

# Multi-step organic synthesis using solid-supported reagents and scavengers: a new paradigm in chemical library generation

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## 1 Review

The use of polymer-supported reagents and scavengers provides an attractive and practical method for the clean and efficient preparation of novel chemical libraries with potential application in the pharmaceutical or agrochemical industries. These methods can be extended in a multi-step fashion to provide access to more complex structures, including biologically active natural products. In this review, an extensive listing of known supported reagents, catalysts and scavenging agents has been included as an aid in the future design of synthesis programmes.

### 1.1 Overview

The creativity and art of organic synthesis has reached an interesting stage in its development. Although we now have some excellent methods to effect the construction of target molecules, with an ever increasing level of complexity, there is a need to find new, strategically important processes which are environmentally cleaner, more efficient and which lead to greater structural variation in a shorter period of time. The demands of modern society for new, functional chemical entities has driven the development of novel technologies which have begun to produce compounds at a greater rate than ever before thought possible. These methods are revolutionising the way we think, plan and optimise chemical processes and have far reaching consequences, particularly in the pharmaceutical and agrochemical sectors. In the future, the impact will be even greater by influencing both materials discovery and catalyst design.

In order to effect high throughput parallel synthesis or combinatorial chemistry, one must understand the key issues associated with molecular assembly, since it introduces complex decision making at all stages of the synthesis process. To be effective, one has to balance experience, creativity and innovation with the practical aspects of the process, using the modern computational aids, state of the art instrumentation and all of the analytical methods which are available. Indeed, management of these resources is a crucial factor in efficient synthesis programmes.

There is no generic way to make a molecule and even the decision of what to make is a non-trivial problem. At the synthesis planning stage one has to define a strategy using a retrosynthetic analysis, which can also incorporate invention and the best of the modern synthetic methods. The larger the molecule however, the more pathways there are that can be adopted often leading to a daunting problem of which direction to pursue. Again, these decisions will have to be based upon

product requirements (*e.g.* quantity and purity), experience, safety issues, efficiency and economics, not all of which will be consistent with one another. The synthesis itself is a juggling act of gigantic proportions as it requires the interplay and control of many variables ranging from the substrates and reagents used, solvent(s), temperature, stoichiometry, and the reaction times *etc.* Also, the reactions will often require substantial analysis and variation of conditions to produce an optimum yield of the desired product at any stage of a multi-step process. Moreover, there can be a large number of reagents available to achieve a particular transformation and it is necessary to make an optimal choice, again based on a large number of variables such as cost, availability, safety, likelihood of success *etc.* Having come this far, the task is by no means over owing to the need to work-up the reaction and obtain the product in an acceptable yield and purity. This final aspect of the synthesis process can be the most frustrating and depends critically on the quality of the earlier decision making. It also depends upon the skill and ability of the synthetic chemist to master all of the available analytical, separative and purification techniques which are under constant technological development. If a combination of the above processes has worked effectively, one has been able to devise, synthesise and isolate a new molecule with potential biological or other functions.

With the ever increasing demand for new compounds, synthetic chemists have been expected to greatly accelerate their rate of production of chemical entities. In response to this, over the last few years enormous advances have been made to enhance the synthesis and design of molecules which fit a set of parameters rather than just indiscriminately and wastefully synthesising a vast number of compounds. Indeed, the current trend in compound library generation is towards well designed, individual, pure and fully characterised compounds with quantities in excess of 20 mg. However, these criteria are also subject to change as new technologies develop. One should also not lose sight of the fact that we still need to invent new synthetic methods which provide strategic advantages. The methods of combinatorial multiparallel synthesis can aid this discovery process if correctly harnessed.

## 1.2 Solid-phase organic synthesis (SPOS)

In order to overcome some of the problems associated with classical multi-step synthesis in solution and to produce large numbers of compounds in a multiparallel fashion, a modification of the techniques introduced by Merrifield<sup>1</sup> and Letsinger<sup>2</sup> has been extensively developed. This involves using a polymeric resin or other solid material to support a substrate, which can then be elaborated using an excess of reagents and coupling components to drive reactions to completion. The desired molecule is then detached from the support material and isolated following a simple filtration. This general process has become the backbone of modern combinatorial chemistry and is now a widely used technique.<sup>3-5</sup>

Despite the success and advantages of this type of solid-phase organic synthesis, there are also severe limitations to this approach which are worth noting. Firstly, the reactions can be slow relative to their solution-phase counterparts and it can be difficult to monitor reaction progress. Although considerable improvements have been made in this area in recent years (*e.g.* FTIR, MALDI-MS, Gelpase and MAS NMR *etc.*),<sup>6,7</sup> these techniques still do not provide the same quality of analysis as rapidly and conveniently as conventional solution-phase techniques (*e.g.* TLC, GC-MS, LC-MS, SFC-MS, NMR *etc.*). A second fundamental feature of this approach is that additional steps are required to attach and detach products from the resins: often a vestigial part of the linker unit is found in the final product and linker compatibility with the reagents used can be a source of problems or limitations. It is also not

possible to undertake convergent syntheses using this methodology and the resin loading and swelling characteristics can be poor, necessitating the use of solvents which are perhaps not optimal for the chemistry being carried out. However, the most frustrating aspect of this type of chemistry, is usually the time consuming process of attempting to optimise solution-phase chemistry on a polymer-supported substrate, particularly where a long synthetic sequence is required.

## 1.3 Beyond conventional solid-phase organic synthesis

Owing to these problems, a number of alternative and innovative approaches have also been developed for chemical library generation, some of which are now beginning to show considerable promise. The use of fluororous molecules as reagents and scavengers in conjunction with fluororous solvents, for example, is an attractive concept designed to exploit multi-reaction and separation phases.<sup>8</sup> Many believe that the advantages of solution-phase chemistry so far outweigh the disadvantages, that their efforts focus around improved high-throughput purification technology to clean-up the products from complex reaction streams.<sup>9</sup> Others have concentrated their efforts on using insoluble polymer<sup>10</sup> and other solid-supported<sup>11-13</sup> agents to scavenge by-products and excess starting materials thereby purifying reaction products produced in solution.<sup>14</sup> The idea that one can use a suitably functionalised polymer-support to selectively capture the required product away from any contaminating impurities, filter and then re-release it (catch and release) in a pure form is also an important purification concept.<sup>15</sup> Perhaps most significant is that both hetero- and homogeneous<sup>16,17</sup> polymer-supported reagents, including immobilised enzymes, which have been known and used for a long time, are making a noticeable comeback and are likely to have a crucial impact in the future on how this whole area will develop.

## 1.4 The review

This review is divided into two sections. The first emphasises those processes which involve the application of more than one solid-supported species, to either effect reactions or product clean-up or employ catch and release techniques. We believe that the combined application of these methods is the best way of preparing libraries of truly significant functional molecules in a clean, effective and general manner. The second section of the review tabulates the literature on known solid-supported reagents, catalysts and scavengers together with catch and release materials. Due to the pictorial fashion in which it is presented, it should provide an accessible and comprehensive reference to the large amount of data which has now been published. The intention is also to stimulate new work by presenting the reagents currently available for incorporation into multi-step parallel synthesis programmes and to highlight areas which would benefit from the development of new or improved supported materials.

## 1.5 Some definitions

A large number of terms, phrases and buzz-words have been introduced into the vocabulary during the application of these new technologies to organic synthesis programmes, not all of which have been helpful or informative. Therefore it is pertinent to define some expressions that will be used commonly during this review.

*Supported reagents* are reactive species which are associated with a support material. They transform a substrate (or substrates) to a new chemical product (or products) and the excess or spent reagent may be removed by filtration.

*Supported catalysts* are reactive species which are associated with a support material. They are used in sub-stoichiometric quantities to transform a substrate (or substrates) to a new

chemical product (or products) and may be removed by filtration and recycled.

*Supported scavengers* are reactive species which are associated with a support material. They selectively quench or sequester by-products of the reaction or remove excess or unreacted starting materials and may be removed by filtration. Also referred to as 'sequestering agents' or 'quenching agents' and variants thereof.

*Catch and release* is a technique used to selectively trap the desired product of a solution-phase reaction onto a functionalised support material. Following filtration (and washing) to remove solution-phase contaminants, the compound may then be released from the support. Also referred to as 'capture and release' and variants thereof.

### 1.6 Solid-supported reagents and scavengers

Solid-supported reagents,<sup>18–23</sup> and scavengers,<sup>24,25,14</sup> have been used in organic synthesis programmes from 1946<sup>26</sup> although key contributions appeared somewhat later from Frechet, Cainelli, Camps, Font, Hodge, Leznoff and Sherrington among others. However, if anything this work was before its time since these reagents were regarded by many to be either prohibitively expensive or too difficult to recycle or that reaction times were too slow to be generally useful. It is unfortunate to note that, in the current fever to find new chemical approaches to synthesis, these earlier contributions from the literature have often been poorly cited. In recent years however, many new and several improved solid-supported reagents have been developed, an ever increasing number of which are becoming commercially available. The increased level of interest has largely been due to the need to generate large numbers of new compounds in a cleaner, faster and more efficient manner, and the potential of these reagents to achieve this.

The reasons why solid-supported reagents are so attractive in combinatorial chemistry programmes are numerous. A key advantage is that it is possible to use excess reagent to drive reactions to completion and, as work-up is by simple filtration to remove products, the chemistry is clean. This filtration also results in isolation of the solid-supported species which is a crucial feature in cases either where the reagent acts as a catalyst, or where the spent material can be regenerated and recycled. Another attractive aspect is that toxic, noxious or hazardous reagents and their by-products, can be immobilised and therefore not released into solution thereby improving their general acceptability, utility and safety profile. More than one reagent can be used simultaneously and, due to site isolation of reagents, even species that are incompatible in solution may be used together to achieve one-pot transformations that are not possible in homogenous solution. Furthermore, if the reactions proceed poorly or generate by-products and impurities, scavengers or catch and release techniques can lead to isolation of pure products in a simple fashion without the need for conventional work-up and purification procedures. The fact that only simple work-up operations are necessary, involving filtration and solvent removal or exchange, is a crucial feature for library generation as the chemistry should then be suitable for automation using robotic devices.

What has particularly attracted us and others is that reactions can be optimised and scaled up extremely readily because they can be constantly monitored using conventional methods (TLC, LC-MS, GC-MS, SFC-MS, NMR *etc.*). Additionally, because the chemistry is carried out in solution, they often require only minimal optimisation compared to that involved in transferring a solution-phase reaction onto a polymer-bound substrate. This is a considerable advantage over conventional solid-phase organic synthesis as both long linear syntheses (*i.e.* in excess of ten steps) and convergent strategies now become possible in a general sense.

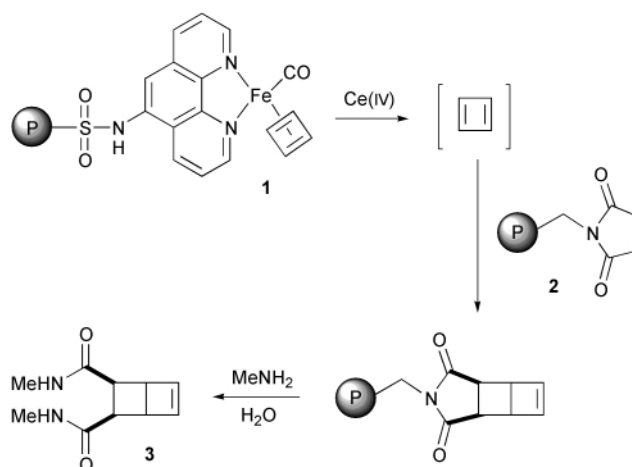
### 1.7 Multi-step use of solid-supported reagents and scavenging reagents

The preparation of biologically active and many other functional materials from small, commercially available building blocks inevitably involves more than one synthetic step. For example, the synthesis of most modern drugs requires at least ten transformations and for more complex molecules, it is not uncommon to use in excess of twenty steps. Also, while there are a large number of *simple* starting materials currently available for synthesis, industry would like to have available more sophisticated scaffolds for combinatorial decoration and more functionalised monomer sets to lead more rapidly to drug-like molecules.

In order to address these goals, we believe that a much better practical solution for the preparation of large chemical libraries would be to use solid-supported reagents in a designed, sequential, and multi-step fashion. Not only would this solve many of the problems associated with conventional solid-phase organic synthesis but, in combination with the fundamentally important developments using scavenging agents and catch and release techniques, even greater opportunities for organic synthesis become apparent.

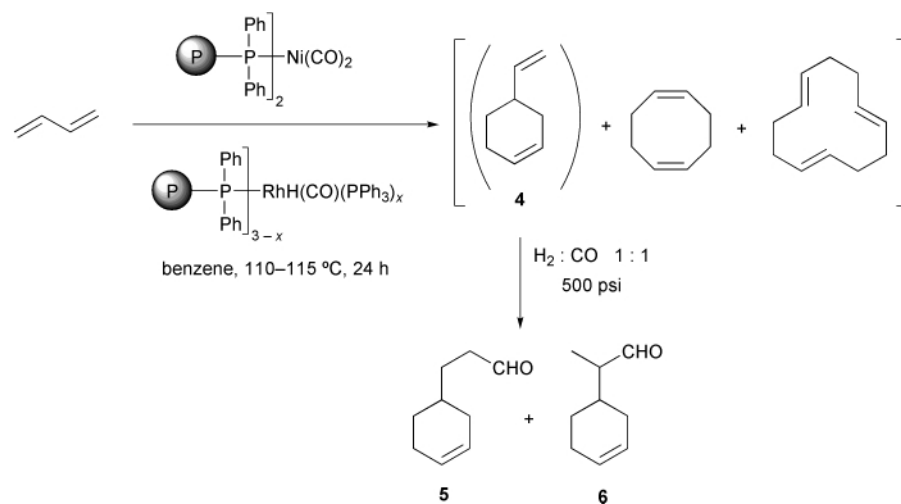
This section of the review describes, in an approximately chronological order, how polymer-supported reagents and scavengers have been and may be used to effect sequential steps in organic synthesis programmes.

In an early experiment (1974), designed to exploit different phases for the generation and capture of reactive intermediates, Rebek showed that a polymer-supported cyclobutadiene iron complex (**1**) could be treated with an oxidant (ceric ammonium nitrate) to release the unstable parent cyclobutadiene. This was then immediately trapped in a Diels–Alder reaction by a second polymer (**2**) containing a succinimide functional group.<sup>27</sup> Upon subsequent reaction with methylamine this released the diamide (**3**) into solution (Scheme 1). In addition to providing evidence for an uncomplexed cyclobutadiene species, this work represents the first example of two polymeric reagents being used in conjunction for the synthesis of an organic product.



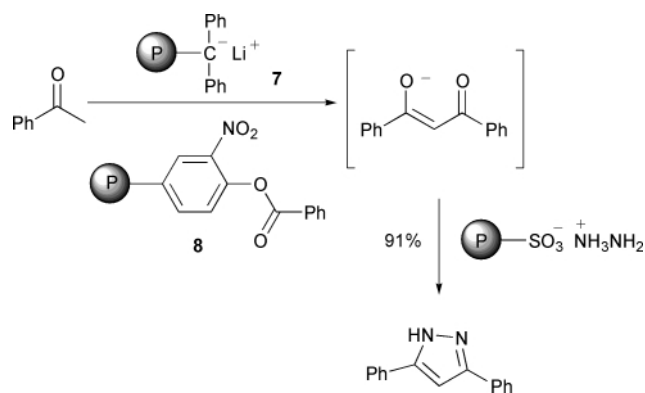
Scheme 1

In 1975, Pittman described the use of various polymer-bound nickel, rhodium and ruthenium catalysts to effect sequential cyclooligomerisation and hydrogenation or hydroformylation reactions.<sup>28</sup> For example, butadiene reacts with a mixture of polymer-bound triphenylphosphine ligated nickel and rhodium catalysts to give a mixture of cyclooligomerised products. Upon sequential treatment with H<sub>2</sub> and CO at 500 psi in the presence of the same catalysts, aldehydes (**5**) and (**6**) are formed *via* selective hydroformylation of the exocyclic double bond of (**4**) (Scheme 2). However, although a number of other catalytic reactions were reported, none were directed towards synthesis programmes.



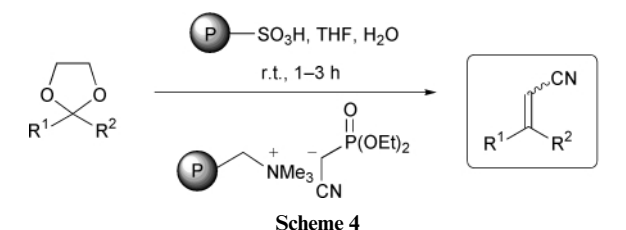
Scheme 2

The next advance in the area came from the work of the Cohen group in 1977, who reported what they described as a “wolf and lamb” reaction.<sup>29</sup> The initial part of this process involves the use of a polymer-bound trityllithium base (**7**) to remove an acidic proton from acetophenone. The anion generated then undergoes a *C*-acylation reaction with a benzoyl-transfer polymer (**8**) and is passed without isolation into Amberlyst A-15 resin (hydrazine form), affording 3,5-diphenylpyrazole in 91% yield when filtered from the spent polymer reagent (Scheme 3). Once again, this interesting early example illustrates a key concept in that, due to site isolation of the polymer-bound reagents, mutually incompatible species may be used in conjunction with one another to achieve reaction sequences that are not possible in one-pot processes with homogeneous reagents. Simple filtration affords products in high yield and purity. In the above example, the spent polymeric reagents from the first step were recovered and separated *via* a selective flotation protocol and recycled for use in further reactions. Although this particular reaction sequence has not been exploited in chemical library generation, additional examples using similar approaches have subsequently been reported.<sup>30</sup>



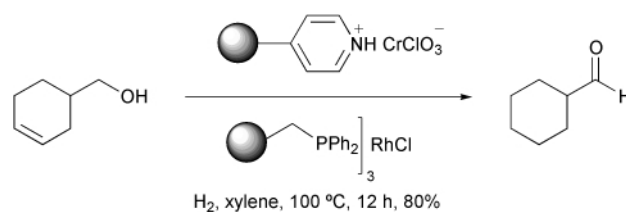
Scheme 3

In 1979 Cainelli, one of the champions of polymer-supported reagents, described a simple but effective two-step procedure which provides a source of unsaturated nitriles from acetals (Scheme 4).<sup>31</sup> The simultaneous use of acidic Amberlyst 15-H and basic Amberlyst A-26 (phosphonate form) allowed sequential acetal deprotection and Horner–Wittig alkene formation. Once again, mutually incompatible reagents were supported on polymers and used together, in order to accomplish in one-pot a transformation that is not conceivable in homogeneous solution. Work-up of the products consisted of filtration and evaporation to obtain pure material in yields ranging from 40–98%, depending upon the substrate used.



Scheme 4

In a further demonstration of this principle, a two step process involving an alcohol oxidation with poly(vinylpyridiniumchlorochromate) (PVPCC), previously described by Frechet,<sup>32</sup> and concurrent alkene reduction with a polyethylene diphenylphosphine immobilised Wilkinson’s catalyst was achieved in generally good yields for a range of unsaturated alcohols (Scheme 5).<sup>33</sup> Under the reaction conditions, the supported Wilkinson’s catalyst is homogeneous and product isolation consisted of cooling the reaction to precipitate the supported catalyst, followed by subsequent filtration. An efficient method for recovery of the catalyst involving soxhlet extraction with hot toluene is also reported.



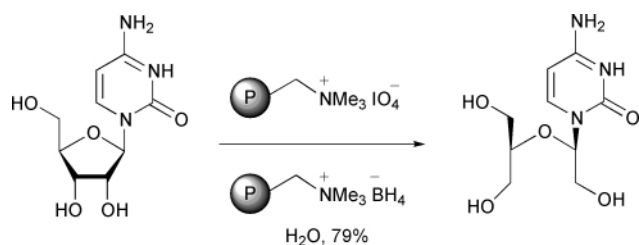
Scheme 5

An attractive one-pot cleavage reaction of 1,2-diols to primary alcohols, as a route towards antiviral precursors, has also been described.<sup>34</sup> This process also uses mutually incompatible reagents, but in this case reactions were carried

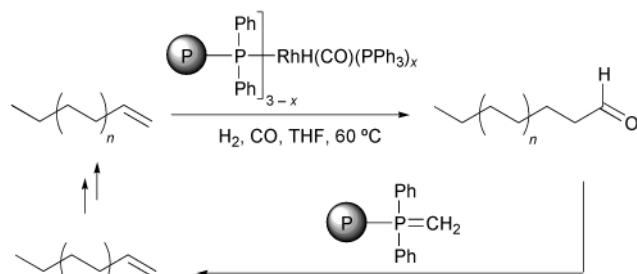
out by simply pumping the reaction solution through a column packed with a 1:1 mixture of the polymers, until TLC indicated good conversion (Scheme 6). A particular advantage in this case is that the unstable dialdehyde resulting from diol cleavage is immediately reduced *in situ* by the polymer-supported borohydride, thus minimising the lifetime of this species and improving the overall yield for the two step process. This protocol has subsequently been used in the cleavage of 1,2:5,6-di-*o*-isopropylidene-mannitol in a synthesis of Bolaform phosphatidylcholines.<sup>35</sup>

In a further demonstration of two reagents being combined in one-pot, Regen reported a chain homologation of alkenes (Scheme 7).<sup>36</sup> In this strategy, a polystyrene supported rhodium catalyst effects a hydroformylation of the alkene with synthesis gas to generate aliphatic aldehydes. These then react with a





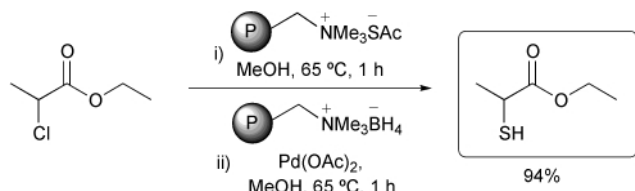
Scheme 6



Scheme 7

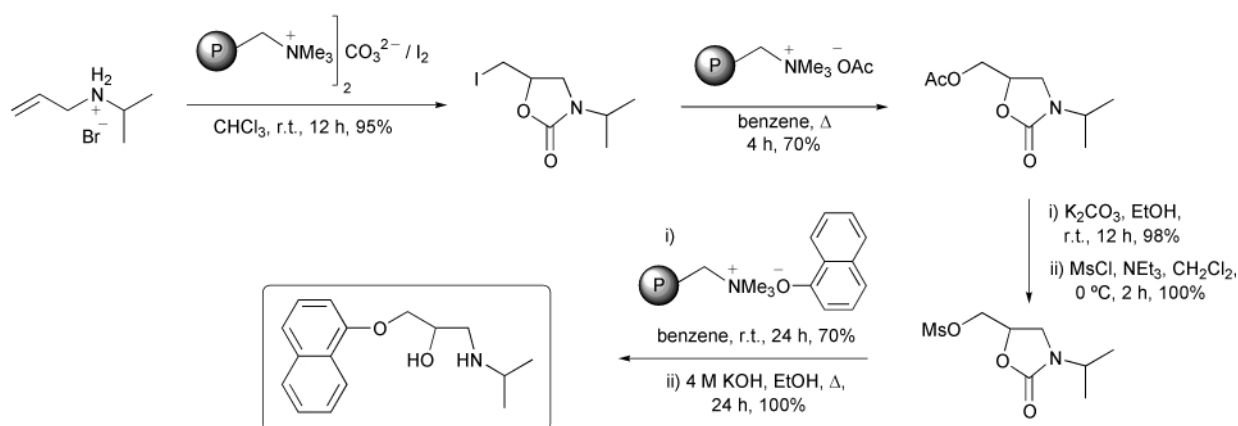
polystyrene-supported Wittig reagent to produce two-carbon homologated alkenes which can then re-enter the reaction cycle. Advantages of this strategy include milder reaction conditions and less complex mixtures than traditional alkene homologation methods.

A convenient method for the synthesis of thiols from alkyl halides or tosylates has also been reported.<sup>37</sup> In this strategy, displacement of the leaving group with a supported thioacetate reagent afforded the intermediate thioester. Subsequent addition of palladium-supported borohydride with a catalytic quantity of palladium acetate resulted in reduction of the thioacetate to the thiol (Scheme 8).



Scheme 8

In a significant piece of work by Cardillo, a new polymeric reagent was developed by adsorbing iodine onto Amberlyst A-26 (carbonate form).<sup>38</sup> This allowed the synthesis of oxazolidin-2-ones from allylic amines and was used in the synthesis of ( $\pm$ )-propranolol, a  $\beta$ -adrenergic receptor agonist (Scheme 9). Although use of the polymer-bound reagents



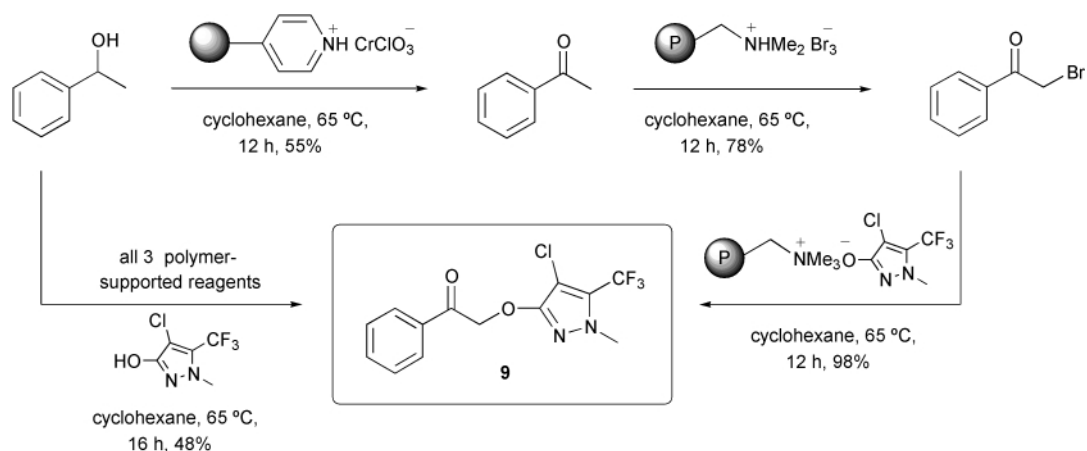
Scheme 9

obviated the need for an aqueous work-up, silica gel chromatography was used after each step to give pure products.

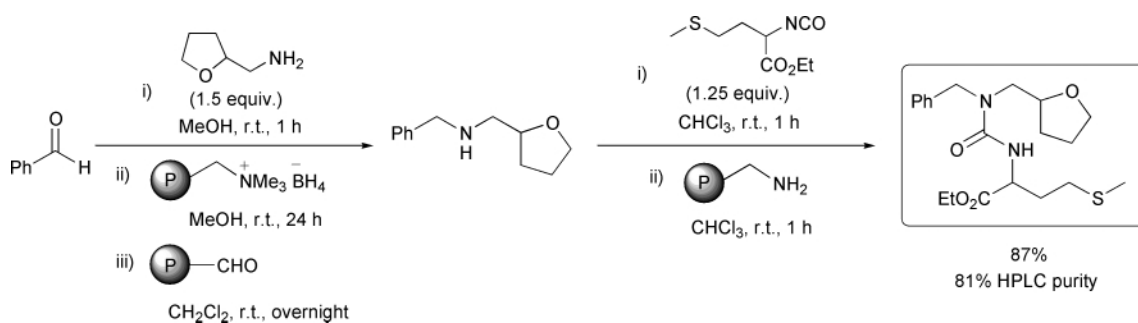
Following these early results, the field lay relatively dormant until in 1995, Parlow accomplished a transformation involving a combination of three different polymeric reagents in a single reaction vessel to afford the pyrazole (**9**) in 48% overall yield (Scheme 10).<sup>39</sup> Despite being an impressive example of multi-step synthesis using supported reagents, only a single example was reported and no mention was made of how these processes could be used in combinatorial chemistry or parallel synthesis programmes. However, this work stimulated our interest in the area and in conjunction with the exciting developments in solid-supported scavengers, which were beginning to appear for small library generation in solution, tremendous opportunities for synthesis became apparent.

Although the principles of using polymeric reagents to scavenge unwanted by-products or excess starting materials at the end of a reaction were well established by the early pioneers, the need to rapidly prepare large numbers of new chemical entities for drug discovery programmes stimulated renewed interest in these systems. Key advances in the area have been made by several industrial laboratories including Eli-Lilly, Warner-Lambert/Parke-Davis and Searle/Monsanto and it has now been established as a highly desirable and useful technology. These methods are therefore becoming widespread in chemical library preparation, particularly as they are amenable to automation techniques.

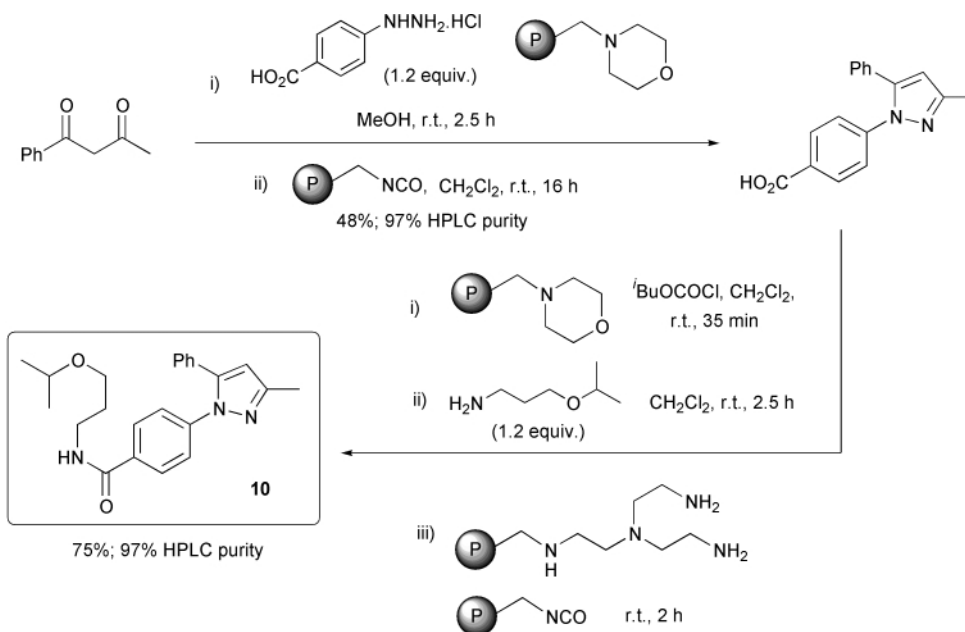
Kaldor, Siegel *et al.*<sup>40</sup> were the first to show the power of these solid-supported scavengers in the expedient construction of parallel arrays. In this work, involving amine alkylation and acylation reactions, various scavengers were reported, including an immobilised amine, isocyanate, aldehyde and acid chloride to effect reaction clean-up and impressive purities of relatively complex products were reported (90–95%). Scheme 11 is a representative example and neatly illustrates the complementary use of polymer-supported reagents and scavengers in a two-step synthesis. The first reductive amination requires the use of an excess of amine to drive the imine formation reaction to completion. Following treatment with polymer-bound borohydride, this excess is then scavenged by polystyrene-bound carbaldehyde. The resulting secondary amine is subsequently reacted with an excess of a functionalised isocyanate and gives the final urea after scavenging any unreacted isocyanate with an aminomethylated polystyrene resin. The authors report that thousands of amides, sulfonamides, ureas and thioureas have been prepared for biological evaluation using these general concepts. Kaldor went on to use these methods to discover antirhinoviral leads with sub-micromolar potency by screening a combinatorial library of ureas, which was prepared using aminomethylpolystyrene as a covalent scavenger to remove isocyanate impurities.<sup>41</sup>



Scheme 10



Scheme 11



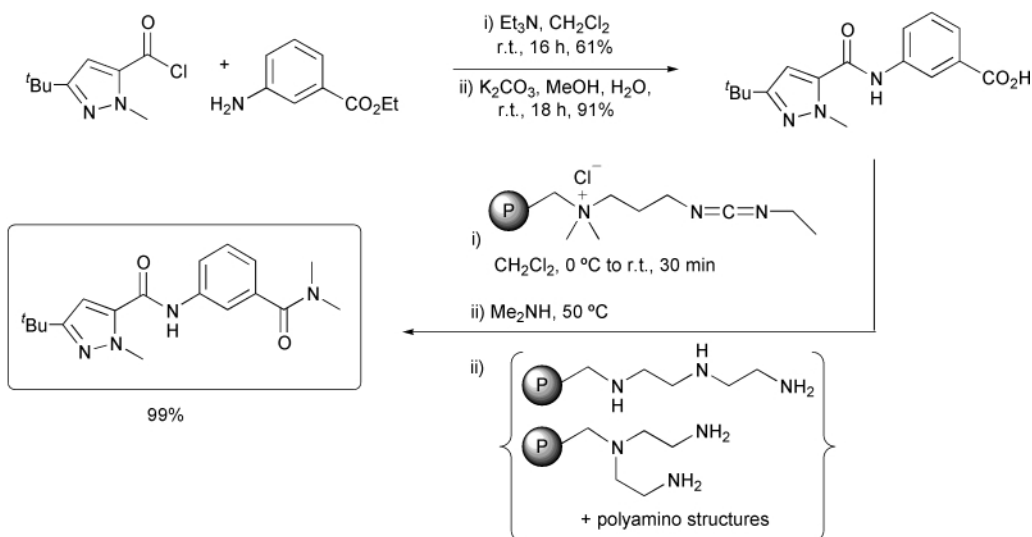
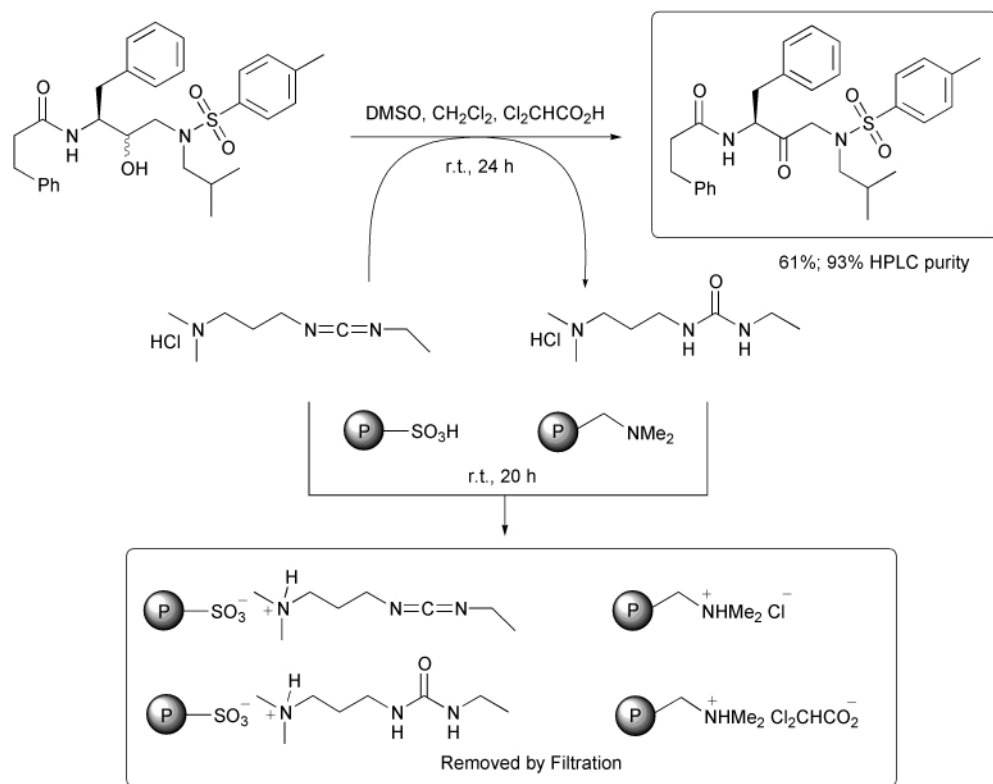
Scheme 12

Booth and Hodges also demonstrated the utility of solid-supported scavengers in parallel purification.<sup>42</sup> Several different compound classes were prepared including many drug-like substances and by way of example, the pyrazole (**10**) was obtained in excellent purity after two synthetic steps (Scheme 12). In this case, scavengers are used to remove hydrochloric acid and excess hydrazine in the first step. In the second stage, following acid activation and coupling to form an amide, polymers again remove unreacted starting materials to give a clean product.

Work from the Searle/Monsanto chemists employs a strategy for chemical library purification based on similar principles of complementary molecular reactivity and recognition.<sup>43</sup> Whilst they too describe many alternative sequences and strategies, the parallel oxidation of hydroxyethylamines under Moffat con-

ditions illustrates the designed choice of functionalised reagents and polymeric agents used to effect reaction and product clean-up (Scheme 13). In this protocol, solution-phase reagents (*e.g.* a carbodiimide) are modified with a functional group (*e.g.* a tertiary amine) which enables removal of excess reagent and reagent derived by-products upon reaction completion with a complementary polymer-supported reagent (*e.g.* an acid). Once again, the principle of polymer-bound site isolation allows mutually incompatible species to be used in conjunction, to effect a simultaneous acid and base quench thus further simplifying the work-up procedure.

These complementary reactivity and recognition concepts were refined further to provide better scavenging reagents and subsequently used in the solution-phase synthesis of

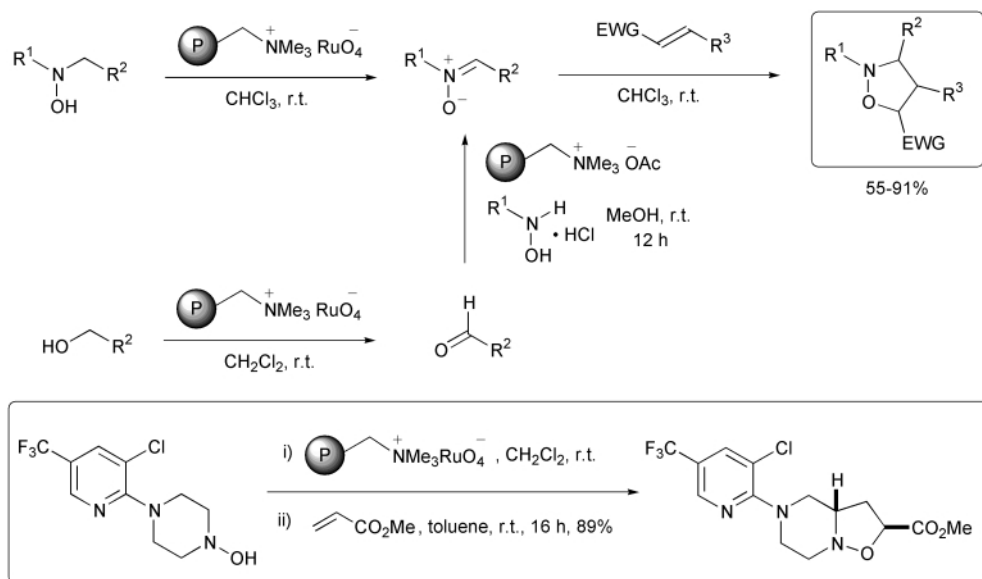


heterocyclic amide based libraries (Scheme 14).<sup>44</sup> Over 400 compounds were produced during this programme of work, resulting in the identification of an active herbicide with a four-fold increase in potency over the original lead compound.

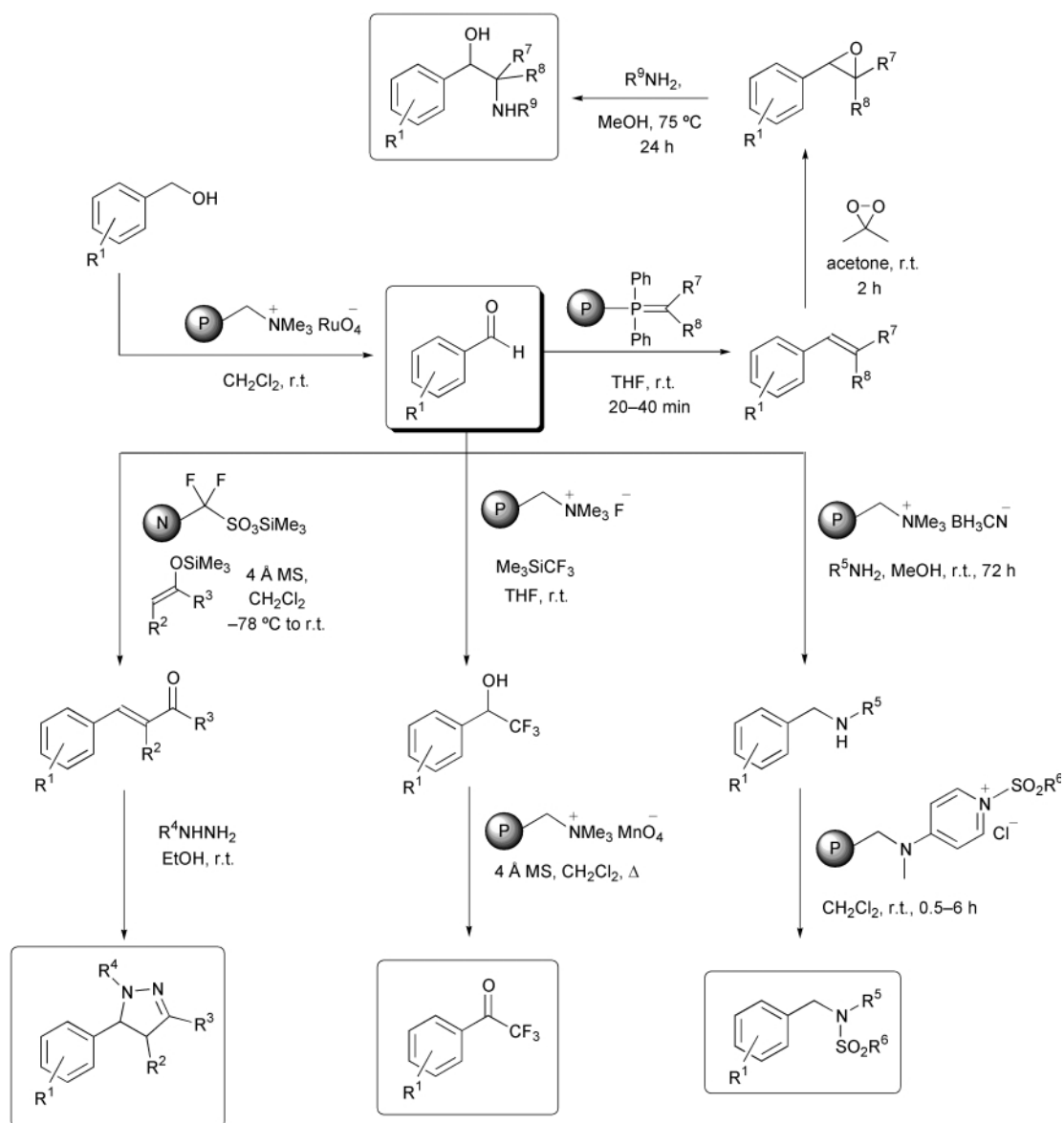
In 1998, the number of papers published utilising solid-supported reagents and particularly scavengers in multi-step sequences increased dramatically. In an effort to prepare chemical libraries with potential pharmaceutical or agrochemical use, our group devised a new route to isoxazolidines using only polymer-supported reagents.<sup>45</sup> In order to increase the diversity in the reaction products, two routes were used which employed different starting materials. Secondary hydroxylamines, readily prepared from amines by *in situ* treatment with dimethyldioxirane, may be oxidised directly to nitrones with polymer-supported perruthenate (PSP). Alternatively, alcohols can be used as starting materials which upon oxidation with polymer-supported perruthenate give aldehydes.

These in turn condense with primary hydroxylamines, mediated by polymer-bound acetate, to produce nitrones. The nitrones produced using either method then undergo a 1,3-dipolar cycloaddition with various alkenes to give the corresponding isoxazolidines (Scheme 15).

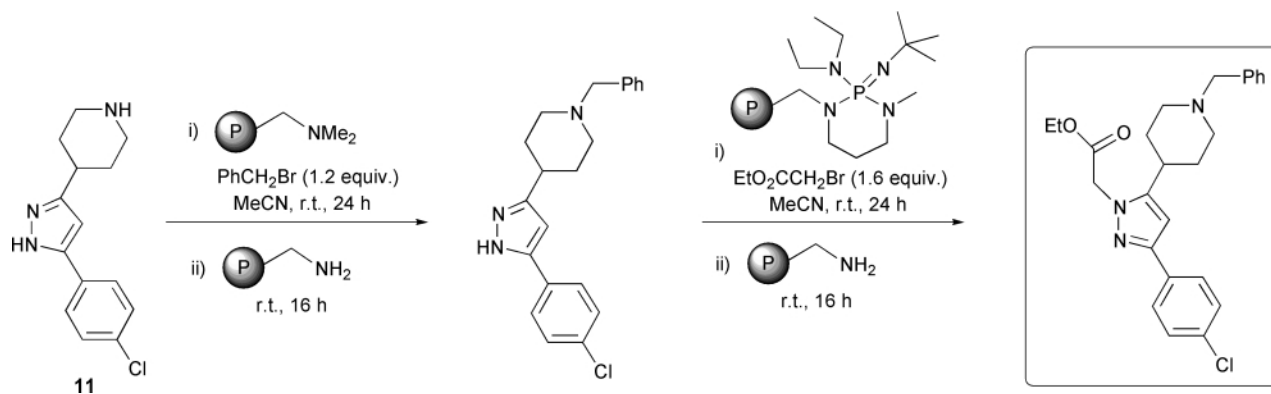
The use of catalytic polymer-supported perruthenate<sup>46,47</sup> to cleanly convert readily available alcohols to aldehydes is an important transformation since it can be carried out on multi-gramme scale and can provide starting materials for combinatorial chemistry programmes that would not necessarily be available from chemical suppliers. Aldehydes are versatile starting materials in synthesis and the ability to make these in large-scale quantities using polymer-supported reagents allows the opportunity for splitting of the batch and diversion to many different synthesis projects. In the first example, if a portion were reacted separately with silyl enol ethers to achieve a Mukaiyama aldol reaction, when Nafion-TMS is used as



Scheme 15



Scheme 16

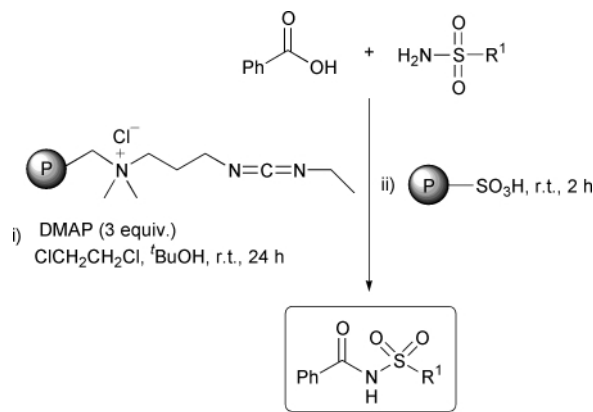


Scheme 17

a catalyst the direct conversion to unsaturated carbonyl compounds is realised.<sup>48</sup> These products are similarly very useful building blocks in organic synthesis and, upon reaction with hydrazines, dihydro-1*H*-pyrazoles are obtained in excellent yield (Scheme 16). Compounds of this type have found many useful applications as antibiotics and as antioxidants. In an alternative pathway, reaction with trifluoromethyl anion, generated from  $\text{Me}_3\text{SiCF}_3$  and polymer-supported fluoride, affords alcohols which can be oxidised with solid-supported oxidants to generate trifluoroacetyl derivatives<sup>49</sup> (Scheme 16). Alternatively, if the aldehyde is subjected to reductive amination using polymer-supported cyanoborohydride, secondary amines are obtained which in turn can be used further in library generation.<sup>50</sup> For example, sulfonylation is possible using a polymer-bound aminomethylpyridine sulfonylating agent and a small library of compounds was therefore generated using an ACT 496 synthesiser (Scheme 16). Finally, if the aldehyde is split into a fourth channel and then reacted with polymer-supported Wittig reagents, alkenes are obtained as the products<sup>51</sup> (Scheme 16). This reaction is particularly useful since the phosphine oxide by-product is attached to the polymeric support and therefore completely removed by filtration. Alkenes produced by this method also serve as excellent precursors for further synthesis and consequently, upon treatment with dimethyldioxirane, a clean preparation of epoxides ensues. In principle, these too could be diverted to other synthesis programmes in a multi-parallel fashion but in this particular work they were reacted further with amines to give  $\beta$ -hydroxyamino compounds which are considered to be privileged structural motifs in pharmaceutical products (Scheme 16).

The methods reported above, using carefully designed, multi-step polymer-supported reagent sequences, allow the conversion of readily available alcohols into a range of structural motifs. These protocols may be useful in the generation of compounds for screening purposes or alternatively, in the formation of novel monomer sets for other combinatorial chemistry programmes.

A further example of the multi-step use of polymer-bound species was reported as a convenient method for the *N*-alkylation of weakly acidic heterocycles.<sup>52</sup> The use of polymer-supported 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphinine (P-BEMP) as a base to promote these reactions was described (Scheme 17) and, following scavenging with aminomethylpolystyrene, very high yields and product purities were obtained. In this elegant example of a two-step, one-pot reaction sequence, the differing acidities of the amino functionalities of (**11**) are exploited. Selective alkylation of the piperidinyl-*N* was achieved with a polymer-supported tertiary amine base and excess alkyl halide was conveniently removed by treatment with aminomethylpolystyrene resin. Subsequent treatment with P-BEMP in the presence of alkyl halide resulted in regioselective alkylation of a pyrazole-*N*

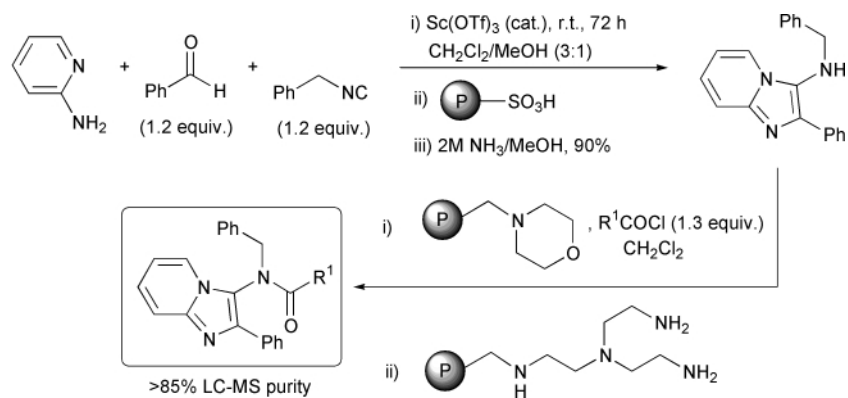


Scheme 18

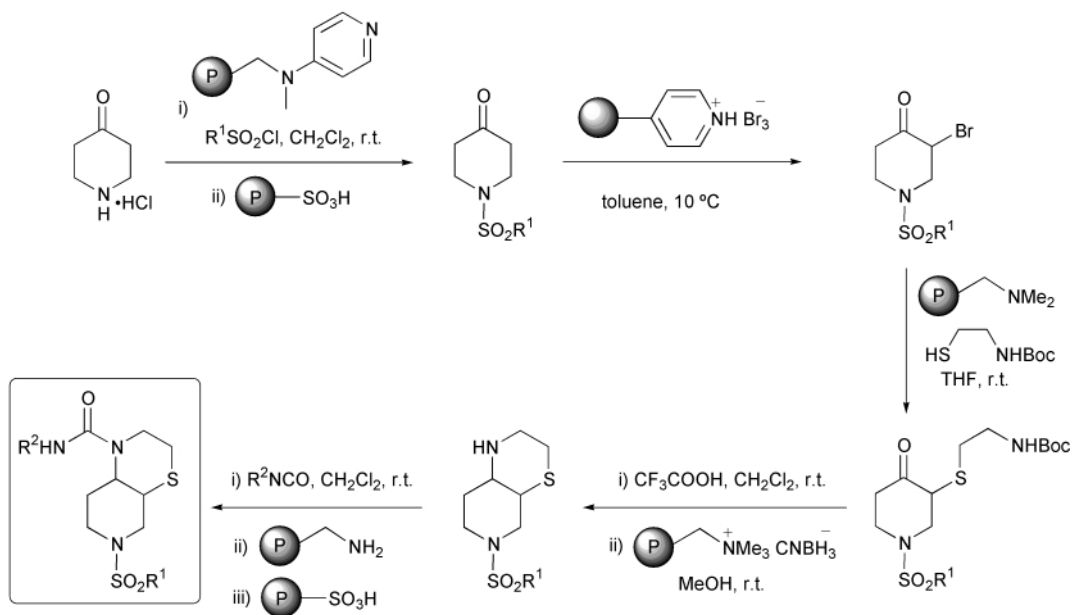
which, upon treatment with aminomethylpolystyrene resin and filtration, afforded amines in high yields (95–98%) and purities (86–96% by HPLC). This work complements previous studies by this group which used polymer-supported guanidinium bases for *O*- and *N*-alkylation reactions.<sup>53</sup> The use of P-BEMP for the alkylation of other weakly acidic heterocycles, in combination with a polymeric trisamine scavenger, has recently been reported.<sup>54</sup>

The Merck Frosst group<sup>55</sup> have described an efficient preparation of acylsulfonamide libraries using two resin-bound reagents. Firstly, polymer-supported 1-(3-dimethylamino-propyl)-3-ethylcarbodiimide was used to activate the carboxylic acid component. This was then reacted with a primary sulfonamide, in the presence of 3 equivalents of dimethylaminopyridine (DMAP), to give the coupled product. Scavenging of the DMAP with Amberlyst A-15 resin followed by simple filtration afforded some 25 acylsulfonamide products in respectable yields (56–81%) and excellent purities (85–92% by HPLC) (Scheme 18).

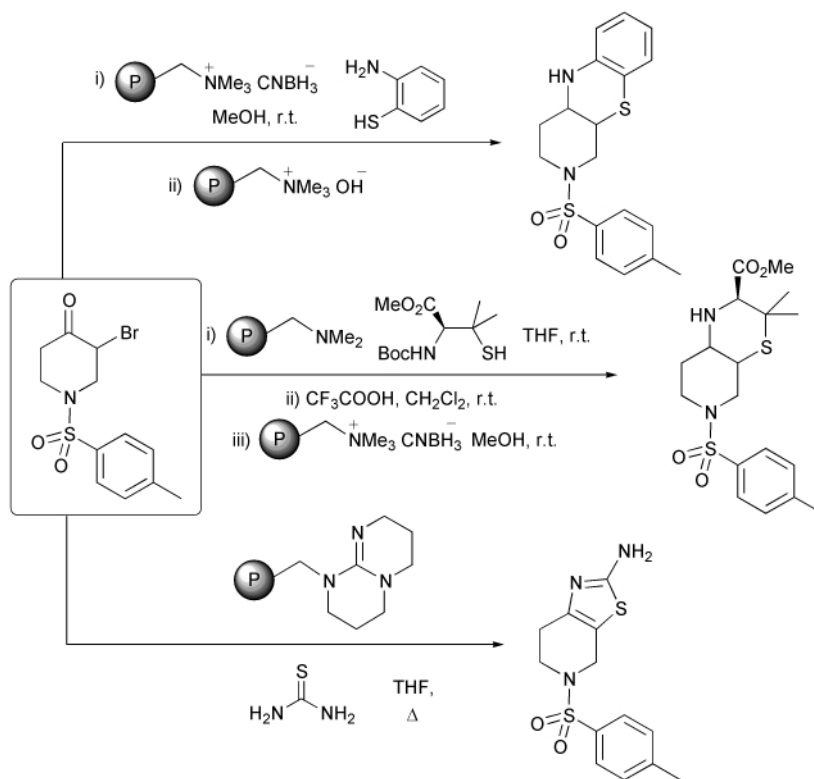
Multi-component condensation reactions, such as those developed by Ugi, Passerini, Biginelli and others, are attractive for combinatorial chemistry programmes since a single reaction step can produce medicinally useful compounds. Using a new three-component condensation, scientists at Millennium Pharmaceuticals developed a parallel synthesis of 3-aminoimidazo[1,2-*a*]pyridines and pyrazines.<sup>56</sup> The key reaction uses scandium triflate catalysis in  $\text{CH}_2\text{Cl}_2$ -MeOH at room temperature for 72 hours and the major product of the reactions was captured in a second step onto a strongly acidic cation exchange resin, thereby removing it from contaminating impurities and unreacted aldehyde and isonitrile. Pure product was released from the resin by treatment with methanolic ammonia (Scheme 19). In order to decorate the product further, it was acylated in the presence of a polymer-supported morpholine catalyst with excess acid chloride being scavenged by a polymer-supported tris(2-aminoethyl)amine derivative (Scheme 19). This report is



Scheme 19



Scheme 20



Scheme 21

significant in that functionalised polymers are utilised not only as reagents and scavengers, but also to effect a catch and release purification.

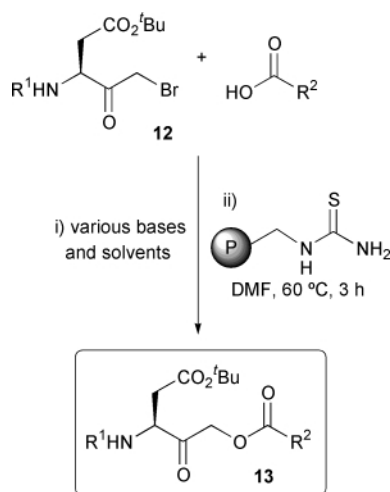
Another significant development in the area demonstrated that it was possible to generate a piperidinothiomorpholine library, using up to *seven* polymer-supported reagents and scavengers in a multi-step synthesis.<sup>57</sup> Scheme 20 is representative of only one of the possible reaction combination profiles. Filtration and evaporation at each stage allowed isolation of essentially pure products. Therefore, in addition to the final library members, the intermediates from each variant sequence could also be screened for biological or other activity and a large number of compounds could be prepared in a relatively short period of time.

Alternatively, the intermediates at various stages of the reaction sequence could be incorporated into different reaction schemes. An example of this is illustrated below with reference to the variety of transformations that can be carried out on just one intermediate from the previous reaction sequence (Scheme 21). In this way, functionality may easily be varied and introduced to certain points of the heterocyclic template. This may have many uses, particularly in establishing structure activity relationships in drug discovery programmes. Whilst all of the specific reactions and polymer-supported reagents are

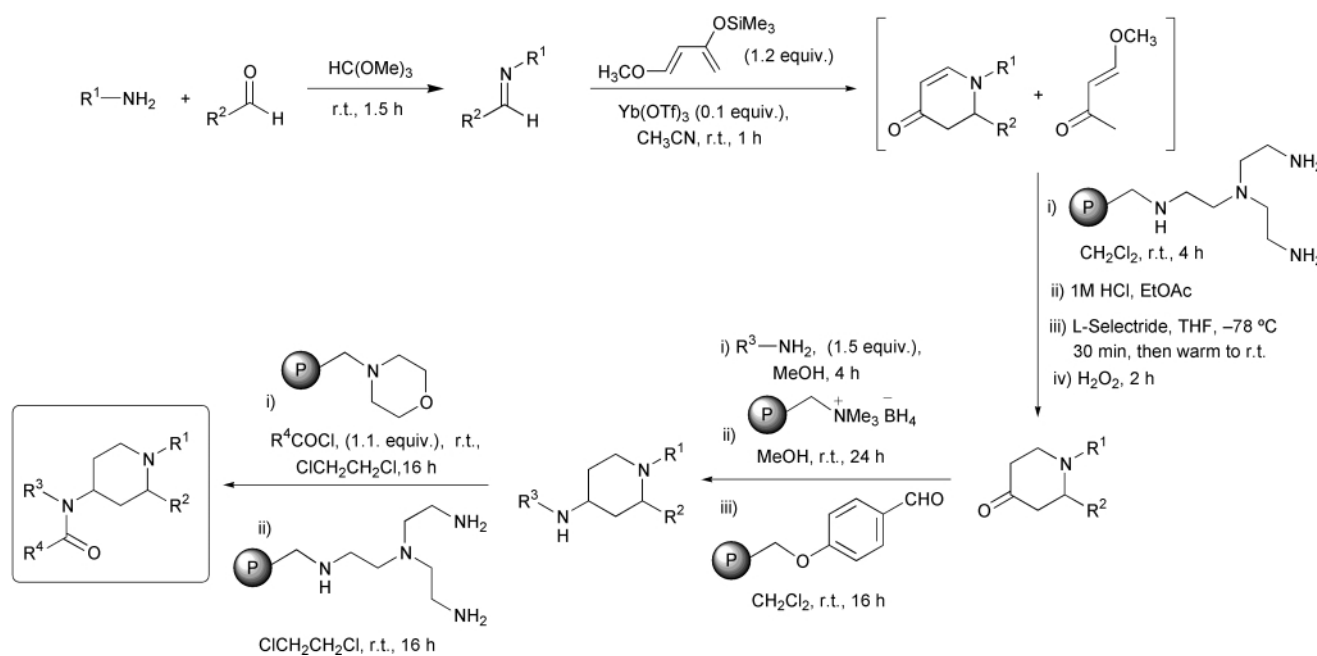
well established, it is their combined use which distinguishes this work and gives confidence that much longer synthetic routes can be contemplated using these concepts. This could then lead directly to drug substances, new materials and even natural products.

Further developments in the use of solution-phase methods have been reported for the rapid optimisation of the synthesis of an interleukin-1 $\beta$  converting enzyme inhibitor, using multiple reaction conditions in a parallel array.<sup>58</sup> This was an important study in that it compared a large range of reaction conditions including organic and inorganic acids and bases, solid-supported reagents and scavenging agents during the conversion of a  $\beta$ -*tert*-butyl aspartic acid bromoethylketone (**12**) to the corresponding acyloxyketone (**13**) (Scheme 22). While this work reports the sequential use of two polymeric reagents in just a few examples, optimisation of the reaction sequence was accomplished in just three to four days and in excess of 200 different reaction conditions were evaluated. A polymer-supported thiourea was also developed to scavenge out any unreacted  $\alpha$ -bromoketone. Eventually, over 500 compounds were then prepared using these conditions. What is noteworthy about these studies is how easily polymer-supported reagents and scavengers can be incorporated into such optimisation studies and synthetic routes.

The first full paper in the area, utilising mainly polymer-supported reagents and scavengers, reports the construction of an acylaminopiperidine library (Scheme 23).<sup>59</sup> The reaction sequence involves the ytterbium triflate catalysed hetero Diels–Alder reaction of imines, formed *in situ* from aldehydes and amines, with Danishefsky's diene. This is followed by the use of a scavenging resin to remove any unreacted imine as well as by-products derived from diene hydrolysis. An aqueous acidic work-up produces dihydropyridones in good yields and purities. The double bond was reduced with L-selectride and then treated with aqueous hydrogen peroxide to obtain the product. The ketone functionality could be reductively aminated using polymer-supported borohydride with a variety of amines and scavenging by a polymer-supported aldehyde to remove any excess primary amine. Acylation in the presence of polymer-bound morpholine and use of a basic scavenger to remove any excess acid chloride afforded the final products (Scheme 23). This sequence is impressive both in the number of steps involved and in the number of points of diversity in the final heterocyclic framework.



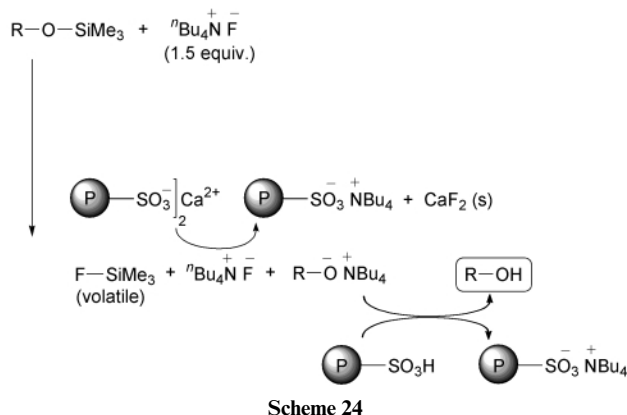
Scheme 22



Scheme 23

Tetrabutylammonium salts can be difficult to remove from synthesised products. However, Parlow has shown that simultaneous use of a calcium sulfonate polymer and a sulfonic acid polymer may be used to quench and purify a trimethylsilyl deprotection reaction involving tetrabutylammonium fluoride (Scheme 24).<sup>60</sup> The calcium sulfonate polymer reacts with any excess tetrabutylammonium fluoride to afford insoluble calcium fluoride whilst the acidic polymer protonates the ammonium alkoxide, with each then giving the polymer-bound ammonium salt. Filtration and removal of volatile fluoro-trimethylsilane *in vacuo* affords clean alcohol. This eliminates the need for a liquid extractive protocol and thus may easily be introduced into multi-step and parallel synthesis programmes.

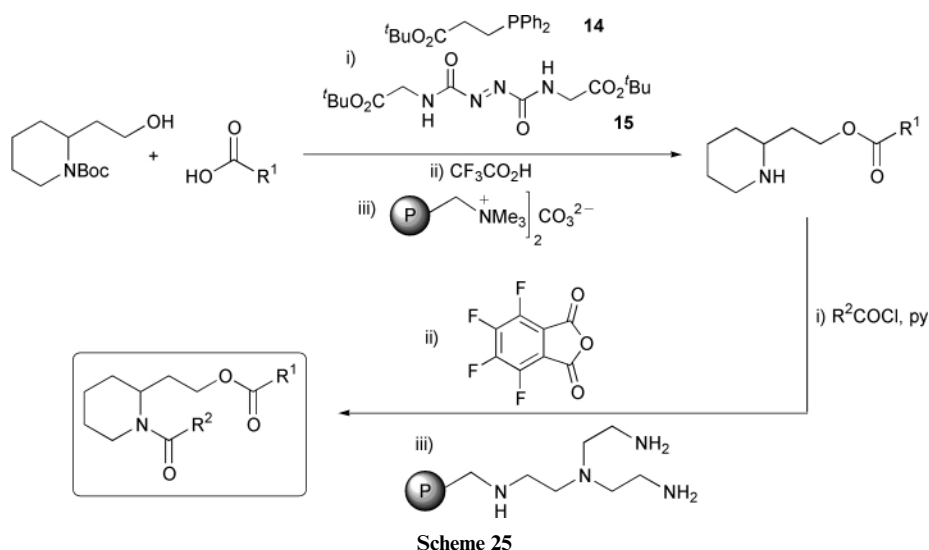
In an extension to the complementary molecular recognition reagents described earlier, chemically modified Mitsunobu reagents have been utilised in the synthesis of solution-phase libraries (Scheme 25).<sup>61</sup> The specially designed phosphine (**14**) and azodicarboxylate (**15**) reagents achieve the initial Mitsunobu process. Following treatment with trifluoroacetic acid, the *tert*-butyl ester groups contained within these excess reagents and the by-products derived from them are hydrolysed to acids which can then be readily scavenged with polymer-supported methylammonium carbonate. This also removes the Boc protecting group from the 2° amine, which can then be further acylated. Treatment with tetrafluorophthalic anhydride<sup>62</sup> derivatises any hydroxylic starting materials and is removed, along with any remaining acid chloride, by a polyamino scavenging resin (Scheme 25). This whole process, although appearing convoluted, solves a difficult problem in solution-phase synthesis using the Mitsunobu reaction, namely how to efficiently remove spent and contaminating reagents from the main synthesis product without using traditional purification methods.



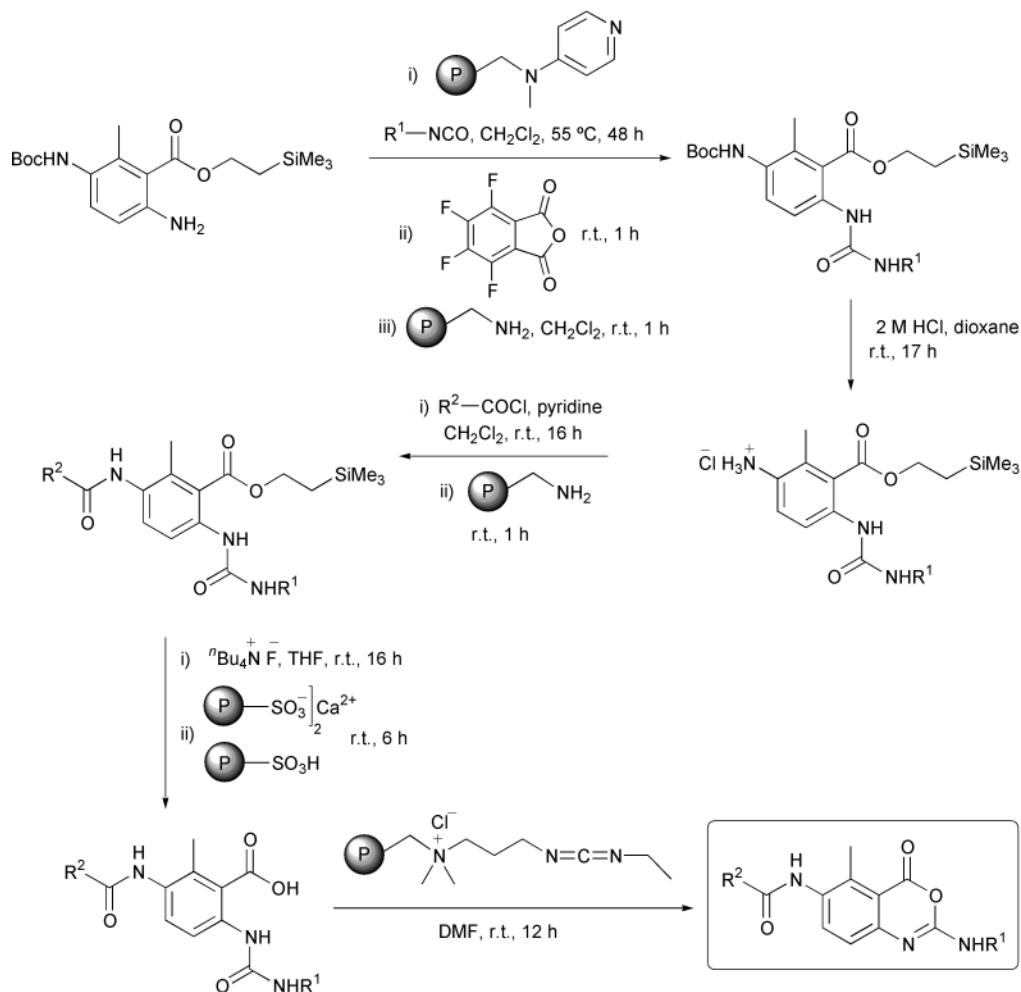
Several features introduced previously (Schemes 24 and 25) have been brought together in an elegant synthesis of a benzoxazinone library (Scheme 26).<sup>63</sup> Coupling of a substituted aniline with a range of electrophiles was mediated by polymer-supported dimethylaminopyridine and reactions were subsequently cleaned-up by derivatisation with tetrafluorophthalic anhydride followed by scavenging with aminomethylpolystyrene resin. Acid-catalysed removal of the Boc group unmasked a second aniline group which could in turn be reacted with a range of different electrophiles. Deprotection of the 2-(trimethylsilyl)ethyl ester with tetrabutylammonium fluoride proceeded smoothly, and the reaction mixture was then quenched and purified using the combination of a calcium sulfonate resin and sulfonic acid resin described above. Cyclodehydration to afford the benzoxazinone framework was then achieved using polymer-supported 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide and gave the products in respectable yields and purities for this five-step sequence.

Solid-supported scavengers have also found application in the synthesis of a new family of chiral ligands for enantioselective catalysis.<sup>64</sup> In this case, 1,2-diamines are reacted with a number of amino-acid derived sulfonyl chlorides, to give a 30-membered library of interesting chiral ligands (Scheme 27). The reaction is catalysed by polymer-bound dimethylaminopyridine and excess sulfonyl chloride is subsequently removed with an amino scavenging resin.

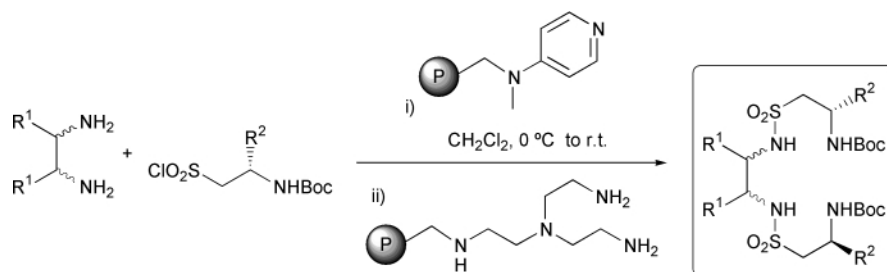
A solution-phase synthesis of ureas has also been devised using nitrophenylcarbamates which react with amines to give ureas with reactions being purified with polymer-supported scavengers (Scheme 28A).<sup>65</sup> The disadvantage of this approach is that the initial nitrophenyl carbamates must themselves be prepared from the reaction of nitrophenyl chloroformate with amines. In addition, the clean-up depends upon which components must be used in excess to drive the reactions to completion. Any excess amine may be removed with either a polymer-bound chloroformate or isocyanate and the *p*-nitrophenol by-product is sufficiently acidic to be readily removed using a polymer-bound amine scavenger. The Searle-Monsanto group have also reported a range of resins designed to scavenge both active ester and leaving group by-products during amide bond formation (Scheme 28B),<sup>66</sup> somewhat similar to the above reaction. However, in this study a wider range of active ester groups and scavenging resins were investigated. A recent report has utilised the reaction of acyl and sulfonyl chlorides with a range of nitrogen nucleophiles.<sup>67</sup> The combined use of solid-supported reagents and scavengers then allowed the preparation of a 300 membered library of cathepsin D inhibitors (Scheme 28C).







Scheme 26



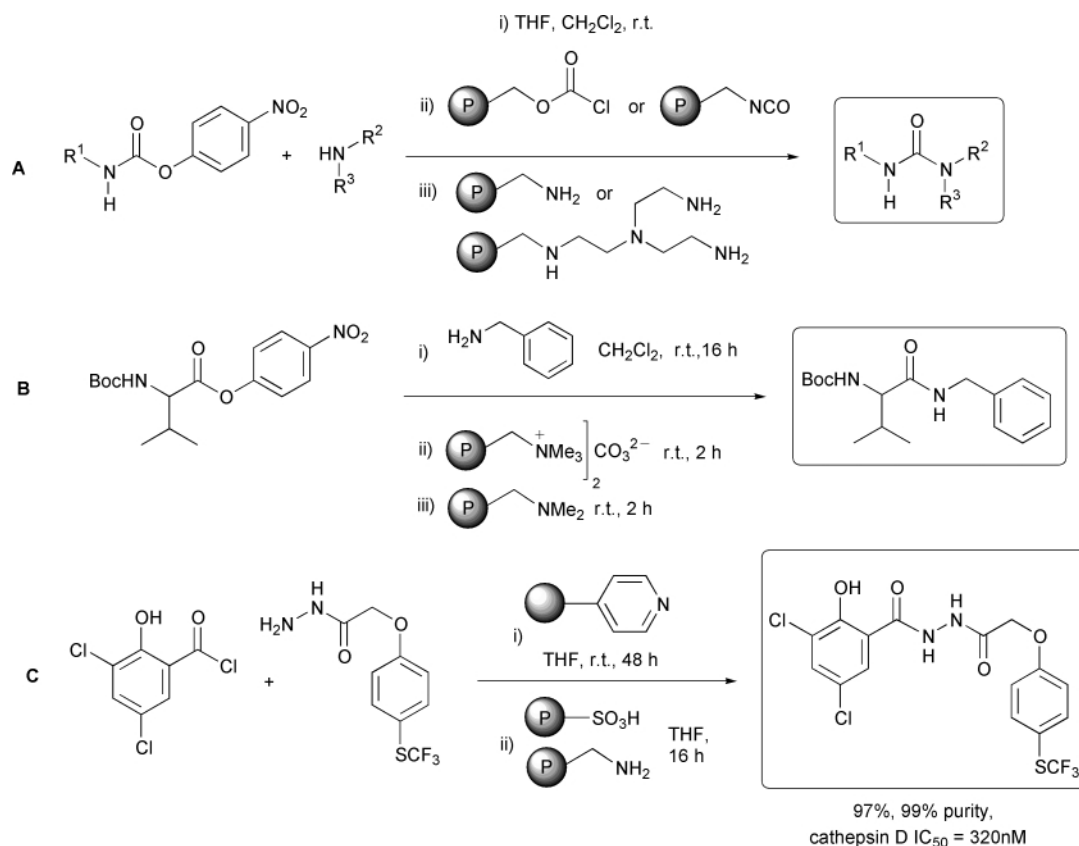
Scheme 27

The Dess–Martin reagent is an important oxidant for the conversion of alcohols to carbonyl compounds under mild conditions. However, the spent or excess reagent can be difficult to remove, often necessitating chromatographic work-up. In an effort to scavenge the by-products and excess oxidant, a new thiosulfate resin has been developed and these oxidations can now be easily incorporated into parallel synthesis programmes.<sup>68</sup> Upon completion of reactions, treatment with thiosulfate resin results in any remaining I(v) and I(III) species being reduced to 2-iodobenzoic acid. This may then be readily removed by a basic scavenger resin (Scheme 29).

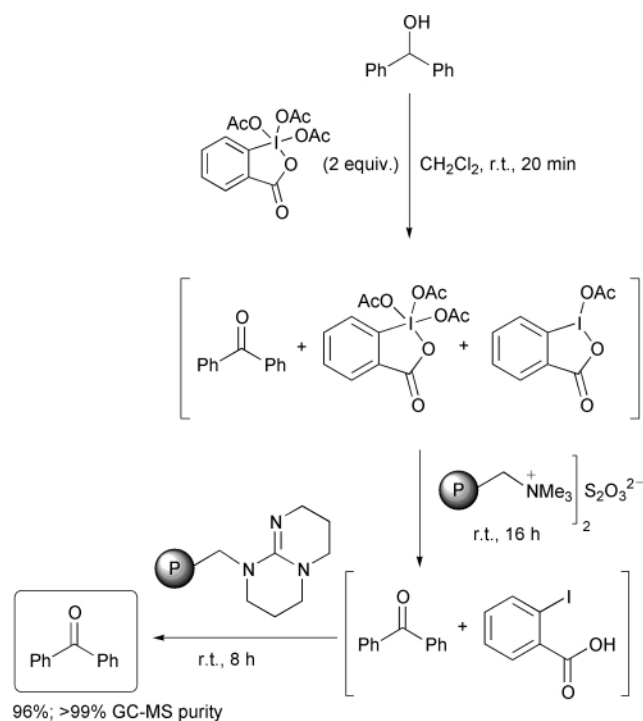
A catch and release strategy has been employed during the preparation of some 1,2,3-thiadiazoles, in yields ranging from 48 to 98%.<sup>69</sup> A Weinreb amide derivative is used as the starting point and reacted with a number of Grignard reagents in order to add diversity. The products are worked-up by protonation with sulfonic acid resin and then captured by addition of a sulfonyl hydrazine functionalised polystyrene resin. The thiadiazoles are then released by a Hurd–Mori reaction with thionyl chloride and filtered through liquid–liquid extraction

cartridges to give the products after solvent evaporation (Scheme 30).

Further multi-step sequences involving polymer-supported reagents and scavengers have also been reported by our group. In the first of these, a route to pyrrole derivatives was developed since these compounds have important medical and agricultural applications.<sup>70</sup> The route begins with the oxidation of readily available alcohols to aldehydes using polymer-supported permanganate (PSM). These are then condensed with nitroalkanes using Amberlite IRA-420 (hydroxide form) to promote a Henry reaction, conditions which were found to be superior to the literature report of Amberlyst A-21 for a similar process.<sup>71</sup> The products were then eliminated to afford nitrostyrene derivatives using trifluoroacetic anhydride followed by triethylamine. Work-up of these reactions was achieved using aminomethylpolystyrene and acidic Amberlyst A-15 as scavengers to give clean products. The pyrrole ring was then constructed by addition of *tert*-butyl isocyanate to the nitrostyrenes in the presence of the polymer-supported guanidine base 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD-P) in tetrahydro-

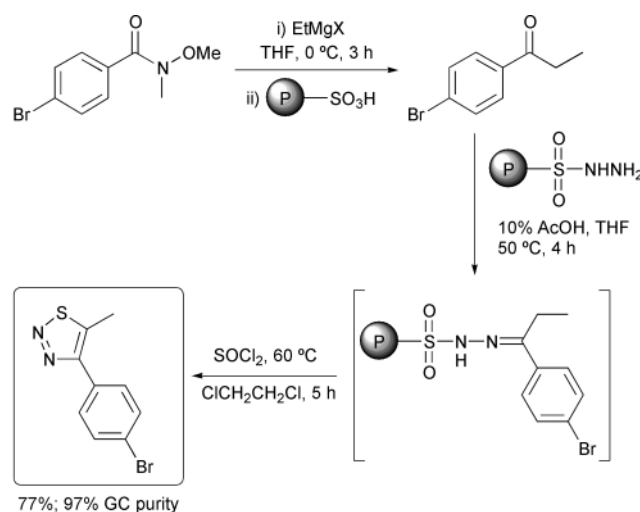


Scheme 28



Scheme 29

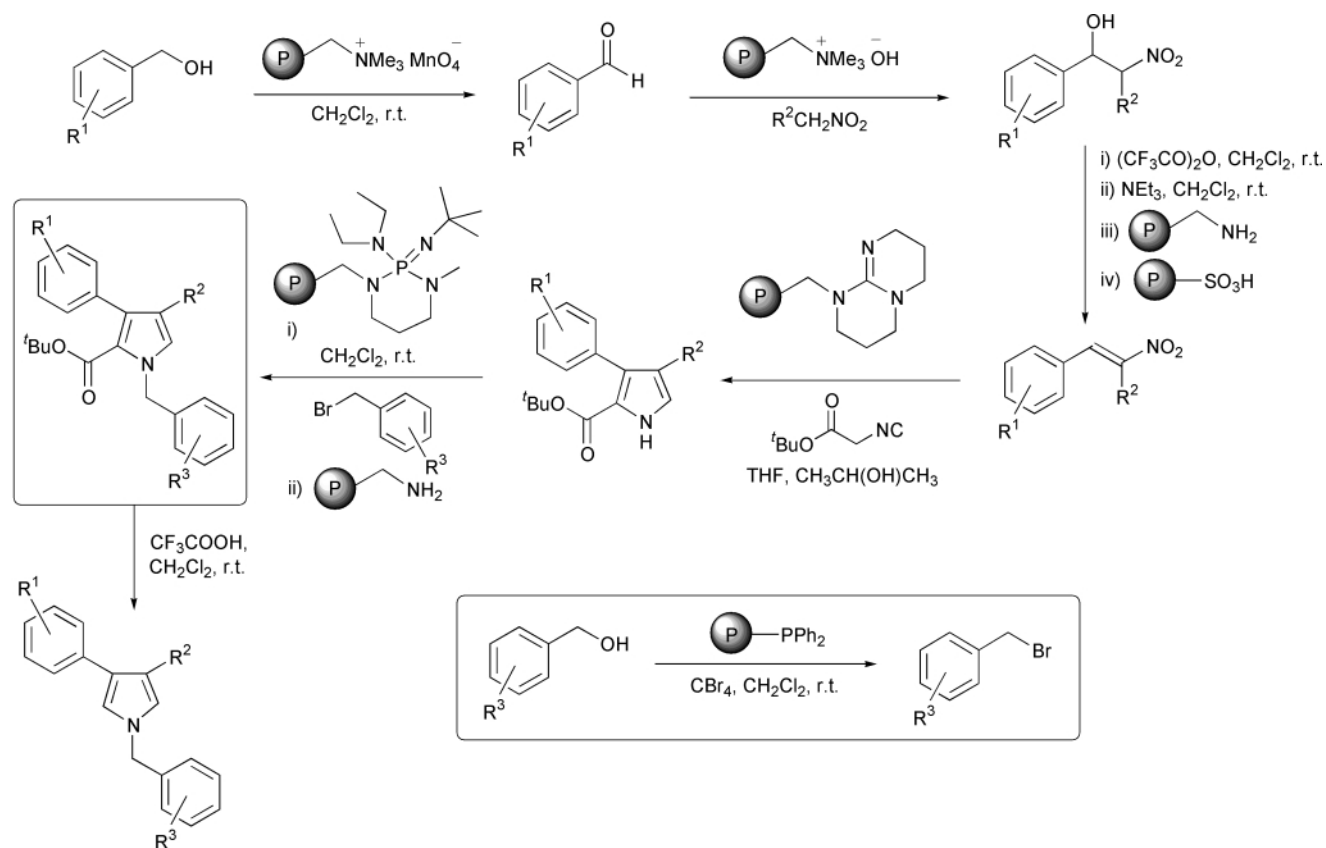
furan and propan-2-ol (Scheme 31). These pyrrole products were further decorated using a polymer-supported phosphazene base to mediate an *N*-alkylation reaction with alkyl halides and excess halide was removed with aminomethyl-polystyrene in the normal way. Importantly, benzylic halides which are not commercially available can be prepared from the corresponding alcohols and carbon tetrabromide with polymer-supported triphenylphosphine, further increasing the potential diversity of this process. Further modification of the product pyrroles is also possible since, upon treatment with trifluoro-



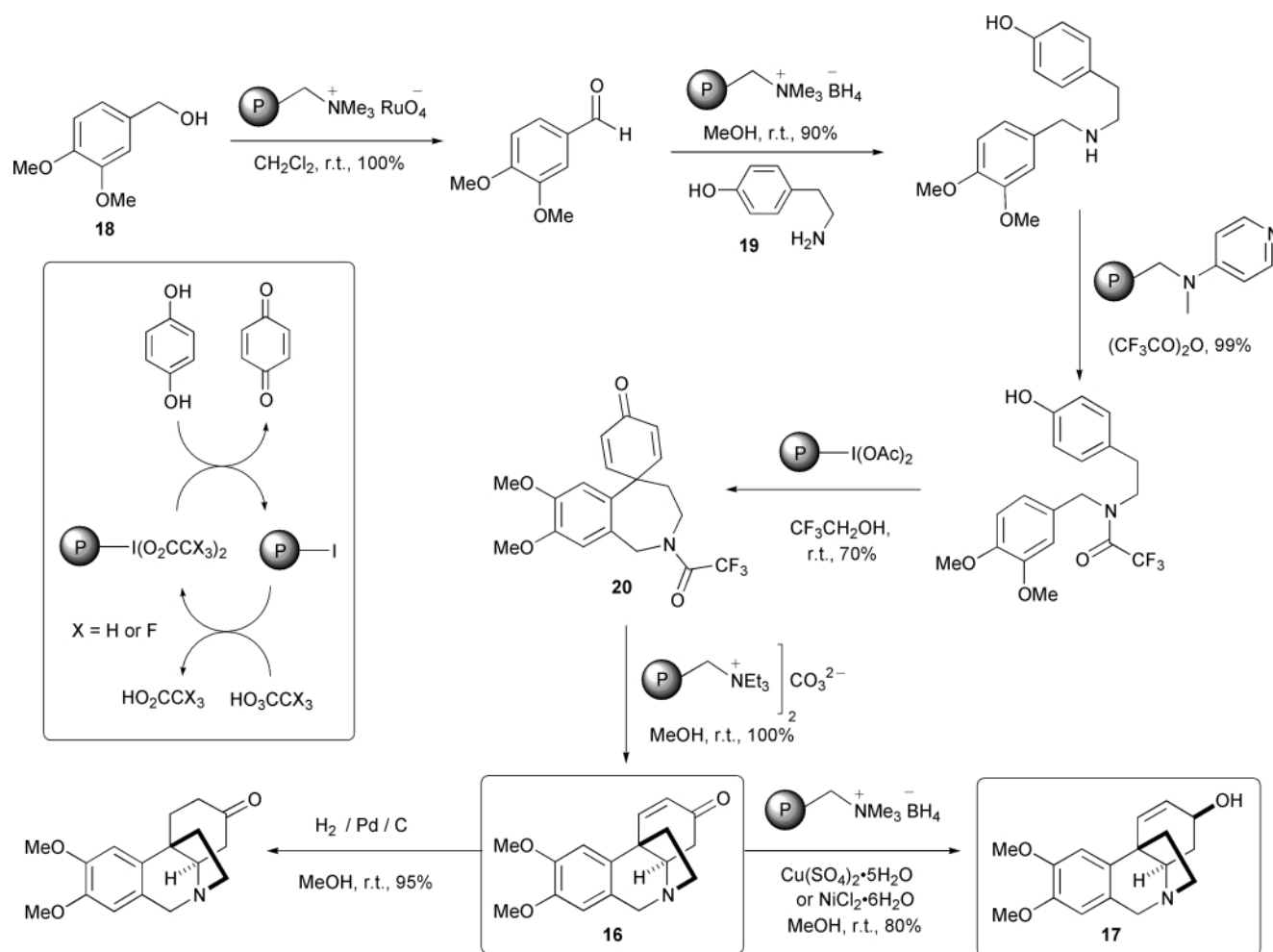
Scheme 30

acetic acid, cleavage of the *tert*-butyl esters occurs followed by *in situ* decarboxylation to give the parent pyrroles (Scheme 31).

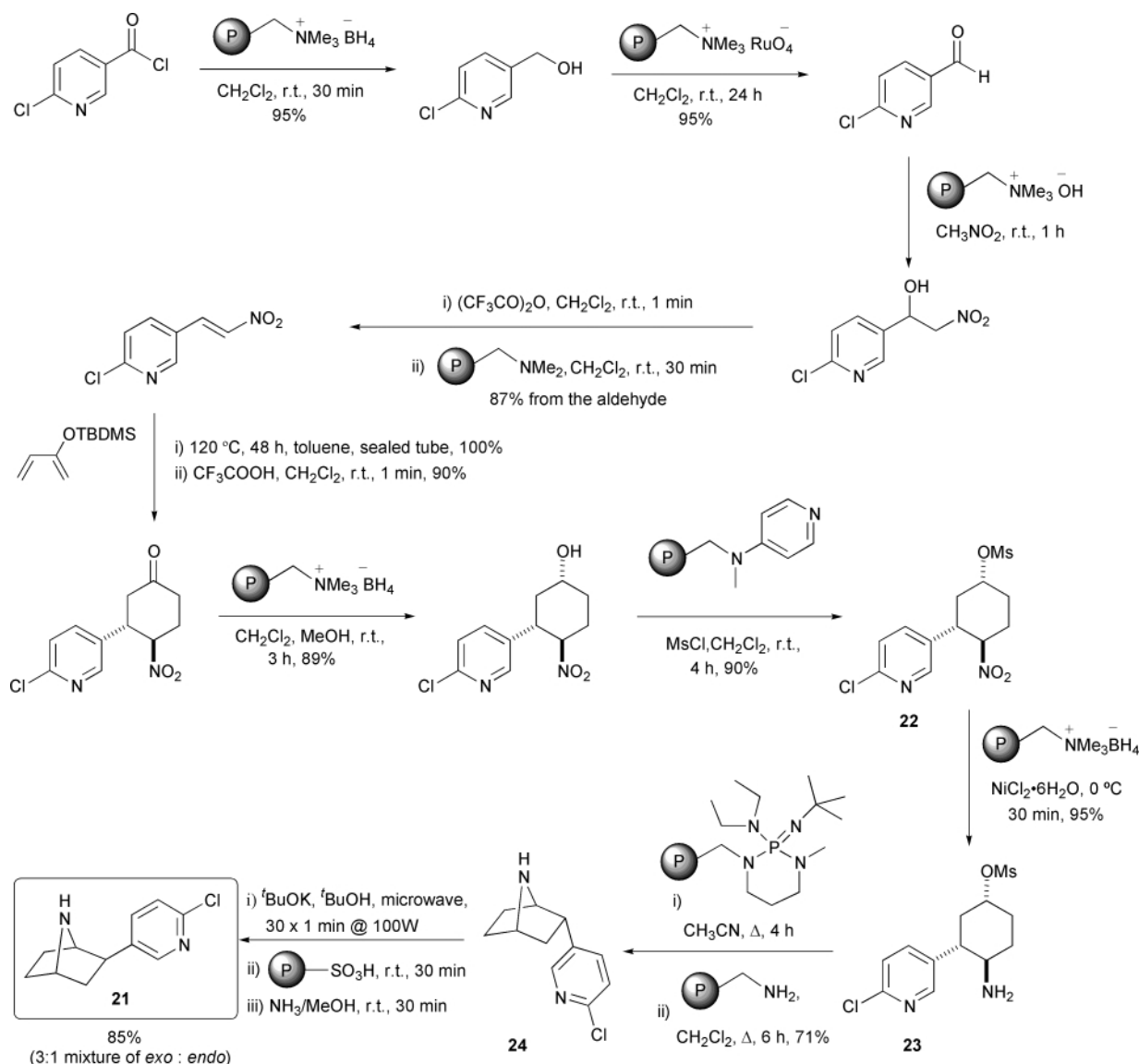
In order to broaden the scope of chemistry amenable to this multi-polymer approach, it is often necessary to develop new immobilised reagents and scavengers or alternatively, to modify existing systems that have been reported in the literature. In keeping with this philosophy, we have developed polymer-supported hypervalent iodine reagents<sup>72</sup> as it was anticipated that the rich, diverse chemistry known for these reagents in solution might translate well to an immobilised variant.<sup>73,74</sup> A range of polymer-supported hypervalent iodine reagents were prepared and characterised and then shown to facilitate a variety of oxidative processes, for example oxidation of hydroquinones to quinones using polymer-supported diacetoxyiodobenzene (PSDIB) (Scheme 32). We attempted to demonstrate the utility of these new polymer-supported tools in the synthesis of natural products. Indeed, in just five or six steps



Scheme 31



Scheme 32

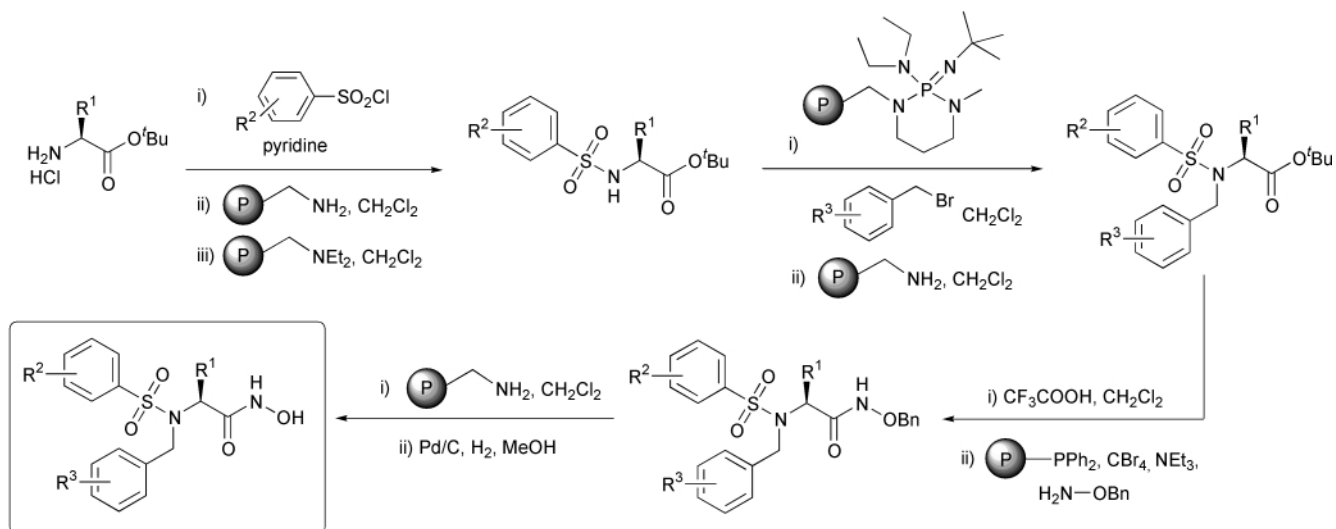


Scheme 33

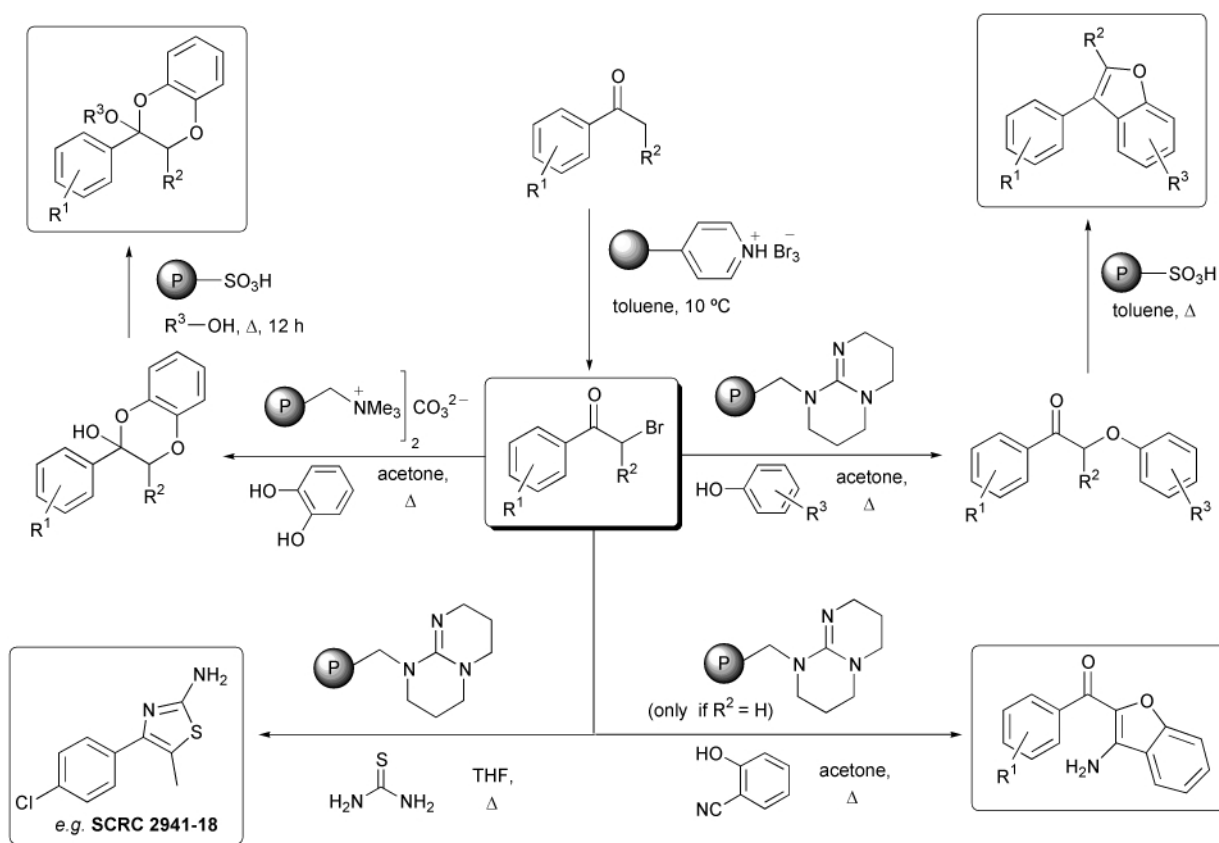
respectively, the syntheses of the alkaloids ( $\pm$ )-oxomaritidine (**16**) and ( $\pm$ )-epimaritidine (**17**) were achieved in high overall yield in a sequence using only polymer-supported reagents.<sup>75</sup> The route begins with polymer-supported perruthenate oxidation of the alcohol (**18**) to provide the corresponding aldehyde in quantitative yield. This in turn is subjected to reductive amination with amine (**19**) using immobilised borohydride and following selective protection of the secondary amino function as the trifluoroacetate, oxidative intramolecular phenolic cyclisation affords the spirodienone (**20**). This oxidation was best achieved using polymer-supported diacetoxyiodobenzene in trifluoroethanol and led directly to the desired *para-para* coupled product in 70% yield with no other products detected by LC-MS. An advantage of this polymer-supported variant is that the iodobenzene by-product is localised on resin and, following removal by filtration, may be conveniently recycled by treatment with peracetic acid, increasing the overall efficiency of this process. Deprotection of (**20**) with polymer-supported carbonate in methanol resulted in spontaneous intramolecular 1,4-addition to give ( $\pm$ )-oxomaritidine (**16**). This in turn could be elaborated to a further natural product ( $\pm$ )-epimaritidine (**17**), by stereoselective reduction with supported borohydride in the presence of a catalytic quantity of nickel(II) chloride or copper sulfate (Scheme 32). These reactions can readily be scaled up and therefore, significant quantities of both intermediates and the natural products can be obtained and used

as starting materials for other combinatorial programmes. Furthermore, the route could also be readily adapted to provide unnatural analogues using this general strategy. What is significant from this work is that only minimal optimisation is required since the route is derived from a known solution-phase synthesis by Kita,<sup>76</sup> but uses complementary polymer-supported reagents to accomplish the same transformations. However, work-up at any stage requires no chromatography or conventional purification methods and rather the product is obtained in high yield and purity only by filtration and solvent removal.

The natural product epibatidine (**21**), which has extraordinarily potent analgesic properties, has also been synthesised using a sequence of polymer-supported reagents (Scheme 33).<sup>77</sup> In this case, no less than *ten* polymer-bound reagents were used to effect the synthesis, including reagents and scavengers together with resin catch and release techniques. Rather than commenting on each individual step, attention is focused on the last few steps of the synthesis. The selective reduction of the aliphatic nitro group of (**22**) was carried out with immobilised nickel boride in the presence of the mesylate and without concomitant reductive dechlorination of the pyridyl ring. The key transannular displacement of mesylate by the amino group of (**23**) proceeded well under dilute conditions in the presence of the polymer-supported phosphazine base P-BEMP and any impurities were conveniently removed by scavenging with



Scheme 34

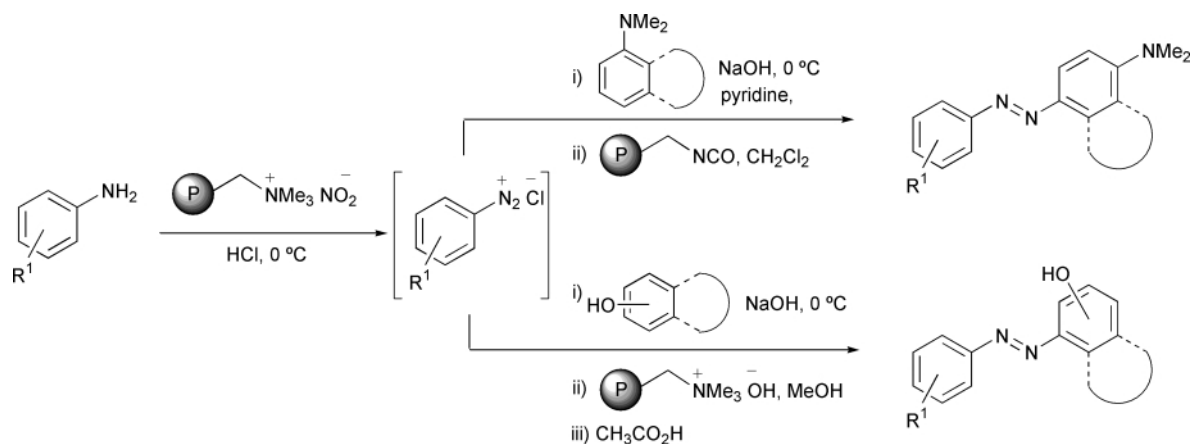


Scheme 35

aminomethyl polystyrene resin. However, the final step in the synthesis, namely the epimerisation of (**24**) to ( $\pm$ )-epibatidine (**21**), required extensive optimisation. It was eventually found that microwave irradiation not only accelerated the reaction considerably, but also shifted the equilibrium in favour of the desired *exo* isomer (**21**) relative to previously reported conditions which gave a 1:1 mixture of *exo* (**21**) and *endo* (**24**) isomers.<sup>78</sup> The amine product was then captured onto a sulfonic acid ion exchange resin (Amberlyst A-15) and washed to remove any non-basic impurities. Finally, treatment of the resin with ammonia in methanol afforded a 3:1 mixture of easily separable *exo* (**21**) and *endo* (**24**) isomers (Scheme 33). This work clearly demonstrates the potential of what may now be possible using polymer-supported species in multi-step organic synthesis.

In an effort to demonstrate the power of these methods when applied to contemporary drug design, the synthesis of an array of potential matrix metalloprotease (MMP) inhibitors has been carried out.<sup>79</sup> A series of amino acid sulfonamides, containing the key hydroxyamino acid feature common to other MMP inhibitors, was prepared using six polymeric reagents and scavengers in succession. Noteworthy in this work is the use of carbon tetrabromide and polymer-supported diphenylphosphine to convert an acid to the reactive acyl bromide *in situ*, prior to formation of the protected hydroxyamino acid (Scheme 34). This procedure has proven to be very reliable and has been used in other synthetic programmes.

Previously, this review has highlighted the fact that  $\alpha$ -bromoketones are attractive precursors for synthesis (Scheme 21) and two recent reports further illustrate their potential.



Scheme 36

Bromination of commercially available acetophenones with polymer-supported pyridinium perbromide proceeded well for an electronically diverse range of examples. Careful control of the reaction temperature is required in order to avoid polybromination but conditions are readily optimised using LC-MS analysis. The resultant  $\alpha$ -bromoketones were then converted to benzofurans by one of two routes (Scheme 35).<sup>80</sup> Reaction with substituted phenols in the presence of solid-supported 1,5,7-triazobicyclo[4.4.0]dec-5-ene (TBD-P) affords the substitution product and, upon treatment with Amberlyst A-15, 3-arylbenzofurans are produced. In an alternative route, reaction of  $\alpha$ -bromoketones with 2-cyanophenol leads directly to 3-aminobenzofurans. In a complementary study it was shown that if these  $\alpha$ -bromoketones were treated with catechols in the presence of a carbonate resin, 1,4-benzodioxanes were produced.<sup>81</sup> These could be further modified upon hemiacetal exchange with alcohols in the presence of an acidic resin (Scheme 35). Also,  $\alpha$ -bromoketones undergo reaction with thiourea in the presence of a polymer-supported guanidinium base to give 2-amino-4-phenyl-1,3-thiazole derivatives. This aspect of the chemistry was used to synthesise a number of compounds including SCRC 2941-18, a compound recently found to inhibit the interleukin-6 (IL-6) induction stimulated by parathyroidal hormone in osteoblastic MC3 T3-E1 cells.

The combination of polymer-supported reagents and scavengers could also find application in materials science programmes. A method for the construction of both phenolic and amino azo-dyes has been reported using a polymer-supported nitrite reagent to effect diazotisation of aromatic amines (Scheme 36). Waste minimisation and operational simplicity are key advantages of polymer-supported reagents in this area.<sup>82</sup>

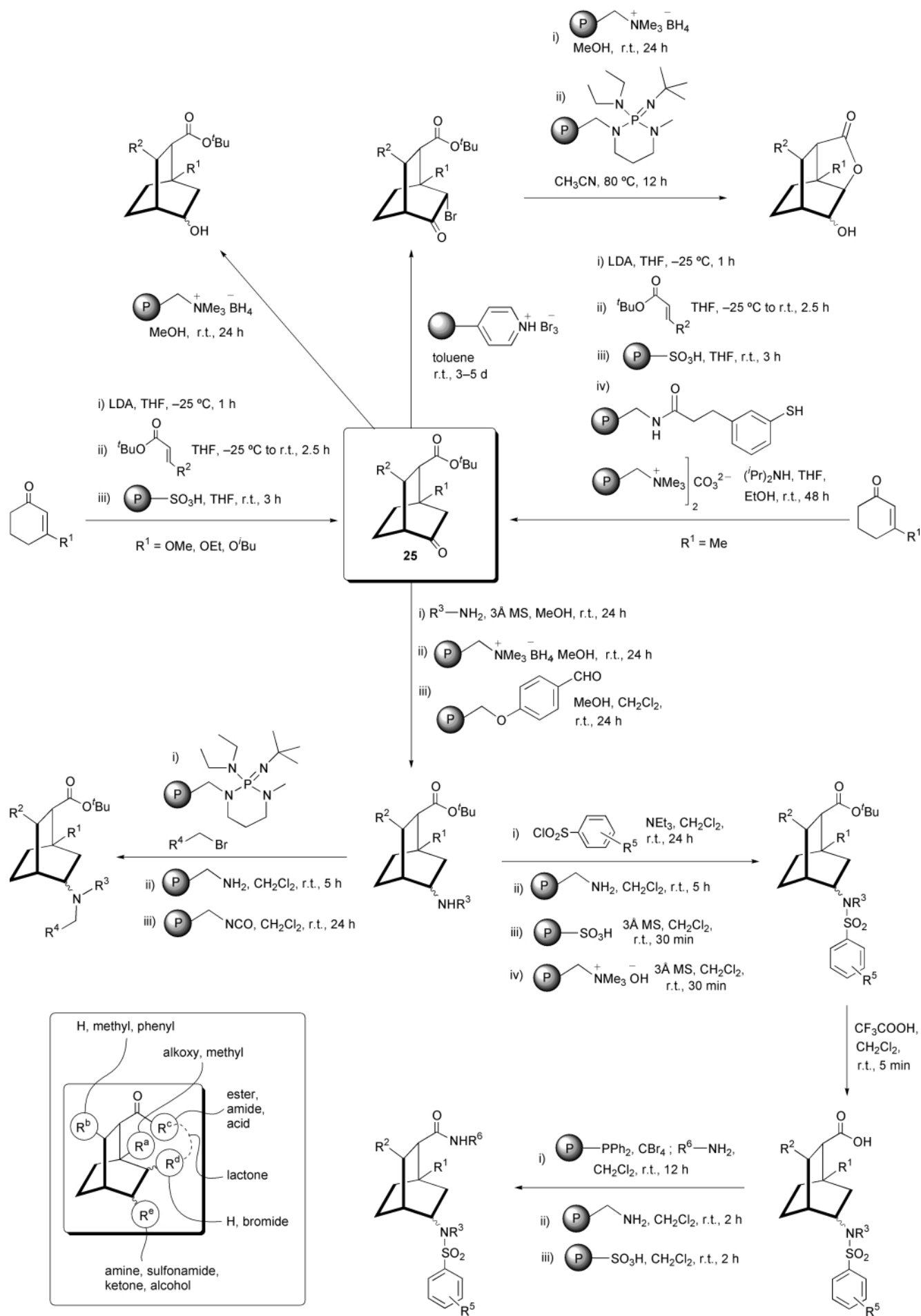
In perhaps the most comprehensive demonstration of the scope of polymer-supported reagents to date, a rigid bicyclo-[2.2.2]octane scaffold (**25**) has been cleanly constructed and subsequently decorated utilising no less than *eleven* different reagents and scavenging resins (Scheme 37).<sup>83</sup> A range of reactions including bromination, ketone reduction, lactonisation, reductive amination, *N*-alkylation, sulfonylation and amide formation were used to alter the functionality at various points on this bicyclic framework. The absence of any conventional work-up or chromatographic purification at any stage during this programme of work significantly reduced the time required to generate library members and suggests considerable potential for the way in which structure-activity relationship studies for example, could be carried out in the future. It is also of considerable interest to note that a structurally similar library was previously constructed using conventional solid-phase organic synthesis on a Wang resin support.<sup>84</sup> In this case however, a significantly less diverse library was generated with a

much greater development time required compared with the routes presented in Scheme 37.

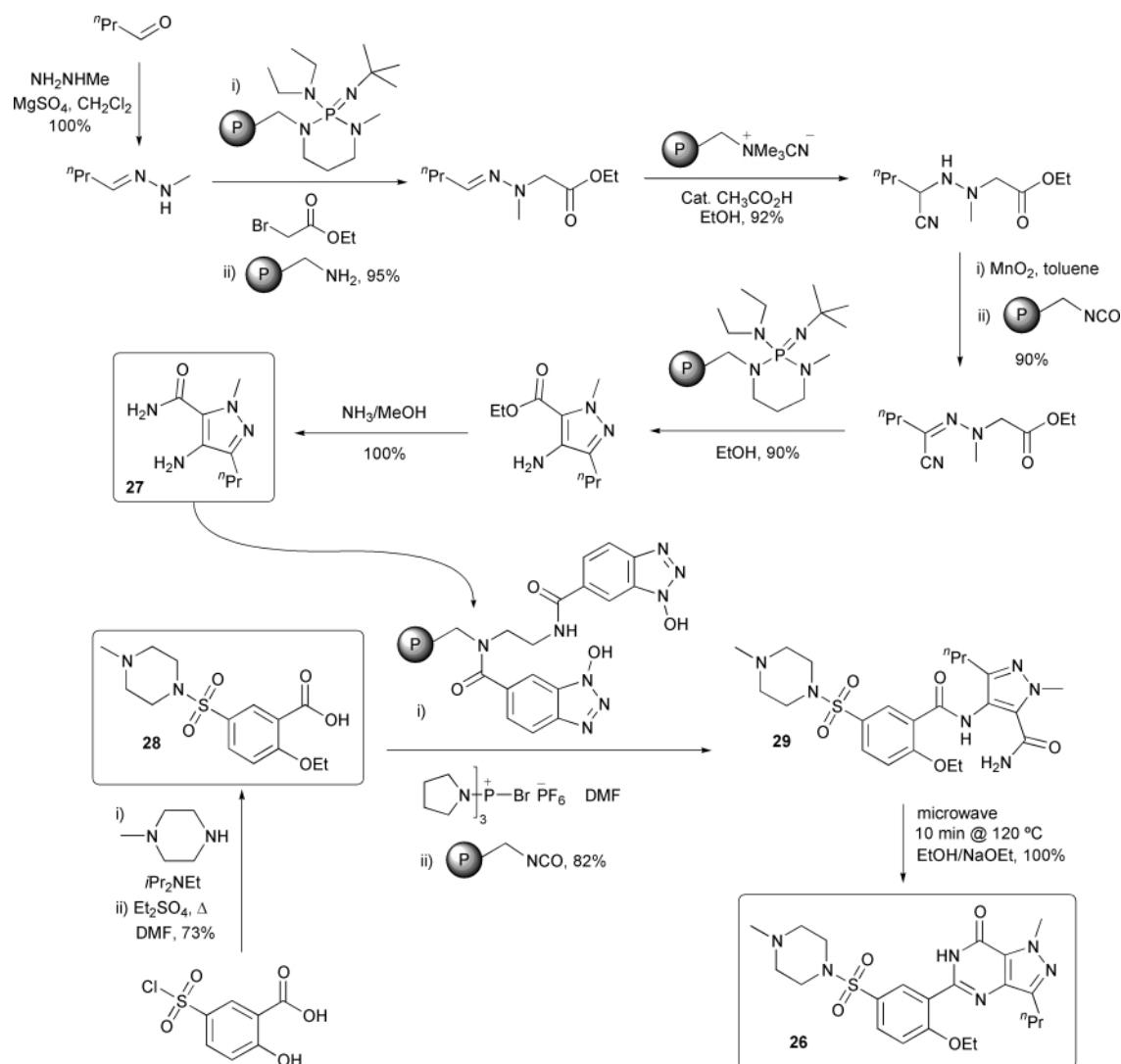
Finally, the synthesis of Sildenafil (**26**) (Viagra<sup>TM</sup>),<sup>85</sup> a potent and selective inhibitor of the enzyme phosphodiesterase type five (PDE-5), has recently been completed by our group (Scheme 38). A key feature of this work is that a convergent synthetic strategy was used. The heterocyclic amine (**27**) was assembled in six steps from readily available *n*-butanal. A polymer-supported hydroxybenzotriazole mediated coupling to the carboxylic acid (**28**) proceeded smoothly in the presence of bromo-trispyrrolidinophosphonium hexafluorophosphate (PyBrOP). This process allows simultaneous activation of the acid (**28**) and purification from ester impurities by simple filtration. Reaction of the resin-bound activated ester with amine (**27**) resulted in amide bond formation with any excess amine being scavenged by polymer-supported isocyanate. Cyclodehydration of (**29**) was then effected using sodium ethoxide under microwave irradiation conditions to afford gram quantities of Sildenafil (**26**) in excellent overall yield.

## 1.8 Conclusions and future perspective

This review has attempted to bring together a large amount of literature data on polymer-supported reagents and scavengers (together with catch and release agents) and also illustrates how they may be utilised in multi-step organic synthesis programmes. These methods are particularly attractive for applications in combinatorial chemistry but their potential is much wider and one can envisage a much greater impact in the future upon the way that organic synthesis is carried out in general. The limitations of *some* of the current technologies, for example the cost of such materials, will undoubtedly change as demand increases. However, improved, higher loading solid-supported reagents and scavengers are required and the potential of alternative supporting materials such as cellulose, mesoporous solids, dendritic systems and aerogels should be fully investigated. The presentation format of the reagents should also be modified so as to have more practically useful devices, particularly for automation, which could include plug-in cartridges and porous pouches for example. New approaches to process-scale synthesis can also be envisaged, perhaps utilising stacked reactors, flow systems and surface immobilised reagents. The development of more catalytic and recyclable systems will also become a priority if these systems are to be properly integrated into reaction scale-up programmes. Due to the importance of these tools for complex, multi-step, molecular assembly, we should therefore expect a rapid development of all of these methods and hence, their increased application in modern organic synthesis programmes.



Scheme 37



Scheme 38

## 2 Introduction to the tables

### 2.1 Organisation of tables (reagent and catalyst section)

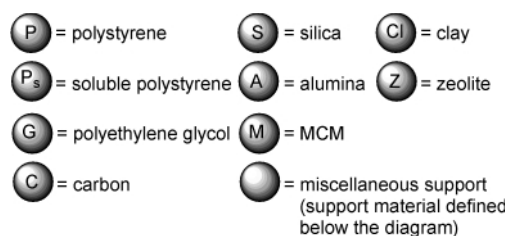
Data entries are generally grouped into tables according to the type of functionality produced. The heading of each table is included in the alphabetical contents for easy reference. Within each individual table, entries are further grouped according to type of reaction (*e.g.* aldol, Diels–Alder, alkylation, palladium coupling) to facilitate comparison of the large amount of available reagents which can be used to carry out these transformations. A miscellaneous section is also included, containing data entries that could not clearly be categorised into the existing tables.

### 2.2 Representative data entry (reagent and catalyst section)

#### Aldehydes/Ketones

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Perruthenate form (1.0-1.3 mmol g <sup>-1</sup> )	 $\text{R}^1\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{O}_2, \text{O}} \text{R}^1\text{CH}_2\text{CHO}$ 23 examples R <sup>1</sup> = alkyl, aryl, pyridyl R <sup>2</sup> = H, alkyl, aryl	Y:56-100	Selectively oxidises primary alcohols to aldehydes without over-oxidation to the respective carboxylic acid.  General procedure.  Used in a multi-step synthesis 1.	2	3

**Reagent:** Diagram of the solid-supported reagent with additional information about the support type (*e.g.* Amberlyst, Amberlite) is shown with the reagent loading given below. The following abbreviations are used for the various types of support:





In cases of supported metal catalysts, unless the coordinated structure is explicitly described in the paper, a blank bead is shown with the metal, oxidation state and support structure defined beneath.

**Transformation:** A diagram of the general reaction scheme with any additional reagents and the number of examples is reported. The type of reactant substitution is also detailed in this section. Specific reaction conditions, *e.g.* solvent and temperature, are not given as in many cases a range of conditions were used.

**Data/%:** A range of yields (Y), conversions (C) or purity (P) is given for the examples reported. Stereochemical information (ee, de) or ratios of products in the case of mixtures is also summarised.

**Comments:** Additional information about the reactions, especially regarding functional group compatibility, stability of the reagent and methods for regenerating or recycling is presented here. General procedure indicates that a sample experimental method is reported either within the main text of the paper, in the reference section or at the end. 'Experimental section' indicates the fact that additional characterisation data is reported and 'Full experimental section' indicates characterisation data is reported for all examples in addition to detailed experimental information. References to additional related reagents or further examples are also included.

**Ref.:** The reference number of the paper (or group of papers) is given.

**Prep. Ref.:** The reference number of a paper detailing the preparation of the solid-supported reagent.

### 2.3 Organisation of Tables (scavenging agents section):

In this section, data entries are grouped according to the type of functionality scavenged. Within the comments section, other functionality that is scavenged by the reagent is included to facilitate the appropriate choice of scavenger.

### 2.4 Representative data entry (scavenging agents section)

#### Alcohols

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: alcohols, alkoxyamines, amidines, carboxylic acids, guanidines, hydrazines, hydroxylamines and thiols.	1	1

## 3 Tables of reagents and catalysts

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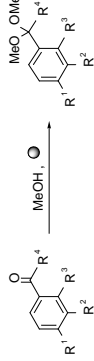

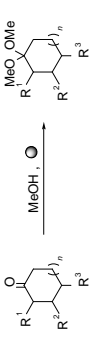

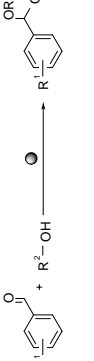



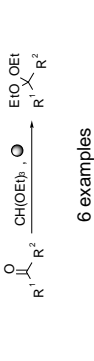
**Multi-step organic synthesis using solid-  
supported reagents and scavengers: a  
new paradigm in chemical library  
generation**

**Tables of reagents and catalysts  
Tables of scavengers**





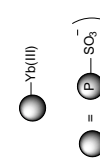

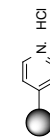

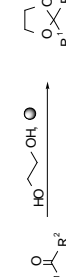

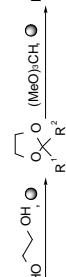
### 3 Tables of reagents and catalysts

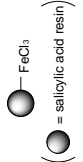



#### 3.1 Acetals and thioacetals

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (0.25 mmol g <sup>-1</sup> )	$  \begin{array}{c}  \text{O} \\  \parallel \\  \text{R}^1-\text{C}-\text{R}^2 \\  \xrightarrow{\text{MeHSi}(\text{OTMS})_2, \text{O}} \\  \text{HO}-\text{C}-\text{R}^1-\text{R}^2  \end{array}  $ 4 examples R <sup>1</sup> = alkyl, benzyl, aryl R <sup>2</sup> = H, alkyl		Polymer could be reused without loss of activity.	86	86
 MCM-41	$  \begin{array}{c}  \text{O} \\  \parallel \\  \text{R}^1-\text{C}-\text{R}^2 \\  \xrightarrow{\text{MeOH}, \text{O}} \\  \text{MeO}-\text{C}-\text{R}^1-\text{R}^2  \end{array}  $ 9 examples R <sup>1</sup> = alkyl, aryl, het R <sup>2</sup> = H, alkyl	Y:18-100	Resin was used without drying prior to reaction. General procedure. Also see reference 87.	88	89
 Nafion-TMS	$  \begin{array}{c}  \text{O} \\  \parallel \\  \text{R}^1-\text{C}-\text{R}^2 \\  \xrightarrow{\text{R}^3\text{OH}, \text{O}} \\  \text{R}^3\text{O}-\text{C}-\text{R}^1-\text{R}^2  \end{array}  $ 2 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl R <sup>3</sup> = alkyl	Y:93-96	Reagent is stable to moisture.	90	91
 PVP (0.91 mmol g <sup>-1</sup> )	$  \begin{array}{c}  \text{O} \\  \parallel \\  \text{R}^1-\text{C}-\text{R}^2 \\  \xrightarrow{\text{R}^3\text{OH}, \text{O}} \\  \text{R}^3\text{O}-\text{C}-\text{R}^1-\text{R}^2  \end{array}  $ 11 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl R <sup>3</sup> = alkyl	Y:27-100	Several polymers investigated. Best results given. Resin was air stable and could be recycled after use. Experimental section.	92	92
 Montmorillonite K 10	$  \begin{array}{c}  \text{O} \\  \parallel \\  \text{R}^1-\text{C}-\text{R}^2 \\  \xrightarrow{\text{MeOH}, \text{O}} \\  \text{MeO}-\text{C}-\text{R}^1-\text{R}^2  \end{array}  $ 5 examples R <sup>1</sup> = alkyl, aryl, het R <sup>2</sup> = H, alkyl	Y:0-100	Experimental section.	93	93

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Montmorillonite K 10	 <p>9 examples</p> <p>R<sup>1</sup> = H, alkyl, Br, Cl, M-alkyl, nitro, O-alkyl            R<sup>2</sup>, R<sup>3</sup> = H, alkyl            R<sup>4</sup> = H, alkyl, aryl</p>	Y:18-99	Acetalisation could be carried out on molecules possessing acid sensitive groups. Experimental section.	93	93
 Montmorillonite K 10	 <p>12 examples</p> <p>R<sup>1</sup> = H, alkyl, Cl            R<sup>2</sup> = H, alkyl            R<sup>3</sup> = H, alkyl, aryl            n = 0, 1, 2, 3</p>	Y:20-95	Acetalisation could be carried out on molecules possessing acid sensitive groups. Order of reactivity for metal ions: Ce <sup>3+</sup> > Fe <sup>2+</sup> , Al <sup>3+</sup> , Zr <sup>4+</sup> >> Zn <sup>2+</sup> , Na <sup>+</sup> . Experimental section.	93	93
 AlCl <sub>3</sub>	 <p>7 examples</p> <p>R<sup>1</sup> = H, aryl, chloro, nitro, O-alkyl            R<sup>2</sup> = alkyl</p>	Y:0-62	General procedure.	94	95
 SO <sub>3</sub> H Amberlyst A-15 Proton form	 <p>3 examples</p> <p>R<sup>1</sup> = alkyl, aryl            R<sup>2</sup> = H, alkyl</p>	Y:98-100	Comparable to montmorillonite K 10. General procedure.	96	
 SO <sub>3</sub> H Amberlyst A-15 Proton form	 <p>6 examples</p> <p>R<sup>1</sup> = alkyl, aryl            R<sup>2</sup> = H, alkyl</p>	Y:62-100	The enol ether was formed if the double bond was conjugated. General procedure. Also see reference 97.	98	

3.1 Acetals and thioacetals—continued


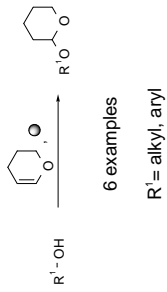

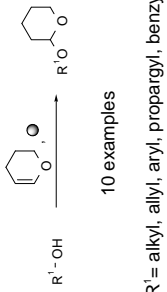

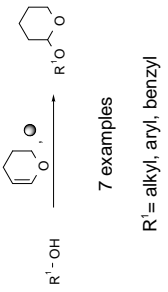

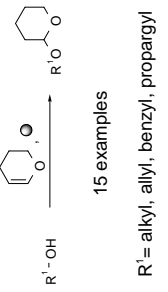

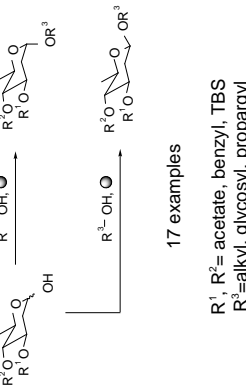
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Nafion-H/ Montmorillonite K 10	 1 example	Y:67	Combination of Nafion and clay worked better than individual components. Also see references 99, 100, 101.	102	102
 Montmorillonite K 10	 10 examples $R^1 = \text{alkyl, aryl}$ $R^2 = \text{H, alkyl, aryl, vinyl}$	Y:91-100	General procedure.	96	
 Amberlyst XN-1010 Ytterbium form (0.76 mmol g <sup>-1</sup> )	 2 examples $R = \text{alkyl, aryl}$	Y:95-100	Also used for aldo and imine condensations. General procedure.	103	103
  (5.1 mmol g <sup>-1</sup> )	 3 examples $R^1 = \text{alkyl}$ $R^2 = \text{H, alkyl}$	Y:62-96	Acetalisation could be carried out in the presence of acid sensitive functionality. Experimental section. Also see references 104, 105.	105	105
 Na <sup>+</sup> exchanged zeolites	 10 examples $R^1 = \text{alkyl, aryl, benzyl}$ $R^2 = \text{H, alkyl}$	Y:38-96	Hydrolytic cleavage of acetals was also described. (Y:71-97%) Kinetic study. Experimental section.	106	106

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Salicylic acid resin	$  \begin{array}{c}  \text{O} \\  \parallel \\  \text{R}^1-\text{C}-\text{R}^2 \\  \xrightarrow{\text{HO}-\text{CH}_2-\text{OH}} \\  \text{O} \\  \parallel \\  \text{R}^1-\text{C}-\text{O}-\text{CH}_2-\text{CH}_2-\text{OH} \\  \text{R}^1, \text{R}^2 = \text{alkyl}  \end{array}  $ 10 examples	Y:41-99	Also used as a catalyst for esterification reactions.	107	107
Hydrous Zirconium Oxide	$  \begin{array}{c}  \text{O} \\  \parallel \\  \text{R}^1-\text{C}-\text{R}^2 \\  \xrightarrow{\text{HO}-\text{CH}_2-\text{OH}} \\  \text{O} \\  \parallel \\  \text{R}^1-\text{C}-\text{O}-\text{CH}_2-\text{CH}_2-\text{OH} \\  \text{R}^1 = \text{alkyl, aryl} \\  \text{R}^2 = \text{H, alkyl, vinyl}  \end{array}  $ 13 examples	Y:15-98	General procedure.	108	108
 Envirocat EPZG	$  \begin{array}{c}  \text{O} \\  \parallel \\  \text{R}^1-\text{C}-\text{R}^2 \\  \xrightarrow{\text{HO}-\text{C(CH}_3)_2-\text{OH}} \\  \text{O} \\  \parallel \\  \text{R}^1-\text{C}-\text{O}-\text{C(CH}_3)_2-\text{OH} \\  \text{R}^1 = \text{H, alkyl} \\  \text{R}^2 = \text{aryl, furyl}  \end{array}  $ 11 examples	Y:80-98	Acid catalyst which exhibited both Bronsted and Lewis acid characteristics. General procedure. Also see references 109, 110, 111, 112, 113.	114	
 Envirocat EPZG	$  \begin{array}{c}  \text{O} \\  \parallel \\  \text{R}^1-\text{C}-\text{R}^2 \\  \xrightarrow{(\text{MeCO})_2\text{O}} \\  \text{O} \\  \parallel \\  \text{R}^1-\text{C}-\text{O}-\text{C(CH}_3)_2-\text{OAc} \\  \text{R}^1 = \text{alkyl, aryl, het}  \end{array}  $ 11 examples	Y:69-99	General procedure.	115	
 $\text{H}_2\text{SO}_4$	$  \begin{array}{c}  \text{OH} \\    \\  \text{R}^1-\text{C}-\text{R}^2 \\  \xrightarrow{\text{C}_6\text{H}_5\text{O}-\text{R}^3} \\  \text{O} \\    \\  \text{R}^1-\text{C}-\text{O}-\text{C}_6\text{H}_5 \\  \text{R}^1 = \text{alkyl, alkynyl, allyl, cholesteryl} \\  \text{R}^2 = \text{alkyl, cholesteryl} \\  \text{R}^3 = \text{H, alkyl}  \end{array}  $ 11 examples	C:93-100	Also successful with phenols. Experimental section.	116	116


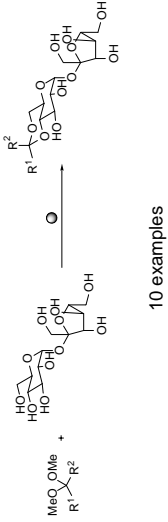
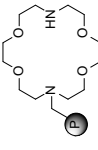
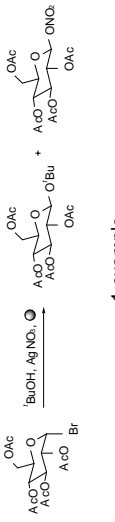
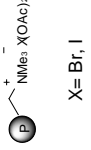
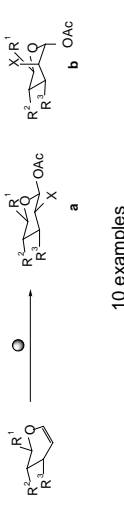
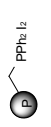
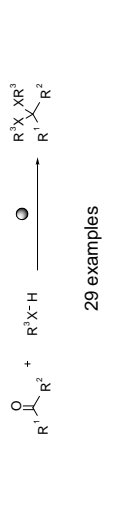
3.1 Acetals and thioacetals—continued

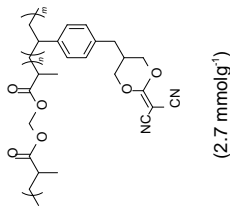


Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Reillex 425 HCl (5.0 mmol g <sup>-1</sup> )	 9 examples R <sup>1</sup> = alkyl, aryl, benzyl	Y:84-98	Resin could be reused without regeneration of acid function. General procedure.	104	104
 Amberlyst A-15 Proton form	 13 examples R <sup>1</sup> = alkyl, aryl	Y:90-98	Worked on sterically hindered substrates. General procedure.	117	
 Dowex 50W x2 Proton form	 23 examples R <sup>1</sup> , R <sup>2</sup> = H, alkyl n = 0-9	Y:64-96	Resin must be wet in order to achieve good selectivity of mono over di-protection. General procedure.	118	
 Nafion-H	 11 examples R <sup>1</sup> = alkyl, benzyl	Y:50-97	Dihydro-4H-pyran must be added slowly to alcohol and Nafion to prevent polymerization. General procedure.	119	
 Envirocat EPZG	 13 examples R <sup>1</sup> = alkyl, allyl, aryl, benzyl	Y:76-99	The clay exhibited both Bronsted and Lewis acid characteristics. General procedure. Montmorillonite K 10 may also be used. <sup>120</sup>	109	




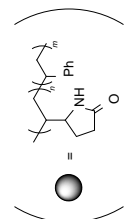

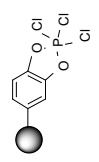

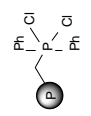
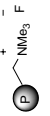
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 MCM-41	 <p>6 examples R<sup>1</sup> = alkyl, aryl</p>	C:64-99	Reagent could be reactivated and reused. General procedure.	121	121
 Kaolinitic clay	 <p>10 examples R<sup>1</sup> = alkyl, allyl, aryl, propargyl, benzyl</p>	Y:0-91	Yields were generally >80%. Phenol failed to react.	122	123
 Spanish Sepiolite Clay	 <p>7 examples R<sup>1</sup> = alkyl, aryl, benzyl</p>	Y:27-99	Silica and alumina supports were unsuccessful.	124	
	 <p>15 examples R<sup>1</sup> = alkyl, allyl, benzyl, propargyl</p>	Y:75-90	Reagent could be reactivated and reused. Reagent was stored under N <sub>2</sub> . General procedure. Alumina could also be used as a catalyst. <sup>126</sup>	126	126
 Montmorillonite K 10	 <p>17 examples R<sup>1</sup>, R<sup>2</sup> = acetate, benzyl, TBS R<sup>3</sup> = alkyl, glycosyl, propargyl</p>	Y:21-96	Use of 3-O-Ac-4-O-TBS (R <sup>1</sup> = OAc, R <sup>2</sup> = TBS) gave the corresponding α-product in high selectivity. Use of 4-O-Ac-3-O-TBS gave preferentially the corresponding β-anomer. General procedure given.	127	

### 3.1 Acetals and thioacetals—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-15W Ytterbium form	 10 examples $R^1 = \text{aryl, vinyl}$ $R^2 = \text{H, alkyl}$	Y:8-80	Several lanthanide exchange resins were investigated. Experimental section.	128	128 103
 (0.2-0.5 mmol g <sup>-1</sup> )	 1 example	Y:75-95	Several polymers investigated. Yield and product ratio depended on the type of polymer. Experimental section.	129	129
 $X = \text{Br, I}$	 10 examples $R^1 = \text{alkyl}$ $R^2, R^3 = \text{ether, ester}$ $X = \text{Br, I}$	Y:71-98	Reagent stable below 0 °C for weeks. Thirteen more examples of 1,2-haloacetoxylation of simple alkenes can be found in reference. The ratio of products (a:b) ranged between 4.2:1 and 1.2:5. General procedure.	130, 131	130
 (1.2 mmol g <sup>-1</sup> )	 29 examples $R^1 = \text{alkyl, aryl}$ $R^2 = \text{H, alkyl, aryl}$ $R^3 = \text{alkyl}$ $X = \text{O, S}$	Y:80-98	Both cyclic and acyclic acetals could be synthesised using this procedure. Experimental section.	132	132

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>(2.7 mmol g<sup>-1</sup>)</p>	$\begin{matrix} R^2 \\ \diagup \\ X \\ \diagdown \\ R^1 \end{matrix} \begin{matrix} OMe \\ OMe \end{matrix} \xrightarrow{PhSX, O} \begin{matrix} R^2 \\ \diagup \\ X \\ \diagdown \\ R^1 \end{matrix} \begin{matrix} OMe \\ SPh \end{matrix}$ <p>7 examples  R<sup>1</sup> = alkyl, aryl  R<sup>2</sup> = H, alkyl  X = H, SiMe<sub>3</sub></p>	Y:14-88	Good selectivity for monothioacetalisation was observed. General procedure.	133	133
 <p>Nafion-H</p>	$\begin{matrix} R^1 \\ \diagup \\ O \\ \diagdown \\ R^2 \end{matrix} \begin{matrix} OR^3 \\ R^3 \end{matrix} \xrightarrow{HS-CH_2-CH_2-SH, O} \begin{matrix} R^1 \\ \diagup \\ O \\ \diagdown \\ R^2 \end{matrix} \begin{matrix} S \\ R^3 \end{matrix}$ <p>14 examples  R<sup>1</sup> = alkyl  R<sup>2</sup> = alkyl, aryl  R<sup>3</sup> = H, alkyl, aryl</p>	Y:75-98	Catalyst could be regenerated and reused. General procedure. Also see reference 99.	134	
 <p>Montmorillonite K 10</p>	$\begin{matrix} O \\ \parallel \\ R^2 \\   \\ \text{C}_6\text{H}_4 \\   \\ R^1 \end{matrix} \xrightarrow{(MeO)_2HC-CH(O)Me_2} \begin{matrix} O \\ \parallel \\ R^2 \\   \\ \text{C}_6\text{H}_4 \\   \\ R^1 \end{matrix} \begin{matrix} CH(O)Me_2 \\ R^2 \end{matrix}$ <p>3 examples  R<sup>1</sup> = H, O-alkyl  R<sup>2</sup> = H, alkyl</p>	Y:83-86	Both Ti <sup>3+</sup> and Ti <sup>4+</sup> that were generated during the reaction were tightly bound to the support. Various inorganic supports were tried but the acidic K 10 was the best one. Reagent was stable and could be stored for months.	135	135

### 3.2 Acyl and sulfonyl halides

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
  (3.2 mmol g <sup>-1</sup> )	$\text{R}^1-\text{C}(=\text{O})\text{Cl} \xrightarrow{\bullet} \text{R}^1-\text{C}(=\text{O})\text{F}$ <p>5 examples R<sup>1</sup> = alkyl, aryl, benzyl</p>	Y:71-100	Reagent had comparable reactivity to KF on CaF <sub>2</sub> and was much more reactive than KF alone.	136	136
 (2.5 mmol g <sup>-1</sup> )	$\text{R}^1-\text{C}(=\text{O})\text{OH} \xrightarrow{\text{CCl}_4, \bullet} \text{R}^1-\text{C}(=\text{O})\text{Cl}$ <p>8 examples R<sup>1</sup> = alkyl, aryl</p>	Y:50-90	Products isolated as aryl chloride derivatives. General procedures.	137	137
 (3.9 mmol g <sup>-1</sup> )	$\text{R}^1-\text{C}(=\text{O})\text{OR}^2 \xrightarrow{\bullet} \text{R}^1-\text{C}(=\text{O})\text{Cl}$ <p>3 examples R<sup>1</sup> = alkyl R<sup>2</sup> = H, O-acetyl</p>	Y:8-35	Reagent could be recycled by treatment with PCl <sub>5</sub> . Experimental section.	138	138
 Amberlite IRA-93 (2.0 mmol g <sup>-1</sup> )	$\text{R}^1-\text{C}(=\text{O})\text{OH} \xrightarrow{\text{CCl}_4, \bullet} \text{R}^1-\text{C}(=\text{O})\text{Cl}$ <p>9 examples R<sup>1</sup> = alkyl, aryl, alkenyl</p>	Y:48-91	Phosphorus by-products retained on polymer. General procedure.	139	139
	$\text{R}^1-\text{C}(=\text{O})\text{OH} \xrightarrow{\bullet} \text{R}^1-\text{C}(=\text{O})\text{Cl}$ <p>4 examples R<sup>1</sup> = aryl, benzyl</p>	Y:87-100	Kinetic studies. Experimental section.	140	140
 BIO-RAD AG1-X10	$\text{R}^1-\text{S}(=\text{O})_2\text{Cl} \xrightarrow{\bullet} \text{R}^1-\text{S}(=\text{O})_2\text{F}$ <p>8 examples R<sup>1</sup> = aryl</p>	Y:71-94	Reaction could be carried out on a multi-gram scale. General procedures.	141	141

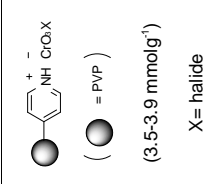
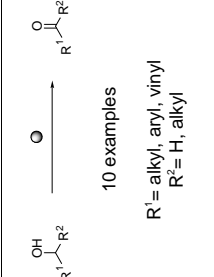
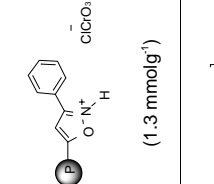
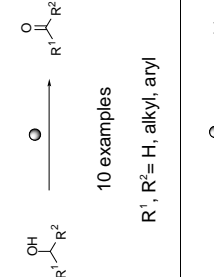
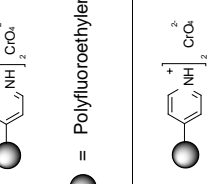
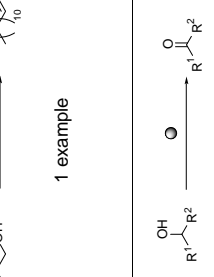
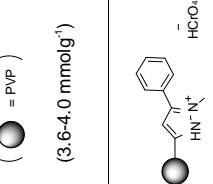
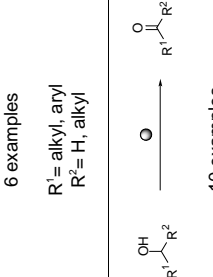
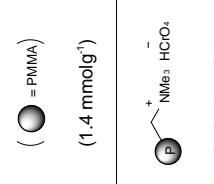
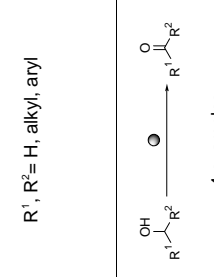

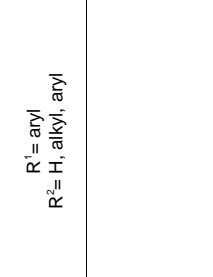
### 3.3 Aldehydes/ketones

#### 3.3.1 Aldehydes/ketones (From alcohols with Cr based oxidants)

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
  (0.50-0.60 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{O}} \text{R}^1-\text{C}(=\text{O})-\text{R}^2$ <p>22 examples            R<sup>1</sup> = alkyl, aryl, vinyl            R<sup>2</sup> = H, alkyl</p>	Y:62-81	Convenient procedure for the oxidation of 2° alcohols to ketones. Experimental section. Also see references 142, 143.	144	144
 (0.50-0.60 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{O}} \text{R}^1-\text{C}(=\text{O})-\text{R}^2$ <p>11 examples            R<sup>1</sup> = alkyl, aryl, vinyl            R<sup>2</sup> = H, alkyl</p>	Y:75-95	Catalyst is stable to air and will also oxidise α-keto alcohols.	145	145
 (1.4 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{MW, O}} \text{R}^1-\text{C}(=\text{O})-\text{R}^2$ <p>12 examples            R<sup>1</sup> = alkyl, aryl            R<sup>2</sup> = H, acyl, alkyl, aryl</p>	Y:85-97	Reaction rates enhanced by microwave irradiation. Experimental section.	146	146
 (1.4 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{O}} \text{R}^1-\text{C}(=\text{O})-\text{R}^2$ <p>4 examples            R<sup>1</sup> = alkyl, aryl            R<sup>2</sup> = H, alkyl, aryl</p>	Y:30-90	A variety of solvents were tested. The reagent was stable at room temperature but showed some loss of activity upon regeneration. Experimental section.	147	147
 (1.3 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{O}} \text{R}^1-\text{C}(=\text{O})-\text{R}^2$ <p>5 examples            R<sup>1</sup> = alkyl, aryl            R<sup>2</sup> = H, alkyl, aryl</p>	Y:65-90	Experimental section.	147	147

3.3.1 Aldehydes/ketones (From alcohols with Cr based oxidants)—continued




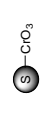

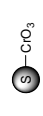
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Chlorochromate form (2.3 mmol g <sup>-1</sup> )	 5 examples R <sup>1</sup> = alkyl, aryl, vinyl R <sup>2</sup> = H, alkyl	Y:73-98	A range of supports and chromates were investigated. The most effective is shown. The reagent is suitable for allylic alcohols and may be regenerated post-reaction. Experimental section.	148	148
 (0.80 mmol g <sup>-1</sup> )	 1 example	Y:67	The reagent was not acidic enough to cleave the THP group. Experimental section.	149	150
	 8 examples R <sup>1</sup> = alkyl, aryl, vinyl R <sup>2</sup> = H, alkyl	Y:45-98	General procedure.	151	152
 ( = PVP )	 1 example	Y:5-80	A variety of different polymer-supports were investigated. General experimental procedures.	153	153
 ( = PVP ) (2.7-2.9 mmol g <sup>-1</sup> ) X = Br, Cl, F	 7 examples R <sup>1</sup> = alkyl, aryl, vinyl R <sup>2</sup> = H, aryl	Y:80-96	No over-oxidation of primary alcohols was observed. Spent reagent may be regenerated. General procedure.	154	154
	 13 examples R <sup>1</sup> = alkyl, aryl, vinyl R <sup>2</sup> = H, alkyl	Y:56-92	Experimental section.	155	155

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 ( = PVP ) (3.5-3.9 mmol g <sup>-1</sup> ) X = halide	 10 examples R <sup>1</sup> = alkyl, aryl, vinyl R <sup>2</sup> = H, alkyl	Y:61-100	No over-oxidation observed. Reagent may be regenerated and reused. General procedure.	151	151
 (1.3 mmol g <sup>-1</sup> )	 10 examples R <sup>1</sup> , R <sup>2</sup> = H, alkyl, aryl	Y:80-88	Similar resins were also used. The best example is shown. The reagent may be regenerated without loss of activity. Experimental section.	156	156
 ( = Polyfluoroethylene )	 1 example	Y:96	Several other resins were tested. The best example is shown.	157	157
 ( = PVP ) (3.6-4.0 mmol g <sup>-1</sup> )	 6 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl	C:82-100	Reagent can be regenerated. Experimental section. Also see references 152, 158.	159	159
 ( = PMMA ) (1.4 mmol g <sup>-1</sup> )	 10 examples R <sup>1</sup> , R <sup>2</sup> = H, alkyl, aryl	Y:80-88	A range of resins were tested. The best example is shown. The reagent could be regenerated without loss of activity. Experimental section.	160, 161	160, 161
 Amberlyst A-26 Chromate form	 4 examples R <sup>1</sup> = aryl R <sup>2</sup> = H, alkyl, aryl	Y:80-100	The reagent successfully oxidises benzylic alcohols to aldehydes without further oxidation to the carboxylic acids. Polar solvents gave better results. General procedure. Also see reference 162.	163	163





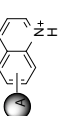
3.3.1 Aldehydes/ketones (From alcohols with Cr based oxidants)—continued

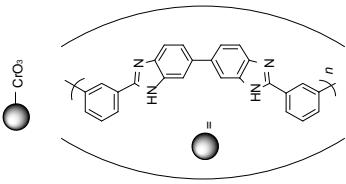
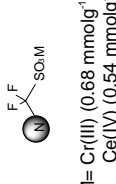
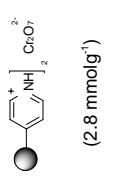
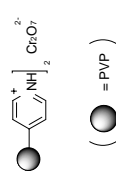
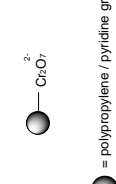
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Chromate form (3.8 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\bullet} \text{R}^1-\text{C}(\text{O})-\text{R}^2$ <p>15 examples                      R<sup>1</sup>, R<sup>2</sup>= H, alkyl, aryl, vinyl</p>	Y:73-98	Reactions were fastest for allylic and benzylic alcohols. The reagent is stable in air at room temperature for several weeks. General procedures.	164	164
 (4.3 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\bullet} \text{R}^1-\text{C}(\text{O})-\text{R}^2$ <p>4 examples                      R<sup>1</sup>= H, alkyl, Ph                      R<sup>2</sup>= H, Cl</p>	Y:69-80	General procedure.	165	166
 (2.0 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\bullet} \text{R}^1-\text{C}(\text{O})-\text{R}^2$ <p>5 examples                      R<sup>1</sup>= H, alkyl, aryl</p>	Y:74-90	Reagent may be stored under vacuum and in the dark for several weeks without loss of activity. General procedure.	167	167
 (3.7 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\bullet} \text{R}^1-\text{C}(\text{O})-\text{R}^2$ <p>10 examples                      R<sup>1</sup>, R<sup>2</sup>= H, alkyl, aryl</p>	Y:90-96	Reagent may be regenerated. Experimental section.	168	168
 (4.1 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\bullet} \text{R}^1-\text{C}(\text{O})-\text{R}^2$ <p>10 examples                      R<sup>1</sup>, R<sup>2</sup>= H, alkyl, aryl</p>	Y:90-98	Reagent may be regenerated. Optimisation studies are described. Experimental section.	169	169



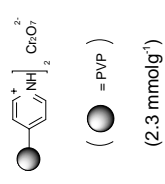
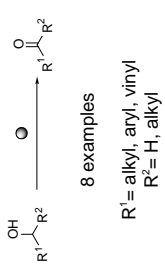
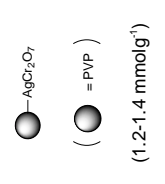
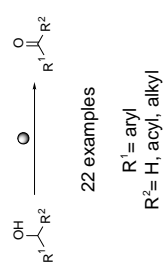
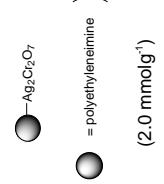
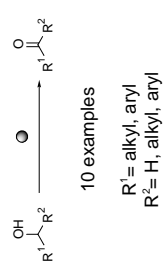
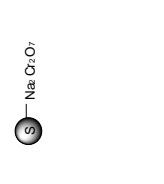
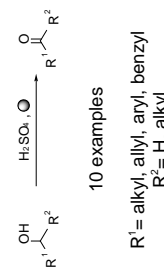
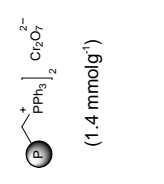
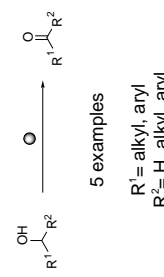
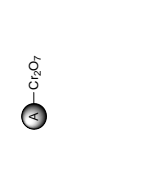
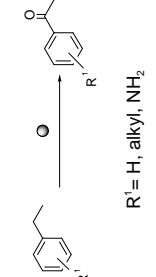
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (2.0-2.5 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{O}} \text{R}^1-\text{C}(=\text{O})-\text{R}^2$ 10 examples R <sup>1</sup> , R <sup>2</sup> = H, alkyl, aryl	Y:87-94	No over-oxidation of aldehydes to carboxylic acids was observed. The effects of altering the spacer were studied. Experimental section.	170	170
 (1.7 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{O}_2 \text{ or TBHP, A}} \text{R}^1-\text{C}(=\text{O})-\text{R}^2$ 17 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl, aryl	Y:80-97	The reagent can be stored without significant loss of activity. Experimental section. Magtrieve may also be used. <sup>71</sup>	172	172
 (0.29 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{O}_2 \text{ or TBHP, A}} \text{R}^1-\text{C}(=\text{O})-\text{R}^2$ 5 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl	C:26-78	Primary benzylic alcohols were partially over-oxidised to their carboxylic acids. General procedure.	173	173
 (1.0 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{O}_2} \text{R}^1-\text{C}(=\text{O})-\text{R}^2$ 1 example	Y:52	The reagent works best if prepared fresh. Stable <i>in vacuo</i> and in the dark for one week. Full experimental section.	174	174
	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{O}_2, \text{ MW, A}} \text{R}^1-\text{C}(=\text{O})-\text{R}^2$ 9 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl, aryl	Y:72-90	Reactions carried out in the absence of solvent.	175	175
 (2 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{O}_2} \text{R}^1-\text{C}(=\text{O})-\text{R}^2$ 7 examples R <sup>1</sup> = alkyl, aryl, vinyl R <sup>2</sup> = H, alkyl	Y:46-85	No over-oxidation of aldehydes to acids observed. The reagent is stable to storage in a desiccator for two months. General procedure.	176	176

3.3.1 Aldehydes/ketones (From alcohols with Cr based oxidants)—continued

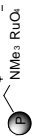
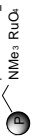

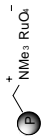
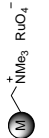
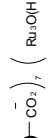
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (Si:Cr = 140:1)	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{BuOOH}, \text{O}} \text{R}^1-\text{C}(=\text{O})-\text{R}^2$ 9 examples R <sup>1</sup> = aryl R <sup>2</sup> = H, alkyl, aryl	Y:15-43	Only activated alcohols were oxidised. Yields were increased by using CCl <sub>4</sub> as solvent instead of MeOH and by adding a phase transfer catalyst. General procedure.	177	178
 Chromia pillared montmorillonite (0.25 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{BuOOH}, \text{O}} \text{R}^1-\text{C}(=\text{O})-\text{R}^2$ 10 examples R <sup>1</sup> = H, alkyl R <sup>2</sup> = alkyl, aryl, vinyl	Y:82-96	2° alcohols were oxidised more rapidly than 1° in the same molecule. No over-oxidation of 1° alcohols was observed.	179	
 (1.5 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{O}} \text{R}^1-\text{C}(=\text{O})-\text{R}^2$ 10 examples R <sup>1</sup> = alkyl, aryl, vinyl R <sup>2</sup> = H, alkyl	Y:72-99	The reaction was facilitated by microwave irradiation under solvent free conditions. The reagent can be stored for three months. Experimental section.	180	166
 (1.5 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{O}} \text{R}^1-\text{C}(=\text{O})-\text{R}^2$ 22 examples R <sup>1</sup> = alkyl, aryl, vinyl R <sup>2</sup> = H, alkyl, CN, CO <sub>2</sub> Et	Y:71-99	Allylic alcohols undergo some double bond cleavage. No over-oxidation of aldehydes to acids observed. Experimental section.	181	181
 (1.4 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{O}} \text{R}^1-\text{C}(=\text{O})-\text{R}^2$ 23 examples R <sup>1</sup> = alkyl, aryl, vinyl R <sup>2</sup> = H, alkyl	Y:56-91	Experimental section.	182	182

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (1.7-2.3 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{H}_2, \text{O}} \text{R}^1-\text{C}(=\text{O})-\text{R}^2$ <p>3 examples            R<sup>1</sup>= alkyl, aryl            R<sup>2</sup>= H, alkyl</p>	Y: 69-94	Reagent may be recycled with minimal loss of activity. Experimental section.	183	183
 M= Cr(III) (0.68 mmol g <sup>-1</sup> ); Ce(IV) (0.54 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{t-BuOOH}, \text{O}} \text{R}^1-\text{C}(=\text{O})-\text{R}^2$ <p>10 examples            R<sup>1</sup>= alkyl, aryl, vinyl            R<sup>2</sup>= alkyl, aryl</p>	Y: 71-98	Primary alcohols were poor substrates. Secondary alcohols were oxidised preferentially if NaBrO <sub>3</sub> was used as a co-oxidant. Neither catalyst was the best for every reaction. General procedures. <sup>184</sup> Experimental section. <sup>185</sup>	184, 185	184, 185
 (2.8 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{O}} \text{R}^1-\text{C}(=\text{O})-\text{R}^2$ <p>7 examples            R<sup>1</sup>= aryl, vinyl</p>	Y: 75-89	Selective oxidation of allylic alcohol over alkyl alcohol was observed. General procedure.	186	186
 ( = PVP ) (2.3 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{O}} \text{R}^1-\text{C}(=\text{O})-\text{R}^2$ <p>1 example</p>	Y: 55	Reaction carried out as part of a one-pot multi-step synthesis. Also see references 187, 188, 189, 190.	39	
 ( = polypropylene / pyridine graft )	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{O}} \text{R}^1-\text{C}(=\text{O})-\text{R}^2$ <p>4 examples            R<sup>1</sup>= alkyl, aryl, vinyl            R<sup>2</sup>= H, alkyl</p>	C: 27-99	Polymer used as a fabric rather than as beads. Experimental section. Also see references 187, 188, 189, 190.	191	191

3.3.1 Aldehydes/ketones (From alcohols with Cr based oxidants)—continued

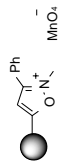





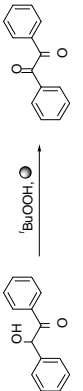
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 ( = PVP ) (2.3 mmolg <sup>-1</sup> )	 8 examples R <sup>1</sup> = alkyl, aryl, vinyl R <sup>2</sup> = H, alkyl	C:66-99	Reagent recyclable. Experimental section. Also see references 187, 188, 189, 190.	32	32
 ( = PVP ) (1.2-1.4 mmolg <sup>-1</sup> )	 22 examples R <sup>1</sup> = aryl R <sup>2</sup> = H, acyl, alkyl	Y:80-100	Two resins were examined. The best results are presented here. General procedures.	188 192	192
 ( = polyethyleneimine ) (2.0 mmolg <sup>-1</sup> )	 10 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl, aryl	Y:73-98	Reagent can be regenerated without significant loss of activity. General procedures. Also see reference 193.	194	194
	 10 examples R <sup>1</sup> = alkyl, allyl, aryl, benzyl R <sup>2</sup> = H, alkyl	Y:93-97 P:77-100	Experimental section.	155	155
 (1.4 mmolg <sup>-1</sup> )	 5 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl, aryl	Y:65-90	A range of solvents was studied. The reagent showed some loss of activity upon regeneration. The reagent was stable at room temperature. Experimental section.	195	195
	 R <sup>1</sup> = H, alkyl, NH <sub>2</sub>	C:0-41	General procedure.	196	

### 3.3.2 Aldehydes/ketones (From alcohols with Ru, Mn, and Mo based oxidants)





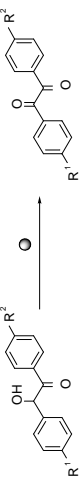

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst IR-27 Perruthenate form (1.0 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}_2-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{N-ox. id.}} \text{R}^1-\text{CH}_2-\text{C}(=\text{O})-\text{R}^2$ <p>10 examples            R<sup>1</sup> = alkyl, aryl, vinyl            R<sup>2</sup> = H, alkyl</p>	Y:64-95	NMO or TMAO used as co-oxidant. Oxidises 1° alcohols to aldehydes without over-oxidation to carboxylic acid. General procedures.	46	46
 Amberlyst A-26 Perruthenate form	$\text{R}^1-\text{CH}_2-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{O}_2} \text{R}^1-\text{CH}_2-\text{C}(=\text{O})-\text{R}^2$ <p>7 examples            R<sup>1</sup> = alkyl, aryl, vinyl</p>	Y:56-95%	Primary alcohols were oxidised selectively in the presence of secondary alcohols. General procedure.	47	46
 Amberlyst A-26 Perruthenate form	$\text{R}^1-\text{C}_6\text{H}_3(\text{R}^2, \text{R}^3, \text{X})-\text{CH}_2-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{O}_2} \text{R}^1-\text{C}_6\text{H}_3(\text{R}^2, \text{R}^3, \text{X})-\text{C}(=\text{O})-\text{R}^2$ <p>8 examples            R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> = H, O-alkyl, Cl            X = CH, N</p>	Y:95-100	General procedure.	48, 75, 77	48, 46
 Amberlyst A-26 Perruthenate form (1.0-1.3 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}_2-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{O}_2} \text{R}^1-\text{CH}_2-\text{C}(=\text{O})-\text{R}^2$ <p>23 examples            R<sup>1</sup> = alkyl, aryl, pyridyl            R<sup>2</sup> = H, alkyl, aryl</p>	Y:56-100	Selectively oxidised 1° alcohols to aldehydes without over-oxidation to the respective carboxylic acid. General procedure. Used in a multi-step synthesis. <sup>51</sup>	51, 47	46
 MCM-41 Perruthenate form	$\text{R}^1-\text{CH}_2-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{O}_2} \text{R}^1-\text{CH}_2-\text{C}(=\text{O})-\text{R}^2$ <p>12 examples            R<sup>1</sup> = aryl, pyridyl, vinyl            R<sup>2</sup> = H, alkyl</p>	Y:100	Recyclable reagent. No metal leaching observed.	197	
 (Ru(OH <sub>2</sub> O) <sub>7</sub> ) <sup>+</sup> ( = polyethylene)	$\text{R}^1-\text{CH}_2-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{O}_2} \text{R}^1-\text{CH}_2-\text{C}(=\text{O})-\text{R}^2$ <p>3 examples            R<sup>1</sup> = alkyl, vinyl            R<sup>2</sup> = H, alkyl</p>		Kinetic study. Experimental section.	198	198

3.3.2 Aldehydes/ketones (From alcohols with Ru, Mn, and Mo based oxidants)—continued

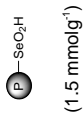
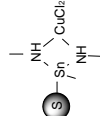
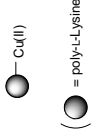
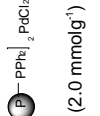

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-27 Permanganate form	 6 examples R <sup>1</sup> = aryl, pyridyl	Y:95-100	One step of a multi-step synthesis. Molecular sieves have also been used as a support. <sup>109</sup>	70	70
 ( = PVP ) (2.0-2.3 mmol g <sup>-1</sup> )	 5 examples R <sup>1</sup> = aryl, vinyl R <sup>2</sup> = H, aryl	Y:68-100	The spent reagent may be regenerated and reused. Cyclic 2° alcohols are inert to this procedure. General procedure. Silica <sup>200</sup> and Montmorillonite K 10 <sup>201</sup> have also been used as supports.	202	202
 (3.3 mmol g <sup>-1</sup> )	 6 examples R <sup>1</sup> = alkyl, aryl, vinyl R <sup>2</sup> = H, acyl, alkyl	C:30-99	Experimental section.	203	203
 (1.4 mmol g <sup>-1</sup> )	 10 examples R <sup>1</sup> , R <sup>2</sup> = H, alkyl, aryl	Y:78-88	Regenerated resin retained the same activity. No over-oxidation of primary alcohols to the corresponding carboxylic acids was observed. Experimental section.	204	204
 ( = PMMA ) (1.7 mmol g <sup>-1</sup> )	 10 examples R <sup>1</sup> , R <sup>2</sup> = H, alkyl, aryl	Y:83-90	Regenerated resin retained the same activity. Primary alcohols were oxidised to aldehydes. Experimental section.	205	205

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
  (1.4-1.5 mmolg <sup>-1</sup> )	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{O}} \text{R}^1-\text{C}(=\text{O})-\text{R}^2$ <p>10 examples            R<sup>1</sup>= alkyl, aryl            R<sup>2</sup>= H, acyl, alkyl</p>	Y:81-89	Two other support types were used. The best results are given. The polymer may be regenerated and reused without loss of activity. General procedure.	206	206
 (S)-MnO <sub>2</sub>	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{MnO}_2} \text{R}^1-\text{C}(=\text{O})-\text{R}^2$ <p>9 examples            R<sup>1</sup>= aryl, vinyl            R<sup>2</sup>= H, alkyl, aryl</p>	Y:67-88	No over-oxidation of 1° alcohols to carboxylic acids was observed. All reaction times were ≤1 min. General procedure.	207	
 (A)-KMinO <sub>4</sub>	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{O}} \text{R}^1-\text{C}(=\text{O})-\text{R}^2$ <p>21 examples            R<sup>1</sup>= aryl, het, vinyl            R<sup>2</sup>= H, alkyl, aryl, benzyl, α-ketone</p>	Y:91-99	Reaction was carried out under solvent free conditions with a pestle and mortar. Primary alcohols were selectively oxidised over secondary alcohols. General procedure.	208	
 [MoO(O <sub>2</sub> ) <sub>2</sub> (O <sub>2</sub> C-C <sub>6</sub> H <sub>4</sub> -NH <sub>2</sub> )] <sup>-</sup> Amberlyst A-26 (0.9-1.2 mmolg <sup>-1</sup> )	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{O}} \text{R}^1-\text{C}(=\text{O})-\text{R}^2$ <p>21 examples            R<sup>1</sup>= alkyl, aryl, vinyl            R<sup>2</sup>= H, acyl, alkyl</p>	Y:88-98	Reagent may be regenerated. General procedures. Also see reference 209.	210	210
 (P)-salicylaldoxime (0.30 mmolg <sup>-1</sup> ) R <sup>1</sup> = (sal-H) <sub>2</sub> , salphen	 $\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{BaOOH}_2} \text{R}^1-\text{C}(=\text{O})-\text{R}^2$ <p>1 example</p>	Y:90	Recyclable reagent. Similar vanadium catalysts were also studied.	211	212

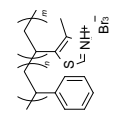
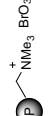
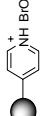
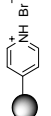
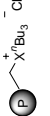
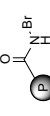
### 3.3.3 Aldehydes/ketones (From alcohols with miscellaneous oxidants)


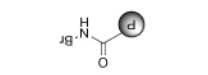
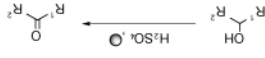
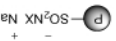
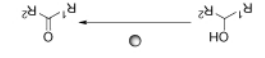
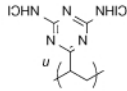

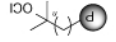

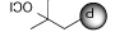

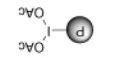
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Montmorillonite K 10	$\text{R}^1\text{-CH(OH)-R}^2 \xrightarrow{\text{K}_2\text{FeO}_4 \cdot \text{O}} \text{R}^1\text{-C(=O)-R}^2$ <p>5 examples</p> <p>R<sup>1</sup>= H, alkyl, aryl R<sup>2</sup>= alkyl, aryl, cinnamyl, furfuryl</p>	Y:54-98	Generally >90% conversion. Some compounds are degraded on the clay surface, leading to lower yields. General procedure.	213	
 (0.50 mmol g <sup>-1</sup> )	$\text{R}^1\text{-CH(OH)-R}^2 \xrightarrow{\text{O}} \text{R}^1\text{-C(=O)-R}^2$ <p>12 examples</p> <p>R<sup>1</sup>= alkyl, aryl, R<sup>2</sup>= H, alkyl</p>	Y:30-75	1 <sup>o</sup> , 2 <sup>o</sup> and benzylic alcohols are good substrates. No over-oxidation of aldehydes to acids was observed. General procedure. Montmorillonite K 10 may also be used as a support. <sup>214</sup>	215	215
 Clayfen®	$\text{R}^1\text{-CH(OH)-R}^2 \xrightarrow{\text{MW, O}} \text{R}^1\text{-C(=O)-R}^2$ <p>8 examples</p> <p>R<sup>1</sup>= alkyl, aryl R<sup>2</sup>= H, alkyl, aryl</p>	Y:87-96	The reactions were conducted under solvent free conditions. General procedure.	216	216
 Montmorillonite K 10 (1.5 mmol g <sup>-1</sup> )	 <p>5 examples</p> <p>R<sup>1</sup>, R<sup>2</sup>= H, alkyl, O-alkyl</p>	Y:85-97	General procedure.	217	214
 Celite (1.8 mmol g <sup>-1</sup> )	$\text{R}^1\text{-CH(OH)-R}^2 \xrightarrow{\text{O}} \text{R}^1\text{-C(=O)-R}^2$ <p>15 examples</p> <p>R<sup>1</sup>= alkyl, vinyl R<sup>2</sup>= H, alkyl</p>	Y:61-100	Reagent was sensitive to steric hindrance. Acetals and thioacetals were stable under the reaction conditions. General procedure.	218	218




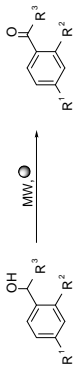
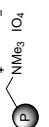
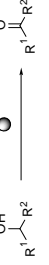
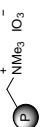

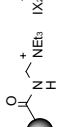
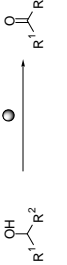
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (1.5 mmol g <sup>-1</sup> )	$\text{R}^1\text{CH}_2\text{CH(OH)R}^2 \xrightarrow{\text{BuCOOH}, \text{O}} \text{R}^1\text{CH}_2\text{C(=O)R}^2$ 9 examples R <sup>1</sup> = aryl, vinyl R <sup>2</sup> = H, aryl	Y:69-100	Recyclable reagent. Primary alcohols were oxidised exclusively to aldehydes. Alcohols must be activated to react.	219	219
ZrO <sub>2</sub> / V <sub>2</sub> O <sub>5</sub>	$\text{R}^1\text{CH}_2\text{CH(OH)R}^2 \xrightarrow{\text{O}} \text{R}^1\text{CH}_2\text{C(=O)R}^2$ 8 examples R <sup>1</sup> = alkyl, aryl, vinyl R <sup>2</sup> = H, alkyl	Y:37-100	No leaching of vanadium observed. Reagent may be regenerated and recycled. An increase in activity was observed on recycling.	220	220
	$\text{MeOH} \xrightarrow{\text{O}_2, \text{O}} \text{HCHO}$ 1 example	Y:100	No over-oxidation to acid was observed. Catalyst may be used several times without loss of activity. General procedure.	221	221
 ( = poly-L-Lysine )	$\text{HO-C}_6\text{H}_3(\text{OH})_2\text{CH}_2\text{CH(COOH)NH}_2 \xrightarrow{\text{Air}, \text{O}} \text{HO-C}_6\text{H}_3(\text{OH})_2\text{CH}_2\text{CH(COOH)NH}_2$ 1 example	C:>65	Kinetic study showed that the rate of oxidation was pH dependent. The polymeric catalyst was soluble in the aqueous phase. Experimental section.	222	222
 (2.0 mmol g <sup>-1</sup> )	$\text{R}^1\text{CH}_2\text{CH(OH)R}^2 \xrightarrow{\text{KCO}_3, \text{O}} \text{R}^1\text{CH}_2\text{C(=O)R}^2$ 8 examples R <sup>1</sup> , R <sup>2</sup> = alkyl	Y:75-90	A range of steroids were oxidised. β,γ-Unsaturated alcohols were doubly oxidised to α,β,γ,δ-unsaturated ketones. The reagent was recycled although a drop in reaction yield was observed. A mechanism is proposed.	223	224
	$\text{R}^1\text{CH}_2\text{CH(OH)R}^2 \xrightarrow{\text{MW}, \text{O}} \text{R}^1\text{CH}_2\text{C(=O)R}^2$ 7 examples R <sup>1</sup> , R <sup>2</sup> = aryl, het	Y:81-96	Reactions were carried out under solvent free conditions.	225	225

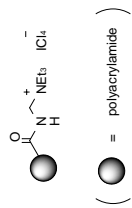
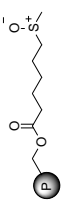
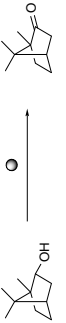
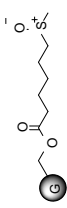
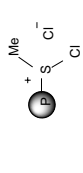
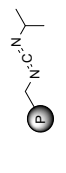
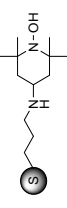
3.3.3 Aldehydes/ketones (From alcohols with miscellaneous oxidants)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (1.9 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{NaOH}, \bullet} \text{R}^1-\text{C}(=\text{O})-\text{R}^2$ 21 examples R <sup>1</sup> = alkyl, aryl, vinyl R <sup>2</sup> = H, acyl, alkyl	Y:81-100	Secondary alcohols were oxidised more readily than primary. No over-oxidation of aldehydes to acids was observed. General procedure.	226	227
 Amberlyst A-26 Bromate form (3.2 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\bullet} \text{R}^1-\text{C}(=\text{O})-\text{R}^2$ 2 examples R <sup>1</sup> , R <sup>2</sup> = alkyl	Y:92-95	Hydrogen bromide formed during the reaction was absorbed onto the resin. General procedure.	228	228
 ( = PVP ) (2.7 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\bullet} \text{R}^1-\text{C}(=\text{O})-\text{R}^2$ 5 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl	Y:70-95	A polystyrene analogue of this reagent oxidises primary alcohols to aldehydes. With the PVP-based resin, some over-oxidation occurred. General procedure.	229	229
 ( = PVP ) (2.0 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\text{electric current}, \bullet} \text{R}^1-\text{C}(=\text{O})-\text{R}^2$ 8 examples R <sup>1</sup> , R <sup>2</sup> = H, alkyl	C:35-100	Recyclable reagent. Polymer used catalytically. General procedure.	230	230
 X = N, P	$\text{C}_6\text{H}_5-\text{CH}_2-\text{OH} \xrightarrow{\text{electric current}, \bullet} \text{C}_6\text{H}_5-\text{CHO}$ 1 example	C:>90	Kinetic study. The mechanism of anodic oxidation in the presence of the catalyst was studied. General procedures.	231	231
 ( = polyacrylamide ) (2.3-7.3 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}(\text{OH})-\text{R}^2 \xrightarrow{\bullet} \text{R}^1-\text{C}(=\text{O})-\text{R}^2$ 10 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl, acyl	Y:87-99	This non-corrosive and easily handled reagent is stable under normal laboratory conditions and can be stored indefinitely. The reagent was also shown to oxidise thiols to sulfides, brominate aromatics and alkenes and to α-brominate ketones. Experimental section.	232, 233	232, 233

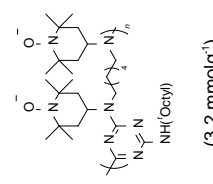
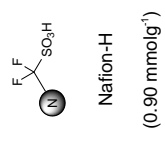
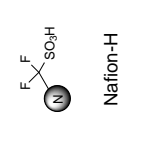
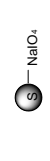
Prep. Ref.	Ref.	Comments	Data/%	Transformation	Reagent (Loading)
	234	The effects of cross-linking were investigated. This non-corrosive and easily handled reagent can be stored indefinitely.	Y:100	 <p>1 example</p>	 <p>( = polyacrylamide )</p> <p>(1.1-6.7 mmol<sup>g</sup><sup>-1</sup>)</p>
235	235	General procedure. Polymer was regenerated and reused without loss of activity.	Y:51-98	 <p>4 examples</p> <p>R<sup>1</sup> = alkyl, aryl R<sup>2</sup> = H, alkyl, aryl</p>	 <p>X = Cl, Br</p> <p>(3.2-3.5 mmol<sup>g</sup><sup>-1</sup>)</p>
236	236	General procedure. Secondary alcohols were oxidised more rapidly than primary.	Y:70-98	 <p>7 examples</p> <p>R<sup>1</sup> = alkyl, aryl R<sup>2</sup> = H, alkyl, aryl</p>	
237, 238	237, 238	Spent resins were regenerated and recycled without loss of activity. Experimental section.	Y:76-98	 <p>6 examples</p> <p>R<sup>1</sup> = alkyl, aryl R<sup>2</sup> = H, alkyl, aryl</p>	 <p>n = 0, 1, 3</p> <p>(1.4-3.0 mmol<sup>g</sup><sup>-1</sup>)</p>
239	239	Reagent may be regenerated. Reagent cannot be stored for long periods.	Y:77-98	 <p>7 examples</p> <p>R<sup>1</sup> = alkyl, aryl R<sup>2</sup> = H, alkyl, aryl</p>	 <p>(0.60-2.4 mmol<sup>g</sup><sup>-1</sup>)</p>
72	72	General procedure. Polymer was regenerated and reused without loss of activity.	Y:100 P:>95	 <p>4 examples</p> <p>R<sup>1</sup> = H, Cl, NO<sub>2</sub>, O-alkyl</p>	 <p>(3.5 mmol<sup>g</sup><sup>-1</sup>)</p>

3.3.3 Aldehydes/ketones (From alcohols with miscellaneous oxidants)—continued

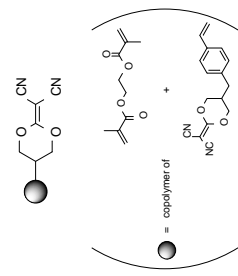
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
	 <p>7 examples  <math>R^1 = \text{H, alkyl, aryl, O-alkyl}</math>  <math>R^2 = \text{H, alkyl}</math>  <math>R^3 = \text{H, alkyl, acyl}</math></p>	Y:89-96	General procedure.	240	
 <p>Amberlyst A-26 Periodate form (1.4 mmolg<sup>-1</sup>)            Amberlite IRA-904 Periodate form (1.6 mmolg<sup>-1</sup>)</p>	 <p>12 examples  <math>R^1, R^2 = \text{aryl}</math></p>	Y:0-100	The supported periodate was also used for the cleavage of 1,2-diols, oxidation of sulfides to sulfoxides and oxidation of phosphines to phosphine oxides. The Amberlite IRA-904 derivative was the most active reagent. Experimental section.	241	241
 <p>Amberlyst A-26 Iodate form (1.4 mmolg<sup>-1</sup>)</p>	 <p>6 examples  <math>R^1, R^2 = \text{aryl}</math></p>	Y:69-100	The reagent was less active than the periodate form. Experimental section.	241	241
 <p>(0.70-1.8 mmolg<sup>-1</sup>)  <math>X = \text{Br, Cl}</math></p>	 <p>9 examples  <math>R^1 = \text{alkyl, aryl}</math>  <math>R^2 = \text{H, alkyl, aryl}</math></p>	Y:61-89	The bromine containing polymer was more reactive than the chlorine form. General procedure.	242, 243, 244	242, 243, 244

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 ( = polyacrylamide ) (1.1-2.4 mmol g <sup>-1</sup> )	$\text{R}^1\text{-CH(OH)-R}^2 \xrightarrow{\text{O}} \text{R}^1\text{-C(=O)-R}^2$ 8 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, aryl	Y:70-83	Reagent may be recycled. General procedure.	242, 243	242
 (2.6 mmol g <sup>-1</sup> )	 1 example	Y:100	The polymeric reagent is odourless. Two equivalents were required for complete conversion. General procedure.	245	245
 (3.0 mmol g <sup>-1</sup> )	$\text{R}^1\text{-CH(OH)-R}^2 \xrightarrow{(\text{COCl})_2, \text{NEt}_3, \text{O}} \text{R}^1\text{-C(=O)-R}^2$ 7 examples R <sup>1</sup> = alkyl, aryl	Y:91-99	The reagent was regenerated with no loss of activity. Experimental section.	246	246
 Amberlite XE-305 (3.61 mmol g <sup>-1</sup> )	$\text{R}^1\text{-CH(OH)-R}^2 \xrightarrow{\text{NEt}_3, \text{O}} \text{R}^1\text{-C(=O)-R}^2$ 5 examples R <sup>1</sup> = alkyl, benzyl	Y:53-100	Full experimental section.	247	247
 (0.70-2.4 mmol g <sup>-1</sup> )	$\text{R}^1\text{-CH(OH)-R}^2 \xrightarrow{\text{DMSO}, \text{O}} \text{R}^1\text{-C(=O)-R}^2$ 14 examples R <sup>1</sup> = alkyl, aryl vinyl R <sup>2</sup> = H, alkyl	Y:66-97	Suitable for sensitive compounds. General procedure.	248, 249	250, 249, 251
 (0.87 mmol g <sup>-1</sup> )	$\text{R}^1\text{-CH(OH)-R}^2 \xrightarrow{\text{NaOCl}, \text{KBr}, \text{O}} \text{R}^1\text{-C(=O)-R}^2$ 10 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl	Y:60-96	Recyclable reagent. Can selectively oxidise 1° alcohols in the presence of 2° alcohols. No racemisation of optically active starting materials. General procedures.	252	252




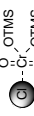
3.3.3 Aldehydes/ketones (From alcohols with miscellaneous oxidants)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (3.2 mmol g <sup>-1</sup> )	$\text{R}^1\text{CH}(\text{OH})\text{R}^2 \xrightarrow{\text{HOCl, K}_2\text{CO}_3, \text{O}} \text{R}^1\text{C}(\text{O})\text{R}^2$ <p>9 examples            R<sup>1</sup> = alkyl, aryl            R<sup>2</sup> = H, alkyl</p>	Y:70-100	Reaction of primary aliphatic alcohols produces a mixture of aldehyde and carboxylic acid, unless performed in MTBE. Resin may be reused with only 5% loss of activity. General procedure.	253	253
 Nafion-H (0.90 mmol g <sup>-1</sup> )	$\text{R}^1\text{CH}(\text{OH})\text{CH}(\text{OH})\text{R}^2 \xrightarrow{\text{O}} \text{R}^1\text{C}(\text{O})\text{R}^2$ <p>3 examples            R<sup>1</sup>, R<sup>2</sup> = H, alkyl</p>	C:55-100 Y:61-80	Comparison made between Nafion-H and NaHX-Zeolite. Nafion-H gave better yields and conversions. Experimental section.	254	
 Nafion-H	$\text{R}^1\text{CH}(\text{OH})\text{C}(\text{OH})(\text{R}^2)\text{R}^2 \xrightarrow{\text{O}} \text{R}^1\text{C}(\text{O})\text{R}^2$ <p>4 examples            R<sup>1</sup>, R<sup>2</sup> = alkyl, aryl</p>	Y:82-92	Catalyst may be regenerated. General procedure.	255	
 NaIO <sub>4</sub>	$\text{R}^1\text{CH}(\text{OH})\text{CH}(\text{OH})\text{R}^2 \xrightarrow{\text{O}} \text{R}^1\text{C}(\text{O})\text{R}^2 + \text{R}^2\text{C}(\text{O})\text{R}^2$ <p>10 examples            R<sup>1</sup> = alkyl, ester            R<sup>2</sup> = H, alkyl, ester</p>	Y:90-100	Full experimental section.	256	256

### 3.3.4 Aldehydes/ketones (From acetals and thioacetals)

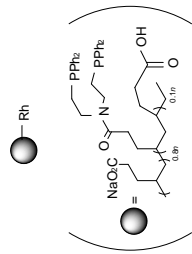

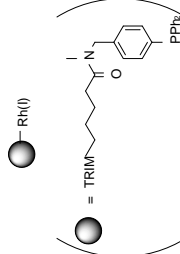

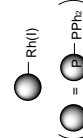

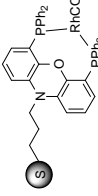

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
<p>CO<sub>2</sub></p> <p>Magtrieve®</p>	$\begin{array}{c} \text{R}^3\text{O} \diagup \text{OR}^3 \\ \text{R}^1 \diagdown \text{R}^2 \end{array} \xrightarrow{\text{H}_2\text{O}, \text{O}} \begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1-\text{C}-\text{R}^2 \end{array}$ <p>10 examples</p> <p>R<sup>1</sup> = alkyl, aryl, vinyl R<sup>2</sup> = H, alkyl R<sup>3</sup> = alkyl</p>	Y:32-98	Some over-oxidation of aldehydes to acids observed. General procedure.	257	
<p>⊙-KHSO<sub>4</sub></p>	$\begin{array}{c} \text{R}^3\text{O} \diagup \text{OR}^3 \\ \text{R}^1 \diagdown \text{R}^2 \end{array} \xrightarrow{\text{MW}, \text{O}} \begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1-\text{C}-\text{R}^2 \end{array}$ <p>8 examples</p> <p>R<sup>1</sup> = alkyl, aryl, het, vinyl R<sup>2</sup> = H, alkyl R<sup>3</sup> = alkyl</p>	Y:84-94	TBDMS and trityl groups were stable under these conditions. General procedure.	258	
 <p>⊙ = copolymer of</p>	$\begin{array}{c} \text{OR}^3 \\ \diagup \\ \text{R}^1-\text{C}-\text{OR}^3 \\ \diagdown \\ \text{R}^2 \end{array} \xrightarrow{\text{O}} \begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1-\text{C}-\text{R}^2 \end{array}$ <p>16 examples</p> <p>R<sup>1</sup> = alkyl, aryl, vinyl R<sup>2</sup> = H, alkyl R<sup>3</sup> = alkyl</p>	Y:17-100	The catalyst also removed some silicon protecting groups, although acetals were hydrolysed faster. The polymer was recycled without loss of activity. General procedure.	259	
<p>⊙-SO<sub>3</sub>H</p> <p>Amberlyst A-15 Proton form</p>	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1-\text{C}-\text{R}^2 \end{array} \xrightarrow{\text{H}_2\text{O}, \text{O}} \begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1-\text{C}-\text{R}^2 \end{array}$ <p>11 examples</p> <p>R<sup>1</sup> = H, alkyl R<sup>2</sup> = alkyl, aryl</p>	Y:64-97	Used in conjunction with a Horner-Emmons reaction for a two-step, one-pot reaction. Saturated aldehydes failed to react. Full experimental section. Nafion-H may also be used as the acid catalyst. <sup>99</sup>	260	260

3.3.4 Aldehydes/ketones (From acetals and thioacetals)—continued

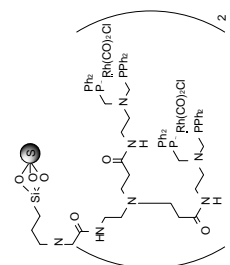
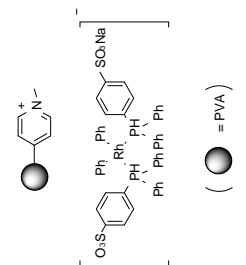
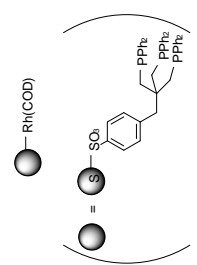
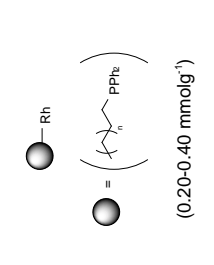
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Montmorillonite K 10 Clayfen®	$  \begin{array}{c}  \text{R}^3\text{S} \\    \\  \text{R}^1\text{C} \\    \\  \text{R}^2  \end{array}  \xrightarrow{\text{MW, } \bullet}  \begin{array}{c}  \text{O} \\     \\  \text{R}^1\text{C} \\    \\  \text{R}^2  \end{array}  $ <p>9 examples                      R<sup>1</sup> = alkyl, aryl                      R<sup>2</sup> = H, alkyl, aryl                      R<sup>3</sup> = alkyl</p>	Y:87-97	Difunctionalized thiols usually bind to the clay. Monofunctionalized thiols do not bind to the clay but are simply removed by washing with hexane. Experimental section.	261	
 Bentonite K-10 Clayfen®	$  \begin{array}{c}  \text{R}^3\text{S} \\    \\  \text{R}^1\text{C} \\    \\  \text{R}^2  \end{array}  \xrightarrow{\bullet}  \begin{array}{c}  \text{O} \\     \\  \text{R}^1\text{C} \\    \\  \text{R}^2  \end{array}  $ <p>11 examples                      R<sup>1</sup> = alkyl, aryl                      R<sup>2</sup> = H, alkyl, aryl                      R<sup>3</sup> = alkyl</p>	Y:62-100	Clay supported copper(II) nitrate gave similar results. General procedure.	262	262
 Amberlyst A-15 Proton form	$  \begin{array}{c}  \text{S} \\    \\  \text{R}^1\text{C} \\    \\  \text{R}^2  \end{array}  \xrightarrow{\text{H}_2\text{O, CH}_3\text{O, } \bullet}  \begin{array}{c}  \text{O} \\     \\  \text{R}^1\text{C} \\    \\  \text{R}^2  \end{array}  $ <p>8 examples                      R<sup>1</sup>, R<sup>2</sup> = H, alkyl, aryl</p>	Y:50-80	Aliphatic aldehydes are unreactive. Acid sensitive groups are not affected. $\alpha$ -Stereocentres do not epimerise. Experimental section.	263	
 Montmorillonite K 10 (1.6 mmol g <sup>-1</sup> )	$  \begin{array}{c}  \text{O} \\    \\  \text{R}^1\text{C} \\    \\  \text{R}^2  \end{array}  \xrightarrow{\bullet}  \begin{array}{c}  \text{O} \\     \\  \text{R}^1\text{C} \\    \\  \text{R}^2  \end{array}  $ <p>10 examples                      R<sup>1</sup> = alkyl, aryl, vinyl                      R<sup>2</sup> = H, alkyl, aryl</p>	Y:75-92	Microwave facilitated under solvent free conditions. Experimental section.	264	264

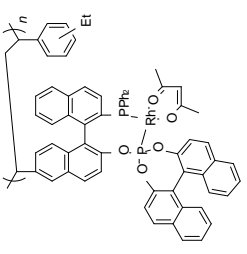
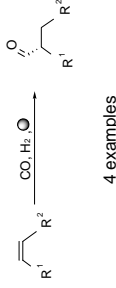
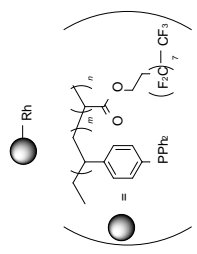
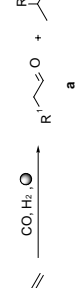
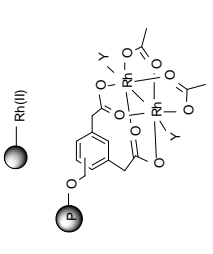
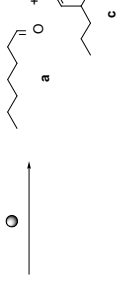
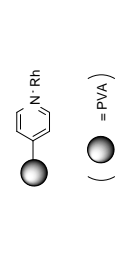
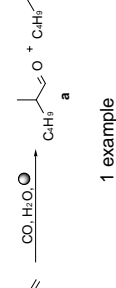
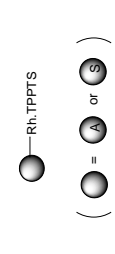
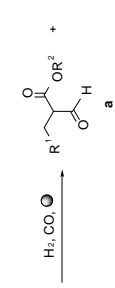


### 3.3.5 Aldehydes/ketones (From alkenes)

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>(0.30 mmol g<sup>-1</sup>)</p>	 <p>11 examples R<sup>1</sup> = H, alkyl R<sup>2</sup> = H, aryl, O-alkyl, O-aryl</p>	C:17-100	This soluble polymer gives regioselective formation of branched aldehydes from vinyl ethers and vinyl arenes. Experimental section.	265	265
 <p>(0.35 mmol g<sup>-1</sup>)</p>	 <p>1 example</p>	C:>80	No hydrogenation side reaction was observed. Ratio <b>a:b</b> = 5:1 - 3.7:1. General procedure.	266	267
 <p>(0.40 mmol g<sup>-1</sup>)</p>	 <p>4 examples r = 5-11</p>	Y:0-45	These reactions are part of a catalytic chain homologation process. Experimental section. Alternative supports <sup>268</sup> including PMMA <sup>269</sup> have also been used. For a resin bound catalyst that releases rhodium under the reaction conditions but immobilises it when cooled see reference 270. For a resin bound catalyst which manifests inverse temperature-dependent solubility in water see reference 271.	36	
 <p>Sol gel</p>	 <p>1 example</p>	C:69	Catalyst may be recycled without loss of activity. No leaching of rhodium was observed. Experimental section.	272	272

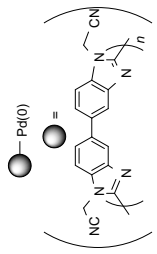
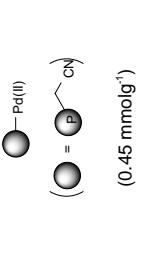
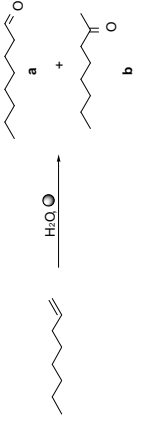
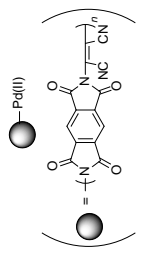
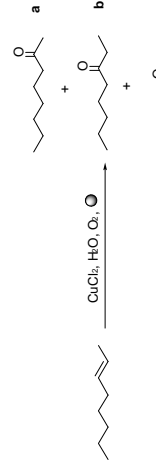
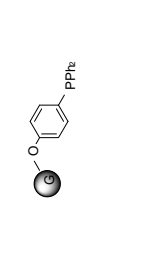
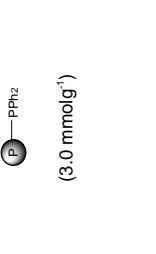
3.3.5 Aldehydes/ketones (From alkenes)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>(0.38 mmol g<sup>-1</sup>)</p>	$R^1-CH=CH_2 \xrightarrow{H_2, CO, \bullet} R^1-CH_2-CH_2-CHO + R^1-CH=CH-CHO$ <p>R<sup>1</sup> = alkyl, aryl, ester 8 examples</p>	C:52-99	Catalyst may be stored under an inert atmosphere at room temperature. A variety of dendrimer generations were studied. Product ratios were dependent upon reaction conditions. Experimental section.	273	273
 <p>( = PVA )</p>	$R^1-CH=CH_2 \xrightarrow{H_2, CO, \bullet} R^1-CH_2-CH_2-CHO$ <p>2 examples r = 0, 5</p>		Two other catalysts were investigated. The best catalyst is shown.	274	274
 <p>(0.20 mmol g<sup>-1</sup>)</p>	$R^1-CH=CH_2 \xrightarrow{H_2, CO_2, \bullet} R^1-CH_2-CH_2-COOH$ <p>3 examples R<sup>1</sup> = alkyl, aryl</p>	C:100	No rhodium leaching was observed. Experimental section. Also see reference 275.	276	276
 <p>(0.20-0.40 mmol g<sup>-1</sup>)</p>	$R^1-CH=CH-R^2 \xrightarrow{CO, CO, \bullet} R^1-CH_2-CH_2-COO-R^2$ <p>4 examples R<sup>1</sup> = alkyl, aryl R<sup>2</sup> = H, alkyl</p>	Y:15-95	Conversion of cyclic olefins was generally lower than for acyclic ones. General procedure.	277	278

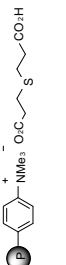
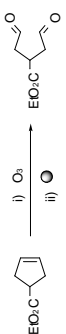
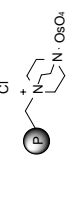

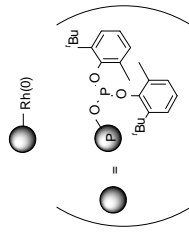
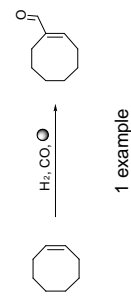
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
	 <p>4 examples R<sup>1</sup> = alkyl, ester, phenyl R<sup>2</sup> = H, alkyl</p>	C:67-87 ee:81-92	Several polymers were made. The best example is shown. Experimental section. Also see reference 279.	280	280
	 <p>4 examples R<sup>1</sup> = alkyl, aryl, ester</p>	C:78-100	Polymer was soluble in fluoruous solvents, but insoluble in normal organic solvents. Catalyst may be reused with some loss of activity. Ratio <b>a:b</b> was from 0:100 to 6:1. General procedure.	281	281
 <p>(0.50-1.0 mmol g<sup>-1</sup>) Y = MeOH</p>	 <p>1 example</p>	Y:100	The catalyst can be stored for long periods of time. No leaching was observed. Ratio <b>a:b+c</b> = 1:1.	267	267
 <p>( = PVA )</p>	 <p>1 example</p>	C:24	Ratio <b>a:b</b> = 3:1. General procedure.	282	282
 <p>( = S or S )</p>	 <p>5 examples R<sup>1</sup> = H, alkyl R<sup>2</sup> = alkyl</p>	C:100	A small decrease in yield was observed when the reagent was recycled. The reaction is carried out under phase transfer conditions. General procedure. Also see reference 283.	284	284

3.3.5 Aldehydes/ketones (From alkenes)—continued

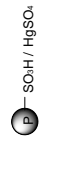
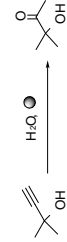
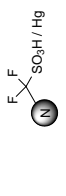

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 $\text{CH}_2\text{CH}_2\text{-PPh}_2$ $\text{Ph-CO(CO)}_2\text{-Co(CO)}_3$ (2.0 mmol g <sup>-1</sup> )	 1 example	Y:98	A range of polymer-bound catalysts was examined. The best example is shown. Ratio <b>a:b+c</b> = 3.4:1 which compares well with the homogeneous catalyst system. Experimental section.	285	285
 $\text{OC}^-\text{Co(CO)}_2$ $(\text{CO})_2\text{Co} \xrightarrow{\text{X}} \text{Co(CO)}_3$ X = P, As	 5 examples R <sup>1</sup> = alkyl, vinyl R <sup>2</sup> = H, alkyl	Y:53-86	The reaction produced a mixture of regioisomers. General procedure. For an example with a Ru-Co bimetallic complex see reference 286.	287	287
 = Co-polymer of polypropylene and 4-vinylpyridine (1.7 mmol g <sup>-1</sup> )	 1 example	C:100	Some alcohol/aldehyde condensation products were also observed. The ratio of <b>a:(b+c)</b> = 1.83:1 was higher than for many other heterogeneous and homogeneous conditions studied. Full experimental.	288	288
 $\text{Ph}_2\text{P}(\text{CO})_2\text{-Co(CO)}_2$ $\text{Cl}^-\text{SnCl}_2$	 1 example	C:9-40 ee:73	The catalyst was recovered after the reaction and re-used with no loss of activity or optical yield.	289, 290	290
 $\text{Ph}_2\text{P}(\text{CO})_2\text{-Co(CO)}_2$	 4 examples R <sup>1</sup> = alkyl, amide, aryl, O-acyl	C:22-100 ee:20-65	Experimental section.	291	291

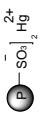
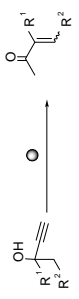
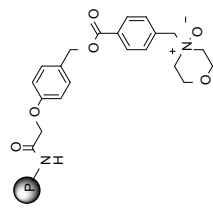
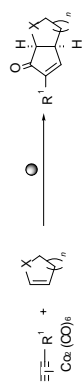

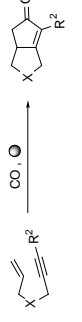


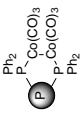
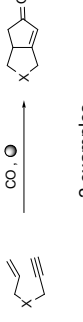
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (1.3-1.7 mmol g <sup>-1</sup> )	$R^1-CH=CH_2 \xrightarrow{O} R^1-CH_2-CH_2-O$ 5 examples R <sup>1</sup> = aryl	Y:100	Several polymers were studied and the best results are shown.	292	293
 (0.45 mmol g <sup>-1</sup> )	 1 example	C:100	The catalyst was more stable at high temperatures than the analogous homogeneous catalyst. Less anti-Markovnikov product was formed when using the polymer catalyst. Ratio <b>a:b</b> = 2.2:1. For a rhodium variant see references 294, 295.	296	296
 (1.1 mmol g <sup>-1</sup> )	 1 example	Y:100	Palladium leaching ceased after the first cycle and activity stabilised after six cycles. The support demonstrated enhanced thermo-oxidative stability compared to polystyrene. Ratio <b>a:b:c</b> = 31:13:6 General procedure.	297	297
 (3.0 mmol g <sup>-1</sup> )	$R^1-CH=CH-R^2 \xrightarrow[i) O_2]{i) O_3} R^1-CH_2-CH_2-O-R^2$ 5 examples R <sup>1</sup> = alkyl, aryl, het R <sup>2</sup> = H, alkyl	Y:63-98	Yields were comparable to those obtained with the solution phase equivalent. Also see reference 298.	299	299
 (3.0 mmol g <sup>-1</sup> )	$R^1-CH=CH-R^2 \xrightarrow[i) O_2]{i) O_3} R^1-CH_2-CH_2-O-R^2$ 7 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> , R <sup>3</sup> = H, alkyl	Y:80-92	Experimental section. Also see reference 300.	301	

### 3.3.5 Aldehydes/ketones (From alkenes)—continued



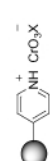



Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Dowex SBR (2.6 mmol g <sup>-1</sup> )	 1 example	Y:92	Resin used for the reductive quenching of ozonolysis reactions. General procedure.	302	302
 (0.20 mmol g <sup>-1</sup> )	 12 examples R <sup>1</sup> = H, alkyl, aryl R <sup>2</sup> = alkyl, aryl, ester, ketone	Y:65-90	General procedure.	303	303
 Rh(0)	 1 example		Kinetic study.	304	304

### 3.3.6 Aldehydes/ketones (From alkynes)





Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Zeo-Karb225 Mercury sulfate form	 1 example	Y:80	Full experimental section.	305	305
 Nafion-Hg Mercury form	 8 examples R <sup>1</sup> = H, aryl R <sup>2</sup> = H, alkyl, aryl	Y:65-93	The catalyst was reused without loss of activity. General procedure.	306	306

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Dowex 50WX2 Mercury form	 3 examples R <sup>1</sup> , R <sup>2</sup> = alkyl	Y:75-84	Experimental section.	307	307
 ArgoGel	 8 examples R <sup>1</sup> = alkyl, aryl, silyl X = CH <sub>2</sub> , O n = 1, 2	Y:51-99	Heterogeneous Pauson-Khand reaction. On work up the oxidised cobalt residues remain bound to the polymer. Reusable reagent. General procedure.	308	308
 SBA-15 (1.5-1.7 mmolg <sup>-1</sup> )	 4 examples R <sup>1</sup> = alkyl, ester, Ts R <sup>2</sup> = H, alkyl, aryl X = CR <sub>2</sub> , NR <sup>1</sup> , O	Y:88-98	Heterogeneous Pauson-Khand reaction. Catalyst may be reused. General procedure.	309	309
 SBA-15 (1.5-1.7 mmolg <sup>-1</sup> )	 2 examples	Y:11-36	Heterogeneous Pauson-Khand reaction. Catalyst may be reused. General procedure.	309	309
 SBA-15 (0.35 mmolg <sup>-1</sup> )	 2 examples R <sup>1</sup> = ester, Ts X = CR <sub>2</sub> , NR <sup>1</sup>	Y:57-66	Heterogeneous Pauson-Khand reaction. General procedure.	310	310

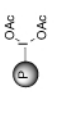



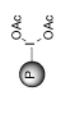

### 3.3.7 Aldehydes/ketones (From oximes and related compounds)

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (1.2-1.4 mmol <sup>g</sup> <sup>-1</sup> ) = PVP	$\text{HO}_2\text{N}-\text{C}(\text{R}^1)=\text{C}(\text{R}^2) \xrightarrow{\text{Ag}_2\text{O}_7} \text{O}=\text{C}(\text{R}^1)-\text{C}(\text{R}^2)$ 8 examples R <sup>1</sup> = aryl R <sup>2</sup> = H, alkyl, aryl	Y:60-90	General procedure.	192	192
 (1.9-2.0 mmol <sup>g</sup> <sup>-1</sup> ) = PVP	$\text{HO}_2\text{N}-\text{C}(\text{R}^1)=\text{C}(\text{R}^2) \xrightarrow{\text{Cr}_2\text{O}_7^{2-}} \text{O}=\text{C}(\text{R}^1)-\text{C}(\text{R}^2)$ 6 examples R <sup>1</sup> = aryl, alkyl R <sup>2</sup> = H, alkyl	Y:25-80	Reagent may be regenerated. Solution phase analogue is more effective but flammable. General procedure.	311	311
 (2.7-2.9 mmol <sup>g</sup> <sup>-1</sup> ) = PVP X = Br, F	$\text{HO}_2\text{N}-\text{C}(\text{R}^1)=\text{C}(\text{R}^2) \xrightarrow{\text{NH}^+\text{C}_{10}\text{H}_8\text{X}^-} \text{O}=\text{C}(\text{R}^1)-\text{C}(\text{R}^2)$ 4 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl	Y:89-96	General procedure.	154	154
 (2.5 mmol <sup>g</sup> <sup>-1</sup> )	$\text{HO}_2\text{N}-\text{C}(\text{R}^1)=\text{C}(\text{R}^2) \xrightarrow{\text{MW}, \text{O}} \text{O}=\text{C}(\text{R}^1)-\text{C}(\text{R}^2)$ 15 examples R <sup>1</sup> , R <sup>2</sup> = alkyl, aryl, vinyl	Y:57-95	General procedure.	312	312
	$\text{HO}_2\text{N}-\text{C}(\text{R}^1)=\text{C}(\text{R}^2) \xrightarrow{\text{MW}, \text{O}} \text{O}=\text{C}(\text{R}^1)-\text{C}(\text{R}^2)$ 12 examples R <sup>1</sup> , R <sup>2</sup> = alkyl, aryl	Y:72-94	General procedure.	313	313
	$\text{HO}_2\text{N}-\text{C}(\text{R}^1)=\text{C}(\text{R}^2) \xrightarrow{\text{MW}, \text{O}} \text{O}=\text{C}(\text{R}^1)-\text{C}(\text{R}^2)$ 10 examples R <sup>1</sup> , R <sup>2</sup> = alkyl, aryl	Y:68-93	The reaction was also performed under standard thermal conditions but required prolonged heating. General procedure.	314	314


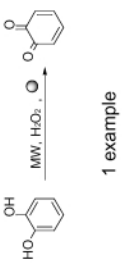

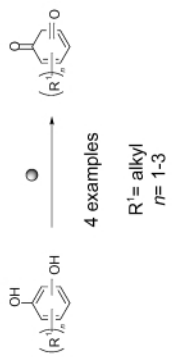



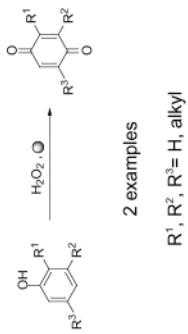

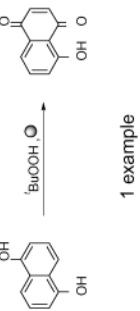


Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (3.0 mmol g <sup>-1</sup> )	 3 examples R <sup>1</sup> = aryl R <sup>2</sup> = H, aryl R <sup>3</sup> = NHPh, NHTs, hydroxy	Y:71-78	This soluble resin was as active as the solution phase equivalent. Spent reagent was regenerated and recycled without loss of activity. Experimental section.	315	315
 Amberlyst A-15 Proton form	 20 examples R <sup>1</sup> , R <sup>2</sup> = H, alkyl, aryl, vinyl R <sup>3</sup> = NHPh, hydroxy, NHTs, urea	Y:61-98 P:>97	Acid sensitive groups survived under these conditions. Experimental section.	316	269

### 3.3.8 Aldehydes/ketones (From miscellaneous)


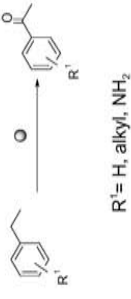
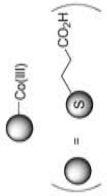
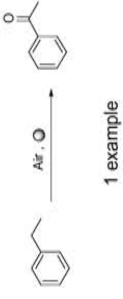


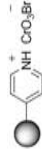




Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (3.5 mmol g <sup>-1</sup> )	 5 examples R <sup>1</sup> = H, ester, CH <sub>2</sub> OH, NHAc, sulfide	Y:100 P:>95	The polymer was regenerated and reused without loss of activity. General procedure.	72	72
 (3.0 mmol g <sup>-1</sup> )	 1 example	Y:63	The soluble resin was as active as the solution-phase equivalent. Spent reagent may be regenerated and recycled without loss of activity. Experimental section.	315	315
	 1 example MW, H <sub>2</sub> O	Y:69	Thermal reactions were less efficient than the microwave conditions. General procedure.	240	




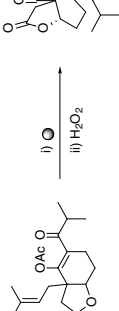

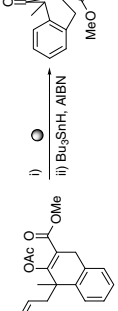

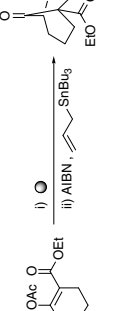

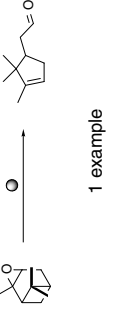
3.3.8 Aldehydes/ketones (From miscellaneous)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
		Y:43	General procedure.	240	
		Y:36-92	The polymeric reagent gave similar yields to reactions carried out with diacetoxyiodobenzene. The reagent was also shown to effect a number of other oxidations and the iodination of aromatics. Spent reagent was regenerated and reused. Full experimental section.	74	74
 Claycop		Y:71	General procedure.	317	
 MCM-41		Y:62-63	General procedure.	318	318
 (1.5 mmol <sup>-1</sup> )		Y:70	Reagent may be recycled. Reagent also oxidises other hydroquinones to quinones.	219	219


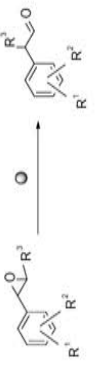
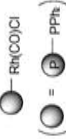
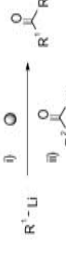
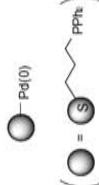





Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 ( = PVA ) (2.9 mmol g <sup>-1</sup> )	 1 example	Y:91	General procedure.	154	154
 (0.85 mmol g <sup>-1</sup> )	 5 examples R <sup>1</sup> = H, alkyl, hal, hydroxy R <sup>2</sup> = H, alkyl, hydroxy R <sup>3</sup> = H, alkyl, hal		Kinetic study. Experimental section.	319	319
 (2.0 mmol g <sup>-1</sup> )	 1 example	Y:69	Several similar polymers were synthesised. The best results are given. General procedure.	320	320
 (2.7 mmol g <sup>-1</sup> )	 5 examples R <sup>1</sup> = H, alkyl, Br, Cl, O-alkyl	Y:31-68	The reagent was stable for six months. Efficient and mild oxidant for benzylic oxidation. General procedure.	321	321
 (2.7 mmol g <sup>-1</sup> )	 3 examples R <sup>1</sup> = H, alkyl, phenyl	Y:40-98	Resin also oxidises hydroquinones to quinones and primary alcohols to carboxylic acids.	229	229


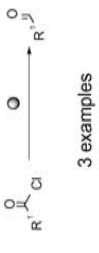





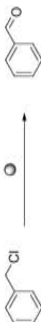
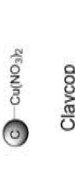

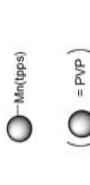

3.3.8 Aldehydes/ketones (From miscellaneous)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
	 R <sup>1</sup> = H, alkyl, NH <sub>2</sub>	C:0-41	Chromium pillared clay has also been used to mediate this transformation. Also see references 322, 323.	196	
	 1 example	Y:70	Catalyst may be reused with only a minimal loss of activity. General procedure.	324	324
	 23 examples R <sup>1</sup> = alkyl, aryl	Y:0-100	Oxidation is specific to the benzylic position. Alcohols are formed if the benzylic position is tertiary. General procedure.	325	325
 (  ) (2.9 mmol g <sup>-1</sup> )	 1 example	Y:92	General procedure.	154	154
 X= hal R <sup>1</sup> = H, alkyl	 7 examples R <sup>2</sup> , R <sup>3</sup> = H, alkyl, aryl	Y:32-57	Several polymers were tested. The best example is shown.	326	

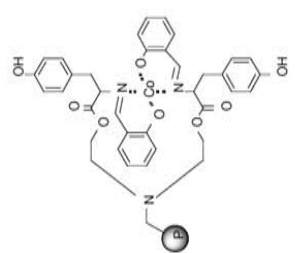
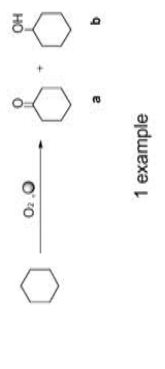
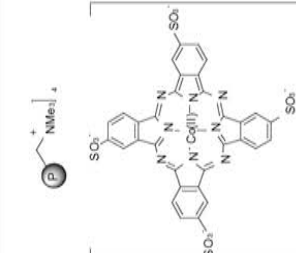
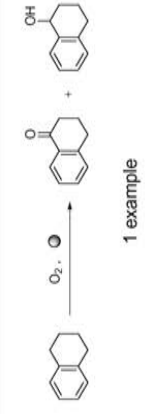
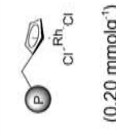
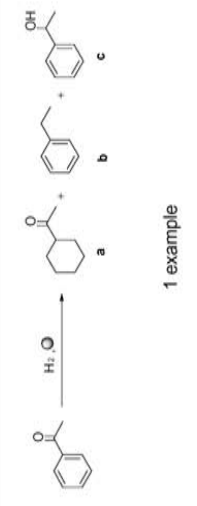
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (1.8 mmol g <sup>-1</sup> )	 <p>6 examples R<sup>1</sup> = alkyl</p>	Y:68-85	The reaction gave better yields under microwave irradiation. The reagent is specific for allylic oxidation. General procedure. Chromium pillared clay has also been used for this transformation. <sup>327</sup>	328	328
 (1.8 mmol g <sup>-1</sup> )	 <p>1 example</p>	Y:90	A resin-bound seleno intermediate was cleaved in the second step.	329	330
 (1.8 mmol g <sup>-1</sup> )	 <p>1 example</p>	Y:85	A resin-bound seleno intermediate was cleaved in the second step.	329	330
 (1.8 mmol g <sup>-1</sup> )	 <p>1 example</p>	Y:37	A resin-bound seleno intermediate was cleaved in the second step.	329	330
 (2.0 mmol g <sup>-1</sup> )	 <p>1 example</p>	C:50-100	The catalyst is 69–80% selective for aldehyde formation over other rearrangement products. Several other catalysts were tested. The best example is shown.	331	331

3.3.8 Aldehydes/ketones (From miscellaneous)—continued

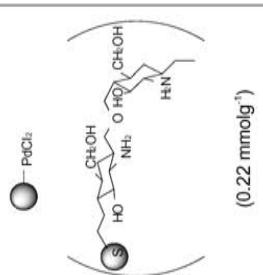
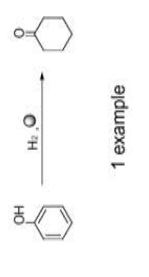
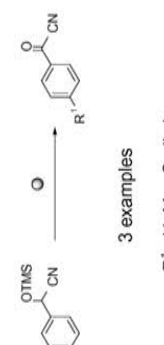
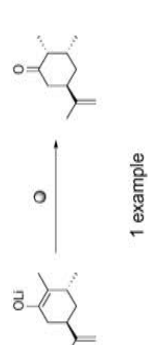
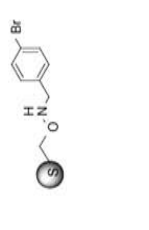
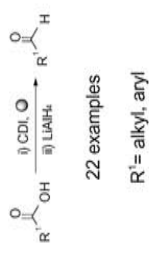
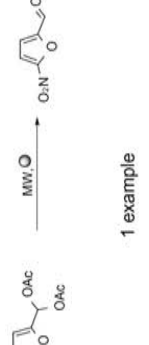
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Nafion-H	 7 examples R <sup>1</sup> = H, alkyl, F, O-alkyl R <sup>2</sup> = H, alkyl R <sup>3</sup> = H, aryl	Y:60-98	No ketone product was observed.	332	
 (0.03 mmol g <sup>-1</sup> )	 14 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = alkyl, aryl, vinyl	Y:0-83	No rhodium leaching was observed. Spent polymer may be recycled. General procedure.	333	333
 (0.03 mmol g <sup>-1</sup> )	 6 examples R <sup>1</sup> = H, alkyl, Cl, O-alkyl, NO <sub>2</sub>	Y:57-80	Useful method for the preparation of unsymmetrical biaryls. Experimental section.	334	334
 Amberlyst A-26 Tetracarbonylhydridoferrate form (1.5 mmol g <sup>-1</sup> )	 9 examples R <sup>1</sup> = alkyl, aryl	Y:53-94	General procedure.	335	335
 (0.60 mmol g <sup>-1</sup> )	 1 example	Y:73	Yield was lower than that of the solution phase equivalent. Experimental section.	336	336

Reagent (Loading)	Transformation	Data/Y%	Comments	Ref.	Prep. Ref.
 (1.6 mmol g <sup>-1</sup> )	 3 examples R <sup>1</sup> = alkyl, aryl	Y:96-100	Reagent may be regenerated. Experimental section. Borohydride supported on Amberlyst A-26 <sup>337</sup> and HFe(CO) <sub>4</sub> supported on Amberlyst A-26 may also be used. <sup>338</sup>	338	338
	 6 examples R <sup>1</sup> = aryl, vinyl R <sup>2</sup> = H, alkyl, aryl X = Br, Cl	Y:95-98	General procedure.	339	
 Amberlyst A-26 Tetracarbonylhydridoferrate form (1.5 mmol g <sup>-1</sup> )	 10 examples R <sup>1</sup> = aryl, vinyl R <sup>2</sup> = H, alkyl, aryl	Y:60-92	Experimental section.	340	340
	 1 example		Kinetic study.	341	341
	 6 examples R <sup>1</sup> = aryl R <sup>2</sup> = H, aryl R <sup>3</sup> = H, Br, CN, CO <sub>2</sub> H, NH <sub>2</sub>	Y:69-83	Triphenylphosphine was also oxidised by this reagent. General procedure.	317	
	 4 examples R <sup>1</sup> , R <sup>2</sup> = alkyl, fluorenyl, phenyl	Y:18-60	The reagent also catalyses the formation of epoxides from alkenes. The manganese porphyrin remains stable and strongly bound to the resin during the reaction. KF supported on Al <sub>2</sub> O <sub>3</sub> has also been used for this transformation. <sup>342</sup>	343	344, 345

3.3.8 Aldehydes/ketones (From miscellaneous)—continued

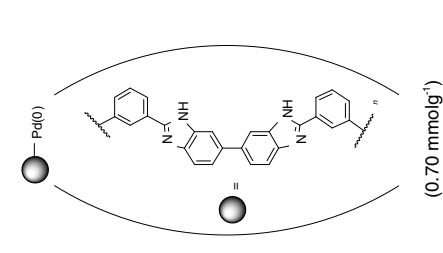
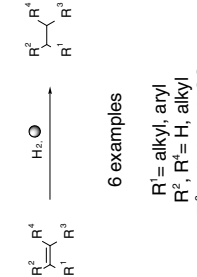
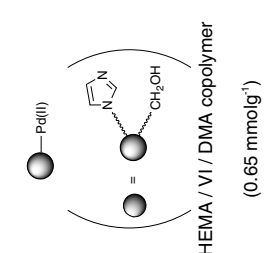
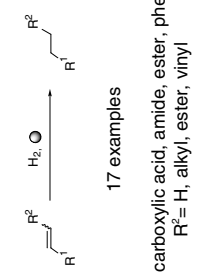
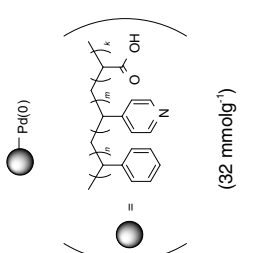
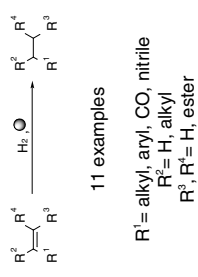
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (0.40 mmol g <sup>-1</sup> )	 1 example	C:5-20	Product ratio depended upon the conditions employed. Ratio of products a:b is 1:2 - 2:1. Experimental section. Also see reference 346.	347	347
 (0.10-4.0 mmol g <sup>-1</sup> )	 1 example	C:100	Also used to catalyse halide displacement with cyanide. General procedure.	348	
 (0.20 mmol g <sup>-1</sup> )	 1 example	Y:100	Ratio of products a:b:c is 48:45:7. Experimental section.	349	349

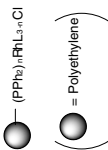
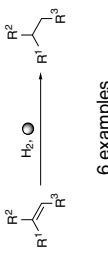
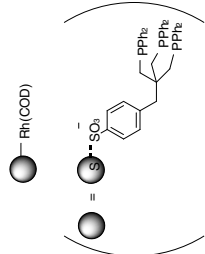
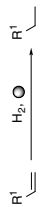
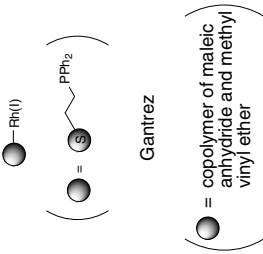
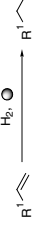
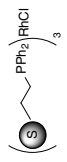
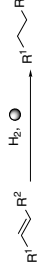
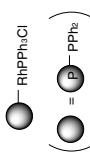
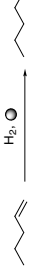


Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>(0.22 mmol g<sup>-1</sup>)</p>	 <p>1 example</p>	C:95	The polymer may be reused without loss of activity. General procedure.	350	350
 <p>3 examples R<sup>1</sup> = H, Me, O-alkyl</p>	Y:83-86	Experimental section.	181	181	
 <p>1 example</p>	de:66-86	Polymer may be reused. Diastereomeric excess increases with <i>n</i> .	351		
 <p><i>n</i> = 1-9</p>	 <p>22 examples R<sup>1</sup> = alkyl, aryl</p>	Y:88-98 P:67-98	Used in a library synthesis. Experimental section.	352	352
 <p>1 example</p>	Y:78	Reaction conditions are milder than normal solution-phase hydrolysis procedures. Experimental section.	353		

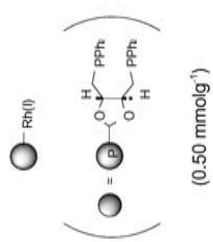
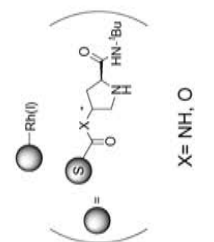
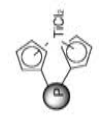
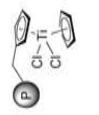

### 3.4 Alkanes

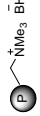
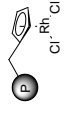
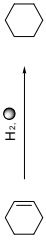
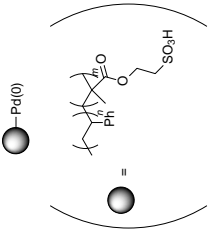
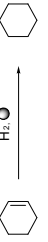
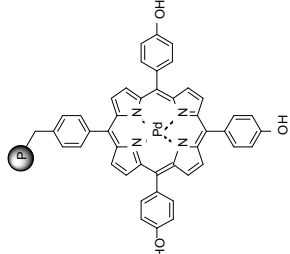
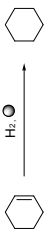
#### 3.4.1 Alkanes (From alkenes and alkynes)

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>(0.70 mmol g<sup>-1</sup>)</p>	 <p>6 examples  R<sup>1</sup> = alkyl, aryl  R<sup>2</sup>, R<sup>4</sup> = H, alkyl  R<sup>3</sup> = alkyl, aryl, CO</p>	Y:86-100	<p>If ketone present some reduction to alcohol is observed. Alternative bound palladium species have also been reported.<sup>354, 355</sup></p> <p>Experimental section.</p> <p>Also see reference 183.</p>	183	183
 <p>HEMA / VI / DMA copolymer  (0.65 mmol g<sup>-1</sup>)</p>	 <p>17 examples  R<sup>1</sup> = alkyl, carboxylic acid, amide, ester, phenyl, vinyl  R<sup>2</sup> = H, alkyl, ester, vinyl</p>		<p>Kinetic study. Several polymer catalysts investigated. Best results given. Catalyst may be recycled without loss of activity.</p> <p>General procedure.</p>	356	356
 <p>(32 mmol g<sup>-1</sup>)</p>	 <p>11 examples  R<sup>1</sup> = alkyl, aryl, CO, nitrile  R<sup>2</sup> = H, alkyl  R<sup>3</sup>, R<sup>4</sup> = H, ester</p>		<p>Kinetic study. Polymer compared to other palladium polymer catalysts. Good selectivity for monohydrogenation of dienes.</p> <p>Experimental section.</p> <p>Also see references 357, 358, 359, 360, 361, 362.</p>	363	363

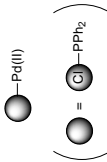
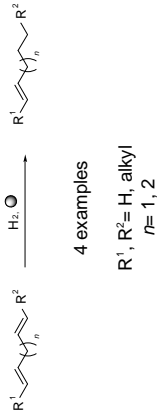
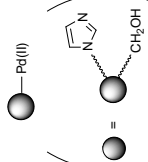
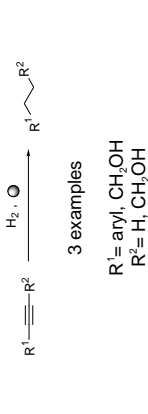
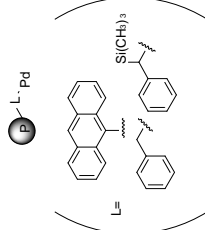
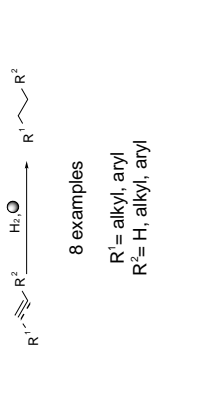
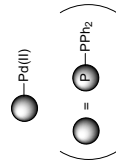
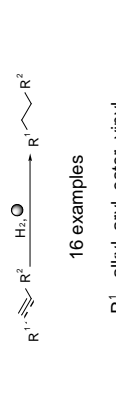
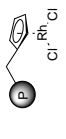
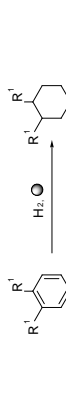
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (0.60 μmolg <sup>-1</sup> )	 6 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> , R <sup>3</sup> = H, alkyl	Y:90-100	The polymer is soluble at reaction temperature but precipitates upon cooling to room temperature. Lower yields with recycled catalyst. General procedure.	364	364
 (0.20 mmolg <sup>-1</sup> )	 3 examples R <sup>1</sup> = H, alkyl aryl	C:100	No rhodium leaching observed. Experimental section. Also see references 365, 366, 367, 368.	276	276
 Gantrez = copolymer of maleic anhydride and methyl vinyl ether	 6 examples R <sup>1</sup> = alkyl, aryl	Y:88->95	Reagent may be recycled. Activity comparable to solution phase Rh(I) catalysts. Soluble polyethylene <sup>369</sup> and related supports <sup>370</sup> have also been reported.	371	371
	 4 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl	C:8-89	Significant isomerization was also observed.	372	372
	 1 example	Y:100	The soluble polymeric catalyst is separated after reaction by membrane filtration. Also see references 373, 374, 375, 376.	377	378

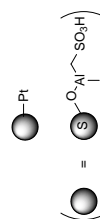
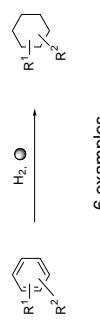
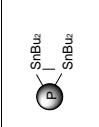
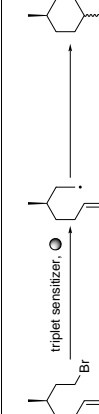
3.4.1 Alkanes (From alkenes and alkynes)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>(0.50 mmol g<sup>-1</sup>)</p>	$\begin{matrix} R^1 \\   \\ C=C \\   \\ R^2 \end{matrix} \xrightarrow{H_2, \odot} \begin{matrix} R^1 \\   \\ CH_2 \\   \\ R^2 \end{matrix}$ <p>2 examples R<sup>1</sup> = phenyl R<sup>2</sup> = alkyl, ester</p>	Y:100 ee:0.6-2.4	Ee's are lower than those obtained with the soluble Rh-diop complex. General procedure. Also see references 379, 380. For a palladium variant see reference 381.	382	382
 <p>X = NH, O (0.10 mmol g<sup>-1</sup>)</p>	$\begin{matrix} R^1 & R^4 \\   &   \\ C=C & \\   &   \\ R^2 & R^3 \end{matrix} \xrightarrow{H_2, \odot} \begin{matrix} R^1 & R^4 \\   &   \\ CH_2 & \\   &   \\ R^2 & R^3 \end{matrix}$ <p>5 examples R<sup>1</sup> = H, alkyl R<sup>2</sup> = alkyl, aryl R<sup>3</sup> = alkyl, amide R<sup>4</sup> = H, ester</p>	ee:76-88	Four different catalysts were studied, including some based on zeolite supports. The catalysts could be recycled. Kinetic study. Full experimental section.	383	383
	$\begin{matrix} R^1 & R^2 \\   &   \\ C \equiv C \end{matrix} \xrightarrow{H_2, \odot} \begin{matrix} R^1 & R^2 \\   &   \\ CH_2-CH_2 \end{matrix}$ <p>12 examples R<sup>1</sup>, R<sup>2</sup> = H, alkyl, aryl</p>		Rates of hydrogenation given. Catalyst is 25–120 times more effective than the corresponding non-polymeric catalyst. General procedure.	384	384
 <p>(0.79 mmol g<sup>-1</sup>)</p>	$\begin{matrix} R^1 & R^2 \\   &   \\ C=C \end{matrix} \xrightarrow{H_2, \odot} \begin{matrix} R^1 & R^2 \\   &   \\ CH_2-CH_2 \end{matrix}$ <p>7 examples R<sup>1</sup> = alkyl, aryl R<sup>2</sup> = H, alkyl, vinyl</p>		Kinetic studies were undertaken. General procedure.	385	385
 <p>Amberlite IRA-400 Borohydride form (3.0 mmol g<sup>-1</sup>)</p>	$\begin{matrix} R^1 & R^2 \\   &   \\ C=C \end{matrix} \xrightarrow{Cu_2SO_4, \odot} \begin{matrix} R^1 & R^2 \\   &   \\ CH_2-CH_2 \end{matrix}$ <p>23 examples R<sup>1</sup> = alkyl, aryl, vinyl R<sup>2</sup> = H, alkyl</p>	Y:0-100	Steric hindrance decreases yield of double bond reduction. Alkynes only partially reduced. Experimental section. CoCl <sub>2</sub> has also been used as a co-catalyst. <sup>386</sup>	387	387

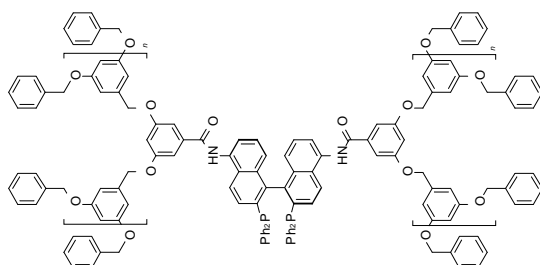

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlite IRA-400 Borohydride form (3.3 mmol g <sup>-1</sup> )	$R^1-CH=CH-R^2 \xrightarrow{Ni(OAc)_2 \cdot 2H_2O} R^1-CH_2-CH_2-R^2$ <p>17 examples            R<sub>1</sub> = alkyl, aryl, ester            R<sub>2</sub> = H, alkyl, nitrile</p>	Y:100	Some more stable structures e.g. benzene, indole could not be hydrogenated even at 65°C. General procedure. Also see reference 388.	389	389
 (0.20 mmol g <sup>-1</sup> )	 <p>1 example</p>	Y:100	Experimental section.	349	349
 (0.010-0.11 mmol g <sup>-1</sup> )	 <p>1 example</p>	C:100	Kinetic study and physical characteristics of resin examined. Experimental section.	390	390
	 <p>1 example</p>	Y:100	Kinetic study. Aromatics are not reduced with this catalyst. Chemoselective for unsubstituted alkenes over nitro groups, carbonyl groups and substituted alkenes.	391	391

3.4.1 Alkanes (From alkenes and alkynes)—continued

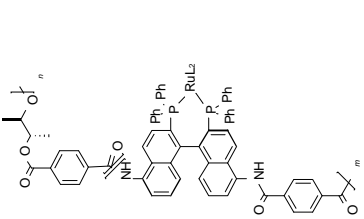
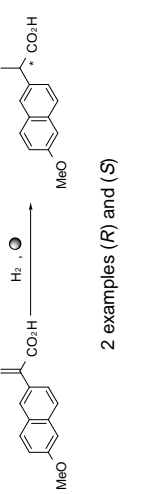
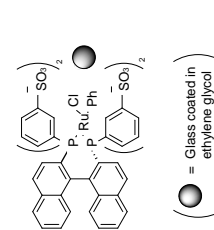
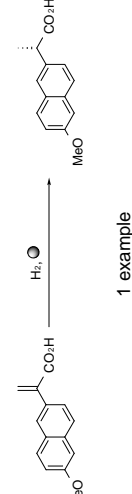
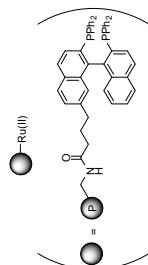
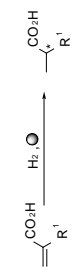
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Montmorillonite K 10	 4 examples $R^1, R^2 = H, \text{alkyl}$ $n = 1, 2$	Y:85-99	Non-conjugated dienes, are selectively reduced to the monoene. Terminal double bonds are reduced preferentially.	392	
 HEMA / VI / DMA co-polymer (0.65 mmol g <sup>-1</sup> )	 3 examples $R^1 = \text{aryl}, \text{CH}_2\text{OH}$ $R^2 = H, \text{CH}_2\text{OH}$		Kinetic study. Several polymer catalysts investigated and the best results are given. Catalyst may be recycled without loss of activity. Alkynes are reduced more rapidly than alkenes. General procedure.	356	356
	 8 examples $R^1 = \text{alkyl}, \text{aryl}$ $R^2 = H, \text{alkyl}, \text{aryl}$	C:100	Three Pd/polystyrene catalysts were prepared and their activity as hydrogenation catalysts compared well to commercial Pd/C. Rates given. Experimental section.	354	354
	 16 examples $R^1 = \text{alkyl}, \text{aryl}, \text{ester}, \text{vinyl}$ $R^2 = H, \text{alkyl}$		Kinetic study. Investigation into catalytic properties of supported Pd catalyst. General procedure.	393	393
 (0.20 mmol g <sup>-1</sup> )	 2 examples $R^1 = H, \text{alkyl}$	Y:100	Also see reference 394. Experimental section.	349	349

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>(0.050 mmol g<sup>-1</sup>)</p>	 <p>6 examples</p> <p>R<sup>1</sup> = alkyl, carboxylic acid, hydroxy R<sup>2</sup> = H, alkyl</p>	Y:26-100	Benzyl groups can also be cleaved using this reagent. Modified catalysts have also been used. <sup>395</sup> Also see references 396, 397.	398	398
 <p>(1.3 mmol g<sup>-1</sup>)</p>	 <p>1 example</p>	Y:89	Acetone/toluene or acetone/propan-2-ol used as sensitizers. General procedures.	399	399

### 3.4.2 Alkanes (From $\alpha,\beta$ -unsaturated carbonyls and related compounds)

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p><math>n = 0, 1, 2</math></p>	 <p>1 example</p>	C:10-69 ee:90-92	Polymeric catalyst gave better enantioselectivity than monomeric equivalent. Catalyst may be reused without loss of activity.	400	400

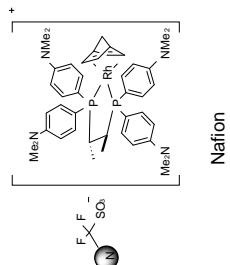
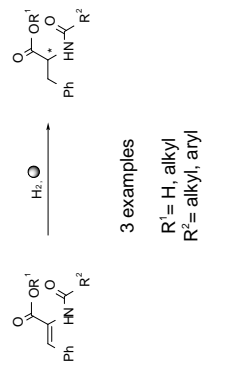
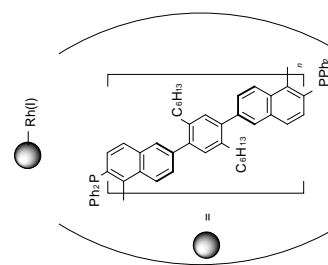
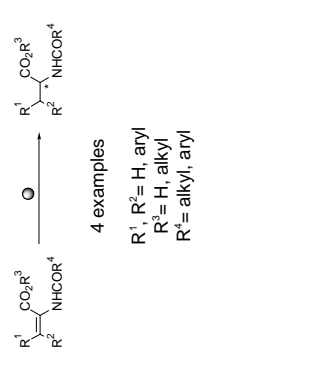
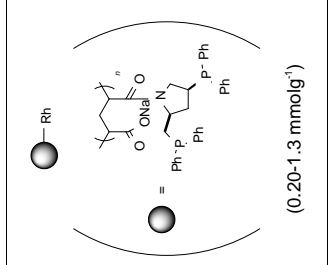
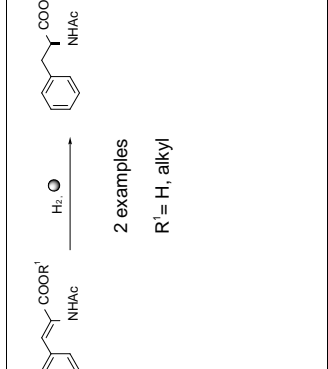
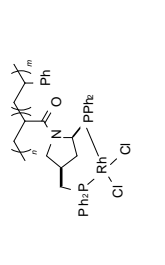
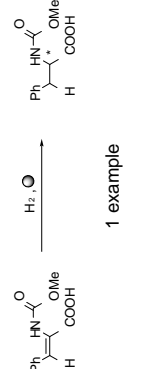
3.4.2 Alkanes (From  $\alpha,\beta$ -unsaturated carbonyls and related compounds)—continued

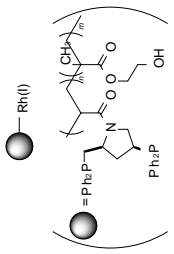
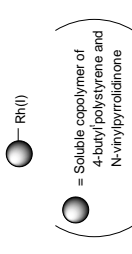
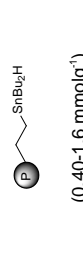
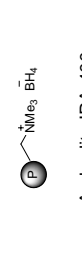
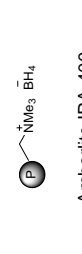
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>soluble copolymer (<i>R</i>) and (<i>S</i>) derivatives were synthesised</p>	 <p>2 examples (<i>R</i>) and (<i>S</i>)</p>	C:100 ee:93	<p>Polymer insoluble in methanol. Reagent may be reused. Tested over ten cycles with no loss in activity. (<i>R</i>) and (<i>S</i>) enantiomers were synthesised giving (<i>R</i>) and (<i>S</i>) products as required. Different polymer compositions compared.</p> <p>General procedure.</p> <p>A variety of alternative supports have also been investigated.<sup>401,402</sup></p>	403	403
 <p>( = Glass coated in ethylene glycol )</p>	 <p>1 example</p>	C:100 ee:96	No leaching of catalyst observed.	404	404
 <p>( = Glass coated in ethylene glycol )</p> <p>(0.18 mmol g<sup>-1</sup>)</p>	 <p>2 examples R<sup>1</sup> = CH<sub>2</sub>CO<sub>2</sub>H, NHAC</p>	Y:90-95 ee:56-64	Catalyst may be reused with a small reduction in ee. Experimental section.	405	405



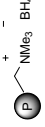
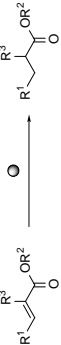
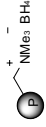

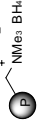

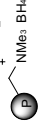
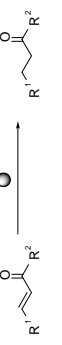
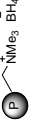

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
<p>X = H, O(CH<sub>2</sub>)<sub>2</sub>OH</p>	$\begin{array}{c} \text{CO}_2\text{H} \\   \\ \text{R}^1-\text{C}=\text{C}-\text{R}^2 \\   \\ \text{H}_2, \text{O} \\ \downarrow \\ \text{CO}_2\text{H} \\   \\ \text{R}^1-\text{C}-\text{C}-\text{R}^2 \\   \quad   \\ \text{H} \quad \text{H} \end{array}$ <p>3 examples R<sup>1</sup> = H, phenyl R<sup>2</sup> = aryl, amide</p>	C:100 ee:52-86	Reagent may be recycled. The ee decreases upon repeated use. Polystyrene <sup>406</sup> and other <sup>407</sup> supports have been used with Rh. An alumina supported palladium system has also been reported. <sup>408</sup>	409, 410	
	$\begin{array}{c} \text{OR}^1 \\   \\ \text{R}^3-\text{C}=\text{C}-\text{C}-\text{OR}^1 \\   \quad   \\ \text{R}^2 \quad \text{OR}^1 \\   \\ \text{H}_2, \text{O} \\ \downarrow \\ \text{OR}^1 \\   \\ \text{R}^3-\text{C}-\text{C}-\text{C}-\text{OR}^1 \\   \quad   \\ \text{R}^2 \quad \text{OR}^1 \end{array}$ <p>4 examples R<sup>1</sup> = H, alkyl R<sup>2</sup> = alkyl, NHAc R<sup>3</sup> = H, alkyl, aryl</p>	C:100 ee:70-94	Catalyst can be reused without loss of either activity or enantioselectivity. General procedure.	411	411
<p>X = H, O(CH<sub>2</sub>)<sub>2</sub>OH</p>	$\begin{array}{c} \text{CO}_2\text{H} \\   \\ \text{R}^1-\text{C}=\text{C}-\text{R}^2 \\   \\ \text{H}_2, \text{O} \\ \downarrow \\ \text{CO}_2\text{H} \\   \\ \text{R}^1-\text{C}-\text{C}-\text{R}^2 \\   \quad   \\ \text{H} \quad \text{H} \end{array}$ <p>5 examples R<sup>1</sup> = aryl R<sup>2</sup> = alkyl, amido</p>	Y:68-92	Enantioselectivity is very low but asymmetric induction arising from the helical conformation of the polymer was observed. Experimental section. Also see reference 412.	413	413
	$\begin{array}{c} \text{CO}_2\text{H} \\   \\ \text{R}^1-\text{C}=\text{C}-\text{NHAc} \\   \\ \text{H}_2, \text{O} \\ \downarrow \\ \text{CO}_2\text{H} \\   \\ \text{R}^1-\text{C}-\text{C}-\text{NHAc} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$ <p>4 examples R<sup>1</sup> = H, aryl</p>	C:70-100 ee:59-83	Reagent may be recycled. The ee decreases upon re-use.	409	

3.4.2 Alkanes (From  $\alpha,\beta$ -unsaturated carbonyls and related compounds)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>Nafion</p>	 <p>3 examples R<sup>1</sup> = H, alkyl R<sup>2</sup> = alkyl, aryl</p>	ee:41-76	Several ion exchange supports were investigated. Best results shown. General procedure.	414	414
	 <p>4 examples R<sup>1</sup>, R<sup>2</sup> = H, aryl R<sup>3</sup> = H, alkyl R<sup>4</sup> = alkyl, aryl</p>	Y:>99 ee:32-75	Catalyst may be reused without loss of activity of enantioselectivity. General procedure.	415	415
 <p>(0.20-1.3 mmol g<sup>-1</sup>)</p>	 <p>2 examples R<sup>1</sup> = H, alkyl</p>	C:50-100 ee:21-89	Catalysts with various phosphorus to carboxylic acid loadings used. Highest ee's obtained using catalyst with lowest loading. Full experimental section. Also see references 416, 417, 418, 419, 420.	421	421
	 <p>1 example</p>	ee:90	Catalyst may be reused with no loss in enantioselectivities obtained and only a small loss in rate.	289	290

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>(<math>\text{P} = \text{P}(\text{H})\text{P}</math>)  <math>\text{P}(\text{H})\text{P}</math></p>	$\text{R}^1-\text{C}(\text{NHC}(\text{O}^-\text{N}(\text{Ac}))\text{COOH})=\text{C}(\text{COOH}) \xrightarrow{\text{H}_2, \text{Et}_3\text{N}, \text{O}} \text{R}^1-\text{CH}_2-\text{CH}(\text{COOH})-\text{CH}_2-\text{COOH}$ <p>4 examples  <math>\text{R}^1 = \text{aryl}</math></p>	ee:33-91	The addition of catalytic $\text{Et}_3\text{N}$ was essential for high optical yields. No yield given in paper. General procedure. Also see reference 422. For a silica-supported variant see reference 423.	424	424
 <p>(<math>\text{P} = \text{Soluble copolymer of 4-butyl polystyrene and N-vinylpyrrolidone}</math>)</p>	$\text{AcHN}-\text{C}(\text{OH})=\text{C}(\text{OH}) \xrightarrow{\text{H}_2, \text{O}} \text{AcHN}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{OH}$ <p>1 example</p>	C:50 ee:87	Full experimental section.	425	425
 <p>(0.40-1.6 mmol g<sup>-1</sup>)</p>	$\text{R}^1-\text{X} + \text{CH}_2=\text{CH}-\text{CN} \longrightarrow \text{R}^1-\text{CH}_2-\text{CH}_2-\text{CN}$ <p>2 examples  <math>\text{R}^1 = \text{alkyl}</math>  <math>\text{X} = \text{Br}, \text{I}</math></p>	Y:80-95	Reagent may be recycled. Tin contaminants remain attached to the polymer. Variety of conditions examined. Experimental section. Also see reference 388.	426 428	427 428
 <p>Amberlite IRA-400 Borohydride form (3.0 mmol g<sup>-1</sup>)</p>	$\text{R}^2-\text{C}(\text{CN})=\text{C}(\text{R}^1) \xrightarrow{\text{Ni}(\text{OAc})_2, \text{O}} \text{R}^2-\text{CH}_2-\text{CH}(\text{CN})-\text{R}^1$ <p>13 examples  <math>\text{R}^1 = \text{H, alkyl, aryl}</math>  <math>\text{R}^2 = \text{H, alkyl}</math>  <math>\text{R}^3 = \text{alkyl}</math></p>	Y:30-93	General procedure.	429	429
 <p>Amberlite IRA-400 Borohydride form (3.0 mmol g<sup>-1</sup>)</p>	$\text{R}^2-\text{C}(\text{OR}^3)=\text{C}(\text{R}^1) \xrightarrow{\text{Ni}(\text{OAc})_2, \text{O}} \text{R}^2-\text{CH}_2-\text{CH}(\text{OR}^3)-\text{R}^1$ <p>14 examples  <math>\text{R}^1, \text{R}^2 = \text{H, alkyl}</math>  <math>\text{R}^3 = \text{alkyl}</math>  <math>\text{R}^4 = \text{alkyl}</math></p>	Y:68-95	Radical mechanism proposed. General procedure.	429, 430	429

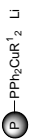

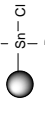
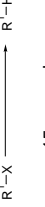
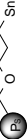
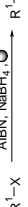
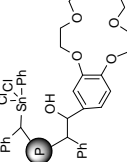
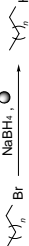
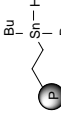
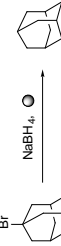
3.4.2 Alkanes (From  $\alpha,\beta$ -unsaturated carbonyls and related compounds)—continued

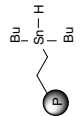
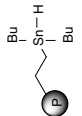
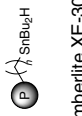
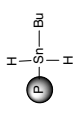
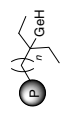
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 SeraLite SRA-400 Borohydride form (3.3 mmol g <sup>-1</sup> )	 12 examples R <sup>1</sup> = H, alkyl, aryl R <sup>2</sup> = alkyl R <sup>3</sup> = H, ester	Y:25-80	Aldehydes are reduced to the unsaturated alcohol. General procedure. Also see reference 431.	432	
 Amberlite IRA-400 Borohydride form (3.0 mmol g <sup>-1</sup> )	 15 examples R <sup>1</sup> = H, alkyl, aryl, ester R <sup>2</sup> , R <sup>3</sup> = H, alkyl R <sup>4</sup> = alkyl	Y:85-100	For slow reducing systems the addition of 0.05 eq. of Ni(OAc) <sub>2</sub> increased the reaction rate. Only $\alpha,\beta$ -unsaturated alkenes reduced. General procedure.	433	433
 Amberlite IRA-400 Borohydride form (3.0 mmol g <sup>-1</sup> )	 3 examples R <sup>1</sup> = H, alkyl, aryl R <sup>2</sup> , R <sup>3</sup> = H, alkyl	Y:94-96	For slow reducing systems the addition of 0.05 eq. of Ni(OAc) <sub>2</sub> increased reaction rate. Non-conjugated alkenes are unreactive. Experimental section.	433	433
 SeraLite SRA-400 Borohydride form (3.3 mmol g <sup>-1</sup> )	 2 examples R <sup>1</sup> , R <sup>2</sup> = alkyl	Y:90-95	Also reduces $\alpha,\beta$ -unsaturated aldehydes to unsaturated alcohol.	432	432
 Amberlite IRA-400 Borohydride form (3.0 mmol g <sup>-1</sup> )	 14 examples R <sup>1</sup> , R <sup>2</sup> , R <sup>3</sup> = alkyl	Y:2-89	Cyclic and acyclic ketones. General procedure.	429	429

### 3.4.3 Alkanes (From haloalkanes)

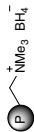
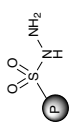
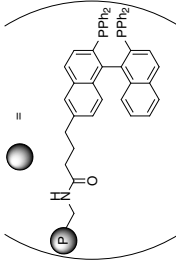
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlite IRA-400 Borohydride form (3.3 mmol g <sup>-1</sup> )	$\text{R}^1\text{-X} \xrightarrow{\text{Ni(OAc)}_2 \cdot \text{O}} \text{R}^1\text{-R}^2$ 25 examples R <sup>1</sup> = alkyl, benzyl R <sup>2</sup> = H, alkyl X = Br, Cl, I, OTs	Y:93-100	A one-pot reduction of tosylates was also illustrated.	434	434
 Amberlite IRA-400 Borohydride form (3.0 mmol g <sup>-1</sup> )	$\text{R}^1\text{-X} \xrightarrow{\text{CuSO}_4 \cdot \text{O}} \text{R}^1\text{-H}$ 13 examples R <sup>1</sup> = alkyl, aryl X = Br, Cl, I	Y:0-100	Experimental section.	387	387
 M = K, Li, Na (2.5 mmol g <sup>-1</sup> )	$\text{R}^1\text{-X} \xrightarrow{\text{O}} \text{R}^1\text{-H}$ 3 examples R <sup>1</sup> = H, alkyl X = Br, I		Kinetic study. Experimental section.	435	435
 Amberlyst A-26 Cyanoborohydride form (3.3 mmol g <sup>-1</sup> )	$\text{R}^1\text{-X} \xrightarrow{\text{O}} \text{R}^1\text{-H}$ 2 examples X = Br, I	Y:77-89	HMPA is required as solvent for this reaction. General procedure.	436	436
 MCM-41 (0.20 mmol g <sup>-1</sup> )	$\text{R}^1\text{-X} \xrightarrow{\text{H}_2 \cdot \text{O}} \text{R}^1\text{-H}$ 10 examples R <sup>1</sup> = alkyl, aryl, benzyl X = Br, Cl	Y:36-92	Aromatic nitro groups are also reduced to anilines. General procedure.	437	437
 Graphite (C <sub>6</sub> K)	$\text{R}^1\text{-X} \xrightarrow{\text{O}} \text{R}^1\text{-H}$ 15 examples R <sup>1</sup> = alkyl, aryl X = Br, Cl, OMs, OTs	Y:0-100	Low yields with tosylates: sulfur-oxygen cleavage is the predominant reaction. Thus alcohols are the main reaction products. Other metal dopants tried but not as successful. Experimental section.	438	439

3.4.3 Alkanes (From haloalkanes)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (0.80-2.6 mmol <sup>g</sup> <sup>-1</sup> ) R <sup>1</sup> = alkyl	 2 examples	C:100	Several resins used and the best results are given. Severe leaching. General procedure.	440	440, 140, 359
 (= Polyethylene) (0.60 mmol <sup>g</sup> <sup>-1</sup> )	 15 examples R <sup>1</sup> = alkyl, aryl X = Br, I	Y:51-100	Excess NaBH <sub>4</sub> and catalytic benzo-15-crown-5 are employed. The polymer is soluble at reaction temperature but precipitates upon cooling to room temperature.	441	441
 (2.6 mmol <sup>g</sup> <sup>-1</sup> )	 10 examples R <sup>1</sup> = alkyl, aryl, benzyl X = Cl, Br, I	Y:60-96	Less than 10 ppm residual tin was detected in products. General procedure.	442	442
 (0.30 mmol <sup>g</sup> <sup>-1</sup> crown ether) (0.40 mmol <sup>g</sup> <sup>-1</sup> Sn)	 2 examples n = 6, 8	Y:64	When multiple functional groups are placed on the same polymer, the overall activity of the catalytic system is increased compared to polymeric systems that contain only one of the reactive sites. Experimental section.	443	443
 (1.0 mmol <sup>g</sup> <sup>-1</sup> )	 1 example	C:72	Various resins investigated. Considered the effects of resin swelling properties and structure/pore size etc. Experimental section.	444, 445	444, 445

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (0.90 mmol g <sup>-1</sup> )	$R^1-X \xrightarrow{\bullet} R^1-H$ 7 examples R <sup>1</sup> = alkyl, benzyl X = Br, Cl	Y:72-100	The reagent can be regenerated. The reagent also facilitates Barton-type dehydroxylation of alcohols and the deamination of amines via isonitriles. General procedure.	428	427
 (1.2 mmol g <sup>-1</sup> )	$X-CH(R^1)-R^2 \xrightarrow{\bullet} H-CH(R^1)-R^2$ 10 examples R <sup>1</sup> = alkyl, aryl, het R <sup>2</sup> = H, alkyl, aryl, het R <sup>3</sup> = H, aryl, het X = Br, OC(S)OPh	Y:65-100	Spent reagent may be regenerated and recycled without loss of activity. No leaching of tin was observed.	446	446
 Amberlite XE-305 Stannane form n = 1, 4 (0.70-1.4 mmol g <sup>-1</sup> )	$Br-CH_2-CH_2-CH_2 \xrightarrow{\bullet} H-CH_2-CH_2-CH_2$ 1 example	Y:>98	Hydride can be regenerated with NaBH <sub>4</sub> . Very low level of tin contamination found in the product. General procedure.	447	447
 Amberlite XE-305 Stannane form (1.2 mmol g <sup>-1</sup> )	$X-CH(R^1)-R^2 \xrightarrow{\bullet} R^1-CH_2-R^2$ 9 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl X = I, Br	Y:80-98	Spent reagent may be regenerated, but only shows 30–60% original hydride content. The suggested reason is tin–tin bonding. Experimental section.	448	448
 n = 0-2 (3.8-4.0 mmol g <sup>-1</sup> )	$R^1-CH_2-X \xrightarrow{Bu-O-O-Bu \cdot \bullet} R^1-CH_2-H$ 4 examples R <sup>1</sup> = alkyl, aryl X = Br, Cl, I	Y:0-60	Halides are reduced in the order I>Br>Cl. Polymer with n = 2 is most reactive. General procedure.	449	449

### 3.4.4 Alkanes (From miscellaneous)

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlite IRA-400 Borohydride form (3.0 mmol g <sup>-1</sup> )	$\text{R}^1-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}^2 \xrightarrow{\text{Ni}(\text{OAc})_2, \text{O}} \text{R}^1-\text{CH}_3$ <p>11 examples R<sup>1</sup> = aryl</p>	Y:78-98	Also reduces nitro groups to amines. General procedure.	450	
 (0.77-0.91 mmol g <sup>-1</sup> )	$\text{R}^1-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}^2 \xrightarrow[\text{(ii) NaBH}_4]{\text{(i) O}} \text{R}^1-\text{R}^2$ <p>6 examples R<sup>1</sup> = alkyl, aryl R<sup>2</sup> = H, alkyl, aryl</p>	Y:6-31	Experimental section.	451	451
 (0.18 mmol g <sup>-1</sup> )	$\text{R}^1-\overset{\text{X}}{\parallel}{\text{C}}-\text{R}^2 \xrightarrow{\text{O}} \text{R}^1-\overset{\text{XH}}{\parallel}{\text{C}}-\text{R}^2$ <p>R<sup>1</sup> = CH<sub>2</sub>, O R<sup>2</sup> = alkyl, amide, carboxylic acid X = CH<sub>2</sub>, O 4 examples</p>	Y:70-100 ee:64-99	Catalyst isolated by filtration and product free of contamination. Catalyst can be re-used with only slight loss in activity. Experimental section. Also see reference 401.	405	405



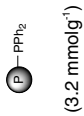
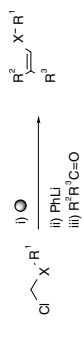

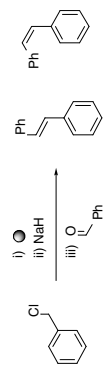
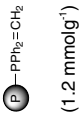

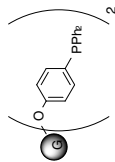
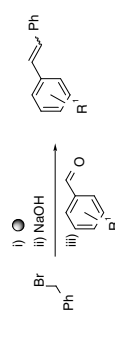
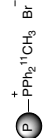
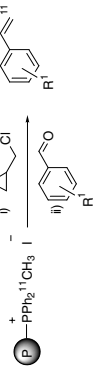
### 3.5 Alkenes

#### 3.5.1 Alkenes (From aldehydes/ketones)

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
$\text{P}-\text{PPh}_2$ (1.4 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}_2-\text{X} \xrightarrow[\text{iii) } \text{R}^2-\text{C}(=\text{O})-\text{R}^3]{\text{i) } \text{O} \quad \text{ii) Base}} \text{R}^1-\text{CH}=\text{CH}-\text{R}^2$ <p>7 examples</p> <p>R<sup>1</sup> = alkyl ester, aryl            R<sup>2</sup> = aryl            X = Br, Cl</p>	Y:24-98	Leads exclusively to monocondensation products. Full experimental section. Also see reference 452.	453	454
$\text{P}-\text{PPh}_2$ (0.70-2.1 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}_2-\text{X} \xrightarrow[\text{iii) } \text{R}^2-\text{C}(=\text{O})-\text{R}^3]{\text{i) } \text{O} \quad \text{ii) Base}} \text{R}^1-\text{CH}=\text{CH}-\text{R}^2$ <p>13 examples</p> <p>R<sup>1</sup>, R<sup>2</sup> = alkyl, aryl            X = Br, Cl</p>	Y:0-68	Dialdehydes gave dienes in amounts equivalent to solution phase reagents (0–62%). Full experimental section.	455	456
$\text{P}-\text{PPh}_2$ (2.3-3.5 mmol g <sup>-1</sup> ) (P = – microporous – linear – Amberlite XE-305)	$\text{R}^1-\text{CH}_2-\text{X} \xrightarrow[\text{iii) } \text{R}^2-\text{C}(=\text{O})-\text{R}^3]{\text{i) } \text{O} \quad \text{ii) Base}} \text{R}^1-\text{CH}=\text{CH}-\text{R}^2$ <p>16 examples</p> <p>R<sup>1</sup> = allyl, aryl, benzyl            R<sup>2</sup> = H, allyl, aryl            X = Br, Cl</p>	Y:0-100	Ketones unreactive. Hydrolysis of phosphonium salt was observed. E:Z ratios similar to solution-phase reactions. Also see reference 457.	458	140
$\text{P}-\text{PPh}_2$ (1.0-1.5 mmol g <sup>-1</sup> )	$\text{R}^1-\text{CH}_2-\text{X} \xrightarrow[\text{iii) } \text{R}^2-\text{C}(=\text{O})-\text{R}^3]{\text{i) } \text{O} \quad \text{ii) Base}} \text{R}^1-\text{CH}=\text{CH}-\text{R}^2$ <p>9 examples</p> <p>R<sup>1</sup>, R<sup>2</sup> = H, alkyl, aryl            R<sup>3</sup> = alkyl, aryl</p>	C:58-93 Y:24-72	E:Z ratio were similar to the corresponding solution phase reactions. General procedure.	459	459

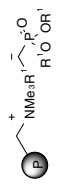
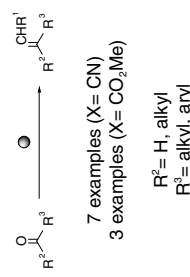
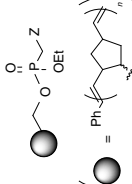
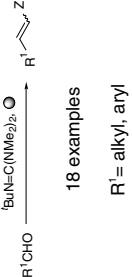

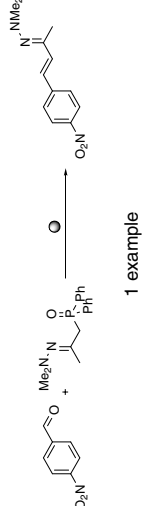
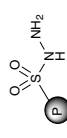
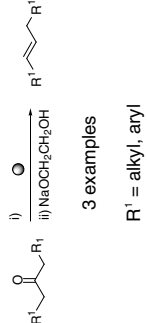
3.5.1 Alkenes (From aldehydes/ketones)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
$\text{P}-\text{PPh}_2$ (1.1-2.4 mmolg <sup>-1</sup> )	$\text{R}^1-\text{CH}_2-\text{X} \xrightarrow[\text{iii) } \text{R}^2-\text{C}(=\text{O})-\text{R}^3]{\text{i) } \text{O} \quad \text{ii) Base}} \text{R}^1-\text{CH}=\text{C}(\text{R}^2)-\text{R}^3$ <p>9 examples                      R<sup>1</sup> = alkyl, aryl                      R<sup>2</sup> = alkyl, allyl, aryl                      R<sup>3</sup> = H, alkyl, aryl                      X = Br, I</p>	Y:89-99	Experimental section. Also see references 460, 461.	460 461	460
$\text{P}-\text{PPh}_2$ (1.8-3.0 mmolg <sup>-1</sup> )	$\text{R}^1-\text{CH}_2-\text{X} \xrightarrow[\text{iii) } \text{R}^3-\text{C}(=\text{O})-\text{R}^4]{\text{i) } \text{O} \quad \text{ii) Base}} \text{R}^1-\text{CH}=\text{C}(\text{R}^2)-\text{R}^3$ <p>10 examples                      R<sup>1</sup>, R<sup>2</sup> = H, alkyl, I, nitrile                      R<sup>3</sup> = aryl</p>	Y:70-100	The Wittig reagents were used in a multi-step synthesis. <sup>51</sup>	51	460
$\text{P}-\text{PPh}_2$ (2.1-3.2 mmolg <sup>-1</sup> )	$\text{R}^1-\text{CH}_2-\text{X} \xrightarrow[\text{iii) } \text{R}^3-\text{C}(=\text{O})-\text{R}^4]{\text{i) } \text{O} \quad \text{ii) Base}} \text{R}^1-\text{CH}=\text{C}(\text{R}^2)-\text{R}^3$ <p>5 examples                      R<sup>1</sup> = alkyl, aryl                      R<sup>2</sup> = H, alkyl, aryl                      R<sup>3</sup> = alkyl, aryl                      R<sup>4</sup> = H, benzyl                      X = Br, I</p>	Y:0-100	General procedure.	462	462
$\text{P}-\text{PPh}_2$ (1.5 mmolg <sup>-1</sup> )	$\text{Br}-\text{CH}_2-\text{R}^1 \xrightarrow[\text{iii) } \text{R}^3-\text{C}(=\text{O})-\text{R}^4]{\text{i) } \text{O} \quad \text{ii) Base}} \text{R}^1-\text{CH}=\text{C}(\text{R}^2)-\text{R}^3$ <p>5 examples                      R<sup>1</sup>, R<sup>2</sup> = alkyl, aryl                      R<sup>3</sup>, R<sup>4</sup> = H, alkyl, aryl</p>		Both inter- and intramolecular Wittig reactions were observed. Experimental section.	463	463

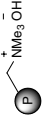
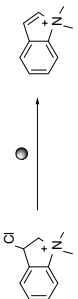


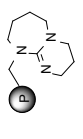

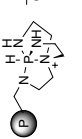


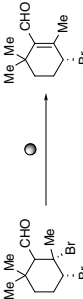
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (3.2 mmol g <sup>-1</sup> )	 8 examples R <sup>1</sup> = alkyl R <sup>2</sup> , R <sup>3</sup> = H, alkyl, aryl X = O, S	Y:79-92	An additional route for the preparation of β-styryl ethers was also discussed briefly. Experimental section.	464	465
	 1 example	Y:40-60	Yield was base dependent. Best results were obtained with sodium hydride.	454	454
 (1.2 mmol g <sup>-1</sup> )	 4 examples r = 4-8	Y:2-45	Wittig reaction was part of a chain homologation reaction cycle with polymer-supported Rh(I) species.	36	460
	 5 examples R <sup>1</sup> = H, alkyl, Cl, NO <sub>2</sub> , O-alkyl	Y:49-95	Maximum <i>E:Z</i> ratio of 3:1 was observed.	299	299
	 3 examples R <sup>1</sup> = H, NO <sub>2</sub> , O-alkyl	Y:29-65	General procedure.	452	452


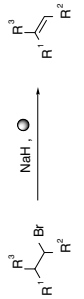

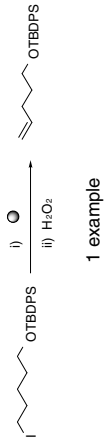

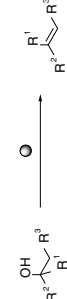
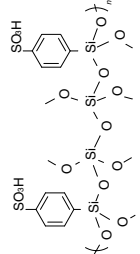
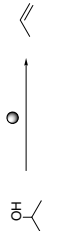

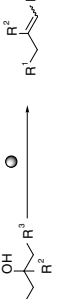

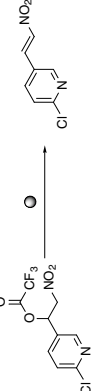
3.5.1 Alkenes (From aldehydes/ketones)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (1.4-1.5 mmol <sup>-1</sup> ) R <sup>1</sup> = Me R <sup>1</sup> = Et (1.2-1.3 mmol <sup>-1</sup> )	 3 examples R <sup>1</sup> = H, NO <sub>2</sub> , OMe	Y:2-99	General procedure.	452	452
 (1.4 mmol <sup>-1</sup> )	 4 examples R <sup>1</sup> = H, alkyl R <sup>2</sup> = alkyl	Y:20-40	Full experimental section.	466	466
 (1.4 mmol <sup>-1</sup> )	 3 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl	Y:11-63	Solvent effects studied. Full experimental section.	467	467
 R <sup>1</sup> = alkyl	 2 examples R <sup>1</sup> = alkyl R <sup>2</sup> = aryl	Y:58-89		468	468

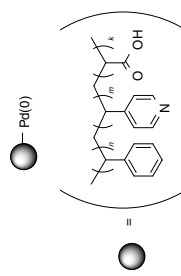
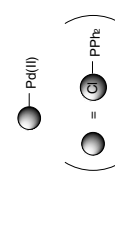
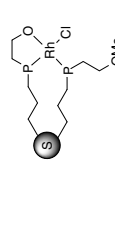

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>Amberlyst A-26 Phosphonate form</p> <p>R<sup>1</sup> = CN (3.4 mmol g<sup>-1</sup>)</p> <p>R<sup>1</sup> = CO<sub>2</sub>Me (2.5 mmol g<sup>-1</sup>)</p>	 <p>7 examples (X = CN) 3 examples (X = CO<sub>2</sub>Me)</p> <p>R<sup>2</sup> = H, alkyl R<sup>3</sup> = alkyl, aryl</p>	Y:64-97 E/Z:50-99	Used in conjunction with a polymer mediated acetal deprotection for a one-pot, two-reagent synthesis. Full experimental section.	260	260
 <p>ROMP Gel (3.3 mmol g<sup>-1</sup>)</p> <p>Z = CN, CO<sub>2</sub>Et</p>	 <p>18 examples R<sup>1</sup> = alkyl, aryl</p>	Y:82-98 P: <sup>&gt;</sup> 95	E:Z ratios of between 70:30 and 100:0. General procedure.	469	469
	 <p>1 example</p>	Y:65	Experimental section.	470	471
 <p>(0.77-0.91 mmol g<sup>-1</sup>)</p>	 <p>3 examples R<sup>1</sup> = alkyl, aryl</p>	Y:9-77	Experimental section.	451	451

### 3.5.2 Alkenes (From elimination)

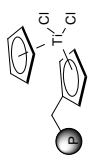
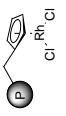
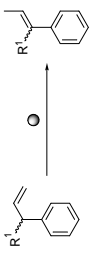

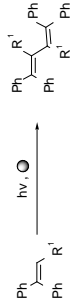
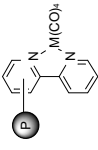

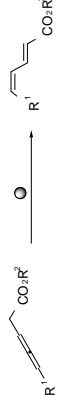
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlite IRA-400 Hydroxide form	 1 example	Y:75	Full experimental section.	472	
 R = Et, iPr, tBu	 3 examples R <sup>1</sup> = alkyl, aryl		The objective of this study was to test the suitability of amine residues as dehydrohalogenating agents.	473	473
 (1.4- 2.9 mmolg <sup>-1</sup> )	 2 examples R <sup>1</sup> = H, alkyl R <sup>2</sup> = alkyl, aryl		Kinetic study using resins with different loadings.	474	474
 (1.0 mmolg <sup>-1</sup> )	 9 examples R <sup>1</sup> = alkyl, aryl, het R <sup>2</sup> = H, alkyl, aryl R <sup>3</sup> = H, Br	C:38-99	Reactive form of catalyst was obtained by treatment of resin with NaH <i>in situ</i> . Experimental section.	475	475
 Amberlyst A-26 Fluoride form	 1 example	Y:100	Full experimental section.	476	477

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (6.7 mmol g <sup>-1</sup> )	 6 examples R <sup>1</sup> = alkyl, aryl, O-aryl R <sup>2</sup> = H, Br R <sup>3</sup> = H, alkyl	Y:14-88	When primary bromides were used, some hydrolysis was also observed. General procedure.	478	478
	 1 example	Y:78		330	330
	 3 examples R <sup>1</sup> , R <sup>2</sup> , R <sup>3</sup> = H, alkyl	Y:100	Rate of reactivity 3 <sup>o</sup> >2 <sup>o</sup> >1 <sup>o</sup> . General procedure.	479	
 (1.7-2.4 mmol g <sup>-1</sup> )	 1 example	Y:90	Several polysiloxanes investigated and the best result is shown. Reactions were carried out in a flow reactor. General procedure.	480	480
	 4 examples R <sup>1</sup> , R <sup>2</sup> , R <sup>3</sup> = H, aryl	Y:5-23	Halogenation also carried out (2 examples given). Experimental section.	481	481
	 1 example	Y:95 P: <sup>&gt;</sup> 95	One step of a multi-step natural product synthesis.	77	


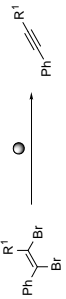
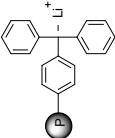
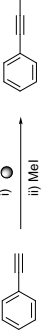
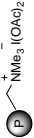
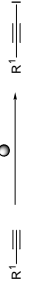
### 3.5.3 Alkenes (From alkynes/alkenes/allenes)

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>(32 mmol g<sup>-1</sup>)</p>	$R^1-C\equiv C-R^2 \xrightarrow{H_2, \bullet} R^1-CH=CH-R^2$ <p>2 examples R<sup>1</sup> = alkyl, CH<sub>2</sub>OH</p>	Y:71-80	Good selectivity for <i>cis</i> alkene was observed. Experimental section. Alternative catalysts have also been used. <sup>360,482,483</sup>	363	363
 <p>Montmorillonite K 10</p>	$R^1-C\equiv C-R^2 \xrightarrow{H_2, \bullet} R^1-CH=CH-R^2$ <p>9 examples R<sup>1</sup> = alkyl, acetal, aryl, ester R<sup>2</sup> = alkyl, aryl, ester, vinyl</p>	Y:87-97	The <i>cis</i> alkene was the only product. No over reduction was observed.	392	
 <p>Sol gel</p>	$Ph-C\equiv C-Ph \xrightarrow{H_2, \bullet} Ph-CH=CH-Ph$ <p>1 example</p>	C: 92	Catalyst may be reused with a slight decrease in activity. Full experimental section.	484	484
	$R^1-C\equiv C-R^2 \xrightarrow{H_2, \bullet} R^1-CH=CH-R^2$ <p>7 examples R<sup>1</sup> = alkyl, ester, OAc, Ts R<sup>2</sup>, R<sup>3</sup> = H, alkyl X = CR<sub>2</sub>, NR, O m, n = 1, 2</p>	C:40-100	Catalyst may be reused, but with some loss of activity. Loss of activity may be minimised by addition of hex-1-ene to the reaction. General procedure.	485	485



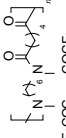
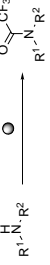
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (0.0032 mmol g <sup>-1</sup> )	$R^1-CH=CH_2 \xrightarrow{R^2/M} R^1-CH=CH-R^2$ <p>3 examples            R<sup>1</sup> = alkyl, aryl            R<sup>2</sup> = alkyl            M = Li, MgX</p>	Y:72-84	E/Z ratios were very high. Choice of catalytic organometallic reagent was important to promote isomerization. General procedure.	486	
 (0.20 mmol g <sup>-1</sup> )	 <p>3 examples            R<sup>1</sup> = alkyl</p>	Y:68-75	Experimental section.	349	349
	 <p>3 examples            R<sup>1</sup> = H, alkyl</p>	Y:50-80	Experimental section.	487	487
 M = Mo, W	$R^1-CH=CH-R^2 \xrightarrow{Et_3Al} R^1-CH=CH-R^2 + R^1-CH=CH-R^2 + R^2-CH=CH-R^2$ <p>1 example            R<sup>1</sup>, R<sup>2</sup> = alkyl</p>	C:100	The polymer bound catalyst was more reactive than the solution phase equivalent. The catalyst could be reused without loss of activity. Experimental section.	488	488
	 <p>8 examples            R<sup>1</sup>, R<sup>2</sup> = alkyl</p>	Y:57-87 P:91-100	Mechanism investigated. Experimental section.	489, 490	

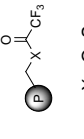
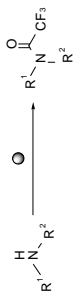
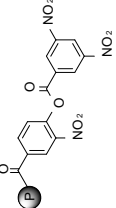
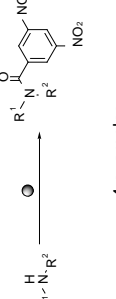
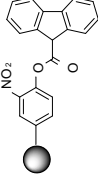
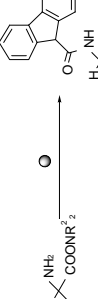
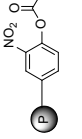
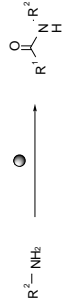
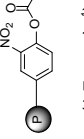
### 3.6 Alkynes and haloalkynes

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (6.7 mmolg <sup>-1</sup> )	 <p>2 examples R<sup>1</sup>= H, aryl</p>	Y:70-89	General procedure. Also see reference 491.	491	491
 (1.5 mmolg <sup>-1</sup> )	 <p>1 example</p>	Y:94	Reagent is air and moisture sensitive. Experimental section.	30	30
	 <p>4 examples R<sup>1</sup>= alkyl, aryl</p>	Y:70-83	General procedure.	131	131

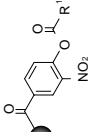
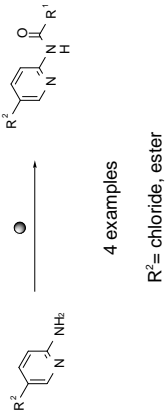
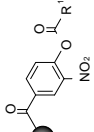
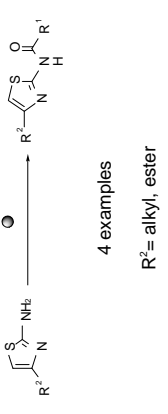
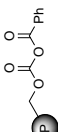

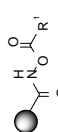
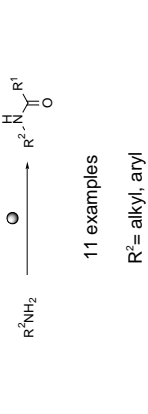
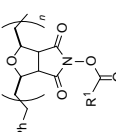
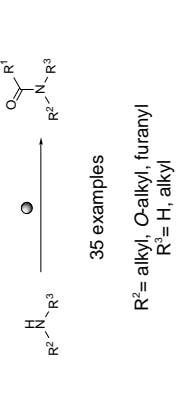
### 3.7 Amides

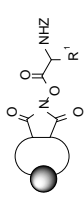
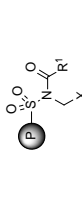
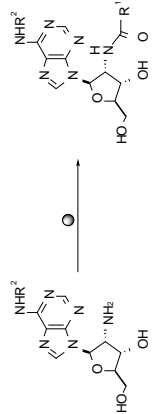
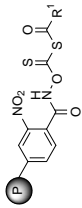
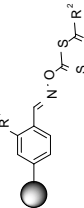
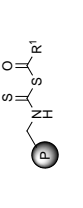
#### 3.7.1 Amides (From amines)

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Nylon (2.4 mmolg <sup>-1</sup> )	 <p>7 examples R<sup>1</sup>= alkyl, aryl, benzyl R<sup>2</sup>= H, alkyl</p>	Y:40-96	Experimental section.	492	492

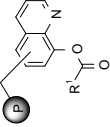
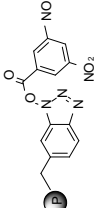
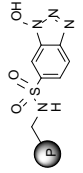
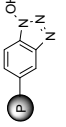
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 X= O, S (0.75-0.86 mmolg <sup>-1</sup> )	 9 examples R <sup>1</sup> = H, alkyl R <sup>2</sup> = alkyl, aryl, benzyl	Y:67-93	Polymer could be stored for long periods at room temperature. Experimental section.	493	493
 (0.62 mmolg <sup>-1</sup> )	 4 examples R <sup>1</sup> = alkyl R <sup>2</sup> = H, alkyl	C:65-95	Function of reagent was derivatisation of aliphatic amines, aminoalcohols and amino-acids. Used to analyse quantities of amphetamine by derivatisation using resin and HPLC analysis. General procedure.	494	494
	 4 examples R <sup>1</sup> = alkyl, phenyl R <sup>2</sup> = alkyl		Reagent used to modify amino acid prior to analysis. Experimental section.	495	495
 (1.0-5.0 mmolg <sup>-1</sup> ) R <sup>1</sup> = alkyl, aryl	 28 examples R <sup>2</sup> = amino acid derivatives	Y:67-99	Could be stored at room temperature without decomposition. General procedure. Synthesis of luteinizing hormone releasing hormone was made using this system. <sup>486</sup>	497, 498	497, 498
 (1.7 mmolg <sup>-1</sup> )	Pentapeptide Boc-Tyr(Obzl)-Gly-Gly-Phe-Leu-Obzl prepared in peptide synthesis cycle.	Y:92	Loading given was of the polymer before coupling with R <sup>1</sup> CO <sub>2</sub> H. Negligible racemisation of phenylalanine was observed when the activated ester was used. Experimental section. Also see reference 499.	500	500

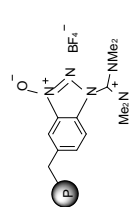
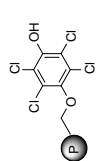
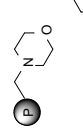
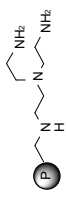
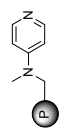
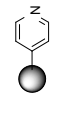
3.7.1 Amides (From amines)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>R<sup>1</sup> = benzyl</p>	 <p>4 examples R<sup>2</sup> = chloride, ester</p>	Y:12-23 P:84-99	Amberlite IRA-120 acidic resin was employed to scavenge unreacted starting material. Low yields were attributed to simultaneous scavenging of the amide product. General procedure.	54	
 <p>R<sup>1</sup> = benzyl</p>	 <p>4 examples R<sup>2</sup> = alkyl, ester</p>	Y:43-94 P:95-99	Amberlite IRA-120 acidic resin was employed to scavenge unreacted starting material. Low yields were attributed to simultaneous scavenging of the amide product. General procedure.	54	
 <p>(1.3 mmol g<sup>-1</sup>)</p>	 <p>5 examples R<sup>1</sup> = alkyl, aryl, benzyl</p>	Y:80-100	Some carboxylic acid side product was observed.	501	501
 <p>( = PMMA) R<sup>1</sup> = alkyl, aryl</p>	 <p>11 examples R<sup>2</sup> = alkyl, aryl</p>	Y:79-97	Reagent could be regenerated. Product was purified by an acid wash. Several polymers were tested and the best example is shown.	502	502
 <p>R<sup>1</sup> = alkyl, aryl, N-alkyl, O-alkyl (2.1-3.8 mmol g<sup>-1</sup>)</p>	 <p>35 examples R<sup>2</sup> = alkyl, O-alkyl, furanyl R<sup>3</sup> = H, alkyl</p>	Y:80-98 P:>95	The reagent was synthesized by ring opening metathesis polymerisation giving high functional loadings. No racemisation of substrate asymmetric centres was observed. Amine hydrochloride salts could be used directly if triethylamine and P-TBD were also introduced. The reagent has also been applied to the production of Weinreb amides, carbamates, hydroxamic acids and ureas from a range of acids and amines.	503	503

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (● = Polymeric ester of Boc-L-Ala) R <sup>1</sup> = alkyl	$R^2NH_2 \xrightarrow{\text{O}} R^2-NH-C(=O)-NHZ$ <p>2 examples</p> <p>R<sup>2</sup> = Triglycine, Boc-L-AlaGlyGly</p>	65-76	No racemisation was detected. Applied successfully to the synthesis of diastereomeric dipeptides. Experimental section. Also see references 504, 505.	506	
 R <sup>1</sup> = alkyl, aryl X = H, nitrile (0.010 mmol g <sup>-1</sup> )	 8 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = benzyl	Y:70-97 P:85-98	Full experimental section.	507	507
 (1.8-5.1 mmol g <sup>-1</sup> ) R <sup>1</sup> = alkyl, aryl	$R^2NH_2 \xrightarrow[2) HCl]{1) \text{O}} R^2-NH-C(=O)-R^1$ <p>11 examples</p> <p>R<sup>2</sup> = alkyl, aryl</p>	Y:62-79	Reagent could be recycled. Several polymers were examined and the best example is shown. General procedure.	508	508
 (1.2-2.1 mmol g <sup>-1</sup> ) R <sup>1</sup> = H, NO <sub>2</sub> R <sup>2</sup> = alkyl, aryl	$R^2-NH_2 \xrightarrow{\text{O}} R^2-NH-C(=O)-R^1$ <p>12 examples</p> <p>R<sup>2</sup> = alkyl, aryl</p>	Y:32-84	Spent polymer could be regenerated and reused. See reference 509 for data on structural properties of resin, and effect of cross-linking on reactivity. General procedure.	510, 511, 509, 512	510, 511, 512
 3 examples R <sup>1</sup> = alkyl, aryl (0.30-0.40 mmol g <sup>-1</sup> )	$R^2-NH_2 \xrightarrow{E_6N} R^2-NH-C(=O)-R^1$ <p>21 examples</p> <p>R<sup>2</sup> = H, alkyl, aryl            R<sup>3</sup> = H, alkyl</p>	Y:65-97	Full experimental section. Also see reference 513.	514	514

3.7.1 Amides (From amines)—continued


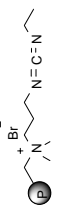
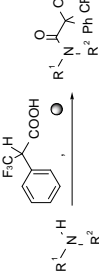
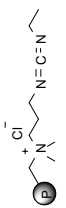
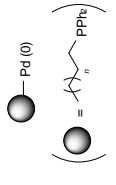

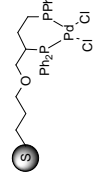
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>R<sup>1</sup> = alkyl, aryl (2.2 mmol g<sup>-1</sup>)</p>	$\text{R}^2\text{-N(R}^3\text{)-H} + \text{O} \longrightarrow \text{R}^2\text{-N(R}^3\text{)-C(=O)-R}^1$ <p>9 examples R<sup>2</sup> = alkyl, aryl, benzyl R<sup>3</sup> = H, alkyl</p>	Y:67-95	Polymer may be regenerated and reused. 1° and 2° amines are acylated at room temperature, but anilines require heating. General procedure.	515	515
 <p>(0.30 mmol g<sup>-1</sup>)</p>	$\text{R}^1\text{-N(R}^2\text{)-H} + \text{O} \longrightarrow \text{R}^1\text{-N(R}^2\text{)-C(=O)-Ar-NO}_2$ <p>4 examples R<sup>1</sup> = alkyl R<sup>2</sup> = H, alkyl</p>	C:60-90	Function of reagent was derivatisation of aliphatic amines, aminoalcohols and amino-acids. Used to analyse quantities of amphetamine by derivatisation using resin and HPLC analysis. General procedure.	494	494
 <p>(0.8-1.0 mmol g<sup>-1</sup>)</p>	$\text{R}^1\text{-C(=O)-OH} + \text{R}^2\text{-N(R}^3\text{)-H} \longrightarrow \text{R}^1\text{-C(=O)-N(R}^2\text{)(R}^3\text{)}$ <p>39 examples R<sup>1</sup>, R<sup>2</sup> = alkyl, aryl, het R<sup>3</sup> = H, alkyl</p>	Y:0-91	Experimental section.	516	516
 <p>(0.25 mmol g<sup>-1</sup>)</p>	$\text{R}^1\text{-C(=O)-X} \xrightarrow[\text{ii) R}^2\text{R}^3\text{NH}]{\text{i) Y, O}} \text{R}^1\text{-C(=O)-N(R}^2\text{)(R}^3\text{)}$ <p>22 examples R<sup>1</sup> = acyl, benzyl, pyrenecarboxy R<sup>2</sup> = H, alkyl R<sup>3</sup> = alkyl, benzyl X = OH, Y = DCC X = R<sup>1</sup>CO<sub>2</sub>, Y = Pyridine</p>	Y:70-100	This reagent displays high reactivity, was recyclable and could be used with a variety of solvents, including water. Experimental section. Also see references 517, 518.	519	519

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>P-TBTU</p>	$AA-NH_2 + AA^x-CO_2H \xrightarrow{Et_3N, \bullet} AA^x-AA^2$ <p>12 examples AA = amino acid</p>	Y:15-82	Spent catalyst may be regenerated and reused without loss of activity. General procedure.	520	520
 <p>(0.70 mmol g<sup>-1</sup>)</p>	$R^1-CO-Cl \xrightarrow[i) R^2-N-R^3]{i) \bullet} R^1-CO-N-R^3$ <p>19 examples R<sup>1</sup> = alkyl, aryl R<sup>2</sup> = alkyl, aryl, benzyl, amino acid R<sup>3</sup> = H, alkyl</p>	Y:75-85	General procedure.	521	521
<p><b>A</b></p>  <p><b>B</b></p> 	$X-NH-R^1 \xrightarrow[i) \bullet]{i) R^2-COCl, \bullet} X-N(R^2)-R^1$ <p>4 examples R<sup>1</sup> = alkyl, aryl, benzyl R<sup>2</sup> = alkyl, aryl R<sup>3</sup> = aryl X = CH, N</p>	Y:70-80	Reaction was carried out using a polymer-supported base ( <b>A</b> ) and then excess acid chloride was removed using a scavenger ( <b>B</b> )	56	
	$HO-C_6H_4-NH-C_6H_4-OMe \xrightarrow{(CF_3CO_2)_2O, \bullet} HO-C_6H_4-N(CF_3)-C_6H_4-OMe$ <p>1 example</p>	Y:99	One step of a multi-step solid-supported reagent mediated synthesis. Conditions were selective for N, over O-alkylation.	75	
 <p>(non cross-linked) ( = PVP)</p>	$R^1-CO-Cl \xrightarrow[i) R^1-NH_2]{i) \bullet} R^1-CO-NH-R^1$ <p>9 examples R<sup>1</sup> = aryl, benzyl</p>	Y:77-97	Several resins tested. Best example given. General procedure.	522	

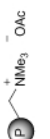
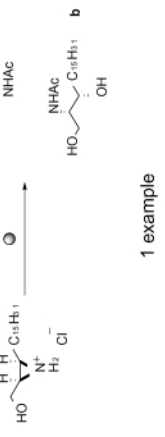
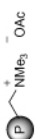
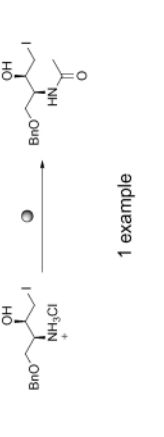

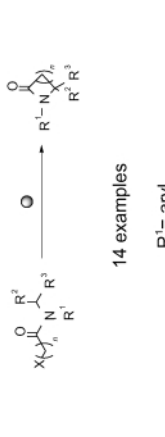
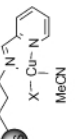
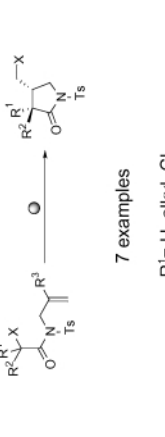
3.7.1 Amides (From amines)—continued




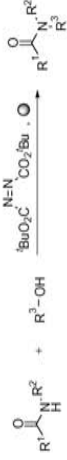






Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 ( = PVP)	 3 examples R <sup>1</sup> = aryl, furyl	Y:90-98 P:92-99	Removal of excess acid chloride afforded the products in good purity. General procedure.	523	
 P-BEMP	 25 examples R <sup>1</sup> = aryl R <sup>2</sup> = alkyl, aryl, benzyl	Y:63-99 P:33-97	A library of compounds was made using a polymeric trisamine resin to scavenge unreacted starting material without simultaneously sequestering product amides.	54	
 P-BEMP	 16 examples R <sup>1</sup> = alkyl, benzyl R <sup>2</sup> = alkyl	Y:37-99 P:75-99	Excess acid chloride was removed with amino-silica gel. General procedure.	524	
 Amberlyst A-21 Hydroxide form	 4500 examples R <sup>1</sup> = alkyl, aryl, het, halogen R <sup>2</sup> = alkyl, aryl, het X = CH, N	P:>85	Library of 4500 compounds created. Resin removed the acid by-product. General procedure.	525	
 (2.7 mmol g <sup>-1</sup> )	 9 examples R <sup>1</sup> = alkyl, benzyl, ester R <sup>2</sup> = alkyl, benzyl R <sup>3</sup> = amino acid	Y:78-100	CBz, Boc and Fmoc groups were tolerated. There was negligible epimerisation at the $\alpha$ -carbon centre during coupling. Experimental section.	526	





Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
	$\begin{matrix} R^1-AA^1-OH \\ H-AA^2-OR^2 \end{matrix} \xrightarrow{\text{imidazole, } \bullet} R^1-AA^1-AA^2-OR^2$ <p>13 examples  <math>R^1 = \text{Boc, CBz, Fmoc}</math>  <math>R^2 = \text{alkyl, allyl, benzyl}</math></p>	Y:90-99	No racemisation was observed. Full experimental section.	527	528
	 <p>6 examples  <math>R^1 = \text{H, alkyl}</math>  <math>R^2 = \text{alkyl}</math></p>	Y:70-95	By using $\text{CDCl}_3$ as reaction solvent, estimation of optical purity could be achieved promptly. General procedure.	529	530
	$R^1-COOH \xrightarrow[\text{ii) } R^2R^3NH]{\text{i) } \bullet} R^1-C(=O)-N(R^2)R^3$ <p>10 examples  <math>R^1, R^2 = \text{alkyl, aryl, het}</math>  <math>R^3 = \text{H, alkyl, aryl, het}</math></p>	Y:72-100	It was essential that chloroform be used as solvent. Excess carboxylic acid remained on the polymer. Reagent could be stored at $0^\circ\text{C}$ for months without loss of activity. General procedure.	530	530
	 <p>9 examples  <math>R^1 = \text{H, alkyl, ester, NO}_2, \text{O-alkyl}</math></p>		Electronics of aryl ring substituents on rate of carbonylation is discussed. General procedure.	277	278
	$R^1-X + \text{PHNH}_2 \xrightarrow{\text{CO, } t\text{BuNH}_2, \bullet} R^1-N(Ph)H$ <p>10 examples  <math>X = \text{I, Br, Cl}</math>  <math>R^1 = \text{aryl}</math></p>	Y:5-86	No leaching was observed. Catalyst could be recycled. General procedures.	531	531

### 3.7.2 Amides (From miscellaneous)

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Acetate form (3.8 mmol g <sup>-1</sup> )	 1 example	Y:74	Products derivatised to triacetates prior to isolation. Product ratio of <b>a:b</b> = 18:56. Full experimental section.	532	
 Amberlyst A-26 Acetate form (3.8 mmol g <sup>-1</sup> )	 1 example	Y:100	Full experimental section.	533	
 Amberlite IRA-400 Hydroxy form	 14 examples R <sup>1</sup> = aryl R <sup>2</sup> = aryl, ester, ketone R <sup>3</sup> = ester n= 1, 2 X= Cl, Br	Y:83-95	Resin could easily be regenerated by washing with dilute sodium hydroxide solution. Experimental section.	534	534
 (0.68-0.74 mmol g <sup>-1</sup> ) X= Cl, Br	 7 examples R <sup>1</sup> = H, alkyl, Cl R <sup>2</sup> = alkyl, aryl, Cl R <sup>3</sup> = H, alkyl	Y:75-96	Catalyst may be recycled with some loss of activity. No leaching of copper observed. Experimental procedure.	535	535





Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 -KF	 <p>15 examples X = Cl, I R<sup>1</sup>, R<sup>2</sup> = H, alkyl, amide, aryl, vinyl R<sup>3</sup> = alkyl, benzyl</p>	Y:61-100	General procedure.	536	537
 -PPh <sub>3</sub> (3.0 mmol g <sup>-1</sup> )	 <p>6 examples R<sup>1</sup> = alkyl, aryl R<sup>2</sup> = amide, ketone R<sup>3</sup> = alkyl, benzyl</p>	Y:66-100 P:92-92	Azodicarboxylate was removed by treatment with TFA and an aqueous wash using a hydrophobic separation tube. Unconverted starting material was removed using resin bound carbonate. General procedure.	538	
 -Yb(OTf) <sub>3</sub>	 <p>10 examples R<sup>1</sup> = alkyl, O-alkyl, O-benzyl R<sup>2</sup> = H, alkyl, aryl, benzyl</p>	Y:96-100	Useful for acid sensitive compounds. General procedure.	539	540
 -NH n = 2, 4, 6	 <p>3 examples R<sup>1</sup> = H, Cl</p>	Y:90-96	The by-products remained bound to the resin, which allowed easy purification. Experimental section.	541	541
 -PBu <sub>3</sub> <sup>+</sup> Br <sup>-</sup>	 <p>1 example</p>	Y:95	Three polymers were tested with the best result shown.	542	542

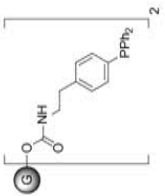






### 3.7.2 Amides (From miscellaneous)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlite IRA-400 Hydroxide form	 1 example	Y:>90		543	

### 3.8 Amines

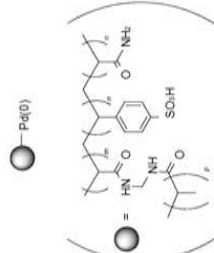
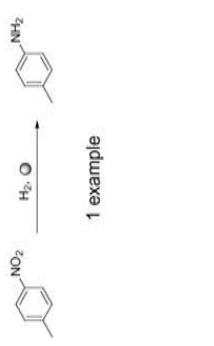
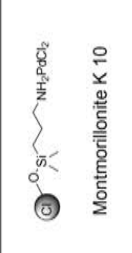
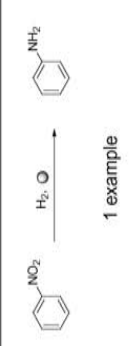
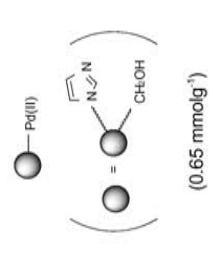
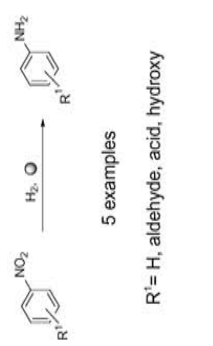
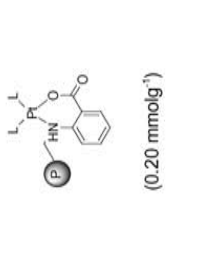
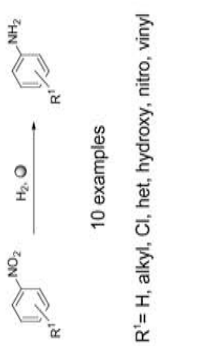
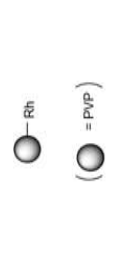
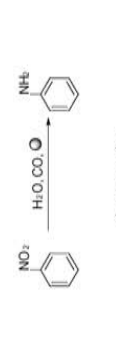
#### 3.8.1 Amines (From azides and nitro compounds)

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlite IRA-400 Borohydride form (3.3 mmol g <sup>-1</sup> )	$R^1-N_3 \xrightarrow{\text{O}} R^1-NH_2$ 11 examples R <sup>1</sup> = alkyl, benzyl, ester	Y:90-96	Reagent does not reduce chloro, ester, acetal, nitrile, epoxide or tosylate functional groups. General procedure.	544	544
 (2.5 mmol g <sup>-1</sup> )	$R^1-N_3 \xrightarrow{\text{O}} R^1-NH_2$ 16 examples R <sup>1</sup> = aryl	Y:93-97	The reagent will not reduce aliphatic azides. Resin can be recycled. General procedure given.	545	545
 Amberlite IRA-400 Borohydride form (3.0 mmol g <sup>-1</sup> )	$R^1-N_3 \xrightarrow{CuSO_4, \text{O}} R^1-NH_2$ 4 examples R <sup>1</sup> = alkyl, aryl, benzyl	Y:85-97	Reagent selectively reduced azides in the presence of alkenes.	387	387
 (● = Poly- <i>n</i> -pyrazine)	$R^1-N_3 \xrightarrow{\text{O}} R^1-NH_2$ 7 examples R <sup>1</sup> = alkyl, aryl, benzyl	Y:83-97	Reagent also reduces ketones, aldehydes and acid chlorides. General procedures.	546	546


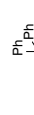



Reagent (Loading)	Transformation	Data <sup>9/</sup>	Comments	Ref.	Prep. Ref.
 (0.50 mmol g <sup>-1</sup> )	$R^1-N_3 \xrightarrow{O} R^1-NH_2$ <p>4 examples R<sup>1</sup> = alkyl, phenyl</p>	Y:90-98	Polystyrene supported triphenylphosphine was not as effective as this reagent.	547	547
 MCM 41 (0.20 mmol g <sup>-1</sup> )	$R^1-N_3 \xrightarrow{H_2, O} R^1-NH_2$ <p>13 examples R<sup>1</sup> = alkyl, aryl, arylsulfonyl</p>	Y:84-99	The catalyst was reused five times with no loss of activity. This selective reduction was also applied to the reduction of 3,4-diazido-1-benzopyrrolidine to the corresponding diamine without debenzoylation or racemisation. General procedures given.	548	548
 (3.2 mmol g <sup>-1</sup> )	 <p>8 examples R<sup>1</sup> = H, trityl R<sup>2</sup> = nucleoside base</p>	Y:89-100	Experimental section.	549	549
 Amberlite IRA-400 Borohydride form (3.0 mmol g <sup>-1</sup> )	$R^1-NO_2 \xrightarrow{CuSO_4, O} R^1-NH_2$ <p>4 examples R<sup>1</sup> = alkyl, aryl</p>	Y:93-100	Nitro groups were selectively reduced in the presence of alkenes. Reagent also reduces N-oxides, nitroso and oxime compounds.	387	387
 (3.0 mmol g <sup>-1</sup> )	 <p>10 examples R<sup>1</sup> = H, aryl, hal, ester, ketone R<sup>2</sup> = H, alkyl, nitro, O-alkyl</p>	Y:15-95	Chloro groups were unaffected under the reaction conditions. Ketones were reduced. General procedure.	550	

3.8.1 Amines (From azides and nitro compounds)—continued

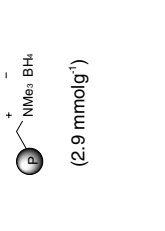
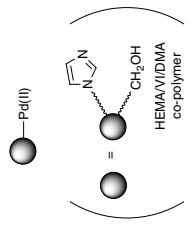
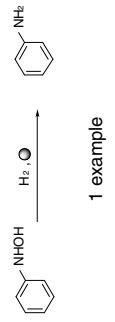
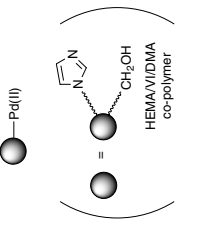
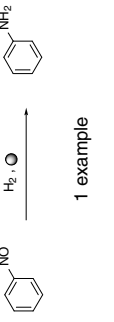
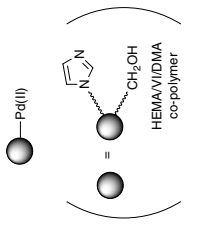
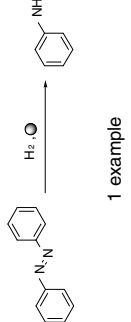
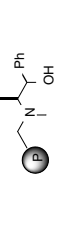
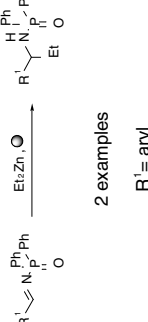
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlite IRA-400 Borohydride form (3.3 mmolg <sup>-1</sup> )	$R^1-NO_2 \xrightarrow{Ni(OAc)_2 \cdot O} R^1-NH_2$ 22 examples R <sup>1</sup> = alkyl, aryl	Y:78-98	Reagent was selective for reduction of the nitro group in the presence of halogen, nitrile and O-alkyl functionality at 0 °C. General procedure.	551	551
 Amberlite IRA-400 Borohydride form	 1 example	Y:95	One step of a multi-step natural product synthesis. Reduction does not remove chloride group on pyridine ring.	77	544
 Amberlite IRA-400 Borohydride form (0.50 mmolg <sup>-1</sup> )	$R^1-NO_2 \xrightarrow{PdCl_2 \cdot O} R^1-NH_2$ R <sup>1</sup> = aryl 14 examples	Y:87-99	Selective for nitro group over other reducible groups. Selective for aromatic nitro over alkyl nitro. Experimental section.	552	552
 Pd(0) (0.70 mmolg <sup>-1</sup> )	 5 examples R <sup>1</sup> = H, alkyl	Y:73-100	Polymer became insoluble once complexed with the palladium. No leaching of palladium was observed. Other catalysts loaded onto polystyrene were also investigated. Experimental section. Palladium on MCM-41 has also been used for this transformation. <sup>583</sup>	183	183

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
		C:100	Physical data about the resin characteristics are also described. Experimental section.	554	554
			Kinetic studies were undertaken. General procedure.	555	
 (0.65 mmol g <sup>-1</sup> )			Kinetic study. The rate of reaction is unaffected by the nature of the ring substituent.	356	356
 (0.20 mmol g <sup>-1</sup> )		Y:0-98	Catalyst may be reused. After five recycles activity is 50% of original. Experimental section.	556	556
 (= PVP)		C:7	General procedure. A chemoselective polymer-supported rhodium carbonyl catalyst has also been reported. <sup>557</sup>	282	282

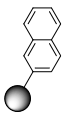
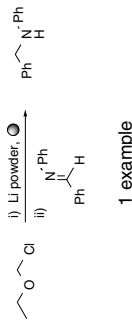
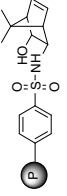
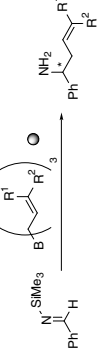
### 3.8.2 Amines (From oximes, imines and related compounds)

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlite IRA-400 Borohydride form (3.0 mmol g <sup>-1</sup> )	$\text{HO}_2\text{N}-\text{C}(\text{R}^1)=\text{C}(\text{R}^2) \xrightarrow{\text{Ni}(\text{OAc})_2, \text{O}} \text{NH}_2-\text{C}(\text{R}^1)-\text{C}(\text{R}^2)$ <p>8 examples R<sup>1</sup> = aryl, furfuryl</p>	Y:68-94	Also reduces nitro compounds to amines. General procedure.	558	558
 (0.70 mmol g <sup>-1</sup> )	$\text{R}^1\text{O}_2\text{N}-\text{C}(\text{Ph})=\text{C}(\text{Ph}) \xrightarrow{\text{B}_2\text{H}_6, \text{O}} \text{NH}_2-\text{C}(\text{Ph})-\text{C}(\text{Ph})$ <p>3 examples R<sup>1</sup> = alkyl, benzyl</p>	Y:100 ee:18-99	Polymer was regenerated and reused without loss of activity. Enantioselectivity was improved upon addition of a Lewis acid, or use of a swollen gel polymer. Experimental section. Also see reference 559.	560, 561	560, 561
 Amberlyst A-15 Proton form	$\text{HO}_2\text{N}-\text{C}(\text{R}^1)=\text{C}(\text{R}^2) \xrightarrow{\text{NaBH}_4, \text{LiCl}, \text{O}} \text{NH}_2-\text{C}(\text{R}^1)-\text{C}(\text{R}^2)$ <p>7 examples R<sup>1</sup> = alkyl, allyl, aryl R<sup>2</sup> = H, alkyl</p>	Y:75-90	Phenyl hydrazones were also used to obtain phenyl hydrazines.	562	
	$\text{HO}_2\text{N}-\text{C}(\text{R}^1)=\text{C}(\text{OR}^2) \xrightarrow{\text{R}^3\text{OH}, \text{O}} \text{NH}_2-\text{C}(\text{R}^1)-\text{C}(\text{OR}^2)$ <p>3 examples R<sup>1</sup> = alkyl, benzyl R<sup>2</sup> = H, alkyl R<sup>3</sup> = alkyl</p>	Y:50-60 C:100	Experimental section.	563	563
 (0.50 mmol g <sup>-1</sup> )	$\text{HO}_2\text{N}-\text{C}(\text{CO}_2\text{H})=\text{C}(\text{CO}_2\text{H}) \xrightarrow{\text{H}_2, \text{O}} \text{NH}_2-\text{C}(\text{CO}_2\text{H})-\text{C}(\text{CO}_2\text{H})$ <p>2 examples R<sup>1</sup> = alkyl, aryl</p>	Y:12-95 ee:1.7-5.1	Experimental section.	408	408


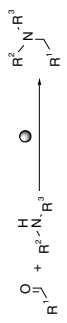

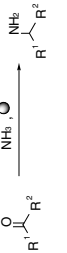


Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (2.9 mmolg <sup>-1</sup> )	$\text{R}^1\text{-N}(\text{R}^2)\text{-NO} \xrightarrow{\text{CuSO}_4 \cdot \text{H}_2\text{O}} \text{R}^1\text{-N}(\text{R}^2)\text{-H}$ <p>9 examples</p> <p>R<sup>1</sup> = alkyl, aryl, benzyl R<sup>2</sup> = alkyl, benzyl</p>	Y:85-99	Aromatic chloro substituents and ester groups are not reduced by the resin. General procedure.	564	564
 (0.65 mmolg <sup>-1</sup> )	 <p>1 example</p>		Kinetic study. General procedure.	356	356
 (0.65 mmolg <sup>-1</sup> )	 <p>1 example</p>		Kinetic study. General procedure.	356	356
 (0.65 mmolg <sup>-1</sup> )	 <p>1 example</p>		Kinetic study. General procedure.	356	356
	 <p>2 examples</p> <p>R<sup>1</sup> = aryl</p>	Y:61-80 ee:84-85	A pronounced solvent effect was observed. General procedure.	565	566

### 3.8.2 Amines (From oximes, imines and related compounds)—continued

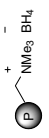
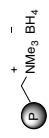
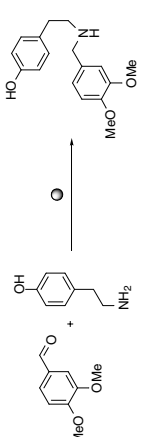
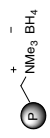
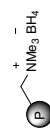
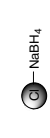
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 = co-polymer of 2-vinylnaphthalene, styrene and divinylbenzene	 1 example	Y:58	Catalyst was recyclable with no loss of activity. Chlorotrimethylsilane was also reduced by this reagent. General procedures.	567, 568	567, 568
 = co-polymer of 2-vinylnaphthalene, styrene and divinylbenzene	 3 examples R <sup>1</sup> , R <sup>2</sup> = H, alkyl	Y:81-99 ee:84-90	General procedures.	569	

### 3.8.3 Amines (From reductive amination of carbonyls)

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Cyanoborohydride form (1.0 mmolg <sup>-1</sup> )	 96 examples R <sup>1</sup> = aryl, het R <sup>2</sup> = alkyl, aryl R <sup>3</sup> = H, alkyl	P:35-92	One step of a multi-step solid-supported reagent synthesis of a library of compounds. General procedure.	50	50
 Amberlyst A-26 Cyanoborohydride form (3.3 mmolg <sup>-1</sup> )	 2 examples R <sup>1</sup> = aryl, alkyl R <sup>2</sup> = alkyl	Y:49-66	Similar yields are obtained to those produced by sodium cyanoborohydride. General procedure.	436	436

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Cyanoborohydride form (3.3 mmol g <sup>-1</sup> )	$R^1-NH_2 \xrightarrow{H_2, CO, O} R^1-NMe_3$ <p>2 examples R<sup>1</sup> = aryl, benzyl</p> <p>3 examples R<sup>1</sup> = H, F, O-alkyl</p>	Y:78-84	Catalytic acid was required for reactions to proceed. General procedure.	436	436
 Amberlyst A-26 Cyanoborohydride form	<p>15 examples R<sup>1</sup> = alkyl R<sup>2</sup>, R<sup>3</sup> = alkyl, benzyl</p>	Y:60-100	One step of a multi-step library synthesis. For complete conversion, a large excess of the aldehyde component was required.	57	
 Amberlyst A-26 Cyanoborohydride form (3.3 mmol g <sup>-1</sup> )	$R^1-CHO + R^2-NH-R^3 \longrightarrow R^1-NH-R^2$	Y:50-99 P:80-95	Used in the synthesis of a non-peptidic library. Acid chloride resin was added to remove excess amine.	570	
 Amberlite IRA-400 Borohydride form (3.3 mmol g <sup>-1</sup> )	$R^1-CHO + R^2-NH-R^3 \longrightarrow R^1-NH-R^2$ <p>26 examples R<sup>1</sup>, R<sup>2</sup> = alkyl, benzyl R<sup>3</sup>, R<sup>4</sup> = H, alkyl.</p>	Y:25-94	Good yields for primary and secondary amines. General procedure.	571	
 Amberlite IRA-400 Borohydride form (2.5 mmol g <sup>-1</sup> )	$R^1-NH_2 + R^2-CHO \longrightarrow R^1-NH-R^2$ <p>Used for library generation - 218 aldehydes - 111 ketones - 240 amines</p>	Y:>73 P:>90	A polymer-supported aldehyde was used to scavenge excess amine. General procedure.	572, 40	
 Amberlyst A-26 Borohydride form	$R^1-NH_2 + R^2-CHO \longrightarrow R^1-NH-R^2$ <p>Library - 217 aldehydes 182 amines</p>		Large library preparation. Imine formed prior to reduction. Patent.	573	

### 3.8.3 Amines (From reductive amination of carbonyls)—continued

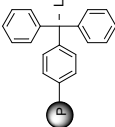
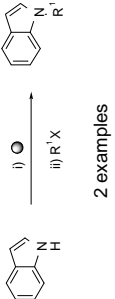
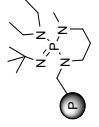

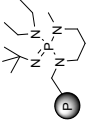
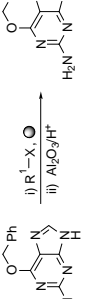
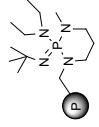
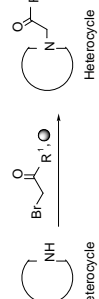
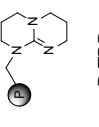
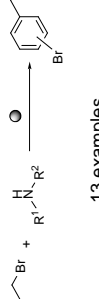
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlite IRA-400 Borohydride form (2.6 mmol g <sup>-1</sup> )	$R^1-C(=O)-R^2 \xrightarrow{Me_3NH, Et_3NHCl, \text{ bead}} R^1-CH_2-NH-R^2$ <p>18 examples</p> <p>R<sup>1</sup> = alkenyl, alkyl, aryl R<sup>2</sup> = H, alkyl, aryl</p>	Y:85-98	ZnCl <sub>2</sub> was added to improve the yields obtained with electron-rich aromatic ketones. General procedure.	574	575
 Amberlite IRA-400 Borohydride form (2.6 mmol g <sup>-1</sup> )	 <p>1 example</p>	Y:90	One step of a multi-step solid-supported reagent synthesis.	75	575
 Amberlite IRA-400 Borohydride form (2.9 mmol g <sup>-1</sup> )	$R^1-C(=O)-R^2 \xrightarrow{NH_2NH_2 \cdot 2HCl, Ni(OAc)_2, \text{ bead}} R^1-CH_2-NH-NH-R^2$ <p>12 examples</p> <p>R<sup>1</sup> = alkyl, aryl R<sup>2</sup> = H, alkyl</p>	Y:58-88	General procedure.	576	577, 551
 Amberlite IRA-400 Borohydride form (2.5 mmol g <sup>-1</sup> )	$R^1-C(=O)-R^2 + H-NH-R^3 \xrightarrow{\text{bead}} R^1-CH_2-NH-R^3$ <p>5 examples</p> <p>R<sup>1</sup> = alkyl R<sup>2</sup> = alkyl, benzyl</p>	Y:50-99 P:80-95	Used in the synthesis of a non-peptidic library. Wang aldehyde resin was added to remove excess amine.	570	
	$R^1-C(=O)-R^2 + H-NH-R^3 \xrightarrow{MW, \text{ bead}} R^1-CH_2-NH-R^3$ <p>24 examples</p> <p>R<sup>1</sup> = alkyl, aryl, benzyl, het R<sup>2</sup>, R<sup>3</sup> = H, alkyl R<sup>3</sup> = alkyl, aryl, benzyl</p>	Y:78-97	Reaction rate increased when wet clay was used. General procedure.	578	578

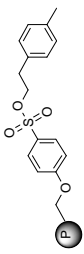
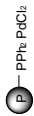



Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
	$R^1-\text{CHO} + R^2-\text{N}-R^3 \xrightarrow[\text{ii) Nu}^-]{\text{i) O}}$ <p>37 examples</p> <p>R<sup>1</sup> = alkyl, aryl, het R<sup>2</sup>, R<sup>3</sup> = alkyl, aryl, benzyl Nu = H, vinyl</p>	Y:0-65 P:40-100	Other resins were investigated. The best example is given. Experimental section.	579	579
	$R^1-\text{CHO} + R^2-\text{N}-R^3 \xrightarrow{\text{MgSO}_4 \cdot \text{R}^3}$ <p>24 examples</p> <p>R<sup>1</sup> = alkyl, aryl, het, PhCO, vinyl R<sup>2</sup> = aryl R<sup>3</sup> = enol ether, CN</p>	Y:73-99	Catalyst was reused without loss of activity. Magnesium sulfate was used as an additive for water sensitive enol ethers.	580	580
	$R^1-\text{CHO} + \text{Ph}-\text{NH}_2 \xrightarrow{\text{Bu}_3\text{SnCN}}$ <p>1 example</p>	Y:77	Strecker-type reactions performed in water. Catalyst may be recovered and reused without loss of activity. General procedure.	581	581

### 3.8.4 Amines (From miscellaneous)

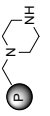
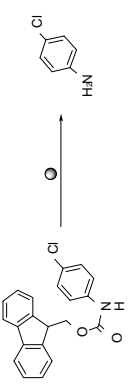
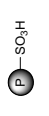
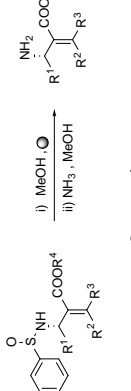
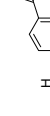
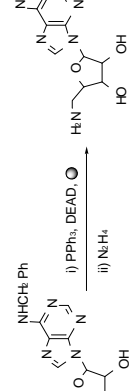
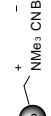
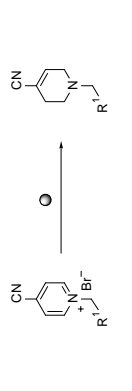
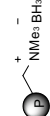
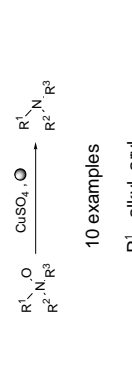
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
	$R^1-\text{X} \cdot \text{O} \xrightarrow{\text{HN-N}}$ <p>4 examples</p> <p>R<sup>1</sup> = acyl, aryl</p>	Y:95-99 P:86-96	Selective reaction. General procedure.	52	
	$\text{HN-N} \xrightarrow{\text{MeI} \cdot \text{O}}$ <p>1 example</p>	Y:61	General procedure.	536	537

3.8.4 Amines (From miscellaneous)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (1.5 mmol g <sup>-1</sup> )	 2 examples R <sup>1</sup> = alkyl, benzyl X = Br, Cl	Y: 96-98	Reagent is air and moisture sensitive. Experimental section.	30	30
 PS-BEMP (2.3 mmol g <sup>-1</sup> )	 16 examples R <sup>1</sup> = aryl R <sup>2</sup> = alkyl R <sup>3</sup> = alkyl, benzyl X = Br, I	Y: 60-100 P: 85->98	This reaction is one step in a multi-step synthesis.	70	582
 PS-BEMP	 4 examples R <sup>1</sup> = alkyl, benzyl	Y: 30-75 P > 99	The N7/N9 purine mixture was purified by filtration over a pad of alumina. General procedure.	524	
 PS-BEMP	 3 examples R <sup>1</sup> = alkyl, aryl	Y: 93-98 P: 93-99	Aminomethyl polystyrene was used to scavenge excess bromide.	52	
 P-TBD (2.2 mmol g <sup>-1</sup> )	 13 examples R <sup>1</sup> = alkyl, benzyl R <sup>2</sup> = alkyl		Reaction was carried out as part of a two-step library synthesis. Yields of final products were 43-63% with purities of 59-99%. Full experimental section.	583	

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
	$R^1-NH-R^2 \xrightarrow{Im, \bullet} R^1-N(R^2)-CH_2-CH_2-C_6H_4-CH_3$ <p>14 examples  <math>R^1 = \text{alkyl, aryl}</math>  <math>R^2 = H, \text{alkyl, aryl}</math></p>	Y:10-95 P:56-95	Reaction also works with sulfur nucleophiles. General procedure. A similar catalyst has been employed for the preparation of unsymmetrical secondary amines. <sup>364</sup>	585	585
	$R^1-NH-R^2 + \text{alkene} \longrightarrow R^1-N(R^2)-alkene$ <p>8 examples  <math>R^1 = H, \text{alkyl}</math>  <math>R^2 = \text{alkyl}</math></p>	Y:11-100	Full experimental section.	586	586
 Amberlyst A-15 Proton form (3.5 mmolg <sup>-1</sup> )	$R^1-NH-R^2 \xrightarrow[\text{ii) } NH_3]{\text{i) } \bullet} R^1-NH-R^2$ <p>10 examples  <math>R^1 = \text{alkyl, aryl, benzyl}</math>  <math>R^2 = H, \text{alkyl}</math></p>	Y:80-99	Primary and secondary Boc amines were deprotected. Boc deprotection step also acts as a purification procedure (catch and release). Experimental section.	587	
	$R^1-NH-R^2 \xrightarrow{MV, \bullet} R^1-NH-R^2$ <p>5 examples  <math>R^1, R^2 = \text{alkyl, benzyl, het}</math></p>	Y:56-98	Boc amides may be deprotected selectively in the presence of Boc amines. General procedure.	588	
 AG 50W-X2 Proton form (5.2 mmolg <sup>-1</sup> )	$R^1-NH-R^2 \xrightarrow[\text{ii) } NH_3, MeOH]{\text{i) } BH_3 \cdot THF} R^1-NH-R^2$ <p>5 examples  <math>R^1 = \text{alkyl, aryl}</math>  <math>R^2, R^3, R^4 = H, \text{alkyl}</math></p>	Y:51-84	Acid resin used to break boron-amine complex. Product remained attached to resin allowing purification. Release was effected by treatment with ammonia. General procedure.	589	

3.8.4 Amines (From miscellaneous)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 XE-305 (1.7 mmol g <sup>-1</sup> )	 1 example	Y:100	Dibenzofulvene formed in reaction was only partially scavenged by the resin. Experimental section.	590	590
 Amberlite IR-120 Proton form	 6 examples R <sup>1</sup> = aryl, het R <sup>2</sup> = H, alkyl, aryl R <sup>3</sup> = alkyl, aryl R <sup>4</sup> = alkyl	Y:84-100	Deprotected product bound to resin and was released by treatment with ammonia. No racemization was detected. General procedure.	591	
 (0.74 mmol g <sup>-1</sup> )	 1 example	Y:96	Full experimental section.	592	592
 Amberlyst A-26 Cyanoborohydride form (3.3 mmol g <sup>-1</sup> )	 2 examples R <sup>1</sup> = aryl	Y:50-75	Reactions are carried out in a mixture of 1:1 ethanol/water.	436	436
 Amberlite IRA-400 Borohydride form (3.0 mmol g <sup>-1</sup> )	 10 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> , R <sup>3</sup> = alkyl	Y:91-96	A large variety of functional groups were tolerated.	593	593



3.9 Amino acids (synthesis & coupling of amino acids and protected forms)

Ref. Prep.	Ref.	Comments	Data/%	Transformation	Reagent (Loading)
594	594	Several other resins were tested. The best example is shown.	C:90-95	<p>4 examples</p> <p><math>R^1 = H, \text{alkyl, benzyl}</math></p>	
595	595	General procedure.	Y:53-62 ee:57-63	<p>3 examples</p> <p><math>R^1 = \text{alkyl, benzyl}</math> <math>X = Br, I</math></p>	
598	598	Tosyl and benzyl protection were compatible with this reaction.  Also see references 596, 597, 251, 598, 599.		<p>3 examples</p> <p><math>R^1 = \text{alkyl}</math></p>	
596	596	General procedure.	Y:92	<p>1 example</p>	


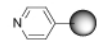
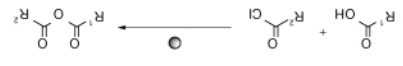
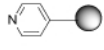

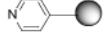
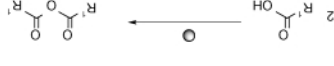
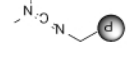
3.9 Amino acids (synthesis & coupling of protected forms)—continued

Ref. Prep. Ref.	Comments	Data/%	Transformation	Reagent (Loading)
600	Reagent could be regenerated. Experimental section.		6 examples $7 \text{ H}_2\text{N}-\text{CH}(\text{R}^1)-\text{CO}_2\text{Me} + 2 \text{ Me}_3\text{C}-\text{N}(\text{H})-\text{CH}_2-\text{CO}_2\text{H} \xrightarrow{\text{MCH}} \text{Me}_3\text{C}-\text{N}(\text{H})-\text{CH}_2-\text{CH}(\text{R}^1)-\text{CO}_2\text{Me} + 2 \text{ H}_2\text{N}-\text{CH}(\text{R}^1)-\text{CO}_2\text{H}$ $\text{M} = \text{Pd, Pt}$	
601	General procedure.	Y:82-93	3 examples $\text{AA}^1-\text{OH} + \text{AA}^2-\text{OR}^1-\text{HO} \xrightarrow{\text{Et}_3\text{N}} \text{AA}^1-\text{AA}^2$	
140	Spent polymer could be reduced using trichlorosilane and reused. General procedure.	Y:65-88	4 examples $\text{Z}-\text{AA}^1 + \text{AA}^2-\text{OEt} \xrightarrow{\text{Z}^+, \text{Et}_3\text{N}} \text{Z}-\text{AA}^1-\text{AA}^2-\text{OEt}$ $\text{AA} = \text{Val, Gly, Phe}$	Amberlite XE-305 
505	Products were obtained in chromatographically pure form.	Y:42-100	17 examples $\left( \text{AA}^1 \right)_n-\text{NH}_2 \xrightarrow{\text{AA}^2-\text{NH}_2} \left( \text{AA}^1 \right)_n-\text{AA}^2-\text{NH}_2$	
603	Racemisation comparable to DCC coupling. Reagent could be stored for over three months without loss of activity. Analogous coupling carried out with dipeptide and amino acid (Y:84%).	Y:84	2 examples $\text{X}-\text{Leu}-\text{OH} + \text{H}-\text{Gly}-\text{OEt} \xrightarrow{\text{X}-\text{Leu}-\text{Gly}-\text{OEt}} \text{X}-\text{Leu}-\text{Gly}-\text{OEt}$	(1.3 mmol) <sup>1</sup> 
518	Reaction used for polypeptide synthesis. General procedures. Also see reference 605.	Y:51-97	11 examples $\text{BocHN}-\text{AA}^1 + \text{HN}-\text{AA}^2-\text{OP} \xrightarrow{\text{DCC}} \text{BocHN}-\text{AA}^1-\text{AA}^2-\text{OP}$	(1.0 mmol) <sup>1</sup> 

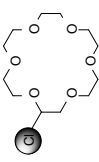
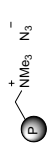
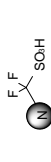
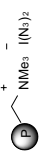
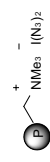
3.10 Amino alcohols

Ref. Prep.	Comments	Data/%	Transformation	Reagent (Loading)
607	Some leaching of osmium was observed, although recycled catalyst maintained high activity.	Y:30-81 ee:88-99	<p>8 examples</p> <p><math>R^1 = \text{H, O-alkyl, nitro}</math>  <math>R^2 = \text{alkyl}</math>  <math>R^3 = \text{alkyl, O-alkyl}</math>  <math>X = \text{H, Br}</math></p>	<p>Co(II)-salen</p>
606				<p>Co(II)-salen</p>
608	Recyclable reagent. This was a one-pot reaction where the supported species catalysed both the epoxidation and the <i>trans</i> ring-opening.	Y:30-70	<p>12 examples</p> <p><math>R^1 = \text{alkyl, aryl, benzyl}</math>  <math>R^2 = \text{aryl}</math></p>	<p>Co(II)-salen</p>
609	General procedure.	Y:25-91	<p>13 examples</p> <p><math>R^1 = \text{alkyl, aryl}</math>  <math>R^2, R^3 = \text{H, alkyl}</math>  <math>R^4 = \text{alkyl}</math></p>	<p>Montmorillonite K 10</p>
610, 611, 612	Product may hydrolyse under the reaction conditions to give the corresponding amidol acetate salt. Experimental section.	Y:18-100	<p>5 examples</p> <p><math>R^1, R^2 = \text{H, alkyl}</math>  <math>X = \text{Cl, Cl}_2\text{CO}_2</math></p>	<p>Amberlyst A-26          Acetate form          (3.8 mmol/g)</p>

3.11 Anhydrides

Ref. Prep.	Comments	Data/%	Transformation	Reagent (Loading)
522	Several polymers with different cross-linkings were used. The best example is shown here. General procedure. Also see references 613, 614.	Y:80-86	 <p>3 examples</p>	 <p>(non cross-linked) = PVP</p>
613	Both symmetrical and mixed anhydrides could be generated. Mixed anhydride synthesis sometimes produced small quantities of symmetric anhydrides. Hydrochloric acid generated was scavenged by the polymer. General procedure.	Y:65-98	 <p>21 examples (mixed anhydrides) 3 examples (symmetric anhydrides) R<sup>1</sup> = alkyl, aryl, O-alkyl R<sup>2</sup> = alkyl, aryl, vinyl</p>	 <p>Reillex 425 = copolymer of polyvinylpyrrolidone, divinylbenzene and 4-ethylstyrene (7.0 mmol<sup>-1</sup>)</p>
614	Batch and flow-column procedures were investigated. General procedure.	Y:56-100 (batch) Y:89-99 (column)	 <p>18 examples R<sup>1</sup> = alkyl, vinyl, aryl</p>	 <p>Reillex 425 = copolymer of polyvinylpyrrolidone, divinylbenzene and 4-ethylstyrene (7.0 mmol<sup>-1</sup>)</p>
250	Spent reagent was regenerated and reused, with only a small decrease in activity. General procedure.	Y:65-100	 <p>2 examples R<sup>1</sup> = glutaric acid, stearic acid</p>	 <p>(2.4 mmol<sup>-1</sup>)</p>

### 3.12 Azides

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Montmorillonite K 10	$R^1-Br \xrightarrow{NaN_3, \text{O}} R^1-N_3$ <p>7 examples</p> <p>R<sup>1</sup> = alkyl, allyl, aryl, benzyl</p>	Y:59-91	Best results were obtained with R <sup>1</sup> = benzyl.	615	615
 Amberlite IRA-400 Azide form (2.6 mmol g <sup>-1</sup> )	$R^1-X \xrightarrow{\text{O}} R^1-N_3$ <p>16 examples</p> <p>R<sup>1</sup> = alkyl, benzyl            X = Br, Cl, I, OTs</p>	Y:60-100	Polymeric reagent could be regenerated. The reagent was found to be stable and not explosive. General procedure. Also see reference 616.	617	617
 Nafion-H Proton form	$R^1 \text{ (alkene)} \xrightarrow{TMSN_3, NBS, \text{O}} R^1 \text{ (azide)}$ <p>7 examples</p> <p>R<sup>1</sup> = alkyl            R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> = H, alkyl</p>	Y:52-77	General procedure. Also see reference 618.	619	
 (2.9 mmol g <sup>-1</sup> )	$R^1 \text{ (alkene)} \xrightarrow{\text{O}} R^1 \text{ (azide)}$ <p>15 examples</p> <p>R<sup>1</sup> = alkyl, aryl, het, O-alkyl            R<sup>2</sup> = H, alkyl, O-alkyl            R<sup>3</sup> = H, alkyl, aryl</p>	Y:38-98	Azido iodination of alkenes proceeded with <i>anti</i> -selectivity. Free hydroxy groups were tolerated in the substrate. Experimental section.	620	620
 (2.9 mmol g <sup>-1</sup> )	$R^1 \text{ (alkene)} \xrightarrow{\text{O}} R^1 \text{ (azide)}$ <p>2 examples</p> <p>R<sup>1</sup> = alkyl            R<sup>2</sup>, R<sup>3</sup> = ester, ether</p>	Y:82-86	The ratio of products (a,b) ranged from 1:1 to 9:1. General procedure.	130	130

### 3.12 Azides—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst IRA-400 Azide form	 5 examples $R^1, R^2 = \text{H, hydroxy}$ $X = \text{N, CH}$	Y:50-86	Epoxide opening of polyaromatic hydrocarbon substrates was stereo- and regioselective. Full experimental section. Calcium cation exchanged zeolite clay has also been used for a similar transformation. <sup>621</sup>	622	622

### 3.13 Aziridines

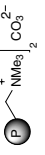
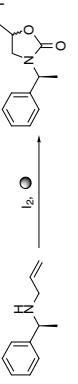
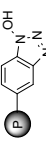
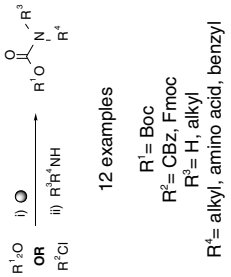
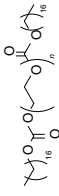
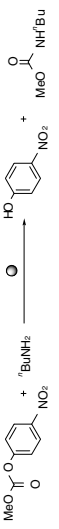
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Carbonate form (3.7 mmol g <sup>-1</sup> )	 1 example $R^1 = n\text{-C}_{13}\text{H}_{27}$	Y:100	Reagent could be regenerated. Experimental section.	611	623
 Amberlyst A-26 Carbonate form (3.7 mmol g <sup>-1</sup> )	 4 examples $R^1, R^2 = \text{H, alkyl}$ $R^3 = \text{H, OH}$ $X = \text{Cl, Cl}_3\text{CO}_2$	Y:95-96	Reagent could be regenerated. Experimental section.	610	623
 Amberlyst A-26 Carbonate form (3.8 mmol g <sup>-1</sup> )	 1 example	Y:90	Full experimental section.	624	

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Carbonate form (3.8 mmol g <sup>-1</sup> )	 1 example	Y:100	Full experimental section.	532	

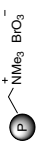

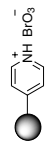

### 3.14 Carbonates and carbamates

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Carbonate form (3.8 mmol g <sup>-1</sup> )	 2 examples R <sup>1</sup> = alkyl	Y:84-87	Full experimental section.	625	623
 $n = 1-7$ X = P, N (0.40-3.2 mmol g <sup>-1</sup> )	 5 examples R <sup>1</sup> = alkyl, aryl, allyl, benzyl, vinyl	Y:86-91	Several catalysts were tested and the best results are given. General procedure.	626	626
 Amberlyst A-26 Carbonate form (3.7 mmol g <sup>-1</sup> )	 6 examples R <sup>1</sup> = alkyl R <sup>2</sup> = H, benzyl	Y:80-95	The reagent could be regenerated. <i>E:Z</i> ratios were between 99:1 and 45:55. Full experimental section.	38, 625	623

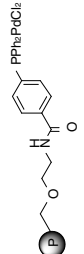
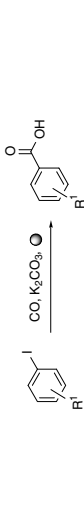
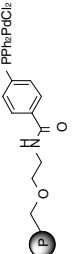
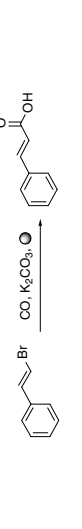
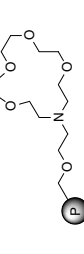
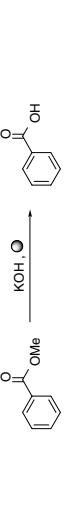
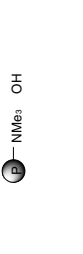

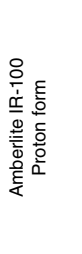
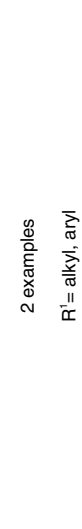
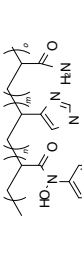
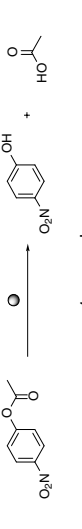
### 3.14 Carbonates and carbamates—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Carbonate form (3.7 mmol g <sup>-1</sup> )	 1 example	Y:100	The reagent could be regenerated. The product was a 1:1 mixture of diastereoisomers. Experimental section.	627	623
 (0.25 mmol g <sup>-1</sup> )	 12 examples R <sup>1</sup> = Boc R <sup>2</sup> = CBz, Fmoc R <sup>3</sup> = H, alkyl R <sup>4</sup> = alkyl, amino acid, benzyl	Y:21-99	Water had no effect on the reactivity or recovery of products and could be used as a co-solvent. This was particularly useful for amines, for example amino acids which were only slightly soluble in the usual organic solvents. General procedure.	628	519
 PEG	 1 example		Kinetic study.	629	

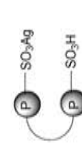
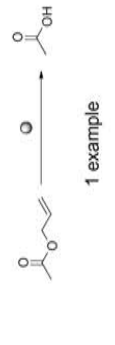
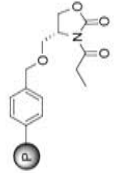
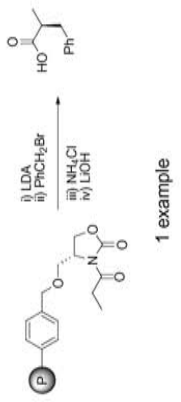

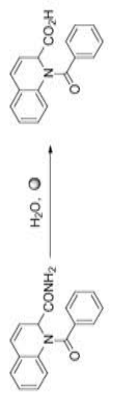
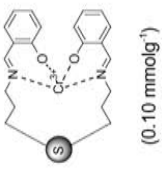
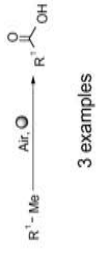
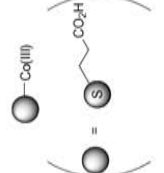


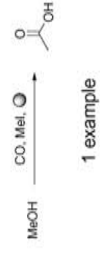
### 3.15 Carboxylic acids

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Bromate form (3.2 mmol g <sup>-1</sup> )	 6 examples R <sup>1</sup> = aryl	Y:80-100	HBr was removed by the resin. General procedure.	228	228
 (= PVP) (2.7 mmol g <sup>-1</sup> )	 3 examples R <sup>1</sup> = alkyl, aryl	Y:80-95	Reagent can be regenerated. Two polymers were investigated and the best example is shown. Secondary alcohols were oxidised to ketones. General procedure.	229	229

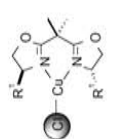



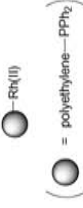
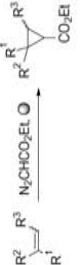
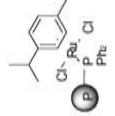

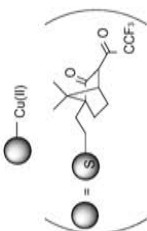



Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Atggel (0.41 mmol g <sup>-1</sup> )	 17 examples R <sup>1</sup> = alkyl, hal, nitro, O-alkyl	Y:45-100	Reaction carried out in aqueous phase. General procedure.	630	
 Atggel (0.41 mmol g <sup>-1</sup> )	 1 example	Y:92	General procedure.	630	
 (0.40-2.2 mmol g <sup>-1</sup> )	 1 example	Y:99	Resin may be reused without loss of activity. Experimental section.	631	631
 Amberlite IR-100 Proton form	 12 examples R <sup>1</sup> , R <sup>2</sup> = alkyl		Kinetic studies were undertaken. Rates of ester hydrolysis were similar to those observed when using sodium hydroxide. General procedures.	632	
 Amberlite IR-100 Proton form	 2 examples R <sup>1</sup> = alkyl, aryl		Kinetic study. Wofatit C studied as a comparison but Amberlite IR-100 was found to be superior. Experimental section.	633	
	 1 example		Complementary nucleophilic groups increase hydrolysis rate. Kinetic study.	634	634

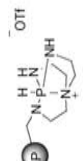



3.15 Carboxylic acids—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlite IR-120 Proton / Silver form	 1 example		General procedure.	635	635
	 1 example	Y:42 ee:96	Yield based on loading of original Merrifield polymer. General procedure.	636	636
 Amberlite IR-120 Proton form	 1 example	Y:61	Selective hydrolysis. General procedure.	637	
 (0.10 mmol g <sup>-1</sup> )	 3 examples R <sup>1</sup> = aryl	Y:7-29	General procedure.	638	638
 (0.68 mmol g <sup>-1</sup> )	 2 examples R <sup>1</sup> = H, Cl	Y:6-25	Catalyst may be reused with only a minimal loss of activity. General procedure.	324	324
	 1 example		Kinetic study.	639	639







### 3.16 Cyclopropanes

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 R <sup>1</sup> = aryl, benzyl	 1 example	Y:13-56 ee:0-45	The catalysts were recoverable and retained most of their catalytic activity. Reaction specificity was solvent dependent. General procedure.	640	640
 R <sup>1</sup> = aryl, benzyl	 3 examples R <sup>1</sup> , R <sup>2</sup> = H, alkyl, Cl, ester R <sup>3</sup> = alkyl, aryl	Y:11-91	Catalyst may be reused. No leaching of copper was observed. General procedure.	641	641
 (0.20 mmol g <sup>-1</sup> )	 6 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> , R <sup>3</sup> = H, alkyl	Y:56-96	It was possible to recycle the reagent with no leaching of the metal. The catalyst was soluble in toluene at 100 °C but insoluble at 25 °C. Copper(II) and ruthenium(II) polymeric catalysts were also investigated and found to have similar catalytic activity. General procedure. Similar reactions were carried out with sodium/copper cross-zeolites, <sup>642</sup> Cu and Rh zeolite complexes <sup>643</sup> and with chiral Cu(I) complexes on zeolite bound pyrrolidine ligands. <sup>644</sup>	645	645
 (2.5 mmol g <sup>-1</sup> )	 3 examples R <sup>1</sup> , R <sup>2</sup> = H, alkyl	Y:68-80	No leaching of catalyst into solution was observed. Catalyst may be reused without loss of activity. General procedure.	646	646
 (0.14 mmol g <sup>-1</sup> )	 1 example	Y:43 ee:98	Catalyst may be reused with only minor loss of activity. General procedure.	647	647




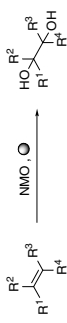



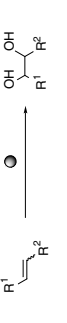


### 3.16 Cyclopropanes—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (1.0 mmol g <sup>-1</sup> )	 1 example	Y:99	The catalyst may be reused. Experimental section.	648	648
	 1 example	Y:100	The reagent was stable to the reaction conditions and storage. General procedure.	649	


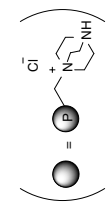
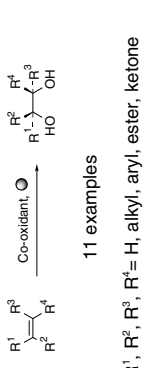
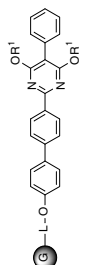
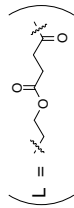
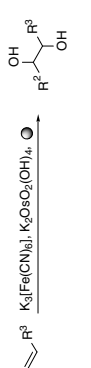
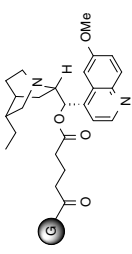
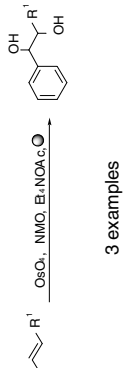
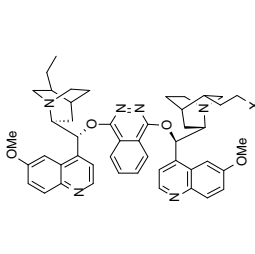
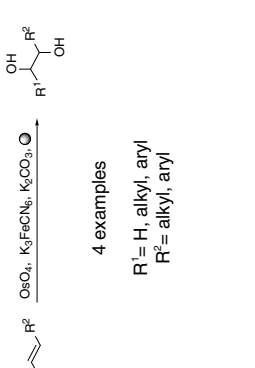
### 3.17 Diazo compounds

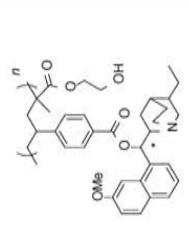

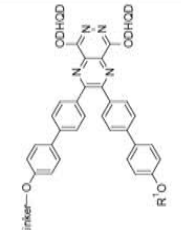
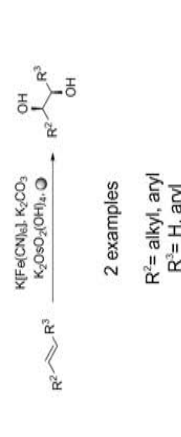
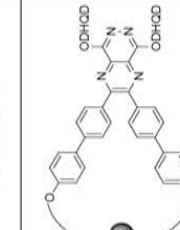
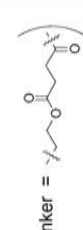

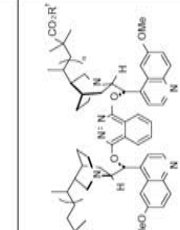
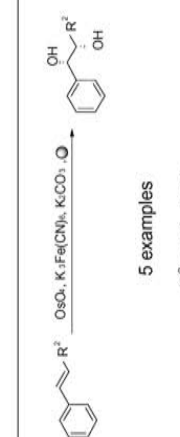
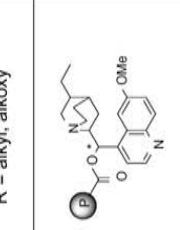
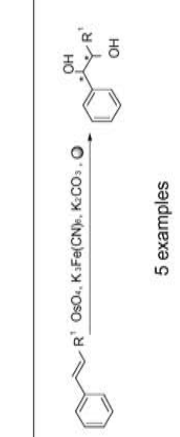
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (3.7 mmol g <sup>-1</sup> )	 7 examples R <sup>1</sup> , R <sup>2</sup> = alkyl, aryl, O-alkyl	Y:68-97	The resin was stable at room temperature and non-explosive when heated. General procedure.	650	650
	 10 examples R <sup>1</sup> = ketone, O-alkyl R <sup>2</sup> = ester, nitrile, phosphonate	Y:46-96	Four examples of cyclic ketones were included. Experimental section.	651	651
	 4 examples R <sup>1</sup> = alkyl R <sup>2</sup> = ester, ketone	Y:50-70	The polymeric reagent was slightly less active than the solution-phase tosyl azide, although it showed greater thermal stability. Experimental section.	652	652

### 3.18 Diols

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Microencapsulated Osmium tetraoxide	 11 examples $R^1, R^3 = \text{H, alkyl}$ $R^2 = \text{alkyl}$	Y:63-89	No leaching of osmium was observed. Catalyst was recycled.	653	
 Microencapsulated Osmium tetraoxide	 10 examples $R^1 = \text{alkyl, aryl}$ $R^2, R^3, R^4 = \text{H, alkyl}$	Y:73-100	Catalyst may be reused with no loss of activity. Complete recovery of the toxic osmium catalyst was achieved. General procedure.	654	654
 Microencapsulated Osmium tetraoxide	 6 examples $R^1 = \text{alkyl, aryl}$ $R^2, R^3, R^4 = \text{H, alkyl}$	Y:36-97 ee:60-92	Catalyst may be reused with no loss of activity. Chiral ligand may be recovered by an acid/base extraction. Complete recovery of the toxic osmium catalyst was achieved. General procedure.	654	654
 Microencapsulated Osmium tetraoxide (2.0 mmol g <sup>-1</sup> )	 2 examples $R^1, R^2 = \text{alkyl}$	Y:8-75	Almost no epoxide was isolated due to the acidic sulfonic acid groups which catalysed hydrolysis. Experimental section.	655	
 Microencapsulated Osmium tetraoxide (1.5 mmol g <sup>-1</sup> )	 5 examples $R^1 = \text{alkyl}$ $R^2 = \text{H, alkyl}$	Y:41-89	Reagent also oxidised allylic alcohols to carbonyl compounds. Experimental section.	219	219

3.18 Diols—continued

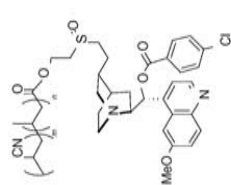

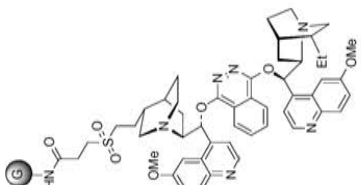

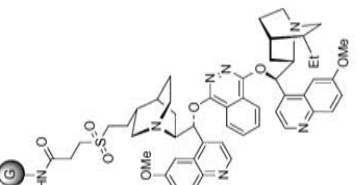
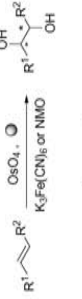
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
  (0.20 mmol g <sup>-1</sup> )	 11 examples R <sup>1</sup> , R <sup>2</sup> , R <sup>3</sup> , R <sup>4</sup> = H, alkyl, aryl, ester, ketone	Y:68-95	Various co-oxidants were studied and trimethylamine N-oxide was found to be the best. Experimental section. Also see reference 656.	303	303
 (L =  ) R <sup>1</sup> = DHQD, DHQ	 4 examples R <sup>2</sup> = alkyl, aryl R <sup>3</sup> = H, aryl	Y:84-88 ee:74-90	Reagent may be recycled. R <sup>1</sup> defines the stereochemical configuration of diol product. A silica-supported variant has also been used. <sup>657</sup>	658	
	 3 examples R <sup>1</sup> = H, alkyl, aryl	Y:80-89 ee:60-88	Patent. The soluble polymer was much more efficient than an insoluble one. It also exhibited comparable reactivity and selectivity to the free ligand. Experimental section. Also see references 659, 660, 661, 662, 663, 664.	665	
 X = S, SO <sub>2</sub>	 4 examples R <sup>1</sup> = H, alkyl, aryl R <sup>2</sup> = alkyl, aryl	Y:80-95 ee:97->99	Patent. A range of polymers were investigated. The reagent was soluble under the reaction conditions, but could be precipitated with ether. Enantioselectivity was superior to insoluble polymer bound species and comparable to the free ligand. Experimental section.	665	665

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
	 <p>2 examples R<sup>1</sup>= aryl, ester</p>	Y:82-84 ee:87-93	Several polymers were studied and the best results are given. Experimental section.	666	666
 <p>R<sup>1</sup> = H, alkyl</p>	 <p>2 examples R<sup>2</sup> = alkyl, aryl R<sup>1</sup> = H, aryl</p>	Y:51-93 ee:90-99	Reagent may be recycled. Various linkers were investigated. As a result of leaching from the support, a small amount of osmium had to be added to maintain the catalytic activity.	657	
 <p>(linker = )</p>	 <p>3 examples R<sup>1</sup> = aryl R<sup>2</sup> = H, alkyl R<sup>3</sup> = H, aryl</p>	Y:89-92 ee:95-99	Reagent may be recycled. General procedure.	658	
 <p>R<sup>1</sup> = alkyl, alkoxy</p>	 <p>5 examples R<sup>2</sup> = aryl, ester</p>	Y:65-93 ee:98-100	Catalyst may be reused without loss of activity. General procedure.	667	667
	 <p>5 examples R<sup>1</sup> = aryl, ester</p>	Y:74-82 ee:30-93	Several other supports and co-oxidants were investigated. The best results are given. Experimental section.	666	666

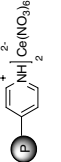
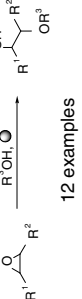
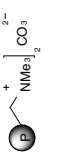
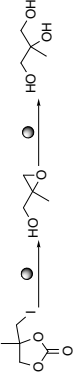
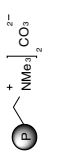
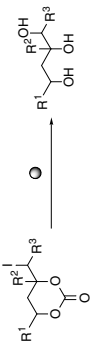
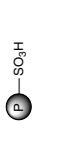
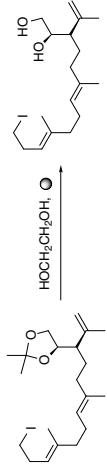
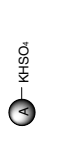
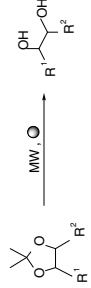
3.18 Diols—continued



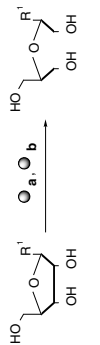
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
<p>(S)  (G) </p>	$\text{R}^1 \text{---} \text{C}(\text{Ph}) \text{---} \text{C}(\text{R}^2) \text{---} \text{OH} \xrightarrow{\text{OsO}_4, \text{K}_2\text{Fe}(\text{C}_6\text{H}_5)_2, \text{NMO}} \text{R}^1 \text{---} \text{C}(\text{Ph}) \text{---} \text{C}(\text{R}^2) \text{---} \text{OH}$ <p>4 examples  <math>\text{R}^1 = \text{H}, \text{alkyl}</math>  <math>\text{R}^2 = \text{alkyl, aryl, ester}</math></p>	Y:88-96 ee:92-99	Enantiomeric excesses were comparable to solution phase analogues. The catalyst was successfully recycled without addition of extra $\text{OsO}_4$ . General procedure.	607	607
<p>(S)  (G) </p>	$\text{R}^3 \text{---} \text{C}(\text{R}^4) \text{---} \text{C}(\text{R}^2) \text{---} \text{OH} \xrightarrow{\text{OsO}_4, \text{K}_2\text{Fe}(\text{C}_6\text{H}_5)_2, \text{H}_2\text{O}} \text{R}^3 \text{---} \text{C}(\text{R}^4) \text{---} \text{C}(\text{R}^2) \text{---} \text{OH}$ <p>4 examples  <math>\text{R}^2 = \text{alkyl, aryl}</math>  <math>\text{R}^3, \text{R}^4 = \text{H, alkyl, aryl}</math></p>	Y:85-90 ee:91-99	Three resins were examined and the best results are given. The polymer was recycled after addition of extra $\text{OsO}_4$ . Also see references 668, 669.	670	670
<p>(S)  (G) </p>	$\text{R}^1 \text{---} \text{C}(\text{R}^2) \text{---} \text{C}(\text{R}^1) \text{---} \text{OH} \xrightarrow{\text{OsO}_4, \text{NMO}} \text{R}^1 \text{---} \text{C}(\text{R}^2) \text{---} \text{C}(\text{R}^1) \text{---} \text{OH}$ <p>8 examples  <math>\text{R}^1 = \text{alkyl, aryl}</math>  <math>\text{R}^2 = \text{H, alkyl, aryl, ester}</math></p>	Y:79-87 ee:22-85	Polymer may be reused without addition of extra $\text{OsO}_4$ . Polymer with $m:n=9:1$ most effective. General procedure.	671	671




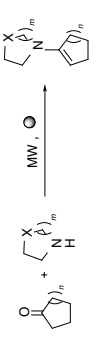



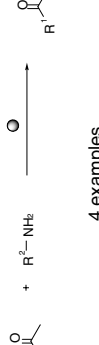
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
	 <p>1 example</p>	Y:75-87 ee:85-93	Several similar polymers were tested and the best result is given. Polymer may be reused without addition of extra osmium.	672	673
	 <p>5 examples R<sup>1</sup> = H, alkyl</p>	C:60-98 ee:98	Insoluble polymer-supported substrate was asymmetrically dihydroxylated using a soluble PEG supported catalyst. Experimental section.	674, 675	674
	 <p>4 examples R<sup>1</sup> = alkyl, aryl R<sup>2</sup> = H, alkyl, aryl</p>	Y:84-98 ee:97-99	General procedure.	676	676

3.18 Diols—continued

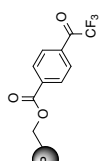
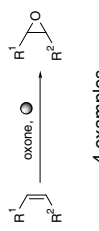
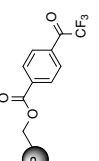
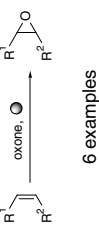
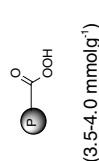
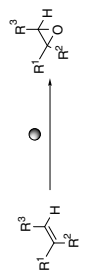
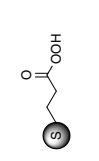
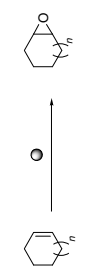
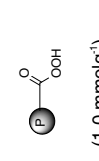
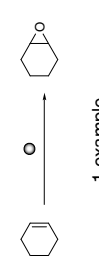
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Carbonate form (1.1 mmol g <sup>-1</sup> )	 12 examples R <sup>1</sup> = H, alkyl, aryl R <sup>2</sup> = H, alkyl R <sup>3</sup> = alkyl	Y:77-90	Catalyst was regenerated and reused without loss of activity. General procedure.	677	677
 Amberlyst A-26 Carbonate form (3.7 mmol g <sup>-1</sup> )	 1 example	Y:80	Reagent may be regenerated. The product was scavenged by the polymer. Experimental section.	623	623
 Amberlyst A-26 Carbonate form	 10 examples R <sup>1</sup> , R <sup>2</sup> , R <sup>3</sup> = H, alkyl	Y:78-90	Some stereoselectivity was observed. Full experimental section.	678	
 Amberlyst IR-120 Proton form	 1 example	Y:80	Reagent was used in the total synthesis of (+)-desepoxyasperdiol. Full experimental section.	679	
 Amberlyst A-26 Carbonate form	 5 examples R <sup>1</sup> = alkyl, sugar R <sup>2</sup> = H, alkyl	Y:73-90	TBDMS and trityl groups were sometimes cleaved under these reaction conditions. General procedure.	258	258


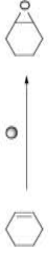








Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
<p><b>a</b> </p> <p><b>b</b> </p>	 <p>4 examples</p> <p>R<sup>1</sup> = adenine, cytosine, guanine, uracil</p>	Y:40-79	The intermediate dialdehyde was unstable. Simultaneous use of the resins improved the yield. General procedure.	34	

### 3.19 Enamines

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
<p></p> <p>Envirocat EPZG</p>	 <p>5 examples</p> <p>X = C, O</p> <p>n = 1, 2</p> <p>m = 1, 2</p>	Y:90-96	General procedure.	680	
<p></p> <p>Montmorillonite K 10</p>	 <p>5 examples</p> <p>R<sup>1</sup> = H, alkyl</p> <p>R<sup>2</sup> = alkyl</p> <p>n = 1, 2</p>	Y:75-97	Reaction takes place under solvent free conditions. General procedure.	681	
<p></p>	 <p>4 examples</p> <p>R<sup>1</sup> = alkyl, aryl</p> <p>R<sup>2</sup> = alkyl, benzyl</p>	Y:85-99	Reactions carried out under solvent free conditions. Montmorillonite K 10 can be used as an alternative. General procedure.	682	

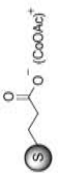
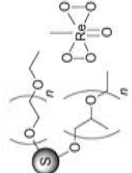

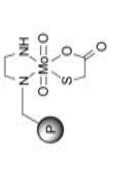
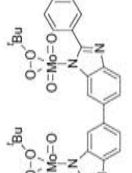
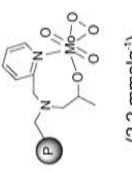
### 3.20 Epoxides

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (0.40 mmol g <sup>-1</sup> )	 4 examples R <sup>1</sup> , R <sup>2</sup> = alkyl, aryl	Y:9-64	General procedure.	683	683
 TentaGel (0.10 mmol g <sup>-1</sup> )	 6 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = alkyl, aryl, O-alkyl	Y:13-97	General procedure.	683	683
 (3.5-4.0 mmol g <sup>-1</sup> )	 25 examples R <sup>1</sup> , R <sup>2</sup> , R <sup>3</sup> = H, alkyl, aryl	Y:1-95	Polymeric peroxyacids were found to be stable and not explosive. They degrade slowly at room temperature, but are stable for long periods at -20 °C. Experimental section.	684, 685	684, 685
 (2.9-3.5 mmol g <sup>-1</sup> )	 2 examples n = 1, 3	Y:55-62	General procedure.	686	686
 (1.0 mmol g <sup>-1</sup> )	 1 example	Y:86	Optimisation studies are reported. Reagent may be regenerated. Reagent should be stored in a refrigerator. Experimental section.	687	687

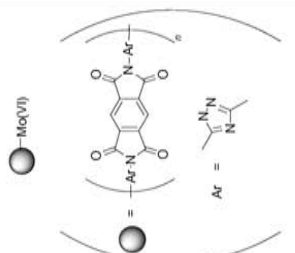

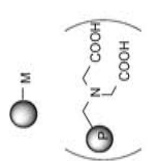
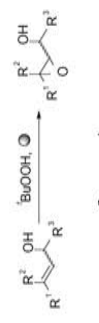
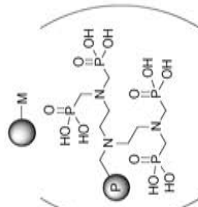

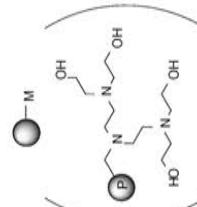

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Duolite C433 (6.0 mmol <sup>-1</sup> ) Duolite C436 (2.5-3.0 mmol <sup>-1</sup> ) Amberlite IRC-50 (0.5 mmol <sup>-1</sup> )	 1 example	C:5-98	The degree of conversion was solvent dependant. Experimental section. Alternative catalysts have also been described. <sup>688,689</sup>	163	690
 (2.5 mmol <sup>-1</sup> ) Bio-Rad 50W Peracid form	 5 examples R <sup>1</sup> = alkyl, aryl, ester R <sup>2</sup> = H, alkyl, aryl	Y:80	The reagent may also be used for Baeyer-Villiger oxidation and disulfide cleavage. General procedure.	691	691
 (2.5 mmol <sup>-1</sup> )	 2 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl	Y:73-82	Polymer may be regenerated without loss of activity. Also oxidises amines to nitro or N-oxides. Experimental section.	692	692
 (6.3 mmol <sup>-1</sup> )	 13 examples R <sup>1</sup> = alkyl, aryl, O-alkyl, vinyl R <sup>2</sup> = H, ester, sulfonate R <sup>3</sup> = alkyl, aryl	Y:0-100	Non-conjugated double bonds were not epoxidised. General procedure.	693	693
 Bio beads S-XI Chloride form (0.90 mmol <sup>-1</sup> )	 3 examples R <sup>1</sup> = H, alkyl R <sup>2</sup> = alkyl	Y:40-70	α,β-Epoxynitriles were also prepared. Optical yields obtained were very low. Experimental section.	694	694

3.20 Epoxides—continued

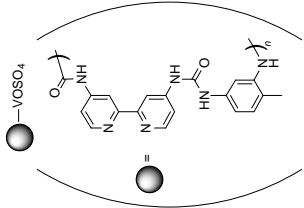


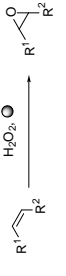
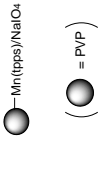

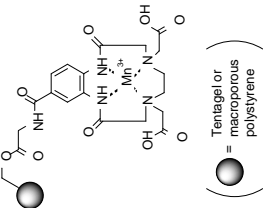

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlite IRA-900 Bromide form	$\text{R}^1\text{-CH=CH-R}^2 \xrightarrow{\text{H}_2\text{O, Electric current, } \ominus} \text{epoxide}$ 7 examples R <sup>1</sup> = alkyl, phenyl R <sup>2</sup> = alkyl	Y:21-83	General procedure. Fe(III) catalysts supported on Amberlite <sup>®</sup> and Dowex <sup>®</sup> have also been used.	697	344, 345
 (2.3 mmolg <sup>-1</sup> ) R <sup>1</sup> = H, alkyl	$\text{R}^1\text{-C(=O)-R}^2 \xrightarrow{\text{NaOH, H}_2\text{O, } \ominus} \text{epoxide}$ 5 examples R <sup>2</sup> = aryl R <sup>3</sup> = H, alkyl, aryl	Y:98-100	Reagent may be regenerated. The reaction was tried in a triphasic medium with tetrabutylammonium iodide used as a phase transfer catalyst. Triphasic conditions gave no loss of catalytic activity upon recycling.	698	698
 M = M(II) Co, Ni, Cu M = M(III) Fe	$\text{R}^1\text{-CH=CH-R}^2 \xrightarrow{\text{H}_2\text{O}_2, \text{OH}^-, \ominus} \text{epoxide}$ 2 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl		Different levels of cross-linking were investigated. 10% crosslinked showed enhanced catalytic activity. Kinetic study. A polystyrene supported tellurium catalyst has also been used for this transformation. <sup>699</sup>	700	700
 Montmorillonite K 10 Claynaic	$\text{R}^1\text{-CH=CH-R}^2 \xrightarrow{\text{O}_2, \text{BuCHO, } \ominus} \text{epoxide}$ 33 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl, aryl	Y:29-100	Environmentally friendly non-chlorinated solvents may be employed. General procedure.	701	701
 XAD-2	$\text{R}^1\text{-CH=CH-R}^2 \xrightarrow{\text{H}_2\text{O}_2, \ominus} \text{epoxide}$ 10 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl		Relative rates were determined. General procedure.	699	699

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (0.30 mmol g <sup>-1</sup> )	$R^1-CH=CH-R^2 \xrightarrow{BuCHO, O} R^1-CH_2-CH_2-R^2$ <p>6 examples R<sup>1</sup>= alkyl, aryl R<sup>2</sup>= H, alkyl</p>	Y:30-95	Very low levels of cobalt leaching were detected. General procedure.	702	
	$R^2-CH=CH-R^1 \xrightarrow{H_2O_2, O} R^2-CH(OH)-CH_2-R^1$ <p>7 examples R<sup>1</sup>= alkyl, aryl R<sup>2</sup>= H, alkyl</p>	Y:34-100(a) Y:0-66(b)	Recycled reagent had a lower activity than fresh reagent. General procedure.	703	703
 (0.50-1.3 mmol g <sup>-1</sup> )	$Cyclohexene \xrightarrow{H_2O, O} Cyclohexanol$ <p>1 example</p>	C:69-79	Reagent could be successfully recycled and reused. Low crosslinked and macroporous variants were studied. Other phosphorous containing ligands were also investigated and found to be less satisfactory for continuous flow reactors. Full experimental section.	704	704
 (1.5 mmol g <sup>-1</sup> )	$R^1-CH=CH-R^2 \xrightarrow{BuOOH, O} R^1-CH_2-CH_2-R^2$ <p>8 examples R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>= H, alkyl</p>	C:10-78	Full experimental section.	705	705
 (1.8 mmol g <sup>-1</sup> )	$R^1-CH=CH_2 \xrightarrow{O} R^1-CH_2-CH_2-OH$ <p>2 examples R<sup>1</sup>= alkyl</p>	Y:59-100	Several other polymers were tested. The best example is given. No leaching of molybdenum was detected and the activity increased upon recycling. Experimental section. Also see references 706, 707.	708, 709	708
 (2.2 mmol g <sup>-1</sup> )	$Cyclohexene \xrightarrow{BuOOH, O} Cyclohexanol$ <p>1 example</p>	Y:100	Kinetic study. Experimental section. A chiral dioxomolybdenum complex supported on a zeolite has also been reported for the epoxidation of allylic alcohols. <sup>710</sup> Also see references 711, 712.	713	713

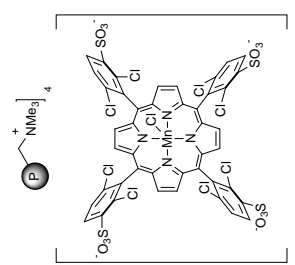
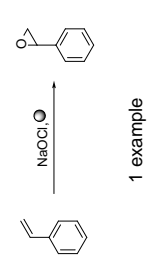
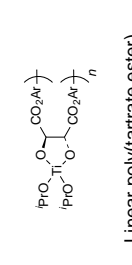
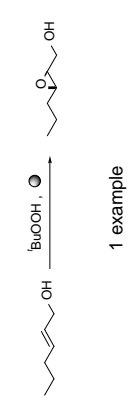
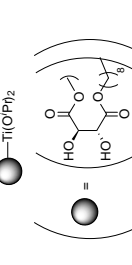
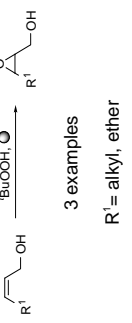
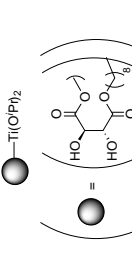
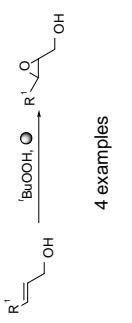
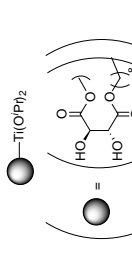
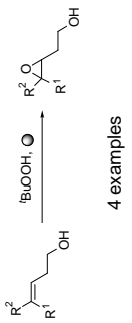
3.20 Epoxides—continued

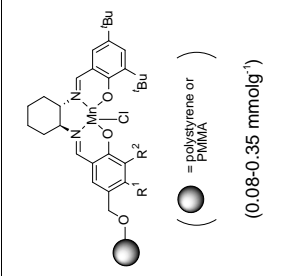
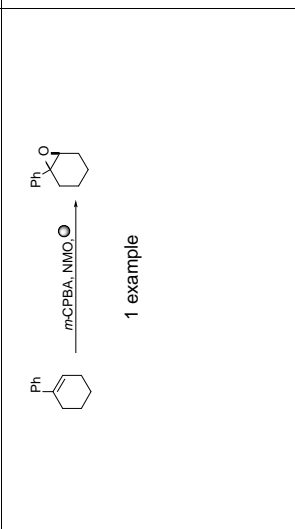
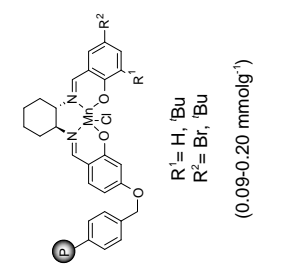
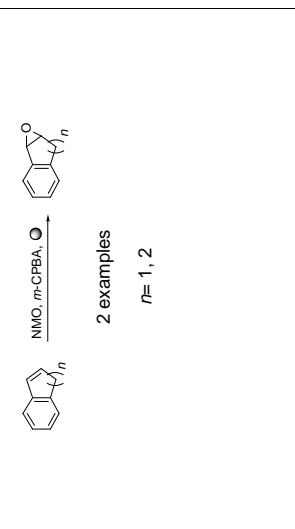
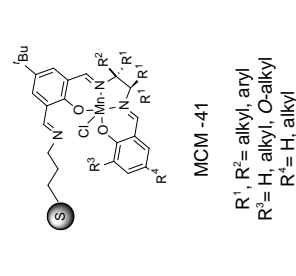
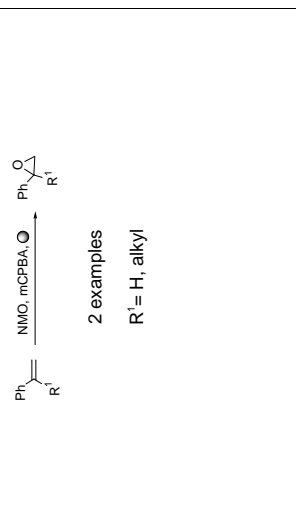
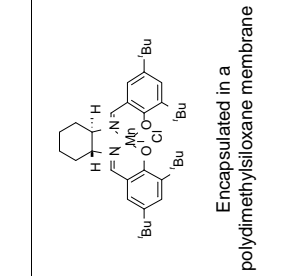
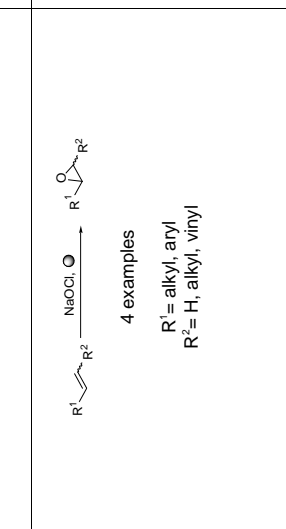
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>(2.1 mmol g<sup>-1</sup>)</p>	 <p>1 example</p>	Y:100	<p>Good stability of catalyst reported.</p> <p>General procedure.</p> <p>Amberlite IRA-400<sup>TM</sup> activated carbon<sup>715</sup> and other supports<sup>716,717</sup> have also been used.</p>	718	718
 <p>M = V(V), Mo(VI)</p>	 <p>3 examples R<sup>1</sup>, R<sup>3</sup> = alkyl R<sup>2</sup> = H, alkyl</p>	C:70-100	<p>Macroreticular resins gave faster conversions than gel type resins. Selectivity for allylic alcohol double bond epoxidation was observed. Between 15–25% loss of metal ion was observed.</p> <p>Experimental section.</p>	719	719
 <p>M = V(V), Mo(VI)</p>	 <p>3 examples R<sup>1</sup>, R<sup>3</sup> = alkyl R<sup>2</sup> = H, alkyl</p>	C:48-100	<p>Macroreticular resins gave faster conversions than gel type resins. Selectivity for allylic alcohol double bond epoxidation was observed. Between 15–25% loss of metal ion was observed.</p> <p>Experimental section.</p>	719, 720	719, 720
 <p>M = V(V), Mo(VI)</p>	 <p>3 examples R<sup>1</sup>, R<sup>3</sup> = alkyl R<sup>2</sup> = H, alkyl</p>	C:70-100	<p>Macroreticular resins gave faster conversions than gel type resins. Selectivity for allylic alcohol double bond epoxidation was observed. Between 15–25% loss of metal ion was observed.</p> <p>Experimental section.</p>	719, 720	719, 720



Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
	 <p>12 examples  <math>R^1, R^2 = \text{alkyl}</math>  <math>R^2 = \text{H, alkyl}</math></p>	Y:3-57	Cyclic olefins were selectively epoxidised, in the presence of acyclic olefins. The resin may be recycled up to five times without loss of activity. Experimental section. Also see reference 721.	722	722
	 <p>5 examples  <math>R^1, R^2 = \text{alkyl}</math></p>	Y:15-100	Polymer may be recycled and reused.	723	724
	 <p>9 examples  <math>R^1 = \text{alkyl, aryl}</math>  <math>R^2 = \text{H, alkyl, aryl}</math></p>	Y:40-95 C:40-100	Z alkenes give predominantly <i>cis</i> epoxides. General procedure.	343	
	 <p>1 example</p>	Y:96	Several catalysts were made as part of an evolutionary approach to a library of catalysts.	725	

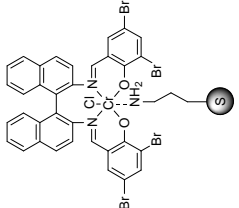
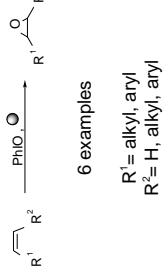
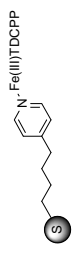
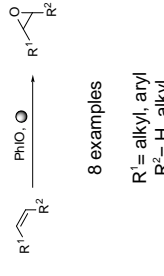
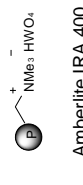

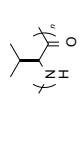

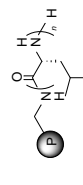
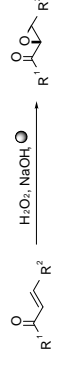
3.20 Epoxides—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>Colloidal resin</p>	 <p>1 example</p>	C:71-81	The resin gave a greater conversion than an analogous solution phase catalyst. Aliphatic alkenes were unreactive under these conditions. Full experimental section. Also see reference 726.	727	727
 <p>Linear poly(tartrate ester)</p>	 <p>1 example</p>	Y:21-92 ee:8-79	Various constructs of the polymer backbone were investigated.	728, 729	728
	 <p>3 examples R<sup>1</sup> = alkyl, ether</p>	Y:18-57 ee:35-86	Polymers with different degrees of crosslinking were investigated. High levels of cross-linking resulted in a significant drop in enantioselectivity. General procedure. Also see reference 730.	731	729
	 <p>4 examples R<sup>1</sup> = alkyl, aryl</p>	Y:13-95 ee:26-98	Polymers with different degrees of crosslinking were tested. High levels of cross-linking resulted in a significant drop in enantioselectivity. Full experimental section. Also see reference 732.	733	733
	 <p>4 examples R<sup>1</sup>, R<sup>2</sup> = H, alkyl</p>	Y:20-75 ee:34-80	Absolute configuration of epoxides is opposite to that obtained with allylic alcohols. Experimental section. A silica supported variant has also been reported. <sup>734</sup>	735, 729	733

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>(0.08-0.35 mmolg<sup>-1</sup>)</p>	 <p>1 example</p>	Y:5-49 ee:0-91	Five polymer-bound catalysts, based on polystyrene or polymethylmethacrylate, were studied. Optimisation studies carried out. (R,R) catalyst gave (S,S) product. General procedures.	736	736
 <p>(0.09-0.20 mmolg<sup>-1</sup>)</p>	 <p>2 examples n= 1, 2</p>	Y:<2-79 ee:0-20	Several polymer supports were investigated. The porous polymers worked better than the gel polymers. Full experimental section.	737	737
 <p>MCM-41 R<sup>1</sup>, R<sup>2</sup> = alkyl, aryl R<sup>3</sup> = H, alkyl, O-alkyl R<sup>4</sup> = H, alkyl</p>	 <p>2 examples R<sup>1</sup> = H, alkyl</p>	C:51-98 ee:43-89	Several catalysts investigated. Catalyst may be reused without loss of activity, up to four times with no leaching of manganese. General procedure. Also see references 738, 739, 740, 741, 742, 743.	744	744
 <p>Encapsulated in a polydimethylsiloxane membrane</p>	 <p>4 examples R<sup>1</sup> = alkyl, aryl R<sup>2</sup> = H, alkyl, vinyl</p>	C:8-84 P:64-80 ee:18-57	The catalyst is retained in the membrane by steric restrictions. Catalyst may be reused without loss of activity. Experimental section. Also see reference 745.	746	746

3.20 Epoxides—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
<p>(0.13 mmol g<sup>-1</sup>)</p>	<p>3 examples Alkene = dihydronaphthalene cis-β-methylstyrene styrene</p>	C:23-100 Y:7-56 ee:7-79	Good stability under stresses such as sonication. Experimental section.	747, 748	747
<p>(0.11 mmol g<sup>-1</sup>)</p>	<p>3 examples R<sup>1</sup> = alkyl R<sup>2</sup> = aryl</p>	Y:82-96 ee:78-95	Catalyst underwent degradation under reaction conditions. m-CPBA / NMO were also investigated as oxidants. General procedure.	749	749
<p>( = Co-polymer with EGDMA )</p>	<p>4 examples R<sup>1</sup> = aryl R<sup>2</sup> = H, aryl</p>	Y:55-72 ee:<28	A related catalyst was also investigated and the best result is shown. General procedures.	750	750
<p>( = PVP )</p> <p>R<sup>1</sup> = H, alkyl, aryl R<sup>2</sup> = alkyl, aryl (0.010 mmol g<sup>-1</sup>)</p>	<p>4 examples R<sup>1</sup> = H, alkyl, Cl, nitro</p>	C:25-65 ee:16-46	Catalyst may be recycled upto ten times without loss of activity. Experimental section.	751	751

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>MCM-41 (0.34 mmol g<sup>-1</sup>)</p>	 <p>6 examples R<sup>1</sup> = alkyl, aryl R<sup>2</sup> = H, alkyl, aryl</p>	Y:26-62 ee:42-73	Catalyst may be reused with only a slight loss of activity and enantioselectivity after four recycles.	752	752
 <p>TDCPP = 5,10,15,20-tetra(2,6-dichlorophenyl) porphyrin (3.0-5.0 mmol g<sup>-1</sup>)</p>	 <p>8 examples R<sup>1</sup> = alkyl, aryl R<sup>2</sup> = H, alkyl</p>	Y:0-97	Reaction does not work on ( <i>E</i> )-alkenes. General procedure.	753	753
 <p>Amberlite IRA 400 Hydrogentungstate form (0.020-0.10 mmol g<sup>-1</sup>)</p>	 <p>1 example</p>		Kinetic studies were undertaken. General procedure.	754, 755	754
 <p>Polyoleucine</p>	 <p>18 examples R<sup>1</sup> = alkyl, aryl R<sup>2</sup> = alkyl, aryl, carbonyl, vinyl</p>	Y:51-100 ee:62-98	Full experimental section.	756	
 <p>(0.30 mmol g<sup>-1</sup>) n = 4-33</p>	 <p>8 examples R<sup>1</sup>, R<sup>2</sup> = aryl</p>	Y:56-98 ee:76-99	Catalyst could be reused up to twelve times without loss of yield or enantioselectivity. Experimental section.	757	757


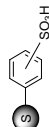




### 3.20 Epoxides—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Hydroxide form	 10 examples R <sup>1</sup> , R <sup>2</sup> , R <sup>3</sup> = H, alkyl	Y:40-91	Stereoselectivity is observed. Experimental section.	678	
 (6.7 mmol g <sup>-1</sup> )	 1 example	Y:61	Resin is stable to reaction conditions and storage. General procedure.	649	
	 1 example	Y:82	General procedure.	478	478

### 3.21 Esters

#### 3.21.1 Esters (From acids)


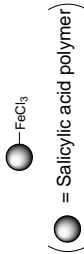
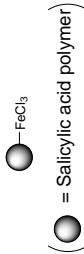



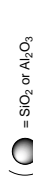


Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-15 Proton form	 13 examples R <sup>1</sup> = alkyl, aryl, benzyl, vinyl	Y:60-98	Higher temperature is needed for the esterification of aromatic and conjugated acids. General procedure.	758	
 Rexyn 101 R231 Proton form	 3 examples R <sup>1</sup> = alkyl	Y:73-100	Several polymer based acids were investigated and the best example is shown. General procedure.	759	

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Graphite Bisulfate	$  \begin{array}{c}  \text{R}^1-\text{C}(=\text{O})-\text{OH} \\  \text{R}^2-\text{OH}  \end{array}  \xrightarrow{\text{O}}  \begin{array}{c}  \text{R}^1-\text{C}(=\text{O})-\text{OR}^2  \end{array}  $ 16 examples $\text{R}^1 = \text{H, alkyl, carbonyl}$ $\text{R}^2 = \text{alkyl, benzyl}$	Y:50-99	Excess of alcohol is not required to obtain a maximum yield. General procedure.	760	
 (0.30 mmol g <sup>-1</sup> )	$  \begin{array}{c}  \text{OH} \\    \\  \text{C} \\    \\  \text{OH}  \end{array}  \xrightarrow{\text{O}}  \begin{array}{c}  \text{C} \\    \\  \text{O}  \end{array}  $ 1 example		Comparison to kinetic study for Amberlyst A-15. Catalytic activity loss after first run. Some activity can be recovered by treatment with sulfuric acid. Experimental section.	761	761
 Amberlyst A-15 Proton form	$  \begin{array}{c}  \text{HO}-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{OH} \\  + \\  \text{HO}-\text{C}(=\text{O})-\text{CH}_2-\text{CH}_3  \end{array}  \xrightarrow{\text{MW, O}}  \begin{array}{c}  \text{HO}-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{CH}_2-\text{CH}_3  \end{array}  $ 1 example		Comparison of kinetics of conventionally heated and MW irradiated heterogeneous reactions. Experimental section.	762	
 Coated silica gel (0.70 mmol g <sup>-1</sup> )	$  \begin{array}{c}  \text{R}^1-\text{C}(=\text{O})-\text{OH} \\  \text{HO}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{OH}  \end{array}  \xrightarrow{\text{O}}  \begin{array}{c}  \text{R}^1-\text{C}(=\text{O})-\text{O}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{OH}  \end{array}  $ 5 examples $\text{R}^1 = \text{fatty acid residue}$	Y:31-62	Various polyols apart from glycerol were used. Comparison of eight catalysts. Best example is shown. Substantial amounts of multiply substituted polyols were detected. General procedure.	763	763
 (1.7-2.6 mmol g <sup>-1</sup> )	$  \begin{array}{c}  \text{HO}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{OH} \\  \text{HO}-\text{C}(=\text{O})-\text{CH}_2-\text{CH}_3  \end{array}  \xrightarrow{\text{O}}  \begin{array}{c}  \text{HO}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{CH}_2-\text{CH}_3  \end{array}  $ 1 example		Various supports were examined. Sulfonic acid coated silica was the most effective and was utilised on 4 other polyol systems. Experimental section. Graphite / H <sub>2</sub> SO <sub>4</sub> has also been used. <sup>760</sup>	763	763
 (1.7-2.6 mmol g <sup>-1</sup> )	$  \begin{array}{c}  \text{HO}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{OH} \\  \text{HO}-\text{C}(=\text{O})-\text{CH}_2-\text{CH}_3  \end{array}  \xrightarrow{\text{O}}  \begin{array}{c}  \text{HO}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{CH}_2-\text{CH}_3  \end{array}  $ 1 example	C:60	Several polysiloxanes investigated and the best result is given. Reactions carried out in a flow reactor. General procedure.	480	480


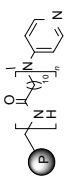
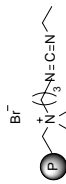

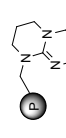
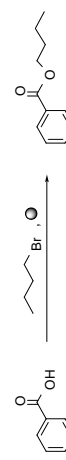
3.21.1 Esters (From acids)—continued

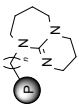
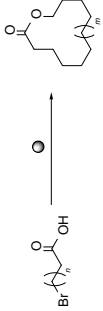
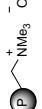

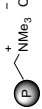

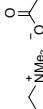

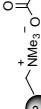
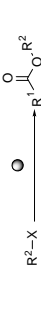
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Nafion-H	$  \begin{array}{c}  \text{R}^1-\text{C}(=\text{O})-\text{OH} \\  \text{R}^2-\text{OH}  \end{array}  \longrightarrow  \begin{array}{c}  \text{R}^1-\text{C}(=\text{O})-\text{OR}^2  \end{array}  $ <p>14 examples  <math>\text{R}^1 = \text{alkyl, aryl, benzyl}</math>  <math>\text{R}^2 = \text{alkyl, benzyl}</math></p>	Y:18-100	Reactions carried out under standard conditions and under flow reactor conditions. General procedure.	764	
 Nafion-H	$  \begin{array}{c}  \text{R}^1-\text{C}(=\text{O})-\text{OH} \\  \text{R}^2-\text{OH}  \end{array}  \longrightarrow  \begin{array}{c}  \text{R}^1-\text{C}(=\text{O})-\text{OR}^2  \end{array}  $ <p>25 examples  <math>\text{R}^1, \text{R}^2 = \text{alkyl}</math></p>	Y:8-100	Yield is strongly influenced by steric bulk of $\text{R}^2$ . Addition of a drying agent increases yields over other literature procedures.	765	
 Nafion-H (0.010-5.0 mmol g <sup>-1</sup> )	$  \begin{array}{c}  \text{R}^1-\text{C}(=\text{O})-\text{OH} \\  \text{MeO}-\text{C}_6\text{H}_4-\text{OH}  \end{array}  \longrightarrow  \begin{array}{c}  \text{MeO}-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{OR}^1  \end{array}  $ <p>4 examples  <math>\text{R}^1 = \text{alkyl}</math></p>	Y:58-75	Reaction does not work with benzyl alcohol. General procedure.	766	
 ( = PVP ) (5.1 mmol g <sup>-1</sup> )	$  \begin{array}{c}  \text{R}^1-\text{C}(=\text{O})-\text{OH} \\  \text{R}^2-\text{OH}  \end{array}  \longrightarrow  \begin{array}{c}  \text{R}^1-\text{C}(=\text{O})-\text{OR}^2  \end{array}  $ <p>2 examples  <math>\text{R}^1 = \text{alkyl}</math></p>	Y:27-100	Esterification may be carried out in the presence of acid sensitive functionality. Experimental section.	105	105
 ( = PVP ) (5.1 mmol g <sup>-1</sup> )	$  \begin{array}{c}  \text{R}^1-\text{C}(=\text{O})-\text{OH} \\  \text{R}^2-\text{OH}  \end{array}  \longrightarrow  \begin{array}{c}  \text{R}^1-\text{C}(=\text{O})-\text{OR}^2  \end{array}  $ <p>3 examples  <math>\text{R}^1, \text{R}^2 = \text{alkyl}</math></p>	C:0-100	Several polymers tested and the best results given. Experimental section.	92	92
 $\text{R}^1 = \text{alkyl}$	$  \begin{array}{c}  \text{R}^2-\text{C}(=\text{O})-\text{OH} \\  \text{R}^1-\text{C}(=\text{O})-\text{OH}  \end{array}  \longrightarrow  \begin{array}{c}  \text{R}^2-\text{C}(=\text{O})-\text{OR}^1  \end{array}  $ <p>24 examples  <math>\text{R}^2 = \text{alkyl, vinyl}</math></p>	Y:55-90	Reaction carried out in the absence of solvent. General procedure.	767	767



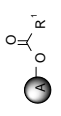

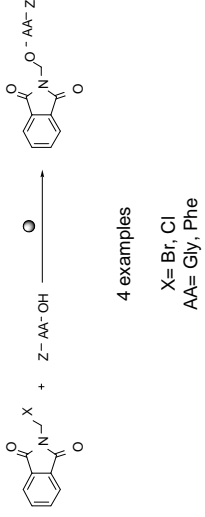
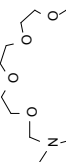
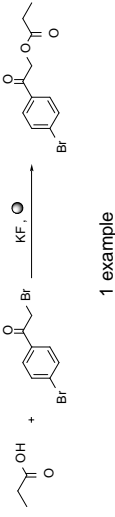
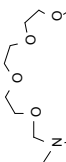
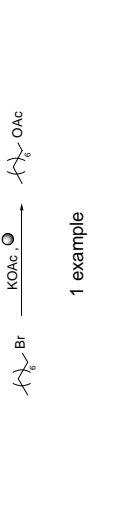

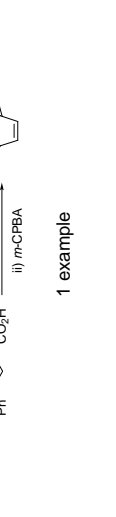
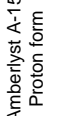
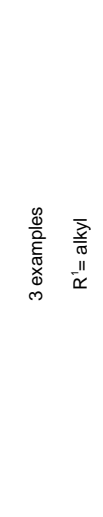
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 -FeCl <sub>3</sub>  (  = Salicylic acid polymer)	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1-\text{C}-\text{OH} \\   \\ \text{OH} \end{array} + \text{R}^2-\text{OH} \longrightarrow \begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1-\text{C}-\text{OR}^2 \end{array}$ 10 examples R <sup>1</sup> , R <sup>2</sup> = alkyl	Y:95-97	Resin may be recycled without loss of activity. AlCl <sub>3</sub> on polystyrene has also been used. <sup>768</sup>	107	107
 -Fe(ClO <sub>4</sub> ) <sub>3</sub> (EOA) <sub>0.6</sub>	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1-\text{C}-\text{OH} \\   \\ \text{OH} \end{array} + \begin{array}{c} \text{OH} \\   \\ \text{R}^2-\text{C}-\text{R}^3 \end{array} \longrightarrow \begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1-\text{C}-\text{OEt} \\   \\ \text{OAc} \\   \\ \text{R}^3 \end{array}$ 16 examples R <sup>1</sup> = alkyl, amide, vinyl R <sup>2</sup> , R <sup>3</sup> = H, alkyl, aryl	Y:49-93	Reaction carried out under solvent free conditions. General procedure.	769	769,
 -AlCl <sub>3</sub>	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}^2-\text{C}-\text{OH} \end{array} + \text{R}^1-\text{OH} \longrightarrow \begin{array}{c} \text{O} \\ \parallel \\ \text{R}^2-\text{C}-\text{OR}^1 \end{array}$ 7 examples R <sup>1</sup> = alkyl R <sup>2</sup> = alkyl, aryl	Y:0-97	Tightly bound complex between AlCl <sub>3</sub> and the polymer. Ideal for condensation reactions in which very mild reaction conditions are required. General procedures.	768	95
 -OTi(OPh) <sub>3</sub>  (1.1 atoms Ti per nm <sup>2</sup> )	$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{OH} \\   \\ \text{OH} \end{array} + \begin{array}{c} \text{OH} \\   \\ \text{C}-\text{C}-\text{C} \\   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \end{array} \longrightarrow \begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{O}-\text{C}-\text{C}-\text{C}-\text{C} \\   \quad   \quad   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$ 1 example	Y:90-97	The catalyst can be recycled. Full experimental section. TiCl <sub>4</sub> on polystyrene <sup>770</sup> and other Zr and Ti supported Lewis acids <sup>771</sup> have also been reported.	772	772
 -N <sup>+</sup> (OMe) <sub>2</sub> C(OMe) <sub>2</sub> (0.27-2.1 mmol g <sup>-1</sup> )	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1-\text{C}-\text{OH} \end{array} + \text{R}^2-\text{OH} \xrightarrow{\text{PPh}_3, \text{O}} \begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1-\text{C}-\text{OR}^2 \end{array}$ 4 examples R <sup>1</sup> = alkyl, amino acid, aryl, benzyl R <sup>2</sup> = alkyl, benzyl	Y:42-65	Resins prepared from hydroxymethyl polystyrene and phosgene. The reagent is recyclable and not shock sensitive. Chromatography necessary to separate triphenylphosphine oxide. Full experimental section.	773	773
 -PPh <sub>2</sub> (3.0 mmol g <sup>-1</sup> )	$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{OH} \\   \\ \text{OH} \end{array} + \text{R}^1-\text{OH} \xrightarrow[\text{CO}_2/\text{Bu}_3\text{N}]{\text{BuOC}} \begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{OR}^1 \\   \\ \text{OH} \end{array}$ 3 examples R <sup>1</sup> = alkyl, benzyl	Y:70-93 P:93-97	Azodicarboxylate was removed by treatment with TFA and an aqueous wash using a hydrophobic phase separation tube. Unconverted starting material was scavenged with resin bound carbonate. General procedure.	538	

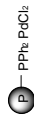
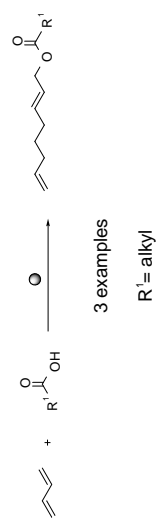
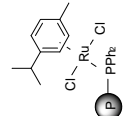
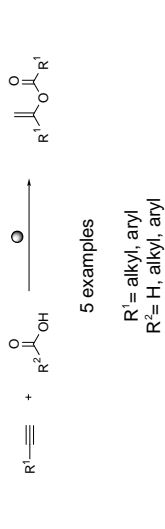
3.21.1 Esters (From acids)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (3.0 mmol g <sup>-1</sup> )	$R^1-C(=O)OH + R^2-OH \xrightarrow{Et_3CN=NO_2Et} R^1-C(=O)OR^2$ 12 examples R <sup>1</sup> = alkyl, aryl, vinyl R <sup>2</sup> = alkyl, benzyl	Y:10-99	Compatible with a variety of functional groups. Experimental section.	774	774
 r = 0, 1 (0.60-1.6 mmol g <sup>-1</sup> )	$R^1-C(=O)OH + R^2-OH \xrightarrow{DCC} R^1-C(=O)OR^2$ 6 examples R <sup>1</sup> = alkyl, aryl, vinyl R <sup>2</sup> = alkyl, benzyl	Y:0-98	The activity of the resin was not linker-dependant. Resin may be reused without loss of activity. General procedure.	775	775
	$R^1-C(=O)OH + R^2-OH \xrightarrow{HOSu \text{ or } OPFP} R^1-C(=O)OR^2$ 18 examples R <sup>1</sup> = het, steroid, amino acid R <sup>2</sup> = OSu, OPFP	Y:53-98	Useful for the preparation of water soluble active esters that cannot be purified by extraction. General procedure.	776	530
 X = Br, Cl, I (2.7 mmol g <sup>-1</sup> )	$R^1-C(=O)OH + R^2-OH \xrightarrow{X} R^1-C(=O)OR^2$ 13 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = alkyl	Y:84-98	Best example given with X=I. If X=Br, double bonds may be attacked. Experimental section.	777	777
 P-TBD (1.1-2.7 mmol g <sup>-1</sup> )	 1 example	Y:100	Polymer with low loading was most efficient. Kinetic study. General procedure.	474, 778	474, 778

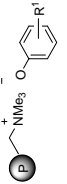
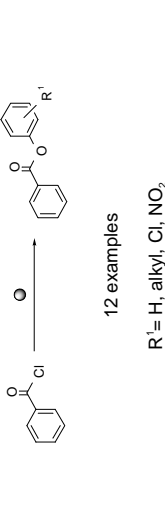
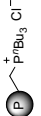
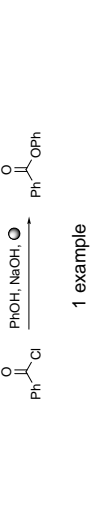

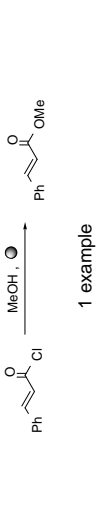
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (0.14-0.30 mmol g <sup>-1</sup> ) <i>n</i> = 1, 7	 6 examples <i>n</i> = 9, 12, 13 <i>m</i> = 1, 4, 5	Y:20-61	The yield is greatest for the low loading resins. Some oligomers detected. Experimental section. For an alternative solid-supported DBU, see reference 779.	780	474
 Amberlite IRA-904 Hydroxide form	 13 examples <i>R</i> <sup>1</sup> = alkyl, aryl, vinyl <i>R</i> <sup>2</sup> = alkyl, aryl, ester <i>X</i> = Br, I, OTs	Y:0-99	General procedure.	781	781
 Amberlite IRA-400 Chloride form (0.90-1.5 mmol g <sup>-1</sup> )	 8 examples <i>R</i> <sup>1</sup> = allyl, aryl, benzyl	Y:89-95	General procedure. Also see reference 782.	783	783
 Amberlite IRA-400 Carboxylate form (1.0 mmol g <sup>-1</sup> )	 4 examples <i>R</i> <sup>1</sup> = aryl <i>R</i> <sup>2</sup> = alkyl, allyl <i>X</i> = I, Br	Y:60-97	Reaction is independent of the nature of the solvent. Polymeric reagent appears to increase nucleophilicity of the anions.	784	784
 Amberlite IRA-904 Carboxylate form	 13 examples <i>R</i> <sup>1</sup> = alkyl, aryl <i>R</i> <sup>2</sup> = alkyl, benzyl <i>X</i> = Cl, Br, I, OTs	Y:28-99	Reaction also proceeds in non-polar solvents. General procedure.	612, 139	612

3.21.1 Esters (From acids)—continued

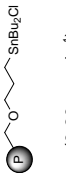
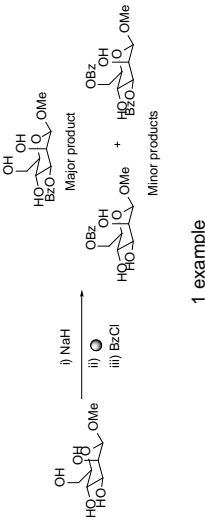
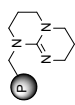
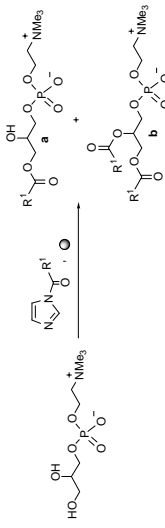

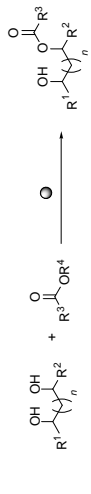
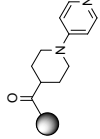
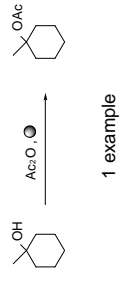
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (10 mmolg <sup>-1</sup> ) R <sup>1</sup> = alkyl, aryl	$R^2-Br \xrightarrow{\text{O}} R^1-C(=O)OR^2$ 7 examples R <sup>2</sup> = alkyl	Y:50-97	The anion is generated on basic Al <sub>2</sub> O <sub>3</sub> (NaOEt adsorbed on Al <sub>2</sub> O <sub>3</sub> ). General procedure.	785	785
 Amberlyst A-26 Fluoride form (2.4 mmolg <sup>-1</sup> )	 4 examples X = Br, Cl AA = Gly, Phe	Y:72-78	The use of polymer-supported fluoride generally gave better yields than with KF. General procedure.	786	
	 1 example	Y:96	Resin is stable to reaction conditions and storage. General procedures.	649	
	 1 example	Y:89	Resin is stable to reaction conditions and storage. General procedures.	649	
	 1 example	Y:56	Three different resins were investigated and the best one is shown. General procedure.	787	787
 Amberlyst A-15 Proton form	 3 examples R <sup>1</sup> = alkyl	C:8-25 Y:36-100	Kinetic study. A number of polymeric cation exchange resins were tested. The best result is shown.	788	

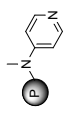
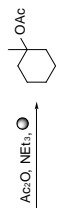
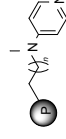

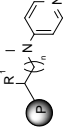

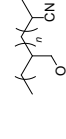
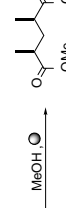
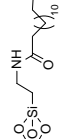

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 $\text{P-PPh}_3\text{-PdCl}_2$	 3 examples $R^1 = \text{alkyl}$	Y:79-86	Full experimental section.	586	586
 $(2.5 \text{ mmol g}^{-1})$	 5 examples $R^1 = \text{alkyl, aryl}$ $R^2 = \text{H, alkyl, aryl}$	Y:73-90	No leaching of catalyst into solution was observed. Catalyst may be reused without loss of activity. General procedure.	646	646

### 3.21.2 Esters (From miscellaneous)

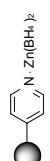
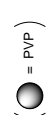
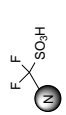
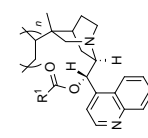
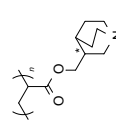
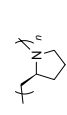
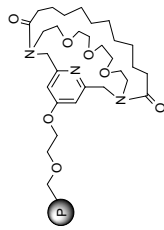
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlite IRA-400 Phenoxide form $(1.0 \text{ mmol g}^{-1})$	 12 examples $R^1 = \text{H, alkyl, Cl, NO}_2$	Y:90-95	Polymer may be recycled. General procedure.	789	789
 $(1.2 \text{ mmol g}^{-1})$	 1 example		Resin was used as a phase transfer catalyst and reactions were carried out in a slurry reactor. Kinetic study. Experimental section.	790	
 $(\text{P} = \text{PVP})$	 1 example	Y:77	General procedure.	791	190, 189

3.21.2 Esters (From miscellaneous)—continued


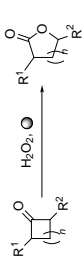




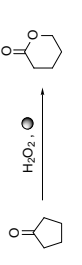
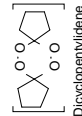

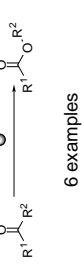
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (0.90 mmol g <sup>-1</sup> )	 1 example	Y:60	Major:minor ratio is 5:1. Toxic tin species remains polymer bound. General procedure.	792	792
 P-TBD (1.9 mmol g <sup>-1</sup> )	 5 examples R <sup>1</sup> = alkyl	Y:22-71	Selectivity is for product <b>a</b> over <b>b</b> . General procedure.	793	
 SO <sub>3</sub> A <sub>2</sub> b	 11 examples R <sup>1</sup> , R <sup>2</sup> , R <sup>3</sup> = H, alkyl R <sup>4</sup> = alkyl n = 0-14	Y:69-96	Selective mono-esterification of diols.	794	
 ( = A variety of insoluble polymers with spacers ) (1.0-1.2 mmol g <sup>-1</sup> )	 1 example		Effects of polymer type, spacer, loading and temperature are discussed. Experimental section. Also see reference 795.	796	796

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (0.70-3.8 mmol <sup>-1</sup> )	 1 example	Y:68-94	A range of polymerisation techniques and cross-linking percentages were studied along with spacer lengths. Experimental section.	797	797
 (1.6-1.9 mmol <sup>-1</sup> ) $n = 0, 4-7$	 1 example	Y:50-100	Several bases tested to investigate the effect of loading and spacer length on acetylation. Experimental section.	798, 799	798, 799
 (1.0-2.1 mmol <sup>-1</sup> ) $R^1 = H, CH_3$ $n = 0, 3, 6, 8, 14$	 1 example	Y:35-97	Use of polymer base allows easy separation of product, which usually co-runs with solution phase base. Experimental section.	800	800
 $n = 0, 3, 6, 8, 14$	 1 example	Y:95 ee:32	Several resins with different linker chains investigated and the best results are given. Experimental section.	673	673
 $n = 0, 3, 6, 8, 14$	 4 examples $R^1 = \text{alkyl}$ $Y = \text{acyl}$ $M = Na, K$	Y:78-91	General procedure. Also see references 801, 802.	803	


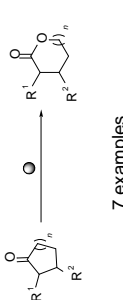







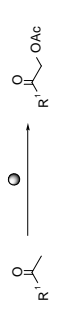
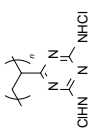
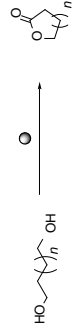
3.21.2 Esters (From miscellaneous)—continued


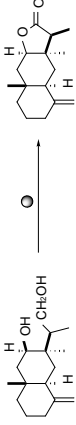



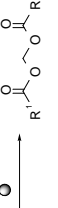
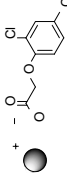
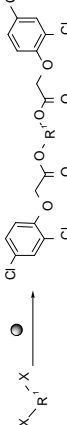

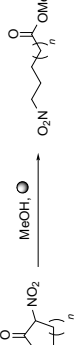
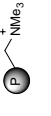
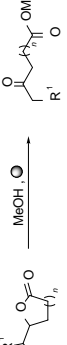
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
  (3.0 mmol g <sup>-1</sup> )	$R^1-CH_2-CHO \xrightarrow{EtOAc, \bullet} R^1-CH_2-CH(OAc)-H$ <p>5 examples R<sup>1</sup> = alkyl, allyl, aryl</p>	Y:80-90	Reaction was selective for aldehydes. Ketones gave very low yields (0–8%).	804	805
 Nafion-H	$R^1-CH_2-CH(OMe)-CO_2Me \xrightarrow{Ac_2O, \bullet} R^1-CH_2-CH(OMe)-CO_2Ac$ <p>2 examples R<sup>1</sup> = alkyl, vinyl</p>	Y:79-94	Experimental section.	806	
	$Ph-CH_2-C(=O)-O- \xrightarrow{MeOH, \bullet} Ph-CH_2-C(=O)-OMe$ <p>1 example</p>	Y:70 ee:35	Several polymers were investigated and the best results are given. The maximum enantiomeric excesses obtained are shown. Experimental section.	807	807
	$Ph-CH_2-C(=O)-O- \xrightarrow{MeOH, \bullet} Ph-CH_2-C(=O)-OMe$ <p>1 example</p>	ee:<20	Several polymers were investigated with the best example given. Experimental section.	808	808
	$Ph-CH_2-C(=O)-O- \xrightarrow{MeOH, \bullet} Ph-CH_2-C(=O)-OMe$ <p>1 example</p>	ee:10		809	
 (0.30 mmol g <sup>-1</sup> )	$R^1-CH(OH)-CH(OH)-R^2 \xrightarrow{Ph-C(=O)-O-} R^1-CH(OH)-CH(OH)-C(=O)-O-Ph$ <p>2 examples R<sup>1</sup>, R<sup>2</sup> = H, alkyl</p>	Y:92	Concave environment of pyridine base facilitates selective protection of less hindered hydroxy group. Yield given is combined for <b>a+b</b> . Full experimental section.	810	810



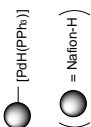
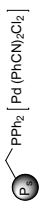
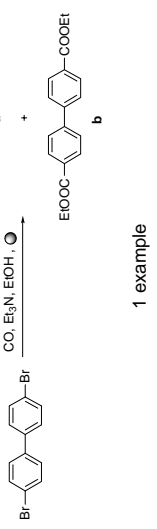
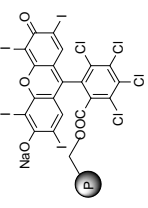


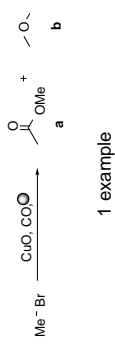
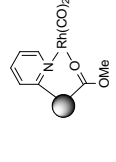
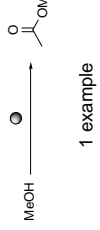
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 $\text{P-SO}_3\text{H}$	 5 examples $R^1, R^2 = \text{H, alkyl}$	Y:71-98	Reagent also oxidises hydroquinones and alcohols. General procedure.	219	219
 $(2.7 \text{ mmol g}^{-1})$	 15 examples $R^1 = \text{alkyl}$ $R^2 = \text{alkyl, aryl}$	Y:0-100	Catalyst may be reused. Experimental section.	724	724
Various zeolites or  Nafion-(13% in $\text{SiO}_2$ ) Nafion-(40% in $\text{SiO}_2$ ) or  Amberlyst A-15 Amberlyst XN-1010	 1 example  Dicyclopentylidene peroxide	C:100 Y:75 (A-15)	All reactions were performed under aqueous conditions and Amberlyst A-15 gave the best selectivity for valerolactone formation.  The major by-product was dicyclopentylidene diperoxide, which was formed in high yield in the presence of very strongly acidic materials like Nafion-H in a silica matrix. These catalysts enable the use of dilute $\text{H}_2\text{O}_2$ (30%) for the epoxidation process.  General procedure.	811	
 $(2.5 \text{ mmol g}^{-1})$ Bio-Rad 50W Peracid form	 6 examples $R^1, R^2 = \text{alkyl, aryl}$	Y:81-99	Resin also epoxidises olefins. General procedure. An alternative catalyst has also been reported. <sup>689</sup>	691	691



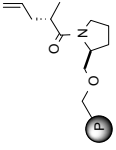
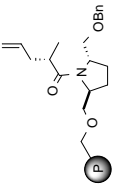


3.21.2 Esters (From miscellaneous)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (S-oxone)	 <p>7 examples R<sup>1</sup>, R<sup>2</sup> = H, alkyl n = 1, 2, 3</p>	Y:23-85	General procedure.	812	812
 (2.4 mmol g <sup>-1</sup> )	 <p>1 example R<sup>1</sup> = aryl</p>	Y:95	General procedure.	73	73
 (2.4 mmol g <sup>-1</sup> )	 <p>3 examples R<sup>1</sup> = aryl</p>	Y:81-89	Reagent may be regenerated. Also iodinated aromatic species. General procedure.	73	73
 (2.4 mmol g <sup>-1</sup> )	 <p>2 examples R<sup>1</sup> = aryl</p>	Y:41	Some by-product detected. General procedure.	73	73
 (3.0 mmol g <sup>-1</sup> )	 <p>1 example R<sup>1</sup> = aryl</p>	Y:72	Soluble resin is as active as solution phase equivalent. Spent reagent may be regenerated and reused without loss of activity. Experimental section.	315	315
	 <p>2 examples n = 1, 2</p>	Y:53-76	Experimental section.	236	236

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Ag <sub>2</sub> CO <sub>3</sub> Celite	 1 example	Y:100	General procedure.	813	218
 Ti(NO <sub>3</sub> ) <sub>3</sub> Montmorillonite K 10	 7 examples R <sup>1</sup> = H, alkyl, Br, F, O-alkyl R <sup>2</sup> = H, alkyl	Y:84-98	Thalium <sup>3+</sup> and Thalium <sup>+</sup> generated during the reaction were tightly bound to the support. Various inorganic supports were investigated but the acidic Montmorillonite K 10 was the best. The reagent was stable and could be stored for months.	135	135
 Amberlite IRA-400 Carboxylate form (1.2-1.4 mmol g <sup>-1</sup> )	 11 examples R <sup>1</sup> = alkyl, aryl, benzyl	Y:50-98	General procedure.	814	814
 Tulison A-27 (2.0 mmol g <sup>-1</sup> )	 7 examples R <sup>1</sup> = alkyl, aryl	Y:37-81	General procedure.	815	815
 Amberlyst A-21	 8 examples n = 1-4, 6-8, 11	Y:75-99	Experimental section.	816	
 Amberlyst A-26 Fluoride form (3.3 mmol g <sup>-1</sup> )	 5 examples R <sup>1</sup> = H, alkyl n = 1, 2	Y:72-83	Substitution of the lactone ring is tolerated allowing access to functionalised 1,4- and 1,5-heteroesters. Experimental section.	817	

3.21.2 Esters (From miscellaneous)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 ( = Nafion-H )	$R^1-CH=CH_2 \xrightarrow{CO, MeOH, \bullet} R^1-CH_2-CH_2-O-C(=O)Me$ <p>3 examples R<sup>1</sup> = alkyl</p>	Y:19-47	General procedure. Also see reference 818.	819	819
	 <p>1 example</p>	C:100	Optimum conditions gave 96% of <b>a</b> and 0.2% of <b>b</b> . Different polymers with varying quantities of palladium were investigated. The reagent may be recycled. General procedure.	820	820
	 <p>1 example</p>	Y:95	Polymer-supported Rose Bengal is used to sensitize the generation of singlet molecular oxygen.	821	821
 graphite intercalation	 <p>1 example</p>	Y:0-53(a) Y:0-74(b)	Ratio of products depends on conditions employed. Experimental section.	822	
 ( = copolymer of 2-vinylpyridine / MMA / ethene diacrylate ) (0.020 mmol g <sup>-1</sup> )	 <p>1 example</p>		Kinetic study. Leaching of 20% of the rhodium occurred during each run. General procedure. A zeolite supported Rh catalyst has also been reported. <sup>823</sup> Also see reference 824.	825	825

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (1.0 mmol g <sup>-1</sup> ) X = Br, Cl, I	$R^1-OH \xrightarrow[DMF, \bullet]{\quad} R^1-O$ 8 examples R <sup>1</sup> = alkyl	Y:78-96	Some addition of bromine to unsaturated systems was observed when X = Br. Full experimental section.	826	826
	$R^1-OH \xrightarrow[\bullet]{\quad} R^1-O$ 6 examples R <sup>1</sup> = amide, carboxylic acid, nitro, SO <sub>3</sub> H	Y: <sup>&gt;</sup> 90	Two polymers were studied. The best example is given	827	827
 (1.0 mmol g <sup>-1</sup> )	$\text{Chiral auxiliary} \xrightarrow{H_2O, I_2} \text{Product}$ 1 example	ee:30	Polymer may be reused.	828	828
	$\text{Chiral auxiliary} \xrightarrow{H_2O, I_2} \text{Product}$ 1 example	Y:34 ee:87 de:100	Polymer may be reused.	829	829
 Amberlyst A-15 Proton form	$R^1-NH_2 \xrightarrow{R^2OH, \bullet} R^1-NH-OR^2$ 13 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl	Y:63-95	In many cases reactions were very slow but the purity of the isolated products was always very high. Full experimental section.	830	830
 Amberlyst A-15 Proton form	$R^1-NH_2 \xrightarrow{R^2OH, \bullet} R^1-NH-OR^2$ 3 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = alkyl	Y:62-78	In many cases reactions were very slow but the purity of the isolated products was always very high. Full experimental section.	830	830

### 3.21.2 Esters (From miscellaneous)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Phenoxide form (1.7 mmol g <sup>-1</sup> )	 10 examples R <sup>1</sup> = alkyl, aryl, benzyl, het, vinyl	Y:54-58	General procedure.	831	

### 3.22 Ethers





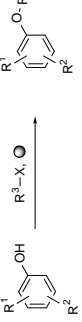

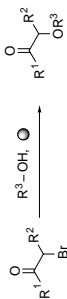
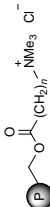
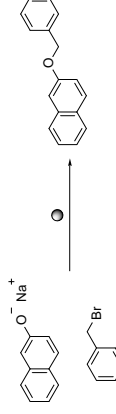
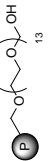

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Phenoxide form (1.7 mmol g <sup>-1</sup> )	 6 examples R <sup>1</sup> = carbohydrate	Y:40-98	Exclusively the β-anomers were obtained from a mixture of α/β starting material. General procedure.	832	832
 Amberlyst A-26 Phenoxide form R = alkyl ester (1.0 mmol g <sup>-1</sup> )	 15 examples R <sup>2</sup> = alkyl, allyl X = hal	Y:75-98	General procedure. Also see references 833, 834.	835	835
 Amberlyst A-26 Phenoxide form (1.5 mmol g <sup>-1</sup> )	 9 examples R <sup>1</sup> = alkyl, benzyl X = Br, Cl, I	Y:60-99	General procedure. Also see references 783, 836.	837	837

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlite IRA-900 Phenoxide form (2.3 mmol g <sup>-1</sup> )	 1 example	Y:98	Reaction carried out as part of a one-pot multi-step synthesis.	39	838
 Amberlite IRA-400 Phenoxide form (1.0 mmol g <sup>-1</sup> ) R <sup>1</sup> = aryl	 11 examples	Y:66-99	Polymer enhances the nucleophilicity of the supported phenoxides. High yields were also obtained with nitrophenols. General procedure.	839, 840	839
 Amberlite IRA-400 Phenoxide form R <sup>1</sup> = aryl	 9 examples	Y:89-95	Spent resin may be regenerated and reused without loss of activity. General procedure.	834	834
 Amberlite IRA-400 Phenoxide form R <sup>1</sup> = aryl (1.3-1.4 mmol g <sup>-1</sup> )	 2 examples		Used as part of a synthesis of atenolol and propranolol. Experimental section.	841	841
 Amberlite IRA-900 Phenoxide form (1.0 mmol g <sup>-1</sup> ) R <sup>1</sup> = aryl	 16 examples R <sup>2</sup> = alkyl, allyl, benzyl X = Br, Cl, I, OMs	Y:0-100	Yields were sensitive to steric hindrance at R <sup>2</sup> . There was no reaction with BuX. Experimental section.	833	833

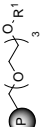
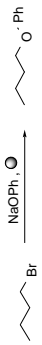
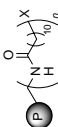



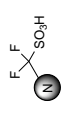


3.22 Ethers—continued

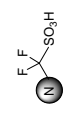
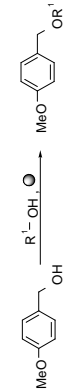



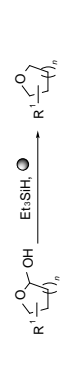
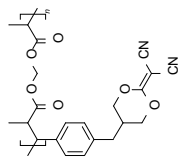
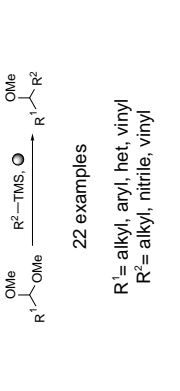
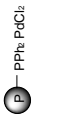
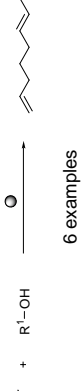
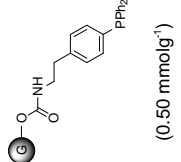
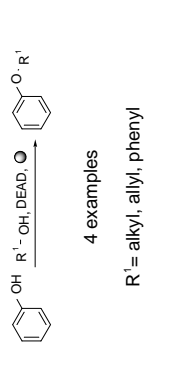
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlite IRA-900 Chloride form	 20 examples $R^1 = \text{alkyl}$ $R^2, R^3 = \text{H, alkyl, aryl}$ $X = \text{CH, N}$	Y:62-100	Resin may be recycled. General procedure.	842	842
 (0.90 mmol g <sup>-1</sup> )	 2 examples $R^1 = \text{vinyl, aryl}$		Polymers with various loadings were examined and the best example is shown. Kinetic study. Also see reference 843.	844, 845	844, 845
 Dowex MSA-1 Fluoride form	 2 examples $R^1 = \text{H, nitro}$	Y:50		846	846
 (0.60 mmol g <sup>-1</sup> )	 1 example		Mechanistic study. Same reaction carried out with Amberlyst A-27 (phenoxide form) and Amberlyst A-27 (bromide form). <i>ortho</i> and <i>meta</i> Alkylation also observed. Experimental section. A similar cellulose supported reagent has also been reported. <sup>847</sup>	848	849
 Amberlite IRA-400 Hydroxide form (1.4 mmol g <sup>-1</sup> )	 11 examples $R^1 = \text{aryl}$	Y:0-90	Experimental section.	850	
 Amberlite IRA-400 Hydroxide form (1.4 mmol g <sup>-1</sup> )	 3 examples $R^1 = \text{alkyl}$	Y:1-37	The yields were moderate but the products were obtained in pure form. The anion was generated on "basic Al <sub>2</sub> O <sub>3</sub> " (NaOEt adsorbed on Al <sub>2</sub> O <sub>3</sub> ). General procedure.	785	785



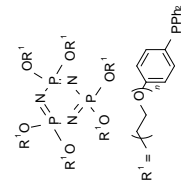
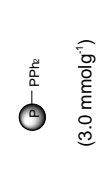

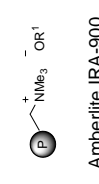

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
	$R^1-OH \xrightarrow{Me_2SO, \text{O}} R^1-O-Me$ <p>3 examples R<sup>1</sup> = aryl</p>	Y:18-49	General procedure.	785	785
	 <p>1 example</p>	Y:97	Several supports investigated, best results given. Alumina supported KF was found to be more reactive than unsupported KF. Works also on aliphatic alcohols. General procedure.	537	537
 P-TBD	 <p>13 examples</p> <p>R<sup>1</sup> = H, alkyl, hal, nitro R<sup>2</sup> = H, alkyl, aryl, hal, nitro R<sup>3</sup> = alkyl, allyl, benzyl, phenyl</p>	Y:47-98 P:71-99	Alkyl halides do not need to be activated.	53	
 P-TBD	 <p>27 examples</p> <p>R<sup>1</sup>, R<sup>3</sup> = aryl R<sup>2</sup> = alkyl</p>	Y:30-95 P:75-95	One step in the synthesis of a benzofuran library using polymer-supported reagents.	80	
 n = 5, 11	 <p>1 example</p>	Y:65-98	Five macrorreticular and microporous resins tested. Negligible chloro-alkylation observed. Resin acts as an immobilised phase transfer catalyst.	851	
 13	 <p>1 example</p>	Y:60	Kinetic study. Also see reference 852.	853	853

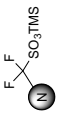



3.22 Ethers—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 R <sup>1</sup> = alkyl	 1 example	Y:14-99	Several polymer catalysts used. Lower loading catalysts seem more effective.	854	
 X = Br, Cl n = 0-2	 1 example		Reaction is selective for O over C alkylation.	855	855
 PPh <sub>3</sub>	 15 examples R <sup>1</sup> = aryl R <sup>2</sup> = alkyl, benzyl, het	Y:63-94	Polymer by-product is the supported triphenylphosphine oxide which can be easily removed.	856	
 Nafion-H	 10 examples R <sup>1</sup> = alkyl	Y:92-98	Resin may be regenerated and recycled. General procedure.	857, 858	
 Amberlyst A-15 Proton form (4.9 mmol g <sup>-1</sup> )	 1 example	Y:94		859	
 Amberlyst A-15 Proton form	 1 example		Kinetic study. General procedure.	860	

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Nafion-H	 4 examples $R^1 = \text{alkyl}$	Y:78-87	General procedure.	766	
 Dowex 50 W Proton form	 8 examples $R^1 = \text{aryl}$ $R^2, R^3, R^4 = \text{alkyl}$	Y:90-98 P:94-95	Used within a multi-step library synthesis.	81	
 Amberlyst A-15 Proton form	 8 examples $R^1 = \text{alkyl, aryl}$ $n = 1, 2$	Y:67-99	Experimental section.	861	
	 22 examples $R^1 = \text{alkyl, aryl, het, vinyl}$ $R^2 = \text{alkyl, nitrile, vinyl}$	Y:0-100	Reaction also occurs with aldehydes and ketones. General procedure.	862	
 $\text{P} - \text{PPh}_2 \text{PdCl}_2$	 6 examples $R^1 = \text{H, alkyl, aryl}$	Y:6-92	Full experimental section.	586	586
 (0.50 mmol $g^{-1}$ )	 4 examples $R^1 = \text{alkyl, allyl, phenyl}$	Y:75-88	Polystyrene supported triphenylphosphine is also useful for this reaction. General procedure.	547	547

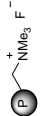


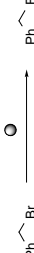
3.22 Ethers—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>Soluble polymer</p>	$R^2-OH + \text{Phenol} \xrightarrow{DEAD, \bullet O} R^2-O-Phenol$ <p>4 examples</p> <p><math>R^2 = \text{alkyl, allyl, benzyl}</math></p>	Y:68-93	Soluble polymer may be completely recovered from solution by precipitation with ether. General procedure.	863	863
 <p>(3.0 mmol g<sup>-1</sup>)</p>	$HO-C_6H_4-NO_2 + R^1-OH \xrightarrow{Bu_3O-C-N=N-CO_2^+ Bu_3O} R^1-O-C_6H_4-NO_2$ <p>3 examples</p> <p><math>R^1 = \text{alkyl, benzyl}</math></p>	Y:33-80 P:78-95	Azodicarboxylate was removed by treatment with TFA and aqueous wash using a hydrophobic phase separation tube. Unconverted starting material was removed with resin bound carbonate. General procedure.	538	
	$Cl-C_6H_3(NO_2) + \text{Phenol} \xrightarrow{KOH, PhCH_3, \bullet O} \text{Ether}$ <p>1 example</p>	Y:64	Some hydrolysis to phenol observed. Experimental section.	864	
 <p>Amberlite IRA-900 Phenoxide form (1.0-1.7 mmol g<sup>-1</sup>)</p> <p><math>R^1 = \text{aryl}</math></p>	$Cl-C_6H_3(NO_2) + \text{Phenol} \xrightarrow{\bullet O} \text{Ether}$ <p>14 examples</p>	Y:81-98	General procedure.	865	865
 <p>Envirocat EPZG</p>	$R^1-OH + CH_2(OMe)_2 \xrightarrow{\bullet O} R^1-OMOM$ <p>11 examples</p> <p><math>R^1 = \text{alkyl, benzyl, het}</math></p>	Y:68-99	Chiral alcohols undergo protection without racemisation. General procedure.	111	

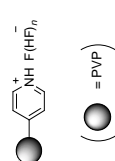
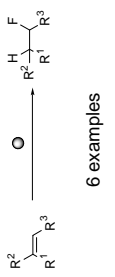
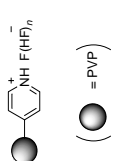
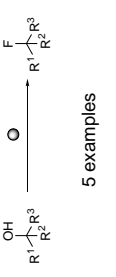
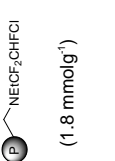
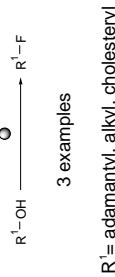
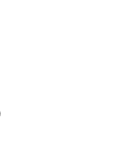
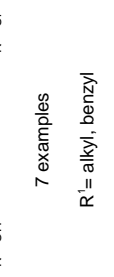
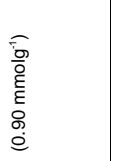
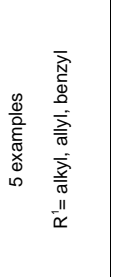
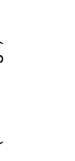
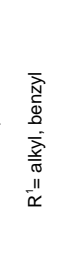
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Nafion-TMS	 1 example	Y:92	Reagent is moisture stable.	90	
 Intercalated graphite	 3 examples X= Cl, Br, F	Y:67-91	Some MeF by-product observed. Also see reference 95.	866	






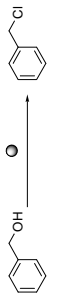

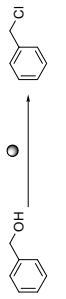



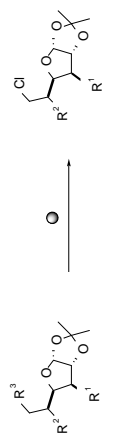
### 3.23 Haloalkanes

#### 3.23.1 Haloalkanes (Monohalogenated)

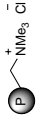
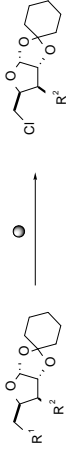
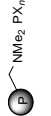


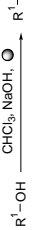


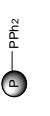
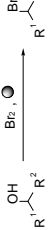
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Fluoride form (4.0 mmol g <sup>-1</sup> )	 11 examples R <sup>1</sup> = alkyl, aryl, benzyl R <sup>2</sup> = H, alkyl X = Br, Cl, OMs, OTs	Y:1-73	Halogen exchange reactions were also carried out on alkyl halides using bromide, chloride and iodide resins. Alkene by-products were often observed (Y:0-73%) in these cases particularly for secondary alkyl halides. Experimental section. Also see reference 867.	477	477
 (3.2 mmol g <sup>-1</sup> )	 1 example	Y:32	Potassium fluoride supported on calcium fluoride <sup>868</sup> and polyethylene glycol <sup>869</sup> have also been reported.	136	136

3.23.1 Haloalkanes (Monohalogenated)—continued





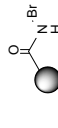

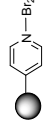


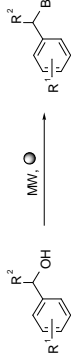

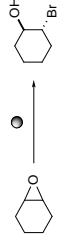
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 ( = PVP)	 6 examples R <sup>1</sup> , R <sup>3</sup> = alkyl R <sup>2</sup> = H, alkyl	Y:60-81	Standard laboratory glassware may be used for these reactions. General procedure	870, 871	870, 871
 ( = PVP)	 5 examples R <sup>1</sup> , R <sup>2</sup> = alkyl R <sup>3</sup> = H, alkyl	Y:65-95	Secondary alcohols were fluorinated more slowly than tertiary alcohols. Standard laboratory glassware could be used for these reactions. General procedure.	871, 870	871, 870
 (1.8 mmol g <sup>-1</sup> )	 3 examples R <sup>1</sup> = adamantyl, alkyl, cholesteryl	Y:>90	The resin was stable for several months when stored under nitrogen.	872	872
 (0.90 mmol g <sup>-1</sup> )	 7 examples R <sup>1</sup> = alkyl, benzyl	Y:60-99	Primary and secondary alcohols were compatible with this protocol. The resin may be recycled by reduction of the oxide. Experimental section.	873, 874	873
 (0.90 mmol g <sup>-1</sup> )	 5 examples R <sup>1</sup> = alkyl, allyl, benzyl	C:62-82 Y:45-72	Several resins with different cross-linking were used. The best results were obtained with 15% cross-linking. Experimental section.	875	875
 (2.5 mmol g <sup>-1</sup> )	 7 examples R <sup>1</sup> = alkyl, benzyl	Y:40-98	General procedure. A soluble polyethylene-supported reagent has also been used. <sup>876</sup>	137	137

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
	$R^1-OH \xrightarrow{CCl_4, \bigcirc} R^1-Cl$ 3 examples $R^1 = \text{alkyl, aryl}$	Y:22-99	This resin was also used for elimination reactions. Experimental section.	481	481
	$R^1-OH \xrightarrow{CCl_4, \bigcirc} R^1-Cl$ 3 examples $R^1 = \text{alkyl, benzyl}$		No yields were quoted. The polymeric reagent reacted at a greater rate than its solution phase equivalent. General procedure.	877	
  (0.70 mmol g <sup>-1</sup> )	$R^1-OH \xrightarrow{CCl_4, \bigcirc} R^1-Cl$ 6 examples $R^1 = \text{alkyl, aryl}$	Y:41-99	The polymer was soluble at reaction temperatures but precipitated at room temperature. Partial recycling of the phosphine oxide by-product was achieved using HSCl <sub>3</sub> .	876	876
 (1.7 mmol g <sup>-1</sup> )	$R^1-OH \xrightarrow{CCl_4, \bigcirc} R^1-Cl$ 4 examples $R^1 = \text{alkyl, aryl, benzyl}$  1 example	C:41-100	Experimental section.	878	878
 (1.7 mmol g <sup>-1</sup> )	 1 example	Y:40-100	Polymer could be regenerated and reused without loss of activity. Experimental section.	879	879
 (1.7 mmol g <sup>-1</sup> )	 1 example	Y:51-57	Semi-empirical calculations were carried out to investigate reactivity differences with the diphenyl analogue. Experimental section.	880	880
 Amberlite IRA-410 Chloride form	 3 examples $R^1, R^2 = \text{OMs, OTs}$ $R^3 = \text{H, OBn, OMs, OTs}$	Y:63-75	Selective displacement of the primary tosylate / mesylate over the secondary was observed.	881	

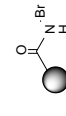
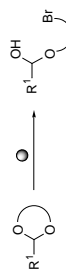
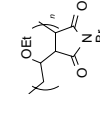
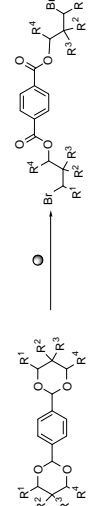
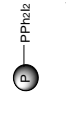
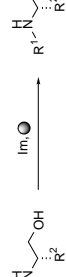
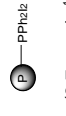
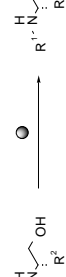
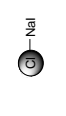
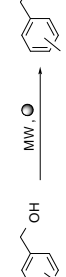
3.23.1 Haloalkanes (Monohalogenated)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlite IRA-410 Chloride form	 2 examples R <sup>1</sup> = OMes, OTs R <sup>2</sup> = H, OBn, OMes, OTs	Y:70-75	Selective displacement of the primary tosylate / mesylate over the secondary was observed.	881	
 Amberlite IRA-93 a X = Cl; n = 5 b X = Br; n = 3 a (~2.0 mmol g <sup>-1</sup> ) b (~1.0 mmol g <sup>-1</sup> )	 a: 9 examples b: 7 examples R <sup>1</sup> = alkyl, allyl, benzyl, allylic	Y:35-98	Phosphorous by-products were retained on polymer. Regeneration of the resin was possible. General procedure.	139	139
	 2 examples R <sup>1</sup> = alkyl, benzyl	Y:56-65	Resin was stable to reaction conditions and to storage. General procedure.	649	
	 5 examples R <sup>1</sup> = alkyl, benzyl M = Na, K X = Cl, F, I	Y:10-93	Resin was stable to reaction conditions and to storage. General procedure.	649	
 (1.3-3.2 mmol g <sup>-1</sup> )	 7 examples R <sup>1</sup> = alkyl, allyl R <sup>2</sup> = H, alkyl	Y:0-100	Experimental section.	882	882



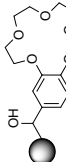
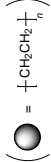

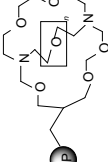

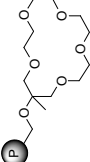

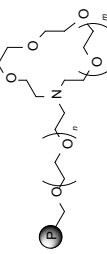

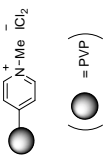

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (1.3-3.2 mmol g <sup>-1</sup> )	 11 examples R <sup>1</sup> = alkyl, allyl R <sup>2</sup> = H, alkyl	Y:80-98	The polymer selectively brominated alcohols in the presence of alkenes. Experimental section.	882, 883	882
	 3 examples R <sup>1</sup> = H, O-alkyl, nitro		The polymer was used to generate benzyl bromides for use in <i>N</i> -alkylation reactions.	70	
 (= polyacrylamide) (5.2-5.7 mmol g <sup>-1</sup> )	 1 example	Y:60-90	This non-corrosive and easily handled reagent was stable under normal laboratory conditions and could be stored indefinitely. The reagent could also be used to oxidise alcohols to aldehydes or ketones, thiols to sulfides, to $\alpha$ -brominate ketones and to brominate alkenes. Experimental section. Also see reference 884.	232	232
 (= PVP)	 9 examples R <sup>1</sup> = atyl	Y:63-85	The spent polymer could be regenerated and reused with no loss of activity.	885	886
 Montmorillonite K 10 (10 mmol g <sup>-1</sup> )	 7 examples R <sup>1</sup> = H, alkyl, O-alkyl R <sup>2</sup> = H, alkyl	Y:60-95	Analogous reactions were unsuccessful with tertiary, benzylic, propargylic and saturated alcohols. General procedure.	887	887
	 1 example	Y:83	Experimental section.	888	888

3.23.1 Haloalkanes (Monohalogenated)—continued



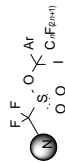
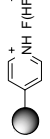
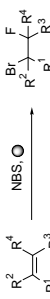
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 = polyacrylamide (2.0-2.8 mmol g <sup>-1</sup> )	 8 examples R <sup>1</sup> = alkyl, aryl	Y:15-72	Other polymers were prepared and the best example is shown. General procedure.	889	889
 (1.4-2.5 mmol g <sup>-1</sup> )	 6 examples R <sup>1</sup> , R <sup>2</sup> , R <sup>3</sup> = H, alkyl R <sup>4</sup> = H, alkyl, OH	C:26-87	The reagent could be stored without loss of activity. Full experimental section.	890, 891	890
 (2.7 mmol g <sup>-1</sup> )	 13 examples R <sup>1</sup> = Boc, CBz, Fmoc R <sup>2</sup> = alkyl, aryl, benzyl	Y:76-95	No racemisation was observed. Reagent was formed <i>in situ</i> prior to substrate addition. General procedure.	892	892
 (2.7 mmol g <sup>-1</sup> )	 13 examples R <sup>1</sup> = Boc, CBz, Fmoc Amino alcohols: Abu, Ala, Asp (OBn), Leu, Phe, Phyl, Tyr (OBn), Val	Y:78-94	No racemisation was observed. Reagent was formed <i>in situ</i> prior to substrate addition. General procedure.	528	528
 Montmorillonite K 10 (4.5 mmol g <sup>-1</sup> )	 4 examples R <sup>1</sup> = H, hydroxy, O-alkyl	Y:55-90	No conversion was observed with aliphatic alcohols, phenol and proparagyl alcohol. General procedure.	893	893

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
	 1 example		Kinetic study. Experimental section. Also see reference 894.	855	855
	$R^1-X \xrightarrow{KI, O} R^1-I$ 2 examples $R^1 = \text{alkyl}$	Y:45-98	Reactions were carried out in a flow reactor. Up to five cycles of reagent were required to give 98% yield.	542	542
	$R^1-Br \xrightarrow{KX, O} R^1-X$ 3 examples $R^1 = \text{alkyl}$ $X = I, \text{ nitrile, SCN}$	Y:85-98	Five reagents were investigated as phase transfer catalysts. The best example is shown. A loss in activity was found after the first cycle but activity then remained constant.	542, 895, 896	
	$R^1-Br \xrightarrow{KX, O} R^1-X$ 3 examples $X = I, CN, C_6H_5S$	C:50-98	Four polymers were tested. The best results are shown. Also see reference 897.	898	898
	$R^1-Br \xrightarrow{KX, O} R^1-X$ 2 examples $X = I, SPh$		Kinetic study.	899	899
	$R^1-Br \xrightarrow{KI, O} R^1-I$ 1 example	C:70	Kinetic study. Experimental section.	855	855
	$R^1-Br \xrightarrow{KI, O} R^1-I$ 1 example		Kinetic study. Experimental section.	855	855

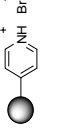
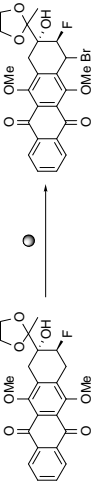
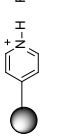

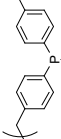
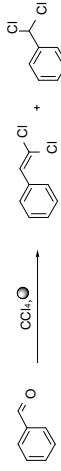
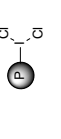
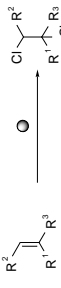
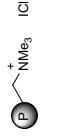
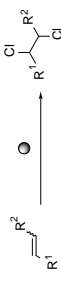
3.23.1 Haloalkanes (Monohalogenated)—continued

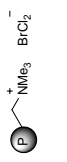
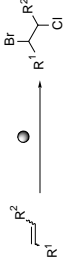
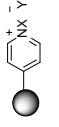
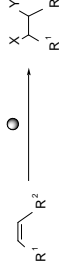
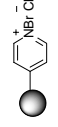
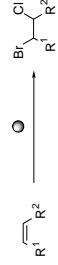
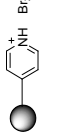
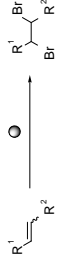
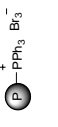
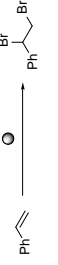
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
  (0.40 mmol g <sup>-1</sup> )	 1 example	Y:90	Other catalysts were described but this one was used on a preparative scale. The catalyst could be recycled and was soluble on heating but precipitated when cooled. Full experimental section. Also see references 900, 901.	902	902
 (0.80-1.1 mmol g <sup>-1</sup> ) n= 1,2	 4 examples M= Na, K X= I, CN	Y:63-100	The catalyst could be recycled. Some loss of activity was observed upon reuse however the reagent could be regenerated by treatment with sodium thiosulfate.	903	903
 (1.8-2.0 mmol g <sup>-1</sup> )	 1 example	Y:95	Generally better yields were obtained using the polymer rather than using the monomeric catalyst.	904	904
 n=0,1 m=1,2 0.60-2.0 mmol g <sup>-1</sup>	 1 example		Kinetic studies were undertaken. Polymers with m=1 gave faster reactions due to increased chelating ability of the polymer. Other similar polymer catalysts were also tested. Experimental section.	905, 906	905, 906
 (2.2 mmol g <sup>-1</sup> )	 21 examples R' = aryl, α-keto alcohol, pyridyl	Y:52-90	Iodination of aromatic rings and positions α to a ketone were carried out. Some chlorination and diiodination were observed. Experimental section.	907, 908	907, 908

### 3.2.3.2 Haloalkanes (Dihalogenated)


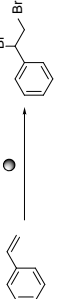


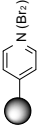
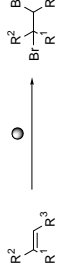
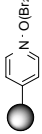
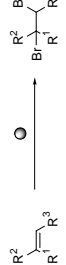

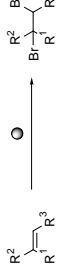
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (1.1 mmol g <sup>-1</sup> )	 6 examples R <sup>1</sup> = H, phenyl R <sup>2</sup> = H, alkyl	Y:85-96	General procedure. Also see reference 909.	910, 911	911
 ( = PVP )	 8 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl, aryl	Y:28-96	FBr generated <i>in situ</i> . General procedure.	912	
 ( = PVP ) n = 2-7	 2 examples R <sup>1</sup> = H, alkyl R <sup>2</sup> = alkyl	Y:56-59	General procedure.	871, 870	871, 870
 (0.30-0.40 mmol g <sup>-1</sup> ) n = 2, 3, 4, 6, 8	 6 examples R <sup>1</sup> = aryl, het	Y:89-95		913	913
 ( = PVP ) n = 2-7	 7 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> , R <sup>3</sup> , R <sup>4</sup> = H, alkyl	Y:71-81	General procedure.	871, 870	871, 870

3.23.2 Haloalkanes (Dihalogenated)—continued

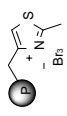

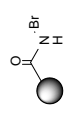
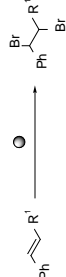
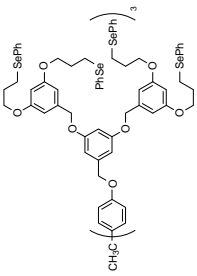
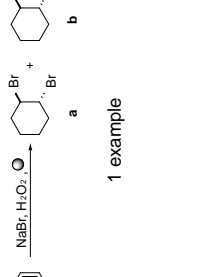
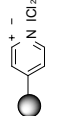
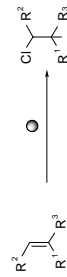
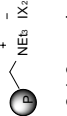
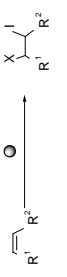
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 ( = PVP ) (2.4 mmol g <sup>-1</sup> )	 1 example	C:50-60	The reaction was stopped at 50% conversion to prevent dibromination. Also see reference 885.	914	
 ( = PVP )	 7 examples R <sup>1</sup> = H, alkyl, aryl R <sup>2</sup> = H, alkyl, F	Y:12-71	Yield was measured after one hour. Reagent can be recycled successfully.	915	916
 (1.1 mmol g <sup>-1</sup> )	 1 example	Y:1-64	Ratio of products varied depending on the polymer used.	878	878
 (1.1 mmol g <sup>-1</sup> )	 3 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl R <sup>3</sup> = H, aryl	Y:53-88	Some stereoselectivity observed, and some mono-chlorination Experimental section.	917,	917
 Amberlyst A-26 iodo-chloride form (2.5 mmol g <sup>-1</sup> )	 2 examples R <sup>1</sup> , R <sup>2</sup> = alkyl	Y:75-82	A four-fold excess of reagent was used. Equimolar amounts of reagent and substrate led to a 1:1 mixture of dichloro- and chloriodo-compounds. Reagent may be regenerated. General procedure.	918	918

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Bromo-chloride form (2.5 mmol g <sup>-1</sup> )	 3 examples R <sup>1</sup> = alkyl R <sup>2</sup> = H, alkyl	Y:62-85	A 10% decrease in reagent activity was observed after three months storage at room temperature. Reagent may be regenerated. General procedure.	919	919
 ( = PVP ) X= Br Y= Br, Cl	 3 examples R <sup>1</sup> = alkyl, phenyl R <sup>2</sup> = H, alkyl	Y:80-100	General procedure.	920	920
 ( = PVP )	 3 examples R <sup>1</sup> = alkyl, phenyl R <sup>2</sup> = H, alkyl	Y:80-100	General procedure.	920	920
 ( = PVP ) (5.6 mmol g <sup>-1</sup> )	 6 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl, aryl	Y:55-99	The reagent was regenerated and reused without loss of reactivity. Also used for $\alpha$ -bromination of ketones. Experimental section.	886	886
 (3.6 mmol g <sup>-1</sup> )	 1 example	Y:85	General procedure.	921	921

3.23.2 Haloalkanes (Dihalogenated)—continued

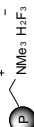
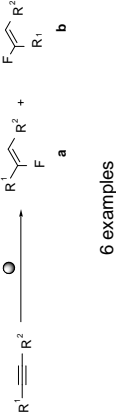

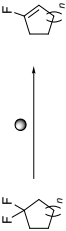
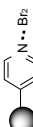
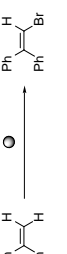
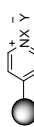
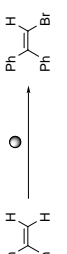
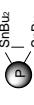
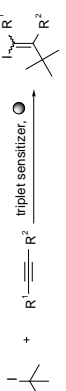
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (● = PMMA) (1.2 mmol g <sup>-1</sup> )	 1 example	Y:93	Stable at room temperature for long periods. General procedure.	922	922
 Amberlyst A-26 Perbromide form (2.5 mmol g <sup>-1</sup> )	 1 example R <sup>1</sup> , R <sup>2</sup> = alkyl	Y:85	A 10% decrease in reagent activity was observed after three months storage at room temperature. Reagent may be regenerated. General procedure.	919	919
 (● = PVP) (2.3 mmol g <sup>-1</sup> ) n = 1, 2	 3 examples R <sup>1</sup> , R <sup>2</sup> , R <sup>3</sup> = H, alkyl, aryl	Y:95-100	Addition of bromine is highly stereospecific for the <i>anti</i> isomer. General procedure.	923	916
 (● = PVP) (2.5 mmol g <sup>-1</sup> ) n = 1, 2	 2 examples R <sup>1</sup> , R <sup>2</sup> , R <sup>3</sup> = H, alkyl	Y:93-100	Addition of bromine is highly stereospecific. General procedure.	923	916
 (● = PVP) (1.7 mmol g <sup>-1</sup> )	 3 examples R <sup>1</sup> , R <sup>2</sup> , R <sup>3</sup> = H, alkyl, aryl	Y:94-100	Three resins were investigated. The most reactive is shown. Addition of bromine is highly stereospecific. General procedure.	923	916

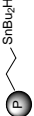
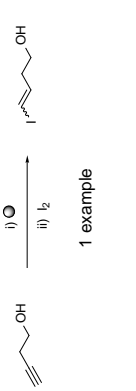
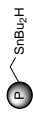
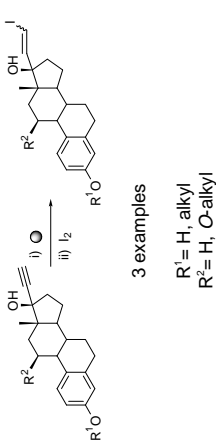

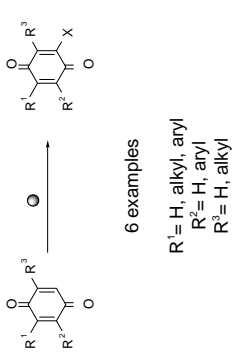


Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (1.6 mmol g <sup>-1</sup> )	 2 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl	Y:100	A range of other resins were synthesised, but only this resin was used in bromination. General procedure.	227	227
 (= polyacrylamide) (5.2-5.7 mmol g <sup>-1</sup> )	 3 examples R <sup>1</sup> = H, aryl, carboxylic acid	Y:73-77	This non-corrosive and easily handled reagent was stable under normal laboratory conditions and could be stored indefinitely. The reagent was also used to oxidise alcohols to aldehydes or ketones, thiols to sulfides and to α-brominate ketones and brominate alkenes. Experimental section.	232	232
	 1 example		Catalyst may be reused without loss of activity. Product ratio for <b>a</b> : <b>b</b> = 38:68. General procedure.	924	924
	 4 examples R <sup>1</sup> = aryl R <sup>2</sup> , R <sup>3</sup> = H, alkyl	C:100	Stereospecific <i>trans</i> -Markovnikov addition occurred.	925	
 (1.2-1.8 mmol g <sup>-1</sup> ) X = Br, Cl	 7 examples R <sup>1</sup> = alkyl, aryl, carboxylic acid, nitrile R <sup>2</sup> = H, alkyl	Y:45-74	Addition was Markovnikov. General procedure.	926	926


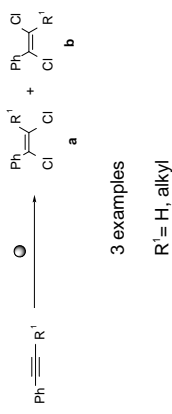
### 3.24 Haloalkenes

#### 3.24.1 Haloalkenes (Monohalogenated)

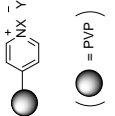
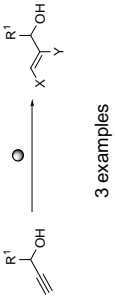
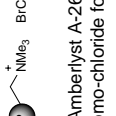
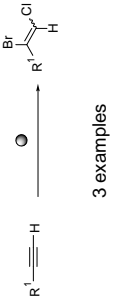
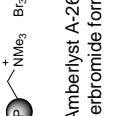
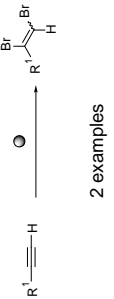
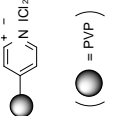
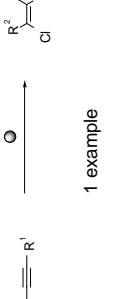
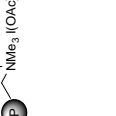
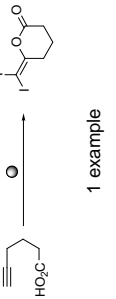
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Dihydrogenotrifluoride form	$R^1-C\equiv C-R^2 \xrightarrow{\bullet} R^1-C(F)=C(R^2) + \bullet$ <p style="text-align: center;">6 examples</p> <p style="text-align: center;">R<sup>1</sup> = alkyl, aryl, ester            R<sup>2</sup> = aldehyde, ester, ketone, nitrile</p> 	Y:0-95	Ratio of products <b>a</b> : <b>b</b> is between 1:2 and 8:1 Only electrophilic alkenes react. General procedure.	927	927
	 <p style="text-align: center;">6 examples r = 1, 2, 3, 7</p>	Y:20-96	Experimental section.	928	
 (= PVP) (2.0 mmol g <sup>-1</sup> )	 <p style="text-align: center;">1 example</p>	Y:100	Three resins were investigated and the best example is shown. General procedure.	929	929
 (= PVP) X = Br, H Y = Br, Br <sub>3</sub> , OBr <sub>4</sub>	 <p style="text-align: center;">1 example</p>	Y:100	Three resins were investigated and the best example is shown. Reagent may be regenerated. General procedure.	916	916
 (1.3 mmol g <sup>-1</sup> )	 <p style="text-align: center;">3 examples R<sup>1</sup> = aryl, ester R<sup>2</sup> = H, ester</p>	Y:66-78	Acetone/toluene or acetone/propan-2-ol were used as sensitizers. General procedure.	399	399

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
		Y:100	Ratios of <i>E:Z</i> isomers = 1:1.	930	930
 Amberlite XE-305 (0.83 mmol g <sup>-1</sup> )		Y:40-60	<i>E:Z</i> ratios of between 48:1 and 6:1 were obtained. Experimental section.	931	931
 X = Br, Cl		Y:20-80	Halogenation is specific to the quinoid position. General procedure.	932	932

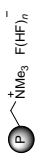
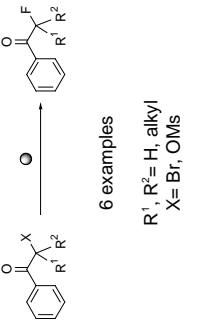
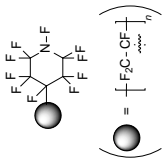
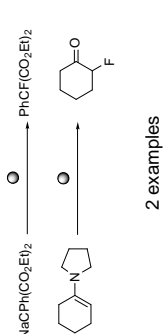
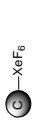
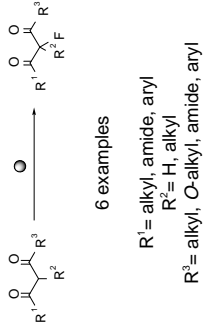
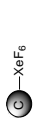
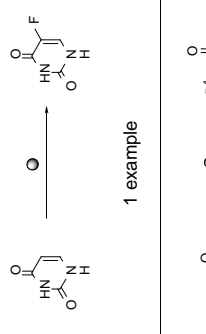
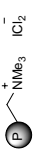
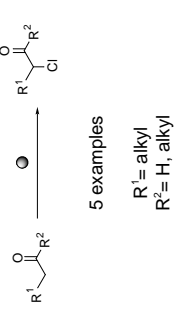
### 3.2.4.2 Haloalkenes (Dihaloalkenated)

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (1.1 mmol g <sup>-1</sup> )			Ratio <i>a:b</i> = 1.4:1 to 11:1. Experimental section.	917	917


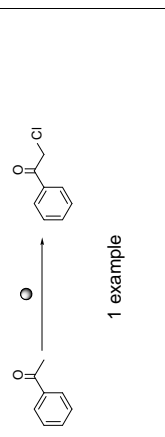
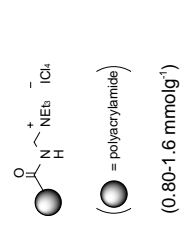
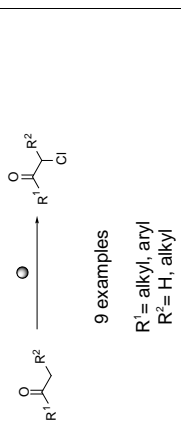
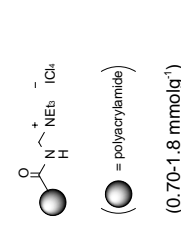
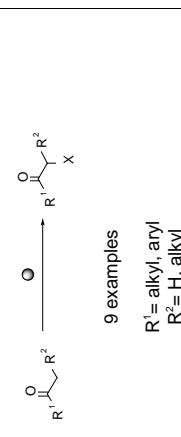
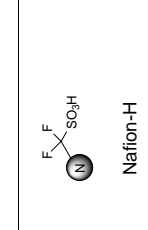
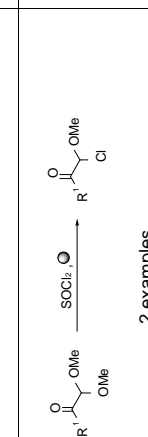
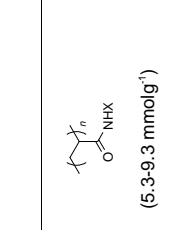
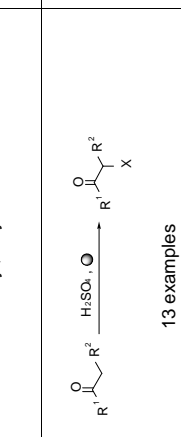
3.2.4.2 Haloalkenes (Dihalogenated)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (● = PVP) X = Br Y = Br, Cl	 3 examples R <sup>1</sup> = H, alkyl	Y:55-80	General procedure.	920	920
 Amberlyst A-26 Bromo-chloride form (2.5 mmol g <sup>-1</sup> )	 3 examples R <sup>1</sup> = alkyl, aryl	Y:62-96	A 10% decrease in reagent activity was observed after three months storage at room temperature. R <sup>1</sup> = alkyl gave mainly the <i>E</i> -isomer. R <sup>1</sup> = aryl gave mainly the <i>Z</i> -isomer. Reagent may be regenerated. General procedure.	919	919
 Amberlyst A-26 Perbromide form (2.5 mmol g <sup>-1</sup> )	 2 examples R <sup>1</sup> = alkyl, aryl	Y:92-94	10% decrease in reagent activity was observed after three months storage at room temperature. Mainly the <i>E</i> -isomer was generated. Reagent may be regenerated. General procedure.	919	919
 (● = PVP)	 1 example R <sup>1</sup> = aryl R <sup>2</sup> = H, alkyl		Stereoselective for <i>trans</i> alkyl substituted alkene formation.	925	
 (● = PVP)	 1 example	Y:57	General procedure.	131	131

### 3.25 $\alpha$ -Halocarbonyls

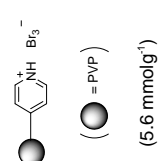
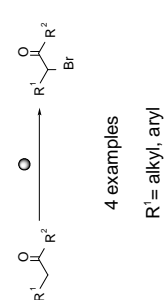
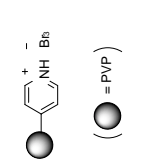
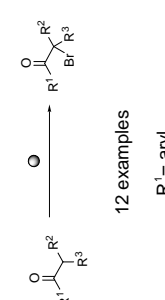
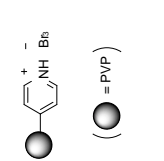
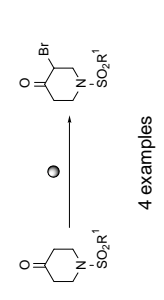
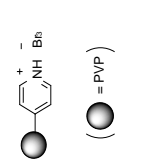
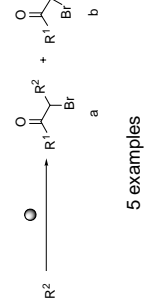
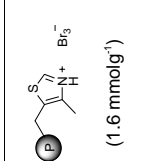
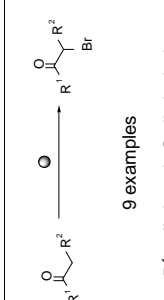
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Amberlyst IRA-900 $n = 0, 1, 2$ (4.0 mmol g <sup>-1</sup> )	 <p>6 examples  <math>R^1, R^2 = H, \text{alkyl}</math>  <math>X = Br, \text{OMs}</math></p>	Y:20-98	Best yields of fluoro substitution were obtained when $n=2$ as $H_2F_3^-$ is less basic and more nucleophilic than $F^-$ . Experimental section.	933	933
 (0.7 mmol g <sup>-1</sup> )	 <p>2 examples</p>	Y:17 (a) Y:15 (b)	Electrophilic fluorinating agent. General procedure.	934	934
 Graphite C <sub>10</sub> XeF <sub>6</sub>	 <p>6 examples  <math>R^1 = \text{alkyl}, \text{amide}, \text{aryl}</math>  <math>R^2 = H, \text{alkyl}</math>  <math>R^3 = \text{alkyl}, \text{O-alkyl}, \text{amide}, \text{aryl}</math></p>	Y:40-68	The reagent is more stable than XeF <sub>6</sub> . No difluorination was observed.	935	936
 Graphite C <sub>10</sub> XeF <sub>6</sub>	 <p>1 example</p>	Y:90	The reagent is more stable than XeF <sub>6</sub> . No difluorination was observed.	935	936
 Amberlyst A-26 Iodochloride form (2.5 mmol g <sup>-1</sup> )	 <p>5 examples  <math>R^1 = \text{alkyl}</math>  <math>R^2 = H, \text{alkyl}</math></p>	Y:45-88	Polychlorinated products were obtained as by-products from ketones. The reagent is stable at room temperature for storage. Regeneration of the resin is possible. General procedure.	918	918

3.25  $\alpha$ -Halocarbonyls—continued

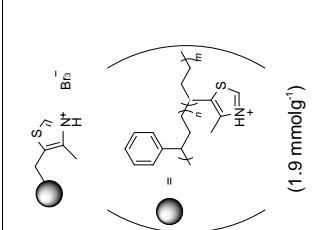
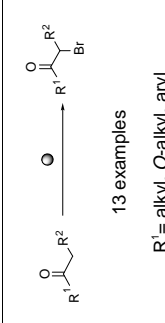
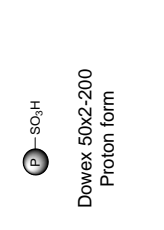
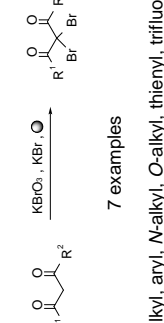
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (2.2 mmol g <sup>-1</sup> )	 1 example	Y:42-97	Some iodinated product was observed. Experimental section.	937	937
 (0.80-1.6 mmol g <sup>-1</sup> )	 9 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl	Y:62-86	General experimental.	242, 938	242
 (0.70-1.8 mmol g <sup>-1</sup> )	 9 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl X = Br, Cl	Y:60-85	The equivalent bromination reagent was more reactive than the chlorination reagent. General procedure.	242	242
 Nafion-H	 2 examples R <sup>1</sup> = alkyl, vinyl	Y:59-91	Experimental section.	806	
 (5.3-9.3 mmol g <sup>-1</sup> ) X = Br, Cl, I	 13 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl	Y:0-85	Spent polymer may be regenerated and recycled. Experimental section.	891	891

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Perbromide form (1.6 mmol g <sup>-1</sup> )	 5 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = alkyl	Y:55-78	It was not possible to obtain completely perbrominated polymer, however the presence of Br <sup>-</sup> on the polymer has no drawbacks in the bromination of ketones. General procedure.	939, 940	939
 Amberlyst A-26 Perbromide form (2.5 mmol g <sup>-1</sup> )	 7 examples R <sup>1</sup> = alkyl, allyl, aryl R <sup>2</sup> = H, alkyl	Y:65-97	Selective for most substituted position $\alpha$ to the carbonyl in the presence of AIBN. A variety of solvents were tolerated, including water. Aldehydes generally gave higher yields than ketones. A 10% decrease in reagent activity after three months storage at room temperature was observed. The resin could be regenerated. Experimental section.	919	919, 939
 Amberlyst A-26 Perbromide form	 1 example	Y:65	Experimental section.	941	939
 Amberlyst A-26 Perbromide form (1.0 mmol g <sup>-1</sup> )	 1 example	Y:78	Reaction carried out as part of a one-pot multi-step synthesis.	39	
 Amberlyst A-26 Perbromide form (3.6 mmol g <sup>-1</sup> )	 3 examples R <sup>1</sup> , R <sup>2</sup> = H, alkyl, aryl	Y:75-90	This reagent was a stable, odourless resin which could be stored at room temperature for long periods without appreciable loss of bromine. General procedure.	921	921
 Amberlyst A-26 Perbromide form (1.2 mmol g <sup>-1</sup> )	 3 examples R <sup>1</sup> = aryl	Y:69-80	This reagent was stable at room temperature for long periods. General procedure.	922	922

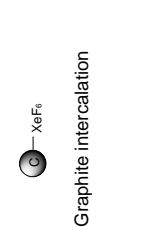
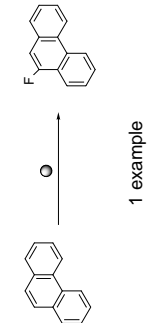
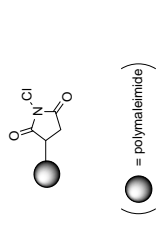
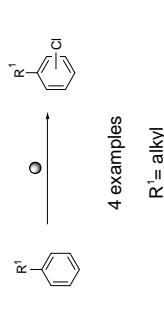
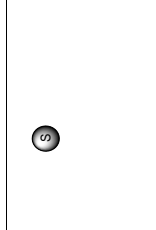
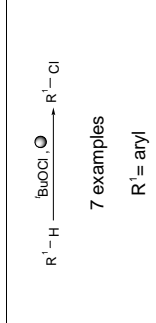
3.25  $\alpha$ -Halocarbonyls—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
	 <p>4 examples R<sup>1</sup> = alkyl, aryl R<sup>2</sup> = alkyl</p>	Y:80-100	The reagent may be regenerated without loss of activity. Experimental section.	886	886
	 <p>12 examples R<sup>1</sup> = aryl R<sup>2</sup> = H, alkyl R<sup>3</sup> = H, alkyl</p>	Y:70-100 P:87-95	Dibromination could be avoided by control of reaction temperature. Also see reference 942.	80, 81	886, 189, 190
	 <p>4 examples R<sup>1</sup> = aryl, aryl</p>	Y:42-85 P:85-90	One step of a multi-step synthesis.	57	886, 189, 190
	 <p>5 examples R<sup>1</sup> = aryl R<sup>2</sup> = H, alkyl</p>	Y:100	Ratio of mono- to di-bromo ketone may be controlled by reaction conditions.	943	886, 189, 190
	 <p>9 examples R<sup>1</sup> = alkyl, aryl, O-alkyl, vinyl R<sup>2</sup> = alkyl, ketone, ester</p>	Y:40-100	In cases of unsymmetric ketones, the more substituted bromide is generally favoured. General procedure.	227	227

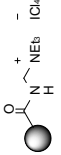
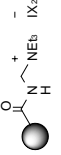
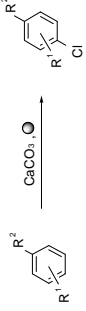
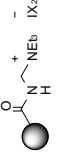
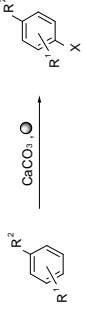
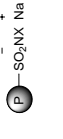


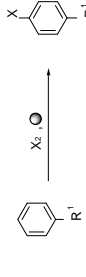


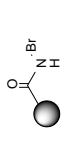
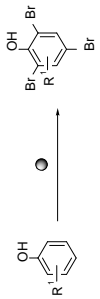
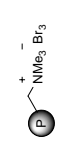
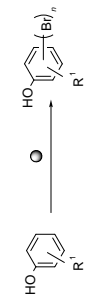
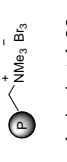
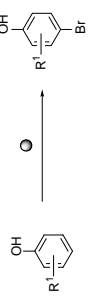
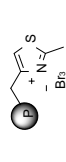
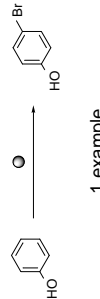
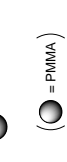
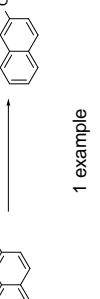
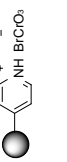
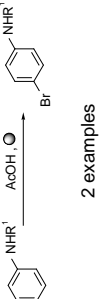
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (1.9 mmol g <sup>-1</sup> )	 13 examples R <sup>1</sup> = alkyl, O-alkyl, aryl R <sup>2</sup> = alkyl, ester	Y:15-100	Resin also used to brominate double bonds. Resin may be regenerated. Experimental section.	944	944
 Dowex 50X2-200 Proton form	 7 examples R <sup>1</sup> , R <sup>2</sup> = alkyl, aryl, N-alkyl, O-alkyl, thienyl, trifluoromethyl	Y:78-95	Full experimental section.	945	

### 3.26 Aryl halides

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Graphite intercalation	 1 example	Y:34	Caution in handling the reagent is recommended. General procedure.	936	936
 (= polymaleimide)	 4 examples R <sup>1</sup> = alkyl	Y:70-88 P:100	No alkyl chlorination was observed. Supported reagent was better than the solution phase analogue.	884	
 (= polymaleimide)	 7 examples R <sup>1</sup> = aryl	Y:70-100	Mixtures of isomers were generated. Very mild reaction conditions. The type of silica was important. Water slows reaction.	946	

3.26 Aryl halides—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
  (1.6 mmol g <sup>-1</sup> ) (= polyacrylamide)	 16 examples R <sup>1</sup> = H, alkyl, aryl, Cl, amine, nitro, O-alkyl R <sup>2</sup> = hydroxy, amine	Y:50-86	The reagent was selective for mono-iodination. General procedure.	947	947
 (1.4-1.8 mmol g <sup>-1</sup> ) X = Cl, Br (= polyacrylamide)	 22 examples R <sup>1</sup> = H, alkyl, aryl, Cl, amine, nitro, O-alkyl R <sup>2</sup> = hydroxy, amine	Y:50-90	The reagent was selective for mono-iodination. General procedure.	947	947
 (3.2-3.5 mmol g <sup>-1</sup> ) X = Cl, Br	 3 examples R <sup>1</sup> = hydroxy, amine	Y:30-90	Polymer was regenerated and reused without loss of activity. General procedure.	235	235
 Bentonitic clay	 3 examples X = Br, Cl R <sup>1</sup> = H, alkyl	Y:80-90	Experimental section.	948	

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (● = polyacrylamide) (5.2-5.7 mmol g <sup>-1</sup> )	 4 examples R <sup>1</sup> = H, hydroxy	Y:60-90	The reagent was non-corrosive, easily handled and could be stored indefinitely. Reagent was also used to oxidise alcohols to aldehydes and ketones and oxidise thiols to sulfides. Experimental section.	232	232
 (● = polyacrylamide) (5.2-5.7 mmol g <sup>-1</sup> )	 30 examples R <sup>1</sup> = alkyl, Br, Cl, ester, nitro, O-alkyl n = 1-3	Y:91-99	The reaction was carried out in a flow reactor. Reagent may be regenerated and reused. General procedure.	949	949
 Amberlyst A-26 Perbromide form (1.1 mmol g <sup>-1</sup> )	 5 examples R <sup>1</sup> = H, Me, O-alkyl, Cl	Y:60-90	The reaction was selective for <i>para</i> bromination over <i>ortho</i> . Only a trace of di-bromination was observed. General procedure.	950	
 (1.6 mmol g <sup>-1</sup> )	 1 example	Y:100	Good selectivity for mono-bromination. <i>Para:ortho</i> ratio = 10:1. General procedure.	227	227
 (● = PMMA) (1.2 mmol g <sup>-1</sup> )	 1 example	Y:80	The reagent was stable at room temperature. General procedures.	922	922
 (● = PVP) (2.7-2.9 mmol g <sup>-1</sup> )	 2 examples R <sup>1</sup> = H, acyl	Y:84-89	General procedure.	154	154

3.26 Aryl halides—continued

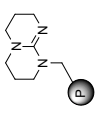
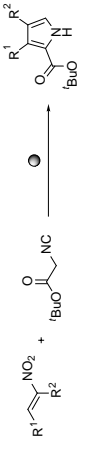
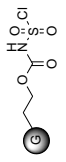
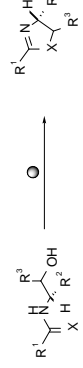
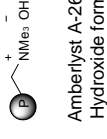
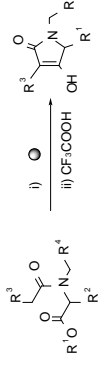

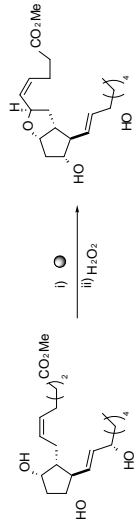
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 ( = PVP ) (1.4 mmolg <sup>-1</sup> )	 4 examples R <sup>1</sup> = alkyl	Y:72-87	A mixture of <i>ortho</i> and <i>para</i> products was formed.	951	951
 ( = PMMA ) (1.2 mmolg <sup>-1</sup> )	 1 example	Y:74	The reagent was stable at room temperature. General procedures.	922	922
	 9 examples R <sup>1</sup> = alkyl, aryl, het, O-alkyl	Y:56-99	Reagent may be regenerated. A mixture of mono- and di- iodo compounds was formed.	73	73
	 9 examples R <sup>1</sup> = aryl	Y:43-94	Polyiodinated products were also formed, especially at high temperatures and with electron rich substrates. Full experimental section.	74	74
 ( = PVP ) (2.2 mmolg <sup>-1</sup> )	 4 examples R <sup>1</sup> , R <sup>2</sup> = H, hydroxy, O-alkyl	Y:68-85	Experimental section.	907	907


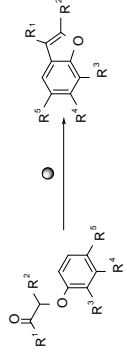

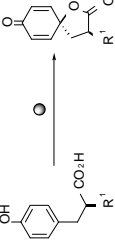
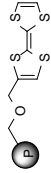
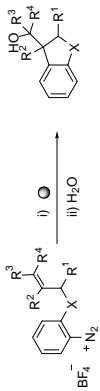

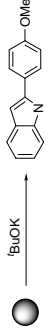
### 3.27 Heterocycles

#### 3.27.1 Heterocycles (5 Ring or smaller)

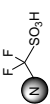
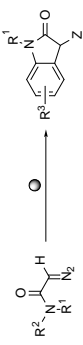
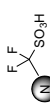
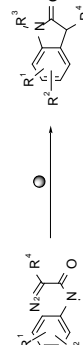

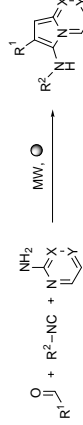
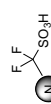
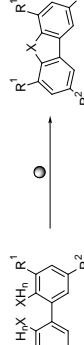
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Carbonate form (3.8 mmol g <sup>-1</sup> )	 1 example	Y:69	Ratio <b>a:b</b> = 21:48 Full experimental section.	532	
 Amberlyst A-26 Carbonate form (3.8 mmol g <sup>-1</sup> )	 1 example	Y:93	Ratio <b>a:b</b> = 63:30 Full experimental section.	533	
 Amberlyst A-26 Carbonate form (3.8 mmol g <sup>-1</sup> )	 1 example	Y:70	Full experimental section.	624	
 Amberlyst A-15 Proton form (4.9 mmol g <sup>-1</sup> )	 1 example	Y:99	This reaction was easily adapted to continuous operation. Experimental section.	859	
 Amberlyst A-15 Proton form (4.9 mmol g <sup>-1</sup> )	 4 examples R <sup>1</sup> = alkyl, aryl, benzyl	Y:90-99	Reactions were carried out under solvent free conditions. General procedure.	682	

3.27.1 Heterocycles (5 Ring or smaller)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 PS-TBD (2.2 mmol g <sup>-1</sup> )	 8 examples R <sup>1</sup> = aryl R <sup>2</sup> = alkyl	Y:83-100 P:>95	This 1,3-dipolar cycloaddition is one step in a multi-step synthesis.	70	
	 7 examples R <sup>1</sup> , R <sup>2</sup> , R <sup>3</sup> = amino acid X = O, S	Y:76-98	The resin gave better results than its solution phase counterpart. Less than 2% racemisation was observed.  General procedure.	952	952
 Amberlyst A-26 Hydroxide form	 10 examples R <sup>1</sup> , R <sup>2</sup> = H, alkyl, benzyl R <sup>3</sup> = aryl R <sup>4</sup> = aryl, nitrile, phosphonate, S-alkyl	Y:70-87 P:71-94	After Dieckman condensation, the products remain bound to the resin, allowing a catch and release purification upon treatment with trifluoroacetic acid.  Experimental section.	953	
	 1 example	Y:94	A 2:1 ratio of epimers was observed.	330	330

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-15 Proton form	 <p>25 examples</p> <p> <math>R^1 = \text{aryl}</math>  <math>R^2 = \text{H, alkyl}</math>  <math>R^3 = \text{H, alkyl, aryl, Br, CF}_3</math>  <math>R^4 = \text{H, aryl}</math>  <math>R^5 = \text{H, O-alkyl, nitro}</math> </p>	Y:57-100 P:75-95	This is the final step in the synthesis of a library generated using polymer-supported reagents.	80	
 (3.5 mmol g <sup>-1</sup> )	 <p>5 examples</p> <p> <math>R^1 = \text{H, NHAc, NHBoc, NHFmoc, NHZ}</math> </p>	Y:75-96 P:90->95	The polymer may be regenerated and reused without loss of activity. General procedure.	72	72
	 <p>5 examples</p> <p> <math>R^1 = \text{H, alkyl}</math>  <math>R^2 = \text{H, allyl, alkyl}</math>  <math>R^3, R^4 = \text{H, alkyl}</math>  <math>X = \text{NMS, O}</math> </p>	Y:25-42	Spent polymer may be regenerated and reused with some loss of activity.	954	954
 + PPh <sub>3</sub> Br <sup>-</sup>	 <p>1 example</p>			463	463

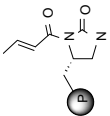
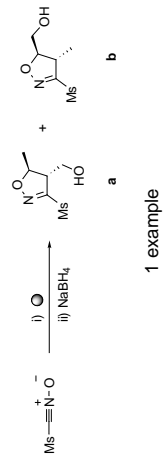

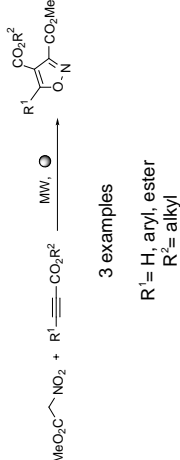

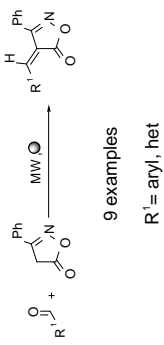
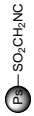
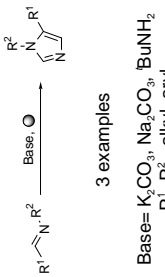

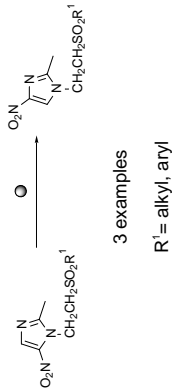
3.27.1 Heterocycles (5 Ring or smaller)—continued


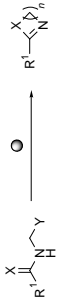

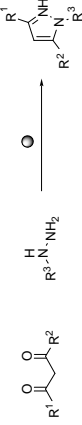
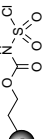
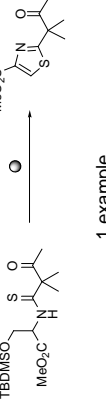
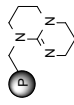
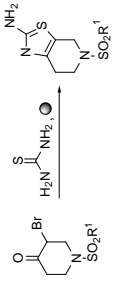
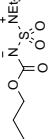
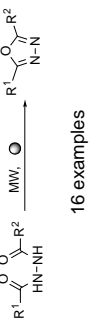
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Nafion-H	 9 examples $R^1 = \text{alkyl, benzyl}$ $R^2 = \text{aryl}$ $Z = \text{H, acyl}$	Y:89-97	Yields of 2-indolinones were greater than those obtained with rhodium carboxylate catalysis even though higher reaction temperatures were required to initiate decomposition. Full experimental section.	955	
 Nafion-H	 11 examples $R^1, R^2 = \text{H, alkyl, O-alkyl}$ $R^3 = \text{alkyl, benzyl}$ $R^4 = \text{H, alkyl}$	Y:28-79	Some examples gave $\beta$ -lactams as the side products. General procedure.	956	
 Montmorillonite K 10	 14 examples $R^1 = \text{alkyl, aryl, vinyl}$ $R^2 = \text{alkyl, benzyl}$ $X, Y = \text{CH, N}$	Y:56-88	Reactions were carried out in the absence of solvent. Yields were generally in excess of 80%. General procedure.	957	
 Nafion-H	 5 examples $R^1, R^2 = \text{H, alkyl}$ $X = \text{N, O}$	Y:0-96	Full experimental section.	958, 959	



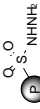
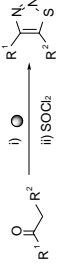

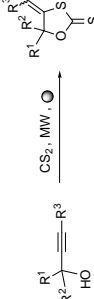
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Kaolinitic clay	$R^1-CN + H_2N-CH(OH)-R^2 \longrightarrow \text{Resin-}R^1-N^+(Me)_3-CH(OH)-R^2$ 13 examples $R^1 = \text{alkyl, aryl, het}$	Y:56-96	One example with L-valine as the $\beta$ -amino alcohol, gave the oxazoline with no loss of optical purity. The clay may be recycled. General procedure.	960	
 Ambersep-900 Hydroxide form (0.90 mmolg <sup>-1</sup> )	$R^1-O-C(=O)-R^2 + TsO-CH_2-NC \longrightarrow \text{Resin-}R^1-O-C(=O)-R^2$ 13 examples $R^1 = \text{aryl, het}$	Y:54-85 P:57-94	Sulfonic acid byproduct remains bound to the ion-exchange resin. General procedure.	961	
 $R^1 = H, \text{alkyl, aryl, nitrile, nitro}$ $R^2 = H, F, Br$ $R^3 = H, \text{alkyl, nitro}$	$R^1-CHO + Bu_4NOH \cdot O \longrightarrow \text{Resin-}R^1-CH(OH)-R^2$ 10 examples $R^1 = H, \text{alkyl, aryl, nitrile, nitro}$ $R^2 = H, F, Br$ $R^3 = H, \text{alkyl, nitro}$	Y:25-50	Solid version of TosMIC. Tentagel support also tested but proved unstable to basic conditions.	962	962
 $R^1 = \text{aryl}$ $R^2 = \text{alkyl}$	$Ph-N^+(R^1)-O-C(=O)-R^2 + OR^3 \xrightarrow{AlMe_3 \cdot O} \text{Resin-}Ph-N^+(R^1)-O-C(=O)-R^2$ 5 examples $R^1 = \text{aryl}$ $R^2 = \text{alkyl}$	Y:72-97 ee:93-99	Enantioselectivity was almost identical to that obtained using an equivalent monomeric catalyst. Catalyst may be reused without loss of activity. General procedure.	963	
 (0.89-1.0 mmolg <sup>-1</sup> )	$Ph-N^+(R^1)-O-C(=O)-R^2 \xrightarrow{i) O, ii) NaBH_4} \text{Resin-}Ph-N^+(R^1)-O-C(OH)-R^2$ 1 example	Y:20-43 ee:81-89 (a)	Wang and Merrifield resins were tried as supports. Spent resin may be regenerated and reused, with a small loss of ee. The ratio of a:b was between 56:44 and 30:70.	964	964

3.27.1 Heterocycles (5 Ring or smaller)—continued


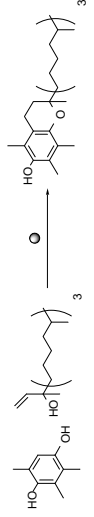

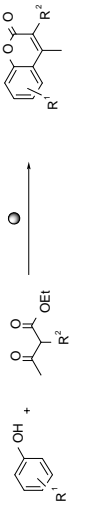
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (0.89-1.0 mmol g <sup>-1</sup> )	 1 example	Y:51-62 ee:33-60 (a)	Wang and Merrifield resins were tried as supports. Spent reagent may be regenerated and reused, with a small loss of ee. The ratio of <b>a:b</b> = 7:3	964	964
	 3 examples R <sup>1</sup> = H, aryl, ester R <sup>2</sup> = alkyl	Y:65	The other regioisomer was also formed.	965	
	 9 examples R <sup>1</sup> = aryl, het	Y:71-92	Experimental section.	966	
 (0.60 mmol g <sup>-1</sup> )	 3 examples Base = K <sub>2</sub> CO <sub>3</sub> , Na <sub>2</sub> CO <sub>3</sub> , BuNH <sub>2</sub> R <sup>1</sup> , R <sup>2</sup> = alkyl, aryl	Y:44-66	The spent polymer may be regenerated in a two step procedure. The polymer was soluble under the reaction conditions. Experimental section.	967	967
	 3 examples R <sup>1</sup> = alkyl, aryl	Y:93-95	General procedure.	968	968


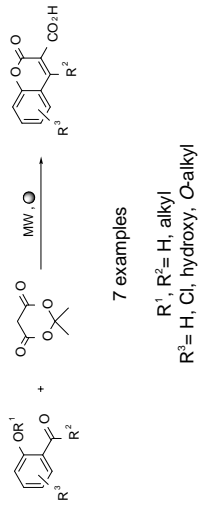

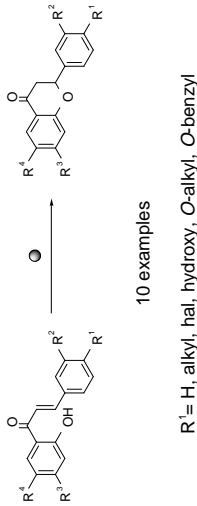
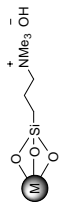
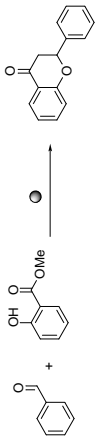

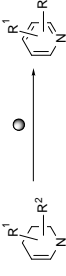

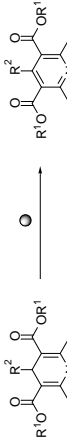
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (40% KF)	 10 examples R <sup>1</sup> = alkyl, aryl, fluoroalkyl X = O, S Y = Cl, Br r = 2,3	Y:76-93	Full experimental section.	969	651
	 7 examples R <sup>1</sup> , R <sup>2</sup> = alkyl, aryl R <sup>3</sup> = H, alkyl, aryl	Y:90-99	Reactions were carried out under solvent free conditions. The other regioisomer was also formed. General procedure.	682	
 (1.0 mmol g <sup>-1</sup> )	 1 example	Y:64	The reagent was stable under wet and oxidative conditions. Experimental section.	970	952
 P-TBD	 4 examples R <sup>1</sup> = aryl	Y:47-80 P:95	This reaction was used within a multi-step library synthesis.	81	
 (2.7 mmol g <sup>-1</sup> )	 16 examples R <sup>1</sup> = α-amino acid, aniline, aryl, furyl, pyridyl, thiophenyl R <sup>2</sup> = alkyl, aniline, aryl	Y:70-98 P:89->99	Supported Burgess reagent. General procedure.	971	952

### 3.27.1 Heterocycles (5 Ring or smaller)—continued

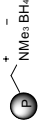
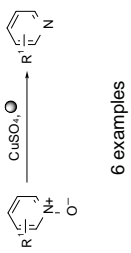

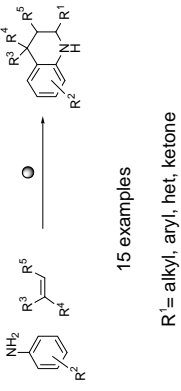
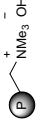
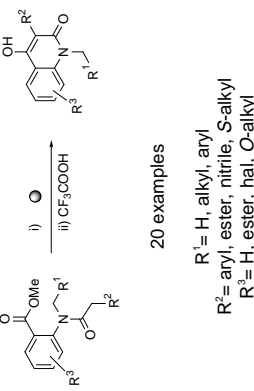

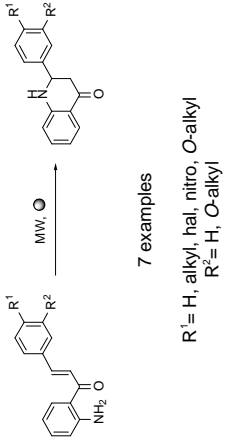
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (2.4 mmol g <sup>-1</sup> )	 13 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = alkyl, aryl, vinyl	Y:48-100 P:71-100	Resin is used in a "catch and release" protocol. Parallel synthesis of ketones used as starting material also described. General procedure.	69	
	 5 examples R <sup>1</sup> , R <sup>3</sup> = H, alkyl R <sup>2</sup> = alkyl	Y:57-94	Experimental section.	972	

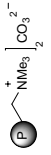
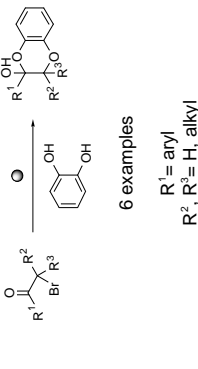
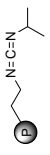
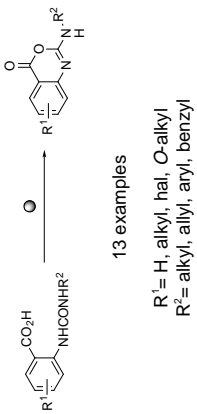
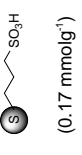
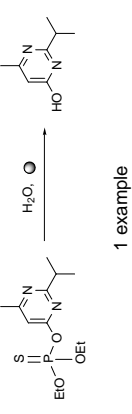

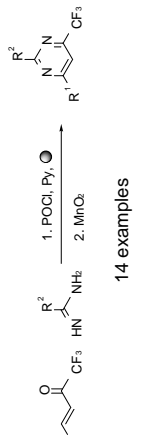

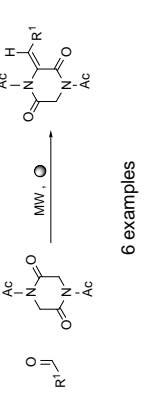
### 3.27.2 Heterocycles (6 Ring or bigger)

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Nafion-H NIR-50	 1 example	C:95 Y:92	Nafion-H better than Dowex 50WX8 or Amberlite 200. Experimental section.	973	
 Amberlite IR-120 Proton form	 12 examples R <sup>1</sup> = H, alkyl, hydroxy R <sup>2</sup> = H, alkyl	Y:9-80	Synthesis of coumarins via the von Pechmann reaction requires only a catalytic quantity of acid. General procedure.	974	

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Envirocat EPZG	 <p>7 examples  <math>R^1, R^2 = \text{H, alkyl}</math>  <math>R^3 = \text{H, Cl, hydroxy, O-alkyl}</math></p>	Y:64-97	Other clay catalysts were investigated. General procedure.	975	
 (50%wt KF)	 <p>10 examples  <math>R^1 = \text{H, alkyl, hal, hydroxy, O-alkyl, O-benzyl}</math>  <math>R^2 = \text{H, O-alkyl}</math>  <math>R^3 = \text{H, hydroxy, O-alkyl}</math>  <math>R^4 = \text{H, aryl, prenyl}</math></p>	Y:42-85	Full experimental section.	976	
 MCM-41 (0.90-1.2 mmol g <sup>-1</sup> )	 <p>1 example</p>	C:65	The reagent was able to catalyse the successive aldol condensation and intramolecular Michael addition in solvent free conditions with a selectivity of 78%. General procedure. Also see reference 977.	978	
 Fe(NO <sub>3</sub> ) <sub>3</sub>	 <p>7 examples  <math>R^1 = \text{alkyl}</math>  <math>R^2 = \text{H, alkyl, aryl, hal}</math></p>	Y:73-98	General procedure.	215	215
 Fe(NO <sub>3</sub> ) <sub>3</sub> (0.50 mmol g <sup>-1</sup> )	 <p>7 examples  <math>R^1 = \text{alkyl}</math>  <math>R^2 = \text{H, alkyl, aryl}</math></p>	Y:73-98	Oxidation of Hantzsch 1,4-dihydropyridines carried out in refluxing chloroform. CrO <sub>3</sub> supported on silica has also been reported. 979.	215	215

3.27.2 Heterocycles (6 Ring or bigger)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlite IRA-400 Borohydride form (3.0 mmol g <sup>-1</sup> )	 6 examples R <sup>1</sup> = H, alkyl, O-alkyl, aryl	Y:61-94	Many functional groups tolerated. Must be stored under nitrogen and kept cool.	593	593
 (0.44 mmol g <sup>-1</sup> )	 15 examples R <sup>1</sup> = alkyl, aryl, het, ketone R <sup>2</sup> = H, aryl, hal, O-alkyl R <sup>3</sup> = H, alkyl, S-alkyl R <sup>4</sup> = aryl, O-alkyl, vinyl R <sup>5</sup> = H, alkyl, benzyl	Y:65-100	Polymer is partially soluble under reaction conditions and may be precipitated using hexane. General procedure.	980	980
 Amberlyst A-26 Hydroxide form	 20 examples R <sup>1</sup> = H, alkyl, aryl R <sup>2</sup> = aryl, ester, nitrile, S-alkyl R <sup>3</sup> = H, ester, hal, O-alkyl	Y:72-97 P:79-99	Following Claisen condensation, products remain bound to the resin, allowing a catch and release purification upon treatment with CF <sub>3</sub> COOH.	981	
 Montmorillonite K 10	 7 examples R <sup>1</sup> = H, alkyl, hal, nitro, O-alkyl R <sup>2</sup> = H, O-alkyl	Y:70-80	Reactions are carried out under solvent free conditions. General procedure.	982	

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
	 <p>6 examples R<sup>1</sup> = aryl R<sup>2</sup>, R<sup>3</sup> = H, alkyl</p>	Y:90-98 P:93-95	Excess catechol removed by amine scavenger resin, which also removes any unreacted bromide.	81	
	 <p>13 examples R<sup>1</sup> = H, alkyl, hal, O-alkyl R<sup>2</sup> = alkyl, allyl, aryl, benzyl</p>	Y:73-94 P:80-97		983	530
	 <p>1 example</p>	C:>99	Colloidal catalyst compared with Nafion, Amberlyst A-15, HCl and Dowex 50W-X4. Kinetic study. Conversion of trityl fluoride to trityl alcohol was also carried out. Experimental section.	984	984
	 <p>14 examples R<sup>1</sup>, R<sup>2</sup> = alkyl, aryl</p>	Y:9-86	One-pot procedure. General procedures.	985	985
	 <p>6 examples R<sup>1</sup> = aryl</p>	Y:70-98	Can form double addition products. General procedure.	986	

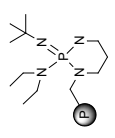
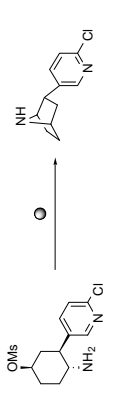
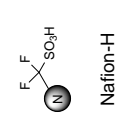

3.27.2 Heterocycles (6 Ring or bigger)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Bromide form	 22 examples R <sup>1</sup> = ester R <sup>2</sup> = aryl, ester R <sup>3</sup> = alkyl, het	Y:83-96	Experimental section.	987	
	 1 example R <sup>1</sup> = aryl	Y:80 P:>97	One step of a multi-step library synthesis. General procedure.	57	
	 6 examples R <sup>1</sup> = aryl R <sup>2</sup> , R <sup>3</sup> = H, alkyl R <sup>4</sup> = H, CO <sub>2</sub> Me	Y:90-100 P:85-98	One step of a multi-step library synthesis.	57	
	 1 example	Y:76 P:>98	One step of a multi-step library synthesis. General procedure.	57	

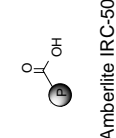
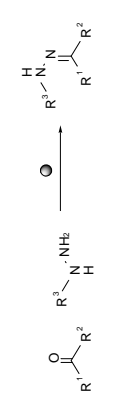
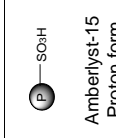
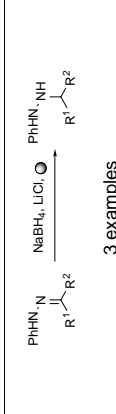


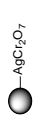

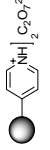

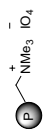
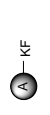

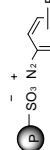
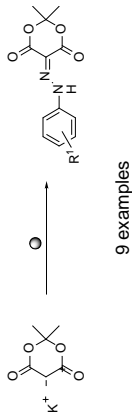
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
	<p>5 examples  <math>R^1 = \text{H, amide}</math>  <math>R^2 = \text{H, alkyl}</math>  <math>R^3 = \text{alkyl}</math>  <math>X = \text{O, S}</math></p>	Y:17-71	Full experimental section.	988	988
	<p>12 examples  <math>R^1, R^2 = \text{H, alkyl}</math>  <math>R^3, R^4 = \text{H, alkyl, aryl}</math>  <math>R^5 = \text{alkyl}</math></p>	Y:29-99	Yields generally >75%. Products are virtually free from tin. Quinone isomers also shown to undergo the same transformation. General procedure.	989	428, 388
	<p>1 example  <math>R^1 = \text{benzyl}</math></p>	Y:97	Resin ylide was formed and isolated immediately prior to use. Reagent can be regenerated. Full experimental section.	471	471
	<p>1 example</p>	Y:70	One step of a multi-step solid-supported reagent synthesis. Trifluoroethanol as a solvent is essential for this reaction.	75	72
	<p>1 example</p>	Y:100	One step of a multi-step solid-supported reagent synthesis.	75	623

### 3.27.2 Heterocycles (6 Ring or bigger)—continued

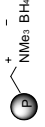
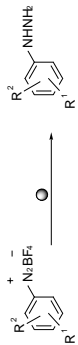
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 PS-BEMP	 1 example	P:>85	The reaction mixture is purified using an amine scavenger resin. General procedure.	77	
 Nafion-H	 2 examples R' = H, alkyl	Y:58-79	Full experimental section.	990	

### 3.28 Hydrazines and hydrazones

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlite IRC-50	 6 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl, aryl R <sup>3</sup> = acyl		The hydrazone was used as a protecting group in a three-step process. The least sterically hindered carbonyl group was selectively protected. Experimental section.	991, 992	
 Amberlyst-15 Proton form	 3 examples R <sup>1</sup> , R <sup>2</sup> = alkyl, aryl	Y:80-85	The analogous reduction of oximes to amines was also successful.	562	

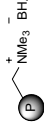
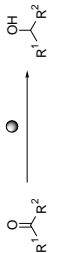
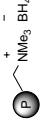
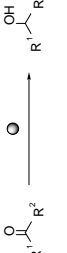
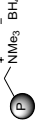

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
  (1.2 mmol g <sup>-1</sup> )	$R^1-NH_2 \xrightarrow{\text{O}} R^1-N=N-R^1$ 4 examples R <sup>1</sup> = alkyl, aryl	Y:0-30	The reagent was non-acidic and therefore compatible with acid sensitive groups. General procedure.	192	192
  (1.9-2.0 mmol g <sup>-1</sup> )	$ArNH_2 \xrightarrow{\text{O}} Ar-N=N-Ar'$ 2 examples R <sup>1</sup> = aryl	Y:25-35	The reagent could also oxidise alcohols, thiols and oximes. Experimental section.	311	311
 Amberlyst A-26 Periodate form (2.5 mmol g <sup>-1</sup> )	$R^1-C(=O)-NH_2 \xrightarrow{\text{O}} R^1-C(=O)-N=N-R^1$ 11 examples R <sup>1</sup> = alkyl, aryl, benzyl	Y:90-95	General procedure.	993	993
	 4 examples R <sup>1</sup> = alkyl, allyl, benzyl Y = O, S n = 0, 1 X = Br, I	Y:31-62	Reaction is carried out without solvent. General procedure.	994	994
 Amberlite IRA 120 Aryldiazonium form (2.0 mmol g <sup>-1</sup> )	 9 examples R <sup>1</sup> = Br, Cl, nitro, O-alkyl	Y:82-96	Diazonium salts were prepared in solution and then captured onto resin. General procedure.	995	995

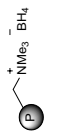
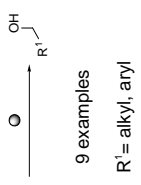
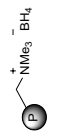
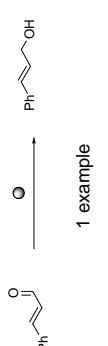
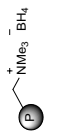
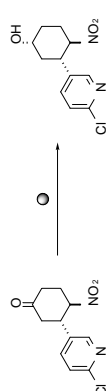
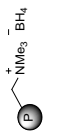
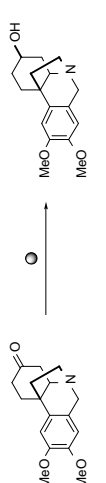
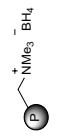
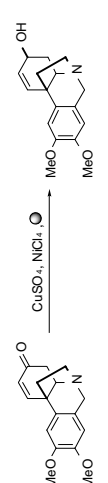
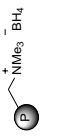
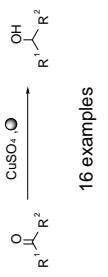
### 3.28 Hydrazines and hydrazones—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Tulsion A-27 Borohydride form (3.0 mmol g <sup>-1</sup> )	 9 examples R <sup>1</sup> = Br, Cl, NO <sub>2</sub> R <sup>2</sup> = H, Br, F	Y:60-91	General procedure.	996	996







### 3.29 Hydroxy

#### 3.29.1 Hydroxy (From aldehydes/ketones – delivery of H from B or Al species)

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlite IRA-400 Borohydride form Amberlite IRA-401S CP Borohydride form	 2 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl		The first example of borohydride exchange resin.	575	575
 Amberlite IRA-400 Borohydride form (2.5 mmol g <sup>-1</sup> )	 7 examples R <sup>1</sup> = allyl, aryl R <sup>2</sup> = H, alkyl, aryl	Y:85-99	Aldehydes are reduced faster than ketones using this reagent. General procedure.	997, 998	997, 998
 Amberlite IRA-400 Borohydride form (2.5 mmol g <sup>-1</sup> )	 2 examples R <sup>1</sup> , R <sup>2</sup> = aryl	Y:100	Polymer-supported borohydride displayed similar selectivity to sodium borohydride. The selectivity obtained was approximately 70:30 (threo:erythro). Also see reference 999.	1000	1001

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (0.50 mmol g <sup>-1</sup> )	 9 examples R <sup>1</sup> = alkyl, aryl	Y:93-99	Selectivity of the reduction of aldehydes over ketones was >12:1. General procedure.	1002	1002
 (0.50-2.0 mmol g <sup>-1</sup> )	 1 example		Several reagents with differing degrees of divinylbenzene cross-linking were tested. Kinetic study. General procedure.	1003	
 (2.5 mmol g <sup>-1</sup> )	 1 example	Y:89	One step of a multi-step natural product synthesis. Reaction was selective >7:1 for the all equatorial isomer.	77	575
 (2.5 mmol g <sup>-1</sup> )	 1 example	Y:98	One step of a multi-step solid-supported reagent synthesis. Reduction of the ketone was diastereoselective.	75	575
 (2.5 mmol g <sup>-1</sup> )	 1 example	Y:80	One step of a multi-step solid-supported reagent synthesis. Diastereoselective reduction of the ketone in the presence of a double bond. For further examples see reference 577. Lithium chloride was also used as a co-catalyst. <sup>1004</sup>	75	387, 575
 (3.0 mmol g <sup>-1</sup> )	 16 examples R <sup>1</sup> = alkyl, aryl, vinyl R <sup>2</sup> = H, alkyl	Y:0-100	Hindered ketones were not reduced. Vinyl compounds were reduced to the saturated alcohol. Carbonyl functionality was reduced over alkenes. Experimental section.	387	387

3.29.1 Hydroxy (From aldehydes/ketones – delivery of H from B or Al species)—continued


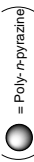


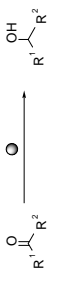

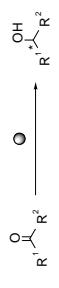
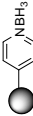

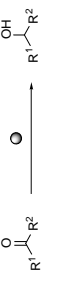


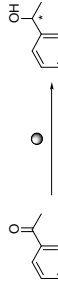

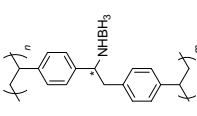

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 $\text{R}^1\text{-C(=O)-R}^2 \longrightarrow \text{R}^1\text{-CH(OH)-R}^2$ 8 examples $\text{R}^1 = \text{alkyl, allyl, aryl}$ $\text{R}^2 = \text{H, alkyl, aryl, ester}$	Y:82-90 P:95	Reagent was unstable to prolonged storage. General procedure. Montmorillonite has also been used as a support. <sup>1006</sup>	1006	1006	
 $\text{R}^1\text{-C(=O)-R}^2 \longrightarrow \text{R}^1\text{-CH(OH)-R}^2$ 22 examples $\text{R}^1 = \text{alkyl, aryl, het}$ $\text{R}^2 = \text{H, alkyl}$	Y:63-100	The material was used in a column format. General procedure.	1007	1007	
 $\text{R}^1\text{-C(=O)-R}^2 \xrightarrow{\text{MW, } \bullet} \text{R}^1\text{-C(OH)(R}^2\text{)-Ar}$ 8 examples $\text{R}^1 = \text{H, alkyl, chloro, nitro}$ $\text{R}^2 = \text{H, alkyl, aryl}$	Y:62-93	Micromole scale reactions have been carried out using a Celite-supported borohydride system. <sup>1007</sup>	1008	1008	
 $\text{R}^1\text{-C(=O)-R}^2 \xrightarrow{\text{NaBH}_4, \bullet} \text{R}^1\text{-CH(OH)-R}^2$ 7 examples $\text{R}^1 = \text{aryl}$ $\text{R}^2 = \text{alkyl}$	Y:80-95 ee:31-57	The asymmetric induction obtained was poor. General procedure.	1009 1010	1011	
 $\text{R}^1\text{-C(=O)-R}^2 \longrightarrow \text{R}^1\text{-CH(OH)-R}^2$ 1 example $\text{R}^1 = \text{alkyl}$	Y:52-72 ee:21-75	Polymers with different pore sizes were compared. High yields gave lower enantiomeric excesses. The best example gave 71% yield, 56% ee. Other polymer examples are given in reference 1012. General procedure.	1013, 1012	1013, 1012	
 $\text{R}^1\text{-C(=O)-R}^2 \longrightarrow \text{R}^1\text{-CH(OH)-R}^2$ 1 example $\text{R}^1 = \text{alkyl}$	Y:63-95 ee:21-52	Polymers with different pore sizes were compared. High yields gave lower enantiomeric excesses. The best overall example gave 80% yield, 48% ee. General procedure.	1013	1013	

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 $\text{PPh}_3 \text{ BH}_4$ (1.7 mmol g <sup>-1</sup> )	 5 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl, aryl, Cl	Y:16-78	Esters were resistant to reduction with this reagent. Experimental section.	1014	1014
 (2.5 mmol g <sup>-1</sup> ) R <sup>1</sup> = <i>endo</i> -borneol and ( <i>S</i> )-2-methylbutan-1-ol	 1 example	C:100	Kinetic study.	435	435
 (2.5 mmol g <sup>-1</sup> ) R <sup>1</sup> = <i>endo</i> -borneol and ( <i>S</i> )-2-methylbutan-1-ol	 10 examples R <sup>2</sup> , R <sup>3</sup> = H, alkyl, benzyl, O-alkyl	C:100 ee:20-40	Kinetic study. Experimental section. Also see reference 1015.	435	435
 R <sup>1</sup> = H, Me (0.48-1.6 mmol g <sup>-1</sup> )	 4 examples R <sup>1</sup> = alkyl, aryl	Y:88-95	The resin catalysts were more active than their monomer counterparts. The activity of the resin increased upon recycling. General procedure.	1016	1016
 (0.40 mmol g <sup>-1</sup> )	 1 example	Y:93	Other catalysts were described but the example given was used on a preparative scale. The catalyst could be recycled and was soluble on heating but precipitated when cooled. Full experimental section.	902	902

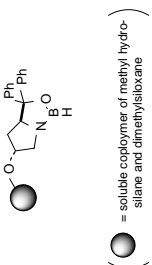
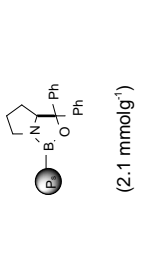
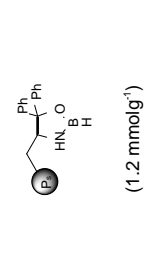
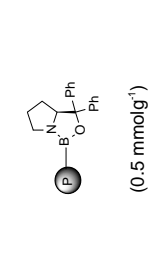
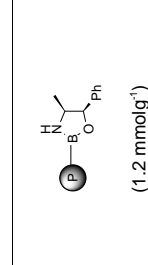
3.29.1 Hydroxy (From aldehydes/ketones – delivery of H from B or Al species)—continued

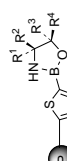

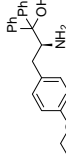

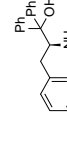


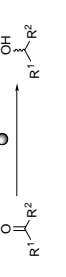
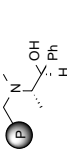
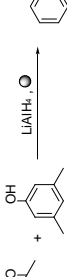
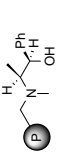
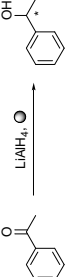
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlite IRA-120 Copper(II) form	$\text{R}^1\text{C}(=\text{O})\text{R}^2 \xrightarrow{\text{NaBH}_4, \bullet} \text{R}^1\text{CH}(\text{OH})\text{R}^2$ <p>8 examples R<sup>1</sup>= alkyl R<sup>2</sup>= alkyl, aryl</p>	Y:52-98	General procedure.	1017	1017
 Amberlyst-15 Proton form	$\text{R}^1\text{C}(=\text{O})\text{R}^2 \xrightarrow{\text{NaBH}_4, \bullet} \text{R}^1\text{CH}(\text{OH})\text{R}^2$ <p>1 example</p>	Y:96	Three polymers were studied with the best example shown.	542	542
 Amberlyst-15 Proton form	$\text{R}^1\text{C}(=\text{O})\text{R}^2 \xrightarrow{\text{NaBH}_4, \bullet} \text{R}^1\text{CH}(\text{OH})\text{R}^2$ <p>9 examples R<sup>1</sup>, R<sup>2</sup>= alkyl, aryl</p>	Y:80-98	The reagent was used in aprotic solvents except where <i>in situ</i> product cyclisation was desired. General procedure.	1018	
 Amberlyst A-26 Cyanoborohydride form (3.3 mmol g <sup>-1</sup> )	<p>1 example</p>	Y:70	The double bond of $\alpha$ -ionone was unaffected.	436	436
 (3.0 mmol g <sup>-1</sup> )	$\text{R}^1\text{C}(=\text{O})\text{H} \xrightarrow{\bullet} \text{R}^1\text{CH}(\text{OH})$ <p>15 examples R<sup>1</sup>= alkyl, aryl</p>	Y:65-95	The reduction of aldehydes was totally selective in the presence of ketones, which were unreactive to this procedure. The reagent could be recycled and stored at room temperature for a number of months. Experimental section.	805	805
 (5.4 mmol g <sup>-1</sup> )	$\text{R}^1\text{C}(=\text{O})\text{R}^2 \xrightarrow{\bullet} \text{R}^1\text{CH}(\text{OH})\text{R}^2$ <p>8 examples R<sup>1</sup>= alkyl, aryl, vinyl R<sup>2</sup>= H, alkyl</p>	Y:80-96	The reagent could be regenerated and stored for a number of months.	1019	805



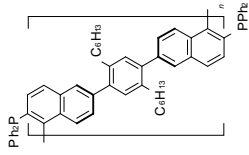

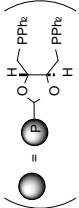
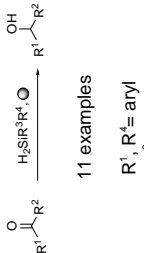
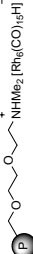
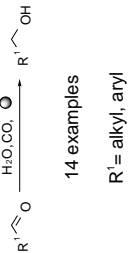
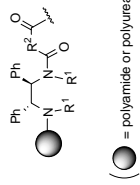

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
  ( = Poly-pyrazine)	 19 examples R <sup>1</sup> = alkyl, aryl, vinyl R <sup>2</sup> = H, alkyl, hal	Y:73-95	General procedure.	546	546
	 13 examples R <sup>1</sup> = aryl, vinyl R <sup>2</sup> = H, alkyl	Y:50-88	Reduction of $\alpha,\beta$ -unsaturated carbonyls yielded the unsaturated alcohol. Nitro groups were not reduced. General procedure.	1020	1020
 (1.4 mmol g <sup>-1</sup> )	 7 examples R <sup>1</sup> = alkyl R <sup>2</sup> = alkyl, aryl	Y:85-96 de:99	Two resins were investigated. The best example is given. Selectivity was for the most stable alcohol. The polymer could be recycled. Experimental section.	1021	1021
  (2.7-7.2 mmol g <sup>-1</sup> )	 10 examples R <sup>1</sup> = alkyl, aryl, het R <sup>2</sup> = alkyl, aryl	Y:4-100	Reactions were carried out in acidic media. The reagent was chemoselective for aldehydes in the presence of carboxylic acids and esters. General procedure. Also see reference 1022.	1023	1023
  ( = Polyproline or polysaccharide)	 1 example  1 example	Y:75-100 ee:0-5	Experimental section.	1024	1024
	 1 example	Y:50 ee:9	The polymeric reagent was more stable than the monomer and could be stored for several weeks without loss of activity. Experimental section.	1025	1025

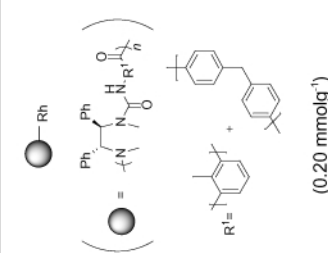
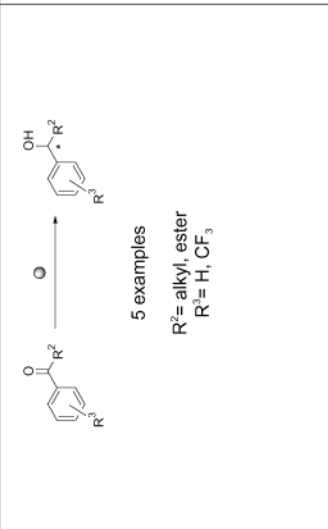
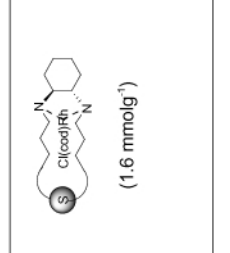
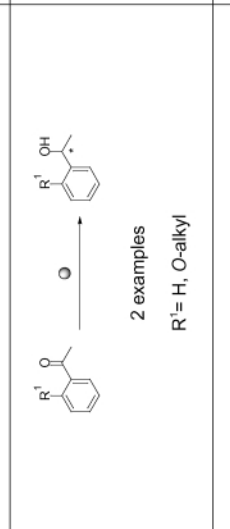
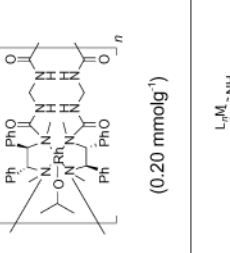
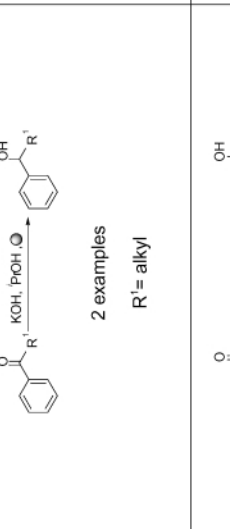
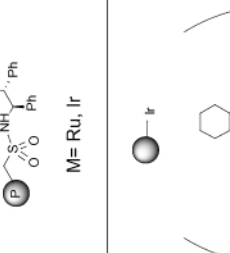
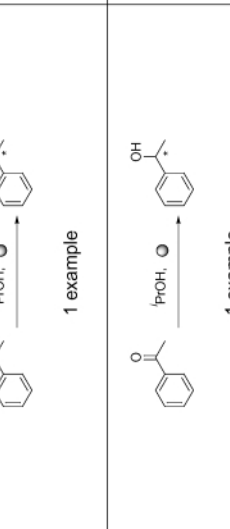
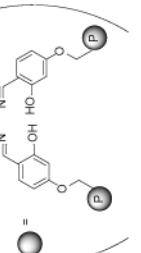

3.29.1 Hydroxy (From aldehydes/ketones – delivery of H from B or Al species)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>( = soluble copolymer of methyl hydro-silane and dimethylsiloxane )</p>	$\text{R}^1\text{C}(=\text{O})\text{R}^2 \xrightarrow{\text{BH}_3 \cdot \text{O}} \text{R}^1\text{C}(\text{OH})\text{R}^2$ <p>3 examples R<sup>1</sup> = aryl R<sup>2</sup> = alkyl</p>	Y:83-88 ee:89-97	Both R and S enantiomers were investigated. The catalyst was isolated after reaction by nano-filtration. General procedure. Also see reference 1025.	1026	1026
 <p>(2.1 mmol g<sup>-1</sup>)</p>	$\text{R}^1\text{C}(=\text{O})\text{R}^2 \xrightarrow{\text{BH}_3 \cdot \text{SMe}_2 \cdot \text{O}} \text{R}^1\text{C}(\text{OH})\text{R}^2$ <p>2 examples R<sup>1</sup> = aryl R<sup>2</sup> = alkyl</p>	C:95-99 ee:90-99	Kinetic study. All reactions gave the R-enantiomer product. The reagent was a soluble polymer contained within a nanofiltration membrane. General procedure.	1027	
 <p>(1.2 mmol g<sup>-1</sup>)</p>	$\text{R}^1\text{C}(=\text{O})\text{R}^2 \xrightarrow{\text{BH}_3 \cdot \text{SMe}_2 \cdot \text{O}} \text{R}^1\text{C}(\text{OH})\text{R}^2$ <p>2 examples R<sup>1</sup> = aryl R<sup>2</sup> = alkyl</p>	C:95-99 ee:84-94	Kinetic study. All reactions gave the R-enantiomer product. The reagent was a soluble polymer contained within a nanofiltration membrane. Also see reference 1028. General procedure.	1027	
 <p>(0.5 mmol g<sup>-1</sup>)</p>	$\text{R}^1\text{C}(=\text{O})\text{R}^2 \xrightarrow{\text{BH}_3 \cdot \text{SMe}_2 \cdot \text{O}} \text{R}^1\text{C}(\text{OH})\text{R}^2$ <p>2 examples R<sup>1</sup> = alkyl, aryl R<sup>2</sup> = alkyl</p>	ee:83-98	The catalyst was only recycled once. Full experimental section.	1029	1029
 <p>(1.2 mmol g<sup>-1</sup>)</p>	$\text{R}^1\text{C}(=\text{O})\text{R}^2 \xrightarrow{\text{Me}_2\text{S} \cdot \text{BH}_3 \cdot \text{O}} \text{R}^1\text{C}(\text{OH})\text{R}^2$ <p>2 examples R<sup>1</sup> = alkyl</p>	Y:67-98 ee:74-89	The reagent could be recycled. Experimental section.	1030	1030

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 15 examples $R^1, R^2, R^3, R^4 = \text{H, alkyl, phenyl}$ (0.30-2.1 mmolg <sup>-1</sup> )	 2 examples $R^1, R^2 = \text{alkyl}$	Y:89->95 ee:56-61	Various polymers were studied. Experimental section.	1031	1031
 (0.70 mmolg <sup>-1</sup> )	 4 examples $R^1 = \text{alkyl}$ $R^2 = \text{phenyl}$	Y:100 ee:76-97	The polymer could be regenerated and reused without loss of activity. Experimental section.	560, 1032, 1033	560
 (0.70 mmolg <sup>-1</sup> )	 2 examples $X = \text{Br, Cl}$	Y:100 ee:51-84	Halogens were not displaced. The resultant halohydrins could be treated with base to generate epoxides. Experimental section.	560, 1034	560
 Amberlite IRA-93 (5.5 mmolg <sup>-1</sup> )	 12 examples $R^1 = \text{H, alkyl, aryl}$ $R^2 = \text{alkyl, aryl}$	Y:51-97	Aluminium derived by-products generally remained linked to the polymer. Hindered compounds were efficiently reduced. General procedure.	1035	1035
 (0.7-2.1 mmolg <sup>-1</sup> )	 1 example	Y:65-97 ee:5-79	Enantiomeric excess increased with decreasing loading of chiral auxiliary. Resin may be reused without loss of enantiomeric excess. Experimental section.	566	566
 (0.7-2.1 mmolg <sup>-1</sup> )	 1 example	ee:20-45	The enantiomeric excess was dependant on the degree of functionalisation of the polymer. General procedure.	1036	1036



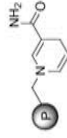

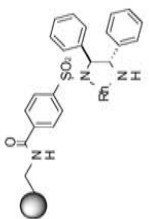

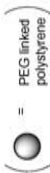


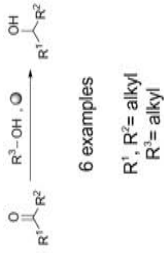
### 3.29.2 Hydroxy (From aldehydes/ketones – delivery of H from other species)

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
	 <p>3 examples R<sup>1</sup> = aryl</p>	Y: >99 ee: 80-92	The catalyst was generated <i>in situ</i> . Catalyst may be reused without loss of activity or ee. General procedure.	415	415
 <p>(0.50 mmol g<sup>-1</sup>)</p>	 <p>11 examples R<sup>1</sup>, R<sup>2</sup> = aryl R<sup>1</sup>, R<sup>2</sup> = alkyl</p>	Y: 33-100 ee: 8-59	Hydroxylation of acetophenone with fresh catalyst gave optical yields very similar to those observed with the homogenous rhodium-dip catalyst. Experimental section. Also see reference 1037.	382	382
	 <p>14 examples R<sup>1</sup> = alkyl, aryl</p>	Y: 27-91	Aldehydes were selectively reduced over ketones. Experimental section.	1038	1038
 <p>( = polyamide or polyurea ) R<sup>1</sup> = H, alkyl R<sup>2</sup> = aryl</p>	 <p>1 example</p>	C: 100 ee: 60	The (S,S) and (R,R) reagent stereochemistries allowed access to (S) or (R) products, respectively. The polyamide catalyst gave significantly lower conversions and ee than the polyurea catalyst. General procedure.	1039	1039

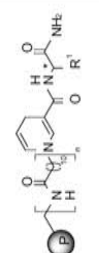
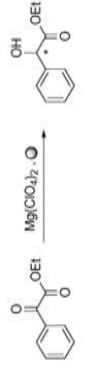
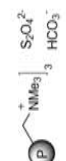

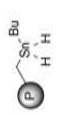





Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>(0.20 mmol g<sup>-1</sup>)</p>	 <p>5 examples R<sup>2</sup>= alkyl, ester R<sup>2</sup>= H, CF<sub>3</sub></p>	C:40-100 ee:24-70	Producing the polymer using chiral imprinting increased the enantiomeric excesses obtained. The degree of cross-linking also affected the polymer performance.	1040, 1041	1041
 <p>(1.6 mmol g<sup>-1</sup>)</p>	 <p>2 examples R<sup>1</sup>= H, O-alkyl</p>	C:30-75 ee:58-80	The reagent was a hybrid material prepared by sol-gel hydrolysis. A 3-dimensional network was created which influenced the properties of the catalyst. General procedure.	1042	1042
 <p>(0.20 mmol g<sup>-1</sup>)</p>	 <p>2 examples R<sup>1</sup>= alkyl</p>	C:89-91 ee:43-66	A molecular imprinting effect was investigated. General procedure. A silica supported ruthenium catalyst has also been described. <sup>1043</sup>	1044	1044
 <p>M= Ru, Ir</p>	 <p>1 example</p>	C:23-96 ee:31-92	Three polymers were investigated with the best example shown. General procedure.	1045	1045
	 <p>1 example</p>	C:90 ee:70	Catalyst recycling was unsatisfactory. General procedure.	1046	1046

3.29.2 Hydroxy (From aldehydes/ketones – delivery of H from other species)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (2.9 mmol g <sup>-1</sup> )	 13 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl		Kinetic study. The catalyst could be recycled without loss of activity. Experimental section.	1047	1047
 (2.6 mmol g <sup>-1</sup> )	 13 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl		Kinetic study. The catalyst could be recycled without loss of activity. Experimental section.	1047	1047
 Montmorillonite K 10 (0.47 mmol g <sup>-1</sup> )	 8 examples R <sup>1</sup> = H, alkyl, O-alkyl R <sup>2</sup> = H, alkyl, aryl, ketone		Kinetic studies were undertaken. Aliphatic carbonyls are not reduced under the reaction conditions. General procedure.	555	555
 Membrane (0.054 μmol cm <sup>-2</sup> )	 1 example	ee:79-92	No ruthenium leaching was observed. The catalyst could be reused without loss of enantiomeric excess. General procedure.	1048	1048
 (0.18 mmol g <sup>-1</sup> )	 2 examples R <sup>1</sup> = alkyl	Y:98-99 ee:88-97	The catalyst was reused but a small reduction in enantiomeric excess was observed. Experimental section.	405	405

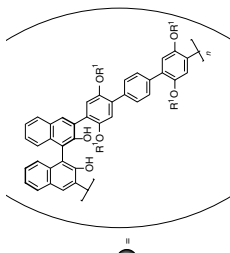
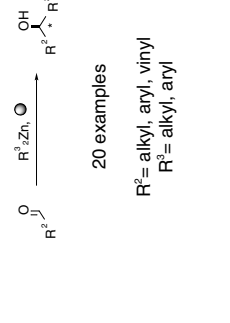
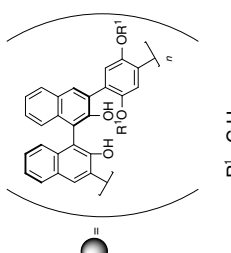
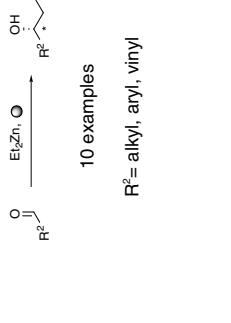
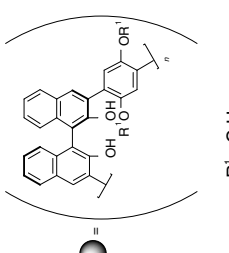
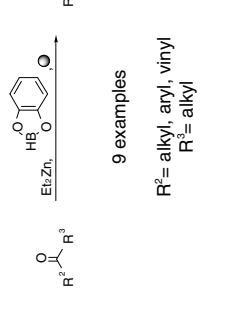
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Montmorillonite K 10		Y:70 P:99	Kinetic study.	1049	1049
 Amberlite (0.30-0.70 mmolg <sup>-1</sup> )		Y:85-90	Some loss of activity was observed upon recycling. General procedure.	686	686
  = (P) (0.7 mmolg <sup>-1</sup> )  = PEG linked polystyrene (0.22 mmolg <sup>-1</sup> )		C:21-100 ee:51-99	A range of conditions were examined. The best result was obtained with PEG linked polystyrene: 97% ee at 96% conversion. The activity of the polymeric catalyst decreased upon reuse.	1050	1050
		Y:58-87 C:100	The thermodynamically most stable isomer was the major product. Experimental section.	563	563

3.29.2 Hydroxy (From aldehydes/ketones – delivery of H from other species)—continued

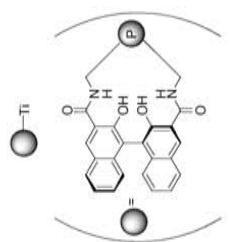
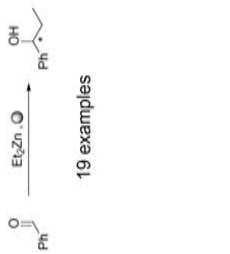

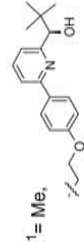

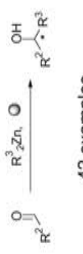
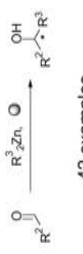




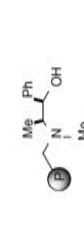
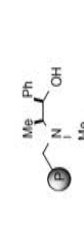
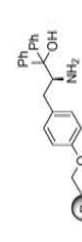
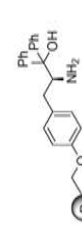
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>R<sup>1</sup> = alkyl, benzyl r = 0, 1</p>	 <p>1 example</p>	Y:11-43 ee:1.1-7.3	The ee was greatest for the resin with a linker unit. The resin may be recovered and reused, but with some loss of activity and ee.	1051	
 <p>Amberlyst A-26 Dithionite form (0.7-0.8 mmol g<sup>-1</sup>)</p>	 <p>9 examples R<sup>1</sup> = alkyl, aryl, benzyl R<sup>2</sup> = H, alkyl</p>	Y:48-78	General procedure.	1052	1052
 <p>(1.2 mmol g<sup>-1</sup>)</p>	 <p>7 examples R<sup>1</sup> = alkyl, aryl R<sup>2</sup> = H, alkyl, aryl</p>	Y:54-92	Experimental section.	448	448
 <p>Amberlite XE-305 (2.0 mmol g<sup>-1</sup>)</p>	 <p>7 examples R<sup>1</sup> = alkyl, aryl, benzyl R<sup>2</sup> = H, alkyl</p>	Y:54-92	The reduction could be greatly accelerated by addition of platinum tetrachloride. The spent reagent could be regenerated, but only showed 30-60% of the original hydride content. Experimental section.	448	448
 <p>(1.3 mmol g<sup>-1</sup>)</p>	 <p>1 example</p>	Y:73	General procedure.	447	447

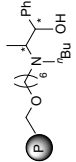
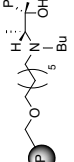
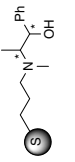
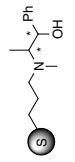
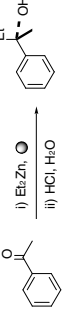
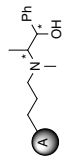
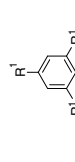


### 3.29.3 Hydroxy (From aldehydes/ketones — delivery of alkyl groups)

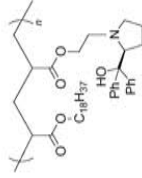
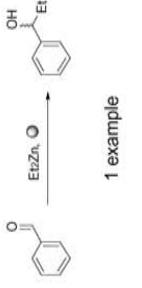
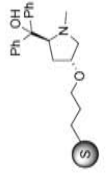

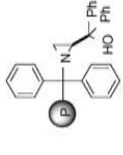
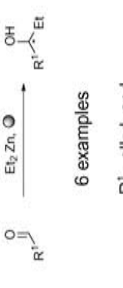


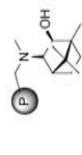

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>R<sup>1</sup> = C<sub>6</sub>H<sub>13</sub> (1.1 mmol g<sup>-1</sup>)</p>	 <p>20 examples R<sup>2</sup> = alkyl, aryl, vinyl R<sup>3</sup> = alkyl, aryl</p>	Y:65-95 ee:91-98	Polymer is soluble in THF, toluene and chloroform and is precipitated with methanol. Experimental section.	1053, 1054	1054
 <p>R<sup>1</sup> = C<sub>6</sub>H<sub>13</sub> (1.1 mmol g<sup>-1</sup>)</p>	 <p>10 examples R<sup>2</sup> = alkyl, aryl, vinyl</p>	Y:65-94 ee:35-93	Enantiomeric excesses are lower for <i>ortho</i> substituted benzaldehydes and aliphatic aldehydes. Polymer is soluble in THF, toluene and chloroform and is precipitated with methanol. General procedure. Also see references 1055, 1055, 1053, 1056, 1054.	1053, 1056, 1054	1056
 <p>R<sup>1</sup> = C<sub>6</sub>H<sub>13</sub> (1.1 mmol g<sup>-1</sup>)</p>	 <p>9 examples R<sup>2</sup> = alkyl, aryl, vinyl R<sup>3</sup> = alkyl</p>	Y:78-92 ee:4-80	Soluble polymer may be recovered and recycled up to three times with no loss of yield or enantioselectivity. Experimental section.	1054	1054

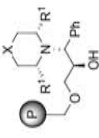

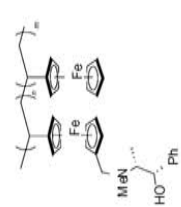

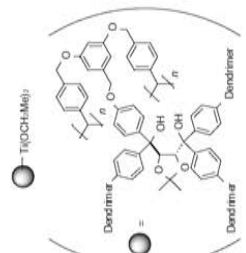

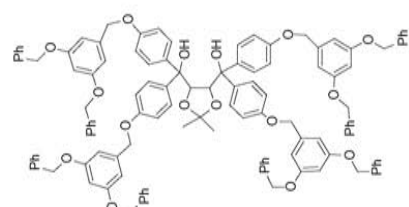

3.29.3 Hydroxy (From aldehydes/ketones — delivery of alkyl groups)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>(0.38 mmol g<sup>-1</sup>)</p>	 <p>19 examples</p>	Y:78-97 ee:57-99	In some cases resin gave better ees than its solution phase counterpart. General procedure.	1057, 1058	1057, 1058
 <p>1 example</p> <p>R<sup>1</sup> = Me,</p> 	 <p>1 example</p>	Y:77-88 P:71-73	A range of polymers was examined. Also see reference 1059.	1060	
 <p>42 examples</p> <p>R<sup>2</sup> = alkyl, aryl R<sup>3</sup> = alkyl</p>	 <p>42 examples</p> <p>R<sup>2</sup> = alkyl, aryl R<sup>3</sup> = alkyl</p>	Y:43-87 ee:21-89	Addition to aliphatic aldehydes generally gave lower ee than addition to aromatic aldehydes. Experimental section.	1061, 1062	1061
 <p>2 examples</p> <p>R<sup>1</sup> = aryl</p>	 <p>2 examples</p> <p>R<sup>1</sup> = aryl</p>	Y:81-98 ee:81-98	Reagent applied within a flow system. Example shown was the best in a family of 3-ephedrine based polymer-supported ligands. Experimental section.	1063	1063
 <p>7 examples</p> <p>R<sup>1</sup> = alkyl, aryl</p>	 <p>7 examples</p> <p>R<sup>1</sup> = alkyl, aryl</p>	Y:78-96 ee:8-99	Several polymers with different cross-linking tested. Best example given. Polymer may be recycled. Experimental section.	1064	1064
 <p>(1.2 mmol g<sup>-1</sup>)</p>	 <p>(1.2 mmol g<sup>-1</sup>)</p>				
 <p>(0.70 mmol g<sup>-1</sup>)</p>	 <p>(0.70 mmol g<sup>-1</sup>)</p>				

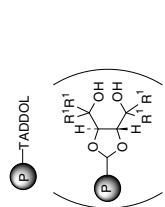
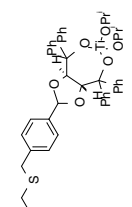
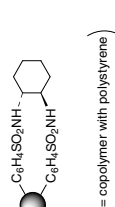
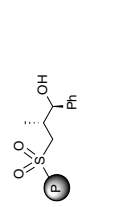
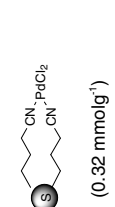
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (0.80 mmol g <sup>-1</sup> )	$R^1-CHO \xrightarrow{R^2-Zn, O} R^1-CH(OH)-R^2$ 4 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = alkyl	Y:75-91 ee:69-82	Various catalysts were investigated. Best results given. General procedure.	1065	1065
	$R^1-CHO \xrightarrow{Et_2Zn, O} R^1-CH(OH)-Et$ 4 examples R <sup>1</sup> = alkyl, aryl, vinyl	Y:53-91 ee:51-82	Several catalysts were examined with the best example shown. Full experimental section.	1066	1066
 (0.30-0.60 mmol g <sup>-1</sup> )	$R^1-CHO \xrightarrow{R^2-Zn, O} R^1-CH(OH)-R^2$ 4 examples R <sup>1</sup> = aryl R <sup>2</sup> = alkyl	Y:12-69 ee:37-40	Catalyst was recycled without loss of activity. Experimental section. Also see reference 1067.	1068	1068
 MCM-41 (0.60-0.90 mmol g <sup>-1</sup> )	 1 example	ee:14-33	Study of various factors affecting efficiency of the catalyst. Kinetic study. Experimental section.	1069	1069
 (0.15 mmol g <sup>-1</sup> )	$R^1-CHO \xrightarrow{R^2-Zn, O} R^1-CH(OH)-R^2$ 5 examples R <sup>1</sup> = aryl R <sup>2</sup> = alkyl	Y:13-81 ee:40-59	Catalyst was recycled without loss of activity. Experimental section.	1068	1068
	$R^1-CHO \xrightarrow{R^2-Zn, O} R^1-CH(OH)-R^2$ 5 examples R <sup>2</sup> = aryl R <sup>3</sup> = alkyl	Y:50-67 ee:77-86	The catalyst is a toluene soluble dendrimer. Catalyst may be reused without loss of activity or ee. General procedure.	1070	1070

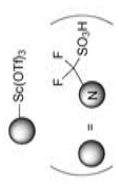
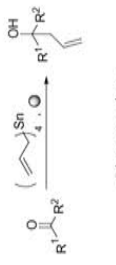
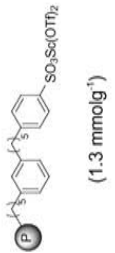
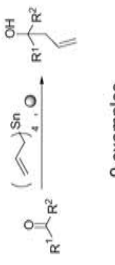
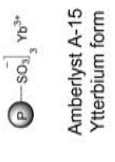


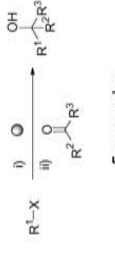
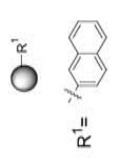
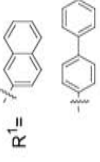

3.29.3 Hydroxy (From aldehydes/ketones — delivery of alkyl groups)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 C <sub>18</sub> H <sub>37</sub>	 1 example	ee:20-80	Ee depends upon reaction conditions. Reactions carried out as flow reactions. Experimental section. Also see reference 1071.	1072	
 SBA-15 (0.37 mmol g <sup>-1</sup> )	 1 example	Y:98 ee:75	Various silica supports were tested. The best example is shown. Capping of free silanol moieties with TMS groups and employment of BuLi also improved the reaction. General procedure.	1073	1073
 (0.70 mmol g <sup>-1</sup> )	 6 examples R <sup>1</sup> = alkyl, aryl	Y:72-92 ee:77-97	Reagent may be recycled without loss of yield or ee. General procedure.	1074	1074
 (0.60-3.3 mmol g <sup>-1</sup> )	 2 examples R <sup>1</sup> = H, hal	Y:89-94 ee:92-98	An ephedrine-based polystyrene catalyst was also investigated. The best results are shown. Experimental section. Also see reference 1075.	1076	1076
	 4 examples R <sup>1</sup> = alkyl, aryl	Y:64-97 ee:70-97	The reagent was suitable for use in a flow reactor for up to ~275 hours, although significant loss of activity was seen during this time. In general high yields and ee were maintained over six runs in a batch reactor.	1063	1063



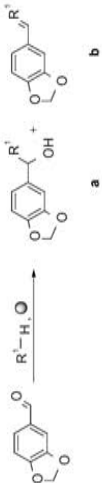
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>R<sup>1</sup> = H, alkyl X = CH<sub>2</sub>, NMe</p>	 <p>1 example</p>	ee:19-69	Full experimental section.	1077	1077
	 <p>1 example</p>	Y:67-85 ee:51-72	Several resins with different monomer ratios were synthesised and investigated.	1078	
	 <p>1 example</p>	C:23-100 ee:2-96	Several polymers and conditions tested. Best results given. Results are better than the equivalent solution phase reaction.	1079	1079
	 <p>1 example</p>	Y:46-100 ee:90-98	Several other dendrimers were investigated. Experimental section.	1080	1080

3.29.3 Hydroxy (From aldehydes/ketones — delivery of alkyl groups)—continued

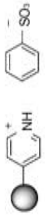


Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>(0.63 mmol g<sup>-1</sup>)</p> <p>R<sup>1</sup> = aryl</p>	$\text{R}^2-\text{C}(=\text{O})-\text{R}^3 \xrightarrow[\text{R}^2-\text{Zn}, \text{O}]{\text{Ti}(\text{O}i\text{Pr})_4, \text{TADDOL}} \text{R}^2-\text{C}(\text{OH})-\text{R}^3$ <p>9 examples</p> <p>R<sup>2</sup> = alkyl, aryl, vinyl R<sup>3</sup> = alkyl</p>	Y:90 ee:76	Polymer beads were contained in a polypropylene pouch to prevent degradation. Yield and ee are given for 1-phenylpropan-1-ol. Full experimental section.	1081	1081
 <p>(0.08-0.32 mmol g<sup>-1</sup>)</p>	$\text{R}^1-\text{C}(=\text{O})-\text{R}^2 \xrightarrow[\text{O}]{\text{Et}_2\text{Zn}} \text{R}^1-\text{C}(\text{OH})-\text{R}^2$ <p>1 example</p>	C:>95 ee:98	Catalyst may be reused up to twenty times with only a slight loss of activity.	1082	1082
 <p>( = copolymer with polystyrene )</p>	$\text{R}^1-\text{C}(=\text{O})-\text{R}^2 \xrightarrow[\text{O}]{\text{ZnEt}_2, \text{Ti}(\text{O}i\text{Pr})_4, \text{Copolymer}} \text{R}^1-\text{C}(\text{OH})-\text{R}^2$ <p>7 examples</p> <p>R<sup>1</sup> = allyl, aryl</p>	Y:71-85 ee:56-98	Loadings were controlled by reagent stoichiometry. The reagent was also used for the cyclopropanation of cinnamyl alcohol. Experimental section.	1083	1083
	$\text{R}^1-\text{C}(=\text{O})-\text{R}^2 + \text{B} \xrightarrow[\text{O}]{\text{ZnEt}_2, \text{Ti}(\text{O}i\text{Pr})_4, \text{Copolymer}} \text{R}^1-\text{C}(\text{OH})-\text{R}^2$ <p>6 examples</p> <p>R<sup>1</sup> = alkyl, aryl R<sup>2</sup> = H, alkyl</p>	Y:51-96 ee:65-92	Several chiral amino alcohol resins were investigated. General procedure.	1084	1084
 <p>(0.32 mmol g<sup>-1</sup>)</p>	$\text{R}^1-\text{C}(=\text{O})-\text{R}^2 + \text{X} \xrightarrow[\text{O}]{\text{SnCl}_4, \text{Copolymer}} \text{R}^1-\text{C}(\text{OH})-\text{R}^2$ <p>15 examples</p> <p>R<sup>1</sup> = alkyl, aryl, vinyl R<sup>2</sup> = H, alkyl X = Cl, OAc</p>	Y:54-89	Full experimental section.	1085	1047

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Nafion NR50 Scandium triflate form	 11 examples R <sup>1</sup> = alkyl, aryl, het, sugar, vinyl R <sup>2</sup> = H, alkyl, ester	Y:57-98	Reagent reused without loss of activity. Reaction was also carried out using a flow reactor. General procedure.	1086	1086
 (1.3 mmol g <sup>-1</sup> )	 9 examples R <sup>1</sup> = alkyl, aryl, het, vinyl R <sup>2</sup> = H, alkyl, ester	Y:72-100	Reactions were performed in water. Catalyst may be recovered and reused without loss of activity. General procedure.	581	581
 Amberlyst A-15 Ytterbium form (0.80-1.5 mmol g <sup>-1</sup> )	 1 example	Y:91	Catalyst may be recycled without loss of activity. Experimental section.	103	103
 Lithium deposited on polyethylene (7.1 mmol g <sup>-1</sup> )	 5 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> , R <sup>3</sup> = alkyl X = Br, Cl	Y:56-79	Supported lithium was non-pyrophoric and was stored under hexane for over three months. Full experimental section.	1087	1087
 R <sup>1</sup> = 	 16 examples R <sup>2</sup> = alkyl, allyl, benzyl R <sup>3</sup> = alkyl, aryl R <sup>4</sup> = H, alkyl	Y:48-99	The catalyst was successfully recycled. No loss of activity was detected in experiments using recycled catalyst. General procedures.	567 568	567 568

### 3.29.3 Hydroxy (From aldehydes/ketones — delivery of alkyl groups)—continued

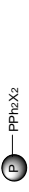
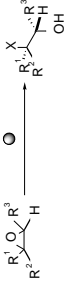

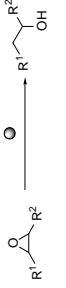
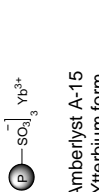

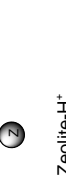

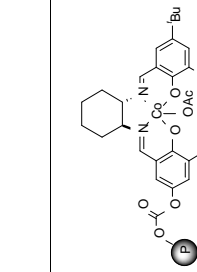
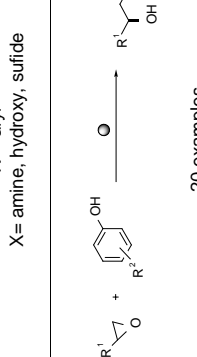
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Zinc deposited on polyethylene	$R^1-X \xrightarrow[\text{ii) } \begin{array}{c} \text{O} \\ \parallel \\ R^2-C-R^3 \end{array}]{\text{i) } \text{O}} R^1-CH(OH)-R^2$ 11 examples R <sup>1</sup> = allyl, ester, R <sup>2</sup> = alkyl, aryl R <sup>3</sup> = H, alkyl, haloalkyl X= Br, Cl	Y:40-99	Used for Barbier and Reformatski type reactions. Full experimental section.	1087	1087
 KF	$R^1-CHO \xrightarrow{R^1-H, O} R^1-CH(OH)-R^2$  2 examples R <sup>1</sup> = phenyl acetylene, fluorene	Y:25-54 (a) Y:0-64 (b)	General procedure.	1088	

### 3.29.4 Hydroxy (From acetals)

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Resin with SO <sub>3</sub> <sup>-</sup> and NH <sup>+</sup> groups	$R^1-O-CH_2-CH_2-O \xrightarrow{O} R^1-OH$ 9 examples R <sup>1</sup> = alkyl, aryl, benzyl	Y:86-100	Acid labile epoxides remain untouched. Polymer may be reused. General procedure.	1089	
 Dowex-50W-X8 Proton form	$R^1-O-CH_2-CH_2-O \xrightarrow{O} R^1-OH$ 4 examples R <sup>1</sup> = alkyl	Y:97-99	This represents a useful procedure for removal of a THP protecting group under mild conditions. General procedure.	1090	
 Nafion-H	$R^1-O-CH_2-CH_2-O \xrightarrow{O} R^1-OH$ 10 examples R <sup>1</sup> = alkyl, benzyl	Y:95-99	General procedure. Amberlyst A-15 has also been used. <sup>117</sup>	119	

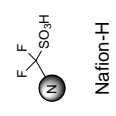
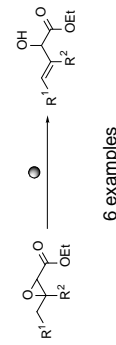
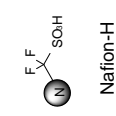
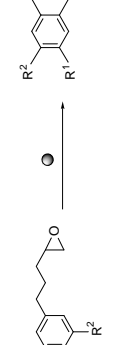


### 3.29.5 Hydroxy (From epoxides)

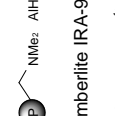
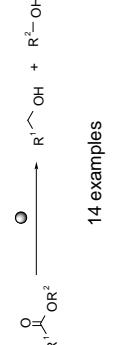
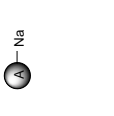
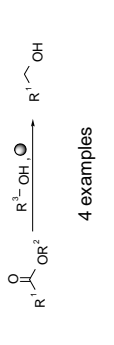
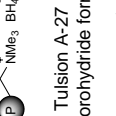
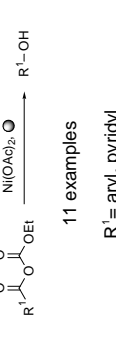
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (2.7 mmol g <sup>-1</sup> ) X = Br, Cl, I	 6 examples R <sup>1</sup> , R <sup>2</sup> , R <sup>3</sup> = H, alkyl	Y:94-98	Diastereomeric mixtures were obtained. Full experimental section.	1091	1091
 (1.8 mmol g <sup>-1</sup> )	 9 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl	Y:85-98	The least substituted alcohol was obtained exclusively. General procedure.	1092	1092
 (0.80-1.5 mmol g <sup>-1</sup> )	 1 example	Y:97	Experimental section. Ratio <b>a:b</b> = 1.7-1	103	103
 Zeolite-H <sup>+</sup>	 14 examples R <sup>1</sup> = alkyl, allyl R <sup>2</sup> = aryl X = amine, hydroxy, sulfide	Y:0-92	Full experimental section. Ratio <b>a:b</b> = 3:2 – 39:1	1093	
	 20 examples R <sup>1</sup> = alkyl R <sup>2</sup> = H, alkyl, aryl, Br, CF <sub>3</sub> , O-alkyl, O-aryl	Y:55-100 P:93-100 ee:81->99	Catalyst may be reused without loss of activity.	1094	1095

3.29.5 Hydroxy (From epoxides)—continued

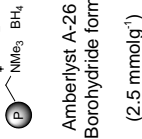
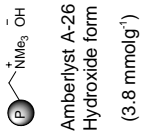
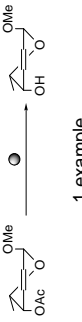
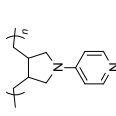

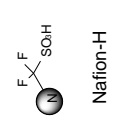
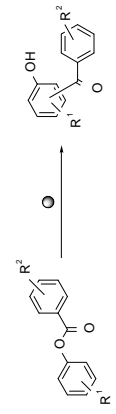
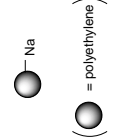
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
	$\text{Epoxide} \xrightarrow{\text{H}_2\text{O}} \text{Diol}$ <p style="text-align: center;">4 examples</p> <p style="text-align: center;">R<sup>1</sup> = aryl, haloalkyl, hydroxyalkyl</p>	ee:93-96 (a)	The immobilised catalysts have been adapted for use in a continuous flow process. Full experimental section.	1095	1095
	$\text{Epoxide} \xrightarrow{\text{R}^1\text{-OH, O}_2} \text{Diol}$ <p style="text-align: center;">2 examples</p> <p style="text-align: center;">R<sup>1</sup> = aryl R<sup>2</sup> = alkyl, haloalkyl</p>	Y:90-98 ee:96-99	Repeated recycling resulted in no loss of reactivity or enantioselectivity. Full experimental section.	1095	1095
	<p style="text-align: center;">3 examples</p> <p style="text-align: center;">r = 3, 4, 9 m = 4, 9</p>	Y:70-87	The olefin formed always possessed <i>E</i> geometry. The polymer overcame the need for high dilution. General procedure.	1096	
	<p style="text-align: center;">6 examples</p> <p style="text-align: center;">R<sup>1</sup>, R<sup>2</sup> = alkyl</p>	Y:44-91	Mixed products in many cases. <i>Exo-endo</i> isomerization occurred where possible. General procedure.	1097	

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Nafion-H	 6 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = alkyl	Y:69-99	Experimental section.	1098	
 Nafion-H	 7 examples R <sup>1</sup> = H, alkyl, Cl, F, O-alkyl R <sup>2</sup> = H, alkyl, O-alkyl	Y:31-88	Five examples gave only the target molecule. Two examples gave a 1:1 mixture with another isomer. Full experimental section.	1099	1099

### 3.29.6 Hydroxy (From esters)

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlite IRA-93 (5.5 mmolg <sup>-1</sup> )	 14 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = alkyl		Aluminium derived by-products generally remain linked to the polymer. Hindered compounds were efficiently reduced.	1035	1035
	 4 examples R <sup>1</sup> = alkyl, benzyl R <sup>2</sup> , R <sup>3</sup> = alkyl	Y:65-70 C:100	Experimental section.	563	563
 Tulsion A-27 Borohydride form (3.0 mmolg <sup>-1</sup> )	 11 examples R <sup>1</sup> = aryl, pyridyl	Y:62-93	Mixed anhydrides of dicarboxylic acids were completely reduced to the corresponding diols. General procedure.	1100	

3.29.6 Hydroxy (From esters)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Borohydride form (2.5 mmol g <sup>-1</sup> )	$\text{R}^1\text{-OAc} \xrightarrow{\text{O}} \text{R}^1\text{-OH}$ <p>4 examples R<sup>1</sup> = aryl</p>	Y:92-95	Alkyl substituted aromatics remained unreduced. General procedure.	1101	1101
 Amberlyst A-26 Hydroxide form (3.8 mmol g <sup>-1</sup> )	 <p>1 example</p>	Y:90	Experimental section.	1102	
	$\text{R}^1\text{-O-CO-C}_6\text{H}_4\text{-NO}_2 \xrightarrow{\text{H}_2\text{O}, \text{O}} \text{R}^1\text{-OH}$ <p>6 examples R<sup>1</sup> = alkyl</p>		Kinetic study. Experimental section.	1103	1103
	$\text{R}^1\text{-O-CO-OBn} \xrightarrow{\text{IMW, O}} \text{R}^1\text{-OH}$ <p>7 examples R<sup>1</sup> = aryl, amino alcohol, alkylamine</p>	Y:89-95	Reactions were carried out under solvent free conditions. General procedure.	1104	
	 <p>6 examples R<sup>1</sup> = H, alkyl R<sup>2</sup> = alkyl, Cl</p>	Y:63-75	Fries rearrangement. Resin may be regenerated and reused. General procedure.	1105	
 ( = polyethylene) (2.2 mmol g <sup>-1</sup> )	$\text{R}^1\text{-O-CO-OR}^2 \xrightarrow{\text{O}} \text{R}^1\text{-OH}$ <p>4 examples R<sup>1</sup>, R<sup>2</sup> = alkyl</p>	Y:48-81	Various solid supports were investigated. The best results are shown. Experimental section.	1087	1087

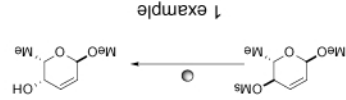
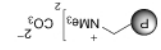
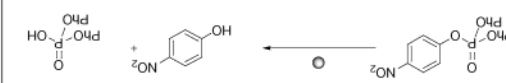
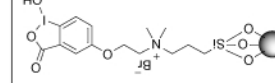
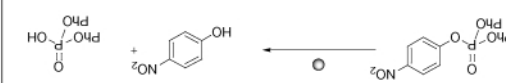
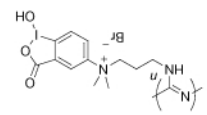


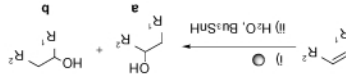
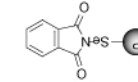
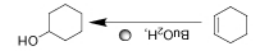
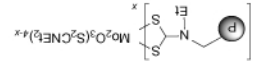
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Fluoride form (3.3 mmol g <sup>-1</sup> )	 5 examples R <sup>1</sup> , R <sup>2</sup> , R <sup>3</sup> = H, alkyl	Y:68-82	Reagent may be regenerated. Highest yields are obtained with five-membered iodocarbonates. Experimental section.	817	

### 3.29.7 Hydroxy (From halides)

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Carbonate form (3.7 mmol g <sup>-1</sup> )	 7 examples R <sup>1</sup> = alkyl, aryl X = Cl, Br, I	Y:>85	Reagent may be regenerated. When used with secondary alkyl halides, elimination predominated. Experimental section.	623	623
 Amberlyst A-26 Hydrogen carbonate form (3.5 mmol g <sup>-1</sup> )	 14 examples R <sup>1</sup> = alkyl, allyl X = Br, Cl	Y:26-92	Two other resins were investigated, best results given. Experimental section.	1106	1106
 (0.40-2.2 mmol g <sup>-1</sup> )	 1 example	Y:>90	Kinetic study.	853	853
 (0.40-2.2 mmol g <sup>-1</sup> )	 5 examples r = 4, 6 M = Na, K X = O-aryl, SCN, I, hydroxy	Y:78-94	The resin may be reused without loss of activity. Experimental section.	631	631

3.29.8 Hydroxy (From miscellaneous)

Ref. Prep. Ref.	Comments	Data/%	Transformation	Reagent (Loading)
1107	The reagent may be regenerated.	Y:89-94	<p>5 examples</p> <p>R<sup>1</sup> = OSiPh<sub>2</sub> Bu → R<sup>1</sup> - OH</p> <p>R<sup>1</sup> = carbohydrate</p>	<p>Amberlyst A-26 Fluoride form (3.8 mmolg<sup>-1</sup>)</p>
1108	The reagent was more reactive than tetra- <i>n</i> -butyl ammonium fluoride. Experimental section.	Y:72-100	<p>5 examples</p> <p>R<sup>2</sup> = H, alkyl, alkenyl, aryl R<sup>2</sup> = alkyl, aryl, phosphate ester</p>	<p>R<sup>1</sup> = H, Me (3.1-4.5 mmolg<sup>-1</sup>)</p>
1109	Phenolic silyl ethers were deprotected faster than primary and secondary alcohols. General procedure.	Y:68-93	<p>7 examples</p> <p>R<sup>1</sup> = alkyl, aryl, het</p>	
259	Primary alcohols were deprotected selectively in the presence of secondary alcohols. TBDPS groups were generally not removed (MOM, THP) were not affected. General procedures.	Y: 17-100	<p>9 examples</p> <p>R<sup>1</sup> = alkyl, aryl, vinyl R<sup>2</sup> = H, alkyl R<sup>2</sup> = TMS, TBDMS, TBDPS</p>	
1110	Removal of the dimethoxy trityl group from oligonucleotides was much easier using the resin than acetic acid.		<p>3 examples</p> <p>R<sup>1</sup> = oligonucleotide</p>	<p>Dowex 50WX</p>

Ref. Prep.	Ref.	Comments	Data/%	Transformation	Reagent (Loading)
	623	The reagent may be regenerated. Experimental section.	Y:80	1 example 	Amberlyst A-26 Carbonate form (3.7 mmol <sup>g</sup> <sup>-1</sup> ) 
	1112	Kinetic study. Experimental section.	1112	1 example 	(0.10 mmol <sup>g</sup> <sup>-1</sup> ) 
	1112	Kinetic study. Experimental section.	1112	1 example 	Nylon (0.30 mmol <sup>g</sup> <sup>-1</sup> ) 
	575	One step of a multi-step natural product synthesis. 77	Y:95	1 example 	Amberlite IRA-400 Borohydride form (2.5 mmol <sup>g</sup> <sup>-1</sup> ) 
	330	The ratio of products <b>a</b> : <b>b</b> = 2:1. General procedure.	Y:80-82	2 examples 	
	1113	Some leaching of metal occurs when treated with butyl hydrogen peroxide. Experimental section.	Y:70	1 example 	(0.73 mmol <sup>g</sup> <sup>-1</sup> ) 

Ref. Prep. Ref.	Ref.	Comments	Data/%	Transformation	Reagent (Loading)
1114	1114	The least substituted alcohol was formed exclusively.	Y:70-95 de:10-50	10 examples $\text{R}^1 \text{C}(\text{R}^2)=\text{C}(\text{R}^3)\text{OH} \xleftarrow{\ominus} \text{R}^1 \text{C}(\text{R}^2)=\text{C}(\text{R}^3)$ $\text{R}^1 = \text{alkyl, aryl}$ $\text{R}^2, \text{R}^3 = \text{H, alkyl, aryl}$	$\text{S} - \text{Zn}(\text{BH}_4)_2$
1114	1114	General procedure.	Y:75-96	7 examples $\text{R}^1 \text{C}(\text{R}^2)=\text{C}(\text{R}^3)\text{OH} + \text{R}^1 \text{C}(\text{R}^2)=\text{C}(\text{R}^3) \xleftarrow{\ominus} \text{R}^1 \text{C}(\text{R}^2)=\text{C}(\text{R}^3)\text{OH}$ $\text{R}^1 = \text{H, alkyl, aryl}$ $\text{R}^2 = \text{H, alkyl, aryl}$	$\text{S} - \text{Zn}(\text{BH}_4)_2$
1115	1115	Acylation was also achieved using an acetic acid buffer.	Y:82-85	3 examples $\text{R}^1 \text{C}(\text{R}^2)=\text{C}(\text{R}^3)\text{OH} + \text{R}^1 \text{C}(\text{R}^2)=\text{C}(\text{R}^3) \xleftarrow{\text{Ascorbic acid, } \ominus} \text{R}^1 \text{C}(\text{R}^2)=\text{C}(\text{R}^3)\text{OH}$ $\text{R}^1 = \text{H, alkyl, aryl}$	$\text{Cu(I)}$ $\left( \text{NH}_2 \right)$ (0.40 mmol <sup>-1</sup> )
1116	1116	Asymmetric induction was greater in the presence of the polymer than with the analogous solution phase reaction. Ration of products a:b = 6:1	Y:85-92 ee:2-4	1 example $\text{R}^1 \text{C}(\text{R}^2)=\text{C}(\text{R}^3)\text{OH} + \text{R}^1 \text{C}(\text{R}^2)=\text{C}(\text{R}^3) \xleftarrow{\text{Ascorbic acid, } \ominus} \text{R}^1 \text{C}(\text{R}^2)=\text{C}(\text{R}^3)\text{OH}$	$\text{Cu(I)}$ (PMA) (1.2 mmol <sup>-1</sup> )
72	72	Polymer could be regenerated and reused without loss of activity. General procedure.	Y:100 P:>95	4 examples $\text{R}^1 \text{C}(\text{R}^2)=\text{C}(\text{R}^3)\text{OH} \xleftarrow{\text{CF}_3\text{CO}_2\text{H, } \ominus} \text{R}^1 \text{C}(\text{R}^2)=\text{C}(\text{R}^3)\text{OH}$ $\text{R}^1 = \text{H, Cl, nitro, O-alkyl}$	$\text{P}$ (3.5 mmol <sup>-1</sup> )



Ref. Prep. Ref.	Comments	Data/%	Transformation	Reagent (Loading)	35	74	35	725	1118
	Some $\alpha$ -dimethoxy product was also formed. Full experimental section.	Y: 34-70	<p>3 examples</p> <p>R<sup>1</sup> = aryl</p>						
	Two reagents were used simultaneously in a one-pot reaction. Full experimental section.	35	<p>1 example</p>	<p>A</p> <p>Amberlite A-27 Periodate form</p> <p>B</p> <p>Amberlite A-27 borohydride form</p>					
	Several catalysts were made as part of an evolution approach to a library of catalysts.	Y: 18	<p>1 example</p>	<p>= Tetragel or macroporous polystyrene</p>					
	This transformation is important industrially. There was no leaching of the metal and the particles were mechanically robust. A polyethylene glycol / acac / iron(III) system has also been used with hydrogen peroxide for the oxidation of cyclohexane. <sup>1117</sup>	Y: 30	<p>1 example</p>	<p>(0.37 mmol g<sup>-1</sup>)</p>					

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
Wang	<p>3 examples R<sup>1</sup> = alkyl, benzyl</p>	Y:12-66 ee:71-90	Merrifield and Tentagel polymeric supports were also used although polystyrene was the best support. General procedure.	1119	1119

## 3.30 Imines, haloimines and related compounds

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
A	<p>11 examples R<sup>1</sup> = alkyl, aryl R<sup>2</sup> = H, alkyl, aryl R<sup>3</sup> = aryl, benzyl</p>	Y:51-99	Reactions were carried out under solvent free conditions. General procedure.	1120	
Envirocac EPZG	<p>6 examples R<sup>1</sup> = H, alkyl, hydroxy, O-alkyl</p>	Y:90-97	Reaction times were very short. General procedure.	680	
Montmorillonite K 10	<p>5 examples R<sup>1</sup> = H, amino, hydroxy, O-alkyl</p>	Y:95-98	The reaction was carried out under solvent free conditions. General procedure.	681	

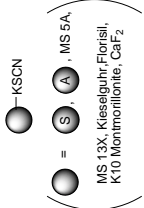
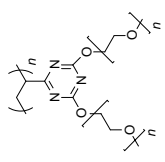
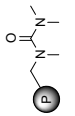



Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
$\text{CaCO}_3$	<p>11 examples  <math>R^1 = \text{H, halogen, O-alkyl, O-acyl}</math>  <math>R^2 = \text{H, O-alkyl, O-acyl}</math>  <math>R^3 = \text{H, alkyl, halogen}</math></p>	Y:52-91	Reaction is carried out under solvent free conditions.	1121	
$\text{P}^+\text{Ph}_2\text{Br}^-$	<p>2 examples  <math>R^1 = \text{H, aryl}</math></p>	Y:78-93	The resin may be regenerated and reused. Experimental section.	140	140
$\text{P}^+\text{PPh}_2$ (2.9 mmol g <sup>-1</sup> )	<p>2 examples  <math>R^1 = \text{aryl}</math>  <math>R^2 = \text{alkyl, aryl}</math></p>	Y:88-90	General procedure.	1122	1122
$\text{P}^+\text{PPh}_2$ (2.9 mmol g <sup>-1</sup> )	<p>1 example  <math>R^1, R^2 = \text{aryl}</math></p>	Y:88	General procedure.	1122	
$\text{P}^+\text{Ph}_2\text{Br}^-$ (2.2 mmol g <sup>-1</sup> )	<p>1 example</p>			465	465
$\text{P}^+\text{NMe}_3\text{CN}^-$ Amberlite IRA-400 Cyanide form	<p>8 examples  <math>R^1 = \text{aryl}</math>  <math>R^2 = \text{alkyl, aryl}</math></p>	Y:75-90	Polymer is non-toxic and may be stored without decomposition. General procedure.	1123	1124

### 3.31 Isocyanates

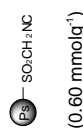

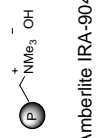
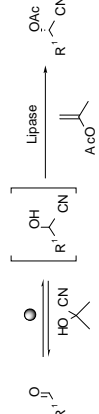
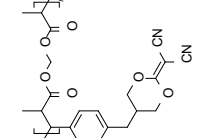
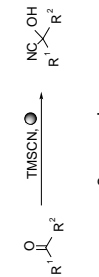
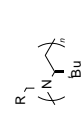
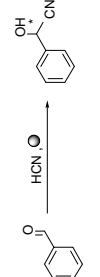
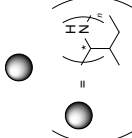
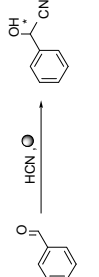
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Isocyanate form (3.9 mmolg <sup>-1</sup> )	$R^1-X \xrightarrow{\bullet} R^1-NCO$ <p>8 examples</p> <p>R<sup>1</sup>= alkyl, allyl, benzyl X= Br, Cl</p>	Y:38-93	The reagent must be refrigerated to prevent decomposition. The isocyanates decomposed spontaneously to ureas under the reaction conditions. In ethanol, <i>N</i> -substituted urethanes were isolated. Full experimental section.	1125	1125


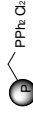
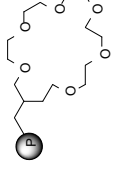


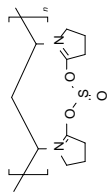
### 3.32 Isothiocyanates and thiocyanates

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Thiocyanate form (4.0 mmolg <sup>-1</sup> )	$R^1 \begin{array}{c} R^1 \\   \\ R^2 - C - X \\   \\ R^3 \end{array} \xrightarrow{\bullet} R^1 \begin{array}{c} R^1 \\   \\ R^2 - C - SCN \\   \\ R^3 \end{array}$ <p>14 examples</p> <p>R<sup>1</sup>= H, alkyl, benzyl R<sup>2</sup>, R<sup>3</sup>= H, alkyl X= Br, Cl</p>	Y:28-98	The reagent could be regenerated. Best results were obtained using hydrocarbon solvents. Isothiocyanate formation was also observed, although control of physio-chemical parameters allowed the exclusive formation of only the thiocyanate isomers. Experimental section (ref. 1126).	1126, 1127	1126, 1127
 Amberlyst A-26 Thiocyanate form (3.9 mmolg <sup>-1</sup> )	$R^1-X \xrightarrow{\bullet} R^1-SCN$ <p>4 examples</p> <p>R<sup>1</sup>= alkyl, benzyl</p>	Y:49-91	The reagent could be stored without decomposition at room temperature. Full experimental section.	1125	1125
 Amberlyst A-26 Thiocyanate form (2.1 mmolg <sup>-1</sup> )	$R^1-X \xrightarrow{\bullet} R^1-SCN$ <p>4 examples</p> <p>R<sup>1</sup>= alkyl, benzyl X= Br, Cl, I</p>	Y:76-94	The reagent was stable at room temperature. Experimental section.	1014	1014


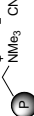




Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>MS 13X, Kieselguhr, Florisil, K10 Montmorillonite, CaF<sub>2</sub></p> <p>(0.50-10.0 mmol g<sup>-1</sup>)</p>	$R^1-X \xrightarrow{O} R^1-SCN \xrightarrow{R^2-NCS} R^1-N(R^2)-SCN$ <p>9 examples R<sup>1</sup> = alkyl, allyl, benzyl X = Br, Cl</p>	C:6-100	A number of supports were investigated and SiO <sub>2</sub> was found to be the best. The reaction without solvent was most effective. Selectivity was usually for <b>a</b> over <b>b</b> . Experimental section.	1128	1128
 <p>r = 1-3</p>	$Y-Br \xrightarrow{M, SCN, O} Y-SCN$ <p>3 examples M = Li, Na, K</p>	Y:44-88	Experimental section.	1129	1129
	$Y-Br \xrightarrow{KSCN, O} Y-SCN$ <p>1 example</p>	Y:67	The resin could be reused without loss of activity. Experimental section.	1130	1130
 <p>(1.4-5.5 mmol g<sup>-1</sup>)</p>	$Y-Br \xrightarrow{M, X} Y-X$ <p>3 examples M = K, Na X = CN, I, SCN</p>	Y:20-99	Several polymers were prepared with different degrees of cross-linking. The best results are given. Experimental section.	1131	1131
<p>a = </p> <p>b = </p>	$R^1, R^2, R^3 \xrightarrow{O, a, b} R^1, R^2, R^3-SCN$ <p>6 examples R<sup>1</sup> = alkyl, aryl, O-alkyl R<sup>2</sup> = alkyl, O-alkyl R<sup>3</sup> = alkyl, benzyl</p>	Y:18-89	This two-step, one-pot "wolf and lamb" process would not be possible in the solution phase. Reaction worked best when R <sup>3</sup> was not bulky.	1132	1132

### 3.33 Nitriles

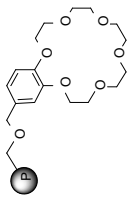
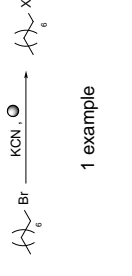
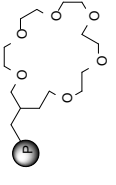
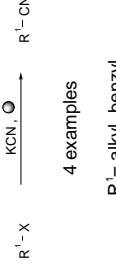
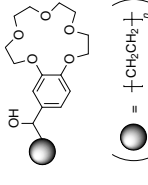
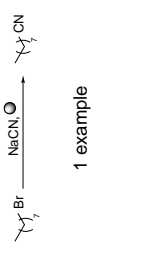
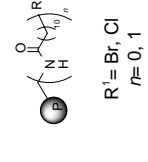
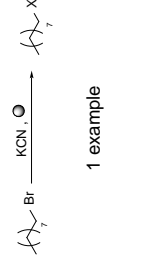
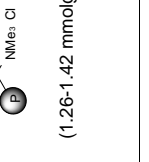
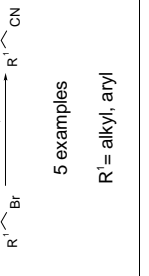
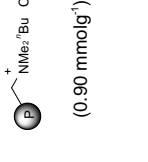
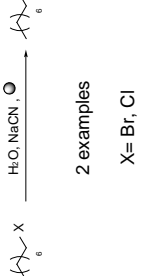
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (0.60 mmolg <sup>-1</sup> )	 4 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl	Y:24-88	Polymer can be regenerated in a two step procedure. Polymer is soluble under reaction conditions. Experimental section.	967	967
 (2.5 mmolg <sup>-1</sup> )	 14 examples R <sup>1</sup> = alkyl, aryl, het	Y:20-96 ee:15-91	Dynamic resolution by a lipase, or resolution of cyanohydrins formed and racemised <i>in situ</i> , by a basic anion exchange resin. Full experimental section.	1133	
 (2.5 mmolg <sup>-1</sup> )	 6 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl	Y:0-96	General procedure.	862	862
 (2.5 mmolg <sup>-1</sup> )	 1 example	Y:61-91 ee:0-20	It was found that the polymer was responsible for racemization of products. Experimental section.	1134	1134
 (2.5 mmolg <sup>-1</sup> )	 1 example	Y:52	Some enantiomeric excess observed. Other resins tested with best result shown.	1134	1134

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Oxone (1.0 mmol g <sup>-1</sup> )	$\text{R}^1-\text{C}(=\text{O})-\text{NHPH} \xrightarrow{\text{NH}_2\text{OH}\cdot\text{HCl, MW, } \ominus} \text{R}^1-\text{C}(\text{N}=\text{O})-\text{CN}$ <p>10 examples R<sup>1</sup> = alkyl, aryl</p>	Y:70-95	Solvent free conversion under microwave conditions. General procedure.	1135	
	$\text{Ph}-\text{C}(=\text{O})-\text{NHPH} \xrightarrow{\ominus} \text{Ph}-\text{C}(\text{N}=\text{O})-\text{CN}$ <p>1 example</p>	Y:78	Resin may be regenerated and reused. Experimental section.	140	140
	$\text{Ph}-\text{C}(=\text{O})-\text{NH}_2 \xrightarrow{\text{NaOH, } \ominus} \text{Ph}-\text{C}(\text{N}=\text{O})-\text{CN}$ <p>1 example</p>	Y:100	Resin is stable to reaction conditions and storage. General procedures.	649	
 (2.8 mmol g <sup>-1</sup> )	$\text{R}^1-\text{C}(=\text{O})-\text{NH}_2 \xrightarrow{\text{CCl}_4 \text{ OR DCE, } \ominus} \text{R}^1-\text{C}(\text{N}=\text{O})-\text{CN}$ <p>7 examples R<sup>1</sup> = alkyl, aryl, benzyl, naphthyl</p>	Y:61-100	General procedure.	1122	1122
 (2.8 mmol g <sup>-1</sup> )	$\text{R}^1-\text{C}(=\text{O})-\text{N}(\text{OH})-\text{Ph} \xrightarrow{\text{CCl}_4 \text{ OR DCE, } \ominus} \text{R}^1-\text{C}(\text{N}=\text{O})-\text{CN}$ <p>1 example R<sup>1</sup> = aryl</p>	Y:76	Montmorillonite K 10 can also be used. <sup>1136</sup>	1122	
	$\text{R}^1-\text{C}(=\text{O})-\text{N}(\text{OH})-\text{Ph} \xrightarrow{\ominus} \text{R}^1-\text{C}(\text{N}=\text{O})-\text{CN}$ <p>13 examples R<sup>1</sup> = alkyl, aryl</p>	Y:86-95	General procedure.	1137	1137


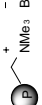

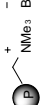

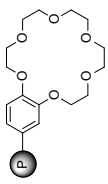
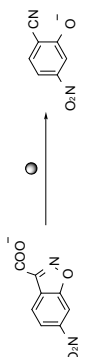
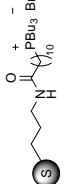
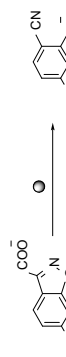
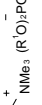

3.33 Nitriles—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Envirocat EPZG	$\text{R}^1\text{-CH}_2\text{-N}^+\text{(OH)-} \bigcirc \longrightarrow \text{R}^1\text{-CN}$ 7 examples R <sup>1</sup> = aryl, furyl	Y:67-92	Clay exhibits acid characteristics. General procedure. Cesium exchanged zeolite can also be used. <sup>1138</sup>	110	
 Amberlite IRA-400 Cyanide form (1.0 mmolg <sup>-1</sup> )	$\text{R}^1\text{-X} \bigcirc \longrightarrow \text{R}^1\text{-CN}$ 7 examples R <sup>1</sup> = alkyl, benzyl X = Br, Cl	Y:43-98	Choice of solvent had minimal effect on the reaction. Dowex 21 (Cyanide form) was also tested but found to be less successful. Experimental section. Also see references 1139, 1140, 1141.	1124	1124
 KCN	$\text{R}^1\text{-Br} \bigcirc \longrightarrow \text{R}^1\text{-CN}$ 7 examples R <sup>1</sup> = alkyl	Y:50-97	Reaction of primary and secondary alkyl bromides was successful. Dibromides converted to dinitriles. General procedure.	785	785
 (0.90 mmolg <sup>-1</sup> )	$\text{R}^1\text{-X} \xrightarrow{\text{NaCN}, \bigcirc} \text{R}^1\text{-CN}$ 4 examples R <sup>1</sup> = alkyl, benzyl		Aqueous conditions employed. Polymer functions as a colloidal phase transfer catalyst. Kinetics, particle sizes and cross-linking were investigated. Also see references 1142, 1143.	348, 1144	1144
 X = Br, Cl (0.96-1.2 mmolg <sup>-1</sup> )	$\text{R}^1\text{-CH}_2\text{-X} \xrightarrow{\text{MY}, \bigcirc} \text{R}^1\text{-Y}$ 6 examples R <sup>1</sup> = alkyl, aryl Y = CN, O-acyl, I M = Na, K		Resin used to probe parameters of triphase catalysis and spacer effects. Experimental section.	1145, 1146, 1147, 1148, 1149, 1150	1145, 1146, 1147
 R <sup>1</sup> = H, alkyl (0.48-1.6 mmolg <sup>-1</sup> )	$\text{R}^1\text{-Br} \xrightarrow{\text{MX}, \bigcirc} \text{R}^1\text{-X}$ 4 examples M = K, Na X = CN, I	Y:82-95	The polymeric catalysts are more active than their monomeric analogues. The activity of the resin increases on recycling. General procedure.	1016	1016

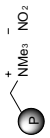
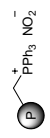
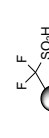
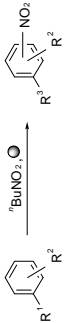
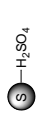
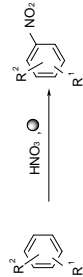
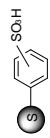


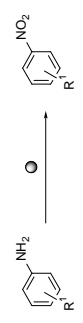


Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (2.1 mmol g <sup>-1</sup> )	 1 example	Y:100	Several linkers used to investigate properties of resins as phase transfer catalysts. Experimental section.	1151	1151
	 4 examples R <sup>1</sup> = alkyl, benzyl X = Br, Cl	Y:0-100	Resin was stable to reaction conditions and storage. General procedures.	649	
 (0.40 mmol g <sup>-1</sup> )	 1 example	Y:85	Other catalysts described but this one has also been used on a preparative scale. Recyclable catalyst is soluble on heating but precipitates when cooled. Full experimental section. Also see reference 900.	902	902
 R <sup>1</sup> = Br, Cl n = 0, 1	 1 example	Y:100	Reaction carried out on multi-gram scale. Experimental section.	855	855
 (1.26-1.42 mmol g <sup>-1</sup> )	 5 examples R <sup>1</sup> = alkyl, aryl		Resin used to probe parameters of triphase catalysis. Experimental section.	1145, 1146	1145, 1146
 (0.90 mmol g <sup>-1</sup> )	 2 examples X = Br, Cl	Y:50-92	Triphase catalyst.	1143	

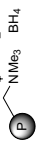
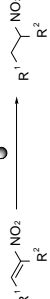

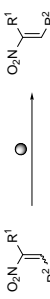
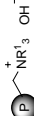
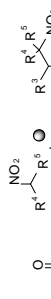
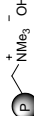
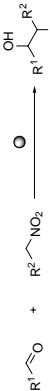
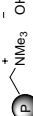

3.33 Nitriles—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 X = S, SO, SO <sub>2</sub> (2.6-3.5 mmol g <sup>-1</sup> )	$R^1-CH_2-Br \xrightarrow{KCN, \bullet} R^1-CH_2-CN$ 2 examples R <sup>1</sup> = alkyl	C:20-74	Several other polymers investigated, best example given. Experimental section.	1152, 1131	1152, 1131
 Seralite SRA-400 Borohydride form (3.3 mmol g <sup>-1</sup> )	 3 examples R <sup>1</sup> = alkyl	Y:95	Resin may be regenerated and reused. General procedure.	432	
 Amberlite IRA-400 Borohydride form (3.0 mmol g <sup>-1</sup> )	 3 examples R <sup>1</sup> , R <sup>2</sup> , R <sup>3</sup> = H, alkyl	Y:92-99	For slow reducing systems the addition of 0.05 eq. of Ni(OAc) <sub>2</sub> increased the reaction rate. Only α,β-unsaturated alkenes reduced. General procedure.	433	433
	 1 example		Kinetic study.	1153	1154
 (1.1 mmol g <sup>-1</sup> )	 1 example		Reaction used to investigate catalytic properties of phase transfer catalyst.	1155	542
 (3.4 mmol g <sup>-1</sup> ) R <sup>1</sup> = alkyl	 4 examples R <sup>2</sup> , R <sup>3</sup> = alkyl R <sup>4</sup> = alkyl, aryl	Y:40-98	General procedure.	260	260

### 3.34 Nitro compounds

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst IRA-900 Nitrite form	$R^1-X \xrightarrow{\bullet} R^1-NO_2$ <p>7 examples  <math>R^1 = \text{alkyl, benzyl}</math>  <math>X = \text{Br, Cl}</math></p>	Y:10-100	Experimental section.	833	833
 (1.0 mmol g <sup>-1</sup> )	$R^1-X \xrightarrow{\bullet} R^1-NO_2$ <p>3 examples  <math>R^1 = \text{alkyl, benzyl}</math>  <math>X = \text{Br, Cl}</math></p>	Y:33-98	Experimental section.	1014	1014
 Nafion-H	 <p>9 examples  <math>R^1 = \text{H, alkyl, amine}</math>  <math>R^2 = \text{H, alkyl}</math></p>	Y:77-98	No di-nitration was observed. <i>Ortho-para</i> substitution was favoured. General procedure. Also see references 1156, 1157.	1158	
 (11.0 mmol g <sup>-1</sup> )	 <p>11 examples  <math>R^1 = \text{H, alkyl, hal, nitro}</math>  <math>R^2 = \text{H, Cl}</math></p>	C:90-100	Little over-nitration observed. General procedure. $Fe(NO_3)_3$ on Montmorillonite K 10 has also been used. <sup>1159, 1160, 1161</sup>	1162	1162
 (2.6 mmol g <sup>-1</sup> )	 <p>1 example</p>	Y:93	Reaction performed in the vapour phase in a flow reactor. Also see references 1163, 480.	1164	
 (2.5 mmol g <sup>-1</sup> )	 <p>6 examples  <math>R^1 = \text{H, alkyl, hydroxy, O-alkyl}</math></p>	Y:78-88	Polymer may be regenerated without loss of activity. Experimental section.	692	692

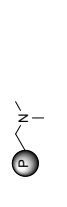
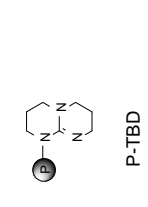
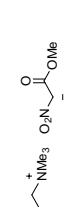

3.34 Nitro compounds—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlite IRA-400 Borohydride form (2.5 mmol g <sup>-1</sup> )	 7 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl	Y:78-83	Store under nitrogen at room temperature. General procedure. Also see reference 1165.	431	575, 431
 Amberlite IR-400 Hydroxide form	 6 examples R <sup>1</sup> = alkyl R <sup>2</sup> = alkyl, aryl	Y:65-100	Polymeric reagent is comparable to triphenylphosphine and superior to triethylamine.	1166	
 Amberlite IR-4B Hydroxide form R <sup>2</sup> = H, alkyl	 18 examples R <sup>3</sup> = H, alkyl, aryl R <sup>1</sup> , R <sup>2</sup> = H, alkyl	C:0-69	Comparison of the resins shown. Ketones give low conversions. Experimental section.	1167	
 Amberlite IRA-420 Hydroxide form DOWEX-1 Hydroxide form	 8 examples R <sup>1</sup> = aryl R <sup>2</sup> = alkyl	Y:27-77 P:90->98	Without an excess of the nitromethylene compound, Amberlite IRA-420 hydroxide form effected a Cannizzaro reaction. In combination with a solid-supported oxidant, this reaction could be used to generate benzoic acids.	70	70
 Amberlyst A-21 Hydroxide form	 1 example	Y:>79	Experimental section.	71	


Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 P-TBD (2.2 mmol g <sup>-1</sup> )	 R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = H, alkyl, aryl, O-alkyl	Y:74-95	The polymeric reagent was as effective as the monomeric guanidine base. Vinylogous nitroaldol reactions also demonstrated.	1168	1168
 A	 4 examples R <sup>1</sup> = H, alkyl R <sup>2</sup> = alkyl, aryl	Y:3-73	Yields are low. KF works more effectively. Full experimental section.	1169	
 B Envirocat EPZG	 11 examples R <sup>1</sup> = alkyl, aryl, het R <sup>2</sup> = H, alkyl	Y:90-97	General procedure.	112	
 P(NMe <sub>2</sub> ) <sub>3</sub>	 1 example	Y:70	Experimental section.	470	471
 Amberlite IRA-420 Hydroxide form	 8 examples R <sup>1</sup> = H, F, O-alkyl, nitro R <sup>2</sup> = H, alkyl	Y:100	One step of a multi-step natural product synthesis. The Henry product was found to be unstable, and therefore derivatised immediately.	77, 70	
 Amberlyst IRA-400 (2.2-2.5 mmol g <sup>-1</sup> )	 6 examples R <sup>1</sup> = alkyl, benzyl X= Br, I	Y:35-70	Resin stable in dry state for several months. Reagent was also used to effect Michael additions. General procedure.	1170	1170

3.34 Nitro compounds—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (3.5 mmol g <sup>-1</sup> )	 14 examples R <sup>1</sup> , R <sup>3</sup> = alkyl R <sup>2</sup> = H, alkyl, aryl R <sup>4</sup> = alkyl, O-Alkyl	Y:0-100	If β-carbon atom was hindered yields were low. Mono-Michael adducts were always formed. General procedure.	1171	1171
 (6.7 mmol g <sup>-1</sup> )	 1 example	Y:74	General procedure.	478	478
 Amberlite IRA-400 Hydroxide form Amberlite IRA-410 Hydroxide form	 1 example	Y:91	Resin was stable to reaction conditions and storage. General procedures.	649	
 Amberlite IRA-400 Hydroxide form Amberlite IRA-410 Hydroxide form	 8 examples R <sup>1</sup> = alkyl R <sup>2</sup> = H, alkyl R <sup>3</sup> = ester, ketone, nitrile	Y:36-90	Addition of β-ketoesters and malonates also described but yields were generally low.	1172	
 Amberlyst A-27 Chloride form	 22 examples R <sup>1</sup> = H, alkyl R <sup>2</sup> = alkyl R <sup>3</sup> = H, alkyl R <sup>4</sup> = ester, ketone, nitrile, sulfonate	Y:55-93	Reactions carried out in the absence of solvent and did not require excess nitroalkane as other methods did. General procedure.	1173	

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-21	$R^1-NO_2 \xrightarrow{CO_2CH_3} R^1-NO_2-CO_2CH_3$ 9 examples $R^1 = \text{alkyl, aryl}$	Y:51-85	Procedure works well on gram scale and good results were obtained with acid- or base-sensitive substrates. Experimental section.	1174	
 P-TBD (2.2 mmol g <sup>-1</sup> )	$R^1-CH=CH-R^2 \xrightarrow{CH_3NO_2} R^1-CH(NO_2)-CH_2-R^2$ $R^1-CH=CH-R^2 \xrightarrow{O_2N-CH_2-CO-R^3} R^1-CH(O_2N-CH_2-CO-R^3)-CH_2-R^2$ $R^3 = H, \text{ alkyl, aryl, O-alkyl}$	Y:70-95	The polymeric reagent was as effective as the monomeric guanidine base. Nitroaldol Henry reaction was also demonstrated	1168	1168
 Amberlyst IRA-400 (2.2-2.5 mmol g <sup>-1</sup> )	$CH_2=CH-X \xrightarrow{MeO-CO-CH_2-NO_2} MeO-CO-CH_2-CH_2-CH_2-X$ 2 examples $R^1 = H, O\text{-alkyl}$ $X = \text{ester, nitrile}$	Y:62-75	Resin stable in dry state for several months. Reagent can also be used to effect Michael additions. General procedure.	1170	1170
 Amberlyst A-26 Nitrate form	$R^1-OR^2 \xrightarrow{ONO_2} R^1-ONO_2$ 4 examples $R^1 = \text{alkyl}$ $R^2 = \text{alkyl, aryl}$ $R^3 = Ms, Ts$	Y:80-90	General procedure.	1175	1175

### 3.35 Nitrones

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst IR-27 Perruthenate form (1.0 mmol g <sup>-1</sup> )	$R^1-N(R^2)-OH \xrightarrow{O} R^1-N^+(R^2)=O^-$ 3 examples $R^1, R^2 = \text{alkyl}$	Y:55-91	The product was used in conjunction with a dipolarophile to form isoxazolidines. Yields quoted were over the two-step process. General procedure.	45	45

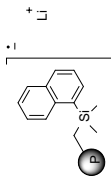
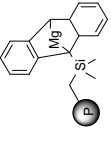
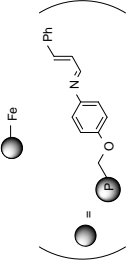

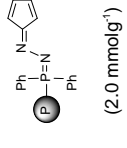
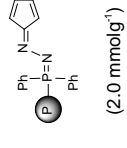
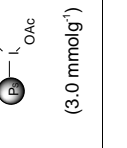
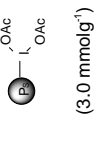
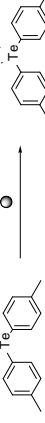
### 3.36 N-Oxides

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (2.5 mmol g <sup>-1</sup> )	 4 examples R <sup>1</sup> = H, alkyl R <sup>2</sup> = H, alkyl, amine	Y:80-85	Polymer may be regenerated without loss of activity. Experimental section.	692	692


### 3.37 Organometallics

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 ( = copolymer of 2-vinylnaphthalene, styrene and divinylbenzene )	$R^1-Cl \xrightarrow[\text{Li powder}]{\bullet} R^1-Li$ 22 examples R <sup>1</sup> = alkyl, benzyl	Y:48-99	Catalyst recyclable. Lithiated species was subsequently reacted with aldehydes, ketones, imines and silyl chlorides. There was no detected loss of activity in experiments using recycled catalyst. General procedure.	568	568
 ( = copolymer of 2-vinylnaphthalene, styrene and divinylbenzene )	$R^1-Cl \xrightarrow[\text{Li powder}]{\bullet} R^1-Li$ 19 examples R <sup>1</sup> = alkyl, benzyl	Y:58-98	Catalyst recyclable. Lithiated species was subsequently reacted with aldehydes, ketones, imines and silyl chlorides. No detected loss of activity in experiments using recycled catalyst. General procedure.	567, 568	567, 568
	$R^1-X \xrightarrow{\bullet} R^1-Li$ 8 examples R <sup>1</sup> = alkyl, aryl X = hal, nitrile	Y:>75	Recyclable reagent. Reaction also carried out with sodium. General procedure.	1176	1176, 1177
	$R^1-H \xrightarrow{\bullet} R^1-Li$ 4 examples R <sup>1</sup> = alkyl, aryl	Y:>75	Resin may be regenerated and reused without loss of activity. General procedure.	1177	1177


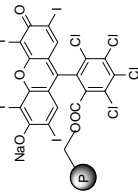
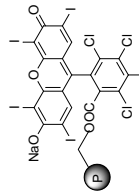


Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
	$R^1-CN \xrightarrow{\text{O}} R^1-\overset{NH}{C}-Li$ 2 examples $R^1 = \text{alkyl, aryl}$	Y:>75	Resin may be regenerated and reused without loss of activity. General procedure.	1177	1177
 (1.3-4.1 mmol g <sup>-1</sup> )	$R^1-X \xrightarrow{\text{O}} R^1-\overset{MgX}{C}$ 26 examples $R^1 = \text{allyl, aryl}$ $X = Cl, I$	Y:80-95	Reagent is as effective as the monomeric analogue. Full experimental section.	1178, 1179	1178
	 1 example	Y:83	Irontricarboxyl transfer reagent may be regenerated and reused up to six times.	1180	1180
 (2.0 mmol g <sup>-1</sup> )	$\text{Re(CO)}_3(\text{C-HCN})_3 \xrightarrow{\text{TiO}^-} \text{Re(CO)}_3(\text{C-HCN})_2 \text{OC(O)R}^1$ 5 examples $R^1 = \text{alkyl, aryl}$	Y:60-71	Reagent is considerably more stable than solution phase counterpart. Experimental section.	1181	1181
 (2.0 mmol g <sup>-1</sup> )	$\text{Re(CO)}_3(\text{C-HCN})_3 \xrightarrow{\text{TiO}^-} \text{Re(CO)}_3(\text{C-HCN})_2 \text{OC(O)R}^1$ 5 examples $R^1 = \text{alkenyl, aryl}$	Y:41-56	Experimental section.	1181	1181
 (3.0 mmol g <sup>-1</sup> )	$\text{Ph}^1\text{-Te-Te-Ph} \xrightarrow{\text{O}} \text{Ph}^1\text{-Te-Te-OC(O)R}^1$ 1 example	Y:72	Soluble resin is as active as solution phase equivalent. Used reagent may be regenerated and recycled without loss of activity. Experimental section.	315	315
 (3.0 mmol g <sup>-1</sup> )	 1 example	Y:71	Soluble resin is as active as solution phase equivalent. Used reagent may be regenerated and recycled without loss of activity. Experimental section.	315	315

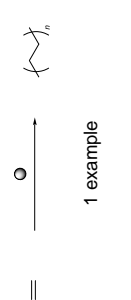
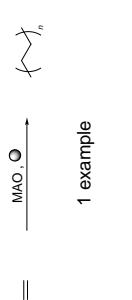
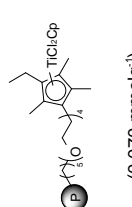
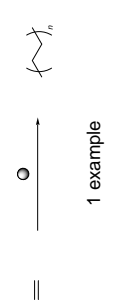
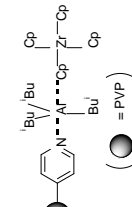
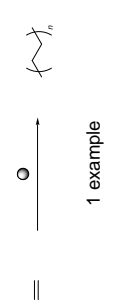
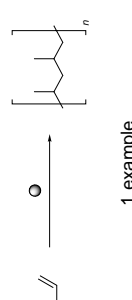
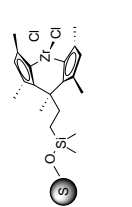
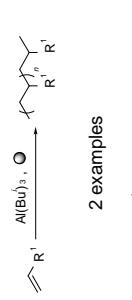
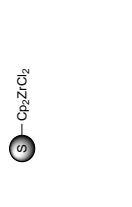
### 3.38 Oximes

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-27	$\text{R}^1-\text{C}(=\text{O})-\text{R}^2 \xrightarrow{\text{NH}_2\text{OH}\cdot\text{HCl}} \text{R}^1-\text{C}(\text{N}^+\text{OH})-\text{R}^2$ <p>18 examples  <math>\text{R}^1 = \text{alkyl, aryl}</math>  <math>\text{R}^2 = \text{H, alkyl, aryl}</math></p>	Y:70-100	Labile functional groups were not affected.	1182	

### 3.39 Peroxides

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (2.5 mmol g <sup>-1</sup> ) Bio-Rad 50W Peroxid form	$\text{R}^1-\text{C}(=\text{O})-\text{OH} \xrightarrow{\text{O}_2} \text{R}^1-\text{C}(=\text{O})-\text{O}-\text{O}-\text{H}$ <p>5 examples  <math>\text{R}^1 = \text{aryl}</math></p>	Y:85-95	General procedure.	691	691
	$\text{C}_6\text{H}_6 \xrightarrow{\text{O}_2} \text{C}_6\text{H}_6\text{O}_2$ <p>1 example</p>	Y:69	Polymer-supported Rose Bengal is used to sensitize the generation of singlet molecular oxygen.	821	821
	$\text{C}_6\text{H}_6 \xrightarrow{\text{O}_2} \text{C}_6\text{H}_6\text{O}_2$ <p>1 example</p>	Y:82	Polymer-supported Rose Bengal is used to sensitize the generation of singlet molecular oxygen.	821	821

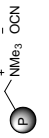
### 3.40 Polymers

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>TiCl<sub>4</sub> (= Polythene) 1 example</p>	1185	1185	Polythene produced has a low distribution of molecular weight. Experimental section. Also see references 1183, 1184.	1185	1185
 <p>MAO,  1 example</p>	1186	1186	Resin fully characterised using a range of analytical techniques.	1186	1186
 <p> 1 example</p>	1191	1191	Kinetic study. Catalyst produces polymers with low molecular weight distribution. Experimental section. Also see references 1187, 1188, 1189, 1190.	1191	1191
 <p>Ni(COD) (1.2 mmol g<sup>-1</sup>) 1 example</p>	1194	1194	Catalyst can be recovered and recycled. Experimental section. Also see references 1192, 1193.	1194	1194
 <p> 1 example</p>	1198	1198	Polymer is C <sub>2</sub> -symmetric but does not give an isotactic polymer. Also see references 1195, 1196, 1197.	1198	1198
 <p> 2 examples R<sup>1</sup> = H, alkyl</p>	1199	1199	Negligible leaching of catalyst observed. Consistent molecular weight polymers. Experimental procedure.	1199	1199

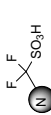


3.40 Polymers—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
$\left( \text{P} \begin{array}{c} \text{CO}_2 \\   \\ \text{CO}_2 \end{array} \right)_n \text{LnCl}_{3-n}$ <p>Ln= Nd (0.86 mmolg<sup>-1</sup>) Ln= Ce (1.2 mmolg<sup>-1</sup>)</p>	<p>R<sup>1</sup> = alkyl</p>		Catalyst may be recycled. Experimental section.	1200	1200
<p>(0.10-0.60 mmolg<sup>-1</sup>) L = Ph, Cy</p>	<p>1 example</p>		Experimental section.	1201	1201
<p>H N—RuCl₂(PPPh)₂</p>			Ethyl 2-bromoisobutyrate used to initiate reaction. On recycling there is a 25% decrease in activity of the catalyst. Experimental section.	1202	1202
<p>V(v)</p> <p>Glycidymethacrylate-ethylene glycol dimethylacrylate polymer</p>	<p>1 example</p>	Y:100	Polymer does not leach metal and may be successfully recycled. Experimental section.	1203	1203
<p>Fe(II)</p>	<p>1 example</p>		Polymer weight and yield greater than that obtained from homogeneous catalyst. Experimental section.	1204	1204


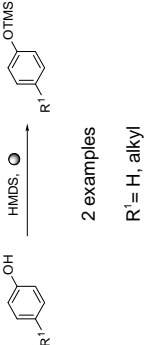


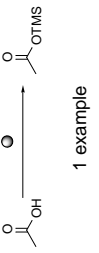

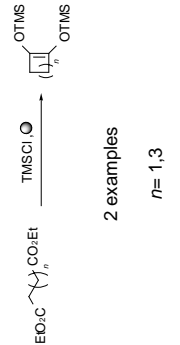


### 3.41 Ureas

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Cyanate form (3.9 mmol g <sup>-1</sup> )	$R^1-X \xrightarrow{\bullet} [R^1-NCO] \longrightarrow R^1-NH-C(=O)-N^+R^1$ <p>8 examples            R<sup>1</sup> = alkyl, allyl, benzyl</p>	Y:38-93	The reagent must be refrigerated to prevent decomposition. The isocyanates decompose spontaneously to ureas under the reaction conditions. In ethanol, <i>N</i> -substituted urethanes were isolated. Full experimental section.	1125	1125

### 3.42 Silyl containing compounds

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Nafion-H	$R^1-OH + \text{SiMe}_3 \longrightarrow R^1-OTMS$ <p>9 examples            R<sup>1</sup> = alkyl, aryl, carbonyl</p>	Y:89-97	General procedure.	119	
 Kaolinitic clay	$R^1-OH \xrightarrow{HMDS, \bullet} R^1-OTMS$ <p>6 examples            R<sup>1</sup> = alkyl, allyl, aryl</p>	Y:85-95	Easy protection of acid sensitive alcohols.	122	123
 Envirocat EPZG	$R^1-OH \xrightarrow{HMDS, \bullet} R^1-OTMS$ <p>6 examples            R<sup>1</sup> = alkyl, aryl            R<sup>2</sup> = H, alkyl, ketone            R<sup>3</sup> = H, alkyl</p>	Y:70-92	Silylation was selective for alcohols over thiols. General procedure.	1205	

3.42 Silyl containing compounds—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Envirocat EPZG	 2 examples R <sup>1</sup> = H, alkyl	Y:94-96	Silylation was selective for phenols over thiophenols. General procedure.	1205	
 Nafion-TMS (0.80 mmol g <sup>-1</sup> )	$R^1-XH \longrightarrow R^1-XTMS$ 4 examples R <sup>1</sup> = alkyl, aryl X = O, S, N-alkyl	Y:86-100	Reagent is air stable. General procedure.	91, 90	91
 Nafion-TMS (0.80 mmol g <sup>-1</sup> )	 1 example	Y:54	General procedure.	91	91
 ( = polyethylene) (2.2 mmol g <sup>-1</sup> )	 2 examples n = 1, 3	Y:44-70	Trimethylsilyl modification of the acyl/oin reaction. Experimental section.	1087	1087
 Kraton D1102	 1 example		Kinetic studies.	1206	1206

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 $\text{[Rh(COD)Cl]P}$	 1 example		Experimental section.	1207	1207
 Kraton D11102	$\text{R}^1\text{C}=\text{C} \xrightarrow{\text{HSiEt}_3} \text{R}^1\text{CH}_2\text{CH}(\text{SiEt}_3)$ 2 examples $\text{R}^1 = \text{alkyl, aryl}$		Kinetic studies. Also see references 1208, 374, 1209, 1210, 1211.	1206	1206
 (0.084 mmol <sup>-1</sup> )	$\text{R}^1\text{C}=\text{C}(\text{R}^2) \xrightarrow{\text{R}^3\text{R}^4_2\text{SiH}_4} \text{R}^1\text{CH}_2\text{CH}(\text{SiR}^3\text{R}^4_2)\text{R}^2$ 7 examples $\text{R}^1 = \text{alkyl}$ $\text{R}^2 = \text{H, alkyl}$ $\text{R}^3 = \text{alkyl, O-alkyl}$ $\text{R}^4 = \text{alkyl, Cl, O-alkyl}$	Y:0-95	Catalyst may be reused without loss of activity. Experimental section.	1212	1212
 $\text{P-PPh}_2\text{PdCl}_2$	 1 example	Y:85	Full experimental section.	586	586

### 3.43 Sulfur containing compounds

#### 3.43.1 Sulfur containing compounds (Thiols)

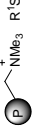
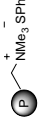

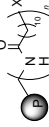
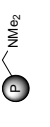
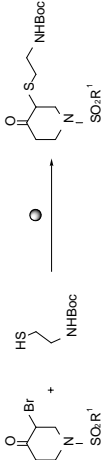
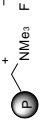
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Tulsion A-27 Hydrosulfide form	$\text{R}^1\text{-X} \xrightarrow{\text{S}} \text{R}^1\text{-SH}$ 7 examples $\text{R}^1 = \text{alkyl, benzyl}$ $\text{X} = \text{Hal}$	Y:93-98	Tulsion A-27 supported hydrosulfide has more nucleophilic character than NaSH. Experimental section. Also see reference 1213.	1214	1214

3.43.1 Sulfur containing compounds (Thiols)—continued

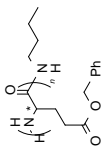
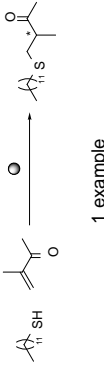




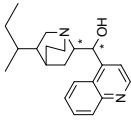
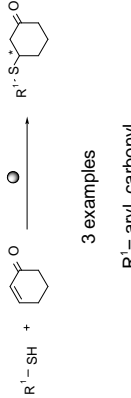
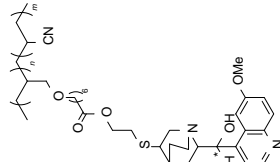
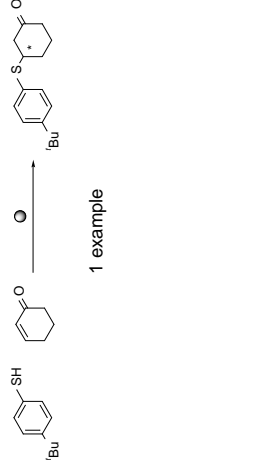
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
<p>Amberlite IRA-400 Borohydride form (3.0 mmol g<sup>-1</sup>)</p>	$R^1-SAC \xrightarrow{Pd(OAc)_2 \cdot O} R^1-SH$ <p>8 examples R<sup>1</sup> = alkyl, aryl, benzyl</p>	Y:91-98	General procedure.	37	37
<p><b>A</b></p> <p>Amberlite IRA-400 Thioacetate form (3.7 mmol g<sup>-1</sup>)</p> <p><b>B</b></p> <p>Amberlite IRA-400 Borohydride form (3.0 mmol g<sup>-1</sup>)</p>	$R^1-X \xrightarrow{MeOH, O^A} R^1-SAC \xrightarrow{Pd(OAc)_2 \cdot O^B} R^1-SH$ <p>10 examples R<sup>1</sup> = alkyl, benzyl, vinyl X = Br, Cl, OTs</p>	Y:87-98	Two polymer bound reagents used in a one-pot conversion of alkyl halides to thiols. General procedure.	37	37
<p>Bio-Rad 50W Peracid form</p>	$R^1, R^2-S-S \xrightarrow{\text{General schematic given}} R^1-SH + R^2-SH$ <p>4 examples R<sup>1</sup> = amino acid</p>	C:>90	General procedure.	691	691
<p>( = aminoethyl cellulose or Sephadex or Sepharose )</p>	$R^1, R^2-S-S \xrightarrow{\text{General schematic given}} R^1-SH + R^2-SH$ <p>General schematic given</p>		R <sup>1</sup> and R <sup>2</sup> not defined in the paper. The polymeric reagent is stable at room temperature when dry. Experimental section.	1215	1215

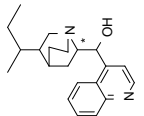
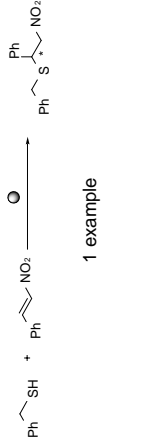
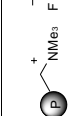
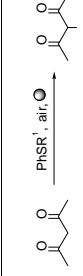
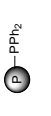

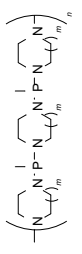
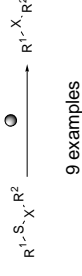
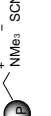
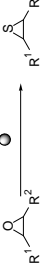


### 3.43.2 Sulfur containing compounds (Sulfides)

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Sulfide form R <sup>1</sup> = alkyl, aryl (1.5 mmol g <sup>-1</sup> )	$R^2-X \xrightarrow{\text{O}} R^1-S-R^2$ 7 examples R <sup>2</sup> = alkyl X = Br, Cl, OTs	Y:72-95	Spent reagent can be regenerated. Experimental section.	1216	1216
 Amberlite IRA-400 Arylsulfide form	$X-C(R^1)-R^2 \xrightarrow{\text{O}} R^1-S(R^2)-SPh$ 35 examples R <sup>1</sup> = alkyl, propargyl, benzyl, ketone R <sup>2</sup> = H, alkyl X = hal, OTs	Y:0-95	No sulfur contamination of product observed. Experimental section.	1217	1217
 (2.7 mmol g <sup>-1</sup> )	$R^1-Br \xrightarrow{\text{O}} R^1-S-R^1$ 4 examples R <sup>1</sup> = aryl	Y:13-65	Used for the preparation of various cyclic thioethers. General procedure.	1218	1218
 X = Br, Cl r = 0-1	$R^1-Br \xrightarrow{KSPH_2O} R^1-SPh$ 1 example	Y:97-100	Reaction carried out on multi-gram scale. Experimental section.	855	855
 Amberlyst A-21	 4 examples R <sup>1</sup> = aryl		One step of a multi-step library synthesis.	57	
 Dowex-MSA-1 Fluoride form	$R^1-SPh \xrightarrow{PhSH_2O} R^1-SPh$ 1 example	Y:80	Also see reference 1219.	846	846

3.43.2 Sulfur containing compounds (Sulfides)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
		ee:47	Several other polyamino acids were investigated. The best result is displayed.	1220	
	 R <sup>1</sup> = H, alkyl, aryl R <sup>2</sup> = H, alkyl R <sup>3</sup> = alkyl, aryl, N-alkyl, O-alkyl	C:40-100	Some enantioselectivity observed.	1221	1221
 (6.7 mmol g <sup>-1</sup> )	 R <sup>1</sup> = aryl	ee:10-24	Polymer gives greater enantioselectivity than monomer. General procedure.	1222	1222
 (0.65 mmol g <sup>-1</sup> )	 R <sup>1</sup> = aryl, carbonyl	Y:74-98 ee:18-45	Experimental section.	1223	1223
	 R <sup>1</sup> = aryl	Y:89 ee:8	Several resins with different linker chains investigated, best results given. Experimental section.	673	673



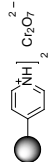

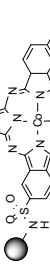
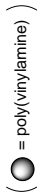

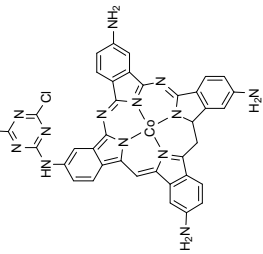
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (0.65 mmol g <sup>-1</sup> )	 1 example	Y:99-100 ee:12-15	Various cinchona alkaloids derived catalysts were investigated. The best example is shown. Experimental section.	1223	1223
 Dowex-MSA-1 Fluoride form	 2 examples R <sup>1</sup> = H, SPh	Y:75		846	846
 (3.3 mmol g <sup>-1</sup> )	 10 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = alkyl, aryl, vinyl	Y:81-99	Broad tolerance of functional groups. Experimental section.	1224	1224
 2 examples m = 1, 2	 9 examples R <sup>1</sup> , R <sup>2</sup> = alkyl, aryl, benzyl X = S, SO, SO <sub>2</sub>	Y:58-99	The polymers exhibited the anticipated properties of aminophosphines and reacted with carbon tetrachloride, alcohols and water. General procedure.	1225	1225
 Amberlite IRA-400 Thiocyanate form (1.7 mmol g <sup>-1</sup> )	 5 examples R <sup>1</sup> = aryl, alkyl R <sup>2</sup> = H, alkyl	Y:80-93	Spent reagent can be regenerated. General procedure.	1226	1226

### 3.43.2 Sulfur containing compounds (Sulfides)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Fluoride form (3.4 mmol g <sup>-1</sup> )	$\text{(ClCH}_2\text{)}_2\text{S} \xrightarrow{\text{O}} \text{(CH}_2\text{)}_2\text{S}$ 1 example	Y:32-57	Optimisation study. Full experimental section.	1227	1227
 R <sup>1</sup> =alkyl n=1-7 X=P, N (1.4-3.2 mmol g <sup>-1</sup> )	 6 examples R <sup>2</sup> , R <sup>3</sup> = alkyl, aryl	Y:67-89	Kinetic study. Experimental section.	1228	1228
 (1.9 mmol g <sup>-1</sup> )	 1 example	Y:82	Experimental section.	1229	

### 3.43.3 Sulfur containing compounds (Disulfides)

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (= PVP) (3.8 mmol g <sup>-1</sup> )	$\text{R}^1\text{-SH} \xrightarrow{\text{O}} \text{R}^1\text{-S-S-R}^1$ 9 examples R <sup>1</sup> = alkyl, amino acid, aryl	Y:36-96	Other functionality tolerated. Experimental section.	1230	1230
 (3.0 mmol g <sup>-1</sup> )	$\text{R}^1\text{-SH} \xrightarrow{\text{O}} \text{R}^1\text{-S-S-R}^1$ 3 examples R <sup>1</sup> = aryl, benzyl	Y:89-93	Soluble resin is as active as the solution phase equivalent. Used reagent may be regenerated and recycled without loss of activity Experimental section.	315	315

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
  (1.2 mmol g <sup>-1</sup> )	$R^1-SH \xrightarrow{\text{O}} R^1-S-S-R^1$ 4 examples R <sup>1</sup> = alkyl, aryl, benzyl, het	Y:80-100	Reagent also oxidises alcohols, amines and oximes. General procedure.	192	192
  (1.9-2.0 mmol g <sup>-1</sup> )	$R^1-SH \xrightarrow{\text{O}} R^1-S-S-R^1$ 3 examples R <sup>1</sup> = aryl, benzyl, het	Y:80-100	Reagent also oxidises alcohols, amines and oximes. General procedure.	311	311
  ( = poly(vinylamine) )	$\sim SH \xrightarrow{O_2, \text{O}} \sim S-S \sim$ 1 example		The polymeric catalyst exhibits enzyme-like behaviour which resembles the catalytic action of vitamin B12 in the oxidation of thiols. Experimental section.	1231, 1232	1231, 1232
 	$HO \sim SH \xrightarrow{O_2, \text{O}} HO \sim S-S \sim OH$ 1 example		Kinetic study. Catalyst may be reused without loss of activity. General procedure.	1233	1233


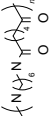
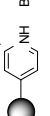


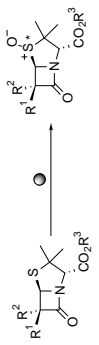

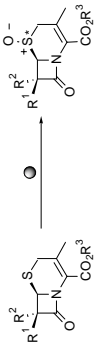
3.43.3 Sulfur containing compounds (Disulfides)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Bromate form (3.2 mmol g <sup>-1</sup> )	 1 example	Y:80	HBr is removed by the resin. General procedure. Fe(NO <sub>3</sub> ) <sub>3</sub> supported on Montmorillonite K 10 has also been used. <sup>1,234</sup>	228	228
 (0.21 mmol g <sup>-1</sup> )	 8 examples	Y:73-92	Intramolecular disulfide formation in peptides. No cysteine dimers are formed. Full experimental section.	1235	1235
 (1.2-1.5 mmol g <sup>-1</sup> )	$R^1-X \xrightarrow{\text{O}} R^1-S-S-R^1$ 11 examples R <sup>1</sup> = alkyl, allyl, benzyl, ester X = Br, Cl, OTs	Y:46-97	Reagent can be regenerated. Experimental section.	1216	1216
 Amberlyst A-26 Disulfide form (1.2-1.5 mmol g <sup>-1</sup> )	 7 examples R <sup>1</sup> = alkyl, allyl, aryl, benzyl	Y:83-98	Reagent can be regenerated. General procedure.	1236	1236
 Kaolinitic clay	$R^1-H \xrightarrow{S_2Cl_2, \text{O}} R^1-S-S-R^1$ 9 examples R <sup>1</sup> = vinyl, aryl	Y:65-85	Catalyst may be reused without loss of activity.	1237	

### 3.43.4 Sulfur containing compounds (Sulfoxides)




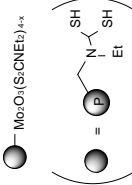
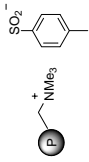
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
<p><b>A</b> <math>\text{AlO}_4</math> (0.94 mmol g<sup>-1</sup>)</p>	$\text{R}^1-\text{S}-\text{R}^2 \xrightarrow{\text{MW, O}} \text{R}^1-\overset{\text{O}}{\text{S}}-\text{R}^2$ <p>8 examples R<sup>1</sup>, R<sup>2</sup> = alkyl, aryl, benzyl</p>	Y:76-85	Alumina must be wet for reaction to occur. Less than 5% of the sulfone is formed. General procedure. Also see references 1238, 1239.	1240	1240
<p><b>B</b> <math>\text{NMe}_3^+ \text{IO}_4^-</math> Amberlyst A-26 Periodate form (1.4 mmol g<sup>-1</sup>) Amberlite IRA-904 Periodate form (1.6 mmol g<sup>-1</sup>)</p>	$\text{R}^1-\text{S}-\text{R}^2 \xrightarrow{\text{O}} \text{R}^1-\overset{\text{O}}{\text{S}}-\text{R}^2$ <p>5 examples R<sup>1</sup>, R<sup>2</sup> = alkyl, aryl, benzyl</p>	Y:81-99	Supported periodate can also be used for cleavage of 1,2-diols and oxidation of alcohols to carbonyls. Experimental section.	241	241
<p><b>F</b> <math>\begin{matrix} \text{OAc} \\   \\ \text{P} \\   \\ \text{OAc} \end{matrix}</math> (3.0 mmol g<sup>-1</sup>)</p>	$\text{R}^1-\text{S}-\text{R}^2 \xrightarrow{\text{MW, O}} \text{R}^1-\overset{\text{O}}{\text{S}}-\text{R}^2$ <p>3 examples R<sup>1</sup> = aryl, benzyl</p>	Y:65-80	Soluble resin is as active as the solution phase equivalent. Spent reagent may be regenerated and recycled without loss of activity. Experimental section.	315	315
<p><b>P</b> <math>\begin{matrix} \text{OAc} \\   \\ \text{P} \\   \\ \text{OAc} \end{matrix}</math></p>	$\text{R}^1-\text{S}-\text{R}^2 \xrightarrow{\text{O}} \text{R}^1-\overset{\text{O}}{\text{S}}-\text{R}^2$ <p>3 examples R<sup>1</sup>, R<sup>2</sup> = alkyl, aryl</p>	Y:2-84	Sulfoxides were the major products when R <sup>1</sup> and R <sup>2</sup> were alkyl. Sulfones were formed preferentially when R <sup>1</sup> and R <sup>2</sup> were aryl.	74	74
<p><b>G</b> <math>\text{Fe}(\text{NO}_3)_3</math> Clayfen</p>	$\text{R}^1-\text{S}-\text{R}^2 \xrightarrow{\text{MW, O}} \text{R}^1-\overset{\text{O}}{\text{S}}-\text{R}^2$ <p>9 examples R<sup>1</sup>, R<sup>2</sup> = alkyl, benzyl, phenyl</p>	Y: 15-91	Less than 5% over-oxidation observed. General procedure.	1241	
<p><b>S</b> MMPP</p>	$\text{R}^1-\text{S}-\text{R}^2 \xrightarrow{\text{O}} \text{R}^1-\overset{\text{O}}{\text{S}}-\text{R}^2$ <p>20 examples R<sup>1</sup> = alkyl, aryl, vinyl R<sup>2</sup> = alkyl, allyl, aryl, vinyl</p>	Y:89-100	Steric bulk has no effect on this procedure. Reactions can be carried out in the presence of other oxidisable functional groups. Full experimental section.	1242	1242

3.43.4 Sulfur containing compounds (Sulfoxides)—continued




Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 $R^1-S-R^2$ 14 examples $R^1, R^2 = \text{alkyl, aryl, allyl}$	$R^1-S-R^2 \xrightarrow{H_2O, O} R^1-S^+(R^2)-O^-$	Y:80-100	Reactions can be carried out in the presence of other oxidisable functional groups. Full experimental section.	1243	1243
 $R^1-S-R^2$ $R^1 = \text{aryl, benzyl}$ $R^2 = \text{alkyl, aryl, benzyl}$	$R^1-S-R^2 \xrightarrow{H_2O, O} R^1-S^+(R^2)-O^-$	Y:92-100	When reaction is carried out in $^{18}O$ labelled water, full incorporation of $^{18}O$ is observed.	1244	1245
  $R^1-S-R^2 + H_2O \xrightarrow{\text{electric current, } \bullet} R^1-S-R^2$ 4 examples $R^1 = \text{alkyl, aryl}$ $R^2 = \text{alkyl}$	$R^1-S-R^2 \xrightarrow{\text{electric current, } \bullet} R^1-S-R^2$	Y:78-100	The resin may be reused without loss of activity. General procedure.	1246	230
 $R^1-S-R^2$ 9 examples $R^1 = \text{H, amide, hal, phthalimide}$ $R^2 = \text{H, hal}$ $R^3 = \text{H, alkyl, aryl}$	 $R^1-S-R^2 \xrightarrow{\bullet} R^1-S^+(R^2)-O^-$	Y:69-100 P:71-100	Stereoselectivity for (R)- or (S)-sulfoxide is observed. General procedure.	1247	1247
 $R^1-S-R^2$ 3 examples $R^1 = \text{amide}$ $R^2 = \text{H}$ $R^3 = \text{H, alkyl, aryl}$	 $R^1-S-R^2 \xrightarrow{\bullet} R^1-S^+(R^2)-O^-$	Y:90-100 P:98-100	Stereoselectivity for (R)- or (S)-sulfoxide is observed. General procedure.	1247	1247




### 3.43.5 Sulfur containing compounds (Sulfones)

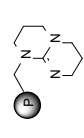
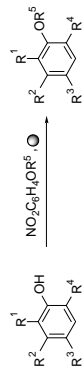
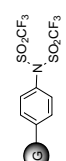
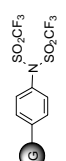
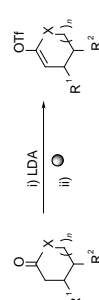
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 $R^1-S-R^2 \xrightarrow{MW, O} R^1-S(=O)-R^2$ 8 examples $R^1, R^2 = \text{alkyl, benzyl, aryl}$	$R^1-S-R^2 \xrightarrow{O} R^1-S(=O)-R^2$ 2 examples (L)-Methionine Tetrahydrothiophene	Y:72-93	Supported reagent must be wet. General procedure.	1240	1240
 (3.9 mmol g <sup>-1</sup> )	$R^1-S-R^2 \xrightarrow{BuOH, O} R^1-S(=O)-R^2$ 3 examples $R^1 = \text{alkyl, aryl}$ $R^2 = \text{aryl, benzyl}$	Y:94-100	Using more than two equivalents of reagent, the reaction can be forced to completion, yielding only the sulfone product. General procedure. Also see reference 1248.	1247	684
	$-S- \xrightarrow{BuOH, O} -S(=O)-$ 1 example	Y:4-95	Chemoselective oxidation of sulfide in the presence of alkenes. General procedure.	1249	1249
 (0.70 mmol g <sup>-1</sup> )	$R^1-X \xrightarrow{O} R^1-S(=O)-$ 10 examples $R^1 = \text{alkyl, allyl, benzyl}$ $X = \text{Br, Cl, I}$	Y:70	Some leaching of metal occurs when treated with <sup>t</sup> BuO <sub>2</sub> H. Experimental section.	1113	1113
 Amberlite IRA-400 <i>p</i> -Toluene sulfinate form (1.0 mmol g <sup>-1</sup> )		Y: 89-99	General procedure. Amberlyst A-26 has also been used. Also see reference 1250.	1251	1251

### 3.43.5 Sulfur containing compounds (Sulfones)—continued

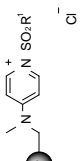

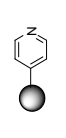
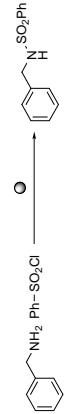
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (0.80–1.5 mmol g <sup>-1</sup> )	$R^1-X \xrightarrow{\text{PhSO}_3\text{Na, MW, O}} \text{Ph-SO}_2\text{-R}^1$ <p>8 examples</p> <p>R<sup>1</sup> = alkyl, aryl, ester, ketone, nitrile, vinyl X = Br, Cl, I</p>	Y:30-99	Several supports were investigated. Alumina gave best yields. Sonication can be used instead of MW with comparable yields. General procedure.	1252	1252
 Amberlyst A-26 Sulfonate form (3.5 mmol g <sup>-1</sup> )	$R^1-X \xrightarrow{\text{O}_2\text{O}} \text{R}^1\text{-SO}_2\text{-R}^2$ <p>11 examples</p> <p>R<sup>1</sup> = alkyl, allyl, benzyl R<sup>2</sup> = H, alkyl X = Br, Cl, I</p>	Y:60-95	Reagent may be regenerated and reused. Experimental section.	1250	1250
 KF	$\text{Ph-SO}_2\text{-R}^1 + \text{R}^2\text{-CHO} \xrightarrow{\text{MW, O}} \text{Ph-SO}_2\text{-R}^1\text{-CH(R}^2\text{)-CHO}$ <p>12 examples</p> <p>R<sup>1</sup> = ester, ketone, nitrile R<sup>2</sup> = aryl</p>	Y:50-88	General procedure.	1253	

### 3.43.6 Sulfur containing compounds (Sulfonates)

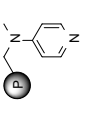
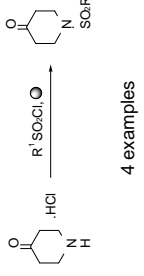
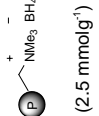
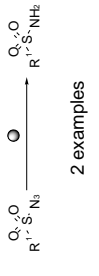
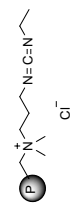

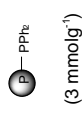
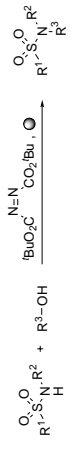
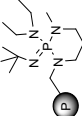
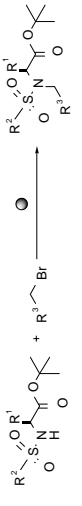
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 N	$\text{Cl-C}_6\text{H}_3\text{(NO}_2\text{)-N} \xrightarrow{\text{MeCl, O}} \text{OMe-C}_6\text{H}_3\text{(NO}_2\text{)-N}$ <p>1 example</p>	Y:90	One step of a multi-step natural product synthesis.	77	

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 P-TBD	 $\text{NO}_2\text{-C}_6\text{H}_4\text{-OR}^5\text{-O}$ 10 examples $\text{R}^1 = \text{H, alkyl, aryl}$ $\text{R}^2 = \text{H, aryl, aldehyde}$ $\text{R}^3 = \text{H, alkyl, O-alkyl, I}$ $\text{R}^4 = \text{H, alkyl, O-alkyl}$ $\text{R}^5 = \text{OTf, NTf}$	Y:65-100	Spent polymer may be regenerated and reused without loss of activity. Residual nitrophenoxide by-product remained attached to resin. General procedure.	1254	
 (0.60 mmol g <sup>-1</sup> )	$\text{R}^1\text{-OH} \xrightarrow{\text{O}} \text{R}^1\text{-OTf}$ 8 examples $\text{R}^1 = \text{aryl, het}$	Y:87-95	Spent polymer may be regenerated and reused. General procedure.	1255	1255
 (0.60 mmol g <sup>-1</sup> )	 6 examples $\text{R}^1, \text{R}^2, \text{R}^3 = \text{H, alkyl}$ $\text{X} = \text{CHR}^1, \text{O}$ $n = 1, 2$	Y:72-92	Spent polymer may be regenerated and reused. Regioselectivity of deprotonation was the same as observed that with the solution phase equivalent reagent. General procedure.	1255	1255

### 3.43.7 Sulfur containing compounds (Sulfonamides)

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 $\text{R}^1 = \text{alkyl, aryl, het}$ (1.8 mmol g <sup>-1</sup> )	 7 examples	Y:>90	One step of a multi-step solid-supported reagent synthesis of a library.	50	50
 ( = PVP )	 1 example	Y:84	Removal of the excess sulfonyl chloride affords a 92% purity of product. General procedure.	523	


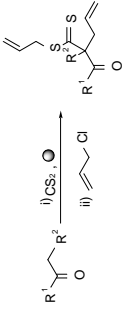

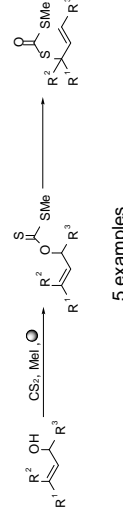

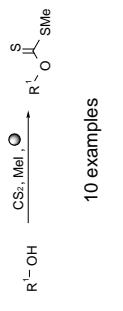

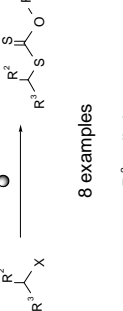


3.43.7 Sulfur containing compounds (Sulfonamides)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (2.5 mmol g <sup>-1</sup> )	 4 examples R <sup>1</sup> = aryl	Y:32-94 P:90-95	One step of a library synthesis. General procedure.	57	
 (2.5 mmol g <sup>-1</sup> )	 2 examples R <sup>1</sup> = aryl	Y:97-98	Reaction requires the use of alcoholic solvents. General procedure.	545	545
	 25 examples R <sup>1</sup> = alkyl, aryl, het	Y:56-81 P:85-92	Amberlyst A-15 scavenges the DMAP and unreacted benzoic acid remains attached to the resin.	55	55
 (3 mmol g <sup>-1</sup> )	 4 examples R <sup>1</sup> = aryl R <sup>2</sup> = alkyl, aryl R <sup>3</sup> = alkyl, benzyl	Y:77-95 P:21-86	Azodicarboxylate was removed by treatment with TFA and aqueous wash with a hydrophobic phase separation tube. Unconverted starting material was removed with polymer-supported carbonate. General procedure.	538	
 PS-BEMP (2.3 mmol g <sup>-1</sup> )	 27 examples R <sup>1</sup> = H, alkyl, aryl R <sup>2</sup> , R <sup>3</sup> = aryl	Y:89-100 P:92->98	One reaction in a multi-step sequence towards a hydroxamic acid library. Polymer-supported amine was used to remove excess bromides.	79	

3.43.8 Sulfur containing compounds (Thiocarbonyls, thioesters and related compounds)

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
<p>Amberlyst A-26 Thiolate form R<sup>1</sup> = alkyl, aryl (1.6 mmol g<sup>-1</sup>)</p>	<p>11 examples R<sup>2</sup> = alkyl, aryl</p>	Y:85-97	Spent reagent can be regenerated.	1256	1256
<p>Amberlyst A-26 Thioacetate form (3.0 mmol g<sup>-1</sup>)</p>	<p>12 examples X = Br, Cl, OTs R<sup>1</sup> = alkyl, allyl, benzyl, ester</p>	Y:56-96	Reagent can be regenerated following reaction.	1257	1257
<p>Amberlyst A-26 Dithiocarboxylate form R<sup>1</sup> = alkyl, aryl</p>	<p>11 examples R<sup>1</sup> = amino acid, steroid R<sup>2</sup> = alkyl, aryl, benzyl, het</p>	Y:34-86 P: <sup>&gt;</sup> 98	General procedure.	1258	530
	<p>6 examples R<sup>1</sup> = aryl, ferrocenyl, het</p>	Y:95-98	Experimental section.	1259	
<p>Amberlyst A-26 Dithiocarboxylate form R<sup>1</sup> = alkyl, aryl</p>	<p>4 examples R<sup>2</sup> = aryl</p>	Y:66-75	Alkyl halides also used as electrophiles. General procedures.	1260	1260

3.43.8 Sulfur containing compounds (Thiocarbonyls, thioesters and related compounds)—continued

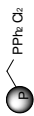




Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 -KF	 <p>4 examples R<sup>1</sup> = alkyl, aryl R<sup>2</sup> = alkyl, aryl, ketone</p>	Y:40-95	General procedure.	1261	
 -KF	 <p>5 examples R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> = alkyl</p>	Y:40-90	General procedure.	1262	
 -KF	 <p>10 examples R<sup>1</sup> = alkyl, aryl, benzyl</p>	Y:0-97	Order of reactivity; primary > secondary >> tertiary alcohols. General procedure.	1263	1263
 -NMe <sub>3</sub> <sup>+</sup> S <sup>-</sup> O <sup>-</sup> R <sup>1</sup> Amberlyst A-26 Dithiocarbonate form (3.8 mmol g <sup>-1</sup> ) R <sup>1</sup> = H, alkyl	 <p>8 examples R<sup>2</sup> = alkyl R<sup>3</sup> = alkyl, aryl, vinyl X = Br, Cl, I</p>	Y:52-99	Primary and secondary halides may be used in this reaction. Experimental section.	1264	1264
 -NMe <sub>3</sub> <sup>+</sup> S <sup>-</sup> N <sup>-</sup> R <sup>1</sup> Amberlyst A-26 Dithiocarbonate form R <sup>1</sup> = alkyl	 <p>R<sup>2</sup> = alkyl, benzyl, propargyl X = Br, I</p>	Y:59-96		1265	

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
KF 5 examples R <sup>1</sup> = aryl		Y:30-90		1266	
KF 9 examples R <sup>1</sup> = aryl		Y:58-98	General procedure.	1266	

### 3.44 Phosphorus containing compounds

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Periodate form (1.4 mmolg <sup>-1</sup> )		Y:86-99	Cleavage of 1,2-diols, oxidation of alcohols to carbonyls, oxidation of phosphines to phosphine oxides and of sulfides to sulfoxides is also described. Experimental section.	241	241
 Claycop		Y:85	General procedure.	317	
 (3.0 mmolg <sup>-1</sup> )		Y:72	Soluble resin is active as solution phase equivalent. Spent reagent may be regenerated and recycled without loss of activity Experimental section.	315	315
 (0.70-1.1 mmolg <sup>-1</sup> ) R <sup>1</sup> = H, alkyl		Y:31-74 ee:62-89	R <sup>1</sup> = Me gave the best results. General procedure.	1267, 1268, 1269	1267, 1268, 1269

3.44 Phosphorus containing compounds—continued


Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
	$\text{R}^1-\text{P}(\text{OMe})_2 + \text{R}^2-\text{C}(\text{Cl})-\text{R}^3 \longrightarrow \text{R}^1-\text{P}(\text{OMe})_2-\text{C}(\text{OR}^2)-\text{R}^3$ <p>2 examples R<sup>1</sup> = alkyl</p>	Y:78-97		1270	
	$\text{R}^1-\text{C}(\text{OR}^2)-\text{R}^3 + \text{H}-\text{P}(\text{OR}^4)-\text{OR}^5 \longrightarrow \text{R}^1-\text{C}(\text{OR}^2)-\text{P}(\text{OR}^4)(\text{OR}^5)-\text{R}^3$ <p>8 examples R<sup>1</sup> = H, alkyl, aryl, ester, vinyl R<sup>2</sup> = H, alkyl R<sup>3</sup> = alkyl</p>	Y:78-96	General procedure.	1271	
 P-TBD (2.2 mmol g <sup>-1</sup> )	$\text{R}^1-\text{C}(\text{OR}^2)-\text{R}^3 + \text{H}-\text{P}(\text{OR}^4)(\text{OR}^5)-\text{OR}^6 \longrightarrow \text{R}^1-\text{C}(\text{OR}^2)-\text{P}(\text{OR}^4)(\text{OR}^5)(\text{OR}^6)-\text{R}^3$ <p>R<sup>1</sup> = alkyl, aryl R<sup>2</sup> = H, alkyl, aryl, O-alkyl R<sup>3</sup> = alkyl</p>	Y:70-98	The polymeric reagent was as effective as the monomeric guanidine base.	1168	1168
 P-TBD (2.2 mmol g <sup>-1</sup> )	$\text{R}^1-\text{C}(\text{OR}^2)-\text{C}(\text{OR}^3)=\text{C}(\text{OR}^4)-\text{R}^5 + \text{H}-\text{P}(\text{OR}^6)(\text{OR}^7)-\text{OR}^8 \longrightarrow \text{R}^1-\text{C}(\text{OR}^2)-\text{C}(\text{OR}^3)=\text{C}(\text{OR}^4)-\text{P}(\text{OR}^6)(\text{OR}^7)(\text{OR}^8)-\text{R}^5$ <p>R<sup>1</sup> = alkyl, aryl R<sup>2</sup>, R<sup>3</sup> = H, alkyl, aryl, O-alkyl R<sup>4</sup> = alkyl</p>	Y:70-98	The polymeric reagent was as effective as the monomeric guanidine base.	1168	1168
	$\text{R}^1-\text{C}(\text{OR}^2)-\text{C}(\text{OR}^3)=\text{C}(\text{OR}^4)-\text{R}^5 + \text{HO}-\text{P}(\text{OR}^6)(\text{OR}^7)-\text{OR}^8 \longrightarrow \text{R}^1-\text{C}(\text{OR}^2)-\text{C}(\text{OR}^3)=\text{C}(\text{OR}^4)-\text{P}(\text{OR}^6)(\text{OR}^7)(\text{OR}^8)-\text{R}^5$ <p>3 examples R<sup>1</sup> = Alkyl</p>	Y:70		1272	1272



### 3.45 Selenium containing compounds

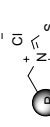
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlyst A-26 Arylselenide form (1.9 mmolg <sup>-1</sup> )	$R^1-X \xrightarrow{\text{O}} R^1-SePh$ <p>R<sup>1</sup> = acyl, alkyl, allyl, benzyl X = hal</p>	Y:76-100 P:93-97	General procedure.	1273	1273
 (1.9 mmolg <sup>-1</sup> )	$R^1-X \xrightarrow{\text{O}} R^1-Se-R^1$ <p>6 examples R<sup>1</sup> = alkyl, benzyl X = hal, tosylate</p>	Y:84-98	Resin has no odour associated with the selenium. General procedure.	1274	1274

### 3.46 Tin containing compounds

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Lithium deposited on polyethylene (7.1 mmolg <sup>-1</sup> )	$R^1-X \xrightarrow[\text{ii) } R^2_3SnCl]{\text{i) } \text{O}} (R^1)_2SnR^2$ <p>2 examples R<sup>1</sup> = aryl, stannane R<sup>2</sup> = alkyl, aryl X = Br, Cl</p>	Y:62-82	Supported lithium is non-pyrophoric and may be stored under hexane for over 3 months. Full experimental section.	1087	1087


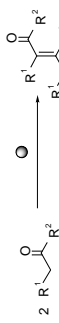



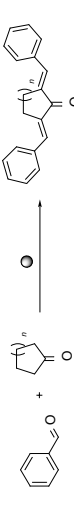

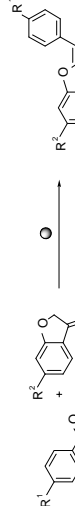

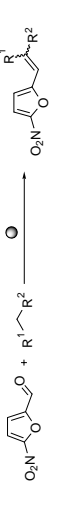
### 3.47 Reactions

#### 3.47.1 Reactions (Aldol and related reactions)


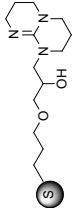

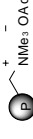

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (3.3 mmolg <sup>-1</sup> )	$R^1-O \xrightarrow{\text{O}} R^1-C(=O)-R^2$ <p>5 examples R<sup>1</sup> = alkyl, aryl, het</p>	Y:53-100	Catalyst may be recycled. General procedure.	1275	1275

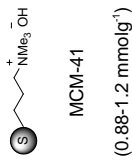

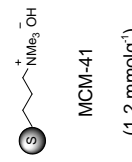
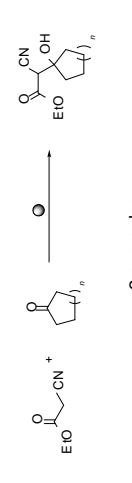
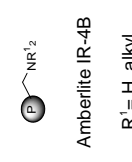
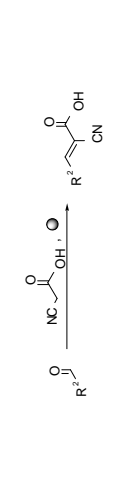
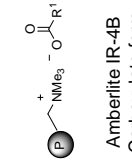
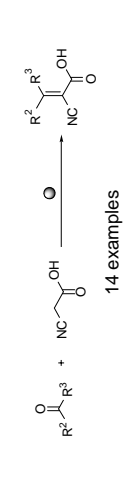
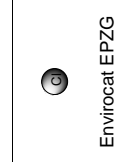
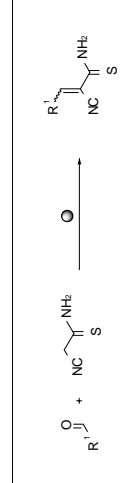
3.47.1 Reactions (Aldol and related reactions)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 $\text{P}-\text{N}(\text{Me})_3^+ \text{CN}^-$ R <sup>1</sup> = alkyl, alkaloid (0.41–0.60 mmol g <sup>-1</sup> )	 2 examples R <sup>2</sup> = aryl, het	Y:26-35 ee:0-5	Where applicable the <i>R</i> -enantiomer was obtained as the major product.	1276	1276
 $\text{P}-\text{N}R_3^+ \text{CN}^-$ 4 examples R <sup>1</sup> = alkyl, alkaloid (1.8–2.3 mmol g <sup>-1</sup> )	 2 examples R <sup>2</sup> = aryl, het	Y:5-61 ee:0-23	Where applicable the <i>R</i> -enantiomer was obtained as the major product.	1276	1276
 $\text{P}-\text{N}(\text{Me})_3^+ \text{Ph}^-$	 1 example	Y:77 ee:75	Several chiral polymeric bases were investigated. The best results were obtained with soluble polymers and lithium chloride. Best result shown. General procedure.	1277	1277
 $\text{P}-\text{N}(\text{Me})_3^+ \text{OH}^-$ Amberlite IRA-400 Hydroxide form	 3 examples	Y:39-45	Experimental section.	1278	1278
 Zeolite encapsulated (0.40 mmol g <sup>-1</sup> )	 1 example	Y:100	The monomer gives 90% yield of the $\alpha,\beta$ -unsaturated product. Ratio of products <b>a</b> : <b>b</b> = 14:86	1279	1279


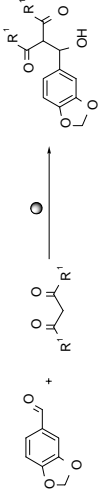

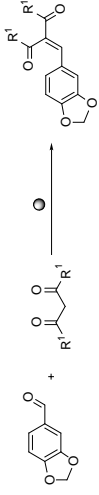

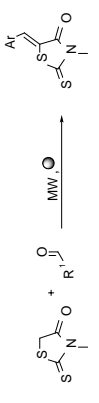

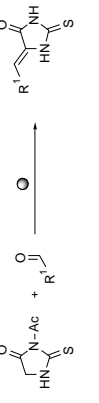

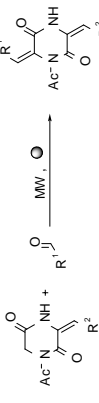
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 -SO <sub>3</sub> H Dowex 50 W Proton form	 <p>5 examples            R<sup>1</sup> = H, alkyl            R<sup>2</sup> = alkyl, aryl</p>	C:60-85	Reactions carried out on >500 g scale. Experimental section.	1280	
	 <p>4 examples            R<sup>1</sup> = H, ester, nitro            R<sup>2</sup> = H, O-alkyl</p>	Y:72-83	Reactions took place under solvent free conditions. General procedure.	1281	
	 <p>2 examples            n = 1, 2</p>	Y:94-96	Reactions took place under solvent free conditions. General procedure.	1281	
	 <p>8 examples            R<sup>1</sup> = H, amine, Cl, ester, hydroxy, O-alkyl, nitro            R<sup>2</sup> = H, O-acetyl</p>	Y:86-93	Concomitant dehydration was observed. General procedure.	1282	
 -ZnCl <sub>2</sub> Montmorillonite K 10	 <p>8 examples            R<sup>1</sup> = amide, ester, ketone, nitrile            R<sup>2</sup> = amide, aryl, ester, ketone, nitrile</p>	Y:62-98	Removing zinc complex was sometimes a problem. Experimental section.	353	1283


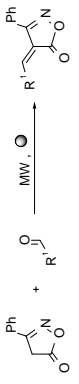

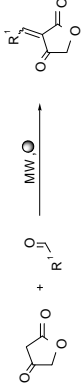

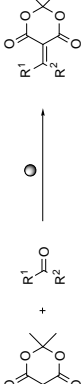

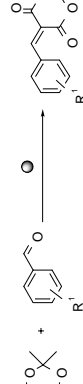


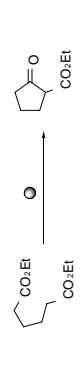

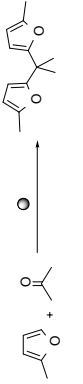
3.47.1 Reactions (Aldol and related reactions)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (0.68-0.79 mmol g <sup>-1</sup> ) R <sup>1</sup> = H, alkyl	$R^2-\overset{O}{\parallel}C-R^3 + R^4-CH_2-R^5 \longrightarrow R^2-\overset{O}{\parallel}C-CH(R^4)-CH(R^5)-R^3$ <p>22 examples            R<sup>2</sup> = aryl, vinyl            R<sup>3</sup> = H, alkyl            R<sup>4</sup>, R<sup>5</sup> = ester, ketone, nitrile</p>	C:0-100 Y:0-98	Reactions were carried out in a flow reactor. General procedure.	1284	1284
 MCM-41 (0.35 mmol g <sup>-1</sup> )	$R^1-\overset{O}{\parallel}C + NC-CH_2-R^2 \longrightarrow R^1-\overset{O}{\parallel}C-CH_2-NC-CH_2-R^2$ <p>6 examples            R<sup>1</sup> = aryl            R<sup>2</sup> = ester, nitrile</p>	Y:9-98	General procedure.	1285	1285
 MCM-41 (0.90-1.2 mmol g <sup>-1</sup> )	$NC-CH_2-R^1 + Ph-\overset{O}{\parallel}C \longrightarrow Ph-\overset{O}{\parallel}C-CH_2-NC-CH_2-R^1$ <p>2 examples            R<sup>1</sup> = ester, sulfone</p>	Y:77-95	Kinetic study. General procedure. Also see reference 978.	977	
 Dowex 3 Acetate form (4.9 mmol g <sup>-1</sup> )	$R^1-\overset{O}{\parallel}C + NC-CH_2-R^2 \longrightarrow R^1-\overset{O}{\parallel}C-CH_2-NC-CH_2-R^2$ <p>33 examples            R<sup>1</sup>, R<sup>2</sup> = alkyl, aryl            R<sup>3</sup> = nitrile, carbonyl</p>	C:3-100	Experimental section.	1286	1286
 (6.7 mmol g <sup>-1</sup> )	$R^1-\overset{O}{\parallel}C + NC-CH_2-R^2 \longrightarrow R^1-\overset{O}{\parallel}C-CH_2-NC-CH_2-R^2$ <p>3 examples            R<sup>1</sup>, R<sup>2</sup> = alkyl, aryl            R<sup>3</sup> = aryl, CN</p>	Y:55-86	General procedure.	478	478


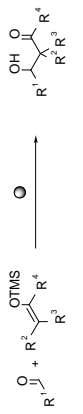
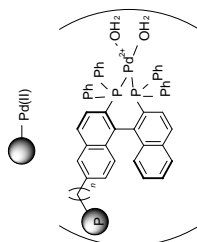


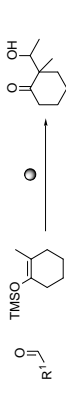
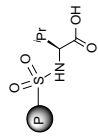
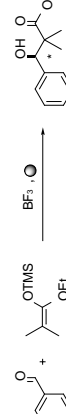

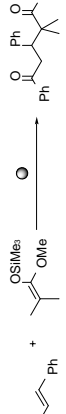
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 MCM-41 (0.88-1.2 mmol g <sup>-1</sup> )	 1 example	Y:77-95	General procedure. Also see reference 977.	978	978
 MCM-41 (1.2 mmol g <sup>-1</sup> )	 2 examples <i>n</i> = 1, 2	Y:35-50	General procedure.	978	978
 Amberlite IR-4B R <sup>1</sup> = H, alkyl	 12 examples R <sup>2</sup> = alkyl, aryl	C:20-100	With the exception of cyclohexanone, ketones did not react satisfactorily (C:65%). Experimental section.	1287	
 Amberlite IR-4B Carboxylate form R <sup>1</sup> = alkyl, aryl	 14 examples R <sup>2</sup> = alkyl, aryl, het R <sup>3</sup> = H, alkyl	C:6-100	Best results were achieved using aliphatic aldehydes. General procedure.	1288	1288
 Envirocat EPZG	 9 examples R <sup>1</sup> = aryl, het	Y:95-98	General procedure.	1289	

3.47.1 Reactions (Aldol and related reactions)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
	 <p>4 examples R<sup>1</sup> = alkyl, aryl</p>	Y:43-54	General procedure.	1088	
	 <p>3 examples R<sup>1</sup> = aryl, amide, O-alkyl</p>	Y:54-70	General procedure.	1088	
	 <p>15 examples R<sup>1</sup> = aryl</p>	Y:70-98	Full experimental section.	1290	
	 <p>6 examples R<sup>1</sup> = alkyl, aryl, het</p>	Y:72-95	Very rapid condensation and elimination reactions. General procedure.	1291	
	 <p>6 examples R<sup>1</sup> = alkyl, aryl R<sup>2</sup> = aryl</p>	Y:70-100	High levels of microwave irradiation were required. Experimental section.	986	

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
	 <p>9 examples R<sup>1</sup> = aryl, het</p>	Y:71-92	General procedure.	966	
 Montmorillonite K 10	 <p>8 examples R<sup>1</sup> = aryl, het</p>	Y:54-92	Several support types investigated. The best results are given. E/Z ratio was substrate dependent. General procedure.	1292	
	 <p>9 examples R<sup>1</sup>, R<sup>2</sup> = alkyl aryl, het</p>	Y:100	Large quantities of alumina were required. General procedure.	1293	
 Kaolin	 <p>7 examples R<sup>1</sup> = amine, hydroxy, O-alkyl</p>	Y:82-91	Reaction did not proceed with ketones. Several other inorganic solids were tested. The best example is shown. General procedure.	1294	
  ( = polyethylene)	 <p>1 example</p>	Y:89	Reagent was more effective at promoting Dieckmann condensation than colloidal potassium. Experimental section.	1087	1087
 MCM-41 (1.0-1.5 mmol g <sup>-1</sup> )	 <p>1 example</p>	C:57-85	Investigation into acidity of catalyst was performed.	1295	1295

3.47.1 Reactions (Aldol and related reactions)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Montmorillonite K 10	 <p>18 examples</p> <p>R<sup>1</sup> = alkyl, aryl, carboxylic acid, het                      R<sup>2</sup>, R<sup>3</sup> = H, alkyl                      R<sup>4</sup> = alkyl, aryl, het, O-alkyl</p>	Y:51-90	Reactions were carried out in water or under solvent free conditions. Experimental section.	1296	
 (0.40 mmol g <sup>-1</sup> )	 <p>1 example</p>	Y:94 ee:74	Reagent could be regenerated without significant loss of activity. General procedures.	1297	1297
 Amberlyst A-15 Ytterbium form (0.80-1.5 mmol g <sup>-1</sup> )	 <p>3 examples</p> <p>R<sup>1</sup> = H, aryl</p>	Y:34-87	Reaction with benzaldehyde was diastereoselective. A simple example with an imine was also given. Experimental section.	103	103
 (0.77 mmol g <sup>-1</sup> )	 <p>1 example</p>	Y:28-70 ee:18-90	A second chiral polymer and various reaction conditions were investigated.	1298	1298
 Encapsulated (2.7 mmol g <sup>-1</sup> )	 <p>1 example</p>	Y:95-97	No loss of activity on reuse of catalyst was observed. Catalyst was suitable for aldol and Michael reactions.	1299	1299



Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
	<p>4 examples R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> = alkyl</p>	Y:79-96	Reactions were carried out in both batch and flow systems. Spent catalyst may be regenerated and reused. General procedure.	1300	1300
	<p>5 examples R<sup>1</sup> = alkyl, aryl, O-alkyl R<sup>2</sup>, R<sup>3</sup> = H, alkyl R<sup>4</sup> = alkyl, aryl, O-alkyl R<sup>5</sup> = H, alkyl</p>	Y:79-95	Reactions were carried out in both batch and flow systems. Spent catalyst may be regenerated and reused. General procedure.	1300	1300
	<p>14 examples R<sup>1</sup>, R<sup>2</sup> = alkyl R<sup>3</sup> = alkyl, aryl, het</p>	Y:68-97	Dimethyl acetal could be used instead of the aldehyde component. Other solid acids investigated. The most effective is shown. Full experimental procedure.	1301	1301
	<p>1 example</p>	C:32 ee:26	Polymer could be easily removed by precipitation with pentane.	1302	1302
<p>Soluble polystyrene (0.50 mmol g<sup>-1</sup>)</p>	<p>1 example</p>	C:100	Several polybinaphthyls investigated. No enantioselectivity was observed. Experimental section.	1303	1303

3.47.1 Reactions (Aldol and related reactions)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 $\text{SO}_3\text{Sc}(\text{OTf})_2$ (1.3 mmol g <sup>-1</sup> )	 1 example	Y:98	Reactions were performed in water. Catalyst may be recovered and reused without loss of activity. General procedure.	581	581
 Nafion-TMS	 10 examples R <sup>1</sup> = aryl R <sup>2</sup> = H, alkyl R <sup>3</sup> = alkyl	Y:8-95	General procedure.	48	
 (0.40 mmol g <sup>-1</sup> Pd)	 1 example	Y:95 ee:81	Reagent could be regenerated with some loss of activity. General procedure.	1297	1297
 (0.40 mmol g <sup>-1</sup> )	 5 examples R <sup>1</sup> = alkyl, aryl, het R <sup>2</sup> = aryl R <sup>3</sup> = aryl, S-alkyl R <sup>4</sup> = H, alkyl	Y:58-99	Competition experiments indicated that the polymer selectively activates imines over aldehydes, reversing the usual reactivity. General procedure.	1304	980
 Encapsulated (2.7 mmol g <sup>-1</sup> )	 1 example	Y:88-90	No loss of activity on reuse of catalyst. Imines may also be formed <i>in situ</i> from benzaldehyde and benzylamine.	1299	1299

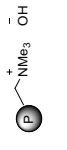
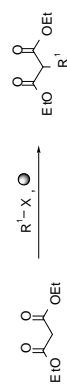
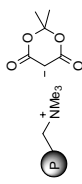
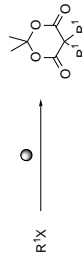
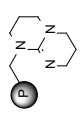
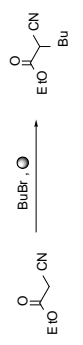
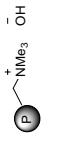
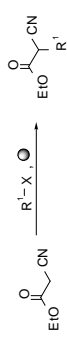
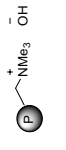
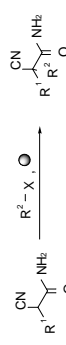
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
	<p>35 examples</p> <p>R<sup>1</sup> = aryl R<sup>2</sup> = H, alkyl R<sup>3</sup> = alkyl, aryl, benzyl R<sup>4</sup> = alkyl, aryl, O-alkyl R<sup>5</sup>, R<sup>6</sup> = H, alkyl</p>	Y:0-100	Mannich type reaction was performed under neutral conditions and showed excellent aldimine selectivity in the presence of aldehydes. Catalyst may be reused without loss of activity.	1305	1305
	<p>7 examples</p> <p>R<sup>1</sup> = alkyl, aryl</p>	Y:51-68	<i>syn:anti</i> ratio = 1:>7 (higher than monomeric catalyst). Experimental section.	1306	1306

### 3.47.2 Reactions (Alkylation, Michael and related reactions)

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
	<p>1 example</p>	Y:100 C:68	Reaction could be carried out on multi-gram scale. Experimental section.	855	855
	<p>1 example</p>	Y:84	Experimental section.	470	471

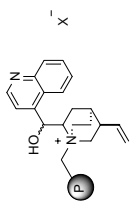
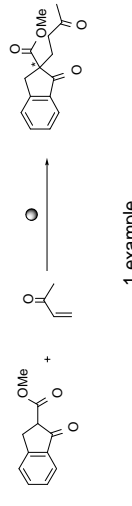
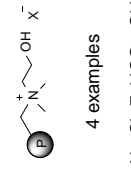
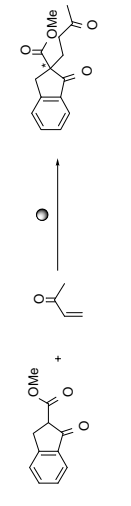
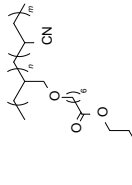
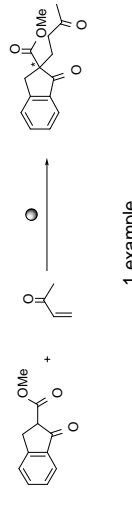
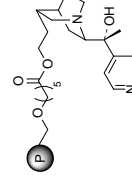
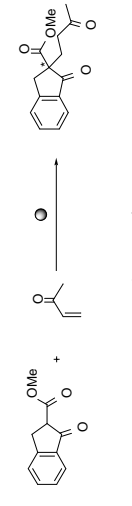
3.47.2 Reactions (Alkylation, Michael and related reactions)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
G	<p>1 example</p>	Y:100		1307	
<p>Amberlyst A-27 Fluoride form</p>	<p>1 example</p>	Y:60-70	General procedure.	846	846
<p>( = Celite )</p>	<p>1 example</p>		Reagent gave exclusively the mono-substituted product. General procedure.	537	537
	<p>1 example</p>	Y:84	Reagent gave exclusively the di-substituted product. General procedure.	537	537
<p>Amberlyst IRA-900 β-Diketonate form</p> <p>R<sup>1</sup>, R<sup>2</sup> = alkyl R<sup>3</sup> = H, alkyl</p>	<p>3 examples</p>	Y:80-95	Mono C-alkylation, di C-alkylation and O-alkylation by-products were observed in varying quantities. Experimental section.	833	833

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlite IRA-400 Hydroxide form	 3 examples $R^1 = \text{alkyl, vinyl}$ $X = \text{Br, I}$	Y:55-72	Some dialkylation was observed. Experimental section.	1308	
 Amberlite IRA-400 (1 mmol g <sup>-1</sup> )	 5 examples $R^1 = \text{alkyl, benzyl}$	Y:78-89	Resin was regenerated and reused. Experimental section.	1309	1309
 P-TBD (1.1-2.4 mmol g <sup>-1</sup> )	 1 example	Y:44	Good selectivity for mono- over di-alkylation was observed. Kinetic study. General procedure.	778	778
 Amberlite IRA-400 Hydroxide form	 3 examples $R^1 = \text{alkyl, allyl}$ $X = \text{Br, I}$	Y:31-51	Some dialkylation was observed. Experimental section.	1308	
 Amberlite IRA-400 Hydroxide form	 17 examples $R^1 = \text{H, alkyl, amide, aryl}$ $R^2 = \text{alkyl, allyl}$ $X = \text{Br, I}$	Y:13-82	Experimental section.	1308	

3.47.2 Reactions (Alkylation, Michael and related reactions)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Amberlite IRA-400 Hydroxide form Amberlite IRA-410 Hydroxide form	 28 examples R <sup>1</sup> , R <sup>3</sup> , R <sup>4</sup> = H, alkyl, aryl R <sup>2</sup> = aldehyde, ketone, ester, nitrile R <sup>5</sup> = ester, ketone, nitrile	Y:0-75	Different types of resin were tested.	1172, 1310	
 (1.0 mmol g <sup>-1</sup> )	 5 examples R <sup>1</sup> = alkyl R <sup>2</sup> = H, alkyl R <sup>3</sup> = alkyl, benzyl, allyl X = Br, Cl, I	Y:60-72	Primary and secondary bromides were unreactive in this procedure. General procedure.	1311	1311
 MCM-41 (1.2 mmol g <sup>-1</sup> )	 4 examples R <sup>1</sup> = alkyl, O-alkyl R <sup>2</sup> = alkyl, ester, nitrile	Y:10-85	General procedure.	978	978
 MCM-41 (0.90-1.2 mmol g <sup>-1</sup> )	 5 examples R <sup>1</sup> = alkyl R <sup>2</sup> , R <sup>4</sup> = H, alkyl R <sup>3</sup> = ester, ketone, nitrile	Y:10-85	Double addition products were sometimes observed, although rearrangements, dimerisations and other condensations were not detected. General procedure.	978	978

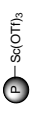
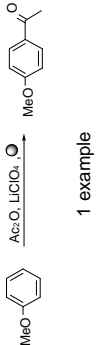
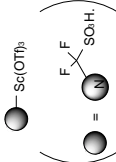
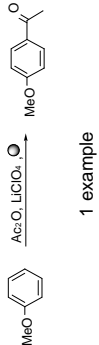
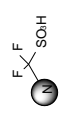



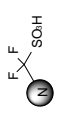

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>4 examples X = Cl, F, HCO<sub>3</sub>, OH (0.73 mmolg<sup>-1</sup>)</p>	 <p>1 example</p>	Y:33-100 ee:5-27	X = Fluoride and bicarbonate gave the best results. Full experimental section.	1312	1312
 <p>4 examples X = Cl, F, HCO<sub>3</sub>, OH (2.7-3.7 mmolg<sup>-1</sup>)</p>	 <p>1 example</p>	Y:20-100	Effect of the degree of cross-linking of the resin was investigated. Resin with a ligand of the opposite stereochemistry, gave the product with opposite stereochemistry. Full experimental section.	1312	1312
	 <p>1 example</p>	Y:88 ee:65	Several resins with different linker chains were investigated. The best results are given. Experimental section.	673	673
 <p>(0.30 mmolg<sup>-1</sup>)</p>	 <p>1 example</p>	Y:85 ee:87	Other catalysts were also prepared from both quinine and quinidine by varying the length of the spacer between the polymer and the ester linkage. Best example shown. General procedure.	1313	1313

3.47.2 Reactions (Alkylation, Michael and related reactions)—continued




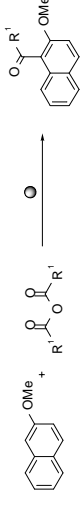



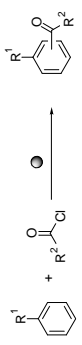


Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
	<p>1 example</p>	Y:78	Reaction gave higher yield than using alumina alone. General procedure.	1088	
<p>Encapsulated scandium triflate</p>	<p>1 example</p>	Y:92-97	Catalyst may be reused without loss of activity. General procedure.	1299	1299
<p>A = (1.5 mmol g<sup>-1</sup>)</p> <p>B = (2.5-2.8 mmol g<sup>-1</sup>)</p> <p>R<sup>1</sup> = O-alkyl, aryl</p>	<p>9 examples</p> <p>R<sup>2</sup> = amide, aryl, O-alkyl R<sup>3</sup> = H, alkyl, aryl</p>	Y:88-98	Trityllithium polymer was prepared <i>in situ</i> . Reagent was air and moisture sensitive. Solid-supported reagent gave better yields than the solution phase equivalent. It also generated polymeric lithium diisopropylamide. Experimental section.	30, 29	30
<p>A = (1.5 mmol g<sup>-1</sup>)</p> <p>B = (2.5-2.8 mmol g<sup>-1</sup>)</p> <p>R<sup>1</sup> = O-alkyl, aryl</p>	<p>3 examples</p> <p>R<sup>2</sup> = H, aryl</p>	Y:90-94	Reagent was air and moisture sensitive. Solid-supported reagent gave better yields than the solution phase equivalent. Experimental section.	29, 30	30

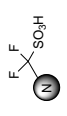
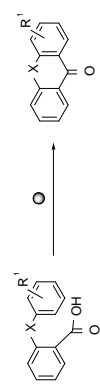
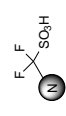
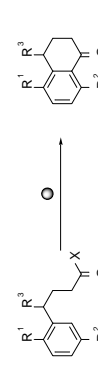
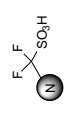
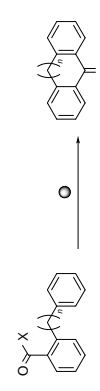
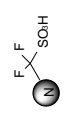
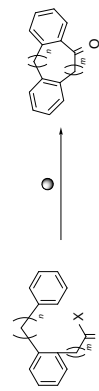

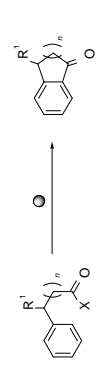


### 3.47.3 Reactions (Friedel–Crafts acylation and alkylation)

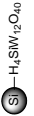
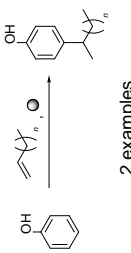
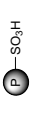
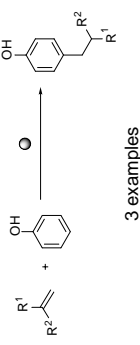
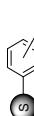
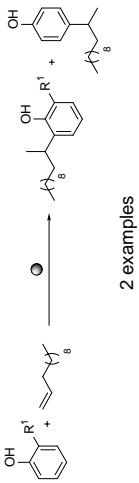

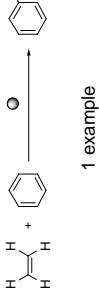

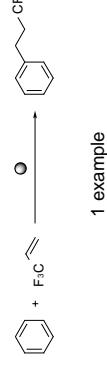
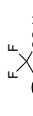
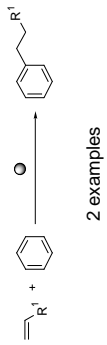
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Encapsulated scandium triflate (2.7 mmol g <sup>-1</sup> )	 1 example	Y:76-81	There was no loss of activity on catalyst reuse.	1299	1299
 Nafion NR-50 Scandium triflate form	 1 example	Y:68	The reagent was reused without loss of activity. Nitromethane was used as the solvent for this Friedel-Crafts acylation.	1086	1086
 Nafion-H	 9 examples R <sup>1</sup> = alkyl, hydroxy R <sup>2</sup> = Cl, O-alkyl R <sup>3</sup> = CF <sub>3</sub> , CCl <sub>3</sub> , O-alkyl	C:2-80	A mixture of isomers was produced. General procedure.	1314	
 Amberlyst IR-120 Proton form	 20 examples R <sup>1</sup> = H, alkyl, aryl R <sup>2</sup> = alkyl, aryl	Y:0-84	Carboxylic acids were also used effectively to replace the anhydride. Experimental section.	1315	
 Nafion-H	 11 examples R <sup>1</sup> = alkyl, aryl, vinyl	Y:0-94	Resin may be reused, but with a loss in activity after each recycle. General procedure.	1316	


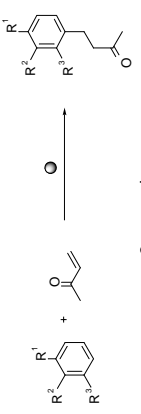

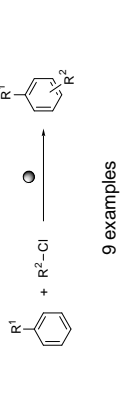



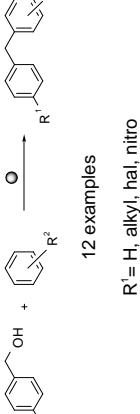

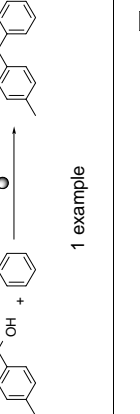

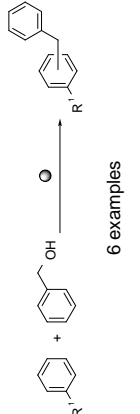
3.47.3 Reactions (Friedel–Crafts acylation and alkylation)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Sodium exchanged HY zeolite	 <p>4 examples</p> <p>R<sup>1</sup> = alkyl, O-alkyl                      R<sup>2</sup> = aryl, benzyl                      R<sup>3</sup> = Cl, OH</p>	Y:71	A range of catalyst compositions was examined. Kinetic study. Full experimental section.	1317	
 H-MCM-41	 <p>3 examples</p> <p>R<sup>1</sup> = alkyl, aryl</p>	C:31-59	Reagent may be recycled without loss of activity. Experimental section.	1318	1318
 Silferc (1.0 mmol g <sup>-1</sup> )	 <p>5 examples</p> <p>R<sup>1</sup> = H, alkyl, O-alkyl, hal</p>	Y:32-72	The catalyst may be stored for two months. General procedure.	1319	1319
 Mo(CO) <sub>3</sub> (0.10 mmol g <sup>-1</sup> )	 <p>6 examples</p> <p>R<sup>1</sup> = alkyl, O-alkyl                      R<sup>2</sup> = aryl, aryl, benzyl</p>	Y:0-81	The <i>para</i> -substituted product was the main compound isolated. The reagent was successfully stored in the cold under nitrogen. When R = alkyl, no reaction was observed. Full experimental section.	1320	1320
 Nafion-H	 <p>11 examples</p> <p>R<sup>1</sup> = H, alkyl, Cl, F                      R<sup>2</sup> = H, alkyl, Cl</p>	Y:63-88	General procedure. Fe(NO <sub>3</sub> ) <sub>3</sub> supported on Montmorillonite K 10 has also been used for this transformation. <sup>1,321</sup>	1322	


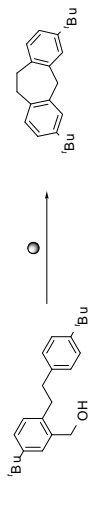
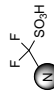
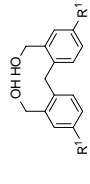
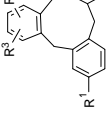

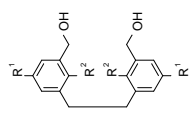
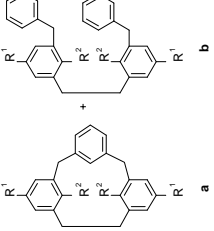
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Nafion-H	 7 examples X = CO, CH <sub>2</sub> , O, NH R <sup>1</sup> = H, COOH	Y:82-95	General procedure.	1323	
 Nafion-H	 4 examples R <sup>1</sup> , R <sup>2</sup> , R <sup>3</sup> = H, alkyl X = Cl, hydroxy	Y:88-96	Five-membered rings could not be produced with the same reagent.	1324	
 Nafion-H	 4 examples X = Cl, hydroxy n = 1, 2	Y:71-100	Uncyclised side-products were also produced due to the competing intermolecular reaction of the substrate. General procedures.	1324	
 Nafion-H	 6 examples X = Cl, hydroxy n = 1, 2 m = 0, 1	Y:26-100	The resin was reused without loss of activity. General procedure.	1325	
 Nafion-H	 6 examples R <sup>1</sup> = H, alkyl X = Cl, hydroxy n = 1, 2	Y:0-96	Resin may be reused without loss of activity. General procedure.	1325	

3.47.3 Reactions (Friedel-Crafts acylation and alkylation)—continued

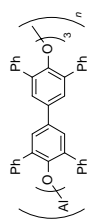
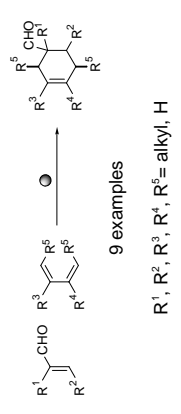
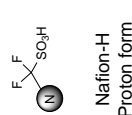
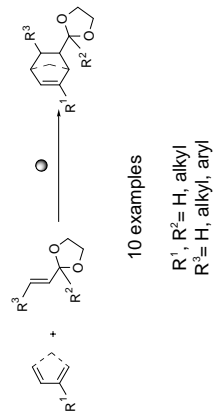
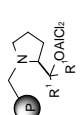
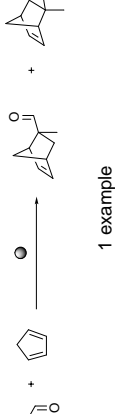
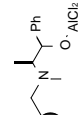
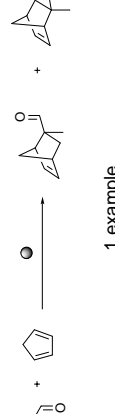
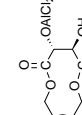
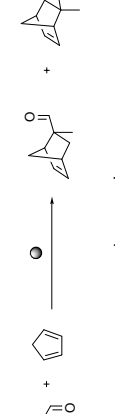
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 $\text{Si}-\text{H}_x\text{SW}_{12}\text{O}_{40}$ (0.30-1.9 mmol g <sup>-1</sup> )	 2 examples $n = 5, 6$	C:95-98	Catalyst shows good selectivity for mono, <i>para</i> -substitution. General procedure.	1326	1326
 Amberlite IR-112 Proton form	 3 examples $R^1 = \text{alkyl}$ $R^2 = \text{H, alkyl}$	Y:77-98	A number of acid ion exchange resins were tried. The reaction is highly selective for <i>para</i> -substitution. Experimental section.	1327	
 (0.30 mmol g <sup>-1</sup> )	 2 examples $R^1 = \text{H, alkyl}$	C:53	Kinetic study. Comparison with kinetic study for Amberlyst-15 and Nafion-H. Monoalkylation predominates. Experimental section.	761	761
 Graphite intercalation	 1 example	C:62	Several reaction conditions were used. The best results from these are given. Severe leaching of AlCl <sub>3</sub> observed.	479	
	 1 example	Y:27	General description.	1328	
 Nafion-H	 2 examples $R^1 = \text{H, alkyl}$	C:29-44	Several reaction conditions were used. The best results from these are given. Also see reference 1329.	479	

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Montmorillonite K 10 (0.40-0.70 mmol g <sup>-1</sup> )	 <p>3 examples</p> <p>R<sup>1</sup> = amine, hydroxy, O-alkyl R<sup>2</sup>, R<sup>3</sup> = H, aryl</p>	Y:18-58	Several other metal ion exchanged clays were used. Good selectivity for <i>para</i> substitution was observed. Experimental section.	1330	1330
 (0.10 mmol g <sup>-1</sup> )	 <p>9 examples</p> <p>R<sup>1</sup> = alkyl, O-alkyl, O-aryl R<sup>2</sup> = aryl, benzyl</p>	Y:0-100	The resin could be stored refrigerated under nitrogen indefinitely. The molybdenum carbonyl moiety is $\pi$ -bonded to the arene ring of the <i>ortho</i> and <i>para</i> derivatives. Full experimental section.	1320	1320
 (0.20 mmol g <sup>-1</sup> )	 <p>5 examples</p> <p>R<sup>1</sup> = H, alkyl, O-alkyl, hal R<sup>2</sup> = H, alkyl</p>	Y:58-85	Supported ZnCl <sub>2</sub> was also investigated, but yields were lower for each substrate. Reagents can be stored for six months. General procedure.	1331	1331
 Nafion-H	 <p>12 examples</p> <p>R<sup>1</sup> = H, alkyl, hal, nitro R<sup>2</sup> = H, alkyl</p>	Y:68-97	Some dimerisation of the phenol is observed. General procedure.	1332	
 Silica and Nafion-H	 <p>1 example</p>		Kinetic study. Experimental section.	1333	
 (0.010-5.0 mmol g <sup>-1</sup> )	 <p>6 examples</p> <p>R<sup>1</sup> = H, alkyl, nitro, O-alkyl</p>	Y:68-85	<i>N,N</i> -dimethylaniline did not react with benzyl alcohol under the same conditions.	1334	

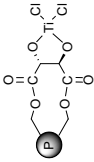
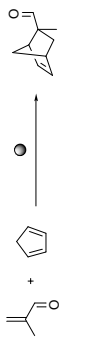
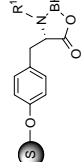
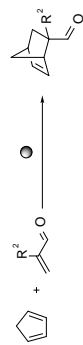
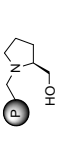

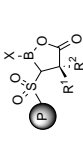
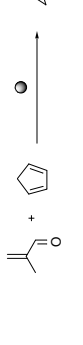
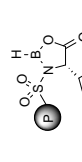
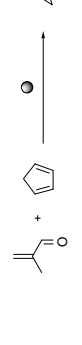
3.47.3 Reactions (Friedel–Crafts acylation and alkylation)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Nafion-H	 1 example	Y:95	Experimental section.	1335	
 Nafion-H	  5 examples R <sup>1</sup> = H, alkyl R <sup>2</sup> = alkyl, O-alkyl R <sup>3</sup> = H, hydroxy	Y:30-97 (a) Y:0-40 (b)	Experimental section.	1336, 1337, 1338	
 Nafion-H	 +  2 examples R <sup>1</sup> , R <sup>2</sup> = H, alkyl	Y:26-31 (a) Y:69-74 (b)		1339, 1340	

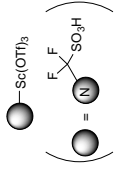
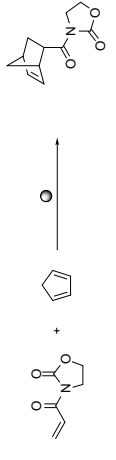
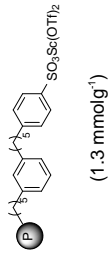
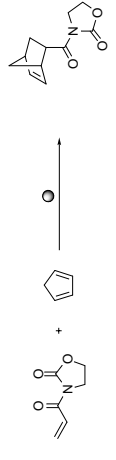
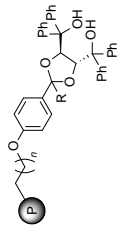
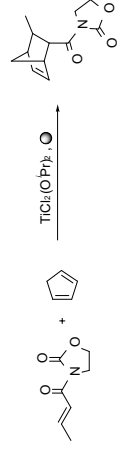
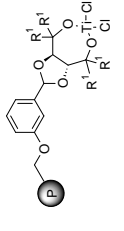
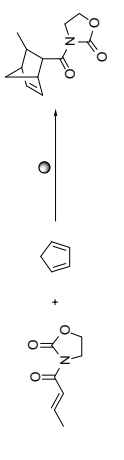
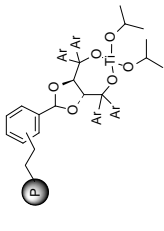
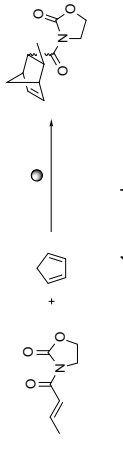
### 3.47.4 Reactions (Diels–Alder and related cycloadditions)

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
	 <p>9 examples</p> <p><math>R^1, R^2, R^3, R^4, R^5 = \text{alkyl, H}</math></p>	Y:40-99	Lower yields were caused by the formation of Tischenko adducts. The <i>endo/exo</i> product ratio varied from 24:1 to 1:8. The polymer was recovered quantitatively and reused up to seven times without any loss of activity.	1341	1341
 <p>Nafion-H Proton form</p>	 <p>10 examples</p> <p><math>R^1, R^2 = \text{H, alkyl}</math> <math>R^3 = \text{H, alkyl, aryl}</math></p>	Y:68-94	Yields and <i>endo</i> selectivity were generally greater than with 5 M lithium perchlorate in ether. The acetal functionality was not cleaved during the reaction. Full experimental section.	1342	
 <p><math>R^1 = \text{H, aryl}</math> (0.70-0.80 mmol g<sup>-1</sup>)</p>	 <p>1 example</p>	C:98 ee:14 ( $R^1 = \text{H}$ )  C:70 ee:7 ( $R^1 = \text{aryl}$ )	Reagent may be regenerated. Limited <i>endo/exo</i> selectivity was observed. Experimental section. For similar reactions see 1343. A range of inorganic supports have also been used for this transformation. <sup>1344,1345,1346</sup>	1347	1347
 <p>(0.60 mmol g<sup>-1</sup>)</p>	 <p>1 example</p>	C:95 ee:0	Limited <i>endo/exo</i> selectivity was observed. Experimental section.	1347	1347
 <p>(0.20 mmol g<sup>-1</sup>)</p>	 <p>1 example</p>	Y:74 ee:13	Limited <i>endo/exo</i> selectivity was observed. Experimental section.	1347	1347


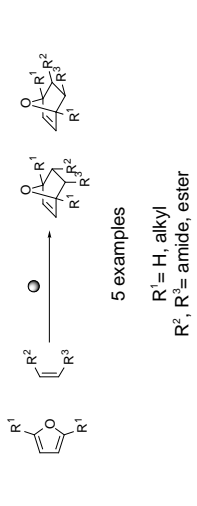
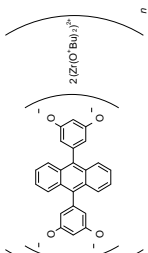
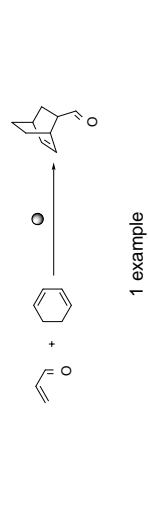
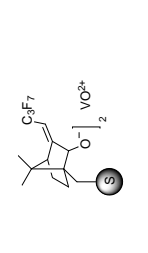
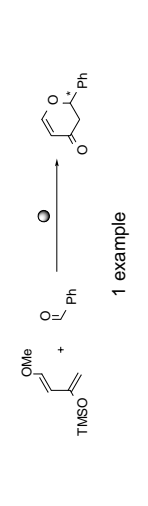
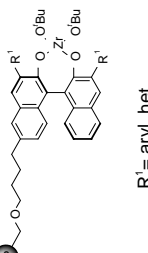
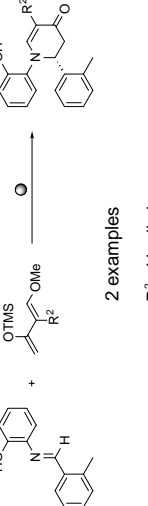
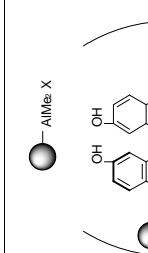
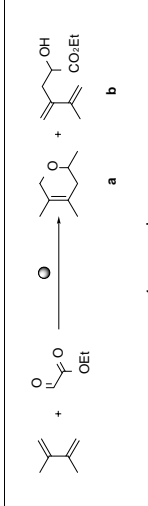
3.47.4 Reactions (Diels–Alder and related cycloadditions)—continued

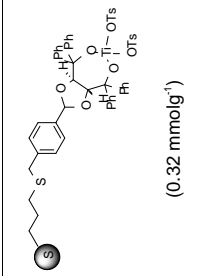
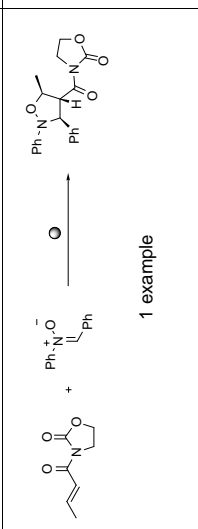
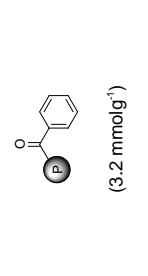
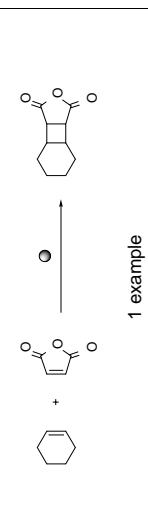
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (0.30 mmol g <sup>-1</sup> )	 1 example	Y:96 ee:3	The catalyst was successfully recycled. Limited <i>endo/exo</i> selectivity was observed. Experimental section.	1347	1347
 R <sup>1</sup> = DNB, Ts (0.20-0.50 mmol g <sup>-1</sup> )	 2 examples R <sup>2</sup> = alkyl, Br	C:51-90 <i>exo:endo</i> 9:1 ee:0	Full experimental section. Silica supported catalysts have also been used for this transformation. <sup>1348</sup> Proline based supports have also been used (up to 54% ee). <sup>1349</sup>	1350	1350
 (0.20-1.1 mmol g <sup>-1</sup> )	 1 example	C:76-98 ee:2-25	Polystyrene with different degrees of cross-linking was tested. Polymerisation vs. grafting was also compared. <i>exo/endo</i> ratio remained constant (9:1). Highest enantiomeric excess obtained for highest degree of cross-linking. Experimental section.	1351	1351
 (0.80-2.5 mmol g <sup>-1</sup> ) R <sup>1</sup> = H, aryl R <sup>2</sup> = H, alkyl X= H, Br	 1 example	Y:65-99 ee:1-95	A number of different polymers were investigated yielding <i>endo/exo</i> ratios between 1:99 and 13:87. The catalyst could be recovered and reused many times or used in a continuous flow system. Experimental section.	1352, 1353	1352, 1353
 (0.80 mmol g <sup>-1</sup> )	 1 example	Y:93 ee:65	Several polymers and reaction conditions were investigated leading to <i>endo:exo</i> ratios of 1:99. The best results are given. The reaction was also carried out in a flow reactor. General procedure.	1354, 1355	1354, 1355



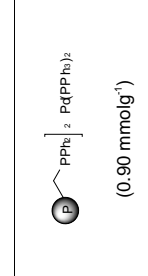
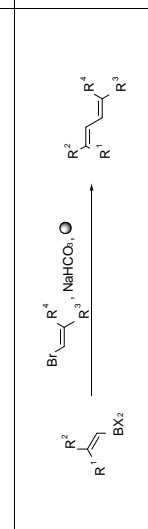
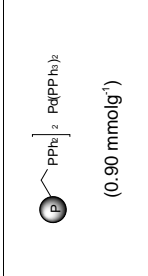
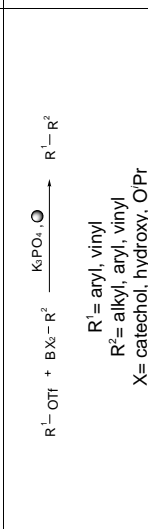
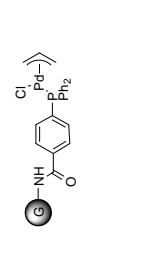

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Nafion-NR 50 Scandium triflate form (0.30 mmol g <sup>-1</sup> )	 1 example	Y:92-97	Reagent was reused without loss of activity. <i>endo:exo</i> ratio varied with the solvent used.	1086	
 (1.3 mmol g <sup>-1</sup> )	 1 example	Y:100	Reactions were performed in water. Catalyst may be recovered and reused without loss of activity. <i>endo:exo</i> ratio = 92:8. General procedure.	581	581
	 1 example	C:100 ee :0-53	Catalyst lost reactivity and gave poorer enantiomeric excesses on recycling. The enantiomeric excess of the <i>endo</i> product is shown ( <i>endo:exo</i> = 8:2-9:1). Experimental section.	1356	1356
 (0.40 mmol g <sup>-1</sup> ) R <sup>1</sup> = 3,5-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> , 2-naphthyl	 1 example	C:50-100 ee:17-40	<i>endo-exo</i> selectivity 7:3. Enantioselectivity was found to reverse depending on whether the Titanium-Taddolite was grafted onto the polymer or was obtained by polymerisation of a Titanium-Taddol monomer. Best results were obtained with the latter. General procedure.	1357	1357
 (0.65 mmol g <sup>-1</sup> ) Ar = 3,5-dimethylbenzene	 1 example	Y:95 ee:25	Nine other variations of resin synthesised. Best example is shown. The <i>endo:exo</i> ratio was 71:29. Experimental section.	1358	1358

3.47.4 Reactions (Diels–Alder and related cycloadditions)—continued


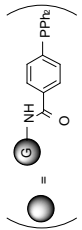
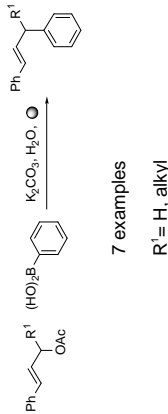
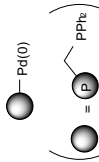
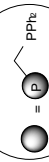
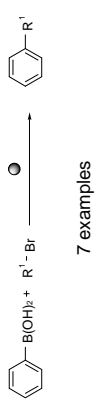
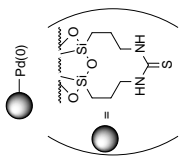
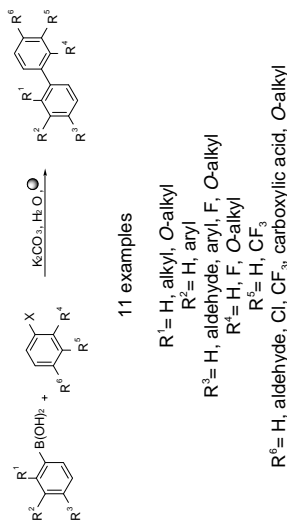
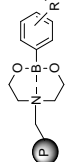
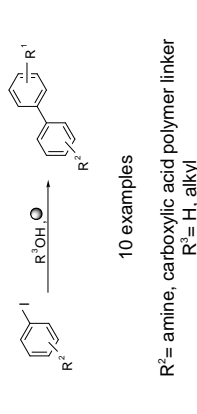
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>Montmorillonite K 10</p>	 <p>5 examples R<sup>1</sup> = H, alkyl R<sup>2</sup>, R<sup>3</sup> = amide, ester</p>	Y:52-100	The reaction was also carried out on dimethyl acetylenedicarboxylate. <i>exo:endo</i> ratios ranged from 2.5:1 to 1:3 (with maleic anhydride).	1359	
 <p>2(Zr(O<sup>t</sup>Bu)<sub>2</sub>)<sub>n</sub></p>	 <p>1 example</p>	Y:98	The solid reagent acted as a catalyst. The <i>endo</i> product was favoured over <i>exo</i> . No zirconium leaching was observed.	1360	1360
 <p>C<sub>6</sub>F<sub>7</sub></p>	 <p>1 example</p>	Y:73-89 ee:32-40	The enantioselectivity observed was opposite to that obtained with the ligand in solution. Experimental section.	1361	1361
 <p>R<sup>1</sup> = aryl, het</p>	 <p>2 examples R<sup>2</sup> = H, alkyl</p>	Y:87-99 ee:80-91	Catalyst library made to find best R <sup>1</sup> . (R <sup>1</sup> = 3-CF <sub>3</sub> -Ph gave best results).	1362	1362
 <p>R = C<sub>6</sub>H<sub>13</sub> X = Me, Cl (1.8 mmol g<sup>-1</sup>)</p>	 <p>1 example</p>	Y:10-80 (a+b) ee:42-95 (a) ee:4-46 (b)	Ratio a:b = 2:1–5:1 Soluble polymer may be precipitated using methanol. Reactions give varying mixtures of the hetero-Diels–Alder adduct, and <i>endo</i> product depending upon reaction conditions. Polymer may be reused without loss of activity. General procedure.	1363	1364

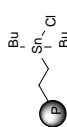
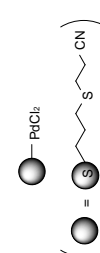
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (0.32 mmol g <sup>-1</sup> )	 1 example	C:91 de:83 ee:85	Catalyst may be reused up to twenty times with only a slight loss of activity.	1082	
 (3.2 mmol g <sup>-1</sup> )	 1 example		This reagent acted as a photo-sensitiser. Experimental section.	1365	1365

### 3.47.5 Reactions (Palladium coupling reactions)

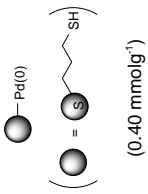
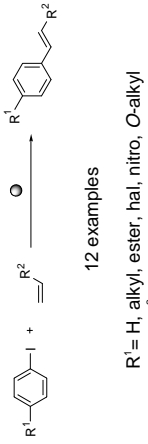
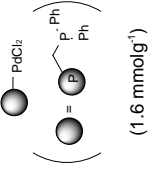
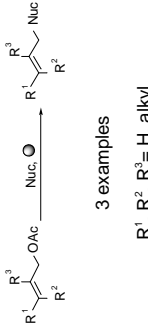
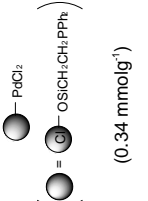
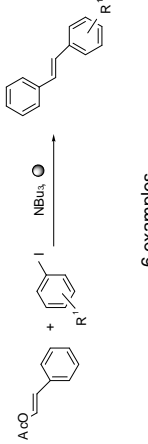
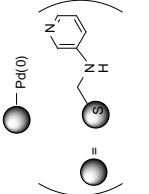

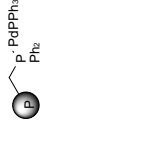
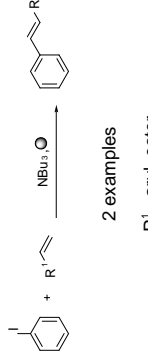
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (0.90 mmol g <sup>-1</sup> )	 13 examples R <sup>1</sup> , R <sup>2</sup> , R <sup>3</sup> , R <sup>4</sup> = H, alkyl, aryl R <sup>2</sup> = H, alkyl X = catechol, siamyl, cyclohexyl	Y:78-96	Polymer may be reused up to ten times without loss of activity. General procedure.	1366	1366
 (0.90 mmol g <sup>-1</sup> )	 R <sup>1</sup> = aryl, vinyl R <sup>2</sup> = alkyl, aryl, vinyl X = catechol, hydroxy, OPr	Y:85-98	The Suzuki coupling of vinyl and aryl triflates proceeds in similar yields to the homogeneous catalyst Pd(PPh <sub>3</sub> ) <sub>4</sub> . General procedure.	1366	1366
 (0.90 mmol g <sup>-1</sup> )	 4 examples R <sup>1</sup> = H, alkyl R <sup>2</sup> = H, alkyl, O-alkyl X = hal	Y:82-91	General procedure.	1367	1367

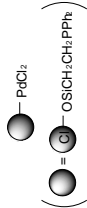

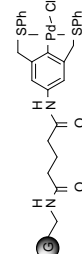
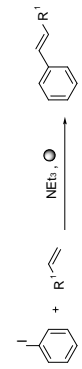

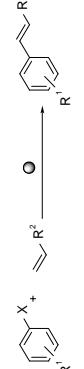
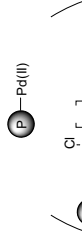

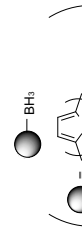

3.47.5 Reactions (Palladium coupling reactions)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 PdCl  PPh <sub>3</sub>	 <p>7 examples R<sup>1</sup> = H, alkyl</p>	Y:45-99	General procedure.	1367	1367
 Pd(0)  PPh <sub>3</sub> (0.70 mmol g <sup>-1</sup> )	 <p>7 examples R<sup>1</sup> = aryl</p>	Y:56-98	Several analogues of the catalyst were compared for Suzuki cross-coupling. The catalysts were stable for at least a year stored in air at 20 °C. Catalysts were reused at least five times without any loss in catalytic activity. General procedure.	1368	1368
 Pd(0) Deloxan THP II	 <p>11 examples R<sup>1</sup> = H, alkyl, O-alkyl R<sup>2</sup> = H, aryl R<sup>3</sup> = H, aldehyde, aryl, F, O-alkyl R<sup>4</sup> = H, F, O-alkyl R<sup>5</sup> = H, CF<sub>3</sub> R<sup>6</sup> = H, aldehyde, Cl, CF<sub>3</sub>, carboxylic acid, O-alkyl X = Br, I</p>	Y:27-99	Catalyst may be reused with some loss of activity after two to three cycles. General procedure.	1369	1369
 Pd(0) R <sup>1</sup> = alkyl, amide, amine	 <p>10 examples R<sup>2</sup> = amine, carboxylic acid polymer linker R<sup>3</sup> = H, alkyl</p>	Y:55-100 P>90	Resin was used to perform Suzuki coupling with resin-bound aryl iodides. R <sup>3</sup> OH acted as transesterification agent, therefore providing a boronic ester in solution.	1370	1371

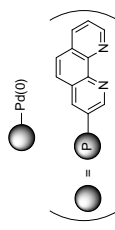
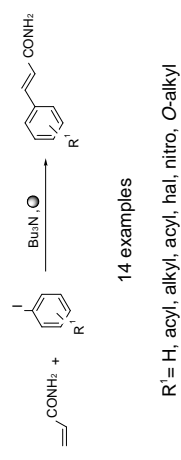
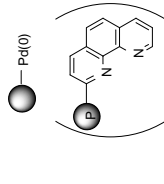
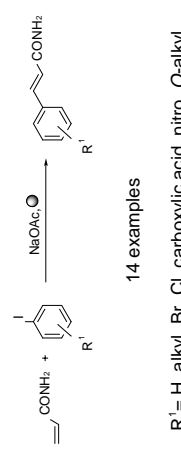
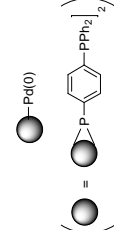
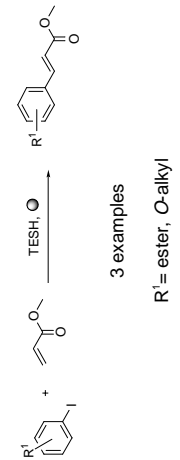
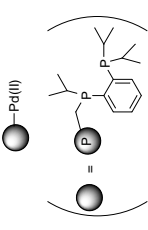
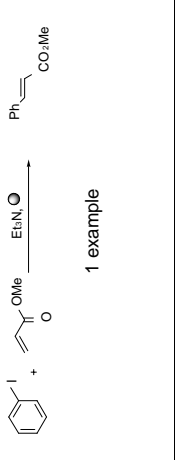
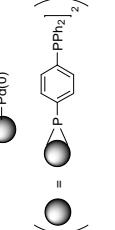
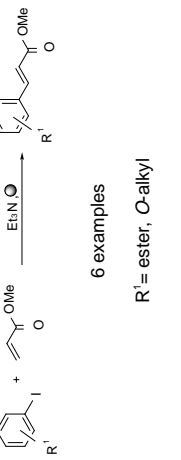
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 $R^1-MgX \xrightarrow{i) \text{ } \text{P}(\text{Bu})_2\text{Sn}(\text{Bu})\text{R}^1 \text{ ii) Pd cat. R}^2\text{Y}$ 10 examples $R^1 = \text{alkynyl, allyl, vinyl}$ $R^2 = \text{alkyl, carbonyl}$ $Y = \text{Cl, OTf}$	$R^1-R^2 \xrightarrow{\text{Pd cat. R}^2\text{Y}}$ 10 examples $R^1 = \text{alkynyl, allyl, vinyl}$ $R^2 = \text{alkyl, carbonyl}$ $Y = \text{Cl, OTf}$	Y:51-96	No tin residue was found in the product after Stille reaction. Resin may be reused without loss of reactivity. General procedure.	1372	426
 $R^1 = \text{alkynyl, allyl, vinyl}$ (1.5 mmol g <sup>-1</sup> )	$R^2-X \xrightarrow{\text{Pd cat. R}^2\text{Y}}$ 10 examples $R^2 = \text{acyl, vinyl}$ $X = \text{Hal, OTf}$	Y:51-96	No tin residue was found in the product after the Stille reaction. The resin may be reused without loss of reactivity. General procedure.	1372	426
 (0.50 mmol g <sup>-1</sup> )	$R^1-SnBu_3 \quad R^2-I \xrightarrow{\text{Pd cat. R}^2\text{Y}}$ 12 examples $R^1 = \text{alkynyl, aryl, het, vinyl}$ $R^2 = \text{aryl}$	Y:71-89	The reagent may be reused but the yield drops by 5% per cycle. Experimental section.	1373	1373
 (0.030 mmol g <sup>-1</sup> )	$R^1-I \xrightarrow{\text{NaBPh}_4}$ 6 examples $R^1 = \text{aryl}$	Y:74-84	The phenylation of aryl bromides under the same conditions was very slow and only trace products were obtained. Experimental section. Use of supported Pd with PPh <sub>3</sub> or NEt <sub>3</sub> has also been described. <sup>1374</sup>	334	334
 (0.24 mmol g <sup>-1</sup> )	$X \xrightarrow{\text{Pd(OAc)}_2, R^1, O}$ $R^1 = \text{CH(COMe)}_2, \text{PhCH}_2\text{NH}$	Y:74-83	Several resins were used. The best results are shown. General procedure.	1375	1375
 (0.24 mmol g <sup>-1</sup> )	$X \xrightarrow{R^1-H, \text{Base}}$ 6 examples $R^1 = 2^\circ \text{ amine, 1,3-dicarbonyl}$ $X = \text{O-alkyl, O-aryl}$	Y:55-96	Best results were obtained in the presence of triphenylphosphine. Experimental section.	1376	1376

3.47.5 Reactions (Palladium coupling reactions)—continued

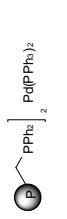
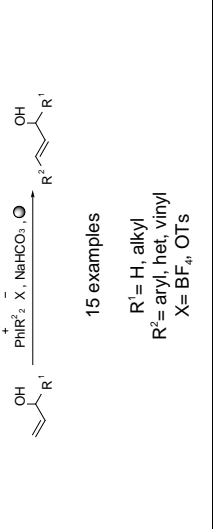
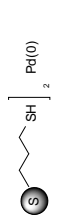
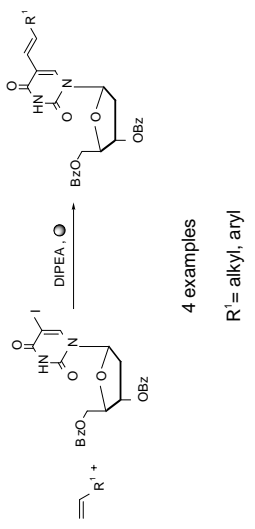
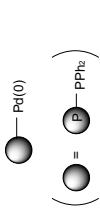
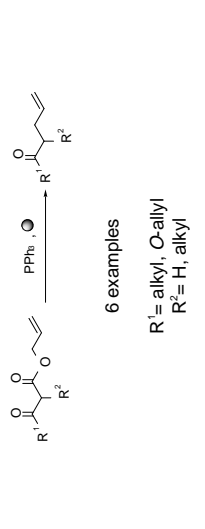
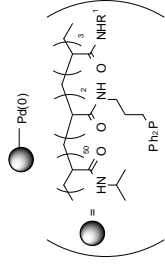
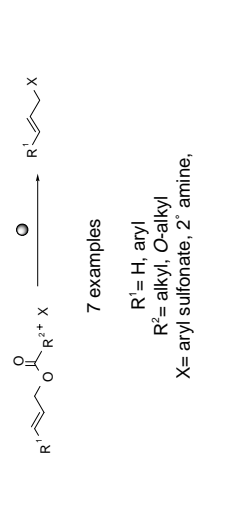
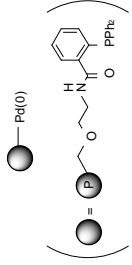
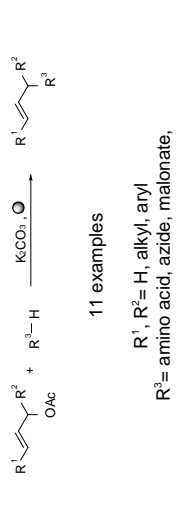
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>(0.40 mmol g<sup>-1</sup>)</p>	 <p>12 examples R<sup>1</sup> = H, alkyl, ester, hal, nitro, O-alkyl R<sup>2</sup> = aryl, carboxylic acid</p>	Y:86-96	Good selectivity for <i>E</i> double bond. Experimental section.	1377	1377
 <p>(1.6 mmol g<sup>-1</sup>)</p>	 <p>3 examples R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> = H, alkyl R<sup>4</sup> = amine, 1,3-dicarbonyl Nuc = (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH, CH<sub>2</sub>CO<sub>2</sub>Me</p>	Y:58-83	Reaction proceeded with complete retention of stereochemistry. Similar results were obtained using a silica support. General procedure. Also see reference 1378.	1379	1379
 <p>(0.34 mmol g<sup>-1</sup>)</p>	 <p>6 examples R<sup>1</sup> = alkyl, O-alkyl</p>	Y:84-86	When conducted in solution phase, these couplings were unsuccessful. General procedure.	1380, 1381	1380
 <p>(0.34 mmol g<sup>-1</sup>)</p>	 <p>13 examples R<sup>1</sup> = H, hal, O-alkyl R<sup>2</sup> = amide, aryl, ester</p>	Y: 71-98	Several silica supported catalysts were investigated. The best results are given. The silica supported catalysts, were more stable and leached less Pd than polystyrene supported catalysts. General procedure.	1382	1382
 <p>(0.34 mmol g<sup>-1</sup>)</p>	 <p>2 examples R<sup>1</sup> = aryl, ester</p>	Y:59-98	The catalyst may be recycled with some loss of activity. General procedure.	1383	1383

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (0.34 mmol g <sup>-1</sup> )	 10 examples R <sup>1</sup> = ester, nitrile	Y:90-98	No reaction with hex-1-ene. General procedure.	1380	1380
 PEG <sub>5000</sub> (1.8 mmol g <sup>-1</sup> )	 2 examples R <sup>1</sup> = aryl, ester	Y:85-95	The catalyst could be recycled with no loss of activity over three cycles. Other resins were studied. The best example is shown. Experimental section.	1384	1384
Montmorillonite K 10 	 8 examples R <sup>1</sup> = H, Cl, O-alkyl R <sup>2</sup> = aryl, ester X = Br, Cl, I	Y:0-93	Several catalysts were used. The best results are given. The catalyst is easy to prepare and may be reused without loss of activity. General procedure.	1385	1385
 (0.10-0.50 mmol g <sup>-1</sup> )	 X = I, Br Y = H, nitro R <sup>3</sup> = acyl, aryl	C:100	Four different catalysts were tried, with Pd:P ratios of 1:1, 1:2, 1:3 and 1:5 respectively. A 1:1 ratio gave the best result. General procedure. Also see reference 1386.	1387	1388
	 3 examples R <sup>1</sup> = alkyl, carbonyl R <sup>2</sup> = H, alkyl R <sup>3</sup> = H, O-alkyl	Y:56-72	Several resins were used. The best results are given. General procedure.	1375	1375

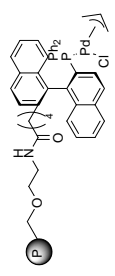
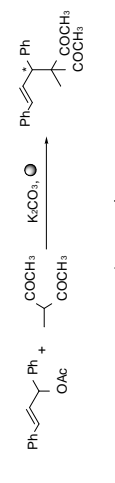
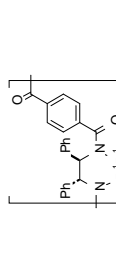

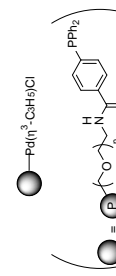
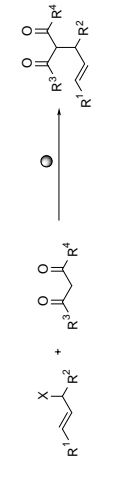
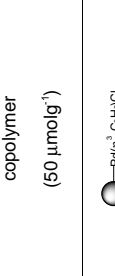
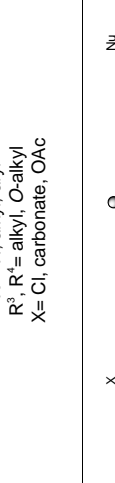
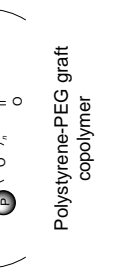
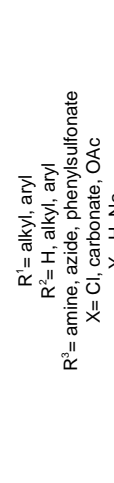
3.47.5 Reactions (Palladium coupling reactions)—continued

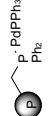

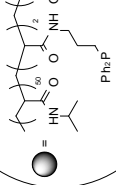


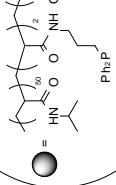
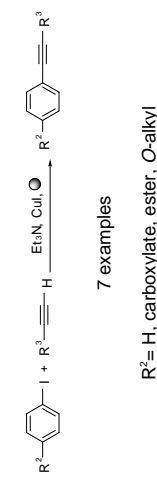
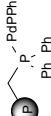

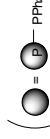


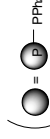
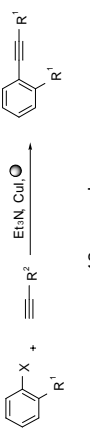
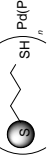


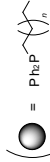

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (0.50 mmol g <sup>-1</sup> )	 14 examples R <sup>1</sup> = H, acyl, alkyl, acyl, hal, nitro, O-alkyl	Y:71-99	Some palladium leaches from the polymer during the reaction. General procedure.	1389, 1390, 1391, 1392	1389, 1390, 1391, 1392
 Pd(0)	 14 examples R <sup>1</sup> = H, alkyl, Br, Cl, carboxylic acid, nitro, O-alkyl	Y:71-99	The resin catalyst appeared to be more reactive than the analogous homogeneous catalyst. Experimental section.	1393, 1394	1393, 1394
 Zirconium support	 3 examples R <sup>1</sup> = ester, O-alkyl	C:100	The reagent was recycled with no loss of activity, provided it was stored under an inert atmosphere. General procedure.	1395	1395
 Pd(II)	 1 example		The kinetic study used compared the polymer catalyst with the solution catalyst. The polymer was successfully recycled.	1396	1396
 (ZrO <sub>2</sub> ) <sub>n</sub>	 6 examples R <sup>1</sup> = ester, O-alkyl	C:87-92	The catalyst may be reused without loss of activity. In competitive reactions the smallest product was the major one produced. General procedure.	1395	1395







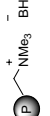


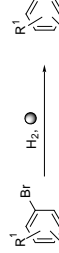

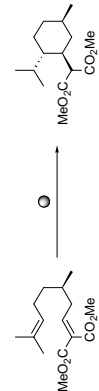
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (0.90 mmol g <sup>-1</sup> )	 15 examples R <sup>1</sup> = H, alkyl R <sup>2</sup> = aryl, het, vinyl X = BF <sub>4</sub> <sup>-</sup> , OTs	Y:80-92	The polymer may be reused without loss of activity. These Heck reactions may be run in the absence of NaHCO <sub>3</sub> with only a minimal effect on yield. General procedure.	1397	1397
 Pd(0)	 4 examples R <sup>1</sup> = alkyl, aryl	Y:79-85	Olefins containing carboxylic acids or unprotected amines were not compatible with this protocol for the Heck reaction. General procedure.	1398	1398
 (0.24 mmol g <sup>-1</sup> )	 6 examples R <sup>1</sup> = alkyl, O-allyl R <sup>2</sup> = H, alkyl	Y:46-100	Experimental section.	1376	1376
 Pd(0)	 7 examples R <sup>1</sup> = H, aryl R <sup>2</sup> = alkyl, O-alkyl X = aryl sulfonate, 2° amine,	Y:86-96	The catalyst can be recovered efficiently by solvent or thermal precipitation methods. General procedures.	1399	1399
 Tentagel	 11 examples R <sup>1</sup> , R <sup>2</sup> = H, alkyl, aryl R <sup>3</sup> = amino acid, azide, malonate,	Y:79-100	Reagent may be recycled without loss of activity.	1400	1400


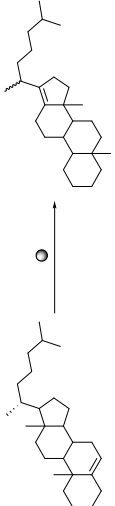

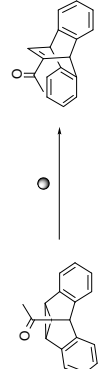

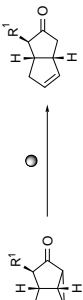

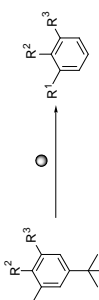

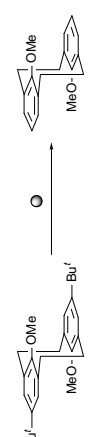
3.47.5 Reactions (Palladium coupling reactions)—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 <p>Tentagel</p>	 <p>1 example</p>	Y:75 ee:81	Seven polymeric catalysts were tested. The best result is shown.	1401	1401
 <p>R¹ = H, alkyl</p>	 <p>3 examples</p> <p>R², R³ = alkyl, aryl</p>	C:38-80 ee:25-80	(R)-enantiomers were obtained as major products. Full experimental section.	1402	1402
 <p>Polystyrene-PEG graft copolymer (50 μmolg⁻¹)</p>	 <p>10 examples</p> <p>R¹ = alkyl, aryl R² = H, alkyl, aryl R³, R⁴ = alkyl, O-alkyl X = Cl, carbonate, OAc</p>	Y:68-100	Resin may be recycled without loss of activity. The reactions were carried out in water. Experimental section.	1403	1403
 <p>Polystyrene-PEG graft copolymer (50 μmolg⁻¹)</p>	 <p>10 examples</p> <p>R¹ = alkyl, aryl R² = H, alkyl, aryl R³ = amine, azide, phenylsulfonate X = Cl, carbonate, OAc Y = H, Na</p>	Y:86-98	Resin may be recycled without loss of activity. The reactions were carried out in water. Experimental section.	1403	1403
 <p>Polystyrene-PEG graft copolymer (50 μmolg⁻¹)</p>	 <p>13 examples</p> <p>R¹ = H, aryl, CF(CF₃)₂, ketone, TMS R² = alkyl R³ = alkyl, aryl</p>	Y:1-96	The catalyst can be reused repeatedly. The yields were better than those obtained using Pd/C. Experimental section.	354, 1374	354


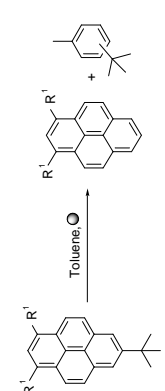

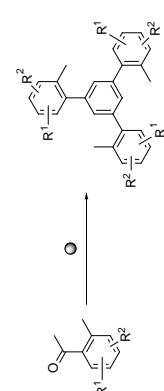

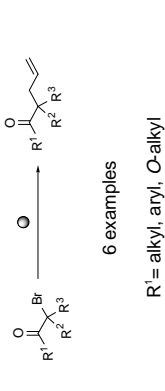
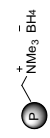
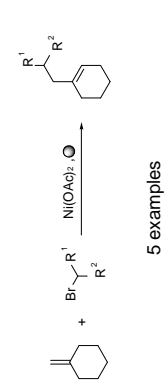
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
   $R^1 = H, iPr$	 1 example	Y:98	The catalyst may be recycled with some loss of activity. General procedure.	1383	1383
  $R^1 = H, iPr$	 7 examples $R^2 = H, \text{carboxylate, ester, O-alkyl}$ $R^3 = \text{alkyl, aryl}$	Y:88-96	The catalyst can be recovered efficiently by solvent or thermal precipitation methods. General procedure.	1399	1399
  	 2 examples $R^1 = \text{alkyl, aryl}$		The catalyst may be recycled with some loss of activity. General procedure.	1383	1383
 	 12 examples $R^1 = NH_2, NHAc, CO_2Me, CO_2H, CH_2OH$ $R^2 = \text{alkyl, aryl, silyl}$ $X = Br, I$	Y:50-95	The catalyst may be recycled, with a loss of ~20% activity.	1404	1404
 (4.6 mmol g <sup>-1</sup> )	 12 examples $R^1 = H, Cl, \text{alkyl}$ $R^2 = \text{alkyl, aryl, alcohol, ether}$	Y:86-95	An unusual application of sulfur ligands in palladium chemistry. Full experimental section.	1405	1405
  (0.60 mmol g <sup>-1</sup> )	 6 examples $R^1 = \text{alkyl}$ $R^2, R^3 = H, \text{alkyl}$	Y:13-100	The catalyst was oxidised by O <sub>2</sub> at elevated temperatures. The catalyst is soluble when heated but precipitates when cooled. If oxidation by adventitious oxygen is avoided, catalyst may be recycled many times. Experimental section.	278	278

3.48 Miscellaneous

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 SO <sub>3</sub> H Amberlyst A-15 (4.3 mmol g <sup>-1</sup> ) Amberlyst 1010 (3.3 mmol g <sup>-1</sup> ) Dowex 50W-X8 (4.8 mmol g <sup>-1</sup> )	 <p>6 examples</p> <p>R<sup>1</sup> = alkyl, amine, hal, hydroxy, O-alkyl X = H, D, T</p>		Deactivated compounds such as nitrobenzene could not be labelled using the Dowex type resin. A variety of regioisomers of isotope incorporation were produced.	1406	
 SO <sub>3</sub> H Nafion-H (0.9 mmol g <sup>-1</sup> )	 <p>4 examples</p> <p>R<sup>1</sup> = alkyl, amine, halo, hydroxy, O-alkyl X = D, T</p>		All examples given were compounds of biological interest.	1406	
 NMe <sub>3</sub> <sup>+</sup> BH <sub>4</sub> <sup>-</sup>	 <p>20 examples</p> <p>R<sup>1</sup> = H, alkyl, carbonyl, hydroxy, nitrile, O-alkyl X = hal</p>	Y:0-100		1407	551
 NH <sub>2</sub> <sup>+</sup> P-Cl <sub>2</sub> Montmorillonite K 10 (0.47 mmol g <sup>-1</sup> )	 <p>9 examples</p> <p>R<sup>1</sup> = H, aldehyde, aryl, ketone, nitro R<sup>2</sup> = H, aryl, nitro</p>	Y:85-98	Nitro groups are not reduced. General procedure.	1408	555
 FeCl <sub>3</sub>	 <p>1 example</p>	Y:92 de:98	Experimental section.	1409	1409

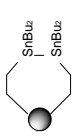
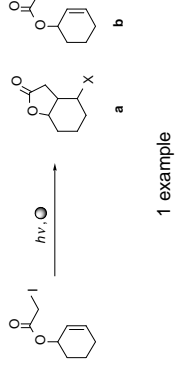
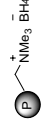



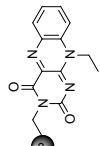
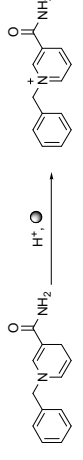
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Montmorillonite K 10	 1 example	Y:92	Conversion was faster than under standard solution phase conditions. Experimental section.	1410	
 Nafion-TMS	 5 examples	Y:81-99	One rearrangement is shown, but other similar rearrangements were also described. General procedure.	1411	
 Nafion-TMS	 2 examples R <sup>1</sup> = H, alkyl	Y:85-90	General procedure.	1411	
 Nafion-H	 17 examples R <sup>1</sup> , R <sup>2</sup> = H, alkyl, hydroxy R <sup>3</sup> = alkyl, <i>N</i> -alkyl	Y:80-98	Some di- <i>tert</i> -butylation was observed. Experimental section.	1412	
 Nafion-H	 1 example	Y:34	Experimental section.	1413	

3.48 Miscellaneous—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 Nafion	 2 examples $R^1 = \text{alkyl, O-alkyl}$	Y:78-80	Full experimental section.	1414, 1415	
 Nafion-H	 10 examples $R^1 = \text{H, alkyl, hal, nitro, O-alkyl}$ $R^2 = \text{H, hal, O-alkyl}$	Y:0-74	<i>ortho</i> substituted acetophenone gave no condensation product. General procedures.	1416	
 (0.96 mmol g <sup>-1</sup> )	 6 examples $R^1 = \text{alkyl, aryl, O-alkyl}$ $R^2, R^3 = \text{H, alkyl}$	Y:50-73	Reaction was successful only with $\alpha$ -bromo carbonyls. Tin by-products can be removed after precipitation of the resin using methanol and subsequent filtration. Less than 7 ppm residual tin was detected in products. The reagent was selective for the most electron deficient bromine. General procedure.	1417	1417
	 5 examples $R^1 = \text{H, alkyl}$ $R^2 = \text{amide, ester, nitrile}$	Y:51-91	Mechanism for the reaction is discussed in the paper. Experimental section.	1201	1201

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
  R <sup>1</sup> = AcCO <sub>2</sub> <sup>-</sup> , AllylCO <sub>2</sub> <sup>-</sup> , AlkylCO <sub>2</sub> <sup>-</sup> , NaphthylO <sup>-</sup> (1.1–2.0 mmolg <sup>-1</sup> )	$R^2-X \xrightarrow{\bullet} R^2-R^1$ <p>12 examples            R<sup>1</sup> = alkyl, benzyl            X = Br, Cl, I</p>	Y:50-90	General procedure.	1418	1418
	$R^1-R^2 \xrightarrow{I_2, \bullet} R^1(R^2)-R^1$ <p>3 examples            R<sup>1</sup> = CN, ester            R<sup>2</sup> = aryl, CN, ester</p>	Y:31-52	The ratio of products may be altered by varying the stoichiometry of iodine to alkane. General procedure.	1419	
	$R^1(R^2)-R^2 \xrightarrow{I_2, \bullet} R^1(R^2)(R^3)-R^1$ <p>3 examples            R<sup>1</sup> = aryl, ester, S-alkyl            R<sup>2</sup> = CN, S-alkyl, S-aryl            R<sup>3</sup> = aryl, S-alkyl, S-aryl</p>	Y:58-83	Better yields were obtained with increasing substitution. General procedure.	1419	
	$R^1-R^2 \xrightarrow{I_2, \bullet} R^1(R^2)-R^1$ <p>7 examples            R<sup>1</sup> = CN, ester            R<sup>2</sup> = aryl, CN, ester, phosphate ester, S-aryl</p>	Y:60-90	Radical reaction. General procedure.	1419	
 (1.0-1.1 mmolg <sup>-1</sup> )	<p>1 example</p>	Y:68	Starting material (30%) recovered, but no radical debromination was observed. Experimental section.	1420	1420

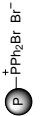
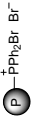
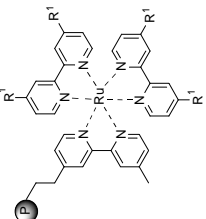
3.48 Miscellaneous—continued

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (1.0-1.1 mmolg <sup>-1</sup> )	 1 example X= H, I	Y:35-41 (a) Y:50-61 (b)	Low levels (0.02–0.1 mol%) of tin contamination were observed. Experimental section.	1420	1420
	 13 examples R <sup>1</sup> = alkyl, benzyl R <sup>2</sup> = H, alkyl X= I, H	Y:40-88	Experimental section.	1421	
 Amberlyst A-15 Proton form	 4 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = alkyl	Y:72-84	Enol ether was formed if the alkene was stabilised, otherwise an acetal was formed. General procedure.	98	
 PS-Flavin (1-6 μmolg <sup>-1</sup> )	 1 example		Kinetic study. Tested various polymers: XAD-2, HP-50, μ-styragel 10 <sup>5</sup> . Merrifield. The reagent was successfully recycled.	1422	1422




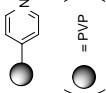


Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (0.60 mmol g <sup>-1</sup> )	 3 examples R <sup>1</sup> = H, alkyl	Y:88-94	Several polymers with different loadings were used. The best example is given. Experimental section.	1423	1423
 (3.0 mmol g <sup>-1</sup> )	 1) TFA ii) CBr <sub>4</sub> , Et <sub>3</sub> N, BrO-NH <sub>2</sub> iii) R <sup>2</sup> -NH <sub>2</sub> iv) Pd/C, H <sub>2</sub> 27 examples R <sup>1</sup> = H, alkyl, benzyl R <sup>2</sup> , R <sup>3</sup> = aryl	Y:59-100 P:90->98	<i>tert</i> -Butyl ester was cleaved, then coupled with <i>O</i> -benzyl hydroxylamine. Removal of unreacted acid with polymer-supported amine is followed by hydrogenolysis of the benzyl protection.	79	
 ( = PVP )	 3 examples R <sup>1</sup> = alkyl, benzyl	Y:75-98	The products were cleanly converted to hydroxylamines using sodium methoxide in methanol. Full experimental section.	1424	
 (0.27 mmol g <sup>-1</sup> )	 1) DCCO ii) N-hydroxysuccinimide 9 examples R <sup>1</sup> = alkyl, amino acid, aryl, het R <sup>2</sup> = H, AC	Y:56-100	This very stable reagent may be reused without loss of activity. Attempted use of pentafluorophenol as the nucleophile did not afford any activated ester product. When the anhydride was used, DCC was not required.	1425	517
 (1.7-2.4 mmol g <sup>-1</sup> )	 1) O ii) R <sup>2</sup> -NH <sub>2</sub> iii) NC-N 5 examples R <sup>1</sup> = alkyl, aryl R <sup>2</sup> = alkyl	Y:59-90	By changing the reaction conditions, one can obtain exclusively symmetric or asymmetric products. Experimental section.	1426	

3.48 Miscellaneous—continued

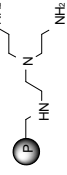
Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
 (2.2 mmol g <sup>-1</sup> )	$  \begin{array}{c}  \text{R}^1 \\    \\  \text{O} \\     \\  \text{N}^+ \text{R}^2 \\    \\  \text{H}  \end{array}  \xrightarrow{\text{NEt}_3}  \begin{array}{c}  \text{R}^1 \\    \\  \text{N} \\     \\  \text{R}^2  \end{array}  $ <p>4 examples R<sup>1</sup>, R<sup>2</sup> = alkyl, aryl</p>	Y:70-90	General procedure.	465	465
 (2.2 mmol g <sup>-1</sup> )	$  \begin{array}{c}  \text{X} \\    \\  \text{R}^1 \text{N}^+ \text{R}^2 \\    \\  \text{H}  \end{array}  \xrightarrow{\text{NEt}_3}  \begin{array}{c}  \text{R}^1 \\    \\  \text{N} \\     \\  \text{R}^2  \end{array}  $ <p>4 examples X = O, S R<sup>1</sup>, R<sup>2</sup> = Ph, C<sub>6</sub>H<sub>11</sub></p>	Y:76-92	Recovered polymer was regenerated by reduction with trichlorosilane. Experimental section.	465	465
 (0.18-0.24 mmol g <sup>-1</sup> ) R <sup>1</sup> = H, CO <sub>2</sub> H	$  \text{H}_2\text{O} \xrightarrow{h\nu} \text{H}_2 + \text{O}_2  $ <p>1 example</p>		Catalyst is stable in the dark. Leaching of complexes into solution is a problem. Full experimental section.	1427	1427

## 4 Tables of scavengers

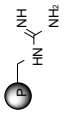
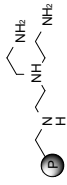


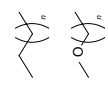
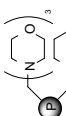
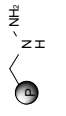
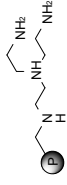

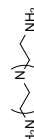

### 4.1 Acids

Reagent (Loading)	Comments	Ref.	Prep. Ref.
 (3 mmolg <sup>-1</sup> )	Scavenges HCl, acid anhydride, and carboxylic acid.	63	
 ( = PVP )	Effective as a tetrafluoroboric acid scavenger.	1428	189, 190, 1424
 (3.4 mmolg <sup>-1</sup> )	Used to scavenge acid by-product from the formation of amides from acid chlorides and amines.	59	42
 Amberlyst A-21	Used for the scavenging of hydrochloric acid residues.	79	

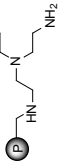
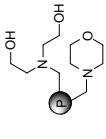
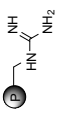
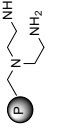
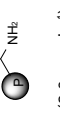
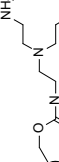
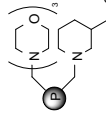
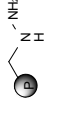
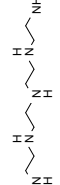
### 4.2 Acyl halides

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: acid chlorides, acid anhydrides, activated esters, aldehydes, epoxides, alkyl halides, alkylsulfonates, enones, imidazoles, isocyanates, isothiocyanates, ketones, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and $\alpha,\beta$ -unsaturated esters.	1431	1431

4.2 Acyl halides—continued

Reagent (Loading)	Comments	Ref.	Prep. Ref.
 (4.3 mmol g <sup>-1</sup> )	Removes: acid chlorides, acid anhydrides, activated esters, alkyl halides, alkylsulfonates, α-diketones, β-diketones, enones, epoxides, imidazolides, isocyanates, isothiocyanates, ketones, β-ketoesters, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and α,β-unsaturated esters.	1431	1431
 (3.4 mmol g <sup>-1</sup> )	Full experimental section.	42	42
 (3 mmol g <sup>-1</sup> )	Examples are given for N-alkylation reactions, where excess starting material was removed using the scavenging resin.	52	
 L =  R = H, alkyl n = 0-10 (● = Polystyrene, polyacrylamide, cellulose, silica, alumina, glass)	Amide library synthesised using the coupling reaction between 235 primary and 169 secondary amines reacted with 340 acid chlorides. Purified with scavenger used in conjunction with solid-supported base to scavenge acid. Aminomethylpolystyrene was the main example given.	1432, 40	
 (3.4 mmol g <sup>-1</sup> )	Removes: acid anhydrides, acid chlorides, activated esters, alkyl halides, alkylsulfonates, α-haloketones, imidazoles, isocyanates, isothiocyanates, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides, silyl triflates and sulfonyl chlorides.	1431	1431
 (3.4 mmol g <sup>-1</sup> )	Removes: acid anhydrides, acid chlorides, activated esters, aldehydes, alkyl halides, alkylsulfonates, α-diketones, β-diketones, enones, epoxides, imidazolides, isocyanates, isothiocyanates, ketones, β-ketoesters, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and α,β-unsaturated esters.	1431	1431
 (3.4 mmol g <sup>-1</sup> )	Used to remove excess acid chloride in amide condensations. Isocyanate resin was used simultaneously to sequester unreacted amine.	59	
 (3 mmol g <sup>-1</sup> )	Full experimental section.	63, 43	
 (3 mmol g <sup>-1</sup> )	Excess acid chloride used for preparation of amides was removed by reaction with pentaerythritolamine and 1,4-phenylene diisocyanate. Filtration of insoluble polyurea afforded clean products. General procedure.	523	
 (3 mmol g <sup>-1</sup> )	Removes: acid chlorides, acid anhydrides, activated esters, alkyl halides, alkylsulfonates, boronic acids, diazoalkanes, epoxides, α-haloketones, imidazoles, isocyanates, isothiocyanates, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, silyl triflates and silyl triflates.	1431	1431

### 4.3 Acid anhydrides

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: acid chlorides, acid anhydrides, activated esters, aldehydes, epoxides, alkyl halides, alkylsulfonates, enones, imidazoles, isocyanates, isothiocyanates, phosphonyl chlorides, Meerwein reagent, phosphoryl chlorides and $\alpha,\beta$ -unsaturated esters.	1431	1431
	Removes: acid chlorides, acid anhydrides, activated esters, alkyl halides, alkylsulfonates, boronic acids, diazoalkanes, epoxides, $\alpha$ -haloketones, imidazoles, isocyanates, isothiocyanates, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, silyl triflates and silyl triflates.	1431	1431
	Removes: acid chlorides, acid anhydrides, activated esters, alkyl halides, alkylsulfonates, $\alpha$ -diketones, $\beta$ -diketones, enones, epoxides, imidazolides, isocyanates, isothiocyanates, $\beta$ -ketoesters, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and $\alpha,\beta$ -unsaturated esters.	1431	1431
 (2.4 mmol g <sup>-1</sup> )	A library of 37 compounds was purified by this scavenger resin.	44	44
 (3.0 mmol g <sup>-1</sup> )	Also scavenges HCl, acid anhydrides and carboxylic acids.	63	
	Removes: acid chlorides, acid anhydrides, activated esters, imidazoles, isocyanates, isothiocyanates, sulfonyl chlorides, phosphoryl chlorides, phosphoryl chlorides, alkyl halides, alkylsulfonates, epoxides, enones, unsaturated esters and thiourea.	1431	1431
	Removes: acid anhydrides, acid chlorides, activated esters, alkyl halides, alkylsulfonates, $\alpha$ -haloketones, imidazoles, isocyanates, isothiocyanates, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, silyl triflates and sulfonyl chlorides.	1431	1431
	Removes: acid anhydrides, acid chlorides, activated esters, aldehydes, alkyl halides, alkylsulfonates, $\alpha$ -diketones, $\beta$ -diketones, enones, epoxides, imidazolides, isocyanates, isothiocyanates, ketones, $\beta$ -ketoesters, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and $\alpha,\beta$ -unsaturated esters.	1431	1431
 Carbon fibre		1433	1433

#### 4.4 Acid hydrazines

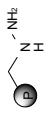
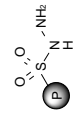
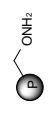
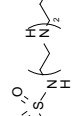
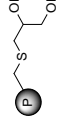
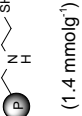

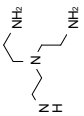
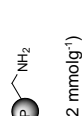
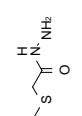
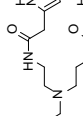
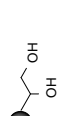
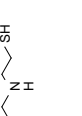
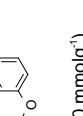
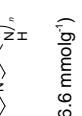
Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: primary and secondary amines, alcohols, carboxylic acids, guanidines, amidines, hydrazines, acid hydrazines, hydroxylamines, alkoxyamines and thiols.	1431	1431

#### 4.5 Alcohols

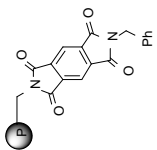
Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: alcohols, alkoxyamines, amidines, carboxylic acids, guanidines, hydrazines, hydroxylamines and thiols.	1431	1431
	Removes: alcohols, primary and secondary amines, carbanions, carboxylic acids, phenols, silanols and thiols.	1431	1431

#### 4.6 Aldehydes


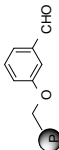
Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: acid chlorides, acid anhydrides, activated esters, aldehydes, epoxides, alkyl halides, alkylsulfonates, enones, imidazoles, isocyanates, isothiocyanates, ketones, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and $\alpha,\beta$ -unsaturated esters.	1431	1431

Reagent (Loading)	Comments	Ref.	Prep. Ref.
 (3.2 mmol g <sup>-1</sup> )	Removes: acid anhydrides, acid chlorides, activated esters, aldehydes, alkyl halides, alkylsulfonates, α-diketones, β-diketones, enones, epoxides, imidazolides, isocyanates, isothiocyanates, ketones, β-ketoesters, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and α,β-unsaturated esters.	1431	1431
 (1.2 mmol g <sup>-1</sup> )	Aldehydes, ketones and α-haloketones were scavenged.	1435	
 (8.0 mmol g <sup>-1</sup> )	Used for reversible binding of steroidal ketones and sugars. Experimental section.	1437	1437
 (0.65-1.4 mmol g <sup>-1</sup> )	Aromatic and aliphatic aldehydes were scavenged. Experimental section.	1438	1438
 (1.4 mmol g <sup>-1</sup> )	Scavenged aldehyde or ketone may be detached from the polymer using p-TSA in water. Experimental section.	1439	1439
 (3.0 mmol g <sup>-1</sup> )	Used in the purification of a thiazolidinone library to remove excess mercaptoacetic acid and carbonyl compounds. General procedure.	1434	1434
 (1.1 mmol g <sup>-1</sup> )	Primary amines were selectively removed in the presence of the secondary amine products of reductive aminations. Experimental section.	59	
	Used to remove unreacted amine in amide condensations. Tris amine resin was used simultaneously to sequester excess acid chloride.	59	
Reagent (Loading)	Comments	Ref.	Prep. Ref.
 (3.2 mmol g <sup>-1</sup> )	Used in the purification of a thiazolidinone library to remove excess mercaptoacetic acid and carbonyl compounds. General procedure.	1434	
 (1.2 mmol g <sup>-1</sup> )	Scavenger used for the parallel purification of a compound library.	1436	
 (3.9-6.6 mmol g <sup>-1</sup> )	Used for reversible binding of steroidal ketones and sugars. Experimental section.	1437	1437
 (3.0 mmol g <sup>-1</sup> )	Removes: aldehydes, alkyl halides, alkylsulfonates, chloroformates, imines, isocyanates, isothiocyanates, ketones, phosgene and thiophosgene.	1431	1431
 (3.9-6.6 mmol g <sup>-1</sup> )	Aldehydes and ketones were scavenged.	1440	
 (3.0 mmol g <sup>-1</sup> )	Removes: aldehydes, alkyl halides, alkylsulfonates, disulfides, epoxides, α-haloketones, ketones, Meerwein reagent, oxidants, silyl chlorides, silyl triflates and thiols.	1431	1431
 (3.9-6.6 mmol g <sup>-1</sup> )	Primary amines were selectively removed in the presence of the secondary amine products of a reductive aminations. Experimental section.	59	
 (3.9-6.6 mmol g <sup>-1</sup> )	The aldehyde could be recovered. The reagent was regenerated the by treatment with 1 M hydrochloric acid. Experimental section.	1441	

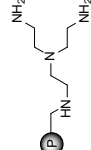
#### 4.7 Alkoxides

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: alkoxides, primary and secondary amines, carbanions, hydroxides and hydride reducing agents.	1431	1431

#### 4.8 Alkoxyamines

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: alkoxyamines, primary amines, 1,2-aminoalcohols, 1,3-aminoalcohols, 1,3-aminothiols, carbanions, 1,3-diols, 1,2-dithiols, 1,3-dithiols, glycols, hydrazines, hydride reducing agents and hydroxylamines.	1431	1431
	Removes: carbanions, primary amines, hydroxylamines, alkoxyamines, hydrazines, glycols, 1,3-diols, 1,2-dithiols, 1,3-dithiols, 1,2-aminoalcohols, 1,3-aminoalcohols, 1,2-aminothiols, 1,3-aminothiols and hydride reducing agents.	1431	1431

#### 4.9 Alkyl halides

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: acid chlorides, acid anhydrides, activated esters, aldehydes, epoxides, alkyl halides, alkylsulfonates, enones, imidazoles, isocyanates, isothiocyanates, ketones, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and $\alpha,\beta$ -unsaturated esters.	1431	1431

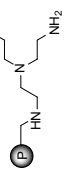
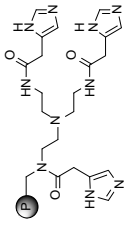
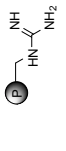
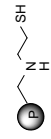
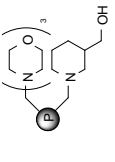
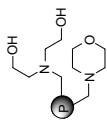
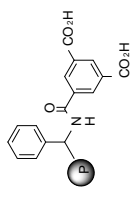
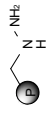
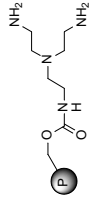


Removes: acid chlorides, acid anhydrides, activated esters, alkyl halides, alkylsulfonates, boronic acids, diazoalkanes, epoxides, $\alpha$ -haloketones, imidazoles, isocyanates, isothiocyanates, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, silyl chlorides and silyl triflates.	1431	1431	1431	1431	1431	1431
Removes: acid chlorides, acid anhydrides, activated esters, alkyl halides, alkylsulfonates, $\alpha$ -diketones, $\beta$ -diketones, enones, epoxides, imidazolides, isocyanates, $\beta$ -ketoesters, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and $\alpha,\beta$ -unsaturated esters.	1431	1431	1431	1431	1431	1431
Removes: aldehydes, alkyl halides, alkylsulfonates, chloroformates, imines, isocyanates, isothiocyanates, ketones, phosgene and thiophosgene.	1431	1431	1431	1431	1431	1431
Removes: alkyl halides, alkylsulfonates, diazoalkanes, $\alpha$ -haloketones, silyl chlorides and silyl triflates.	1431	1431	1431	1431	1431	1431
Removes: alkyl halides, alkylsulfonates and $\alpha$ -haloketones.	1431	1431	1431	1431	1431	1431

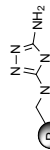
#### 4.10 Alkyl sulfonates

Removes: alkyl halides, alkylsulfonates, disulfides, epoxides, $\alpha$ -haloketones, oxidants, silyl chlorides, silyl triflates and thiols.	1431	1431	1431	1431	1431	1431
Removes: alkyl halides, alkylsulfonates, $\alpha$ -haloketones, oxidants, vinyl bromides and vinyl triflates.	1431	1431	1431	1431	1431	1431
Removes: alkyl halides, alkylsulfonates, $\alpha$ -haloketones.	1431	1431	1431	1431	1431	1431

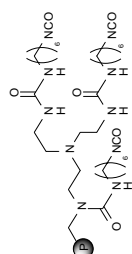
4.10 Alkyl sulfonates—continued

	<p>Removes: acid chlorides, acid anhydrides, activated esters, aldehydes, epoxides, alkyl halides, alkylsulfonates, enones, imidazoles, isocyanates, isothiocyanates, ketones, Meerwein reagent, phosphoryl chlorides, sulfonyl chlorides and <math>\alpha,\beta</math>-unsaturated esters.</p>	1431	1431
	<p>Removes: aldehydes, alkyl halides, alkylsulfonates, chloroformates, imines, isocyanates, isothiocyanates, ketones, phosgene and thiophosgene.</p>	1431	1431
	<p>Removes: acid chlorides, acid anhydrides, activated esters, alkyl halides, alkylsulfonates, <math>\alpha</math>-diketones, <math>\beta</math>-diketones, enones, epoxides, imidazolides, isocyanates, isothiocyanates, <math>\beta</math>-ketoesters, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and <math>\alpha,\beta</math>-unsaturated esters.</p>	1431	1431
	<p>Removes: aldehydes, alkyl halides, alkylsulfonates, disulfides, epoxides, <math>\alpha</math>-haloketones, ketones, Meerwein reagent, oxidants, silyl chlorides, silyl triflates and thiols.</p>	1431	1431
	<p>Removes: acid anhydrides, acid chlorides, activated esters, alkyl halides, alkylsulfonates, <math>\alpha</math>-haloketones, imidazoles, isocyanates, isothiocyanates, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, silyl chlorides, silyl triflates and sulfonyl chlorides.</p>	1431	1431
	<p>Removes: acid chlorides, acid anhydrides, activated esters, alkyl halides, alkylsulfonates, boronic acids, diazoalkanes, epoxides, <math>\alpha</math>-haloketones, imidazoles, isocyanates, isothiocyanates, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, silyl chlorides and silyl triflates.</p>	1431	1431
	<p>Removes: alkyl halides, alkylsulfonates, diazoalkanes, <math>\alpha</math>-haloketones, silyl chlorides and silyl triflates.</p>	1431	1431
	<p>Removes: acid anhydrides, acid chlorides, activated esters, aldehydes, alkyl halides, alkylsulfonates, <math>\alpha</math>-diketones, <math>\beta</math>-diketones, enones, epoxides, imidazolides, isocyanates, isocyanates, isothiocyanates, ketones, <math>\beta</math>-ketoesters, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and <math>\alpha,\beta</math>-unsaturated esters.</p>	1431	1431
	<p>Removes: acid chlorides, acid anhydrides, activated esters, imidazoles, isocyanates, isothiocyanates, sulfonyl chlorides, phosphoryl chlorides, phosphoryl chlorides, alkyl halides, alkylsulfonates, epoxides, enones, unsaturated esters, carbonyls and thiourea.</p>	1431	1431

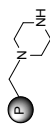
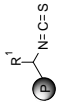
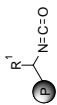
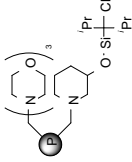
#### 4.11 Amides

Reagent (Loading)	Comments	Ref.	Prep. Ref.	Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: $\alpha$ -diketones, $\beta$ -diketones, $\alpha$ -haloketones, $\beta$ -ketoesters, $\alpha$ -ketoesters, $\alpha$ -ketoamides, $\beta$ -ketoamides, vinyllogous esters and vinyllogous amides.	1431	1431				






#### 4.12 Amidines



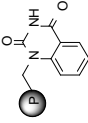






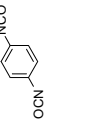


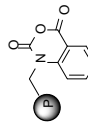

Reagent (Loading)	Comments	Ref.	Prep. Ref.	Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: alcohols, alkoxyamines, amidines, carboxylic acids, guanidines, hydrazines, hydroxyamines and thiols.	1431	1431				

#### 4.13 Amines

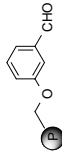
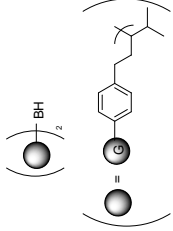
Reagent (Loading)	Comments	Ref.	Prep. Ref.	Reagent (Loading)	Comments	Ref.	Prep. Ref.
 (2.4 mmol g <sup>-1</sup> )	Preparation given.		1442	 R <sup>1</sup> = H, alkyl		56	
 R <sup>1</sup> = H, alkyl		1431	1431		Removes: alcohols, primary and secondary amines, carbanions, carboxylic acids, phenols, silanols and thiols.	1431	1431

4.13 Amines continued

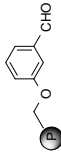
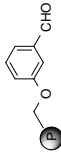
	<p>Removes: primary and secondary amines, dienes and sulfides.</p>	<p>1431</p>	<p>1431</p>	<p>Removes: alkoxides, primary and secondary amines, carbanions, hydroxides and hydride reducing agents.</p>	<p>1431</p>	<p>1431</p>	<p>1431</p>
	<p>Removes: alkoxyamines, primary amines, 1,2-aminoalcohols, 1,3-aminoalcohols, 1,3-aminothiols, 1,2-aminothiols, 1,3-dithiols, glycols, hydrazines, hydride reducing agents and hydroxylamines.</p>	<p>1431</p>	<p>1431</p>	<p>Removes: carbanions, primary amines, hydroxylamines, alkoxyamines, hydrazines, glycols, 1,3-dithiols, 1,3-dithiols, 1,2-aminoalcohols, 1,3-aminothiols, 1,2-aminothiols, 1,3-aminothiols and hydride reducing agents.</p>	<p>1431</p>	<p>1431</p>	<p>1431</p>
	<p>Scavenges amine used as excess component in epoxide opening and halide displacement reactions.</p> <p>Also see reference 1430.</p>	<p>40</p>	<p>65</p>	<p>Also scavenges amines.</p>	<p>65</p>	<p>65</p>	<p>65</p>
	<p>Also scavenges amines.</p>	<p>65</p>	<p>65</p>	<p>Amine converted to amide and then scavenged. Scavenger also scavenges excess activator.</p> <p>Full experimental.</p>	<p>62, 63</p>	<p>62, 63</p>	<p>62, 63</p>
 <p> <math>L = \text{O}(\text{CH}_2)_x</math>  <math>\text{NR}^1(\text{CH}_2)_x</math>  <math>\text{NR}^2(\text{CH}_2)_x</math> </p> <p> <math>\text{R}^1 = \text{NCO, NCS, COF, COCl, COBr, COI}</math>  <math>\text{R}^2 = \text{C1-C10}</math>  <math>\text{X} = \text{C1-C40}</math> </p>	<p>A total of 218 aldehydes and 111 ketones were reacted with 240 primary amines in library generation (Reductive amination).</p> <p>Main polymer-support used was polystyrene (1.0 mmol<sup>g</sup><sup>-1</sup>). Primary amines scavenged in the presence of secondary.</p> <p>Experimental section.</p>	<p>40, 572</p>	<p>573</p>	<p>Used for removal of primary and secondary amines.</p>	<p>573</p>	<p>573</p>	<p>573</p>

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Scavenges amine used as excess component in reductive amination.	40	
 Amberlyst A-15 Proton form	Scavenges tertiary amine tagged carbodiimide reagent. Experimental section.	43	
 (3.2 mmolg <sup>-1</sup> )	Product purity 97–99%.	1445	1445
 (1.0 mmolg <sup>-1</sup> )	Removes excess amines from thiourea and amide formations. Full experimental section.	42	42
 Amberlyst A-15 Proton form	Scavenger used in the purification of a library.	77	
 Varian SCX column	Used as a purification technique for the catch and release of amines.	1444	
	Resin used to scavenge dimethylamine formed during a hetero Diels–Alder reaction.	1447	
Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Scavenger for primary and secondary amines. The reagent scavenges secondary amines at a slower rate than primary amines. General procedures.	1443	
	Scavenger utilised in synthesis of a urea library. Product purity 95–98%. General procedures.	1444	
	Excess of amine used for the preparation of amides/sulfonamides was removed by reaction with 1,4-phenylene diisocyanate and filtration of the insoluble polyurea formed. General procedure.	523	
 SCX- Column	Amine is captured onto the SCX resin, and then released by washing with NH <sub>3</sub> in MeOH.	1446	
 Amberlyst A-15 Proton form	Scavenger used in the purification of a library.	57	
 (1.5–3.2 mmolg <sup>-1</sup> )	Removes excess amine in the synthesis of thioureas. General procedure.	1445	1445
 Amberlyst A-15 Proton form	Amines are retained as the salt and can be recovered. Over 40 examples demonstrated. General procedure.	1446	

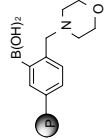
#### 4.14 Aminoalcohol

Reagent (Loading)		Comments	Ref.	Prep. Ref.
	Removes: alkoxyamines, primary amines, 1,2-aminoalcohols, 1,3-aminoalcohols, 1,3-aminothiols, 1,2-aminothiols, carbanions, 1,3-diols, 1,2-dithiols, 1,3-dithiols, glycols, hydrazines, hydride reducing agents and hydroxylamines.	1431	1431	1431
Reagent (Loading)		Used in the purification of a library of amino alcohols. Reagent is moisture sensitive and is best stored as a solution in toluene. Experimental section.	1448	1448
	Removes: carbanions, primary amines, hydroxylamines, alkoxyamines, hydrazines, glycols, 1,3-diols, 1,2-dithiols, 1,3-dithiols, 1,2-aminoalcohols, 1,3-aminoalcohols, 1,2-aminothiols, 1,3-aminothiols and hydride reducing agents	1431	1431	1431

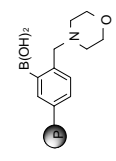
#### 4.15 Aminothiols

Reagent (Loading)		Comments	Ref.	Prep. Ref.
	Removes: alkoxyamines, primary amines, 1,2-aminoalcohols, 1,3-aminoalcohols, 1,3-aminothiols, 1,2-aminothiols, carbanions, 1,3-diols, 1,2-dithiols, 1,3-dithiols, glycols, hydrazines, hydride reducing agents and hydroxylamines.	1431	1431	1431
Reagent (Loading)		Removes: carbanions, primary amines, hydroxylamines, alkoxyamines, hydrazines, glycols, 1,3-diols, 1,2-dithiols, 1,3-dithiols, 1,2-aminoalcohols, 1,3-aminoalcohols, 1,2-aminothiols, 1,3-aminothiols and hydride reducing agents	1431	1431

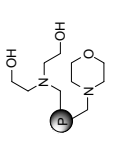
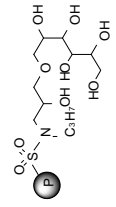
#### 4.16 Aryl halides

Reagent (Loading)		Comments	Ref.	Prep. Ref.
	Removes: aryl iodides, aryl bromides, aryl triflates, vinyl iodides, vinyl bromides and vinyl triflates.	1431	1431	1431
Reagent (Loading)		Comments	Ref.	Prep. Ref.

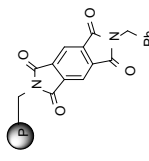
#### 4.17 Aryl triflates

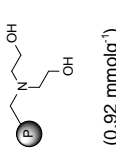
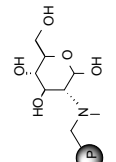
Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: aryl iodides, aryl bromides, aryl triflates, vinyl iodides, vinyl bromides and vinyl triflates.	1431	1431

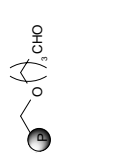
#### 4.18 Boronic acids

	Removes: acid chlorides, acid anhydrides, activated esters, alkyl halides, alkylsulfonates, boronic acids, diazoalkanes, epoxides, $\alpha$ -haloketones, imidazoles, isocyanates, isothiocyanates, Meerwein reagent, phosphonyl chlorides, phosphoryl chlorides, silyl chlorides and silyl triflates.	1431	1431
	Efficient and specific sorbent for the removal of boronic acids. The resin may be regenerated and reused. Experimental section.	1449	1449

#### 4.19 Carbanions

	Removes: alkoxides, primary and secondary amines, carbanions, hydroxides and hydride reducing agents.	1431	1431
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	Nine examples of boronic acids scavenged. Experimental section.	1371	1371
	Resin cannot be regenerated through acidic treatment.	1449	1449

	Removes: alkoxyamines, primary amines, 1,2-aminoalcohols, 1,3-aminoalcohols, 1,3-aminothiols, 1,2-aminothiols, carbanions, 1,3-diols, 1,2-dithiols, 1,3-dithiols, glycols, hydrazines, hydride reducing agents and hydroxylamines.	1431	1431
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#### 4.19 Carbanions—continued

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: alcohols, primary and secondary amines, carbanions, carboxylic acids, phenols, silanols and thiols.	1431	1431
	Removes: carbanions, primary amines, hydroxylamines, alkoxyamines, hydrazines, glycols, 1,3-diols, 1,2-dithiols, 1,3-dithiols, 1,2-aminoalcohols, 1,3-aminoalcohols, 1,2-aminothiols, 1,3-aminothiols and hydride reducing agents.	1431	1431

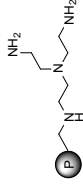

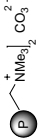
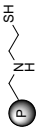
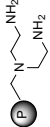

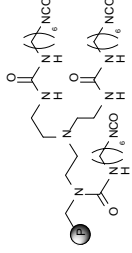
#### 4.20 Carbocations

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: chlorine, bromine, iodine carbocations and electrophilic reagents.	1431	1431

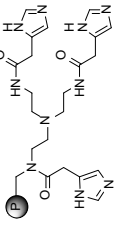
#### 4.21 Carboxylic acids

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: alcohols, primary and secondary amines, carbanions, carboxylic acids, phenols, silanols and thiols.	1431	1431

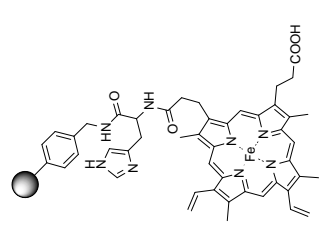


<p>Reagent (Loading)</p>  <p>(1.6-3.2 mmolg<sup>-1</sup>)</p>	<p>Comments</p> <p>Scavenger used for the removal of all excess carboxylic acid and ketone reagents present in the synthesis of a library of 4-thiazolidinones. More sterically hindered and less reactive ketones gave poor results. General procedure.</p>	<p>Ref.</p> <p>1434</p>	<p>Prep. Ref.</p>
<p>Reagent (Loading)</p>  <p>(3.0 mmolg<sup>-1</sup>)</p>	<p>Comments</p> <p>Scavenges HCl and anhydride as well as carboxylic acid.</p>	<p>Ref.</p> <p>63</p>	<p>Prep. Ref.</p>
<p>Reagent (Loading)</p>  <p>(1.4 mmolg<sup>-1</sup>)</p>	<p>Comments</p> <p>Resin used to scavenge DEAD reagent tagged with carboxylic acid. Carboxylic acid functionality is masked with <i>tert</i>-butyl ester prior to removal using the scavenging reagent.</p>	<p>Ref.</p> <p>61</p>	<p>Prep. Ref.</p>
<p>Reagent (Loading)</p>  <p>(1.4 mmolg<sup>-1</sup>)</p>	<p>Comments</p> <p>Scavenger used for the removal of all excess carboxylic acid and ketone reagents present in the synthesis of a library of 4-thiazolidinones. More sterically hindered and less reactive ketones gave poor results. General procedure.</p>	<p>Ref.</p> <p>1434</p>	<p>Prep. Ref.</p>
<p>Reagent (Loading)</p>  <p>(2.4 mmolg<sup>-1</sup>)</p>	<p>Comments</p> <p>Library of 37 compounds purified by scavenger resin.</p>	<p>Ref.</p> <p>44</p>	<p>Prep. Ref.</p> <p>44</p>
<p>Reagent (Loading)</p>  <p>(0.80 mmolg<sup>-1</sup>)</p>	<p>Comments</p> <p>Product purity 75–99%.</p>	<p>Ref.</p> <p>1450</p>	<p>Prep. Ref.</p>
<p>Reagent (Loading)</p> 	<p>Comments</p> <p>Removes: alcohols, alkoxyamines, amidines, carboxylic acids, guanidines, hydrazines, hydroxylamines and thiols.</p>	<p>Ref.</p> <p>1431</p>	<p>Prep. Ref.</p> <p>1431</p>

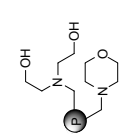
#### 4.22 Chloroformates

<p>Reagent (Loading)</p> 	<p>Comments</p> <p>Removes: aldehydes, alkyl halides, alkylsulfonates, chloroformates, imines, isocyanates, isothiocyanates, ketones, phosphene and thiophosgene.</p>	<p>Ref.</p> <p>1431</p>	<p>Prep. Ref.</p> <p>1431</p>
<p>Reagent (Loading)</p>	<p>Comments</p>	<p>Ref.</p>	<p>Prep. Ref.</p>

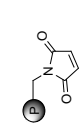
### 4.23 Cyanide ions

Reagent (Loading)	Comments	Ref.	Prep. Ref.
 <p>(0.40 mmol g<sup>-1</sup>)</p>	Cyanide ions may be removed from resin by washing with NaOH. Experimental section.	1451	1451

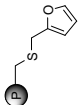
### 4.24 Diazoalkanes

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: acid chlorides, acid anhydrides, activated esters, alkyl halides, alkylsulfonates, boronic acids, diazoalkanes, epoxides, $\alpha$ -haloketones, imidazoles, isocyanates, isothiocyanates, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, silyl chlorides and silyl triflates.	1431	1431

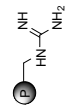
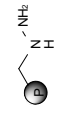
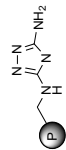
### 4.25 Dienes and 1,3-dipoles

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: primary and secondary amines, dienes, dipoles and sulfides.	1431	1431


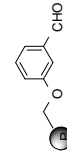
#### 4.26 Dienophiles and dipolarophiles

Reagent (Loading)	Comments	Ref.	Prep. Ref.	Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: dienophiles, dipolarophiles, chlorine, bromine, iodine and oxidants.	1431	1431				


#### 4.27 Diketones

Reagent (Loading)	Comments	Ref.	Prep. Ref.	Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: acid chlorides, acid anhydrides, activated esters, alkyl halides, alkylsulfonates, $\alpha$ -diketones, $\beta$ -diketones, enones, epoxides, imidazolides, isocyanates, isothiocyanates, $\beta$ -ketoesters, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and $\alpha,\beta$ -unsaturated esters.	1431	1431		Removes: acid anhydrides, acid chlorides, activated esters, aldehydes, alkyl halides, alkylsulfonates, $\alpha$ -diketones, $\beta$ -diketones, $\beta$ -ketoesters, enones, epoxides, imidazolides, isocyanates, isothiocyanates, ketones, $\beta$ -ketoesters, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and $\alpha,\beta$ -unsaturated esters.	1431	1431
	Removes: $\alpha$ -diketones, $\beta$ -diketones, $\alpha$ -haloketones, $\beta$ -ketoesters, $\alpha$ -ketoesters, $\alpha$ -ketoamides, $\beta$ -ketoamides, vinylogous esters and vinylogous amides.	1431	1431				

#### 4.28 Diols

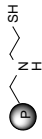
Reagent (Loading)	Comments	Ref.	Prep. Ref.	Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: alkoxyamines, primary amines, 1,2-aminoalcohols, 1,3-aminoalcohols, 1,3-aminothiols, 1,2-aminothiols, carbanions, 1,3-dithiols, 1,3-dithiols, glycols, hydrazines, hydride reducing agents and hydroxyamines. Also see reference 1452.	1431	1431		Removes: carbanions, primary amines, hydroxyamines, alkoxyamines, hydrazines, glycols, 1,3-dithiols, 1,3-dithiols, 1,2-aminoalcohols, 1,3-aminoalcohols, 1,2-aminothiols, 1,3-aminothiols, 1,2-aminothiols, 1,3-aminothiols and hydride reducing agents.	1431	1431

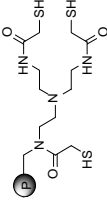
#### 4.28 Diols—continued

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Selective for <i>cis</i> diols over <i>trans</i> diols. The diol may be recovered from polymer by aqueous cleavage. The recovered resin may be recycled.	1453	1454


Reagent (Loading)	Comments	Ref.	Prep. Ref.

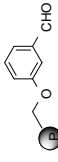
#### 4.29 Disulfides

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: aldehydes, alkyl halides, alkylsulfonates, disulfides, epoxides, $\alpha$ -haloketones, ketones, Meerwein reagent, oxidants, silyl chlorides, silyl triflates and thiols.	1431	1431

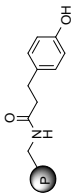
Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: alkyl halides, alkylsulfonates, disulfides, epoxides, $\alpha$ -haloketones, oxidants, silyl chlorides, silyl triflates and thiols.	1431	1431

#### 4.30 Dithiols

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: alkoxyamines, primary amines, 1,2-aminoalcohols, 1,3-aminoalcohols, 1,3-aminothiols, 1,2-aminothiols, carbanions, 1,3-diols, 1,2-dithiols, 1,3-dithiols, glycols, hydrazines, hydride reducing agents and hydroxylamines.	1431	1431

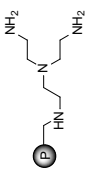
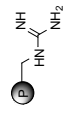
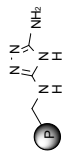
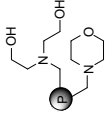
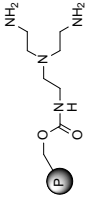
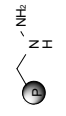
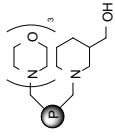
Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: carbanions, primary amines, hydroxylamines, alkoxyamines, hydrazines, glycols, 1,3-diols, 1,2-dithiols, 1,3-dithiols, 1,2-aminoalcohols, 1,3-aminoalcohols, 1,2-aminothiols, 1,3-aminothiols and hydride reducing agents.	1431	1431

#### 4.31 Electrophilic reagents

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: chlorine, bromine, iodine carbocations and electrophilic reagents.	1431	1431

Reagent (Loading)	Comments	Ref.	Prep. Ref.

### 4.32 Esters

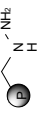
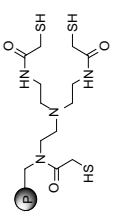
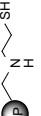
	<p>Removes: acid chlorides, acid anhydrides, activated esters, aldehydes, epoxides, alkyl halides, alkylsulfonates, enones, imidazoles, isocyanates, isothiocyanates, phosphoryl chlorides, Meerwein reagent, phosphonyl chlorides and <math>\alpha,\beta</math>-unsaturated esters.</p> <p>Also see reference 1430.</p>	1431	1431
	<p>Removes: acid chlorides, acid anhydrides, activated esters, alkyl halides, alkylsulfonates, <math>\alpha</math>-diketones, <math>\beta</math>-diketones, enones, epoxides, imidazolides, isocyanates, isothiocyanates, <math>\beta</math>-ketoesters, Meerwein reagent, phosphonyl chlorides, phosphoryl chlorides, sulfonyl chlorides and <math>\alpha,\beta</math>-unsaturated esters.</p>	1431	1431
	<p>Removes: <math>\alpha</math>-diketones, <math>\beta</math>-diketones, <math>\alpha</math>-haloketones, <math>\beta</math>-ketoesters, <math>\alpha</math>-ketoesters, <math>\alpha</math>-ketoamides, <math>\beta</math>-ketoamides, vinylogous esters, and vinylogous amides.</p>	1431	1431
	<p>Removes: acid chlorides, acid anhydrides, activated esters, alkyl halides, alkylsulfonates, boronic acids, diazoalkanes, epoxides, <math>\alpha</math>-haloketones, imidazoles, isocyanates, isothiocyanates, Meerwein reagent, phosphonyl chlorides, phosphoryl chlorides, silyl chlorides and silyl triflates.</p>	1431	1431
	<p>Removes: acid chlorides, acid anhydrides, activated esters, imidazoles, isocyanates, isothiocyanates, sulfonyl chlorides, phosphoryl chlorides, phosphoryl chlorides, alkyl halides, alkylsulfonates, epoxides, enones, unsaturated esters, carbonyls and thiourea.</p>	1431	1431
	<p>Removes: acid anhydrides, acid chlorides, activated esters, aldehydes, alkyl halides, alkylsulfonates, <math>\alpha</math>-diketones, <math>\beta</math>-diketones, enones, epoxides, imidazolides, isocyanates, isothiocyanates, ketones, <math>\beta</math>-ketoesters, Meerwein reagent, phosphonyl chlorides, phosphoryl chlorides, sulfonyl chlorides and <math>\alpha,\beta</math>-unsaturated esters.</p>	1431	1431
	<p>Removes: acid anhydrides, acid chlorides, activated esters, alkyl halides, alkylsulfonates, <math>\alpha</math>-haloketones, imidazoles, isocyanates, isothiocyanates, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, silyl chlorides, silyl triflates and sulfonyl chlorides</p>	1431	1431

### 4.33 Enones

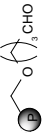
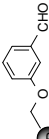
Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: acid chlorides, acid anhydrides, activated esters, aldehydes, epoxides, alkyl halides, alkylsulfonates, enones, imidazoles, isocyanates, isothiocyanates, ketones, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and $\alpha,\beta$ -unsaturated esters.	1431	1431
	Removes: acid chlorides, acid anhydrides, activated esters, alkyl halides, alkylsulfonates, $\alpha$ -diketones, $\beta$ -diketones, enones, epoxides, imidazolides, isocyanates, isothiocyanates, ketones, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and $\alpha,\beta$ -unsaturated esters.	1431	1431

### 4.34 Epoxides

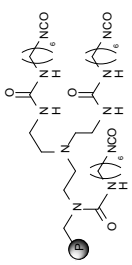
Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: acid chlorides, acid anhydrides, activated esters, aldehydes, epoxides, alkyl halides, alkylsulfonates, enones, imidazoles, isocyanates, isothiocyanates, ketones, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and $\alpha,\beta$ -unsaturated esters.	1431	1431
	Removes: acid chlorides, acid anhydrides, activated esters, alkyl halides, alkylsulfonates, $\alpha$ -diketones, $\beta$ -diketones, enones, epoxides, imidazolides, isocyanates, isothiocyanates, ketones, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and $\alpha,\beta$ -unsaturated esters.	1431	1431

		<p>Removes: acid anhydrides, acid chlorides, activated esters, aldehydes, alkyl halides, alkylsulfonates, <math>\alpha</math>-diketones, <math>\beta</math>-diketones, enones, epoxides, imidazolides, isocyanates, isothiocyanates, ketones, <math>\beta</math>-ketoesters, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and <math>\alpha,\beta</math>-unsaturated esters.</p>	1431	1431
		<p>Removes: aldehydes, alkyl halides, alkylsulfonates, disulfides, epoxides, <math>\alpha</math>-haloketones, <math>\alpha</math>-haloketones, ketones, Meerwein reagent, oxidants, silyl chlorides, silyl triflates and thiols.</p>	1431	1431

#### 4.35 Glycols

		<p>Removes: alkoxyamines, primary amines, 1,2-aminoalcohols, 1,3-aminoalcohols, 1,3-aminothiols, 1,2-aminothiols, carbanions, 1,3-dials, 1,2-dithiols, 1,3-dithiols, glycols, hydrazines, hydride reducing agents and hydroxyamines.</p>	1431	1431
		<p>Removes: carbanions, primary amines, hydroxyamines, alkoxyamines, hydrazines, glycols, 1,3-dials, 1,2-dithiols, 1,3-dithiols, 1,2-aminoalcohols, 1,3-aminoalcohols, 1,2-aminothiols, 1,3-aminothiols and hydride reducing agents.</p>	1431	1431

#### 4.36 Guanidines

		<p>Removes: alcohols, alkoxyamines, amidines, carboxylic acids, guanidines, hydrazines, hydroxyamines and thiols.</p>	1431	1431

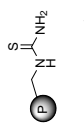
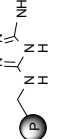
### 4.37 Haloformates

Reagent (Loading)	Comments	Ref.	Prep. Ref.
<p> <math>n = 0-10</math>  <math>R' = H, \text{ alkyl}</math>            ( ) = Polystyrene, polyacrylamide, cellulose, silica, alumina, glass         </p>	49 haloformates plus 404 1° and 2° amines reacted together to give carbamate library. Purified with scavenger. Mainly aminomethylpolystyrene used as reagent. General procedure.	1432	

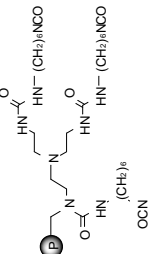

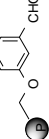

### 4.38 $\alpha$ -Haloketones

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: acid chlorides, acid anhydrides, activated esters, alkyl halides, alkylsulfonates, boronic acids, diazoalkanes, epoxides, $\alpha$ -haloketones, imidazoles, isocyanates, isothiocyanates, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, silyl chlorides and silyl triflates.	1431	1431
	Removes: aldehydes, alkyl halides, alkylsulfonates, disulfides, epoxides, $\alpha$ -haloketones, ketones, Meerwein reagent, oxidants, silyl chlorides, silyl triflates and thiols.	1431	1431
	Removes: alkyl halides, alkylsulfonates, disulfides, epoxides, $\alpha$ -haloketones, oxidants, silyl chlorides, silyl triflates and thiols.	1431	1431

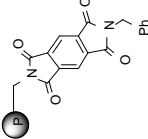
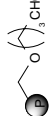


 (2.2 mmol g <sup>-1</sup> )		<p>α-Bromo ketone scavenged from a mixture containing carboxylic acids.</p> <p>Removes: α-diketones, β-diketones, α-halo ketones, β-ketoesters, α-ketoesters, α-ketoamides, β-ketoamides, vinylogous esters and vinylogous amides.</p>	Ref. 58 Prep. Ref. 58	Ref. 1431 Prep. Ref. 1431	Comments: Aldehydes and ketones and α-halo ketones are scavenged.	Ref. 1435 Prep. Ref.
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#### 4.39 Hydrazines

 (CH <sub>2</sub> ) <sub>2</sub>		<p>Removes: alcohols, alkoxyamines, amidines, carboxylic acids, guanidines, hydrazines, hydroxyamines and thiols.</p> <p>Removes: carbanions, primary amines, hydroxyamines, alkoxyamines, hydrazines, glycols, 1,3-diols, 1,2-dithiols, 1,3-dithiols, 1,2-aminoalcohols, 1,3-aminoalcohols, 1,2-aminothiols, 1,3-aminothiols and hydride reducing agents.</p>	Ref. 1431 Prep. Ref. 1431	Ref. 1431 Prep. Ref. 1431	Comments: Removes: alkoxyamines, primary amines, 1,2-aminoalcohols, 1,3-aminoalcohols, 1,3-aminothiols, 1,2-aminothiols, carbanions, 1,3-diols, 1,2-dithiols, 1,3-dithiols, glycols, hydrazines, hydride reducing agents and hydroxyamines.	Ref. 1431 Prep. Ref. 1431
	 (1.0 mmol g <sup>-1</sup> )	<p>Full experimental section.</p>	Ref. 1431 Prep. Ref. 1431	Ref. 42 Prep. Ref. 42	Comments: Full experimental section.	Ref. 42 Prep. Ref. 42

#### 4.40 Hydride reducing agents

		<p>Removes: alkoxides, primary and secondary amines, carbanions, hydroxides and hydride reducing agents.</p>	Ref. 1431 Prep. Ref. 1431	Ref. 1431 Prep. Ref. 1431	Comments: Removes: alkoxyamines, primary amines, 1,2-aminoalcohols, 1,3-aminoalcohols, 1,3-aminothiols, 1,2-aminothiols, carbanions, 1,3-diols, 1,2-dithiols, 1,3-dithiols, glycols, hydrazines, hydride reducing agents and hydroxyamines.	Ref. 1431 Prep. Ref. 1431
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#### 4.40 Hydride reducing agents—continued

Reagent (Loading)	Comments	Ref.	Prep. Ref.	Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: carbanions, primary amines, hydroxylamines, alkoxyamines, hydrazines, glycols, 1,3-diols, 1,2-dithiols, 1,3-dithiols, 1,2-aminoalcohols, 1,3-aminoalcohols, 1,2-aminothiols, 1,3-aminothiols and hydride reducing agents.	1431	1431				

#### 4.41 Hydroxides

Reagent (Loading)	Comments	Ref.	Prep. Ref.	Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: alkoxides, primary and secondary amines, carbanions and hydroxides, hydride reducing agents.	1431	1431				

#### 4.42 Hydroxylamines

Reagent (Loading)	Comments	Ref.	Prep. Ref.	Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: alcohols, alkoxyamines, amidines, carboxylic acids, guanidines, hydrazines, hydroxylamines and thiols.	1431	1431		Removes: alkoxyamines, primary amines, 1,2-aminoalcohols, 1,3-aminoalcohols, 1,3-aminothiols, 1,2-aminothiols, carbanions, 1,3-diols, 1,2 dithiols, 1,3-dithiols, glycols, hydrazines, hydride reducing agents and hydroxylamines.	1431	1431
	Removes: carbanions, primary amines, hydroxylamines, alkoxyamines, hydrazines, glycols, 1,3-diols, 1,2 dithiols, 1,3-dithiols, 1,2-aminoalcohols, 1,3-aminoalcohols, 1,2-aminothiols, 1,3-aminothiols and hydride reducing agents.	1431	1431				

#### 4.43 Imidazoles

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: acid chlorides, acid anhydrides, activated esters, aldehydes, epoxides, alkyl halides, alkylsulfonates, enones, imidazoles, isocyanates, isothiocyanates, phosphonyl chlorides, Meerwein reagent, phosphoryl chlorides and $\alpha,\beta$ -unsaturated esters.	1431	1431
	Removes: acid chlorides, acid anhydrides, activated esters, alkyl halides, alkylsulfonates, Boronic acids, diazoalkanes, epoxides, $\alpha$ -haloketones, imidazoles, isocyanates, isothiocyanates, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, silyl chlorides and silyl triflates.	1431	1431
	Removes: acid chlorides, acid anhydrides, activated esters, alkyl halides, alkylsulfonates, $\alpha$ -diketones, $\beta$ -diketones, enones, epoxides, imidazolides, isocyanates, isothiocyanates, $\beta$ -ketoesters, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and $\alpha,\beta$ -unsaturated esters.	1431	1431

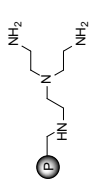
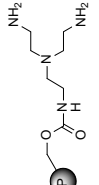
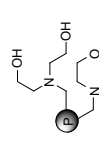
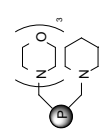
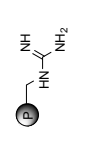
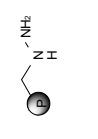
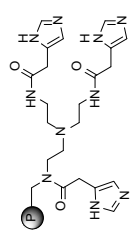
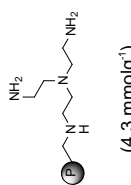
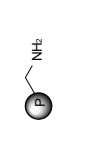
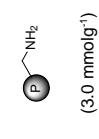
#### 4.44 Imines

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: aldehydes, alkyl halides, alkylsulfonates, chloroformates, imines, isocyanates, isothiocyanates, ketones, phosgene and thiophosgene.	1431	1431

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: acid chlorides, acid anhydrides, activated esters, imidazoles, isocyanates, isothiocyanates, sulfonyl chlorides, phosphoryl chlorides, phosphoryl chlorides, alkyl halides, alkylsulfonates, enones, unsaturated esters, carbonyls and thiourea.	1431	1431
	Removes: acid anhydrides, acid chlorides, activated esters, alkyl halides, alkylsulfonates, $\alpha$ -haloketones, imidazoles, isocyanates, isothiocyanates, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, silyl chlorides, silyl triflates and sulfonyl chlorides.	1431	1431
	Removes: acid anhydrides, acid chlorides, activated esters, aldehydes, alkyl halides, alkylsulfonates, $\alpha$ -diketones, $\beta$ -diketones, enones, epoxides, imidazolides, isocyanates, isothiocyanates, ketones, $\beta$ -ketoesters, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and $\alpha,\beta$ -unsaturated esters.	1431	1431

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Used to remove a number of alkyl and benzyl N-imines from a hetero-Diels-Alder reaction.	59	

#### 4.45 Isocyanates

	<p>Removes: acid chlorides, acid anhydrides, activated esters, aldehydes, epoxides, alkyl halides, alkylsulfonates, enones, imidazoles, isocyanates, isothiocyanates, phosphonyl chlorides, Meerwein Reagent, phosphonyl chlorides, phosphonyl chlorides, sulfonyl chlorides and <math>\alpha,\beta</math>-unsaturated esters.</p>	<p>1431</p>	<p>1431</p>		<p>Removes: acid chlorides, acid anhydrides, activated esters, imidazoles, isocyanates, isothiocyanates, sulfonyl chlorides, phosphonyl chlorides, phosphonyl chlorides, alkyl halides, alkylsulfonates, epoxides, enones, unsaturated esters, carbonyls and thiourea.</p>	<p>1431</p>	<p>1431</p>
	<p>Removes: acid chlorides, acid anhydrides, activated esters, alkyl halides, alkylsulfonates, boronic acids, diazoalkanes, epoxides, <math>\alpha</math>-haloketones, imidazoles, isocyanates, isothiocyanates, Meerwein reagent, phosphonyl chlorides, phosphonyl chlorides, silyl chlorides and silyl triflates.</p>	<p>1431</p>	<p>1431</p>		<p>Removes: acid anhydrides, acid chlorides, activated esters, alkyl halides, alkylsulfonates, <math>\alpha</math>-haloketones, imidazoles, isocyanates, isothiocyanates, Meerwein reagent, phosphonyl chlorides, phosphonyl chlorides, silyl chlorides, silyl triflates and sulfonyl chlorides.</p>	<p>1431</p>	<p>1431</p>
	<p>Removes: acid chlorides, acid anhydrides, activated esters, alkyl halides, alkylsulfonates, <math>\alpha</math>-diketones, <math>\beta</math>-diketones, enones, epoxides, imidazolides, isocyanates, isothiocyanates, <math>\beta</math>-ketoesters, Meerwein reagent, phosphonyl chlorides, phosphonyl chlorides, sulfonyl chlorides and <math>\alpha,\beta</math>-unsaturated esters.</p>	<p>1431</p>	<p>1431</p>		<p>Removes: acid anhydrides, acid chlorides, activated esters, aldehydes, alkyl halides, alkylsulfonates, <math>\alpha</math>-diketones, <math>\beta</math>-diketones, enones, epoxides, imidazolides, isocyanates, isothiocyanates, ketones, <math>\beta</math>-ketoesters, Meerwein Reagent, phosphonyl chlorides, phosphonyl chlorides, sulfonyl chlorides and <math>\alpha,\beta</math>-unsaturated esters.</p>	<p>1431</p>	<p>1431</p>
	<p>Removes: aldehydes, alkyl halides, alkylsulfonates, chloroformates, imines, isocyanates, isothiocyanates, ketones, phosgene and thiophosgene.</p>	<p>1431</p>	<p>1431</p>	 <p>(4.3 mmolg<sup>-1</sup>)</p>	<p>Also scavenges isothiocyanates and sulfonyl chlorides as well as isocyanates. Full experimental section.</p>	<p>42</p>	<p>42</p>
	<p>Scavenger used in the purification of a library.</p>	<p>57</p>	<p>63</p>	 <p>(3.0 mmolg<sup>-1</sup>)</p>	<p>Scavenges HCl, anhydride, and carboxylic acid.</p>	<p>63</p>	<p>63</p>

<p>Reagent (Loading)</p> <p>L = Polystyrene, polyacrylamide, cellulose, silica, alumina, glass</p> <p>R' = H, alkyl</p> <p>n = 0-10</p>	<p>Comments</p> <p>Library of ureas synthesised by reaction of 404 amines (1° and 2°) with 122 isocyanates. The use of thioisocyanates (8 examples) is also described.</p> <p>General procedure given.</p>	<p>Ref.</p> <p>40</p>	<p>Prep. Ref.</p>
<p>Reagent (Loading)</p>	<p>Comments</p> <p>Full experimental section.</p>	<p>Ref.</p> <p>43</p>	<p>Prep. Ref.</p>
<p>Reagent (Loading)</p>	<p>Comments</p> <p>Treatment of isocyanate with 1-(2-hydroxyphenyl)piperazine gives a product which can then be scavenged by the resin.</p>	<p>Ref.</p> <p>1444</p>	<p>Prep. Ref.</p>

#### 4.46 Isothiocyanates

<p>Reagent (Loading)</p>	<p>Comments</p> <p>Removes: acid chlorides, acid anhydrides, activated esters, aldehydes, epoxides, alkyl halides, alkylsulfonates, enones, imidazoles, isocyanates, isothiocyanates, ketones, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and <math>\alpha,\beta</math>-unsaturated esters.</p>	<p>Ref.</p> <p>1431</p>	<p>Prep. Ref.</p> <p>1431</p>
<p>Reagent (Loading)</p>	<p>Comments</p> <p>Removes: acid chlorides, acid anhydrides, activated esters, alkyl halides, alkylsulfonates, boronic acids, diazoalkanes, epoxides, <math>\alpha</math>-haloketones, imidazoles, isocyanates, isothiocyanates, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, silyl chlorides and silyl triflates.</p>	<p>Ref.</p> <p>1431</p>	<p>Prep. Ref.</p> <p>1431</p>
<p>Reagent (Loading)</p>	<p>Comments</p> <p>Removes: acid chlorides, acid anhydrides, activated esters, imidazoles, isocyanates, isothiocyanates, sulfonyl chlorides, phosphoryl chlorides, phosphoryl chlorides, alkyl halides, alkylsulfonates, enones, unsaturated esters, carbonyls and thiourea.</p>	<p>Ref.</p> <p>1431</p>	<p>Prep. Ref.</p> <p>1431</p>
<p>Reagent (Loading)</p>	<p>Comments</p> <p>Removes: acid anhydrides, acid chlorides, activated esters, alkyl halides, alkylsulfonates, <math>\alpha</math>-haloketones, imidazoles, isocyanates, isothiocyanates, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, silyl chlorides, silyl triflates and sulfonyl chlorides.</p>	<p>Ref.</p> <p>1431</p>	<p>Prep. Ref.</p> <p>1431</p>

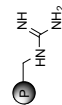
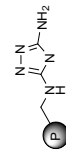
#### 4.46 Isothiocyanates—continued

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: acid chlorides, acid anhydrides, activated esters, alkyl halides, alkylsulfonates, $\alpha$ -diketones, $\beta$ -diketones, enones, epoxides, imidazolides, isocyanates, isothiocyanates, $\beta$ -ketoesters, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and $\alpha,\beta$ -unsaturated esters.	1431	1431
	Removes: aldehydes, alkyl halides, alkylsulfonates, chloroformates, imines, isocyanates, isothiocyanates, ketones, phosgene and thiophosgene.	1431	1431
	Scavenger used in the purification at one stage of a multi-step library synthesis.	57	
	Removes: acid anhydrides, acid chlorides, activated esters, aldehydes, alkyl halides, alkylsulfonates, $\alpha$ -diketones, $\beta$ -diketones, enones, epoxides, imidazolides, isocyanates, isothiocyanates, $\beta$ -ketoesters, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and $\alpha,\beta$ -unsaturated esters.	1431	1431
	Scavenges isocyanates and sulfonyl chlorides as well as isothiocyanates. Full experimental section.	42	42

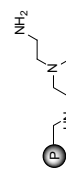
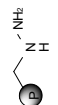
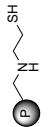
#### 4.47 Ketoamides

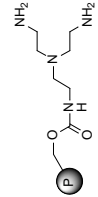
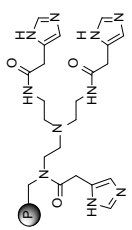
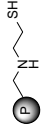
Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: $\alpha$ -diketones, $\beta$ -diketones, $\alpha$ -haloketones, $\beta$ -ketoesters, $\alpha$ -ketoesters, $\alpha$ -ketoamides, $\beta$ -ketoamides, vinylogous esters and vinylogous amides.	1431	1431

#### 4.48 $\beta$ -Ketoesters



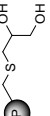

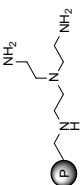
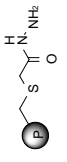
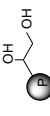
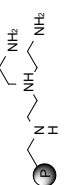
Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: acid chlorides, acid anhydrides, activated esters, alkyl halides, alkylsulfonates, $\alpha$ -diketones, $\beta$ -diketones, enones, epoxides, imidazolides, isocyanates, isothiocyanates, $\beta$ -ketoesters, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and $\alpha,\beta$ -unsaturated esters.	1431	1431
	Removes: $\alpha$ -diketones, $\beta$ -diketones, $\alpha$ -haloketones, $\beta$ -ketoesters, $\alpha$ -ketoesters, $\alpha$ -ketoamides, $\beta$ -ketoamides, vinylogous esters and vinylogous amides.	1431	1431

#### 4.49 Ketones

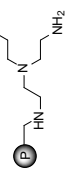
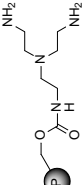
Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: acid chlorides, acid anhydrides, activated esters, aldehydes, epoxides, alkyl halides, alkylsulfonates, enones, imidazoles, isocyanates, isothiocyanates, ketones, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and $\alpha,\beta$ -unsaturated esters.	1431	1431
	Removes: acid anhydrides, acid chlorides, activated esters, aldehydes, alkyl halides, alkylsulfonates, $\alpha$ -diketones, $\beta$ -diketones, enones, epoxides, imidazolides, isocyanates, isothiocyanates, ketones, $\beta$ -ketoesters, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and $\alpha,\beta$ -unsaturated esters.	1431	1431
	Removes: aldehydes, alkyl halides, alkylsulfonates, disulfides, epoxides, $\alpha$ -haloketones, ketones, Meerwein reagent, oxidants, silyl chlorides, silyl triflates and thiols.	1431	1431

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: acid chlorides, acid anhydrides, activated esters, imidazoles, isocyanates, isothiocyanates, sulfonyl chlorides, phosphoryl chlorides, phosphoryl chlorides, alkyl halides, alkylsulfonates, epoxides, enones, unsaturated esters, carbonyls and thiourea.	1431	1431
	Removes: aldehydes, alkyl halides, alkylsulfonates, chloroformates, imines, isocyanates, isothiocyanates, ketones, phosphene and thiophosgene.	1431	1431
	Scavenger reagent used for the removal of all excess carboxylic acid and ketone reagents present in the synthesis of a library of 4-thiazolidinones.	1434	

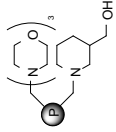
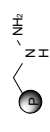
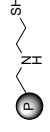
#### 4.49 Ketones—continued

Reagent (Loading)	Comments	Ref.	Prep. Ref.
 (1.2 mmol g <sup>-1</sup> )	Scavenger used for the parallel purification of a compound library.	1436	
	Removes: aldehydes, ketones, α-haloketones.	1435	
 (0.65–1.4 mmol g <sup>-1</sup> )	Scavenged ketone or aldehyde may be detached from the polymer with <i>p</i> -TSA in water. Experimental section.	1439	1439
	Used for reversible binding of steroidal ketones and sugars Experimental section.	1437	1437
 (1.6 mmol g <sup>-1</sup> )	Scavenger reagent used for the removal of all excess carboxylic acid and ketone reagents present in the synthesis of a library of 4-thiazolidinones. More sterically hindered and less reactive ketones gave poor results. General procedure.	1434	
 (4.0 mmol g <sup>-1</sup> )	Used for reversible binding of steroidal ketones and sugars. Experimental section.	1437	1437
	Removes: aldehydes and ketones.		
 (3.4 mmol g <sup>-1</sup> )	Sequestered the α,β-unsaturated ketone by-product of a hetero-Diels–Alder reaction using Danishefsky's diene and an imine. Unreacted imine was also scavenged. Experimental section.	59	

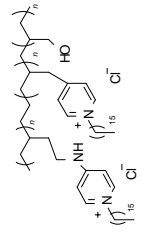
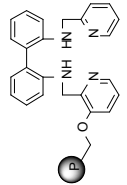
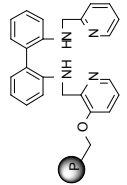
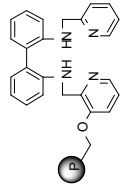
#### 4.50 Meerwein reagent

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: acid chlorides, acid anhydrides, activated esters, aldehydes, epoxides, alkyl halides, alkylsulfonates, enones, imidazoles, isocyanates, isothiocyanates, ketones, Meerwein reagent, and phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and α,β-unsaturated esters.	1431	1431
	Removes: acid chlorides, acid anhydrides, activated esters, imidazoles, isocyanates, isothiocyanates, sulfonyl chlorides, phosphoryl chlorides, phosphoryl chlorides, alkyl halides, alkylsulfonates, epoxides, enones, unsaturated esters, carbonyls and thiourea	1431	1431

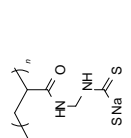
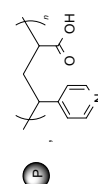
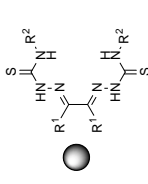
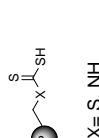
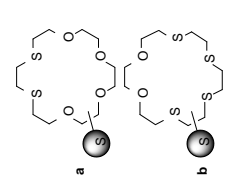
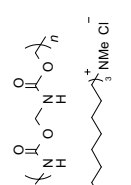
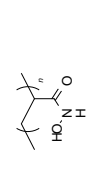
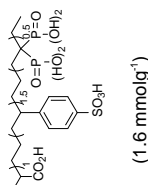
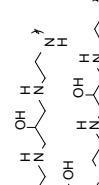
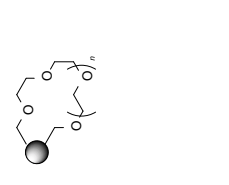


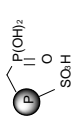
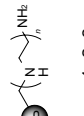
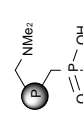
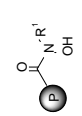
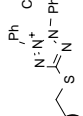
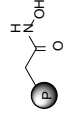
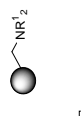
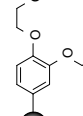
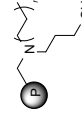
Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: acid chlorides, acid anhydrides, activated esters, alkyl halides, alkylsulfonates, Boronic acids, diazoalkanes, epoxides, $\alpha$ -haloketones, imidazoles, isocyanates, isothiocyanates, Meerwein reagent, phosphoryl chlorides, phosphonyl chlorides, silyl chlorides and silyl triflates.	1431	1431
	Removes: acid chlorides, acid anhydrides, activated esters, alkyl halides, alkylsulfonates, $\alpha$ -diketones, $\beta$ -diketones, enones, epoxides, imidazolides, isothiocyanates, $\beta$ -ketoesters, Meerwein reagent, phosphoryl chlorides, phosphonyl chlorides, sulfonyl chlorides and $\alpha,\beta$ -unsaturated esters.	1431	1431
	Removes: aldehydes, alkyl halides, alkylsulfonates, disulfides, epoxides, $\alpha$ -haloketones, ketones, Meerwein reagent, oxidants, silyl chlorides, silyl triflates and thiols.	1431	1431

#### 4.51 Metal ions

Reagent (Loading)	Comments	Ref.	Prep. Ref.
 (0.70 mmol g <sup>-1</sup> )	Resin scavenges $\text{UO}_2^{2+}$ from aqueous solution. Also scavenges in order of affinity $\text{Hg}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Cr}^{3+} > \text{Co}^{2+} > \text{Ni}^{2+}$ . Experimental section.	1455	1455
 (1.7 mmol g <sup>-1</sup> )	Resin used to scavenge the following metal ions from aqueous solution: $\text{Fe}^{3+}$ , $\text{Cd}^{2+}$ , $\text{Co}^{2+}$ , $\text{Cr}^{6+}$ , $\text{Cu}^{2+}$ , $\text{Ni}^{2+}$ , $\text{Zn}^{2+}$ , $\text{Sr}^{2+}$ .	1456	
	Resin is designed to scavenge Hg from victims of poisoning. Resin also binds Pd, Cd, Li and Ni. Experimental section.	1457	1457
	Polymer selective for $\text{Cu}^{2+}$ and $\text{Ag}^+$ over $\text{Fe}^{2+}$ , $\text{Co}^{2+}$ and $\text{Ni}^{2+}$ .	1458	

4.51 Metal ions—continued

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Resin used to selectively scavenge metal ions. The order of affinity is: $\text{Hg}^{2+} \gg \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+}$ . Paper contains physical data. Experimental section.	1459	1459
 <p>Interpenetrating polymer network</p>	Evaluated for application in metal ion separation. The order of affinity is: $\text{Cu}^{2+} > \text{Hg}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Eu}^{3+}$ .	1461	1462
 <p>Amberlite XAD4/7/16 R<sup>1</sup>=H, alkyl R<sup>2</sup>=H, aryl</p>	Dithiosemicarbazones were absorbed onto Amberlite resin and used to determine ion concentrations of $\text{Cu}^{2+}$ , $\text{Cd}^{2+}$ , $\text{Hg}^{2+}$ , $\text{Pb}^{2+}$ , $\text{Pt}^{4+}$ , $\text{Pd}^{2+}$ . General procedure.	1463, 1464	1463, 1464
 <p>X= S, NH</p>	Removes 3.5–4.4mg copper per gram of resin from pH 6 aqueous solution. Experimental section.	1466	1466
 <p>a: (0.14 mmol g<sup>-1</sup>) b: (0.30 mmol g<sup>-1</sup>)</p>	Crowns covalently attached to silica gel. Removes $\text{Pd}^{2+}$ , $\text{Au}^{3+}$ , $\text{Ag}^{+}$ and $\text{Hg}^{2+}$ from aqueous solutions. Metals can be quantitatively recovered.	1468	1468
	Metal ions $\text{Ta}^{5+}$ , $\text{Nb}^{5+}$ are extracted from a solution in HF.	1460	1460
 <p>(4.5 mmol g<sup>-1</sup>)</p>	Resins with varying degrees of cross-linking investigated, for metal binding properties $\text{Cu}^{2+}$ , $\text{Fe}^{3+}$ , $\text{UO}_2^{2+}$ , $\text{V}^{5+}$ . Experimental section.	1462	1462
 <p>(1.6 mmol g<sup>-1</sup>)</p>	Binding capacity of resin for $\text{Eu}^{3+}$ demonstrated. Experimental section.	1465	1465
	Removes transition metal cations and their counter anions from aqueous solution. Experimental section.	1467	1467
	Various pseudocrown ethers synthesised for binding the transition metal halide complexes of Zn, Au, Fe, Co and Cd. Experimental section.	1469	1469

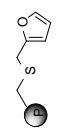
Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Resin is used to complex $\text{Eu}^{3+}$ ions from aqueous solution. General procedure.	1470	1470
 $n = 1, 2, 3$	Resins used to investigate $\text{Cu}^{2+}$ uptake. General procedure.	1472	1472
 (3.3 mmol g <sup>-1</sup> )	Bifunctional polymer for metal ion separation. Polymer scavenges $\text{Fe}^{3+}$ , $\text{Hg}^{2+}$ , $\text{Ag}^+$ , $\text{Mn}^{2+}$ and $\text{Zn}^{2+}$ .	1474	1154
 $\text{R}^1 = \text{H, alkyl, aryl}$ Amberlite XAD-4 (1.1-1.8 mmol g <sup>-1</sup> )	Polymer scavenges $\text{Fe}^{3+}$ , $\text{Al}^{3+}$ , $\text{Cu}^{2+}$ , $\text{Th}^{4+}$ , $\text{U}^{6+}$ , $\text{Ni}^{2+}$ , $\text{Cu}^{2+}$ and $\text{Ca}^{2+}$ . Extraction of metal ions as a function of pH was investigated.	1475, 1476	1476
 (1.1-1.9 mmol g <sup>-1</sup> )	Polymer used to scavenge metal ions, particularly platinum. Experimental section.	1478	1478
Reagent (Loading)	Comments	Ref.	Prep. Ref.
	General for a range of $\text{M}^{2+}$ and $\text{M}^{3+}$ ions.	1471	1471
 (6.5 mmol g <sup>-1</sup> )	Removal and recovery of metal ions including, $\text{Cu}^{2+}$ , $\text{Ni}^{2+}$ , $\text{Co}^{2+}$ , $\text{Cd}^{2+}$ , $\text{Zn}^{2+}$ .	1473	
	Scavenges $\text{Li}^+$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{Rb}^+$ , $\text{Cs}^+$ , $\text{Ba}^{2+}$ , $\text{NH}_4^+$ from aqueous solution. Experimental section.	1154	1154
	Polymer scavenges $\text{Cu}^{2+}$ , $\text{Hg}^{2+}$ , $\text{Cd}^{2+}$ , $\text{Ni}^{2+}$ and $\text{Co}^{2+}$ . Experimental section.	1477	1477

#### 4.52 Miscellaneous

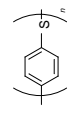
	1479	1479	1479	Resin used to scavenge SO <sub>2</sub> from industrial waste gases. Works at high temperature.	60, 63	60
	68	68	68	Mixture of resins used to scavenge DMP. Thiosulfate resin reduces DMP to give a carboxylic acid, which is then scavenged by the basic resin.	65	65
	65	65	65	Resin used to scavenge carbamate functional group. Alcohol produced during scavenging reaction is removed by isocyanate resin.	1480	1480
	1481	1481	1481	Mixed bed ion exchange resin. Resins used in conjunction to facilitate reduction of DDQ to DDQH (Amberlyst A-26, ascorbate form) and subsequently scavenge DDQH from the solution (Amberlyst A-26, bicarbonate form). Products obtained in good yields (70–100%) and purities (83–100%). General procedure.		

#### 4.53 Oxidants

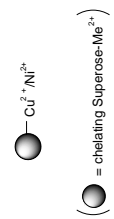

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: aldehydes, alkyl halides, alkylsulfonates, disulfides, epoxides, $\alpha$ -haloketones, ketones, Meerwein reagent, oxidants, silyl chlorides, silyl triflates and thiols.	1431	1431
	Removes: alkyl halides, alkylsulfonates, disulfides, epoxides, $\alpha$ -haloketones, silyl chlorides, silyl triflates and thiols.	1431	1431

Reagent (Loading)	Comments	Ref.	Prep. Ref.	Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: dienophiles, dipolarophiles, chlorine, bromine, iodine and oxidants.	1431	1431				

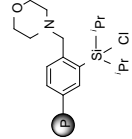
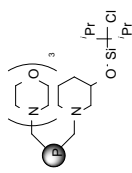
#### 4.54 Ozone

Reagent (Loading)	Comments	Ref.	Prep. Ref.	Reagent (Loading)	Comments	Ref.	Prep. Ref.
 noXon	Applied to the analysis of oxygenated terpenes in air.	1482	1482				

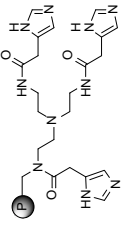
#### 4.55 Peptides

Reagent (Loading)	Comments	Ref.	Prep. Ref.	Reagent (Loading)	Comments	Ref.	Prep. Ref.
 (  = chelating Superose-Me <sup>2+</sup> )	Scavenges cysteine containing peptides. General procedure.	1483					

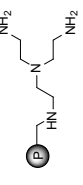
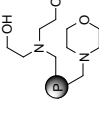
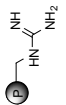
#### 4.56 Phenols

Reagent (Loading)	Comments	Ref.	Prep. Ref.	Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: alcohols, primary and secondary amines, carbanions, carboxylic acids, phenols, silanols and thiols.	1431	1431		Removes: alcohols, primary and secondary amines, carbanions, carboxylic acids, phenols, silanols and thiols.	1431	1431

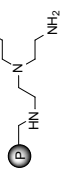
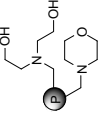
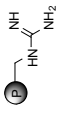
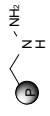
#### 4.57 Phosgene

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: aldehydes, alkyl halides, alkylsulfonates, chloroformates, imines, isocyanates, isothiocyanates, ketones, phosgene and thiophosgene.	1431	1431

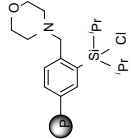
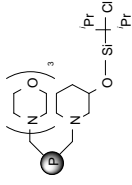
#### 4.58 Phosphonyl chlorides

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: acid chlorides, acid anhydrides, activated esters, aldehydes, epoxides, alkyl halides, alkylsulfonates, enones, imidazoles, isocyanates, isothiocyanates, ketones, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and $\alpha,\beta$ -unsaturated esters.	1431	1431
	Removes: acid chlorides, acid anhydrides, activated esters, alkyl halides, alkylsulfonates, boronic acids, diazoalkanes, epoxides, $\alpha$ -haloketones, imidazoles, isocyanates, isothiocyanates, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and silyl triflates.	1431	1431
	Removes: acid chlorides, acid anhydrides, activated esters, alkyl halides, alkylsulfonates, $\alpha$ -diketones, $\beta$ -diketones, enones, epoxides, imidazolides, isocyanates, isothiocyanates, $\beta$ -ketoesters, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and $\alpha,\beta$ -unsaturated esters.	1431	1431

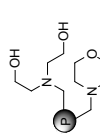
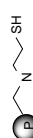
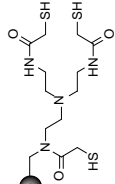
#### 4.59 Phosphoryl chlorides

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: acid chlorides, acid anhydrides, activated esters, aldehydes, epoxides, alkyl halides, alkylsulfonates, enones, imidazoles, isocyanates, isothiocyanates, ketones, Meerwein reagent, phosphoryl chlorides, sulfonyl chlorides and $\alpha,\beta$ -unsaturated esters.	1431	1431
	Removes: acid chlorides, acid anhydrides, activated esters, alkyl halides, alkylsulfonates, boronic acids, diazoalkanes, epoxides, $\alpha$ -haloketones, imidazoles, isocyanates, isothiocyanates, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, silyl chlorides and silyl triflates.	1431	1431
	Removes: acid chlorides, acid anhydrides, activated esters, alkyl halides, alkylsulfonates, $\alpha$ -diketones, $\beta$ -diketones, enones, epoxides, imidazolides, isocyanates, isothiocyanates, $\beta$ -ketoesters, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and $\alpha,\beta$ -unsaturated esters.	1431	1431
	Removes: acid anhydrides, acid chlorides, activated esters, aldehydes, alkyl halides, alkylsulfonates, $\alpha$ -diketones, $\beta$ -diketones, enones, epoxides, isothiocyanates, ketones, $\beta$ -ketoesters, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and $\alpha,\beta$ -unsaturated esters.	1431	1431

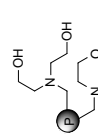
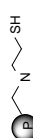
#### 4.60 Silanols

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: alcohols, primary and secondary amines, carbanions, carboxylic acids, phenols, silanols and thiols.	1431	1431
	Removes: alcohols, primary and secondary amines, carbanions, carboxylic acids, phenols, silanols and thiols.	1431	1431

#### 4.61 Silyl chlorides

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: acid chlorides, acid anhydrides, activated esters, alkyl halides, alkylsulfonates, boronic acids, diazoalkanes, epoxides, $\alpha$ -haloketones, imidazoles, isocyanates, isothiocyanates, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, silyl chlorides and silyl triflates.	1431	1431
	Removes: aldehydes, alkyl halides, alkylsulfonates, disulfides, epoxides, $\alpha$ -haloketones, ketones, Meerwein reagent, oxidants, silyl chlorides, silyl triflates and thiols.	1431	1431
	Removes: alkyl halides, alkylsulfonates, disulfides, epoxides, $\alpha$ -haloketones, oxidants, silyl chlorides, silyl triflates and thiols.	1431	1431

#### 4.62 Silyl triflates

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: acid chlorides, acid anhydrides, activated esters, alkyl halides, alkylsulfonates, boronic acids, diazoalkanes, epoxides, $\alpha$ -haloketones, imidazoles, isocyanates, isothiocyanates, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, silyl chlorides and silyl triflates.	1431	1431
	Removes: aldehydes, alkyl halides, alkylsulfonates, disulfides, epoxides, $\alpha$ -haloketones, ketones, Meerwein reagent, oxidants, silyl chlorides, silyl triflates and thiols.	1431	1431



Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: alkyl halides, alkylsulfonates, disulfides, epoxides, $\alpha$ -haloketones, oxidants, silyl chlorides, silyl triflates and thiols.	1431	1431

#### 4.63 Sulfides

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: primary and secondary amines, dienes, dipoles and sulfides.	1431	1431

#### 4.64 Sulfonyl chlorides

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: acid chlorides, acid anhydrides, activated esters, aldehydes, epoxides, alkyl halides, alkylsulfonates, enones, imidazoles, isocyanates, isothiocyanates, ketones, Meerwein reagent, phosphoryl chlorides and $\alpha,\beta$ -unsaturated esters.	1431	1431
	Removes: acid anhydrides, acid chlorides, activated esters, alkyl halides, alkylsulfonates, $\alpha$ -haloketones, imidazoles, isocyanates, isothiocyanates, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, silyl triflates and sulfonyl chlorides.	1431	1431

4.64 Sulfonyl chlorides—continued

<p>Reagent (Loading)</p>	<p>Comments</p> <p>Removes: acid chlorides, acid anhydrides, activated esters, alkyl halides, alkylsulfonates, <math>\alpha</math>-diketones, <math>\beta</math>-diketones, enones, epoxides, imidazolides, isocyanates, isothiocyanates, <math>\beta</math>-ketoesters, Meerwein reagent, phosphoryl chlorides, phosphoryl chlorides, sulfonyl chlorides and <math>\alpha,\beta</math>-unsaturated esters.</p>	<p>Ref.</p> <p>1431</p>	<p>Prep. Ref.</p> <p>1431</p>
<p>Reagent (Loading)</p> <p>L = CH<sub>2</sub></p> <p>L =</p> <p>R = H, alkyl</p> <p>n = 0-10</p> <p>● = Polystyrene, polyacrylamide, cellulose, silica, alumina, glass</p>	<p>Comments</p> <p>Library of sulfonamides synthesised by amines (primary and secondary) with 49 organosulfonyl halides.</p> <p>Aminomethylpolystyrene was the main example given. Used in conjunction with solid-supported base to remove acid.</p>	<p>Ref.</p> <p>1432, 40</p>	<p>Prep. Ref.</p> <p>1431</p>
<p>Reagent (Loading)</p> <p>(4.3 mmolg<sup>-1</sup>)</p>	<p>Comments</p> <p>Scavenges isocyanates and thiocyanates as well as sulfonyl chlorides.</p> <p>Full experimental section.</p>	<p>Ref.</p> <p>42</p>	<p>Prep. Ref.</p> <p>42</p>
<p>Reagent (Loading)</p> <p>(0.30-0.50 mmolg<sup>-1</sup>)</p>	<p>Comments</p> <p>Several macroporous polymer bases were investigated using a non-swelling solvent such as acetonitrile.</p> <p>General procedure.</p>	<p>Ref.</p> <p>1484</p>	<p>Prep. Ref.</p> <p>1484</p>

#### 4.65 Thiols

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: aldehydes, alkyl halides, alkylsulfonates, disulfides, epoxides, $\alpha$ -haloketones, ketones, Meerwein reagent, oxidants, silyl chlorides, silyl triflates and thiols.	1431	1431
	Removes: alcohols, 1° and 2° amines, carbanions, carboxylic acids, phenols, silanols and thiols.	1431	1431
	Removes: alcohols, 1° and 2° amines, carbanions, carboxylic acids, phenols, silanols and thiols.	1431	1431

#### 4.66 Thiophosgene

Reagent (Loading)	Comments	Ref.	Prep. Ref.
	Removes: aldehydes, alkyl halides, alkylsulfonates, chloroformates, imines, isocyanates, isothiocyanates, ketones, phosphosgene and thiophosgene.	1431	1431

### 4.67 Catch and release

Reagent (Loading)	Transformation	Data/%	Comments	Ref.	Prep. Ref.
<p>(0.20–0.50 mmol g<sup>-1</sup>)</p>	<p>4 examples n = 1–4</p>		Acids scavenged by supported HOBt. Treatment with TFA removes the Boc group and neutralisation with Et <sub>3</sub> N effects the cyclisation and release of lactam product.	1485	517
<p>Wang</p>	<p>18 examples R<sup>1</sup> = amide (N-linked) R<sup>2</sup> = alkyl, aryl</p>	Y:25–100	Product released as carboxylic acid by treatment with TFA.	1486	
<p>(0.20 mmol g<sup>-1</sup>)</p>	<p>37 examples R<sup>1</sup> = O-aryl R<sup>2</sup> = alkyl, aryl, benzyl R<sup>3</sup> = H, alkyl</p>	Y:60–99 P:80–99	Amino alcohols purified by catch and release protocol. Acid treatment releases product from polymer as amino alcohol. Experimental section.	1448	1448
<p>(2.4 mmol g<sup>-1</sup>)</p>	<p>7 examples R<sup>1</sup> = alkyl, aryl R<sup>2</sup> = H, alkyl, aryl, vinyl</p>	Y:71–80 P:85–93	Ketones scavenged by treatment with a sulfonyl hydrazine resin and released by Hund-Mori reaction to give 1,2,3-thiadiazoles.	69	
<p>(3.7 mmol g<sup>-1</sup>)</p>	<p>5 examples R<sup>1</sup> = H, alkyl, benzyl R<sup>2</sup>, R<sup>3</sup> = H, alkyl</p>	Y:52–60 P:86–100	Enolisable esters are trapped as silyl ketene acetals which undergo Ireland-Claisen rearrangement reaction. Treatment with acid releases product into solution. General procedure.	1487	

## 5 Other relevant reviews

This section comprises full reference lists with titles of all of the relevant reviews that were used in compiling this paper. These are listed under the categories of *insoluble polymers, soluble polymers, inorganic solids, miscellaneous supports and purification strategies*. Within these broad categories there is further grouping, wherever appropriate, into sections which cover *structure and physical properties, general chemistry and reactions*. Also a *miscellaneous* subsection is often included containing any remaining reviews not already covered in the other sections.

### 5.1 Insoluble polymers

#### 5.1.1 Structure and physical properties (insoluble polymers)

- A. J. Mendonca and X. Y. Xiao, **Optimization of Solid Supports for Combinatorial Chemical Synthesis**, *Med. Res. Rev.*, 1999, **19**, 451.
- W. T. Ford, **Catalysis in Polymer Latexes**, *React. Polym.*, 1997, **33**, 147.
- S. Schlick, E. Bortel and K. Dyrek, **Catalysis on Polymer Supports**, *Acta Polym.*, 1996, **47**, 1.
- A. Akelah, **The Use Of Functionalized Polymers as Polymeric Reagents in Solid-Phase Organic Synthesis — A Review**, *React. Polym.*, 1988, **8**, 273.
- R. Solaro, S. Dantone and E. Chiellini, **Anion Exchange-Type Resins in Preparative Organic Chemistry — Structure Activity Relationship**, *React. Polym.*, 1988, **9**, 155.
- W. T. Ford, **Synthesis with Tethered Molecules**, *Chemtech*, 1987, **17**, 246.
- S. J. Sondheimer, N. J. Bunce and C. A. Fyfe, **Structure and Chemistry of Nafion-H — A Fluorinated Sulfonic-Acid Polymer**, *J. Macromol. Sci. Rev. Macromol. Chem. Phys.*, 1986, **C26**, 353.
- J. B. Roucis and J. G. Ekerdt, **The Influence of Intraparticle Mass-Transfer on the Activity of a Gel-Form Polymer-Bound Transition-Metal Catalyst**, *J. Catal.*, 1984, **86**, 32.
- D. C. Sherrington, **The Effect of Polymer Structure on the Reactivity of Bound Functional-Groups**, *Nouv. J. Chim.*, 1982, **6**, 661.
- J. I. Crowley and H. Rapoport, **Solid-Phase Organic Synthesis: Novelty or Fundamental Concept?**, *Acc. Chem. Res.*, 1976, **9**, 135.
- C. G. Overberger, **Polymers as Reagents in Organic Synthesis**, *Angew. Chem., Int. Ed. Engl.*, 1974, **13**, 99.

#### 5.1.2 General (insoluble polymers)

- D. H. Drewry, D. M. Coe and S. Poon, **Solid-Supported Reagents in Organic Synthesis**, *Med. Res. Rev.*, 1999, **19**, 97.
- J. P. Montheard, C. Jegat and M. Camps, **Vinylbenzylchloride (chloromethylstyrene), Polymers, and Copolymers. Recent Reactions and Applications**, *J. Macromol. Sci.-Rev. Macromol. Chem. Phys.*, 1999, **C39**, 135.
- A. J. Mendonca and X. Y. Xiao, **Optimization of Solid Supports for Combinatorial Chemical Synthesis**, *Med. Res. Rev.*, 1999, **19**, 451.
- M. J. Palmer and M. Wills, **Asymmetric Transfer Hydrogenation of C=O and C=N bonds**, *Tetrahedron: Asymmetry*, 1999, **10**, 2045.
- A. Chesney, **Selected Highlights in the Application of Ion-Exchangers as Supports for Reagents in Organic Synthesis**, *Green Chem.*, 1999, **1**, 209.
- S. J. Shuttleworth, S. M. Allin and P. K. Sharma, **Functionalised Polymers: Recent Developments and New Applications in Synthetic Organic Chemistry**, *Synthesis*, 1997, 1217.
- D. Kriz, O. Ramstrom and K. Mosbach, **Molecular Imprinting — New Possibilities for Sensor Technology**, *Anal. Chem.*, 1997, **69**, A345.
- A. D. Baxter, **Synthesis Utilizing Insoluble Polymers: New Reactions and Small Molecules**, *Curr. Opin. Chem. Biol.*, 1997, **1**, 79.
- S. W. Kaldor and M. G. Siegel, **Combinatorial Chemistry Using Polymer-Supported Reagents**, *Curr. Opin. Chem. Biol.*, 1997, **1**, 101.

- J. H. Clark and D. J. Macquarrie, **Environmentally Friendly Catalytic Methods**, *Chem. Soc. Rev.*, 1996, **25**, 303.
- D. Seebach, R. E. Marti and T. Hintermann, **Polymer- and Dendrimer-Bound Ti-TADDOLates in Catalytic (and Stoichiometric) Enantioselective Reactions: Are Pentacoordinate Cationic Ti Complexes the Catalytically Active Species?**, *Helv. Chim. Acta*, 1996, **79**, 1710.
- M. Kempe and K. Mosbach, **Molecular Imprinting Used for Chiral Separations**, *J. Chromatogr. A*, 1995, **694**, 3.
- A. Chakrabarti and M. M. Sharma, **Cationic Ion-Exchange Resins as Catalyst**, *React. Polym.*, 1993, **20**, 1.
- A. Akelah, **The Use of Functionalized Polymers as Polymeric Reagents in Solid-Phase Organic Synthesis — A Review**, *React. Polym.*, 1988, **8**, 273.
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## 7 Abbreviations

AA	amino acid
Ac	acetate
Acac	acetylacetone
ACT	advanced chemical technologies
Ar	aryl
9-BBN	9-borabicyclo[3.3.1]nonane
BER	borohydride exchange resin
Bz	benzoyl
Boc	<i>tert</i> -butoxycarbonyl
B.p.	boiling point
Bn	benzyl
Cat.	catalytic
Cbz	benzyloxycarbonyl
CDI	carbonyl-1,1'-diimidazole
COD	cycloocta-1,5-diene
CSA	camphor-10-sulfonic acid
DBP	dibenzoyl peroxide
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DEAD	diethyl azodicarboxylate
DHQ	dihydroquinine
DHQD	dihydroquinidine
DMAP	4-dimethylaminopyridine
DMF	<i>N,N</i> -dimethylformamide
DMSO	dimethyl sulfoxide
DNB	2,4-dinitrobenzene
DNP	2,4-dinitrophenyl
EGDMA	ethylene glycol dimethyl acetate
Et	ethyl
Equiv.	equivalent(s)
ether	diethyl ether
EWG	electron withdrawing group
Fmoc	fluoren-9-ylmethoxycarbonyl
FTIR	Fourier transform infrared spectroscopy
GC	gas-phase chromatography
HEMA	2-hydroxyethyl methacrylate
het	heterocycle
HOBT	1-hydroxybenzotriazole
HMPA	hexamethylphosphoramide
HPLC	high performance liquid chromatography
h	hour(s)
Im	imidazole
IR	infrared
IUPAC	International Union of Pure and Applied Chemistry
LC	liquid chromatography
LDA	lithium diisopropylamide
M	mol dm <sup>-3</sup> or undefined metal
MAS	magic angle spinning
<i>m</i> -CPBA	<i>m</i> -chloroperbenzoic acid
MCM	Mobil corporation mesopore
Me	methyl
min	minute(s)
Ms	mesylate

MS	mass spectrometry or molecular sieve
N	normal
NBS	<i>N</i> -bromosuccinimide
NCS	<i>N</i> -chlorosuccinimide
NIS	<i>N</i> -iodosuccinimide
NMO	<i>N</i> -methylmorpholine <i>N</i> -oxide
NMR	nuclear magnetic resonance
Nu	nucleophile
OPA	orthophosphoric acid
PCC	pyridinium chlorochromate
P-BEMP	polystyrene bound 2- <i>tert</i> -butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphinine
PEG	polyethylene glycol
Ph	phenyl
PMMA	poly(methyl methacrylate)
ppm	parts per million
PPTS	3-[5-(sulfonatophenyl)-2-pyridyl]-1,2,4-triazin-5-ylbenzenesulfonic acid, disodium salt
PTSA	toluene- <i>p</i> -sulfonic acid
Pr	propyl
PSDIB	polymer-supported diacetoxiodobenzene
psi	per square inch
PSM	polymer-supported permanganate
PSP	polymer-supported perruthenate
PVA	poly(vinyl alcohol)
PVP	poly(vinyl pyridine)
PVPCC	poly(4-vinylpyridiniumchlorochromate)
Py	pyridine
R	unspecified group
ROMP	ring opening metathesis polymerisation
rt	room temperature
(Sal-H) <sub>2</sub>	salicylaldehyde
Salphen	<i>O</i> -phenylene bis(salicylaldehyde)
SFC	supercritical fluid chromatography
TBAF	tetrabutylammonium fluoride
TBDMS	<i>tert</i> -butyldimethylsilyl
TBDPS	<i>tert</i> -butyldiphenylsilyl
TBD-P	polystyrene bound 1,5,7-triazabicyclo[4.4.0]-dec-5-ene
TBSCI	<i>tert</i> -butyldimethylsilyl chloride
TDCPP	5,10,15,20-tetra(2,6-dichlorophenyl)porphyrin
TFA	trifluoroacetic acid
THF	tetrahydrofuran
THP	tetrahydropyran
TLC	thin layer chromatography
TMS	trimethylsilyl
TRIM	trimethylolpropanetriacrylate
TRIP	triisopropylphenyl
Trityl	triphenylmethyl
Ts	tosyl
X	unspecified heteroatom

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