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α,β-Unsaturated ketones via copper(II) bromide mediated oxidation

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ABSTRACT

A protocol for effecting a rapid Saegusa-type oxidation of enol acetates is reported. This new method relies on the in situ elimination of an α-bromo intermediate to generate α,β-unsaturated ketones using copper(II) bromide. The methodology developed was applied to a range of substrates including a cyclohexanone, which could be directly converted to the corresponding phenol derivative. A catalytic system in which a non-masked ketone was successfully oxidised using substoichiometric $CuBr_2$ was also developed as a proof of principle.

1. Introduction

Copper salts are cheap, readily abundant and possess relatively low toxicity which offers significant scope for utilizing them synthetically, especially if they replace a more expensive metallic reagent. One such example would be in the Saegusa oxidation (Fig. 1).[1] This synthetically important transformation often requires relatively high palladium loadings and thus restricts its use at scale. Interestingly, copper(II) halides have, for over half a century, been known to effect α-bromination or chlorination of ketones.[2–4] The employment of a copper redox system to effect an α-bromination followed by an elimination would offer a comparable process to the Saegusa oxidation, where the use of palladium could be completely avoided.

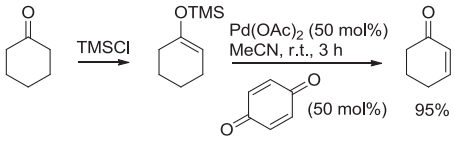

Fig. 1. The Saegusa oxidation of ketones.

While this Saegusa type-oxidation approach would be applicable to a range of transformations, we elected to specifically target the preparation of dehydrohedione (**1b**, Fig. 2), (DHH) as an industrially interesting illustrative example.

Hedione® (**1**, Fig. 2), (methyldihydrojasmonate) is an important fragrance component used in many commercial blends. Of all the possible isomers the (1*R*,2*S*)-(+)-*cis* isomer[7,8] is the most desirable, being almost entirely responsible for the characteristic odour of methyldihydrojasmonate.[5,9] Whilst enantioselective routes to this compound have been developed,[10–14] they are prohibitively expensive and poorly scalable, hence, '*cis*-enhancement' of Hedione®

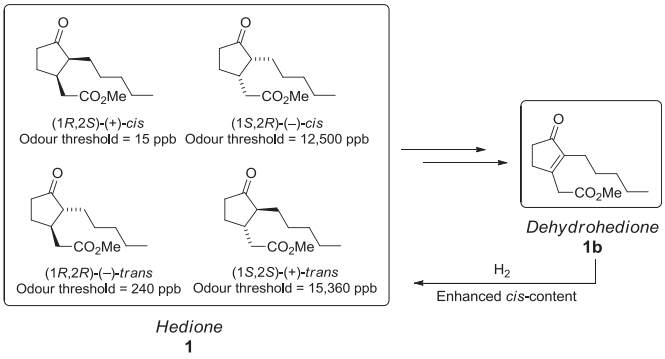

Fig. 2. Methyldihydrojasmonate diastereomer odour thresholds.[5,6]

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is still the favoured approach within the fragrance industry. This is primarily achieved through hydrogenation of DHH (**1b**, its α,β-unsaturated analogue). Although several novel syntheses of DHH have been developed,[15–20] the preferred method of DHH synthesis at scale still remains the direct oxidation of Hedione®.[21]

Herein, we report a convenient and operationally simple means of effecting the oxidative transformation of enol acetates to α,β-unsaturated ketones in a single step using superstoichiometric amounts of copper(II) bromide.

2. Results and discussion

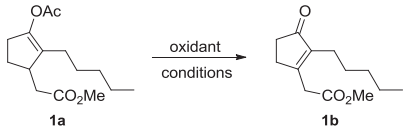
Initial investigations involved the oxidation of the Hedione® enol acetate (**1a**), which was regioselectively prepared in order to direct the initial bromination towards the desired more substituted position. This was accomplished in high yield and with excellent selectivity by treatment of the parent ketone with either acetic anhydride or isopropenyl acetate under mildly acidic conditions. The latter reagent was preferred as less of the acetylating agent was required (2 equiv) and only acetone was generated as a by-product, which could be easily evaporated from the reaction medium. The subsequent oxidation was also achieved under mild conditions with full conversion to the α,β-unsaturated cyclic ketone observed after just 5 min at reflux in acetonitrile.

The above experiments demonstrated the viable formation of DHH (**1b**) from the relevant enol acetate (**1a**) in high yield (99% isolated, 92% NMR yield) using $CuBr_2$ (2 equiv) in acetonitrile, at reflux after only 5 min. Of the other solvents screened, only methanol gave any appreciable amount of the product; this is consistent with previous literature observations in which $CuBr_2$ was used in MeCN.[22] Of the additional copper(II) salts evaluated (chloride, acetate and triflate), none yielded any of the desired product, reinforcing the likelihood of bromine transfer to generate an α-brominated intermediate. Reducing the equivalents of $CuBr_2$ was found to be detrimental to the yield, suggesting that a catalytic system would be hard to achieve. For comparison, conditions under which a similar bromination was known to be catalytic in the literature[22,23] were emulated (Table 1, entry 15 and 16) but these failed to generate any of the desired product. It was speculated that coordination of the bases used (DIPEA and pyridine) to copper led to deactivation of the bromination system. However, the proposed use of 2,6-di-*tert*-butylpyridine as a non-coordinating base/proton sponge to negate decomposition was also unsuccessful (Table 1, entry 17). It was therefore concluded that the scavenging of protons by the bases was in fact causing deactivation and that the reaction is incompatible with a basic environment. This may be to do with the redox characteristics of the system.

The system described in Scheme 1 is proposed as the principle mechanistic pathway, in which 2 equiv of $CuBr_2$ are required. Initially a transient α-bromo intermediate (**1e**) is formed which undergoes rapid elimination to give DHH. The evolution of acidic gas was also observed, this was presumably due to HBr which can promote competitive deacetylative decomposition of the starting material **1a**, giving the saturated compound **1c**. The rate of the oxidation pathway is far quicker than the decomposition which is, in turn, quicker than the reoxidation of Cu(I) to Cu(II) by the following known equation; $2HBr+½O_2+2CuBr \rightarrow 2CuBr_2+H_2O$.[22,23] Sequestering of the HBr by formation of AcBr would also be destructive with regards to the potential copper reoxidation sequence.

These indications imply that making the system work catalytically would be very difficult based upon the current acyl enol starting material **1a**. The potential alternative approach, utilizing the parent ketone directly, which eliminates any potential decomposition, unfortunately creates alternative problems based upon regioselective bromination/oxidation. This was found to be the case upon direct treatment of Hedione® with $CuBr_2$ in MeCN which resulted in a mixture of secondary elimination (**1b**) and bromination (**1d**) products (2.1:1, respectively (GC–MS)).

Table 1
Screening of reaction conditions (1 mmol scale, 0.2 M solution, reflux unless stated otherwise)

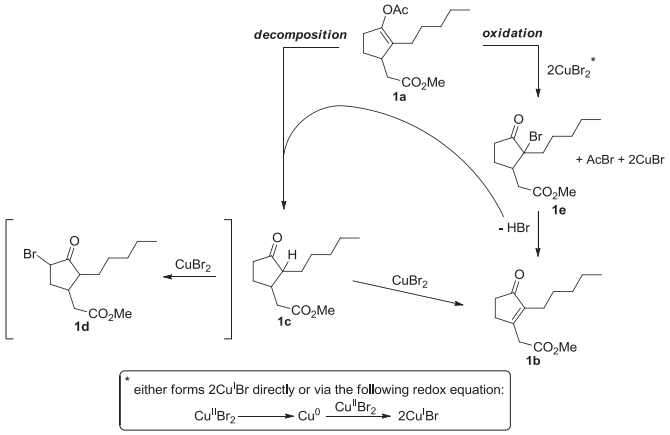


1a 1b

Entry	Solvent	Oxidant (equiv)	Time	Consumption [a] (%)	Yield [a] (%)
1	MeCN	$CuBr_2$ (2.0)	5 min	100	92
2	Toluene	$CuBr_2$ (2.0)	30 min	40	0
3	MeOH	$CuBr_2$ (2.0)	30 min	100	64
4	CH_2Cl_2	$CuBr_2$ (2.0)	30 min	66	0
5	$CHCl_3$	$CuBr_2$ (2.0)	30 min	45	0
6	THF	$CuBr_2$ (2.0)	30 min	23	0
7[b]	DMSO	$CuBr_2$ (2.0)	30 min	84	0
8	MeCN	$CuCl_2$ (2.0)	18 h	44	0
9	MeCN	$Cu(OTf)_2$ (2.0)	18 h	0	0
10	MeCN	$Cu(OAc)_2$ (2.0)	18 h	0	0
11	MeCN	$CuBr_2$ (1.75)	5 min	100	77
12	MeCN	$CuBr_2$ (1.5)	5 min	100	72
13	MeCN	$CuBr_2$ (1.0)	5 min	100	53
14	MeCN	$CuBr_2$ (0.5)	5 min	100	28
15[c, d, g]	MeCN	$CuBr_2$ (0.5)	24 h	0	0
16[c, e, g]	MeCN	$CuBr_2$ (0.5)	24 h	23	0
17[c, f, g]	MeCN	$CuBr_2$ (0.5)	24 h	0	0

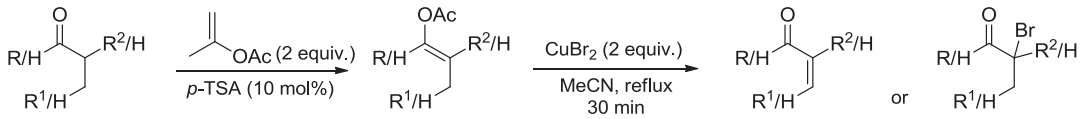
[a] Yield/starting material consumption quantified using 2-nitrotoluene as an internal ^1H NMR standard.
[b] Conducted at 100 °C.
[c] Carried out in an O_2 atmosphere.
[d] DIPEA (5.0 equiv) added.
[e] Pyridine (2.0 equiv) added.
[f] 2,6-di-*tert*-Butylpyridine (2.0 equiv) added.
[g] Conducted at room temperature.

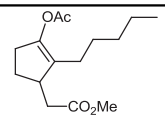
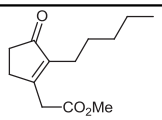
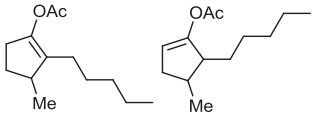
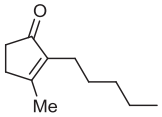
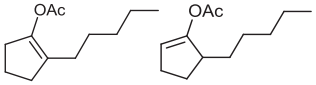
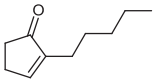
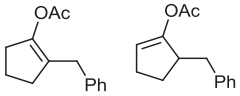
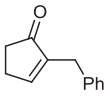
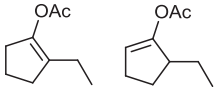
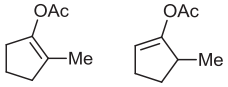
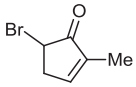
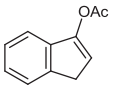
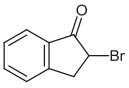
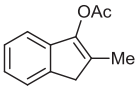
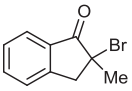
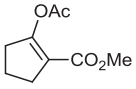
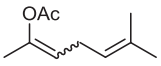
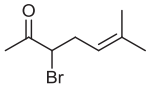
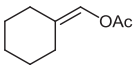
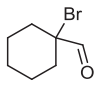
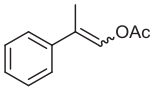
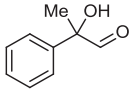
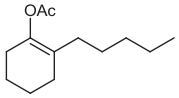
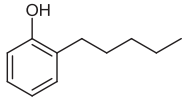
With a viable set of conditions in hand, the scope of the transformation was further investigated (Table 2). As indicated above, for unsymmetrical enolisable ketones, double bond regioselectivity could be problematic in the initial enol acetate forming step leading to mixtures of products further down the line. Using Hedione, which exclusively gave a single enol acetate, none of the undesired enol bond isomer was observed. This was only problematic in certain cases (**2a**–**6a**, ratios given) as easily identified by the characteristic olefinic signal in the ^1H NMR (typically ~5.5 ppm). This is an obvious limitation to the methodology as these, if not separated, give rise to α-bromo intermediates which



Scheme 1. Proposed oxidation/decomposition pathway for enol acetate, **1a**.

Table 2
Substrate scope investigation



Entry	Starting material	Yield (%)[a]	Entry	Product	Yield (%)[a]
1a		97[b]	**1b**		99[b]
2a		64 (3:1)	**2b**		90[c]
3a		70 (8:1)	**3b**		89[c]
4a		78 (2:1)	**4b**		20[c]
5a		75 (1:1)	**5b**		62[c]
6a		53 (6:1)	**6b**		17
7a		76	**7b**		31
8a		73	**8b**		83
9a		55	**9b**		68
10a		74	**10b**	—	N/A
11a		67	**11b**		46
12a		64[d]	**12b**		86
13a		89	**13b**		57
14a		57	**14b**		42[e]

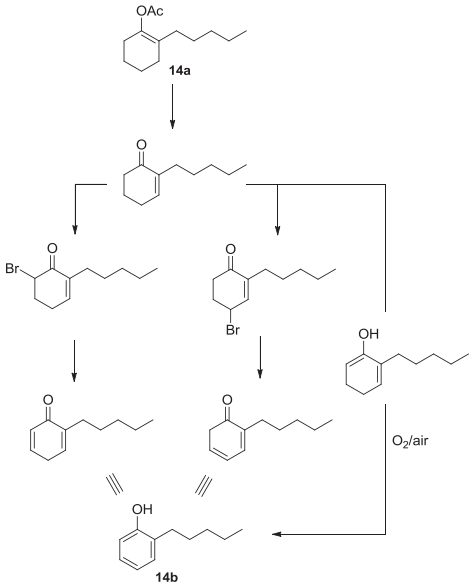
[a] Isolated yields after SiO_2 column chromatography.
[b] Chromatography not necessary.
[c] Yields reported relative to correct enol acetate isomer.
[d] MsOH (10 mol%) and 4 equiv isopropenyl acetate was used.
[e] Unoptimised and based on 2 equiv of $CuBr_2$.

lead to different products. A selection of substrates for which this would not be an issue were therefore also investigated (Table 2, entries 7–13).

Starting material consumption was quantitative in all cases (as determined by TLC). A general trend was observed regarding spontaneous elimination of the initially formed bromo intermediate. For the 2-substituted cyclopentanone derivatives, the pendant alkyl chain induced elimination at lengths down to the ethyl, where incomplete elimination was observed. For both α-methyl cyclopentanone (**6b**) and α-methyl indanone (**9b**) mixtures of α-bromo and α,β-unsaturated products were observed. In the case of **6a**, a complex mixture of products was obtained with **6b** being the only isolable product after flash column chromatography. The unfunctionalised derivatives, **7a** and **8a**, yielded exclusively α-bromo adducts (**7b** and **8b**, respectively). This trend suggests that steric impingement at the α-position is key in determining whether the substrate undergoes full elimination under the reaction conditions. Interestingly, the oxidation of **4a** led exclusively to the formation of the endocyclic, less conjugated double bond isomer. Of the linear carbonyls tested, only α-bromination was observed. For the phenylpropenyl acetate, **13a**, the α-bromo adduct formed initially, but underwent rapid hydrolysis during purification.

Interestingly, the cyclohexanone derivative, **14a**, underwent successive oxidation furnishing the corresponding phenol (**14b**). The formation of phenols from α,β-unsaturated cyclohexanone starting materials using copper(II) salts is a known process and was first reported over 50 years ago.[4] However, taking an enol-cyclohexanone through a single-step, two-level oxidation process, to our knowledge, has never been performed. A plausible mechanistic rationalization is depicted in Scheme 2.

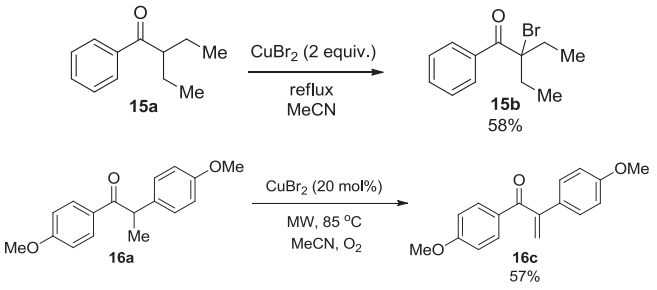
Based upon the information acquired from the above studies, the potential for a catalytic system was again considered (in



Scheme 2. Possible phenol formation mechanistic routes.

which a ketone would be treated with substoichiometric $CuBr_2$) (Scheme 3). In this system, bromination should be biased to only occur on one side of the ketone, leading to an elimination product which could not be brominated a second time. It was hoped that this would allow for complete conversion of the ketone by using substoichiometric quantities of $CuBr_2$ as a basic proof of principle.

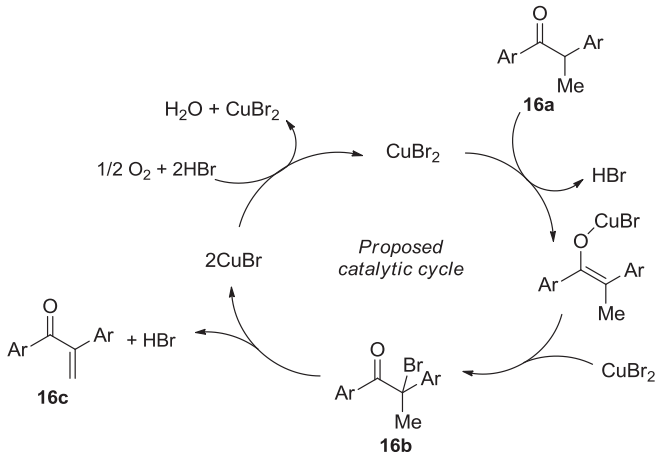
The first of these (**15a**) was unsuccessful due to the formation of exclusively the α-bromo adduct, **15b**. No subsequent elimination



Scheme 3. Substrates employed for catalytic system.

was observed; even upon treatment with 2 equiv of $CuBr_2$, only product **15b** was isolated (58% yield). A second substrate, a desoxyanisoin derivative, **16a**, was treated with 20 mol % of $CuBr_2$ and subjected to microwave heating (85 °C). The reaction progress was monitored by GC–MS analysis and the solvent was purged with further O_2 between each sampling period. After 132 h, >85% conversion of the starting material (**16a**) was estimated and the reaction was worked-up. After purification by column chromatography and removal of a decomposition product (**17**) under high vacuum, **16c** was obtained in 57% isolated yield. To be sure that the oxidation was not proceeding via an alternative route, for example, an α-hydroxylation, the reaction was repeated in an O_2 atmosphere with $Cu(OAc)_2$ and without a copper catalyst. Neither of these resulted in any conversion of the starting material. The α-bromo adduct (**16b**), was observed in the crude reaction mixture by ASAP-MS (accurate mass obtained, Δ=0.9 ppm) supporting the proposed catalytic cycle (Scheme 4; Fig. 3).

In our proposed cycle (Scheme 4), elimination leads to the formation of HBr which allows for the reoxidation of Cu(I) in the



Scheme 4. Proposed catalytic cycle for the oxidation of **16a**.

presence of oxygen, regenerating the brominating agent, $CuBr_2$. Decomposition of the product to 4-acetylanisole (**17**) was also observed under the acidic reaction conditions; this was presumably aided by the electron donating *para*-methoxy group on the aromatic rings. A possible mechanism for the formation of compound **17** is given in Scheme 5.

The cycle described highlights the key attributes of the process and acts as a proof of concept, revealing that $CuBr_2$ can be used as

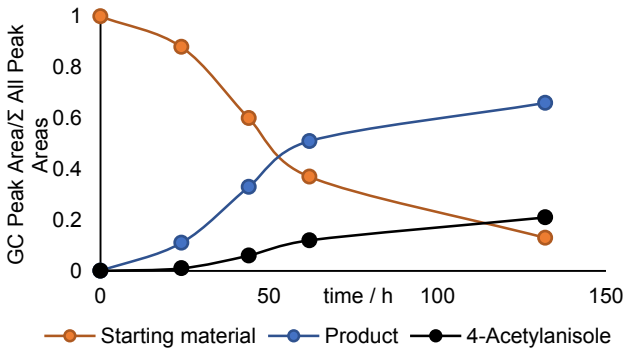
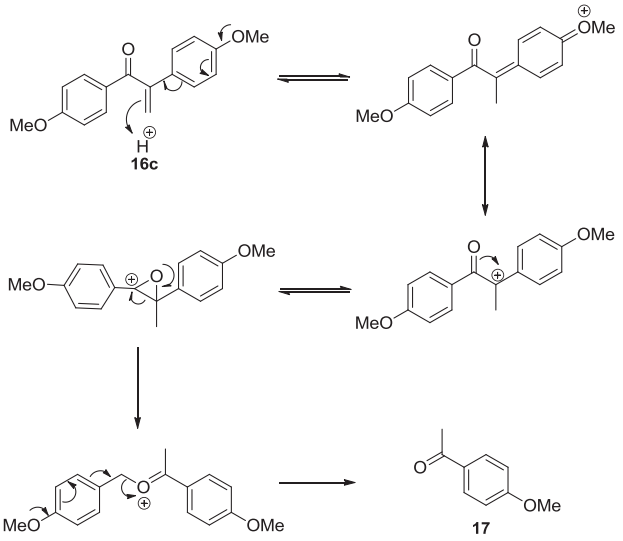


Fig. 3. Reaction progression for the catalytic oxidation of **16a**.



Scheme 5. Possible mechanistic pathway for the acid catalysed decomposition of **16c**.

a catalytic oxidant to convert certain ketones to their corresponding α,β-unsaturated analogues. Further work is underway to gain more insight into the potential of this process for use in industrial oxidation processes.

3. Conclusions

In conclusion, the methodology developed proved highly effective for the two-step synthesis of DHH from Hedione® and its applicability to other substrates was demonstrated. We have shown that in situ elimination is specific to substrates bearing sufficiently bulky functional groups at the α-position. In addition, a catalytic system was developed which served as a mechanistic probe to gain better insight into the process. Efforts directed towards further development of the catalytic system are currently underway and work towards a system in which phenols can be formed from cyclohexanones, catalytically is also ongoing.

4. Experimental

4.1. General procedure for acetylation of ketones/aldehydes

For a typical 10.0 mmol scale reaction, the starting material was dissolved in isopropenyl acetate (2.2 mL, 20 mmol, 2 equiv) and *para*-toluene sulfonic acid (0.20 g, 1 mmol, 10 mol %) was added. The resulting mixture was stirred at 90 °C until full conversion was achieved (TLC). Saturated aqueous $NaHCO_3$ (15 mL) and Et_2O (20 mL) were added and the products were extracted using further Et_2O (2×20 mL). After drying over Na_2SO_4 and concentration in vacuo, crude products were purified using SiO_2 column chromatography (hexane/EtOAc) where necessary.

*4.1.1. Methyl 2-(3-acetoxy-2-pentylcyclopent-2-en-1-yl)acetate (**1a**).*[24] Pale brown liquid (5 mmol scale, 1.31 g, 98%), R_f (9:1, hexane:EtOAc) 0.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.70 (s, 3H), 3.07 (m, 1H), 2.56 (dd, *J*=4.4, 14.8 Hz, 1H), 2.48 (m, 2H), 2.14 (s, 3H), 2.07–2.24 (m, 3H),1.80 (m, 1H), 1.63 (m, 1H), 1.42 (m, 1H), 1.27 (m. 5H), 0.90 (t, *J*=7.9 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 173.3, 168.6, 145.2, 128.3, 51.5, 39.5, 38.6, 31.7, 29.6, 27.1, 26.7, 24.4, 22.4, 20.8, 14.0 ppm; FTIR ν_{max} 1008 (m), 1204 (s), 1368 (m), 1436 (w), 1737 (s), 2930 (w) cm^{-1}; GC–MS R_t 4.79 min, *m*/*z* 268 [M]$^+$, 226 [M–Ac]$^+$.

*4.1.2. 3-Methyl-2-pentylcyclopent-1-en-1-yl acetate (**2a**).* Starting material obtained by organocuprate conjugate addition of 2-pentyl cyclopent-2-enone.[16] Pale yellow liquid (2 mmol scale, 375 mg, 86%), (3:1 isomer ratio), R_f (9:1, hexane:EtOAc) 0.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.70 (m, 1H), 2.45 (m, 2H), 2.16 (s, 3H), 2.15–1.81 (m, 2H), 1.51–1.22 (m, 8H), 1.05 (d, *J*=6.9 Hz, 3H), 0.90 (t, *J*=7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 168.8, 143.8, 130.8, 37.3, 31.7, 29.7, 29.4, 26.7, 24.4, 22.4, 20.8, 19.6, 14.0 ppm; FTIR ν_{max} 1202 (s), 1180 (s), 1369 (w), 1756 (m), 2859 (w), 2929 (w), 2956 (w) cm^{-1}; GC–MS R_t 3.85 min, *m*/*z* 210 [M]$^+$, 168 [M–Ac]$^+$.

*4.1.3. 2-Pentylcyclopent-1-en-1-yl acetate (**3a**).*[16] Starting material obtained by hydrogenation of 2-pentyl cyclopent-2-enone (aldol product of cyclopentanone and pentanal).[25] Colourless liquid (2.5 mmol scale, 295 mg, 70%), (8:1 isomer ratio), R_f (9:1, hexane:EtOAc) 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.48 (m, 2H), 2.31 (m, 2H), 2.17 (s, 3H), 2.03–1.88 (m, 4H), 1.42–1.21 (m, 6H), 0.90 (t, *J*=7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 168.9, 143.8, 126.9, 31.6, 31.1, 31.0, 26.8, 26.4, 22.5, 20.8, 19.8, 14.0 ppm; FTIR ν_{max} 1210 (s), 1739 (s), 2859 (w), 2930 (m), 2956 (m) cm^{-1}; GC–MS R_t 3.76 min, *m*/*z* 196 [M]$^+$, 154 [M–Ac]$^+$.

*4.1.4. 2-Benzylcyclopent-1-en-1-yl acetate (**4a**).*[26] Starting material obtained from 2-cyclopentylidene-1,1-dimethylhydrazine.[27] Colourless liquid (3.5 mmol scale, 592 mg, 78%), (2:1 isomer ratio), R_f (8:2, hexane:EtOAc) 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.16 (m, 5H), 3.34 (s, 2H), 2.51–2.58 (m, 2H), 2.26–2.19 (m, 2H), 2.17 (s, 3H), 1.97–1.87 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 169.0, 144.9, 139.0, 128.7, 128.3, 126.0, 125.9, 33.0, 31.1, 31.0, 20.8, 19.7 ppm; FTIR ν_{max} 699 (m), 753 (m), 1205 (s), 1366 (s), 1746 (s), 2970 (m) cm^{-1}; GC–MS R_t 4.80 (major) +4.86 min, *m*/*z* 216 [M]$^+$, 174 [M–Ac]$^+$.

*4.1.5. 2-Ethylcyclopent-1-en-1-yl acetate (**5a**).* Starting material obtained from 2-cyclopentylidene-1,1-dimethylhydrazine.[27] Colourless oil (1 mmol scale, 115 mg, 75%), (1:1 isomer ratio), R_f (9:1, hexane:EtOAc) 0.5. ^{1}H NMR (700 MHz, $CDCl_3$) δ 2.47–2.42 (m, 2H), 2.32–2.28 (m, 2H), 2.13 (s, 3H), 2.01–1.96 (m, 2H), 1.89 (m, 2H), 0.95 (t, *J*=7.6 Hz, 3H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$) δ_C 168.9, 143.0, 128.1, 31.0, 30.7, 21.1, 19.7, 19.6, 11.9 ppm; FTIR ν_{max} 1178 (s), 1199 (s), 1369 (m), 1751 (m), 2971 (m) cm^{-1}; GC–MS R_t 2.99 min, *m*/*z* 154 [M]$^+$, 112 [M–Ac]$^+$.

*4.1.6. 2-Methylcyclopent-1-en-1-yl acetate (**6a**).* Starting material obtained from 2-cyclopentylidene-1,1-dimethylhydrazine.[27] Colourless liquid (1 mmol scale, 74 mg, 53%), (6:1 isomer ratio), R_f (9:1, hexane:EtOAc) 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.47 (m, 2H), 2.31 (m, 2H), 2.17 (s, 3H), 1.97–1.88 (m, 2H), 1.56 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 168.9, 143.9, 122.7, 33.5, 30.9, 20.8, 19.7,

11.9 ppm; FTIR ν_{max} 1073 (w), 1180 (s), 1208 (s), 1369 (w), 1751 (m), 2925 (w) cm^{-1}; GC–MS R_t 2.70 min, *m/z* 140 $[M]^+$, 98 $[M-Ac]^+$.

*4.1.7. Cyclopent-1-en-1-yl acetate (**7a**).*[28] Pale brown liquid (20 mmol scale, 1.90 g, 76%), R_f (8:2, hexane:EtOAc) 0.6. ^1H NMR (400 MHz, $CDCl_3$) δ 5.41 (m, 1H), 2.46 (m, 2H), 2.38 (m, 2H), 2.16 (s, 3H), 1.95 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 168.7, 150.9, 113.1, 30.9, 28.6, 21.1, 21.0 ppm; FTIR ν_{max} 1153 (w), 1201 (s), 1341 (w), 1370 (w), 1666 (w), 1755 (s), 2856 (w), 2928 (m) cm^{-1}; GC–MS R_t 3.62 min, *m/z* 126 $[M]^+$, 84 $[M-Ac]^+$.

*4.1.8. 1H-Inden-3-yl acetate (**8a**).*[29,30] White crystalline solid, mp 48–49 °C (petroleum ether), (lit. 48.5–49.5 °C), (1.4 mmol scale, 182 mg, 73%), R_f (9:1, hexane:EtOAc) 0.5. ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J*=7.3 Hz, 1H), 7.36–7.25 (m, 3H), 6.36 (t, *J*=2.3 Hz, 1H), 3.45 (d, *J*=2.4 Hz, 2H), 2.37 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 168.3, 149.1, 141.8, 139.0, 126.3, 125.7, 124.1, 118.0, 115.6, 35.0, 21.2 ppm; FTIR ν_{max} 1007 (m), 1074 (m), 1112 (m), 1166 (m), 1207 (s), 1361 (m), 1725 (s) cm^{-1}; GC–MS R_t 4.07 min, *m/z* 174 $[M]^+$, 132 $[M-Ac]^+$.

*4.1.9. 2-Methyl-1H-inden-3-yl acetate (**9a**).*[31] Starting material obtained from 2-(2,3-dihydro-1*H*-inden-1-ylidene)-1,1-dimethylhydrazine.[27] Yellow oil (5 mmol scale, 515 mg, 55%), R_f (9:1, hexane:EtOAc) 0.4. ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J*=7.6 Hz, 1H), 7.27 (m, 1H), 7.17 (td, *J*=7.4, 1.2 Hz, 1H), 7.09 (d, *J*=7.6 Hz, 1H), 3.36 (s, 2H), 2.39 (s, 3H), 2.01 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 168.4, 144.4, 140.2, 139.8, 128.4, 126.2, 124.6, 123.7, 117.1, 39.1, 20.6, 12.3 ppm; FTIR ν_{max} 715 (m), 749 (s), 1122 (m), 1197 (s), 1365 (m), 1752 (s) cm^{-1}; GC–MS R_t 4.07 min, *m/z* 188 $[M]^+$, 146 $[M-Ac]^+$.

*4.1.10. Methyl 2-acetoxycyclopent-1-enecarboxylate (**10a**).*[32] Colourless liquid (5 mmol scale, 680 mg, 74%), R_f (9:1, hexane:EtOAc) 0.4. ^1H NMR (400 MHz, $CDCl_3$) δ 3.73 (s, 3H), 2.70–2.61 (m, 4H), 2.25 (s, 3H), 2.01–1.94 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 167.7, 164.1, 160.0, 118.0, 51.3, 33.5, 29.4, 20.9, 19.1 ppm; FTIR ν_{max} 1043 (m), 1132 (m), 1174 (s), 1217 (s), 1366 (s), 1717 (s), 1739 (s), 2971 (m) cm^{-1}; GC–MS R_t 3.65 min, *m/z* 184 $[M]^+$, 142 $[M-Ac]^+$.

*4.1.11. 6-Methylhepta-2,5-dien-2-yl acetate (**11a**).*[33] Pale yellow liquid (20 mmol scale, 2.25 g, 67%), (~1:1 mixture of *E*/*Z* isomers), R_f (9:1, hexane:EtOAc) 0.4. ^1H NMR (400 MHz, $CDCl_3$) δ 4.75–5.14 (m, 2H), 2.20–2.74 (m, 2H), 2.18 (s, 1.5H), 2.16 (s, 1.5H), 1.89 (m, 3H), 1.70 (m, 3H), 1.63 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 169.2, 168.9, 156.2, 144.6, 132.5, 122.9, 121.5, 115.8, 101.3, 33.4, 25.7, 25.6, 25.1, 24.5, 21.1, 20.8, 19.5, 17.7, 17.6, 15.2 ppm; FTIR ν_{max} 1217 (s), 1370 (s), 1752 (s), 2971 (m) cm^{-1}; GC–MS R_t 3.16+3.29 min, *m/z* 168 $[M]^+$, 126 $[M-Ac]^+$.

*4.1.12. Cyclohexylidenemethyl acetate (**12a**).*[34] Methanesulfonic acid (10 mol %) and 4 equiv of isopropenyl acetate used. Pale yellow liquid (10 mmol scale, 980 mg, 64%), R_f (9:1, hexane:EtOAc) 0.5. ^1H NMR (400 MHz, $CDCl_3$) δ 6.87 (t, *J*=1.2 Hz, 1H), 2.25 (m, 2H), 2.15 (s, 3H), 2.06 (m, 2H), 1.61–1.48 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 168.6, 127.1, 125.7, 30.6, 27.9, 26.8, 26.5, 26.2, 20.8; FTIR ν_{max} 1204 (s), 1220 (s), 1745 (s), 2854 (w), 2927 (m) cm^{-1}; GC–MS R_t 3.27 min, *m/z* 154 $[M]^+$, 112 $[M-Ac]^+$.

*4.1.13. 2-Phenylprop-1-en-1-yl acetate (**13a**).*[35] Yellow liquid (10 mmol scale, 1.56 g, 89%), (3.3:1 mixture of *E*:*Z* isomers), R_f (9:1, hexane:EtOAc) 0.5. ^1H NMR (400 MHz, $CDCl_3$) δ 7.57–7.22 (m, 6H), 2.25 (s, 3H, (***E***)), 2.15 (s, 3H, (***Z***)), 2.12 (d, *J*=1.5 Hz, 3H, (***E***)), 2.05 (d, *J*=1.5 Hz, 3H, (***Z***)) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C ***E***: 168.0, 139.1, 132.6, 128.5, 127.3, 125.8, 121.6, 20.9, 13.6 ppm; FTIR ν_{max} 1067 (m), 1117 (s), 1209 (s), 1369 (m), 1752 (s) cm^{-1}; GC–MS R_t 3.74+3.91 (major) min, *m/z* 176 $[M]^+$, 134 $[M-Ac]^+$.

*4.1.14. 2-Pentylcyclohex-1-en-1-yl acetate (**14a**).*[36] Starting material obtained by hydrogenation of 2-pentylidenecyclohexanone (aldol product of cyclohexanone and pentanal). Colourless liquid (1.1 mmol scale, 135 mg, 57%), R_f (9:1, hexane:EtOAc) 0.6. ^1H NMR (400 MHz, $CDCl_3$) δ 2.15 (s, 3H), 2.15–2.06 (m, 4H), 1.92 (t, *J*=7.7 Hz, 2H), 1.73–1.62 (m, 4H), 1.40–1.21 (m, 6H), 0.90 (t, *J*=7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 169.4, 141.9, 124.5, 31.7, 30.1, 27.7, 27.1, 26.9, 23.1, 22.5, 22.5, 20.9, 14.0 ppm; FTIR ν_{max} 730 (m), 907 (m), 1111 (m), 1217 (s), 1369 (m), 1750 (s), 2930 (m) cm^{-1}; GC–MS R_t 4.03 min, *m/z* 210 $[M]^+$, 168 $[M-Ac]^+$.

4.2. General procedure for the oxidation/bromination of enol acetates

For a typical 1.0 mmol scale reaction, the enol acetate was dissolved in MeCN (5 mL). Copper(II) bromide (0.45 g, 2.0 mmol, 2 equiv) was then added and the mixture was stirred under reflux until full conversion was observed (TLC). The resultant mixture was allowed to cool and after removal of MeCN in vacuo, was partitioned between H_2O (10 mL) and Et_2O (15 mL). Products were extracted using further Et_2O (2×15 mL). After drying over Na_2SO_4 and concentration in vacuo, crude products were purified using SiO_2 column chromatography (hexane/EtOAc) where necessary.

*4.2.1. Methyl 2-(3-oxo-2-pentylcyclopent-1-en-1-yl)acetate (**1b**).*[19] Colourless liquid (1 mmol scale, 220 mg, 99%), R_f (9:1, hexane:EtOAc) 0.1. ^1H NMR (400 MHz, $CDCl_3$) δ 3.74 (s, 3H), 3.46 (s, 2H), 2.63 (m, 2H), 2.42 (m, 2H), 2.19 (m, 2H), 1.21–1.44 (m, 6H), 0.88 (t, *J*=8.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 209.2, 169.6, 163.3, 143.3, 52.3, 36.6, 34.3, 31.8, 29.7, 28.0, 23.2, 22.5, 14.0 ppm; FTIR ν_{max} 1171 (s), 1194 (s), 1435 (m), 1644 (m), 1698 (s), 1738 (s), 2860 (w), 2929 (w), 2954 (w) cm^{-1}; GC–MS R_t 4.70 min, *m/z* 224 $[M]^+$, 193 $[M-OMe]^+$, 154 $[M-C_5H_{11}]^+$, 151 $[M-CH_2CO_2Me]^+$.

*4.2.2. 3-Methyl-2-pentylcyclopent-2-enone (**2b**).*[37] Colourless liquid (1 mmol scale, 75% isomerically pure starting material, 112 mg, 90%), R_f (9:1, hexane:EtOAc) 0.2. ^1H NMR (400 MHz, $CDCl_3$) δ 2.50 (m, 2H), 2.37 (m, 2H), 2.17 (t, *J*=7.6 Hz, 2H), 2.06 (s, 3H), 1.43–1.21 (m, 6H), 0.88 (t, *J*=7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 209.7, 170.0, 140.8, 34.3, 31.8, 31.5, 28.1, 23.0, 22.5, 17.2, 14.0 ppm; FTIR ν_{max} 1385 (w), 1645 (m), 1695 (s), 2858 (w), 2926 (w), 1956 (w) cm^{-1}; GC–MS R_t 3.89 min, *m/z* 166 $[M]^+$, 151 $[M-Me]^+$.

*4.2.3. 2-Pentylcyclopent-2-enone (**3b**).*[37] Pale yellow liquid (1 mmol scale, 90% isomerically pure starting material, 122 mg, 89%), R_f (9:1, hexane:EtOAc) 0.2. ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (m, 1H), 2.60–2.54 (m, 2H), 2.43–2.38 (m, 2H), 2.17 (m, 2H), 1.54–1.44 (m, 2H), 1.38–1.24 (m, 4H), 0.90 (t, *J*=6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 210.1, 157.2, 146.6, 34.6, 31.6, 27.4, 26.4, 24.7, 22.4, 14.0 ppm; FTIR ν_{max} 1696 (s), 2860 (w), 2926 (w), 2956 (w) cm^{-1}; GC–MS R_t 3.63 min, *m/z* 152 $[M]^+$, 137 $[M-Me]^+$, 123 $[M-Et]^+$.

*4.2.4. 2-Benzylcyclopent-2-enone (**4b**).*[38] Colourless liquid (1 mmol scale, 67% isomerically pure starting material, 22 mg, 20%), R_f (8:2, hexane:EtOAc) 0.2. ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.20 (m, 5H), 7.17 (m, 1H), 3.51 (m, 2H), 2.56 (m, 2H), 2.50–2.42 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 209.2, 158.8, 146.1, 138.9, 128.9, 128.5, 126.3, 34.6, 31.4, 26.5 ppm; FTIR ν_{max} 703 (m), 790 (w), 1001 (w), 1453 (w), 1496 (w), 1695 (s) cm^{-1}; GC–MS R_t 4.37 min, *m/z* 172 $[M]^+$.

*4.2.5. 2-Ethylcyclopent-2-enone (**5b**).*[39] Yellow liquid (1 mmol scale, 50% isomerically pure starting material, 31 mg, 62%), R_f (9:1, hexane:EtOAc) 0.3. ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (m, 1H),

2.61–2.55 (m, 2H), 2.45–2.40 (m, 2H), 2.26–2.17 (m, 2H), 1.12 (t, J=7.5 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 210.0, 156.6, 147.9, 34.7, 26.4, 18.1, 12.1 ppm; FTIR ν_{max} 1262 (w), 1715 (s), 2926 (m) cm^{-1}; GC–MS R_t 2.67 min, m/z 110 [M]$^+$, 95 [M–Me]$^+$.

*4.2.6. 5-Bromo-2-methylcyclopent-2-enone (**6b**).* Colourless liquid (1.4 mmol scale, 85% isomerically pure starting material, 35 mg, 17%), R_f (9:1, hexane:EtOAc) 0.2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (m, 1H), 5.11 (m, 1H), 3.07 (dd, J=19.6, 6.2 Hz, 1H), 2.79 (dd, J=19.6, 1.6 Hz, 1H), 1.88 (t, J=1.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 204.7, 156.2, 143.8, 45.2, 42.1, 10.0 ppm; FTIR ν_{max} 918 (m), 1069 (w), 1187 (w), 1709 (s) cm^{-1}; GC–MS R_t 3.13 min, m/z 176 [M]$^+$, 174 [M]$^+$, 95 [M–Br]$^+$; ASAP-HRMS m/z found [M+H]$^+$ 176.9738, C_6H_8BrO requires 176.9738 (Δ=0 ppm).

*4.2.7. 2-Bromocyclopentanone (**7b**).*[40] Colourless liquid (1 mmol scale, 51 mg, 31%), R_f (8:2, hexane:EtOAc) 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.28–4.22 (m, 1H), 2.48–2.34 (m, 2H), 2.31–2.16 (m, 3H), 2.09–1.98 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 211.2, 48.1, 35.0, 33.9, 20.2 ppm; FTIR ν_{max} 1149 (s), 1741 (s), 2972 (w) cm^{-1}; GC–MS R_t 2.88 min, m/z 164 [M]$^+$, 162 [M]$^+$, 83 [M–Br]$^+$.

*4.2.8. 2-Bromo-1-indanone (**8b**).*[41] Pale yellow crystalline solid, mp 36–38 °C (petroleum ether), (lit. 37–38 °C), (1 mmol scale, 156 mg, 74%), R_f (9:1, hexane:EtOAc) 0.2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J=7.7 Hz, 1H), 7.72–7.66 (m, 1H), 7.49–7.43 (m, 2H), 4.68 (dd, J=7.5, 3.2 Hz, 1H), 3.86 (dd, J=18.4, 7.7 Hz, 1H), 3.45 (dd, J=18.1, 3.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 199.6, 151.1, 136.0, 133.6, 128.3, 126.4, 125.1, 44.1, 38.0 ppm; FTIR ν_{max} 1208 (s), 1275 (s), 1460 (w), 1604 (m), 1717 (s) cm^{-1}; GC–MS R_t 4.35 min, m/z 212 [M]$^+$, 210 [M]$^+$, 132 [M–Br]$^+$.

*4.2.9. 2-Bromo-2-methyl-2,3-dihydro-1H-inden-1-one (**9b**).*[42] White crystalline solid, mp 70–71 °C (petroleum ether), (lit.71–72 °C), (1 mmol scale, 153 mg, 68%), R_f (9:1, hexane:EtOAc) 0.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J=7.6 Hz, 1H), 7.69 (td, J=7.5, 1.2 Hz, 1H), 7.50–7.43 (m, 2H), 3.82 (d, J=18.2 Hz, 1H), 3.51 (d, J=18.2 Hz, 1H), 1.99 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 200.3, 149.1, 135.8, 132.7, 128.3, 126.3, 125.7, 59.5, 46.4, 26.8 ppm; FTIR ν_{max} 1045 (m), 1212 (m), 1286 (m), 1465 (m), 1605 (m), 1715 (s) cm^{-1}; GC–MS R_t 4.27 min, m/z 226 [M]$^+$, 224 [M]$^+$, 145 [M–Br]$^+$.

*4.2.10. 3-Bromo-6-methylhept-5-en-2-one (**11b**).* Brown liquid (1.25 mmol scale, 117 mg, 46%), R_f (9:1, hexane:EtOAc) 0.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (dd, J=11.3, 1.5 Hz, 1H), 2.92–2.65 (m, 2H), 2.21 (s, 3H), 2.09–2.01 (m, 1H), 2.00 (s, 3H), 1.86 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 207.3, 67.9, 66.1, 42.3, 35.0, 30.1, 29.9, 28.8 ppm; FTIR ν_{max} 1097 (s), 1370 (m), 1715 (s), 2977 (w) cm^{-1}; GC–MS R_t 4.07 min, m/z 207 [M+H]$^+$, 205 [M+H]$^+$, 125 [M–Br]$^+$; ASAP-HRMS m/z found [M+H]$^+$ 205.0221, $C_8H_{14}BrO$ requires 205.0228 Δ=3.4 ppm).

*4.2.11. 1-Bromocyclohexanecarbaldehyde (**12b**).*[43] Brown liquid (1 mmol scale, 165 mg, 86%), R_f (9:1, hexane:EtOAc) 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (s, 1H), 2.16–1.96 (m, 4H), 1.88–1.20 (m, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 192.8, 71.6, 34.4, 25.0, 23.2 ppm; FTIR ν_{max} 1723 (s), 2858 (w), 2936 (m) cm^{-1}; GC–MS R_t 3.15 min, m/z 192 [M]$^+$, 190 [M]$^+$, 111 [M–Br]$^+$.

*4.2.12. 2-Hydroxy-2-phenylpropanal (**13b**).*[44] α-Bromo compound (2-bromo-2-phenylpropanal) underwent hydrolysis during purification. Pale yellow oil (1.1 mmol scale, 85 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (s, 1H), 7.52–7.33 (m, 5H), 3.92 (br s, 1H), 1.73 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 199.9, 139.2, 128.9, 128.2, 125.8, 79.1, 23.6 ppm; FTIR ν_{max} 697 (s), 1070 (m), 1729 (m), 2982 (m), 3451 (w, br) cm^{-1}; GC–MS R_t 3.34 min, m/z 133 [M–OH]$^+$, 121 [M–CHO]$^+$.

*4.2.13. 2-Pentylphenol (**14b**).*[45] Colourless liquid (0.6 mmol scale, 42 mg, 42%), R_f (9:1, hexane:EtOAc) 0.2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16–7.07 (m, 2H), 6.89 (td, J=7.4, 1.2 Hz, 1H), 6.79 (dd, J=8.0, 1.2 Hz, 1H), 4.81 (s, 1H), 2.63 (m, 2H), 1.71–1.59 (m, 2H), 1.43–1.33 (m, 4H), 0.96–0.89 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 153.4, 130.2, 128.6, 127.0, 120.8, 115.2, 31.7, 29.9, 29.5, 22.6, 14.1; FTIR ν_{max} 751 (s), 1218 (s), 1230 (s), 1367 (s), 1455 (s), 1740 (s), 2929 (m), 3430 (w, br s) cm^{-1}; GC–MS R_t 3.96 min, m/z 164 [M]$^+$, 107 [M–C_4H_9]$^+$, 77 [C_6H_5]$^+$.

4.3. Procedure for catalytic oxidation of 16a

1,2-Bis(4-methoxyphenyl)propan-1-one (**16a**), (163 mg, 0.60 mmol) was dissolved in MeCN (5 mL) in a microwave vial, the solution was degassed and then saturated with O_2. Copper(II) bromide (27 mg, 0.12 mmol, 20 mol %) was then added and the vial was sealed. The solution was stirred at 85 °C under microwave irradiation for 132 h with 5 min of O_2 purging and monitoring by GC–MS at each of the following intervals; 24 h, 44 h, 62 h, 132 h. The solvent was then removed in vacuo and the product was isolated by SiO_2 column chromatography (8:2, hexane:EtOAc) as an orange oil (decomposition product (4-acetylanisole, **17**) removed under high vacuum), (92 mg, 57%).

*4.3.1. 2-Ethyl-1-phenylbutan-1-one (**15a**).*[46] Prepared by diethylation of acetophenone.[46] Colourless liquid (10 mmol scale, 650 mg, 37%), R_f (9:1, hexane:EtOAc) 0.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–7.97 (m, 2H), 7.61–7.55 (m, 1H), 7.52–7.46 (m, 2H), 3.33 (m, 1H), 1.89–1.54 (m, 4H), 0.90 (t, J=7.4 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 204.5, 137.8, 132.8, 128.6, 128.1, 49.2, 24.9, 11.9 ppm; FTIR ν_{max} 698 (s), 982 (m), 1214 (s), 1447 (m), 1677 (s), 2963 (m) cm^{-1}; GC–MS R_t 3.85 min, m/z 176 [M]$^+$, 105 [M–C_5H_{11}]$^+$.

*4.3.2. 2-Bromo-2-ethyl-1-phenylbutan-1-one (**15b**).* Yellow liquid obtained by reaction of **15a** with $CuBr_2$ (2 equiv) in MeCN (1.2 mmol scale, 179 mg, 58%), R_f (9:1, hexane:EtOAc) 0.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (m, 2H), 7.58–7.38 (m, 3H), 2.32 (m, 4H), 0.97 (t, J=7.3 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 198.0, 136.6, 131.9, 129.4, 128.1, 73.2, 31.6, 9.7 ppm; FTIR ν_{max} 698 (s), 822 (m), 853 (m), 1229 (s), 1446 (m), 1674 (s), 2972 (w) cm^{-1}; GC–MS R_t 4.46 min, m/z 175 [M–Br]$^+$, 105 [M–C_5H_{11}Br]$^+$; ASAP-HRMS: m/z found [M+H]$^+$ 255.0395, $C_{12}H_{16}BrO$ requires 255.0385 (Δ=3.9 ppm).

*4.3.3. 1,2-Bis(4-methoxyphenyl)propan-1-one (**16a**).*[47] Prepared by α-methylation of desoxyanisoin.[47] Thick yellow oil (10 mmol scale, 2.45 g, 91%), R_f (8:2, hexane:EtOAc) 0.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99–7.94 (m, 2H), 7.24–7.19 (m, 2H), 6.90–6.82 (m, 4H), 4.62 (q, J=6.8 Hz, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 1.51 (d, J=6.9 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 199.1, 163.1, 158.4, 134.0, 131.0, 129.5, 128.7, 114.3, 113.6, 55.4, 55.2, 46.6, 19.6 ppm; FTIR ν_{max} 780 (m), 832 (m), 952 (m), 1028 (m), 1165 (s), 1243 (s), 1509 (s), 1598 (s), 1671 (m), 2932 (w) cm^{-1}; GC–MS R_t 6.00 min, m/z 270 [M]$^+$, 135 [$MeOC_6H_4CO$]$^+$+[$MeOC_6H_4C_2H_4$]$^+$.

*4.3.4. 2-Bromo-1,2-bis(4-methoxyphenyl)propan-1-one (**16b**).* Inseparable from starting material (**16a**) and unsaturated product (**16c**) but observed in crude reaction mixture by ASAP-HRMS m/z found [M+H]$^+$ 349.0436, $C_{17}H_{18}BrO_3$ requires 349.0439 (Δ=0.9 ppm).

*4.3.5. 1,2-Bis(4-methoxyphenyl)prop-2-en-1-one (**16c**).*[48] Orange oil (0.6 mmol scale, 92 mg, 57%), decomposition product removed in vacuo, R_f (8:2, hexane:EtOAc) 0.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.93 (m, 2H), 7.40–7.36 (m, 2H), 6.94–6.87 (m, 4H), 5.92 (s,

1H), 5.47 (s, 1H), 3.88 (s, 3H), 3.82 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 196.7, 163.6, 159.7, 147.8, 132.4, 129.9, 129.7, 128.1, 117.0, 114.0, 113.6, 55.5, 55.3 ppm; FTIR ν_{max} 783 (m), 836 (m), 979 (m), 1027 (m), 1162 (s), 1250 (s), 1508 (s), 1595 (s), 1657 (m) cm^{-1}; GC–MS R_t 6.30 min, m/z 268 $[M]^+$, 135 $[MeOC_6H_4CO]^+$, 133 $[MeOC_6H_4C_2H_2]^+$.

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Supplementary data

Supplementary material including characterisation data of the products with corresponding literature references can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2016.04.011.

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