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Manganese(III) acetate based oxidation of substituted α′-position on cyclic α,β-unsaturated ketones

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Abstract—Selective oxidation of the tertiary α′-position on various 2-cyclopentenone, 2-cyclohexenone and aromatic ketone derivatives with manganese(III) acetate is described.

1. Introduction

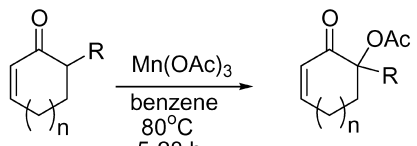
α,β-Unsaturated ketones are among the most versatile building blocks in organic synthesis. Indeed, several natural products have been synthesized using enones as basic starting materials.[1] Selective oxidations yielding α′-hydroxy α,β-unsaturated cyclic ketones possess a central position in synthetic methodology.[2] Some analogues of those oxygenated compounds have interesting biological properties and are used in a number of medical preparations (e.g. monosaccharide carba-analogues as components for anti-viral medicines, hydroxycyclopentenones as anti-cancer drugs, etc.).[3] The regioselective α′-oxidation of enones to α′-acetoxy enones constitutes a valuable procedure for manipulating a common functional group. In 1976, Williams and Hunter reported that the manganese(III) acetate oxidation of enones affords modest yields of α′-acetoxy enones.[4] Watt et al. reinvestigated this procedure and obtained acceptable yields of the desired α′-acetoxy enones.[5] So far, studies on the selective oxidation of cyclic enones in literature have been concerned with substrates that are unsubstituted at α′-positions except for one example of a steroidal substrate involving a tertiary α′-position. However in this exceptional study Ahmad et al. were failed to synthesize α′-acetoxy enones.[6] The lack of a selective oxidation method for the α′-tertiary position of α,β-unsaturated cyclic ketones prompted us toward the development of a new method. In connection with our synthetic studies with $Mn(OAc)_3$,[7] we attempted to prepare α′-acetoxy-α′-alkyl α,β-unsaturated cyclic ketones by $Mn(OAc)_3$ oxidation. We previously published the results of $Mn(OAc)_3$ oxidation of various α′-methyl α,β-unsaturated cyclic ketones.[8] As an extension of the study, we are interested in the $Mn(OAc)_3$ oxidation of various α′-methyl, ethyl and benzyl substituted α,β-unsaturated cyclic ketones and some aromatic ketones. In this report we describe a highly efficient method for the synthesis of α′-acetoxy-α′-substituted α,β-unsaturated cyclic ketones.

2. Results and discussion

2.1. Oxidation of α′-substituted cyclopentenone and cyclohexenone derivatives

α′-Substituted α,β-unsaturated cyclopentanones and cyclohexanones **1** were prepared from the corresponding α,β-unsaturated cyclic ketones using slightly modified literature procedures,[9] with LDA and corresponding alkyl halides at −78°C and subsequently allowed to react with $Mn(OAc)_3$. α′-Alkyl α,β-unsaturated cyclopentanones and cyclohexanones **1** (with dry benzene as the solvent) underwent a selective oxidation with $Mn(OAc)_3$ to afford products **2**. Characterization of the products revealed the introduction of an acetoxy moiety at the α′-position (Scheme 1). The results are summarized in Table 1.

The reaction is thought to proceed through the formation of the Mn(III) enolate **3**, which loses Mn(II) upon one-electron oxidation to give the α′-keto radical **4**[10] (Scheme 2). The



1 **2**

n=0 or 1

R: -CH_3, -CH_2CH_3, -CH_2Ph

Scheme 1.

Keywords: enones; manganese and compounds; oxidation.
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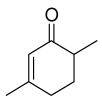
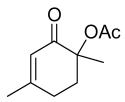
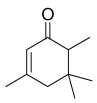
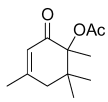
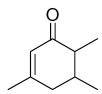
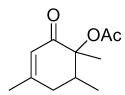
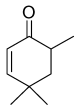
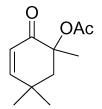
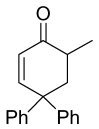
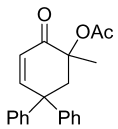
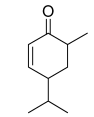
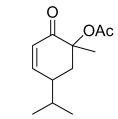
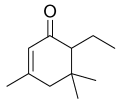
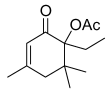
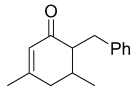
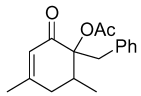
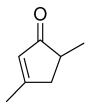
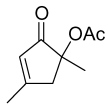
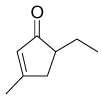
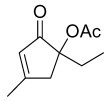
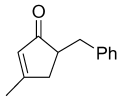
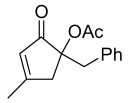
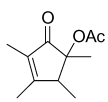
Table 1. Selective oxidation of α′-substituted 2-cyclohexenone and 2-cyclopentenone derivatives with manganese(III) acetate in benzene

Entry	Reactant	Product	2	Yield (%)	Time (h)
1			**2a**	64	10
2			**2b**	76	10
3[a]	 syn/anti=1:1	 syn/anti=1:1	**2c**	81	12
4			**2d**	78	10
5			**2e**	47	28
6[a]	 syn/anti=1:2	 syn/anti=2:8	**2f**	82	12
7			**2g**	53	12
8[a]	 cis/trans=1:9		**2h**[b]	77	5
9			**2i**	72	8
10			**2j**	42	24
11			**2k**	51	18
12			**2l**	68	8

[a] Syn/anti ratio was determined by ^{1}H NMR.
[b] **2h** was isolated as only one stereoisomer and its configuration was not determined.

resultant tertiary radical **4** is prone to further oxidation by another equivalent of $Mn(OAc)_3$. The final oxidation step provides α′-acetoxy α′-alkyl α,β-unsaturated ketones **2**.

The 2-cyclohexenone (entries 1–8) and 2-cyclopentenone (entries 9–12) derivatives afforded different yields in the $Mn(OAc)_3$ oxidations. Among methyl substituted 2-cyclohexenone derivatives, the best yield was observed in the synthesis of 6-acetoxy-6-methyl-4-isopropyl-2-cyclohexen-1-one **2f** (entry 6). The substrates **1a–d** (entries 1–4) gave similar, acceptable yields (64–81%). However, there was a drastic decrease in yield for the diphenyl substituted derivative **2e** (entry 5, 47% yield). Although the reaction time was increased after 10 h to 28 h, there was no change in the yield of product formed.

The acetoxylation yield of **2g** (entry 7) is lower than its methyl substituted derivative **2b** (entry 2). Presumably this can be due to the sterical effect of ethyl group.

Among the oxidation of 2-cyclopentenone derivatives (entries 9–12), compound **1e** (entry 9) gave the best yield. The oxidation yields of α′-ethyl and benzyl substituted 3-methyl cyclopentenones **2j** and **2k** (entry10 and 11) are lower than α′-methyl substituted derivative **2i** (entry 9). Increasing the reaction time beyond 16 h failed to improve the yield of product formed.

2.2. $Mn(OAc)_3$ Oxidation of α′-substituted aromatic ketones

It is well known in the literature that $Mn(OAc)_3$ regioselectively oxidizes the aromatic ketones as well as enones.[11] In this study, we investigated the regioselective oxidation of α′-substituted aromatic ketones (Scheme 3). It can be seen from Table 2 that oxidation of aromatic ketones were completed in 18 h with 30–56% yields.

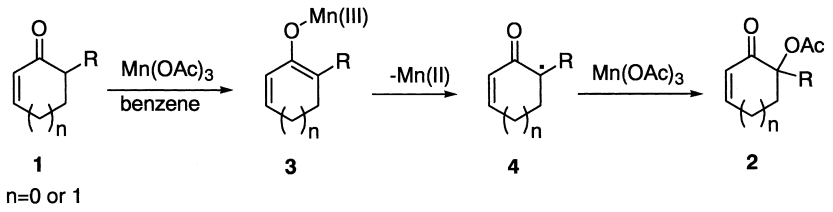
In conclusion, we have demonstrated a synthetically valuable and highly efficient oxidation method with manganese(III) acetate which can be applied to α′-substituted enones. In addition to its simplicity and mild reaction conditions, the method offers acceptable yields of products which makes it a useful and attractive process in the regioselective synthesis of tertiary alcohols.

3. Experimental

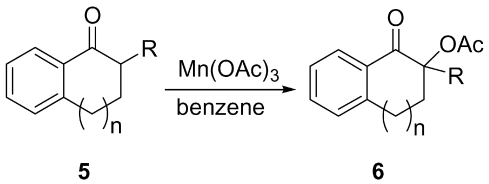
^{1}H NMR spectra were recorded in $CDCl_3$ on Bruker Spectrospin Avance DPX 400 spectrometer. Chemical shifts are given in ppm from tetramethylsilane. IR spectra were obtained using a Perkin–Elmer Model 1600 series FT-IR spectrometer and are reported in cm^{-1}. Mass spectra were recorded with Varian MAT 212. Thin layer chromatography (TLC) was performed on Merck plastic-backed silica gel plates. Compounds were visualized under an UV lamp. Column chromatography was performed using silica gel (Flash Silica 60, 32–63 μm). All the enones, 2-ethyl indanone **5a**, 2-acetyl tetralone **5b** and 2,3,4,5-tetramethyl-2-cyclopenten-1-one **1l** were purchased from Aldrich.

3.1. General procedure for the alkylation and benzylation of α,β-unsaturated ketones

To a stirred solution of freshly distilled diisopropylamine (4.0 mmol) in dry THF (5 mL) at 0°C under argon atmosphere, *n*-BuLi (8.82 mL, 2.45 M) was added. The

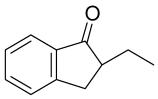
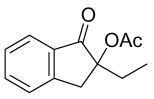
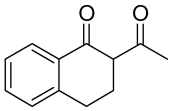
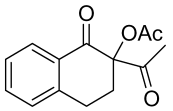
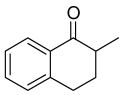
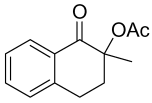


Scheme 2.



Scheme 3.

Table 2. Selective oxidation of α-substituted aromatic compounds.

Entry	Reactant	Product	6	Yield (%)	Time (h)
1			**6a**	30	18
2			**6b**	46	18
3			**6c**	56	18

resultant mixture was cooled down to −78°C and HMPA (4.0 mmol) was added and stirred for 30 min. Then the α,β-unsaturated ketone (4.0 mmol) was gradually added and stirred for an additional 30 min. Finally, alkyl halide (or benzyl halide) (4.2 mmol) was added and stirred for 1 h. Then the mixture was allowed to reach to room temperature and stirred for 12 h. The reaction mixture was diluted with an equal amount of saturated ammonium chloride and extracted with ethyl acetate (2×50 mL). The organic phase was dried over $MgSO_4$ and evaporated in vacuo. The crude product was separated by flash column chromatography using ethyl acetate/hexane as eluent.

Compounds **1a**,[12] **1b**,[13] **1d**,[14] **1e**,[15] **1f**,[16] **1i**[12b] and **1k**[17] were synthesized and all are in accordance with the literature data.

3.1.1. 3,5,6-Trimethyl-2-cyclohexen-1-one 1c. (0.45 g, 74%) as a colourless oil; R_f (EtOAc/hexane 1:4) 0.40; ν_{max} (neat) 3427, 2964, 1678, 1455, 1379 cm^{-1}; δ_H (400 MHz, $CDCl_3$) (1:1 diastereomeric mixture) 5.78 (2×1H, s, =C*H*), 2.21–2.26 (2×1H, m, MeC*H*CO), 1.98–2.05 (2×2H, m, CMeCH_2), 1.87–1.92 (2×1H, m, MeC*H*CH_2), 1.85 (2×3H, s, =C*Me*), 1.60 (3H, d, *J*=7 Hz, *Me*CHCO), 1.20 (3H, d, *J*=7 Hz, *Me*CHCO), 1.06 (3H, d, *J*=7 Hz, *Me*CHCH_2), 1.00 (3H, d, *J*=7 Hz, *Me*CHCH_2); δ_C (100.6 MHz, $CDCl_3$) 202.2, 160.5, 128.4, 126.2, 73.1, 71.6, 47.8, 39.6, 36.4, 24.5, 24.4, 20.3, 20.2, 14.5, 12.7; HRMS (EI): M^+, found 138.1043, $C_9H_{14}O$ requires 138.1045.

3.1.2. 6-Ethyl-3,5,5-trimethyl-2-cyclohexen-1-one 1g. (0.42 g, 62%) as a colourless oil, R_f (EtOAc/hexane 1:3) 0.73; ν_{max} (neat) 3421, 2967, 1680, 1440, 1376 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.71 (1H, s, =C*H*), 2.19 (1H, d, *J*=18 Hz, $Me_2CCH_aH_b$), 1.96 (1H, d, *J*=18 Hz, $Me_2CCH_aH_b$), 1.82 (3H, s, =C*Me*), 1.75–1.78 (1H, dd, *J*=4, 10 Hz, $MeCH_2CH$), 1.48–1.56 (1H, m, $MeCH_aH_bCH$), 1.33–1.41 (1H, m, $MeCH_aH_bCH$), 0.94 (3H, s, Me_aMe_bC), 0.89 (3H, s, Me_aMe_bC), 0.85 (3H, t, *J*=7 Hz, *Me*CH_2); δ_C (100.6 MHz, $CDCl_3$) 203.4, 158.2, 124.9, 59.4, 44.3, 36.4, 29.4, 24.4, 23.3, 19.4, 13.5; HRMS (EI): M^+, found 166.1357, $C_{11}H_{18}O$ requires 166.1358.

3.1.3. 6-Benzyl-3,5-dimethyl-2-cyclohexen-1-one 1h. (0.49 g, 58%) as a colourless oil, R_f (EtOAc/hexane 1:8) 0.27; ν_{max} (neat) 3012, 2961, 1680, 1493 cm^{-1}; δ_H (400 MHz, $CDCl_3$) (1:9 diastereomeric mixture) 7.23–7.28 (2H, m, *Ph*), 7.15–7.20 (3H, m, *Ph*), 5.87 (1H, s, =C*H*), 3.58 (1H, d, *J*=14 Hz, $PhCH_aH_b$), 2.95–2.98 (2H, m, $PhCH_2$), 2.43–2.50 (1H, m, $PhCH_2CH$), 2.29–2.34 (1H, m, MeC*H*), 1.92–2.08 (2H, m, MeCHCH_2), 1.91 (3H, s, major isomer =C*Me*), 1.89 (3H, s, minor isomer =C*Me*), 1.01 (3H, d, *J*=7 Hz, major isomer *Me*CH), 0.91 (3H, d, *J*=7 Hz, minor isomer *Me*CH); δ_C (100.6 MHz, $CDCl_3$) 201.2, 160.0, 140.2, 129.6, 129.3, 128.7, 127.3, 126.5, 126.0, 54.4, 37.4, 34.7, 31.5, 20.4, 14.4; HRMS (EI) M^+, found 214.1356, $C_{15}H_{18}O$ requires 214.1358.

3.1.4. 5-Ethyl-3-methyl-2-cyclopenten-1-one 1j. (0.33 g, 67%) as a colourless oil, R_f (EtOAc/hexane 1:1) 0.63; ν_{max} (neat) 2254, 1690, 1462 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.84 (1H, s, =C*H*), 2.63–2.69 (1H, dd, *J*=6, 18 Hz, =CMeCH_a-H_b), 2.25–2.30 (1H, m, $MeCH_2CH$), 2.19 (1H, d, *J*=18 Hz, =CMeCH_aH_b), 2.06 (3H, s, =C*Me*), 1.72–1.78 (1H, m, MeCH_aH_b), 1.30–1.38 (1H, m, $MeCH_aH_b$), 0.87 (3H, t, *J*=7 Hz, *Me*CH_2); δ_C (100.6 MHz, $CDCl_3$) 212.4, 177.8, 130.4, 53.2, 39.5, 24.6, 19.7, 12.0; HRMS (EI) M^+, found 124.0887, $C_8H_{12}O$ requires 124.0888.

3.2. General procedure for the $Mn(OAc)_3$ oxidations of α′-alkyl α,β-unsaturated ketones

A mixture of $Mn(OAc)_3$ (3.25 g, 14.0 mmol) in benzene (150 mL) was refluxed for 45 min using a Dean-Stark trap. Then, the mixture was cooled to room temperature and the α′-alkyl α,β-unsaturated ketone (7.0 mmol) was gradually

added. The mixture was allowed to reflux until the dark brown colour disappeared (also monitored by TLC). The reaction mixture was diluted with an equal amount of ethyl acetate and the organic phase was washed with 1N HCl (3×50 mL), followed by saturated $NaHCO_3$ (3×50 mL) and brine (2×50 mL). The organic phase was dried over $MgSO_4$ and evaporated in vacuo. The crude product was separated by flash column chromatography using ethyl acetate/hexane as eluent.

3.2.1. 6-Acetoxy-3,6-dimethyl-2-cyclohexen-1-one 2a. (0.81 g, 64%) as a colourless oil; R_f (EtOAc/hexane 1:2) 0.22; ν_{max} (neat) 3342, 2924, 1740, 1678, 1436, 1372, 1251, 1153, 1093, 1025 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.83 (1H, s, C*H*=), 2.77–2.85 (1H, m, =CMeCH_aH_b), 2.26–2.41 (2H, m, CMeOAcCH_2), 1.99 (3H, s, *Me*CO_2), 1.89 (3H, s, =C*Me*), 1.81–1.86 (1H, m, =CMeCH_aH_b), 1.36 (3H, s, COAc*Me*); δ_C (100.6 MHz, $CDCl_3$) 195.9, 170.0, 160.9, 125.5, 80.4, 32.4, 30.2, 24.6, 22.2, 21.9; HRMS (EI): M^+, found 182.0940, $C_{10}H_{14}O_3$ requires 182.0943.

3.2.2. 6-Acetoxy-3,5,5,6-tetramethyl-2-cyclohexen-1-one 2b. (1.12 g, 76%) as a white solid, mp 82–85°C; R_f (EtOAc/hexane 1:3) 0.25; ν_{max} (neat) 3432, 3017, 2975, 2253, 1737, 1686, 1639, 1436, 1372, 1248, 1217 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.70 (1H, s, C*H*=), 2.45 (1H, d, *J*=18 Hz, $CMe_2CH_aH_b$), 1.90 (3H, s, *Me*CO_2), 1.79 (1H, d, *J*=18 Hz, $CMe_2CH_aH_b$), 1.77 (3H, s, =C*Me*), 1.36 (3H, s, COAc*Me*), 1.02 (3H, s, C*Me*$_a$Me$_b$), 0.80 (3H, s, CMe$_a$*Me*$_b$); δ_C (100.6 MHz, $CDCl_3$) 199.1, 172.0, 158.4, 125.5, 87.7, 46.5, 42.8, 26.2, 26.1, 24.8, 23.7, 16.0; HRMS (EI): M^+, found 210.1255, $C_{12}H_{18}O_3$ requires 210.1256.

3.2.3. 6-Acetoxy-3,5,6-trimethyl-2-cyclohexen-1-one 2c. (1.11 g, 81%) as a colourless oil; R_f (EtOAc/hexane 1:5) 0.22; ν_{max} (neat) 3397, 2253, 1735, 1676, 1380, 1257 cm^{-1}; δ_H (400 MHz, $CDCl_3$) (1:1 diastereomeric mixture) 5.83 (1H, s, =C*H*), 5.76 (1H, s, =C*H*), 3.09–3.18 (2×1H, m, MeC*H*), 2.21–2.62 (2×2H, m, CMeCH_2), 2.01 (3H, s, *Me*CO_2), 1.97 (3H, s, *Me*CO_2), 1.88 (3H, s, =C*Me*), 1.84 (3H, s, =C*Me*), 1.49 (3H, s, COAc*Me*), 1.19 (3H, s, COAc*Me*), 0.99 (3H, d, *J*=7 Hz, *Me*CH), 0.93 (3H, d, *J*=7 Hz, *Me*CH); δ_C (100.6 MHz, $CDCl_3$) 196.4, 196.0, 169.8, 169.5, 160.3, 158.1, 125.1, 123.6, 83.4, 82.6, 38.3, 37.1, 33.6, 29.7, 24.1, 23.8, 21.3, 18.8, 16.4, 14.7, 14.0; *m*/*z* (EI) 198 (13), 197 (100), 152 (13), 139 (19), 137 (42); HRMS (EI): M^+, found 196.1105, $C_{11}H_{16}O_3$ requires 196.1100.

3.2.4. 6-Acetoxy-4,4,6-trimethyl-2-cyclohexen-1-one 2d. (1.07 g, 78%) as a colourless oil; R_f (EtOAc/hexane 1:3) 0.27; ν_{max} (neat) 3535, 3155, 2853, 1736, 1689, 1464, 1377 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 6.52 (1H, d, *J*=10 Hz, =CH_β), 5.81 (1H, d, *J*=10 Hz, =CH_α), 2.62 (1H, d, *J*=14 Hz, CH_aH_b), 1.90 (3H, s, *Me*CO_2), 1.79 (1H, d, *J*=14 Hz, CH_aH_b), 1.46 (3H, s, *Me*COAc), 1.16 (3H, s, C*Me*$_a$Me$_b$), 1.14 (3H, s, CMe$_a$*Me*$_b$); δ_C (100.6 MHz, $CDCl_3$) 195.3, 170.5, 157.6, 126.4, 84.3, 45.6, 34.6, 29.6, 25.2, 15.3, 14.5; *m*/*z* (EI) 198 (14), 197 (100), 195 (19), 139 (13), 137 (37); HRMS (EI): M^+, found 196.1103, $C_{11}H_{16}O_3$ requires 196.1100.

3.2.5. 6-Acetoxy-6-methyl-4,4-diphenyl-2-cyclohexen-1-one 2e. (1.05 g, 47%) as a colourless oil, R_f (EtOAc/hexane 1:4) 0.26; ν_{max} (neat) 3717, 3155, 2926, 1709, 1462, 1363, 1095 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.32–7.11 (2×5H and 1H, m, C*PhPh* and =CH_β), 6.21 (1H, d, *J*=10 Hz, =CH_α), 3.66 (1H, d, *J*=14 Hz, CH_aH_b), 2.75 (1H, d, *J*=14 Hz, CH_aH_b), 1.88 (3H, s, *Me*CO_2), 0.97 (3H, s, *Me*COAc); δ_C (100.6 MHz, $CDCl_3$) 195.6, 170.2, 154.4, 147.3, 129.1, 128.9, 128.3, 127.9, 127.5, 127.2, 127.0, 80.2, 50.3, 45.3, 24.2, 21.7; HRMS (EI): M^+, found 320.1412, $C_{21}H_{20}O_3$ requires 320.1413.

3.2.6. 6-Acetoxy-6-methyl-4-isopropyl-2-cyclohexen-1-one 2f. (1.21 g, 82%) as a colourless oil, R_f (EtOAc/hexane 1:4) 0.17; ν_{max} (neat) 3405, 2960, 2867, 2251, 1709, 1674, 1460 cm^{-1}; δ_H (400 MHz, $CDCl_3$) (8:2 diastereomeric mixture) (major isomer) 6.69 (1H, dd, *J*=10, 4 Hz, =CH_β), 5.96 (1H, d, *J*=10 Hz, =CH_α), 2.49–2.53 (1H, m, =CHC*H*), 2.42–2.44 (1H, m, C*H*Me$_2$), 1.99–2.07 (2H, m, CH_2), 1.93 (3H, s, *Me*CO_2), 1.47 (3H, s, *Me*COAc), 0.87 (2×3H, d, *J*=7 Hz, CH*Me*$_2$); (minor isomer) 6.69 (1H, dd, *J*=10, 4 Hz, =CH_β), 5.96 (1H, d, *J*=10 Hz, =CH_α), 2.44–2.48 (1H, m, =CHC*H*), 2.42–2.44 (1H, m, C*H*Me$_2$), 1.99–2.07 (2H, m, CH_2), 1.95 (3H, s, *Me*CO_2), 1.49 (3H, s, *Me*COAc), 0.89 (2×3H, d, *J*=7 Hz, CH*Me*$_2$); δ_C (100.6 MHz, $CDCl_3$) (major isomer) 195.4, 170.2, 152.1, 128.3, 80.8, 40.2, 37.1, 31.6, 21.7, 21.0, 19.6, 19.3; (minor isomer) 191.4, 169.2, 150.3, 125.6, 80.9, 41.2, 37.5, 30.6, 21.8, 21.4, 19.7, 19.1; HRMS (EI): M^+, found 210.1256, $C_{12}H_{18}O_3$ requires 210.1256.

3.2.7. 6-Acetoxy-6-ethyl-3,5,5-trimethyl-2-cyclohexen-1-one 2g. (0.83 g, 53%) as a colourless oil, R_f (EtOAc/hexane 1:4) 0.22; ν_{max} (neat) 3421, 2967, 1735, 1660, 1440, 1376 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.11 (1H, s, =C*H*), 2.47 (1H, d, *J*=18 Hz, CH_aH_b), 2.31 (1H, d, *J*=18 Hz, CH_aH_b), 2.13–2.19 (2H, m, MeCH_2), 2.07 (3H, s, *Me*CO_2), 1.88 (3H, s, =C*Me*), 1.07 (6H, s, *Me*$_2$C), 0.87 (3H, t, *J*=7 Hz, *Me*CH_2); δ_C (100.6 MHz, $CDCl_3$) 208.0, 171.1, 158.1, 124.9, 81.3, 59.4, 47.3, 37.4, 30.0, 27.8, 21.1, 19.2, 13.7; HRMS (EI): M^+, found 224.1416, $C_{13}H_{20}O_3$ requires 224.1413.

3.2.8. 6-Acetoxy-6-benzyl-3,5-dimethyl-2-cyclohexen-1-one 2h. (1.47 g, 77%) as a colourless oil, R_f (EtOAc/hexane 1:5) 0.31; ν_{max} (neat) 3012, 2961, 1730, 1652, 1493 cm^{-1}; δ_H (400 MHz, $CDCl_3$) (only one isomer was isolated) 7.19–7.26 (3H, m, *Ph*), 7.09 (2H, d, *J*=6 Hz, *Ph*), 5.93 (1H, s, =C*H*), 3.58 (1H, d, *J*=14 Hz, PhCH_aH_b), 3.19 (1H, d, *J*=14 Hz, PhCH_aH_b), 2.80–2.83 (1H, m, MeC*H*), 2.44–2.50 (1H, dd, *J*=18, 5 Hz, CH_aH_b), 2.28–2.34 (1H, dd, *J*=18, 5 Hz, CH_aH_b), 2.05 (3H, s, *Me*CO_2), 1.93 (3H, s, =C*Me*), 0.95 (3H, d, *J*=7 Hz, *Me*CH); δ_C (100.6 MHz, $CDCl_3$) 194.5, 170.2, 159.1, 135.3, 130.4, 128.2, 126.9, 125.1, 85.8, 40.3, 37.6, 35.0, 24.2, 21.5, 15.0; *m*/*z* (EI) 274 (17), 273 (100), 214 (8), 213 (47); HRMS (EI) M^+, found 272.1401, $C_{17}H_{20}O_3$ requires 272.1413.

3.2.9. 5-Acetoxy-3,5-dimethyl-2-cyclopenten-1-one 2i. (0.85 g, 72 %) as a colourless oil, R_f (EtOAc/hexane 1:4) 0.17; ν_{max} (neat) 3018, 2400, 1735, 1672, 1521 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.75 (1H, s, =C*H*), 2.80 (1H, d, *J*=18 Hz, CH_aH_b), 2.32 (1H, d, *J*=18 Hz, CH_aH_b), 1.88 (3H, s, *Me*CO_2), 1.82 (3H, s, =C*Me*), 1.16 (3H, s, *Me*COAc); δ_C (100.6 MHz, $CDCl_3$) 205.4, 173.1, 170.2, 127.8, 81.4, 46.3,

30.1, 23.8, 21.3, 20.0; HRMS (EI) M^+, found 168.0782, $C_9H_{12}O_3$ requires 168.0786.

3.2.10. 5-Acetoxy-5-ethyl-3-methyl-2-cyclopenten-1-one 2j. (0.54 g, 42%) as a colourless oil, R_f (EtOAc/hexane 1:4) 0.35; ν_{max} (neat) 2254, 1764, 1709, 1462 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.88 (1H, s, =C*H*), 2.87 (1H, d, *J*= 18 Hz CH_aH_b), 2.51 (1H, d, *J*=18 Hz CH$_a$$H_b$), 2.07 (3H, s, *Me*$CO_2$), 1.99 (3H, s, =C*Me*), 1.55–1.75 (2H, m, MeCH_2), 0.84 (3H, t, *J*=7 Hz, *Me*CH_2); δ_C (100.6 MHz, $CDCl_3$) 205.4, 173.2, 170.3, 128.8, 84.2, 43.7, 30.0, 23.0, 21.3, 8.0; HRMS (EI) M^+, found 182.0942, $C_{10}H_{14}O_3$ requires 182.0943.

3.2.11. 5-Acetoxy-5-benzyl-3-methyl-2-cyclopenten-1-one 2k. (0.87 g, 51%) as a colourless oil, R_f (EtOAc/hexane 1:3) 0.31; ν_{max} (neat) 2254, 1732, 1704, 1469 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.02–7.24 (5H, m, *Ph*), 5.80 (1H, s, =C*H*), 2.70–2.77 (2H, 2d overlapped, *J*=18 Hz, PhCH_a-H_b), 2.20–2.25 (2H, 2d overlapped, *J*=14 Hz, CH_aH_b), 2.03 (3H, s, *Me*CO_2), 1.97 (3H, s, =C*Me*); δ_C (100.6 MHz, $CDCl_3$) 212.3, 178.5, 174.4, 139.2, 130.3, 129.8, 129.4, 128.6, 128.3, 126.2, 84.1, 38.4, 35.7, 20.1, 19.3; HRMS (EI) M^+, found 244.1102, $C_{15}H_{16}O_3$ requires 244.1100.

3.2.12. 5-Acetoxy-2,3,4,5-tetramethyl-2-cyclopenten-1-one 2l. (0.93 g, 68%) as a colourless oil, R_f (EtOAc/hexane 1:4) 0.34; ν_{max} (neat); 2268, 1740, 1715, 1478 cm^{-1}; δ_H (400 MHz, $CDCl_3$) (9:1 diastereomeric mixture) (major isomer) 2.73–2.75 (1H, m, MeC*H*), 1.68 (3H, s, *Me*CO_2), 1.63 (3H, s, *Me*$_\alpha$C=), 1.48 (3H, s, *Me*$_\beta$C=), 0.88 (3H, s, *Me*COAc), 0.82 (3H, d, *J*=8 Hz, *Me*CH); (minor isomer) 2.34–2.36 (1H, m, MeC*H*), 1.70 (3H, s, *Me*CO_2), 1.65 (3H, s, *Me*$_\alpha$C=), 1.48 (3H, s, *Me*$_\beta$C=), 1.04 (3H, s, *Me*COAc), 0.74 (3H, d, *J*=8 Hz, *Me*CH); δ_C (100.6 MHz, $CDCl_3$) (major isomer) 204.5, 169.8, 167.9, 133.0, 83.4, 45.4, 21.3, 19.4, 14.6, 11.9, 8.4; (minor isomer) 204.4, 170.1, 168.5, 132.5, 82.2, 49.6, 24.4, 21.1, 15.1, 12.8, 8.3; HRMS (EI) M^+, found 196.1099, $C_{11}H_{16}O_3$ requires 196.1100.

3.2.13. 2-Acetoxy-2-ethyl-indanone 6a. (0.37 g, 30%) as a colourless oil, R_f (EtOAc/hexane 1:4) 0.31; ν_{max} (neat) 3410, 3019, 1724, 1609, 1466, 1257 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.71 (1H, d, *J*=8 Hz, *Ar*), 7.53 (1H, t, *J*=8 Hz, *Ar*), 7.30–7.33 (2H, m, *Ar*), 3.35 (1H, d, *J*=17 Hz, CH_aH_b), 3.15 (1H, d, *J*=17 Hz, CH$_a$$H_b$), 2.02 (3H, s, *Me*$CO_2$), 1.75–1.86 (1H, m, MeC$H_aH_b$), 1.63–1.72 (1H, m, MeCH$_a$$H_b$), 0.87 (3H, t, *J*=7 Hz, *Me*CH_2); δ_C (100.6 MHz, $CDCl_3$) 202.8, 170.4, 149.8, 135.6, 135.3, 128.1, 126.2, 124.7, 85.1, 37.9, 30.1, 21.2, 8.0; *m/z* (EI) 220 (15), 219 (100), 160 (6), 159 (9); HRMS (EI) M^+, found 218.0937, $C_{13}H_{14}O_3$ requires 218.0943.

3.2.14. 2-Acetoxy-2-acetyl-1-tetralone 6b. (0.79 g, 46%) as a colourless oil, R_f (EtOAc/hexane 1:4) 0.41; ν_{max} (neat) 2254, 1794, 1709, 1662, 1363, 1095, 910, 753, 715 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.58 (1H, d, *J*=8 Hz, *Ar*), 8.20 (1H, d, *J*=8 Hz, *Ar*), 7.35–7.65 (2H, m, *Ar*), 2.79–3.02 (4H, m, CH_2CH_2), 2.26 (3H, s, *Me*CO_2), 2.23 (3H, s, *Me*CO); δ_C (100.6 MHz, $CDCl_3$) 210.3, 204.2, 198.7, 162.6, 143.6, 134.4, 129.0, 127.5, 112.5, 68.4, 32.5, 30.1, 26.3, 25.1; *m/z* (EI) 199 (42), 190 (14), 189 (100), 147 (17); HRMS (EI) M^+, found 246.0902, $C_{14}H_{14}O_4$ requires 246.0892.

3.2.15. 2-Acetoxy-2-methyl-tetralone 6c. (0.86 g, 56%) as a white solid, mp 258–260°C; R_f (EtOAc/hexane 1:3) 0.50; ν_{max} (neat); δ_H (400 MHz, $CDCl_3$) 8.00 (1H, d, *J*=8 Hz, *Ar*), 7.41 (1H, t, *J*=8 Hz, *Ar*), 7.26 (1H, t, *J*=8 Hz, *Ar*), 7.15 (1H, d, *J*=8 Hz, *Ar*), 2.89–2.99 (3H, m, CH_2CH_aH$_b$CMeOAc), 2.00 (3H, s, *Me*CO_2), 1.97–1.99 (1H, m, CH$_2$CH$_a$$H_b$CMeOAc), 1.47 (3H, s, *Me*COAc); δ_C (100.6 MHz, $CDCl_3$) 195.2, 170.1, 142.4, 134.0, 131.6, 129.0, 128.8, 127.4, 81.3, 33.4, 27.3, 22.0, 21.7; HRMS (EI) M^+, found 218.0941, $C_{13}H_{14}O_3$ requires 218.0943.

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