Supporting Information

Dearomatization of naphthols using oxy-allyl cations: efficient construction of α -all-carbon quaternary center-containing 2-(2-oxocycloalkyl)cycloalkyl diketones

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Experimental procedures:

1. General Information

All reactions under standard conditions were carried out under argon atmosphere and were monitored by thin layer chromatography (TLC) on gel F_{254} plates. Solvents were dried by standard methods and distilled under argon. ¹H and ¹³C NMR spectra were recorded on Bruker AX-400 MHz instruments using CDCl₃ as solvent. Chemical shifts of ¹H NMR were recorded in parts per million (ppm, δ) relative to tetramethylsilane ($\delta = 0.00$ ppm) with the solvent resonance as an internal standard (CDCl₃: $\delta = 7.26$ ppm). NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, sept = septet, m = multiplet, br = broad signal. High-resolution mass spectral analysis (HRMS) data were measured on a VG Auto Spec-3000 spectrometer by means of the ESI technique. Column chromatography was performed on silica gel (200–300 mesh). Melting point (m.p.) was measured on a microscopic melting point apparatus.

Compounds **1a-1q**,¹ **2d-2f**,² **2h**² **4a**³ and **4d**³ were prepared according to literature procedures. Compounds **2a**, **2b**, **2c** and **2g** are commercial available.

2. Experimental Details for 1p

Compound **1p** was prepared according to literature procedures.^{1d}



Offwhite amorphous solid: ¹**H NMR** (400 MHz, CDCl₃, ppm): δ 8.01-7.98 (m, 2H), 7.78-7.72 (m, 4H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 8.8 Hz, 1H), 6.16-6.07 (m, 1H), 5.17-5.09 (m, 3H), 3.87 (d, *J* = 5.6 Hz, 2H); ¹³**C NMR** (100 MHz, CDCl₃, ppm): δ 151.3 (C), 140.9 (C), 135.8 (C), 135.6 (CH), 132.4 (C), 129.7 (C), 128.8 (CH), 128.6 (CH), 127.2 (CH), 127.1 (CH), 126.4 (CH), 126.1 (CH), 123.6 (CH), 118.4 (CH), 116.7 (C), 116.0 (CH₂), 29.3 (CH₂); **HRMS** (ESI) calcd for C₁₉H₁₇O₁ [M +H]⁺: 261.1274, found 261.1275.

2. Experimental Details for 4b and 4c

Compound **2b** and **2c** was prepared according to literature procedures.³



4-ethoxy-2-methylnaphthalen-1-yl acetate

Offwhite amorphous solid: ¹**H** NMR (400 MHz, CDCl₃, ppm): δ 8.28 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.53 (td, *J* = 6.8, 1.2 Hz, 1H), 7.46 (td, *J* = 8.0, 1.2 Hz, 1H), 6.65 (s, 1H), 4.19 (q, *J* = 6.8 Hz, 2H), 2.48 (s, 3H), 2.33 (s, 3H),1.55 (t, *J* = 6.8 Hz, 3H); ¹³**C** NMR (100 MHz, CDCl₃, ppm): δ 169.5 (C), 152.5 (C), 137.4 (C), 127.6 (C), 127.0 (CH), 126.1 (C), 125.0 (C), 124.6 (CH), 122.4 (CH), 120.3 (CH), 107.0 (CH), 63.8 (CH₂), 20.5 (CH₃), 16.8 (CH₃), 14.8 (CH₂); **HRMS** (ESI) calcd for C₁₅H₁₆O₃Na₁ [M +Na]⁺: 267.0992, found 267.0991.

4-ethoxy-2-methylnaphthalen-1-ol (4b)

Offwhite amorphous solid: ¹**H NMR** (400 MHz, CDCl₃, ppm): δ 8.22 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 6.59 (s, 1H), 4.69-4.12 (m, 1H), 4.15 (q, *J* = 6.8 Hz, 2H), 2.39 (s, 3H), 1.53 (t, *J* = 6.8 Hz, 1H); ¹³**C NMR** (100 MHz, CDCl₃, ppm): δ 148.7 (C), 142.0 (C), 126.0 (CH), 125.4 (C),

125.2 (C), 124.6 (CH), 122.1 (CH), 120.7 (CH), 116.3 (C), 108.2 (CH), 64.2 (CH₂), 16.2 (CH₃),15.0 (CH₃);; **HRMS** (ESI) calcd for $C_{13}H_{15}O_2$ [M +H]⁺: 203.1067, found 203.1067.



4-(benzyloxy)-2-methylnaphthalen-1-yl acetate

Offwhite amorphous solid: ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.29 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.51-7.48 (m, 3H), 7.43-7.39 (m, 3H), 7.36-7.20 (m, 1H), 6.71 (s, 1H), 5.18 (s, 2H), 2.44 (s, 3H), 2.29 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 169.4 (C), 152.2 (C), 137.8 (C), 136.9 (C), 128.5 (CH), 127.9 (CH), 127.7 (C), 127.4 (CH), 126.1 (C), 125.0 (C), 124.8 (CH), 122.5 (CH), 120.4 (CH), 107.5 (CH), 70.2 (CH₂), 20.5 (CH₃), 16.8 (CH₃); HRMS (ESI) calcd for C₂₀H₁₈O₃Na₁ [M +Na]⁺: 329.1148, found 329.1149.

4-(benzyloxy)-2-methylnaphthalen-1-ol (4c)

Offwhite amorphous solid: ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.29 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.56-7.50 (m, 3H), 7.48-7.42 (m, 3H), 7.39-7.35 (m, 1H), 6.69 (s, 1H), 5.20 (s, 2H), 4.73 (s, 1H), 2.40 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 148.4 (C), 142.3 (C), 137.4 (C), 128.5 (CH), 127.8 (CH), 127.4 (CH), 126.0 (CH), 125.4 (C), 125.2 (C), 124.8 (CH), 122.1 (CH), 120.7 (CH), 116.1 (C), 108.6 (CH), 70.5 (CH₂), 16.1 (CH₃); HRMS (ESI) calcd for C₁₈H₁₇O₂ [M +H]⁺: 265.1223, found 265.1223.

4. Experimental Details for 3

Typical Procedure for dearomatization of naphthols using oxy-allyl cations: efficient Construction of α -all-carbon quaternary center containing 2-(2-oxocycloalkyl)cycloalkyl diketones



Substrate **1** or **4** (0.1 mmol) and Na_2CO_3 were dissolved in HFIP (1 mL) under argon atmosphere. After which 2-haloketone **2** was added, the mixture was stirred at room temperature or 59 °C. The reaction system was monitored by TLC until **1** or **4** disappeared completely. After which, the reaction mixture was concentrated under vacuum. Purification of the residue by column chromatography on silica gel (eluting with ethyl acetate/petroleum ether 20:1-10:1) provided **3**.

1,3-dimethyl-1-(2-oxocyclopentyl)naphthalen-2(1H)-one (3a):



Light yellow oil: ¹**H NMR** (400 MHz, CDCl₃, ppm): δ 7.34-7.33 (m, 2H), 7.26-7.24 (m, 3H), 2.69 (t, *J* = 8.0 Hz, 1H), 2.67-2.49 (m, 1H), 2.25 (dd, *J* = 17.6, 7.6 Hz, 1H), 2.00 (s, 3H), 1.95-1.80 (m, 2H), 1.73-1.58 (m, 4H),

1.41-1.36 (m, 1H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 218.4 (C), 203.9 (C), 145.1 (C), 141.7 (CH),132.4 (C), 129.8 (C), 129.1 (CH), 128.9 (CH), 126.8 (CH), 126.0 (CH), 56.2 (C), 53.2 (CH), 39.9 (CH₂), 27.8 (CH₂), 27.7 (CH₃), 20.6 (CH₂), 15.8 (CH₃); **HRMS** (ESI) calcd for C₁₇H₁₈O₂Na₁ [M +Na]⁺: 277.1199, found 277.1199.

3-ethyl-1-methyl-1-(2-oxocyclopentyl)naphthalen-2(1H)-one (**3b**):



Light yellow oil: ¹**H NMR** (400 MHz, CDCl₃, ppm): δ 7.37-7.30 (m, 2H), 7.28-7.24 (m, 3H), 7.18 (s, 1H), 2.68 (t, J = 9.2 Hz, 1H), 2.61-2.52 (m, 1H), 2.49-2.33 (m, 1H), 2.26 (dd, J = 16.0, 8.0 Hz, 1H), 1.69-1.58 (m, 1H), 1.40-1.30 (m, 1H), 1.14 (t, J = 7.6 Hz, 3H); ¹³**C NMR** (100 MHz, CDCl₃, ppm): δ 218.5 (C), 203.5 (C), 145.0 (C), 139.8 (CH), 137.9 (C), 129.9 (C), 129.1 (CH), 129.1 (CH), 126.8 (CH), 125.9 (CH), 56.6 (C), 52.9 (CH), 40.0 (CH₂), 27.9 (CH₂), 27.6 (CH₃), 22.3 (CH₂), 20.6 (CH₂), 12.5 (CH₃); **HRMS** (ESI) calcd for C₁₈H₂₀O₂Na₁ [M+Na]⁺: 291.1356, found 291.1356.

3-allyl-1-methyl-1-(2-oxocyclopentyl)naphthalen-2(1H)-one (3c):



Offwhite amorphous solid; ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.36-7.33 (m, 2H),7.30-7.25 (m, 2H), 7.21 (s, 1H), 5.94-5.87 (m, 1H), 5.17-5.12 (m, 2H), 3.25-3.04 (m 2H), 2.70 (t, *J* = 9.2 Hz, 1H), 2.58-2.49 (m, 1H), 2.25 (dd, *J* = 17.6, 7.6 Hz, 1H), 1.93-1.80 (m, 2H), 1.65-1.59 (m, 4H), 1.39-1.33 (m, 1H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 218.3 (C), 203.0 (C), 145.1 (C), 141.5 (CH), 134.9 (CH), 134.5 (C), 129.7 (C), 129.3 (CH), 129.3 (CH), 126.9 (CH), 126.0 (CH), 117.1 (CH₂), 56.4 (C), 53.2 (CH), 39.9 (CH₂), 33.2 (CH₂), 27.8 (CH₂), 27.7 (CH₃), 20.6 (CH₂); HRMS (ESI) calcd for C₁₉H₂₀O₂Na₁ [M+Na]⁺: 303.1356, found 303.1353.

3-chloro-1-methyl-1-(2-oxocyclopentyl)naphthalen-2(1H)-one (3d):



Colorless oil: ¹**H** NMR (400 MHz, CDCl₃, ppm): δ 7.66 (s, 1H), 7.46-7.37 (m, 2H), 7.34-7.31 (m, 2H), 2.79 (t, *J* = 5.6 Hz, 1H), 2.51-2.41 (m, 1H), 2.26 (dd, *J* = 18.0, 5.6 Hz, 1H), 2.05-1.91 (m, 1H), 1.90-1.84 (m, 1H), 1.71-1.60 (m, 4H), 1.50-1.40 (m, 1H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 217.3 (C), 196.6 (C), 144.4 (C), 142.6 (CH), 130.4 (CH), 129.6 (CH), 129.5 (C), 128.8 (C), 127.4 (CH), 126.5 (CH), 57.4 (C), 54.4 (CH), 39.6 (CH₂), 27.6 (CH₂), 27.6 (CH₃), 20.6 (CH₂); **HRMS** (ESI) calcd for C₁₆H₁₅ClO₂Na₁ [M+Na]⁺: 297.0653, found 297.0652.

1-methyl-1-(2-oxocyclopentyl)-3-phenylnaphthalen-2(1H)-one (3e):



Light yellow oil: ¹**H NMR** (400 MHz, CDCl₃, ppm): δ 7.51-7.43 (m, 3H), 7.41-7.30 (m, 7H), 2.74 (t, *J* = 9.6 Hz, 1H), 2.70-2.60 (m, 1H), 2.33-2.19 (m, 2H), 2.02-1.95 (m, 1H), 1.90-1.84 (m, 1H), 1.81 (s, 3H), 1.71-1.62 (m, 1H), 1.50-1.40 (m, 1H); ¹³**C NMR** (100 MHz, CDCl₃, ppm): δ 218.6 (C), 202.6 (C), 145.4 (C), 141.6 (CH), 135.4 (C), 135.2 (C), 130.1 (CH), 129.9 (CH), 129.8 (CH), 128.5 (CH), 128.3 (CH), 128.3 (CH), 127.1 (CH), 126.0 (CH), 58.1 (C), 52.4 (CH), 39.9 (CH₂), 28.2 (CH₂), 27.6 (CH₃), 20.7 (CH₂); **HRMS** (ESI) calcd for C₂₂H₂₀O₂Na₁ [M+Na]⁺: 339.1356, found 339.1358.

1-methyl-1-(2-oxocyclopentyl)naphthalen-2(1H)-one (3f):



Light yellow oil: ¹**H** NMR (400 MHz, CDCl₃, ppm): δ 7.44-7.37 (m, 3H), 7.32-7.27 (m, 2H), 6.17 (d, *J* = 10.0 Hz, 1H), 2.70 (t, *J* = 8.0 Hz, 1H), 2.56-2.46 (m, 1H), 2.49 (dd, *J* = 16.0, 8.0 Hz, 1H), 1.94-1.81 (m, 2H), 1.67 (s, 3H), 1.63-1.55 (m, 1H), 1.44-1.34 (m, 1H); ¹³**C** NMR (100 MHz, CDCl₃, ppm): δ 218.2 (C), 203.7 (C), 145.8 (C), 145.2 (CH), 130.3 (CH), 129.8 (CH), 129.3 (C), 126.9 (CH), 126.3 (CH), 125.0 (CH), 56.3 (C), 53.3 (CH), 39.9 (CH₂), 27.8 (CH₂), 27.5 (CH₃), 20.7 (CH₂); **HRMS** (ESI) calcd for C₁₆H₁₆O₂Na₁ [M+Na]⁺: 263.1043, found 263.1043.

1-ethyl-3-methyl-1-(2-oxocyclopentyl)naphthalen-2(1H)-one (**3g**):



Light yellow oil: ¹**H NMR** (400 MHz, CDCl₃, ppm): δ 7.37-7.29 (m, 2H), 7.28-7.26 (m, 3H), 2.74 (t, *J* = 8.8 Hz, 1H), 2.53-2.44 (m, 1H), 2.42-2.33 (m, 1H), 2.24-2.15 (m, 1H), 2.11-2.02 (m, 1H), 1.99 (s, 3H), 1.93-1.85 (m, 1H), 1.84-1.75 (m, 1H), 1.68-1.56 (m, 2H), 1.48-1.38 (m, 1H), 0.52 (t, *J* = 7.6 Hz, 3H); ¹³**C NMR** (100 MHz, CDCl₃, ppm): δ 217.9 (C), 204.5 (C), 142.9 (C), 142.2 (CH), 133.9 (C), 131.6 (C), 128.8 (CH), 128.7 (CH), 126.9 (CH), 126.6 (CH), 59.9 (C), 54.6 (CH), 39.9 (CH₂), 34.2 (CH₂), 27.4 (CH₂), 20.8 (CH₂), 15.7 (CH₃), 8.5 (CH₃); **HRMS** (ESI) calcd for C₁₈H₂₀O₂Na₁ [M+Na]⁺: 291.1356, found 291.1355.

1,3-diethyl-1-(2-oxocyclopentyl)naphthalen-2(1H)-one (3h):



Light yellow oil: ¹**H NMR** (400 MHz, CDCl₃, ppm): δ 7.37-7.25 (m, 4H), 7.20 (s, 1H), 2.73 (t, *J* = 5.6 Hz, 1H), 2.53-2.33 (m, 4H), 2.24-2.17 (m, 1H), 2.12-2.03 (m, 1H), 1.92-1.76 (m, 2H), 1.67-1.55 (m, 1H), 1.45-1.35 (m, 1H), 1.15 (t, *J* = 7.6 Hz, 3H), 0.53 (t, *J* = 7.6 Hz, 3H); ¹³**C NMR** (100 MHz, CDCl₃, ppm): δ 217.9 (C), 204.0 (C), 142.9 (C), 140.4 (CH), 139.3 (C), 131.6 (C), 128.9 (CH), 128.8 (CH), 126.9 (CH), 126.5 (CH), 60.2 (C), 54.2 (CH), 40.0 (CH₂), 34.2 (CH₂), 27.4 (CH₂), 22.4 (CH₂), 20.8 (CH₂), 12.6 (CH₃), 8.5 (CH₃); **HRMS** (ESI) calcd for C₁₉H₂₃O₂ [M+H]⁺: 283.1693, found 283.1693.

1-ethyl-1-(2-oxocyclopentyl)naphthalen-2(1H)-one (3i):



Light yellow oil: ¹**H NMR** (400 MHz, CDCl₃, ppm): δ 7.46-7.31 (m, 5H), 6.25 (d, *J* = 10.0 Hz, 1H), 2.75 (t, *J* = 9.2 Hz, 1H), 2.58-2.49 (m, 1H), 2.41-2.35 (m, 1H), 2.28-2.12 (m, 1H), 2.13-2.04 (m, 1H), 1.93-1.79 (m, 2H), 1.68-1.56 (m, 1H), 1.51-1.41 (m, 1H), 0.55 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 217.7 (C), 204.3 (C), 145.7 (CH), 143.7 (C), 131.0 (C), 130.0 (CH), 129.7 (CH), 127.0 (CH), 126.8 (CH), 126.6 (CH), 60.0 (C), 54.8 (CH), 39.9 (CH₂), 34.2 (CH₂), 27.3 (CH₂), 20.8 (CH₂), 8.5 (CH₃); **HRMS** (ESI) calcd for C₁₇H₁₈O₂Na₁ [M +Na]⁺: 277.1199, found 277.1199.

1-butyl-3-methyl-1-(2-oxocyclopentyl)naphthalen-2(1H)-one (3j):



Light yellow oil: ¹**H NMR** (400 MHz, CDCl₃, ppm): δ 7.36-7.32 (m, 2H), 7.30-7.25 (m, 3H), 2.75 (t, *J* = 9.2 Hz, 1H), 2.47-2.38 (m, 1H), 2.36-2.28 (m, 1H), 2.22-2.16 (m, 1H), 2.05-1.97 (m, 4H), 1.93-1.85 (m, 1H), 1.83-1.74 (m, 1H), 1.68-1.55 (m, 1H), 1.49-1.39 (m, 1H), 1.19-1.05 (m, 2H), 0.88-0.75 (m, 2H), 0.71 (t, *J* = 7.2 Hz, 3H); ¹³**C NMR** (100 MHz, CDCl₃, ppm): δ 217.7 (C), 204.3 (C), 143.3 (C), 142.1 (CH), 133.8 (C), 131.4 (C), 128.8 (CH), 128.7 (CH), 126.8 (CH), 126.5 (CH), 59.2 (C), 55.2 (CH), 40.8 (CH₂), 39.8 (CH₂), 27.2 (CH₂), 26.1 (CH₂), 22.9 (CH₂), 20.8 (CH₂), 15.7 (CH₃), 13.8 (CH₃); **HRMS** (ESI) calcd for C₂₀H₂4O₂Na₁ [M+Na]⁺: 319.1669, found 319.1668.

1-hexyl-3-methyl-1-(2-oxocyclopentyl)naphthalen-2(1H)-one (3k):



Light yellow oil: ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.36-7.31 (m, 2H), 7.29-7.25 (m, 3H), 2.75 (t, *J* = 8.0 Hz, 1H), 2.46-2.38 (m, 1H), 2.36-2.29 (m, 1H), 2.22-2.15 (m, 1H), 2.04-1.97 (m, 4H), 1.93-1.85 (m, 1H), 1.83-1.74 (m, 1H), 1.67-1.57 (m, 1H), 1.48-1.38 (m, 1H), 1.15-1.00 (m, 6H), 0.86-0.75 (m, 5H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 217.7 (C), 204.4 (C), 143.3 (C), 142.1 (CH), 133.8 (C), 131.4 (C), 138.7 (CH), 128.7 (CH), 126.8 (CH), 126.5 (CH), 59.2 (C), 55.2 (CH), 41.1 (CH₂), 39.8 (CH₂), 31.5 (CH₂), 29.5 (CH₂), 27.2 (CH₂), 23.9 (CH₂), 22.5 (CH₃), 20.8 (CH₂), 15.8 (CH₂), 14.0 (CH₃); HRMS (ESI) calcd for C₂₂H₂₈O₂Na₁ [M+Na]⁺: 347.1982, found 347.1983.

(E)-ethyl 3-(2-oxo-1-(2-oxocyclopentyl)-1,2-dihydronaphthalen-1-yl)acrylate (31):

O CO2Et 0 31

Offwhite amorphous solid: ¹**H NMR** (400 MHz, CDCl₃, ppm): δ 7. 45 (d, *J* = 10.0 Hz, 1H), 7.43-7.30 (m, 6H), 6.12 (d, *J* = 10.0 Hz, 1H), 5.36 (d, *J* = 15.6 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.26 (dd, *J* = 10.4, 8.4 Hz, 1H), 2.31

(dd, J = 18.0, 6.8, 1H), 2.09-1.95 (m, 2H), 1.90-1.84 (m, 1H), 1.77-1.65 (m, 2H), 1.24 (t, J = 7.2 Hz, 3H); ¹³**C NMR** (100 MHz, CDCl₃, ppm): δ 218.1 (C), 198.6 (C), 165.8 (C), 149.7 (CH), 145.9 (CH), 140.8 (CH), 130.7 (C), 130.5 (CH), 130.3 (CH), 128.7 (CH), 128.0 (CH), 124.7 (CH), 122.2 (CH), 60.5 (CH), 58.8 (C), 58.3 (CH₂), 39.2 (CH₂), 26.2 (CH₂), 20.5 (CH₂), 14.2 (CH₃); **HRMS** (ESI) calcd for C₂₀H₂₀O₄Na₁ [M+Na]⁺: 347.1254, found 347.1254.

1-allyl-1-(2-oxocyclopentyl)naphthalen-2(1H)-one (**3m**):

White solid: **m.p.** 119-121 °C; ¹**H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.44-7.40 (m, 2H), 7.37-7.28 (m, 3H), 6.18 (d, J = 10.0 Hz, 1H), 5.36-5.26 (m, 1H), 4.85 (d, J = 8.0 Hz, 1H), 4.82 (s, 1H), 3.10 (dd, J = 13.2, 8.0 Hz, 1H), 2.89 (dd, J = 13.2, 6.8 Hz, 1H), 2.74 (t, J = 9.2 Hz, 1H), 2.50-2.40 (m, 1H), 2.28-2.22 (m, 1H), 1.92-1.80 (m, 2H), 1.68-1.53 (m, 2H), 1.47-1.37 (m, 1H); ¹³C **NMR** (100 MHz, $CDCl_3$, ppm): δ 217.7 (C), 203.5 (C), 145.6 (CH), 143.1 (C), 132.1 (CH), 130.6 (C), 129.8 (CH), 129.7 (CH), 127.1 (CH), 127.1 (CH), 126.1 (C), 119.0 (CH₂), 60.0 (C), 53.2 (CH), 44.8 (CH₂), 40.1 (CH₂), 27.4 (CH₂), 20.8 (CH₂); **HRMS** (ESI) calcd for $C_{18}H_{18}O_2Na_1$ [M+Na]⁺: 289.1199, found 289.1200.

1-allyl-6-methoxy-1-(2-oxocyclopentyl)naphthalen-2(1H)-one (3n):



Colorless oil: ¹**H** NMR (400 MHz, CDCl₃, ppm): δ 7. 36 (d, *J* = 10.0 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 6.83 (s, 1H), 6.19 (d, *J* = 9.6 Hz, 1H), 5.36-5.26 (m, 1H), 4.86 (d, *J* = 10.8 Hz, 1H), 4.82 (s, 1H), 3.85 (s, 3H), 3.07 (dd, *J* = 13.2, 8.0 Hz, 1H), 2.84 (dd, *J* = 13.2, 6.8 Hz, 1H), 2.72 (t, *J* = 9.6 Hz, 1H), 2.46-2.37 (m, 1H), 2.26-2.17 (m, 1H), 1.68-1.56 (m, 1H), 1.48-1.38 (m, 1H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 217.8 (C), 203.8 (C), 158.2 (C), 145.4 (C), 135.0 (C), 132.2 (CH), 131.6 (C), 128.3 (CH), 126.6 (CH), 118.9 (CH₂), 115.7 (CH), 114.2 (CH), 59.3 (C), 55.4 (CH), 53.7 (CH₃), 44.9 (CH₂), 40.1 (CH₂), 27.3 (CH₂), 20.8 (CH₂); **HRMS** (ESI) calcd for C₁₉H₂₀O₃Na₁ [M+Na]⁺: 319.1305, found 319.1305.

1-allyl-6-bromo-1-(2-oxocyclopentyl)naphthalen-2(1H)-one (30):



Light yellow oil: ¹**H NMR** (400 MHz, CDCl₃, ppm): δ 7. 52 (dd, J = 8.0, 1.6 Hz, 1H), 7.47 (d, J = 1.6 Hz, 1H), 7.33 (d, J = 10.0 Hz, 1H), 7.23 (d, J = 8.4 Hz, 1H), 6.22 (d, J = 10.0 Hz, 1H), 5.37-5.26 (m, 1H), 4.87 (s, 1H), 4.83 (d, J = 9.2 Hz, 1H), 3.05 (dd, J = 13.2, 7.6 Hz, 1H), 2.86 (dd, J = 13.2, 7.2 Hz, 1H), 2.73 (t, J = 10.4 Hz, 1H), 2.46-2.39 (m, 1H), 2.28-2.17 (m, 1H), 1.94-1.83 (m, 2H), 1.70-1.59 (m, 1H), 1.48-1.38 (m, 1H); ¹³**C NMR** (100 MHz, CDCl₃, ppm): δ 217.2 (C), 202.8 (C), 143.9 (C), 141.7 (C), 132.5 (CH), 132.4 (CH), 132.2 (CH), 131.7 (CH), 128.8 (CH), 127.2 (CH), 120.9 (C), 119.5 (CH₂), 59.6 (C), 53.3 (CH), 44.6 (CH₂), 39.9 (CH₂), 27.3 (CH₂), 20.8 (CH₂); **HRMS** (ESI) calcd for C₁₈H₁₇Br₁O₂Na₁ [M+Na]⁺: 367.0304, found 367.0305.

1-allyl-1-(2-oxocyclopentyl)-6-phenylnaphthalen-2(1H)-one (**3p**):



Colorless oil: ¹**H** NMR (400 MHz, CDCl₃, ppm): δ 7.63-7.61 (m, 3H), 7.54 (d, *J* = 1.6 Hz, 1H), 7.49-7.39 (m, 5H), 6.23 (d, *J* = 10.0 Hz, 1H), 5.40-5.34 (m, 1H), 4.91-4.85 (m, 1H), 3.12 (dd, *J* = 13.2, 7.6 Hz, 1H), 2.93 (dd, *J* = 13.2, 6.8 Hz, 1H), 2.79 (t, *J* = 9.2 Hz, 1H), 2.50-2.41 (m, 1H), 2.26 (ddd, *J* = 17.6, 8.0, 1.2 Hz, 1H), 1.98-1.82 (m, 2H), 1.70-1.58 (m, 1H), 1.53-1.43 (m, 1H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 217.8 (C), 203.5 (C), 145.6 (CH), 141.9 (CH), 140.0 (C), 139.6 (C), 132.1 (CH), 131.0 (C), 129.0 (CH), 128.4 (CH), 128.2 (CH), 127.8 (CH), 127.7 (CH), 127.0 (CH), 126.5 (CH), 119.2 (CH₂), 59.8 (C), 53.4 (CH), 44.8 (CH₂), 40.1 (CH₂), 27.4 (CH₂), 20.8 (CH₂); HRMS (ESI) calcd for C₂₄H₂₂O₂Na₁ [M+Na]⁺: 365.1512, found 365.1511.

1-allyl-7-methoxy-1-(2-oxocyclopentyl)naphthalen-2(1H)-one (**3q**):



Light yellow oil: ¹**H NMR** (400 MHz, CDCl₃, ppm): δ 7. 37 (d, *J* = 9.6 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 6.89 (s, 1H), 6.82 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.06 (d, *J* = 10.0 Hz, 1H), 5.40-5.29 (m, 1H), 4.89-4.84 (m, 1H), 3.86 (s, 3H), 3.10 (dd, *J* = 12.8, 7.6 Hz, 1H), 2.85 (dd, *J* = 13.6, 6.8 Hz, 1H), 2.67 (t, *J* = 9.6 Hz, 1H), 2.52-2.42 (m, 1H), 2.27-2.21 (m, 1H), 1.94-1.80 (m, 2H), 1.68-1.56 (m, 1H), 1.47-1.37 (m, 1H); ¹³C **NMR** (100 MHz, CDCl₃, ppm): δ 217.8 (C), 203.3 (C), 161.2 (C), 145.6 (CH), 145.5 (C), 132.2 (CH), 131.2 (CH), 123.9 (C), 123.6 (CH), 119.0 (CH₂), 114.3 (CH), 111.4 (CH), 60.2 (C), 55.5 (CH₃), 53.2 (CH), 45.1 (CH₂), 40.1 (CH₂), 27.4 (CH₂), 20.8 (CH₂); **HRMS** (ESI) calcd for C₁₉H₂₀O₃Na₁ [M+Na]⁺: 319.1305, found 319.1305.

1,3-dimethyl-1-(2-oxocyclohexyl)naphthalen-2(1H)-one (**3r**):



Light yellow oil: ¹**H** NMR (400 MHz, CDCl₃, ppm): δ 7.31-7.18 (m, 5H), 3.32 (dd, *J* = 12.0, 6.4 Hz, 1H), 2.52-2.44 (m, 2H), 2.27-2.23 (m, 1H), 2.10-1.90 (m, 5H), 1.71-1.59 (m, 2H), 1.30 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 209.8 (C), 204.2 (C), 147.0 (C), 140.3 (CH),132.8 (C), 130.3 (C), 128.8 (CH), 128.4 (CH), 126.3 (CH), 125.2 (CH), 63.5 (CH), 49.1 (C), 42.5 (CH₂), 30.0 (CH₂), 27.1 (CH₂), 26.8 (CH₃), 26.2 (CH₂), 16.1 (CH₃); **HRMS** (ESI) calcd for C₁₈H₂₀O₂Na₁ [M+Na]⁺: 291.1356, found 291.1355.

 $\label{eq:2.1} 3-ethyl-1-methyl-1-(2-oxocyclohexyl)naphthalen-2(1H)-one~(3s):$



Light yellow oil: ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.37-7.19 (m, 5H), 3.32 (t, *J* = 12.0, 6.0 Hz, 1H), 2.52-2.41

(m, 4H), 2.27-2.23 (m, 1H), 2.19-2.11 (m, 1H), 2.03-1.93 (m, 2H), 1.71-1.60 (m, 2H), 1.30 (s, 3H), 1.17 (t, J = 7.6 Hz, 3H); ¹³**C NMR** (100 MHz, CDCl₃, ppm): δ 209.8 (C), 203.7 (C), 146.8 (C), 138.5 (CH), 138.1 (C), 130.3 (C), 129.0 (CH), 128.4 (CH), 126.3 (CH), 125.1 (CH), 63.2 (CH), 49.2 (C), 42.5 (CH₂), 30.0 (CH₂), 27.1 (CH₂), 26.6 (CH₃), 26.2 (CH₂), 22.2 (CH₂), 12.4 (CH₃); **HRMS** (ESI) calcd for C₁₉H₂₂O₂Na₁ [M+Na]⁺: 305.1512, found 305.1512.

3-chloro-1-methyl-1-(2-oxocyclohexyl)naphthalen-2(1H)-one (3t):

White amorphous powder: ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.67 (s, 1H), 7.36-7.23 (m, 4H), 3.35 (dd, J = 11.6, 6.8 Hz, 1H), 2.57-2.48 (m, 2H), 2.28-2.25 (m, 1H), 2.18-2.02 (m, 3H), 1.73-1.61 (m, 2H), 1.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 209.4 (C), 196.5 (C), 146.7 (C), 140.8 (CH), 130.7 (C), 129.7 (CH), 129.3 (CH), 129.3 (C), 126.8 (CH), 125.4 (CH), 64.5 (CH), 51.0 (C), 42.3 (CH₂), 29.8 (CH₂), 27.1 (CH₂), 26.8 (CH₃), 26.2 (CH₂); HRMS (ESI) calcd for C₁₇H₁₇Cl₁O₂Na₁ [M+Na]⁺: 311.0809, found 311.0809.

1-methyl-1-(2-oxocyclohexyl)-3-phenylnaphthalen-2(1H)-one (**3u**):



White amorphous powder: ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.54-7.50 (m, 3H), 7.43-7.30 (m, 7H), 7.28-7.23 (M, 1H), 3.37 (dd, *J* = 12.4, 6.0 Hz, 1H), 2.58-2.43 (m, 2H), 2.30-2.26 (m, 1H), 2.23-2.13 (m, 1H), 2.04-1.96 (m, 2H), 1.69-1.64 (m, 2H), 1.59 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 209.7 (C), 202.5 (C), 147.4 (C), 141.3 (CH), 136.4 (C), 135.9 (C), 130.2 (C), 130.0 (CH), 129.2 (CH), 129.0 (CH), 128.9 (CH), 128.0 (CH), 127.8 (CH), 126.6 (CH), 125.3 (CH), 63.4 (CH), 50.1 (C), 42.5 (CH₂), 30.1 (CH₂), 27.1 (CH₂), 26.5 (CH₃), 26.3 (CH₂); **HRMS** (ESI) calcd for C₂₃H₂₂O₂Na₁ [M+Na]⁺: 353.1512, found 353.1513.

1-methyl-1-(2-oxocyclohexyl)naphthalen-2(1H)-one (**3v**):



Light yellow oil: ¹**H NMR** (400 MHz, CDCl₃, ppm): δ 7.54 (d, *J* = 9.6 Hz, 1H), 7.36-7.31 (m, 3H), 7.26-7.21 (m, 1H), 6.20 (d, *J* = 9.6 Hz, 1H), 3.33 (dd, *J* = 11.2, 6.8 Hz, 1H), 2.51-2.42 (m, 2H), 2.28-2.27 (m, 1H), 2.25-2.08 (m, 1H), 2.04-1.99 (m, 2H), 1.70-1.61 (m, 2H), 1.33 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 209.7 (C), 204.2 (C), 147.6 (C), 143.7 (CH), 129.7 (CH), 129.6 (C), 129.6 (CH), 126.4 (CH), 126.0 (CH), 125.4 (CH), 63.3 (CH), 49.4 (C), 42.5 (CH₂), 30.0 (CH₂), 27.1 (CH₂), 26.6 (CH₃), 26.2 (CH₂); **HRMS** (ESI) calcd for C₁₇H₁₈O₂Na₁ [M +Na]⁺: 277.1199, found 277.1199.

1-ethyl-3-methyl-1-(2-oxocyclohexyl)naphthalen-2(1H)-one (3w):



Light yellow oil: ¹**H** NMR (400 MHz, CDCl₃, ppm): δ 7.28-7.19 (m, 5H), 3.31 (dd, *J* = 12.8, 5.2 Hz, 1H), 2.49-2.32 (m, 2H), 2.23-2.08 (m, 3H), 2.05-1.97 (m, 5H), 1.81-1.72 (m, 1H), 1.69-1.58 (m, 2H), 0.37 (t *J* = 7.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): 210.0 (C), 204.5 (C), 145.1 (C), 140.4 (CH), 134.6 (C), 132.4 (C), 128.4 (CH), 128.3 (CH), 126.3 (CH), 125.4 (CH), 64.8 (CH), 53.5 (C), 42.8 (CH₂), 34.2 (CH₂), 29.7 (CH₂), 27.4 (CH₂), 26.3 (CH₂), 15.9 (CH₃), 7.9 (CH₃); **HRMS** (ESI) calcd for C₁₉H₂₂O₂Na₁ [M+Na]⁺: 305.1512, found 305.1512.

1,3-diethyl-1-(2-oxocyclohexyl)naphthalen-2(1H)-one (3x):



Light yellow oil: ¹**H NMR** (400 MHz, CDCl₃, ppm): δ 7.30-7.25 (m, 3H), 7.24-7.21 (m, 1H), 7.19 (s, 1H), 3.30 (dd, J = 12.8, 7.6 Hz, 1H), 2.51-2.31 (m, 4H), 2.24-2.08 (m, 3H), 2.04-1.96 (m, 2H), 1.82-1.73 (m, 1H), 1.69-1.58 (m, 2H), 1.17 (t, J = 7.2 Hz, 3H), 0.38 (t, J = 7.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 209.9 (C), 204.0 (C), 145.0 (C), 139.9 (C), 138.8 (CH), 132.4 (C), 128.6 (CH), 128.3 (CH), 126.3 (CH), 125.4 (CH), 64.6 (CH), 53.6 (C), 42.8 (CH₂), 34.2 (CH₂), 29.8 (CH₂), 27.4 (CH₂), 26.3 (CH₂), 22.3 (CH₂), 12.6 (CH₃), 7.9 (CH₃); **HRMS** (ESI) calcd for C₂₀H₂₄O₂Na₁ [M+Na]⁺: 319.1669, found 319.1669.

1-ethyl-1-(2-oxocyclohexyl)naphthalen-2(1H)-one (**3y**):



Light yellow oil: ¹**H NMR** (400 MHz, CDCl₃, ppm): δ 7.42 (d, *J* = 9.6 Hz, 1H), 7.36-7.30 (m, 3H), 7.27-7.22 (m, 1H), 6.26 (d, *J* = 9.6 Hz, 1H), 3.32 (dd, *J* = 12.8, 5.2 Hz, 1H), 2.49-2.44 (m, 1H), 2.39-2.29 (m, 1H), 2.24-2.21 (m, 3H), 2.02-1.99 (m, 2H), 1.83-1.74 (m, 1H), 1.69-1.58 (m, 2H), 1.63 (t, *J* = 5.6 Hz, 3H); ¹³**C NMR** (100 MHz, CDCl₃, ppm): δ 209.9 (C), 204.5 (C), 145.8 (C), 143.7 (CH), 131.8 (C), 129.5 (CH), 129.3 (CH), 127.8 (CH), 126.4 (CH), 125.7 (CH), 64.7 (CH), 54.0 (C), 42.7 (CH₂), 34.0 (CH₂), 29.6 (CH₂), 27.4 (CH₂), 7.8 (CH₃); **HRMS** (ESI) calcd for C₁₈H₂₀O₂Na₁ [M+Na]⁺: 291.1356, found 291.1358.

1-butyl-3-methyl-1-(2-oxocyclohexyl)naphthalen-2(1H)-one (**3z**):



Light yellow oil: ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.30-7.18 (m, 5H), 3.30 (dd, J = 12.8, 5.2 Hz, 1H), 2.50-2.45 (m, 1H), 2.39-2.30 (m, 1H), 2.22-2.04 (m, 3H), 2.02-1.96 (m, 5H), 1.75-1.68 (m, 1H), 1.65-1.59 (m, 2H), 1.19-0.94 (m, 2H), 0.90-0.81 (m, 2H), 0.80-0.71 (m, 1H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 210.0 (C), 204.4 (C), 145.5 (C), 140.4 (CH), 134.4 (C), 132.2 (C), 128.4 (CH), 128.3 (CH), 126.3 (CH), 125.4 (CH), 65.0 (CH), 53.0 (C), 42.8 (CH₂), 41.0 (CH₂), 29.7 (CH₂), 27.4 (CH₂), 26.3 (CH₂), 25.3 (CH₂), 23.0 (CH₂), 16.0 (CH₃), 13.7

(CH₃); **HRMS** (ESI) calcd for $C_{21}H_{26}O_2Na_1$ [M+Na]⁺: 333.1825, found 333.1825.

1-allyl-1-(2-oxocyclohexyl)naphthalen-2(1H)-one (3aa):

Colorless oil: ¹**H** NMR (400 MHz, CDCl₃, ppm): δ 7.40-7.19 (m, 6H), 6.22 (d, *J* = 8.0 Hz, 1H), 5.21-5.11 (m, 1H), 4.80-4.73 (m, 2H), 3.36 (dd, *J* = 12.4, 5.6 Hz, 1H), 2.77 (dd, *J* = 12.8, 7.6 Hz, 1H), 2.57 (dd, *J* = 13.2, 7.2 Hz, 1H), 2.46-2.34 (m, 3H), 2.20-2.12 (m, 1H), 2.05-2.00 (m, 2H), 1.67-1.60 (m, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 209.7 (C), 203.7 (C), 145.2 (C), 143.8 (CH), 131.8 (CH), 131.4 (C), 129.5 (CH), 129.4 (CH), 127.3 (CH), 126.6 (CH), 126.1 (CH), 118.5 (CH₂), 63.9 (CH), 53.7 (C), 45.0 (CH₂), 42.8 (CH₂), 29.8 (CH₂), 27.4 (CH₂), 26.2 (CH₂); **HRMS** (ESI) calcd for C₁₉H₂₀O₂Na₁ [M+Na]⁺: 303.1356, found 303.1356.

1-allyl-6-methoxy-1-(2-oxocyclohexyl)naphthalen-2(1H)-one (**3ab**):



Light yellow oil: ¹**H NMR** (400 MHz, CDCl₃, ppm): δ 7.34-7.30 (m, 2H), 6.90 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.81 (d, *J* = 2.8 Hz, 1H), 6.22 (d, *J* = 10.0 Hz, 1H), 5.22-5.12 (m, 1H), 4.81-4.74 (m, 2H), 3.82 (s, 3H), 3.32 (dd, *J* = 12.4, 4.2 Hz, 1H), 2.75 (dd, *J* = 12.8, 7.6 Hz, 1H), 2.57 (dd, *J* = 12.8, 6.8 Hz, 1H), 2.42-2.10 (m, 5H), 2.05-1.98 (m, 2H), 1.70-1.55 (m, 2H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 209.9 (C), 203.9 (C), 157.8 (C), 143.7 (C), 137.1 (C), 132.4 (C), 132.0 (CH), 127.8 (CH), 127.4 (CH), 118.4 (CH₂), 115.5 (CH), 113.8 (CH), 63.9 (C), 55.3 (CH), 53.3 (CH₃), 45.0 (CH₂), 42.8 (CH₂), 29.8 (CH₂), 27.5 (CH₂), 26.2 (CH₂); **HRMS** (ESI) calcd for C₂₀H₂₂O₃Na₁ [M+Na]⁺: 333.1461, found 333.1461.

1-allyl-6-bromo-1-(2-oxocyclohexyl)naphthalen-2(1H)-one (**3ac**):



Light yellow oil: ¹**H NMR** (400 MHz, CDCl₃, ppm): δ 7.46-7.43 (m, 2H), 7.31-7.26 (m, 2H), 6.24 (d, *J* = 9.6 Hz, 1H), 5.21-5.10 (m, 1H), 4.79 (d, *J* = 7.2 Hz, 1H), 4.76 (s, 1H), 3.31 (dd, *J* = 12.4, 5.6 Hz, 1H), 2.76 (dd, *J* = 13.2, 8.0 Hz, 1H), 2.53 (dd, *J* = 12.8, 6.8 Hz, 1H), 2.44-2.33 (m, 2H), 2.27-2.11 (m, 1H), 2.04-2.00 (m, 2H), 1.67-1.58 (m, 2H); ¹³**C NMR** (100 MHz, CDCl₃, ppm): δ 209.7 (C), 202.9 (C), 144.0 (C), 142.1 (CH), 133.4 (C), 132.0 (CH), 131.9 (CH), 131.3 (CH), 128.4 (CH), 127.9 (CH), 120.2 (C), 119.0 (CH₂), 63.9 (CH), 53.6 (C), 44.8 (CH₂), 42.7 (CH₂), 29.7 (CH₂), 27.4 (CH₂), 26.2 (CH₂); **HRMS** (ESI) calcd for C₁₉H₁₉Br₁O₂Na₁ [M+Na]⁺: 381.0461, found 381.0461.

1-allyl-1-(2-oxocyclohexyl)-6-phenylnaphthalen-2(1H)-one (**3ad**):



White amorphous solid: ¹**H** NMR (400 MHz, CDCl₃, ppm): δ 7.60-7.56 (m, 3H), 7.51 (d, J = 2.0 Hz, 1H), 7.47-7.43 (m, 1H), 7.38-7.34 (m, 1H), 6.26 (d, J = 10.0 Hz, 1H), 5.28-5.17 (m, 1H), 4.84-4.77 (m, 2H), 3.40 (dd, J = 12.4, 6.0 Hz, 1H), 2.79 (dd, J = 12.8, 7.6 Hz, 1H), 2.61 (dd, J = 12.8, 6.8 Hz, 1H), 2.47-2.34 (m, 2H), 2.29-2.15 (m, 2H), 2.05-2.01 (m, 2H), 1.72-1.61 (m, 2H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 209.8 (C), 203.6 (C), 144.0 (C), 143.7 (CH), 139.9 (C), 139.4 (C), 131.8 (CH), 131.7 (C), 128.8 (CH), 127.9 (CH), 127.6 (CH), 127.5 (CH), 126.9 (CH), 126.6 (CH), 118.6 (CH₂), 63.9 (CH), 53.5 (C), 44.9 (CH₂), 42.8 (CH₂), 29.8 (CH₂), 27.4 (CH₂), 26.2 (CH₂); **HRMS** (ESI) calcd for C₂₅H₂₄O₂Na₁ [M+Na]⁺: 379.1669, found 379.1669.

1-allyl-7-methoxy-1-(2-oxocyclohexyl)naphthalen-2(1H)-one (3ae):



Colorless oil: ¹**H** NMR (400 MHz, CDCl₃, ppm): δ 7. 35 (d, J = 9.6 Hz, 1H), 7.24 (d, J = 8.0 Hz, 1H), 6.98 (d, J = 2.0 Hz, 1H), 6.77 (dd, J = 8.4, 2.4 Hz, 1H), 6.10 (d, J = 9.6 Hz, 1H), 5.25-5.15 (m, 1H), 4.84-4.76 (m, 2H), 3.84 (s, 3H), 3.31 (dd, J = 12.4, 5.6 Hz, 1H), 2.76 (dd, J = 13.2, 8.0 Hz, 1H), 2.59 (dd, J = 13.2, 6.8 Hz, 1H), 2.39-2.15 (m, 4H), 2.05-1.97 (m, 2H), 1.65-1.60 (m, 2H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 209.9 (C), 203.6 (C), 160.9 (C), 147.4 (C), 143.9 (CH), 132.0 (CH), 130.9 (CH), 124.8 (CH), 118.4 (CH₂), 114.0 (CH), 110.6 (CH), 63.8 (CH), 55.4 (CH₃), 54.1 (C), 45.2 (CH₂), 42.9 (CH₂), 29.9 (CH₂), 27.4 (CH₂), 26.2 (CH₂); HRMS (ESI) calcd for C₂₀H₂₂O₃Na₁ [M+Na]⁺: 333.1461, found 333.1463.

4-methoxy-2-methyl-2-(2-oxocyclopentyl)naphthalen-1(2H)-one (**3af**):



Colorless oil: ¹**H** NMR (400 MHz, CDCl₃, ppm): δ 8.06 (dd, J = 6.8, 1.2 Hz, 1H), 7.78 (dd, J = 8.0, 0.8 Hz, 1H), 7.65 (td, J = 7.6, 1.2 Hz, 1H), 7.43 (td, J = 7.6, 1.2 Hz, 1H), 5.02 (s, 1H), 3.75 (s, 3H), 2.70 (ddd, J = 12.0, 7.6, 0.8 Hz, 1H), 2.38-2.32 (m, 1H), 2.08-1.99 (m, 1H), 1.91-1.83 (m, 2H), 1.70-1.62 (m, 1H), 1.60 (s, 3H), 1.41-1.30 (m, 1H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 219.7 (C), 201.5 (C), 149.7 (C), 135.6 (C), 134.5 (CH), 129.2 (C), 128.5 (CH), 127.1 (CH), 122.6 (CH), 102.9 (CH), 55.6 (CH), 55.0 (CH₃), 49.4 (C), 39.9 (CH₂), 26.9 (CH₂), 24.6 (CH₃), 20.1 (CH₂); **HRMS** (ESI) calcd for C₁₇H₁₈O₃Na₁ [M+Na]⁺: 293.1148, found 293.1149.

4-ethoxy-2-methyl-2-(2-oxocyclopentyl)naphthalen-1(2H)-one (**3ag**):



Colorless oil: ¹**H** NMR (400 MHz, CDCl₃, ppm): δ 8.08 (dd, J = 7.6, 0.8 Hz, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.62 (td, J = 8.0, 1.2 Hz, 1H), 7.43 (td, J = 7.6, 0.8 Hz, 1H), 4.99 (s, 1H), 3.97-3.82 (m, 2H), 3.07-3.03 (m, 1H), 2.27-2.16 (m, 2H), 2.09-1.99 (m, 2H), 1.88-1.74 (m, 2H), 1.43 (t, J = 7.2 Hz, 3H), 1.27 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 217.1 (C), 202.2 (C), 148.7 (C), 135.4 (C), 133.9 (CH), 129.6 (C), 128.3 (CH), 126.8 (CH), 122.6 (CH), 102.8 (CH), 62.9 (CH₂), 58.6 (CH), 48.4 (C), 38.3 (CH₂), 28.3 (CH₂), 25.1 (CH₃), 25.0 (CH₂), 20.9 (CH₂), 14.5 (CH₃); **HRMS** (ESI) calcd for C₁₈H₂₀O₃Na₁ [M+Na]⁺: 307.1305, found 307.1305.

4-(benzyloxy)-2-methyl-2-(2-oxocyclopentyl)naphthalen-1(2H)-one (**3ah**):



White amorphous solid: ¹**H** NMR (400 MHz, CDCl₃, ppm): δ 8.07 (d, J = 7.6 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.46-7.31 (m, 6H), 5.10 (d, J = 12.0 Hz, 1H), 5.07 (s, 1H), 4.96 (d, J = 12.0 Hz, 1H), 2.65 (dd, J = 12.0, 8.0 Hz, 1H), 2.23 (dd, J = 8.0, 7.2 Hz, 1H), 1.83-1.66 (m, 3H), 1.62-1.54 (m, 4H), 1.25-1.13 (m, 1H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 219.7 (C), 201.3 (C), 148.2 (C), 136.8 (C), 135.7 (C), 134.5 (CH), 129.2 (C), 128.6 (CH), 128.5 (CH), 127.9 (CH), 127.2 (CH), 127.1 (CH), 122.8 (CH), 105.1 (CH), 69.2 (CH₂), 55.4 (CH), 49.4 (C), 39.7 (CH₂), 26.7 (CH₂), 24.4 (CH₃), 20.0 (CH₃); **HRMS** (ESI) calcd for C₂₃H₂₃O₃ [M+H]⁺: 347.1642, found 347.1641.

4-((tert-butyldimethylsilyl)oxy)-2-methyl-2-(2-oxocyclopentyl)naphthalen-1(2H)-one (3ai):



Colorless oil: ¹**H** NMR (400 MHz, CDCl₃, ppm): δ 8.08 (dd, *J* = 7.6, 0.4 Hz, 1H), 7.67-7.60 (m, 2H), 7.42 (td, *J* = 8.0, 1.6 Hz, 1H), 5.21 (s, 1H), 3.12-3.07 (m, 1H), 2.27-2.19 (m, 2H), 2.11-1.97 (m, 2H), 1.87-1.70 (m, 2H), 1.25 (s, 3H), 1.03 (s, 9H), 0.20 (s, 3H), 0.17 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 216.9 (C), 202.0 (C), 145.6 (C), 136.9 (C), 133.9 (CH), 130.0 (C), 128.2 (CH), 127.0 (CH), 123.1 (CH), 111.8 (CH), 58.6 (CH), 48.8 (C), 38.1 (CH₂), 25.8 (CH₃), 24.9 (CH₂), 24.6 (CH₃), 20.9 (C), 18.3 (CH₂), -4.3 (CH₃), -4.6 (CH₃); **HRMS** (ESI) calcd for C₂₂H₃₀O₃Si₁Na₁ [M+Na]⁺: 393.1856, found 393.1858.

4-methoxy-2-methyl-2-(2-oxocyclohexyl)naphthalen-1(2H)-one (3aj):



White amorphous solid: ¹**H** NMR (400 MHz, CDCl₃, ppm): δ 8.08 (d, J = 7.6 Hz, 1H), 7.80 (d, J = 7.6 Hz, 1H), 7.62 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 7.2 Hz, 1H), 5.00 (s, 1H), 3.74 (s, 3H), 3.38 (dd, J = 13.6, 6.0 Hz, 1H), 2.34-2.25 (m, 3H), 2.08-2.05 (m, 2H), 1.80-1.55 (m, 2H), 1.15 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 209.3 (C), 202.1 (C), 149.1 (C), 135.1 (C), 133.6 (CH), 129.4 (C), 128.1 (CH), 126.8 (CH), 122.5 (CH), 102.7

(CH), 60.5 (CH), 54.6 (CH₃), 47.1 (C), 41.8 (CH₂), 26.8 (CH₂), 26.7 (CH₂), 25.3 (CH₂), 24.8 (CH₃); **HRMS** (ESI) calcd for $C_{18}H_{20}O_3Na_1$ [M+Na]⁺: 307.1305, found 307.1306.

4-(benzyloxy)-2-methyl-2-(2-oxocyclohexyl)naphthalen-1(2H)-one (3ak):

White amorphous solid: ¹**H** NMR (400 MHz, CDCl₃, ppm): δ 8.10 (d, J = 7.6 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.63 (t, J = 6.4 Hz, 1H), 7. 45-7.33 (m, 6H), 5.07 (s, 1H), 5.00 (d, J = 11.6 Hz, 1H), 4.95 (d, J = 11.6 Hz, 1H), 3.36 (dd, J = 13.2, 5.2 Hz, 1H), 2.29-2.19 (m, 3H), 2.05-2.01 (m, 2H), 1.80-1.70 (m, 1H), 1.61-1.48 (m, 2H), 1.14 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 209.0 (C), 201.9 (C), 148.0 (C), 137.0 (C), 135.0 (C), 133.6 (CH), 129.5 (C), 128.5 (CH), 128.2 (CH), 127.8 (CH), 127.3 (CH), 126.8 (CH), 122.6 (CH), 104.7 (C), 69.2 (CH₂), 60.5 (CH), 47.2 (C), 41.7 (CH₂), 26.7 (CH₂), 26.5 (CH₂), 25.2 (CH₂), 24.6 (CH₃); **HRMS** (ESI) calcd for C₂₄H₂₄O₃Na₁ [M+Na]⁺: 383.1618, found 383.1617.

4-((tert-butyldimethylsilyl)oxy)-2-methyl-2-(2-oxocyclohexyl)naphthalen-1(2H)-one (3al)



Colorless oil: ¹**H NMR** (400 MHz, CDCl₃, ppm): δ 8.06 (dd, J = 7.6, 0.4 Hz, 1H), 7.69 (d, J = 7.6 Hz, 1H), 7.61 (td, J = 7.6, 1.2 Hz, 1H), 7.40 (td, J = 7.6, 0.8 Hz, 1H), 5.23 (s, 1H), 3.35 (dd, J = 13.2, 5.6 Hz, 1H), 2.33-2.20 (m, 3H), 2.08-2.04 (m, 2H), 1.81-1.70 (m, 1H), 1.62-1.50 (m, 2H), 1.12 (s, 3H), 1.03 (s, 9H), 0.18 (s, 3H), 0.17 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 208.9 (C), 202.0 (C), 145.2 (C), 136.8 (C), 133.5 (CH), 129.9 (C), 127.9 (CH), 126.9 (CH), 123.0 (CH), 112.8 (CH), 60.2 (CH), 47.6 (C), 41.8 (CH₂), 26.9 (CH₂), 26.8 (CH₂), 25.9 (CH₃), 25.3 (CH₂), 24.0 (CH₃), 18.4 (C), -4.2 (CH₃), -4.4 (CH₃); **HRMS** (ESI) calcd for C₂₃H₃₂O₃Si₁Na₁ [M+Na]⁺: 407.2013, found 407.2013.

1-(5-ethyl-2-oxocyclohexyl)-1,3-dimethylnaphthalen-2(1H)-one (3am)



^{1e} 3am

Colorless oil: ¹**H NMR** (400 MHz, CDCl₃, ppm): δ 7.31-7.19 (m, 5H), 3.41 (dd, *J* = 12.4, 6.0 Hz, 1H), 2.56 (td, *J* = 132, 4.4 Hz, 1H), 2.30-2.24 (m, 1H), 2.19-2.08 (m, 2H), 2.02 (s, 3H), 1.85-1.82 (m, 3H), 1.66-1.59 (m, 2H), 1.33 (s, 3H), 1.02 (t, *J* = 7.2 Hz, 3H); ¹³**C NMR** (100 MHz, CDCl₃, ppm): δ 210.7 (C), 204.3 (C), 146.8 (C), 140.5 (CH), 132.8 (C), 130.3 (C), 128.8 (CH), 128.4 (CH), 128.4 (CH), 125.5 (CH), 57.8 (CH), 49.3 (C), 38.4 (CH₂), 34.5 (CH₂), 32.5 (CH₂), 29.6 (CH₂), 26.5 (CH₂), 24.5 (CH₃), 16.1 (CH₃), 12.3 (CH₃); **HRMS** (ESI) calcd for C₂₀H₂₄O₂Na₁ [M+Na]⁺: 319.1669, found 319.1669.

1-(5-(tert-butyl)-2-oxocyclohexyl)-1,3-dimethylnaphthalen-2(1H)-one (3an)



Colorless oil: ¹**H** NMR (400 MHz, CDCl₃, ppm): δ 7.30-7.20 (m, 5H), 3.35 (t, *J* = 8.0 Hz, 1H), 2.48-2.41 (m, 1H), 2.29 (ddd, *J* = 18.0, 4.8, 2.0 Hz, 1H), 2.12-2.04 (m, 1H), 2.01 (d, *J* = 0.8 Hz, 3H), 1.97-1.89 (m, 1H), 1.81-1.78 (m, 1H), 1.64-1.53 (m, 1H), 1.42 (s, 3H), 1.40-1.34 (m, 1H), 0.91 (s, 9H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 212.9 (C), 204.6 (C), 146.3 (C), 140.8 (CH), 132.8 (C), 130.3 (C), 128.8 (CH), 128.4 (CH), 126.6 (CH), 125.8 (CH), 58.0 (CH), 50.0 (C), 43.2 (CH), 39.9 (CH₂), 33.2 (CH₂), 27.0 (CH₃), 26.0 (C), 25.5 (CH₂), 22.5 (CH₃), 16.0 (CH₃); HRMS (ESI) calcd for C₂₂H₂₈O₂Na₁ [M+Na]⁺: 347.1982, found 347.1984.

1,3-dimethyl-1-(2-oxo-5-phenylcyclohexyl)naphthalen-2(1H)-one (3ao)



Colorless oil: ¹**H** NMR (400 MHz, CDCl₃, ppm): δ 7.36-7.35 (m, 3H), 7.24-7.12 (m, 6H), 7.04-7.02 (m, 1H), 3.36 (dd, *J* = 10.8, 6.4 Hz, 1H), 3.14-3.12 (m, 1H), 2.85-2.78 (m, 1H), 2.65-2.60 (m, 1H), 2.39-2.33 (m, 1H), 2.19-2.12 (m, 1H), 2.08-2.00 (m, 1H), 1.95 (d, *J* = 1.2 Hz, 3H), 1.29 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 210.3 (C), 204.3 (C), 146.5 (C), 143.3 (C), 140.7 (CH), 132.8 (C), 130.2 (C), 128.8 (CH), 128.8 (CH), 126.7 (CH), 126.5 (CH), 126.3 (CH), 125.4 (CH), 58.2 (CH), 49.4 (C), 39.2 (CH₂), 37.3 (CH), 33.2 (CH₂), 29.5 (CH₂), 26.3 (CH₃), 16.0 (CH₃); **HRMS** (ESI) calcd for C₂₄H₂₄O₂Na₁ [M+Na]⁺: 367.1669, found 367.1671.

Acyclic 2-haloketones 2g and 2h we tested failed to complete the corresponding dearomatization process



4. Experimental Details for 5 and 6



To a solution of **3f** (0.1 mmol) in EtOH (1mL) was added Pd/C (10% w/w, 0.1eq.). the reaction mixture was stirred at room temperature under H_2 atmosphere until the reaction was complete (monitored by TLC). After which, the reaction mixture was filtered by silica gel. The filtrate was concentrated under vacuum. Purification of the residue by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate 15:1) provided **5** (87% yield).

1-methyl-1-(2-oxocyclopentyl)-3,4-dihydronaphthalen-2(1H)-one (5)

Colorless oil: ¹**H NMR** (400 MHz, CDCl₃, ppm): δ 7.20-7.15 (m, 2H), 7.13-7.07 (m, 2H), 3.22-3.14 (m, 1H), 3.01-2.95 (m, 1H), 2.80-2.68 (m, 2H), 2.55 (dt, *J* = 14.0, 4.0 Hz, 1H), 2.30-2.11 (m, 2H), 1.86-1.79 (m, 2H), 1.63 (s, 3H), 1.59-1.40 (m, 2H); ¹³**C NMR** (100 MHz, CDCl₃, ppm): δ 218.0 (C), 213.5 (C), 141.4 (C), 135.8 (C), 128.4 (CH), 127.2 (CH), 126.7 (CH), 126.5 (CH), 55.6 (CH), 54.8 (C), 39.0 (CH₂), 37.4 (CH₂), 29.0 (CH₂), 27.2 (CH₂), 26.8 (CH₃), 20.6 (CH₂); **HRMS** (ESI) calcd for C₁₆H₁₈O₂Na₁ [M+Na]⁺: 265.1199, found 265.1200.



To a solution of **3ai** (0.1 mmol) in AR DCM (1mL) was added TFA (0.1 mL) at room temperature. The reaction mixture was stirred for 5min. After which, the resultant mixture was concentrated and then purified by flash chromatography (PE:EA= 15:1) to give the corresponding product **6** (80% yield).

2-methyl-2-(2-oxocyclopentyl)-2,3-dihydronaphthalene-1,4-dione (6)

Colorless oil: ¹**H** NMR (400 MHz, CDCl₃, ppm): δ 8.10 (dd, J = 7.2, 1.6 Hz, 1H), 7.97 (dd, J = 6.8, 1.6 Hz, 1H), 7.77-7.69 (m, 2H), 3.17 (d, J = 15.6 Hz, 1H), 2.91 (dd, J = 12.8, 8.0 Hz, 1H), 2.69 (d, J = 15.6 Hz, 1H), 2.36 (dd, J = 18.4, 8.0 Hz, 3H), 2.23-2.15 (m, 1H), 2.13-2.02 (m, 2H), 1.86-1.75 (m, 1H), 1.72-1.61 (m, 1H), 1.33 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 217.3 (C), 198.9 (C), 196.1 (C), 134.7 (C), 134.4 (CH), 134.0 (CH), 133.3 (C), 127.8 (CH), 125.9 (CH), 54.8 (CH), 49.2 (C), 46.6 (CH₂), 38.4 (CH₂), 25.0 (CH₂), 23.7 (CH₃), 20.2 (CH₂); **HRMS** (ESI) calcd for C₁₇H₁₈O₃Na₁ [M+Na]⁺: 293.1148, found 293.1149.

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5. X-ray Crystallography of 3m:



X-ray Crystallography of **3m** (the major diastereoisomer) with thermal ellipsoids are drawn at 50% probability level. The crystal structure of **3m** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers (CCDC number): 1831764.

6. Copies of ¹H and ¹³C spectra of new compounds







¹³C NMR spectrum of compound **4-(benzyloxy)-2-methylnaphthalen-1-yl acetate** (100 MHz, CDCl₃)

¹H NMR spectrum of compound **3a** (400 MHz, CDCl₃)

¹H NMR spectrum of compound **3b** (400 MHz, CDCl₃)

¹H NMR spectrum of compound **3c** (400 MHz, CDCl₃)

¹H NMR spectrum of compound **3d** (400 MHz, CDCl₃)

¹H NMR spectrum of compound **3e** (400 MHz, CDCl₃)

¹H NMR spectrum of compound **3f** (400 MHz, CDCl₃)

¹H NMR spectrum of compound **3g** (400 MHz, CDCl₃)

¹H NMR spectrum of compound **3i** (400 MHz, CDCl₃)

¹H NMR spectrum of compound **3j** (400 MHz, CDCl₃)

¹H NMR spectrum of compound **3l** (400 MHz, CDCl₃)

¹H NMR spectrum of compound **3u** (400 MHz, CDCl₃)

¹H NMR spectrum of compound **3v** (400 MHz, CDCl₃)

¹H NMR spectrum of compound **3z** (400 MHz, CDCl₃)

¹H NMR spectrum of compound **3ac** (400 MHz, CDCl₃)

¹H NMR spectrum of compound **3al** (400 MHz, CDCl₃)

