Oxidative Rearrangement of Cyclic Tertiary Allylic Alcohols with IBX in DMSO

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I. General.

IBX,¹ Dess-Martin periodinane,² PhIO₂,³ and PhIO⁴ were prepared according to the literature procedures. Other chemicals and solvents were either purchased from commercial suppliers and used without purification, except for DMSO distilled over CaH₂. All reactions were stirred magnetically, under an argon atmosphere, unless otherwise noted, and monitored with analytical TLC (Merck Kieselgel 60 F₂₅₄). Column chromatography was carried out with silica gel 60 particle size 0.063-0.210 mm. Melting points were taken with Yazawa BY-2 and are uncorrected. NMR spectra were measured in JEOL JNM-AL400 (400 MHz). Chemical

shifts were reported in the δ scale relative to tetramethylsilane (TMS) as 0.00 ppm for ^1H (CDCl_3) and residual CHCl_3 (7.26 ppm for ^1H and 77.00 ppm for ^{13}C), as internal reference. The infrared (IR) spectra were recorded on JASCO IR-700.

II. Synthesis of the tertiary allylic alcohol substrates

Scheme S1

General procedure for 1,2-addition of organolithium reagents to α,β -unsaturated ketones.* Phenyllithium (1.0 M in cyclohexane-diethyl ether), butyllithium (1.6 M in hexane) and methyllithium (1.0M in diethyl ether) were purchased from commercial suppliers. The other aryllithium reagents were prepared *in situ* from the corresponding aryl bromide by the halogen-lithium exchanging protocol[#] using *tert*-butyllithium (1.5M in *n*-pentane) in THF at -78°C . To a solution of α,β -unsaturated ketone in THF (concentration 0.2M) at -78°C was added organolithium reagent (1.5 equiv). After the mixture was stirred at -78°C for 1 hr, H_2O was added and allowed to warm to rt, and the mixture was extracted with Et_2O . The organic extract was washed with brine, dried (MgSO_4), and concentrated. The residue was purified by silica gel column chromatography (EtOAc -hexane = 1 : 4) to give *tert*-allylic alcohol.

1-Phenyl-2-cyclohexen-1-ol (1a)

mp $44-45^\circ\text{C}$ (recrystallized from hexane); IR (neat): 3398 cm^{-1} ; ^1H -NMR δ 7.46 (d, 2H, $J = 7.8\text{ Hz}$), 7.31 (t, 2H, $J = 7.8\text{ Hz}$), 7.22 (tt, 1H, $J = 7.4, 1.2\text{ Hz}$), 6.00 (ddd, 1H, $J = 10.0, 3.9, 3.7\text{ Hz}$), 5.75 (d, 1H, $J = 10.0\text{ Hz}$), 2.16-1.99 (m, 4H), 1.85 (dd, 1H, $J = 12.8, 2.8\text{ Hz}$), 1.82-1.72 (m, 1H), 1.63-1.54 (m, 1H); ^{13}C -NMR (100MHz, CDCl_3) δ 147.7, 132.1, 130.4, 127.9, 126.6, 125.3, 72.1, 39.5, 25.0, 19.2; MS m/z 174 (M^+), 146 (100%); HRMS Calcd. $\text{C}_{12}\text{H}_{14}\text{O}$: 174.1045. Found: 174.1013.

1-Butyl-2-cyclohexen-1-ol (2a)

IR (neat): 3377 cm^{-1} ; $^1\text{H-NMR}$ δ 5.78 (dt, 1H, $J = 10.0, 4.3$ Hz), 5.61 (d, 1H, $J = 10.0$ Hz), 1.97 (m, 2H), 1.58 (m, 7H), 1.27 (m, 4H), 0.91 (t, 3H, $J = 6.3$ Hz); $^{13}\text{C-NMR}$ (100MHz, CDCl_3) δ 132.8, 129.5, 69.6, 42.0, 35.4, 25.7, 25.2, 23.3, 19.1, 14.1; MS m/z 154 (M^+), 97 (100%); HRMS Calcd. $\text{C}_{10}\text{H}_{18}\text{O}$: 154.1358. Found: 154.1342.

1-(4-Acetoxymethylphenyl)-2-cyclohexen-1-ol (3a)

IR (neat): 3455, 1739 cm^{-1} ; $^1\text{H-NMR}$ δ 7.48 (d, 2H, $J = 8.3$ Hz), 7.30 (d, 2H, $J = 8.3$ Hz), 6.03 (dt, 1H, $J = 10.0, 3.2$ Hz), 5.75 (d, 1H, $J = 10.0$ Hz), 5.09 (s, 2H), 2.20-1.90 (m, 4H), 2.09 (s, 3H), 1.88-1.72 (m, 2H), 1.70-1.56 (m, 1H); $^{13}\text{C-NMR}$ (100MHz, CDCl_3) δ 170.8, 147.9, 134.3, 131.9, 130.8, 128.0, 125.6, 72.0, 66.1, 39.6, 25.0, 21.1, 19.2; MS m/z 246 (M^+), 186 (100%)

1-(4-Methoxymethoxymethylphenyl)-2-cyclohexen-1-ol (4a)

IR (neat): 3444 cm^{-1} ; $^1\text{H-NMR}$ δ 7.46 (dt, 2H, $J = 8.3$ Hz), 7.32 (d, 2H, $J = 8.3$ Hz), 6.02 (dt, 1H, $J = 10.0, 3.7$ Hz), 5.77 (d, 1H, $J = 10.0$ Hz), 4.69 (s, 1H), 4.57 (s, 1H), 3.40 (s, 3H), 2.20-2.00 (m, 3H), 1.96 (dd, 1H, $J = 10.3, 8.6$ Hz), 1.88-1.72 (m, 2H), 1.67-1.58 (m, 1H); $^{13}\text{C-NMR}$ (100MHz, CDCl_3) δ 147.3, 136.2, 132.0, 130.6, 127.6, 125.5, 95.5, 72.0, 68.9, 55.3, 39.6, 25.0, 19.2; MS m/z 248 (M^+), 186 (100%); HRMS Calcd. $\text{C}_{15}\text{H}_{20}\text{O}_3$: 248.1412. Found: 248.1397.

1-(4-Hydroxymethylphenyl)-2-cyclohexen-1-ol (S5)

IR (neat): 3348 cm^{-1} ; $^1\text{H-NMR}$ δ 7.47 (dt, 2H, $J = 8.3, 2.07$ Hz), 7.32 (d, 2H, $J = 8.3$ Hz), 6.03 (dt, 1H, $J = 9.8, 3.2$ Hz), 5.76 (d, 1H, $J = 9.8$ Hz), 4.67 (d, 2H, $J = 3.5$ Hz), 2.20-1.70 (m, 6H), 1.70-1.55 (m, 1H); $^{13}\text{C-NMR}$ (100MHz, CDCl_3) δ 147.2, 139.3, 132.0, 130.7, 126.7, 125.6, 72.1, 65.1, 39.6, 25.1, 19.2; MS m/z 204 (M^+), 145 (100%); HRMS Calcd. $\text{C}_{13}\text{H}_{16}\text{O}_2$: 204.1150. Found: 204.1137.

1-[4-(tert-Butyldiphenylsiloxymethyl)-2-cyclohexen-1-ol (5a)

IR (neat): 3390 cm^{-1} ; $^1\text{H-NMR}$ δ 7.69 (d, 4H, $J = 6.6$ Hz), 7.44 (d, 2H, $J = 8.1$ Hz), 7.46 – 7.32 (m, 6H), 7.32 (d, 2H, $J = 8.1$ Hz), 6.03 (dt, 1H, $J = 10.0, 3.7$ Hz), 5.79 (d, 1H, $J = 10.0$ Hz), 2.20-1.95 (m, 3H), 1.90-1.75 (m, 3H), 1.65-1.55 (m, 1H), 1.09 (s, 9H); $^{13}\text{C-NMR}$ (100MHz, CDCl_3) δ 146.3, 139.6, 135.5, 133.4, 132.2, 130.5, 129.6, 127.6, 125.6, 125.3, 72.1, 65.3, 39.6, 26.9, 25.1, 19.4, 19.3; MS m/z 442 (M^+), 199 (100%); HRMS Calcd. $\text{C}_{29}\text{H}_{33}\text{O}_2\text{Si}$ ($\text{M}^+ - \text{H}_2\text{O}$): 424.2222. Found: 424.2201.

1-[4-(tert-Butyldimethylsiloxymethyl)phenyl]-2-cyclohexen-1-ol (6a)

mp 57-58 $^{\circ}\text{C}$ (recrystallized from hexane); IR (neat): 3393 cm^{-1} ; $^1\text{H-NMR}$ δ 7.44 (d, 2H, $J = 8.3$ Hz), 7.28 (d, 2H, $J = 8.3$ Hz), 6.01 (dt, 1H, $J = 10.1, 3.8$ Hz), 5.77 (d, 1H, $J = 10.1$ Hz), 4.72 (s, 2H), 2.20-1.88 (m, 3H), 1.92 (s, 1H), 1.88-1.72 (m, 2H), 1.70-1.56 (m, 1H), 0.93 (s, 9H), 0.09 (s, 6H); $^{13}\text{C-NMR}$ (100MHz, CDCl_3) δ 146.4, 139.9, 132.2, 130.5, 127.6, 125.7, 125.3, 72.1, 64.8, 39.6, 26.0, 25.1, 19.3, -5.1; MS m/z 318 (M^+), 97 (100%); HRMS Calcd. $\text{C}_{19}\text{H}_{30}\text{O}_2\text{Si}$: 318.2015. Found: 318.1990.

1-[3-(*tert*-Butyldimethylsilanyloxy)phenyl]-2-cyclohexen-1-ol (7a)

IR (neat): 3398 cm^{-1} ; $^1\text{H-NMR}$ δ 7.18 (dd, 1H, $J = 8.0, 7.8$ Hz), 7.04 (d, 1H, $J = 7.8$ Hz), 6.97 (s, 1H), 6.71 (d, 1H, $J = 8.0$ Hz), 6.01 (dt, 1H, $J = 10.0, 3.7$ Hz), 5.75 (d, 1H, $J = 10.0$ Hz), 2.20-2.00 (m, 2H), 1.99-1.89 (m, 2H), 1.89-1.71 (m, 2H), 1.68-1.54 (m, 1H), 0.98 (s, 9H), 0.19 (m, 6H); $^{13}\text{C-NMR}$ (100MHz, CDCl_3) δ 155.3, 149.4, 132.0, 130.5, 128.8, 118.3, 117.4, 72.0, 39.5, 25.8, 25.0, 19.2, 18.3, -4.3; MS m/z 304 (M^+), 229 (100%); HRMS Calcd. $\text{C}_{18}\text{H}_{28}\text{O}_2\text{Si}$ (M^+): 304.1859. Found: 304.1859.

1-Phenyl-2-cyclopenten-1-ol (8a)

IR (neat): 3428 cm^{-1} ; $^1\text{H-NMR}$ δ 7.43 (d, 2H, $J = 7.6$ Hz), 7.32 (dd, 2H, $J = 8.7, 7.6$ Hz), 7.23 (d, 1H, $J = 7.2$ Hz), 6.1 (dt, 1H, $J = 5.6, 2.2$ Hz), 5.8 (dt, 1H, $J = 5.5, 2.2$ Hz), 2.63 (m, 1H), 2.45 (m, 1H), 2.24 (t, 2H, $J = 6.3$ Hz), 1.99 (s, 1H); $^{13}\text{C-NMR}$ (100MHz, CDCl_3) δ 146.9, 136.5, 134.7, 128.3, 128.1, 126.7, 126.0, 124.7, 86.9, 42.0, 31.5.

6-Methoxymethoxy-2-phenylbicyclo[3.2.1]oct-3-en-2-ol (9a)

IR (neat): 3441 cm^{-1} ; $^1\text{H-NMR}$ δ 7.50 (d, 2H, $J = 7.8$ Hz), 7.33 (t, 2H, $J = 7.8$ Hz), 7.25 (t, 1H, $J = 7.8$ Hz), 6.12 (dd, 1H, $J = 9.8, 6.3$ Hz), 5.64 (dd, 1H, $J = 9.8, 2.2$ Hz), 4.66 (s, 2H), 4.24 (dt, 1H, $J = 9.5, 5.4$ Hz), 3.39 (s, 3H), 2.64 (dd, 1H, $J = 9.8, 5.6$ Hz), 2.37 (t, 1H, $J = 6.3$ Hz), 2.24 (dd, 1H, $J = 14.5, 9.5$ Hz), 2.20 (s, 1H), 2.14 (dd, 1H, $J = 14.5, 5.6$ Hz), 1.67 (d, 1H, $J = 12.2$ Hz), 1.35 (dt, 2H, $J = 12.2, 4.9$ Hz); $^{13}\text{C-NMR}$ (100MHz, CDCl_3) δ 146.7, 132.3, 130.2, 127.8, 127.1, 126.5, 96.0, 82.4, 79.1, 55.5, 46.1, 38.6, 32.4,

30.4; MS m/z 261 (M^+), 154 (100%); HRMS Calcd. $C_{16}H_{20}O_3$ (M^+): 260.1412. Found: 260.1386.

3-Methyltricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-ol (10a)

IR (neat): 3355 cm^{-1} ; 1H -NMR δ 6.17 (dd, 1H, $J = 5.3, 2.9$ Hz), 5.9 (dd, 1H, $J = 5.3, 3.3$ Hz), 5.45 (dd, 1H, $J = 7.9, 4.3$ Hz), 3.32 (dd, 1H, $J = 7.9, 4.4$ Hz), 2.94 (s, 1H), 2.9 (s, 1H), 2.59 (dd, 1H, $J = 7.8, 4.1$ Hz), 1.55 (t, 1H, $J = 13.1$ Hz), 1.42 (d, 2H, $J = 6.6$ Hz), 1.32 (s, 3H); ^{13}C -NMR (100MHz, $CDCl_3$) δ 139.4, 135.3, 133.1, 132.7, 54.0, 53.5, 52.4, 46.7, 45.1, 30.7; MS m/z 162 (M^+), 66 (100%); HRMS Calcd. $C_{11}H_{14}O$ (M^+): 162.1045. Found: 162.1016.

1-Phenyl-2-cyclohepten-1-ol (11a)

mp 42-43 $^{\circ}C$ (recrystallized from hexane); IR (neat): 3254 cm^{-1} ; 1H -NMR δ 7.50 (dt, 2H, $J = 7.9, 1.0$ Hz), 7.34 (t, 2H, $J = 7.9$ Hz), 7.25 (tt, 1H, $J = 7.9, 1.0$ Hz), 5.96 (dt, 1H, $J = 11.7, 5.8$ Hz), 5.76 (d, 1H, $J = 11.7$ Hz), 2.32-2.15 (m, 2H), 2.15 (m, 2H), 1.97 (s, 1H), 1.83-1.70 (m, 1H), 1.70-1.55 (m, 2H), 1.45 (m, 1H); ^{13}C -NMR (100MHz, $CDCl_3$) δ 146.7, 137.4, 131.7, 128.1, 126.9, 125.6, 78.5, 41.7, 27.6, 26.7, 23.4; MS m/z 188 (M^+), 188 (100%); HRMS Calcd. $C_{13}H_{16}O$ (M^+): 188.1201. Found: 188.1193.

5-Methyl-2-phenylcyclopent-3-en-1-ol (12a)

IR (neat): 3389 cm^{-1} ; 1H -NMR δ 7.43 (dd, 2H, $J = 8.5$ Hz), 7.30 (ddt, 2H, $J = 8.5, 7.6, 1.2$ Hz), 7.23 (d, 1H, $J = 7.6$ Hz), 5.72 (d, 1H, $J = 15.9$ Hz), 2.31 (oct, 1H, $J = 6.6$ Hz), 1.61 (s, 3H), 1.00 (dd, 6H, $J = 6.6, 1.5$ Hz); ^{13}C -NMR (100MHz, $CDCl_3$) δ 147.2, 135.8, 133.9, 128.0, 126.6, 125.1, 74.3, 30.8, 30.3, 22.4; MS m/z 190 (M^+), 147 (100%); HRMS Calcd. $C_{13}H_{18}O$ (M^+): 190.1358. Found: 190.1397.

1,5-Dimethylnon-3-en-5-ol (13a)

IR (neat): 3390 cm^{-1} ; $^1\text{H-NMR}$ δ 5.56 (dd, 1H, $J = 15.8, 6.5$ Hz), 5.45 (d, 1H, $J = 15.8$ Hz), 2.28 (dt, 1H, $J = 12.3, 6.6$ Hz), 1.821 (s, 1H), 1.49 (m, 2H), 1.31 (m, 4H), 1.25 (s, 3H), 0.99 (d, 6H, $J = 6.6$ Hz), 0.90 (t, 3H, $J = 6.7$ Hz); $^{13}\text{C-NMR}$ (100MHz, CDCl_3) δ 134.7, 133.8, 72.7, 42.6, 30.7, 27.8, 26.2, 23.1, 22.5, 14.1; MS m/z 169 ($\text{M}^+ - \text{H}$), 113 (100%); HRMS Calcd. $\text{C}_{11}\text{H}_{21}\text{O}$ ($\text{M}^+ - \text{H}$): 169.1592. Found: 169.1573.

III. Typical experimental procedure for IBX-mediated oxidative rearrangement

To a stirred solution of tertially allylic alcohol (**1a**) (100 mg, 574 μmol) in DMSO (3 ml) was added IBX¹ (320 mg, 1.15 mmol) at room temperature. After IBX was dissolved, the reaction was warmed to 55 $^\circ\text{C}$ and stirred for 1 h. After cooling to rt, water was added and the mixture was extracted with diethyl ether. The organic extract was washed with brine, dried (MgSO_4), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 4) to give enone (**1b**) (84 mg, 488 μmol , 85 %) as a colorless crystal and the dehydrated product (12 mg, 77 μmol , 13 %).

3-Phenyl-2-cyclohexen-1-one (1b)

mp 64-65 °C (recrystallized from hexane); IR (neat): 1663 cm^{-1} ; $^1\text{H-NMR}$ δ 7.56-7.50 (m, 2H), 7.44-7.38 (m, 3H), 6.42 (s, 1H), 2.78 (td, 2H, $J = 6.1, 2.4$ Hz), 2.49 (t, 2H, $J = 6.1$ Hz), 2.16 (qt, 2H, $J = 6.1$ Hz); $^{13}\text{C-NMR}$ (100MHz, CDCl_3) δ 199.7, 159.6, 138.7, 129.9, 128.6, 126.0, 125.3, 37.3, 28.1, 22.9; MS m/z 172 (M^+), 144 (100%); HRMS Calcd. $\text{C}_{15}\text{H}_{16}\text{O}_3$: 172.0888. Found: 172.0856.

3-Butyl-2-cyclohexen-1-one (2b)

IR (neat): 1670 cm^{-1} ; $^1\text{H-NMR}$ δ 5.87 (t, 1H, $J = 1.4$ Hz), 2.35 (ddd, 2H, $J = 7.5, 6.7, 2.2$ Hz), 2.29 (t, 2H, $J = 6.1$ Hz), 2.21 (t, 2H, $J = 7.5$ Hz), 2.05-1.95 (m, 2H), 1.53-1.45 (m, 2H), 1.39-1.29 (m, 2H), 0.92 (td, 2H, $J = 7.3, 2.2$ Hz); $^{13}\text{C-NMR}$ (100MHz, CDCl_3) δ 199.7, 166.5, 125.4, 37.7, 37.3, 29.6, 29.0, 22.7, 22.3, 13.8; MS m/z 152 (M^+), 82 (100%); HRMS Calcd. $\text{C}_{10}\text{H}_{16}\text{O}$: 152.1201. Found: 152.1180.

4-(3-oxo-1-cyclohexenyl)-benzyl acetate (3b)

IR (neat): 1741, 1665 cm^{-1} ; $^1\text{H-NMR}$ δ 7.53 (d, 2H, $J = 8.3$ Hz), 7.39 (d, 2H, $J = 8.3$ Hz), 6.41 (s, 1H), 5.13 (s, 2H), 2.76 (t, 2H, $J = 6.0$ Hz), 2.49 (t, 2H, $J = 6.0$ Hz), 2.16 (qt, 2H, $J = 6.0$ Hz), 2.12 (s, 3H); $^{13}\text{C-NMR}$ (100MHz, CDCl_3) δ 199.5, 170.5, 159.0, 138.5, 137.7, 128.3, 126.3, 125.4, 65.6, 37.2, 28.1, 22.8, 21.0; MS m/z 244 (M^+), 156 (100%); HRMS Calcd. $\text{C}_{15}\text{H}_{16}\text{O}_3$: 244.1099. Found: 244.1097.

3-(4-Methoxymethoxymethylphenyl)-2-cyclohexen-1-one (4b)

mp 45.5-46.5 °C (recrystallized from hexane-diethyl ether); IR (neat): 1660 cm^{-1} ; $^1\text{H-NMR}$ δ 7.52 (d, 2H, $J = 8.2$ Hz), 7.40 (d, 2H, $J = 8.2$ Hz), 6.42 (s, 1H), 4.72 (s, 2H), 4.62 (s, 2H), 3.42 (s, 3H), 2.77 (t, 2H, $J = 6.0$ Hz), 2.49 (t, 2H, $J = 6.0$ Hz), 2.16 (qt, 2H, $J = 6.0$ Hz); $^{13}\text{C-NMR}$ (100MHz, CDCl_3) δ 199.6, 159.2, 139.9, 138.0, 127.9, 126.0, 125.2, 95.7, 68.5, 55.4, 37.2, 28.1, 22.8; MS m/z 246 (M^+), 246 (100%); HRMS Calcd. $\text{C}_{15}\text{H}_{16}\text{O}_3$: 246.1256. Found: 246.1261.

3-[4-(tert-Butyldiphenylsilanyloxymethyl)phenyl]-2-cyclohexen-1-one (5b)

IR (neat): 1667 cm^{-1} ; $^1\text{H-NMR}$ δ 7.68 (dd, 4H, $J = 6.7, 1.1$ Hz), 7.51 (d, 2H, $J = 8.1$ Hz), 7.50 – 7.31 (m, 6H), 7.40 (d, 2H, $J = 8.1$ Hz), 6.43 (s, 1H), 4.79 (s, 2H), 2.78 (t, 2H, $J = 6.0$ Hz), 2.49 (t, 2H, $J = 6.0$ Hz), 2.15 (qt, 2H, $J = 6.0$ Hz), 1.10 (s, 9H); $^{13}\text{C-NMR}$ (100MHz, CDCl_3) δ 199.7, 159.4, 143.1, 137.2, 135.4, 133.2, 129.7, 127.7, 126.1, 125.9, 124.9, 65.1, 37.3, 28.1, 26.9, 22.9, 19.4; MS m/z 383 ($\text{M}^+ - t\text{Bu}$), 383 (100%); HRMS Calcd. $\text{C}_{25}\text{H}_{23}\text{O}_2\text{Si}$: 383.1467. Found: 383.1458.

3-[4-(tert-Butyldimethylsiloxymethyl)phenyl]-2-cyclohexen-1-one (6b)

mp 50-51 °C (recrystallized from hexane); IR (neat): 1660 cm^{-1} ; $^1\text{H-NMR}$ δ 7.51 (d, 2H, $J = 8.1$ Hz), 7.36 (d, 2H, $J = 8.1$ Hz), 6.42 (s, 1H), 4.72 (s, 2H), 4.76 (s, 2H), 2.77 (t, 2H, $J = 5.6$ Hz), 2.49 (t, 2H, $J = 6.3$ Hz), 2.16 (tt, 2H, $J = 6.3, 5.6$ Hz); $^{13}\text{C-NMR}$ (100MHz, CDCl_3) δ 199.8, 159.5, 143.6, 137.1, 126.1, 125.9, 124.9, 64.5, 37.3, 28.1, 26.0, 22.9, 18.5; MS m/z 316 (M^+), 259 (100%); HRMS Calcd. $\text{C}_{19}\text{H}_{28}\text{O}_2\text{Si}$: 316.1859 Found: 316.1845.

4-(3-Oxo-1-cyclohexenyl)-benzaldehyde (S6)

IR (neat): 1700, 1668 cm^{-1} ; $^1\text{H-NMR}$ δ 10.0 (s, 1H), 7.92 (d, 2H, $J = 8.3$ Hz), 7.68 (d, 2H, $J = 8.3$ Hz), 6.46 (s, 1H), 2.80 (t, 2H, $J = 5.6$ Hz), 2.52 (t, 2H, $J = 6.8$ Hz), 2.20 (tt, 2H, $J = 6.8, 5.6$ Hz); $^{13}\text{C-NMR}$ (100MHz, CDCl_3) δ 199.2, 191.3, 157.9, 144.6, 136.8, 29.9, 127.1, 126.6, 37.2, 28.1, 22.8

3-[3-(*tert*-Butyldimethylsiloxy)phenyl]-2-cyclohexen-1-one (7b)

IR (neat): 1668 cm^{-1} ; $^1\text{H-NMR}$ δ 7.26 (dd, 1H, $J = 7.9, 7.7$ Hz), 7.12 (dd, 1H, $J = 7.7, 2.2$ Hz), 6.99 (t, 1H, $J = 2.2$ Hz), 6.88 (dd, 1H, $J = 7.9, 2.2$ Hz), 6.38 (t, 1H, $J = 1.3$ Hz), 2.74 (td, 2H, $J = 6.0, 1.3$ Hz), 2.48 (t, 2H, $J = 6.0$ Hz), 2.15 (qt, 2H, $J = 6.0$ Hz), 1.00 (s, 9H), 0.21 (s, 6H); $^{13}\text{C-NMR}$ (100MHz, CDCl_3) δ 199.7, 159.4, 155.8, 140.1, 129.6, 125.3, 121.5, 119.0, 117.7, 37.3, 28.1, 25.7, 22.8, 18.2; MS m/z 302 (M^+), 245 (100%); HRMS Calcd. $\text{C}_{18}\text{H}_{26}\text{O}_2\text{Si}$: 302.1702. Found: 302.1692.

3-Phenyl-2-cyclopenten-1-one (8b)

mp 81-82 $^{\circ}\text{C}$ (recrystallized from hexane); IR (neat): 1682 cm^{-1} ; $^1\text{H-NMR}$ δ 7.58-7.60 (m, 2H), 7.47-7.38 (m, 3H), 6.56 (d, 1H, $J = 1.0$ Hz), 3.04-2.98 (m, 2H), 2.60-2.52 (m, 2H); $^{13}\text{C-NMR}$ (100MHz, CDCl_3) δ 209.0, 174.0, 133.9, 131.0, 128.7, 127.3, 126.6, 35.2, 28.6; MS m/z 158 (M^+), 158 (100%); HRMS Calcd. $\text{C}_{11}\text{H}_{12}\text{O}$: 158.0732. Found: 158.0723.

7-Methoxymethoxy-4-phenylbicyclo[3.2.1]oct-3-en-2-one (9b)

IR (neat): 1668 cm^{-1} ; $^1\text{H-NMR}$ δ 7.55 (d, 2H, $J = 6.7$ Hz), 7.43-7.39 (m, 3H), 6.29 (s, 1H), 4.75(ddd, 1H, $J = 9.3, 6.3, 3.3$ Hz), 4.69 (d, 1H, $J = 6.7$ Hz), 4.53 (d, 1H, $J = 6.7$ Hz), 3.38-3.26 (m, 2H), 3.33 (s, 3H), 2.59 (ddd, 1H, $J = 13.8, 8.5, 5.4$ Hz), 2.22 (dd, 1H, $J = 11.8, 2.5$ Hz), 1.89 (ddd, 1H, $J = 11.8, 4.4, 4.2$ Hz), 1.82 (dt, 2H, $J = 13.8, 3.1$ Hz); $^{13}\text{C-NMR}$ (100MHz, CDCl_3) δ

199.8, 167.1, 137.2, 129.9, 128.7, 126.2, 123.9, 95.7, 76.6, 55.6, 54.5, 39.3, 38.7, 38.2; MS m/z 258 (M^+), 198 (100%); HRMS Calcd. $C_{16}H_{18}O_3$: 258.1256. Found: 258.1266.

5-Methyltricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one (10b)

IR (neat): 1695 cm^{-1} ; 1H -NMR δ 5.98 (dd, 1H, J = 5.6, 3.0 Hz), 5.79 (dd, 1H, J = 5.6, 2.9 Hz), 5.69 (s, 1H), 3.22 (t, 1H, J = 4.9 Hz), 3.18 (s, 1H), 3.01 (s, 1H), 2.85 (t, 1H, J = 5.1 Hz), 1.98 (s, 3H), 1.77 (d, 1H, J = 8.3 Hz), 1.59 (d, 1H, J = 8.7 Hz); ^{13}C -NMR (100MHz, $CDCl_3$) δ 209.8, 178.06, 133.4, 132.9, 131.4, 52.4, 51.7, 51.1, 44.3, 43.3, 18.2; MS m/z 160 (M^+), 66 (100%); HRMS Calcd. $C_{11}H_{12}O$: 160.0888. Found: 160.0877.

3-Phenyl-2-cyclohepten-1-one (11b)

IR (neat): 1651 cm^{-1} ; 1H -NMR δ 7.44 (d, 2H, J = 8.8 Hz), 7.41 – 7.31 (m, 3H), 6.30 (s, 1H), 2.88 (t, 2H, J = 5.6 Hz), 2.68 (t, 2H, J = 5.8 Hz), 1.95 (dt, 2H, J = 6.3, 5.8 Hz), 1.91 (dt, 2H, J = 6.3, 5.6 Hz); ^{13}C -NMR (100MHz, $CDCl_3$) δ 204.1, 157.4, 142.3, 130.3, 128.8, 128.4, 126.3, 42.0, 32.0, 25.3, 21.0; MS m/z 186 (M^+), 157 (100%); HRMS Calcd. $C_{13}H_{14}O$: 186.1045. Found: 186.1020.

IV. References

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