

Supporting Information

Solvent-controlled Diastereoselective Synthesis of Cyclopentane Derivatives by a [3+2] Cyclization Reaction of α,β -Disubstituted (Alkenyl)(Methoxy)carbene Complexes with Methyl Ketone Lithium Enolates

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(4a*S*^{*,5*R*^{*})-2,3,4,4a,5,6-Hexahydro-7-methoxy-5-(2-methylpropyl)cyclopenta[b]pyran-5-ol (4b).} Silyl enol ether **6b** (103 mg, 0.6 mmol) was treated with BuLi (0.38 mL of 1.6 N solution in hexanes, 0.6 mmol) in Et₂O (10 mL), PMDTA (312 mg, 1.8 mmol) and carbene complex **1a** (180 mg, 0.4 mmol) to afford compound **4b** (75 mg, 83%) as a colorless oil. R_f 0.27 (hexanes:ethyl acetate, 5:1). ¹H NMR (300 MHz, C₆D₆) δ = 3.90-3.85 (m, 1 H; CH₂O), 3.87 (s, 3 H; OMe), 3.27 (ddd, *J* = 12.3, 10.5, 2.4 Hz, 1 H; CH₂O), 2.63 (dd, *J* = 15.2, 1.7 Hz, 1 H; CHC=), 2.43 (d, *J* = 15.2 Hz, 1 H; CHC=), 2.33 (dd, *J* = 12.3, 4.8 Hz, 1 H; CHCOH), 1.98-1.84 (m, 1 H; CHMe₂), 1.55-1.18 (m, 7 H, OH, CH₂CHMe₂ and OCH₂CH₂CH₂), 1.14 (d, *J* = 6.6 Hz, 3 H; Me), 1.03 (d, *J* = 6.8 Hz, 3 H; Me). ¹³C NMR (75 MHz, C₆D₆) δ = 131.2, 128.4, 75.7, 69.2, 57.6, 53.1, 45.2, 43.6, 25.5, 25.4, 25.2, 24.8, 24.4. HRMS (FAB) calcd. for C₁₃H₂₃O₃ (M+H)⁺: 227.1647, found 227.1642. Elemental analysis calcd. for C₁₃H₂₂O₃: C, 68.99, H, 9.80; found C, 69.15, H, 9.69.

(4a*S*^{*,5*S*^{*})-2,3,4,4a,5,6-Hexahydro-7-methoxy-5-isopropylcyclopenta[b]pyran-5-ol (4c).} Silyl enol ether **6c** (95 mg, 0.6 mmol) was treated with BuLi (0.38 mL of 1.6 N solution in hexanes, 0.6 mmol) in Et₂O (10 mL), PMDTA (312 mg, 1.8 mmol) and carbene complex **1a** (180 mg, 0.4 mmol) to afford compound **4c** (76 mg, 89%, 78%de) as a colorless oil. R_f 0.23 (hexanes:ethyl acetate, 5:1). ¹H NMR (300 MHz, C₆D₆) δ = 3.90 (dd, *J* = 10.5, 4.8 Hz, 1 H; CH₂O), 3.86 (s, 3 H; OMe), 3.33 (ddd, *J* = 12.8, 10.5, 2.6 Hz, 1 H; CH₂O), 2.48 (dd, *J* = 15.5, 1.6 Hz, 1 H; CHC=), 2.31 (d, *J* = 15.5 Hz, 1 H; CHC=), 2.29 (ddd, *J* = 12.0, 4.3, 1.6 Hz, 1 H; CHCOH), 1.81-1.23 (m, 5 H; CH₂CH₂CH₂O, CHMe₂ and OH), 1.10 (qd, *J* = 12.0, 3.7 Hz, 1 H; CH₂CH₂CH₂O), 1.01 (d, *J* = 6.8 Hz, 3 H; Me), 0.98 (d, *J* = 6.8 Hz, 3 H; Me). ¹³C NMR (75 MHz, C₆D₆) δ = 132.7, 130.1, 77.0, 70.5, 57.4, 52.2, 42.5, 32.7, 26.7, 26.0, 17.2, 16.9. HRMS (FAB) calcd. for C₁₂H₂₁O₃ (M+H)⁺: 213.1491, found 213.1495.

(4a*S*^{*,5*R*^{*})-2,3,4,4a,5,6-Hexahydro-7-methoxy-5-phenylcyclopenta[b]pyran-5-ol (4e).} Silyl enol ether **6e** (115 mg, 0.6 mmol) was treated with BuLi (0.38 mL of 1.6 N solution in hexanes, 0.6 mmol) in THF (10 mL), PMDTA (312 mg, 1.8 mmol) and carbene complex **1a** (180 mg, 0.4 mmol) at -78°C with slow warming to room temperature to afford compound **4e**

(81 mg, 82%, 93%de) as a colorless oil. R_f 0.29 (hexanes:ethyl acetate, 5:1). ^1H NMR (300 MHz, C_6D_6) δ = 7.56-7.07 (m, 5 H; ArH), 3.82 (s, 3 H; OMe), 3.71-3.61 (m, 1 H; CH HO), 3.06-2.95 (m, 1 H; CH HO), 2.93 (dd, J = 15.1, 1.6 Hz, 1 H; CH HC=), 2.82-2.72 (m, 1 H; CH), 2.71 (dd, J = 15.1, 1.6 Hz, 1 H; CH HC=), 1.41-0.92 (m, 4 H; CH $\text{CH}_2\text{CH}_2\text{O}$ and OH), 0.43 (qd, J = 12.6, 3.7 Hz, 1 H; CH $\text{CH}_2\text{CH}_2\text{O}$). ^{13}C NMR (75 MHz, C_6D_6) δ = 146.1, 131.7, 128.5, 127.4, 126.8, 125.6, 77.4, 68.3, 57.8, 51.7, 46.8, 26.3, 24.9. HRMS (EI) calcd. for $\text{C}_{15}\text{H}_{18}\text{O}_3$: 246.1256, found 246.1262.

(4aS*,5R*)-2,3,4,4a,5,6-Hexahydro-7-methoxy-5-(4-methoxyphenyl)cyclopenta[b]pyran-5-ol (4f). Silyl enol ether **6f** (133 mg, 0.6 mmol) was treated with BuLi (0.38 mL of 1.6 N solution in hexanes, 0.6 mmol) in Et_2O (10 mL), PMDTA (312 mg, 1.8 mmol) and carbene complex **1a** (180 mg, 0.4 mmol) to afford compound **4f** (95 mg, 86%, 73%de) as a colorless oil. R_f 0.43 (hexanes:ethyl acetate, 2:1). ^1H NMR (300 MHz, C_6D_6) δ = 7.51 (d, J = 8.8 Hz, 2 H; ArH), 6.88 (d, J = 8.8 Hz, 2 H; ArH), 3.91 and 3.41 (2xs, 6 H; 2xOMe), 3.79-3.71 (m, 1 H; CH HO), 3.21-3.04 (m, 2 H; CH HO and CH HC=), 2.98-2.87 (m, 2 H; CH HC= and CH), 1.81 (br s, 1 H; OH), 1.53-1.10 (m, 3 H; CH $\text{CH}_2\text{CH}_2\text{O}$), 0.63 (qd, J = 12.8, 3.5 Hz, 1H; CH $\text{CH}_2\text{CH}_2\text{O}$). ^{13}C NMR (75 MHz, C_6D_6) δ = 158.8, 138.3, 131.1, 126.9, 126.5, 113.1, 77.3, 68.3, 57.9, 54.6, 51.7, 46.8, 26.3, 24.9. HRMS (FAB) calcd. for $\text{C}_{16}\text{H}_{21}\text{O}_4$ ($\text{M}+\text{H}$) $^+$: 277.1440, found 277.1431.

(4aS*,5R*)-2,3,4,4a,5,6-Hexahydro-5-(2-furyl)-7-methoxycyclopenta[b]pyran-5-ol (4g). Silyl enol ether **6g** (109 mg, 0.6 mmol) was treated with BuLi (0.38 mL of 1.6 N solution in hexanes, 0.6 mmol) in THF (10 mL), PMDTA (312 mg, 1.8 mmol) and carbene complex **1a** (180 mg, 0.4 mmol) at -78°C with slow warming to room temperature to afford compound **4g** (72 mg, 76%, 83%de) as a colorless oil. R_f 0.13 (hexanes:ethyl acetate, 5:1). ^1H NMR (300 MHz, C_6D_6) δ = 7.06 (d, J = 1.8 Hz, 1 H; =CHO), 6.14 (d, J = 3.2 Hz, 1 H; =CHC), 6.06 (dd, J = 3.2, 1.8 Hz, 1 H; CH=CHO), 3.89 (s, 3 H; OMe), 3.82-3.72 (m, 1 H; CH HO), 3.18 (ddd, J = 12.8, 10.8, 2.6 Hz, 1 H; CH HO), 3.08 (dd, J = 15.4, 1.6 Hz, 1 H; CH HC=), 2.87 (apparent ddt, J = 12.6, 10.8, 1.6 Hz, 1 H; CH), 2.68 (dd, J = 15.4, 1.6 Hz, 1 H; CH HC=), 1.72-1.06 (m; 4 H; CH $\text{CH}_2\text{CH}_2\text{O}$ and OH), 0.68 (qd, J = 12.6, 3.8, 1 H; CH $\text{CH}_2\text{CH}_2\text{O}$). ^{13}C NMR (75 MHz, C_6D_6) δ = 158.4, 141.3, 130.7, 127.2, 110.0, 105.7, 75.1, 68.6, 57.8, 51.9, 43.6, 26.2, 24.9. HRMS (FAB) calcd. for $\text{C}_{13}\text{H}_{17}\text{O}_4$ ($\text{M}+\text{H}$) $^+$: 237.1127, found 237.1118.

(4aS*,5S*)-2,3,4,4a,5,6-Hexahydro-7-methoxy-5-[*(E*)-2-

phenylethenyl]cyclopenta[b]pyran-5-ol (4h). Silyl enol ether **6h** (131 mg, 0.6 mmol) was

treated with BuLi (0.38 mL of 1.6 N solution in hexanes, 0.6 mmol) in THF (10 mL) and carbene complex **1a** (180 mg, 0.4 mmol) to afford compound **4h** (98 mg, 90%) as a colorless oil. R_f 0.45 (hexanes:ethyl acetate, 2:1). ^1H NMR (300 MHz, C_6D_6) δ = 7.31-7.05 (m, 5 H; ArH), 6.78 and 6.38 (2xd, J = 15.9 Hz, 2 H; CH=CH), 3.81-3.71 (m, 1 H; CH HO), 3.78 (s, 3 H; OMe), 3.16 (ddd, J = 12.6, 10.3, 2.6 Hz, 1 H; CH HO), 2.76-2.62 (m, 2 H; CHHC= and CH), 2.56 (dd, J = 14.9, 1.6 Hz, 1 H; CHHC=), 2.19 (br s, 1 H; OH), 1.72-1.10 (m, 4 H; $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$). ^{13}C NMR (75 MHz, C_6D_6) δ = 137.4, 133.9, 130.3, 128.6, 127.7, 127.3, 127.2, 126.6, 76.4, 68.5, 57.7, 50.6, 44.6, 25.5, 24.9. HRMS (EI) calcd. for $\text{C}_{17}\text{H}_{20}\text{O}_3$: 272.1412, found 272.1419. Elemental analysis calcd. for $\text{C}_{17}\text{H}_{20}\text{O}_3$: C, 74.97, H, 7.40; found C, 75.12, H, 7.28.

(4aS*,5S*)-2,3,4,4a,5,6-Hexahydro-7-methoxy-5-[(E)-2-(4-methoxyphenylethenyl)cyclopenta[b]pyran-5-ol (4i]. Silyl enol ether **6i** (149 mg, 0.6 mmol) was treated with BuLi (0.38 mL of 1.6 N solution in hexanes, 0.6 mmol) in THF (10 mL) and carbene complex **1a** (180 mg, 0.4 mmol) to afford compound **4i** (108 mg, 89%, 91%de) as a colorless oil. R_f 0.32 (hexanes:ethyl acetate, 2:1). ^1H NMR (300 MHz, C_6D_6) δ = 7.34 and 6.88 (2xd, J = 8.5 Hz, 4 H; ArH), 6.87 and 6.38 (2xd, J = 16.0 Hz, 2 H; CH=CH), 3.90-3.82 (m, 1 H; CH HO), 3.87 and 3.41 (2xs, 6 H; 2xOMe), 3.28 (td, J = 9.4, 1.7 Hz, 1 H; CH HO), 2.86-2.78 (m, 2 H; CH and CHHC=), 2.69 (dd, J = 15.8, 1.6 Hz, 1 H; CHHC=), 1.84-1.21 (m, 5 H; $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$ and OH). ^{13}C NMR (75 MHz, C_6D_6) δ = 159.4, 131.7, 130.4, 130.1, 127.8, 127.6, 126.7, 114.2, 76.5, 68.5, 57.7, 54.6, 50.7, 44.7, 25.6, 25.0. HRMS (FAB) calcd. for $\text{C}_{18}\text{H}_{23}\text{O}_4$ ($\text{M}+\text{H}$) $^+$: 303.1596, found 303.1603.

(4aS*,5S*)-2,3,4,4a,5,6-Hexahydro-7-methoxy-5-[(E)-1-pentenyl)cyclopenta[b]pyran-5-ol (4j]. Silyl enol ether **6j** (110 mg, 0.6 mmol) was treated with BuLi (0.38 mL of 1.6 N solution in hexanes, 0.6 mmol) in THF, PMDTA (312 mg, 1.8 mmol) and carbene complex **1a** (180 mg, 0.4 mmol) to afford compound **4j** (70 mg, 73%) as a colorless oil. R_f 0.36 (hexanes:ethyl acetate, 5:1). ^1H NMR (300 MHz, C_6D_6) δ = 5.78 (dt, J = 15.4, 6.3 Hz, 1 H; C=CHPr), 5.68 (dd, J = 15.4, 0.8 Hz, 1 H; CH=CHPr), 3.88-3.81 (m, 1 H; CH HO), 3.84 (s, 3 H; OMe), 3.27 (ddd, J = 12.8, 10.5, 2.3 Hz, 1 H; CH HO), 2.68 (dd, J = 14.5, 1.4 Hz, 1 H; CHHC=), 2.71-2.63 (m, 1 H; CH), 2.57 (dd, J = 14.5, 1.7 Hz, 1 H; CHHC=), 2.08-2.00 (m, 2 H; =CHCH₂), 1.73 (br s, 1 H; OH), 1.60-1.20 (m, 7 H; OH, $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$ and CH_2Me), 0.95 (t, J = 7.4 Hz, 3 H; Me). ^{13}C NMR (75 MHz, C_6D_6) δ = 134.2, 130.5, 127.6, 127.1, 75.8, 68.5, 57.7, 50.3, 44.8, 34.4, 25.5, 25.0, 22.8, 13.7. HRMS (EI) calcd. for $\text{C}_{14}\text{H}_{22}\text{O}_3$: 238.1569, found 238.1571. Elemental analysis calcd. for $\text{C}_{14}\text{H}_{22}\text{O}_3$: C, 70.56, H, 9.30; found C, 70.69, H, 9.18.

(4a*S*^{*},5*S*^{*})-2,3,4,4a,5,6-Hexahydro-7-methoxy-5-(2-methyl-1-propenyl)cyclopenta[*b*]pyran-5-ol (4k). Silyl enol ether **6k** (102 mg, 0.6 mmol) was treated with BuLi (0.38 mL of 1.6 N solution in hexanes, 0.6 mmol) in THF (10 mL), PMDTA (312 mg, 1.8 mmol) and carbene complex **1a** (180 mg, 0.4 mmol) to afford compound **4k** (65 mg, 73%, 90%de) as a colorless oil. R_f 0.23 (hexanes:ethyl acetate, 5:1). ¹H NMR (300 MHz, C₆D₆) δ = 5.30-5.28 (m, 1 H; C=CH), 3.83-3.72 (m, 1 H; CHHO), 3.76 (s, 3 H; OMe), 3.18 (td, J = 12.8, 2.3 Hz, 1 H; CHHC= and CH), 2.53 (dd, J = 14.6, 2.0 Hz, 1 H; CHHC=), 1.82 (d, J = 1.3 Hz, 3 H; Me), 1.62 (d, J = 1.7 Hz, 3 H; Me), 1.51-1.13 (m, 5 H; OH and CH₂CH₂CH₂O). ¹³C NMR (75 MHz, C₆D₆) δ = 134.9, 130.5, 129.1, 127.6 76.5, 68.6, 57.6, 51.3, 47.5, 26.9, 25.9, 25.1, 19.4. HRMS (EI) calcd. for C₁₃H₂₀O₃: 224.1412, found 224.1408.

(4a*S*^{*},5*R*^{*})-2,3,4,4a,5,6-Hexahydro-7-methoxy-5-(phenylethynyl)cyclopenta[*b*]pyran-5-ol (4n). ketone **3n** (63 mg, 0.44 mmol) was treated with LDA (0.44 mmol) in THF (10 mL), PMDTA (229 mg, 1.32 mmol) and carbene complex **1a** (180 mg, 0.4 mmol) to afford compound **4n** (93 mg, 86%) as a colorless oil. R_f 0.16 (hexanes:ethyl acetate, 5:1). ¹H NMR (300 MHz, C₆D₆) δ = 7.47-6.92 (m, 5 H; ArH), 3.81-3.72 (m, 1 H; CHHO), 3.72 (s, 3 H; OMe), 3.24 (ddd, J = 12.4, 10.4, 2.6 Hz, 1 H; CHHC=), 3.07 (dd, J = 14.6, 1.6 Hz, 1 H; CHHC=), 2.92 (br s, 1 H; OH), 2.91 (dd, J = 14.6, 1.6 Hz, 1 H; CHHC=), 2.81 (ddt, J = 12.1, 5.4, 1.6 Hz, 1 H; CH), 2.14-2.01 (m, 1 H; CHHCH₂CH₂O), 1.80 (qd, J = 12.8, 3.8 Hz, 1 H; CHHCH₂CH₂O), 1.45 (qt, J = 12.8, 3.6 Hz, 1 H; CHHCH₂O), 1.29-1.16 (m, 1 H; CHHCH₂O). ¹³C NMR (75 MHz, C₆D₆) δ = 131.8, 130.2, 128.3, 128.2, 127.0, 123.2, 92.4, 85.1, 72.3, 68.5, 57.7, 50.0, 46.3, 26.5, 24.6. HRMS (FAB) calcd. for C₁₇H₁₉O₃ (M+H)⁺: 271.1334, found 271.1324. Elemental analysis calcd. for C₁₇H₁₈O₃: C, 75.53, H, 6.71; found C, 75.66, H, 6.59.

(4a*S*^{*},5*R*^{*})-5-(1-Hexinyl)-2,3,4,4a,5,6-hexahydro-7-methoxycyclopenta[*b*]pyran-5-ol (4o). Silyl enol ether **6o** (118 mg, 0.6 mmol) was treated with BuLi (0.38 mL of 1.6 N solution in hexanes, 0.6 mmol) in THF (10 mL), PMDTA (312 mg, 1.8 mmol) and carbene complex **1a** (180 mg, 0.4 mmol) to afford compound **4o** (95 mg, 95%) as a colorless oil. R_f 0.26 (hexanes:ethyl acetate, 5:1). ¹H NMR (300 MHz, C₆D₆) δ = 3.87-3.80 (m, 1 H; CHHO), 3.80 (s, 3 H; OMe), 3.35 (ddd, J = 12.3, 10.8, 2.8 Hz, 1 H; CHHO), 3.03 (dd, J = 14.4, 1.6 Hz, 1 H; CHHC=), 2.90 (dd, J = 14.4, 1.6 Hz, 1 H; CHHC=), 2.76 (ddt, J = 12.0, 5.4, 1.6 Hz, 1 H; CH), 2.34 (br s, 1 H; OH), 2.11 (t, J = 6.9 Hz, 2 H; CH₂Pr), 1.84 (qd, J = 12.0, 4.1 Hz, 1 H; CHHCH₂CH₂O), 2.02-1.96 and 1.52-1.22 (2xm, 7 H; (CH₂)₂Me and CHHCH₂CH₂O), 0.85 (t, J = 7.2 Hz, 3 H, Me). ¹³C NMR (75 MHz, C₆D₆) δ = 130.3, 126.9, 85.1, 83.4, 72.1, 68.4, 57.7,

49.8, 46.7, 30.9, 26.4, 24.7, 22.0, 18.4, 13.5. HRMS (EI) calcd. for C₁₅H₂₂O₃: 250.1569, found 250.1566. Elemental analysis calcd. for C₁₅H₂₂O₃: C, 71.97, H, 8.86; found C, 72.11, H, 8.73.

(4a*S*^{*},5*R*^{*})-2,3,4,4a,5,6-Hexahydro-7-methoxy-5-

(trimethylsilylethynyl)cyclopenta[*b*]pyran-5-ol (4p). Silyl enol ether **6p** (127 mg, 0.6 mmol) was treated with BuLi (0.38 mL of 1.6 N solution in hexanes, 0.6 mmol) in THF (10 mL) and carbene complex **1a** (180 mg, 0.4 mmol) to afford compound **4p** (83 mg, 78%) as a colorless oil. R_f 0.31 (hexanes:ethyl acetate, 5:1). ¹H NMR (300 MHz, C₆D₆) δ = 3.83 (ddt, *J* = 10.8, 4.4, 2.2 Hz, 1 H; CHHO), 3.77 (s, 3 H; OMe), 3.33 (ddd, *J* = 12.8, 10.8, 2.6 Hz, 1 H; CHHO), 3.04 (dd, *J* = 14.8, 1.6 Hz, 1 H; CHC=), 2.84 (dd, *J* = 14.8, 1.6 Hz, 1 H; CHC=), 2.72 (ddt, *J* = 12.1, 5.3, 1.6 Hz, 1 H; CH), 2.19 (br s, 1 H; OH), 1.84 (qd, *J* = 12.1, 3.8 Hz, 1 H; CHHCCH₂O), 2.12-2.03 and 1.54-1.28 (2xm, 3 H; CHHC₂CH₂O), -0.24 (s, 9 H; TMS). ¹³C NMR (75 MHz, C₆D₆) δ = 130.1, 126.8, 108.9, 88.7, 72.0, 68.5, 57.6, 49.6, 43.3, 26.6, 24.7, -0.2. HRMS (EI) calcd. for C₁₄H₂₂O₃Si: 266.1338, found 266.1327. Elemental analysis calcd. for C₁₄H₂₂O₃Si: C, 63.12, H, 8.32; found C, 63.28, H, 8.19.

(1*R*^{*},7a*R*^{*})-2,4,5,6,7,7a-Hexahydro-3-methoxy-1-phenyl-1*H*-inden-1-ol (5b). Silyl enol ether **6e** (115 mg, 0.6 mmol) was treated with BuLi (0.38 mL of 1.6 N solution in hexanes, 0.6 mmol) in THF (10 mL) and carbene complex **1b** (126 mg, 0.4 mmol) to afford compound **5b** (87 mg, 89%) as a colorless oil. R_f 0.38 (hexanes:ethyl acetate, 2:1). ¹H NMR (400 MHz, C₆D₆) δ = 7.51-7.06 (m, 5 H; ArH), 3.33 (s, 3 H; OMe), 3.06 (d, *J* = 16.2 Hz, 1 H; CHHCOH), 2.95 (d, *J* = 13.9 Hz, 1 H; CHC=COMe), 2.72 (d, *J* = 16.2 Hz, 1 H; CHHCOH), 2.48 (dd, *J* = 12.1, 4.8 Hz, 1 H; CH), 2.28 (br s, 1 H; OH), 1.86-1.72 (m, 1 H; CHC=COMe), 1.65-1.50 (m, 2 H; CH₂CHHCHHCH₂), 1.30-1.21 (m, 1 H; CHHCH), 1.16-0.99 (m, 2 H; CH₂CHHCHHCH₂), 0.53 (qd, *J* = 12.1, 3.1 Hz, 1 H; CHHCH). ¹³C NMR (100 MHz, C₆D₆) δ = 145.4, 145.0, 127.7, 126.6, 126.0, 114.7, 80.4, 57.6, 56.4, 46.0, 31.0, 26.3, 26.0, 24.5. HRMS (FAB) calcd. for C₁₆H₂₁O₂ (M+H)⁺: 245.1542, found 245.1546. Elemental analysis calcd. for C₁₆H₂₀O₂: C, 78.65, H, 8.25; found C, 78.76, H, 8.10.

(1*S*^{*},7a*R*^{*})-2,4,5,6,7,7a-hexahydro-3-methoxy-1-[(*E*)-2-phenylethenyl]-1*H*-inden-1-ol

(5c). Silyl enol ether **6h** (131 mg, 0.6 mmol) was treated with BuLi (0.38 mL of 1.6 N solution in hexanes, 0.6 mmol) in THF (10 mL) and carbene complex **1b** (126 mg, 0.4 mmol) to afford compound **5c** (100 mg, 93%) as a colorless oil. R_f 0.24 (hexanes:ethyl acetate, 5:1).

¹H NMR (300 MHz, C₆D₆) δ = 7.47-6.93 (m, 5 H; ArH), 6.86 and 6.35 (2xd, *J* = 16.0 Hz, 2

H; CH=CH), 3.31 (s, 3 H; OMe), 2.95 (d, J = 15.4, 1 H; CHHC=COMe), 2.71 (s, 2 H, CH₂COH), 2.55-2.46 (m, 2 H; CH and OH), 1.96-1.13 (m, 7 H; (CH₂)₃CHHC=COMe). ¹³C NMR (75 MHz, C₆D₆) δ = 144.9, 137.6, 134.3, 128.6, 127.6, 127.1, 126.6, 114.7, 78.9, 57.2, 56.4, 44.8, 30.4, 26.6, 26.2, 24.4. HRMS (EI) calcd. for C₁₈H₂₂O₂: 270.1620, found 270.1619.

(1*R*^{*},7*aR*^{*})-2,4,5,6,7,7a-hexahydro-3-methoxy-1-phenylethynyl-1*H*-inden-1-ol (5d).

Ketone **3n** (63 mg, 0.44 mmol) was treated with LDA (0.44 mmol) in THF (10 mL) and carbene complex **1b** (126 mg, 0.4 mmol) to afford compound **5d** (90 mg, 84%) as a colorless oil. R_f 0.19 (hexanes:ethyl acetate, 5:1). ¹H NMR (300 MHz, C₆D₆) δ = 7.48-6.93 (m, 5 H; ArH), 3.22 (s, 3 H; OMe), 3.09 (dt, J = 15.9, 2.1 Hz, 1 H; CHHCOH), 2.96-2.80 (m, 2 H; CHHC=COMe and CHHCOH), 2.53 (dd, J = 12.3, 4.1, 1 H; CH), 2.43 (br s, 1 H; OH), 2.24-1.12 (m, 7 H; (CH₂)₃CHHC=COMe). ¹³C NMR (75 MHz, C₆D₆) δ = 144.0, 131.7, 128.3, 127.6, 123.4, 114.0, 92.2, 85.6, 73.8, 56.4, 56.4, 47.0, 31.1, 26.3, 26.0, 24.3. HRMS (EI) calcd. for C₁₈H₂₀O₂: 268.1463, found 268.1472. Elemental analysis calcd. for C₁₈H₂₀O₂: C, 80.56, H, 7.51; found C, 80.67, H, 7.41.

(4a*S*^{*},5*S*^{*})-2,3,4,4a,5,6-Hexahydro-7-methoxy-5-methylcyclopenta[*b*]pyran-5-ol (diast-4a). Silyl enol ether **6a** (92 mg, 0.6 mmol) was treated with BuLi (0.38 mL of 1.6 N solution in hexanes, 0.6 mmol) in Et₂O (10 mL) and carbene complex **1a** (180 mg, 0.4 mmol) to afford a 1:1 separable mixture of compounds **4a** (35 mg, 47%) and **diast-4a** (35 mg, 47%) as colorless oils. R_f 0.36 (hexanes:ethyl acetate, 2:1). ¹H NMR (400 MHz, C₆D₆) δ = 3.83-3.75 (m, 1 H; CHHO), 3.78 (s, 3 H; OMe), 3.22 (ddd, J = 11.3, 10.5, 2.8 Hz, 1 H; CHHO), 2.39 (dd, J = 15.1, 1.4 Hz, 1 H; CHHC=), 2.21 (dd, J = 15.1, 1.4 Hz, 1 H; CHHC=), 2.15-2.07 (m, 1 H; CH), 1.51-1.18 (m, 5 H; OH and CH₂CH₂CH₂O), 1.07 (3 H, s, Me). ¹³C NMR (100 MHz, C₆D₆) δ = 131.1, 126.7, 72.4, 68.3, 57.6, 48.3, 45.4, 26.3, 24.6, 22.2. HRMS (EI) calcd. for C₁₀H₁₆O₃: 184.1099, found 184.1097.

(4a*S*^{*},5*R*^{*})-2,3,4,4a,5,6-Hexahydro-7-methoxy-5-(2-propyl)cyclopenta[*b*]pyran-5-ol (diast-4c).

Silyl enol ether **6c** (95 mg, 0.6 mmol) was treated with BuLi (0.38 mL of 1.6 N solution in hexanes, 0.6 mmol) in Et₂O (10 mL) and carbene complex **1a** (180 mg, 0.4 mmol) to afford compound **diast-4c** (75 mg, 88 %) as a colorless oil. R_f 0.23 (hexanes:ethyl acetate, 5:1). ¹H NMR (300 MHz, C₆D₆) δ = 3.83-3.74 (m, 1 H; CHHO), 3.79 (s, 3 H; OMe), 3.22 (ddd, J = 13.3, 10.8, 2.8 Hz, 1 H; CHHO), 2.47 (dd, J = 15.5, 1.7 Hz, 1 H; CHHC=), 2.35-2.27 (m, 1 H; CH), 2.06 (dd, J = 15.5, 1.5 Hz, 1 H; CHHC=), 1.58-1.08 (m, 6 H; OH, CHMe₂ and CH₂CH₂CH₂O), 0.84 (d, J = 7.2 Hz, 3 H; Me), 0.80 (d, J = 7.2 Hz, 3 H; Me). ¹³C NMR

(75 MHz, C₆D₆) δ = 131.3, 128.9, 76.9, 68.4, 57.6, 46.0, 42.8, 37.5, 24.9, 24.2, 17.4, 17.1. HRMS (EI) calcd. for C₁₂H₂₀O₃: 212.1412, found 212.1416. Elemental analysis calcd. for C₁₂H₂₀O₃: C, 67.89, H, 9.50; found C, 68.02, H, 9.36.

(4aS*,5S*)-5-tert-Butyl-2,3,4,4a,5,6-hexahydro-7-methoxycyclopenta[b]pyran-5-ol (*diast-4d*). Silyl enol ether **6d** (103 mg, 0.6 mmol) was treated with BuLi (0.38 mL of 1.6 N solution in hexanes, 0.6 mmol) in Et₂O (10 mL) and carbene complex **1a** (180 mg, 0.4 mmol) to afford compound **diast-4d** (67 mg, 74%) as a colorless oil. R_f 0.31 (hexanes:ethyl acetate, 5:1). ¹H NMR (400 MHz, C₆D₆) δ = 3.83-3.75 (m, 1 H; CHHO), 3.78 (s, 3 H; OMe), 3.19 (ddd, J = 11.1, 9.1, 2.8 Hz, 1 H; CHHO), 2.73 (dd, J = 15.6, 1.6 Hz, 1 H; CHHC=), 2.54-2.45 (m, 1 H; CH), 2.02 (dd, J = 15.6, 1.6 Hz, 1 H; CHH=), 1.64-1.46 and 1.33-1.22 (2xm, 5 H, CH₂CH₂CH₂O and OH), 0.81 (s, 9 H; 3xMe). ¹³C NMR (100 MHz, C₆D₆) δ = 131.2, 127.9, 79.1, 68.5, 57.5, 43.3, 40.7, 37.5, 25.5, 25.3, 25.0. HRMS (EI) calcd. for C₁₃H₂₂O₃: 226.1569, found 226.1568. Elemental analysis calcd. for C₁₃H₂₂O₃: C, 68.99, H, 9.80; found C, 69.11, H, 9.71.

(4aS*,5S*)-2,3,4,4a,5,6-Hexahydro-7-methoxy-5-phenylcyclopenta[b]pyran-5-ol (*diast-4e*). Silyl enol ether **6e** (115 mg, 0.6 mmol) was treated with BuLi (0.38 mL of 1.6 N solution in hexanes, 0.6 mmol) in Et₂O (10 mL) and carbene complex **1a** (180 mg, 0.4 mmol) to afford compound **diast-4e** (91 mg, 92%) as a colorless oil. R_f 0.29 (hexanes:ethyl acetate, 5:1). ¹H NMR (300 MHz, C₆D₆) δ = 7.49-7.08 (m, 5 H; ArH), 3.89-3.78 (m, 1 H; CHHO), 3.86 (s, 3 H; OMe), 3.30 (ddd, J = 14.2, 10.8, 3.2 Hz, 1 H; CHHO), 2.99 (dd, J = 15.6, 1.3 Hz, 1 H; CHHC=), 2.74 (ddt, J = 12.0, 5.6, 1.3 Hz, 1 H; CH), 2.46 (dd, J = 15.6, 1.3 Hz, 1 H; CHHC=), 2.09-1.90 and 1.48-1.18 (m, 4 H; OH and CHHCH₂CH₂O), 1.63 (qd, J = 12.0, 4.3 Hz, 1 H; CHHCH₂CH₂O). ¹³C NMR (75 MHz, C₆D₆) δ = 146.3, 130.7, 128.5, 127.6, 126.8, 125.6, 76.4, 68.6, 57.9, 50.9, 47.2, 24.8, 22.0. HRMS (EI) calcd. for C₁₅H₁₈O₃: 246.1256, found 246.1262. Elemental analysis calcd. for C₁₅H₁₈O₃: C, 73.15, H, 7.37; found C, 73.28, H, 7.22.

(4aS*,5S*)-2,3,4,4a,5,6-Hexahydro-7-methoxy-5-(4'-methoxy)phenylcyclopenta[b]pyran-5-ol (*diast-4f*). Silyl enol ether **6f** (133 mg, 0.6 mmol) was treated with BuLi (0.38 mL of 1.6 N solution in hexanes, 0.6 mmol) in Et₂O (10 mL) and carbene complex **1a** (180 mg, 0.4 mmol) to afford compound **diast-4f** (98 mg, 89%) as a colorless oil. R_f 0.43 (hexanes:ethyl acetate, 2:1). ¹H NMR (400 MHz, C₆D₆) δ = 7.44 and 6.90 (2xd, J = 8.9 Hz, 4 H; ArH), 3.94-3.86 (m, 1 H; CHHO), 3.91 and 3.40 (2xs, 6 H; 2xOMe), 3.37 (ddd, J = 13.1, 10.8, 2.7 Hz, 1

H; CHHO), 3.08 (dd, J = 15.6, 1.5 Hz, 1 H; CHHC=), 2.79 (ddt, J = 12.3, 5.4, 1.5 Hz, 1 H; CH), 2.54 (dd, J = 15.6, 1.5 Hz, 1 H; CHHC=), 2.26 (br s, 1 H; OH), 1.73 (qd, J = 12.3, 3.9 Hz, 1 H; CHHCH₂CH₂O), 1.61-1.28 (m, 3 H; CHHCH₂CH₂O). ¹³C NMR (100 MHz, C₆D₆) δ = 158.7, 138.1, 130.5, 127.1, 126.5, 113.5, 76.1, 68.3, 57.5, 54.6, 50.5, 46.9, 24.6, 21.8. HRMS (EI) calcd. for C₁₆H₂₀O₄: 276.1362, found 276.1365. Elemental analysis calcd. for C₁₆H₂₀O₄: C, 69.54, H, 7.30; found C, 69.67, H, 7.17.

(4aS*,5S*)-2,3,4,4a,5,6-Hexahydro-5-(2-furyl)-7-methoxycyclopenta[b]pyran-5-ol (*diast-4g*). Silyl enol ether **6g** (109 mg, 0.6 mmol) was treated with BuLi (0.38 mL of 1.6 N solution in hexanes, 0.6 mmol) in Et₂O (10 mL) and carbene complex **1a** (180 mg, 0.4 mmol) to afford compound **diast-4g** (77 mg, 81%) as a colorless oil. R_f 0.13 (hexanes:ethyl acetate, 5:1). ¹H NMR (300 MHz, C₆D₆) δ = 7.11 (d, J = 1.5 Hz, 1 H; =CHO), 6.19 (d, J = 3.1 Hz, 1 H; =CHC) and 6.13 (dd, J = 3.1, 1.5 Hz, 1 H; CH=CHO), 3.90-3.81 (m, 1 H; CHHO), 3.83 (s, 3 H; OMe), 3.32 (ddd, J = 12.7, 9.8, 2.4 Hz, 1 H; CHHO), 3.18 (dd, J = 15.4, 1.5 Hz, 1 H; CHHC=), 2.93 (ddt, J = 11.8, 5.8, 1.5 Hz, 1 H; CH), 2.49 (dd, J = 15.4, 1.5 Hz, 1 H; CHHC=), 1.81-1.22 (m, 5 H; OH and CH₂CH₂CH₂O). ¹³C NMR (75 MHz, C₆D₆) δ = 158.5, 141.6, 130.5, 127.1, 110.3, 105.1, 73.2, 68.5, 57.9, 47.5, 44.0, 24.7, 22.2. HRMS (EI) calcd. for C₁₃H₁₆O₄: 236.1049, found 236.1047.

(4aS*,5R*)-2,3,4,4a,5,6-Hexahydro-7-methoxy-5-[(E)-2-phenylethenyl)cyclopenta[b]pyran-5-ol (*diast-4h*). Silyl enol ether **6h** (131 mg, 0.6 mmol) was treated with BuLi (0.38 mL of 1.6 N solution in hexanes, 0.6 mmol) in Et₂O (10 mL) and carbene complex **1a** (180 mg, 0.4 mmol) to afford compound **diast-4h** (91 mg, 84%, 79%de) as a colorless oil. R_f 0.45 (hexanes:ethyl acetate, 2:1). ¹H NMR (300 MHz, C₆D₆) δ = 7.37-7.13 (m, 5 H; ArH), 6.84 and 6.17 (2xd, J = 16.0 Hz, 2 H; CH=CH), 3.91-3.85 (m, 1 H; CHHO), 3.90 (s, 3 H; OMe), 3.37-3.29 (m, 1 H; CHHO), 2.75 (dd, J = 15.4, 1.9 Hz, 1 H; CHHC=), 2.50 (apparent ddt, J = 11.4, 5.8, 1.9 Hz, 1 H; CH), 2.32 (apparent dd, J = 15.4, 1.9 Hz, 1 H; CHHC=), 1.68-1.24 (m, 5 H) (OH and CH₂CH₂CH₂O). ¹³C NMR (75 MHz, C₆D₆) δ = 137.3, 134.5, 130.9, 128.6, 127.9, 127.6, 127.3, 126.6, 75.1, 68.3, 57.7, 48.0, 45.0, 24.6, 21.5. HRMS (EI) calcd. for C₁₇H₂₀O₃: 272.1412, found 272.1416.

(4aS*,5R*)-2,3,4,4a,5,6-Hexahydro-7-methoxy-5-[(E)-2-(4-methoxyphenyl)ethenyl)cyclopenta[b]pyran-5-ol (*diast-4i*). Silyl enol ether **6i** (149 mg, 0.6 mmol) was treated with BuLi (0.38 mL of 1.6 N solution in hexanes, 0.6 mmol) in Et₂O (10 mL) and carbene complex **1a** (180 mg, 0.4 mmol) to afford compound **diast-4i** (102 mg, 84%,

82%de) as a colorless oil. R_f 0.32 (hexanes:ethyl acetate, 2:1). ^1H NMR (300 MHz, C_6D_6) δ = 7.32 and 6.86 (2xd, J = 8.5 Hz, 4 H; ArH), 6.85 and 6.12 (2xd, J = 16.0 Hz, 2 H; $\text{CH}=\text{CH}$), 3.91 and 3.40 (2xs, 6 H; 2xOMe), 3.93-3.88 (m, 1 H; CHHO), 3.36 (dt, J = 10.8, 2.2 Hz, 1 H; CHHO), 2.80 (dd, J = 15.2, 1.5 Hz, 1 H; CHC=), 2.55 (apparent ddt, J = 12.6, 6.0, 1.5 Hz, 1 H; CH), 2.38 (dd, J = 15.2, 1.5 Hz, 1 H; CHC=), 1.86 (br s, 1 H; OH), 1.71-1.31 (m, 4 H; $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$). ^{13}C NMR (75 MHz, C_6D_6) δ = 159.4, 132.3, 130.9, 130.0, 127.8, 127.4, 127.3, 114.1, 75.1, 68.3, 57.7, 54.6, 48.1, 45.1, 24.7, 21.6. HRMS (FAB) calcd. for $\text{C}_{18}\text{H}_{23}\text{O}_4$ ($\text{M}+\text{H}$) $^+$: 303.1596, found 303.1591.

(4a*S*^{*},5*R*^{*})-2,3,4,4a,5,6-Hexahydro-7-methoxy-5-[(*E*)-1-penten-1-yl]cyclopenta[*b*]pyran-5-ol (*diast*-4j). Silyl enol ether **6j** (110 mg, 0.6 mmol) was treated with BuLi (0.38 mL of 1.6 N solution in hexanes, 0.6 mmol) in Et_2O (10 mL) and carbene complex **1a** (180 mg, 0.4 mmol) to afford compound **diast-4j** (76 mg, 80%) as a colorless oil. R_f 0.36 (hexanes:ethyl acetate, 2:1). ^1H NMR (300 MHz, C_6D_6) δ = 5.78 (dt, J = 15.4, 6.7 Hz, 1 H; $=\text{CHPr}$), 5.46 (dt, J = 15.4, 1.1 Hz, 1 H; $\text{CH}=\text{CHPr}$), 3.89-3.80 (m, 1 H; CHHO), 3.86 (s, 3 H; OMe), 3.31 (ddd, J = 13.3, 10.8, 2.9 Hz, 1 H; CHHO), 2.72 (dd, J = 15.3, 1.5 Hz, 1 H; CHHCOH), 2.46 (apparent ddt, J = 9.2, 7.7, 1.5 Hz, 1 H; CHCOH), 2.31 (dd, J = 15.3, 1.5 Hz, 1 H; CHHCOH), 1.98 (qd, J = 6.7, 1.1 Hz, 2 H; $=\text{CHCH}_2\text{Et}$), 1.66-1.28 (m, 7 H; OH, $(\text{CH}_2)_2\text{CH}_2\text{O}$ and CH_2Me), 0.91 (t, J = 7.2 Hz, 3 H; Me). ^{13}C NMR (75 MHz, C_6D_6) δ = 135.0, 130.9, 128.2, 127.5, 74.7, 68.3, 57.6, 47.9, 44.9, 34.4, 24.6, 22.6, 21.5, 13.6. HRMS (EI) calcd. for $\text{C}_{14}\text{H}_{22}\text{O}_3$: 238.1569, found 238.1566. Elemental analysis calcd. for $\text{C}_{14}\text{H}_{22}\text{O}_3$: C, 70.56, H, 9.30; found C, 70.69, H, 9.15.

(4a*S*^{*},5*R*^{*})-2,3,4,4a,5,6-Hexahydro-7-methoxy-5-(2-methyl-1-propen-1-yl)penta[*b*]pyran-5-ol (*diast*-4k). Silyl enol ether **6k** (102 mg, 0.6 mmol) was treated with BuLi (0.38 mL of 1.6 N solution in hexanes, 0.6 mmol) in Et_2O (10 mL) and carbene complex **1a** (180 mg, 0.4 mmol) to afford compound **diast-4k** (81 mg, 90%) as a colorless oil. R_f 0.23 (hexanes:ethyl acetate, 5:1). ^1H NMR (300 MHz, C_6D_6) δ = 5.37-5.35 (m, 1 H; $\text{CH}=$), 3.87-3.83 (m, 1 H; CHHO), 3.86 (s, 3 H; OMe), 3.32 (ddd, J = 12.5, 10.8, 2.3 Hz, 1 H; CHHO), 2.81 (dd, J = 14.8, 1.8 Hz, 1 H; CHC=), 2.62 (dd, J = 14.8, 1.8 Hz, 1 H; CHC=), 2.54 (apparent ddt, J = 9.2, 8.1, 1.8 Hz, 1 H; CH), 1.84 (d, J = 0.8 Hz, 3 H; Me), 1.61-1.29 (m, 5 H) (OH and $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 1.67 (d, J = 1.4 Hz, 3 H; Me). ^{13}C NMR (75 MHz, C_6D_6) δ = 135.1, 131.1, 130.4, 127.6, 74.5, 68.3, 57.3, 50.0, 45.9, 26.8, 24.7, 22.3, 19.0. HRMS (EI) calcd. for $\text{C}_{13}\text{H}_{20}\text{O}_3$: 224.1412, found 224.1410. Elemental analysis calcd. for $\text{C}_{13}\text{H}_{20}\text{O}_3$: C, 69.61, H, 8.99; found C, 69.72, H, 8.87.

(4a*S*^{*},5*S*^{*})-2,3,4,4a,5,6-Hexahydro-5-(5,6-dihydro-4*H*-pyran-2-yl)-7-methoxycyclopenta[*b*]pyran-5-ol (*diast*-4l).

Silyl enol ether **6l** (119 mg, 0.6 mmol) was treated with BuLi (0.38 mL of 1.6 N solution in hexanes, 0.6 mmol) in Et₂O (10 mL) and carbene complex **1a** (180 mg, 0.4 mmol) to afford compound **diast-4l** (94 mg, 93%) as a colorless oil. R_f 0.53 (hexanes:ethyl acetate, 2:1). ¹H (400 MHz, C₆D₆) δ = 4.92 (t, *J* = 3.8 Hz, 1 H; CH=), 3.83-3.76 (m, 1 H; CH₂O from the bicyclic), 3.81 (s, 3 H; OMe), 3.66 (t, *J* = 5.0 Hz, 2 H; CH₂O pyran ring), 3.31 (ddd, *J* = 12.3, 11.0, 2.6 Hz, 1 H; CH₂O from the bicyclic), 3.15 (dd, *J* = 15.4, 1.4 Hz, 1 H; CHC=), 2.93 (apparent tt, *J* = 8.4, 1.4 Hz, 1 H; CH), 2.27 (dd, *J* = 15.4, 1.4 Hz, 1 H; CHC=), 1.89 (br s, 1 H; OH), 1.84-1.19 (m, 8 H; 2xCH₂CH₂CH₂O). ¹³C NMR (100 MHz, C₆D₆) δ = 156.0, 130.9, 128.5, 94.5, 75.1, 68.1, 57.8, 45.7, 42.7, 25.0, 22.6, 22.5, 20.2. HRMS (EI) calcd. for C₁₄H₂₀O₄: 252.1362, found 252.1360. Elemental analysis calcd. for C₁₄H₂₀O₄: C, 66.65, H, 7.99; found C, 66.79, H, 7.82.

(4a*S*^{*},5*S*^{*})-5-(1-Cyclohexenyl)-2,3,4,4a,5,6-hexahydro-7-methoxycyclopenta[*b*]pyran-5-ol (*diast*-4m). Silyl enol ether **6m** (118 mg, 0.6 mmol) was treated with BuLi (0.38 mL of 1.6 N solution in hexanes, 0.6 mmol) in THF (10 mL) and carbene complex **1a** (180 mg, 0.4 mmol) to afford compound **diast-4c** (85 mg, 85%) as a colorless oil. R_f 0.23 (hexanes:ethyl acetate, 5:1). ¹H NMR (300 MHz, C₆D₆) δ = 5.79-5.68 (m, 1 H; C=CH), 3.82-3.73 (m, 1 H; CH₂O), 3.70 (s, 3 H; OMe), 3.26 (ddd, *J* = 11.8, 10.8, 2.6 Hz, 1 H; CH₂O), 2.72 (dd, *J* = 15.2, 1.4 Hz, 1 H; CHHCOH), 2.60 (apparent ddt, *J* = 12.6, 6.7, 1.4 Hz, 1 H; CH), 2.19 (dd, *J* = 15.2, 1.4 Hz, 1 H; CHHCOH), 2.01-1.21 (m, 13 H; OH, CH₂CH₂CH₂O and (CH₂)₄). ¹³C NMR (75 MHz, C₆D₆) δ = 140.1, 131.0, 126.5, 120.4, 76.9, 68.3, 57.7, 45.5, 43.1, 25.3, 25.2, 24.8, 23.1, 22.5. HRMS (EI) calcd. for C₁₅H₂₂O₃: 250.1569, found 250.1572. Elemental analysis calcd. for C₁₅H₂₂O₃: C, 71.97, H, 8.86; found C, 72.11, H, 8.73.

(4a*S*^{*},5*S*^{*})-2,3,4,4a,5,6-Hexahydro-5-(hexin-1-yl)-7-methoxycyclopenta[*b*]pyran-5-ol (*diast*-4o). Silyl enol ether **6o** (118 mg, 0.6 mmol) was treated with BuLi (0.38 mL of 1.6 N solution in hexanes, 0.6 mmol) in Et₂O (10 mL) and carbene complex **1a** (180 mg, 0.4 mmol) to afford compound **diast-4o** (90 mg, 90%) as a colorless oil. R_f 0.26 (hexanes:ethyl acetate, 5:1). ¹H NMR (300 MHz, C₆D₆) δ = 3.84-3.77 (m, 1 H; CH₂O), 3.82 (s, 3 H; OMe), 3.31 (ddd, *J* = 12.1, 10.8, 2.6 Hz, 1 H; CH₂O), 3.10 (dd, *J* = 15.4, 1.3 Hz, 1 H; CHC=), 2.92 (apparent ddt, *J* = 10.5, 5.9, 1.3 Hz, 1 H; CH), 2.68 (dd, *J* = 15.4, 1.3 Hz, 1 H; CHC=), 2.21 (br s, 1 H; OH), 2.03 (t, *J* = 6.8 Hz, 2 H; CH₂Pr), 1.84-1.26 (m, 8 H; (CH₂)₂Me and CH₂CH₂CH₂O), 0.78 (t, *J* = 7.0, 3 H; Me). ¹³C NMR (75 MHz, C₆D₆) δ = 130.4, 127.0, 83.8, 83.3, 68.3, 67.8, 57.7, 50.1, 46.7, 30.8, 24.5, 22.0, 21.9, 18.4, 13.5. HRMS (EI) calcd. for

$C_{15}H_{22}O_3$: 250.1569, found 250.1567. Elemental analysis calcd. for $C_{15}H_{22}O_3$: C, 71.97, H, 8.86; found C, 72.12, H, 8.73.

(4a*S*^{*},5*S*^{*})-2,3,4,4a,5,6-Hexahydro-7-methoxy-5-

(trimethylsilylethynyl)cyclopenta[*b*]pyran-5-ol (*diast*-4p). Silyl enol ether **6p** (127 mg, 0.6 mmol) was treated with BuLi (0.38 mL of 1.6 N solution in hexanes, 0.6 mmol) in Et₂O (10 mL) and carbene complex **1a** (180 mg, 0.4 mmol) to afford compound **diast-4p** (89 mg, 84%) as a colorless oil. R_f 0.31 (hexanes:ethyl acetate, 5:1). ¹H NMR (300 MHz, C₆D₆) δ = 3.81-3.76 (m, 1 H; CH₂), 3.79 (s, 3 H; OMe), 3.27 (ddd, J = 12.8, 10.8, 2.5 Hz, 1 H; CH₂), 3.10 (dd, J = 15.5, 1.3 Hz, 1 H; CHC=), 2.93 (apparent ddt, J = 12.0, 5.7, 1.3 Hz, 1 H; CH), 2.61 (dd, J = 15.5, 1.3 Hz, 1 H; CHC=), 2.24 (br s, 1 H; OH), 1.83-1.77 and 1.29-1.22 (2xm, 2 H; CH₂CH₂CH₂), 1.72 (qd, J = 12.8, 4.0 Hz, 1 H; CH₂CH₂), 1.42 (qt, J = 12.8, 4.0 Hz, 1 H; CH₂CH₂CH₂), 0.25 (s, 9 H; TMS). ¹³C NMR (75 MHz, C₆D₆) δ = 130.2, 126.8, 109.4, 86.8, 68.2, 67.9, 57.7, 49.8, 46.4, 24.3, 21.9, -0.2. HRMS (EI) calcd. for $C_{14}H_{22}O_3Si$: 266.1338, found 266.1334.

General Procedure for the Preparation of Ketones 10 and 14. In a flame dried round-bottom flask under nitrogen a solution of enolates **2a-f,h,k** was prepared by treatment of the corresponding ketones **3** (0.44 mmol) with a solution of lithium diisopropilamide (0.44 mmol) in THF (10 mL) at -30°C for 30 minutes. The mixture was cooled to -60°C and carbene complex **1a,11** (0.4 mmol) was added. Once the intense color from the carbene turned much softer, the reaction was quenched with silica gel and purified by flash column chromatography (hexanes:ethyl acetate 20:1).

(E)-4-Methoxy-4-(tetrahydropyran-2-ylidene)-2-butanone (10a). Acetone (26 mg, 0.44 mmol) was treated with LDA (0.44 mmol) in THF (10 mL) and carbene complex **1a** (180 mg, 0.4 mmol) to afford ketone **10a** (68 mg, 92%) as a colorless oil. R_f 0.66 (hexanes:ethyl acetate, 2:1). ¹H NMR (300 MHz, C₆D₆) δ = 3.52 (t, J = 5.0 Hz, 2 H; CH₂O), 3.28 (s, 2 H; CH₂CO), 3.22 (s, 3 H; OMe), 2.29 (t, J = 6.0 Hz, 2 H; CH₂C(-O-)C), 1.94 (s, 3 H; Me), 1.41-1.18 (m, 4 H; CH₂CH₂CH₂O). ¹³C NMR (75 MHz, C₆D₆) δ = 204.2, 144.2, 138.3, 69.6, 57.4, 41.6, 28.3, 25.8, 23.1. HRMS (EI) calcd. for $C_{10}H_{16}O_3$: 184.1099, found 184.1102.

(E)-1-Methoxy-5-methyl-1-(tetrahydropyran-2-ylidene)-3-hexanone (10b). 4-Methyl-2-pentanone (44 mg, 0.44 mmol) was treated with LDA (0.44 mmol) in THF (10 mL) and carbene complex **1a** (180 mg, 0.4 mmol) to afford ketone **10b** (81 mg, 90%) as a colorless oil. R_f 0.63 (hexanes:ethyl acetate, 5:1). ¹H NMR (300 MHz, CDCl₃) δ = 3.78 (t, J = 5.2 Hz, 2 H;

CH_2O), 3.43 (s, 3 H; OMe), 3.28 (s, 2 H; CH_2CO), 2.38-2.31 (m, 2 H; $\text{CH}_2\text{C}(-\text{O}-)=\text{C}$), 2.34 (d, $J = 6.7$ Hz, 2 H; CH_2CHMe_2), 2.12 (n, $J = 6.7$ Hz, 1 H; CHMe_2), 1.71-1.64 (m, 4 H; $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 0.91 (d, $J = 6.7$ Hz, 6 H; Me₂). ¹³C NMR (75 MHz, CDCl_3) $\delta = 208.3, 143.8, 135.8, 69.9, 58.0, 50.3, 41.1, 25.6, 24.3, 23.0, 22.9, 22.4$. HRMS (EI) calcd. for $\text{C}_{13}\text{H}_{22}\text{O}_3$: 226.1569, found 226.1575.

(E)-1-Methoxy-4-methyl-1-(tetrahydropyran-2-ylidene)-3-pentanone (10c). 3-Methyl-2-butanone (38 mg, 0.44 mmol) was treated with LDA (0.44 mmol) in THF (10 mL) and carbene complex **1a** (180 mg, 0.4 mmol) to afford ketone **10c** (77 mg, 91%) as a colorless oil. R_f 0.61 (hexanes:ethyl acetate, 5:1). ¹H NMR (300 MHz, CDCl_3) $\delta = 3.82-3.73$ (m, 2 H; CH_2O), 3.43 (s, 3 H; OMe), 3.38 (s, 2 H; CH_2CO), 2.78 (h, $J = 6.9$ Hz, 1 H; CHMe_2), 2.39-2.32 (m, 2 H; $\text{CH}_2\text{C}(-\text{O}-)=\text{C}$), 1.72-1.64 (m, 4 H; $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 1.11 (d, $J = 6.9$ Hz, 6 H; Me₂). ¹³C NMR (75 MHz, CDCl_3) $\delta = 212.2, 144.7, 136.1, 70.0, 58.2, 39.5, 38.7, 25.9, 23.3, 23.2, 18.2$. HRMS (EI) calcd. for $\text{C}_{12}\text{H}_{20}\text{O}_3$: 212.1412, found 212.1419.

(E)-1-Methoxy-4,4-dimethyl-1-(tetrahydropyran-2-ylidene)-3-pentanone (10d). Pinacolone (44 mg, 0.44 mmol) was treated with LDA (0.44 mmol) in THF (10 mL) and carbene complex **1a** (180 mg, 0.4 mmol) to afford ketone **10d** (78 mg, 86%) as a colorless oil. R_f 0.63 (hexanes:ethyl acetate, 5:1). ¹H NMR (300 MHz, C_6D_6) $\delta = 3.60$ (t, $J = 5.3$ Hz, 2 H; CH_2O), 3.40 (s, 2 H; CH_2CO), 3.35 (s, 3 H; OMe), 2.33 (t, $J = 6.2$ Hz, 2 H; $\text{CH}_2\text{C}(-\text{O}-)=\text{C}$), 1.43-1.27 (m, 4 H; $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 1.04 (s, 9 H; Me₃). ¹³C NMR (75 MHz, C_6D_6) $\delta = 210.7, 144.0, 137.1, 69.6, 57.9, 44.2, 35.4, 26.3, 25.9, 23.3$. HRMS (EI) calcd. for $\text{C}_{13}\text{H}_{20}\text{O}_3$: 226.1569, found 226.1576.

(E)-3-Methoxy-1-phenyl-3-(tetrahydropyran-2-ylidene)-1-propanone (10e). Acetophenone (53 mg, 0.44 mmol) was treated with LDA (0.44 mmol) in THF (10 mL) and carbene complex **1a** (180 mg, 0.4 mmol) to afford ketone **10e** (93 mg, 94%) as a colorless oil. R_f 0.55 (hexanes:ethyl acetate, 5:1). ¹H NMR (300 MHz, CDCl_3) $\delta = 8.08-7.47$ (m, 5 H; ArH), 3.92 (s, 2 H; CH_2CO), 3.77 (t, $J = 5.4$ Hz, 2 H; CH_2O), 3.50 (s, 3 H; OMe), 2.36 (t, $J = 6.1$ Hz, 2 H; $\text{CH}_2\text{C}(-\text{O}-)=\text{C}$), 1.71-1.62 (m, 4 H; $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$). ¹³C NMR (75 MHz, CDCl_3) $\delta = 197.5, 144.5, 136.5, 136.0, 132.8, 128.3, 69.8, 58.5, 37.1, 25.6, 23.0, 22.9$. HRMS (EI) calcd. for $\text{C}_{15}\text{H}_{18}\text{O}_3$: 246.1256, found 246.1263.

(E)-3-Methoxy-1-(4-methoxyphenyl)-3-(tetrahydropyran-2-ylidene)-1-propanone (10f). 4'-Methoxyacetophenone (66 mg, 0.44 mmol) was treated with LDA (0.44 mmol) in THF (10 mL) and carbene complex **1a** (180 mg, 0.4 mmol) to afford ketone **10f** (106 mg, 96%) as a

colorless oil. R_f 0.44 (hexanes:ethyl acetate, 5:1). ^1H NMR (300 MHz, CDCl_3) δ = 8.03 and 6.94 (2xd, J = 6.9 Hz, 4 H; ArH), 3.90 (s, 5 H; $\text{CH}_2\text{C}=\text{O}$ and OMe), 3.82 (t, J = 5.2 Hz, 2 H, CH_2O), 3.52 (s, 3 H; OMe), 2.38 (t, J = 5.6, 2 H; $\text{CH}_2\text{C}(-\text{O}-)=\text{C}$), 1.75-1.63 (m, 4 H; $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$). ^{13}C NMR (75 MHz, CDCl_3) δ = 196.1, 163.2, 144.2, 136.4, 130.7, 129.6, 113.5, 69.9, 58.5, 55.3, 36.9, 25.7, 22.9, 22.8. HRMS (EI) calcd. for $\text{C}_{16}\text{H}_{20}\text{O}_4$: 276.1362, found 276.1365.

(E)-1-Methoxy-5-methyl-1-(tetrahydropyran-2-ylidene)-4-hexen-3-one (10k). Mesityl oxide (43 mg, 0.44 mmol) was treated with LDA (0.44 mmol) in THF (10 mL) and carbene complex **1a** (180 mg, 0.4 mmol) to afford ketone **10a** (83 mg, 92%) as a colorless oil. R_f 0.56 (hexanes:ethyl acetate, 5:1). ^1H NMR (300 MHz, C_6D_6) δ = 6.81 (s, 1 H; CH=), 3.69 (t, J = 5.4 Hz, 2 H; CH_2O), 3.57 (s, 2 H; CH_2CO), 3.42 (s, 3 H; OMe), 2.44 (d, J = 6.0 Hz, 2 H; $\text{CH}_2\text{C}(-\text{O}-)=\text{C}$), 2.22 and 1.54 (2xs, 6 H; 2xMe), 1.46-1.37 (m, 4 H; $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$). ^{13}C NMR (75 MHz, C_6D_6) δ = 196.6, 154.3, 144.1, 137.0, 123.2, 69.8, 57.5, 42.5, 27.1, 25.9, 23.3, 20.4. HRMS (EI) calcd. for $\text{C}_{13}\text{H}_{20}\text{O}_3$: 224.1412, found 224.1408.

(E,E)-5-Methoxy-6-methyl-1-phenyl-1,4-octadien-3-one (14). Benzylidenacetone (64 mg, 0.44 mmol) was treated with LDA (0.44 mmol) in THF (10 mL) and carbene complex **11** (169 mg, 0.4 mmol) to afford ketone **14** (87 mg, 89%) as a colorless oil. R_f 0.54 (hexanes:ethyl acetate, 5:1). ^1H NMR (400 MHz, C_6D_6) δ = 7.61-7.31 (m, 6 H; ArH and $\text{CH}=\text{CH}$), 6.75 (d, J = 15.9 Hz, 1 H; $\text{CH}=\text{CH}$), 5.55 (s, 1 H; C=CH), 3.99 (apparent h, J = 6.7 Hz, 1 H; CHMe), 3.72 (s, 3 H; OMe), 1.67-1.33 (m, 2 H; CH_2Me), 1.12 (d, J = 6.7 Hz, 3 H; MeCH), 0.82 (t, J = 7.3 Hz, 3 H; MeCH₂). ^{13}C NMR (100 MHz, C_6D_6) δ = 187.6, 181.0, 140.3, 135.0, 129.6, 129.0, 128.6, 127.9, 99.0, 55.4, 36.3, 27.1, 17.5, 11.8. HRMS (EI) calcd. for $\text{C}_{16}\text{H}_{20}\text{O}_2$: 244.1464, found 244.1469.

3-Butyl-4-(5,6-dihydro-4*H*-pyran-2-yl)-4-methoxy-2-cyclopentenone (15b). Ketone **3o** (63 mg, 0.44 mmol) was treated with LDA (0.44 mmol) and carbene complex **1a** (180 mg, 0.4 mmol) in THF to afford, after reflux for 20 hours, compound **15b** (72 mg, 72%) as a colorless oil. R_f 0.36 (hexanes:ethyl acetate, 5:1). ^1H NMR (300 MHz, C_6D_6) δ = 6.12 (s, 1 H; $\text{CBu}=\text{CH}$), 5.28 (t, J = 3.9 Hz, 1 H; =CH pyran ring), 3.61 (td, J = 5.0, 1.7 Hz, 2 H; CH_2O), 2.92 (s, 3 H; OMe), 2.91 (d, J = 17.7 Hz, 1 H; CHHCO), 2.54 (d, J = 17.7, 1 H; CHHCO), 2.26 (tt, J = 8.3, 2.0 Hz, 2 H; CH_2Pr), 1.90-1.82 (m, 2 H; CHCH_2 pyran ring), 1.46-1.19 (m, 6 H; $\text{CH}_2\text{CH}_2\text{O}$ and $(\text{CH}_2)_2\text{Me}$), 0.87 (3 H, t, J = 7.2 Hz, Me). ^{13}C NMR (75 MHz, C_6D_6) δ =

203.0, 177.9, 151.8, 131.5, 96.5, 85.2, 66.1, 50.4, 42.6, 29.0, 26.9, 22.6, 22.3, 19.9, 13.8. HRMS (EI) calcd. for C₁₅H₂₂O₃: 250.1569, found 250.1560.

(E)-3-{(3*S)-3-[(*S**)-1-Hydroxy-1-phenylmethyl]-tetrahydropyran-2-ylidene}-3-methoxy-1-phenyl-1-propanone (19b).** Acetophenone (58 mg, 0.48 mmol), was treated with LDA (0.48 mmol) in THF (10 mL), carbene complex **1a** (180 mg, 0.4 mmol) and benzaldehyde (85 mg, 0.8 mmol) to afford compound **19b** (82 mg, 58%) as a colorless oil. R_f 0.26 (hexanes:ethyl acetate, 2:1). ¹H NMR (300 MHz, CDCl₃) δ = 7.99-7.16 (m, 10 H; ArH), 4.97 (d, *J* = 8.3 Hz, 1 H; CHPh), 4.12-4.03 (m, 1 H; CHHO), 3.85 (d, *J* = 15.7 Hz, 1 H; CHHCO), 3.68 (d, *J* = 15.7 Hz, 1 H; CHHCO), 3.51-3.49 (m, 1 H; CHHO), 3.13-3.06 (m, 1 H; CHCHOH), 2.92 (s, 3 H; OMe), 2.63 (br s, 1 H; OH), 2.24-1.37 (m, 4 H; CH₂CH₂CH₂O). ¹³C NMR (75 MHz, CDCl₃) δ = 197.1, 143.8, 143.3, 137.9, 136.2, 132.9, 128.4, 128.3, 127.7, 127.1, 126.3, 73.8, 70.7, 57.0, 39.9, 36.2, 23.3, 21.6.

(1*E*,5*E*)-5-{(3*S)-3-[(*S**)-1-Hydroxy-1-phenylmethyl]-tetrahydropyran-2-ylidene}-5-methoxy-1-phenyl-1-penten-3-one (19c).** Benzylideneacetone (70 mg, 0.48 mmol), was treated with LDA (0.48 mmol) in THF (10 mL), carbene complex **1a** (180 mg, 0.4 mmol) and benzaldehyde (85 mg, 0.8 mmol) to afford compound **19c** (76 mg, 50%) as a colorless oil. R_f 0.33 (hexanes:ethyl acetate, 2:1). ¹H NMR (300 MHz, CDCl₃) δ = 7.61 (d, *J* = 16.2 Hz, 1 H; =CHPh), 7.54-7.18 (m, 10 H; ArH), 6.78 (d, *J* = 16.2 Hz, 1 H; =CHCO), 5.03 (d, *J* = 8.2 Hz, 1 H; CHPh), 4.24-4.17 (m, 1 H; CHHO), 3.62 (ddd, *J* = 10.8, 9.0, 3.6 Hz, 1 H; CHHO), 3.47 (s, 2 H; CH₂CO), 3.14 (ddd, *J* = 8.2, 5.2, 2.4 Hz, 1 H; CHCHOH), 2.91 (s, 3 H; OMe), 2.31-1.26 (m, 5 H; OH and CH₂CH₂CH₂O). ¹³C NMR (75 MHz, CDCl₃) δ = 197.0, 144.0, 143.3, 142.8, 137.8, 134.5, 130.4, 128.8, 128.3, 127.8, 127.3, 126.4, 124.9, 73.9, 71.1, 56.9, 39.9, 39.2, 23.6, 21.7.

Ethyl (E)-3-{(3*S)-3-[(*S**)-1-hydroxy-1-phenylmethyl]-tetrahydropyran-2-ylidene}-3-methoxypropanoate (19d).** Ethyl acetate (42 mg, 0.48 mmol), was treated with LDA (0.48 mmol) in THF (10 mL), carbene complex **1a** (180 mg, 0.4 mmol) and benzaldehyde (85 mg, 0.8 mmol) to afford compound **19d** (76 mg, 59%) as a colorless oil. R_f 0.13 (hexanes:ethyl acetate, 5:1). ¹H NMR (300 MHz, CDCl₃) δ = 7.41-7.22 (m, 5 H; ArH), 5.02 (d, *J* = 8.8 Hz, 1 H; CHPh), 4.13 (q, *J* = 7.4 Hz, 2 H; MeCH₂O), 4.16-4.08 (m, 1 H; CHHO), 3.62 (dd, *J* = 12.2, 9.0 Hz, 1 H; CHHO), 3.33 (d, *J* = 15.9 Hz, 1 H; CHHCO₂), 3.12-3.02 (m, 1 H; CHCHOH), 3.04 (d, *J* = 15.9 Hz, 1 H; CHHCO₂), 2.89 (s, 3 H; OMe), 2.44 (br s, 1 H; OH), 2.21-1.42 (m, 4 H; CH₂CH₂CH₂O), 1.35 (t, *J* = 7.4 Hz, 3 H; CH₂Me). ¹³C NMR (75 MHz,

CDCl_3) δ = 170.7, 144.1, 143.5, 137.6, 127.8, 127.2, 126.4, 73.8, 71.1, 60.6, 56.9, 40.0, 31.5, 23.5, 21.8, 14.1. Elemental analysis calcd. for $\text{C}_{18}\text{H}_{24}\text{O}_5$: C, 67.48, H, 7.55; found C, 67.56, H, 7.39.

Ethyl (E)-3-{(3*S)-3-[(*S**)-1-Hydroxy-1-(2-furyl)-methyl]-tetrahydropyran-2-ylidene}-3-methoxypropanoate (19e).** Ethyl acetate (42 mg, 0.48 mmol), was treated with LDA (0.48 mmol) in THF (10 mL), carbene complex **1a** (180 mg, 0.4 mmol) and furfural (85 mg, 0.8 mmol) to afford compound **19e** (71 mg, 57%, 94%de) as a colorless oil. R_f 0.26 (hexanes:ethyl acetate, 2:1). ^1H NMR (300 MHz, CDCl_3) δ = 7.40 (s, 1 H; =CHO) and 6.36-6.33 (m, 2 H; CH=CH), 5.06 (d, J = 8.3 Hz, 1 H; CH-2-Fu), 4.20-4.11 (m, 1 H; CHHO), 4.17 (q, J = 7.0 Hz, 2 H; MeCH_2O), 3.64 (td, J = 11.3, 3.1 Hz, 1 H; CHHO), 3.37 (d, J = 16.3 Hz, 1 H; CHHCO_2), 3.35-3.28 (m, 1 H; CHCHOH), 3.26 (s, 3 H; OMe), 3.17 (d, J = 16.3 Hz, 1 H; CHHCO_2), 2.52 (br s, 1 H, OH), 2.30-2.23 (m, 1 H; CHHCH_2O), 2.08 (qt, J = 13.1, 4.4 Hz, 1 H; CHHCH_2O), 1.74 (tt, J = 13.1, 4.8 Hz, 1 H; $\text{CHHCH}_2\text{CH}_2\text{O}$), 1.55-1.48 (m, 1 H; $\text{CHHCH}_2\text{CH}_2\text{O}$), 1.24 (t, J = 7.0 Hz, 3 H; CH_2Me). ^{13}C NMR (75 MHz, CDCl_3) δ = 170.7, 155.4, 143.7, 141.4, 138.0, 110.0, 106.5, 71.0, 67.6, 60.6, 57.5, 37.5, 31.7, 23.7, 21.5, 14.0. Elemental analysis calcd. for $\text{C}_{16}\text{H}_{22}\text{O}_6$: C, 61.92, H, 7.15; found C, 62.16, H, 6.99.

(1*R*,2*S*,5*R*)-5-Methyl-2-(1-methyl-1-phenylethyl)cyclohexyl (E)-3-{(3*S*)-3-[(*S*)-1-hydroxy-1-phenylmethyl]-tetrahydropyran-2-ylidene}-3-methoxypropanoate/ (1*R*,2*S*,5*R*)-5-Methyl-2-(1-methyl-1-phenylethyl)cyclohexyl (E)-3-{(3*R*)-3-[(*R*)-1-hydroxy-1-phenylmethyl]-tetrahydropyran-2-ylidene}-3-methoxypropanoate (19f). (1*R*,2*S*,5*R*)-5-Methyl-2-(1-methyl-1-phenylethyl)cyclohexyl acetate (132 mg, 0.48 mmol), was treated with LDA (0.48 mmol) in THF (10 mL), carbene complex **1a** (180 mg, 0.4 mmol) and benzaldehyde (85 mg, 0.8 mmol) to afford compound **19f** (136 mg, 67%) as a colorless oil. R_f 0.48. Mixture of diastereoisomers 2:1.(hexanes:ethyl acetate, 5:1). ^1H NMR (300 MHz, CDCl_3) δ = 7.40-7.14 (m, 20 H; ArH), 5.02 (d, J = 8.6 Hz, 2 H; CHPh), 4.88-4.71 (m, 2 H; CHOCO), 4.20-4.02 (m, 2 H; CHHO), 3.71-3.52 (m, 2 H; CHCHOH), 3.08-3.00 (m, 2 H; CHHO), 3.02 (d, J = 16.0 Hz, 1 H; CHHCO_2 , major d.), 2.72 (s, 3 H; OMe, minor d.), 2.71 (d, J = 16.0 Hz, 1 H; CHHCO_2 , minor d.), 2.70 (s, 3 H; OMe, major d.), 2.58 (d, J = 16.0 Hz, 1 H; CHHCO_2 , minor d.), 2.49 (d, J = 16.0 Hz, 1 H; CHHCO_2 , major d.), 2.22-0.81 (m, 42 H; $(\text{CH}_2)_2\text{CHMeCH}_2\text{CHCM}_2$ and $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$). ^{13}C NMR (75 MHz, CDCl_3) δ = 169.9, 151.3, 143.9, 143.4, 137.5, 127.9, 127.8, 127.1, 126.3, 125.3, 125.0, 74.8, 73.9, 73.8, 71.1, 70.9, 56.8, 50.3, 41.4, 40.0, 39.7, 34.4, 31.4, 31.2, 27.1, 26.8, 26.6, 26.1, 25.7, 23.3, 21.9, 21.7. **(1*S**,6*S**,7*S**,9*R**,11*S**)-9-*tert*-Butyl-11-methoxy-7-phenyl-2,8,12-**

trioxatricyclo[7.2.1.0^{1,6}]dodecane (20b). Pinacolone (48 mg, 0.48 mmol) was treated with LDA (0.48 mmol), carbene complex **1a** (180 mg, 0.4 mmol), benzaldehyde (85 mg, 0.8 mmol) and CHCl₃ (10 mL) to afford compound **20b** (60 mg, 45%) as a white solid. M.p.: 119-121°C (CHCl₃). R_f 0.53 (hexanes:ethyl acetate, 5:1). ¹H NMR (400 MHz, CDCl₃) δ = 7.41-7.26 (m, 5 H; ArH), 5.43 (d, J = 4.3 Hz, 1 H; CHPh), 3.94-3.76 (m, 2 H; CH₂O), 3.72 (dd, J = 11.0, 4.5 Hz, 1 H; CHOMe), 3.53 (s, 3 H; OMe), 2.66 (dd, J = 14.3, 11.0 Hz, 1 H; CHHCHOMe), 2.06 (dt, J = 12.3, 4.3 Hz, 1 H; CHCHPh), 1.85 (dd, J = 14.3, 4.5 Hz, 1 H; CHHCHOMe), 1.62-1.44 and 0.97-0.86 (2xm, 4 H; CH₂CH₂CH₂O), 1.14 (s, 9 H; t-Bu). ¹³C NMR (100 MHz, CDCl₃) δ = 140.2, 127.9, 126.6, 125.6, 108.8, 104.6, 84.4, 72.8, 64.1, 58.4, 38.1, 37.0, 34.6, 24.6, 18.9 (CH₂). HRMS (FAB) calcd. for C₂₀H₂₉O₄ (M+H)⁺: 333.2066, found 333.2070. Elemental analysis calcd. for C₂₀H₂₈O₄: C, 72.26, H, 8.49; found C, 72.38, H, 8.38.

(1S*,6S*,7S*,9R*,11S*)-9-tert-Butyl-7-(2-furyl)-11-methoxy-2,8,12-

trioxatricyclo[7.2.1.0^{1,6}]dodecane (20c). Pinacolone (48 mg, 0.48 mmol) was treated with LDA (0.48 mmol), carbene complex **1a** (180 mg, 0.4 mmol), furfural (77 mg, 0.8 mmol) and CHCl₃ (10 mL) to afford compound **20c** (41 mg, 32%) as a white solid. M.p.: 95-97°C (CHCl₃). R_f 0.62 (hexanes:ethyl acetate, 5:1). ¹H NMR (300 MHz, CDCl₃) δ = 7.38 (d, J = 1.8 Hz, 1 H; =CHO), 6.36 (dd, J = 3.1, 1.8 Hz, 1 H; CH=CHO), 6.24 (dt, J = 3.1 Hz, 1 H; C=CH), 5.40 (d, J = 4.4 Hz, 1 H; CH-2-Fu), 3.95-3.74 (m, 2 H; CH₂O), 3.66 (dd, J = 11.0, 4.6 Hz, 1 H; CHOMe), 3.48 (s, 3 H; OMe), 2.63 (dd, J = 14.3, 11.0 Hz, 1 H; CHHCHOMe), 2.13 (dt, J = 12.3, 4.4 Hz, 1 H; CHCH-2-Fu), 1.77 (dd, J = 14.3, 4.6 Hz, 1 H; CHHCHOMe), 1.65-1.51 and 1.09-1.02 (2xm, 4 H; CH₂CH₂CH₂O), 1.04 (9 H, s, t-Bu). ¹³C NMR (75 MHz, CDCl₃) δ = 153.6, 141.1, 109.9, 109.2, 105.9, 104.3, 84.2, 69.3, 64.2, 58.4, 36.8, 34.5, 24.5, 19.3. HRMS (FAB) calcd. for C₁₈H₂₇O₅ (M+H)⁺: 323.1859, found 323.1848. Elemental analysis calcd. for C₁₈H₂₆O₅: C, 67.06, H, 8.13; found C, 67.13, H, 8.00.

(1S*,6S*,7S*,9R*,11S*)-7,9-Diphenyl-11-methoxy-2,8,12-

trioxatricyclo[7.2.1.0^{1,6}]dodecane (20d). Acetophenone (58 mg, 0.48 mmol) was treated with LDA (0.48 mmol), carbene complex **1a** (180 mg, 0.4 mmol), benzaldehyde (85 mg, 0.8 mmol) and CHCl₃ (10 mL) to afford compound **20d** (72 mg, 51%) as a white solid. M.p.: 183-185°C (CHCl₃). R_f 0.51 (hexanes:ethyl acetate, 5:1). ¹H NMR (300 MHz, CDCl₃) δ = 7.72-7.26 (m, 10 H; ArH), 5.65 (d, J = 4.1 Hz, 1 H; CHPh), 4.02-3.81 (m, 3 H; CH₂O and CHOMe), 3.57 (s, 3 H; OMe), 2.75 (dd, J = 14.4, 11.0 Hz, 1 H; CHHCHOMe), 2.38 (dd, J = 14.4, 4.4 Hz, 1 H; CHHCHOMe), 2.19 (dt, J = 12.5, 4.1 Hz, 1 H; CHCHPh), 1.71-1.49 and

1.00-0.89 (2xm, 4 H; $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$). ^{13}C NMR (75 MHz, CDCl_3) δ = 141.2, 139.3, 128.2, 128.0, 126.9, 125.8, 125.1, 105.5, 104.4, 84.2, 73.6, 64.4, 58.6, 42.4, 38.2, 24.5, 18.9. HRMS (FAB) calcd. for $\text{C}_{22}\text{H}_{25}\text{O}_4$ ($\text{M}+\text{H}$) $^+$: 353.1753, found 353.1767. Elemental analysis calcd. for $\text{C}_{22}\text{H}_{24}\text{O}_4$: C, 74.98, H, 6.86; found C, 75.09, H, 6.74.

(1*S*^{*,6*S*^{*,7*S*^{*,9*R*^{*,11*S*^{*}}}}}-11-methoxy-9-(4-methoxyphenyl)-7-phenyl-2,8,12-trioxatricyclo[7.2.1.0^{1,6}]dodecane (20e). 4'-Methoxyacetophenone (72 mg, 0.48 mmol) was treated with LDA (0.48 mmol), carbene complex **1a** (180 mg, 0.4 mmol), benzaldehyde (85 mg, 0.8 mmol) and CHCl_3 (10 mL) to afford compound **20e** (73 mg, 48%) as a white solid. M.p.: 131-133°C (CHCl_3). R_f 0.48 (hexanes:ethyl acetate, 5:1). ^1H NMR (300 MHz, CDCl_3) δ = 7.62 (d, J = 8.9 Hz, 2 H; ArH), 7.41-7.22 (m, 5 H; ArH), 6.94 (d, J = 8.9 Hz, 2 H; ArH), 5.63 (d, J = 4.1 Hz, 1 H; CHPh), 3.98-3.91 (m, 2 H; CH_2O), 3.88-3.82 (m, 1 H; CHOMe), 3.84 (s, 3 H; OMe), 3.54 (s, 3 H; OMe), 2.76 (dd, J = 14.4, 11.0 Hz, 1 H; CHHCHOMe), 2.37 (dd, J = 14.4, 4.3, 1 H; CHHCHOMe), 2.18 (dt, J = 12.7, 4.1 Hz, 1 H; CHCHPh), 1.77-1.48 and 0.99-0.92 (2xm, 4 H; $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$). ^{13}C NMR (75 MHz, CDCl_3) δ = 159.5, 139.4, 133.6, 128.0, 126.9, 126.5, 125.8, 113.4, 105.4, 104.4, 84.2, 73.6, 64.4, 58.6, 55.3, 42.3, 38.2, 24.5, 18.9. HRMS (FAB) calcd. for $\text{C}_{23}\text{H}_{27}\text{O}_5$ ($\text{M}+\text{H}$) $^+$: 383.1858, found 383.1845. Elemental analysis calcd. for $\text{C}_{23}\text{H}_{26}\text{O}_5$: C, 72.23, H, 6.85; found C, 72.29, H, 6.74.

(1*S*^{*,6*S*^{*,7*S*^{*,9*R*^{*,11*S*^{*}}}}-7-(2-furyl)-11-methoxy-9-(4-methoxyphenyl)-2,8,12-trioxatricyclo[7.2.1.0^{1,6}]dodecane (20f).} 4'-Methoxyacetophenone (72 mg, 0.48 mmol) was treated with LDA (0.48 mmol), carbene complex **1a** (180 mg, 0.4 mmol), furfural (77 mg, 0.8 mmol) and CHCl_3 (10 mL) to afford compound **20f** (57 mg, 38%) as a white syrup. R_f 0.41 (hexanes:ethyl acetate, 5:1). ^1H NMR (300 MHz, CDCl_3) δ = 7.56 (d, J = 8.9 Hz, 2 H; ArH), 7.41 (d, J = 1.8 Hz, 1 H; =CHO), 6.92 (d, J = 8.9 Hz, 2 H; ArH), 6.37 (dd, J = 3.2, 1.8 Hz, 1 H; $\text{CH}=\text{CHO}$), 6.33 (d, J = 3.2 Hz, 1 H; C=CH), 5.62 (d, J = 4.3 Hz, 1 H; CH-2-Fu), 4.03-3.82 (m, 3 H; CH_2O and CHOMe), 3.84 (s, 3 H; OMe), 3.53 (s, 3 H; OMe), 2.74 (dd, J = 14.5, 11.1 Hz, 1 H; CHHCHOMe), 2.33 (dd, J = 14.5, 4.3 Hz, 1 H; CHHCHOMe), 2.25 (dt, J = 12.8, 4.3 Hz, 1 H; CHCH-2-Fu), 1.93 (qd, J = 12.9, 4.3 Hz, 1 H; $\text{CHHCH}_2\text{CH}_2\text{O}$), 1.66 (qt, J = 12.8, 4.3 Hz, 1 H; CHHCH_2O), 1.21-1.13 (m, 2 H; $\text{CHHCHHCH}_2\text{O}$). ^{13}C NMR (75 MHz, CDCl_3) δ = 159.5, 152.8, 141.4, 133.3, 126.4, 113.4, 110.0, 106.6, 105.1, 104.7, 84.0, 69.9, 64.4, 58.5, 55.3, 42.2, 37.1, 24.5, 19.3. HRMS (FAB) calcd. for $\text{C}_{21}\text{H}_{25}\text{O}_6$ ($\text{M}+\text{H}$) $^+$: 373.1651, found 373.1642.

(1*S*^{*},6*S*^{*},7*S*^{*},9*R*^{*},11*S*^{*})-11-methoxy-7-phenyl-9-[(*E*)-2-phenylethenyl]-2,8,12-trioxatricyclo[7.2.1.0^{1,6}]dodecane (20g). Bencilydenacetone (70 mg, 0.48 mmol) was treated with LDA (0.48 mmol), carbene complex **1a** (180 mg, 0.4 mmol), benzaldehyde (85 mg, 0.8 mmol) and CHCl₃ (10 mL) to afford compound **20g** (68 mg, 45%) as a white solid. M.p.: 108-110°C (CHCl₃). R_f 0.48 (hexanes:ethyl acetate, 5:1). ¹H NMR (300 MHz, CDCl₃) δ = 7.48-7.24 (m, 10 H; ArH), 6.99 and 6.36 (2xd, *J* = 15.9 Hz, 2 H; CH=CH), 5.53 (d, *J* = 4.3 Hz, 1 H; CHPh), 3.99-3.78 (m, 3 H; CH₂O and CHOMe), 3.53 (s, 3 H; OMe), 2.68 (dd, *J* = 14.5, 11.1 Hz, 1 H; CHHCHOMe), 2.21 (dd, *J* = 14.5, 4.3 Hz, 1 H; CHHCHOMe), 2.12 (dt, *J* = 12.5, 4.3 Hz, 1 H; CHCHPh), 1.78-1.48 and 0.99-0.90 (m, 4 H; CH₂CH₂CH₂O). ¹³C NMR (75 MHz, CDCl₃) δ = 139.2, 136.1, 131.1, 128.5, 128.1, 128.0, 127.9, 127.0, 126.8, 125.8, 105.4, 103.4, 84.1, 73.7, 64.4, 58.6, 40.0, 38.3, 24.5, 18.9. HRMS (FAB) calcd. for C₂₄H₂₇O₄ (M+H)⁺: 379.1909, found 379.1900. Elemental analysis calcd. for C₂₄H₂₆O₄: C, 76.17, H, 6.92; found C, 76.25, H, 6.83.

(1*S*^{*},6*S*^{*},7*S*^{*},9*R*^{*},11*S*^{*})-9-(1-cyclohexenyl)-11-methoxy-7-phenyl-2,8,12-trioxatricyclo[7.2.1.0^{1,6}]dodecane (20h). 1-Acetylcylohexene (60 mg, 0.48 mmol) was treated with LDA (0.48 mmol), carbene complex **1a** (180 mg, 0.4 mmol), benzaldehyde (85 mg, 0.8 mmol) and CHCl₃ (10 mL) to afford compound **20h** (60 mg, 42%) as a white solid. M.p.: 127-129°C (CHCl₃). R_f 0.52 (hexanes:ethyl acetate, 5:1). ¹H NMR (300 MHz, CDCl₃) δ = 7.38-7.19 (m, 5 H; ArH), 6.11-6.06 (m, 1 H, =CH), 5.46 (d, *J* = 4.0 Hz, 1 H; CHPh), 3.97-3.72 (m, 3 H; CH₂O and CHOMe), 3.50 (s, 3 H; OMe), 2.65 (dd, *J* = 14.2, 11.1 Hz, 1 H; CHHCHOMe), 2.37-2.03, 1.71-1.46 and 0.97-0.89 (m, 14 H; CHCHPh, CHHCHOMe, (CH₂)₄ and CH₂CH₂CH₂O). ¹³C NMR (75 MHz, CDCl₃) δ = 139.6, 136.6, 128.0, 126.8, 125.8, 123.3, 105.1, 105.0, 84.0, 73.3, 64.3, 58.5, 38.7, 38.2, 24.7, 24.5, 23.5, 22.4, 22.1, 18.9. HRMS (FAB) calcd. for C₂₂H₂₉O₄ (M+H)⁺: 357.2066, found 357.2060. Elemental analysis calcd. for C₂₂H₂₈O₄: C, 74.13, H, 7.92; found C, 74.21, H, 7.86.