Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

for

Angew. Chem. Int. Ed. 200460547

Diastereoselective Synthesis of Cycloheptadienol Derivatives by a Formal [5+2] Carbocyclization Reaction of α,β,γ,δ-Diunsaturated (Methoxy)carbene Complexes with Methyl Ketone Lithium Enolates

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General. All reactions were conducted in flame-dried glassware under an inert atmosphere of nitrogen. TLC was performed on aluminium-backed plates coated with silica gel 60 with F_{254} indicator. Flash column chromatography was carried out on deactivated silica gel 60, 230-240 mesh [silica gel (125 g) was stirred with a 4% aqueous solution of K_2HPO_4 (500 mL) for 3 h. After filtration, the resulting solid was oven-dried at 100°C for 2 d]. ^{1}H NMR spectra were recorded on a Bruker DPX-300 (300 MHz) or an AC-200 (200 MHz). Chemical shifts (δ) are reported in ppm from tetramethylsilane with the residual solvent resonance as the internal standard ($CHCl_3$: δ 7.26; C_6D_6: δ 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s: singlet, d: doublet, dd: double doublet, td: triplet of doublets, t: triplet, q: quartet, br: broad, m: multiplet), coupling constants (*J* in Hz) and integration. ^{13}C NMR spectra were recorded on a Bruker DPX-300

(75 MHz) or an AC-200 (50 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$: δ 76.95, C_6D_6: δ 128.7 ppm). High-resolution mass spectrometry was carried out on a Finnigan-Mat 95 spectrometer. Elemental analyses were carried out on a Perkin-Elmer 2400 microanalyzer. All reagents were obtained from commercial suppliers and used without further purification, unless otherwise indicated. Silyl enol ethers **3**[1] and carbene complexes **1a**,**b**[2] were prepared according to the literature procedures. Tetrahydrofuran was distilled from sodium metal/benzophenone ketyl, and triethylamine was distilled from calcium hydride and stored under nitrogen.

General Procedure for the Synthesis of Carbene Complexes 1c-e To a solution of pentacarbonyl[1-methoxyethylidene]tungsten (3.82 g, 10 mmol) in diethyl ether (100 mL) was successively added the corresponding aldehyde (10 mmol), chlorotrimethylsilane (3.81 mL, 30 mmol), and triethylamine (5.58 mL, 40 mmol) at room temperature. After stirring for 3 days, silica gel (10 g) was added. Solvents were removed under reduced pressure and the resulting crude was purified by flash column chromatography using a mixture of hexanes and dichloromethane as eluent to give the carbene complexes **1c-e**.

Pentacarbonyl[(*E*,*E*)-5-(2-furyl)-1-methoxy-2,4-pentadienylidene]tungsten (1c): Pentacarbonyl[1-methoxyethylidene]tungsten (3.82 g, 10 mmol) and (*E*)-3-(2-furyl)acrolein (1.22 g, 10 mmol)afforded **1c** as a black solid (2.67

g, 55% yield). R_f 0.28 (hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.52 (d, *J* = 1.7 Hz, 1 H; =CHO), 7.37 (d, *J* = 14.5 Hz, 1 H; CH=CW), 7.01 (dd, *J* = 14.5, 11.4 Hz, 1 H; C*H*=CHCW), 6.89 (d, *J* = 15.4 Hz, 1 H; =C*H*-2-Fu), 6.72 (dd, *J* = 15.4, 11.4 Hz, 1 H; C*H*=CH-2-Fu), 6.56 (d, *J* = 3.4 Hz, 1 H; C*H*CH=CHO), 6.47 (dd, *J* = 3.4, 1.7 Hz, 1 H; C*H*=CHO), 4.58 (s, 3 H; OMe). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 304.5, 204.2, 197.8, 153.0, 146.9, 144.7, 135.2, 130.9, 125.8, 113.3, 112.8, 68.8. HRMS (EI) calc. for $C_{15}H_{10}O_7W$: 485.9936. Found: 485.9942.

Pentacarbonyl[(*E*,*E*)-1-methoxy-4-methyl-5-phenyl-2,4-pentadienylidene]tungsten (1d): Pentacarbonyl[1-methoxyethylidene]tungsten (3.82 g, 10 mmol) and (*E*)-α-methylcinnamaldehyde (1.46 g, 10 mmol) afforded **1d** as a black solid (1.94 g, 38%). R_f 0.39 (hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.48 (d, *J* = 16.1 Hz, 1 H; CH=CW), 7.11 (d, *J* = 16.1 Hz, 1 H; C*H*=CHCW), 7.43-7.26 (m, 5 H; ArH), 7.05 (s, 1 H; =C*H*Ph), 4.62 (s, 3 H; OMe), 2.17 (s, 3 H; Me). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 306.3, 203.9, 197.7, 143.8, 143.2, 141.2, 140.5, 133.6, 129.5, 128.4, 128.2, 68.8, 13.6. HRMS (EI) calc. for $C_{18}H_{14}O_6W$: 510.0300. Found: 510.0311.

Pentacarbonyl[(2*E*,4*Z*)-4-chloro-1-methoxy-5-phenyl-2,4-pentadienylidene]tungsten (1e): Pentacarbonyl[1-methoxyethylidene]tungsten (3.82 g, 10 mmol) and α-chlorocinnamaldehyde (1.67 g, 10 mmol) afforded **1e** as a black solid (4.08 g, 77%). R_f 0.63 (hexanes:ethyl acetate, 5:1). ^{1}H NMR

(300 MHz, $CDCl_3$) δ = 7.85-7.38 (m, 5 H; ArH), 7.74 (d, *J* = 14.2 Hz, 1 H; CH=CW), 7.10 (s, 1 H; =C*H*Ph), 6.96 (d, *J* = 14.2 Hz, 1 H; C*H*=CHCW), 4.62 (s, 3 H; OMe). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 306.6, 203.9, 197.2, 191.1, 145.1, 139.0, 134.4, 131.7, 130.2, 129.7, 128.6, 68.9. HRMS (FAB) calc. for $C_{17}H_{12}ClO_6W$ $(M+H)^+$: 530.9832. Found: 530.9841.

Synthesis of pentacarbonyl[(*E*)-3-(1-cyclohexenyl)-1-methoxy-2-propenylidene]tungsten (1f): To a solution of (*E*)-2-(1-cyclohexenyl)-1-iodoethene[2] (94 mg, 4 mmol) in THF (10 mL) *t*-BuLi (10.7 mL, 16 mmol, 1.5 N in pentane) was added at -78°C and the mixture was stirred for 30 min, and then transferred *via* canula to a suspension of hexacarbonyltungsten (141 mg, 4 mmol) in diethyl ether (40 mL) at 0°C. The mixture was warmed to room temperature and stirred for 1 h. Solvent was removed under reduced pressure and the crude solved in dichloromethane (40 mL). The resulting mixture was cooled at 0°C and treated with methyl triflate (0.91 mL, 8 mmol), followed by 20 min stirring. A small portion of sodium bicarbonate as well as silica gel (5 g) were added. Solvents were removed at reduced pressure and the resulting crude was purified by flash column chromatography using a mixture of hexanes and dichloromethane (40:1) as eluent, affording **1f** as a black solid (1.21 g, 64%). R_f 0.62 (hexanes). ^1H NMR (300 MHz, $CDCl_3$) δ = 7.23 (d, *J* = 15.2 Hz, 1 H; CH=CW), 6.91 (d, *J* = 15.2 Hz, 1 H; C*H*=CHCW), 6.48-6.44 (m, 1 H; =C*H*CH_2), 4.59 (s, 3 H; OMe), 2.26-2.18 (m, 4 H; C*H*$_2$$CH_2$$CH_2$C*H*$_2$), 1.78-1.61 (m, 4 H; CH_2C*H*$_2$C*H*$_2$$CH_2$). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 306.7, 203.8, 197.7, 145.1, 140.8,

139.8, 135.8, 68.6 (OMe), 27.4, 24.0, 21.9, 21.8. HRMS (FAB) calc. for $C_{15}H_{15}O_6W$ $(M+H)^+$: 475.0378. Found: 475.0385. Elemental analysis calc. for $C_{15}H_{14}O_6W$: C, 38.00; H, 2.98. Found: C, 38.05; H, 3.03.

Synthesis of carbocycles 4 and 5 and ketone 6. General procedure. To a solution of the corresponding silyl enol ethers **3** (1 mmol) in diethyl ether (10 mL) was added BuLi (0.63 mL of a 1.6 N solution in hexanes, 1 mmol) at 0°C and the mixture was stirred for 30 min. Then, the corresponding carbene complex **1** (0.5 mmol) were added and the resulting mixture was warmed to room temperature and stirred for 1 h. After that, deactivated silica gel (0.5 g) was added. The solvent was removed at reduced pressure and the resulting crude purified by flash column chromatography in deactivated silica gel using mixtures of hexanes and ethyl acetate (40:1 to 10:1) as eluent to give the products **4**, **5**, and **6**.

(1*R,2*S**)-6-Methoxy-1,2-diphenyl-3,5-cycloheptadienol (4a):** Silyl enol ether **3a** (0.19 g, 1 mmol), BuLi (0.63 mL of a 1.6 N solution in hexanes, 1 mmol), and carbene complex **1b** (0.25 g, 0.5 mmol) afforded compound **4a** (126 mg, 86%) as a white solid. M. p. 153-155°C (Et_2O). R_f 0.31 (hexanes:ethyl acetate, 5:1). ^1H NMR (200 MHz, C_6D_6) δ = 7.22-6.71 (m, 10 H; ArH), 5.94 (dd, *J* = 11.7, 7.8 Hz; 1 H; C*H*CH=COMe), 5.64 (dd, *J* = 11.7, 6.7 Hz, 1 H; C*H*CHPh), 4.95 (d, *J* = 7.8 Hz, 1 H; C*H*=COMe), 3.78 (d, *J* = 6.7 Hz, 1 H; C*H*Ph), 3.52 (d, *J* = 16.4 Hz, 1 H; C*H*H), 3.12 (s, 4 H; OMe and OH), 2.81 (d, *J* = 16.4 Hz, 1 H; CH*H*). ^{13}C NMR (75 MHz, C_6D_6) δ = 159.6, 145.6, 141.1, 130.3, 130.3, 128.1, 127.6, 127.4, 126.8, 126.3, 123.4, 95.5, 75.8, 61.3, 54.3, 43.5. HRMS (EI) calc. for $C_{20}H_{20}O_2$:

292.1463. Found: 292.1452. Elemental analysis calc. for $C_{20}H_{20}O_2$: C, 82.16; H, 6.89. Found: C, 82.22; H, 6.83.

(1R*,2S*)-6-Methoxy-1-(4-methoxyphenyl)-2-phenyl-3,5-cycloheptadienol (4b): Silyl enol ether **3b** (0.22 g, 1 mmol), BuLi (0.63 mL of a 1.6 N solution in hexanes, 1 mmol), and carbene complex **1b** (0.25 g, 0.5 mmol) afforded compound **4b** (124 mg, 77%) as a white solid. M. p. 102-104°C (decompose). ^{1}H NMR (300 MHz, C_6D_6) δ = 7.28-6.88 (m, 7 H; ArH), 6.75 (d, *J* = 9.1 Hz, 2 H; ArH), 6.04 (dd, *J* = 11.8, 8.0 Hz; 1 H; C*H*CH=COMe), 5.75 (dd, *J* = 11.8, 6.7 Hz, 1 H; C*H*CHPh), 5.05 (d, *J* = 8.0 Hz, 1 H; C*H*=COMe), 3.89 (d, *J* = 6.7 Hz, 1 H; C*H*Ph), 3.60 (d, *J* = 16.6 Hz, 1 H; C*H*H), 3.33 (s, 4 H; OMe and OH), 3.20 (s, 3 H; OMe), 2.92 (d, *J* = 16.6 Hz, 1 H; CH*H*). ^{13}C NMR (75 MHz, C_6D_6) δ = 159.7, 158.7, 141.3, 137.8, 130.4, 127.6, 127.4, 126.9, 126.7, 123.4, 112.8, 95.5, 75.6, 61.5, 54.4, 54.3, 43.8. HRMS (EI) calc. for $C_{21}H_{22}O_3$: 322.1569. Found: 322.1559. Elemental analysis calc. for $C_{21}H_{22}O_3$: C, 78.23; H, 6.88. Found: C, 78.12; H, 6.99.

(1*R,2*S**)-1-(2-Furyl)-6-methoxy-2-phenyl-3,5-cycloheptadienol (4c):** Silyl enol ether **3c** (0.18 g, 1 mmol), BuLi (0.63 mL of a 1.6 N solution in hexanes, 1 mmol), and carbene complex **1b** (0.25 g, 0.5 mmol) afforded compound **4c** (93 mg, 66%) as a colourless oil along with ***diast*-4c** (23 mg, 16%) as a colourless oil. R_f 0.23 (hexanes:ethyl acetate, 5:1). ^{1}H NMR (300 MHz, C_6D_6) δ = 7.08-6.96 (m, 6 H; ArH and =CHO), 6.08 (dd, *J* = 11.4, 7.1 Hz, 1 H; C*H*CH=COMe), 5.98 (dd, *J* = 3.1, 2.0 Hz, 1 H; C*H*=CHO), 5.91-5.82 (m, 2 H; C*H*CH=CHO and C*H*CHPh), 5.04 (d, *J* = 7.1 Hz, 1 H; C*H*=COMe),

4.31 (d, *J* = 6.3 Hz, 1 H; C*H*Ph), 3.38 (d, *J* = 16.2 Hz, 1 H; CH*H*) and 2.95 (d, *J* = 16.2 Hz, 1 H; C*H*H), 3.19 (s, 3 H; OMe), 2.70 (s, 1 H; OH). ^{13}C NMR (75 MHz, C_6D_6) δ = 159.4, 157.3, 141.1, 140.8, 129.3, 128.1, 127.9, 127.0, 125.0, 110.2, 106.6, 96.1, 77.9, 58.1, 54.3, 42.0. HRMS (EI) Calc. for $C_{18}H_{18}O_3$: 282.1256. Found: 282.1262.

(1*R,2*R**)-1-(2-Furyl)-6-methoxy-2-phenyl-3,5-cycloheptadienol (*diast*-4c):** R_f 0.30 (hexanes:ethyl acetate, 5:1). ^{1}H NMR (300 MHz, C_6D_6) δ = 7.12-7.02 (m, 6 H; 5 ArH and =CHO), 6.45 (d, *J* = 3.1 Hz, 1 H; C*H*CH=CHO), 6.16-6.06 (m, 2 H; C*H*=CHO and C*H*CH=COMe), 5.90 (dd, *J* = 11.4, 6.6 Hz, 1 H; C*H*CHPh), 5.04 (d, *J* = 7.1 Hz, 1 H; C*H*=COMe), 4.37 (d, *J* = 6.6 Hz, 1 H; C*H*Ph), 3.45 (d, *J* = 16.3 Hz, 1 H; C*H*H), 3.21 (s, 3 H; OMe), 3.04 (d, *J* = 16.3 Hz, 1 H; CH*H*), 2.88 (s, 1 H; OH). HRMS (EI) calc. for $C_{18}H_{18}O_3$: 282.1256. Found: 282.1260.

(1*R,2*S**)-1-(1-Hexynyl)-6-methoxy-2-phenyl-3,5-cycloheptadienol (4d):** Silyl enol ether **3d** (0.20 g, 1 mmol), BuLi (0.63 mL of a 1.6 N solution in hexanes, 1 mmol), and carbene complex **1b** (0.25 g, 0.5 mmol) afforded compound **4d** (120 mg, 81%) as a colourless oil. R_f 0.40 (hexanes:ethyl acetate, 5:1). ^{1}H NMR (200 MHz, C_6D_6) δ = 7.50-7.12 (m, 5 H; ArH), 5.98 (dd, *J* = 11.5, 6.9 Hz, 1 H; C*H*CH=COMe), 5.75 (dd, *J* = 11.5, 5.3 Hz, 1 H; C*H*CHPh), 4.90 (d, *J* = 6.9 Hz, 1 H; C*H*=COMe), 3.91 (d, *J* = 5.3 Hz, 1 H; C*H*Ph), 3.14 (s, 5 H; CH_2COH and OMe), 2.27 (s, 1 H; OH), 1.92 (t, *J* = 6.8 Hz, 2 H; CH_2Pr), 1.28-1.19 (m, 4 H; CH_2CH_2Me), 0.75 (t, *J* = 7.0 Hz, 3 H; Me). ^{13}C NMR (75 MHz, C_6D_6) δ = 159.3, 141.2, 130.5, 128.1, 127.1, 126.8, 125.2, 96.0, 86.7, 82.4, 74.8, 58.7, 54.3, 47.0, 30.5, 21.8, 18.3, 13.5.

HRMS (EI) calc. for $C_{20}H_{24}O_2$: 296.1776. Found: 296.1768. Elemental analysis calc. for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 81.13; H, 8.19.

(1*R,2*R**)-2-(2-Furyl)-6-methoxy-1-(2-phenylethyl)-3,5-cycloheptadienol (4e):** Silyl enol ether **3e** (0.22 g, 1 mmol), BuLi (0.63 mL of a 1.6 N solution in hexanes, 1 mmol), and carbene complex **1c** (0.24 g, 0.5 mmol) afforded compound **4e** (53 mg, 34%, 76% de) as a colourless oil. Data of major diastereoisomer. R_f 0.26 (hexanes:ethyl acetate, 5:1). ^{1}H NMR (300 MHz, C_6D_6) δ = 7.18-7.04 (m, 5 H; ArH), 6.95 (d, *J* = 2.0 Hz, 1 H; =CHO), 5.98 (dd, *J* = 3.1, 2.0 Hz, 1 H; C*H*=CHO), 5.93 (d, *J* = 3.1 Hz, 1 H; C*H*CH=CHO), 5.88 (dd, *J* = 11.4, 7.1 Hz; 1 H; C*H*CH-2-Fu), 5.60 (dd, *J* = 11.4, 7.0 Hz, 1 H; C*H*CH=COMe), 4.82 (d, *J* = 7.1 Hz, 1 H; C*H*=COMe), 3.88 (d, *J* = 6.3 Hz, 1 H; C*H*-2-Fu), 3.11 (s, 3 H; OMe), 3.02-2.80 (m, 2 H; CH_2Ph), 2.79 (d, *J* = 15.9 Hz, 1 H; C*H*HCOH), 2.61 (d, *J* = 15.9 Hz, 1 H; CH*H*COH), 2.46 (s, 1 H; OH), 1.96-1.68 (m, 2 H; CH_2Bn). ^{13}C NMR (75 MHz, C_6D_6) δ = 160.5, 155.3, 143.0, 141.6, 128.6, 128.4, 125.7, 124.7, 123.7, 110.3, 108.2, 95.2, 77.1, 54.3, 51.1, 43.7, 42.0, 30.1. HRMS (EI) calc. for $C_{20}H_{22}O_3$: 310.1569: 244.1463. Found: 310.1554.

(1*R,2*R**)-2-(2-Furyl)-6-methoxy-1-phenyl-3,5-cycloheptadienol (4f):** Silyl enol ether **3a** (0.19 g, 1 mmol), BuLi (0.63 mL of a 1.6 N solution in hexanes, 1 mmol), and carbene complex **1c** (0.24 g, 0.5 mmol) afforded compound **4f** (118 mg, 84%, 88% de) as a colourless oil. Data of the major diastereoisomer. R_f 0.40 (hexanes:ethyl acetate, 5:1). ^{1}H NMR (300 MHz, C_6D_6) δ = 7.44-7.00 (m, 5 H; ArH),

6.82 (d, *J* = 2.0 Hz, 1 H; =CHO), 5.96 (dd, *J* = 11.4, 6.2 Hz, 1 H; C*H*CH-2-Fu), 5.88 (dd, *J* = 3.4, 2.0 Hz, 1 H; C*H*=CHO), 5.75 (dd, *J* = 11.4, 6.3 Hz, 1 H; C*H*CH=COMe), 5.71 (d, *J* = 3.4 Hz, 1 H; C*H*CH=CHO), 4.89 (d, *J* = 6.3 Hz, 1 H; C*H*=COMe), 4.07 (d, *J* = 6.2 Hz, 1 H; C*H*-2-Fu), 3.47 (d, *J* = 15.6 Hz, 1 H; C*H*H), 2.77 (d, *J* = 15.6 Hz, 1 H; CH*H*), 3.11 (s, 3 H; OMe), 3.10 (s, 1 H; OH). ^{13}C NMR (75 MHz, C_6D_6) δ = 160.7, 154.7, 145.8, 141.2, 127.6, 126.9, 125.8, 125.6, 125.4, 110.1, 108.0, 95.6, 82.7, 54.4, 53.8, 45.9. HRMS (EI) calc. for $C_{18}H_{18}O_3$: 282.1256. Found: 282.1251.

(1*R,2*R**)-2-(2-Furyl)-6-methoxy-1-trimethylsilylethynyl-3,5-cycloheptadienol (4g):** Silyl enol ether **3f** (0.21 g, 1 mmol), BuLi (0.63 mL of a 1.6 N solution in hexanes, 1 mmol), and carbene complex **1c** (0.24 g, 0.5 mmol) afforded compound **4g** (109 mg, 72%) as a colourless oil. R_f 0.38 (hexanes:ethyl acetate, 5:1). ^{1}H NMR (300 MHz, C_6D_6) δ = 7.13 (d, *J* = 1.7 Hz, 1 H; =C*H*O), 6.27 (d, *J* = 3.4 Hz, 1 H; C*H*CH=CHO), 6.18 (dd, *J* = 3.4, 1.7 Hz, 1 H; C*H*=CHO), 6.02 (dd, *J* = 11.4, 5.4 Hz, 1 H; C*H*CH-2-Fu), 5.94 (dd, *J* = 11.4, 5.4 Hz, 1 H; C*H*CH=COMe), 4.87 (d, *J* = 5.4 Hz, 1 H; C*H*=COMe), 4.09 (d, *J* = 5.4 Hz, 1 H; C*H*-2-Fu), 3.16 (s, 3 H; OMe), 3.05 (d, *J* = 15.1 Hz, 1 H; C*H*H), 3.03 (d, *J* = 15.1 Hz, 1 H; CH*H*), 2.92 (br s, 1 H; OH), 0.13 (s, 9 H; 3xMeSi). ^{13}C NMR (75 MHz, C_6D_6) δ = 160.3, 154.8, 141.7, 124.6, 110.3, 107.7, 107.5, 96.3, 89.4, 79.8, 54.4, 52.2, 45.9, -0.4. HRMS (EI) calc. for $C_{17}H_{22}O_3Si$: 302.1338. Found: 302.1344.

(1*R,2*S**)-6-Methoxy-3-methyl-1,2-diphenyl-3,5-cycloheptadienol (4h):** Silyl enol ether **3a** (0.19 g, 1 mmol), BuLi (0.63 mL of a 1.6

N solution in hexanes, 1 mmol), and carbene complex **1d** (0.26 g, 0.5 mmol) afforded compound **4h** (121 mg, 79%) as a colourless oil. R_f 0.34 (hexanes:ethyl acetate, 5:1). ^{1}H NMR (300 MHz, C_6D_6) δ = 7.48-6.88 (m, 10 H; ArH), 5.82 (d, *J* = 8.8 Hz, 1 H; C*H*CH=COMe), 5.02 (d, *J* = 8.8 Hz, 1 H; C*H*=COMe), 3.71 (s, 1 H; C*H*Ph), 3.63 (d, *J* = 17.4 Hz, 1 H; C*H*H), 3.53 (s, 1 H; OH), 3.21 (s, 3 H; OMe), 2.92 (d, *J* = 17.4 Hz, 1 H; CH*H*), 1.76 (s, 3 H; Me). ^{13}C NMR (75 MHz, C_6D_6) δ = 157.6, 146.1, 134.2, 130.0, 127.7, 127.4, 127.0, 126.8, 126.4, 118.8, 95.1, 72.0, 66.4, 54.1, 42.7, 27.0. HRMS (EI) calc. for $C_{21}H_{21}O$ $(M-OH)^+$: 289.1592. Found: 289.1573. Elemental analysis calc. for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.19; H, 7.36.

(1*S,2*R**)-2-(2-Furyl)-6-methoxy-1-[(*E*)-styryl]-3,5-cycloheptadienol (4i):** Silyl enol ether **3g** (0.22 g, 1 mmol), BuLi (0.63 mL of a 1.6 N solution in hexanes, 1 mmol), and carbene complex **1c** (0.24 g, 0.5 mmol) afforded compound **4i** (74 mg, 48%) as a colourless oil along with compound **5a** (68 mg, 44%) as a colourless oil. R_f 0.42 (hexanes:ethyl acetate, 5:1). ^{1}H NMR (200 MHz, C_6D_6) δ = 7.36-6.97 (m, 6 H; ArH and =CHO), 6.84 (d, *J* = 15.9 Hz, 1 H; C*H*Ph), 6.49 (d, *J* = 15.9 Hz, 1 H; C*H*=CHPh), 6.00-5.98 (m, 3 H; C*H*C*H*=CHO and C*H*CH=COMe), 5.77 (dd, *J* = 11.2, 5.9 Hz; 1 H; C*H*CH-2-Fu), 4.86 (d, *J* = 6.4 Hz, 1 H; C*H*=COMe), 3.97 (d, *J* = 5.9 Hz, 1 H; C*H*-2-Fu), 3.02 (s, 3 H; OMe), 2.96 (d, *J* = 15.6 Hz, 1 H; C*H*H), 2.72 (d, *J* = 15.6 Hz, 1 H; CH*H*), 2.63 (s, 1 H; OH). ^{13}C NMR (75 MHz, C_6D_6) δ = 160.7, 154.9, 141.8, 137.5, 133.6, 128.5, 127.8, 127.3, 126.7, 126.3, 124.4, 110.3, 107.9, 95.7, 80.9, 54.4, 52.3, 45.1. HRMS (EI) calc. for $C_{20}H_{20}O_3$: 308.1412. Found: 308.1419.

***cis*-5-[(*E*)-2-(2-Furyl)ethenyl]-3-methoxy-6-phenyl-2-cycloheptenone (5a):** R_f 0.12 (hexanes:ethyl acetate, 5:1). ^{1}H NMR (200 MHz, C_6D_6) δ = 7.13-6.96 (m, 6 H; ArH and =CHO), 6.02 (d, *J* = 15.9 Hz, 1 H; C*H*-2-Fu), 5.80 (d, *J* = 15.9 Hz, 1 H; C*H*=CH-2-Fu), 6.05 (dd, *J* = 3.3, 2.1 Hz, 1 H; C*H*=CHO), 5.88 (d, *J* = 3.1 Hz, 1 H; C*H*CH=CHO), 5.60 (s, 1 H; C*H*=COMe), 3.30-2.39 (m, 6 H; CH_2C=O, C*H*Ph, C*H*C=, and CH_2COMe), 3.05 (s, 3 H; OMe). ^{13}C NMR (75 MHz, C_6D_6) δ = 198.5, 171.7, 152.7, 142.7, 141.6, 128.4, 128.3, 126.5, 119.7, 111.1, 107.2, 105.9, 54.9, 46.2, 44.0, 43.9, 38.1. HRMS (EI) calc. for $C_{20}H_{20}O_3$: 308.1412. Found: 308.1422.

***cis*-5-[(*Z*)-1-Chloro-2-phenylethenyl]-3-methoxy-6-phenyl-2-cycloheptenone (5b):** Silyl enol ether **3g** (0.22 g, 1 mmol), BuLi (0.63 mL of a 1.6 N solution in hexanes, 1 mmol), and carbene complex **1e** (0.27 g, 0.5 mmol) afforded compound **5b** (86 mg, 49%) as a colourless oil. R_f 0.12 (hexanes:ethyl acetate, 5:1). ^{1}H NMR (300 MHz, C_6D_6) δ = 7.22-7.04 (m, 10 H; ArH), 5.81 (s, 1 H; =C*H*Ph), 5.57 (s, 1 H; C*H*COMe), 3.54 (ddd, *J* = 10.6, 6.2, 3.3 Hz, 1 H; C*H*Ph), 3.41 (dd, *J* = 15.3, 10.6 Hz, 1 H; C*H*HC=O), 3.20-3.02 (m, 3 H; CH*H*C=O, C*H*CCl, and C*H*HCOMe), 3.11 (s, 3 H; OMe), 2.46 (dd, *J* = 12.4, 1.7 Hz, 1 H; CH*H*COMe). ^{13}C NMR (75 MHz, C_6D_6) δ = 199.1, 172.5, 141.1, 135.4, 134.8, 128.9, 128.5, 128.1, 128.0, 127.6, 127.0, 126.7, 105.4, 55.1, 49.7, 46.0, 42.7, 35.5. HRMS (EI) calc. for $C_{22}H_{21}ClO_2$: 352.1230. Found: 352.1216.

***cis*-5-(1-Cyclohexenyl)-3-methoxy-6-phenyl-2-cycloheptenone (5c):** Silyl enol ether **3g** (0.22 g, 1 mmol), BuLi (0.63 mL of a 1.6 N solution in hexanes, 1 mmol), and carbene complex **1f** (0.24 g, 0.5

mmol) afforded compound **5c** (75 mg, 51%) as a colourless oil. R_f 0.16 (hexanes:ethyl acetate, 5:1). ^{1}H NMR (200 MHz, C_6D_6) δ = 7.08-6.81 (m, 5 H; ArH), 5.50 (s, 1 H; C*H*COMe), 4.97-4.88 (m, 1 H; =C*H*CH_2), 3.19 (ddd, *J* = 10.5, 6.1, 4.2 Hz, 1 H; C*H*Ph), 3.08 (dd, *J* = 14.0, 10.5 Hz, 1 H; C*H*HC=O), 3.00 (s, 3 H; OMe), 2.86 (dd, *J* = 14.0, 4.2 Hz, 1 H; CH*H*C=O), 2.79 (dd, *J* = 15.9, 11.5 Hz, 1 H; C*H*HOMe), 2.57 (dd, *J* = 11.5, 6.1 Hz, 1 H; CHC=), 2.33 (d, *J* = 15.9 Hz, 1 H; CH*H*OMe), 1.72-1.22 (m, 8 H; 4xCH_2 cyclohexenyl ring). ^{13}C NMR (50 MHz, C_6D_6) δ = 198.7, 175.2, 142.5, 138.6, 128.6, 128.1, 126.3, 123.1, 105.5, 54.9, 47.6, 42.9, 35.9, 28.5, 25.2, 22.8, 22.2. HRMS (EI) calc. for $C_{20}H_{24}O_2$: 296.1776. Found: 296.1782.

(*E*)-5-(1-Cyclohexenyl)-3-methoxy-1-phenyl-2-penten-1-one (6): Silyl enol ether **3a** (0.19 g, 1 mmol), BuLi (0.63 mL of a 1.6 N solution in hexanes, 1 mmol), and carbene complex **1f** (0.24 g, 0.5 mmol) afforded compound **6** (105 mg, 78%) as a colourless oil. R_f 0.62 (hexanes:ethyl acetate, 5:1). ^{1}H NMR (300 MHz, C_6D_6) δ = 7.94-7.42 (m, 5 H; ArH), 6.10 (s, 1 H; C*H*=COMe), 5.49-5.40 (m, 1 H; =C*H*CH_2), 3.74 (s, 3 H; OMe), 2.96 (t, *J* = 7.3 Hz, 2 H; CH_2COMe), 2.23 (t, *J* = 7.3 Hz, 2 H; CH_2CH=), 2.04-1.50 (m, 8 H; 4xCH_2 cyclohenenyl ring). ^{13}C NMR (75 MHz, C_6D_6) δ = 189.9, 178.1, 140.5, 136.9, 131.6, 128.3, 127.6, 121.3, 95.8, 55.4, 35.5, 31.7, 28.1, 25.2, 22.9, 22.4. HRMS (EI) calc. for $C_{18}H_{22}O_2$: 270.1620. Found: 270.1622.

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