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## Supporting Information

**General:** All reactions involving organometallic species were carried out under an atmosphere of dry N<sub>2</sub> using oven-dried glassware and syringes. All common reagents and solvents were obtained from commercial suppliers and used without further purification unless otherwise indicated. THF and Et<sub>2</sub>O were distilled from sodium benzophenone ketyl under N<sub>2</sub> immediately prior to use, CH<sub>2</sub>Cl<sub>2</sub> from P<sub>2</sub>O<sub>5</sub> and DMF from CaH<sub>2</sub>. Hexane and EtOAc were distilled before use. Ferrocenecarbaldehyde and all the olefins used were commercially available. Ozone was generated in the usual fashion by a Fischer 500 laboratory ozonator using commercial-grade oxygen as a source.<sup>20a</sup> Variable voltage settings (80-90 V), pressures (6-8 lb/in<sup>2</sup>), flow rates (0.02-0.03 ft<sup>3</sup>/min) and reaction times (15-20 min) were employed. The ozonizations were carried out in ordinary schlenks which were nearly filled with solvent and cooled at -78 °C. Ozone was introduced through a glass tube extended very close to the magnetic stirring bar and tipped with a fritted glass disc. TLC was performed on aluminum-backed plates coated with silica gel 60 with F254 indicator (Scharlau). Flash column chromatography was carried out on silica gel 60, 230-240 mesh. <sup>1</sup>H NMR (200, 300 MHz) and <sup>13</sup>C NMR (50.5, 75.5 MHz) spectra were measured on a Bruker AC-200 and AC-300 instruments, respectively, with tetramethylsilane ( $\delta$  = 0.0, <sup>1</sup>H NMR) or CDCl<sub>3</sub> ( $\delta$  = 77.00, <sup>13</sup>C NMR) as internal standard. Carbon multiplicities were assigned by DEPT techniques. Low-resolution electron impact mass spectra (EI-LRMS) were obtained at 70 eV on a HP 5987 A instrument, and the intensities are reported as a percentage relative to the base peak after the corresponding *m/z* value. High-resolution mass spectra (HRMS) were determined on a Finnigan MAT 95 spectrometer. Elemental analysis were carried out on a Perkin-Elmer 2400 microanalyzer.

**(E)-(3-Ferrocenyl-1-methoxy-2-**

**propenylidene)pentacarbonylchromium (1)** To a solution of [(methoxy)(methyl)methylene]pentacarbonylchromium (6.3 g, 25 mmol) in Et<sub>2</sub>O (150 mL) at room temperature were successively added triethylamine (13.94 mL, 100 mmol), ferrocenecarbaldehyde (6.42 g, 30 mmol) and chlorotrimethylsilane (9.52 mL, 75 mmol). The mixture was stirred at room temperature for 48 h. Silica gel (ca. 25 g) was then added, and the solvent was removed under reduced pressure. The residue was loaded onto a silica gel column under N<sub>2</sub>. Elution with hexane gave 8.35 g (18.72 mmol, 75%) of carbene complex **1** as a dark violet solid. M.p. 105-107 °C; *R*<sub>f</sub> = 0.30 (hexane); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 4.22 (s, 5H), 4.60 (br s, 4H), 4.70 (s, 3H), 7.19 (d, *J* = 15.0 Hz, 1H), 7.52 (d, *J* = 15.0 Hz, 1H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>) δ 65.6, 69.9, 70.3, 72.6, 78.3, 137.5, 138.0, 217.1, 224.2, 326.0; IR (KBr) ν 3020 (s), 2401 (w), 2361 (w), 2054 (m), 1939 (s), 1575 (m), 1541 (w), 1423 (w), 1217 (s); LRMS (70 eV, EI) *m/z* (%) 446 (M<sup>+</sup>, 20), 418 (15), 332 (30), 306 (80), 270 (90), 237 (25), 220 (45), 205 (46), 186 (75), 149 (40), 121 (100); HRMS (70 eV, EI) calcd for C<sub>19</sub>H<sub>14</sub>CrFeO<sub>6</sub> (M<sup>+</sup>) 445.9545, found 445.9564. Anal. Calcd for C<sub>19</sub>H<sub>14</sub>CrFeO<sub>6</sub>: C, 51.15; H, 3.16. Found: C, 51.22; H, 3.06.

**General Procedure for the Cyclopropanation Reactions:** A mixture of carbene complex **1** or **4** (0.5 mmol), the corresponding alkene (10 mmol) and 3,5-di-*tert*-butyl-4-methylphenol (BHT, 5 mg, 0.02 mmol) in DMF (20 mL) was refluxed for a period of 25-35 min (1.5 h in the case of compound **5** and 2-2.5 h for compounds **6**, **8** and **11**). Upon cooling to room temperature the solvent was removed under reduced pressure and the resulting residue was dissolved in hexane and filtered through a plug of celite. Evaporation of the volatiles and column chromatography (Silica gel) afforded pure compounds **3**, **5-11**. In the case of compounds **3**, **5**, **7** and **10** the major diastereoisomer was separated by this procedure. Yields are described in

Schemes 2, 3 and Table 1. In the preparation of compound **5** when CH<sub>3</sub>CN or THF were used as solvents the reaction was refluxed for 1.5 h and 6 h respectively.

**(1*S*\*,2*R*\*)-2-Butyl-1-[(*E*)-2-ferrocenylethenyl]-1-**

**methoxycyclopropane (3).** Orange oil; *R*<sub>f</sub> = 0.30 (hexane : CH<sub>2</sub>Cl<sub>2</sub>, 4:1); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.60 (dd, *J* = 7.01, 4.58 Hz, 1H), 0.84-1.00 (m, 5H), 1.42-1.50 (m, 5H), 1.64 (m, 1H), 3.39 (s, 3H), 4.13 (s, 5H), 4.21 (t, *J* = 1.83 Hz, 2H), 4.33 (t, *J* = 1.83 Hz, 2H), 5.64 (d, *J* = 15.8 Hz, 1H), 6.21 (d, *J* = 15.8 Hz, 1H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>) δ 14.1, 18.3, 22.5, 27.4, 28.0, 31.9, 55.5, 65.5, 66.2, 66.4, 68.3, 69.0, 83.3, 124.3, 128.8; LRMS (70 eV, EI) *m/z* (%) 338 (M<sup>+</sup>, 100), 307 (10), 214 (10), 186 (20), 121 (20), 44 (15), 36 (20); HRMS (70 eV, EI) calcd for C<sub>20</sub>H<sub>26</sub>FeO (M<sup>+</sup>) 338.1333, found 338.1332. Anal. Calcd for C<sub>20</sub>H<sub>26</sub>FeO: C, 71.01; H, 7.75. Found: C, 70.79; H, 7.97.

**(1*S*\*,2*R*\*)-2-Butyl-1-[(*E*)-2-Phenylethenyl]-1-**

**methoxycyclopropane (5).** Colorless oil; *R*<sub>f</sub> = 0.27 (hexane : CH<sub>2</sub>Cl<sub>2</sub>, 9:1); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.70 (dd, *J* = 6.41, 4.88 Hz, 1H), 0.87-1.00 (m, 4H), 1.03-1.12 (m, 1H), 1.38-1.49 (m, 5H), 1.59-1.75 (m, 1H), 3.41 (s, 3H), 5.99 (d, *J* = 16.2 Hz, 1H), 6.51 (d, *J* = 16.2 Hz, 1H), 7.20-7.26 (m, 1H), 7.28-7.43 (m, 4H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>) δ 14.1, 18.8, 22.5, 27.5, 28.5, 31.8, 55.8, 65.5, 125.8, 126.4, 126.8, 128.5, 132.3, 137.1; Anal. Calcd for C<sub>16</sub>H<sub>22</sub>O: C, 83.43; H, 9.63. Found: C, 83.54; H, 9.59.

***meso*-(1*R*,6*S*,7*S*)-7-[(*E*)-2-Ferrocenylethenyl]-7-**

**methoxybicyclo[4.1.0]heptane (6).** Was prepared following the general procedure using 1.64 g (20 mmol, 40 equiv) of cyclohexene. Orange oil. Data on the 94.5:5.5 mixture of diastereoisomers; *R*<sub>f</sub> = 0.35 (hexane : EtOAc, 4:1); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.81-1.04 (m, 1H), 1.06-1.12 (m, 1H), 1.26-1.44 (m, 4H), 1.70-1.86 (m, 4H), 3.30 (s, 3H, minor isomer), 3.51 (s,

3H, major isomer), 4.12 (s, 5H), 4.18 (s, 2H), 4.30 (s, 2H), 5.70 (d,  $J = 15.9$  Hz, 1H), 6.12 (d,  $J = 15.9$  Hz, 1H);  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ )  $\delta$  18.7, 21.2, 21.9, 55.5, 66.2, 66.3, 68.4, 69.0, 83.6, 124.2, 130.0; LRMS (70 eV, EI)  $m/z$  (%) 336 ( $\text{M}^+$ , 100), 184 (20), 121 (15); HRMS (70 eV, EI) calcd for  $\text{C}_{20}\text{H}_{24}\text{FeO}$  ( $\text{M}^+$ ) 336.1177, found 336.1175.

***meso*-(1*R*,7*S*,8*S*)-8-[(*E*)-2-Ferrocenylethenyl]-8-methoxybicyclo[5.1.0]octane (7).** Orange solid; M.p. 68-70 °C;  $R_f$  = 0.63 (hexane : EtOAc, 9:1);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.86-1.42 (m, 7H), 1.88-2.03 (m, 5H), 3.39 (s, 3H), 4.11 (s, 5H), 4.20 (t,  $J = 1.83$  Hz, 2H), 4.32 (t,  $J = 1.83$  Hz, 2H), 5.75 (d,  $J = 15.9$  Hz, 1H), 6.16 (d,  $J = 15.9$  Hz, 1H);  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ )  $\delta$  23.6, 29.5, 30.2, 32.6, 56.0, 66.3, 66.5, 68.3, 69.0, 83.5, 124.3, 129.3; LRMS (70 eV, EI)  $m/z$  (%) 350 ( $\text{M}^+$ , 100), 198 (17), 186 (15), 121 (10); HRMS (70 eV, EI) calcd for  $\text{C}_{21}\text{H}_{26}\text{FeO}$  ( $\text{M}^+$ ) 350.1333, found 350.1328. Anal. Calcd for  $\text{C}_{21}\text{H}_{26}\text{FeO}$ : C, 72.01; H, 7.48. Found: C, 72.19; H, 7.38.

Resolvable resonances of the minor isomer:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.34 (s, 3H);  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ )  $\delta$  26.2, 29.7, 30.9, 54.6, 68.5, 68.7, 69.3, 120.1, 129.8.

***meso*-(1*R*,2*S*,3*S*,4*R*,5*S*)-3-[(*E*)-2-Ferrocenylethenyl]-3-methoxytricyclo[3.2.1.0<sup>2,4</sup>]octane (8).** Orange solid. Data on the 95:5 mixture of diastereoisomers;  $R_f$  = 0.30 (hexane : EtOAc, 4:1);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.81 (d,  $J = 5.3$  Hz, 1H), 0.98 (s, 2H), 1.20-1.48 (m, 2H), 1.41-1.62 (m, 2H), 1.92 (d,  $J = 5.3$  Hz, 1H), 2.63 (s, 2H), 3.35 (s, 3H), 4.11 (s, 5H), 4.18 (s, 2H), 4.31 (s, 2H), 5.42 (d,  $J = 15.6$  Hz, 1H), 6.18 (d,  $J = 15.6$  Hz, 1H);  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ )  $\delta$  29.7, 30.9, 32.6, 36.9, 54.9, 66.2, 68.3, 68.6, 68.9, 83.6, 123.5, 129.7; LRMS (70 eV, EI)  $m/z$  (%) 349 (20), 348 ( $\text{M}^+$ , 100) 333 (10), 317 (15); HRMS (70 eV, EI) calcd for  $\text{C}_{21}\text{H}_{24}\text{FeO}$  ( $\text{M}^+$ ) 348.1176, found 348.1168.

**(1*S*\*,2*S*\*)-2-(3-Cyclohexenyl)-1-[(*E*)-2-ferrocenylethenyl]-1-methoxycyclopropane (9).** Orange oil. Data on the 1:1 mixture of diastereoisomers;  $R_f = 0.56$  (hexane : EtOAc, 9:1);  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  0.66, 0.78 (m, 1H), 0.82-0.92 (m, 2H), 1.39-1.60 (m, 2H), 1.82-1.98 (m, 2H), 2.09-2.25 (m, 3H), 3.38 (s, 3H), 4.11 (s, 5H), 4.20 (t,  $J = 1.83$  Hz, 2H), 4.33 (t,  $J = 1.83$  Hz, 2H), 5.60-5.71 (m, 3H), 6.20, 6.22 (2d,  $J = 15.8$  Hz, 1H of each isomer);  $^{13}\text{C}$  NMR (50.0 MHz,  $\text{CDCl}_3$ )  $\delta$  16.8, 25.0, 28.2, 29.2, 31.3, 31.9, 32.8, 33.0, 33.7, 33.9, 55.5, 65.4, 65.7, 66.3, 66.5, 68.4, 69.0, 83.3, 124.3, 126.5, 126.6, 127.1, 128.9; LRMS (70 eV, EI)  $m/z$  (%) 362 ( $\text{M}^+$ , 100), 266 (10), 229 (10), 199 (25), 186 (20), 121 (15); HRMS (70 eV, EI) calcd for  $\text{C}_{22}\text{H}_{26}\text{FeO}$  ( $\text{M}^+$ ) 362.1333, found 362.1337. Anal. Calcd for  $\text{C}_{22}\text{H}_{26}\text{FeO}$ : C, 72.94; H, 7.23. Found: C, 72.66; H, 7.38.

**(1*R*\*,2*S*\*)-2-(Allyloxymethyl-1-[(*E*)-2-ferrocenylethenyl]-1-methoxycyclopropane (10).** Orange oil;  $R_f = 0.51$  (hexane : EtOAc, 4:1);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.74-0.82 (m, 1H), 0.88-1.06 (dd  $J = 9.77, 5.8$  Hz, 1H), 1.26-1.46 (m, 1H), 3.37 (s, 3H), 3.51-3.59 (m, 2H), 3.97-4.16 (m, 7H), 4.20 (t,  $J = 1.72$  Hz, 2H), 4.32 (t,  $J = 1.72$  Hz, 2H), 5.22 (dm,  $J = 10.37$  Hz, 1H), 5.32 (dq,  $J = 17.09, 1.52$  Hz, 1H), 5.68 (d,  $J = 15.8$  Hz, 1H), 5.87-6.10 (m, 1H), 6.25 (d,  $J = 15.8$  Hz, 1H);  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ )  $\delta$  16.6, 26.5, 55.4, 66.4, 66.5, 68.5, 68.6, 69.0, 70.8, 71.5, 82.9, 116.9, 126.1, 127.0, 135.0; LRMS (70 eV, EI)  $m/z$  (%) 352 ( $\text{M}^+$ , 100), 270 (15), 256 (40), 214 (80), 186 (10), 121 (30); HRMS (70 eV, EI) calcd for  $\text{C}_{20}\text{H}_{24}\text{FeO}_2$  ( $\text{M}^+$ ) 352.1126, found 352.1122. Anal. Calcd for  $\text{C}_{20}\text{H}_{24}\text{FeO}_2$ : C, 68.20; H, 6.87. Found: C, 68.52; H, 6.78.

Resolvable resonances of the minor isomer:  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  3.28 (s, 3H), 4.12 (s, 5H), 4.42 (t,  $J = 1.83$  Hz, 2H), 4.51 (t,  $J = 1.83$  Hz, 2H).

**2-Ferrocenyl-4-methoxy-6-(1-methylethenyl)phenol (11).** Orange solid;  $R_f = 0.37$  (hexane :  $\text{CH}_2\text{Cl}_2$ , 4:1);  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  2.23

(s, 3H), 3.80 (s, 3H), 4.07 (s, 5H), 4.42 (t,  $J = 1.77$  Hz, 2H), 4.60 (t,  $J = 1.77$  Hz, 2H), 5.22 (s, 1H), 5.32 (s, 1H), 6.72 (d,  $J = 3.08$  Hz, 1H), 6.79 (d,  $J = 3.08$  Hz, 1H), 6.85 (s, 1H);  $^{13}\text{C}$  NMR (50.5 MHz,  $\text{CDCl}_3$ )  $\delta$  23.5, 55.7, 67.8, 69.2, 69.3, 82.5, 113.0, 113.7, 115.6, 124.0, 131.0, 143.5, 144.1, 152.4; LRMS (70 eV, EI)  $m/z$  (%) 348 ( $\text{M}^+$ , 100), 282 (40), 267 (35), 121 (10); HRMS (70 eV, EI) calcd for  $\text{C}_{20}\text{H}_{20}\text{FeO}_2$  ( $\text{M}^+$ ) 348.0813, found 348.0811. Anal. Calcd for  $\text{C}_{20}\text{H}_{20}\text{FeO}_2$ : C, 68.98; H, 5.79. Found: C, 68.59; H, 5.93.

**General Procedure for the Synthesis of 12 and 13:** A solution of the corresponding cyclopropane derivative **3** or **7** (0.2 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL) and dry MeOH (10 mL) at  $-78^\circ\text{C}$  was ozonized according to the general procedure described above.<sup>20a</sup> After the addition of dimethyl sulfide (3 mL), the reaction mixture was allowed to reach slowly (12 h) rt. Evaporation of readily volatile materials afforded a black sticky oil that was extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 50 mL); the solvent was removed under reduced pressure and the resulting residue was chromatographed using a mixture of hexane/EtOAc (4:1) as eluent. The desired aldehydes **12** or **13** were obtained as colorless oils. Yields are listed in Scheme 4.

**(1*R*\*,2*R*\*)-2-Butyl-1-methoxycyclopropanecarbaldehyde (12).** Colorless oil;  $R_f = 0.47$  (hexane : EtOAc, 9:1);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.87-1.06 (m, 4H), 1.21-1.61 (m, 6H), 3.48 (s, 3H), 9.25 (s, 1H);  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ )  $\delta$  14.0, 19.5, 22.4, 26.8, 29.6, 31.5, 58.0, 71.8, 201.3; LRMS (70 eV, EI)  $m/z$  (%) 156 ( $\text{M}^+$ , 30), 127 (25), 114 (20), 99 (20), 95 (40), 87 (75).

**meso-(1*R*,7*S*,8*R*)-8-Methoxybicyclo[5.1.0]octane-8-carbaldehyde (13).** Colorless oil;  $R_f = 0.42$  (hexane : EtOAc, 9:1);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.15-1.52 (m, 5H), 1.62-1.74 (m, 2H), 1.79-2.05 (m, 5H), 3.55 (s, 3H), 9.22 (s, 1H);  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ )  $\delta$  23.0, 28.6, 31.6, 32.4, 58.4, 75.8, 201.1; LRMS (70 eV, EI)  $m/z$  (%) 168 ( $\text{M}^+$ , 90), 155 (20), 139

(40), 125 (40), 109 (40), 97 (50); HRMS (70 eV, EI) calcd for  $C_{10}H_{16}O_2$  ( $M^+$ ) 168.1150, found 168.1155.

Chart 1

