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[3+2]/[4+1] Cycloaddition Reactions of Fischer Alkoxy(alkenyl)carbene Complexes with Electronically Neutral 1,3-Dienes

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Experimental procedures and spectral and analytical data for all products.

General: All reactions involving organometallic species were carried out under an atmosphere of dry N_2 using oven-dried glassware and syringes. THF and CH_3Ph were distilled from sodium benzophenone ketyl under N_2 immediately prior to use. The solvents used in column chromatography, hexane, EtOAc, CH_2Cl_2 and Et_3N were obtained from commercial suppliers and used without further distillation. TLC was performed on aluminum-backed plates coated with silica gel 60 with F_{254} indicator (Scharlau). Flash column chromatography was carried out on silica gel 60, 230-240 mesh. Deactivated Silica gel was obtained by previous treatment with a mixture of hexane and Et_3N (10%). ^1H NMR (200, 300, 400 MHz) and ^{13}C NMR (50.5, 75.5, 100 MHz) spectra were measured at room temperature on a Bruker AC-200, AC-300 and AMX-400 instruments, respectively, with tetramethylsilane (δ = 0.0, ^1H NMR) or $CDCl_3$ (δ = 77.00, ^{13}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, 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 analyses were carried out on a Perkin-Elmer 2400 and Carlo Erba 1108 microanalyzers. Enantiomeric excesses were determined by HPLC analysis (in comparison with the corresponding

racemic mixtures) carried out with either a Shimadzu (SPD-MA6, UV/Vis detector) or a Waters (LC Module 1 Plus, UV/Vis detector) on a Chiralcel OJ or OB-H (Daicel Chem. Ind.) column (25 x 0.46 cm). Optical rotations were determined at room temperature with a Perkin Elmer 241 polarimeter using a Na lamp; sample concentrations *c* are reported in g cm^{-3} of CH_2Cl_2.

Materials: 2,6-di-*tert*-Butyl-4-methyphenol (BHT), 1,3-butadiene, isoprene, myrcene, 2,3-dimethyl-1,3-butadiene, (*E*)-2-methyl-1,3-pentadiene, 2,4-dimethyl-1,3-pentadiene and common reagents were obtained from commercial suppliers and used without further purification unless otherwise indicated. Carbene complexes **1a**,**b**,**e**,**f**,[22] **1c**,[15], **1d**,[23] **1g**,**h**,**i**[14] and (−)-8-phenylmenthol[24] were prepared as previously described.

General Procedure for the Synthesis of Compounds 3. A mixture of the appropriate carbene complex **1** (1 mmol), the corresponding 1,3-diene **2** (5 mmol) and BHT (0.5 mmol, 10 mmol% with regard to diene) in toluene (15 mL) introduced in a sealed flask was heated at 80 °C (oil bath temperature) until disappearance of the color of the starting carbene complex (reaction times are given in Tables 1 and 2). The initial dark red solution turned brown. The reaction mixture was cooled to room temperature, toluene was removed under reduced pressure, and the remaining residue was dissolved in hexane and exposed to sunlight and air during 0.5-1 h to remove coordinated metal species. The resulting mixture was filtered through a short pad of Celite and the volatiles were

evaporated. The remaining oil was purified by column chromatography (deactivated silica gel, hexane:EtOAc, 95:5) to give compounds **3a-f** each one as a single diastereoisomer. Compound **3d** was not pure and hence submitted to acid hydrolysis without further purification. Compounds **3g-i** were not subjected to column chromatography purification and were characterized as crude products. Yields and ratio of diastereoisomers are listed in Table 1 and 3.

(3*R,5*R**)-1-Methoxy-5-methyl-3-phenyl-5-vinylcyclopentene (3a)**. This compound could not be separated from BHT by column chromatography. The following data were taken from a 2:1 mixture of compound **3a** and BHT, respectively. Colorless oil. R_f = 0.48 (Hexane:EtOAc, 95:5). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.28 (s, 3H), 1.86 (dd, *J* = 12.5, 7.4 Hz, 1H), 2.24 (dd, *J* = 12.8, 8.0 Hz, 1H), 3.66 (s, 3H), 3.90 (td, *J* = 7.7, 1.7 Hz, 1H), 4.56 (d, *J* = 1.7 Hz, 1H), 5.01-5.10 (m, 2H), 5.59 (dd, *J* = 17.4, 10.9 Hz, 1H), 7.18-7.35 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.9, 44.5, 47.7, 49.4, 57.2, 96.7, 112.1, 126.0, 128.2, 128.4, 144.9, 147.1, 165.7.

(3*R,5*R**)-3-(2-Furyl)-1-methoxy-5-methyl-5-vinylcyclopentene (3b)**. Colorless oil. R_f = 0.50 (Hexane: EtOAc, 95.5). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.30 (s, 3H), 2.09 (dd, *J* = 12.8, 6.8 Hz, 1H), 2.20 (dd, *J* = 12.8, 8.0 Hz, 1H), 3.67 (s, 3H), 3.96 (td, *J* = 7.7, 2.1 Hz, 1H), 4.60 (d, *J* = 2.1 Hz, 1H), 5.01-5.04 (m, 1H), 5.10 (dd, *J* = 7.7, 1.3 Hz, 1H), 6.00 (dd, *J* = 17.1, 10.8 Hz, 1H), 6.04 (dt, *J* = 3.1, 0.8 Hz, 1H), 6.31 (dd, *J* = 3.1, 1.9 Hz, 1H), 7.35 (dd, *J* =

1.9, 0.8 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.6, 37.7, 43.3, 48.9, 57.0, 94.1, 103.6, 109.9, 112.0, 140.8, 144.6, 159.6, 165.7. LRMS (70 eV, EI): *m/z* (%): 204 (M^+, 34), 161 (33), 135 (22), 129 (23), 123 (100), 91 (17). HRMS (70 eV, EI) calcd for $C_{13}H_{16}O_2$ (M^+): 204.1150; found: 204.1148.

(3*R,5*R**)-3-Ferrocenyl-1-methoxy-5-methyl-5-vinylcyclopentene (3c)**. Orange solid. R_f = 0.17 (Hexane:CH_2Cl_2, 9:1). M.p. 52-53 °C. ^{1}H NMR (300 MHz, C_6D_6): δ = 1.44 (s, 3H), 2.09 (qd, *J* = 12.8, 7.1 Hz, 1H), 2.18 (dd, *J* = 12.8, 8.0 Hz, 1H), 3.36 (m, 3H), 3.68 (td, *J* = 7.7, 2.0 Hz, 1H), 4.06-4.22 (m with s at 4.17, 9H), 4.60 (t, *J* = 2.0 Hz, 1H), 5.13 (dd, *J* = 10.5, 1.4 Hz, 1H), 5.30 (dd, *J* = 17.7, 1.4 Hz, 1H), 6.22 (dd, *J* = 17.4, 10.5 Hz, 1H). ^{13}C NMR (75 MHz, C_6D_6): δ = 24.4, 39.6, 47.1, 50.4, 57.3, 67.8, 67.9, 68.1, 68.5, 69.3, 95.6, 98.2, 112.7, 146.2, 165.6. LRMS (70 eV, EI): *m/z* (%): 323 (M^++1, 22), 322 (M^+, 100), 228 (16), 201 (12), 129 (11), 128 (14), 121 (65). HRMS (70 eV, EI) calcd for $C_{19}H_{22}FeO$ (M^+): 322.1020; found: 322.1015. Elemental analysis calcd (%) for $C_{19}H_{22}FeO$: C, 70.82; H, 6.88; found: C,70.71; H, 7.21.

(3*R,5*R**)-1-Methoxy-3-phenyl-5-vinylcyclopentene (3e)**. Colorless oil. R_f = 0.48 (Hexane:EtOAc, 95.5). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.59 (dt, *J* = 12.8, 8.0 Hz, 1H), 2.66 (dt, *J* = 13.0, 8.1 Hz, 1H), 3.39-3.47 (m, 1H), 3.71 (s, 3H), 3.88 (apparent tt, *J* = 7.7, 2.0 Hz, 1H), 4.67 (s, 1H), 5.08-5.22 (m, 2H), 5.86 (ddd, *J* = 17.1, 10.3, 8.3 Hz, 1H), 7.22-7.50 (m, 5H). ^{13}C NMR (75 MHz,

$CDCl_3$): δ = 39.9, 46.1, 48.7, 57.1, 98.5, 115.3, 126.0, 127.1, 128.2, 139.9, 147.1, 162.1. LRMS (70 eV, EI): *m/z* (%): 220 (M^+, 31), 205 (100), 133 (29), 115 (48), 91 (63), 77 (62). HRMS (70 eV, EI) calcd for $C_{14}H_{16}O$ (M^+): 200.1201; found: 200.1200.

(3*R,5*R**)-1-Methoxy-5-(4-methyl-3-pentenyl)-3-phenyl-5-vinylcyclopentene (3f)**. Colorless oil. R_f = 0.77 (Hexane: EtOAc, 95:5). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.67 (s, 3H), 1.55-1.79 (m with s at 1.74, 4H), 1.91 (dd, *J* = 13.4, 6.8 Hz, 1H), 1.98-2.15 (s, 3H), 2.42 (dd, *J* = 13.1, 8.5 Hz, 1H), 3.69 (s, 3H), 3.89 (ddd, *J* = 8.5, 6.8, 1.9 Hz, 1H), 4.62 (d, *J* = 2.0 Hz, 1H), 5.04 (dd, *J* = 10.3, 1.1 Hz, 1H), 5.09 (dd, *J* = 3.8, 1.2 Hz, 1H), 5.17-5.24 (m, 1H), 6.05 (dd, *J* = 17.5, 11.0 Hz, 1H), 7.20-7.36 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.5, 23.4, 25.7, 37.2, 43.7, 45.0, 53.1, 56.9, 97.8, 112.2, 124.6, 125.9, 127.2, 128.2, 131.2, 144.1, 147.5, 164.0. LRMS (70 eV, EI): *m/z* (%): 282 (M^+, 45), 211 (100), 198 (77), 167 (28), 91 (32). HRMS (70 eV, EI) calcd for $C_{20}H_{26}O$ (M^+): 282.1984; found: 282.1975.

(3*R,5*R**)-5-Methyl-3-phenyl-1-[(1*R*,2*S*,5*R*)-8-phenylmenthyloxy]-5-vinylcyclopentene (3g)**. Data taken from a 87:13 mixture of diastereoisomers in the crude reaction mixture. Colorless oil. R_f = 0.80 (Hexane: EtOAc, 95:5). ^{1}H NMR (200 MHz, C_6D_6): δ = 0.93 (d, *J* = 6.7 Hz, 3H), 1.38 (s, 3H), 1.49 (s, 3H), 1.50-1.98 (m with s at 1.61, 11H), 2.05-2.20 (m, 2H), 3.81 (td, *J* = 10.1, 4.0 Hz, 1H), 3.94 (td, *J* = 8.0, 1.8 Hz, 1H), 4.44 (d, *J* = 1.8 Hz, 1H), 5.05-

5.20 (m, 2H), 6.20 (dd, *J* = 17.4, 10.8 Hz, 1H), 7.12-7.45 (m, 10H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.6, 22.2, 24.4, 27.0, 30.0, 31.0, 34.5, 39.1, 40.2, 44.5, 46.4, 49.3, 51.0, 78.8, 96.0, 111.4, 124.5, 125.3, 125.6, 126.8, 127.4, 127.9, 144.6, 147.0, 149.6, 162.2. Resolvable resonances of minor isomer: ^{1}H NMR (200 MHz, C_6D_6): δ = 4.55 (d, *J* = 2.1 Hz, 1H), 4.94-5.55 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.4, 23.1, 23.9, 26.1, 28.1, 30.8, 39.2, 41.2, 47.1, 49.8, 50.9, 79.1, 96.5, 111.2, 128.5, 144.6, 147.2, 150.3, 162.0.

(3*R,5*R**)-3-Phenyl-1-[(1*R*,2*S*,5*R*)-8-phenylmenthyloxy]-5-vinylcyclopentene (3h)**. Data for the single diastereoisomer taken in the crude reaction mixture. Colorless oil. R_f = 0.82 (Hexane: EtOAc, 95:5). ^{1}H NMR (300 MHz, C_6D_6): δ = 0.84 (d, *J* = 6.7 Hz, 3H), 1.34-1.75 (m with two s at 1.52, 1.64, 13H), 1.82-1.95 (m, 1H), 2.12-2.27 (m, 1H), 2.41-2.60 (m, 1H), 3.31-3.45 (m, 1H), 3.80-3.95 (m, 2H), 4.51 (s, 1H), 5.02-5.20 (m, 2H), 5.95-6.10 (m, 1H), 7.05-7.45 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2, 24.6, 27.4, 31.0, 31.4, 34.8, 39.4, 39.6, 40.6, 46.3, 49.6, 51.3, 79.6, 98.3, 115.0, 124.5, 125.4, 125.9, 127.1, 128.1, 128.2, 128.9, 140.2, 147.5, 150.0, 158.9.

(3*R,5*R**)-3-Ferrocenyl-1-[(1*R*,2*S*,5*R*)-8-phenylmenthyloxy]-5-vinylcyclopentene (3i)**. Data taken from a 90:10 mixture of diastereoisomers in the crude reaction mixture. Colorless oil. R_f = 0.71 (Hexane:EtOAc, 95:5). ^{1}H NMR (200 MHz, C_6D_6): δ = 0.84 (d, *J* =

6.2 Hz, 3H), 1.25-1.71 (m with two s at 1.48, 1.63, 13H), 1.75-2.01 (m, 2H), 2.39-2.58 (m, 1H), 3.32-3.50 (m, 1H), 3.66 (tt, *J* = 7.6, 1.9 Hz, 1H), 3.84-4.02 (m, 1H), 4.05-4.21 (m with s at 4.17, 9H), 4.74-7.78 (m, 1H), 5.03-5.28 (m, 2H), 6.03 (dd, *J* = 16.9, 8.2 Hz, 1H), 7.15-7.43 (m, 5H). ^{13}C NMR (75 MHz, C_6D_6): δ = 22.9, 25.3, 28.5, 32.3, 35.8, 38.5, 41.0, 41.2, 41.7, 50.8, 52.4, 67.6, 67.8, 68.1, 68.5, 69.3, 80.4, 95.9, 99.9, 115.8, 126.3, 127.2, 128.9, 130.0, 141.6, 151.0, 158.7. Resolvable resonances of minor isomer: ^{1}H NMR (200 MHz, C_6D_6): δ = 4.58-4.72 (m, 1H). ^{13}C NMR (75 MHz, C_6D_6): δ = 26.3, 32.7, 35.5, 38.3, 49.7, 96.0, 99.0, 115.1, 152.1.

General Procedure for the Synthesis of Compounds 4: A mixture of the appropriate carbene complex **1** (1 mmol), the corresponding 1,3-diene **2** (5 mmol) and BHT (0.5 mmol, 10 mmol% with regard to diene) in THF (15 mL) introduced in a sealed flask was heated at 120 °C (oil bath temperature) until disappearance of the color of the starting carbene complex (reaction times are given in Schemes 1 and 2). The initial dark red solution turned yellow. The reaction mixture was cooled to room temperature, solvent was removed under reduced pressure, and the remaining residue was dissolved in hexane and exposed to sunlight and air during 0.5-1 h to remove coordinated metal species. The resulting mixture was filtered through a short pad of Celite and the volatiles were evaporated. The remaining pale yellow oil was purified by column chromatography (silica gel, hexane:EtOAc, 95:5) to yield pure compounds **4**. Yields are reported in Schemes 1 and 2.

4-Methoxy-1-methyl-4-[(*E*)-2-phenylethenyl]cyclopentene (4a). Colorless oil. R_f = 0.16 (Hexane: EtOAc, 95:5). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.75-1.82 (m, 3H), 2.55-2.70 (m, 4H), 3.26 (s, 3H), 5.33 (dd, *J* = 3.7, 1.9 Hz, 1H), 6.37 (d, *J* = 16.4 Hz, 1H), 6.54 (d, *J* = 16.4 Hz, 1H), 7.20-7.45 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.7, 43.1, 47.1, 51.4, 86.7, 121.5, 126.3, 127.4, 128.5, 128.6, 133.7, 136.8, 137.7. LRMS (70 eV, EI): *m/z* (%): 214 (M^+, 20), 182 (90), 167 (100), 123 (26), 91 (22). HRMS (70 eV, EI) calcd for $C_{15}H_{18}O$ (M^+): 214.1357; found: 214.1349. Elemental analysis calcd (%) for $C_{15}H_{18}O$: C, 84.07; H, 8.47; found: C, 83.47; H, 8.67.

4-Methoxy-1-(4-methyl-3-pentenyl)-4-[(*E*)-2-phenylethenyl]cyclopentene (4b). Colorless oil. R_f = 0.28 (Hexane: EtOAc, 95:5). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.62 (s, 3H), 1.69 (s, 3H), 2.10-2.25 (m, 4H), 2.45-2.70 (m, 4H), 3.24 (s, 3H), 5.05-5.18 (m, 1H), 5.33 (bs, 1H), 6.35 (d, *J* = 16.1 Hz, 1H), 6.52 (d, *J* = 16.1 Hz, 1H), 7.20-7.45 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.7, 25.6, 26.1, 31.4, 43.0, 45.4, 51.5, 86.4, 120.5, 124.1, 126.3, 127.4, 128.5, 128.6, 131.6, 133.7, 136.9, 142.0. LRMS (70 eV, EI): *m/z* (%): 282 (M^+, 31), 213 (36), 165 (39), 115 (43), 103 (55), 91 (100), 69 (99). HRMS (70 eV, EI) calcd for $C_{20}H_{26}O$ (M^+): 282.1984; found: 282.1975. Elemental analysis calcd (%) for $C_{20}H_{26}O$: C, 85.06; H, 9.28. found: C, 85.43; H, 8.90.

4-[(*E*)-2-(2-Furyl)ethenyl]-4-methoxy-1-methylcyclopentene (4c). Colorless oil. R_f = 0.22 (Hexane: EtOAc, 95:5). ^{1}H NMR (300 MHz,

$CDCl_3$): δ = 1.75 (bs, 3H), 2.40-2.72 (m, 4H), 3.21 (s, 3H), 5.28 (bs, 1H), 6.24 (d, *J* = 3.1 Hz, 1H), 6.27 (d, *J* = 19.6 Hz, 1H), 6.35 (d, *J* = 20.0 Hz, 1H), 6.38 (dd, *J* = 3.5, 1.6 Hz, 1H), 7.35 (d, *J* = 1.7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.7, 43.1, 47.2, 51.5, 86.5, 107.6, 111.2, 117.2, 121.5, 132.5, 137.7, 141.7.

General Procedure for the Synthesis of Compounds 5 and 6. To a solution of the corresponding alkyl enol ether **3a-f** (methyl) or **3g-i** ((–)-8-phenylmenthyl) (1 mmol) in THF (10 mL) was added at room temperature a solution of HCl 2N (0.5 mL, 1 mmol) and the mixture was stirred at this temperature until consumption of starting material, 10-15 min for compounds **3a-f** and 1 h for **3g-i** (the reaction was monitored by TLC). This procedure was also used to hydrolyze the crude product obtained in the first step of each one of the reactions shown in Table 2. The solvent was removed under reduced pressure and the residue extracted with Et_2O. The organic phase was dried with Na_2SO_4 and concentrated in vacuo. The resulting oil was purified by column chromatography (silica gel, hexane:EtOAc, 95:5) to give the corresponding cyclopentanone **5a**-**h**, **6a**, **(+)-5a** and **(+)-6a,b** as pure compounds and each one as a single diastereoisomer. Yields are listed in Table 1, 2 and 3. After column chromatography the quiral auxiliary group was recovered (60-75%).

(2*R*,4*R*)-2-Methyl-4-phenyl-2-vinylcyclopentanone ((+)-5a). Colorless oil. R_f = 0.33 (Hexane:EtOAc, 95:5). $[\alpha]_D^{20}$ = +19.00

($0.40x10^{-2}$, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.28 (s, 3H), 2.20 (t, *J* = 12.6 Hz, 1H), 2.29 (ddd, *J* = 12.6, 6.5, 2.2 Hz, 1H), 2.46 (dd, *J* = 18.5, 12.6 Hz, 1H), 2.81 (ddd, *J* = 18.3, 7.4, 2.2 Hz, 1H), 3.50 (apparent septet , *J* = 7.0 Hz, 1H), 5.13 (dd, *J* = 6.5, 0.9 Hz, 1H), 5.18 (s, 1H), 6.02 (dd, *J* = 17.9, 10.0 Hz, 1H), 7.23-7.41 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.6, 38.0, 43.8, 45.1, 53.1, 113.8, 126.7, 128.6, 141.0, 142.8, 218.4. LRMS (70 eV, EI): *m/z* (%): 200 (M^+, 84), 143 (92), 128 (35), 104 (100), 91 (17), 77 (16). HRMS (70 eV, EI) calcd for $C_{14}H_{16}O$ (M^+): 200.1201; found: 200.1205. Elemental analysis calcd (%) for $C_{14}H_{16}O$: C, 83.96; H, 8.05; found: C, 84.19; H, 8.35. The enantiomeric excess of **(+)-5a** was determined using a Chiralcel OJ column, hexane as eluant and a flow rate of 0.8 mL min^{-1}, retention times (min): 54.3 (minor), 60.3 (major), 70% ee.

(2*R,4*R**)-4-(2-Furyl)-2-methyl-2-vinylcyclopentanone (5b)**. Colorless oil. R_f = 0.23 (Hexane: EtOAc, 95:5). ^1H NMR (200 MHz, $CDCl_3$): δ = 1.23 (s, 3H), 2.26 (t, *J* = 9.0 Hz, 2H), 2.48 (dd, *J* = 18.5, 11.3 Hz, 1H), 2.76 (ddd, *J* = 8.2, 7.2, 1.0 Hz, 1H), 3.43-3.64 (m, 1H), 5.09 (dd, *J* = 6.5, 0.8 Hz, 1H), 5.13 (s, 1H), 5.96 (dd, *J* = 18.0, 10.3 Hz, 1H), 6.10 (dt, *J* = 3.1, 0.8 Hz, 1H), 6.32 (dd, *J* = 3.1, 1.8 Hz, 1H), 7.36 (dd, *J* = 1.8, 0.8 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.4, 31.7, 41.2, 42.6, 52.5, 104.6, 110.1, 113.9, 140.6, 141.4, 156.2, 218.0. LRMS (70 eV, EI): *m/z* (%): 190

(M^+, 62), 162 (40), 133 (61), 105 (35), 94 (100). HRMS (70 eV, EI) calcd for $C_{12}H_{14}O_2$ (M^+): 190.0994; found: 190.0992.

(2*R,4*R**)-4-Ferrocenyl-2-methyl-2-vinylcyclopentanone (5c)**. Orange solid: R_f = 0.27 (Hexane: EtOAc, 95:5). M.p. 74-75 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.22 (s, 3H), 2.08 (t, *J* = 12.6 Hz, 1H), 2.19 (ddd, *J* = 12.8, 6.6, 2.0 Hz, 1H), 2.39 (dd, *J* = 18.2, 11.7 Hz, 1H), 2.75 (ddd, *J* = 18.2, 7.7, 1.7 Hz, 1H), 3.09-3.22 (m, 1H), 4.05-4.21 (m with s at 4.17, 9H), 5.10 (dd, *J* = 8.0, 0.9 Hz, 1H), 5.15 (s, 1H), 5.98 (dd, *J* = 17.1, 11.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.7, 32.0, 43.8, 45.4, 53.1, 65.9, 66.7, 67.3, 67.4, 68.2, 91.6, 113.7, 141.1, 219.1. LRMS (70 eV, EI): *m/z* (%): 309 (M^++1, 22), 308 (M^+, 100), 212 (24), 186 (9), 121 (14). HRMS (70 eV, EI) calcd for $C_{18}H_{20}FeO$ (M^+): 308.0864; found: 308.0872. Elemental analysis calcd (%) for $C_{18}H_{20}FeO$: C, 70.15; H, 6.54; found: C, 70.19; H, 6.16.

(2*R,4*R**)-4-Butyl-2-methyl-2-vinylcyclopentanone (5d)**. Colorless oil. R_f = 0.47 (Hexane:EtOAc, 95:5). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.80-1.00 (m, 3H), 1.19-1.45 (m, 6H), 1.41 (s, 3H), 1.65 (t, *J* = 12.0 Hz, 1H), 1.85 (dd, *J* = 18.2, 11.1 Hz, 1H), 1.99 (ddd, *J* = 12.5, 6.0, 2.3 Hz, 1H), 2.19-2.28 (m, 1H), 2.51 (ddd, *J* = 18.2, 7.1, 2.3 Hz, 1H), 5.02-5.12 (m, 2H), 5.92 (dd, *J* = 17.1, 11.1 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.0, 22.7, 30.1, 30.3, 32.8, 35.8, 42.6, 44.6, 52.9, 113.4, 141.5, 220.2. LRMS (70 eV,

EI): *m/z* (%): 180 (M^+, 35), 123 (22), 95 (39), 81 (35), 68 (93). HRMS (70 eV, EI) calcd for $C_{12}H_{20}O$ (M^+): 180.1514; found: 180.1512.

(2*R,4*R**)-2-(4-Methyl-3-pentenyl)-4-phenyl-2-vinylcyclopentanone (5e)**. Colorless oil. R_f = 0.29 (Hexane: EtOAc, 95:5). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 58-1.66 (m with s at 1.64, 4H), 1.70 (s, 3H), 1.85-2.05 (m, 3H), 2.14 (t, *J* = 12.4 Hz, 1H), 2.45 (dd, *J* = 18.3, 12.0 Hz, 1H), 2.46 (dd, *J* = 19.4, 2.2 Hz, 1H), 2.80 (ddd, *J* = 18.3, 7.6, 2.2 Hz, 1H), 3.47 (apparent septet, *J* = 7.0 Hz, 1H), 5.03-5.15 (m with d at 5.09, *J* = 17.4 Hz, 2H), 5.19 (d, *J* = 10.8 Hz, 1H), 6.05 (dd, *J* = 17.4, 10.8 Hz, 1H), 7.24-7.45 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 7.6, 22.6, 25.6, 35.3, 37.9, 39.8, 45.0, 57.0, 114.5, 123.4, 126.8, 128.6, 132.3, 139.7, 143.0, 218.0. LRMS (70 eV, EI): *m/z* (%): 268 (M^+, 5), 186 (100), 104 (10), 91 (16), 69 (14). HRMS (70 eV, EI) calcd for $C_{19}H_{24}O$ (M^+): 268.1827; found: 268.1825.

(2*R,4*R**)-2-Methyl-2-(1-methylethenyl)-4-phenylcyclopentanone (5f)**. Colorless oil. R_f = 0.28 (Hexane:EtOAc, 95:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31 (s, 3H), 1.78 (s, 3H), 2.20 (ddd, *J* = 12.8, 6.6, 2.2 Hz, 1H), 2.30 (t, *J* = 12.7 Hz, 1H), 2.47 (dd, *J* = 18.0, 12.7 Hz, 1H), 2.81 (ddd, *J* = 12.0, 7.2, 2.2 Hz, 1H), 3.46 (m, 1H), 4.94-4.96 (m, 2H), 7.12-7.41 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.1, 21.5, 38.1, 44.5, 46.3, 55.5, 112.0, 126.7, 128.7, 142.8, 145.9, 219.2. LRMS (70 eV, EI): *m/z* (%): 214 (M^+, 70), 157 (75), 131 (75), 104 81009, 82 (90). HRMS (FAB^+) calcd for $C_{15}H_{19}O$ (M^++1):

215.1436; found: 215.1435. Elemental analysis calcd (%) for $C_{15}H_{18}O$: C, 84.07, H, 8.47; found: C, 84.38, H, 8.37.

(2*R,4*R**,*E*)-2-Methyl-2-(1-propenyl)-4-phenylcyclopentanone (5g)**. Colorless oil. R_f = 0.39 (Hexane:EtOAc, 95:5). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.24 (s, 3H), 1.72 (d, *J* = 6.0 Hz, 3H), 2.12-2.30 (m, 2H), 2.44 (dd, *J* = 18.2, 12.2 Hz, 1H), 2.79 (ddd, *J* = 18.2, 7.4, 2.0 Hz, 1H), 3.47 (m, 1H), 5.51-5.67 (m, 2H), 7.20-7.41 (m, 5H). ^{13}C NMR (300 MHz, $CDCl_3$) δ = 18.1, 23.0, 38.0, 44.6, 45.1, 52.3, 124.5, 126.6, 126.7, 128.6, 133.9, 142.9, 219.4. LRMS (70 eV, EI): *m/z* (%): 214 (M^+, 100), 171 (73), 157 (100), 143 (89), 129 (69), 104 (100), 91 (67). HRMS (FAB$^+$) calcd for $C_{15}H_{19}O$ (M^++1): 215.1436; found: 215.1428. Elemental analysis calcd (%) for $C_{15}H_{18}O$: C, 84.07, H, 8.47; found: C, 83.80, H, 8.36.

(2*R,4*R**)-2-Methyl-2-(2-methyl-1-propenyl)-4-phenylcyclopentanone (5h)**. Colorless oil. R_f = 0.26 (Hexane:EtOAc, 95:5). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.29 (s, 3H), 1.65 (d, *J* = 1.3 Hz, 3H), 1.75 (d, *J* = 1.3 Hz, 3H), 2.20 (t, *J* = 12.6 Hz, 1H), 2.48 (dd, *J* = 18.5, 12.1 Hz, 1H), 2.53 (ddd, *J* = 18.5, 12.8, 2.1 Hz, 1H), 2.84 (ddd, *J* = 18.5, 7.7, 2.1 Hz, 1H), 3.35-3.57 (m, 1H), 5.41 (q, *J* = 1.3 Hz, 1H), 7.25-7.43 (m, 5H). ^{13}C NMR (300 MHz, $CDCl_3$): δ = 19.8, 24.1, 26.6, 38.3, 44.9, 46.2, 51.4, 126.6, 126.8, 128.4, 128.6, 134.0, 143.1, 221.0. LRMS (70 eV, EI): *m/z* (%): 229 (M^++1, 56), 219 (97), 208 (63), 192 (27), 166 (15), 154 (100). HRMS (FAB$^+$) calcd for $C_{16}H_{21}O$ (M^++1): 229.1592; found: 229.1586.

Elemental analysis calcd (%) for $C_{16}H_{20}O$: C, 84.16, H, 8.83; found: C, 84.50, H, 9.02.

(*R*,*E*)-2-Ethylidene-4-phenylcyclopentanone ((+)-6a). Colorless oil. R_f = 0.34 (Hexane: EtOAc, 95:5); $[\alpha]_D^{20}$ = +16.94 ($0.77x10^{-2}$, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.83 (ddd, *J* = 7.1, 2.3, 1.4 Hz, 3H), 2.52 (dd, *J* = 17.7, 10.4 Hz, 1H), 2.58-2.66 (m, 1H), 2.78 (dd, *J* = 17.7, 7.7 Hz, 1H), 3.12 (dd, *J* = 16.4, 7.6 Hz, 1H), 3.41 (apparent quintet, *J* = 8.6 Hz, 1H), 6.65-6.81 (m, 1H), 7.20-7.49 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.1, 34.9, 38.9, 46.0, 126.5, 128.5, 131.4, 138.1, 143.6, 205.0. LRMS (70 eV, EI): *m/z* (%): 186 (M^+, 94), 115 (17), 104 (29), 91 (17), 82 (100), 77 (23). HRMS (70 eV, EI) calcd for $C_{13}H_{14}O$ (M^+): 186.1045; found: 186.1038. The enantiomeric excess of **(+)-6a** was determined using a Chiralcel OJ column, hexane as eluant and a flow rate of 1 mL min^{-1}, retention times (min): 80.2 (major), 103.2 (minor), >99% ee.

(*R*,*E*)-2-Ethylidene-4-ferrocenylcyclopentanone ((+)-6b). Orange solid. R_f = 0.19 (Hexane: EtOAc, 95:5). M.p. 69-70° C. $[\alpha]_D^{20}$ = + 15.13 ($0.08x10^{-2}$, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.81 (d, *J* = 7.1 Hz, 3H), 2.40-2.57 (m with a dd at 2.46, *J* = 17.8, 9.3 Hz, 2H), 2.70 (dd, *J* = 17.7, 7.7 Hz, 1H), 2.93-3.14 (m with a dd at 2.97, *J* = 16.1, 7.6 Hz, 2H), 4.04 (s, 2H), 4.10-4.11 (m, 2H), 4.12 (s, 5H), 6.56-6.68 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.1, 32.7, 34.7, 46.3, 66.0, 66.5, 67.3, 68.1, 92.4, 131.1, 138.2, 205.3. HRMS (70 eV, EI) calcd for $C_{17}H_{19}FeO$ (M^++1): 295.0785; found

295.0774. Elemental analysis calcd (%) for $C_{17}H_{18}FeO$: C, 69.41; H, 6.17; found: C, 69.45; H, 6.20. The enantiomeric excess of **(+)-6b** was determined using a Chiralcel OB-H column, hexane:2-propanol (150:1) as eluant and a flow rate of 1 mL min^{-1}, retention times (min): 41.0 (major), 52.4 (minor), 79% ee. The absolute configuration was determined by X-Ray analysis of a cristal corresponding to the major enantiomer.

Methyl *(1R*,6R*)*-3,4-dimethyl-6-phenyl-3-cyclohexenecarboxylate (7). Yellow solid. R_f = 0.56 (Hexane: EtOAc, 95:5). M.p. 96-98º C. ^{1}H NMR (300 MHz, C_6D_6): δ = 1.55 (s, 3H), 1.63 (s, 3H), 1.72-1.98 (m, 2H), 2.17-2.46 (m, 2H), 2.84 (td, *J* = 11.4, 5.1 Hz, 1H), 3.89 (s, 3H), 4.50 (td, *J* = 11.1, 4.8 Hz, 1H), 7.05-7.27 (m, 5H). ^{13}C NMR (75 MHz, C_6D_6): δ = 18.6, 18.7, 36.4, 40.2, 44.6, 70.0, 74.4, 123.8, 125.7, 126.4, 127.7, 128.2, 143.2, 197.0. LRMS (70 eV, EI): *m/z* (%): 244 (M^+, 21), 184 (100), 169 (42), 91 (45).

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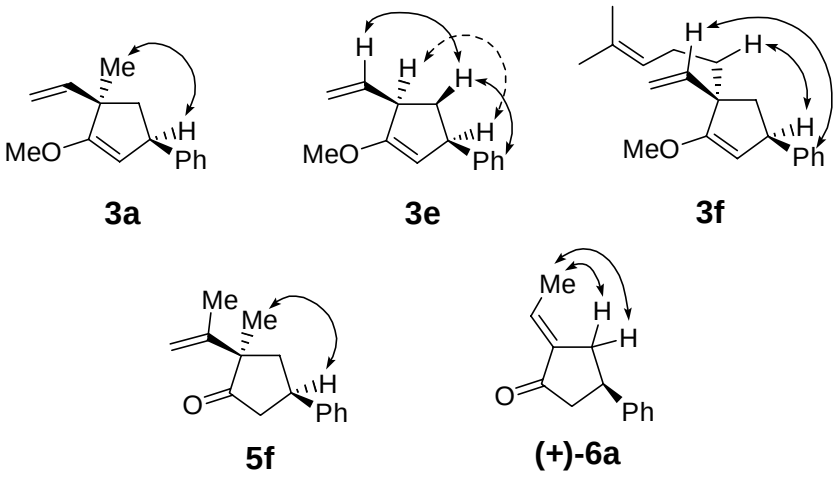

3a **3e** **3f**

5f **(+)-6a**

Figure 1. The arrows stand for the observed significant NOE enhacements (NOESY experiments) of compounds **3a**,**e**,**f**,**5f** and **(+)-6a**.