Supporting Information for:

Highly Chemo-, Regio-, and Stereoselective [3+2]-Cyclization of
Activated and Deactivated Allenes with Alkenyl Fischer Carbene
Complexes: A Straightforward Access to
Alkylidenecyclopentanone Derivatives

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General Methods: ^1H NMR and ^{13}C NMR spectra were recorded at room temperature in CDCl_3 , on a Bruker AC-300 (300 and 75.5 MHz) and Bruker AMX-400 (400 and 100 MHz) spectrometers. Chemical shifts are given in ppm relative to TMS (^1H , 0.0 ppm) or CDCl_3 (^{13}C , 77.0 ppm). Carbon multiplicities were assigned by DEPT techniques. IR spectra were obtained in a Mattson 3000 FTIR spectrometer. Elemental analyses were carried out on a Perkin-Elmer 2400 and Carlo Erba 1108 microanalyzers. TLC was performed on aluminum-backed plates with silica gel 60 with F_{254} indicator. All reactions involving organometallic species were carried out under nitrogen using standard Schlenk techniques. CH_2Cl_2 was distilled from CaH_2 . Flash column chromatography was carried out on silica gel (230-240 mesh). Fischer carbene

complexes **1**, allenes **2**, **3**, and $[\text{Rh}(\text{naphthalene})(\text{cod})][\text{SbF}_6]$ were prepared according to literature methods. All other reagents and solvents used in this work were of the best commercial grade available and used without further purification.

General Procedure for the Rh(I)-Catalyzed [3+2]-Cyclization Reaction of Alkenyl Fischer Carbene Complexes **1 and Electron-rich Allenes **2a-c** and **2e**: Synthesis of Cyclopentene Derivatives **4** and **6**.**

To a solution of the carbene complex **1** (1 equiv) and the corresponding allene (2 equiv for allenes **2a** and **2e**; 1.2 equiv for allenes **2b**, **2c** and **2d**) in CH_2Cl_2 under a CO atmosphere (1 bar) was added the corresponding Rh(I)-catalyst (0.1 equiv, 10%). The mixture was stirred at room temperature until disappearance of the starting carbene complex (checked by TLC; 0.5-18 h). The solvent was distilled under reduced pressure and the residue was dissolved in a mixture of diethylether and CH_2Cl_2 (10:1) and filtered through Celite. The solvents were removed in vacuo and the residue was purified by flash chromatography (SiO_2 , mixtures of hexane and ethyl acetate).

Compound 4a. The general procedure was followed using complex **1a** (184 mg, 0.5 mmol), allene **2a** (123 mg, 1 mmol) and $[\text{Rh}(\text{cod})\text{Cl}]_2$ (24.6 mg, 0.05 mmol) in CH_2Cl_2 (10 mL). Final chromatographic purification using a 2:1 mixture of hexane:ethyl acetate as eluent afforded **4a** (114 mg, 76 %). ^1H -NMR (CDCl_3): 1.98-2.12 (m, 2H), 2.43 (t, $J = 7.5$ Hz, 2H), 3.33 (t, $J = 7.0$ Hz, 2H), 3.70-3.72 (m, 1H), 3.75 (s, 3H), 3.77 (s, 3H), 4.77 (br s, 1H), 5.04 (br s, 1H), 5.07-5.09 (m, 1H), 5.25 (d, $J = 2.5$ Hz, 1H), 6.83 (d, $J = 8.8$

Hz, 2H), 7.11 (d, $J = 8.8$ Hz, 2H); ^{13}C -NMR (CDCl_3): 18.1 (CH_2), 31.2 (CH_2), 42.8 (CH_2), 48.2 (CH), 55.2 (CH_3), 56.4 (CH_3), 60.2 (CH), 104.0 (CH_2), 105.9 (CH), 114.0 (CH), 128.0 (CH), 135.4 (C), 144.2 (C), 157.4 (C), 158.5 (C), 174.9 (C). IR (CH_2Cl_2): ν 1679, 1611, 1512, 1421 cm^{-1} . Anal. Calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_3$: C, 72.22; H, 7.07; N, 4.68; Found: C, 72.36; H, 7.02; N, 4.65.

4b

Compound 4b. The general procedure was followed using complex **1b** (169 mg, 0.5 mmol), allene **2a** (123 mg, 1mmol) and $[\text{Rh}(\text{cod})\text{Cl}]_2$ (24.6 mg, 0.05 mmol) in CH_2Cl_2 (10 mL). Final chromatographic purification using a 2:1 mixture of hexane:ethyl acetate as eluent afforded **4b** (105 mg, 78 %). ^1H -NMR (CDCl_3): 2.01-2.09 (m, 2H), 2.43 (t, $J = 8.1$ Hz, 2H), 3.35 (t, $J = 7.0$ Hz, 2H), 3.74-3.76 (s + m, 4H), 4.79 (br s, 1H), 5.08 (br s, 1H), 5.11-5.14 (m, 1H), 5.27 (d, $J = 2.4$ Hz, 1H), 7.19-7.30 (m, 5H); ^{13}C -NMR (CDCl_3): 18.1 (CH_2), 31.2 (CH_2), 42.8 (CH_2), 49.0 (CH), 56.5 (CH_3), 60.0 (CH), 104.1 (CH_2), 105.7 (CH), 126.8 (CH), 127.0 (CH), 128.6 (CH), 143.3 (C), 144.2 (C), 157.5 (C), 174.9 (C). IR (CH_2Cl_2): ν 1682, 1422 cm^{-1} . Anal. Calcd for $\text{C}_{17}\text{H}_{19}\text{NO}_2$: C, 75.81; H, 7.11; N, 5.20; Found: C, 75.66; H, 7.13; N, 5.31.

4c

Compound 4c. The general procedure was followed using complex **1c** (186 mg, 0.5 mmol), allene **2a** (123 mg, 1mmol) and $[\text{Rh}(\text{cod})\text{Cl}]_2$ (24.6 mg, 0.05 mmol) in CH_2Cl_2

(10 mL). Final chromatographic purification using a 2:1 mixture of hexane:ethyl acetate as eluent afforded **4c** (126 mg, 83 %). $^1\text{H-NMR}$ (CDCl_3): 2.06-2.13 (m, 2H), 2.47 (t, $J = 8.0$ Hz, 2H), 3.36 (t, $J = 7.6$ Hz, 2H), 3.75-3.76 (m, 1H), 3.80 (s, 3H), 4.84 (br s, 1H), 5.07 (br s, 1H), 5.10-5.12 (m, 1H), 5.32 (d, $J = 3.0$ Hz, 1H), 7.18 (d, $J = 8.7$ Hz, 2H), 7.29 (d, $J = 8.7$ Hz, 2H); $^{13}\text{C-NMR}$ (CDCl_3): 18.6 (CH_2), 31.7 (CH_2), 43.2 (CH_2), 49.1 (CH), 57.0 (CH_3), 60.4 (CH), 105.1 (CH_2), 105.5 (CH), 128.9 (CH), 129.2 (CH), 133.0 (C), 142.4 (C), 144.2 (C), 158.3 (C), 175.5 (C). IR (CH_2Cl_2): ν 1680, 1612, 1491, 1422 cm^{-1} . Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{ClNO}_2$: C, 67.21; H, 5.97; N, 4.61; Found: C, 67.43; H, 5.83; N, 4.72.

Compound 4d. The general procedure was followed using complex **1d** (164 mg, 0.5 mmol), allene **2a** (123 mg, 1mmol) and $[\text{Rh}(\text{cod})\text{Cl}]_2$ (24.6 mg, 0.05 mmol) in CH_2Cl_2 (10 mL). Final chromatographic purification using a 2:1mixture of hexane:ethyl acetate as eluent afforded **4d** (104 mg, 80 %). $^1\text{H-NMR}$ (CDCl_3): 1.99-2.09 (m, 2H), 2.45 (t, $J = 7.7$ Hz, 2H), 3.24-3.34 (m, 2H), 3.73 (s, 3H), 3.85-3.87 (m, 1H), 4.79 (br s, 1H), 5.08 (br s, 1H), 5.27 (d, $J = 2.5$ Hz, 1H), 5.34-5.36 (m, 1H), 6.17 (d, $J = 3.1$ Hz, 1H), 6.27-6.29 (m, 1H), 7.33 (br s, 1H); $^{13}\text{C-NMR}$ (CDCl_3): 18.0 (CH_2), 31.1 (CH_2), 42.3 (CH), 42.6 (CH_2), 56.4 (CH_3), 56.8 (CH), 102.7 (CH), 104.1 (CH_2), 105.0 (CH), 110.2 (CH), 141.6 (CH), 143.3 (C), 155.8 (C), 157.4 (C), 175.0 (C). IR (CH_2Cl_2): ν 1682, 1614, 1422 cm^{-1} . Anal. Calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_3$: C, 69.48; H, 6.61; N, 5.40; Found: C, 69.43; H, 6.75; N, 5.44.

Compound 4e. The general procedure was followed using complex **1g** (159 mg, 0.5 mmol), allene **2a** (123 mg, 1mmol) and [Rh(cod)Cl]₂ (24.6 mg, 0.05 mmol) in CH₂Cl₂ (10 mL). Final chromatographic purification using a 2:1 mixture of hexane:ethyl acetate as eluent afforded **4e** (78 mg, 63%). ¹H-NMR (CDCl₃): 0.91 (s, 9H), 1.91-2.06 (m, 2H), 2.33-2.46 (m, 3H), 3.20 (t, *J* = 7.4 Hz, 2H), 3.71 (s, 3H), 4.74 (br s, 1H), 4.98 (br s, 1H), 5.04-5.07 (m, 1H), 5.16 (d, *J* = 2.4 Hz, 1H); ¹³C-NMR (CDCl₃): 18.0 (CH₂), 26.9 (CH₃), 31.3 (CH₂), 33.0 (C), 42.3 (CH₂), 52.7 (CH), 54.0 (CH), 56.2 (CH₃), 103.0 (CH₂), 104.3 (CH), 145.0 (C), 157.1 (C), 174.2 (C). IR (CH₂Cl₂): ν 1672, 1613, 1462, 1424, 1270, 1163 cm⁻¹. Anal. Calcd for C₁₅H₂₃NO₂: C, 72.25; H, 9.30; N, 5.62; Found: C, 72.18; H, 9.15; N, 5.66.

Compound 4f. The general procedure was followed using complex **1h** (171 mg, 0.5 mmol), allene **2a** (123 mg, 1mmol) and [Rh(cod)Cl]₂ (24.6 mg, 0.05 mmol) in CH₂Cl₂ (10 mL). Final chromatographic purification using a 2:1 mixture of hexane:ethyl acetate as eluent afforded **4f** (107 mg, 78%). ¹H-NMR (CDCl₃): 1.54-1.61 (m, 4H), 1.84-2.04 (m, 6H), 2.43 (t, *J* = 7.5 Hz, 2H), 3.02 (br s, 1H), 3.15-3.29 (m, 2H), 3.71 (s, 3H), 4.72 (br s, 1H), 4.89 (br s, 1H), 4.98-5.01 (m, 1H), 5.17 (d, *J* = 2.3 Hz, 1H), 5.45 (br s, 1H); ¹³C-NMR (CDCl₃): 18.0 (CH₂), 22.4 (CH₂), 22.8 (CH₂), 25.1 (CH₂), 26.3 (CH₂), 31.3

(CH₂), 42.5 (CH₂), 50.4 (CH), 56.3 (CH₃), 56.6 (CH), 103.3 (CH₂), 105.1 (CH), 121.8 (CH), 138.6 (C), 144.5 (C), 157.0 (C), 174.8 (C). IR (CH₂Cl₂): ν 1678, 1435, 1102 cm⁻¹. Anal. Calcd for C₁₇H₂₃NO₂: C, 74.69; H, 8.48; N, 5.12; Found: C, 74.72; H, 8.43; N, 5.16.

4g

Compound 4g. The general procedure was followed using complex **1a** (184 mg, 0.5 mmol), allene **2b** (171 mg, 0.6 mmol) and [Rh(cod)Cl]₂ (24.6 mg, 0.05 mmol) in CH₂Cl₂ (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded **4g** (226 mg, 98%). ¹H-NMR (CDCl₃): 2.38 (s, 3H), 3.60 (s, 3H), 3.63-3.65 (m, 1H), 3.84 (s, 3H), 4.70 (br s, 1H), 5.26-5.29 (m, 1H), 5.35 (br s, 1H), 5.40 (d, *J* = 2.5 Hz, 1H), 6.81 (d, *J* = 8.8 Hz, 2H), 7.01- 7.06 (m, 4H), 7.14-7.16 (m, 2H), 7.28-7.35 (m, 5H); ¹³C-NMR (CDCl₃): 21.4 (CH₃), 48.6 (CH), 55.2 (CH₃), 56.1 (CH₃), 69.4 (CH), 105.7 (CH₂), 113.9 (CH), 127.2 (CH), 128.3 (CH), 128.5 (CH), 128.9 (CH), 129.1 (CH), 131.8 (CH), 135.5 (C), 136.8 (C), 138.3 (C), 142.7 (C), 145.9 (C), 156.7 (C), 158.5 (C). Anal. Calcd for C₂₇H₂₇NO₄S: C, 70.26; H, 5.90; N, 3.03; Found: C, 70.21; H, 6.01; N, 3.12.

4h

Compound 4h. The general procedure was followed using complex **1b** (169 mg, 0.5 mmol), allene **2b** (171 mg, 0.6 mmol) and [Rh(cod)Cl]₂ (24.6 mg, 0.05 mmol) in

CH₂Cl₂ (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded **4h** (190 mg, 88 %). ¹H-NMR (CDCl₃): 2.37 (s, 3H), 3.60 (s, 3H), 3.68-3.70 (m, 1H), 4.72 (br s, 1H), 5.33-5.35 (m, 1H), 5.37 (br s, 1H), 5.42 (d, *J* = 2.3 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 2H), 7.10-7.27 (m, 12H); ¹³C-NMR (CDCl₃): 21.4 (CH₃), 49.5 (CH), 56.2 (CH₃), 69.2 (CH), 105.6 (CH), 106.0 (CH₂), 126.8 (CH), 127.3 (CH), 127.6 (CH), 128.3 (CH), 128.6 (CH), 128.9 (CH), 129.2 (CH), 131.9 (CH), 136.8 (C), 138.3 (C), 142.8 (C), 143.6 (C), 145.9 (C), 157.0 (C). IR (CH₂Cl₂): ν 1614, 1422, 1162 cm⁻¹. Anal. Calcd for C₂₆H₂₅NO₃S: C, 72.36; H, 5.84; N, 3.25; Found: C, 72.29; H, 5.91; N, 3.22.

Compound 4i. The general procedure was followed using complex **1e** (223 mg, 0.5 mmol), allene **2b** (171 mg, 0.6 mmol) and [Rh(cod)Cl]₂ (24.6 mg, 0.05 mmol) in CH₂Cl₂ (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded **4i** (267 mg, 99%). ¹H-NMR (CDCl₃): 2.41 (s, 3H), 3.45 (t, *J* = 3.0 Hz, 1H), 3.64 (s, 3H), 3.93 (br s, 1H), 4.07-4.16 (several signals, 8H), 4.91 (br s, 1H), 5.13 (br s, 1H), 5.19-5.22 (m, 1H), 5.31 (d, *J* = 2.4 Hz, 1H), 7.13-7.30 (m, 7H), 7.51 (d, *J* = 8.2 Hz, 2H); ¹³C-NMR (CDCl₃): 21.5 (CH₃), 43.5 (CH), 56.2 (CH₃), 65.9 (CH), 67.4 (CH), 67.5, 67.7 (CH), 68.3 (CH), 91.7 (C), 104.9 (CH), 105.8 (CH₂), 127.6 (CH), 128.3 (CH), 128.8 (CH), 129.3 (CH), 131.9 (CH), 136.8 (C), 138.4 (C), 143.0 (C), 146.3 (C), 156.5 (C). Anal. Calcd for C₃₀H₂₉FeNO₃S: C, 66.79; H, 5.42; N, 2.60; Found: C, 66.90; H, 5.46; N, 2.71.

4j

Compound 4j. The general procedure was followed using complex **1d** (164 mg, 0.5 mmol), allene **2b** (172 mg, 0.6 mmol) and $[\text{Rh}(\text{cod})\text{Cl}]_2$ (24.6 mg, 0.05 mmol) in CH_2Cl_2 (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded **4j** (185 mg, 88 %). ^1H -NMR (CDCl_3): 2.41 (s, 3H), 3.60 (s, 3H), 3.82 (dd, $J = 4.6$ and 2.4 Hz, 1H), 4.71 (br s, 1H), 5.36 (br s, 1H), 5.41 (d, $J = 2.5$ Hz, 1H), 5.53-5.56 (m, 1H), 6.05 (d, $J = 3.1$ Hz, 1H), 6.30-6.32 (m, 1H), 7.10-7.27 (m, 8H), 7.48 (d, $J = 8.0$ Hz, 2H); ^{13}C -NMR (CDCl_3): 21.4 (CH_3), 42.8 (CH), 56.1 (CH_3), 66.0 (CH), 102.1 (CH), 105.7 (CH), 106.0 (CH_2), 110.2 (CH), 127.4 (CH), 128.5 (CH), 128.9 (CH), 129.2 (CH), 132.3 (CH), 136.4 (C), 138.2 (C), 141.5 (CH), 142.9 (C), 145.0 (C), 155.7 (C), 156.9 (C). Anal. Calcd for $\text{C}_{24}\text{H}_{23}\text{NO}_4\text{S}$: C, 68.39; H, 5.50; N, 3.32; Found: C, 68.46; H, 5.33; N, 3.33.

4k

Compound 4k. The general procedure was followed using complex **1g** (159 mg, 0.5 mmol), allene **2b** (171 mg, 0.6 mmol) and $[\text{Rh}(\text{cod})\text{Cl}]_2$ (24.6 mg, 0.05 mmol) in CH_2Cl_2 (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded **4k** (123 mg, 60%). ^1H -NMR (CDCl_3): 0.93 (s, 9H), 2.32 (t, $J = 2.5$ Hz, 1H), 2.39 (s, 3H), 3.49 (s, 3H), 4.61 (br s, 1H), 5.10 (br s, 1H), 5.22 (br s, 1H), 5.28-5.32 (m, 1H), 7.11-7.25 (m, 7H), 7.51 (d, $J = 8.1$ Hz, 2H); ^{13}C -

NMR (CDCl₃): 21.5 (CH₃), 27.3 (CH₃), 33.9 (C), 55.0 (CH), 56.1 (CH₃), 60.3 (CH), 104.1 (CH), 105.9 (CH₂), 127.8 (CH), 128.2 (CH), 128.4 (CH), 129.1 (CH), 132.5 (CH), 136.3 (C), 138.2 (C), 143.0 (C), 147.3 (C), 157.2 (C). Anal. Calcd for C₂₄H₂₉NO₃S: C, 70.04; H, 7.10; N, 3.40; Found: C, 70.17; H, 7.02; N, 3.52.

4l

Compound 4l: The general procedure was followed using complex **1h** (171 mg, 0.5 mmol), allene **2b** (171 mg, 0.6 mmol) and [Rh(cod)Cl]₂ (24.6 mg, 0.05 mmol) in CH₂Cl₂ (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded **4l** (170 mg, 78%). ¹H-NMR (CDCl₃): 1.52-1.66 (m, 4H), 1.89-2.01 (m, 4H), 2.42 (s, 3H), 3.10-3.11 (m, 1H), 3.54 (s, 3H), 4.52 (br s, 1H), 5.21-5.23 (m, 2H), 5.28 (d, *J* = 2.6 Hz, 1H), 5.36 (br s, 1H), 7.10-7.28 (m, 7H), 7.62 (d, *J* = 8.0 Hz, 2H); ¹³C-NMR (CDCl₃): 21.4 (CH₃), 22.4 (CH₂), 22.8 (CH₂), 25.2 (CH₂), 25.3 (CH₂), 51.3 (CH), 56.0 (CH₃), 64.1 (CH), 104.9 (CH), 105.3 (CH₂), 123.4 (CH), 127.6 (CH), 128.2 (CH), 128.7 (CH), 129.2 (CH), 132.3 (CH), 136.5 (C), 138.0 (C), 138.6 (C), 143.0 (C), 16.2 (C), 156.5 (C). Anal. Calcd for C₂₆H₂₉NO₃S: C, 71.69; H, 6.71; N, 3.22; Found: C, 71.54; H, 6.73; N, 3.25.

4m

Compound 4m. The general procedure was followed using complex **1f** (138 mg, 0.5 mmol), allene **2b** (171 mg, 0.6 mmol) and [Rh(cod)Cl]₂ (24.6 mg, 0.05 mmol) in

CH₂Cl₂ (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded **4m** (87 mg, 47%). ¹H-NMR (CDCl₃): 1.11 (d, *J* = 6.8 Hz, 3H), 2.45 (s, 3H), 2.61-2.65 (m, 1H), 3.53 (s, 3H), 4.63 (br s, 1H), 4.93-4.94 (m, 1H), 4.97 (br s, 1H), 5.21 (d, *J* = 2.3 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 2H), 7.27-7.29 (m, 5H), 7.67 (d, *J* = 8.1 Hz, 2H); ¹³C-NMR (CDCl₃): 19.9 (CH₃), 21.5 (CH₃), 38.7 (CH), 56.0 (CH₃), 67.5 (CH), 105.1 (CH₂), 107.1 (CH), 127.6 (CH), 128.3 (CH), 128.7 (CH), 129.4 (CH), 132.2 (CH), 136.7 (C), 138.6 (C), 143.2 (C), 145.8 (C), 155.9 (C). Anal. Calcd for C₂₁H₂₃NO₃S: C, 68.27; H, 6.27; N, 3.79; Found: C, 68.39; H, 6.21; N, 3.83.

Compound 4n. The general procedure was followed using complex **1a** (184 mg, 0.5 mmol), allene **2c** (178 mg, 0.6 mmol) and [Rh(cod)Cl]₂ (24.6 mg, 0.05 mmol) in CH₂Cl₂ (10 mL). Final chromatographic purification using a 3:1 mixture of hexane:ethyl acetate as eluent afforded **4n** (232 mg, 98%). ¹H-NMR (CDCl₃): 2.36 (s, 3H), 3.07 (dd, *J* = 15.2 and 7.2 Hz, 1H), 3.41 (s, 3H), 3.42 (s, 3H), 3.37 (dd, *J* = 15.2 and 3.6 Hz, 1H), 3.68 (s, 3H), 3.79 (s, 3H), 4.04 (t, *J* = 2.8 Hz, 1H), 4.56 (br s, 1H), 4.67-4.71 (m, 2H), 4.88 (t, *J* = 1.8 Hz, 1H), 5.15 (d, *J* = 2.4 Hz, 1H), 6.74 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H); ¹³C-NMR (CDCl₃): 21.2 (CH₃), 47.3 (CH₂), 48.9 (CH), 54.5 (CH₃), 55.0 (CH₃), 55.3 (CH₃), 56.1 (CH₃), 68.0 (CH), 104.0 (CH), 104.7 (CH₂), 106.3 (CH), 113.6 (CH), 127.0 (CH), 128.3 (CH), 129.2 (CH), 135.7 (C), 137.5 (C), 142.9 (C), 144.2 (C), 156.6 (C), 158.3

(C). Anal. Calcd for C₂₅H₃₁NO₆S: C, 63.40; H, 6.60; N, 2.96; Found: C, 63.56; H, 6.54; N, 2.93.

6a

Compound 6a. The general procedure was followed using complex **1a** (184 mg, 0.5 mmol), allene **2e** (132 mg, 1 mmol) and [Rh(CO)₂Cl]₂ (19.4 mg, 0.05 mmol) in CH₂Cl₂ (10 mL). Final chromatographic purification using a 10:1 mixture of hexane:ethyl acetate as eluent afforded **6a** (97 mg, 63%). ¹H-NMR (CDCl₃): 3.80 (s, 3H), 3.84 (s, 3H), 3.90 (t, *J* = 2.3 Hz, 1H); 5.05 (m, 2H), 5.20 (br s, 1H), 5.44 (d, *J* = 1.6 Hz, 1H), 6.80-6.94 (m, 5H), 7.10-7.24 (m, 4H); ¹³C-NMR (CDCl₃): 51.9 (CH), 55.2 (CH₃), 56.5 (CH₃), 83.9 (CH), 106.0 (CH), 106.9 (CH₂), 114.0 (CH), 116.0 (CH), 121.0 (CH), 128.5 (CH), 129.3 (CH), 135.5 (C), 146.4 (C), 156.7 (C), 157.9 (C), 158.5 (C). IR (CH₂Cl₂): ν 1614, 1442, 1164 cm⁻¹. Anal. Calcd for C₂₀H₂₀O₃: C, 77.90; H, 6.54; Found: C, 77.95; H, 6.66.

6b

Compound 6b. The general procedure was followed using complex **1b** (169 mg, 0.5 mmol), allene **2e** (132 mg, 1 mmol) and [Rh(CO)₂Cl]₂ (19.4 mg, 0.05 mmol) in CH₂Cl₂ (10 mL). Final chromatographic purification using a 10:1 mixture of hexane:ethyl acetate as eluent afforded **6b** (82 mg, 59%). ¹H-NMR (CDCl₃): 3.78 (s, 3H), 3.92 (br s, 1H), 5.06 (br s, 2H), 5.19 (br s, 1H), 5.42 (br s, 1H), 6.81 (d, *J* = 7.9 Hz, 2H), 6.93 (t, *J*

= 7.3 Hz, 1H), 7.18-7.36 (m, 7H); ^{13}C -NMR (CDCl_3): 52.7 (CH), 56.5 (CH_3), 83.7 (CH), 105.7 (CH), 107.0 (CH_2), 116.0 (CH), 121.0 (CH), 126.9 (CH), 127.6 (CH), 128.6 (CH), 129.4 (CH), 143.4 (C), 146.4 (C), 156.9 (C), 157.9 (C). IR (CH_2Cl_2): ν 1600, 1500, 1164 cm^{-1} . Anal. Calcd for $\text{C}_{19}\text{H}_{18}\text{O}_2$: C, 81.99; H, 6.52; Found: C, 81.84; H, 6.57.

6c

Compound 6c. The general procedure was followed using complex **1c** (186 mg, 0.5 mmol), allene **2e** (132 mg, 1 mmol) and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (19.4 mg, 0.05 mmol) in CH_2Cl_2 (10 mL). Final chromatographic purification using a 10:1 mixture of hexane:ethyl acetate as eluent afforded **6c** (83 mg, 53%). ^1H -NMR (CDCl_3): 3.83 (s, 3H), 3.95 (t, J = 2.3 Hz, 1H), 5.05-5.06 (m, 2H), 5.24 (br s, 1H), 5.47 (d, J = 1.5 Hz, 1H), 6.85 (d, J = 7.8 Hz, 2H), 6.99 (t, J = 7.3 Hz, 1H), 7.16-7.27 (m, 6H); ^{13}C -NMR (CDCl_3): 52.1 (CH), 56.6 (CH_3), 83.7 (CH), 105.0 (CH), 107.3 (CH_2), 116.0 (CH), 121.2 (CH), 128.8 (CH), 128.9 (CH), 129.4 (CH), 132.6 (C), 142.0 (C), 146.0 (C), 157.2 (C), 157.8 (C). Anal. Calcd for $\text{C}_{19}\text{H}_{17}\text{ClO}_2$: C, 72.96; H, 5.48; Found: C, 73.02; H, 5.51.

6d

Compound 6d. The general procedure was followed using complex **1d** (164 mg, 0.5 mmol), allene **2e** (132 mg, 1 mmol) and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (19.4 mg, 0.05 mmol) in CH_2Cl_2 (10 mL). Final chromatographic purification using a 10:1 mixture of hexane:ethyl

acetate as eluent afforded **6d** (80 mg, 60%). ¹H-NMR (CDCl₃): 3.78 (s, 3H), 4.04 (br s, 1H), 5.01 (br s, 1H), 5.18 (br s, 1H), 5.22 (br s, 1H), 5.41 (br s, 1H), 6.08 (d, *J* = 3.3 Hz, 1H), 6.31-6.33 (m, 1H), 6.93-6.98 (m, 3H), 7.26 (t, *J* = 7.1 Hz, 2H), 7.38 (d, *J* = 1.0 Hz, 1H); ¹³C-NMR (CDCl₃): 46.1 (CH), 56.6 (CH₃), 80.8 (CH), 102.0 (CH), 105.8 (CH), 107.5 (CH₂), 110.3 (CH), 115.9 (CH), 121.2 (CH), 129.4 (CH), 141.8 (CH), 145.5 (C), 155.8 (C), 157.3 (C), 157.9 (C). IR (CH₂Cl₂): ν 1614, 1422, 1164 cm⁻¹. Anal. Calcd for C₁₇H₁₆O₃: C, 76.10; H, 6.01; Found: C, 76.04; H, 5.96.

Compound 6e. The general procedure was followed using complex **1e** (223 mg, 0.5 mmol), allene **2e** (132 mg, 1 mmol) and [Rh(CO)₂Cl]₂ (19.4 mg, 0.05 mmol) in CH₂Cl₂ (10 mL). Final chromatographic purification using a 10:1 mixture of hexane:ethyl acetate as eluent afforded **6e** (131 mg, 68%). ¹H-NMR (CDCl₃): 3.72 (br s, 1H), 3.82 (s, 3H), 4.00 (br s, 1H), 4.08-4.13 (s+m, 8H), 5.01 (br s, 1H), 5.08 (br s, 1H), 5.16 (br s, 1H), 5.31 (d, *J* = 1.6 Hz, 1H), 6.95-6.99 (m, 3H), 7.26-7.31 (m, 2H); ¹³C-NMR (CDCl₃): 46.9 (CH), 56.9 (CH₃), 67.0 (CH), 68.0 (CH), 68.1 (CH), 68.2 (CH), 68.9 (CH), 84.0 (CH), 91.2 (C), 105.0 (CH), 106.8 (CH₂), 116.7 (CH), 121.6 (CH), 129.9 (CH), 146.9 (C), 156.8 (C), 158.6 (C). IR (CH₂Cl₂): ν 1614, 1494, 1421 cm⁻¹. Anal. Calcd for C₂₃H₂₂FeO₂: C, 71.52; H, 5.74; Found: C, 71.60; H, 5.59.

General Procedure for the Rh(I)-Catalyzed [3+2]-Cyclization Reaction of Alkenyl Fischer Carbene Complexes **1 and Electron-Poor Allenes **3a-h**: Synthesis of Cyclopentene Derivatives **7-10**.**

To a solution of the carbene complex **1** (1 equiv) and the corresponding allene (2 equiv for allenes **3c-e**; 3 equiv for allenes **3a-b** and **3f-h**) in CH₂Cl₂ under a CO atmosphere (1 bar) was added [Rh(naphthalene)(cod)][SbF₆] (0.1 equiv, 10%). The mixture was stirred at room temperature until disappearance of the starting carbene complex (checked by TLC; 4-18 h). The solvent was distilled under reduced pressure and the residue was dissolved in a mixture of diethylether and CH₂Cl₂ (10:1) and filtered through Celite. The solvent was removed in vacuo and the residue was purified by flash chromatography (SiO₂, mixtures of hexane and ethyl acetate).

Compound 7a. The general procedure was followed using complex **1a** (184 mg, 0.5 mmol), allene **3a** (147 mg, 1.5 mmol) and [Rh(naphthalene)(cod)][SbF₆] (29 mg, 0.05 mmol) in CH₂Cl₂ (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded **7a** (99 mg, 72 %). ¹H-NMR (CDCl₃): 2.89 (dt, *J* = 19.7 and 2.4 Hz, 1H), 3.58 (ddd, *J* = 19.7, 7.0 and 2.4 Hz, 1H), 3.72 (s, 3H), 3.78 (s, 3H), 3.81 (s, 3H), 3.97 (m, 1H), 5.49 (d, *J* = 2.8 Hz, 1H), 5.96 (t, *J* = 2.4 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H); ¹³C-NMR (CDCl₃): 39.3 (CH₂), 44.8 (CH), 50.9 (CH₃), 55.2 (CH₃), 56.9 (CH₃), 106.6 (CH), 113.9 (CH), 116.1 (CH), 127.8 (CH), 137.1 (C), 158.2 (C), 158.3 (C), 158.7 (C), 167.9 (C). IR (CH₂Cl₂): ν 1703, 1634, 1606, 1511, 1100 cm⁻¹. Anal. Calcd for C₁₆H₁₈O₄: C, 70.06; H, 6.61; Found: C, 70.14; H, 6.59.

7b

Compound 7b. The general procedure was followed using complex **1b** (169 mg, 0.5 mmol), allene **3a** (147 mg, 1.5 mmol) and [Rh(naphthalene)(cod)][SbF₆] (29 mg, 0.05 mmol) in CH₂Cl₂ (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded **7b** (80 mg, 66 %). ¹H-NMR (CDCl₃): 2.93 (dt, *J* = 19.7 and 2.2 Hz, 1H), 3.58-3.72 (m, 1H), 3.72 (s, 3H), 3.79 (s, 3H), 4.01-4.03 (m, 1H), 5.51 (d, *J* = 2.8 Hz, 1H), 5.97 (t, *J* = 2.4 Hz, 1H), 7.16-7.22 (m, 5H); ¹³C-NMR (CDCl₃): 39.1 (CH₂), 45.6 (CH), 51.0 (CH₃), 57.0 (CH₃), 106.7 (CH), 115.8 (CH), 126.5 (CH), 126.9 (CH), 128.5 (CH), 145.0 (C), 158.6 (C), 167.9 (C). Anal. Calcd for C₁₅H₁₆O₃: C, 73.75; H, 6.60; Found: C, 73.66; H, 6.63.

7c

Compound 7c. The general procedure was followed using complex **1c** (186 mg, 0.5 mmol), allene **3a** (147 mg, 1.5 mmol) and [Rh(naphthalene)(cod)][SbF₆] (29 mg, 0.05 mmol) in CH₂Cl₂ (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded **7c** (86 mg, 62 %). ¹H-NMR (CDCl₃): 2.86 (dt, *J* = 19.5 and 2.4 Hz, 1H), 3.58 (ddd, *J* = 19.5, 7.0 and 2.4 Hz, 1H), 3.72 (s, 3H), 3.79 (s, 3H), 3.96-4.00 (m, 1H), 5.45 (d, *J* = 2.6 Hz, 1H), 5.96 (t, *J* = 2.4 Hz, 1H), 7.12 (d, *J* = 8.8 Hz, 2H), 7.26 (d, *J* = 8.8 Hz, 2H); ¹³C-NMR (CDCl₃): 39.0 (CH₂), 45.0 (CH), 51.0 (CH₃), 57.0 (CH₃), 107.1 (CH), 115.1 (CH), 128.3 (CH), 128.6 (CH), 132.2 (C), 143.6

(C), 158.1 (C), 158.9 (C), 167.8 (C). Anal. Calcd for C₁₅H₁₅ClO₃: C, 64.64; H, 5.42; Found: C, 64.42; H, 5.37.

Compound 7d. The general procedure was followed using complex **1e** (223 mg, 0.5 mmol), allene **3a** (147 mg, 1.5 mmol) and [Rh(naphthalene)(cod)][SbF₆] (29 mg, 0.05 mmol) in CH₂Cl₂ (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded **7d** (84 mg, 48 %). ¹H-NMR (CDCl₃): 3.02 (dt, *J* = 19.4 and 2.2 Hz, 1H), 3.46 (ddd, *J* = 19.4, 6.6 and 2.2 Hz, 1H), 3.73 (s, 3H), 3.76 (s, 3H), 4.02-4.14 (m, 10H), 5.51 (d, *J* = 2.6 Hz, 1H), 5.90 (br s, 1H); ¹³C-NMR (CDCl₃): 37.8 (CH₂), 39.4 (CH), 51.0 (CH₃), 56.8 (CH₃), 66.3 (CH), 66.8 (CH), 67.3 (CH), 67.6 (CH), 68.3 (CH), 92.9 (C), 106.3 (CH), 116.1 (CH), 157.6 (C), 158.9 (C), 168.0 (C). Anal. Calcd for C₁₉H₂₀FeO₃: C, 64.79; H, 5.72; Found: C, 64.91; H, 5.71.

Compound 7e. The general procedure was followed using complex **1d** (164 mg, 0.5 mmol), allene **3a** (147 mg, 1.5 mmol) and [Rh(naphthalene)(cod)][SbF₆] (29 mg, 0.05 mmol) in CH₂Cl₂ (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded **7e** (69 mg, 59 %). ¹H-NMR (CDCl₃): 3.06 (dt, *J* = 19.6 and 2.4 Hz, 1H), 3.47 (ddd, *J* = 19.6, 7.2 and 2.4 Hz, 1H), 3.71 (s, 3H), 3.75 (s, 3H), 4.04-4.09 (m, 1H), 5.46 (d, *J* = 2.8 Hz, 1H), 5.93 (t, *J* = 2.4 Hz, 1H), 6.01 (d, *J* = 3.1 Hz, 1H), 6.27 (dd, *J* = 3.1 and 1.9 Hz, 1H), 7.31 (dd, *J* = 1.9 and 0.9 Hz, 1H); ¹³C-

NMR (CDCl₃): 35.4 (CH₂), 38.9 (CH), 51.0 (CH₃), 56.9 (CH₃), 104.2 (CH), 107.1 (CH), 110.1 (CH), 112.3 (CH), 141.4 (CH), 157.2 (C), 157.5 (C), 158.7 (C), 167.8 (C).
 Anal. Calcd for C₁₃H₁₄O₄: C, 66.66; H, 6.02; Found: C, 66.49; H, 6.00.

Compound 7f. The general procedure was followed using complex **1a** (184 mg, 0.5 mmol), allene **3b** (168 mg, 1.5 mmol) and [Rh(naphthalene)(cod)][SbF₆] (29 mg, 0.05 mmol) in CH₂Cl₂ (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded **7f** (75 mg, 52 %). ¹H-NMR (CDCl₃): 1.28 (t, *J* = 7.0 Hz, 3H), 2.86 (dt, *J* = 19.6 and 2.4 Hz, 1H), 3.56 (ddd, *J* = 19.6, 7.0 and 2.4 Hz, 1H), 3.78 (s, 3H), 3.81 (s, 3H), 3.94-3.98 (m, 1H), 4.17 (q, *J* = 7.0 Hz, 2H), 5.46 (d, *J* = 2.9 Hz, 1H), 5.94 (t, *J* = 2.4 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 2H), 7.11 (d, *J* = 8.7 Hz, 2H); ¹³C-NMR (CDCl₃): 14.4 (CH₃), 39.2 (CH₂), 44.8 (CH), 55.3 (CH₃), 56.9 (CH₃), 59.6 (CH₂), 107.1 (CH), 113.9 (CH), 115.9 (CH), 127.9 (CH), 137.2 (C), 158.2 (C), 158.39 (C), 158.41 (C), 167.5 (C). IR (CH₂Cl₂): ν 1696, 1634, 1606, 1421 cm⁻¹. Anal. Calcd for C₁₇H₂₀O₄: C, 70.81; H, 6.99; Found: C, 70.96; H, 6.83.

Compound 7g. The general procedure was followed using complex **1a** (184 mg, 0.5 mmol), allene **3c** (174 mg, 1mmol) and [Rh(naphthalene)(cod)][SbF₆] (29 mg, 0.05 mmol) in CH₂Cl₂ (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded **7g** (98 mg, 56 %). ¹H-NMR (CDCl₃): 2.90 (dt, *J*

= 19.8 and 2.1 Hz, 1H), 3.58 (ddd, J = 19.8, 6.9 and 2.1 Hz, 1H), 3.76 (s, 3H), 3.79 (s, 3H), 3.95-3.97 (m, 1H), 5.16 (s, 2H), 5.47 (d, J = 2.7 Hz, 1H), 6.01 (br s, 1H), 6.83 (d, J = 8.8 Hz, 2H), 7.11 (d, J = 8.8 Hz, 2H), 7.32-7.37 (m, 5H); ^{13}C -NMR (CDCl_3): 39.3 (CH_2), 44.8 (CH), 55.2 (CH_3), 56.9 (CH_3), 65.5 (CH_2), 106.7 (CH), 113.9 (CH), 116.3 (CH), 127.9 (CH), 128.0 (CH), 128.4 (CH), 136.5 (C), 137.0 (C), 158.2 (C), 158.3 (C), 159.2 (C), 167.2 (C). Anal. Calcd for $\text{C}_{22}\text{H}_{22}\text{O}_4$: C, 75.41; H, 6.33; Found: C, 75.53; H, 6.41.

Compound 7h. The general procedure was followed using complex **1d** (164 mg, 0.5 mmol), allene **3c** (174 mg, 1mmol) and $[\text{Rh}(\text{naphthalene})(\text{cod})][\text{SbF}_6]$ (29 mg, 0.05 mmol) in CH_2Cl_2 (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded **7h** (84 mg, 54 %). ^1H -NMR (CDCl_3): 3.11 (dt, J = 19.5 and 2.4 Hz, 1H), 3.51 (ddd, J = 19.5, 7.0, and 2.4 Hz, 1H), 3.77 (s, 3H), 4.08-4.10 (m, 1H), 5.19 (s, 2H), 5.50 (d, J = 2.8 Hz, 1H), 6.01-6.04 (m, 2H), 6.29-6.31 (m, 1H), 7.28-7.39 (m, 6H); ^{13}C -NMR (CDCl_3): 35.4 (CH_2), 38.9 (CH), 56.9 (CH_3), 65.5 (CH_2), 104.2 (CH), 107.1 (CH), 110.1 (CH), 112.4 (CH), 127.9 (CH), 128.1 (CH), 128.4 (CH), 136.4 (C), 141.3 (CH), 157.1 (C), 157.9 (C), 158.6 (C), 167.1 (C). Anal. Calcd for $\text{C}_{19}\text{H}_{18}\text{O}_4$: C, 73.53; H, 5.85; Found: C, 73.58; H, 5.77.

Compound 7i. The general procedure was followed using complex **1a** (184 mg, 0.5 mmol), allene **3d** (210 mg, 1.5 mmol) and $[\text{Rh}(\text{naphthalene})(\text{cod})][\text{SbF}_6]$ (29 mg, 0.05

mmol) in CH₂Cl₂ (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded **7i** (81 mg, 51 %). ¹H-NMR (CDCl₃): 1.46 (s, 9H), 2.81 (dt, J = 19.6 and 2.3 Hz, 1H), 3.53 (ddd, J = 19.7, 7.1, and 2.5 Hz, 1H), 3.74 (s, 3H), 3.78 (s, 3H), 3.90-3.93 (m, 1H), 5.40 (d, J = 2.8 Hz, 1H), 5.84 (d, J = 2.4 Hz, 1H), 6.82 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H); ¹³C-NMR (CDCl₃): 28.4 (CH₃), 39.1 (CH₂), 44.8 (CH₂), 55.3 (CH₃), 56.9 (CH₃), 79.6 (C), 109.1 (CH), 113.9 (CH), 115.2 (CH), 127.9 (CH), 137.4 (C), 157.1 (C), 158.2 (C), 158.6 (C), 167.2 (C). Anal. Calcd for C₁₉H₂₄O₄: C, 72.13; H, 7.65; Found: C, 71.98; H, 7.73.

Compound 8a. The general procedure was followed using complex **1a** (184 mg, 0.5 mmol), allene **3e** (174 mg, 1mmol) and [Rh(naphthalene)(cod)][SbF₆] (29 mg, 0.05 mmol) in CH₂Cl₂ (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded **8a** (122 mg, 70 %). ¹H-NMR (CDCl₃): 3.69 (dd, J = 3.2 and 2.7 Hz, 1H), 3.72 (s, 3H), 3.79 (s, 3H), 3.82 (s, 3H), 3.89 (t, J = 3.2 Hz, 1H), 5.32 (br s, 1H), 5.39-5.40 (m, 1H), 6.83 (d, J = 8.5 Hz, 2H), 7.03 (d, J = 8.5 Hz, 2H), 7.12-7.15 (m, 2H), 7.25-7.33 (m, 3H); ¹³C-NMR (CDCl₃): 51.4 (CH₃), 54.3 (CH), 55.2 (CH₃), 57.2 (CH₃), 59.4 (CH), 111.4 (CH), 112.8 (CH), 113.8 (CH), 126.8 (CH), 128.0 (CH), 128.4 (CH), 128.6 (CH), 136.0 (C), 142.1 (C), 152.9 (C), 157.7 (C), 158.4 (C), 167.4 (C). IR (CH₂Cl₂): ν 1721, 1610, 1470, 1384 cm⁻¹. Anal. Calcd for C₂₂H₂₂O₄: C, 75.41; H, 6.33; Found: C, 75.61; H, 6.17.

8b

Compound 8b. The general procedure was followed using complex **1b** (169 mg, 0.5 mmol), allene **3e** (174 mg, 1mmol) and [Rh(naphthalene)(cod)][SbF₆] (29 mg, 0.05 mmol) in CH₂Cl₂ (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded **8b** (106 mg, 66 %). ¹H-NMR (CDCl₃): 3.69-3.71 (s+m, 4H), 3.83 (s, 3H), 3.92 (t, J = 2.9 Hz, 1H), 5.30 (br s, 1H), 5.41 (br s, 1H), 7.09-7.26 (m, 10H); ¹³C-NMR (CDCl₃): 51.4 (CH₃), 55.0 (CH), 57.2 (CH₃), 59.1 (CH), 111.5 (CH), 112.4 (CH), 126.7 (CH), 126.9 (CH), 127.0 (CH), 128.4 (CH), 128.5 (CH), 128.6 (CH), 142.1 (C), 143.9 (C), 152.8 (C), 157.9 (C), 167.3 (C). IR (CH₂Cl₂): ν 1732, 1614 cm⁻¹. Anal. Calcd for C₂₁H₂₀O₃: C, 78.73; H, 6.29; Found: C, 78.75; H, 6.34.

8c

Compound 8c. The general procedure was followed using complex **1d** (164 mg, 0.5 mmol), allene **3e** (174 mg, 1mmol) and [Rh(naphthalene)(cod)][SbF₆] (29 mg, 0.05 mmol) in CH₂Cl₂ (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded **8c** (101 mg, 65 %). ¹H-NMR (CDCl₃): 3.71 (s, 3H), 3.80 (s, 3H), 3.98-4.02 (m, 2H), 5.35 (br s, 1H), 5.38 (d, J = 1.6 Hz, 1H), 6.03 (d, J = 3.2 Hz, 1H), 6.29 (t, J = 2.4 Hz, 1H), 7.20-7.35 (m, 6H); ¹³C-NMR (CDCl₃): 48.3 (CH), 51.4 (CH₃), 55.0 (CH), 57.2 (CH₃), 105.0 (CH), 109.3 (CH), 110.1 (CH), 112.0 (CH), 127.0 (CH), 128.3 (CH), 128.7 (CH), 141.6 (CH), 142.1 (C), 151.7 (C), 156.3

(C), 157.9 (C), 167.3 (C). IR (CH₂Cl₂): ν 1727, 1614, 1454 cm⁻¹. Anal. Calcd for C₁₉H₁₈O₄: C, 73.53; H, 5.85; Found: C, 73.62; H, 5.92.

Compounds 8d. The general procedure was followed using complex **1a** (184 mg, 0.5 mmol), allene **3f** (154 mg, 1mmol) and [Rh(naphthalene)(cod)][SbF₆] (29 mg, 0.05 mmol) in CH₂Cl₂ (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded **8d** (109 mg, 66 %). ¹H-NMR (CDCl₃): 0.98 (s, 9H), 2.32 (br s, 1H), 3.65 (d, J = 3.1 Hz, 1H), 3.70 (s, 3H), 3.76 (s, 3H), 3.79 (s, 3H), 5.25 (d, J = 2.0 Hz, 1H), 5.66 (br s, 1H), 6.82 (d, J = 8.7 Hz, 2H), 7.12 (d, J = 8.7 Hz, 2H); ¹³C-NMR (CDCl₃): 27.3 (CH₃), 34.6 (C), 47.0 (CH), 51.4 (CH₃), 55.2 (CH₃), 57.1 (CH₃), 62.3 (CH), 112.9 (CH), 113.3 (CH), 113.9 (CH), 128.0 (C), 137.5 (C), 149.7 (C), 158.09 (C), 158.13 (C), 167.4 (C). IR (CH₂Cl₂): ν 1722, 1615, 1510, 1175 cm⁻¹. Anal. Calcd for C₂₀H₂₆O₄: C, 72.70; H, 7.93; Found: C, 72.73; H, 7.93.

Compound 8e. The general procedure was followed using complex **1e** (223 mg, 0.5 mmol), allene **3f** (154 mg, 1mmol) and [Rh(naphthalene)(cod)][SbF₆] (29 mg, 0.05 mmol) in CH₂Cl₂ (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded **8e** (126 mg, 62 %). ¹H-NMR (CDCl₃): 0.94 (s, 9H), 2.16 (br s, 1H), 3.38 (d, J = 3.5 Hz, 1H), 3.71 (s, 3H), 3.76 (s, 3H), 3.94-3.95 (m,

1H), 4.01-4.10 (m, 3H), 4.14 (s, 5H), 5.39-5.41 (m, 1H), 5.56 (br s, 1H); ¹³C-NMR (CDCl₃): 27.3 (CH₃), 34.2 (C), 41.5 (CH), 51.3 (CH₃), 57.1 (CH₃), 62.2 (CH), 66.2 (CH), 67.0 (CH), 67.2 (CH), 67.4 (CH), 68.3 (CH), 93.9 (C), 111.5 (CH), 113.4 (CH), 149.6 (C), 158.1 (C), 167.3 (C). Anal. Calcd for C₂₃H₂₈FeO₃: C, 67.66; H, 6.91; Found: C, 67.85; H, 6.78.

Compounds 8f, 9f and 10f. The general procedure was followed using complex **1a** (184 mg, 0.5 mmol), allene **3g** (210 mg, 1.5 mmol) and [Rh(naphthalene)(cod)][SbF₆] (29 mg, 0.05 mmol) in CH₂Cl₂ (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded **8f** (107 mg, 68 %) and a 1:1 mixture of **9f** and **10f** (16 mg, 10%). **Compound 8f.** ¹H-NMR (CDCl₃): 0.88 (d, J = 6.8 Hz, 3H), 0.97 (d, J = 6.8 Hz, 3H), 1.93-2.00 (m, 1H), 2.62 (dd, J = 3.6 and 1.6 Hz, 1H), 3.58 (br s, 1H), 3.69 (s, 3H), 3.74 (s, 3H), 3.78 (s, 3H), 5.26 (d, J = 1.6 Hz, 1H), 5.61 (br s, 1H), 6.81 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H); ¹³C-NMR (CDCl₃): 16.9 (CH₃), 20.3 (CH₃), 33.1 (CH), 46.1 (CH), 51.5 (CH₃), 55.3 (CH₃), 57.2 (CH₃), 57.4 (CH), 110.1 (CH), 113.9 (CH), 114.8 (CH), 128.3 (CH), 137.7 (C), 152.2 (C), 158.0 (C), 158.2 (C), 167.6 (C). Anal. Calcd for C₁₉H₂₄O₄: C, 72.13; H, 7.65; Found: C, 72.22; H, 7.63.

Compounds 9f and 10f. Spectroscopic data of **9f** and **10f** were obtained from a 1:1 mixture. ¹H-NMR (CDCl₃): 0.74 (d, J = 6.7 Hz, 3H), 0.86 (d, J = 6.7 Hz, 3H), 1.03 (d, J = 6.9 Hz, 3H), 1.09 (d, J = 6.9 Hz, 3H), 1.96-2.01 (m, 1H), 2.35-2.41 (m, 1H), 2.64 (d, J = 3.9 Hz, 1H), 3.39 (br s, 1H), 3.60 (d, J = 2.7 Hz, 1H), 3.66 (d, J = 2.9 Hz, 1H), 3.68 (s, 3H), 3.74 (s, 3H), 3.77 (s, 3H), 3.78 (s, 3H), 5.39 (d, J = 2.9 Hz, 1H), 5.62 (br s, 2H),

5.98 (d, $J = 1.7$ Hz, 1H), 6.79 (d, $J = 8.3$ Hz, 2H), 6.82 (d, $J = 8.4$ Hz, 2H), 7.04 (d, $J = 8.4$ Hz, 2H), 7.07 (d, $J = 8.3$, 2H); ^{13}C -NMR (CDCl_3): 16.1, 16.3, 20.6, 21.5, 31.5, 33.7, 45.6, 46.1, 51.0, 52.3, 55.2, 55.3, 56.9, 59.2, 107.5, 107.8, 113.9, 115.1, 124.5, 128.1, 128.3, 136.8, 137.4, 155.4, 158.1, 158.2, 158.4, 162.9, 166.5, 167.3, 170.6.

9g

10g

Compounds 9g and 10g. The general procedure was followed using complex **1a** (184 mg, 0.5 mmol), allene **3h** (168 mg, 1.5 mmol) and $[\text{Rh}(\text{naphthalene})(\text{cod})][\text{SbF}_6]$ (29 mg, 0.05 mmol) in CH_2Cl_2 (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded an unseparable mixture of **9g** and **10g** (86 mg, 60 %). Spectroscopic and analytical data of **9g** and **10g** were obtained from this mixture. **Compound 9g:** ^1H -NMR (CDCl_3): 1.36 (d, $J = 7.1$ Hz, 3H); 3.40-3.44 (m, 1H), 3.50 (br s, 1H), 3.70 (s, 3H), 3.78 (s, 3H), 5.42 (d, $J = 2.9$ Hz, 1H), 5.97 (d, $J = 1.5$ Hz, 1H), 7.13-7.32 (m, 5H); ^{13}C -NMR (CDCl_3): 21.7 (CH_3), 44.9 (CH), 51.0 (CH), 55.1 (CH_3), 56.9 (CH_3), 107.6 (CH), 113.4 (CH), 126.5 (CH), 126.7 (CH), 127.1 (CH), 144.7 (C), 157.2 (C), 163.6 (C), 167.2 (C). **Compound 10g:** ^1H -NMR (CDCl_3): 1.30 (d, $J = 7.1$ Hz, 3H), 2.63-2.68 (m, 1H), 3.47 (br s, 1H), 3.72 (s, 3H), 3.82 (s, 3H), 5.06 (br s, 1H), 5.67 (m, 1H), otherwise as for the major isomer; ^{13}C -NMR (CDCl_3): 19.4 (CH_3), 49.9 (CH), 52.3 (CH), 55.1 (CH_3), 54.2 (CH_3), 107.1 (CH), 122.3 (CH), 126.8 (CH), 128.5 (CH), 128.6 (CH), 144.0 (C), 155.0 (C), 167.5 (C), 170.7 (C). Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{O}_3$: C, 74.39; H, 7.02; Found: C, 74.53; H, 7.09.

Removal of the Tosyl Group in Compound **4j** with Li/Naphthalene

To a suspension of lithium powder (21 mg, 3.0 mmol), and naphthalene (2 mg, 0.016 mmol) in THF (5 mL) was slowly added a solution of compound **4j** (90 mg, 0.21 mmol) at -78 °C. Stirring was continued for 6 h. The resulting mixture was then hydrolysed with water (5 mL) and extracted with diethyl ether (2 x 20 mL). The organic layer was dried over anhydrous Na₂SO₄. Solvents were evaporated in vacuo and the resulting residue was purified by flash chromatography (SiO₂, hexane:ethyl acetate 5:1) affording compound **5** (32 mg, 57%).

5

¹H-NMR (CDCl₃): 3.79 (s, 3H), 3.91 (t, *J* = 2.6 Hz, 1H), 4.04 (br signal, 1H), 4.51 (d, *J* = 2.0 Hz, 1H), 5.03 (br s, 1H), 5.11 (br s, 1H), 5.32 (d, *J* = 2 Hz, 1H), 6.10 (d, *J* = 3.2 Hz, 1H), 6.32-6.34 (m, 1H), 6.60 (d, *J* = 7.6 Hz, 2H), 6.70-6.74 (m, 1H), 7.16 (d, *J* = 7.2 Hz, 2H), 7.39 (br s, 1H); ¹³C-NMR (CDCl₃): 46.9 (CH), 56.5 (CH₃), 60.4 (CH), 103.0 (CH), 105.0 (CH₂), 105.3 (CH), 110.3 (CH), 113.3 (CH), 117.6 (CH), 129.2 (CH), 141.5 (CH), 146.8 (C), 147.9 (C), 156.9 (C), 157.5 (C). Anal. Calcd for C₁₇H₁₇NO₂: C, 76.38; H, 6.41; N, 5.24; Found: C, 76.27; H, 6.54; N, 5.22.

General Procedure for the Synthesis of 2-Methylenecyclopentanones **11**

2M HCl (1mL) was added to a solution of the corresponding compound (0.1 mmol) in THF (5 mL). The mixture was stirred for 2h at rt. Then water (5 mL) was added and the mixture extracted with diethyl ether (3 x 10 mL). The combined organic layers were

dried (Na₂SO₄). The solvent was removed in vacuo and the resulting residue was purified by flash chromatography (SiO₂, mixtures of hexane:ethyl acetate).

11a

Compound 11a. The general procedure was followed using compound **4b** (27 mg, 0.1 mmol) in THF (5 mL). Final chromatographic purification using a 1:1 mixture of hexane:ethyl acetate as eluent afforded **11a** (25 mg, 98 %). ¹H-NMR (CDCl₃): 2.00-2.07 (m, 2H), 2.28-2.46 (m, 2H), 2.53 (dd, *J* = 18.0 and 12.7 Hz, 1H), 2.87 (dd, *J* = 18.0 and 7.5 Hz, 1H), 3.29-3.44 (m, 3H), 5.22 (d, *J* = 2.7 Hz, 1H), 5.50-5.55 (m, 1H), 6.23 (d, *J* = 3.3 Hz, 1H), 7.26-7.35 (m, 5H); ¹³C-NMR (CDCl₃): 18.4 (CH₂), 30.9 (CH₂), 42.4 (CH₂), 42.8 (CH), 45.7 (CH₂), 57.9 (CH), 118.7 (CH₂), 127.0 (CH), 127.5 (CH), 129.0 (CH), 138.8 (C), 142.5 (C), 175.6 (C), 201.2 (C). IR (CH₂Cl₂): ν 1732, 1682, 1634 cm⁻¹. Anal. Calcd for C₁₆H₁₇NO₂: C, 75.27; H, 6.71; Found: C, 75.32; H, 6.86.

11b

Compound 11b. The general procedure was followed using compound **4h** (43 mg, 0.1 mmol) in THF (5 mL). Final chromatographic purification using a 3:1 mixture of hexane:ethyl acetate as eluent afforded **11b** (39 mg, 95 %). ¹H-NMR (CDCl₃): 2.37 (s, 3H), 2.41 (dd, *J* = 18.2 and 11.6 Hz, 1H), 2.62 (dd, *J* = 18.2 and 8.3 Hz, 1H), 3.02-3.10 (m, 1H), 5.80-5.84 (m, 1H), 6.01 (d, *J* = 2.7 Hz, 1H), 6.50 (d, *J* = 3.1 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 7.21-7.27 (m, 10H); ¹³C-NMR (CDCl₃): 21.4

(CH₃), 43.7 (CH), 46.4 (CH₂), 66.3 (CH), 122.8 (CH₂), 127.2 (CH), 127.4 (CH), 127.5 (CH), 127.7 (CH), 129.1 (CH), 129.2 (CH), 129.3 (CH), 132.6 (CH), 135.5 (C), 137.1 (C), 140.1 (C), 143.2 (C), 144.3 (C), 201.3 (C). Anal. Calcd for C₂₅H₂₃NO₃S: C, 71.92; H, 5.55; N, 3.35; Found: C, 71.80; H, 5.59; N, 3.38.

Compound 11c. The general procedure was followed using compound **6e** (39 mg, 0.1 mmol) in THF (5 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded **11c** (29 mg, 77 %). ¹H-NMR (CDCl₃): 2.69 (dd, *J* = 18.4 and 7.8 Hz, 1H), 3.05 (dd, *J* = 18.4 and 8.6 Hz, 1H), 3.33-3.44 (m, 1H), 4.01-4.02 (m, 1H), 4.03-2.19 (s+m, 8H), 5.13-5.16 (m, 1H), 5.58 (d, *J* = 2.9 Hz, 1H), 6.25 (d, *J* = 2.9 Hz, 1H), 6.96-7.07 (m, 3H), 7.29-7.35 (m, 2H); ¹³C-NMR (CDCl₃): 39.6 (CH), 43.0 (CH₂), 66.1 (CH), 67.8 (CH), 67.9 (CH), 68.0 (CH), 68.5 (CH), 83.1 (CH), 88.9 (C), 115.8 (CH), 121.6 (CH), 122.3 (CH₂), 129.7 (CH), 144.9 (C), 157.8 (C), 202.9 (C). IR (CH₂Cl₂): ν 1727, 1651, 1597, 1493, 1381, 1228, 1097 cm⁻¹. Anal. Calcd for C₂₂H₂₀FeO₂: C, 70.99; H, 5.42; Found: C, 71.16; H, 5.35.

Compound 11d. The general procedure was followed using compound **7a** (27 mg, 0.1 mmol) in THF (5 mL). Final chromatographic purification using a 1:1 mixture of hexane:ethyl acetate as eluent afforded **11d** (23 mg, 89 %). ¹H-NMR (CDCl₃): 2.52 (dd,

J = 18.1 and 10.0 Hz, 1H), 2.80-3.01 (m, 2H), 3.39-3.45 (m, 1H), 3.66-3.71 (m, 1H), 3.78 (s, 3H), 3.80 (s, 3H), 6.58 (t, J = 2.9, 1H), 6.88 (d, J = 8.7 Hz, 2H), 7.15 (d, J = 8.7 Hz, 2H); ^{13}C -NMR (CDCl_3): 37.8 (CH_2), 37.9 (CH), 45.8(CH_2), 51.9 (CH_3), 55.3 (CH_3), 114.2 (CH), 119.5 (CH), 127.6 (CH), 134.8 (C), 150.9 (C), 158.5 (C), 166.0 (C), 205.8 (C). IR (CH_2Cl_2): ν 1714, 1514, 1220 cm^{-1} . Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{O}_4$: C, 69.22; H, 6.20; Found: C, 69.35; H, 6.14.

Compound 11e. The general procedure was followed using compound **8a** (35 mg, 0.1 mmol) in THF (5 mL). Final chromatographic purification using a 1:1 mixture of hexane:ethyl acetate as eluent afforded **11e** (18 mg, 53 %). ^1H -NMR (CDCl_3): 2.68 (dd, J = 18.6 and 6.6 Hz, 1H), 2.96 (dd, J = 18.6 and 8.3 Hz, 1H), 3.41-3.47 (s+m, 4H), 3.80 (s, 3H), 4.60 (dd, J = 5.2 and 2.9 Hz, 1H), 6.83-6.86 (m, 3H), 7.01-7.06 (m, 4H), 7.20-7.23 (m, 1H), 7.26-7.30 (m, 2H); ^{13}C -NMR (CDCl_3): 44.1 (CH_2), 48.1 (CH), 51.6 (CH_3), 55.1 (CH), 55.2 (CH_3), 114.2 (CH), 122.9 (CH), 126.6 (CH), 127.1 (CH), 127.8 (CH), 128.6 (CH), 134.8 (C), 142.6 (C), 151.3 (C), 158.5 (C), 165.7 (C), 206.0 (C). Anal. Calcd for $\text{C}_{21}\text{H}_{20}\text{O}_4$: C, 74.98; H, 5.99; Found: C, 75.07; H, 6.12.