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 Alkylidene cyclopentanone Derivatives

José Barluenga,* Rubén Vicente, Luis A. López, and Miguel Tomás

Instituto Universitario de Química Organometálica “Enrique Moles”, Unidad Asociada al CSIC, Universidad de Oviedo, Julián Clavería 8, 33071 Oviedo, Spain

barluenga@uniovi.es

**General Methods:** $^1$H 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 ($^1$H, 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 Schlenck techniques. CH$_2$Cl$_2$ 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 [Rh(naphthalene)(cod)][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$_2$Cl$_2$ 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$_2$Cl$_2$ (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, 1mmol) and [Rh(cod)Cl]$_2$ (24.6 mg, 0.05 mmol) in CH$_2$Cl$_2$ (10 mL). Final chromatographic purification using a 2:1 mixture of hexane:ethyl acetate as eluent afforded 4a (114 mg, 76 %). $^1$H-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).
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$_2$Cl$_2$): ν 1679, 1611, 1512 cm$^{-1}$. Anal. Calcd for C$_{18}$H$_{21}$NO$_3$: C, 72.22; H, 7.07; N, 4.68; Found: C, 72.36; H, 7.02; N, 4.65.

**Compound 4b.** The general procedure was followed using complex 1b (169 mg, 0.5 mmol), allene 2a (123 mg, 1mmol) and [Rh(cod)Cl]$_2$ (24.6 mg, 0.05 mmol) in CH$_2$Cl$_2$ (10 mL). Final chromatographic purification using a 2:1 mixture of hexane:ethyl acetate as eluent afforded 4b (105 mg, 78 %). $^1$H-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$_2$Cl$_2$): ν 1682, 1422 cm$^{-1}$. Anal. Calcd for C$_{17}$H$_{19}$NO$_2$: C, 75.81; H, 7.11; N, 5.20; Found: C, 75.66; H, 7.13; N, 5.31.

**Compound 4c.** The general procedure was followed using complex 1c (186 mg, 0.5 mmol), allene 2a (123 mg, 1mmol) and [Rh(cod)Cl]$_2$ (24.6 mg, 0.05 mmol) in CH$_2$Cl$_2$
Final chromatographic purification using a 2:1 mixture of hexane:ethyl acetate as eluent afforded 4e (126 mg, 83%). \(^1\)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); \(^{13}\)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\(_2\)Cl\(_2\)): \(\nu\) 1680, 1612, 1422 cm\(^{-1}\). Anal. Calcd for C\(_{17}\)H\(_{18}\)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, 1 mmol) and [Rh(cod)Cl]\(_2\) (24.6 mg, 0.05 mmol) in CH\(_2\)Cl\(_2\) (10 mL). Final chromatographic purification using a 2:1 mixture of hexane:ethyl acetate as eluent afforded 4d (104 mg, 80%). \(^1\)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); \(^{13}\)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\(_2\)Cl\(_2\)): \(\nu\) 1682, 1614, 1422 cm\(^{-1}\). Anal. Calcd for C\(_{15}\)H\(_{17}\)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
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%). \(^\text{1}\)H-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); \(^{13}\)C-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.

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
CH$_2$Cl$_2$ (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded 4h (190 mg, 88%). $^1$H-NMR (CDCl$_3$): 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); $^{13}$C-NMR (CDCl$_3$): 21.4 (CH$_3$), 49.5 (CH), 56.2 (CH$_3$), 69.2 (CH), 105.6 (CH), 106.0 (CH$_2$), 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 (CH$_2$Cl$_2$): $\nu$ 1614, 1422, 1162 cm$^{-1}$. Anal. Calcd for C$_{26}$H$_{25}$NO$_3$S: 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 CH$_2$Cl$_2$ (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded 4i (267 mg, 99%). $^1$H-NMR (CDCl$_3$): 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); $^{13}$C-NMR (CDCl$_3$): 21.5 (CH$_3$), 43.5 (CH), 56.2 (CH$_3$), 65.9 (CH), 67.4 (CH), 67.5, 67.7 (CH), 68.3 (CH), 91.7 (C), 104.9 (CH), 105.8 (CH$_2$), 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 C$_{30}$H$_{29}$FeNO$_3$S: C, 66.79; H, 5.42; N, 2.60; Found: C, 66.90; H, 5.46; N, 2.71.
Compound 4j. The general procedure was followed using complex 1d (164 mg, 0.5 mmol), allene 2b (172 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 4j (185 mg, 88%). ¹H-NMR (CDCl₃): 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); ¹³C-NMR (CDCl₃): 21.4 (CH₃), 42.8 (CH), 56.1 (CH₃), 66.0 (CH), 102.1 (CH), 105.7 (CH), 106.0 (CH₂), 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 C₂₄H₂₃NO₄S: C, 68.39; H, 5.50; N, 3.32; Found: C, 68.46; H, 5.33; N, 3.33.

Compound 4k. The general procedure was followed using complex 1g (159 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 4k (123 mg, 60%). ¹H-NMR (CDCl₃): 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); ¹³C-
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.

**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.

**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
CH$_2$Cl$_2$ (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded 4m (87 mg, 47%). $^1$H-NMR (CDCl$_3$): 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); $^{13}$C-NMR (CDCl$_3$): 19.9 (CH$_3$), 21.5 (CH$_3$), 38.7 (CH), 56.0 (CH$_3$), 67.5 (CH), 105.1 (CH$_2$), 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 C$_{21}$H$_{23}$NO$_3$S: 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 CH$_2$Cl$_2$ (10 mL). Final chromatographic purification using a 3:1 mixture of hexane:ethyl acetate as eluent afforded 4n (232 mg, 98%). $^1$H-NMR (CDCl$_3$): 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); $^{13}$C-NMR (CDCl$_3$): 21.2 (CH$_3$), 47.3 (CH$_2$), 48.9 (CH), 54.5 (CH$_3$), 55.0 (CH$_3$), 55.3 (CH$_3$), 56.1 (CH$_3$), 68.0 (CH), 104.0 (CH), 104.7 (CH$_2$), 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
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.

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}\text{C}-\text{NMR} \ (\text{CDCl}_3): 52.7 \ (\text{CH}), 56.5 \ (\text{CH}_3), 83.7 \ (\text{CH}), 105.7 \ (\text{CH}), 107.0 \ (\text{CH}_2), 116.0 \ (\text{CH}), 121.0 \ (\text{CH}), 126.9 \ (\text{CH}), 127.6 \ (\text{CH}), 128.6 \ (\text{CH}), 129.4 \ (\text{CH}), 143.4 \ (\text{C}), 146.4 \ (\text{C}), 156.9 \ (\text{C}), 157.9 \ (\text{C}). \ \text{IR} \ (\text{CH}_2\text{Cl}_2): \nu 1600, 1500, 1164 \text{ cm}^{-1}. \ \text{Anal. Calcd for C}_{19}\text{H}_{18}\text{O}_2: C, 81.99; H, 6.52; \text{Found: C, 81.84; H, 6.57.}

**Compound 6c.** The general procedure was followed using complex 1c (186 mg, 0.5 mmol), allene 2e (132 mg, 1 mmol) and [Rh(CO)\(_2\text{Cl}\)]\(_2\) (19.4 mg, 0.05 mmol) in CH\(_2\)Cl\(_2\) (10 mL). Final chromatographic purification using a 10:1 mixture of hexane:ethyl acetate as eluent afforded 6c (83 mg, 53%). \(^1\text{H}-\text{NMR} \ (\text{CDCl}_3): 3.83 \ (s, 3H), 3.95 \ (t, J = 2.3 \text{ Hz}, 1H), 5.05-5.06 \ (m, 2H), 5.24 \ (br \ s, 1H), 5.47 \ (d, J = 1.5 \text{ Hz}, 1H), 6.85 \ (d, J = 7.8 \text{ Hz}, 2H), 6.99 \ (t, J = 7.3 \text{ Hz}, 1H), 7.16-7.27 \ (m, 6H); \(^{13}\text{C}-\text{NMR} \ (\text{CDCl}_3): 52.1 \ (\text{CH}), 56.6 \ (\text{CH}_3), 83.7 \ (\text{CH}), 105.0 \ (\text{CH}), 107.3 \ (\text{CH}_2), 116.0 \ (\text{CH}), 121.2 \ (\text{CH}), 128.8 \ (\text{CH}), 128.9 \ (\text{CH}), 129.4 \ (\text{CH}), 132.6 \ (\text{C}), 142.0 \ (\text{C}), 146.0 \ (\text{C}), 157.2 \ (\text{C}), 157.8 \ (\text{C}). \ \text{Anal. Calcd for C}_{19}\text{H}_{17}\text{ClO}_2: C, 72.96; H, 5.48; \text{Found: C, 73.02; H, 5.51.}

**Compound 6d.** The general procedure was followed using complex 1d (164 mg, 0.5 mmol), allene 2e (132 mg, 1 mmol) and [Rh(CO)\(_2\text{Cl}\)]\(_2\) (19.4 mg, 0.05 mmol) in CH\(_2\)Cl\(_2\) (10 mL). Final chromatographic purification using a 10:1 mixture of hexane:ethyl
acetate as eluent afforded **6d** (80 mg, 60%). $^1$H-NMR (CDCl$_3$): 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); $^{13}$C-NMR (CDCl$_3$): 46.1 (CH), 56.6 (CH$_3$), 80.8 (CH), 102.0 (CH), 105.8 (CH), 107.5 (CH$_2$), 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 (CH$_2$Cl$_2$): ν 1614, 1422, 1164 cm$^{-1}$. Anal. Calcd for C$_{17}$H$_{16}$O$_3$: C, 76.10; H, 6.01; Found: C, 76.04; H, 5.96.

![Compound 6e](image)

**Compound 6e.** The general procedure was followed using complex **1e** (223 mg, 0.5 mmol), allene **2e** (132 mg, 1 mmol) and [Rh(CO)$_2$Cl]$_2$ (19.4 mg, 0.05 mmol) in CH$_2$Cl$_2$ (10 mL). Final chromatographic purification using a 10:1 mixture of hexane:ethyl acetate as eluent afforded **6e** (131 mg, 68%). $^1$H-NMR (CDCl$_3$): 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); $^{13}$C-NMR (CDCl$_3$): 46.9 (CH), 56.9 (CH$_3$), 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 (CH$_2$), 116.7 (CH), 121.6 (CH), 129.9 (CH), 146.9 (C), 156.8 (C), 158.6 (C). IR (CH$_2$Cl$_2$): ν 1614, 1494, 1421 cm$^{-1}$. Anal. Calcd for C$_{23}$H$_{22}$FeO$_2$: 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 CH$_2$Cl$_2$ under a CO atmosphere (1 bar) was added [Rh(naphthalene)(cod)][SbF$_6$] (0.1 equiv, 10%). The mixture was stirred at room temperature until dissapereance 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 CH$_2$Cl$_2$ (10:1) and filtered through Celite. The solvent was removed in vacuo and the residue was purified by flash chromatography (SiO$_2$, 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)][SbF$_6$] (29 mg, 0.05 mmol) in CH$_2$Cl$_2$ (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded 7a (99 mg, 72 %). $^1$H-NMR (CDCl$_3$): 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); $^{13}$C-NMR (CDCl$_3$): 39.3 (CH$_2$), 44.8 (CH), 50.9 (CH$_3$), 55.2 (CH$_3$), 56.9 (CH$_3$), 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 (CH$_2$Cl$_2$): ν 1703, 1634, 1606, 1511, 1100 cm$^{-1}$. Anal. Calcd for C$_{16}$H$_{18}$O$_4$: C, 70.06; H, 6.61; Found: C, 70.14; H, 6.59.
**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.

**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 C_{15}H_{15}ClO_3: 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)][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 7d (84 mg, 48 %). ^1H-NMR (CDCl_3): 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 (CDCl_3): 37.8 (CH_2), 39.4 (CH), 51.0 (CH_3), 56.8 (CH_3), 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 C_{19}H_{20}FeO_3: 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)][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 7e (69 mg, 59 %). ^1H-NMR (CDCl_3): 3.06 (dt, J = 19.4 and 2.2 Hz, 1H), 3.47 (ddd, J = 19.6, 7.2 and 2.4 Hz, 1H), 3.71 (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 (CDCl_3): 37.8 (CH_2), 39.4 (CH), 51.0 (CH_3), 56.8 (CH_3), 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).
NMR (CDCl$_3$): 35.4 (CH$_2$), 38.9 (CH), 51.0 (CH$_3$), 56.9 (CH$_3$), 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 C$_{13}$H$_{14}$O$_4$: 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)][SbF$_6$] (29 mg, 0.05 mmol) in CH$_2$Cl$_2$ (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded 7f (75 mg, 52 %). $^1$H-NMR (CDCl$_3$): 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);

$^{13}$C-NMR (CDCl$_3$): 14.4 (CH$_3$), 39.2 (CH$_2$), 44.8 (CH), 55.3 (CH$_3$), 56.9 (CH$_3$), 59.6 (CH$_2$), 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 (CH$_2$Cl$_2$): ν 1696, 1634, 1606, 1421 cm$^{-1}$. Anal. Calcd for C$_{17}$H$_{20}$O$_4$: 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)][SbF$_6$] (29 mg, 0.05 mmol) in CH$_2$Cl$_2$ (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded 7g (98 mg, 56 %). $^1$H-NMR (CDCl$_3$): 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); 13C-NMR (CDCl3): 39.3 (CH2), 44.8 (CH), 55.2 (CH3), 56.9 (CH3), 65.5 (CH2), 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 C22H22O4: 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 [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 7h (84 mg, 54%). 1H-NMR (CDCl3): 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); 13C-NMR (CDCl3): 35.4 (CH2), 38.9 (CH), 56.9 (CH3), 65.5 (CH2), 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 C19H18O4: 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 [Rh(naphthalene)(cod)][SbF6] (29 mg, 0.05
mmol) in CH$_2$Cl$_2$ (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded 7i (81 mg, 51 %). $^1$H-NMR (CDCl$_3$): 1.46 (s, 9H), 2.81 (dt, J = 19.6 and 2.3 Hz, 1H), 3.53 (dd, 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); $^{13}$C-NMR (CDCl$_3$): 28.4 (CH$_3$), 39.1 (CH$_2$), 44.8 (CH$_2$), 55.3 (CH$_3$), 56.9 (CH$_3$), 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 C$_{19}$H$_{24}$O$_4$: 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)][SbF$_6$] (29 mg, 0.05 mmol) in CH$_2$Cl$_2$ (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded 8a (122 mg, 70 %). $^1$H-NMR (CDCl$_3$): 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); $^{13}$C-NMR (CDCl$_3$): 51.4 (CH$_3$), 54.3 (CH), 55.2 (CH$_3$), 57.2 (CH$_3$), 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 (CH$_2$Cl$_2$): ν 1721, 1610, 1470, 1384 cm$^{-1}$. Anal. Calcd for C$_{22}$H$_{22}$O$_4$: C, 75.41; H, 6.33; Found: C, 75.61; H, 6.17.
Compound 8b. The general procedure was followed using complex 1b (169 mg, 0.5 mmol), allene 3e (174 mg, 1 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 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.

Compound 8c. The general procedure was followed using complex 1d (164 mg, 0.5 mmol), allene 3e (174 mg, 1 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 8c (101 mg, 65%). ¹H-NMR (CDCl₃): 3.71 (s, 3H), 3.80 (s, 3H), 3.88-4.02 (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
Compounds 8d. The general procedure was followed using complex 1a (184 mg, 0.5 mmol), allene 3f (154 mg, 1mmol) and [Rh(naphthalene)(cod)][SbF$_6$] (29 mg, 0.05 mmol) in CH$_2$Cl$_2$ (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded 8d (109 mg, 66 %). $^1$H-NMR (CDCl$_3$): 0.98 (s, 9H), 2.32 (br s, 1H), 3.65 8d, 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); $^{13}$C-NMR (CDCl$_3$): 27.3 (CH$_3$), 34.6 (C), 47.0 (CH), 51.4 (CH$_3$), 55.2 (CH$_3$), 57.1 (CH$_3$), 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 (CH$_2$Cl$_2$): v 1722, 1615, 1510, 1175 cm$^{-1}$. Anal. Calcd for C$_{20}$H$_{26}$O$_4$: 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)][SbF$_6$] (29 mg, 0.05 mmol) in CH$_2$Cl$_2$ (10 mL). Final chromatographic purification using a 5:1 mixture of hexane:ethyl acetate as eluent afforded 8e (126 mg, 62 %). $^1$H-NMR (CDCl$_3$): 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, 2H), 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), 7.12 (d, J = 8.4 Hz, 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.

**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 [Rh(naphthalene)(cod)][SbF$_6$] (29 mg, 0.05 mmol) in CH$_2$Cl$_2$ (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:** $^1$H-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:** $^1$H-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 C$_{16}$H$_{18}$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 ºC. 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%).

\[
\begin{align*}
5 \\
\text{OMe} \\
\text{Ph} \\
\text{H}
\end{align*}
\]

\(^1\)H-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); \(^{13}\)C-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 (Na_2SO_4). The solvent was removed in vacuo and the resulting residue was purified by flash chromatography (SiO_2, mixtures of hexane:ethyl acetate).

**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 (CDCl_3): 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 (CDCl_3): 18.4 (CH_2), 30.9 (CH_2), 42.4 (CH_2), 42.8 (CH), 45.7 (CH_2), 57.9 (CH), 118.7 (CH_2), 127.0 (CH), 127.5 (CH), 129.0 (CH), 138.8 (C), 142.5 (C), 175.6 (C), 201.2 (C). IR (CH_2Cl_2): v 1732, 1682, 1634 cm\(^{-1}\). Anal. Calcd for C_{16}H_{17}NO_2: C, 75.27; H, 6.71; Found: C, 75.32; H, 6.86.

**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 (CDCl_3): 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 (CDCl_3): 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$_2$Cl$_2$): ν 1714, 1514, 1220 cm$^{-1}$. Anal. Calcd for C$_{15}$H$_{16}$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 %). $^1$H-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 C$_{21}$H$_{20}$O$_4$: C, 74.98; H, 5.99; Found: C, 75.07; H, 6.12.