Supporting information for:

Metal-Controlled Selective [3+2] Cyclization Reactions of Alkenyl Fischer Carbene Complexes and Allenes

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General methods: All reactions involving organometallic species were carried out under argon using standard Schlenck techniques. CH₂Cl₂ was distilled from CaH₂ and toluene was distilled from sodium benzophenone. TLC was performed on aluminium-backed plates coated with silica gel 60 with F₂₅₄ indicator. Flash column chromatography was carried out on silica gel 60 (230-240 mesh). IR spectra were obtained in a Mattson 3000 FTIR spectrometer. ¹H NMR (200, 300, 400 MHz) and ¹³C NMR (50.5, 75.5, 100 MHz) spectra were measured in CDCl₃ at room temperature on a Bruker AC-200, AC-300 and AMX-400 instruments, respectively, with tetramethylsilane (δ = 0.0, ¹H NMR), CDCl₃ (δ = 76.95, ¹³C NMR) as internal standard. Carbon multiplicities were assigned by DEPT techniques. Elemental analyses were carried out on a Perkin-Elmer 2400 and Carlo Erba 1108 microanalyzers.

Fischer carbene complexes **1**, allenenes, and [(naphthalene)Rh(cod)][SbF₆] were prepared according to the literature methods. All other reagents and solvents used in this work were of the best commercial grade available and used without further purification.

Thermal Reaction of Alkenyl Carbene Complex **1a with 1,1-dimethyl-1,2-propadiene and 1,1-diphenylpropadiene.**

To a solution of complex **1a** (169 mg, 0.5 mmol) in 1,2-dichloroethane (10 mL) was added 1,1-dimethyl allene (102 mg, 1.5 mmol) and the mixture was stirred in a sealed tube at 60 °C until disappearance of the starting carbene complex (checked by TLC; 2h). The solvent was then removed under reduced pressure and the resulting residue was

subjected to flash chromatography (SiO₂, 10:1 hexane: ethyl acetate) to give 4-phenyl-3-buten-2-one **3** (59 mg, 80%).

The reaction with 1,1-diphenyl allene took place under the same reaction conditions to give 51 mg (70%) of compound **3**.

The spectroscopic data of compound **3** were identical to those reported.

General Procedure for the Nickel(0)-Mediated [3+2]-Cyclization Reaction of Alkenyl Fischer Carbene Complexes **1** with Allenes **2**.

To a solution of alkenyl carbene complex **1** (0.5 mmol) and allene **2** (1.5 mmol) in toluene (10 mL) was added Ni(cod)₂ (151 mg, 0.55 mmol) and the mixture was stirred at rt until disappearance of the starting carbene complex (checked by TLC; 2-5h). After exposure of the reaction crude to light (10h) the solvent was removed under reduced pressure and the resulting residue was subjected to flash chromatography (SiO₂, 30:1 hexane : ethyl acetate) to give the alkylidenecyclopentenones **4**.

(4a): Yield 129 mg (70%); ¹H-NMR: 3.10 (d, *J* = 20 Hz, 1H), 3.67 (s, 3H), 3.73 (d, *J* = 20 Hz, 1H), 3.76 (s, 3H), 4.63 (s, 2H), 6.64 (s, 4H), 6.97-6.98 (m, 2H), 7.19-7.26 (m, 8H); ¹³C-NMR: 38.1 (CH₂), 51.1 (CH), 55.1 (CH₃), 56.4 (CH₃), 98.7 (CH), 113.1 (CH), 126.3 (CH), 126.4 (CH), 127.9 (CH), 128.0 (CH), 128.1 (CH), 128.5 (CH), 129.4 (CH), 137.1 (C), 137.2 (C), 139.9 (C), 141.7 (C), 142.3 (C), 157.5 (C), 158.9 (C). **Anal.** Calcd for C₂₆H₂₄O₂: C, 84.75; H, 6.57; Found: C, 84.66; H, 6.69.

(4b): Yield 83 mg (78%) ¹H-NMR: 1.44 (s, 3H), 1.67 (s, 3H), 3.12 (d, *J* = 19 Hz, 1H), 3.30 (d, *J* = 19 Hz, 1H), 3.62 (s, 3H), 4.42 (br s, 1H), 4.64 (m, 1H), 7.16-7.27 (m, 5H); ¹³C-NMR: 20.1 (CH₃), 21.4 (CH₃), 37.2 (CH₂), 51.9 (CH), 56.3 (CH₃), 100.2 (CH),

125.6 (CH), 126.1 (C), 127.4 (CH), 128.2 (CH), 132.4 (C), 146.6 (C), 158.6 (C). **Anal.** **Calcd** for C₁₅H₁₈O: C, 84.07; H, 8.47; Found: C, 84.21; H, 8.60.

(4c): Yield 83 mg (68%); **¹H-NMR**: 1.46 (s, 3H), 1.68 (s, 3H), 3.12 (d, *J* = 19 Hz, 1H), 3.27 (d, *J* = 19 Hz, 1H), 3.63 (s, 3H), 3.80 (s, 3H), 4.39 (br s, 1H), 4.62 (m, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 2H); **¹³C-NMR**: 20.0 (CH₃), 21.4 (CH₃), 37.1 (CH₂), 51.0 (CH), 55.1 (CH₃), 56.3 (CH₃), 100.3 (CH), 113.5 (CH), 125.8 (C), 128.2 (CH), 132.6 (C), 138.8 (C), 157.4 (C), 158.3 (C). **Anal.** **Calcd** for C₁₆H₂₀O₂: C, 78.65; H, 8.25; Found: C, 78.51; H, 8.30.

(4d): Yield 70 mg (69%); **¹H-NMR**: 1.60 (s, 3H), 1.66 (s, 3H), 3.02 (d, *J* = 19 Hz, 1H), 3.19 (d, *J* = 19 Hz, 1H), 3.63 (s, 3H), 4.51 (br s, 1H), 4.64 (br s, 1H), 5.94 (m, 1H), 6.26 (br s, 1H), 7.29 (br s, 1H); **¹³C-NMR**: 20.0 (CH₃), 21.4 (CH₃), 36.3 (CH₂), 44.7 (CH), 56.3 (CH₃), 95.9 (CH), 103.9 (CH), 109.9 (CH), 126.6 (C), 129.5 (C), 140.6 (CH), 158.5 (C), 159.9 (C). **Anal.** **Calcd** for C₁₃H₁₆O₂: C, 76.44; H, 7.90; Found: C, 76.61; H, 7.99.

(4e): Yield 88 mg (72%); **¹H-NMR**: 1.55-1.60 (m, 6H), 2.04-2.16 (m, 4H), 3.08 (d, *J* = 19 Hz, 1H), 3.27 (d, *J* = 19 Hz, 1H), 3.67 (s, 3H), 4.59 (br s, 1H), 4.69 (br s, 1H), 5.97 (br s, 1H), 6.30 (m, 1H), 7.33 (br s, 1H); **¹³C-NMR**: 26.4 (CH₂), 27.3 (CH₂), 27.4 (CH₂), 30.5 (CH₂), 31.8 (CH₂), 35.5 (CH₂), 44.0 (CH), 56.3 (CH₃), 95.8 (CH), 103.6

(CH), 109.9 (CH), 125.9 (C), 134.5 (C), 140.6 (CH), 158.9 (C), 159.9 (C). **Anal. Calcd** for C₁₆H₂₀O₂: C, 78.65; H, 8.25; Found: C, 78.77; H, 8.11.

General Procedure for the Rhodium-Catalyzed [3+2]-Cyclization Reaction of Alkenyl Fischer Carbene Complexes with allenes.

To a solution of carbene complex **1** (0.5 mmol) and the corresponding allene (0.75 mmol except for dimethylallene, in this case 1.5 mmol were used) in CH₂Cl₂ (20 mL) was added [(naphthalene)Rh(cod)]SbF₆ (29 mg, 0.05 mmol). The mixture was stirred at room temperature until disappearance of the starting carbene complex (checked by TLC; 18-24h). The solvent was then removed and the resulting residue was subjected to flash chromatography (SiO₂, 10:1 hexane:ethyl acetate) to give the methylenecyclopentenenes **5**.

(5a): Yield 138 mg (75%); **¹H-NMR**: 3.68 (s, 3H), 3.85 (s, 3H), 4.74 (br s, 1H), 4.79 (br s, 1H), 5.15 (br s, 1H), 5.50 (br s, 1H), 6.49 (d, *J* = 8.5 Hz, 2H), 6.68 (d, *J* = 8.5 Hz, 2H), 6.90-6.95 (m, 5H), 7.27-7.47 (m, 5H); **¹³C-NMR**: 55.0 (CH₃), 56.6 (CH₃), 57.6 (CH), 63.8 (C), 105.5 (CH), 107.4 (CH₂), 112.6 (CH), 125.2 (CH), 125.9 (CH), 126.4 (CH), 127.7 (CH), 128.0 (CH), 130.1 (CH), 130.6 (CH), 134.4 (C), 143.3 (C), 148.7 (C), 153.2 (C), 157.6 (C), 157.8 (C). **Anal. Calcd** for C₂₆H₂₄O₂: C, 84.75; H, 6.57; Found: C, 84.82; H, 6.54.

(5b): Yield 142 mg (84%); **¹H-NMR**: 3.87 (s, 3H), 4.79 (br s, 1H), 4.87 (d, *J* = 2.5 Hz, 1H), 5.20 (br s, 1H), 5.54 (s, 1H), 6.80-6.99 (m, 9H), 7.26-7.35 (m, 6H); **¹³C-NMR**: 56.7 (CH₃), 58.4 (CH), 63.8 (C), 105.3 (CH), 107.6 (CH₂), 125.2 (CH), 125.9 (CH), 126.0 (CH), 126.5 (CH), 127.2 (CH), 127.8 (CH), 128.0 (CH), 129.4 (CH), 130.7 (CH), 142.4 (C), 143.2 (C), 148.8 (C), 153.1 (C), 157.9 (C). **Anal. Calcd** for C₂₅H₂₂O: C, 88.72; H, 6.55; Found: C, 88.81; H, 6.72.

(5c): Yield 151 mg (92%); **¹H-NMR**: 3.88 (s, 3H), 4.80 (br s, 1H), 4.88, (d, $J = 2.6$ Hz, 1H), 5.15 (br s, 1H), 5.59 (s, 1H), 5.87 (d, $J = 3.2$ Hz, 1H), 6.07 (m, 1H), 7.01-7.52 (m, 11H); **¹³C-NMR**: 52.7 (CH), 56.7 (CH₃), 62.8 (C), 101.5 (CH), 107.6 (CH), 107.9 (CH₂), 109.7 (CH), 125.4 (CH), 126.1 (CH), 126.5 (CH), 127.8 (CH), 128.1 (CH), 129.7 (CH), 141.1 (CH), 143.7 (C), 147.4 (C), 152.6 (C), 155.4 (C), 158.3 (C). **Anal.** Calcd for C₂₃H₂₀O₂: C, 84.12; H, 6.14; Found: C, 83.99; H, 6.17.

(5d): Yield 100 mg (82%) **¹H-NMR**: 0.61 (s, 3H), 1.29 (s, 3H), 3.58 (d, $J = 2.5$ Hz, 1H), 3.80 (s, 3H), 3.81 (s, 3H), 4.71 (br s, 1H), 4.99 (br s, 1H), 5.12 (s, 1H), 6.85 (d, $J = 8.7$ Hz, 2H), 7.07 (d, $J = 8.7$ Hz, 2H); **¹³C-NMR**: 26.6 (CH₃), 30.6 (CH₃), 44.1 (C), 55.2 (CH₃), 56.5 (CH), 56.7 (CH₃), 100.2 (CH₂), 105.1 (CH), 113.2 (CH), 129.3 (CH), 134.6 (C), 157.1 (C), 157.7 (C), 158.2 (C). **Anal.** Calcd for C₁₆H₂₀O₂: C, 78.65; H, 8.25; Found: C, 78.52; H, 8.40.

(5e): Yield 104 mg (65%); **¹H-NMR**: 0.58 (s, 3H), 1.17 (s, 3H), 3.38 (br s, 1H), 3.82 (s, 3H), 4.06-4.13 (m, 4H), 4.15 (s, 5H), 4.63 (br s, 1H), 5.04 (s, 1H), 5.16 (br s, 1H); **¹³C-NMR**: 26.5 (CH₃), 29.3 (CH₃), 43.9 (C), 52.2 (CH), 56.4 (CH₃), 67.1 (CH), 67.2 (CH), 67.4 (CH), 68.3 (C), 68.4 (CH), 89.6 (C), 99.8 (CH₂), 104.6 (CH), 157.0 (C), 157.4 (C). **Anal.** Calcd for C₁₉H₂₂FeO: C, 70.82; H, 6.88; Found: C, 70.71; H, 6.93.

(5f): Yield 46 mg (42%); $^1\text{H-NMR}$: 0.98 (s, 3H), 1.24 (s, 3H), 1.61-2.07 (m, 8H), 2.90 (br s, 1H), 3.76 (s, 3H), 4.68 (br s, 1H), 4.85 (br s, 1H), 5.05 (br s, 1H), 5.48 (m, 1H); $^{13}\text{C-NMR}$: 22.6 (CH_2), 22.9 (CH_2), 24.9 (CH_3), 25.3 (CH_2), 29.2 (CH_2), 31.7 (CH_3), 43.3 (C), 56.3 (CH_3), 58.7 (CH), 99.0 (CH_2), 105.0 (CH), 123.0 (CH), 138.8 (C), 156.9 (C), 157.8 (C); **Anal. Calcd** for $\text{C}_{15}\text{H}_{22}\text{O}$: C, 82.52; H, 10.16; Found: C, 82.56; H, 10.21.

(5g): Yield 132 mg (93%); $^1\text{H-NMR}$: 1.24-1.82 (m, 10H), 3.68 (d, $J = 2.8$ Hz, 1H), 3.76 (s, 3H), 3.83 (s, 3H), 4.83 (s, 1H), 5.00 (br s, 1H), 5.20 (s, 1H), 6.85 (d, $J = 8.5$ Hz, 2H), 7.12 (d, $J = 8.5$ Hz, 2H); $^{13}\text{C-NMR}$: 22.0 (CH_2), 23.1 (CH_2), 25.7 (CH_2), 31.9 (CH_2), 41.7 (CH_2), 47.6 (C), 54.2 (CH_3), 55.1 (CH), 56.3 (CH_3), 100.9 (CH_2), 106.9 (CH), 113.0 (CH), 130.2 (CH), 135.1 (C), 157.3 (C), 157.4 (C), 157.9 (C). **Anal. Calcd** for $\text{C}_{19}\text{H}_{24}\text{O}_2$: C, 80.24; H, 8.51; Found: C, 80.42; H, 8.37.

(5h): Yield 104 mg (68%) of a 1.5:1 trans/cis mixture; Spectroscopic data for the major isomer: $^1\text{H-NMR}$: 1.00 (s, 3H), 3.82 (s, 3H), 3.87 (s, 3H), 4.03 (d, $J = 2.3$ Hz, 1H), 4.58 (br s, 1H), 5.05 (br s, 1H), 5.30 (s, 1H), 6.82 (d, $J = 8.5$ Hz, 2H), 6.94 (d, $J = 8.5$ Hz, 2H), 7.28-7.35 (m, 5H); $^{13}\text{C-NMR}$: 25.0 (CH_3), 51.8 (C), 55.2 (CH_3), 56.7 (CH), 59.5 (CH_3), 103.7 (CH_2), 104.6 (CH), 113.3 (CH), 125.8 (CH), 126.7 (CH), 128.0 (CH), 129.4 (CH), 133.6 (C), 149.9 (C), 156.7 (C), 158.2 (C), 158.4 (C). Spectroscopic data for the minor isomer: $^1\text{H-NMR}$: 1.78 (s, 3H), 3.68 (s, 3H), 3.87 (s, 4H), 4.73 (br s, 1H), 4.99 (br s, 1H), 5.38 (s, 1H), 6.52 (d, $J = 8.4$ Hz, 2H), 6.68 (d, $J = 8.4$ Hz, 2H),

7.01-7.35 (m, 5H). **Anal. Calcd** for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24; Found: C, 82.41; H, 7.28.

(5i): Yield 98 mg (78%); **1H -NMR**: 3.83 (s, 3H), 3.96 (m, 2H), 4.65 (m, 1H), 5.12 (br s, 1H), 5.27 (m, 1H), 6.05 (d, J = 3.0 Hz, 1H), 6.31 (dd, J = 3.0 and 2.0 Hz, 1H), 7.14-7.57 (m, 6H); **^{13}C -NMR**: 48.7 (CH), 53.4 (CH), 56.7 (CH₃), 103.0 (CH), 104.1 (CH₂), 104.5 (CH), 110.0 (CH), 126.4 (CH), 127.9 (CH), 128.4 (CH), 141.4 (CH), 144.0 (C), 150.0 (C), 157.6 (C), 158.5 (C). **Anal. Calcd** for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39; Found: C, 80.89; H, 6.47.

(5j): Yield 118 mg (81%); **1H -NMR**: 3.68 (m, 1H), 3.81-3.84 (2s and m, 7H), 4.60 (br s, 1H), 5.12 (m, 1H), 5.23 (d, J = 2.8 Hz, 1H), 6.85 (d, J = 8.7 Hz, 2H), 7.09 (d, J = 8.7 Hz, 2H), 7.07-7.33 (m, 5H); **^{13}C -NMR**: 54.8 (CH₃), 55.2 (CH), 56.7 (CH₃), 57.7 (CH), 103.4 (CH₂), 106.3 (CH), 113.7 (CH), 126.3 (CH), 128.0 (CH), 128.1 (CH), 128.3 (CH), 137.6 (C), 144.5 (C), 151.4 (C), 158.8 (C), 158.9 (C). **Anal. Calcd** for $C_{20}H_{20}O_2$: C, 82.16; H, 6.89; Found: C, 82.22; H, 6.91.

(5k): Yield 100 mg (77%); **1H -NMR**: 1.83-2.01 (m, 2H), 2.71-2.77 (m, 1H), 3.54 (t, J = 2.5 Hz, 1H), 3.73-3.79 (2s and m, 8H), 4.83 (br s, 1H), 4.99 (br s, 1H), 5.18 (m, 1H), 6.83 (d, J = 8.8 Hz, 2H), 7.14 (d, J = 8.8 Hz, 2H); **^{13}C -NMR**: 38.4 (CH₂), 47.3 (CH), 51.1 (CH), 55.2 (CH₃), 56.6 (CH₃), 60.4 (CH₂), 101.7 (CH₂), 107.5 (CH), 113.9 (CH),

128.1 (CH), 138.0 (C), 150.6 (C), 157.8 (C), 158.1 (C). **Anal. Calcd** for C₁₆H₂₀O₃: C, 73.82; H, 7.74; Found: C, 73.98; H, 7.69.

(5l): Yield 116 mg (78%); **¹H-NMR**: 1.55-2.26 (m, 10H), 2.25-2.26 (m, 2H), 2.56-2.59 (m, 1H), 3.36 (d, *J* = 2.0 Hz, 1H), 3.75 (s, 3H), 3.80 (s, 3H), 4.89 (br s, 1H), 5.65 (m, 1H), 6.84 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H); **¹³C-NMR**: 22.6 (CH₂), 26.7 (CH₂), 27.6 (CH₂), 28.5 (CH₂), 28.7 (CH₂), 33.7 (CH₂), 51.0 (CH₃), 53.8 (CH), 55.3 (CH₃), 56.5 (CH), 103.8 (CH), 113.7 (CH), 119.0 (CH), 127.8 (CH), 139.2 (C), 142.9 (C), 157.8 (C), 158.1 (C). **Anal. Calcd** for C₂₀H₂₆O₂: C, 80.50; H, 8.78; Found: C, 80.43; H, 8.90.

(5m): Yield 127 mg (80%) **¹H-NMR**: 1.73 (s, 3H), 1.91-2.00 (m, 4H), 3.91 (s, 3H), 4.12 (t, *J* = 5.0 Hz, 2H), 7.08-7.13 (m, 4H), 7.23-7.27 (m, 6H); **¹³C-NMR**: 9.8 (CH₃), 18.8 (CH₂), 22.7 (CH₂), 59.3 (CH₃), 62.8 (C), 67.2 (CH₂), 118.0 (C), 124.1 (C), 126.0 (CH), 128.1 (CH), 128.2 (CH), 142.5 (C), 148.6 (C), 149.2 (C). **Anal. Calcd** for C₂₂H₂₂O₂: C, 82.99; H, 6.96; Found: C, 83.06; H, 6.88.

Hydrolysis of the compound 4d

To a solution of compound **4d** (51 mg, 0.25 mmol) in 10 ml of THF was added silica gel (90 mg). The mixture was stirred at rt until disappearance of the starting material (checked by TLC; 5h). After filtration the solvent was removed under reduced pressure and the resulting residue was subjected to flash chromatography on silica gel eluting with a mixture of hexane/ethyl acetate 10:1 to yield pure ketone **6**.

(6): Yield 38 mg (80%); $^1\text{H-NMR}$: 1.73 (s, 3H), 1.80 (s, 3H), 2.62 (d, $J = 18.1$ Hz, 1H), 2.75 (dd, $J = 18.1$ and 9.2 Hz, 1H), 2.94 (d, $J = 22.0$ Hz, 1H), 3.06 (d, $J = 22$ Hz, 1H), 4.36 (d, $J = 9.2$ Hz, 1H), 6.00 (d, $J = 2.2$ Hz, 1H), 6.30 (dd, $J = 2.2$ and 0.9 Hz, 1H), 7.35 (d, $J = 0.9$ Hz, 1H); $^{13}\text{C-NMR}$: 19.5 (CH_3), 21.3 (CH_3), 38.2 (CH), 41.0 (CH_2), 45.3 (CH_2), 104.6 (CH), 110.0 (CH), 127.9 (C), 128.6 (C), 141.7 (CH), 156.6 (C), 216.2 (C). Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{O}_2$: C, 75.76; H, 7.42; Found: C, 75.69; H, 7.45.

Hydrolysis of the compound 5d

1N HCl (1mL) was added to a solution of compound **5d** (61 mg, 0.25 mmol) in 3 mL of THF. The mixture was stirred for 15 min at rt. Then, water (5 mL) was added and the mixture extracted with Et_2O (3x10 mL). The combined organic layers were dried (Na_2SO_4). Solvent was removed in vacuo and the product purified by flash chromatography (SiO_2 , 10:1 hexane: ethyl acetate) to give pure methylidene ketone **7**.

(7): Yield 52 mg (90%); $^1\text{H-NMR}$: 0.81 (s, 3H), 1.25 (s, 3H), 2.66 (dd, $J = 18.2$ and 8.2 Hz, 1H), 2.70 (dd, $J = 18.2$ and 10.5 Hz, 1H), 3.07 (dd, $J = 10.5$ and 8.2 Hz, 1H), 3.81 (s, 3H), 5.24 (s, 1H), 6.06 (s, 1H), 6.88 (d, $J = 8.8$ Hz, 2H), 7.09 (d, $J = 8.8$ Hz, 2H); $^{13}\text{C-NMR}$: 24.2 (CH_3), 27.0 (CH_3), 41.4 (CH_2), 43.9 (C), 49.4 (CH), 55.2 (CH_3), 113.5 (CH), 116.0 (CH_2), 129.3 (CH), 130.8 (C), 155.0 (C), 158.5 (C), 206.1 (C). Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_2$: C, 78.23; H, 7.88; Found: C, 78.37; H, 7.92.