Supplementary Material

β,β'- and α,β,β'-Annulation Reactions of Cyclic Enamines: Enantioselective Synthesis of Bicyclo[3.n.1]alkenones (n = 2,3) and Tricyclo[3.3.0.0^{2,8}]octanes from Fischer Alkenyl Carbene Complexes

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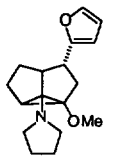
Contents

*Reaction of carbene complex **1** with cyclopentanone-pyrrolidine enamine **2**. Synthesis of semibullvalenes **3**.*

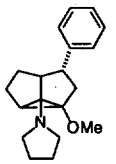
To a solution of carbene complex **1** (1 mmol) in THF (50 mL), 178 mg (1.3 mmol) of cyclopentanone pyrrolidine enamine **2** was added at room temperature. The reaction mixture was heated at 60°C for 1.5 h (**3a-c**) or 6h (**3e-g**). Removed solvent at reduced pressure and column chromatography (hexane-ethyl acetate-triethyl amine 20:1:1) afforded the semibullvalenes **3** as pale yellow oils.

Compound 3a: from pentacarbonyl[(*E*)-2-(2-furyl)ethenyl(methoxy)carbene]tungsten **1a**.



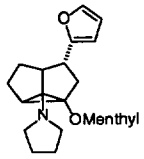
Yield: 85%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.1 (dd, 1H, *J* = 7.1, 12.5 Hz), 1.4 (m, 1H), 1.55 (m, 1H), 1.7 (d, 1H, *J* = 6.5 Hz), 1.8 (m, 4H), 2.05 (m, 1H), 2.1 (dd, 1H, *J* = 10.8, 13.0 Hz), 2.4 (dd, 1H, *J* = 10.3, 13.0 Hz), 2.8 (m, 4H), 3.0 (t, 1H, *J* = 7.1 Hz), 3.35 (s, 3H), 3.4 (m, 1H), 6.0 (m, 1H), 6.25 (m, 1H), 7.3 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 23.9 (2 x CH_2), 25.0 (CH_2), 30.7 (CH_2), 32.8 (CH_2), 36.8 (CH), 42.4 (CH), 45.2 (CH), 51.2 (2 x CH_2), 56.4 (CH_3), 68.1 (C), 75.6 (C), 105.3 (CH), 109.6 (CH), 140.9 (CH), 156.0 (C); HRMS: Calcd for $C_{17}H_{23}NO_2$: 273.1729; Found: 273.1718. Anal. Calcd for $C_{17}H_{23}NO_2$: C, 74.69; H, 8.48; N, 5.12; Found: C, 74.77; H, 8.58; N, 5.09

Compound 3b: from pentacarbonyl[(*E*)-2-phenylethenyl(methoxy)carbene]tungsten **1b**.



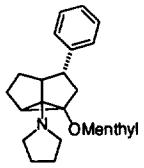
Yield: 88%; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.25 (m, 1H), 1.4-1.6 (m, 2H), 1.7 (d, 1H, *J* = 6.6 Hz), 1.9 (m, 4H), 2.05 (m, 1H), 2.2 (dd, 1H, *J* = 10.8, 13.1 Hz), 2.45 (dd, 1H, *J* = 9.7, 13.1 Hz), 2.85 (m, 4H), 3.0 (t, 1H, *J* = 6.5 Hz), 3.4 (s, 3H), 3.5 (m, 1H), 7.1-7.35 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 23.9 (2 x CH_2), 25.3 (CH_2), 30.7 (CH_2), 31.6 (CH_2), 36.5 (CH), 46.3 (CH), 48.8 (CH), 51.2 (2 x CH_2), 56.4 (CH_3), 68.2 (C), 75.6 (C), 125.7 (CH), 127.7 (2 x CH), 127.9 (2 x CH), 141.3 (C); HRMS: Calcd for $C_{19}H_{25}NO$: 283.1936; Found: 283.1936. Anal. Calcd for $C_{19}H_{25}NO$: C, 80.52; H, 8.89; N, 4.94; Found: C, 80.63; H, 9.00; N, 4.91

Compound 3e: from pentacarbonyl[(*E*)-2-(2-furyl)ethenyl[(1*R*,2*S*,5*R*)-menthyloxy]carbene] chromium **1e**.



Yield: 70%. $[\alpha]_D^{20}$ = -0.184 (*c* 0.43 CH_2Cl_2); ^1H NMR ($CDCl_3$, 300 MHz): δ 0.8 (d, 3H, *J* = 7.0 Hz), 0.85 (d, 3H, *J* = 7.0 Hz), 0.95 (d, 3H, *J* = 6.5 Hz), 0.7-1.0 (m, 2H), 1.1 (dd, 1H, *J* = 6.9, 12.1), 1.3-1.7 (m, 8H), 1.85 (m, 4H), 2.0-2.3 (m, 4H), 2.45 (dd, 1H, *J* = 10.0, 12.6 Hz), 2.8 (m, 4H), 3.05 (t, 1H, *J* = 7.1 Hz), 3.45 (m, 2H), 6.0 (m, 1H), 6.25 (m, 1H), 7.3 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 16.0 (CH_3), 20.8 (CH_3), 22.5 (CH_3), 23.2 (CH_2), 24.0 (2 x CH_2) 24.9 (CH_2), 25.3 (CH), 31.4 (CH), 31.5 (CH_2), 32.3 (CH_2), 34.4 (CH_2), 39.7 (CH), 40.6 (CH_2), 42.7 (CH), 46.2 (CH), 47.2 (CH), 51.0 (2 x CH_2), 65.2 (C), 71.0 (C), 76.7 (CH), 105.3 (CH), 109.7 (CH), 140.8 (CH), 156.2 (C); HRMS Calcd. for $C_{26}H_{39}NO_2$: 397.2981; Found: 397.2968; Anal. Calcd for $C_{26}H_{39}NO_2$: C, 78.54; H, 9.89; N, 3.52; Found: C, 79.02; H, 9.97; N, 3.49

Compound 3f: from pentacarbonyl[(*E*)-2-phenylethenyl[(1*R*,2*S*,5*R*)-menthyloxy]carbene] chromium **1f**.



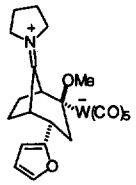
Yield: 73%. $[\alpha]_D^{20}$ = -7.51 (*c* 0.94 CH_2Cl_2); ^1H NMR ($CDCl_3$, 300 MHz): δ 0.8 (d, 3H, *J* = 6.9 Hz), 0.9 (d, 3H, *J* = 7.2 Hz), 0.95 (d, 3H, *J* = 6.7 Hz), 0.7-1.1 (m, 3H), 1.2-1.7 (m, 8H), 1.85 (m, 4H), 2.0-2.5 (m, 5H), 2.9 (m, 4H), 3.05 (t, 1H, *J* = 6.7 Hz), 3.5 (m, 2H), 7.1-7.3 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 16.0 (CH_3), 20.8 (CH_3), 22.5 (CH_3), 23.2 (CH_2), 23.9 (2 x CH_2) 25.2 (CH_2), 25.3 (CH), 31.3 (CH_2), 31.4 (CH_2), 31.5 (CH), 34.4 (CH_2), 39.4 (CH), 40.6 (CH_2), 47.2 (CH), 47.5 (CH), 49.1 (CH), 51.0 (2 x CH_2), 65.2 (C), 71.0 (C), 76.6 (CH), 125.7 (CH), 127.8 (2 x CH), 128.0 (2 x CH), 141.6 (C); HRMS Calcd. for $C_{28}H_{41}NO$: 407.3188; Found: 407.3199; Anal. Calcd for $C_{28}H_{41}NO$: C, 82.50; H, 10.14; N, 3.44; Found: C, 82.73; H, 10.21; N, 3.40

Reaction of carbene complex 1with cyclopentanone-pyrrolidine enamine. Synthesis of complexes 4.

To a solution of carbene complex **1a-d** (1 mmol) in hexane (40 mL) at room 151 mg (1.1 mmol) of cyclopentanone pyrrolidine enamine in hexane (10 mL) was added. The reaction

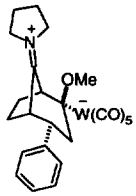
mixture was stirred for 2 h. Filtration of the yellow solid and washing with hexane (2 x 15 mL) yield the complexes **4** as solids.

Compound 4a: from pentacarbonyl[(*E*)-2-(2-furyl)ethenyl(methoxy)carbene]tungsten **1a**.



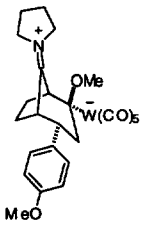
Yield: 95%; yellow solid; Mp: 105-110 °C dec. ^{1}H NMR (THF-*d*8, 300 MHz): δ 1.8-1.9 (m. 1H), 2.05-2.45 (m, 7H), 2.65 (m, 1H), 2.7 (dd, 1H, *J* = 4.4, 15.8 Hz), 3.25 (brd, 1H, *J* = 7.0 Hz), 3.35 (s, 3H), 3.7-3.8 (m, 1H), 3.95 (dd, 1H, *J* = 1.7, 6.6 Hz), 4.05-4.25 (m, 3H), 4.35-4.45 (m, 1H), 6.3 (m, 1H), 6.45 (m, 1H), 7.5 (d, 1H, *J* = 1.3 Hz); ^{13}C NMR (THF-*d*8, 50 MHz): δ 22.2 (CH_2) 26.9 (2 x CH_2), 28.1 (CH_2), 40.5 (CH_2), 47.5 (CH), 50.4 (CH), 54.6 (CH_3), 54.9 (CH_2), 55.8 (CH_2), 64.8 (CH), 108.2 (CH), 108.3 (C), 112.1 (CH), 143.5 (CH), 157.1 (C), 201.4 (C), 206.0 (CO), 206.2 (4 x CO); FAB-MS (*m/z*): 598 (M^+ +1); Anal. Calcd for $C_{22}H_{23}NO_7W$: C, 44.24; H, 3.88; N, 2.35; Found: C, 44.02; H, 3.61; N, 2.30.

Compound 4b: from pentacarbonyl[(*E*)-2-phenylethenyl(methoxy)carbene]tungsten **1b**.



Yield: 94%; yellow solid; Mp: 97-99 °C dec.; ^{1}H NMR (THF-d_8, 300 MHz): δ 1.7 (m, 1H), 2.0-2.5 (m, 7H), 2,6 (m, 1H), 2.65 (dd, 1H, *J* = 4.1, 15.4 Hz), 3.1 (d, 1H, *J* = 6.9 Hz), 3.3 (s, 3H), 3.7 (m, 1H), 3.9 (d, 1H, *J* = 6.1 Hz), 4.0-4.2 (m, 3H), 4.3-4.45 (m, 1H), 7.25 (m, 1H), 7.4 (m, 4H); ^{13}C NMR (THF-d_8, 75 MHz): δ 21.7 (CH_2) 26.5 (2 x CH_2), 28.4 (CH_2), 41.5 (CH_2), 50.1 (CH), 54.6 (CH_3), 55.9 (CH), 56.0 (CH_2), 56.3 (CH_2), 65.0 (CH), 108.5 (C), 128.6 (CH), 129.6 (2 x CH), 130.5 (2 x CH), 143.8 (C), 201.4 (C), 206.0 (CO), 206.3 (4 x CO); FAB-MS (*m/z*): 608 (M^+ +1); Anal. Calcd. for $C_{24}H_{25}NO_6W$: C, 47.46; H, 4.15; N, 2.30; Found: C, 47.18; H, 4.01; N, 2.26

Compound 4c: from pentacarbonyl[(*E*)-2-(4-methoxyphenyl)ethenyl(methoxy)carbene] tungsten **1c**.



Yield: 97%; yellow solid; Mp: 89-91 °C dec. ^{1}H NMR (THF-*d*8, 300 MHz): δ 1.7 (m. 1H), 2.0-2.45 (m, 7H), 2.5 (brs, 1H), 2.6 (dd, 1H, *J* = 4.3, 15.6 Hz), 3.05 (brd, 1H, *J* = 6.8 Hz), 3.3 (s, 3H), 3.6-3.7 (m, 1H), 3.8 (s, 3H), 3.9 (d, 1H, *J* = 6.9 Hz), 4.0-4.2 (m, 3H), 4.3-4.5 (m, 1H), 6.9 (d, 2H, *J* = 8.7 Hz), 7.25 (d, 2H, *J* = 8.7 Hz); ^{13}C NMR (THF-*d*8, 75 MHz): δ 21.6 (CH_2) 26.9 (2 x CH_2), 28.3 (CH_2), 41.6 (CH_2), 50.4 (CH), 54.5 (CH_3), 54.6 (CH_2) 55.1 (CH), 55.8 (CH_2) 56.5 (CH_3), 64.8 (CH), 108.3 (C), 115.7 (2 x CH), 130.4 (2 x CH), 135.6 (C), 160.9 (C), 201.5 (C), 206.0 (CO), 206.2 (4 x CO); FAB-MS (*m/z*): 638 (M^+ +1); Anal. Calcd for $C_{25}H_{27}NO_7W$: C, 47.11; H, 4.27; N, 2.20; Found: C, 47.41; H, 4.51; N, 2.11

Compound 4d: from pentacarbonyl[(*E*)-2-propylethenyl(methoxy)carbene]tungsten **1d**.

^{1}H NMR (THF-*d*8, 300 MHz): δ 1.0 (m, 3H); 1.4 (m, 4H), 1.75 (m. 1H), 2.0-2.5 (m, 9H), 2.85 (brd, 1H, *J* = 7.0 Hz), 3.25 (s, 3H), 3.35 (brs, 1H), 3.7-4.7 (m, 5H); ^{13}C NMR (THF-*d*8, 75 MHz): δ 15.7 (CH_3), 21.2 (CH_2), 22.6 (CH_2) 27.1 (2 x CH_2), 28.3 (CH_2), 37.2 (CH_2) 43.8 (CH_2), 47.7 (CH), 52.6 (CH_3), 54.2 (CH) 54.4 (CH_2), 55.7 (CH_2) 54.9 (CH),110.0 (C), 203.0 (C), 206.1 (CO), 206.4 (4 x CO)

Synthesis of bycyclo[3.2.1]oc-2-en-8-ones ***5***.

Methode A: *Hydrolysis of complexes* ***4***. To a solution of complex **4** (1 mmol) in THF (40 mL) at 0°C 1 mL of trifluoroacetic acid in THF (10 mL) was added. The reaction mixture was stirred 10 min, 10 mL of H_2O was added and the solution was allowed to reach room temperature and stirred for two additional hours. The mixture was extracted with methylene dichloride (3 x 30 mL) and the organic layer washed with 20 mL of saturated solution of sodium hydrogencarbonate and 20 mL of water. The resulting solution was dried over Na_2SO_4.

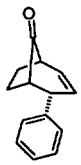
After removal of the solvents, chromatographic purification of the residue on silica gel (5% of ethyl acetate in hexane) gave the pure bycyclic ketones **5**.

***Methode B*:** To 50 mL of a 0.02M THF solution of the alkenyl Fischer carbene complex **1**, at 0°C, 180 mg (1.3 mmol) of the enamine **2** was added. The mixture was stirred at 0°C for 6 h. Then, 1 mL of trifluoroacetic acid and 10 mL of water was subsequently added. The solution was allowed to reach room temperature and stirred for two additional hours. The mixture was extracted with methylene dichloride (3 x 30 mL) and the organic layer washed with 20 mL of saturated solution of sodium hydrogencarbonate and 20 mL of water. The resulting solution was dried over Na_2SO_4. After removal of the solvents, chromatographic purification of the residue on silica gel (5% of ethyl acetate in hexane) gave the pure bycyclic ketones **5**.

Compound (±)-5a:

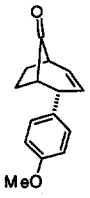
Yield: 87%; colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.7-1.9 (m, 2H), 1.9-2.0 (m, 2H), 2.55 (m, 1H), 2.65 (m, 1H), 4.4 (m, 1H), 5.7 (ddd, 1H, J = 1.2, 2.3, 9.3 Hz), 6.05 (ddd, 1H, J = 2.7, 7.0, 9.4 Hz), 6.15 (m, 1H), 6.35 (m, 1H), 7.4 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 19.8 (CH_2), 28.6 (CH_2), 44.6 (CH), 46.9 (CH), 49.5 (CH), 107.0 (CH), 110.0 (CH), 125.1 (CH), 133.7 (CH), 141.8 (CH), 153.8 (C), 215.1 (C); HRMS Calcd. for $C_{12}H_{12}O_2$: 188.0837; Found:188.0827; Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.42; Found: C, 76.45; H, 6.33

Compound (±)-5b:



Yield: 89%; colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.6-1.8 (m, 2H), 1.9-2.1 (m, 2H), 2.5 (m, 1H), 2.6 (m, 1H), 4.4 (m, 1H), 5.7 (ddd, 1H, J = 1.3, 2.4, 9.2 Hz), 6.1 (ddd, 1H, J = 2.4, 7.0, 9.2 Hz), 7.2-7.4 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 19.0 (CH_2), 28.6 (CH_2), 44.5 (CH), 49.8 (CH), 55.0 (CH), 126.8 (CH), 127.8 (CH), 128.1 (2 x CH), 128.4 (2 x CH), 133.9 (CH), 140.5 (C), 215.8 (C); HRMS Calcd. for $C_{14}H_{14}O$: 198.1045; Found: 198.1031; Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12; Found: C, 84.70; H, 7.04

Compound (±)-5c:



Yield: 91%; white solid; Mp: 110-111 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.6-1.9 (m, 2H), 1.9-2.1 (m, 2H), 2.45 (m, 1H), 2.55 (m, 1H), 3.8 (s, 3H), 4.4 (m, 1H), 5.7 (brd, 1H, J = 9.9 Hz), 6.1 (ddd, 1H, J = 2.5, 7.2, 9.5 Hz), 6.9 (d, 2H, J = 8.6 Hz), 7.1 (d, 2H, J = 8.6 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.9 (CH_2), 28.6 (CH_2), 44.4 (CH), 50.1 (CH), 54.3 (CH_3), 55.0 (CH), 113.8 (2 x CH), 128.1 (CH), 129.0 (2 x CH), 132.6 (C), 133.5 (CH), 158.4 (C), 215.9 (C); HRMS Calcd. for $C_{15}H_{16}O_2$: 228.1150; Found: 228.1144; Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06; Found: C, 78.56; H, 7.14

Compound (±)-5d:

Major isomer; colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.9 (t, 3H, J = 7.1 Hz), 1.2-1.6 (m, 5H), 1.8-2.1 (m, 3H), 2.25 (m, 1H), 2.45 (m, 1H), 2.95 (m, 1H), 5.4 (ddd, 1H, J = 1.5, 2.0, 9.1), 5.8 (ddd, 1H, J = 2.6, 6.6, 9.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.9 (CH_3), 18.3 (CH_2), 19.9 (CH_2), 28.8 (CH_2), 33.8 (CH_2), 45.2 (CH), 46.7 (CH), 50.0 (CH), 130.2 (CH), 130.7 (CH), 220.7 (C); HRMS Calcd. for $C_{11}H_{16}O$: 164.1201; Found: 164.1202; Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82; Found: C, 80.23; H, 9.73

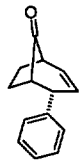
Synthesis of optically active ketones ***5****.*

To a solution of 1 mmol of the alkenyl Fischer carbene complex **1** in 50 mL of THF at -20°C, was added 180 mg (1.3 mmol) of cyclopentanone methoxymethylpyrrolidine enamine **6**. After 6.5 h of stirring at -20°C, 390 μL (5 mmol) of trifluoroacetic acid and stirred 0.5h; 10 mL of water was added and the mixture allowed to react two additional hours at room temperature. Then the mixture was extracted with methylene dichloride (3 x 30 mL) and the organic layer washed with 20 mL of saturated solution of sodium hydrogencarbonate and 20 mL of water and dried over Na_2SO_4. After removal of the solvents, chromatographic purification of the residue on silica gel (5% of ethyl acetate in hexane) gave the optically active ketones **5**.

Compound (+)-5a:

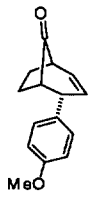
Yield: 85%. $[\alpha]_D^{20}$ = +2.8 (*c* 0.8 CH_2Cl_2). Spectroscopic data, see: (±)-**5a**.
The enantiomeric ratio was determined by HPLC (Chiracel OB-H column, 250 x 4.6 mm, 0.8 mL/min, hexane / isopropanol 50:1): Retention times, 13.6 (6%) and 14.9 (94%) min.

Compound (+)-5b:



Yield: 88%. $[\alpha]_D^{20}$= + 40.57 (*c* 0.53 CH_2Cl_2). Spectroscopic data, see: (±)-**5b**.
The enantiomeric ratio was determined by HPLC (Chiracel OJ column, 250 x 4.6 mm, 0.8 mL/min, hexane / ethanol 500:1): Retention times, 27.9 (4.5%) and 29.7 (95.5%) min.

Compound (+)-5c:



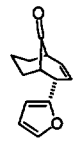
Yield: 90%. $[\alpha]_D^{20}$ = +81 (*c* 0.1 CH_2Cl_2). Spectroscopic data, see: (±)-**5c**.
The enantiomeric ratio was determined by HPLC (Chiracel OJ column, 250 x 4.6 mm, 0.8 mL/min, hexane / isopropanol 50:1): Retention times, 39.8 (3.5%) and 44.7 (96.5%) min.

Synthesis of bycyclo[3.3.1]non-2-en-9-ones ***8****.*

200 mg (1.3 mmol) of the cyclohexanone pyrrolidine enamine was added to a solution of 1 mmol of the alkenyl Fischer carbene complex **2** in 50 mL of THF at 0°C. The mixture was stirred at 0°C for 12 h. Then, 390 μL (5 mmol) of trifluoroacetic acid and 10 mL of water was subsequently added an the solution allowed to reach room temperature and stirred for two additional hours. The resulting mixture was extracted with methylene dichloride (3 x 30 mL) and the organic layer washed with 20 mL of saturated solution of sodium hydrogencarbonate

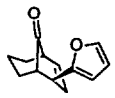
and 20 mL of water, and finally dried over Na_2SO_4. The solvents were removed and subsequent chromatographic purification of the residue on silica gel (5% of ethyl acetate in hexane) yielded the pure bycyclic ketones **8**.

Compound (±)-*endo*-8a:



Yield 67%; white solid; Mp: 49-50 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.3 (m, 1H), 1.4-1.65 (m, 2H), 1.8-2.0 (m, 3H), 2.8 (m, 1H), 2.95 (m, 1H), 4.15 (m, 1H), 5.8 (ddd, 1H, *J* = 2.9, 5.9, 9.9), 6.05 (dd, 1H, *J* = 2.3, 9.9 Hz), 6.2(m 1H), 6.35 (m, 1H), 7.35 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 16.9 (CH_2), 31.4 (CH_2), 32.5 (CH_2), 44.2 (CH), 47.4 (CH), 49.6 (CH), 106.8 (CH), 110.0 (CH), 128.5 (CH), 129.4 (CH), 141.7 (CH), 154.0 (C), 214.7 (C); HRMS Calcd. for $C_{13}H_{14}O_2$: 202.0994; Found: 202.0992; Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98; Found: C, 77.42; H, 6.80

Compound (±)-*exo*-8a:



Yield 13%; colorless oil; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.5-1.7 (m, 2H), 1.8-2.2 (m, 4H), 2.7 (m, 1H), 2.9 (m, 1H), 3.95 (m, 1H), 5.75 (m, 1H), 5.95 (m, 1H), 6.05(m 1H), 6.25 (m, 1H), 7.3 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 17.0 (CH_2), 32.6 (CH_2), 36.0 (CH_2), 47.3 (CH), 47.4 (CH), 41.0 (CH), 105.2 (CH), 110.2 (CH), 128.5 (CH), 129.8 (CH), 141.7 (CH), 155.3 (C), 214.8 (C); HRMS Calcd. for $C_{13}H_{14}O_2$: 202.0994; Found: 202.1002; Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98; Found: C, 77.45; H, 7.09

Compound (±)-*endo*-8b:

Yield 71%; white solid; Mp: 31-33 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.35 (m, 1H), 1.5 (m, 2H), 1.8-2.0 (m, 3H), 2.7 (m, 1H), 3.0 (m, 1H), 4.15 (m, 1H), 5.8 (ddd, 1H, *J* = 2.9, 6.0,

9.9), 6.2 (dd, 1H, J = 2.3, 9.7 Hz), 7.2-7.5 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 17.1 (CH_2), 30.4 (CH_2), 32.9 (CH_2), 47.5 (CH), 49.9 (CH), 51.7 (CH), 126.7 (CH), 127.8 (2 x CH), 128.4 (CH), 128.5 (2 x CH), 132.2 (CH), 140.4 (C), 215.9 (C); HRMS Calcd. for $C_{15}H_{16}O$: 212.1201; Found: 212.1200; Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60; Found: C, 84.79; H, 7.55

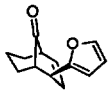
Synthesis of optically active ketones ***8****.*

To 50 mL of a 0.02M solution (in the appropriate solvent) of the alkenyl Fischer carbene complex **1**, 1.3 mmol of the enamine **7** was added. After stirring the mixture at low temperature, 390 μL (5 mmol) of trifluoroacetic acid and 10 mL of water was subsequently added. The solution was allowed to reach room temperature and stirred for two additional hours. The mixture was extracted with methylene dichloride (3 x 30 mL) and the organic layer washed with 20 mL of saturated solution of sodium bicarbonate and 20 mL of water. The resulting solution was dried over Na_2SO_4 and the solvents removed. Purification of the residue by chromatography on silica gel (5% of ethyl acetate in hexane) gave the optically active bycyclic ketones **8**.

Compound (-)-*endo*-8a:

Solvent: CH_2Cl_2; Temperature: -50 °C; Reaction time: 7d; Yield 52%; $[\alpha]_D^{20}$ = -17.6 (*c* 0.23 CH_2Cl_2). Spectroscopic data, see: **(±)-*endo*-8a**.
The enantiomeric ratio was determined by HPLC (Chiracel OJ column, 250 x 4.6 mm, 0.8 mL/min, hexane / isopropanol 200:1): Retention times, 15.8 (1%) and 18.2 (99%) min.

Compound (-)-*exo*-8a:

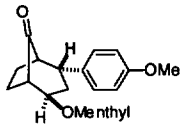


Solvent: THF; Temperature: -20 °C; Reaction time: 72h; *endo*:*exo* ratio 1:2; Spectroscopic data, see: **(±)-*exo*-8a**.
The enantiomeric ratio was determined by HPLC (Chiracel OJ column, 250 x 4.6 mm, 0.8 mL/min, hexane / isopropanol 200:1): Retention times, 20.2 (99%) and 22.3 (1%) min.

Compound (-)-*endo*-8b:

Solvent: THF; Temperature: -30 °C; Reaction time: 7d; $[\alpha]_D^{20}$ = -10.31 (*c* 0.15 CH_2Cl_2).
Spectroscopic data, see: **(±)-*endo*-8b**.
The enantiomeric ratio was determined by HPLC (Chiracel OJ column, 250 x 4.6 mm, 0.8 mL/min, hexane / isopropanol 250:1): Retention times, 23.2 (3%) and 38.9 (97%) min.

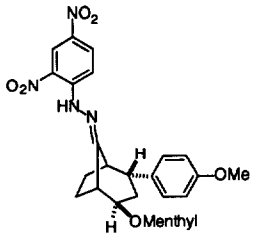
Synthesis of ketone (+)-9.



In a sealed tube, the residue crude from **3g** was dissolved in 30 mL of a mixture of 20 mL of water and 10 mL of methanol and stirred at 170°C for 3 hours. After cooling down, the mixture was extracted with ethyl acetate (3 x 20 mL). The organic layer was washed with water and dried over Na_2SO_4. Evaporation of the solvents and chromatographic purification of the residue on silica gel (hexane: ethyl acetate (3:1)) yielded the ketone **9** (70%).

Colorless oil; $[\alpha]_D^{20}$ = +13.9 (*c* 0.23 CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.7 (d, 3H, *J* = 7.0 Hz), 0.9 (d, 3H, *J* = 7.0Hz), 0.95 (d, 3H, *J* = 7.0 Hz), 0.8-1.0 (m, 3H), 1.3 (m, 2H), 1.5-2.3 (m, 10H), 2.4 (m, 2H), 3.1 (dt, 1H, *J* = 4.4, 10.4 Hz), 3.5 (dd, 1H, *J* = 3.9, 11.8 Hz), 3.8 (s, 3H), 4.1 (s, 1H), 6.9 (d, 2H, *J* = 8.4 Hz), 7.2 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 15.8 (CH_3), 17.3 (CH_2), 20.5 (CH_2), 21.2 (CH_3), 22.3 (CH_3), 22.9 (CH_2), 25.1 (CH), 27.4 (CH_2), 31.5 (CH), 34.4 (CH_2), 40.6 (CH_2), 44.2 (CH), 48.2 (CH), 49.3 (CH), 50.9 (CH), 55.2 (CH_3), 77.1 (CH), 79.5 (CH), 113.8 (2 x CH), 128.1 (2 x CH), 134.1 (C), 158.2 (C), 216.3 (C); HRMS Calcd for $C_{25}H_{36}O_3$: 384.2664; Found: 384.2663; Anal. Calcd for $C_{25}H_{36}O_3$: C, 78.08; H, 9.44; Found: C, 78.25; H, 9.52

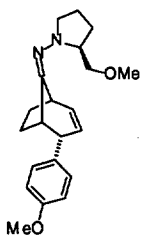
Synthesis of hydrazone (-)-10.



5 mL of concentrated sulfuric acid was added over a stirred suspension of 240 mg (1.2 mmol) of 2,4-dinitrophenylhidrazine in 5 mL of methanol. After almost completely dissolution of the hidrazine the mixture was filtered. To the obtained solution, 192 mg (0.5 mmol) of the ketone **9** was added. After 10 minutes of reaction, the obtained suspension was cooled down to 0°C and the solid separated and washed with cold methanol (3 x 5 mL). The solid was redissolved in hot methanol and filtered again. Slow cooling of the solution precipitates the hidrazone **10** as a pure compound, which was filtered and dried under vacuum.

Yield: 90%; yellow solid; Mp: 146-148 °C; $[\alpha]_D^{20}$ = -683.6 (*c* 0.15 in CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.5-2.3 (m, 24H), 2.9 (m, 1H), 3.1-3.5 (m, 3H), 3.8 (s, 3H), 4.2 (m, 1H), 6.9 (d, 2H, *J* = 8.6 Hz), 7.2 (d, 2H, *J* = 8.6 Hz), 7.9 (d, 1H, *J* = 9.7 Hz), 8.3 (d, 1H, *J* = 9.7 Hz), 9.1 (s, 1H), 11.3 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 15.7 (CH_3), 19.2 (CH_2), 20.9 (CH_3), 22.2 (CH_3), 22.9 (CH_2), 23.7 (CH_2), 25.1 (CH_2), 26.0 (CH_2), 31.3 (CH), 34.1 (CH_2), 39.0 (CH), 41.8 (CH), 46.4 (CH), 48.0 (CH), 48.2 (CH), 55.2 (CH_3), 74.6 (CH), 76.5 (CH), 113.8 (2 x CH), 116.0 (CH), 123.7 (CH), 128.2 (2 x CH), 128.5 (C), 129.6 (CH), 134.1 (C), 137.0 (C), 145.5 (C), 158.3 (C), 173.1 (C); Electro-spray-MS (*m/z*): 565 (M^+ +1); Anal. for $C_{31}H_{40}N_4O_6$ Calcd.: C, 65.94; H, 7.14; N, 9.92; Found: C, 65.91; H, 6.98; N, 9.85

Synthesis of hydrazone (+)-11.



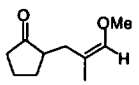
21 mg (0.16 mmol) of (*S*)-(-)-1-amino-2-methoxymethylpyrrolidine in 220 μL of toluene was added to a solution of 51 mg (0.15 mmol) of the ketone **(+)-5c** in 1 mL of toluene. The mixture was stirred at 60°C for 16 hours. After cooling down, 12 mL of water was added and

the two-phase mixture was extracted with diethyl ether (3 x 15 mL). The organic layer was washed with water and dried over Na_2SO_4. The solvents were evaporated and the residue purified by chromatography on silica gel (5 % of ethyl acetate in hexane). The residue was dissolved in pentane and cooled down to -20°C to obtain a whited solid enriched in the mayor estereoisomer of the hidrazone **11**. After two successive cristalizations this isomer could be obtained as a sole compound.

White solid; Mp: 79-81°C; $[\alpha]_D^{20}$= + 472.53 (*c* 0.43 CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.5-1.9 (m, 7H), 2.0 (m, 1H), 2.6 (q, 1H, *J* = 8.7 Hz), 2.7 (m, 1H), 3.3 (m, 4H), 3.4 (s, 3H), 3.5 (m, 1H), 3.8 (s, 3H), 4.1 (m, 1H), 5.6 (ddd, 1H, *J* = 1.3, 2.4, 9.6 Hz), 6.1 (ddd, 1H, *J* = 2.4, 7.0, 9.6 Hz), 6.9 (d, 2H, *J* = 8.6 Hz), 7.1 (d, 2H, *J* = 8.6 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 20.3 (CH_2), 22.0 (CH_2), 26.4 (CH_2), 31.3 (CH_2), 36.5 (CH), 46.8 (CH), 54.0 (CH), 55.2 (CH), 55.6 (CH_2), 59.2 (CH_3), 66.4 (CH_3), 75.2 (CH_2), 113.6 (2 x CH), 128.9 (CH), 129.1 (2 x CH), 133.3 (CH), 133.9 (C), 158.1 (C), 172.8 (C); HRMS Calcd for $C_{21}H_{28}N_2O_2$: 340.2151; Found: 340.2147. Anal. Calcd: C, 74.08; H, 8.28; N, 8.22; Found: C, 74.27; H, 8.51; N, 8.10

*Reaction of pentacarbonyl[1-mehylethenyl(methoxy)carbene]tungsten with cyclopentanone-pyrrolidine enamine **2**. Synthesis of enol-ether **12**.*

To a solution of carbene complex (1 mmol) in THF (50 mL) 178 mg (1.3 mmol) of cyclopentanone pyrrolidine enamine was added at 0°C. The reaction was stirred at 25°C for 2 h. Then, 1 mL of trifluoroacetic acid and 10 mL of water was added. The mixture was extracted with methylene dichloride (3 x 30 mL) and the organic layer washed with water (2 x 20 mL). The resulting solution was dried over Na_2SO_4. After removal of the solvents, chromatographic purification of the residue on silica gel (5% of ethyl acetate in hexane) gave the pure enol-ether **12**.



^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.5 (d, 3H, *J* = 1.32 Hz), 1.5-1.9 (m, 2H), 1.9-2.4 (m, 7H), 3.5 (s, 3H), 5.85 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 17.1 (CH_3), 20.5 (CH_2), 28.9 (CH_2), 29.0 (CH_2), 38.1 (CH_2), 47.2 (CH), 59.1 (CH_3), 111.6 (C), 143.0 (CH), 219.5 (C); HRMS Calcd for $C_{10}H_{16}O_2$: 168.1150; Found: 168.1154. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59; Found: C, 71.57; H, 9.64