

Supplementary Material

Group 6 Heteroatom- and Nonheteroatom-Stabilized Carbene Complexes. β,β' - and α,β,β' -Annulation Reactions of Cyclic Enamines

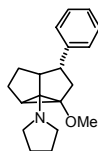
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Contents

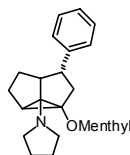
Characterization data of compounds **5b,f**, **6b,d**, **7b,d**, **8b**, **12b,c**, **7-d-b**, **13b**, **15b,c**, (+)-**22**, (-)-**23**, (+)-**24**.

Compound 5b: from pentacarbonyl[(*E*)-2-phenylethenyl(methoxy)carbene]tungsten **2b**.



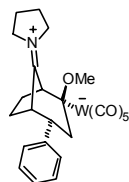
Yield: 88%; ^1H NMR (CDCl_3 , 200 MHz): δ 1.25 (m, 1H), 1.4-1.6 (m, 2H), 1.7 (d, 1H, $J = 6.6$ Hz), 1.9 (m, 4H), 2.05 (m, 1H), 2.2 (dd, 1H, $J = 10.8, 13.1$ Hz), 2.45 (dd, 1H, $J = 9.7, 13.1$ Hz), 2.85 (m, 4H), 3.0 (t, 1H, $J = 6.5$ Hz), 3.4 (s, 3H), 3.5 (m, 1H), 7.1-7.35 (m, 5H); ^{13}C NMR (CDCl_3 , 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 $\text{C}_{19}\text{H}_{25}\text{NO}$: 283.1936; Found: 283.1936. Anal. Calcd for $\text{C}_{19}\text{H}_{25}\text{NO}$: C, 80.52; H, 8.89; N, 4.94; Found: C, 80.63; H, 9.00; N, 4.91

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



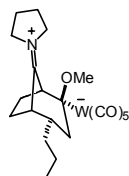
Yield: 73%. $[\alpha]_{\text{D}}^{20} = -7.51$ (c 0.94 CH_2Cl_2); ^1H NMR (CDCl_3 , 300 MHz): δ 0.8 (d, 3H, $J = 6.9$ Hz), 0.9 (d, 3H, $J = 7.2$ Hz), 0.95 (d, 3H, $J = 6.7$ Hz), 0.7-1.1 (m, 3H), 1.2-1.7 (m, 8H), 1.85 (m, 4H), 2.0-2.5 (m, 5H), 2.9 (m, 4H), 3.05 (t, 1H, $J = 6.7$ Hz), 3.5 (m, 2H), 7.1-7.3 (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 $\text{C}_{28}\text{H}_{41}\text{NO}$: 407.3188; Found: 407.3199; Anal. Calcd for $\text{C}_{28}\text{H}_{41}\text{NO}$: C, 82.50; H, 10.14; N, 3.44; Found: C, 82.73; H, 10.21; N, 3.40

Compound 6b: from pentacarbonyl[(*E*)-2-phenylethenyl(methoxy)carbene]tungsten **2b**.



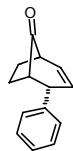
Yield: 94%; yellow solid; Mp: 97-99 °C dec.; ^1H NMR (THF- d_8 , 300 MHz): δ 1.7 (m, 1H), 2.0-2.5 (m, 7H), 2.6 (m, 1H), 2.65 (dd, 1H, $J = 4.1, 15.4$ Hz), 3.1 (d, 1H, $J = 6.9$ Hz), 3.3 (s, 3H), 3.7 (m, 1H), 3.9 (d, 1H, $J = 6.1$ Hz), 4.0-4.2 (m, 3H), 4.3-4.45 (m, 1H), 7.25 (m, 1H), 7.4 (m, 4H); ^{13}C 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 ($\text{M}^+ + 1$); Anal. Calcd. for $\text{C}_{24}\text{H}_{25}\text{NO}_6\text{W}$: C, 47.46; H, 4.15; N, 2.30; Found: C, 47.18; H, 4.01; N, 2.26

Compound 6d: from pentacarbonyl[(*E*)-2-propylethenyl(methoxy)carbene]tungsten **2d**.



^1H 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)

Compound (±)-7b:



Yield: 89%; colorless oil; ^1H 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 $\text{C}_{14}\text{H}_{14}\text{O}$: 198.1045; Found: 198.1031; Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{O}$: C, 84.81; H, 7.12; Found: C, 84.70; H, 7.04

Compound (±)-7d:



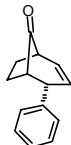
Major isomer; colorless oil; ^1H NMR (CDCl_3 , 300 MHz): δ 0.9 (t, 3H, $J = 7.1$ Hz), 1.2-1.6 (m, 5H), 1.8-2.1 (m, 3H), 2.25 (m, 1H), 2.45 (m, 1H), 2.95 (m, 1H), 5.4 (ddd, 1H, $J = 1.5, 2.0, 9.1$), 5.8 (ddd, 1H, $J = 2.6, 6.6, 9.1$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz): δ 13.9 (CH_3), 18.3 (CH_2), 19.9 (CH_2),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

Compound (±)-endo-8b:



Yield 71%; white solid; Mp: 31-33 °C; ^1H 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 $\text{C}_{15}\text{H}_{16}\text{O}$: 212.1201; Found: 212.1200; Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{O}$: C, 84.87; H, 7.60; Found: C, 84.79; H, 7.55

Compound (+)-7b:



Yield: 88%. $[\alpha]_{\text{D}}^{20} = +40.57$ (c 0.53 CH_2Cl_2). Spectroscopic data, see: (±)-7b.

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.

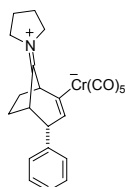
Compound (-)-endo-8b:



Solvent: THF; Temperature: -30 °C; Reaction time: 7d; $[\alpha]_{\text{D}}^{20} = -10.31$ (c 0.15 CH_2Cl_2). Spectroscopic data, see: (±)-endo-8b.

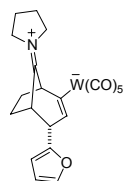
The enantiomeric ratio was determined by HPLC (Chiracel OJ column, 250 x 4.6 mm, 0.8 mL/min, hexane / isopropanol 250:1): Retention times, 23.2 (3%) and 38.9 (97%) min.

Compound 12b



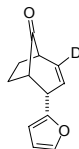
Yield: 64%; yellow solid; Mp; 200-202 dec.; ^1H NMR (CD_2Cl_2 , 300 MHz): δ 1.5-1.7 (m, 2H), 1.8-1.9 (m, 1H), 2.0-2.4 (m, 5H), 2.8 (m, 1H), 3.6 (m, 1H), 3.7-4.1 (m, 4H), 4.8 (m, 1H), 5.5 (m, 1H), 7.2-7.5 (m, 5H); ^{13}C NMR (CD_2Cl_2 , 75 MHz): δ 22.6 (CH_2), 25.5 (CH_2), 25.6 (CH_2), 30.7 (CH_2), 49.3 (CH), 53.0 (CH_2), 54.1 (CH_2), 60.5 (CH), 67.0 (CH), 128.0 (CH), 129.2 (2 x CH), 129.3 (2 x CH), 132.6 (CH), 141.9 (C), 183.3 (C), 199.3 (C), 223.8 (4 x C) 231.0 (C); EI-MS (m/z): 252 [$\text{M}-\text{Cr}(\text{CO})_5+1$]; Anal. Calcd. for $\text{C}_{23}\text{H}_{21}\text{NO}_5\text{Cr}$: C, 62.30; H, 4.77; N, 3.16. Found: C, 62.38; H, 4.72; N, 3.11.

Compound 12c



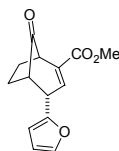
Yield: 67%; yellow solid; Mp; 155-158 dec.; ^1H NMR (CD_2Cl_2 , 300 MHz): δ 1.7-2.4 (m, 8H), 3.2 (brs, 1H), 3.8 (m, 1H), 3.8-4.1 (m, 4H), 4.7 (m, 1H), 5.7 (m, 1H), 6.4 (m, 2H), 7.4 (m, 1H); ^{13}C NMR (CD_2Cl_2 , 75 MHz): δ 22.7 (CH_2), 25.0 (CH_2), 25.1 (CH_2), 30.2 (CH_2), 46.0 (CH), 52.7 (CH_2), 54.0 (CH_2), 61.1 (CH), 62.2 (CH), 109.0 (CH), 110.7 (CH), 130.2 (CH), 142.0 (CH), 154.2 (C), 170.3 (C), 199.7 (C), 203.2 (4 x C) 207.0 (C); FAB-HRMS Calcd. for $\text{C}_{21}\text{H}_{20}\text{NO}_6^{184}\text{W}$: 566.0800; Found: 566.0793; Anal. Calcd. for $\text{C}_{21}\text{H}_{19}\text{NO}_6\text{W}$: C, 44.62; H, 3.39; N, 2.48. Found: C, 44.73; H, 3.29; N, 2.41.

Compound 7-d-b



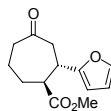
Yield: 93%; colourless oil; ^1H NMR (CDCl_3 , 300 MHz): δ 1.7-1.9 (m, 2H), 1.9-2.0 (m, 2H), 2.55 (m, 1H), 2.65 (m, 1H), 4.4 (m, 1H), 5.7 (s, 1H), 6.15 (m, 1H), 6.35 (m, 1H), 7.4 (m, 1H); ^{13}C NMR (CDCl_3 , 75 MHz): δ 19.8 (CH_2), 28.6 (CH_2), 44.6 (CH), 46.9 (CH), 49.5 (CH), 107.0 (CH), 110.0 (CH), 125.1 (CH), 133.7 (CD, t, $J = 28$ Hz), 141.8 (CH), 153.8 (C), 215.1 (C); HRMS Calcd. for $\text{C}_{12}\text{H}_{11}\text{DO}_2$: 189.0900; Found: 189.0899, Anal. Calcd. for $\text{C}_{12}\text{H}_{11}\text{DO}_2$: C, 76.17; H, 6.92; Found: C, 76.28; H, 6.81.

Compound 13b



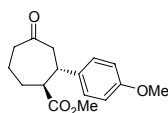
Yield: 64% Method A (from complex **12a**), 57% Method B (from alkenyl Fyscher carbene complex **1,2a**) ; colourless oil; ^1H NMR (CDCl_3 , 300 MHz): δ 1.8-1.9 (m, 1H), 2.0-2.2 (m, 3H), 2.8 (m, 1H), 3.0 (m, 1H), 3.7 (s, 3H), 4.0 (m, 1H), 6.2 (m, 1H), 6.3 (m, 1H), 6.4 (m, 1H), 7.4 (m, 1H); ^{13}C NMR (CDCl_3 , 75 MHz): δ 21.6 (CH_2), 28.2 (CH_2), 44.2 (CH), 45.4 (CH), 52.3 (CH_3), 53.4 (CH), 106.5 (CH), 111.2 (CH), 115.2 (CH), 134.2 (C), 142.8 (CH), 151.4 (C), 171.2 (C), 213.2 (C); HRMS Calcd. for $\text{C}_{14}\text{H}_{14}\text{O}_4$: 246.0892; Found: 246.0881, Anal. Calcd. for $\text{C}_{14}\text{H}_{14}\text{O}_4$: C, 68.28; H, 5.73; Found: C, 68.22; H, 5.67.

Compound (\pm)-15b



Yield: 64%; colourless oil; ^1H NMR (CDCl_3 , 300 MHz): δ 1.8-2.2 (m, 4H), 2.5 (m, 2H), 2.8 (dd, 1H, $J = 2.56, 14.10$ Hz), 3.0 (m, 2H), 3.4 (dt, 1H, $J = 2.57, 10.52$ Hz), 3.6 (s, 3H), 6.0 (m, 1H), 6.3 (m, 1H), 7.3 (m, 1H); ^{13}C NMR (CDCl_3 , 75 MHz): δ 21.3 (CH_2), 30.6 (CH_2), 37.2 (CH), 43.3 (CH_2), 46.0 (CH_2), 51.0 (CH), 51.8 (CH_3), 105.4 (CH), 110.0 (CH), 141.5 (CH), 155.4 (C), 174.4 (C), 211.7 (C); FAB-HRMS (M+1) Calcd. for $\text{C}_{13}\text{H}_{17}\text{O}_4$: 237.1128; Found: 237.1127, Anal. Calcd. for $\text{C}_{16}\text{H}_{16}\text{O}_3$: C, 66.09; H, 6.83; Found: C, 66.15; H, 6.74.

Compound (\pm)-15c



Yield: 61%; white solid; Mp: 108-109° C; ^1H NMR (CDCl_3 , 300 MHz): δ 1.7 (m, 1H), 1.9 (m, 1H), 2.1 (m, 1H), 2.2 (m, 1H), 2.6 (m, 3H), 2.8 (dt, 1H, $J = 2.85, 10.82$ Hz), 3.1 (m, 2H), 3.4 (s, 3H), 3.8 (s, 3H), 6.8 (d, 2H, $J = 8.8$ Hz), 7.1 (d, 2H, $J = 8.8$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz): δ 22.0 (CH_2), 31.9 (CH_2), 43.2 (CH_2), 43.6 (CH), 49.8 (CH_2), 51.4 (CH_3), 55.1 (CH + CH_3), 113.8 (2 x CH), 127.9 (2 x CH), 135.5 (C), 158.2 (C), 174.6 (C), 212.2 (C); HRMS Calcd. for $\text{C}_{16}\text{H}_{20}\text{O}_4$: 276.1362; Found: 276.1362, Anal. Calcd. for $\text{C}_{16}\text{H}_{20}\text{O}_4$: C, 69.54; H, 7.30; Found: C, 69.58; H, 7.28.

Compound (+)-15b

Yield: 54%. $[\alpha]_{\text{D}}^{20} = +11.0$ (c 0.1 CH_2Cl_2). Spectroscopy data, see: (\pm)-15b.

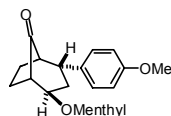
The enantiomeric ratio was determined by HPLC (chiracel OB-H column, 250 x 4.6 mm, 0.8 mL/min, hexane / ethanol 50:1): Retention times, 31.7 (4.5%) and 36.7 (95.5%) min.

Compound (+)-15c

Yield: 55%. $[\alpha]_{\text{D}}^{20} = +55.7$ (c 0.67 CH_2Cl_2). Spectroscopy data, see: (\pm)-15c.

The enantiomeric ratio was determined by HPLC (chiracel OB-H column, 250 x 4.6 mm, 0.8 mL/min, hexane / ethanol / isopropanol 50:1:1): Retention times, 39.1 (98%) and 42.6 (2%) min.

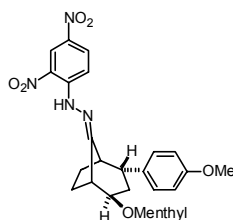
Synthesis of ketone (+)-22.



In a sealed tube, the residue crude from **5g** 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 Na₂SO₄. Evaporation of the solvents and chromatographic purification of the residue on silica gel (hexane: ethyl acetate (3:1)) yielded the ketone **(+)-22** (70%).

Colorless oil; $[\alpha]_D^{20} = +13.9$ (*c* 0.23 CH₂Cl₂); ¹H NMR (CDCl₃, 300 MHz): δ 0.7 (d, 3H, *J* = 7.0 Hz), 0.9 (d, 3H, *J* = 7.0 Hz), 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); ¹³C NMR (CDCl₃, 75 MHz): δ 15.8 (CH₃), 17.3 (CH₂), 20.5 (CH₂), 21.2 (CH₃), 22.3 (CH₃), 22.9 (CH₂), 25.1 (CH), 27.4 (CH₂), 31.5 (CH), 34.4 (CH₂), 40.6 (CH₂), 44.2 (CH), 48.2 (CH), 49.3 (CH), 50.9 (CH), 55.2 (CH₃), 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 C₂₅H₃₆O₃: 384.2664; Found: 384.2663; Anal. Calcd for C₂₅H₃₆O₃: C, 78.08; H, 9.44; Found: C, 78.25; H, 9.52

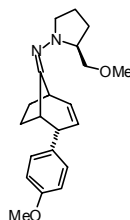
Synthesis of hydrazone (-)-23.



5 mL of concentrated sulfuric acid was added over a stirred suspension of 240 mg (1.2 mmol) of 2,4-dinitrophenylhydrazine in 5 mL of methanol. After almost completely dissolution of the hydrazine the mixture was filtered. To the obtained solution, 192 mg (0.5 mmol) of the ketone (-)-**22** 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 hydrazone (-)-**23** 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 CH₂Cl₂); ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 75 MHz): δ 15.7 (CH₃), 19.2 (CH₂), 20.9 (CH₃), 22.2 (CH₃), 22.9 (CH₂), 23.7 (CH₂), 25.1 (CH₂), 26.0 (CH₂), 31.3 (CH), 34.1 (CH₂), 39.0 (CH), 41.8 (CH), 46.4 (CH), 48.0 (CH), 48.2 (CH), 55.2 (CH₃), 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 C₃₁H₄₀N₄O₆ Calcd.: C, 65.94; H, 7.14; N, 9.92; Found: C, 65.91; H, 6.98; N, 9.85

Synthesis of hydrazone (+)-**24**.



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 (+)-**7c** 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 Na₂SO₄. 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 (-)-**24**. After two successive cristalizaciones this isomer could be obtained as a sole compound.

White solid; Mp: 79-81°C; $[\alpha]_D^{20} = +472.53$ (*c* 0.43 CH₂Cl₂); ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 75 MHz): δ 20.3 (CH₂), 22.0 (CH₂), 26.4 (CH₂), 31.3 (CH₂), 36.5 (CH), 46.8 (CH), 54.0 (CH), 55.2 (CH), 55.6 (CH₂), 59.2 (CH₃), 66.4 (CH₃), 75.2 (CH₂), 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 C₂₁H₂₈N₂O₂: 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