Supplementary Information for

A New Homogeneous Zinc Complex with Increased Reactivity for the Intramolecular Hydroamination of Alkenes

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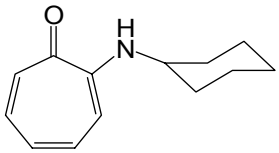
(7 pages)

I. Experimental Procedures

General. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX 500 spectrometer at 353 or 298 K using the deuterated solvent as a lock and residual solvent peak as the internal reference. MS and HRMS were recorded on a Finnigan MAT 95 SQ spectrometer. IR spectra were measured on a Nicolet FT-IR 750 spectrometer. All reactions were, unless otherwise stated, carried out using standard Schlenk and glovebox techniques under an atmosphere of nitrogen. $[PhNMe_2H][B(C_6F_5)_4]$ was purchased from Strem. Benzene-d_6 was dried over 4Å molecular sieves. Aminoalkenes were prepared using modified literature procedures from commercially available starting materials from Aldrich, Acros Organics and Fluka. Prior to use, all substrates were purified either by distillation or recrystallization.
1-Benzyl-2,4,4-trimethylpyrrolidine and 1-benzyl-2-methyl-4,4-diphenylpyrrolidin (entries 3 and 7) have allready been described elsewhere.[1]

General Procedure for NMR-tube scale intramolecular aminoalkynes hydroamination.
A predried NMR-tube was charged with the aminoalkene (430 µmol). A solution of **1** (4 mg, 11 µmol, 2.5 mol%) and $[PhNMe_2H][B(C_6F_5)_4]$ (9 mg, 11 µmol, 2.5 mol%) in 0.5 mL C_6D_6 was added under a nitrogen athmosphere. The NMR-tube was flamesealed under vacuum. The reaction mixture was then heated to 80 °C for the stated duration of time. The reaction progress was monitored by ^{1}H NMR. When the reaction was judged to be completed, the crude reaction mixture was directly subjected to column chromatography on silica. All products were analysed by ^{1}H, ^{13}C, ^{13}C-DEPT, IR, MS, HRMS. The NMR yields were determined by comparing the integration of a well-resolved signal for the starting material with a well-resolved signal for the heterocyclic product.

2-Cyclohexylamino-tropone



2-Tosyloxytropone[2] (2.73 g, 10.0 mmol) was added at once to neat cyclohexylamine (15 mL) at 0 °C. The mixture was allowed to warm to room temperature and stirred over night. All volatiles were removed under reduced pressure, the oliy residue was taken up in 15 mL 2 N NaOH and 30 mL of MTBE. The aqueous phase is extracted with MTBE (2*30 mL). The combined organic phases were washed with brine (20 mL) and dried over $MgSO_4$. Flash Column Chromatographie (SiO_2, Hexanes/MTBE 2:1) gives the product as a yellowish oil (1.87 g, 9.20 mmol, 92 %) which solidifies upon standing.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) = 1.23-1.46 (m, 5 H); 1.64-1.72 (m, 1 H); 1.76-1.86 (m, 2 H); 2.01-2.10 (m, 2 H); 3.45-3.55 (m, 1 H); 6.58 (d, *J* = 10.8 Hz, 1 H); 6.64 (t, *J* = 9.4 Hz, 1 H); 7.15 (t, *J* = *12.4* Hz, 1 H); 7.21-7.37 (m, 1 H).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) = 24.7; 25.6; 32.1; 51.1; 108.8; 121.7; 128.1; 136.2; 137.1; 154.6 (C_q); 176.4 (C_q).

IR (ATR): ν (cm^{-1}) = 3283 (w); 3054 (w); 2931 (m); 2854 (w); 1733 (w); 1602 (s); 1590 (s); 1552 (s); 1508 (s); 1477 (m); 1454 (s); 1406 (m); 1389 (m); 1350 (m); 1267 (m); 1256 (m); 1246 (m); 1223 (m); 1206 (m); 1149 (m); 1107 (m); 1075 (w); 1041 (w); 962 (m); 875 (m); 846 (w); 760 (w); 724 (m); 719 (m).

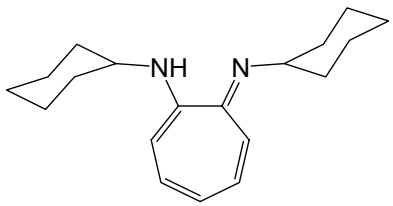
MS (EI, 70 eV): m/z (%) = 203 [M^+] (100); 174 (10); 160 (37); 146 (39); 132 (17); 121 (40); 118 (13); 105 (18); 98 (38); 93 (65); 92 (10); 78 (13); 77 (20); 66 (12); 65 (15); 55 (23).

HRMS: $C_{13}H_{17}NO$ calc: 203.1310
found: 203.1309.

Elemental analysis: calc.: C : 76.81 % H : 8.43 % N : 6.85 %
found: C : 76.60 % H : 8.23 % N : 7.12 %

melting point: 67 °C (from Ethanol)

Cyclohexyl-(7-cyclohexylimino-cyclohepta-1,3,5-trienyl)-amine

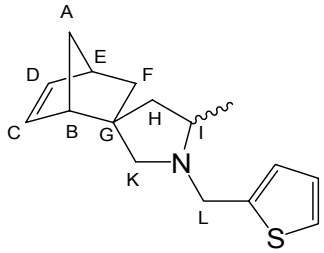


Et_3OBF_4 (1.75 g, 9.21 mmol) was dissolved in 10 mL of CH_2Cl_2. A solution of 2-cyclohexylaminotropone (1.87 g, 9.20 mmol) in 10 mL of CH_2Cl_2 was slowly added. The solution was stirred at rt for 3 h, then it was cooled to 0 °C and cyclohexylamine (20 mL) is solowly added. The soltution is allowed to warm to rt and stirred over night. All volatiles were removed under reduced pressure, the oliy residue was taken up in 10 mL 2 N NaOH and 20 mL of MTBE. The aqueous phase is extracted with MTBE (20 mL). The combined organic phases were washed with brine (20 mL) and dried over $MgSO_4$. Flash Column Chromatographie (SiO_2, Hexanes/MTBE 2:1) gives the product as a yellow oil (2.35 g, 8.26 mmol, 90 %).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) = 1.24-1.47 (m, 10 H); 1.60-1.68 (m, 2 H); 1.72-1.82 (m, 4 H); 1.84-1.95 (m, 4 H); 3.47-3.55 (m, 2 H); 6.05 (t, *J* = 9.2 Hz, 1 H); 6.29 (d, *J* = 11.6 Hz, 2 H); 6.65-6.71 (m, 2 H); 7.88 (bs, 1 H, N**H**).
^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) = 24.8; 26.0; 26.9; 32.9; 53.5; 109.7; 116.9; 132.4; 151.4 (C_q).
IR (ATR): ν (cm^{-1}) = 3189 (w); 3155 (w); 3048 (w); 3019 (w); 2926 (s); 2852 (m); 2665 (w); 1610 (w); 1589 (s); 1537 (s); 1510 (s); 1475 (m); 1464 (s); 1450 (m); 1414 (w); 1385 (m); 1367 (w); 1349 (m); 1339 (w); 1275 (m); 1246 (m); 1226 (w); 1203 (m); 1150 (w); 1111 (w); 1075 (w); 1050 (w); 1025 (w); 965 (m); 928 (w); 887 (w); 881 (w); 860 (w); 846 (w); 743 (w); 702 (m).
MS (EI, 70 eV): m/z (%) = 284 [M^+] (58); 241 (17); 213 (17); 202 (15); 201 (100); 132 (11); 131 (19); 73 (54); 57 (14).
HRMS: $C_{19}H_{28}N_2$ calc.: 284.2252
found: 284.2256
Elemental analysis: calc.: C : 80.23 % H : 9.92 % N : 9.85 %
found: C : 79.92 % H : 9.98 % N : 9.51 %

II. Characterisation of new cyclization products

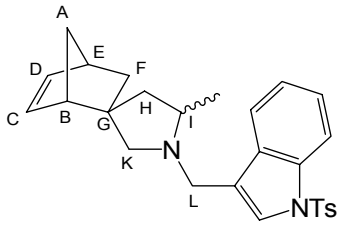
3-Methyl-2-thiophen-2-ylmethyl-2-aza-spiro[4.6]-bicylo[2.2.1]undecane



Diastereomer I:
^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) = 1.17 (d, *J* = 6.0 Hz, 3 H, CH_3); 1.37-1.40 (m, 3 H, H_A, H_F); 1.69 (dd, *J* = 8.8 Hz, *J* = 12.6 Hz, 1 H, H_H); 1.76 (dd, *J* = 3.8 Hz, *J* = 12.1 Hz, 1 $H_{F'}$); 1.96 (dd, *J* = 7.2 Hz, *J* = 12.6 Hz, 1 H, $H_{H'}$); 2.21 (d, *J* = 9.4 Hz, 1 H, H_K); 2.40 (bs, 1 H, H_B); 2.50-2.58 (m, 1 H, H_I); 2.56 (d, *J* = 9.4 Hz, 1 H, $H_{K'}$); 2.78 (bs, 1 H, H_E); 3.55 (d, *J* = 14.1 Hz, 1 H, H_L); 4.07 (dd, *J* = 0.7 Hz, *J* = 14.1 Hz, 1 H, $H_{L'}$); 6.00 (dd, *J* = 2.9 Hz, *J* = 5.4 Hz, 1 H, H_D); 6.07-6.11 (m, 1 H, H_C); 6.85-6.87 (m, 1 H, H_{ar}); 6.93 (m, 1 H, H_{ar}); 7.19 (m, 1 H, H_{ar}).
^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) = 19.1; 43.0; 45.7 (C_q); 47.6; 48.9; 49.7; 51.6; 52.9; 59.3; 68.0; 125.1; 125.3; 134.5; 138.1; 142.9 (C_q).
Diastereomer II:
^{1}H-NMR ($CDCl_3$, 400 MHz): δ = (ppm) 1.03 (d, *J* = 11.6 Hz, 1 H, H_F); 1.17 (d, *J* = 6.0 Hz, 3 H, CH_3); 1.40-1.43 (m, 2 H, H_A); 1.56 (dd, *J* = 8.8 Hz, *J* = 12.4 Hz, 1 H, H_H); 1.66 (dd, *J* = 3.8 Hz, *J* = 11.6 Hz, 1 H, $H_{F'}$); 2.01 (dd, *J* = 7.4 Hz, *J* = 12.4 Hz, 1 H, $H_{H'}$); 2.03 (d, *J* = 9.9 Hz, 1 H, H_K); 2.62 (bs, 1 H, H_B); 2.74 (bs, 1 H, H_E); 2.79 (d, *J* = 9.9 Hz, 1 H, $H_{K'}$); 3.49 (d, *J* = 14.1 Hz, 1 H, H_L); 4.06 (dd, *J* = 0.7 Hz, *J* = 14.1 Hz, 1 H, $H_{L'}$); 6.05 (dd, *J* = 2.8 Hz, *J* = 5.1 Hz, 1 H, H_D); 6.07-6.11 (m, 1 H, H_C); 6.85-6.87 (m, 1 H, H_{ar}); 6.93 (m, 1 H, H_{ar}); 7.19 (m, 1 H, H_{ar}).
^{13}C-NMR ($CDCl_3$, 100 MHz): δ = (ppm) 19.3; 42.7; 44.6; 46.0 (C_q); 48.3; 50.1; 51.5; 52.7; 58.6; 66.4; 124.4; 126.3; 135.2; 137.8; 142.5 (C_q).

IR (ATR): ν (cm^{-1}) = 3138 (w); 3104 (w); 3059 (w); 2960 (bs); 2937 (s); 2866 (m); 2781 (m); 2675 (w); 2583 (w); 1716 (w); 1694 (w); 1676 (w); 1589 (w); 1571 (w); 1538 (w); 1511 (w); 1458 (w); 1444 (w); 1375 (m); 1356 (m); 1332 (m); 1310 (m); 1273 (m); 1263 (m); 1211 (m); 1169 (m); 1142 (m); 1096 (m); 1077 (m); 1038 (w); 1025 (w); 971 (w); 954 (w); 938 (w); 907 (w); 853 (m); 823 (m); 801 (m); 713 (s); 695 (s).
MS (EI, 70 eV): m/z (%) = 259 [M^+] (13); 244 (38); 193 (10); 192 (20); 97 (100); 66 (11).
HRMS: $C_{16}H_{21}NS$ calc.: 259.1394
found: 259.1399

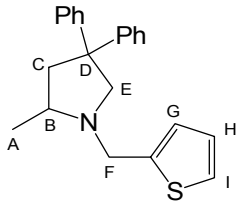
3-Methyl-2-)-[1-toluene-4-sulfonyl)-1*H*-indol -2-ylmethyl-2-aza-spiro[4.6]-bicylo[2.2.1]undecane



Diastereomer I:
^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) = 1.25 (dd, *J* = 2.4 Hz, *J* = 11.8 Hz, H_F); 1.20 (d, *J* = 6.0 Hz, 3 H, CH_3); 1.35-1.42 (m, X H, H_A); 1.64 (dd, *J* = 4.2 Hz, *J* = 12.7 Hz, H_H); 1.71 (dd, *J* = 3.7 Hz, *J* = 11.8Hz, 1 H, $H_{F'}$); 1.97 (dd, *J* = 7. 5 Hz, *J* = 12.7 Hz, 1 H, $H_{H'}$); 2.07 (d, *J* = 9.3 Hz, 1 H, H_K); 2.32 (s, 3 H, CH_3 of Ts); 2.37 (d, *J* = 9.3 Hz, 1 H, $H_{K'}$); 2.37 (bs, 1 H, H_B); 2.47-2.55 (m, 1 H, H_I); 2.72 (bs, 1 H, H_E); 3.25 (d, *J* = 13.9 Hz, 1 H, H_L); 3.99 (dd, *J* = 2.6 Hz, *J* = 13.8 Hz, 1 H, $H_{L'}$); 5.78 (dd, *J* = 3.0 Hz, *J* = 5.6 Hz, 1 H, H_D); 6.03 (dd, *J* = 3.0 Hz, *J* = 5.8 Hz, 1 H, H_C); 7.15-7.23 (m, 3 H, H_{ar}); 7.25-7.32 (m, 1 H, H_{ar}); 7.40 (s, 1 H, H_{ar}); 7.61-7.75 (m, 3 H, H_{ar}); 7.95 (dd, *J* = 3.8 Hz, *J* = 8.3 Hz, 1 H, H_{ar}).
^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) = 19.4; 21.5; 27.0; 42.6; 45.8 (C_q); 48.2; 48.8; 50.1; 52.9; 60.2; 66.9; 113.6; 120.4; 121.2 (C_q); 123.0; 124.0; 124.5 (C_q); 126.7; 129.7; 131.0 (C_q); 135.1; 135.3 (C_q); 135.5 (C_q); 137.7; 144.6 (C_q).
Diastereomer II:
^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 0.98 (dd, *J* = 2.0 Hz, *J* = 11.6 Hz, 1 H, H_F); 1.19 (d, *J* = 5.8 Hz, 3 H, CH_3); 1.35-1.42 (m, 2 H, H_A); 1.54 (dd, *J* = 8.8 Hz, *J* = 12.3 Hz, 1 H, H_H); 1.66 (dd, *J* = 3.6 Hz, *J* = 11.6 Hz, 1 H, $H_{F'}$); 1.87 (d, *J* = 9.9 Hz, 1 H, H_K); 2.03 (dd, *J* = 7.7 Hz, *J* = 12.6 Hz, 1 H, $H_{H'}$); 2.32 (s, 3 H, CH_3 of Ts); 2.47-2.55 (m, 1 H, H_I); 2.56 (bs, 1 H, H_B); 2.57 (d, *J* = 9.9 Hz, 1 H, $H_{K'}$); 2.75 (bs, 1 H, H_E); 3.28 (d, *J* = 13.9 Hz, 1 H, H_L); 4.00 (dd, *J* = 2.8 Hz, *J* = 13.9 Hz, 1 H, $H_{L'}$); 5.93 (dd, *J* = 3.0 Hz, *J* = 5.8 Hz, 1 H, H_D); 6.04 (dd, *J* = 3.0 Hz, *J* = 6.1 Hz, 1 H, H_C); 7.15-7.23 (m, 3 H, H_{ar}); 7.25-7.32 (m, 1 H, H_{ar}); 7.40 (s, 1 H, H_{ar}); 7.61-7.75 (m, 3 H, H_{ar}); 7.95 (dd, *J* = 3.8 Hz, *J* = 8.3 Hz, 1 H, H_{ar}).
^{13}C-NMR ($CDCl_3$, 100 MHz): δ 19.8; 21.5; 27.0; 42.9; 44.1; 46.1 (C_q); 47.5; 48.4; 49.8; 52.6; 59.1; 59.6; 65.1; 113.6; 121.4 (C_q); 123.0; 124.2; 124.6; 126.7; 129.7; 131.0 (C_q); 135.3 (C_q); 135.4 (C_q); 137.9; 144.6 (C_q).
IR (ATR): ν (cm^{-1}) = 3114 (w); 3056 (w); 2960 (m); 2936 (w); 2866 (w); 2786 (w); 1598 (w); 1570 (w); 1494 (w); 1446 (m); 1399 (w); 1372 (m); 1322 (w); 1306 (w); 1293 (w); 1276 (w); 1246 (w); 1206 (w); 1187 (m); 1174 (s); 1121 (m); 1106 (m); 1019 (w); 976 (m); 939 (w); 907 (w); 812 (m); 798 (w); 773 (w); 746 (m); 715 (w); 704 (w); 673 (m).
MS (EI, 70 eV): m/z (%) = 446 [M^+] [14); 285 (33); 284 (100); 225 (10); 162 (18); 155 (29); 130 (19); 129 (18); 91 (54); 66 (11).
HRMS: $C_{27}H_{30}N_2O_2S$ calc.: 446.2028
found: 446.2021
Elemental analysis: calc.: C : 72.61 % H : 6.77 % N : 6.27 %

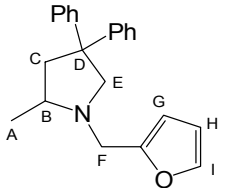
found: C : 72.94 % H : 7.01 % N : 5.97 %

2-Methyl-4,4-diphenyl-1-thiophen-2-ylmethyl-pyrrolidine



^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) = 1.17 (d, *J* = 5.9 Hz, 3 H, Me); 2.16 (m, 1 H, H_C); 2.80-2.95 (m, 3 H, H_B, $H_{C'}$, H_E); 3.61 (d, *J* = 14.0 Hz, 1 H, H_F); 3.77 (d, *J* = 9.8 Hz, 1 H, $H_{E'}$); 4.17 (dd, *J* = 0.1 Hz, *J* = 14.0 Hz, 1 H, $H_{F'}$); 6.91-6.96 (m, 2 H, H_G, H_A); 7.09-7.16 (m, 1 H, H_I); 7.16-7.31 (m, 10 H, H_{ar}).
^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) = 19.4; 48.0; 52.2; 52.4 (C_q); 59.3; 66.4; 124.7; 124.7; 124.9; 125.4; 125.8; 126.3; 127.3; 127.4; 127.9; 128.2; 143.6 (C_q); 148.5 (C_q); 150.5 (C_q).
IR (ATR): ν (cm^{-1}) = 3104 (w); 3083 (w); 3057 (w); 3026 (w); 2962 (m); 2925 (w); 2868 (w); 2789 (bm); 2738 (w); 2681 (w); 2581 (w); 1946 (w); 1871 (w); 1802 (w); 1736 (w); 1597 (w); 1581 (w); 1539 (w); 1493 (m); 1476 (w); 1445 (m); 1376 (m); 1355 (w); 1348 (w); 1335 (w); 1313 (w); 1264 (w); 1233 (w); 1212 (w); 1189 (w); 1170 (w); 1155 (w); 1133 (w); 1106 (w); 1076 (w); 1063 (w); 1035 (m); 1016 (w); 1002 (w); 951 (w); 908 (w); 852 (w); 829 (w); 803 (w); 773 (w); 761 (m); 724 (w); 698 (s); 657 (w).
MS (EI, 70 eV): m/z (%) = 333 [M^+] (25); 318 (29); 179 (12); 178 (14); 165 (19); 153 (40); 115 (13); 111 (22); 97 (94); 91 (14); 56 (100).
HRMS: $C_{22}H_{23}NS$ calc.: 333.1551
found: 333.1552
Elemental analysis: calc.: C : 79.23 % H : 6.95 % N : 4.20 %
found: C : 79.15 % H : 7.10 % N : 4.54 %

1-Furan-2-ylmethyl-2-methyl-4,4-diphenyl-pyrrolidine

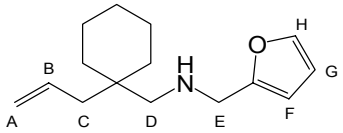


^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) = 1.15 (d, *J* = 5.9 Hz, 3 H, H_A); 2.20 (dd, *J* = 7.6 Hz, *J* = 12.1 Hz, 1 H, H_C); 2.76-2.90 (m, 1 H, H_B); 2.86 (d, *J* = 12.1 Hz, 1 H, $H_{C'}$); 3.00 (d, *J* = 10.0 Hz, 1 H, H_E); 3.50 (d, *J* = 14.4 Hz, 1 H, H_F); 3.75 (d, *J* = 10.0 Hz, 1 H, $H_{E'}$); 3.96 (d, *J* = 14.4 Hz, 1 H, $H_{F'}$); 6.19 (d, *J* = 3.1 Hz, 1 H, H_G); 6.33 (dd, *J* = 1.8 Hz, *J* = 3.1 Hz, 1 H, H_H); 7.09-7.29 (m, 10 H, H_{ar}); 7.39 (dd, *J* = 0.7 Hz, *J* = 1.8 Hz, H_I).
^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) = 19.2; 47.9; 49.3; 52.5 (C_q); 58.8; 66.1; 107.8; 110.0; 125.5; 125.8; 127.2; 127.4; 128.0; 128.2; 141.8; 148.7 (C_q); 150.3 (C_q); 153.0 (C_q).
IR (ATR): ν (cm^{-1}) = 3084 (w); 3057 (w); 3025 (w); 2963 (m); 2925 (w); 2870 (w); 2797 (m); 1947 (w); 1872 (w); 1803 (w); 1741 (w); 1598 (m); 1493 (m); 1446 (m); 1376 (m); 1356 (m); 1336 (w); 1315 (w); 1268 (w); 1223 (w); 1188 (w); 1148 (m); 1107 (w); 1075 (w); 1033 (m); 1010 (m); 938 (w); 917 (w); 885 (w), 810 (w); 761 (m); 734 (m); 700 (s).

MS (EI, 70 eV): m/z (%) = 317 [M^+] (28); 302 (35); 165 (10); 137 (55); 81 (65); 56 (100).
HRMS: $C_{22}H_{23}NO$ calc.: 317.1780
found: 317.1780

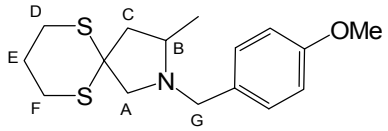
Elemental analysis: calc.: C : 83.24 % H : 7.30 % N : 4.41 %
found: C : 83.39 % H : 6.91 % N : 4.50 %
melting point: 69 °C

2-Furan-2-ylmethyl-3-methyl-2-aza-spiro[4.5]decanamine



^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) = 1.27-1.46 (m, 10 H, H_{Ring}); 2.09 (td, *J* = 1.0 Hz, *J* = 7.5 Hz, 2 H, H_C); 2.40 (s, 2 H, H_D); 3.75 (s, 2 H, H_E); 4.97-4.99 (m, 1 H, H_A); 5.00-5.03 (m, 1 H, $H_{A'}$); 5.70-5.81 (m, 1 H, H_B); 6.15 (dd, *J* = 0.4 Hz, *J* = 3.1 Hz, 1 H, H_F); 6.30 (dd, *J* = 1.8 Hz, *J* = 3.1 Hz, 1 H, H_G); 7.35 (dd, *J* = 0.7 Hz, *J* = 1.8 Hz, 1 H, H_H).
^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) = 21.5; 26.4; 34.0; 35.5 (C_q); 40.6; 47.1; 55.5; 106.6; 110.0; 116.7; 135.1; 141.5; 154.6 (C_q).
IR (ATR): ν (cm^{-1}) = 3341 (w); 3114 (w); 3073 (w); 3001 (w); 2974 (w); 2924 (vs); 2850 (m); 2672 (w); 1828 (w); 1713 (w); 1637 (m); 1598 (w); 1548 (w); 1505 (m); 1464 (m); 1451 (m); 1437 (m); 1414 (w); 1335 (m); 1298 (w); 1273 (w); 1241 (w); 1217 (w); 1186 (w); 1148 (m); 1108 (m); 1078 (w); 1008 (m), 913 (s); 884 (m); 848 (w); 804 (m); 775 (m); 731 (s); 699 (m).
MS (EI, 70 eV): m/z (%) = 234 [M^++H] (47); 233 [M^+] (26); 232 (5); 138 (7); 136 (7); 110 (41); 82 (7); 81 (100); 67 (5); 53 (15).
HRMS: $C_{15}H_{24}NO$ [M^+-H] calc.: 234.1858
found: 234.1862
Elemental analysis: calc.: C : 77.21 % H : 9.93 % N : 6.00 %
found: C : 76.77 % H : 9.77 % N : 5.93 %

2-(4-Methoxybenzyl)-3-methyl-6,10-dithia-2-aza-spiro[4.5]decane

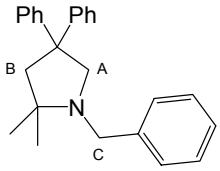


^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) = 1.20 (d, *J* = 6.0 Hz, 3 H, CH_3); 1.93 (dd, *J* = 9.3 Hz, *J* = 13.3 Hz, H_C); 1.95-2.00 (m, 2 H, H_E); 2.46 (dd, *J* = 6.7 Hz, *J* = 13.3 Hz, 1 H, $H_{C'}$); 2.62 (d, *J* = 10.6 Hz, 1 H, H_A); 2.75-2.90 (m, 5 H, H_B, H_D, H_F); 3.24 (d, *J* = 13.2 Hz, 1 H, H_G); 3.39 (d, *J* = 10.6 Hz, 1 H, $H_{A'}$); 3.80 (s, 3 H, OCH_3); 4.00 (d, *J* = 13.2 Hz, 1 H, $H_{G'}$); 6.85 (d, *J* = 8.6 Hz, 2 H, H_{ar}); 7.24 (d, *J* = 8.6 Hz, 2 H, H_{ar}).
^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) = 18.5; 25.3; 28.7; 29.1; 50.5; 50.7 (C_q); 55.3; 56.4; 58.4; 68.4; 113.6; 129.7; 130.9 (C_q); 158.6 (C_q).
IR (ATR): ν (cm^{-1}) = 3061 (w); 3031 (w); 2995 (w); 2959 (m); 2930 (m); 2901 (m); 2832 (m); 2800 (m); 2726 (w); 1884 (w); 1726 (w); 1611 (m); 1585 (w); 1511 (s); 1463 (m); 1440 (m); 1422 (m); 1375 (m); 1356 (w); 1344 (w); 1301 (m); 1275 (m); 1247 (s); 1170 (m); 1145 (w); 1102 (m); 1035 (m); 997 (w); 952 (w); 907 (w); 867 (w); 849 (w); 822 (m); 804 (m); 764 (w); 750 (w); 714 (w); 673 (w).
MS (EI, 70 eV): m/z (%) = 309 [M^+] (11); 177 (16); 122 (7); 121 (100); 56 (29).
HRMS: $C_{16}H_{23}NOS_2$ calc.: 309.1221

found: 309.1222

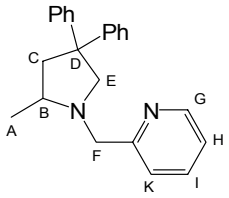
Elemental analysis: calc.: C : 62.09 % H : 7.49 % N : 7.49 %
found: C : 61.80 % H : 4.61 % N : 7.45 %

1-Benzyl-2,2-dimethyl-4,4-diphenyl-pyrrolidine



^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) = 1.13 (s, 6 H, 2 × CH_3); 2.61 (s, 2 H, H_B); 3.28 (s, 2 H, H_A); 3.61 (s, 2 H, H_C); 7.09-7.39 (m, 15 H, H_{ar}).
^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) = 25.1; 51.6 (C_q); 52.4; 54.4; 60.5 (C_q); 63.1; 125.5; 126.7; 127.2; 127.8; 128.1; 128.5; 140.9 (C_q); 149.7 (C_q).
IR (ATR): ν (cm^{-1}) = 3085 (w); 3059 (m); 3026 (m); 2959 (m); 2924 (m); 2868 (w); 2795 (m); 2699 (w); 1946 (w); 1872 (w); 1805 8w); 1714 (w); 1599 (m); 1494 (m); 1453 (m); 1446 (m); 1380 (m); 1363 (m); 1334 (w); 1311 (w); 1291 (w); 1264 (w); 1222 (m); 1208 (w); 1191 (w); 1154 (m); 1123 (w); 1070 (w); 1050 (m); 1028 (m); 1002 (w); 962 (w); 952 (w); 907 (w); 865 (w); 826 (w); 775 (m); 760 (m); 747 (m); 730 (m); 697 (s); 654 (w).
MS (EI, 70 eV): m/z (%) = 341 [M^+] (4); 327 (22); 326 (100); 207 (6); 161 (6); 129 (5); 92 (5); 91 (75); 70 (38); 65 (5); 55 (12).
HRMS: $C_{25}H_{27}N$ calc.: 341.2143
found: 341.2150
Elemental analysis: calc.: C : 87.93 % H : 7.97 % N : 4.10 %
found: C : 88.28 % H : 8.01 % N : 4.04 %

2-Methyl-4,4-diphenyl-1-pyrridin-2-ylmethyl-pyrrolidine



^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) = 1.18 (d, *J* = 5.8 Hz, 3 H, Me); 2.25-2.31 (m, 1 H, H_C); 2.85-2.96 (m, 2 H, H_B,$H_{C'}$); 3.00 (d, *J* = 9.9 Hz, 1 H, H_E); 3.58 (d, *J* = 14.4 Hz, 1 H, H_F); 3.67 (d, *J* = 9.9 Hz, 1 H, $H_{E'}$); 4.17 (d, *J* = 14.4 Hz, 1 H, $H_{F'}$); 7.10-7.29 (m, 11 H, H_{ar}); 7.44 (d, *J* = 7.6 Hz, *J* = 7.6 Hz, 1 H, H_K); 7.63 (td, *J* = 1.8 Hz, *J* = 7.6 Hz, 1 H, H_I); 8.54 (qd, *J* = 0.9 Hz, *J* = 4.9 Hz, 1 H, H_G).
^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) = 19.5; 47.8; 52.8 (C_q); 59.6; 59.7; 66.5; 121.8; 122.8; 125.5; 125.8; 127.2; 127.9; 128.2; 136.4; 148.5 (C_q); 148.9; 150.4 (C_q); 160.4 (C_q).
IR (ATR): ν (cm^{-1}) = 3084 (w); 3058 (w); 3027 (w); 3021 (w); 2959 (m); 29214 (w); 2868 (w); 2803 (m); 2792 8M); 2733 (w); 2684 (w); 1951 (w); 1878 (w); 1812 (w); 1664 (w); 1588 (m); 1569 (m); 1491 (m); 1476 (m); 1445 (m); 1432 (m); 1375 (m); 1358 (w); 1355 (w); 1319 (w); 1287 (w); 1251 (w); 1230 (w); 1193 (w); 1160 (w); 1147 (w); 1134 (w); 1113 (w);

1104 (w); 1088 (w); 1066 (w); 1046 (w); 1038 (w); 1032 (w); 993 (w); 966 (w); 950 (w); 907 (w); 836 (w); 804 (w); 774 (m); 768 (m); 760 (s); 730 (w); 703 (s); 659 (w).

MS (EI, 70 eV): m/z (%) = 329 (54) [M^+-H]; 328 (1) [M^+]; 237 (19); 236 (100); 178 (5); 165 (5); 93 (43); 92 (6); 56 (10).

HRMS: $C_{22}H_{25}N_2$ [M^+-H] calc: 329.2018
found: 329.2020

Elemental analysis: calc.: C : 84.11 % H : 7.37 % N : 8.53 %
found: C : 83.65 % H : 7.47 % N : 8.28 %

melting point: 93 °C

III. References

1 C. F. Bender and R. A. Widenhoefer, *J. Am. Chem. Soc.,* 2005, **127**, 1070.
2 W. von E. Doering and C. Hiskey, *J. Am. Chem. Soc.,* 1952, 74, 5688.