Supporting Information

Isolation of the Key Intermediates of Base-Promoted Borylene-Carbonyl Coupling Reactions

Holger Braunschweig, Thomas Kramer, Krzysztof Radacki, Rong Shang, Eva Siedler and Christine Werner*

Institut für Anorganische Chemie

Julius-Maximilians-Universität Würzburg

Am Hubland, 97074 Würzburg (Germany)

Fax: (+49)931-31-84623

E-Mail: h.braunschweig@uni-wuerzburg.de

Experimental Section

General considerations: All syntheses were carried out under an argon atmosphere with standard Schlenk and glovebox techniques unless otherwise stated. The complex [(η^5-C_5H_5)(OC)$_2$MnB*t*Bu] (**1**) was prepared according to published procedures.[1-2] Pentane, hexane and benzene were dried by distillation over Na/K alloy under argon and stored over molecular sieves. Toluene and C_6D_6 were dried over Na, distilled under argon and stored over molecular sieves. Elemental analyses were obtained from an Elementar Vario MICRO cube instrument. NMR spectra were recorded on a Bruker Avance 400 (^{1}H: 400.1 MHz, ^{11}B: 128.3 MHz, ^{13}C{^{1}H}: 100.6 MHz) and/or a Bruker Avance 500 FT-NMR spectrometer (^{1}H: 500 MHz, ^{11}B: 160 MHz, ^{13}C{^{1}H}: 126 MHz). Chemical shifts are given in ppm, and are referenced against external $SiMe_4$ (^{1}H, ^{13}C{^{1}H}), $BF_3{\cdot}Et_2O$ (^{11}B) and 85% H_3PO_4 (^{31}P).

Synthesis of [(η^5-C_5H_5)(OC)Mn{κ^2-*C,C′*-C(O)B(*t*Bu)(PMe_3)C(O)}] (3)

To a hexane solution of the borylene complex [(η^5-C_5H_5)(OC)$_2$MnB*t*Bu] (**1**) (10.0 mg, 0.041 mmol) was added two drops of trimethylphosphine (2–3 eqv.) via a syringe. The resulting solution was connected to CO atmosphere (1 bar) at room temperature. An instantaneous reaction occurred, from which a red orange solid precipitated from the reaction mixture. The pale orange supernatant was removed via a cannula and the resulting red solid was washed with pentane (2×2 mL). Further drying of the red solid in *vacuum* lead to an analytically pure sample of the title compound (12 mg, 84%). IR (solid): 1892 (s), 1682 (br, s) (νCO) cm^{-1}. ^{1}H NMR (C_6D_6): δH 4.49 [s, (η^5-C_5H_5)], 1.02 [s, C(CH_3)$_3$], 0.80 (d, 2J$_{HP}$ = 8). ^{13}C{^{1}H} NMR (C_6D_6): δC 265.6 (s, br, bridging *C*O), 232.9 (s, sh, terminal *C*O), 88.53 [s, br, (η^5-C_5H_5)], 31.88 (d, ^{4}J$_{CP}$ = 5), 20.79 (m, br, BC(CH_3)$_3$), 12.46 (d, ^{1}JCP = 39). ^{11}B NMR (C_6D_6): δB −52.5 (sh, d, ^{1}J$_{BP}$ = 105). ^{31}P{^{1}H} NMR (C_6D_6): δP −3.30 (br, m). ^{1}H NMR (d_8-Tol): δH 4.44 [s, (η^5-C_5H_5)], 0.95 (s, C(CH_3)$_3$), 0.81 (d, ^{2}J$_{HP}$ = 12). ^{13}C{^{1}H} NMR (d_8-Tol): δC 265.9 (s, br, CO), 88.46 (s, br, Cp), 31.83 (d, ^{4}J$_{CP}$ = 5), 12.44 (d, ^{1}J$_{CP}$ = 39).

^{1}H NMR (500 MHz, −30 °C, d_8-Tol): δH 4.42 [s, (η^5-C_5H_5)], 0.95 (s, C(CH_3)$_3$), 0.72 (d, ^{2}J$_{HP}$ = 12, P(CH_3)$_3$). ^{13}C{^{1}H} NMR (125.8 MHz, −30 °C, d^8-Tol): δC 265.5 (s, br, μ-CO), 232.9 (s, CO), 88.48 [s, (η^5-C_5H_5)], 31.68 (d, ^{4}J$_{CP}$ = 5), 11.90 (d, ^{1}J$_{CP}$ = 39). ^{11}B NMR (160.5 MHz, −30 °C, d_8-Tol): δB −54.0 (sh, d, ^{1}J$_{BP}$ = 105). ^{31}P{^{1}H} NMR (202.5 MHz, −30 °C, d_8-Tol): δP −3.16 (d, ^{1}J$_{BP}$ = 105). Anal. Found: C, 51.83; H, 6.81. Calcd. data for $C_{15}H_{23}O_3MnBP$: C, 51.76; H, 6.66.

Synthesis of [(η^5-C_5H_5)(OC)$_2$MnB(*t*Bu)(DMAP)] (4) and detection of [(η^5-C_5H_5)(OC)$_2$Mn-B(*i*Bu)(DMAP)] (4a)

In a glove box charged with Ar atmosphere, a solid mixture of the borylene complex [(η^5-C_5H_5)(OC)$_2$Mn=B(*t*Bu)] (**1**) (10 mg, 0.041 mmol) and dimethylaminopyridine (DMAP, 5 mg, 0.041 mmol) was charged into a small Schlenk tube, to which hexane (4 mL) was added. The titled compound formed immediately as a glittering gold precipitate, which settled at the bottom of the Schlenk tube. The clear supernatant was removed and the product was obtained in quantitative yield after being washed with n-pentane (2 × 3 mL). At room temperature, the NMR spectra showed very broad signals for the DMAP moiety. Low temperature NMR (at −30 °C) experiments were conducted for characterization. IR (solid): 1874, 1795 (s) (νCO) cm^{-1}. ^{1}H NMR (500 MHz, −30 °C, d_8-Tol): δH 7.43, 5.44 (4 H, 2 × CH), 4.48 [5 H, (η^5-C_5H_5)], 1.84 [6 H, N(CH_3)$_2$], 1.35 [9 H, BC(CH_3)$_3$]. ^{13}C{^{1}H} NMR (125.8 MHz, −30 °C, d_8-Tol): δC 234.2 (s), 104.6 [s, (Me_2N(CH)$_2$], 83.73 [s, (η^5-C_5H_5)], 38.12 [s, (CH_3)$_2$N], 35.43 [BC(*C*H$_3$)$_3$], 29.11 [B*C*(CH_3)$_3$]. ^{11}B NMR (C_6D_6): δB 122.2 (s, br). The carbon signals at the *ortho*-

positions pyridine were not observed due to the overlapping solvent signals. Anal. Found: C, 58.83; H, 6.71; N, 7.70. Calcd. data for $C_{18}H_{27}O_2N_2BMn$: C, 59.05; H, 6.61; N, 7.65.

Crystallization of 4: in a small thin glass vial, DMAP was dissolved in 1mL of benzene and layered with a couple of drops of toluene. To this, slowly a hexane solution of **1** was carefully transferred to the vial as the top layer. The vial containing the reaction mixture was left in the glove box at room temperature over night. Needle-shaped yellow-brown crystals formed at where the toluene layer was. When a sample is left at room temperature for a few weeks, the isomer [(η^5-C_5H_5)$(OC)_2$MnB(*i*Bu)(DMAP)] (**4a**) was observed in the crystal lattice (around 5%) according to refinement. See details in the X-ray crystallography section. No analytically pure sample of **4a** was able to be isolated.

Synthesis of [(η^5-C_5H_5)$(OC)_2$MnB(*t*Bu)(Lutidin)] (5)

3,5-Lutidine (10.7 mg, 0.10 mmol) was added to a solution of 20 mg (0.082 mmol) [(η^5-C_5H_5)$(CO)_2$MnB*t*Bu] in 2 mL hexane. Immediately a red precipitate formed. The solvent was decanted from the precipitate. The title compound was isolated as a red solid in 79% yield (22 mg). Red single crystals of **5** suitable for X−ray diffraction were obtained by recrystallization from toluene at –30 °C.

IR (solid): 1876 (s), 1809 (s) (νCO) cm^{-1}. NMR: ^1H (500.1 MHz, d_8-Tol, −40 °C): δH 7.54 (br, 2H, o-C*H* of NC_7H_9), 6.03 (br, 1H, p-C*H* of NC_7H_9), 4.28 (s, 5H, C_5H_5), 1.48 (br, 6H, C*H*$_3$ of NC_7H_9), 1.22 (s, 9H, *t*Bu); $^{11}B\{^1H\}$ (160.5 MHz, d_8-Toluol, −40 °C) δB = 116.1 (br); $^{13}C\{^1H\}$ (125.8 MHz, d_8-Toluol, −40 °C): δC = 234.0 (s, CO), 133.8 (s, *C*H of NC_7H_9), 84.2 (s, C_5H_5), 28.4 (s, C(*C*H$_3$)$_3$), 18.1 (CH_3 of NC_7H_9). Only one aromatic carbon was observed from the $^{13}C\{^1H\}$ spectrum due to the overlapping solvent signals. At room temperature, due to the lability of the lutidin ligand, average signals of the starting material **1** and the final product are observed. Anal. Found: C 61.02, H 6.75, N 4.08. Calcd. data for $C_{18}H_{23}BMnNO_2$: C 61.57, H 6.60, N 3.99.

Synthesis of [(η^5-C_5H_5)$(OC)_2$MnB(*t*Bu)(IMe)] (6)

One equivalent of IMe (:C[N(Me)CH]$_2$, 39.4 mg, 0.041 mmol) was added to a solution of 100.0 mg (0.041 mmol) [(η^5-C_5H_5)$(CO)_2$MnB*t*Bu] in 0.6 mL benzene. Slow evaporation of the solvent yielded the title compound [(η^5-C_5H_5)$(OC)_2$MnB(*t*Bu)(IMe)] (**6**) as yellow crystals in 88% yield (119.6 mg).

IR (CH_2Cl_2): 1890 (s), 1820 (s) (νCO) cm^{-1}; (solid): 1884 (s), 1805(s) (νCO) cm^{-1}. ^1H NMR (400.1 MHz, C_6D_6): δH 5.60 (s, 2H, NC*H*C*H*N), 4.33 (s, 5H, C_5H_5), 2.66 (s, 6H, N-C*H*$_3$), 1.33 (s, 9H, *t*Bu); $^{11}B\{^1H\}$ NMR (C_6D_6, 128.4 MHz) δB 129.8 (br); $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6 MHz): δC 235.0 (s, CO), 119.8 (s, N*C*H*C*HN), 83.6 (s, C_5H_5), 35.5 (s, N-*C*H$_3$), 30.4 (s, C(*C*H$_3$)$_3$). Anal. Found: C 56.71, H 6.28, N 8.08. Calcd. data for $C_{16}H_{22}BMnN_2O_2$: C 56.50, H 6.53, N 8.23.

Synthesis of [(η^5-C_5H_5)$(OC)_2$MnB(*i*Bu)(IMe)] (6a)

A sample of **6** (30.0 mg, 0.088 mmol) was dissolved in 1 mL of benzene. The solution was heated at 60 °C for 4h. Slow evaporation of the solvent yielded [(η^5-C_5H_5)$(CO)_2$MnB(*i*Bu)(IMe)] as orange crystals in 93% yield (27.9 mg) suitable for X−ray diffraction analysis.

IR (CH_2Cl_2): 1909 (s), 1828 (s) (νCO) cm^{-1}. (solid): 1872 (s), 1801(s) (νCO) cm^{-1}. ^1H NMR (C_6D_6, 400.1 MHz): δH 5.76 (s, 2H, NC*H*C*H*N), 4.43 (s, 5H, C_5H_5), 2.79 (s, 6H, N-C*H*$_3$), 2.37 (d, 2H, $^3J_{HH}$ = 6.6 Hz, BC*H*$_2$), 1.50 (m, 1H, C*H*(CH$_3$)$_2$), 0.99 [d, 6H, $^3J_{HH}$ = 6.5 Hz, CH(C*H*$_3$)$_2$]; $^{11}B\{^1H\}$ NMR (C_6D_6, 128.4 MHz) δB 125.3 (br); $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): δC 233.8 (s, CO), 120.1 (s, N*C*H*C*HN), 83.9 (s, C_5H_5), 50.3 (br, B*C*H$_2$), 34.8 (s, N-*C*H$_3$), 28.3 (s, *C*H(CH$_3$)$_2$), 26.4 (s, C(*C*H$_3$)$_2$). Anal. Found: C, 55.94; H, 6.63; N, 8.32. Calcd. data for $C_{16}H_{22}BMnN_2O_2$: C, 56.50; H, 6.53; N 8.23.

Synthesis of [(η^5-C_5H_5)(OC)Mn{κ^2-*C,C′*-C(O)B(*t*Bu)(DMAP)C(O)}] (7)

One equivalent of **1** (10.0 mg, 0.041 mmol) and DMAP (5 mg, 0.041 mmol) was dissolved and transferred to a *J-Young*-NMR tube. After 2 hours at room temperature, the reaction mixture was connected to an atmosphere of CO. After brief shaking, the yellow orange color of the solution turned to intense red and red crystals precipitated out of the solution. The supernatant was decanted and the crystals of **7** were washed with benzene (3 x 0.7 mL) and pentane (1 mL) and then dried under vacuum (82% yield). Complex **7** is sparingly soluble in hexane and pentane, moderately soluble in benzene and toluene, and soluble in dichloromethane. At room temperature, it decomposes readily in benzene and toluene, and very quickly in CH_2Cl_2.

IR (C_6H_6): 1907 (s), 1668, 1637, (s), (νCO) cm^{-1}. ^{1}H NMR (500 MHz, −50 °C, CD_2Cl_2): δH 8.25, 6.48 (d, $^3J_{HH}$= 6 Hz, 4 H, 2 × CH), 4.34 [5 H, (η^5-C_5H_5)], 3.08 [6 H, N(CH_3)$_2$], 0.65 [9 H, BC(CH_3)$_3$]. ^{13}C{^{1}H} NMR (125.8 MHz, −50 °C, CD_2Cl_2): δC 271.0 (s, bridging *C*O), 228.8 (s, terminal *C*O), 144.8 [s, N(*C*H)$_2$(CH)$_2$NMe$_2$], 106.7 [s, (Me$_2$N(CH)$_2$], 87.66 [s, (η^5-C_5H_5)], 39.81 [s, (CH_3)$_2$N], 26.82 [BC(CH_3)$_3$], 22.10 [BC(CH_3)$_3$]. ^{11}B NMR (160.462 MHz, −50 °C, CD_2Cl_2): δB –49.44 (s).

Synthesis of [(η^5-C_5H_5)(OC)Mn{κ^2-*C,C′*-C(O)B(*t*Bu)(IMe)C(O)}] (8)

A sample of **6** (20 mg, 0.059 mmol) was dissolved in C_6D_6 in a *J-Young*-NMR tube and the solution was frozen using a –50 °C cooling bath. After replacing the argon atmosphere in the tube by a CO atmosphere, the reaction mixture was allowed to warm to room temperature. Slow evaporation of the solvent yielded the title compound **7** as red crystals suitable for X–ray diffraction in 58% yield (12.6 mg).

IR (C_6H_6): 1913 (s), 1684 (s) (νCO) cm^{-1}. ^{1}H NMR (400.1 MHz, C_6D_6): δH 5.37 (s, 2H, NC*H*C*H*N), 4.01 (s, 5H, C_5H_5), 3.37 (s, 6H, N-C*H*$_3$), 1.17 (s, 9H, *t*Bu). ^{11}B{^{1}H} NMR (128.4 MHz, C_6D_6) δB −40.1 (s). ^{1}H NMR ($CDCl_3$, 400.1 MHz): δH 6.92 (s, 2H, NC*H*C*H*N), 4.15 (s, 5H, C_5H_5), 4.08 (s, 6H, N-C*H*$_3$), 0.84 (s, 9H, *t*Bu); ^{11}B{^{1}H} NMR (128.4 MHz, $CDCl_3$,) δB −40.1 (br); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δC 122.5 (s, N*C*H*C*HN), 85.4 (s, C_5H_5), 38.5 (s, N-*C*H$_3$), 31.4 (s, *C*(CH_3)$_3$), 30.3 (s, C(*C*H$_3$)$_3$). Anal. Found: C, 55.49; H, 6.02; N, 7.69. Calcd. data for $C_{17}H_{22}BMnN_2O_3$: C, 55.47; H, 6.02; N, 7.61. Due to the low concentration of the sample, no carbonyl signals were found in the ^{13}C{^{1}H} NMR spectrum.

Synthesis of B(H)(*t*Bu){κ^2-C^a,C^b-$C^aH_2C(CH_3)_2\overline{\mathrm{N(CHCHN(}t\mathrm{Bu)C}^b}$ } (10)

Two equivalents of I*t*Bu (:C[N(*t*Bu)CH]$_2$, 74.0 mg, 0.41 mmol) were added to a solution of **1** (50.0 mg, 0.20 mmol) in 5 ml toluene. After stirring for 1h, the yellow solution was then freed of all volatiles under vacuum. The remained solid provided a mixture of [(η^5-C_5H_5)(CO)$_2$Mn(I*t*Bu)] (**9**) and the title compound **10**. Compound **10** was separated by sublimation (60 °C, 1×10^{-3} mbar). The sublimed solid was dissolved in 1 mL of benzene. Slow evaporation of the solvent yielded colorless crystals suitable for X–ray diffraction in 79% yield (39 mg).

Spectroscopy data for 9: ^{1}H NMR (400.1 MHz, C_6D_6): δH 6.68 (s, 2H, NC*H*C*H*N), 4.21 (s, 5H, C_5H_5), 1.62 (s, 9H, C(C*H*$_3$)$_3$); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δH 235.8 (s, *C*O), 200.2 (s, N*C*N), 119.8 (s, N*C*H*C*HN), 85.6 (s, *C*$_5$H$_5$), 61.1 (N*C*(CH_3)$_2$), 33.0 (s, C(*C*H$_3$)$_3$).

Spectroscopy data for 10: ^{1}H NMR (400.1 MHz, C_6D_6): δH 6.33 (d, 1H, $^3J_{HH}$ = 2.0 Hz, NC*H*C*H*N), 6.09 (d, 1H, $^3J_{HH}$ = 2.0 Hz, NC*H*C*H*N), 2.77 (br, m, 1H, B*H*), 1.83 (m, 1H, BC*H*$_2$), 1.54 (m, 1H, BC*H*$_2$), 1.43 (s, 9H, C(C*H*$_3$)$_3$), 1.38 (s, 3H, NC(C*H*$_3$)$_2$), 1.35 (s, 9H, C(C*H*$_3$)$_3$), 1.19 [s, 3H, NC(C*H*$_3$)$_2$]; ^{11}B{^{1}H} NMR (128.3 MHz, C_6D_6): δH −10.8 (d, $^1J_{BH}$ = 90.4 Hz); ^{13}C{^{1}H} NMR (100.6 MHz,

C_6D_6): δH 120.3 (s, N*C*H*C*HN), 112.6 (s, NCH*C*HN), 62.7 (N*C*(CH_3)$_2$), 57.6 (N*C*(CH_3)$_3$), 33.7 (s, C(*C*H_3)$_3$), 32.0 (s, C(*C*H_3)$_2$), 30.7 (s, C(*C*H_3)$_2$), 30.6 (s, C(*C*H_3)$_3$). Anal. Found: C, 72.27; H, 11.64; N, 11.46. Calcd. data for $C_{15}H_{29}BN_2$: C, 72.58; H, 11.78; N, 11.29.

Crystal structure determination

The crystal data were collected on a *Bruker D8-Quest* (**3, 4**) and a *Bruker X8-Apex 2* diffractometer (**4', 5, 6, 6a,** and **10**) with a CCD area detector and multi-layer mirror or graphite (**4'**) monochromated $Mo_{K\alpha}$ radiation. The structures were solved using direct methods, refined with the *Shelx* software package[17] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized geometric positions and included in structure factors calculations. The *Shelx* was interfaced with *ShelXLe* GUI for most of refinement steps.[18] The pictures of molecules were prepared using *Pov-Ray* 3.6.[19] Crystallographic data can be obtained from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

Crystal data for 3: $C_{15}H_{23}BMnO_3P$, $M_r = 348.05$, orange needle, 0.14×0.04×0.03 mm^3, Hexagonal space group $P6_3/m$, $a = 16.5774(7)$ Å, $b = 16.5774(7)$ Å, $c = 10.5446(5)$ Å, $\alpha = 90.00°$, $\beta = 90.00°$, $\gamma = 120.00°$, $V = 2509.54(19)$ Å^3, $Z = 6$, $\rho_{calcd} = 1.382$ g·cm^{-3}, $\mu = 0.890$ mm^{-1}, $F(000) = 1092$, $T = 100(2)$ K, $R_1 = 0.0491$, $wR^2 = 0.1050$, 1816 independent reflections [$2\theta \le 52.72°$] and 113 parameters. CCDC-976330.

Crystal data for 4: $C_{18}H_{24}BMnN_2O_2$, $M_r = 366.14$, yellow needle, 0.163×0.146×0.065 mm^3, Monoclinic space group $P2_1/c$, $a = 24.302(2)$ Å, $b = 7.8695(7)$ Å, $c = 21.291(2)$ Å, $\beta = 115.979(7)°$, $V = 3660.4(6)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.329$ g·cm^{-3}, $\mu = 0.733$ mm^{-1}, $F(000) = 1536$, $T = 293(2)$ K, $R_1 = 0.0619$, $wR^2 = 0.1056$, 7403 independent reflections [$2\theta \le 52.74°$] and 496 parameters. CCDC-976331.

The crystal was twined by (1 0 0) 2-fold axis and was refined with final BASF parameter of 48%. The displacement parameters of the opposite methyl-carbon atoms belonging to disordered *tert*-butyl residues were constrained to the same value. The position of boron-bound carbon was kept at the same coordinates for all three butyl-residues. The low occupancy of *iso*-Bu in structure allows only geometry-restrained refinement. The carbon 1–2 distances were restraint during refinement to the value of 1.54 Å and the 1–3 to 2.55 Å (DFIX restraint). The U_{ii} displacement parameters of carbons in butyl-groups were restrained with ISOR keyword to approximate isotropic behavior. The 'rigid bond' restraint was used for all bonds in these groups (DELU).

Crystal data for 4a: $C_{18}H_{24}BMnN_2O_2$, $M_r = 366.14$, orange block, 0.43×0.22×0.22 mm^3, Orthorhombic space group *Pna*21, $a = 21.1662(11)$ Å, $b = 7.9276(11)$ Å, $c = 21.8218(4)$ Å, $V = 3661.6(5)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.328$ g·cm^{-3}, $\mu = 0.733$ mm^{-1}, $F(000) = 1536$, $T = 100(2)$ K, $R_1 = 0.0561$, $wR^2 = 0.1201$, 9112 independent reflections [$2\theta \le 56.66°$] and 475 parameters. CCDC-976332.

Data set was refined as racemic twin with final BASF value 0.474(19). The displacement parameters of the opposite methyl-carbon atoms belonging to disordered *t*Bu residues were constrained to the same value. The position of boron-bound carbon was kept at the same coordinates for *tert*-butyl residues (EXYZ). The low occupancy of *iso*-Bu in structure allow only geometry-constrained refinement. The positions of atoms belonging to *iso*-Bu group were fitted to idealized geometry and U_{ii} displacement parameters of carbons in these groups were refined isotropic. The 'rigid bond' restraint was used for all bonds in these groups (DELU).

Crystal data for 5: $C_{18}H_{23}BMnNO_2$, $M_r = 351.12$, red block, $0.256\times0.248\times0.12$ mm^3, Monoclinic space group $C2/c$, $a = 24.5671(14)$ Å, $b = 8.1978(5)$ Å, $c = 18.4064(10)$ Å, $\beta = 111.169(2)°$, $V = 3456.8(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.349$ g·cm^{-3}, $\mu = 0.771$ mm^{-1}, $F(000) = 1472$, $T = 100(2)$ K, $R_1 = 0.0316$, $wR^2 = 0.0776$, 3533 independent reflections [$2\theta \le 52.74°$] and 213 parameters. CCDC-976333.

Crystal data for 6: $C_{16}H_{22}BMnN_2O_2$, $M_r = 340.11$, yellow block, $0.26\times0.12\times0.08$ mm^3, Monoclinic space group $P2_1/c$, $a = 14.4606(11)$ Å, $b = 12.5027(9)$ Å, $c = 18.2085(13)$ Å, $\beta = 93.815(3)°$, $V = 3284.7(4)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.375$ g·cm^{-3}, $\mu = 0.811$ mm^{-1}, $F(000) = 1424$, $T = 100(2)$ K, $R_1 = 0.0955$, $wR^2 = 0.1856$, 6489 independent reflections [$2\theta \le 52.04°$] and 421 parameters. CCDC-976334.

The crystal was a pseudo-merohedral twin with domains rotated by 180° around real axis (0 1 0). The BASF parameter was refined to 50%. 12 of reported least-squares restraints as shown by _refine_ls_number_restraints key are attributed to DELU keyword in ShelXL input ('rigid bond' restraint for all bonds in the connectivity list. s1=0.005 and s2=0.01 were used). The displacement parameters of related atoms B1 > C5 of the residues 3 and 13 were constrained to the same value. The coordinates of pairs of atoms B1_3 and B1_13, and of C2_3 and C2_13 were constrained to the same value. The Uii displacement parameters of atoms C2_3 > C5_3 and C2_13 > C5_13 were restrained with ISOR keyword to approximate isotropic behavior.

Crystal data for 6a: $C_{16}H_{22}BMnN_2O_2 \times ½(C_6H_6)$, $M_r = ¼(1516.64)$, yellow block, $0.22\times0.20\times0.18$ mm^3, Monoclinic space group $P2_1/c$, $a = 15.2676(7)$ Å, $b = 8.5852(4)$ Å, $c = 15.8554(7)$ Å, $\beta = 113.8480(10)°$, $V = 1900.81(15)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.325$ g·cm^{-3}, $\mu = 0.708$ mm^{-1}, $F(000) = 796$, $T = 100(2)$ K, $R_1 = 0.0302$, $wR^2 = 0.0718$, 3888 independent reflections [$2\theta \le 52.74°$] and 288 parameters. CCDC-976335.

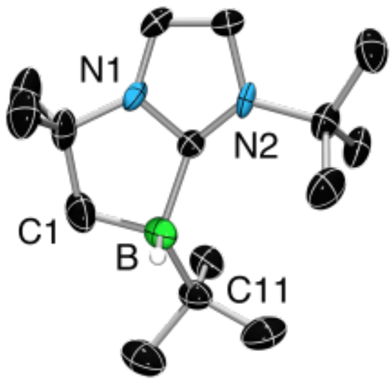
The 24 of 240 for the solvent reported least-squares restraints as shown by _refine_ls_number_restraints key are attributed to DELU keyword in ShelXL input ('rigid bond' restraint for all bonds in the connectivity list. The parameters s1=0.005 and s2=0.01 were used). The displacement parameters of atoms C1 > C6 of the residues 1 and 2 were restrained to the same value with similarity restraint SIMU. The U_{ii} displacement parameters of atoms C1 > C6 of the residues 1 and 2 were restrained with ISOR keyword to approximate isotropic behavior.

Crystal data for 7: $C_{19}H_{24}BMnN_2O_3$, $M_r = 486.28$, orange plate, $0.133\times0.12\times0.04$ mm^3, Orthorhombic space group $Pnma$, $a = 13.024(8)$ Å, $b = 9.225(4)$ Å, $c = 19.975(9)$ Å, $V = 2400(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.346$ g·cm^{-3}, $\mu = 0.580$ mm^{-1}, $F(000) = 1024$, $T = 100(2)$ K, $R_1 = 0.0507$, $wR^2 = 0.1156$, 2609 independent reflections [$2\theta \le 52.744°$] and 164 parameters. CCDC-976336.

The displacement parameters of close atoms of solvent molecules were restrained to the same value with similarity restraint SIMU.

Crystal data for 10: $C_{15}H_{29}BN_2$, $M_r = 248.21$, colorless block, $0.23\times0.18\times0.10$ mm^3, Orthorhombic space group $Pbca$, $a = 14.3661(7)$ Å, $b = 12.0848(6)$ Å, $c = 18.9620(9)$ Å, $V = 3292.0(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.002$ g·cm^{-3}, $\mu = 0.057$ mm^{-1}, $F(000) = 1104$, $T = 100(2)$ K, $R_1 = 0.0821$, $wR^2 = 0.1690$, 3502 independent reflections [$2\theta \le 53.52°$] and 234 parameters. CCDC-976337.

The 104 of 462 reported least-squares restraints as shown by _refine_ls_number_restraints key are attributed to DELU keyword in ShelXL input ('rigid bond' restraint for all bonds in the connectivity list. Standard values of 0.01 for both parameters s1 and s2 were used). The displacement parameters of atoms B1 > C4 and B101 > C104, and C11 > C15 and C111 > C115 were constrained to the same value. The displacement parameters of atoms C21 > C24 and C121 > C124, and C31 > C34 and C131 > C134 were restrained to the same value with similarity restraint SIMU. The distances between atoms C101 and C102, C131 and C132 and C131 and C134 were restrained to the value of 1.56. The distances between atoms B1 and C11, and B101 and C111 were restrained during refinement to the same value. The U$_{ii}$ displacement parameters of atoms C1 > C4 and C101 > C104, C11 > C15 and C111 > C115, C22 > C24, C32 > C34, C122 > C124 and C132 > C134 were restrained with ISOR keyword to approximate isotropic behavior.



10

Figure 1. Molecular structure of **10** in the solid state. Thermal ellipsoids are shown at the 50% probability level. Selected bond distances (Å) and angles (°) for **10**: B–C11 1.651(8), B–C1 1.678(6).

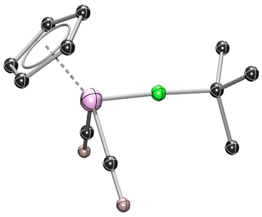
Computational Details Section

General considerations

The gas-phase geometry pre-optimizations were performed using *Turbomole 6.2*.[1] The final optimizations and the preparation of wave-functions files were performed using *Gaussian 03* program.[2] The B3LYP hybrid functional and Def2-SVP basis set were used for all these computations.[3] We ensured that the calculated geometries are respectively minima on the potential energy surface carrying out harmonic frequency calculations (zero negative eigenvalues of the Hessian). The Wiberg Bond Index (WBI) values given in the text as well as the Natural Bond Orbitals analysis were obtained using the *NBO 5* program.[4] The NBO analysis was performed using wave-functions obtained with *Gaussian 03*. Illustrations of the NBO orbitals were prepared with the *Molekel 4.3*.[5] The pictures of computed molecules were prepared using customized version of XMakeMol 5.14 and Pov-Ray 3.6.[6]

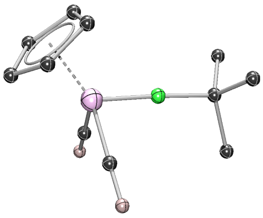
The total energies E_h and the Zero Point Vibration Energy (ZPVE, in Hartrees) carbonyle IR-frequencies and ^{11}B- and carbonyl ^{13}C-NMR shifts for computed molecules follow. The computed NMR chemical shifts were referenced *via* tetramethylsilane and diborane(6). The given symmetry symbol indicates not necessarily the highest point group of the calculated molecule but rather one used during computations. The IRED gives a count of negative eigenvalues of Hessian. Hydrogen atoms are omitted for clarity in all graphic representations.

1 (C_1) IRED = 0



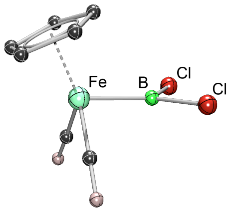
		IR [ν, cm^{-1}]		^{11}B and ^{13}C NMR [δ, ppm]	
Energy	ZPVE	CO (sym)	CO (asym)	B	CO
−1753.32647285	0.226980	2076.43	2034.39	151.3	223.0
experimental		*1968*	*1912*	*144.0*	*223.6*

1 (C_s) IRED = 1, transition state *via* rotation of Cp-ring around centroid-Mn axis



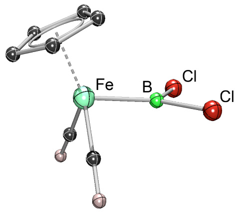
		IR [ν, cm^{-1}]		^{11}B and ^{13}C NMR [δ, ppm]	
Energy	ZPVE	CO (sym)	CO (asym)	B	CO
−1753.32615741	0.226943	2135.75	2097.62	–	–

FpBCl$_2$·(C_s) IRED = 0



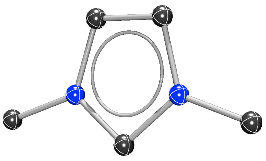
		IR [ν, cm^{-1}]		^{11}B and ^{13}C NMR [δ, ppm]	
Energy	ZPVE	CO (sym)	CO (asym)	B	CO
−2628.55884446	0.109248	2134.88	2096.94	106.7	220.4
experimental[7]		*2026*	*1974*	*90.0*	*213.1*

FpBCl$_2$ (C_s) IRED = 1, transition state *via* rotation of Cp-ring around centroid-Fe axis



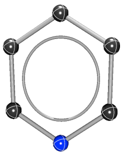
		IR [ν, cm^{-1}]		^{11}B and ^{13}C NMR [δ, ppm]	
Energy	ZPVE	CO (sym)	CO (asym)	B	CO
−2628.55653318	0.109182	2135.75	2097.62	–	–

IMe (C_{2v}) IRED = 0



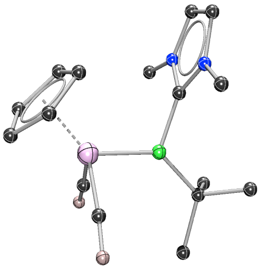
		IR [ν, cm^{-1}]		^{11}B and ^{13}C NMR [δ, ppm]	
Energy	ZPVE	CO (sym)	CO (asym)	B	CO
−304.557264802	0.126186	–	–	–	–

py (C_{2v}) IRED = 0



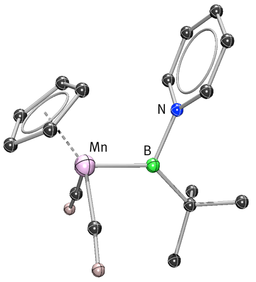
		IR [ν, cm^{-1}]		^{11}B and ^{13}C NMR [δ, ppm]	
Energy	ZPVE	CO (sym)	CO (asym)	B	CO
−248.094099112	0.088745	–	–	–	–

6 (***C_1***) IRED = 0



		IR [ν, cm^{-1}]		^{11}B and ^{13}C NMR [δ, ppm]	
Energy	ZPVE	CO (sym)	CO (asym)	B	CO
–2057.92433096	0.357573	2027.5766	1974.0828	130.3	232.4, 237.4
experimental		*1890*	*1820*	*129.8*	*235.0*

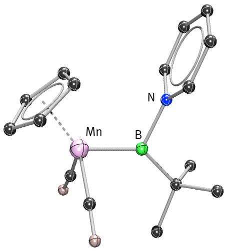
5' – Cp(CO)$_2$B(*t*Bu)(py) (***C_1***) IRED = 0



		IR [ν, cm^{-1}]		^{11}B and ^{13}C NMR [δ, ppm]	
Energy	ZPVE	CO (sym)	CO (asym)	B	CO
–2057.92433096	0.357573	2027.5766	1974.0828	116.9	232.4, 237.4
*experimental **5***[†]		*1876*	*1809*	*116.1*	*234.0*

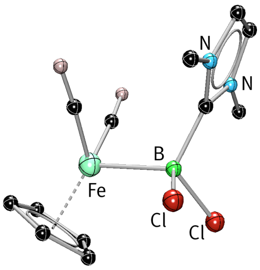
[†] The experimental data are for *meta*-dimethylpyridine complex rather, than for unsusbtituted base.

5’ – Cp(CO)$_2$B(*t*Bu)(py) (*C*$_s$) IRED = 1



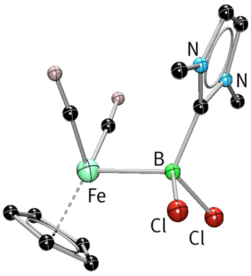
		IR [ν, cm^{-1}]		^{11}B and ^{13}C NMR [δ, ppm]	
Energy	ZPVE	CO (sym)	CO (asym)	B	CO
−2001.42488181	0.319054	2035.8096	1992.1840	–	–

FpBCl·IMe (*C*$_1$) IRED = 0



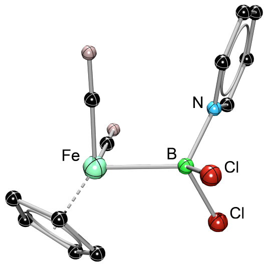
		IR [ν, cm^{-1}]		^{11}B and ^{13}C NMR [δ, ppm]	
Energy	ZPVE	CO (sym)	CO (asym)	B	CO
−2933.16958929	0.240077	2069.4612	2027.5429	18.4	229.3, 230.1

FpBCl·IMe (*C*$_s$) IRED = 1



		IR [ν, cm^{-1}]		^{11}B and ^{13}C NMR [δ, ppm]	
Energy	ZPVE	CO (sym)	CO (asym)	B	CO
−2933.16957267	0.240013	2069.2894	2027.4617	–	–

FpBCl·py (**C_s**) IRED = 0



		IR [ν, cm^{-1}]		^{11}B and ^{13}C NMR [δ, ppm]	
Energy	ZPVE	CO (sym)	CO (asym)	B	CO
−2876.67940773	0.201393	2081.58	2040.82	18.4	227.3
experimenta†l[13]		*1976*	*1916*	18.8	−‡

† the experimental data are for *para*-methylpyridine complex rather, than for unsusbtituted base.

‡ Carbonyle ^{13}C chemical shifts were not reported in the paper.

Bond Dissociation Energy (D_0) – comparison of borylene (1) and boryl (FpBCl$_2$) base adducts

The single point total energies E_h (in Hartrees) for fragments in geometry found in optimized base adducts are as follows:

1 in 1·IMe	−1753.28330048
1 in 1·py	−1753.28961457
FpBCl$_2$ in FpBCl$_2$·IMe:	−2628.50464596
FpBCl$_2$ in FpBCl$_2$·py:	−2628.51602952
IMe in **1**·IMe:	−304.55425528
IMe in FpBCl$_2$·IMe:	−304.54959694
py in **1**·IMe:	−248.09284026
py in FpBCl$_2$·IMe:	− 248.09270115

These, and above listed numbers for optimized geometries, result in the following energy decomposition schema (in kJ·mol^{-1}):

	Borylene·IMe	Boryl·IMe	Borylene·py	Boryl·py
preparation energy for base	7.90	20.13	3.31	3.67
preparation energy for boryl/ene	113.35	142.30	96.77	112.41
instantaneous interaction energies (ΔE_{int})	−227.83	−302.84	−113.39	−185.56
bond dissociation energy (D_0)	−106.58	−140.41	−11.32	−69.48
bond dissociation energy incl. ZPV correction	−95.01	−128.22	−2.15	−60.55

Natural Bond Orbital Analysis (NBO) for compound 6

The NBOs that account for the main contribution to the covalent interactions between Mn and B are presented in Figure 2. They are consistent with the Kohn-Sham frontier orbitals of **6** presented in main part of the paper. Both suggest a σ- as well as a π-type interaction between both atoms.

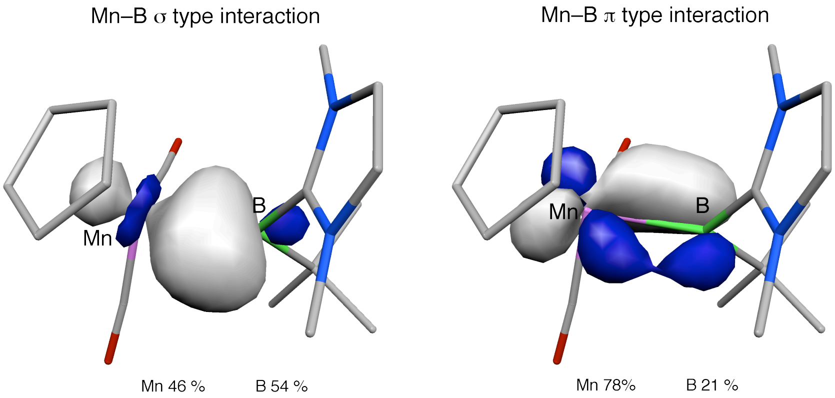


Figure 2. Interactions between boron and manganese atoms in the two-center Mn–B bond. Contributions of manganese and boron atomic orbitals to the NBO-orbital are given below of each figure (in %).

References

[1] R. Ahlrichs *et al.*, *Turbomole 6.2*, Turbomole GmbH, Karlsruhe (Germany), (**2010**).

[2] M. J. Frisch *et al.*, *Gaussian 03, Revision E.01*, Gaussian, Inc., Pittsburgh PA (USA), (**2004**).

[3] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, 3297; Def2-SVP basis set was obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 1.2.2, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352 (USA), and funded by the U.S. Department of Energy.

[4] E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, F. Weinhold, *NBO 5.0*, Theoretical Institute, University of Wisconsin, Madison (USA), (**2001**).

[5] P. Flükiger, H. P. Lüthi, S. Portmann, J. Weber, *Molekel 4.0*, Swiss Center for Scientific Computing, Manno (Switzerland), (**2000**).

[6] M. P. Hodges, XMakeMol 5.14, http://www.nongnu.org/xmakemol, (2003).

[7] H. Braunschweig, K. Radacki, F. Seeler, G. R. Whittell, *Organometallics* **2004**, *23*, 4178–4180.

NMR-Spectra of 5 and 6a

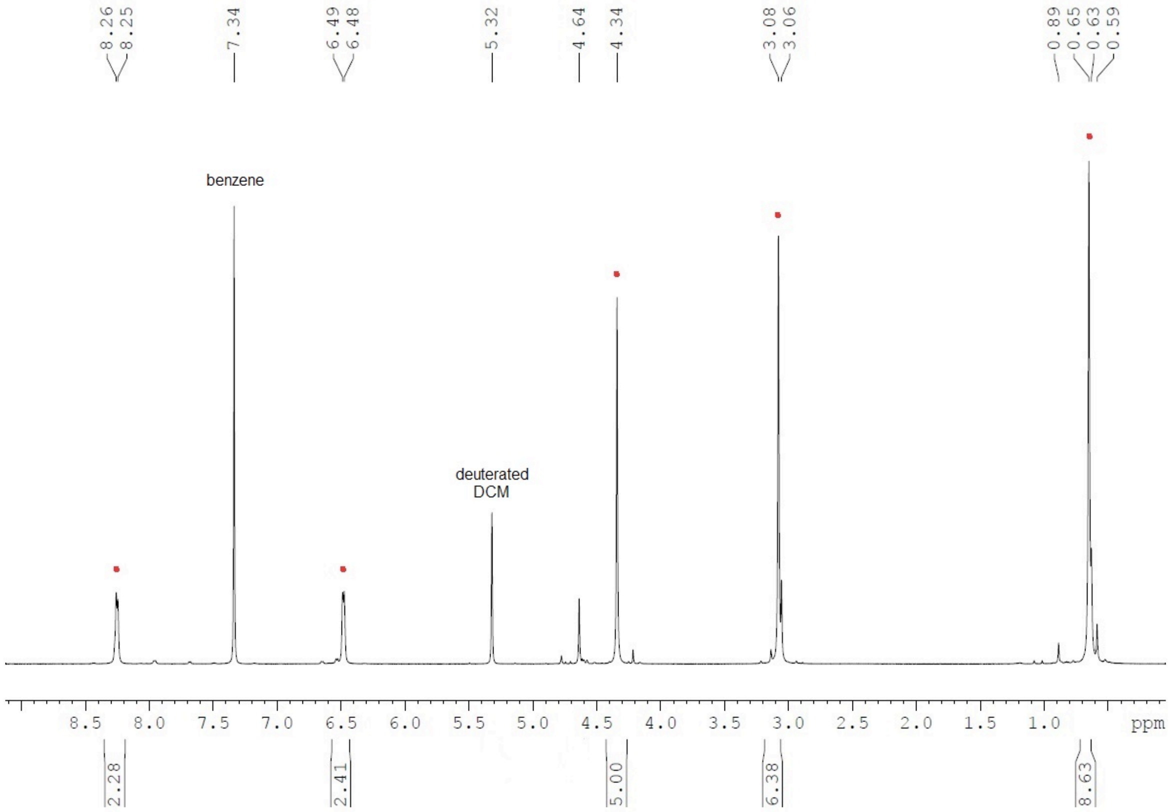


Figure 3. ^{1}**H NMR spectra of compound** 5**.** Signals that belong to **5** are marked with red dots.

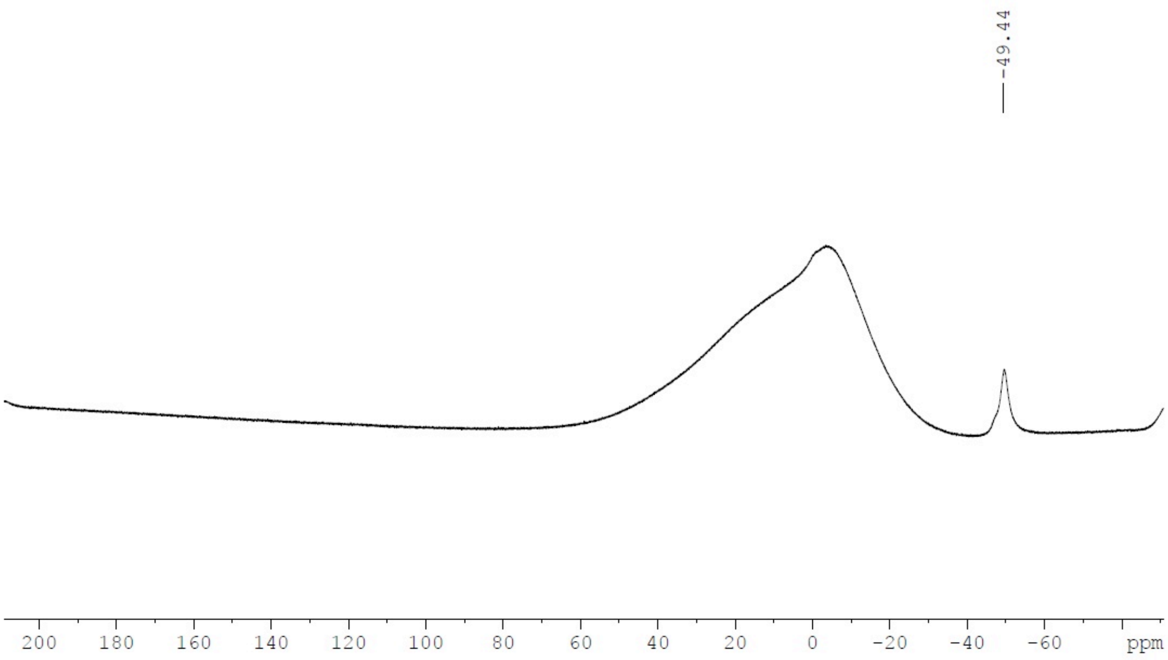


Figure 4. ^{11}B NMR spectra of compound **5**.

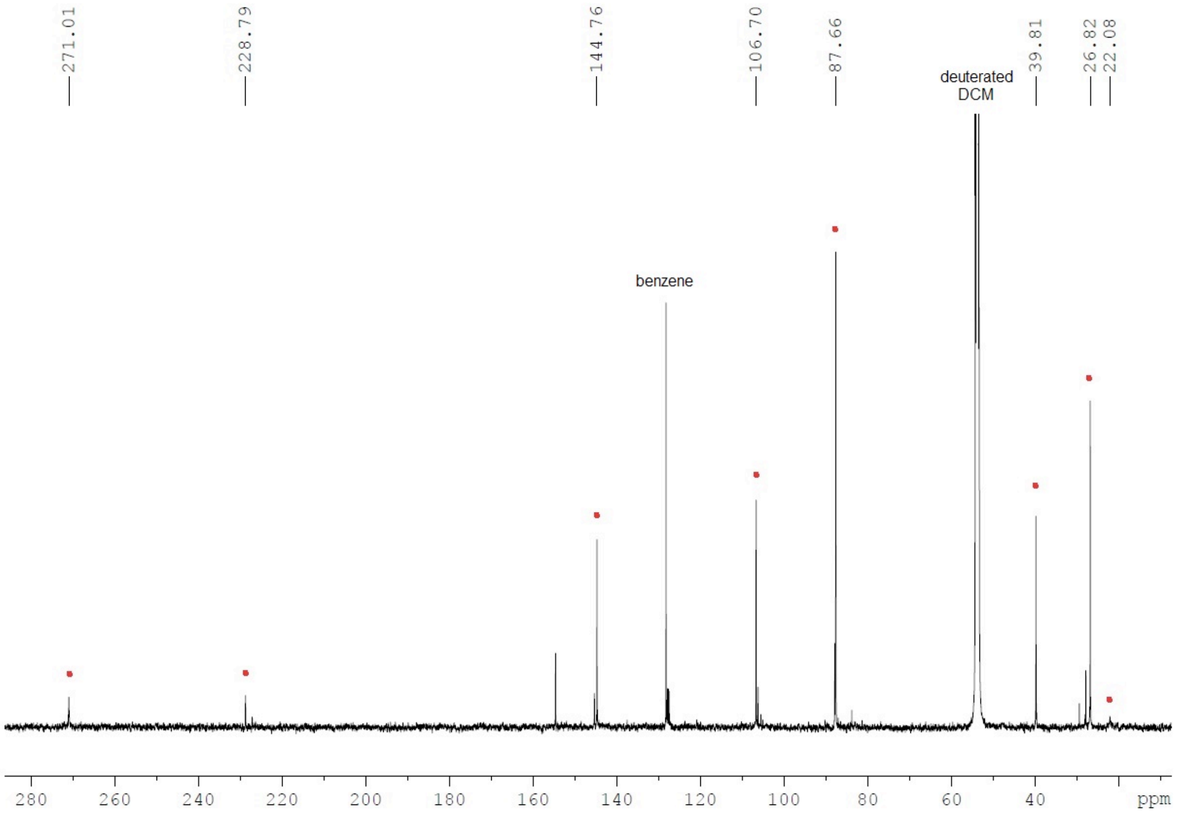


Figure 5. ^{13}C NMR spectra of compound **5**. Signals that belong to **5** are marked with red dots.

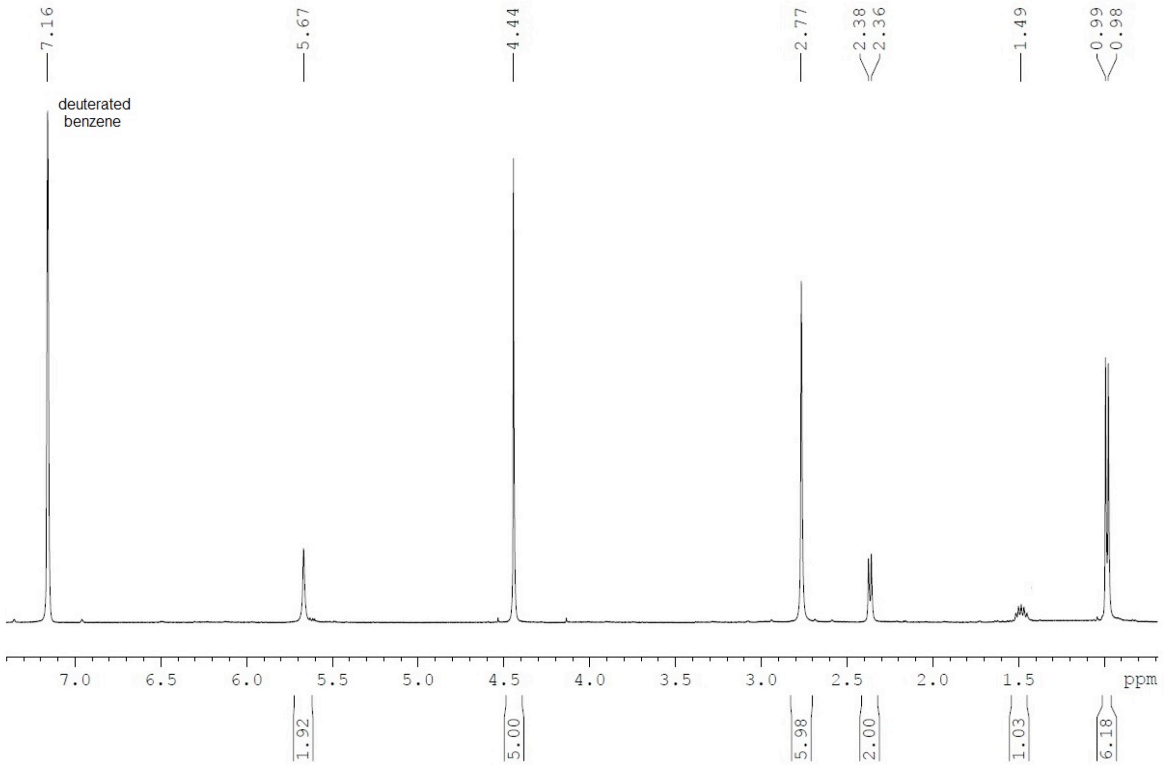


Figure 6. ^{1}H NMR spectra of compound **6a**.