Supplementary Material

Ln(III) Methyl and Methylidene Complexes Stabilized by a Bulky Hydrotris(pyrazolyl)borate Ligand

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Experimental Details

General Procedures. All operations were performed with rigorous exclusion of air and water, using standard *Schlenk*, high-vacuum, and glovebox techniques (MBraun MBLab; <1 ppm O_2, <1 ppm H_2O). Hexane and toluene were purified by using *Grubbs* columns (MBraun SPS, solvent purification system) and stored in a glovebox. C_6D_6 and toluene-d_8 were obtained from *Aldrich*, degassed, dried over Na for 24 h, and filtered. $AlMe_3$ was purchased from *Aldrich* and used as received. Homoleptic $Ln(AlMe_4)_3$ (**1**) (Ln = Lu, Y) were prepared according to literature methods.[17] $(Tp^{tBu,Me})H$ was synthesized by a modification of the published procedure for $(PhTp^{tBu})H$.[31] The NMR spectra of air and moisture sensitive compounds were recorded by using *J. Young* valve NMR tubes at 25 °C on a *Bruker*-BIOSPIN-AV500 (5 mm BBO, ^1H: 500.13 Hz; ^{13}C: 125.77 MHz) and a *Bruker*-BIOSPIN-AV600 (5 mm cryo probe, ^1H: 600.13 MHz; ^{13}C: 150.91 MHz). ^1H and ^{13}C shifts are referenced to internal solvent resonances and reported in *parts per million* relative to TMS. ^{27}Al NMR spectra were recorded on the AV500 at 130.33 MHz. 2000 scans were averaged. The ^{27}Al chemical shifts are reported relative to an external reference: a solution of $AlCl_3$ in D_2O with a drop of concentrated HCl $[Al(D_2O)_6^{3+}]$. ^{11}B NMR (161 MHz) spectra were referenced to an external standard of boron trifluoride diethyl etherate (0.0 ppm, C_6D_6). IR spectra were recorded on a *NICOLET Impact 410 FTIR* spectrometer as Nujol mulls sandwiched between CsI plates. Elemental analyses were performed on an *Elementar Vario EL III.*

General procedure for the synthesis of $(Tp^{tBu,Me})Ln(AlMe_4)(Me)$ (2): In a glovebox $Ln(AlMe_4)_3$ (**1**) was dissolved in 3 mL of hexane and added to a stirred solution of $(Tp^{tBu,Me})H$ in 4 mL of hexane. Instant gas formation and the formation of a white precipitate were observed. The reaction mixture was stirred another 15 min at ambient temperature. The product was separated by centrifugation, washed four times with 5 mL of hexane, and dried under vacuum to yield **2** as powdery white solids.

(Tp$^{t\mathrm{Bu,Me}}$)Lu(AlMe$_4$)(Me) (2a): Following the procedure described above, Lu(AlMe$_4$)$_3$ (**1a**, 91 mg, 0.21 mmol) and (Tp$^{t\mathrm{Bu,Me}}$)H (89 mg, 0.21 mmol) yielded **2a** as a powdery white solid (89 mg, 0.13 mmol, 61%).

^{1}H NMR (500 MHz, C$_6$D$_6$, 25 °C): $\delta = 5.61$ (s, $\Delta\nu_{1/2} = 3$ Hz, 3 H, 4-pz-*H*), 4.44 (d v br, $^{1}J_{\mathrm{B\text{-}H}} \cong 119$ Hz, 1 H, B*H*), 1.93 (s, $\Delta\nu_{1/2} = 6$ Hz, 9 H, pz-C*H*$_3$), 1.33 (s, $\Delta\nu_{1/2} = 2$ Hz, 27 H, pz-C(C*H*$_3$)$_3$), 0.07 (s br, $\Delta\nu_{1/2} = 170$ Hz, 3 H, Lu-C*H*$_3$), −0.32 (s br, $\Delta\nu_{1/2} = 110$ Hz, 12 H, Al(C*H*$_3$)). ^{1}H NMR (500 MHz, tol-d_8, −40 °C): 5.60 (s br, $\Delta\nu_{1/2} = 30$ Hz, 2 H, 4-pz-*H*), 5.36 (s br, $\Delta\nu_{1/2} = 57$ Hz, 1 H, 4-pz-*H*), 4.38 (s v br, $^{1}J_{\mathrm{B\text{-}H}} \cong 130$ Hz, 1 H, B*H*), 2.08 (s br, $\Delta\nu_{1/2} = 30$ Hz, 9 H, pz-C*H*$_3$), 1.36 (s br, $\Delta\nu_{1/2} = 19$ Hz, 27 H, pz-C(C*H*$_3$)$_3$), 0.46 (s, $\Delta\nu_{1/2} = 5$ Hz, 3 H, Lu-C*H*$_3$), 0.03 (s, $\Delta\nu_{1/2} = 7$ Hz, 3 H, Al(μ-C*H*$_3$)), −0.31 (s, $\Delta\nu_{1/2} = 4$ Hz, 9 H, Al(C*H*$_3$)). ^{13}C NMR (126 MHz, C$_6$D$_6$, 25 °C): $\delta = 166.5$ (3-pz-*C*), 148.6 (5-pz-*C*), 105.0 (4-pz-*C*), 32.3 (pz-*C*(CH$_3$)$_3$), 31.1 (pz-C(*C*H$_3$)$_3$), 12.9 (pz-*C*H$_3$), −5.1 (Lu-*C*H$_3$), −6.1 (Al(*C*H$_3$)$_4$). ^{27}Al NMR (130 MHz, C$_6$D$_6$, 25 °C): $\delta = 164$ (s br, *Al*(CH$_3$)$_4$) ppm. ^{11}B{^{1}H} NMR (161 MHz, C$_6$D$_6$, 25 °C): $\delta = -9.1$ (s br) ppm. IR (Nujol, cm^{-1}): 2561 m (B-H), 1551 s, 1463 vs Nujol, 1375 vs Nujol, 1323 m, 1246 m, 1204 s, 1163 vs, 1070 s, 1033 s, 987 m, 811 s, 769 s, 728 s, 686 s, 650 m, 588 w, 526 m. Elemental analysis: calculated C (49.72), H (7.91), N (12.00); found C (49.96), H (7.98), N (11.84).

(Tp$^{t\mathrm{Bu,Me}}$)Y(AlMe$_4$)(Me) (2b): Following the procedure described above, Y(AlMe$_4$)$_3$ (**1b**, 154 mg, 0.44 mmol) and (Tp$^{t\mathrm{Bu,Me}}$)H (186 mg, 0.44 mmol) yielded **2b** as a powdery white solid (135 mg, 0.22 mmol, 50%).

^{1}H NMR (500 MHz, C$_6$D$_6$, 25 °C): $\delta = 5.57$ (s, 3 H, 4-pz-*H*), 4.46 (d v br, $^{1}J_{\mathrm{B\text{-}H}} \cong 116$ Hz, 1 H, B*H*), 1.95 (s, $\Delta\nu_{1/2} = 4$ Hz, 9 H, pz-C*H*$_3$), 1.32 (s, $\Delta\nu_{1/2} = 4$ Hz, 27 H, pz-C(C*H*$_3$)$_3$), 0.25 (s br, $\Delta\nu_{1/2} = 100$ Hz, 3 H, Y-C*H*$_3$), −0.36 (s br, $\Delta\nu_{1/2} = 30$ Hz, 12 H, Al(C*H*$_3$)). ^{1}H NMR (500 MHz, Tol-d_8, -60 °C): 5.49 (s br, $\Delta\nu_{1/2} = 15$ Hz, 2 H, 4-pz-*H*), 5.22 (s br, $\Delta\nu_{1/2} = 32$ Hz, 1 H, 4-pz-*H*), 4.35 (s v br, $\Delta\nu_{1/2} = 70$ Hz, 1 H, B*H*), 1.88 (s br, $\Delta\nu_{1/2} = 13$ Hz, 9 H, pz-C*H*$_3$), 1.36 (s br, $\Delta\nu_{1/2} = 13$ Hz, 27 H, pz-C(C*H*$_3$)$_3$), 0.43 (s, $\Delta\nu_{1/2} = 6$ Hz, 3 H, Y-C*H*$_3$), −0.14 (s, $\Delta\nu_{1/2} = 20$ Hz, 3 H, Al(μ-C*H*$_3$)), −0.21 (s, $\Delta\nu_{1/2} = 10$ Hz, 9 H, Al(C*H*$_3$)). ^{13}C NMR (126 MHz, C$_6$D$_6$, 25 °C): $\delta = 165.4$ (3-pz-*C*), 148.6

(5-pz-*C*), 104.4 (4-pz-*C*), 32.2 (pz-$C(CH_3)_3$), 31.1 (pz-$C(CH_3)_3$), 12.7 (pz-CH_3), −0.5 (Y-CH_3), −4.3 ($Al(CH_3)_4$). ^{27}Al NMR (130 MHz, C_6D_6, 25 °C): $\delta = 162$ (s br, $Al(CH_3)_4$) ppm. $^{11}B\{^1H\}$ NMR (161 MHz, C_6D_6, 25 °C): $\delta = -9.0$ (s br) ppm. IR (Nujol, cm^{-1}): 2566 m (B-H), 1551 s, 1458 vs Nujol, 1375 vs Nujol, 1328 s, 1251 m, 1204 s, 1168 vs, 1147 s, 1064 m, 1033 s, 992 m, 904 w, 805 s, 764 s, 728 m, 681 s, 645 m, 593 w, 526 m. Elemental analysis: calculated C (56.68), H (9.02), N (13.68); found C (56.94), H (9.07), N (13.44).

Procedure for the synthesis of $\{(Tp^{tBu,Me})AlMe\}^+\{Y(AlMe_4)[(\mu\text{-}CH_2)(\mu\text{-}Me)AlMe_2]_2(AlMe_2)\}^-$ (3): Following the procedure described for the synthesis of compounds **2b**, the supernatant and the hexane washing solutions were combined and stored at −30 °C. Colorless single crystals of **3** suitable for X-ray diffraction analysis were obtained after four weeks (192 mg, 0.22 mmol, 50% calculated on $Y(AlMe_4)_3$).

^{1}H NMR (600 MHz, C_6D_6, 25 °C): $\delta = 5.80$ (s, 1 H, 4-pz-*H*), 5.56 (s, 2 H, 4-pz-*H*), 4.30 (s v br, 1 H, B*H*), 2.19 (s, 3 H, pz-CH_3), 2.02 (s, 6 H, pz-CH_3), 1.37 (s, 9 H, pz-$C(CH_3)_3$), 1.10 (s, 18 H, pz-$C(CH_3)_3$), 0.64 (s, 3 H, Al-CH_3), 0.35 (d, $^2J_{Y\text{-}H} \cong 3.5$ Hz, 2 H, (μ-CH_2)), 0.23 (d, $^2J_{Y\text{-}H} \cong 1.2$ Hz, 2 H, (μ-CH_2)), −0.02 (d, $^2J_{Y\text{-}H} \cong 1.2$ Hz, 12 H, $Y(Al(CH_3)_4)$, −0.06 (d, $^2J_{Y\text{-}H} \cong 1.2$ Hz, 6 H), −0.15 (s, 6 H), −0.17 (s, 3 H), −0.25 (d, $^2J_{Y\text{-}H} \cong 1.8$ Hz, 9 H). ^{13}C NMR (151 MHz, C_6D_6, 25 °C): $\delta = 167.0$, 164.9 (3-pz-*C*), 149.7, 147.2 (5-pz-*C*), 107.0, 106.6 (4-pz-*C*), 33.0 (pz-$C(CH_3)_3$), 31.8 (pz-$C(CH_3)_3$), 31.3, 31.0, (Y-CH_2), 30.7 (pz-$C(CH_3)_3$), 13.6, 12.7 (pz-CH_3), 2.5, 0.5, 0.3, −0.3, −0.4 (Y-CH_3, $Al(CH_3)$)). ^{27}Al NMR (130 MHz, C_6D_6, 25 °C): $\delta = 160$ (s br, $Al(CH_3)_4$) ppm. $^{11}B\{^1H\}$ NMR (161 MHz, C_6D_6, 25 °C): $\delta = -7.7$ (s br) ppm. Elemental analysis: calculated C (53.80), H (9.61), N (9.65); found C (54.13), H (9.72), N (10.03).

31 J. L. Kisko, T. Hascall, C. Kimblin and G. Parkin, *J. Chem. Soc. Dalton Trans.*, 1999, 1929.

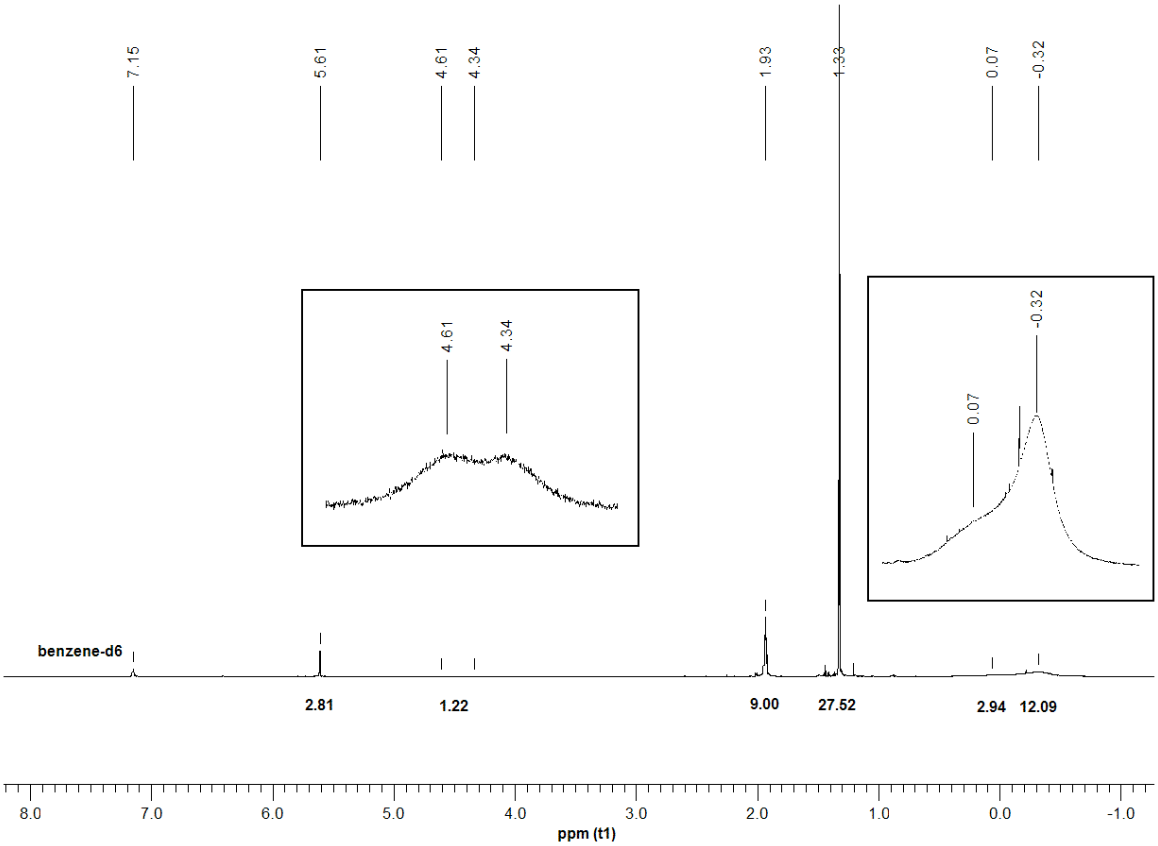

Fig. S1 ^{1}H NMR spectrum of compound **2a** in benzene-d_6 at 25 °C.

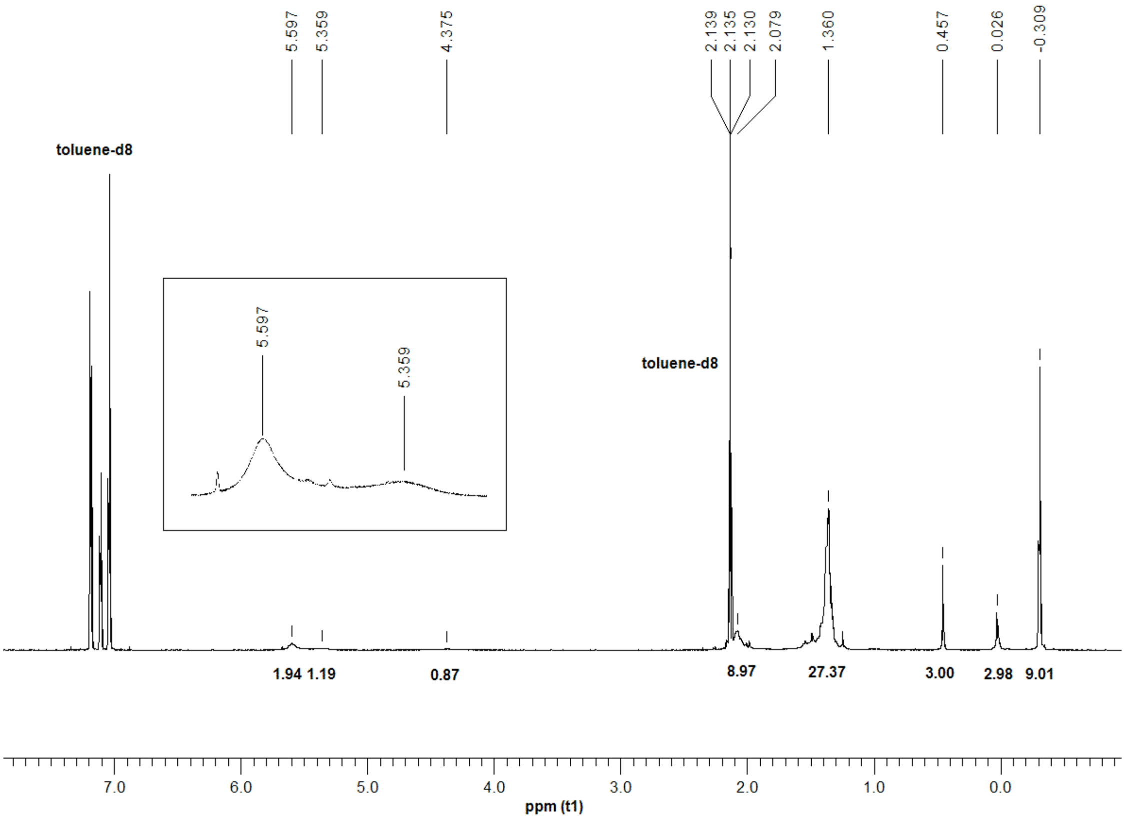

Fig. S2 ^{1}H NMR spectrum of compound **2a** in toluene-d_8 at −40 °C. At −40 °C significant broadening of the resonances associated with the pyrazolylborate ligand is observed. While well-separated signals are already observed for H-4 ($\Delta\nu_{½}$ = 30 Hz and 57 Hz) the signals for the pz-CH_3 ($\Delta\nu_{½}$ = 30 Hz) and the pz-C(CH_3)$_3$ ($\Delta\nu_{½}$ = 19 Hz) appear only significantly broadened.

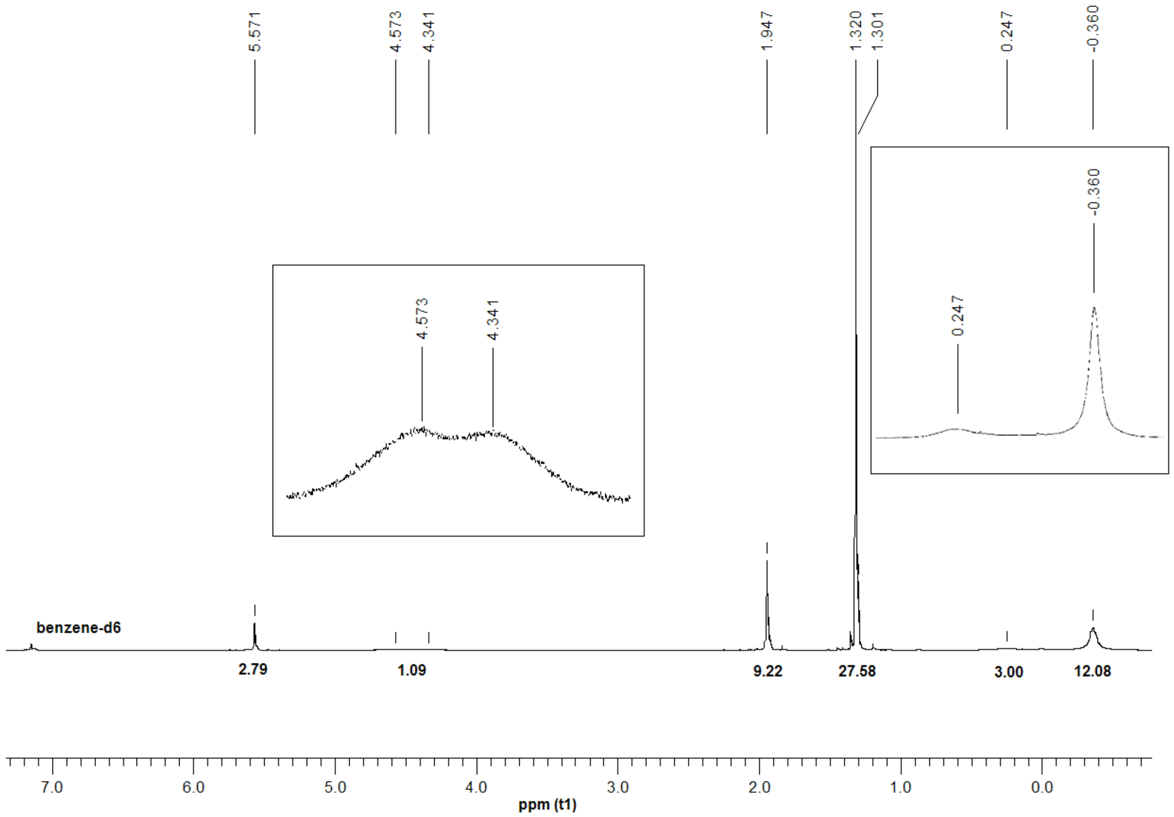

Fig. S3 ^{1}H NMR spectrum of compound **2b** in benzene-d_6 at 25 °C.

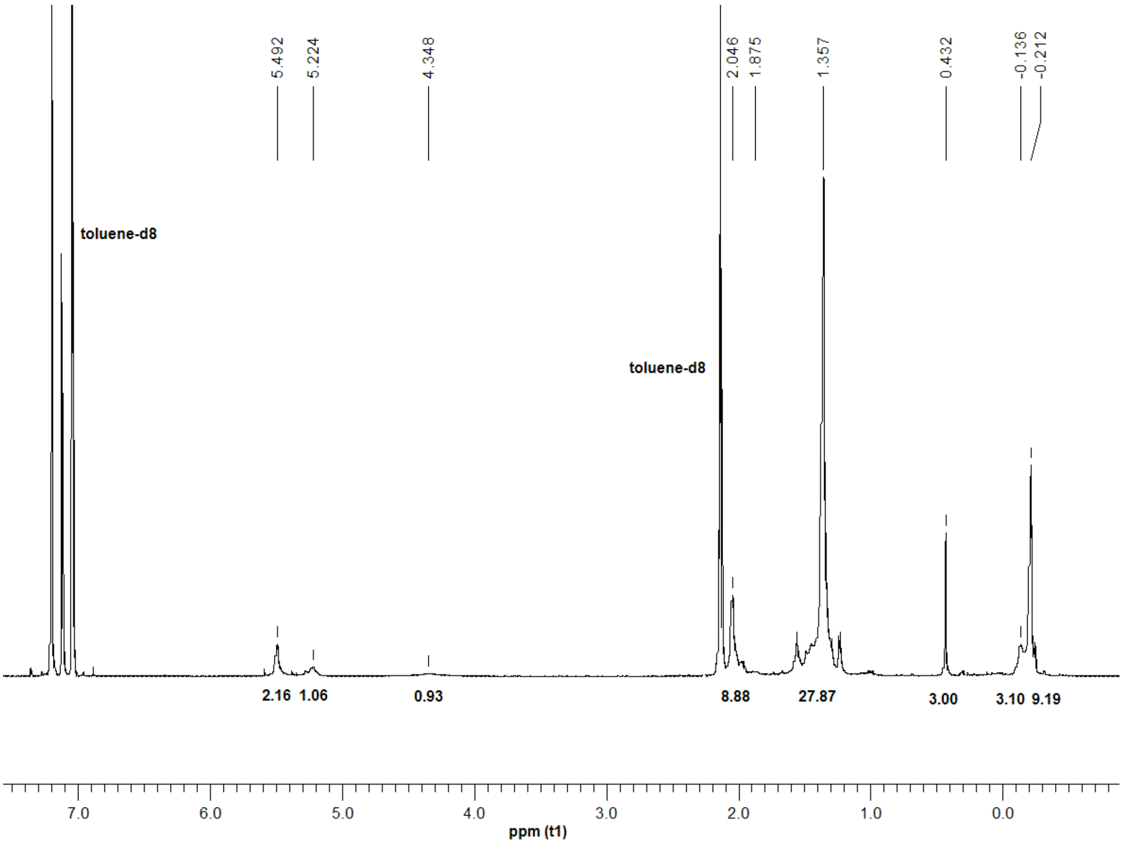

Fig. S4 ^{1}H NMR spectrum of compound **2b** in toluene-d_8 at −60 °C. At −60 °C significant broadening of the resonances associated with the pyrazolylborate ligand is observed. While well-separated signals are already observed for H-4 ($\Delta\nu_{½}$ = 15 Hz and 32 Hz) the signals for the pz-CH_3 ($\Delta\nu_{½}$ = 13 Hz) and pz-C(CH_3)$_3$ ($\Delta\nu_{½}$ = 13 Hz) groups appear only significantly broadened.

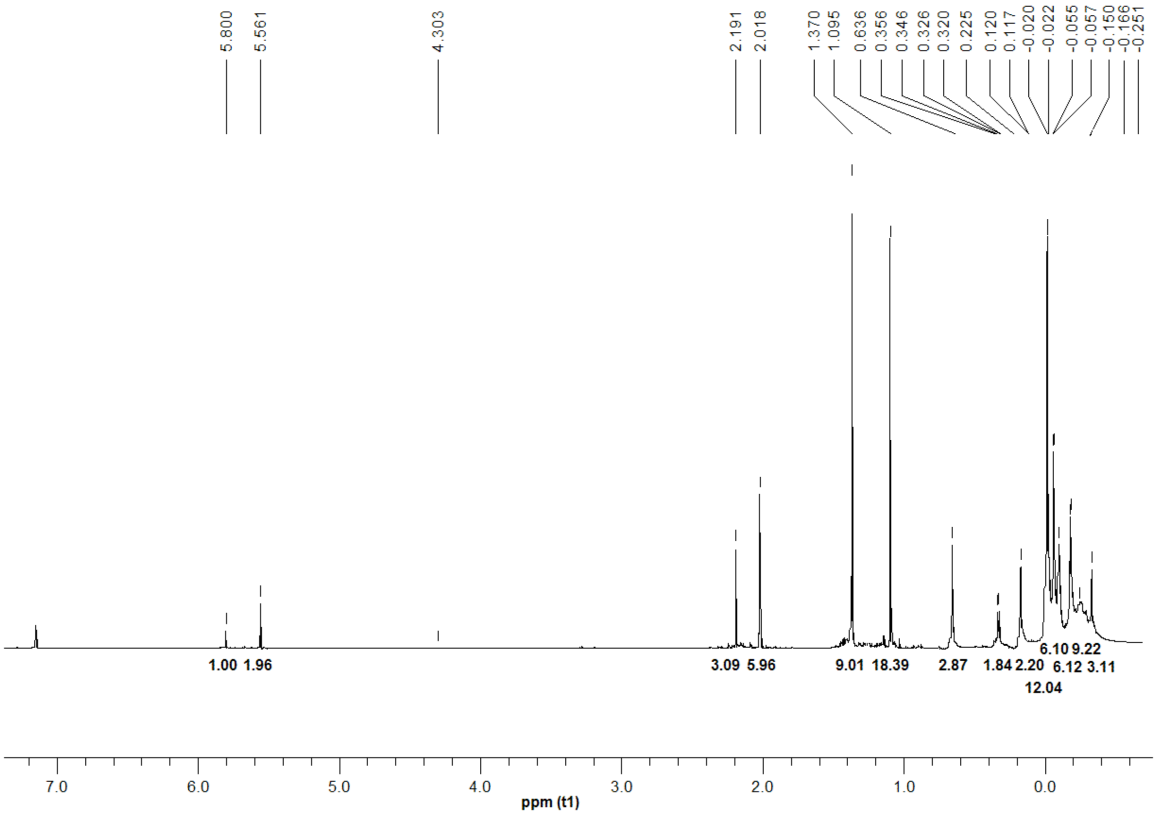

Fig. S5 ^{1}H NMR spectrum of compound **3** in benzene-d_8 at 25 °C.