Characterization of β-B-Agostic Isomers in Zirconocene Amidoborane Complexes

*Taryn D. Forster, Heikki M. Tuononen,[†] Masood Parvez, and Roland Roesler**

Contribution from the Department of Chemistry, University of Calgary, 2500 University Drive NW, Calgary, AB, T2N 1N4 Canada, and Department of Chemistry, University of Jyväskylä, P.O. Box 35, FIN-40014 Jyväskylä, Finland[†]

roesler@ucalgary.ca

- Supporting Information -

Topic | Page

Experimental Section

General considerations. All operations were carried out with careful exclusion of air and moisture using standard Schlenk and glove box techniques. The solvents were dried and deoxygenated prior to use. Starting materials were purchased from commercial suppliers and used as received. All NMR spectra were run on either a Bruker Avance DRX-400 or a DRY-400 instrument and chemical shifts are reported in δ units (ppm) using the solvent as an internal reference: C_6D_5H (7.15 ppm, ^1H) and C_6D_6 (128.39, ^{13}C); THF-d_7 (3.58 ppm, ^1H) and THF-d_8 (67.57 ppm, ^{13}C); toluene-d_7 (2.09 ppm, ^1H), and toluene-d_8 (20.4 ppm, ^{13}C). $BF_3{\cdot}Et_2O$ (0 ppm) was used as reference for the ^{11}B NMR measurements. The infrared spectra were recorded using KBr pellets on a Nicolet Nexus 470 CSI optics FT-IR instrument while the Raman spectra were recorded using a Bruker Vortex 70 RT-DLaTGS RAM II instrument. The powder X-ray diffraction pattern was recorded on a Rigaku multiflex diffractometer.

Synthesis of $Cp_2Zr(H)NH_2BH_3$, 1

THF (30 mL) was condensed over a mixture of ammonia borane (0.302 g, 9.8 mmol) and Cp_2ZrCl_2 (1.43 g, 4.9 mmol). The reactants dissolved upon warming up to room temperature and the solution was subsequently cooled to -78 ˚C. *n*BuLi (1.6 M in hexanes, 6.07 mL, 9.7 mmol) was added, the mixture was stirred at -78 ˚C for 2 hours and then allowed to warm to room temperature. The solvent was removed in vacuum, benzene (25 mL) was added to the remaining solid and the slurry was filtered. $Cp_2Zr(H)NH_2BH_3$ (0.98 g, 3.5 mmol, 71%) was isolated upon removal of benzene in vacuum. X-ray quality single crystals were obtained by cooling a saturated toluene solution to -35 °C. The solid compound could be handled in the air for short periods of time, but showed signs of hydrolysis with formation of ammonia borane after exposure to the air for a few hours.

EA: Calcd.: C 47.60, H 6.41, N, 5.55. Found: C 47.49, H 6.45, N 5.42.

IR (KBr): ν(cm^{-1}) = 3377 (w, NH), 3305 (m, NH), 3081 (w, CH), 2376 (s, BH_{term}), 2304 (m, BH_{term}), 1899 (w, $BH_{bridging}$), 1824 (m, $BH_{bridging}$), 1553 (s, ZrH).

Raman: ν(cm^{-1})= 3115 (m, CH), 3085 (m, CH), 2380 (m, BH_{term}), 2308 (w, BH_{term}).

^1H NMR (C_6D_6, 400 MHz, 20 °C): **Isomer 1** (~50%) δ (ppm) = 0.15 (q, br, 3H, $B\underline{H}_3$, $^1J_{BH}$ = 91.0 Hz), 0.49, (s, br, 2H, $N\underline{H}_2$), 3.58 (s, 1H, $Zr\underline{H}$), 5.43 (s, 10H, $C_5\underline{H}_5$); **Isomer 2** (~50%) δ (ppm) =

0.10, (s, br, 2H, N$\underline{H}_2$), 0.15 (q, br, 3H, B$\underline{H}_3$ $^1J_{BH}$ = 91.0 Hz), 3.61 (s, 1H, Zr$\underline{H}$), 5.29 (s, 10H, $C_5\underline{H}_5$).

^{1}H NMR (THF-d_8, 400 MHz, 20 °C): **Isomer 1** (~66%) δ (ppm) = -0.44 (q, br, 3H, B$\underline{H}_3$, $^1J_{BH}$ = 88.0 Hz), 1.41 (s, br, 2H, N$\underline{H}_2$), 3.12 (s, 1H, Zr$\underline{H}$), 5.71 (s, 10H, $C_5\underline{H}_5$); **Isomer 2** (~33%) δ (ppm) = -0.44(q, br, 3H, B$\underline{H}_3$, $^1J_{BH}$ = 88.0 Hz), 1.41 (s, br, 2H, N$\underline{H}_2$), 3.49 (s, 1H, Zr$\underline{H}$), 5.76 (s, 10H, $C_5\underline{H}_5$).

^{1}H NMR (toluene-d_8, 400 MHz, 20 °C): **Isomer 1** (identified as **1a**) (~50%) δ (ppm) = -0.34 (q, br, 3H, B$\underline{H}_3$, 0.44, (s, br, 2H, N$\underline{H}_2$), 3.51 (s, 1H, Zr$\underline{H}$), 5.41 (s, 10H, $C_5\underline{H}_5$); **Isomer 2** (identified as **1b**) (~50%) δ (ppm) = 0.06, (s, br, 2H, N$\underline{H}_2$), 0.06 (q, br, 3H, B$\underline{H}_3$ $^1J_{BH}$ = 91.0 Hz), 3.51 (s, 1H, Zr$\underline{H}$), 5.28 (s, 10H, $C_5\underline{H}_5$).

^{1}H NMR (toluene-d_8, 400 MHz, 60 °C): **Isomer 1** (identified as **1a**) (~50%) δ (ppm) = -0.38 (q, br, 3H, B$\underline{H}_3$, 0.45, (s, br, 2H, N$\underline{H}_2$), 3.56 (s, 1H, Zr$\underline{H}$), 5.43 (s, 10H, $C_5\underline{H}_5$); **Isomer 2** (identified as **1b**) (~50%) δ (ppm) = 0.01 (q, br, 3H, B$\underline{H}_3$ $^1J_{BH}$ = 91.0 Hz), 0.09, (s, br, 2H, N$\underline{H}_2$), 3.53 (s, 1H, Zr$\underline{H}$), 5.31 (s, 10H, $C_5\underline{H}_5$).

^{1}H NMR (toluene-d_8, 400 MHz, -60 °C): **Isomer 1** (identified as **1a**) (~50%) δ (ppm) = -2.88 (q, br, 1H, B-$\mu\underline{H}$-Zr), 0.53, (s, br, 2H, N$\underline{H}_2$), 1.11 (q, br, 3H, B$\underline{H}_2$, 3.49 (s, 1H, Zr$\underline{H}$), 5.36 (s, 10H, $C_5\underline{H}_5$); **Isomer 2** (identified as **1b**) (~50%) δ (ppm) = 0.16, (s, br, 2H, N$\underline{H}_2$), 0.26 (q, br, 3H, B$\underline{H}_3$ $^1J_{BH}$ = 91.0 Hz), 3.40 (s, 1H, Zr$\underline{H}$), 5.21 (s, 10H, $C_5\underline{H}_5$).

^{11}B NMR (C_6D_6, 128.4 MHz, 20 °C): **Isomer 1** δ (ppm) = -33.9 (q, $^1J_{BH}$ = 91.0 Hz); **Isomer 2** δ (ppm) = -33.5 (q, $^1J_{BH}$ = 91.0 Hz).

^{11}B NMR (THF-d_8, 128.4 MHz, 20 °C): **Isomer 1** δ (ppm) = -34.0 (q, $^1J_{BH}$ = 88.0 Hz); **Isomer 2** δ (ppm) = -34.3 (q, $^1J_{BH}$ = 88.0 Hz).

^{11}B NMR (toluene-d_8, 128.4 MHz, 20 °C): **Isomer 1** δ (ppm) = -33.5 (q, $^1J_{BH}$ = 88.0 Hz); **Isomer 2** δ (ppm) = -33.9 (q, $^1J_{BH}$ = 88.0 Hz).

^{13}C NMR (C_6D_6, 100.6 MHz, 20 °C): **Isomer 1** δ 103.88 ($\underline{C}_5H_5$); **Isomer 2** δ 103.91 ($\underline{C}_5H_5$).

^{13}C NMR (THF-d_8, 100.6 MHz, 20 °C): **Isomer 1** δ (ppm) = 104.25 ($\underline{C}_5H_5$); **Isomer 2** δ (ppm) = 104.16 ($\underline{C}_5H_5$).

^{13}C NMR (toluene-d_8, 100.6 MHz, 20 °C): **Isomer 1** δ (ppm) = 103.84 ($\underline{C}_5H_5$); **Isomer 2** δ (ppm) = 103.87 ($\underline{C}_5H_5$).

Synthesis of $Cp^*_2Zr(H)NH_2BH_3$, 2

THF (30 mL) was condensed over a mixture of ammonia borane (0.1 g, 3.2 mmol) and $Cp^*_2ZrCl_2$ (0.7 g, 1.6 mmol). The reactants dissolved upon warming up to room temperature and the solution was subsequently cooled to -78 ˚C. *n*BuLi (1.6 M in hexanes, 2.02 mL, 3.2mmol) was added, the mixture was stirred at -78 ˚C for 2 hours and then allowed to warm to room temperature. The solvent was removed in vacuum, benzene (25 mL) was added to the remaining solid and the slurry was filtered. $Cp^*_2Zr(H)NH_2BH_3$ (0.52 g, 2.06 mmol, 64%) was isolated upon removal of benzene in vacuum. X-ray quality single crystals were obtained by slow evaporation of a toluene solution.

IR (KBr): $\nu(cm^{-1})$ = 3430 (w, NH), 3366 (w, NH), 2903 (m, CH), 2390 (m, BH_{term}), 2318 (m, BH_{term}), 1892 (w, $BH_{bridging}$), 1819 (w, $BH_{bridging}$), 1531 (m ZrH).

Raman: $\nu(cm^{-1})$ = 2904 (vs, CH), 2397 (w, BH_{term}), 2321 (w, BH_{term}).

^1H NMR (C_6D_6, 400 MHz, 20 °C): **Isomer 1** (~80): ^1H NMR δ (ppm) = -0.10, (s, br, 2H, $N\underline{H}_2$), -0.05 (q, br, 3H, $B\underline{H}_3$, $^1J_{BH}$ = 90 Hz), 1.76 (s, 30H, $C_5(C\underline{H}_3)_5$), 4.15 (s, 1H, $Zr\underline{H}$); **Isomer 2** (~20%) δ (ppm) = -0.05 (q, br, 3H, $B\underline{H}_3$, $^1J_{BH}$ = 90 Hz), 0.40, (s, br, 2H, $N\underline{H}_2$), 1.84 (s, 30H, $C_5(C\underline{H}_3)_5$), 4.08 (s, 1H, $Zr\underline{H}$).

^{11}B NMR (C_6D_6, 128.4 MHz, 20 °C): **Isomer 1** δ (ppm) = -29.6 (q, $^1J_{BH}$ = 90 Hz); **Isomer 2** δ (ppm) = -31.9 (q, $^1J_{BH}$ = 90 Hz).

^{13}C NMR (C_6D_6, 100.6 MHz, 20 °C): **Isomer 1** δ (ppm) = 11.76 ($C_5(\underline{C}H_3)_5$), 114.06 ($\underline{C}_5(CH_3)_5$); **Isomer 2** δ (ppm) = 12.26 ($C_5(\underline{C}H_3)_5$), 115.09 ($\underline{C}_5(CH_3)_5$).

Synthesis of $Cp_2Zr(Cl)NH_2BH_3$, 3

THF (30 mL) was condensed over a mixture of ammonia borane (0.3 g, 9.7 mmol) and Cp_2ZrCl_2 (2.84 g, 9.7 mmol). The reactants dissolved upon warming up to room temperature and the solution was subsequently cooled to -78 °C. *n*BuLi (1.6 M in hexanes, 6.07 mL, 9.7 mmol) was added, the mixture was stirred at -78 °C for 2 hours and then allowed to warm to room temperature. The solvent was removed in vacuum, benzene (25 mL) was added to the remaining solid and the slurry was filtered. $Cp_2Zr(Cl)NH_2BH_3$ (1.48 g, 5.9 mmol, 60%) was isolated upon removal of benzene in vacuum. X-ray quality single crystals were obtained by cooling a saturated toluene solution to -35 °C.

EA: Calcd.: C 41.88, H 5.28, N, 4.89. Found: C 41.92, H 5.34, N 3.95.

IR (KBr): ν(cm^{-1}) = 3384 (m, NH), 3280 (s, NH), 3097 (m, CH), 2393 (s, BH_{term}), 2320 (m, BH_{term}), 1868 (m, $BH_{bridging}$), 1792 (m, $BH_{bridging}$).

Raman: ν(cm^{-1})= 3115 (m, CH), 3091 (m, CH), 2395 (s, BH_{term}), 2323 (m, BH_{term}).

^{1}H NMR (C_6D_6, 400 MHz, 20 °C): **Isomer 1** (~80%) δ (ppm) = 0.36 (q, br, 3H, B$\underline{H}_3$, $^{1}J_{BH}$ = 93.7 Hz), 1.46, (s, br, 2H, N$\underline{H}_2$), 5.61 (s, 10H, $C_5\underline{H}_5$); **Isomer 2** (~20%) δ (ppm) = 0.36 (q, br, 3H, B$\underline{H}_3$, $^{1}J_{BH}$ = 93.7 Hz), 1.46, (s, br, 2H, N$\underline{H}_2$), 6.01 (s, 10H, $C_5\underline{H}_5$).

^{1}H NMR (THF-d_8, 400 MHz, 20 °C): **Isomer 1** (~85%) ^{1}H NMR δ (ppm) = 0.20 (q, br, 3H, B$\underline{H}_3$, $^{1}J_{BH}$ = 94.4 Hz), 2.76, (s, br, 2H, N$\underline{H}_2$), 6.08 (s, 10H, $C_5\underline{H}_5$); **Isomer 2** (~15%) δ (ppm) = 0.20 (q, br, 3H, B$\underline{H}_3$, $^{1}J_{BH}$ = 94.4 Hz), 2.76, (s, br, 2H, N$\underline{H}_2$), 6.37 (s, 10H, $C_5\underline{H}_5$);

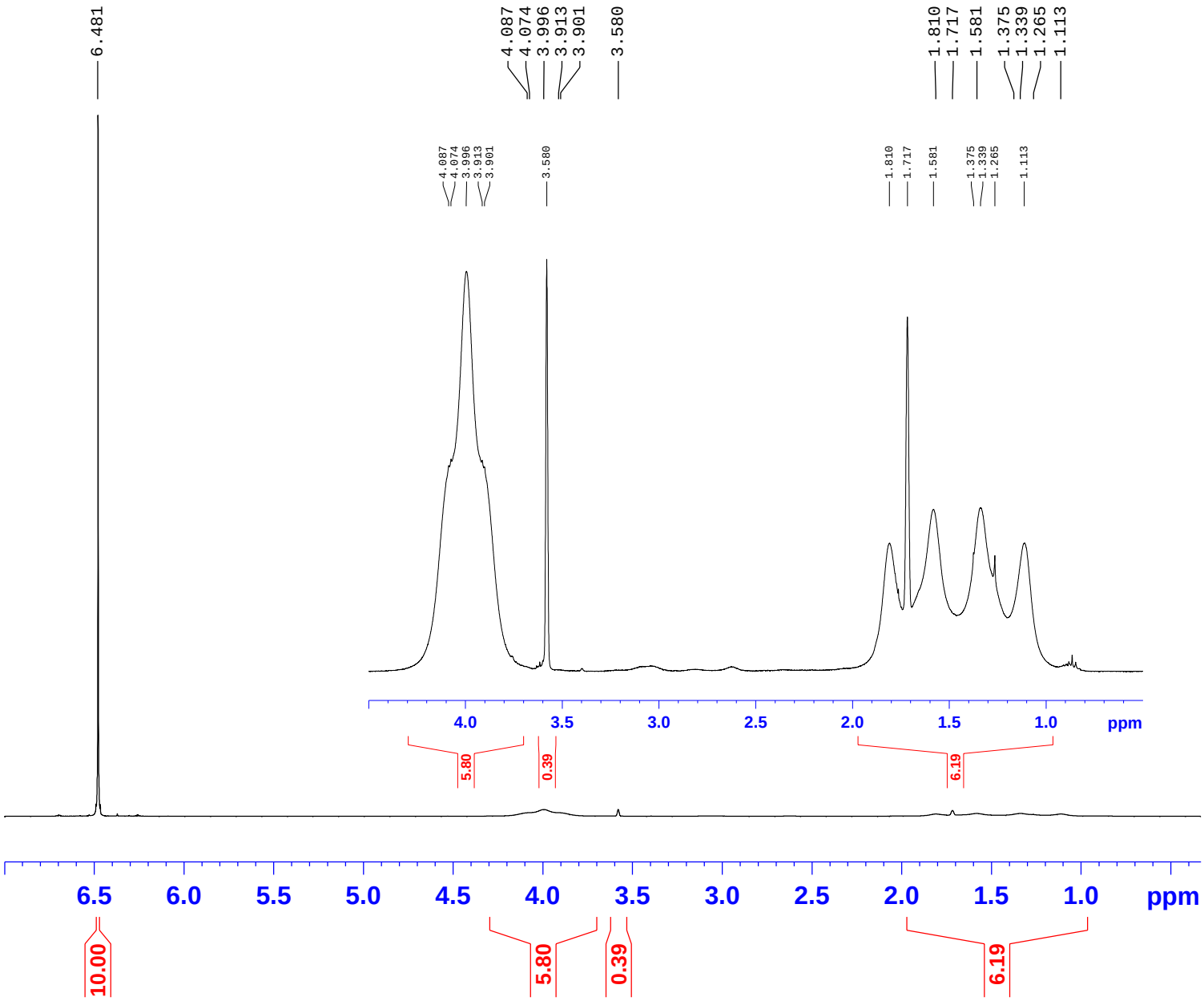
^{11}B NMR (C_6D_6, 128.4 MHz, 20 °C): **Isomer 1** δ (ppm) = -22.6 (q, $^{1}J_{BH}$ = 93.7 Hz); **Isomer 2** δ (ppm) = -21.2 (q, $^{1}J_{BH}$ = 93.7 Hz).

^{11}B NMR (THF-d_8, 128.4 MHz, 20 °C): **Isomer 1** δ (ppm) = -23.0 (q, $^{1}J_{BH}$ = 94.4 Hz); **Isomer 2** δ (ppm) = -22.4 (q, $^{1}J_{BH}$ = 94.4 Hz).

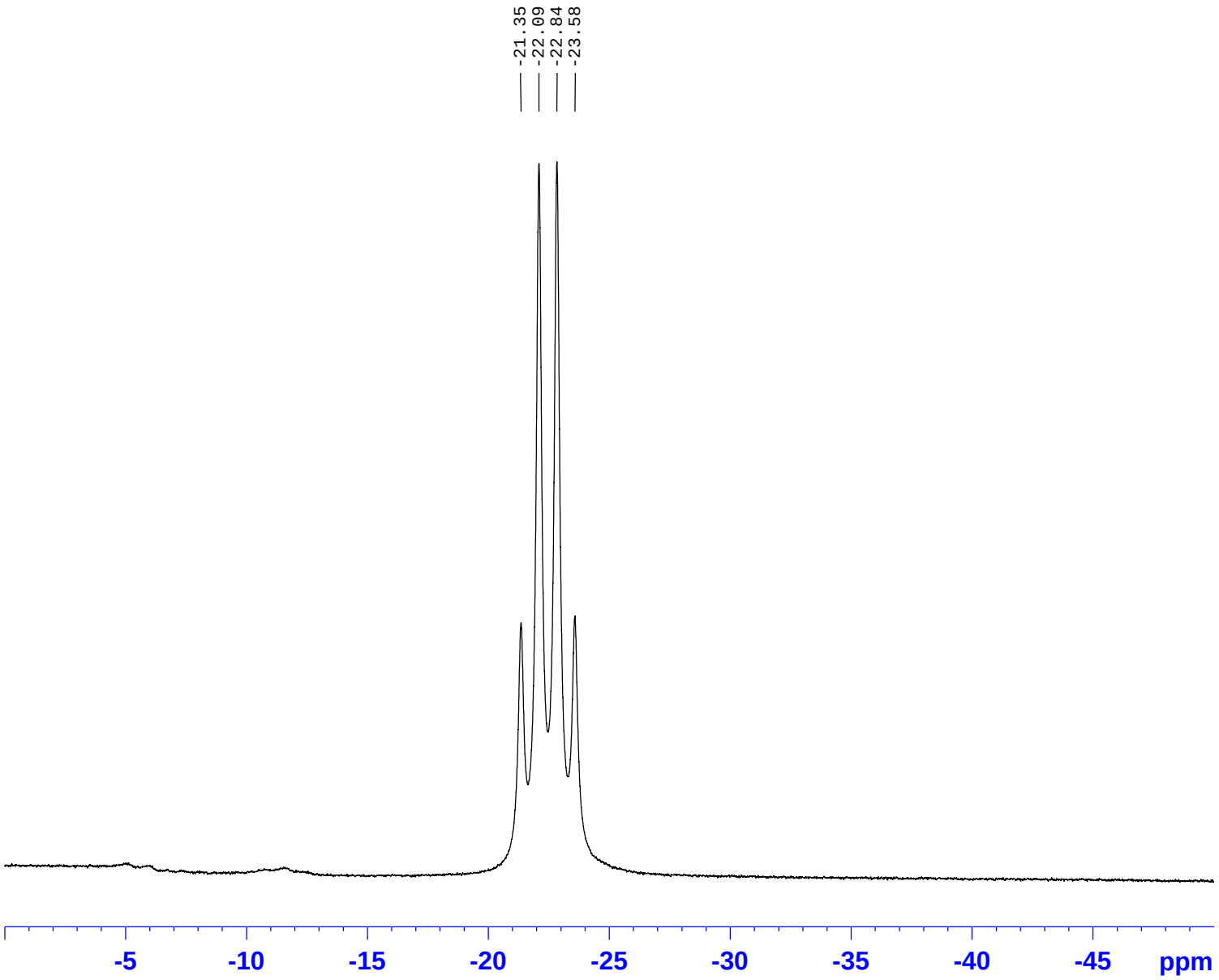
^{13}C NMR (C_6D_6, 100.6 MHz, 20 °C): **Isomer 1** δ (ppm) = 111.72 ($\underline{C}_5H_5$); **Isomer 2** δ (ppm) = 114.50 ($\underline{C}_5H_5$).

^{13}C NMR (THF-d_8, 100.6 MHz, 20 °C): **Isomer 1** δ (ppm) = 112.20 ($\underline{C}_5H_5$); δ (ppm) = 115.07 ($\underline{C}_5H_5$).

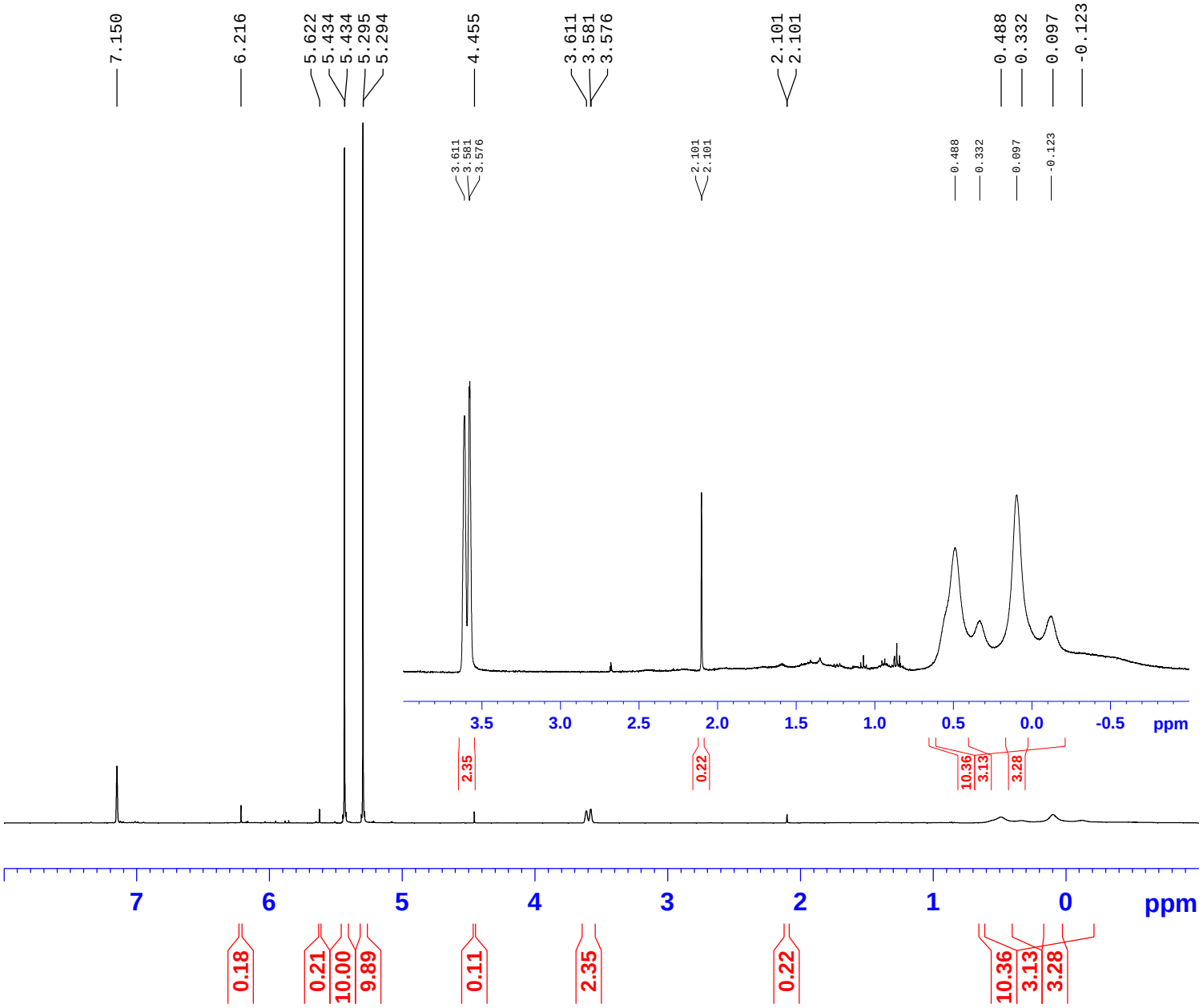
Cp_2ZrCl_2 – NH_3BH_3 1 :1 mixture, ^1H NMR in THF-d_8, 20 °C



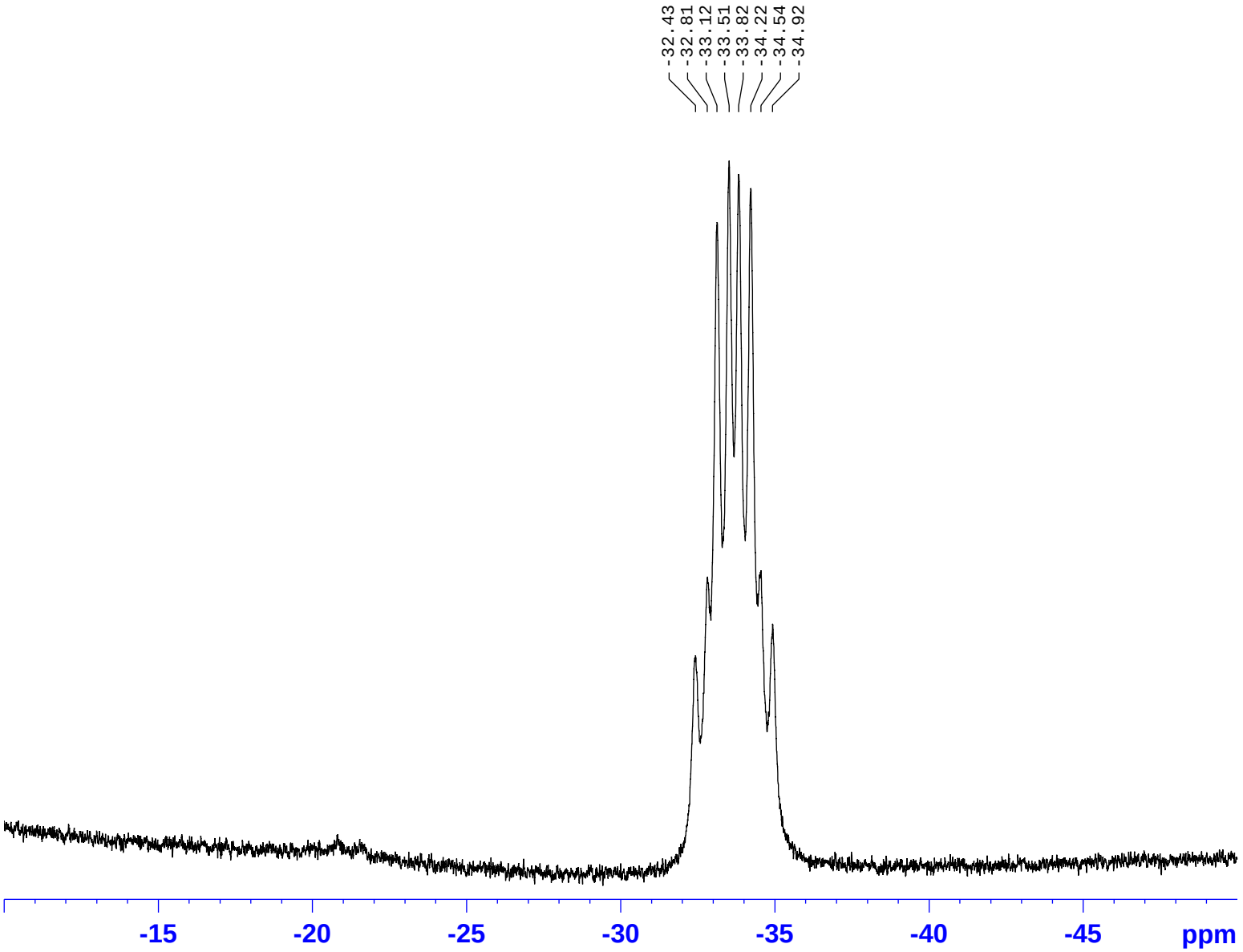
Cp_2ZrCl_2 – NH_3BH_3 1 :1 mixture, ^{11}B NMR in THF-d_8, 20 °C



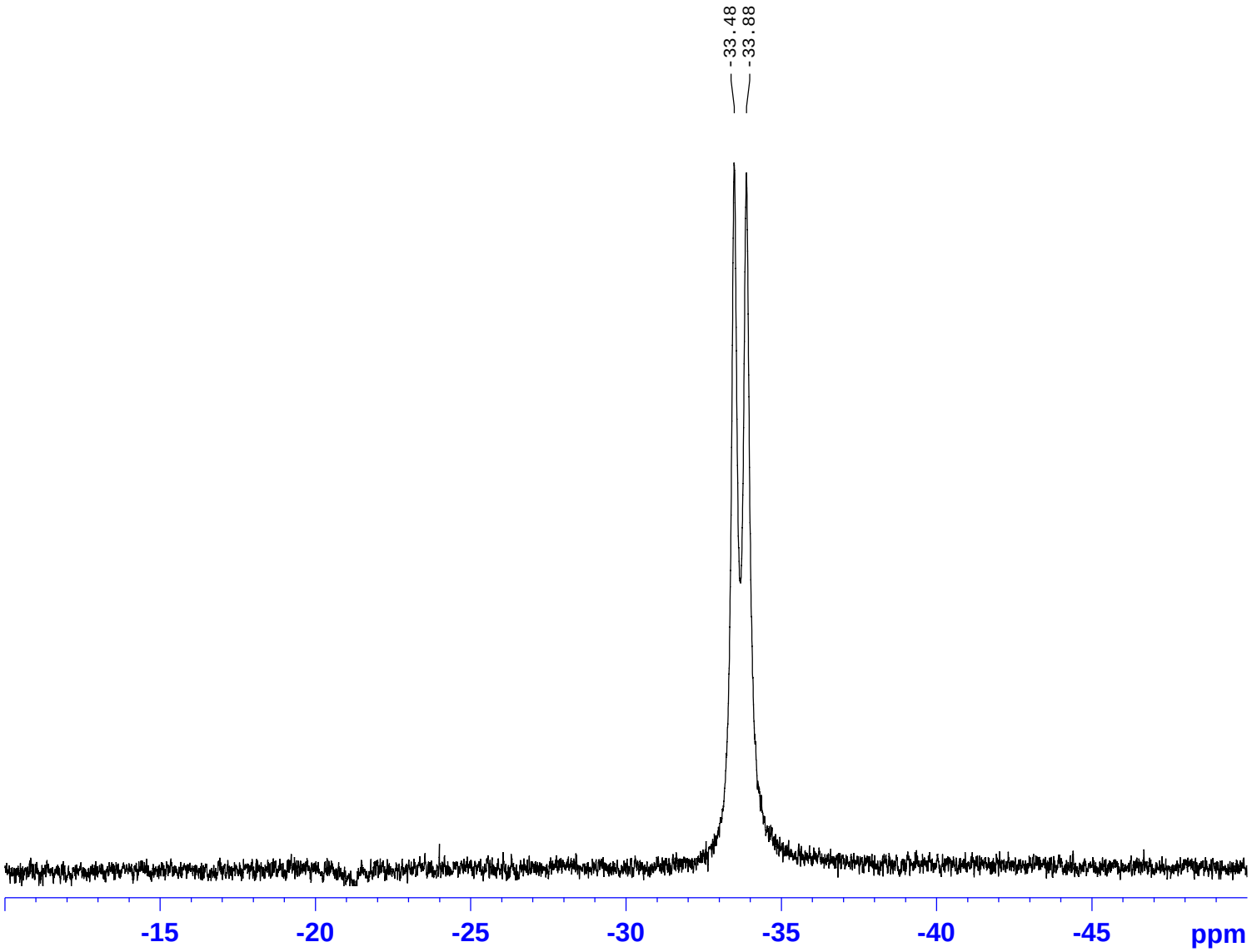
15 mg $Cp_2Zr(H)NH_2BH_3$, **1**, ^1H NMR in C_6D_6



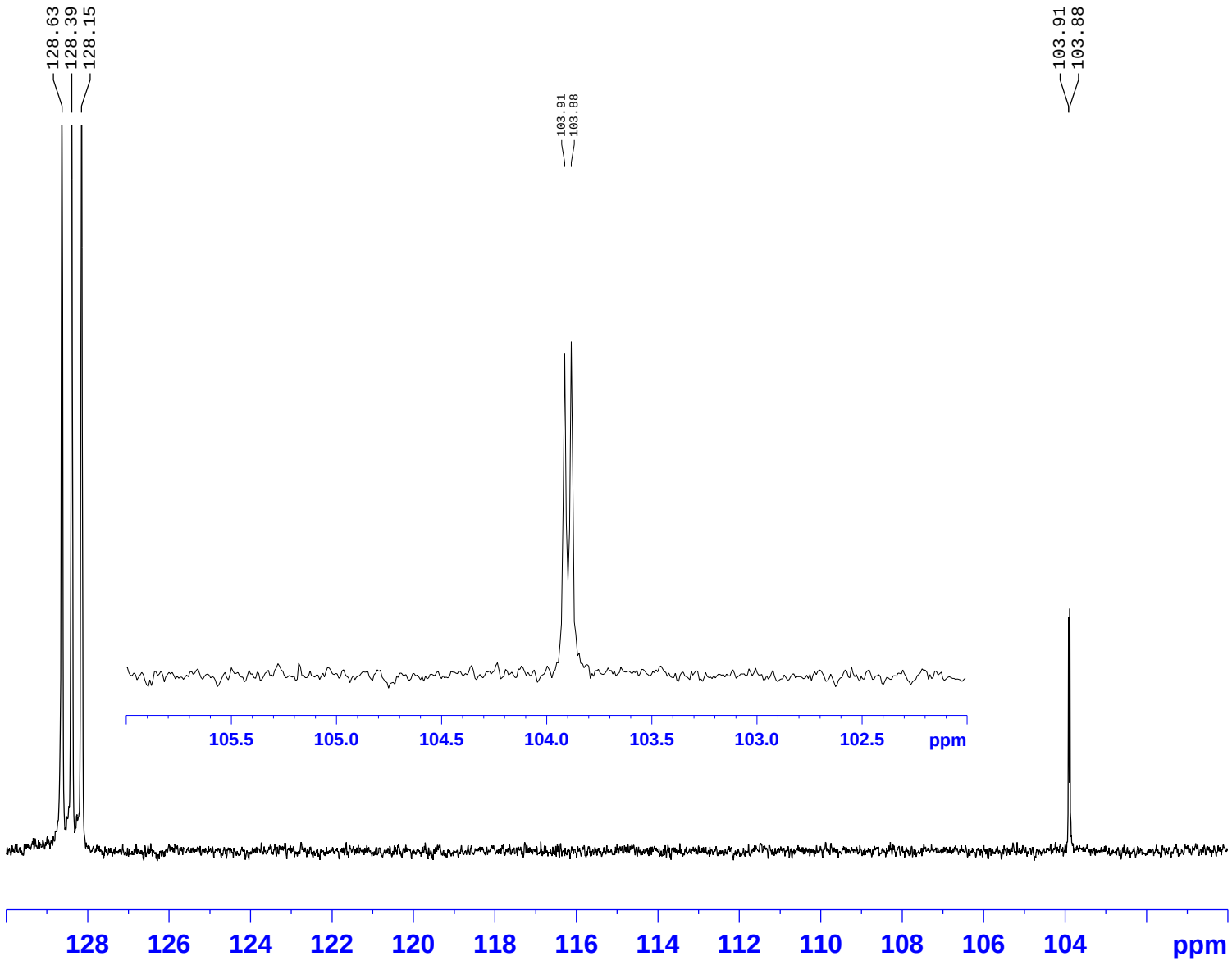
15 mg $Cp_2Zr(H)NH_2BH_3$, **1**, ^{11}B NMR in C_6D_6



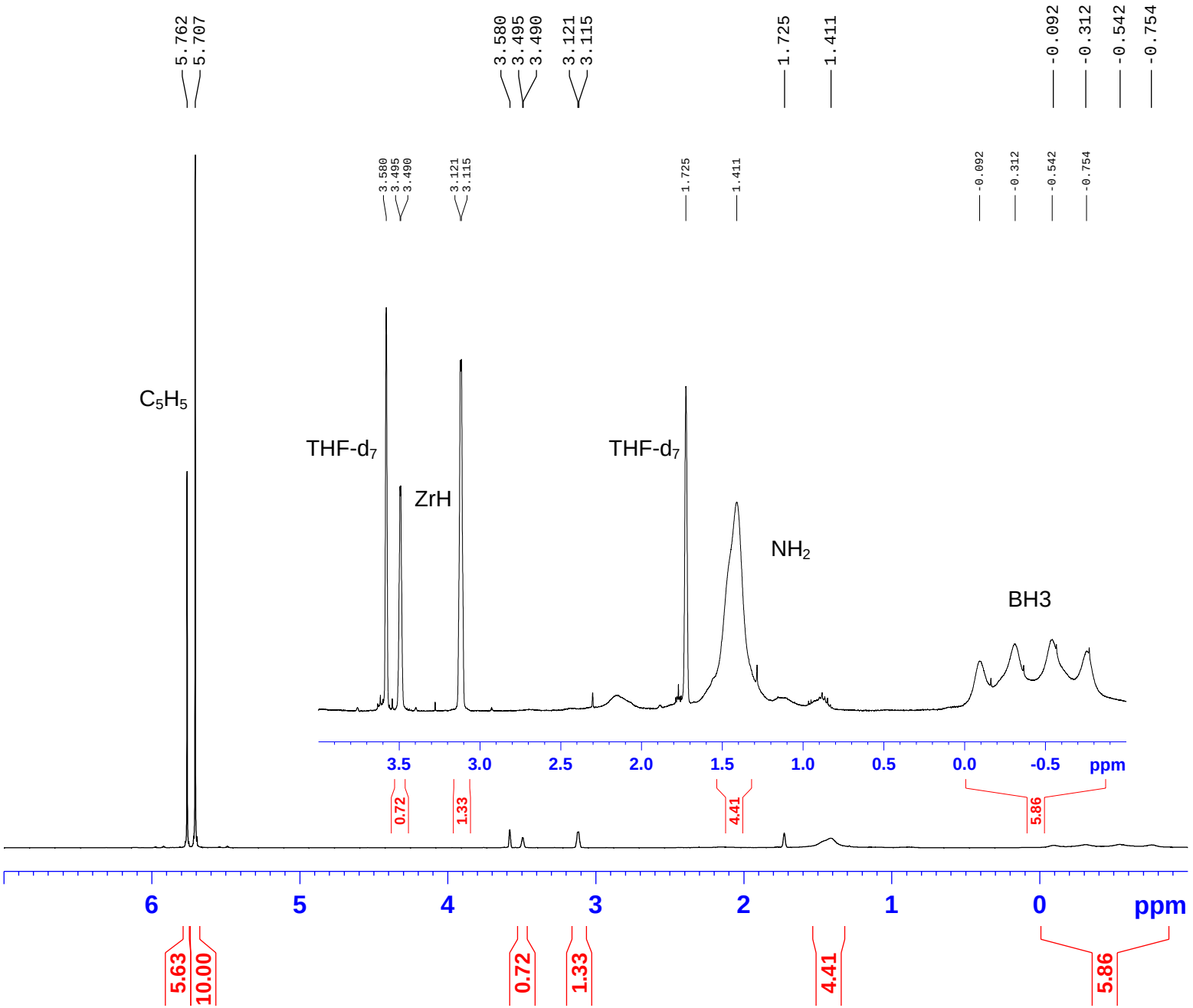
15 mg $Cp_2Zr(H)NH_2BH_3$, **1**, $^{11}B\{^1H\}$ NMR in C_6D_6



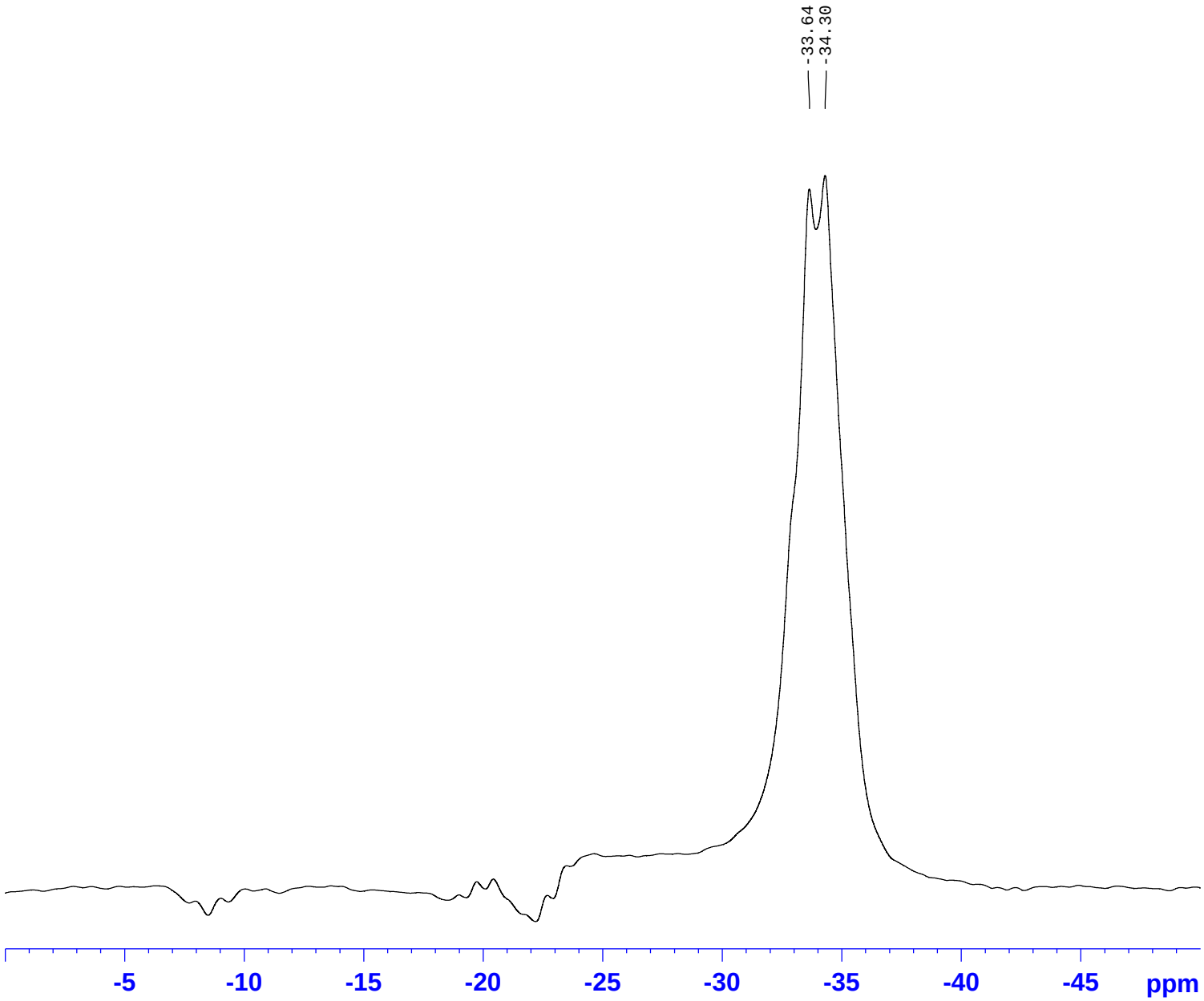
15 mg $Cp_2Zr(H)NH_2BH_3$, **1**, ^{13}C NMR in C_6D_6



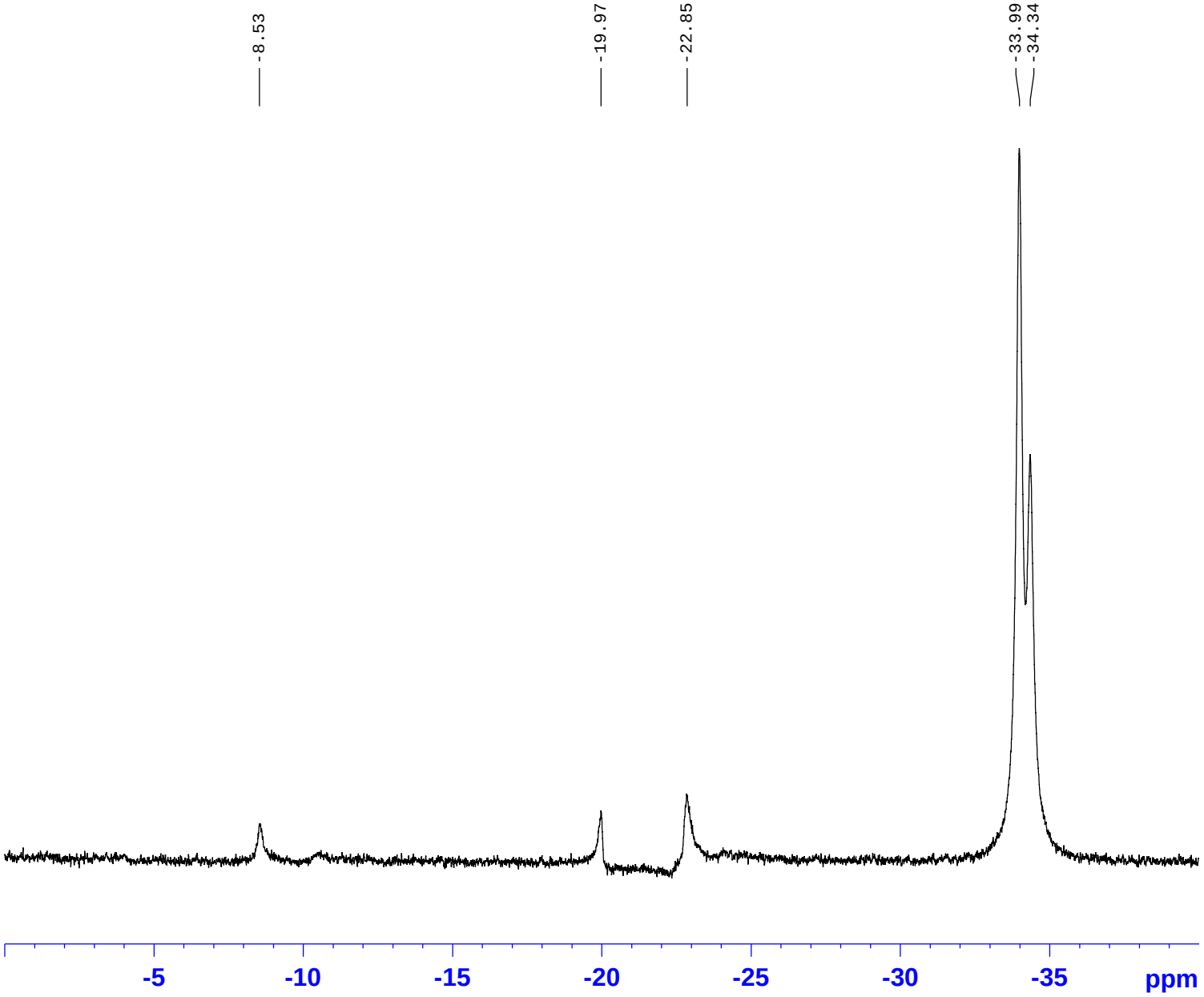
$Cp_2Zr(H)NH_2BH_3$, **1**, ^1H NMR in THF-d_8, 20 °C



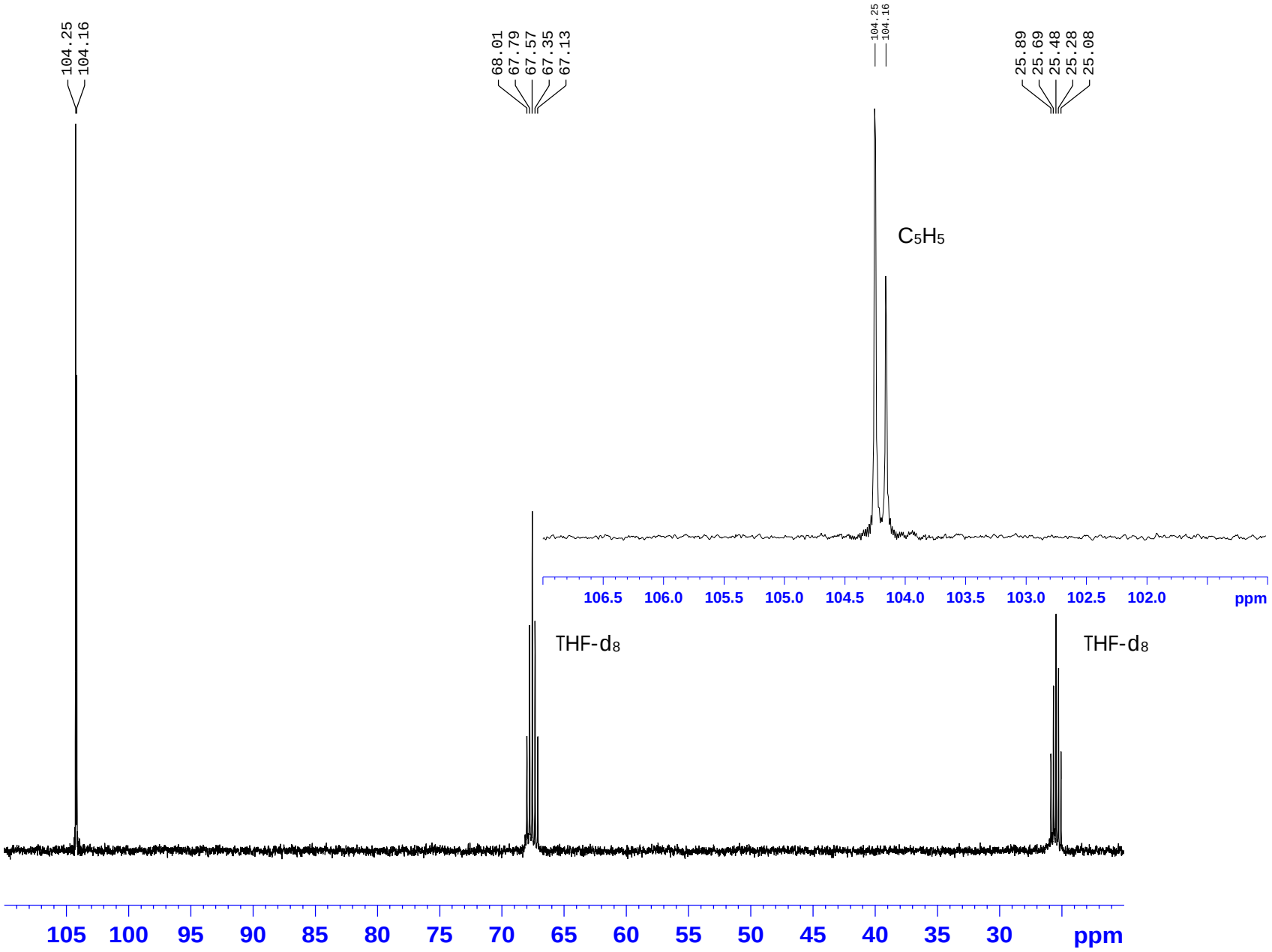
$Cp_2Zr(H)NH_2BH_3$, **1**, ^{11}B NMR in THF-d_8, 20 °C



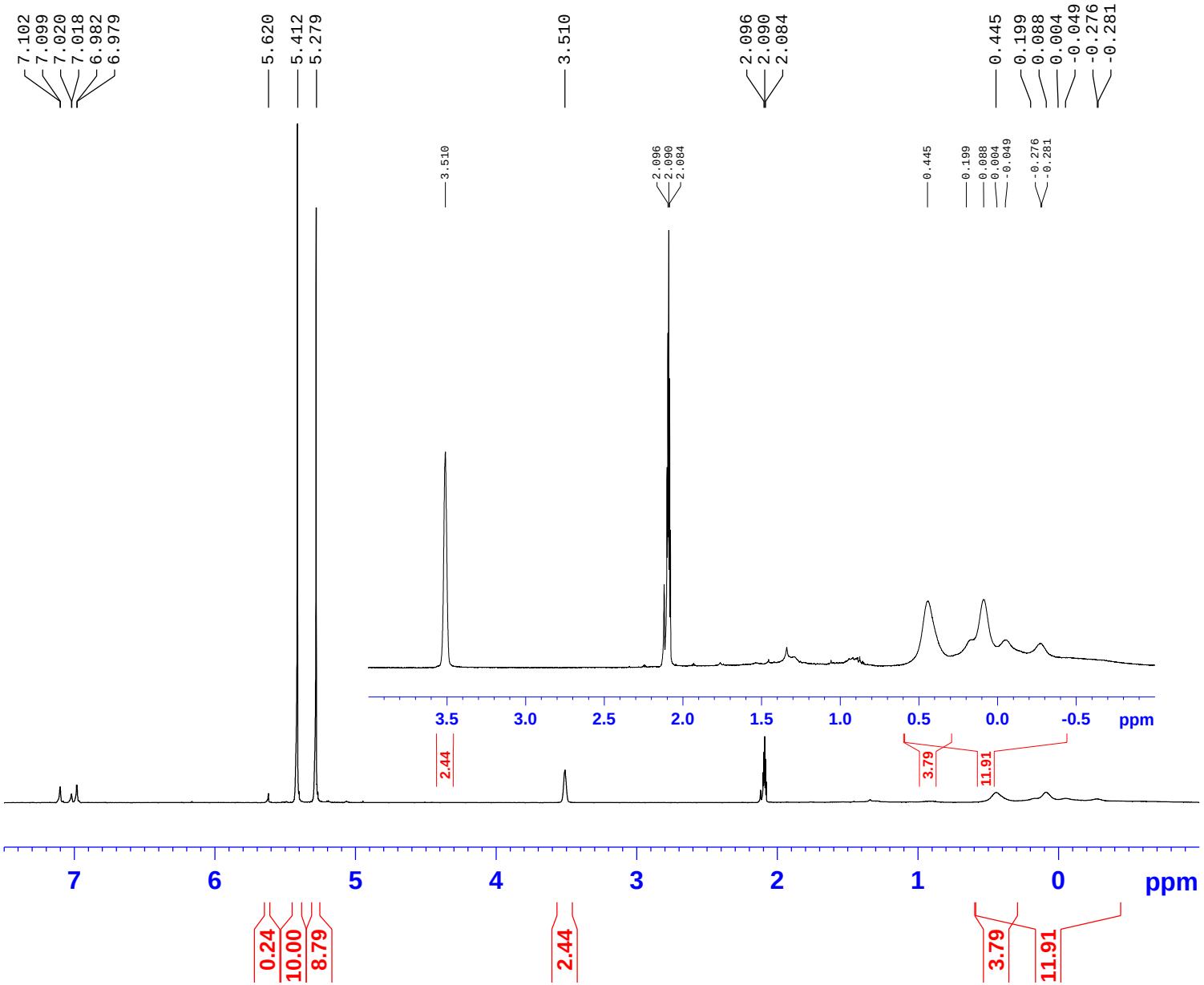
$Cp_2Zr(H)NH_2BH_3$, **1**, $^{11}B\{^1H\}$ NMR in THF-d_8, 20 °C



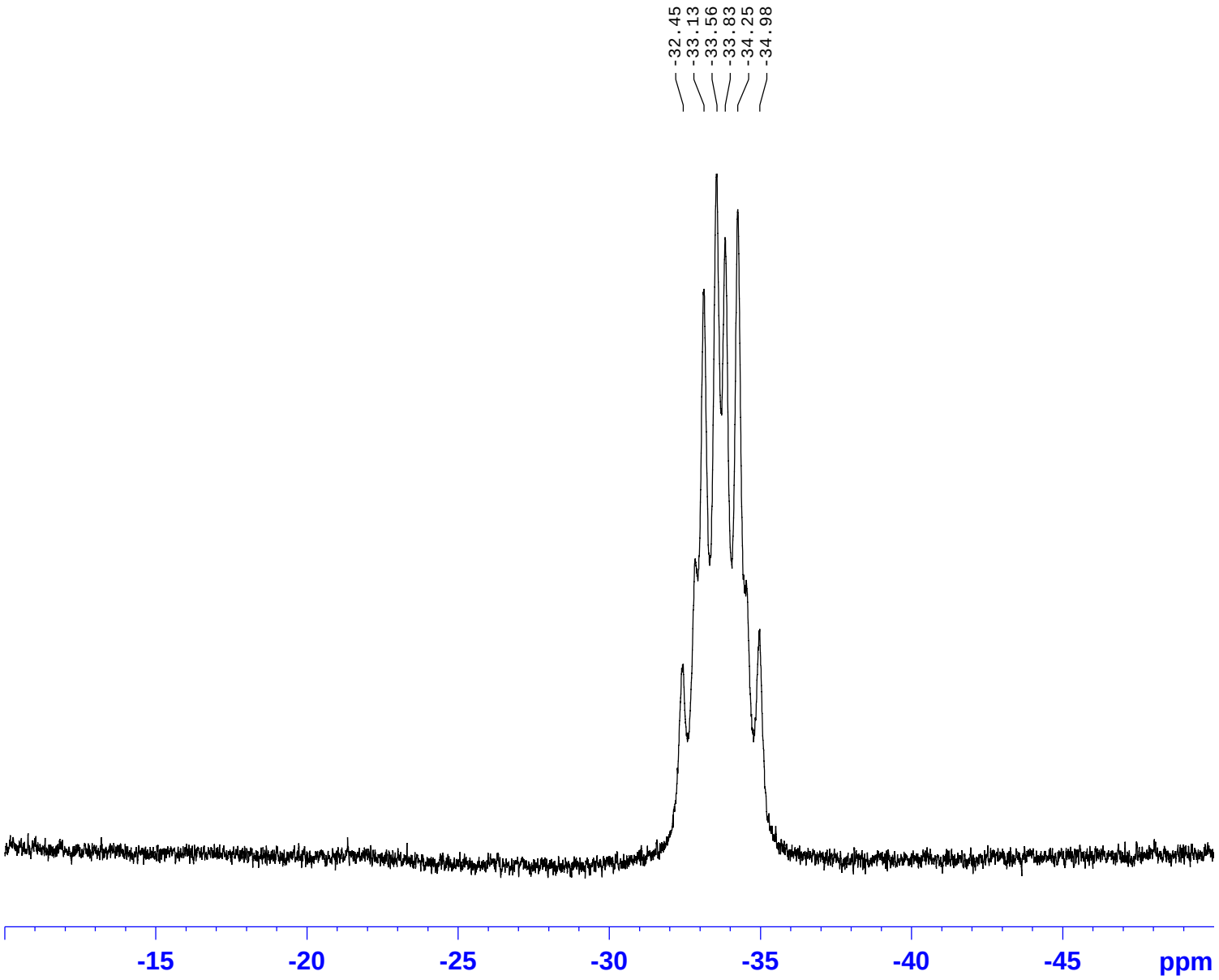
$Cp_2Zr(H)NH_2BH_3$, **1**, $^{13}C\{^1H\}$ NMR in THF-d_8, 20 °C



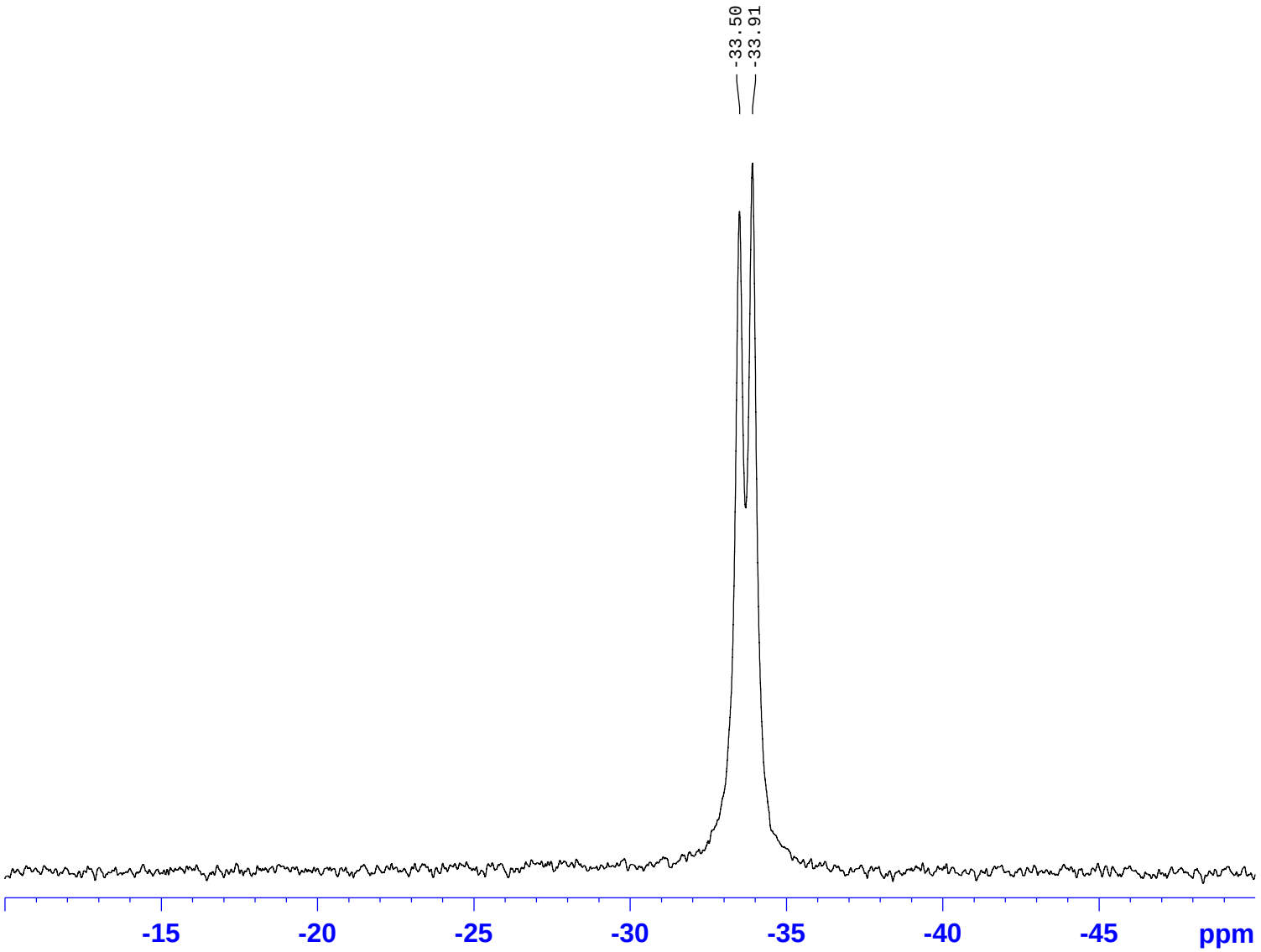
15 mg $Cp_2Zr(H)NH_2BH_3$, **1**, ^1H NMR in tol-d_8, 20 °C



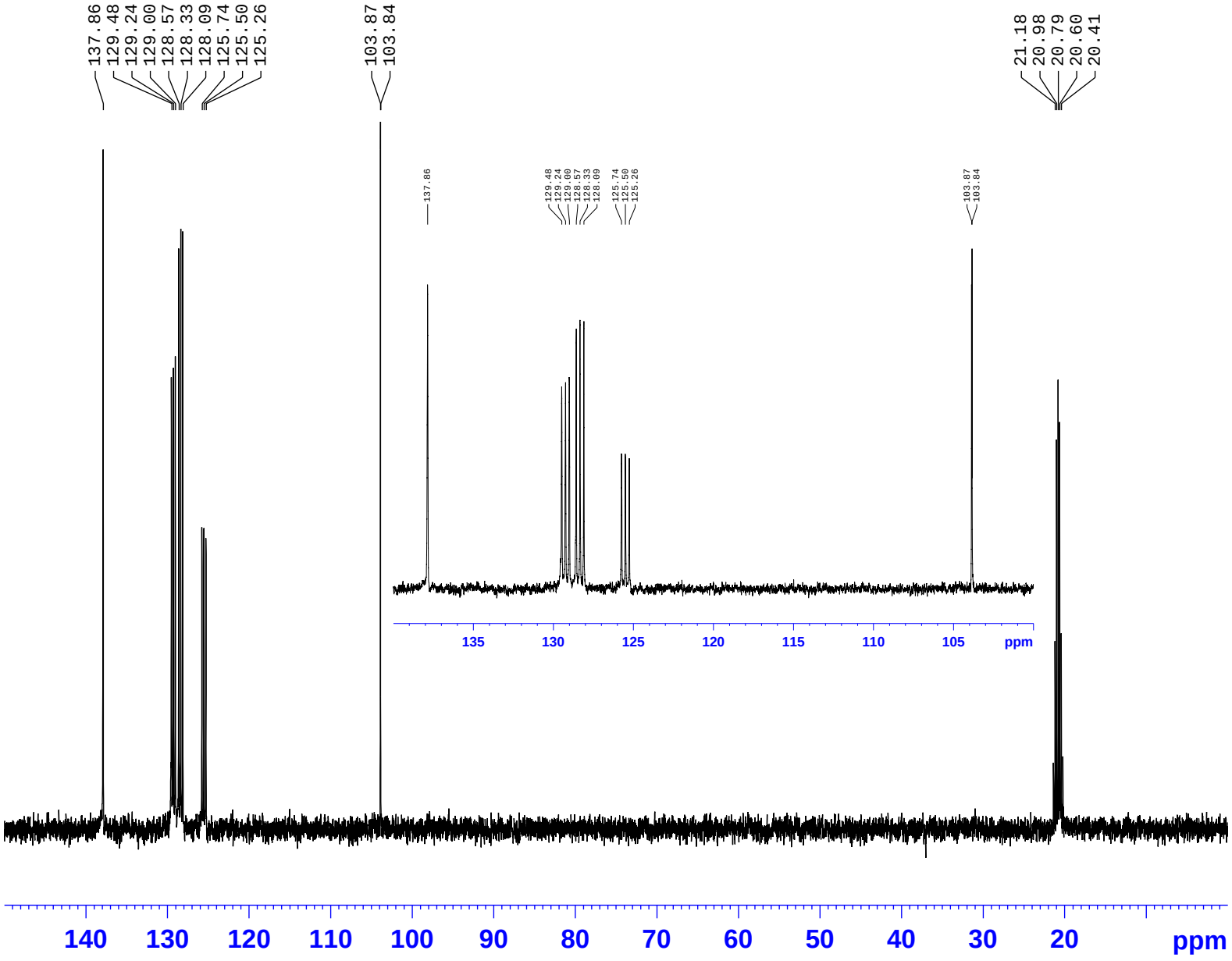
15 mg $Cp_2Zr(H)NH_2BH_3$, **1**, ^{11}B NMR in tol-d_8, 20 °C



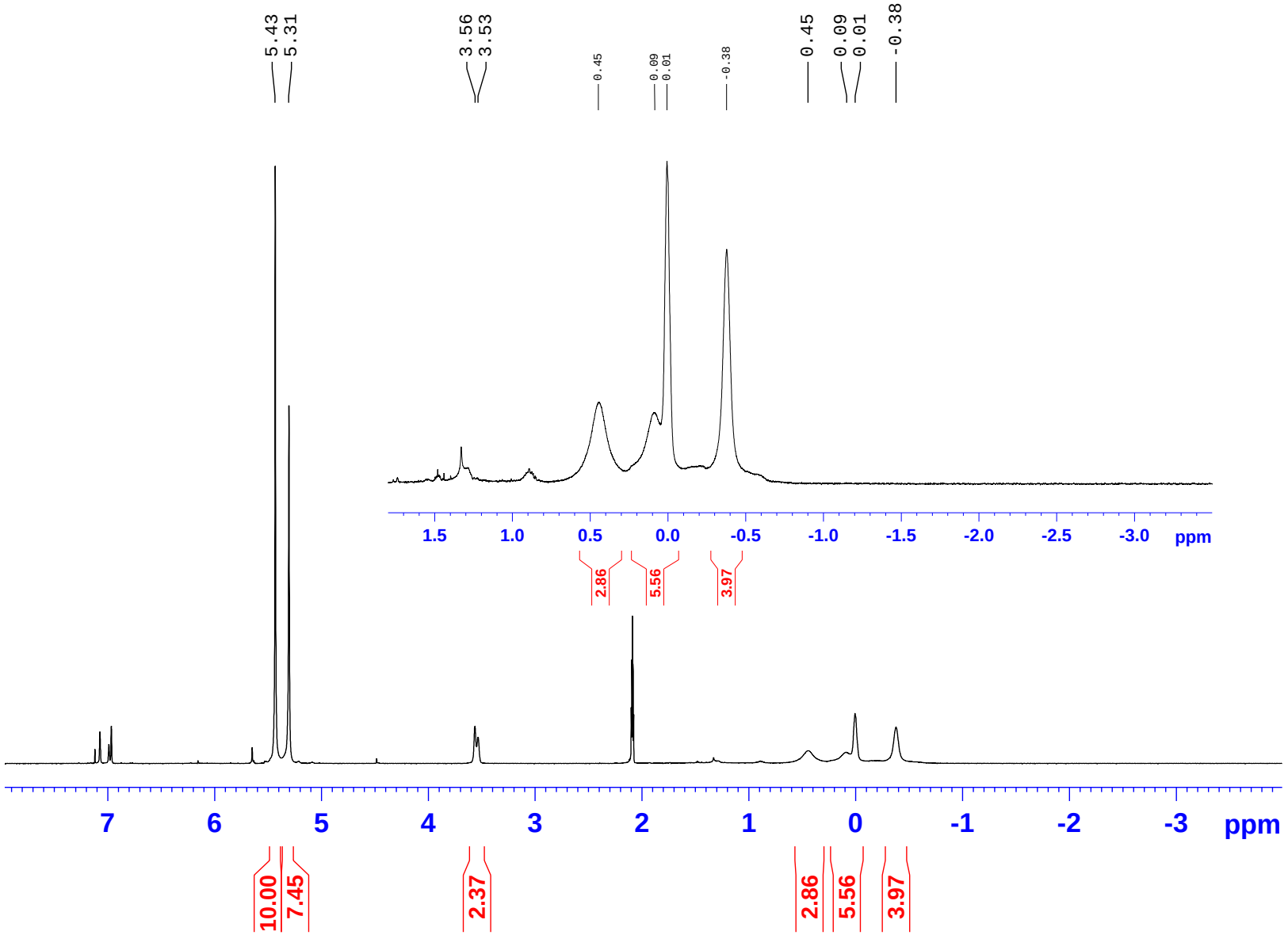
15 mg $Cp_2Zr(H)NH_2BH_3$, **1**, $^{11}B\{^1H\}$ NMR in tol-d_8, 20 °C



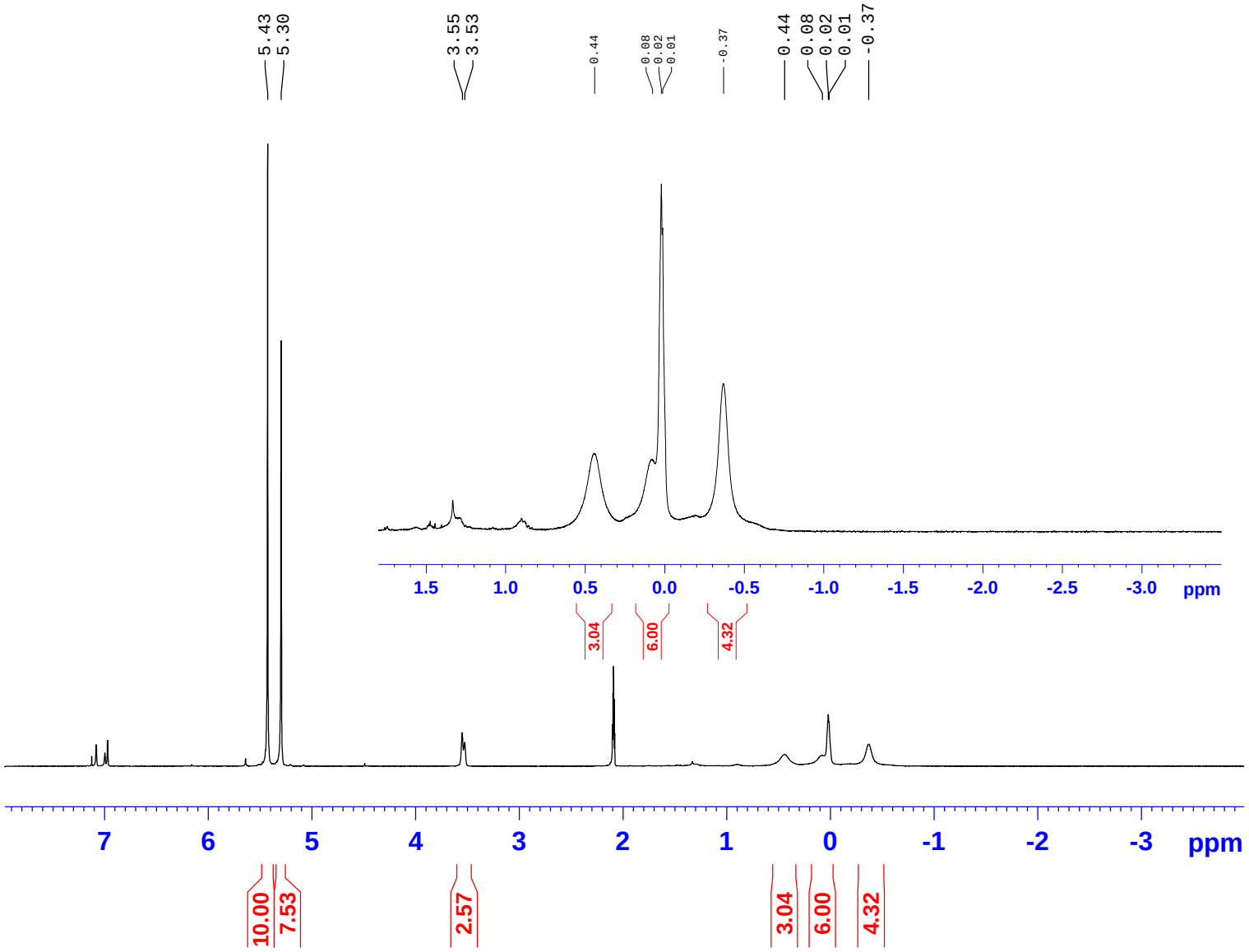
15 mg $Cp_2Zr(H)NH_2BH_3$, **1**, $^{13}C\{^1H\}$ NMR in tol-d_8, 20 °C



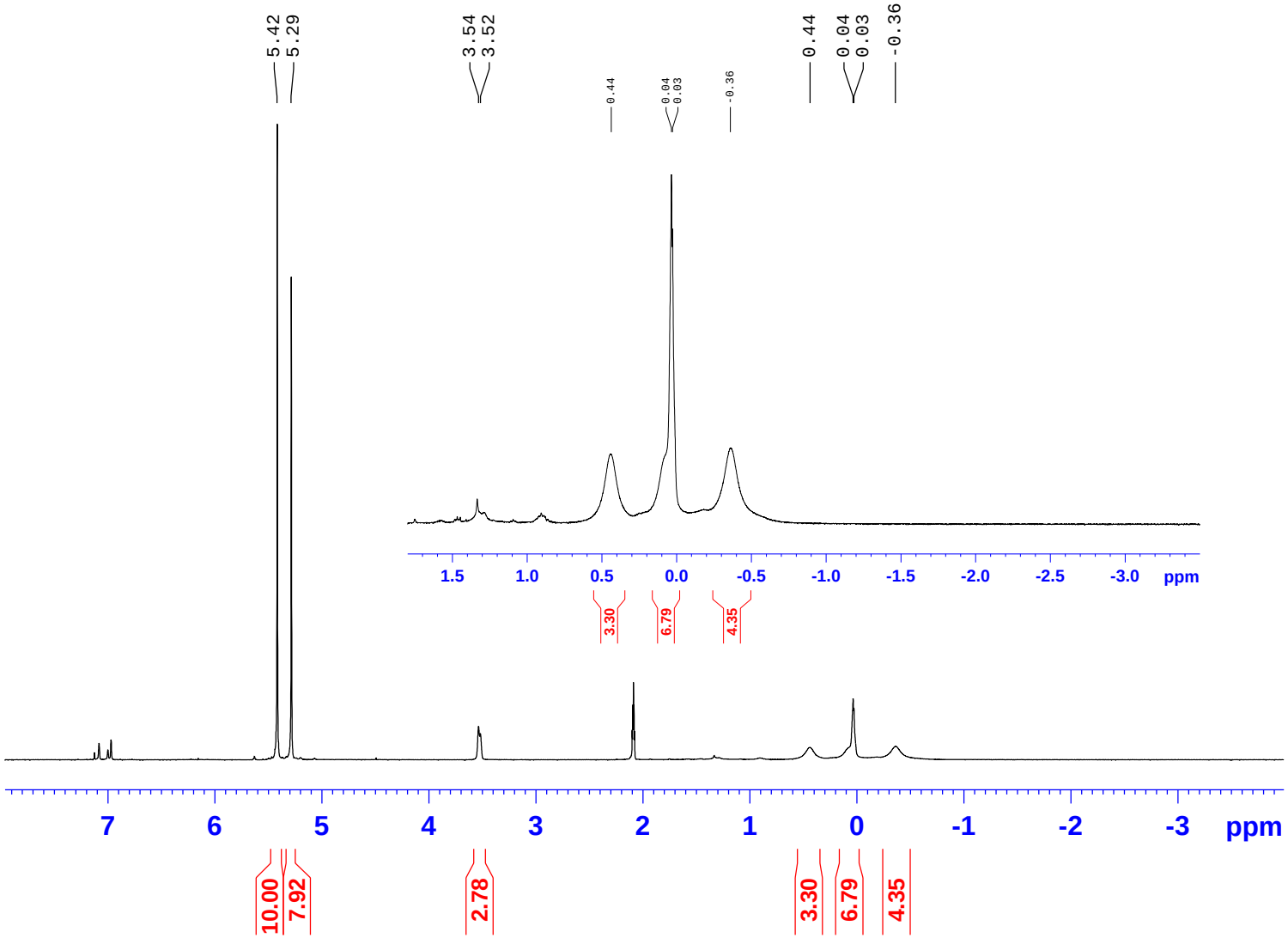
$Cp_2Zr(H)NH_2BH_3$, **1**, $^1H\{^{11}B\}$ NMR in tol-d_8, 60 °C



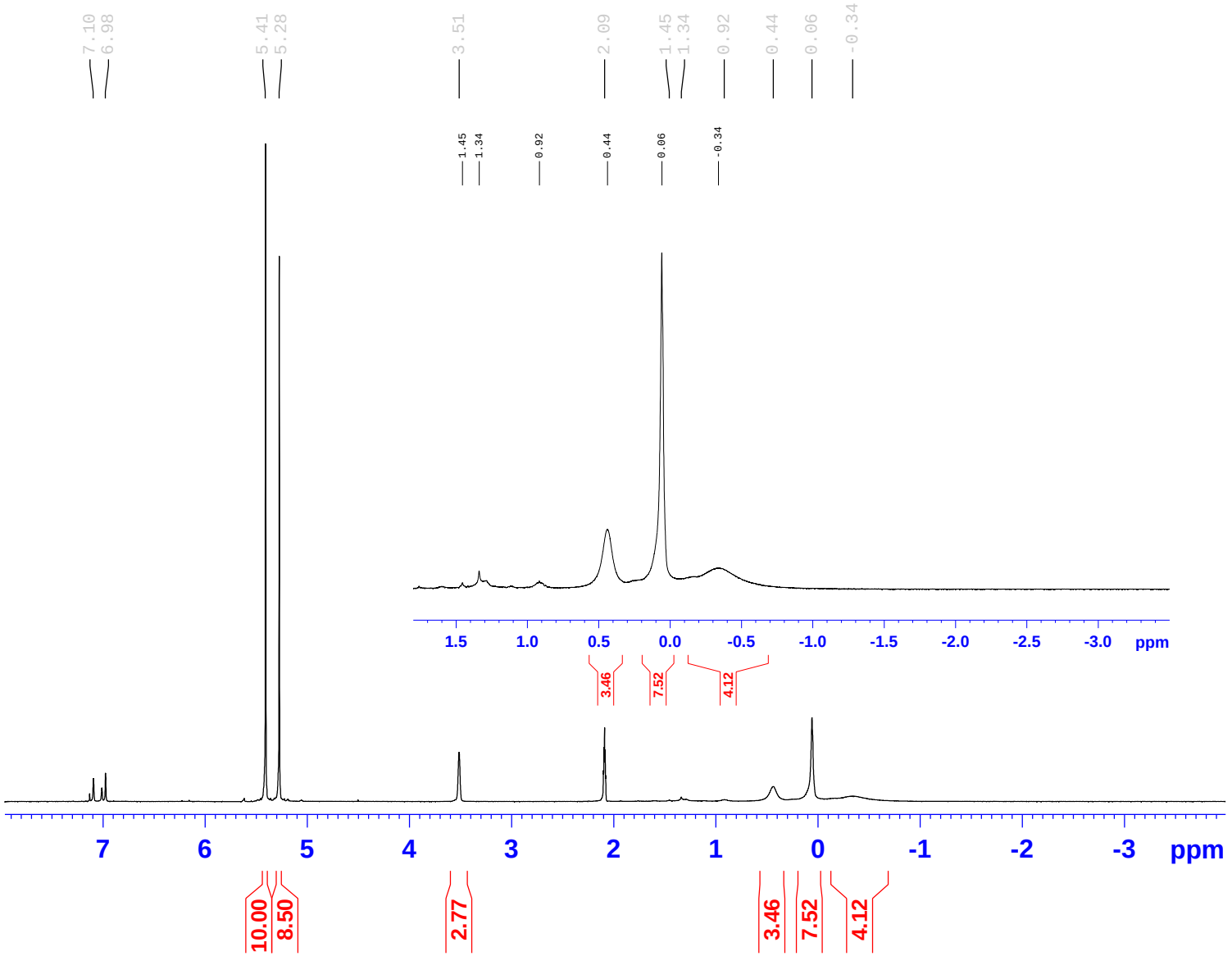
$Cp_2Zr(H)NH_2BH_3$, **1**, $^1H\{^{11}B\}$ NMR in tol-d_8, 50 °C



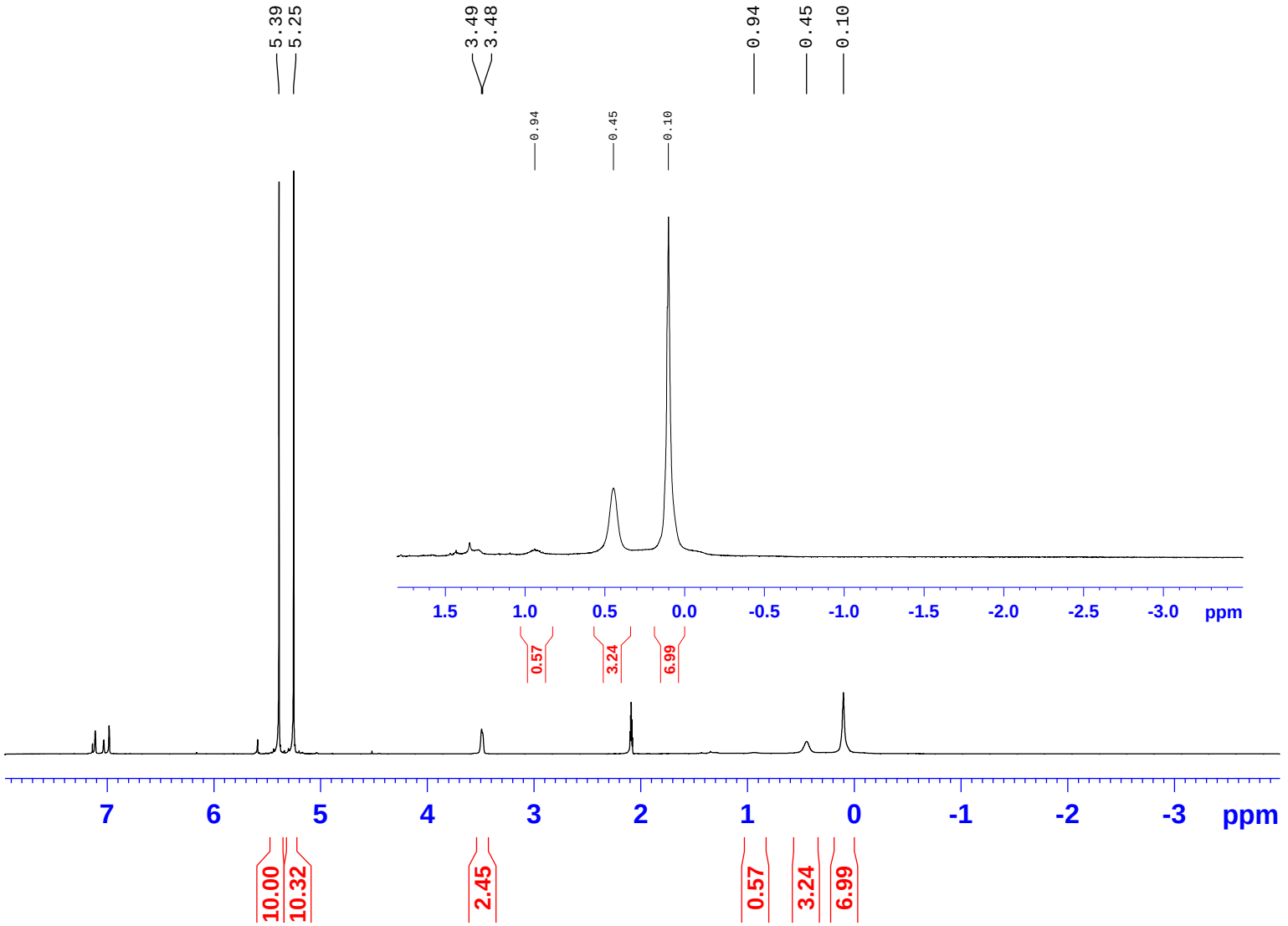
$Cp_2Zr(H)NH_2BH_3$, **1**, $^1H\{^{11}B\}$ NMR in tol-d_8, 40 °C



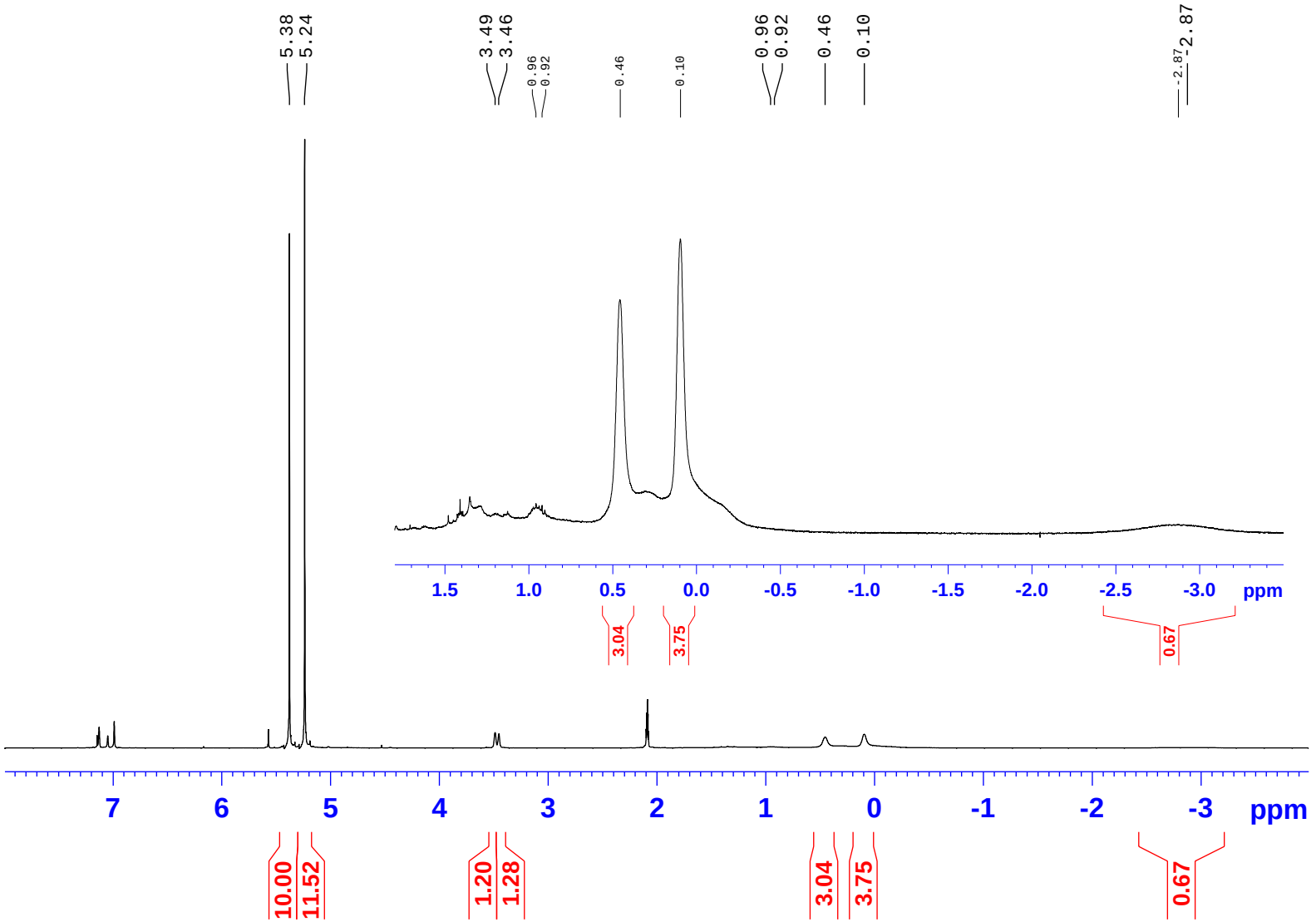
$Cp_2Zr(H)NH_2BH_3$, **1**, $^1H\{^{11}B\}$ NMR in tol-d_8, 25 °C



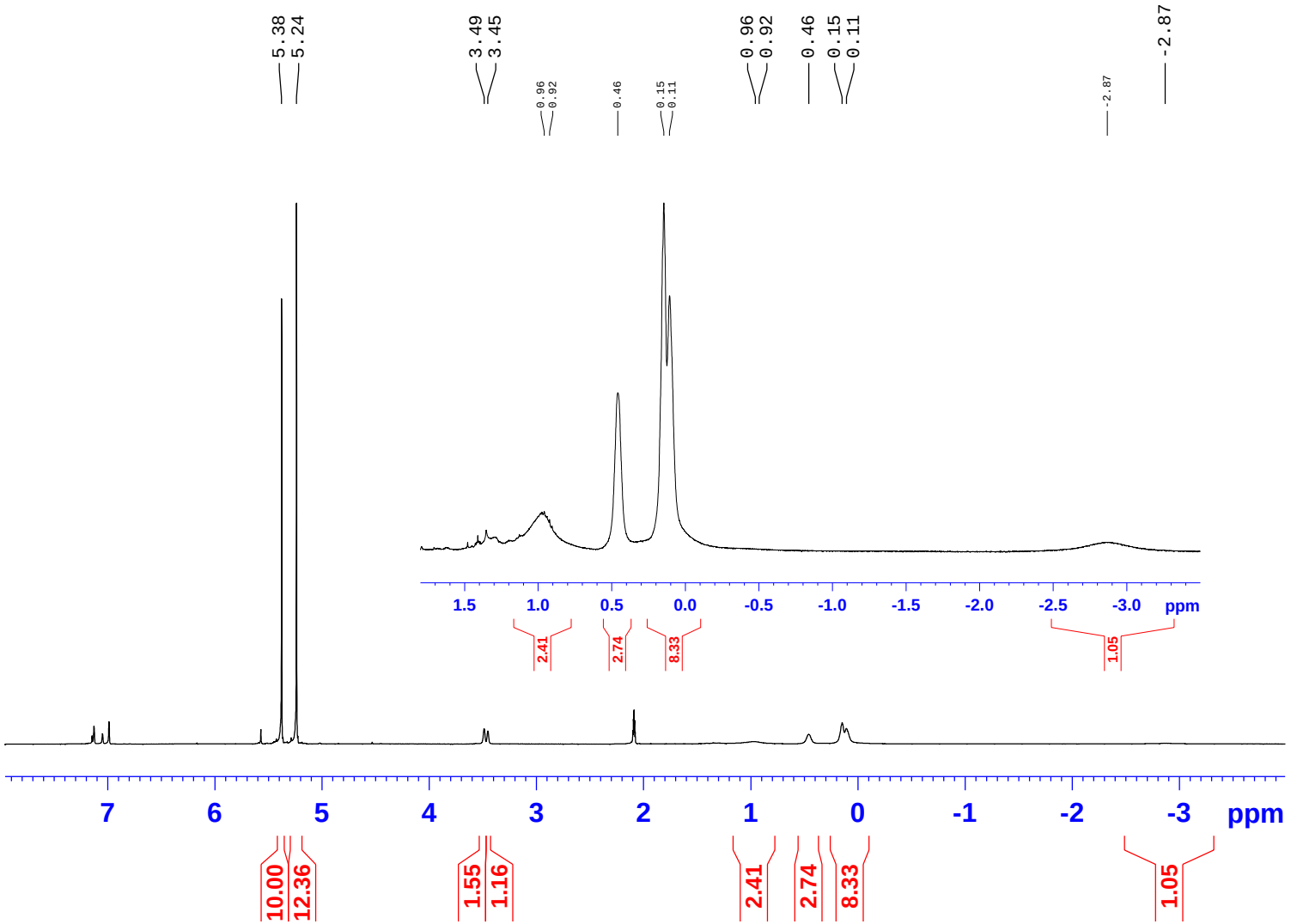
$Cp_2Zr(H)NH_2BH_3$, **1**, $^1H\{^{11}B\}$ NMR in tol-d_8, 0 °C



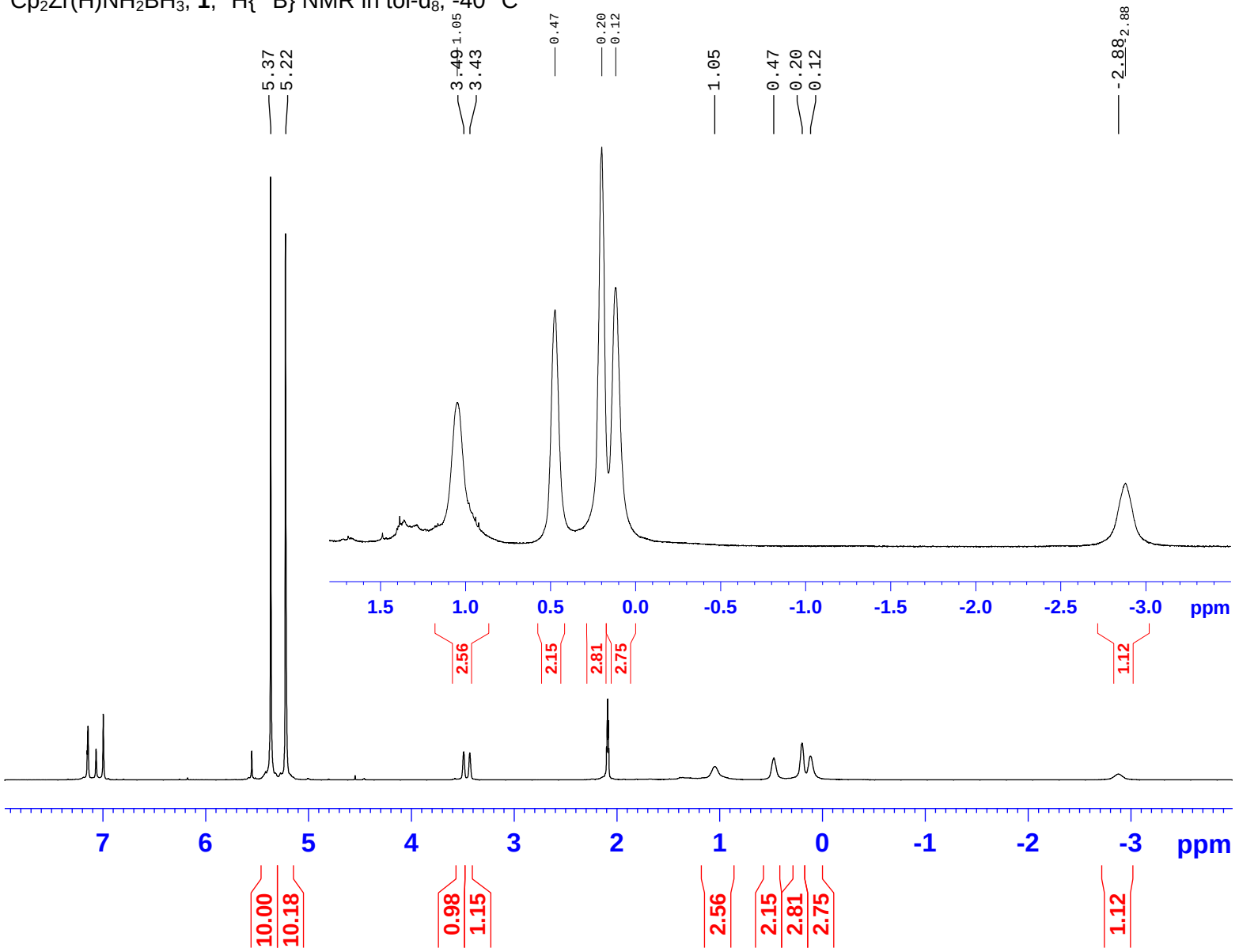
$Cp_2Zr(H)NH_2BH_3$, **1**, ^1H NMR in tol-d_8, -20 °C



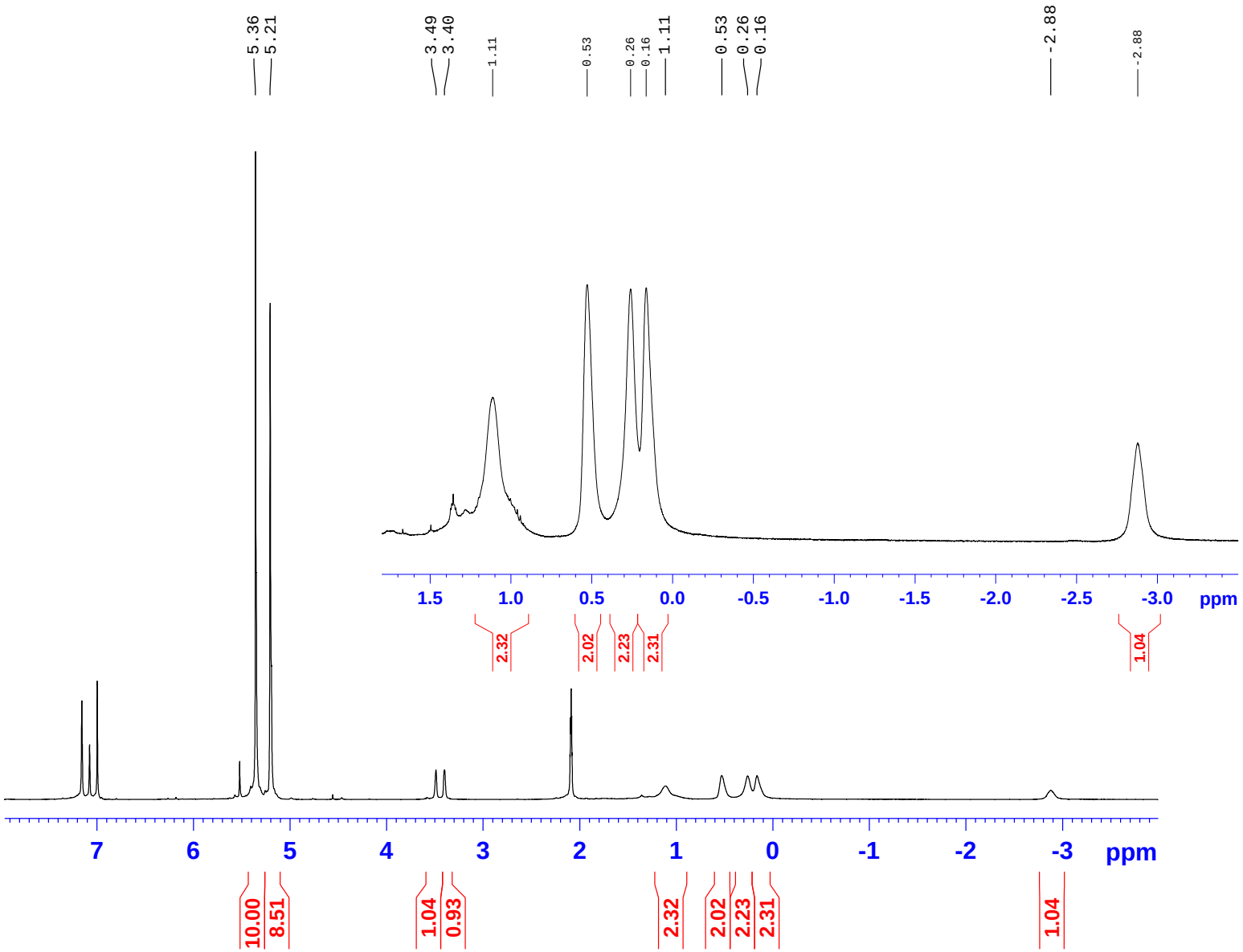
$Cp_2Zr(H)NH_2BH_3$, **1**, $^1H\{^{11}B\}$ NMR in tol-d_8, -20 °C



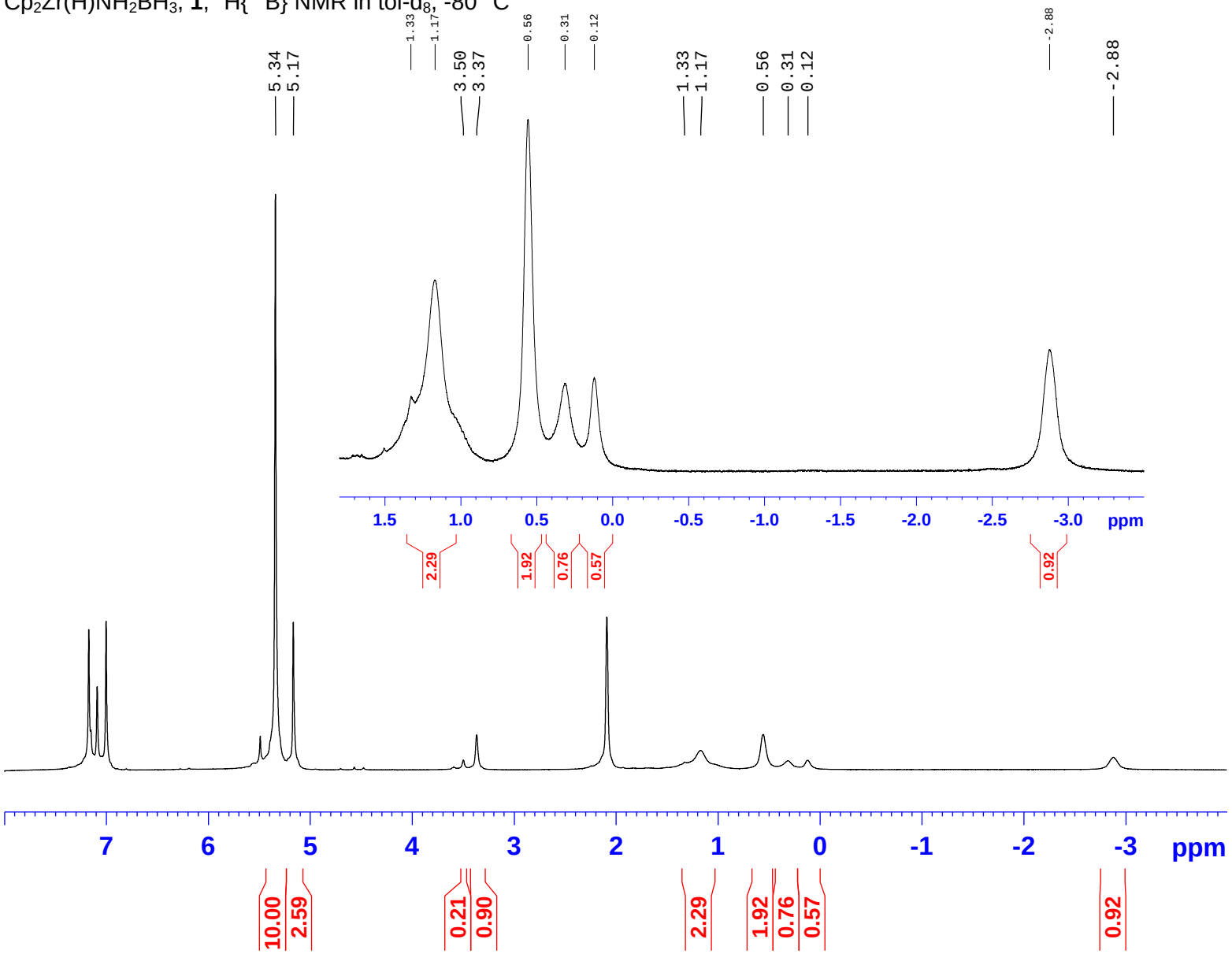
$Cp_2Zr(H)NH_2BH_3$, **1**, $^1H\{^{11}B\}$ NMR in tol-d_8, -40 °C



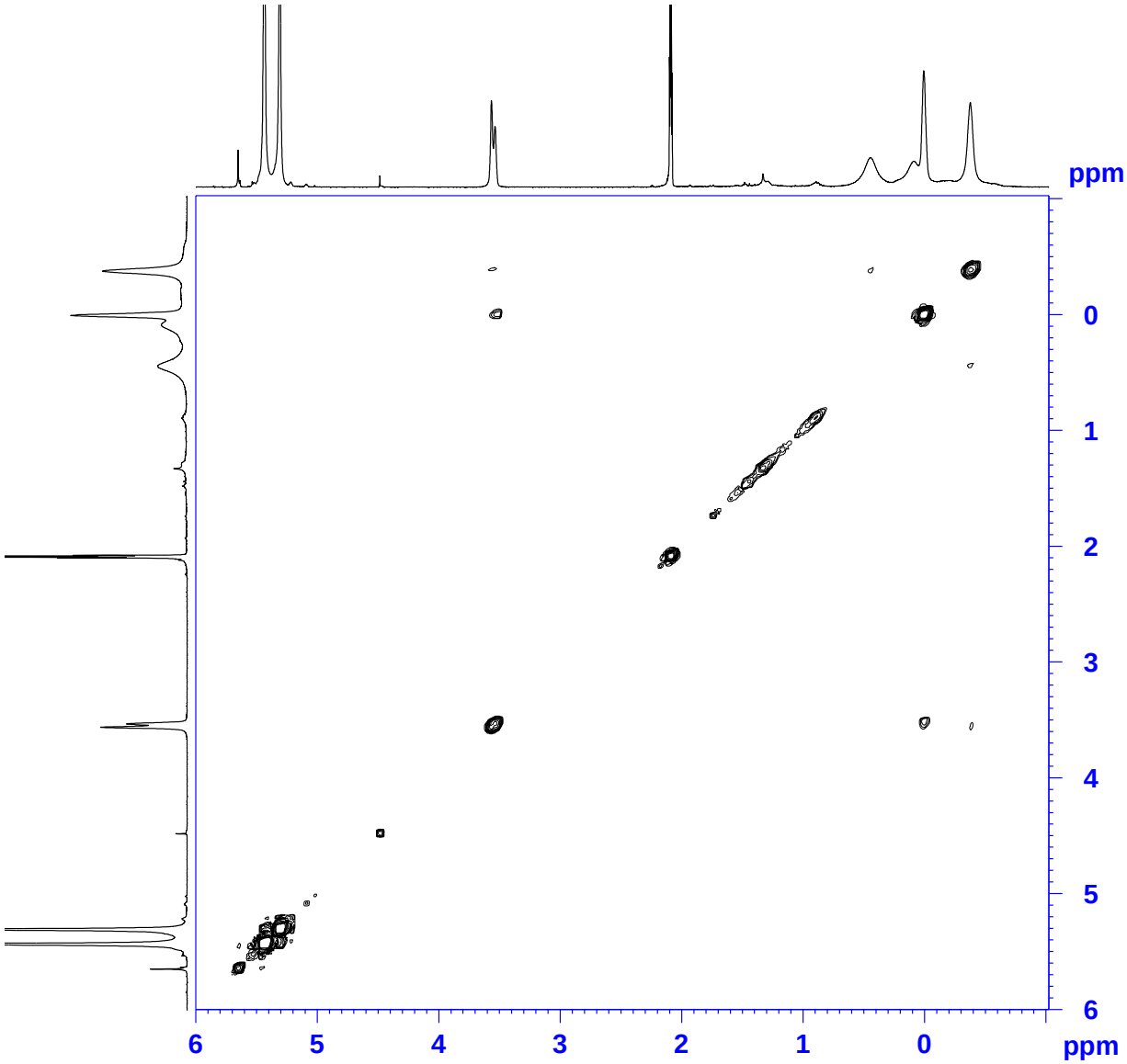
$Cp_2Zr(H)NH_2BH_3$, **1**, $^{1}H\{^{11}B\}$ NMR in tol-d_8, -60 °C



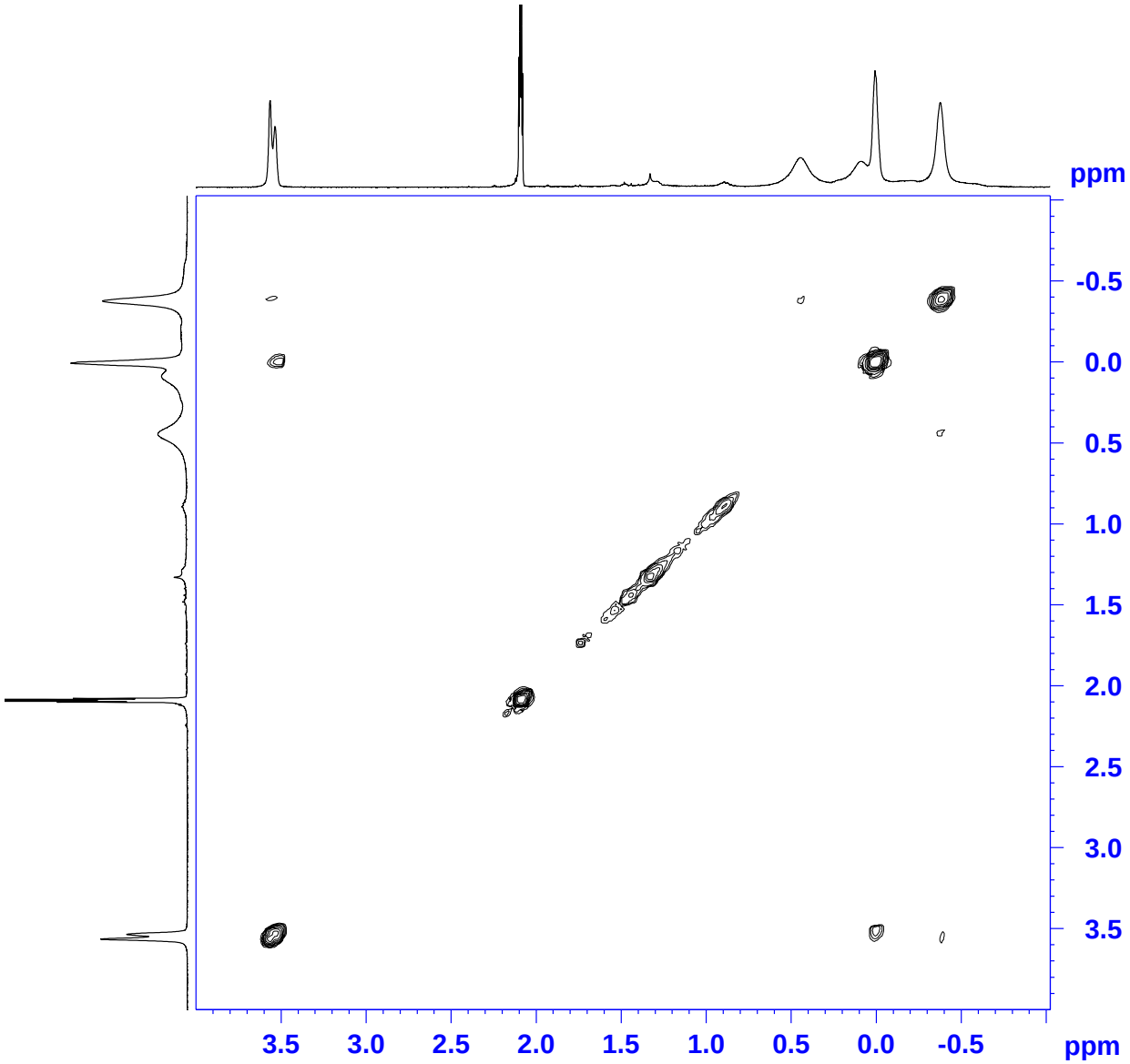
$Cp_2Zr(H)NH_2BH_3$, **1**, $^{1}H\{^{11}B\}$ NMR in tol-d_8, -80 °C



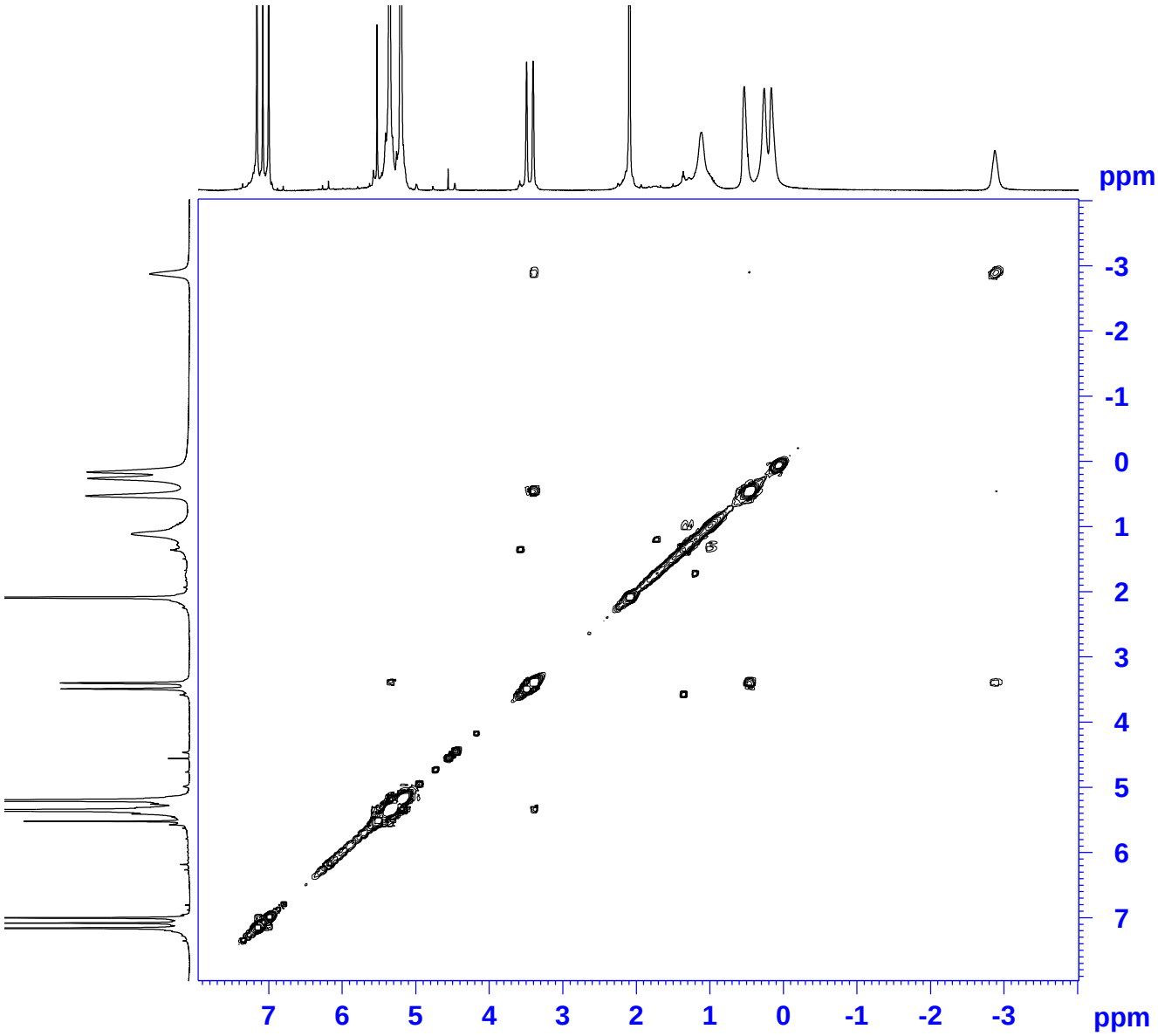
$Cp_2Zr(H)NH_2BH_3$, **1**, COSY{^{11}B} in tol-d_8, 60 °C



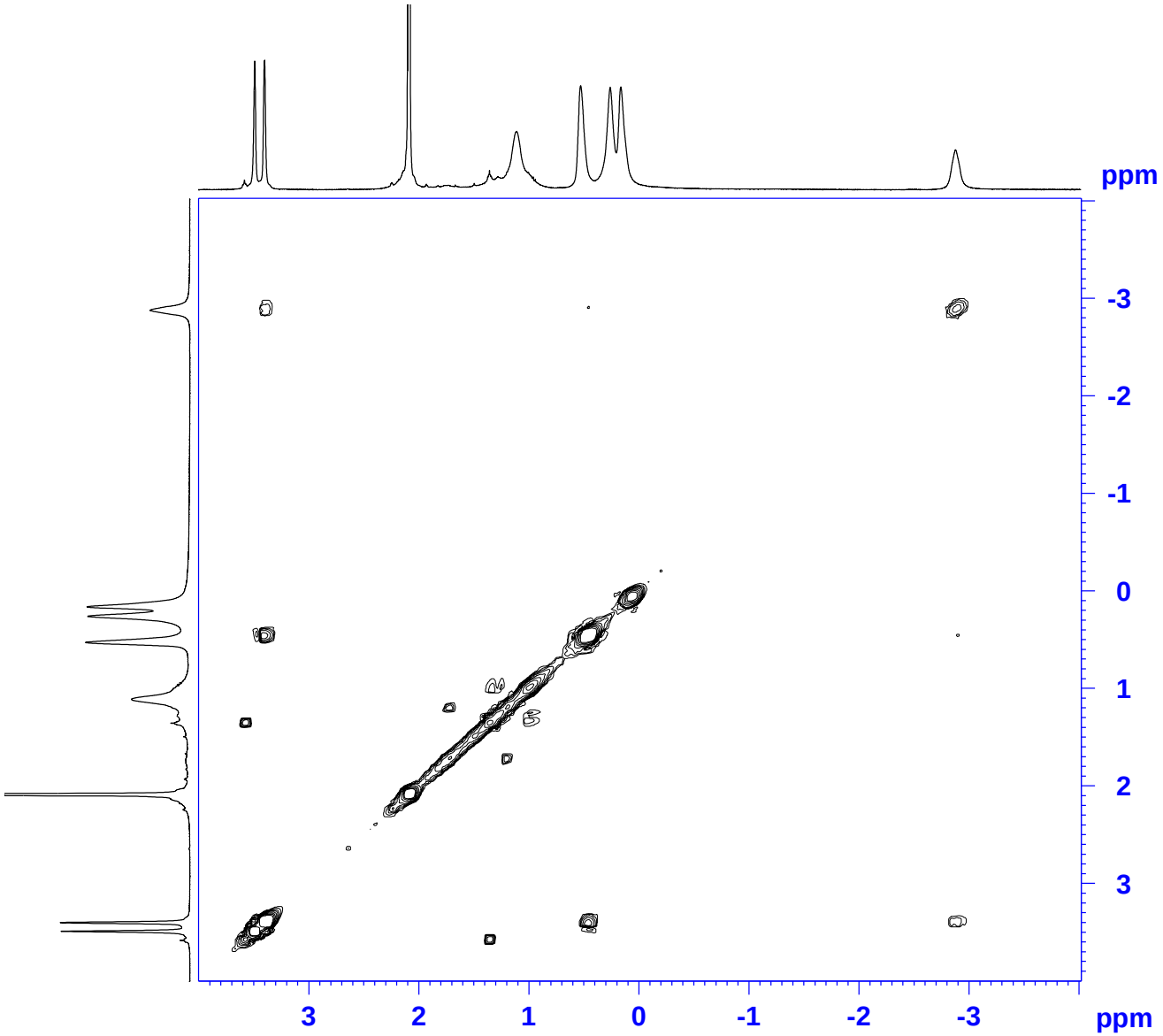
$Cp_2Zr(H)NH_2BH_3$, **1**, COSY{^{11}B} in tol-d_8, 60 °C, detail



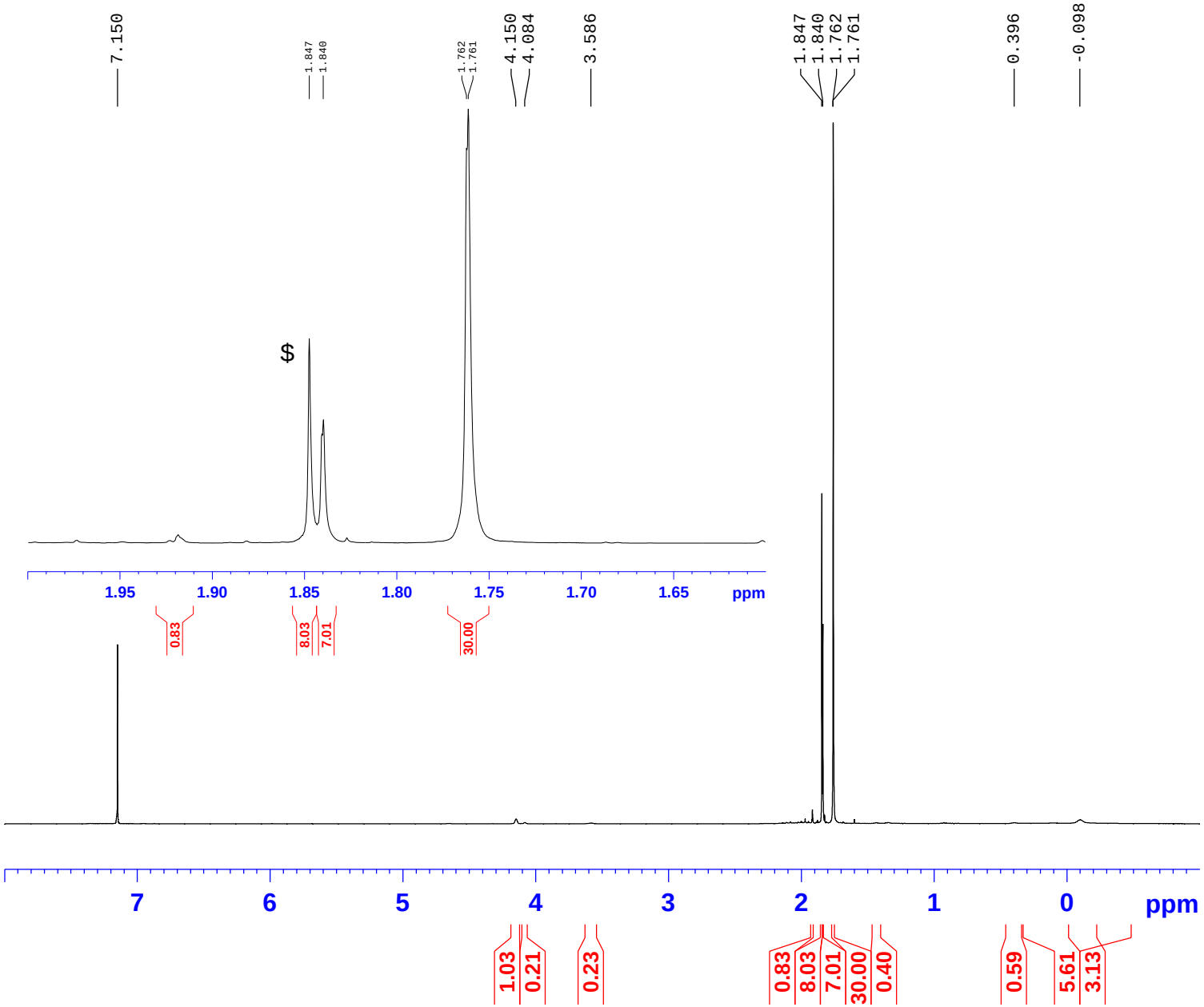
$Cp_2Zr(H)NH_2BH_3$, **1**, COSY{^{11}B} in tol-d_8, -60 °C



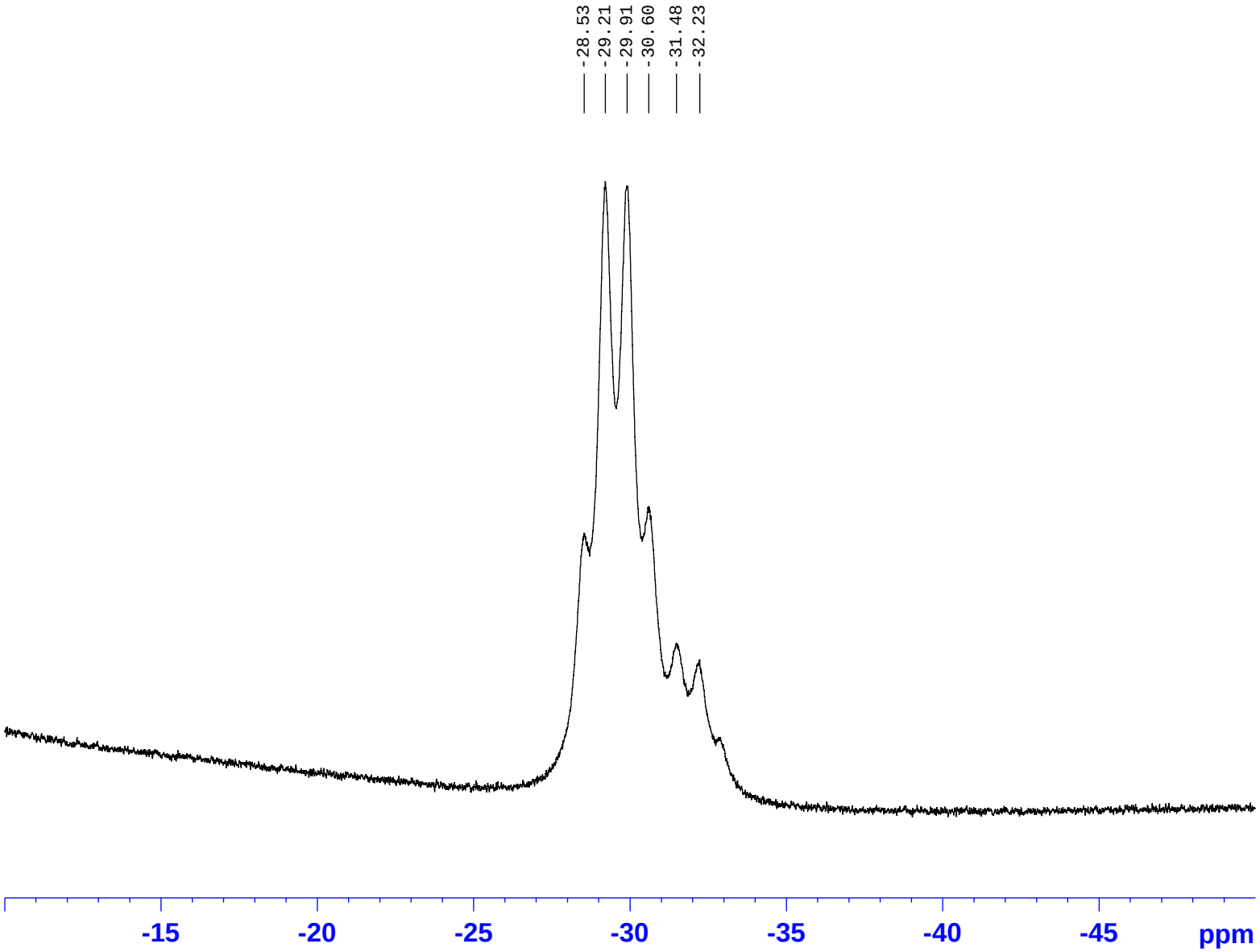
$Cp_2Zr(H)NH_2BH_3$, **1**, COSY{^{11}B} in tol-d_8, -60 °C, detail



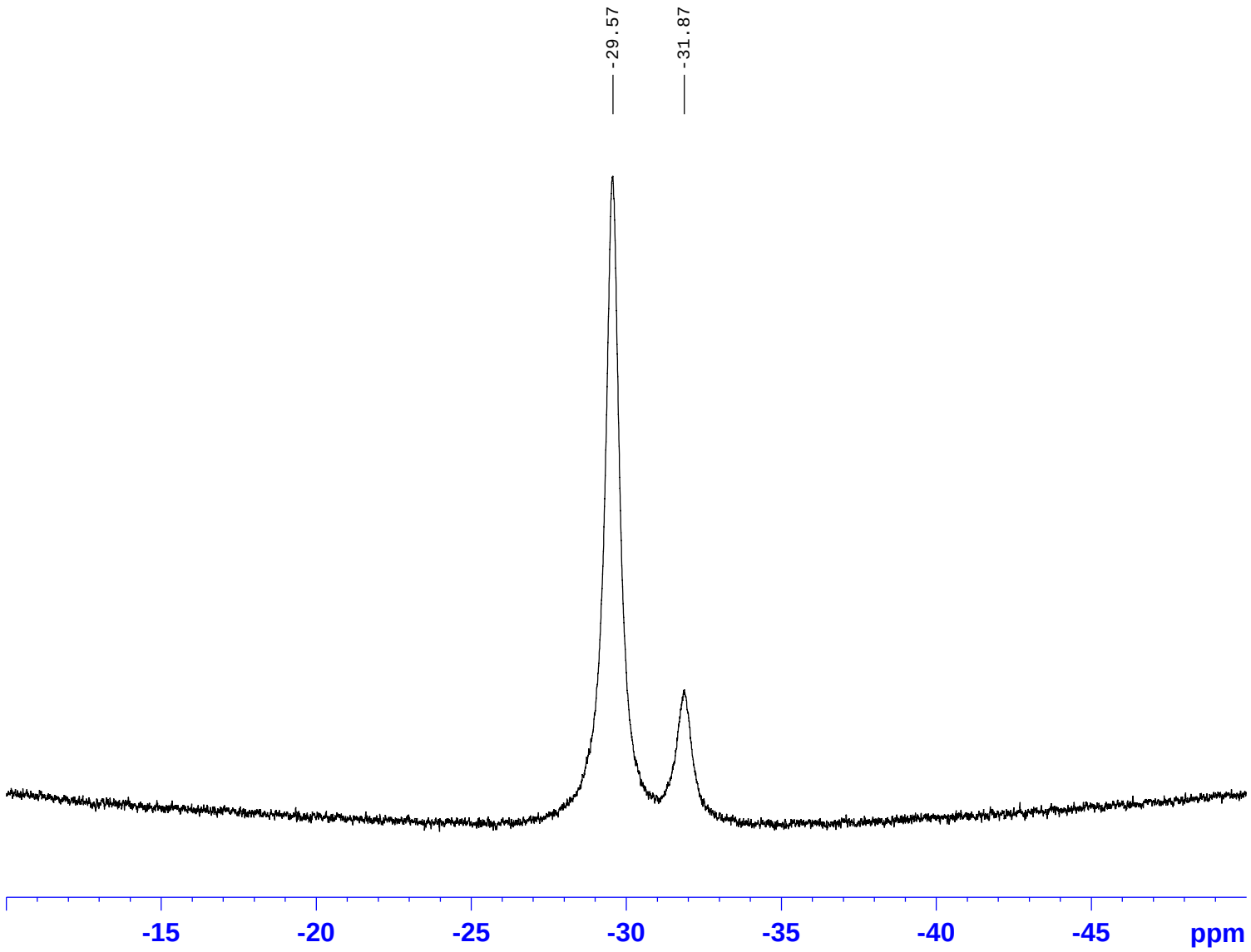
Cp*$_2$Zr(H)NH$_2$BH$_3$, **2**, ^{1}H NMR in C_6D_6, 20 °C ($ indicates Cp*$_2$ZrCl$_2$ impurity)



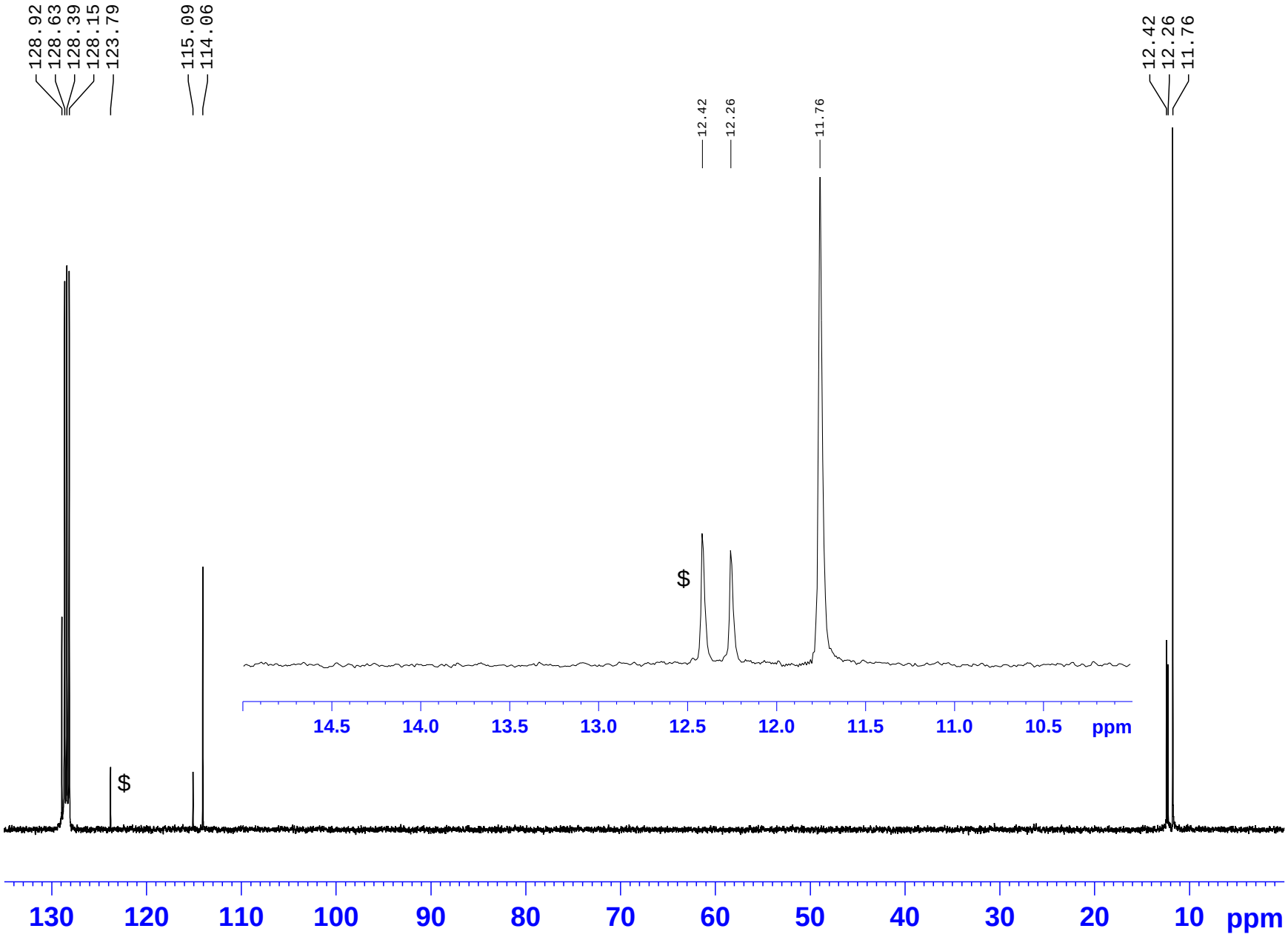
Cp*$_2$Zr(H)NH$_2$BH$_3$, **2**, ^{11}B NMR in C_6D_6, 20 °C



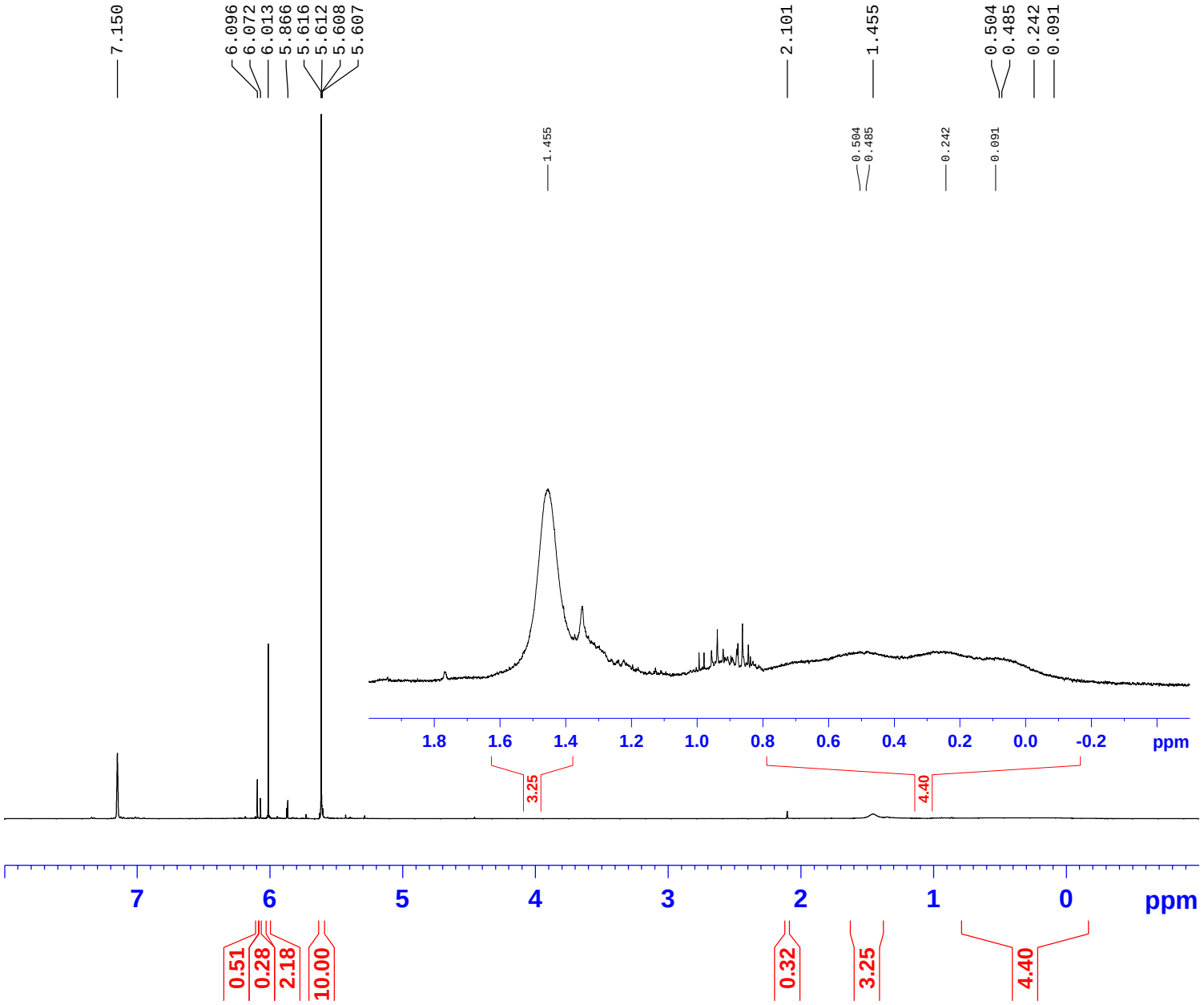
Cp*$_2$Zr(H)NH$_2$BH$_3$, **2**, ^{11}B{^{1}H} NMR in C_6D_6, 20 °C



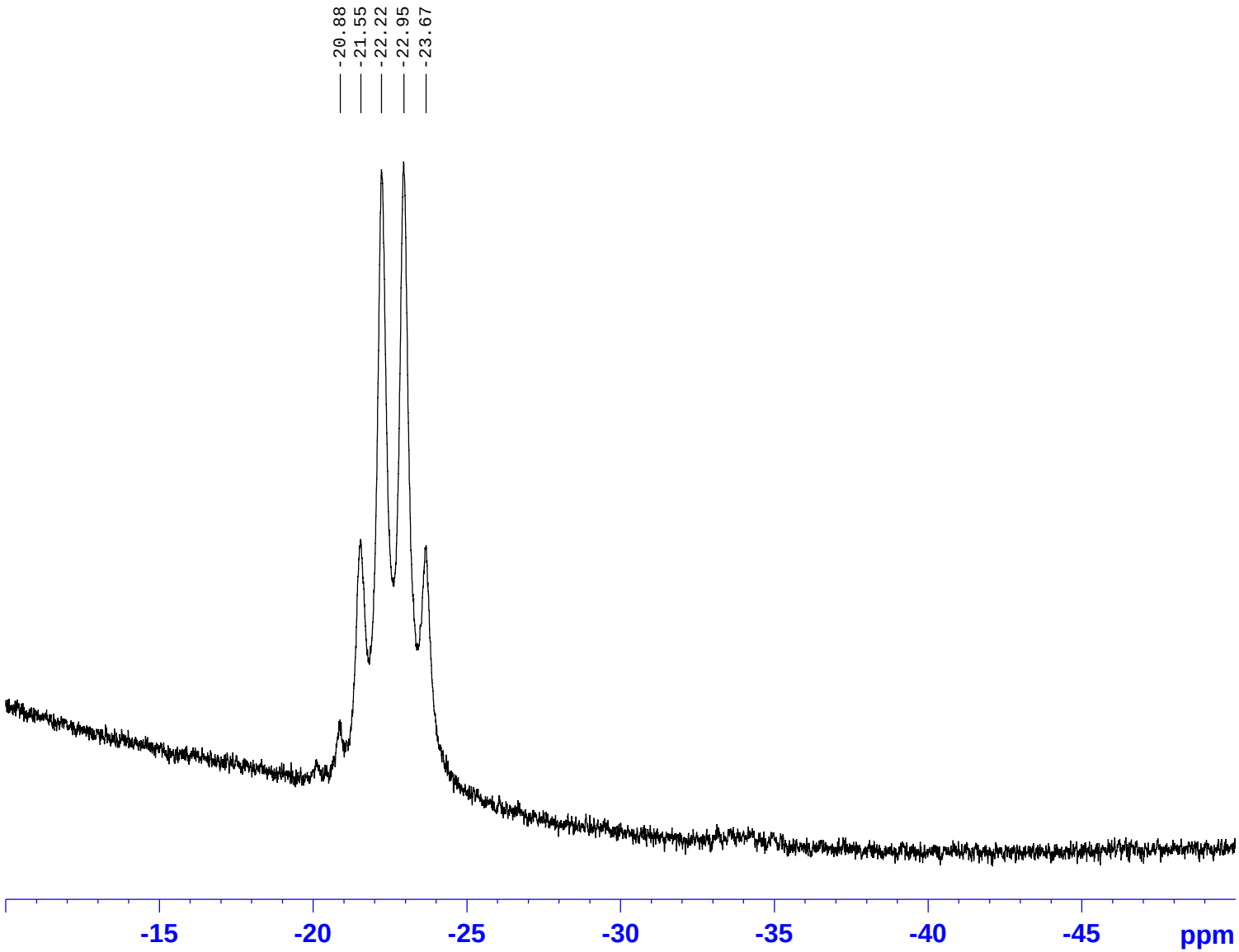
$Cp^*_2Zr(H)NH_2BH_3$, **2**, $^{13}C\{^1H\}$ NMR in C_6D_6, 20 °C ($ indicates $Cp^*_2ZrCl_2$ impurity)



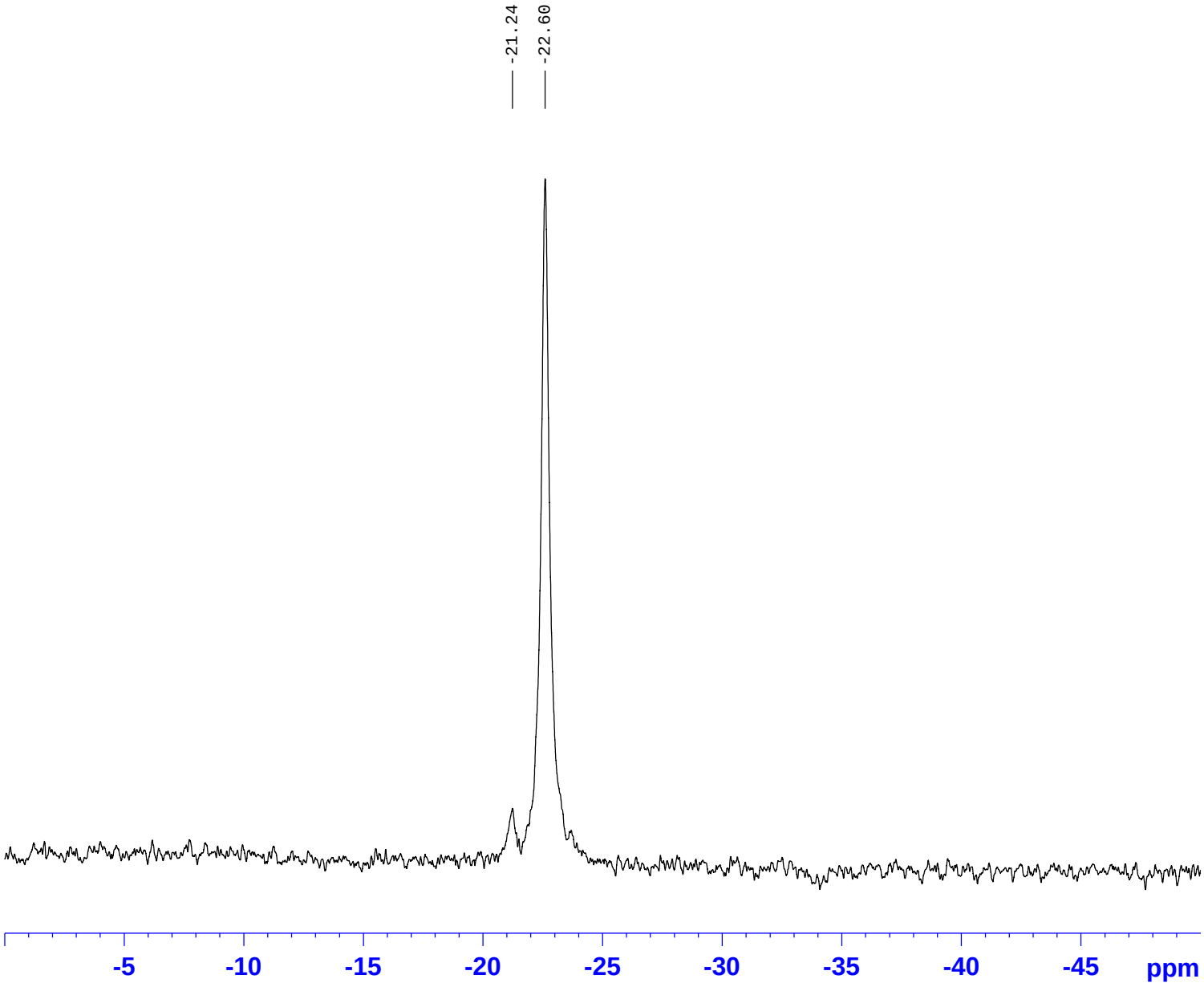
$Cp_2Zr(Cl)NH_2BH_3$, **3**, ^1H NMR in C_6D_6, 20 °C



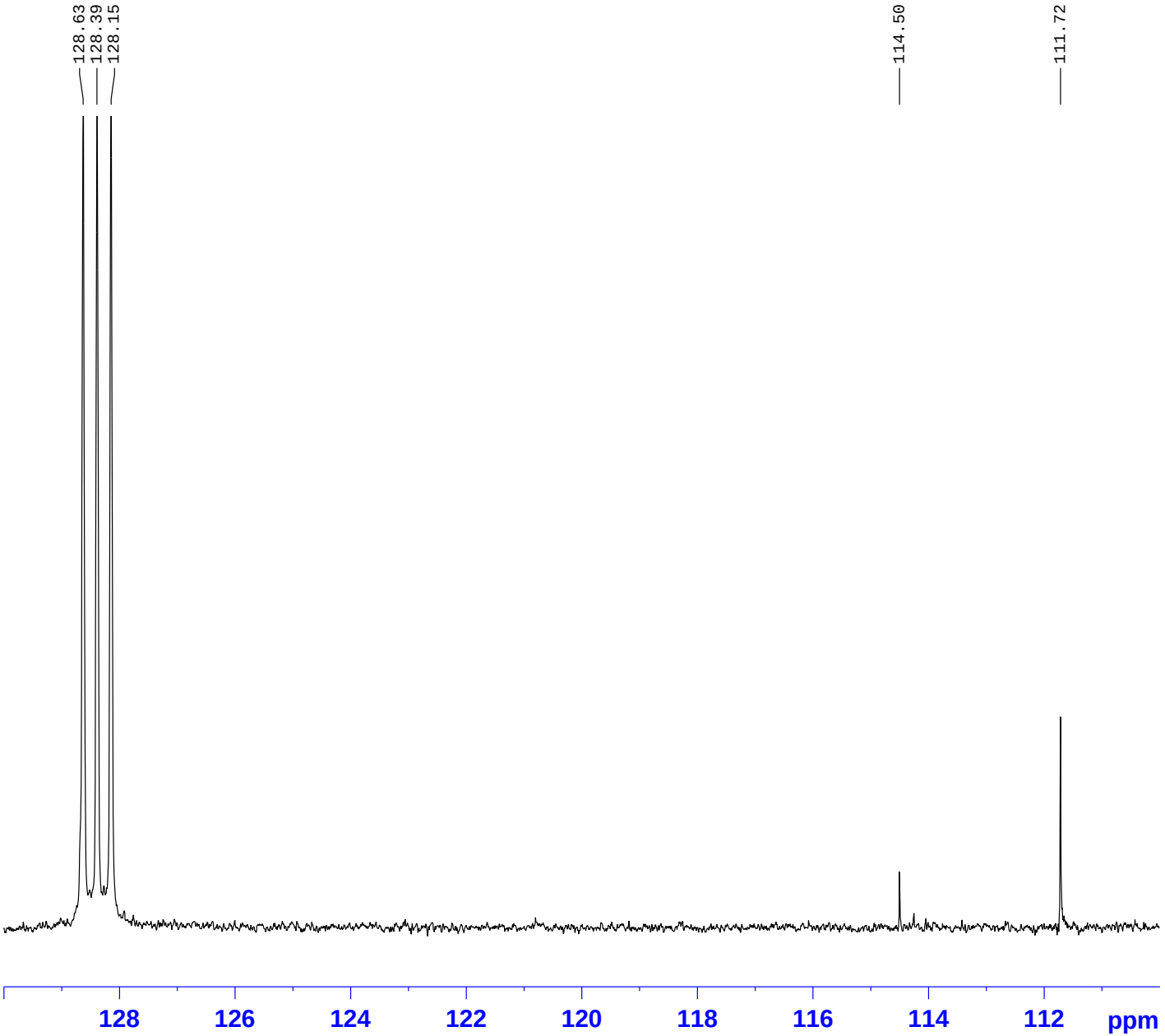
$Cp_2Zr(Cl)NH_2BH_3$, **3**, ^{11}B NMR in C_6D_6, 20 °C



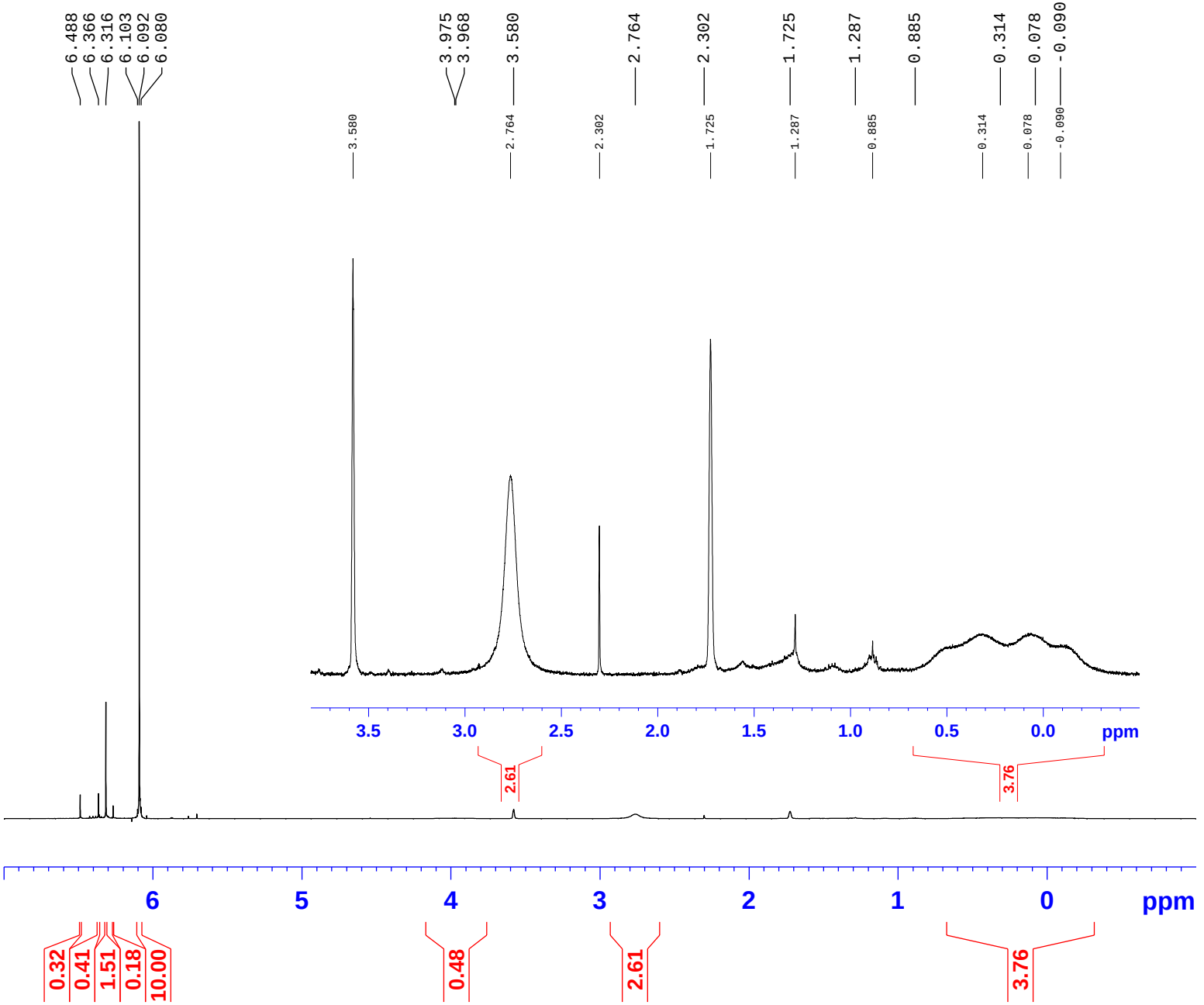
$Cp_2Zr(Cl)NH_2BH_3$, **3**, $^{11}B\{^1H\}$ NMR in C_6D_6, 20 °C



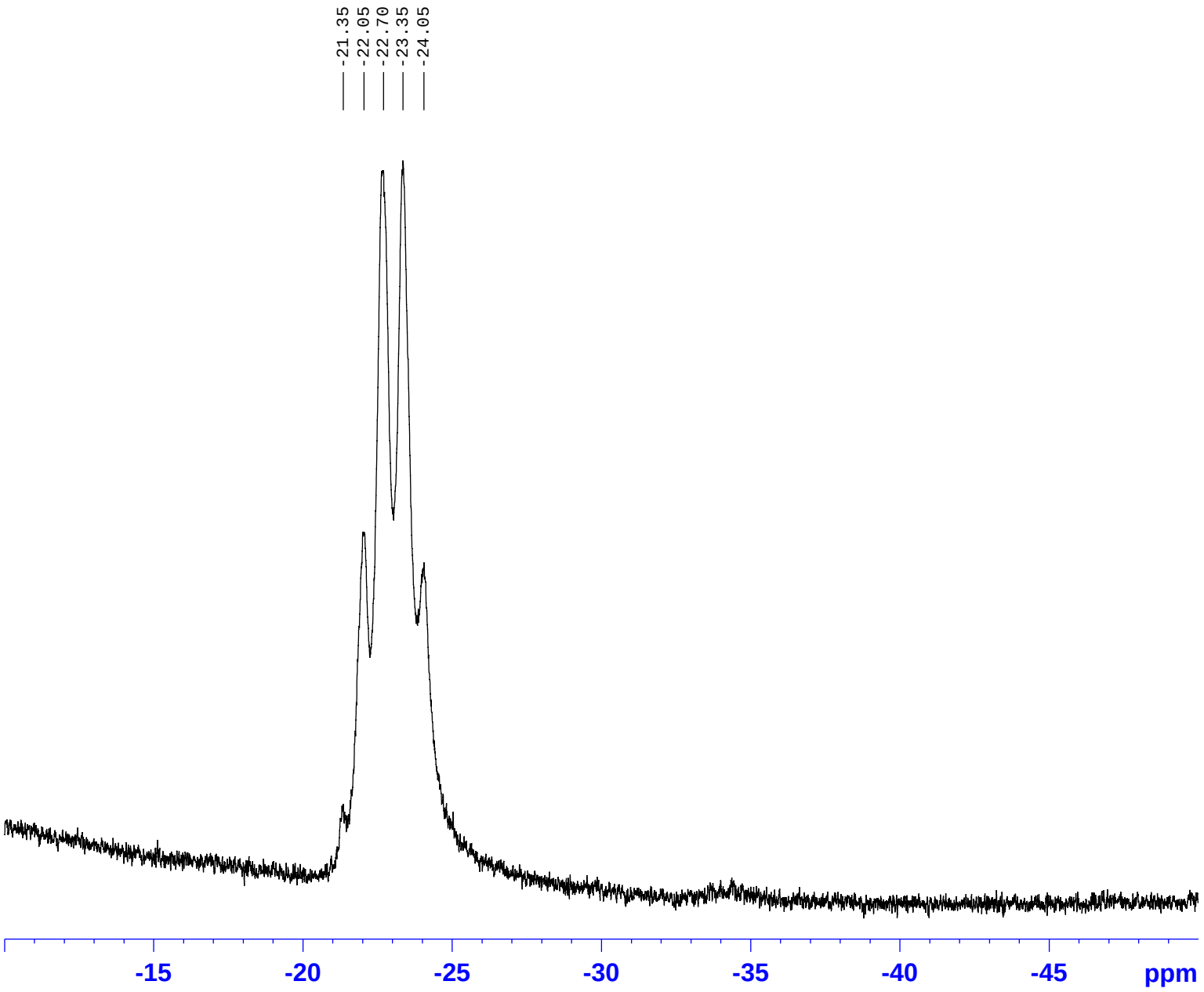
$Cp_2Zr(Cl)NH_2BH_3$, **3**, ^{11}C NMR in C_6D_6, 20 °C



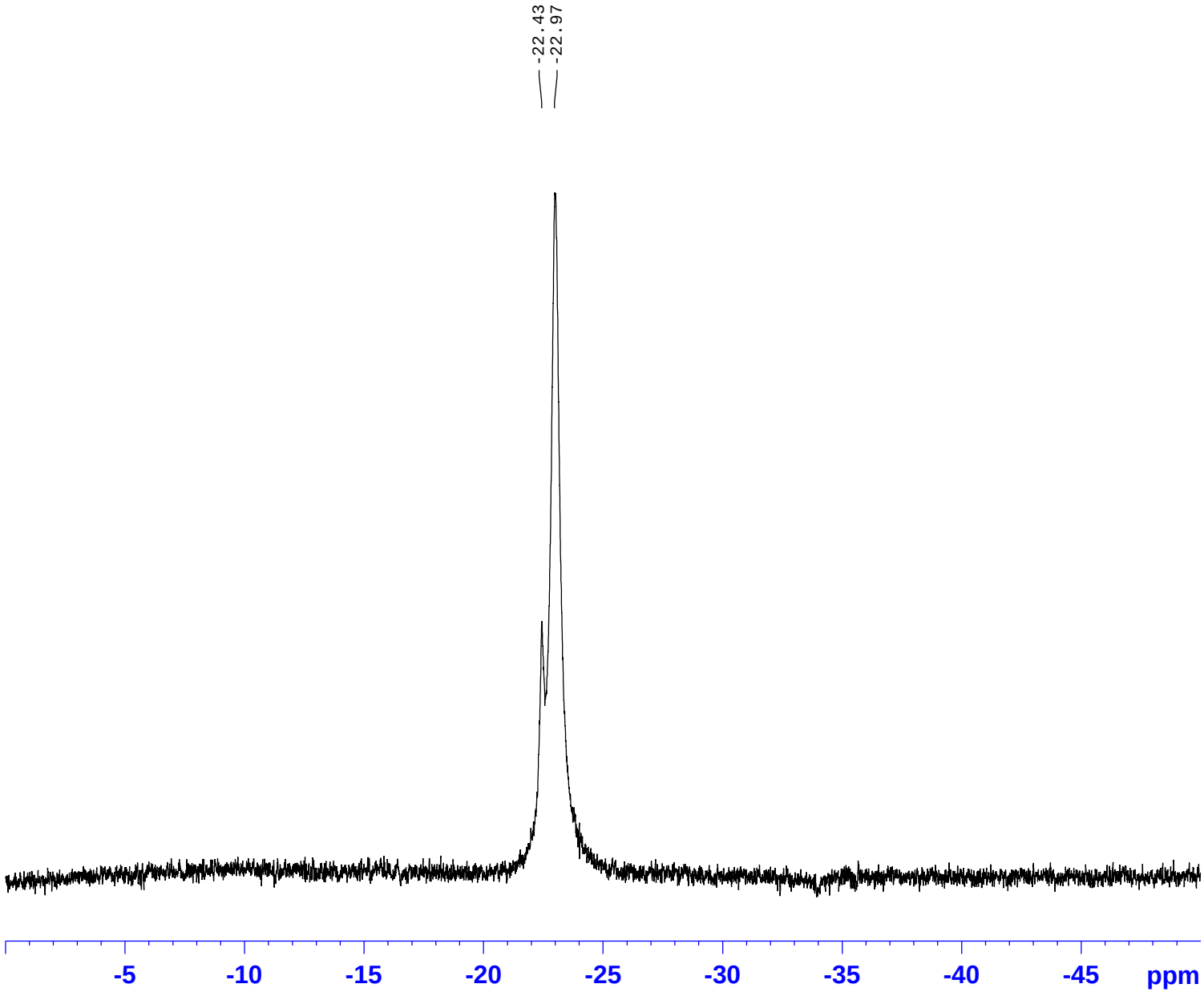
$Cp_2Zr(Cl)NH_2BH_3$, **3**, ^1H NMR in THF-d_8, 20 °C



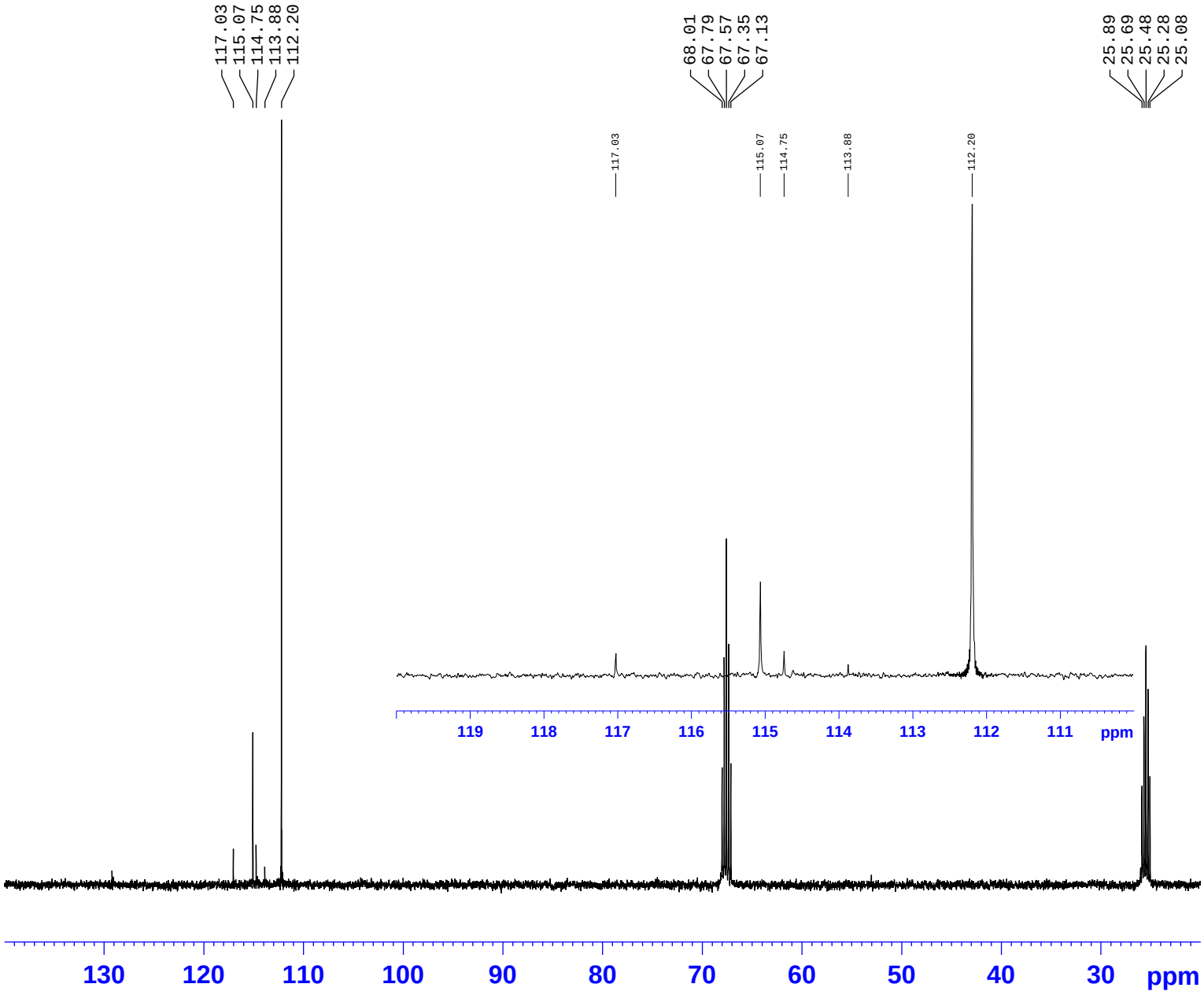
$Cp_2Zr(Cl)NH_2BH_3$, **3**, ^{11}B NMR in THF-d_8, 20 °C

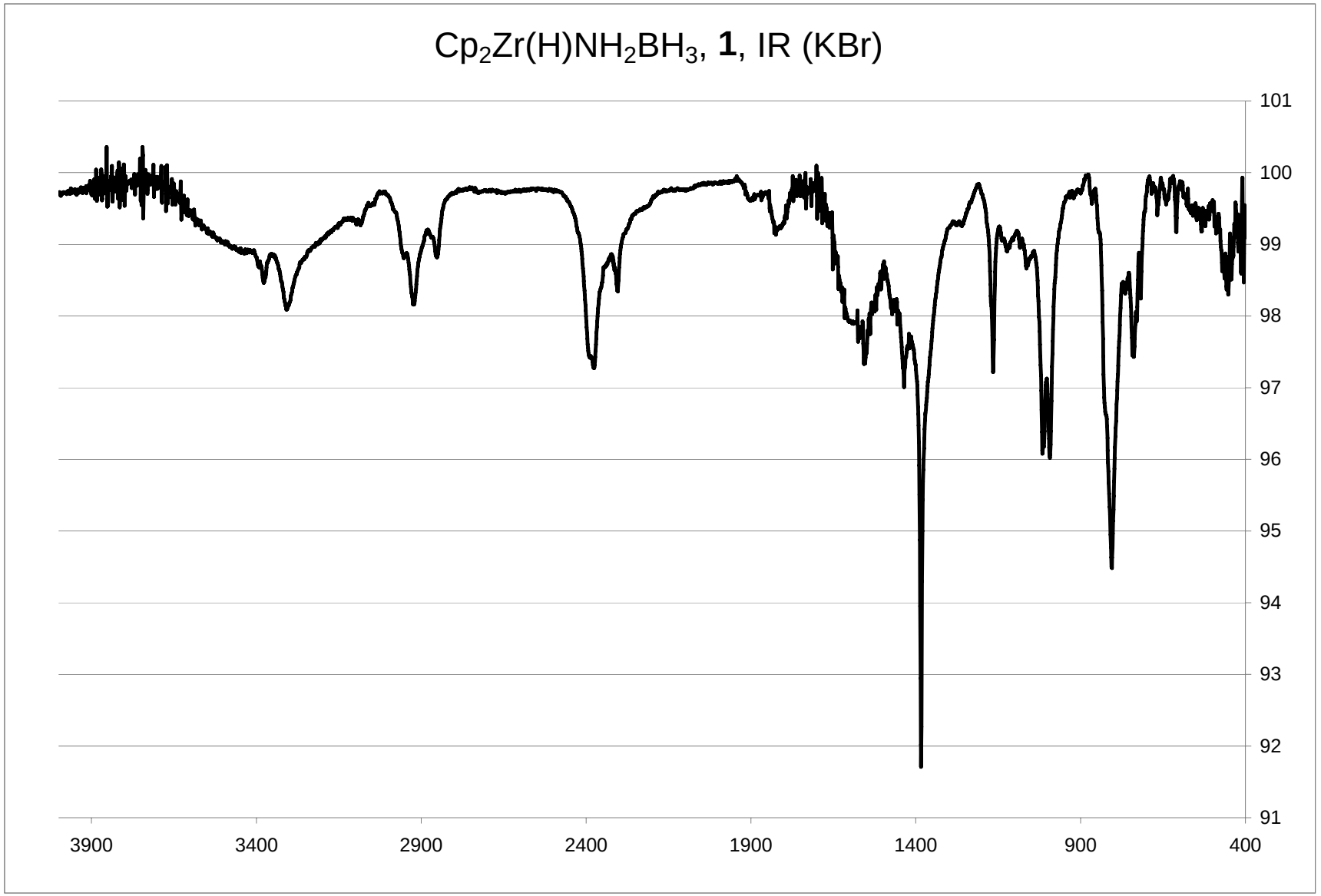


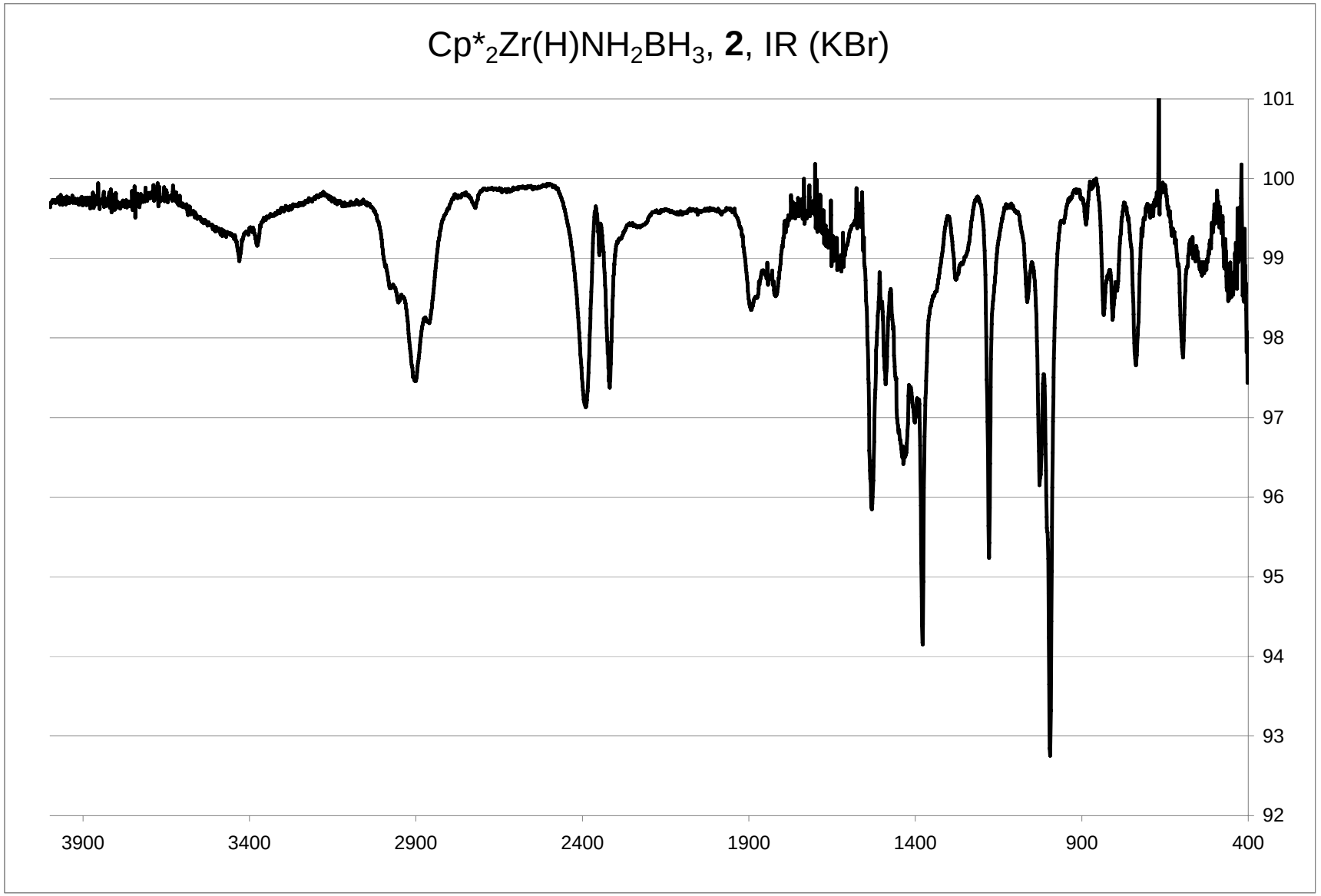
$Cp_2Zr(Cl)NH_2BH_3$, **3**, $^{11}B\{^1H\}$ NMR in THF-d_8, 20 °C

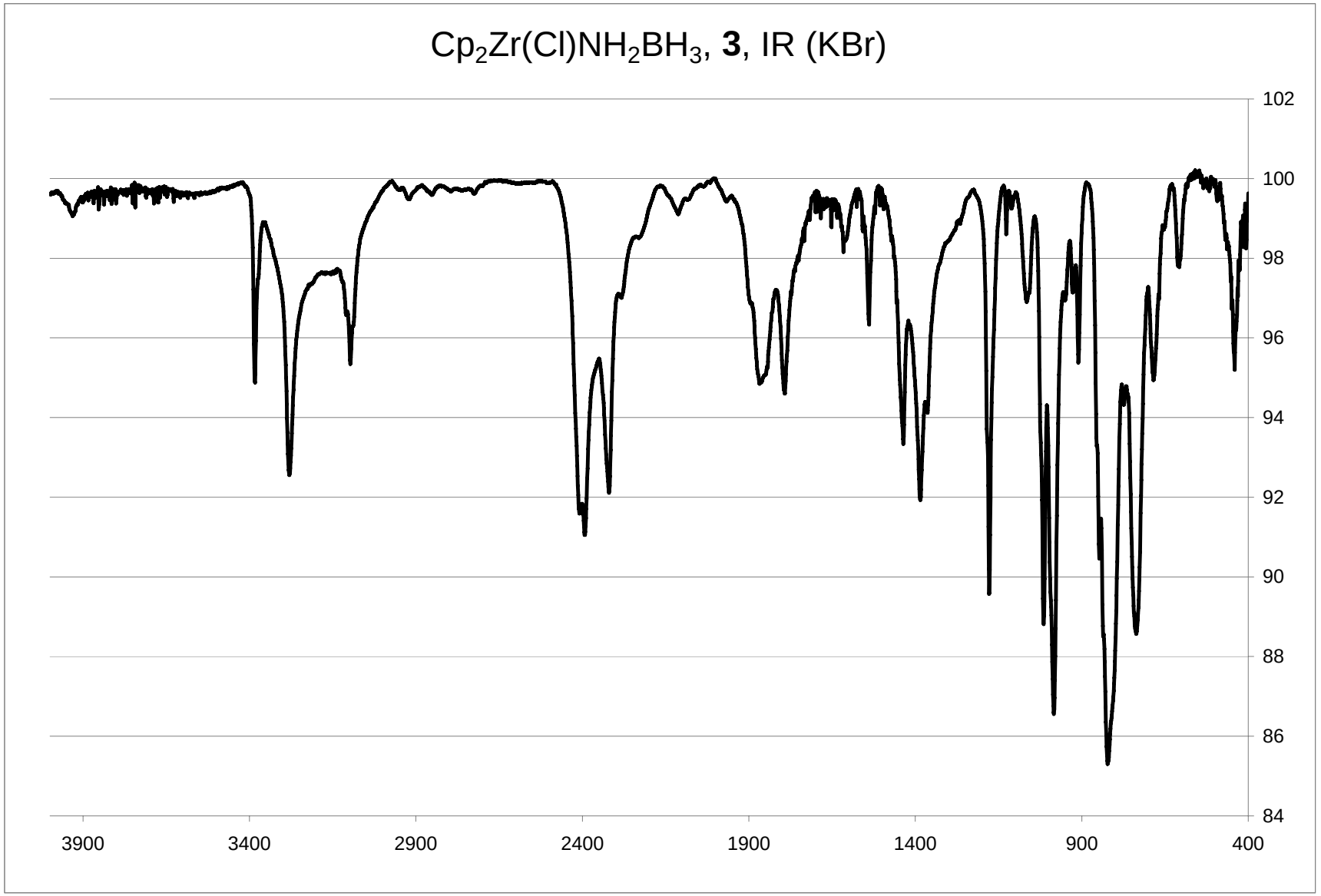


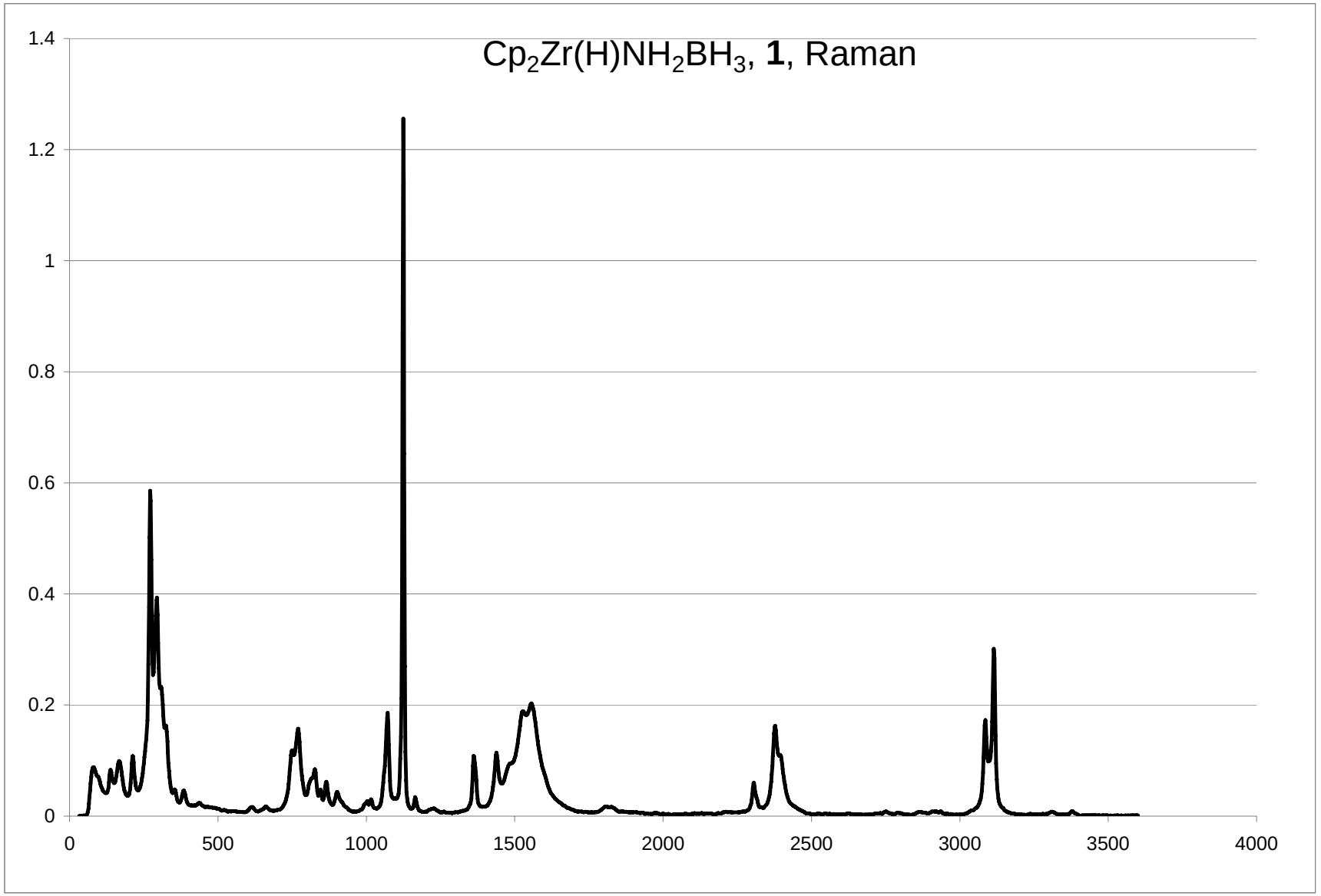
$Cp_2Zr(Cl)NH_2BH_3$, **3**, $^{13}C\{^1H\}$ NMR in THF-d_8, 20 °C

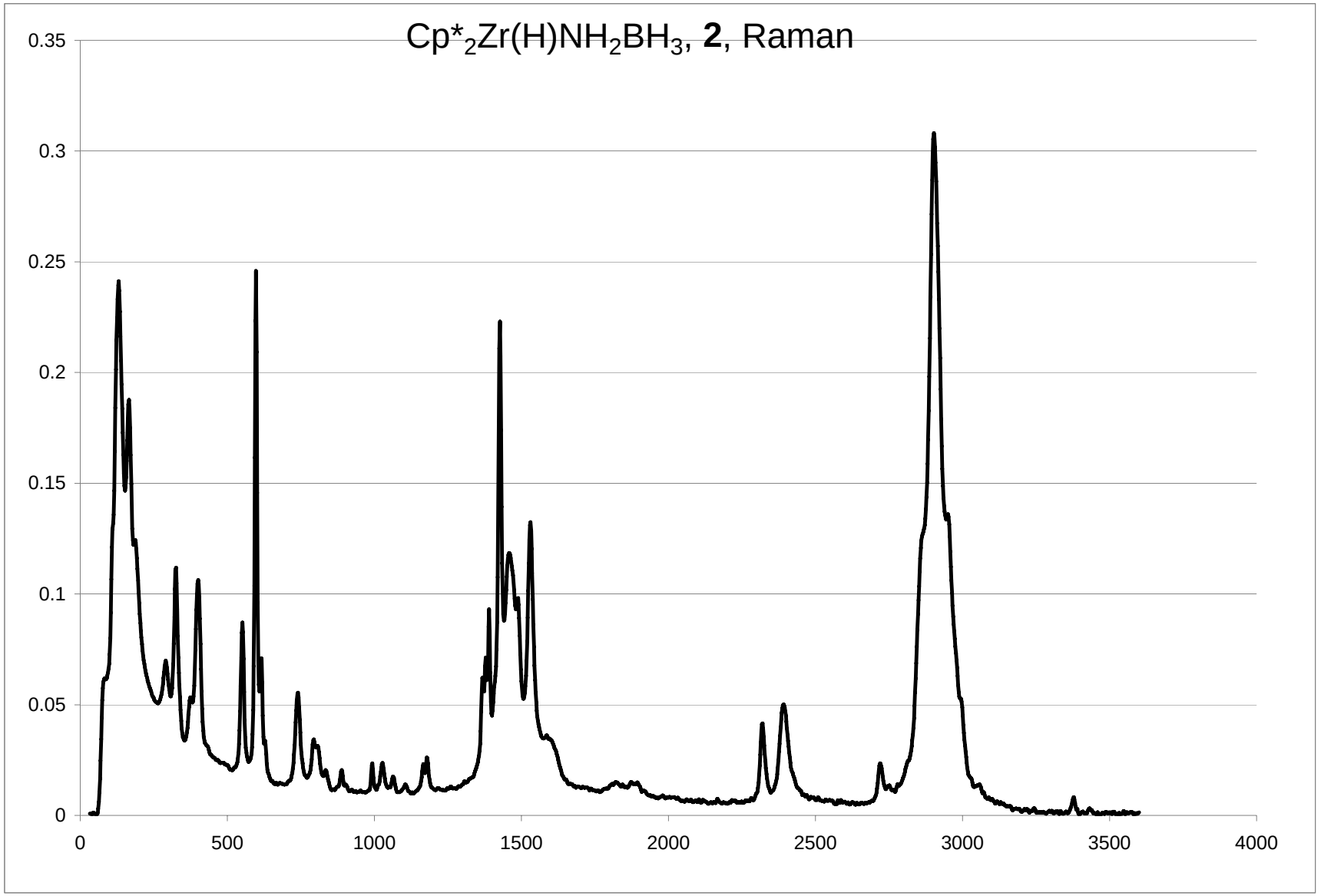


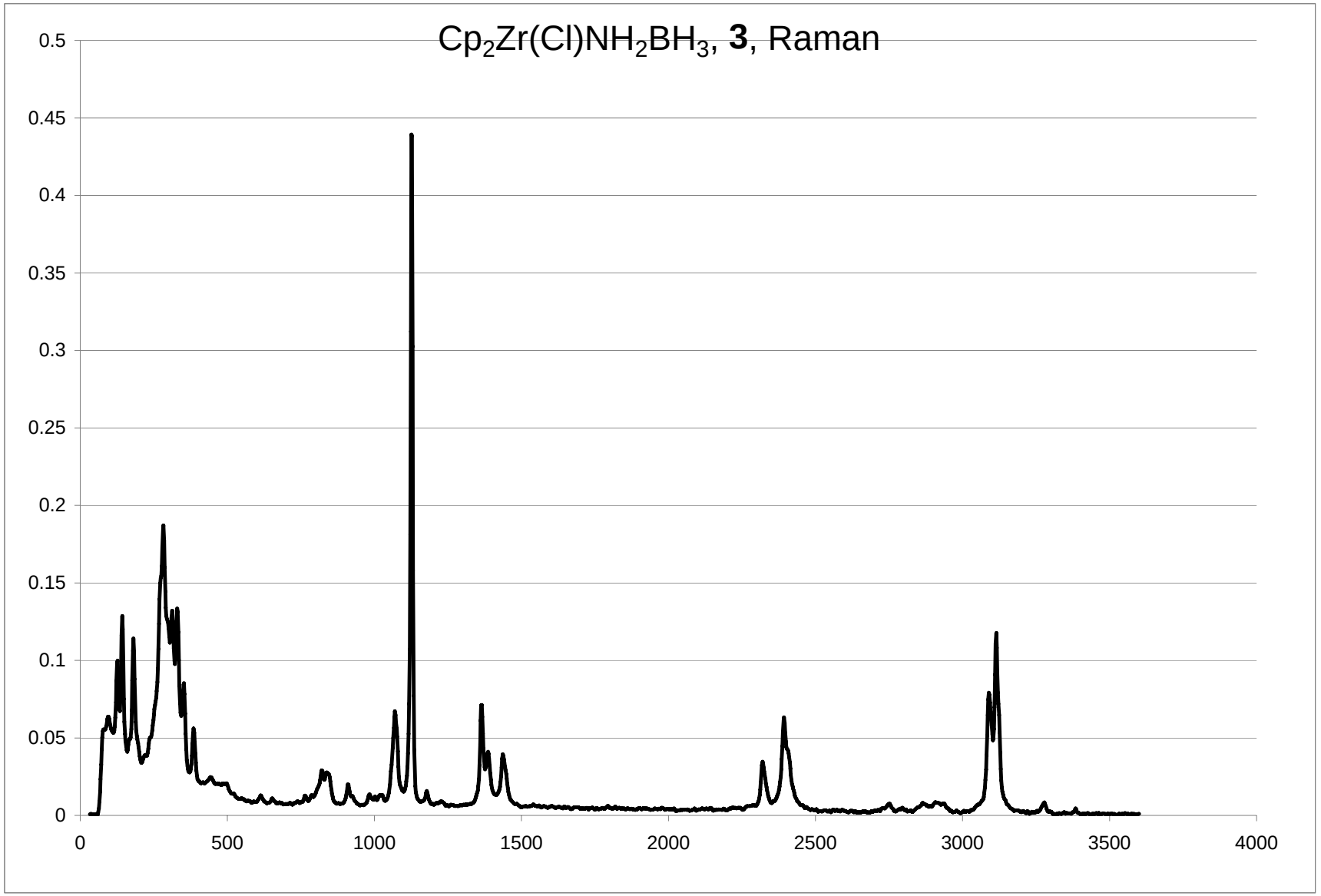

Cp2Zr(H)NH2BH3, 1, IR (KBr)
101
100
99
98
97
96
95
94
93
92
91
3900
3400
2900
2400
1900
1400
900
400


Cp*2Zr(H)NH2BH3, 2, IR (KBr)
101
100
99
98
97
96
95
94
93
92
3900
3400
2900
2400
1900
1400
900
400

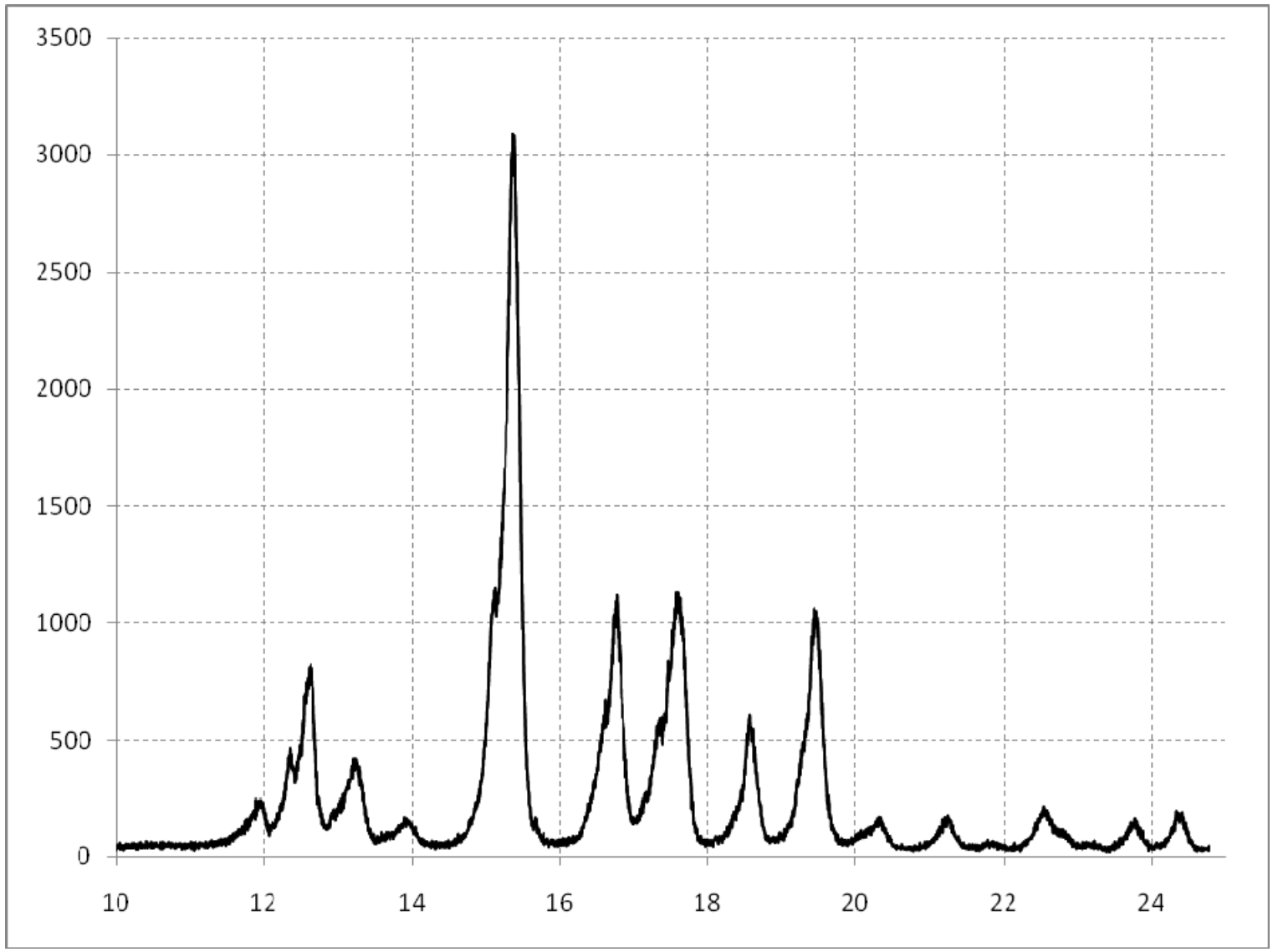

Cp2Zr(Cl)NH2BH3, 3, IR (KBr)
102
100
98
96
94
92
90
88
86
84
3900
3400
2900
2400
1900
1400
900
400


Cp2Zr(H)NH2BH3, 1, Raman
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
500
1000
1500
2000
2500
3000
3500
4000


Cp*2Zr(H)NH2BH3, 2, Raman
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
500
1000
1500
2000
2500
3000
3500
4000


Cp2Zr(Cl)NH2BH3, 3, Raman
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
500
1000
1500
2000
2500
3000
3500
4000

$Cp_2Zr(H)NH_2BH_3$, **1**, powder X-ray pattern



Single crystal X-ray diffraction data for $Cp_2Zr(H)NH_2BH_3$, **1bII**

A colorless needle crystal of **1bII**, was coated with Paratone 8277 oil (Exxon) and mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo-K_α radiation. Details of crystal data, data collection[1,2] and structure refinement have been provided in Table 1. The data were corrected for Lorentz and polarization effects and for absorption using multi-scan method[1].

The structure was solved by the direct methods[3] and expanded using Fourier techniques[4]. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms on nitrogen, boron, and zirconium were refined isotropically, and the cyclopentadienyl hydrogen atoms were included at geometrically idealized positions and were not refined. The final cycle of full-matrix least-squares refinement using SHELXL97[5] converged with unweighted and weighted agreement factors, R = 0.0323 and wR = 0.0665 (all data), respectively, and goodness of fit, S = 1.048. The weighting scheme was based on counting statistics and the final difference map had no chemically significant features.

Table 1. Crystal data and structure refinement for $Cp_2Zr(H)NH_2BH_3$, **1bII**.

Identification code	tf840	
Empirical formula	$C_{20}H_{32}B_2N_2Zr_2$	
Formula weight	504.54	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 16.4630(6) Å	α= 90°.
	b = 15.4550(5) Å	β= 123.341(2)°.
	c = 10.1380(3) Å	γ = 90°.
Volume	2154.92(12) $Å^3$	
Z	4	
Density (calculated)	1.555 Mg/m^3	
Absorption coefficient	0.973 mm^{-1}	
F(000)	1024	
Crystal size	0.14 x 0.08 x 0.07 mm^3	
Theta range for data collection	2.41 to 27.48°.	
Index ranges	-21<=h<=21, -19<=k<=20, -13<=l<=13	
Reflections collected	9977	
Independent reflections	2459 [R(int) = 0.0682]	
Completeness to theta = 27.48°	99.6 %	
Absorption correction	'Multi-scan'	
Max. and min. transmission	0.9350 and 0.8758	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2459 / 0 / 143	
Goodness-of-fit on F^2	1.048	
Final R indices [I>2sigma(I)]	R1 = 0.0268, wR2 = 0.0640	
R indices (all data)	R1 = 0.0323, wR2 = 0.0665	
Extinction coefficient	0.0025(4)	
Largest diff. peak and hole	0.484 and -0.524 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $Cp_2Zr(H)NH_2BH_3$, **1bII**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(6)	3955(2)	1574(2)	8690(4)	48(1)
C(7)	3671(2)	1094(2)	7319(3)	41(1)
C(8)	3620(2)	227(2)	7650(3)	35(1)
C(9)	3842(2)	181(2)	9192(3)	39(1)
C(10)	4054(2)	1013(2)	9824(3)	45(1)
N(1)	1460(1)	-61(1)	5894(2)	23(1)
B(1)	1337(2)	-445(2)	7166(3)	27(1)
C(1)	1032(2)	1875(2)	5284(3)	39(1)
C(2)	626(2)	1690(2)	6162(3)	38(1)
C(3)	1154(2)	2154(2)	7591(3)	33(1)
C(4)	1898(2)	2605(2)	7610(3)	33(1)
C(5)	1814(2)	2441(2)	6174(3)	37(1)
Zr(1)	2288(1)	1031(1)	7653(1)	19(1)

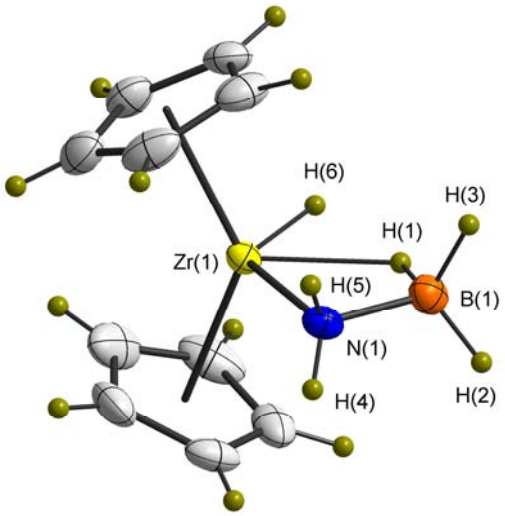


Figure 1. Solid-state molecular structures of **1bII** with thermal ellipsoids at 50% probability.

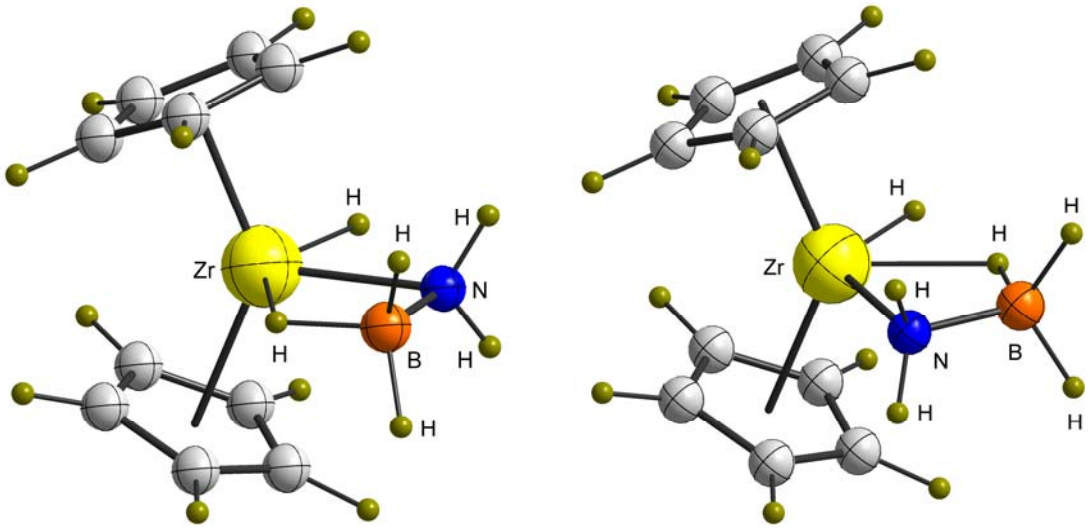


Figure 2. Optimized molecular structures of **1a** (left) and **1b** (right).

Table 3. Bond lengths [Å] and angles [°] for $Cp_2Zr(H)NH_2BH_3$, **1bII**.

N(1)-Zr(1)	2.2843(18)	N(1)-B(1)	1.531(3)
N(1)-H(4)	0.86(3)	N(1)-H(5)	0.84(3)
B(1)-Zr(1)	2.657(2)	B(1)-H(3)	1.11(3)
B(1)-H(1)	1.24(2)	B(1)-H(2)	1.11(3)
C-C	1.376(4) - 1.409(4)	C-Zr	2.480(2) - 2.524(2)
B(1)-N(1)-Zr(1)	85.86(12)	H(4)-N(1)-H(5)	111(2)
B(1)-N(1)-H(4)	116.5(16)	B(1)-N(1)-H(5)	112.7(17)
Zr(1)-N(1)-H(4)	116.7(17)	Zr(1)-N(1)-H(5)	112.6(17)
N(1)-B(1)-Zr(1)	59.05(10)	Zr(1)-B(1)-H(1)	45.0(11)
Zr(1)-B(1)-H(3)	117.0(13)	Zr(1)-B(1)-H(2)	124.8(17)
N(1)-B(1)-H(1)	103.9(11)	N(1)-B(1)-H(2)	115.3(16)
H(1)-B(1)-H(2)	104(2)	N(1)-B(1)-H(3)	112.9(12)
H(1)-B(1)-H(3)	104.6(17)	H(2)-B(1)-H(3)	115(2)
N(1)-Zr(1)-B(1)	35.09(7)	N(1)-Zr(1)-H(1)	61.4(7)
B(1)-Zr(1)-H(1)	26.3(7)	N(1)-Zr(1)-H(6)	123.0(8)
B(1)-Zr(1)-H(6)	87.9(8)	H(1)-Zr(1)-H(6)	61.8(10)
C-C-C	107.5(2) - 108.3(2)		

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for $Cp_2Zr(H)NH_2BH_3$, **1bII**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(6)	30(1)	40(1)	79(2)	-19(1)	32(1)	-15(1)
C(7)	34(1)	57(2)	46(1)	14(1)	31(1)	7(1)
C(8)	20(1)	41(1)	44(1)	-13(1)	18(1)	1(1)
C(9)	22(1)	51(2)	44(1)	19(1)	19(1)	11(1)
C(10)	18(1)	81(2)	29(1)	-16(1)	8(1)	-3(1)
N(1)	20(1)	26(1)	22(1)	-5(1)	12(1)	0(1)
B(1)	25(1)	27(1)	29(1)	-4(1)	16(1)	-4(1)
C(1)	46(2)	34(1)	23(1)	2(1)	10(1)	16(1)
C(2)	25(1)	29(1)	44(1)	-3(1)	10(1)	6(1)
C(3)	34(1)	29(1)	39(1)	-1(1)	23(1)	10(1)
C(4)	41(1)	24(1)	33(1)	-4(1)	18(1)	2(1)
C(5)	51(2)	27(1)	36(1)	7(1)	27(1)	9(1)
Zr(1)	18(1)	21(1)	17(1)	-2(1)	10(1)	0(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $Cp_2Zr(H)NH_2BH_3$, **1bII**.

	x	y	z	U(eq)
H(12)	4060	2182	8810	58
H(13)	3538	1319	6348	49
H(14)	3462	-247	6953	42
H(15)	3847	-330	9718	46
H(16)	4236	1167	10860	55
H(1)	1810(18)	52(16)	8310(30)	32(6)
H(2)	1690(20)	-1084(18)	7630(40)	49(9)
H(3)	577(19)	-399(16)	6860(30)	31(6)
H(4)	1779(19)	-367(16)	5620(30)	27(6)
H(5)	932(19)	105(16)	5100(30)	25(6)
H(6)	2450(20)	1082(15)	9500(30)	32(7)
H(7)	815	1655	4266	47
H(8)	90	1318	5847	45
H(9)	1027	2159	8399	39
H(10)	2376	2960	8445	40
H(11)	2218	2674	5862	44

Single crystal X-ray diffraction data for $Cp_2Zr(H)NH_2BH_3$, **1bI**

A colorless needle crystal of **1bI**, was coated with Paratone 8277 oil (Exxon) and mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo-Kα radiation. Details of crystal data, data collection[1,2] and structure refinement have been provided in Table 6. The data were corrected for Lorentz and polarization effects and for absorption using multi-scan method[1].

The structure was solved by the direct methods[3] and expanded using Fourier techniques[4]. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were refined isoropically. The final cycle of full-matrix least-squares refinement using SHELXL97[5] converged with unweighted and weighted agreement factors, R = 0.0819 and wR = 0.0841 (all data), respectively, and goodness of fit, S = 1.144. The weighting scheme was based on counting statistics and the final difference map had no chemically significant features.

Table 6. Crystal data and structure refinement for $Cp_2Zr(H)NH_2BH_3$, **1bI**.

Identification code	tf903	
Empirical formula	$C_{10}\ H_{16}\ B\ N\ Zr$	
Formula weight	252.27	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 2_1/c 1	
Unit cell dimensions	a = 7.9840(5) Å	α= 90.000(3)°.
	b = 14.8370(5) Å	β= 117.830(3)°.
	c = 10.3050(5) Å	γ = 90.000(2)°.
Volume	1079.52(9) $Å^3$	
Z	4	
Density (calculated)	1.552 Mg/m^3	
Absorption coefficient	0.971 mm^{-1}	
F(000)	512	
Crystal size	0.06 x 0.02 x 0.02 mm^3	
Theta range for data collection	2.62 to 27.58°.	
Index ranges	-10<=h<=10, -19<=k<=19, -13<=l<=13	
Reflections collected	16239	
Independent reflections	2488 [R(int) = 0.1289]	
Completeness to theta = 27.58°	99.3 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9808 and 0.9440	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2488 / 0 / 182	
Goodness-of-fit on F^2	1.144	
Final R indices [I>2sigma(I)]	R1 = 0.0536, wR2 = 0.0762	
R indices (all data)	R1 = 0.0819, wR2 = 0.0841	
Largest diff. peak and hole	0.636 and -0.648 $e.Å^{-3}$	

Table 7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $Cp_2Zr(H)NH_2BH_3$, **1bI**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	3168(7)	2210(4)	2651(7)	41(1)
C(2)	3272(7)	1302(4)	2956(6)	43(1)
C(3)	2701(7)	836(4)	1637(7)	38(1)
C(4)	2258(6)	1465(4)	540(5)	36(1)
C(5)	2557(7)	2319(4)	1172(6)	38(1)
C(6)	7233(9)	238(4)	3802(7)	47(2)
C(7)	8607(8)	908(4)	4308(6)	39(1)
C(8)	9119(8)	1079(4)	3217(6)	39(1)
C(9)	8087(8)	513(4)	2029(7)	45(2)
C(10)	6913(9)	7(4)	2396(7)	50(2)
B(1)	7095(9)	3225(4)	2207(6)	33(1)
N(1)	7161(6)	2822(3)	3607(5)	27(1)
Zr(1)	5760(1)	1579(1)	2210(1)	20(1)

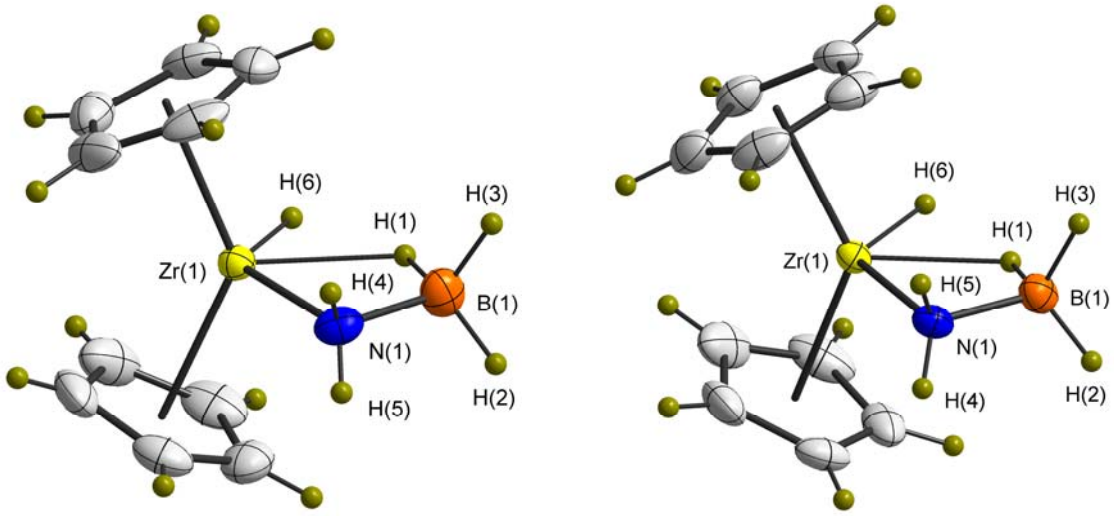


Figure 3. Solid-state molecular structures of **1bI** (left) and **1bII** (right) with thermal ellipsoids at 50% probability.

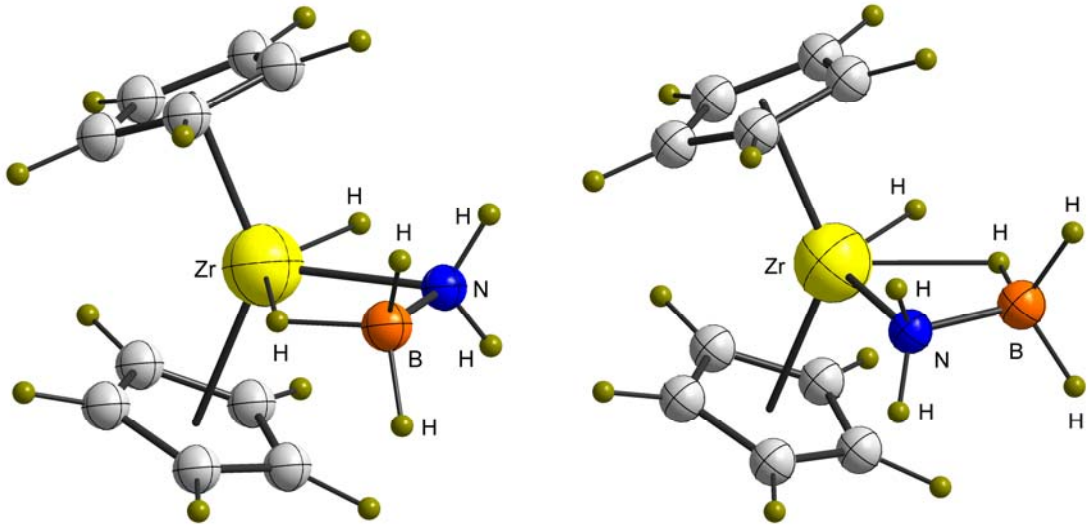


Figure 4. Optimized molecular structures of **1a** (left) and **1b** (right).

Table 8. Bond lengths [Å] and angles [°] for $Cp_2Zr(H)NH_2BH_3$, **1bI**.

B(1)-N(1)	1.539(7)	N(1)-Zr(1)	2.286(4)
B(1)-Zr(1)	2.665(5)	B(1)-H(1)	1.22(4)
N(1)-H(4)	0.81(5)	B(1)-H(2)	1.09(5)
N(1)-H(5)	0.81(6)	B(1)-H(3)	1.10(4)
Zr(1)-H(6)	1.71(4)	Zr(1)-H(1)	2.02(4)
C-Zr	2.477(5) - 2.517(5)	C-C	1.375(8) - 1.398(8)
N(1)-Zr(1)-H(1)	60.9(13)	B(1)-Zr(1)-H(1)	25.7(13)
N(1)-Zr(1)-H(6)	125.1(14)	B(1)-Zr(1)-H(6)	90.0(14)
B(1)-N(1)-Zr(1)	86.0(3)	H(1)-Zr(1)-H(6)	64.4(19)
H(1)-B(1)-H(3)	104(3)	H(2)-B(1)-H(3)	111(3)
Zr(1)-N(1)-H(4)	116(3)	Zr(1)-N(1)-H(5)	119(4)
B(1)-N(1)-H(4)	115(3)	H(4)-N(1)-H(5)	110(5)
B(1)-N(1)-H(5)	108(4)	N(1)-B(1)-Zr(1)	58.8(2)
Zr(1)-B(1)-H(1)	46(2)	Zr(1)-B(1)-H(3)	122(2)
Zr(1)-B(1)-H(2)	125(3)	H(1)-B(1)-H(2)	109(3)
N(1)-B(1)-H(1)	105(2)	N(1)-B(1)-H(3)	115(2)
N(1)-B(1)-H(2)	112(3)	C(10)-C(9)-C(8)	106.6(6) - 109.4(6)

Table 9. Anisotropic displacement parameters ($Å^2$x 10^3)for $Cp_2Zr(H)NH_2BH_3$, **1bI**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	21(3)	59(4)	48(4)	-24(3)	20(3)	-3(2)
C(2)	24(3)	78(4)	32(3)	18(3)	17(2)	5(3)
C(3)	30(3)	30(3)	59(4)	3(3)	24(3)	1(2)
C(4)	19(2)	59(4)	26(3)	-8(3)	7(2)	-2(2)
C(5)	23(3)	34(3)	51(4)	9(3)	14(2)	7(2)
C(6)	43(4)	41(3)	61(4)	30(3)	26(3)	18(3)
C(7)	36(3)	44(3)	33(3)	3(3)	12(3)	19(2)
C(8)	27(3)	41(3)	52(4)	1(3)	20(3)	5(2)
C(9)	46(4)	50(4)	42(3)	0(3)	24(3)	25(3)
C(10)	42(4)	26(3)	57(4)	-6(3)	2(3)	3(3)
B(1)	38(3)	28(3)	30(3)	-4(2)	13(3)	-5(2)
N(1)	23(2)	32(2)	27(2)	-7(2)	12(2)	1(2)
Zr(1)	19(1)	24(1)	19(1)	1(1)	9(1)	1(1)

Table 10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $Cp_2Zr(H)NH_2BH_3$, **1bI**.

	x	y	z	U(eq)
H(1)	6370(60)	2640(30)	1280(50)	35(13)
H(2)	8510(70)	3370(30)	2340(50)	50(15)
H(3)	6160(60)	3810(30)	1750(50)	34(13)
H(4)	6550(70)	3090(30)	3930(50)	34(15)
H(5)	8260(80)	2790(40)	4230(60)	54(19)
H(6)	5330(60)	1430(30)	430(50)	35(13)
H(7)	3360(80)	2600(40)	3230(60)	52(19)
H(8)	3650(70)	1010(30)	3830(50)	38(14)
H(9)	2520(60)	240(30)	1480(50)	27(13)
H(10)	1790(60)	1340(30)	-400(50)	32(13)
H(11)	2410(70)	2830(30)	720(50)	41(15)
H(12)	6700(90)	50(40)	4300(70)	90(30)
H(13)	9070(70)	1160(30)	5140(50)	34(15)
H(14)	9970(70)	1480(40)	3270(50)	49(16)
H(15)	8200(90)	510(40)	1220(70)	70(20)
H(16)	6210(70)	-350(30)	1880(50)	32(15)

Single crystal X-ray diffraction data for $Cp^*_2Zr(H)NH_2BH_3$, **2**

Severe disorder of the Cp* groups prevented the location of the hydrogen atoms on the Fourier map and the structure was not included in this study.

Table 11. Crystal data and structure refinement for $Cp^*_2Zr(H)NH_2BH_3$, **2**.

Identification code	tf909	
Empirical formula	C_{20} H_{35} B N Zr	
Formula weight	391.52	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 2_1 2_1 2_1	
Unit cell dimensions	a = 8.1330(2) Å	α= 90°.
	b = 11.1820(4) Å	β= 90°.
	c = 22.3460(9) Å	γ = 90°.
Volume	2032.22(12) Å^3	
Z	8	
Density (calculated)	2.559 Mg/m^3	
Absorption coefficient	1.082 mm^{-1}	
F(000)	1656	

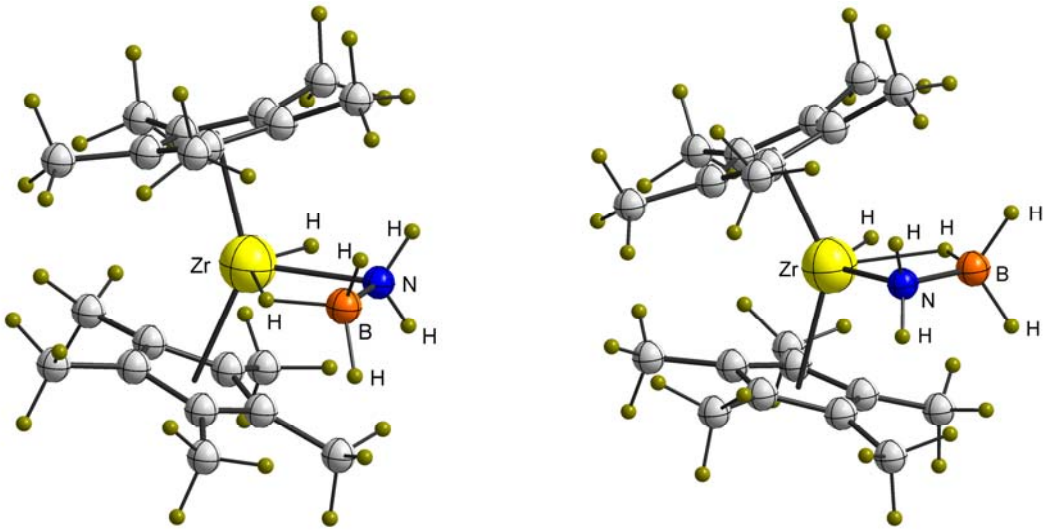


Figure 5. Optimized molecular structures of **2a** (left) and **2b** (right).

Single crystal X-ray diffraction data for $Cp_2Zr(Cl)NH_2BH_3$, **3a**

A colorless needle crystal of **3a** was coated with Paratone 8277 oil (Exxon) and mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo-Kα radiation. Details of crystal data, data collection[1,2] and structure refinement have been provided in Table 12. The data were corrected for Lorentz and polarization effects and for absorption using multi-scan method[1].

The structure was solved by the direct methods[3] and expanded using Fourier techniques[4]. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement using SHELXL97[5] converged with unweighted and weighted agreement factors, R = 0.0624 and wR = 0.0781 (all data), respectively, and goodness of fit, S = 1.042. The weighting scheme was based on counting statistics and the final difference map had no chemically significant features.

Table 12. Crystal data and structure refinement for $Cp_2Zr(Cl)NH_2BH_3$, **3a**.

Identification code	tf823	
Empirical formula	C_{10} H_{15} B Cl N Zr	
Formula weight	286.71	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 2_1/c 1	
Unit cell dimensions	a = 8.1000(4) Å	α= 90°.
	b = 10.7920(6) Å	β= 119.120(3)°.
	c = 15.0870(6) Å	γ = 90°.
Volume	1152.14(10) $Å^3$	
Z	4	
Density (calculated)	1.653 Mg/m^3	
Absorption coefficient	1.145 mm^{-1}	
F(000)	576	
Crystal size	0.10 x 0.05 x 0.04 mm^3	
Theta range for data collection	3.03 to 27.45°.	
Index ranges	-9<=h<=10, -14<=k<=13, -19<=l<=19	
Reflections collected	10749	
Independent reflections	2626 [R(int) = 0.0704]	
Completeness to theta = 27.45°	99.7 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9556 and 0.8941	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2626 / 0 / 188	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2sigma(I)]	R1 = 0.0354, wR2 = 0.0691	
R indices (all data)	R1 = 0.0624, wR2 = 0.0781	
Extinction coefficient	0.0071(9)	
Largest diff. peak and hole	0.636 and -0.983 e.$Å^{-3}$	

Table 13. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $Cp_2Zr(Cl)NH_2BH_3$, **3a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	7946(5)	7732(4)	2618(2)	37(1)
C(2)	7050(5)	6591(4)	2246(3)	37(1)
C(3)	5192(5)	6823(4)	1499(3)	36(1)
C(4)	4943(5)	8119(4)	1394(3)	34(1)
C(5)	6633(5)	8668(3)	2110(3)	35(1)
C(6)	9866(5)	7423(3)	324(3)	31(1)
C(7)	8834(5)	6332(3)	27(3)	33(1)
C(8)	9099(6)	5706(3)	906(3)	40(1)
C(9)	10348(5)	6405(4)	1748(3)	43(1)
C(10)	10789(5)	7469(4)	1394(3)	35(1)
B(1)	4322(6)	6884(4)	-894(3)	32(1)
N(1)	5165(4)	8177(3)	-755(2)	31(1)
Zr(1)	7344(1)	7608(1)	839(1)	21(1)
Cl(1)	8244(1)	9890(1)	810(1)	31(1)

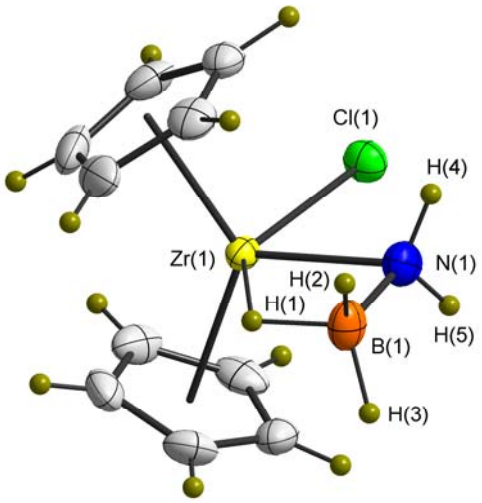


Figure 6. Solid-state molecular structures of **3a** with thermal ellipsoids at 50% probability.

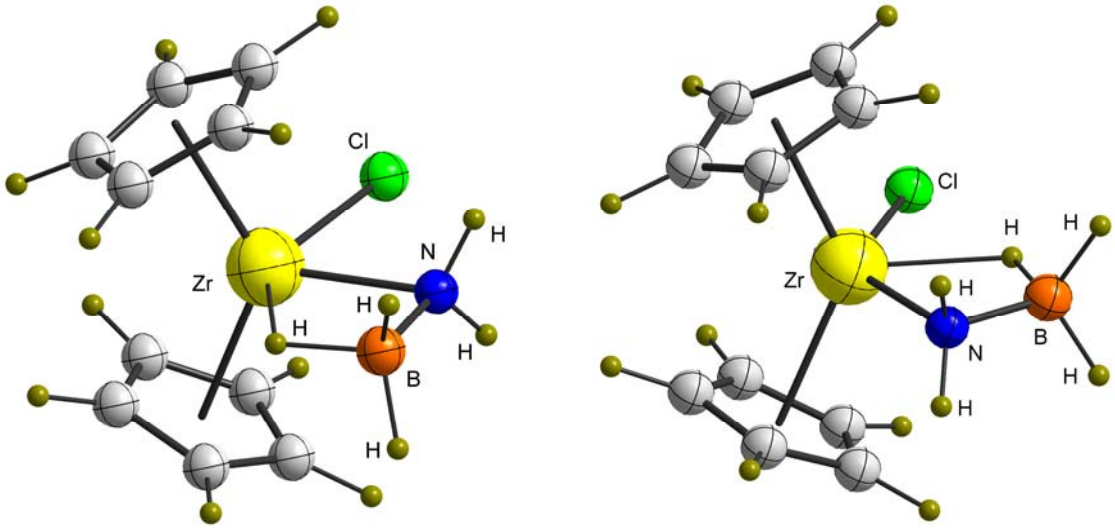


Figure 7. Optimized molecular structures of **3a** (left) and **3b** (right).

Table 14. Bond lengths [Å] and angles [°] for $Cp_2Zr(Cl)NH_2BH_3$, **3a**

B(1)-Zr(1)	2.685(4)	B(1)-N(1)	1.523(5)
N(1)-Zr(1)	2.268(3)	Zr(1)-Cl(1)	2.5742(8)
N(1)-H(4)	0.98(4)	B(1)-H(1)	1.24(3)
N(1)-H(5)	0.93(5)	B(1)-H(3)	1.13(3)
Zr(1)-H(1)	2.02(3)	B(1)-H(2)	1.09(4)
C(6)-C(10)	1.384(5) - 1.412(5)	C(3)-Zr(1)	2.471(3) - 2.537(3)
N(1)-B(1)-Zr(1)	57.59(15)	B(1)-N(1)-Zr(1)	87.89(19)
N(1)-B(1)-H(1)	102.8(15)	N(1)-B(1)-H(3)	113(2)
Zr(1)-B(1)-H(1)	45.6(15)	Zr(1)-B(1)-H(3)	117.5(16)
H(1)-B(1)-H(3)	107(2)	Zr(1)-B(1)-H(2)	122.6(18)
N(1)-B(1)-H(2)	114.8(19)	H(1)-B(1)-H(2)	101(2)
H(3)-B(1)-H(2)	116(3)	Zr(1)-N(1)-H(4)	112(2)
B(1)-N(1)-H(4)	118(2)	B(1)-N(1)-H(5)	114(3)
Zr(1)-N(1)-H(5)	110(3)	N(1)-Zr(1)-Cl(1)	78.68(8)
H(4)-N(1)-H(5)	112(4)	N(1)-Zr(1)-H(1)	60.4(9)
Cl(1)-Zr(1)-H(1)	139.1(9)	C(7)-C(6)-C(10)	107.4(3) - 108.7(3)

Table 15. Anisotropic displacement parameters ($Å^2$x 10^3)for $Cp_2Zr(Cl)NH_2BH_3$, **3a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	26(2)	66(3)	18(2)	-2(2)	10(1)	-3(2)
C(2)	45(2)	42(2)	35(2)	17(2)	28(2)	12(2)
C(3)	33(2)	45(2)	37(2)	-5(2)	23(2)	-12(2)
C(4)	27(2)	48(2)	33(2)	7(2)	19(2)	7(2)
C(5)	51(2)	35(2)	39(2)	-7(2)	37(2)	-5(2)
C(6)	27(2)	40(2)	31(2)	4(2)	19(1)	7(2)
C(7)	37(2)	37(2)	33(2)	-6(2)	23(2)	6(2)
C(8)	45(2)	28(2)	60(3)	14(2)	36(2)	17(2)
C(9)	35(2)	62(3)	32(2)	18(2)	16(2)	29(2)
C(10)	20(2)	53(2)	30(2)	-6(2)	10(1)	5(2)
B(1)	29(2)	33(2)	24(2)	1(2)	4(2)	0(2)
N(1)	28(2)	36(2)	25(1)	2(1)	9(1)	1(1)
Zr(1)	18(1)	25(1)	19(1)	1(1)	9(1)	2(1)
Cl(1)	33(1)	26(1)	34(1)	-1(1)	17(1)	-2(1)

Table 16. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $Cp_2Zr(Cl)NH_2BH_3$, **3a**.

	x	y	z	U(eq)
H(6)	9110(50)	7820(30)	3080(30)	34(10)
H(7)	7570(40)	5830(30)	2450(20)	21(8)
H(8)	4280(50)	6280(30)	1140(30)	35(10)
H(9)	3910(50)	8500(40)	980(30)	47(11)
H(10)	6880(50)	9510(30)	2220(20)	34(9)
H(11)	9840(50)	8040(40)	-140(30)	46(11)
H(12)	8050(40)	6090(30)	-650(20)	21(8)
H(13)	8490(40)	5020(30)	880(20)	19(8)
H(14)	10690(60)	6180(40)	2420(30)	60(12)
H(15)	11490(50)	8050(40)	1770(30)	46(12)
H(1)	5450(40)	6350(30)	-100(20)	36(9)
H(3)	2910(50)	6880(30)	-910(20)	37(9)
H(2)	4440(50)	6310(30)	-1460(30)	48(10)
H(4)	5750(50)	8410(40)	-1170(30)	47(11)
H(5)	4400(60)	8810(50)	-730(30)	72(15)

$Cp^*_2Zr(Cl)NH_2BH_3$, **4a** and **4b**

These compounds were not observed experimentally.

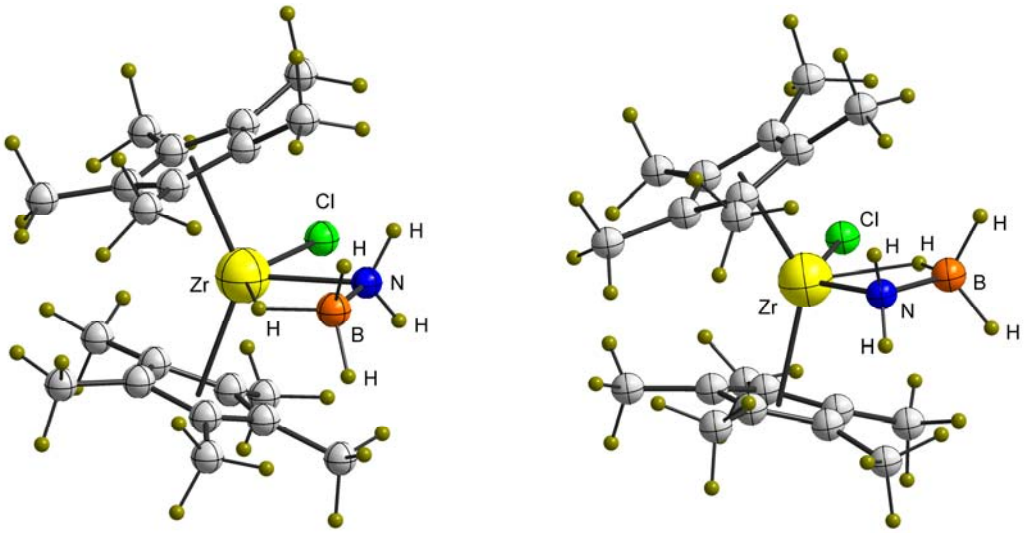


Figure 8. Optimized molecular structures of $Cp^*_2Zr(Cl)NH_2BH_3$, **4a** (left) and **4b** (right). These compounds were not observed experimentally.

Computational Details

Molecular Structures were optimized using density functional theory. ThePBE1PBE hybrid functional[6] was used in together with the def2-TZVP basis set.[7] Frequency calculations were performed on the optimized structures to ensure that they represent stable minima on the potential energy surface. All calculations were performed with the Gaussian 03 program package.[8]

Optimized coordinates of 1a in mol2 format (Figure 2 and 4):

```
@<TRIPOS>MOLECULE
 Molden generated mol2
    29     36      1
 SMALL
 NO_CHARGES
 ****
 ****
@<TRIPOS>ATOM
     1  C     7.7865     8.2849     1.3131  C.3   1 RES1    0.0000
     2  C     7.5218     7.6625     0.0730  C.3   1 RES1    0.0000
     3  C     6.9875     6.3792     0.3272  C.3   1 RES1    0.0000
     4  C     6.8984     6.2147     1.7214  C.3   1 RES1    0.0000
     5  C     7.3892     7.3945     2.3325  C.3   1 RES1    0.0000
     6 ZR     5.2897     8.0486     1.1565 ZR     1 RES1    0.0000
     7  C     3.8235     9.1466     2.8762  C.3   1 RES1    0.0000
     8  C     4.3669     7.9897     3.4717  C.3   1 RES1    0.0000
     9  C     3.8341     6.8580     2.8056  C.3   1 RES1    0.0000
    10  C     2.9617     7.3181     1.8016  C.3   1 RES1    0.0000
    11  C     2.9664     8.7295     1.8326  C.3   1 RES1    0.0000
    12  H     5.7782     9.8035     1.4234  H     1 RES1    0.0000
    13  N     4.7907     9.1356    -0.8016  N.4   1 RES1    0.0000
    14  B     4.3019     7.7803    -1.3113  B     1 RES1    0.0000
    15  H     5.0518     7.9711     4.3062  H     1 RES1    0.0000
    16  H     4.0383     5.8245     3.0423  H     1 RES1    0.0000
    17  H     2.4058     6.7052     1.1087  H     1 RES1    0.0000
    18  H     2.3960     9.3755     1.1814  H     1 RES1    0.0000
    19  H     4.0170    10.1647     3.1717  H     1 RES1    0.0000
    20  H     7.7107     8.0817    -0.9044  H     1 RES1    0.0000
    21  H     6.6824     5.6646    -0.4217  H     1 RES1    0.0000
    22  H     6.5386     5.3350     2.2338  H     1 RES1    0.0000
    23  H     7.4701     7.5743     3.3940  H     1 RES1    0.0000
    24  H     8.2223     9.2602     1.4564  H     1 RES1    0.0000
    25  H     4.4865     6.9431    -0.3292  H     1 RES1    0.0000
    26  H     3.1078     7.7325    -1.4895  H     1 RES1    0.0000
    27  H     4.9867     7.3193    -2.1936  H     1 RES1    0.0000
    28  H     5.5963     9.5351    -1.2575  H     1 RES1    0.0000
    29  H     4.1001     9.8625    -0.6958  H     1 RES1    0.0000
@<TRIPOS>BOND
     1      1      2      1
     2      1      5      1
     3      1      6      1
     4      1     24      1
     5      2      3      1
     6      2      6      1
```

```
     7      2     20      1
     8      3      4      1
     9      3      6      1
    10      3     21      1
    11      4      5      1
    12      4      6      1
    13      4     22      1
    14      5      6      1
    15      5     23      1
    16      6      7      1
    17      6      8      1
    18      6      9      1
    19      6     10      1
    20      6     11      1
    21      7      8      1
    22      7     11      1
    23      7     19      1
    24      8      9      1
    25      8     15      1
    26      9     10      1
    27      9     16      1
    28     10     11      1
    29     10     17      1
    30     11     18      1
    31     13     14      1
    32     13     28      1
    33     13     29      1
    34     14     25      1
    35     14     26      1
    36     14     27      1
@<TRIPOS>SUBSTRUCTURE
      1 RES1       1
```

Optimized coordinates of 1b in mol2 format (Figure 2 and 4):

```
@<TRIPOS>MOLECULE
 Molden generated mol2
    29     36      1
 SMALL
 NO_CHARGES
 ****
 ****
@<TRIPOS>ATOM
     1  C    -0.4420     3.6675     4.9696  C.3   1 RES1    0.0000
     2  C    -1.3960     2.7939     4.4190  C.3   1 RES1    0.0000
     3  C    -2.4577     2.6599     5.3444  C.3   1 RES1    0.0000
     4  C    -2.1677     3.4739     6.4609  C.3   1 RES1    0.0000
     5  C    -0.9159     4.0842     6.2363  C.3   1 RES1    0.0000
     6 ZR    -0.4594     1.6356     6.4580 ZR     1 RES1    0.0000
     7  C     2.0362     1.9174     6.3688  C.3   1 RES1    0.0000
     8  C     1.8154     0.5291     6.4018  C.3   1 RES1    0.0000
     9  C     1.2267     0.2032     7.6438  C.3   1 RES1    0.0000
    10  C     1.1110     1.3935     8.3971  C.3   1 RES1    0.0000
    11  C     1.5997     2.4533     7.6053  C.3   1 RES1    0.0000
    12  N    -0.8334    -0.1455     5.0563  N.4   1 RES1    0.0000
```

```
     13  B    -1.7941    -0.6269     6.1646  B     1 RES1    0.0000
     14  H     2.0612    -0.1645     5.6114  H     1 RES1    0.0000
     15  H     0.9155    -0.7804     7.9627  H     1 RES1    0.0000
     16  H     0.7280     1.4733     9.4011  H     1 RES1    0.0000
     17  H     1.6515     3.4907     7.9002  H     1 RES1    0.0000
     18  H     2.4838     2.4700     5.5561  H     1 RES1    0.0000
     19  H    -1.3279     2.3187     3.4515  H     1 RES1    0.0000
     20  H    -3.3350     2.0417     5.2240  H     1 RES1    0.0000
     21  H    -2.7938     3.6081     7.3276  H     1 RES1    0.0000
     22  H    -0.4175     4.7673     6.9077  H     1 RES1    0.0000
     23  H     0.4798     3.9786     4.5006  H     1 RES1    0.0000
     24  H    -1.4200    -1.6404     6.7054  H     1 RES1    0.0000
     25  H    -2.9520    -0.6277     5.8196  H     1 RES1    0.0000
     26  H    -1.7599     0.2601     7.1156  H     1 RES1    0.0000
     27  H    -1.2799     0.0560     4.1751  H     1 RES1    0.0000
     28  H    -0.0578    -0.7640     4.8777  H     1 RES1    0.0000
     29  H    -1.2924     1.8177     8.0696  H     1 RES1    0.0000
@<TRIPOS>BOND
      1      1      2      1
      2      1      5      1
      3      1      6      1
      4      1     23      1
      5      2      3      1
      6      2      6      1
      7      2     19      1
      8      3      4      1
      9      3      6      1
     10      3     20      1
     11      4      5      1
     12      4      6      1
     13      4     21      1
     14      5      6      1
     15      5     22      1
     16      6      7      1
     17      6      8      1
     18      6      9      1
     19      6     10      1
     20      6     11      1
     21      7      8      1
     22      7     11      1
     23      7     18      1
     24      8      9      1
     25      8     14      1
     26      9     10      1
     27      9     15      1
     28     10     11      1
     29     10     16      1
     30     11     17      1
     31     12     13      1
     32     12     27      1
     33     12     28      1
     34     13     24      1
     35     13     25      1
     36     13     26      1
@<TRIPOS>SUBSTRUCTURE
       1 RES1       1
```

Optimized coordinates of 2a in mol2 format (Figure 5):

```
@<TRIPOS>MOLECULE
 Molden generated mol2
    59     66      1
 SMALL
 USER_CHARGES
 ****
 ****
@<TRIPOS>ATOM
     1  C    -2.4815    -0.6762    -0.4963  C.3   1 RES1    0.0387
     2  C    -2.1510     0.5368    -1.1628  C.3   1 RES1    0.1347
     3  C    -1.7663     1.4800    -0.1775  C.3   1 RES1   -0.0026
     4  C    -1.8587     0.8513     1.0986  C.3   1 RES1    0.0167
     5  C    -2.3258    -0.4692     0.8993  C.3   1 RES1    0.0806
     6 ZR     0.0086    -0.3416    -0.1723 ZR    1 RES1   -0.0947
     7  C     1.7482     1.1343     0.9696  C.3   1 RES1    0.0192
     8  C     1.8143     1.4279    -0.4220  C.3   1 RES1    0.0487
     9  C     2.3007     0.2764    -1.0919  C.3   1 RES1    0.1681
    10  C     2.5205    -0.7314    -0.1215  C.3   1 RES1   -0.0820
    11  C     2.1733    -0.2034     1.1548  C.3   1 RES1    0.1272
    12  N     0.0951    -2.5235    -0.8652  N.4   1 RES1   -0.3723
    13  B    -0.0152    -2.9092     0.6104  B     1 RES1   -0.1983
    14  H     0.0400    -0.2824    -2.0075  H     1 RES1   -0.0689
    15  C    -1.5993     2.9441    -0.4171  C.3   1 RES1   -0.4407
    16  C    -1.7938     1.5267     2.4296  C.3   1 RES1   -0.4399
    17  C    -2.7707    -1.3862     1.9875  C.3   1 RES1   -0.3956
    18  C    -3.0681    -1.8887    -1.1406  C.3   1 RES1   -0.5052
    19  C    -2.3902     0.8367    -2.6050  C.3   1 RES1   -0.4214
    20  C     2.7043     0.2177    -2.5272  C.3   1 RES1   -0.4292
    21  C     3.2056    -2.0352    -0.3659  C.3   1 RES1   -0.4488
    22  C     2.4086    -0.8813     2.4639  C.3   1 RES1   -0.4281
    23  C     1.5328     2.1270     2.0630  C.3   1 RES1   -0.4460
    24  C     1.6724     2.7690    -1.0624  C.3   1 RES1   -0.4632
    25  H    -0.0688    -1.7941     1.2671  H     1 RES1    0.0949
    26  H    -1.0508    -3.4687     0.8794  H     1 RES1   -0.0486
    27  H     0.9628    -3.4616     1.0570  H     1 RES1   -0.0409
    28  H     0.9572    -2.7620    -1.3318  H     1 RES1    0.2463
    29  H    -0.6721    -2.7964    -1.4601  H     1 RES1    0.2515
    30  H     2.7729    -2.8473     0.2209  H     1 RES1    0.1667
    31  H     3.1724    -2.3152    -1.4214  H     1 RES1    0.1231
    32  H     4.2648    -1.9649    -0.0958  H     1 RES1    0.1392
    33  H     2.5738    -0.7795    -2.9486  H     1 RES1    0.1309
    34  H     2.1143     0.9038    -3.1344  H     1 RES1    0.1368
    35  H     3.7607     0.4899    -2.6398  H     1 RES1    0.1335
    36  H     1.7451    -0.5031     3.2435  H     1 RES1    0.1228
    37  H     2.2520    -1.9579     2.3899  H     1 RES1    0.1573
    38  H     3.4375    -0.7138     2.8028  H     1 RES1    0.1350
    39  H     1.1032     1.6731     2.9565  H     1 RES1    0.1343
    40  H     2.4896     2.5733     2.3569  H     1 RES1    0.1452
    41  H     0.8800     2.9448     1.7567  H     1 RES1    0.1154
    42  H     1.1520     3.4791    -0.4218  H     1 RES1    0.1289
    43  H     2.6608     3.1907    -1.2773  H     1 RES1    0.1437
    44  H     1.1340     2.7180    -2.0116  H     1 RES1    0.1407
    45  H    -3.8076    -1.1592     2.2615  H     1 RES1    0.1335
    46  H    -2.7212    -2.4316     1.6879  H     1 RES1    0.1400
    47  H    -2.1631    -1.2749     2.8869  H     1 RES1    0.1317
```

```
     48  H    -2.8052     1.7540     2.7857  H     1 RES1    0.1418
     49  H    -1.3230     0.9024     3.1920  H     1 RES1    0.1339
     50  H    -1.2496     2.4692     2.3893  H     1 RES1    0.1270
     51  H    -4.1615    -1.8265    -1.1682  H     1 RES1    0.1406
     52  H    -2.7328    -1.9962    -2.1750  H     1 RES1    0.1392
     53  H    -2.8118    -2.8016    -0.5983  H     1 RES1    0.1671
     54  H    -3.4076     1.2186    -2.7526  H     1 RES1    0.1314
     55  H    -1.6960     1.5881    -2.9820  H     1 RES1    0.1315
     56  H    -2.2724    -0.0516    -3.2255  H     1 RES1    0.1343
     57  H    -2.5789     3.4358    -0.4232  H     1 RES1    0.1428
     58  H    -1.0064     3.4277     0.3600  H     1 RES1    0.1150
     59  H    -1.1281     3.1560    -1.3770  H     1 RES1    0.1364
@<TRIPOS>BOND
      1      1      2      1
      2      1      5      1
      3      1      6      1
      4      1     18      1
      5      2      3      1
      6      2      6      1
      7      2     19      1
      8      3      4      1
      9      3      6      1
     10      3     15      1
     11      4      5      1
     12      4      6      1
     13      4     16      1
     14      5      6      1
     15      5     17      1
     16      6      7      1
     17      6      8      1
     18      6      9      1
     19      6     10      1
     20      6     11      1
     21      7      8      1
     22      7     11      1
     23      7     23      1
     24      8      9      1
     25      8     24      1
     26      9     10      1
     27      9     20      1
     28     10     11      1
     29     10     21      1
     30     11     22      1
     31     12     13      1
     32     12     28      1
     33     12     29      1
     34     13     25      1
     35     13     26      1
     36     13     27      1
     37     15     57      1
     38     15     58      1
     39     15     59      1
     40     16     48      1
     41     16     49      1
     42     16     50      1
     43     17     45      1
     44     17     46      1
```

```
    45     17     47      1
    46     18     51      1
    47     18     52      1
    48     18     53      1
    49     19     54      1
    50     19     55      1
    51     19     56      1
    52     20     33      1
    53     20     34      1
    54     20     35      1
    55     21     30      1
    56     21     31      1
    57     21     32      1
    58     22     36      1
    59     22     37      1
    60     22     38      1
    61     23     39      1
    62     23     40      1
    63     23     41      1
    64     24     42      1
    65     24     43      1
    66     24     44      1
@<TRIPOS>SUBSTRUCTURE
      1 RES1       1
```

Optimized coordinates of 2b in mol2 format (Figure 5):

```
@<TRIPOS>MOLECULE
 Molden generated mol2
    59     66      1
 SMALL
 NO_CHARGES
 ****
 ****
@<TRIPOS>ATOM
     1  C    -1.7021     1.4268     0.4758  C.3   1 RES1    0.0000
     2  C    -1.9171     0.2769     1.2894  C.3   1 RES1    0.0000
     3  C    -2.4326    -0.7474     0.4520  C.3   1 RES1    0.0000
     4  C    -2.4742    -0.2605    -0.8753  C.3   1 RES1    0.0000
     5  C    -2.0245     1.0869    -0.8612  C.3   1 RES1    0.0000
     6 ZR     0.0000    -0.3194    -0.2585 ZR    1 RES1    0.0000
     7  C     1.8377     1.4264    -0.4070  C.3   1 RES1    0.0000
     8  C     1.7568     1.0790     0.9695  C.3   1 RES1    0.0000
     9  C     2.1532    -0.2733     1.1020  C.3   1 RES1    0.0000
    10  C     2.5106    -0.7558    -0.1880  C.3   1 RES1    0.0000
    11  C     2.3103     0.2931    -1.1185  C.3   1 RES1    0.0000
    12  N     0.0231    -2.4523     0.5699  N.4   1 RES1    0.0000
    13  B    -0.0768    -2.8798    -0.9091  B     1 RES1    0.0000
    14  C    -3.0009    -2.0465     0.9160  C.3   1 RES1    0.0000
    15  C    -3.0202    -0.9793    -2.0624  C.3   1 RES1    0.0000
    16  C    -2.0853     2.0351    -2.0114  C.3   1 RES1    0.0000
    17  C    -1.5042     2.8225     0.9685  C.3   1 RES1    0.0000
    18  C    -1.8372     0.2129     2.7809  C.3   1 RES1    0.0000
    19  C     2.3579    -0.9774     2.4033  C.3   1 RES1    0.0000
    20  C     3.1846    -2.0537    -0.4860  C.3   1 RES1    0.0000
    21  C     2.6954     0.2672    -2.5596  C.3   1 RES1    0.0000
    22  C     1.6561     2.7811    -1.0085  C.3   1 RES1    0.0000
```

```
     23  C     1.5840     2.0102     2.1236  C.3   1 RES1    0.0000
     24  H    -1.1528    -3.3584    -1.1856  H     1 RES1    0.0000
     25  H     0.8590    -3.5387    -1.2926  H     1 RES1    0.0000
     26  H    -0.0030    -1.8021    -1.6215  H     1 RES1    0.0000
     27  H     0.8745    -2.7319     1.0330  H     1 RES1    0.0000
     28  H    -0.7535    -2.7444     1.1439  H     1 RES1    0.0000
     29  H    -0.0126     0.0593    -2.0498  H     1 RES1    0.0000
     30  H    -2.4774     3.3207     1.0458  H     1 RES1    0.0000
     31  H    -1.0501     2.8563     1.9574  H     1 RES1    0.0000
     32  H    -0.8958     3.4246     0.2931  H     1 RES1    0.0000
     33  H    -2.8329     0.2725     3.2345  H     1 RES1    0.0000
     34  H    -1.3804    -0.7163     3.1328  H     1 RES1    0.0000
     35  H    -1.2512     1.0373     3.1885  H     1 RES1    0.0000
     36  H    -4.0947    -1.9961     0.9231  H     1 RES1    0.0000
     37  H    -2.7243    -2.8788     0.2635  H     1 RES1    0.0000
     38  H    -2.6954    -2.2820     1.9384  H     1 RES1    0.0000
     39  H    -4.0799    -0.7394    -2.2060  H     1 RES1    0.0000
     40  H    -2.4885    -0.6990    -2.9730  H     1 RES1    0.0000
     41  H    -2.9308    -2.0600    -1.9514  H     1 RES1    0.0000
     42  H    -3.0637     2.5281    -2.0548  H     1 RES1    0.0000
     43  H    -1.3305     2.8188    -1.9322  H     1 RES1    0.0000
     44  H    -1.9260     1.5194    -2.9585  H     1 RES1    0.0000
     45  H     2.1476     1.0181    -3.1285  H     1 RES1    0.0000
     46  H     3.7669     0.4694    -2.6748  H     1 RES1    0.0000
     47  H     2.4884    -0.7013    -3.0160  H     1 RES1    0.0000
     48  H     3.0427    -2.3521    -1.5238  H     1 RES1    0.0000
     49  H     4.2619    -1.9668    -0.3050  H     1 RES1    0.0000
     50  H     2.8223    -2.8785     0.1307  H     1 RES1    0.0000
     51  H     1.0507     2.7445    -1.9172  H     1 RES1    0.0000
     52  H     1.1816     3.4756    -0.3156  H     1 RES1    0.0000
     53  H     2.6246     3.2129    -1.2828  H     1 RES1    0.0000
     54  H     2.5190    -2.0488     2.2682  H     1 RES1    0.0000
     55  H     3.2467    -0.5936     2.9168  H     1 RES1    0.0000
     56  H     1.5137    -0.8492     3.0858  H     1 RES1    0.0000
     57  H     1.1481     2.9619     1.8260  H     1 RES1    0.0000
     58  H     0.9663     1.5873     2.9188  H     1 RES1    0.0000
     59  H     2.5623     2.2285     2.5672  H     1 RES1    0.0000
@<TRIPOS>BOND
     1      1      2      1
     2      1      5      1
     3      1      6      1
     4      1     17      1
     5      2      3      1
     6      2      6      1
     7      2     18      1
     8      3      4      1
     9      3      6      1
    10      3     14      1
    11      4      5      1
    12      4      6      1
    13      4     15      1
    14      5      6      1
    15      5     16      1
    16      6      7      1
    17      6      8      1
    18      6      9      1
    19      6     10      1
```

```
    20      6     11      1
    21      7      8      1
    22      7     11      1
    23      7     22      1
    24      8      9      1
    25      8     23      1
    26      9     10      1
    27      9     19      1
    28     10     11      1
    29     10     20      1
    30     11     21      1
    31     12     13      1
    32     12     27      1
    33     12     28      1
    34     13     24      1
    35     13     25      1
    36     13     26      1
    37     14     36      1
    38     14     37      1
    39     14     38      1
    40     15     39      1
    41     15     40      1
    42     15     41      1
    43     16     42      1
    44     16     43      1
    45     16     44      1
    46     17     30      1
    47     17     31      1
    48     17     32      1
    49     18     33      1
    50     18     34      1
    51     18     35      1
    52     19     54      1
    53     19     55      1
    54     19     56      1
    55     20     48      1
    56     20     49      1
    57     20     50      1
    58     21     45      1
    59     21     46      1
    60     21     47      1
    61     22     51      1
    62     22     52      1
    63     22     53      1
    64     23     57      1
    65     23     58      1
    66     23     59      1
@<TRIPOS>SUBSTRUCTURE
      1 RES1       1
```

Optimized coordinates of 3a in mol2 format (Figure 7):

```
@<TRIPOS>MOLECULE
 Molden generated mol2
    29     36      1
 SMALL
 NO_CHARGES
```

```
 ****
 ****
@<TRIPOS>ATOM
     1 CL     6.0675    10.6352     1.0575 CL     1 RES1    0.0000
     2  N     4.6739     8.8413    -0.9716  N.4   1 RES1    0.0000
     3  B     4.1439     7.4219    -1.1507  B     1 RES1    0.0000
     4 ZR     5.3449     8.2213     1.1090 ZR     1 RES1    0.0000
     5  C     4.4993     8.3898     3.4588  C.3   1 RES1    0.0000
     6  C     3.1065     7.3799     1.9556  C.3   1 RES1    0.0000
     7  C     4.0529     7.1362     2.9645  C.3   1 RES1    0.0000
     8  C     2.9756     8.7811     1.8083  C.3   1 RES1    0.0000
     9  C     7.7855     8.0145     0.4404  C.3   1 RES1    0.0000
    10  C     7.1607     6.8425    -0.0067  C.3   1 RES1    0.0000
    11  C     3.8121     9.3980     2.7597  C.3   1 RES1    0.0000
    12  C     6.7182     6.1193     1.1290  C.3   1 RES1    0.0000
    13  C     7.1089     6.8406     2.2762  C.3   1 RES1    0.0000
    14  C     7.7416     8.0247     1.8557  C.3   1 RES1    0.0000
    15  H     5.2208     8.5468     4.2471  H     1 RES1    0.0000
    16  H     4.3679     6.1637     3.3119  H     1 RES1    0.0000
    17  H     2.5849     6.6352     1.3758  H     1 RES1    0.0000
    18  H     2.3226     9.2851     1.1113  H     1 RES1    0.0000
    19  H     3.9517    10.4589     2.8865  H     1 RES1    0.0000
    20  H     8.1910     8.8014    -0.1765  H     1 RES1    0.0000
    21  H     7.0005     6.5515    -1.0339  H     1 RES1    0.0000
    22  H     6.2015     5.1713     1.1114  H     1 RES1    0.0000
    23  H     6.9364     6.5455     3.3003  H     1 RES1    0.0000
    24  H     8.1204     8.8104     2.4907  H     1 RES1    0.0000
    25  H     4.4760     6.8152    -0.0427  H     1 RES1    0.0000
    26  H     2.9390     7.3498    -1.1622  H     1 RES1    0.0000
    27  H     4.7222     6.7781    -1.9923  H     1 RES1    0.0000
    28  H     5.4514     9.1309    -1.5480  H     1 RES1    0.0000
    29  H     4.0071     9.5991    -0.9533  H     1 RES1    0.0000
@<TRIPOS>BOND
     1      1      4      1
     2      2      3      1
     3      2      4      1
     4      2     28      1
     5      2     29      1
     6      3      4      1
     7      3     25      1
     8      3     26      1
     9      3     27      1
    10      4      5      1
    11      4      6      1
    12      4      7      1
    13      4      8      1
    14      4      9      1
    15      4     10      1
    16      4     11      1
    17      5      7      1
    18      5     11      1
    19      5     15      1
    20      6      7      1
    21      6      8      1
    22      6     17      1
    23      7     16      1
    24      8     11      1
```

```
    25      8     18      1
    26      9     10      1
    27      9     14      1
    28      9     20      1
    29     10     12      1
    30     10     21      1
    31     11     19      1
    32     12     13      1
    33     12     22      1
    34     13     14      1
    35     13     23      1
    36     14     24      1
@<TRIPOS>SUBSTRUCTURE
      1 RES1       1
```

Optimized coordinates of 3b in mol2 format (Figure 7):

```
@<TRIPOS>MOLECULE
 Molden generated mol2
    29     36      1
 SMALL
 NO_CHARGES
 ****
 ****
@<TRIPOS>ATOM
     1  C    -0.1942     0.0155     0.8764  C.3   1 RES1    0.0000
     2  C     0.6316     0.1986     2.0035  C.3   1 RES1    0.0000
     3  C     1.9766     0.0889     1.5735  C.3   1 RES1    0.0000
     4  C     1.9761    -0.1384     0.1907  C.3   1 RES1    0.0000
     5  C     0.6340    -0.1683    -0.2486  C.3   1 RES1    0.0000
     6 ZR     1.0337     2.2043     0.5161 ZR     1 RES1    0.0000
     7  C    -0.9084     3.2213    -0.7217  C.3   1 RES1    0.0000
     8  C    -1.4137     2.8584     0.5450  C.3   1 RES1    0.0000
     9  C    -0.7830     3.6606     1.5137  C.3   1 RES1    0.0000
    10  C     0.0940     4.5458     0.8391  C.3   1 RES1    0.0000
    11  C     0.0064     4.2802    -0.5357  C.3   1 RES1    0.0000
    12  N     1.9195     2.8872     2.5135  N.4   1 RES1    0.0000
    13  B     3.1694     3.2933     1.6913  B     1 RES1    0.0000
    14  H     2.8594     0.1902     2.1881  H     1 RES1    0.0000
    15  H     2.8470    -0.2141    -0.4409  H     1 RES1    0.0000
    16  H     0.3100    -0.2979    -1.2695  H     1 RES1    0.0000
    17  H    -1.2728     0.0044     0.8766  H     1 RES1    0.0000
    18  H     0.2916     0.3661     3.0151  H     1 RES1    0.0000
    19  H    -0.9579     3.6171     2.5786  H     1 RES1    0.0000
    20  H     0.7397     5.2833     1.2938  H     1 RES1    0.0000
    21  H     0.5876     4.7522    -1.3114  H     1 RES1    0.0000
    22  H    -1.1665     2.7718    -1.6684  H     1 RES1    0.0000
    23  H    -2.1640     2.1081     0.7384  H     1 RES1    0.0000
    24  H     4.1331     2.6086     1.9348  H     1 RES1    0.0000
    25  H     3.3688     4.4839     1.6922  H     1 RES1    0.0000
    26  H     2.8864     3.0273     0.4722  H     1 RES1    0.0000
    27  H     1.4653     3.6600     2.9759  H     1 RES1    0.0000
    28  H     2.0946     2.1742     3.2051  H     1 RES1    0.0000
    29 CL     1.9877     2.2629    -1.8011 CL     1 RES1    0.0000
@<TRIPOS>BOND
     1      1      2      1
     2      1      5      1
```

```
     3      1      6      1
     4      1     17      1
     5      2      3      1
     6      2      6      1
     7      2     18      1
     8      3      4      1
     9      3      6      1
    10      3     14      1
    11      4      5      1
    12      4      6      1
    13      4     15      1
    14      5      6      1
    15      5     16      1
    16      6      7      1
    17      6      8      1
    18      6      9      1
    19      6     10      1
    20      6     11      1
    21      7      8      1
    22      7     11      1
    23      7     22      1
    24      8      9      1
    25      8     23      1
    26      9     10      1
    27      9     19      1
    28     10     11      1
    29     10     20      1
    30     11     21      1
    31     12     13      1
    32     12     27      1
    33     12     28      1
    34     13     24      1
    35     13     25      1
    36     13     26      1
@<TRIPOS>SUBSTRUCTURE
      1 RES1       1
```

Optimized coordinates of 4a in mol2 format (Figure 8):

```
@<TRIPOS>MOLECULE
 Molden generated mol2
    59     66      1
 SMALL
 NO_CHARGES
 ****
 ****
@<TRIPOS>ATOM
     1  C    -1.9406    -0.0213     1.3912  C.3   1 RES1    0.0000
     2  C    -2.5057    -0.6933     0.2765  C.3   1 RES1    0.0000
     3  C    -2.5024     0.1902    -0.8224  C.3   1 RES1    0.0000
     4  C    -1.9498     1.4320    -0.3905  C.3   1 RES1    0.0000
     5  C    -1.6417     1.3084     0.9881  C.3   1 RES1    0.0000
     6 ZR    -0.0073    -0.2210    -0.2725 ZR     1 RES1    0.0000
     7  C     2.3388    -0.7341     0.7236  C.3   1 RES1    0.0000
     8  C     1.8165     0.3730     1.4300  C.3   1 RES1    0.0000
     9  C     1.7479     1.4745     0.5230  C.3   1 RES1    0.0000
    10  C     2.2034     1.0290    -0.7386  C.3   1 RES1    0.0000
```

```
     11  C     2.5285    -0.3511    -0.6296  C.3   1 RES1    0.0000
     12 CL    -0.0706    -2.6240     0.5029 CL     1 RES1    0.0000
     13  N    -0.0765    -1.3615    -2.2331  N.4   1 RES1    0.0000
     14  B     0.0193    -0.0224    -2.9557  B     1 RES1    0.0000
     15  C     1.6536     0.4208     2.9139  C.3   1 RES1    0.0000
     16  C     1.6164     2.9190     0.8779  C.3   1 RES1    0.0000
     17  C     2.5279     1.9345    -1.8777  C.3   1 RES1    0.0000
     18  C     3.1658    -1.1935    -1.6850  C.3   1 RES1    0.0000
     19  C     2.8082    -2.0019     1.3446  C.3   1 RES1    0.0000
     20  C    -3.1690    -2.0258     0.3040  C.3   1 RES1    0.0000
     21  C    -3.2115    -0.0628    -2.1110  C.3   1 RES1    0.0000
     22  C    -1.9272     2.6943    -1.1883  C.3   1 RES1    0.0000
     23  C    -1.4145     2.4487     1.9225  C.3   1 RES1    0.0000
     24  C    -1.8947    -0.5624     2.7814  C.3   1 RES1    0.0000
     25  H     0.0311     0.8558    -1.9943  H     1 RES1    0.0000
     26  H     1.0657     0.1387    -3.5305  H     1 RES1    0.0000
     27  H    -0.9483     0.2737    -3.6079  H     1 RES1    0.0000
     28  H    -0.9284    -1.8952    -2.3317  H     1 RES1    0.0000
     29  H     0.7010    -2.0001    -2.3245  H     1 RES1    0.0000
     30  H    -4.2930    -0.0757    -1.9352  H     1 RES1    0.0000
     31  H    -3.0001     0.7055    -2.8508  H     1 RES1    0.0000
     32  H    -2.9558    -1.0260    -2.5595  H     1 RES1    0.0000
     33  H    -4.2396    -1.8979     0.5040  H     1 RES1    0.0000
     34  H    -3.0749    -2.5529    -0.6468  H     1 RES1    0.0000
     35  H    -2.7502    -2.6687     1.0760  H     1 RES1    0.0000
     36  H    -2.8825     3.2243    -1.1033  H     1 RES1    0.0000
     37  H    -1.1476     3.3783    -0.8483  H     1 RES1    0.0000
     38  H    -1.7499     2.4951    -2.2459  H     1 RES1    0.0000
     39  H    -2.3786     2.7525     2.3461  H     1 RES1    0.0000
     40  H    -0.7699     2.1917     2.7626  H     1 RES1    0.0000
     41  H    -0.9962     3.3201     1.4229  H     1 RES1    0.0000
     42  H    -2.8977    -0.5805     3.2217  H     1 RES1    0.0000
     43  H    -1.5087    -1.5839     2.7948  H     1 RES1    0.0000
     44  H    -1.2653     0.0448     3.4327  H     1 RES1    0.0000
     45  H     2.6313     0.5083     3.4011  H     1 RES1    0.0000
     46  H     1.0590     1.2750     3.2368  H     1 RES1    0.0000
     47  H     1.1820    -0.4833     3.3031  H     1 RES1    0.0000
     48  H     2.6045     3.3912     0.8383  H     1 RES1    0.0000
     49  H     0.9781     3.4705     0.1849  H     1 RES1    0.0000
     50  H     1.2309     3.0653     1.8844  H     1 RES1    0.0000
     51  H     3.8237    -1.8574     1.7330  H     1 RES1    0.0000
     52  H     2.1698    -2.3140     2.1701  H     1 RES1    0.0000
     53  H     2.8334    -2.8230     0.6298  H     1 RES1    0.0000
     54  H     4.2565    -1.0982    -1.6563  H     1 RES1    0.0000
     55  H     2.9371    -2.2527    -1.5438  H     1 RES1    0.0000
     56  H     2.8388    -0.9019    -2.6847  H     1 RES1    0.0000
     57  H     3.4695     2.4566    -1.6697  H     1 RES1    0.0000
     58  H     2.6445     1.3895    -2.8119  H     1 RES1    0.0000
     59  H     1.7608     2.6948    -2.0341  H     1 RES1    0.0000
@<TRIPOS>BOND
     1      1      2      1
     2      1      5      1
     3      1      6      1
     4      1     24      1
     5      2      3      1
     6      2      6      1
     7      2     20      1
```

8	3	4	1
9	3	6	1
10	3	21	1
11	4	5	1
12	4	6	1
13	4	22	1
14	5	6	1
15	5	23	1
16	6	7	1
17	6	8	1
18	6	9	1
19	6	10	1
20	6	11	1
21	7	8	1
22	7	11	1
23	7	19	1
24	8	9	1
25	8	15	1
26	9	10	1
27	9	16	1
28	10	11	1
29	10	17	1
30	11	18	1
31	13	14	1
32	13	28	1
33	13	29	1
34	14	25	1
35	14	26	1
36	14	27	1
37	15	45	1
38	15	46	1
39	15	47	1
40	16	48	1
41	16	49	1
42	16	50	1
43	17	57	1
44	17	58	1
45	17	59	1
46	18	54	1
47	18	55	1
48	18	56	1
49	19	51	1
50	19	52	1
51	19	53	1
52	20	33	1
53	20	34	1
54	20	35	1
55	21	30	1
56	21	31	1
57	21	32	1
58	22	36	1
59	22	37	1
60	22	38	1
61	23	39	1
62	23	40	1
63	23	41	1
64	24	42	1

```
    65     24     43      1
    66     24     44      1
@<TRIPOS>SUBSTRUCTURE
      1 RES1       1
```

Optimized coordinates of 4b in mol2 format (Figure 8):

```
@<TRIPOS>MOLECULE
 Molden generated mol2
    59     66      1
 SMALL
 NO_CHARGES
 ****
 ****
@<TRIPOS>ATOM
     1  C     2.4637     0.8524    -0.2098  C.3   1 RES1    0.0000
     2  C     1.9140     0.8839     1.0994  C.3   1 RES1    0.0000
     3  C     1.6911    -0.4602     1.5073  C.3   1 RES1    0.0000
     4  C     2.0426    -1.3084     0.4315  C.3   1 RES1    0.0000
     5  C     2.5278    -0.4932    -0.6302  C.3   1 RES1    0.0000
     6 ZR    -0.0014     0.0416    -0.3815 ZR    1 RES1    0.0000
     7  C    -2.1504     1.0239     0.6666  C.3   1 RES1    0.0000
     8  C    -1.7033     0.0187     1.5539  C.3   1 RES1    0.0000
     9  C    -1.8174    -1.2379     0.8906  C.3   1 RES1    0.0000
    10  C    -2.3816    -0.9942    -0.3879  C.3   1 RES1    0.0000
    11  C    -2.5489     0.4016    -0.5461  C.3   1 RES1    0.0000
    12  C    -1.5253     0.2429     3.0190  C.3   1 RES1    0.0000
    13  C    -1.6492    -2.5905     1.5029  C.3   1 RES1    0.0000
    14  C    -2.9132    -2.0313    -1.3190  C.3   1 RES1    0.0000
    15  C    -3.1805     1.0819    -1.7128  C.3   1 RES1    0.0000
    16  C    -2.3744     2.4488     1.0381  C.3   1 RES1    0.0000
    17  C     1.7960     2.1087     1.9443  C.3   1 RES1    0.0000
    18  C     1.4974    -0.9389     2.9066  C.3   1 RES1    0.0000
    19  C     2.1410    -2.7958     0.5188  C.3   1 RES1    0.0000
    20  C     3.2145    -0.9650    -1.8679  C.3   1 RES1    0.0000
    21  C     3.0523     2.0095    -0.9395  C.3   1 RES1    0.0000
    22  N     0.0552    -1.7964    -1.7255  N.4   1 RES1    0.0000
    23  B    -0.0743    -0.8032    -2.9067  B     1 RES1    0.0000
    24  H    -1.1232    -0.9058    -3.5005  H     1 RES1    0.0000
    25  H     0.8961    -0.7844    -3.6239  H     1 RES1    0.0000
    26  H    -0.1147     0.3562    -2.3878  H     1 RES1    0.0000
    27  H     0.9177    -2.3175    -1.7275  H     1 RES1    0.0000
    28  H    -0.7030    -2.4589    -1.6664  H     1 RES1    0.0000
    29 CL    -0.0370     2.4681    -1.0580 CL    1 RES1    0.0000
    30  H    -2.5052     0.4383     3.4693  H     1 RES1    0.0000
    31  H    -1.1049    -0.6210     3.5288  H     1 RES1    0.0000
    32  H    -0.9015     1.1103     3.2408  H     1 RES1    0.0000
    33  H    -2.6232    -3.0361     1.7329  H     1 RES1    0.0000
    34  H    -1.1283    -3.2891     0.8427  H     1 RES1    0.0000
    35  H    -1.0909    -2.5470     2.4379  H     1 RES1    0.0000
    36  H    -4.0073    -2.0318    -1.2813  H     1 RES1    0.0000
    37  H    -2.6305    -1.8472    -2.3589  H     1 RES1    0.0000
    38  H    -2.5944    -3.0376    -1.0366  H     1 RES1    0.0000
    39  H    -4.2435     1.2666    -1.5219  H     1 RES1    0.0000
    40  H    -2.7006     2.0408    -1.9136  H     1 RES1    0.0000
    41  H    -3.1004     0.4767    -2.6165  H     1 RES1    0.0000
```

```
     42  H    -3.2884     2.5357     1.6379  H     1 RES1    0.0000
     43  H    -1.5502     2.8558     1.6259  H     1 RES1    0.0000
     44  H    -2.4834     3.0776     0.1569  H     1 RES1    0.0000
     45  H     2.6518     2.9547    -0.5788  H     1 RES1    0.0000
     46  H     4.1391     2.0174    -0.7947  H     1 RES1    0.0000
     47  H     2.8566     1.9621    -2.0113  H     1 RES1    0.0000
     48  H     3.1116    -0.2528    -2.6857  H     1 RES1    0.0000
     49  H     4.2843    -1.0978    -1.6711  H     1 RES1    0.0000
     50  H     2.8425    -1.9251    -2.2318  H     1 RES1    0.0000
     51  H     1.3288     2.9247     1.3886  H     1 RES1    0.0000
     52  H     1.2032     1.9273     2.8416  H     1 RES1    0.0000
     53  H     2.7834     2.4511     2.2719  H     1 RES1    0.0000
     54  H     2.2815    -3.2608    -0.4591  H     1 RES1    0.0000
     55  H     3.0086    -3.0851     1.1229  H     1 RES1    0.0000
     56  H     1.2634    -3.2502     0.9834  H     1 RES1    0.0000
     57  H     1.1020    -0.1663     3.5621  H     1 RES1    0.0000
     58  H     0.8457    -1.8108     2.9700  H     1 RES1    0.0000
     59  H     2.4692    -1.2409     3.3144  H     1 RES1    0.0000
@<TRIPOS>BOND
     1      1      2      1
     2      1      5      1
     3      1      6      1
     4      1     21      1
     5      2      3      1
     6      2      6      1
     7      2     17      1
     8      3      4      1
     9      3      6      1
    10      3     18      1
    11      4      5      1
    12      4      6      1
    13      4     19      1
    14      5      6      1
    15      5     20      1
    16      6      7      1
    17      6      8      1
    18      6      9      1
    19      6     10      1
    20      6     11      1
    21      7      8      1
    22      7     11      1
    23      7     16      1
    24      8      9      1
    25      8     12      1
    26      9     10      1
    27      9     13      1
    28     10     11      1
    29     10     14      1
    30     11     15      1
    31     12     30      1
    32     12     31      1
    33     12     32      1
    34     13     33      1
    35     13     34      1
    36     13     35      1
    37     14     36      1
    38     14     37      1
```

```
     39      14      38       1
     40      15      39       1
     41      15      40       1
     42      15      41       1
     43      16      42       1
     44      16      43       1
     45      16      44       1
     46      17      51       1
     47      17      52       1
     48      17      53       1
     49      18      57       1
     50      18      58       1
     51      18      59       1
     52      19      54       1
     53      19      55       1
     54      19      56       1
     55      20      48       1
     56      20      49       1
     57      20      50       1
     58      21      45       1
     59      21      46       1
     60      21      47       1
     61      22      23       1
     62      22      27       1
     63      22      28       1
     64      23      24       1
     65      23      25       1
     66      23      26       1
@<TRIPOS>SUBSTRUCTURE
      1 RES1       1
```

References:

1. Otwinowski, Z.; Minor, W. *Methods in Enzymology,* Macromolecular Crystallograpy, Carter, Jr., C. W.; Sweet, R. M. Eds., Academic Press **1997**, *276A*, 307-326.
2. Hooft, R. *COLLECT*: Users Manual, Nonius B.V., Delft. The Netherlands, **1998**.
3. Altomare, A., Cascarano, M., Giacovazzo, C.& Guagliardi, A. *J. Appl. Cryst.*, **1993***, 26*, 343-350.
4. Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M., The *DIRDIF-94* program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, **1994**.
5. Sheldrick, G. M. *Acta Cryst.* **2008** *A64,* 112-122.
6. (a) Perdew, J. P.; Burke, K.; Ernzerhof, M. Phys. Rev. Lett. 1996, 77, 3865. (b) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1997**, *78*, 1396. (c) Perdew, J. P.; Ernzerhof, M.; Burke, K. *J. Chem. Phys.* **1996**, *105*, 9982.
7. (a) Schäfer, A.; Huber, C.; Ahlrichs, R. J. Chem. Phys. 1994, 100, 5829. (b) Eichkorn, K.; Weigend, F.; Treutler, O.; Ahlrichs, R. Theor. Chem. Acc. 1997, 97, 119.
8. Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, **2004**.