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Supporting Information for

Dialkynyldiboranes(4) and the selectable reactivity of their C–H, C≡C and B–B bonds

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Contents

Methods and materials

All manipulations were performed either under an atmosphere of dry argon or *in vacuo* using standard Schlenk line or glovebox techniques. Deuterated solvents were dried over molecular sieves and degassed by three freeze-pump-thaw cycles prior to use. All other solvents were distilled and degassed from appropriate drying agents. Both deuterated and non-deuterated solvents were stored under argon over activated 4 Å molecular sieves. NMR spectra were acquired either on a Bruker Avance 500 or a Bruker Avance 400 NMR spectrometer. Chemical shifts (δ) are reported in ppm and internally referenced to the carbon nuclei ($^{13}C\{^{1}H\}$) or residual protons (^{1}H) of the solvent. Heteronuclei NMR spectra are referenced to external standards (^{11}B: $BF_3{\cdot}OEt_2$, ^{29}Si: $Si(CH_3)_4$). Solid-state IR spectra were recorded on a Bruker FT-IR spectrometer ALPHA II inside a glovebox. Microanalyses (C, H, N, S) were performed on an Elementar vario MICRO cube elemental analyser. High-resolution mass spectrometry (HRMS) data were obtained from a Thermo Scientific Exactive Plus spectrometer.

Unless otherwise noted, solvents and reagents were purchased from Sigma-Aldrich, Fisher Scientific or Alfa Aesar. $B_2Cl_2(NMe_2)_2$,[1] $B_2(NMe_2)_2(OTf)_2$,[2] were synthesised by following literature procedures.

Synthetic procedures

Sodium propynylide

Propyne was bubbled through a solution of sodium hexamethyldisilazide (1.00 g, 5.45 mmol) in a 4:1 mixture of hexane/ether (50 mL) for 15 min and subsequently stirred for 1 h at room temperature. The resulting colourless suspension was filtered and the solid was washed with 10 mL of pentane. Drying the residue *in vacuo* yielded sodium propynylide (270 mg, 4.35 mmol, 80% yield) as a colourless solid, which was used without further purification.

$B_2(CCSiMe_3)_2(NMe_2)_2$, 1a

A 1.6 molar solution of *n*-butyllithium (6.38 mL, 10.2 mmol, 2.2 equiv) in hexane was added dropwise to a solution of trimethylsilylacetylene (1.00 g, 10.2 mmol, 2.2 equiv) in 500 mL of hexane. The resulting off-white suspension was stirred for 2 h at room temperature prior to cooling to –78 °C. Bis(dimethylamino)dichlorodiborane(4) (829 mg, 4.59 mmol) dissolved in 50 mL of hexane was then added dropwise over a period of 30 min. The resulting suspension was stirred at this temperature for 6 h prior to warming to room temperature. The resulting orange suspension was stirred at ambient temperature for 2 h. After evaporation of all volatiles the residue obtained was suspended with hexane and filtered through a 5 cm column of silica. The resulting orange solution was stored at –70 °C and **1a** was obtained as colourless solid and washed with cold pentane. Drying *in vacuo* yielded **1a** (1.09 g, 3.58 mmol, 78% yield) as a colourless solid. Colourless single crystals were obtained by slow evaporation of a concentrated hexane solution at –30 °C. ^{1}H NMR (500 MHz, C_6D_6, 297 K): δ = 2.86 (s, 6H, N(CH_3)$_2$), 2.69 (s, 6H, N(CH_3)$_2$), 0.20 (s, 18H, Si(CH_3)$_3$) ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 297 K): δ = 116.9 (SiC_q), 43.2 (N(CH$_3$)$_2$), 42.3 (N(CH$_3$)$_2$), 0.3 (Si(CH$_3$)$_3$) ppm. *Note: the BC_q resonance could not be detected by HMBC.* ^{11}B NMR (160 MHz, C_6D_6, 297 K): δ = 37.3 (s) ppm. ^{29}Si NMR (99 MHz, C_6D_6, 297 K): δ = –20.0 (s) ppm. Solid-state IR: ν(C≡C) = 2112 cm^{-1}. Elemental analysis for [$C_{14}H_{30}B_2N_2Si_2$] (M_w = 304.20): calcd. C 55.28, H 9.94, N 9.21%; found C 55.37, H 9.90, N 9.15%. HRMS ASAP for $[C_{14}H_{30}B_2N_2Si_2]^+ = [M + H]^+$: calcd. 305.2206; found 305.2203.

$B_2(CCMe)_2(NMe_2)_2$, 1b

Bis(dimethylamino)bis(triflato)diborane(4) (3.00 g, 7.35 mmol) dissolved in 20 mL of hexane was added to a suspension of sodium propynylide (912 mg, 14.7 mmol, 2 equiv) in 140 mL of hexane. Diethyl ether (40 mL) was then added and the suspension was stirred for 16 h at ambient temperature prior to removing all volatiles. The obtained residue was suspended in pentane and filtered through a 2 cm silica column. The resulting orange solution was stored at –70 °C and **1b** was obtained as an off-white solid and washed with cold pentane. Drying *in vacuo* yielded **1b** (960 g, 5.11 mmol, 70% yield) as an off-white solid. Colourless single crystals were obtained by slow evaporation of a concentrated hexane solution at –30 °C. ^{1}H NMR (500 MHz, C_6D_6, 297 K): δ = 2.96 (s, 6H, N(CH_3)$_2$), 2.76 (s, 6H,

N(C*H*$_3$)$_2$), 1.71 (s, 6H, C$_q$C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (126 MHz, C$_6$D$_6$, 297 K): δ = 107.5 (*C$_q$*CH$_3$), 87.9 (B*C$_q$*), 43.2 (N(*C*H$_3$)$_2$), 41.9 (N(*C*H$_3$)$_2$), 5.2 (*C*H$_3$) ppm. ^{11}B NMR (160 MHz, C$_6$D$_6$, 297 K): δ = 38.4 (s) ppm. Solid-state IR: ν(C≡C) = 2171 cm^{-1}. Elemental analysis for [C$_{10}$H$_{18}$B$_2$N$_2$] (M$_w$ = 187.89): calcd. C 63.93, H 9.66, N 14.91%; found C 63.89, H 9.76, N 14.81%. HRMS ASAP for [C$_{10}$H$_{18}$B$_2$N$_2$]$^+$ = [M + H]$^+$: calcd. 189.1729; found 189.1726.

B$_2$(CCH)$_2$(NMe$_2$)$_2$, 1c

Bis(dimethylamino)bis(triflato)diborane(4) (3.00 g, 7.35 mmol) dissolved in 20 mL of pentane was added to a suspension of sodium acetylide (706 mg, 14.7 mmol, 2 equiv) in 140 mL of hexane. 40 mL of diethyl ether were added and the suspension was stirred for 16 h at ambient temperature prior to removing all volatiles at –15 °C. The residue obtained was suspended in pentane and filtered through a 2 cm silica column. The resulting orange solution was evaporated at –15 °C and after sublimation (40 °C, 0.01 mbar) **1c** (952 g, 5.95 mmol, 81% yield) was obtained as a colourless solid. Colourless single crystals were obtained by slow evaporation of a concentrated hexane solution at –30 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$, 297 K): δ = 2.94 (s, 2H, C*H*), 2.83 (s, 6H, N(C*H*$_3$)$_2$), 2.63 (s, 6H, N(C*H*$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (126 MHz, C$_6$D$_6$, 297 K): δ = 98.2 (*C$_q$*H), 91.9 (B*C$_q$* identified by HMBC), 43.1 (N(*C*H$_3$)$_2$), 42.1 (N(*C*H$_3$)$_2$) ppm. ^{11}B NMR (160 MHz, C$_6$D$_6$, 297 K): δ = 37.2 (s) ppm. Solid-state IR: ν(C≡C–H) = 3255 cm^{-1}; ν(C≡C) = 2041 cm^{-1}. Elemental analysis for [C$_8$H$_{14}$B$_2$N$_2$] (M$_w$ = 159.83): calcd. C 60.12, H 8.83, N 17.53%; found C 59.09, H 8.89, N 17.07%. HRMS ASAP for [C$_8$H$_{14}$B$_2$N$_2$]$^+$ = [M + H]$^+$: calcd. 161.1416; found 161.1415.

OB$_2$(CCSiMe$_3$)$_2$(NMe$_2$)$_2$, 2a

Trimethylamine *N*-oxide (16.0 mg, 213 µmol) dissolved in 2 mL of benzene was added to a solution of **1a** (65.0 mg, 213 µmol) in 2 mL of benzene. The colourless suspension was stirred for 5 h at ambient temperature prior to removing all volatiles. The obtained residue was suspended in pentane and filtered. The resulting colourless solution was stored at –30 °C and **2a** was obtained as colourless solid and washed with cold pentane. Drying *in vacuo* yielded **2a** (63.0 mg, 196 µmol, 92% yield) as a colourless solid. Colourless single crystals were obtained by slow evaporation of a concentrated hexane solution at –30 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$, 297 K): δ = 2.76 (s, 6H, N(C*H*$_3$)$_2$), 2.48 (s, 6H, N(C*H*$_3$)$_2$), 0.22 (s, 18H, Si(C*H*$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR (126 MHz, C$_6$D$_6$, 297 K): δ = 110.1 (Si*C*), 39.0 (N(*C*H$_3$)$_2$), 35.5 (N(*C*H$_3$)$_2$), 0.1 (Si(*C*H$_3$)$_3$) ppm. *Note: the BC$_q$ resonance could not be detected by HMBC.* ^{11}B NMR (160 MHz, C$_6$D$_6$, 297 K): δ = 21.5 (s) ppm. ^{29}Si NMR (99 MHz, C$_6$D$_6$, 297 K): δ = –19.3 (s) ppm. Solid-state IR: ν(C≡C) = 2111 cm^{-1}. Elemental analysis for [C$_{14}$H$_{30}$B$_2$N$_2$OSi$_2$] (M$_w$ = 320.20): calcd. C 52.52, H 9.44, N 8.75%; found C 51.62, H 9.26, N 8.29%. HRMS ASAP for [C$_{14}$H$_{30}$B$_2$N$_2$OSi$_2$]$^+$ = [M + H]$^+$: calcd. 321.2156; found 321.2149.

$OB_2(NMe)_2(CCMe_2)_2$, 2b

Trimethylamine *N*-oxide (16.0 mg, 213 µmol) dissolved in 2 mL of benzene was added to a solution of **1b** (40.0 mg, 213 µmol) in 2 mL of benzene. The colourless suspension was stirred for 5 h at ambient temperature prior to removing all volatiles. The obtained residue was suspended in pentane and filtered. The resulting colourless solution was stored at –30 °C and **2b** was obtained as a colourless solid and washed with cold pentane. Drying *in vacuo* yielded **2b** (39.0 mg, 190 µmol, 89% yield) as a colourless solid. Colourless single crystals were obtained by slow evaporation of a concentrated hexane solution at –30 °C. ^{1}H NMR (500 MHz, C_6D_6, 297 K): δ = 2.84 (s, 6H, N(C*H*$_3$)$_2$), 2.59 (s, 6H, N(C*H*$_3$)$_2$), 1.59 (s, 6H, C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 297 K): δ = 99.7 (C_qCH$_3$), 82.2 (BC_q identified by HMBC), 39.0 (N(*C*H$_3$)$_2$), 35.6 (N(*C*H$_3$)$_2$), 4.5 (*C*H$_3$) ppm. ^{11}B NMR (160 MHz, C_6D_6, 297 K): δ = 22.0 (s) ppm. Solid-state IR: ν(C≡C) = 2193 cm^{-1}. Elemental analysis for [$C_{10}H_{18}B_2N_2O$] (M_w = 203.89): calcd. C 58.91, H 8.90, N 13.74%; found C 59.29, H 9.11, N 13.53%. HRMS ASAP for [$C_{10}H_{18}B_2N_2O$]$^+$ = [M + H]$^+$: calcd. 205.1678; found 205.1677.

$OB_2(CCH)_2(NMe_2)_2$, 2c

Trimethylamine *N*-oxide (16.0 mg, 213 µmol) dissolved in 2 mL of pentane was added to a solution of **1c** (34.0 mg, 213 µmol) in 2 mL of pentane. The colourless suspension was stirred for 5 h at ambient temperature prior to removing all volatiles at 0 °C and 100 mbar. The obtained residue was suspended in pentane, filtered and all volatiles were removed at 0 °C and 100 mbar. ^{1}H NMR (400 MHz, C_6D_6, 297 K): δ = 2.71 (s, 6H, N(C*H*$_3$)$_2$), 2.67 (s, 2H, C*H*), 2.46 (s, 6H, N(C*H*$_3$)$_2$) ppm. ^{11}B NMR (129 MHz, C_6D_6, 297 K): δ = 21.8 (s) ppm. *Note: All attempts to further purify this compound failed.*

$B_2(CCSiMe_3Co_2(CO)_6)_2(NMe_2)_2$, 3a

Dicobaltoctacarbonyl (146.0 mg, 426 µmol, 2 equiv) dissolved in 15 mL of DCM was added to a solution of **1a** (65.0 mg, 213 µmol) in 10 mL of DCM. The brown suspension was stirred for 16 h at ambient temperature prior to removing all volatiles. The obtained residue was suspended in hexane and filtered. The resulting brown solution was stored at –30 °C and **3a** was obtained as a dark red solid and washed with cold pentane. Drying *in vacuo* yielded **3a** (162 mg, 185 µmol, 87% yield) as a dark red solid. Dark red single crystals were obtained by slow evaporation of a concentrated hexane solution at –30 °C. ^{1}H NMR (500 MHz, C_6D_6, 297 K): δ = 2.87 (s, 6H, N(C*H*$_3$)$_2$), 2.74 (s, 6H, N(C*H*$_3$)$_2$), 0.37 (s, 18H, Si(C*H*$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 297 K): δ = 202.3 (OC_q), 202.2 (OC_q), 96.1 (BC_q), 89.4 (SiC_q), 44.8 (N(*C*H$_3$)$_2$), 41.4 (N(*C*H$_3$)$_2$), 1.7 (Si(*C*H$_3$)$_3$) ppm. ^{11}B NMR (160 MHz, C_6D_6, 297 K): δ = 42.1 (s) ppm. ^{29}Si NMR (99 MHz, C_6D_6, 297 K): δ = –0.1 (s) ppm. Solid-state IR: ν(C≡O) = 2076, 2034, 1979 cm^{-1}. Elemental analysis for [$C_{26}H_{30}B_2Co_4N_2O_{12}Si_2$] ($M_w$ = 876.05): calcd. C 35.65, H 3.45, N 3.20%; found C 35.97, H 3.72, N 3.06%. HRMS ASAP for [$C_{23}H_{30}B_2Co_4N_2O_9Si_2$] = [M – 3 CO]: calcd. 792.9032; found 792.8992. *Note: The only signal detected in the HRMS stems from the loss of three carbonyl ligands from **3a**.*

$B_2(CCMeCo_2(CO)_6)_2(NMe_2)_2$, 3b

Dicobaltoctacarbonyl (146.0 mg, 426 µmol, 2 equiv) dissolved in 15 mL of DCM was added to a solution of **1b** (40.0 mg, 213 µmol) in 10 mL of DCM. The brown suspension was stirred for 5 h at ambient temperature prior to removing all volatiles. The obtained residue was suspended in hexane and filtered. The resulting brown solution was stored at –30 °C and **3b** was obtained as dark red solid and washed with cold pentane. Drying *in vacuo* yielded **3b** (146.0 mg, 192 µmol, 90% yield) as dark red solid. Dark red single crystals were obtained by slow evaporation of a concentrated hexane solution at –30 °C. ^{1}H NMR (500 MHz, C_6D_6, 297 K): δ = 2.75 (s, 6H, N(C*H*$_3$)$_2$), 2.69 (s, 6H, N(C*H*$_3$)$_2$), 2.51 (s, 6H, C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 297 K): δ = 201.7 (OC_q), 201.5 (OC_q), 105.5 (C_qCH$_3$), 82.4 (BC_q), 44.9 (N(*C*H$_3$)$_2$), 39.7 (N(*C*H$_3$)$_2$), 22.28 (*C*H$_3$) ppm.^{11}B NMR (160 MHz, C_6D_6, 297 K): δ = 42.8 (s) ppm. Solid-state IR: ν(C≡O) = 2076, 2032, 1975 cm^{-1}. Elemental analysis for [$C_{22}H_{18}B_2Co_4N_2O_{12}$] ($M_w$ = 759.74): calcd. C 34.78, H 2.39, N 3.69%; found C 34.82, H 2.37, N 3.69%. HRMS ASAP for [$C_{19}H_{18}B_2Co_4N_2O_9$] = [M – 3 CO]: calcd. 675.8521; found 675.8521. *Note: The only signal detected in the HRMS stems from the loss of three carbonyl ligands from **3b**.*

$B_2(CCHCo_2(CO)_6)_2(NMe_2)_2$, 3c

Dicobaltoctacarbonyl (146.0 mg, 426 µmol, 2 equiv) dissolved in 15 mL of DCM was added to a solution of **1c** (34.0 mg, 213 µmol) in 10 mL of DCM. The brown suspension was stirred for 5 h at ambient temperature prior to removing all volatiles. The obtained residue was suspended in hexane and filtered. The resulting brown solution was stored at –30 °C and **3c** was obtained as a dark red solid and washed with cold pentane. Drying *in vacuo* yielded **3c** (139 mg, 190 µmol, 89% yield) as a dark red solid. Dark red single crystals were obtained by slow evaporation of a concentrated hexane solution at –30 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 297 K): δ = 6.23 (s, 2H, C_q*H*), 2.81 (s, 6H, N(C*H*$_3$)$_2$), 2.73 (s, 6H, N(C*H*$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 297 K): δ = 201.0 (OC_q), 87.6 (C_qH), 79.0 (BC_q), 44.6 (N(*C*H$_3$)$_2$), 38.8 (N(*C*H$_3$)$_2$) ppm.^{11}B NMR (160 MHz, $CDCl_3$, 297 K): δ = 42.3 (s) ppm. Solid-state IR: ν(C≡O) = 2084, 2042, 2019, 2002,. 1984 cm^{-1}. Elemental analysis for [$C_{20}H_{14}B_2Co_4N_2O_{12}$] ($M_w$ = 731.69): calcd. C 32.83, H 1.93, N 3.83%; found C 32.87, H 2.01, N 3.76%. HRMS ASAP for [$C_{17}H_{14}B_2Co_4N_2O_9$] = [M – 3 CO]: calcd. 647.8208; found 647.8204. *Note: The only signal detected in the HRMS stems from the loss of three carbonyl ligands from **3c**.*

$B_2(CCPh)_2(NMe_2)_2$, 4

A solution of **1c** (10.0 mg, 62.6 µmol) in 1 mL of triethylamine was added to a solution of iodobenzene (27.0 mg, 131 µmol, 2 equiv), copper(I) iodide (1.20 mg, 6.26 µmol, 0.1 equiv) and tetrakis-(triphenylphosphine)palladium(0) (1.00 mg, 626 nmol, 0.01 equiv) in 1 mL of triethylamine. The grey suspension was stirred for 1 h at ambient temperature prior to removing all volatiles. The obtained residue was suspended in hexane and filtered. The resulting colourless solution was stored at –30 °C and **4** was obtained as a colourless solid and washed with cold pentane. Drying *in vacuo* yielded **4**

(18.4 mg, 58.8 mmol, 94% yield) as a colourless solid. *Note: The ^{1}H, ^{13}C and ^{11}B NMR data are in line with previously reported data.*[2]

NMR spectra of isolated compounds

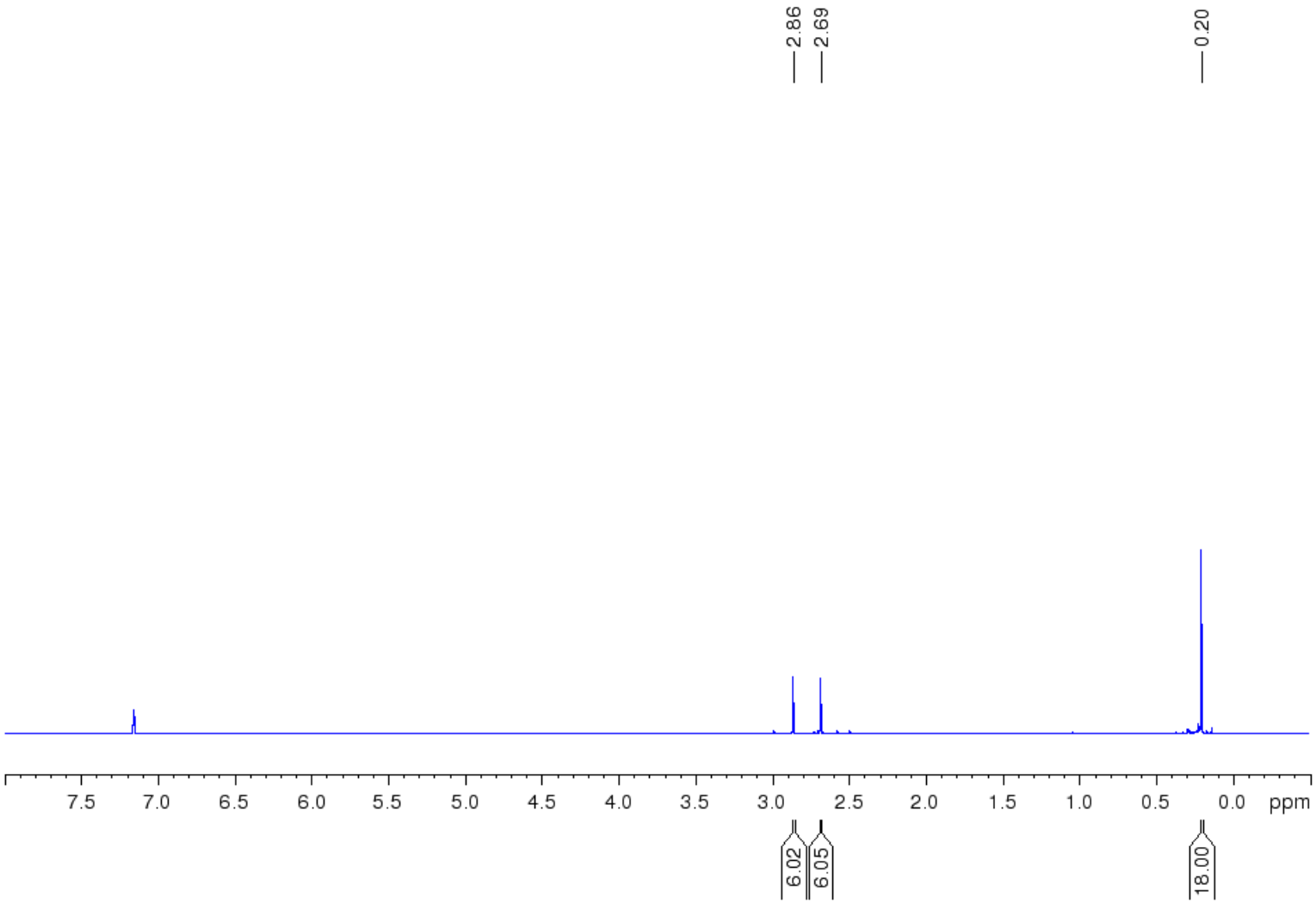

Figure S1. ^{1}H NMR spectrum of $\mathbf{B_2(CCSiMe_3)_2(NMe_2)_2}$, **1a** in C_6D_6.

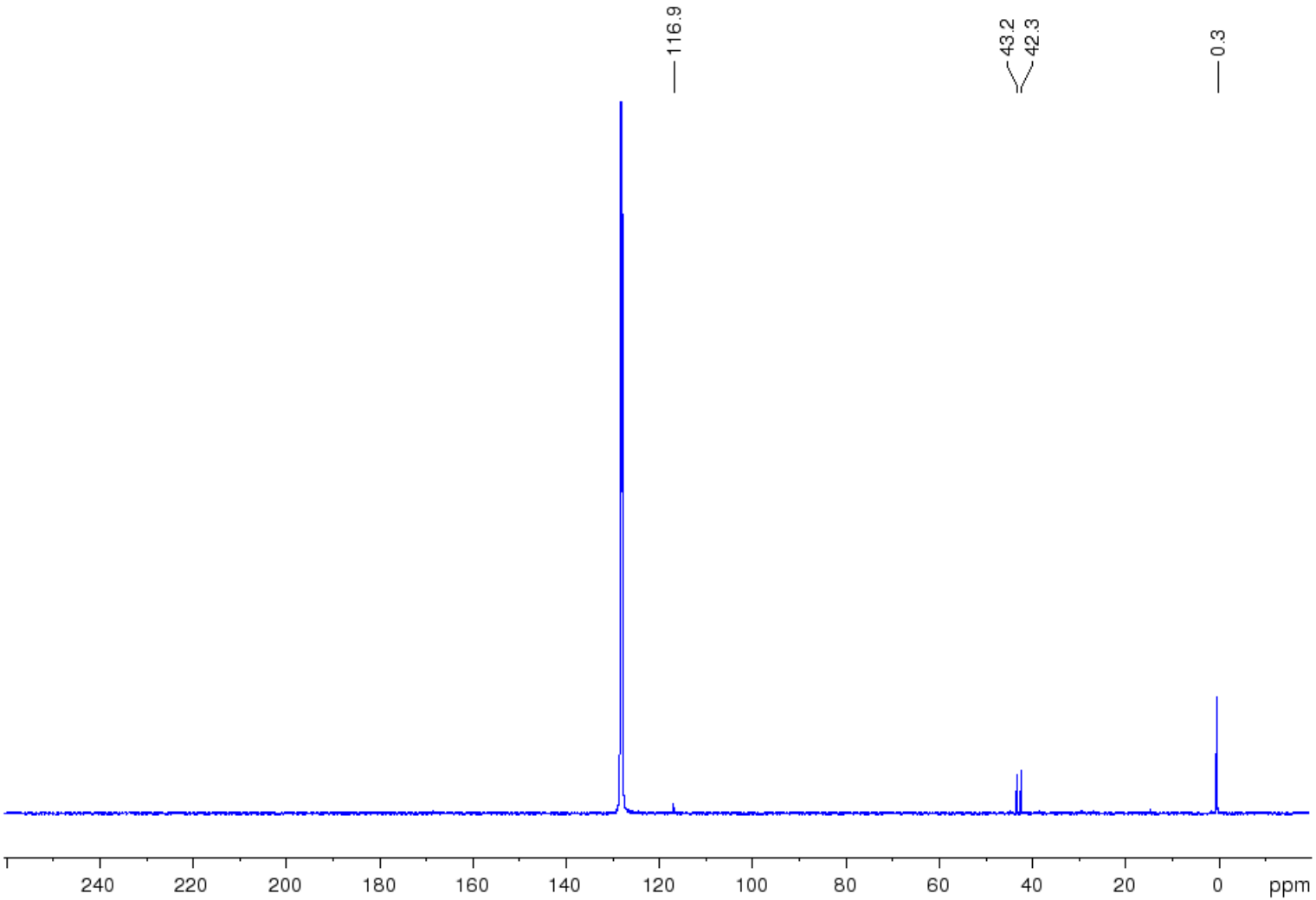

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **$B_2(CCSiMe_3)_2(NMe_2)_2$**, **1a** in C_6D_6.

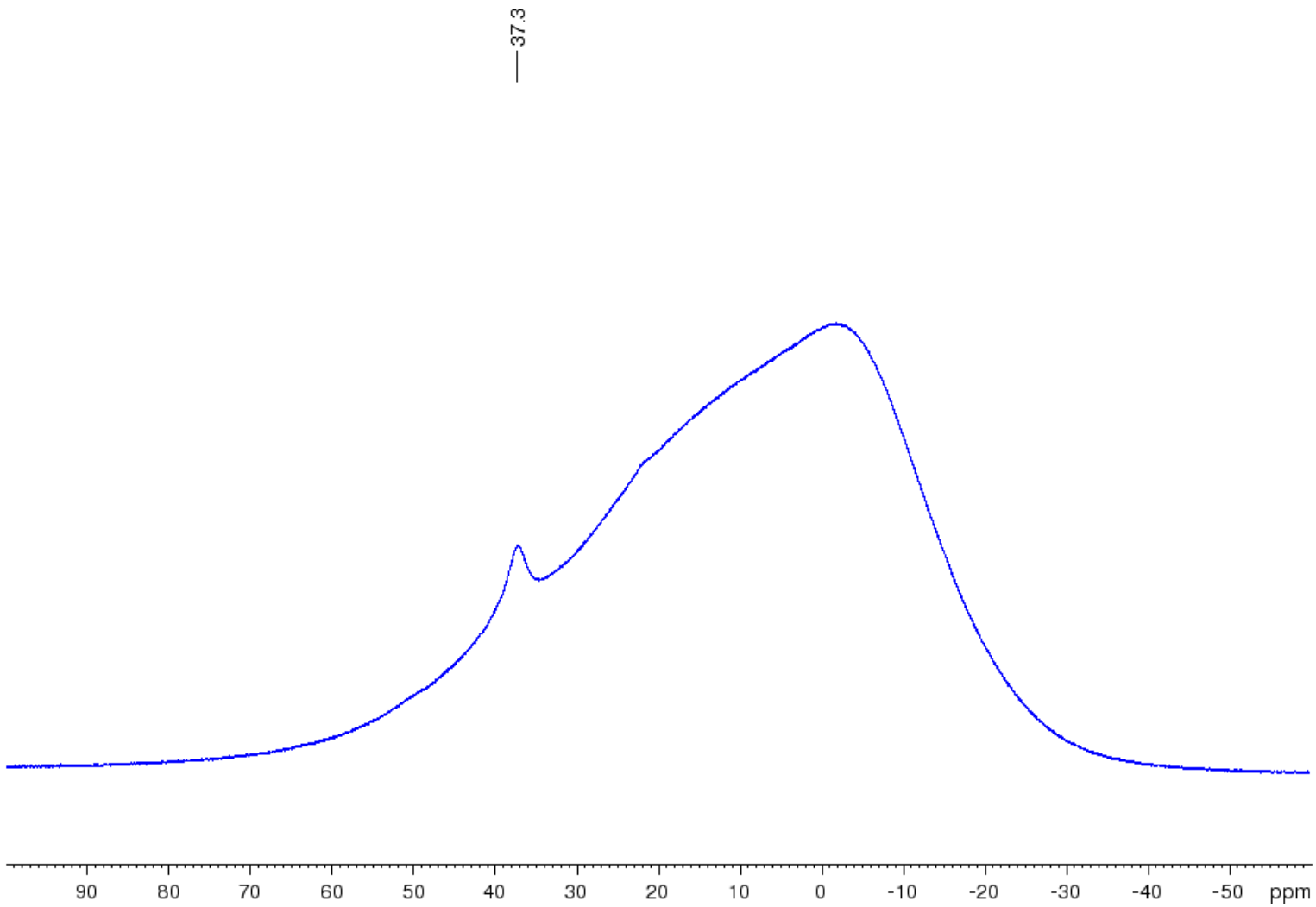

Figure S3. ^{11}B NMR spectrum of **$B_2(CCSiMe_3)_2(NMe_2)_2$**, **1a** in C_6D_6.

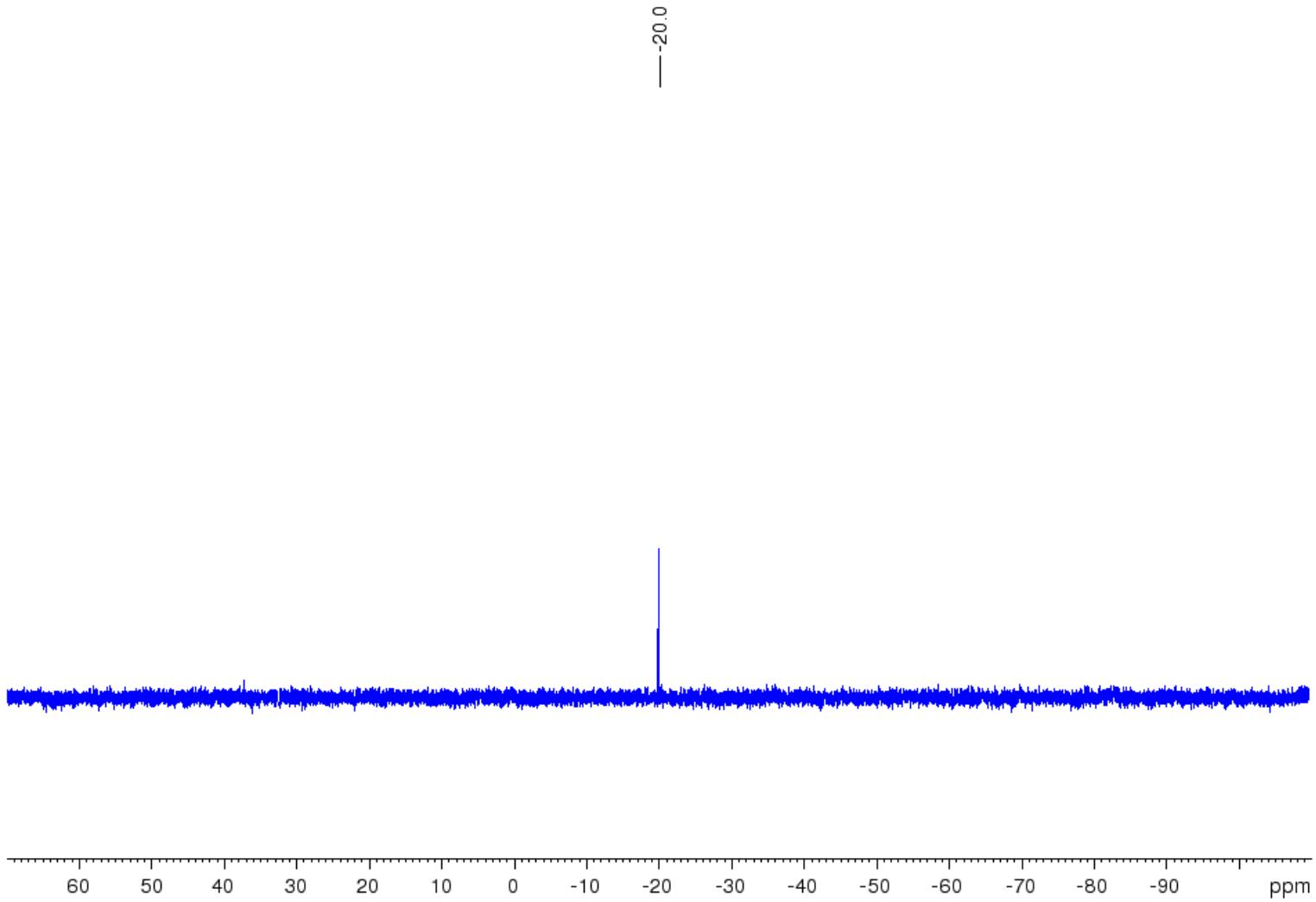

Figure S4. ^{29}Si NMR spectrum of **$B_2(CCSiMe_3)_2(NMe_2)_2$**, **1a** in C_6D_6.

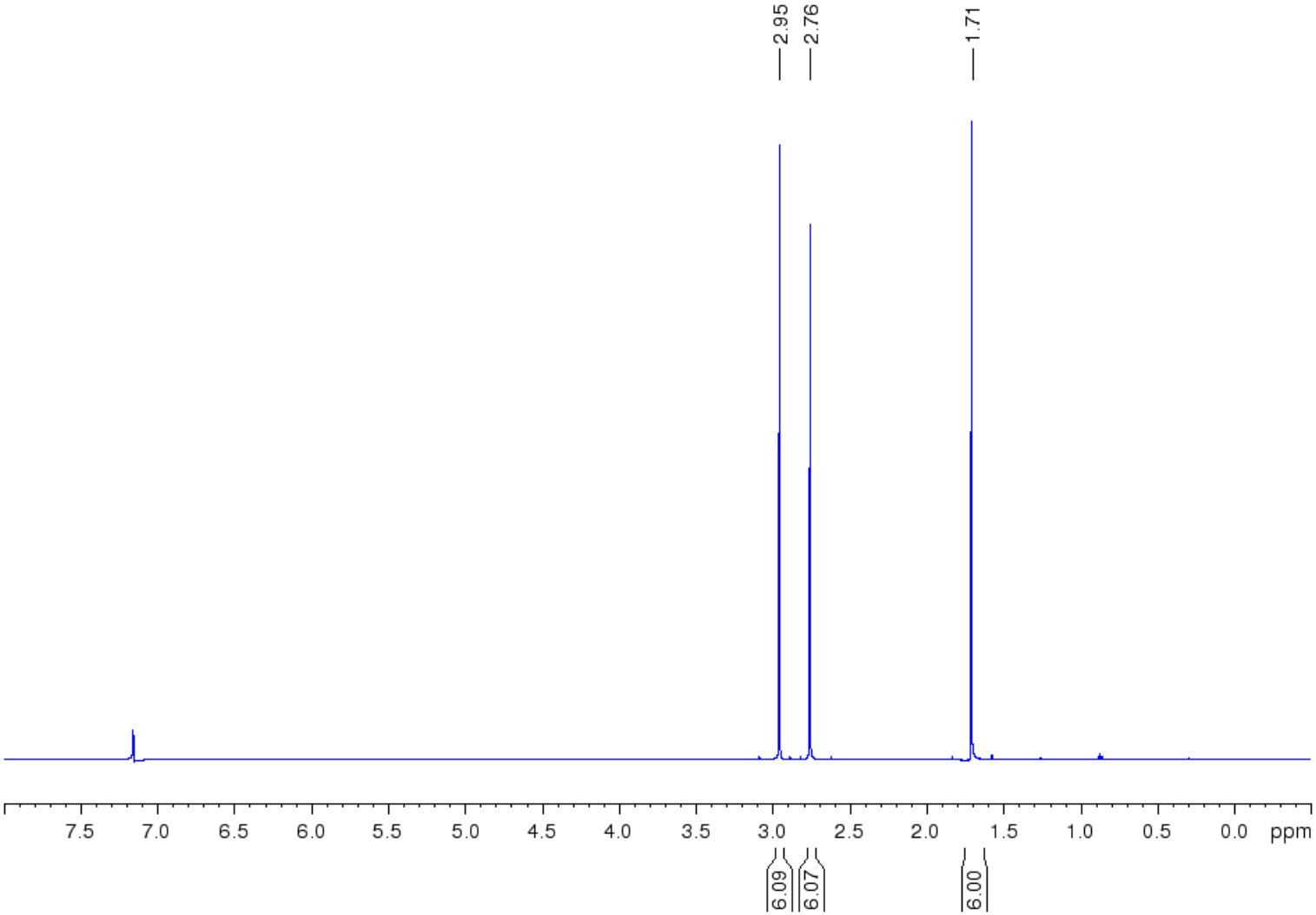

Figure S5. ^{1}H NMR spectrum of **$B_2(CCMe)_2(NMe_2)_2$, 1b** in C_6D_6.

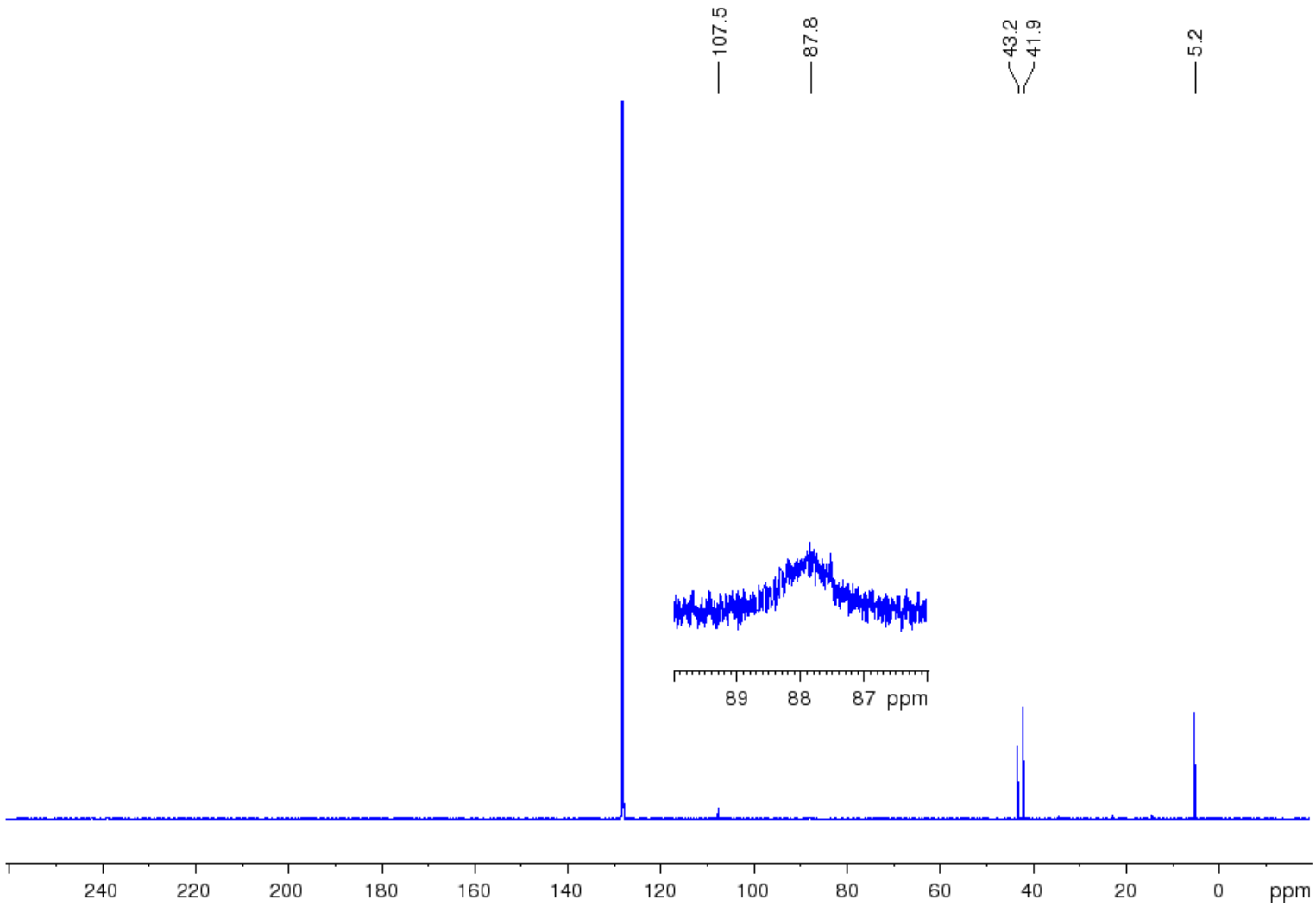

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **$B_2(CCMe)_2(NMe_2)_2$, 1b** in C_6D_6.

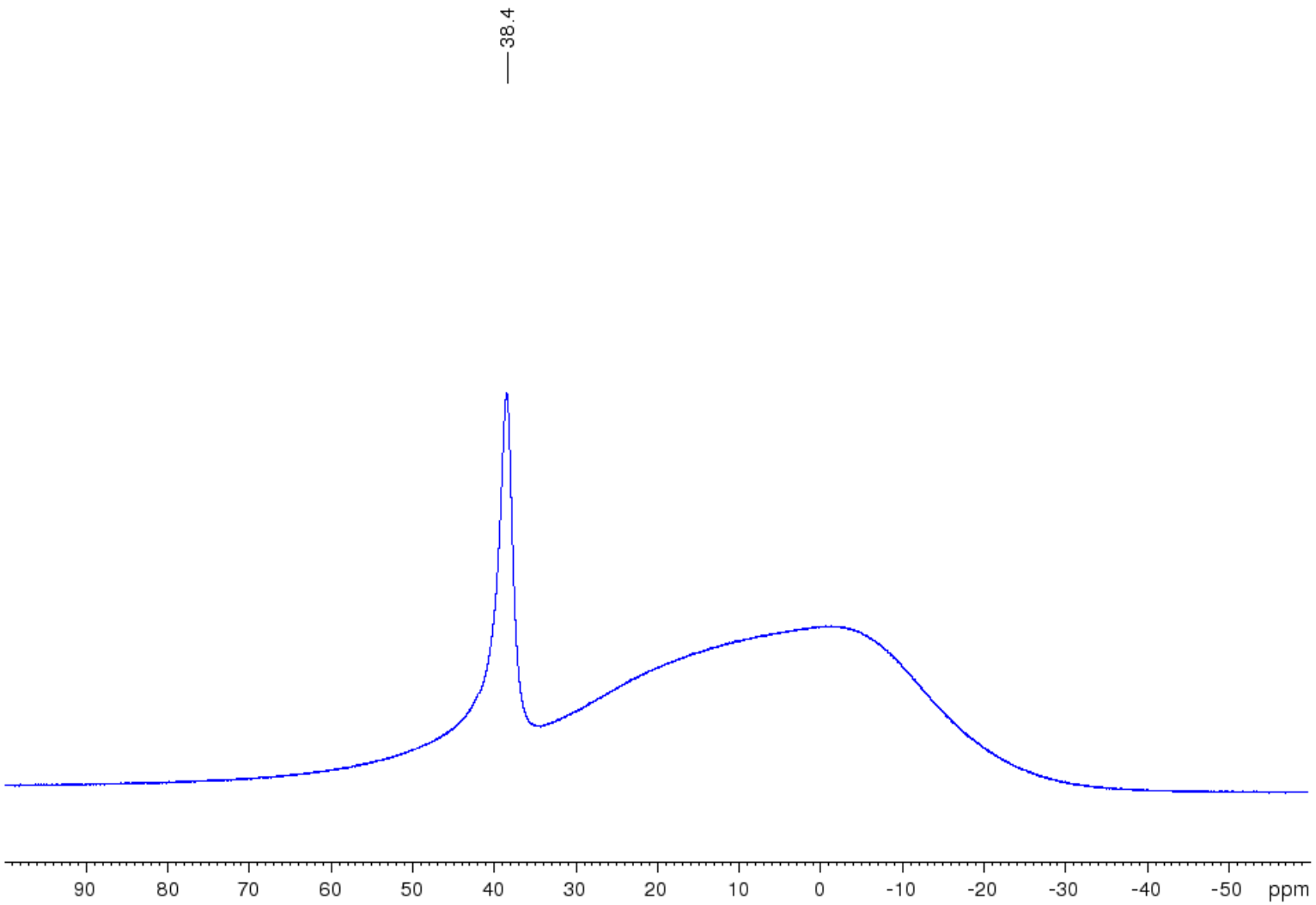

Figure S7. ^{11}B NMR spectrum of of **$B_2(CCMe)_2(NMe_2)_2$, 1b** in C_6D_6.

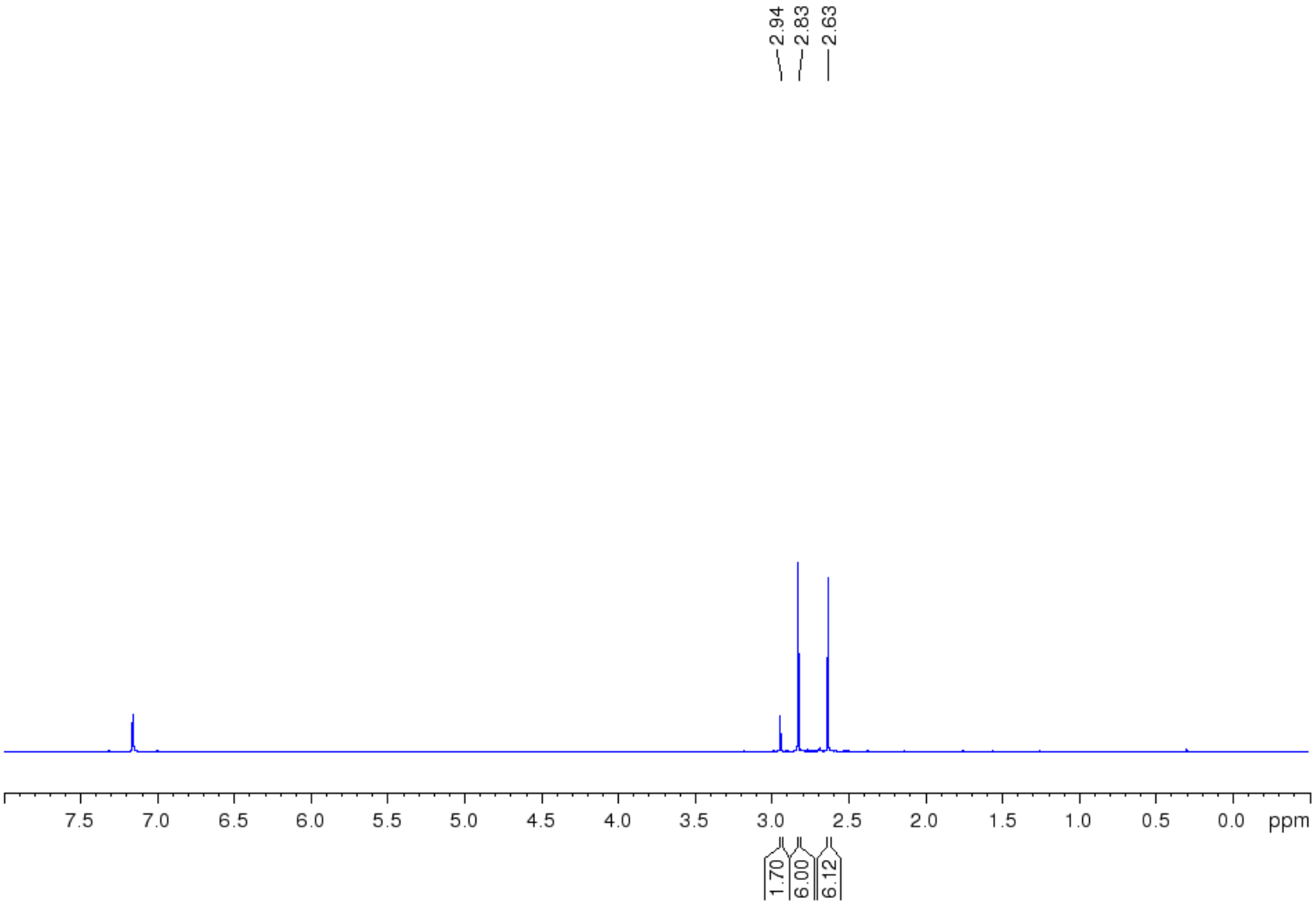

Figure S8. ^{1}H NMR spectrum of **$B_2(CCH)_2(NMe_2)_2$, 1c** in C_6D_6.

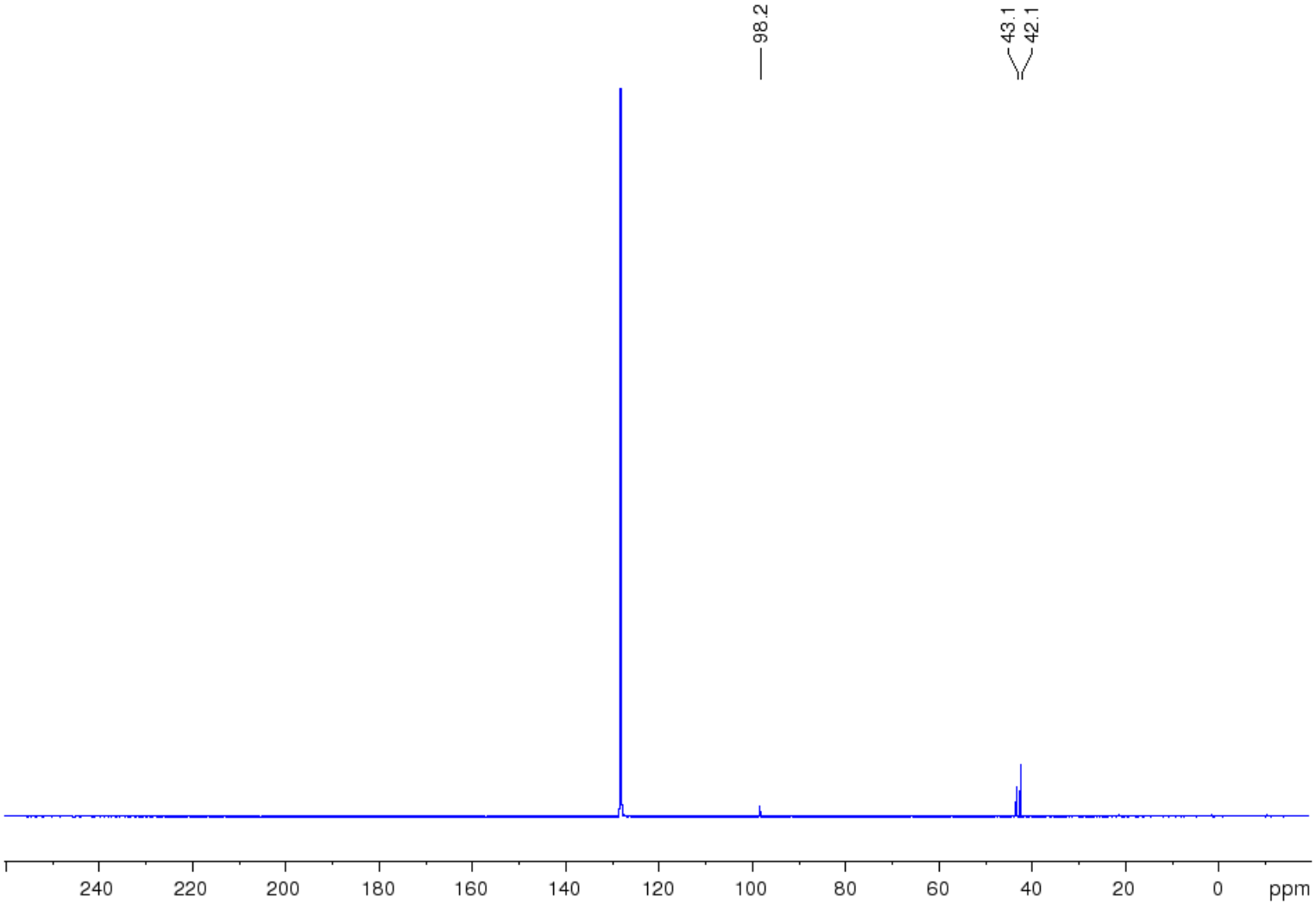

Figure S9. $^{13}C\{^{1}H\}$ spectrum of **$B_2(CCH)_2(NMe_2)_2$, 1c** in C_6D_6.

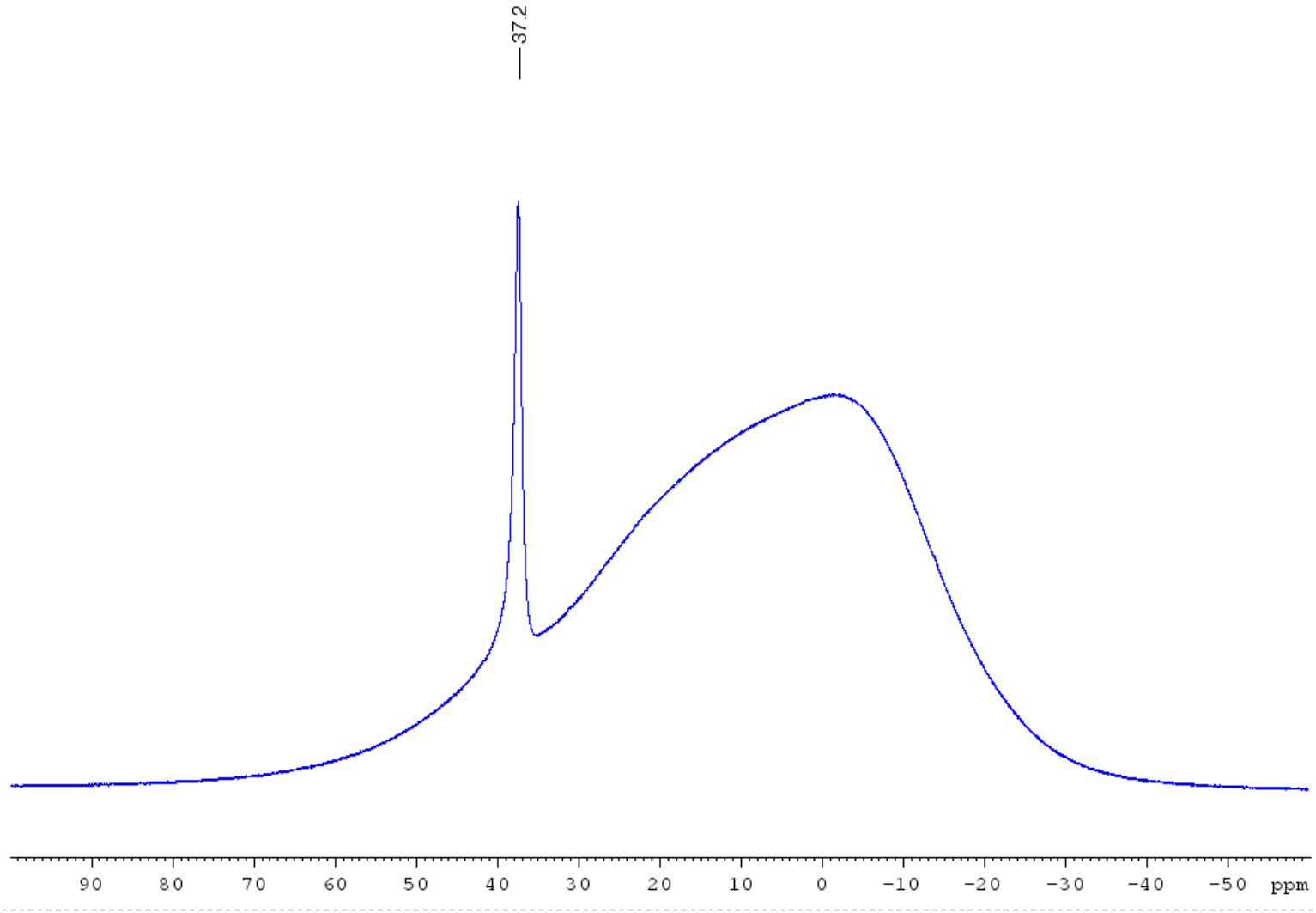

Figure S10. ^{11}B spectrum of **$B_2(CCH)_2(NMe_2)_2$, 1c** in C_6D_6.

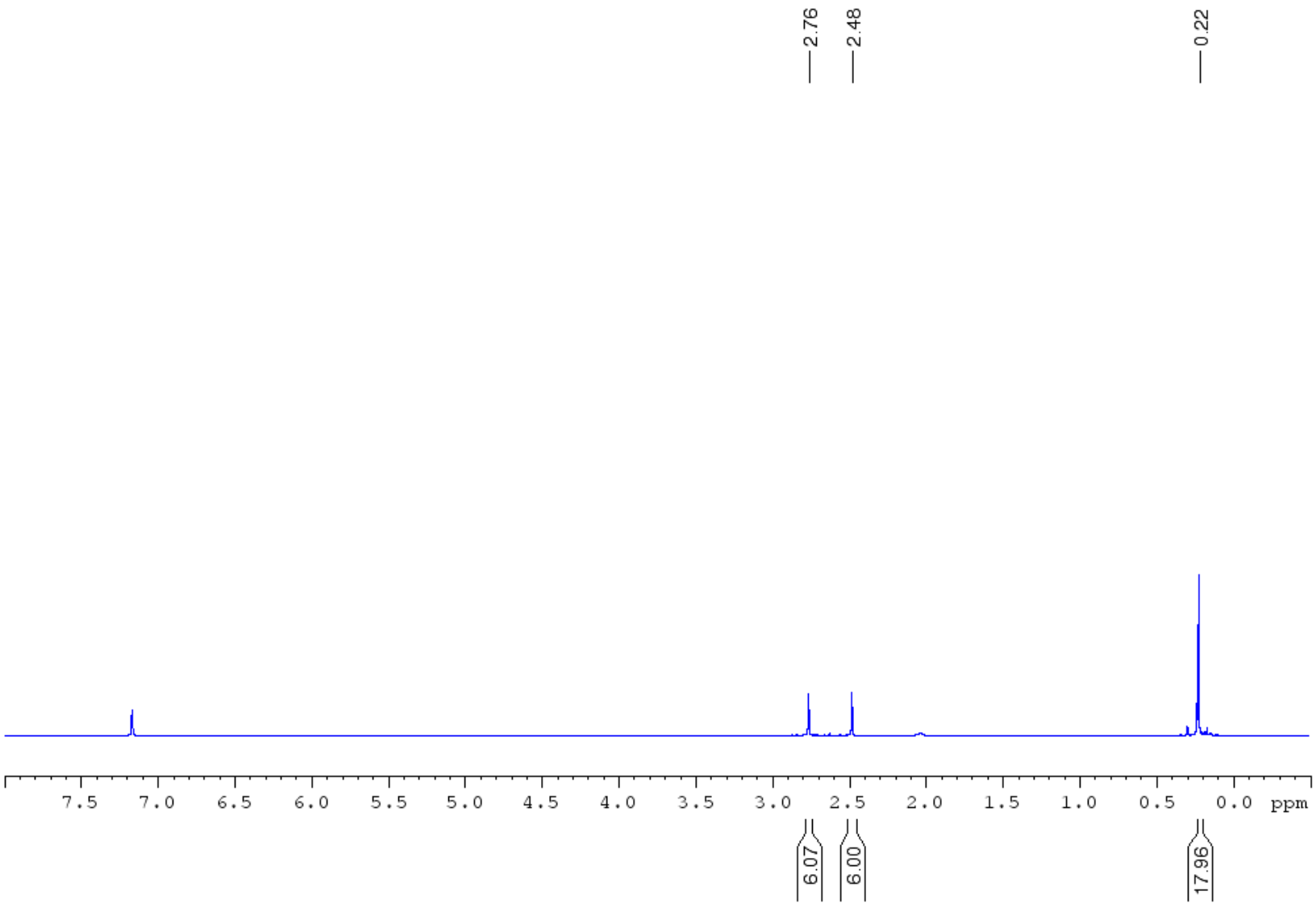

Figure S11. ^{1}H NMR spectrum of **$OB_2(CCSiMe_3)_2(NMe_2)_2$, 2a** in C_6D_6.

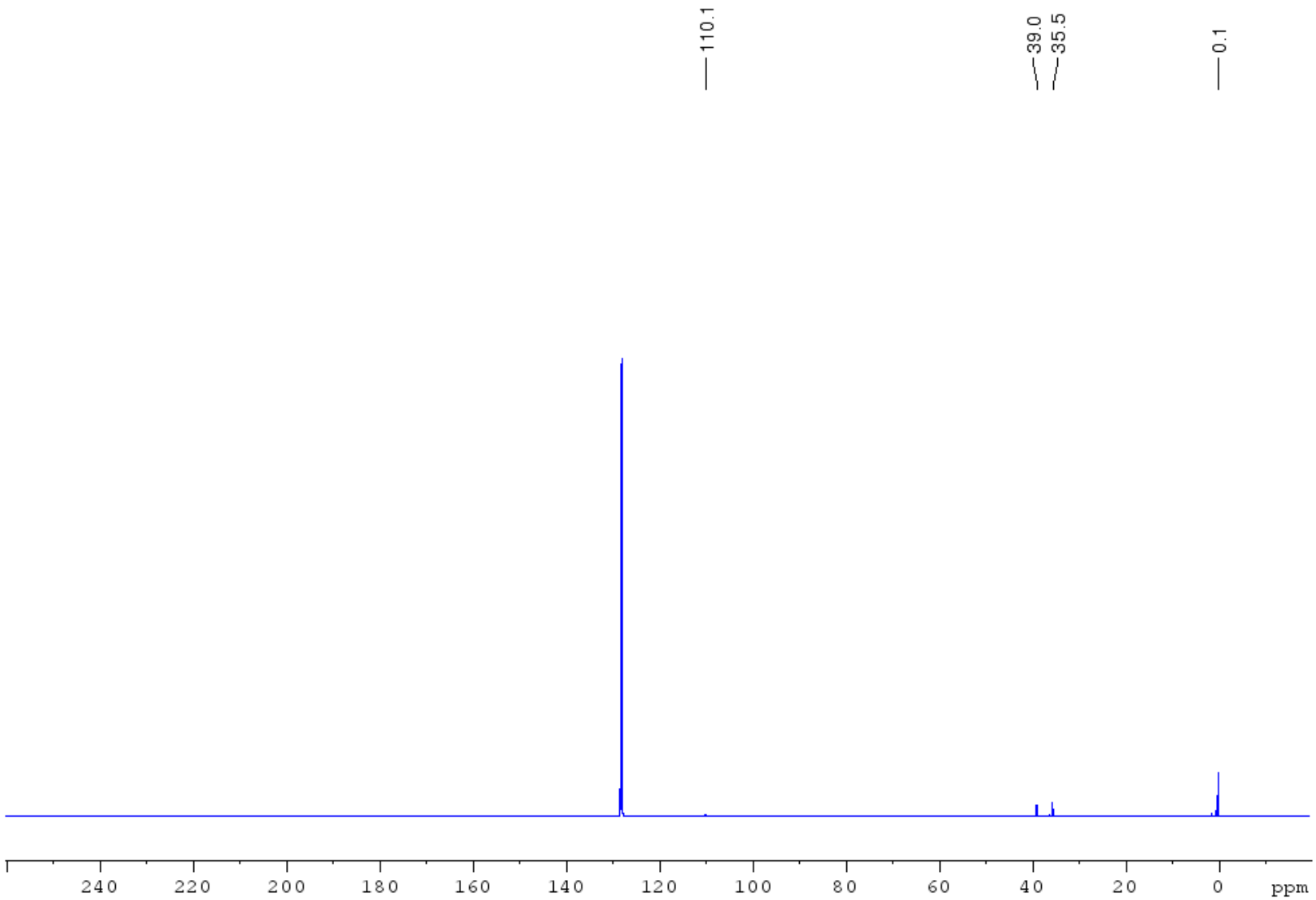

Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of **$OB_2(CCSiMe_3)_2(NMe_2)_2$, 2a** in C_6D_6.

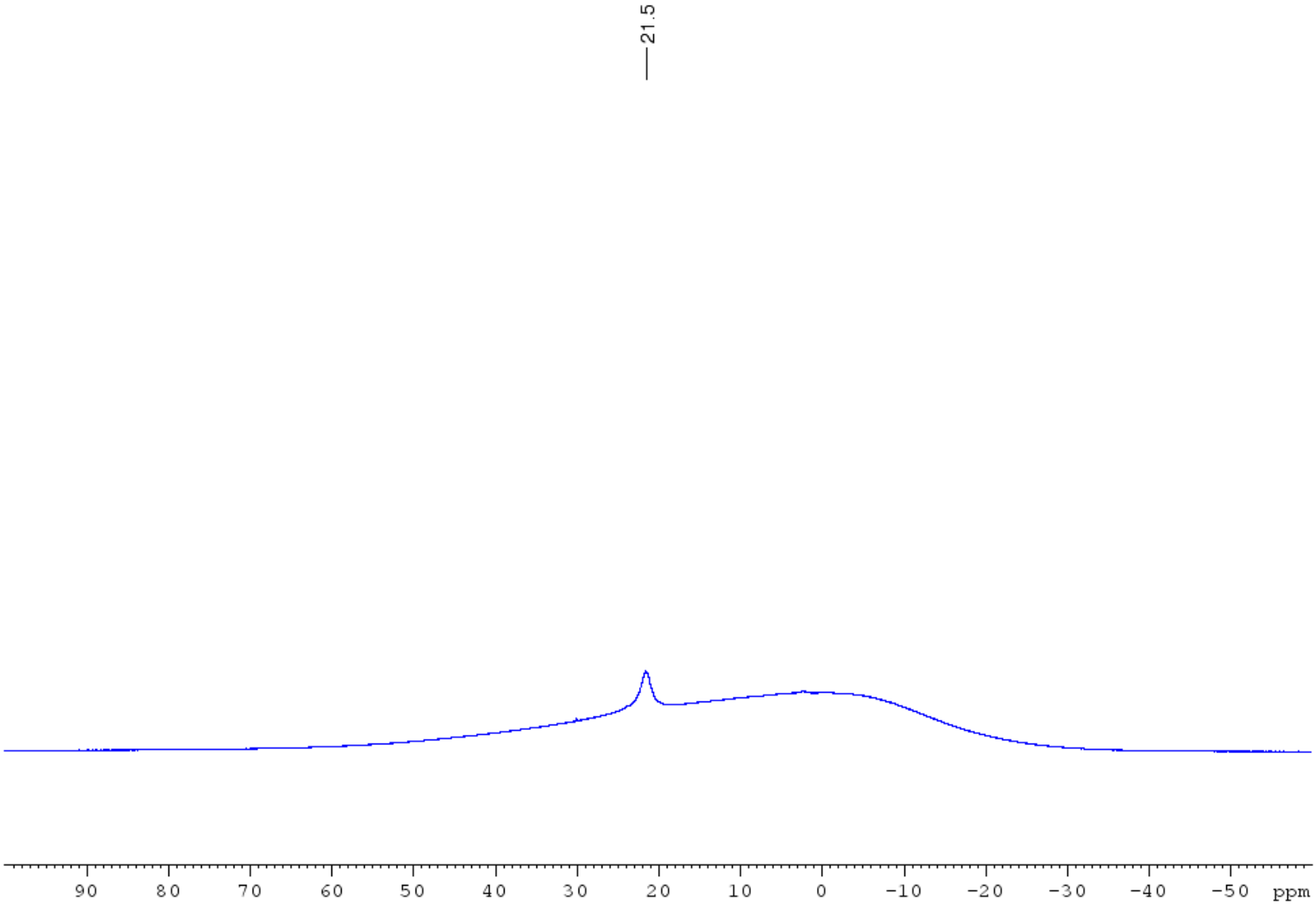

Figure S13. ^{11}B NMR spectrum of **$OB_2(CCSiMe_3)_2(NMe_2)_2$, 2a** in C_6D_6..

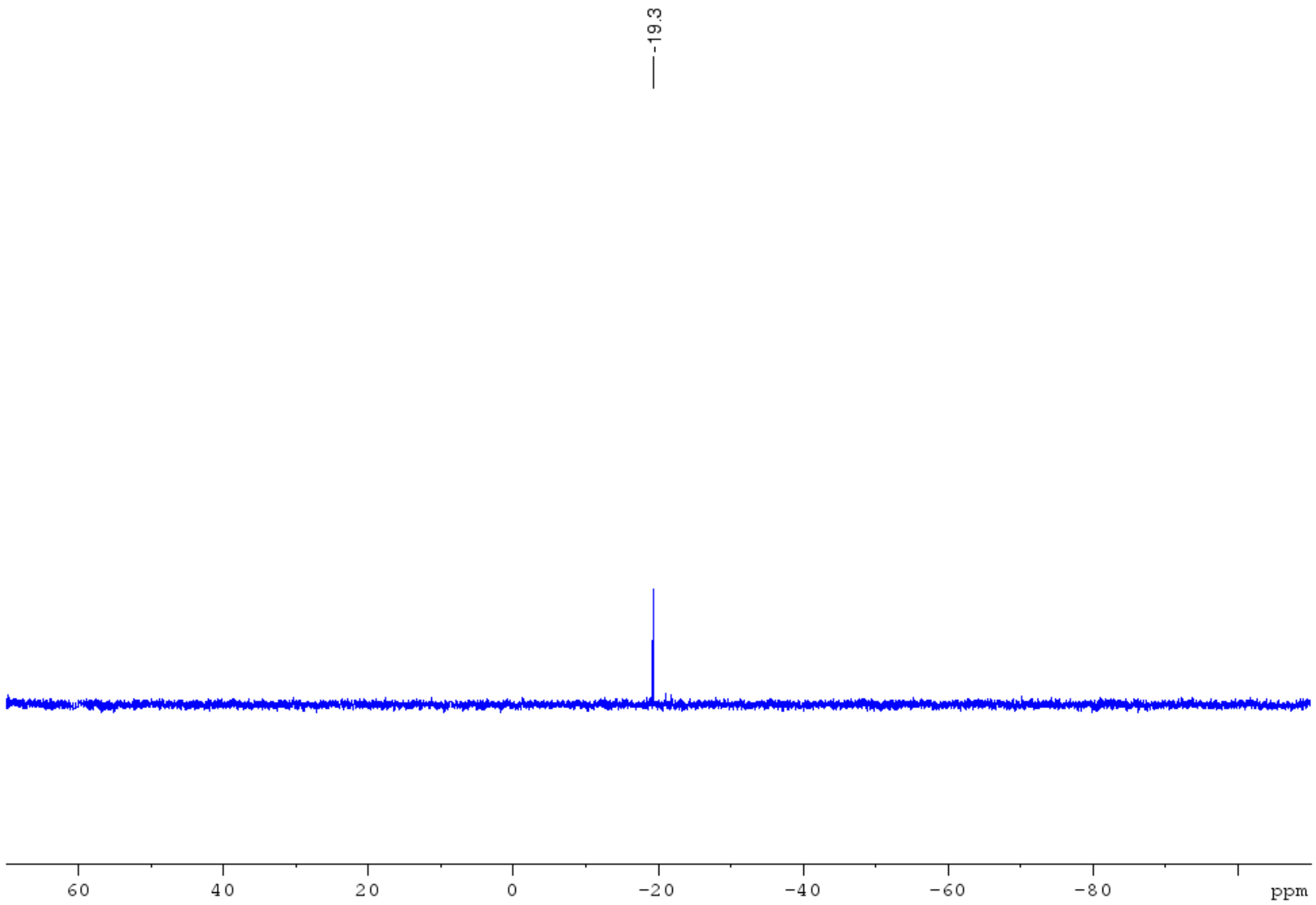

Figure S14. ^{29}Si NMR spectrum of **$OB_2(CCSiMe_3)_2(NMe_2)_2$, 2a** in C_6D_6.

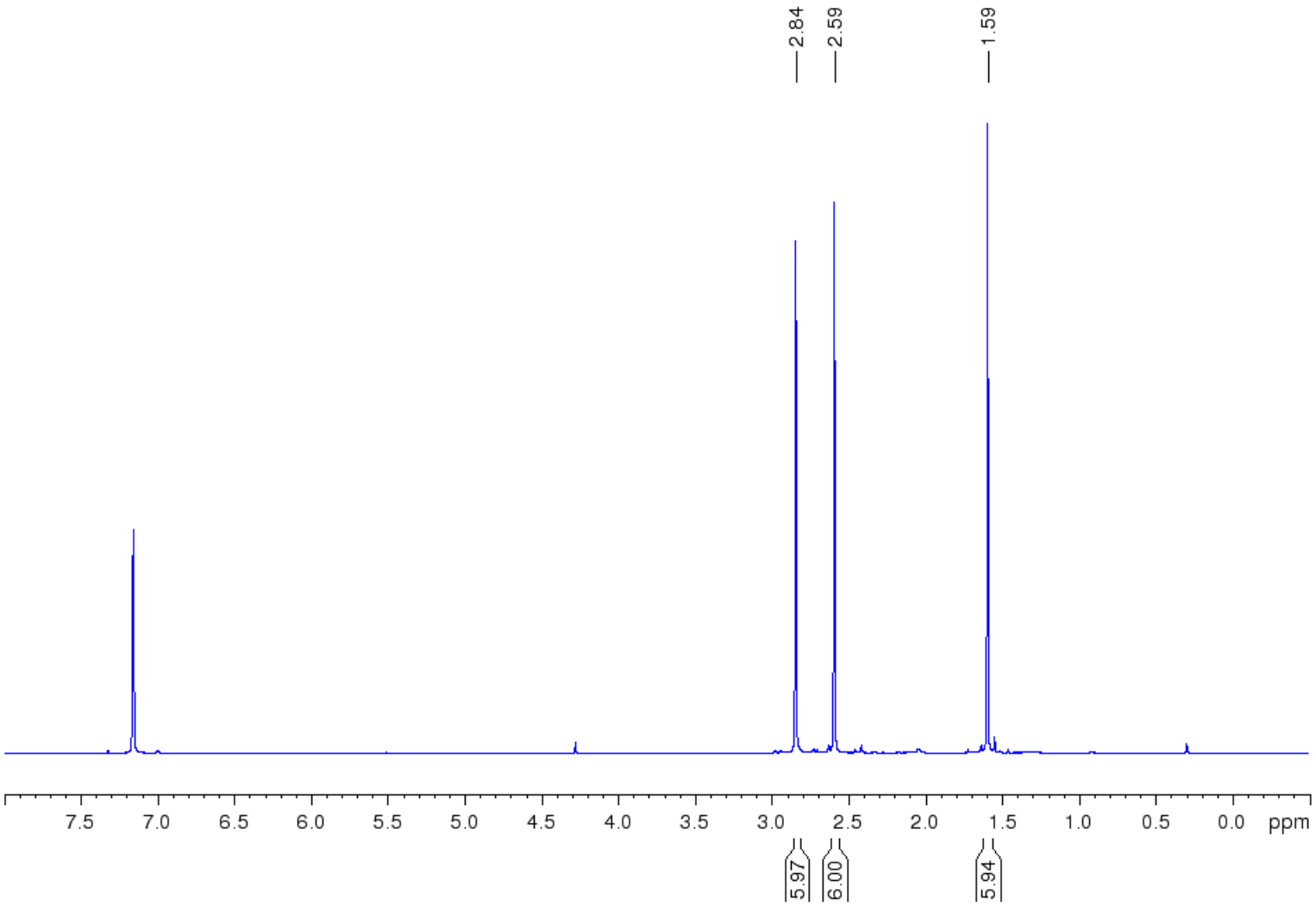

Figure S15. ^{1}H NMR spectrum of **$OB_2(CCMe)_2(NMe_2)_2$, 2b** in C_6D_6.

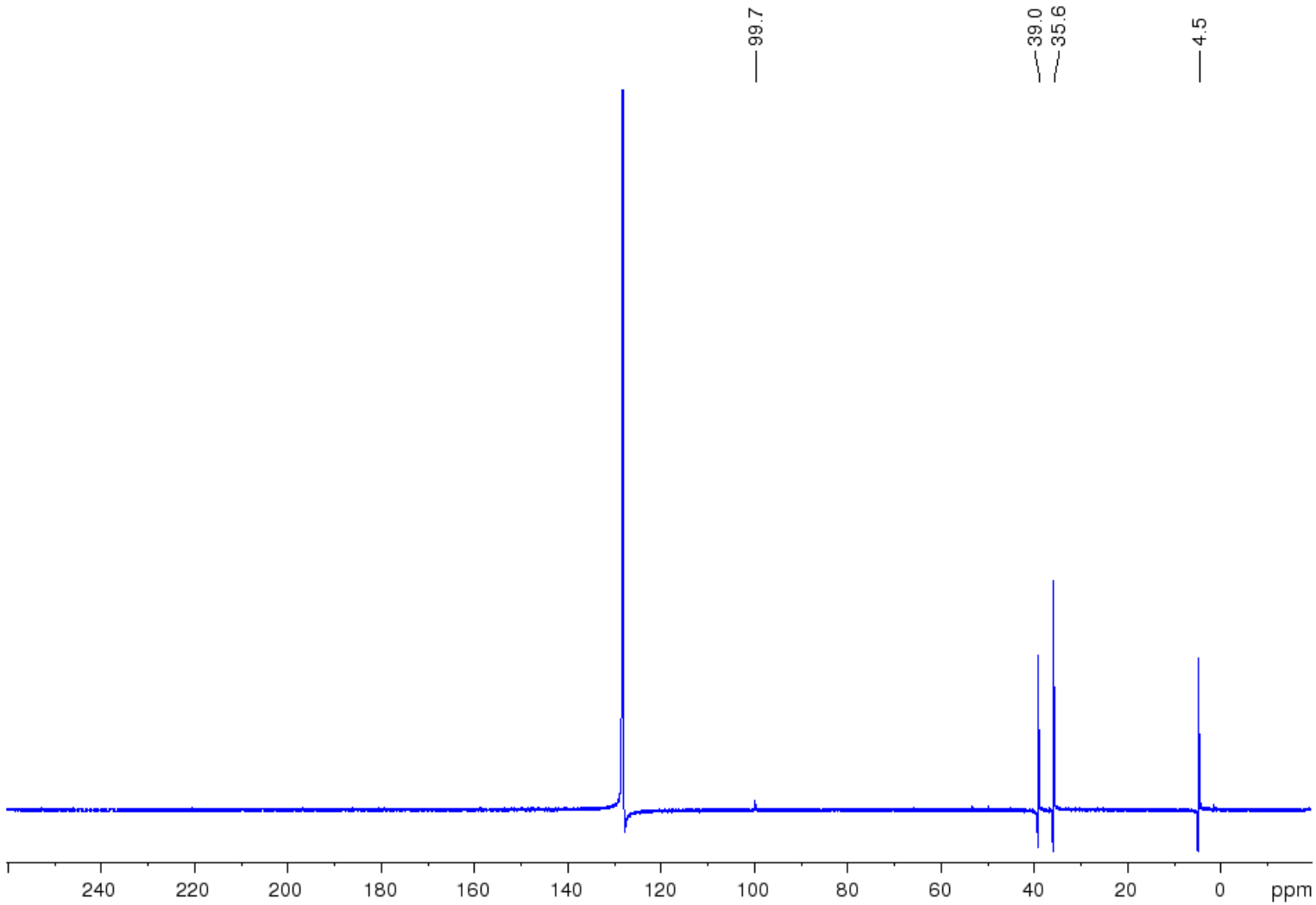

Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of **$OB_2(CCMe)_2(NMe_2)_2$, 2b** in C_6D_6.

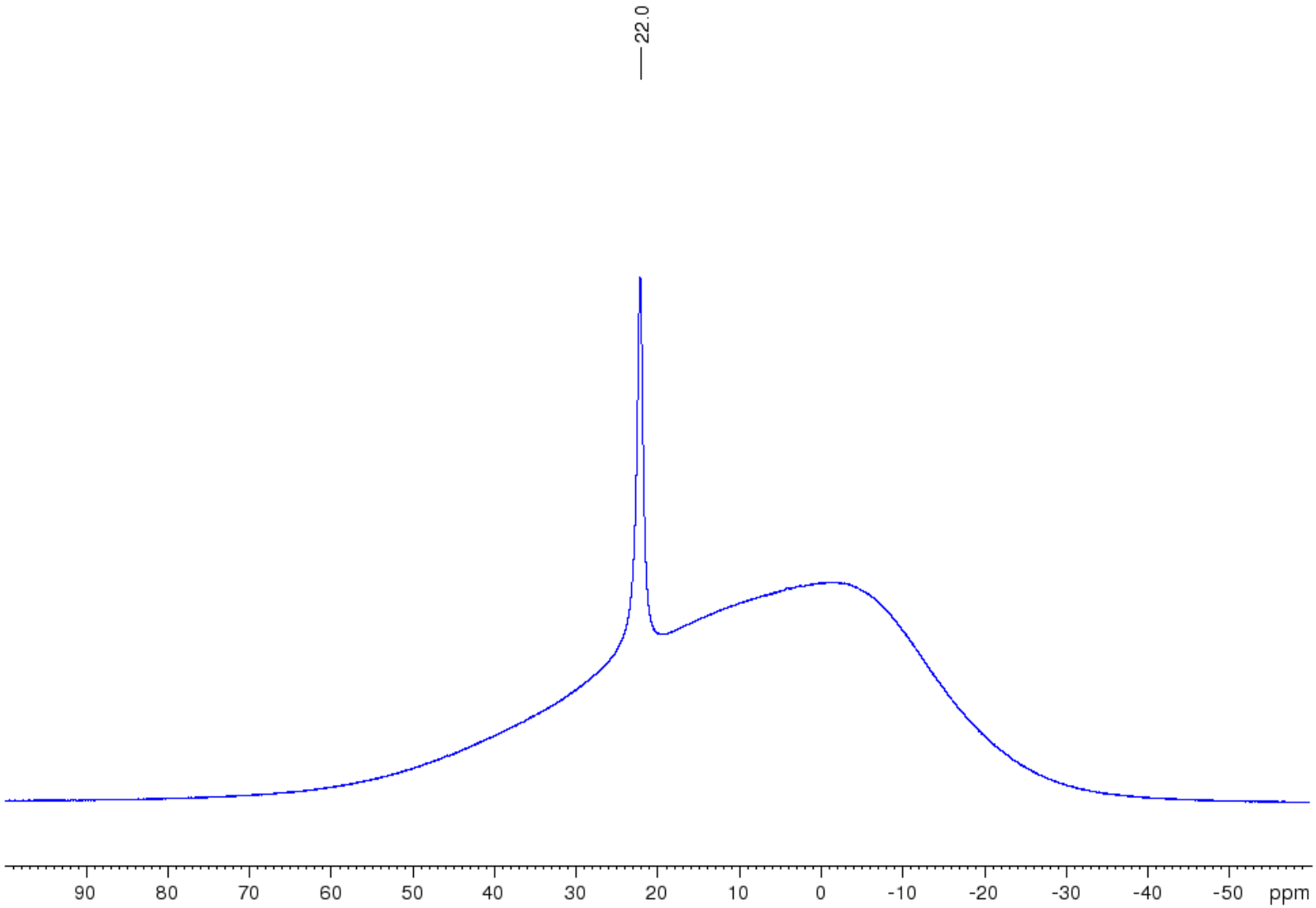

Figure S17. ^{11}B NMR spectrum of **$OB_2(CCMe)_2(NMe_2)_2$, 2b** in C_6D_6.

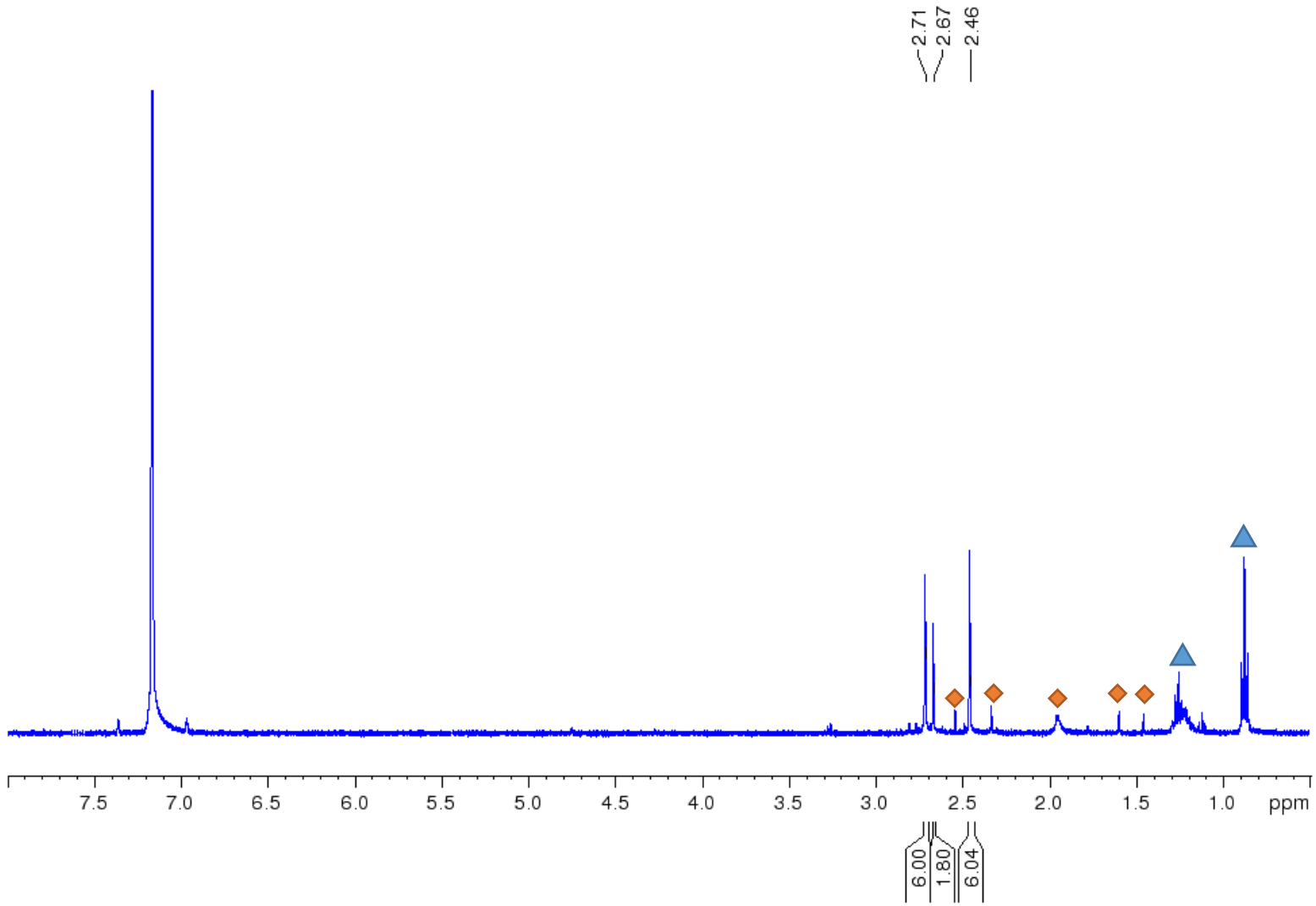

Figure S18. ^{1}H NMR spectrum of **$OB_2(CCH)_2(NMe_2)_2$, 2c** in C_6D_6. The resonances marked with ▲ correspond to residual pentane. The resonances marked with ◆ correspond to unkown impurities.

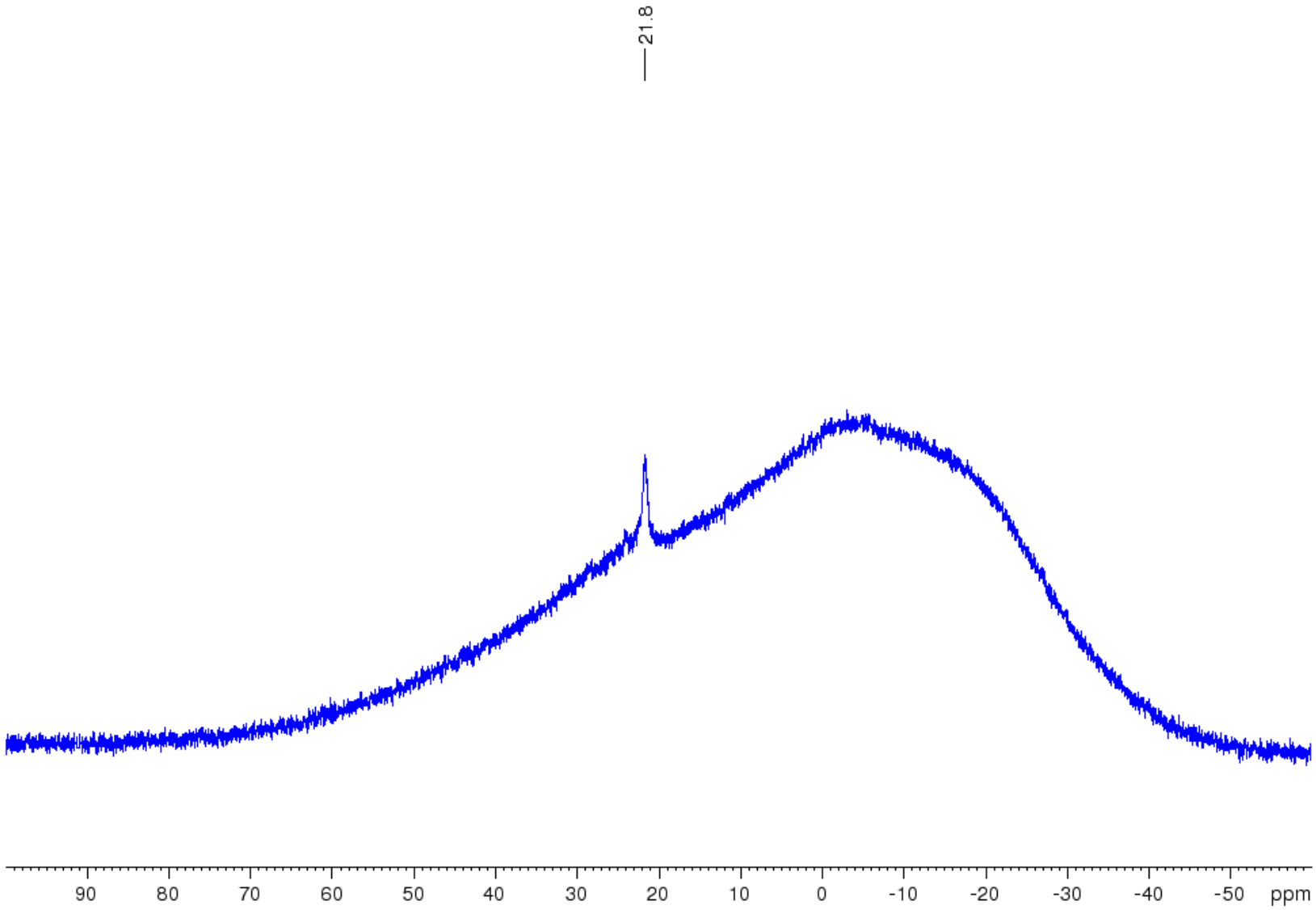

Figure S19. ^{11}B NMR spectrum of **$OB_2(CCH)_2(NMe_2)_2$, 2c** in C_6D_6.

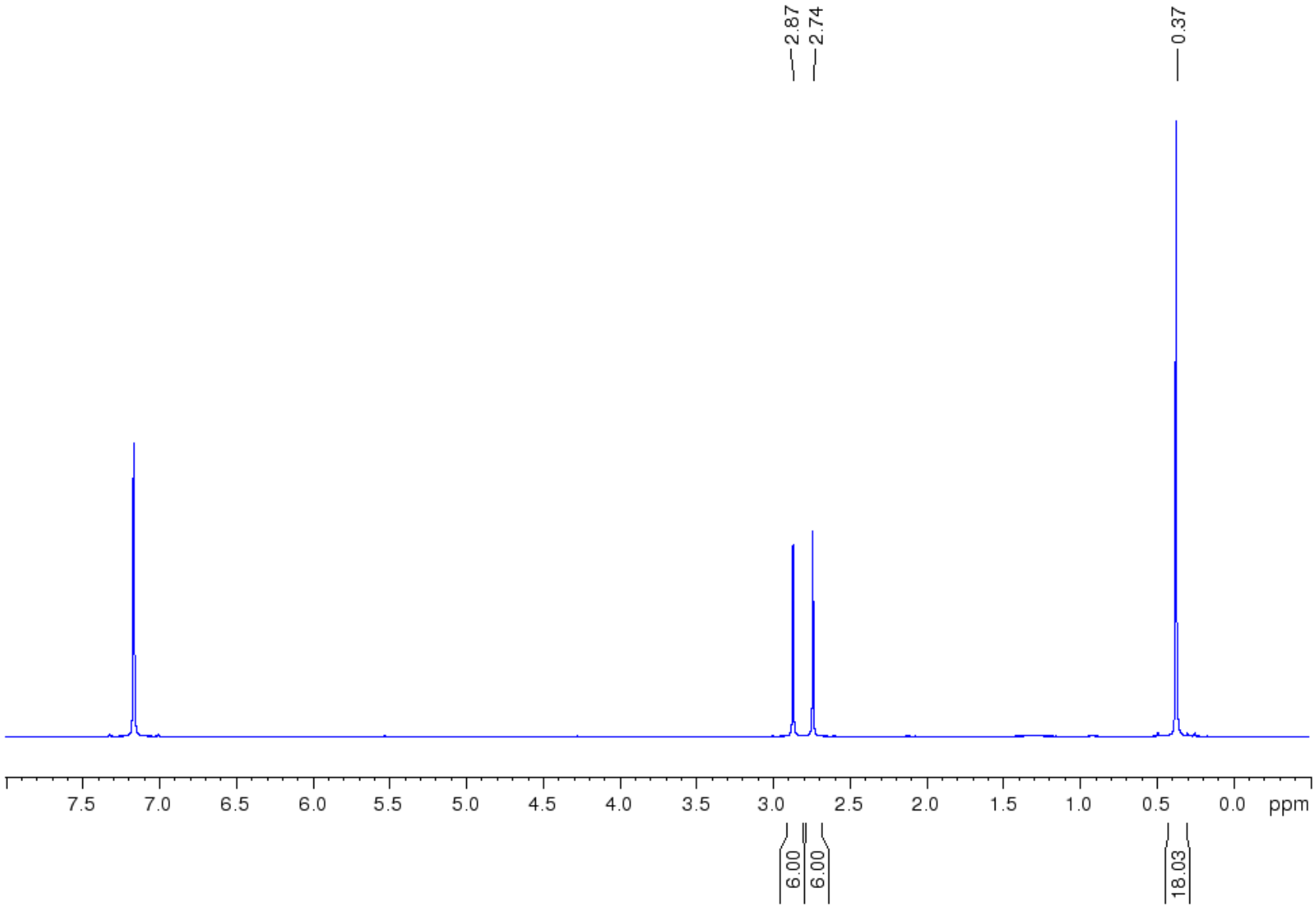

Figure S20. ^{1}H NMR spectrum of **$B_2(CCSiMe_3Co_2(CO)_6)_2(NMe_2)_2$, 3a** in C_6D_6.

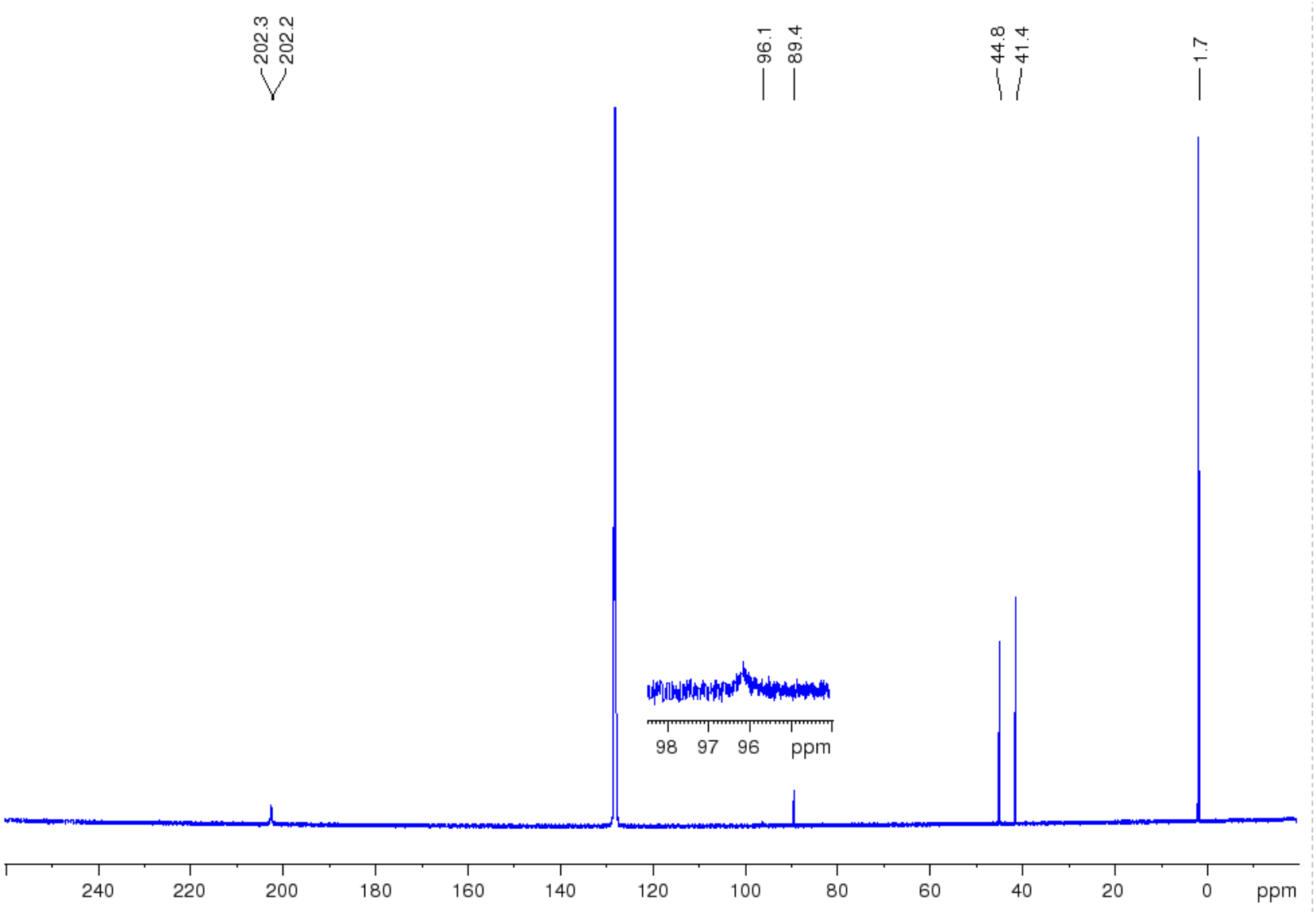

Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of **$B_2(CCSiMe_3Co_2(CO)_6)_2(NMe_2)_2$, 3a** in C_6D_6.

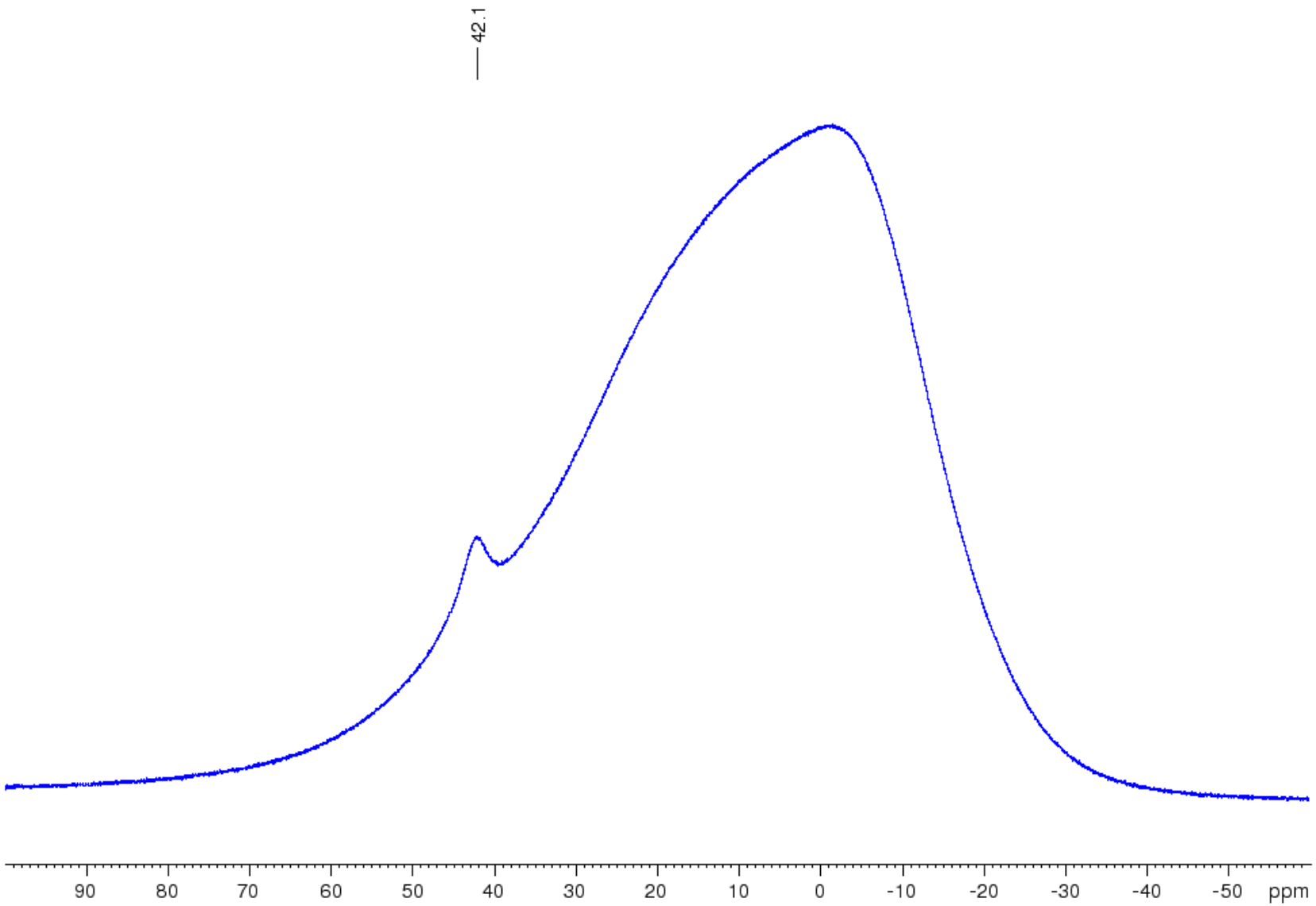

Figure S22. ^{11}B NMR spectrum of **$B_2(CCSiMe_3Co_2(CO)_6)_2(NMe_2)_2$, 3a** in C_6D_6.

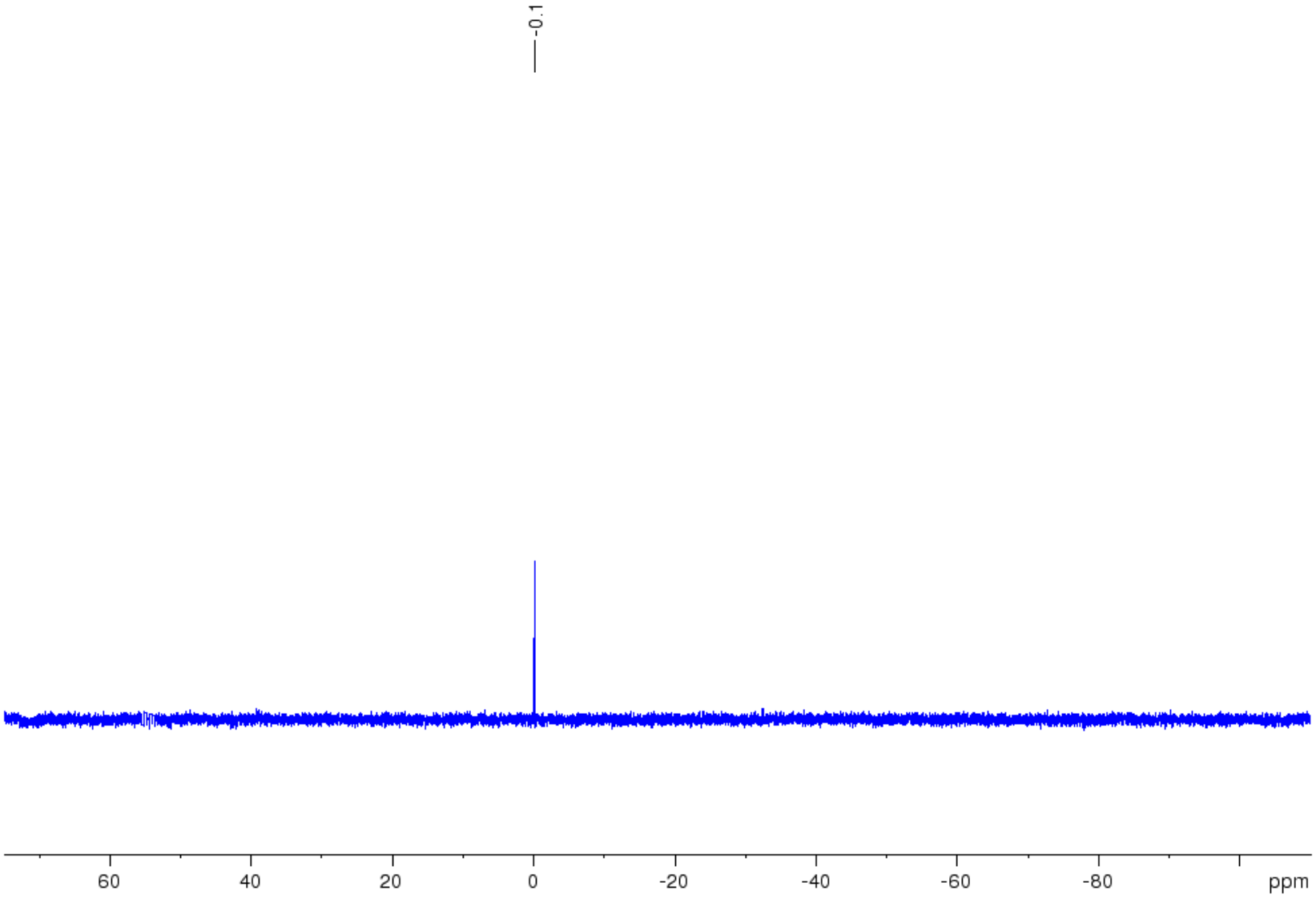

Figure S23. ^{29}Si NMR spectrum of **$B_2(CCSiMe_3Co_2(CO)_6)_2(NMe_2)_2$, 3a** in C_6D_6.

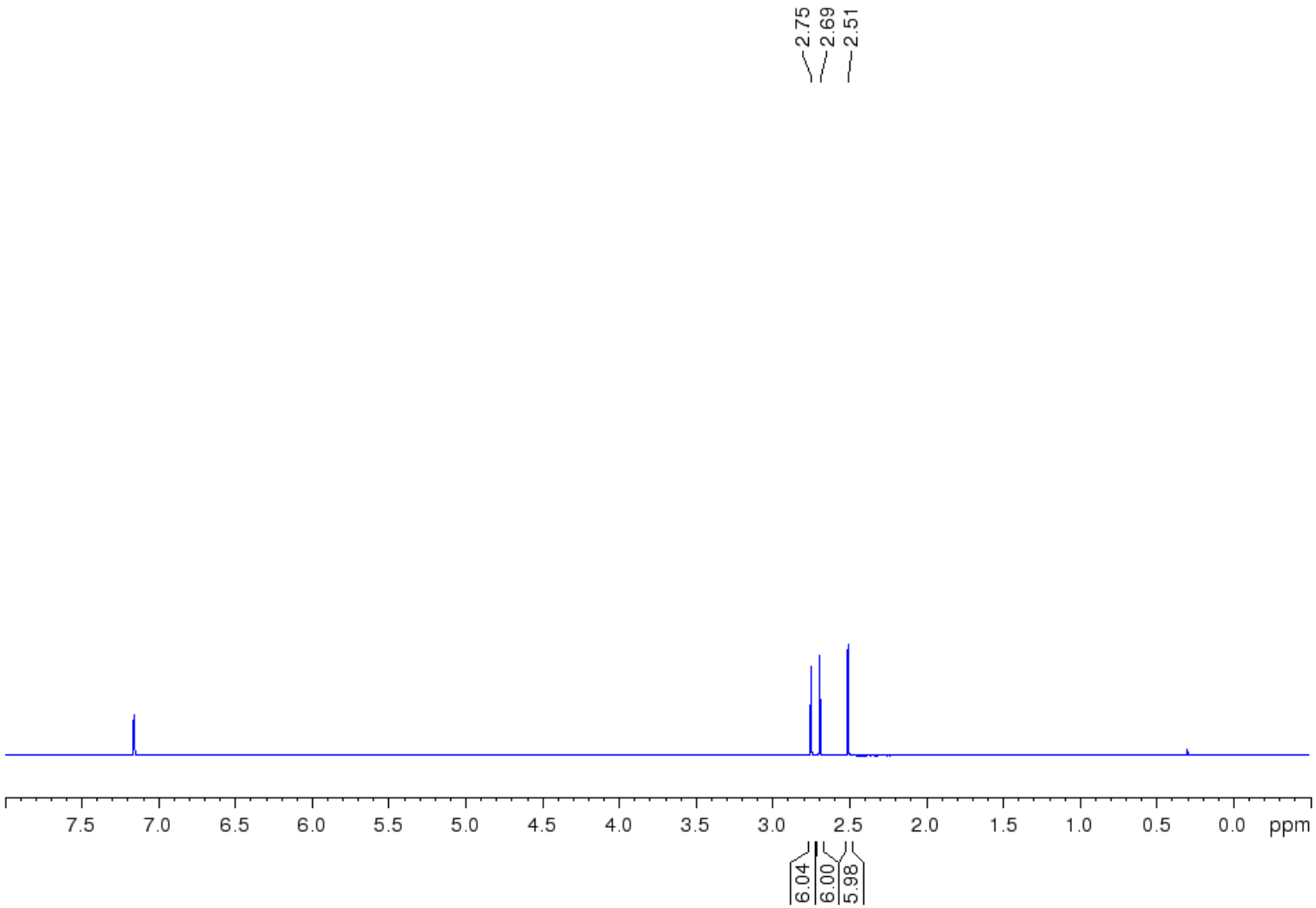

Figure S24. ^{1}H NMR spectrum of **$B_2(CCMeCo_2(CO)_6)_2(NMe_2)_2$, 3b** in C_6D_6.

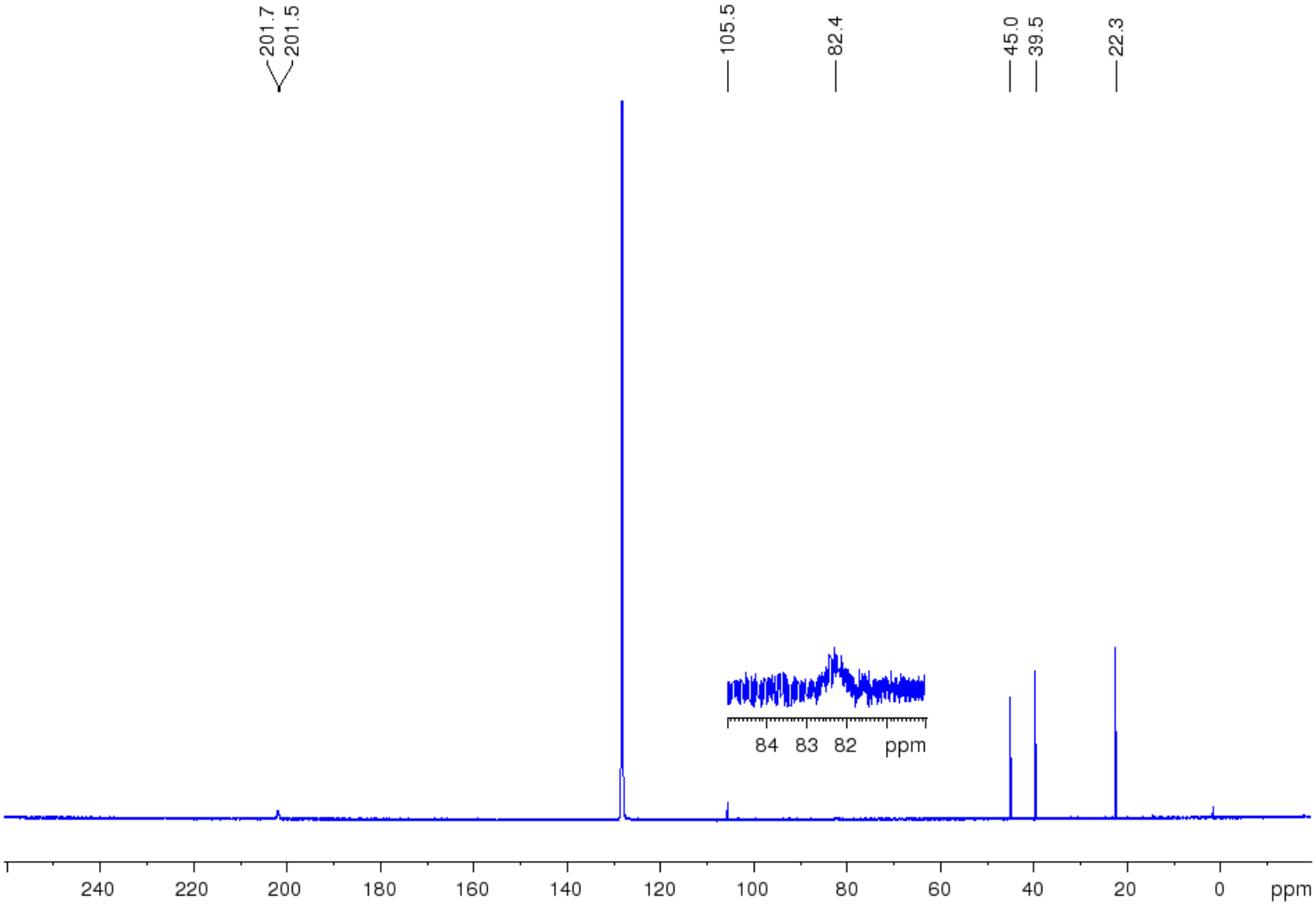

Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum of **$B_2(CCMeCo_2(CO)_6)_2(NMe_2)_2$, 3b** in C_6D_6.

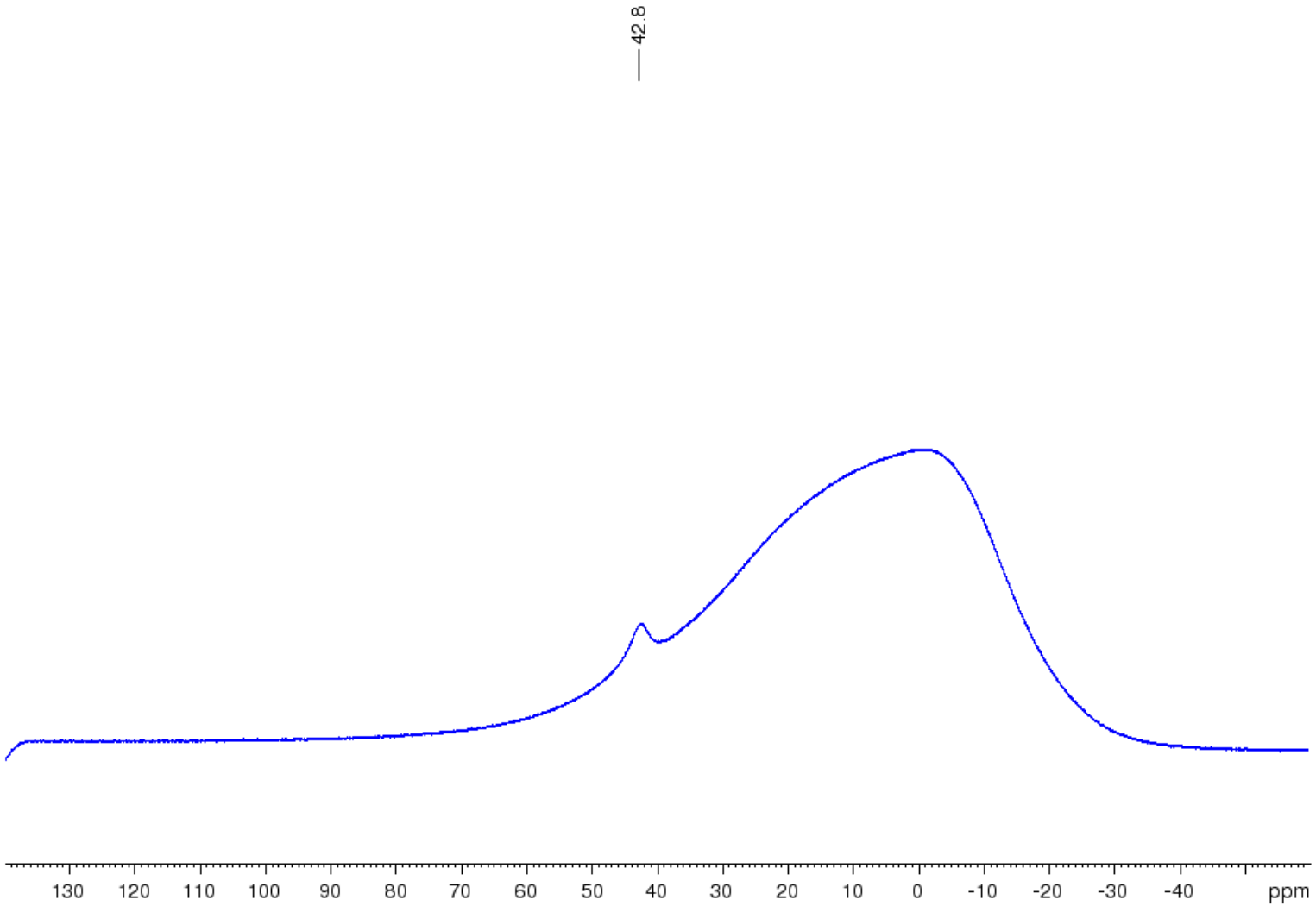

Figure S26. ^{11}B NMR spectrum of **$B_2(CCMeCo_2(CO)_6)_2(NMe_2)_2$, 3b** in C_6D_6.

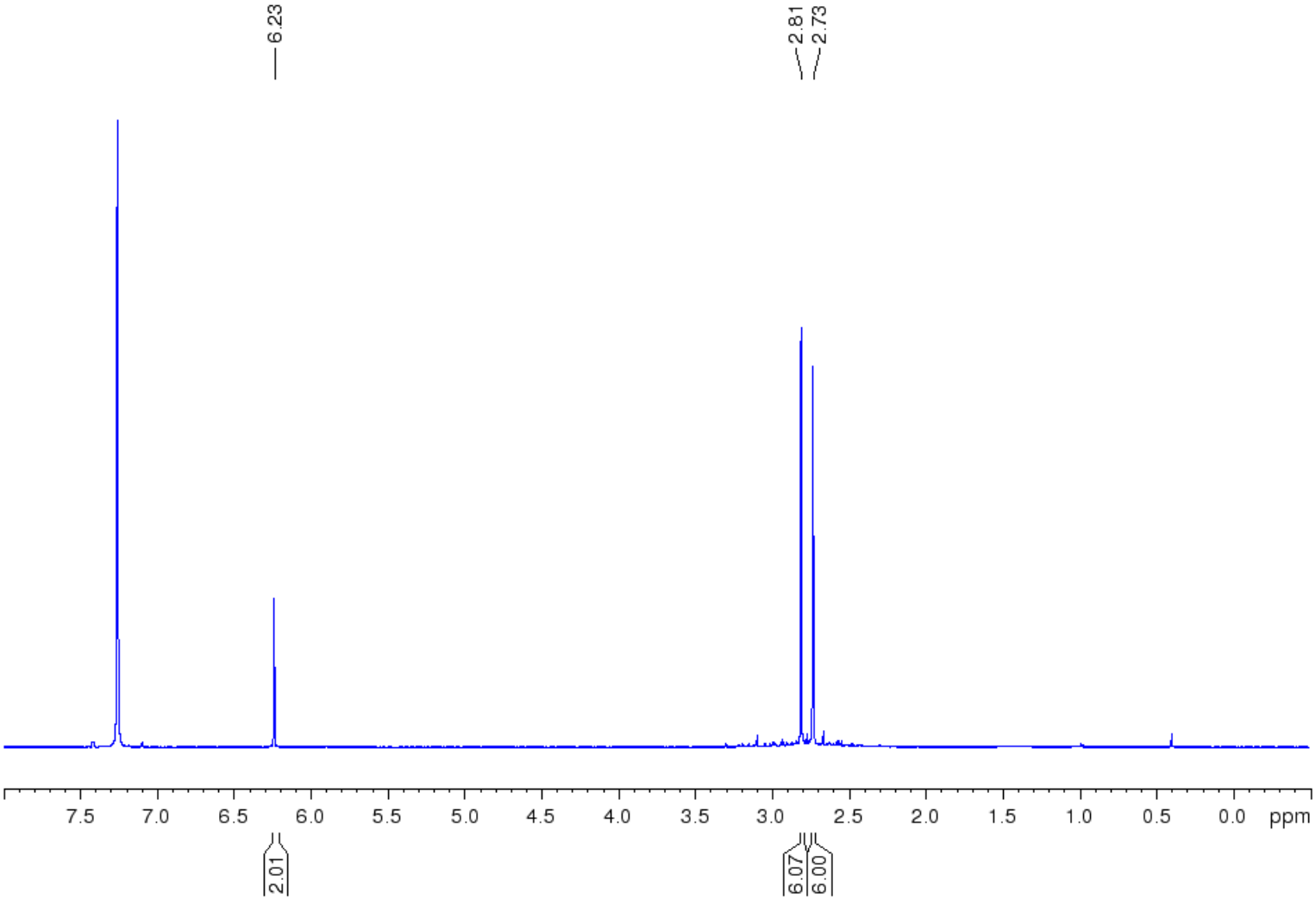

Figure S27. ^{1}H NMR spectrum of **$B_2(CCHCo_2(CO)_6)_2(NMe_2)_2$, 3c** in C_6D_6.

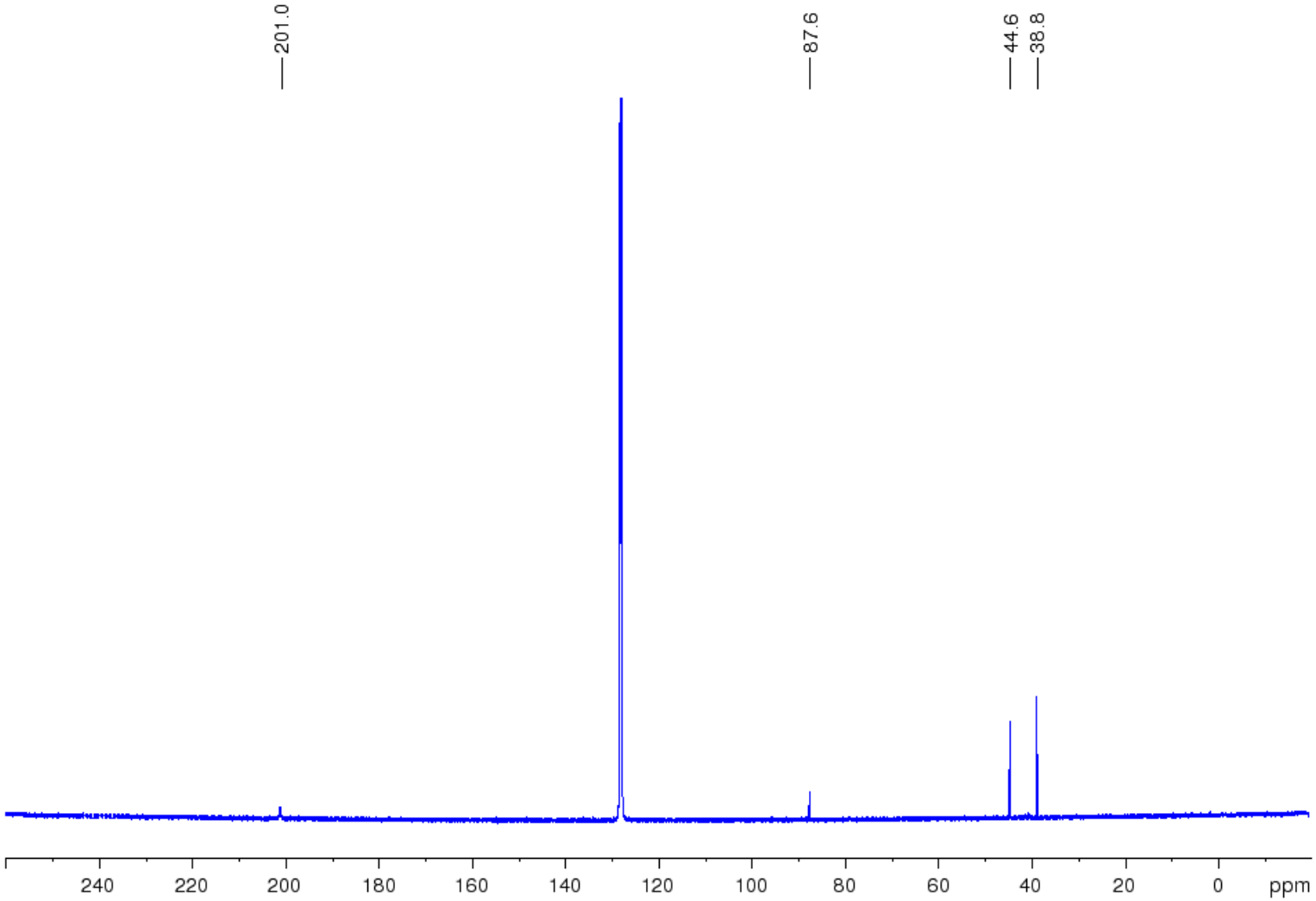

Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum of **$B_2(CCHCo_2(CO)_6)_2(NMe_2)_2$, 3c** in C_6D_6.

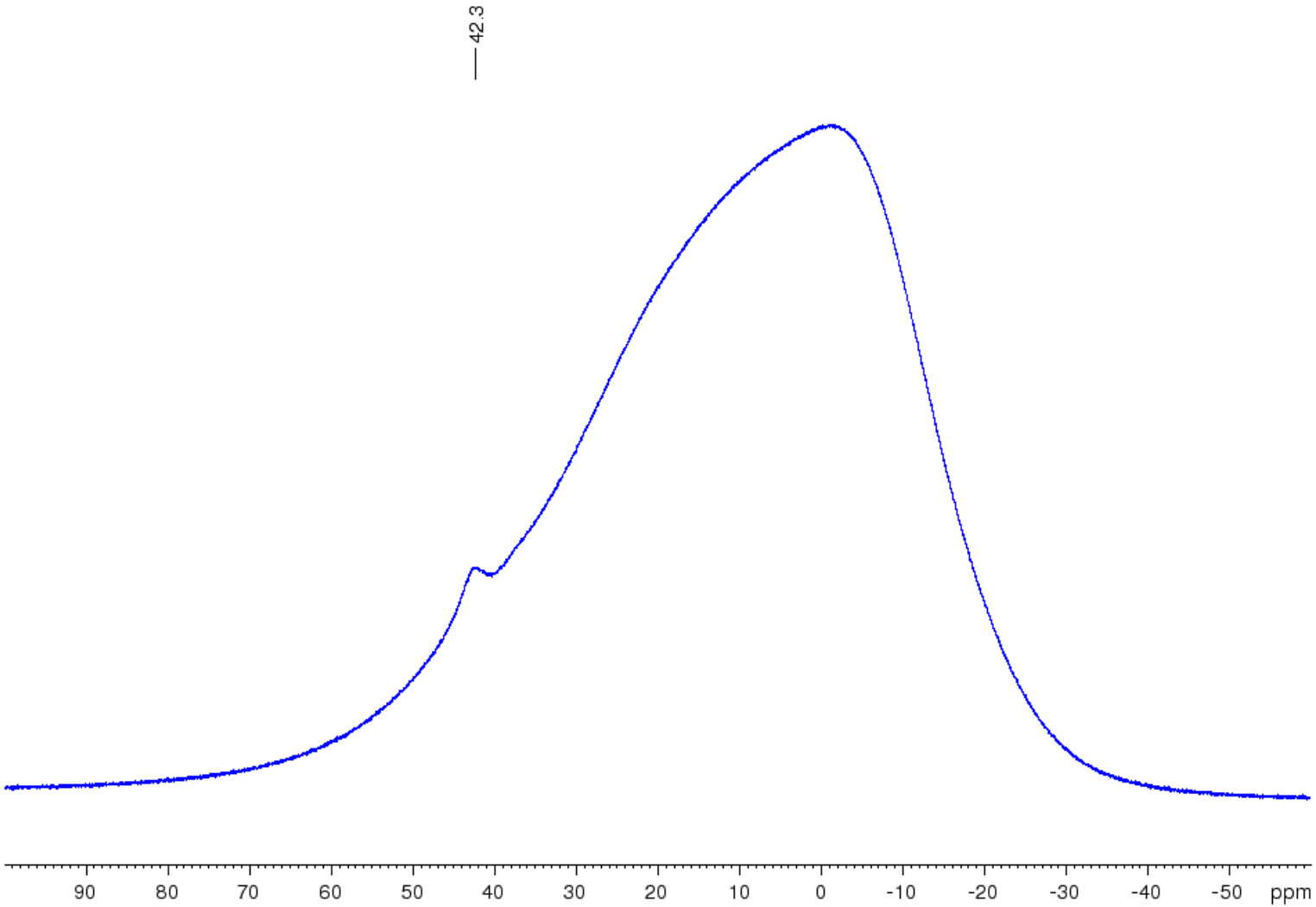

Figure S29. ^{11}B NMR spectrum of **$B_2(CCHCo_2(CO)_6)_2(NMe_2)_2$, 3c** in C_6D_6.

IR spectra

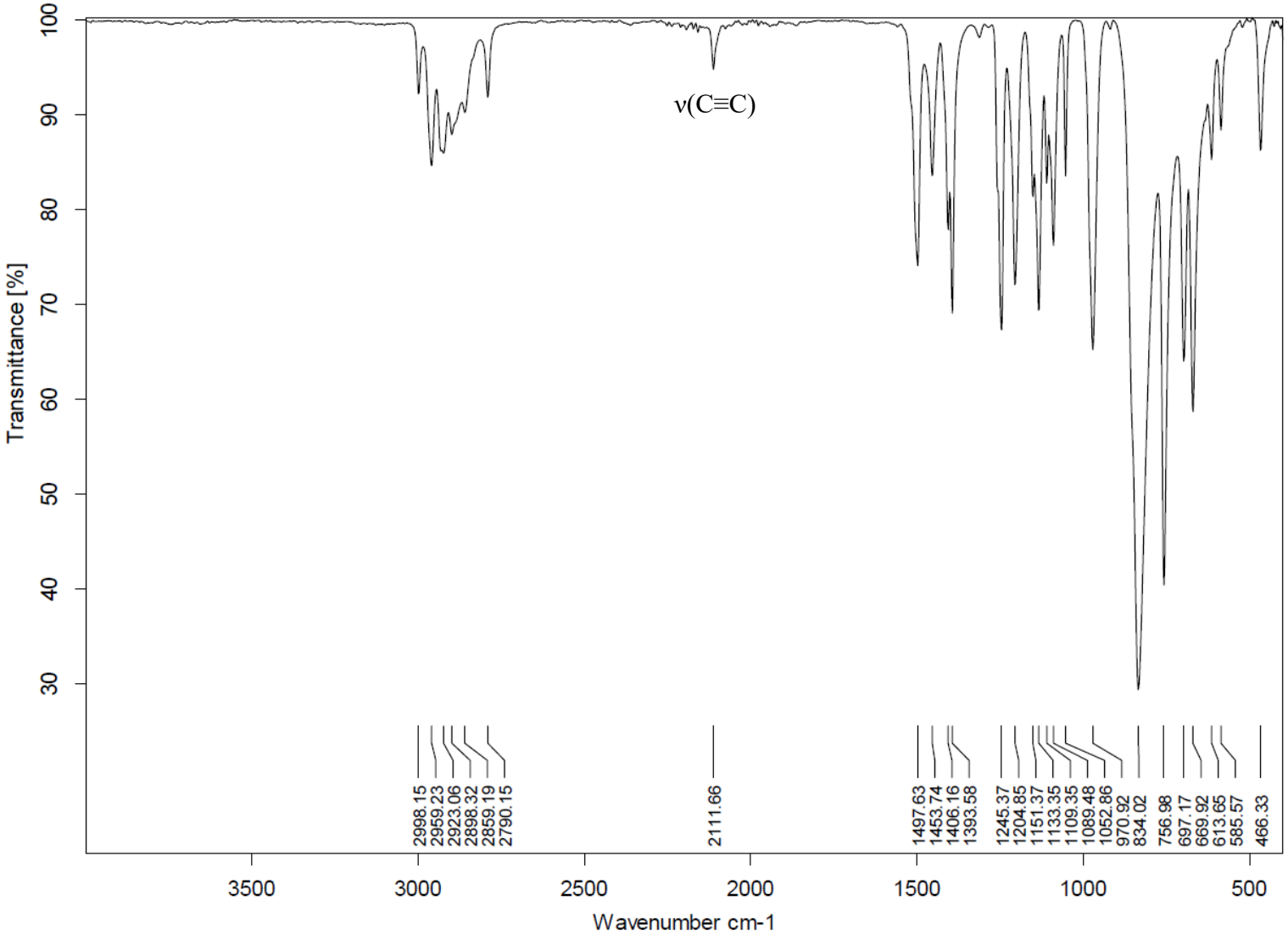

Figure S30. Solid-state IR spectrum of **$B_2(CCSiMe_3)_2(NMe_2)_2$, 1a**.

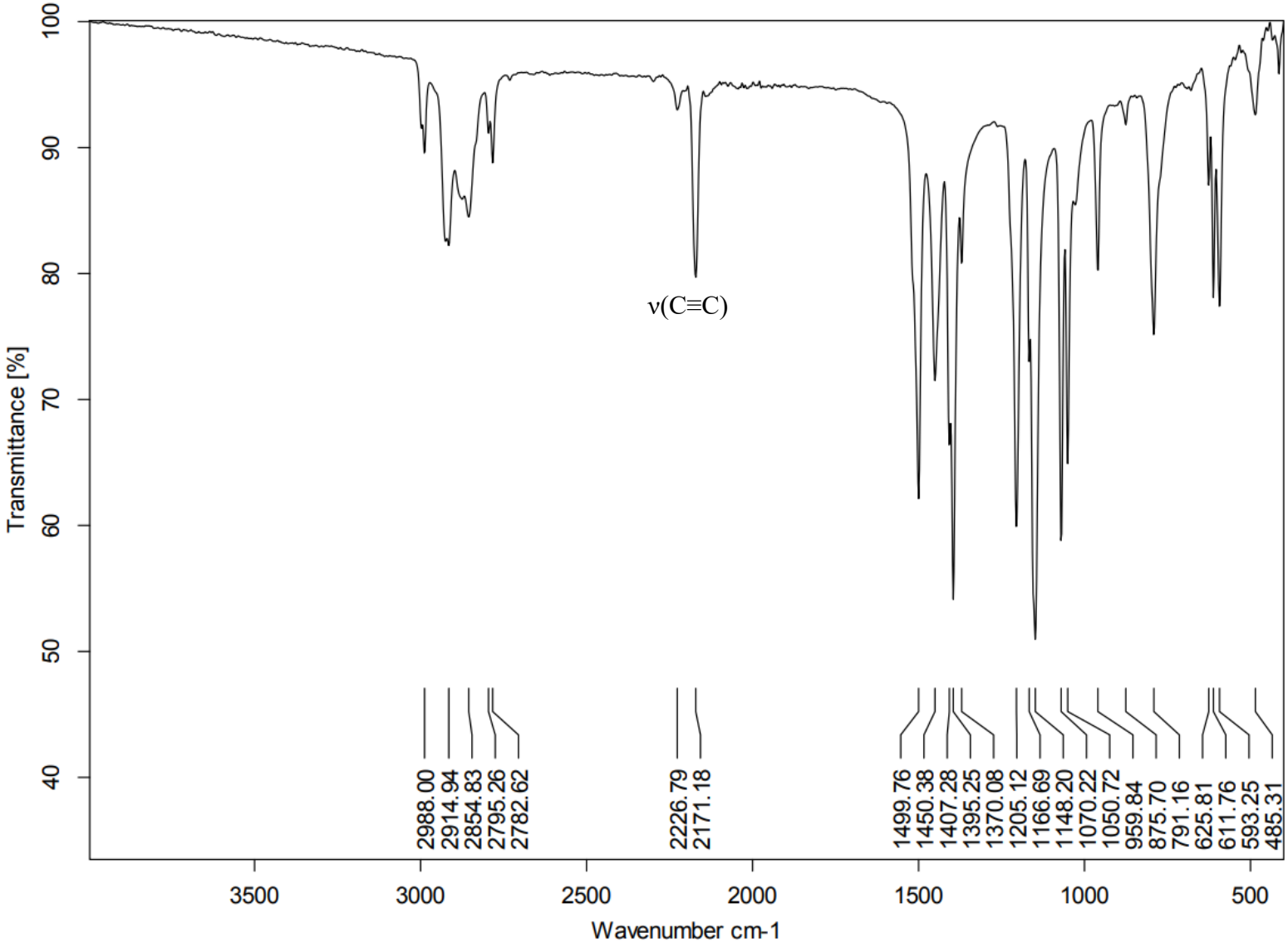

Figure S31. Solid-state IR spectrum of **$B_2(CCMe)_2(NMe_2)_2$, 1b**.

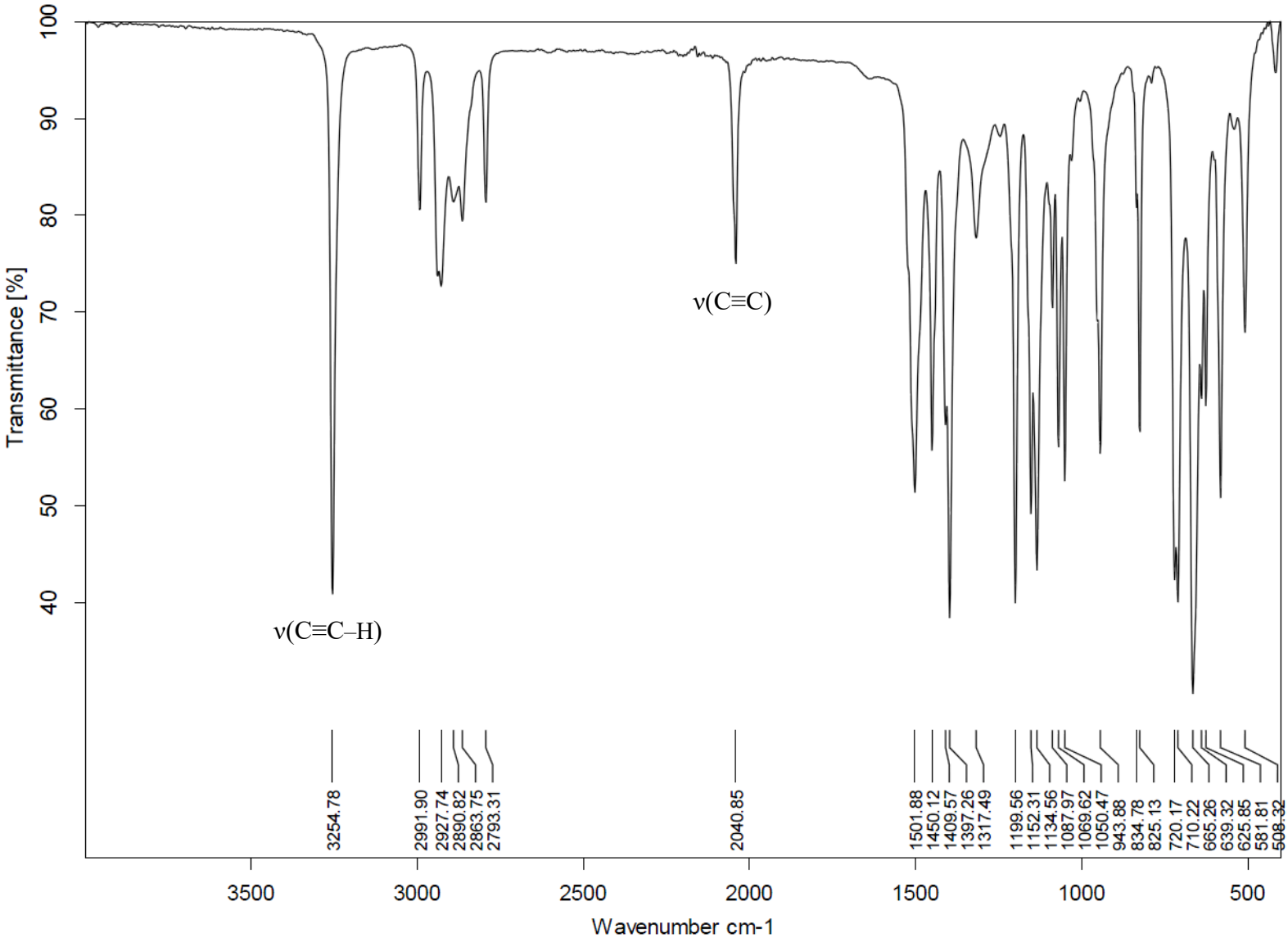

Figure S32. Solid-state IR spectrum of **$B_2(CCH)_2(NMe_2)_2$, 1c**.

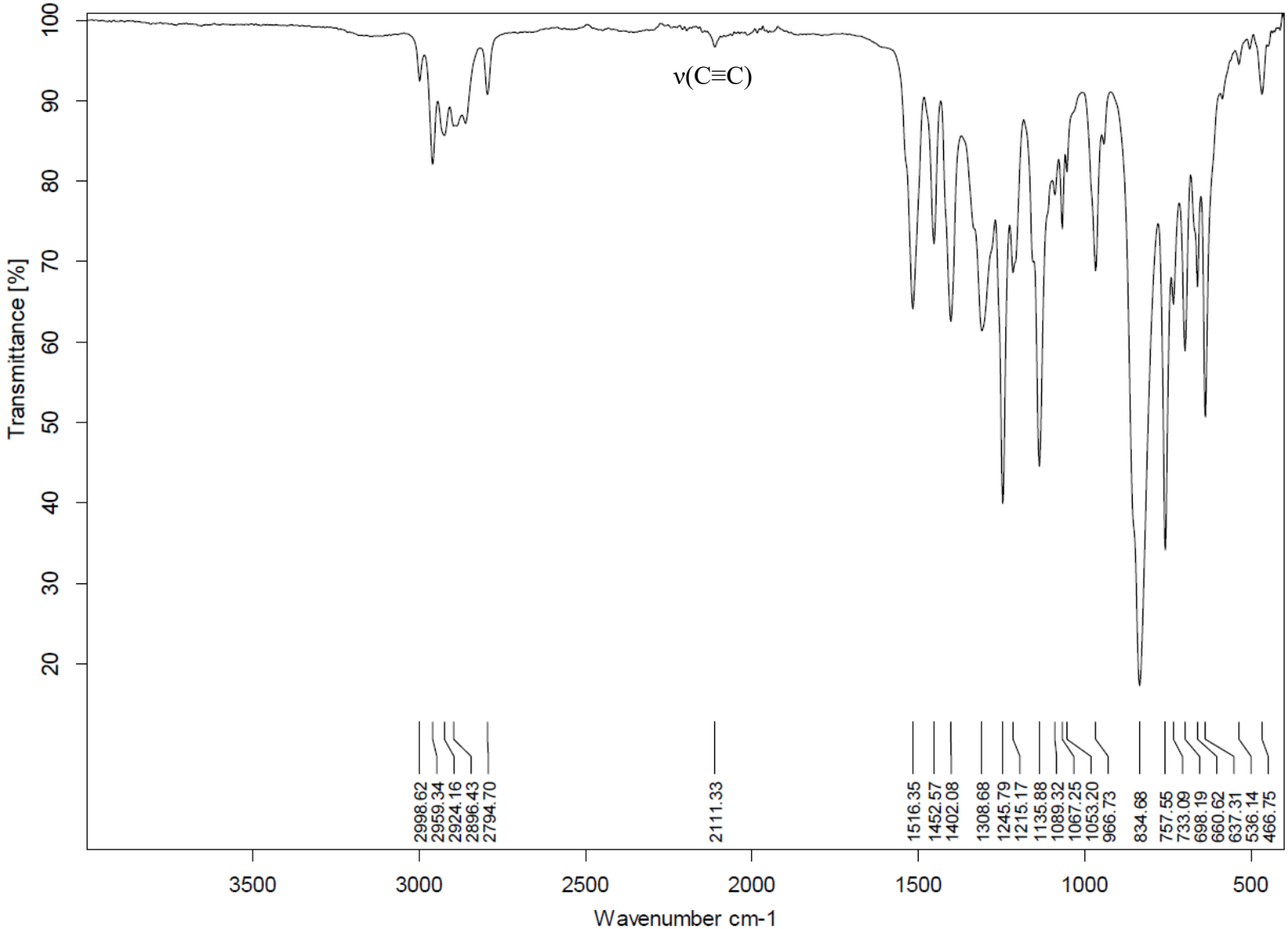

Figure S33. Solid-state IR spectrum of **$OB_2(CCSiMe_3)_2(NMe_2)_2$, 2a**

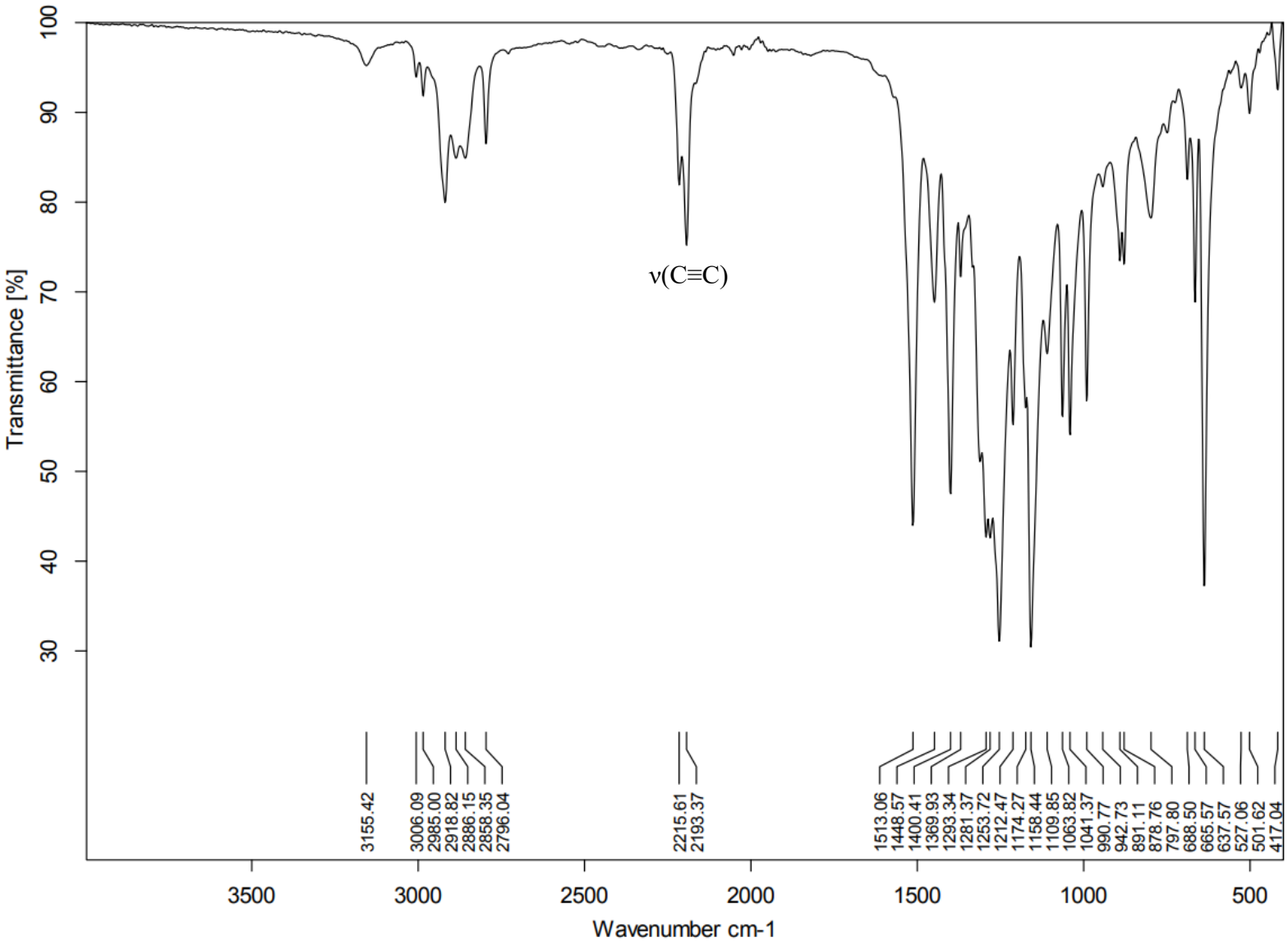

Figure S34. Solid-state IR spectrum of **$OB_2(CCMe)_2(NMe_2)_2$, 2b**.

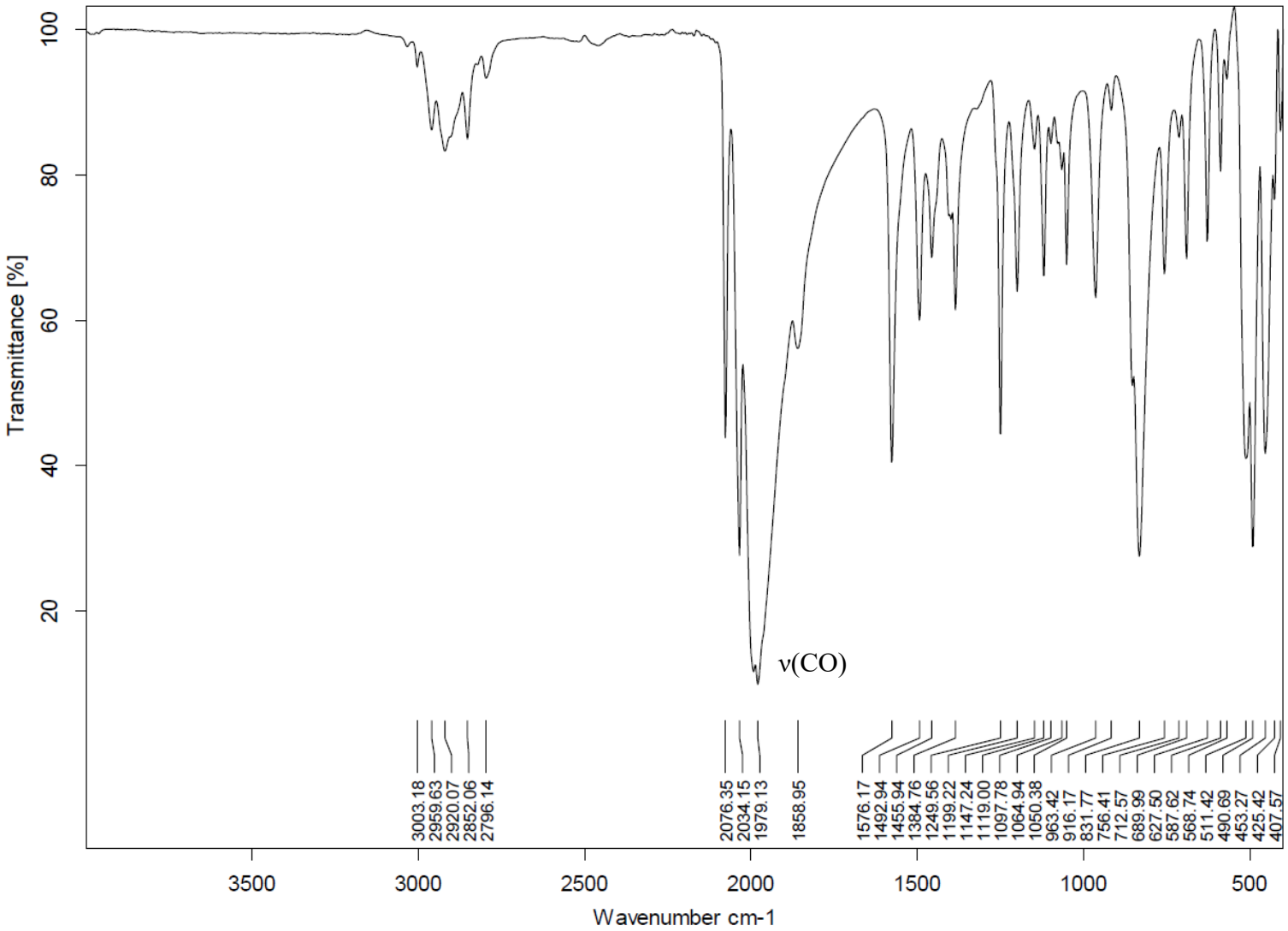

Figure S35. Solid-state IR spectrum of **$B_2(CCSiMe_3Co_2(CO)_6)_2(NMe_2)_2$, 3a**.

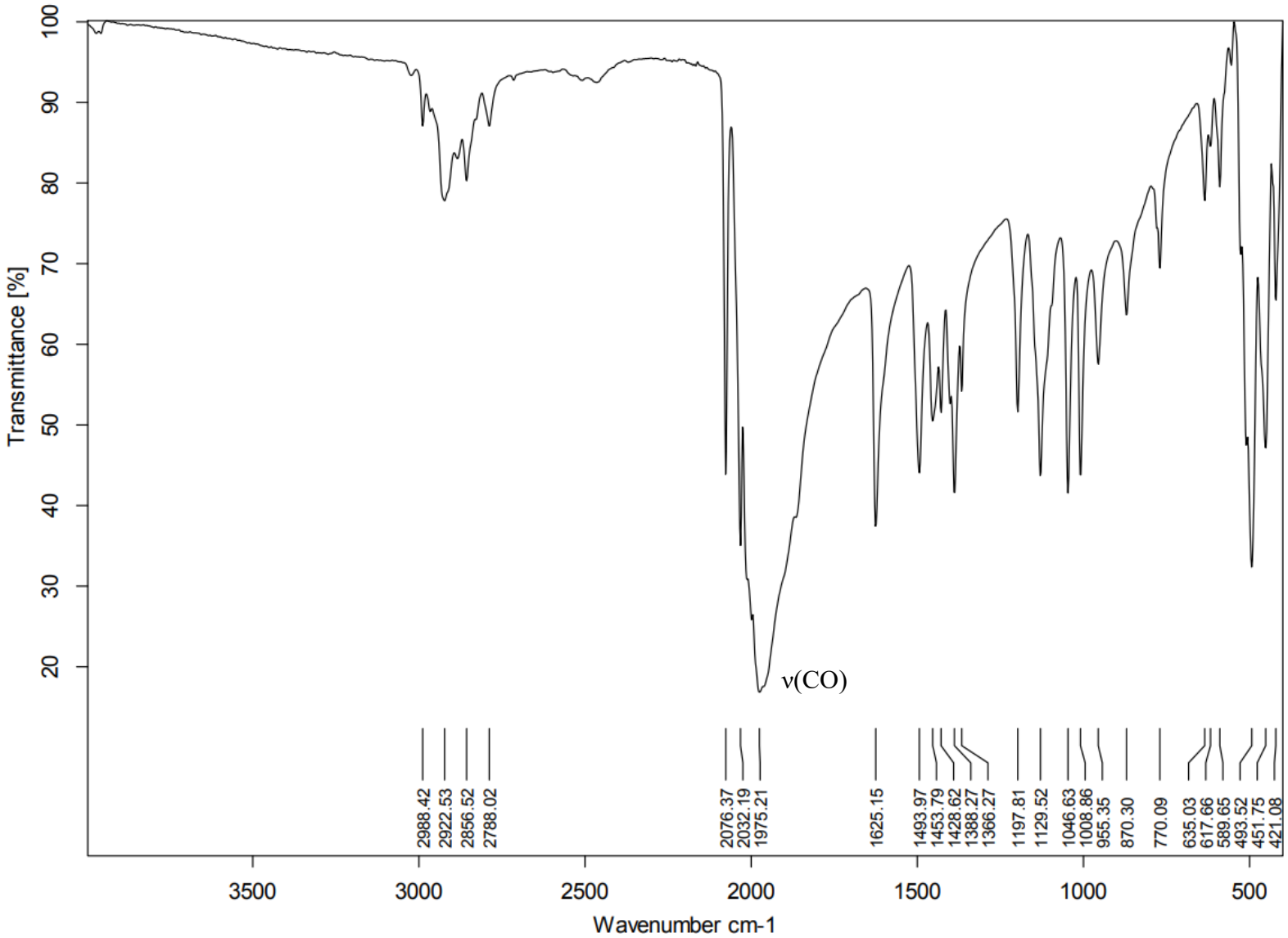

Figure S36. Solid-state IR spectrum of **$B_2(CCMeCo_2(CO)_6)_2(NMe_2)_2$, 3b**.

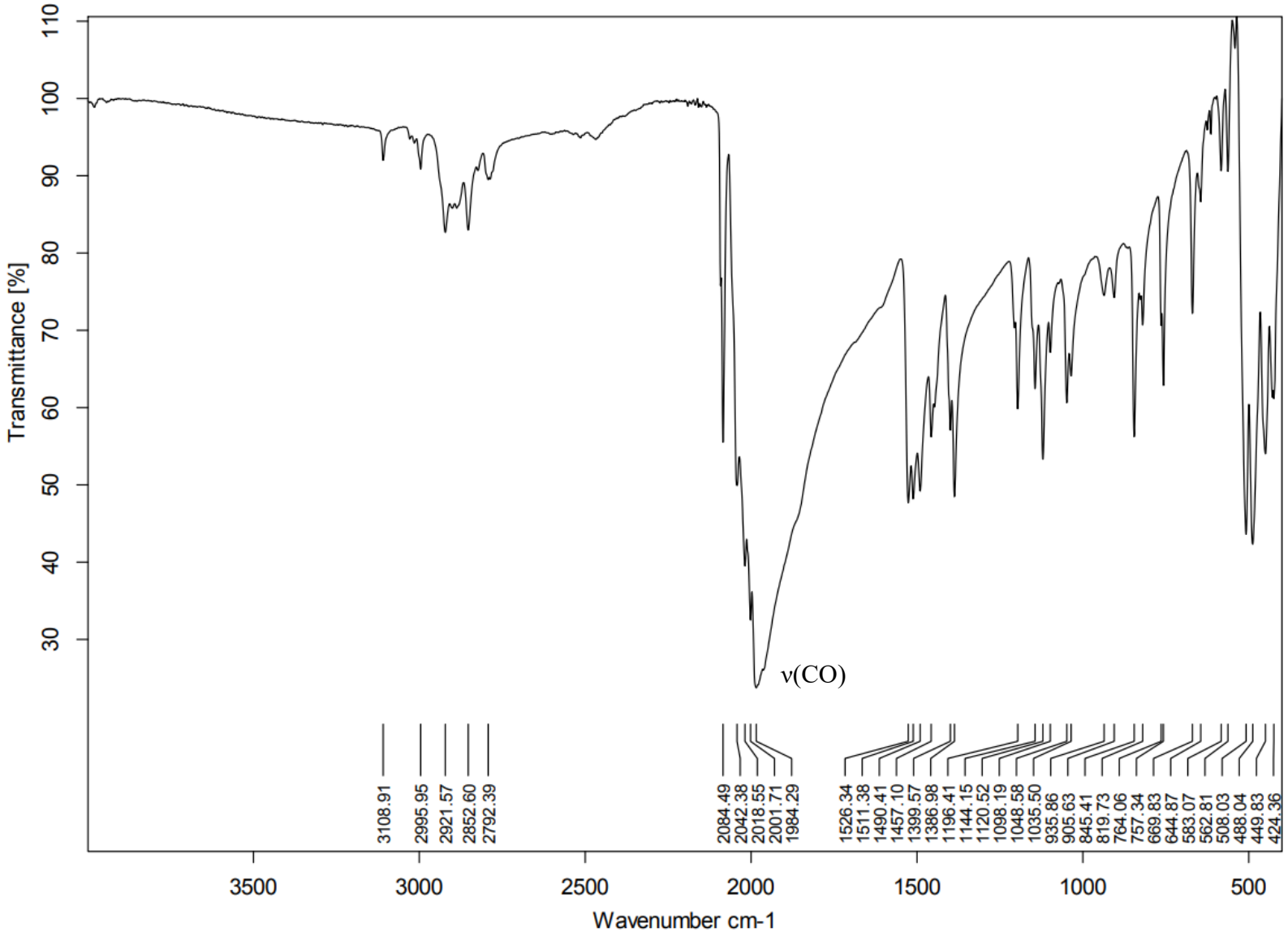

Figure S37. Solid-state IR spectrum of **$B_2(CCHCo_2(CO)_6)_2(NMe_2)_2$, 3c**.

UV-vis spectra

UV-vis spectra were measured on a METTLER TOLEDO UV-vis-Excellence UV5 spectrophotometer inside a glovebox.

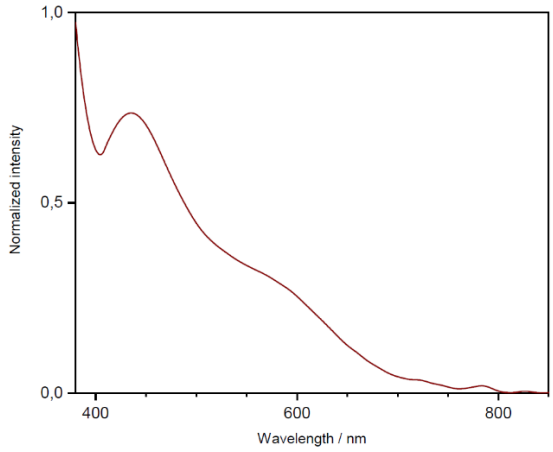

Figure S38. UV-vis absorption spectrum of **3a** in pentane at 25 °C.

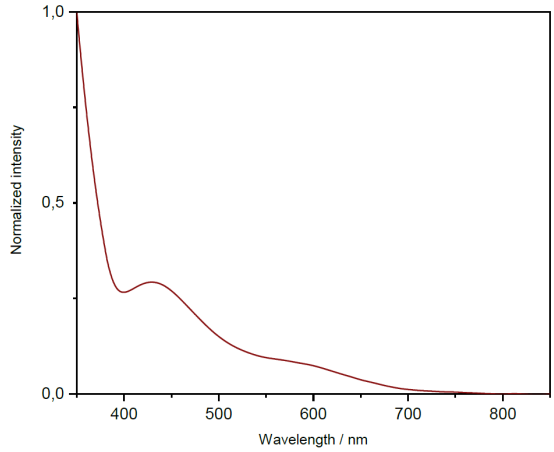

Figure S39. UV-vis absorption spectrum of **3b** in pentane at 25 °C.

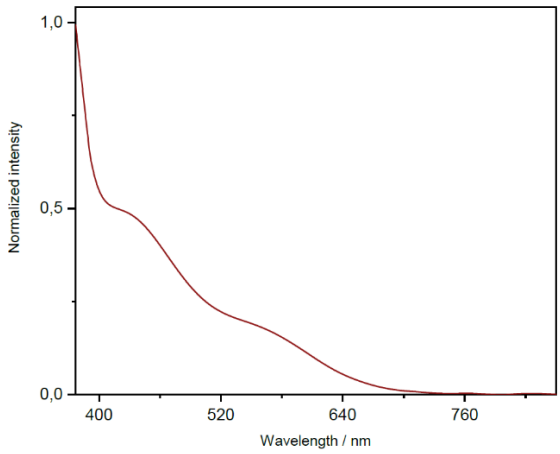

Figure S40. UV-vis absorption spectrum of **3c** in pentane at 25 °C.

X-ray crystallographic data

The crystal data of **1b**, **1c** and **2b** were collected on a Bruker D8 Quest diffractometer with a CMOS area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The crystal data of **1a**, **2a**, **3a**, **3b** and **3c** were collected on a BRUKER X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structures were solved using the intrinsic phasing method,[3] refined with the ShelXL program[4] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms except terminal H7 bound to the metallahedrane moiety of **3c** were assigned to idealized geometric positions. The coordinates of H7 were refined freely.

Special refinement details for 2a: B2 and N2 showed thermal vibration along the bond axis, therefore a restraint was used. The displacement parameters of atoms B2 and C2 were restrained to the same value with similarity restraint SIMU.

Special refinement details for 3a: One of the $SiMe_3$ groups showed a translational disorder. The displacement parameters of atoms Si1, C1, C2 and C3 of residues 2 and 12 were restrained to the same value with similarity restraint SIMU. The Uii displacement parameters of atoms Si1, C1, C2 and C3 of residues 2 and 12 were restrained with the ISOR keyword to approximate isotropic behaviour. The atomic displacement parameters of atoms Si1, C1, C2 and C3 of residues 2 and 12 were restrained with the RIGU keyword in the ShelXL input ('enhanced rigid bond' restraint for all bonds in the connectivity list. Standard values of 0.004 for both parameters s1 and s2 were used). A solvent molecule was found on an inversion center. The displacement parameters of atoms C1, C2, C3, C4, C5 and C6 of residue 4 were restrained to the same value with similarity restraint SIMU. The most disagreeable reflections were omitted (2 0 0; 0 2 0; 3 1 0; 2 7 11; 6 2 10).

Crystal data for **1a**: $C_{14}H_{30}B_2N_2Si_2$, M_r = 304.20, colourless block, 0.558×0.536×0.494 mm^3, monoclinic space group *C2/c*, a = 28.1055(15) Å, b = 5.9611(4) Å, c = 12.3603(8) Å, β = 103.971(3)°, V = 2009.6(2) Å^3, Z = 4, ρ_{calcd} = 1.005 g·cm^{-3}, μ = 0.170 mm^{-1}, F(000) = 664, T = 100(2) K, R_1 = 0.0422, wR^2 = 0.0975, 1980 independent reflections [2θ≤52.014°] and 96 parameters. CCDC: 2055858.

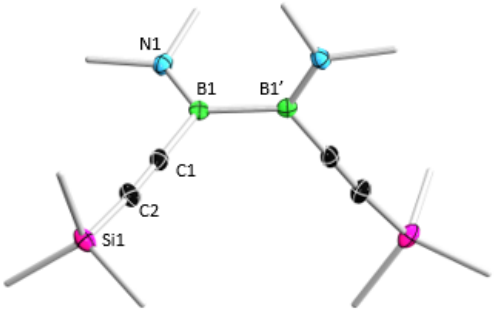

Figure S41. Crystallographically-derived molecular structure of **1a**. Thermal ellipsoids drawn at the 50% probability level. Ellipsoids on terminal methyl groups and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): C1–C2 1.214(2), B1–C1 1.550(2), B1–B1' 1.720(2); C1-B1-B1'-C1' 86.8(2).

Crystal data for **1b**: $C_{10}H_{18}B_2N_2$, M_r = 187.88, colourless plate, 0.526×0.483×0.206 mm^3, orthorhombic space group *Pbcn*, a = 17.5863(7) Å, b = 5.6213(2) Å, c = 11.9738(5) Å, V = 1183.70(8) Å^3, Z = 4, ρ_{calcd} = 1.054 g·cm^{-3}, μ = 0.060 mm^{-1}, F(000) = 408, T = 100(2) K, R_1 = 0.0474, wR^2 = 0.1060, 1162 independent reflections [2θ≤52.036°] and 67 parameters. CCDC: 2055852.

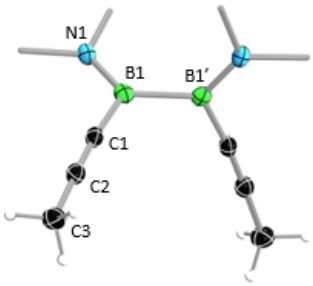

Figure S42. Crystallographically-derived molecular structure of **1b**. Thermal ellipsoids drawn at the 50% probability level. Ellipsoids on aminomethyl groups and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): C1–C2 1.204(2), B1–C1 1.547(2), B1–B1' 1.725(2); C1-B1-B1'-C1' 81.1(1).

Crystal data for **1c**: $C_8H_{14}B_2N_2$, M_r = 159.83, colourless block, 0.514×0.492×0.401 mm^3, monoclinic space group *C*2/*c*, a = 13.8008(9) Å, b = 6.3504(4) Å, c = 12.1141(7) Å, β = 90.588(3)°, V = 1061.63(11) Å^3, Z = 4, ρ_{calcd} = 1.000 g·cm^{-3}, μ = 0.058 mm^{-1}, F(000) = 344, T = 100(2) K, R_1 = 0.0469, wR^2 = 0.1027, 1044 independent reflections [2θ≤52.038°] and 57 parameters. CCDC: 2055857.

Crystal data for **2a**: $C_{14}H_{30}B_2N_2OSi_2$, $M_r = 320.20$, colourless block, 0.354×0.266×0.258 mm^3, monoclinic space group $P2_1/c$, $a = 16.2232(6)$ Å, $b = 10.2407(4)$ Å, $c = 12.6695(5)$ Å, $\beta = 94.201(3)°$, $V = 2099.22(14)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.013$ g·cm^{-3}, $\mu = 0.169$ mm^{-1}, $F(000) = 696$, $T = 100(2)$ K, $R_1 = 0.0722$, $wR^2 = 0.1181$, 4126 independent reflections [2θ≤52.044°] and 200 parameters. CCDC: 2055853.

Crystal data for **2b**: $C_{10}H_{18}B_2N_2O$, $M_r = 203.88$, colourless block, 0.729×0.434×0.262 mm^3, monoclinic space group $C2/c$, $a = 18.1518(12)$ Å, $b = 6.7454(4)$ Å, $c = 12.0546(8)$ Å, $\beta = 124.587(2)°$, $V = 1215.12(14)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.114$ g·cm^{-3}, $\mu = 0.070$ mm^{-1}, $F(000) = 440$, $T = 100(2)$ K, $R_1 = 0.0476$, $wR^2 = 0.1241$, 1193 independent reflections [2θ≤52.014°] and 72 parameters. CCDC: 2055859.

Crystal data for **3a**: $C_{29}H_{37}B_2Co_4N_2O_{12}Si_2$, $M_r = 919.12$, red block, 0.557×0.413×0.358 mm^3, orthorhombic space group $Pbcn$, $a = 20.8512(3)$ Å, $b = 21.3528(3)$ Å, $c = 18.4332(3)$ Å, $V = 8207.0(2)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.488$ g·cm^{-3}, $\mu = 1.702$ mm^{-1}, $F(000) = 3736$, $T = 100(2)$ K, $R_1 = 0.0608$, $wR^2 = 0.1337$, 8103 independent reflections [2θ≤52.044°] and 498 parameters. CCDC: 2055855.

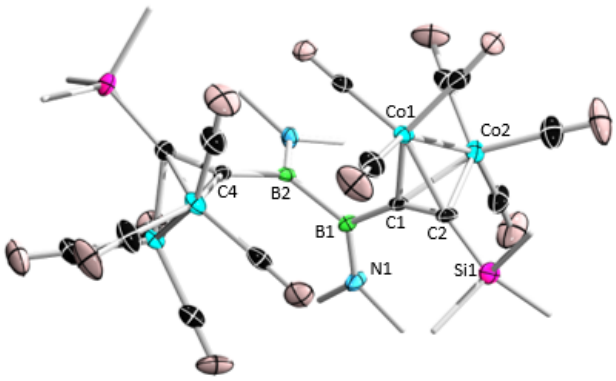

Figure S43. Crystallographically-derived molecular structure of **3a**. Thermal ellipsoids drawn at the 50% probability level. Ellipsoids on methyl groups and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles(°): C1–C2 1.324(6), B1–C1 1.574(6); B1-C1-C2 152.9(4).

Crystal data for **3b**: $C_{22}H_{18}B_2Co_4N_2O_{12}$, $M_r = 759.72$, red plate, 0.274×0.255×0.116 mm^3, monoclinic space group $P2_1/c$, $a = 15.6359(6)$ Å, $b = 11.9136(5)$ Å, $c = 16.3810(6)$ Å, $\beta = 102.757(2)°$, $V = 2976.1(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.696$ g·cm^{-3}, $\mu = 2.251$ mm^{-1}, $F(000) = 1512$, $T = 100(2)$ K, $R_1 = 0.0379$, $wR^2 = 0.0716$, 5862 independent reflections [2θ≤52.042°] and 385 parameters. CCDC: 2055854.

Crystal data for **3c**: $C_{20}H_{14}B_2Co_4N_2O_{12}$, M_r = 731.67, red block, 0.373×0.276×0.084 mm^3, monoclinic space group *C*2/*c*, *a* = 17.582(3) Å, *b* = 14.6013(18) Å, *c* = 11.2104(17) Å, β = 107.223(7)°, *V* = 2748.9(7) Å^3, *Z* = 4, ρ_{calcd} = 1.768 g·cm^{-3}, μ = 2.433 mm^{-1}, *F*(000) = 1448, *T* = 296(2) K, R_1 = 0.0540, wR^2 = 0.0669, 2703 independent reflections [2θ≤52.038°] and 186 parameters. CCDC: 2055856.

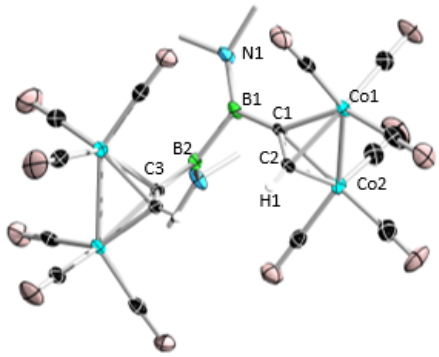

Figure S44. Crystallographically-derived molecular structure of **3c**. Thermal ellipsoids drawn at the 50% probability level. Ellipsoids on methyl groups and most hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles(°): C1–C2 1.336 (4), B1–C1 1.559(4); B1-C1-C2 143.2(18).

Computational details

Geometry optimisations and Hessian calculations were performed for **1a**, **1b**, **1c** and **4** at the density functional theory level. The PBE0[5] functional was employed in conjunction with the def2-SVP[6] basis set. Dispersion corrections were considered using Grimme's D3[7] model with the Becke-Johnson (BJ)[8] damping function. All optimised structures were characterised as minimum energy structures by the analysis of the computed vibrational frequencies, as in all cases only positive eigenvalues were found. The canonical Kohn–Sham molecular orbitals of **1a**, **1b**, **1c** and **4** and their corresponding HOMO-LUMO gaps were obtained at their corresponding optimised structures at the PBE0-D3(BJ)/def2-SVP level. All calculations were performed using Gaussian 16, revision B.01.[9]

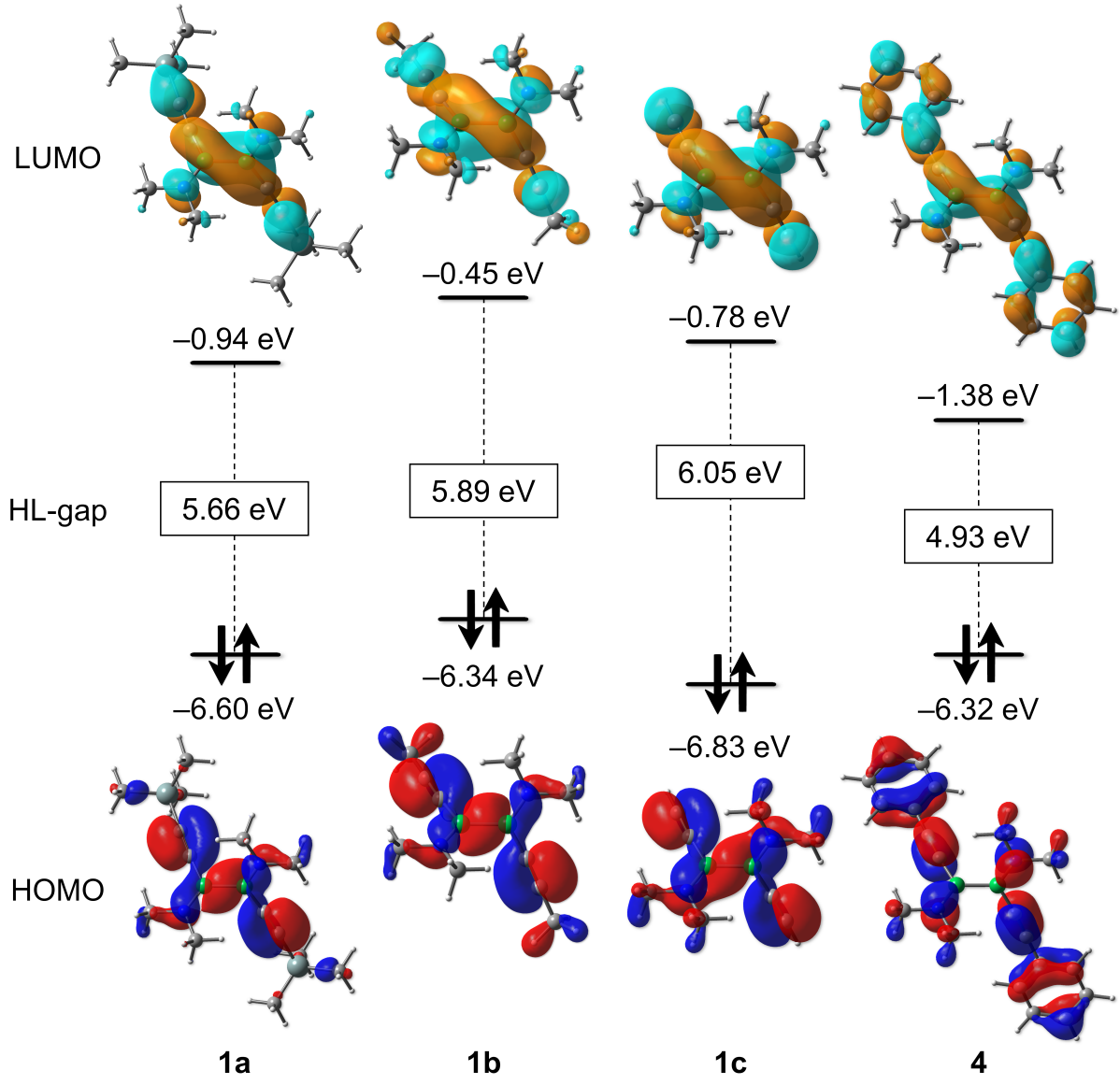

Figure S45. Canonical Kohn-Sham molecular orbitals of **1a**, **1b**, **1c** and **4** at the PBE0-D3(BJ)/def2-SVP level of theory.

Cartesian coordinates

1a

B	0.621695154	0.594952076	-1.032757962
C	2.955434345	1.351896881	-1.576779940
H	3.269483940	1.630613612	-2.598777923
H	3.841460769	0.939572706	-1.061177087
H	2.630689751	2.257040161	-1.048769098
N	1.883974080	0.383963208	-1.610337482
C	2.241528923	-0.833782284	-2.297238508
H	2.495374212	-0.633889721	-3.354082903
H	1.414982667	-1.553769471	-2.262486496
H	3.124042134	-1.305779343	-1.829128414
C	-2.241528923	4.973140856	0.469257496
H	-2.600918096	5.896279073	0.951616087
H	-2.958513003	4.167621411	0.690807703
H	-2.238131129	5.134860254	-0.619779152
Si	-0.523106033	4.521349916	1.084192080
C	0.001257114	2.970938011	0.238707755
C	0.329645339	1.929974685	-0.325540733
C	0.697786006	5.888869427	0.668633303
H	1.711337146	5.624982174	1.008010194
H	0.408393258	6.833863205	1.155757514
H	0.738198817	6.062029611	-0.417856953
C	-0.548529462	4.205631302	2.936179083
H	0.449984618	3.916472999	3.298251645
H	-1.247448590	3.392308651	3.184444092
H	-0.863528284	5.109844490	3.481323059
B	-0.621695154	-0.594952076	-1.032757962
C	-2.955434345	-1.351896881	-1.576779940
H	-3.269483940	-1.630613612	-2.598777923
H	-3.841460769	-0.939572706	-1.061177087
H	-2.630689751	-2.257040161	-1.048769098
N	-1.883974080	-0.383963208	-1.610337482
C	-2.241528923	0.833782284	-2.297238508
H	-2.495374212	0.633889721	-3.354082903
H	-1.414982667	1.553769471	-2.262486496

H	-3.124042134	1.305779343	-1.829128414
C	2.241528923	-4.973140856	0.469257496
H	2.600918096	-5.896279073	0.951616087
H	2.958513003	-4.167621411	0.690807703
H	2.238131129	-5.134860254	-0.619779152
Si	0.523106033	-4.521349916	1.084192080
C	-0.001257114	-2.970938011	0.238707755
C	-0.329645339	-1.929974685	-0.325540733
C	-0.697786006	-5.888869427	0.668633303
H	-1.711337146	-5.624982174	1.008010194
H	-0.408393258	-6.833863205	1.155757514
H	-0.738198817	-6.062029611	-0.417856953
C	0.548529462	-4.205631302	2.936179083
H	-0.449984618	-3.916472999	3.298251645
H	1.247448590	-3.392308651	3.184444092
H	0.863528284	-5.109844490	3.481323059

1b

B	-0.708178465	0.488102055	-0.181380697
C	-1.914790934	2.601337813	-0.823077599
H	-2.271176952	2.796566038	-1.851018667
H	-1.673748707	3.579502024	-0.368258772
H	-2.728208953	2.138668476	-0.250508368
N	-0.760029871	1.735775520	-0.828942005
C	0.352154229	2.277245890	-1.570478290
H	0.093994986	2.414986145	-2.636685027
H	1.220248620	1.609532852	-1.502623315
H	0.649327838	3.265185793	-1.174171189
C	-1.941819921	-0.020310820	0.582751736
B	0.708177470	-0.488107988	-0.181375278
C	1.914796612	-2.601342962	-0.823061560
H	2.271188466	-2.796570959	-1.851000664
H	1.673754189	-3.579507400	-0.368243414
H	2.728210572	-2.138671498	-0.250488278
N	0.760033480	-1.735783516	-0.828931998
C	-0.352147079	-2.277258251	-1.570470369
H	-0.093983942	-2.415001099	-2.636675825

H	-1.220242863	-1.609546579	-1.502620267
H	-0.649320233	-3.265197461	-1.174161251
C	1.941817185	0.020312695	0.582754683
C	2.875907043	0.504627261	1.203655553
C	-2.875913213	-0.504615643	1.203655077
C	-3.987028080	-1.072587075	1.946426118
H	-4.181498920	-0.494954173	2.864374847
H	-4.913013223	-1.063363076	1.349368033
H	-3.786787906	-2.114433608	2.243185862
C	3.987020566	1.072604956	1.946423858
H	4.181012548	0.495403819	2.864745647
H	4.913176204	1.062719247	1.349641258
H	3.787069519	2.114683877	2.242562046

1c

B	-0.836865519	-0.196934486	0.196677163
C	-3.217422630	0.316416632	-0.435265577
H	-3.602127478	0.187785444	-1.462925486
H	-3.779133601	1.148966429	0.025084323
H	-3.418549519	-0.599709184	0.133328063
N	-1.800410748	0.596110228	-0.444898214
C	-1.462494953	1.788412717	-1.184752537
H	-1.747057351	1.691088390	-2.248153672
H	-0.384890891	1.985967925	-1.126390087
H	-1.993868716	2.668002896	-0.779641085
C	-1.285106875	-1.459466566	0.959448974
B	0.836846474	0.196938930	0.196665433
C	3.217398208	-0.316410927	-0.435293977
H	3.602098882	-0.187769161	-1.462954114
H	3.779110598	-1.148966000	0.025044984
H	3.418528448	0.599707998	0.133309781
N	1.800385771	-0.596102317	-0.444924572
C	1.462467065	-1.788397879	-1.184789029
H	1.747002936	-1.691057645	-2.248195837
H	0.384867037	-1.985968443	-1.126401056
H	1.993861498	-2.667987063	-0.779701999
C	1.285096276	1.459454866	0.959460478

C	1.558223149	2.477912236	1.572734480
H	1.802185799	3.372169425	2.116929356
C	-1.558130389	-2.477929456	1.572758547
H	-1.801936646	-3.372258358	2.116905167

4

B	0.526637037	1.235394287	-0.679862249
C	1.033689171	1.827782155	-3.071668387
H	1.297192860	2.852900237	-3.389215806
H	0.517514018	1.343295750	-3.920236444
H	1.958237608	1.275825487	-2.862141778
N	0.191113792	1.848250662	-1.899763236
C	-1.044409402	2.565274209	-2.101845143
H	-0.854370686	3.626598820	-2.345213294
H	-1.669260707	2.517454069	-1.201413149
H	-1.619935551	2.133244441	-2.940349529
C	1.868077913	0.499168001	-0.547641021
B	-0.526633873	1.235268411	0.680073639
C	-1.033675275	1.827202441	3.071993726
H	-1.297160141	2.852263880	3.389739882
H	-0.517510791	1.342541631	3.920468615
H	-1.958234772	1.275305242	2.862358603
N	-0.191098621	1.847882683	1.900093565
C	1.044435284	2.564848808	2.102314904
H	0.854412322	3.626129842	2.345885508
H	1.669287743	2.517192222	1.201875189
H	1.619953241	2.132649439	2.940737373
C	-1.868090496	0.499097298	0.547709089
C	-2.918694982	-0.096247714	0.343091494
C	2.918672275	-0.096229280	-0.343124247
C	4.140376852	-0.789213854	-0.100150094
C	4.363223943	-1.429316798	1.133055370
C	5.144288240	-0.845624784	-1.084255295
C	5.555338162	-2.104206257	1.370892233
H	3.584608176	-1.388542966	1.897220598
C	6.334311468	-1.521634156	-0.838809086
H	4.974387264	-0.350868846	-2.042534819

C	6.544042245	-2.152542789	0.387695426
H	5.715454709	-2.598141445	2.332237698
H	7.105954663	-1.557833642	-1.611487389
H	7.479807700	-2.683618033	0.577489042
C	-4.140391166	-0.789207482	0.100004368
C	-5.144270476	-0.845858172	1.084128319
C	-4.363263034	-1.429042129	-1.133336073
C	-6.334286437	-1.521839699	0.838569829
H	-4.974350502	-0.351310538	2.042512017
C	-5.555369913	-2.103904886	-1.371285105
H	-3.584671948	-1.388081990	-1.897516519
C	-6.544041874	-2.152481251	-0.388067759
H	-7.105904391	-1.558227409	1.611264415
H	-5.715506039	-2.597630307	-2.332735061
H	-7.479801720	-2.683534767	-0.577949759

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