Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for

1,2-Dialkylnyldiboranes: B–B versus C≡C bond reactivity

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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 ($^{13}C\{^1H\}$) or residual protons (^1H) of the solvent. Heteronuclei NMR spectra are referenced to external standards (^{11}B: $BF_3{\cdot}OEt_2$, ^{19}F: Cl_3CF, ^{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. $B_2(CCSiMe_3)_2(NMe_2)_2$ (**1**$^{\mathbf{TMS}}$),[1] $B_2(CCMe)_2(NMe_2)_2$ (**1**$^{\mathbf{Me}}$),[1] $B_2(CCH)_2(NMe_2)_2$ (**1**$^{\mathbf{H}}$),[1] all azides,[2] Mes_2BH (Mes = 2,4,6-$Me_3C_6H_2$),[3] and I*i*Pr (1,3-di*iso*propylimidazol-2-ylidene)[4] were synthesised by following literature procedures.

Synthetic procedures

PhN{B(CCSiMe$_3$)(NMe$_2$)}$_2$, 2^{TMS}-Ph

Azidobenzene (35.3 mg, 296 µmol, 1.50 equiv) was added to a solution of **1^{TMS}** (60.0 mg, 197 µmol) in 1 mL of benzene. The yellow solution was stirred for 16 h at 80 °C prior to removing all volatiles. The resulting residue was suspended in hexane and the solution filtered. The resulting colourless solution was stored at –30 °C and **2^{TMS}-Ph** was obtained as colourless solid and washed with cold pentane. Drying *in vacuo* yielded **2^{TMS}-Ph** (60.9 mg, 154 µmol, 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, CDCl$_3$, 297 K): δ = 7.14 (m, 2H, Ar–*H*), 6.95 (tt, ^4J= 1.1 Hz, ^3J= 7.35 Hz, 1H, Ar–*H*), 6.86 (m, 2H, Ar–*H*), 2.96 (br s, 6H, N*CH*$_3$), 2.53 (br s, 6H, N*CH*$_3$), 0.03 (s, 18H, Si*CH*$_3$) ppm. ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$, 297 K): δ = 148.5 (NC_q^{Ar}), 127.8 (HC_{ortho}^{Ar}), 126.7 (HC_{meta}^{Ar}), 122.3 (HC_{para}^{Ar}), 113.3 (BC_q), 110.9 (SiC_q), 41.0 (N*C*H$_3$), 39.3 (N*C*H$_3$), 0.0 (Si*C*H$_3$) ppm. ^{11}B NMR (128.6 MHz, CDCl$_3$, 297 K): δ = 25.5 (s) ppm. ^{29}Si NMR (99 MHz, CDCl$_3$, 297 K): δ = –19.4 (s) ppm. *Note: the solid-state IR C≡C band was not detected.* Elemental analysis for [$C_{20}H_{35}B_2N_3Si_2$] (M_w = 395.31): calcd. C 60.77, H 8.92, N 10.63%; found C 59.42, H 8.60, N 10.51%. HRMS LIFDI for [$C_{20}H_{35}B_2N_3Si_2$]$^+$ = [M]$^+$: calcd. 395.2550; found 395.2550.

Ph^{CN}N{B(CCSiMe$_3$)(NMe$_2$)}$_2$, 2^{TMS}-Ph^{CN}

4-Cyanoazidobenzene (28.4 mg, 197 µmol) was added to a solution of **1^{TMS}** (60.0 mg, 197 µmol) in 1 mL of benzene. The yellow solution was stirred for 16 h at 80 °C prior to removing all volatiles. The resulting residue was suspended in hexane and filtered. The resulting colourless solution was stored at –30 °C and **2^{TMS}-Ph^{CN}** was obtained as a colourless solid and washed with cold pentane. Drying *in vacuo* yielded **2^{TMS}-Ph^{CN}** (71.0 mg, 169 µmol, 86% 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, CDCl$_3$, 297 K): δ = 7.10 (d, ^3J= 8.7 Hz, 2H, Ar–*H*), 6.72 (d, ^3J= 8.7 Hz, 2H, Ar–*H*), 2.86 (br s, 6H, N*CH*$_3$), 2.30 (br s, 6H, N*CH*$_3$), 0.05 (s, 18H, Si*CH*$_3$) ppm. ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$, 297 K): δ = 152.8 (NC_q^{Ar}), 132.1 (HC_{ortho}^{Ar}), 126.2 (HC_{meta}^{Ar}), 120.4 (BC_q), 119.6 (N≡C_q), 112.1 (SiC_q), 105.7 (CC_q^{Ar}), 40.8 (N*C*H$_3$), 38.9 (N*C*H$_3$), 0.2 (Si*C*H$_3$) ppm. ^{11}B NMR (161 MHz, CDCl$_3$, 297 K): δ = 25.3 (s) ppm. ^{29}Si NMR (99 MHz, CDCl$_3$, 297 K): δ = –19.2 (s) ppm. Solid-state IR: $\tilde{\nu}$ = 2220 cm^{-1} (C≡C). Elemental analysis for [$C_{21}H_{34}B_2N_4Si_2$] (M_w = 420.25): calcd. C 60.01, H 8.15, N 13.33%;

found C 59.90, H 8.19, N 13.21%. HRMS LIFDI for $[C_{21}H_{34}B_2N_4Si_2]^+ = [M]^+$: calcd. 420.2503; found 420.2501.

Ph^{OMe}N{B(CCSiMe$_3$)(NMe$_2$)}$_2$, 2^{TMS}-Ph^{OMe}

4-Methoxyazidobenzene (16.0 mg, 108 µmol, 1.10 equiv) was added to a solution of **1^{TMS}** (30.0 mg, 98.6 µmol) in 1 mL of benzene. The yellow solution was stirred for 16 h at 80 °C prior to removing all volatiles. The resulting residue was suspended in hexane and filtered. The resulting colourless solution was stored at –30 °C and **2^{TMS}-Ph^{OMe}** was obtained as colourless solid and washed with cold pentane. Drying *in vacuo* yielded **2^{TMS}-Ph^{OMe}** (65.5 mg, 154 µmol, 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 = 7.01 (d, ^{3}J= 8.9 Hz, 2H, Ar–*H*), 6.78 (d, ^{3}J= 8.9 Hz, 2H, Ar–*H*), 3.35 (s, 3H, 2.96 OCH_3), (br s, 6H, NCH_3), 2.48 (br s, 6H, NCH_3), 0.08 (s, 18H, SiCH_3) ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 297 K): δ = 156.4 (OC_q^{Ar}), 142.0 (NC_q^{Ar}), 128.4 (HC_{meta}^{Ar}), 113.7 (HC_{ortho}^{Ar}), 111.0 (SiC_q), 55.0 (OCH$_3$), 40.9 (NCH$_3$), 39.0 (NCH$_3$), 0.0 (SiCH$_3$) ppm. *Note: The resonance for the boron-bound carbon atom was not detected.* ^{11}B NMR (161 MHz, C_6D_6, 297 K): δ = 25.4 (s) ppm. ^{29}Si NMR (99 MHz, C_6D_6, 297 K): δ = –19.7 (s) ppm. *Note: the solid-state IR C≡C band was not detected.* Elemental analysis for $[C_{21}H_{37}B_2N_3OSi_2]$ (M_w = 425.34): calcd. C 59.30, H 8.77, N 9.88%; found C 58.72, H 8.87, N 9.91%. HRMS LIFDI for $[C_{21}H_{37}B_2N_3OSi_2]^+ = [M]^+$: calcd. 425.2656; found 425.2650.

***o*TolN{B(CCSiMe$_3$)(NMe$_2$)}$_2$, 2^{TMS}-*o*Tol**

4-Methylazidobenzene (40.0 mg, 296 µmol, 1.50 equiv) was added to a solution of **1^{TMS}** (60.0 mg, 197 µmol) in 1 mL of benzene. The yellow solution was stirred for 16 h at 80 °C prior to removing all volatiles. The resulting residue was suspended in hexane and filtered. The resulting colourless solution was stored at –30 °C and **2^{TMS}-*o*Tol** was obtained as colourless solid and washed with cold pentane. Drying *in vacuo* yielded **2^{TMS}-*o*Tol** (50.8 mg, 124 µmol, 63% 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 = 7.02 (d, ^{3}J= 8.7 Hz, 2H, Ar–*H*), 6.97 (d, ^{3}J= 8.6 Hz, 2H, Ar–*H*), 2.96 (br s, 6H, NCH_3), 2.48 (br s, 6H, NCH_3), 2.15 (s, 6H, ArCH_3), 0.08 (s, 18H, SiCH_3) ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 297 K): δ = 146.3 (NC_q^{Ar}), 131.9 (CH$_3$$C_q^{Ar}$), 128.9 (H$C_{meta}^{Ar}$), 127.1 (H$C_{ortho}^{Ar}$), 120.4 (B$C_q$), 110.9 (Si$C_q$), 41.0 (N$CH_3$), 39.0 (N$CH_3$), 20.9 ($C_q^{Ar}$$CH_3$), 0.0 (Si$CH_3$) ppm. ^{11}B NMR (161 MHz, C_6D_6, 297 K): δ = 25.4 (s) ppm. ^{29}Si NMR (99 MHz, C_6D_6, 297 K): δ = –19.7 (s) ppm. *Note: the solid-state IR C≡C band was not detected.* Elemental analysis for [$C_{21}H_{37}B_2N_3Si_2$] (M_w = 409.34): calcd. C 61.62, H 9.11, N 10.27%; found C 61.50, H 9.00, N 10.39%. HRMS LIFDI for [$C_{21}H_{37}B_2N_3Si_2$]$^+$ = [M]$^+$: calcd. 409.2707; found 409.2704.

Ph^{CF3}N{B(CCSiMe$_3$)(NMe$_2$)}$_2$, 2^{TMS}-Ph^{CF3}

4-Trifluoromethylazidobenzene (55.4 mg, 296 µmol, 1.50 equiv) was added to a solution of **1^{TMS}** (60.0 mg, 197 µmol) in 1 mL of benzene. The yellow solution was stirred for 16 h at 80 °C prior to removing all volatiles. The resulting residue was suspended in hexane and filtered. The resulting colourless solution was stored at –30 °C and **2^{TMS}-Ph^{CF3}** was obtained as a colourless solid and washed with cold pentane. Drying *in vacuo* yielded **2^{TMS}-Ph^{CF3}** (76.4 mg, 165 µmol, 84% 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, $CDCl_3$, 257 K): δ = 7.38 (d, ^3J= 8.4 Hz, 2H, Ar–*H*), 6.93 (d, ^3J= 8.2 Hz, 2H, Ar–*H*), 2.98 (s, 6H, N*C*H_3), 2.50 (s, 6H, N*C*H_3), 2.15 (s, 6H Ar*C*H_3), 0.00 (s, 18H, Si*C*H_3) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 257 K): δ = 151.5 (NC_q^{Ar}), 125.9 (HC_{ortho}^{Ar}), 124.8 (q, $^1J_{C-F}$= 271 Hz, $C_q^{Ar}CF_3$), 124.6 (q, $^3J_{C-F}$= 3.7 Hz, HC_{meta}^{Ar}), 123.3 (q, $^2J_{C-F}$= 32.2 Hz, $CF_3C_q^{Ar}$), 112.0 (BC_q), 111.4 (SiC_q), 41.0 (N*C*H_3), 39.4 (N*C*H_3), 0.3 (Si*C*H_3) ppm. ^{11}B NMR (161 MHz, $CDCl_3$, 257 K): δ = 24.5 (s) ppm. ^{19}F NMR (471 MHz, $CDCl_3$, 257 K): δ = –61.1 (s) ppm. ^{29}Si NMR (99 MHz, $CDCl_3$, 257 K): δ = –19.0 (s) ppm. *Note: the solid-state IR C≡C band was not detected.* Elemental analysis for [$C_{21}H_{34}B_2F_3N_3Si_2$] ($M_w$ = 463.31): calcd. C 54.44, H 7.40, N 9.07%; found C 54.05, H 7.33, N 9.40%. HRMS LIFDI for [$C_{21}H_{34}B_2F_3N_3Si_2$]$^+$ = [M]$^+$: calcd. 463.2424; found 463.2420.

PhN{B(CCMe)(NMe$_2$)}$_2$, 2^{Me}-Ph

Azidobenzene (95.0 mg, 798 µmol, 3.00 equiv) was added to a solution of **1^{Me}** (50.0 mg, 266 µmol) in 1 mL of benzene. The yellow solution was stirred for 16 h at 80 °C prior to removing all volatiles. The resulting residue was suspended in hexane and filtered. The resulting colourless solution was stored at –30 °C and **2^{Me}-Ph** was obtained as colourless solid and washed with cold pentane. Drying *in vacuo* yielded **2^{Me}-Ph** (66.0 mg, 237 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 (500.1 MHz, CD_2Cl_2): δ = 7.17 (m, 2H, Ar–*H*), 6.94 (m, 1H, Ar–*H*), 6.81 (m, 2H, Ar–*H*), 2.97 (br s, 6H, N*C*H_3), 2.54 (br s, 6H, N*C*H_3), 1.78 (s, 2H, C_q*C*H_3) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2): δ = 148.9 (NC_q^{Ar}), 128.2

(HC^{Ar}_{meta}), 126.0 (HC^{Ar}_{ortho}), 121.9 (HC^{Ar}_{para}), 100.5 (CH_3C_q), 84.5 (BC_q), 40.7 (NCH_3), 39.1 (NCH_3), 4.7 (C_qCH_3) ppm. ^{11}B NMR (128.6 MHz, CD_2Cl_2): δ = 25.6 (s) ppm. Solid-state IR: $\tilde{\nu}$ = 2178 cm^{-1} (C≡C). Elemental analysis for [$C_{16}H_{23}B_2N_3$] (M_w = 279.00): calcd. C 68.88, H 8.31, N 15.06%; found C 68.79, H 8.41, N 15.01%. HRMS ASAP for $[C_{16}H_{24}B_2N_3]^+$ = $[M+H]^+$: calcd. 280.2151; found 280.2147.

oTolN{B(CCMe)(NMe$_2$)}$_2$, 2^{Me}-oTol

1-Azido-2-methylbenzene (46.0 mg, 346 µmol, 1.30 equiv) was added to a solution of **1^{Me}** (50.0 mg, 266 µmol) in 1 mL of benzene. The yellow solution was stirred for 28 h at 80 °C prior to removing all volatiles. The resulting residue was suspended in hexane and filtered. The resulting colourless solution was stored at –30 °C and **2^{Me}-oTol** was obtained as a colourless solid and washed with cold pentane. Drying *in vacuo* yielded **2^{Me}-oTol** (54.0 mg, 184 µmol, 69% yield) as a colourless solid. Colourless single crystals were obtained by slow evaporation of a concentrated hexane solution at –30 °C. ^{1}H NMR (500.1 MHz, CD_2Cl_2): δ = 7.11 (m, 1H, Ar–H), 7.04 (m, 1H, Ar–H), 6.95 (td, ^4J= 1.1 Hz, ^3J= 7.4 Hz, 1H, Ar–H), 6.76 (m, 1H, Ar–H), 2.92 (br s, 6H, NCH_3), 2.52 (br s, 6H, NCH_3), 2.16 (s, 3H, $ArCH_3$), 1.73 (s, 6H, C_qCH_3) ppm. $^{13}C\{^1H\}$ NMR (125.8 MHz, CD_2Cl_2): δ = 148.5 (NC^{Ar}_q), 135.5 ($CH_3C^{Ar}_q$), 130.4 (HC^{Ar}_{meta}), 129.1 (HC^{Ar}_{para}), 126.1 (HC^{Ar}_{meta}), 123.8 (HC^{Ar}_{ortho}), 100.2 (CH_3C_q), 40.8 (NCH_3), 38.8 (NCH_3), 19.0 ($C^{Ar}_qCH_3$), 4.6 (C_qCH_3) ppm. *Note: The boron-bound carbon atom was not detected.* ^{11}B NMR (128.6 MHz, CD_2Cl_2): δ = 25.5 (s) ppm. Solid-state IR: $\tilde{\nu}$ = 2211 cm^{-1}, 2181 cm^{-1} (C≡C). Elemental analysis for [$C_{17}H_{25}B_2N_3$] (M_w = 293.03): calcd. C 69.68, H 8.60, N 14.34%; found C 69.25, H 8.51, N 14.47%. HRMS LIFDI for $[C_{17}H_{25}B_2N_3]^+$ = $[M]^+$: calcd. 293.2229; found 293.2224.

PhN{B(CCH)(NMe$_2$)}$_2$, 2^{H}-Ph

Azidobenzene (120 mg, 1.00 mmol, 2.00 equiv) was added to a solution of **1^{H}** (80.0 mg, 500 µmol) in 1 mL of benzene. The yellow solution was stirred for 8 h at 80 °C prior to removing all volatiles. The resulting residue was suspended in hexane and filtered. The resulting colourless solution was stored at –30 °C and **2^{H}-Ph** was obtained as colourless solid and washed with cold pentane. Drying *in vacuo* yielded **2^{H}-Ph** (104 mg, 415 µmol, 83% yield) as a colourless solid. Colourless single crystals were obtained by slow evaporation of a concentrated hexane solution at –30 °C. ^{1}H NMR (500.1 MHz, C_6D_6): δ = 7.16 (m, 2H, Ar–H), 7.07 (m, 2H, Ar–H), 6.94 (tt, ^4J= 1.2 Hz, ^3J= 7.3 Hz, 1H, Ar–H), 2.88 (br s, 6H, NCH_3), 2.42

(br s, 6H, NCH_3), 2.22 (s, 2H, C_qH) ppm. $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6): δ = 148.4 (NC_q^{Ar}), 128.6 (HC_{ortho}^{Ar}), 128.4 (BC_q), 126.8 (HC_{meta}^{Ar}), 123.0 (HC_{para}^{Ar}), 91.8 (HC_q), 40.6 (NCH_3), 38.9 (NCH_3) ppm. ^{11}B NMR (128.6 MHz, C_6D_6): δ = 25.7 (s) ppm. Solid-state IR: $\tilde{\nu}$ = 2061 cm^{-1} (C≡C). Elemental analysis for [$C_{14}H_{19}B_2N_3$] (M_w = 250.95): calcd. C 67.01, H 7.63, N 16.74%; found C 66.61, H 7.63, N 16.85%. HRMS ASAP for $[C_{14}H_{20}B_2N_3]^+$ = $[M+H]^+$: calcd. 252.1838; found 252.1834.

***o*TolN{B(CCH)(NMe$_2$)}$_2$, 2^H-*o*Tol**

1-Azido-2-methylbenzene (54.0 mg, 403 µmol, 1.30 equiv) was added to a solution of **1^H** (50.0 mg, 313 µmol) in 1 mL of benzene. The yellow solution was stirred for 16 h at 80 °C prior to removing all volatiles. The resulting residue was suspended in hexane and filtered. The resulting colourless solution was stored at –30 °C and **2^H-*o*Tol** was obtained as colourless solid and washed with cold pentane. Drying *in vacuo* yielded **2^H-*o*Tol** (60.0 mg, 228 µmol, 73% yield) as a colourless solid. Colourless single crystals were obtained by slow evaporation of a concentrated hexane solution at –30 °C. ^1H NMR (500.1 MHz, CD_2Cl_2): δ = 7.13 (m, 1H, Ar–*H*), 7.07 (m, 1H, Ar–*H*), 7.00 (td, ^4J= 1.4 Hz, ^3J= 7.4 Hz, 1H, Ar–*H*), 6.81 (m, 1H, Ar–*H*), 2.97 (br s, 6H, NCH_3), 2.56 (br s, 6H, NCH_3), 2.47 (s, 2H, C_q–*H*), 2.18 (s, 3H, ArCH_3) ppm. $^{13}C\{^1H\}$ NMR (125.8 MHz, CD_2Cl_2): δ = 147.6 (NC_q^{Ar}), 135.5 ($CH_3C_q^{Ar}$), 130.6 (HC_{meta}^{Ar}), 129.2 (HC_{para}^{Ar}), 126.4 (HC_{ortho}^{Ar}), 124.5 (HC_{meta}^{Ar}), 90.9 (HC_q), 40.8 (NCH_3), 38.9 (NCH_3), 18.9 ($C_q^{Ar}CH_3$) ppm. *Note: The boron-bound carbon atom was not detected.* ^{11}B NMR (128.6 MHz, CD_2Cl_2): δ = 25.1 (s) ppm. Solid-state IR: $\tilde{\nu}$ = 3279 cm^{-1} (C≡CH), 2065 cm^{-1} (C≡C). Elemental analysis for [$C_{15}H_{21}B_2N_3$] (M_w = 264.97): calcd. C 67.99, H 7.99, N 15.86%; found C 68.05, H 7.78, N 16.07%.HRMS ASAP for $[C_{15}H_{22}B_2N_3]^+$ = $[M+H]^+$: calcd. 266.1994; found 266.1989.

{B(C(H)C(Me)BMes$_2$)(NMe$_2$)}$_2$, 4^{Me}

Dimesitylborane (80.0 mg, 318 µmol, 3.00 equiv) was added to a solution of **1^{Me}** (20.0 mg, 106 µmol) in 1 mL of benzene. The colourless suspension was stirred for 1 h at ambient temperature prior to removing all volatiles. The resulting residue was suspended in hexane and filtered. The resulting colourless solution was stored at –30 °C and **4^{Me}** was obtained as colourless solid and washed with cold pentane. Drying *in vacuo* yielded **4^{Me}** (61.0 mg, 88.0 µmol, 83% yield) as a colourless solid. Colourless single crystals were obtained by slow evaporation of a concentrated hexane solution at –30 °C. ^1H NMR (500.1 MHz, CD_2Cl_2): δ = 6.73 (s, 8H, Ar–*H*), 6.42 (s, 2H, C*H*), 2.83 (s, 6H, NCH_3), 2.73 (s, 6H, NCH_3), 2.25 (s, 12H, ArCH_3), 2.04 (s, 24H, ArCH_3), 1.69 (d, ^4J = 1.0 Hz, 6H, CCH_3) ppm. $^{13}C\{^1H\}$ NMR (125.8 MHz, CD_2Cl_2): δ = 157.6 (BB*C*H), 155.1 (Mes_2B*C*Me), 142.9 (BC^{Ar}_{q}), 140.5 ($CH_3C^{Ar}_{ortho}$), 137.9 ($CH_3C^{Ar}_{para}$), 128.2 (HC^{Ar}_{meta}), 44.4 (NCH_3), 41.3 (NCH_3), 22.8 ($C^{Ar}_{ortho}CH_3$), 21.2 ($C^{Ar}_{para}CH_3$), 20.6 (C_qCH_3) ppm. ^{11}B NMR (128.6 MHz, CD_2Cl_2): δ = 74.5 (br s), 48.2 (br s) ppm. Solid-state IR: $\tilde{\nu}$ = 1605 cm^{-1} (C=C). HRMS ASAP for $[C_{46}H_{64}B_4N_{22}]^+$ = $[M]^+$: calcd. 688.5436; found 688.5438.

{B(C(H)C(H)BMes$_2$)(NMe$_2$)}$_2$, 4^{H}

Dimesitylborane (93.0 mg, 564 µmol, 3.00 equiv) was added to a solution of **1^{H}** (30.0 mg, 188 µmol) in 1 mL of benzene. The colourless suspension was stirred for 1 h at ambient temperature prior to removing all volatiles. The resulting residue was suspended in hexane and filtered. The resulting colourless solution was stored at –30 °C and **4^{H}** was obtained as a colourless solid and washed with cold pentane. Drying *in vacuo* yielded **4^{H}** (97.0 mg, 147 µmol, 78% yield) as a colourless solid. Colourless single crystals were obtained by slow evaporation of a concentrated hexane solution at –30 °C. ^1H NMR (500.1 MHz, C_6D_6): δ = 7.59 (d, ^3J = 20.5 Hz, 2H, C*H*), 7.53 (d, ^3J = 20.5 Hz, 2H, C*H*), 6.91 (s, 8H, Ar–*H*), 2.74 (s, 6H, NCH_3), 2.63 (s, 6H, NCH_3), 2.44 (s, 24H, ArCH_3), 2.29 (s, 12H, ArCH_3) ppm. $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6): δ = 163.0 (BB*C*H), 156.1 (Mes_2B*C*H), 143.0 (BC^{Ar}_{q}), 140.8 ($CH_3C^{Ar}_{ortho}$), 138.3 ($CH_3C^{Ar}_{para}$), 128.8 (HC^{Ar}_{meta}), 44.8 (NCH_3), 39.6 (NCH_3), 23.8 ($C^{Ar}_{ortho}CH_3$), 21.3 ($C^{Ar}_{para}CH_3$) ppm. ^{11}B NMR (128.6 MHz, C_6D_6): δ = 71.9 (br s), 47.2 (br s) ppm. Solid-state IR: $\tilde{\nu}$ = 1606 cm^{-1} (C=C). HRMS ASAP for $[C_{44}H_{60}B_4N_2]^+$ = $[M]^+$: calcd. 660.5123; found 660.5133.

(I*i*Pr)BH(*n*Pr)(NMe$_2$), 6^{Me}

A catalytic amount of Pd/C 10 wt% (5.0 mg, 4.7 µmol, 2.9 mol%) was added to a solution of **1^{Me}** (30 mg, 0.16 mmol) in 1 mL of diethyl ether. The argon atmosphere was exchanged against a hydrogen atmosphere *via* three freeze-pump-thaw cycles. The colourless suspension was stirred for 15 min at ambient temperature. The volatile parts (Et_2O + **5^{Me}**) were condensed to a new vessel and a solution of I*i*Pr (24 mg, 0.16 mmol) in 1 mL of diethyl ether was added. The pale-yellow solution was stirred for 30 min at ambient temperature, prior to removing all volatiles. The resulting residue was suspended in hexane and filtered. The resulting colourless solution was stored at –30 °C and **6^{Me}** was obtained as colourless solid and washed with cold pentane. Drying *in vacuo* yielded **6^{Me}** (17 mg, 67 µmol, 42% yield) as a colourless solid. Colourless single crystals were obtained by slow evaporation of a concentrated hexane solution at –30 °C. ^{1}H NMR (500.1 MHz, C_6D_6): δ = 6.30 (s, 2H, N*CH*), 6.15 (s, 2H, CH_3*CH*), 3.39 (m, 1H, B*H*), 2.61 (s, 6H, NCH_3), 1.35 (m, 1H, BCH_2), 1.07 (t, ^3J = 7.7 Hz, 3H, CH_2CH_3), 1.01 (m, 12H, CHCH_3) 0.81 (m, 1H, BCH_2) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 174.9 (BC_q), 114.5 (N*C*H), 47.5 (CH_3*C*H), 47.4 (NCH_3), 31.7 (br s, BCH_2,), 24.0 (CHCH_3), 23.4 (CHCH_3), 22.8 (CH_3CH_2), 19.9 (CH_2CH_3) ppm. ^{11}B NMR (128.6 MHz, C_6D_6): δ = –4.1 (d, $^1J_{B\text{-}H}$ = 82.3 Hz) ppm. Solid-state IR: $\tilde{\nu}$ = 2054 cm^{-1} (B–H).

(I*i*Pr)BH(Et)(NMe$_2$), 6^H

A catalytic amount of Pd/C 10 wt% (5.0 mg, 4.7 µmol, 3.6 mol%) was added to a solution of **1^H** (20 mg, 0.13 mmol) in 1 mL of diethyl ether. The argon atmosphere was exchanged against a hydrogen atmosphere *via* three freeze-pump-thaw cycles. The colourless suspension was stirred for 15 min at ambient temperature. The volatile parts (Et_2O + **5^H**) were condensed to a new vessel and a solution of I*i*Pr (19 mg, 0.13 mmol) in 1 mL of diethyl ether was added. The pale-yellow solution was stirred for 30 min at ambient temperature, prior to removing all volatiles. The resulting residue was suspended in hexane and filtered. The resulting colourless solution was stored at –30 °C and **6^H** was obtained as a colourless solid and washed with cold pentane. Drying *in vacuo* yielded **6^H** (14 mg, 56 µmol, 45% yield) as a colourless solid. Colourless single crystals were obtained by slow evaporation of a concentrated hexane solution at –30 °C. ^{1}H NMR (500.1 MHz, C_6D_6): δ = 6.19 (s, 2H, N*CH*), 6.03 (s, 2H, CH_3*CH*), 2.69 (t, ^3J = 5.4 Hz, 1H, B*H*), 1.70 (m, 1H, BCH_2), 1.53 (m, 1H, BCH_2), 1.39 (t, ^3J = 7.2 Hz, 3H, CH_2CH_3), 1.26 (s, 3H, NCH_3), 1.24 (s, 3H, NCH_3), 1.12 (d, ^3J = 6.7 Hz, 12H, CHCH_3) 1.02 (m, 2H, CH_3CH_2) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 170.9 (BC_q), 115.3 (N*C*H), 48.4 (CH_3*C*H), 46.7 (NCH_3), 23.4 (CHCH_3), 22.7 (CHCH_3), 14.7 (q, $^1J_{B\text{-}C}$ = 45.4 Hz, BCH_2,), 13.8 (CH_2CH_3) ppm. ^{11}B NMR (128.6 MHz, C_6D_6): δ = –6.3 (d, $^1J_{B\text{-}H}$ = 85.8 Hz) ppm. Solid-state IR: $\tilde{\nu}$ = 2121 cm^{-1} (B–H). HRMS ASAP for $[C_{13}H_{29}BN_3]^+$ = $[M+H]^+$: calcd. 238.2449; found 238.2447.

BI(CCMe)(NMe$_2$), 7^{Me}-I

Iodine (40.6 mg, 160 µmol) was added to a solution of **1^{Me}** (30.0 mg, 160 µmol) in 1 mL of C_6D_6. The pink solution was stirred for 5 min at ambient temperature. Due to its low boiling point and slow decomposition, **7^{Me}-I** was characterised *in situ*. ^{1}H NMR (500.1 MHz, C_6D_6): δ = 2.65 (s, 3H, NCH_3), 2.60 (s, 3H, NCH_3), 1.47 (s, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 109.5 (BC_q), 87.0 (CH_3C_q), 44.3 (NCH_3), 41.4 (NCH_3), 4.8 (C_qCH_3) ppm. *Note: The* *boron-bound carbon atom was not detected.* ^{11}B NMR (128.6 MHz, C_6D_6): δ = 19.9 (s) ppm. Solid-state IR: $\tilde{\nu}$ = 2197 cm^{-1} (C≡C). *Note: Due to its low boiling point and decomposition, characterization via HRMS was not possible.*

BI(C_2I_2Me)(NMe_2), 8^{Me}-I

Iodine (120 mg, 480 µmol, 3.00 equiv) was added to a solution of **1^{Me}** (30.0 mg, 160 µmol) in 1 mL of benzene. The pink solution was stirred for 36 h at ambient temperature prior to removing all volatiles. The resulting residue was suspended in hexane and filtered. Removing all volatiles yielded **8^{Me}-I** (35.0 mg, 104 µmol, 65% yield) as a pale yellow liquid. ^{1}H NMR (500.1 MHz, C_6D_6): δ = 2.58 (s, 3H, C*H*$_3$), 2.32 (s, 3H, NC*H*$_3$), 2.21 (s, 3H, NC*H*$_3$) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 104.2 (B*C*$_q$), 97.3 (CH$_3$*C*$_q$), 44.5 (N*C*H$_3$), 39.3 (N*C*H$_3$), 37.9 (C$_q$*C*H$_3$) ppm. ^{11}B NMR (128.6 MHz, C_6D_6): δ = 28.9 (s) ppm. Solid-state IR: $\tilde{\nu}$ = 1625 cm^{-1} (C=C). HRMS ASAP for $[C_5H_{10}BI_3N]^+$ = $[M+H]^+$: calcd. 475.8035; found 475.8023.

BBr(CCMe)(NMe_2), 7^{Me}-Br

A solution of bromine (0.5 M, 320 µL, 160 µmol) in C_6D_6 was added to a solution of **1^{Me}** (30.0 mg, 160 µmol) in 1 mL of C_6D_6. The pale-yellow solution was stirred for 5 min at ambient temperature. Due to its low boiling point and slow decomposition, **7^{Me}-Br** was characterised *in situ*. ^{1}H NMR (500.1 MHz, C_6D_6): δ = 2.63 (s, 3H, NC*H*$_3$), 2.53 (s, 3H, NC*H*$_3$), 1.48 (s, 3H, C$_q$C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 106.6 (B*C*$_q$), 83.4 (CH$_3$*C*$_q$), 41.3 (N*C*H$_3$), 40.3 (N*C*H$_3$), 4.6 (C$_q$*C*H$_3$) ppm. ^{11}B NMR (128.6 MHz, C_6D_6): δ = 25.1 (s) ppm. Solid-state IR: $\tilde{\nu}$ = 2199 cm^{-1} (C≡C). *Note: Due to its low boiling point and decomposition, characterisation via HRMS was not possible.*

BBr(C_2Br_2Me)(NMe_2), 8^{Me}-Br

A solution of bromine (0.5 M, 960 µL, 480 µmol, 3.00 equiv.) in benzene was added to a solution of **1^{Me}** (30.0 mg, 160 µmol) in 1 mL of benzene. The red solution was stirred for 3 h at ambient temperature prior to removing all volatiles. The resulting residue was suspended in hexane and filtered. Removing all volatiles yielded **8^{Me}-Br** (35.0 mg, 106 µmol, 66% yield) as a pale yellow liquid. The ^{11}B NMR spectrum also shows the presence of ca. 3% of the dimeric species **[8^{Me}-Br]$_2$**. ^{1}H NMR (500.1 MHz, C_6D_6): δ = 2.50 (s, 3H, NC*H*$_3$), 2.38 (s, 3H, NC*H*$_3$), 2.06 (s, 3H, C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 122.4 (CH$_3$*C*$_q$), 117.9 (B*C*$_q$), 40.5 (N*C*H$_3$), 39.7 (N*C*H$_3$), 26.9 (C$_q$*C*H$_3$) ppm. ^{11}B NMR (128.6 MHz, C_6D_6): δ = 31.3 (s, monomer), 0.9 (s, dimer) ppm. Solid-state IR: $\tilde{\nu}$ = 1636 cm^{-1} (C=C). HRMS LIFDI for $[C_5H_{10}BBr_3N]^+$ = $[M+H]^+$: calcd. 333.8430; found 333.8426.

BI(CCH)(NMe₂), 7ᴴ-I

Iodine (32.0 mg, 125 µmol) was added to a solution of **1^H** (20.0 mg, 125 µmol) in 1 mL of C_6D_6. The pink solution was stirred for 5 min at ambient temperature. Due to its low boiling point and slow decomposition, **7^H-I** was characterised *in situ*. ^{1}H NMR (500.1 MHz, C_6D_6): δ = 2.80 (s, 1H, C*H*), 2.52 (s, 3H, N*CH*$_3$), 2.48 (s, 3H, N*CH*$_3$) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 98.7 (B*C*$_q$), 82.9 (C$_q$*C*H), 44.2 (N*C*H$_3$), 41.5 (N*C*H$_3$) ppm. ^{11}B NMR (128.6 MHz, C_6D_6): δ = 19.7 (s) ppm. Solid-state IR: $\tilde{\nu}$ = 3287 cm^{-1} (C≡CH), 2069 cm^{-1} (C≡C). *Note: Due to its low boiling point and decomposition, characterisation via HRMS was not possible.*

$BI(C_2I_2H)(NMe_2)$, 8^H-I

Iodine (95.0 mg, 375 µmol, 3.00 equiv) was added to a solution of **1^H** (20.0 mg, 125 µmol) in 1 mL of benzene. The pink solution was stirred for 12 h at ambient temperature prior to removing all volatiles. The resulting residue was suspended in hexane and filtered. Removing all volatiles yielded **8^H-I** (42.0 mg, 91.3 µmol, 78% yield) as a pale yellow liquid. ^{1}H NMR (500.1 MHz, C_6D_6): δ = 6.51 (s, 1H, C*H*), 2.50 (s, 3H, N*CH*$_3$), 2.25 (s, 3H, N*CH*$_3$) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 104.6 (B*C*$_q$), 82.9 (C$_q$*C*H), 44.4 (N*C*H$_3$), 39.4 (N*C*H$_3$) ppm. ^{11}B NMR (128.6 MHz, C_6D_6): δ = 29.2 (s) ppm. Solid-state IR: $\tilde{\nu}$ = 1583 cm^{-1} (C=C). HRMS LIFDI for $[C_4H_7BI_3N]^+$ = $[M]^+$: calcd. 460.7800; found 460.7790.

$BBr(CCH)(NMe_2)$, 7^H-Br

A solution of bromine (0.5 M, 250 µL, 125 µmol) in C_6D_6 was added to a solution of **1^H** (20.0 mg, 125 µmol) in 1 mL of C_6D_6. The pale-yellow solution was stirred for 5 min at ambient temperature. Due to its low boiling point and slow decomposition, **7^H-Br** was characterised *in situ*. ^{1}H NMR (500.1 MHz, C_6D_6): δ = 2.58 (s, 1H, C*H*), 2.49 (s, 3H, N*CH*$_3$), 2.40 (s, 3H, N*CH*$_3$) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 96.4 (C$_q$*C*H), 41.3 (N*C*H$_3$), 40.2 (N*C*H$_3$) ppm. *Note: The boron-bound carbon atom was not detected.* ^{11}B NMR (128.6 MHz, C_6D_6): δ = 24.8 (s) ppm. Solid-state IR: $\tilde{\nu}$ = 3289 cm^{-1} (C≡CH), 2073 cm^{-1} (C≡C). *Note: Due to its low boiling point and decomposition, characterisation via HRMS was not possible.*

$BBr(C_2Br_2H)(NMe_2)$, 8^H-Br

A solution of bromine (0.5 M, 750 µL, 375 µmol, 3.00 equiv) in benzene was added to a solution of $B_2(CCH)_2(NMe_2)_2$ (20.0 mg, 125 µmol) in 1 mL of benzene. The red solution was stirred for 1 h at ambient temperature prior to removing all volatiles. The resulting residue was suspended in hexane and filtered. Removing all volatiles yielded **8^H-Br** (27.0 mg, 83.8 µmol, 67% yield) as a pale yellow liquid, as an *E*/*Z* mixture in a 3:1 molar ratio. The ^{11}B NMR spectrum also shows the presence of ca. 10% of the dimeric species **[8^H-Br]$_2$**. **(*E*)-8^H-Br** (75%): ^1H NMR (500.1 MHz, C_6D_6): δ = 6.21 (s, 1H, C*H*), 2.43 (s, 3H, NC*H*$_3$), 2.29 (s, 3H, NC*H*$_3$) ppm. $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6): δ = 118.5 (B*C*$_q$), 109.2 (C_q*C*H), 40.5 (N*C*H$_3$), 39.8 (N*C*H$_3$) ppm. **(*Z*)-8^H-Br** (25%): ^1H NMR (500.1 MHz, C_6D_6): δ = 6.43 (s, 1H, C*H*), 2.39 (s, 3H, NC*H*$_3$), 2.12 (s, 3H, NC*H*$_3$) ppm. $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6): δ = 122.2 (B*C*$_q$), 115.4 (C_q*C*H), 41.3 (N*C*H$_3$), 40.1 (N*C*H$_3$) ppm. ^{11}B NMR (128.6 MHz, C_6D_6): δ = 31.3 (s, monomer) 0.8 (s, dimer) ppm. Solid-state IR: $\tilde{\nu}$ = 1600 cm^{-1} (C=C). HRMS LIFDI for $[C_4H_8BBr_3N]^+$ = $[M+H]^+$: calcd. 319.8274; found 319.8269.

NMR spectra of isolated compounds

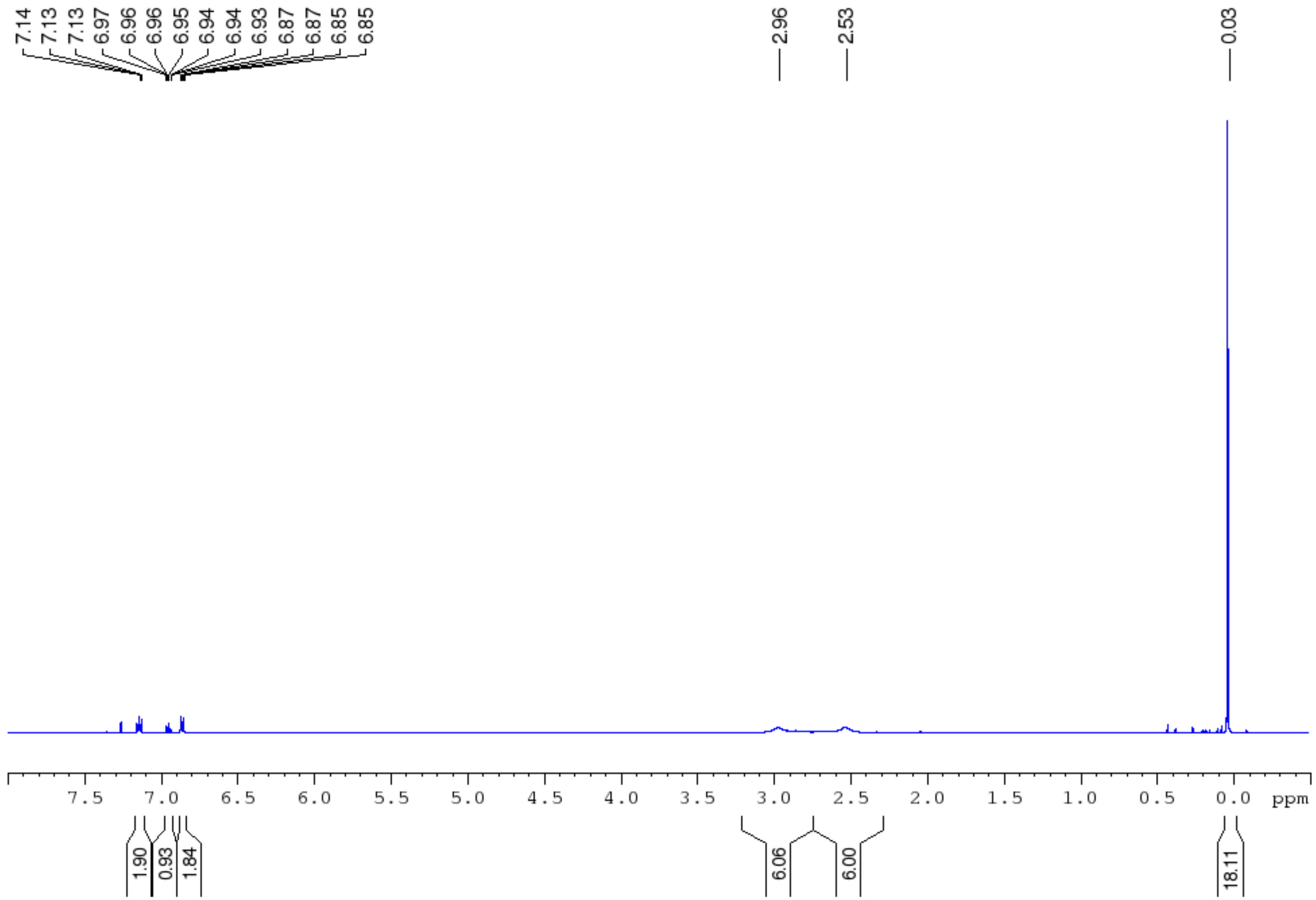

Figure S1. ^{1}H NMR spectrum of **2^{TMS}-Ph** in $CDCl_3$.

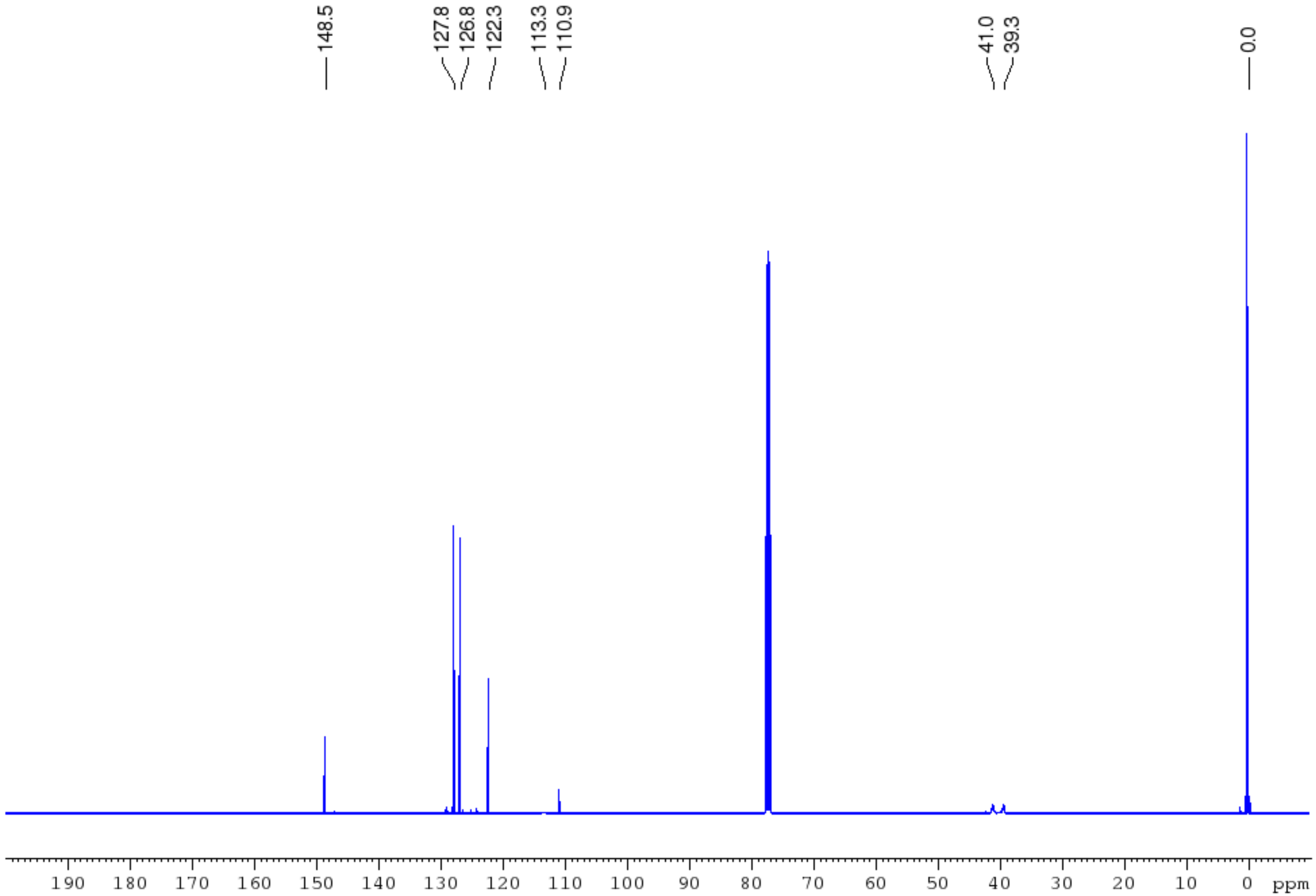

Figure S2. $^{13}C\{^1H\}$ NMR spectrum of **2^{TMS}-Ph** in $CDCl_3$.

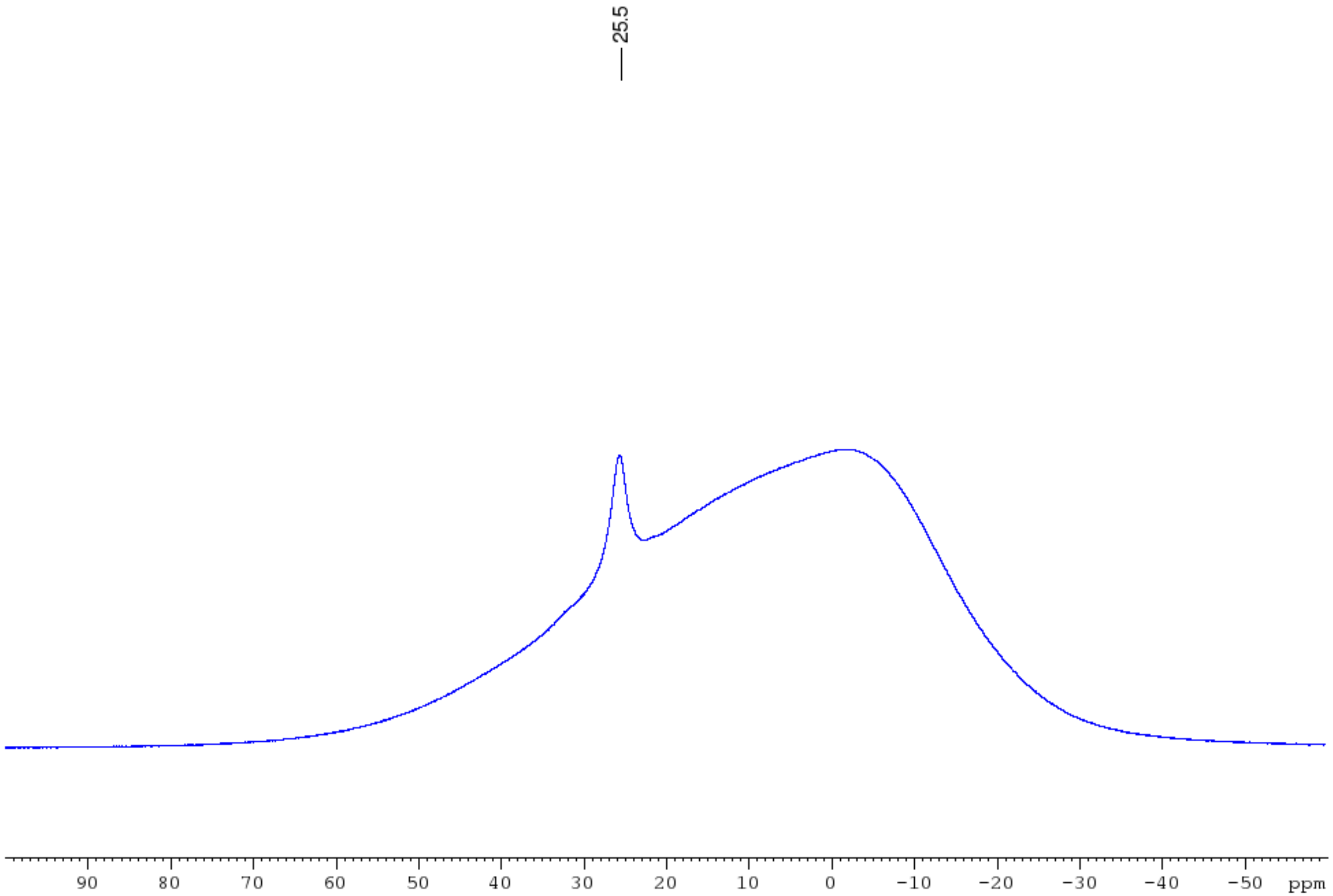

Figure S3. ^{11}B NMR spectrum of **2^{TMS}-Ph** in $CDCl_3$.

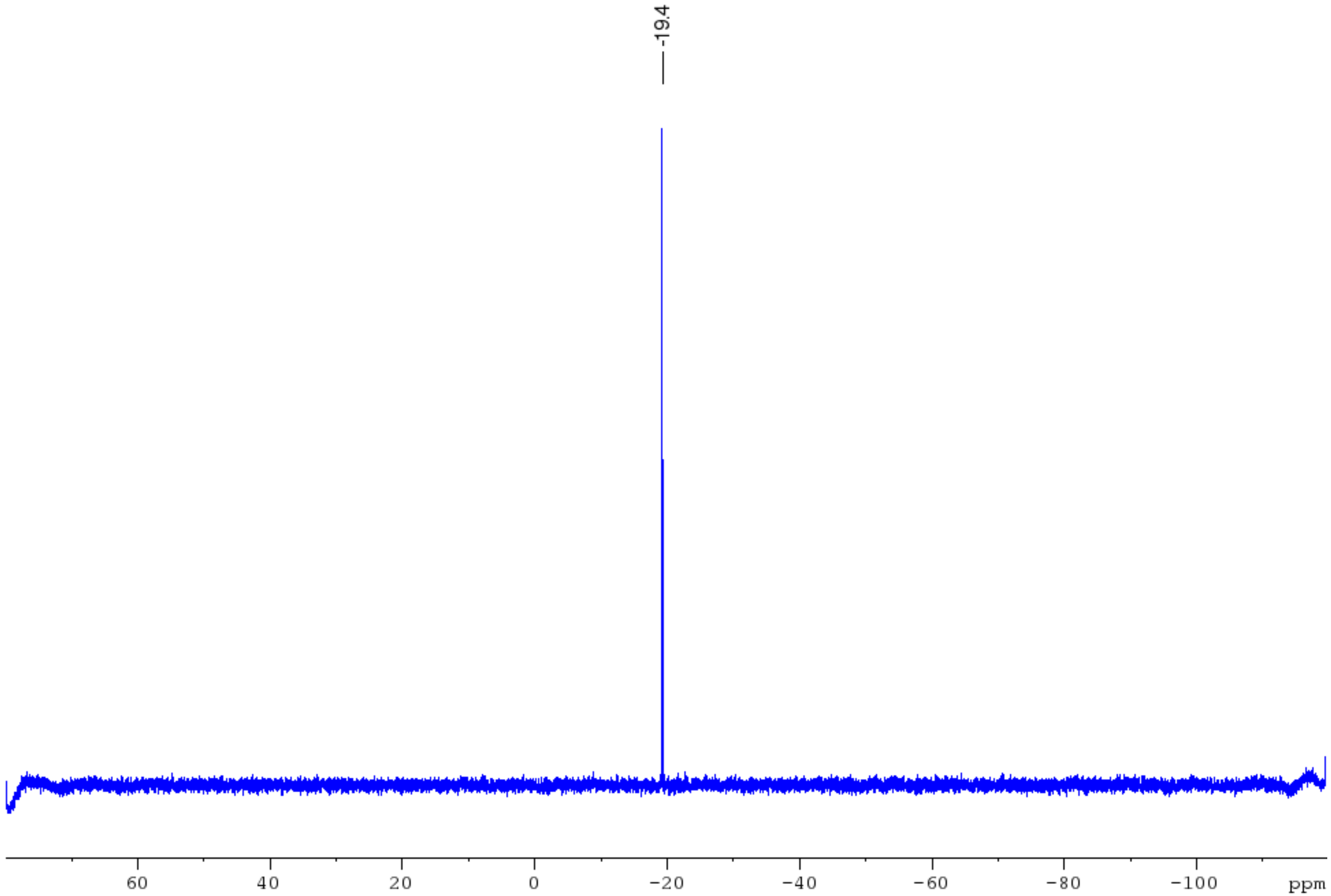

Figure S4. ^{29}Si NMR spectrum of **2^{TMS}-Ph** in $CDCl_3$.

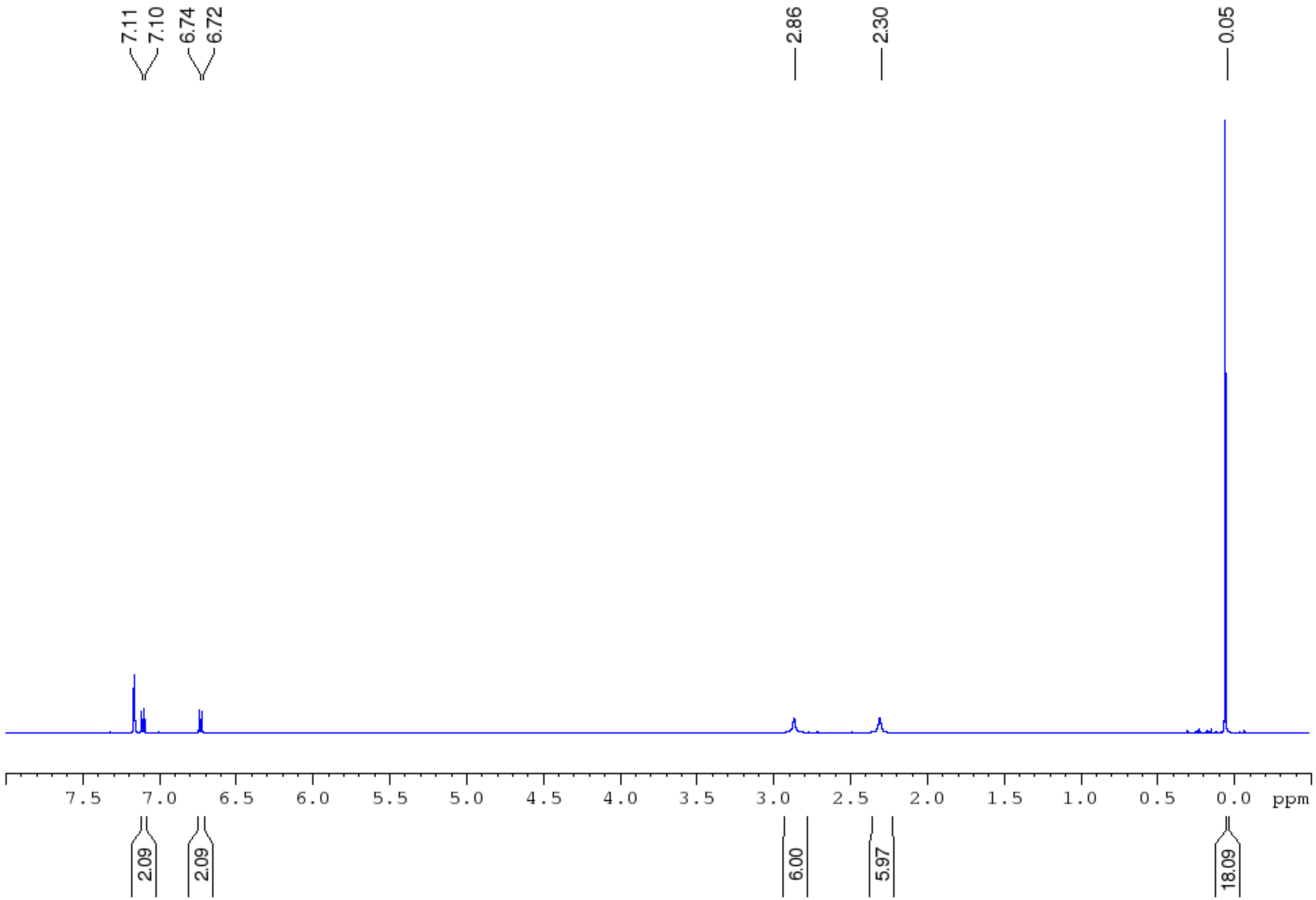

Figure S5. ¹H NMR spectrum of $\mathbf{2^{TMS}}$**-Ph**$^{\mathbf{CN}}$ in $CDCl_3$.

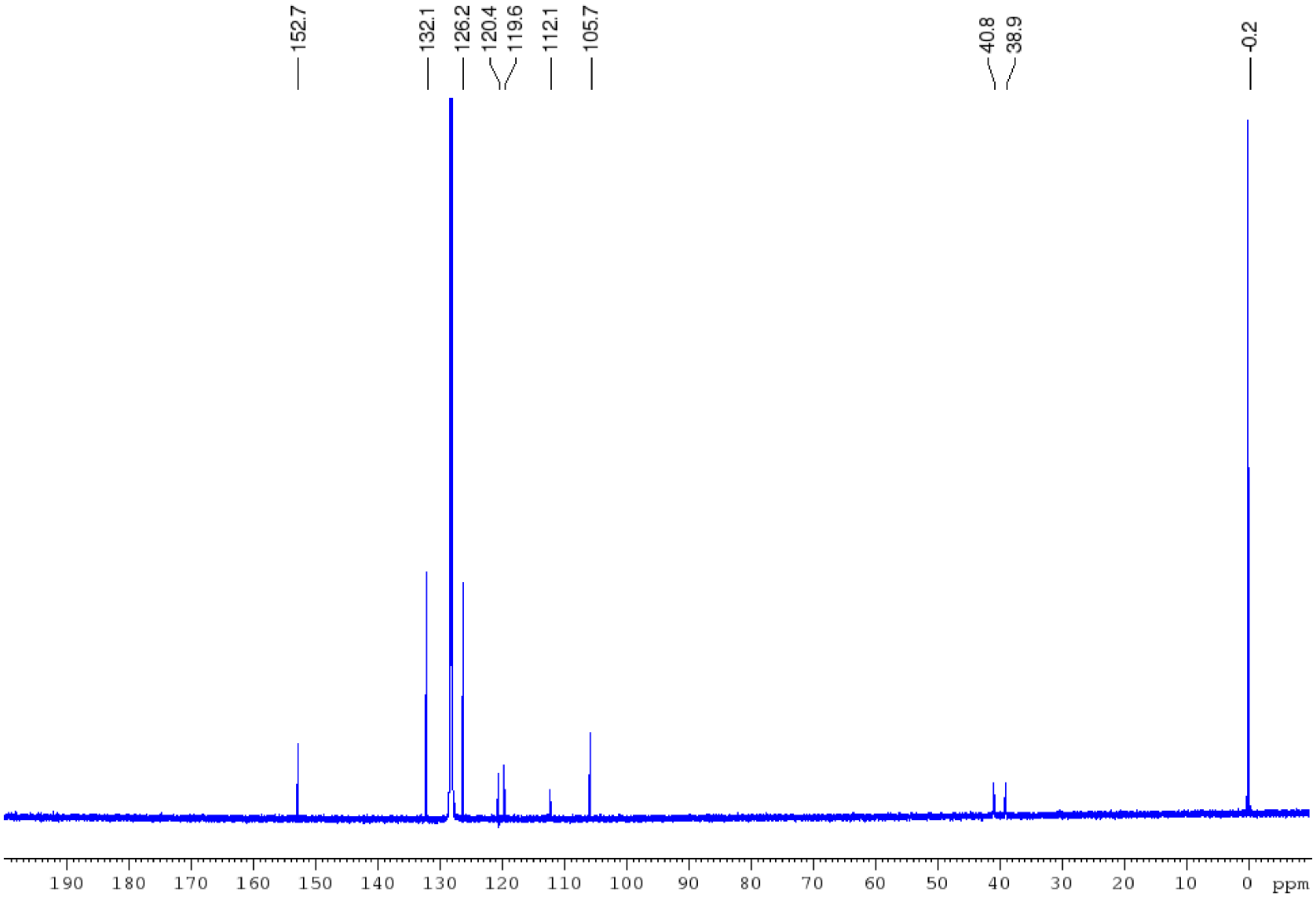

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of $\mathbf{2^{TMS}}$**-Ph**$^{\mathbf{CN}}$ in $CDCl_3$.

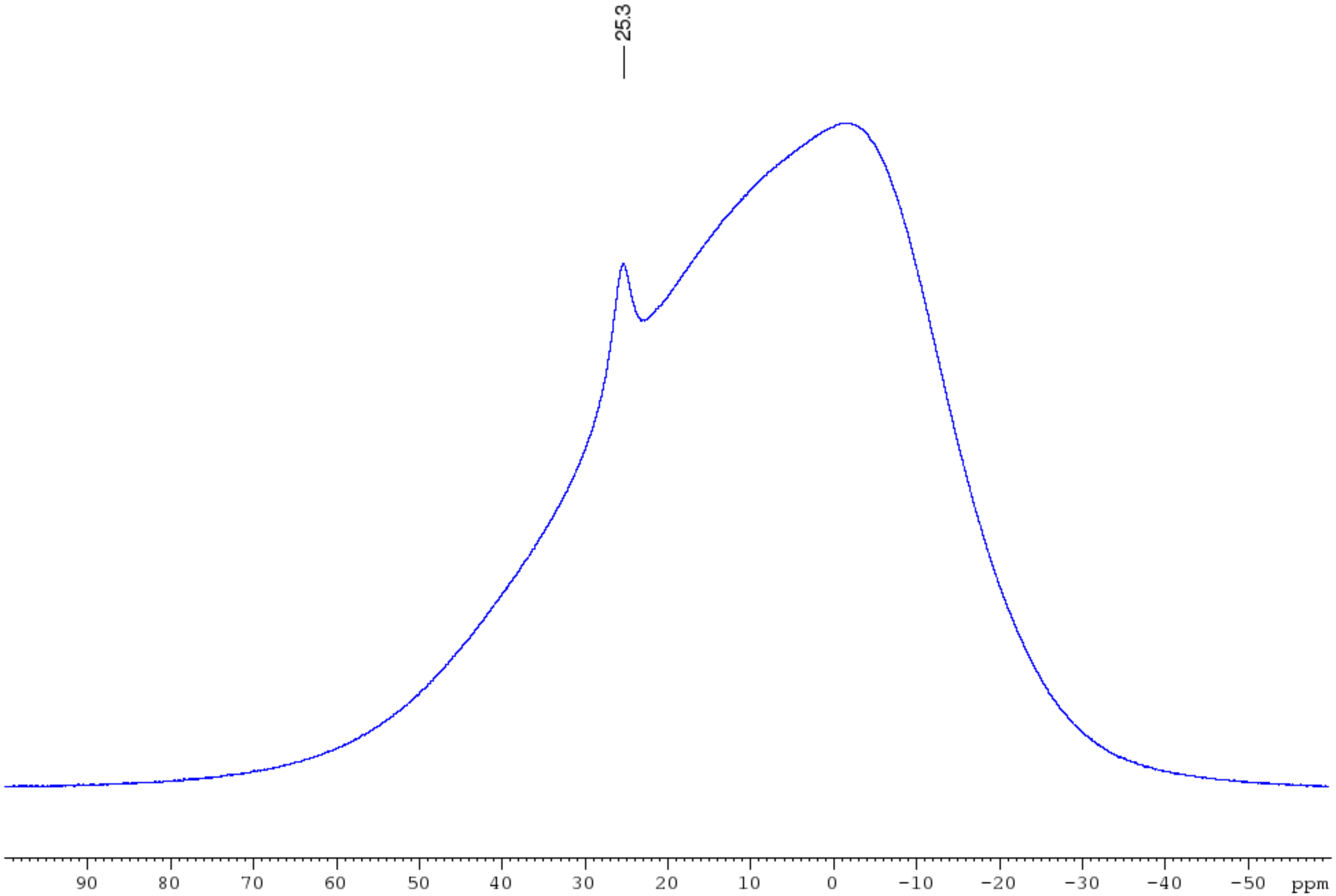

Figure S7. ^{11}B NMR spectrum of $\mathbf{2^{TMS}}$-$\mathbf{Ph^{CN}}$ in $CDCl_3$.

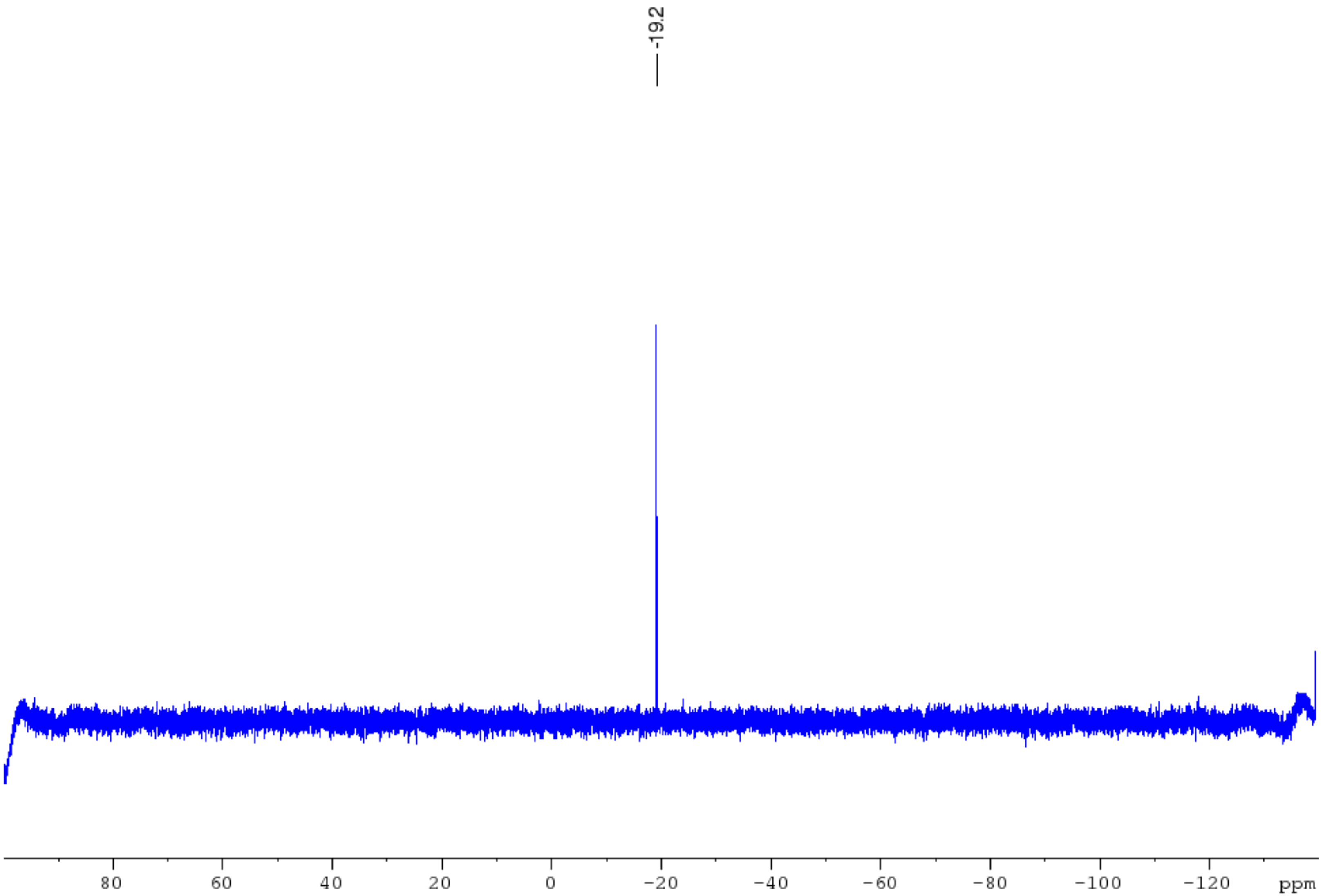

Figure S8. ^{29}Si NMR spectrum of $\mathbf{2^{TMS}\text{-}Ph^{CN}}$ in $CDCl_3$.

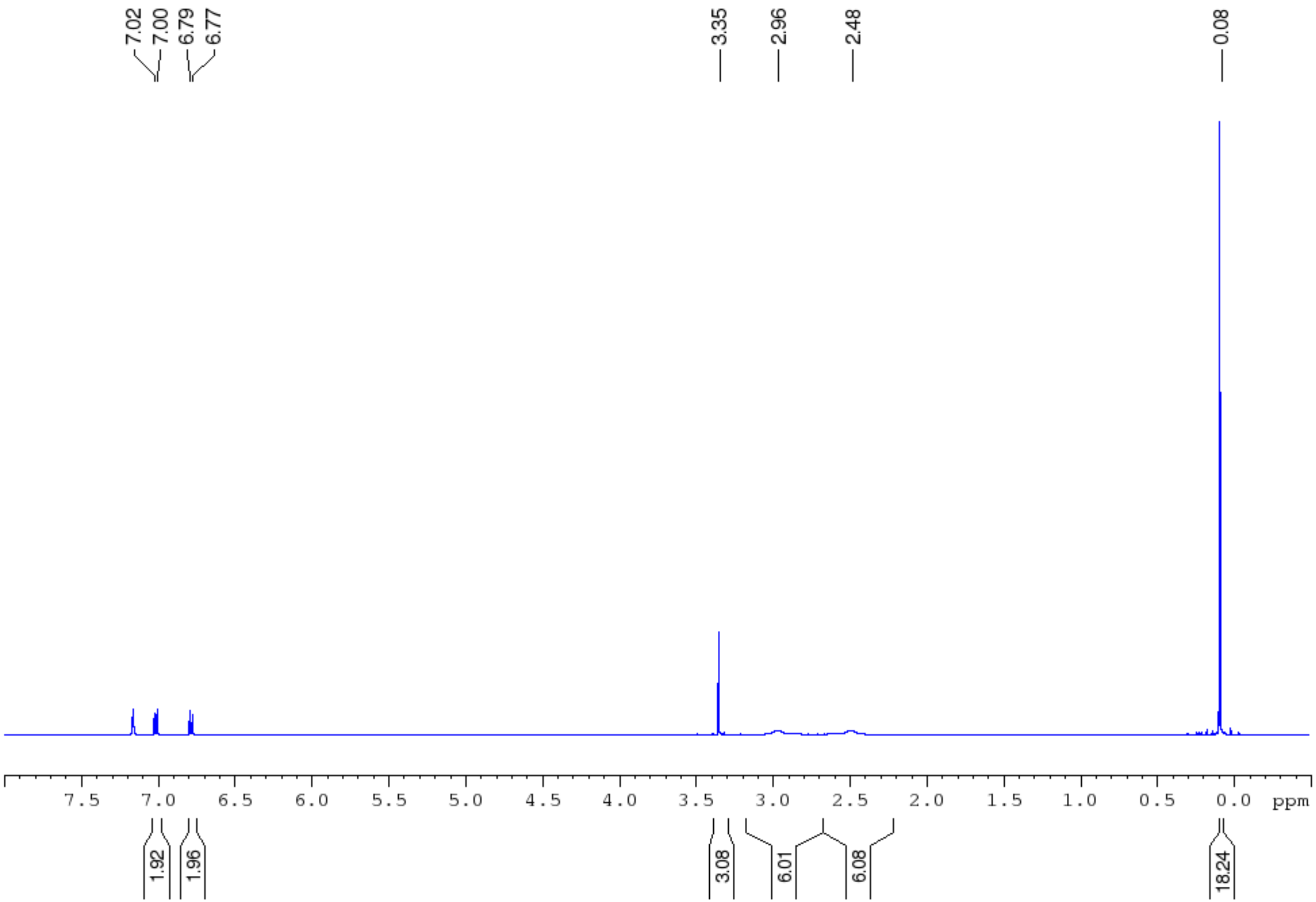

Figure S9. [1]H NMR spectrum of $\mathbf{2^{TMS}}$**-Ph**$^{\mathbf{OMe}}$ in C_6D_6.

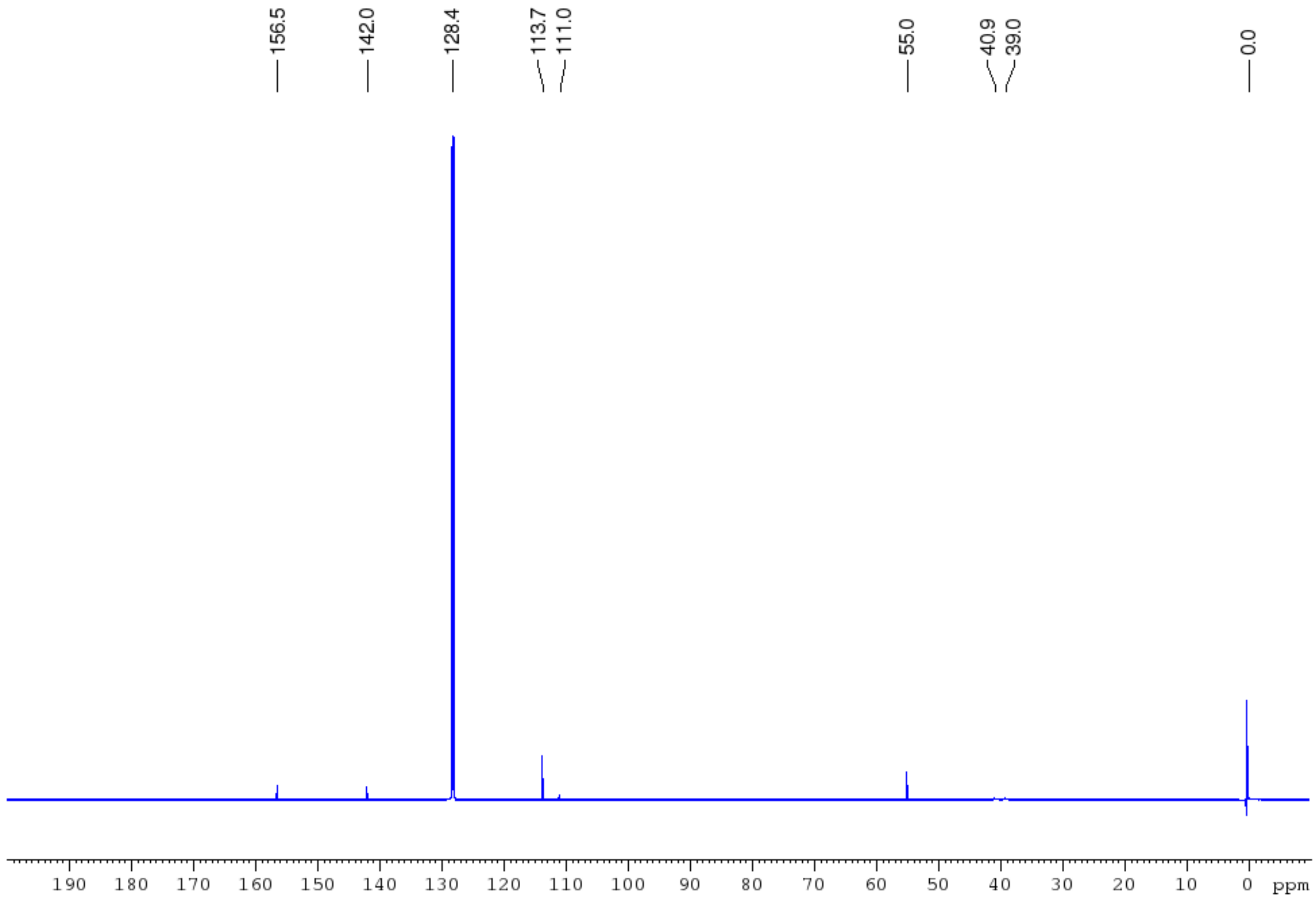

Figure S10. $^{13}C\{^{1}H\}$ spectrum of **2^{TMS}-Ph^{OMe}** in C_6D_6.

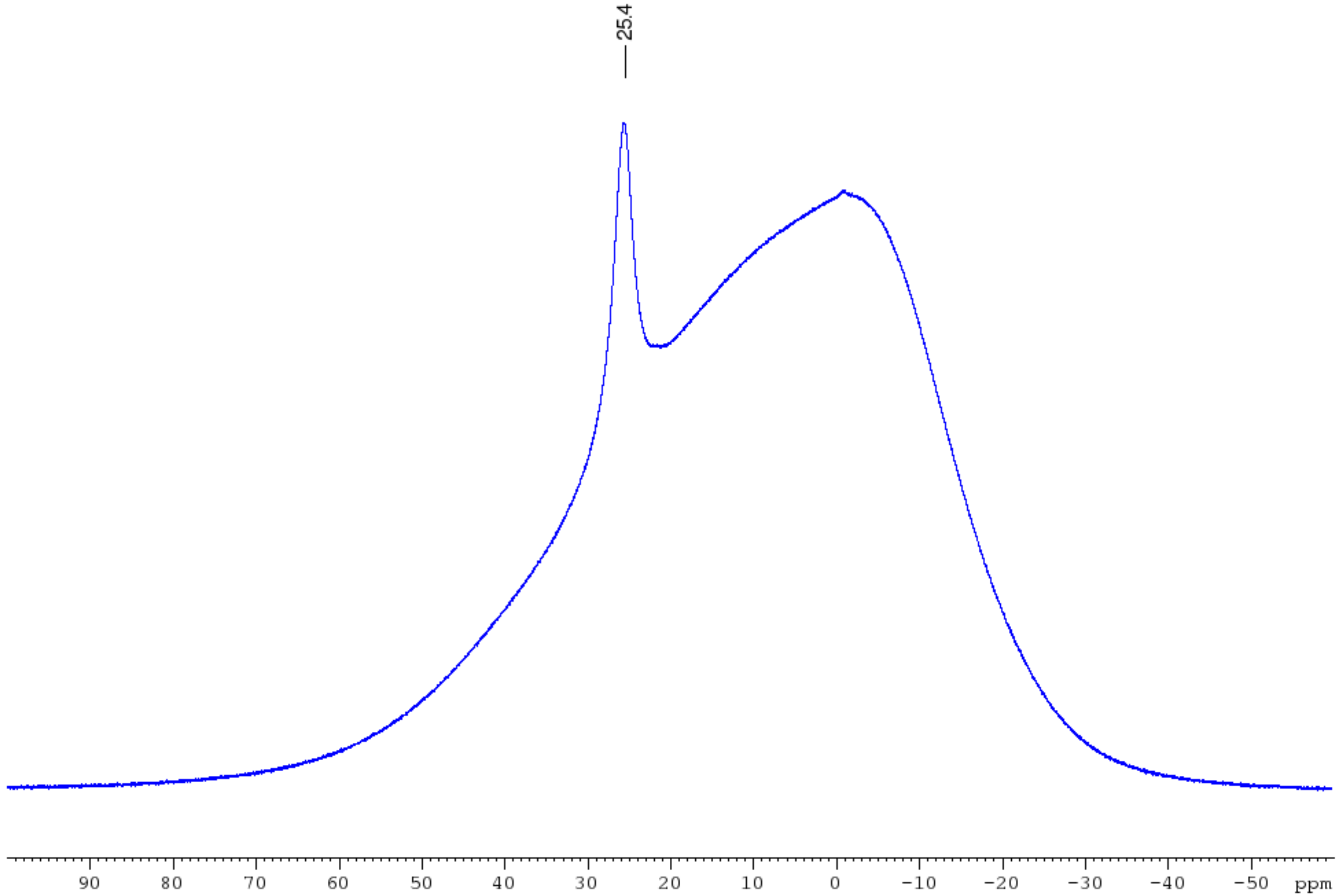

Figure S11. ^{11}B spectrum of $\mathbf{2^{TMS}}$**-Ph**$^{\mathbf{OMe}}$ in C_6D_6.

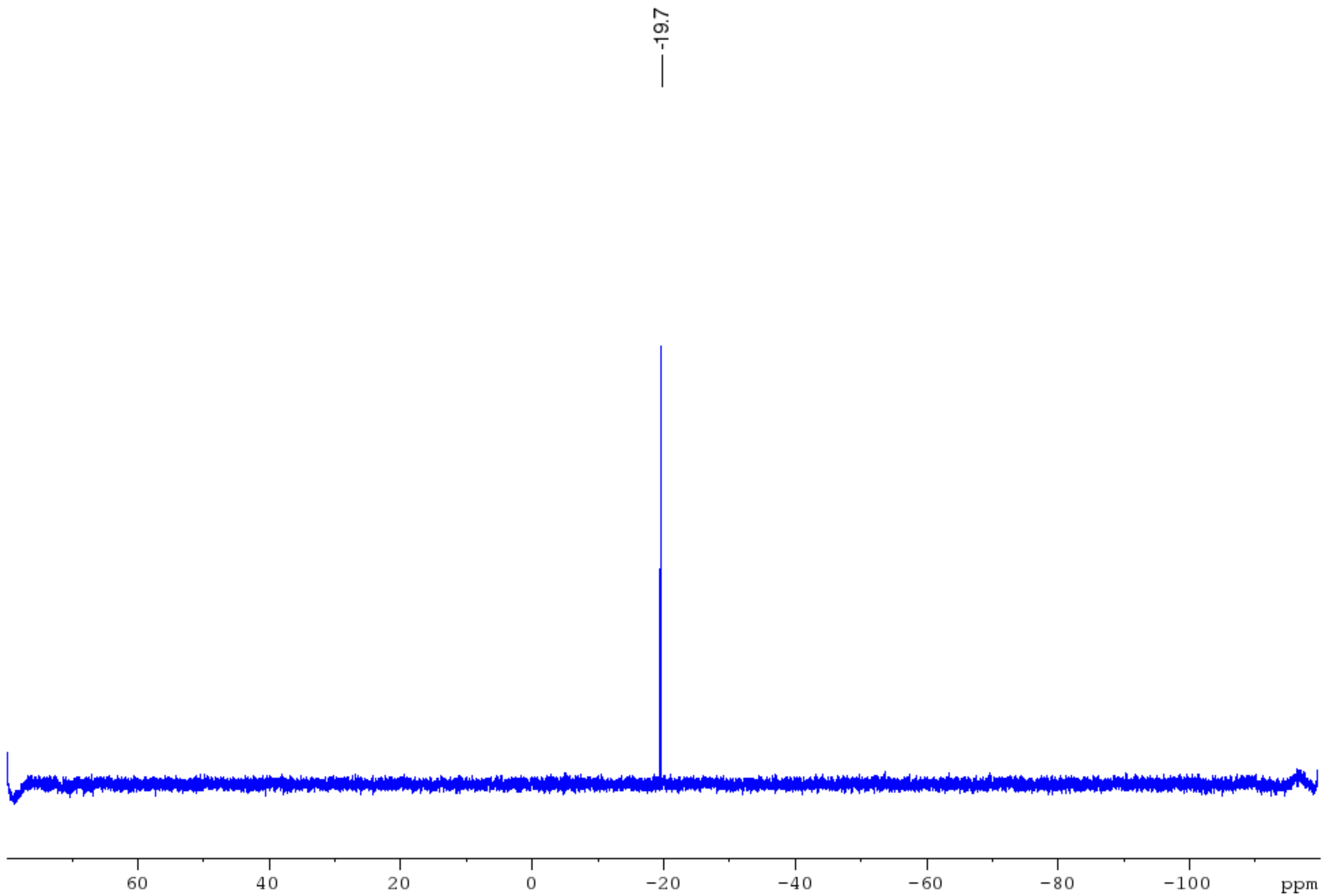

Figure S12. ^{29}Si NMR spectrum of **2^{TMS}-Ph^{OMe}** in C_6D_6.

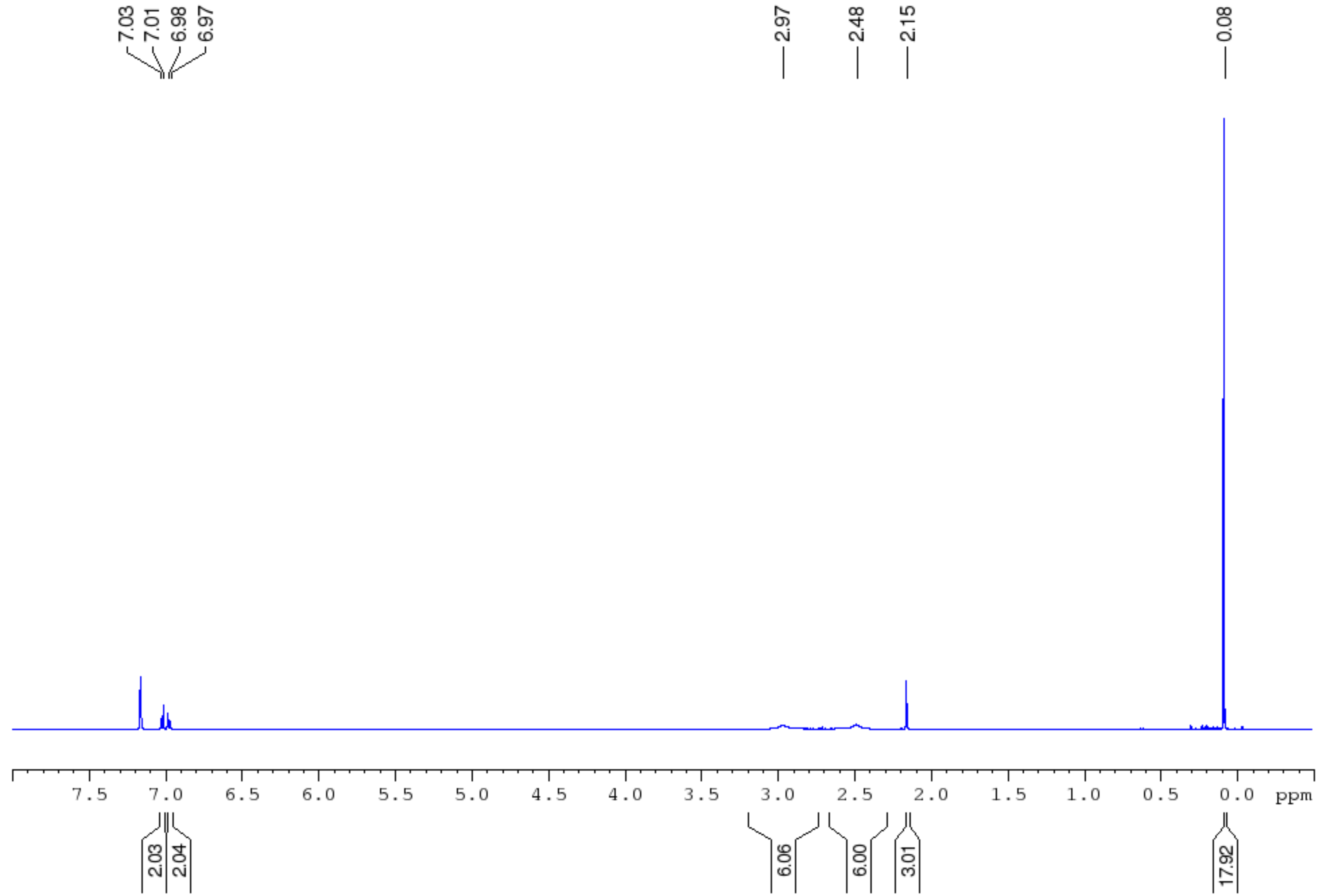

Figure S13. [1]H NMR spectrum of **2^{TMS}-*p*Tol** in C_6D_6.

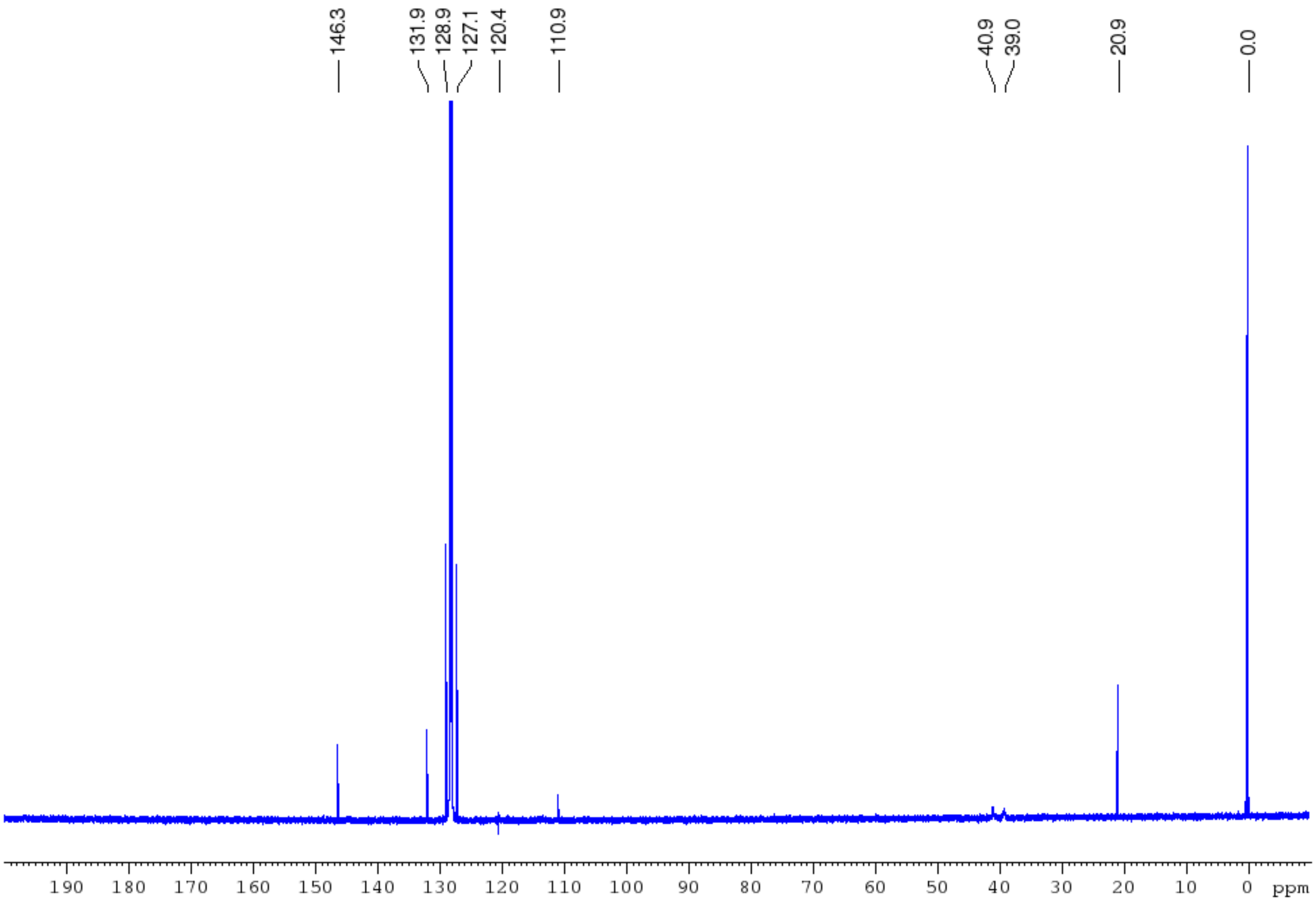

Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of $\mathbf{2^{TMS}}$-***p*Tol** in C_6D_6.

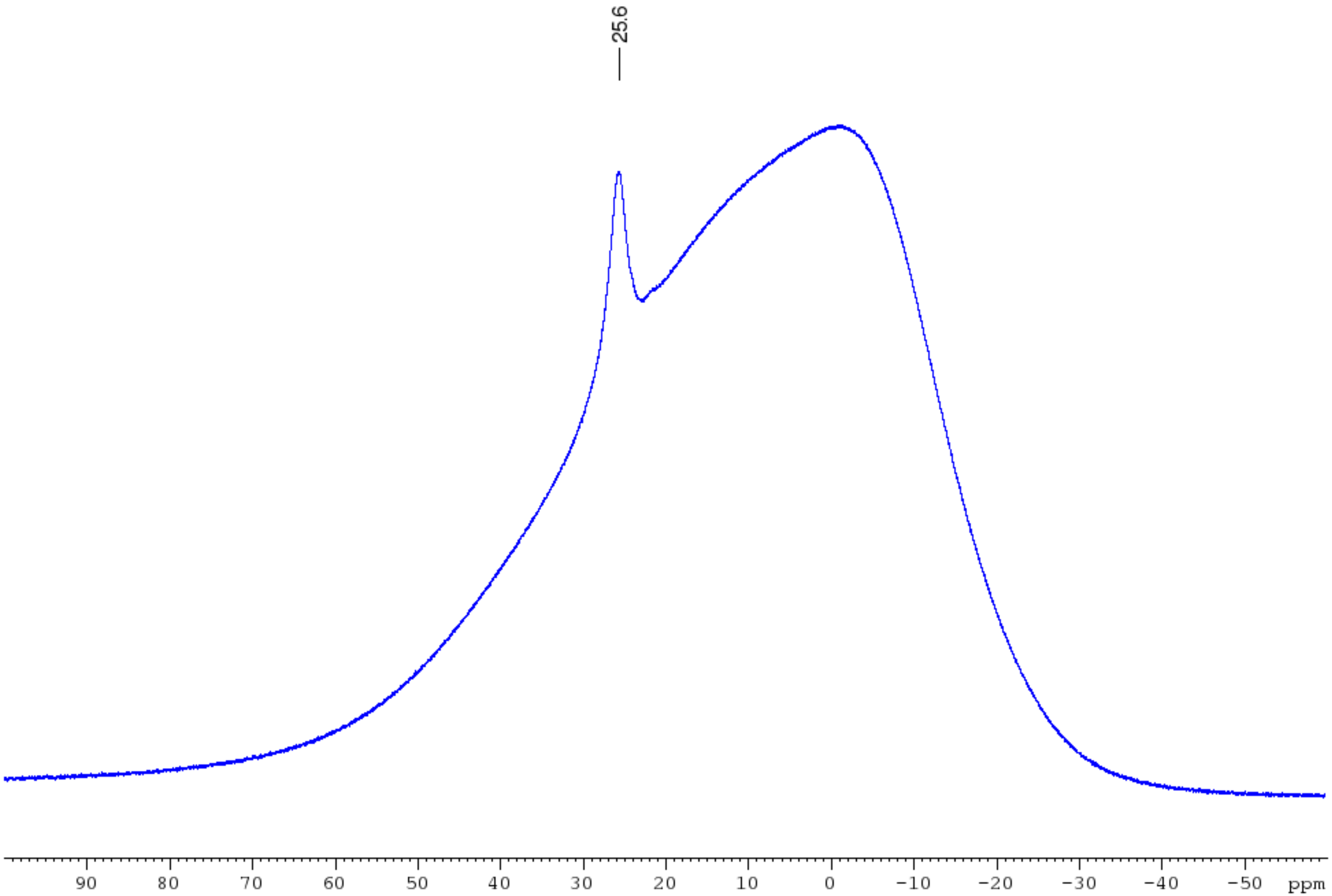

Figure S15. ^{11}B NMR spectrum of **2^{TMS}-*p*Tol** in C_6D_6.

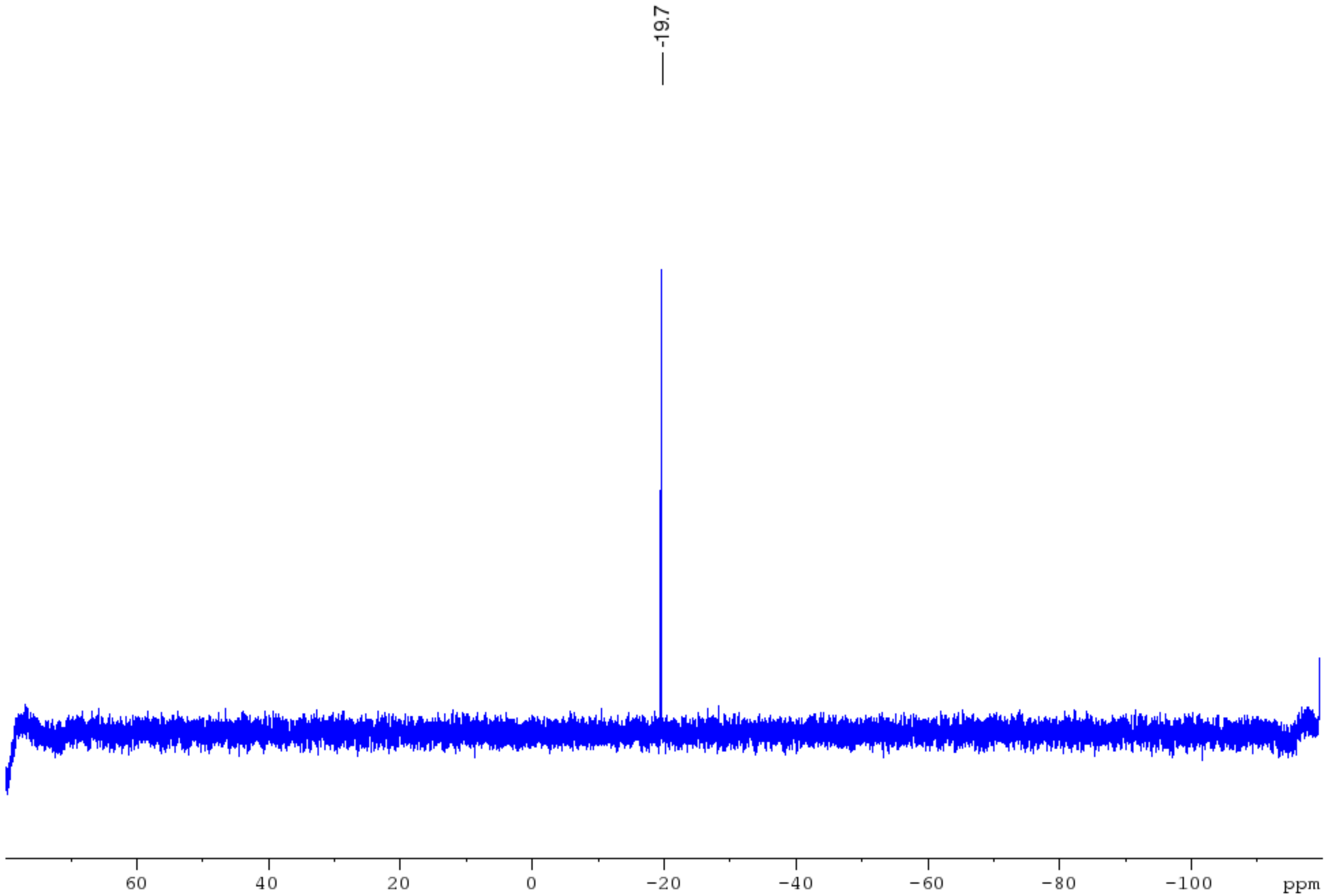

Figure S16. ^{29}Si NMR spectrum of **2^{TMS}-*p*Tol** in C_6D_6.

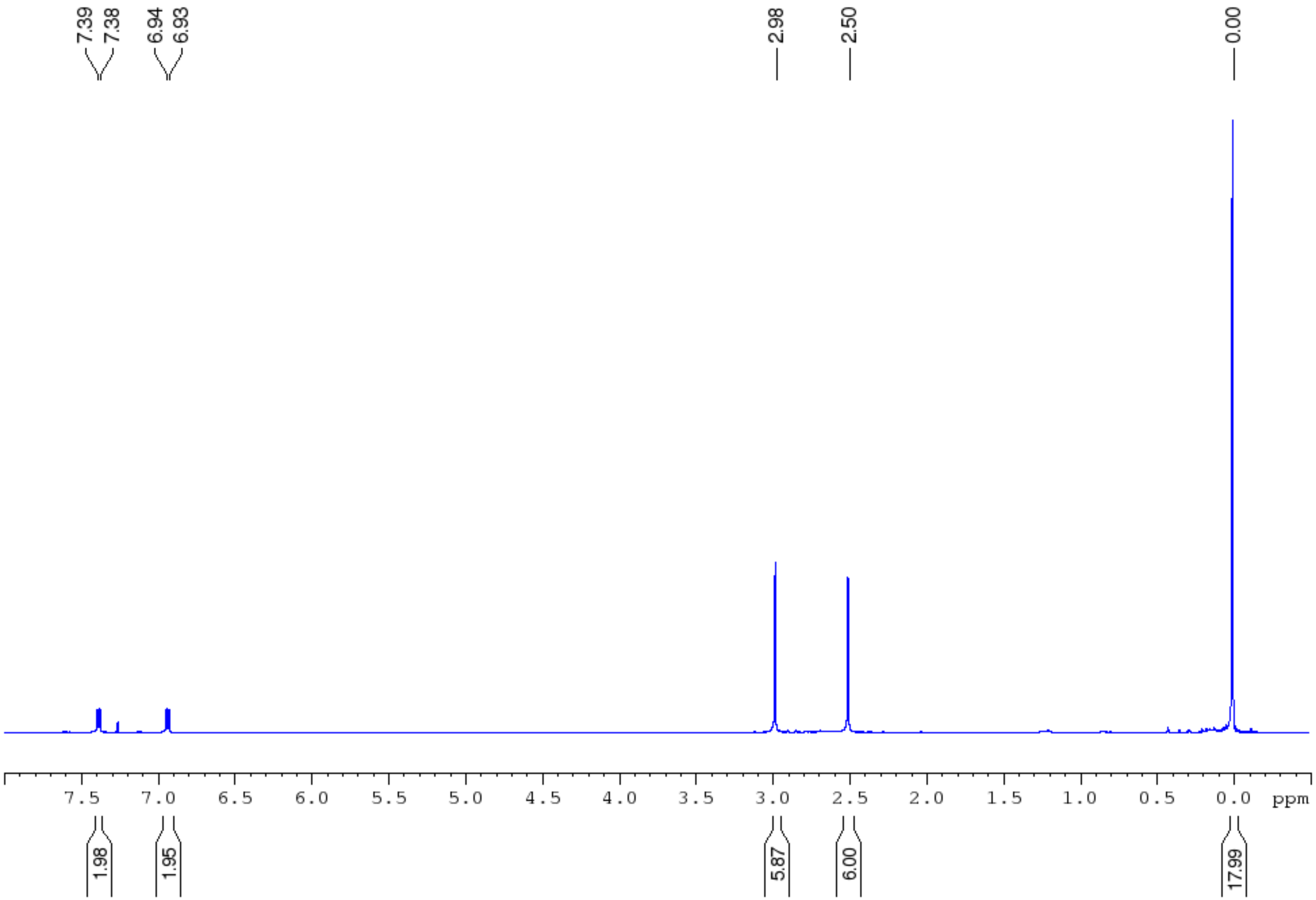

Figure S17. ^{1}H NMR spectrum of $\mathbf{2^{TMS}}$**-**$\mathbf{Ph^{CF3}}$ in $CDCl_3$.

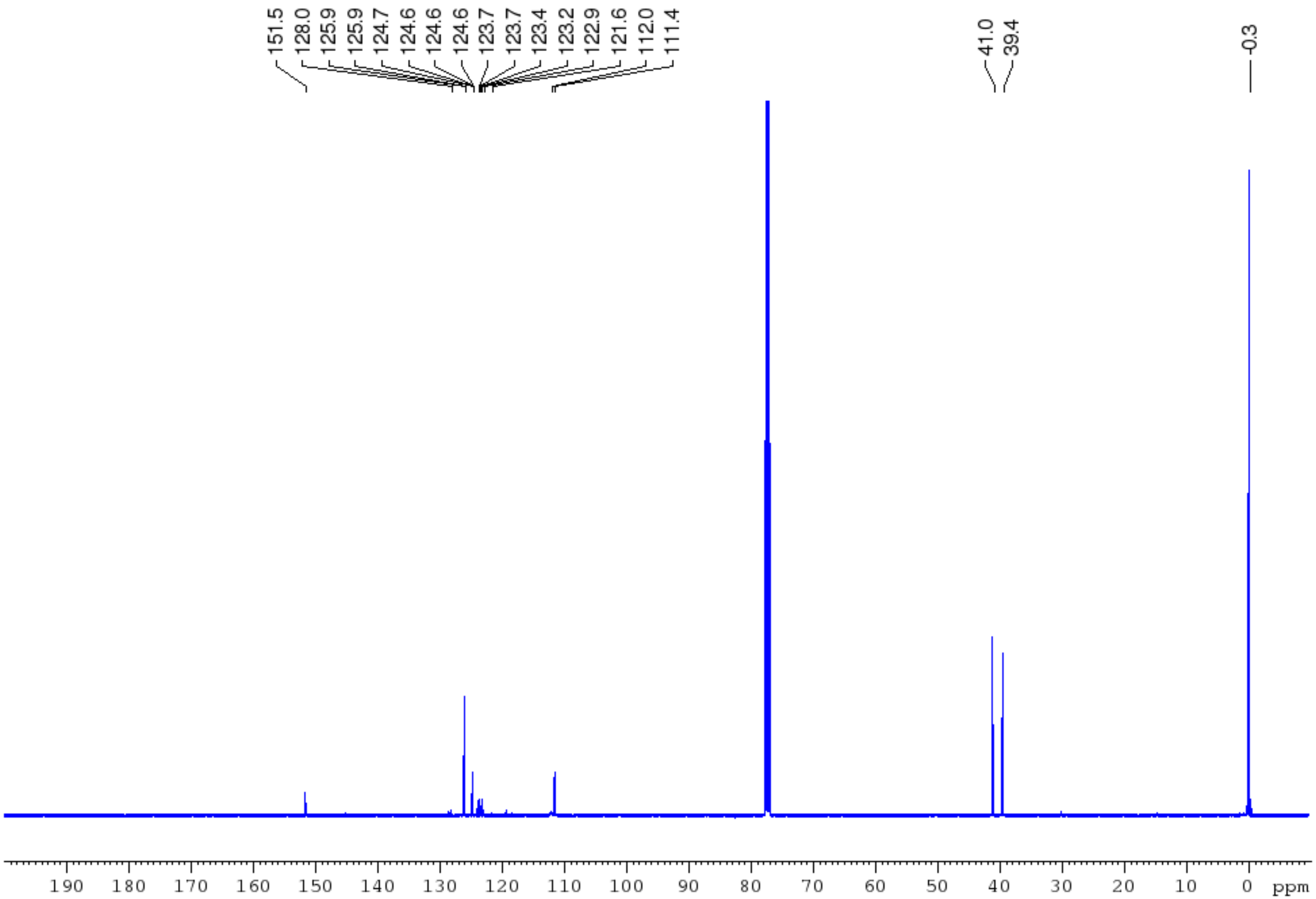

Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of **2^{TMS}-Ph^{CF3}** in $CDCl_3$.

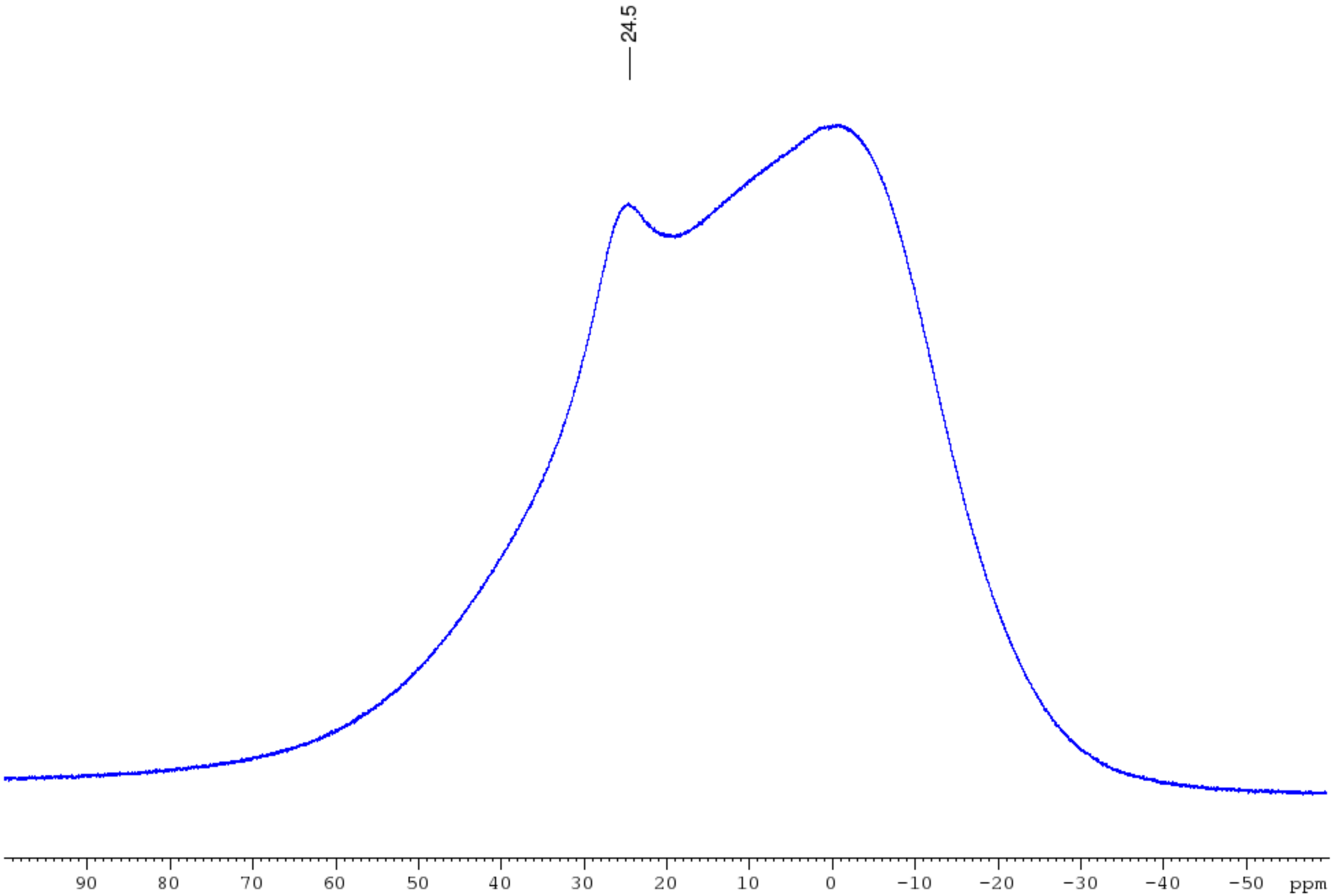

Figure S19. ^{11}B NMR spectrum of $\mathbf{2^{TMS}}$**-Ph**$^{\mathbf{CF3}}$ in $CDCl_3$.

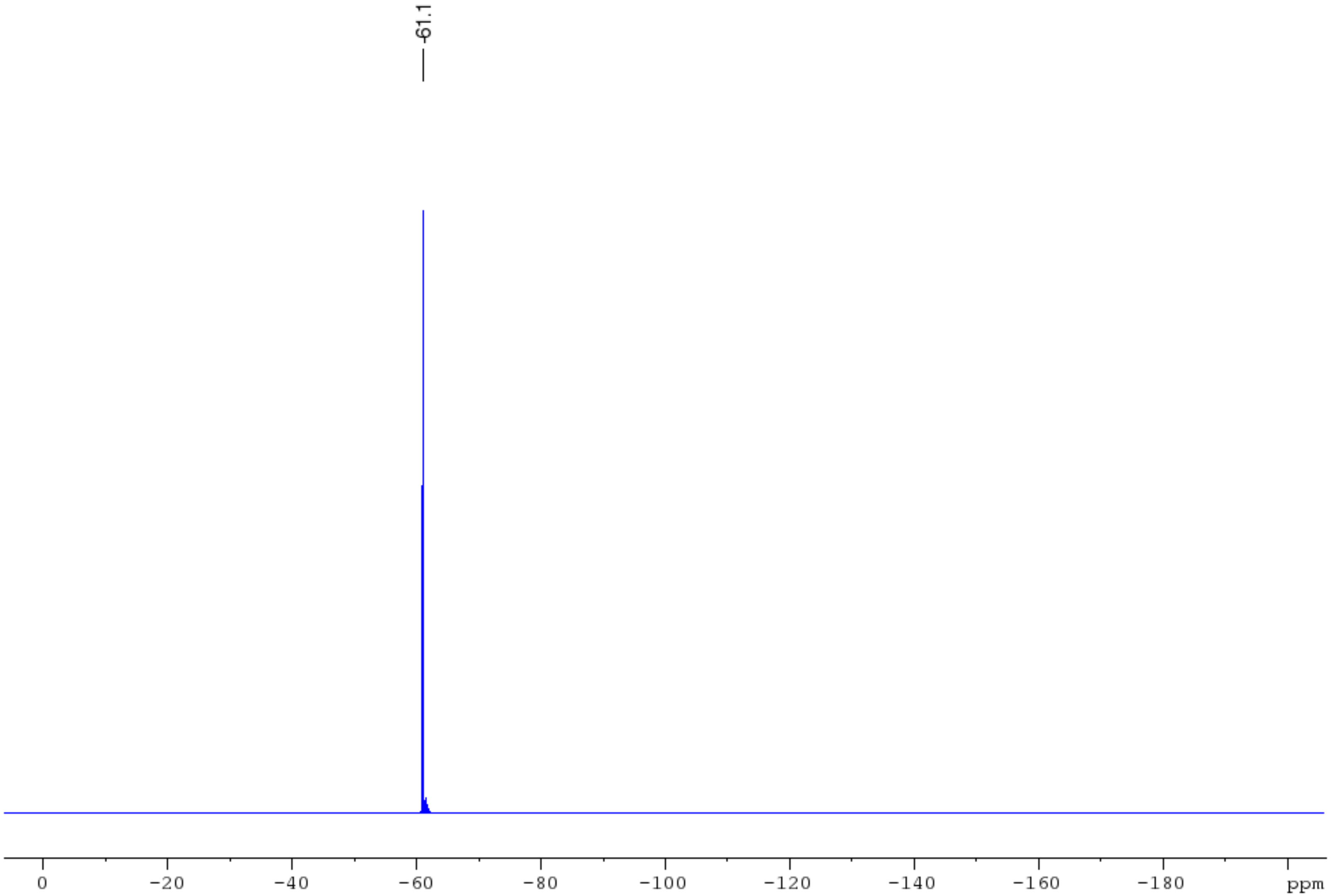

Figure S20. ^{19}F NMR spectrum of **2^{TMS}-Ph^{CF3}** in $CDCl_3$.

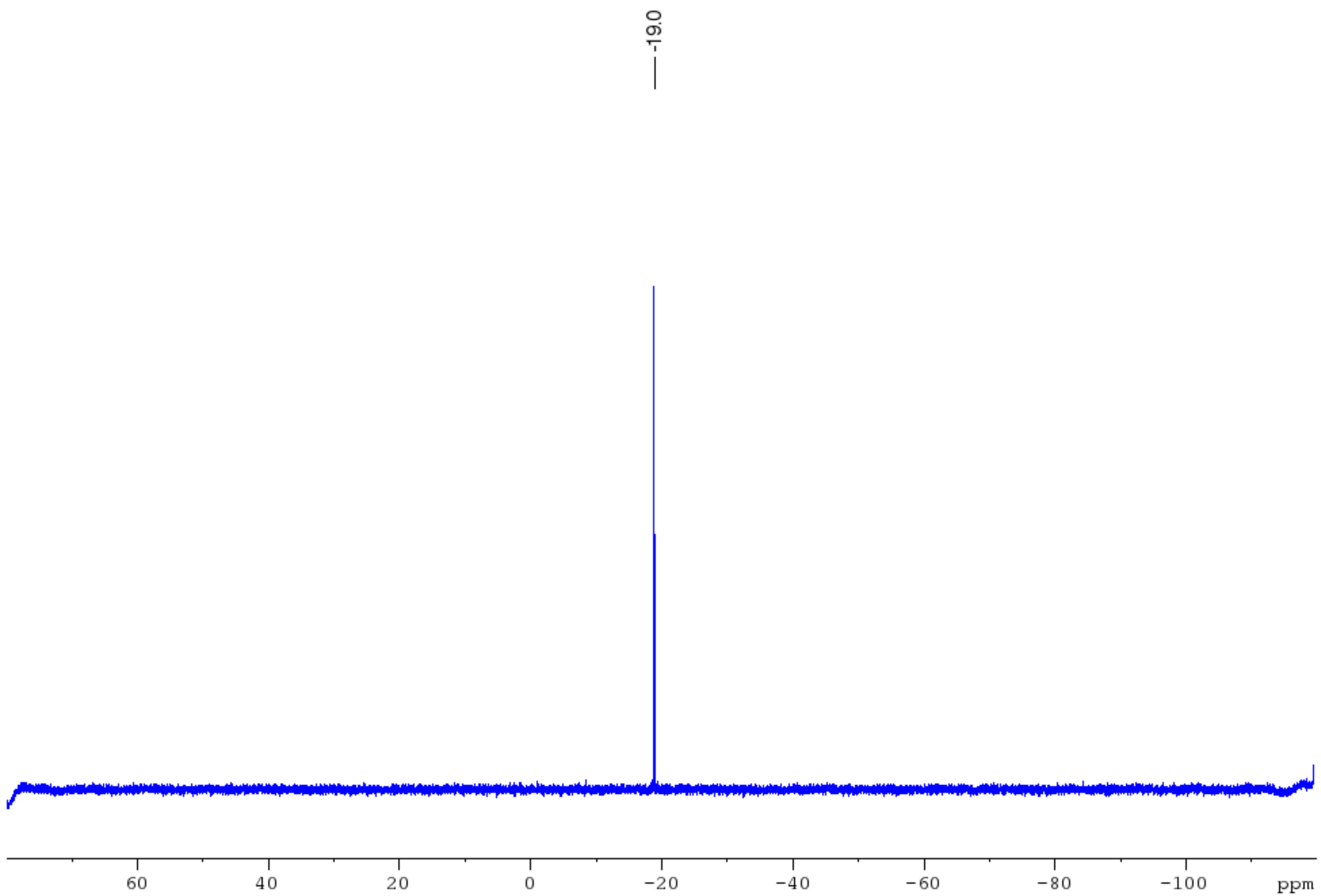

Figure S21. ^{29}Si NMR spectrum of **2^{TMS}-Ph^{CF3}** in $CDCl_3$.

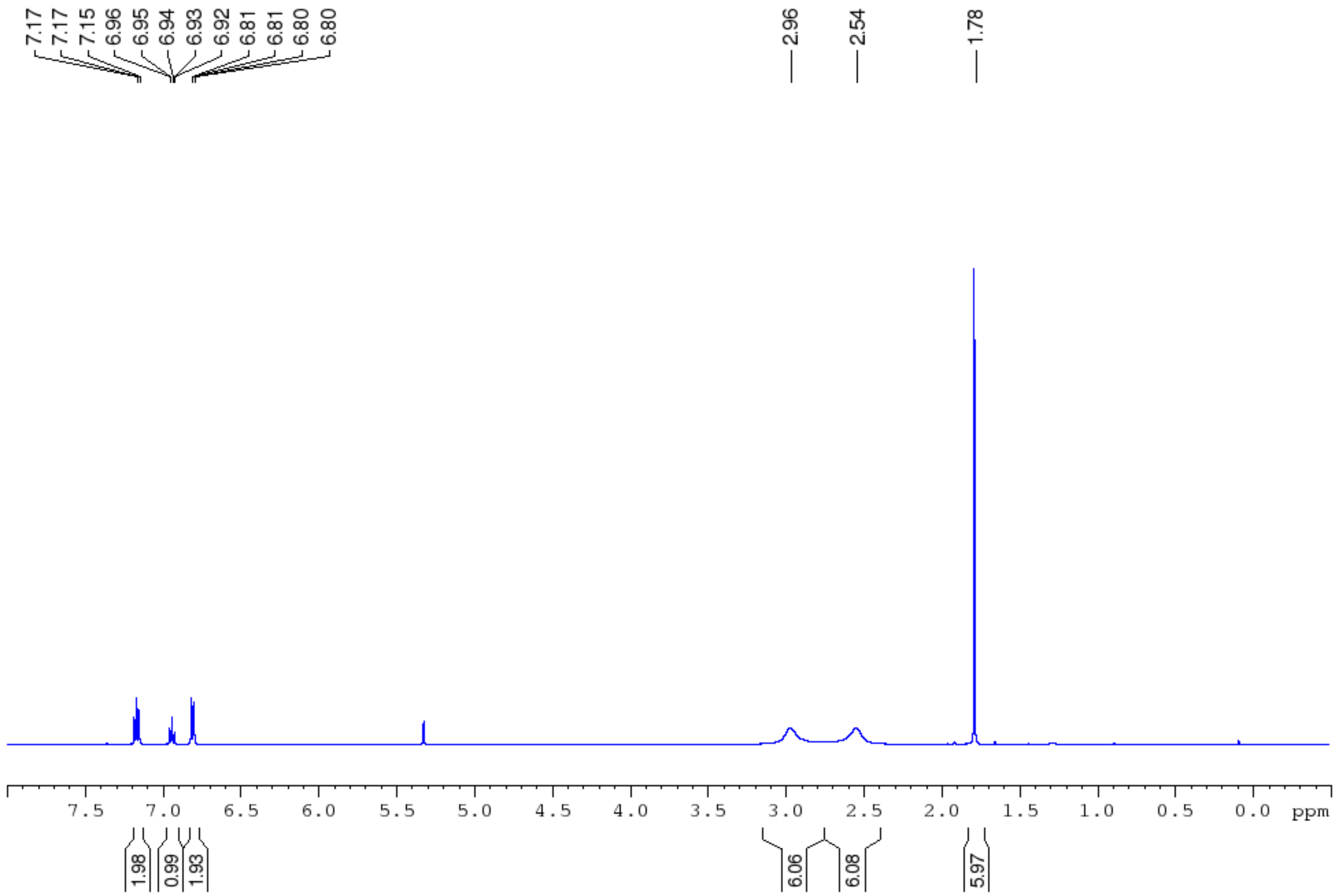

Figure S22. ^{1}H NMR spectrum of **2^{Me}-Ph** in CD_2Cl_2.

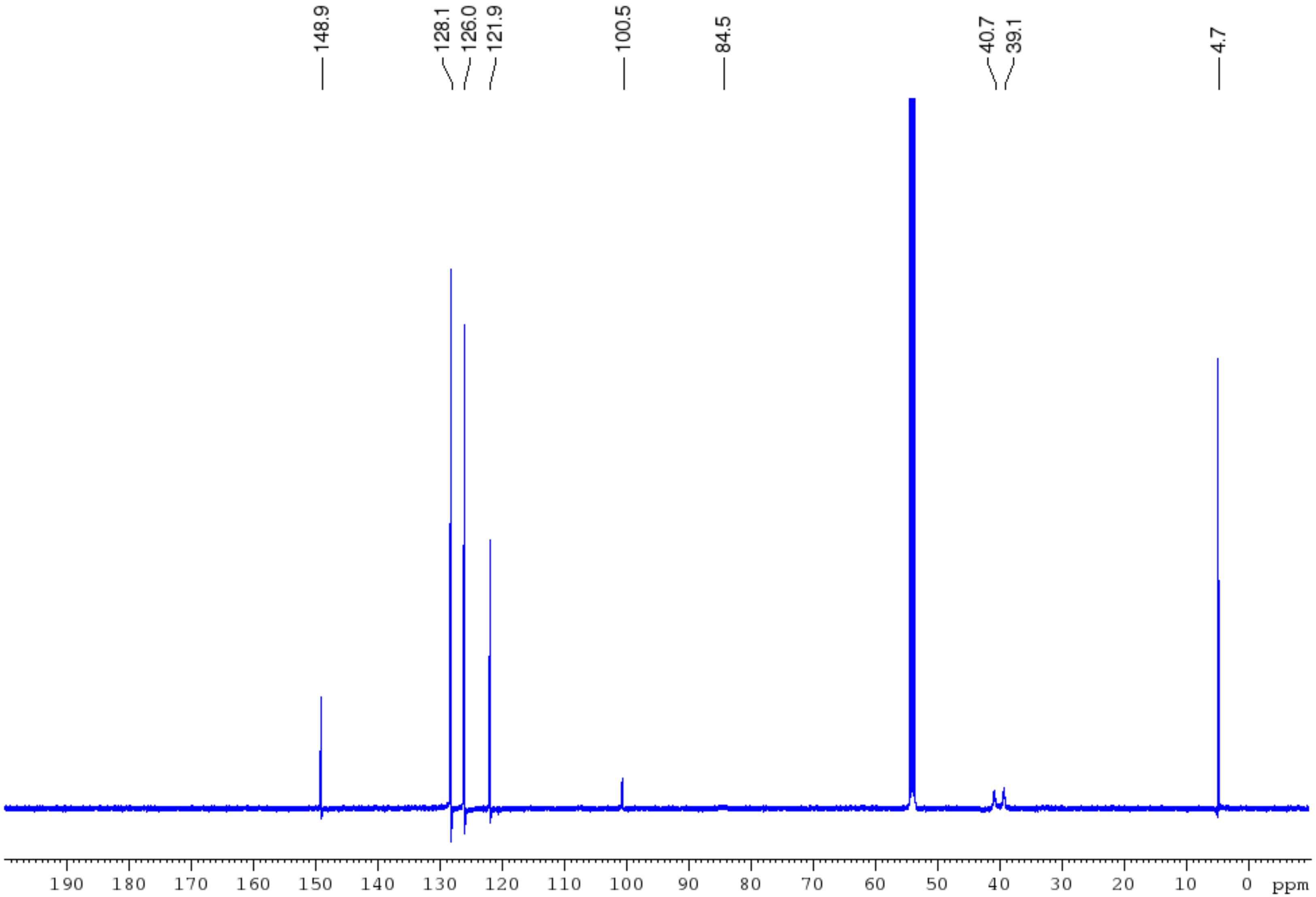

Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of **2^{Me}-Ph** in CD_2Cl_2.

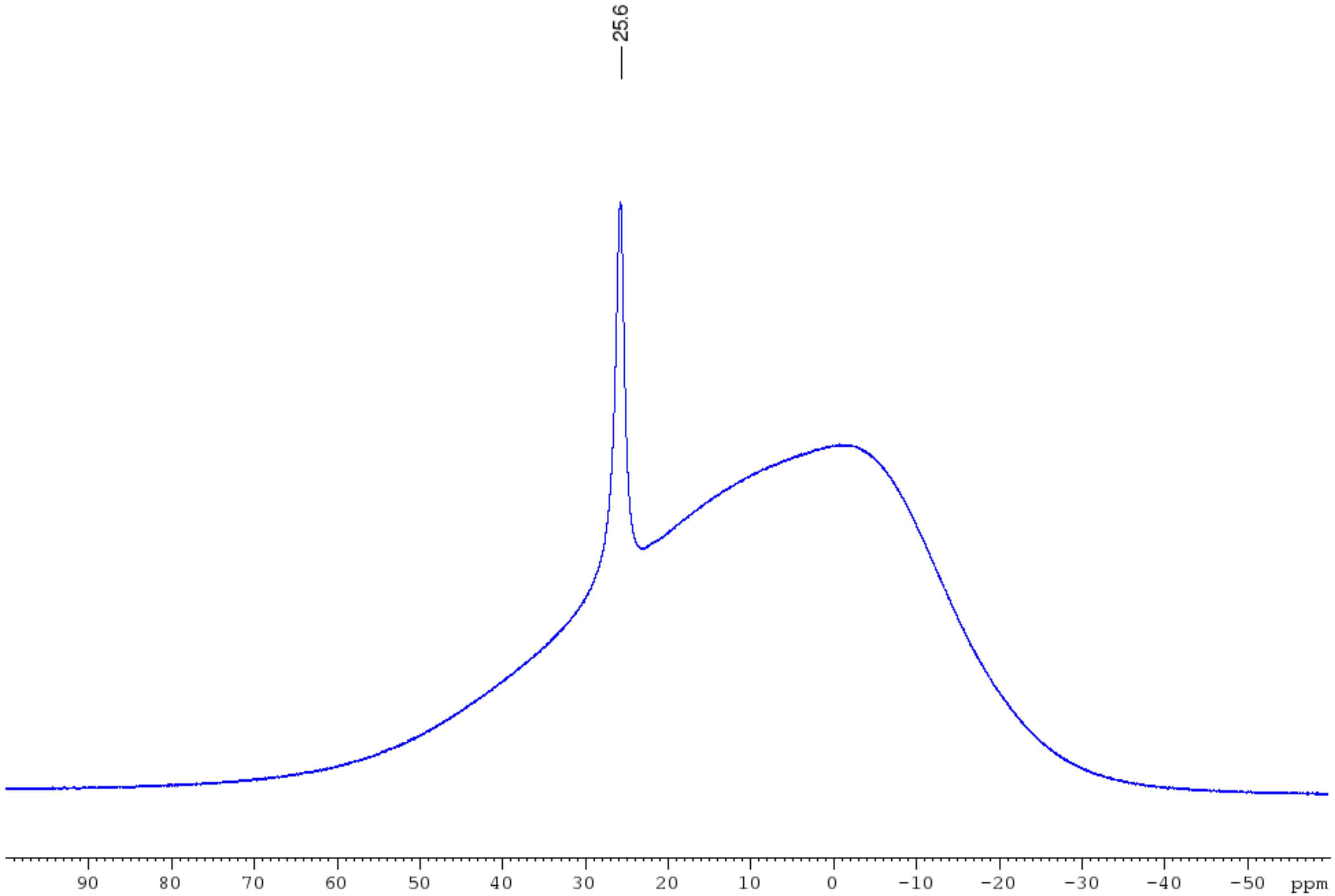

Figure S24. ^{11}B NMR spectrum of **2^{Me}-Ph** in CD_2Cl_2.

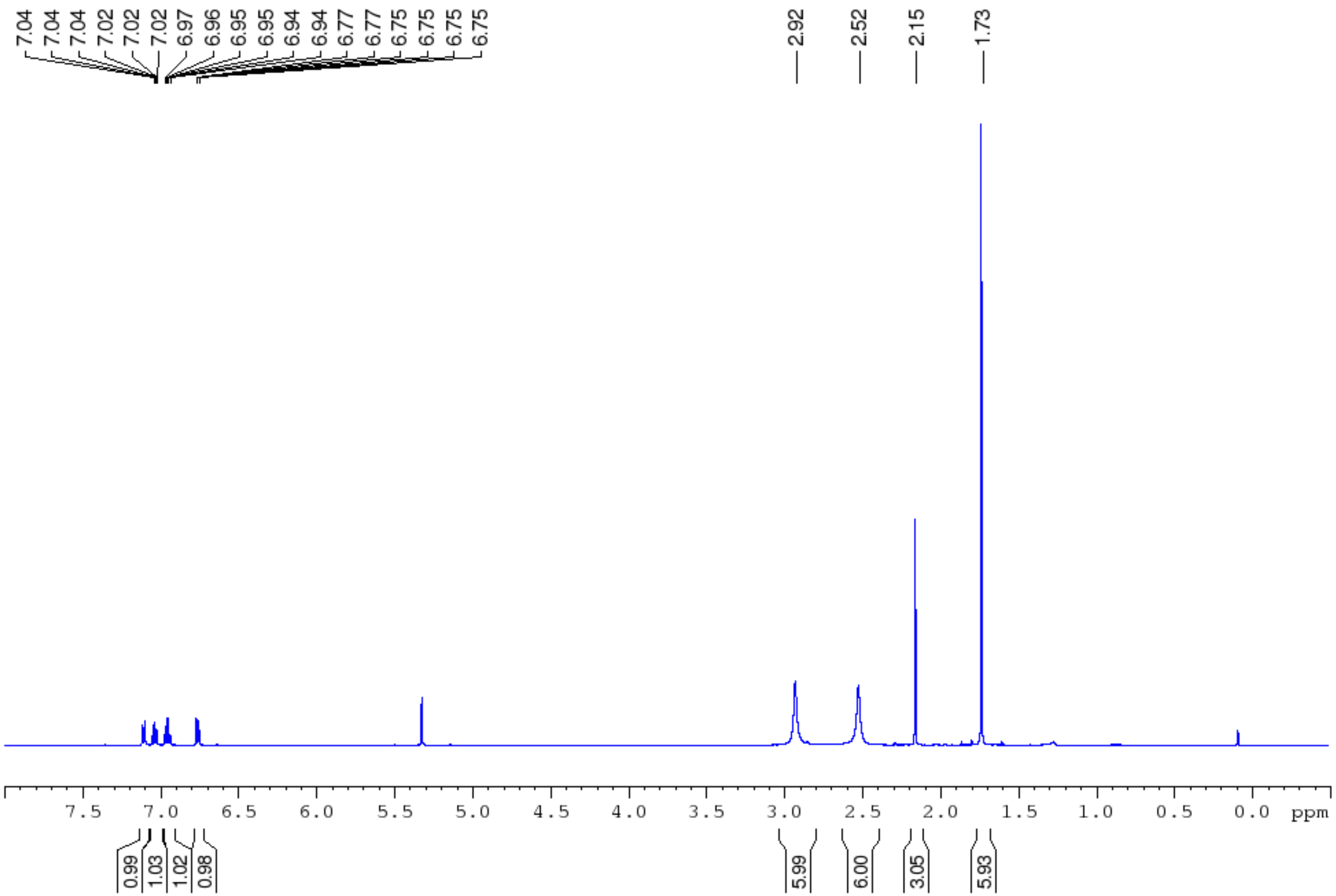

Figure S25. ^{1}H NMR spectrum of **2^{Me}-*o*Tol** in CD_2Cl_2.

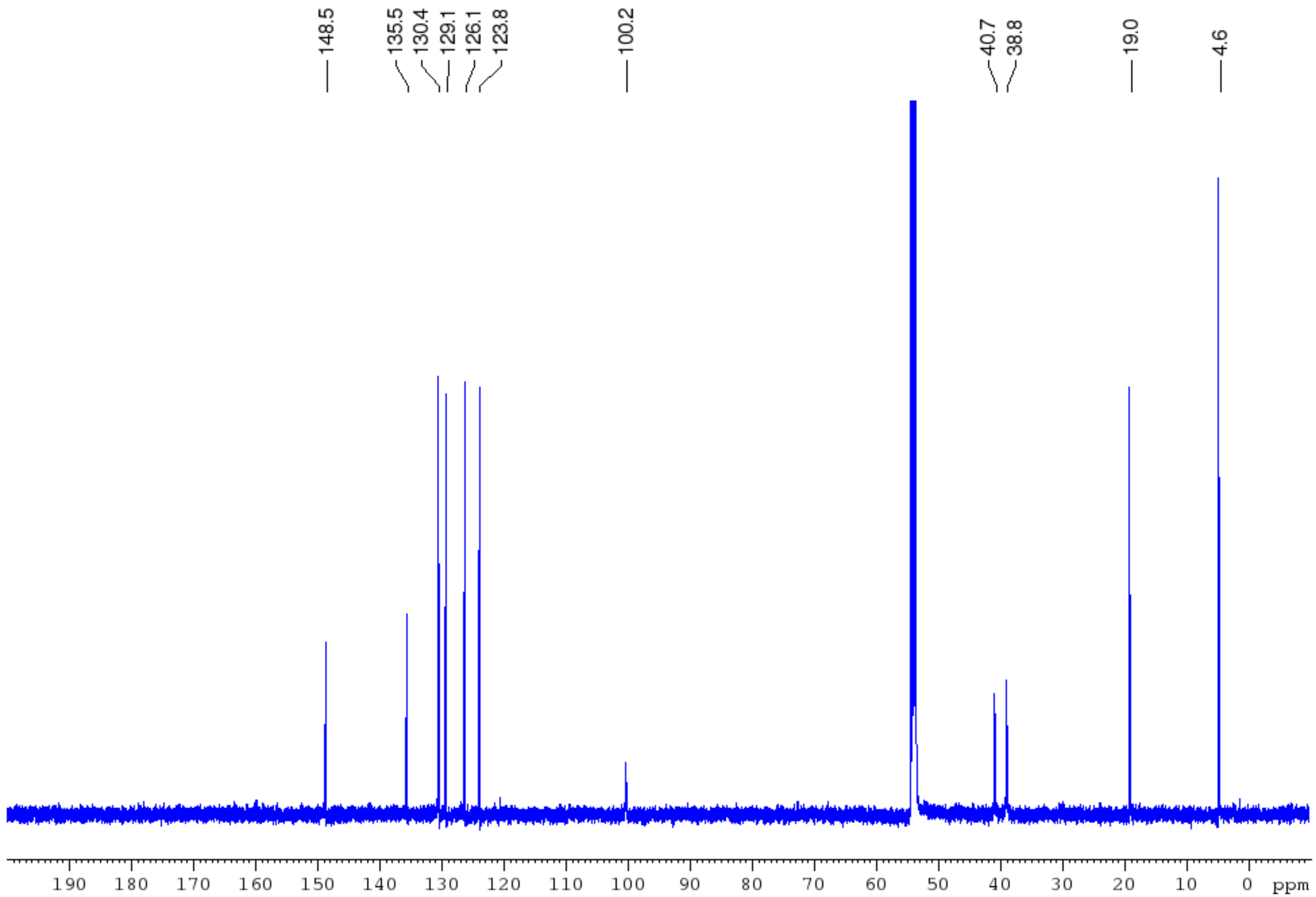

Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum of **2^{Me}-*o*Tol** in CD_2Cl_2.

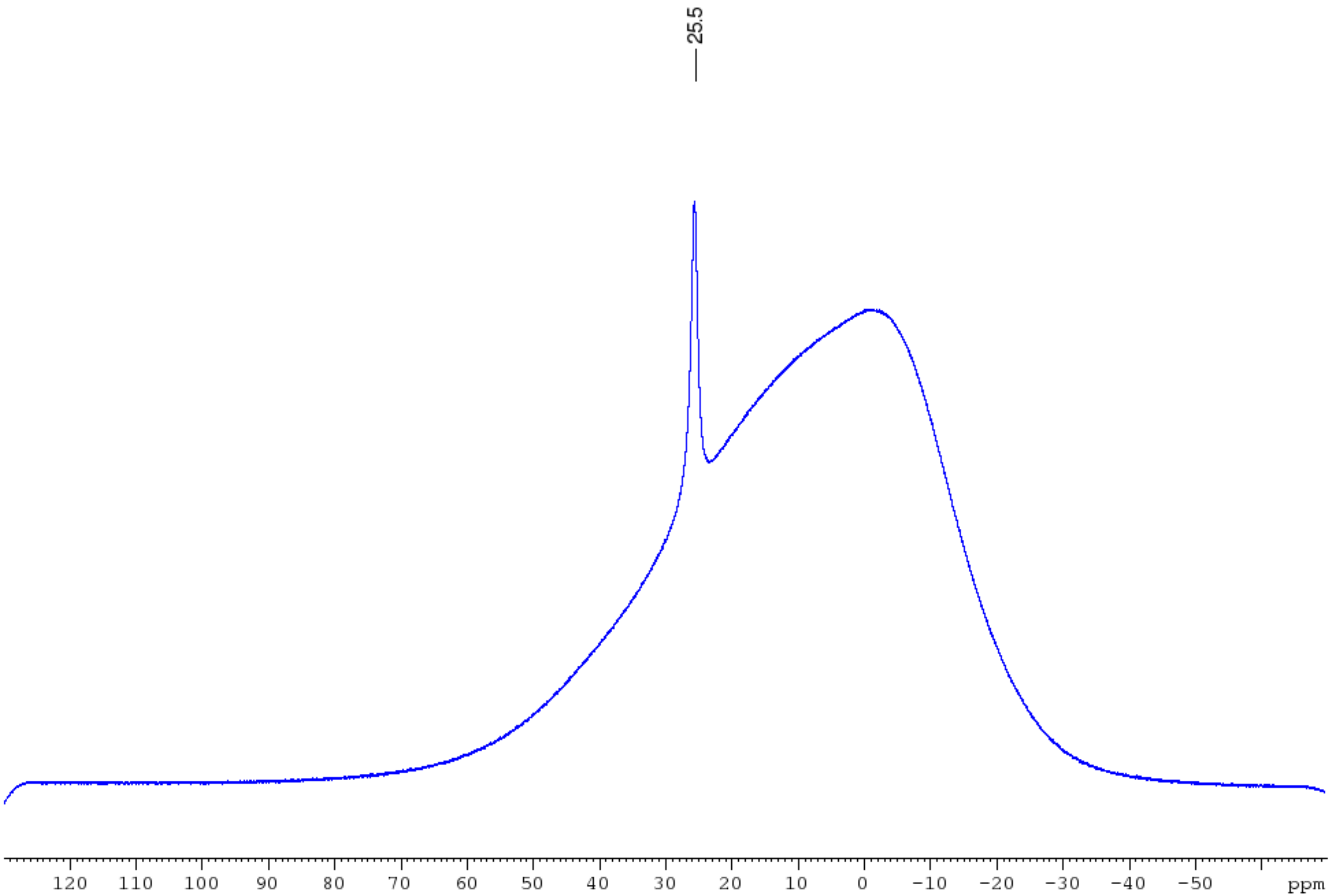

Figure S27. ^{11}B NMR spectrum of **2^{Me}-*o*Tol** in CD_2Cl_2.

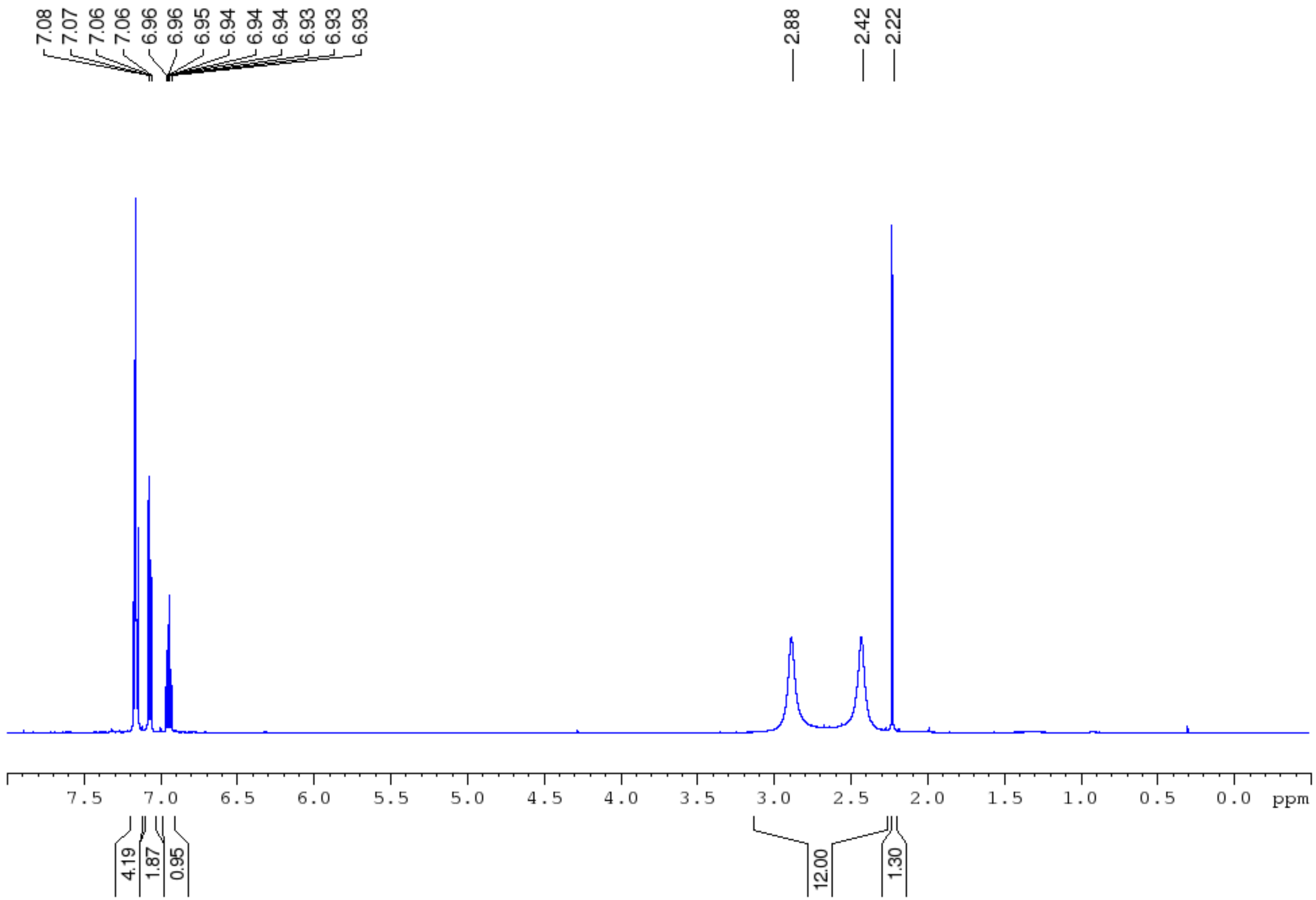

Figure S28. [1]H NMR spectrum of **2^{H}-Ph** in C_6D_6.

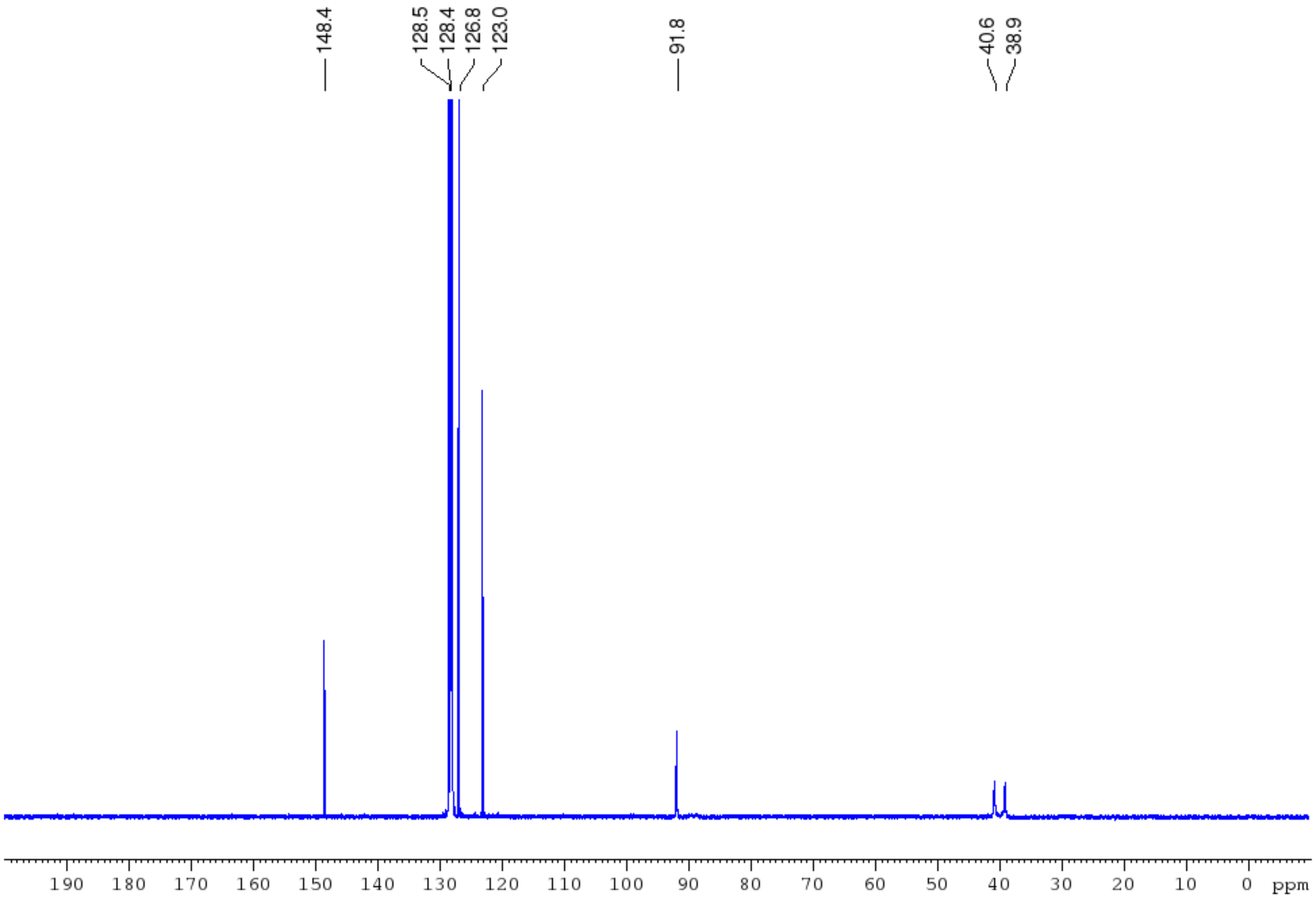

Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum of **2^{H}-Ph** in C_6D_6.

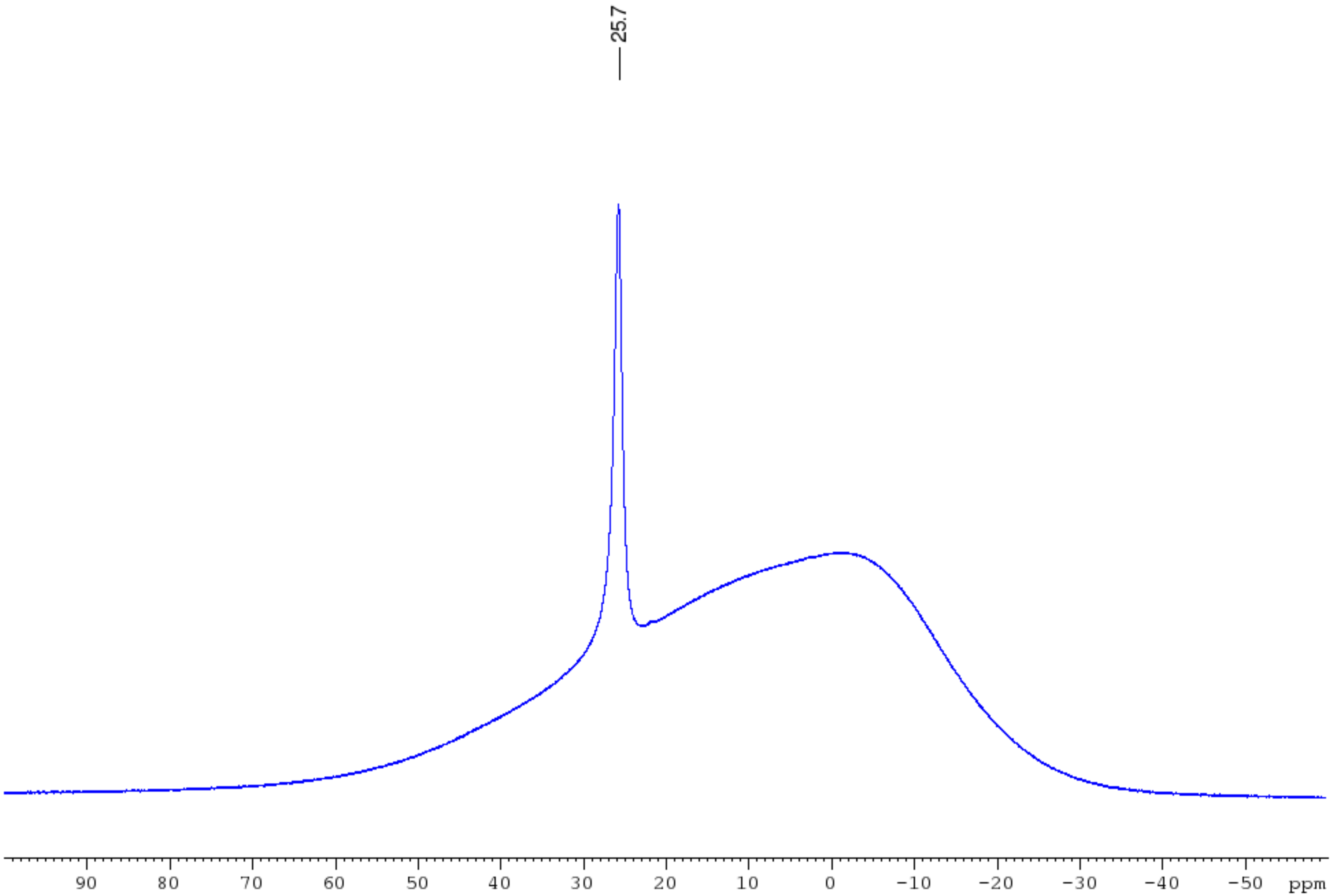

Figure S30. ^{11}B NMR spectrum of **2^{H}-Ph** in C_6D_6.

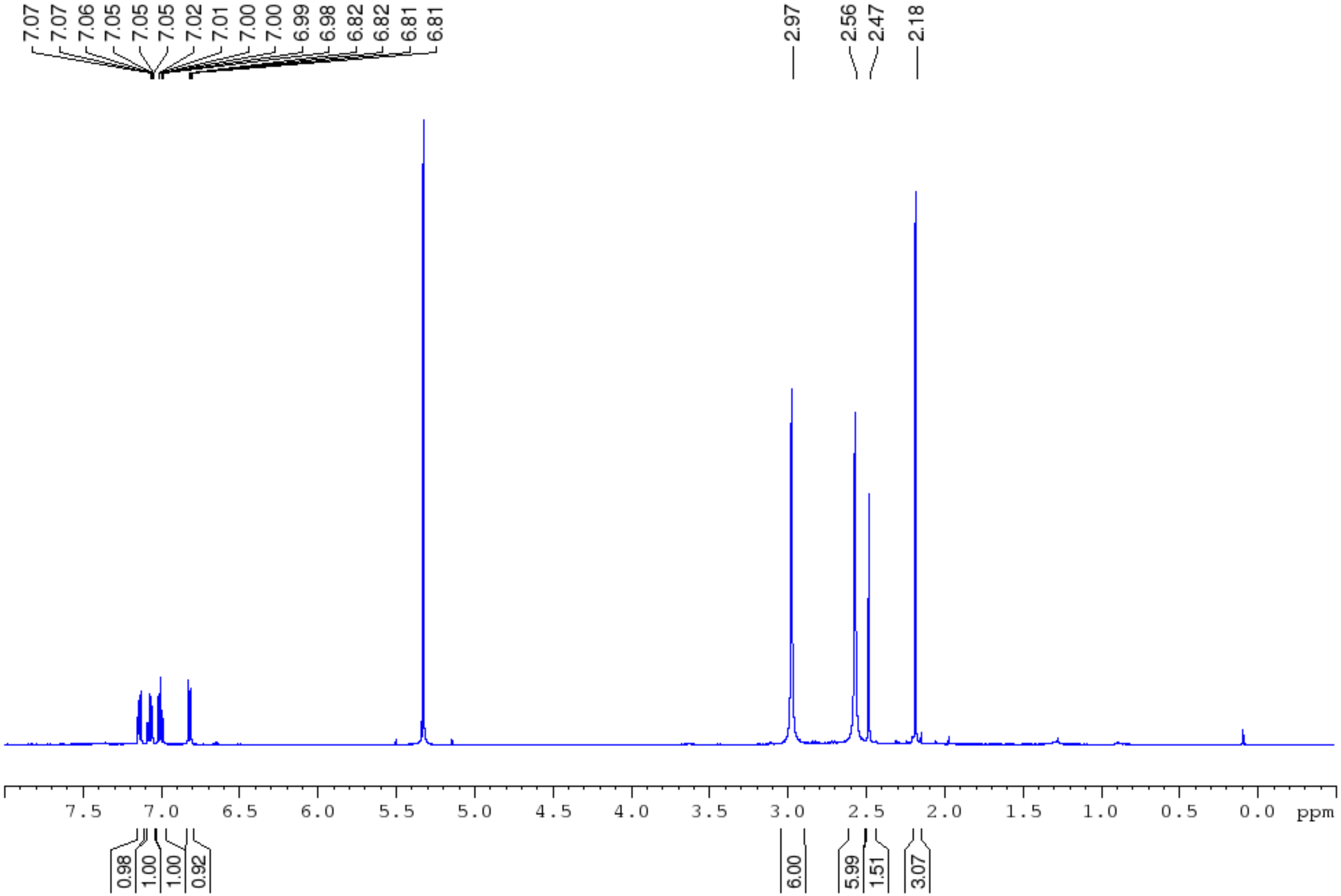

Figure S31. [1]H NMR spectrum of **2^{H}-*o*Tol** in CD_2Cl_2.

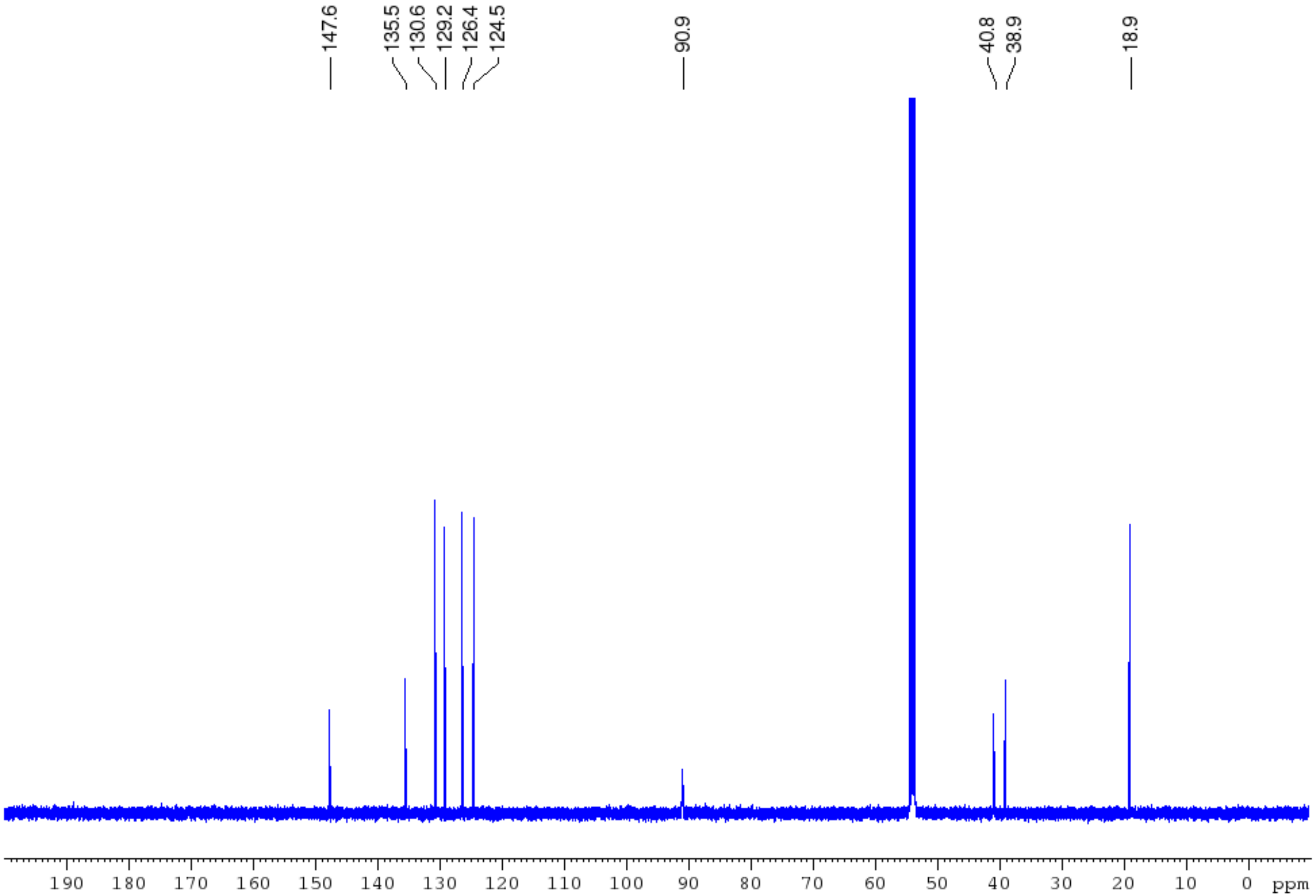

Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum of **2^{H}-*o*Tol** in CD_2Cl_2.

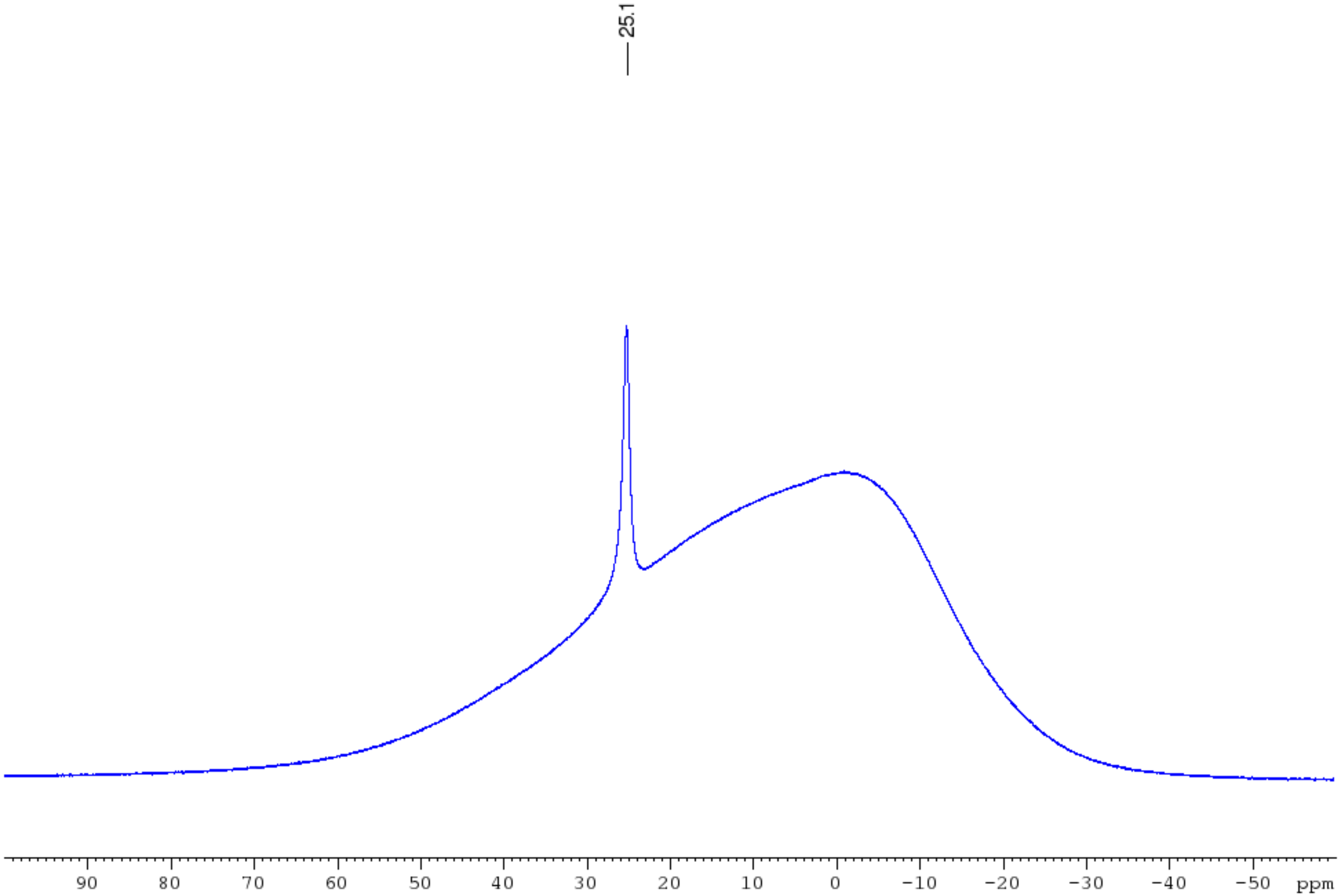

Figure S33. ^{11}B NMR spectrum of **2^H-*o*Tol** in CD_2Cl_2.

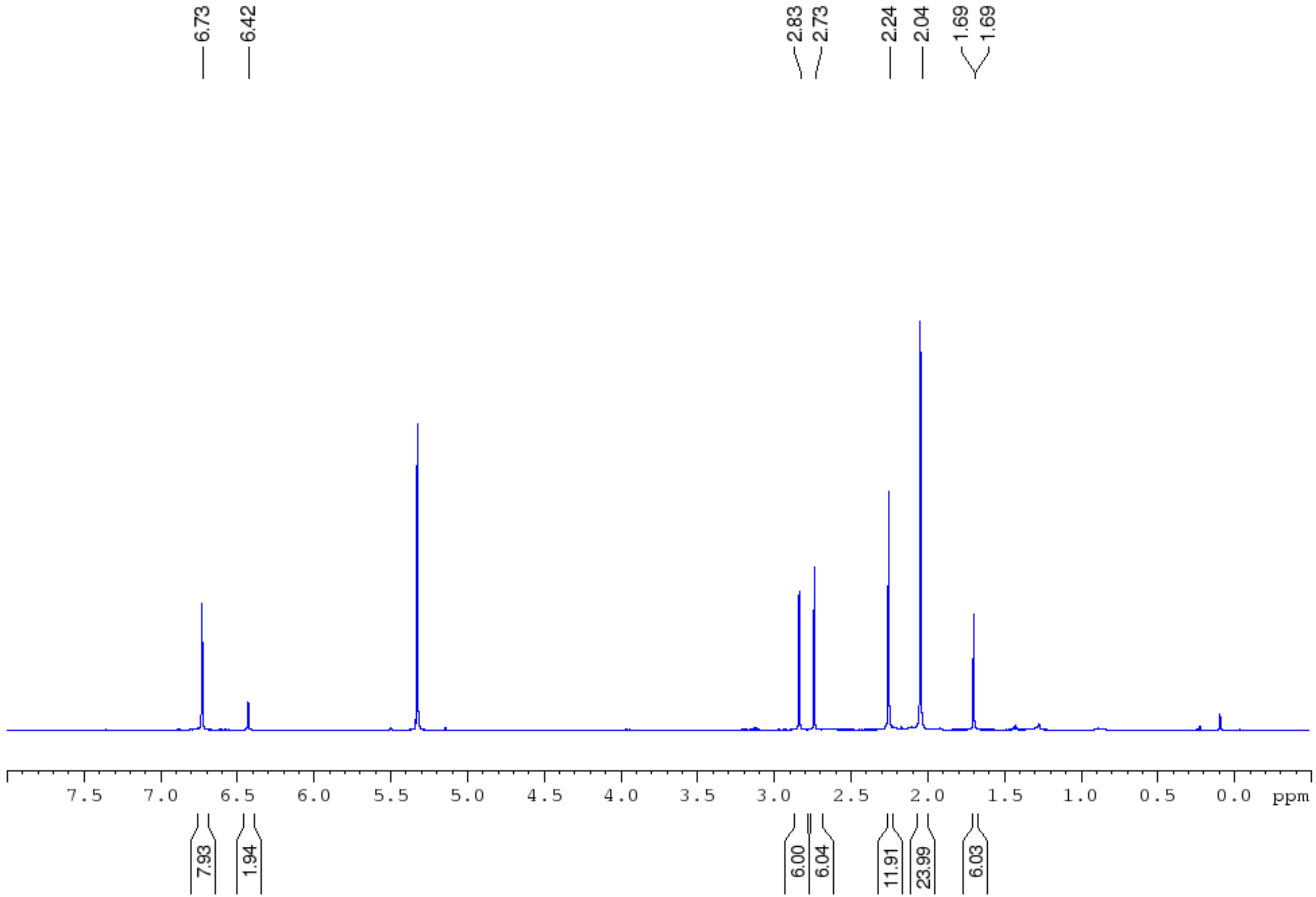

Figure S34. [1]H NMR spectrum of **4^{Me}** in CD_2Cl_2.

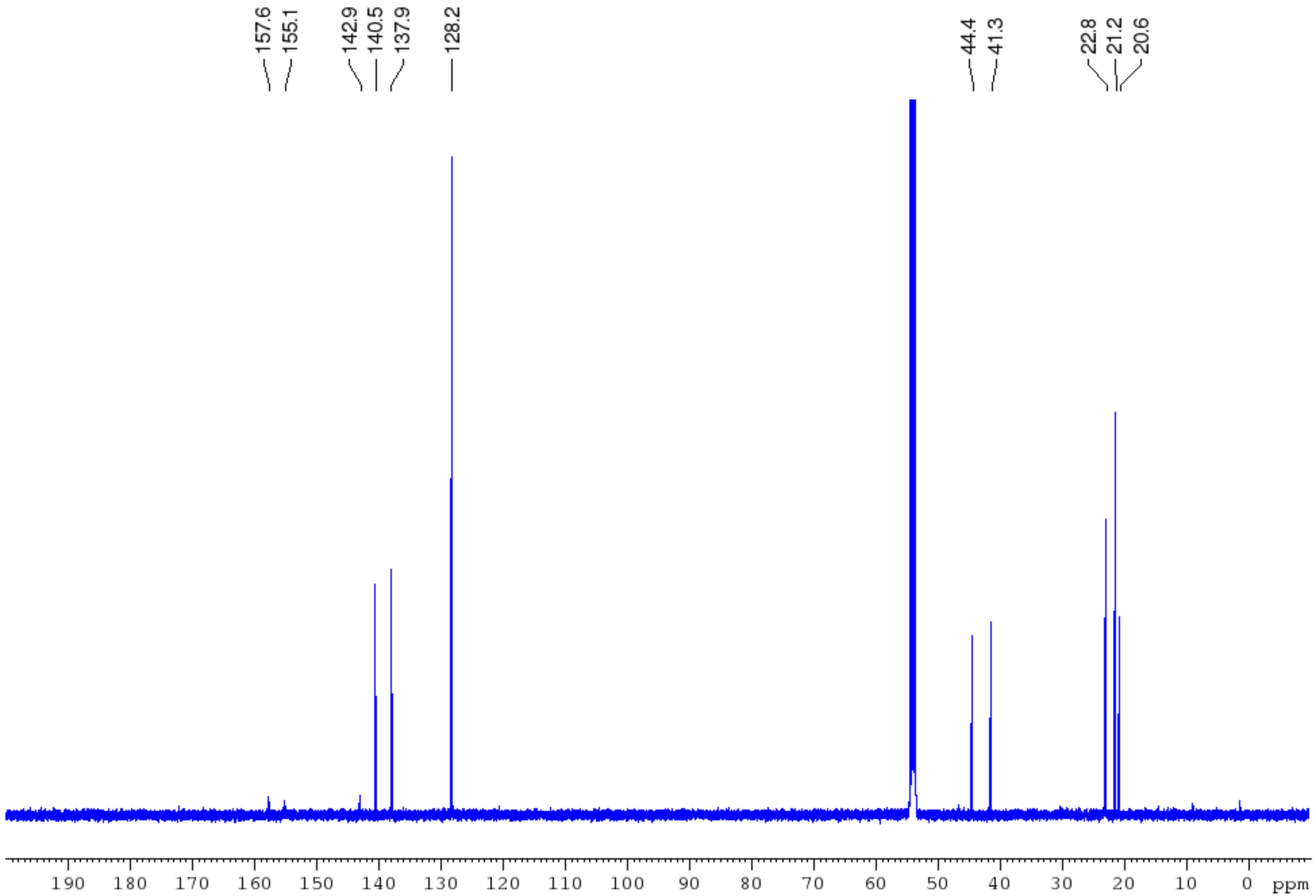

Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum of $\mathbf{4^{Me}}$ in CD_2Cl_2.

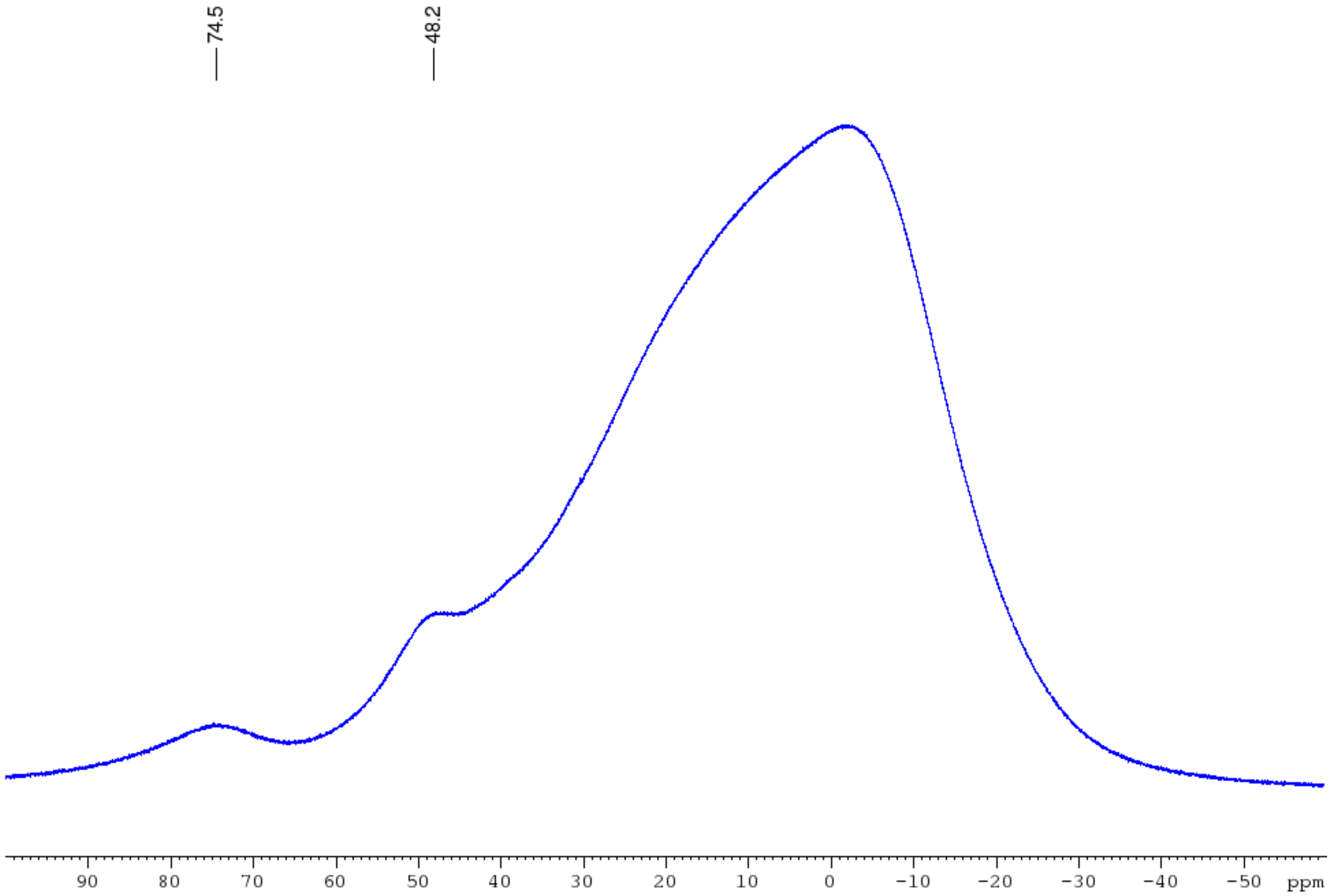

Figure S36. ^{11}B NMR spectrum of $\mathbf{4^{Me}}$ in CD_2Cl_2.

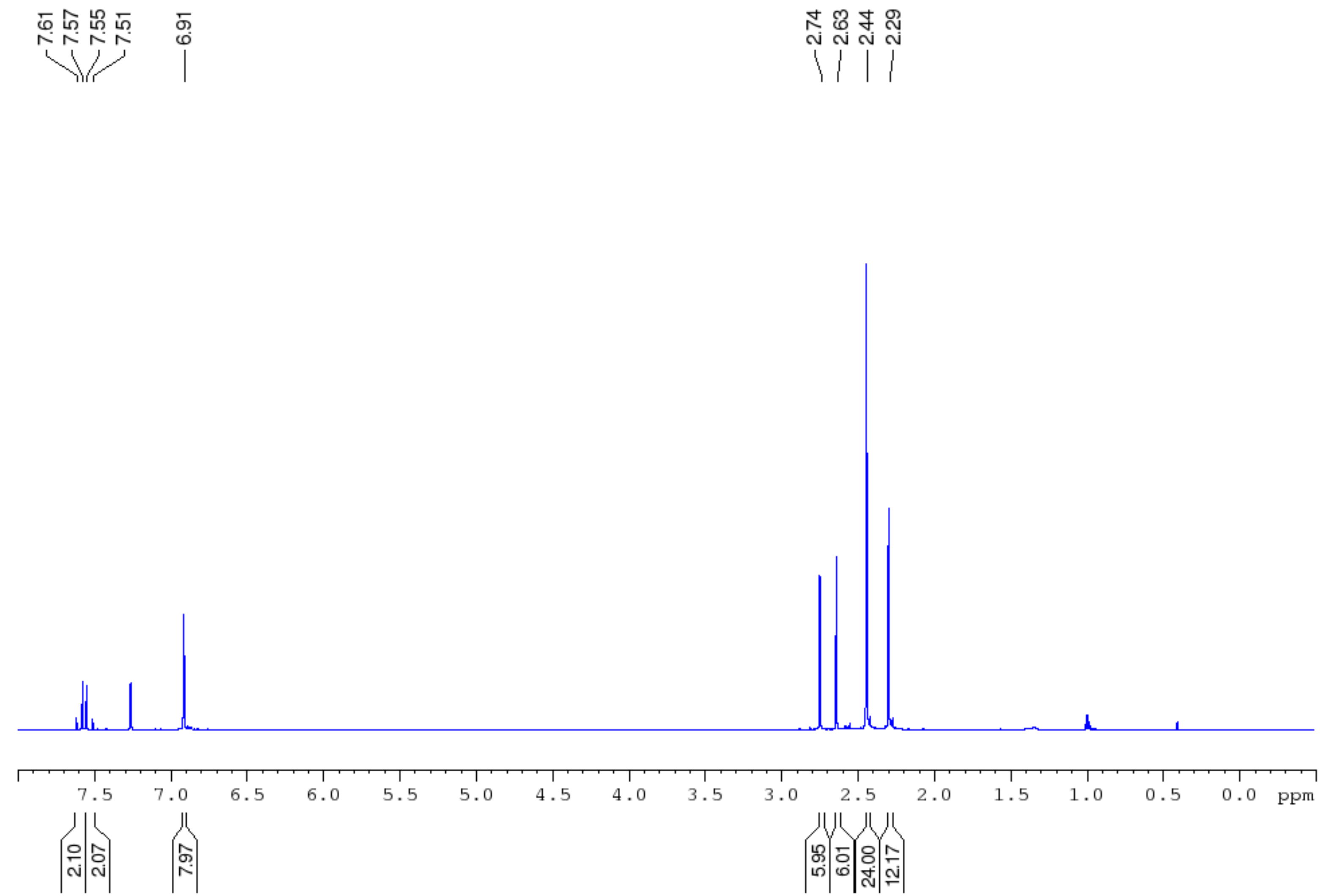

Figure S37. [1]H NMR spectrum of **4^H** in C_6D_6.

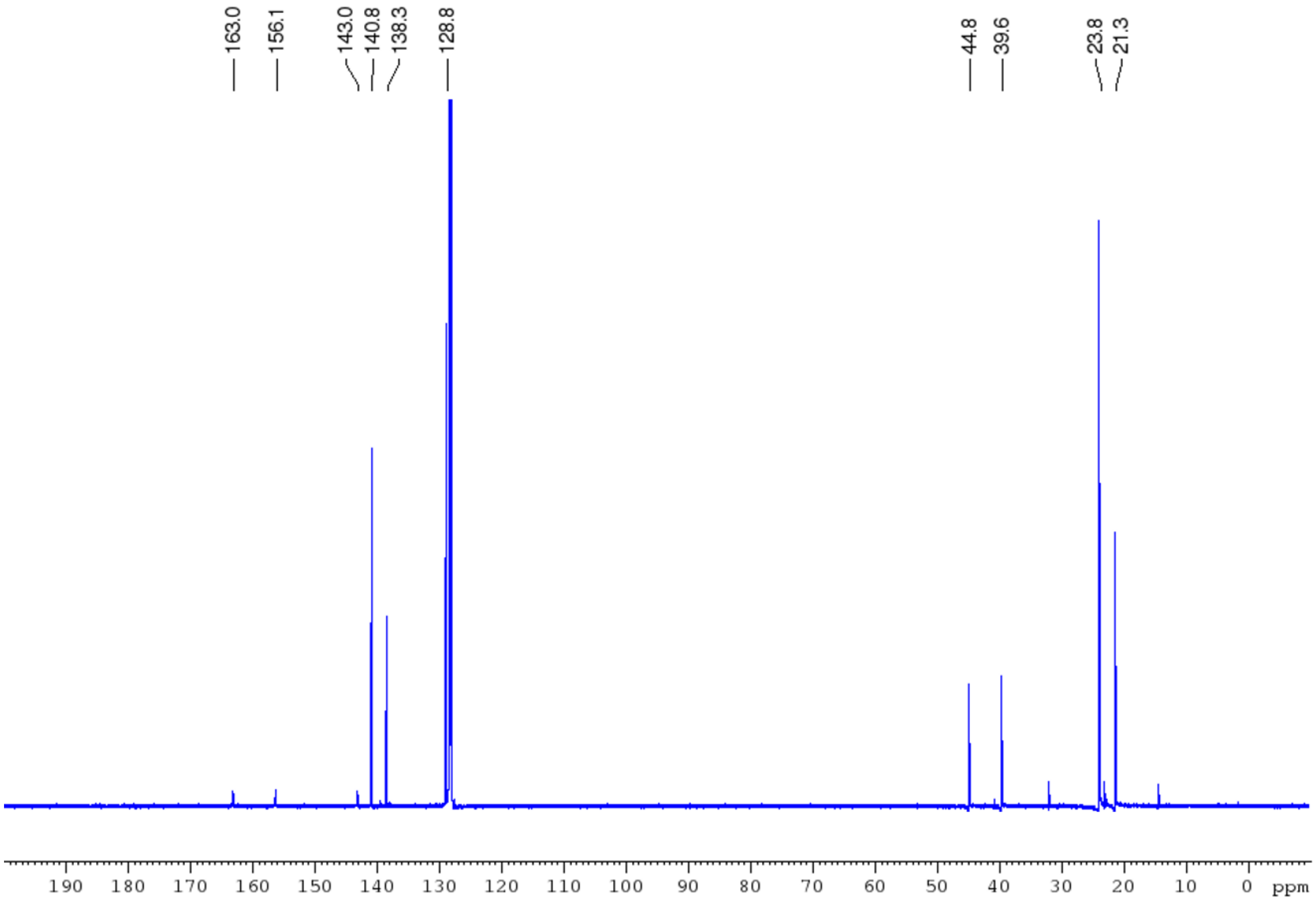

Figure S38. $^{13}C\{^1H\}$ NMR spectrum of $\mathbf{4^H}$ in C_6D_6.

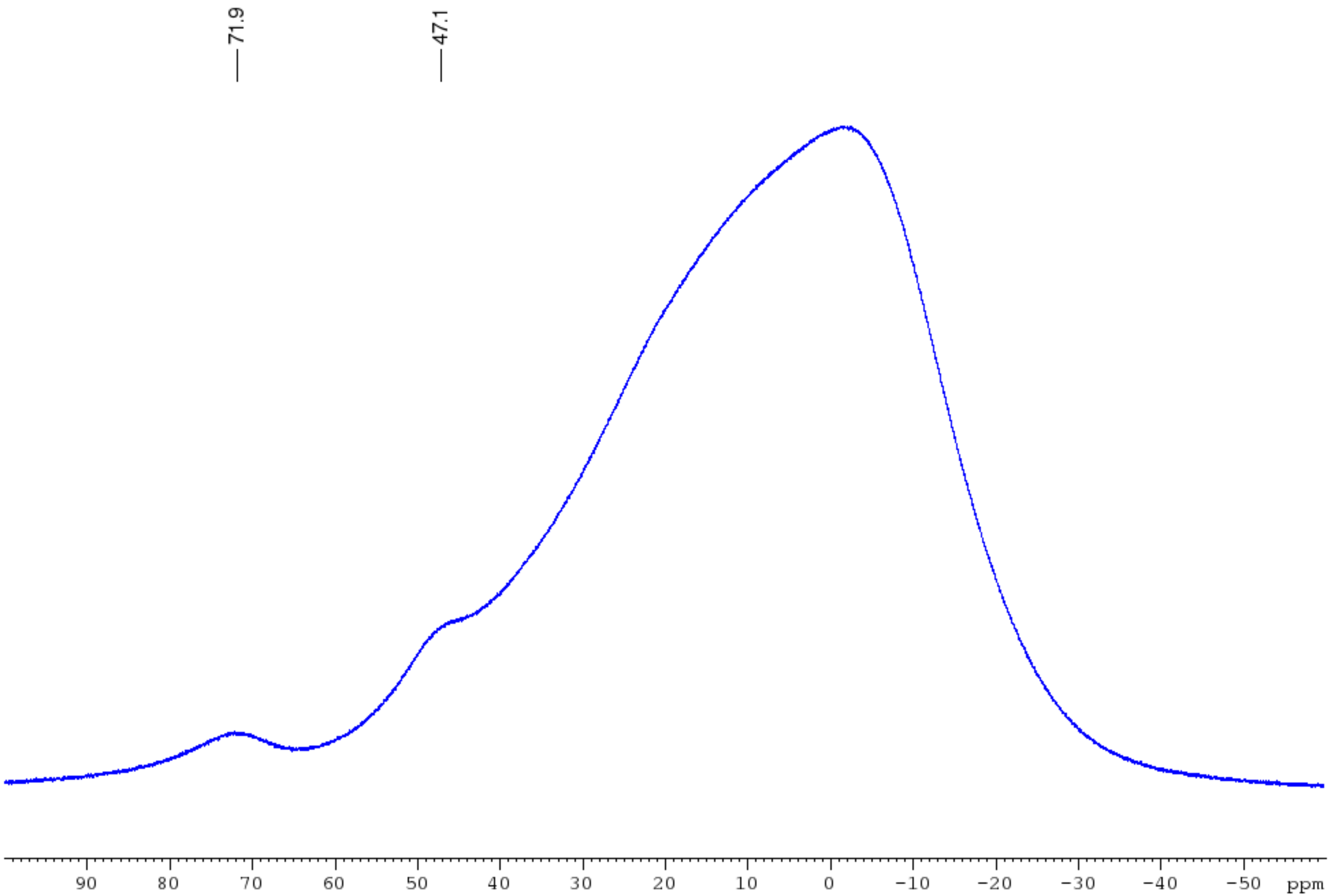

Figure S39. ^{11}B NMR spectrum of $\mathbf{4^H}$ in C_6D_6.

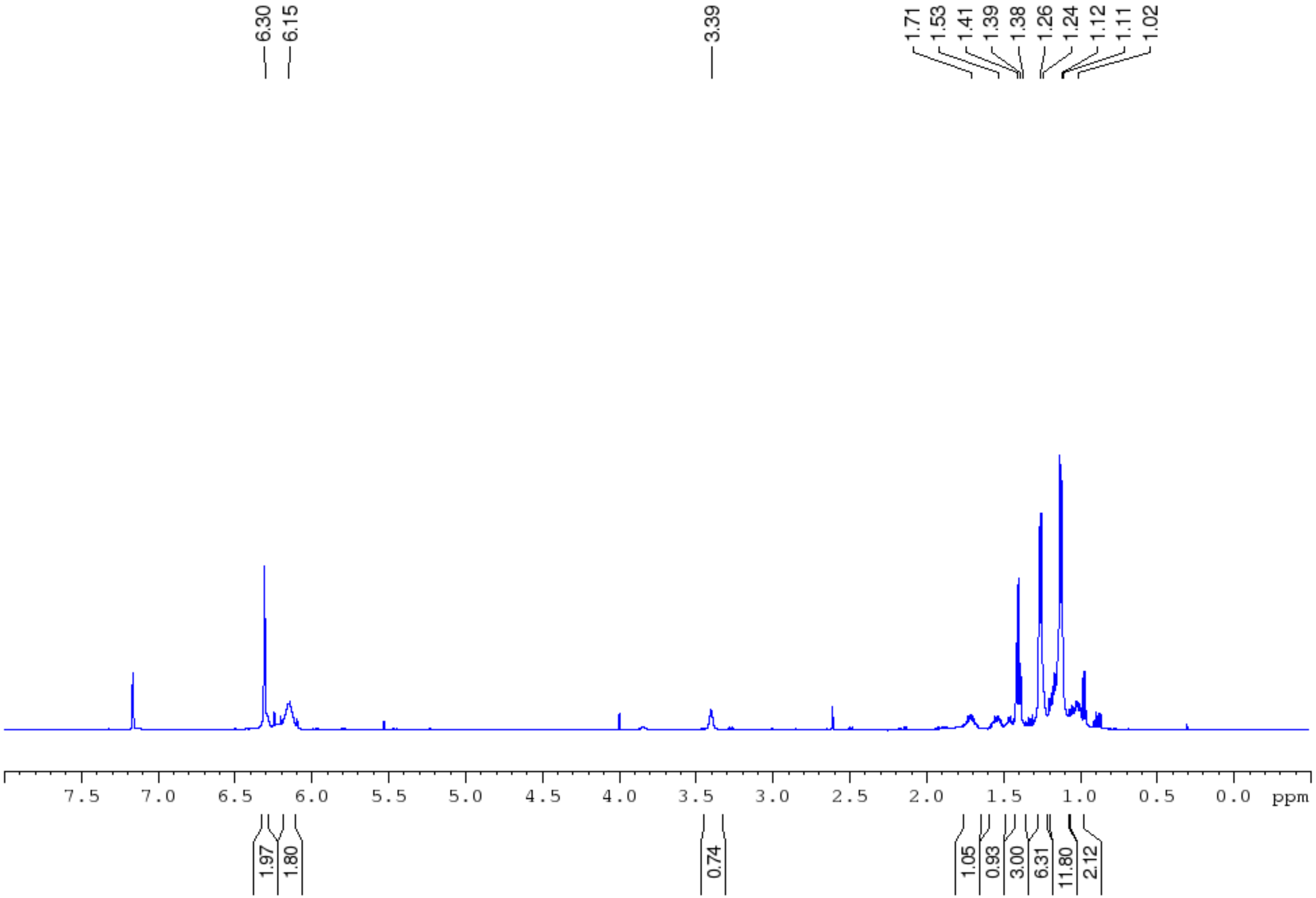

Figure S40. ^{1}H NMR spectrum of $\mathbf{6^{Me}}$ in C_6D_6.

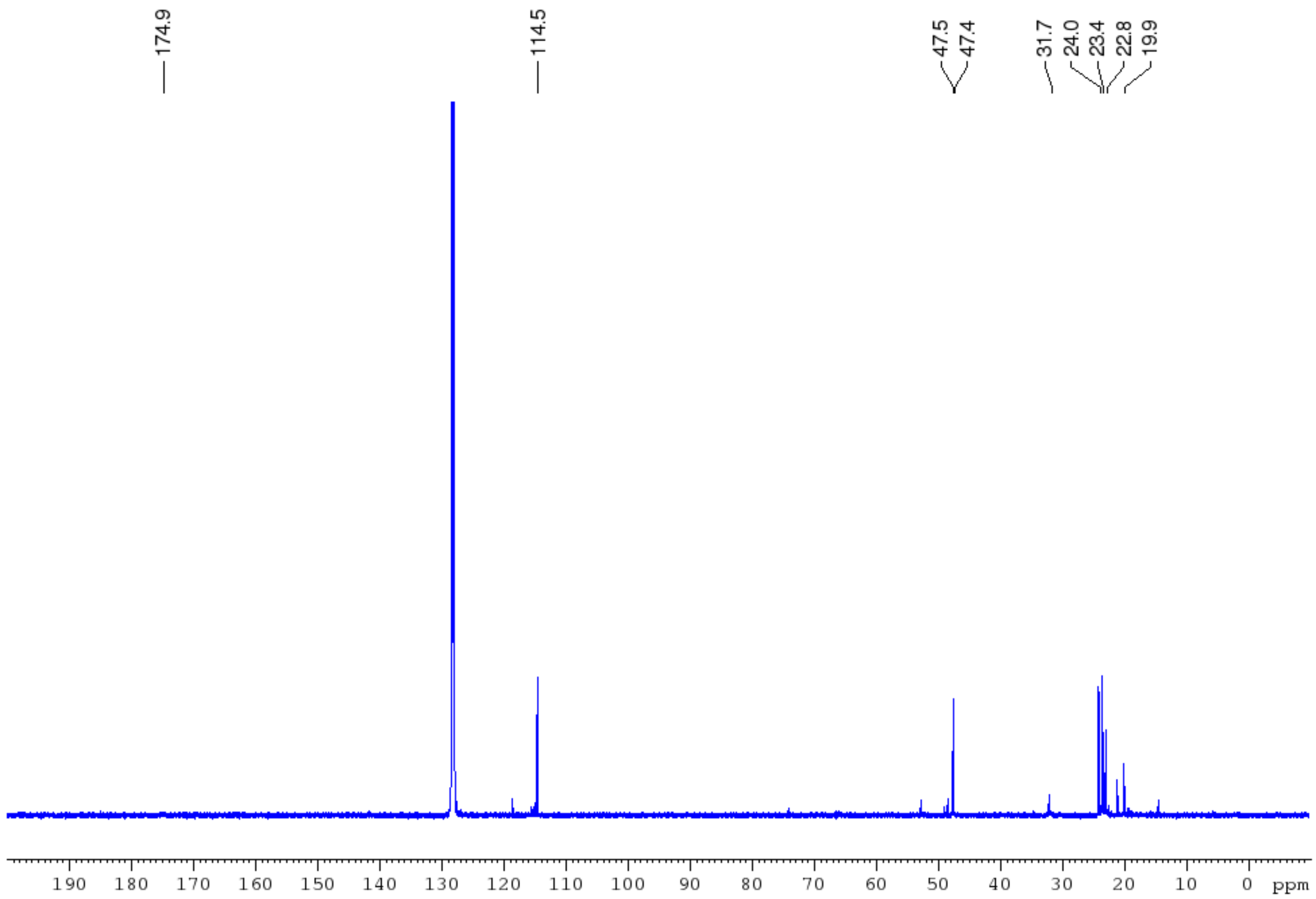

Figure S41. $^{13}C\{^1H\}$ NMR spectrum of $\mathbf{6^{Me}}$ in C_6D_6.

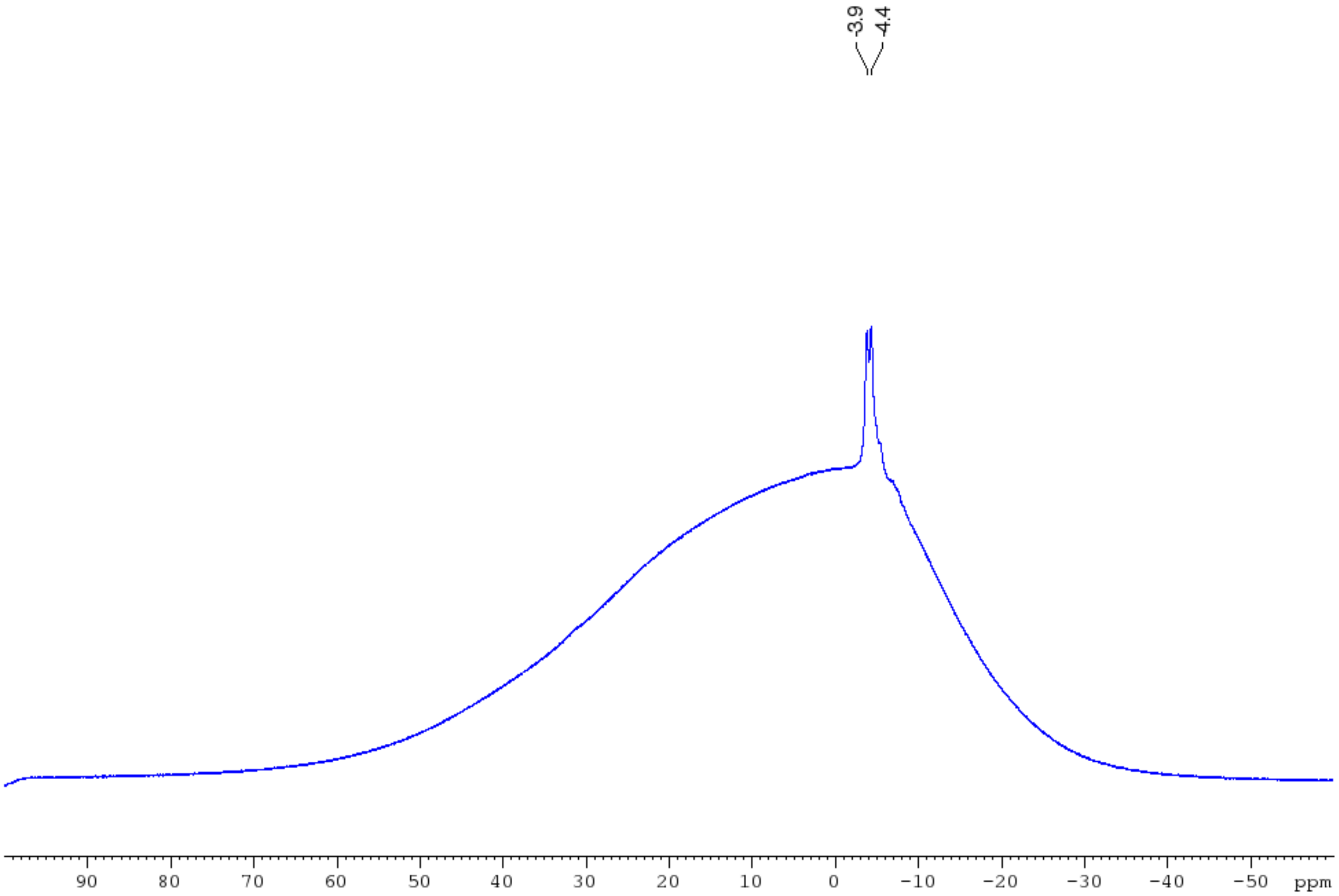

Figure S42. ^{11}B NMR spectrum of **6^{Me}** in C_6D_6.

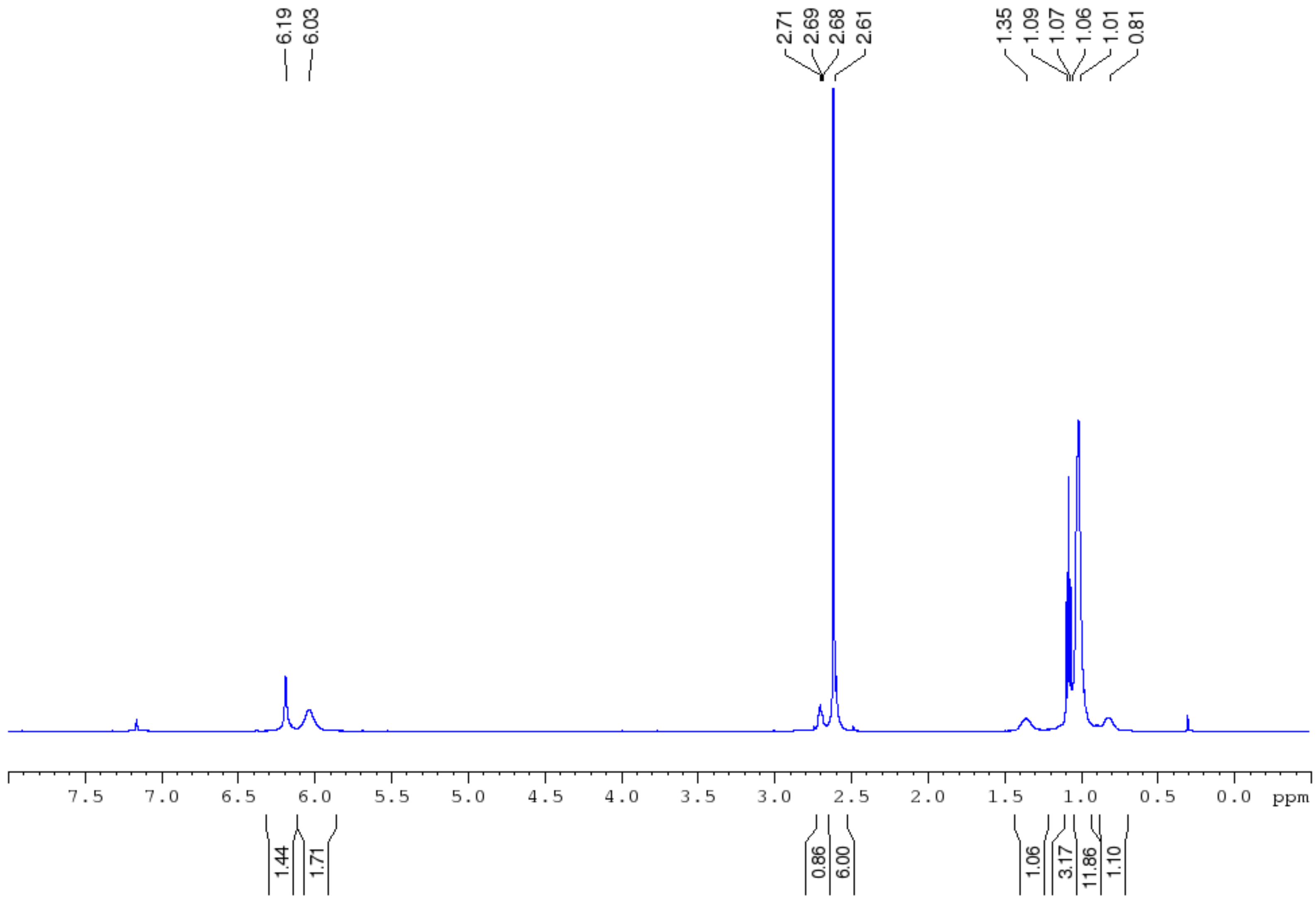

Figure S43. ^{1}H NMR spectrum of $\mathbf{6^{H}}$ in C_6D_6.

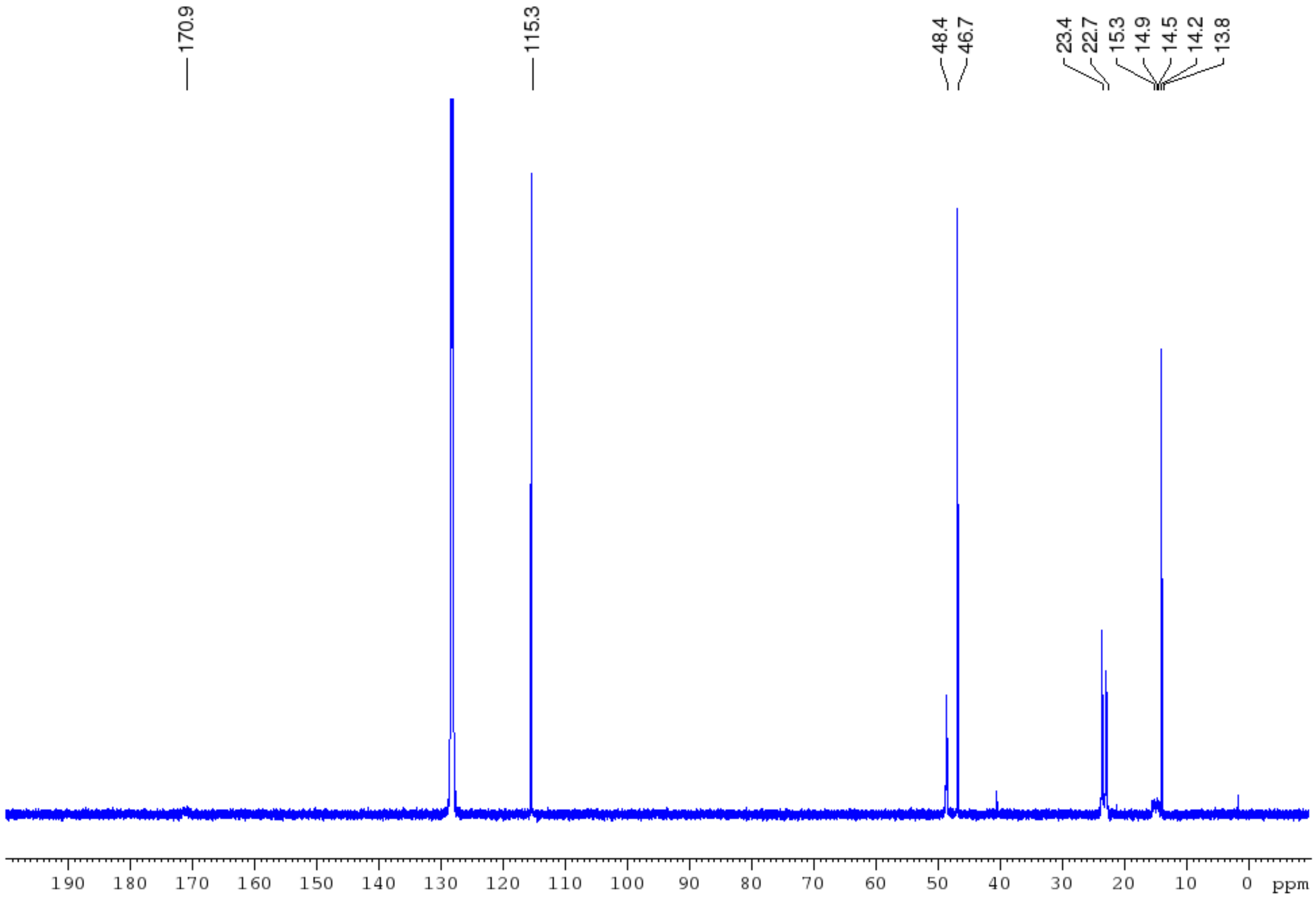

Figure S44. $^{13}C\{^{1}H\}$ NMR spectrum of $\mathbf{6^{H}}$ in C_6D_6.

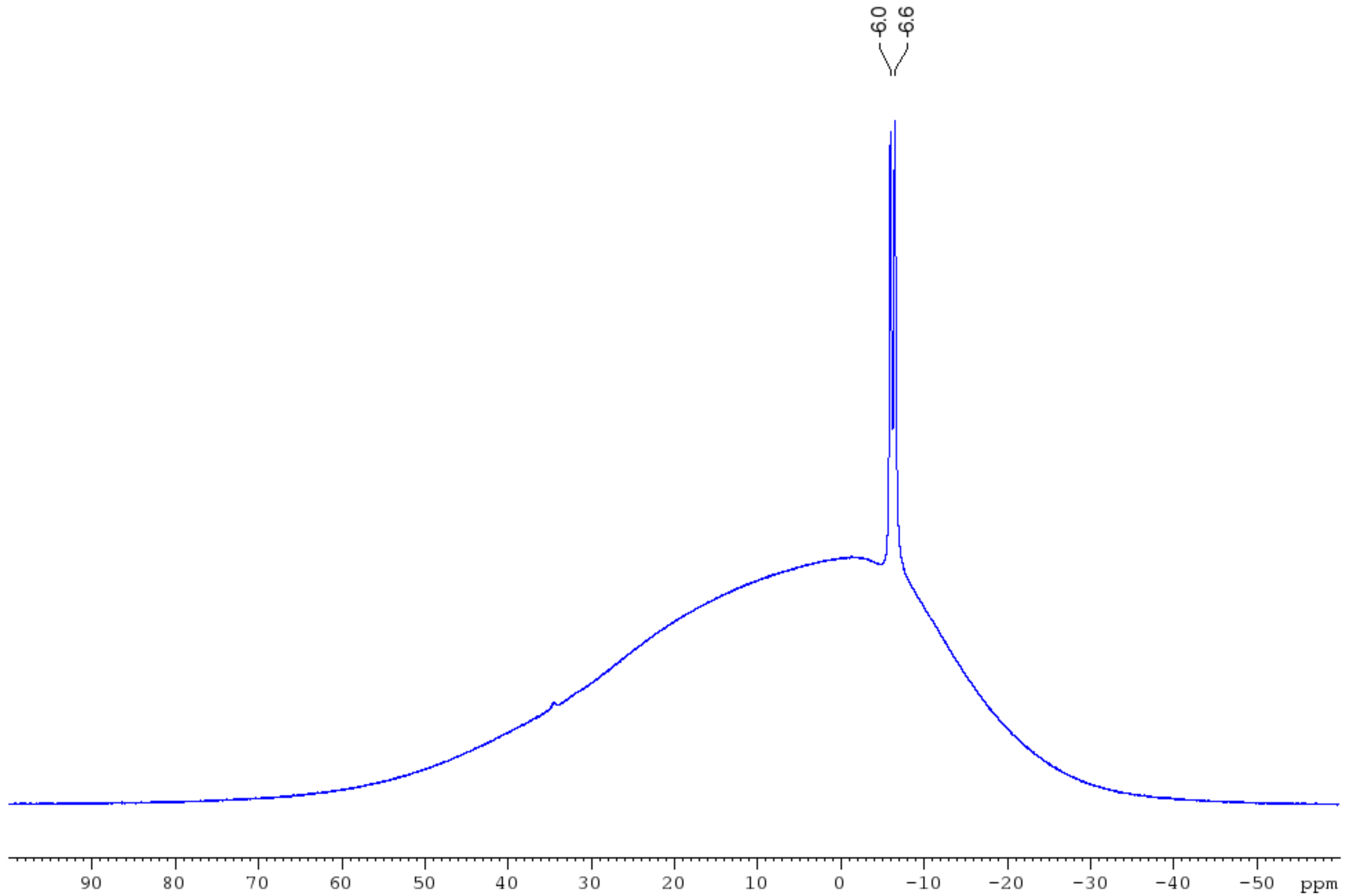

Figure S45. ^{11}B NMR spectrum of **6^H** in C_6D_6.

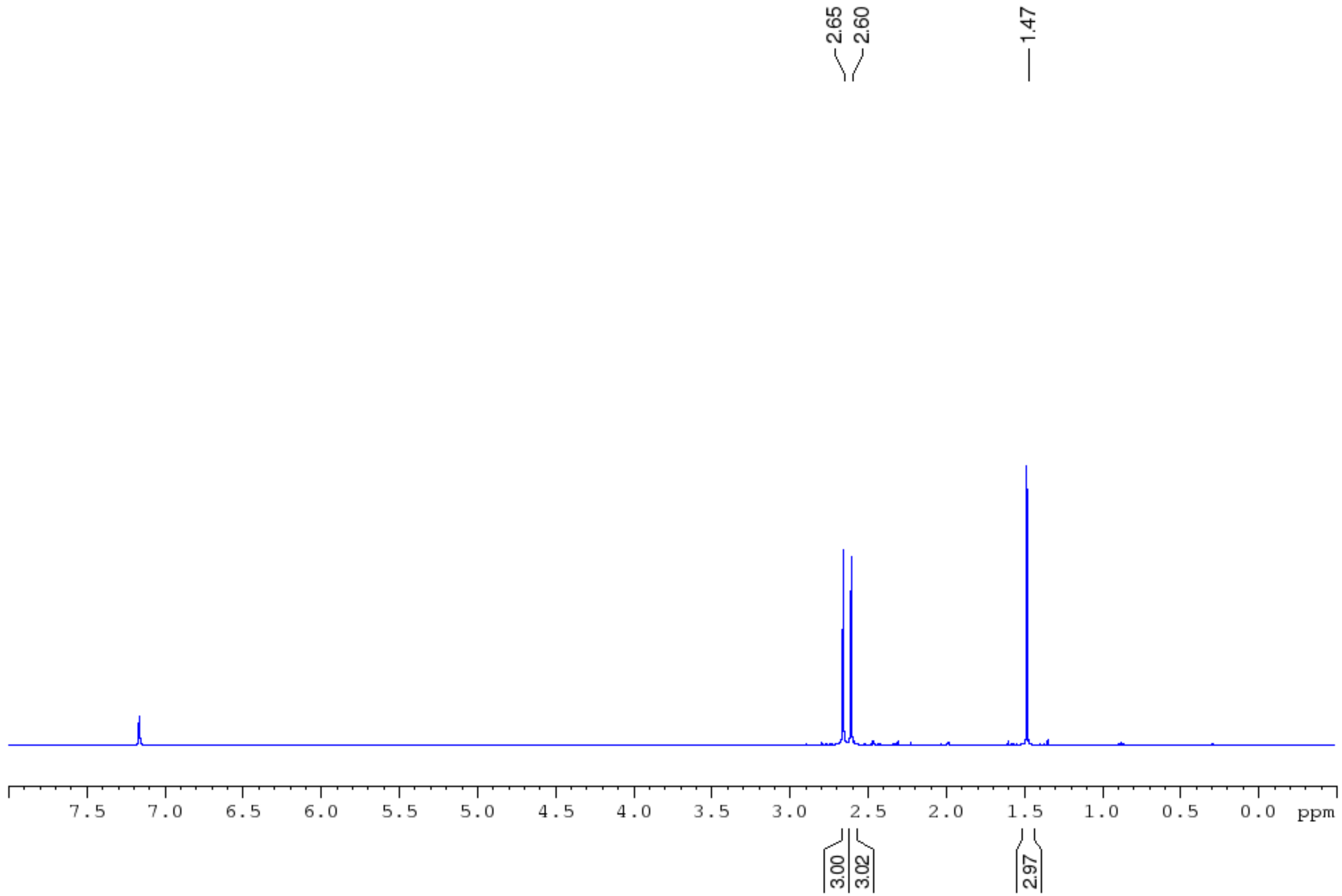

Figure S46. ^{1}H NMR spectrum of **7^{Me}-I** in C_6D_6.

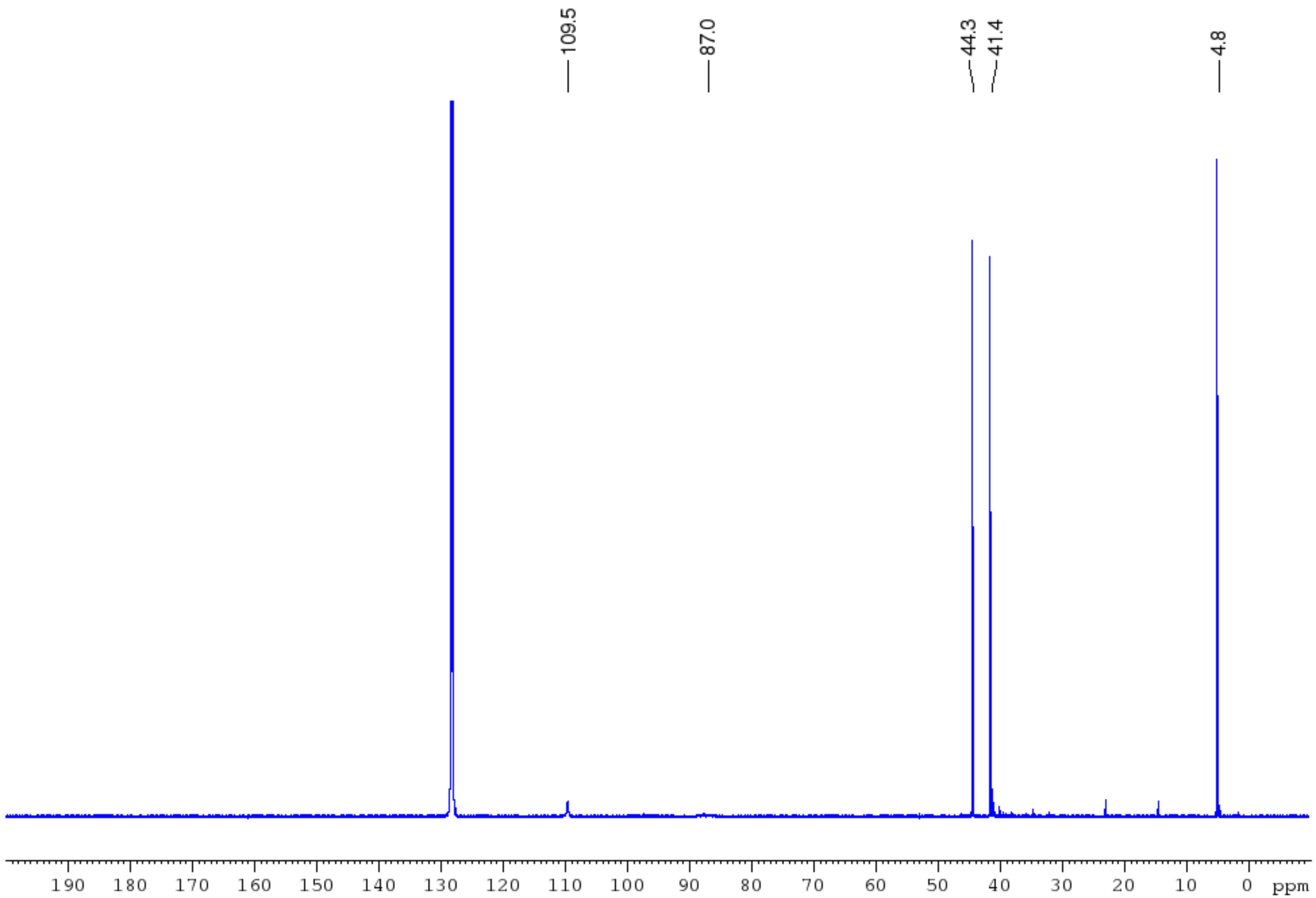

Figure S47. $^{13}C\{^1H\}$ NMR spectrum of $\mathbf{7^{Me}}$**-I** in C_6D_6.

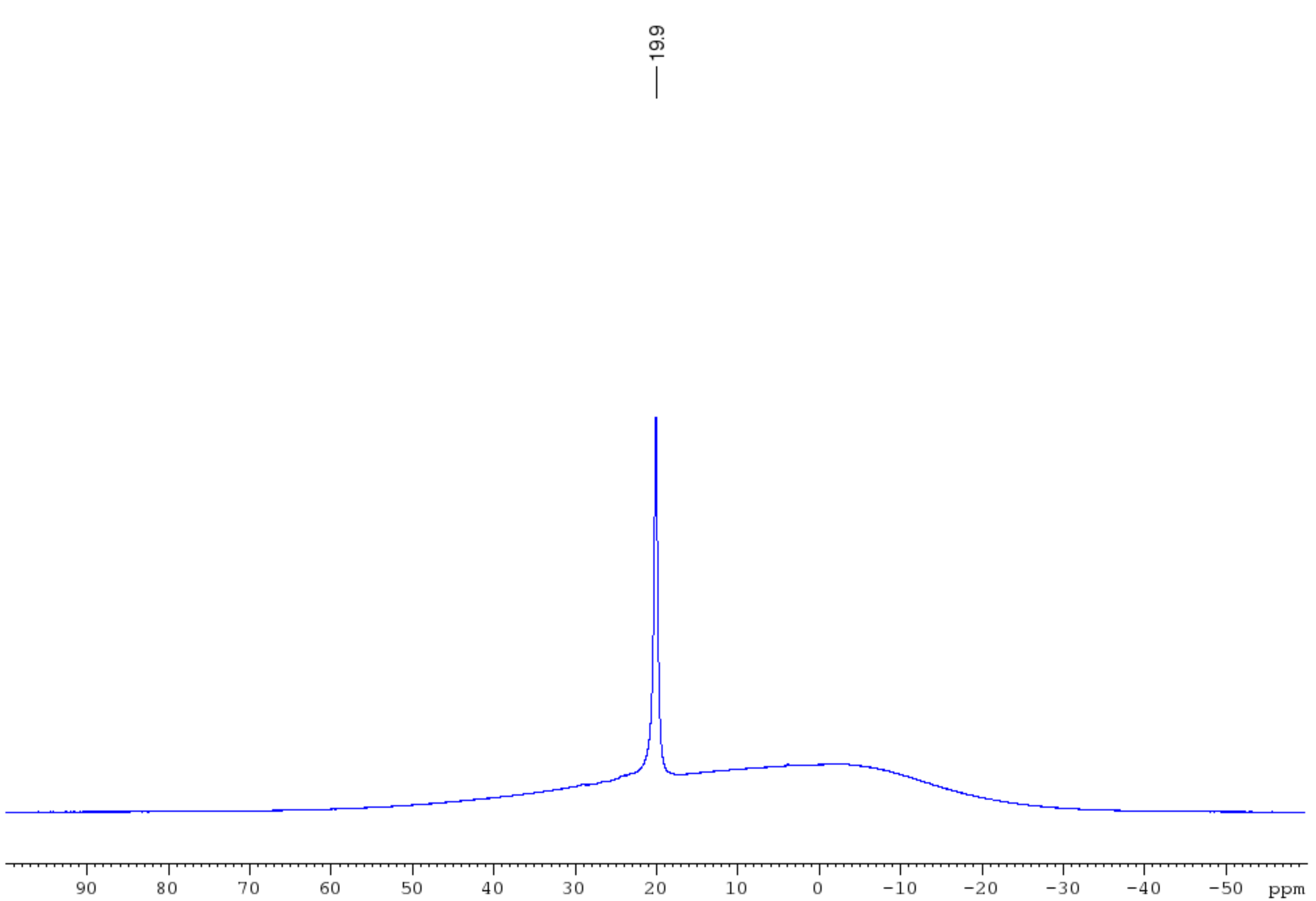

Figure S48. ^{11}B NMR spectrum of $\mathbf{7^{Me}\text{-}I}$ in C_6D_6.

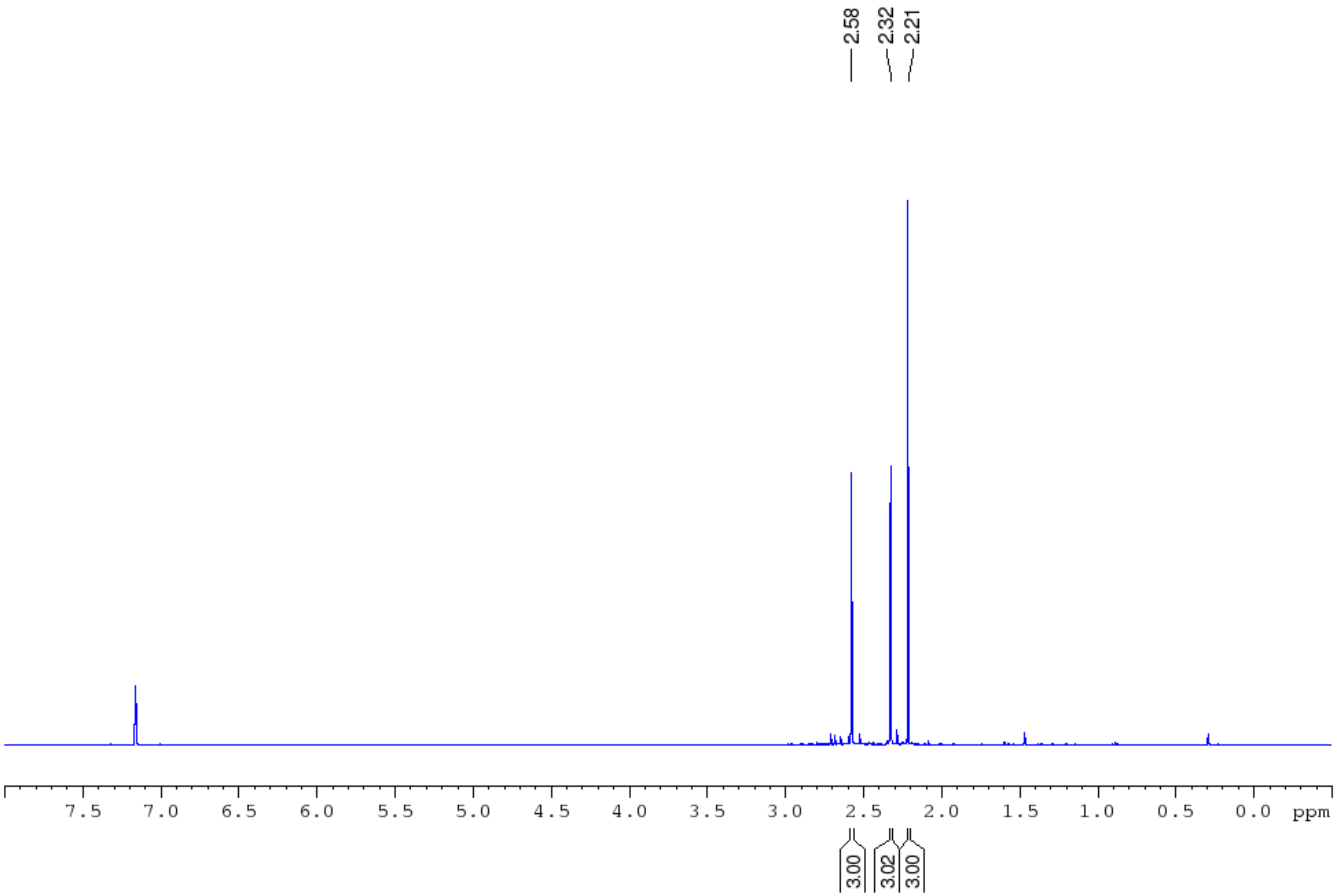

Figure S49. ^{1}H NMR spectrum of **8^{Me}-I** in C_6D_6.

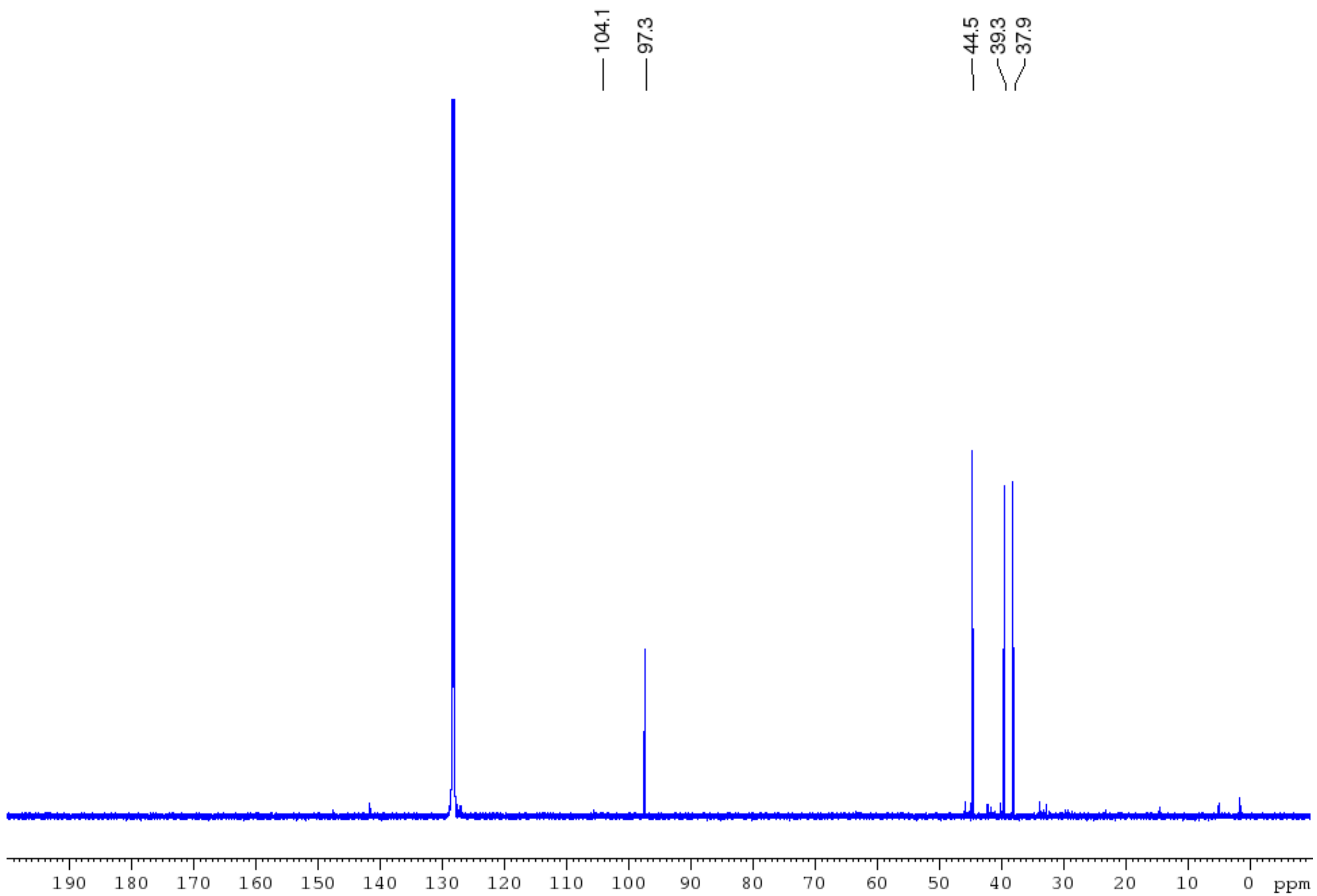

Figure S50. $^{13}C\{^1H\}$ NMR spectrum of $\mathbf{8^{Me}}$**-I** in C_6D_6.

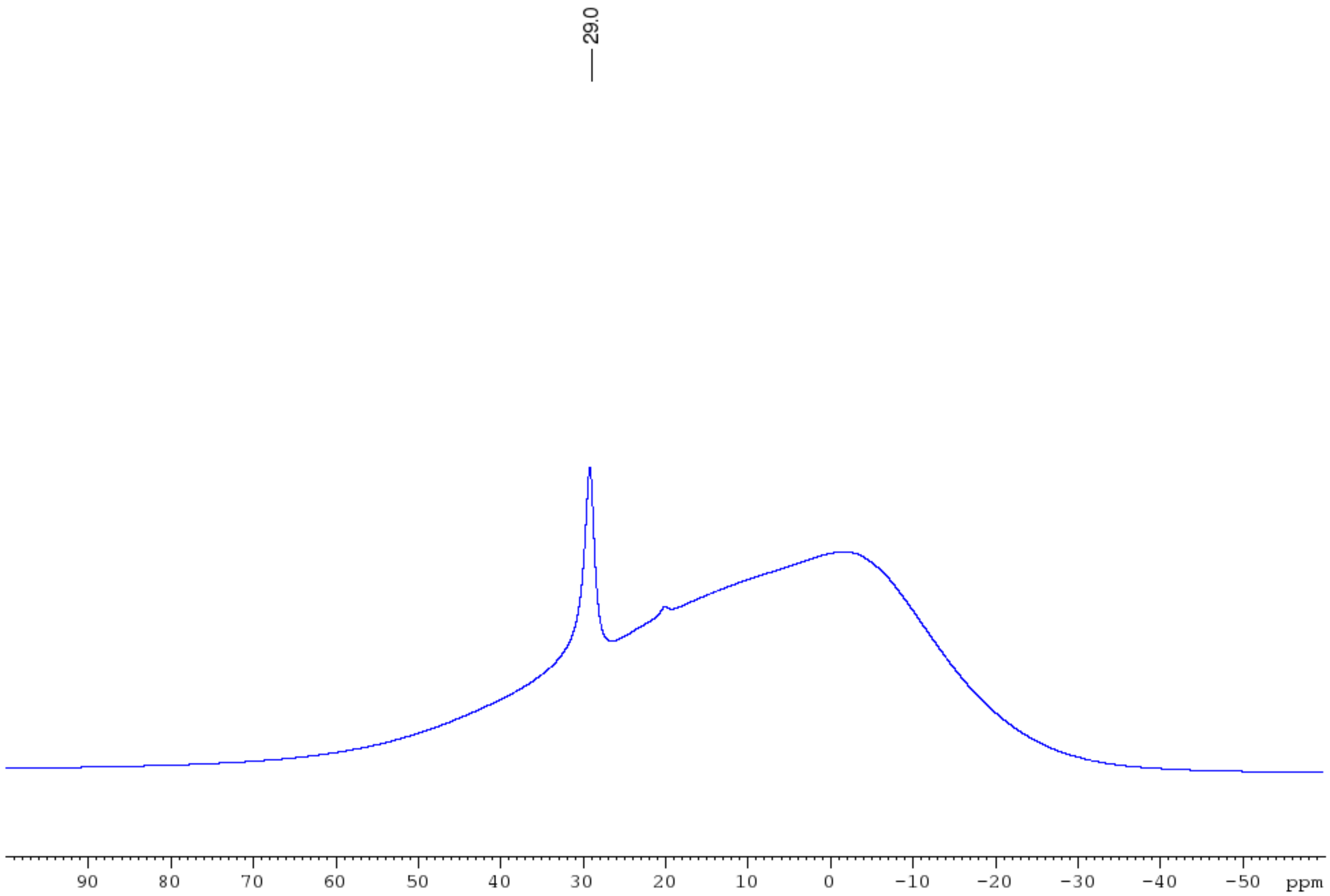

Figure S51. ^{11}B NMR spectrum of **8^{Me}-I** in C_6D_6.

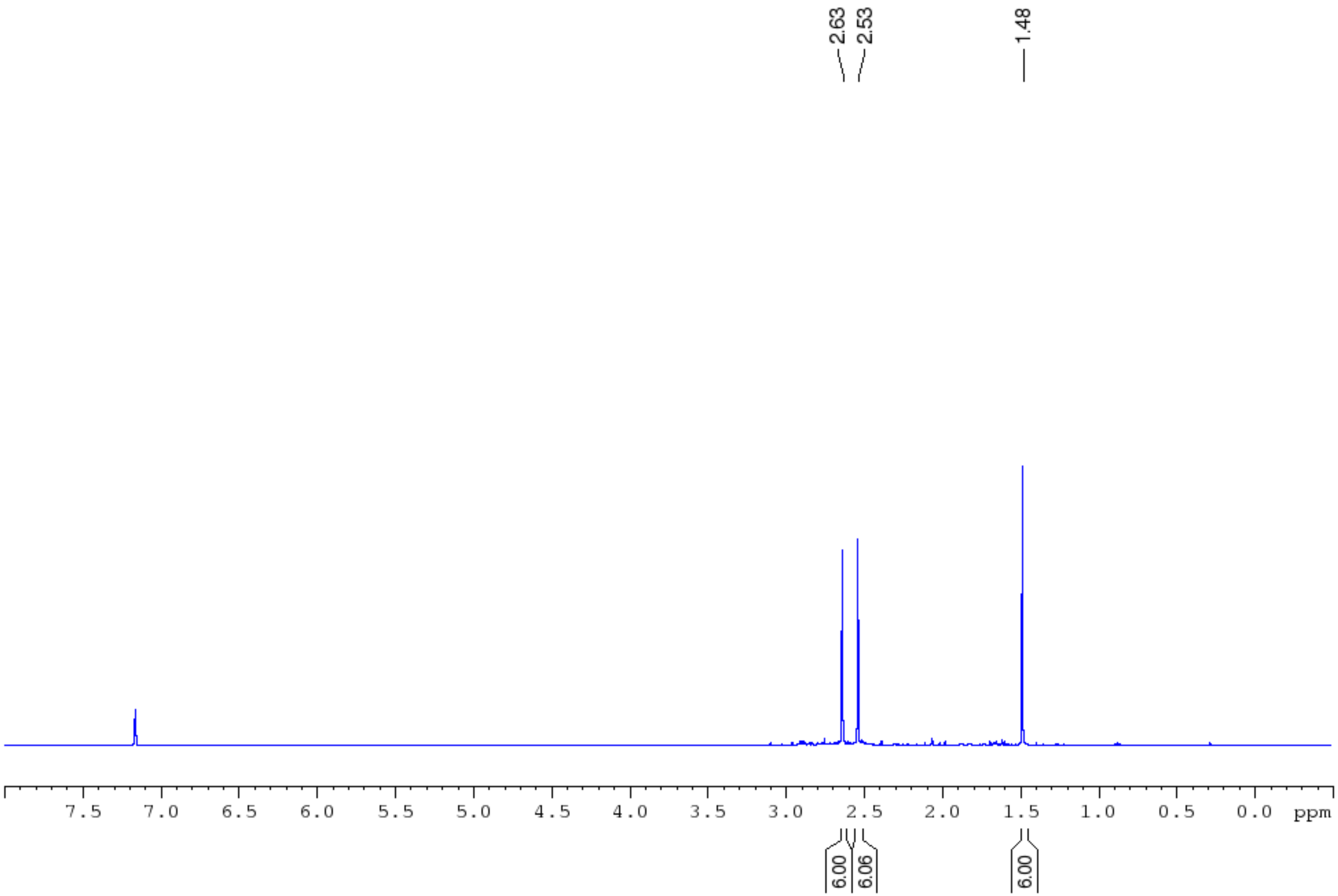

Figure S52. ^{1}H NMR spectrum of $\mathbf{7^{Me}}$**-Br** in C_6D_6.

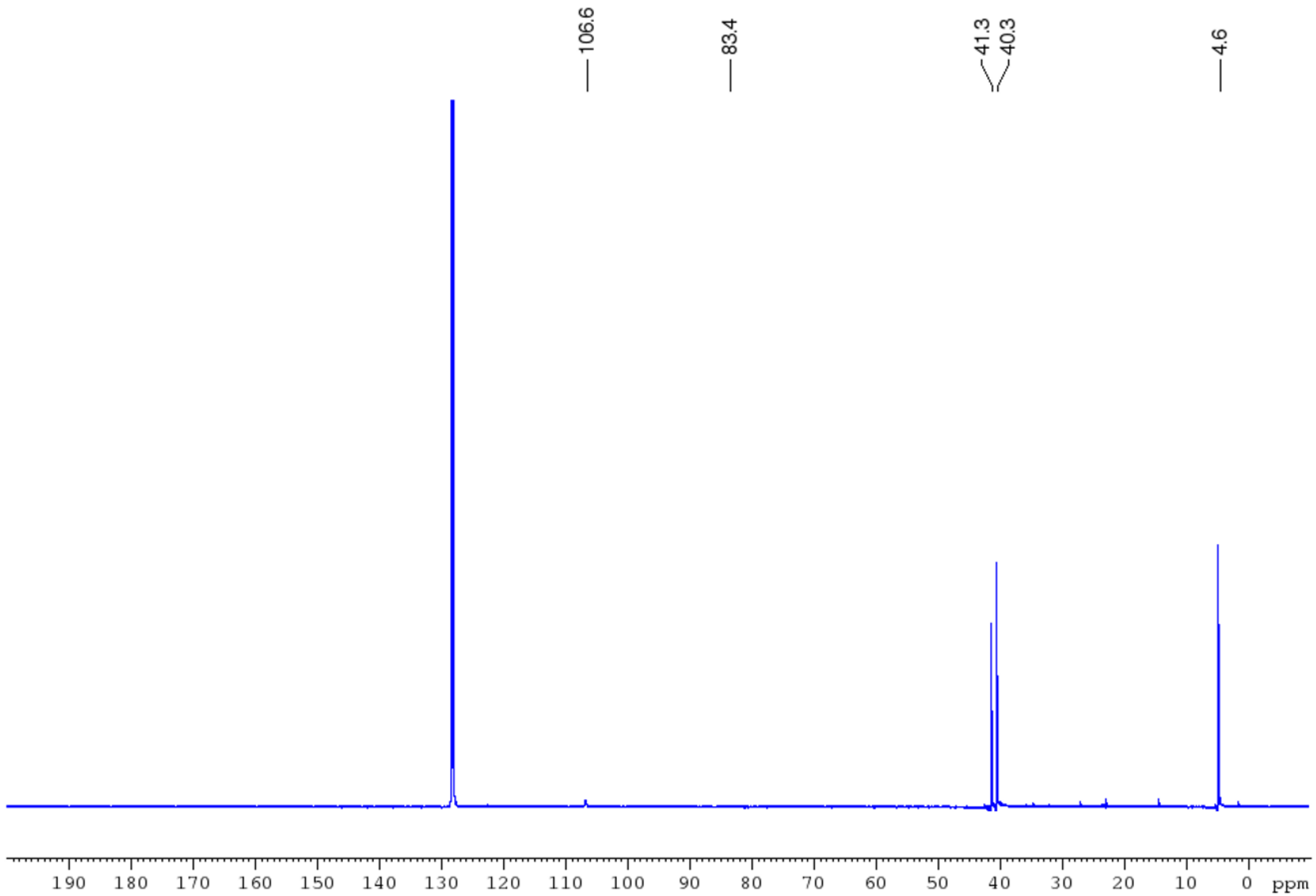

Figure S53. $^{13}C\{^1H\}$ NMR spectrum of **7^{Me}-Br** in C_6D_6.

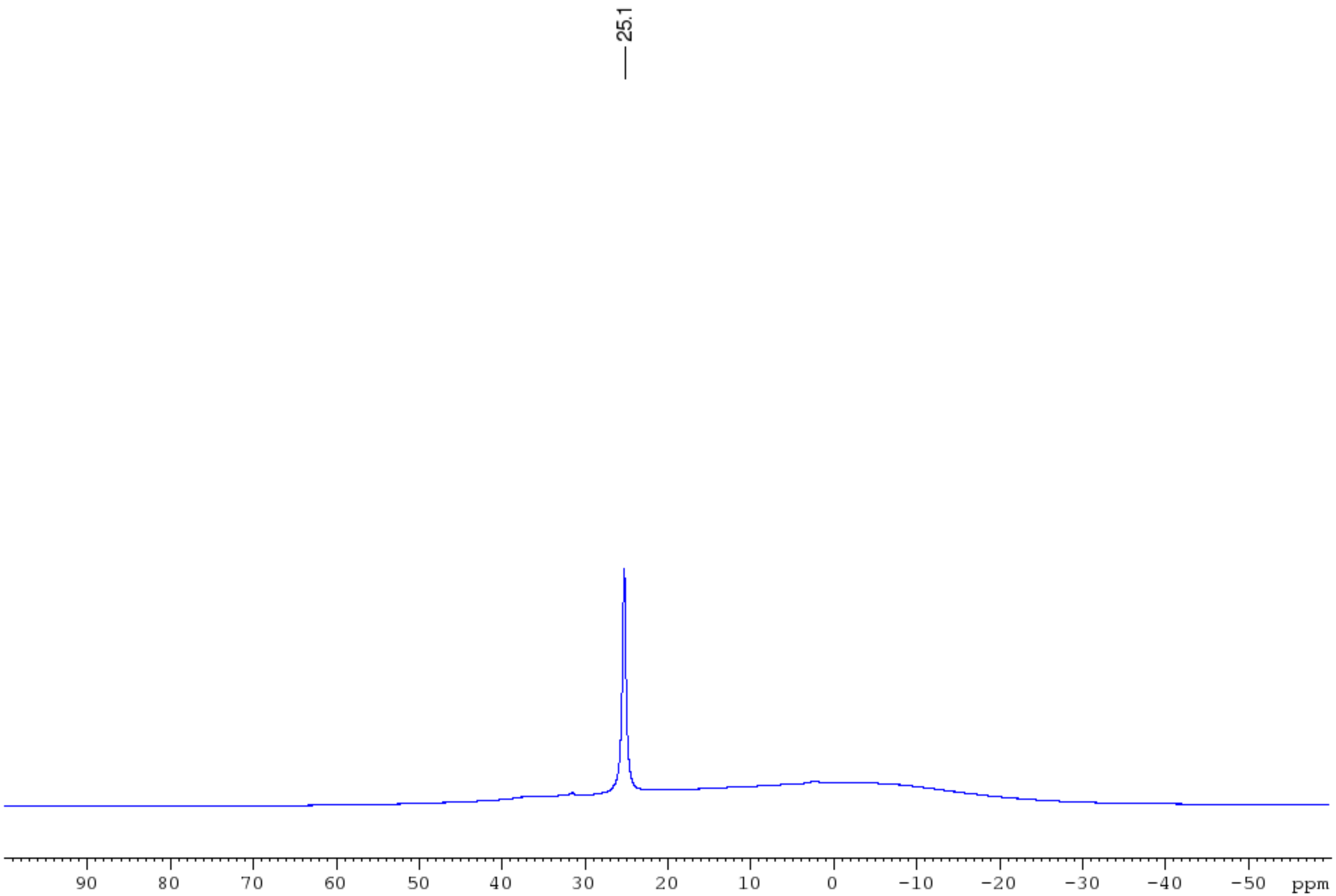

Figure S54. ^{11}B NMR spectrum of **7^{Me}-Br** in C_6D_6.

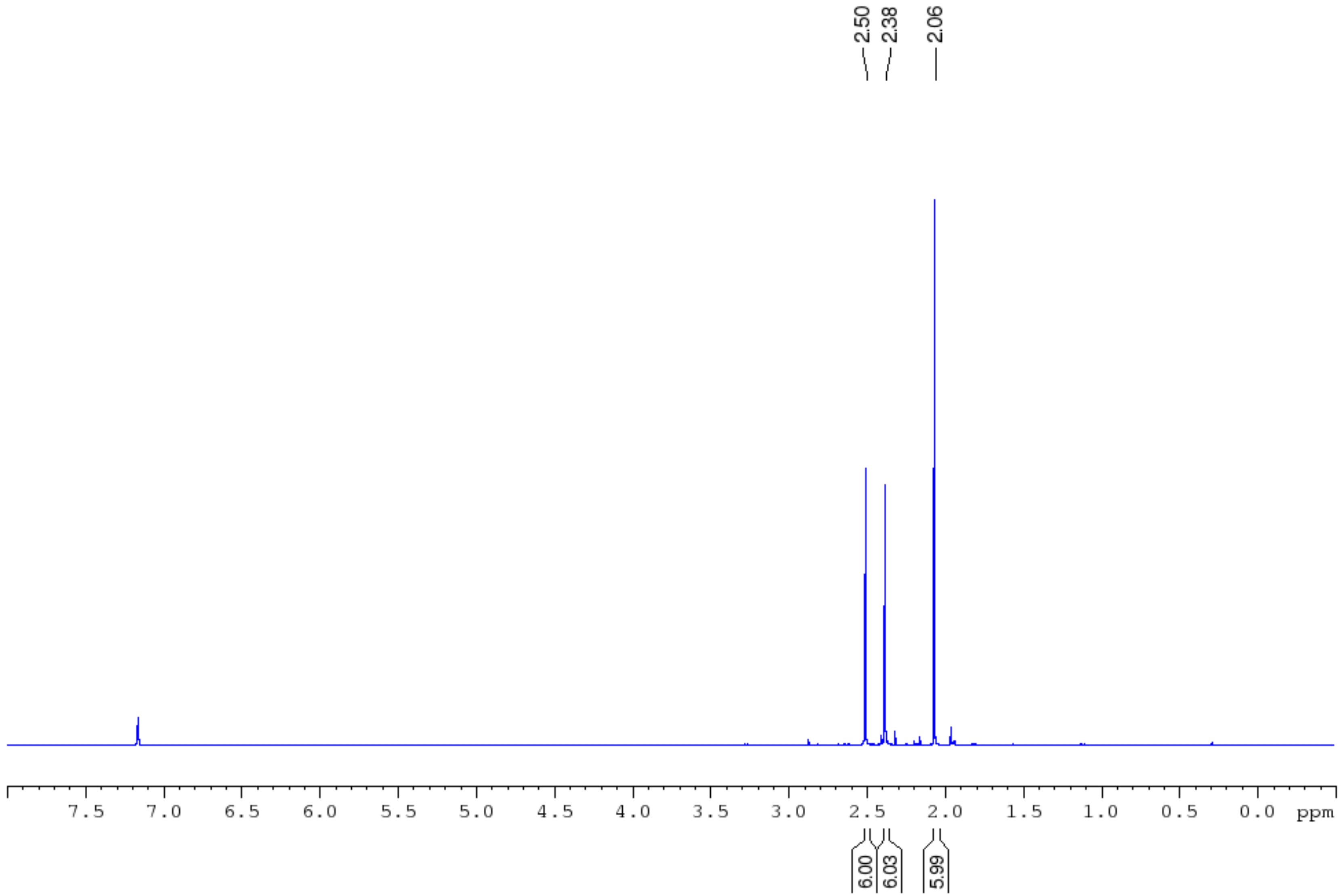

Figure S55. ^{1}H NMR spectrum of **8^{Me}-Br** in C_6D_6.

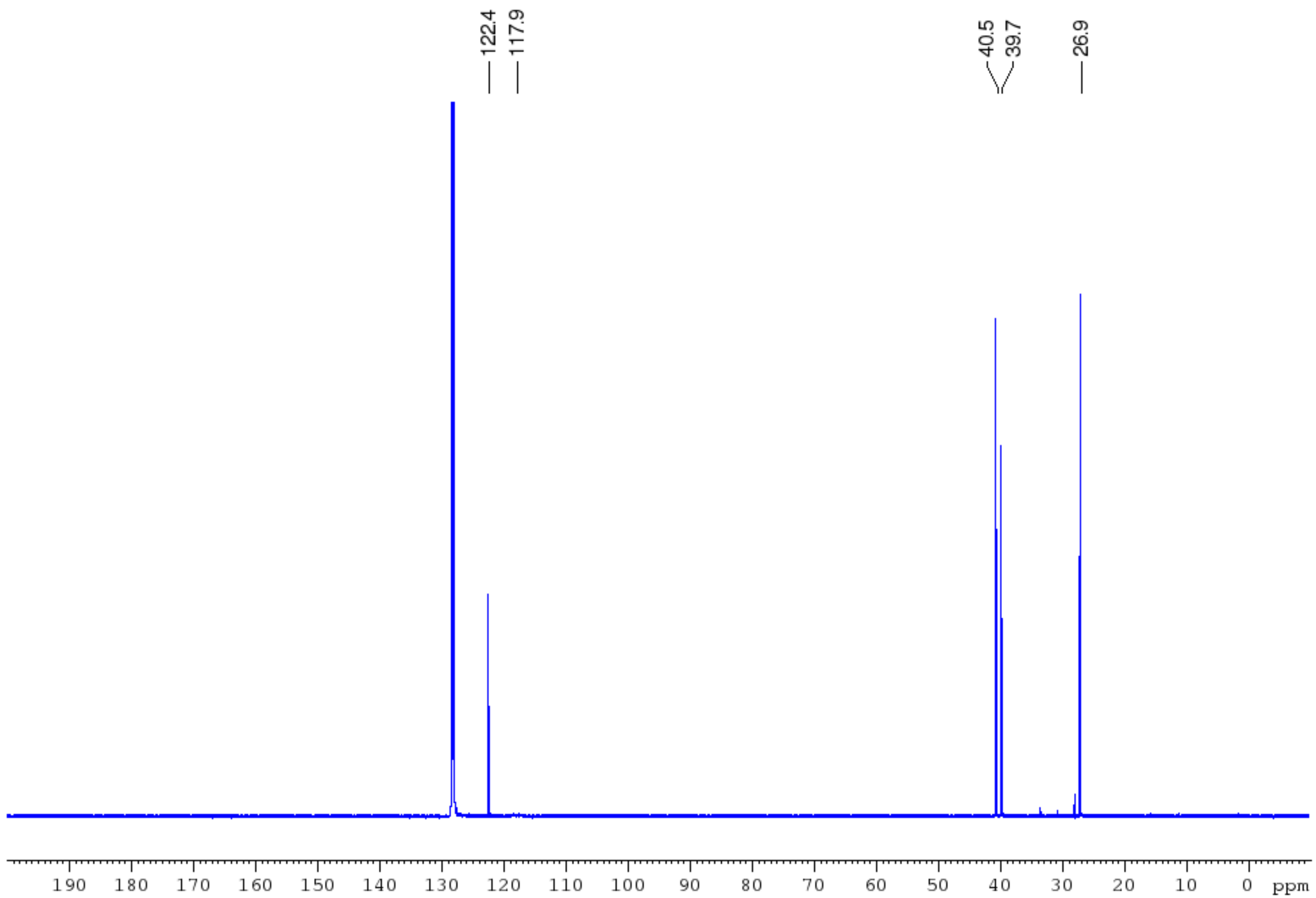

Figure S56. $^{13}C\{^1H\}$ NMR spectrum of **8^Me^-Br** in C_6D_6.

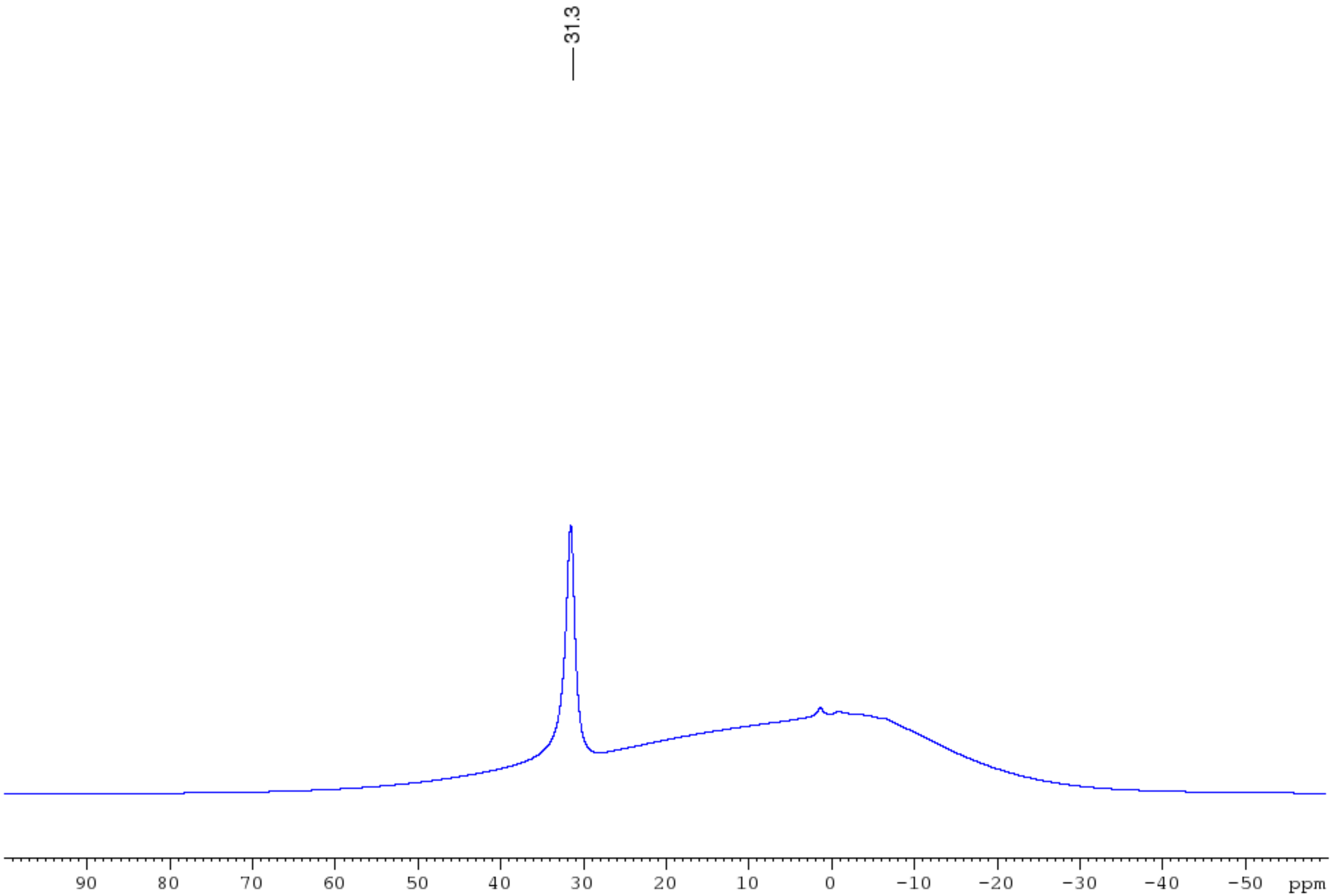

Figure S57. ^{11}B NMR spectrum of **8^{Me}-Br** in C_6D_6. The resonance around 0.9 ppm (ca. 3%) is likely the dimerisation product **[8^{Me}-Br]$_2$**.

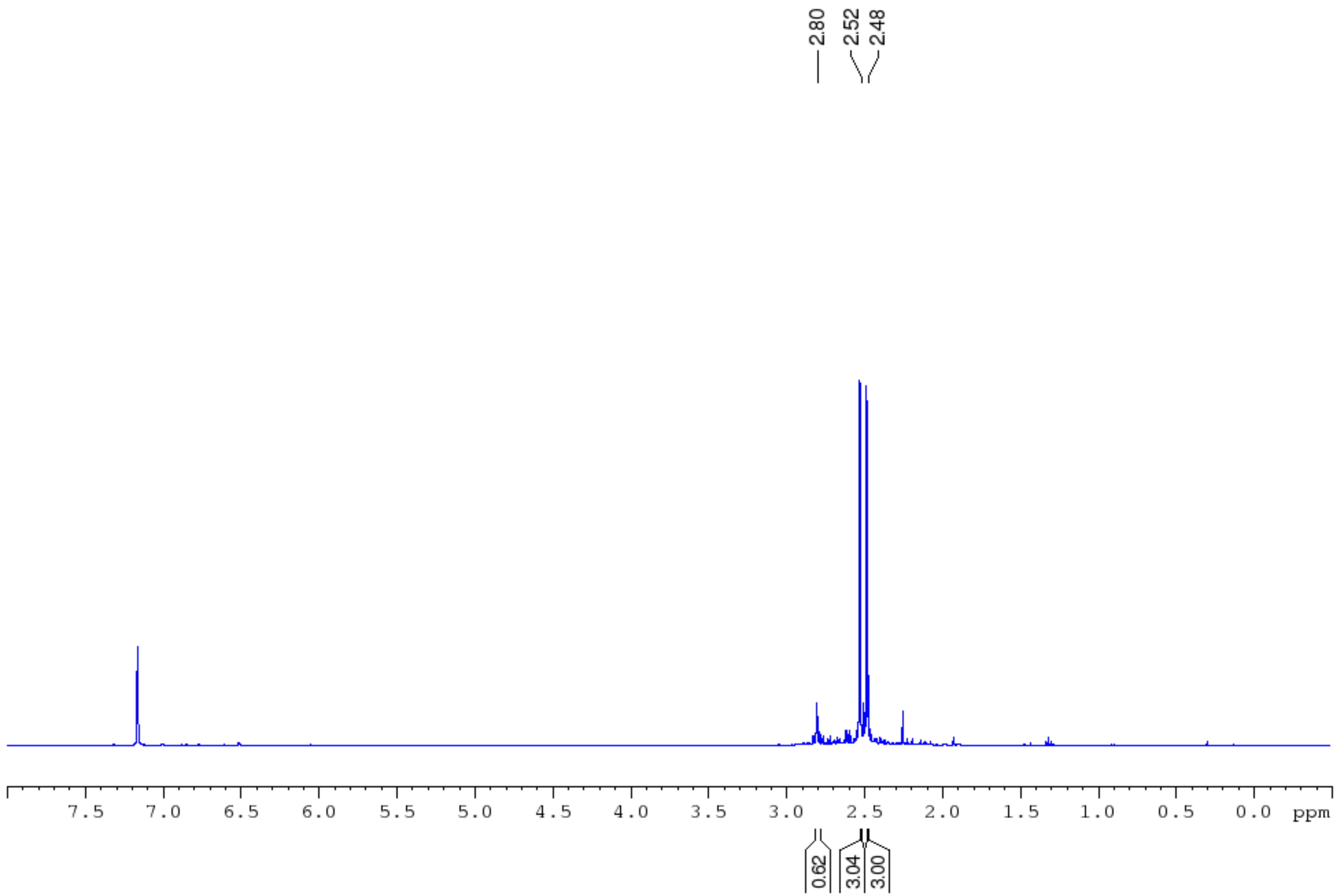

Figure S58. ^{1}H NMR spectrum of **7$^{\mathbf{H}}$-I** in C_6D_6.

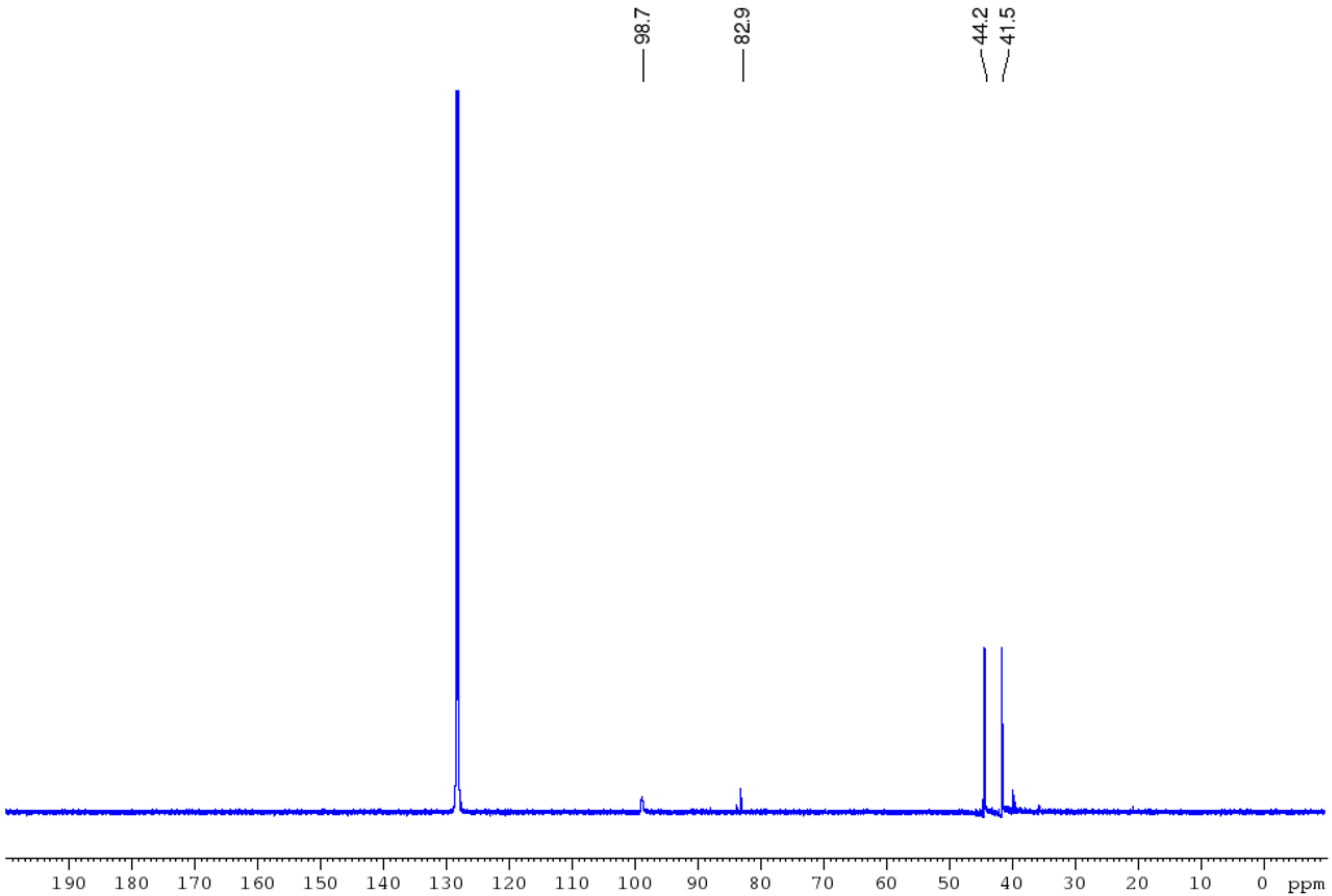

Figure S59. $^{13}C\{^{1}H\}$ NMR spectrum of $\mathbf{7^{H}}$**-I** in C_6D_6.

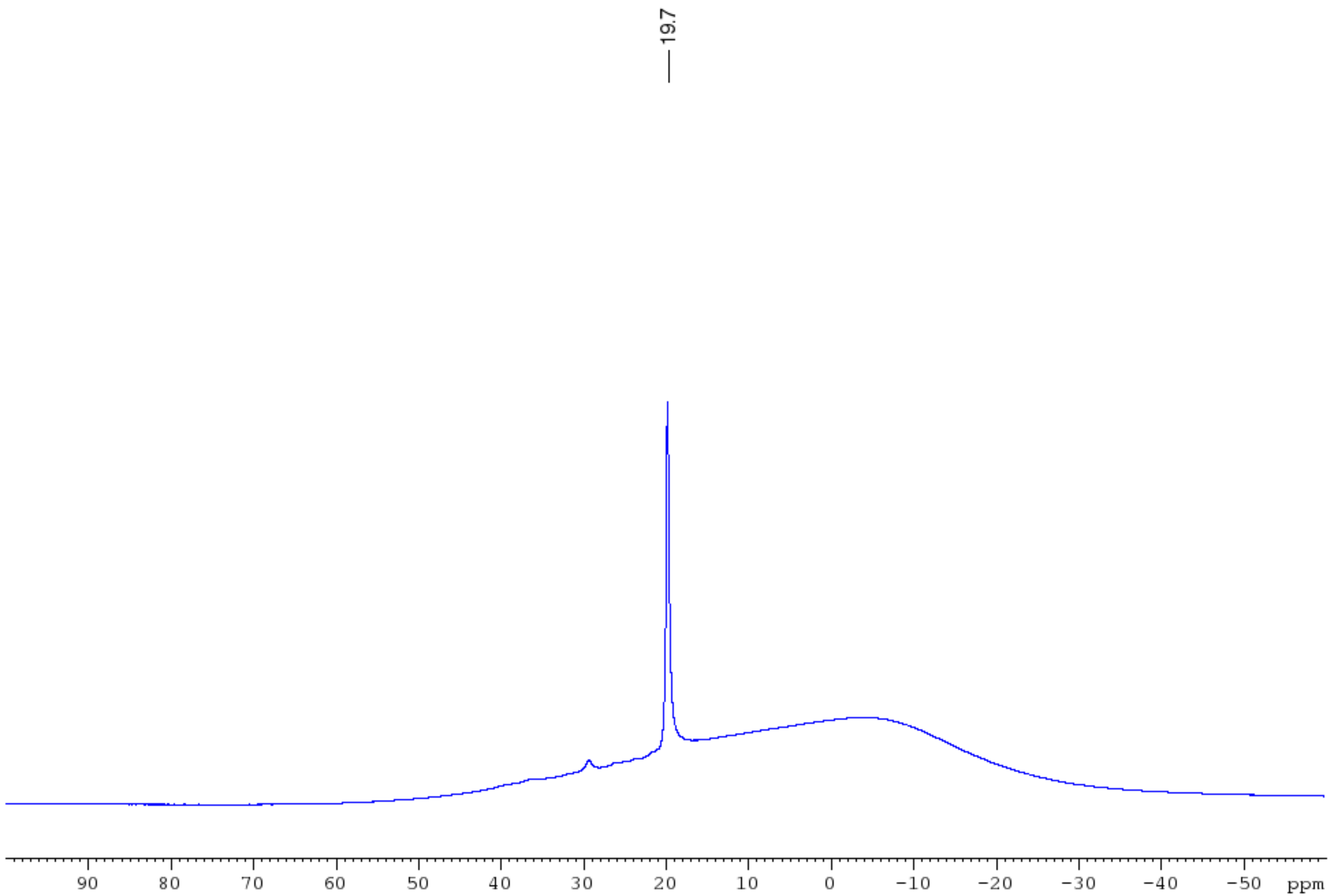

Figure S60. ^{11}B NMR spectrum of **7^H-I** in C_6D_6.

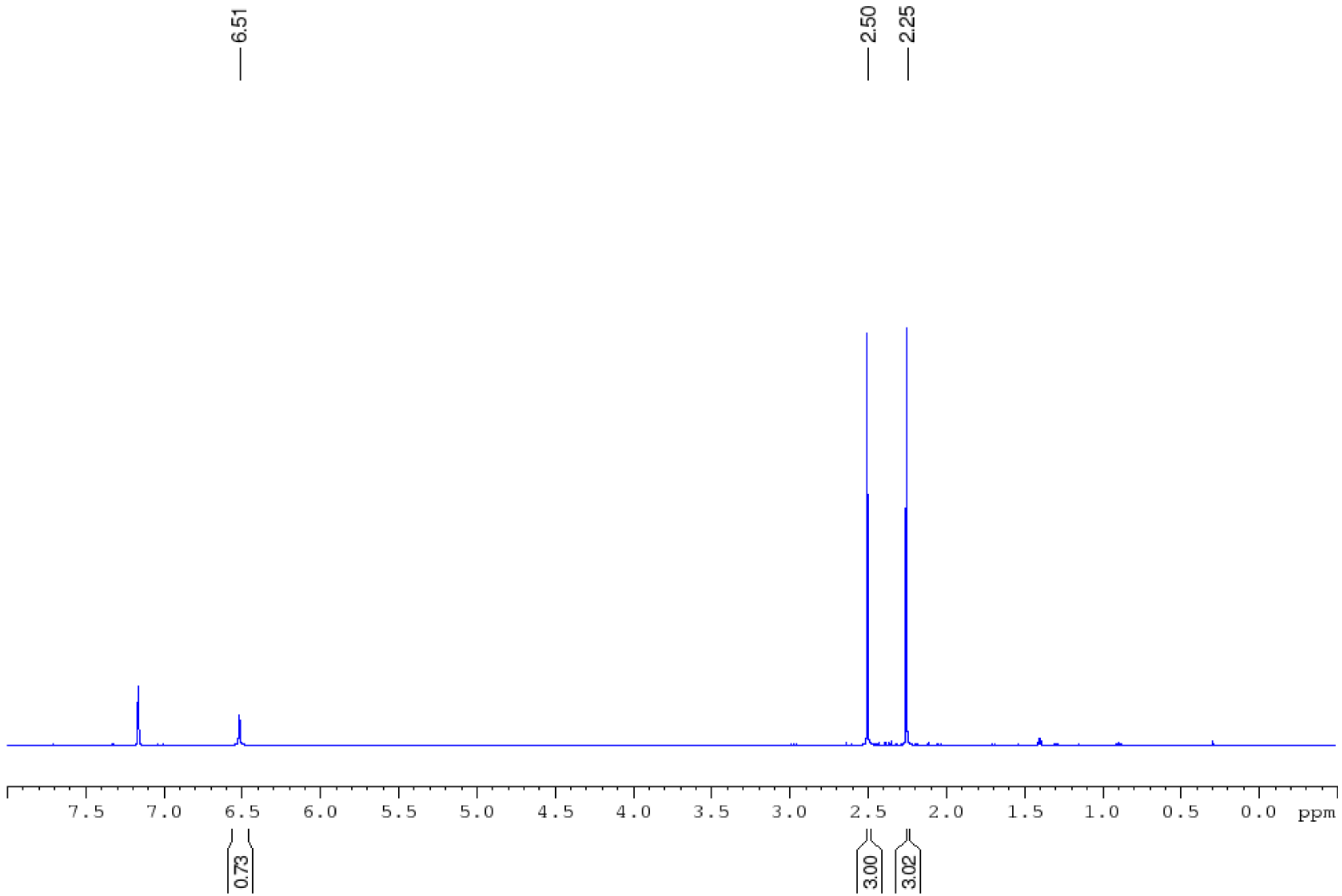

Figure S61. ^{1}H NMR spectrum of **8^{H}-I** in C_6D_6.

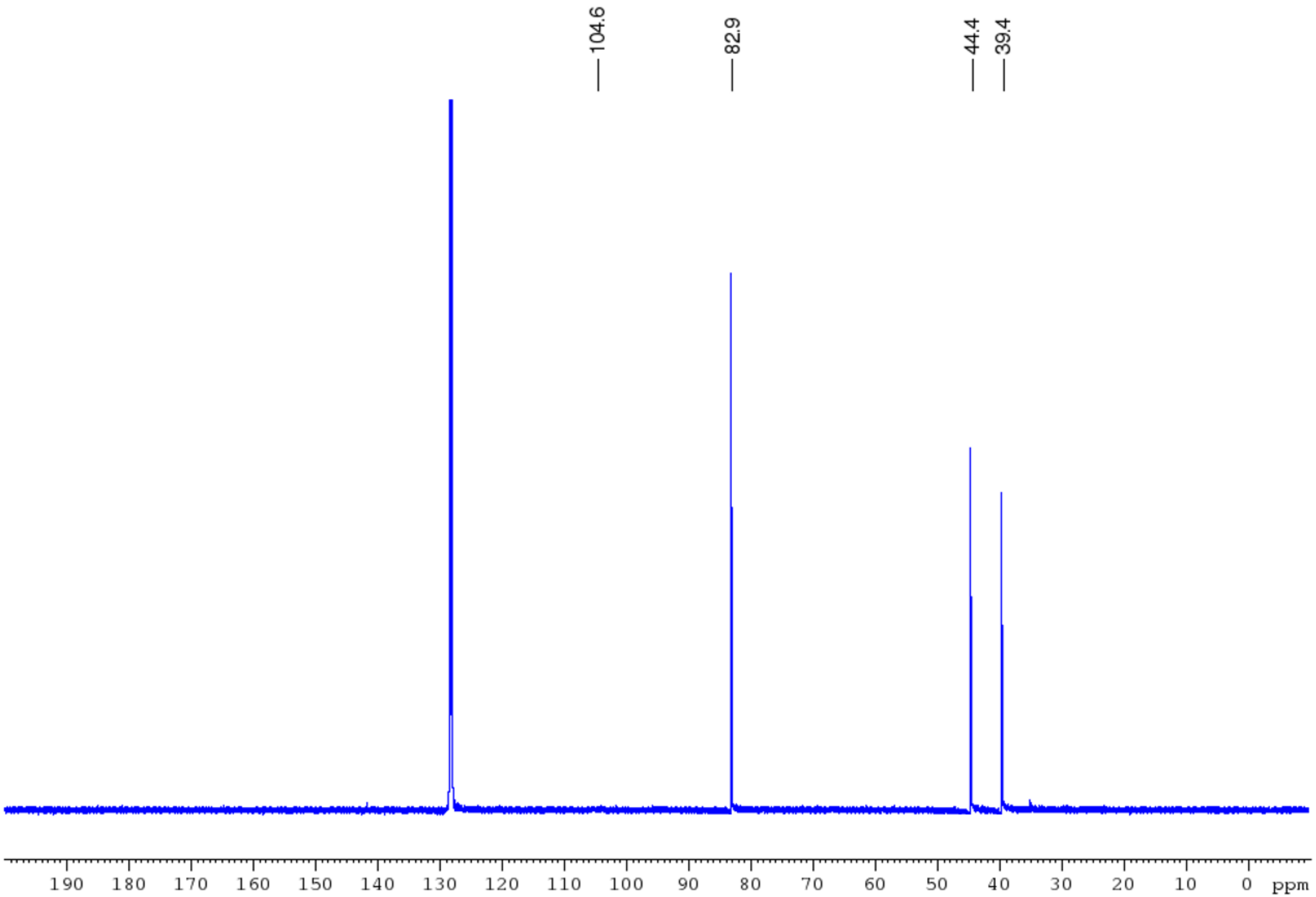

Figure S62. $^{13}C\{^1H\}$ NMR spectrum of **8^H-I** in C_6D_6.

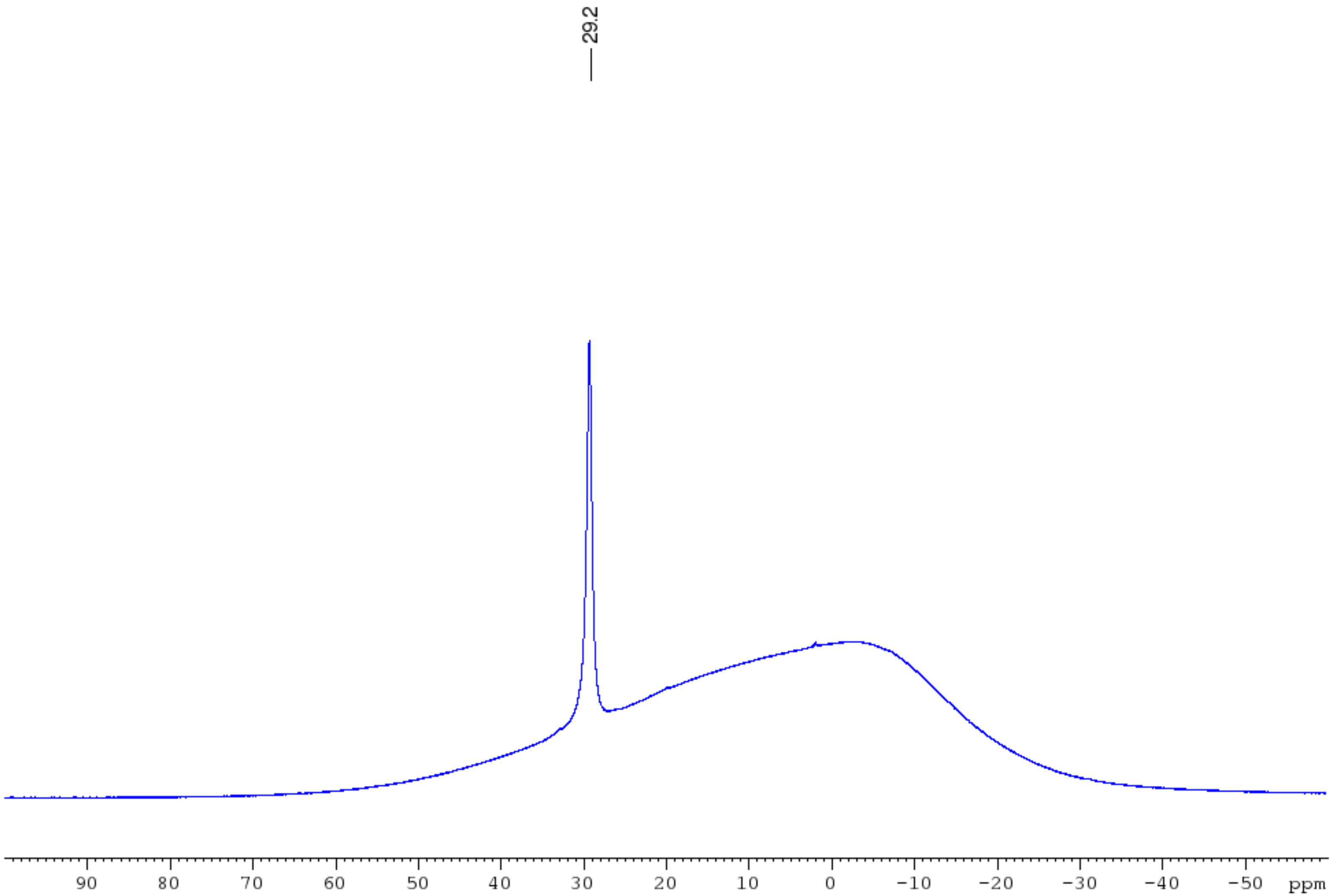

Figure S63. ^{11}B NMR spectrum of **8^H-I** in C_6D_6.

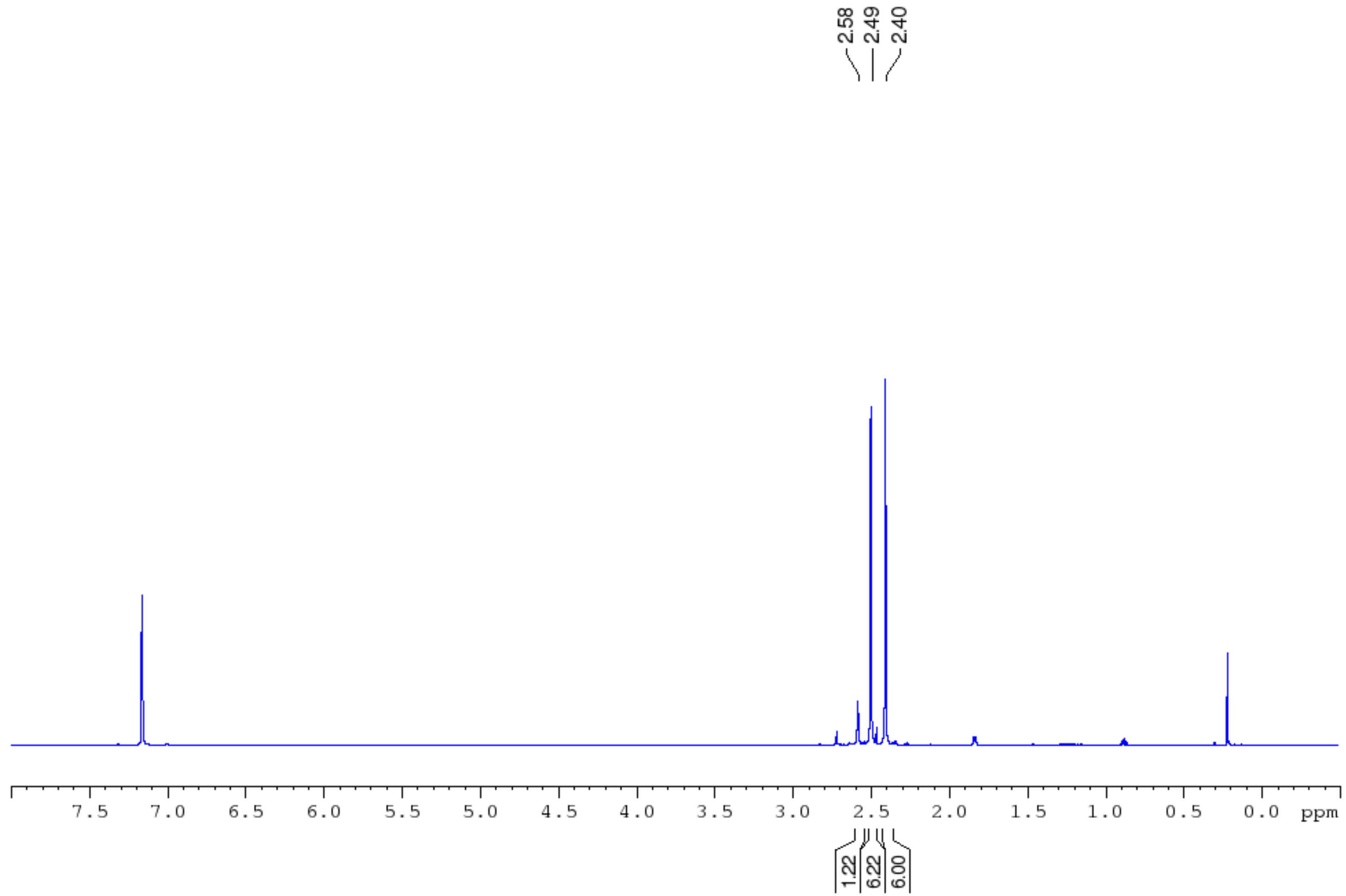

Figure S64. ^{1}H NMR spectrum of **7^{H}-Br** in C_6D_6.

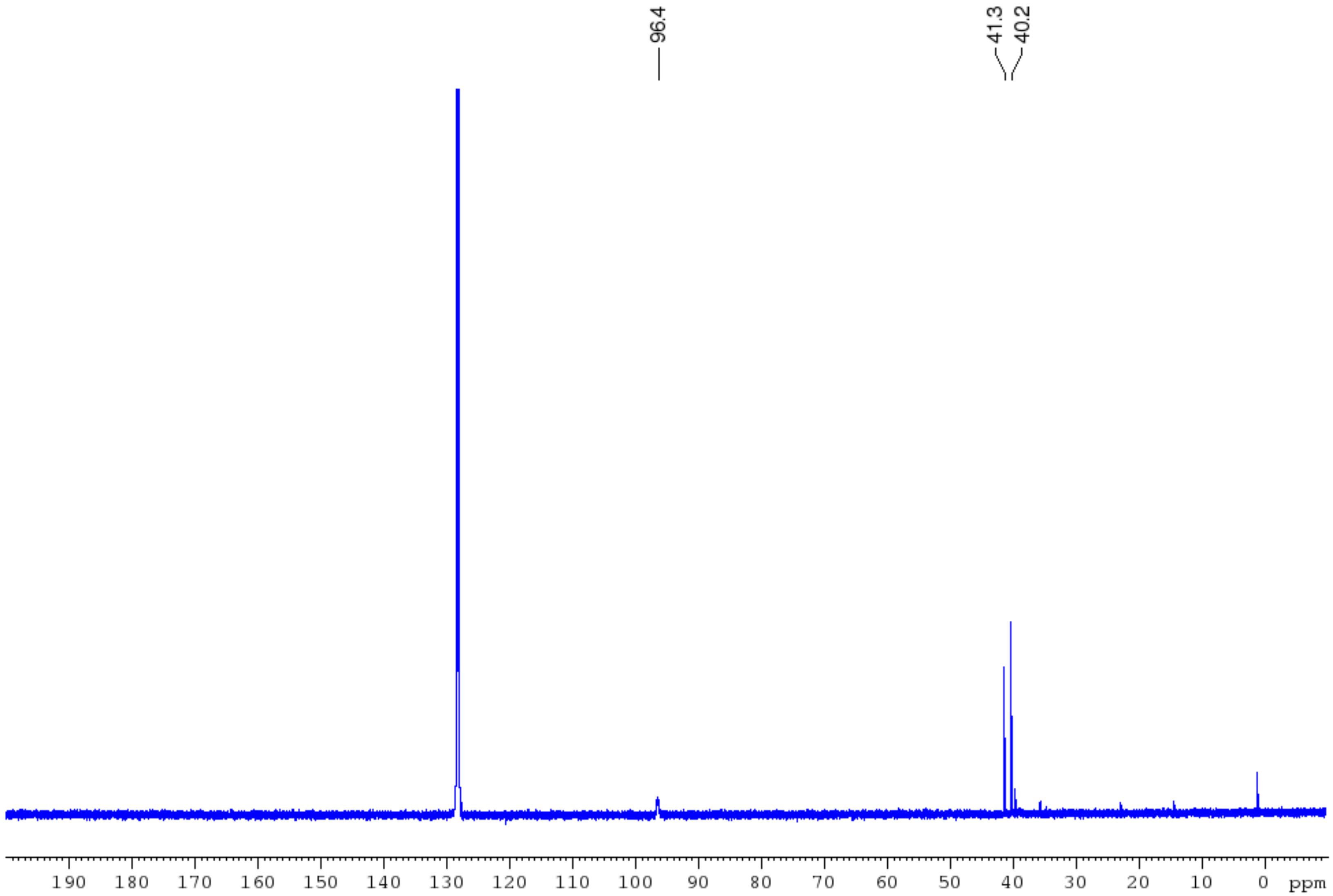

Figure S65. $^{13}C\{^{1}H\}$ NMR spectrum of **7^{H}-Br** in C_6D_6.

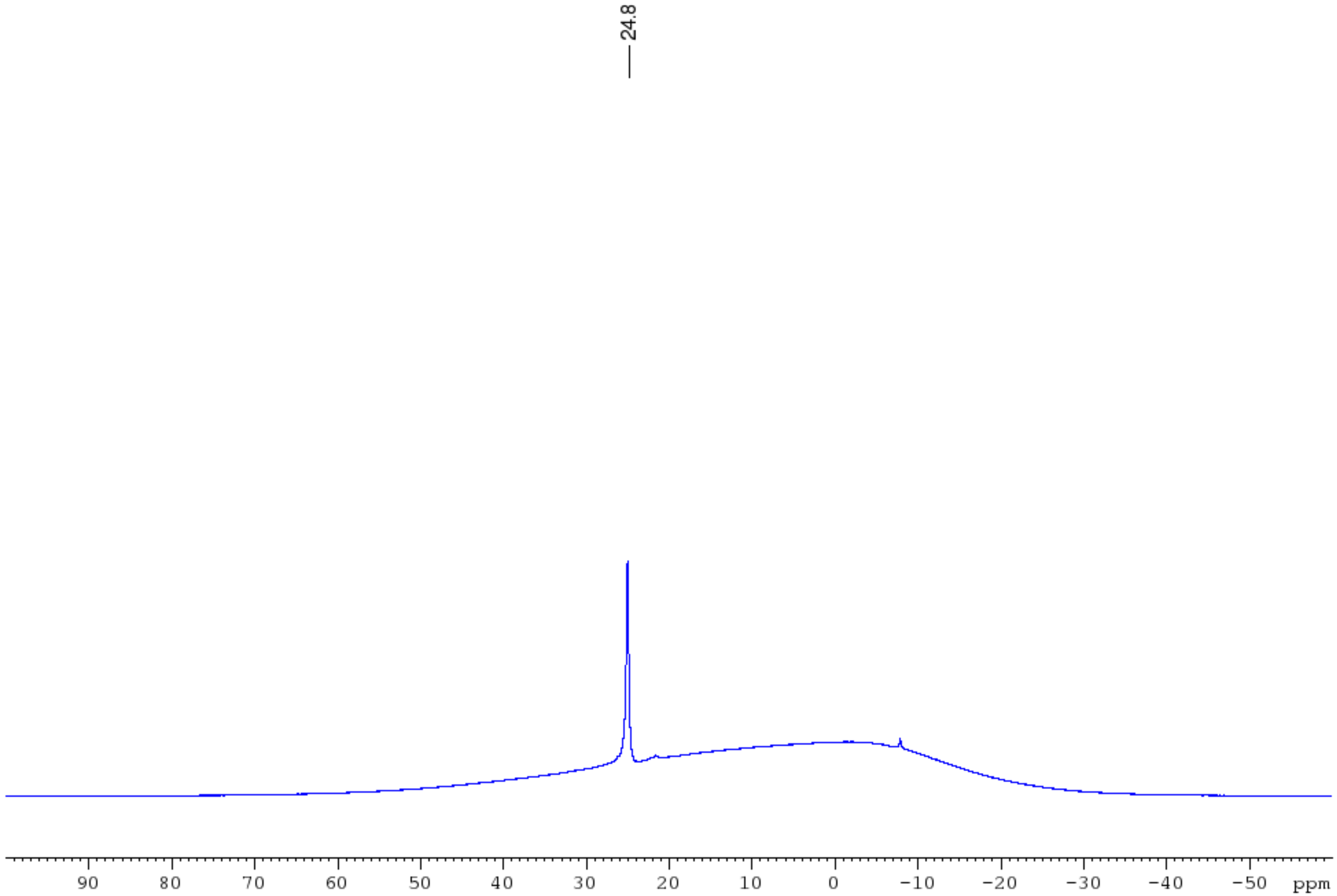

Figure S66. ^{11}B NMR spectrum of **7^{H}-Br** in C_6D_6.

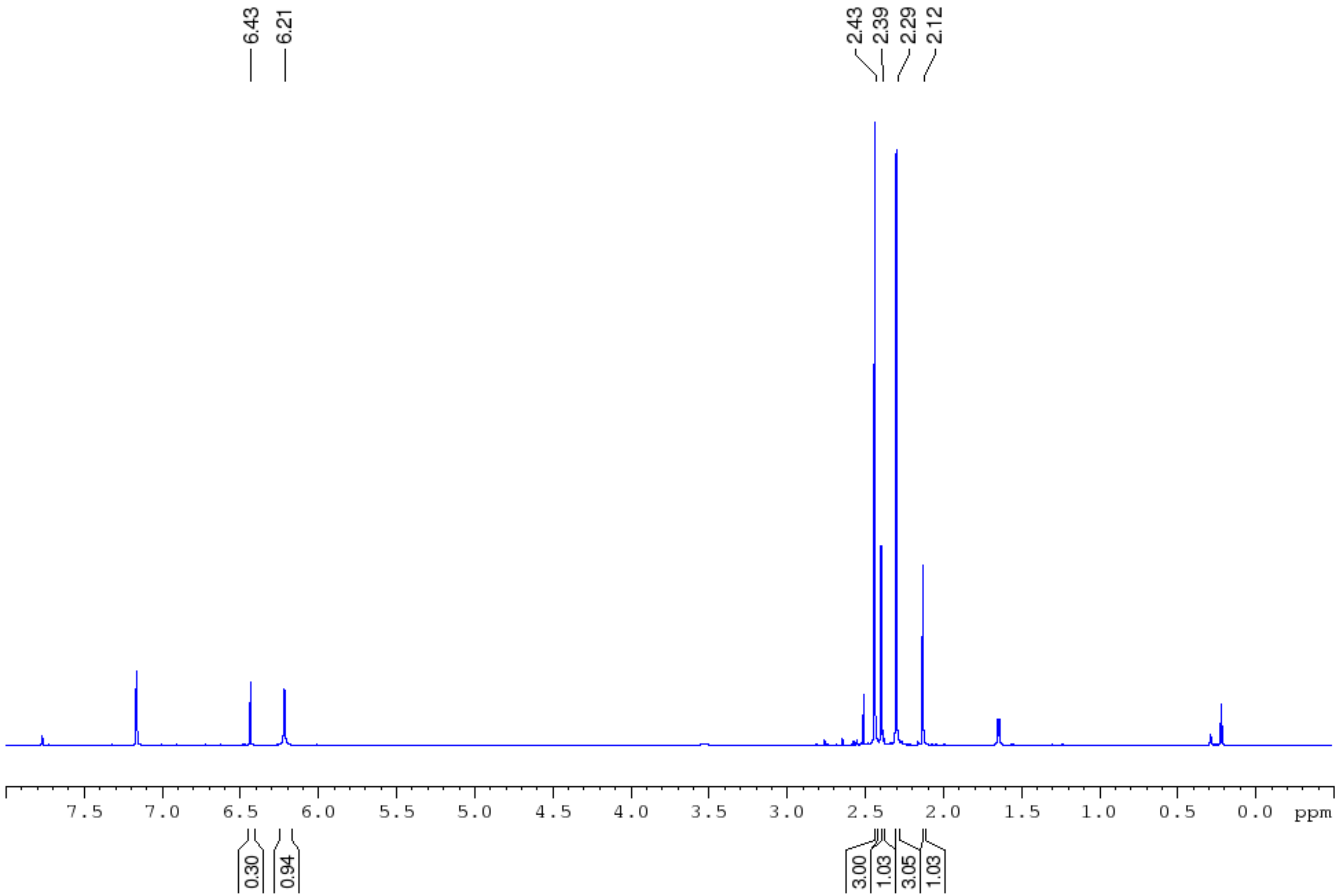

Figure S67. [1]H NMR spectrum of the 3:1 mixture of ***(E)*****-** and ***(Z)*****-8$^{\mathbf{H}}$-Br** in C_6D_6.

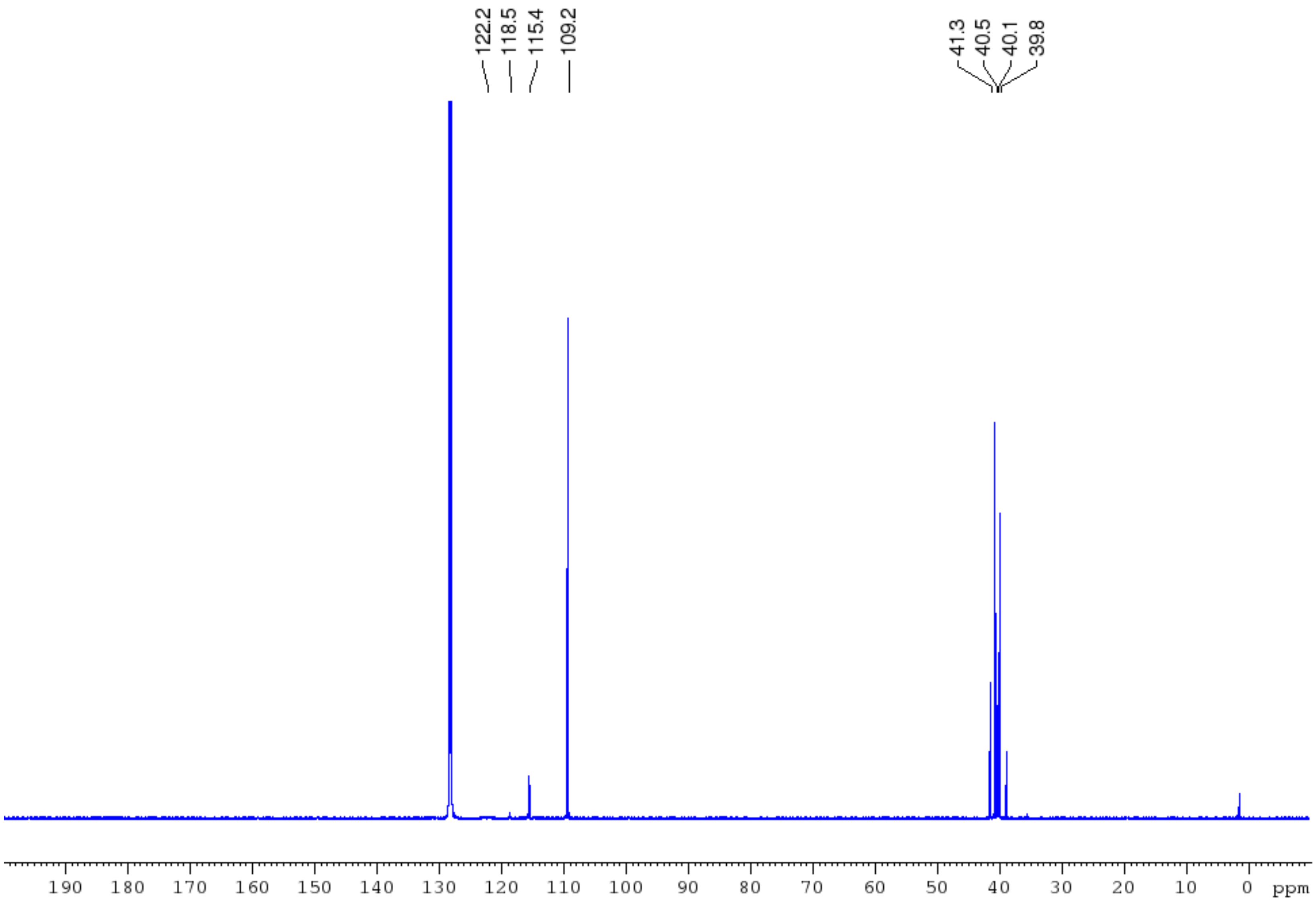

Figure S68. $^{13}C\{^{1}H\}$ NMR spectrum of the 3:1 mixture of **(*E*)-** and **(*Z*)-8^{H}-Br** in C_6D_6.

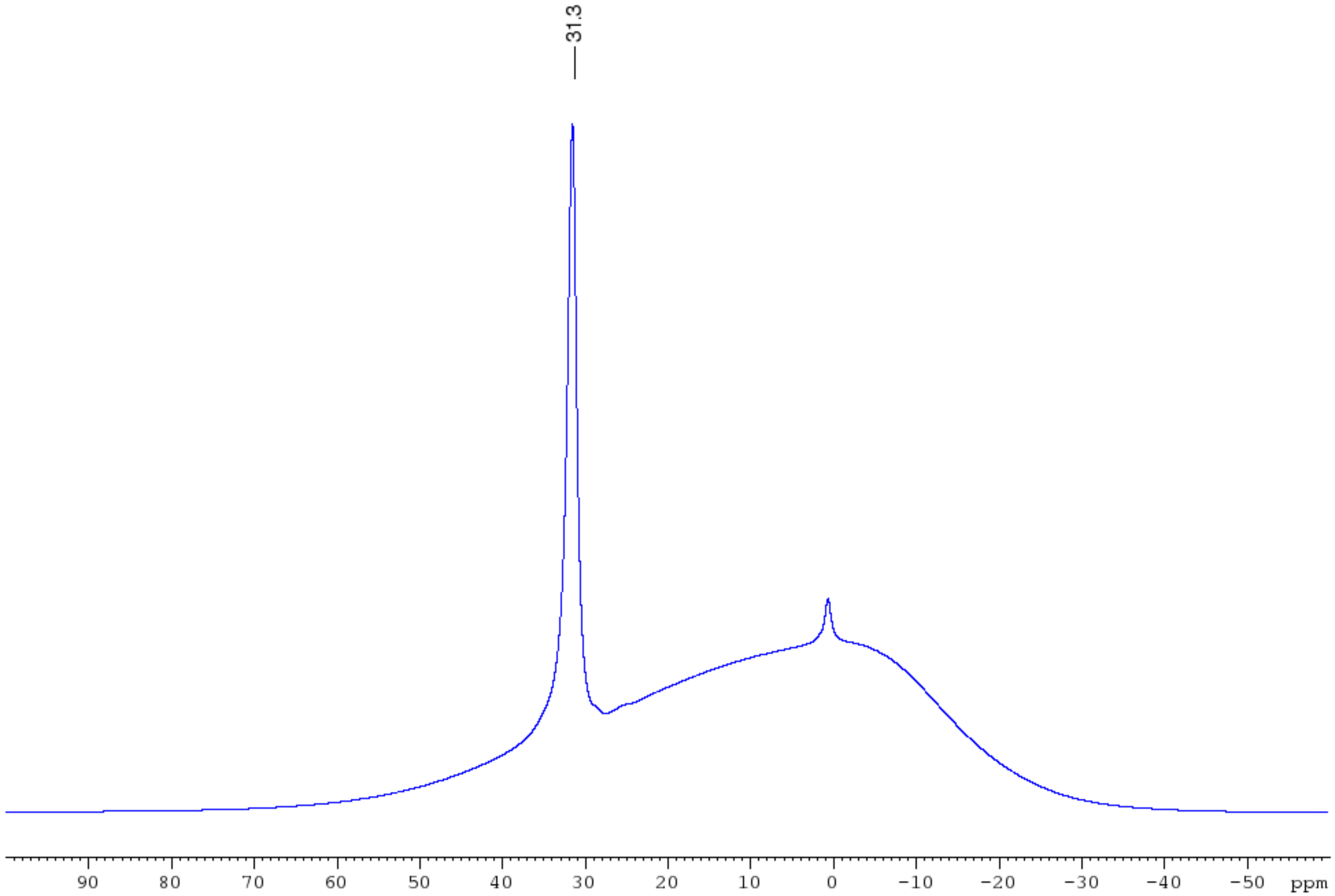

Figure S69. ^{11}B NMR spectrum of **8^H-Br** in C_6D_6. The resonance at 0.8 ppm (ca. 10%) is likely the dimerisation product **[8^H-Br]$_2$**.

Dimerisation of 5^R

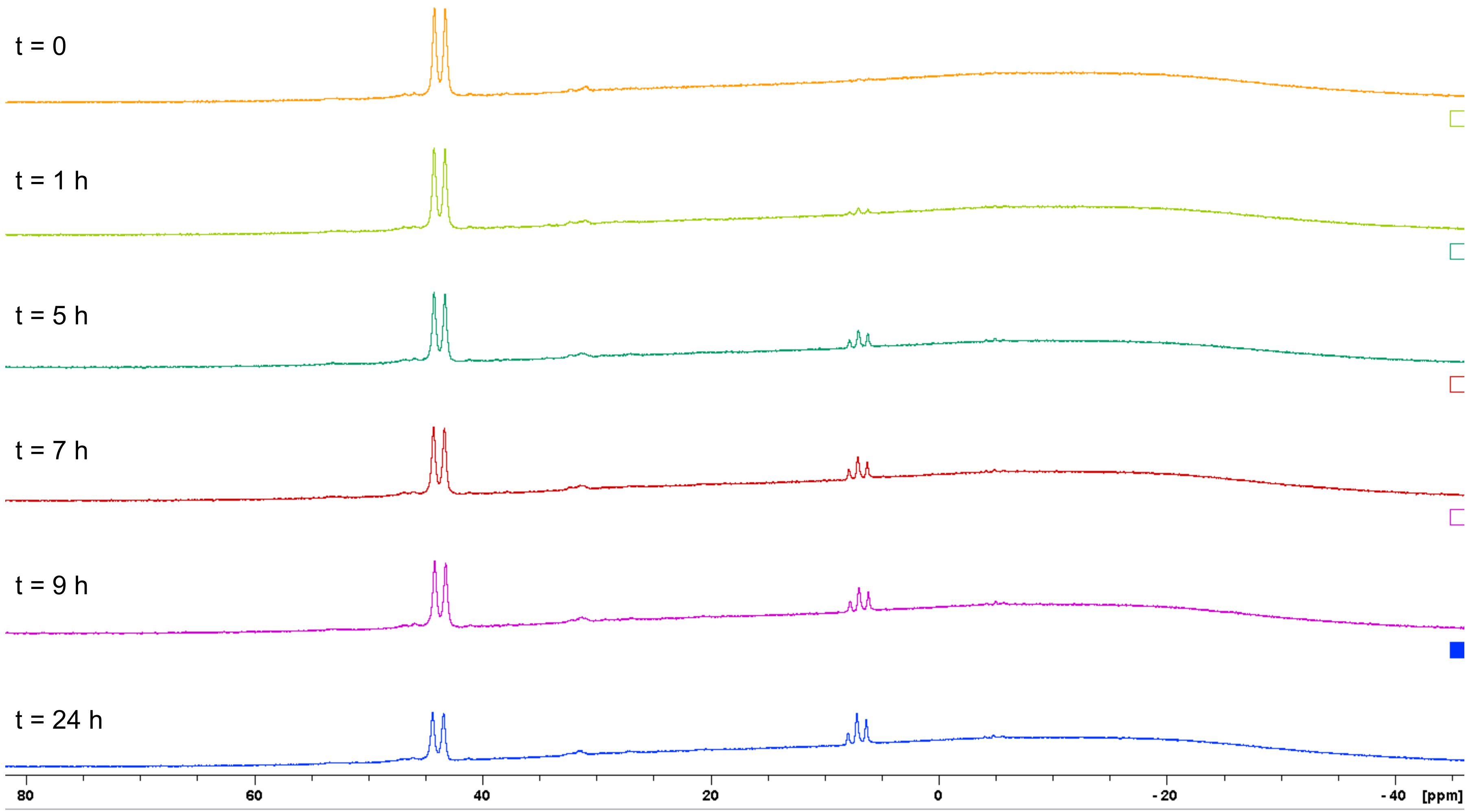

Figure S70. ^{11}B NMR stack-plot showing the dimerisation of $\mathbf{5^H}$ in C_6D_6 at rt over a period of 24 h.

Decomposition of 7^{H}-I

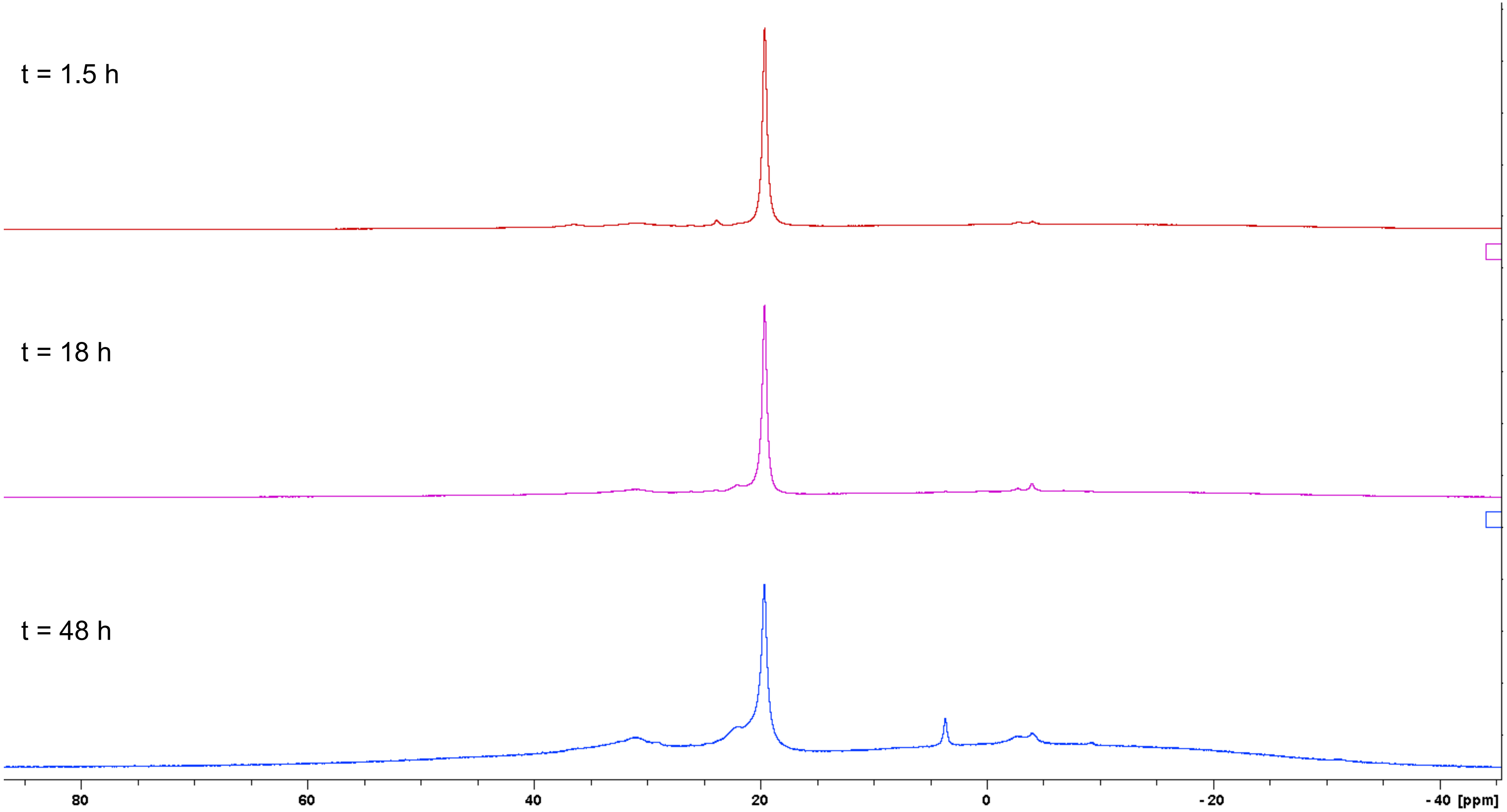

Figure S71. ^{11}B NMR stack-plot showing the decomposition of **7^{H}-I** in C_6D_6 at 80 °C over a period of 24 h.

IR spectra

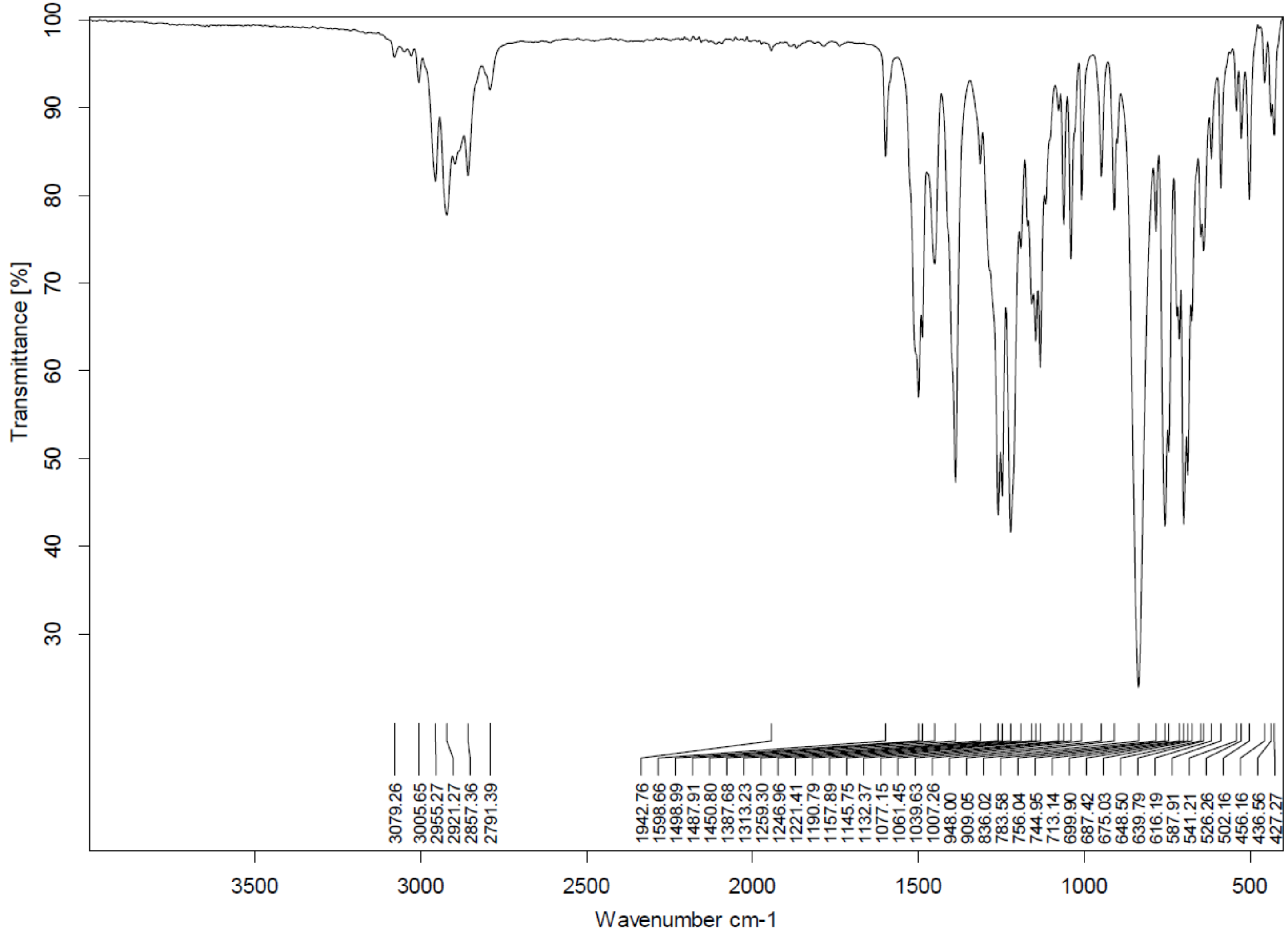

Figure S72. Solid-state IR spectrum of **2^{TMS}-Ph**.

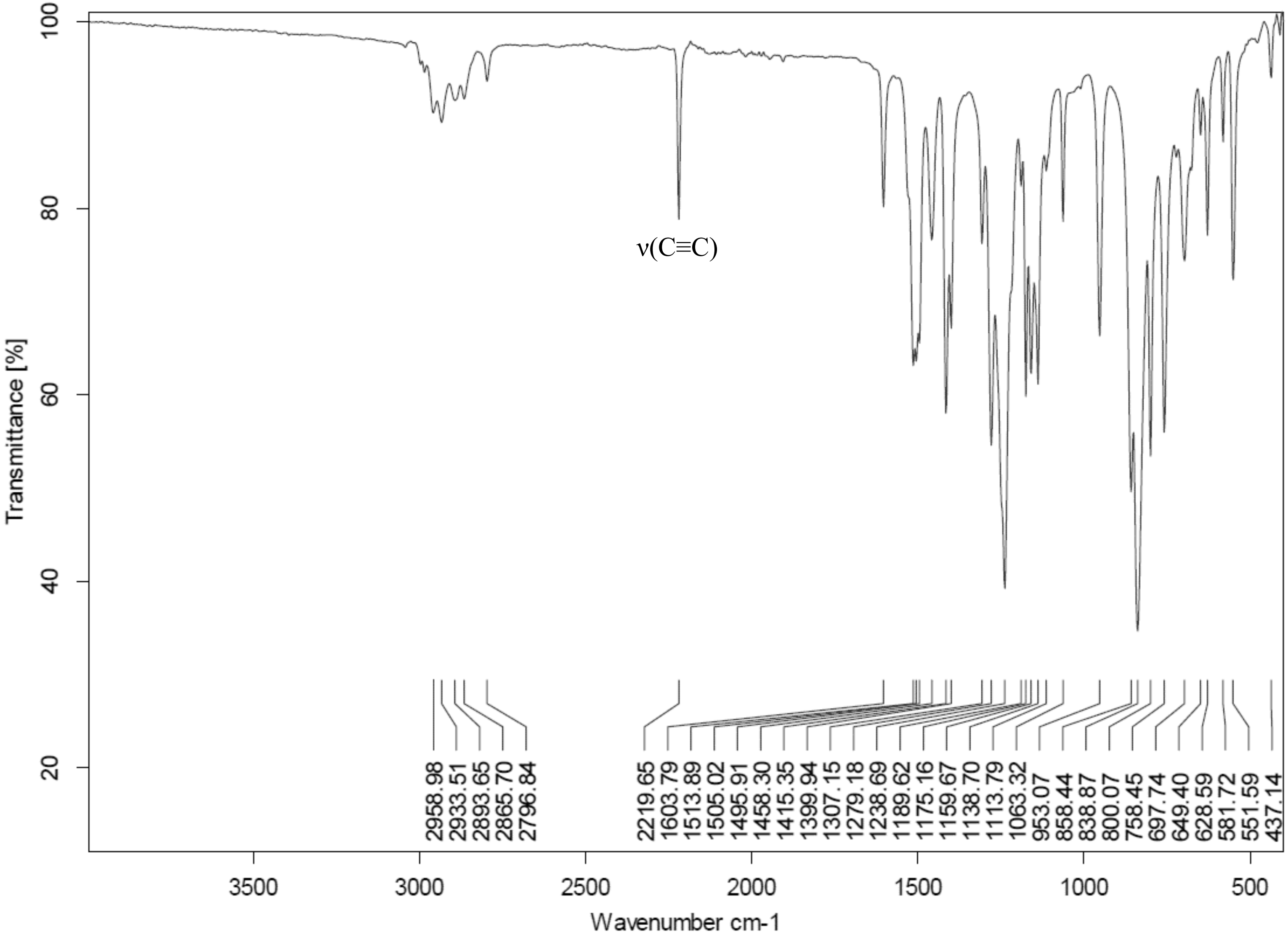

Figure S73. Solid-state IR spectrum of $\mathbf{2^{TMS}}$**-Ph**$^{\mathbf{CN}}$.

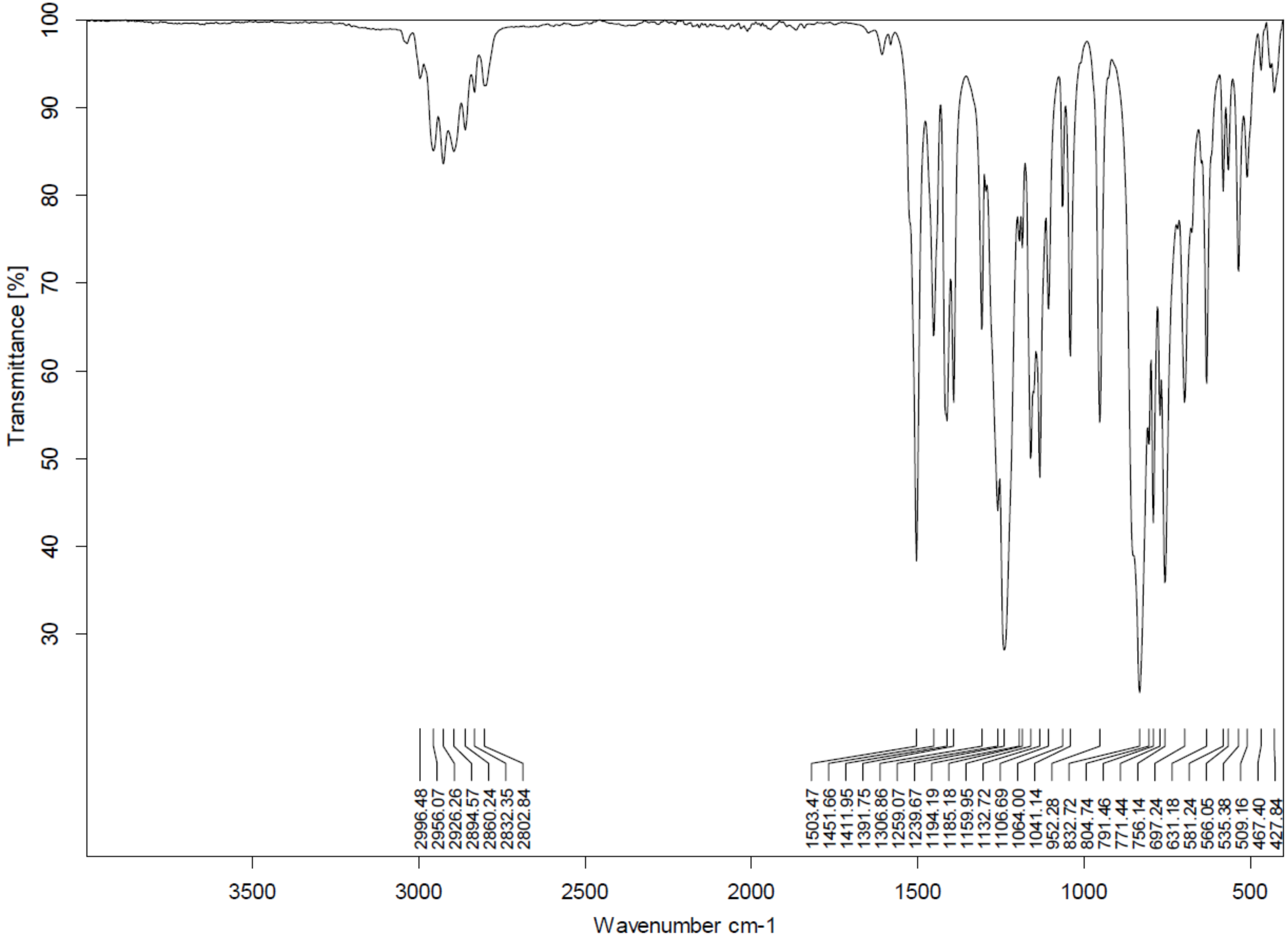

Figure S74. Solid-state IR spectrum of **2^{TMS}-Ph^{OMe}**.

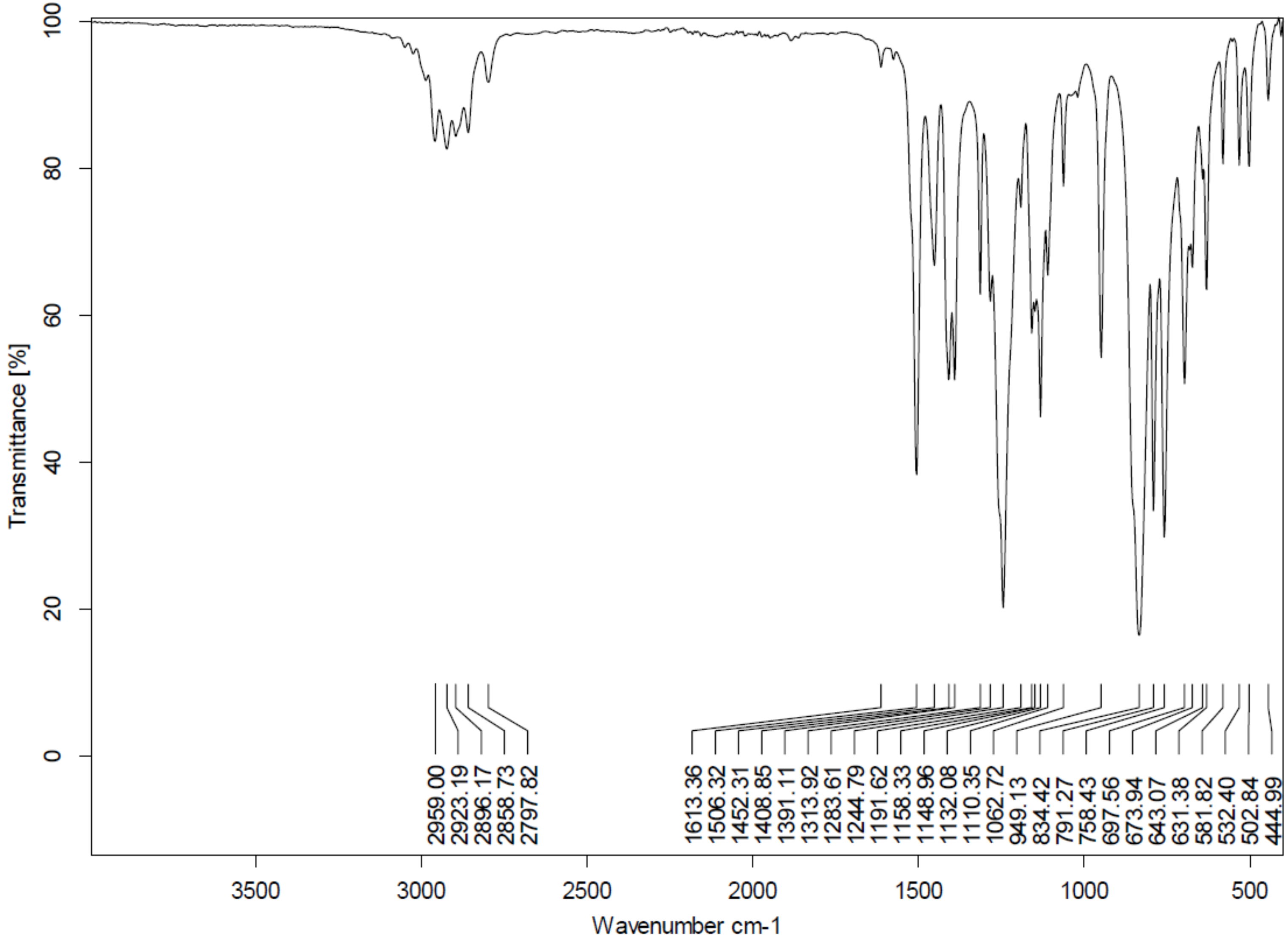

Figure S75. Solid-state IR spectrum of $\mathbf{2^{TMS}}$-***pTol***.

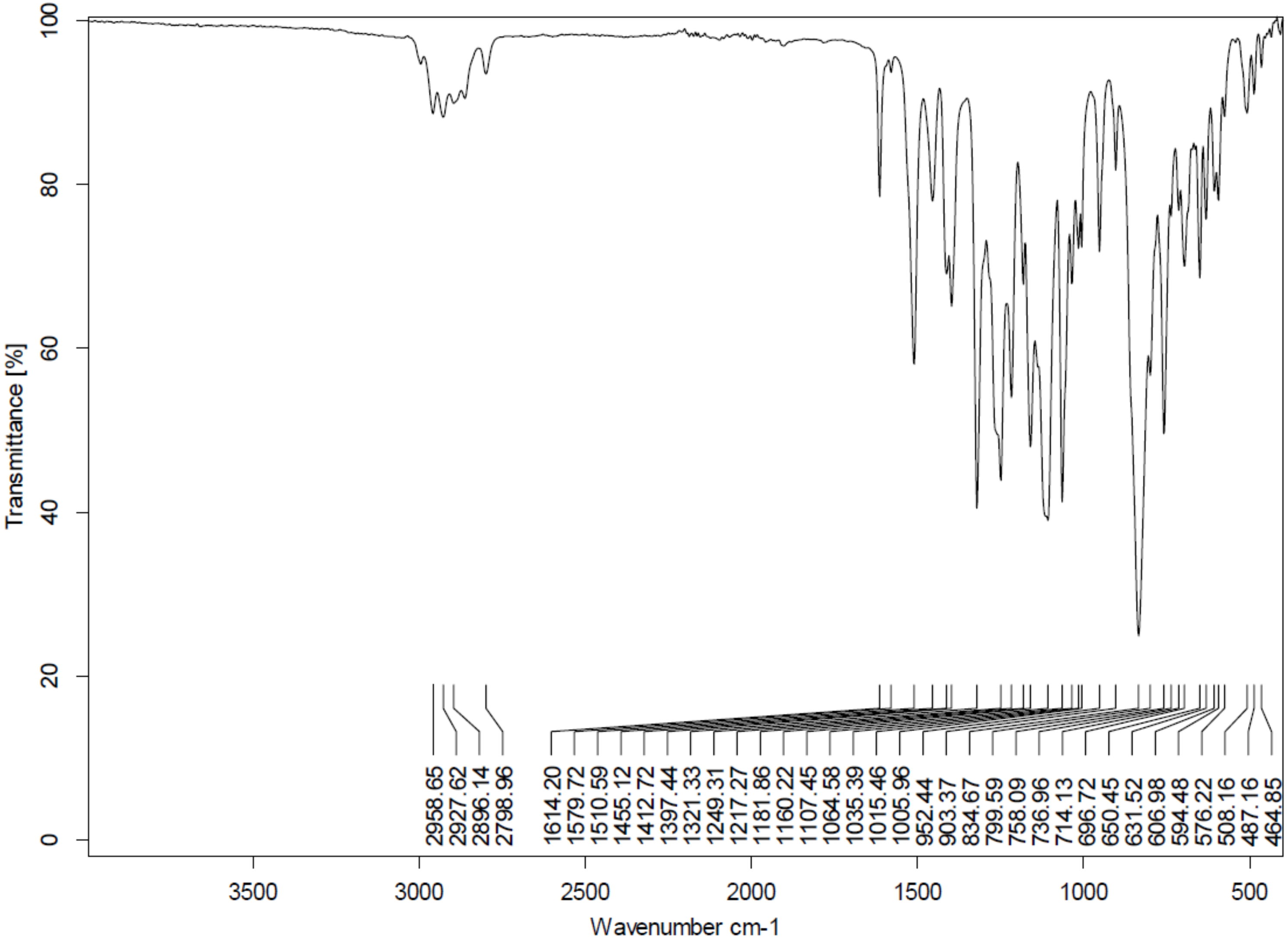

Figure S76. Solid-state IR spectrum of $\mathbf{2^{TMS}}$-$\mathbf{Ph^{CF3}}$.

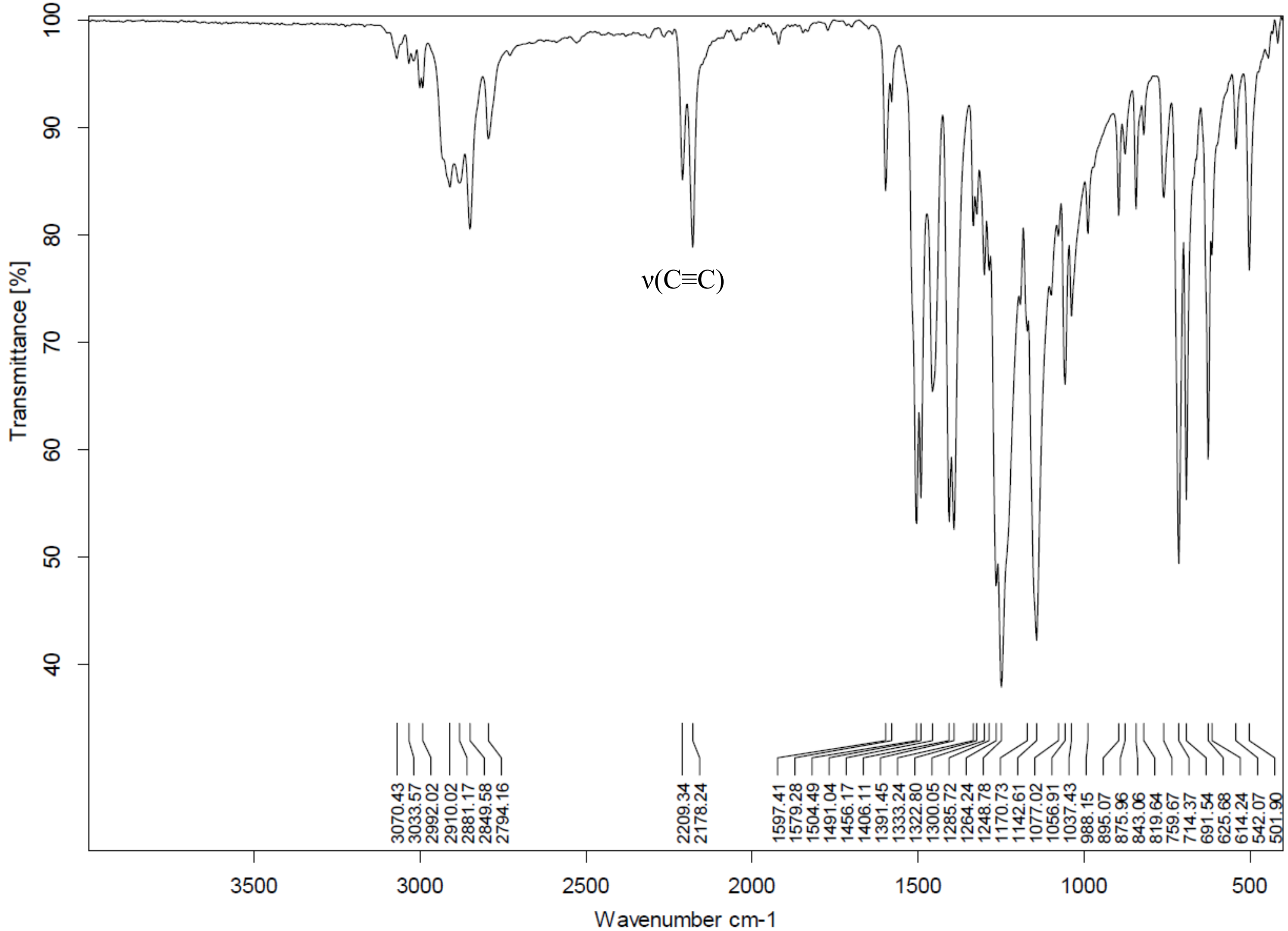

Figure S77. Solid-state IR spectrum of $\mathbf{2^{Me}}$**-Ph**.

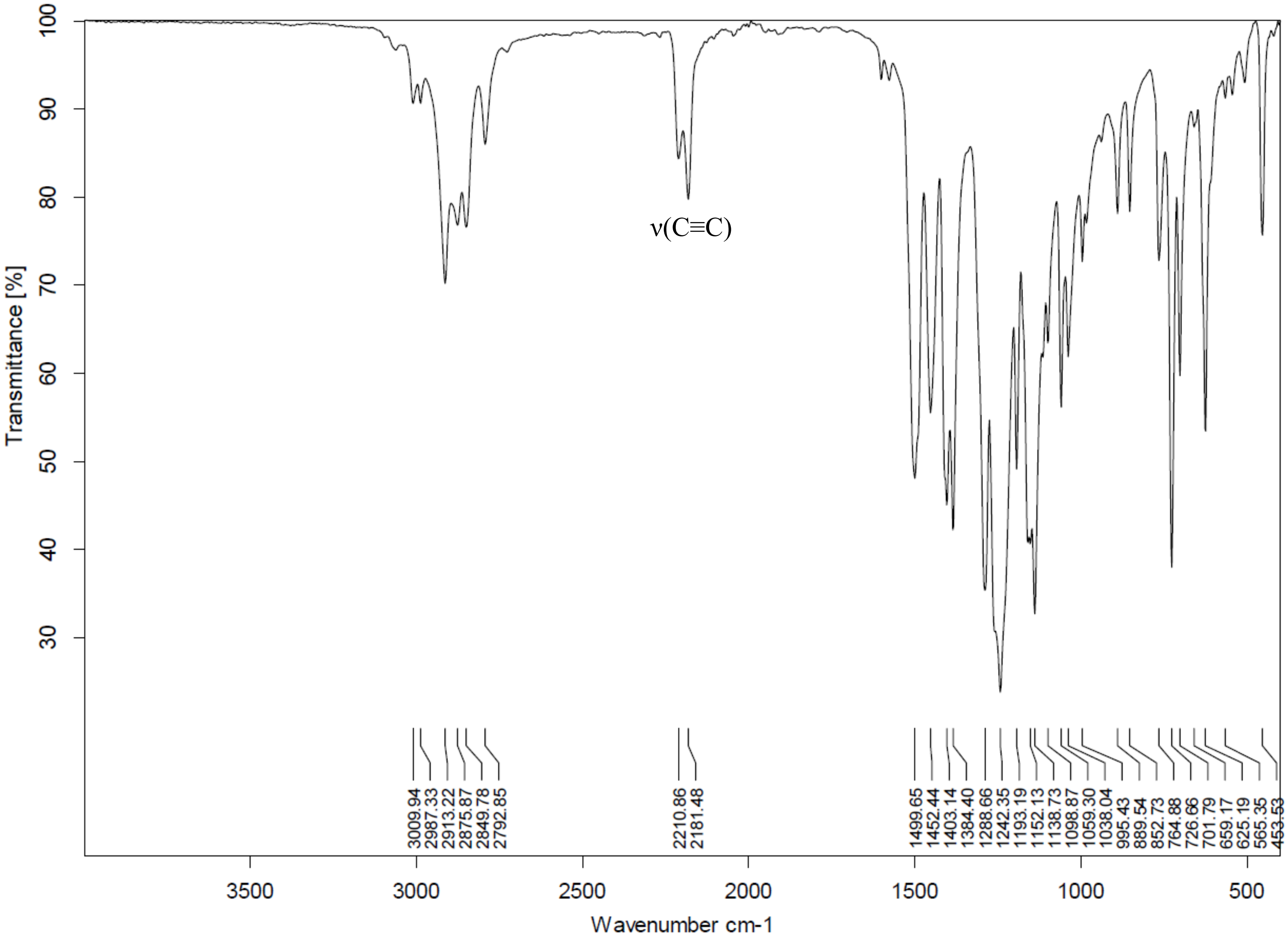

Figure S78. Solid-state IR spectrum of **2^{Me}-*o*Tol**.

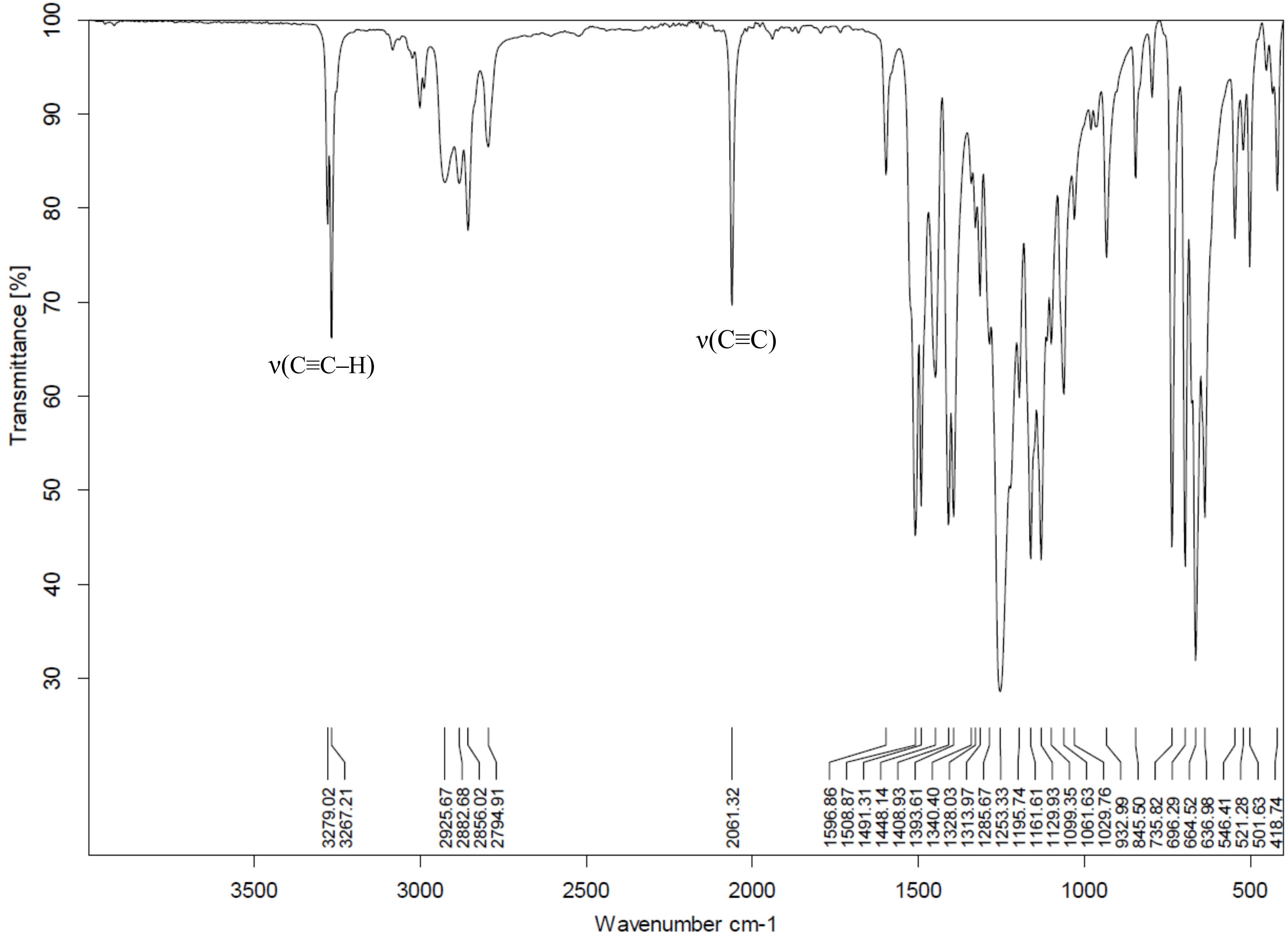

Figure S79. Solid-state IR spectrum of **2^{H}-Ph**.

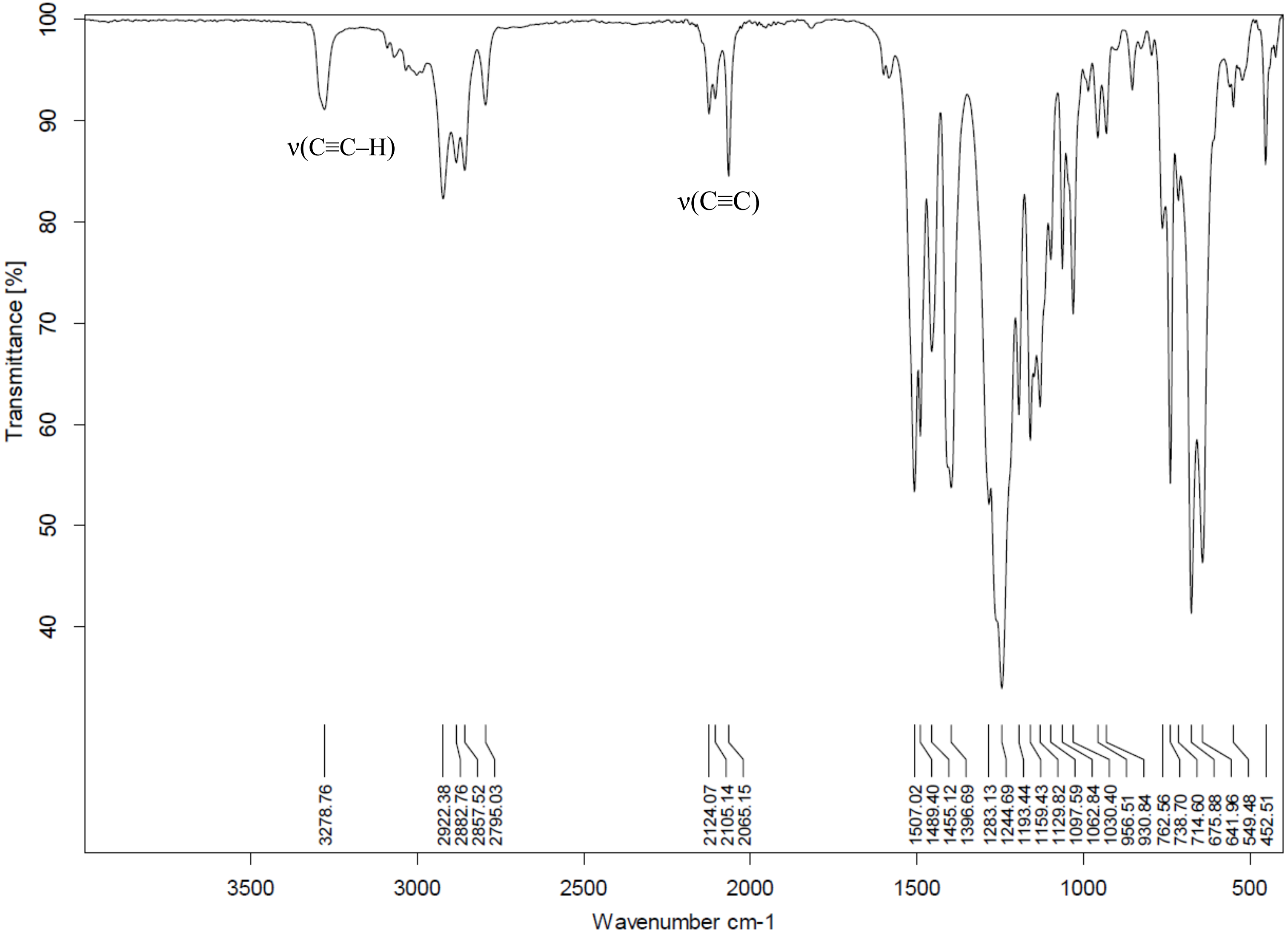

Figure S80. Solid-state IR spectrum of **2^{H}-*o*Tol**.

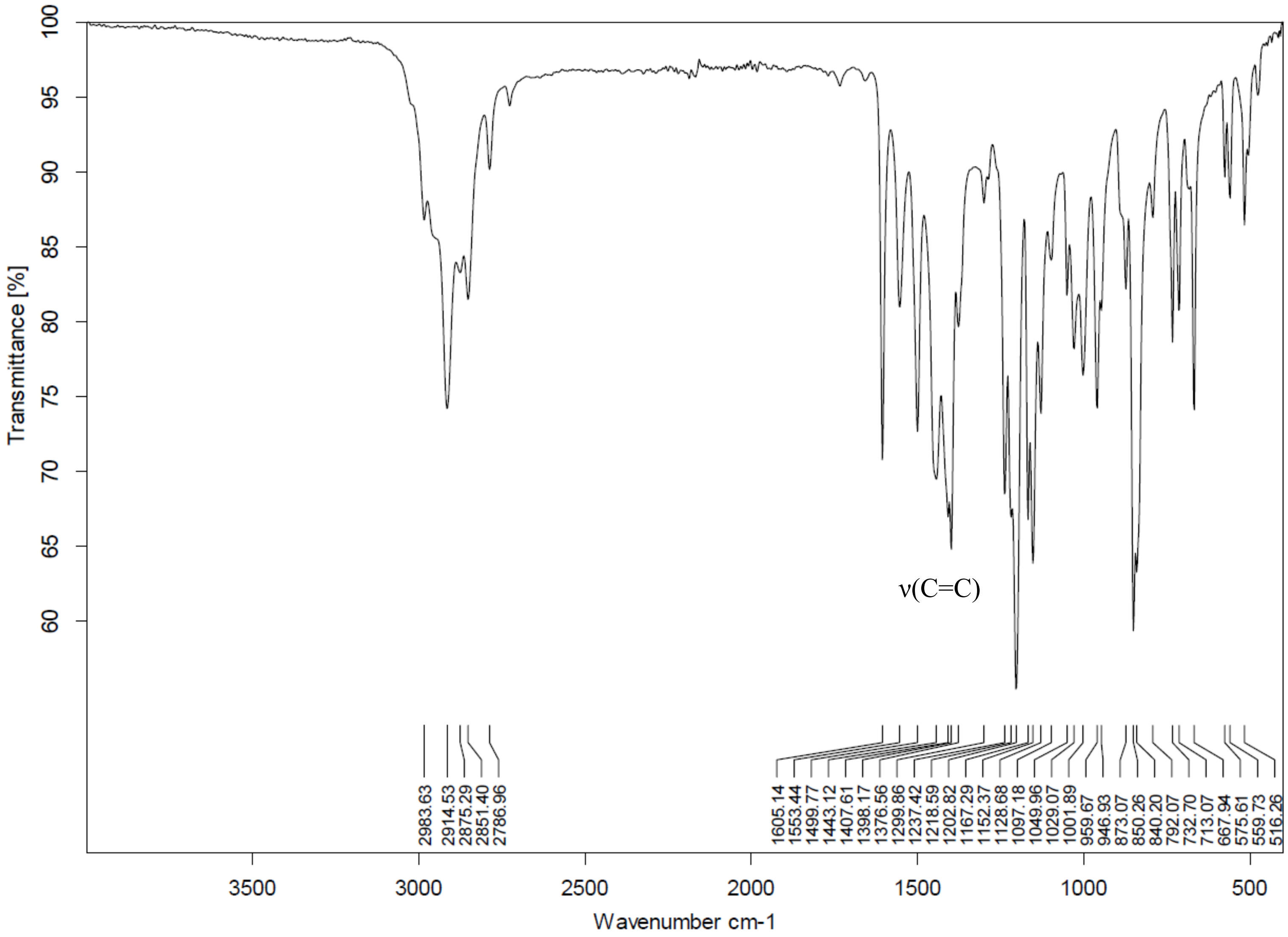

Figure S81. Solid-state IR spectrum of $\mathbf{4^{Me}}$.

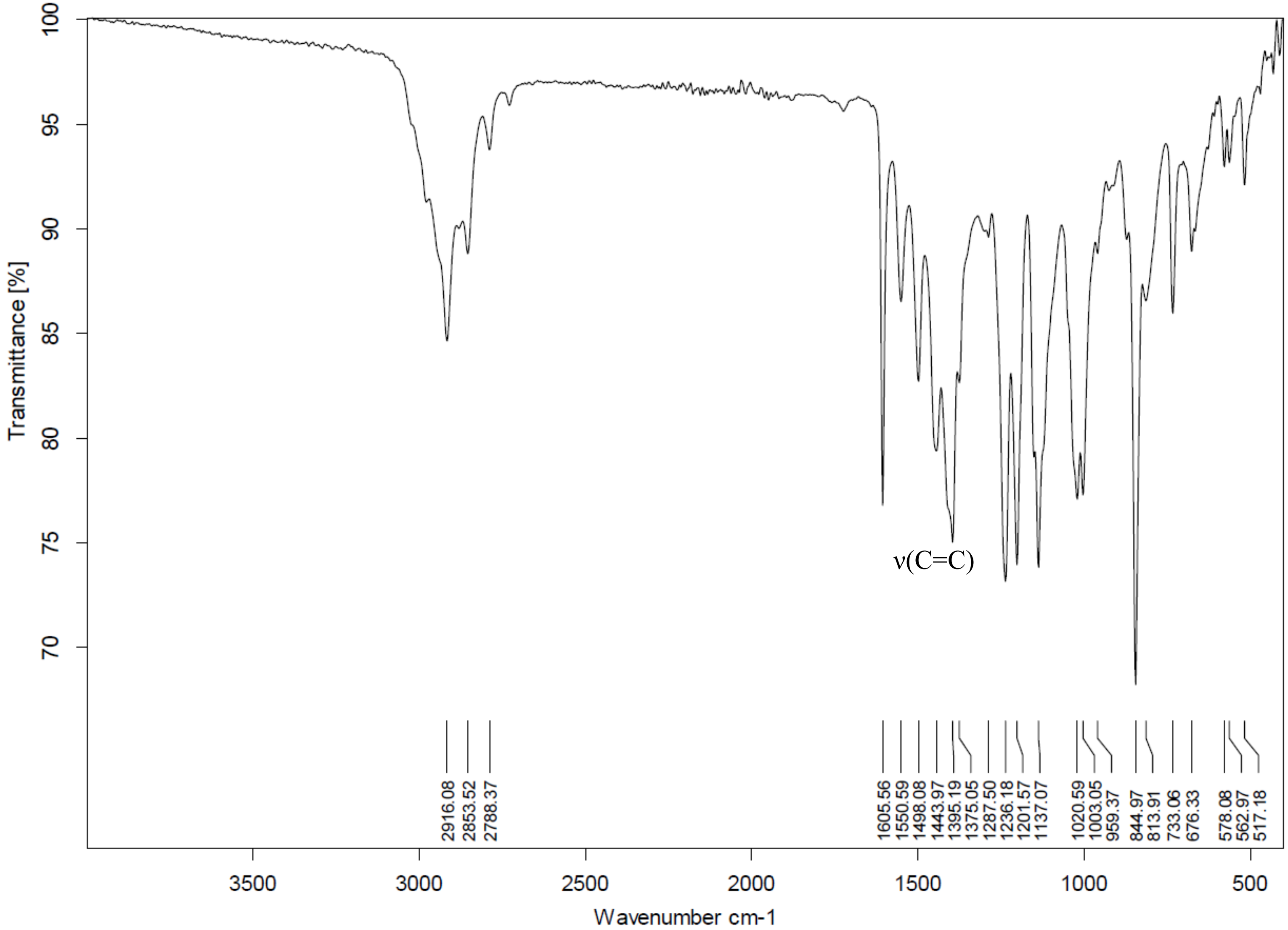

Figure S82. Solid-state IR spectrum of $\mathbf{4^{H}}$.

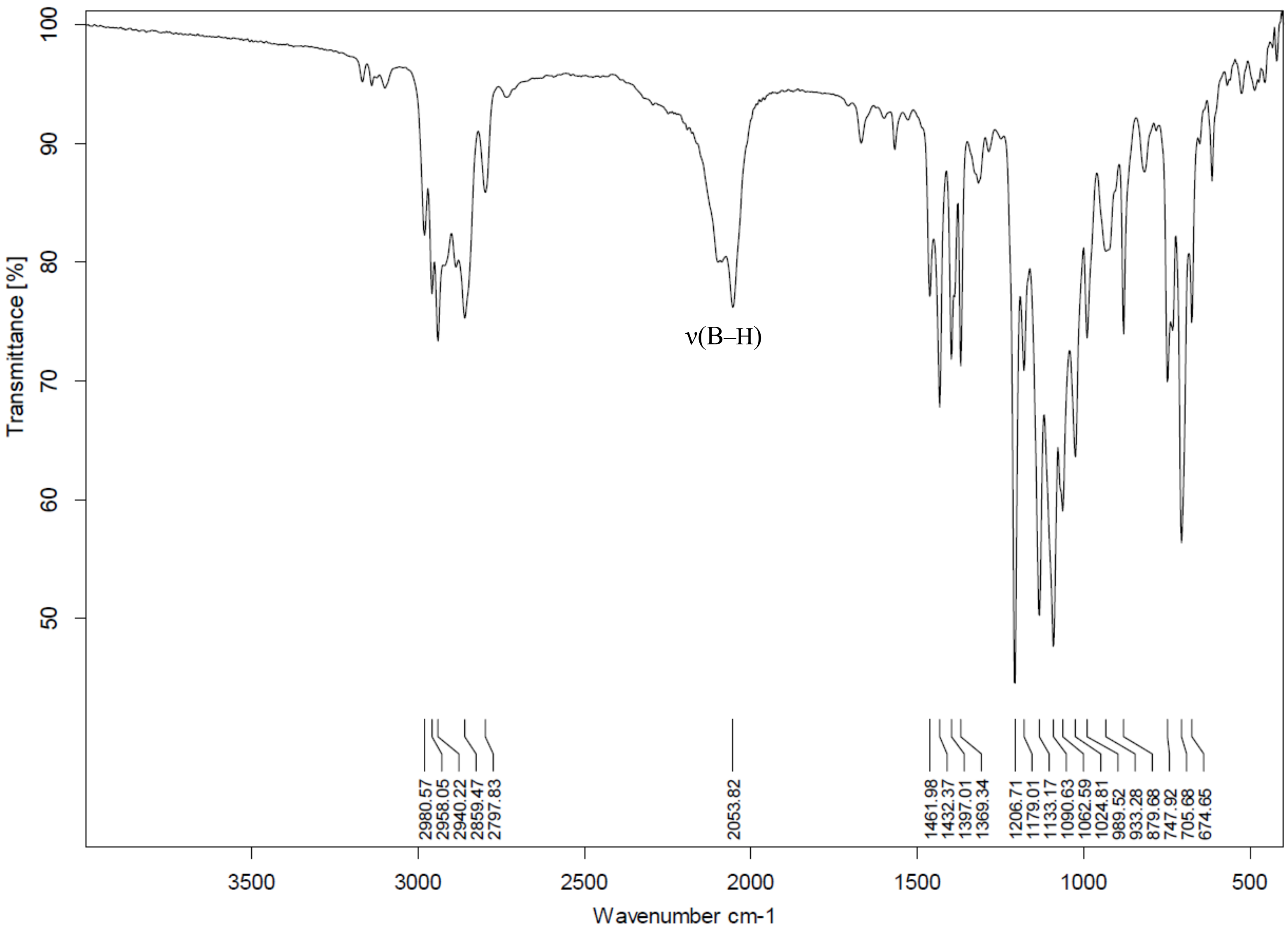

Figure S83. Solid-state IR spectrum of $\mathbf{6}^{\mathbf{Me}}$.

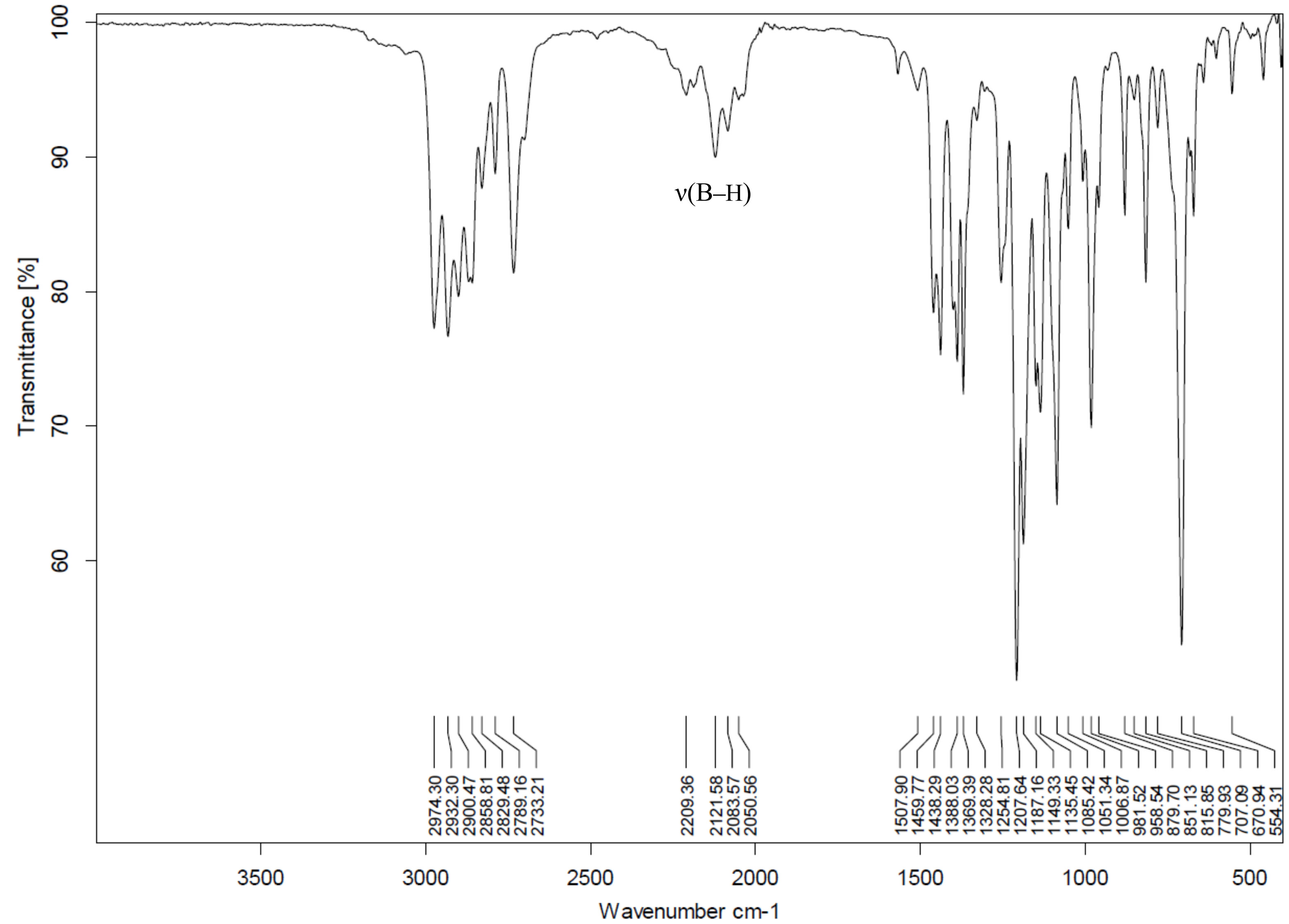

Figure S84. Solid-state IR spectrum of $\mathbf{6^H}$.

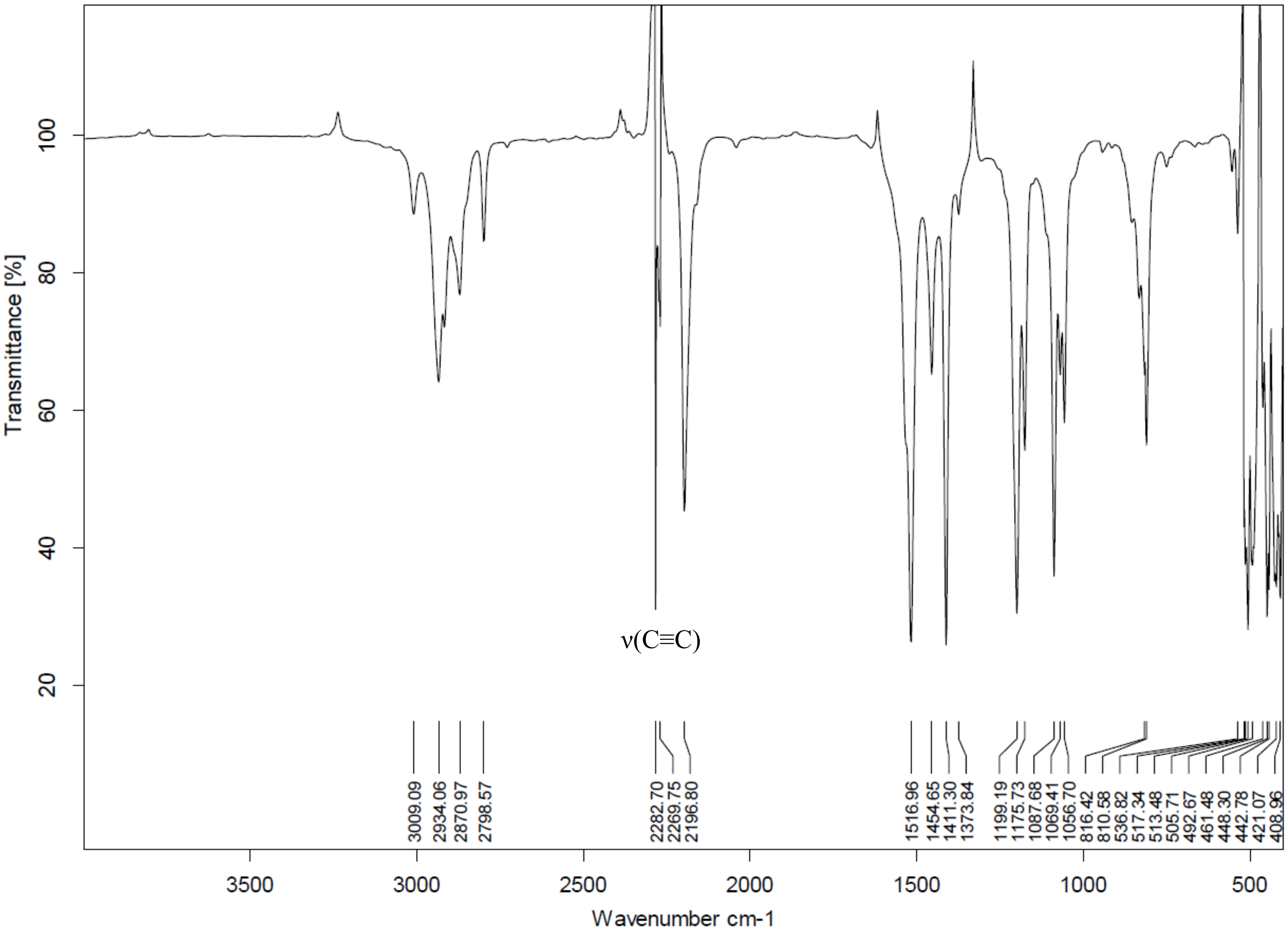

Figure S85. Solid-state IR spectrum of $\mathbf{7^{Me}}$**-I**.

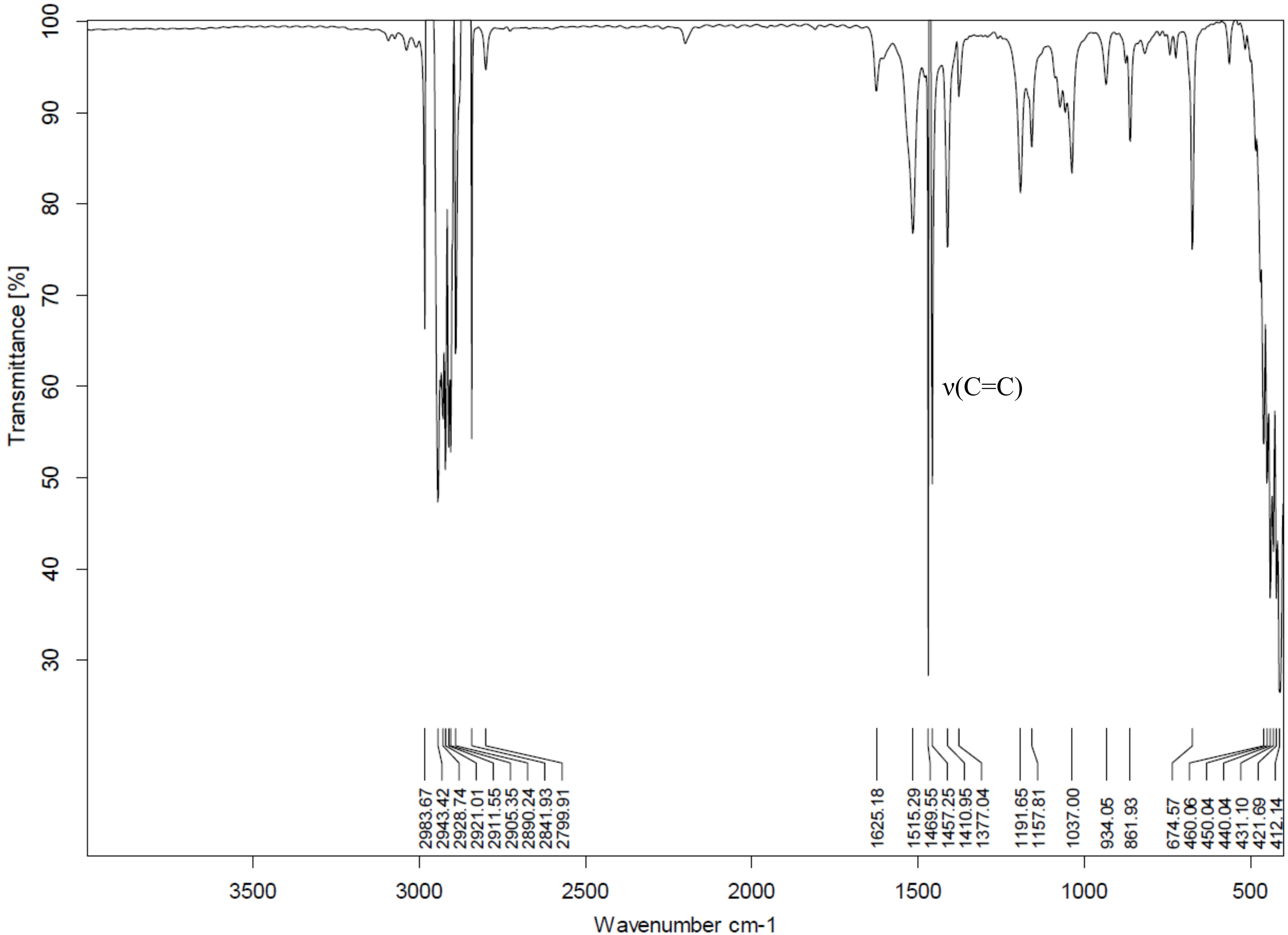

Figure S86. Solid-state IR spectrum of $\mathbf{8^{Me}}$**-I**.

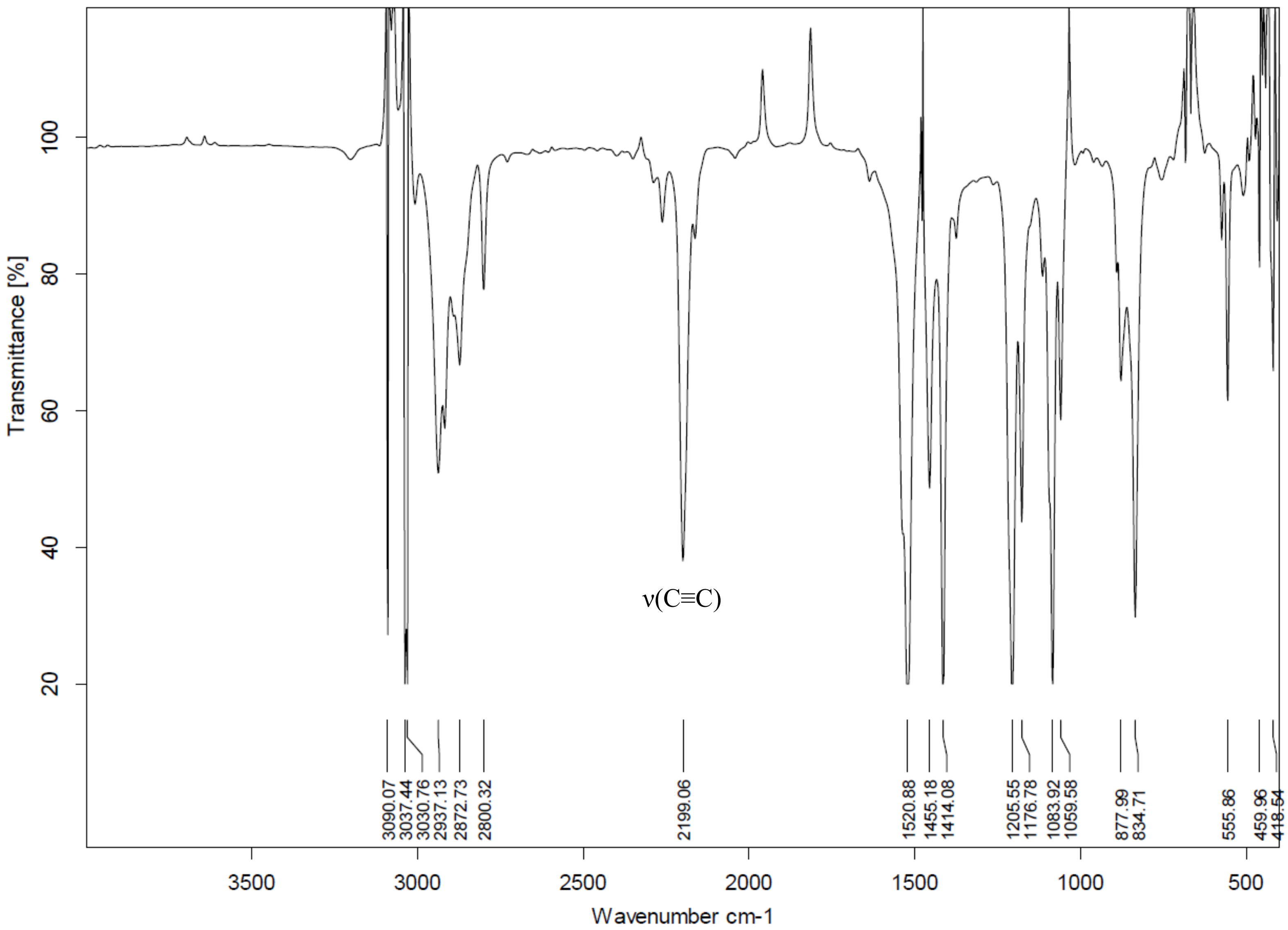

Figure S87. Solid-state IR spectrum of $\mathbf{7^{Me}}$**-Br**.

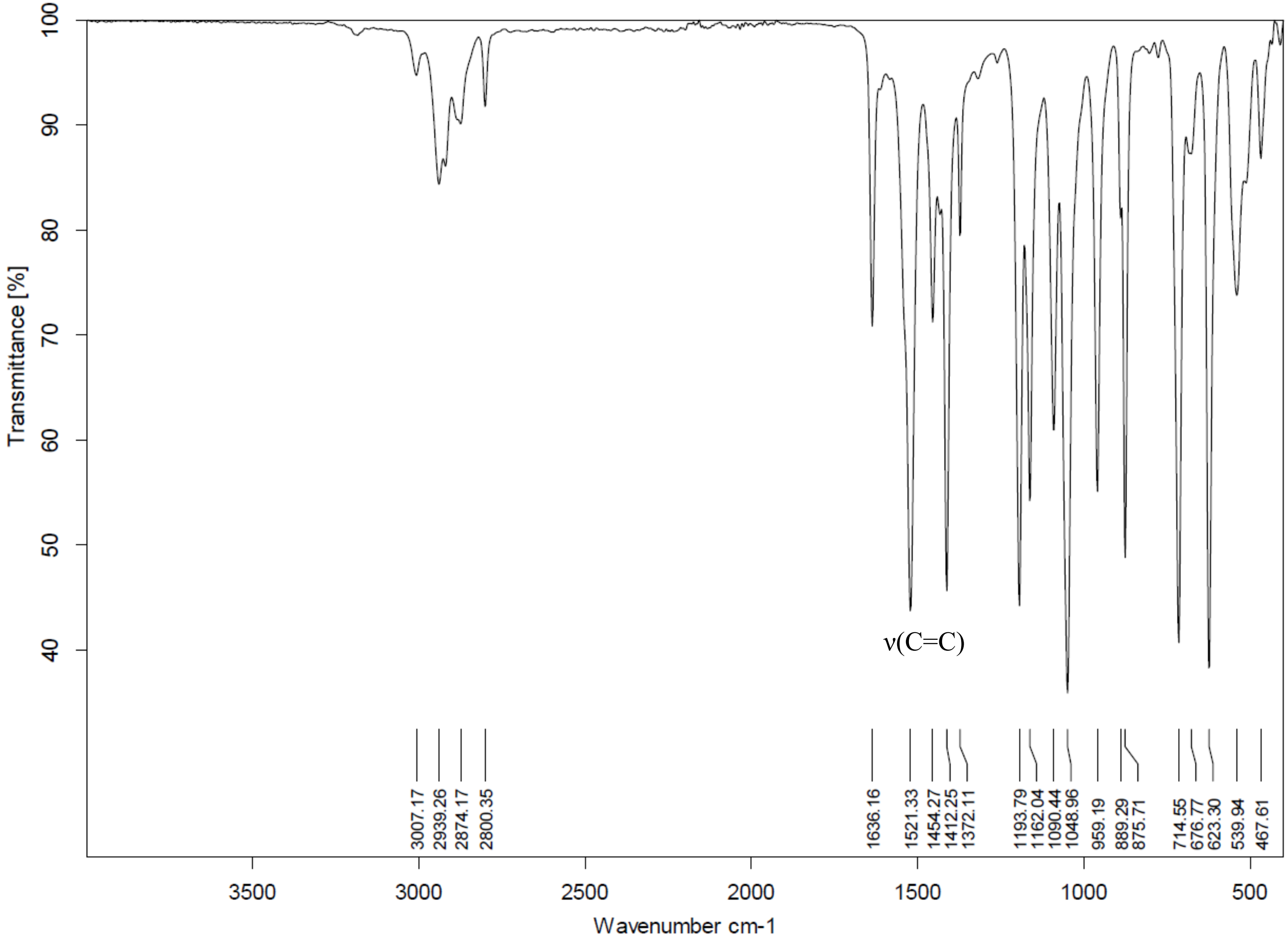

Figure S88. Solid-state IR spectrum of **8^{Me}-Br**.

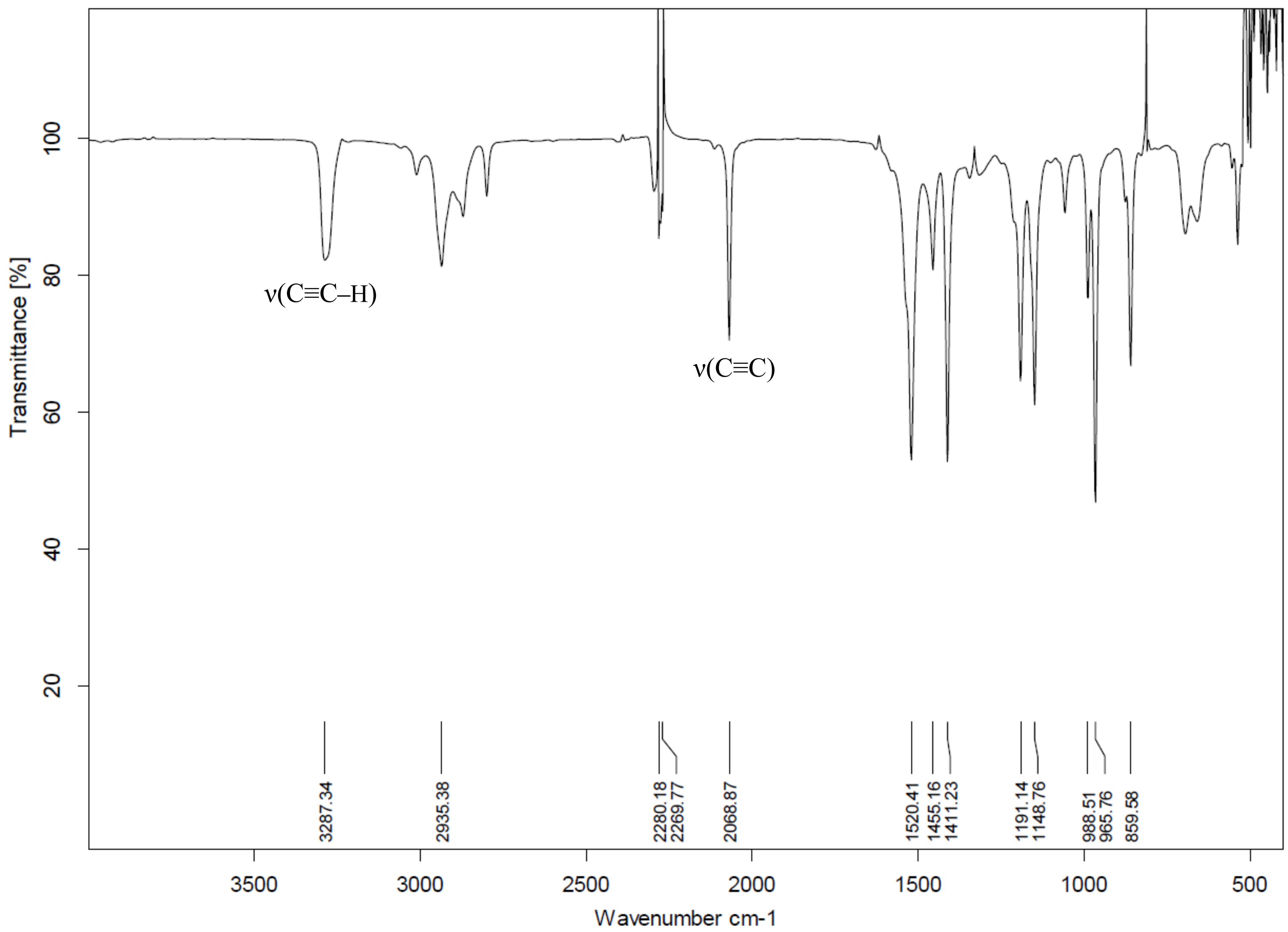

Figure S89. Solid-state IR spectrum of $\mathbf{7^{H}}$**-I**.

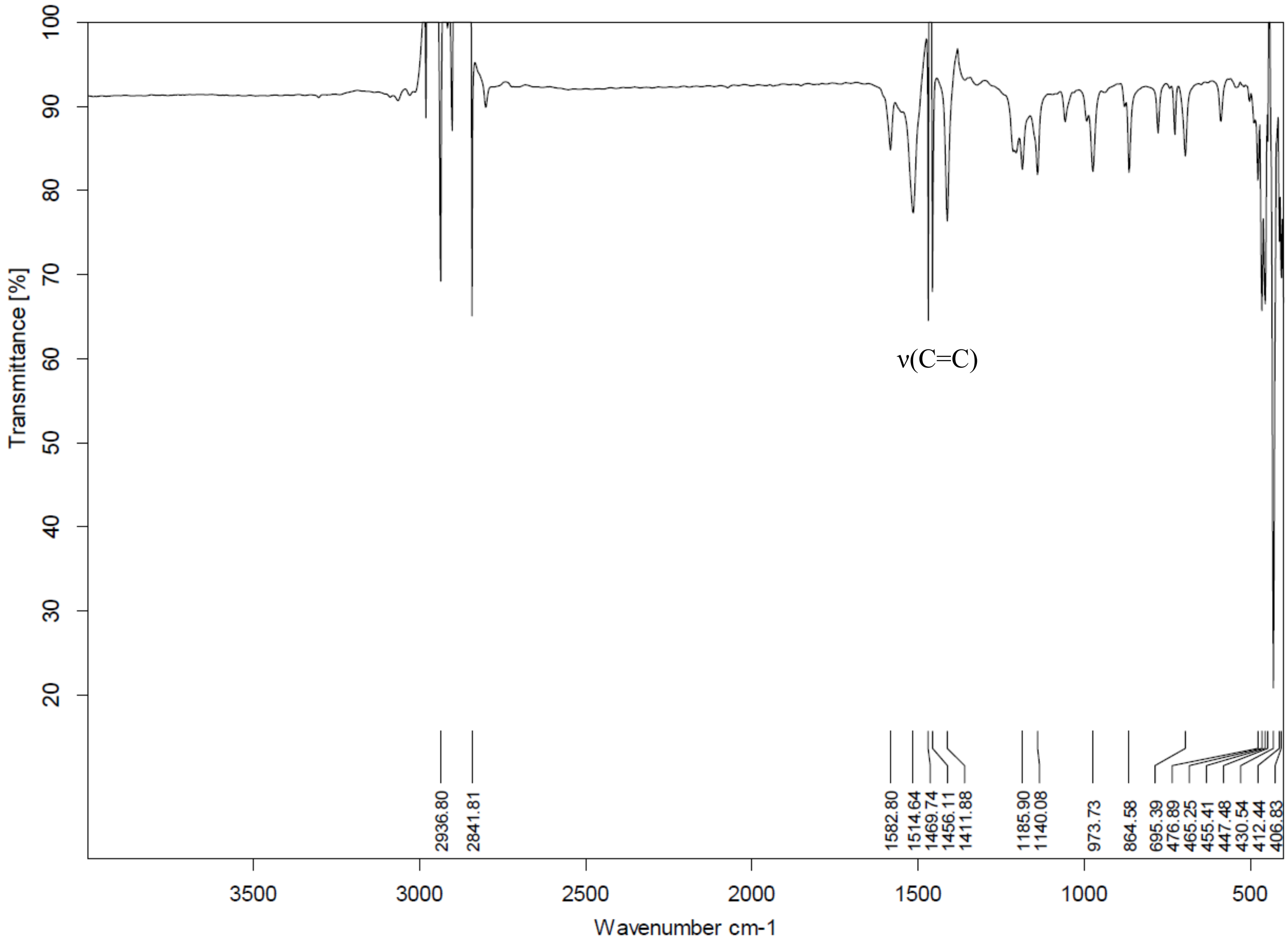

Figure S90. Solid-state IR spectrum of **8^{H}-I**.

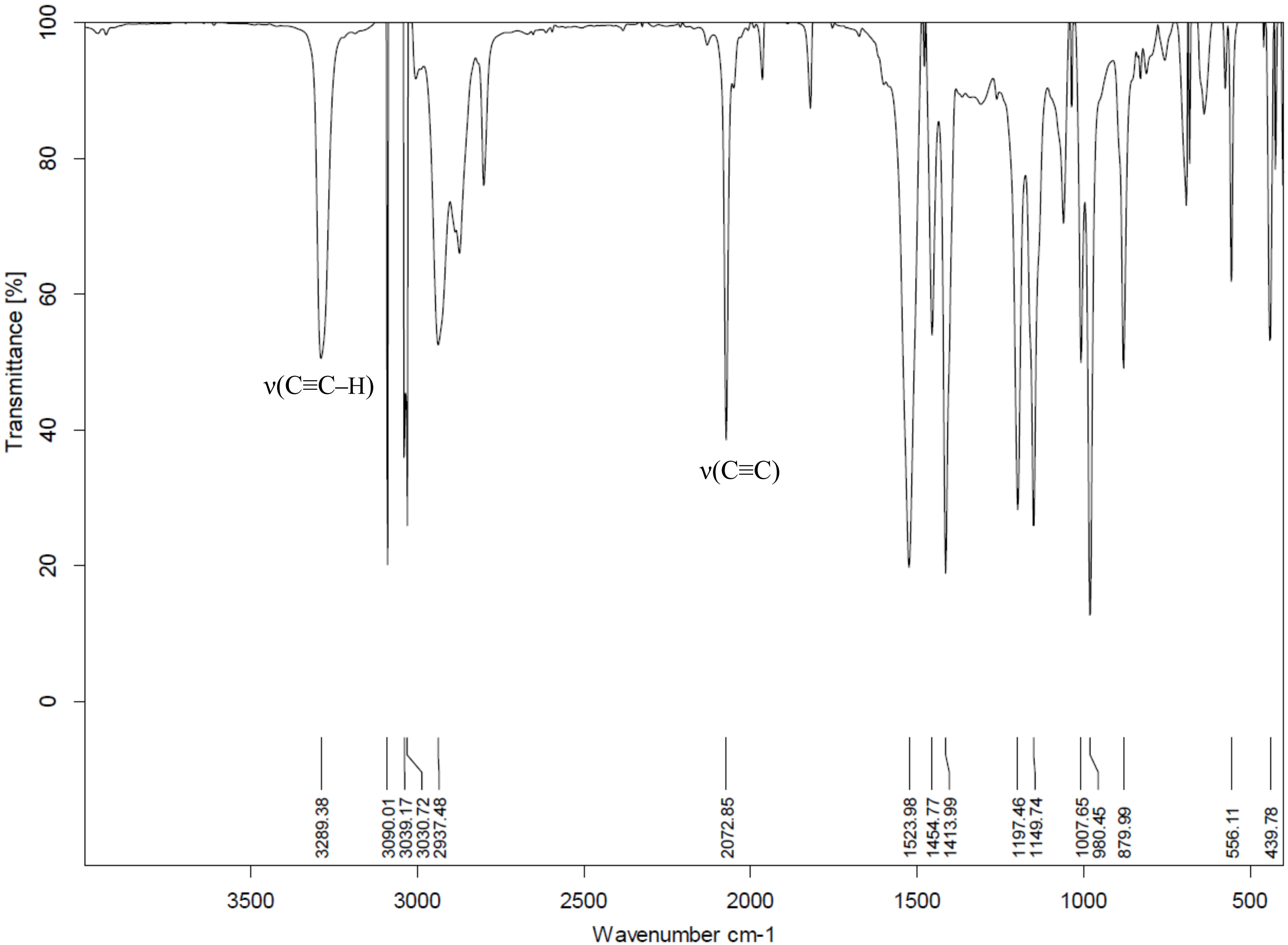

Figure S91. Solid-state IR spectrum of **7[H]-Br**.

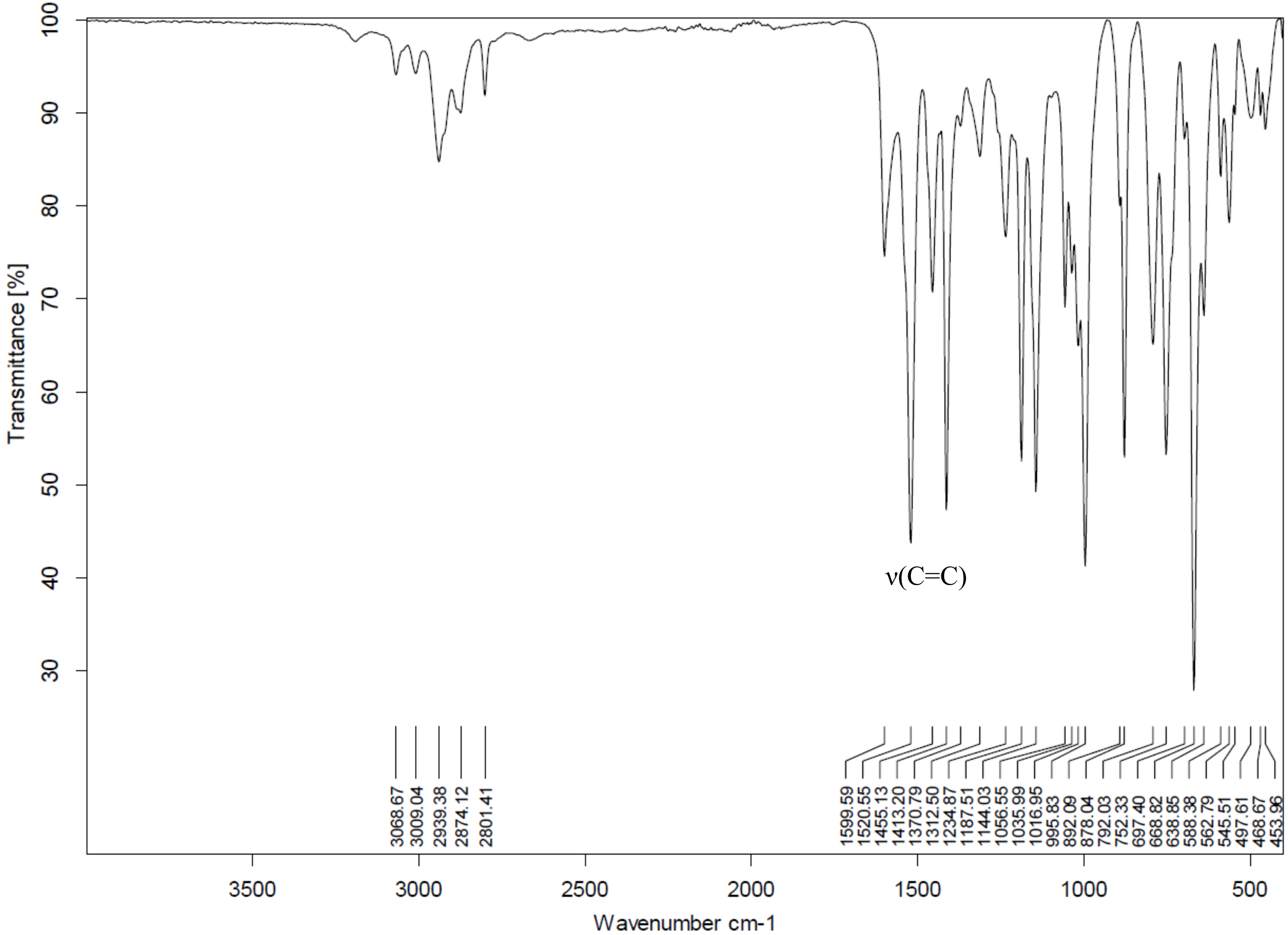

Figure S92. Solid-state IR spectrum of **8^{H}-Br**.

X-ray crystallographic data

The crystal data of **2^{TMS}-Ph^{OMe}**, **2^{TMS}-*p*Tol**, **2^{Me}-Ph**, **2^{H}-*o*Tol**, **4^{Me}** and **4^{H}** 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 **2^{TMS}-Ph**, **2^{TMS}-Ph^{CN}**, **2^{Me}-*o*Tol** and **2^{H}-Ph** were collected on a BRUKER X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The crystal data of **2^{TMS}-Ph^{CF3}** and **6^{H}** were collected on a *XtaLAB Synergy Dualflex HyPix* diffractometer with a Hybrid Pixel array detector and multi-layer mirror monochromated $Cu_{K\alpha}$ radiation. The structures were solved using the intrinsic phasing method,[5] refined with the ShelXL program[6] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms except boron-bound ones were assigned to idealised geometric positions. The coordinates of boron-bound hydrogen atoms were refined freely.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC 2124001-2124012. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Special refinement details for 2^{TMS}-Ph: The phenyl group (C15 > C20) was modelled as twofold disordered in a 57:43 ratio. ADPs within this disorder were restrained with SIMU 0.01 and the rings idealised with AFIX 66. Three reflections with $I_{obs} > 10\ I_{calc}$ were omitted.

Crystal data for 2^{TMS}-Ph: $C_{20}H_{35}B_2N_3Si_2$, $M_r = 395.31$, colourless plate, $0.158 \times 0.192 \times 0.247$ mm^3, monoclinic space group $P2_1/n$, $a = 15.038(3)$ Å, $b = 6.4555(13)$ Å, $c = 26.212(5)$ Å, $\beta = 96.313(6)°$, $V = 2529.2(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.038$ g·cm^{-3}, $\mu = 0.149$ mm^{-1}, $F(000) = 856$, $T = 100(2)$ K, $R_1 = 0.0893$, $wR_2 = 0.1611$, 4964 independent reflections [$2\theta \leq 52.042°$] and 285 parameters.

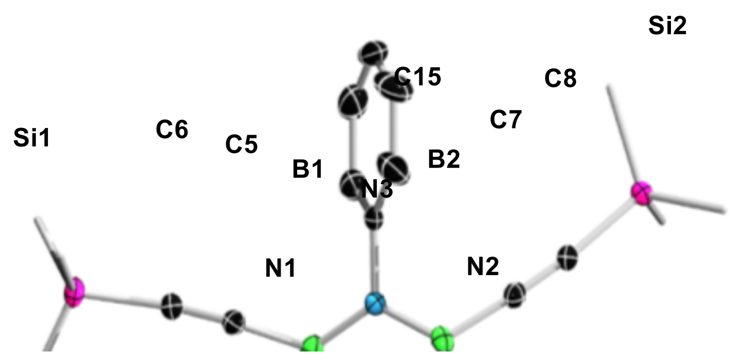

Figure S93. Crystallographically-determined solid-state structure of **2^{TMS}-Ph**. Atomic displacement ellipsoids represented at 50%. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity.

Crystal data for 2^{TMS}-Ph^{CN}: $C_{21}H_{34}B_2N_4Si_2$, M_r = 420.32, colourless block, 0.282×0.209×0.117 mm^3, triclinic space group $P\bar{1}$, a = 11.2067(11) Å, b = 11.2717(11) Å, c = 12.9033(13) Å, α = 70.688(3)°, β = 69.069(3)°, γ = 66.393(3)°, V = 1361.0(2) Å^3, Z = 2, ρ_{calcd} = 1.026 g·cm^{-3}, μ = 0.143 mm^{-1}, F(000) = 452, T = 100(2) K, R_1 = 0.0501, wR_2 = 0.1029, 5348 independent reflections [2θ≤52.038°] and 272 parameters.

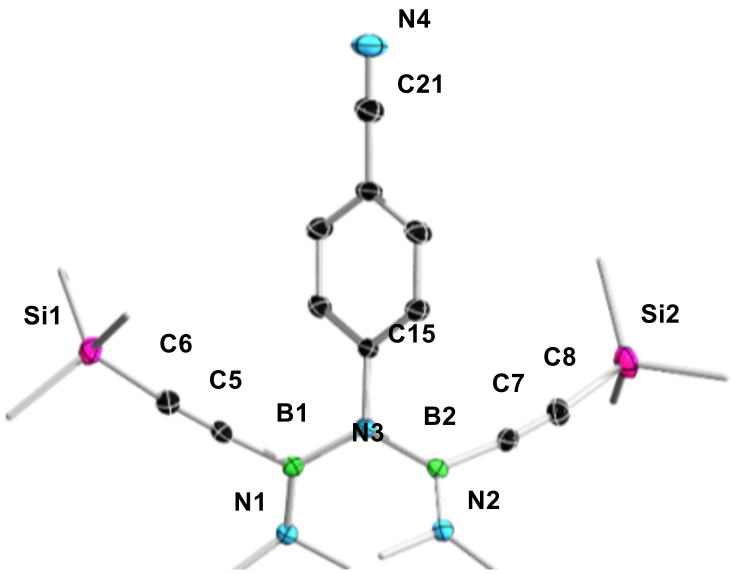

Figure S94. Crystallographically-determined solid-state structure of **2^{TMS}-Ph^{CN}**. Atomic displacement ellipsoids represented at 50%. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity.

Special refinement details for 2^{TMS}-Ph^{OMe}: Two reflections were affected by the beamstop and therefore omitted.

Crystal data for 2^{TMS}-Ph^{OMe}: $C_{21}H_{37}B_2N_3OSi_2$, $M_r = 425.33$, colourless block, 0.551×0.403×0.25 mm^3, triclinic space group $P\bar{1}$, $a = 10.3348(4)$ Å, $b = 11.1942(4)$ Å, $c = 12.3913(4)$ Å, $\alpha = 97.2110(10)°$, $\beta = 111.7480(10)°$, $\gamma = 94.4550(10)°$, $V = 1308.93(8)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.079$ g·cm^{-3}, $\mu = 0.151$ mm^{-1}, $F(000) = 460$, $T = 100(2)$ K, $R_1 = 0.0432$, $wR_2 = 0.0868$, 5144 independent reflections [$2\theta \leq 52.038°$] and 273 parameters.

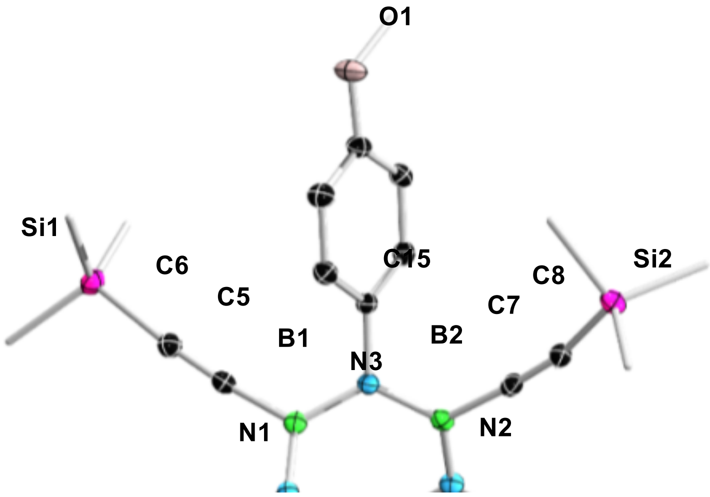

Figure S95. Crystallographically-determined solid-state structure of **2^{TMS}-Ph^{OMe}**. Atomic displacement ellipsoids represented at 50%. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity.

Crystal data for $\mathbf{2^{TMS}}$-*o*Tol: $C_{21}H_{37}B_2N_3Si_2$, $M_r = 409.33$, colourless plate, 0.35×0.229×0.14 mm^3, monoclinic space group $P2_1/c$, $a = 12.0127(10)$ Å, $b = 10.1425(7)$ Å, $c = 22.1185(17)$ Å, $\beta = 102.046(3)°$, $V = 2635.6(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.032$ g·cm^{-3}, $\mu = 0.145$ mm^{-1}, $F(000) = 888$, $T = 100(2)$ K, $R_1 = 0.0843$, $wR_2 = 0.1201$, 5183 independent reflections [$2\theta \leq 52.038°$] and 264 parameters.

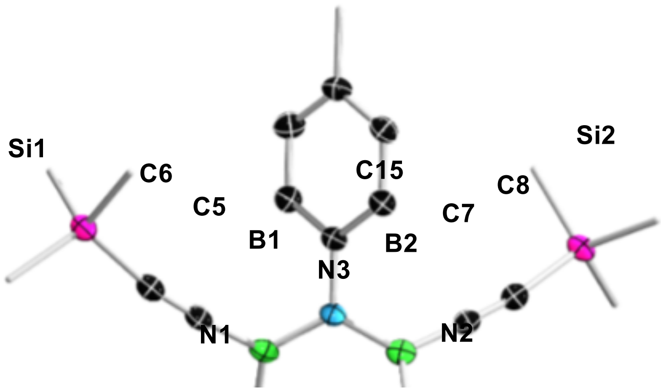

Figure S96. Crystallographically-determined solid-state structure of $\mathbf{2^{TMS}}$-*o*Tol. Atomic displacement ellipsoids represented at 50%. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity.

Special refinement details for $\mathbf{2^{TMS}}$-$\mathbf{Ph^{CF3}}$: Refined as a two-component pseudo-merohedral twin using the HKLF5 keyword and BASF refined to 28%. Three reflections with $I_{obs} > 10\ I_{calc}$ were omitted.

Crystal data for $\mathbf{2^{TMS}}$-$\mathbf{Ph^{CF3}}$: $C_{21}H_{34}B_2F_3N_3Si_2$, $M_r = 463.31$, colourless plate, 0.258×0.121×0.024 mm^3, monoclinic space group $P2_1/c$, $a = 11.7482(5)$ Å, $b = 21.4022(7)$ Å, $c = 10.7780(4)$ Å, $\beta = 91.715(4)°$, $V = 2708.78(17)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.134$ g·cm^{-3}, $\mu = 1.469$ mm^{-1}, $F(000) = 980.000$, $T = 100.00(10)$ K, $R_1 = 0.0988$, $wR_2 = 0.2635$, 5085 independent reflections [$2\theta \leq 155.831°$] and 291 parameters.

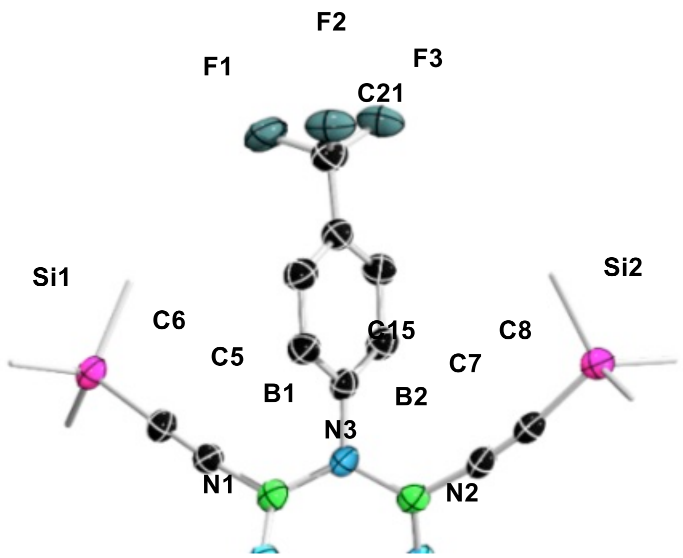

Figure S97. Crystallographically-determined solid-state structure of $\mathbf{2^{TMS}}$-$\mathbf{Ph^{CF3}}$. Atomic displacement ellipsoids represented at 50%. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity.

Crystal data for 2^{Me}-Ph: $C_{16}H_{23}B_2N_3$, M_r = 278.99, colourless block, 0.729×0.414×0.36 mm^3, monoclinic space group $P2_1/n$, a = 13.446(2) Å, b = 9.2578(15) Å, c = 13.4729(19) Å, β = 100.440(6)°, V = 1649.4(5) Å^3, Z = 4, ρ_{calcd} = 1.124 g·cm^{-3}, μ = 0.066 mm^{-1}, F(000) = 600, T = 100(2) K, R_1 = 0.0679, wR_2 = 0.1589, 3226 independent reflections [$2\theta \leq 52.032°$] and 196 parameters.

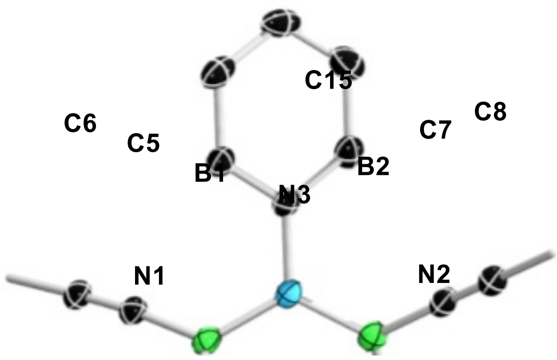

Figure S98. Crystallographically-determined solid-state structure of **2^{Me}-Ph**. Atomic displacement ellipsoids represented at 50%. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity.

Special refinement details for 2^{Me}-*o*Tol: The *o*-tolyl group (C15 > C21) was modelled as twofold disordered in a 71:29 ratio. The aryl rings within this disorder were idealised with AFIX 66 and ADPs restrained with SIMU 0.005

Crystal data for 2^{Me}-*o*Tol: $C_{17}H_{25}B_2N_3$, $M_r = 293.02$, colourless block, $0.414 \times 0.295 \times 0.142$ mm^3, monoclinic space group $P2_1/n$, $a = 8.639(2)$ Å, $b = 14.083(4)$ Å, $c = 14.346(4)$ Å, $\beta = 91.720(15)°$, $V = 1744.6(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.116$ g·cm^{-3}, $\mu = 0.065$ mm^{-1}, $F(000) = 632$, $T = 100(2)$ K, $R_1 = 0.0792$, $wR^2 = 0.1535$, 3448 independent reflections [$2\theta \leq 52.042°$] and 247 parameters.

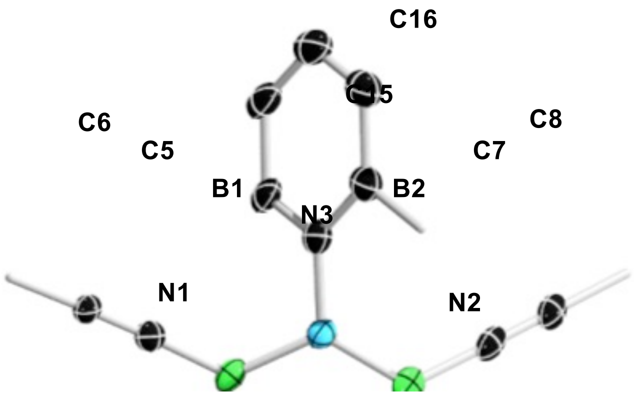

Figure S99. Crystallographically-determined solid-state structure of 2^{Me}-*o*Tol. Atomic displacement ellipsoids represented at 50%. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity.

Crystal data for 2^{H}-Ph: $C_{14}H_{19}B_2N_3$, M_r = 250.94, colourless block, 0.357×0.154×0.146 mm^3, monoclinic space group $P2_1/n$, a = 8.0065(5) Å, b = 7.0312(5) Å, c = 27.5295(16) Å, β = 95.020(4)°, V = 1543.84(17) Å^3, Z = 4, ρ_{calcd} = 1.080 g·cm^{-3}, μ = 0.063 mm^{-1}, F(000) = 536, T = 100(2) K, R_1 = 0.0683, wR_2 = 0.1177, 3038 independent reflections [$2\theta \leq 52.04°$] and 176 parameters.

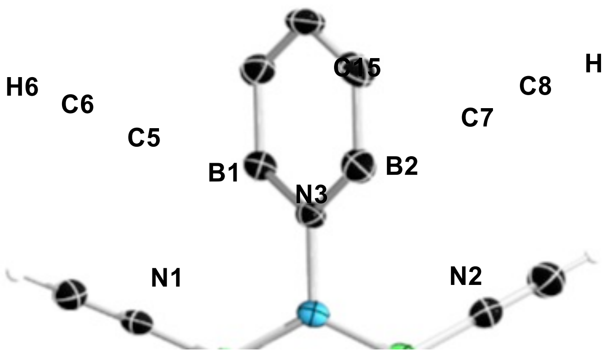

Figure S100. Crystallographically-determined solid-state structure of **2^{H}-Ph**. Atomic displacement ellipsoids represented at 50%. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity.

Special refinement details for 2^{H}-*o*Tol: An extinction coefficient was applied.

Crystal data for 2^{H}-*o*Tol: $C_{15}H_{21}B_2N_3$, M_r = 264.97, colourless plate, 0.348×0.34×0.15 mm^3, monoclinic space group $P2_1/n$, a = 9.1998(11) Å, b = 16.7464(19) Å, c = 11.1726(14) Å, β = 108.512(4)°, V = 1632.2(3) $Å^3$, Z = 4, ρ_{calcd} = 1.078 $g{\cdot}cm^{-3}$, μ = 0.063 mm^{-1}, $F(000)$ = 568, T = 100(2) K, R_1 = 0.1164, wR_2 = 0.1403, 3223 independent reflections [$2\theta \leq 52.04°$] and 187 parameters.

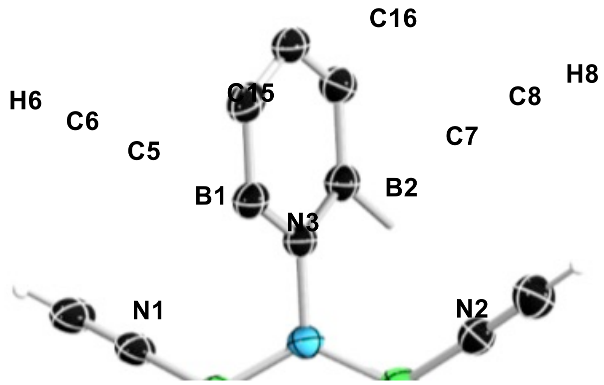

Figure S101. Crystallographically-determined solid-state structure of **2^{H}-*o*Tol**. Atomic displacement ellipsoids represented at 50%. Ellipsoids of ligand periphery and hydrogen atoms, except for terminal alkynyl hydrogens, omitted for clarity.

Special refinement details for 4^Me^: The most disagreeable reflections were omitted (1 0 0, 1 1 0, 1 2 0)

Crystal data for $\mathbf{4^{Me}}$: $C_{46}H_{64}B_4N_2$, M_r = 688.23, colourless needle, 0.527×0.407×0.176 mm^3, monoclinic space group $P2_1/c$, a = 15.1340(10) Å, b = 35.027(2) Å, c = 8.2612(5) Å, β = 103.043(3)°, V = 4266.3(5) Å^3, Z = 4, ρ_{calcd} = 1.071 g·cm^{-3}, μ = 0.059 mm^{-1}, F(000) = 1496, T = 100(2) K, R_1 = 0.1351, wR_2 = 0.1605, 8405 independent reflections [$2\theta \leq 52.042°$] and 487 parameters.

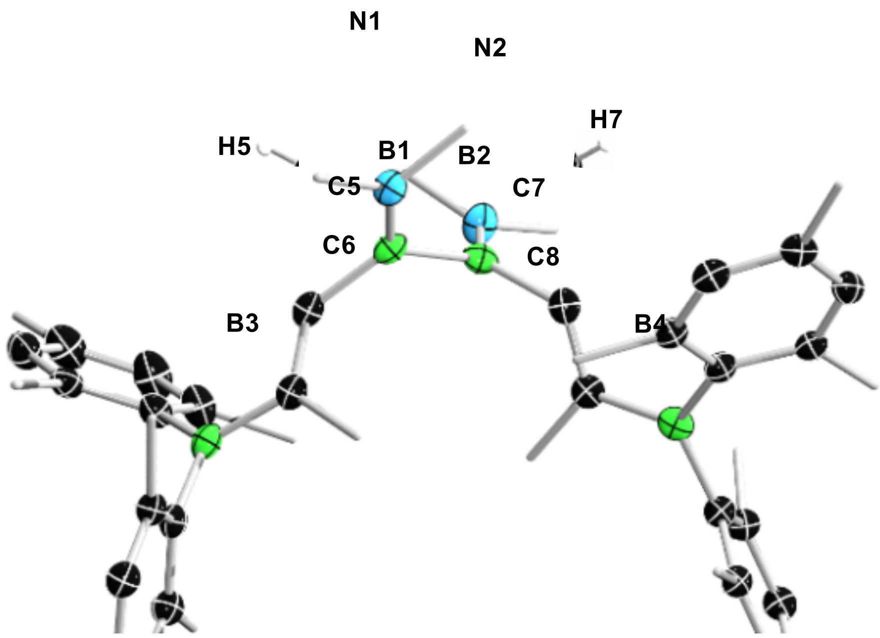

Figure S102. Crystallographically-determined solid-state structure of $\mathbf{4^{Me}}$. Atomic displacement ellipsoids represented at 50%. Ellipsoids of ligand periphery and hydrogen atoms, except for vinylic hydrogens, omitted for clarity.

Special refinement details for 4^{H}: An extinction coefficient was applied.

Crystal data for 4^{H}: $C_{44}H_{60}B_4N_2$, M_r = 660.18, colourless needle, 0.245×0.225×0.086 mm^3, monoclinic space group $P2_1/c$, a = 14.7580(11) Å, b = 18.7438(13) Å, c = 14.9750(11) Å, β = 97.863(4)°, V = 4103.5(5) $Å^3$, Z = 4, ρ_{calcd} = 1.069 g·cm^{-3}, μ = 0.059 mm^{-1}, $F(000)$ = 1432, T = 140(2) K, R_1 = 0.0687, wR_2 = 0.1708, 8060 independent reflections [$2\theta \leq 52.044°$] and 468 parameters.

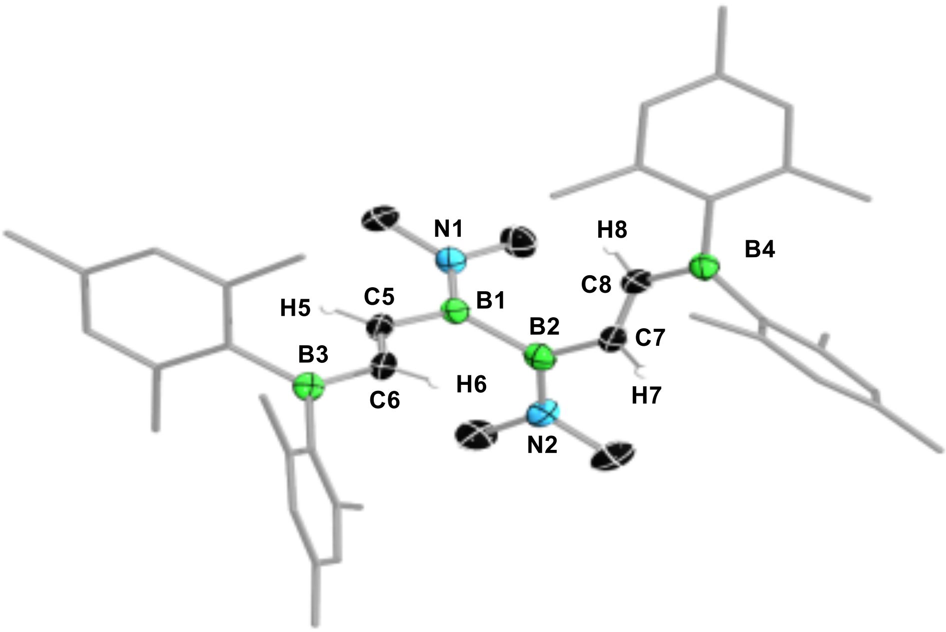

Figure S103. Crystallographically-determined solid-state structure of 4^{H}. Atomic displacement ellipsoids represented at 50%. Ellipsoids of ligand periphery and hydrogen atoms, except for vinylic hydrogens, omitted for clarity.

Special refinement details for 6^H: The asymmetric unit contains four crystallographically distinct molecules of the compounds (RESI 1, 2, 3, 4 MAIN), with different orientations of the ethyl substituent and different degrees of disorder. RESI 2 and 3 MAIN are not disordered. RESI 1: The BHEt(NMe_2) unit (RESI 7 and 71 BNCH) and one half of the I*i*Pr ligand (N2, C8 > C12, RESI 8 and 81 I*i*Pr) were modelled as twofold disordered in a 93:7 ratio. 1,2- and 1,3-distances in both parts of the disorder were restrained to similarity with SAME. ADPs were restrained to similarity with SIMU 0.005. RESI 4: The BHEt(NMe_2) unit (RESI 9 and 91 BNCH) and one half of the I*i*Pr ligand (N2, C8 > C12, RESI 5 and 51 I*i*Pr) were modelled as twofold disordered in a 83:17 ratio. 1,2- and 1,3-distances in both parts of the disorder were restrained to similarity with SAME. ADPs were restrained to similarity with SIMU 0.006 (RESI BCNH) and SIMU 0.003 (RESI I*i*Pr), respectively.

Crystal data for 6^H: $C_{13}H_{28}BN_3$, $M_r = 237.19$, colourless plate, $0.244\times0.203\times0.096$ mm^3, triclinic space group $P\bar{1}$, $a = 8.72540(10)$ Å, $b = 18.0882(4)$ Å, $c = 20.4041(3)$ Å, $\alpha = 105.493(2)°$, $\beta = 92.5810(10)°$, $\gamma = 91.617(2)°$, $V = 3097.44(9)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.013$ g·cm^{-3}, $\mu = 0.451$ mm^{-1}, $F(000) = 1050$, $T = 100.00(11)$ K, $R_1 = 0.0664$, $wR_2 = 0.1619$, 11722 independent reflections [$2\theta \leq 134.152°$] and 898 parameters.

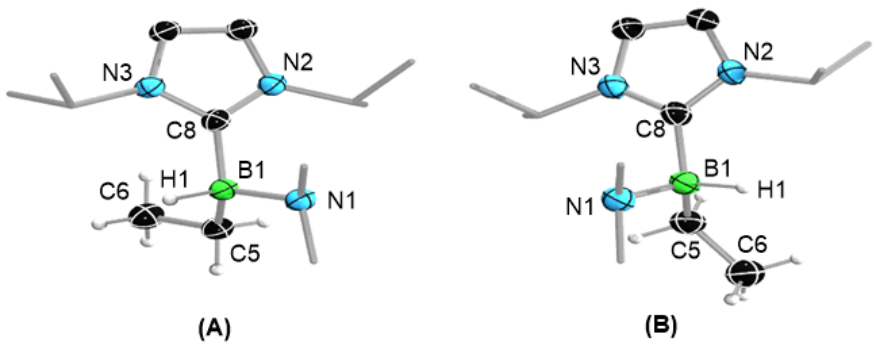

Figure S104. Crystallographically-determined solid-state structures of the two conformers of 6^H present in the asymmetric unit. Atomic displacement ellipsoids at 50%. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity, except for the boron-bound hydride and ethyl protons resulting from the hydrogenation reaction.

Computational details

Geometry optimisations and Hessian calculations were performed for **1^R**, **2^R-Ph**, and **3^R-Ph** (R = H, Me, Ph, and $SiMe_3$) at the density functional theory level. The PBE0[7,8] functional was employed in conjunction with the def2-SVP[9] basis set. Dispersion corrections were considered using Grimme's D3[10] model with the Becke-Johnson (BJ)[11] damping function. The reaction mechanism of the formal nitrene insertion into **1^H** was also investigated. The transition states were optimised at the same level of theory. All optimised geometries were characterised either as minimum energy structures (only positive eigenvalues) or transition states (one negative eigenvalue) by vibrational frequency calculations. In order to attest the connectivity of transition states and their corresponding minimum energy structures, inspection of the imaginary modes and additional intrinsic reaction coordinate (IRC)[12] calculations were performed. To estimate the Gibbs free energies in solution, single-point calculations at the optimised geometries were performed at the PBE0-D3(BJ)/def2-QZVPP[13] level, with the inclusion of implicit solvent effects by the Solvation Model for Density (SMD)[14] method (solvent = benzene, $\varepsilon = 2.2706$). The thermal corrections to the Gibbs free energies (G_{corr}) obtained at the PBE0-D3(BJ)/def2-SVP were added to the solvent-corrected single-point energies. A concentration correction (G_{conc}) of $\Delta G^{0\rightarrow*} = RT\ln(24.46) = 1.89$ kcal mol^{-1} ($T = 298.15$ K) was also included in the free energies of all species in order to account for the change in standard states in going from gas phase (1 atm) to the condensed phase (1 M) and to properly describe associative/dissociative steps.[15,16] All calculations were performed using Gaussian 16, revision C.01.[17] Images of 3D structures were obtained using CYLview.[18]

Table S1. Energy components (Hartree) of the species investigated in this work. Level of theory: PBE0-D3(BJ)/def2-QZVPP+SMD(Benzene)//PBE0-D3(BJ)/def2-SVP.

Species	E	E+ZPE	G_{corr}	G_{conc}	G
N_2	-109.446079	-109.440316	-0.012674	0.003018	-109.455735
1^{H}	-472.073446	-471.858686	0.17261	0.003018	-471.897817
1^{Me}	-550.667304	-550.39633	0.219792	0.003018	-550.444494
1^{Ph}	-933.877562	-933.497469	0.319098	0.003018	-933.555445
1^{SiMe3}	-1289.094831	-1288.675345	0.354024	0.003018	-1288.737789
PhN_3	-395.563564	-395.458485	0.07327	0.003018	-395.487276
2^{H}-Ph	-758.352238	-758.038567	0.264725	0.003018	-758.084494
2^{Me}-Ph	-836.947578	-836.577583	0.31346	0.003018	-836.631099
2^{Ph}-Ph	-1220.158332	-1219.679359	0.412041	0.003018	-1219.743273
2^{SiMe3}-Ph	-1575.37521	-1574.856982	0.444834	0.003018	-1574.927358
A^{H}-Ph	-867.6461228	-867.3257248	0.264799	0.003018	-867.378306
TS1	-867.607881	-867.288412	0.268243	0.003018	-867.336620
B^{H}-Ph	-867.7075054	-867.3844384	0.271126	0.003018	-867.433361
TS2	-867.6745025	-867.3544295	0.26925	0.003018	-867.402234
3^{H}-Ph	-867.7524408	-867.7524408	0.275423	0.003018	-867.474000
3^{Me}-Ph	-946.3349404	-945.9516864	0.325216	0.003018	-946.006706
3^{Ph}-Ph	-1329.548579	-1329.056766	0.425714	0.003018	-1329.119847
3^{SiMe3}-Ph	-1684.759696	-1684.22871	0.459063	0.003018	-1684.297615

Cartesian coordinates

All values are given in Å.

N_2			
N	0.000000000	0.000000000	-0.048878000
N	0.000000000	0.000000000	1.048878000

PhN_3			
C	-2.512421000	0.475157000	0.000000000
C	-2.203892000	-0.885566000	0.000000000
C	-0.879615000	-1.309054000	0.000000000
C	0.152878000	-0.365257000	0.000000000
C	-0.150967000	1.002374000	0.000000000
C	-1.480652000	1.413116000	0.000000000
H	-3.553618000	0.803869000	0.000000000
H	-3.004840000	-1.628454000	0.000000000
H	-0.619993000	-2.368968000	0.000000000
H	0.652413000	1.743559000	0.000000000
H	-1.710773000	2.481118000	0.000000000
N	1.466822000	-0.865291000	0.000000000
N	2.411386000	-0.090251000	0.000000000
N	3.362482000	0.524722000	0.000000000

1^{H}			
B	-0.836865000	-0.196934000	0.196677000
C	-3.217422000	0.316417000	-0.435266000
H	-3.602127000	0.187785000	-1.462925000
H	-3.779133000	1.148966000	0.025084000
H	-3.418549000	-0.599709000	0.133328000
N	-1.800411000	0.596110000	-0.444898000
C	-1.462495000	1.788413000	-1.184752000
H	-1.747057000	1.691088000	-2.248154000
H	-0.384891000	1.985968000	-1.126390000

H	-1.993869000	2.668003000	-0.779641000
C	-1.285107000	-1.459466000	0.959449000
B	0.836846000	0.196939000	0.196665000
C	3.217398000	-0.316411000	-0.435294000
H	3.602099000	-0.187769000	-1.462954000
H	3.779110000	-1.148966000	0.025045000
H	3.418528000	0.599708000	0.133310000
N	1.800386000	-0.596102000	-0.444925000
C	1.462467000	-1.788398000	-1.184789000
H	1.747003000	-1.691058000	-2.248196000
H	0.384867000	-1.985968000	-1.126401000
H	1.993861000	-2.667987000	-0.779702000
C	1.285096000	1.459455000	0.959460000
C	1.558223000	2.477912000	1.572734000
H	1.802186000	3.372169000	2.116929000
C	-1.558130000	-2.477929000	1.572758000
H	-1.801937000	-3.372258000	2.116905000

1^Me^

B	-0.708178000	0.488102000	-0.181381000
C	-1.914791000	2.601338000	-0.823078000
H	-2.271177000	2.796566000	-1.851019000
H	-1.673749000	3.579502000	-0.368259000
H	-2.728209000	2.138668000	-0.250508000
N	-0.760030000	1.735775000	-0.828942000
C	0.352154000	2.277246000	-1.570478000
H	0.093995000	2.414986000	-2.636685000
H	1.220249000	1.609533000	-1.502623000
H	0.649328000	3.265186000	-1.174171000
C	-1.941820000	-0.020311000	0.582752000
B	0.708177000	-0.488108000	-0.181375000
C	1.914796000	-2.601343000	-0.823061000
H	2.271188000	-2.796571000	-1.851001000

H	1.673754000	-3.579507000	-0.368243000
H	2.728210000	-2.138671000	-0.250488000
N	0.760033000	-1.735783000	-0.828932000
C	-0.352147000	-2.277258000	-1.570470000
H	-0.093984000	-2.415001000	-2.636676000
H	-1.220243000	-1.609546000	-1.502620000
H	-0.649320000	-3.265197000	-1.174161000
C	1.941817000	0.020313000	0.582755000
C	2.875907000	0.504627000	1.203655000
C	-2.875913000	-0.504616000	1.203655000
C	-3.987028000	-1.072587000	1.946426000
H	-4.181499000	-0.494954000	2.864375000
H	-4.913013000	-1.063363000	1.349368000
H	-3.786788000	-2.114433000	2.243186000
C	3.987020000	1.072605000	1.946424000
H	4.181012000	0.495404000	2.864745000
H	4.913176000	1.062719000	1.349641000
H	3.787069000	2.114684000	2.242562000

1^Ph^

B	0.526637000	1.235394000	-0.679862000
C	1.033689000	1.827782000	-3.071668000
H	1.297193000	2.852900000	-3.389216000
H	0.517514000	1.343296000	-3.920236000
H	1.958237000	1.275825000	-2.862142000
N	0.191114000	1.848251000	-1.899763000
C	-1.044409000	2.565274000	-2.101845000
H	-0.854371000	3.626599000	-2.345213000
H	-1.669261000	2.517454000	-1.201413000
H	-1.619935000	2.133244000	-2.940349000
C	1.868078000	0.499168000	-0.547641000
B	-0.526634000	1.235268000	0.680074000
C	-1.033675000	1.827202000	3.071994000

H	-1.297160000	2.852264000	3.389740000
H	-0.517511000	1.342542000	3.920468000
H	-1.958235000	1.275305000	2.862358000
N	-0.191099000	1.847883000	1.900093000
C	1.044435000	2.564849000	2.102315000
H	0.854412000	3.626130000	2.345885000
H	1.669288000	2.517192000	1.201875000
H	1.619953000	2.132649000	2.940737000
C	-1.868090000	0.499097000	0.547709000
C	-2.918695000	-0.096248000	0.343091000
C	2.918672000	-0.096229000	-0.343124000
C	4.140377000	-0.789214000	-0.100150000
C	4.363224000	-1.429317000	1.133055000
C	5.144288000	-0.845625000	-1.084255000
C	5.555338000	-2.104206000	1.370892000
H	3.584608000	-1.388543000	1.897220000
C	6.334311000	-1.521634000	-0.838809000
H	4.974387000	-0.350869000	-2.042535000
C	6.544042000	-2.152543000	0.387695000
H	5.715454000	-2.598141000	2.332238000
H	7.105954000	-1.557834000	-1.611487000
H	7.479807000	-2.683618000	0.577489000
C	-4.140391000	-0.789207000	0.100004000
C	-5.144270000	-0.845858000	1.084128000
C	-4.363263000	-1.429042000	-1.133336000
C	-6.334286000	-1.521840000	0.838570000
H	-4.974350000	-0.351311000	2.042512000
C	-5.555370000	-2.103905000	-1.371285000
H	-3.584672000	-1.388082000	-1.897516000
C	-6.544041000	-2.152481000	-0.388068000
H	-7.105904000	-1.558227000	1.611264000
H	-5.715506000	-2.597630000	-2.332735000
H	-7.479801000	-2.683535000	-0.577950000

1^{SiMe3}			
B	0.621695000	0.594952000	-1.032758000
C	2.955434000	1.351897000	-1.576780000
H	3.269484000	1.630613000	-2.598778000
H	3.841460000	0.939573000	-1.061177000
H	2.630690000	2.257040000	-1.048769000
N	1.883974000	0.383963000	-1.610337000
C	2.241529000	-0.833782000	-2.297238000
H	2.495374000	-0.633890000	-3.354083000
H	1.414983000	-1.553769000	-2.262486000
H	3.124042000	-1.305779000	-1.829128000
C	-2.241529000	4.973140000	0.469257000
H	-2.600918000	5.896279000	0.951616000
H	-2.958513000	4.167621000	0.690808000
H	-2.238131000	5.134860000	-0.619779000
Si	-0.523106000	4.521350000	1.084192000
C	0.001257000	2.970938000	0.238708000
C	0.329645000	1.929975000	-0.325541000
C	0.697786000	5.888869000	0.668633000
H	1.711337000	5.624982000	1.008010000
H	0.408393000	6.833863000	1.155757000
H	0.738199000	6.062029000	-0.417857000
C	-0.548529000	4.205631000	2.936179000
H	0.449985000	3.916473000	3.298251000
H	-1.247449000	3.392308000	3.184444000
H	-0.863528000	5.109844000	3.481323000
B	-0.621695000	-0.594952000	-1.032758000
C	-2.955434000	-1.351897000	-1.576780000
H	-3.269484000	-1.630613000	-2.598778000
H	-3.841460000	-0.939573000	-1.061177000
H	-2.630690000	-2.257040000	-1.048769000
N	-1.883974000	-0.383963000	-1.610337000

C	-2.241529000	0.833782000	-2.297238000
H	-2.495374000	0.633890000	-3.354083000
H	-1.414983000	1.553769000	-2.262486000
H	-3.124042000	1.305779000	-1.829128000
C	2.241529000	-4.973140000	0.469257000
H	2.600918000	-5.896279000	0.951616000
H	2.958513000	-4.167621000	0.690808000
H	2.238131000	-5.134860000	-0.619779000
Si	0.523106000	-4.521350000	1.084192000
C	-0.001257000	-2.970938000	0.238708000
C	-0.329645000	-1.929975000	-0.325541000
C	-0.697786000	-5.888869000	0.668633000
H	-1.711337000	-5.624982000	1.008010000
H	-0.408393000	-6.833863000	1.155757000
H	-0.738199000	-6.062029000	-0.417857000
C	0.548529000	-4.205631000	2.936179000
H	-0.449985000	-3.916473000	3.298251000
H	1.247449000	-3.392308000	3.184444000
H	0.863528000	-5.109844000	3.481323000

2^{H}-Ph

N	-1.834888000	-1.433115000	0.838810000
C	-2.662558000	-2.612406000	0.760947000
H	-2.791882000	-3.071092000	1.757543000
H	-2.207414000	-3.352572000	0.091649000
H	-3.670646000	-2.369335000	0.377141000
B	-0.654521000	-1.276351000	0.078946000
N	-1.835069000	1.433165000	-0.838475000
C	-2.351075000	-0.427698000	1.733745000
H	-1.582770000	0.321436000	1.964981000
H	-2.669063000	-0.894063000	2.682043000
H	-3.226795000	0.098706000	1.311361000
B	-0.654422000	1.276509000	-0.079007000

C	-2.662500000	2.612648000	-0.760810000
H	-2.791038000	3.071715000	-1.757346000
H	-2.207644000	3.352497000	-0.090971000
H	-3.670892000	2.369672000	-0.377782000
N	0.046285000	0.000059000	-0.000116000
C	-2.351530000	0.427693000	-1.733193000
H	-2.669867000	0.894004000	-2.681403000
H	-3.227087000	-0.098697000	-1.310475000
H	-1.583283000	-0.321425000	-1.964677000
C	-0.097706000	-2.486611000	-0.708686000
C	-0.097248000	2.486851000	0.708199000
C	1.456926000	-0.000074000	-0.000019000
C	2.173180000	-0.885661000	0.816584000
H	1.626126000	-1.567316000	1.472169000
C	3.564557000	-0.891216000	0.808136000
H	4.102844000	-1.592226000	1.450910000
C	4.269616000	-0.000283000	0.000073000
H	5.361937000	-0.000370000	0.000112000
C	3.564749000	0.890787000	-0.808043000
H	4.103202000	1.591710000	-1.450772000
C	2.173393000	0.885433000	-0.816569000
H	1.626426000	1.567172000	-1.472136000
C	0.336277000	-3.413742000	-1.367568000
H	0.733954000	-4.226968000	-1.947183000
C	0.337123000	3.414000000	1.366787000
H	0.735094000	4.227277000	1.946120000

2^{Me}-Ph

N	1.169487000	-1.952625000	1.170601000
C	2.327613000	-2.782755000	1.390468000
H	2.520681000	-2.917602000	2.470207000
H	3.212348000	-2.324852000	0.931022000
H	2.189695000	-3.789570000	0.953533000

B	1.218531000	-0.768328000	0.397543000
N	-1.168662000	-1.953105000	-1.170529000
C	-0.030052000	-2.467237000	1.780456000
H	-0.814408000	-1.699687000	1.808381000
H	0.177604000	-2.780958000	2.818397000
H	-0.431005000	-3.345913000	1.241659000
B	-1.218206000	-0.768884000	-0.397381000
C	-2.326486000	-2.783606000	-1.390573000
H	-2.519716000	-2.918033000	-2.470337000
H	-3.211323000	-2.326287000	-0.930738000
H	-2.188064000	-3.790567000	-0.954132000
N	0.000000000	-0.067437000	0.000080000
C	0.031086000	-2.467219000	-1.780394000
H	-0.176462000	-2.781100000	-2.818308000
H	0.432460000	-3.345676000	-1.241552000
H	0.815094000	-1.699317000	-1.808401000
C	2.583541000	-0.207679000	-0.049629000
C	-2.583448000	-0.208715000	0.049671000
C	-0.000289000	1.341142000	0.000036000
C	0.663511000	2.060077000	1.004408000
H	1.169591000	1.513517000	1.803460000
C	0.670363000	3.451537000	0.997655000
H	1.196303000	3.989613000	1.790476000
C	-0.000923000	4.157385000	-0.000053000
H	-0.001176000	5.249788000	-0.000089000
C	-0.671886000	3.451170000	-0.997730000
H	-1.198055000	3.988969000	-1.790586000
C	-0.664402000	2.059720000	-1.004395000
H	-1.170216000	1.512866000	-1.803414000
C	3.637343000	0.261110000	-0.444794000
C	-3.637412000	0.259763000	0.444763000
C	-4.879944000	0.845466000	0.913763000
H	-4.856524000	1.942069000	0.811373000

H	-5.746392000	0.469425000	0.347409000
H	-5.047855000	0.615737000	1.978033000
C	4.879715000	0.847087000	-0.913864000
H	4.856573000	1.943589000	-0.810315000
H	5.746376000	0.470389000	-0.348259000
H	5.047094000	0.618352000	-1.978423000

2^{Ph}-Ph			
N	-0.985879000	2.674315000	1.335660000
C	-2.112139000	3.478053000	1.741751000
H	-2.122445000	3.622744000	2.837098000
H	-3.049814000	2.991459000	1.445125000
H	-2.079058000	4.481198000	1.277363000
B	-1.137781000	1.477893000	0.598383000
N	0.985953000	2.674271000	-1.335899000
C	0.287502000	3.217681000	1.734259000
H	1.079353000	2.462794000	1.643203000
H	0.246087000	3.542928000	2.788222000
H	0.579584000	4.094588000	1.127112000
B	1.137836000	1.477933000	-0.598512000
C	2.112245000	3.477944000	-1.742042000
H	2.122607000	3.622482000	-2.837408000
H	3.049900000	2.991379000	-1.445300000
H	2.079149000	4.481152000	-1.277793000
N	-0.000019000	0.785918000	-0.000137000
C	-0.287413000	3.217634000	-1.734552000
H	-0.245971000	3.542834000	-2.788527000
H	-0.579481000	4.094569000	-1.127444000
H	-1.079268000	2.462759000	-1.643463000
C	-2.533906000	0.855508000	0.411555000
C	2.533924000	0.855559000	-0.411446000
C	0.000005000	-0.625138000	-0.000229000
C	-0.427132000	-1.342620000	1.125633000

H	-0.746197000	-0.795438000	2.015541000
C	-0.436172000	-2.734348000	1.120931000
H	-0.776359000	-3.272189000	2.009395000
C	0.000124000	-3.439968000	-0.000441000
H	0.000165000	-4.532388000	-0.000523000
C	0.436361000	-2.734146000	-1.121710000
H	0.776595000	-3.271828000	-2.010250000
C	0.427204000	-1.342419000	-1.126200000
H	0.746237000	-0.795069000	-2.016017000
C	-3.584549000	0.262438000	0.218050000
C	3.584488000	0.262424000	-0.217712000
C	4.762260000	-0.504166000	0.015922000
C	6.043641000	0.044076000	-0.167706000
C	4.643880000	-1.842931000	0.434142000
C	7.176597000	-0.728327000	0.064525000
H	6.136500000	1.081978000	-0.493517000
C	5.782329000	-2.608296000	0.659946000
H	3.646589000	-2.266107000	0.573017000
C	7.050292000	-2.054771000	0.477763000
H	8.168081000	-0.292437000	-0.079432000
H	5.680136000	-3.647147000	0.982626000
H	7.942603000	-2.658946000	0.658065000
C	-4.762344000	-0.504143000	-0.015523000
C	-6.043702000	0.043942000	0.168784000
C	-4.644029000	-1.842723000	-0.434326000
C	-7.176689000	-0.728430000	-0.063377000
H	-6.136505000	1.081700000	0.495071000
C	-5.782513000	-2.608066000	-0.660056000
H	-3.646766000	-2.265797000	-0.573702000
C	-7.050444000	-2.054697000	-0.477215000
H	-8.168151000	-0.292664000	0.081105000
H	-5.680361000	-3.646780000	-0.983192000
H	-7.942780000	-2.658852000	-0.657459000

2^{SiMe3}-Ph			
Si	-5.039463000	-0.921540000	-0.220930000
N	-1.025833000	2.585660000	1.310955000
C	-2.167072000	3.382915000	1.688873000
H	-2.204770000	3.527272000	2.783598000
H	-3.094234000	2.890535000	1.369025000
H	-2.128034000	4.386181000	1.225415000
B	-1.152995000	1.391180000	0.567842000
N	1.025814000	2.585687000	-1.310997000
Si	5.039409000	-0.921507000	0.221044000
C	0.234798000	3.134257000	1.742102000
H	1.031431000	2.382031000	1.672540000
H	0.164463000	3.460488000	2.794164000
H	0.539397000	4.011472000	1.141762000
B	1.152987000	1.391219000	-0.567874000
C	2.167030000	3.382996000	-1.688875000
H	2.204719000	3.527408000	-2.783591000
H	3.094206000	2.890623000	-1.369055000
H	2.127960000	4.386234000	-1.225365000
N	-0.000010000	0.700916000	-0.000039000
C	-0.234828000	3.134252000	-1.742160000
H	-0.164507000	3.460438000	-2.794236000
H	-0.539422000	4.011490000	-1.141850000
H	-1.031449000	2.382021000	-1.672554000
C	-2.545370000	0.764774000	0.342763000
C	-3.597679000	0.175220000	0.124054000
C	-4.580053000	-2.630845000	0.408279000
H	-5.374582000	-3.361697000	0.188022000
H	-4.418980000	-2.613847000	1.497203000
H	-3.645926000	-2.974199000	-0.062862000
C	-6.557397000	-0.262776000	0.669655000
H	-7.428297000	-0.913254000	0.489775000

H	-6.810216000	0.750369000	0.320618000
H	-6.385069000	-0.214837000	1.755939000
C	-5.327352000	-0.950756000	-2.077293000
H	-6.168729000	-1.615183000	-2.331491000
H	-4.430311000	-1.314565000	-2.601394000
H	-5.558893000	0.056313000	-2.456912000
C	2.545375000	0.764865000	-0.342721000
C	3.597685000	0.175329000	-0.123965000
C	4.579706000	-2.630833000	-0.407898000
H	5.374124000	-3.361806000	-0.187650000
H	4.418442000	-2.613960000	-1.496793000
H	3.645583000	-2.973956000	0.063429000
C	5.327438000	-0.950519000	2.077385000
H	6.168668000	-1.615089000	2.331659000
H	4.430326000	-1.314043000	2.601574000
H	5.559188000	0.056562000	2.456850000
C	6.557346000	-0.263007000	-0.669729000
H	7.428195000	-0.913518000	-0.489680000
H	6.810257000	0.750187000	-0.320904000
H	6.385044000	-0.215318000	-1.756023000
C	0.000035000	-0.711327000	-0.000089000
C	-0.449736000	-1.428120000	1.116829000
H	-0.788084000	-0.880521000	1.999362000
C	-0.458795000	-2.819652000	1.112050000
H	-0.817996000	-3.357923000	1.992731000
C	0.000199000	-3.525117000	-0.000147000
H	0.000271000	-4.617484000	-0.000166000
C	0.459092000	-2.819553000	-1.112314000
H	0.818352000	-3.357741000	-1.993021000
C	0.449867000	-1.428018000	-1.117039000
H	0.788142000	-0.880358000	-1.999563000

A^{H}-Ph

N	1.220499000	-0.820034000	-1.800571000
C	0.900381000	-2.101394000	-2.382409000
H	-0.151026000	-2.128110000	-2.721509000
H	1.041755000	-2.897509000	-1.641628000
H	1.539380000	-2.310435000	-3.259002000
B	1.593249000	-0.639380000	-0.460391000
N	3.141919000	1.355889000	0.623035000
C	1.097057000	0.278404000	-2.726739000
H	1.278749000	1.233106000	-2.216998000
H	0.084380000	0.316041000	-3.167146000
H	1.814294000	0.180652000	-3.561906000
B	1.872395000	0.910610000	0.225663000
C	3.392019000	2.636298000	1.241967000
H	3.833532000	2.508760000	2.246784000
H	2.454447000	3.197566000	1.338993000
H	4.102930000	3.233855000	0.643278000
N	-1.548932000	-1.582607000	0.204625000
C	4.332949000	0.558640000	0.456966000
H	4.831318000	0.385190000	1.427503000
H	5.062035000	1.062299000	-0.203552000
H	4.083658000	-0.418083000	0.023291000
C	1.735313000	-1.860951000	0.467851000
C	0.640836000	1.808538000	0.437642000
C	-2.357687000	-0.440709000	0.097922000
C	-3.039983000	0.126210000	1.181416000
H	-2.951611000	-0.315392000	2.177035000
C	-3.824549000	1.259292000	0.986367000
H	-4.355262000	1.694994000	1.836408000
C	-3.935351000	1.836795000	-0.278580000
H	-4.554853000	2.724043000	-0.426199000
C	-3.251402000	1.268003000	-1.354358000
H	-3.328736000	1.713127000	-2.349045000
C	-2.467125000	0.135696000	-1.171657000

H	-1.922611000	-0.318954000	-1.999938000
C	1.877284000	-2.763823000	1.276155000
H	1.994851000	-3.560248000	1.988278000
C	-0.402327000	2.430275000	0.551875000
H	-1.337993000	2.952014000	0.643792000
N	-1.430688000	-2.145625000	1.282695000
N	-1.244505000	-2.755726000	2.217171000

TS1 (imaginary frequency: –313.0 cm^{-1})

	-0.004270000	1.751299000	0.245632000
C	0.561789000	2.643984000	1.216923000
H	1.655698000	2.756883000	1.077019000
H	0.379067000	2.269576000	2.231713000
H	0.116905000	3.652986000	1.130613000
B	-0.547701000	0.439630000	0.529943000
N	-2.927225000	-1.064232000	0.185674000
C	0.173979000	2.184377000	-1.111668000
H	1.235733000	2.109829000	-1.423678000
H	-0.134703000	3.237211000	-1.237531000
H	-0.431616000	1.575397000	-1.796143000
B	-2.157028000	0.046858000	-0.223493000
C	-4.358696000	-1.153366000	0.030317000
H	-4.629943000	-2.011883000	-0.610492000
H	-4.750068000	-0.235841000	-0.424148000
H	-4.848326000	-1.304878000	1.009234000
N	0.581546000	-0.699250000	-0.339123000
C	-2.354561000	-2.248696000	0.773852000
H	-2.780301000	-2.434869000	1.775722000
H	-1.270065000	-2.145955000	0.889181000
H	-2.568109000	-3.133603000	0.147566000
C	-0.570921000	0.052743000	2.045066000
C	-2.895939000	1.210386000	-0.917421000
C	1.985489000	-0.617848000	-0.280175000

C	2.790337000	-0.863541000	-1.399393000
H	2.327015000	-1.155532000	-2.344611000
C	4.172069000	-0.737923000	-1.298434000
H	4.793026000	-0.936717000	-2.175105000
C	4.761419000	-0.353847000	-0.094305000
H	5.846061000	-0.250680000	-0.021015000
C	3.953688000	-0.106696000	1.015017000
H	4.404395000	0.188434000	1.965443000
C	2.571084000	-0.242426000	0.933120000
H	1.934687000	-0.069815000	1.801858000
C	-0.629830000	-0.267113000	3.220429000
H	-0.685616000	-0.549443000	4.255812000
C	-3.434943000	2.154468000	-1.469823000
H	-3.910157000	2.985325000	-1.958492000
N	0.018578000	-1.192122000	-1.357553000
N	-1.027177000	-1.210820000	-1.849804000

B^{H}-Ph

N	0.130899000	1.902636000	-0.178559000
C	-0.425060000	3.169479000	0.231218000
H	0.373962000	3.910241000	0.412401000
H	-1.007409000	3.049915000	1.152690000
H	-1.085365000	3.574112000	-0.555471000
B	-0.079080000	0.716334000	0.527706000
N	-3.388737000	-0.816629000	0.024309000
C	0.917843000	1.973292000	-1.385007000
H	1.136506000	0.968825000	-1.763361000
H	1.873106000	2.499818000	-1.209956000
H	0.359601000	2.519944000	-2.163192000
B	-2.123644000	-0.887188000	-0.588705000
C	-4.468666000	-0.006640000	-0.471258000
H	-5.378730000	-0.613284000	-0.631314000
H	-4.189104000	0.459211000	-1.424754000

H	-4.728332000	0.795261000	0.244754000
N	0.678845000	-0.518895000	0.171919000
C	-3.672158000	-1.510363000	1.252065000
H	-4.602051000	-2.099439000	1.158417000
H	-3.803995000	-0.805649000	2.093576000
H	-2.845428000	-2.189887000	1.496158000
C	-0.962598000	0.690976000	1.787733000
C	-1.850432000	-0.181906000	-1.936792000
C	2.089112000	-0.540646000	0.161535000
C	2.775175000	-1.529124000	-0.556372000
H	2.201988000	-2.282512000	-1.096978000
C	4.166256000	-1.541510000	-0.566503000
H	4.689214000	-2.320125000	-1.127174000
C	4.892603000	-0.565503000	0.115630000
H	5.984492000	-0.574189000	0.094805000
C	4.209595000	0.420115000	0.826206000
H	4.764288000	1.184320000	1.375996000
C	2.818143000	0.429560000	0.861072000
H	2.290625000	1.188083000	1.443527000
C	-1.584761000	0.683128000	2.834143000
H	-2.130420000	0.669903000	3.760270000
C	-1.613809000	0.340756000	-3.011239000
H	-1.410060000	0.794817000	-3.963889000
N	0.097196000	-1.742627000	0.089724000
N	-1.122020000	-1.805169000	-0.085405000

TS2 (imaginary frequency: –321.4 cm^{-1})

N	-1.042838000	1.511905000	-1.167648000
C	-1.902136000	2.611572000	-1.535385000
H	-1.373323000	3.324832000	-2.192351000
H	-2.239552000	3.146142000	-0.638940000
H	-2.788554000	2.248048000	-2.084721000
B	-0.697526000	1.218429000	0.156613000

N	-2.187342000	-1.335513000	-0.036020000
C	-0.539264000	0.761071000	-2.293603000
H	-0.003081000	-0.135439000	-1.960443000
H	0.155256000	1.371482000	-2.898148000
H	-1.368008000	0.446719000	-2.949199000
B	-0.815493000	-1.518006000	0.357666000
C	-2.696670000	-1.761219000	-1.311718000
H	-3.541678000	-2.466115000	-1.191312000
H	-1.914702000	-2.266531000	-1.892282000
H	-3.073072000	-0.905987000	-1.906738000
N	0.178016000	0.060766000	0.470002000
C	-3.182887000	-0.690489000	0.779274000
H	-3.556987000	0.241964000	0.313580000
H	-2.788546000	-0.424457000	1.767897000
H	-4.056016000	-1.352240000	0.934344000
C	-1.234523000	2.072881000	1.319493000
C	0.033431000	-2.557827000	-0.418877000
C	1.558403000	0.183443000	0.224788000
C	2.442648000	-0.849552000	0.583064000
H	2.057627000	-1.764295000	1.031764000
C	3.810436000	-0.716021000	0.370930000
H	4.475992000	-1.533533000	0.658649000
C	4.334960000	0.443733000	-0.198092000
H	5.410191000	0.541832000	-0.362869000
C	3.470152000	1.480163000	-0.543928000
H	3.863273000	2.401829000	-0.979960000
C	2.101151000	1.355838000	-0.330824000
H	1.436765000	2.180423000	-0.598301000
C	-1.625546000	2.728424000	2.267695000
H	-1.966243000	3.304507000	3.109163000
C	0.695977000	-3.369076000	-1.037775000
H	1.284386000	-4.085497000	-1.581686000
N	-0.048763000	-0.545228000	2.168440000

N	-0.619846000	-1.539565000	1.936641000

3^{H}-Ph

B	2.386269000	0.978105000	0.154307000
C	3.474536000	2.887100000	-1.082582000
H	3.026881000	3.333438000	-1.988628000
H	4.571168000	2.984347000	-1.175820000
H	3.144215000	3.460628000	-0.207895000
N	3.089273000	1.501616000	-0.944570000
C	3.489029000	0.687118000	-2.067427000
H	3.046684000	1.062918000	-3.007311000
H	3.162447000	-0.350200000	-1.920256000
H	4.586938000	0.694678000	-2.194893000
C	1.969130000	1.934152000	1.292097000
B	1.903260000	-0.671140000	0.257454000
C	2.526659000	-3.107869000	0.573634000
H	2.800004000	-3.494412000	1.572183000
H	3.106544000	-3.684556000	-0.169559000
H	1.459506000	-3.281736000	0.394753000
N	2.838201000	-1.697147000	0.470445000
C	4.245223000	-1.430877000	0.654712000
H	4.589801000	-1.787923000	1.641951000
H	4.447848000	-0.354017000	0.589045000
H	4.853224000	-1.949283000	-0.109601000
C	0.362341000	-0.937798000	0.104907000
C	-5.717829000	0.853957000	-0.147711000
C	-4.705233000	1.606706000	0.443820000
C	-3.402025000	1.119169000	0.496284000
C	-3.111178000	-0.127588000	-0.061416000
C	-4.119447000	-0.891060000	-0.654946000
C	-5.418782000	-0.395701000	-0.690251000
H	-6.739210000	1.238890000	-0.182840000
H	-4.929679000	2.582429000	0.880537000

H	-2.619569000	1.702167000	0.984472000
H	-3.864612000	-1.864036000	-1.074776000
H	-6.206387000	-0.994074000	-1.153890000
N	-1.791040000	-0.629928000	-0.029856000
N	-1.554658000	-1.943354000	-0.199764000
N	-0.290898000	-2.128958000	-0.118535000
C	-0.625608000	0.031406000	0.155458000
H	-0.564785000	1.105014000	0.306150000
C	1.595059000	2.623705000	2.226723000
H	1.273938000	3.230785000	3.053721000

3^{Me}-Ph			
B	1.566354000	0.721267000	0.143373000
C	1.082022000	3.199263000	-0.021739000
H	1.633340000	3.882969000	-0.691754000
H	0.778837000	3.787799000	0.864051000
H	0.181762000	2.863227000	-0.549360000
N	1.911176000	2.072310000	0.334350000
C	3.204602000	2.473879000	0.837289000
H	3.736502000	3.107268000	0.104699000
H	3.825860000	1.593078000	1.041091000
H	3.106131000	3.058448000	1.770230000
C	0.112417000	0.312343000	-0.296396000
B	2.715819000	-0.543588000	0.339701000
C	3.489879000	-2.660966000	1.456753000
H	2.963468000	-3.620742000	1.304154000
H	3.936156000	-2.686823000	2.467735000
H	4.295949000	-2.582660000	0.716863000
N	2.582346000	-1.547714000	1.316230000
C	1.493951000	-1.582872000	2.259727000
H	0.904926000	-2.512287000	2.154871000
H	0.818536000	-0.733510000	2.097484000
H	1.863432000	-1.542497000	3.301093000

C	3.913702000	-0.579994000	-0.622629000
C	-6.178616000	-0.517076000	-0.183650000
C	-5.597040000	0.748167000	-0.136529000
C	-4.215864000	0.892920000	-0.246469000
C	-3.412114000	-0.240663000	-0.384139000
C	-3.989365000	-1.512478000	-0.438554000
C	-5.370750000	-1.643260000	-0.343748000
H	-7.262350000	-0.625793000	-0.102522000
H	-6.223257000	1.636658000	-0.028421000
H	-3.766201000	1.886098000	-0.249635000
H	-3.339807000	-2.379016000	-0.565700000
H	-5.820276000	-2.637838000	-0.389048000
N	-2.008764000	-0.125049000	-0.491584000
N	-1.340665000	-0.943963000	-1.328219000
N	-0.091631000	-0.695331000	-1.206665000
C	4.835119000	-0.526378000	-1.422803000
C	-1.138701000	0.679856000	0.186089000
C	5.923045000	-0.475353000	-2.383217000
H	6.156431000	0.561175000	-2.674664000
H	6.842499000	-0.929682000	-1.980781000
H	5.655508000	-1.024384000	-3.300417000
C	-1.522491000	1.615154000	1.275689000
H	-1.862500000	2.593250000	0.898675000
H	-2.331199000	1.200228000	1.895662000
H	-0.650637000	1.799627000	1.917485000

3^{Ph}-Ph

B	1.122832000	1.209059000	1.148503000
C	1.379113000	0.054265000	3.370824000
H	0.712949000	-0.783243000	3.645381000
H	1.675423000	0.566623000	4.303901000
H	2.276820000	-0.357271000	2.893451000
N	0.710097000	0.961148000	2.469013000

C	-0.478329000	1.547759000	3.035508000
H	-1.212006000	0.767868000	3.311198000
H	-0.952218000	2.228346000	2.316888000
H	-0.242615000	2.117964000	3.952205000
C	2.403553000	0.531881000	0.628845000
B	0.231366000	2.222538000	0.075024000
C	0.186920000	4.377500000	-1.274282000
H	0.817424000	4.485377000	-2.175806000
H	0.104780000	5.377903000	-0.812578000
H	-0.818124000	4.050629000	-1.560680000
N	0.787380000	3.441958000	-0.346683000
C	2.077905000	3.896242000	0.116842000
H	2.763116000	4.070675000	-0.732573000
H	2.541140000	3.155045000	0.779976000
H	1.988054000	4.851007000	0.666313000
C	-1.198069000	1.748637000	-0.394790000
C	-6.119507000	-2.215488000	-1.069210000
C	-4.812973000	-2.566772000	-1.405670000
C	-3.781955000	-1.637979000	-1.295024000
C	-4.065938000	-0.353865000	-0.826715000
C	-5.371678000	0.009661000	-0.492316000
C	-6.395504000	-0.924211000	-0.620698000
H	-6.924767000	-2.947578000	-1.161954000
H	-4.590934000	-3.572573000	-1.769052000
H	-2.762138000	-1.905046000	-1.573553000
H	-5.565076000	1.025497000	-0.145895000
H	-7.417998000	-0.639854000	-0.362139000
N	-3.038038000	0.611588000	-0.699374000
N	-3.279082000	1.885169000	-1.057397000
N	-2.201831000	2.551797000	-0.880919000
C	-1.751159000	0.472834000	-0.272091000
C	3.386524000	0.007692000	0.120730000
C	4.514543000	-0.630493000	-0.471614000

C	5.097627000	-0.114139000	-1.643488000
C	5.058889000	-1.796133000	0.099084000
C	6.192707000	-0.745697000	-2.222518000
H	4.676312000	0.788936000	-2.089413000
C	6.151386000	-2.424620000	-0.488452000
H	4.609500000	-2.198148000	1.009460000
C	6.722490000	-1.902033000	-1.649114000
H	6.636960000	-0.333390000	-3.131594000
H	6.563656000	-3.329593000	-0.035779000
H	7.582061000	-2.396656000	-2.107484000
C	-1.193339000	-0.778145000	0.254797000
C	-0.023746000	-1.315566000	-0.294334000
C	-1.809662000	-1.437476000	1.329227000
C	0.529474000	-2.482237000	0.229227000
H	0.458193000	-0.807562000	-1.131221000
C	-1.258664000	-2.605209000	1.845316000
H	-2.724043000	-1.024188000	1.761119000
C	-0.086074000	-3.129515000	1.297706000
H	1.452927000	-2.878216000	-0.199224000
H	-1.744717000	-3.108815000	2.684293000
H	0.347450000	-4.044703000	1.707920000

3^{SiMe3}-Ph

B	2.075433000	-1.818122000	-0.474612000
C	3.446381000	-2.867671000	-2.297361000
H	3.037773000	-3.041159000	-3.309050000
H	4.195726000	-3.656921000	-2.105624000
H	3.950968000	-1.893248000	-2.284456000
N	2.397505000	-2.898356000	-1.305918000
C	1.686665000	-4.154856000	-1.256555000
H	1.310726000	-4.427366000	-2.257839000
H	0.815401000	-4.076943000	-0.594967000
H	2.343750000	-4.973961000	-0.910771000

C	2.556278000	3.489776000	-1.166387000
H	2.866510000	4.546832000	-1.146683000
H	1.659230000	3.383051000	-0.537056000
H	2.277905000	3.232610000	-2.199973000
Si	3.940494000	2.375286000	-0.550183000
C	3.329276000	0.639734000	-0.611831000
C	2.833617000	-0.484910000	-0.601135000
C	5.460649000	2.551380000	-1.639778000
H	6.266239000	1.882443000	-1.299827000
H	5.841291000	3.585079000	-1.617370000
H	5.225396000	2.295106000	-2.684258000
C	4.358992000	2.781999000	1.236900000
H	5.151535000	2.118151000	1.615274000
H	3.473573000	2.653301000	1.878312000
H	4.707877000	3.822740000	1.332320000
B	0.805010000	-1.839387000	0.679029000
C	0.015912000	-2.087432000	3.062745000
H	0.151090000	-1.270967000	3.796799000
H	0.050041000	-3.038194000	3.623810000
H	-0.977534000	-1.987206000	2.609272000
N	1.039370000	-2.054555000	2.045549000
C	2.366116000	-2.258094000	2.577081000
H	2.623460000	-1.473787000	3.312425000
H	3.108873000	-2.223870000	1.769707000
H	2.447637000	-3.233130000	3.090404000
C	-1.775119000	2.546745000	0.086680000
H	-1.576915000	3.516527000	0.571265000
H	-2.836826000	2.520069000	-0.199833000
H	-1.170752000	2.498080000	-0.832851000
Si	-1.310263000	1.146968000	1.253063000
C	-1.539778000	-0.494831000	0.338493000
C	-0.648337000	-1.552487000	0.141558000
C	0.495292000	1.323630000	1.728844000

H	0.785990000	0.629087000	2.529430000
H	0.661860000	2.350257000	2.094592000
H	1.166070000	1.147335000	0.875166000
C	-2.343221000	1.235605000	2.827284000
H	-2.214931000	0.330202000	3.440695000
H	-3.415317000	1.369140000	2.624450000
H	-2.009817000	2.096403000	3.429422000
C	-6.075850000	1.368880000	-1.263875000
C	-5.779392000	0.959975000	0.035652000
C	-4.628367000	0.217974000	0.289705000
C	-3.764668000	-0.091980000	-0.759699000
C	-4.062480000	0.297711000	-2.065550000
C	-5.221975000	1.026804000	-2.312990000
H	-6.980304000	1.948408000	-1.461825000
H	-6.455436000	1.207699000	0.857136000
H	-4.397871000	-0.137191000	1.294854000
H	-3.375875000	0.026091000	-2.868625000
H	-5.456694000	1.337473000	-3.333542000
N	-2.572552000	-0.812302000	-0.506057000
N	-2.343464000	-1.951645000	-1.166049000
N	-1.197435000	-2.393693000	-0.790648000

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