

Supporting Information for

The forgotten borole: synthesis, properties and reactivity of a 1-boraindene

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Experimental section

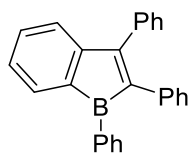
General considerations

All syntheses were carried out with standard Schlenk and glovebox techniques under an argon atmosphere. Solvents were dried by distillation from suitable desiccants (benzene (K), toluene (Na), dichloromethane (P_2O_5), hexane and pentane (Na/K alloy)) under argon and were stored over molecular sieves. All solvents and reagents were purchased from commercial sources. Azidotrimethylsilane was purchased from commercial sources and distilled prior to use. 1-Azido-2,4,6-trimethylbenzene^[1] and dibromo(phenyl)borane^[2] were synthesized according to published procedures.

Liquid-phase NMR spectra were acquired on a range of Bruker Avance spectrometers operating at either 400, 500 or 600 MHz. Chemical shifts (δ) are provided in ppm and internally referenced to the carbon nuclei ($^{13}C\{^1H\}$) or residual protons (1H) of the solvent. Multinuclear NMR spectra are referenced to external standards (^{11}B : $BF_3 \cdot OEt_2$, ^{31}P : 85% H_3PO_4).

High-resolution mass spectrometry (HRMS) was carried out on an Exactive Plus spectrometer with a Orbitrap detector from ThermoFisher Scientific. The ion source was a LIFDI [m/z] calculated for 700 unit from Linden CMS. All UV-Vis experiments were conducted in an argon-filled glovebox using a JASCO V-660 UV-Vis spectrometer. All cyclic voltammetry experiments were conducted in an argon-filled glovebox, using a Gamry Instruments Reference 600 potentiostat. A standard three-electrode cell configuration was employed using a platinum disk working electrode, a platinum wire counter electrode, and a silver wire, separated by a Vycor tip, serving as the reference electrode. Formal redox potentials are reported versus the ferrocene/ferrocenium (Fc/Fc^+) redox couple obtained by using ferrocene (Fc) as an internal standard. Compensation for resistive losses (iR drop) was employed for all measurements.

Synthesis of **1**



A solution of 1,1-dimethyl-2,3-diphenyl-1-stannaindene^[3] (1.08 g, 2.68 mmol, 1.0 equiv) in toluene (50 mL) was cooled to $-78\text{ }^{\circ}\text{C}$. A solution of dibromo(phenyl)borane (664 mg, 2.68 mmol, 1.0 equiv) in toluene (30 mL) was added and the mixture was stirred for 5 min, during which it turned from colorless to red. The solution was allowed to reach room temperature and stirred for 16 h. All volatiles were removed *in vacuo* and the side product dimethyltin dibromide was removed from the product by sublimation at $60\text{ }^{\circ}\text{C}$. The remaining solid was washed with *n*-hexane ($4 \times 50\text{ mL}$) and dried again, yielding **1** as a red solid (605 mg, 1.77 mmol, 66%). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated benzene solution at room temperature.

¹H NMR (500 MHz, CD_2Cl_2): $\delta = 7.75$ (d, 2H, $^3J_{\text{H,H}} = 7.6\text{ Hz}$, Ar-CH), 7.67 (d, 1H, $^3J_{\text{H,H}} = 6.7\text{ Hz}$, Ar-CH), 7.65 (t, 1H, $^3J_{\text{H,H}} = 7.4\text{ Hz}$, Ar-CH), 7.37 (t, 2H, $^3J_{\text{H,H}} = 7.6\text{ Hz}$, Ar-CH), 7.34–7.27 (m, 3H, Ar-CH), 7.24 (m, 2H, Ar-CH), 7.19–7.11 (m, 5H, Ar-CH), 6.96 (dd, 2H, $^4J_{\text{H,H}} = 0.7\text{ Hz}$, $^3J_{\text{H,H}} = 7.0\text{ Hz}$, Ar-CH), 6.81 (d, 1H, $^3J_{\text{H,H}} = 7.0\text{ Hz}$, Ar-CH) ppm.

¹¹B NMR (160 MHz, CD_2Cl_2): $\delta = 65.26$ (s, BPh) ppm.

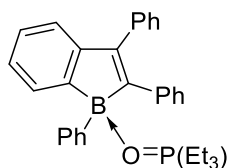
¹³C{¹H} NMR (126 MHz, CD_2Cl_2): $\delta = 165.90$ (C_q , Ar-C), 155.13 (C_q , Ar-C), 146.94 (C_q , CB), 139.89 (C_q , Ar-C), 139.39 (C_q , CB), 138.52 (C_q , CB), 136.39 (CH, Ar-CH), 135.74 (C_q , Ar-C), 133.37 (C_t , Ar-CH), 132.60 (C_t , Ar-CH), 132.47 (C_t , Ar-CH), 129.23 (C_t , 2 Ar-CH), 128.69 (C_t , 2 Ar-CH), 128.26 (C_t , Ar-CH), 128.16 (C_t , 2 Ar-CH), 128.01 (C_t , Ar-CH), 127.71 (C_t , 2 Ar-CH), 127.66 (C_t , 2 Ar-CH), 125.78 (C_t , Ar-CH), 121.57 (C_t , Ar-CH) ppm.

UV-Vis (CH_2Cl_2): $\lambda_{\text{max}} = 485\text{ nm}$.

Anal. Calcd for $\text{C}_{26}\text{H}_{19}\text{B}$: C 91.25, H 5.60; found: C 91.09, H 5.63.

HRMS (LIFDI): calcd. for $\text{C}_{26}\text{H}_{19}\text{B}$: 342.1580; found: 342.1574.

Synthesis of **1-OPEt₃**



To a solution of **1** (20.0 mg, 58.4 μmol , 1.0 equiv) in C_6D_6 (0.5 mL) was added triethylphosphine oxide (7.84 mg, 58.4 μmol , 1.0 equiv), resulting in a color change from red to colorless. All volatiles were removed *in vacuo*. The remaining solid was washed with pentane (3 \times 1 mL) and dried again, yielding **1-OPEt₃** as a white solid (23.0 mg, 48.3 μmol , 83%). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated benzene solution at room temperature.

¹H NMR (400 MHz, C_6D_6): δ = 7.91 (d, 2H, $^3J_{\text{H,H}} = 7.0$ Hz, Ar-CH), 7.57 (d, 2H, $^3J_{\text{H,H}} = 7.3$ Hz, Ar-CH), 7.46 (t, 2H, $^3J_{\text{H,H}} = 7.4$ Hz, Ar-CH), 7.43–7.35 (m, 4H, Ar-CH), 7.33–7.25 (m, 3H, Ar-CH), 7.23–7.11 (m, 3H, Ar-CH), 6.92 (t, 2H, $^3J_{\text{H,H}} = 7.5$ Hz, Ar-CH), 6.83 (t, 1H, $^3J_{\text{H,H}} = 7.2$ Hz, Ar-CH), 1.15–0.81 (m, 6H, Et-CH₂), 0.59–0.29 (m, 9H, Et-CH₃) ppm.

¹¹B NMR (128 MHz, C_6D_6): δ = 6.77 (s, 1B, R₃BO) ppm.

³¹P{¹H} NMR (162 MHz, C_6D_6): δ = 75.64 (s, 1P, Et₃PO) ppm.

¹³C{¹H} NMR (101 MHz, C_6D_6): δ = 159.06* (br C_q, CB), 158.60* (br C_q, CB), 153.91* (br C_q, CB), 152.74 (C_q, Ar-C), 147.00 (C_q, Ar-C), 143.21 (C_q, Ar-C), 140.78 (C_q, Ar-C), 131.46 (C_t, 2 Ar-CH), 130.26 (C_t, 2 Ar-CH), 130.19 (C_t, 2 Ar-CH), 129.36 (C_t, Ar-CH), 128.87 (C_t, 2 Ar-CH), 127.74 (C_t, 2 Ar-CH), 127.71 (C_t, 2 Ar-CH), 126.65 (C_t, Ar-CH), 126.62 (C_t, Ar-CH), 125.31 (C_t, Ar-CH), 125.05 (C_t, Ar-CH), 124.84 (C_t, Ar-CH), 120.95 (C_t, Ar-CH), 17.31 (C_s, 3 Et-CH₂), 5.01 (C_p, 3 Et-CH₃) ppm.

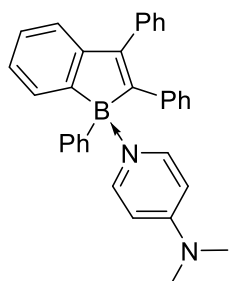
The resonances marked with an asterisk (*) were identified by 2D NMR spectroscopy.

HRMS (LIFDI): calcd. for C₃₂H₃₄BOP: 476.2440; found: 476.2427.

For the Gutmann-Beckett studies, samples were prepared with a 1:1 stoichiometric ratio between the borane and Et₃PO. NMR samples were prepared in a glovebox under argon for subsequent ³¹P{¹H} NMR spectroscopy in C_6D_6 .

AN (**1**) = 2.21 * ($\delta(^{31}\text{P}) - 41$) = 76.9 (C_6D_6)

Synthesis of **1-DMAP**



To a solution of **1** (30.0 mg, 87.7 μ mol, 1.0 equiv) in C₆D₆ (0.5 mL) was added 4-dimethylaminopyridine (10.7 mg, 87.7 μ mol, 1.0 equiv), resulting in a color change from red to colorless. All volatiles were removed *in vacuo*. The remaining solid was washed with pentane (3 \times 1 mL) and dried again, yielding **1-DMAP** as a white solid (35.8 mg, 77.1 μ mol, 88%). Single crystals suitable for X-ray diffraction analysis were obtained by layering a saturated benzene solution with pentane at room temperature.

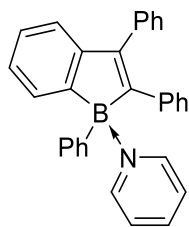
¹H NMR (500 MHz, CD₂Cl₂): δ = 8.11–8.08 (d, 2H, ³J_{H,H} = 7.6 Hz, NC₅H₄(NMe₂)), 7.39–7.36 (m, 2H, Ar-CH), 7.33–7.28 (m, 5H, Ar-CH), 7.25–7.16 (m, 3H, Ar-CH), 7.14–7.10 (m, 1H, Ar-CH), 7.07–6.91 (m, 6H, Ar-CH), 6.85–6.82 (m, 2H, Ar-CH), 6.48 (d, 2H, ³J_{H,H} = 7.6 Hz, NC₅H₄(NMe₂)), 3.05 (s, 6H, Py-N(CH₃)₂) ppm.

¹¹B NMR (160 MHz, CD₂Cl₂): δ = 2.22 (s, R₃BN) ppm.

¹³C{¹H} NMR (126 MHz, CD₂Cl₂): δ = 159.7 (br. C_q, CB), 158.4 (br. C_q, CB), 155.9 (C_q, Ar-C), 152.9 (C_q, Ar-C), 151.8 (br. C_q, CB), 148.1 (C_q, Ar-C), 145.5 (C_t, 2 Py-CH), 144.3 (C_q, Py-C(NMe₂)), 140.0 (C_q, Ar-C), 133.4 (C_t, 2 Ar-CH), 130.5 (C_t, 2 Ar-CH), 129.3 (C_t, 2 Ar-CH), 128.3 (C_t, 2 Ar-CH), 128.3 (C_t, Ar-CH), 127.6 (C_t, 2 Ar-CH), 127.6 (C_t, 2 Ar-CH), 126.3 (C_t, Ar-CH), 126.1 (C_t, Ar-CH), 125.5 (C_t, Ar-CH), 125.0 (C_t, Ar-CH), 124.7 (C_t, Ar-CH), 120.7 (C_t, Ar-CH), 106.8 (C_t, 2 Py-CH), 39.7 (C_p, Py-N(CH₃)₂) ppm.

HRMS (LIFDI): calcd. for C₃₃H₂₉BN₂: 464.2424; found: 464.2418.

Synthesis of **1-Py**



To a solution of **1** (20.0 mg, 58.5 μmol , 1.0 equiv) in C_6D_6 (0.5 mL) was added pyridine (10.0 mg, 126 μmol , 2.2 equiv), resulting in a color change from red to colorless. All volatiles were removed *in vacuo*. The remaining solid was washed with pentane (3×1 mL) and dried again, yielding **1-Py** as a white solid (18.5 mg, 43.8 μmol , 75%). Single crystals suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of pentane into a saturated benzene solution at room temperature.

^1H NMR (600 MHz, C_6D_6): δ = 8.44–8.42 (m, 2H, Py-CH), 7.63–7.60 (m, 2H, (B)Ph-CH), 7.55–7.49 (m, 4H, 5-CH/ 6-CH/ 7-CH/ Ph-CH), 7.32 (t, $^3J_{\text{H,H}} = 7.3$ Hz, 2H, (B)Ph-CH), 7.28–7.22 (m, 3H, 4-CH/ (B)Ph-CH/ Ph-CH), 7.18 (t, $^3J_{\text{H,H}} = 7.7$ Hz, 2H, Ph-CH), 7.13–7.10 (m, 2H, Ph-CH), 7.07 (tt, $^3J_{\text{H,H}} = 7.4$ Hz, $^4J_{\text{H,H}} = 1.2$ Hz, 1H, Ph-CH), 6.96–6.92 (m, 2H, Ph-CH), 6.86 (tt, $^3J_{\text{H,H}} = 7.4$ Hz, $^4J_{\text{H,H}} = 1.2$ Hz, 1H, Ph-CH), 6.48 (tt, $^3J_{\text{H,H}} = 7.7$ Hz, $^4J_{\text{H,H}} = 1.5$ Hz, 1H, Py-CH), 6.08–6.05 (m, 2H, Py-CH) ppm.

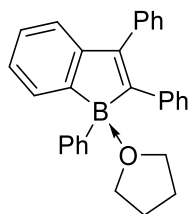
^{11}B NMR (193 MHz, C_6D_6): δ = 4.18 (s, R_3BN) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6): δ = 158.6 (C_q , 1-CB), 157.3 (C_q , 8-CB), 153.1 (C_q , 3-C), 150.3 (C_q , Ph-CB), 149.7 (C_q , 2-C), 146.1 (C_t , 2 Py-CH), 144.2 (C_q , Ph-C), 139.7 (C_t , Py-CH), 139.6 (C_q , Ph-C), 133.7 (C_t , 2 Ph-CH), 130.6 (C_t , 6-CH/ 7-CH), 129.9 (C_t , 5-CH), 129.5 (C_t , Ph-CH), 128.5 (C_t , Ph-CH), 128.4 (C_t , Ph-CH), 128.1 (C_t , 2 Ph-CH), 128.0 (C_t , 2 Ph-CH), 127.1 (C_t , 4-CH), 126.6 (C_t , Ph-CH), 126.2 (C_t , Ph-CH), 125.7 (C_t , Ph-CH), 125.2 (C_t , Ph-CH), 124.7 (C_t , 2 Py-CH), 121.7 (C_t , Ph-CH) ppm.

The resonances marked with an asterisk (*) were identified by 2D NMR spectroscopy.

HRMS (LIFDI): calcd. for $\text{C}_{31}\text{H}_{24}\text{BN}$: 421.2002; found: 421.1992.

Synthesis of **1-THF**



1 (30.0 mg, 87.7 μmol , 1.0 equiv) was suspended in pentane (2.0 mL) and thf (0.1 mL) was added. The formation of a white solid was observed. The supernatant was decanted and the remaining solid was washed with pentane (3 x 1 mL) and dried by slow vapor diffusion, yielding **1-THF** as a white solid (32.0 mg, 77.2 μmol , 88%). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated thf solution at $-30\text{ }^{\circ}\text{C}$.

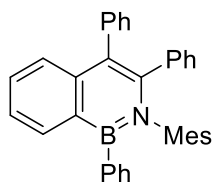
^1H NMR (400 MHz, C_6D_6): δ = 7.70–7.66 (m, 2H, Ar-CH), 7.45–7.41 (m, 1H, Ar-CH), 7.39–7.34 (m, 3H, Ar-CH), 7.33–7.29 (m, 2H, Ar-CH), 7.26 (dt, 1H, $^3J_{\text{H,H}} = 7.2\text{ Hz}$, $^4J_{\text{H,H}} = 1.5\text{ Hz}$, Ar-CH), 7.24–7.20 (m, 2H, Ar-CH), 7.16–7.11 (m, 4H, Ar-CH), 7.08–6.99 (m, 3H, Ar-CH), 6.91 (tt, 1H, $^3J_{\text{H,H}} = 7.4\text{ Hz}$, $^4J_{\text{H,H}} = 1.3\text{ Hz}$, Ar-CH), 3.63 (m, 4H, thf-CH₂), 3.63 (m, 4H, thf-CH₂) ppm.

^{11}B NMR (129 MHz, C_6D_6): δ = 17.4 (s, R_3BO) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6): δ = 153.9 (C_q , Ar-C), 153.7 (br. C_q , CB), 151.5 (C_q , Ar-C), 149.6 (br. C_q , CB), 146.04 (br. C_q , CB), 143.3 (C_q , Ar-C), 138.9 (C_q , Ar-C), 133.9 (C_t , 2 Ar-CH), 130.7 (C_t , Ar-CH), 130.2 (C_t , 2 Ar-CH), 129.7 (C_t , 2 Ar-CH), 128.5 (C_t , 2 Ar-CH), 128.2 (C_t , Ar-CH), 127.9 (C_t , 2 Ar-CH), 127.8 (C_t , 2 Ar-CH), 127.8 (C_t , Ar-CH), 127.1 (C_t , Ar-CH), 126.8 (C_t , Ar-CH), 126.0 (C_t , Ar-CH), 125.3 (C_t , Ar-CH), 121.4 (C_t , Ar-CH), 72.2 (C_s , 2 thf-CH₂), 24.8 (C_s , 2 thf-CH₂) ppm.

HRMS (LIFDI): calcd. for $\text{C}_{31}\text{H}_{24}\text{BN}$: 421.2002; found: 421.1992.

Synthesis of **2**



To a solution of **1** (20.0 mg, 58.4 μmol , 1.0 equiv) in C_6D_6 (0.5 mL) was added 1-azido-2,4,6-trimethylbenzene (18.8 mg, 117 μmol , 2.0 equiv), resulting in a color change from red to yellow. All volatiles were removed *in vacuo*. The remaining solid was washed with cold *n*-hexane (3×1 mL, -30 $^\circ\text{C}$) and dried again, yielding **2** as a yellow solid (22.0 mg, 46.3 μmol , 79%). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated *n*-hexane solution at room temperature.

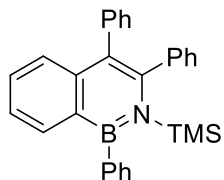
^1H NMR (600 MHz, CD_2Cl_2): δ = 8.31 (dd, 1H, $^3J_{\text{H,H}} = 7.7$ Hz, $^4J_{\text{H,H}} = 0.9$ Hz, Ar-CH), 7.64 (d, 1H, $^3J_{\text{H,H}} = 8.2$ Hz, Ar-CH), 7.50–7.48 (m, 2H, Ar-CH), 7.43–7.39 (m, 1H, Ar-CH), 7.27 (td, 1H, $^3J_{\text{H,H}} = 7.3$ Hz, $^4J_{\text{H,H}} = 1.1$ Hz, Ar-CH), 7.25–7.22 (m, 2H, Ar-CH), 7.18–7.16 (m, 2H, Ar-CH), 7.11–7.04 (m, 5H, Ar-CH), 6.93 (tt, 1H, $^3J_{\text{H,H}} = 7.5$ Hz, $^4J_{\text{H,H}} = 1.3$ Hz, Ar-CH), 6.70 (t, 2H, $^3J_{\text{H,H}} = 6.7$ Hz, Ar-CH), 6.61 (tt, 1H, $^3J_{\text{H,H}} = 7.5$ Hz, $^4J_{\text{H,H}} = 1.2$ Hz, Ar-CH), 6.38 (s, 2H, Mes-CH), 2.07 (s, 6H, Mes-CH₃), 1.74 (s, 3H, Mes-CH₃) ppm.

^{11}B NMR (190 MHz, CD_2Cl_2): δ = 38.91 (s, BC_2N) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2): δ = 143.01 (C_q , 1C, Ar-C), 142.83 (C_q , 1C, Ar-C), 141.48 (C_q , 1C, Mes-CN), 140.29 (C_q , 1C, Ar-C), 137.70 (C_q , 1C, Ar-C), 137.32 (C_t , 1C, Ar-CH), 135.96 (C_q , 1C, Mes-C), 134.42 (C_q , 1C, Mes-C), 133.31 (C_t , 2C, Ar-CH), 132.57 (C_t , 2C, Ar-CH), 131.27 (C_t , 1C, Ar-CH), 130.64 (C_t , 2C, Ar-CH), 128.75 (C_t , 2C, Mes-CH), 128.35 (C_t , 2C, Ar-CH), 128.14 (C_q , 1C, Mes-C), 128.09 (C_q , 1C, Ar-CN), 127.98 (C_q , 1C, Ar-CB), 127.61 (C_t , 1C, Ar-CH), 127.24 (C_t , 2C, Ar-CH), 127.17 (C_t , 1C, Ar-CH), 126.71 (C_t , 2C, Ar-CH), 126.53 (C_t , 1C, Ar-CH), 126.50 (C_t , 1C, Ar-CH), 125.54 (C_q , 1C, Ar-CB), 125.08 (C_t , 1C, Ar-CH), 20.73 (C_s , 1C, Mes-CH₃), 19.45 (C_s , 2C, Mes-CH₃) ppm.

HRMS (LIFDI): calcd. for $\text{C}_{35}\text{H}_{30}\text{BN}$: 475.2471; found: 475.2466.

Synthesis of **3**



To a solution of **1** (20.0 mg, 58.4 μmol , 1.0 equiv) in CD_2Cl_2 (0.5 mL) was added trimethylsilyl azide (10.1 mg, 87.7 μmol , 1.5 equiv), resulting in a color change from red to orange. The mixture was stirred for 4 d at room temperature before all volatiles were removed *in vacuo*. The remaining solid was washed with cold pentane ($3 \times 1 \text{ mL}$, $-30 \text{ }^\circ\text{C}$) and dried again, yielding **3** as an off-white solid (21.5 mg, 50.1 μmol , 86%). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated pentane solution at room temperature.

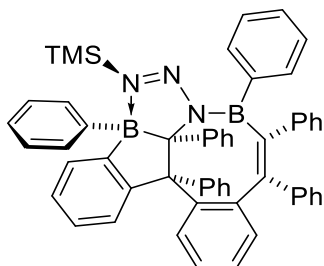
^1H NMR (600 MHz, CD_2Cl_2): δ = 8.01 (dd, 1H, $^3J_{\text{H,H}} = 7.7 \text{ Hz}$, $^4J_{\text{H,H}} = 0.8 \text{ Hz}$, 7-CH), 7.80–7.77 (m, 2H, Ph-CH), 7.52–7.47 (m, 3H, Ph-CH), 7.47–7.44 (m, 1H, 5-CH), 7.31 (td, 1H, $^3J_{\text{H,H}} = 7.0 \text{ Hz}$, $^4J_{\text{H,H}} = 1.2 \text{ Hz}$, 6-CH), 7.28–7.23 (m, 4H, Ph-CH), 7.21 (m, 1H, Ph-CH), 7.18 (d, 1H, $^3J_{\text{H,H}} = 8.1 \text{ Hz}$, 4-CH), 7.16–7.11 (m, 3H, Ph-CH), 7.10–7.08 (m, 2H, Ph-CH), -0.16 (s, 9H, TMS- CH_3) ppm.

^{11}B NMR (193 MHz, CD_2Cl_2): δ = 44.75 (s, 1B, R_2BN) ppm.

^{13}C NMR (151 MHz, CD_2Cl_2): δ = 144.74 (C_q , Ph-C), 143.25 (br. C_q , 1-C), 142.35 (C_q , 3-C), 141.18 (C_q , Ph-C), 140.52 (C_q , Ph-C), 136.11 (C_t , 7-CH), 134.81 (C_t , 2 Ph-CH), 133.01 (br. C_q , 8-C), 132.72 (C_t , 2 Ph-CH), 132.49 (C_t , 2 Ph-CH), 131.31 (C_t , 5-CH), 128.24 (C_t , Ph-CH), 128.12 (C_t , 2 Ph-CH), 127.51 (C_t , 3 Ph-CH), 127.03 (C_t , 2 Ph-CH), 126.41 (C_t , Ph-CH), 126.17 (C_q , 2-C), 125.80 (C_t , 4-CH), 124.78 (C_t , 6-CH), 5.78 (C_p , 3 TMS- CH_3) ppm.

HRMS (LIFDI): calcd. for $\text{C}_{29}\text{H}_{28}\text{BNSi}$: 429.2084; found: 429.2079.

Synthesis of **4**



A) To a solution of **1** (20.0 mg, 58.4 μmol , 1.0 equiv) in C_6D_6 (0.5 mL) was added trimethylsilyl azide (7.40 mg, 64.3 μmol , 1.1 equiv). The mixture was stirred for 16 h at 80 $^\circ\text{C}$. The product was crystallized by layering the benzene solution with pentane (3 mL) for 3 d at room temperature. The supernatant was decanted and the remaining solid was dried *in vacuo*, yielding **4** as a white solid (7.50 mg, 9.38 μmol , 32%). Single crystals suitable for X-ray diffraction analysis were obtained from the synthetic procedure.

B) A solution of **5** (40.0 mg, 52.4 μmol , 1.0 equiv) in C_6D_6 (0.5 mL) was heated at 80 $^\circ\text{C}$ for 5 d (20 d at room temperature). All volatiles were removed *in vacuo*. The remaining solid was washed with *n*-pentane (3 \times 1 mL) and dried *in vacuo*, yielding **4** as a white solid (31.0 mg, 38.76 μmol , 74%). Single crystals suitable for X-ray diffraction analysis were obtained by layering the benzene solution with pentane at room temperature.

^1H NMR (600 MHz, CD_2Cl_2): δ = 7.95 (dd, 1H, $^3J_{\text{H,H}} = 7.1$ Hz, $^4J_{\text{H,H}} = 1.2$ Hz, Ar-CH), 7.90 (dd, 2H, $^3J_{\text{H,H}} = 8.0$ Hz, $^4J_{\text{H,H}} = 1.5$ Hz, Ar-CH), 7.70 (d, 1H, $^3J_{\text{H,H}} = 8.0$ Hz, Ar-CH), 7.58–7.47 (m, 4H, Ar-CH), 7.44–7.39 (m, 1H, Ar-CH), 7.37 (s, 2H, Ar-CH), 6.99–6.80 (m, 19H, Ar-CH), 6.69–6.63 (m, 4H, Ar-CH), 6.52 (t, 1H, $^3J_{\text{H,H}} = 7.3$ Hz, Ar-CH), 6.40 (t, 2H, $^3J_{\text{H,H}} = 7.7$ Hz, Ar-CH), 6.29 (d, 1H, $^3J_{\text{H,H}} = 7.9$ Hz, Ar-CH), 0.03 (s, 9H, TMS- CH_3) ppm.

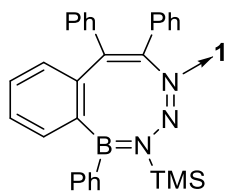
^{11}B NMR (190 MHz, CD_2Cl_2): δ = 51.08 (s, BC_2N), 9.68 (s, BC_3LB) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2): δ = 156.60 (C_q , Ar-C), 150.90 (C_q , Ar-C), 148.21 (C_q , Ar-C), 145.11 (C_q , Ar-C), 143.21 (C_q , Ar-C), 143.20 (C_q , Ar-C), 141.28 (C_q , Ar-C), 141.01 (C_q , Ar-C), 136.86 (C_t , 2 Ar-CH), 134.86 (C_t , Ar-CH), 134.22 (C_t , Ar-CH), 133.88 (C_t , Ar-CH), 133.35 (C_t , Ar-CH), 132.04 (C_t , 2 Ar-CH), 131.71 (C_t , Ar-CH), 130.62 (C_t , 2 Ar-CH), 129.90 (C_t , Ar-CH), 128.72 (C_q , 4 Ar-C), 128.23 (C_t , 2 Ar-CH), 128.07 (C_t , Ar-CH), 127.79 (C_t , 2 Ar-CH), 127.57 (C_t , Ar-CH), 127.41 (C_t , Ar-CH), 127.36 (C_q , Ar-CB), 127.34 (C_t , Ar-CH), 127.13 (C_t , 2 Ar-CH), 126.84 (C_t , Ar-CH), 126.70 (C_t , 2 Ar-CH), 126.52 (C_t , 4 Ar-CH), 126.16 (C_t , Ar-CH), 125.13 (C_t , Ar-CH), 125.62 (C_t , Ar-CH), 125.37 (C_t , Ar-CH), 124.24 (C_t , Ar-CH), 75.60 (C_q , R_2CBN), -0.28 (C_s , 3 TMS- CH_3) ppm.

The signals for two quaternary carbons adjacent to boron atoms were not observed in the spectrum.

HRMS (LIFDI): calcd. for $C_{55}H_{47}B_2N_3Si$: 799.3725; found: 799.3720.

Synthesis of **5**



To a solution of **1** (47.5 mg, 139 μmol , 1.0 equiv) in toluene (3 mL) was added trimethylsilyl azide (8.00 mg, 69.5 μmol , 0.5 equiv). The product was crystallized by layering the toluene solution with pentane (2 mL) for 5 d at $-30\text{ }^\circ\text{C}$. The supernatant was decanted and the remaining solid was washed with pentane ($3 \times 1\text{ mL}$) and dried *in vacuo*, yielding **5** as a red solid (40.6 mg, 50.7 μmol , 73%). The synthetic procedure yielded single crystals suitable for X-ray diffraction analysis.

^1H NMR (400 MHz, CD_2Cl_2): δ = 7.64 (t, 1H, $^3J_{\text{H,H}} = 6.9\text{ Hz}$, Ar-CH), 7.53–7.56 (br s, 1H, Ar-CH), 7.52–7.48 (m, 1H, Ar-CH), 7.44–7.39 (m, 4H, Ar-CH), 7.35–7.24 (m, 5H, Ar-CH), 7.14–6.98 (m, 10H, Ar-CH), 6.97–6.93 (m, 6H, Ar-CH), 6.89–6.85 (m, 2H, Ar-CH), 6.79 (d, $^3J_{\text{H,H}} = 7.5\text{ Hz}$, 2H, Ar-CH), 6.74 (br. s, 2H, Ar-CH), 6.58–6.52 (m, 2H, Ar-CH), -0.10 (s, 9H, TMS- CH_3) ppm.

^{11}B NMR (128 MHz, CD_2Cl_2): δ = 49.2 (br. s, 1B, PhBR_2), 4.7 (br. s, 1B, R_3BN) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2): δ = 154.23 (C_q , Ar-C), 153.32 (C_q , 2 Ar-C), 144.13 (C_q , Ar-C), 141.07 (C_q , Ar-C), 138.32 (C_q , 2 Ar-C), 137.59 (C_t , Ar-CH), 136.86 (C_t , Ar-CH), 136.25 (br. C_q , Ar-C), 135.69 (C_t , Ar-CH), 134.80 (C_t , Ar-CH), 134.04 (C_t , Ar-CH), 133.20 (C_q , 3 Ar-C), 132.71 (C_q , Ar-C), 132.53 (br. C_t , Ar-CH), 132.48 (C_t , Ar-CH), 132.23 (C_t , Ar-CH), 132.18 (C_t , Ar-CH), 131.68 (C_t , Ar-CH), 131.32 (C_t , Ar-CH), 130.41 (C_t , 3 Ar-CH), 130.01 (C_t , 3 Ar-CH), 129.85 (C_t , Ar-CH), 129.74 (C_t , Ar-CH), 129.15 (C_t , Ar-CH), 128.88 (C_t , Ar-CH), 128.58 (C_t , Ar-CH), 128.40 (C_t , 3 Ar-CH), 128.31 (C_t , 3 Ar-CH), 128.22 (C_t , 2 Ar-CH), 127.7 (C_q , Ar-C), 127.62 (C_t , 3 Ar-CH), 127.49 (C_t , 2 Ar-CH), 127.34 (br C_t , Ar-CH), 127.33 (C_q , Ar-C), 125.27 (br C_t , Ar-CH), 121.00 (br C_t , Ar-CH), 0.97 (C_s , 3 TMS- CH_3) ppm.

Note: The spectrum contains **4** (0.1 eq.) due to the rearrangement of **5** to **4** in solution.

HRMS (LIFDI): calcd. for $\text{C}_{29}\text{H}_{28}\text{BN}_3\text{Si}$ [**5-1**]: 457.2146; found: 457.2111.

NMR spectra of isolated compounds

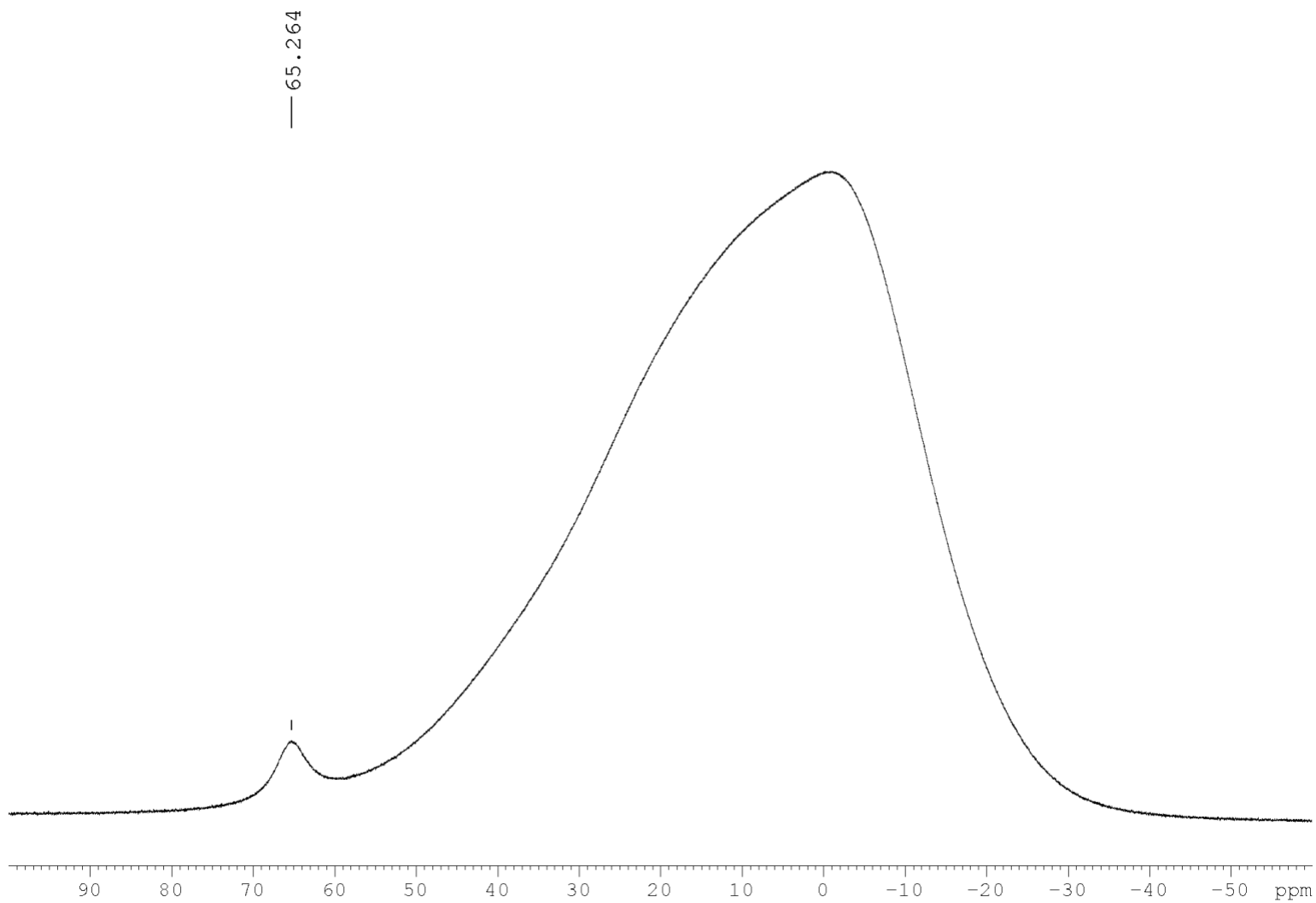


Figure S1: ^{11}B NMR spectrum of **1** in CD_2Cl_2 .

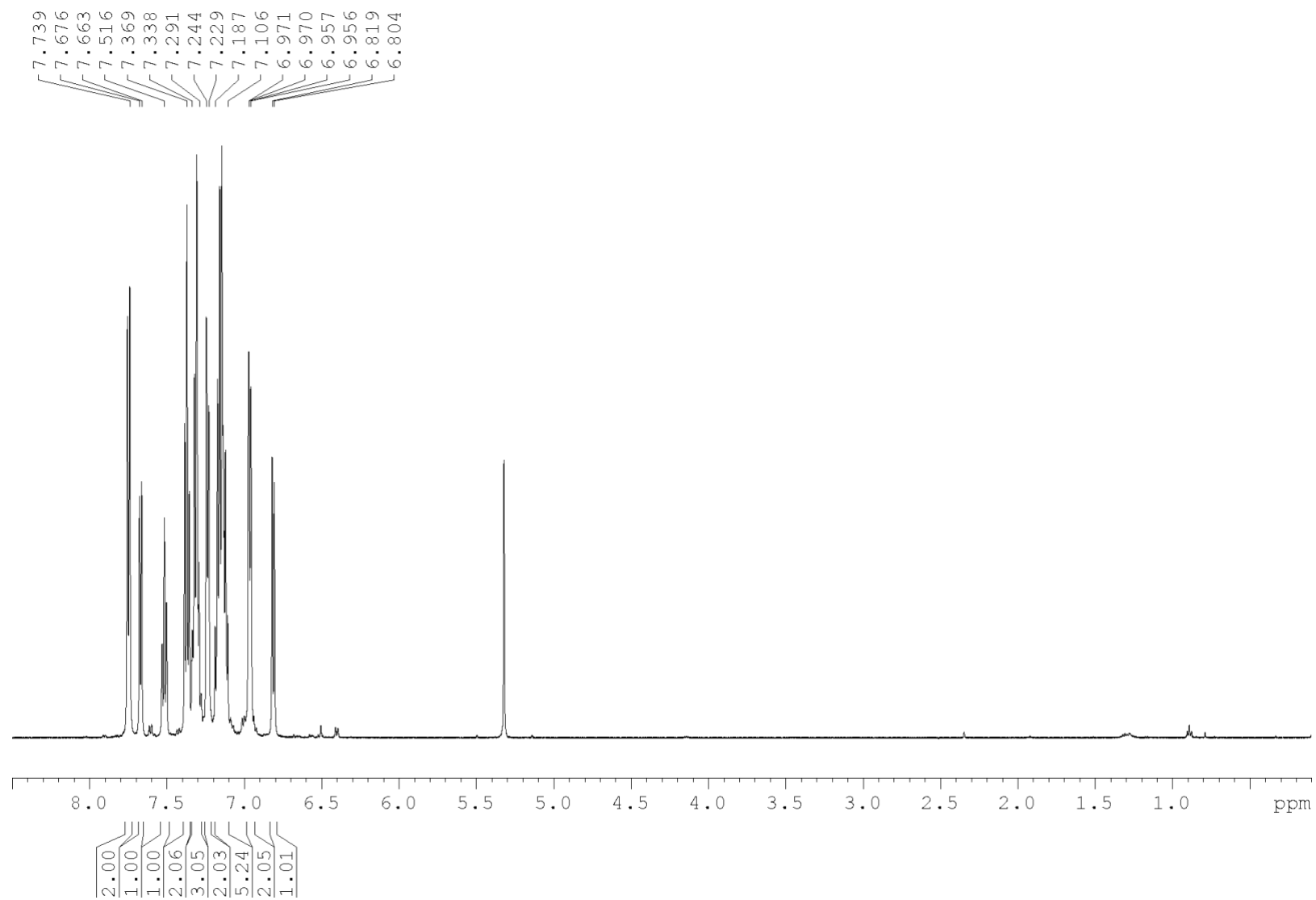


Figure S2: ^1H NMR spectrum of **1** in CD_2Cl_2 .

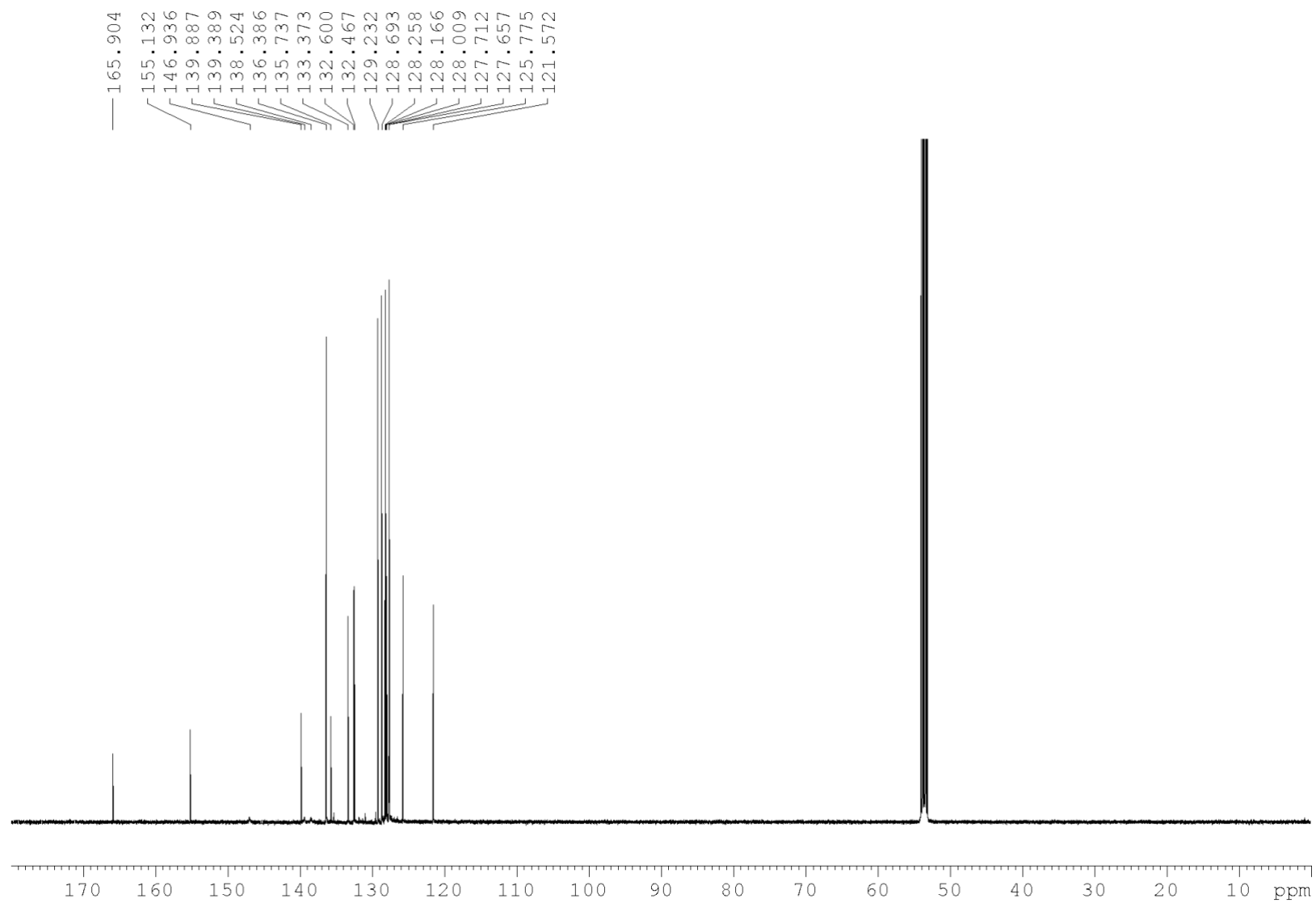


Figure S3: ^{13}C NMR spectrum of **1** in CD_2Cl_2 .

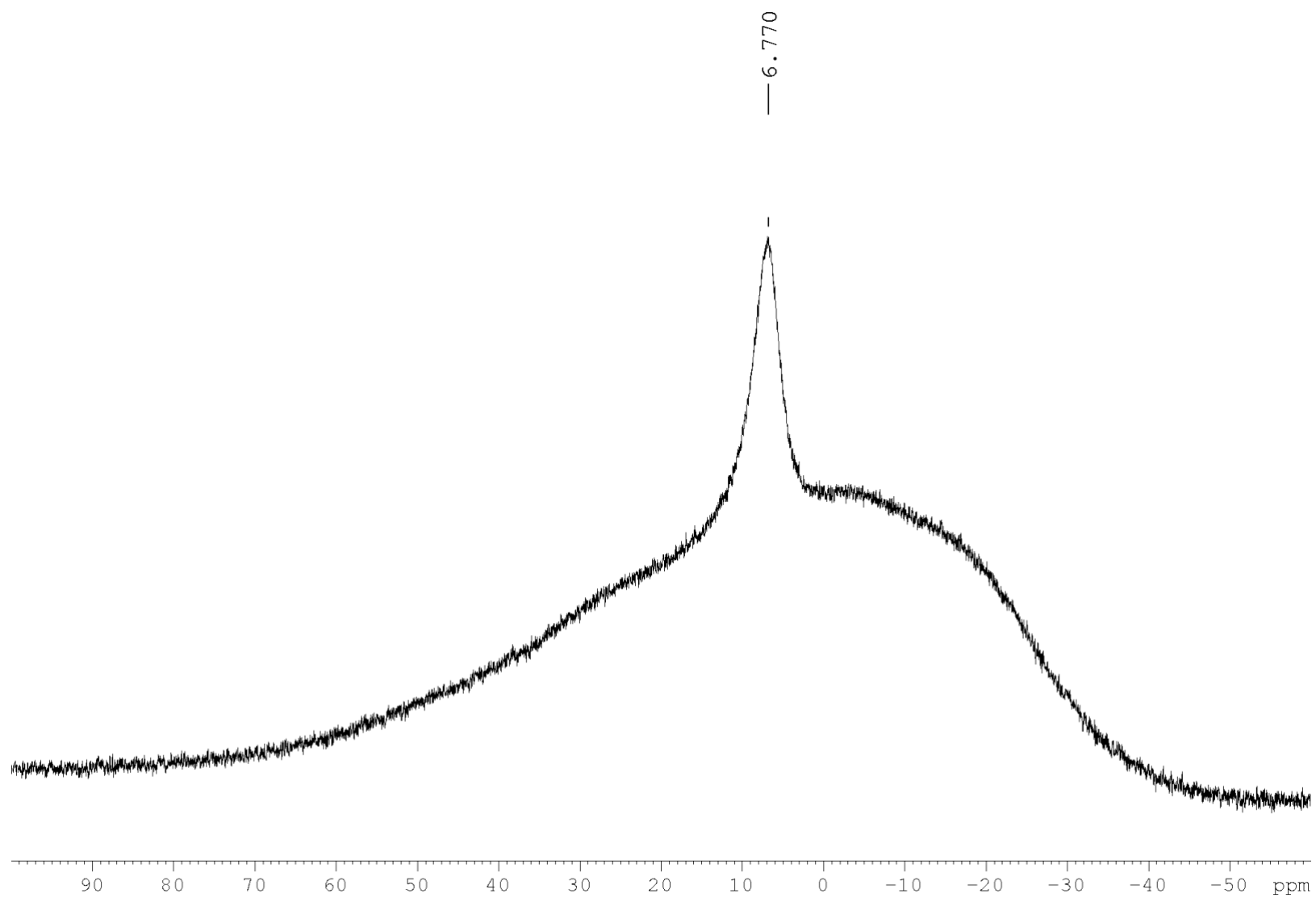


Figure S4: ^{11}B NMR spectrum of 1- Et_3PO in C_6D_6 .

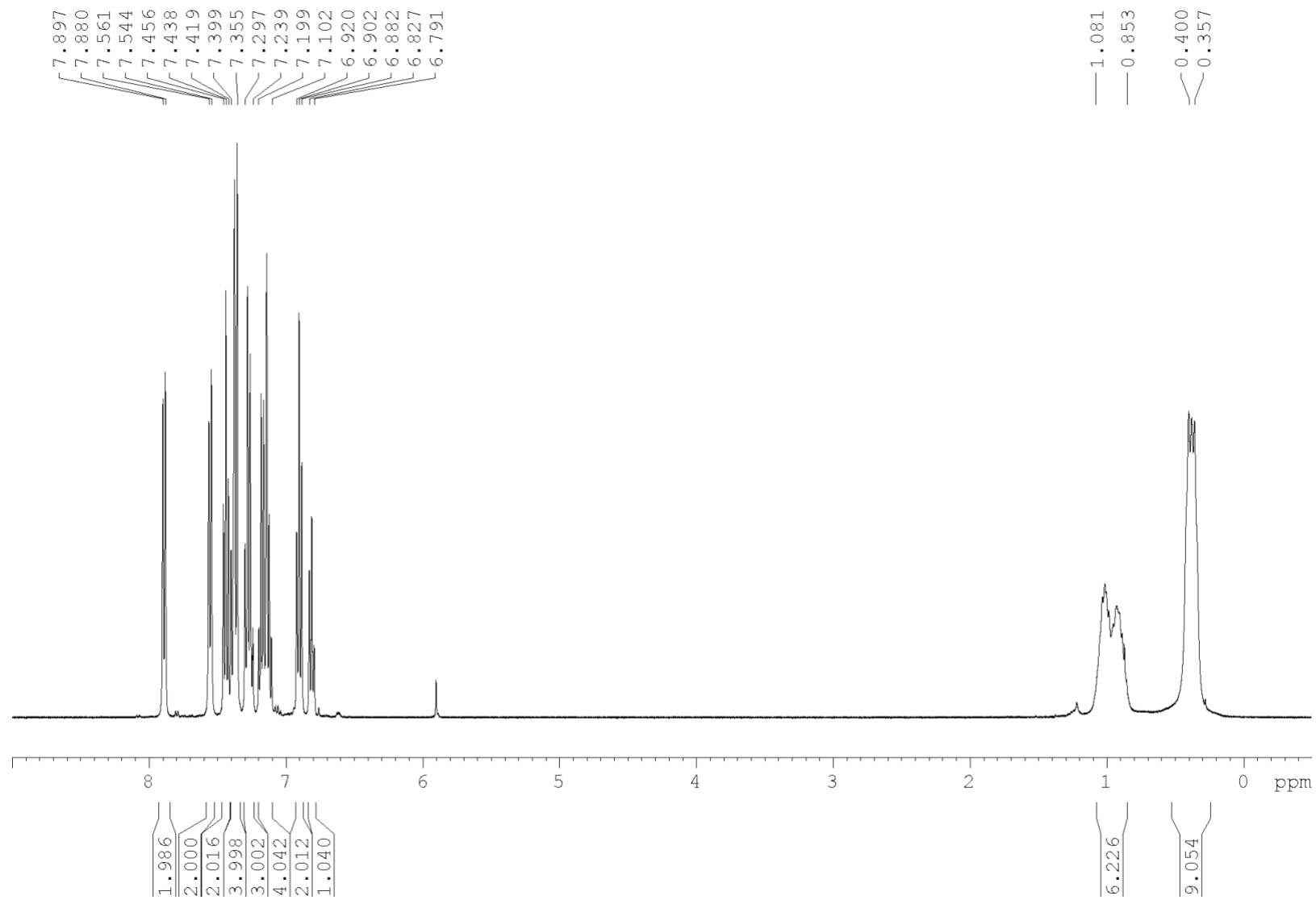


Figure S5: ^1H NMR spectrum of 1- Et_3PO in C_6D_6 .

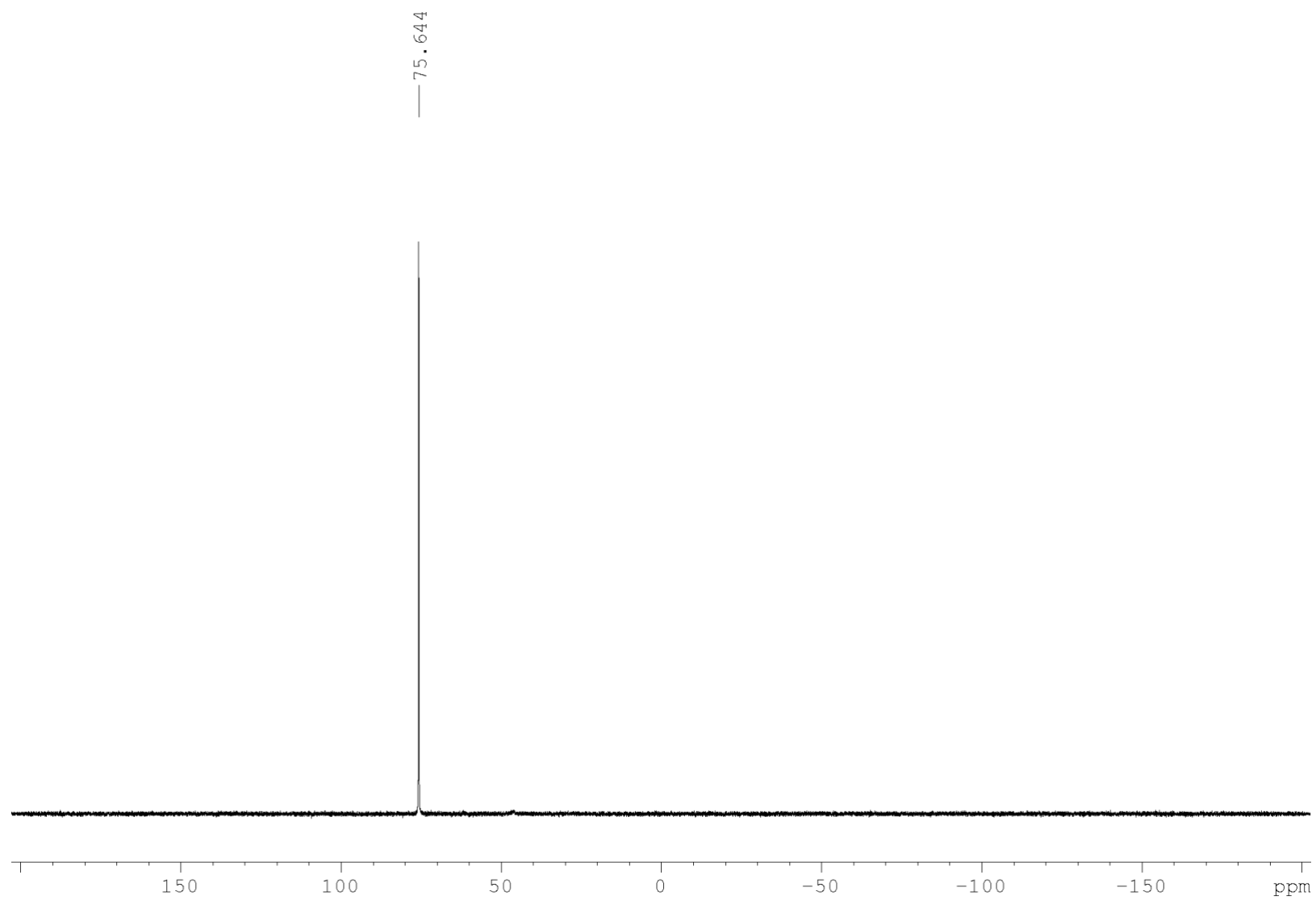


Figure S6: ^{31}P NMR spectrum of **1-Et₃PO** in C_6D_6 .

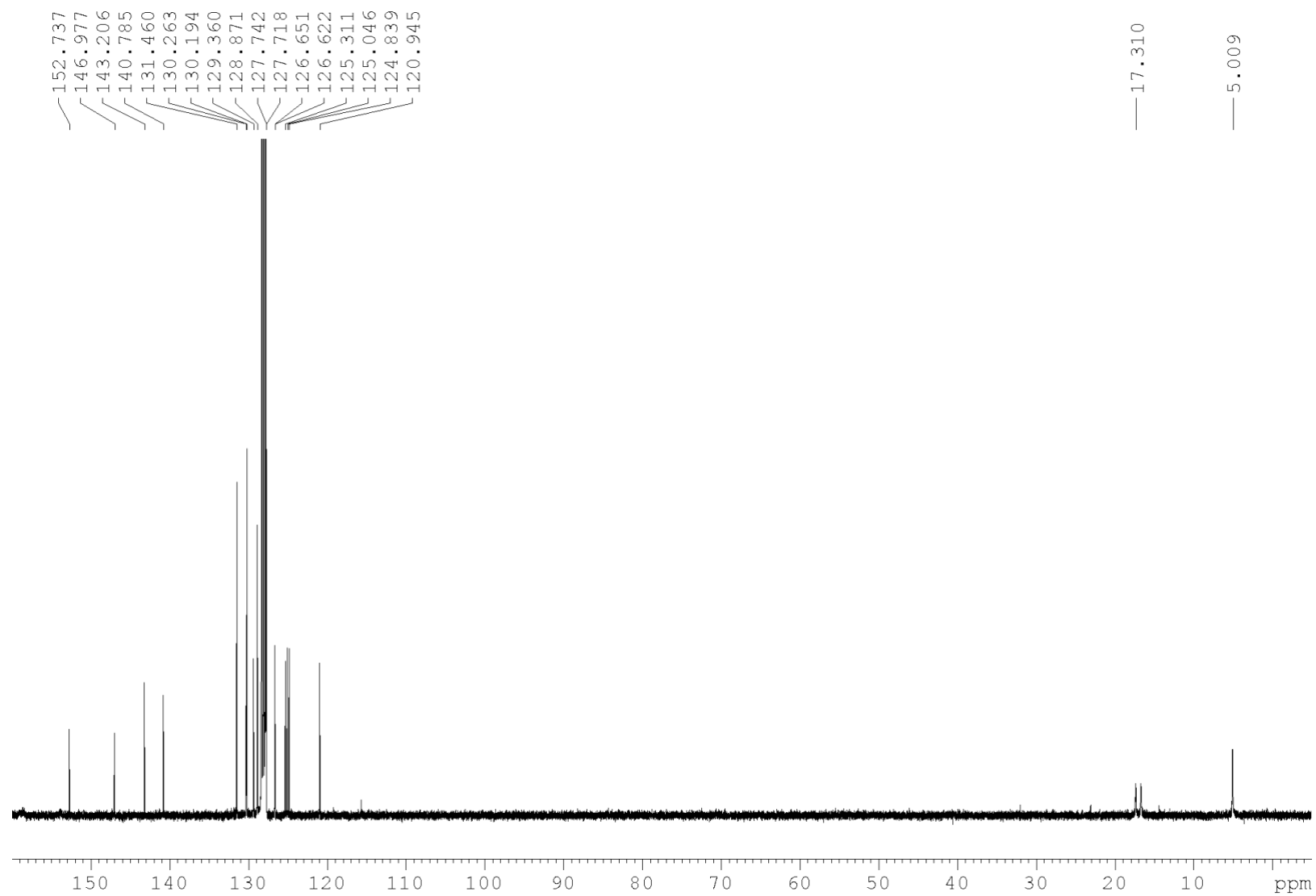


Figure S7: ^{13}C NMR spectrum of 1-Et₃PO in C₆D₆.

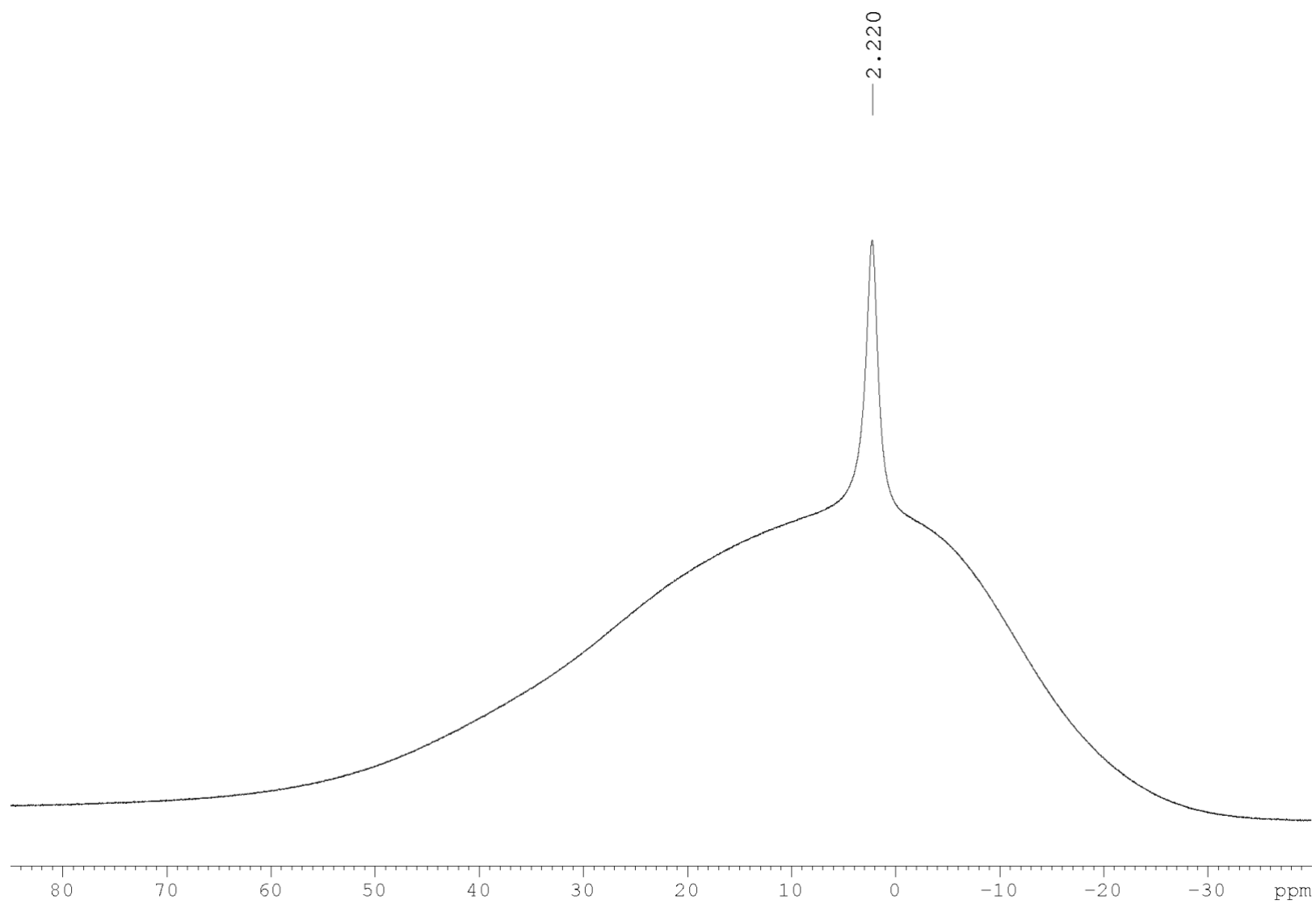


Figure S8: ^{11}B NMR spectrum of **1-DMAP** in CD_2Cl_2 .

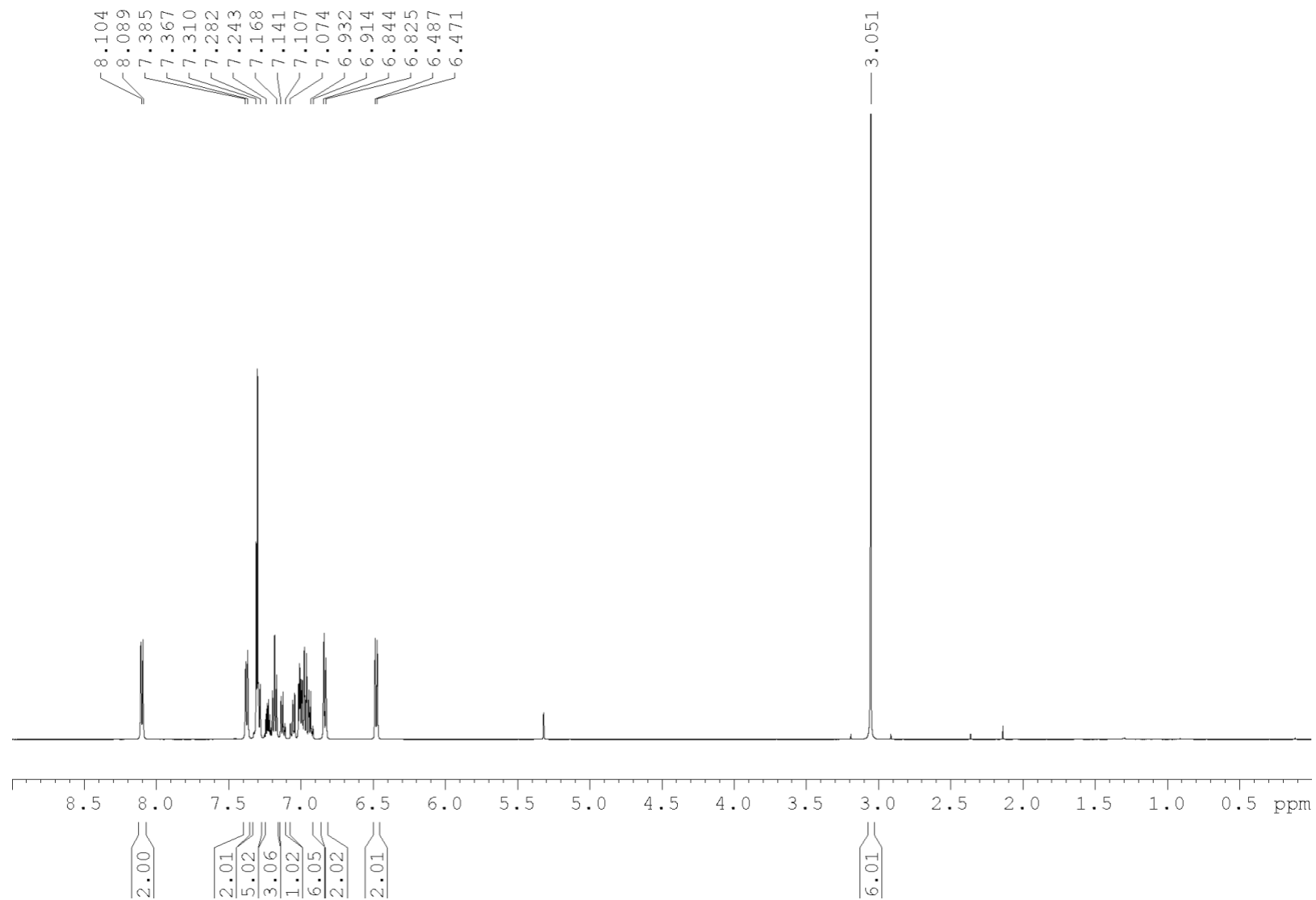


Figure S9: ^1H NMR spectrum of **1-DMAP** in CD_2Cl_2 .

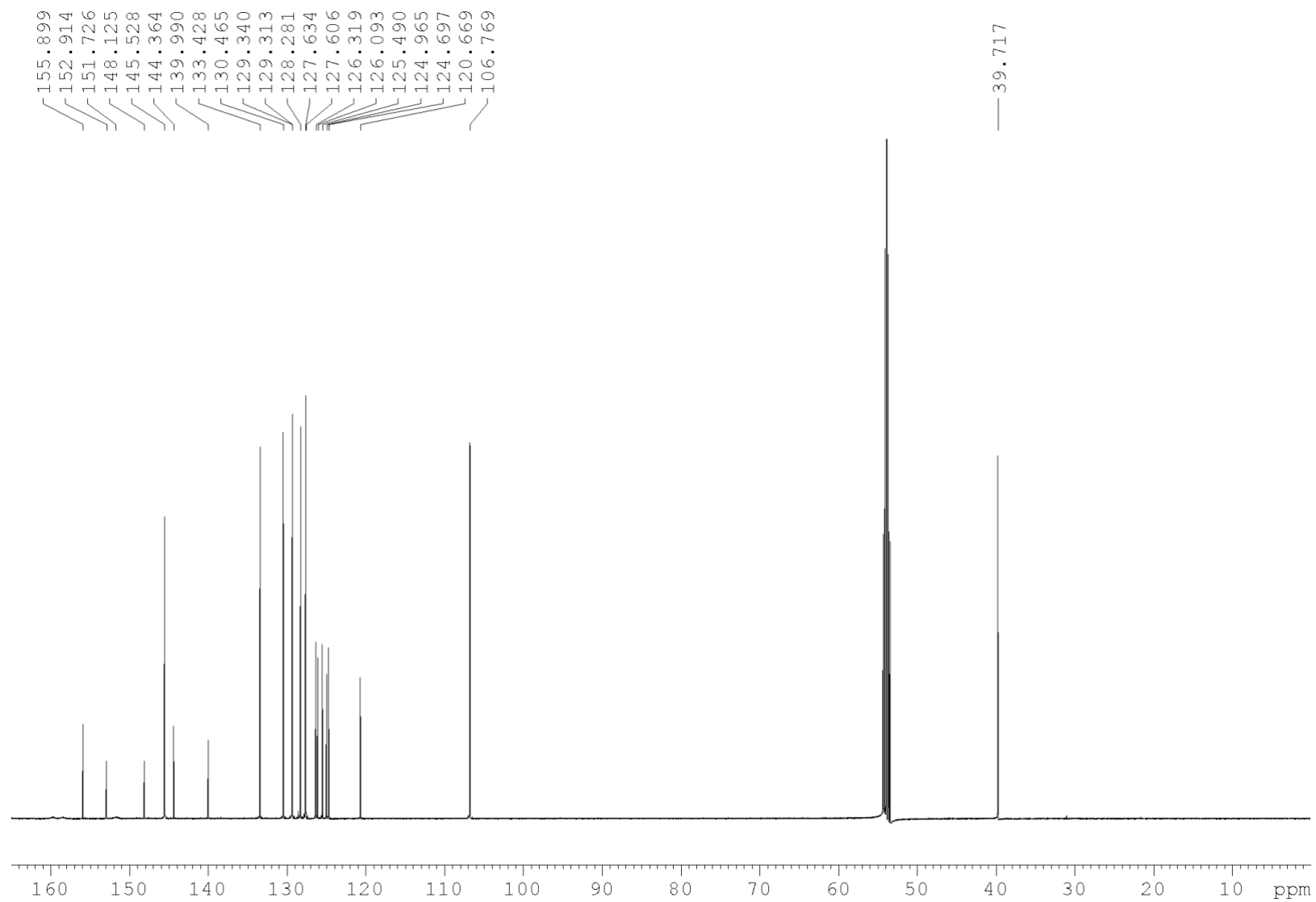


Figure S10: ^{13}C NMR spectrum of **1-DMAP** in CD_2Cl_2 .

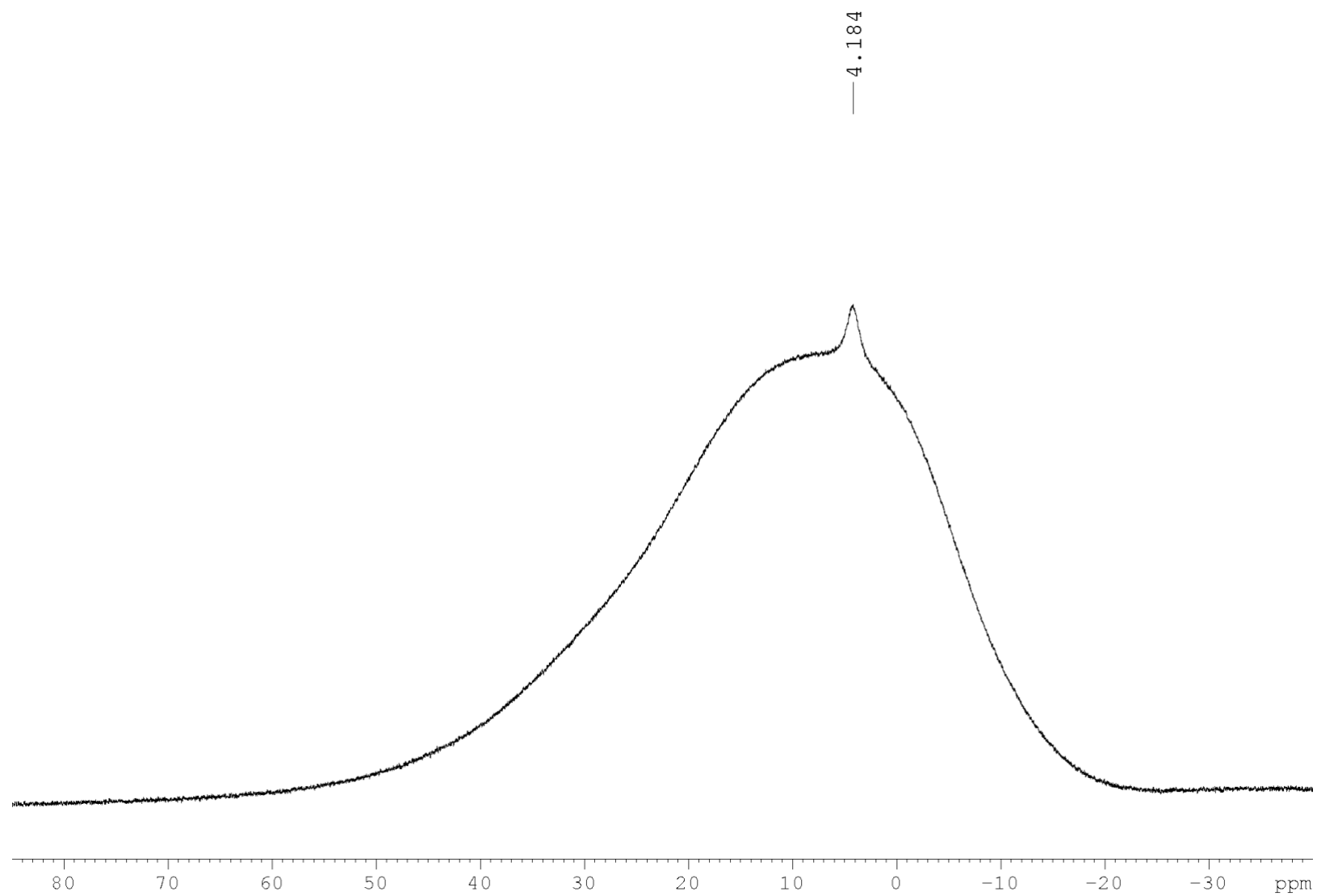


Figure S11: ^{11}B NMR spectrum of 1-Py in C_6D_6 .

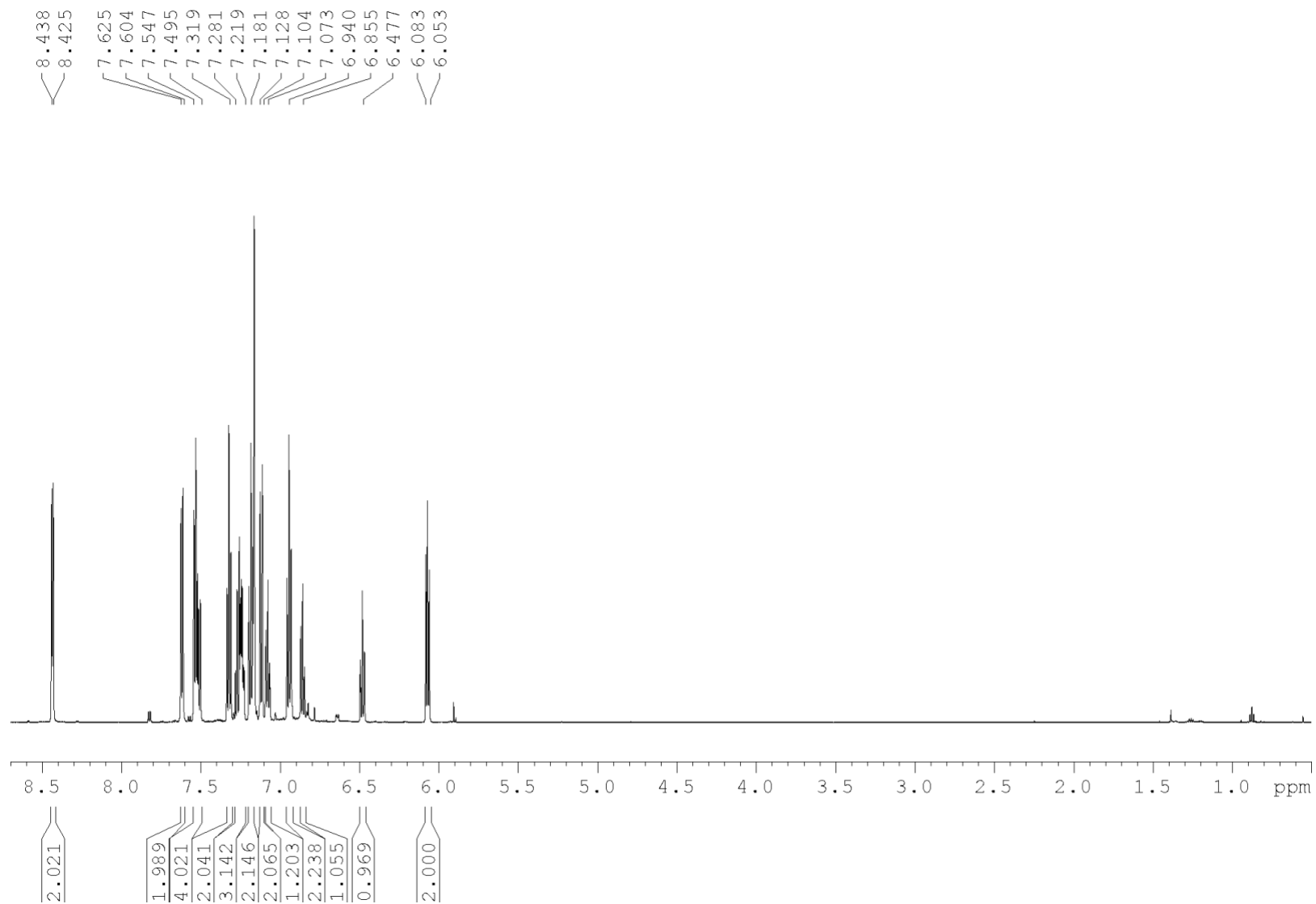


Figure S12: ^1H NMR spectrum of **1-Py** in C_6D_6 .

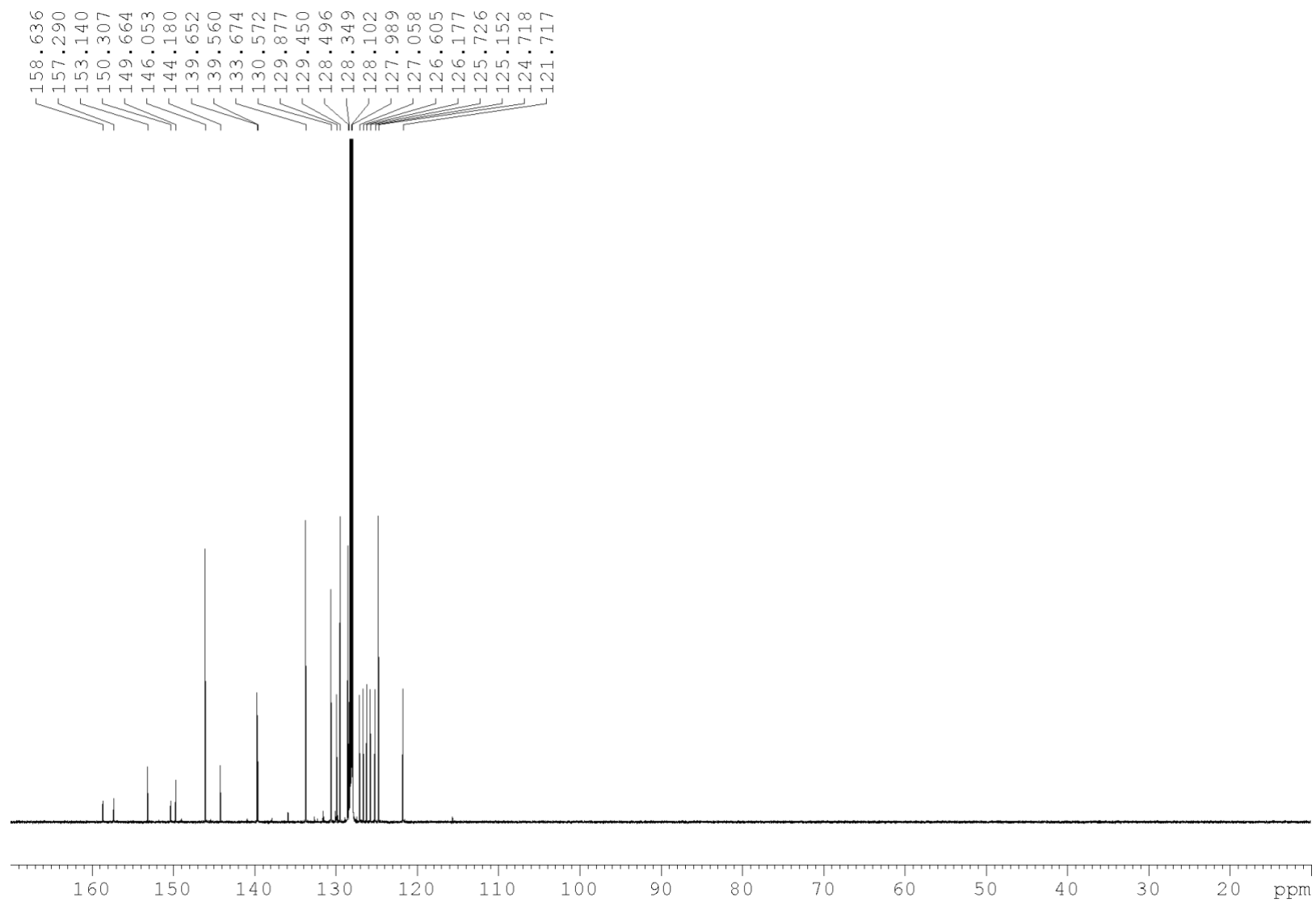


Figure S13: ^{13}C NMR spectrum of **1-Py** in C_6D_6 .

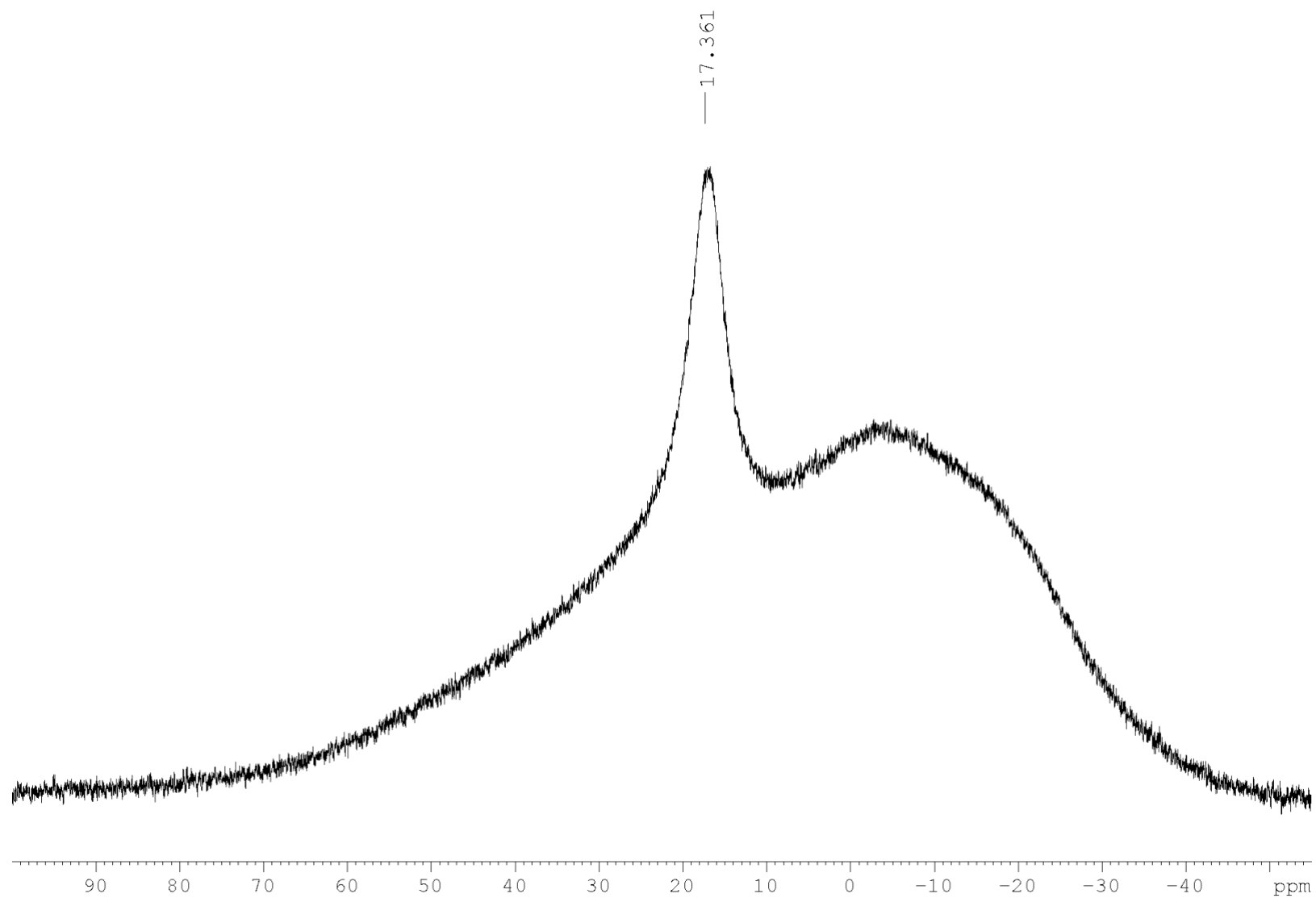


Figure S14: ^{11}B NMR spectrum of **1-THF** in C_6D_6 .

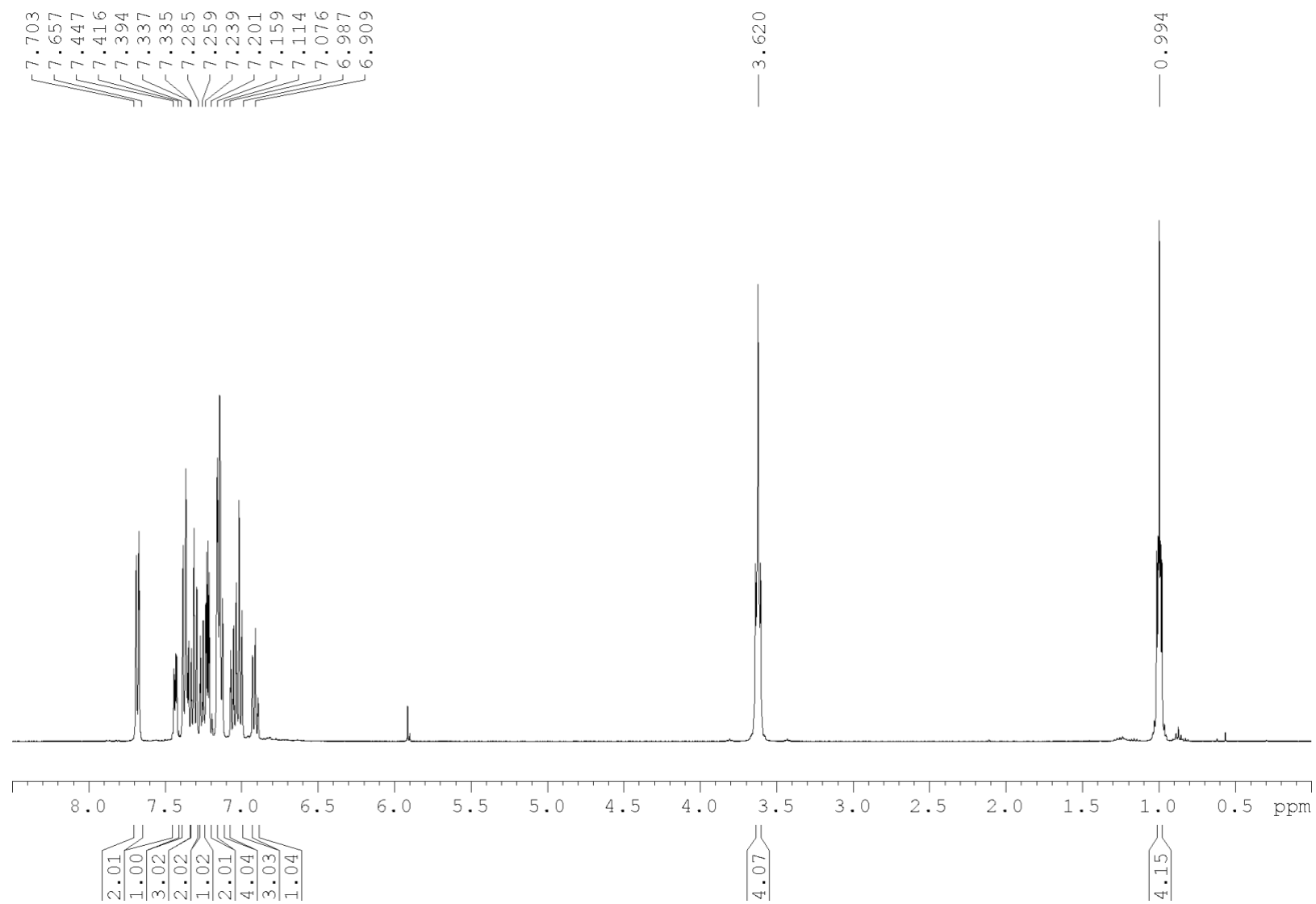


Figure S15: ^1H NMR spectrum of **1-THF** in C_6D_6 .

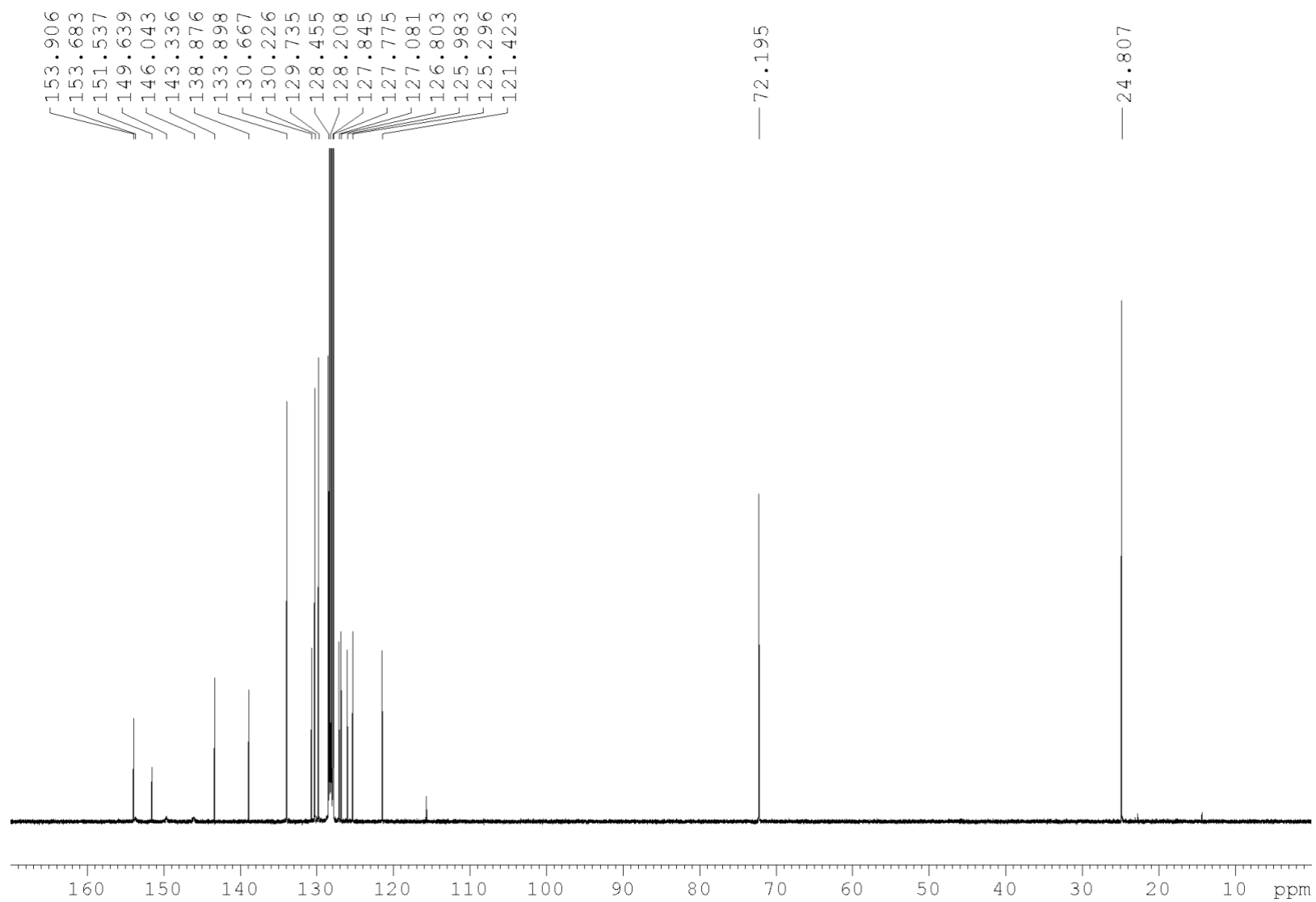


Figure S16: ^{13}C NMR spectrum of 1-THF in C_6D_6 .

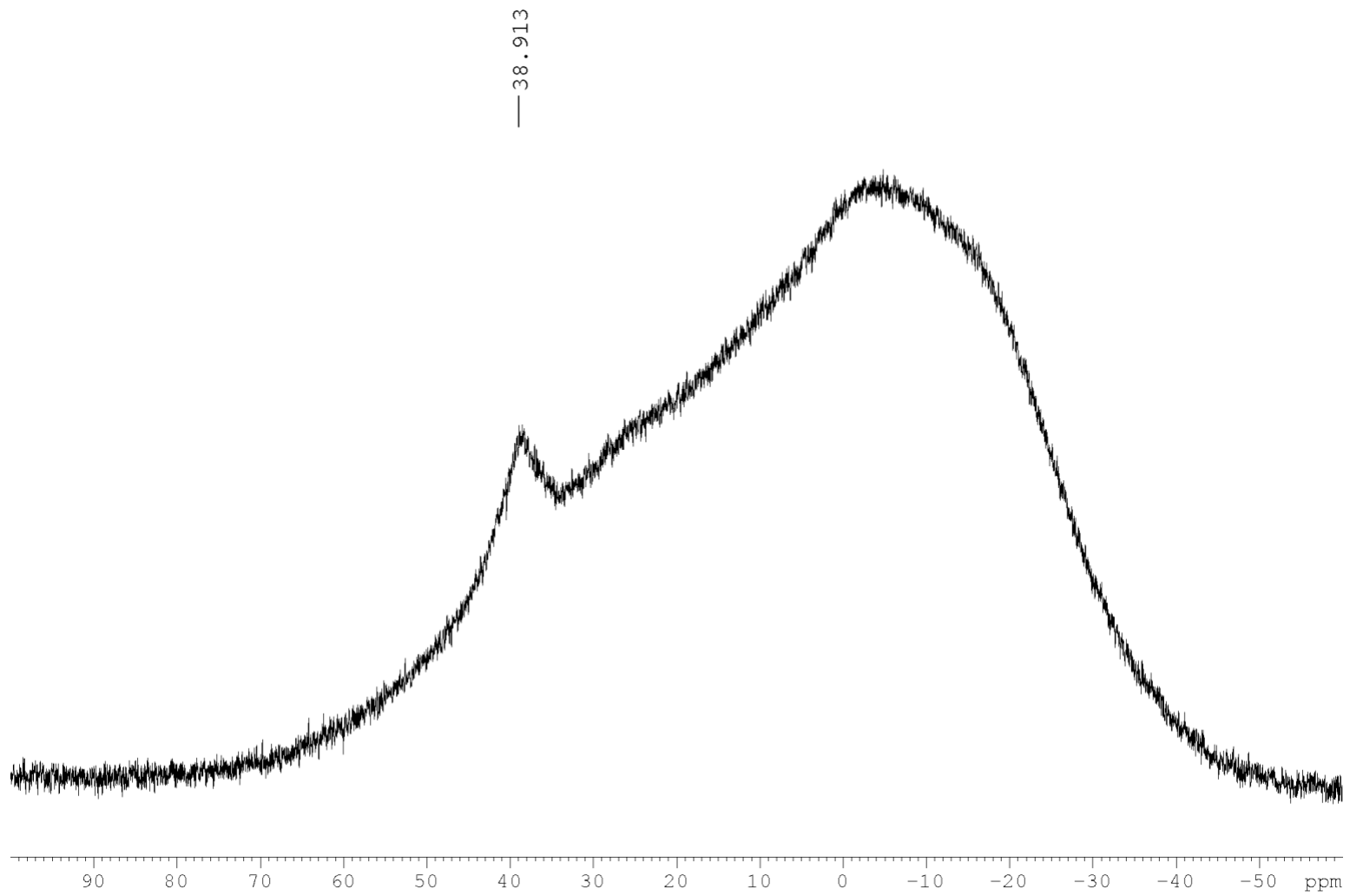


Figure S17: ^{11}B NMR spectrum of **2** in C_6D_6 .

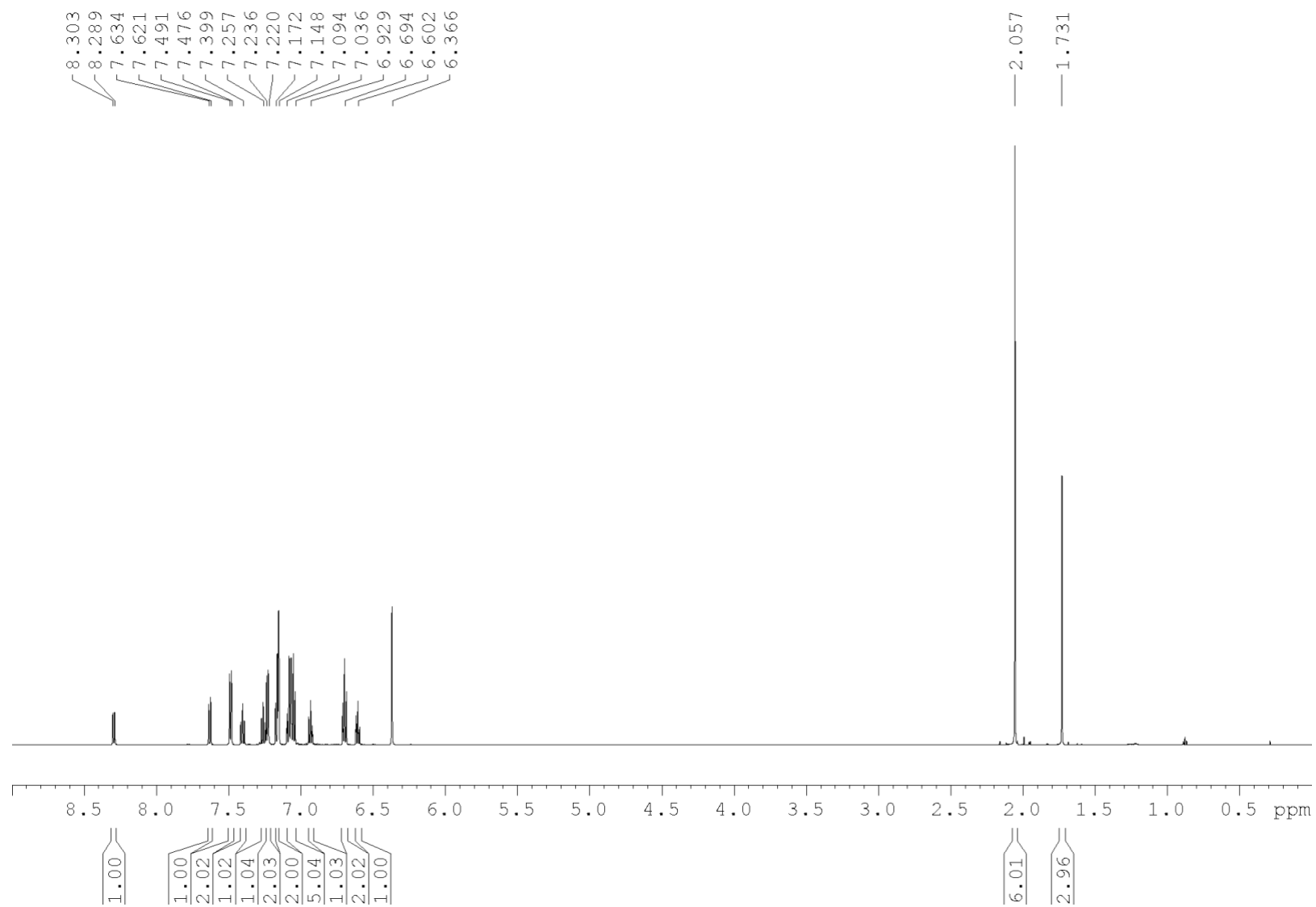


Figure S18: ¹H NMR spectrum of **2** in C₆D₆.

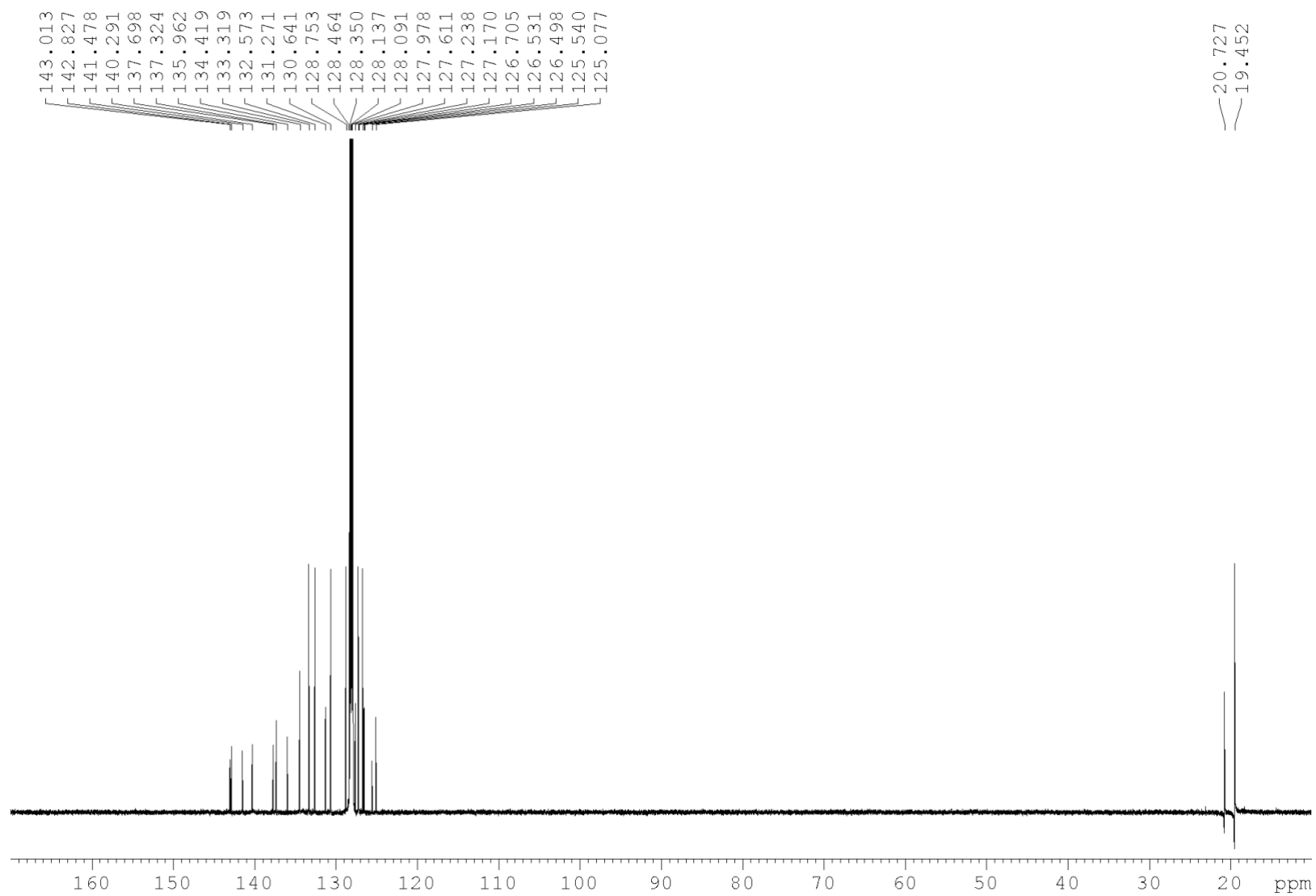


Figure S19: ^{13}C NMR spectrum of **2** in C_6D_6 .

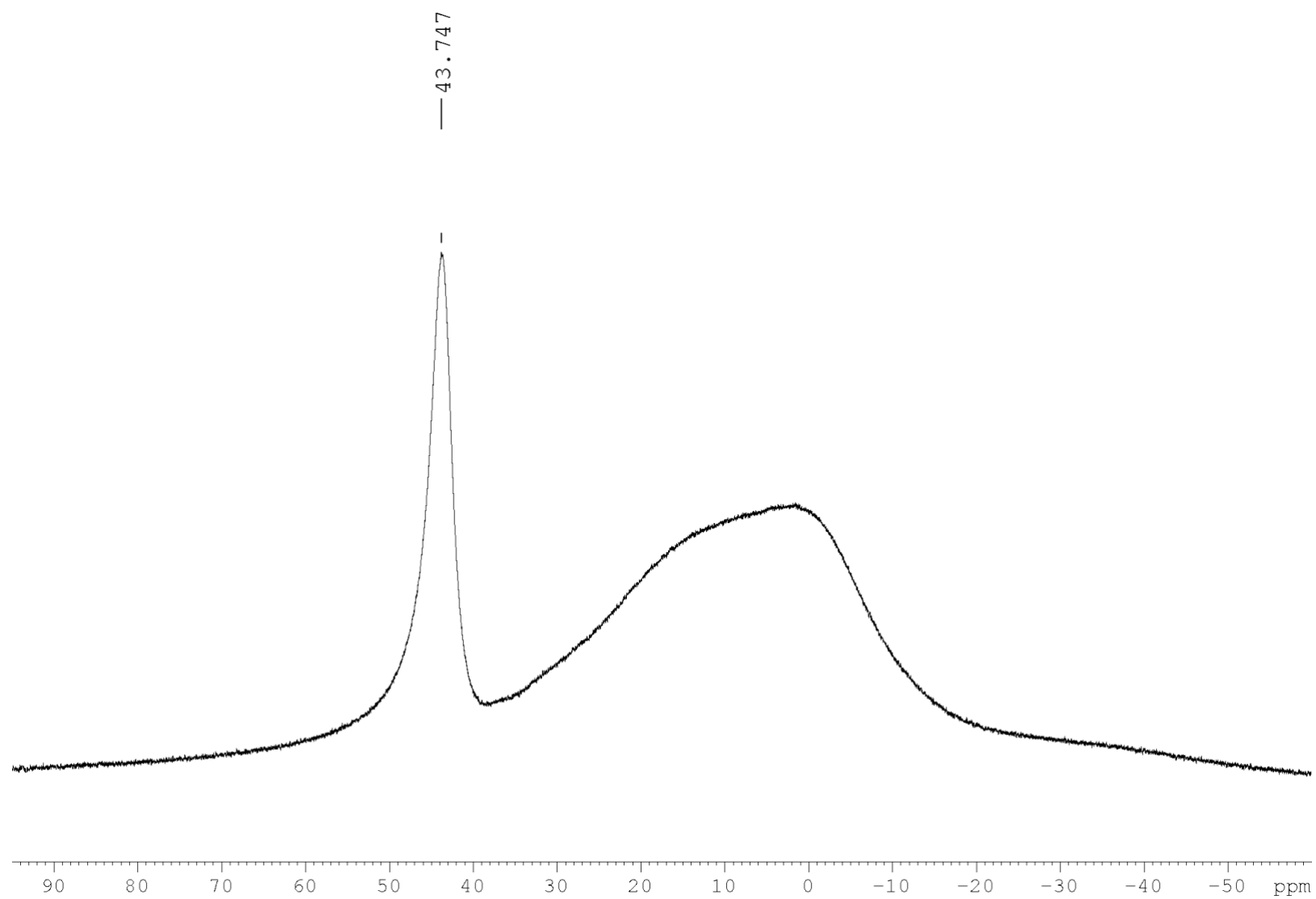


Figure S20: ^{11}B NMR spectrum of **3** in CD_2Cl_2 .

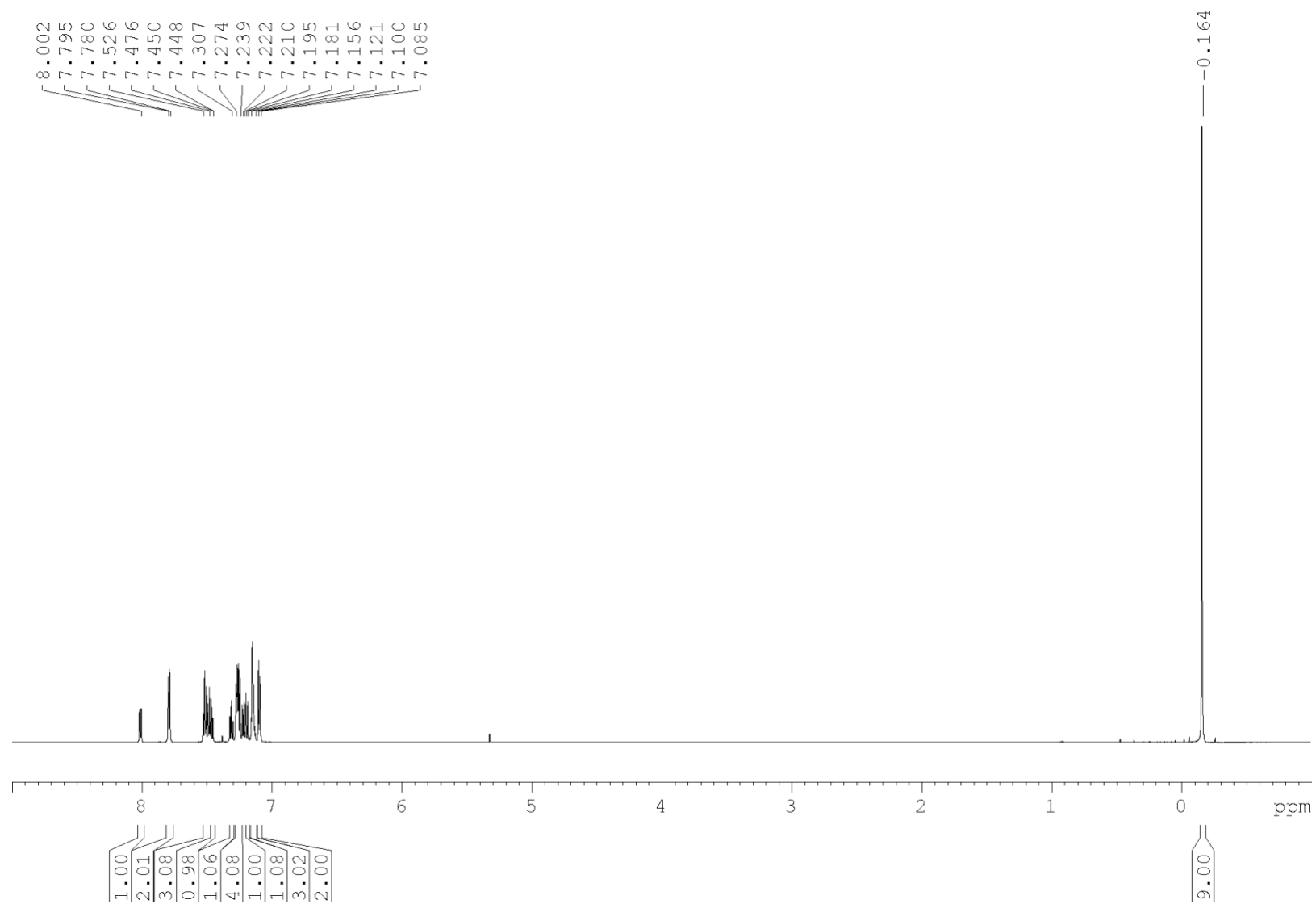


Figure S21: ^1H NMR spectrum of **3** in CD_2Cl_2 .

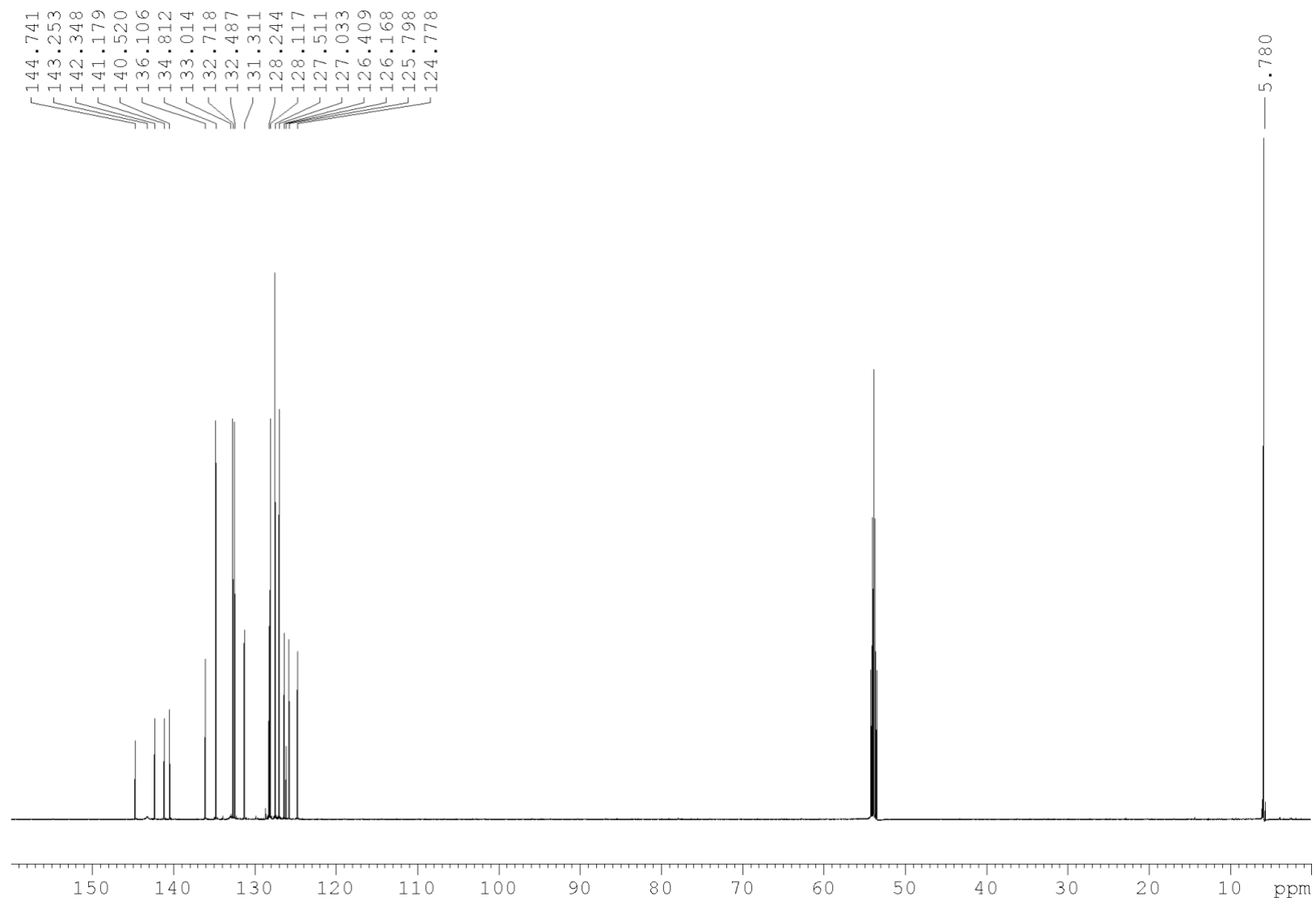


Figure S22: ^{13}C NMR spectrum of **3** in CD_2Cl_2 .

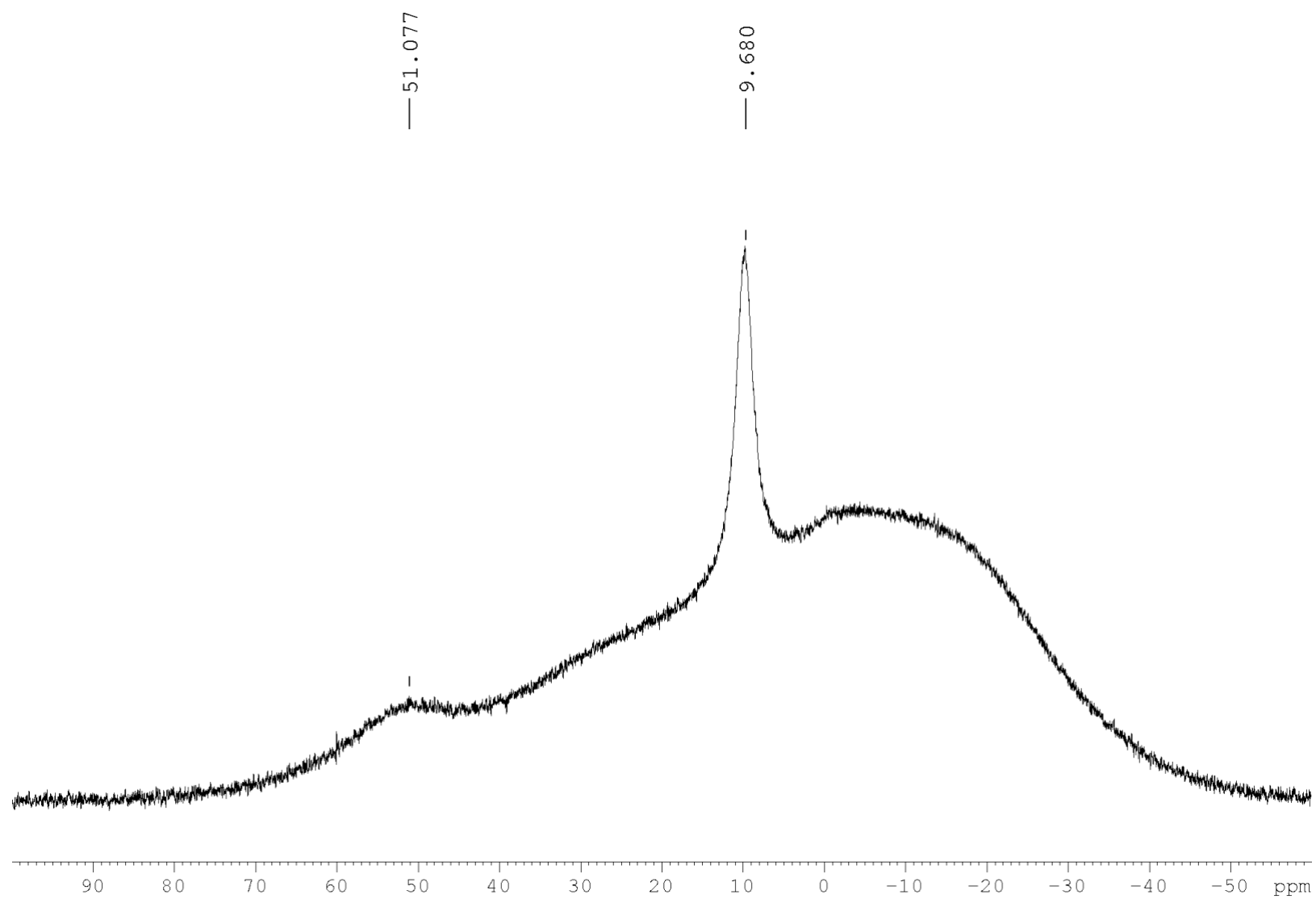


Figure S23: ^{11}B NMR spectrum of **4** in CD_2Cl_2 .

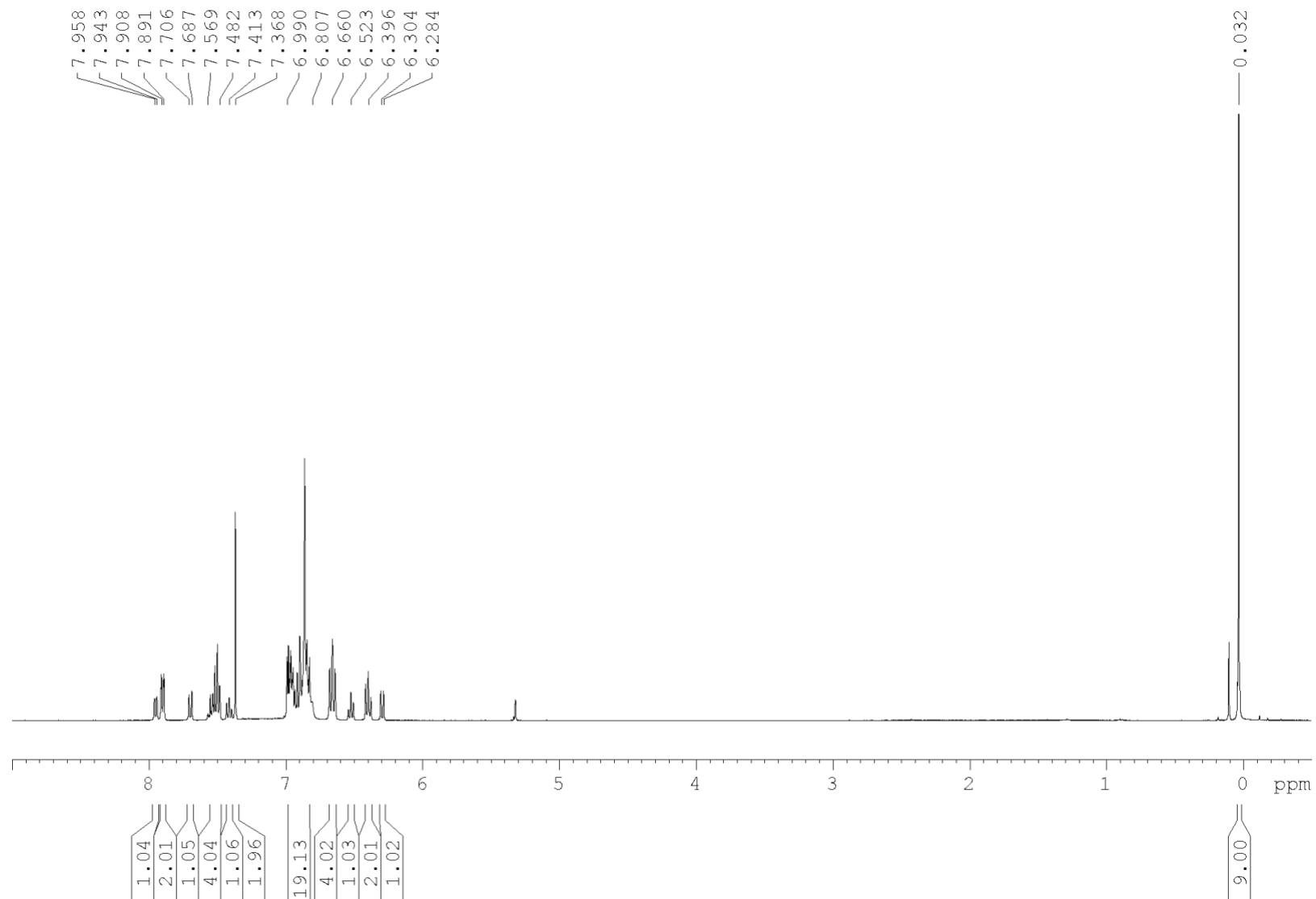


Figure S24: ^1H NMR spectrum of **4** in CD_2Cl_2 .

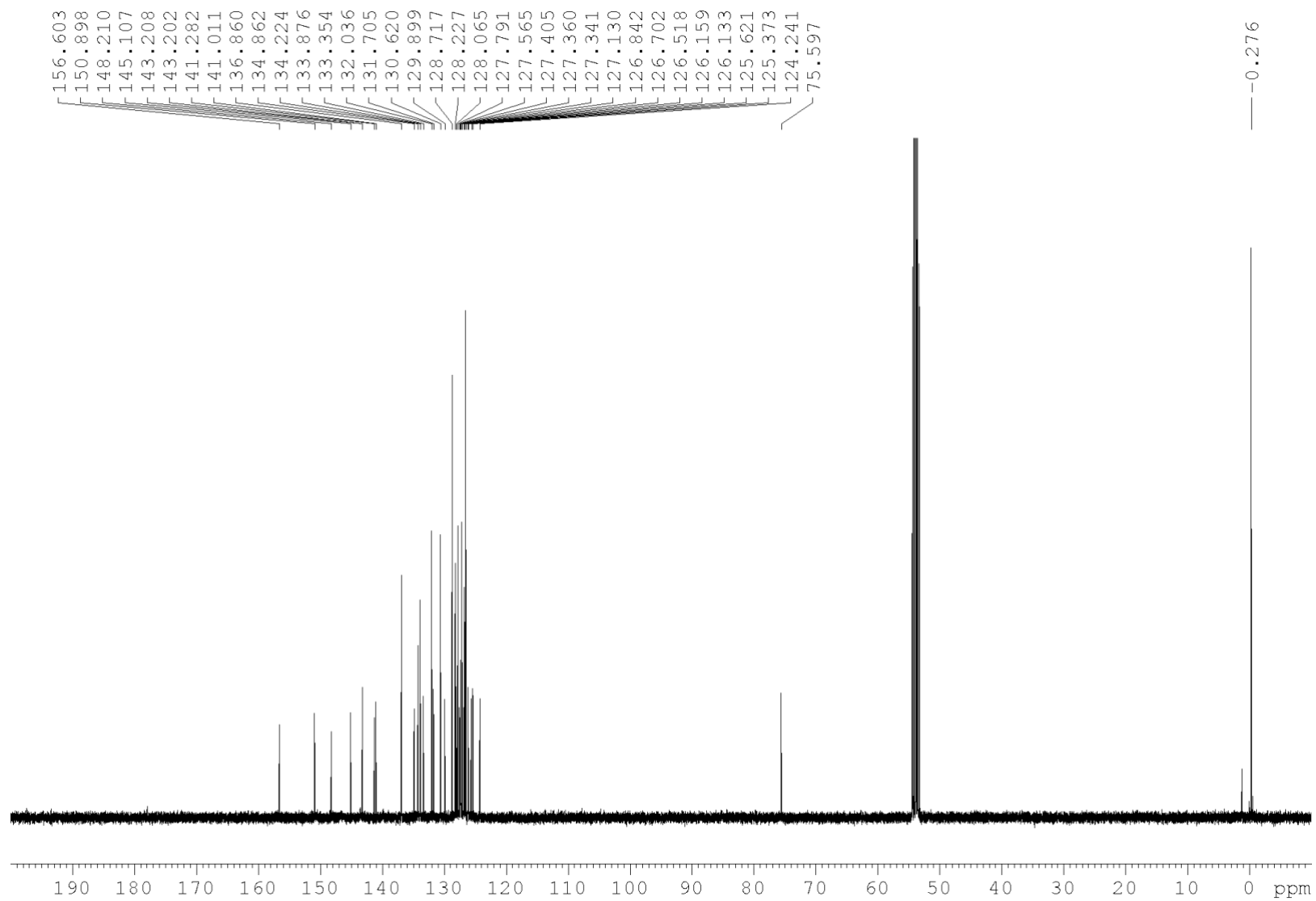


Figure S25: ^{13}C NMR spectrum of **4** in CD_2Cl_2 .

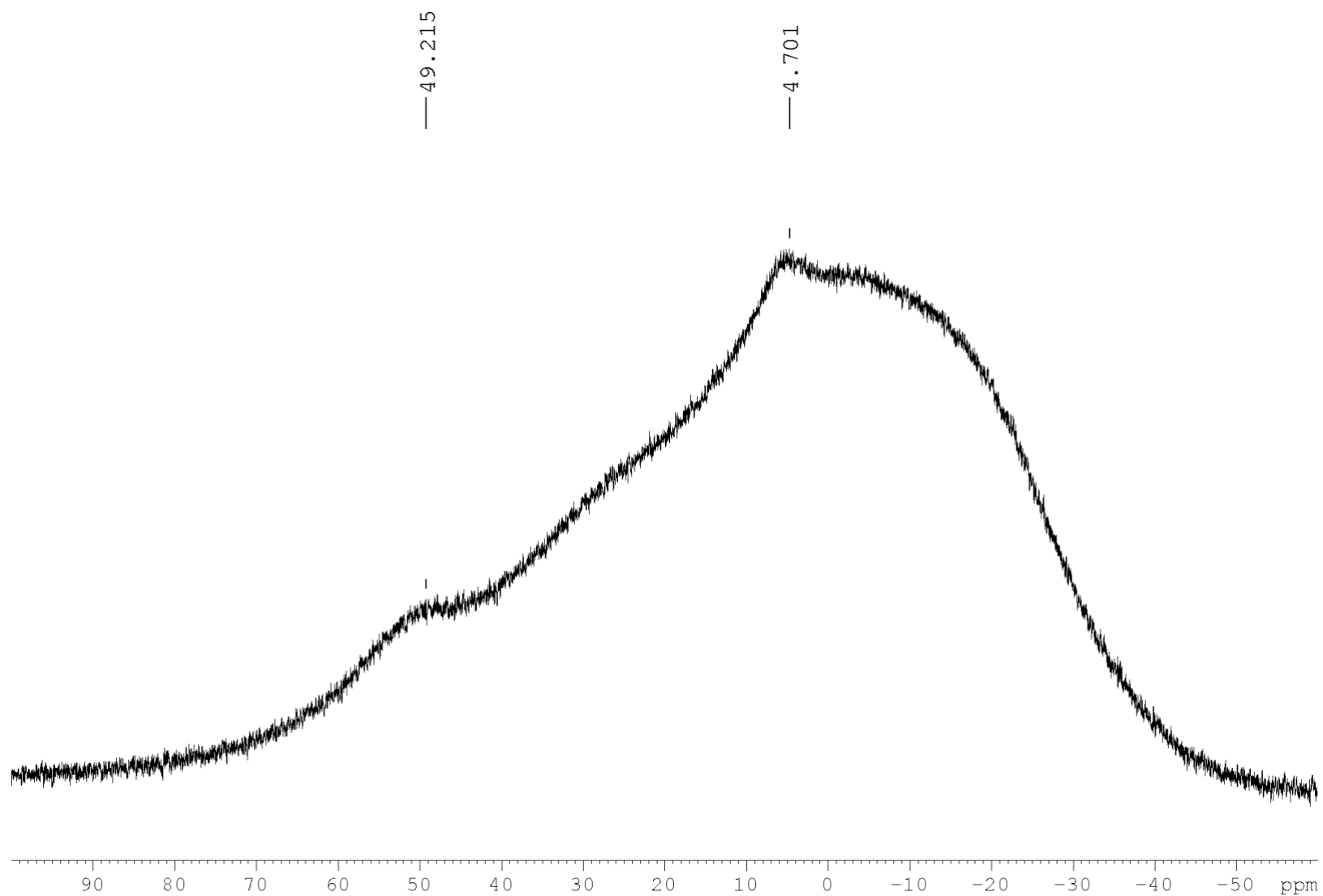


Figure S26: ^{11}B NMR spectrum of **5** in CD_2Cl_2 .

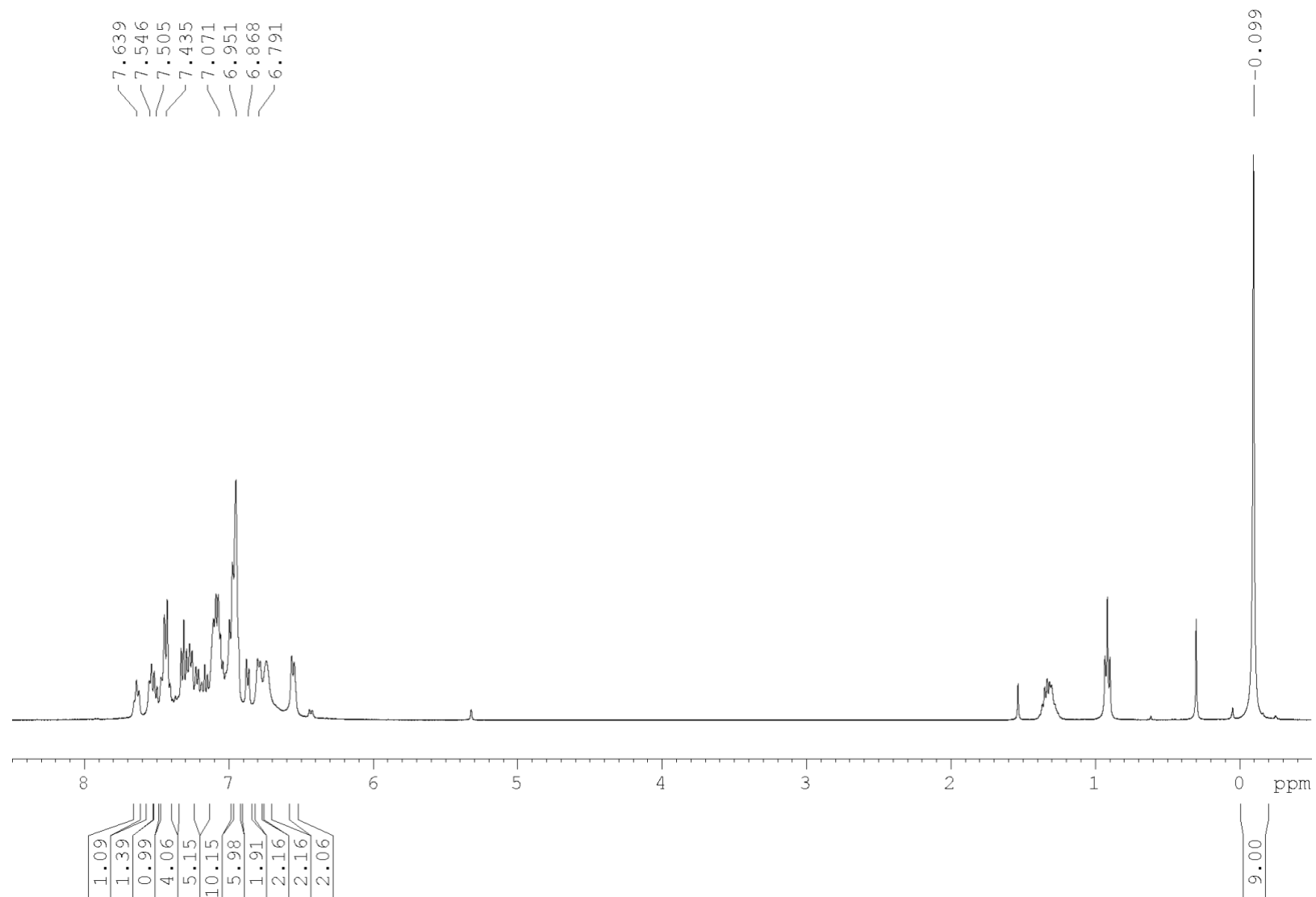


Figure S27: ^1H NMR spectrum of **5** in CD_2Cl_2 .

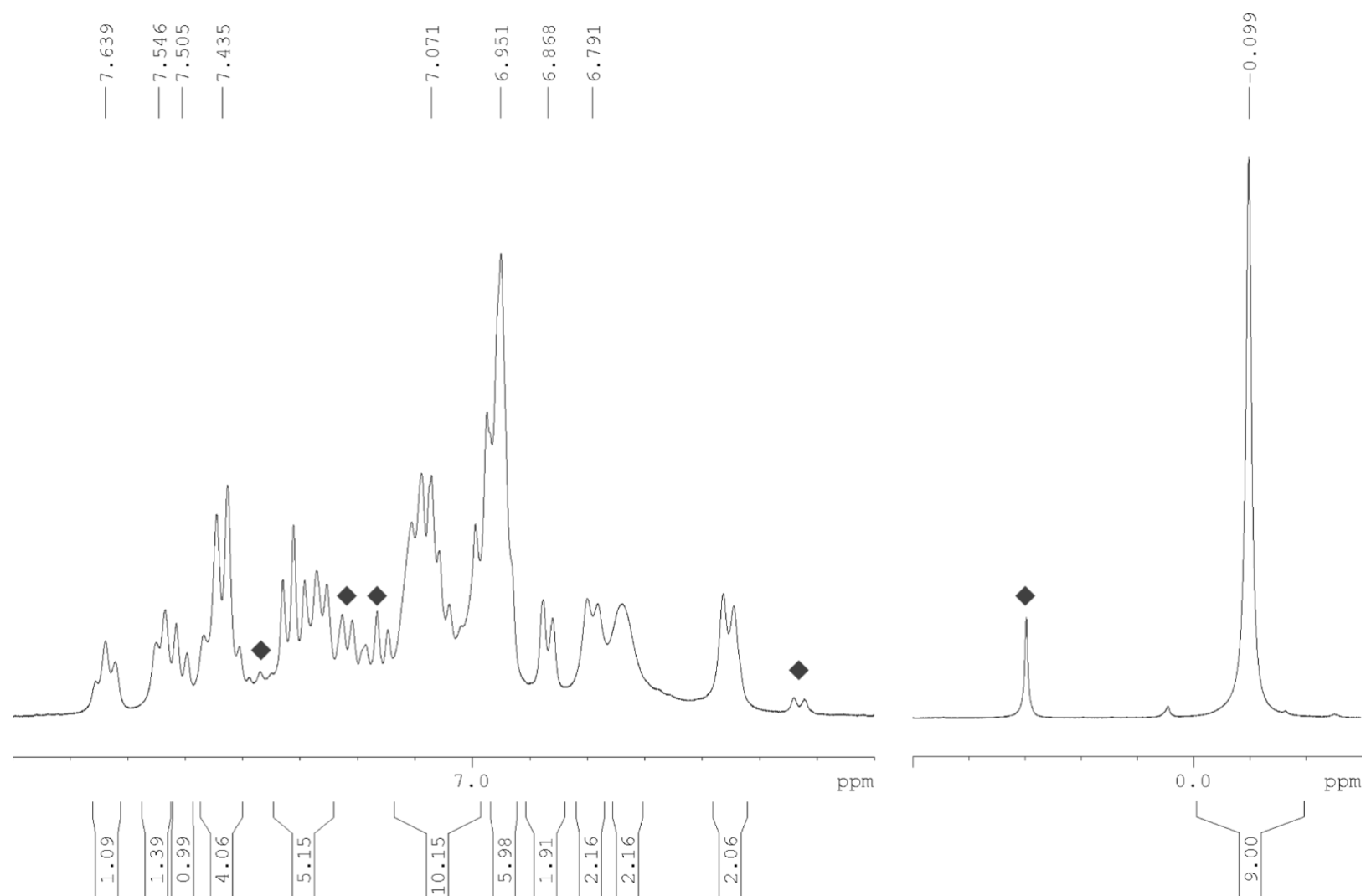


Figure S28: ^1H NMR spectrum of **5** in CD_2Cl_2 (marked signals correspond to the rearrangement product **4** (♦)).

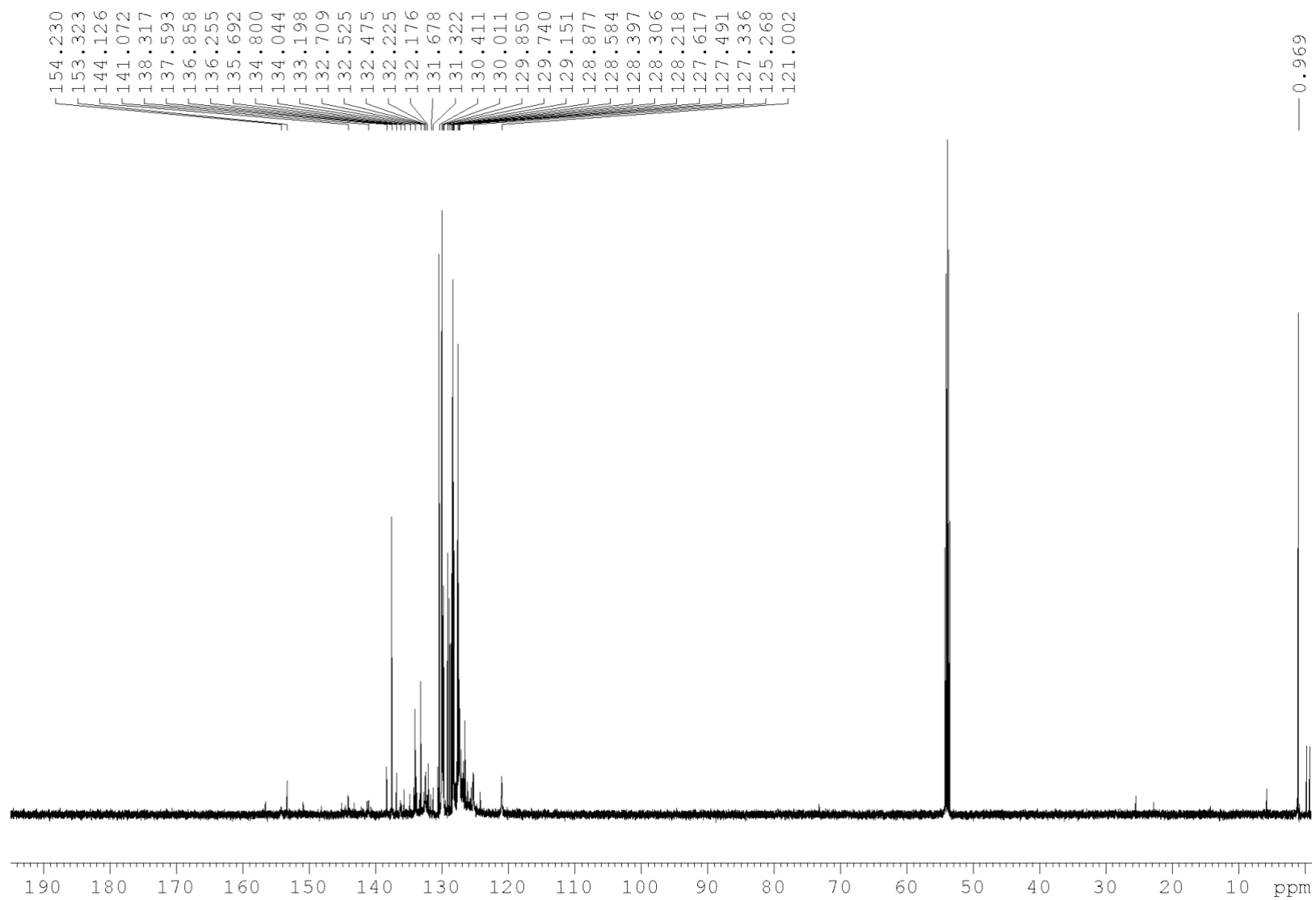


Figure S29: ^{13}C NMR spectrum of **5** in CD_2Cl_2 .

UV-Vis spectra

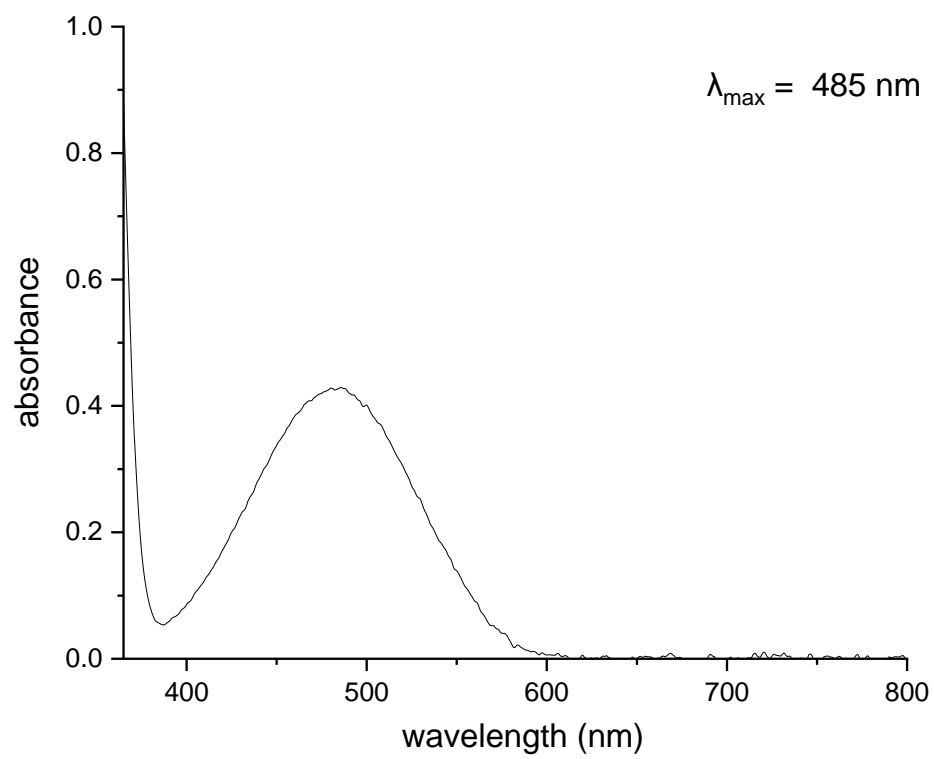


Figure S30: UV-Vis spectrum of **1** in CH₂Cl₂.

Cyclic voltammetry

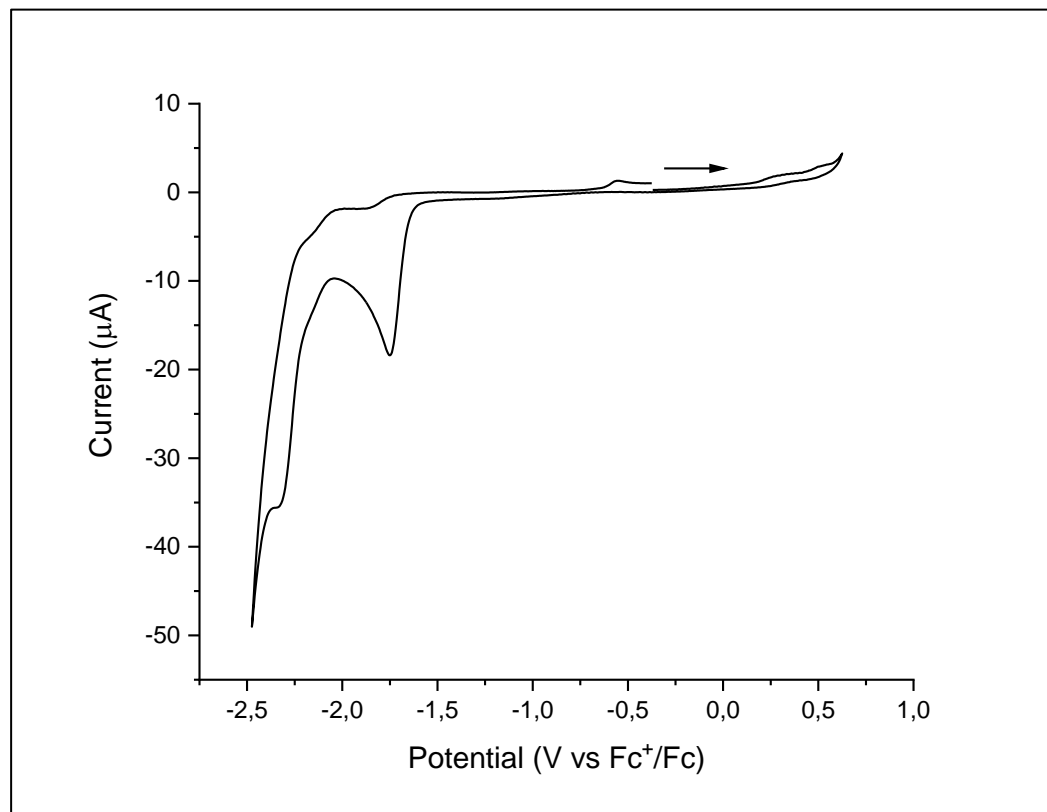


Figure S31: Cyclic voltammogram of **1** in CH₂Cl₂ solution with a scan rate 100 mVs⁻¹. Potential is reported versus Fc/Fc⁺ as internal standard. Two sequential reductions occur at -1.75 V and -2.35 V.

Crystal structure determination

The crystal data of all compounds were collected on a XTALAB DUALFLEX HYPIX diffractometer with a Hybrid Pixel array detector and multi-layer mirror monochromated $\text{Cu}_{K\alpha}$ radiation. The structures were solved using intrinsic phasing method,^[4] refined with the SHELXL program^[5] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealized geometric positions.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-2360675 (**1**), CCDC-2360676 (**1-DMAP**), CCDC-2360677 (**1-OPe_t3**), CCDC-2360678 (**1-Py**), CCDC-2360679 (**1-THF**), CCDC-2360680 (**2**), CCDC-2360681 (**3**), CCDC-2360682 (**4**), CCDC-2360683 (**5**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Refinement details for 1: The displacement parameters of all atoms of one disordered benzene were restrained to the same value with similarity restraint SIMU. The geometry of this solvent molecule (benzene) was fitted to the idealized structure using AFIX 66.

Crystal data for **1**: $C_{29}H_{22}B$, $M_r = 381.27$, clear light red plate, $0.190 \times 0.150 \times 0.090$ mm³, monoclinic space group $P2/n$, $a = 18.3373(4)$ Å, $b = 6.01900(10)$ Å, $c = 24.2331(4)$ Å, $\beta = 104.751(2)^\circ$, $V = 2586.51(9)$ Å³, $Z = 4$, $\rho_{calcd} = 0.979$ g·cm⁻³, $\mu = 0.412$ mm⁻¹, $F(000) = 804$, $T = 100(2)$ K, $R_1 = 0.0874$, $wR_2 = 0.1734$, 5149 independent reflections [$2\theta \leq 147.934^\circ$] and 271 parameters.

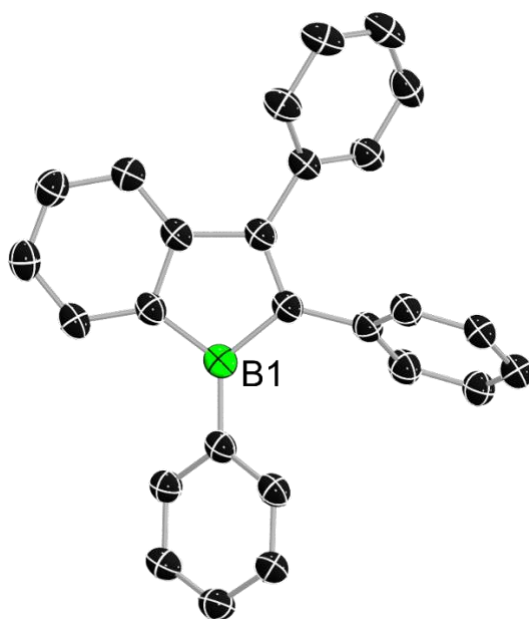


Figure S32: Solid-state structure of **1**. Atomic displacement ellipsoids represented at 50%. Ellipsoids of carbon atoms of aryl groups, hydrogen atoms and two benzene molecules are omitted for clarity.

Refinement details for 1-OPEt₃: The atomic displacement parameters of the atoms in the disordered benzene moiety were restrained with the RIGU keyword in ShelXL input ('enhanced rigid bond' restraint for all bonds in the connectivity list). The displacement parameters of the atoms in the disordered benzene moiety were restrained to the same value using similarity restraint SIMU.

Crystal data for **1-OPEt₃**: C₃₂H₃₄BOP, *M_r* = 476.37, colourless block, 0.120×0.120×0.110 mm³, monoclinic space group *P2₁/n*, *a* = 12.3326(2) Å, *b* = 16.0720(2) Å, *c* = 13.3588(2) Å, $\alpha = 90^\circ$, $\beta = 92.4270(10)^\circ$, $\gamma = 90^\circ$, *V* = 2645.47(7) Å³, *Z* = 4, $\rho_{\text{calcd}} = 1.196 \text{ g}\cdot\text{cm}^{-3}$, $\mu = 1.077 \text{ mm}^{-1}$, *F*(000) = 1016, *T* = 100(2) K, *R*₁ = 0.0506, *wR*₂ = 0.1140, 5420 independent reflections [$2\theta \leq 150.686^\circ$] and 350 parameters.

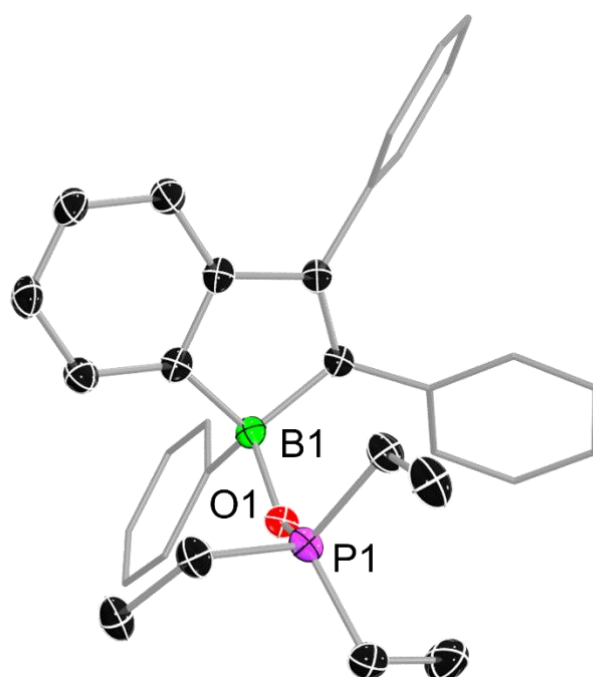


Figure S33: Solid-state structure of **1-Et₃PO**. Atomic displacement ellipsoids represented at 50%. Ellipsoids of carbon atoms of aryl and alkyl groups and hydrogen atoms are omitted for clarity.

Crystal data for **1-DMAP**: $C_{36}H_{32}BN_2$, $M_r = 503.44$, colourless block, $0.278 \times 0.164 \times 0.138 \text{ mm}^3$, space group $P2_1/n$, $a = 10.93990(10) \text{ \AA}$, $b = 13.5758(2) \text{ \AA}$, $c = 19.8961(2) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 104.7630(10)^\circ$, $\gamma = 90^\circ$, $V = 2857.38(6) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.170 \text{ g}\cdot\text{cm}^{-3}$, $\mu = 0.510 \text{ mm}^{-1}$, $F(000) = 1068$, $T = 100.01(10) \text{ K}$, $R_1 = 0.0485$, $wR_2 = 0.1175$, 5864 independent reflections [$2\theta \leq 150.316^\circ$] and 356 parameters.

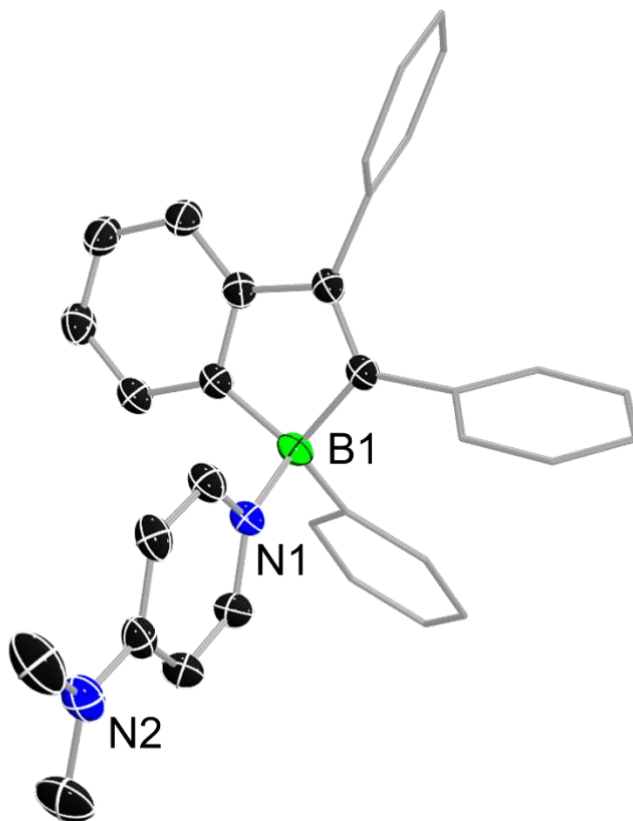


Figure S34: Solid-state structure of **1-DMAP**. Atomic displacement ellipsoids represented at 50%. Ellipsoids of carbon atoms of aryl groups, one benzene molecule and hydrogen atoms are omitted for clarity.

Crystal data for **1-Py**: $C_{31}H_{24}BN$, $M_r = 421.32$, colourless block, $0.380 \times 0.160 \times 0.100 \text{ mm}^3$, monoclinic space group Cc , $a = 13.62580(10) \text{ \AA}$, $b = 13.3900(2) \text{ \AA}$, $c = 12.53570(10) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 98.7320(10)^\circ$, $\gamma = 90^\circ$, $V = 2260.62(4) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.238 \text{ g}\cdot\text{cm}^{-3}$, $\mu = 0.534 \text{ mm}^{-1}$, $F(000) = 888$, $T = 100(2) \text{ K}$, $R_1 = 0.0319$, $wR_2 = 0.0808$, Flack parameter = $0.0(3)$, 3575 independent reflections [$2\theta \leq 150.262^\circ$] and 298 parameters.

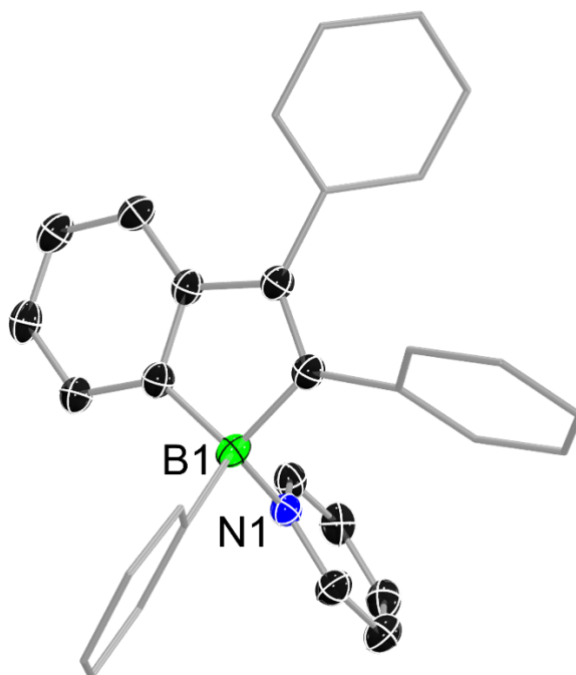


Figure S35: Solid-state structure of **1-Py**. Atomic displacement ellipsoids represented at 50%. Ellipsoids of carbon atoms of aryl groups and hydrogen atoms are omitted for clarity.

Refinement details for 1-THF: The atomic displacement parameters of all atoms in the thf residue were restrained with the RIGU keyword in ShelXL input ('enhanced rigid bond' restraint for all bonds in the connectivity list). The displacement parameters of atoms in the thf residue were restrained to the same value with similarity restraint SIMU. The 1–2 and 1–3 distances in the disordered thf residue were restrained to the same values with SAME.

Crystal data for **1-THF**: $C_{30}H_{27}BO$, $M_r = 414.32$, colourless plate, $0.310 \times 0.280 \times 0.100$ mm³, monoclinic space group $P2_1/n$, $a = 10.9933(2)$ Å, $b = 12.0387(2)$ Å, $c = 17.7494(3)$ Å, $\beta = 106.511(2)^\circ$, $V = 2252.18(7)$ Å³, $Z = 4$, $\rho_{calcd} = 1.222$ g·cm⁻³, $\mu = 0.544$ mm⁻¹, $F(000) = 880$, $T = 100(2)$ K, $R_1 = 0.0555$, $wR_2 = 0.1189$, 4516 independent reflections [$2\theta \leq 149.892^\circ$] and 335 parameters.

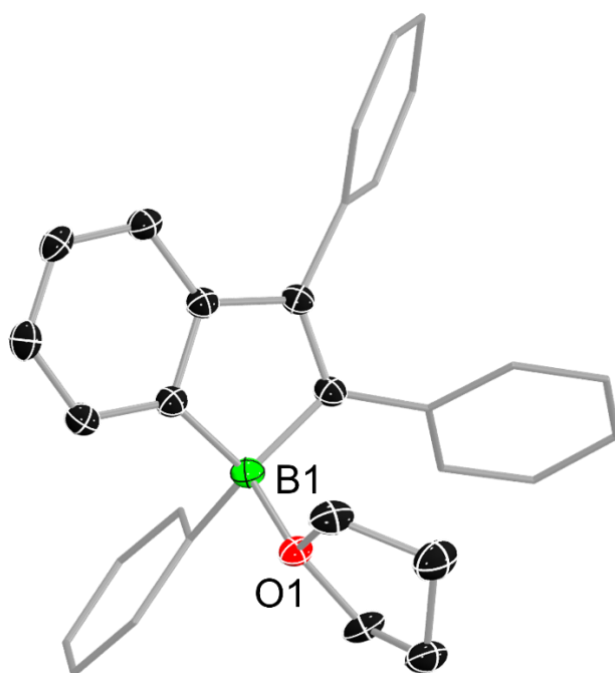


Figure S36: Solid-state structure of **1-THF**. Atomic displacement ellipsoids represented at 50%. Ellipsoids of carbon atoms of aryl groups and hydrogen atoms are omitted for clarity.

Crystal data for **2**: $C_{35}H_{30}BN$, $M_r = 475.41$, clear colourless needle, $0.103 \times 0.041 \times 0.027 \text{ mm}^3$, space group $P2_1/c$, $a = 13.2512(2) \text{ \AA}$, $b = 14.86320(10) \text{ \AA}$, $c = 14.8307(2) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 113.055(2)^\circ$, $\gamma = 90^\circ$, $V = 2687.68(7) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.175 \text{ g}\cdot\text{cm}^{-3}$, $\mu = 0.503 \text{ mm}^{-1}$, $F(000) = 1008$, $T = 100.00(10) \text{ K}$, $R_1 = 0.0542$, $wR_2 = 0.1128$, 5488 independent reflections [$2\theta \leq 149.926^\circ$] and 337 parameters.

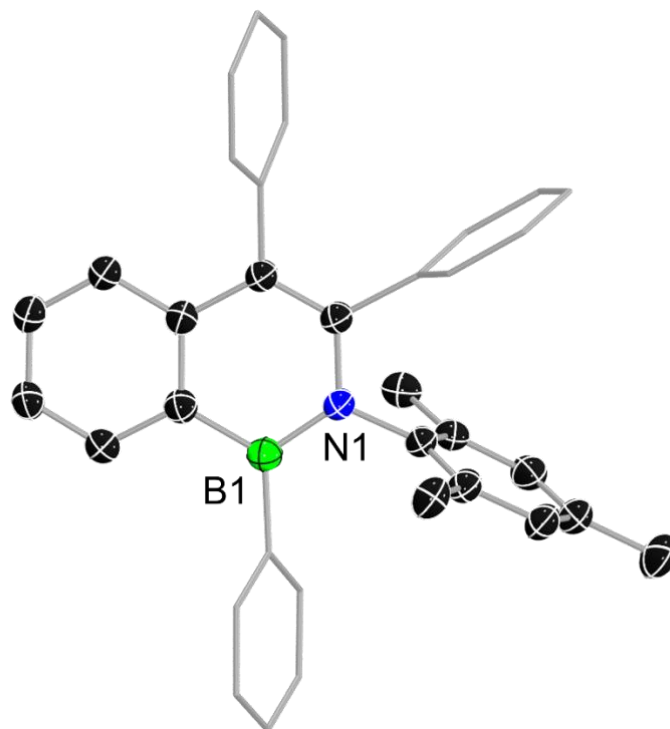


Figure S37: Solid-state structure of **2**. Atomic displacement ellipsoids represented at 50%. Ellipsoids of carbon atoms of aryl groups and hydrogen atoms are omitted for clarity.

Crystal data for **3**: C₂₉H₂₈BNSi, $M_r = 429.42$, colourless block, 0.180×0.092×0.066 mm³, space group $P2_1/n$, $a = 13.0612(2) \text{ \AA}$, $b = 11.32090(10) \text{ \AA}$, $c = 16.7015(2) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 106.2250(10)^\circ$, $\gamma = 90^\circ$, $V = 2371.20(5) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.203 \text{ g}\cdot\text{cm}^{-3}$, $\mu = 0.980 \text{ mm}^{-1}$, $F(000) = 912$, $T = 100.00(10) \text{ K}$, $R_1 = 0.0521$, $wR_2 = 0.1214$, 4819 independent reflections [$2\theta \leq 150.436^\circ$] and 292 parameters.

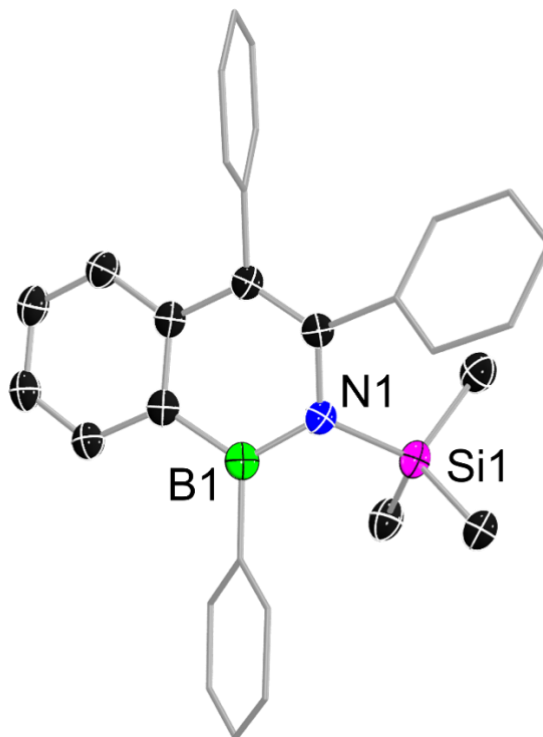


Figure S38: Solid-state structure of **3**. Atomic displacement ellipsoids represented at 50%. Ellipsoids of carbon atoms of aryl groups and hydrogen atoms omitted for clarity.

Refinement details for 4: The displacement parameters of the benzene residue were restrained to the same value with similarity restraint SIMU. The U_{ii} displacement parameters of atoms of the benzene residue were restrained with ISOR keyword to approximate isotropic behavior.

Crystal data for **4**: $C_{61}H_{53}B_2N_3Si$, $M_r = 877.77$, clear pale colourless block, $0.525 \times 0.345 \times 0.251 \text{ mm}^3$, space group $P2_1/c$, $a = 13.45630(10) \text{ \AA}$, $b = 30.1996(2) \text{ \AA}$, $c = 11.78090(10) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 97.8290(10)^\circ$, $\gamma = 90^\circ$, $V = 4742.84(6) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.229 \text{ g} \cdot \text{cm}^{-3}$, $\mu = 0.767 \text{ mm}^{-1}$, $F(000) = 1856$, $T = 100.00(10) \text{ K}$, $R_1 = 0.0461$, $wR_2 = 0.1173$, 9732 independent reflections [$2\theta \leq 150.504^\circ$] and 607 parameters.

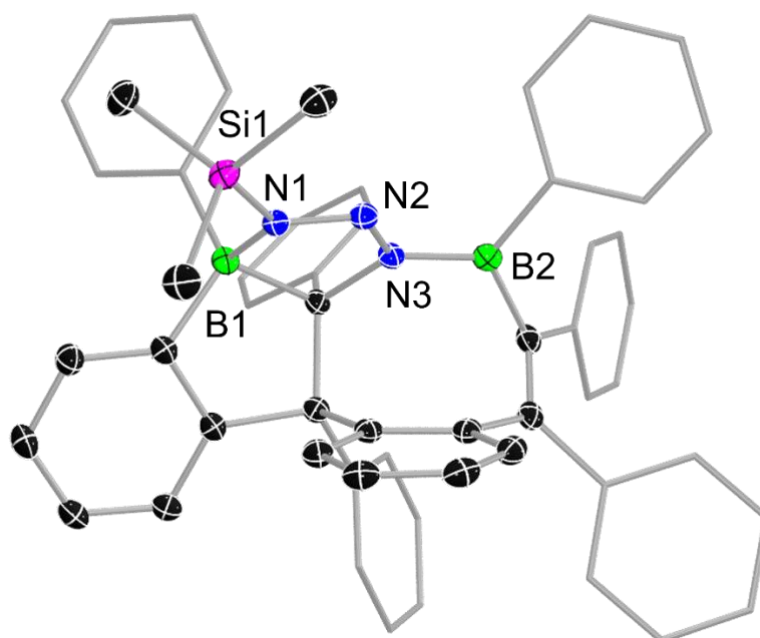


Figure S39: Solid-state structure of **4**. Atomic displacement ellipsoids represented at 50%. Ellipsoids of carbon atoms of aryl groups, hydrogen atoms and one benzene molecule are omitted for clarity.

Refinement details for 5: The compound was refined as a two-component twin. Component 2 was rotated by 6.0699° around [0.90–0.24–0.37] (reciprocal) or [0.98–0.10–0.17] (direct). The BASF parameter was refined to 52.7%. The atomic displacement parameters of the atoms C1 to C7 of toluene were restrained using the DELU keyword in ShelXL input ('rigid bond' restraint for the bonds in the connectivity list). The atomic displacement parameters of the atoms C1 to C7 in the toluene residue (TOL) were restrained with the RIGU keyword in ShelXL input ('enhanced rigid bond' restraint for all bonds in the connectivity list). The displacement parameters of all atoms of the residue TOL were restrained to the same value with the similarity restraint SIMU. The U_{ii} displacement parameters of the atoms in TOL were restrained with the ISOR keyword to approximate isotropic behavior.

Crystal data for **5**: $C_{62}H_{55}B_2N_3Si$, $M_r = 891.80$, red block, $0.321 \times 0.132 \times 0.090$ mm³, triclinic space group $P\bar{1}$, $a = 9.9393(2)$ Å, $b = 15.2431(2)$ Å, $c = 16.3736(3)$ Å, $\alpha = 85.6500(10)^\circ$, $\beta = 86.819(2)^\circ$, $\gamma = 89.3620(10)^\circ$, $V = 2469.68(7)$ Å³, $Z = 2$, $\rho_{calcd} = 1.199$ g·cm⁻³, $\mu = 0.744$ mm⁻¹, $F(000) = 944$, $T = 100(2)$ K, $R_1 = 0.0927$, $wR_2 = 0.2381$, 20203 independent reflections [$2\theta \leq 151.054^\circ$] and 659 parameters.

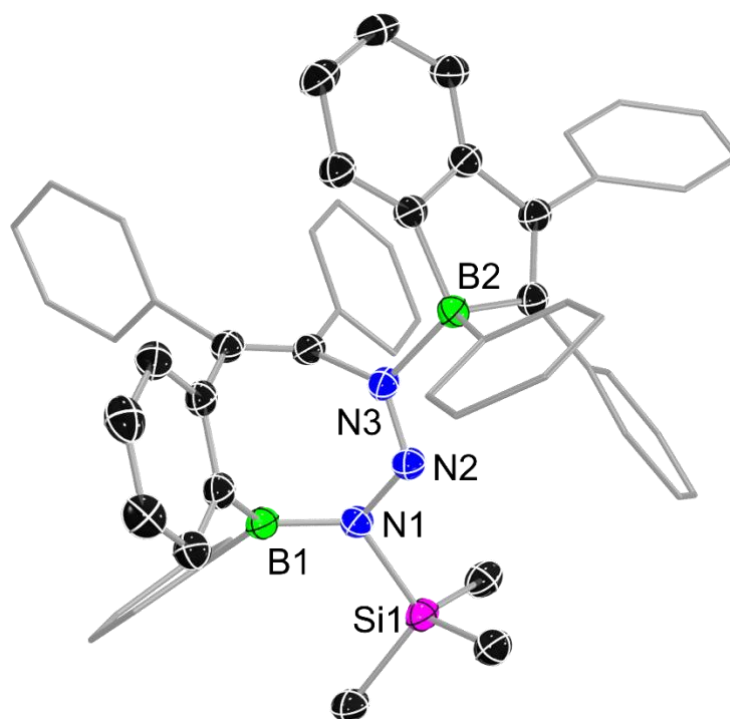


Figure S40: Solid-state structure of **5**. Atomic displacement ellipsoids represented at 50%. Ellipsoids of carbon atoms of aryl groups, hydrogen atoms and one toluene molecule are omitted for clarity.

Computational details

DFT geometry optimizations of all compounds were carried out with the Gaussian 98 g16, Revision C.01 program package^[6] using the PBE1PBE functional^[7] in combination with the 6-311+G(d,p) basis set^[8] in the gas phase. The D3-version of Grimmes dispersion model with the initial D3-dampening function and additional Becke-Johnson-dampening function was used. All structures were fully optimized and confirmed as minima on the corresponding potential energy surface by vibrational frequency computations, which revealed that all eigenvalues of the Hessian matrices are positive. The frontier molecular orbitals were visualized with the Chemcraft 1.8 program^[9] and their energetic level is given at the PBE1PBE / 6-311+G(d,p) / SMD(benzene) level of theory. To assess the aromatic character of the systems, calculations of the nucleus-independent chemical shifts (NICS)^[10] were carried out, using the PBE1PBE functional, the 6-311+G(d,p) basis set, the D3-version of Grimmes dispersion model with the initial D3-dampening function and additional Becke-Johnson-dampening function and the gauge-independent atomic orbital (GIAO) method.^[11] The corresponding values were obtained by placing dummy atoms in the centers of BC₄ rings and at distances of 0.1 Å along the axis perpendicular to the ring centers (see Table S2). For the NICS_{zz} scan, the zz component of the magnetic shielding tensor was used (see Figure S41).^[12]

Frontier molecular orbitals

Table S1: Calculated HOMO and LUMO energies for 1-phenylborole (**HB**), pentaphenylborole (**PPB**), 9-phenyl-9-borafluorene (**PhBF**), 1,2,3-triphenylboraindene (**1**, ^{Ph}**PhBI**), and 1-phenylboraindene (^H**PhBI**; PBE1PBE/ 6-311+G(d,p)/D3(BJ)/SCRF(SMF, solvent=benzene).

compound	HOMO energy (eV)	LUMO energy (eV)	HOMO-LUMO gap (eV)
HB	-6.3790776428808	-2.66908279094964	3.70999485193116
PPB	-5.6828690745736	-2.78764506823920	2.89522400633440
PhBF	-6.3119231148584	-2.38080488563060	3.93111822922780
^{Ph} PhBI (1)	-6.0653167381248	-2.54656799610616	3.51874874201864
^H PhBI	-6.3514748761308	-2.52273503190072	3.82873984423008

NICS values

Table S2: Calculated NICS and NICS_{zz} values of **HB**, **PPB**, **PhBF**, ^{Ph}**PhBI** (**1**) and ^H**PhBI** (PBE1PBE/6-311+G(d,p)/ D3(BJ)).

compound	NICS _{iso} (0)	NICS _{iso} (-1/+1)	NICS _{zz} (0)	NICS _{zz} (-1/+1)
HB	15.86 ppm	8.12 / 8.12 ppm	54.70 ppm	28.06 / 28.05 ppm
PPB	13.37 ppm	7.12 / 7.13 ppm	49.72 ppm	24.55 / 24.88 ppm
PhBF	14.03 ppm	6.01 / 6.01 ppm	52.93 ppm	24.62 / 24.62 ppm
^{Ph} PhBI * (1)	14.48 ppm	7.68 / 7.33 ppm	53.76 ppm	26.88 / 27.90 ppm
^H PhBI	15.46 ppm	7.39 / -7.14 ppm	55.26 ppm	27.94 / 27.11 ppm

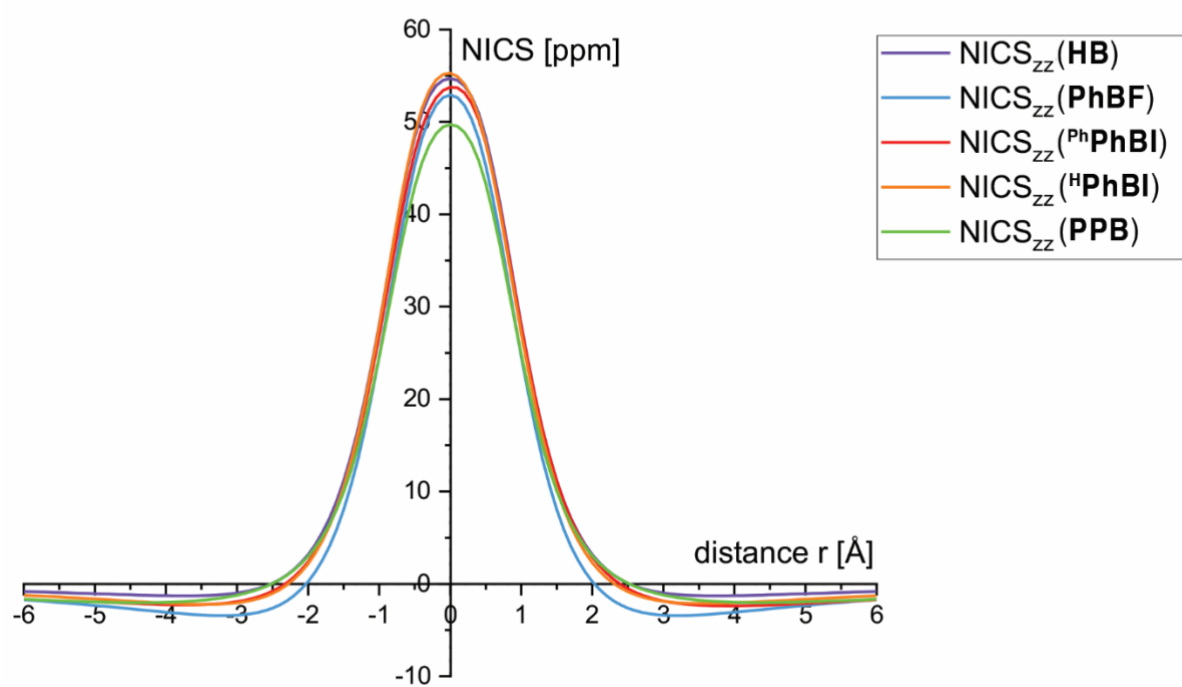


Figure S41: NICS_{zz} scans of **HB**, **PhBF**, **^{Ph}PhBI (1)**, **^HPhBI**, and **PPB** (PBE1PBE/6-311+G(d,p)/D3(BJ)).

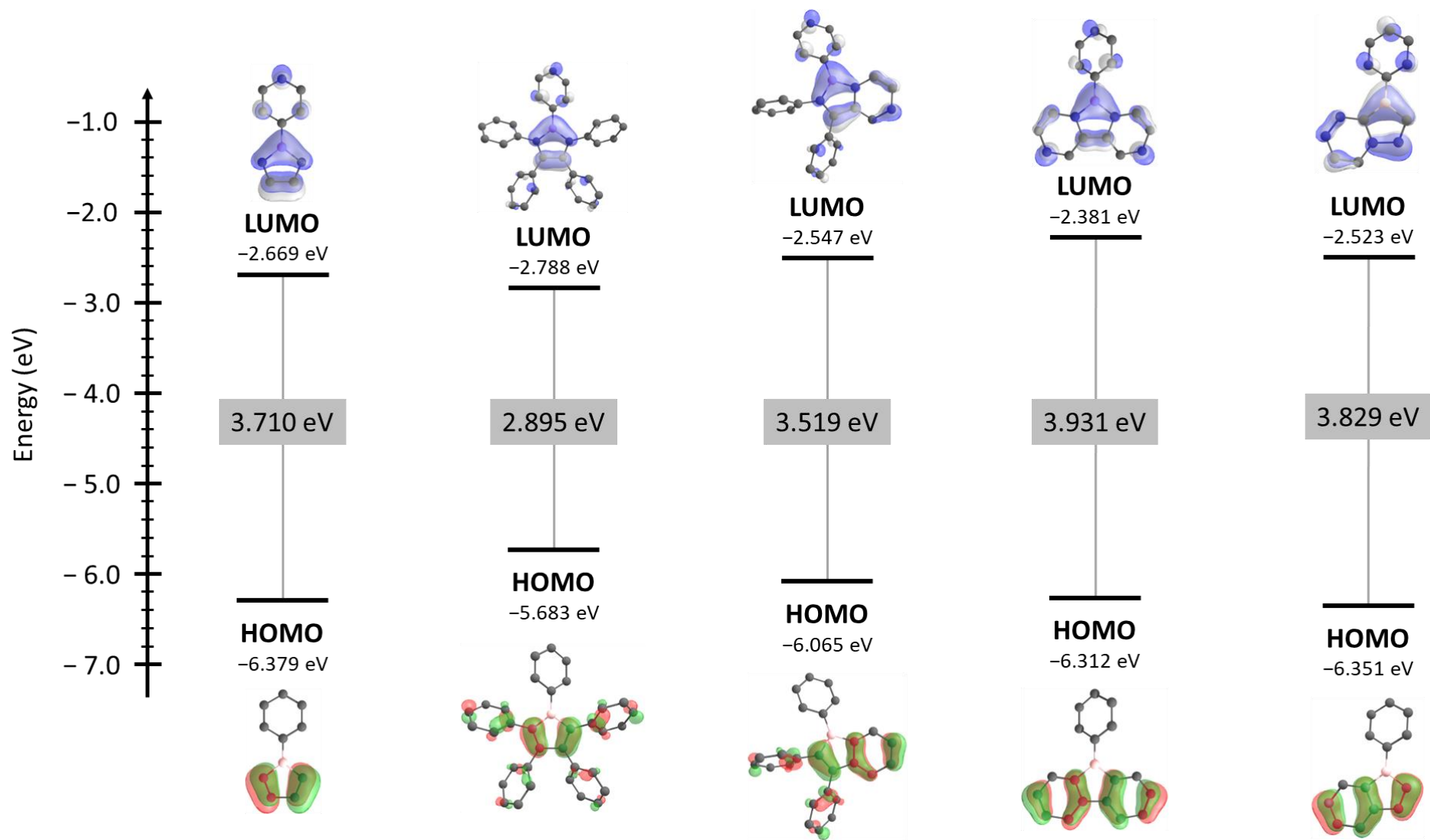
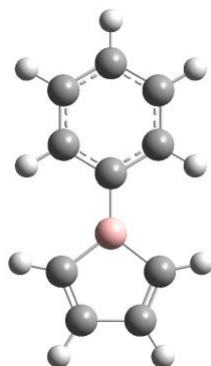


Figure S42: Calculated frontier molecular orbitals (isovalue 0.04 a.u.) of **HB**, **PPB**, **^{Ph}PhBI (1)**, **PhBF** and **^HPhBI** with their corresponding energetic level (PBE1PBE/ 6-311+G(d,p) /D3(BJ)/SCRF(SMF, solvent=benzene)).

Optimized structures (.xyz-files)

Compound **HB** @ PBE1PBE/6-311+G(d,p)/D3(BJ)

Energy + Zero-point correction = -410.742374 E_h



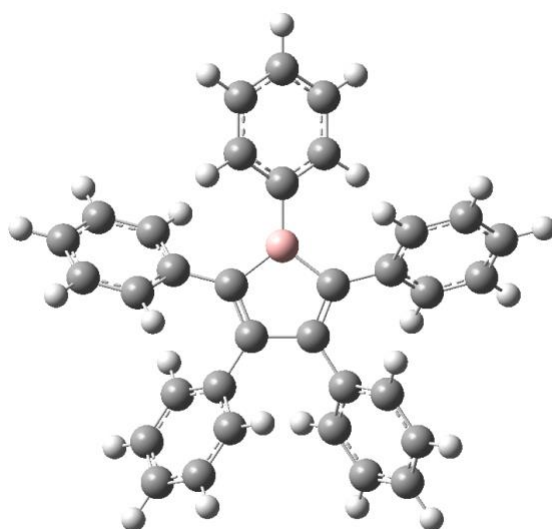
0 1

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C	3.26394400	-0.75126800	0.00012700
C	3.26393600	0.75127600	-0.00052400
C	2.01824200	1.24895600	0.00022700
H	1.80834900	-2.31242500	0.00262100
H	4.18699400	-1.32580400	0.00149500
H	4.18698000	1.32581900	-0.00244000
H	1.80832300	2.31242100	-0.00213700
B	1.04712300	-0.00000700	0.00026600
C	-0.49025500	-0.00000600	0.00012800
C	-1.21694900	1.20317000	0.00042200
C	-1.21695800	-1.20317500	-0.00030000
C	-2.60392500	1.20732400	0.00046700
H	-0.67858800	2.14571000	0.00071000
C	-2.60393200	-1.20732100	-0.00061100

H	-0.67860200	-2.14571900	-0.00048700
C	-3.29715800	0.00000400	-0.00014000
H	-3.14882600	2.14560900	0.00049500
H	-3.14883900	-2.14560200	-0.00073900
H	-4.38260000	0.00000800	-0.00024800

Compound **PPB** @ PBE1PBE/6-311+G(d,p)/D3(BJ)

Energy + Zero-point correction = -1333.825813E_h



0 1

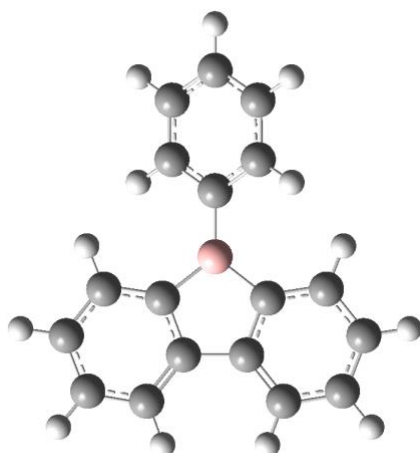
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C	-0.75940500	-0.87374400	-0.01136200
C	-1.25279200	0.38903200	-0.02108100
B	-0.00106400	1.35319000	-0.00030900
C	-0.00212300	2.89378800	0.00034600
C	1.02694200	3.62147700	-0.62408500
C	-1.03217100	3.61976800	0.62507700

C	1.01607700	5.00872000	-0.64265300
H	1.83938400	3.08928800	-1.10720500
C	-1.02314100	5.00701600	0.64442200
H	-1.84398100	3.08620800	1.10777200
C	-0.00397700	5.70285700	0.00110300
H	1.80964300	5.55141800	-1.14595200
H	-1.81744800	5.54838500	1.14798200
H	-0.00468200	6.78844900	0.00143300
C	-2.67424300	0.75546200	0.00326800
C	-3.55736300	0.20447000	0.93987600
C	-3.17570500	1.69270800	-0.90784000
C	-4.89590800	0.56966800	0.95652600
H	-3.18207900	-0.51544500	1.65947200
C	-4.51761900	2.05041900	-0.89778500
H	-2.50146200	2.13899100	-1.63166500
C	-5.38380100	1.49104600	0.03497400
H	-5.56239900	0.13340000	1.69369800
H	-4.88668400	2.77266800	-1.61894400
H	-6.43108800	1.77438000	0.04750600
C	-1.54348900	-2.11654900	-0.01120300
C	-1.28272700	-3.13266600	0.91458700
C	-2.57688000	-2.29868700	-0.93648900
C	-2.04805300	-4.29074300	0.92562100
H	-0.48044900	-3.00912000	1.63383000
C	-3.32852900	-3.46435400	-0.93555000
H	-2.78361700	-1.51568700	-1.65784500

C	-3.06976100	-4.46268900	-0.00146900
H	-1.83971900	-5.06504300	1.65657500
H	-4.12182600	-3.59323000	-1.66452300
H	-3.66089400	-5.37256800	0.00161300
C	1.54636600	-2.11426800	0.01135900
C	2.58044400	-2.29410100	0.93636200
C	1.28696200	-3.13141000	-0.91367100
C	3.33407400	-3.45846700	0.93583800
H	2.78610600	-1.51034200	1.65720200
C	2.05427400	-4.28819300	-0.92430400
H	0.48414800	-3.00973400	-1.63263200
C	3.07665800	-4.45782100	0.00245100
H	4.12787000	-3.58553400	1.66458500
H	1.84694000	-5.06329200	-1.65469500
H	3.66941000	-5.36664600	-0.00038700
C	2.67299800	0.75910200	-0.00420400
C	3.55652500	0.20995500	-0.94150700
C	3.17352800	1.69628100	0.90748500
C	4.89457500	0.57695600	-0.95835700
H	3.18193900	-0.50992300	-1.66149800
C	4.51496300	2.05578100	0.89722700
H	2.49894900	2.14108500	1.63190000
C	5.38155500	1.49829300	-0.03627800
H	5.56139300	0.14213400	-1.69608600
H	4.88335000	2.77793300	1.61883200
H	6.42845800	1.78304300	-0.04894200

Compound **PhBF** @ PBE1PBE/6-311+G(d,p)/D3(BJ)

Energy + Zero-point correction = -717.706089 E_h



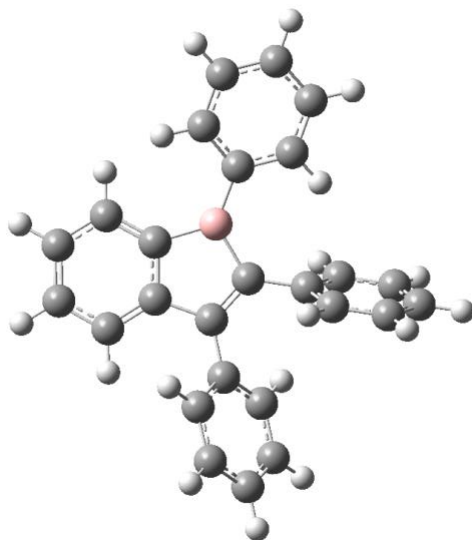
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C	-0.61646900	1.23210700	0.03829400
C	-1.94203200	0.73961600	0.02885100
C	-3.02458200	1.59980900	0.08352900
H	-3.63061900	3.66034800	0.19732100
H	-1.33077100	4.54676000	0.24743100
H	0.60368900	3.00076400	0.17149200
H	-4.04306600	1.22375200	0.07785300
C	-0.61648600	-1.23211800	-0.03822500
C	-0.40572300	-2.60226300	-0.12876500
C	-1.49398800	-3.47617300	-0.18055600
C	-2.78952200	-2.97552900	-0.15416300
C	-3.02460000	-1.59978600	-0.08361400
C	-1.94204200	-0.73960700	-0.02886700

H	0.60365800	-3.00079000	-0.17133200
H	-1.33081900	-4.54676400	-0.24736900
H	-3.63065600	-3.66031700	-0.19743000
H	-4.04308000	-1.22371700	-0.07801800
B	0.35077300	-0.00001600	0.00007800
C	1.89575700	-0.00001800	0.00005900
C	2.62333500	-1.00851700	0.65240900
C	2.62325400	1.00849900	-0.65235900
C	4.01140700	-1.00262400	0.66717200
H	2.08930000	-1.79479700	1.17704200
C	4.01132500	1.00263000	-0.66726300
H	2.08914800	1.79477400	-1.17692900
C	4.70774900	0.00000800	-0.00008100
H	4.55346400	-1.78250300	1.19234000
H	4.55331700	1.78251900	-1.19248300
H	5.79310600	0.00001600	-0.00013600

Compound **^{Ph}PhBI (1)** @ PBE1PBE/6-311+G(d,p)/D3(BJ)

Energy + Zero-point correction = -1025.765634 E_h



0 1

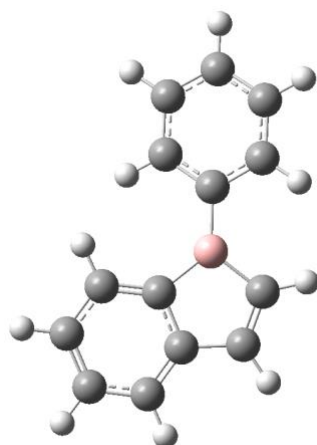
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C	0.55703000	4.48646900	-0.42608700
C	-0.82178200	4.50731100	-0.53171100
C	-1.55211900	3.31021900	-0.46233700
C	0.00641700	-0.20393400	-0.23227100
C	1.01708100	0.70468000	-0.11332100
H	2.32616500	3.26159200	-0.21105500
H	1.11808000	5.41360300	-0.48603600
H	-1.33967100	5.44970400	-0.67712100
H	-2.63115300	3.34347700	-0.57871400
B	-1.34592100	0.59693800	-0.19626400
C	-2.76969300	0.05418000	0.05850800

C	-3.11721800	-1.28866500	-0.17274700
C	-3.76980500	0.89969000	0.57206200
C	-4.40216900	-1.75424400	0.06704200
H	-2.36813500	-1.97744200	-0.54501900
C	-5.05087600	0.43554700	0.83260700
H	-3.52695000	1.93265800	0.79551900
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H	-4.64755000	-2.79318800	-0.12822200
H	-5.80122900	1.10577000	1.23949100
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C	0.69475200	-2.29301700	0.96058700
C	-0.03588200	-2.44843300	-1.32106100
C	0.90027400	-3.66652500	0.98739900
H	0.90224900	-1.69341300	1.84085000
C	0.17653900	-3.82120600	-1.29819500
H	-0.39780100	-1.96957600	-2.22647900
C	0.64385600	-4.43616200	-0.14161300
H	1.26466300	-4.13761500	1.89468300
H	-0.02315400	-4.41217200	-2.18642900
H	0.80691400	-5.50857800	-0.12079300
C	2.44415800	0.40326100	0.06609300
C	3.09124800	-0.53179400	-0.74795900
C	3.17738300	1.03858400	1.07449700
C	4.43494800	-0.82078100	-0.55954800
H	2.53242600	-1.02873900	-1.53250700

C	4.51750900	0.73499800	1.27280800
H	2.68249200	1.75588100	1.72110400
C	5.15153100	-0.19239800	0.45346000
H	4.92430100	-1.54327900	-1.20431400
H	5.06853300	1.22438100	2.06926100
H	6.20069000	-0.42457500	0.60375000

Compound ¹PhBI @ PBE1PBE/6-311+G(d,p)/D3(BJ)

Energy + Zero-point correction = -564.226549 E_h



0 1

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C	-3.62598900	0.40809000	0.07424500
C	-3.93485900	-0.95432400	-0.06351300
C	-2.92718400	-1.89173300	-0.19958300
C	-1.58073800	-1.49027300	-0.19003400
C	-0.39250400	2.16343600	0.10150900
C	-1.73894100	2.15452200	0.17229300

H	-4.42070000	1.14231500	0.16842800
H	-4.97269200	-1.27175000	-0.07053700
H	-3.17727100	-2.94105800	-0.31675500
H	-0.80934700	-2.24361200	-0.31704000
B	0.09159200	0.67538100	0.00791900
C	1.55465100	0.18671100	0.01263600
C	2.59780000	1.08675000	-0.26474200
C	1.90497500	-1.14420500	0.29520100
C	3.92313400	0.67659600	-0.28323600
H	2.35799600	2.12378000	-0.47848800
C	3.22906800	-1.55800600	0.29844100
H	1.12647200	-1.85928300	0.53758600
C	4.23959200	-0.64805800	0.00167400
H	4.71181700	1.38639000	-0.51071700
H	3.47821400	-2.58848700	0.53007300
H	5.27583500	-0.97122700	-0.00290500
H	0.18247300	3.08132900	0.16265200
H	-2.37807600	3.02773200	0.28354600

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