Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Reactions of Hydrazones and Hydrazides with Lewis Acidic Boranes

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1 Experimental

1.1 General experimental

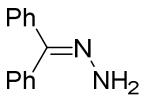
With the exception of the starting materials, all reactions and manipulations were carried out under an atmosphere of dry, O_2-free nitrogen using standard double-manifold techniques with a rotary oil pump. A nitrogen-filled glove box (MBraun) was used to manipulate solids including the storage of starting materials, room temperature reactions, product recovery and sample preparation for analysis. All solvents (toluene, pentane, DCM) were dried by employing a solvent purification system MB SPS-800 and stored under a nitrogen atmosphere. Benzene, THF and diethyl ether were distilled over sodium and stored over 4 Å molecular sieves under a nitrogen atmosphere. Deuterated solvents were distilled and/or dried over molecular sieves before use. Chemicals were purchased from commercial suppliers and used as received, including benzhydrazide from Sigma-Aldrich. ^{1}H, ^{13}C, ^{11}B and ^{19}F NMR spectra were recorded on a Bruker Avance II 400 or Bruker Avance 500 spectrometers. Chemical shifts are expressed as parts per million (ppm, δ) downfield of tetramethylsilane (TMS) and are referenced to $CDCl_3$ (7.26/77.16 ppm) as internal standards. NMR spectra were referenced to $CFCl_3$ (^{19}F), $BF_3{\cdot}Et_2O/CDCl_3$ (^{11}B). The description of signals includes s = singlet, d = doublet, t = triplet, m = multiplet and br. = broad. All coupling constants are absolute values and are expressed in Hertz (Hz). ^{13}C NMR was measured as ^{1}H decoupled. Yields are given as isolated yields.

1.2 Synthesis of starting materials

General Procedure **A**:[1]

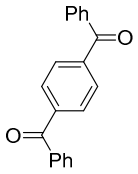
The ketone was added to a stirred solution of excess hydrazine monohydrate in ethanol (20 mL). Acetic acid (0.2 mL) was added drop wise to the same reaction mixture. The reaction mixture was heated at reflux for 12 hrs. The resultant solid filtered washed with water followed by pentane to afford the desired product.

*Synthesis of (diphenylmethylene)hydrazone (**1a**)*



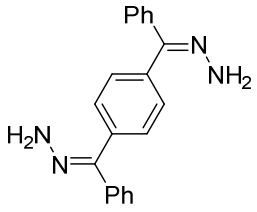
1a was synthesised according to general procedure **A** using benzophenone (5 g, 27.4 mmol, 1 equiv.) and hydrazine monohydrate (4.8 mL, 156.0 mmol, 4 equiv.). The title compound was isolated as white crystalline solid (4.46 g, 22.7 mmol, 83%). The spectral data shows good agreement with the literature reported values.[2] **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 7.33 – 7.30 (m, 2H), 7.26 – 7.23 (m, 3H), 7.09 – 7.04 (m, 5H), 5.21 (s, 2H, NH_2); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 149.3, 138.5, 133.1, 129.5, 129.0, 128.9, 128.26, 128.23,126.5; **HRMS** (ES+) m/z calculated for $[C_{13}H_{13}N_2]^+$ $[M+H]^+$: 197.1073, found: 197.1080.

Synthesis of 1,4-phenylenebis(phenylmethanone)



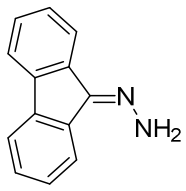
Terrephthaloyl chloride (4.00 g, 19.7 mmol, 1 equiv.) in 25 mL of dry benzene was added slowly to the stirred solution of $AlCl_3$ (3.15 g., 23.6 mmol, 1.2 equiv.) in dry benzene (20 mL) and the reaction mixture was brought to reflux for 2 hrs. The reaction mixture was extracted using DCM, washed with $NaHCO_3$, brine, dried over magnesium sulphate and concentrated using vacuum. The title compound was isolated as a white powder (2.26 g, 12.4 mmol, 63%). The spectral data shows good agreement with the literature reported values.[3] **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 7.89 (s, 4H), 7.85 – 7.84 (m, 4H), 7.65 – 7.62 (m, 2H), 7.53 – 7.50 (m, 4H).

*Synthesis of 1,4-bis-hydrazoneylidene(phenyl)methyl)benzene (**1b**)*



Synthesised according to General Procedure **A** using 1,3-phenylene - bis(phenylmethanone) (1.2 g, 4.2 mmol, 1 equiv.) and hydrazine monohydrate (1 mL, 20.9 mmol, 5 equiv.) The title compound (**1b**) was isolated as a pale-yellow powder (1.15 g, 3.6 mmol, 87%). **^{1}H NMR** (500 MHz, DMSO-d_6, 298 K) δ/ppm: 7.56 – 7.53 (m, 4H), 7.47 – 7.44 (m, 2H), 7.23 – 7.19 (m, 8H), 6.23 (s, 4H, NH_2); **^{13}C{^{1}H} NMR** (126 MHz, DMSO-d_6, 298 K) δ/ppm: 144.7, 138.1, 133.5, 129.9, 129.1, 129.0, 125.6; **HRMS** (ES+) m/z calculated for $[C_{20}H_{19}N_4]^+$ $[M+H]^+$: 315.1604, found: 315.1614.

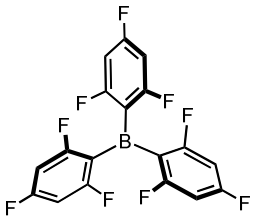
*Synthesis of (9H-fluoren-9-ylidene)hydrazone(**1c**)*



1c was synthesised according to General Procedure **A** using 9H-fluoren-9-one (2.5 g, 13.8 mmol, 1 equiv.) and hydrazine monohydrate (4 mL, 82.4 mmol, 5 equiv.) The title compound (**1c**) was isolated as yellow crystals (2.44 g, 12.5 mmol, 91%). The spectral data shows good agreement with the literature reported values.[4] **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 7.80 (d, $^3J_{HH}$ = 10 Hz, 1H), 7.67 – 7.63 (m, 2H), 7.56 – 7.54 (m, 1H), 7.33 (t, $^3J_{HH}$ = 10 Hz, 1H), 7.26 – 7.15 (m, 3H), 6.30 (s, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 145.6, 141.4, 138.6, 137.8, 130.3, 129.8, 128.6, 128.0, 127.8, 125.6, 120.8, 120.6, 119.6; **HRMS** (ES+) m/z calculated for $[C_{13}H_{11}N_2]^+$ $[M+H]^+$: 195.0917, found: 195.0918.

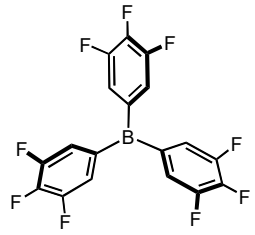
1.3 Synthesis of boranes

Synthesis of tris(2,4,6-trifluorophenyl)borane



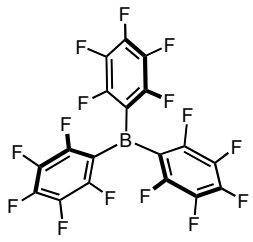
Synthesised according to a literature procedure.[5] 1-bromo-2,4,6-trifluorobenzene (3.5 mL, 30 mmol, 3 equiv.) was dissolved in freshly distilled THF (100 mL) and cooled to -20 °C. ^{i}PrMgCl (2.0 M in THF), (15 mL, 30 mmol, 3 equiv.) was added portion wise. The reaction was allowed to warm up for an hour, until the temperature reached 0 °C. Upon cooling to -50 °C, $BF_3 \cdot Et_2O$ (1.23 mL, 10 mmol, 1 equiv.) was added. The reaction was left for 1 hr at -50 °C, whereupon it was allowed to warm up to room temperature. Removal of all volatiles, followed by a two-fold sublimation (120 °C, 1 x 10^{-3} mbar) of the crude product generated tris(2,4,6-trifluorophenyl)borane as a white solid (3.35 g, 8.3 mmol, 83%). The spectroscopic data agrees with literature established values.[5] **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 6.64 (dd,$^{3}J_{HF}$ = 8 Hz,14 Hz, 6H); **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ/ppm: -95.74 (d, $^{3}J_{FH}$ = 9 Hz, 6F), - 100.30 (t, $^{3}J_{FH}$ = 14 Hz, 9F); **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) δ/ppm: -59.6 (br., s).

Synthesis of tris(3,4,5-trifluorophenyl)borane



Mg turnings (3.05 g, 12 mmol.) were suspended in Et_2O and cooled to 0 °C. 1,2-dibromoethane (0.1 mL, 1.1 mmol, 9 equiv.) and 1-bromo-3,4,5-fluorobenzene (15 mL, 0.1 mmol, 1 equiv.) were added drop wise with vigorous stirring. After addition, the reaction mixture was allowed to warm to room temperature and was stirred until all the magnesium turnings were consumed. The solution was then cooled to 0 °C and added drop wise to a solution of $BF_3.Et_2O$ (5.2 mL, 0.04 mmol, 3 equiv.) in Et_2O, also at 0 °C. The solution was allowed to warm to room temperature and stirred for a further hour. All volatiles were removed *in vacuo*, and sublimation of the resultant solid (120 °C, 1 x 10^{-3} mbar) resulted in oily yellow crystals. These yellow crystals were washed with pentane (3 x 5 mL), and sublimed again (120 °C, 1 x 10^{-3} mbar) to afford pure tris(3,4,5-trifluorophenyl)borane as white crystals (2.03 g, 5.02 mmol, 11.9%). The spectroscopic data agrees with literature established values.[6] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.20 – 7.13 (m, 6H); **^{19}F NMR** (376 MHz, $CDCl_3$,298 K) δ/ppm: -133.18 (d,$^{3}J_{FF}$ = 25 Hz,6F), -152.38 (t, $^{3}J_{FF}$ = 25 Hz, 3F); **^{11}B NMR**(128 MHz, $CDCl_3$, 298 K) δ/ppm: 65.9 (br., s).

Synthesis of tris(pentafluorophenyl)borane



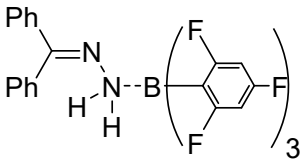
Tris(pentafluorophenyl)borane was synthesised using a literature procedure.[7] Magnesium turnings (1.1 g, 45 mmol, 1 equiv.) were suspended in Et_2O (100 mL). C_6F_5Br (5.6 mL, 45 mmol, 3 equiv.) was added drop wise over the course of half an hour under vigorous stirring, without allowing the mixture to reach reflux. The mixture was allowed to stir for half an hour at room temperature, whereby the mixture was transferred *via* filter cannula to a stirred solution of $BF_3{\cdot}OEt_2$ (1.9 mL, 15 mmol, 1 equiv.) in toluene (150 mL). The Et_2O solvent was removed *in vacuo* leaving the mixture as a toluene solution. The reaction was then heated to 100 °C for 1 hr then left to cool to ambient temperature. The remaining solvent was removed under reduced pressure whilst gently heating in an oil bath until a white brown cake remains. This was then subjected to a two-fold sublimation (110 °C, 1 x 10^{-3} mbar) that yielded pure $B(C_6F_5)_3$ as a white microcrystalline solid (6.7 g, 13.2 mmol, 88%). The spectroscopic data agrees with literature established values.[7] **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ/ppm: - 127.87 (br., s, 6F), -142.68 (br., s, 3F), -159.99 (br., s, 6F); **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) δ/ppm: 58.6 (br., s).

1.4 Synthesis of products

General Procedure **B***:*

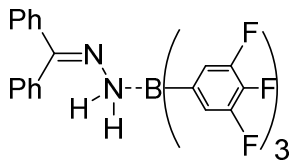
In a Schlenk tube equipped with a magnetic stirring bar, the hydrazone **1** (1 equiv.) was dissolved in toluene and the borane (1 equiv.) was added portion wise to the same reaction tube. The resultant solution was allowed to stir for 10 hrs at room temperature. Subsequently all volatiles were removed *in vacuo*. The desired product was obtained by recrystallisation.

*Synthesis of compound **2a***



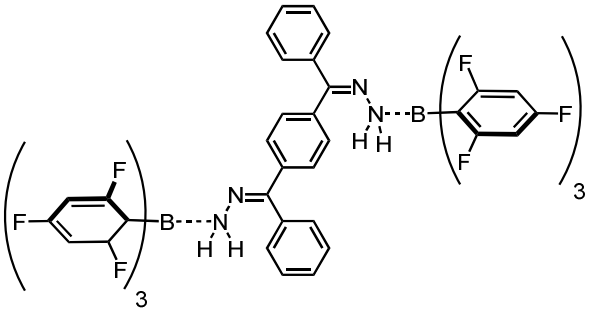
Synthesised according to General Procedure **B** using tris (2,4,6-trifluorophenyl) borane (200 mg, 0.5 mmol, 1 equiv.) and (diphenylmethylene)hydrazone (**1a**) (100 mg, 0.5 mmol, 1 equiv.) in toluene (10 mL). Recrystallisation from a DCM/Pentane mixture afforded desired compound (**2a**) as white crystals (187 mg, 0.3 mmol, 61%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 7.58 – 7.52 (m, 5H), 7.45 – 7.42 (m, 1H), 7.35 – 7.28 (m, 4H), 6.93 (d, $^{3}J_{HH}$ = 10 Hz, 2H), 6.48 – 6.45 (t,$^{3}J_{HH}$ = 10 Hz, 6H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 172.8, 165.1 (m), 162.1 (m), 135.3, 132.1, 131.3, 129.9, 129.2, 128.6, 128.0, 99.5 (m), carbon atom attached to boron could not be observed; **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ/ppm -112.79 (s, 2F), -99.92 (s, 4F); **^{11}B NMR** (160 MHz, 298 K, $CDCl_3$) δ/ppm: -6.1 (br., s); **HRMS** (ES+) m/z calculated for $[C_{13}H_{13}N_2]^+$ [M – $B(C_6F_3H_2)_3]^+$: 197.1073 found: 197.1091; **EA** expected C 62.03, H 3.02, N 4.67: obtained C 60.91, H 2.28, N 4.59.

*Synthesis of compound **2b***



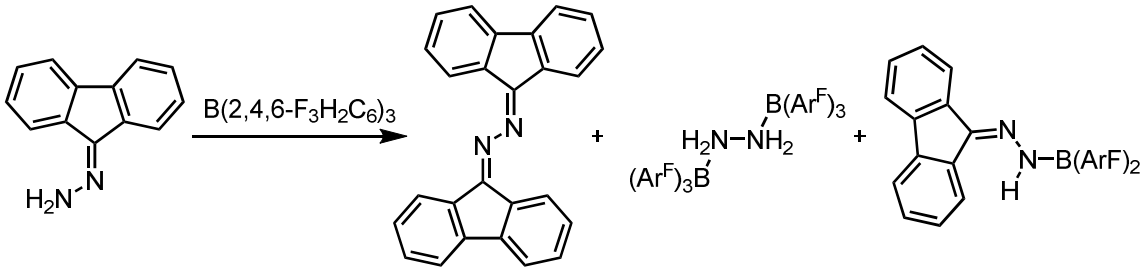
Synthesised according to General Procedure **B** using tris(3,4,5-trifluorophenyl) borane (200 mg, 0.5 mmol, 1 equiv.) and (diphenylmethylene)hydrazone (**1a**) (100 mg, 0.5 mmol, 1 equiv.) in toluene (10 mL). The desired compound (**2b**) was yielded as white crystals (195 mg, 0.3 mmol, 65%) following recrystallisation from a DCM/Pentane. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 7.69 – 7.67 (m, 1H), 7.61 – 7.58 (m, 2H), 7.54 – 7.51 (m, 1H), 7.46 – 7.38 (m, 4H), 6.78 – 6.75 (m, 4H), 6.62 – 6.59 (m, 6H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 151.0 (m), 138.6 (m), 134.4, 132.7, 131.7, 130.4, 129.6, 129.0, 129.0, 127.7, 117.2 (m), carbon atom attached to boron could not be observed; **^{19}F NMR** (471 MHz, $CDCl_3$, 296 K) δ/ppm: -135.66 (dd, $^{3}J_{FF}$ = 19 Hz, $^{3}J_{FH}$= 9.0 Hz, 6F), -163.24 (m, 3F); **^{11}B NMR** (160 MHz, 298 K, $CDCl_3$) δ/ppm: δ -2.6 (br., s); **EA** expected C 62.03, H 3.02, N 4.67: obtained C 61.92, H 2.95, N 4.63.

*Synthesis of compound **2c***



Synthesised according to General Procedure **B** using tris(2,4,6-trifluoro-phenyl) borane (50 mg, 0.2 mmol, 2 equiv.) and 1,4-bis-hydrazoneylidene (phenyl) methylbenzene (**1b**) (20 mg, 0.1 mmol, 1 equiv.) in toluene (5 mL). Recrystallisation from a DCM/Pentane mixture gave the desired compound (**2c**) as white crystals (36 mg, 0.2 mmol, 56%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 7.59 – 7.51 (m,10H), 7.27 – 7.26 (m, 4H), 6.86 (d,$^{3}J_{HH}$= 5 Hz, 4H), 6.46 – 6.42 (m, 12H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 171.7 (m), 165.5 (m), 162.1 (m), 138.3, 131.6, 130.1, 129.1, 127.9, 127.9, 127.7, 99.6 (m); **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ/ppm: -99.90 (s, 12F). -112.54 (s, 6F); **^{11}B NMR** (160 MHz, $CDCl_3$,298 K) δ/ppm: -6.2 (br., s).

*Reaction of **1c** with tris(2,4,6-trifluorophenyl)borane (synthesis of **3**,**4** and**5**)*



1c **3** **4** **5**

Synthesised according to General Procedure **B** using tris(2,4,6-trifluorophenyl)borane (40 mg, 0.1 mmol, 1 equiv.) and (9H-fluoren-9-ylidene)hydrazone (**1c**) (20 mg, 0.1 mmol, 1 equiv.) in toluene (5 mL) at room temperature. Recrystallisation of the reaction mixture from a DCM/Pentane mixture gives an inseparable mixture of **3**, **4** and **5** (32 mg, 0.1 mmol, 72%).

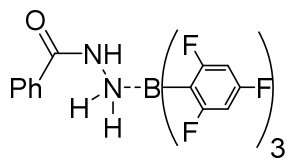
*Characterisation of **3***[8]

Synthesised according to General Procedure **B** using tris(2,4,6-trifluorophenyl) borane (40 mg, 0.1 mmol, 1 equiv.) and (9H-fluoren-9-ylidene) hydrazone (**1c**) (20 mg, 0.1 mmol, 1 equiv.) in toluene (5 mL). Recrystallisation of the reaction mixture from a DCM/Pentane mixture afforded **3** (32 mg, 0.1 mmol, 72%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 8.15 – 8.05 (m, 4H), 7.67 – 7.65 (m, 4H), 7.49 – 7.39 (m, 6H), 7.24 – 7.23 (m, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 154.7, 142.1, 141.1, 136.4, 131.3, 131.2, 130.8, 129.7, 128.2, 128.1, 122.8, 120.0, 119.9; **HRMS** (ES+) m/z calculated for $[C_{26}H_{18}N_2]$ + [M+H] +: 357.1396, found: 357.1392.

*Independent synthesis and characterisation of **5***

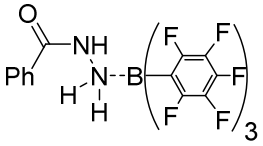
In a microwave vial equipped with a magnetic stirring bar, tris(2,4,6-trifluorophenyl) borane (50 mg, 0.1 mmol, 1 equiv.) was dissolved in toluene (5 mL) and (9H-fluoren-9-ylidene) hydrazone (**1c**) (24 mg, 0.1 mmol, 1 equiv.) was added portion wise to the same reaction vial. The resultant solution was cooled to 0 °C and allowed to stir for 12 hrs. Subsequently all volatiles were removed in vacuo. The desired product was obtained by recrystallisation from a DCM/pentane mixture (21 mg, 0.1 mmol, 46%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 8.07 (s, 1H), 7.67 – 7.64 (m, 4H), 7.55 – 7.50 (m, 2H), 7.44 – 7.31 (m, 2H), 7.25 – 7.21 (m, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 166.7, 164.3, 144.1, 140.4, 135.3, 133.6, 132.6, 129.0, 128.9, 128.5, 126.0, 123.7, 121.4, 119.9, 99.5 (m), carbon atom attached to boron could not be observed; **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ/ppm: -99.90 (s, 4F). -112.54 (s, 2F); **^{11}B NMR** (160 MHz, $CDCl_3$, 298 K) δ/ppm: -4.2 (br., s). **HRMS** (ES+) m/z calculated for $[C_{25}H_{14}BF_6N_2]$+ [M+H]+: 467.1149, found: 467.1142.

*Synthesis of compound **6a***



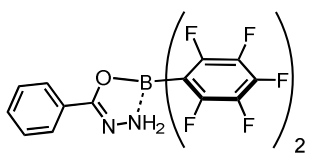
Synthesised according to General Procedure **B** using tris(2,4,6-trifluorophenyl) borane (30 mg, 0.2 mmol, 1 equiv.) and benzhydrazide (80 mg, 0.2 mmol, 1 equiv.) in toluene (10 mL). Recrystallisation from a DCM/Pentane mixture afforded the desired compound (**6a**) as white crystals (76 mg, 0.1 mmol, 56%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 7.74 – 7.70 (m, 3H), 7.60 – 7.57 (m, 1H), 7.52 – 7.51 (m, 2H), 7.46 – 7.42 (m, 2H), 6.55 – 6.52 (m, 6H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 166.9, 165.7 (m), 162.7 (m) 133.8, 129.3, 129.2, 127.1, 100.8 (m), carbon attached to boron cannot be observed; **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ/ppm: -105.32 (s, 6F), -110.68 (m, 3F); **^{11}B NMR** (160 MHz, $CDCl_3$,298 K) δ/ppm:-6.1 (br., s).

Synthesis of compound ***6b***



Synthesised according to General Procedure **B** using tris(pentafluorophenyl)borane (50 mg, 0.1 mmol, 1 equiv.) and benzhydrazide (13 mg, 0.1 mmol, 1 equiv.) in toluene (8 mL) to afford the desired compound (**6b**) as white crystals (45 mg, 0.1 mmol, 71%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.97 (br. s, 2H, NH_2), 7.68 – 7.64 (m, 2H), 7.55 – 7.47 (m, 4H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 166.9, 149.1 (m), 146.7 (m),138.6 (m), 134.4, 129.4, 128.0, 127.0; carbon attached to boron cannot be observed; **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ/ppm: -135.60 (dd, $^{3}J_{FF}$ = 20.1, 6.6 Hz, 6F), -153.98 (t, $^{3}J_{FF}$ = 20.3 Hz, 3 F), -161.64 (m, 6F).; **^{11}B NMR** (128 MHz, 298 K, $CDCl_3$): δ/ppm: -6.2 (br. s).

*Synthesis of compound **7***



Synthesised according to General Procedure **B** using tris(pentafluorophenyl)borane (108 mg, 0.2 mmol, 1 equiv.) and benzhydrazide (30 mg, 0.2 mmol, 1 equiv.) in toluene (5 mL).The desired compound (**7**) was yielded as pink crystal (97 mg, 0.2 mmol, 82%) following recrystallisation from a DCM/Pentane. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.04 – 8.01 (m, 2H), 7.61 – 7.56 (m, 1H), 7.49 – 7.45 (m, 2H), 7.14 (br., s, 2H, NH_2); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$, 298 K) δ/ppm: 173.1, 147.5 (m), 141.0 (m), 137.3 (m), 133.0, 128.6, 128.5, 125.9, carbon attached to boron cannot be observed; **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ/ppm: -135.6 (dd, $^{3}J_{FF}$ = 19 Hz, 4F), -153.98 (t,$^{3}J_{FF}$ = 18 Hz, 2F), -161.64 (m, 4F); **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) δ/ppm: δ -4.3 (br., s); HRMS (ES+) m/z calculated for $[C_{19}H_8BF_{10}N_2O]^+$ [M +H]$^+$: 480.0606, found: 480.0609.

2 NMR spectra

2.1 NMR of starting materials

Figure S1 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of (diphenylmethylene)hydrazone (**1a**).

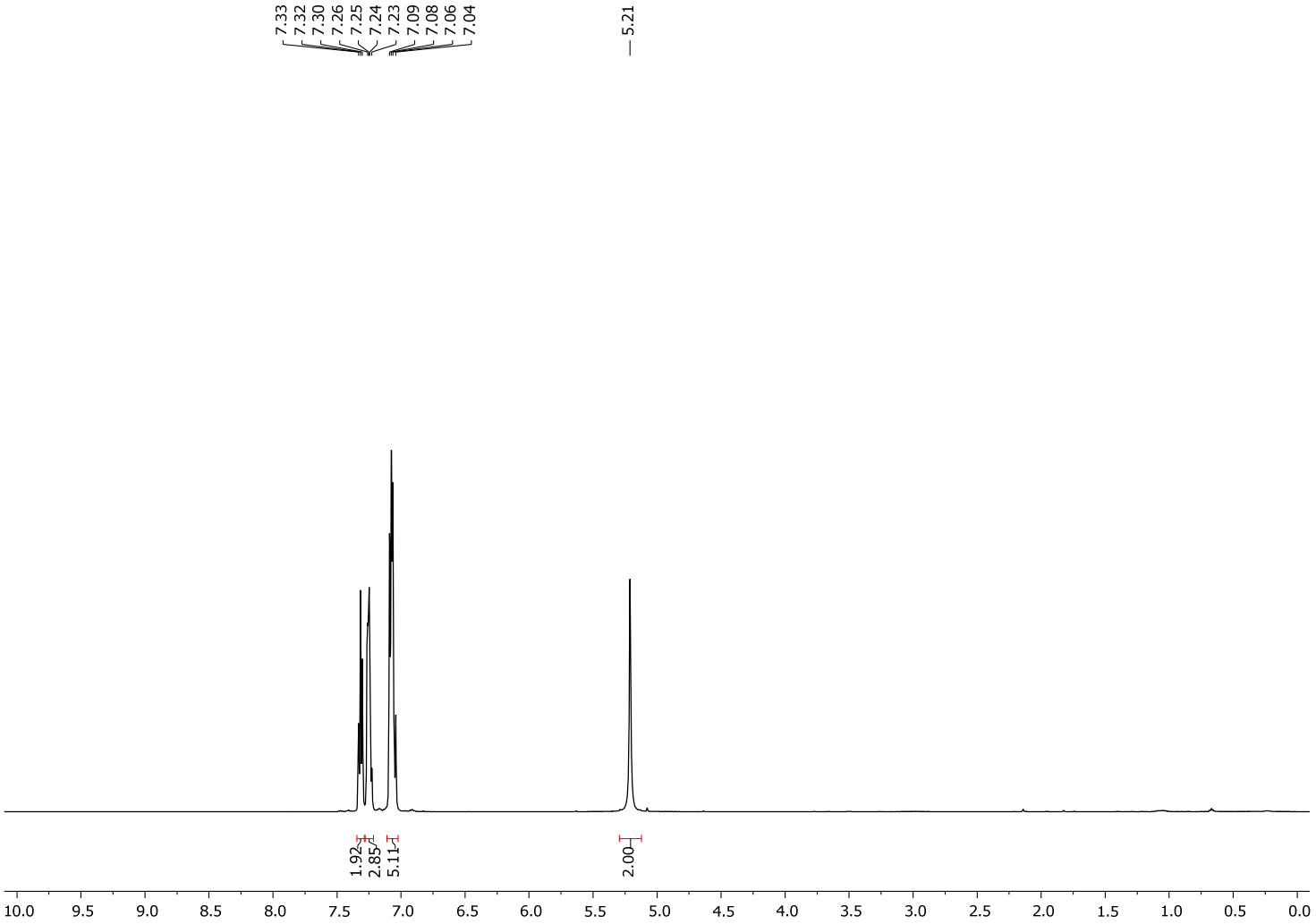


Figure S2 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of (diphenylmethylene)hydrazone (**1a**).

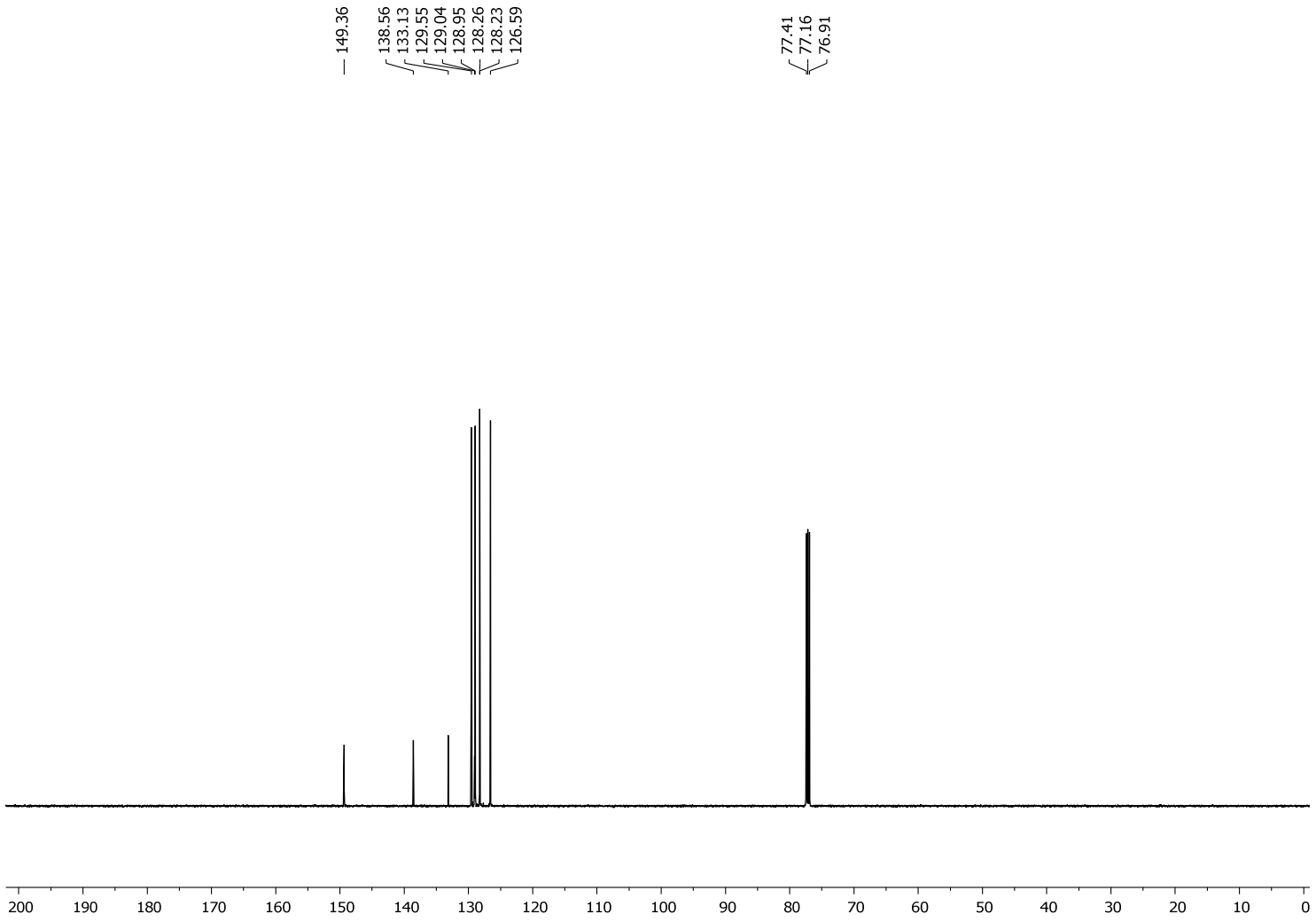


Figure S3 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of 1,4-phenylene bis(phenylmethanone).

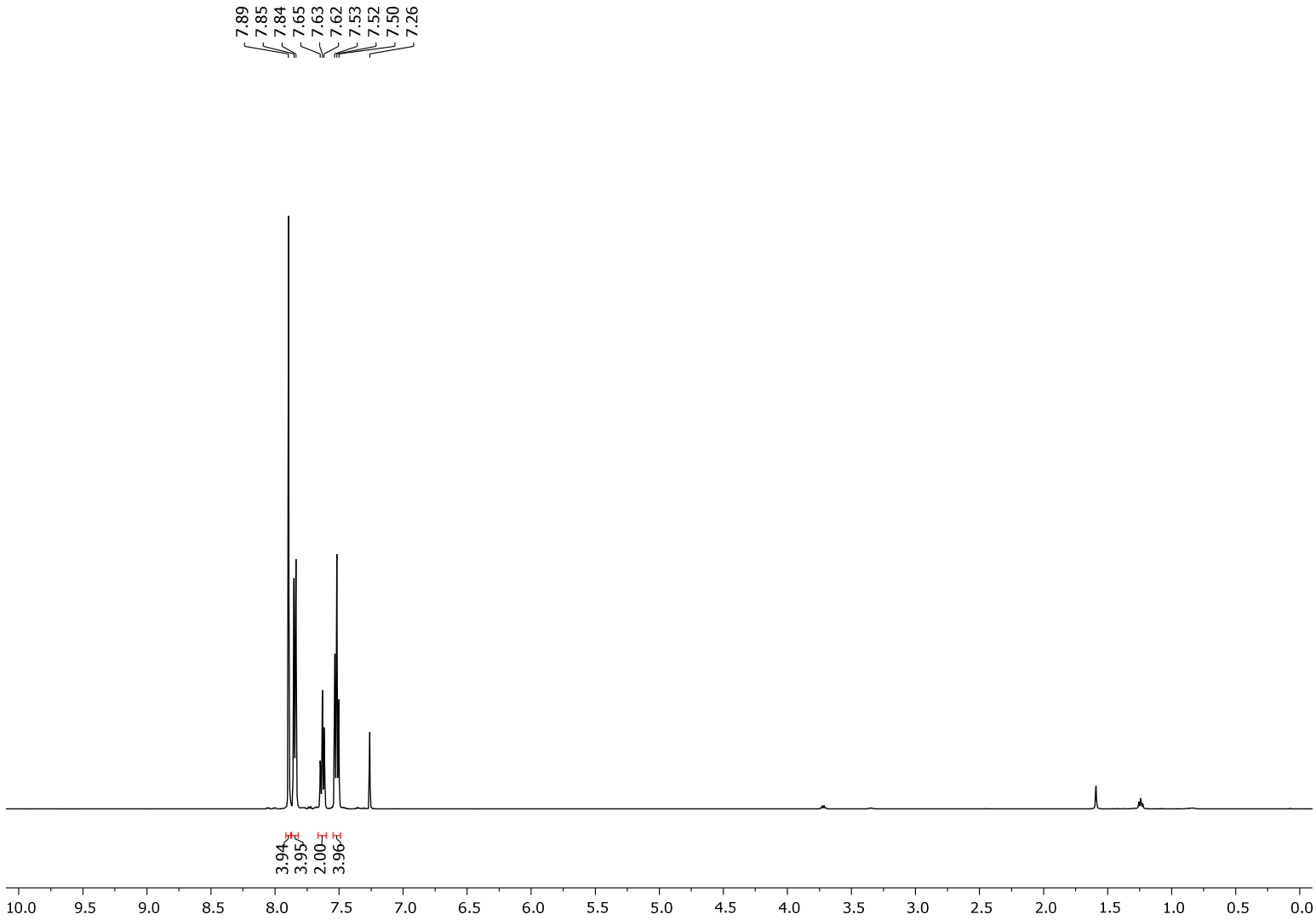


Figure S4 ^{1}H NMR (500 MHz, DMSO-d_6, 298 K) spectrum of 1,4-bis-hydrazoneylidene(phenyl)methyl)benzene (**1b**).

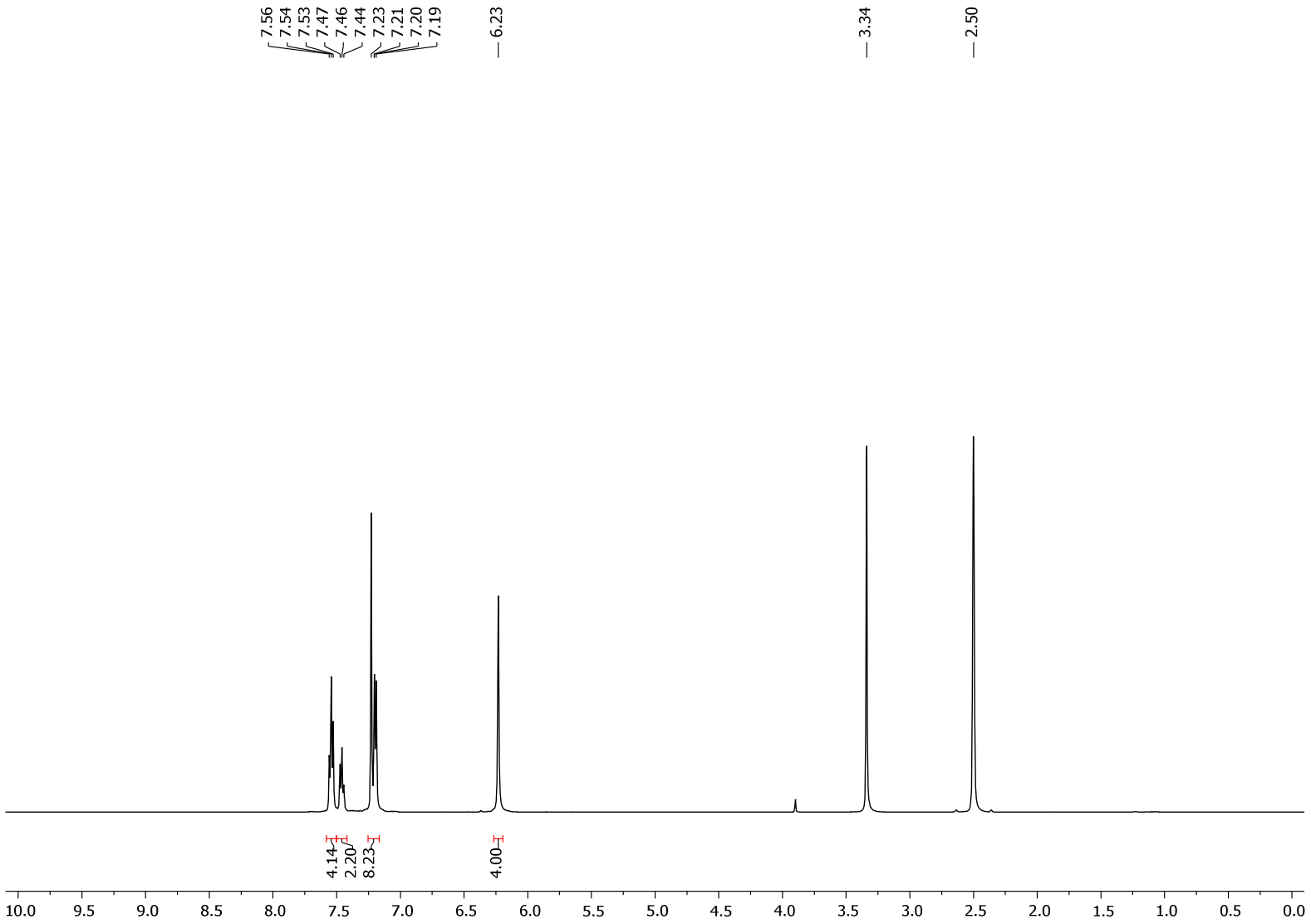


Figure S5 $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6, 298 K) spectrum of 1,4-bis-hydrazoneylidene(phenyl)methyl)benzene (**1b**).

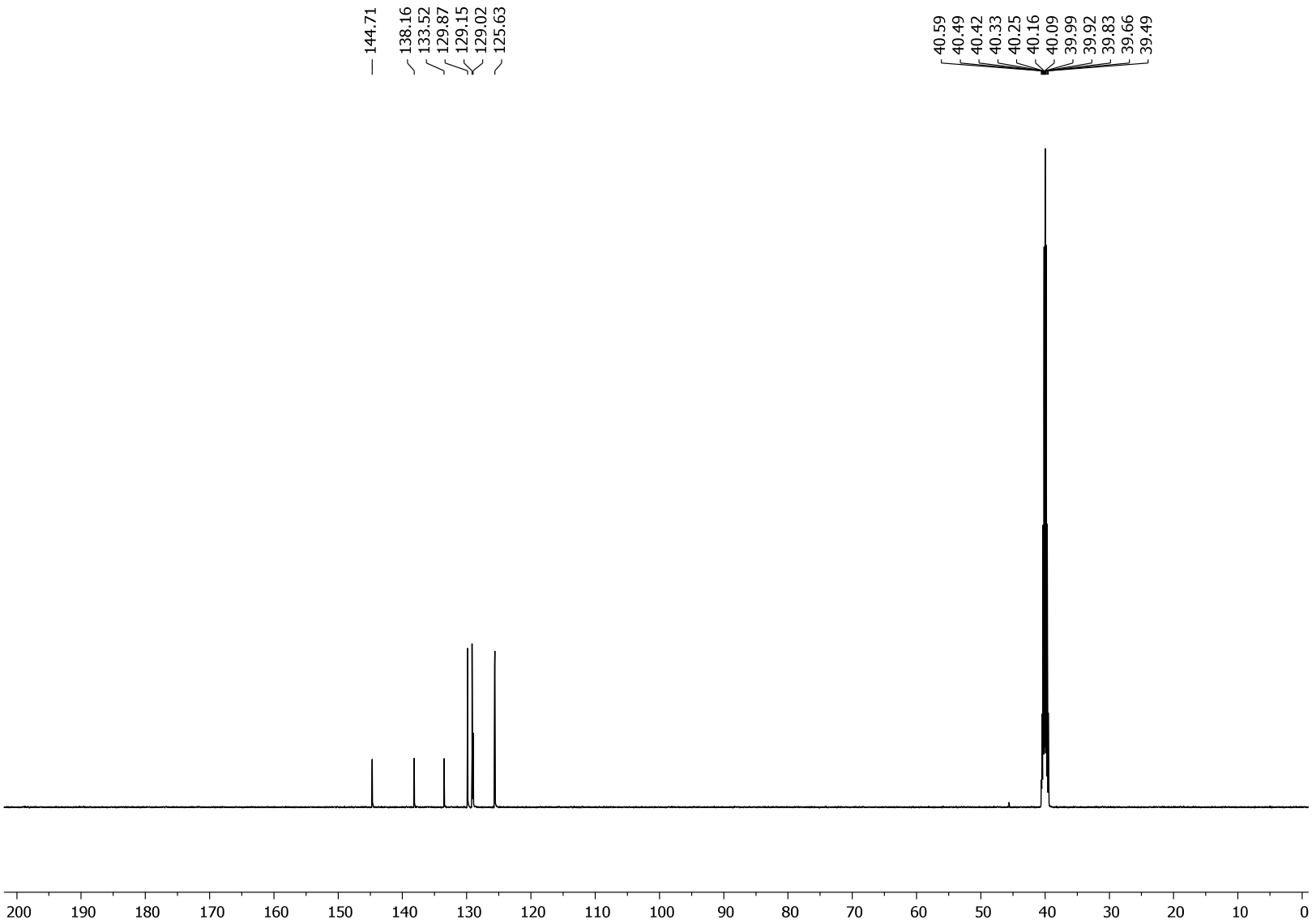


Figure S6 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of (9H-fluoren-9-ylidene)hydrazone (**1c**).

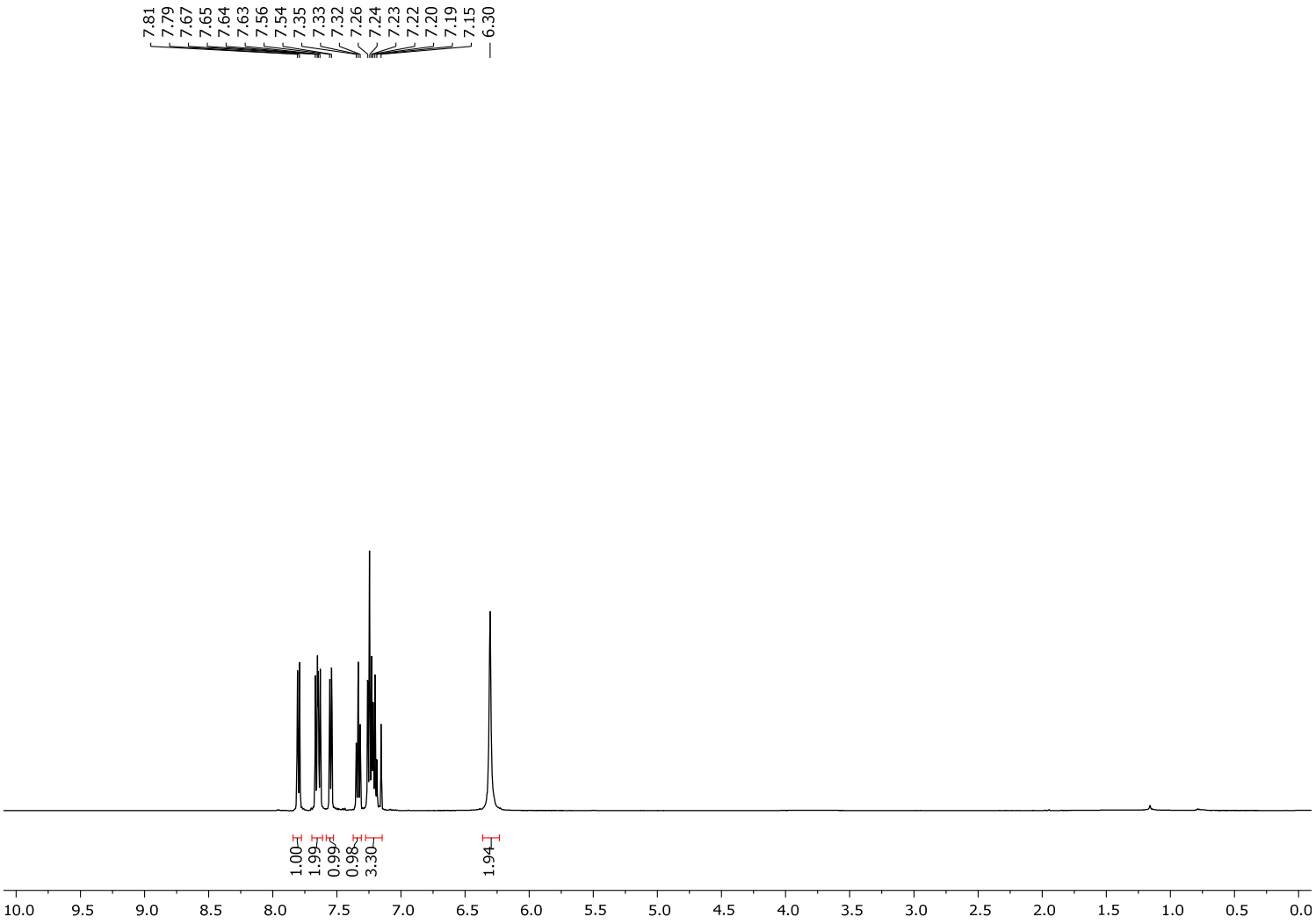
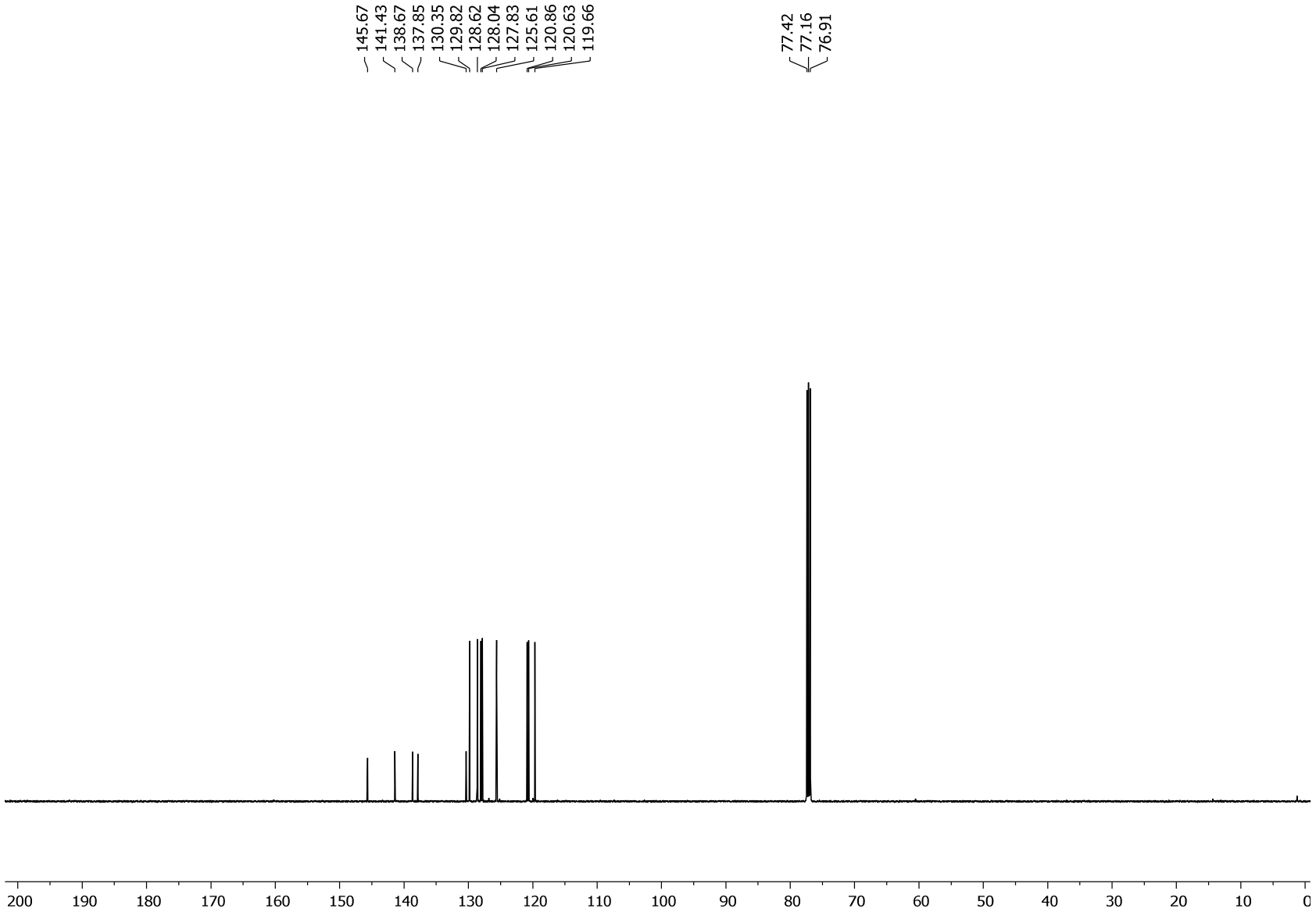


Figure S7 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of (9H-fluoren-9-ylidene)hydrazone (**1c**).



2.2 NMR of triarylfluoroboranes

Figure S8 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of tris(2,4,6-trifluorophenyl)borane.

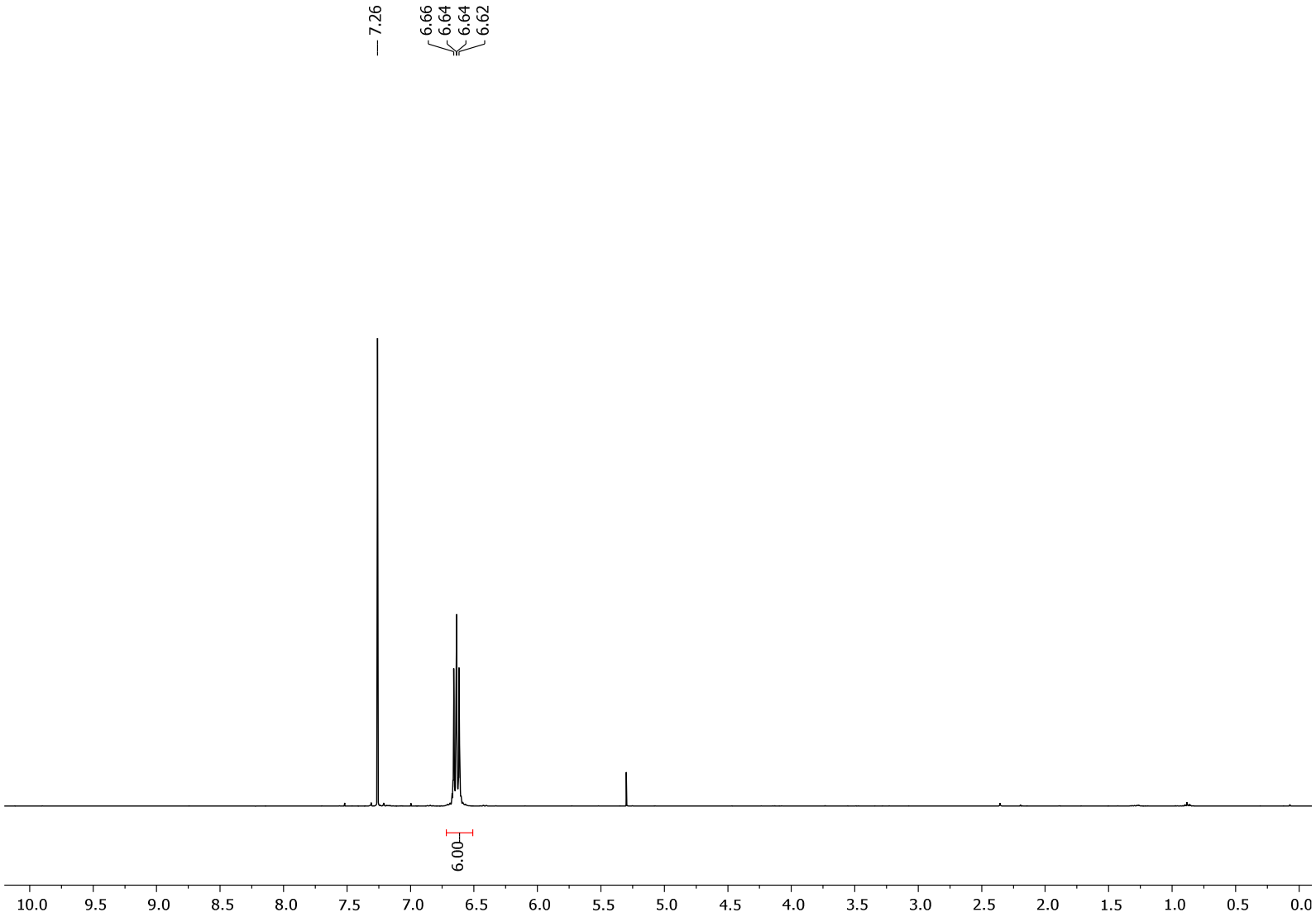


Figure S9 ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) spectrum of tris(2,4,6-trifluorophenyl)borane.

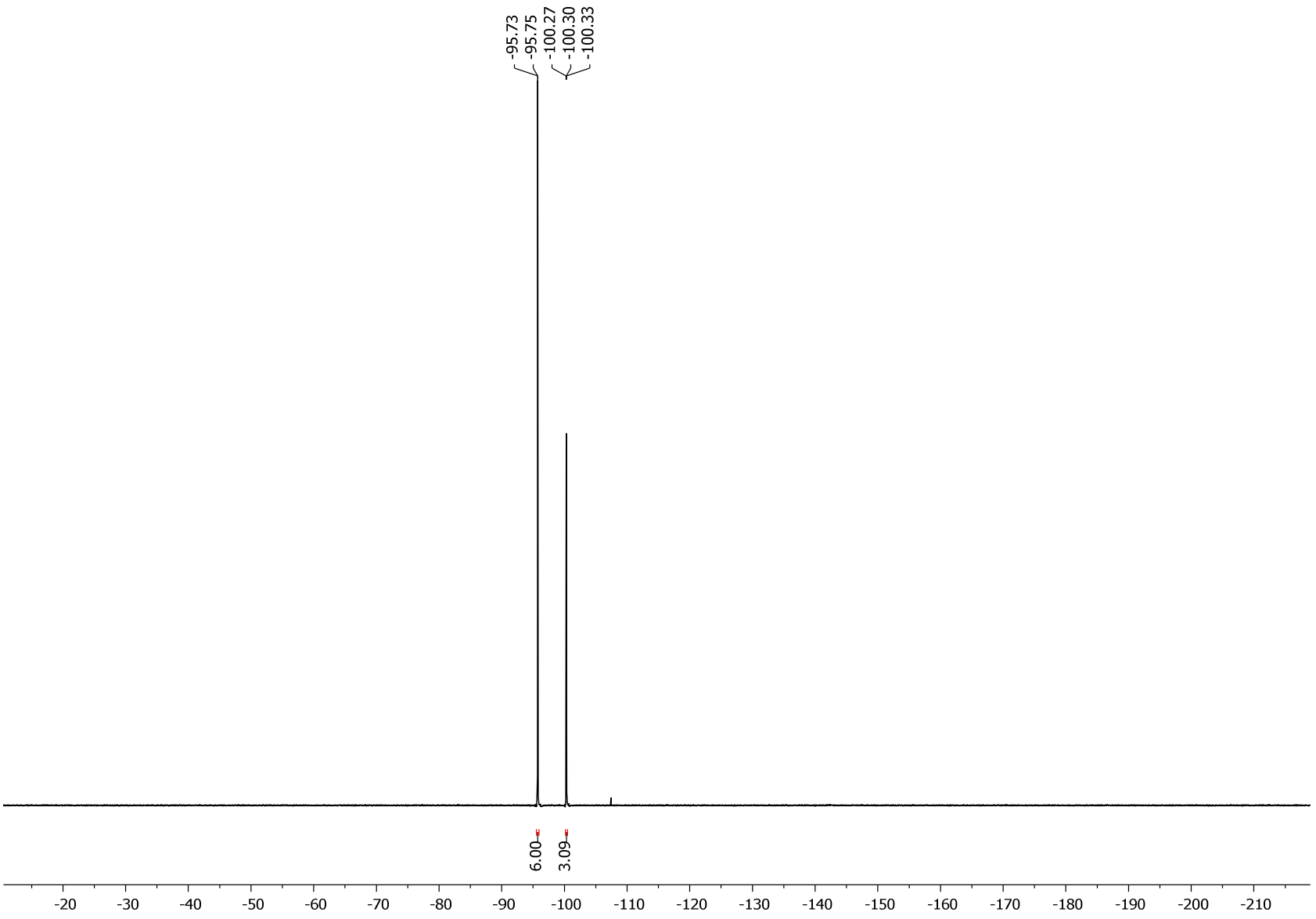


Figure S10 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of tris(2,4,6-trifluorophenyl)borane.

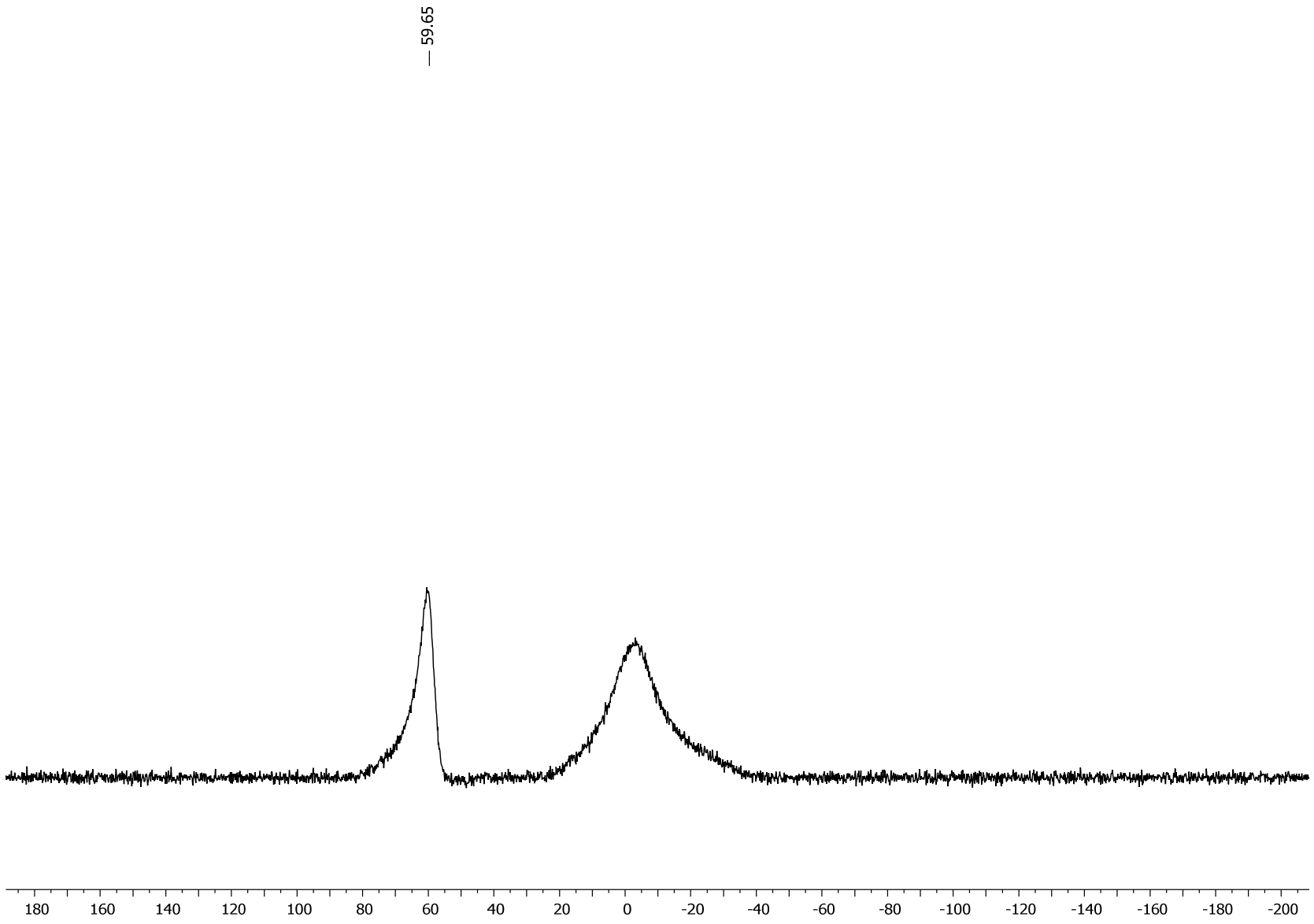


Figure S11 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of tris(3,4,5-trifluorophenyl)borane.

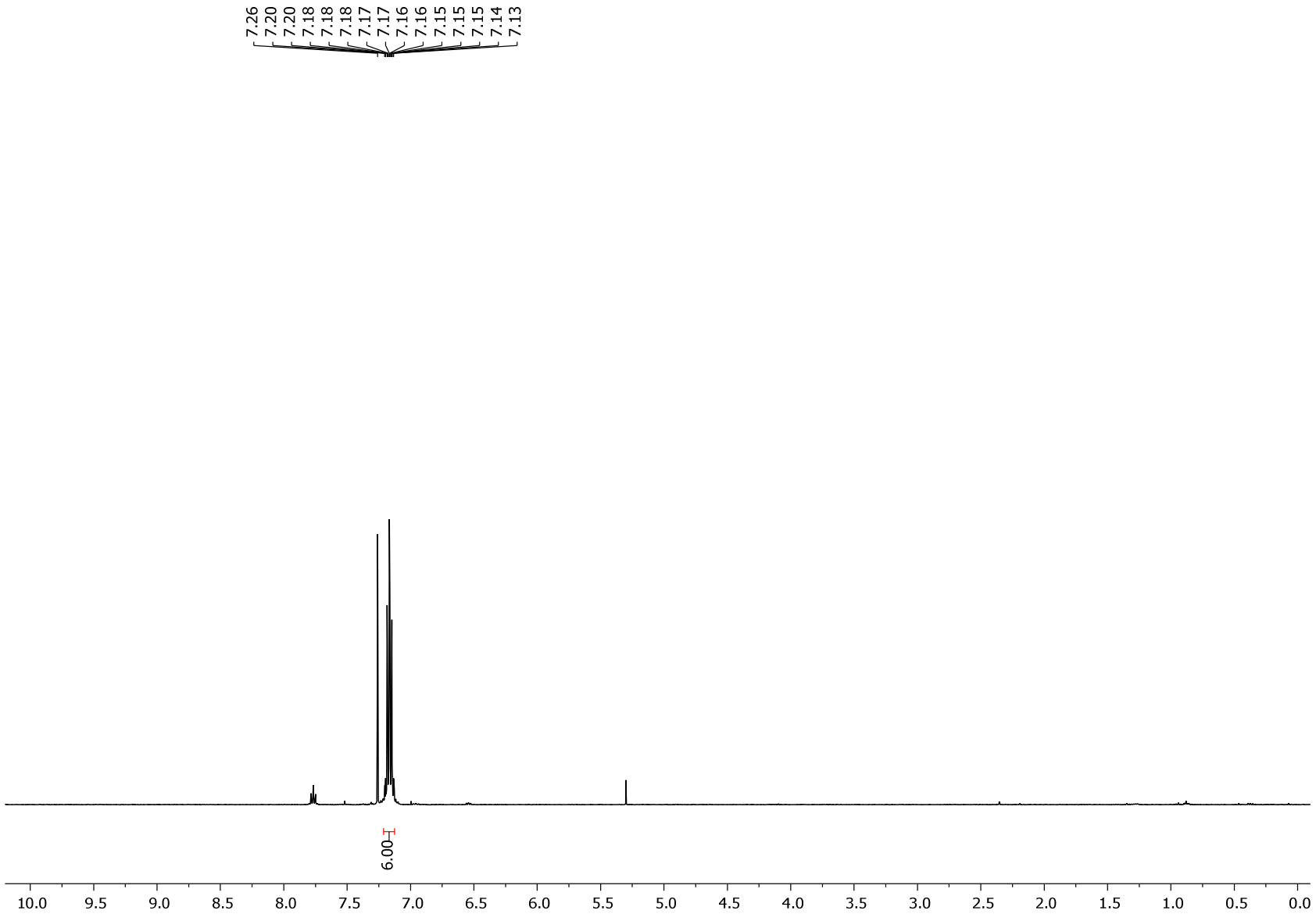


Figure S12 ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) spectrum of tris(3,4,5-trifluorophenyl)borane.

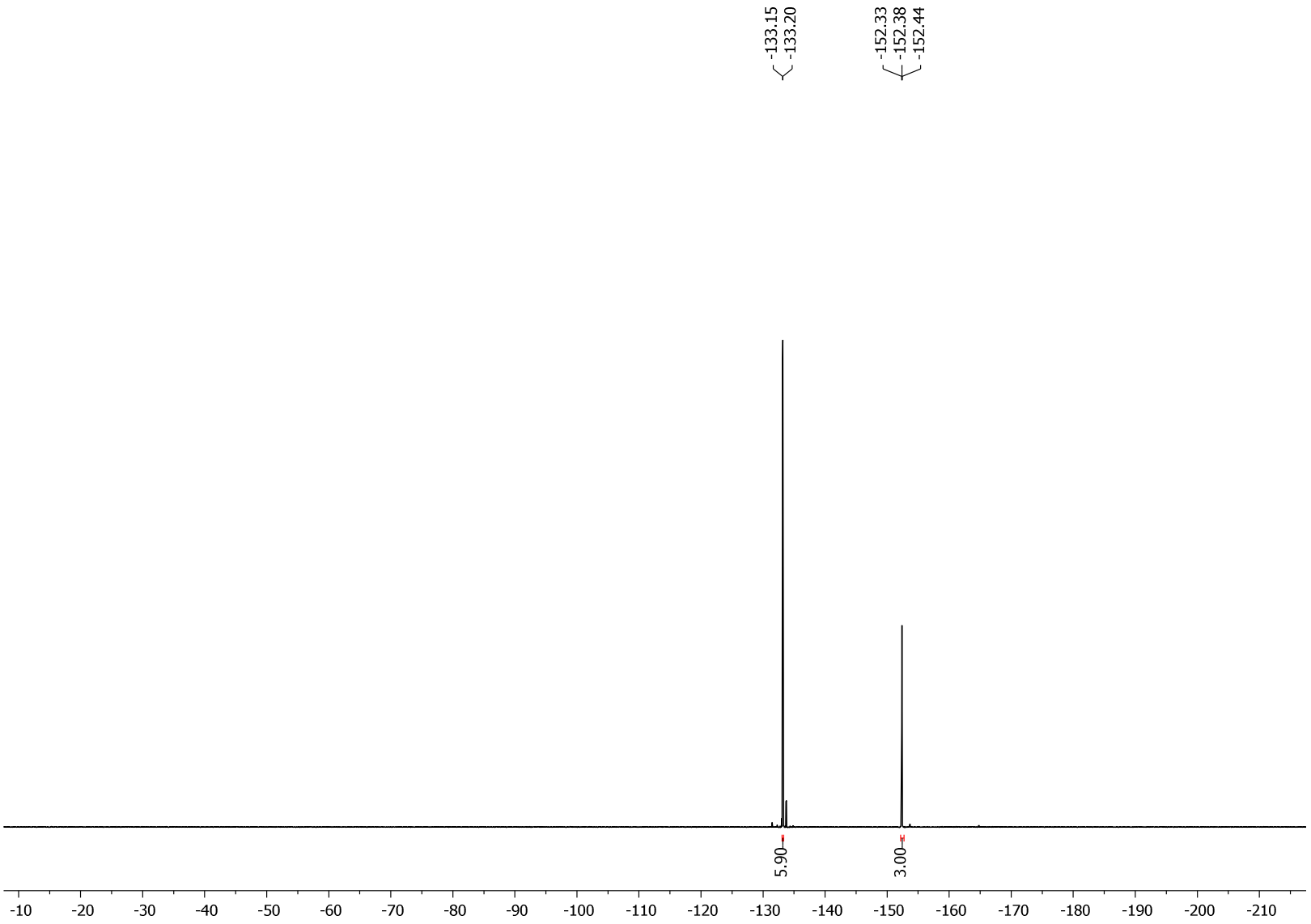


Figure S13 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of tris(3,4,5-trifluorophenyl)borane.

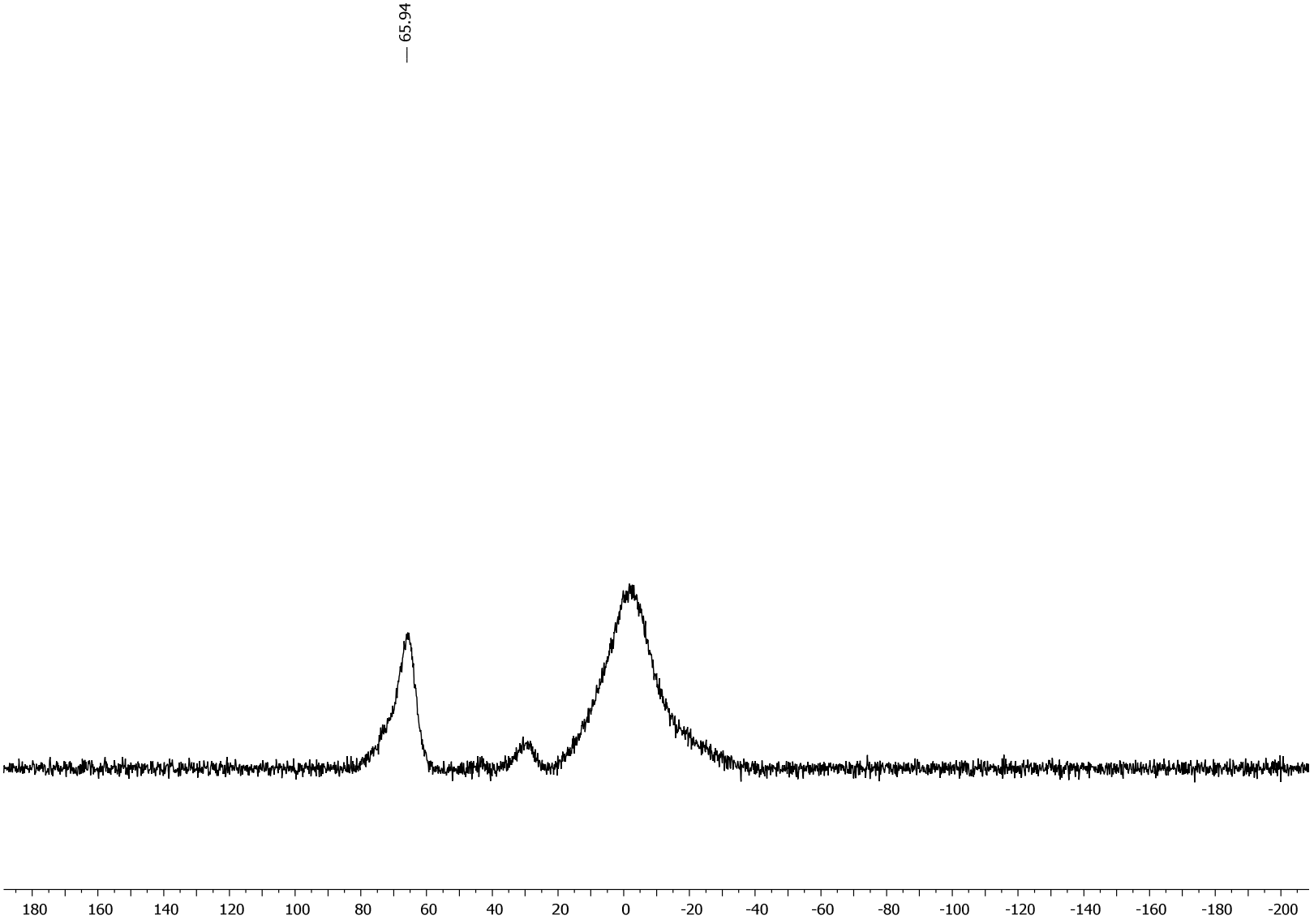


Figure S14 ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) spectrum of tris(pentafluophenyl)borane.

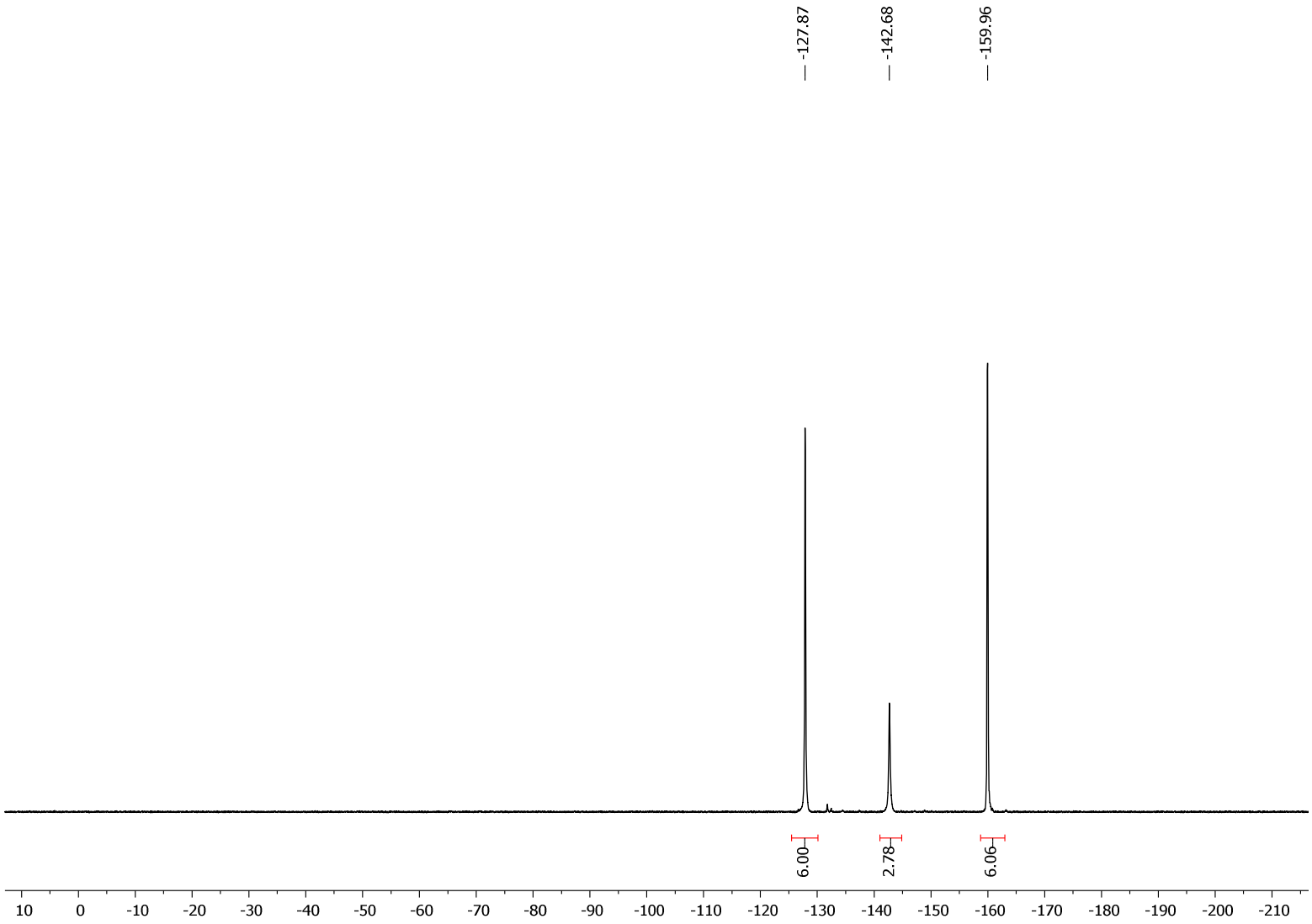
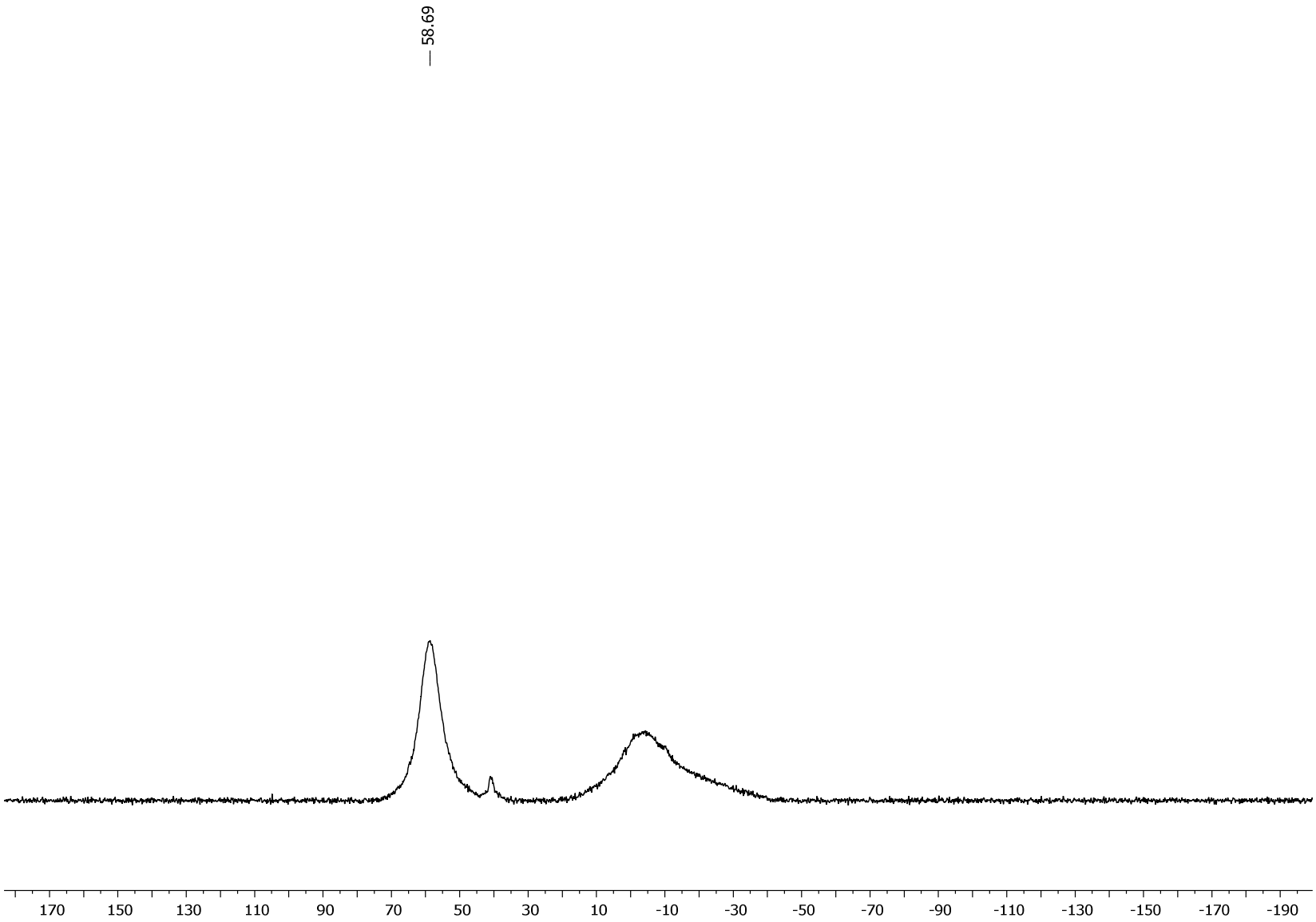


Figure S15 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum oftris(pentafluophenyl)borane.



2.3 NMR of products

Figure S16 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of **2a**.

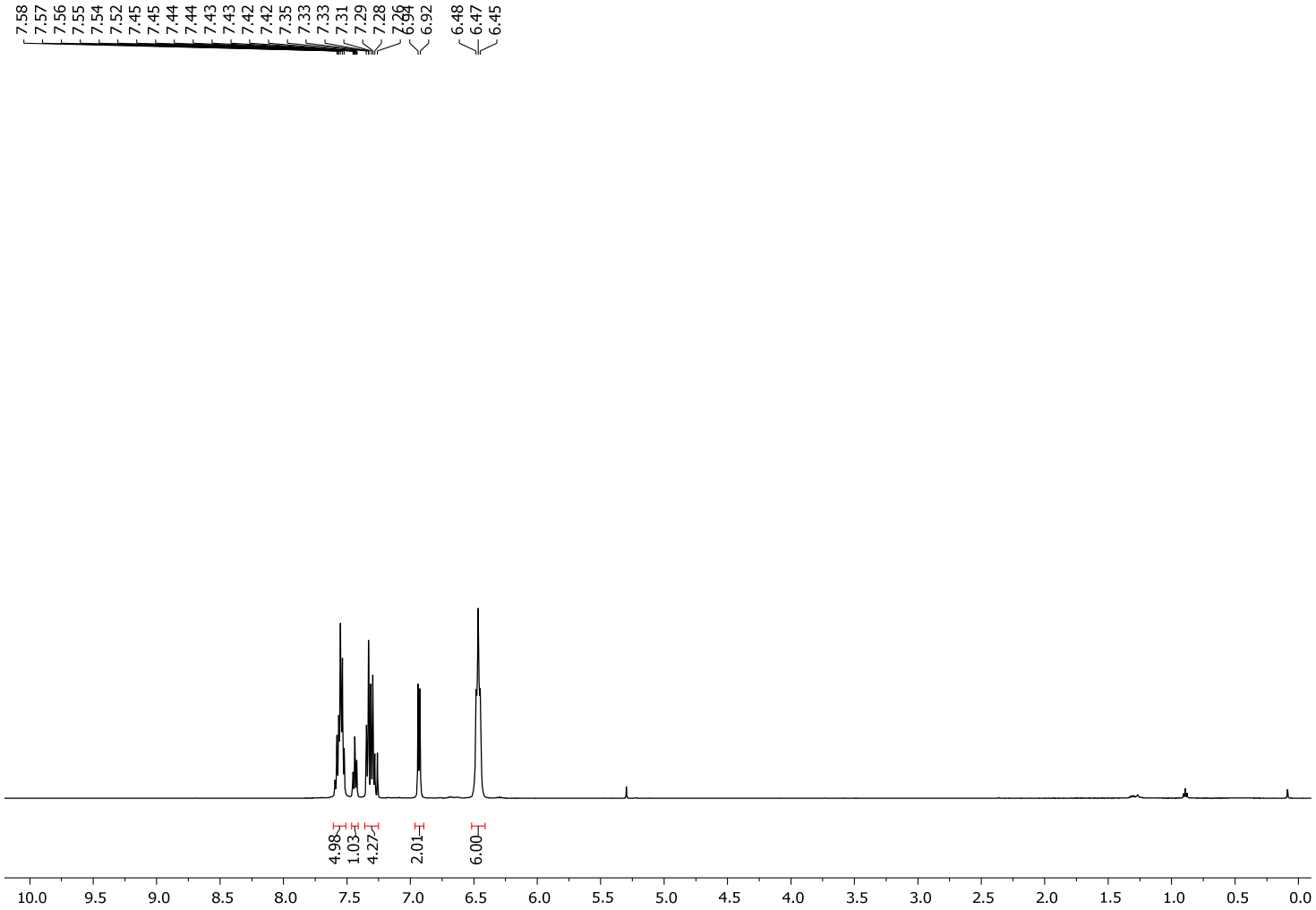


Figure S17 $^{13}C\{^{1}H\}$NMR (126 MHz, $CDCl_3$, 298 K) spectrum of **2a**.

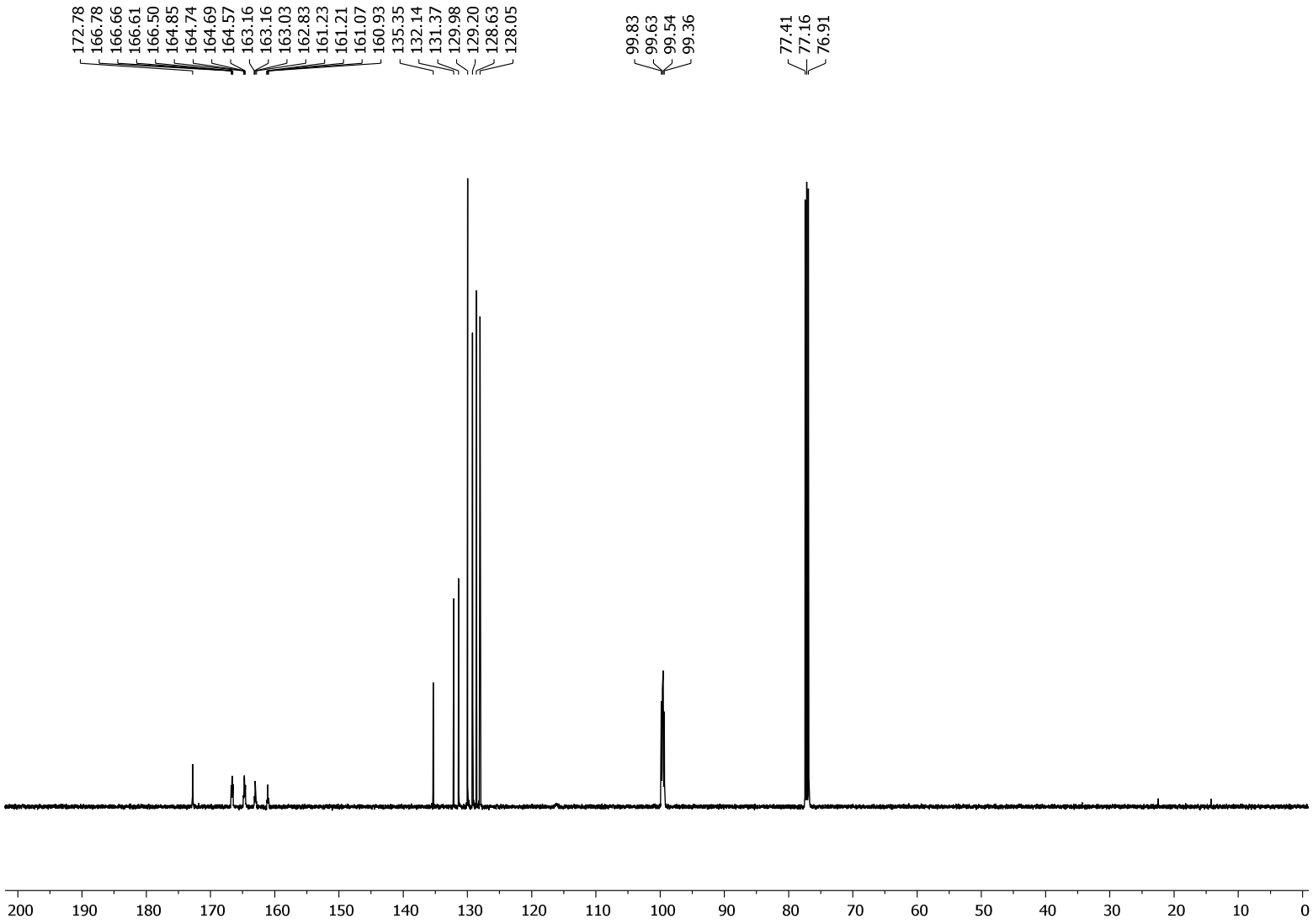


Figure S18 ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) spectrum of **2a**.

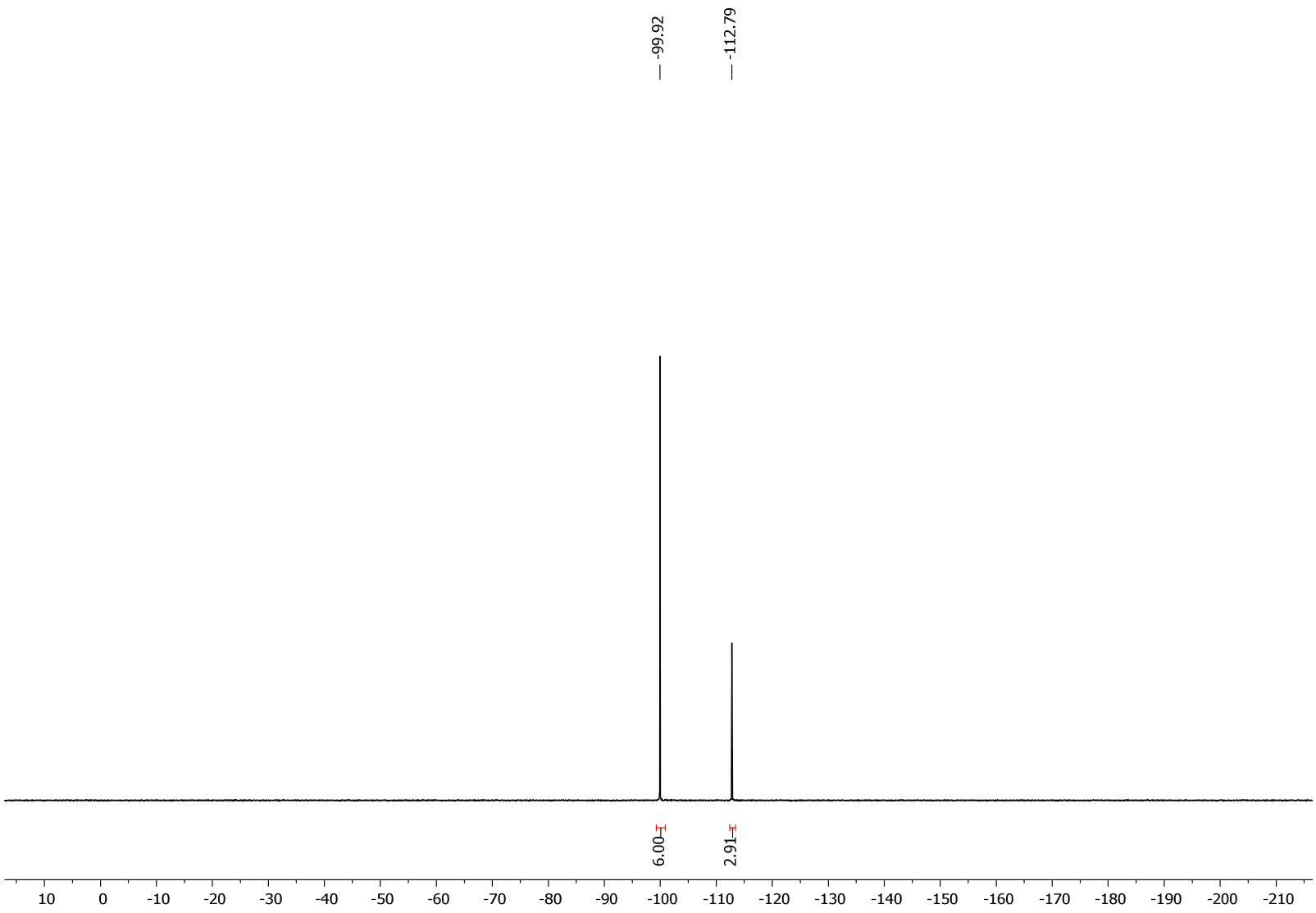


Figure S19 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of **2a**.

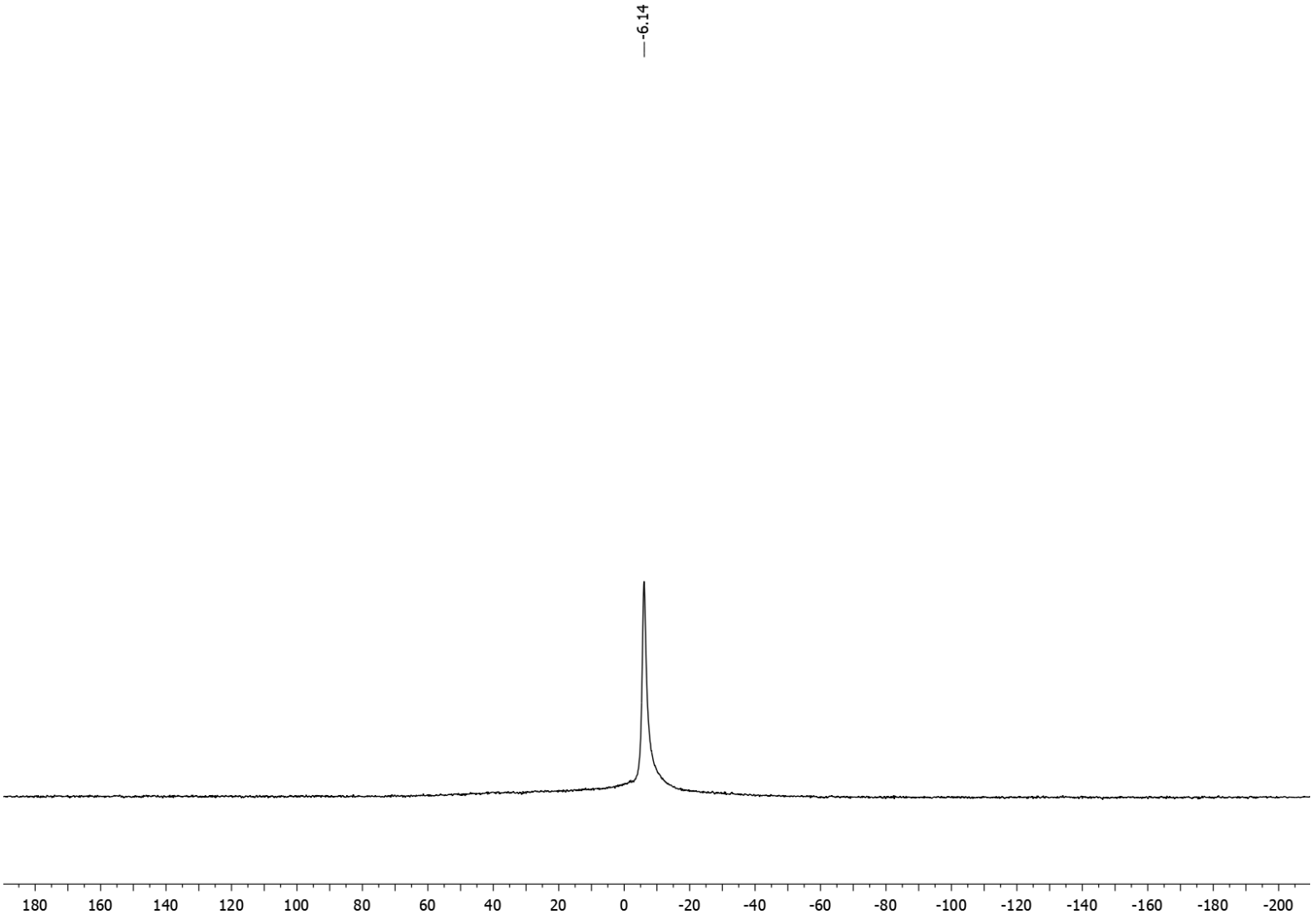


Figure S20 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of **2b**.

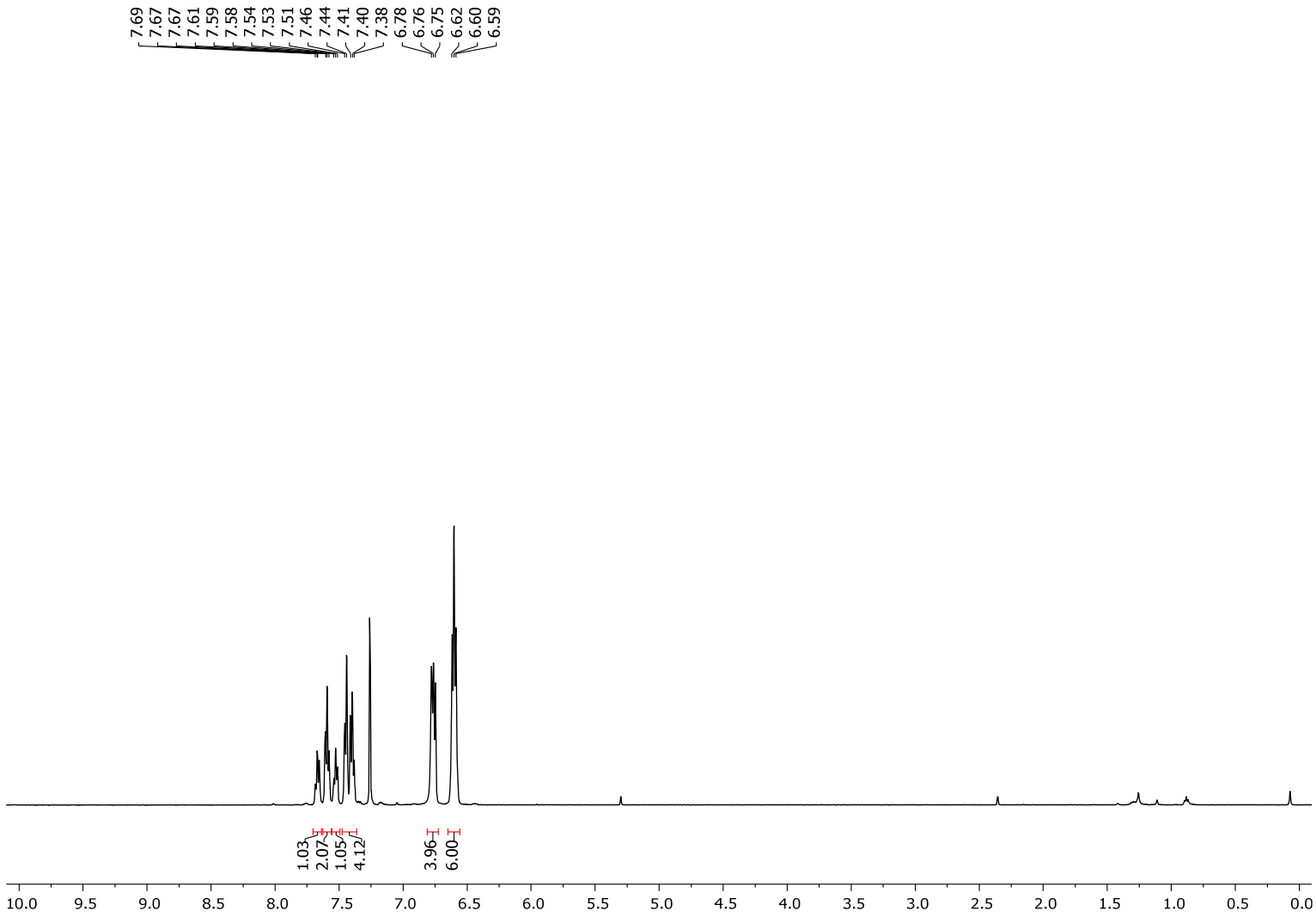


Figure S21 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of **2b**.

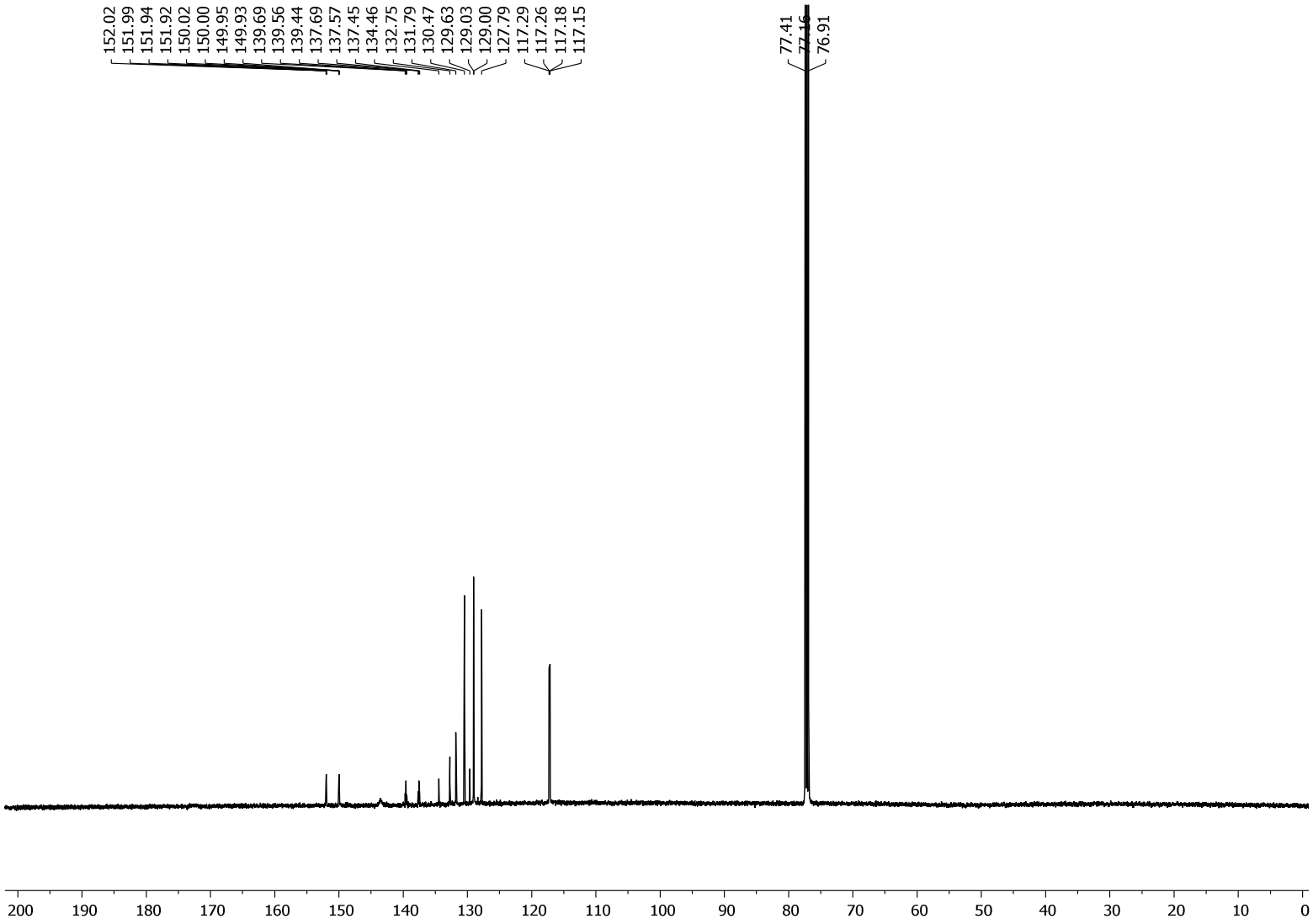


Figure S22 ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) spectrum of **2b**.

Figure S23 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of **2b**.

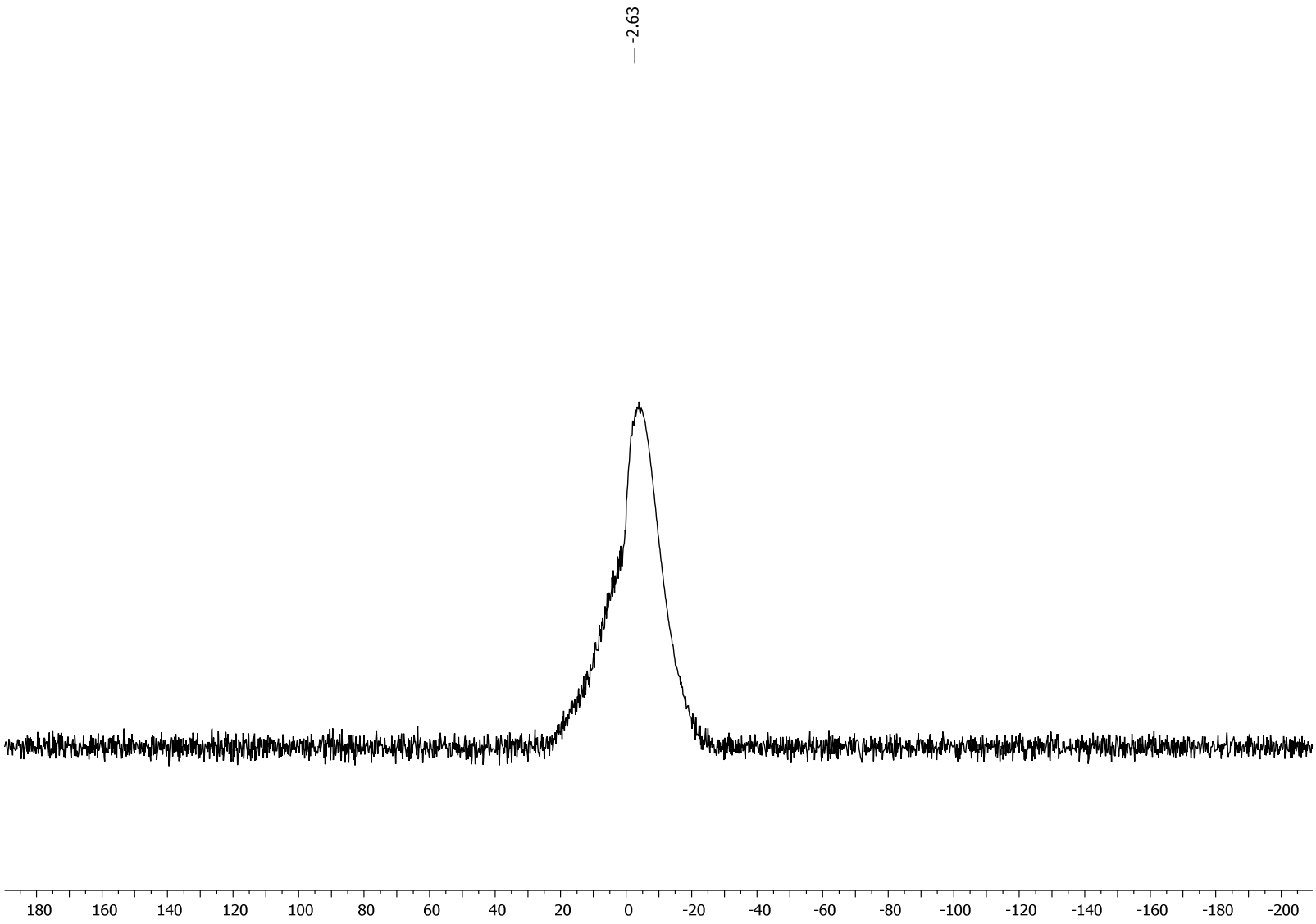


Figure S24 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of **2c**.

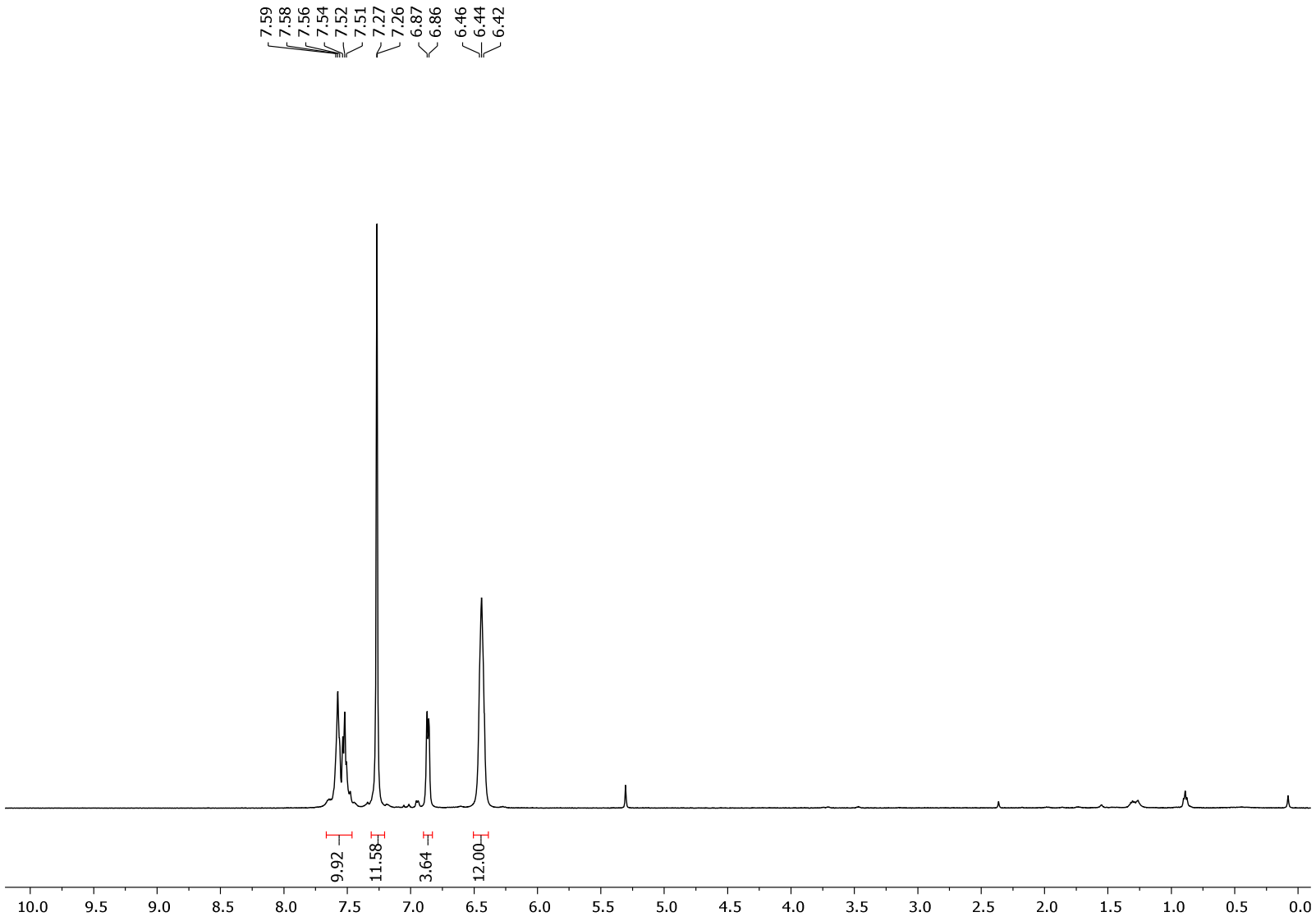


Figure S25 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of **2c**.

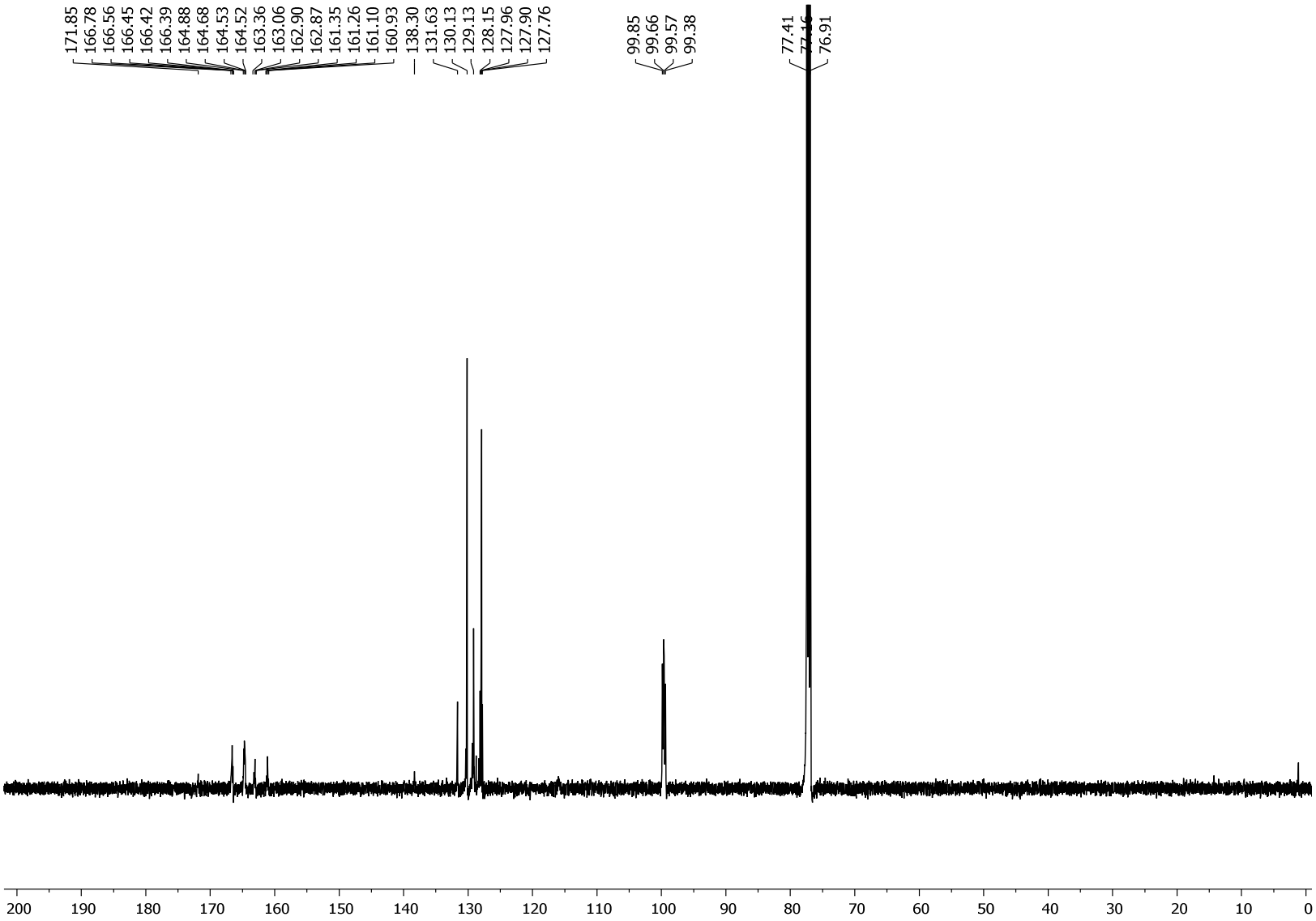


Figure S26 ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) spectrum of **2c**.

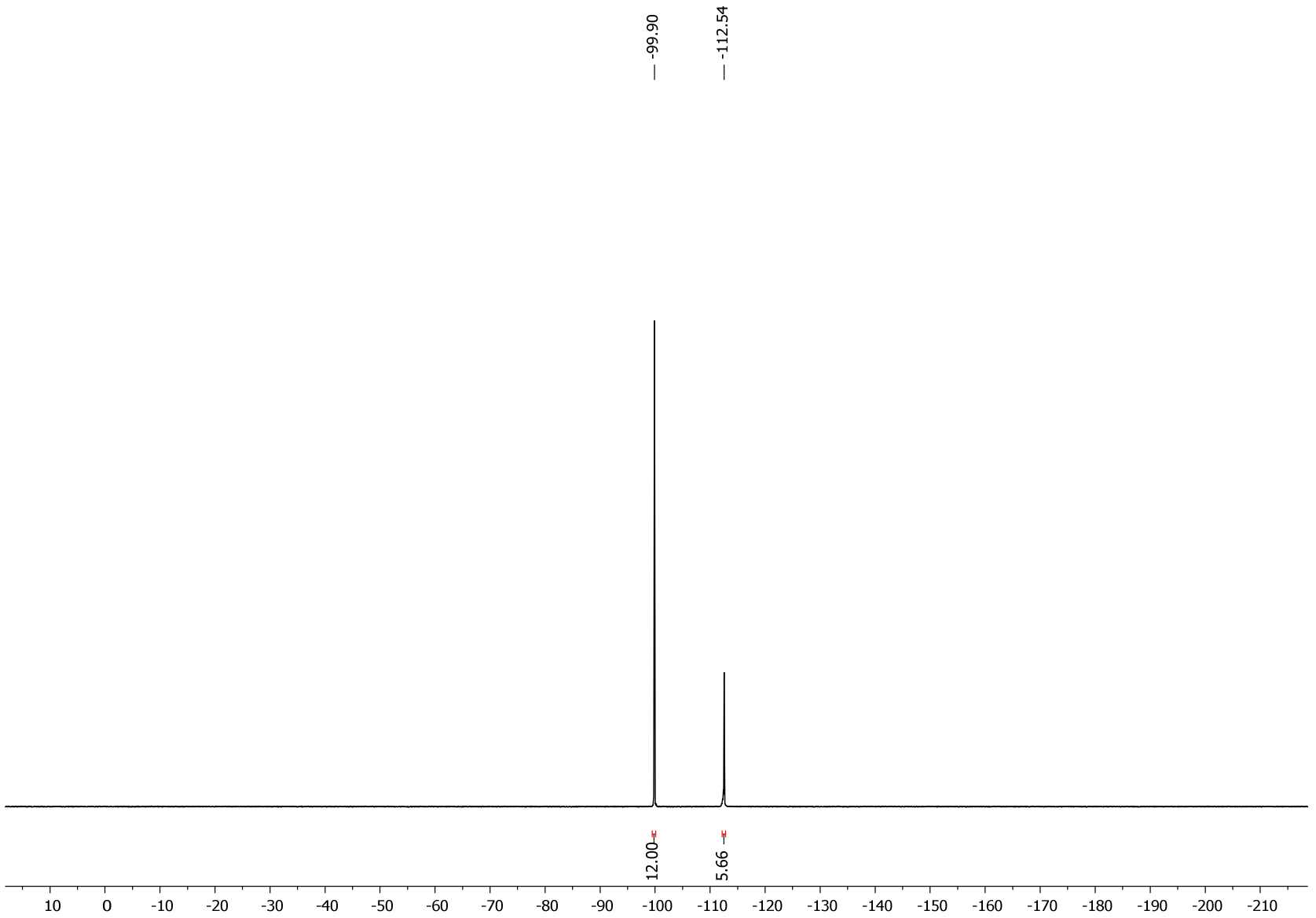


Figure S27 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of **2c**.

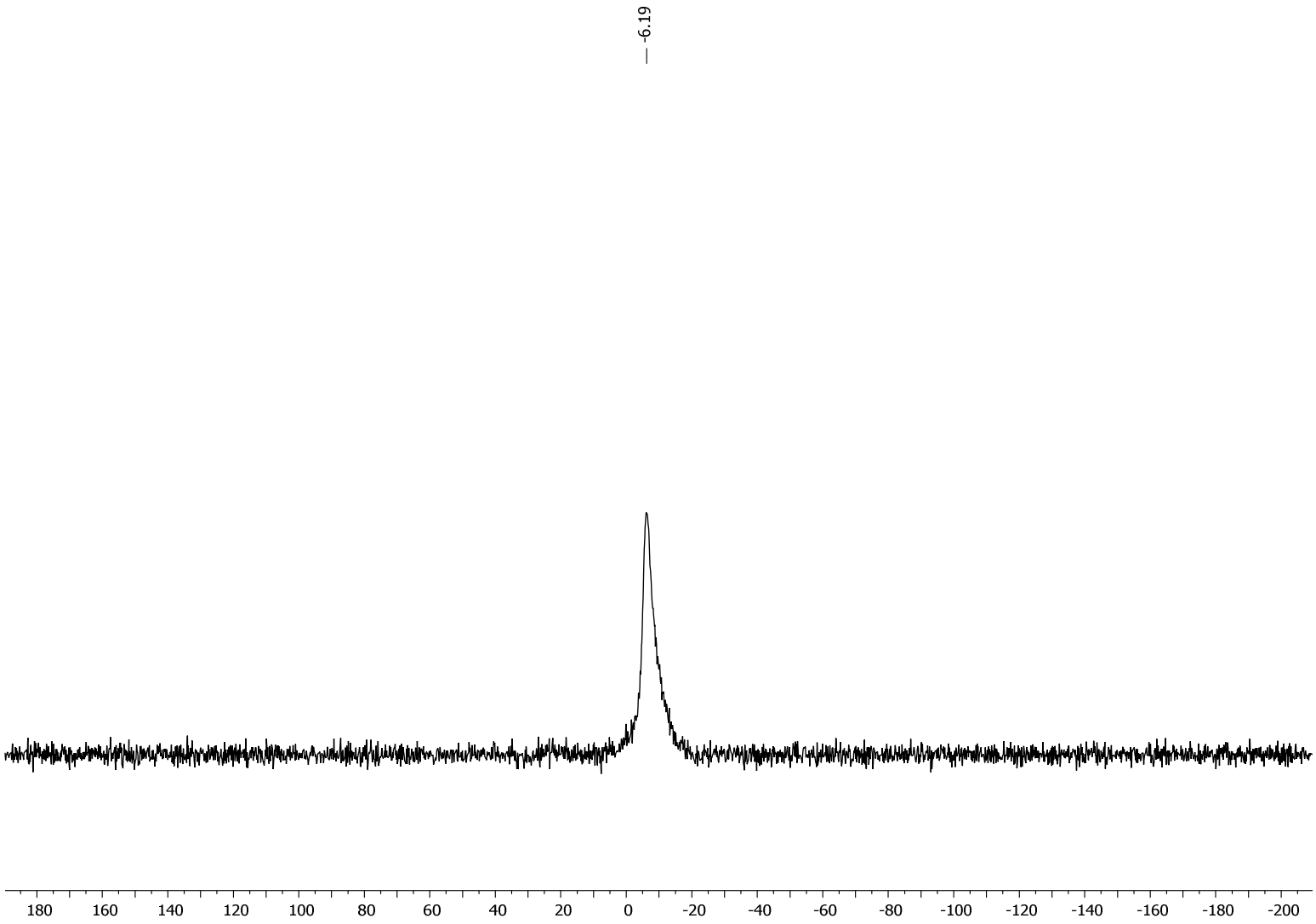


Figure S28 ^{1}H NMR (500 MHz, $CDCl_3$, 298K) spectrum of **3.**

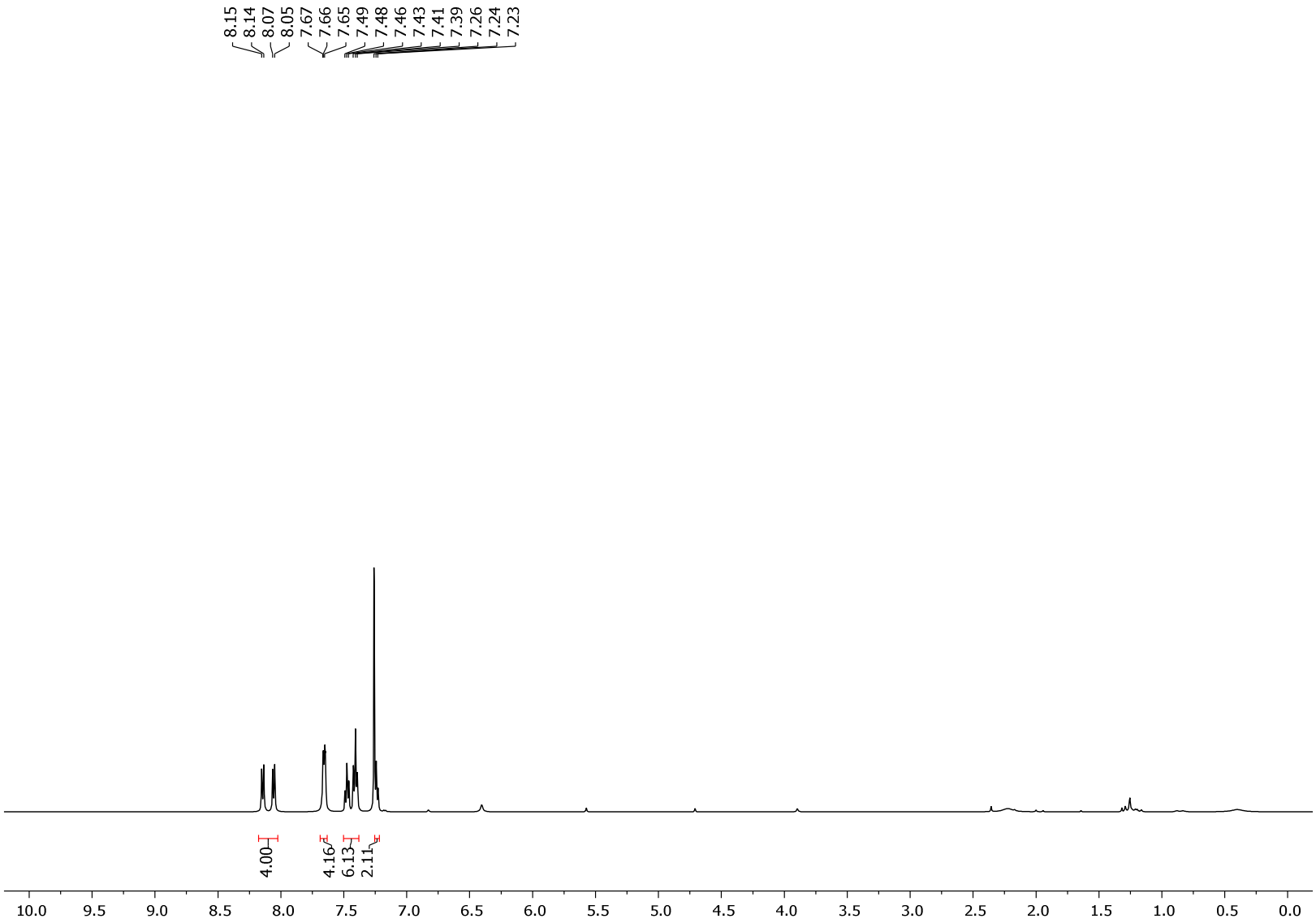


Figure S29 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of **3**.

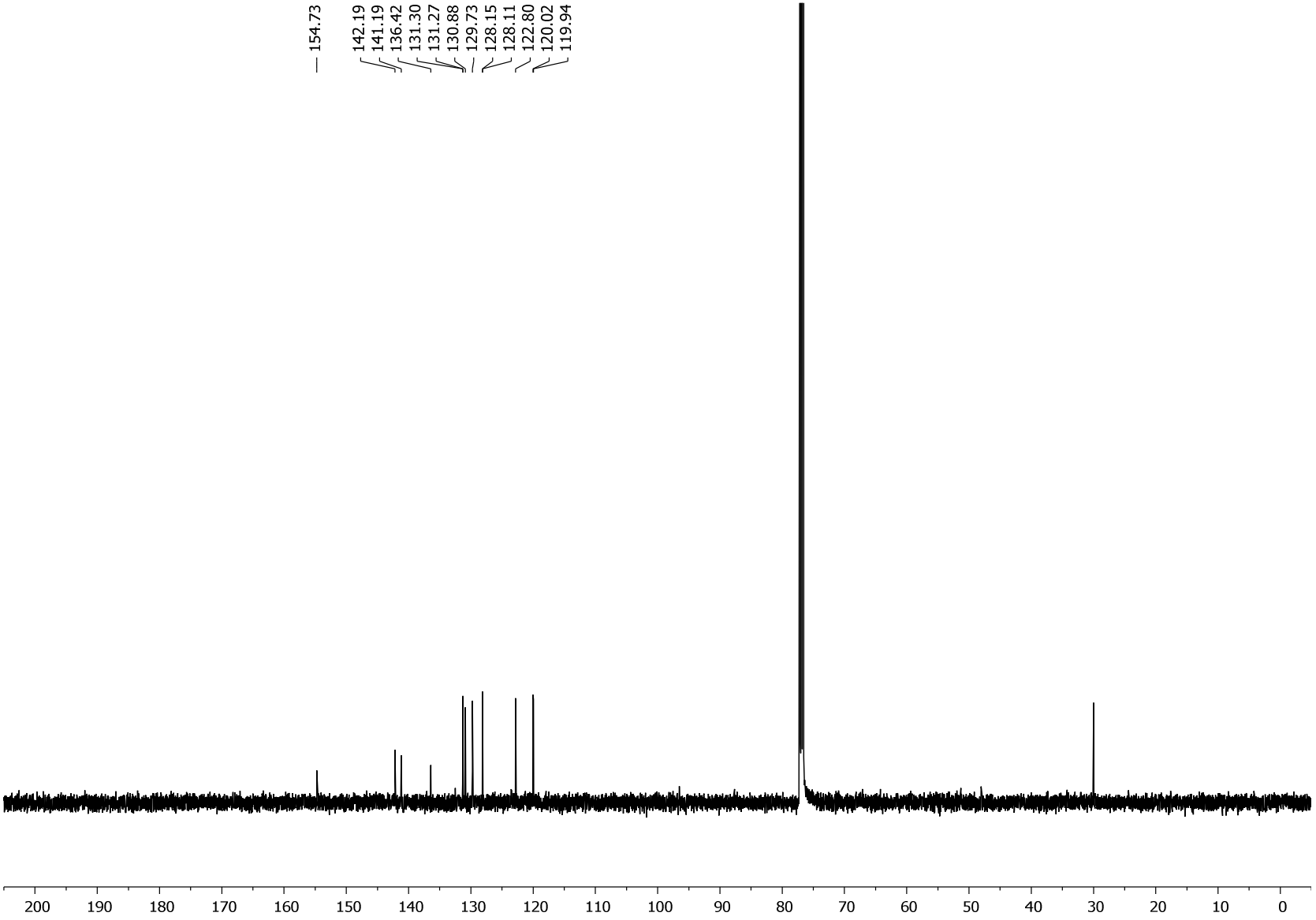


Figure S30 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of.**5**.

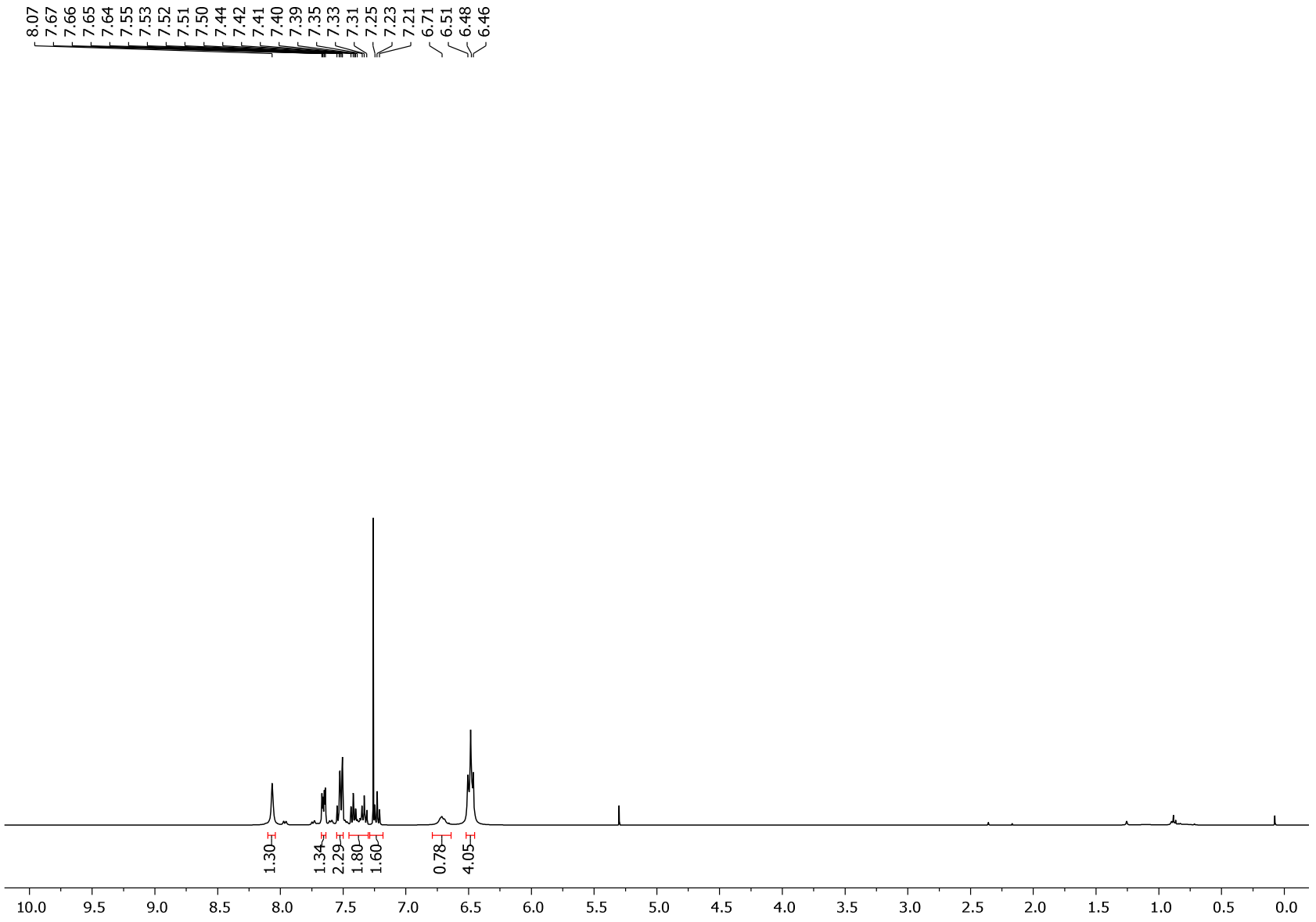


Figure S31 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of **5**

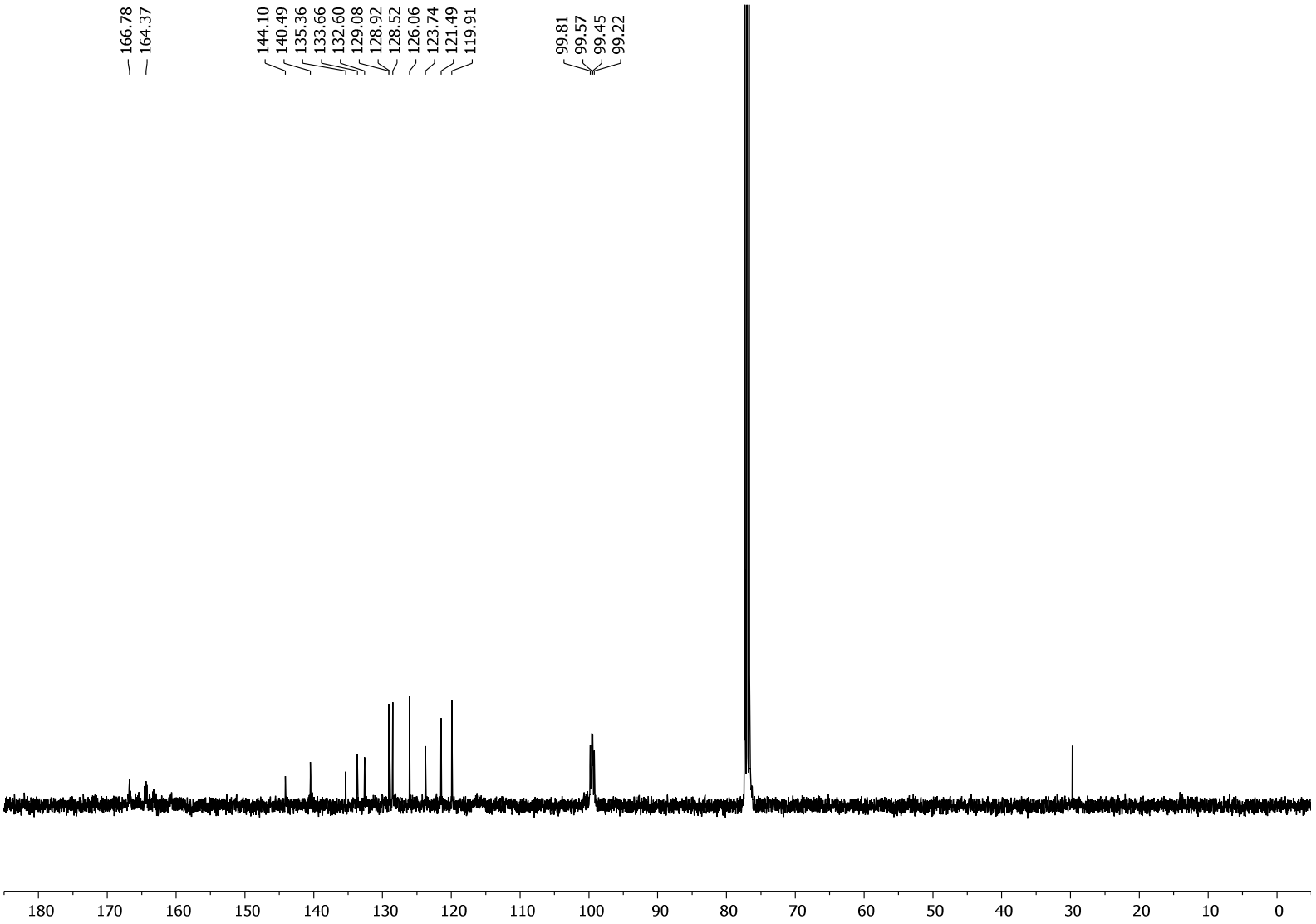


Figure S32 ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) spectrum of **5**.

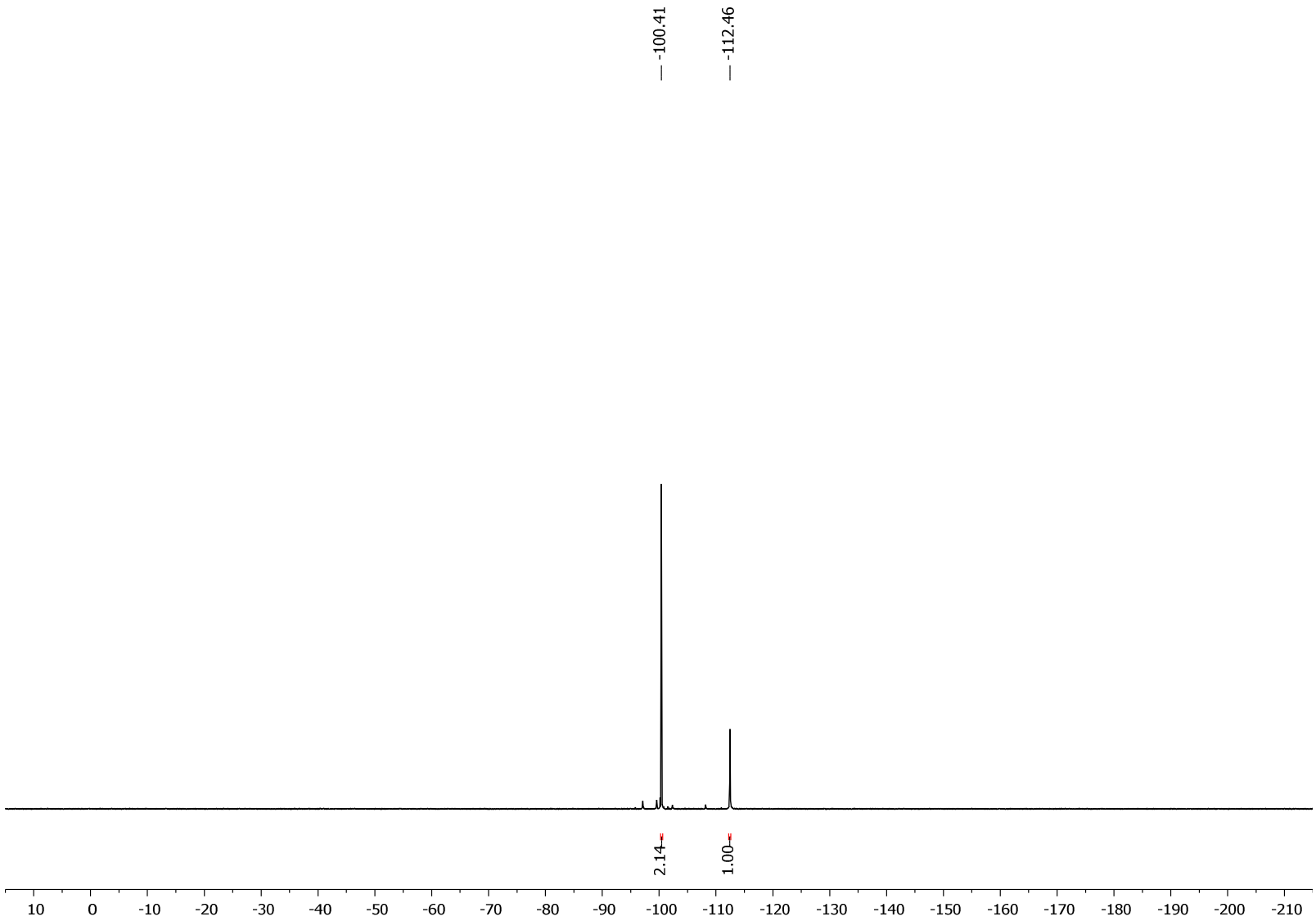


Figure S33 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of **5**.

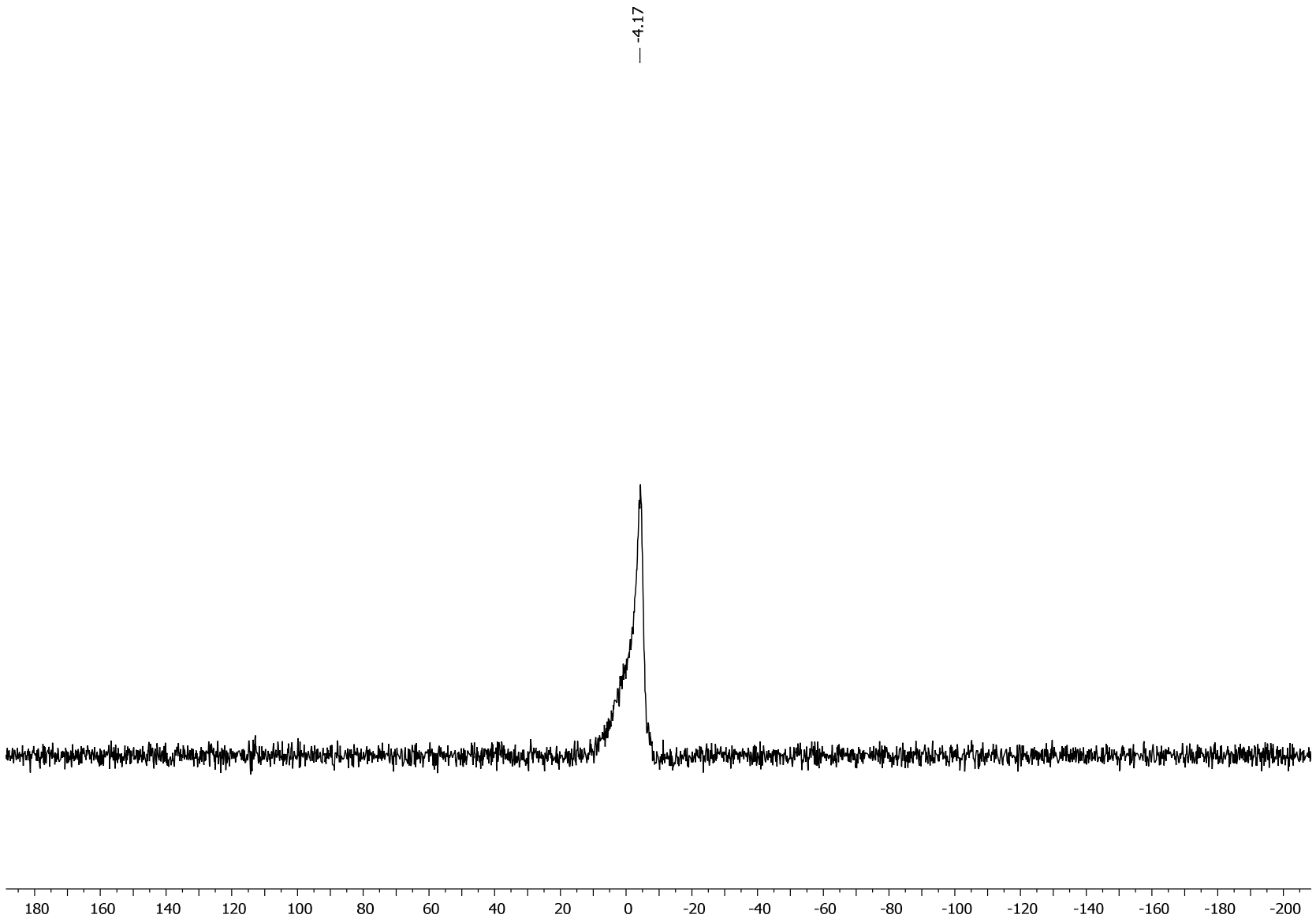


Figure S34 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of **6a**.

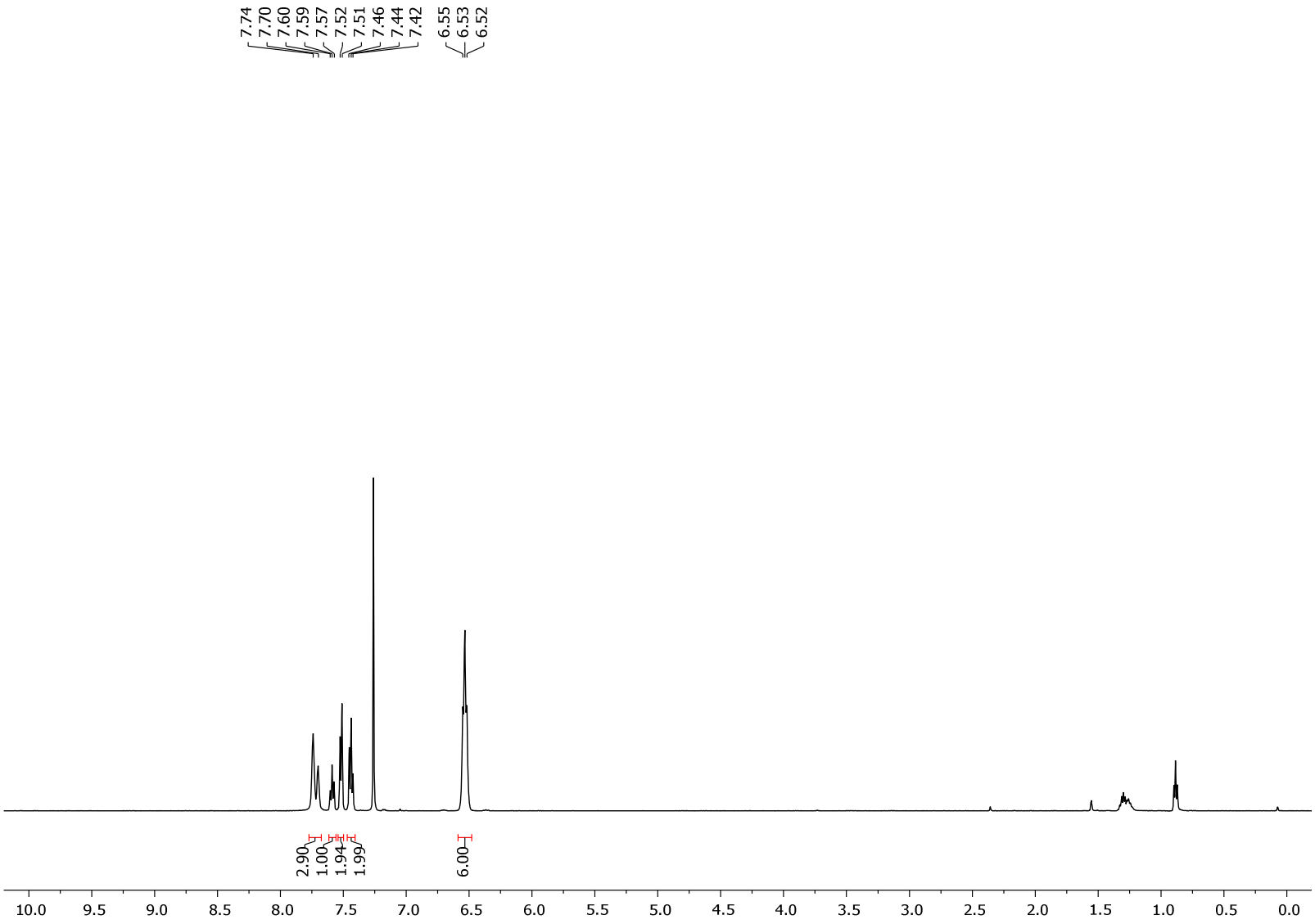


Figure S35 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of **6a**.

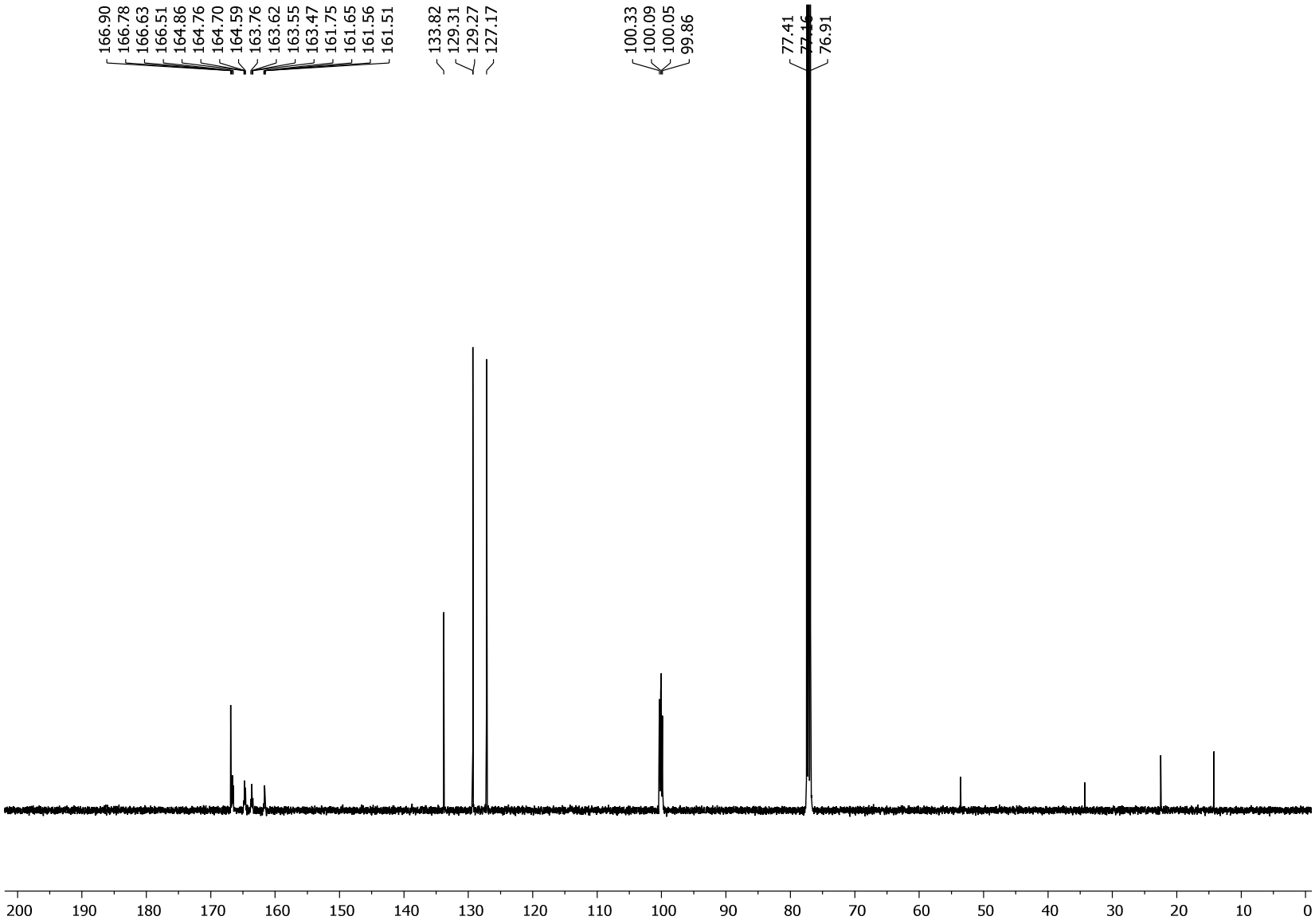


Figure S36 ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) spectrum of **6a**.

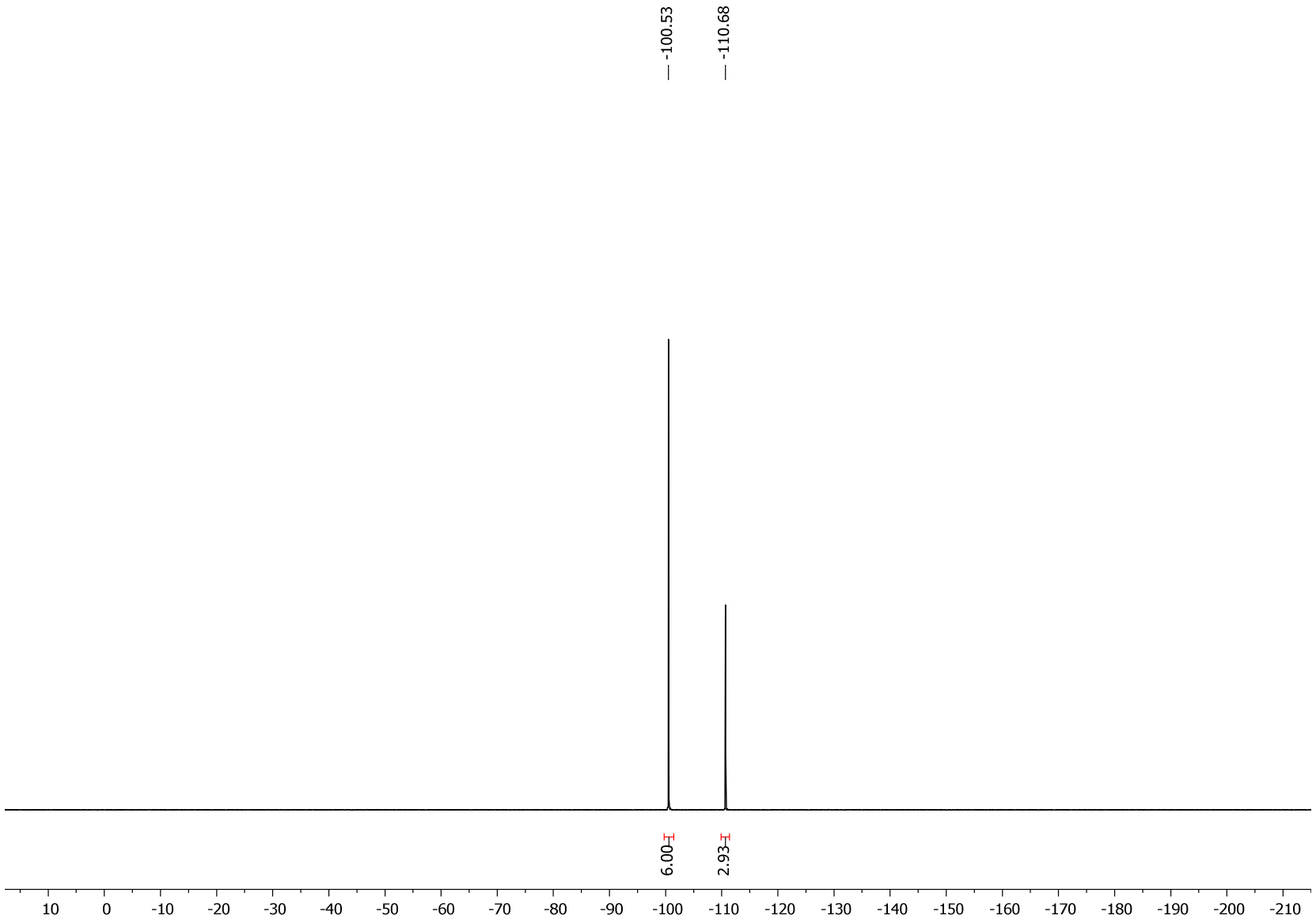


Figure S37 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of **6a**.

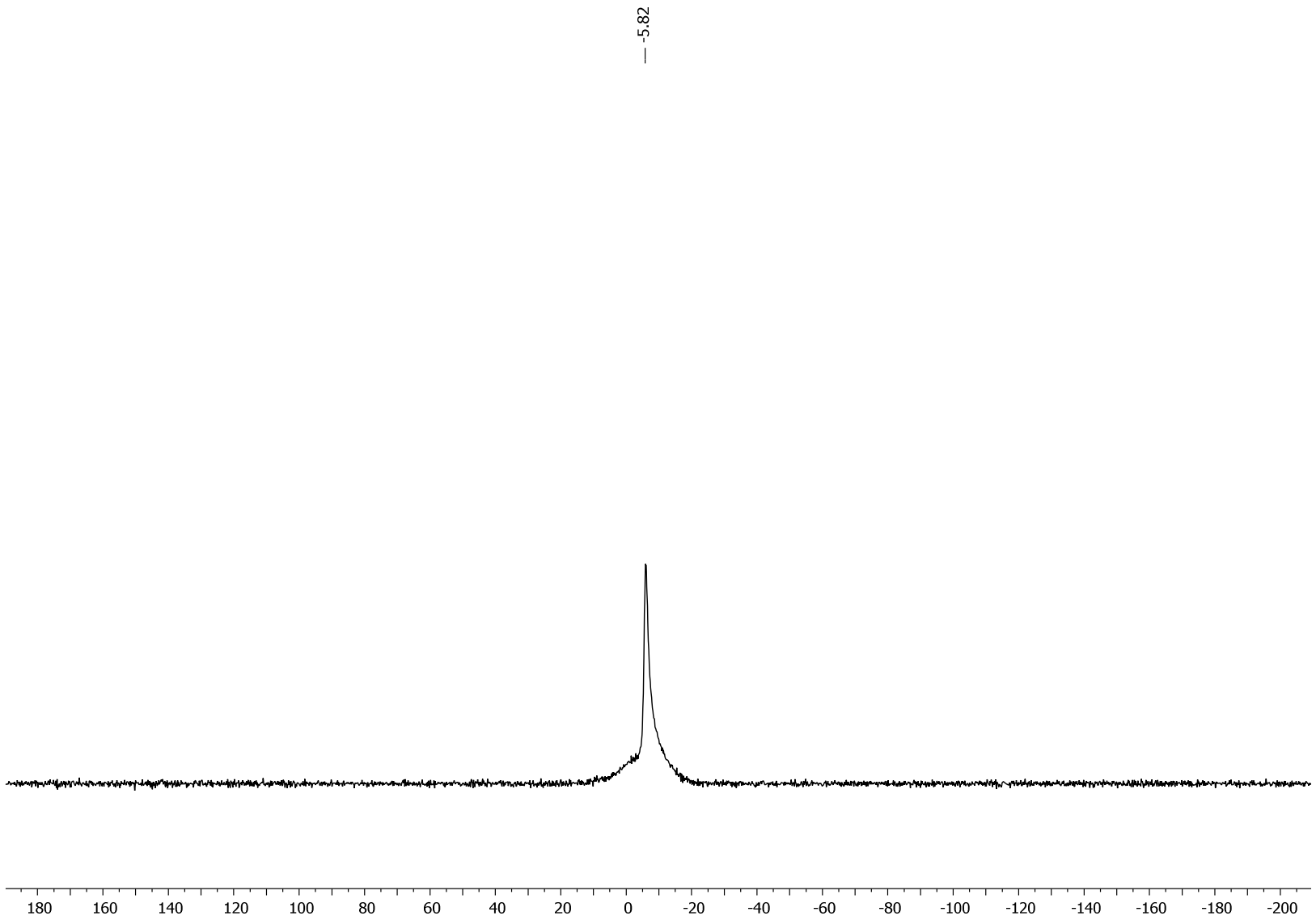


Figure S38 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of **6b**.

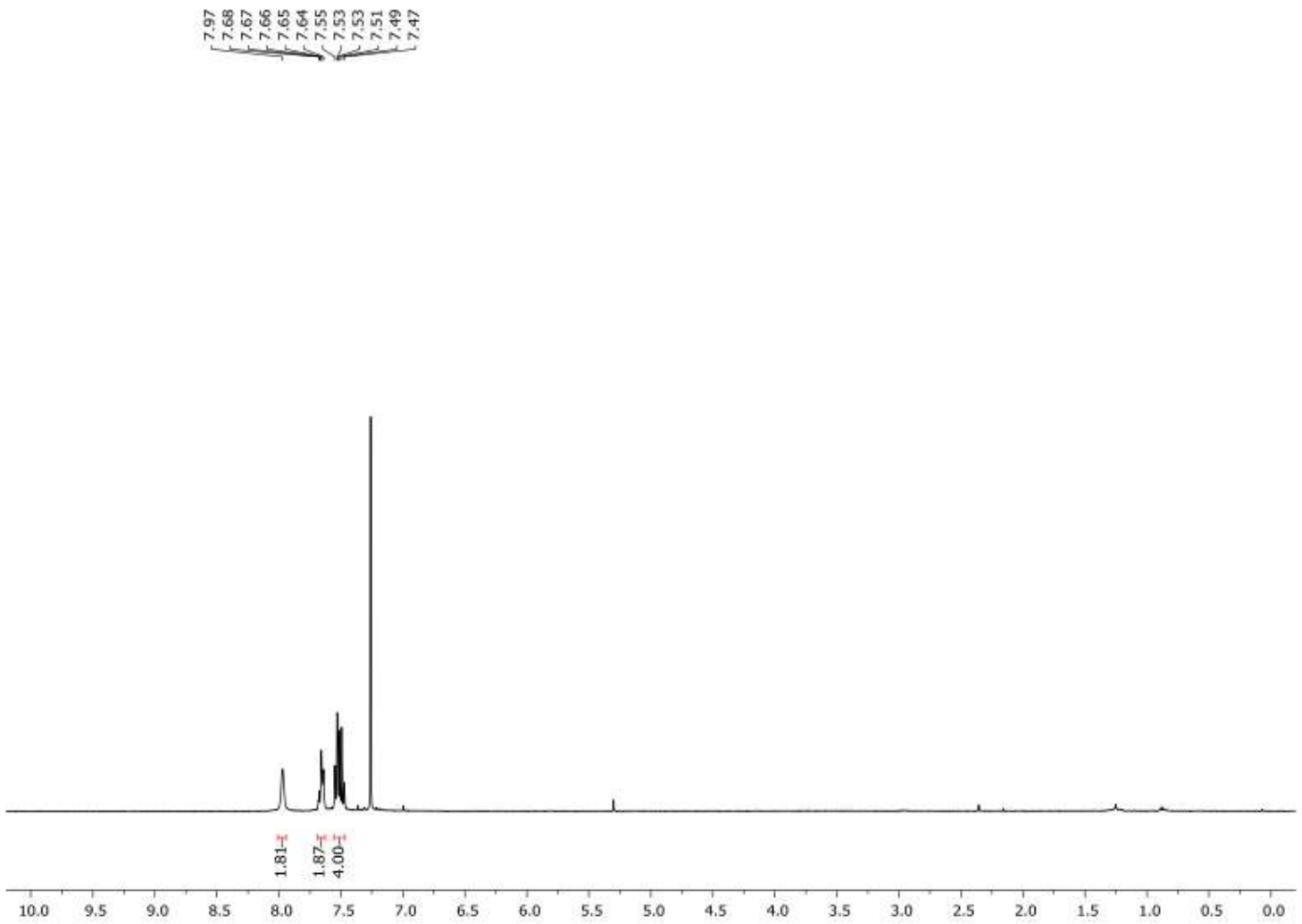


Figure S 39 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of **6b**.

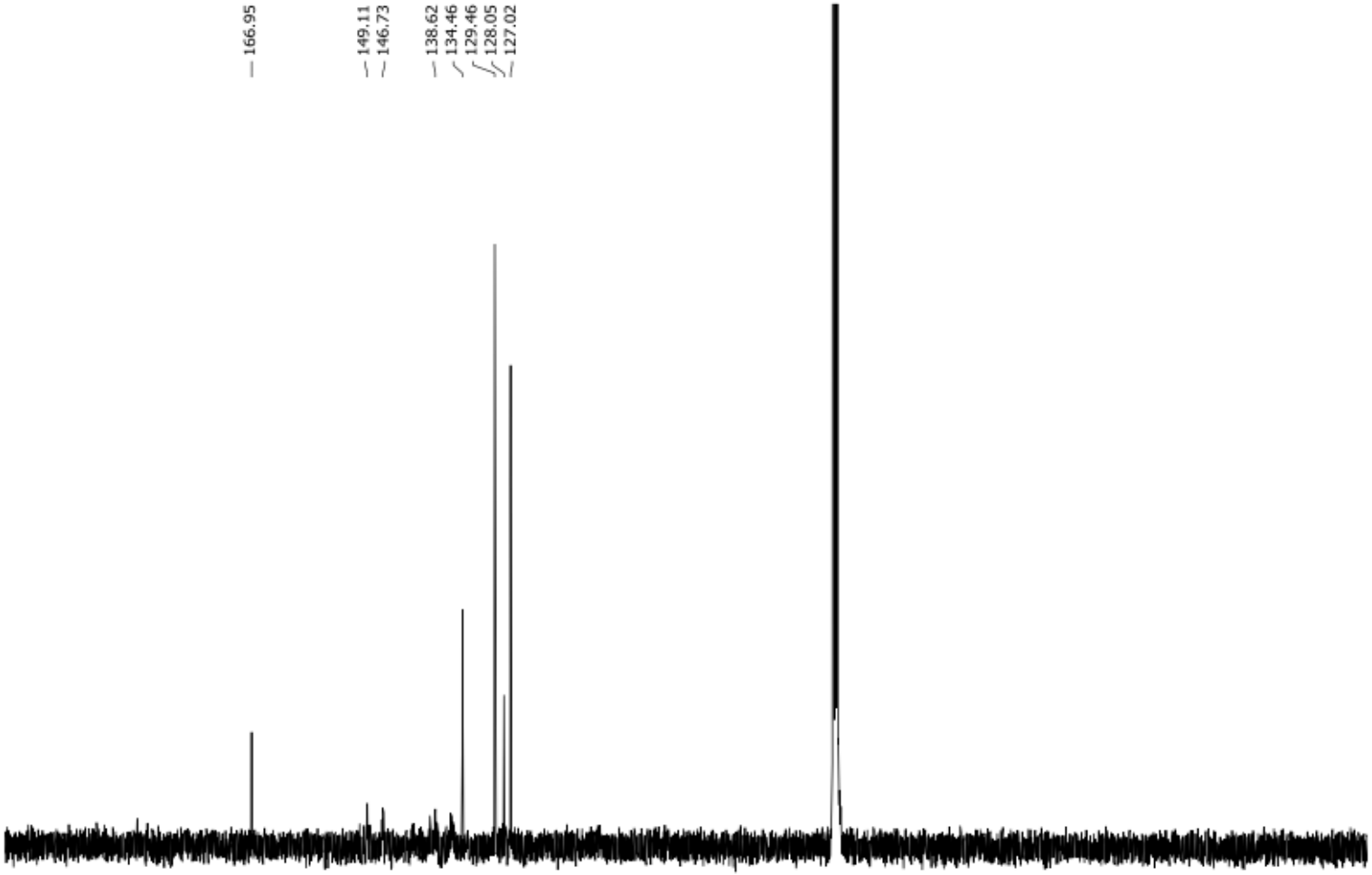


Figure S40 ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) spectrum of **6b**.

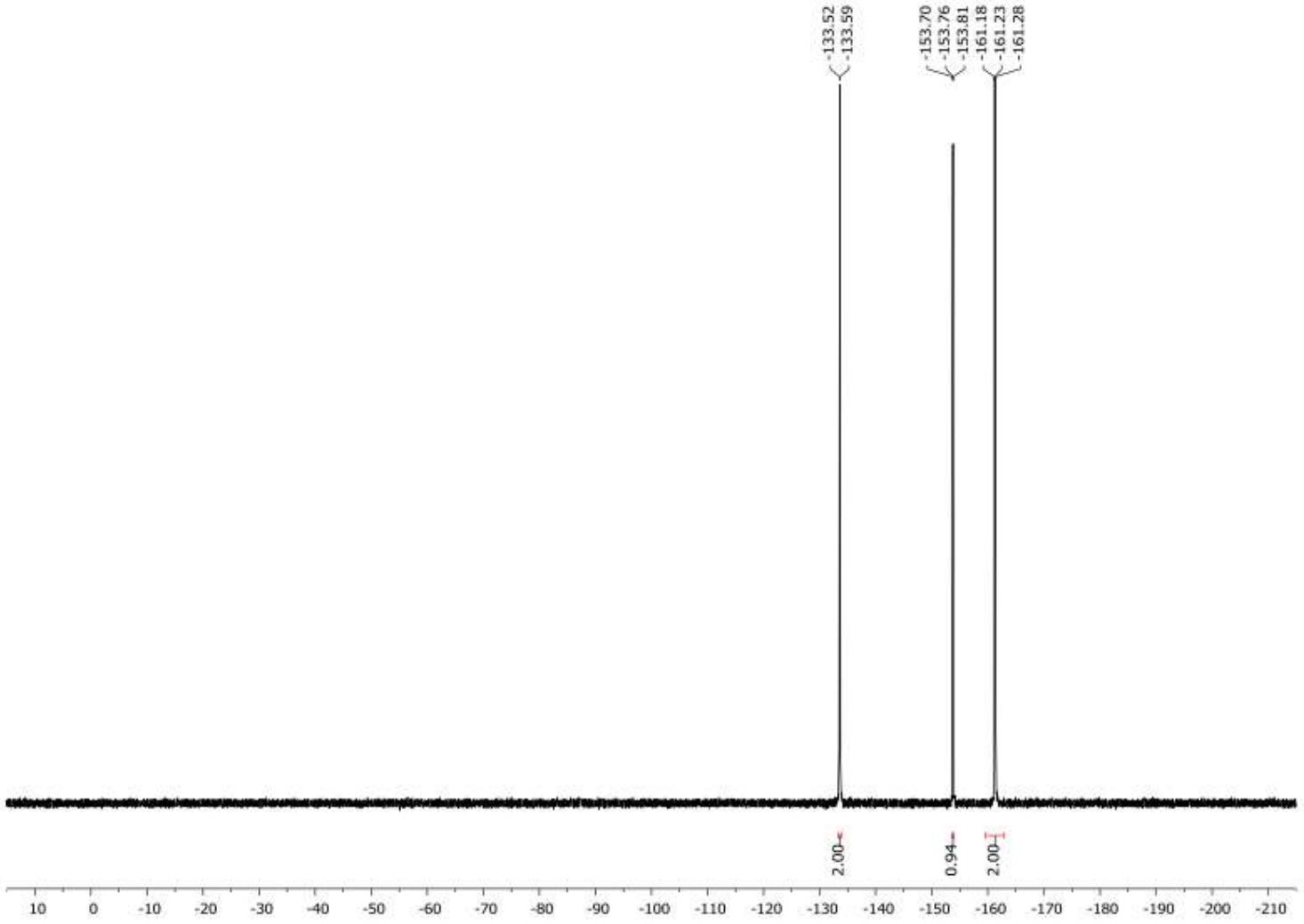


Figure S41 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of **6b**.

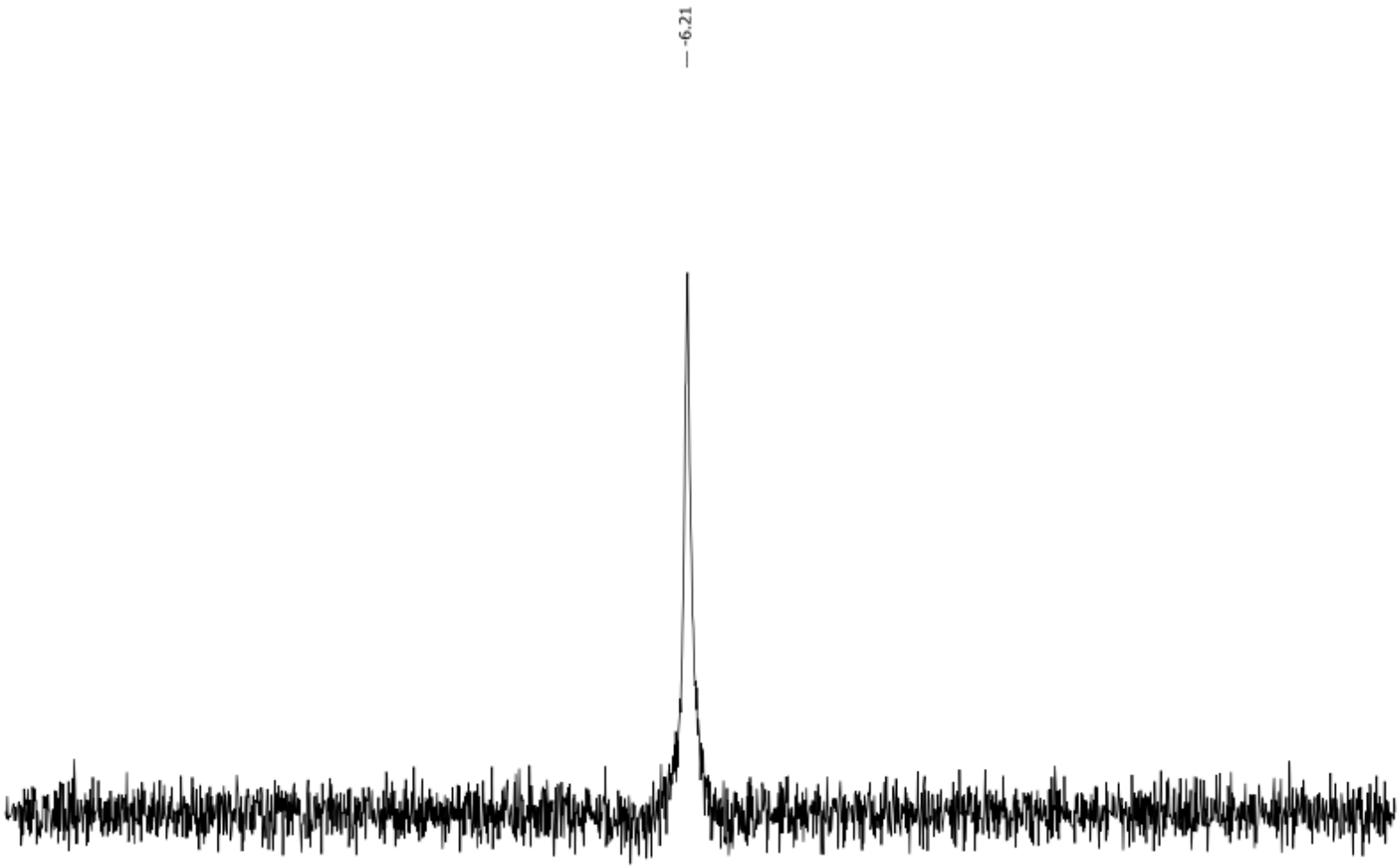


Figure S42 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **7**.

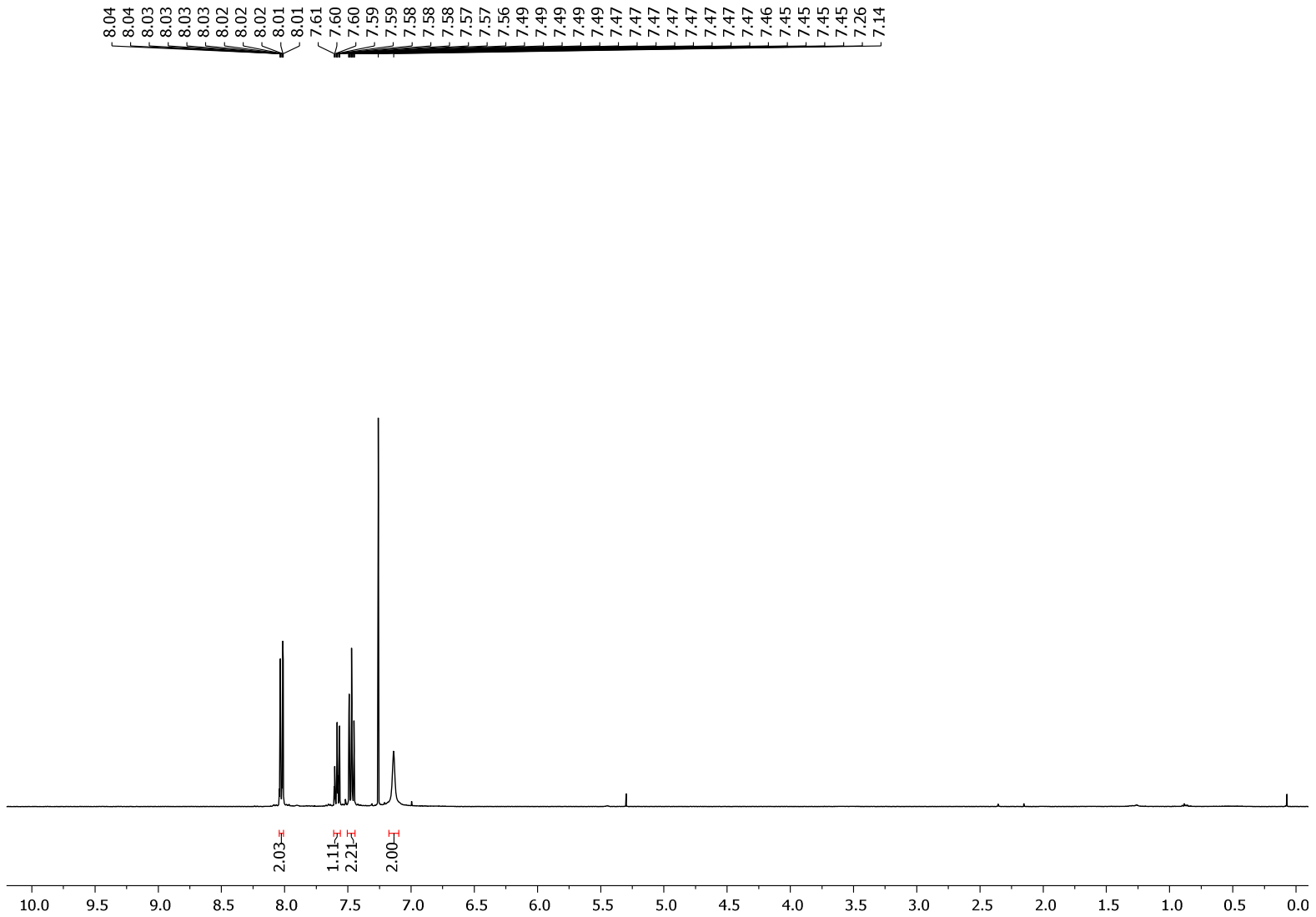


Figure S43 $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) spectrum of **7**

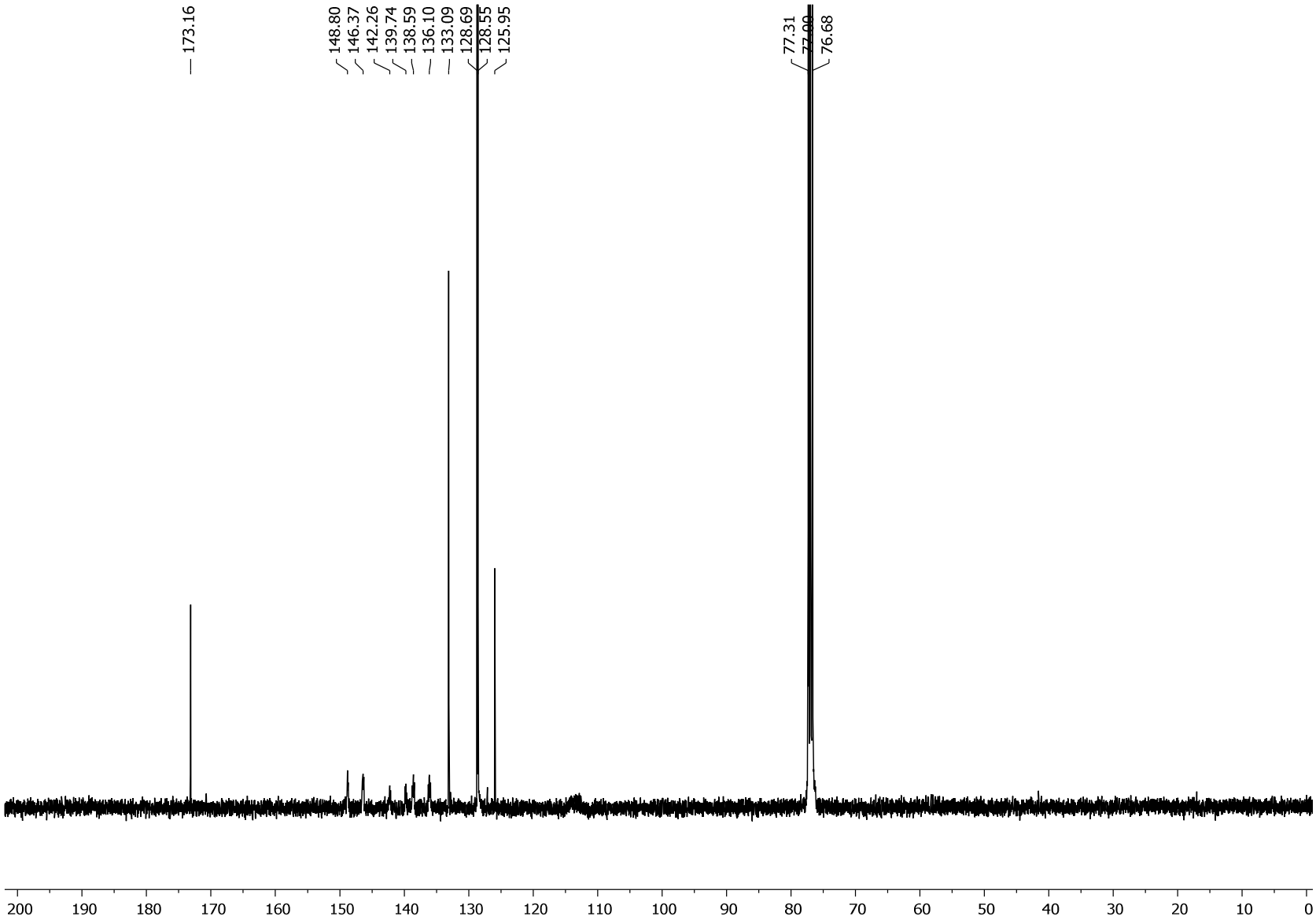


Figure S44 ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) spectrum of **7**.

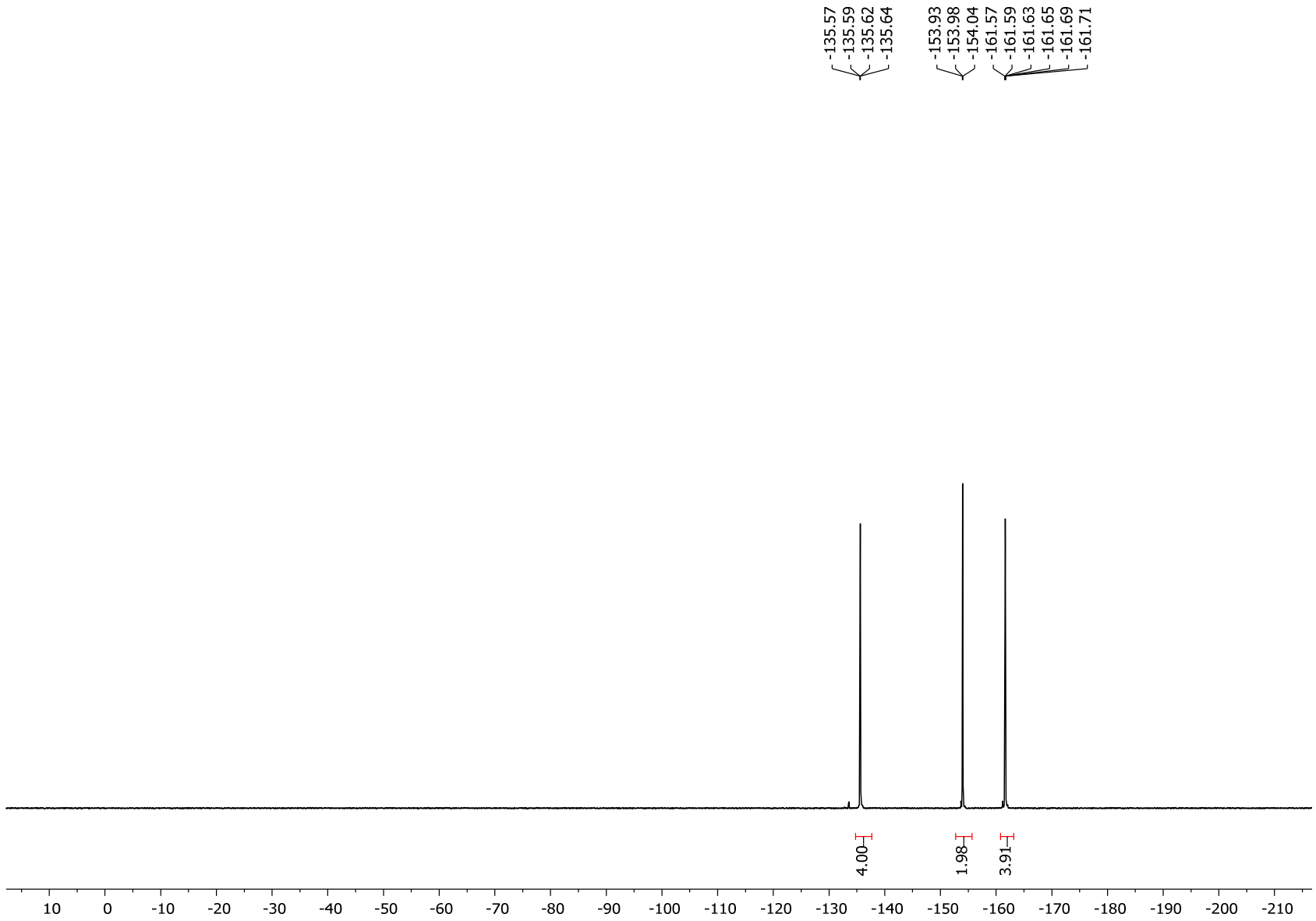
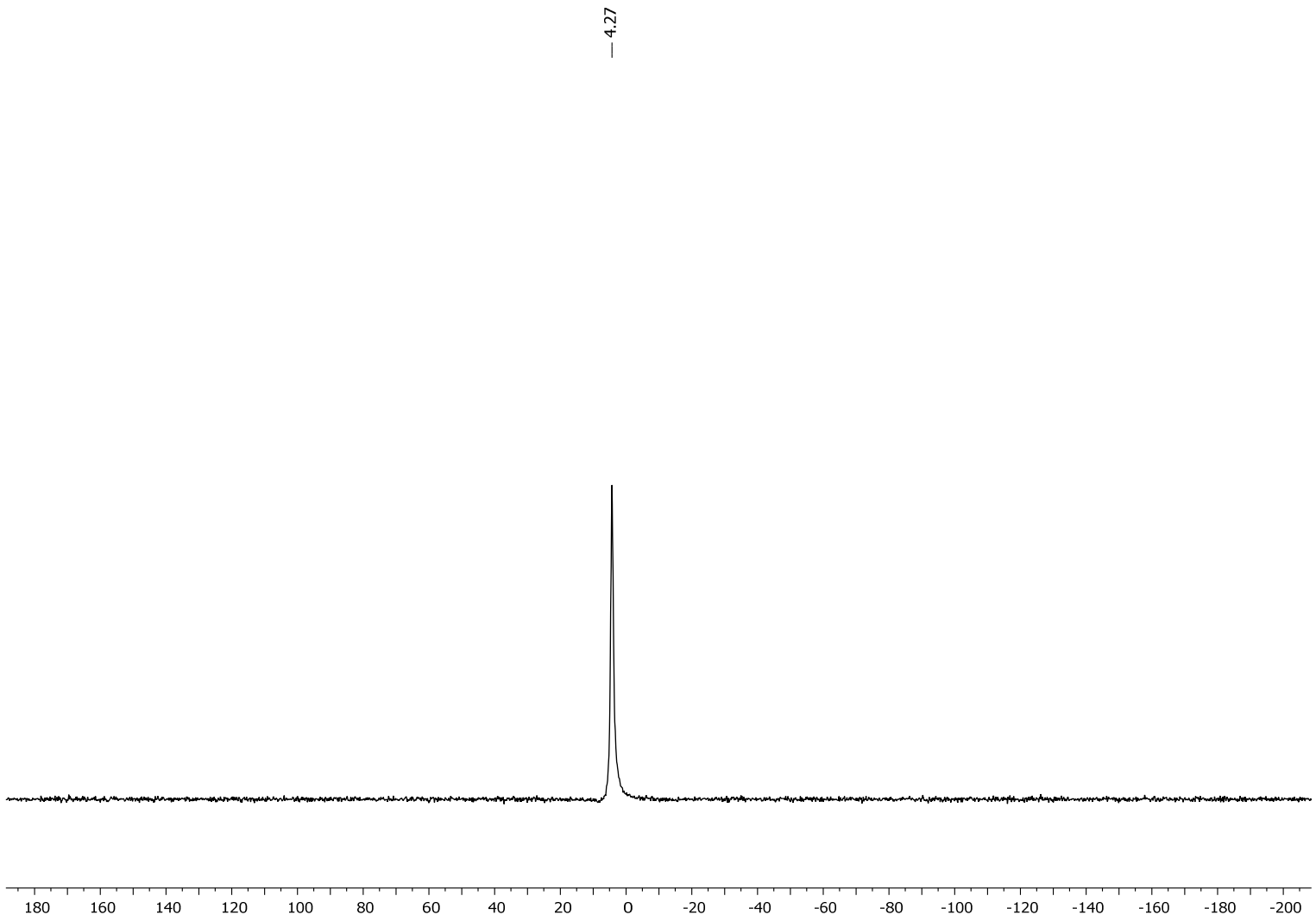


Figure S45 ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of **7**



3 Crystallographic data

Single crystals were grown under an inert atmosphere. Crystallographic studies were undertaken of a single crystal mounted in paratone and studied on an Agilent Super Nova diffractometer using Mo-Kα radiation and a CCD detector. Measurements were carried out at 150(2) K with temperatures maintained using an Oxford cryostream unless otherwise stated. Data were collected and integrated and data corrected for absorption using a numerical absorption correction based on gaussian integration over a multifaceted crystal model within CrysAlisPro.[9] The structures were solved by direct methods and refined against F^2 within SHELXL-2013.[10] The structures are deposited with the Cambridge Structural Database (CCDC deposition numbers 1897205-1897211, 1903201). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

3.1 X-ray refinement data

Table S1 Crystal data and structure refinement for compound **2a-c**.

Compound	**2a**	**2b**	**2c**
Empirical Formula	$C_{31}H_{18}BF_9N_2$	$C_{31}H_{18}BF_9N_2$	$C_{56}H_{30}B_2F_{18}N_4 \cdot 2(CH_2Cl_2)$
Crystal System	Monoclinic	Triclinic	Triclinic
Space Group	$P2_1/n$	P-1	P-1
a/Å	9.5166(4)	9.7975(7)	9.4053(6)
b/Å	21.8157(8)	10.9639(11)	11.2224(7)
c/Å	13.1104(5)	13.8619(15)	13.6936(8)
α/Å	90	106.193(9)	103.791(5)
β/Å	99.132(4)	102.430(7)	98.886(5)
γ/Å	90	105.643(7)	90.099(5)
V/Å^3	2687.37(18)	1307.3(2)	1385.73(16)
Z	4	2	1
T /K	150(2)	150(2)	150(2)
D_C/g.cm^{-3}	1.484	1.525	1.549
Crystal size/mm	0.21 × 0.18 × 0.11	0.20 × 0.16 × 0.11	0.12 × 0.04 × 0.03
Total data	14715	10154	10704
Unique data	6315	6080	6091
R_{int}	0.022	0.031	0.041
$R_1[F^2>2\ \sigma(F^2)]$	0.042	0.056	0.065
wR2 (all data)	0.105	0.149	0.169
GoF	1.06	1.08	1.030
ρ_{min}/ρ_{max}/eÅ^{-3}	-0.22/0.28	-0.30/0.25	-0.39/0.66
CCDC code	1897205	1897206	1897207

Table S2 Crystal data and structure refinement for compound **4**, **5** and **6a**.

Compound	**4**	**5**	**6a**
Empirical Formula	$C_{36}H_{16}B_2F_{18}N_2$	$C_{25}H_{13}BF_6N_2$	$C_{25}H_{14}BF_9N_2O$
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space Group	I2/*a*	$P2_1/c$	C2/*c*
a/Å	15.7866(8)	14.8884(9)	25.9971(10)
b/Å	9.6410(4)	10.6742(5)	15.1972(6)
c/Å	22.4406(11)	14.1291(7)	13.0295(4)
α/°	90	90	90
β/°	108.694(6)	115.392(7)	94.668(3)
γ/°	90	90	90
V/Å^3	3235.2(3)	2028.5(2)	5130.7(3)
Z	4	4	8
T /K	150(2)	170(2)	200(2)
D_C/g.cm^{-3}	1.725	1.526	1.399
Crystal size/mm	0.82 × 0.28 × 0.09	0.57 × 0.27 × 0.12	0.50 × 0.37 × 0.16
Total data	8430	10152	10904
Unique data	3884	4614	5055
R_{int}	0.020	0.020	0.017
$R_1[F^2>2\ \sigma(F^2)]$	0.037	0.041	0.124
wR2 (all data)	0.095	0.113	0.405
GoF	1.02	1.04	1.82
ρ_{min}/ρ_{max}/eÅ^{-3}	-0.21/0.35	-0.23/0.30	-0.38/4.7
CCDC code	1897208	1897209	1897210

Table S3 Crystal data and structure refinement for compound **6b** and **7**.

Compound	**6b**	**7**
Empirical Formula	$C_{25}H_8BF_{15}N_2O$	$C_{19}H_7BF_{10}N_2O$
Crystal System	Monoclinic	Triclinic
Space Group	P21/c	*P*-1
a/Å	10.8497(5)	11.8326(5)
b/Å	16.1722(8)	12.0001(7)
c/Å	13.6947(6)	13.9711(6)
α/°	90	73.338(4)
β/°	104.795(5)	89.047(3)
γ/°	90	75.159(4)
V/Å^3	104.795(5)	1833.64(16)
Z	2323.27(19)	4
T /K	3	150(2)
D_C/g.cm^{-3}	200	1.739
Crystal size/mm	1.853	0.45 × 0.33 × 0.22
Total data	0.30x0.27x0.16	15395
Unique data	12738	8650
R_{int}	5617	0.031
$R_1[F^2>2\ \sigma(F^2)]$	0.021	0.052
wR2 (all data)	0.040	0.147
GoF	1.03	1.04
ρ_{min}/ρ_{max}/eÅ^{-3}	-0.29/0.28	-0.38/0.35
CCDC code	1903201	1897211

Figure S46 Solid-state structure of compound **2a**, thermal ellipsoids drawn at the 50% probability level. H-atoms except for those on nitrogen omitted for clarity.

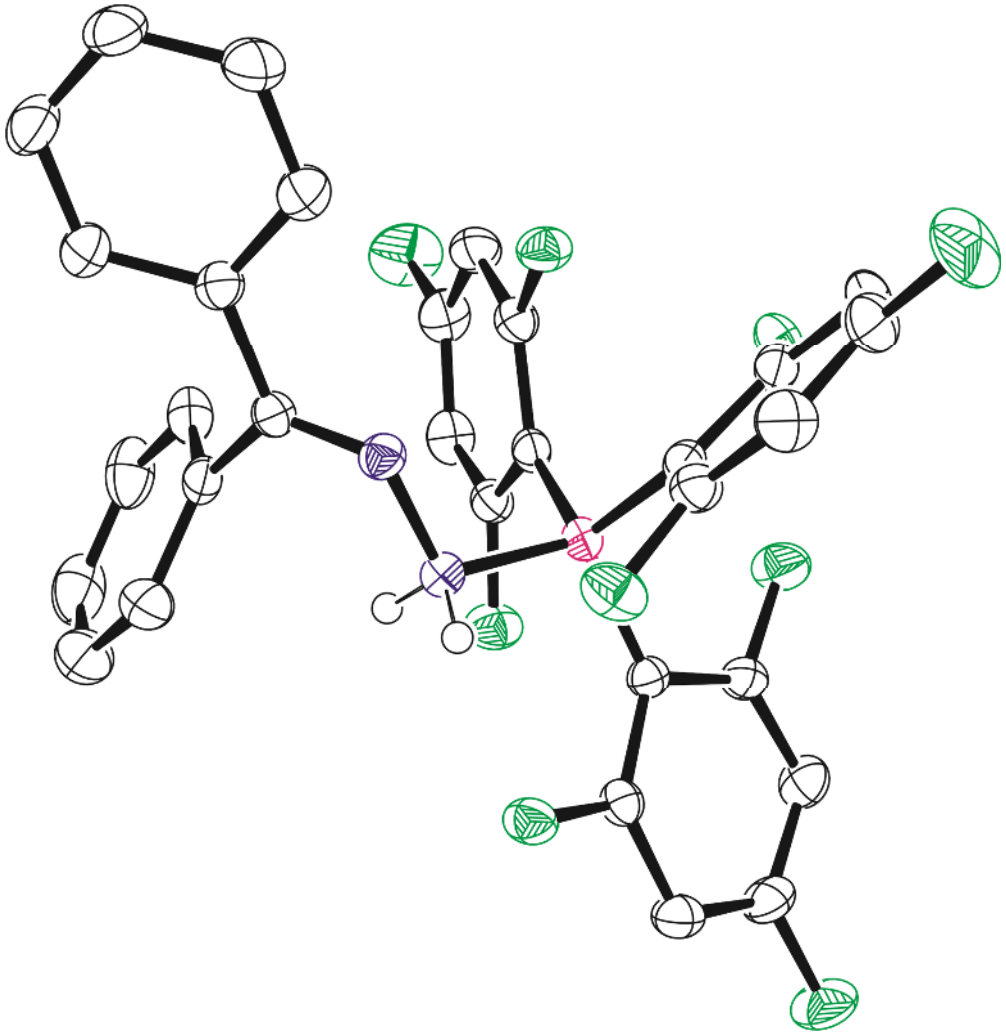


Figure S47 Solid-state structure of compound **2b**, thermal ellipsoids drawn at the 50% probability level.H-atoms except for those on nitrogen omitted for clarity.

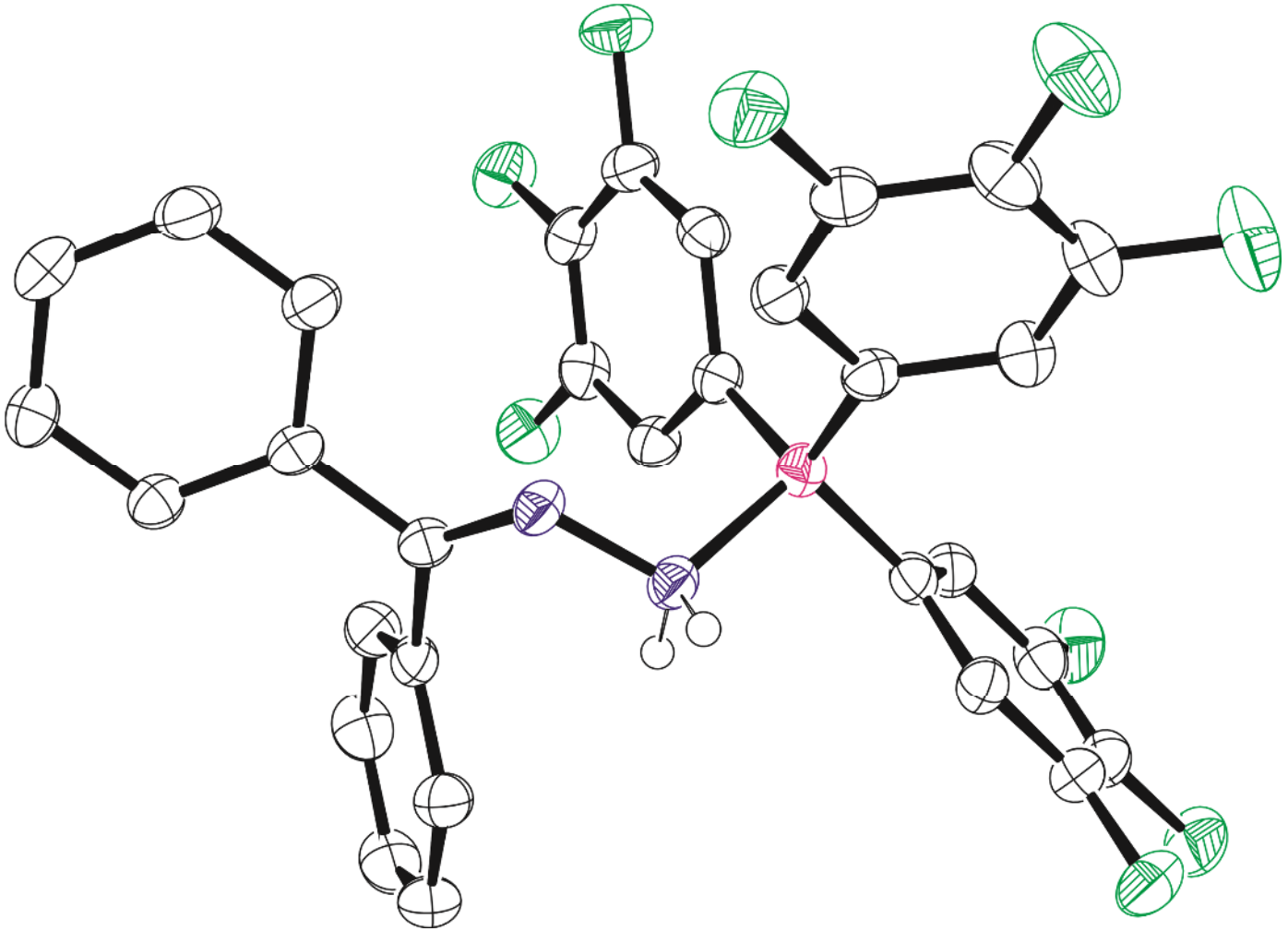


Figure S48 Solid-state structure of compound **2c**, thermal ellipsoids drawn at the 50% probability level.H-atoms except for those on nitrogen omitted for clarity.

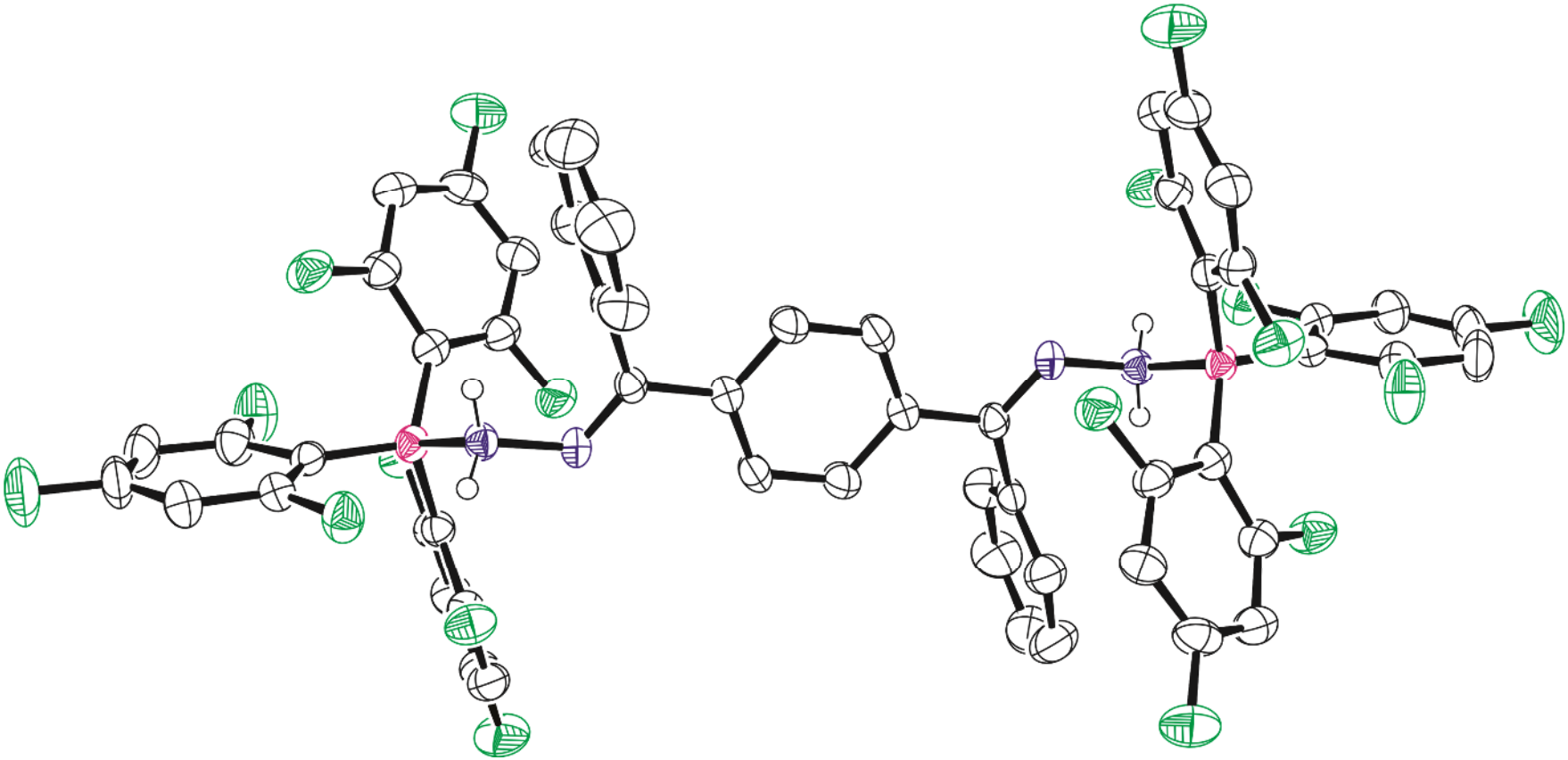


Figure S49 Solid-state structure of compound **4**, thermal ellipsoids drawn at the 50% probability level. H-atoms except for those on nitrogen omitted for clarity.

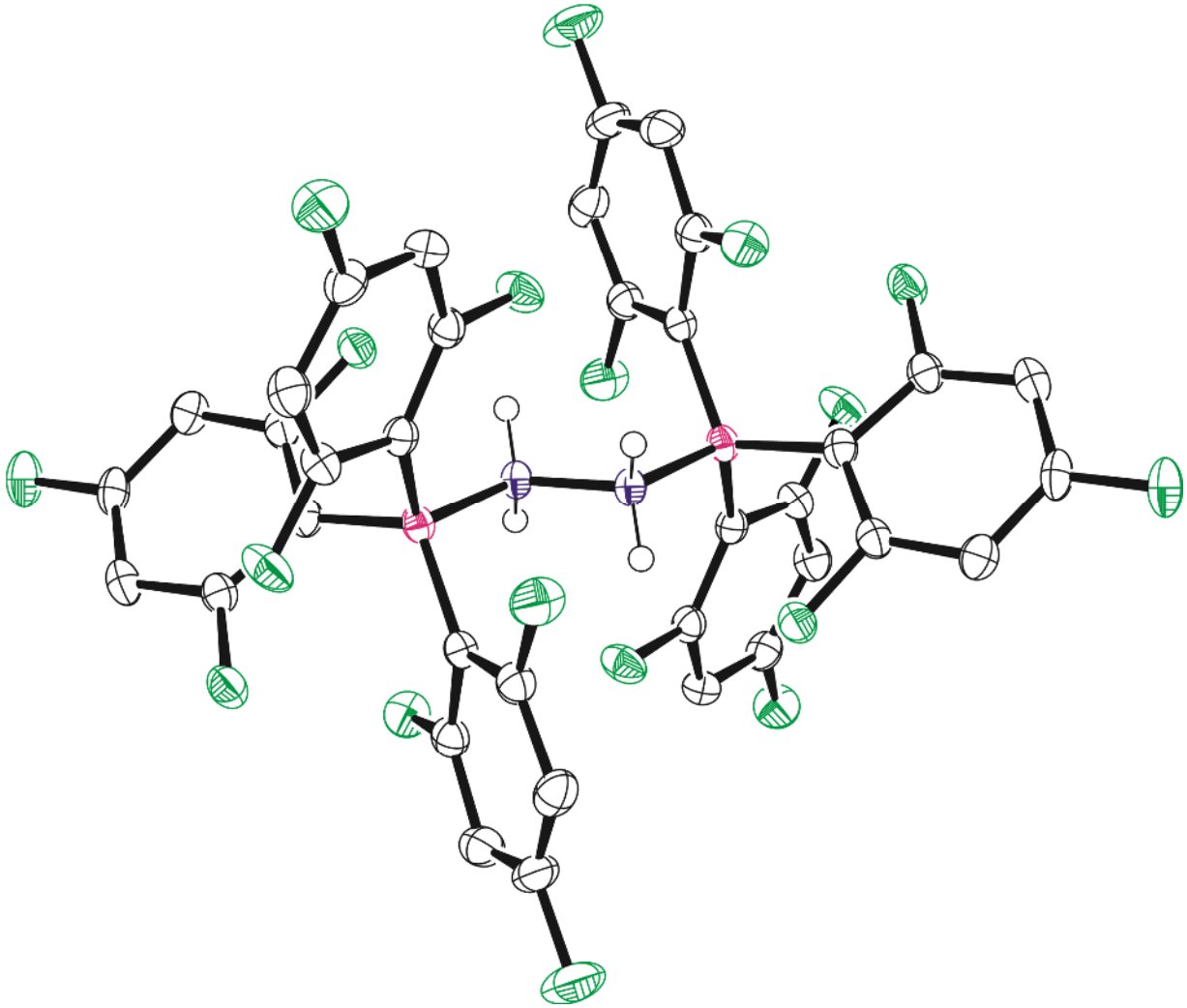


Figure S50 Solid-state structure of compound **5**, thermal ellipsoids drawn at the 50% probability level. H-atoms except for those on nitrogen omitted for clarity.

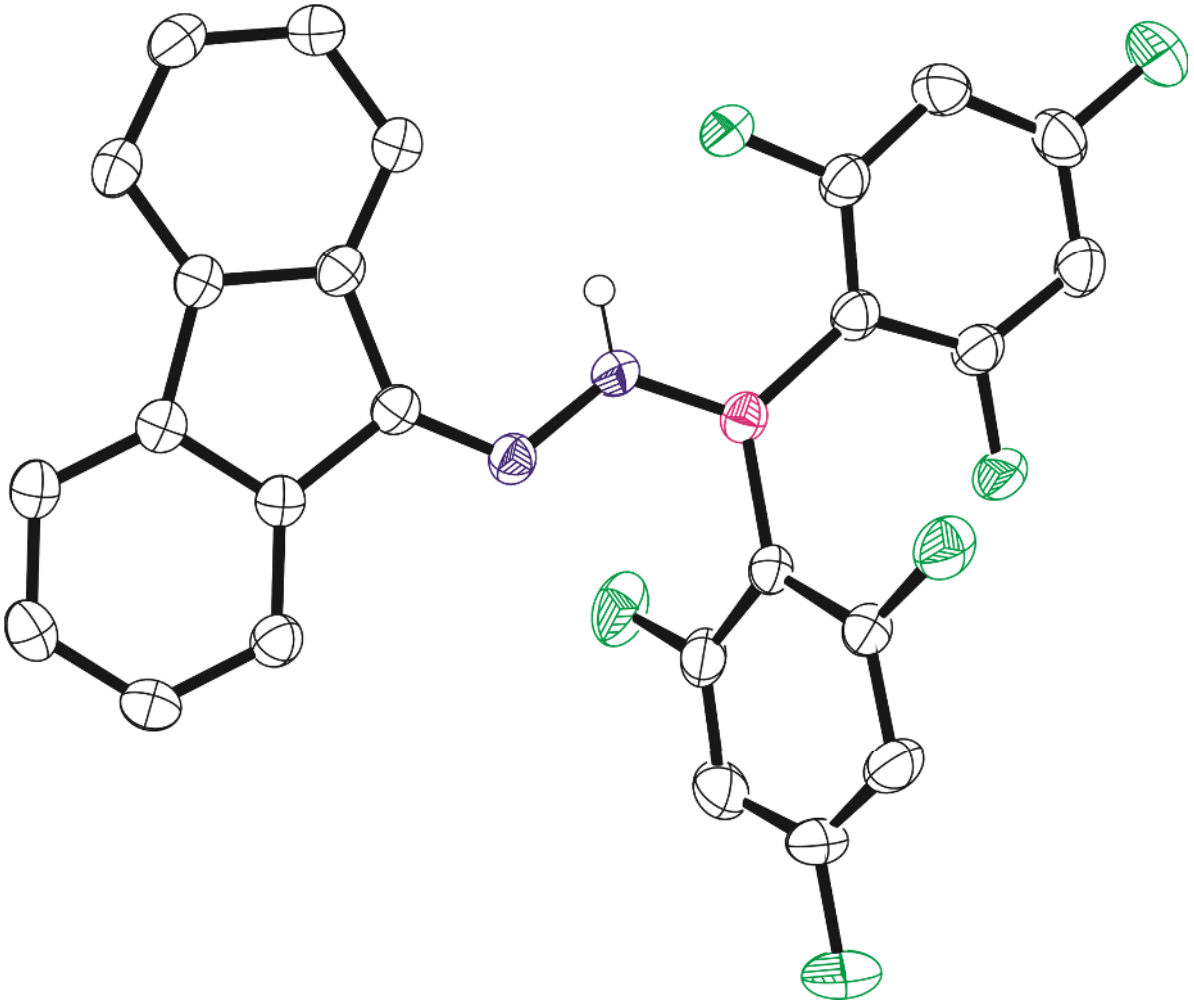


Figure S51 Solid-state structure of compound **6a**, thermal ellipsoids drawn at the 50% probability level. H-atoms except for those on nitrogen omitted for clarity.

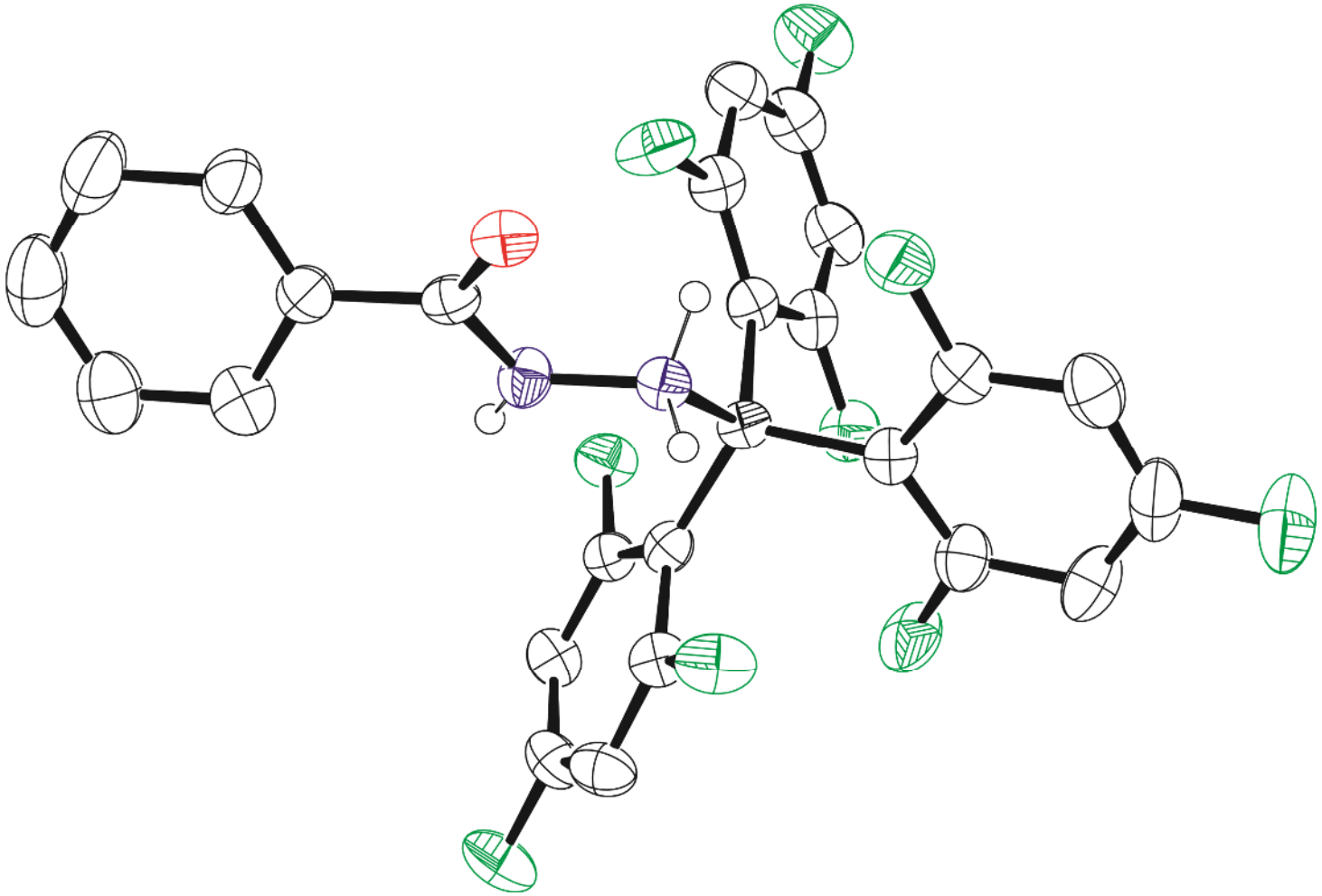


Figure S52 Solid-state structure of compound **6b**, thermal ellipsoids drawn at the 50% probability level. H-atoms except for those on nitrogen omitted for clarity.

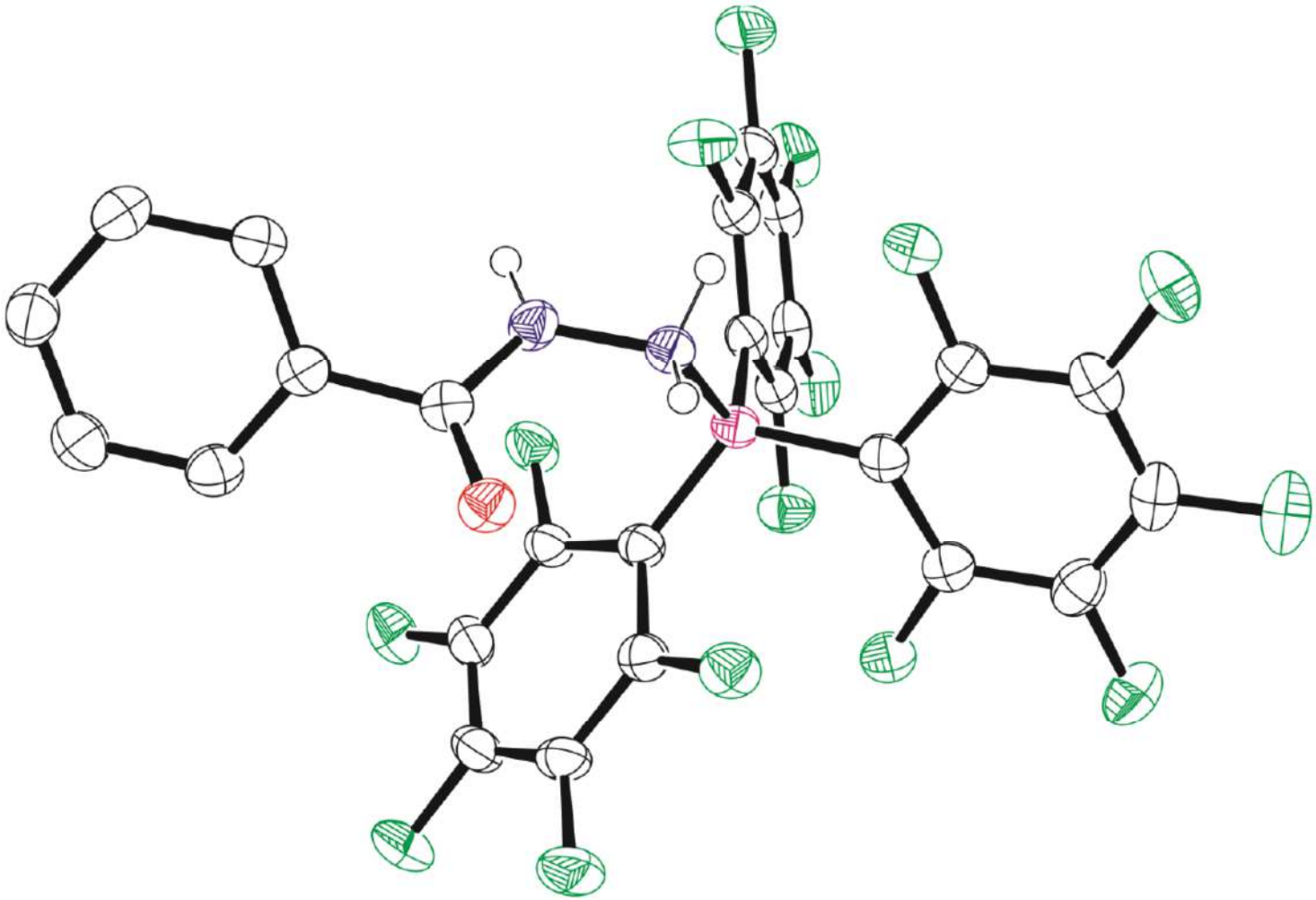
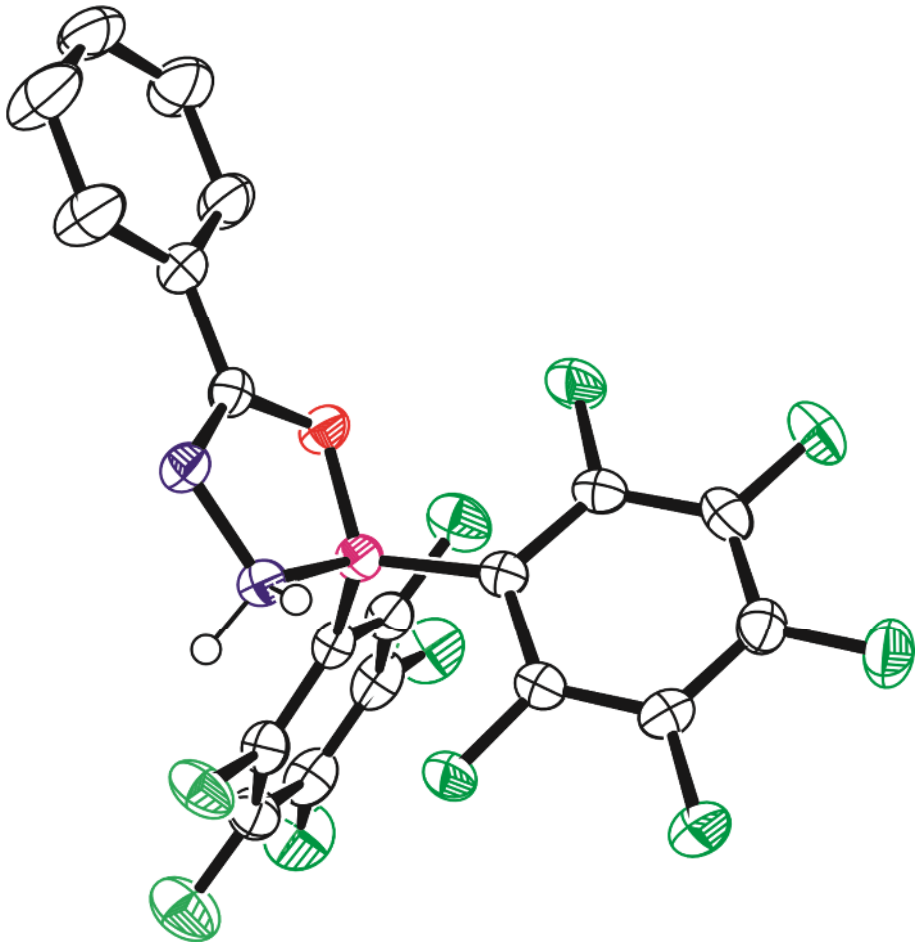


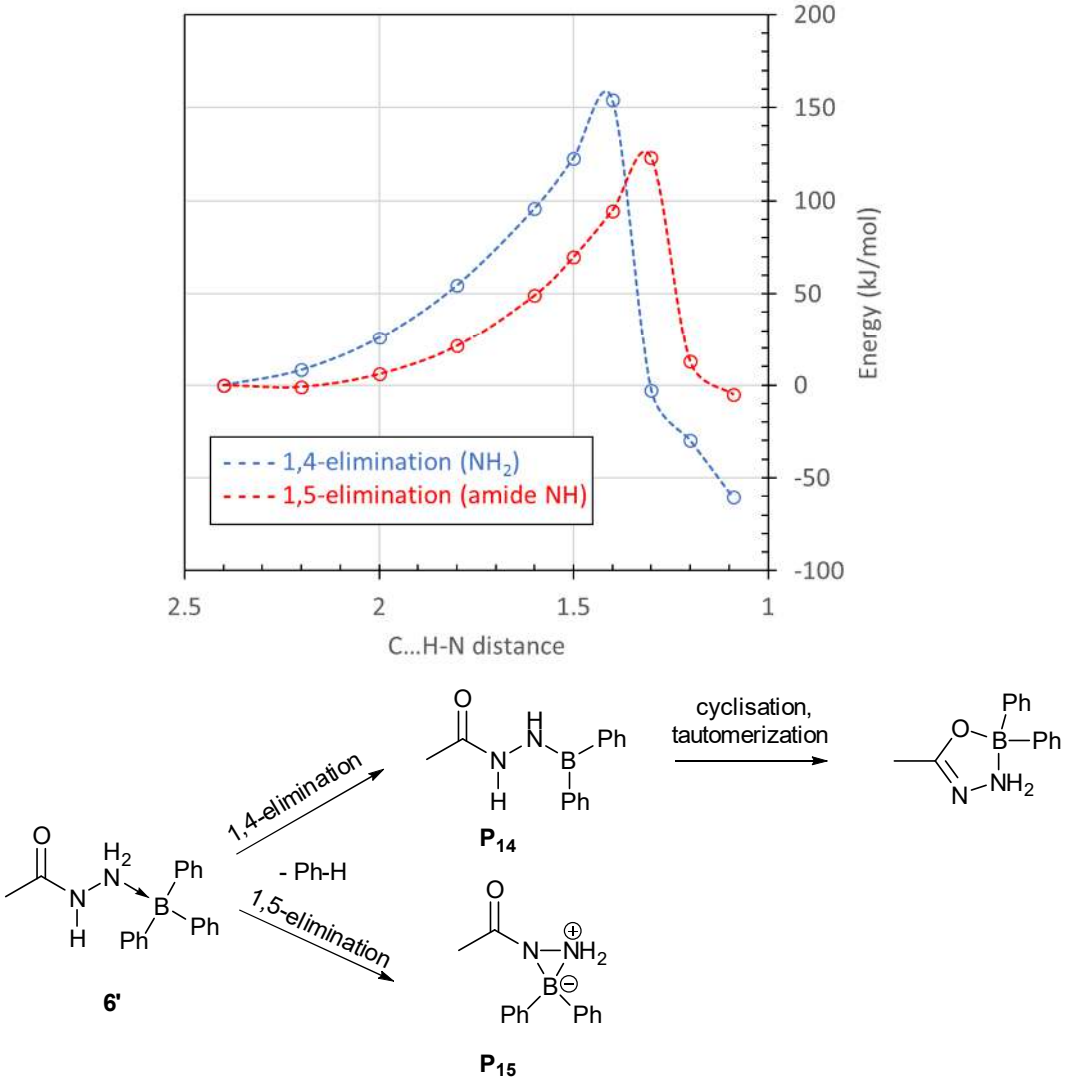
Figure S53 Solid-state structure of compound **7**, thermal ellipsoids drawn at the 50% probability level. H-atoms except for those on nitrogen omitted for clarity.



4 DFT Studies

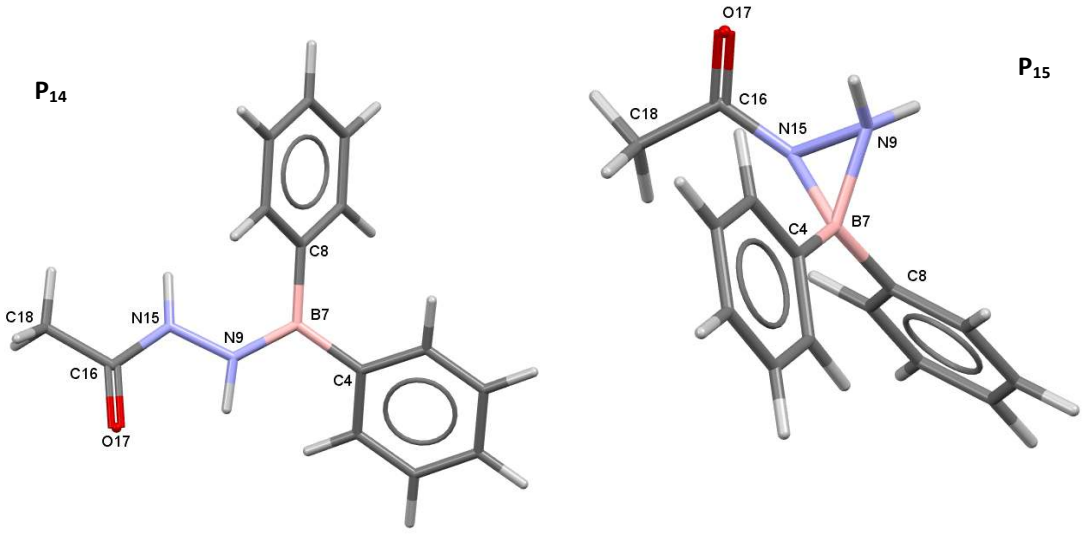
The observed elimination of Ar-H from **6a** – **6b** was probed by DFT with a view to probing the relative ease of 1,4- vs 1,5-elimination. A slightly simplified model (**6'**, Figure S54) was used in which the phenyl group of **6a** was replaced by a methyl group and the fluoroaryl rings of the borane were replaced by phenyl rings. This structure was initially geometry minimized using an initial force field model, followed by a full DFT geometry-optimization. All calculations implemented the B3LYP functional and 6-31G(d,p) basis set within Jaguar[11] using an a posteriori D3-correction for dispersion.[12]

Figure S54 Molecular structure of **6'** implemented for elimination calculations



The possibility of elimination was considered using both the amide N-H group (a 1,5-elimination) and the amine NH_2 group (a 1,4-elimination) affording products **P_{15}** and **P_{14}** respectively (Figure S54). In each case, a series of geometry-optimizations (B3LYP-D3/6-31G(d,p)) were undertaken using restricted intramolecular N-H···C-B distances ranging from 2.40 to 1.09 Å, permitting the geometry to relax during each step in the C···H bond forming process. The dispersion term proved not to affect the reaction profiles significantly and the computed energy dependence for 1,4- and 1,5-elimination (excluding the D3 correction) are plotted in Figure S54. Initial shortening of the N-H···C-B distance is more easily achieved for the less-strained 1,5-elimination, i.e. implementing the amide N-H group but converged to a strained three-membered BN_2 ring (**P_{15}**), an overall near energy-neutral process (Figure S54). The 1,4-elimination requires a higher activation energy but leads to a more energetically favorable product (**P_{14}**) in which the core structure is close to planarity reflecting extensive π-conjugation throughout the structure and can be formally considered a 5 centre (OCNNB), 6π e^- system (Figure S55). Thus 1,4-elimination appears as the thermodynamic process whereas 1,5-elimination appears to be the kinetic process. The flexibility in the initially-formed acyclic **P_{14}** framework should favour intramolecular C=O→B coordination (at the expense of some loss in π-stabilization) and cyclization, followed by tautomerization to form the observed cyclic product (tautomerization prior to ring closure appears less likely as it will break the π-conjugation in the system).

Figure S55 Structures and selected geometric parameters for elimination products **P_{14}** and **P_{15}** (sum of angles for an idealized trigonal planar geometry = 360° and for a tetrahedral geometry = 656.82°)



Distances/Å			**Distances/Å**	
C18-C16		1.515	C18-C16	1.507
C16-O17		1.233	C16-O17	1.230
C16-N15		1.363	C16-N15	1.384
N15-N9		1.394	N15-N9	1.449
N9-B7	1.408		N9-B7	1.656
B7-C4	1.570		B7-C4	1.593
B7-C8	1.578		B7-C8	1.588
			B7-N15	1.536
Sum of angles/º			**Sum of angles/º**	
C16	360.0		C16	360.0
N15	357.9		N15	317.5
N9	360.0		N9	641.2
B7	360.0		B7	637.9

5 References

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