Supporting Information

Charge Transfer Fluorescence in Imine Borane Adducts Towards a Vapochromic Litmus Test

Yashar Soltani, Samuel J. Adams, Jennifer Börger, Lewis C. Wilkins, Paul D. Newman, Simon J. A. Pope*, Rebecca L. Melen*

School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, Cymru/Wales, United Kingdom

Contents

1. Experimental

1.1 General experimental

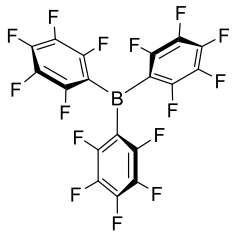
All reactions and manipulations were carried out under an atmosphere of dry, O_2-free nitrogen using standard double-manifold techniques with a rotary oil pump. An argon- or nitrogen-filled glove box (MBraun) was used to manipulate solids including the storage of starting materials, room temperature reactions, product recovery and sample preparation for analysis. The solvent (CH_2Cl_2) was dried by employing a Grubbs-type column system (Innovative Technology) or a solvent purification system MB SPS-800 and stored under a nitrogen atmosphere. The NEt_3 used in the imine formation reactions was dried over 3 Å molecular sieves. The $CHCl_3$ for the UV/vis and Fluorescence measurements was dried over CaH_2, distilled and degassed. Deuterated solvents were distilled and/or dried over molecular sieves before use. Chemicals were purchased from commercial suppliers and used as received. ^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR spectra were recorded on a Bruker Avance 300 or Bruker Avance II 400. 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 PPh_3 (^{31}P), and $BF_3{\cdot}Et_2O/CDCl_3$ (^{11}B). The description of signals include: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sep = septet, 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. Mass spectra were measured on a Waters LCT Premier/XE or a Waters GCT Premier spectrometer.

UV-Visible absorption studies were performed on a Shimadzu UV-1800 spectrophotometer a $CHCl_3$ solutions (1×10^{-5} M) unless otherwise stated. Photophysical data were obtained on a JobinYvon–Horiba Fluorolog spectrometer fitted with a JY TBX picosecond photodetection module as $CHCl_3$ solutions unless otherwise stated. Solid-state luminescence samples were prepared by filling a cuvette with a 10^{-3} M solution of the compound and then removing the solvent under vacuum to leave a film on the wall of the cuvette. Emission spectra were uncorrected and excitation spectra were instrument corrected. The pulsed source was a Nano-LED configured for 295 nm output operating at 1 MHz. Luminescence lifetime profiles were obtained using the JobinYvon–Horiba FluoroHub single photon counting module and the data fits yielded the lifetime values using the provided DAS6 deconvolution software.

1.2 Synthesis of starting materials.

1.2.1 Synthesis of the borane reagents.

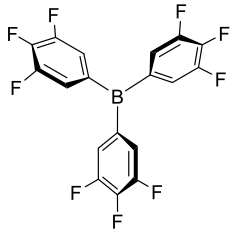
Tris(pentafluorophenyl) borane.



Tris(pentafluorophenyl)borane was synthesised in a procedure used previously[1] whereby magnesium turnings (1.1 g, 45 mmol, 1 equiv.) were suspended in Et_2O (100 ml) to which C_6F_5Br (5.6 ml, 45 mmol, 3 equiv.) was added dropwise over the course of 30 minutes whilst stirring, without allowing the mixture to reach reflux. After stirring at ambient temperature for 30 mins, this 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 (100 ml). The excess Et_2O solvent was removed under vacuum leaving the mixture as a toluene solution. The reaction was then set to react at 100 °C for 1 h then left to cool to ambient temperature. The remaining solvent was removed under reduced pressure whilst gently heating in an oil bath until a brown cake remains. This was the subject to a two-fold sublimation (110 °C, 1 x 10^{-3} mbar) whereupon the pure $B(C_6F_5)_3$ was collected as a white microcrystalline solid. Yield: 6.7 g, 13.2 mmol, 88%. The spectroscopic data agrees with literature established values.[1] **^{11}B NMR** (128 MHz, $CDCl_3$, 298

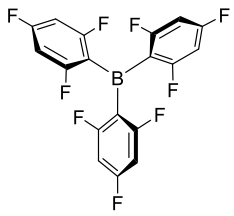
K) δ/ppm: 59.6 (br. s). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ/ppm: -127.73 (br. s, 6F, *o*-F), -142.46 (br. s, 3F, *p*-F), -159.83 (br. s, 6F, *m*-F).

Tris(3,4,5-trifluorophenyl) borane.



A solution of 5-Bromo-1,2,3-trifluorobenzene (3.5 ml, 29.4 mmol, 1 equiv) in diethylether (50 ml, dry) was cooled to -78 °C under nitrogen and ^{n}BuLi (20 ml, 1.47 M, 29.4 mmol, 1 equiv) in hexane was added dropwise. The solution turns yellow and is stirred for an additional 2 h to turn in to a white suspension. $BF_3{\cdot}OEt_2$ (1.2 ml, 9.8 mmol, 0.33 equiv) was added dropwise and the mixture was allowed to warm to room temperature and stirred overnight. After removing the solvent *in vacuo*, the solid residue was sublimed and the yielding oily yellow crystals were washed with pentane and sublimed again to give white crystals (0.65 g, 1.61 mmol 16%). Spectroscopic data agrees with literature values.[2] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.07 (t, $^{3}J_{HF}$ = 7.4 Hz, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$, 298 K) δ/ppm: 151.3 (ddd, $^{1}J_{CF}$ = 254.0 Hz, $^{2}J_{CF}$ = 9.6 Hz, $^{3}J_{CF}$ = 2.7 Hz), 143.0 (dt, $^{1}J_{CF}$ = 260.9, $^{2}J_{CF}$ = 15.0 Hz), 136.5–136.0 (m), 122.0 (dd, $^{2}J_{CF}$ = 13.6, $^{3}J_{CF}$ = 5.4 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ/ppm: -133.2 (d, $^{3}J_{FF}$ = 20.1 Hz, *m*-F), -152.4 (t, $^{3}J_{FF}$ = 20.1 Hz, *p*-F). **^{11}B NMR** (160 MHz, $CDCl_3$, 298 K) δ/ppm: 64.6 ppm.

Tris(2,4,6-trifluorophenyl) borane.

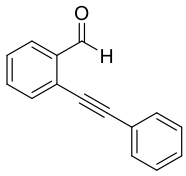


According to the literature,[3] using 1-bromo-2,4,6-trifluorobenzene (3.50 ml, 30 mmol, 3 equiv.) was dissolved in freshly distilled THF (100 ml) and cooled to -20 °C. At this temperature ^{i}PrMgCl (15 ml, 30 mmol, 3 equiv.) was added dropwise. The reaction mixture was then allowed to reach 0 °C and after 1 h at this temperature cooled again to -50 °C. Subsequently, $BF_3{\cdot}Et_2O$ (1.23 ml, 10 mmol, 1 equiv.) was added dropwise and after 1 h the cooling bath was removed and the reaction mixture warmed to room temperature within another hour. Removal of all volatiles and a two-fold sublimation of the remaining solid (120 °C, 1 x 10^{-3} mbar) afforded the pure product (3.35 g, 8.3 mmol, 83%). Spectroscopic analyses agree with literature values.[3] **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 6.64 (t, $^{3}J_{HF}$ = 8.3 Hz, 6H, aryl). **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) δ/ppm: 58.4 (br. s). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ/ppm: -95.75 (d, $^{4}J_{FF}$ = 10.4 Hz, 6F, *o*-F), -100.31 (t, $^{4}J_{FF}$ = 10.4 Hz, 3F, *p*-F).

1.2.2 Synthesis of the aldehyde reagents.

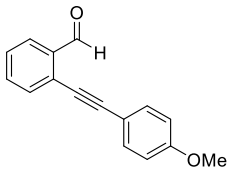
General procedure 1: In accordance with the literature[4] CuI (1 mol%), $Pd(PPh_3)_2Cl_2$ (2 mol%) and the corresponding aldehyde (1.0 equiv.) were stirred in dry NEt_3. The acetylene reagent (1.2 equiv.) was added slowly at room temperature. The reaction mixture was heated up to 60 °C for 19 h. After cooling the solution to room temperature, the suspension was filtered using a silica plug and washed with Et_2O (2 x 10 ml). The solvent was removed *in vacuo* and the crude product was purified by column chromatography. The resultant oil was distilled to give the desired product.

2-(phenylethynyl)benzaldehyde (1a).



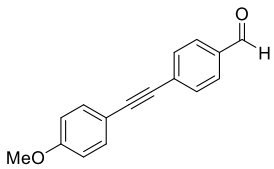
In accordance to *General procedure 1*, CuI (20.6 mg, 0.11 mmol, 1 mol%), $Pd(PPh_3)_2Cl_2$ (151 mg, 0.22 mmol, 2 mol%) and 2-bromobenzaldehyde (1.26 ml, 11 mmol, 1.0 equiv.) and phenylacetylene (1.42 mL, 13 mmol, 1.2 equiv.) in dry NEt_3 (40 ml) were used to synthesis the compound **1a**. The crude product was purified by column (SiO_2, hexane/EtOAc, 50:1). The oil was distilled (180 °C, 15 mmHg) to give the desired product as an oil. Yield: 2.19 g, 9.70 mmol, 90%. Spectroscopic data agrees with literature known values.[4] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 10.66 (d, $^4J_{HH}$ = 0.8 Hz, 1H), 7.95 (ddd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.5 Hz, $^4J_{HH}$ = 0.6 Hz, 1H), 7.63 (ddd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.5 Hz, $^4J_{HH}$ = 0.6 Hz, 1H), 7.59–7.53 (m, 3H), 7.49–7.44 (m, 1H), 7.40–7.35 (m, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 191.8 (s), 135.9 (s), 133.9 (s), 133.3 (s), 131.8 (s), 129.2 (s), 128.7 (s), 128.6 (s), 127.3 (s), 126.9 (s), 122.4 (s), 96.4 (s), 85.0 (s).

2-((4-methoxyphenyl)ethynyl)benzaldehyde (1b).



In accordance to *General procedure 1*, CuI (42 mg, 0.22 mmol, 4 mol%), $Pd(PPh_3)_2Cl_2$ (78 mg, 0.11 mmol, 2 mol%), 2-ethynylbenzaldehyde (0.94 g, 7.22 mmol, 1.3 equiv.) and 4-iodoanisol (1.30 g, 11 mmol, 1.0 equiv.) in dry NEt_3 (50 ml) were used to synthesise compound **1b**. The crude product was purified by column (SiO_2, hexane/EtOAc, 40:1, gradient to 35:1). The resulting orange oil was recrystallised from CH_2Cl_2/Hexane. The product was isolated as a colourless solid. Yield: 0.602 g, 2.5 mmol, 46%. Spectroscopic data agrees with literature known values.[4] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 10.65 (d, $^4J_{HH}$ = 0.8 Hz, 1H), 7.94 (ddd, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.4 Hz, $^4J_{HH}$ = 0.6 Hz, 1H), 7.65–7.55 (m, 2H), 7.54–7.48 (m, 2H), 7.43 (m, 1H), 6.94–6.88 (m, 2H), 3.85 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 192.0 (s), 160.4 (s), 135.8 (s), 133.9 (s), 133.4 (s), 133.2 (s), 128.4 (s), 127.5 (s), 127.3 (s), 114.5 (s), 114.3 (s), 96.7 (s), 83.9 (s), 55.5 (s).

4-((4-methoxyphenyl)ethynyl)benzaldehyde (1c).



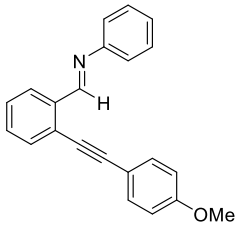
In accordance with *General procedure 1*, CuI (15 mg, 0.08 mmol, 1 mol%), $Pd(PPh_3)_2Cl_2$ (114 mg, 0.17 mmol, 2 mol%), 4-ethynylanisole (1.05 ml, 8.1 mmol, 1.0 equiv.) and 4-bromobenzaldehyde (1.80 g, 9.7 mmol, 1.2 equiv.) in dry NEt_3 (60 ml) were used to synthesise compound **1c**. The crude product was purified by column (SiO_2, hexane/EtOAc, 40:1, gradient to 10:1). The product was isolated as a white solid. Yield: 1.29 g, 5.5 mmol, 67%. Spectroscopic data agrees with literature known values.[4] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 10.01 (s, 1H), 7.89–7.81 (m, 2H), 7.68–7.62 (m, 2H), 7.53–7.48 (m, 2H), 6.95–6.87 (m, 2H), 3.85 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 191.6 (s), 160.3 (s), 135.2 (s), 133.5 (s), 132.0 (s), 130.2 (s), 129.7 (s), 114.7 (s), 114.3 (s), 93.9 (s), 87.6 (s), 55.5 (s).

1.2.3 Synthesis of the imine reagents.

General procedure 2: The aldehyde (1.0 equiv.) was dissolved in dry CH_2Cl_2 with molecular sieves. The amine (4.0 equiv.) was added slowly. The reaction mixture was stirred for 18 h at room temperature. The solution was filtered and washed with CH_2Cl_2 (2 x 10 ml). The solvent was removed *in vacuo*. The crude product was dried under vacuum to remove any unreacted amine.

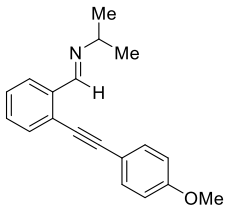
General procedure 3: The aldehyde (1.0 equiv.) was solved in dry CH_2Cl_2 with $MgSO_4$. The amine (4.0 equiv.) was added slowly. The reaction mixture was stirred for 18 h at room temperature. The solution was filtrated and washed with CH_2Cl_2. The solvent was removed *in vacuo* with the crude product being dried over $MgSO_4$, and the volatiles removed *in vacuo*.

_N_-(2-((4-methoxyphenyl)ethynyl)benzylidene)aniline (2a).



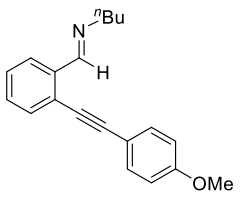
In accordance with *General procedure 2*, **2a** was synthesised using **1b** (100 mg, 0.42 mmol, 1.0 equiv.) and aniline (0.15 ml, 1.7 mmol, 4.0 equiv.) in CH_2Cl_2 (2.5 ml). The product was isolated as an orange oil. Yield: 83 mg, 0.27 mmol, 63%. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 9.10 (s, 1H), 8.30–8.24 (m, 1H), 7.61–7.57 (m, 1H), 7.50–7.46 (m, 2H), 7.44–7.40 (m, 2H), 7.18–7.13 (m, 2H), 6.91–6.87 (m, 2H), 6.76 (tt, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.0 Hz, 1H), 6.71–6.68 (m, 2H), 3.84 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 160.1 (s), 159.2 (s), 152.4 (s), 136.6 (s), 133.2 (s), 132.7 (s), 131.0 (s), 129.4 (s), 129.4 (s), 128.5 (s), 126.7 (s), 126.2 (s), 121.2 (s), 118.7 (s), 115.2 (s), 114.3 (s), 95.7 (s), 85.2 (s), 55.5 (s). **HRMS** (ES^+) *m/z* calculated for $[C_{22}H_{18}NO]^+$ $[M+H]^+$: 312.1388, found: 312.1388.

_N_-isopropyl-1-(2-((4-methoxyphenyl)ethynyl)phenyl)methanimine (2b).



In accordance with *General procedure 2*, **2b** was synthesised using **1b** (150 mg, 0.64 mmol, 1.0 equiv.) and isopropylamine (0.22 ml, 2.6 mmol, 4.0 equiv.) in CH_2Cl_2 (2.5 ml). The product was isolated as a yellow oil. Yield: 58 mg, 0.21 mmol, 33%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.90 (d, $^4J_{HH}$ = 0.8 Hz, 1H), 8.09–8.03 (m, 1H), 7.57–7.46 (m, 3H), 7.41–7.29 (m, 2H), 6.94–6.87 (m, 2H), 3.85 (s, 3H), 3.63 (pd, $^3J_{HH}$ = 6.3 Hz, $^4J_{HH}$ = 0.8 Hz, 1H), 1.29 (d, $^3J_{HH}$ = 6.3 Hz, 6H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ/ppm: 160.0 (s), 157.2 (s), 137.0 (s), 133.1 (s), 132.4 (s), 130.1 (s), 128.4 (s), 126.5 (s), 124.3 (s), 115.2 (s), 114.2 (s), 95.0 (s), 85.4 (s), 62.0 (s), 55.5 (s), 24.4 (s). **HRMS** (ES^+) *m/z* calculated for $[C_{19}H_{20}NO]^+$ $[M+H]^+$: 278.1545, found: 278.1552.

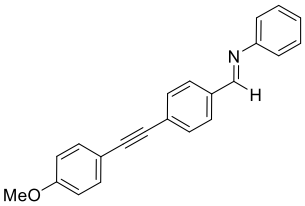
_N_-butyl-1-(2-((4-methoxyphenyl)ethynyl)phenyl)methanimine (2c).



In accordance with *General procedure 2*, **2c** was synthesised using **1b** (270 mg, 1.1 mmol, 1.0 equiv.) and *n*-butylamine (0.45 ml, 4.4 mmol, 4.0 equiv.) in CH_2Cl_2 (4 ml). The product was isolated as a yellow solid. Yield: 191 mg, 0.65 mmol, 57%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.87 (d, $^4J_{HH}$ = 1.4 Hz, 1H), 8.04 (dd, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.9 Hz, 1H), 7.58–7.46 (m, 3H), 7.42–7.29 (m, 2H), 6.97–6.86 (m, 2H), 3.84 (s, 3H), 3.68 (td, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 1.4 Hz, 2H), 1.79–1.66 (m, 2H), 1.49–1.34 (m, 2H), 0.96 (t, $^3J_{HH}$ = 7.4 Hz,

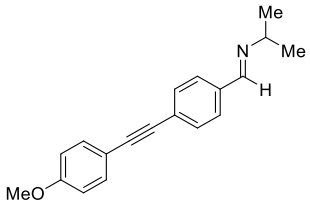
3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 207.2 (s), 160.0 (s), 159.7 (s), 136.8 (s), 133.1 (s), 132.5 (s), 130.1 (s), 128.4 (s), 126.3 (s), 124.4 (s), 115.2 (s), 114.2 (s), 95.0 (s), 85.4 (s), 61.8 (s), 55.5 (s), 33.1 (s), 20.6 (s), 14.1 (s). **HRMS** (ES^+) *m/z* calculated for $[C_{20}H_{22}NO]^+$ $[M+H]^+$ 292.1701 found: 292.1700.

1-(4-((4-methoxyphenyl)ethynyl)phenyl)-*N*-phenylmethanimine (2d).



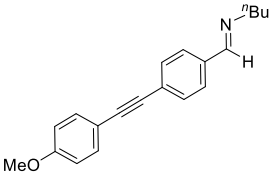
In accordance with *General procedure 3*, **2d** was synthesised using **1c** (150 mg, 0.63 mmol, 1.0 equiv.) and aniline (0.23 ml, 2.5 mmol, 4.0 equiv.) in CH_2Cl_2 (2 ml). The product was isolated as a light-yellow solid. Yield: 52.3 mg, 0.17 mmol, 26%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.46 (s, 1H), 7.92–7.85 (m, 2H), 7.64–7.58 (m, 2H), 7.53–7.47 (m, 2H), 7.44–7.38 (m, 2H), 7.29–7.20 (m, 3H), 6.93–6.87 (m, 2H), 3.84 (d, $^{4}J_{HH}$ = 0.5 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ/ppm: 207.2 (s), 160.0 (s), 159.6 (s), 152.0 (s), 135.6 (s), 133.3 (s), 131.9 (s), 129.4 (s), 129.3 (s), 128.8 (s), 126.8 (s), 126.3 (s), 121.0 (s), 115.2 (s), 115.1 (s), 114.2 (s), 92.1 (s), 88.1 (s), 55.5 (s). **HRMS** (ES^+) *m/z* calculated for $[C_{22}H_{18}NO]^+$ $[M+H]^+$: 312.1388 found: 312.1387.

***N*-isopropyl-1-(4-((4-methoxyphenyl)ethynyl)phenyl)methanimine (2e).**



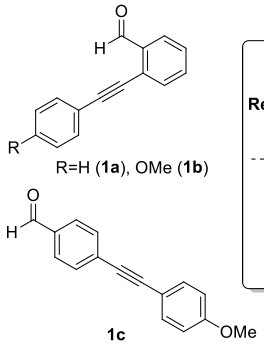
In accordance with *General procedure 2*, **2e** was synthesised using **1c** (250 mg, 1.1 mmol, 1.0 equiv.) and isopropylamine (0.36 ml, 4.2 mmol, 4.0 equiv.) in CH_2Cl_2 (4 ml). The product was isolated as a yellow solid. Yield: 50 mg, 0.18 mmol, 17%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.29 (s, 1H), 7.72–7.68 (m, 2H), 7.56–7.52 (m, 2H), 7.50–7.46 (m, 2H), 6.91–6.86 (m, 2H), 3.83 (s, 3H), 3.61–3.49 (m, 1H), 1.27 (d, $^{3}J_{HH}$ = 6.3 Hz, 6H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 159.9 (s), 157.8 (s), 135.9 (s), 133.3 (s), 131.7 (s), 128.1 (s), 125.7 (s), 115.3 (s), 114.2 (s), 91.3 (s), 88.1 (s), 61.9 (s), 55.5 (s), 24.3 (s). **HRMS** (ES^+) *m/z* calculated for $[C_{19}H_{20}NO]^+$ $[M+H]^+$: 277.1467, found: 277.1469.

***N*-butyl-1-(4-((4-methoxyphenyl)ethynyl)phenyl)methanimine (2f).**



In accordance with *General procedure 3*, **2f** was synthesised using **1c** (500 mg, 2.1 mmol, 1.0 equiv.) and *n*-butylamine (0.84 ml, 8.5 mmol, 4.0 equiv.) in CH_2Cl_2 (8 ml). The product was isolated as a yellow solid. Yield: 523 mg, 1.8 mmol, 85%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.26 (t, $^{4}J_{HH}$ = 1.3 Hz, 1H), 7.73–7.65 (m, 2H), 7.58–7.52 (m, 2H), 7.50–7.43 (m, 2H), 6.94–6.84 (m, 2H), 3.83 (s, 3H), 3.62 (td, $^{3}J_{HH}$ = 7.0 Hz, $^{4}J_{HH}$ = 1.3 Hz, 2H), 1.77–1.63 (m, 2H), 1.47–1.33 (m, 2H), 0.95 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ/ppm: 160.5 (s), 160.2 (s), 136.1 (s), 133.6 (s), 132.1 (s), 128.3 (s), 126.1 (s), 115.6 (s), 114.5 (s), 91.7 (s), 88.4 (s), 62.0 (s), 55.8 (s), 33.5 (s), 21.0 (s), 14.4 (s). **HRMS (ES^+)** *m/z* calculated for $[C_{20}H_{21}NO]^+$ $[M+H]^+$ 292.1701, found 292.1700.

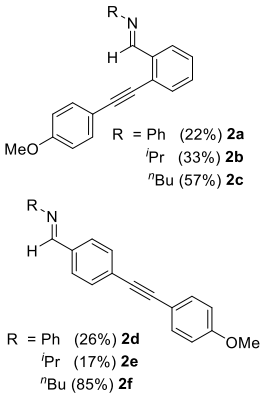
1.3 ^{11}B-NMR-Shifts of the adducts of aldehydes 1a–c and 2a–f with various boranes.



BR_3 R =	C_6F_5	2,4,6-$F_3C_6H_2$	C_6H_5
Relative Lewis acidity	100%	88%	68%
	Adduct Formation?		
1a	✓	✗	✗
1b	✓	✓	✗
1c	✓	✓	✗

Table 1: ^{11}B-NMR-Shift of the adducts of aldehydes **1a–c** and different boranes

Substrate	$B(C_6F_5)_3$	2,4,6-$BArF_9$	BPh_3
1a	4.5 ppm	✗	✗
1b	4.1 ppm	22.1 ppm	✗
1c	4.1 ppm	22.3 ppm	✗



BR_3 R =	C_6F_5	2,4,6-$F_3C_6H_2$	C_6H_5
Relative Lewis acidity	100%	88%	68%
	Adduct Formation?		
2a	✓	✗	✗
2b	✓	✓	✗
2c	✓	✓	✓
2d	✓	✗	✗
2e	✓	✓	✗
2f	✓	✓	✓

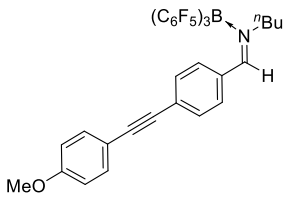
Table 2: ^{11}B-NMR-Shift of the adducts of imines **2a–e** with different boranes

Compound	$B(C_6F_5)_3$	2,4,6-$BArF_9$	BPh_3
2a	-5.3 ppm	✗	✗
2b	-5.0 ppm	-4.7 ppm	✗
2c	-3.7 ppm	-3.3 ppm	-1.8 ppm
2d	-5.1 ppm	✗	✗
2e	-4.0 ppm	-4.4 ppm	✗
2f	-3.5 ppm	-3.1 ppm	5.3 ppm

1.4 Synthesis of the borane adducts for UV-vis. measurements.

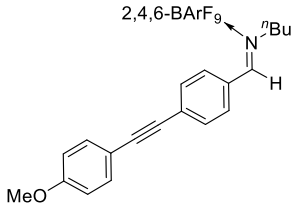
General procedure 4: The imine **2** (1.0 equiv.) was dissolved in $CDCl_3$ with subsequent addition to the borane (1.0 equiv.).

***N*-butyl-1-(4-((4-methoxyphenyl)ethynyl)phenyl)methanimine adduct with $B(C_6F_5)_3$.**



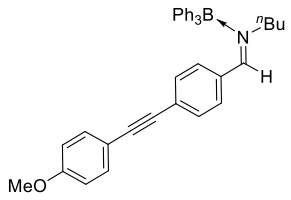
In accordance with *General procedure 4*, the adduct was synthesised using **2f** (29.1 mg, 0.10 mmol, 1.0 equiv.) and $B(C_6F_5)_3$ (51.2 mg, 0.10 mmol, 1.0 equiv.). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.57 (s, 1H), 7.74–7.68 (m, 2H), 7.66–7.60 (m, 2H), 7.54–7.49 (m, 2H), 6.97–6.88 (m, 2H), 4.25–3.96 (m, 2H), 3.85 (s, 3H), 1.07–0.91 (m, 2H), 0.59 (t, $^3J_{HH}$ = 7.3 Hz, 3H), 0.09 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 169.8 (s), 160.7 (s), 148.2 (dm, $^1J_{CF}$ = 247.5 Hz), 140.4 (dm, $^1J_{CF}$ = 248.9 Hz), 137.4 (dm, $^1J_{CF}$ = 255.2 Hz), 133.7 (s), 132.5 (s), 130.1 (s), 129.5 (s), 128.9 (s), 117.2 (s), 114.4 (s), 114.2 (s), 95.4 (s), 87.1 (s), 55.5 (s), 52.9 (s), 30.4 (s), 20.4 (s), 13.1 (s).**^{11}B NMR** (160 MHz, $CDCl_3$, 298 K) δ/ppm: -3.5 (br. s). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ/ppm: -127.83 (br. s, 1F), -128.72 (br. s, 1F), -129.23 (br. d, 1F), -130.55 (d, $^2J_{FF}$ = 21.8 Hz, 1F), -131.24 (br. s, 2F), -134.80 (s, 1F), -155.51 (br. d, 1F), -157.18 (t, $^2J_{FF}$ = 20.1 Hz, 1F), -159.94 (br. s, 1F), -162.92 (br. s, 2F), -163.39 (t, $^2J_{FF}$ = 18.8 Hz, 1F), -163.96 (m, 3F).

***N*-butyl-1-(4-((4-methoxyphenyl)ethynyl)phenyl)methanimine adduct with 2,4,6-$BArF_9$.**



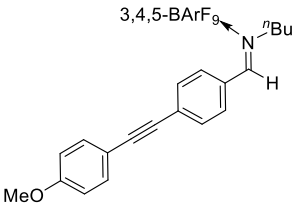
In accordance with *General procedure 4*, the adduct was synthesised using **2f** (29.1 mg, 0.10 mmol, 1.0 equiv.) and 2,4,6-$BArF_9$ (40.4 mg, 0.10 mmol, 1.0 equiv.). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.61 (s, 1H), 7.71–7.65 (m, 2H), 7.61–7.56 (m, 2H), 7.55–7.49 (m, 2H), 6.96–6.88 (m, 2H), 6.51 (t, $^3J_{HH}$ = 9.1 Hz, 6H), 4.08 (t, $^3J_{HH}$ = 11.6 Hz, 2H), 3.85 (s, 3H), 0.90 (pent., $^3J_{HH}$ = 7.2 Hz, 2H), 0.54 (t, $^3J_{HH}$ = 7.3 Hz, 3H), 0.10 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 168.1 (s), 166.1 (dt, $^2J_{CF}$ = 29.9 Hz, $^3J_{CF}$ = 12.4 Hz), 162.3 (dt, $^1J_{CF}$ = 244.9 Hz, $^3J_{CF}$ = 15.8 Hz), 160.5 (s), 133.6 (s), 132.3 (s), 130.2 (s), 128.9 (s), 128.7 (s), 117.4 (s), 114.4 (s), 114.4 (s), 100.1–99.1 (m), 94.1 (s), 87.2 (s), 55.5 (s), 52.7 (s), 30.5 (s), 20.6 (s), 13.2 (s).**^{11}B NMR** (160 MHz, $CDCl_3$, 298 K) δ/ppm: -3.1 (br. s).

***N*-butyl-1-(4-((4-methoxyphenyl)ethynyl)phenyl)methanimine adduct with BPh_3.**



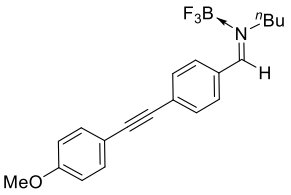
In accordance with *General procedure 4*, the adduct was synthesised using **2f** (29.1 mg, 0.10 mmol, 1.0 equiv.) and BPh_3 (24.2 mg, 0.10 mmol, 1.0 equiv.). **^{1}H NMR** (400 MHz, $CDCl_3$) δ/ppm: 8.16 (s, 1H), 7.61–7.36 (m, 21H), 6.82–6.75 (m, 2H), 3.72 (s, 3H), 1.64–1.55 (m, 2H), 1.36–1.25 (m, 2H), 1.17 (s, 2H), 0.86 (t, $^3J_{HH}$ = 7.4 Hz, 3H). **^{11}B NMR** (128 MHz, $CDCl_3$) δ/ppm: 4.3 (br. s). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 168.6 (s), 160.2 (s), 159.9 (s), 138.7 (s), 135.8 (s), 133.3 (s), 132.2 (s), 131.7 (s), 130.1 (s), 128.1 (s), 127.5 (s), 114.2 (s), 91.4 (s), 88.1 (s), 61.7 (s), 55.4 (s), 33.2 (s), 20.6 (s), 14.1 (s).

***N*-butyl-1-(4-((4-methoxyphenyl)ethynyl)phenyl)methanimine adduct with 3,4,5-$BArF_9$.**



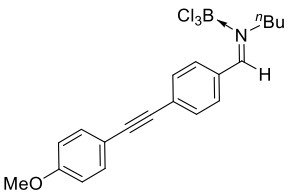
In accordance with *General procedure 4*, the adduct was synthesised using **2f** (29.1 mg, 0.10 mmol, 1.0 equiv.) and 3,4,5-$BArF_9$ (40.4 mg, 0.10 mmol, 1.0 equiv.). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.40 (s, 1H), 7.73 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 7.58 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 7.54–7.48 (m, 2H), 6.96–6.89 (m, 2H), 6.81 (dd, $^3J_{HH}$ = 8.9 Hz, $^3J_{HH}$ = 6.8 Hz, 6H), 3.85 (s, 3H), 3.82 (m, 2H), 1.29–1.18 (m, 3H), 1.14 (q, $^3J_{HH}$ = 7.1 Hz, 2H), 0.72 (t, $^3J_{HH}$ = 7.2 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ/ppm: 170.4 (s), 160.8 (s), 151.0 (ddd, $^1J_{CF}$ = 250.7 Hz, $^3J_{CF}$ = 9.2 Hz, $^4J_{CF}$ = 2.8 Hz), 145.6 (s), 138.3 (dt, $^1J_{CF}$ = 250.5 Hz, $^3J_{CF}$ = 15.5 Hz), 133.7 (s), 132.60 (s), 131.2 (s), 130.8 (s), 127.6 (s), 117.6 (dd, $^3J_{CF}$ = 13.5 Hz, $^4J_{CF}$ = 4.4 Hz), 114.4 (s), 114.1 (s), 96.1 (s), 87.0 (s), 55.5 (s), 52.2 (s), 30.7 (s), 20.0 (s), 13.3 (s). **^{11}B NMR** (160 MHz, $CDCl_3$, 298 K) δ/ppm: 2.9 (br. s). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ/ppm: -135.64 (d, $^3J_{FF}$ = 20.3 Hz, 2F), -163.82 (d, $^3J_{FF}$ = 20.3 Hz, 1F).

***N*-butyl-1-(4-((4-methoxyphenyl)ethynyl)phenyl)methanimine adduct with BF_3.**



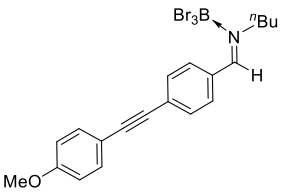
In accordance with *General procedure 4*, the adduct was synthesised using **2f** (29.1 mg, 0.10 mmol, 1.0 equiv.) and $BF_3{\cdot}OEt_2$ (12.7 µl, 0.10 mmol, 1.0 equiv.). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.29 (br. s, 1H), 7.98–7.92 (m, 2H), 7.61–7.56 (m, 2H), 7.51–7.45 (m, 2H), 6.92–6.83 (m, 2H), 3.82 (s, 3H), 1.84 (p, $^3J_{HH}$ = 7.5 Hz, 2H), 1.45–1.33 (m, 2H), 0.97 (t, $^3J_{HH}$ = 7.4 Hz, 3H), 0.91–0.81 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 170.4 (s), 160.5 (s), 133.6 (s), 131.5 (s), 130.5 (s), 128.2 (s), 114.4 (s), 114.3 (s), 95.1 (s), 87.6 (s), 61.1 (s), 55.5 (s), 32.3 (s), 32.3 (s), 20.0 (s), 13.7 (s). **^{11}B NMR** (160 MHz, $CDCl_3$, 298 K) δ/ppm: -0.1 (s). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ/ppm: -144.19 (s, 1F).

***N*-butyl-1-(4-((4-methoxyphenyl)ethynyl)phenyl)methanimine adduct with BCl_3.**



In accordance with *General procedure 4*, the adduct was synthesised using **2f** (29.1 mg, 0.10 mmol, 1.0 equiv.) and BCl_3 (100 µl, 1 M solution in CH_2Cl_2, 0.10 mmol, 1.0 equiv.). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 9.33 (dd, $^3J_{HH}$ = 9.7 Hz, $^4J_{HH}$ = 4.1 Hz, 1H), 8.15 (d, $^3J_{HH}$ = 8.6 Hz, 1H), 7.78 – 7.71 (m, 2H), 7.63–7.58 (m, 1H), 7.53–7.47 (m, 2H), 6.94–6.87 (m, 2H), 4.32–4.18 (m, 2H), 3.84 (s, 3H), 2.09–1.86 (m, 2H), 1.51–1.39 (m, 2H), 1.04–0.93 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 169.3 (s), 160.8 (s), 133.7 (s), 132.6 (s), 132.5 (s), 131.6 (s), 114.4 (s), 113.9 (s), 96.8 (s), 87.1 (s), 55.5 (s), 51.2 (s), 30.9 (s), 20.3 (s), 13.6 (s). **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) δ/ppm: 8.1 (s).

***N*-butyl-1-(4-((4-methoxyphenyl)ethynyl)phenyl)methanimine adduct with BBr_3.**



In accordance with *General procedure 4*, the adduct was synthesised using **2f** (29.1 mg, 0.10 mmol, 1.0 equiv.) and BBr_3 (9.5 µl, 0.10 mmol, 1.0 equiv.). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 9.61 (s, 1H), 7.82–7.72 (m, 4H), 7.54–7.50 (m, 2H), 6.94–6.90 (m, 2H), 3.85 (s, 3H), 1.54–1.40 (m, 2H), 1.25 (s, 3H), 1.02–0.94 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 170.6 (s), 160.8 (s), 133.8 (s), 132.8 (s), 132.6 (s), 131.6 (s), 130.5 (s), 114.4 (s), 113.9 (s), 97.3 (s), 87.3 (s), 55.5 (s), 52.4 (s), 29.8 (s), 20.3 (s), 13.6 (s). **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) δ/ppm: -7.1 (s).

1.5 Assessing Lewis acidity *via* the Gutmann-Beckett method.

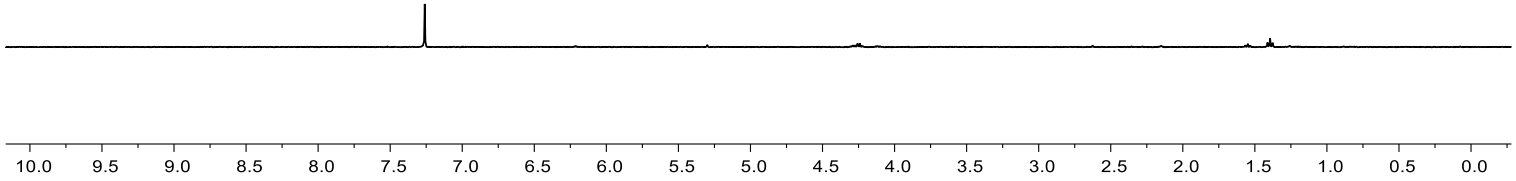
General procedure 5: The Lewis acidity was determined using the Gutmann-Beckett method. The borane (1.7 equiv.) was dissolved in $CDCl_3$ (0.5 ml) and added to triethylphosphine oxide (1.0 equiv.). A capillary with PPh_3 in $CHCl_3$ was added as a standard. The shift of the PPh_3 in $CDCl_3$ was calibrated to δ = -5.21 ppm according to Demchuk *et al.*[5] The acceptor number was calculated according to Beckett *et al.*[6] Relative Lewis acidities were calculated using the benchmark of $B(C_6F_5)_3$ as 100%.

Borane	^{31}P NMR chemical shift (δ/ppm)	Acceptor Number	Relative Lewis Acidity (%)
$B(C_6F_5)_3$	76.0	77.5	100
2,4,6-$BArF_9$	71.9	68.5	88
BPh_3	64.9	52.9	68
3,4,5-$BArF_9$	77.0	79.8	103
$BF_3{\cdot}OEt_2$	78.7	83.5	108
BCl_3	85.3	98.1	127
BBr_3	88.5	105.2	136

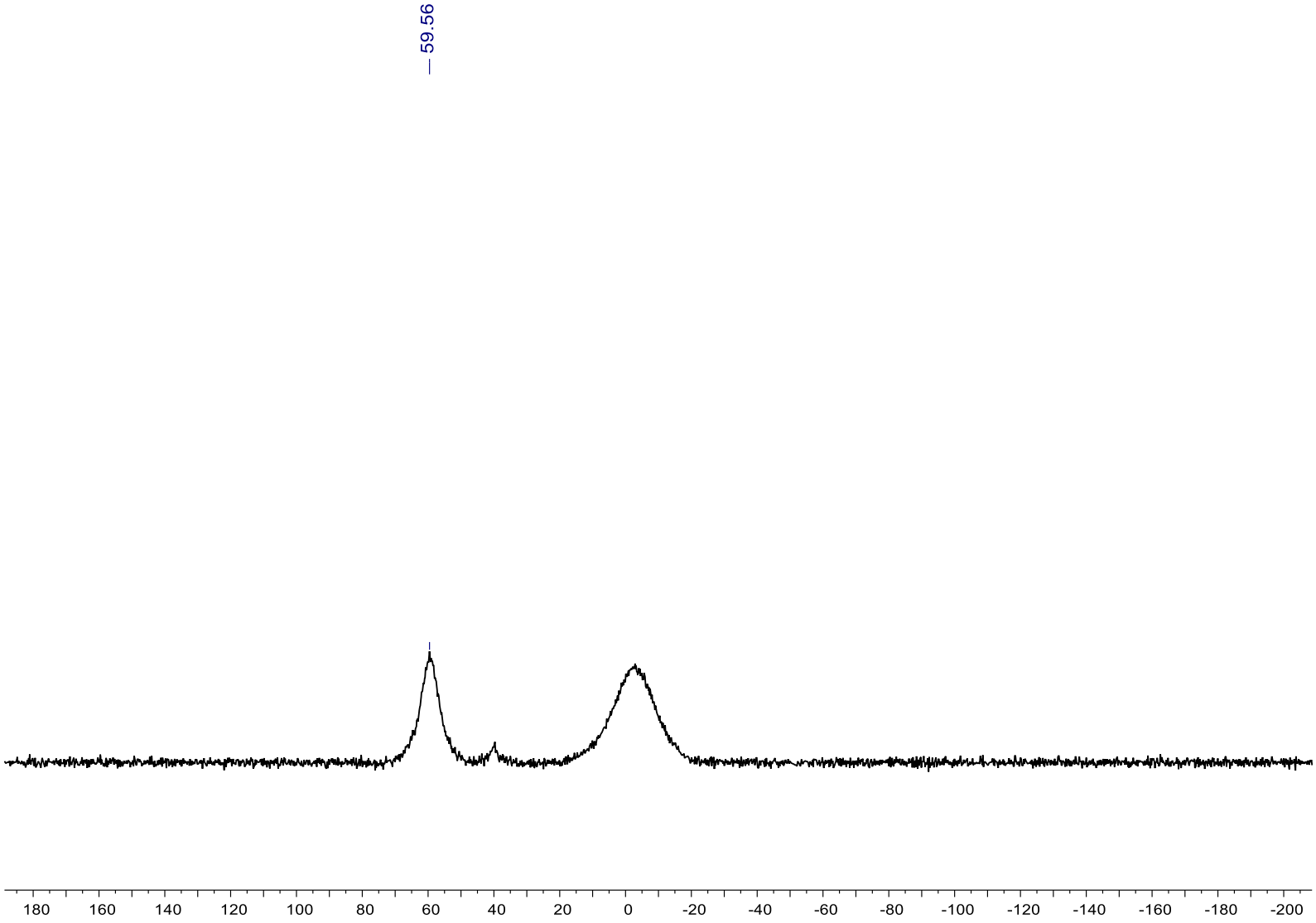
2. NMR spectra.

2.1 NMR spectra of borane reagents and starting materials **1**–**2**.

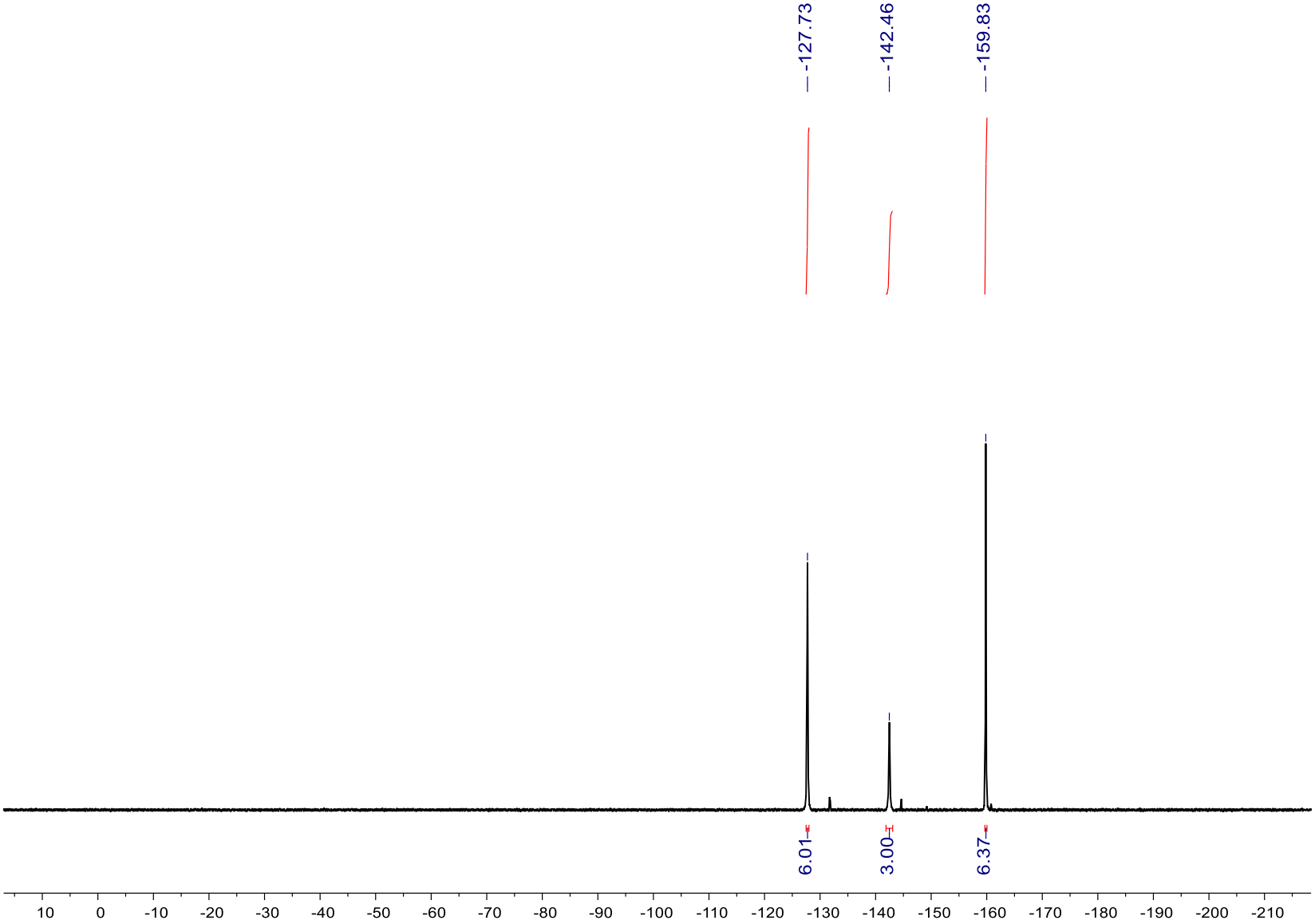
S1 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of tris(pentafluorophenyl)borane.



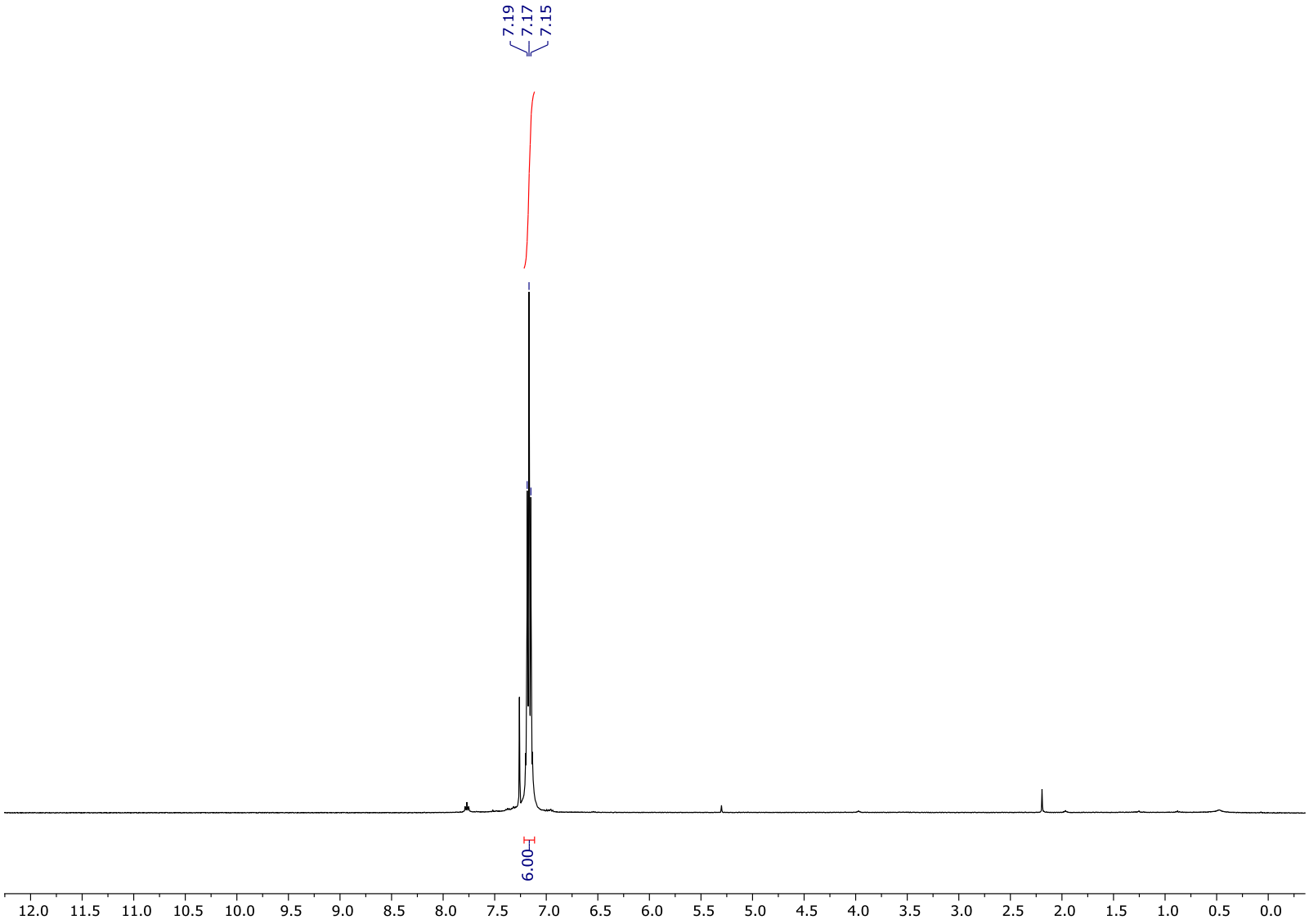
S2 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of tris(pentafluorophenyl)borane.



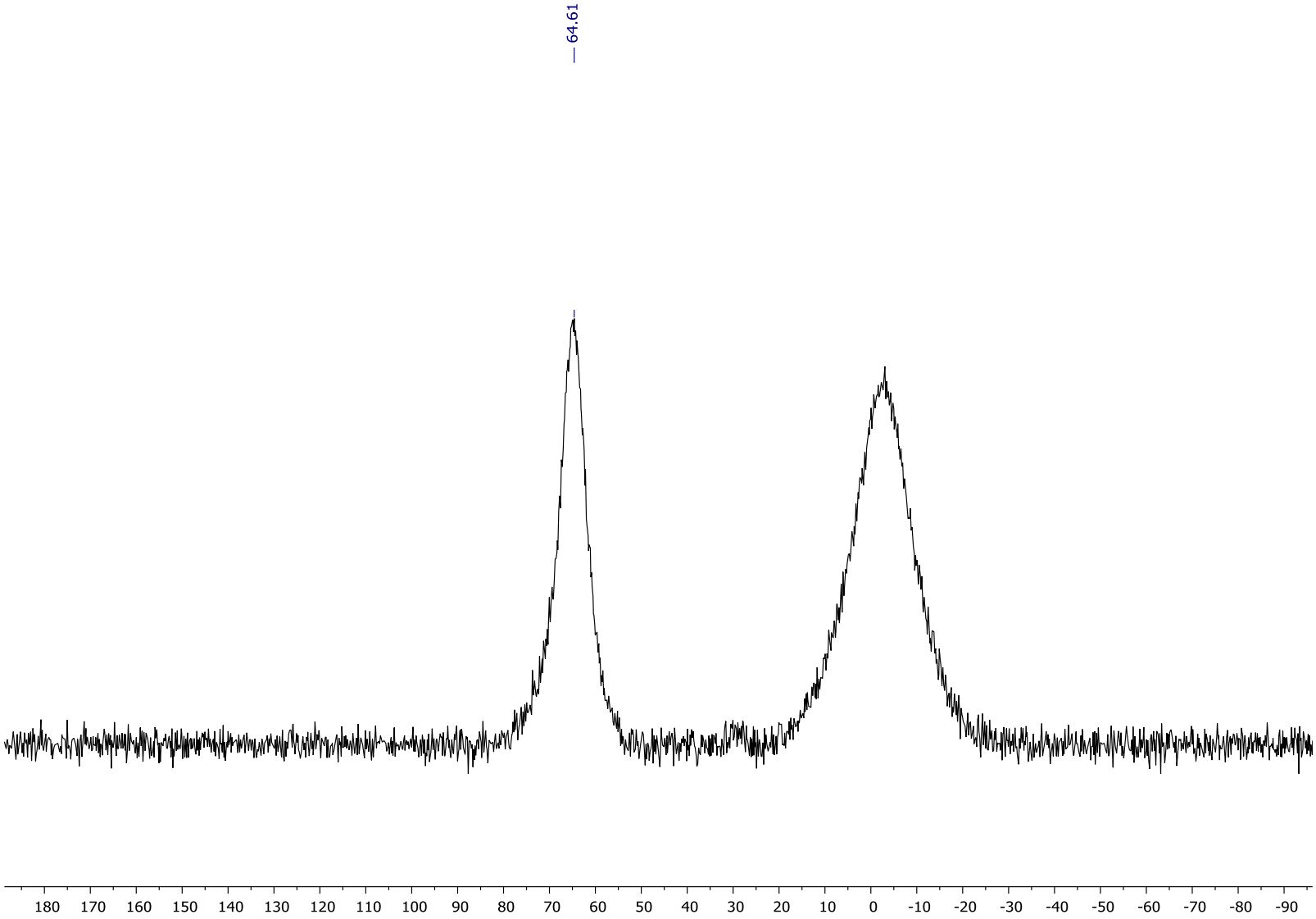
S3 ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) spectrum of tris(pentafluorophenyl)borane.



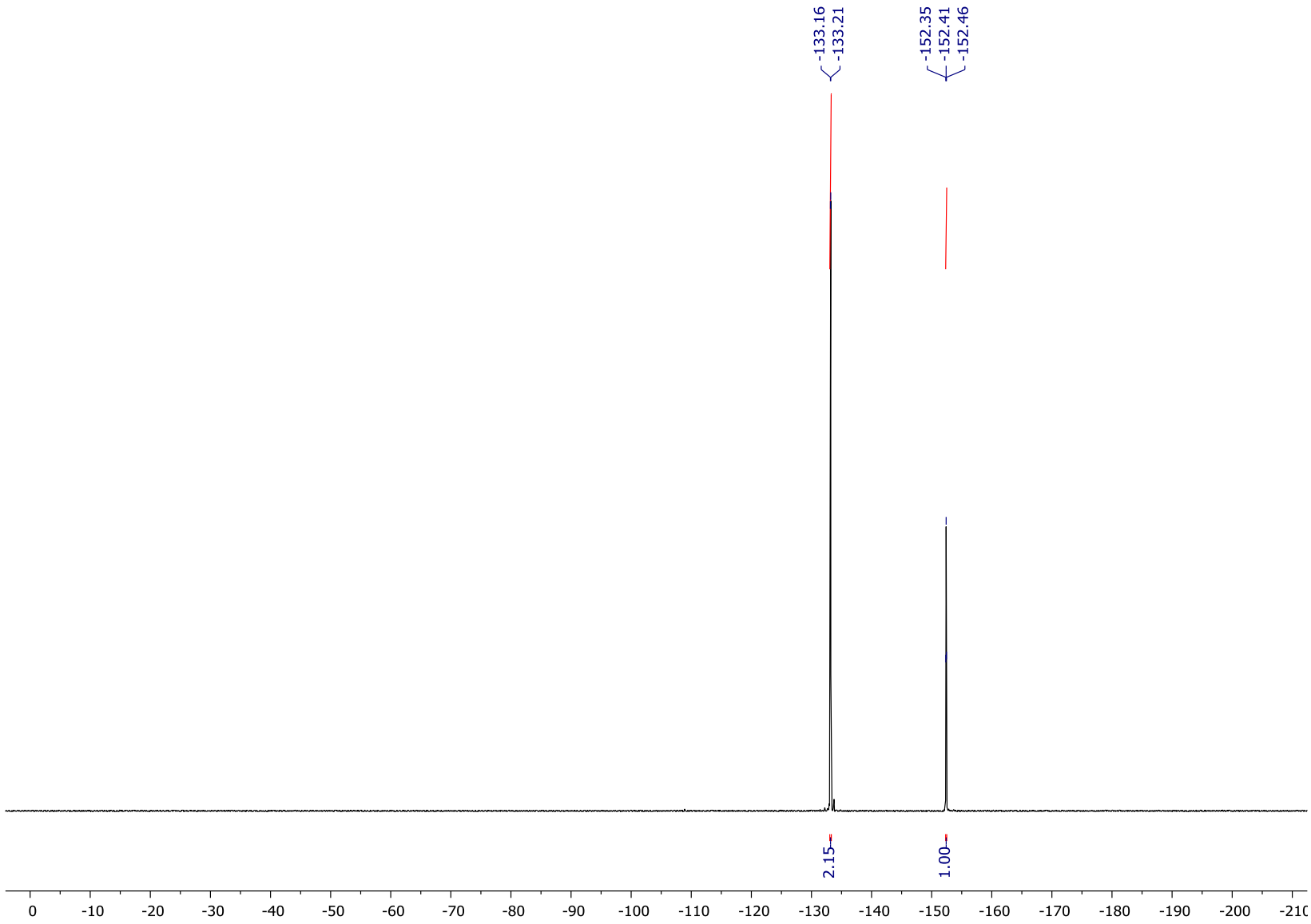
S4 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of tris(3,4,5-trifluorophenyl)borane.



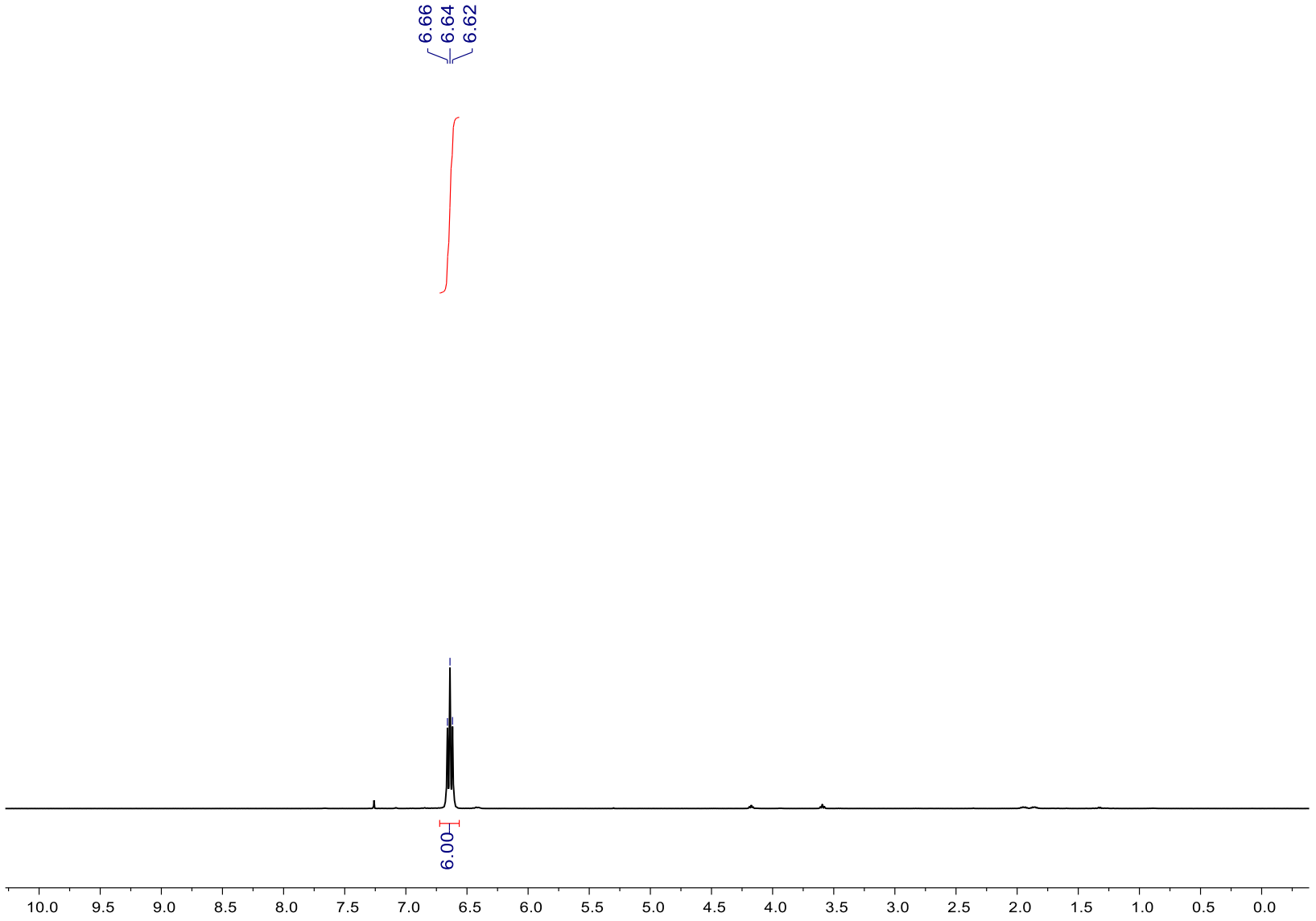
S5 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of tris(3,4,5-trifluorophenyl)borane.



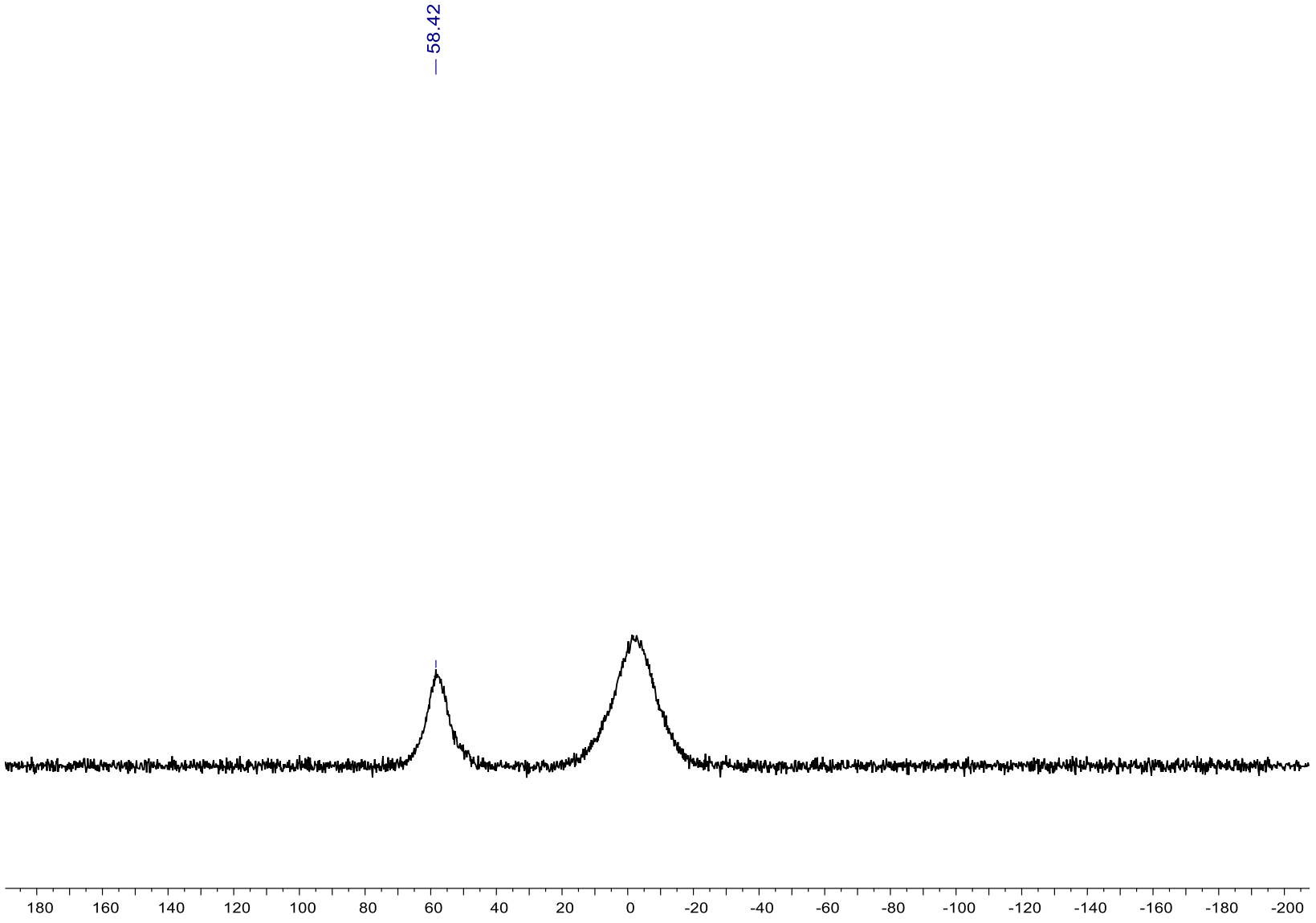
S6 ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) spectrum of tris(3,4,5-trifluorophenyl)borane.



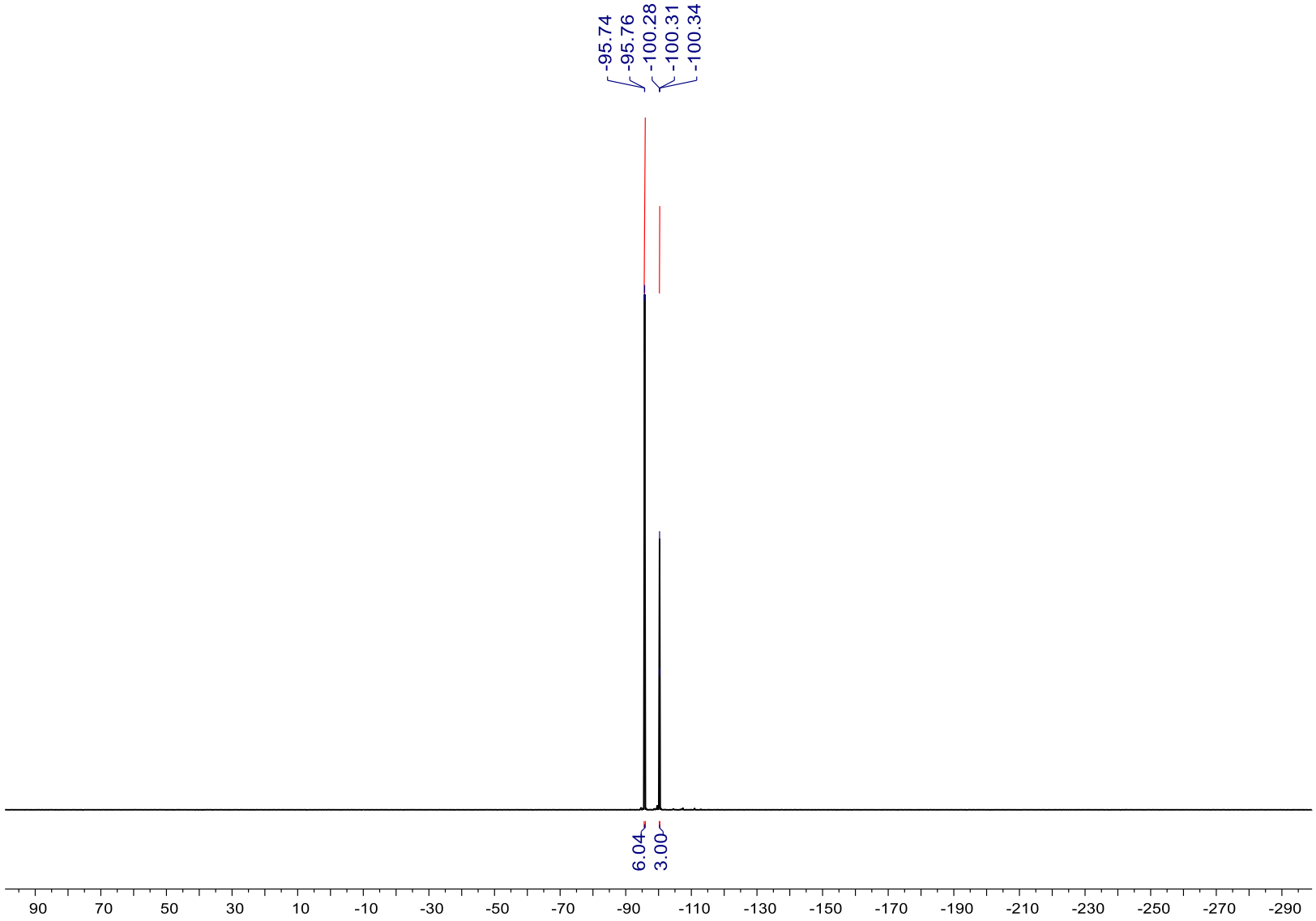
S7 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of tris(2,4,6-trifluorophenyl)borane.



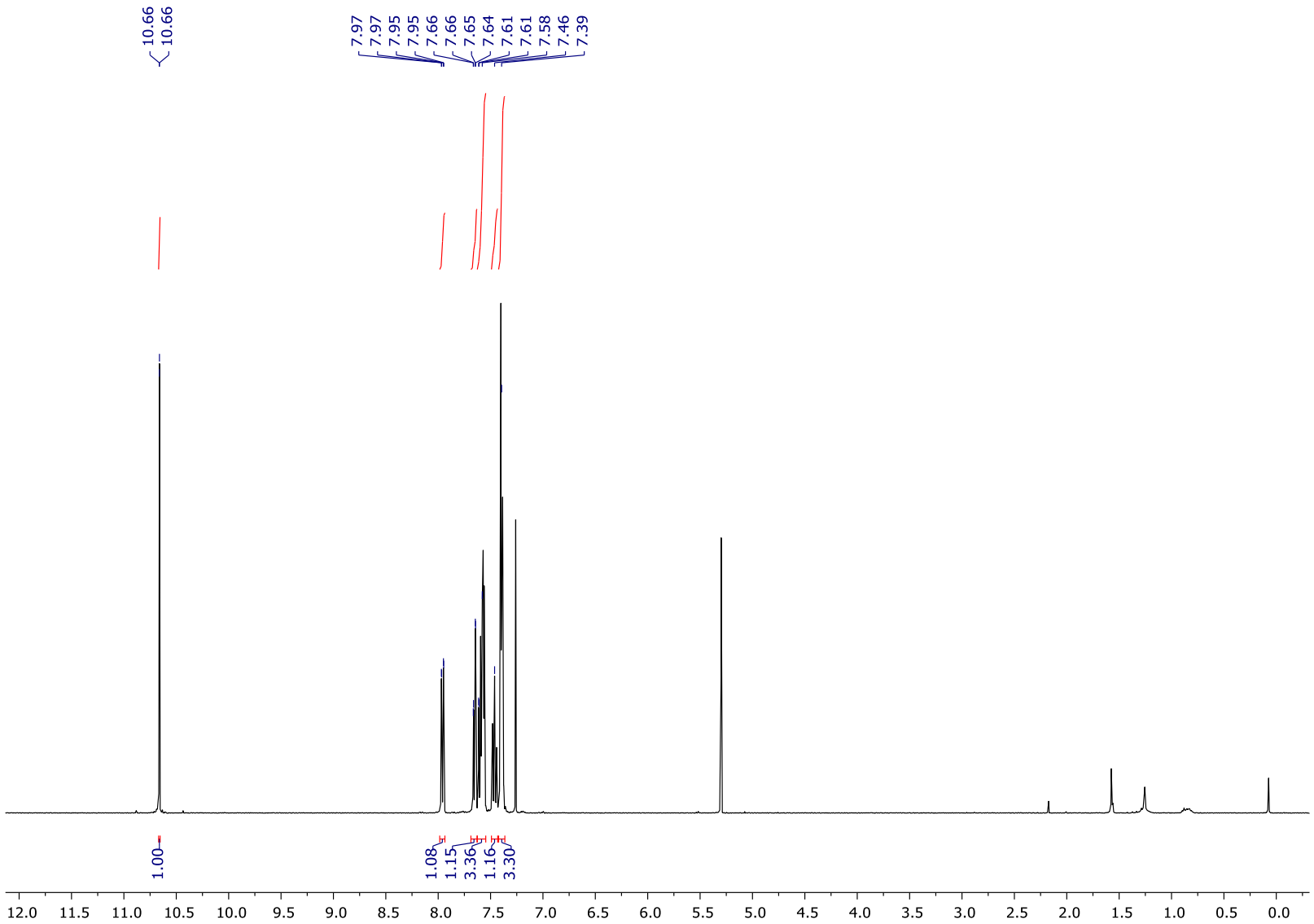
S8 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of tris(2,4,6-trifluorophenyl)borane.



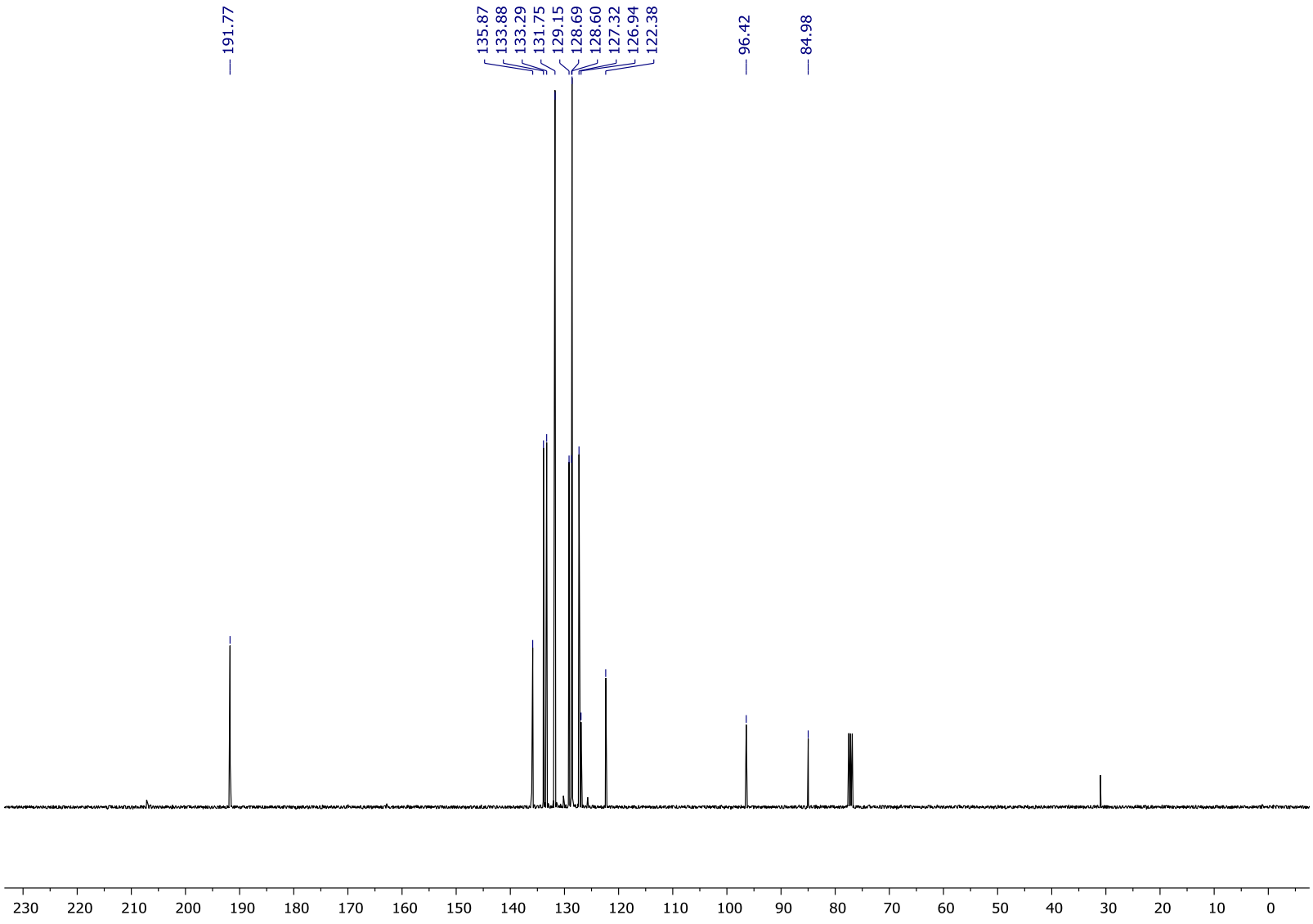
S9 ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) spectrum of tris(2,4,6-trifluorophenyl)borane.



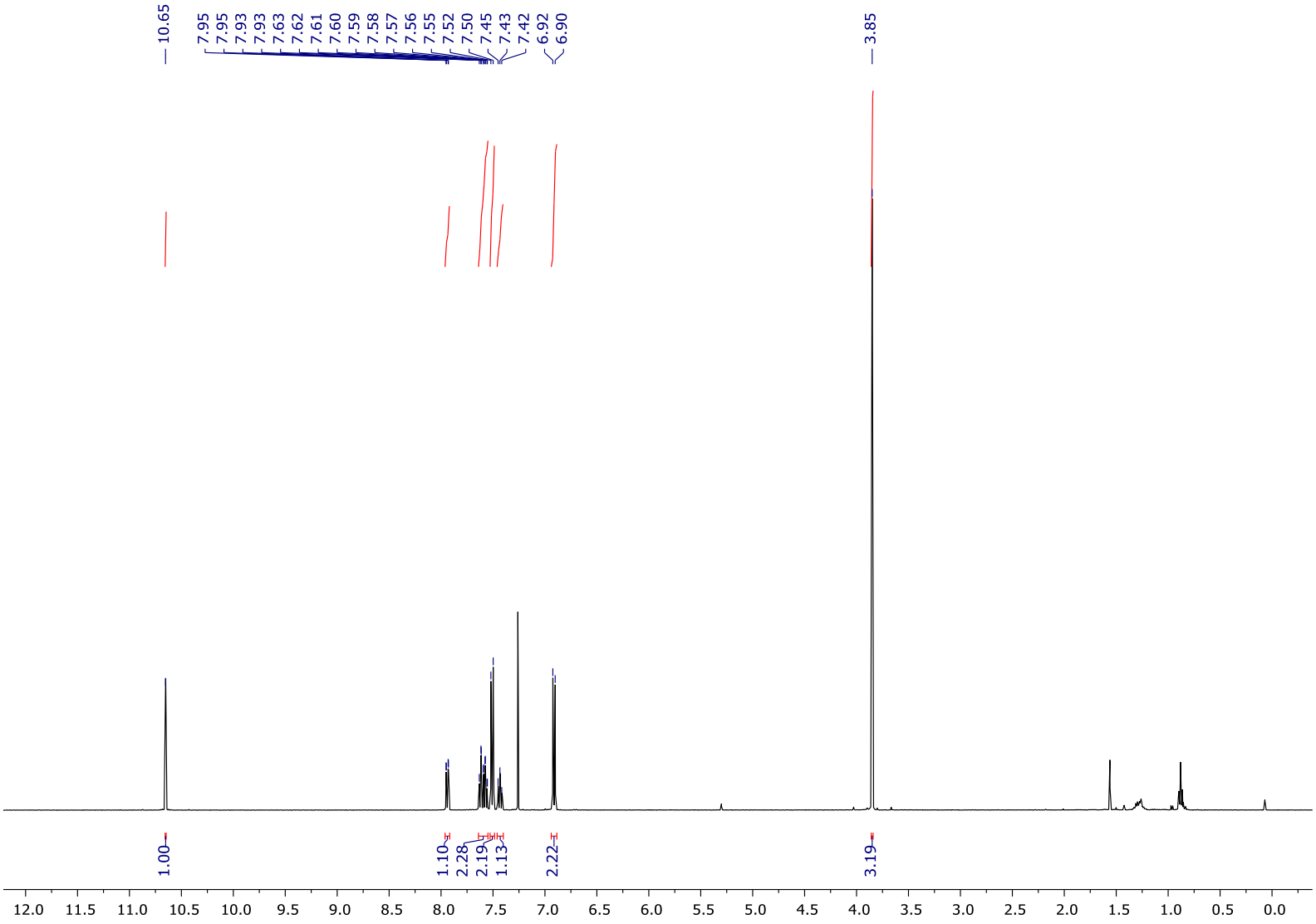
S10 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of 2-(phenylethynyl)benzaldehyde (**1a**).



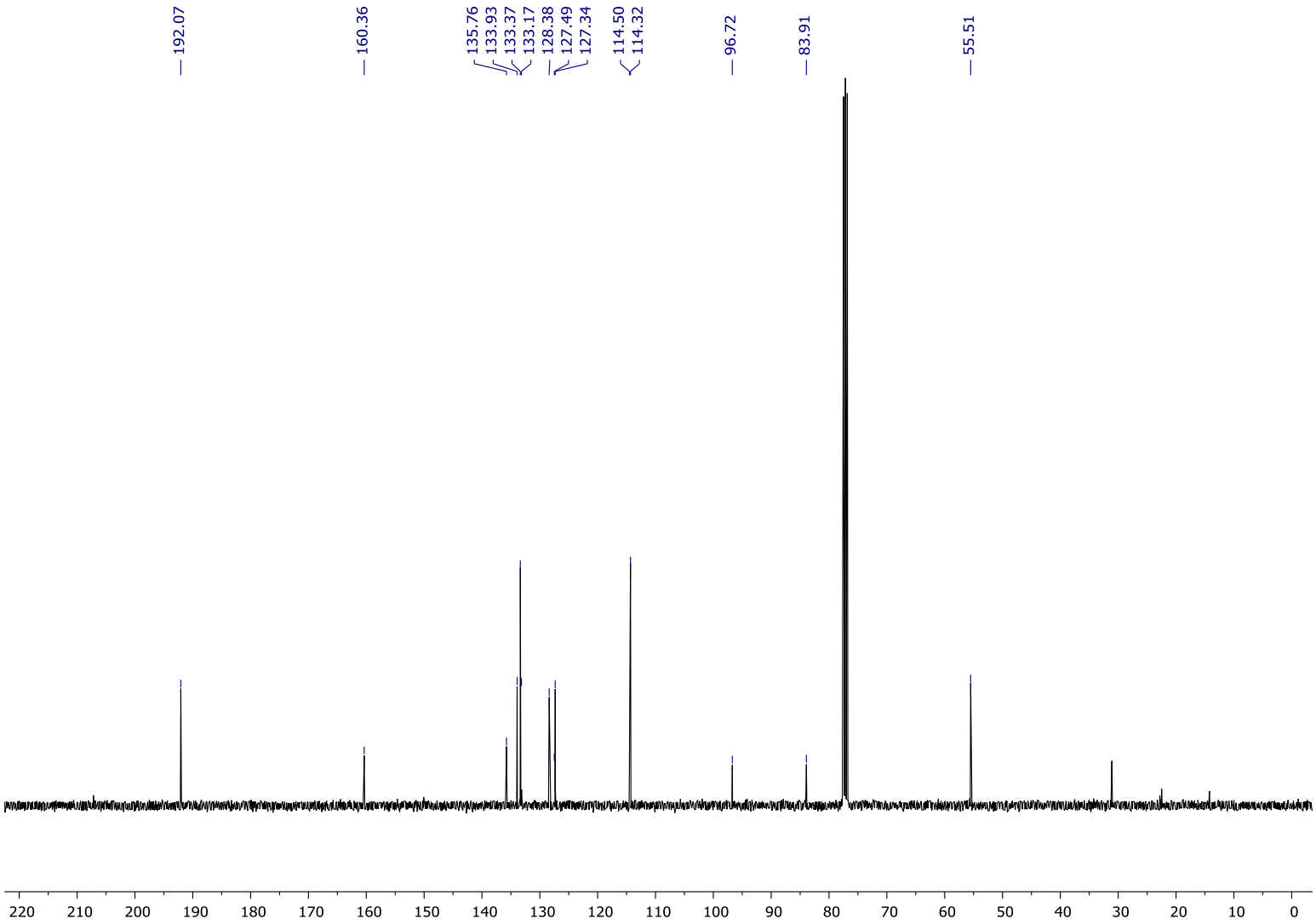
S11 $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) spectrum of 2-(phenylethynyl)benzaldehyde (**1a**).



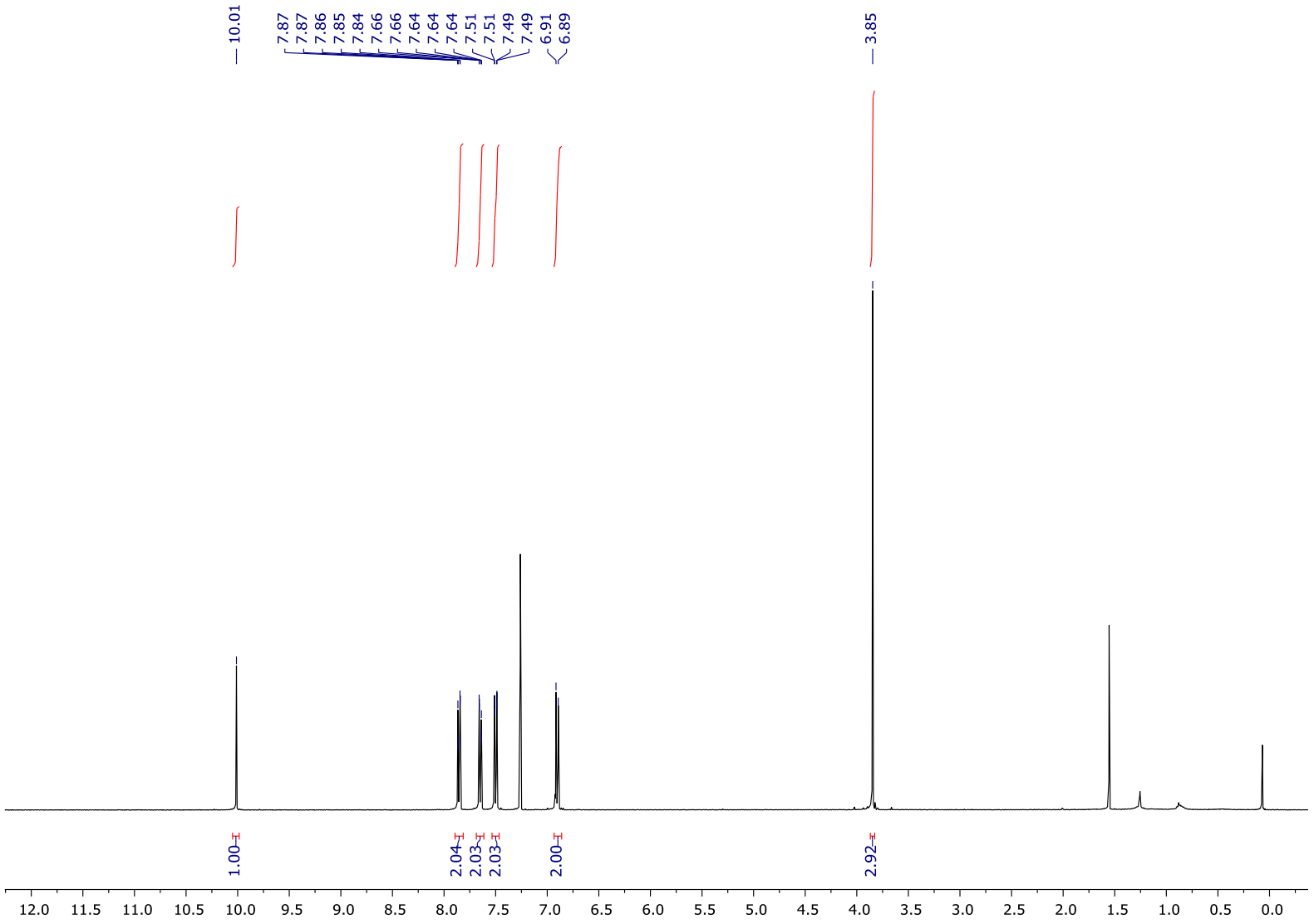
S12 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of 2-((4-methoxyphenyl)ethynyl)benzaldehyde (**1b**).



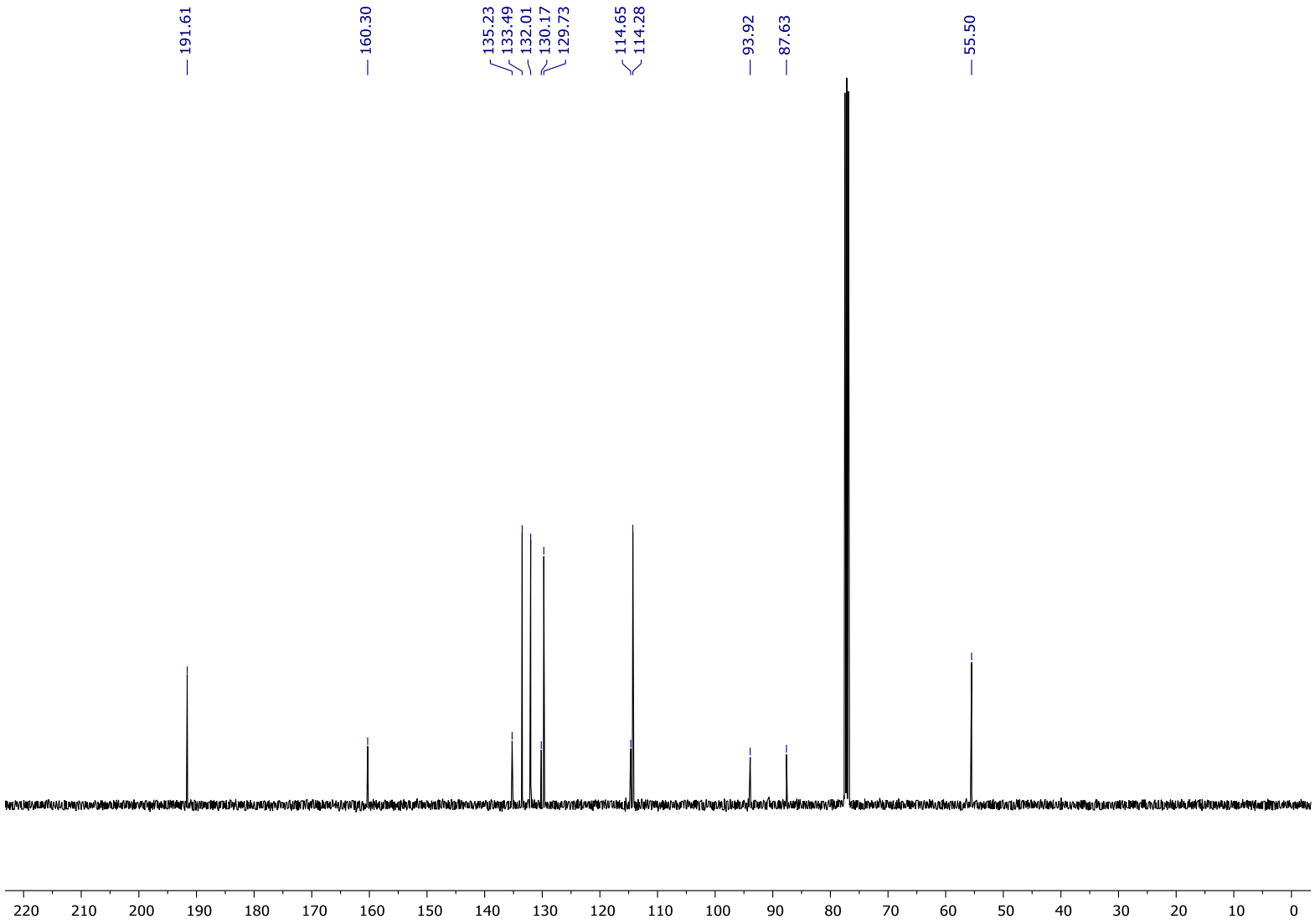
S13 $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) spectrum of 2-((4-methoxyphenyl)ethynyl)benzaldehyde (**1b**).



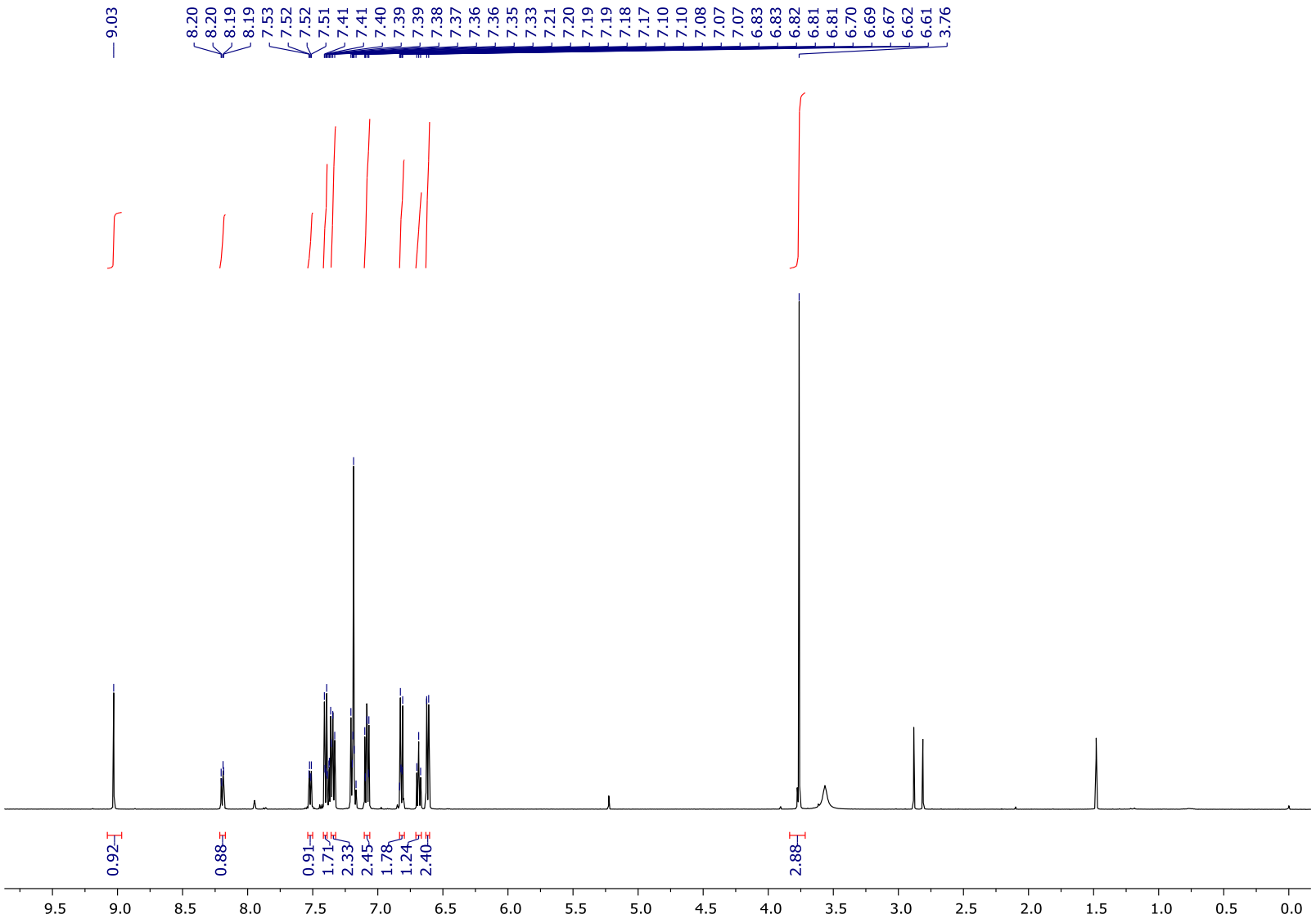
S14 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of 4-((4-methoxyphenyl)ethynyl)benzaldehyde (**1c**).



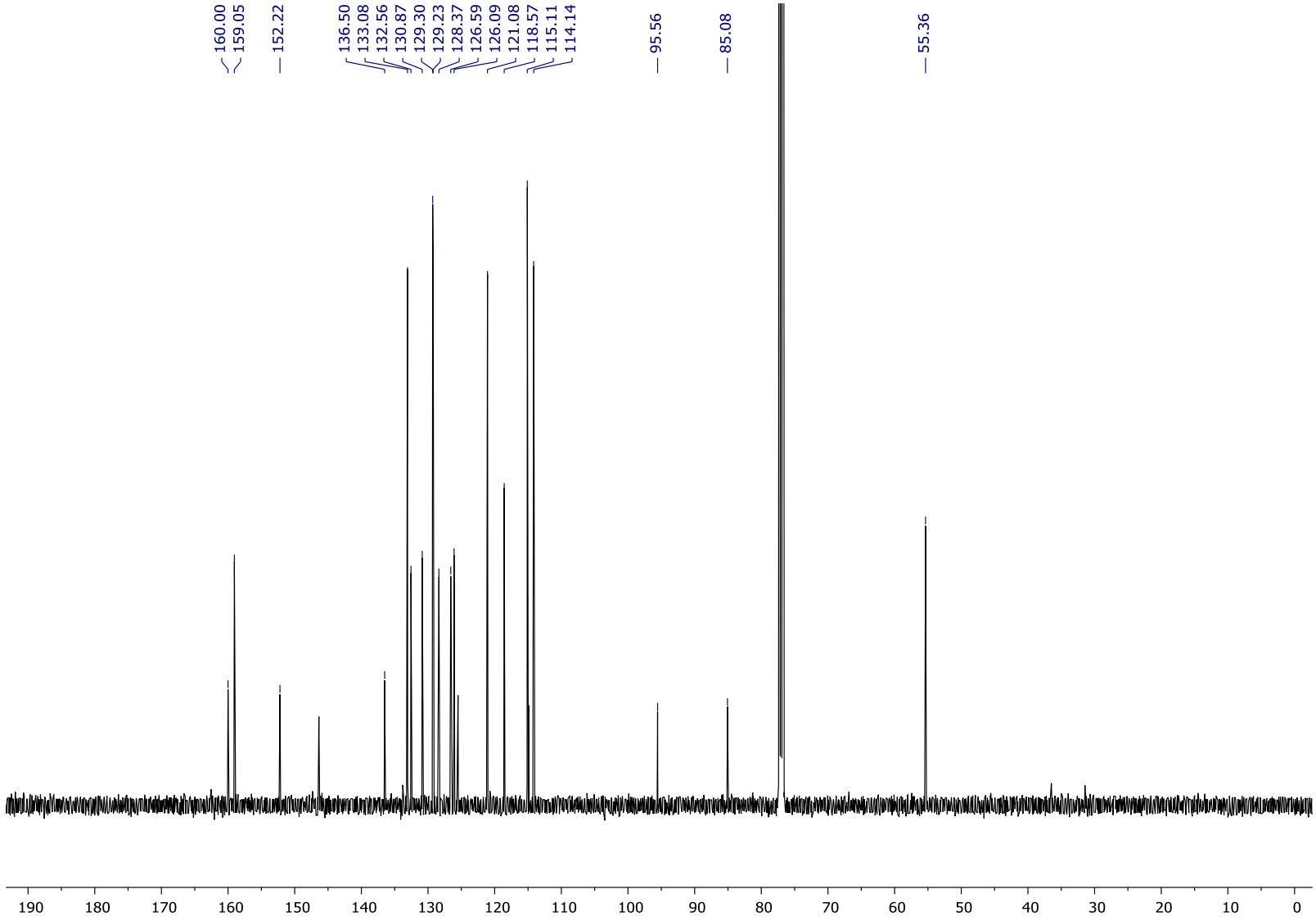
S15 $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) spectrum of 4-((4-methoxyphenyl)ethynyl)benzaldehyde (**1c**).



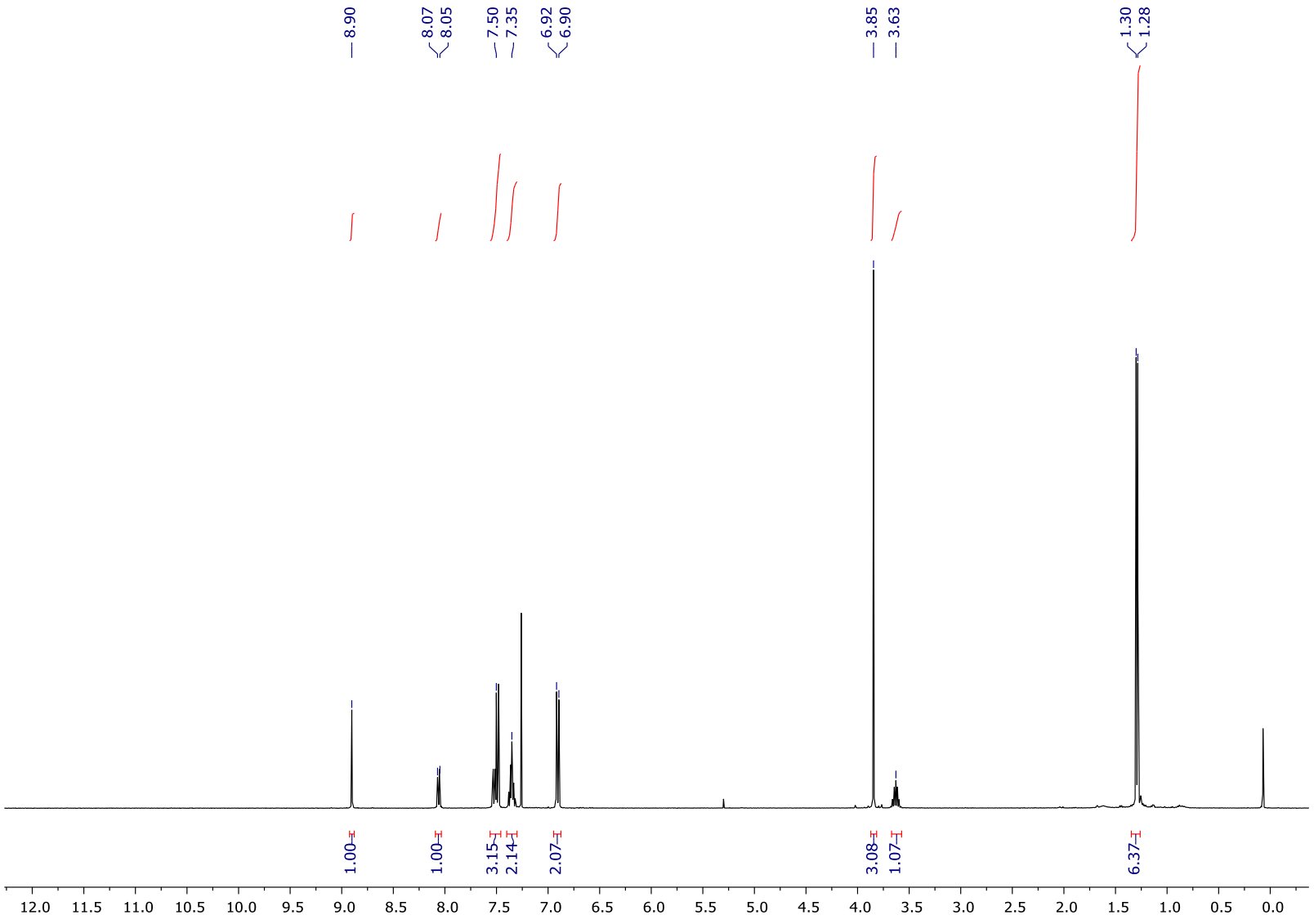
S16 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of *N*-(2-((4-methoxyphenyl)ethynyl)benzylidene)aniline (**2a**).



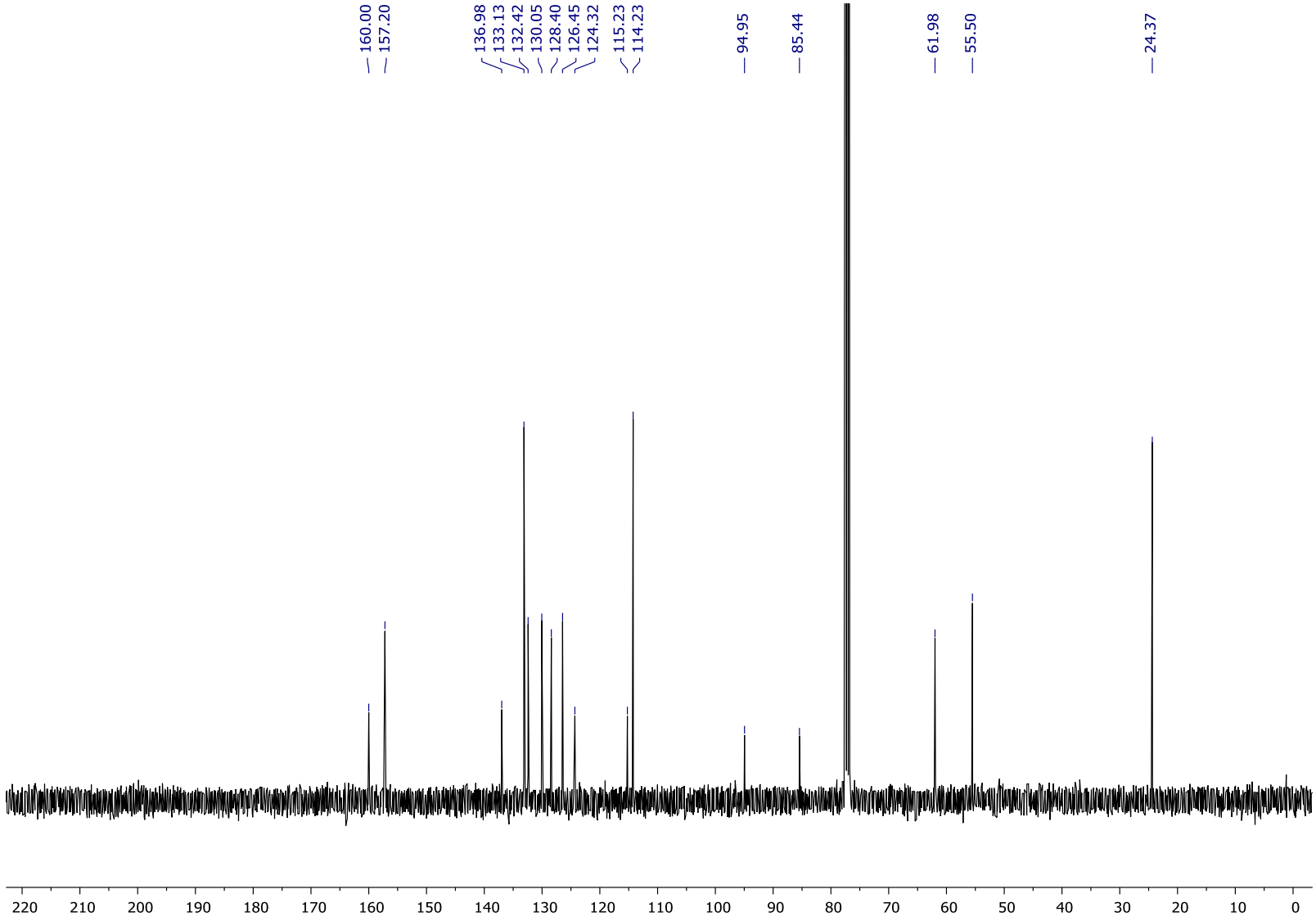
S17 ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) spectrum of *N*-(2-((4-methoxyphenyl)ethynyl)benzylidene)aniline (**2a**).



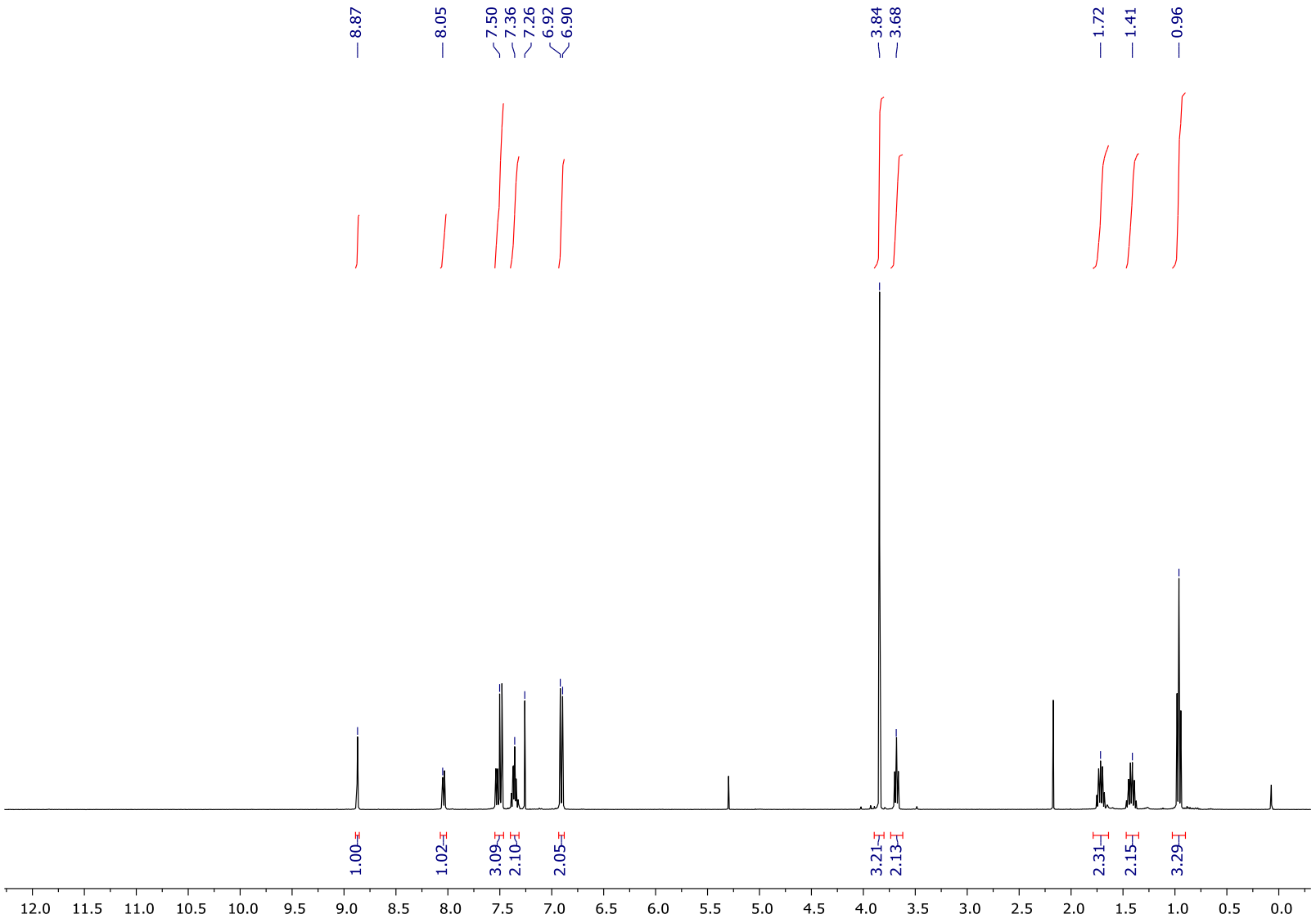
S18 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of *N*-isopropyl-1-(2-((4-methoxyphenyl)ethynyl)phenyl)methanimine (**2b**).



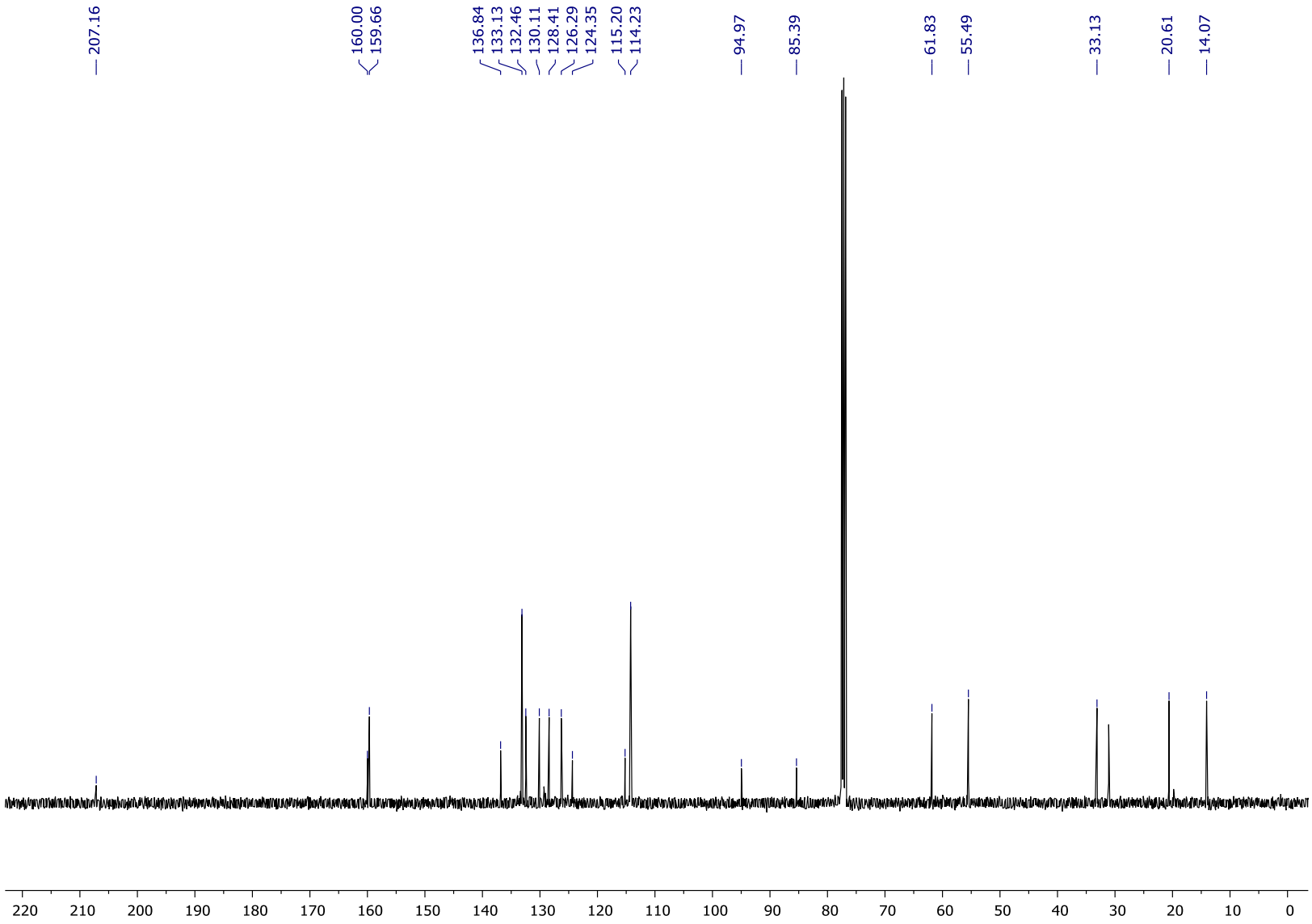
S19 $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) spectrum of *N*-isopropyl-1-(2-((4-methoxyphenyl)ethynyl)phenyl)methanimine (**2b**).



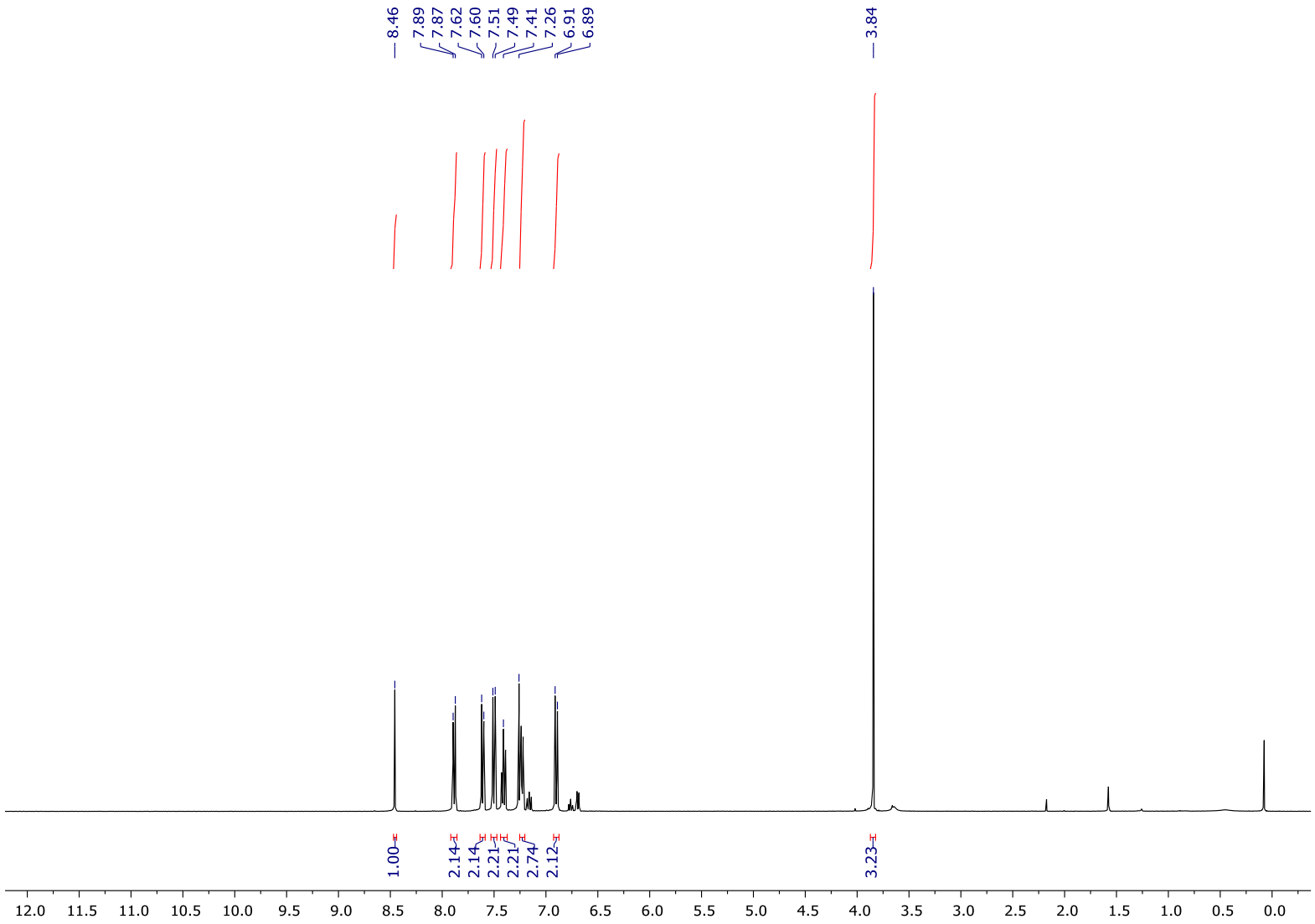
S20 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of *N*-butyl-1-(2-((4-methoxyphenyl)ethynyl)phenyl)methanimine (**2c**).



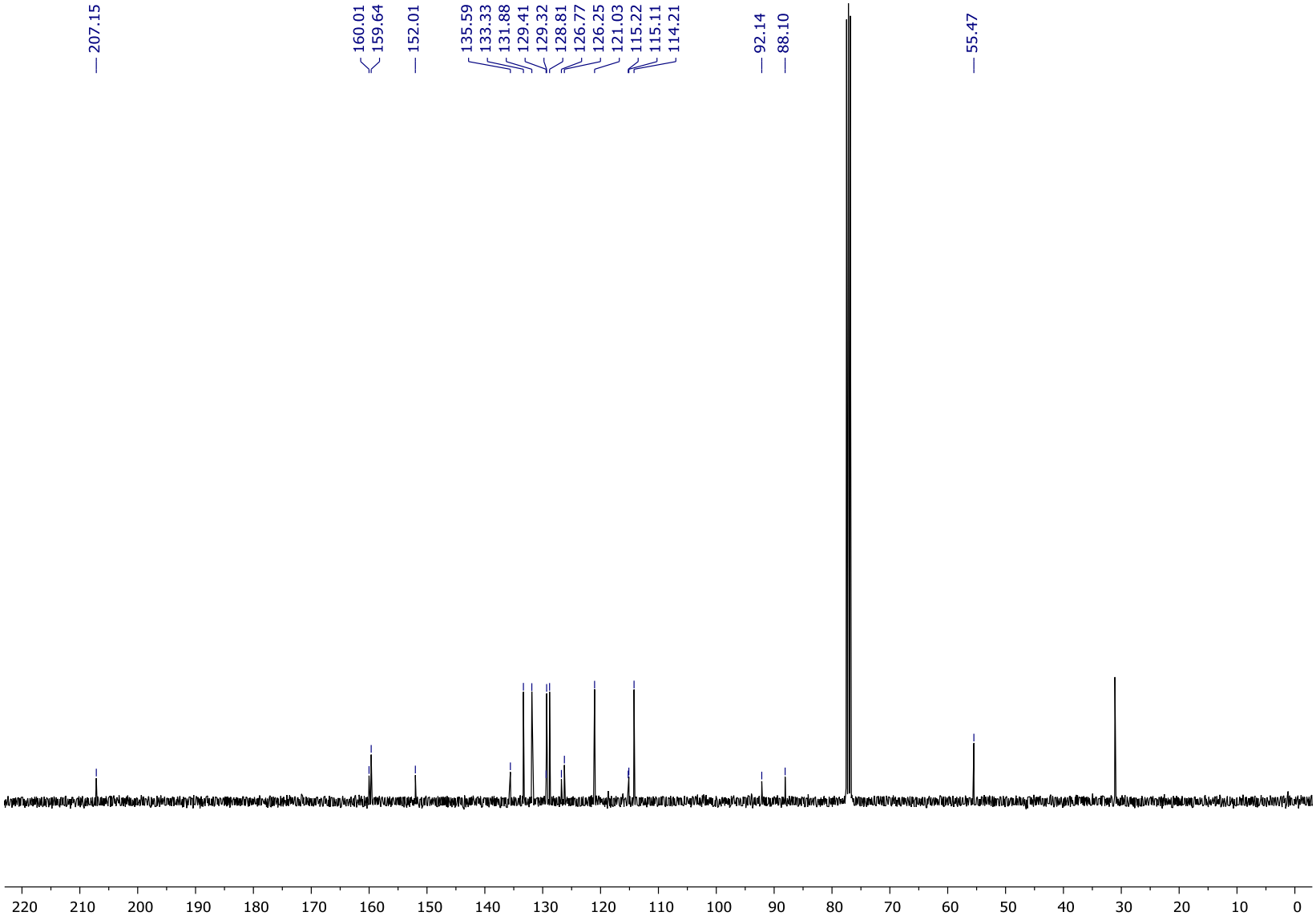
S21 $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) spectrum of *N*-butyl-1-(2-((4-methoxyphenyl)ethynyl)phenyl)methanimine (**2c**).



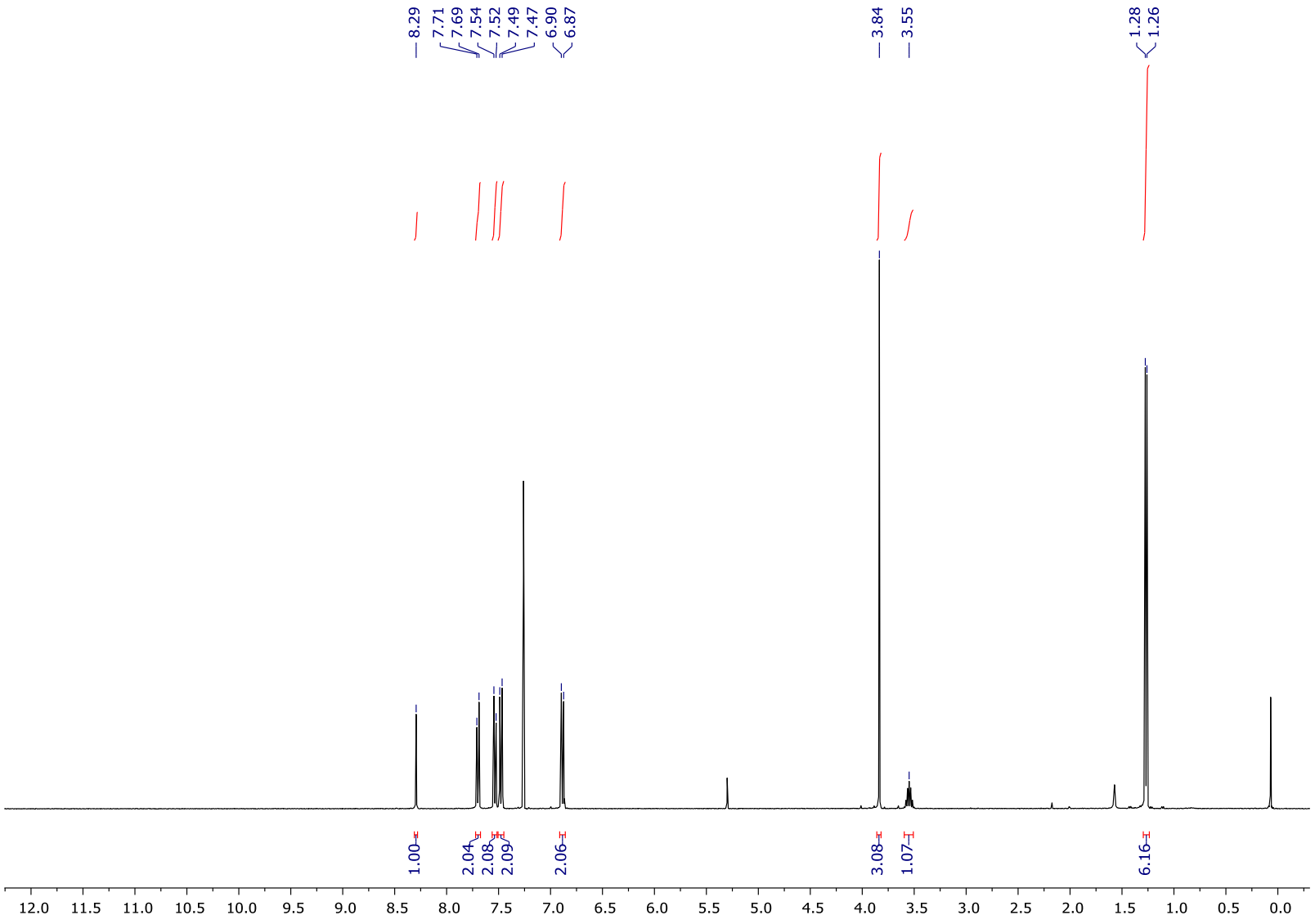
S22 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of 1-(4-((4-methoxyphenyl)ethynyl)phenyl)-*N*-phenylmethanimine (**2d**).



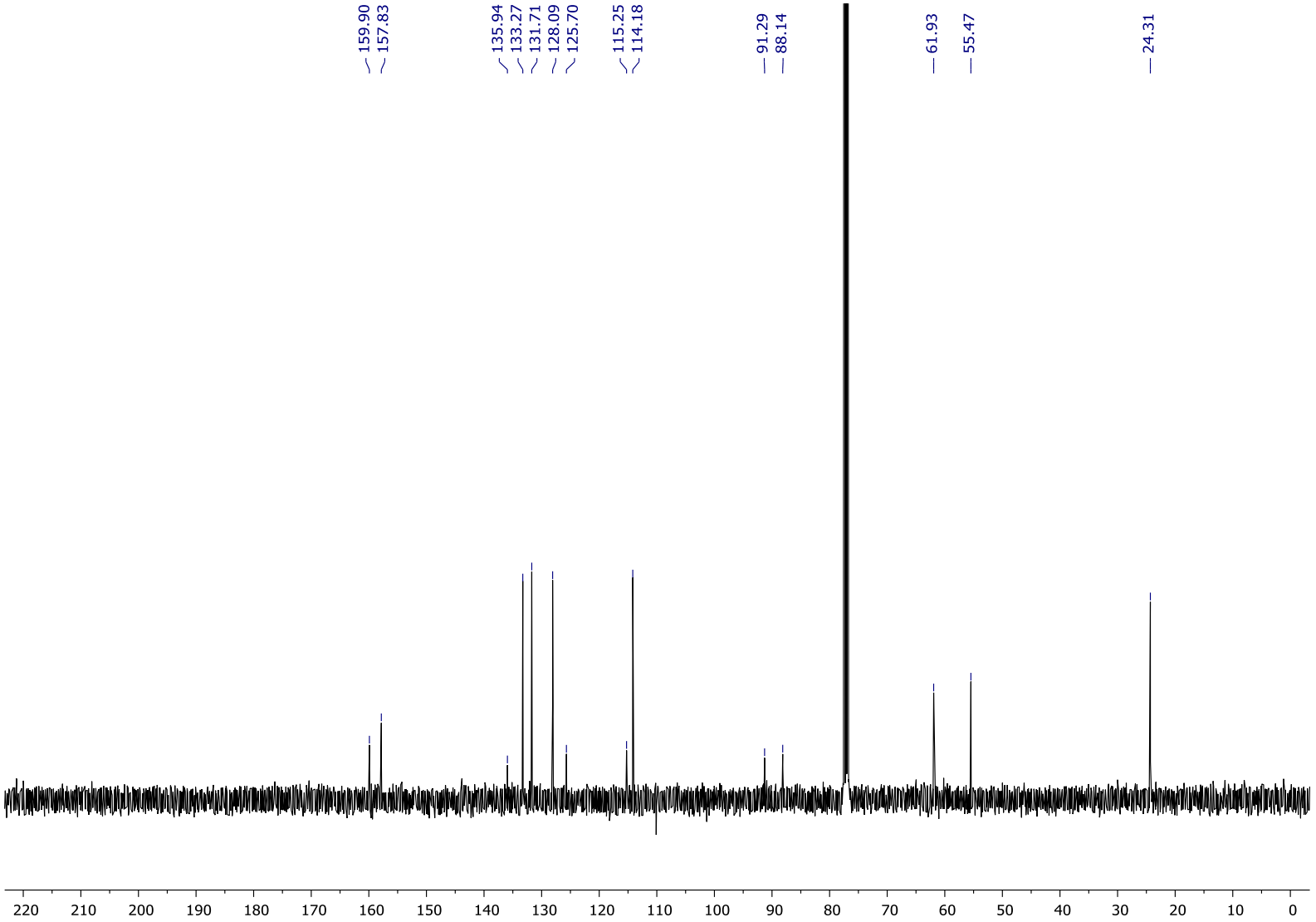
S23 $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) spectrum of 1-(4-((4-methoxyphenyl)ethynyl)phenyl)-*N*-phenylmethanimine (**2d**).



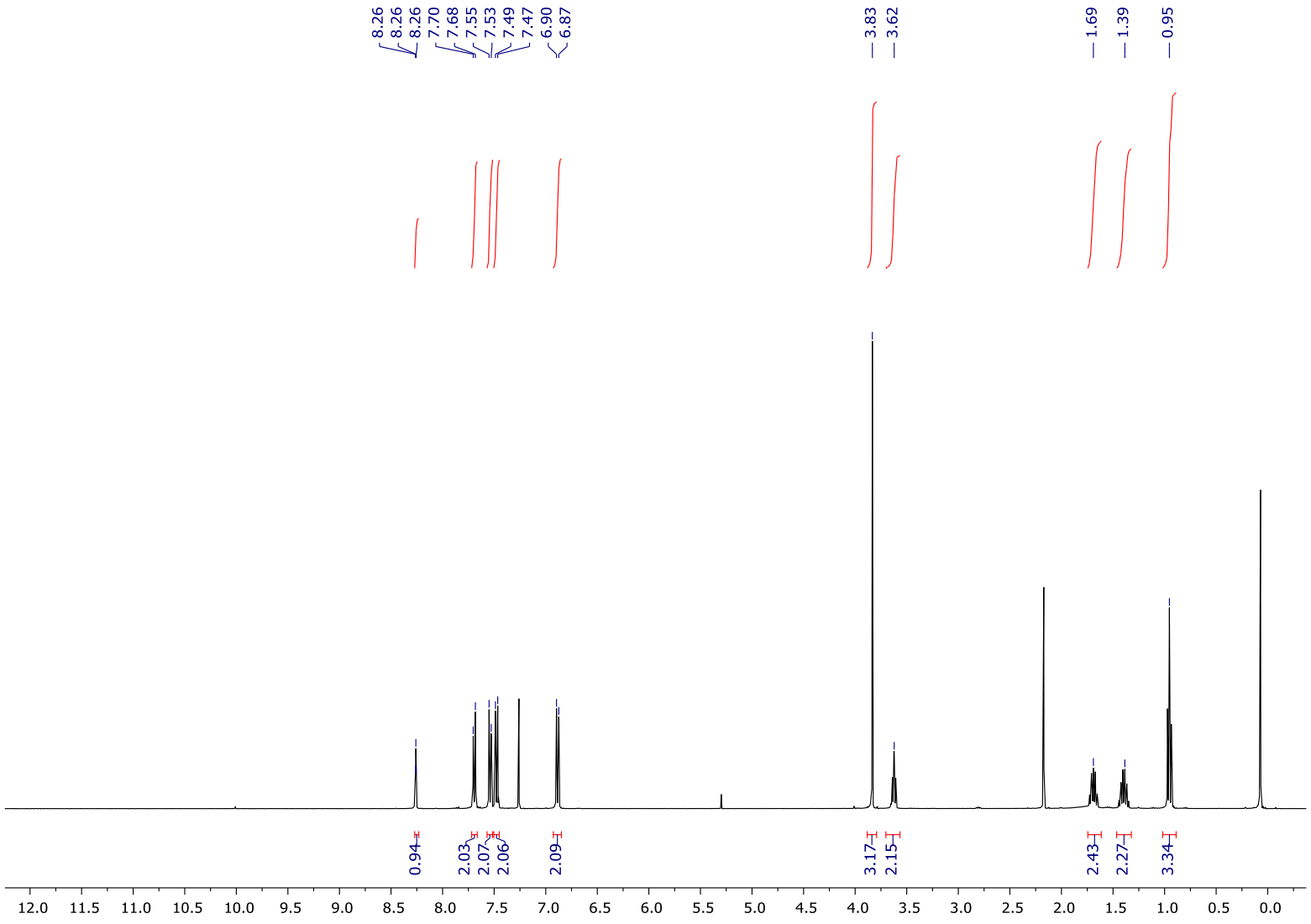
S24 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of *N*-isopropyl-1-(4-((4-methoxyphenyl)ethynyl)phenyl)methanimine (**2e**).



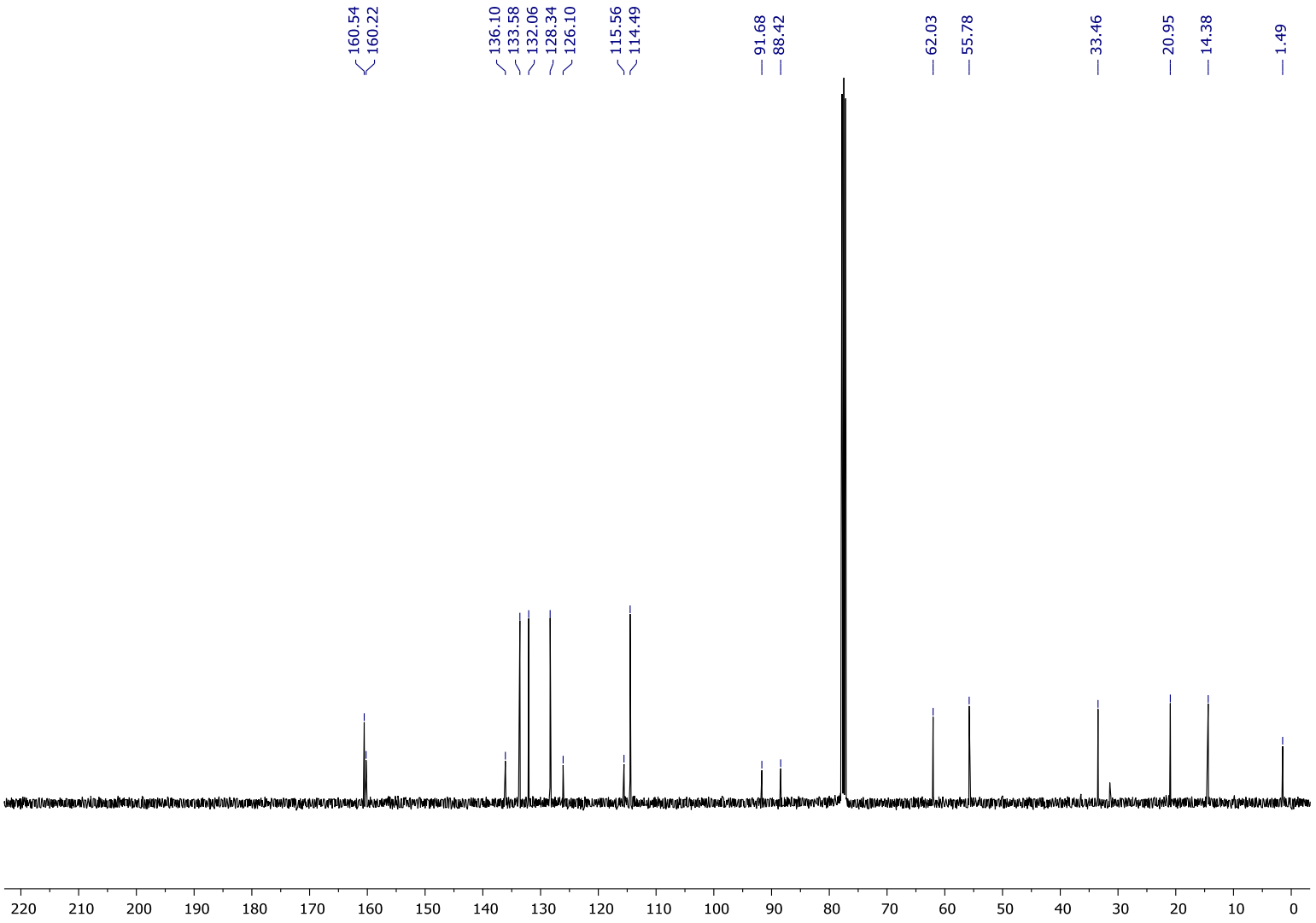
S25 $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) spectrum of *N*-isopropyl-1-(4-((4-methoxyphenyl)ethynyl)phenyl)methanimine (**2e**).



S26 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of *N*-butyl-1-(4-((4-methoxyphenyl)ethynyl)phenyl)methanimine (**2f**).

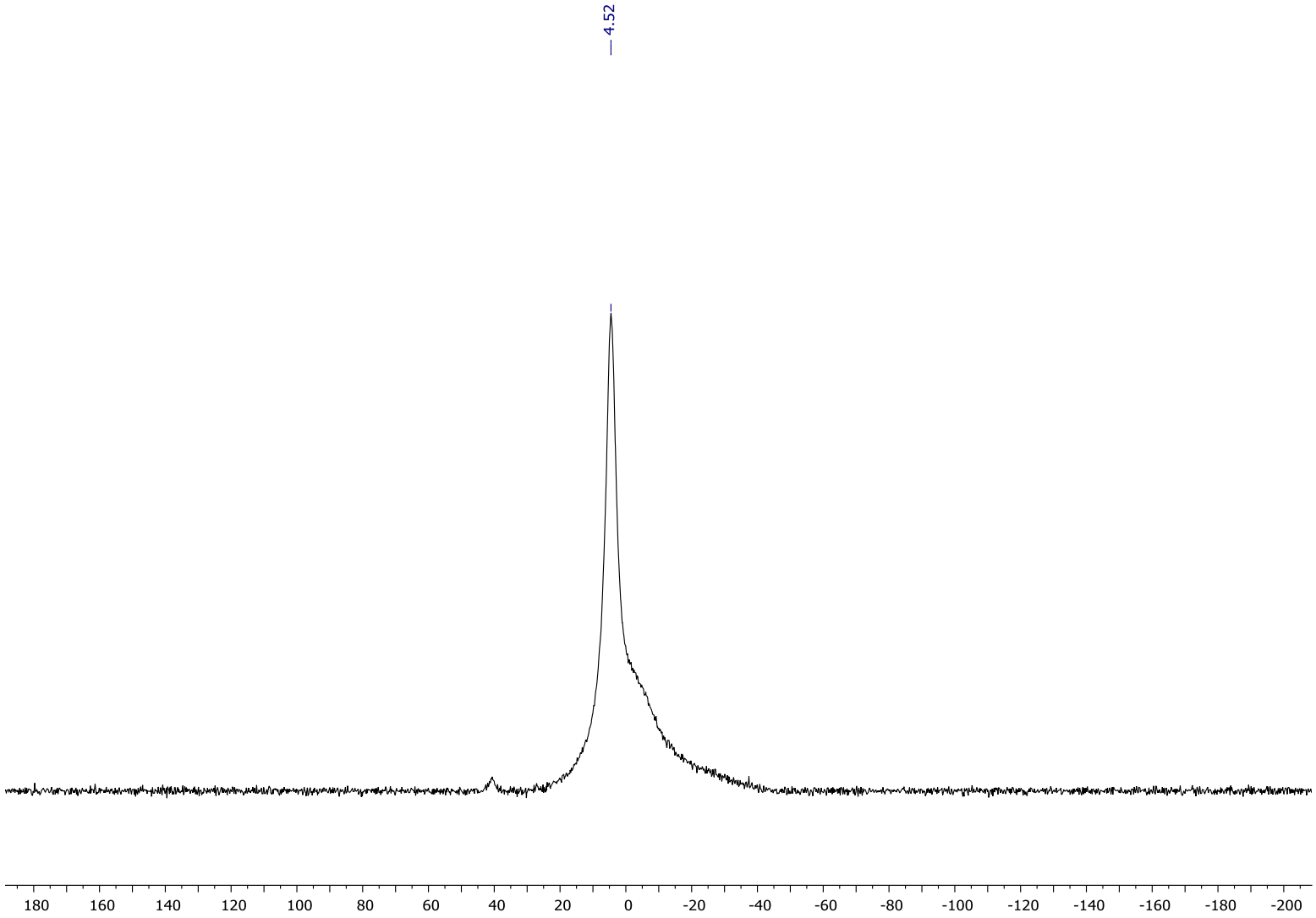


S27 $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) spectrum of *N*-butyl-1-(4-((4-methoxyphenyl)ethynyl)phenyl)methanimine (**2f**).

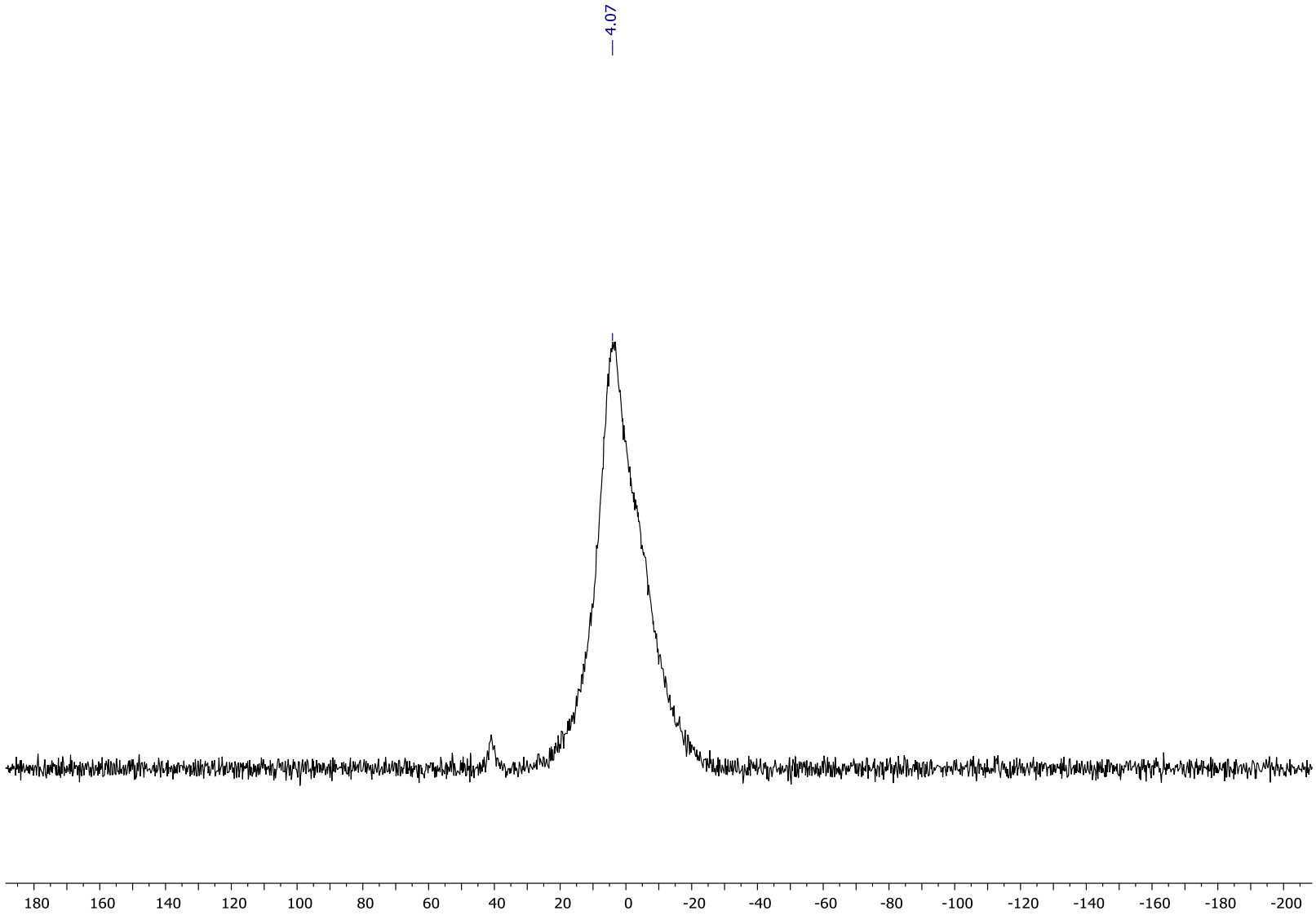


2.2 NMR spectra of borane adducts of aldehydes 1a–c and 2a–f with various boranes

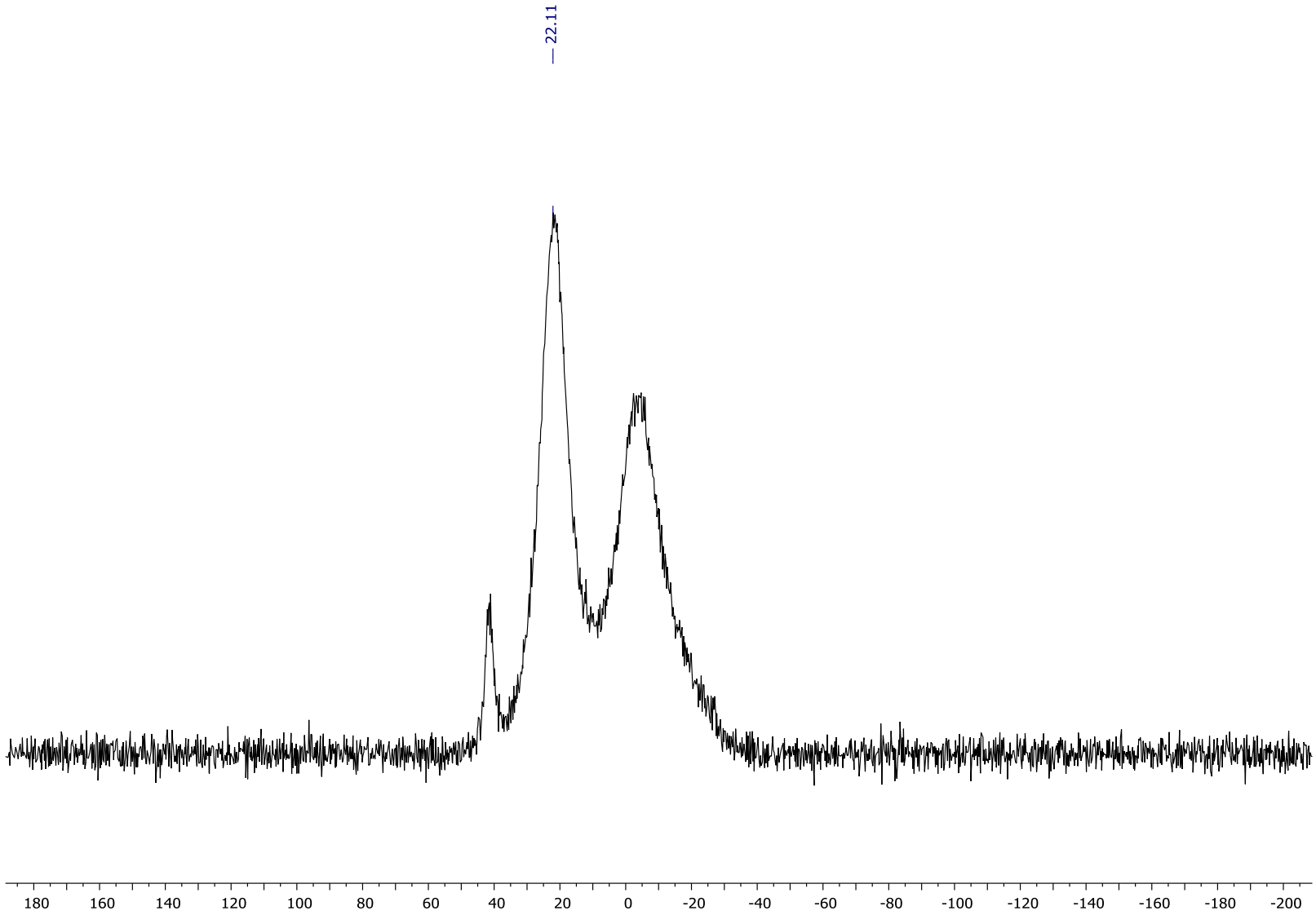
S28 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of adduct between **1a** and $B(C_6F_5)_3$.



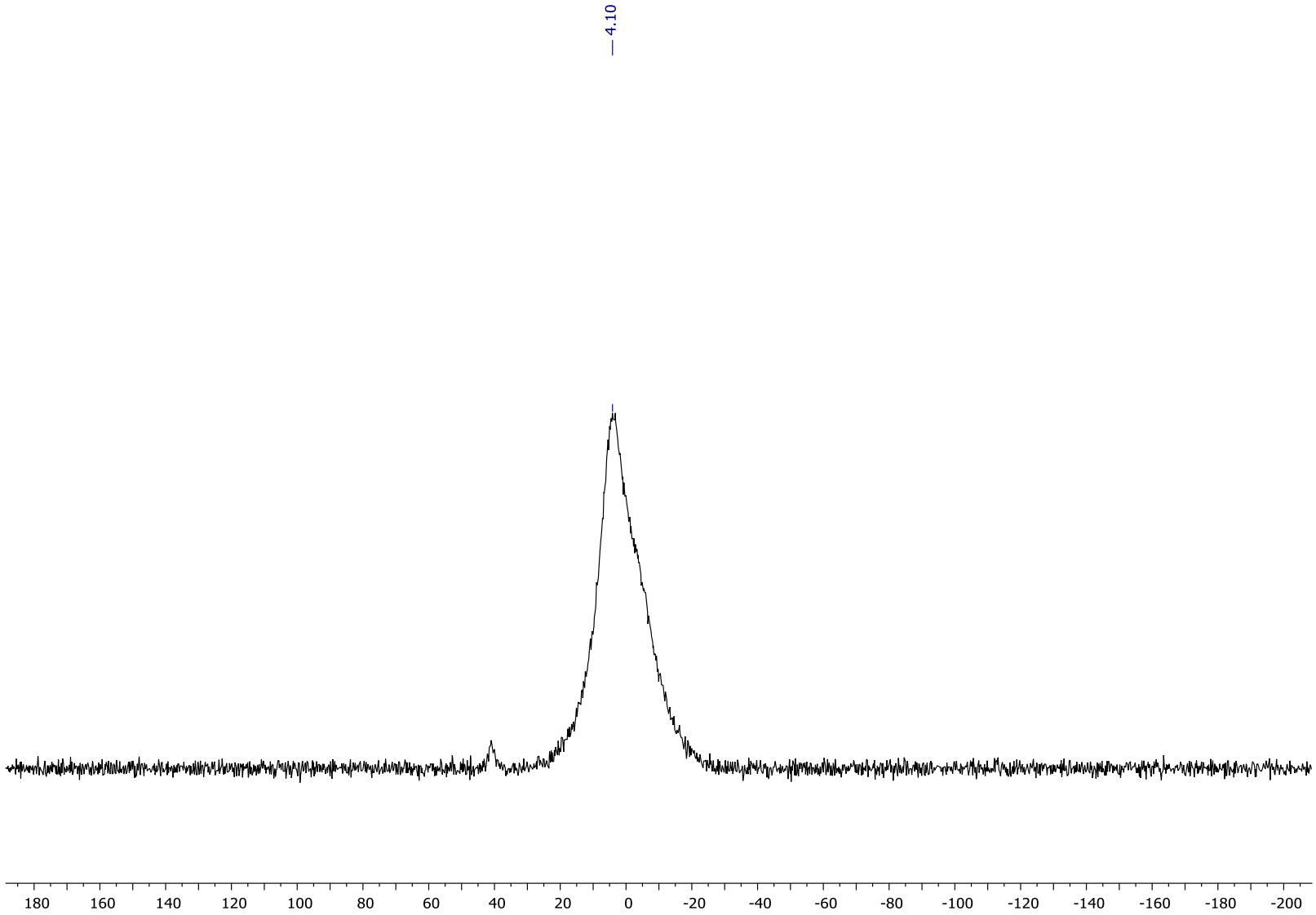
S29 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of adduct between **1b** and $B(C_6F_5)_3$.



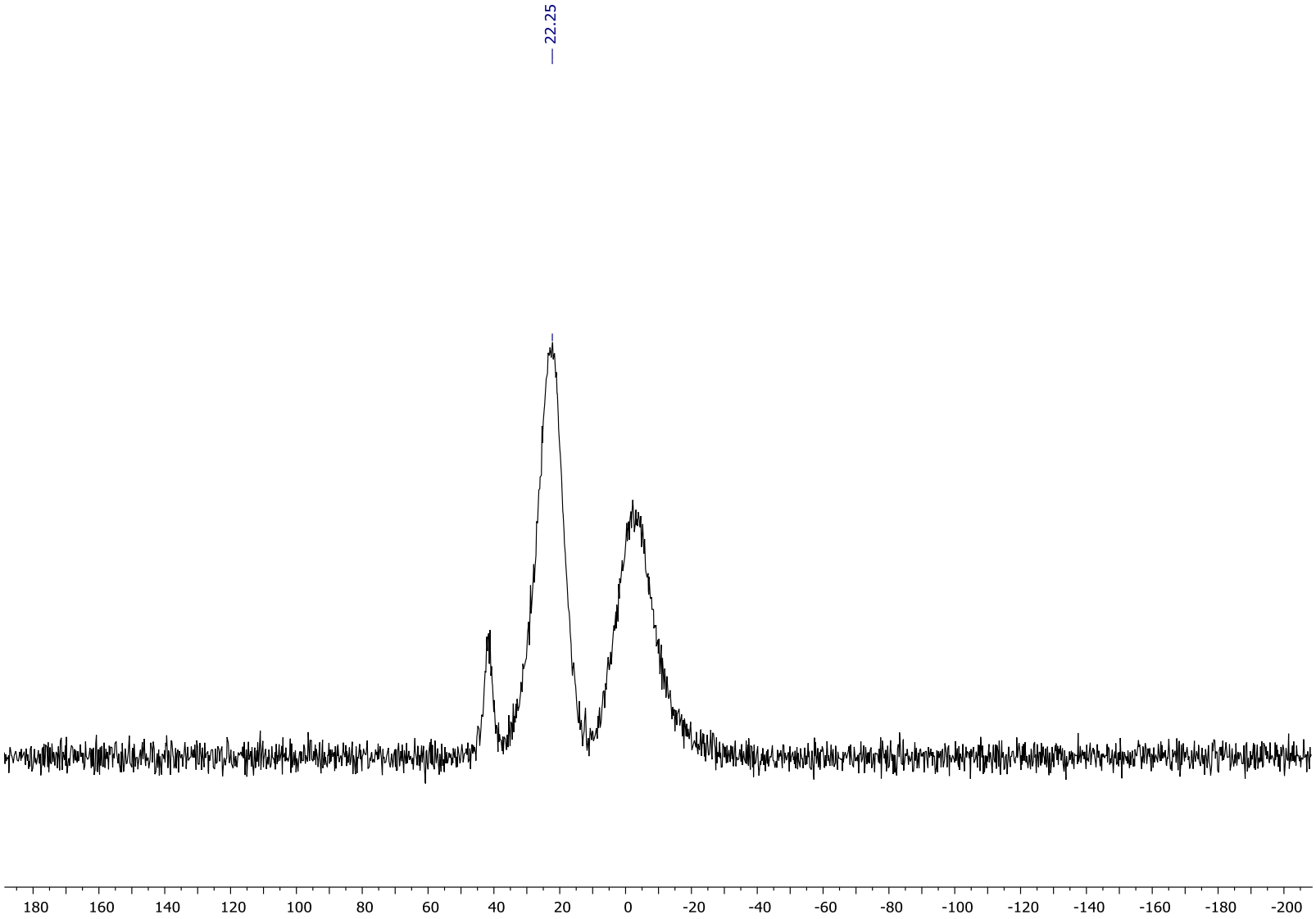
S30 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of adduct between **1b** and 2,4,6-$BArF_6$.



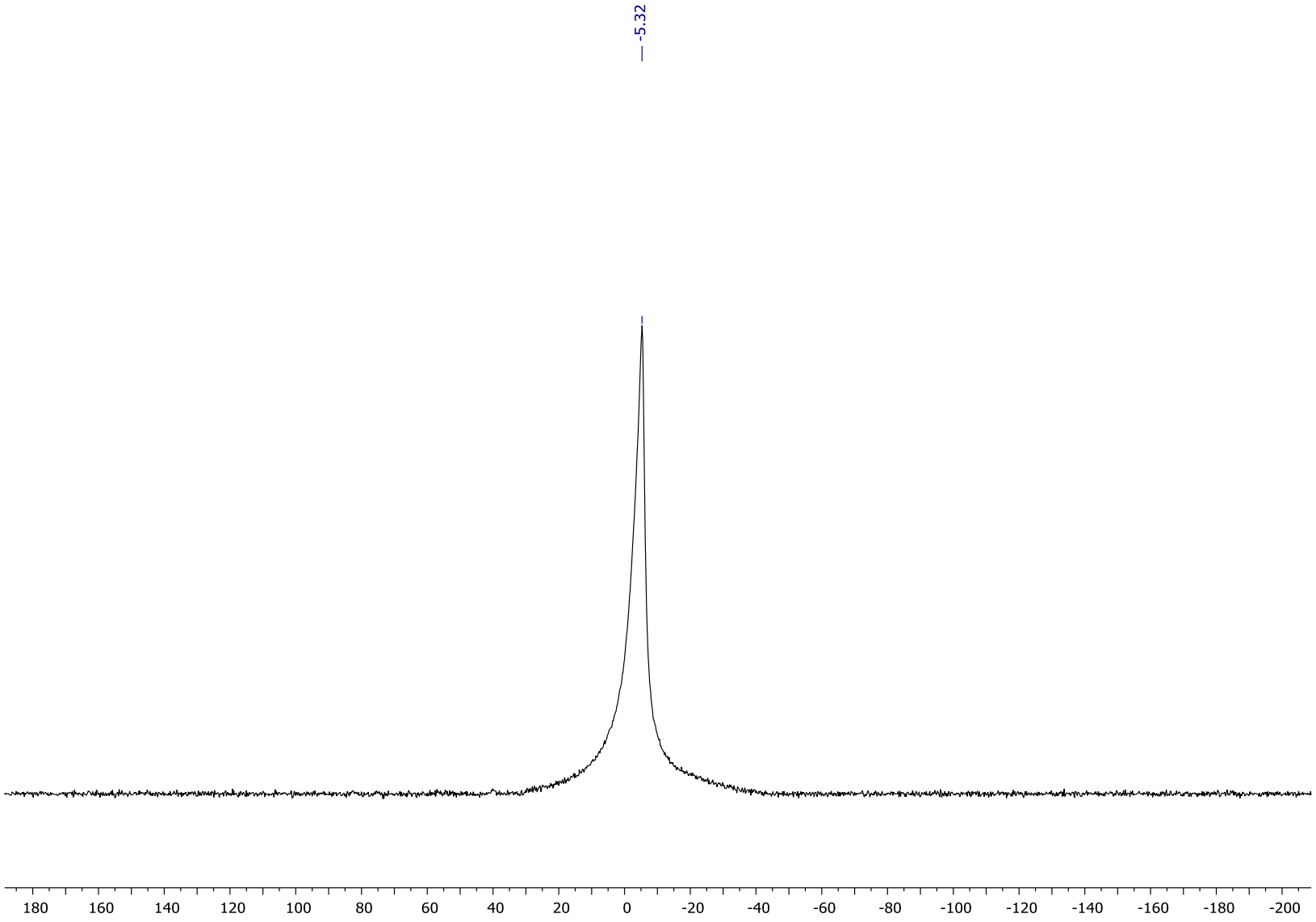
S31 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of adduct between **1c** and $B(C_6F_5)_3$.



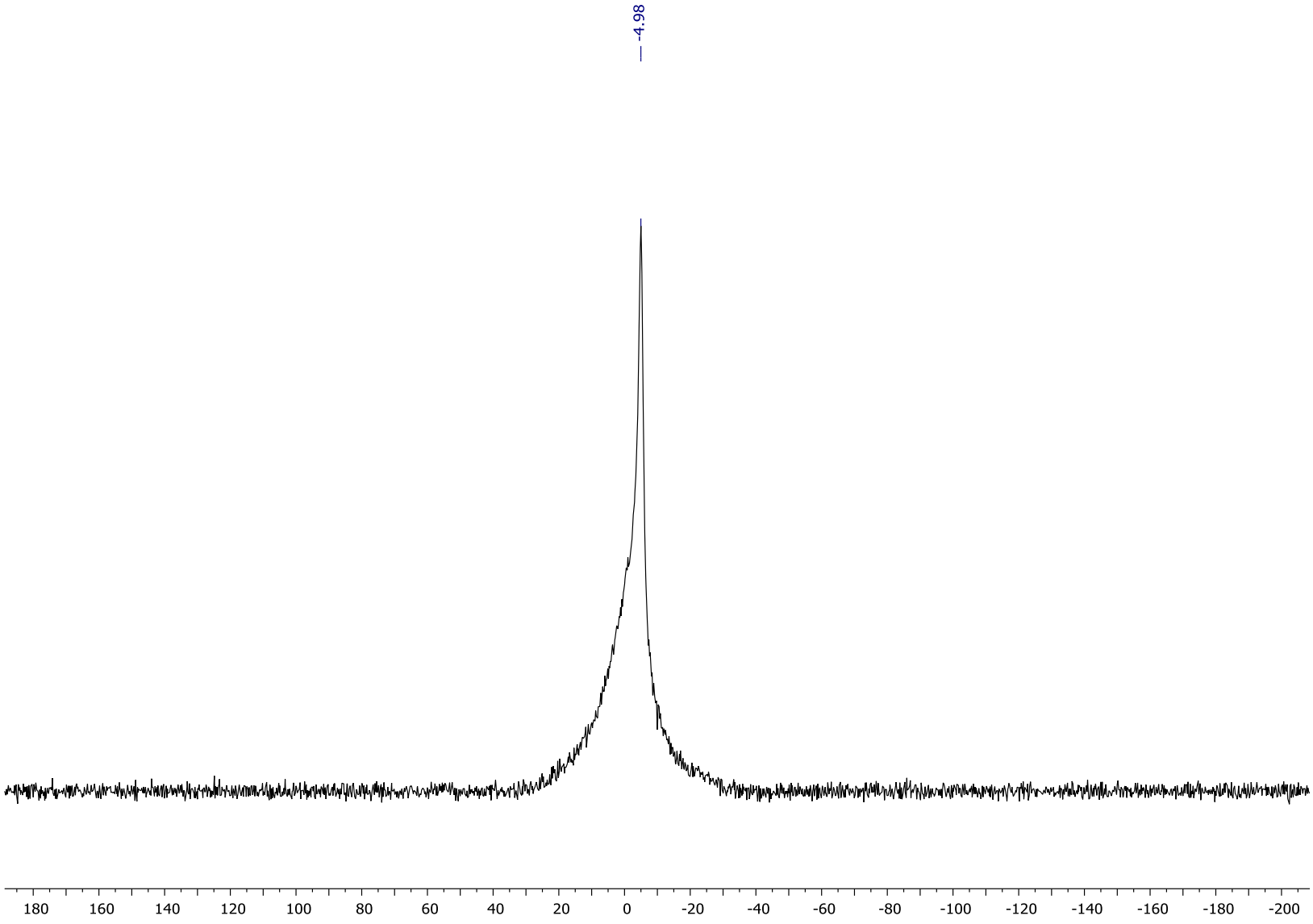
S32 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of adduct between **1c** and 2,4,6-$BArF_9$.



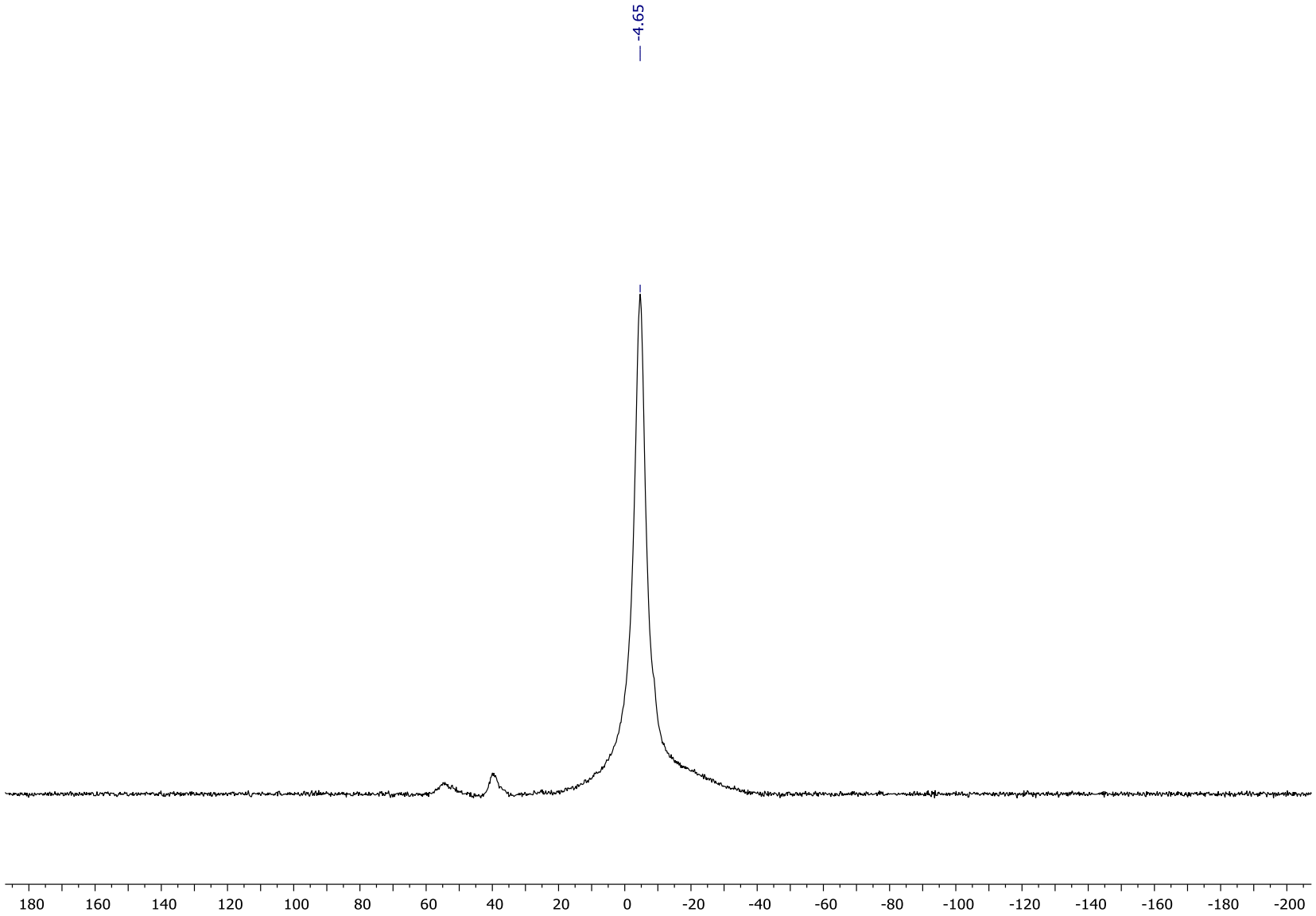
S33 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2a** and $B(C_6F_5)_3$.



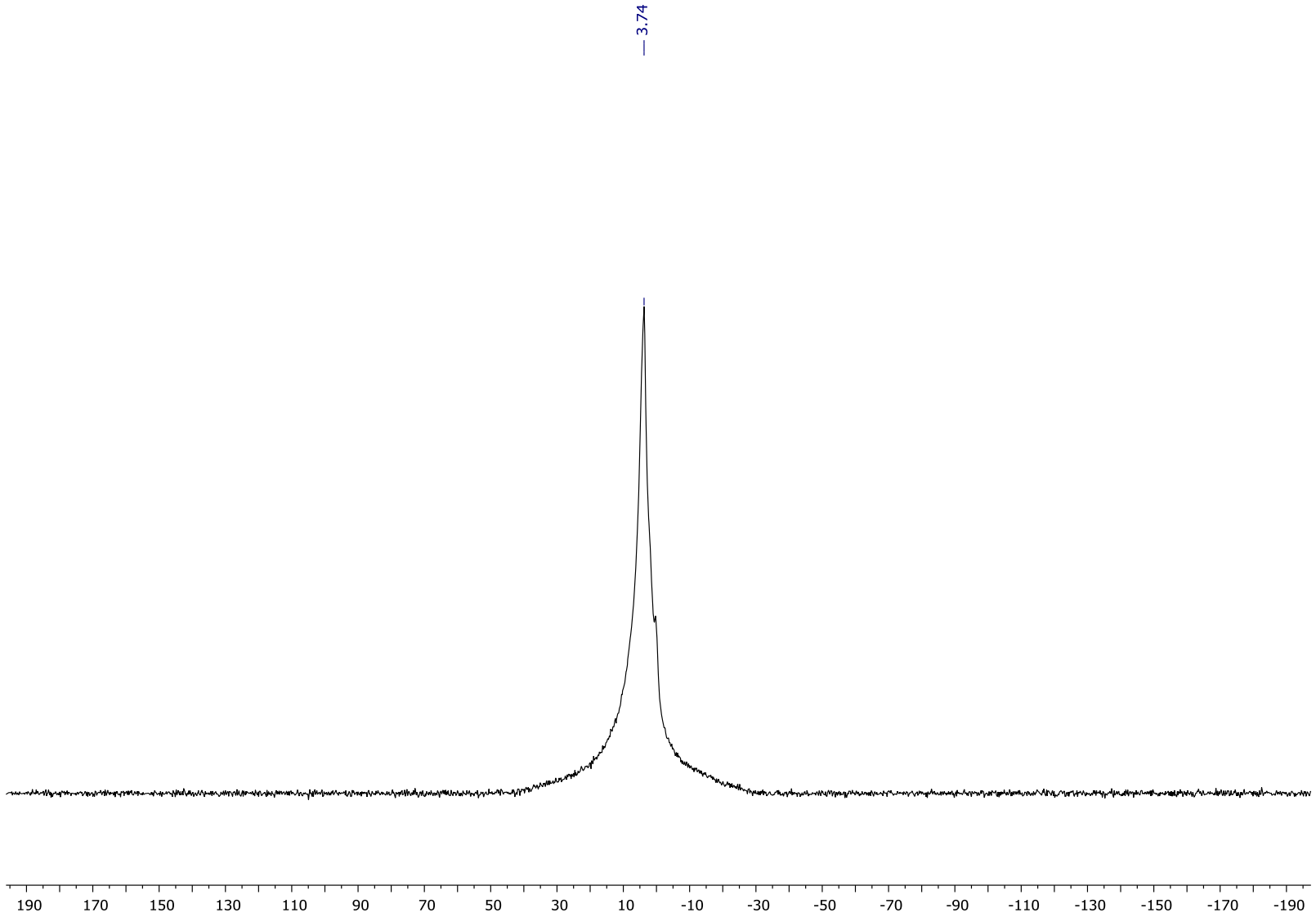
S34 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2b** and $B(C_6F_5)_3$.



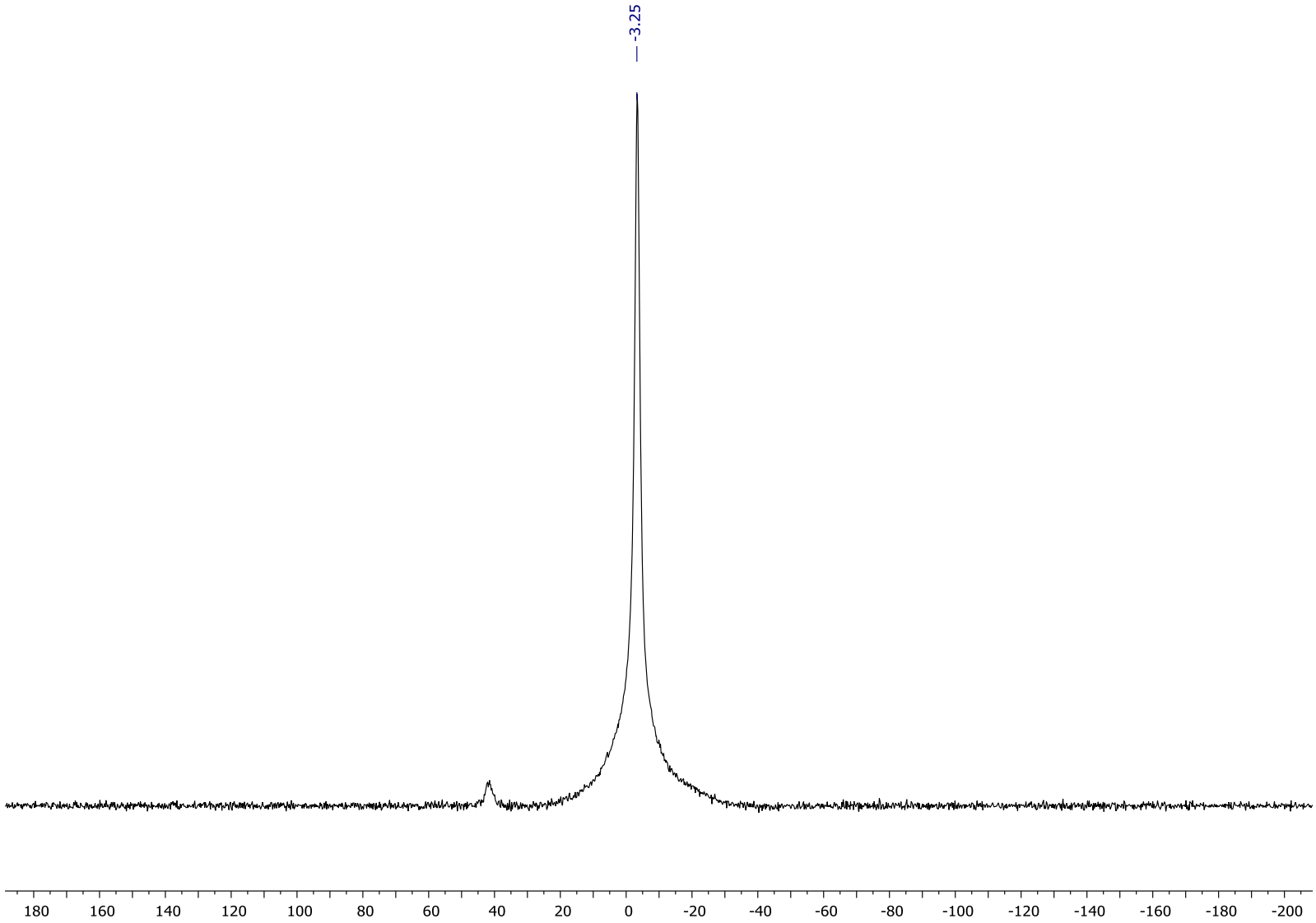
S35 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2b** and 2,4,6-$BArF_9$.



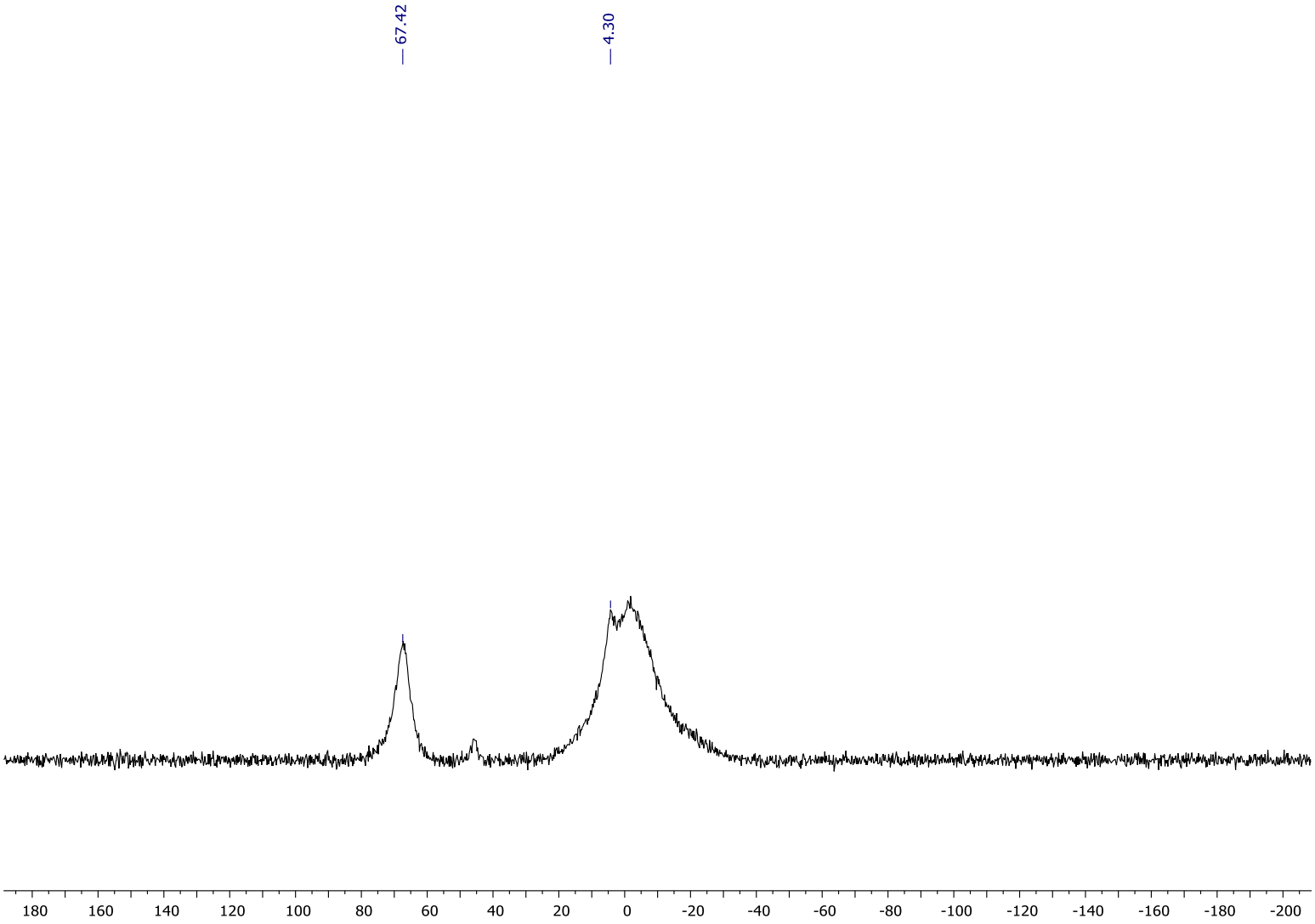
S36 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2c** and $B(C_6F_5)_3$.



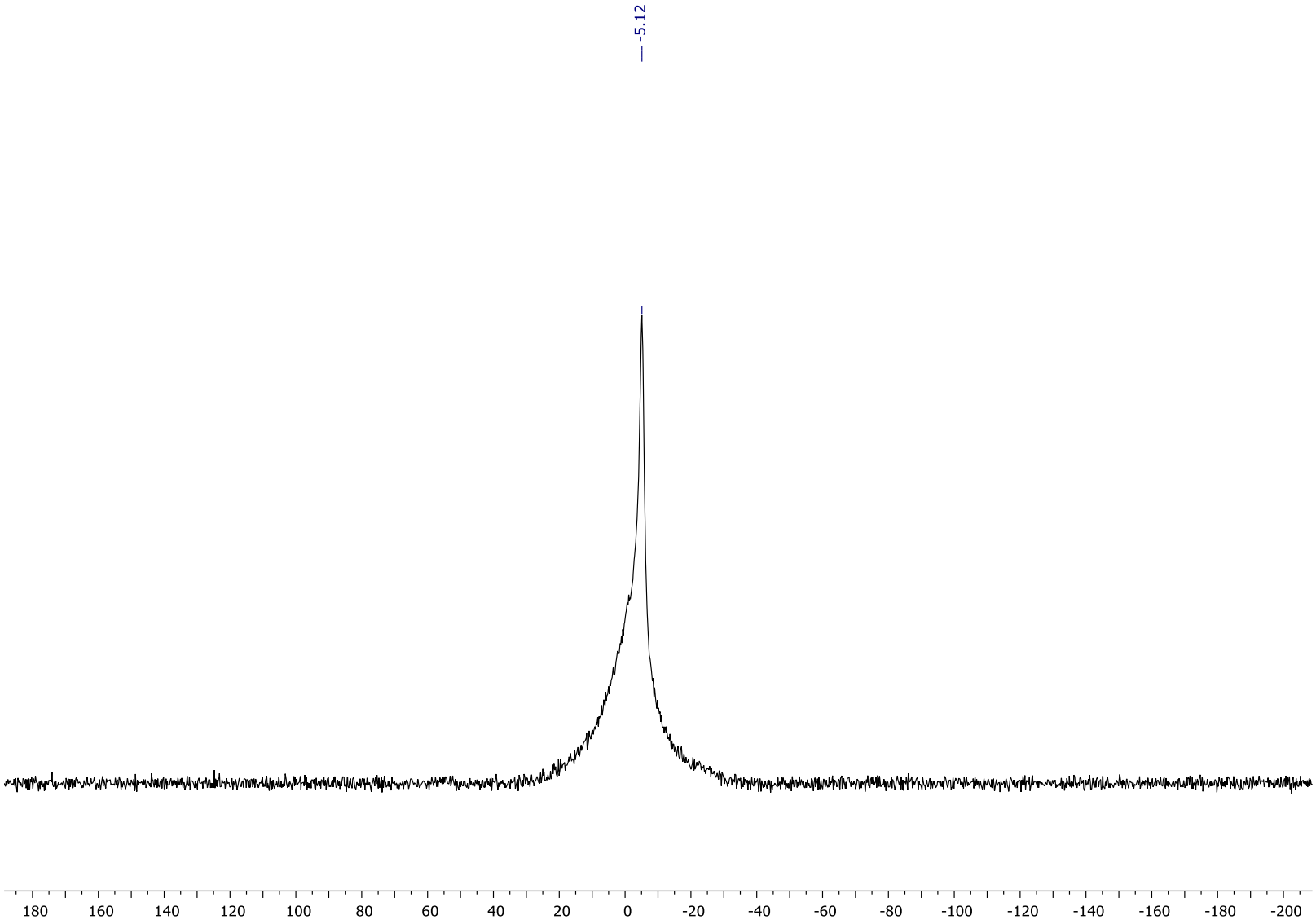
S37 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2c** and 2,4,6-$BArF_9$.



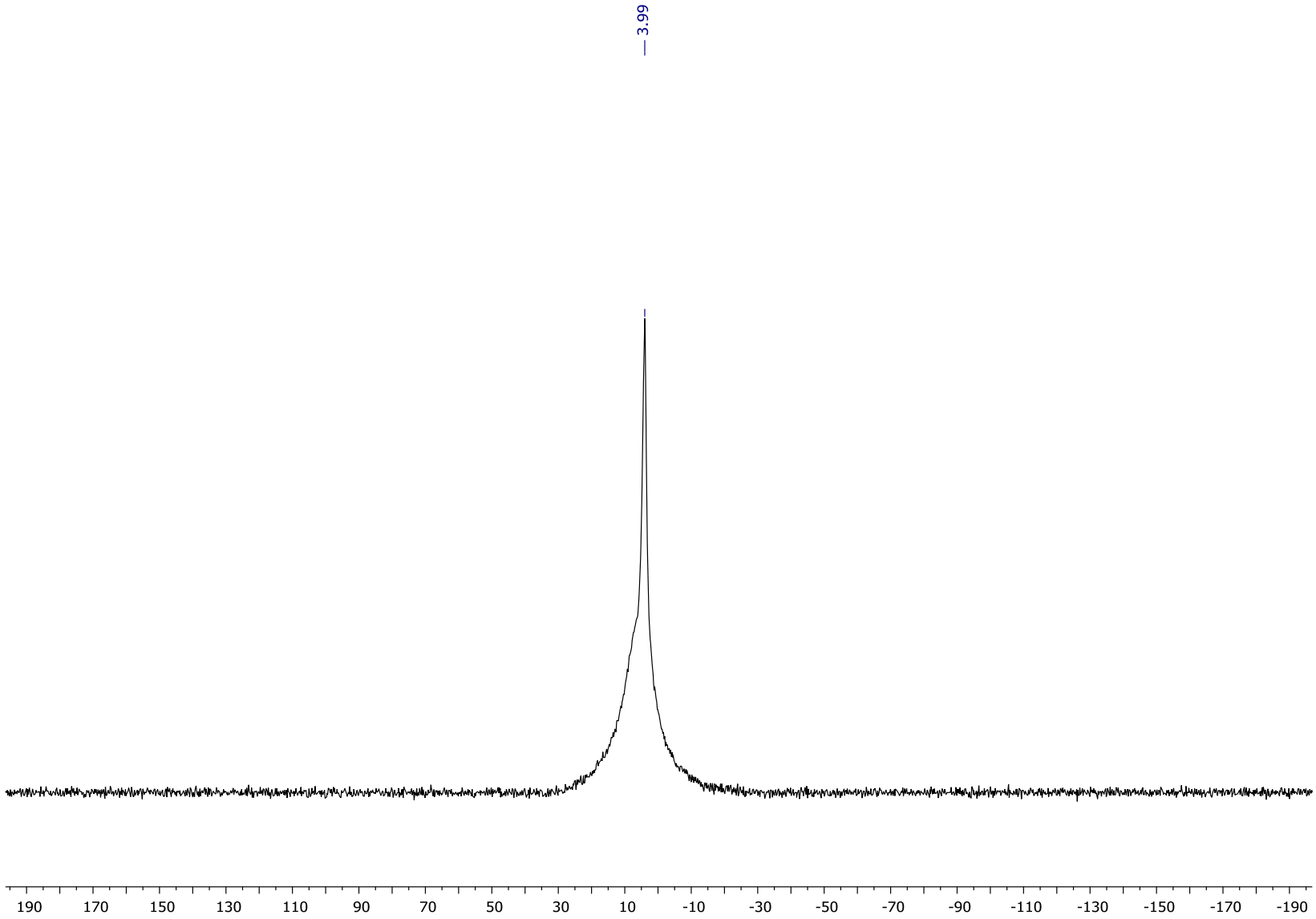
S38 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2c** and BPh_3.



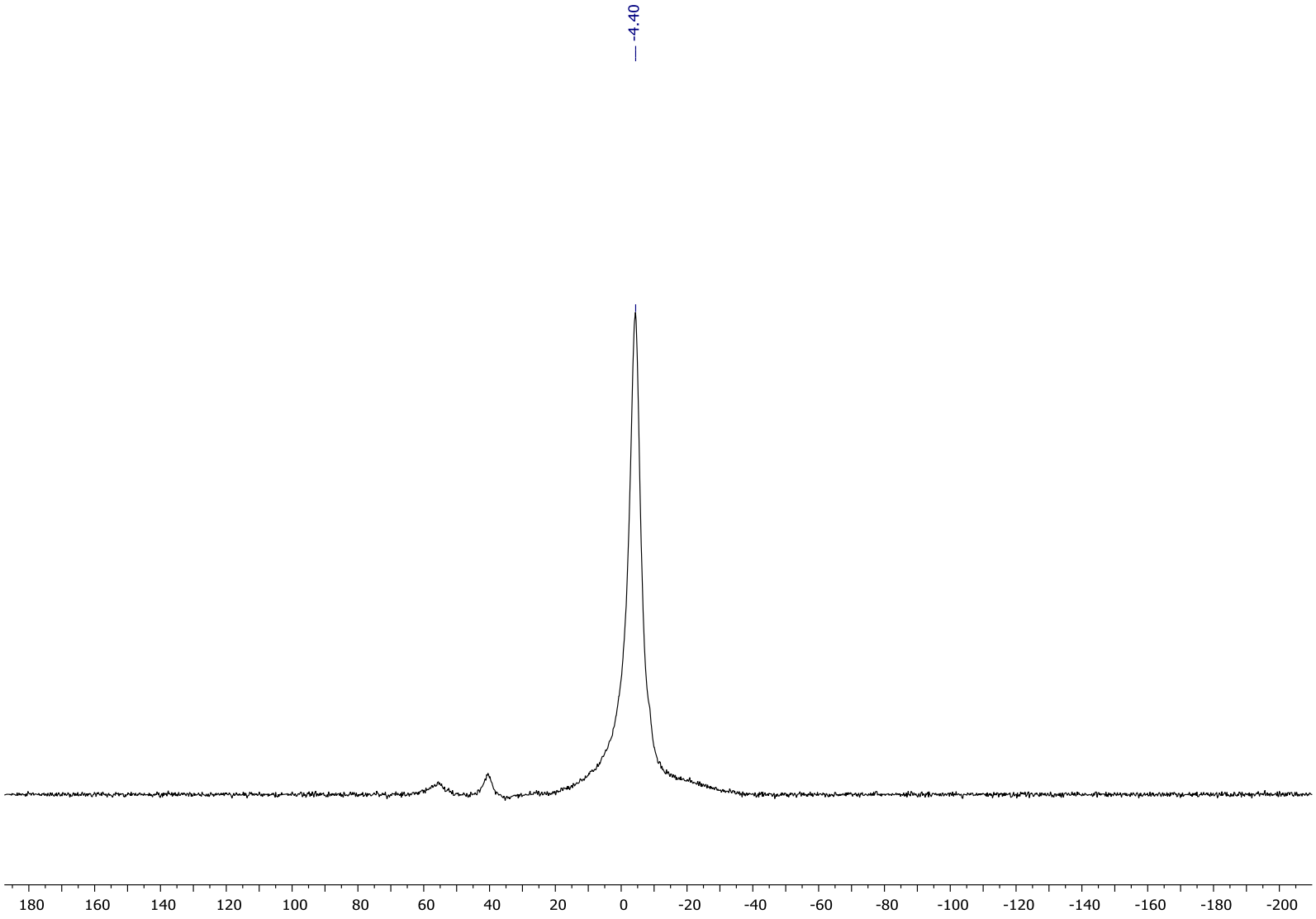
S39 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2d** and $B(C_6F_5)_3$.



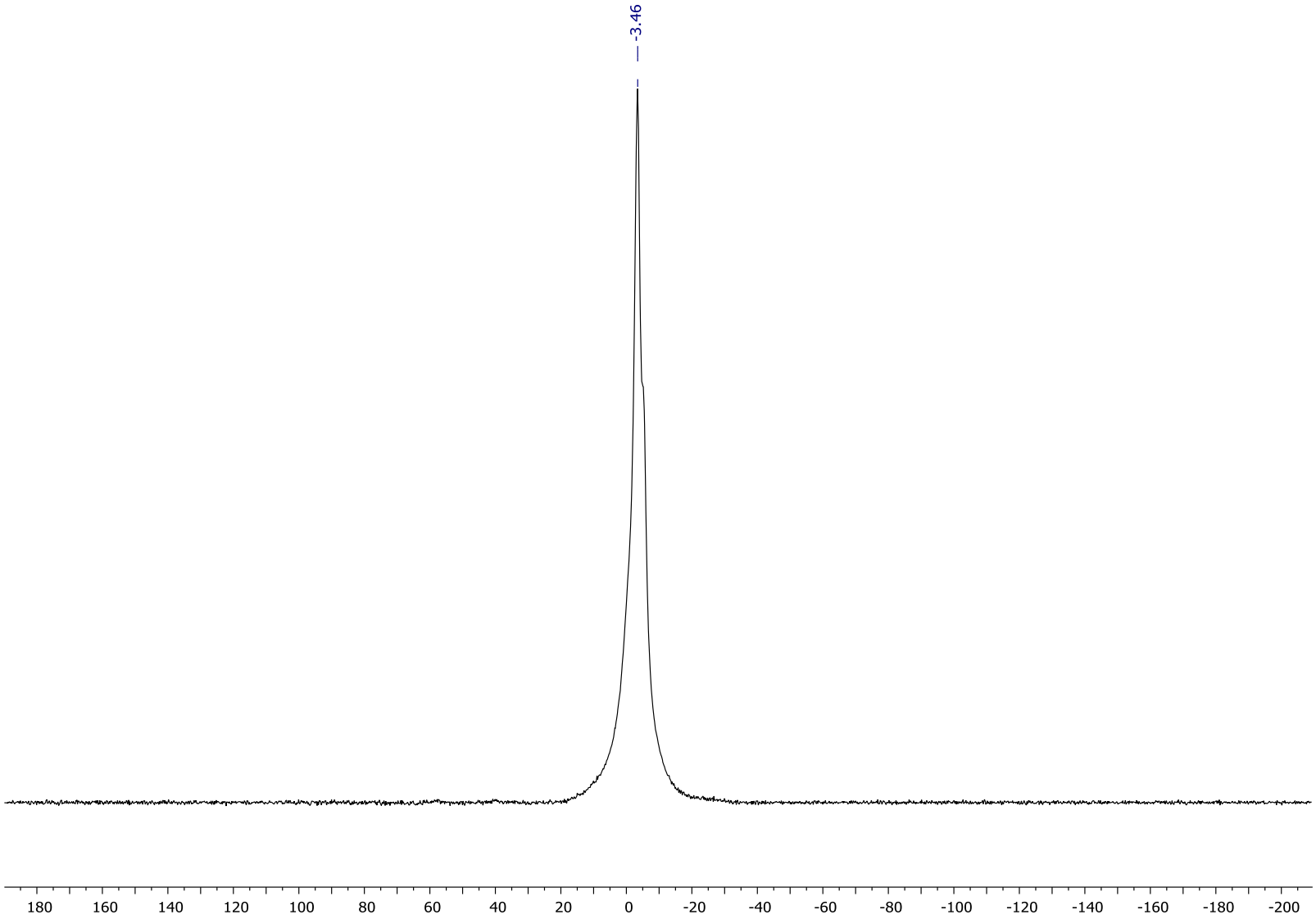
S40 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2e** and $B(C_6F_5)_3$.



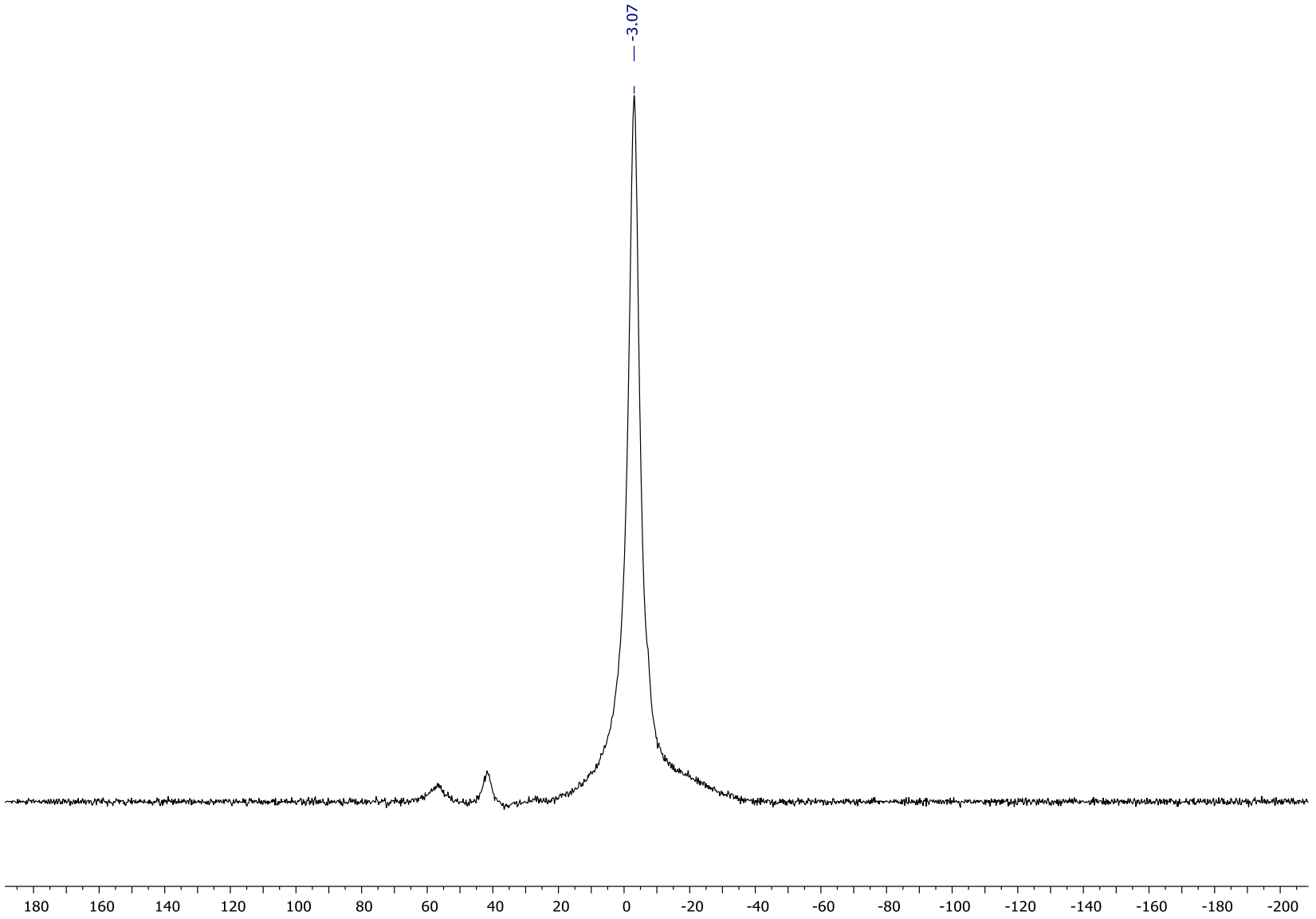
S41 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2e** and 2,4,6-$BArF_9$.



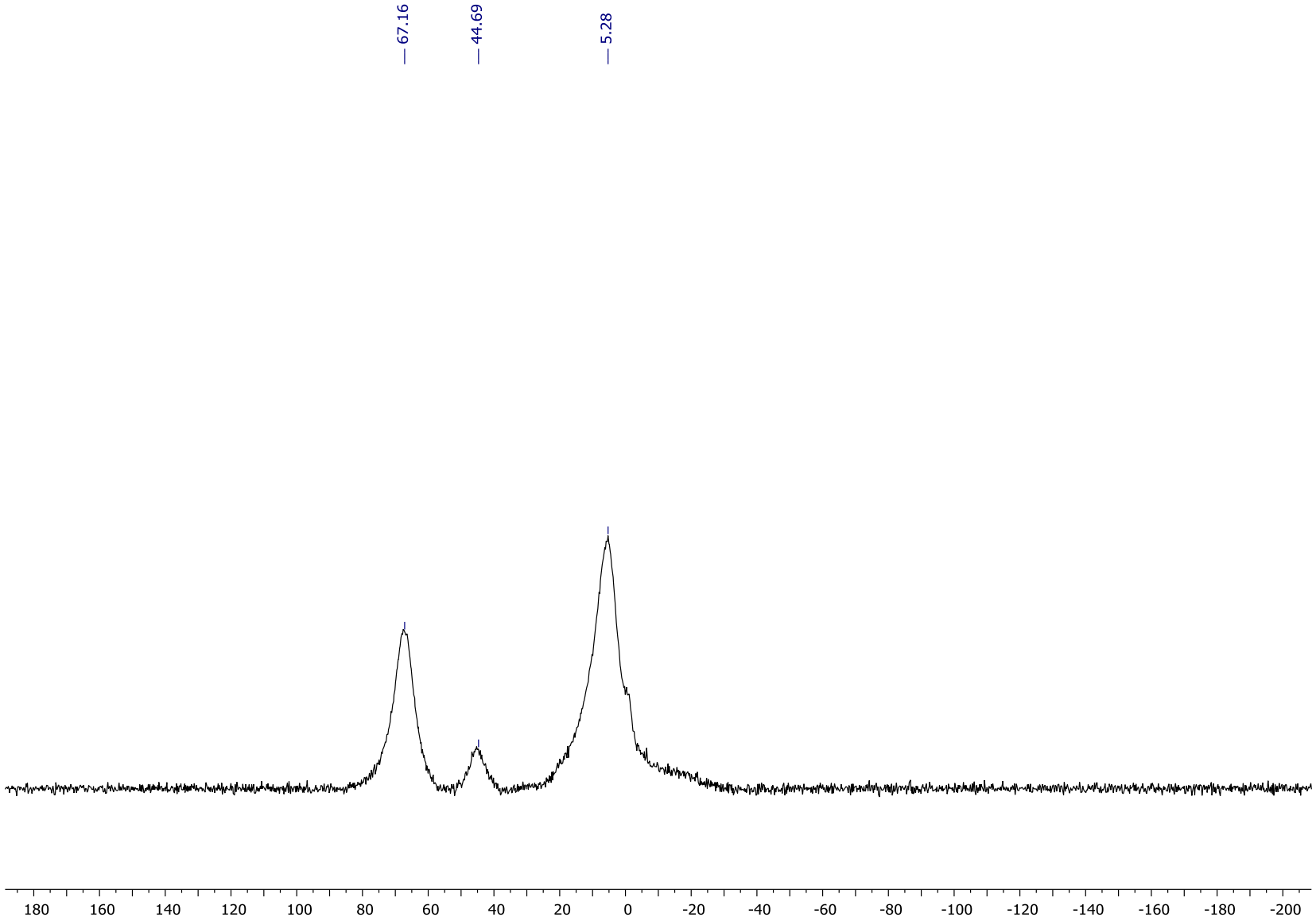
S42 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2f** and $B(C_6F_5)_3$.



S43 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2f** and 2,4,6-$BArF_9$.

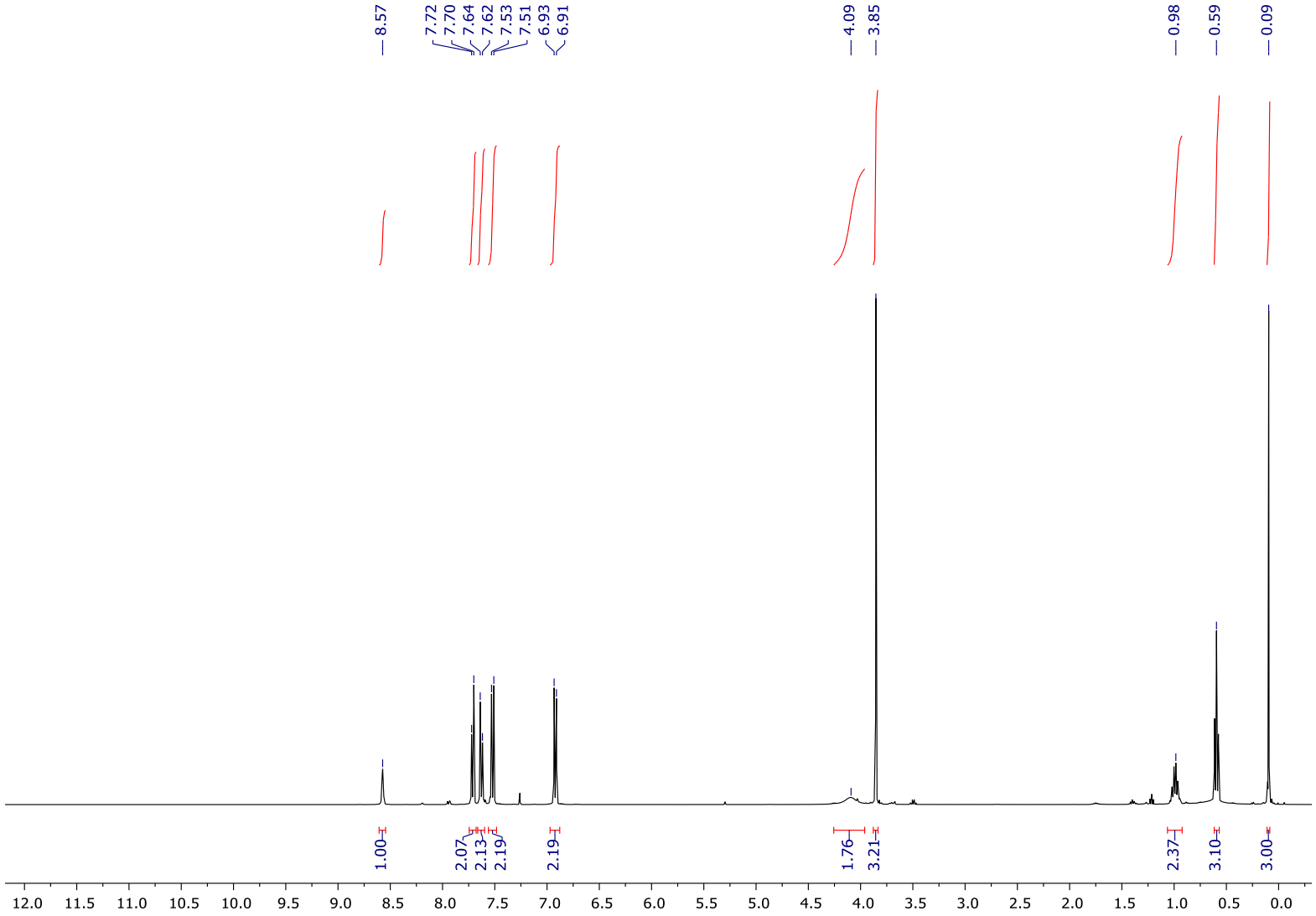


S44 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2f** and BPh_3.

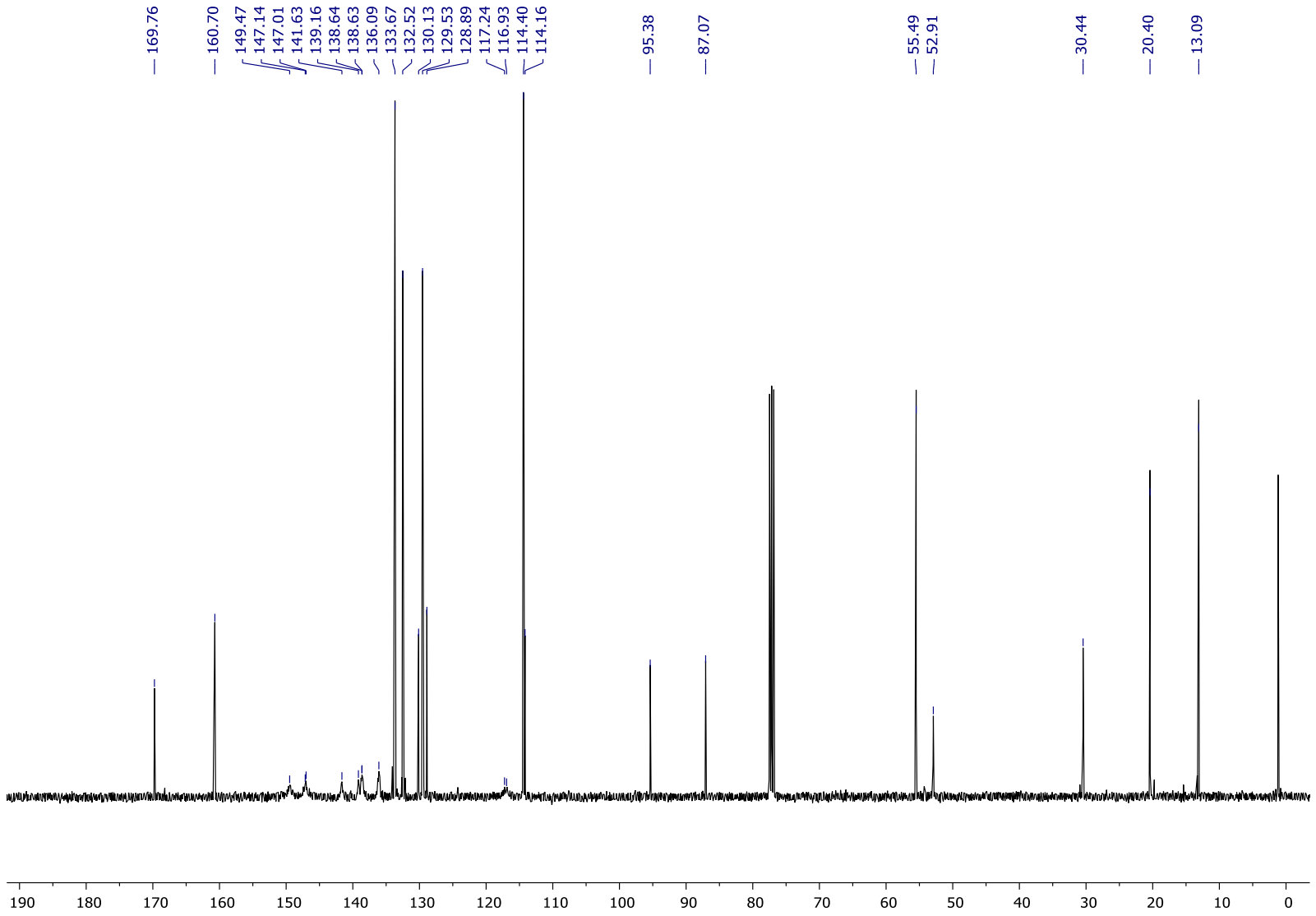


2.3 NMR spectra of borane adducts for UV-vis. measurements

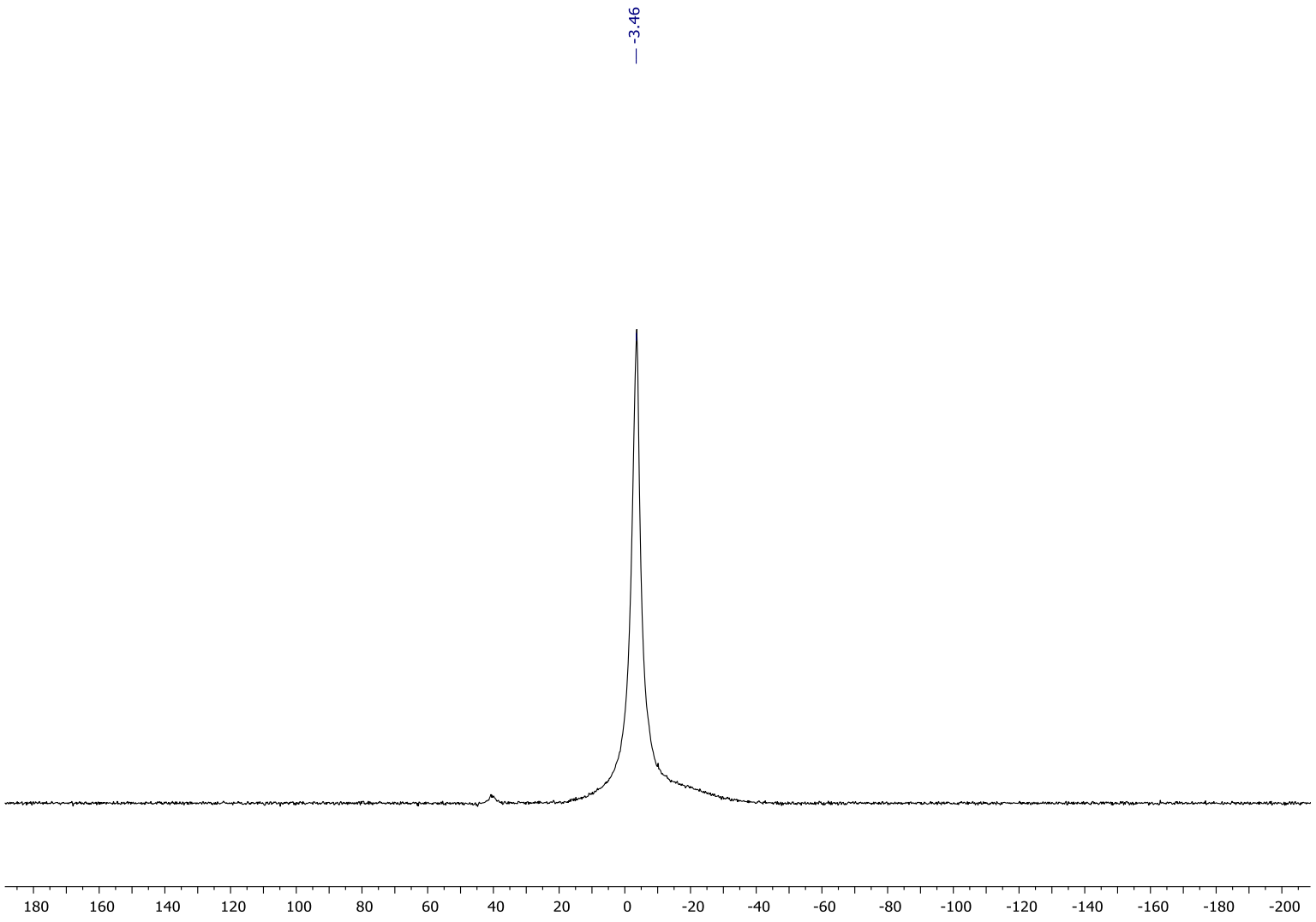
S45 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2f** and $B(C_6F_5)_3$.



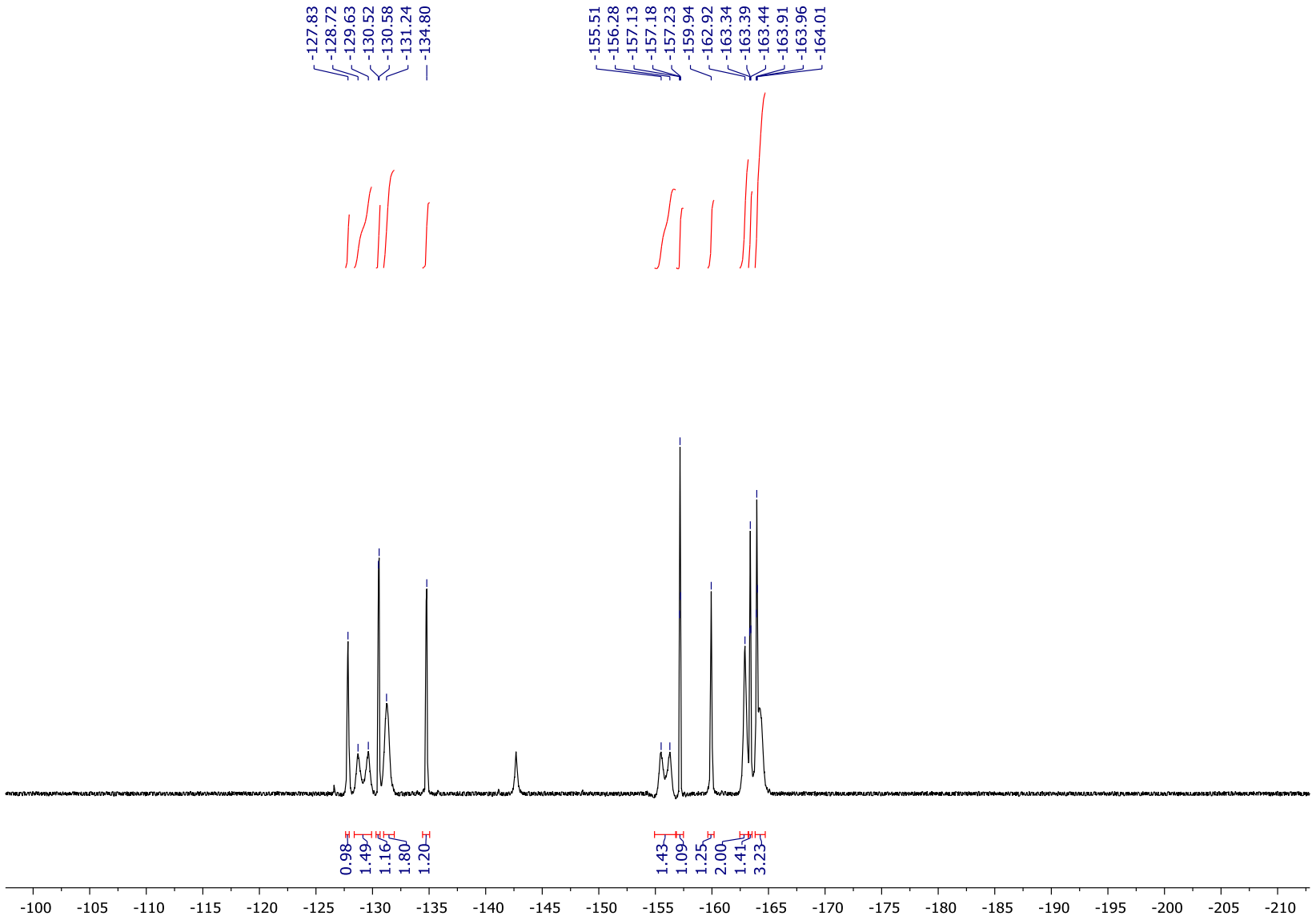
S46 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2f** and $B(C_6F_5)_3$.



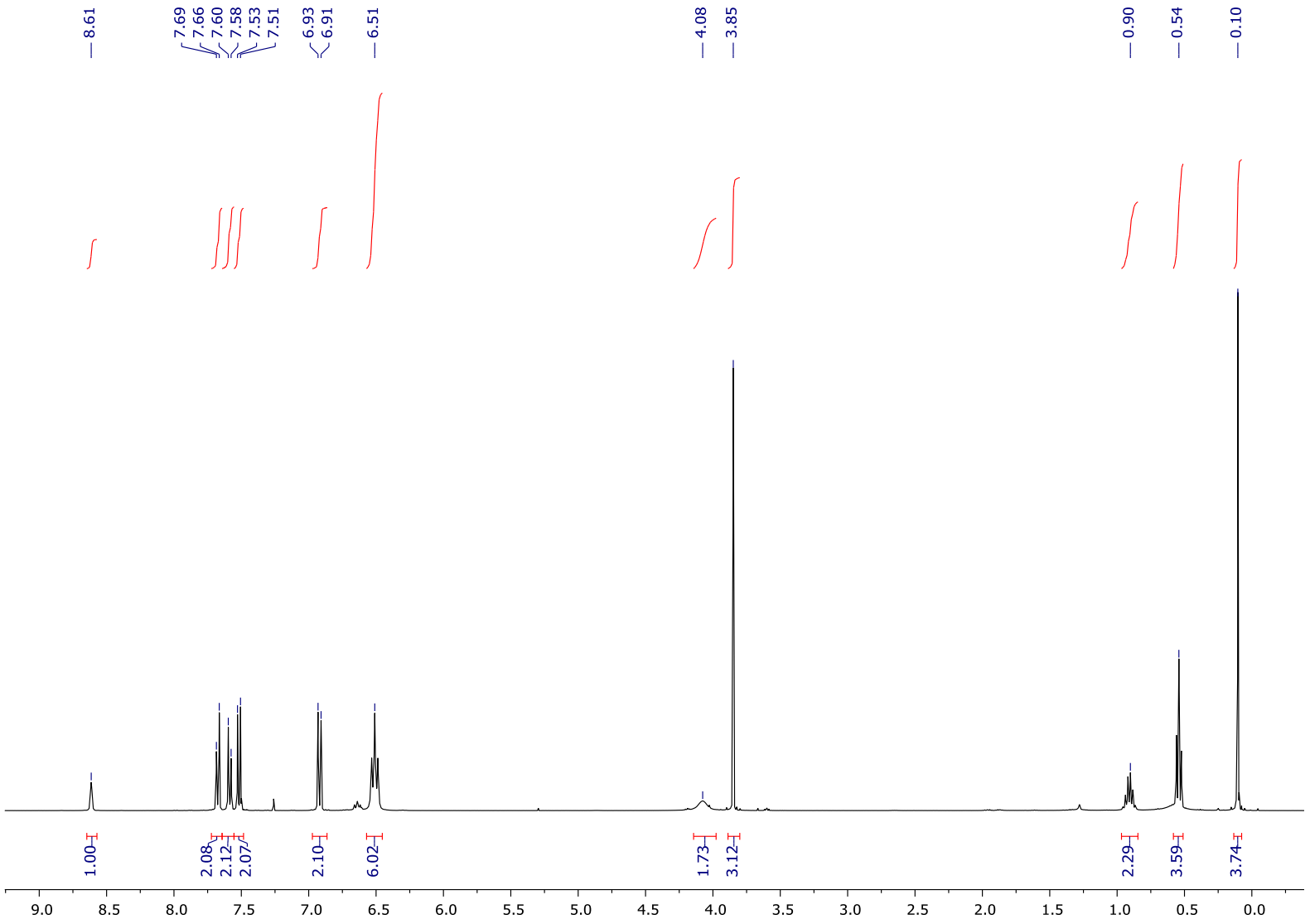
S47 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2f** and $B(C_6F_5)_3$.



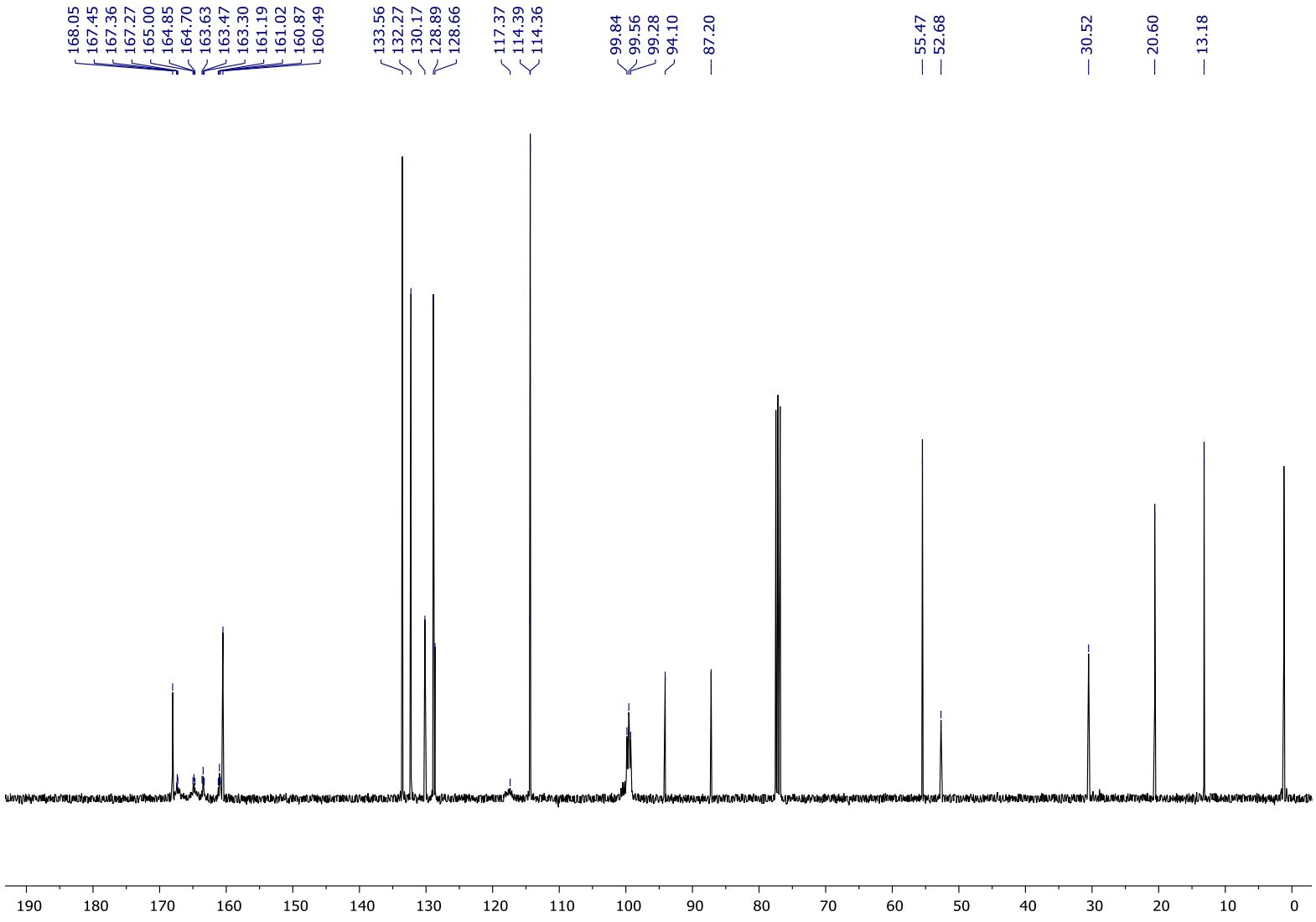
S48 ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2f** and $B(C_6F_5)_3$.



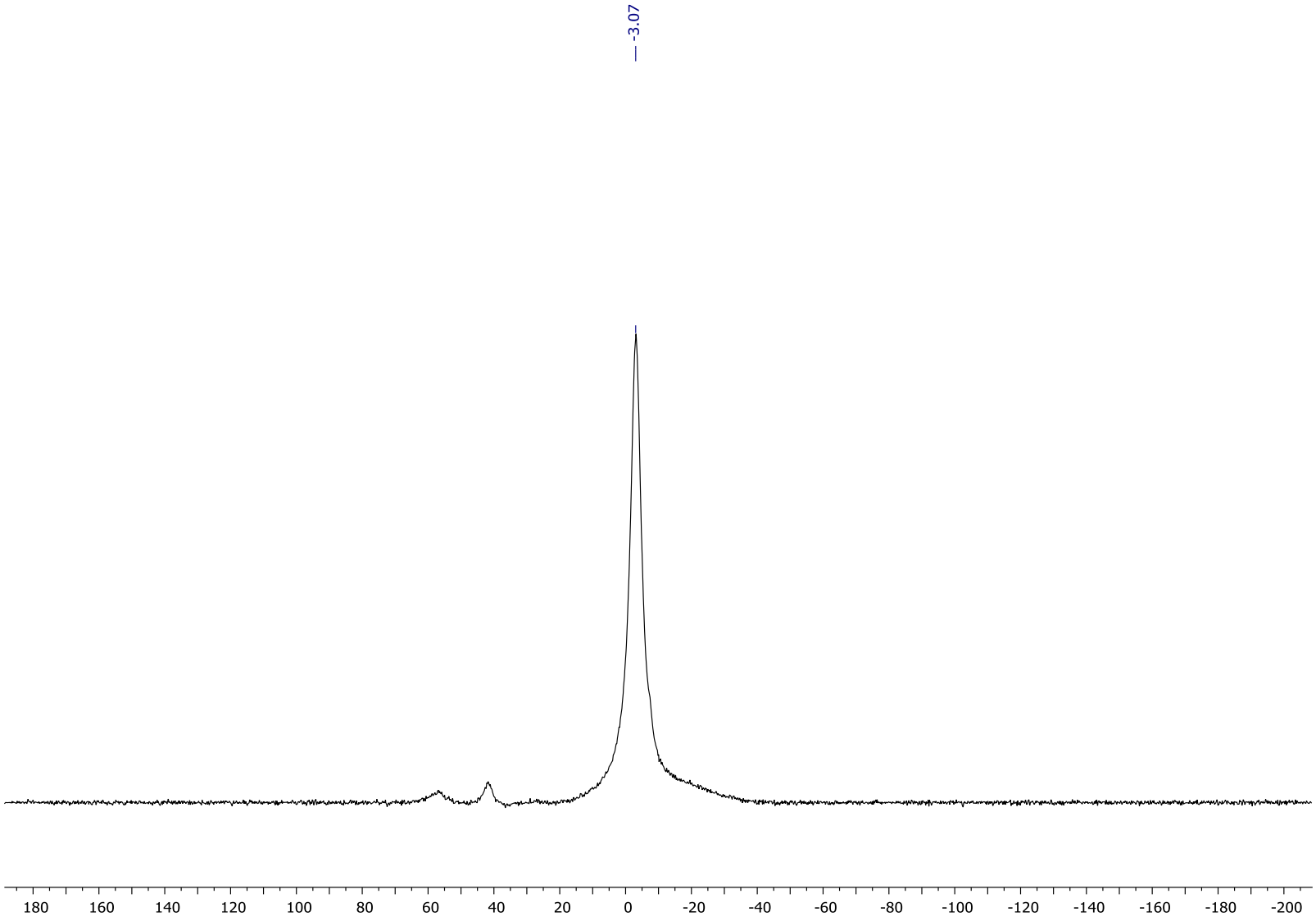
S49 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2f** and 2,4,6-$BArF_9$.



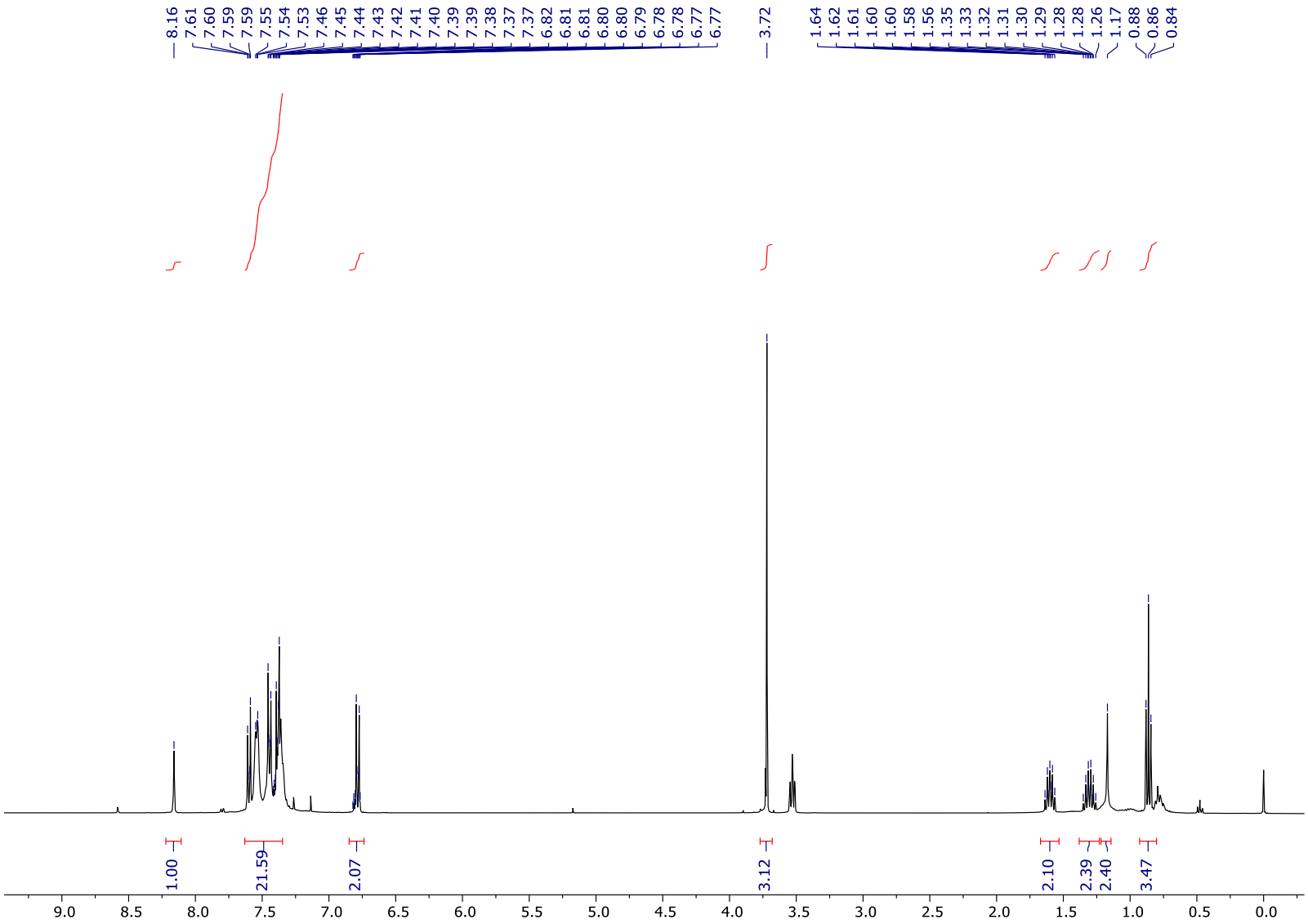
S50 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2f** and 2,4,6-$BArF_9$



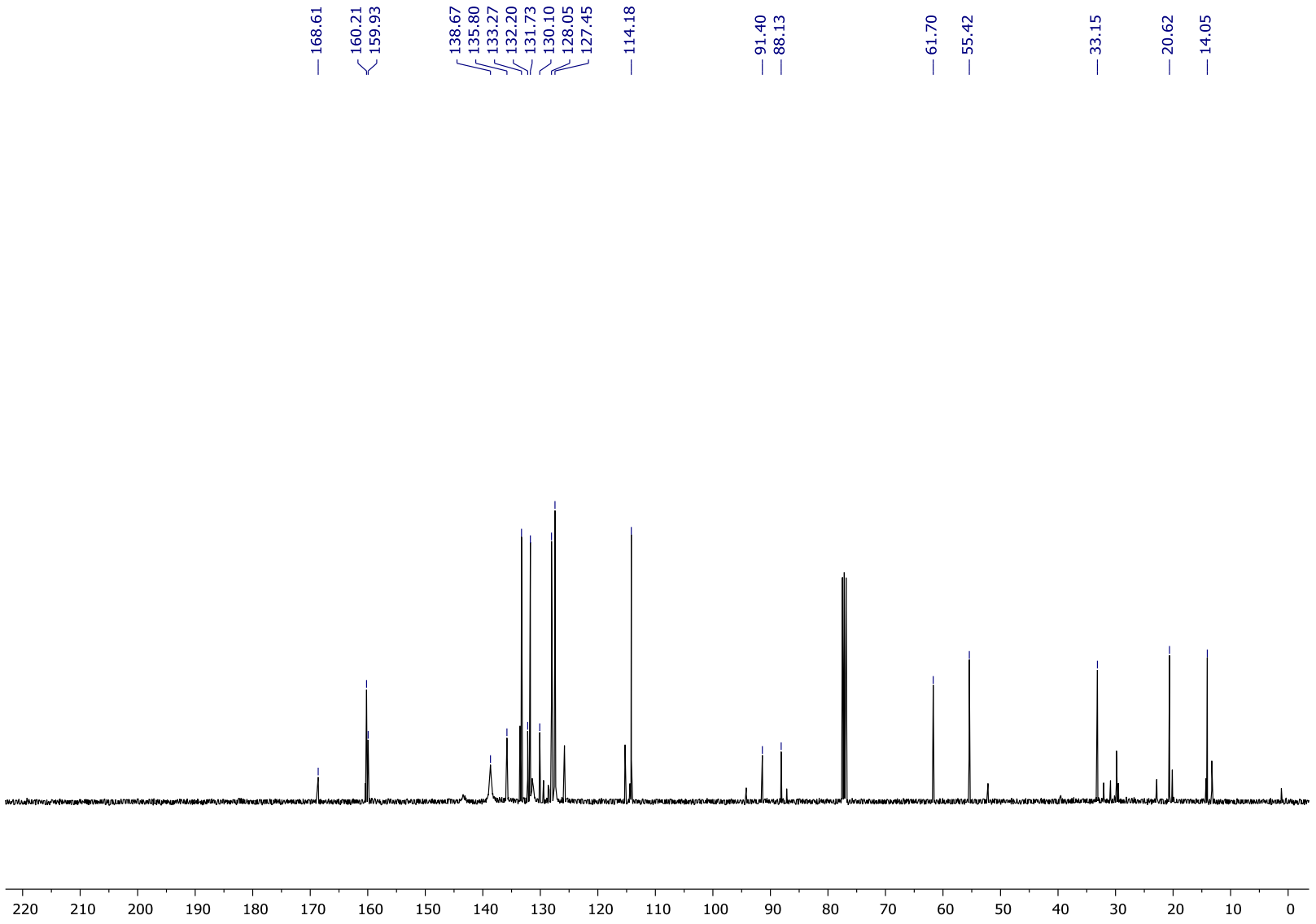
S51 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2f** and 2,4,6-$BArF_9$.



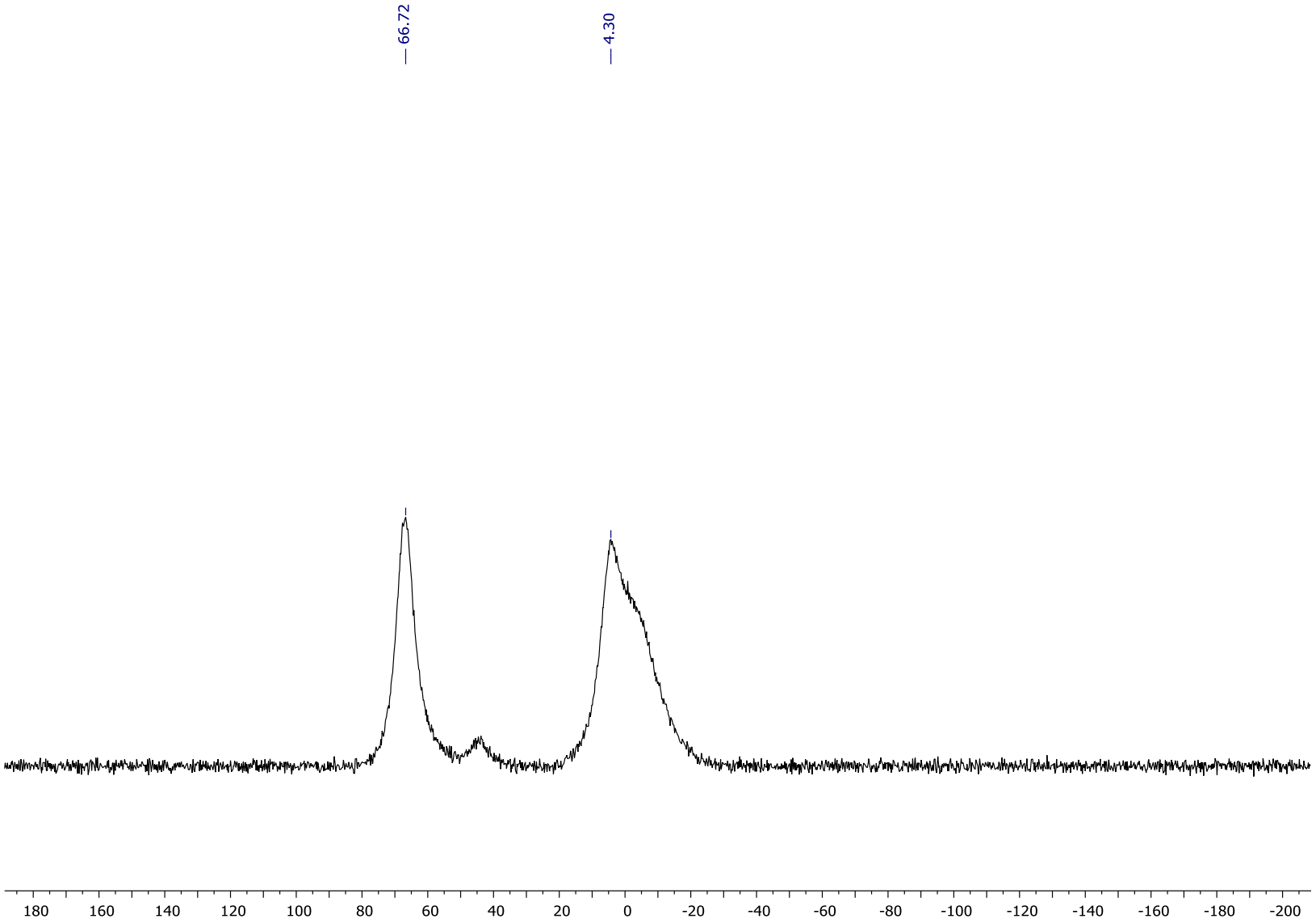
S52 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2f** and BPh_3.



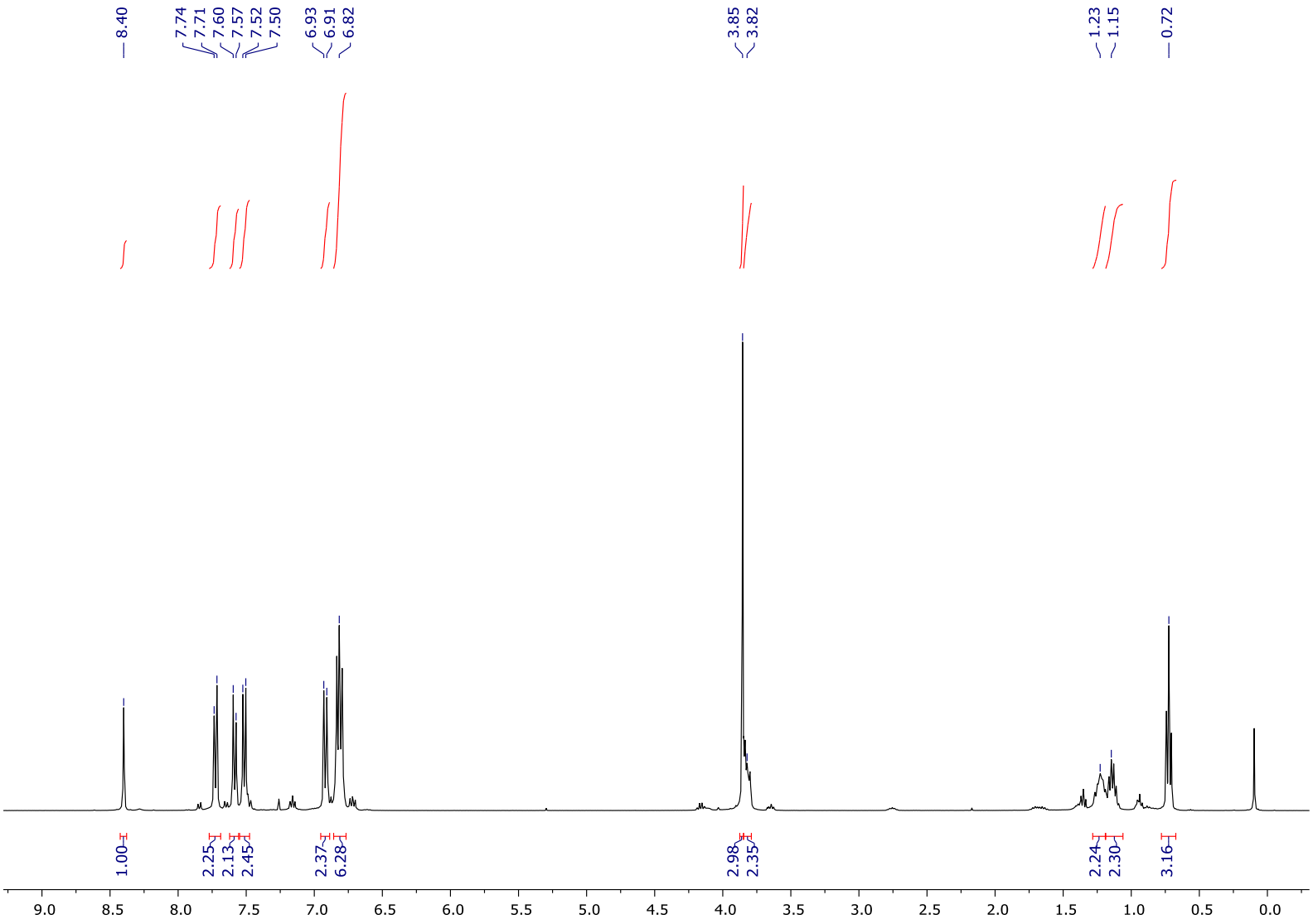
S53 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2f** and BPh_3.



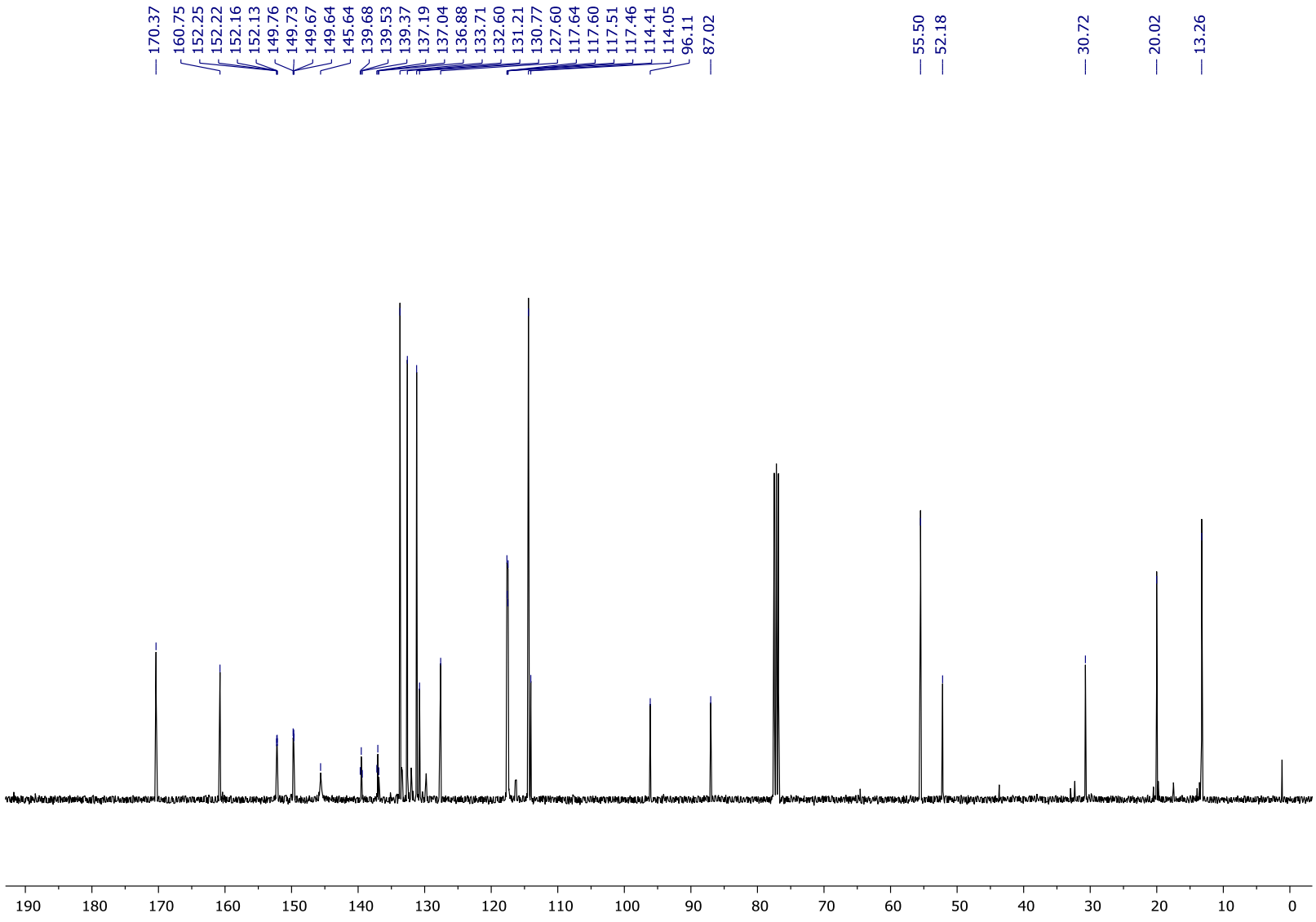
S54 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2f** and BPh_3.



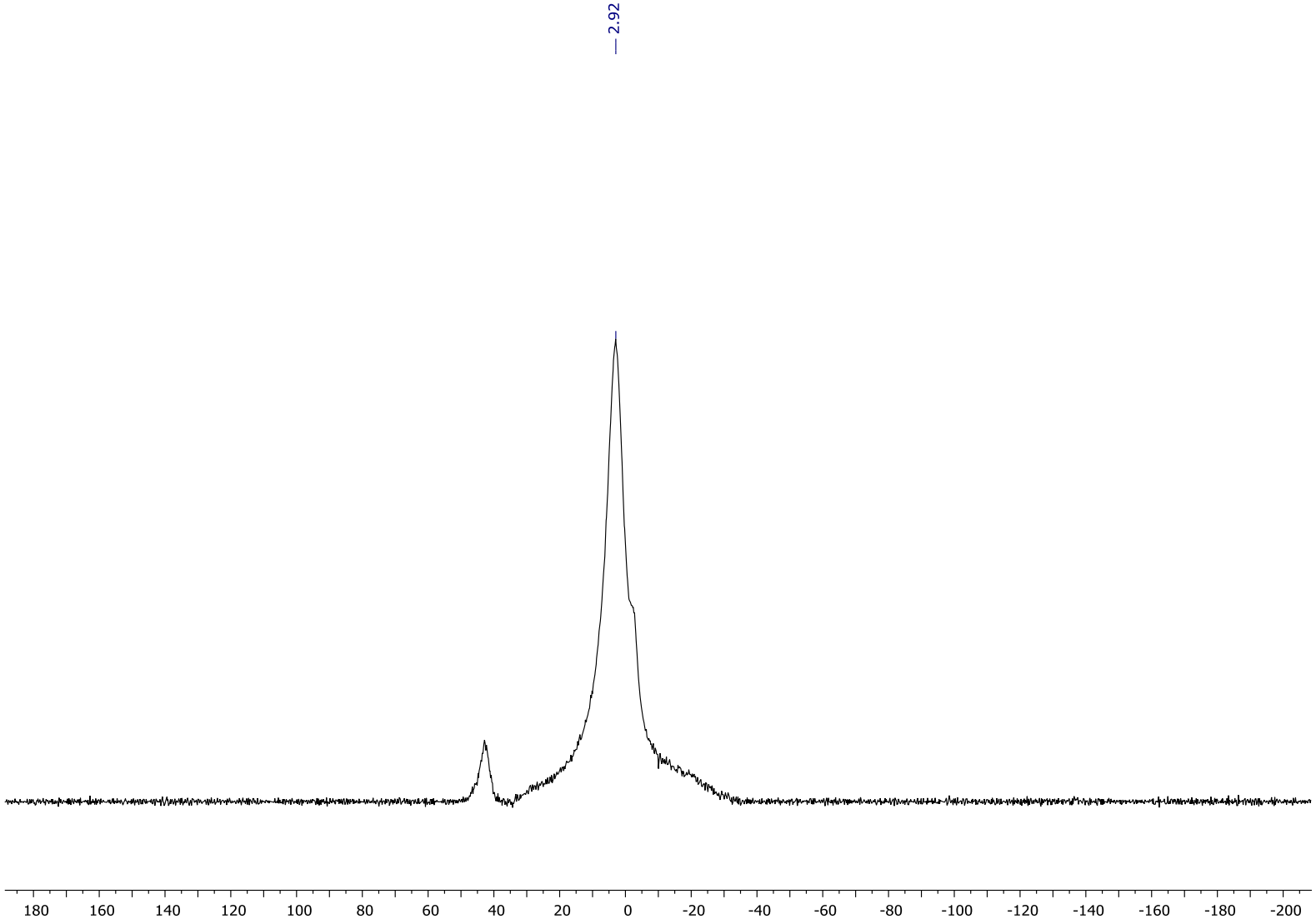
S55 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2f** and 3,4,5-$BArF_9$.



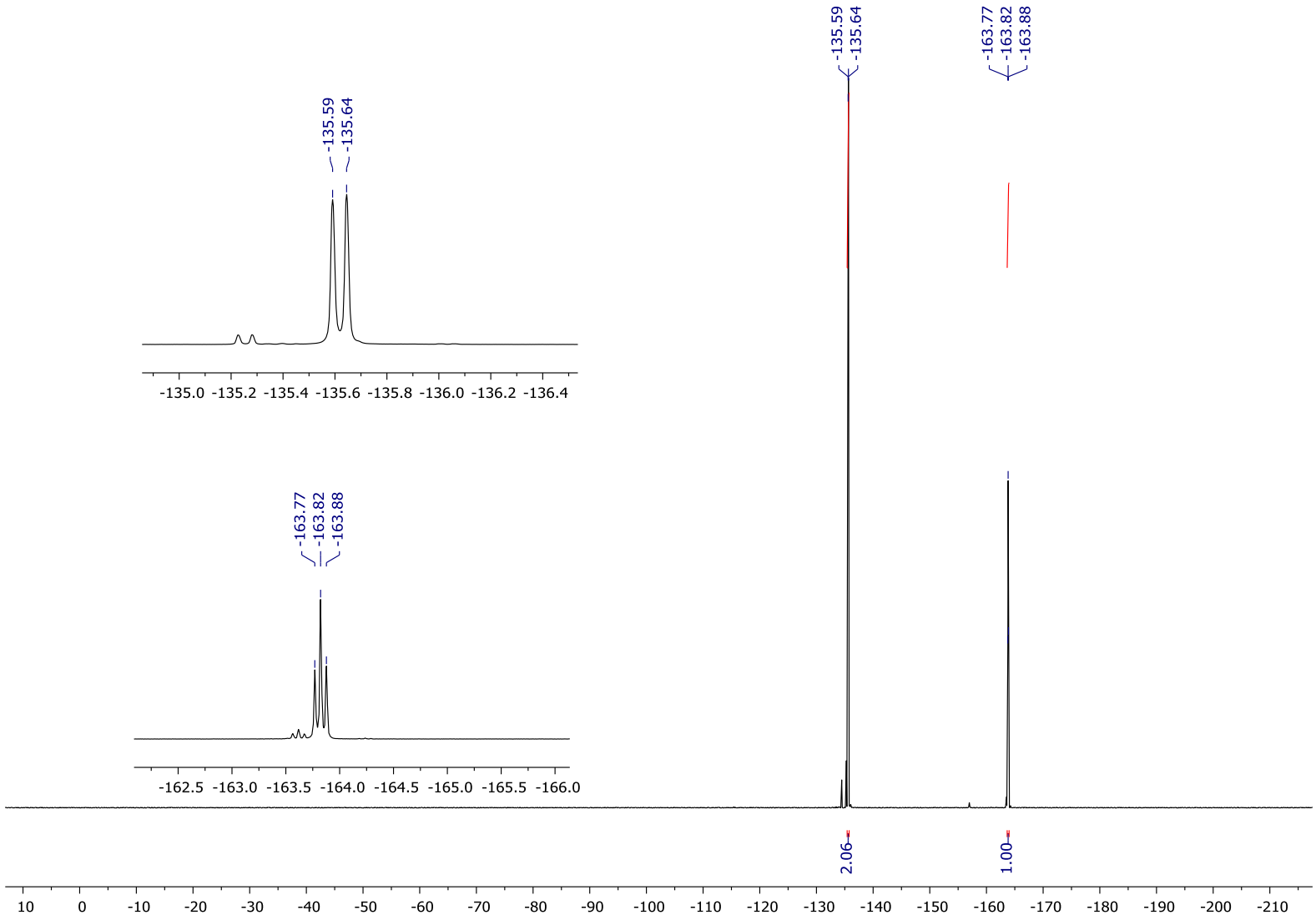
S56 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2f** and 3,4,5-$BArF_9$.



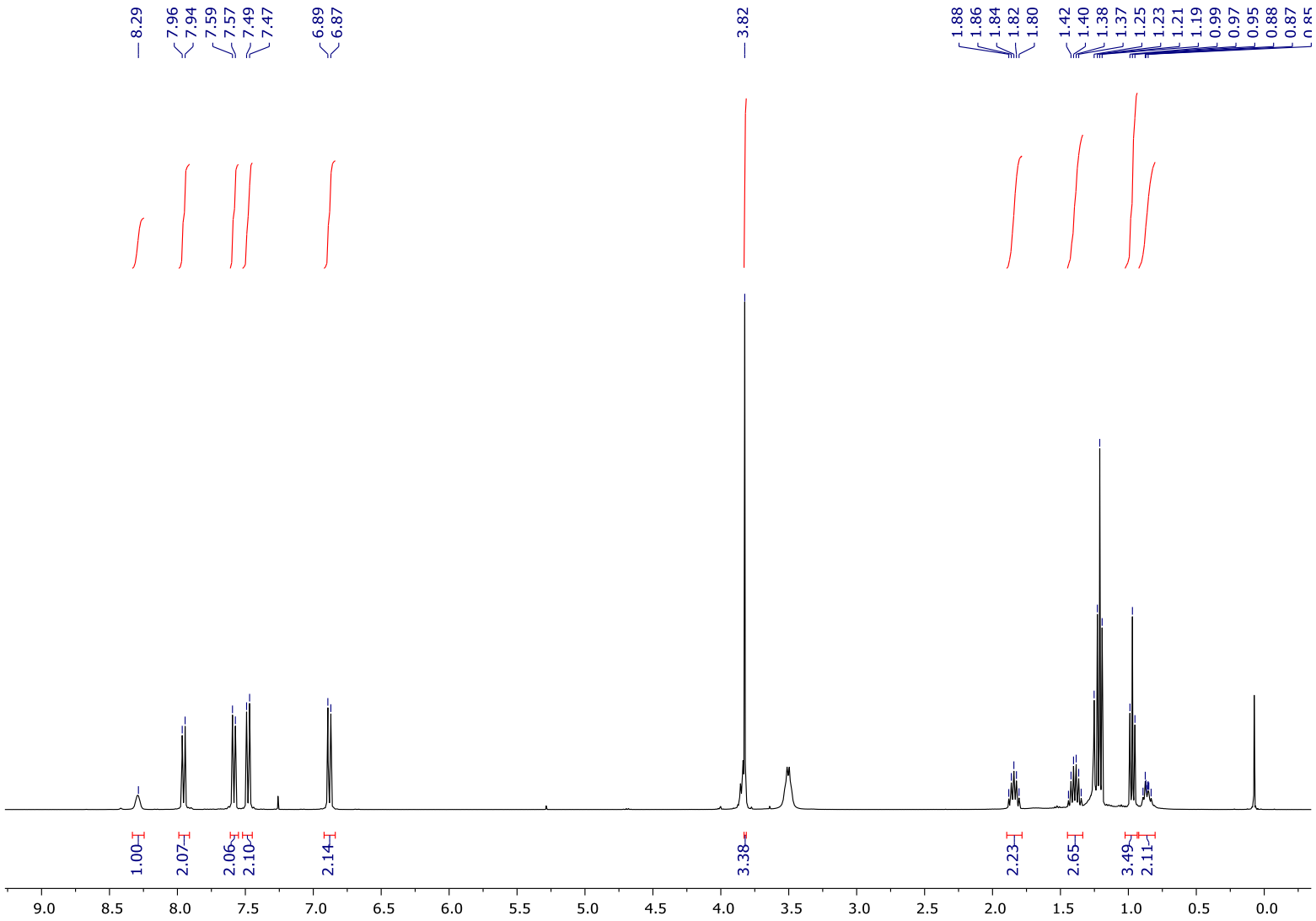
S57 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2f** and 3,4,5-$BArF_9$.



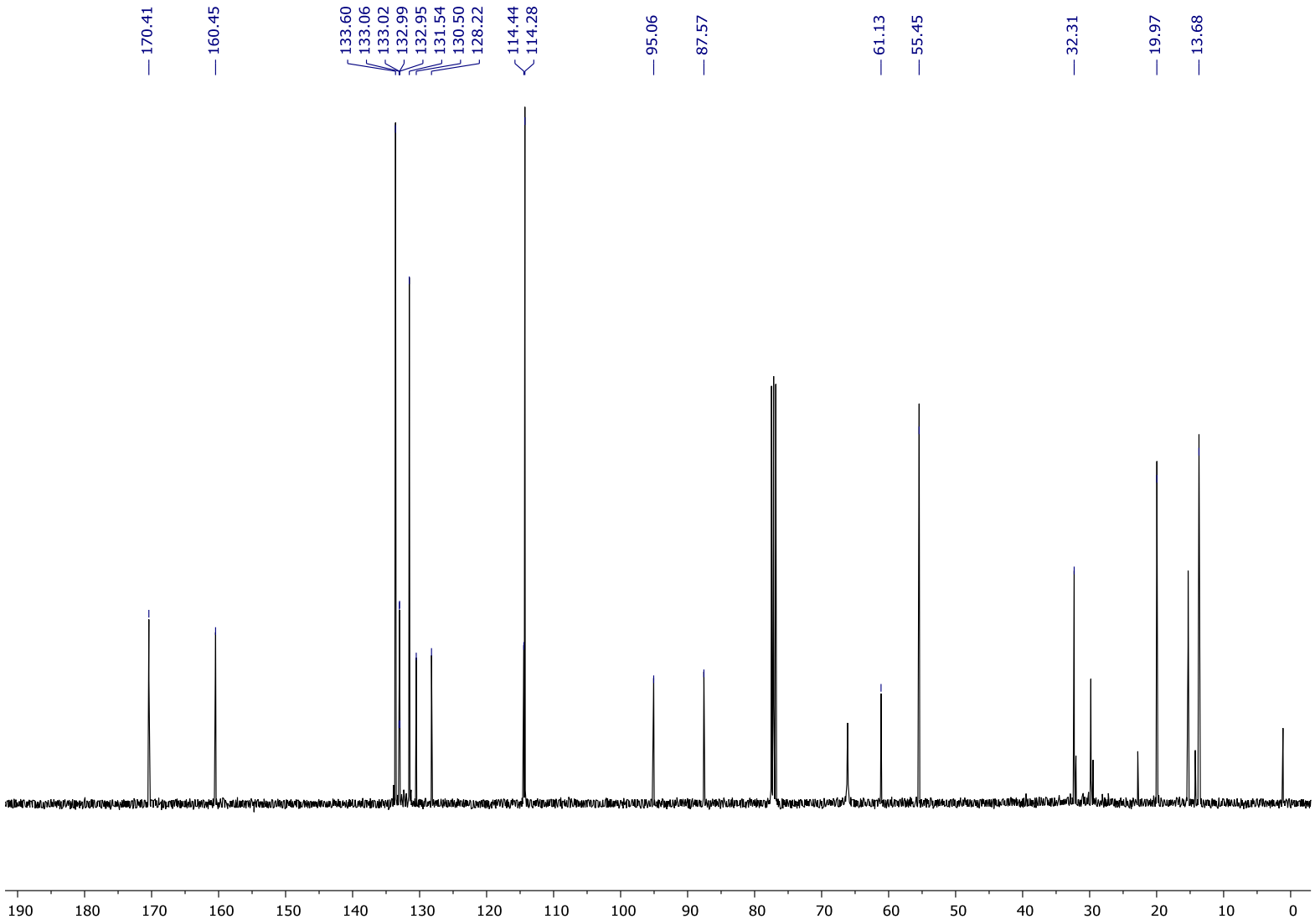
S58 ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2f** and 3,4,5-$BArF_9$.



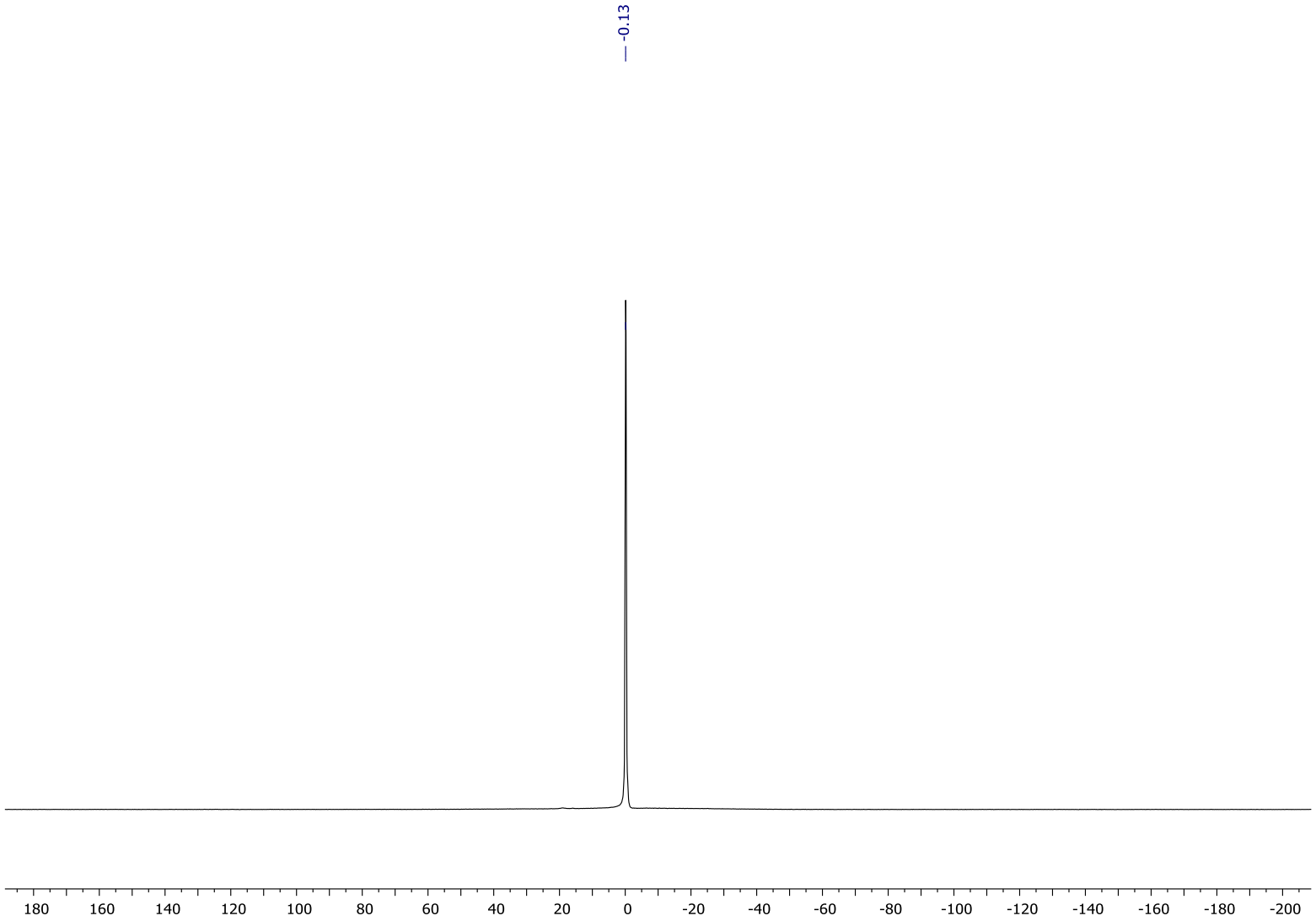
S59 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2f** and BF_3.



S60 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2f** and BF_3.

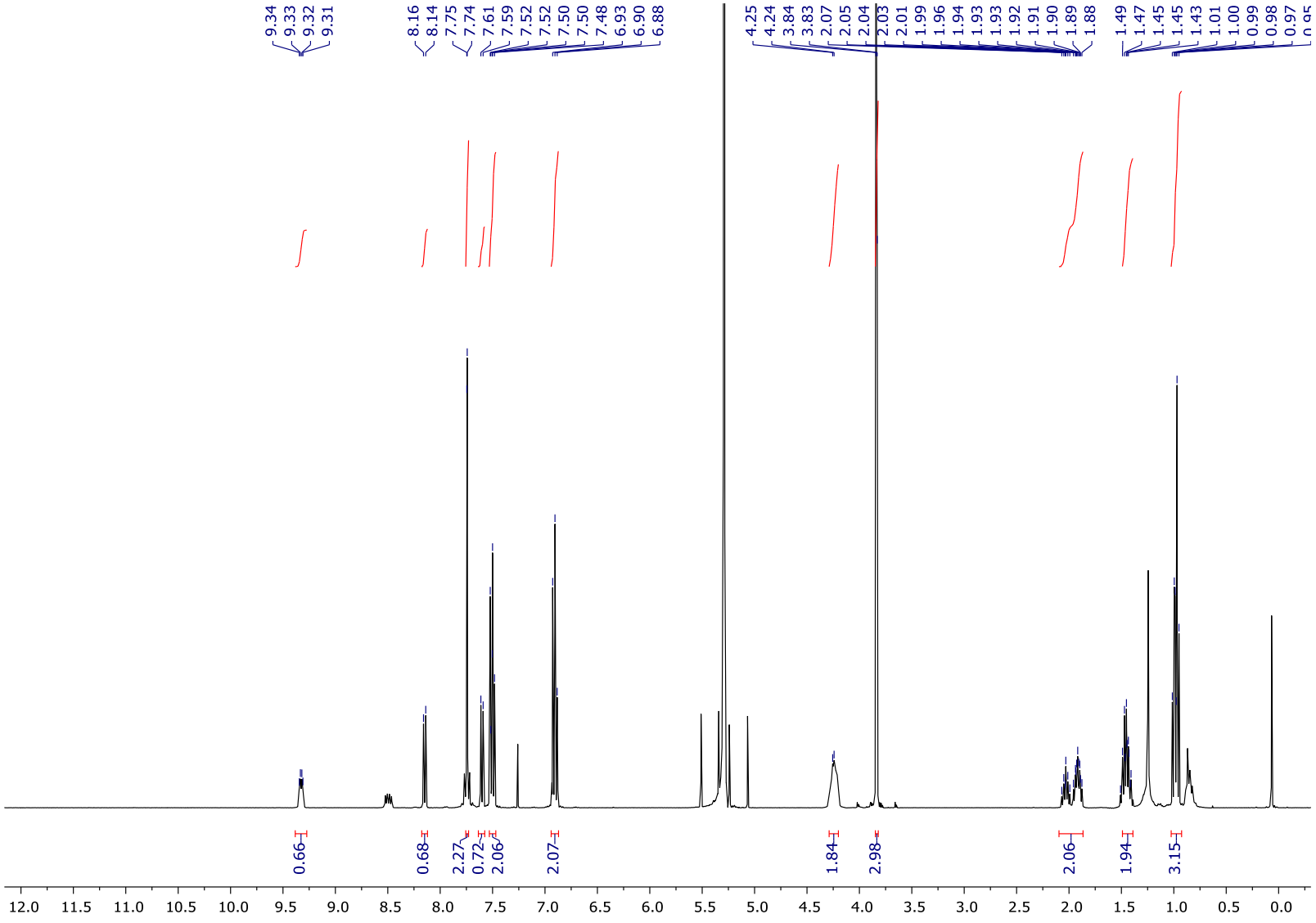


S61 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2f** and BF_3.

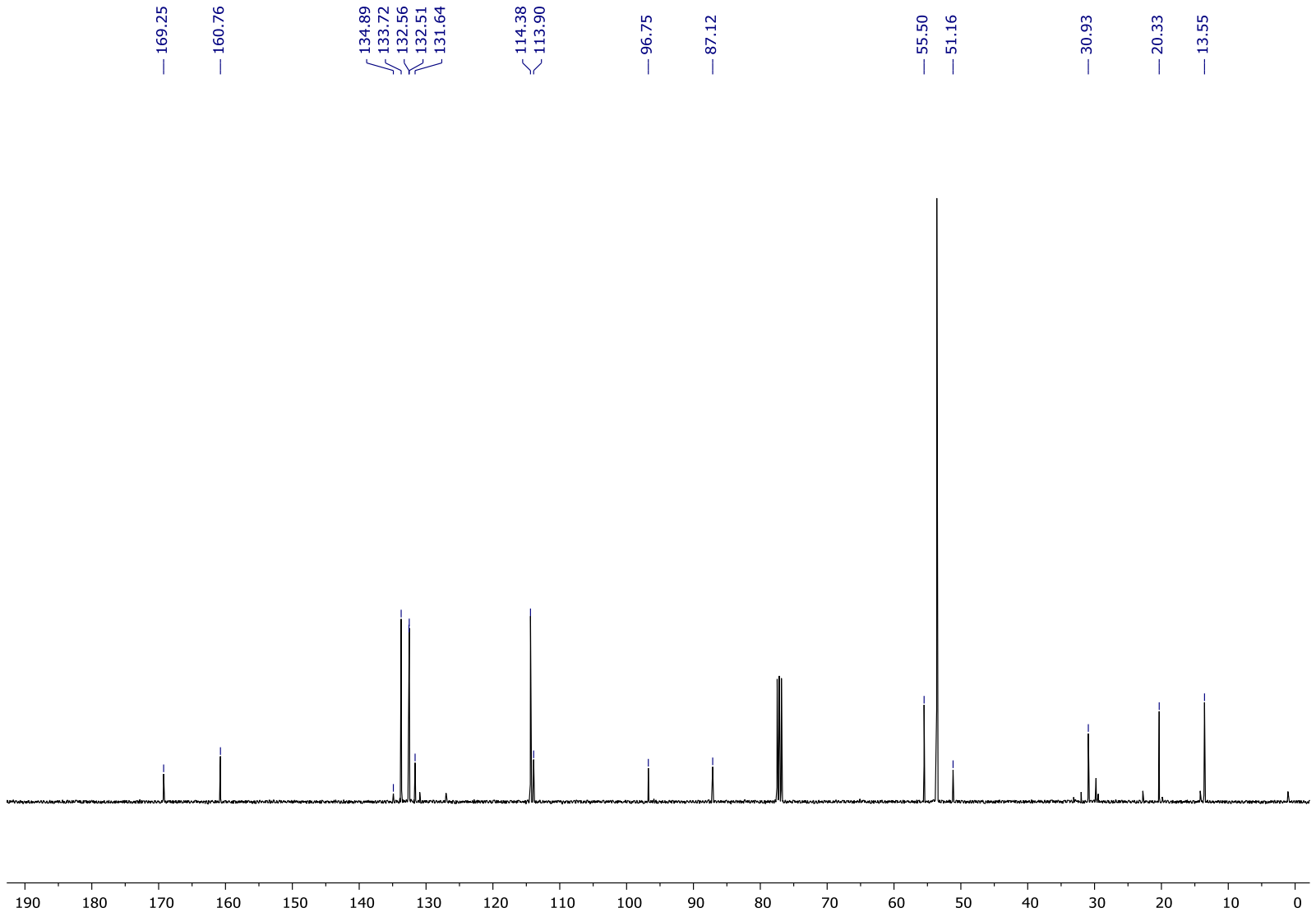


S62 ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2f** and BF_3.

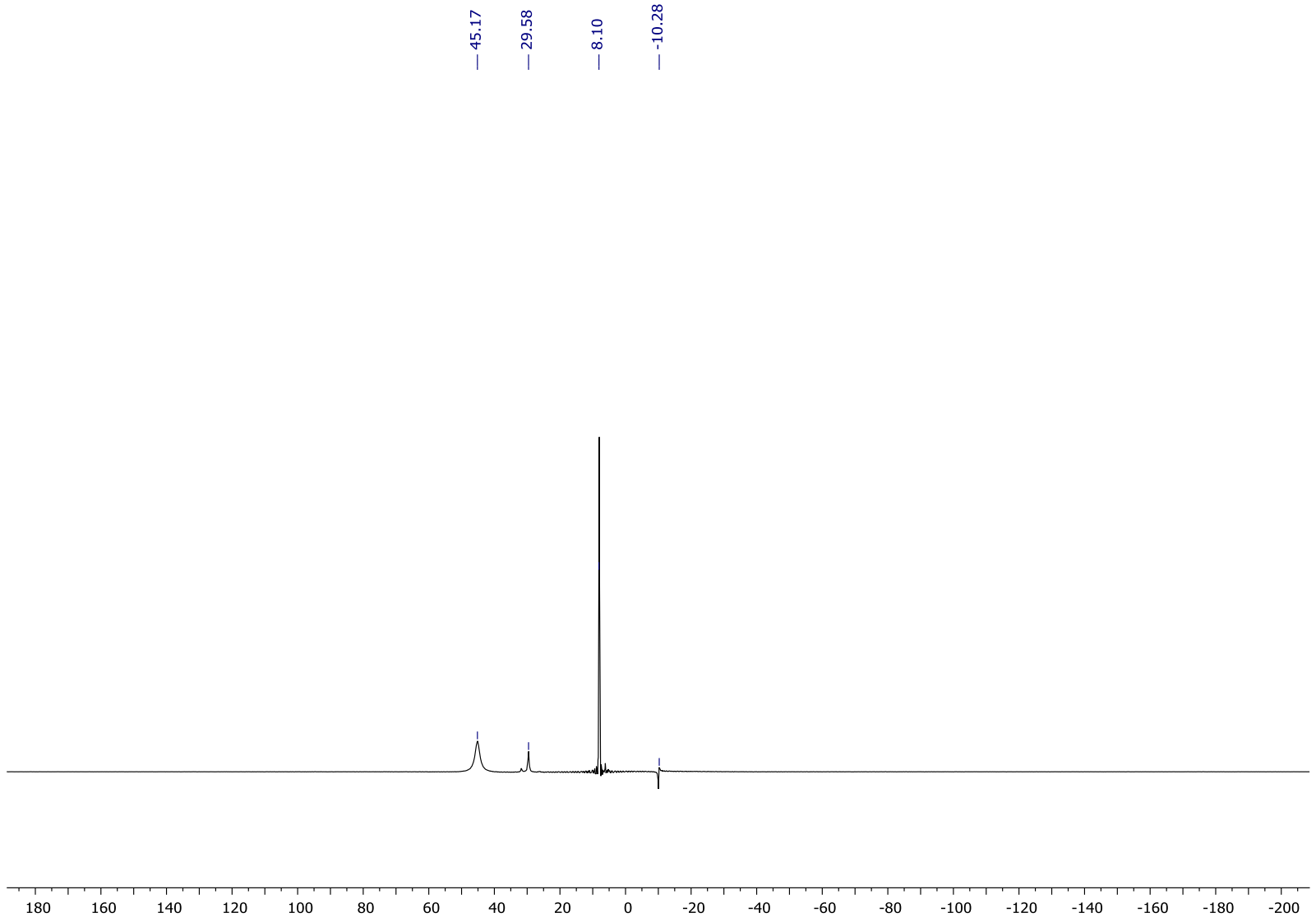
S63 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2f** and BCl_3.



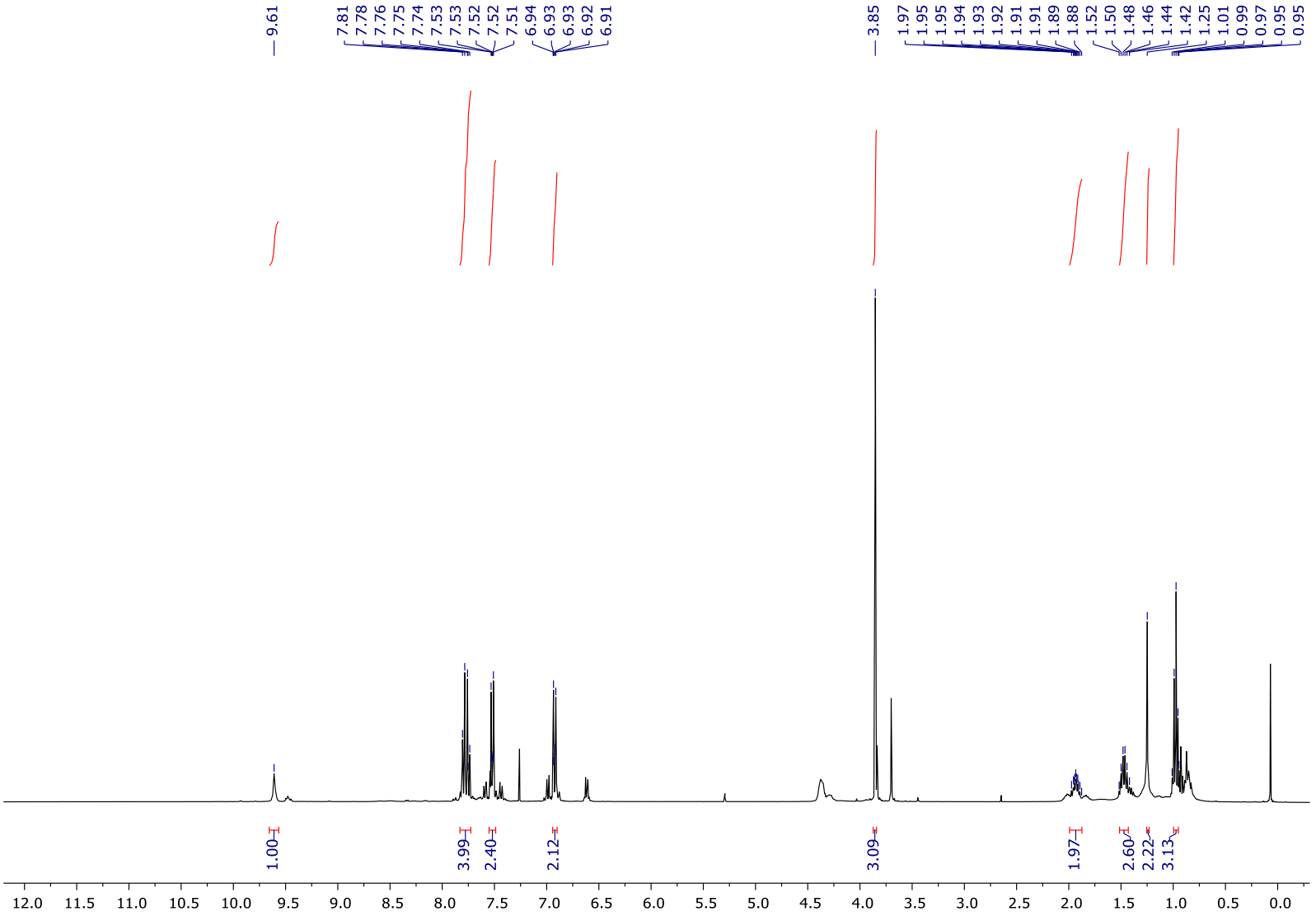
S64 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2f** and BCl_3.



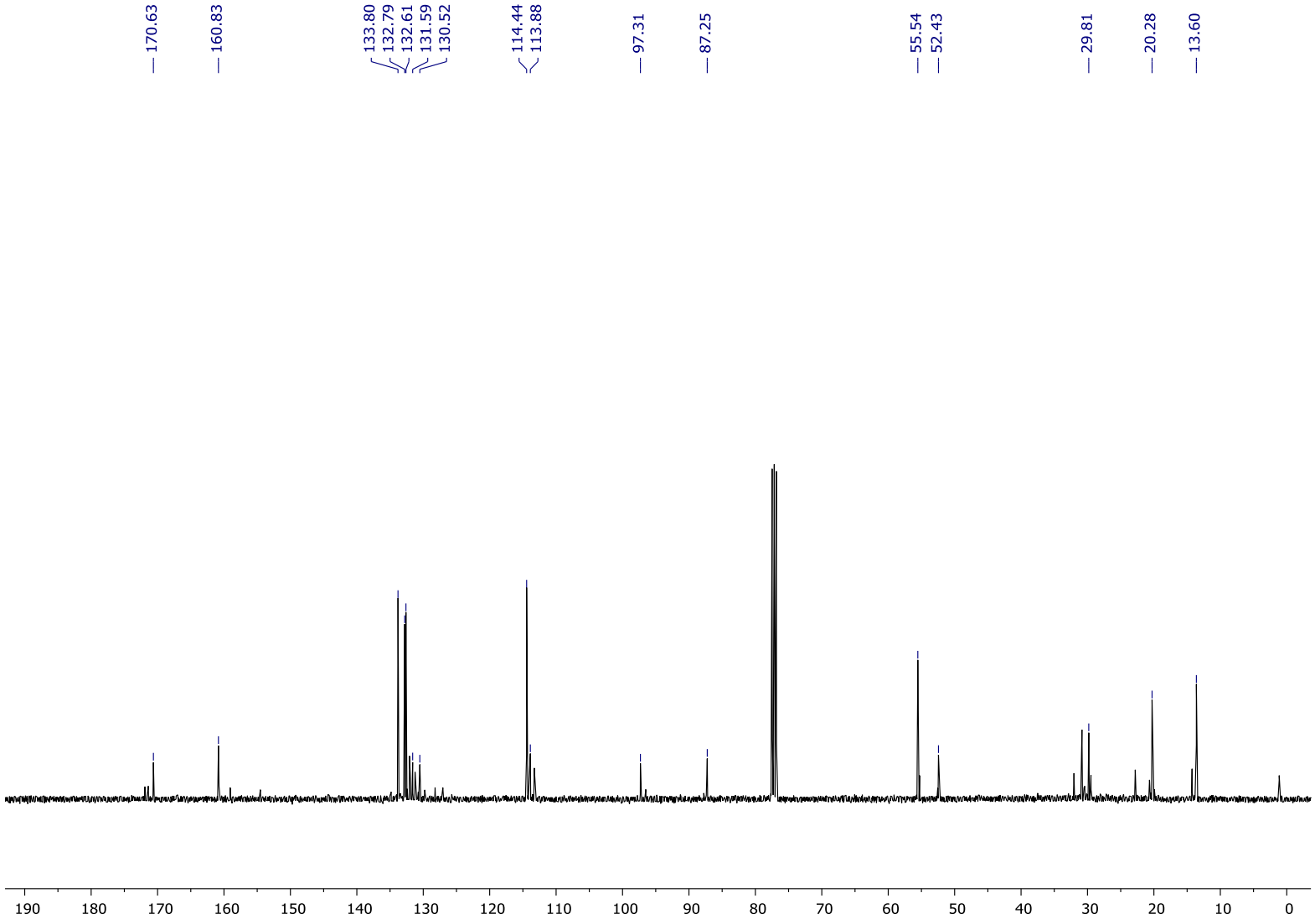
S65 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2f** and BCl_3.



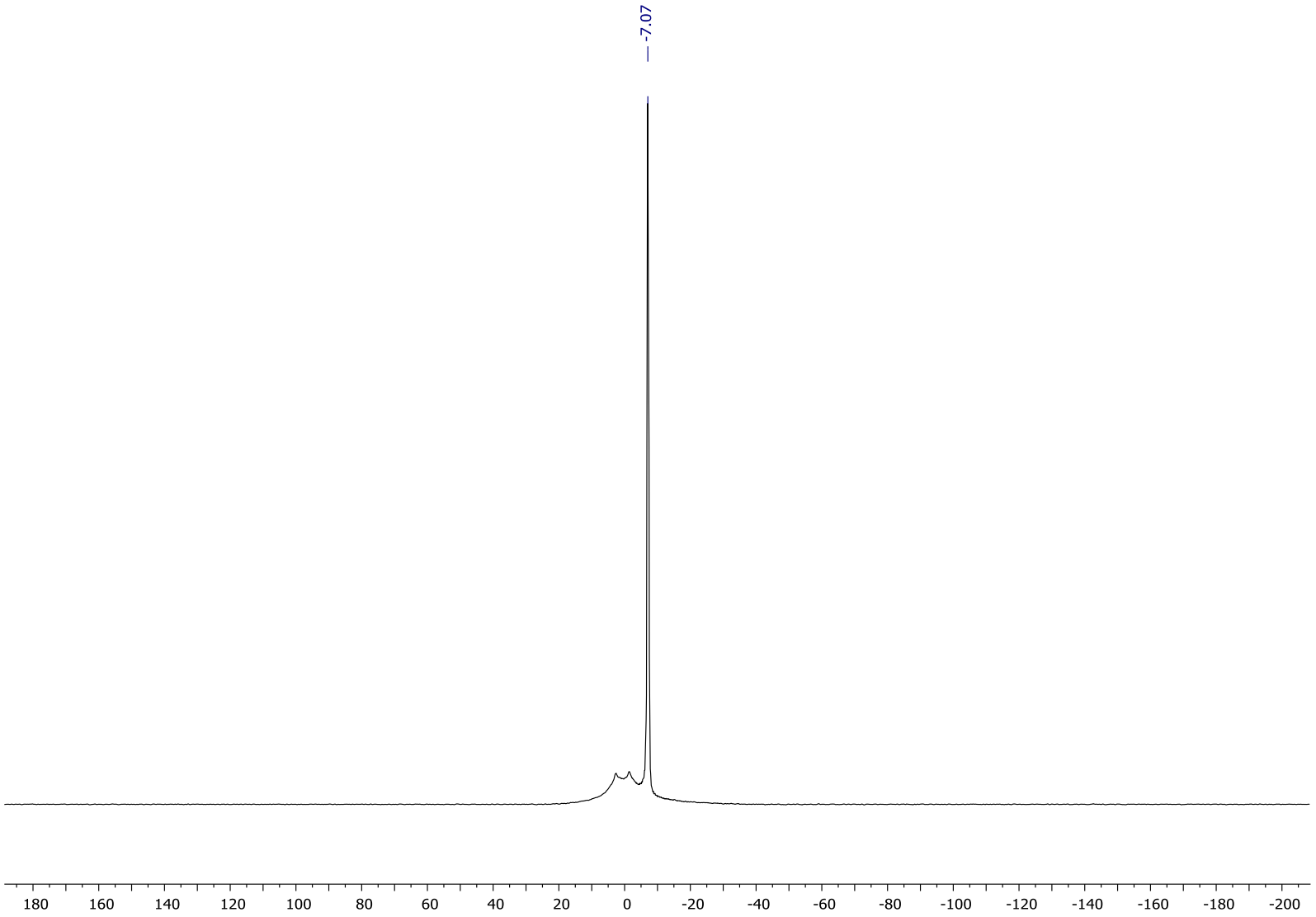
S66 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2f** and BBr_3.



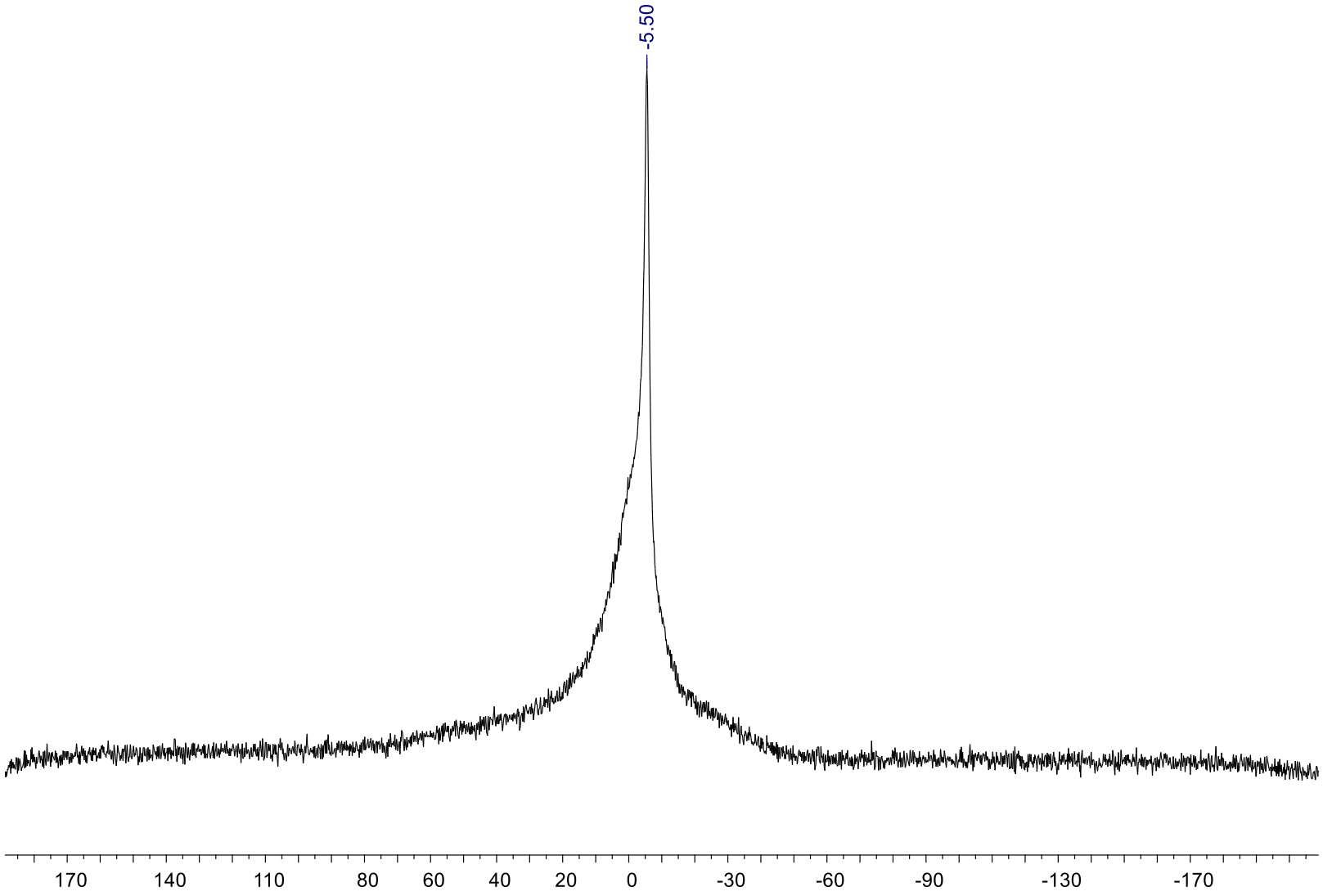
S67 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2f** and BBr_3.



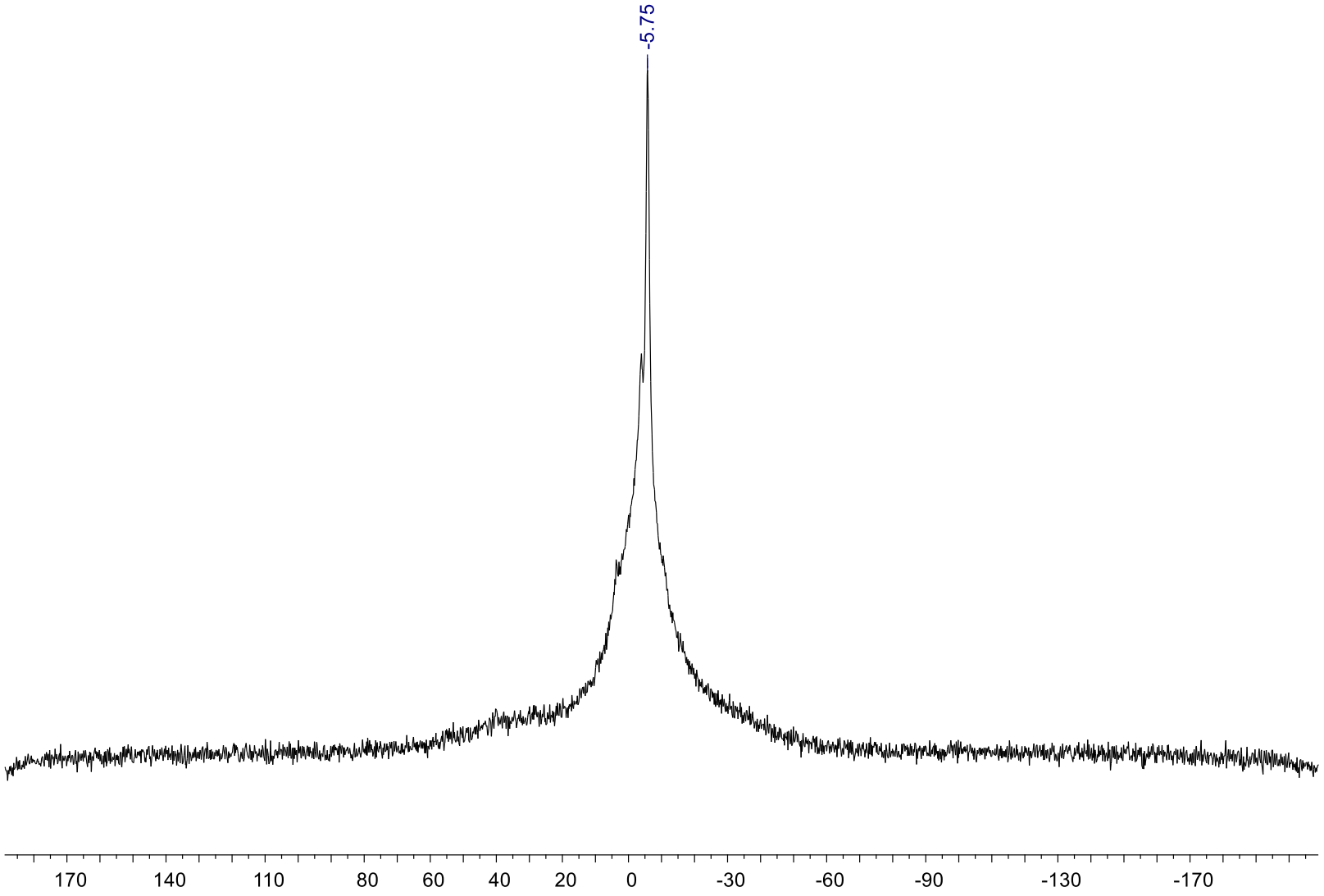
S68 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2f** and BBr_3.



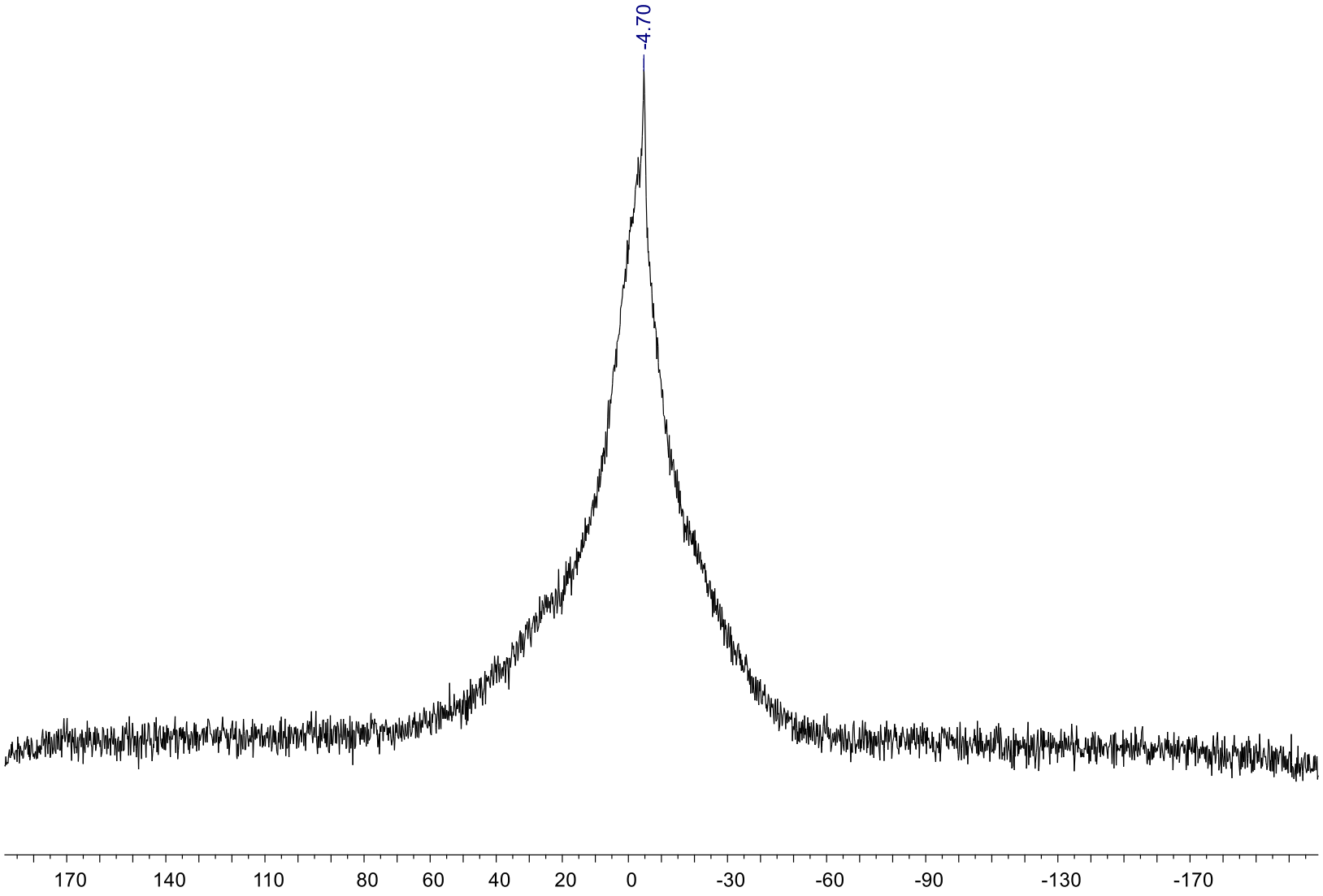
S69 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of adduct between **2f** and $B(C_6F_5)_3$ in $CDCl_3$.



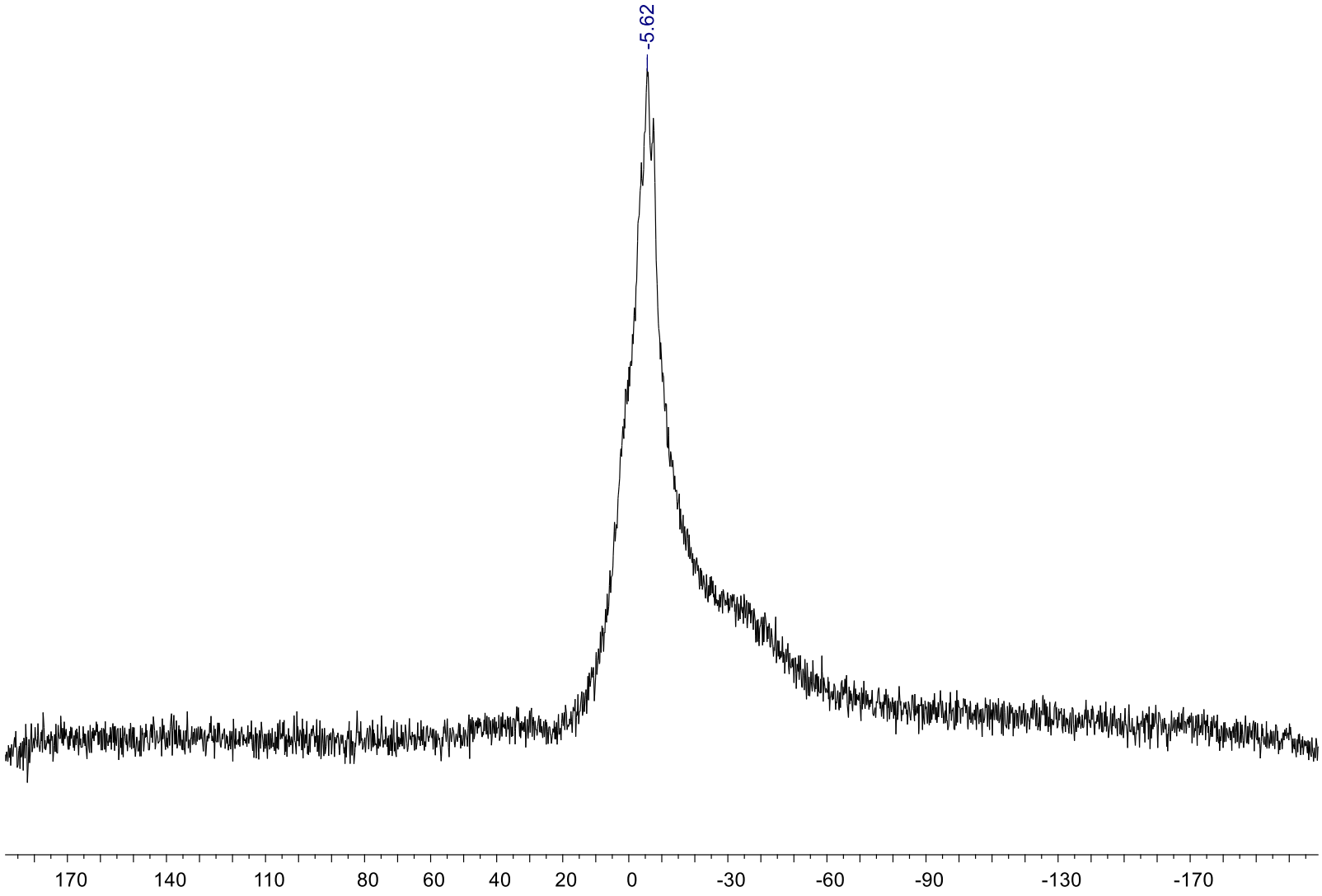
S70 ^{11}B NMR (160 MHz, CH_2Cl_2, 298 K) spectrum of adduct between **2f** and $B(C_6F_5)_3$ in CH_2Cl_2.



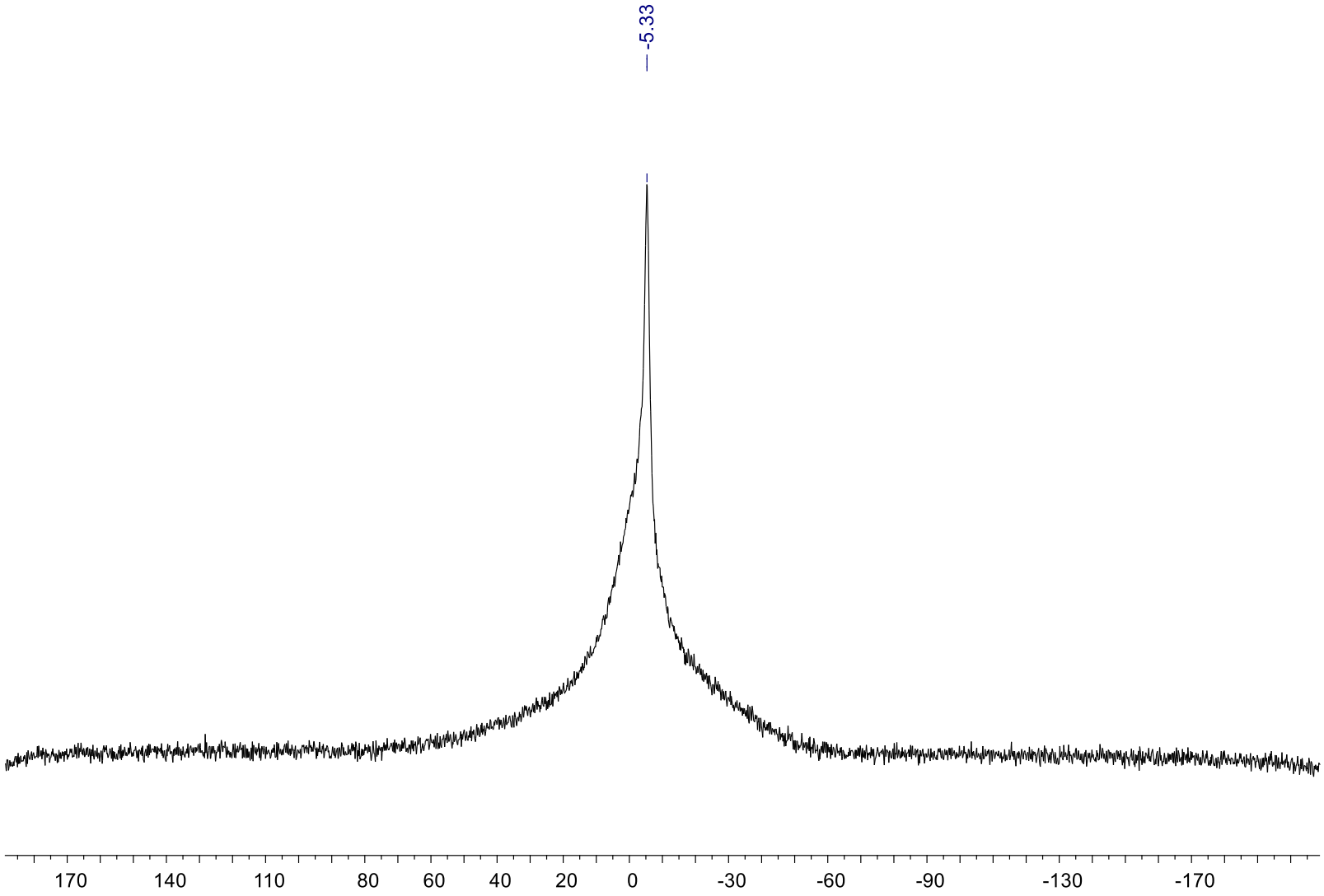
S71 ^{11}B NMR (160 MHz, hexane, 298 K) spectrum of adduct between **2f** and $B(C_6F_5)_3$ in hexane.



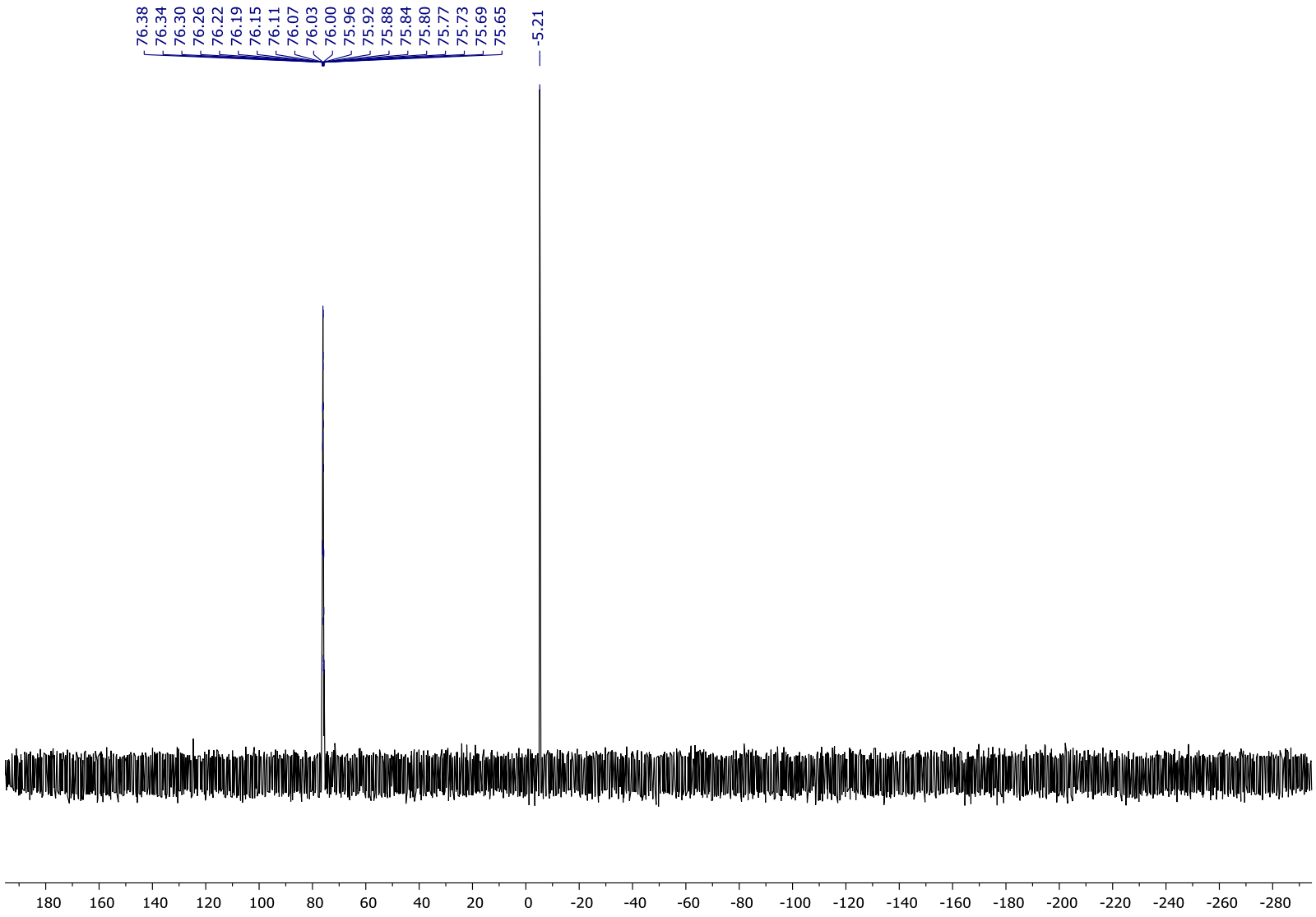
S72 ^{11}B NMR (160 MHz, C_6H_5Cl, 298 K) spectrum of adduct between **2f** and $B(C_6F_5)_3$ in chlorobenzene.



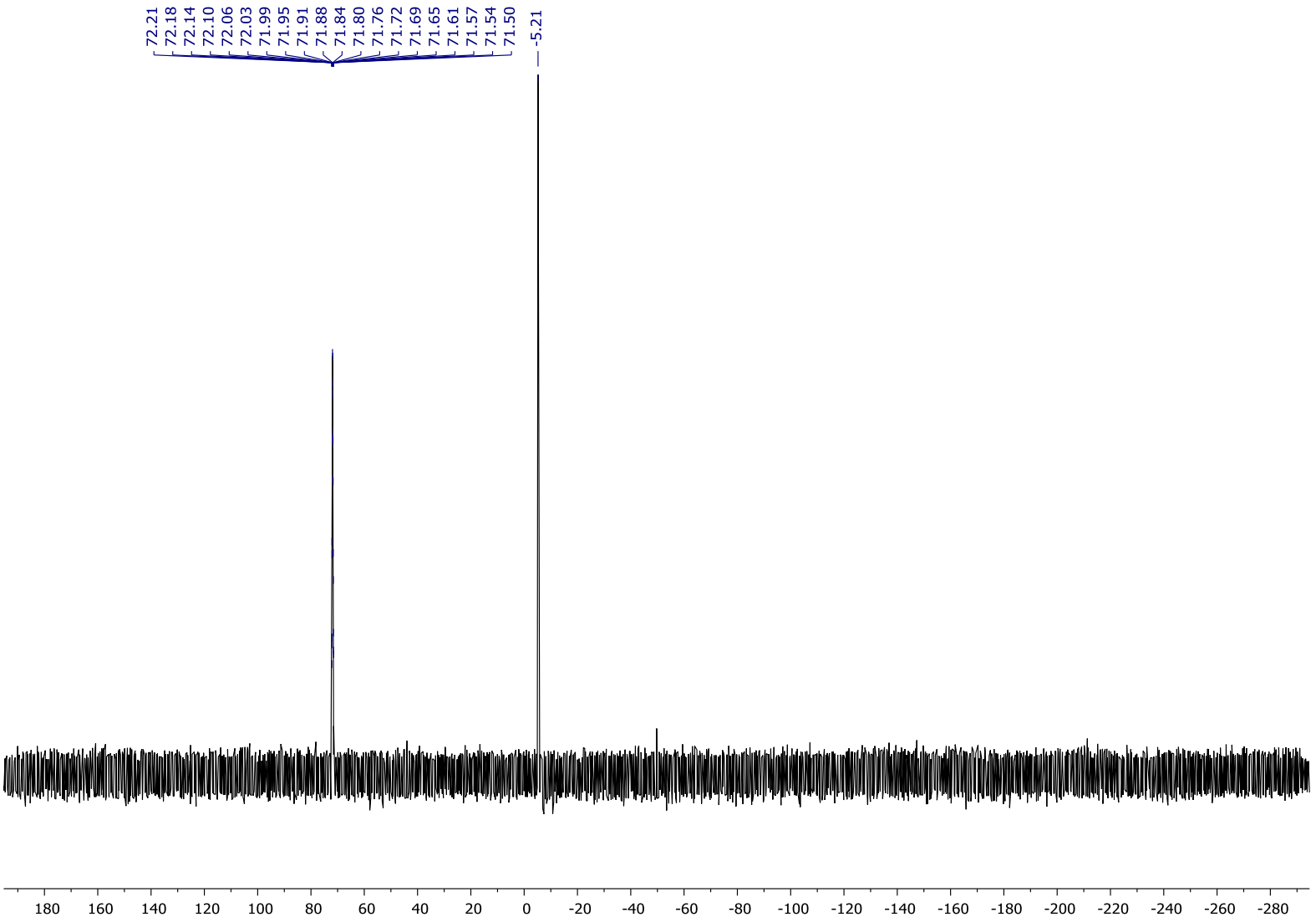
S73 ^{11}B NMR (160 MHz, toluene, 298 K) spectrum of adduct between **2f** and $B(C_6F_5)_3$ in toluene.



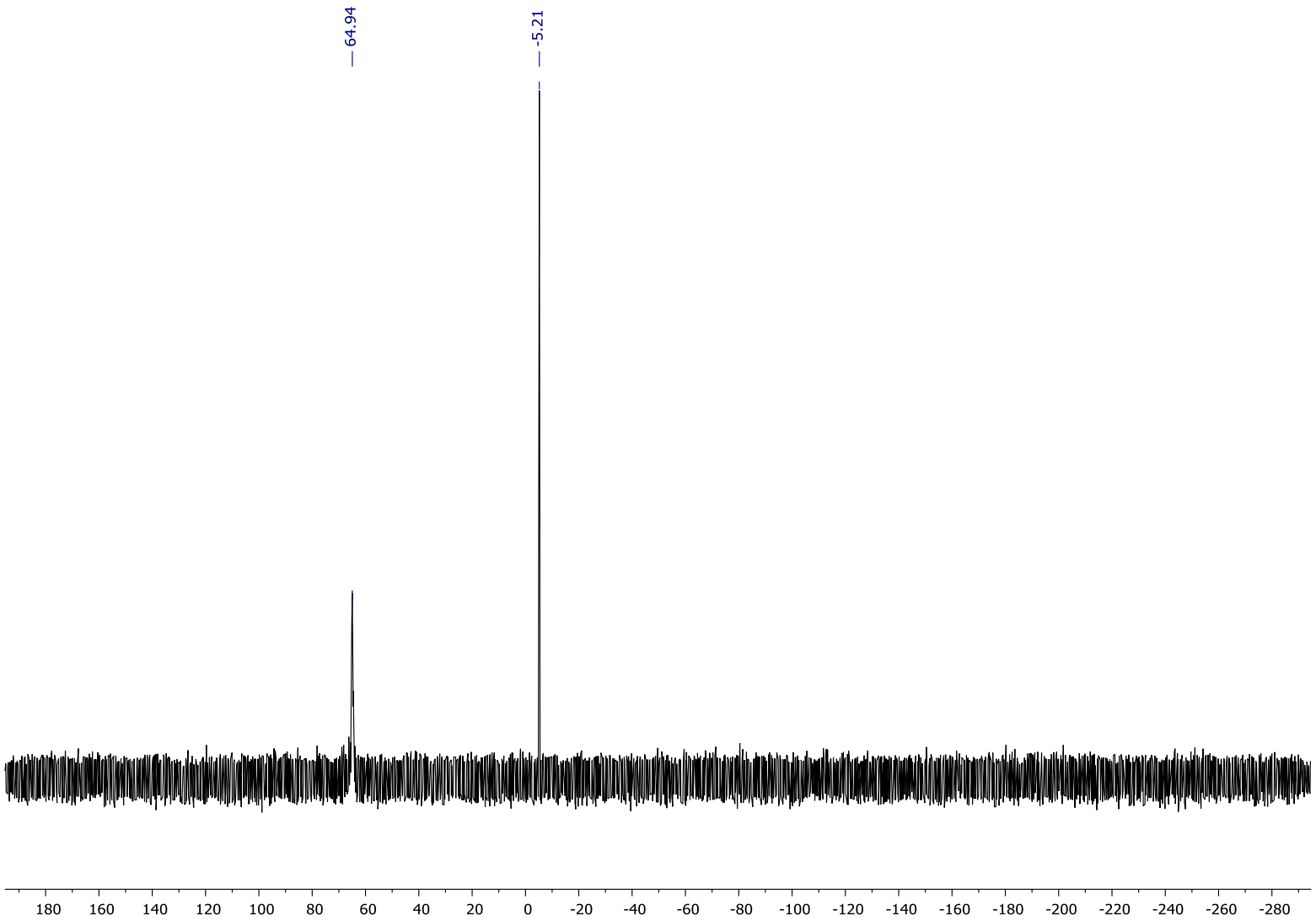
S74 ^{31}P NMR (162 MHz, $CDCl_3$, 298 K) spectrum of Gutmann-Beckett Lewis acidity test of $B(C_6F_5)_3$.



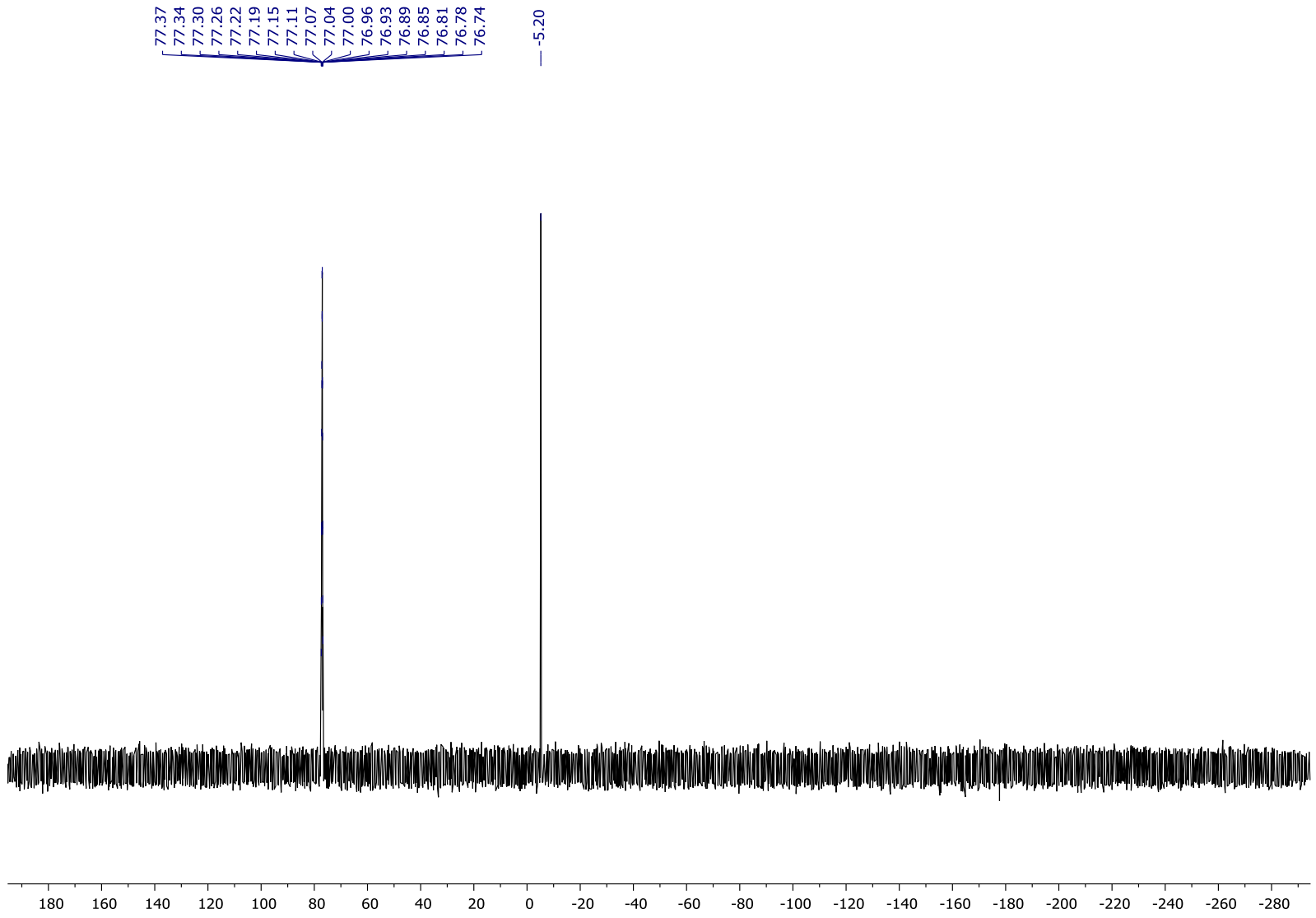
S75 ^{31}P NMR (162 MHz, $CDCl_3$, 298 K) spectrum of Gutmann-Beckett Lewis acidity test of 2,4,6-$BArF_9$.



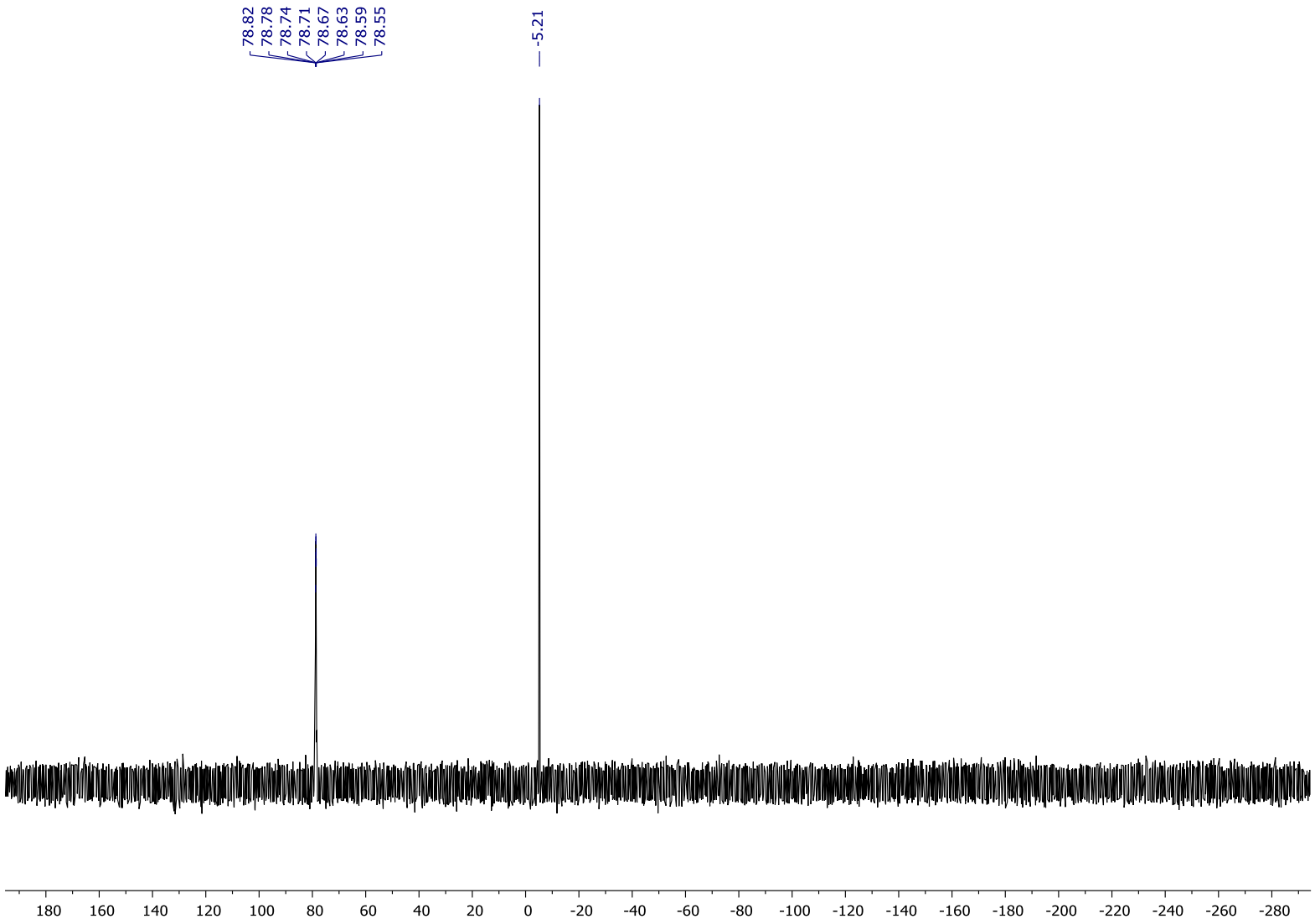
S76 ^{31}P NMR (162 MHz, $CDCl_3$, 298 K) spectrum of Gutmann-Beckett Lewis acidity test of BPh_3.



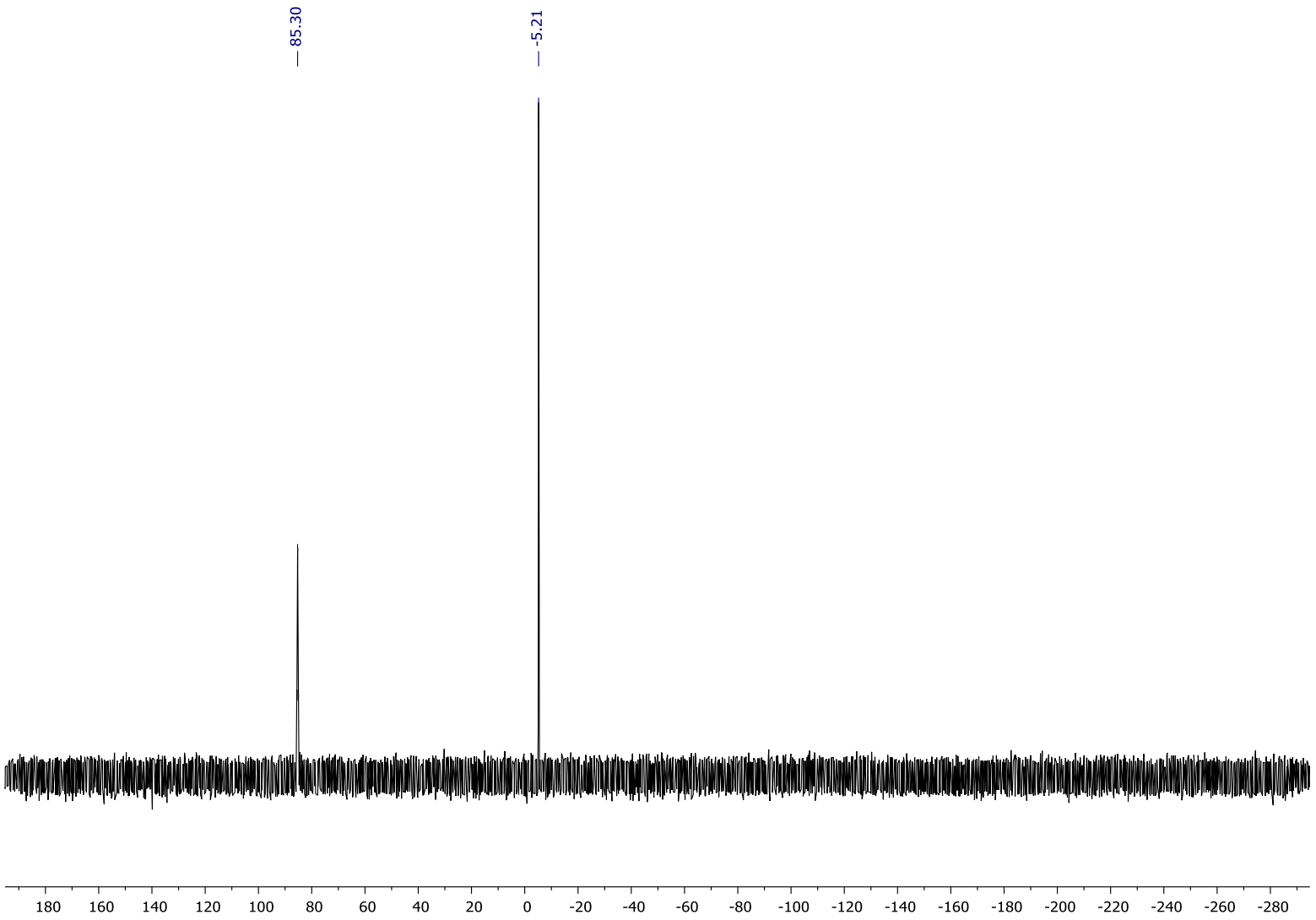
S77 ^{31}P NMR (162 MHz, $CDCl_3$, 298 K) spectrum of Gutmann-Beckett Lewis acidity test of 3,4,5-$BArF_9$.



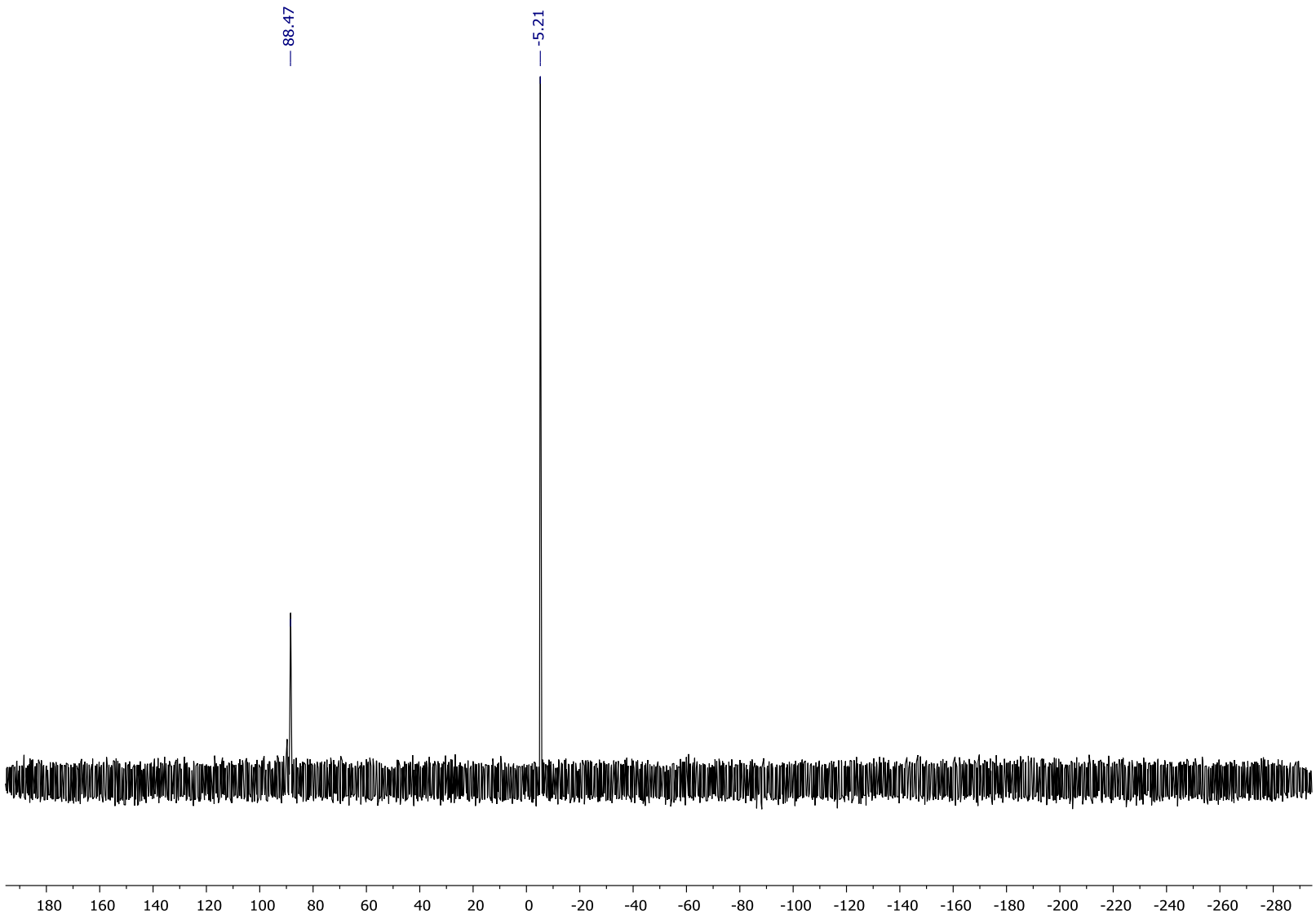
S78 ^{31}P NMR (162 MHz, $CDCl_3$, 298 K) spectrum of Gutmann-Beckett Lewis acidity test of BF_3.



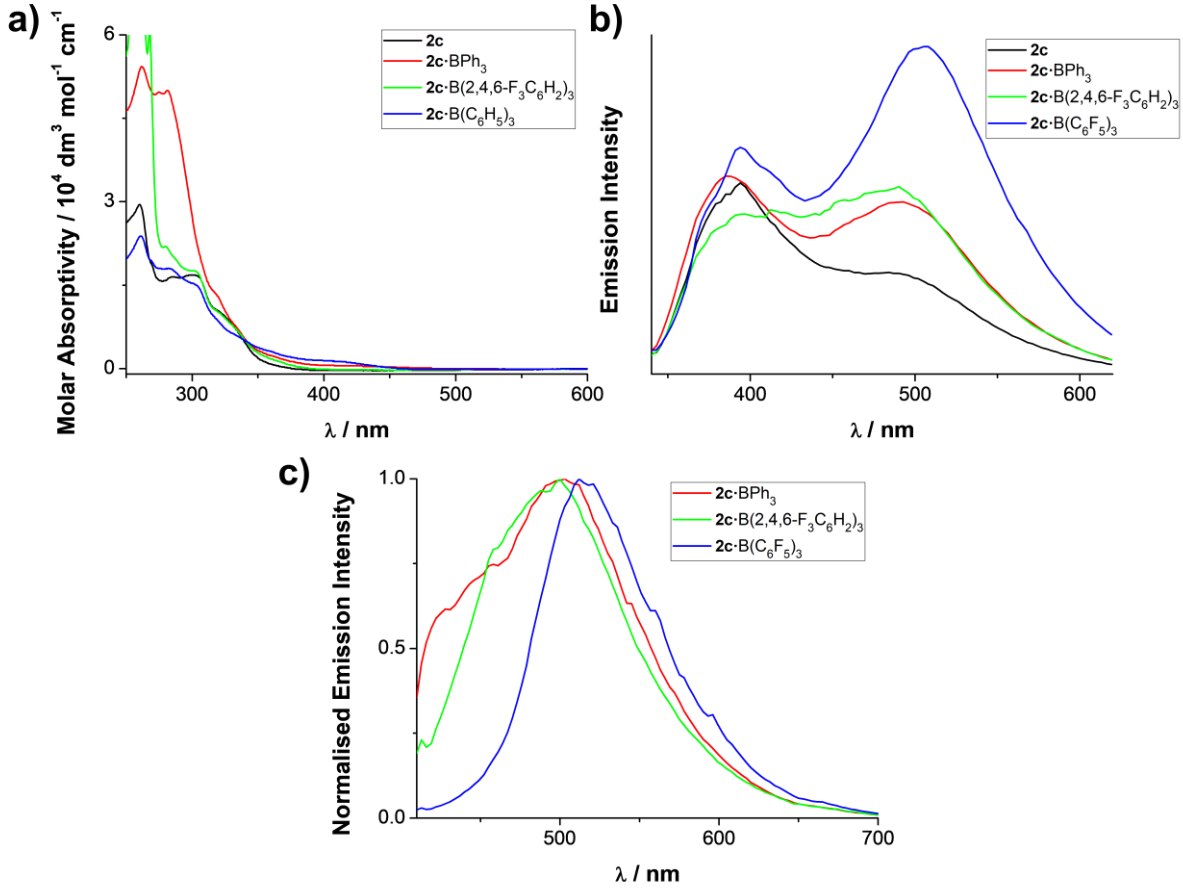
S79 ^{31}P NMR (162 MHz, $CDCl_3$, 298 K) spectrum of Gutmann-Beckett Lewis acidity test of BCl_3.



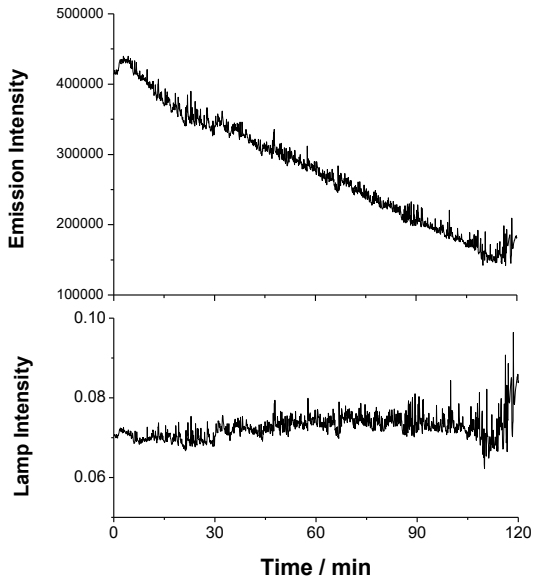
S80 ^{31}P NMR (162 MHz, $CDCl_3$, 298 K) spectrum of Gutmann-Beckett Lewis acidity test of BF_3.



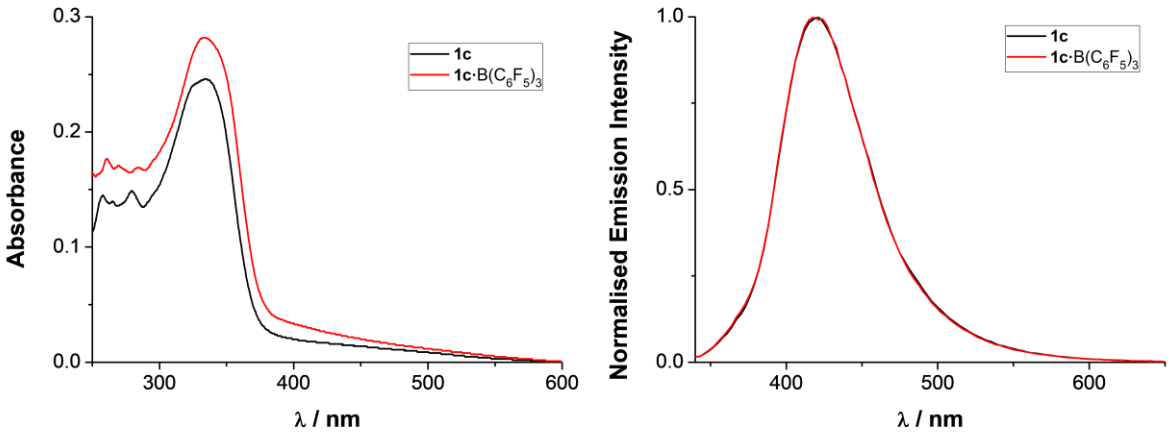
3. Photophysical studies.



S81 UV-Visible absorption spectra (a) and steady state emission spectra of **2c** and adducts in chloroform solution. b – λ_{ex} = 330 nm, c – λ_{ex} = 400 nm. C = 10^{-5} mol dm^{-3}, Emission spectra are not corrected for spectral response.



S82 Time based steady-state emission plot of **2f**·$B(C_6F_5)_3$ adduct in chloroform after exposure to air. λ_{ex} = 400 nm, λ_{em} = 500 nm.



S83 UV-Visible absorption (left) and steady state emission spectrum (right) of **1c** and its adduct with $B(C_6F_5)_3$ in chloroform solution. λ_{ex} = 330 nm. C = 10^{-5} mol dm^{-3}, emission spectra are not corrected for spectral response.

4. Vapochromic Studies.

Small strips of filter paper were impregnated with **2f**·$B(C_6F_5)_3$ from a 25 mM orange coloured solution of **2f** and $B(C_6F_5)_3$ in a glove box. After drying the paper strips under vacuum they were then subjected to atmospheres of different solvents by suspending them in a closed 15 mL vial above 3 mL of various coordinating and non-coordinating solvents. The change of visible colour and fluorescence (excitation using a hand-held UV-light at ex. 365 nm) were monitored over a time period of 48 h.

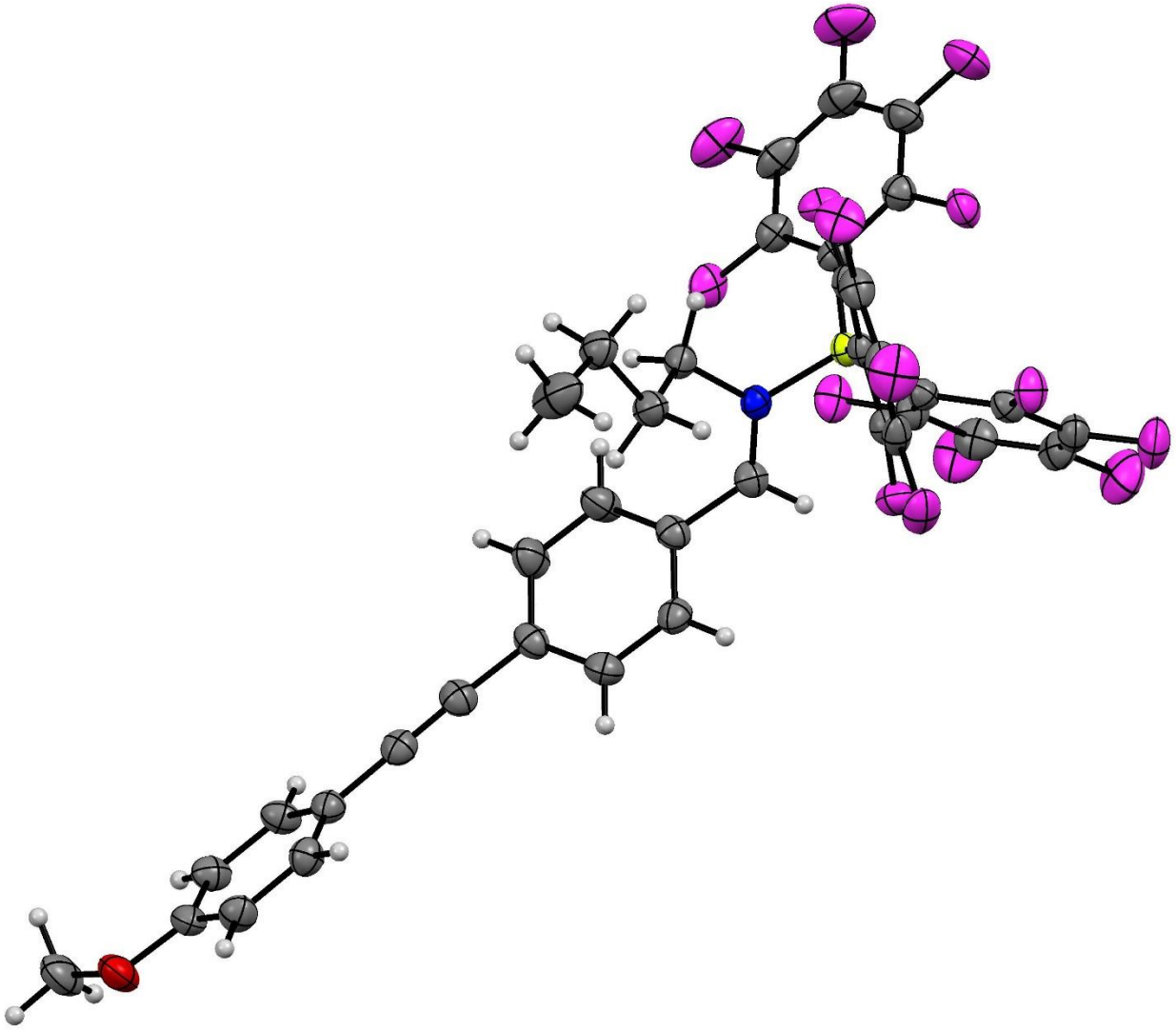
S84 Set-up for vapochromic solvent test.

5. Crystallographic studies.

Single crystals were grown under an inert atmosphere. Crystallographic studies were undertaken of a single crystal mounted in paratone and studied on an Agilent SuperNova diffractometer using Cu- or 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.[11] The structures were solved by direct methods and refined against F^2 within SHELXL-2013.[12] The structures are deposited with the Cambridge Structural Database (CCDC deposition numbers 1836219). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Compound	**2f**·$B(C_6F_5)_3$
Empirical Formula	$C_{38}H_{21}BF_{15}NO$
Crystal System	Triclinic
Space Group	*P*-1
a/Å	10.8591(5)
b/Å	11.0549(4)
c/Å	15.5476(7)
a/Å	75.088(4)
b/Å	69.996(4)
c/Å	84.603(4)
V/Å^3	1694.73(14)
Z	2
T /K	150(2)
D_c/g.cm^{-3}	1.574
Crystal size/mm	0.263 x 0.233 x 0.155
Total data	15186
Unique data	3784
R_{int}	0.0458
$R_1[F^2>2\ \sigma(F^2)]$	0.0489
wR2 (all data)	0.1380
GoF	1.016
ρ_{min}/ρ_{max}/eÅ^{-3}	-0.278/0.242
CCDC code	1836219

S85 Thermal ellipsoid plot (50% probability) of solid-state structure of **2f**·$B(C_6F_5)_3$.



6. References.

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(2) Yin, Q.; Soltani, Y.; Melen, R. L.; Oestreich, M. *Organometallics* **2017**, *36*, 2381.

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(4) Hansmann, M. M.; Lõpez-Andarias, A.; Rettenmeier, E.; Egler-Lucas, C.; Rominger, F.; Hashmi, A. S. K.; Romero-Nieto, C. *Angew. Chem. Int. Ed.* **2016**, *55*, 1196.

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(6) Beckett, M. A.; Strickland, G. C.; Holland, J. R.; Varma, K. S. *Polym. Commun.* **1996**, *37*, 4629.