Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

1,3-Carboboration of Iodonium Ylides

Theodore A. Gazis, Bayan A. J. Mohajeri Thaker, Darren Willcox, Darren M. C.Ould, Jan Wenz, Jeremy M. Rawson, Michael S. Hill, Thomas Wirth and Rebecca L. Melen

Table of Contents

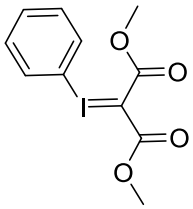
1 Experimental
1.1 General experimental

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, product recovery and sample preparation for analysis. All solvents (toluene, pentane, CH_2Cl_2) with the exception of ethanol were dried by employing a solvent purification system MB SPS-800 and stored under a nitrogen atmosphere. THF and diethyl ether were distilled over molten potassium and sodium benzophenone respectively. They were stored over 3 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. ^{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). ^{13}C NMR and ^{11}B were measured as ^{1}H decoupled. The description of signals includes: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br. = broad. All coupling constants are absolute values and are expressed in Hertz (Hz). Yields are given as isolated yields.

1.2 Synthesis of starting materials

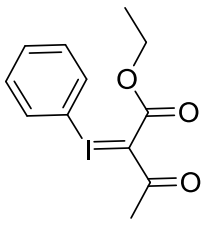
General Procedure **A**:[1]
To a suspension of KOH (6.0 equiv.) in acetonitrile (20 mL) was added the appropriate 1,4 dicarbonyl compound (1.0 equiv.) The heterogeneous mixture was stirred vigorously for 5 min. at 0 ˚C. To this was added phenyliodonium diacetate (1.1 equiv.) in one portion and stirred at 0 ˚C for a further 2 h. Water was subsequently added to the resultant mixture and stirred for 1 min. The faint yellow biphasic mixture was filtered and the solid was washed with water (2 x 5 mL) being careful to completely remove the solvent between each wash. A final wash with ethanol (10 mL) yielded the desired iodonium ylide, which was dried under reduced pressure.

Synthesis of *bis(methoxycarbonyl)(phenyliodinio)methanide (**2a**)*



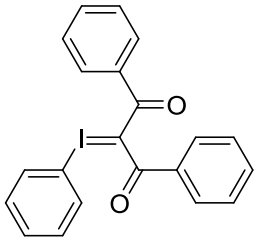
2a was synthesised according to General Procedure **A** using iodobenzene diacetate (1.72 g, 5.3 mmol, 1.0 equiv.), potassium hydroxide (1.8 g, 32.0 mmol, 6.0 equiv.) and dimethyl malonate (0.6 mL, 5.3 mmol, 1.0 equiv.). The title compound was isolated as an off-white solid (1.15 g, 3.4 mmol, 65%). The spectral data shows good agreement with the literature reported values.[1] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ: 7.75–7.72 (m, 2H, Ar-H), 7.55–7.51 (m, 1H, Ar-H), 7.43–7.38 (m, 2H, Ar-H), 3.74 (s, 6H, O-CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ: 166.5 (2C, C=O), 131.7 (Ar), 131.5 (Ar), 130.4 (Ar), 114.5 (Ar-I), 52.5 (2C, O-CH_3), ylide carbon could not be observed. The product partially degraded during preparation of the NMR sample.[1]

Synthesis of *ethyl 3-oxo-2-(phenyliodaneylidene)butanoate (**2b**)*



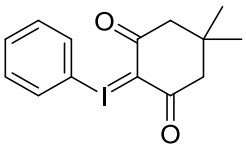
2b was synthesised according to General Procedure **A** using iodobenzene diacetate (2.56 g, 7.9 mmol, 1.0 equiv.), potassium hydroxide (2.66 g, 47.3 mmol, 6.0 equiv.) and dimethyl malonate (1.0 mL, 7.9 mmol, 1.0 equiv.). The title compound was isolated as an off white solid (423 mg, 1.3 mmol, 16%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ: 7.78–7.77 (m, 2H, Ar-H), 7.54–7.51 (m, 1H, Ar-H), 7.40–7.37 (m, 2H, Ar-H), 4.13 (q, *J* = 7.1 Hz, 2H, $C\underline{H_2}CH_3$), 2.59 (s, 3H, CH_3), 1.22 (t, *J* = 7.1 Hz, 3H, $CH_2C\underline{H_3}$); **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ: 187.2 (1C, C=O), 165.2 (1C, C=O), 133.2 (Ar), 131.6 (Ar), 131.4 (Ar), 112.8 (C-I), 60.6 (1C, $C\underline{H_2}CH_3$), 26.0 (1C,$CH_{3)}$, 14.8, 1C, CH_3).

Synthesis of *1,3-diphenyl-2-(phenyliodaneylidene)propane-1,3-dione (**2c**)*[2]



A solution of potassium hydroxide (6.90 g, 123.1 mmol, 20.0 equiv.) in methanol (10 mL) was added to dibenzoyl methane (1.38 g, 6.0 mmol, 1.0 equiv.) in methanol (10 mL) at -5 ˚C. Subsequently, a solution of iodobenzene diacetate (2.00 g, 6 mmol, 1.0 equiv.) in methanol (20 mL) was added portionwise while the temperature was not allowed to exceed 0 ˚C. Stirring was continued for 30 minutes at 0 ˚C. The resultant mixture was poured onto ice water (50 mL) and the product was extracted with CH_2Cl_2 (3 × 20 mL) and dried with magnesium sulfate. The solvent was removed *in vacuo* and the solid residue was recrystallised from cold ethanol to give **2c** as a yellow powder (538 mg, 1.3 mmol, 21%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ: 8.03–8.00 (m, 2H, Ar), 7.57–7.52 (m, 1H), Ar, 7.43–7.38 (m, 2H, Ar), 7.24–7.22 (m, 4H, Ar), 7.05–7.01 (m, 2H, Ar), 6.93–6.91 (m, 4H, Ar); **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ: 186.4 (C=O), 139.1 (Ar), 137.6 (Ar), 134.5 (Ar), 131.6 (Ar), 130.4 (Ar), 129.8 (Ar), 129.2 (Ar), 127.5 (Ar), 112.1 (C-I). **HRMS** (ASAP+) m/z calculated for $[C_{15}H_1O_2]$ $[M - C_6H_5I]^+$: 223.0754 found: 223.0756.

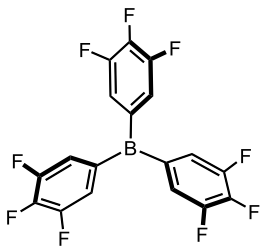
*Synthesis of 5,5-dimethyl-2-(phenyliodaneylidene)cyclohexane-1,3-dione (**2d**)*[3]



To iodobenzene diacetate (1 g, 3.1 mmol, 1.0 equiv.) in CH_2Cl_2 (15 mL) at 10–15 ˚C was added in one portion KOH (1.73 g, 30.9 mmol, 10.0 equiv) and dimedone (581 mg, 4.1 mmol, 1.3 equiv.). The reaction mixture was allowed to stir for 50 minutes until complete conversion was confirmed by TLC analysis (8% MeOH in CH_2Cl_2). The crude was diluted with CH_2Cl_2 (15 mL), filtered through cotton and glass wool, washed with CH_2Cl_2 (20 mL) and dried over Na_2SO_4. The drying agent was filtered off and the solvent removed under reduced pressure at room temperature. Precipitation at −20 ˚C for 1 h using CH_2Cl_2 (15 mL) and hexane (40 mL) afforded the iodonium ylide which was further washed with hexane prior to being dried in high vacuum. The title compound was isolated as a white fibrous solid (564 mg, 1.7 mmol, 53%). The spectral data shows good agreement with the literature reported values.[3] **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ: 7.82 (d, *J* = 6.9 Hz, 2H, Ar), 7.53–7.50 (m, 1H, Ar), 7.37–7.34 (m, 2H, Ar), 2.50 (s, 4H, -CH_2), 1.05 (s, 6H, -CH_3); **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ: 188.5 (C=O), 134.0 (Ar), 131.7 (Ar), 131.5 (Ar), 111.9 (Ar), 94.6 (1C, C-I), 50.8 (2C, -CH_2), 32.1 (1C, -$\underline{C}(CH_3)_2$), 28.2 (2C, -CH_3).

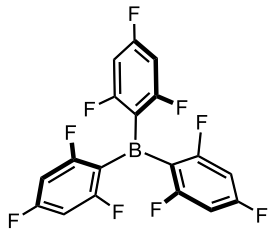
1.3 Synthesis of boranes

Synthesis of *tris(3,4,5-trifluorophenyl)borane* (**1a**)



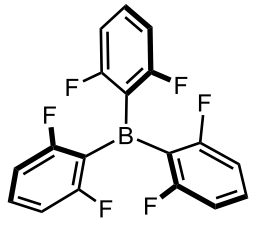
Synthesised according to the literature procedure.[4] Mg turnings (3.05 g, 125 mmol, 3.0 equiv.) were suspended in Et_2O and cooled to 0 °C. 1,2-dibromoethane (0.1 mL, 1.1 mmol) and 1-bromo-3,4,5-fluorobenzene (15 mL, 125 mmol, 3.0 equiv.) were added dropwise with vigorous stirring. After addition, the 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 dropwise to a solution of $BF_3{\cdot}Et_2O$ (5.2 mL, 42 mmol, 1.0 equiv.) in Et_2O, also at 0 °C. The solution was allowed to warm to room temperature and stirred for 60 minutes. 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.[4] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ: 7.20–7.13 (m, 6H); **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ: −133.18 (d, *J* = 25 Hz, 6F), −152.38 (t, *J* = 25 Hz, 3F); **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) δ: 65.9 (br., s).

Synthesis of *tris(2,4,6-trifluorophenyl)borane* (**1b**)



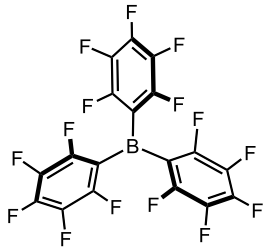
Synthesised according to the literature procedure.[4] 1-bromo-2,4,6-trifluorobenzene (3.5 mL, 30 mmol, 3.0 equiv.) was dissolved in freshly distilled THF (100 mL) and cooled to −20 ˚C. ^{i}PrMgCl (2.0 M in THF), (15 mL, 30 mmol, 3.0 equiv.) was added portion wise. The reaction was allowed to warm up for 60 minutes, until the temperature reached 0 ˚C. Upon cooling to −50 ˚C, $BF_3{\cdot}Et_2O$ (1.23 mL, 10 mmol, 1.0 equiv.) was added. The reaction was held at −50 ˚C for 60 minutes, then warmed 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.[4] **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ: 6.64 (dd, *J* = 14 Hz, 8 Hz, 6H); **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ: −95.74 (d, *J* = 9 Hz, 6F), −100.30 (t, *J* = 14 Hz, 9F); **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) δ: 59.6 (br., s).

Synthesis of *tris(2,6-trifluorophenyl)borane* (**1c**)



Synthesised according to the literature procedure.[4] 1-bromo-2,6-difluorobenzene (3.4 mL, 30 mmol, 3.0 equiv.) was dissolved in freshly distilled THF (100 mL) and cooled to −20 ˚C. ^{i}PrMgCl (2.0 M in THF), (6.00 mL, 40 mmol, 4.0 equiv.) was added dropwise. The reaction was allowed to warm up to 0 ˚C. Upon cooling to −50 ˚C, $BF_3{\cdot}Et_2O$ (1.2 mL, 10 mmol, 1.0 equiv) was added dropwise. The reaction was held at -50 ˚C for 60 minutes then warmed 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 microcrystalline solid (2.3 g, 6.6 mmol, 66%). The spectroscopic data agrees with literature established values.[4] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ: 7.42–7.35 (m, 3H), 6.86–6.82 (m, 6H) **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ: −100.46 (s, 6F); **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) δ: 63.2 (br., s).

Synthesis of *tris(pentafluorophenyl)borane* (**1e**)



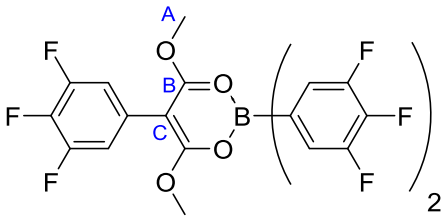
Synthesised according to a literature procedure.[5] Magnesium turnings (1.1 g, 45 mmol, 3.0 equiv.) were suspended in Et_2O (100 mL). C_6F_5Br (5.6 mL, 45 mmol, 3.0 equiv.) was added drop wise over the course of 30 minutes under vigorous stirring, without allowing the mixture to reach reflux. The mixture was allowed to stir for 30 minutes at room temperature and was then transferred *via* filter cannula to a stirred solution of $BF_3{\cdot}OEt_2$ (1.9 mL, 15 mmol, 1.0 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 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 light brown cake remained. 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.[5] **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ: −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: 58.6 (br., s).

1.4 Synthesis of products

General Procedure **B***:*

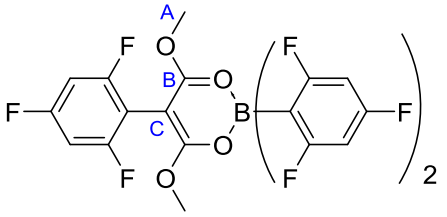
To a Schlenk tube equipped with a magnetic stirring bar, the appropriate iodonium ylide **1** (1.0 equiv.) was dissolved in toluene and the appropriate borane (1.0 equiv.) was added portion wise. The resultant solution was allowed to stir for 12 h at 50 ˚C. Subsequently all volatiles were removed *in vacuo*. The desired product was obtained by successive washes of the crude with pentane.

Synthesis of compound ***3a***



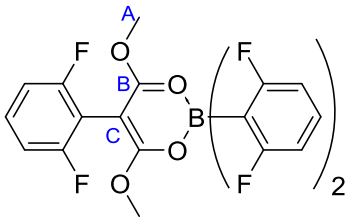
Synthesised according to General Procedure **B** using 3,4,5-tris(trifluorophenyl)borane (123 mg, 0.3 mmol, 1.0 equiv.) and dimethyl 2-(phenyliodaneylidene)malonate (**2a**) (102 mg, 0.3 mmol, 1.0 equiv.) in toluene (15 mL) to afford the desired compound (**3a**) as a white solid (120 mg, 0.2 mmol, 74%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ: 6.94–6.90 (m, 4H, Ar), 6.79–6.76 (m, 2H, Ar), 4.08 (s, 6H, HA); **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ: 172.8 (s, C^B), 152.5 (m, Ar), 150.0 (m, Ar), 139.1 (m, Ar), 129.2 (m, Ar), 128.4 (s, Ar), 115.6 (m, Ar), 114.2 (m, Ar), 82.3 (s, C^C), 55.9 (s, C^A), carbon atom attached to boron could not be observed; **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ: −135.04 (d, *J* = 20.7 Hz, 2F), −135.70 (d, *J* = 20.1 Hz, 4F), −161.32 (t, *J* = 20.8 Hz, 1F), −162.82 (t, *J* = 20.1 Hz, 2F); **^{11}B NMR** (128 MHz, 298 K, $CDCl_3$) δ: 7.5 (br., s); **HRMS** (ASAP+) m/z calculated for $[C_{17}H_{10}O_4{}^{10}BF_6]^+$ [M – C_6F_5]$^+$: 403.0571 found: 403.0567.

Synthesis of compound ***3b***



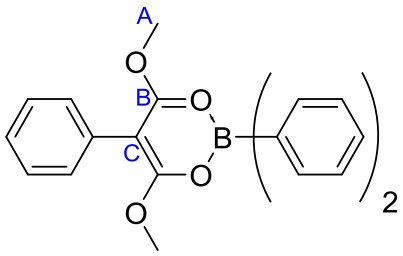
Synthesised according to General Procedure **B** using 2,4,6-tris(trifluorophenyl)borane (95 mg, 0.2 mmol, 1.0 equiv.) and dimethyl 2-(phenyliodaneylidene)malonate (**1a**) (79 mg, 0.2 mmol, 1.0 equiv.) in toluene (15 mL) to afford the desired compound (**3b**) as a white solid (62 mg, 0.1 mmol, 50%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ: 6.68–6.65 (m, 2H, Ar), 6.55–6.51 (m, 4H, Ar), 3.99 (s, 6H, H^A); **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ: 173.2 (s, C^B), 166.0 (m, Ar), 164.1 (m, Ar), 162.6 (m, Ar), 161.2 (m, Ar), 103.5 (m, Ar), 99.9 (m, Ar), 99.5 (s, Ar), 70.1 (s, C^C), 56.0 (s, C^A), carbon atom attached to boron could not be observed; **^{19}F NMR** (470 MHz, $CDCl_3$, 298 K) δ: −103.27 (d, *J* = 7.5 Hz, 4F, −106.77 (d, *J* = 6.7 Hz, 2F), −107.88 (t, *J* = 6.7 Hz), −110.98 – −111.00 (m, 2F); **^{11}B NMR** (160 MHz, 298 K, $CDCl_3$) δ: 6.6 (br., s); **HRMS** (ASAP+) m/z calculated for $[C_{23}H_{11}O_4{}^{10}BF_9]$+ [M - H]$^+$: 533.0618 found: 533.0607.

Synthesis of compound ***3c***



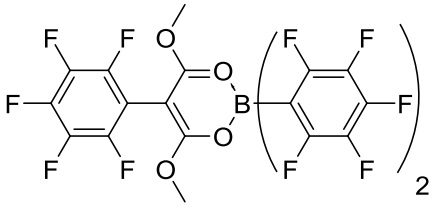
Synthesised according to General Procedure **B** using tris(2,6-difluorophenyl)borane (250 mg, 0.7 mmol, 1.0 equiv.) and dimethyl 2-(phenyliodaneylidene)malonate (**2a**) (238.6 mg, 0.7 mmol, 1.0 equiv.) in toluene (10 mL) to afford the desired compound (**3c**) as a white solid (230 mg, 0.5 mmol, 67%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ: 7.30–7.24 (m, 1H, Ar), 7.23–7.15 (m, 2H, Ar), 6.90–6.86 (m, 2H, Ar), 6.79 – 6.75 (m, 4H, Ar), 4.01 (s, 6H, H^A); **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ: 173.2 (s, C^B), 165.9 (m, Ar), 161.4 (m, Ar) 129.9 (m, Ar), 129.3 (m, Ar), 111.3 (m, Ar) , 110.8 (s, Ar), 107.3 (m, Ar), 70.7 (s, C^C), 55.9 (s, C^A), carbon atom attached to boron could not be observed; **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ: −105.85 (s, 2F), −109.69 (s, 4F); **^{11}B NMR** (128 MHz, 298 K, $CDCl_3$) δ: 6.9 (br., s); **HRMS** (ASAP+) m/z calculated for $[C_{23}H_{14}O_4{}^{10}BF_6]^+$ $[M - H]^+$: 481.1046 found: 481.1057.

Synthesis of compound ***3d***



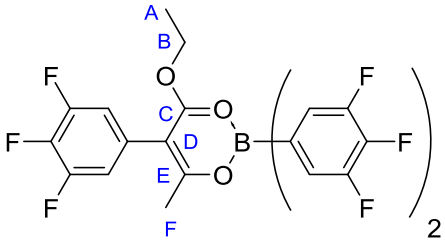
Synthesised according to General Procedure **B** using triphenylborane (250 mg, 1 mmol, 1.0 equiv.) and dimethyl 2-(phenyliodaneylidene)malonate (**2a**) (345 mg, 1 mmol, 1.0 equiv.) in toluene (10 mL) to afford the desired compound (**3d**) as an off-white solid (132 mg, 0.4 mmol, 43%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ: 7.54–7.52 (m, 4H, Ar), 7.37–7.24 (m, 9H, Ar), 7.17–7.14 (m, 2H, Ar), 4.02 (s, 6H, H^A); **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ: 173.1 (s, C^B) 134.7 (s, Ar), 131.4 (s, Ar), 131.1 (s, Ar), 128.0 (s, Ar), 127.4 (s, Ar), 127.1 (s, Ar), 126.8 (s, Ar), 83.5 (s, C^C), 54.9 (s, C^A), carbon atom attached to boron could not be observed; **^{11}B NMR** (128 MHz, 298 K, $CDCl_3$) δ: 9.18 (br., s); **HRMS** (ASAP+) m/z calculated for $[C_{23}H_{20}O_4{}^{10}B]^+$ $[M - H]^+$: 371.1457 found: 371.1455.

Synthesis of compound ***3e***



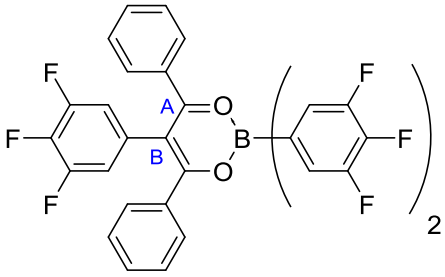
Synthesised according to General Procedure **B** using tris(pentafluorophenylborane (250 mg, 0.5 mmol, 1.0 equiv.) and dimethyl 2-(phenyliodaneylidene)malonate (**1a**) (163 mg, 0.5 mmol, 1.0 equiv.) in toluene (15 mL) to afford a mixture of products as a white solid. Crystals were obtained from a CH_2Cl_2/pentane mixture at room temperature.

Synthesis of compound ***3f***



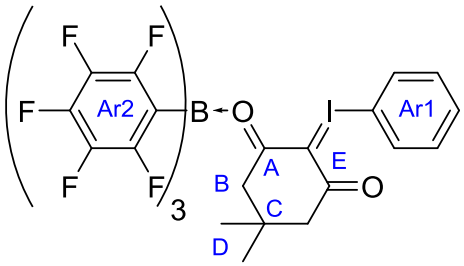
Synthesised according to General Procedure **B** using 3,4,5 tris(trifluorophenylborane (100 mg, 0.3 mmol, 1.0 equiv.) and methyl 3-oxo-2-(phenyliodaneylidene)butanoate (**2b**) (83 mg, 0.3 mmol, 1.0 equiv.) in toluene (10 mL) to afford the desired compound (**3f**) as a white powder (78 mg, 0.3 mmol, 61%). Crystals were obtained from a CH_2Cl_2/pentane mixture at -30 ˚C. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ: 6.96–6.92 (m, 4H, Ar), 6.77–6.73 (m, 2H, Ar), 4.57 (q, *J* = 7.2 Hz, 2H, H^B), 2.14 (s, 3H, H^F), 1.39 (t, 7.2 Hz, 3H, H^A); **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ: 185.4 (s, C^E), 172.5 (s, C^C), 152.3 (m, Ar), 149.8 (m, Ar), 140.5 (m, Ar), 138.0 (m, Ar), 127.3 (m, Ar), 115.5 (m, Ar), 114.0 (m, Ar), 100.6 (s, Ar), 66.5 (s, C^B), 22.7 (s, C^F) , 14.1 (s, C^A), carbon atom attached to boron could not be observed; **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ: −133.59 (d, *J* = 22.5 Hz, 2F), −136.14 (d, *J* = 20.1 Hz, 4F), −160.06 (t, *J* = 20.6Hz, 1F), −163.47 (t, *J* = 22.4 Hz, 2F); **^{11}B NMR** (128 MHz, 298 K, $CDCl_3$) δ: 7.7 (br., s); **HRMS** (ASAP+) m/z calculated for $[C_{24}H_{14}{}^{10}BF_9O_3]^+$ $[M - H]^+$: 532.0887 found: 532.0881.

Synthesis of compound ***3g***



Synthesised according to General Procedure **B** using 3,4,5 tris(trifluorophenyl)borane (95 mg, 0.2 mmol, 1.0 equiv.) and 1,3-diphenyl-2-(phenyliodaneylidene)propane-1,3-dione (**2c**) (100 mg, 0.2 mmol, 1.0 equiv.) in toluene (5 mL) to afford the desired compound (**3g**) as a yellow powder (103 mg, 0.2 mmol, 70%). Crystals were obtained from a CH_2Cl_2/pentane mixture. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ: 7.58–7.50 (m, 2H, Ar), 7.40–7.32 (m, 8H, Ar), 7.06–7.02 (m, 4H, Ar), 6.53 (m, 2H, Ar); **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ: 186.3 (s, C^A), 151.3 (m, Ar), 140.7 (m, Ar), 138.2 (m, Ar), 133.7 (s, Ar), 133.6(s, Ar), 130.5 (s, Ar), 129.5 (s, Ar), 129.2 (m, Ar), 128.8 (s, Ar), 116.8 (s, Ar), 114.2 (s, Ar), 113.4 (s, C^B), carbon atom attached to boron could not be observed; **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ: −132.06 (d, *J* = 20.5 Hz, 2F), −135.99 (d, *J* = 20.2 Hz, 4F), −158.96 (t, *J* = 20.7 Hz, 1F), −163.34 (t, *J* = 20.1 Hz, 2F); **^{11}B NMR** (128 MHz, 298 K, $CDCl_3$) δ: 7.3 (br., s); **HRMS** (ASAP+) m/z calculated for $[C_{33}H_{15}{}^{10}BF_9O_2]^+$ $[M - H]^+$: 626.1214 found: 626.1185.

Synthesis of compound **4**



Synthesised according to General Procedure **B** using tris(pentafluorophenyl)borane (200 mg, 0.4 mmol, 1.0 equiv.) and 5,5-dimethyl-2-(phenyliodaneylidene)cyclohexane-1,3-dione (**2d**) (163 mg, 0.4 mmol, 1.0 equiv.) in toluene (15 mL) to afford the desired compound (**4**) as a faint brown solid (156 mg, 0.2 mmol, 48%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ: 7.84–7.81 (m, 2H, Ar), 7.61–7.58 (m, 1H, Ar), 7.40–7.37 (m, 2H, Ar), 2.35 (s, 2H, H^B), 2.25 (s, 2H, H^E), 0.81 (s, 6H, H^D); **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ: 189.5 (s, C^A), 187.7 (s, C^A), 147.7 (m,Ar2), 139.9 (m, Ar2), 137.1 (m, Ar2), 135.7 (s, Ar1), 133.2 (s, Ar2), 132.6 (s, Ar1), 110.6 (s, Ar1), 99.7 (s, C^E), 50.3 (s, C^B), 45.0 (S, C^B), 332. (s, C^C), 27.6 (s, C^D). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ: −133.78 (d, *J* = 29.3 Hz), −157.75 (t, *J* = 20.4 Hz), −163.93 (t, *J* = 26.9 Hz); **^{11}B** NMR (160 MHz, 298 K, $CDCl_3$) δ: -1.86 (br., s); **HRMS** (ASAP-) m/z calculated for $[C_{32}H_{14}O_2{}^{127}I^{10}BF_{15}]^-$ [M + H]$^-$: 851.9928 found: 851.9910.

2. NMR Spectra

2.1 NMR of starting materials

Figure S1 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **2a**.

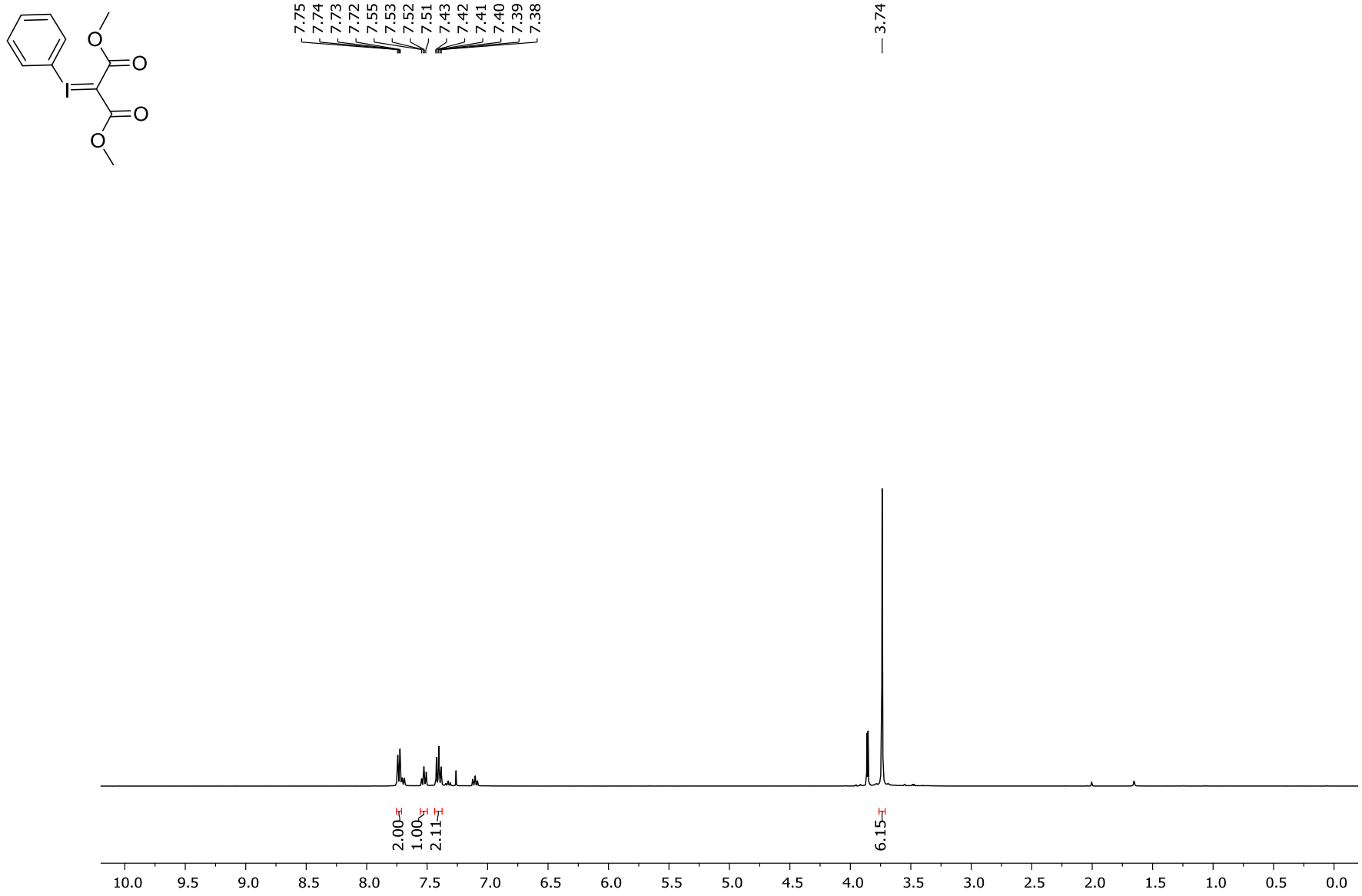


Figure S2 $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **2a**.

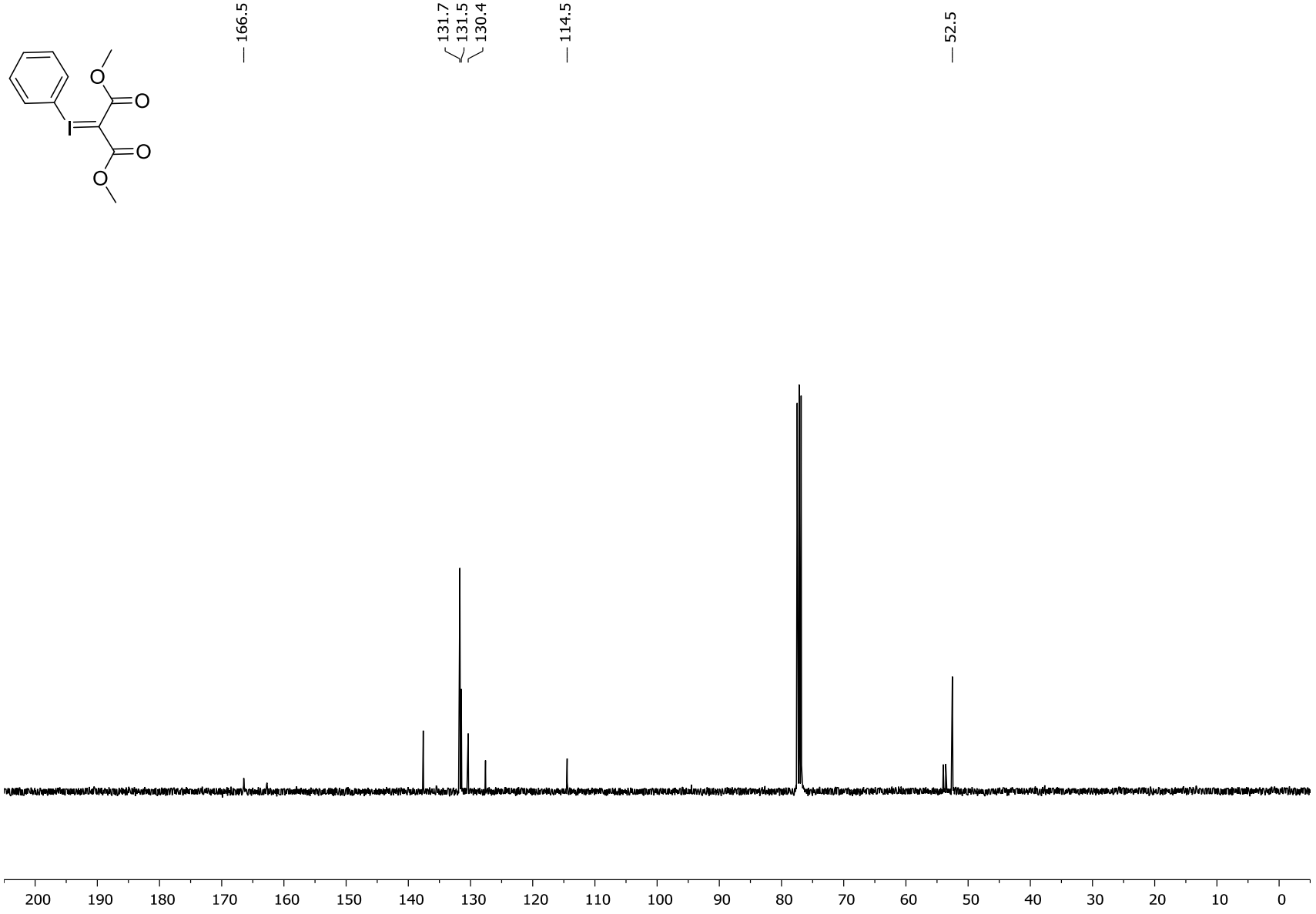


Figure S3 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **2b**.

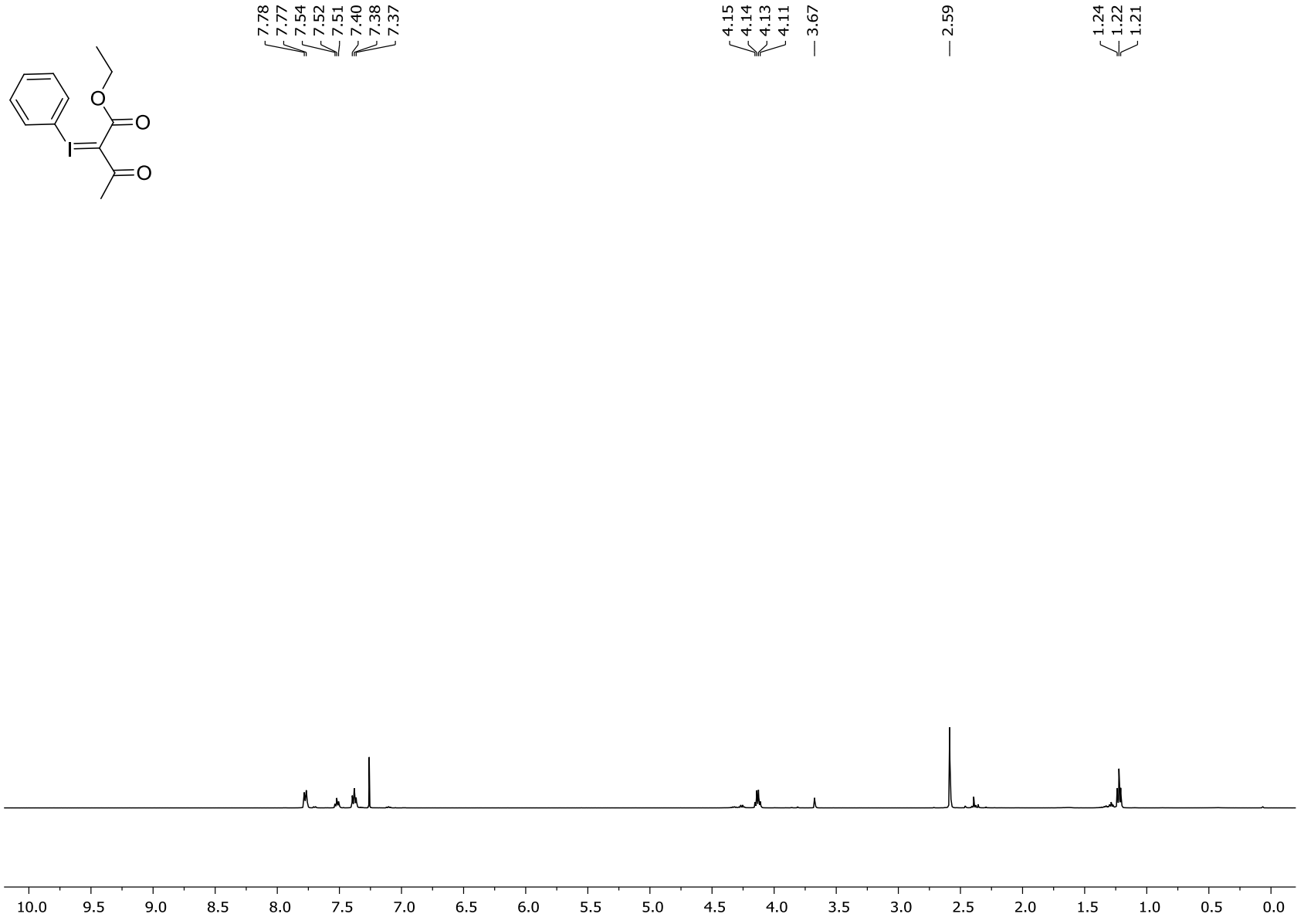


Figure S4 $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **2b**.

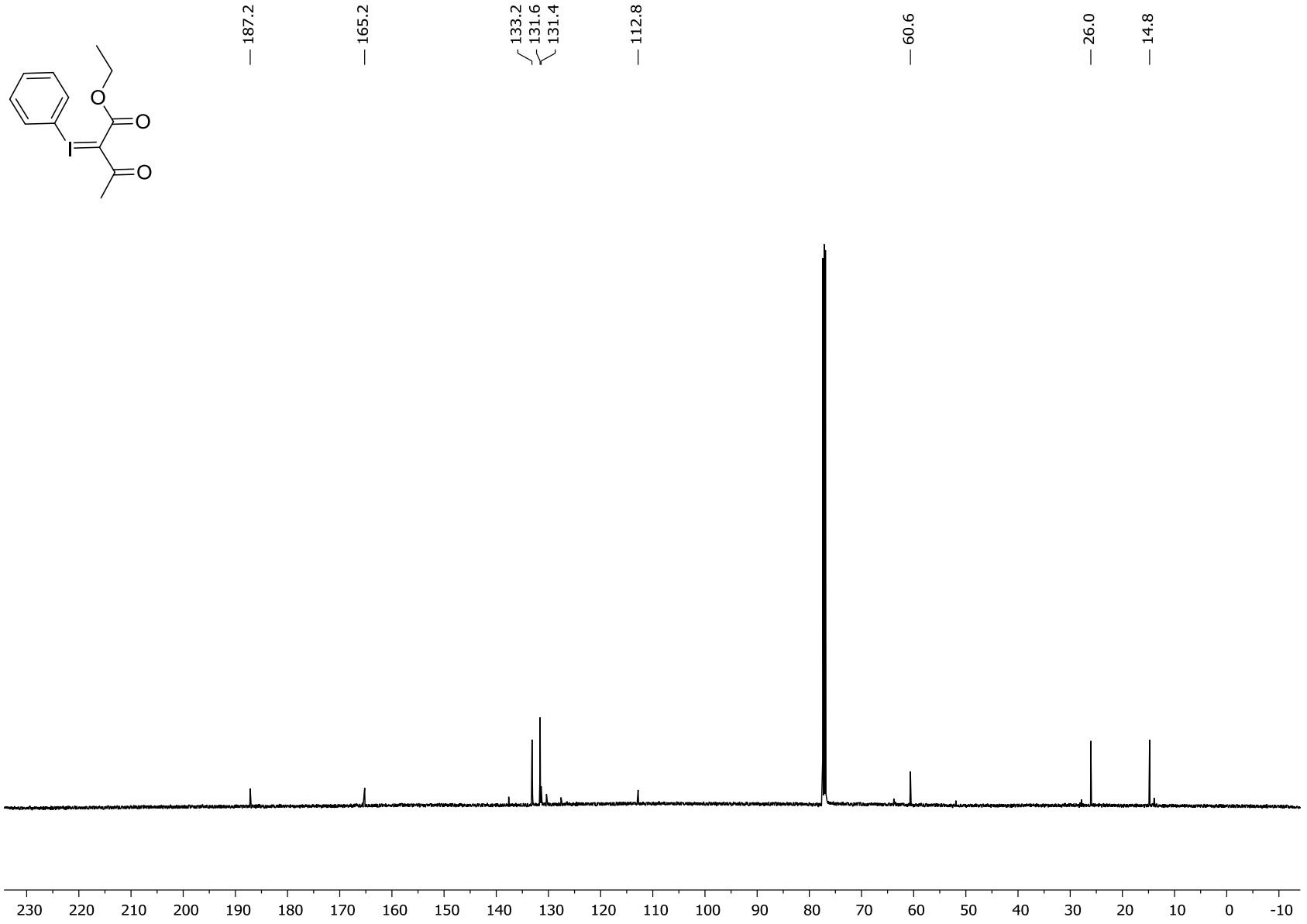


Figure S5 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **2c**.

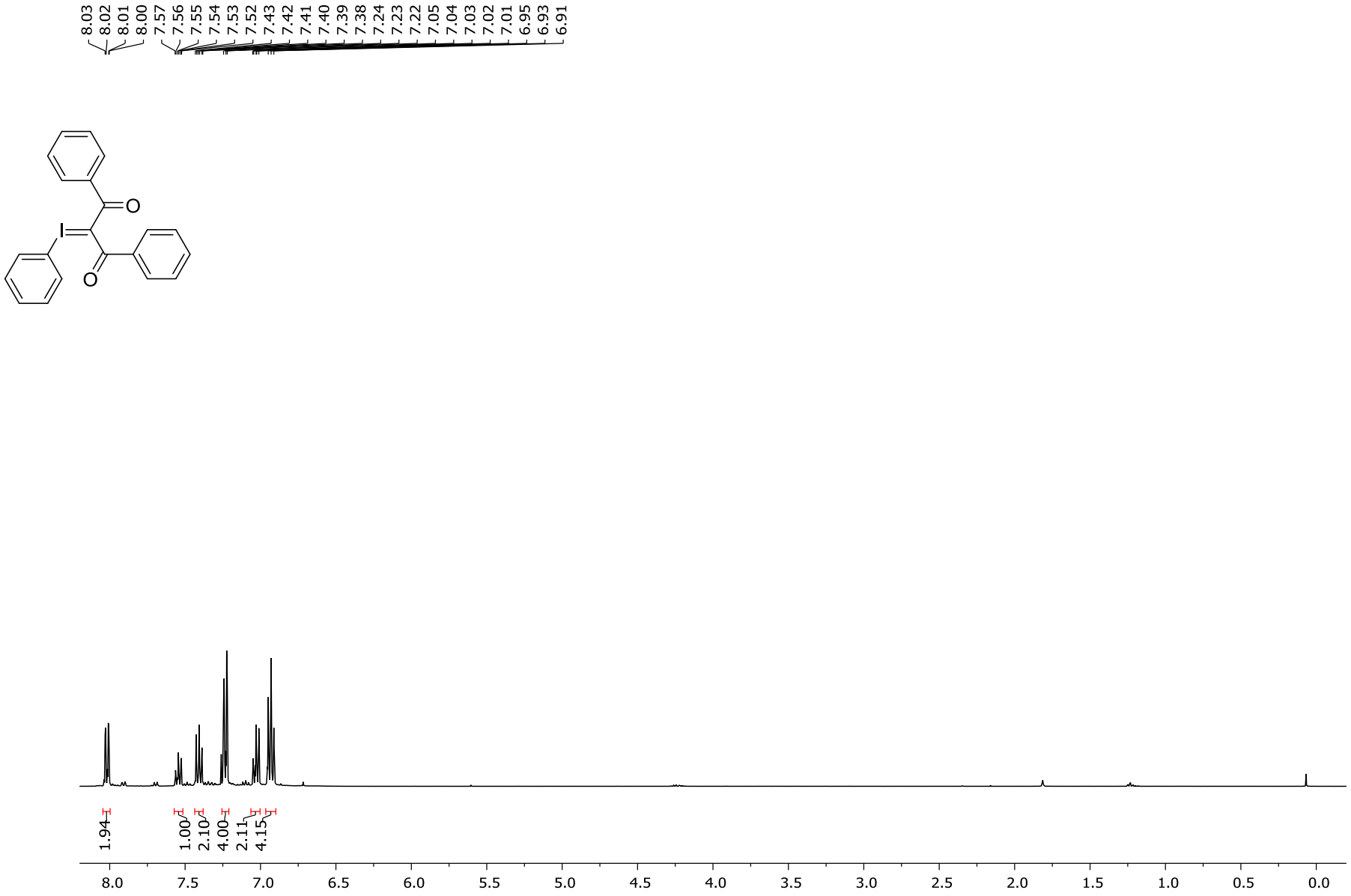


Figure S6 $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **2c**.

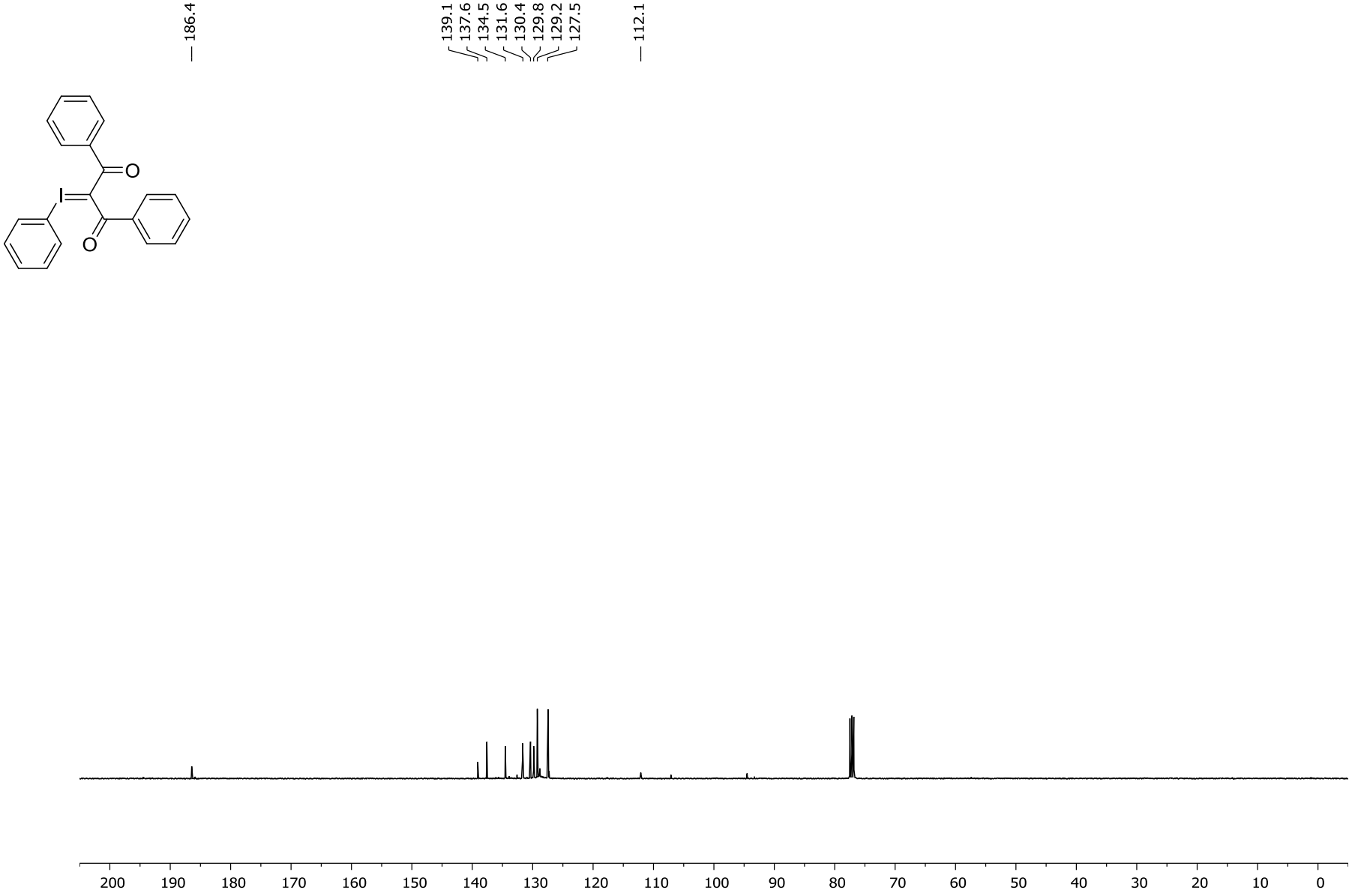


Figure S7 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of **2d**.

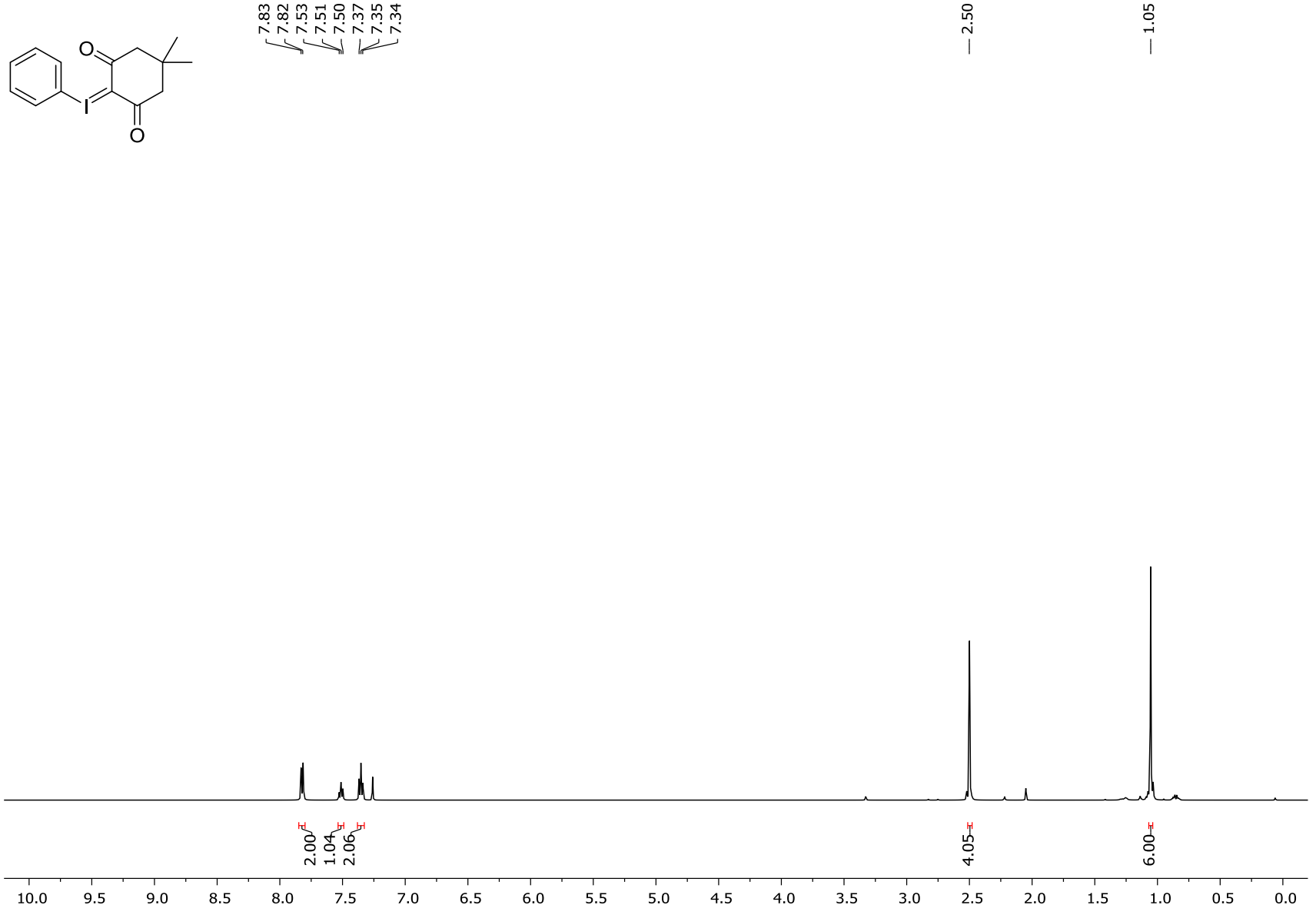
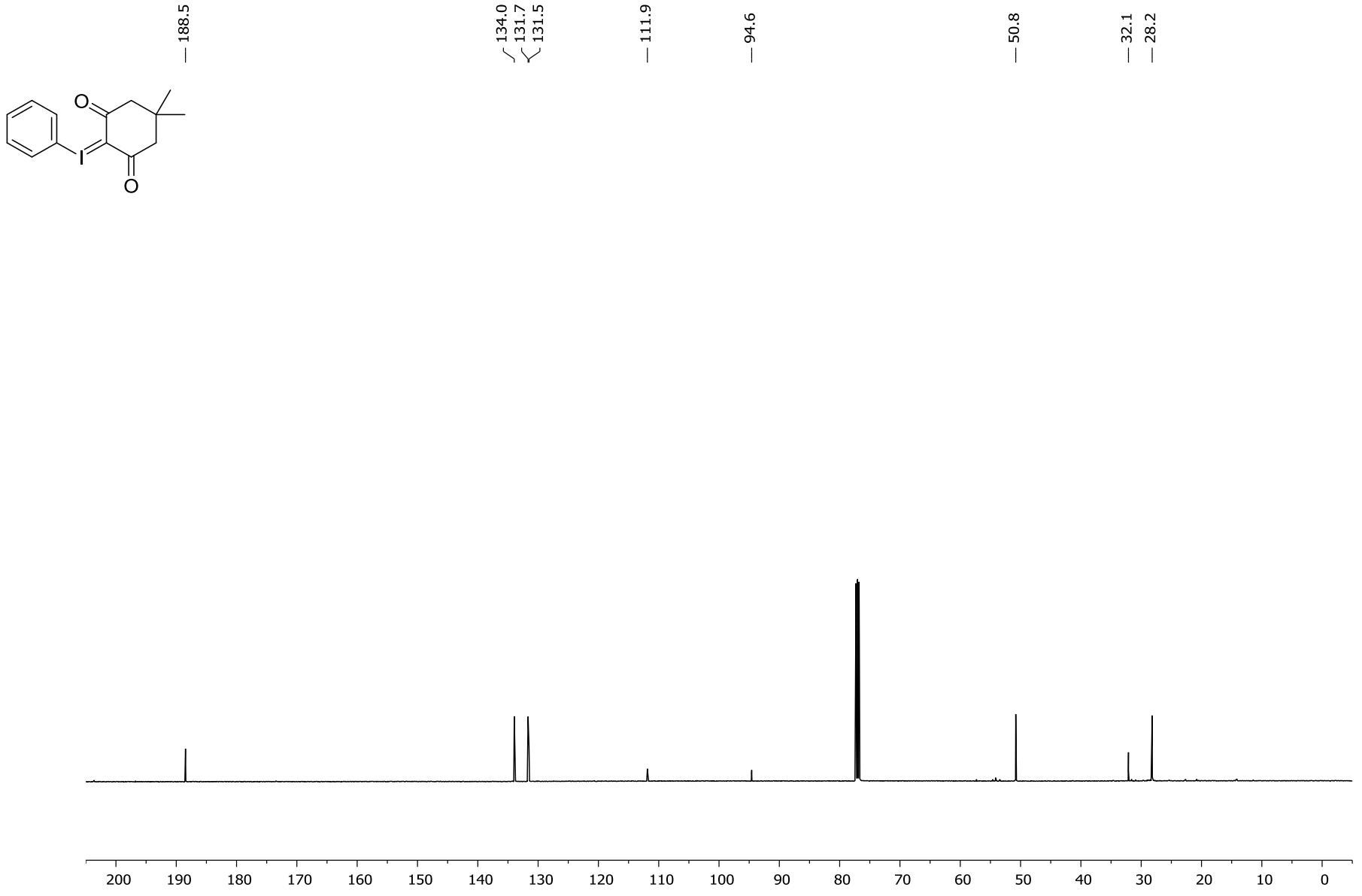
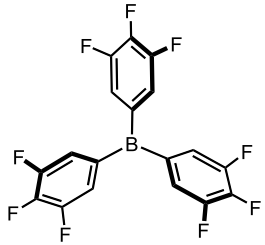


Figure S8 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of **2d**.



2.2 NMR of triaryl fluoroboranes

Figure S9 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of tris(3,4,5-trifluorophenyl)borane (**1a**).



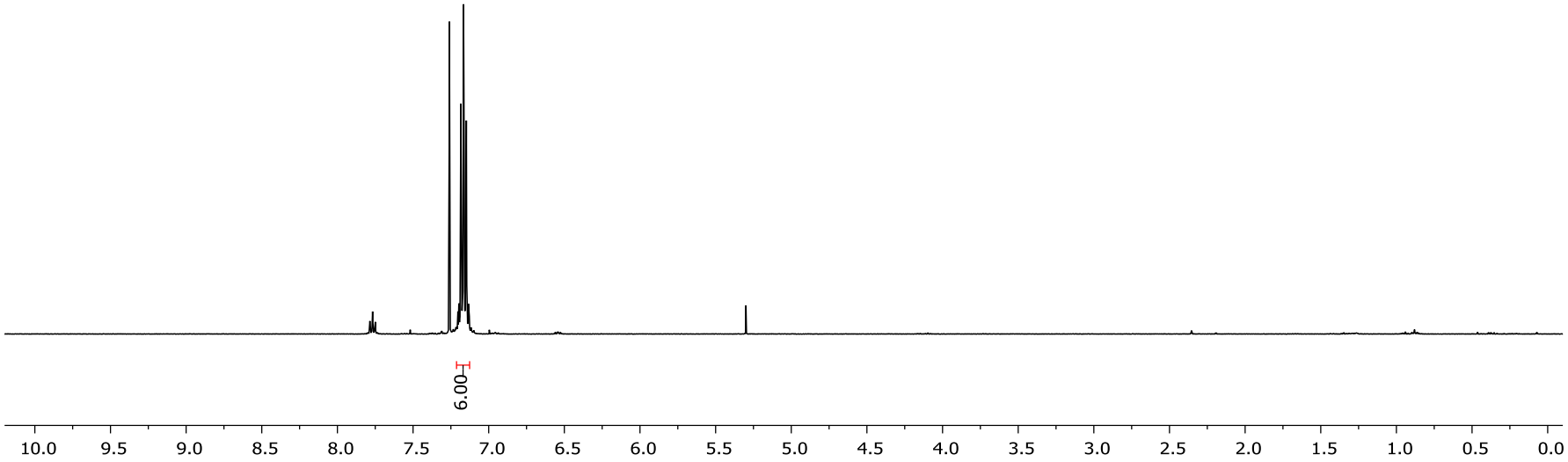


Figure S10 ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) spectrum of tris(3,4,5-trifluorophenyl)borane (**1a**).

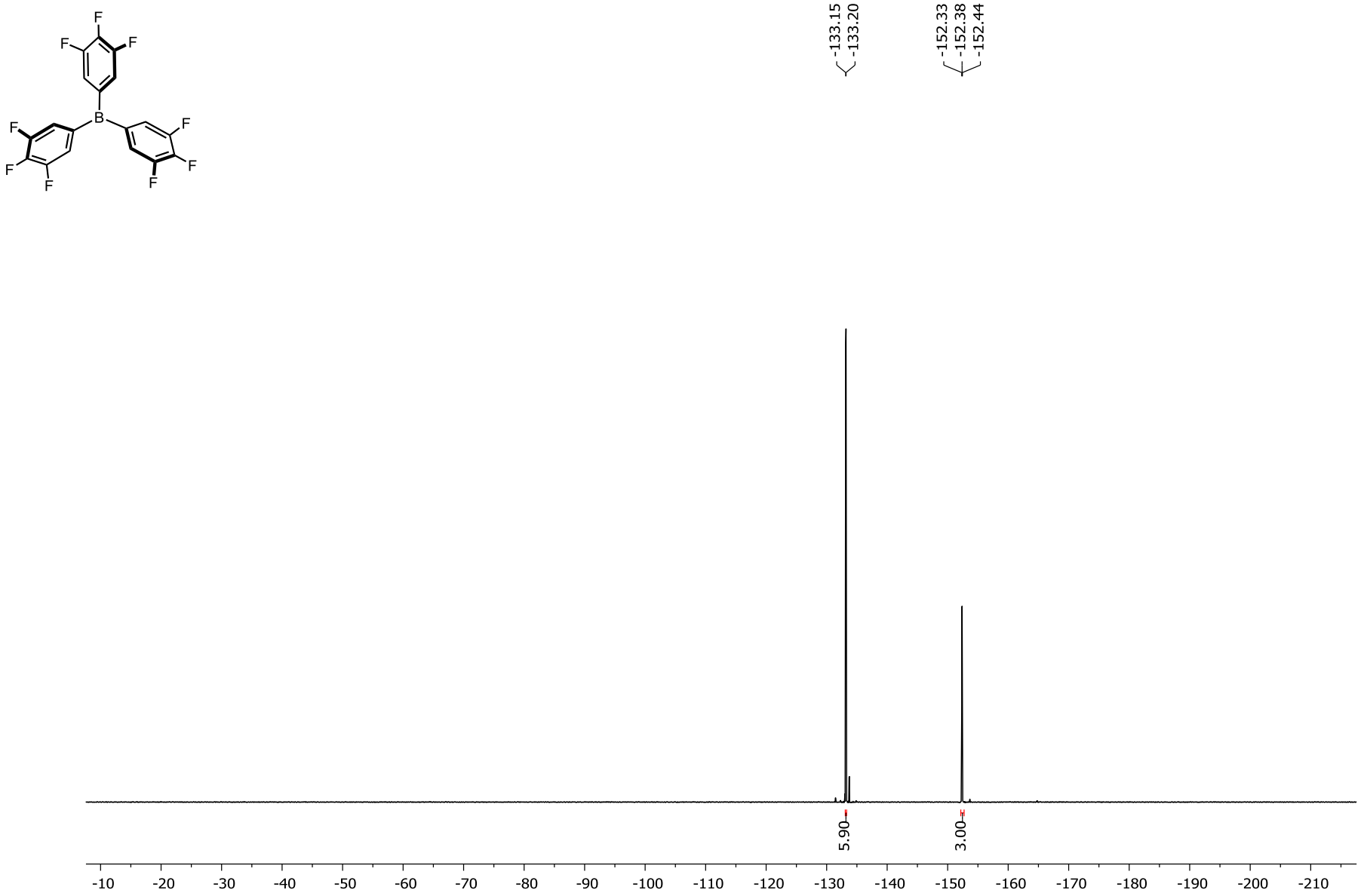


Figure S11 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of tris(3,4,5-trifluorophenyl)borane (**1a**).

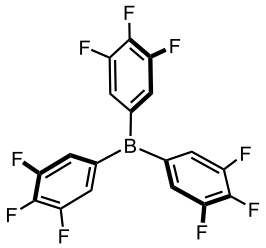


Figure S12 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of tris(2,4,6-trifluorophenyl)borane (**1b**).

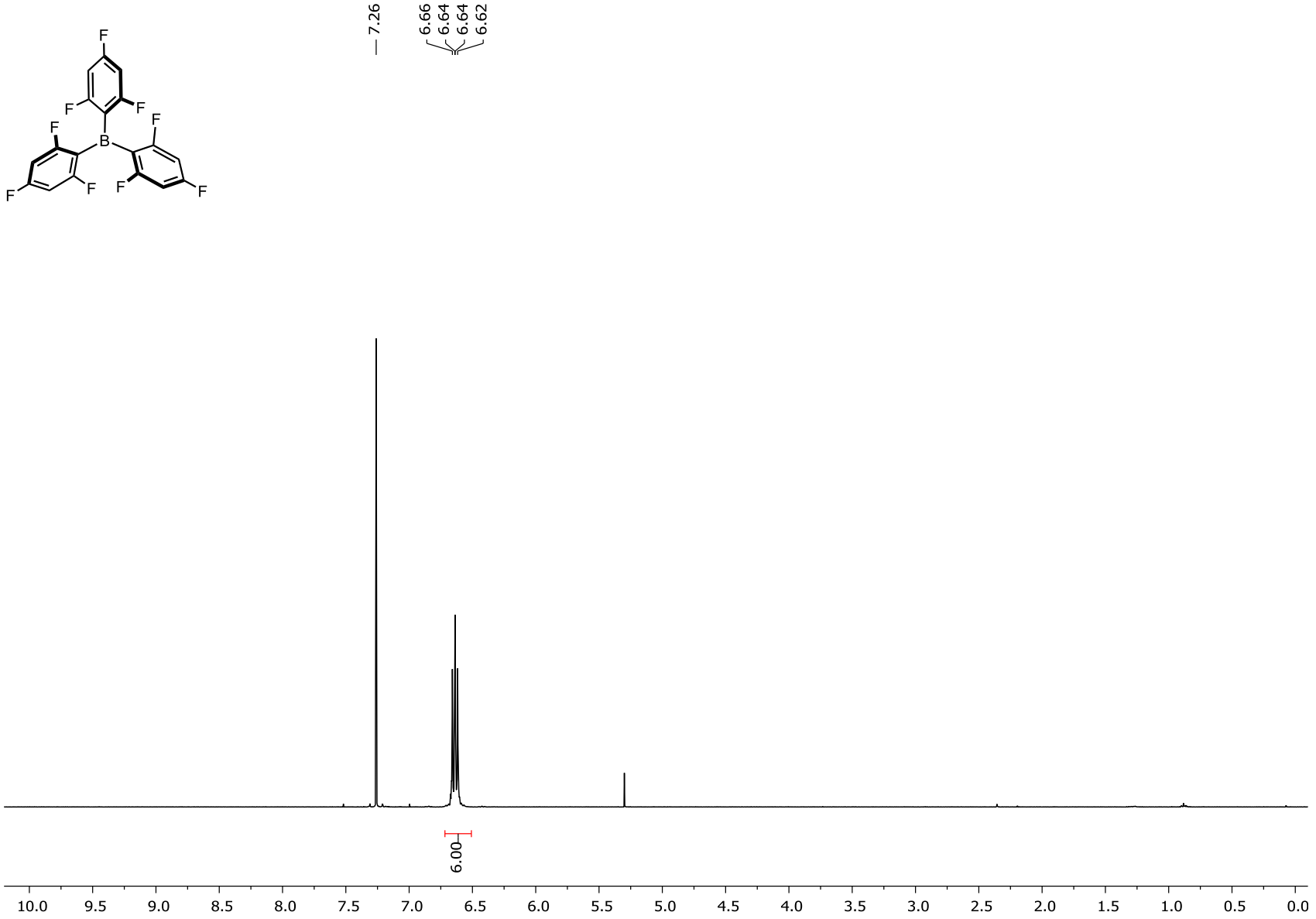


Figure S13 ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) spectrum of tris(2,4,6-trifluorophenyl)borane (**1b**).

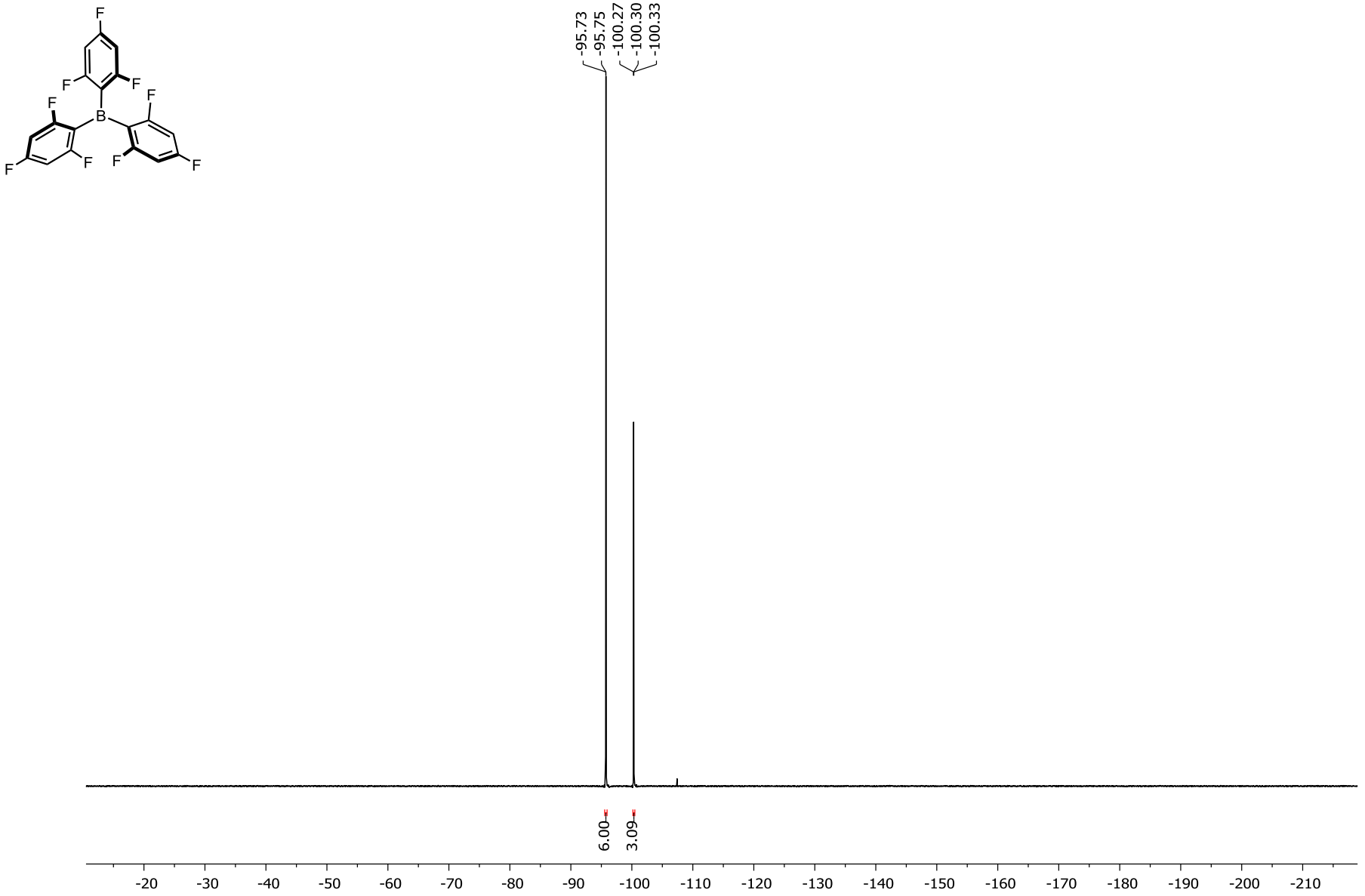


Figure S14 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of tris(2,4,6-trifluorophenyl)borane (**1b**).

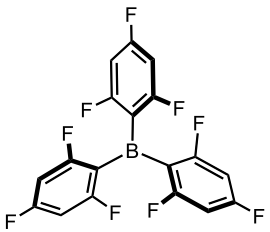


Figure S15 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of tris(2,6-trifluorophenyl)borane (**1c**).

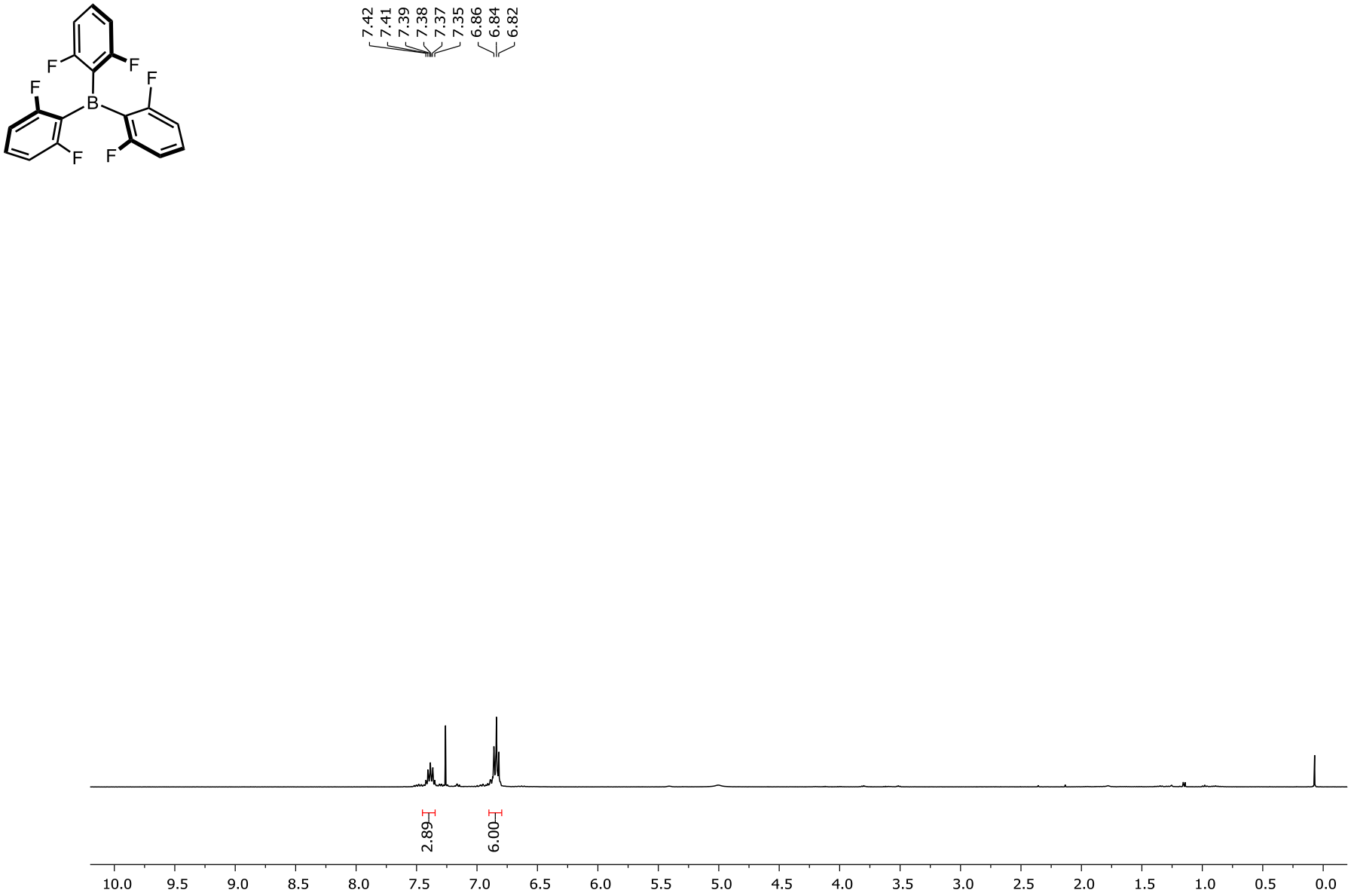


Figure S16 ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) spectrum of tris(2,6-trifluorophenyl)borane (**1c**).

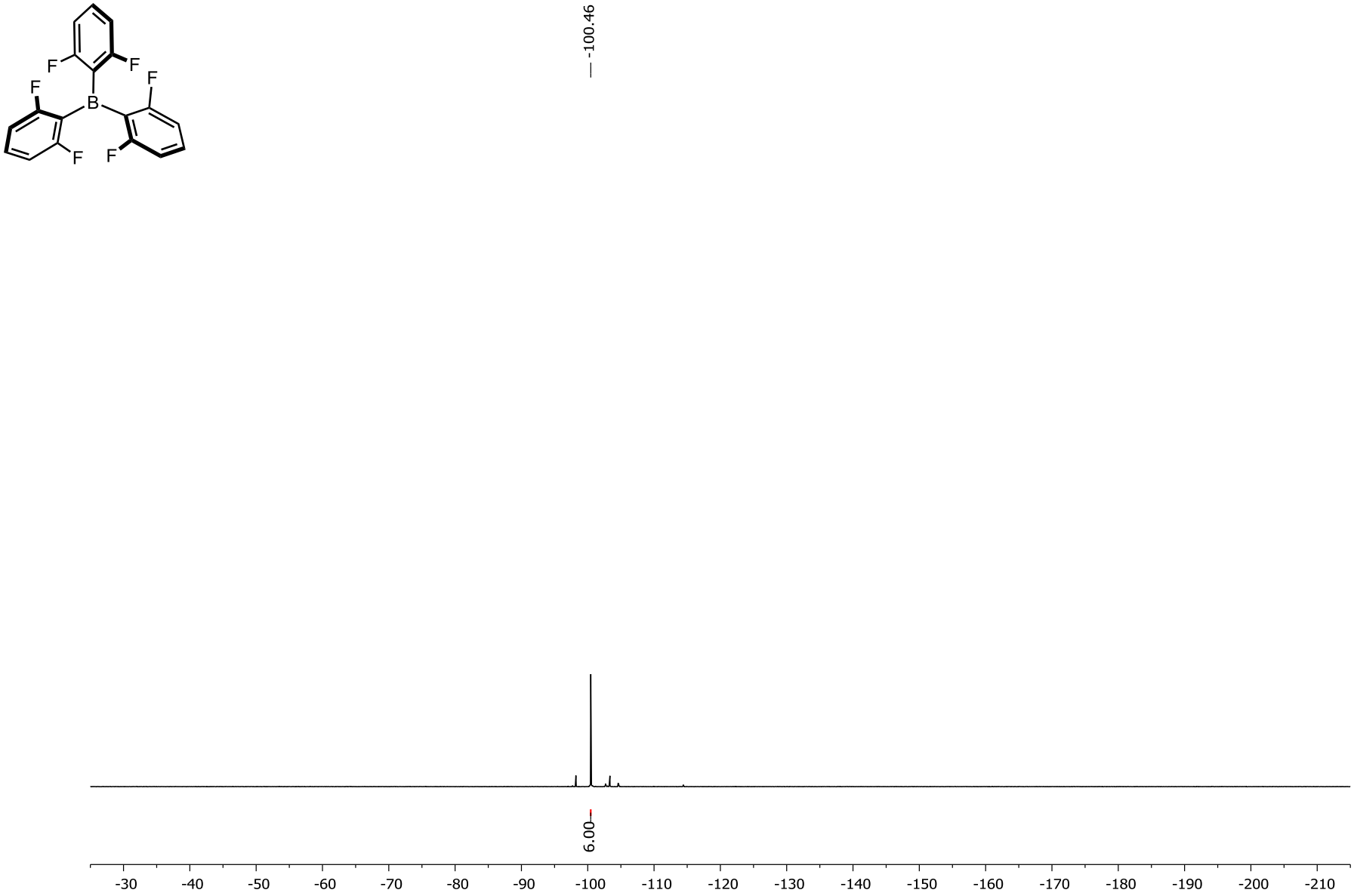


Figure S17 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of tris(2,6-trifluorophenyl)borane (**1c**).

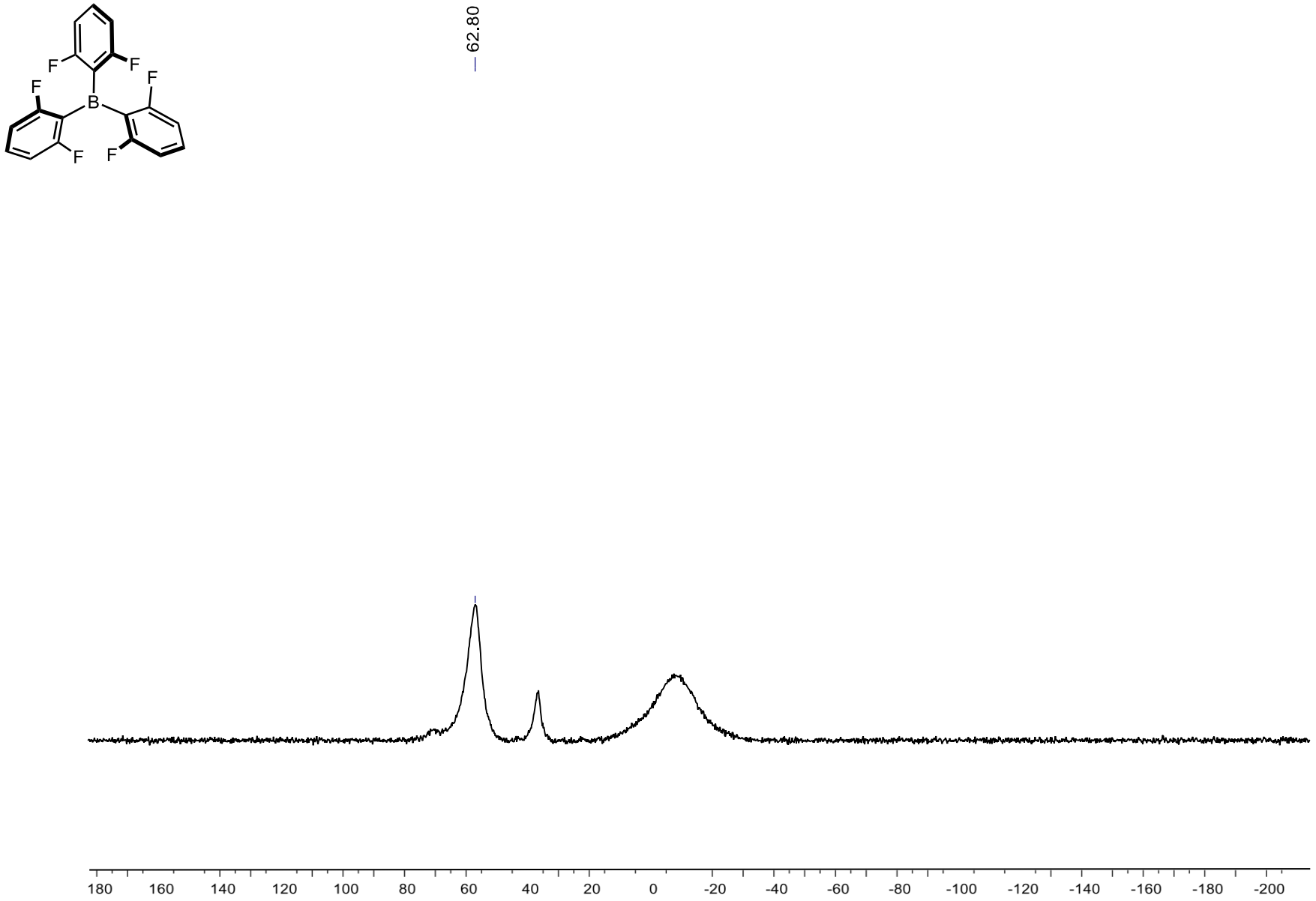


Figure S18 ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) spectrum of tris(pentafluophenyl)borane (**1e**).

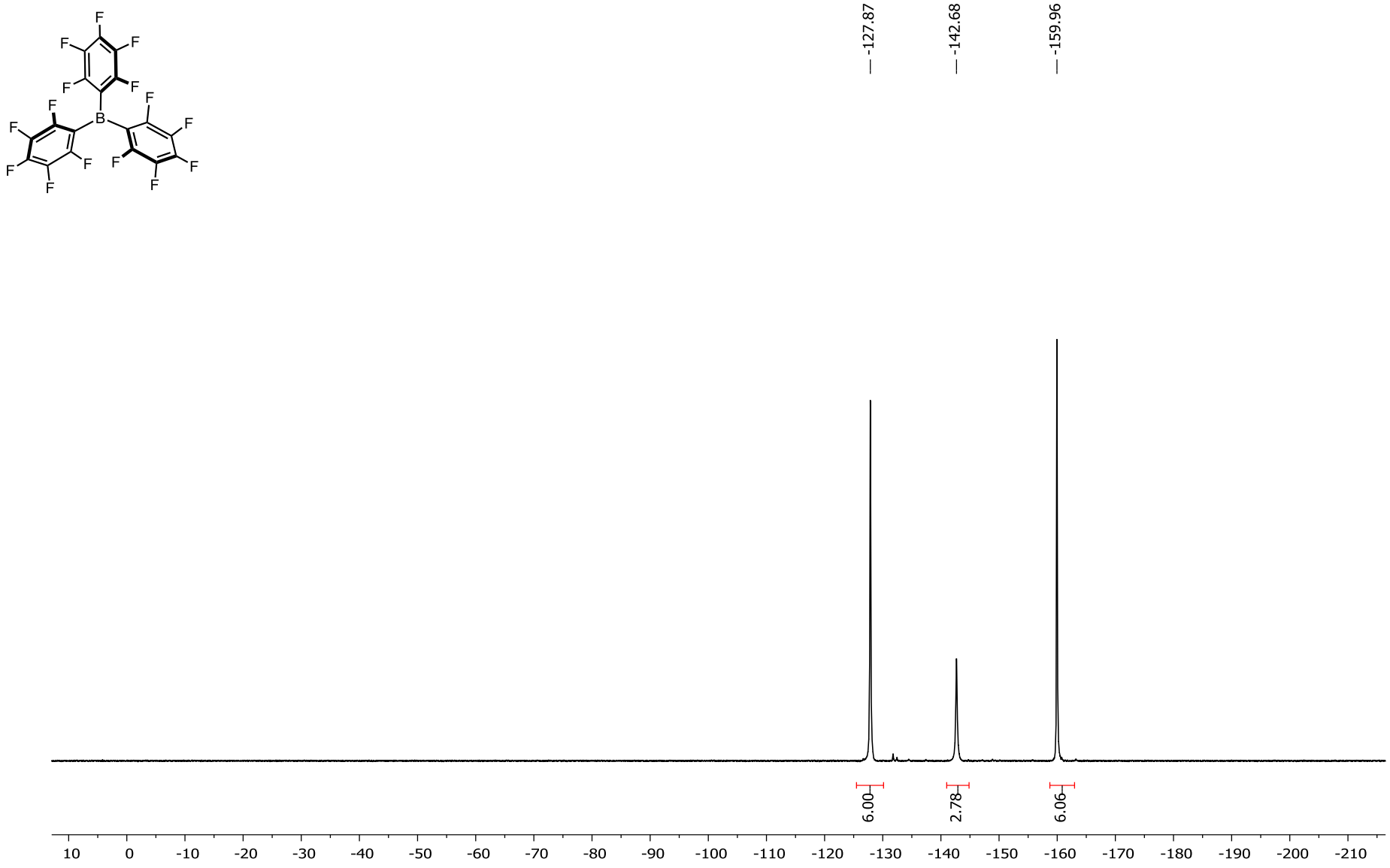
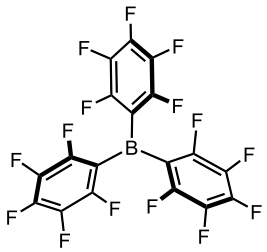


Figure S19 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of tris(pentafluophenyl)borane (**1e**).



2.3 NMR of products

Figure S20 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **3a**.

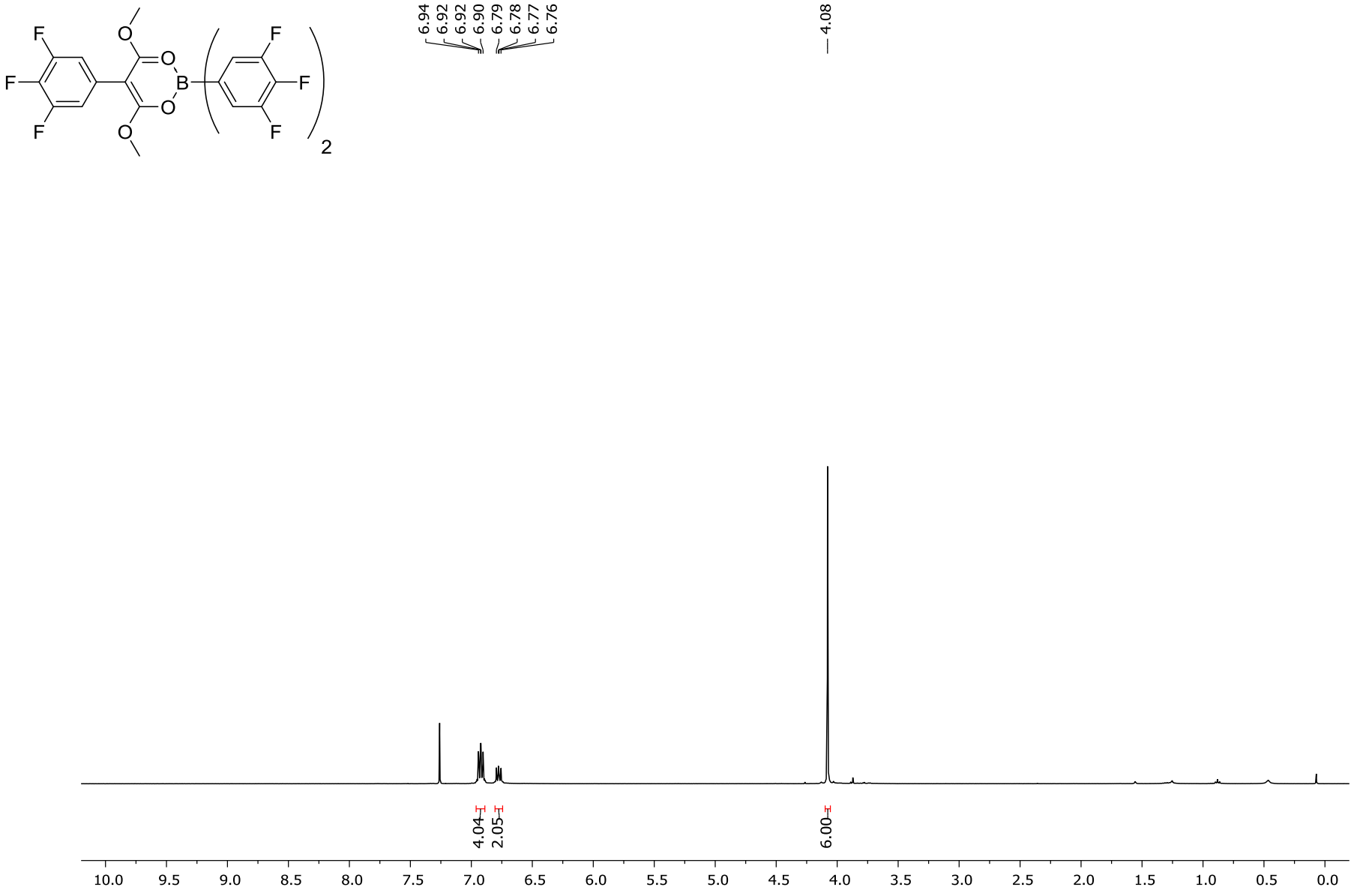


Figure S21 $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **3a**.

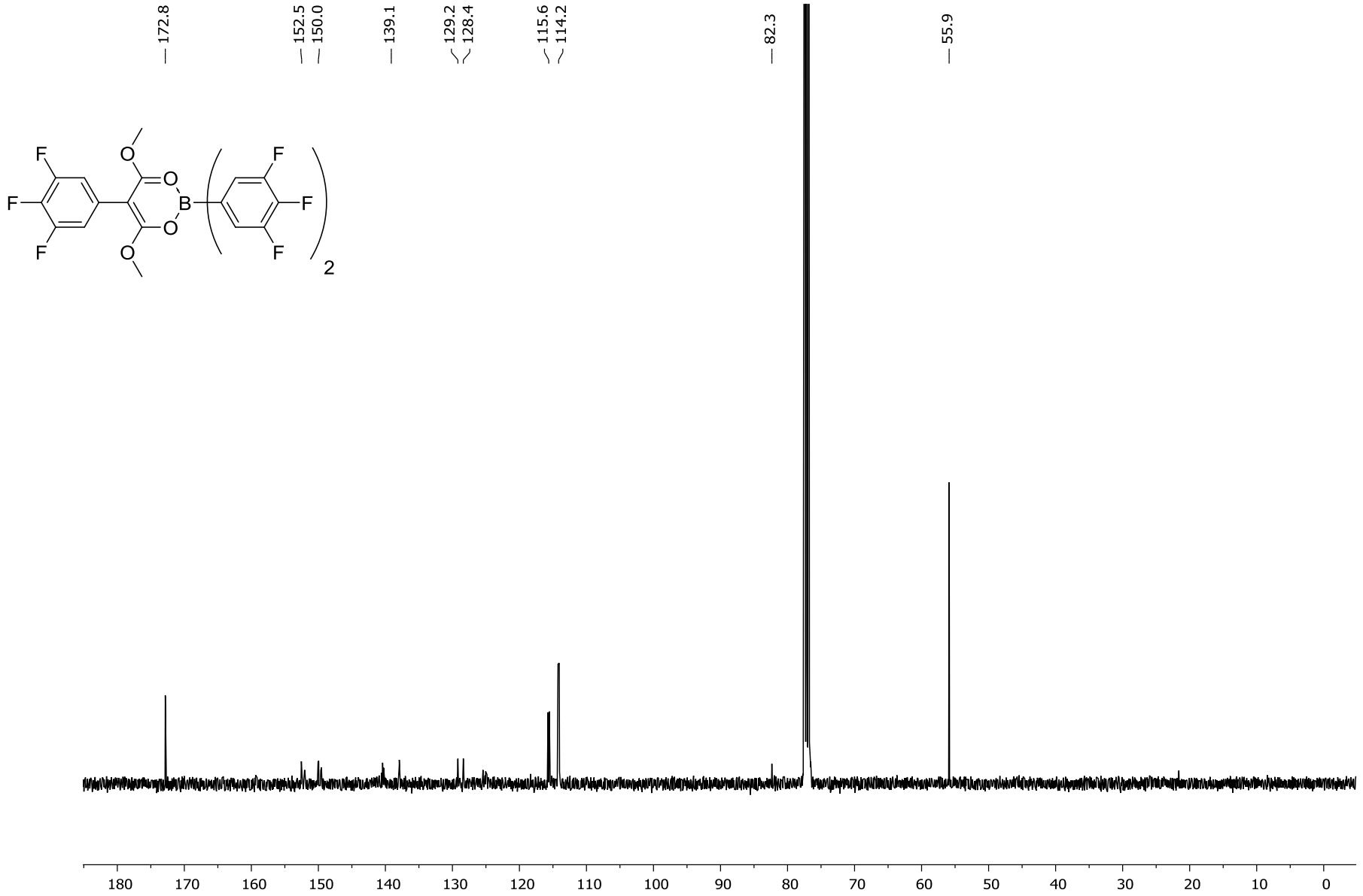


Figure S22 ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) spectrum of **3a**.

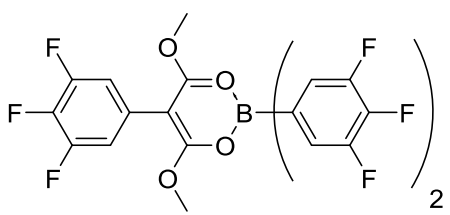


Figure S23 ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of **3a**.

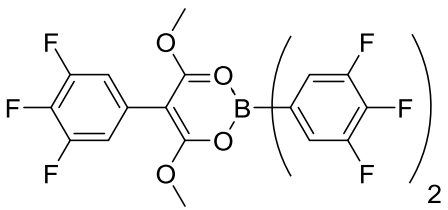


Figure S24 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of **3b**.

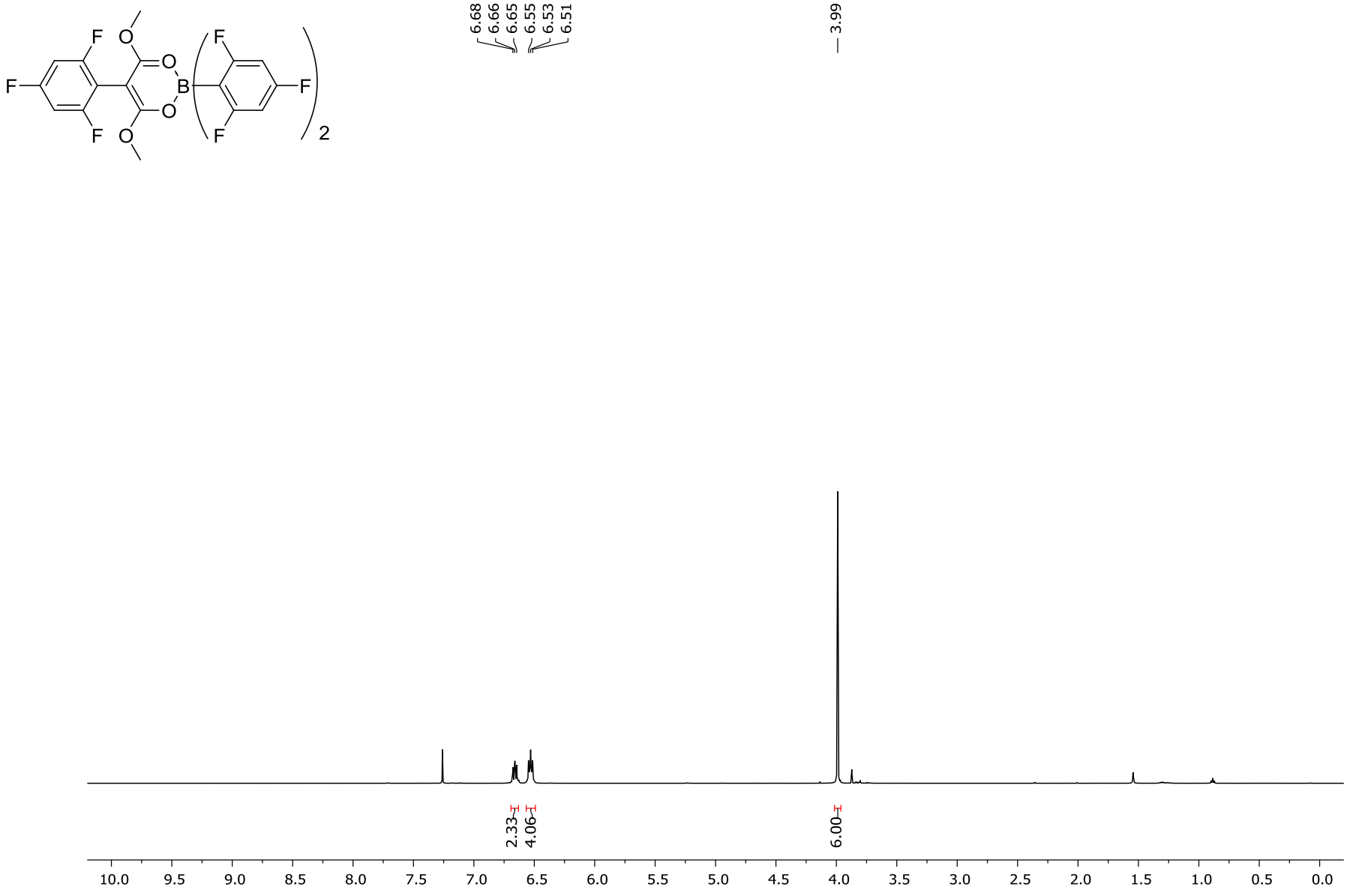


Figure S25 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of **3b**.

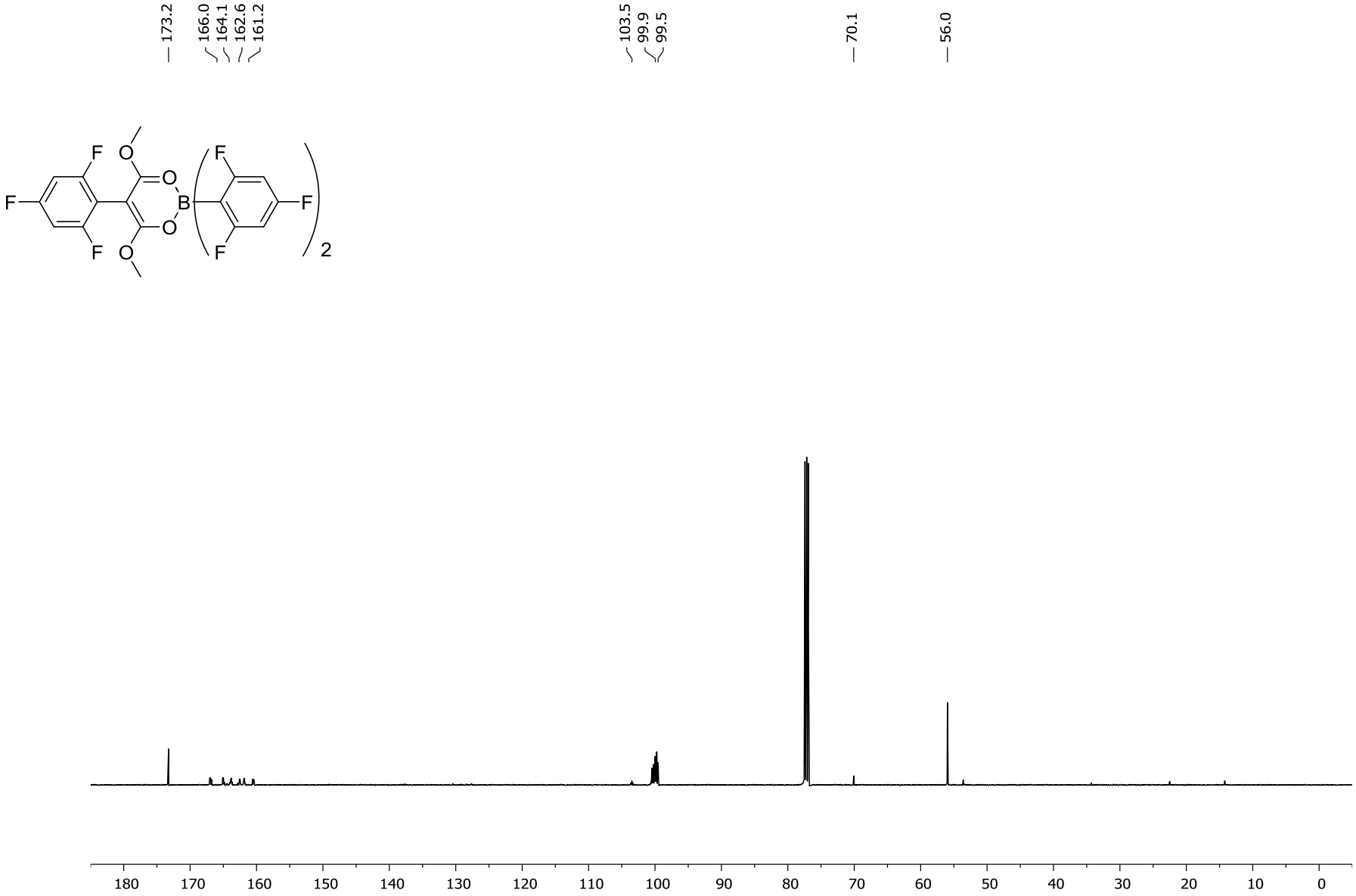


Figure S26 ^{19}F NMR (470 MHz, $CDCl_3$, 298 K) spectrum of **3b**.

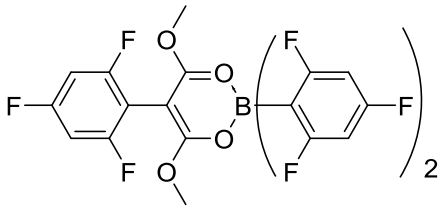


Figure S27 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of **3b**.

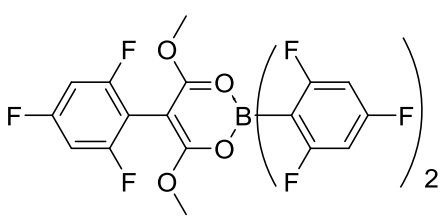


Figure S28 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **3c**.

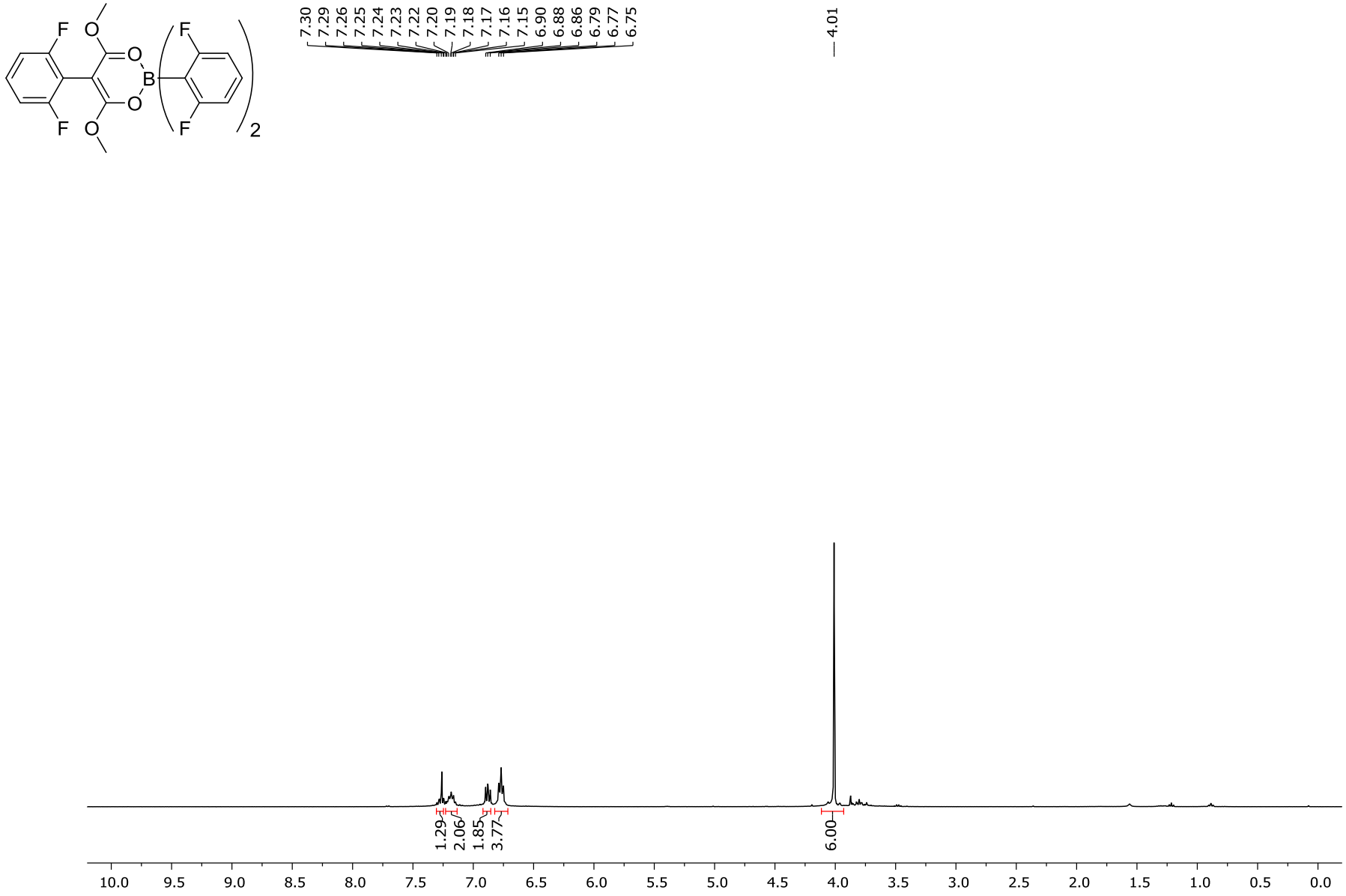


Figure S29 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of **3c**.

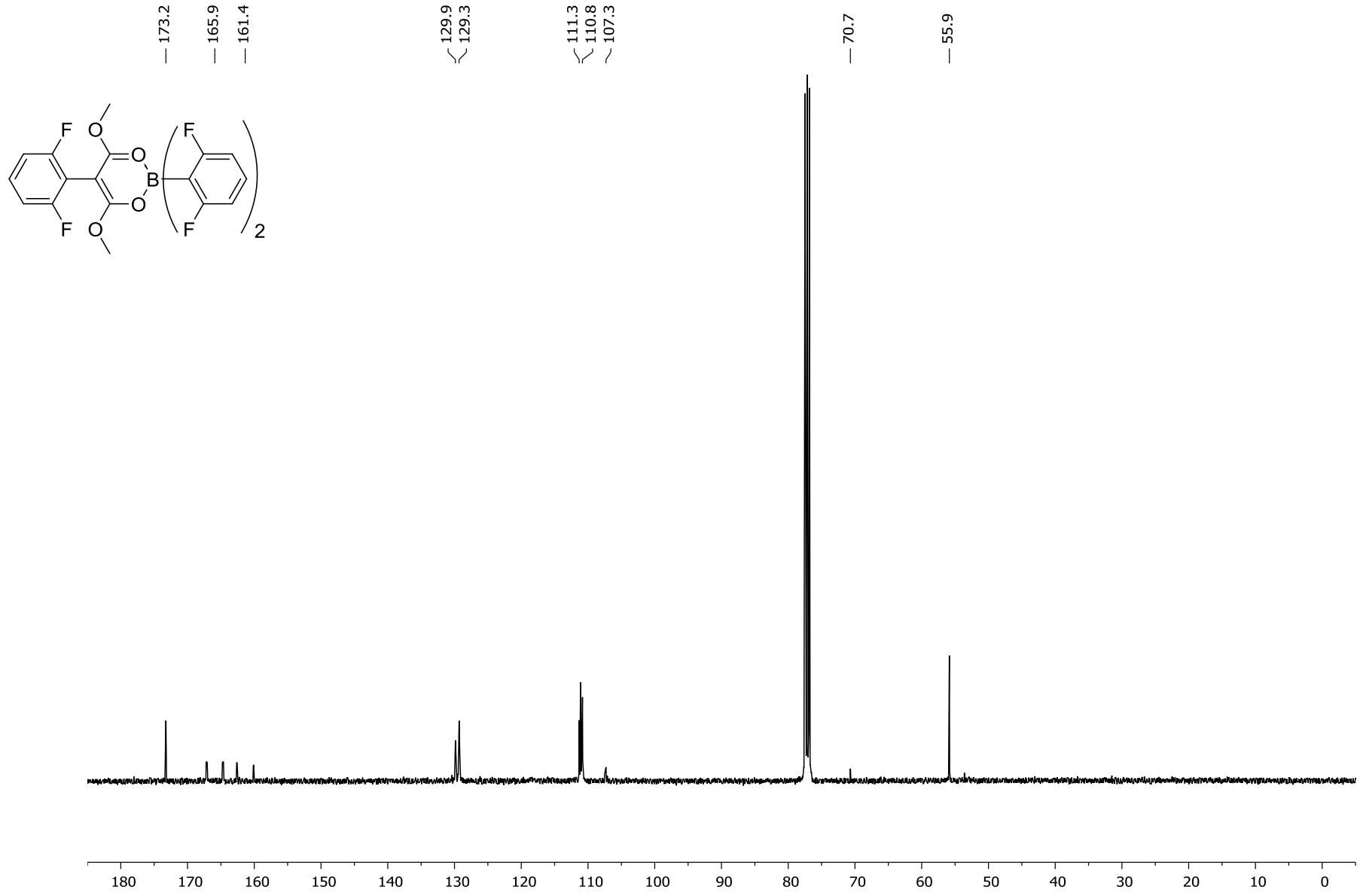


Figure S30 ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) spectrum of **3c**.

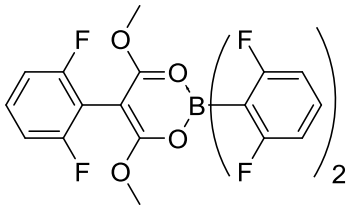


Figure S31 ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of **3c**.

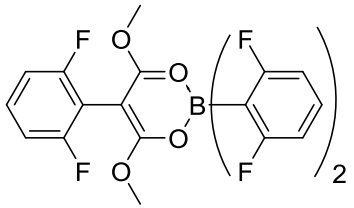


Figure S32 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **3d**.

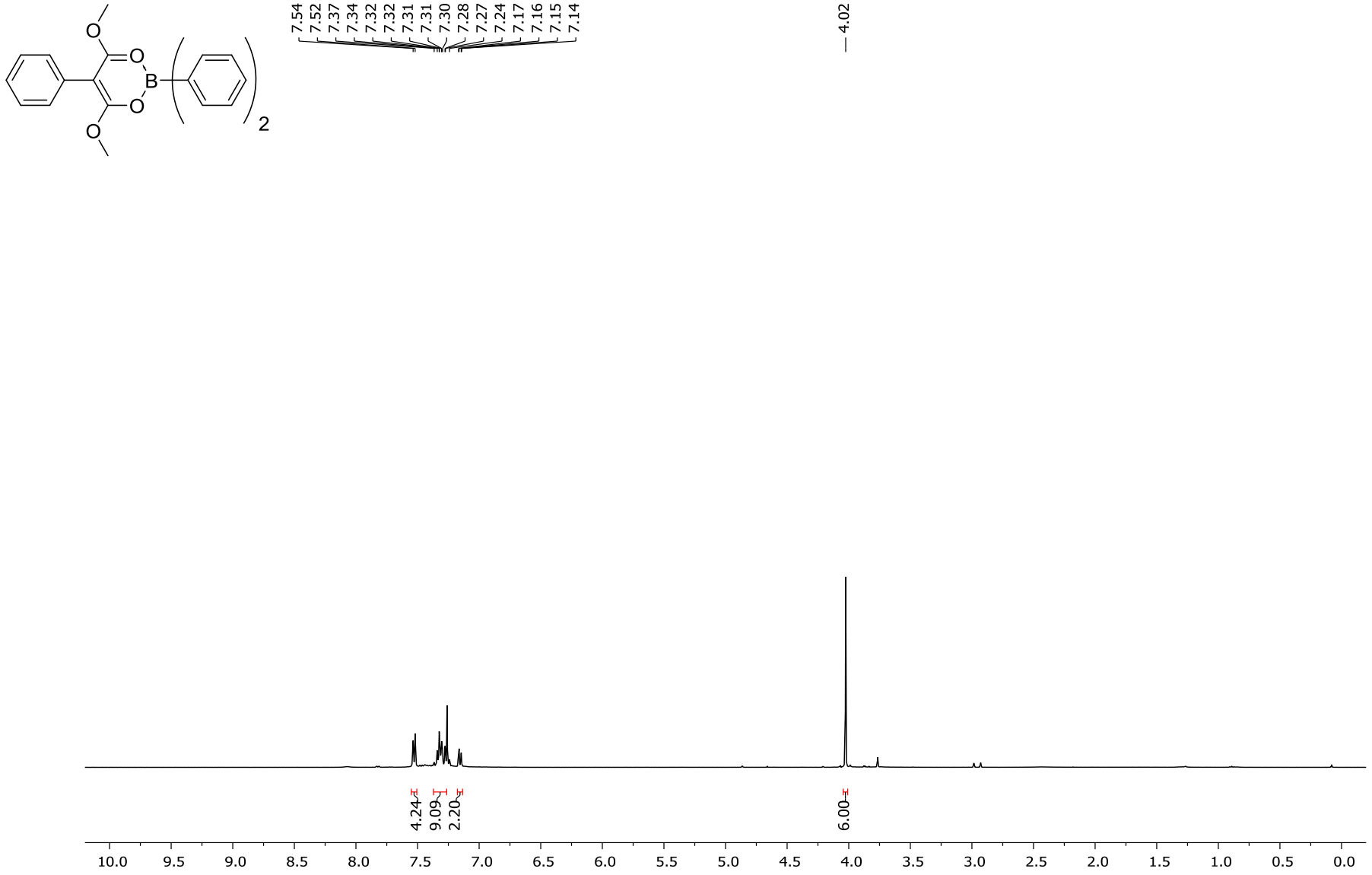


Figure S33 $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **3d**.

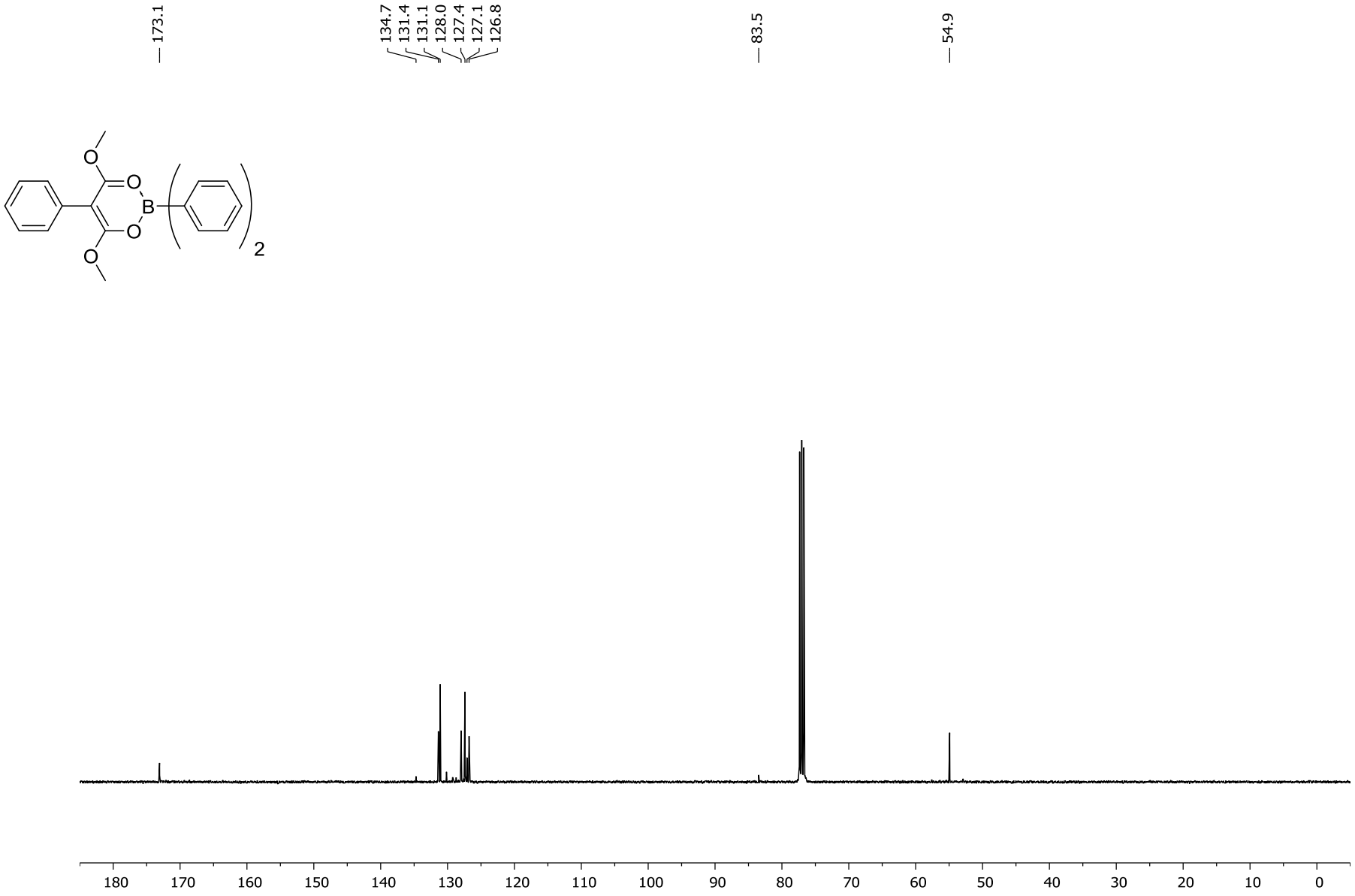


Figure S34 ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of **3d**.

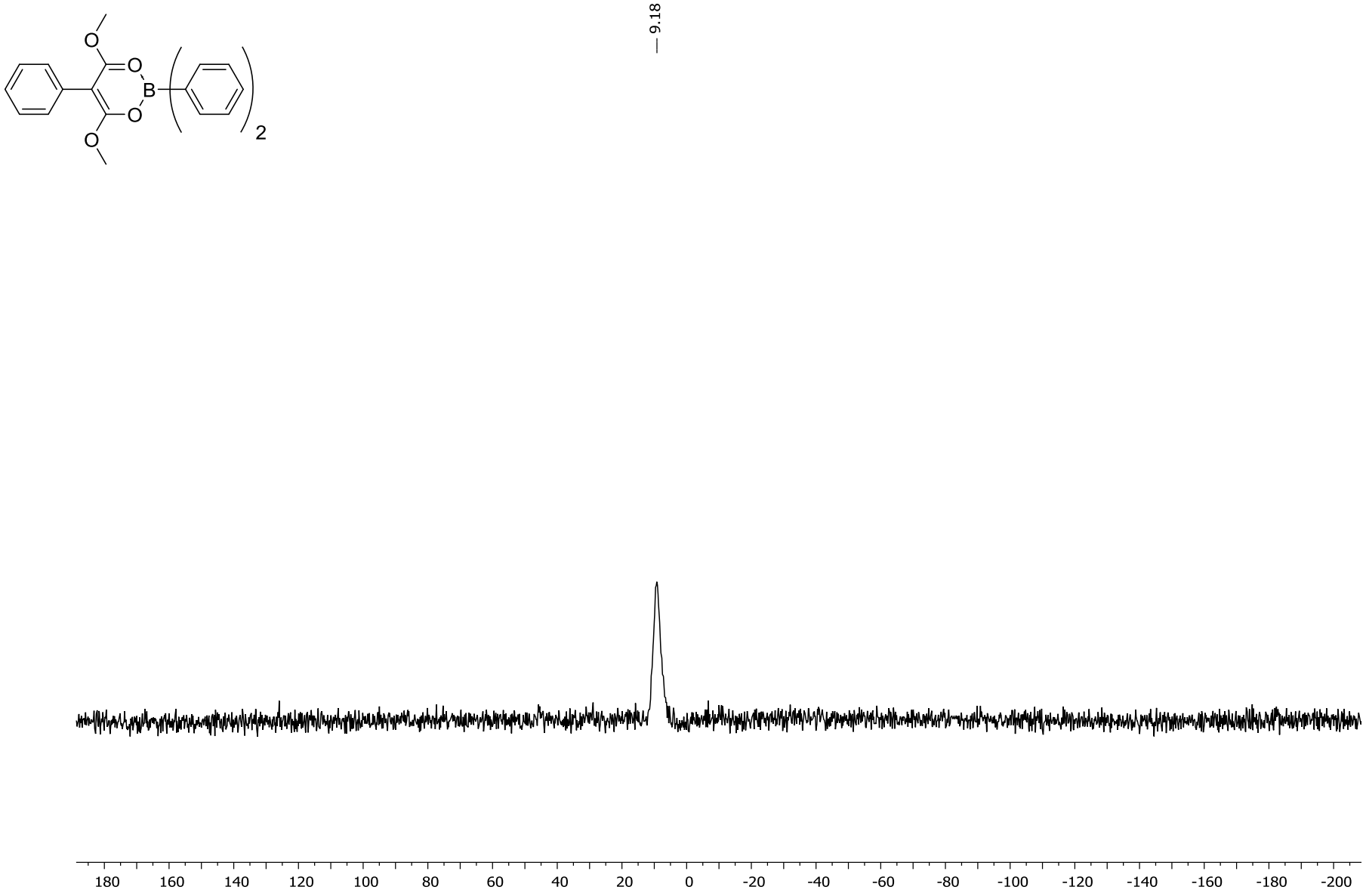


Figure S35 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **3f**.

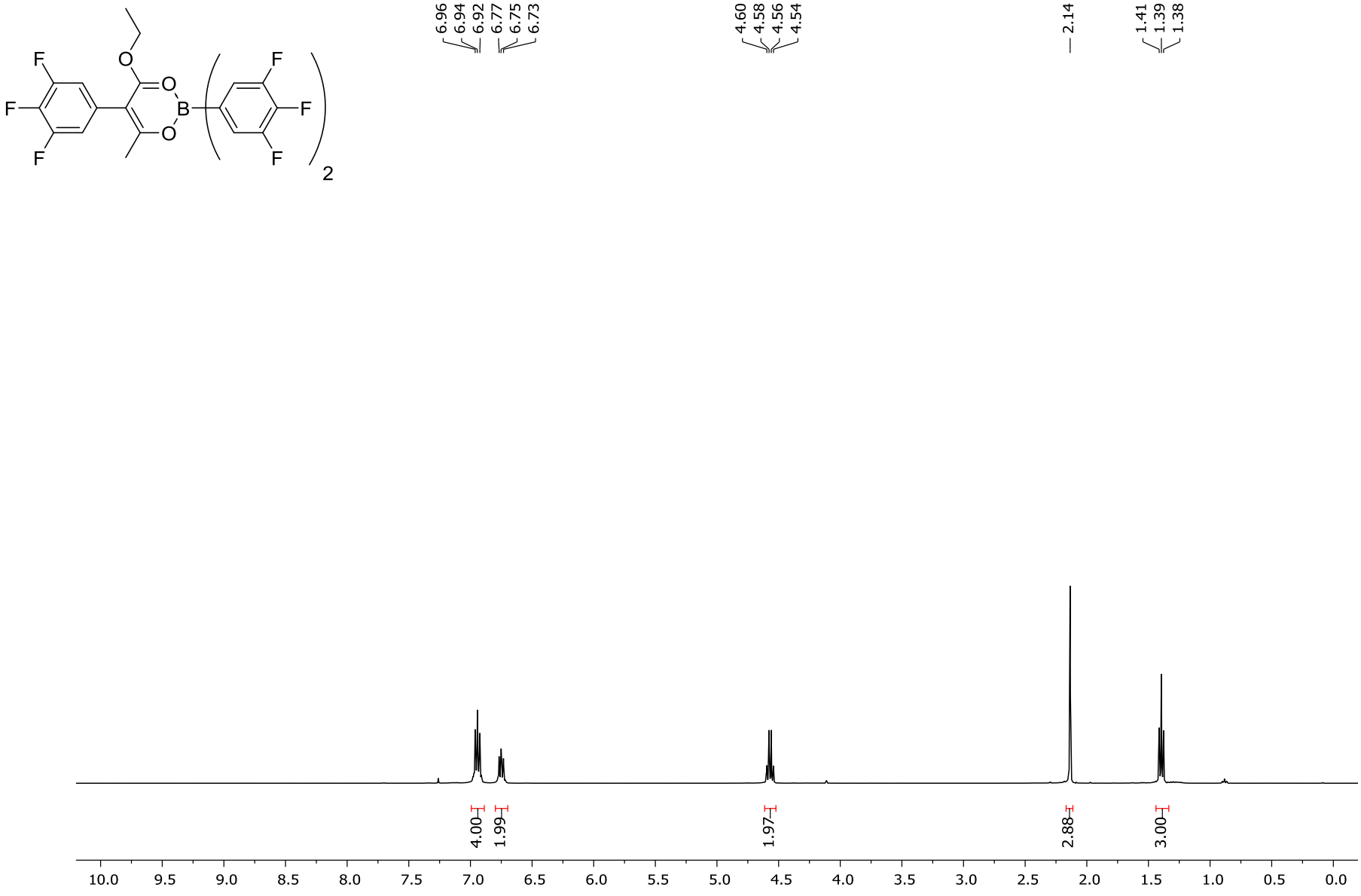


Figure S36 $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **3f**.

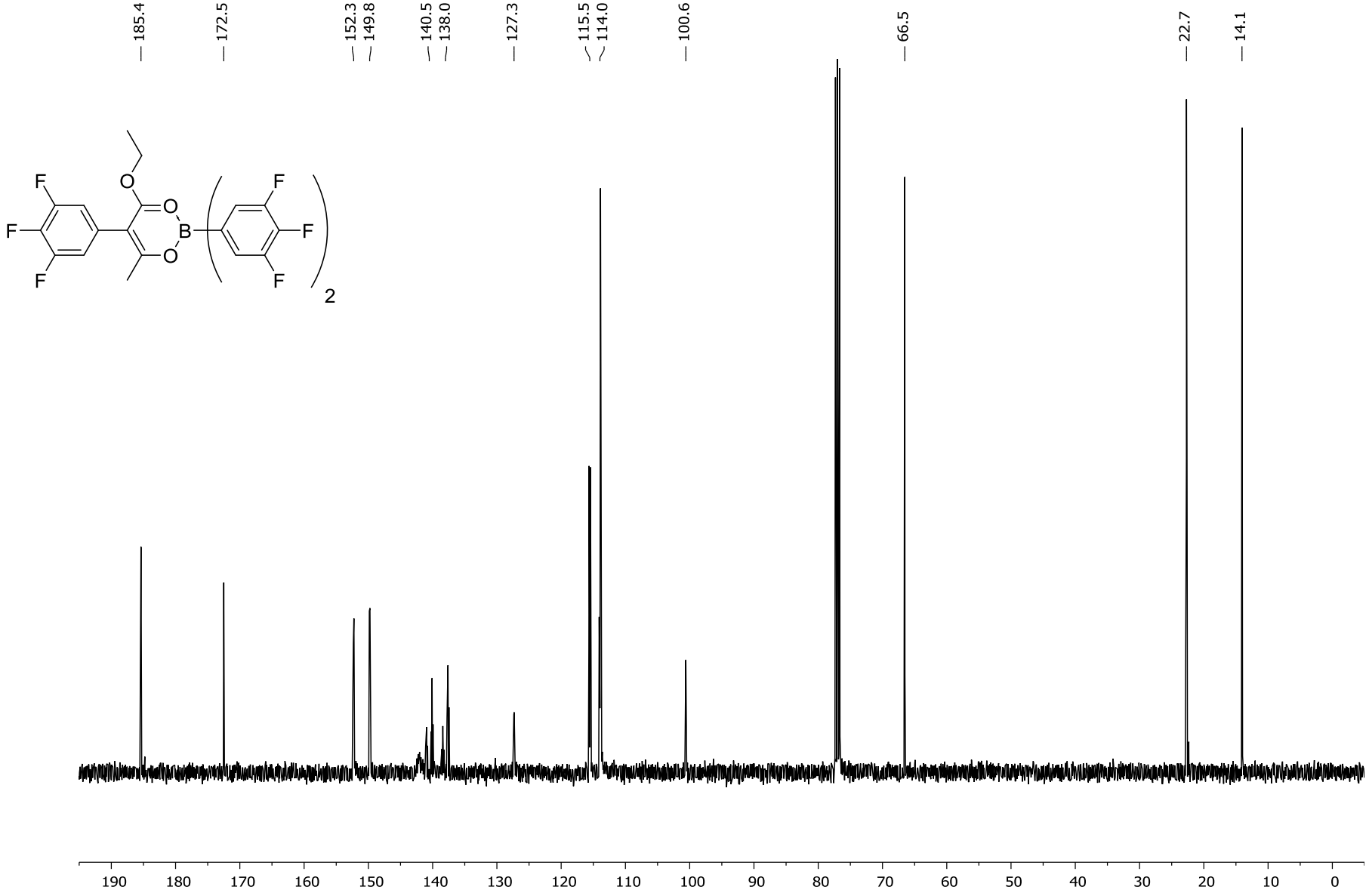


Figure S37 ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) spectrum of **3f**.

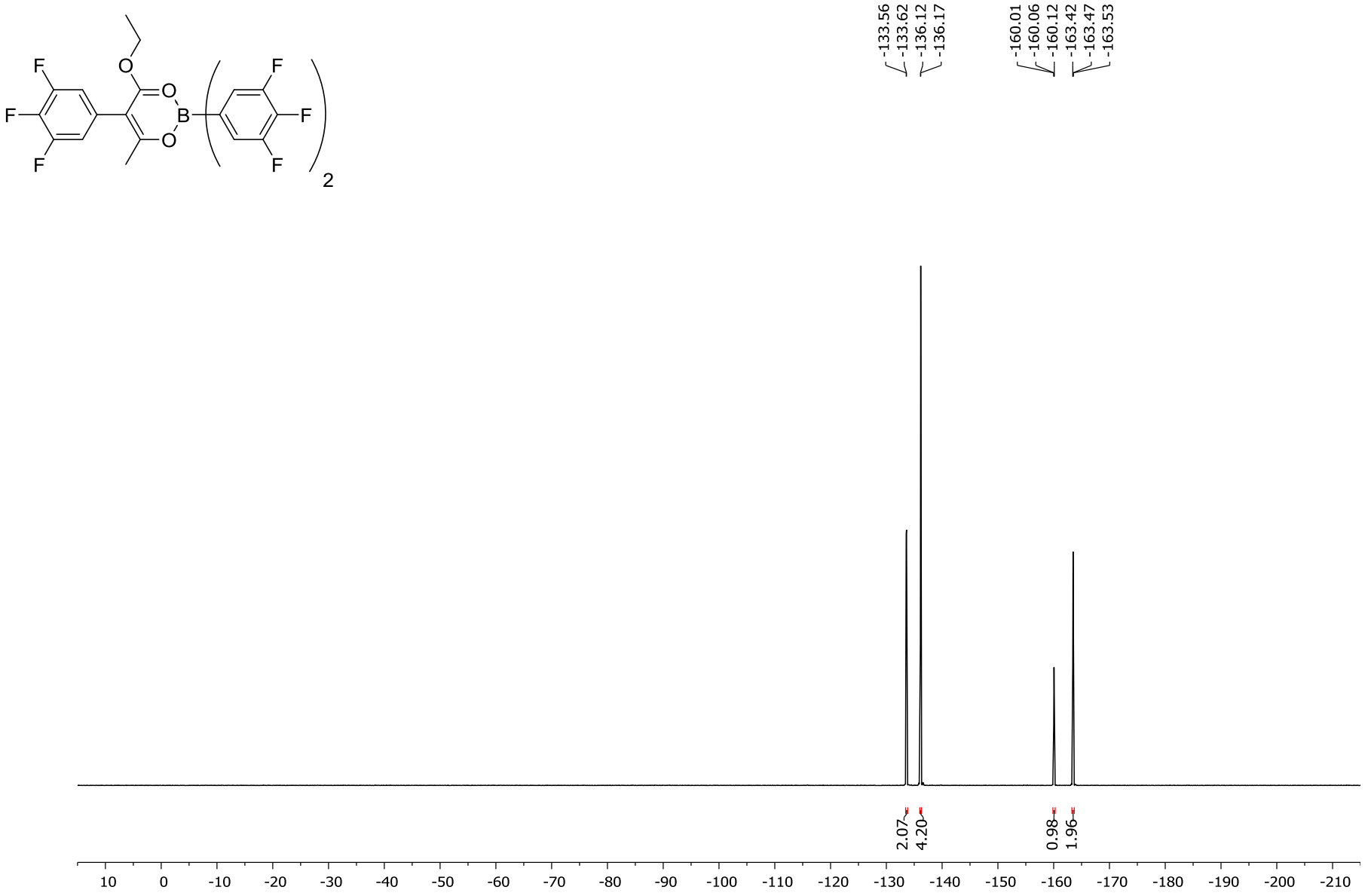


Figure S38 ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of **3f**.

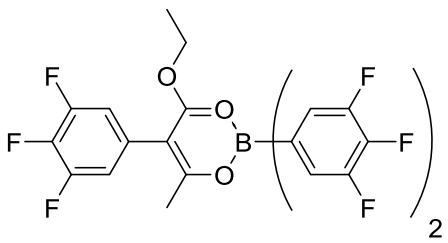


Figure S39 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **3g**.

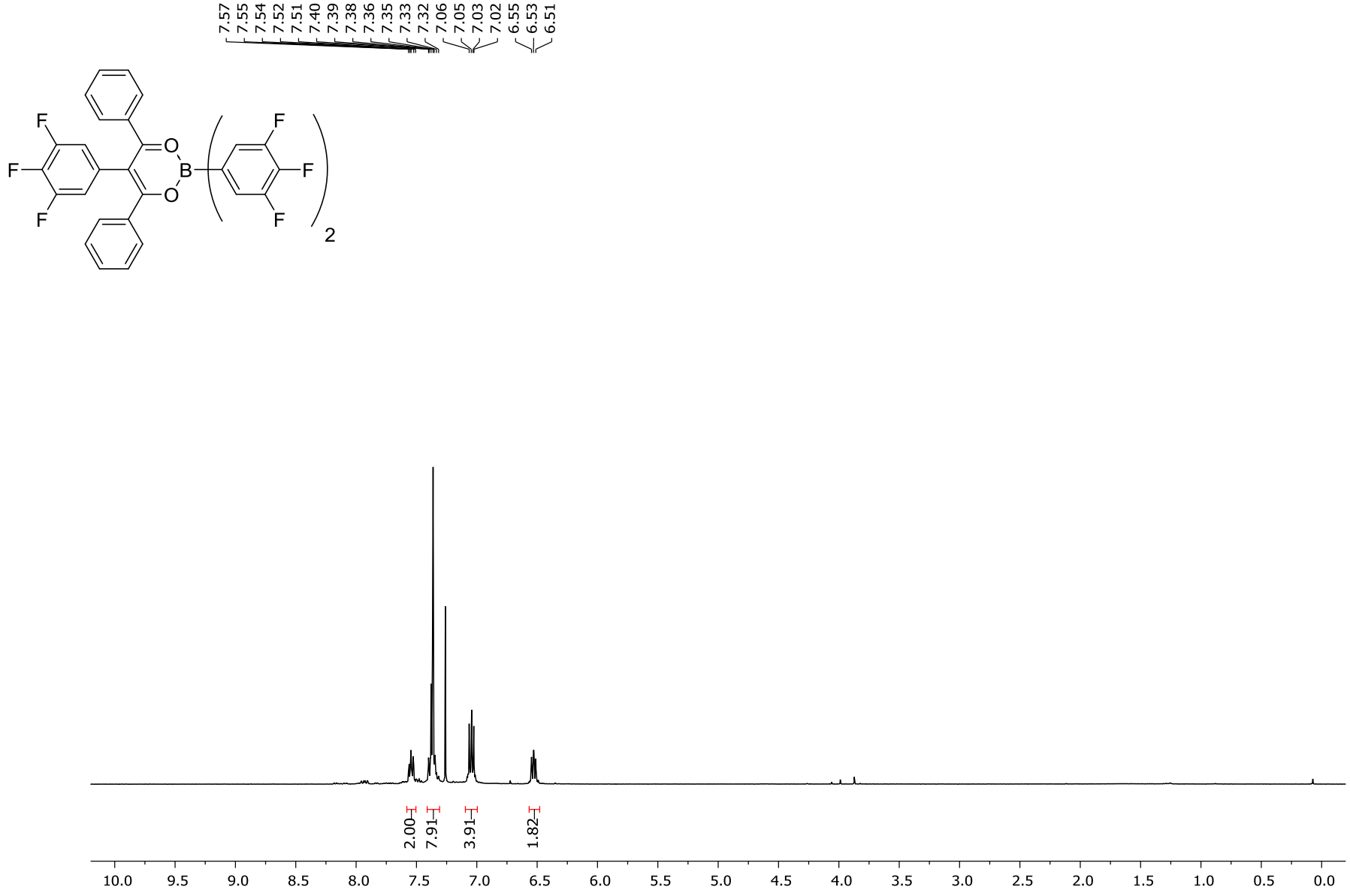


Figure S40 $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **3g**.

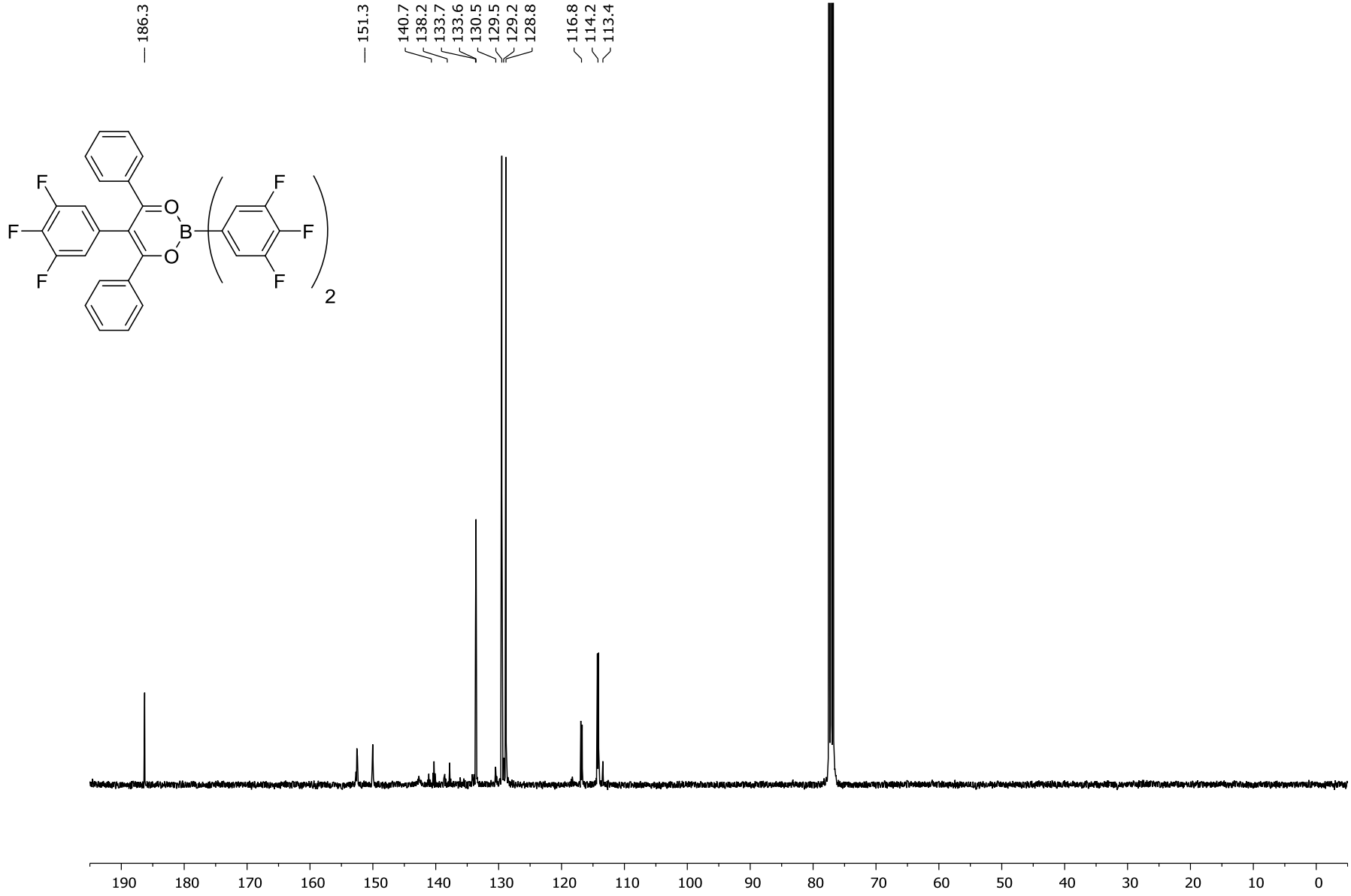


Figure S41 ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) spectrum of **3g**.

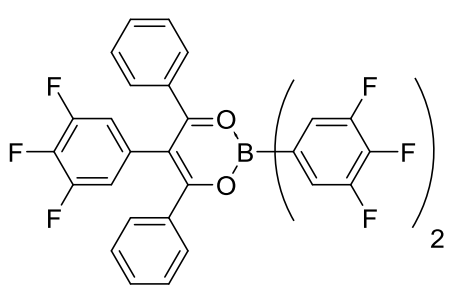


Figure S42 ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of **3g**.

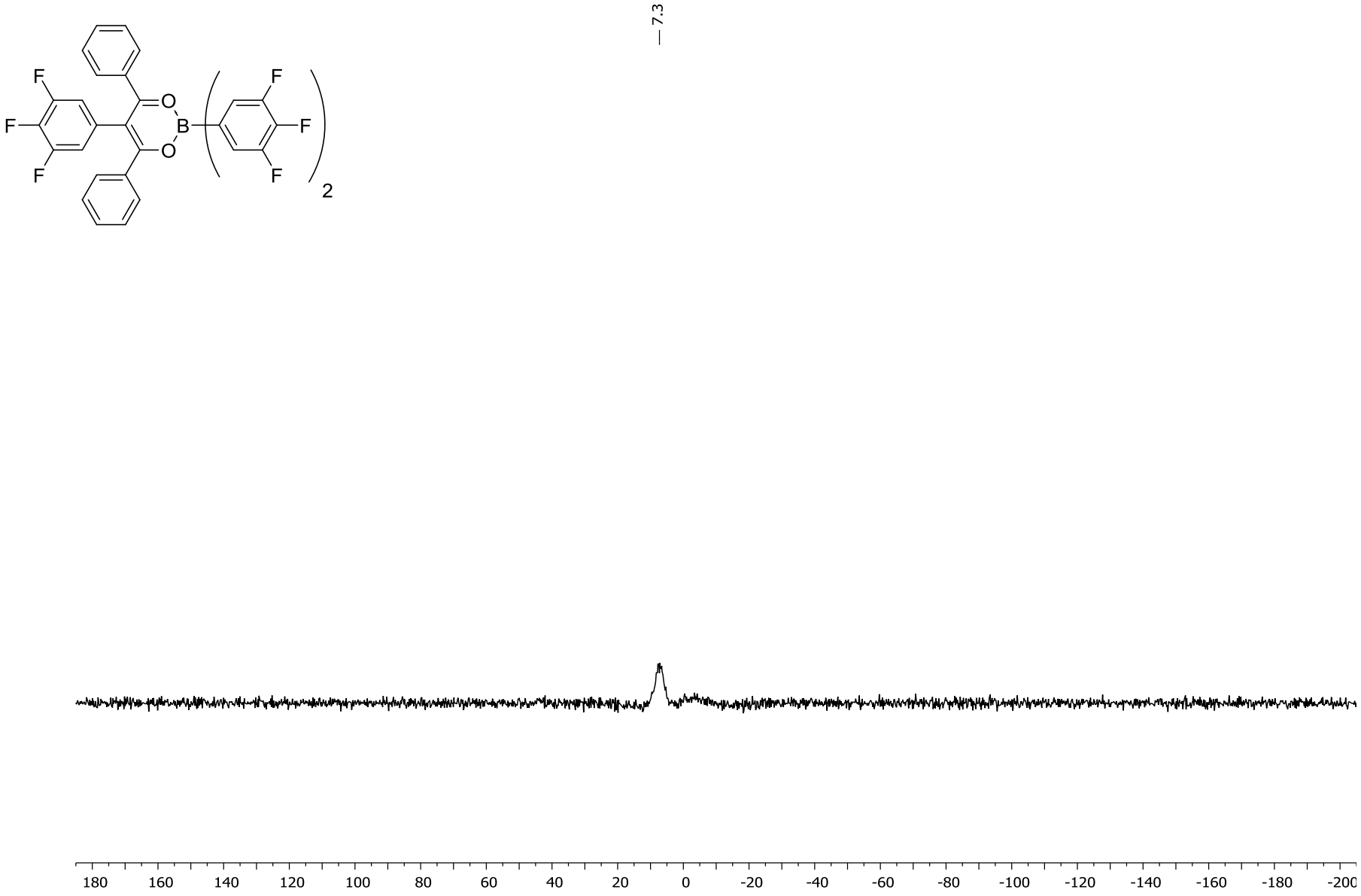


Figure S43 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of **4**.

Figure S44 $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **4**.

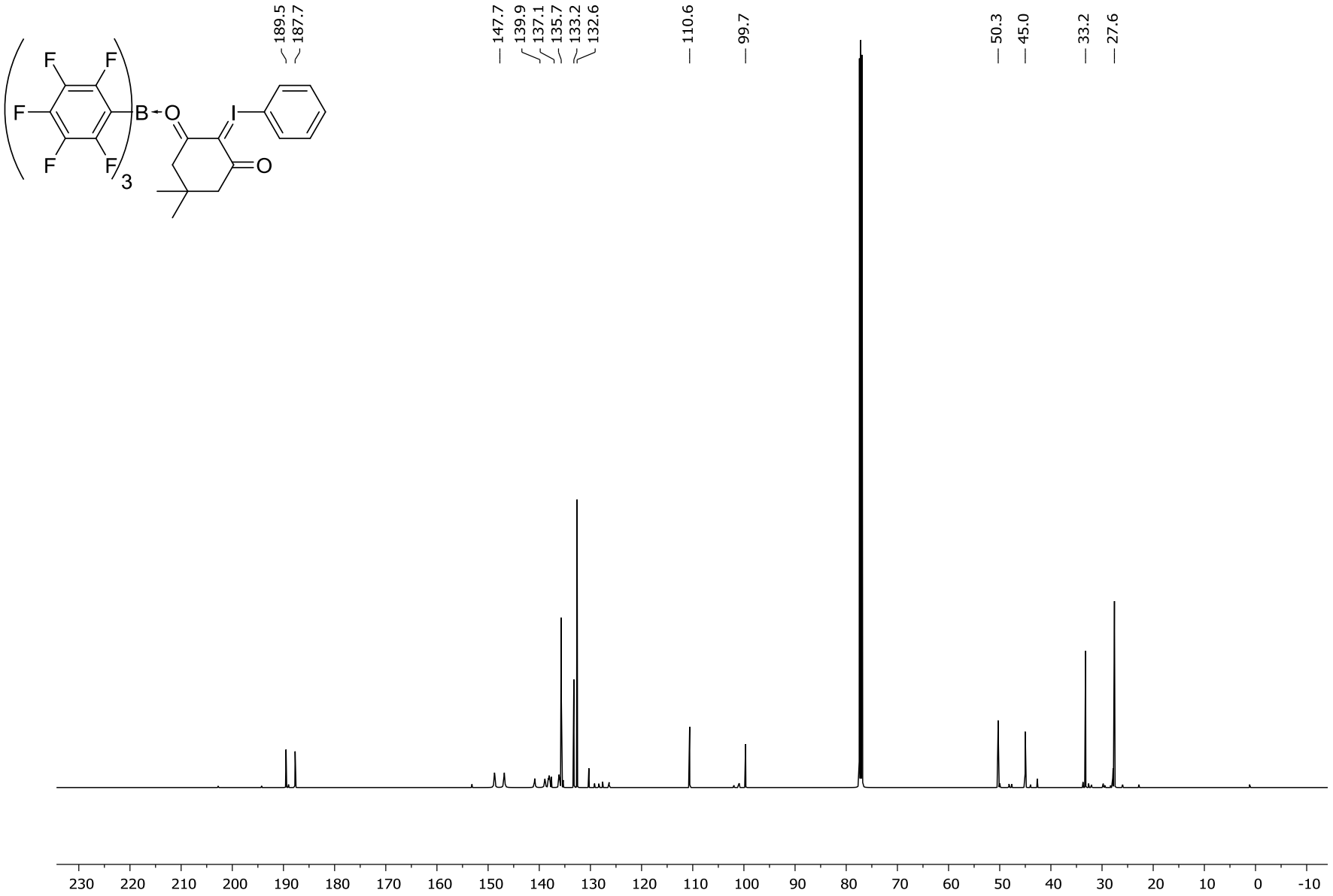


Figure S45 ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) spectrum of **4**.

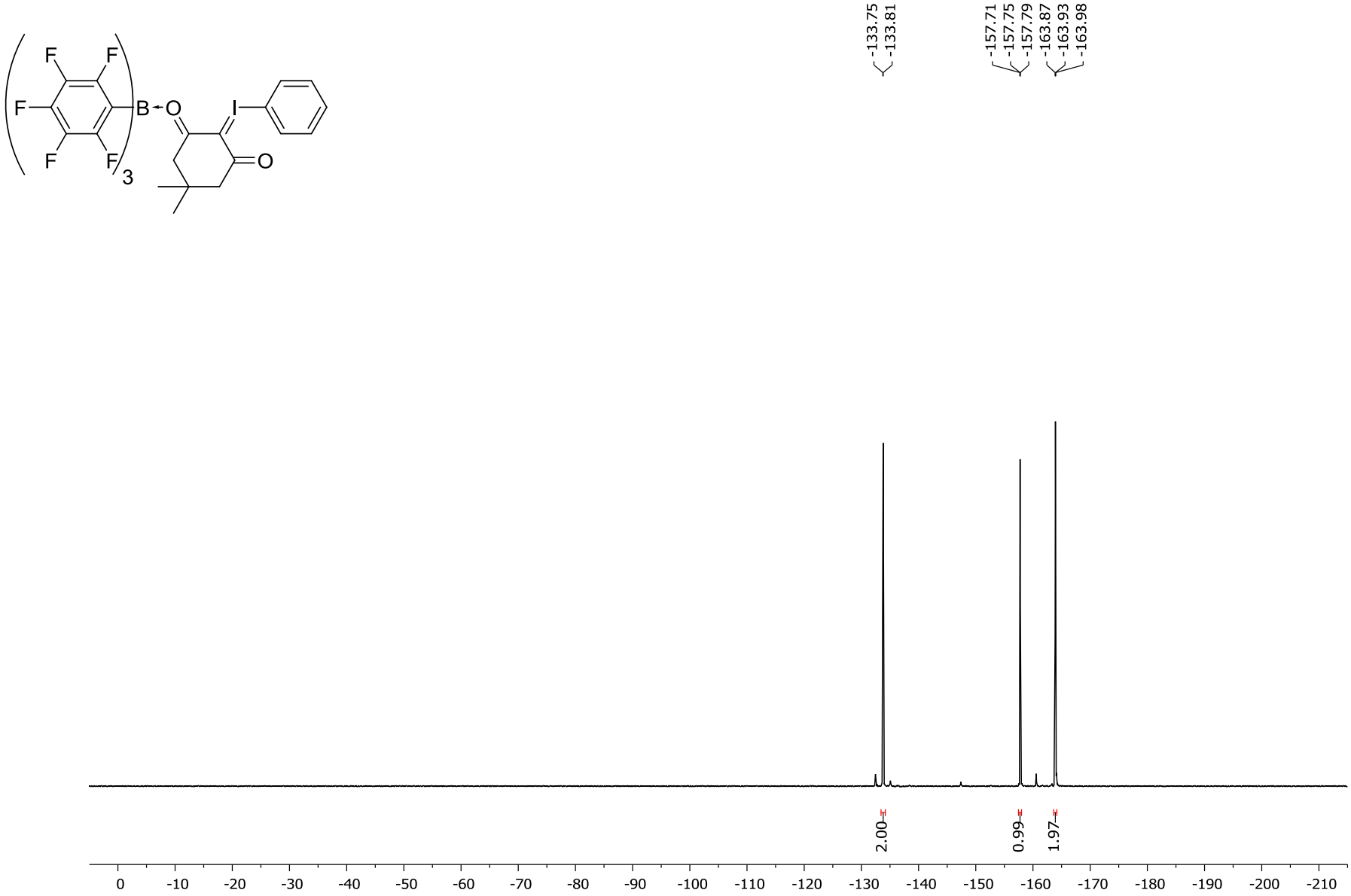
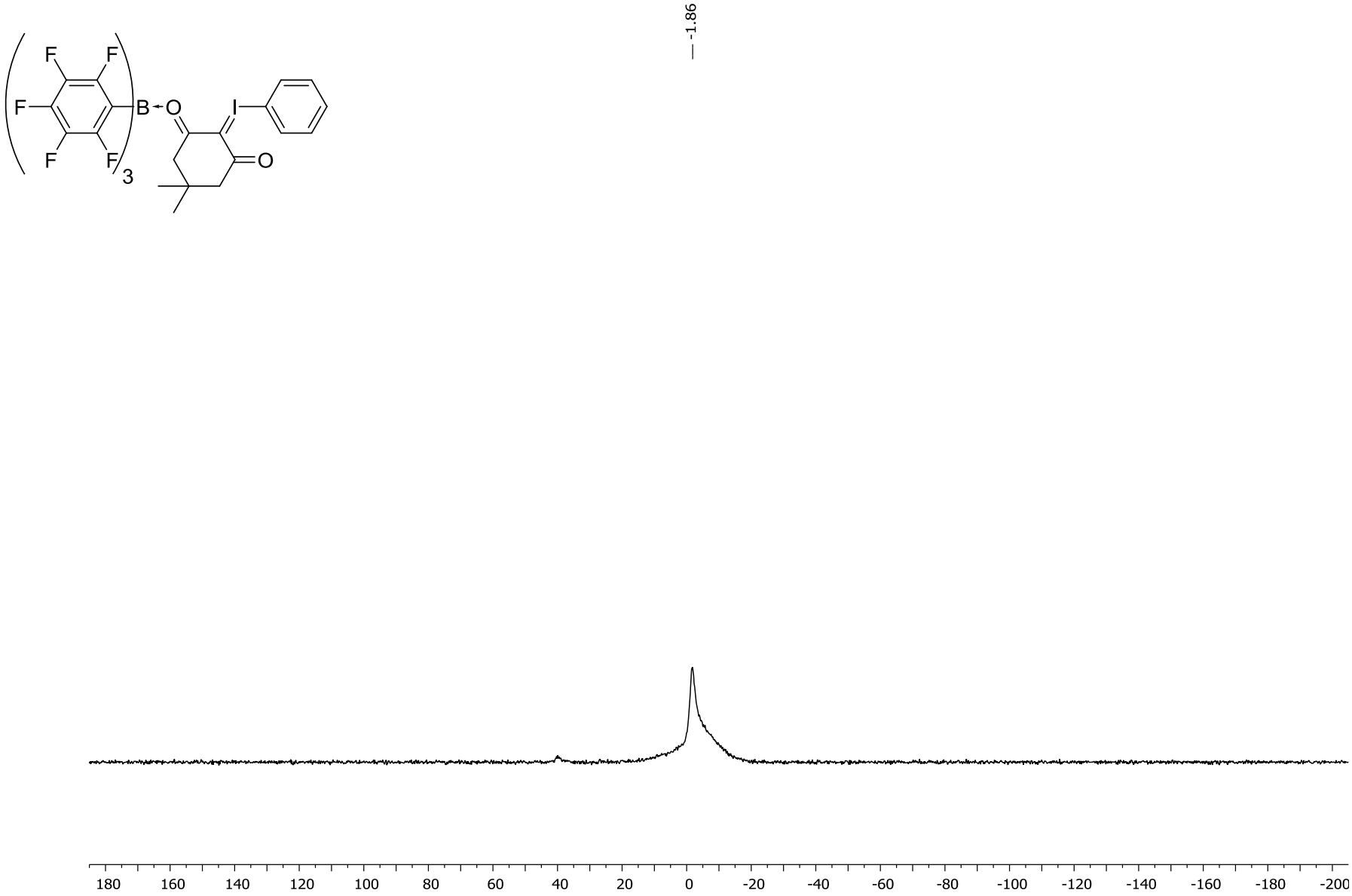


Figure S46 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of **4**.



3 Crystallographic Data

Crystallographic studies were undertaken of a single crystal mounted in paratone and studied on an Agilent SuperNova diffractometer using Mo-Kα radiation and a CCD detector. Measurements were carried out at temperatures ranging between 150(2) K and 293(2) K, and are detailed in Tables S1 and S2. Temperatures were maintained using an Oxford cryostream unless otherwise stated. Data were collected, integrated and corrected for absorption using a numerical absorption correction based on Gaussian integration over a multifaceted crystal model within CrysAlisPro.[6] The structures were solved by direct methods and refined against F^2 within SHELXL-2013.[7] OLEX2 was used for analysis.[8] The structures are deposited with the Cambridge Structural Database (CCDC deposition numbers: 1935886, 1935888, 1935890, 1936166, 1963748). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Compound **3a** contained a severely disordered CH_2Cl_2 molecule located about a symmetry element (1, 1.5, 0). After applying SQUEEZE,[9] R1 and wR2 improved significantly with SQUEEZE reporting 43 e^- per solvent accessible void per unit cell comparable with that computed for a unique CH_2Cl_2 molecule (42 e^-).

Compound **3f** was found to be twinned with the R1 and wR2 values stalling at unacceptably high levels during refinement. The structure of **3f** was finally refined from a HKLF5 file, generated from TWINROTMAT within PLATON[10] and the subsequent refinement as a two-component twin afforded an acceptable R1 value of 6%.

Compound **4** was found to possess disordered lattice solvent. One lattice solvent was clearly identified as a $CHCl_3$ molecule on a general position but with significant rotational disordered about the C-H bond. The second region of electron density was located about a special position (1,1, ½) and again appeared disordered over multiple sites, exacerbated by the symmetry position. Using a value of 1.5 $CHCl_3$ molecules per lattice solvent per asymmetric unit, this leads to 348 electrons per unit cell which is reasonable agreement with the estimate based on SQUEEZE[9] within PLATON[10] (396 electrons). Subsequent refinement proceeded smoothly.

3.1 X-ray refinement data

Table S1 Crystal data and structure refinement for compound **3a** and **3e**.

Compound	**3a**	**3e**
Empirical Formula	$C_{23}H_{12}BF_9O_4 \bullet 0.5(CH_2Cl_2)$*	$C_{23}H_6BF_{15}O_4$
Formula Weight	576.60	642.09
Crystal System	Triclinic	Monoclinic
Space Group	*P-1*	$P2_1/n$
a/Å	7.8542(4)	13.3140(16)
b/Å	10.5570(10)	10.1081(14)
c/Å	15.6690(9)	18.044(3)
α/Å	71.330(5)	90
β/Å	75.721(5)	111.202(16)
γ/Å	84.401(4)	90
V/Å^3	1193.50(12)	2263.9(6)
Z	2	4
T/K	200.0(2)	293(2)
D_C/g.cm^{-3}	1.604	1.884
Crystal size/mm	0.77 × 0.55 × 0.30	0.35 × 0.26 × 0.17
Total data	8874	12879
Unique data	4677	5342
R_{int}	0.019	0.080
$R_1[F^2>2\ \sigma(F^2)]$	0.064	0.070
wR2 (all data)	0.185	0.180
GoF	1.05	1.00
ρ_{min}/ρ_{max}/eÅ^{-3}	-0.96/1.02	-0.34/0.28
CCDC code	1935888	1935890

* The part occupancy CH_2Cl_2 molecule was disordered and latter stages of refinement used a solvent mask.

Table S2 Crystal data and structure refinement for compound **3f**, **3g** and **4**.

Compound	**3f**	**3g**	**4**
Empirical Formula	$C_{24}H_{14}BF_9O_3$	$C_{33}H_{16}BF_9O_2$	$C_{32}H_{15}BF_{15}IO_2$ •1.5 $CHCl_3$*
Formula Weight	532.16	626.27	854.15
Crystal System	Monoclinic	Triclinic	Monoclinic
Space Group	*$P2_1/c$*	*P-1*	*$P2_1/n$*
a/Å	9.0378(8)	9.7170(4)	16.1557(4)
b/Å	17.4814(12)	10.2493(5)	37.6672(11)
c/Å	14.4485(10)	15.4586(9)	16.7091(4)
α/°	90	85.283(4)	90
β/°	96.721(7)	75.672(4)	104.564(3)
γ/°	90	66.7463(4)	90
V/Å^3	2267.1(3)	1367.33(13)	9841.5(5)
Z	4	2	12
T /K	150(2)	200.0(2)	293
D_C/g.cm^{-3}	1.559	1.521	1.729
Crystal size/mm	1.0 x 0.47 x 0.20	0.44 x 0.28 x 0.19	0.33 × 0.13 × 0.10
Total data	5375	6362	22003
Unique data	5375	4319	15239
R_{int}	0.0285	0.021	0.050
$R_1[F^2>2\ \sigma(F^2)]$	0.061	0.047	0.053
wR2 (all data)	0.161	0.158	0.139
GoF	1.03	0.95	1.04
ρ_{min}/ρ_{max}/eÅ^{-3}	-0.26/0.32	-0.21/0.28	-1.31/2.53
CCDC code	1936166	1935886	1963748

* The 1.5 $CHCl_3$ molecules were disordered and latter stages of refinement used a solvent mask.

Figure S47 Solid-state structure of compound **3a**, thermal ellipsoids drawn at the 50% probability level. C: black, O: red, F: green, B: pink. H-atoms omitted for clarity.

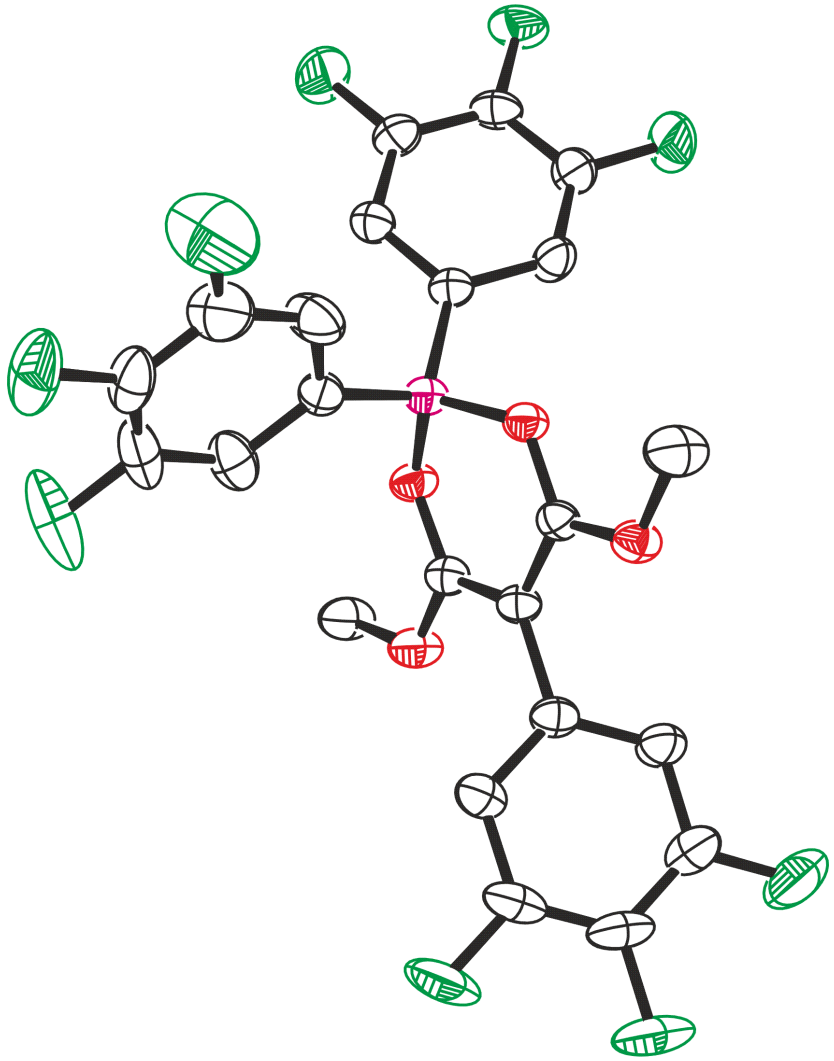


Figure S48 Solid-state structure of compound **3e**, thermal ellipsoids drawn at the 50% probability level. C: black, O: red, F: green, B: pink. H-atoms omitted for clarity.

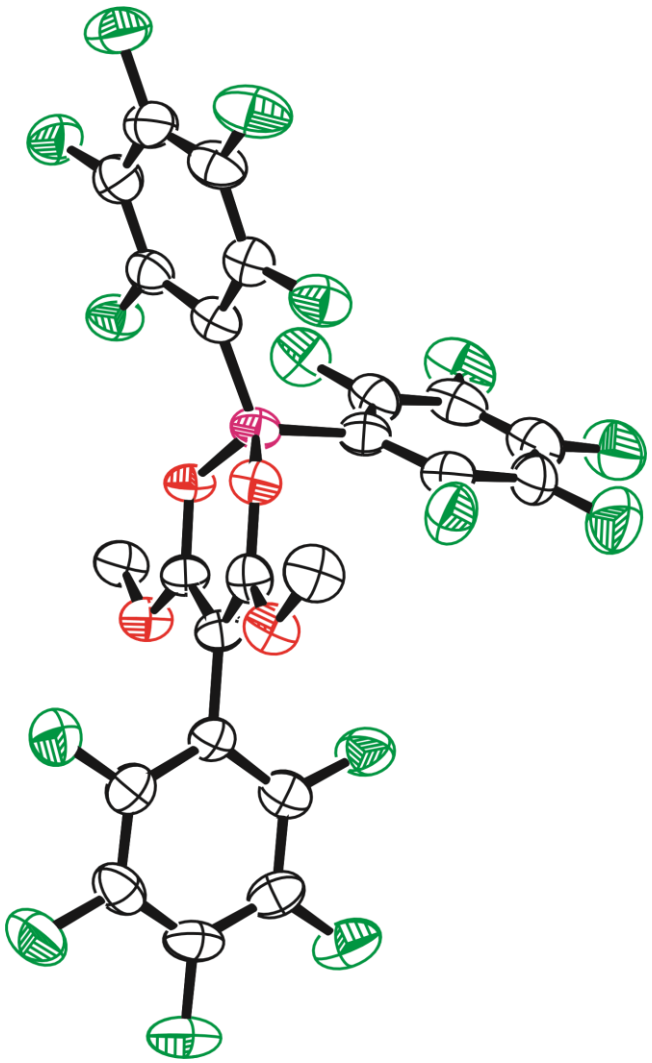


Figure S49 Solid-state structure of compound **3f**, thermal ellipsoids drawn at the 50% probability level. C: black, O: red, F: green, B: pink. H-atoms omitted for clarity.

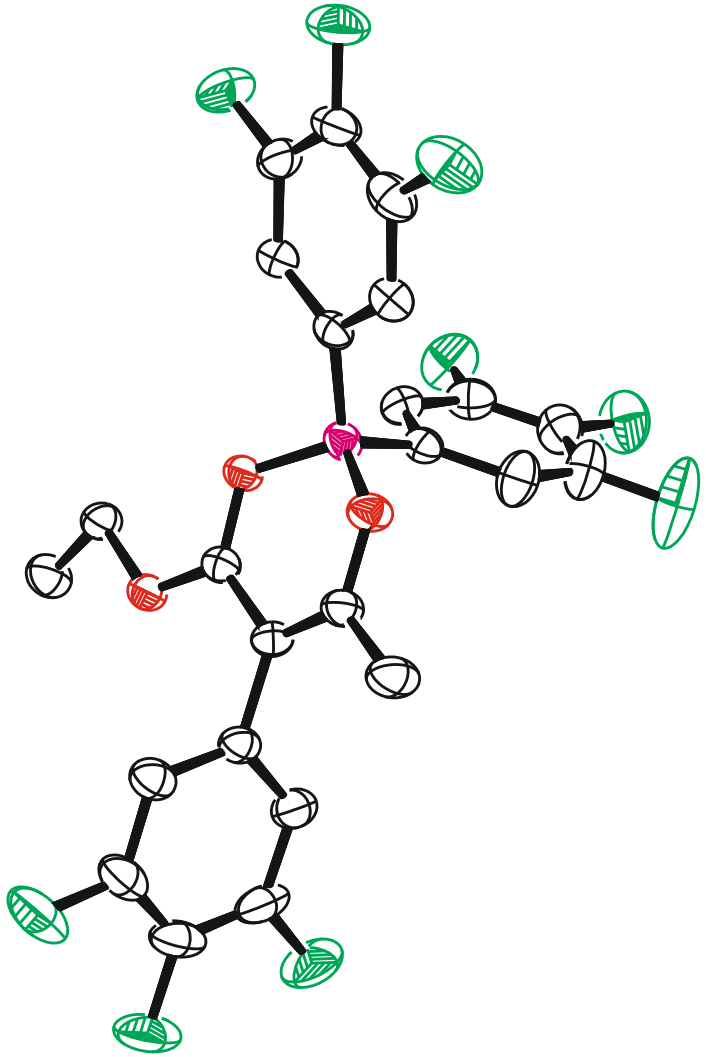


Figure S50 Solid-state structure of compound **3g**, thermal ellipsoids drawn at the 50% probability level. C: black, O: red, F: green, B:pink. H-atoms omitted for clarity.

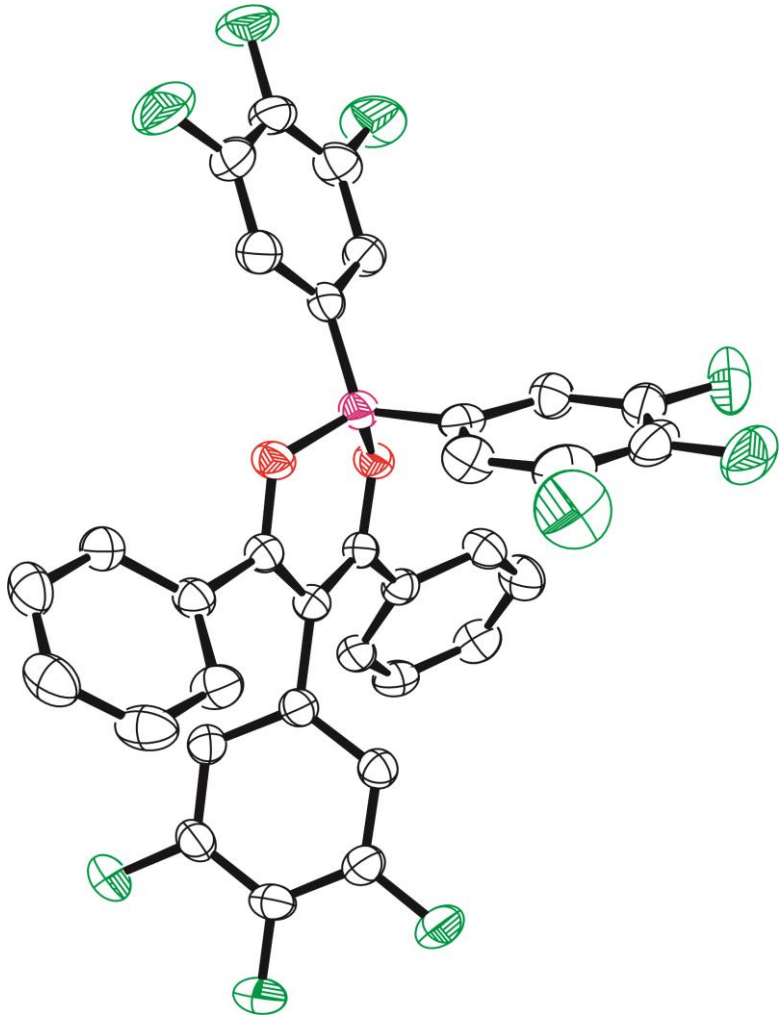
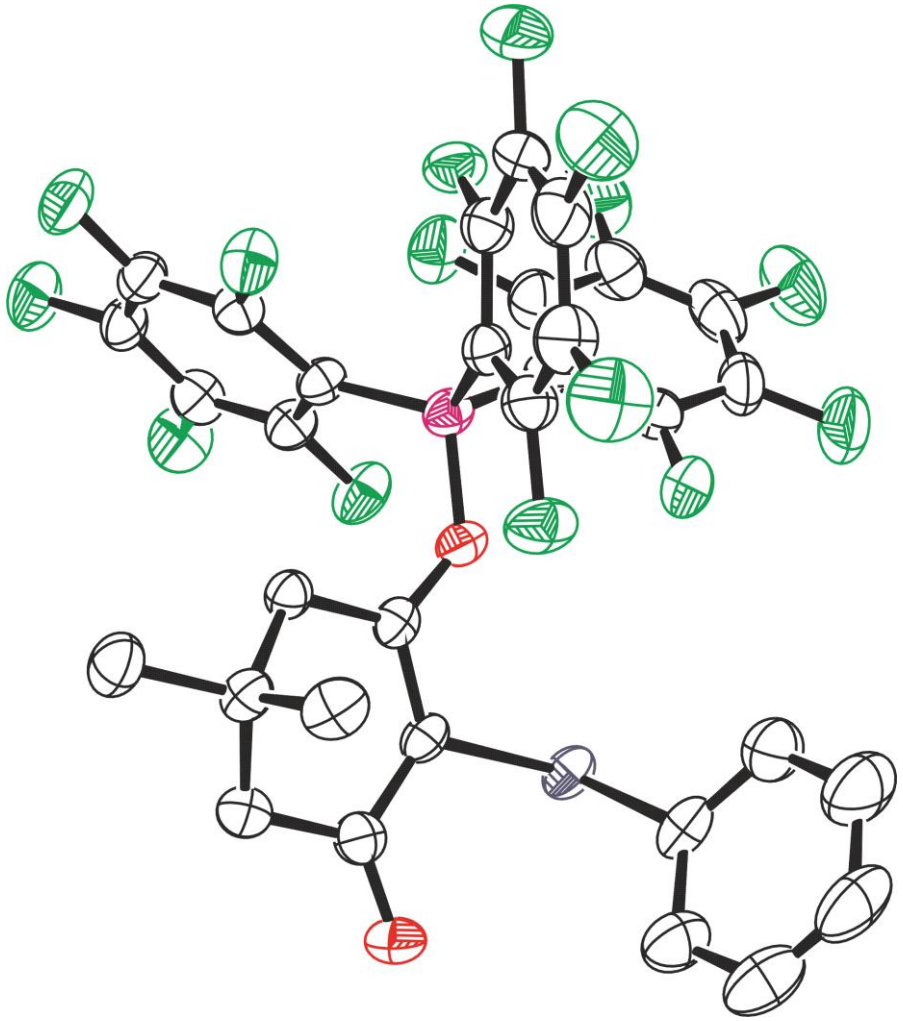


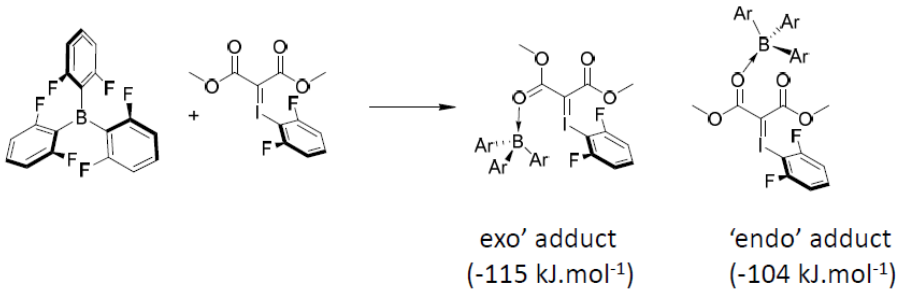
Figure S51 Solid-state structure of compound **4**, thermal ellipsoids drawn at the 50% probability level. C: black, O: red, F: green, B:pink. H-atoms omitted for clarity. The asymmetric unit comprises three molecules of 4 but only one is shown here for clarity.



4 Computational Studies

DFT calculations were undertaken using Jaguar v 9.8.[11] The starting point for the calculations comprised the crystal structure of $B(2,6\text{-}F_2C_6H_3)_3$ taken from the Cambridge Structural Database [CSD code: GIMBEL][12] while the structure of $2,6\text{-}F_2C_6H_3I{=}C(CO_2Me)_2$ was generated from the crystal structure of the closely related derivative, $2\text{-}MeOC_6H_4I{=}C(CO_2Me)_2$ [CSD code: NAXBOF][13] with the MeO and H atoms at the 2' and 6' positions replaced by F. Initial attempts using the M06-2X functional and cc-PVTZ-PP basis set to handle the heavier I atom failed to converge well, in agreement with previous studies.[14] We therefore switched from cc-PVTZ-PP to the LACVP+ basis set which implements an effective core potential for iodine but incorporating the outermost core orbitals explicity and a 6-31G+ basis for lighter atoms.

We optimised the energies of the two starting materials (Scheme S4.1) as well as optimised geometries for two conformations of the 1:1 adducts formed through O→B bond formation. All structures were identified as minima on the potential energy surface with no imaginary frequencies. These revealed adduct formation to be a favourable process in conjunction with previous studies,[15] with the "exo" conformer energetically more favourable than the more sterically crowded conformer by *ca.* 11 kJ.mol^{-1}.



Scheme S4.1. Initial adduct formation between the iodonium ylide and the Lewis acidic BAr_3 [Ar = $2,6\text{-}C_6H_3F_2$].

We then studied migration of the aryl group from the borane to the ylidic carbon through a series of geometry optimisations in which the $C_{Ar}\cdots C{=}I$ distance was steadily decreased. Calculations revealed that migration commencing from the preferred 'exo' adduct proceeded via a lower activation pathway (95 kJ.mol^{-1}) with aryl group migration being energetically favourable (ΔE = –260 kJ.mol^{-1}) and is accompanied by elimination of the aryl iodide, Ar–I. Subsequent ring closure leads to the six-membered cyclic product as the substantially most energetically favourable product from the reaction (overall ΔE = -471 kJ.mol^{-1}). Coordinates for the optimised starting materials and adducts (Scheme S4.1) are presented in Tables T4.1

– T4.4. The optimised geometries after migration and ring closure alongside the transition state for ring closure are presented in Tables 4.5 – 4.7 with transition states exhibiting one imaginary frequency and intermediates/products showing no imaginary frequencies.

Table T4.1: Final atomic coordinates for $B(Ar)_3$

atom	x	y	z
F1	10.3883123355	-0.4222112272	5.7169455903
F2	10.4745171799	3.7878018241	4.2213743693
F3	7.6359016466	0.3771634069	6.0052901978
B4	9.1512063732	1.2478326788	3.6717542201
C5	9.1512265439	-0.3170799269	3.6711012792
C6	9.7484649968	-1.0862305349	4.6745114707
C7	9.7768842059	-2.4695008377	4.7049996304
H8	10.2740374917	-2.9767822430	5.5207393974
C9	9.1499843827	-3.1635882803	3.6687230389
H10	9.1495488384	-4.2464890680	3.6678415348
C11	9.0608961873	2.0307178849	5.0237200873
C12	9.7049419219	3.2513264177	5.2493557677
C13	9.6586028741	3.9676760385	6.4324917711
H14	10.2001360303	4.9003163817	6.5152568832
C15	8.9003799367	3.4518084097	7.4848348119
H16	8.8393521850	3.9925513226	8.4210963767
C17	8.2205426709	2.2418726656	7.3354792240
H18	7.6221137314	1.8150855078	8.1289886896
C19	8.3304176427	1.5771464657	6.1267029994
F20	7.9142550528	-0.4179924180	1.6249532200
F21	7.8241768106	3.7847523187	3.1193360579
F22	10.6695026153	0.3779494715	1.3383552855
C23	8.5533429168	-1.0842856273	2.6664468785
C24	8.5236864007	-2.4674250915	2.6335577993
H25	8.0262096365	-2.9729148665	1.8168790062
C26	9.2417227515	2.0298552612	2.3191114545
C27	8.5952379162	3.2490298481	2.0920464130
C28	8.6401474213	3.9644063546	0.9082163513
H29	8.0967624447	4.8958914194	0.8245094911
C30	9.3993591100	3.4490472094	-0.1436294735
H31	9.4592727883	3.9889453857	-1.0804644114
C32	10.0815002939	2.2405855522	0.0069202328
H33	10.6806670342	1.8142276068	-0.7862743137
C34	9.9729997033	1.5766843976	1.2163556246

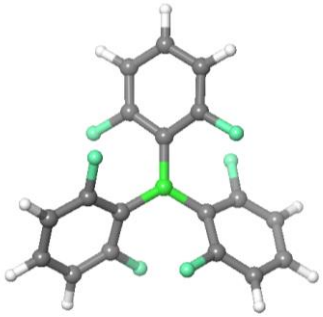


Table T4.2: Final atomic coordinates for ArI=C(COOMe)$_2$

atom	x	y	z
I1	7.6021958613	5.3194094619	7.1086419419
C2	6.6127018869	4.4975556386	5.5021339256
C3	5.2123490273	4.3108137253	5.7369974035
O4	4.5883710522	3.6032853308	4.7574200172
C5	3.1564242651	3.3963563201	4.9274660444
O6	4.5903094443	4.7398579011	6.7306326572
C7	7.4054278718	4.1032908067	4.3823517355
O8	7.0255166636	3.6596506078	3.2948591261
O9	8.7688824822	4.2561455269	4.6445793130
C10	9.6705905904	3.9325174981	3.5543316675
C11	8.7552087185	3.6494453848	7.6831964905
C12	10.1117375096	3.5806714442	7.4001323898
F13	10.7363431436	4.6900972755	6.8617726727
C15	10.8666027426	2.4455809661	7.6513817885
C16	10.2289786854	1.3327931656	8.2049762990
C17	8.8650050198	1.3619250989	8.5018271207
C18	8.1569650041	2.5226757928	8.2296507940
H19	2.8568361624	2.8311585228	4.0491286415
H20	2.6397671024	4.3559746029	4.9762356216
H21	2.9648259256	2.8364215861	5.8440679077
H22	10.6656239029	4.1411859165	3.9410217389
H23	9.4484397931	4.5537126342	2.6850545239
H24	9.5632563657	2.8819886604	3.2790482532
H28	11.9216156730	2.4438246408	7.4111615772
H29	10.8001690735	0.4350262683	8.4053927994
H30	8.3491356655	0.5115145266	8.9275833426
F27	6.8031415480	2.5607494195	8.4979140691

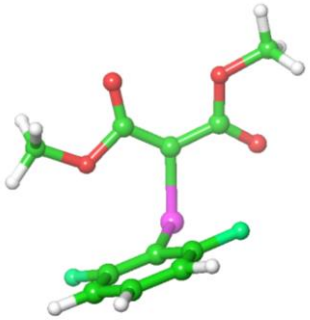


Table T4.3: Final atomic coordinates for "exo" ArI=C(COOMe)$_2$·BAr$_3$

atom	x	y	z
C1	-0.1900712404	0.1272646543	-0.0595519624
I2	-0.7685824709	1.7810115292	-1.1475391900
C3	-0.0354251360	3.3460627299	0.0712992979
C4	1.1905386088	-0.0057402669	0.0492981383
C5	-1.1982043475	-0.6588579204	0.6039951829
O6	-1.0095573377	-1.6145481186	1.3566531410
O7	-2.4737834353	-0.2234420912	0.3000404035
O8	1.6608680591	-1.1045846668	0.6291598853
O9	1.9643172081	0.9493670417	-0.3870350869
C10	2.9834909448	-1.1334913120	1.2649724955
C11	0.5777810852	3.2137834695	1.3086105922
C12	1.1393464050	4.3015935603	1.9607879312
C13	1.0713737235	5.5606602812	1.3672297764
C14	0.4402559092	5.7343771058	0.1324892700
C15	-0.0889220760	4.6156886405	-0.4807885631
F16	0.6088644429	1.9894251341	1.9388336260
F17	-0.7153986020	4.7288179036	-1.7201933470
B18	3.2006901595	0.9158968258	-1.3830195911
C19	-3.5670779837	-0.9412155304	0.9389307786
C20	4.5461426342	1.3448507620	-0.5903650953
C21	3.1746809615	-0.5758572086	-2.0345488063
C22	2.8744649614	2.1287303531	-2.4280523632
C23	2.6789344902	3.4228547853	-1.9402489820
C24	2.4044721794	4.5479650050	-2.7024278593
C25	2.3190917467	4.3960976199	-4.0876204431
C26	2.5290816384	3.1409476973	-4.6557031521
C27	2.8042920692	2.0661023182	-3.8188870783
C28	5.7412423853	1.4242457060	-1.3043100807
C29	6.9576073230	1.8553278125	-0.8070413674
C30	7.0066787168	2.2657749263	0.5277975847
C31	5.8490463725	2.2365066585	1.3040863384
C32	4.1484762030	-1.5649522235	-1.9214730441
C33	4.0625223455	-2.8443722361	-2.4561976210
C34	2.9125194525	-3.1959663447	-3.1591570031
C35	1.8803634410	-2.2664176646	-3.3063567503
C36	2.0553035897	-1.0171880781	-2.7426564676
H37	3.0950597218	-2.1673156722	1.5786096457
H38	3.7665308346	-0.8565845950	0.5616953282
H39	2.9754082643	-0.4553006270	2.1174461337
H40	1.6293411502	4.1369110499	2.9113468752
H41	1.5127557691	6.4133787706	1.8672775208
H42	0.3631208203	6.7000774326	-0.3498979315
H43	-4.4704956854	-0.4586414639	0.5753706220
H44	-3.5394534386	-1.9936581890	0.6539903065
H45	-3.4850664080	-0.8575712333	2.0234879936
F48	2.7821608512	3.6240222521	-0.5561289484
H47	2.2772845201	5.5088951023	-2.2194642547
H48	2.1041574814	5.2507652695	-4.7173288475
H49	2.4920787832	2.9814014178	-5.7255980970
F52	3.0323180656	0.8504466899	-4.4595322122
F53	5.6942119249	1.0331436025	-2.6451483108
H52	7.8297836342	1.8654140481	-1.4475926312
H53	7.9400468314	2.6094971054	0.9567085456
F58	5.3060047303	-1.2956876339	-1.1829397988
H55	4.8820692452	-3.5362508800	-2.3111577219
H56	2.8163047061	-4.1868256134	-3.5854821427
H57	0.9688248821	-2.4958814838	-3.8424371687
F62	0.9919203555	-0.1063668190	-2.9002488737
C63	4.6688887914	1.7878565971	0.7221749983
F60	3.5410407791	1.7984664935	1.5557035854
H61	5.8439888491	2.5576687510	2.3379990460

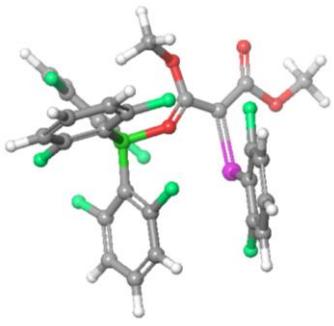


Table T4.4: Final atomic coordinates for 'endo' ArI=C(COOMe)$_2$·BAr$_3$

atom	x	y	z
C1	0.5144468353	2.5830943125	-1.0965026665
I2	-0.9599904089	3.3699878372	0.1556323998
C3	-0.6882558269	2.0040464896	1.7192119951
C4	1.7946233308	2.5375355408	-0.5475790202
C5	0.0913508001	2.2643309969	-2.4325699976
O6	0.7515655658	1.7039451055	-3.3029503171
O7	-1.1995534438	2.7014495651	-2.6698772146
O8	1.9211107956	3.1059473427	0.6795165179
O9	2.8533252454	2.0290686770	-1.0306119569
C10	3.2148375342	2.9601385789	1.3530535756
C11	0.0076429575	2.3472459329	2.8698925556
C12	0.2753404477	1.4276522839	3.8707124032
C13	-0.1828529276	0.1177784377	3.7101736663
C14	-0.8925047001	-0.2608828094	2.5697389337
C15	-1.1191888580	0.6907877557	1.5883499095
F16	0.4198447928	3.6551524850	3.0310731739
F17	-1.7972758141	0.3345582723	0.4409814686
B18	3.3197612296	0.8000041196	-1.8965985770
C19	-1.7432257404	2.4033168219	-3.9881110384
C20	4.6658424316	0.3537511763	-1.0853265189
C21	2.1345293361	-0.3052984636	-1.8173085700
C22	3.7332020467	1.3581075382	-3.3503949196
C23	3.4729203075	2.6223831431	-3.8688475462
C24	3.8976243093	3.0726708467	-5.1122052899
C25	4.6421277260	2.2105294137	-5.9166822003
C26	4.9464477279	0.9258998519	-5.4608607266
C27	4.4870161534	0.5606399481	-4.2075412059
C28	4.9951626094	-0.9276657444	-0.6486181468
C29	6.1551241494	-1.2688023694	0.0356062391
C30	7.0806543411	-0.2659598835	0.3193072493
C31	6.8280786074	1.0437563898	-0.0934069126
C32	1.5499719781	-0.6600067488	-0.6043431424
C33	0.5804613452	-1.6313970222	-0.4166247119
C34	0.1137823960	-2.3139440574	-1.5400545932
C35	0.6278769269	-1.9993627561	-2.7971482973
C36	1.6067068488	-1.0192668506	-2.8932664127
H37	3.0805726081	3.4777776794	2.2996358202
H38	3.4266892323	1.8990272312	1.4940585827
H39	3.9965135150	3.4180095224	0.7468977014
H40	0.8257407231	1.7406624780	4.7480956745
H41	0.0158468898	-0.6149384661	4.4821210789
H42	-1.2630592487	-1.2679344450	2.4310919976
H43	-2.7470438994	2.8201680881	-3.9805979876
H44	-1.1256804921	2.8694905922	-4.7564446433
H45	-1.7647633890	1.3239456452	-4.1434572332
F48	2.7353438580	3.5471851465	-3.1147171573
H47	3.6444406939	4.0767568449	-5.4280004728
H48	4.9837373211	2.5367423942	-6.8916331696
H49	5.5160785952	0.2216765046	-6.0531784002
F52	4.7944309672	-0.7297300034	-3.7622737151
F53	4.1179495836	-1.9822001935	-0.9082411521
H52	6.3165951869	-2.2994825706	0.3243753181
H53	7.9957140022	-0.5033214977	0.8483141681
F58	1.9774584157	0.0181863709	0.5639080450
H55	0.2227916610	-1.8539559972	0.5797144549
H56	-0.6420309169	-3.0831484240	-1.4362385767
H57	0.2912612112	-2.4988390974	-3.6965606807
F62	2.0649156489	-0.7512804120	-4.1756040466
C63	5.6473289732	1.2974650927	-0.7758082218
F60	5.4456862975	2.6218746666	-1.1855922499
H61	7.5261599250	1.8506677245	0.0900529802

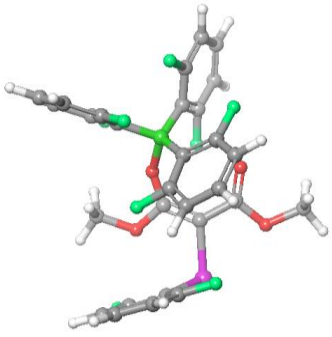


Table T4.5: Final atomic coordinates for the transition state for Ar migration commencing from the endo adduct.

atom	x	y	z
C1	0.8735699587	2.4331450375	-1.4089721401
I2	-0.8482573876	2.4110812249	-0.2026126194
C3	-1.4078107073	4.4479892648	0.0786803533
C4	1.9843157543	3.0331473653	-0.7707926177
C5	0.5773837070	2.6425057825	-2.8318655323
O6	1.3384116249	3.1916488795	-3.6221734934
O7	-0.6242349573	2.1169928610	-3.1965656364
O8	1.8208296658	3.8359378313	0.2878734268
O9	3.1695219376	2.6906609684	-1.1093288783
C10	3.0190433712	4.1024770722	1.1022710599
C11	-1.4370564943	5.3421220539	-0.9802046052
C12	-1.7157907336	6.6890899864	-0.8118715386
C13	-1.9802603517	7.1550124440	0.4780796627
C14	-1.9636931648	6.2854618251	1.5717002313
C15	-1.6719251179	4.9504440500	1.3425216866
F16	-1.1667011825	4.8612232663	-2.2499521208
F17	-1.6513900309	4.0669075528	2.4113933309
B18	3.3381719771	1.3174580569	-1.8721491175
C19	-0.9539877035	2.2066455937	-4.6144052171
C20	4.5708594186	0.5704853774	-1.1148832608
C21	1.8591682868	0.5885037588	-1.5984324937
C22	3.8038602865	1.5892613458	-3.3892068784
C23	4.1157022273	2.8191010639	-3.9649528886
C24	4.6036072319	2.9801282776	-5.2558827484
C25	4.8166246418	1.8479703048	-6.0414511196
C26	4.5502969713	0.5798595214	-5.5197984619
C27	4.0682718670	0.5070728034	-4.2247832889
C28	4.6647438897	-0.7716237636	-0.7472351310
C29	5.7743270693	-1.3626471594	-0.1558162051
C30	6.8984535519	-0.5776535122	0.0931074853
C31	6.8915380479	0.7698171302	-0.2698988794
C32	1.5934501061	0.1040933647	-0.2995884944
C33	0.6260259281	-0.7999797296	0.0638905167
C34	-0.1127813696	-1.4188382093	-0.9627454978
C35	0.1670016995	-1.0943670517	-2.2872609971

Atom	x	y	z
C36	1.1511317348	-0.1524950562	-2.5542176412
H37	2.6636090915	4.7437444235	1.9033112793
H38	3.4053221485	3.1558337032	1.4816354775
H39	3.7700278495	4.5953522207	0.4863460635
H40	-1.7188661454	7.3435451948	-1.6735375065
H41	-2.2017469324	8.2034148783	0.6325389403
H42	-2.1682478852	6.6228814693	2.5792816248
H43	-1.9244575180	1.7264565677	-4.7065955226
H44	-0.9996749678	3.2549220563	-4.9139731016
H45	-0.1923266430	1.6826544230	-5.1925560044
F48	3.9509212695	3.9876745498	-3.2282727832
H47	4.8076836936	3.9784400728	-5.6210957200
H48	5.1959341638	1.9512545766	-7.0510393198
H49	4.7116037061	-0.3267193423	-6.0884665116
F52	3.8332174010	-0.7671051505	-3.6951654151
F53	3.5873472732	-1.6276119336	-0.9830218504
H52	5.7427759792	-2.4163152982	0.0899720814
H53	7.7767826792	-1.0137228997	0.5533022257
F58	2.2518327540	0.7902508376	0.7425006944
H55	0.4745873017	-1.0418472260	1.1089328685
H56	-0.8672715880	-2.1577001610	-0.7236583321
H57	-0.3573041275	-1.5572552708	-3.1137586533
F62	1.3236656887	0.1840360150	-3.9019805704
C63	5.7470203171	1.2819199769	-0.8612057611
F60	5.8014237915	2.6211270315	-1.2555234374
H61	7.7486938955	1.4133295957	-0.1187443570

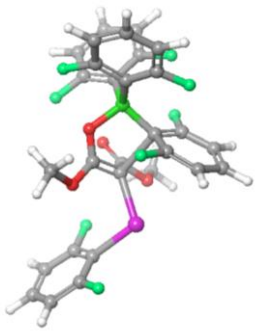


Table T4.6: Final atomic coordinates for intermediate after ArI elimination

atom	x	y	z
C1	1.9258760000	1.9132970000	-2.9061760000
C4	2.9068810000	2.5951650000	-2.2620600000
C5	1.1237900000	2.5408930000	-3.9532200000
O6	1.2971870000	3.6461500000	-4.4736990000
O7	0.0863590000	1.7294170000	-4.3224740000
O8	3.1239620000	3.9012380000	-2.4148180000
O9	3.7092360000	1.9915840000	-1.3227600000
C10	4.3004240000	4.5251550000	-1.8189470000
B18	4.4536770000	0.8251380000	-1.4390320000
C19	-0.8391990000	2.2675250000	-5.3037620000
C20	5.0072900000	0.2245870000	-0.1109530000
C21	1.5762580000	0.5503440000	-2.4607240000
C22	4.7523490000	0.1957560000	-2.8383960000
C23	5.0148870000	0.9426610000	-3.9841020000
C24	5.2695400000	0.4102550000	-5.2349790000
C25	5.2614760000	-0.9793930000	-5.3649280000
C26	5.0123400000	-1.7954050000	-4.2580560000
C27	4.7734900000	-1.1837900000	-3.0411280000
C28	4.3009440000	0.2365920000	1.0933070000
C29	4.7679790000	-0.3038310000	2.2815090000
C30	6.0301010000	-0.8989840000	2.2862430000
C31	6.7905360000	-0.9538430000	1.1158150000
C32	1.0901250000	0.2983120000	-1.1798270000
C33	0.7481490000	-0.9634760000	-0.7170140000
C34	0.8736720000	-2.0442130000	-1.5913690000
C35	1.3362120000	-1.8504360000	-2.8967150000
C36	1.6743190000	-0.5666090000	-3.2859180000
H37	4.2123300000	5.5707850000	-2.1001200000
H38	4.2769680000	4.4077540000	-0.7354780000
H39	5.2062500000	4.0879420000	-2.2395670000
H43	-1.5760830000	1.4828600000	-5.4534300000
H44	-1.3061240000	3.1737170000	-4.9128650000
H45	-0.3132380000	2.4996050000	-6.2312440000
F48	5.0581850000	2.3306720000	-3.8445190000
H47	5.4584620000	1.0680130000	-6.0728700000
H48	5.4458240000	-1.4287970000	-6.3329630000
H49	4.9986120000	-2.8749580000	-4.3313210000
F52	4.5046160000	-1.9973060000	-1.9421030000
F53	3.0286340000	0.7820630000	1.1000080000
H52	4.1501940000	-0.2578020000	3.1685690000
H53	6.4208740000	-1.3259800000	3.2018010000
F58	0.9224580000	1.3836970000	-0.3353240000
H55	0.3923480000	-1.0797360000	0.2985360000
H56	0.6159420000	-3.0412490000	-1.2559710000
H57	1.4502900000	-2.6710150000	-3.5933390000
F62	2.1840280000	-0.3683450000	-4.5626740000
C63	6.2534110000	-0.4013380000	-0.0332660000
F60	7.0256670000	-0.4596060000	-1.1899800000
H61	7.7703400000	-1.4114280000	1.0852840000

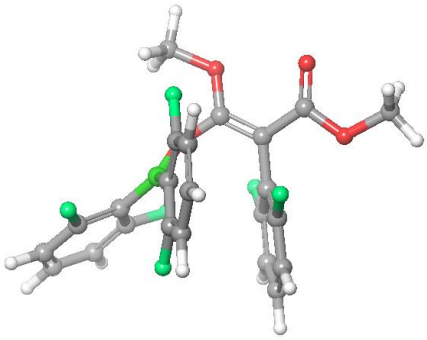
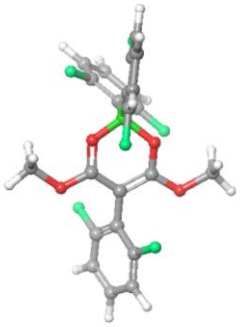


Table T4.7: Final atomic coordinates after ring closure

atom	x	y	z
C1	1.7871389818	1.1543703239	-2.2153007467
C4	2.2889035403	0.7919174500	-0.9624128216
C5	2.7406993635	1.4593009573	-3.1929675199
O6	4.0216817573	1.2917983217	-3.0386535036
O7	2.3321206536	1.9736209999	-4.3484360402
O8	1.4473963700	0.5678252881	0.0335237744
O9	3.5671652674	0.6842324611	-0.7045934004
C10	1.9837253733	0.1559178259	1.3342044130
B18	4.5933151869	0.5042153066	-1.8216377053
C19	3.3300993438	2.2315763932	-5.3903500970
C20	5.9203929183	1.2632420210	-1.3668335273
C21	0.3497432082	1.2652087410	-2.4868204859
C22	4.6677115000	-1.0307632942	-2.3004703580
C23	5.5244455264	-1.3746059299	-3.3456434096
C24	5.6727481694	-2.6411522604	-3.8806598199
C25	4.8922039822	-3.6706224166	-3.3469326065
C26	3.9959542332	-3.4026962745	-2.3137215103
C27	3.9134854947	-2.1016788123	-1.8351021541
C28	5.8696547844	2.6381146240	-1.1387049684
C29	6.9430692128	3.4264875062	-0.7596789947
C30	8.1800134345	2.8020626916	-0.5802699153
C31	8.3042252364	1.4264314424	-0.7734269730
C32	-0.5040484000	2.0816882402	-1.7481873153
C33	-1.8654406616	2.1874882695	-1.9835643604
C34	-2.4178048646	1.4479793772	-3.0309071805
C35	-1.6103019460	0.6225551850	-3.8167117002
C36	-0.2598787433	0.5543196072	-3.5199847285
H37	1.1010214565	0.0063776692	1.9485095956
H38	2.5532684999	-0.7641343793	1.2122193308
H39	2.6150719193	0.9492920241	1.7330215574
H43	2.7459513158	2.5677484272	-6.2416348737
H44	4.0215115857	3.0013368322	-5.0491972277
H45	3.8740364886	1.3142852501	-5.6139113235
F48	6.2962891898	-0.3479985214	-3.8918600131
H47	6.3778807622	-2.8096555272	-4.6838670618
H48	4.9803373490	-4.6760772117	-3.7395700929
H49	3.3662784508	-4.1710013106	-1.8845846949
F52	2.9768115520	-1.8843638018	-0.8112089613
F53	4.6351364449	3.2759542975	-1.2989337027
H52	6.8066886572	4.4895110788	-0.6098182250
H53	9.0428009984	3.3867910614	-0.2857080243
F58	0.0513805993	2.8494917586	-0.7363605151
H55	-2.4644577106	2.8428137519	-1.3652919906
H56	-3.4785226019	1.5167751309	-3.2373657772
H57	-2.0091766983	0.0376404083	-4.6348272850
F62	0.5440953782	-0.2790074137	-4.2867934275
C63	7.1775094818	0.7096561850	-1.1530551962
F60	7.3390264355	-0.6660422213	-1.3125304443
H61	9.2446208439	0.9091034533	-0.6359623246



5 References

[1] S. R. Goudreau, D. Marcoux and A. B. Charette, *J. Org. Chem.*, 2009, **74**, 470 – 473.
[2] H. Huang, Y. Yang, X. Zhang, W. Zeng and Y. Liang, *Tetrahedron Lett.*, 2013, **54**, 6049 – 6052.
[3] J. Cardinale and J. Ermert, *Tetrahedron Lett.*, 2013, **54**, 2067 – 2069.
[4] Y. Soltani, L. C. Wilkins and R. L. Melen, *Angew. Chem. Int. Ed.*, 2017, **56**, 11995 – 11999.
[5] Q. Yin, Y. Soltani, R. L. Melen and M. Oestreich, *Organometallics*, 2017, **36**, 2381 – 2384.
[6] CrysAlisPro, Agilent Technologies, Version 1.171.37.33 (release 27-03-2014 CrysAlis171.NET).
[7] SHELXL-2013, G.M. Sheldrick, University of Göttingen, Germany (2013).
[8] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339 – 341.
[9] SQUEEZE: A. L. Spek, *Acta Cryst.*, 2015, **C71**, 9-18.
[10] PLATON: A. L. Spek, *Acta Cryst.*, 2009, **D65**, 148-155.
[11] A. D. Bochevarov, E. Harder, T. F. Hughes, J. R. Greenwood, D. A. Braden, D. M. Philipp, D. Rinaldo, M. D. Halls, J. Zhang and R. A. Friesner, *Int. J. Quantum Chem.*, 2013, **113**, 2110 – 2142.
[12] L. Greb, C. G. Daniliuc, K. Bergander and J. Paradies, *Angew. Chem. Int. Ed.*, 2013, **52**, 5876 – 5879.
[13] C. Zhu, A. Yoshimura, L. Ji, Y. Wei, V. N. Nemykin and V. V. Zhdankin, *Org. Lett.*, 2012, **14**, 3170 – 3173.
[14] A. Varadwaj, P. R. Varadwaj, H. M. Marques and K. Yamashita, *PCCP*, 2018, **20**, 15316 – 15329; A. Bauza´, D. Quinonero, P. M. Deya and A. Frontera, *J. Phys. Chem. A*, 2013, **117**, 2651 – 2655.
[15] A. Bähr, L. C. Wilkins, K. Ollegott, B. M. Kariuki and R. L. Melen, *Molecules*, 2015, **20(3)**, 4530 – 4547.