Supporting Information

Visible Light-Induced Borylation of C–O, C–N, and C–X Bonds

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Materials and experimental details

Materials: Anhydrous acetonitrile was distilled from ground 3Å molecular sieves under the atmosphere of nitrogen and collected fresh before use. Compounds **PTH4**,[1] **S1-S18**,[2] **S26-S29**[3] were prepared according to the previously reported procedures. The potassium salt of **PTH1** was prepared by reacting **PTH1** with potassium hexamethyldisilazide. All other chemicals were used as commercially available.

Experimental equipment: Glovebox work was carried out in a nitrogen-filled LC Technology Solutions LCPW-220 glovebox. Photoinduced reactions were carried out in a test-tube rack placed on a stirplate and flanked with two 36W LED lights (λ_{max} = 400 nm, 420 nm, or 450 nm) thermostated with continuous air flow supply at 22 °C (default

method, unless otherwise specified), or without the air flow supply at 35−40 °C, allowing to carry out up to eight parallel reactions at the same time. Carrying out reactions without the air flow supply allowed to improve the yields by ~ 20%. The same improvement can also be achieved by carrying out the reaction with added water (1 equiv.)

Purification: Column chromatography was performed using CombiFlash Rf-200 (Teledyne-Isco) automated flash chromatography system, as well as manually. Thin layer chromatography was carried out on silica gel-coated glass plates (Merck Kieselgel 60 F254). Plates were visualized under ultraviolet light (254 nm) and using a potassium permanganate stain.

Characterization: ^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR spectra were recorded at 500 MHz (^{1}H), 125 MHz (^{13}C), 202 MHz (^{31}P), 470.5 MHz (^{19}F), and 160.4 MHz (^{11}B) on Bruker AVANCE III 500 instruments in $CDCl_3$ or other specified deuterated solvents with and without tetramethylsilane (TMS) as an internal standard at 25 °C, unless specified otherwise. Chemical shifts (δ) are reported in parts per million (ppm) from tetramethylsilane (^{1}H and ^{13}C), $BF_3{\cdot}OEt_2$ (^{11}B), and $CFCl_3$ (^{19}F). Coupling constants (*J*) are in Hz. Proton multiplicity is assigned using the following abbreviations: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint.), septet (sept.), multiplet (m), broad (br).

Infrared measurements were carried out neat on a Bruker Vector 22 FT-IR spectrometer fitted with a Specac diamond attenuated total reflectance (ATR) module. The UV/Vis absorption spectra were obtained on a Shimadzu UV-2600 spectrophotometer.

General Procedures

General procedure for the visible light-mediated photocatalytic C–O, C–N and C–X borylation (GP1)

An oven-dried 8 mL reaction tube was charged with a magnetic stir bar, substrate (0.2 mmol), B_2pin_2 (0.24−1.0 mmol, 1.2−5.0 equiv.), **PTH1** (0.2−12 mol%), Cs_2CO_3 (0.24−1.0 mmol, 1.2−5.0 equiv.) and CH_3CN (1.5−4.5 mL). The reaction mixture was purged with

argon via a needle extended to the mixture surface for 5 seconds. The tube was sealed with a plastic cap and then irradiated with an LED light of the appropriate wavelength (400 nm, 420 nm, or 450 nm) for 16–72 h. Water (4 mL) was added, and the reaction mixture was extracted with ethyl acetate (3 × 8 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated. The resulting crude mixture can be purified by flash column chromatography on silica gel (6–15 minutes per column) to give the corresponding boronate ester or by GP2–GP5 to give boronic acids, organotrifluoroborates and diborylarenes.

General procedure for the isolation as organotrifluoroborates with potassium fluoride and tartaric acid (GP2)

To the reaction mixture was added methanol (2 mL) and then acetonitrile (2 mL), followed by a solution of potassium fluoride (0.8 mmol, 4 equiv.) in water (0.4 mL), and the mixture was stirred for 5 minutes at room temperature. A solution of L-(+)-tartaric (0.41 mmol, 2.05 equiv.) in THF (5 mL) was added dropwise to the stirring mixture over 5 minutes, resulting in formation of a white precipitate. The reaction mixture was stirred for 15 minutes, diluted with acetonitrile (5 mL) and then filtered. The flask and the filtered solids were rinsed with acetonitrile (3 × 15 mL) and the combined filtrate was concentrated. The mixture was dried azeotropically with acetonitrile (4 × 3 mL) and washed with diethyl ether (2 × 10 mL). The solid residue was dried in vacuum, acetone (50 mL) was added and the mixture was sonicated for 5 minutes and warmed up to effect dissolution if necessary. The acetone solution was passed through a Celite® pad, and the filtrate was concentrated under reduced pressure. The product was recrystallized from an acetone/diethyl ether mixture to afford the desired potassium organotrifluoroborate. For basic nitrogen group-containing substrates, the substrate was dissolved in CH_3CN (10 mL) and stirred with K_2CO_3 (10 equiv.) for 2 h then passed through a Celite® pad, and

the filtrate was concentrated under reduced pressure to afford the desired potassium organotrifluoroborate.

General procedure for the isolation as organotrifluoroborates with potassium hydrogen difluoride (GP3)

The mixture was purified by a rapid column chromatography (6–15 min) to eliminate B_2pin_2 then methanol (5 mL) and 4.5M solution of potassium hydrogen difluoride (0.8 mmol, 4.0 equiv.) were added. The mixture was stirred for 20 minutes and the volatile components were removed under reduced pressure. The mixture was dried azeotropically with acetonitrile (4 × 3 mL) and washed with pentane (2 × 10 mL). The solid residue was dried in vacuum, acetone (50 mL) was added and the mixture was sonicated for 5 minutes and gently warmed up if necessary to effect dissolution. The acetone solution was passed through a Celite® pad, and the filtrate was concentrated under reduced pressure. The product was crystallized from an acetone/diethyl ether mixture to afford the desired potassium organotrifluoroborate. For basic nitrogen group-containing substrates, the substrate was dissolved in CH_3CN (10 mL) and stirred with K_2CO_3 (10 equiv.) for 2 h then passed through a Celite® pad, and the filtrate was concentrated under reduced pressure to afford the desired potassium organotrifluoroborate.

General procedure for the isolation as boronic acids/organotrifluoroborates with methylboronic acid (GP4)

To the mixture was added acetone (5 mL), 0.2M aqueous solution of hydrochloric acid (5 mL) and methylboronic acid (2 mmol, 10 equiv.). The reaction mixture was stirred overnight then concentrated under reduced pressure and dried azeotropically with acetonitrile (5 × 5 mL) and then with a 1 : 1 v/v acetonitrile/methanol mixture (5 × 6 mL) in heated water bath (40–45 °C). The resulting mixture was converted to

organotrifluoroborate according to GP3 or as a boronic acid, as in this procedure. Thus, the resulting solid was dissolved in a mixture of 1M aqueous solution of fructose (5 mL) and 1M aqueous solution of sodium carbonate (5 mL). Ethyl acetate (15 mL) was added, and the organic portion was separated and discarded. The aqueous phase was acidified to pH 2 using 2M aqueous solution of hydrochloric acid, then extracted with ethyl acetate (4 × 10 mL). The combined organic portions as dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure to yield the desired boronic acid.

General procedure for the isolation of diborylarenes with Kugelrohr distillation (GP5)

The flask with the crude material was placed onto a rotary evaporator (IKA RV10) with a vertically aligned vapor tube. The material was then heated at 140–165 ^{0}C for 1.5–2 h under reduced pressure (vacuum pressure: 1.5 torr, KNF UN842.3FTP vacuum pump) by means of an electrothermal vacuum oven (Chem-Dry, Laboratory Devices, Inc.). The volatile by-products and the unreacted starting material (typically, ArBpin, pinacolone, B_2pin_2) condensed in the distillation trap adapter. The desired bisdioxaborolane remained in the distillation flask and can be further purified by recrystallization.

General procedure for the visible light-mediated photocatalytic C–N borylation with in situ quaternization of arylamines (GP6)

An oven-dried 8 mL reaction tube was charged with a magnetic stir bar, aryl amine (0.2 mmol), Cs_2CO_3 (0–0.8 mmol, 0–4 equiv.), methyl trifluoromethanesulfonate (0.24–1.28 mmol, 1.2–6.4 equiv.) and CH_3CN (1.5–3 mL). The mixture was stirred for 20 minutes at room temperature before adding B_2pin_2 (0.6–1.2 mmol, 3–6 equiv.), Cs_2CO_3 (0.5–1.0 mmol, 2.5–5.0 equiv.), **PTH1** (5–10 mol%) and CH_3CN (0.5–2 mL). The reaction mixture was

purged with argon via a needle extended to the mixture surface for 5 seconds. The tube was sealed with a plastic cap and then irradiated with an LED light of the appropriate wavelength (400 nm, 420 nm, or 450 nm) for 16–36 h. Water (4 mL) was added, and the reaction mixture was extracted with ethyl acetate (3 × 8 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated. The resulting crude mixture can be purified by flash column chromatography on silica gel (6–15 minutes per column) to give the corresponding boronate ester or by GP2–GP5 to give boronic acids, organotrifluoroborates and diborylarenes.

General procedure for the synthesis of diethyl aryl phosphates (GP7)

According to literature procedure[4], a substituted phenol (3.1 mmol) was dissolved in carbon tetrachloride or THF (8–20 mL) and this was cooled to 0 °C, triethylamine (0.55 mL, 3.85 mmol) and diethyl phosphite or diethyl chlorophosphate (0.48 mL, 3.85 mmol) were added. After warming the solution to room temperature a white precipitate formed and this was left to stir at this temperature overnight. Water was added followed by dichloromethane and the organic phase was washed with HCl (1 M), saturated sodium chloride solution, dried over sodium sulphate and the solvent was removed under reduced pressure. The crude mixture can be purified by flash column chromatography on silica gel to give the corresponding product.

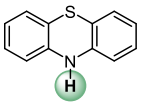
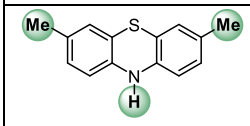
Mechanistic studies

Excited state reduction potentials of phenothiazines

Singlet excited state reduction potentials of phenothiazines **PTH1**, **PTH2**, and **PTH4** were calculated by the equation $E_{ox}(\mathbf{PTH}^{\bullet+}/{}^1\mathbf{PTH}^*) = E(\mathbf{PTH}^{\bullet+}/\mathbf{PTH}) - E_{0\text{-}0}({}^1\mathbf{PTH}^*)$.[5] Reduction potentials $E_{1/2}(\mathbf{PTH}^{\bullet+}/\mathbf{PTH})$ for phenothiazines **PTH1**, **PTH2**, and **PTH4** were determined by cyclic voltammetry. The singlet excited state energies of the phenothiazines $E_{0\text{-}0}({}^1\mathbf{PTH}^*)$ were determined from the intersection of the normalized emission and excitation spectra

(Figure S1).[5] For **PTH3**, the singlet excited state reduction potential (−2.51 V) was previously reported.[6]

Table S1. Ground and excited state reduction potentials and singlet excited state energies of phenothiazines **PTH1**, **PTH2**, and **PTH4**.[a]

Phenothiazine	$E_{1/2}$(**PTH**$^{\bullet+}$/**PTH**), V	$E_{0\text{-}0}$ (^{1}**PTH***), eV	E_{ox}(**PTH**$^{\bullet+}$/**PTH***), V
 PTH1	0.60	3.20	−2.60
 PTH2	0.70	3.28	−2.58
 PTH4	0.48	3.17	−2.71

[a] Reduction potentials are reported for solutions in acetonitrile vs. SCE.

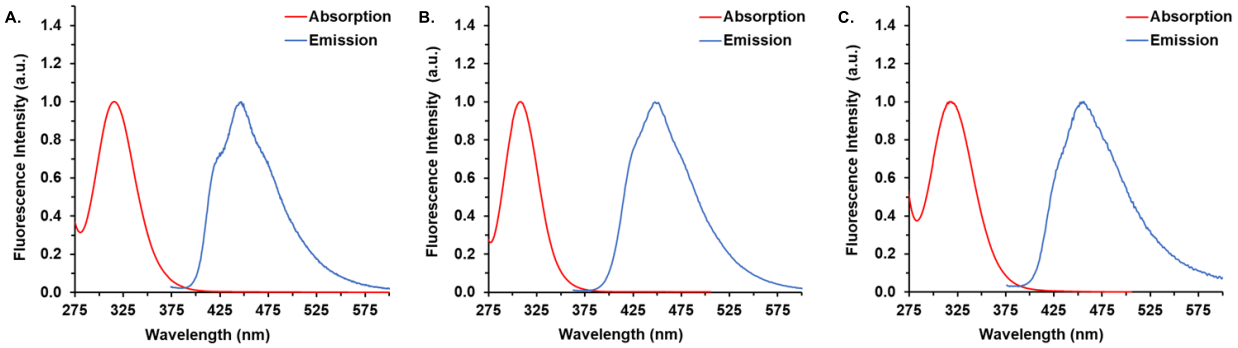


Figure S1. Normalized emission and excitation spectra. **A. PTH1**. **B. PTH2**. C. **PTH4**.

Cyclic voltammetry studies

Cyclic voltammetry (CV) measurements were performed on a CHI 650D potentiostat using a three-electrode cell with a glassy-carbon working electrode, a Ag|AgCl (1M KCl) reference electrode and a platinum counter electrode. CV was conducted at a scan rate of 50 mV s^{-1} in anhydrous degassed acetonitrile with tetrabutylammonium hexafluorophosphate as an electrolyte. Inflection-point potentials (E_{red}) were used to

characterize irreversible redox processes, since they were shown to provide the best approximation of standard electrochemical potentials for irreversible redox systems.[7] The half-wave potential for the Fc^+/Fc redox couple was measured to ensure consistency, and a value of $E_{1/2}$ = 0.39 V vs. Ag|AgCl was recorded. All measured potentials vs. Ag|AgCl were converted to the potentials vs. SCE by subtracting 0.02 V.[8]

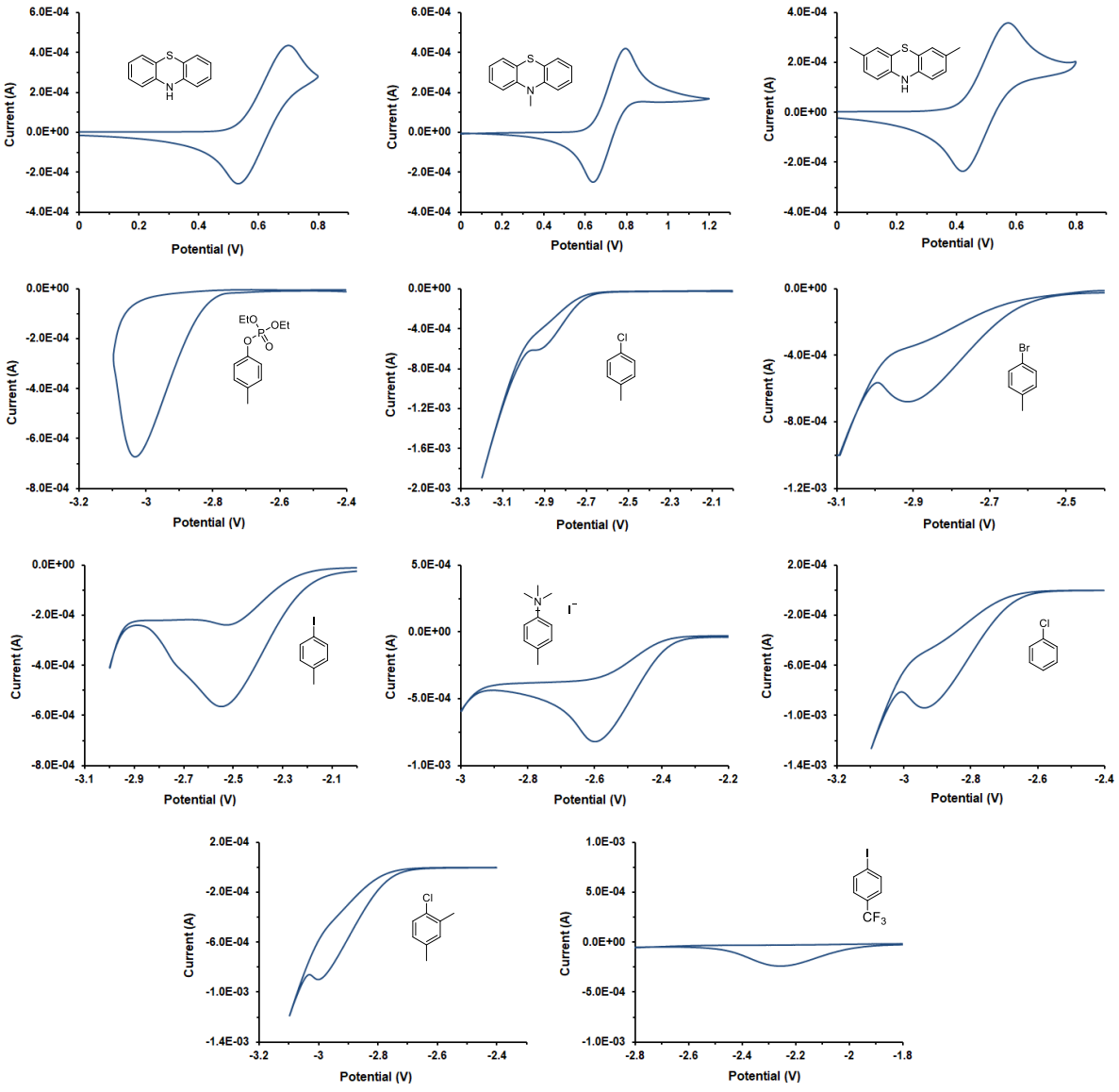


Figure S2. Cyclic voltammograms for phenothiazine catalysts and representative substrates.

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Influence of additives on redox behavior of substrates: For *p*-tolyl diethyl phosphate, *p*-chlorotoluene, and *p*-bromotoluene, reduction potentials were also measured in the presence of B_2Pin_2 (3 equiv., commensurate with the molar ratio in a reaction mixture) or Cs_2CO_3 (3 equiv., commensurate with the molar ratio in a reaction mixture), and both B_2Pin_2 and Cs_2CO_3 (3 equiv. for both, commensurate with the molar ratio in a reaction mixture) in order to ensure that their reduction potentials are not affected by the additives. In all cases, the reduction potentials remained unchanged, indicating that B_2Pin_2 and Cs_2CO_3 do not have any influence on the redox properties of the substrates.

^{1}H NMR spectroscopic studies of PTH1 behavior in the presence of B_2pin_2, Cs_2CO_3, and crown ethers

^{1}H NMR spectra of **PTH1**, potassium salt of **PTH1** (**PTH1**-K), as well as **PTH1** (0.05M) in the presence of Cs_2CO_3, B_2pin_2, and crown ethers 18-crown-6 and 12-crown-4 were recorded in acetonitrile. An aliquot of solutions of **PTH1** (0.05M) in the presence of Cs_2CO_3 (0.025M), B_2pin_2 (0.5M), and crown ethers 18-crown-6 and 12-crown-4 (0.025M) was placed in an NMR tube that contained a sealed coaxial capillary with d_{12}-cyclohexane.

UV/Vis measurements of PTH1 in the presence of B_2pin_2 and cesium carbonate and the potassium salt of PTH1 (PTH1-K)

The UV/Vis spectra of **PTH1** and of the potassium salt of **PTH1** (**PTH1-K**) are shown in Figure S3.A. Deprotonation of **PTH1** leads to significant shift of the absorption to the red with a strong shoulder in the 430−500 nm range that results in a bright yellow color of the salt even in a dilute (0.4 mM) solution. **PTH1**, on the other hand, lacks strong absorption in the range, as evidenced by the large difference in molar attenuation coefficients for **PTH1** (ε = 7.5 $M^{-1}\cdot cm^{-1}$) and salt **PTH1-K** (ε = 2875 $M^{-1}\cdot cm^{-1}$) at 440 nm. Addition of cesium carbonate to **PTH1** or B_2pin_2 to **PTH1** did not lead to any changes in the UV/Vis spectrum.

On the other hand, addition of both B_2pin_2 and cesium carbonate led to a weak bathochromic shift (Figure S3.B). However, the absorptions of the phenothiazine anion (**PTH1-K**) were not present in the UV/Vis spectrum, indicating that the phenothiazine anion is not formed in the borylation reaction mixture, in line with the conclusions made from the ^{1}H NMR study of **PTH1** solutions in the presence of B_2pin_2 and cesium carbonate.

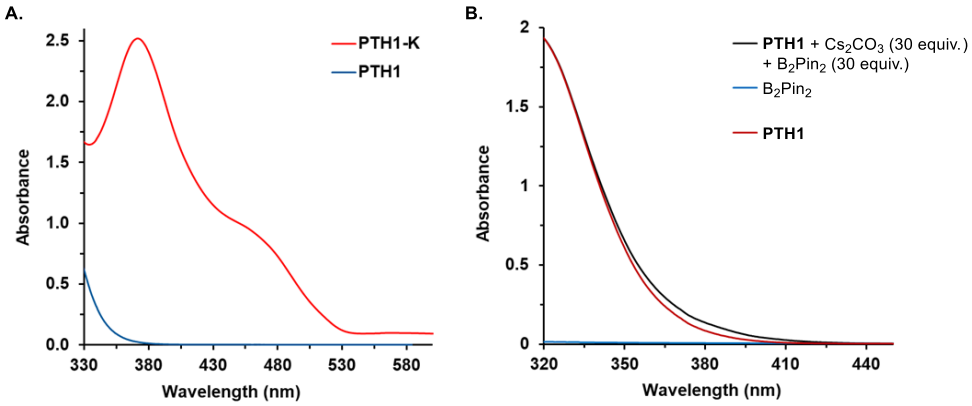


Figure S3. UV/Vis absorption studies of **PTH1** speciation in acetonitrile solution in the presence of B_2pin_2 and cesium carbonate. **A.** UV/Vis absorption spectra of phenothiazine (**PTH1**) and the potassium salt of phenothiazine (**PTH1-K**) in acetonitrile at 0.4mM. **B.** UV/Vis absorption spectra of phenothiazine (**PTH1**) in the absence and in the presence of B_2pin_2 and cesium carbonate in acetonitrile at 0.4mM for **PTH1**. The ratio of concentrations of B_2pin_2 and cesium carbonate to the concentration of **PTH1** (30 : 1) corresponds to the initial concertation ratios of the reagents in the borylation reaction.

Fluorescence quenching measurements with PTH1 and PTH1/Cs_2CO_3/18-crown-6

The steady-state fluorescence emission spectra were acquired on an Edinburgh FLS1000 (Edinburgh Instruments). Fluorescence quenching experiments were carried out with 0.4mM solutions of **PTH1** in anhydrous and degassed acetonitrile in the absence and in the presence of cesium carbonate (30 equiv.) and 18-crown-6 (0.012M) to match the reactant ratios in the borylation reaction. Preliminary experiments were carried out with

18-crown-6 in the absence of cesium carbonate and with cesium carbonate in the absence of 18-crown-6 to exclude the influence of these additives on the fluorescence of **PTH1**.

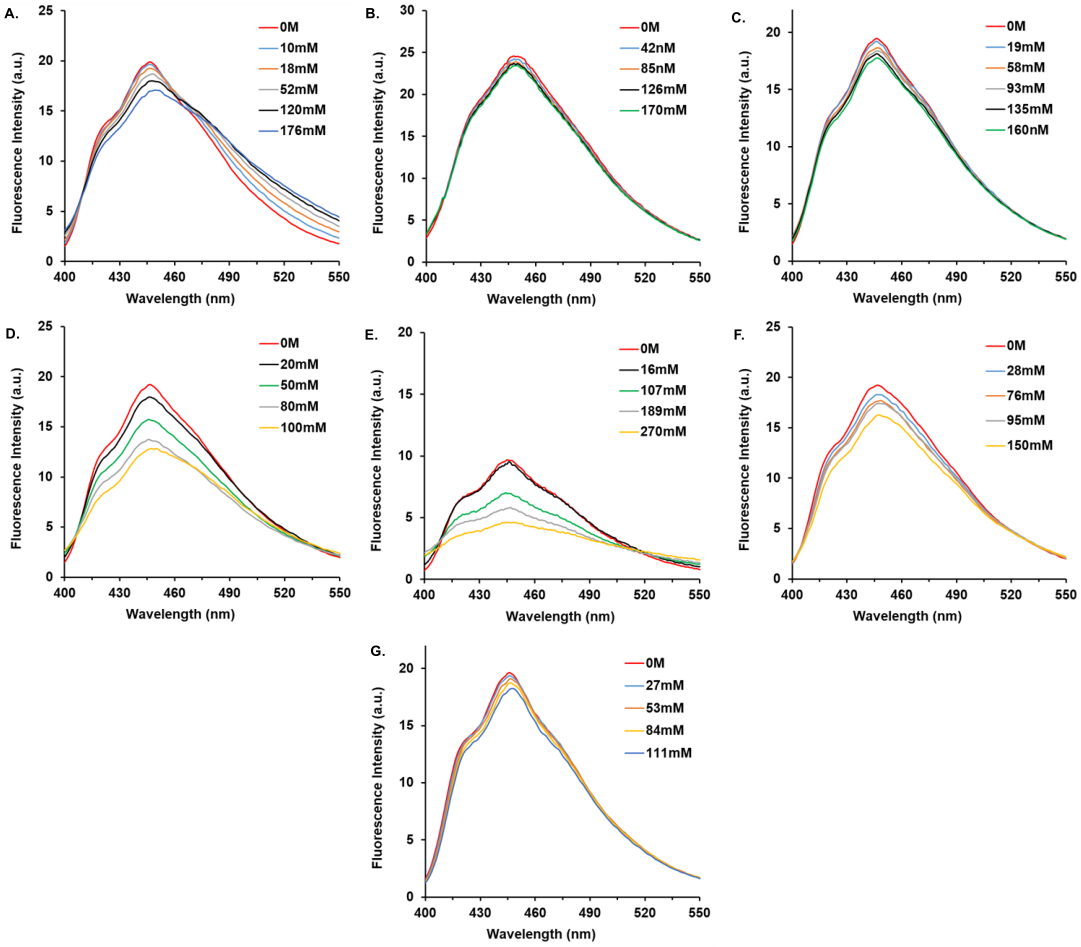
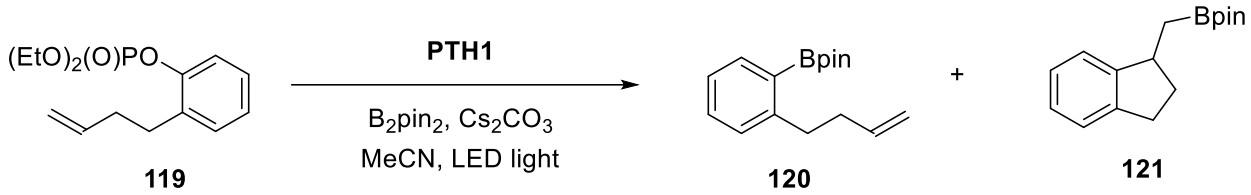


Figure S4. Fluorescence spectra of **PTH1** with substrates added at various concentrations. The corresponding Stern-Vollmer graphs are shown in Figure 3 in the paper. **A.** In the presence of cesium carbonate and 18-crown-6 with phosphate ester **117** as a quencher. **B.** In the presence of cesium carbonate and 18-crown-6 with *p*-chlorotoluene as a quencher. **C.** In the presence of cesium carbonate and 18-crown-6 with *p*-bromotoluene as a quencher. **D.** In the presence of cesium carbonate and 18-crown-6 with *p*-iodotoluene as a quencher. **E.** In the absence of cesium carbonate and 18-crown-6 with *p*-iodotoluene as a quencher. **F.** In the presence of cesium carbonate and 18-crown-6 with phenyltrimethylammonium iodide as a quencher. **G.** In the absence of cesium carbonate and 18-crown-6 with phenyltrimethylammonium iodide as a quencher.

Radical clock experiments

The general procedure GP1 was followed with phosphate ester **119** (57 mg, 0.2 mmol), B_2pin_2 (3.0, 6.0 or 10.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) and CH_3CN (2 mL). The yields of products **120** and **121** were determined by ^1H NMR using 1,4-dimethoxybenzene as an internal standard.



$$\frac{[\mathbf{120}]}{[\mathbf{121}]} = \frac{k_{\mathbf{120}} \times [R\cdot] \times [B_2pin_2]}{k_{\mathbf{121}} \times [R\cdot]}$$

$$\frac{[\mathbf{120}]}{[\mathbf{121}]} = \frac{[B_2pin_2]}{k_{\mathbf{121}}} \times k_{\mathbf{120}}$$

Given that k_{121} = 4.0 x 10^8 s^{-1},[9] experimental data (Table S2) and linear fitting analysis (Figure S5) produce k_{120} = 1.1 x 10^8 s^{-1}.

Table S2. Experimental data for the radical clock experiments with phosphate ester **119**.

[**120**]/[**121**] ratio	$[B_2pin_2]_{start}$, M	$[B_2pin_2]_{end}$, M	$[B_2pin_2]$, M	$[B_2pin_2]/k_{121}$ ratio, M·s
0.055556	0.3	0.27	0.285	7.125E-10
0.125	0.6	0.57	0.585	1.4625E-09
0.25	1	0.97	0.985	2.4625E-09

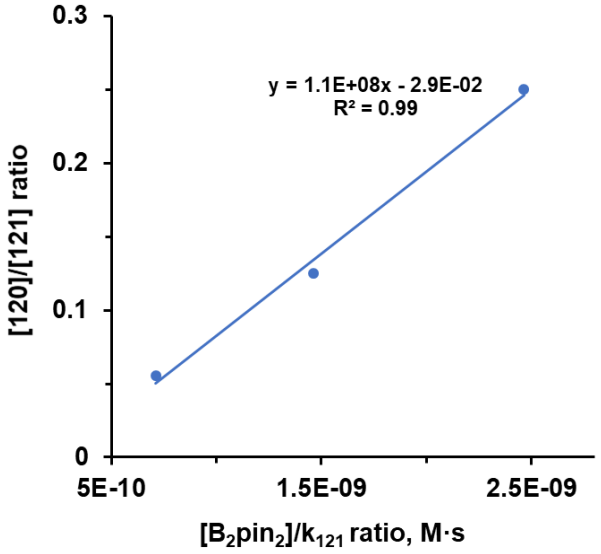
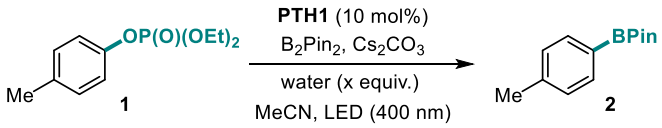


Figure S5. Linear fitting analysis for the radical clock experiments with phosphate ester **119**.

Table S3. Influence of added water on the borylation reaction performance.[a]

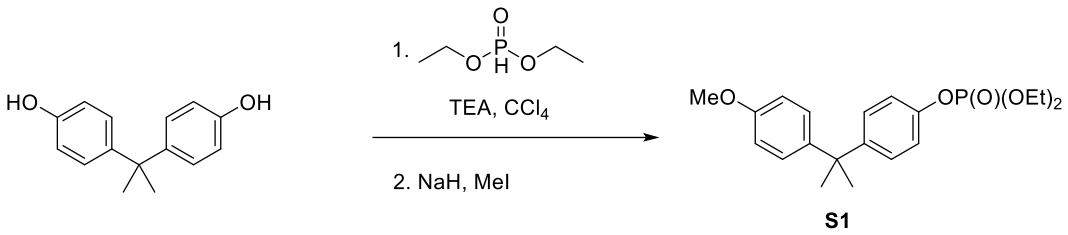


Entry	Water (x equiv.)	Yield, %
1	0	41
2	0.5	71
3	1	73

[a] The reaction was carried out a described in GP1 with phosphate **1** (0.2 mmol), **PTH1** (10 mol%), B_2Pin_2 (0.6 mmol), Cs_2CO_3 (0.6 mmol), MeCN (2 mL), LED light (400 nm), for 12 h. The yields were determined by ^1H NMR spectroscopy with 1,4-dimethoxybenzene as an internal standard.

Synthesis of starting materials

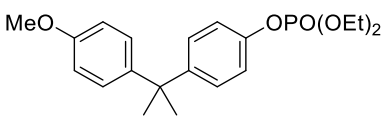
Diethyl (4-(2-(4-methoxyphenyl)propan-2-yl)phenyl) phosphate (S1)



S1

The general procedure GP7 was followed with 4,4'-(propane-2,2-diyl)diphenol (878 mg, 3.85 mmol), triethylamine (0.55 mL, 3.85 mmol), diethyl phosphite (0.48 mL, 3.85 mmol), THF (10 mL) and carbon tetrachloride (10 mL). The mixture was stirred at room temperature overnight. Purification flash chromatography on silica gel (EtOAc/hexane, 3 : 2 v/v) afforded diethyl (4-(2-(4-methoxyphenyl)propan-2-yl)phenyl) phosphate (1.09 g, 78%) as a colorless oil.

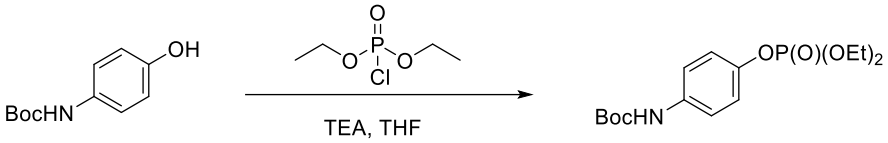
The monophosphate was dissolved in THF (50 mL) and cooled to 0 °C then NaH (4.42 mmol, 1.15 equiv.) was added slowly to the solution under nitrogen. The mixture was stirred for 30 minutes then added MeI (11.55 mmol, 3 equiv.). The mixture was stirred at room temperature for 2 h, concentrated, and 50 mL of ethyl acetate and 30 mL of water were added. The two layers were separated, and the aqueous layer was extracted with ethyl acetate (3 × 50 mL). The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. The residue was purified by column chromatography over silica gel (EtOAc/hexane, 1 : 1 v/v) to afford compound **S1** (837 mg, 60%) a colorless oil.



^{1}H NMR (500 MHz, $CDCl_3$): 7.17 (2 H, d, *J* = 8.7 Hz), 7.12 (2 H, d, *J* = 8.8 Hz), 7.09 (2 H, d, *J* = 8.8 Hz), 6.80 (2 H, d, *J* = 8.8 Hz), 4.21 (4 H, pt, *J* = 7.1, 3.0 Hz), 3.78 (3 H, s), 1.63 (6 H, s), 1.34 (6 H, t, *J* = 7.1 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 157.6, 148.6 (d, *J* = 7.1 Hz), 147.8, 142.6, 128.1, 127.8, 119.4 (d, *J* = 4.7 Hz), 113.4, 64.63, 64.58, 55.3, 42.1, 31.1, 16.23, 16.17 ppm. – ^{31}P NMR (202 Hz, $CDCl_3$):

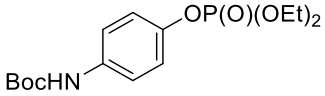
−6.1 ppm. – IR: 2970, 1747, 1614, 1506, 1445, 1369, 1297, 1218, 1176, 1100, 1030, 972, 888 cm^{-1}. – HRMS: calcd for $C_{20}H_{28}O_5P$: 379.1669, found 379.1666 [$M+H^+$].

tert-Butyl (4-((diethoxyphosphoryl)oxy)phenyl)carbamate (S122)



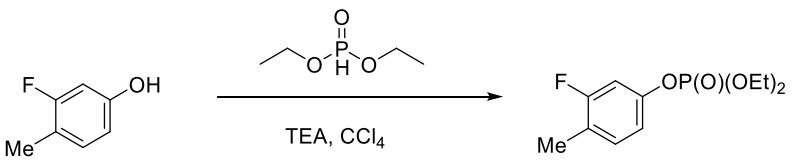
S122

The general procedure GP7 was followed with *tert*-butyl (4-hydroxyphenyl)carbamate (848 mg, 3.1 mmol), triethylamine (0.55 mL, 3.85 mmol), diethyl chlorophosphate (0.48 mL, 3.85 mmol) and THF (10 mL). The mixture was stirred at room temperature overnight. Purification flash chromatography on silica gel (EtOAc/hexane, 2 : 3 v/v) afforded product **S122** (802 mg, 75%) as a colorless oil.



^{1}H NMR (500 MHz, $CDCl_3$): 7.31 (2 H, d, *J* = 8.4 Hz), 7.11 (2 H, d, *J* = 5.9 Hz), 6.69 (1 H, s), 4.24–4.12 (4 H, m), 1.48 (9 H, q, *J* = 3.3, 2.8 Hz), 1.32 (6 H, dd, *J* = 9.3, 4.9 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 153.0, 146.1, 135.6, 120.5, 119.9, 80.6, 64.6 (d, *J* = 6.2 Hz), 28.4, 16.2 (d, *J* = 6.7 Hz) ppm. – ^{31}P NMR (202 Hz, $CDCl_3$): −6.1 ppm. – IR: 2980, 1720, 1606, 1357, 1508, 1455, 1409, 1392, 1367, 1311, 1261, 1156, 1026, 960 cm^{-1}. – HRMS: calcd for $C_{15}H_{28}N_2O_6P$: 363.1679, found 363.1684 [$M+NH_4^+$].

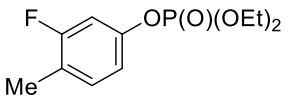
Diethyl (3-fluoro-4-methylphenyl) phosphate (S2)



S2

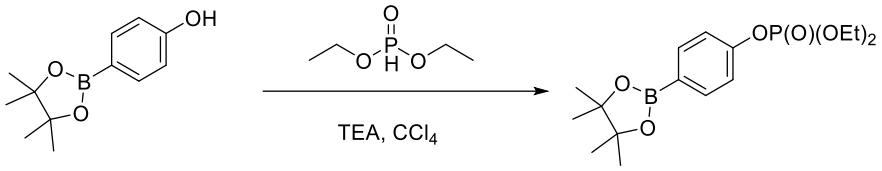
The general procedure GP7 was followed with 3-fluoro-4-methylphenol (391 mg, 3.1 mmol), triethylamine (0.55 mL, 3.85 mmol), diethyl phosphite (0.48 mL, 3.85 mmol) and

carbon tetrachloride (8 mL). The mixture was stirred at room temperature overnight. Purification flash chromatography on silica gel (EtOAc/hexane, 1 : 1 v/v) afforded product **S2** (700 mg, 89%) as a colorless oil.



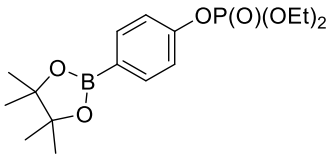
^{1}H NMR (500 MHz, $CDCl_3$): 7.11 (1 H, t, *J* = 8.5 Hz), 6.92 (1 H, s), 6.90 (1 H, s), 4.29–4.12 (4 H, m), 2.22 (3 H, s), 1.34 (6 H, t, *J* = 7.4 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 161.1 (d, *J* = 246.4 Hz), 149.4 (dd, *J* = 11.0, 6.8 Hz), 131.7 (d, *J* = 6.4 Hz), 121.6 (d, *J* = 17.2 Hz), 115.5 (t, *J* = 4.3 Hz), 107.8 (dd, *J* = 25.6, 5.3 Hz), 64.8 (d, *J* = 6.1 Hz), 16.2 (d, *J* = 6.6 Hz), 14.1 (d, *J* = 3.0 Hz) ppm. – ^{19}F NMR (470.5 Hz, $CDCl_3$): −114.0 (t, *J* = 9.4 Hz) ppm. – ^{31}P NMR (202 Hz, $CDCl_3$): −6.4 ppm. – IR: 3443, 2113, 1737, 1634, 1580, 1456, 1382, 1214, 1207, 1158, 1028, 975 cm^{-1}. – HRMS: calcd for $C_{17}H_2NO_5P$: 303.0992, found 303.0993 [$M+H^+$].

Diethyl (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) phosphate (S3)



S3

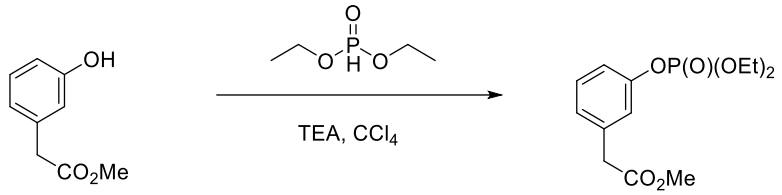
The general procedure GP7 was followed with (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (682 mg, 3.1 mmol), triethylamine (0.55 mL, 3.85 mmol), diethyl phosphite (0.48 mL, 3.85 mmol) and carbon tetrachloride (10 mL). The mixture was stirred at room temperature overnight. Purification flash chromatography on silica gel (EtOAc/hexane, 2 : 3 v/v) afforded product **S3** (993 mg, 90%) as a colorless oil.



^{1}H NMR (500 MHz, $CDCl_3$): 7.77 (2 H, d, *J* = 7.9 Hz), 7.20 (2 H, d, *J* = 7.7 Hz), 4.64–3.88 (4 H, m), 1.41–1.02 (18 H, m) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 153.3 (d, *J* = 6.6 Hz), 136.6, 119.4 (d, *J* = 4.9 Hz), 84.0, 64.8, 64.7, 25.0, 16.2 (d, *J* = 6.6 Hz) ppm. – ^{31}P NMR (202 Hz, $CDCl_3$): −6.7

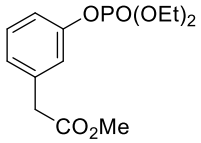
ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.1 ppm. – IR: 2980, 1603, 1397, 1360, 1321, 1270, 1216, 1166, 1144, 1090, 1030, 963, 935 cm^{-1}. – HRMS: calcd for $C_{16}H_{27}BO_6P$: 357.1633, found 357.1636 [$M+H^+$].

Methyl 2-(3-((diethoxyphosphoryl)oxy)phenyl)acetate (S4)



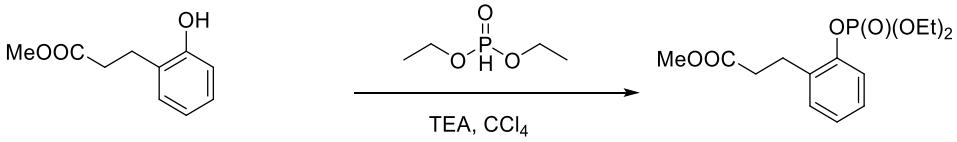
S4

The general procedure GP7 was followed with methyl 2-(3-hydroxyphenyl)acetate (515 mg, 3.1 mmol), triethylamine (0.55 mL, 3.85 mmol), diethyl phosphite (0.48 mL, 3.85 mmol) and carbon tetrachloride (8 mL). The mixture was stirred at room temperature overnight. Purification flash chromatography on silica gel (EtOAc/hexane, 2 : 1 v/v) afforded product **S4** (768 mg, 81%) as a colorless oil.



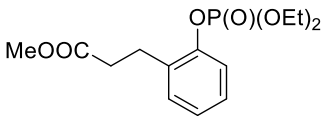
^{1}H NMR (500 MHz, $CDCl_3$): 77.27 (1 H, t, *J* = 7.8 Hz), 7.13 (1 H, s), 7.12 (1 H, d, *J* = 9.6 Hz), 7.07 (1 H, d, *J* = 7.6 Hz), 4.20 (4 H, td, *J* = 7.6, 3.2 Hz), 3.67 (3 H, s), 3.60 (2 H, s), 1.33 (6 H, t, *J* = 7.1 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 171.6, 150.9 (d, *J* = 6.6 Hz), 135.9, 129.8, 126.0, 121.0 (d, *J* = 5.2 Hz), 118.8 (d, *J* = 4.9 Hz), 64.7 (d, *J* = 6.2 Hz), 52.2, 40.9, 16.2 (d, *J* = 6.6 Hz) ppm. – ^{31}P NMR (202 Hz, $CDCl_3$): −6.4 ppm. – IR: 3441, 1737, 1609, 1588, 1488, 1446, 1394, 1370, 1344, 1254, 1150, 1027, 981 cm^{-1}. – HRMS: calcd for $C_{13}H_{20}O_6P$: 303.0992, found 303.0993 [$M+H^+$].

Methyl 3-(2-((diethoxyphosphoryl)oxy)phenyl)propanoate (S5)



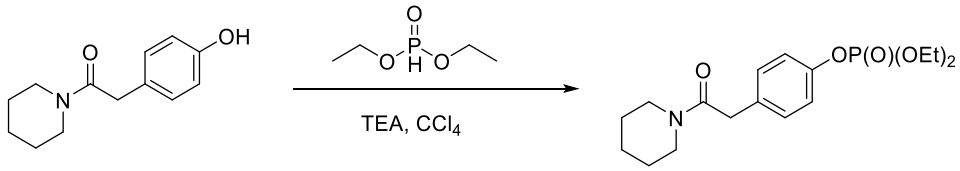
S5

The general procedure GP7 was followed with methyl 3-(2-hydroxyphenyl)propanoate (558 mg, 3.1 mmol), triethylamine (0.55 mL, 3.85 mmol), diethyl phosphite (0.48 mL, 3.85 mmol) and carbon tetrachloride (8 mL). The mixture was stirred at room temperature overnight. Purification flash chromatography on silica gel (EtOAc/hexane, 2 : 1 v/v) afforded product **S5** (793 mg, 81%) as a colorless oil.



^{1}H NMR (500 MHz, $CDCl_3$): 7.32 (1 H, d, *J* = 6.4 Hz), 7.22–7.14 (2 H, m), 7.08 (1 H, d, *J* = 7.0 Hz), 4.24–4.18 (4 H, m), 3.65 (3 H, s), 3.37–2.87 (2 H, m), 2.79–2.44 (2 H, m), 1.34 (6 H, td, *J* = 7.2, 2.7 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 171.6, 150.9 (d, *J* = 6.6 Hz), 135.9, 129.8, 126.0, 121.0 (d, *J* = 5.2 Hz), 118.8 (d, *J* = 4.9 Hz), 64.8, 64.7, 52.2, 40.9, 16.2, 16.1 ppm. – ^{31}P NMR (202 Hz, $CDCl_3$): −6.2 ppm. – IR: 3440, 2985, 1736, 1492, 1453, 1395, 1266, 1165, 1103, 1028, 967 cm^{-1}. – HRMS: calcd for $C_{14}H_{22}O_6P$: 317.1149, found 317.1142 [M+H$^+$].

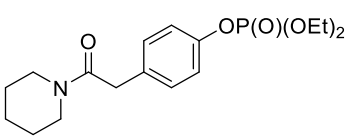
Diethyl (4-(2-oxo-2-(piperidin-1-yl)ethyl)phenyl) phosphate (S6)



S6

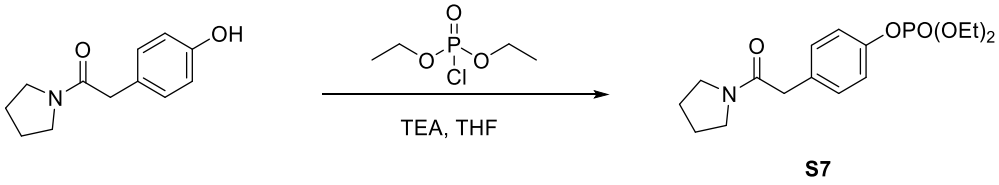
The general procedure GP7 was followed with 2-(4-hydroxyphenyl)-1-(piperidin-1-yl)ethan-1-one (679 mg, 3.1 mmol), triethylamine (0.55 mL, 3.85 mmol), diethyl phosphite (0.48 mL, 3.85 mmol) and carbon tetrachloride (10 mL). The mixture was stirred at room

temperature overnight. Purification flash chromatography on silica gel (EtOAc/DCM, 3 : 2 v/v) afforded product **S6** (561 mg, 51%) as a colorless oil.



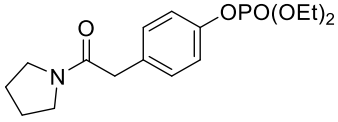
^{1}H NMR (500 MHz, $CDCl_3$): 7.18 (2 H, d, *J* = 8.1 Hz), 7.13 (2 H, d, *J* = 8.0 Hz), 4.17 (4 H, tt, *J* = 7.5, 5.5 Hz), 3.65 (2 H, s), 3.53 (2 H, t, *J* = 5.5 Hz), 3.33 (2 H, t, *J* = 5.5 Hz), 1.55 (2 H, q, *J* = 6.0 Hz), 1.48 (2 H, q, *J* = 5.3 Hz), 1.39–1.33 (2 H, m), 1.31 (6 H, t, *J* = 7.2 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 169.0, 149.6 (d, *J* = 7.0 Hz), 132.2, 129.9, 120.1 (d, *J* = 4.9 Hz), 64.6 (d, *J* = 6.1 Hz), 47.3, 42.9, 40.3, 26.3, 25.5, 24.4, 16.1 (d, *J* = 6.8 Hz) ppm. – ^{31}P NMR (202 Hz, $CDCl_3$): −6.4 ppm. – IR: 3409, 2939, 1737, 1615, 1507, 1446, 1370, 1258, 1217, 1167, 1028, 970 cm^{-1}. – HRMS: calcd for $C_{17}H_2NO_5P$: 303.0992, found 303.0993 [$M+H^+$].

Diethyl (4-(2-oxo-2-(pyrrolidin-1-yl)ethyl)phenyl) phosphate (S7)



S7

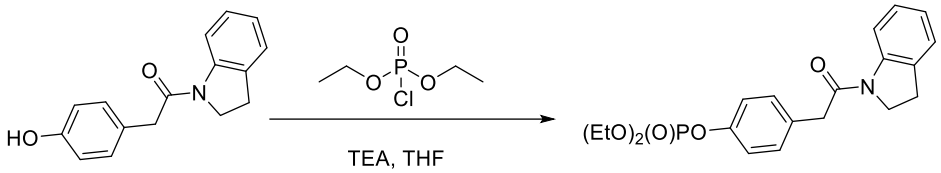
The general procedure GP7 was followed with 2-(4-hydroxyphenyl)-1-(pyrrolidin-1-yl)ethan-1-one (635 mg, 3.1 mmol), triethylamine (0.55 mL, 3.85 mmol), diethyl chlorophosphate (0.48 mL, 3.85 mmol) and THF (15 mL). The mixture was stirred at room temperature overnight. Purification flash chromatography on silica gel (EtOAc/DCM, 3 : 2 v/v) afforded product **S7** (623 mg, 59%) as a colorless oil.



^{1}H NMR (500 MHz, $CDCl_3$): 7.23 (2 H, d, *J* = 8.3 Hz), 7.14 (2 H, d, *J* = 8.3 Hz), 4.30–4.03 (4 H, m), 3.59 (2 H, s), 3.46 (2 H, t, *J* = 6.8 Hz), 3.40 (2 H, t, *J* = 6.8 Hz), 1.94–1.87 (2 H, m), 1.86–1.78 (2 H, m), 1.33 (6 H, t, *J* = 7.1 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 169.3, 149.6, 131.7, 130.3, 120.1 (d, *J* = 4.8 Hz), 64.6 (d, *J* = 6.1 Hz), 47.0, 46.0, 41.5, 26.2, 24.4, 16.2 (d, *J* = 6.7 Hz) ppm. – ^{31}P NMR (202 Hz, $CDCl_3$): −6.3 ppm. – IR: 3400, 2981, 1705, 1621, 1508, 1452, 1394, 1370,

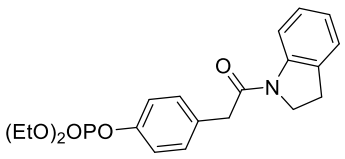
1262, 1217, 1166, 1028, 969 cm^{-1}. – HRMS: calcd for $C_{16}H_{25}NO_5P$: 342.1465, found 342.1460 [M+H^+].

Diethyl (4-(2-(indolin-1-yl)-2-oxoethyl)phenyl) phosphate (S8)



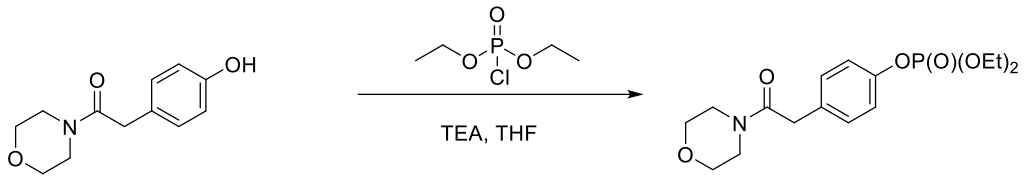
S8

The general procedure GP7 was followed with 2-(4-hydroxyphenyl)-1-(indolin-1-yl)ethan-1-one (784 mg, 3.1 mmol), triethylamine (0.55 mL, 3.85 mmol), diethyl chlorophosphate (0.48 mL, 3.85 mmol) and THF (15 mL). The mixture was stirred at room temperature overnight. Purification flash chromatography on silica gel (EtOAc/hexane, 4 : 1 v/v) afforded product **S8** (603 mg, 50%) as a colorless solid.



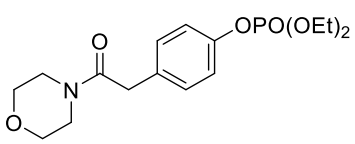
M.p.: 57−60 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 8.24 (1 H, d, *J* = 8.1 Hz), 7.27 (2 H, d, *J* = 8.3 Hz), 7.18 (3 H, d, *J* = 8.2 Hz), 7.16 (1 H, d, *J* = 6.9 Hz), 7.01 (1 H, t, *J* = 7.4 Hz), 4.32–4.14 (4 H, m), 4.05 (2 H, t, *J* = 8.4 Hz), 3.76 (2 H, s), 3.16 (2 H, t, *J* = 8.4 Hz), 1.34 (6 H, t, *J* = 7.1 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 168.9, 149.9 (d, *J* = 7.0 Hz), 143.0, 131.2, 131.0, 130.6, 130.5, 127.6, 124.6, 124.0, 120.3 (d, *J* = 4.8 Hz), 117.2, 64.71, 64.66, 48.3, 42.7, 28.1, 16.2 (d, *J* = 6.6 Hz) ppm. – ^{31}P NMR (202 Hz, $CDCl_3$): −6.3 ppm. – IR: 1660, 1597, 1507, 1479, 443, 1423, 1410, 1395, 1370, 1274, 1210, 1165, 1112, 1017, 967, 940 cm^{-1}. – HRMS: calcd for $C_{20}H_{25}NO_5P$: 390.1465, found 390.1462 [M+H^+].

Diethyl (4-(2-morpholino-2-oxoethyl)phenyl) phosphate (S9)



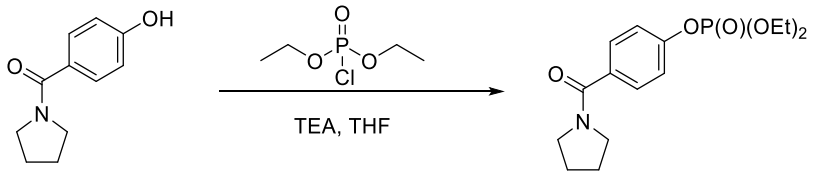
S9

The general procedure GP7 was followed with 2-(4-hydroxyphenyl)-1-morpholinoethan-1-one (685 mg, 3.1 mmol), triethylamine (0.55 mL, 3.85 mmol), diethyl chlorophosphate (0.48 mL, 3.85 mmol) and THF (15 mL). The mixture was stirred at room temperature overnight. Purification flash chromatography on silica gel (EtOAc/DCM, 3 : 2 v/v) afforded product **S9** (641 mg, 59%) as a colorless oil.



^{1}H NMR (500 MHz, $CDCl_3$): 7.18 (2 H, d, *J* = 8.7 Hz), 7.15 (2 H, d, *J* = 8.8 Hz), 4.26–4.11 (4 H, m), 3.66 (2 H, s), 3.61 (4 H, s), 3.52–3.44 (2 H, m), 3.40 (2 H, t, *J* = 4.8 Hz), 1.32 (6 H, t, *J* = 7.1 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 169.4, 149.8 (d, *J* = 6.9 Hz), 131.5, 130.0, 120.3 (d, *J* = 4.8 Hz), 66.8, 66.5, 64.7 (d, *J* = 6.2 Hz), 46.5, 42.2, 39.9, 16.2 (d, *J* = 6.8 Hz) ppm. – ^{31}P NMR (202 Hz, $CDCl_3$): −6.4 ppm. – IR: 3391, 1738, 1626, 1508, 1444, 1394, 1370, 1259, 1217, 1167, 1112, 1031, 969 cm^{-1}. – HRMS: calcd for $C_{16}H_{25}NO_6P$: 358.1414, found 358.1412 [$M+H^+$].

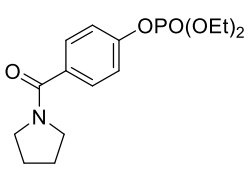
Diethyl (4-(pyrrolidine-1-carbonyl)phenyl) phosphate (S10)



S10

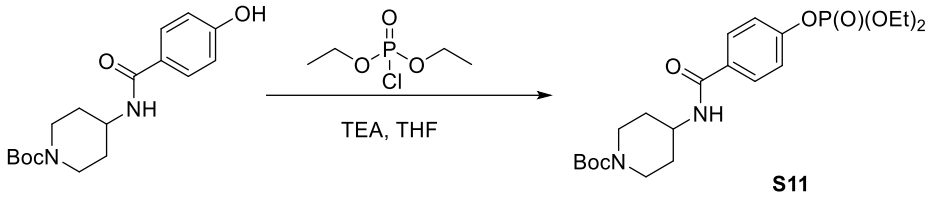
The general procedure GP7 was followed with (4-hydroxyphenyl)(pyrrolidin-1-yl)methanone (592 mg, 3.1 mmol), triethylamine (0.55 mL, 3.85 mmol), diethyl chlorophosphate (0.48 mL, 3.85 mmol) and THF (15 mL). The mixture was stirred at room

temperature overnight. Purification flash chromatography on silica gel (EtOAc/DCM, 3 : 2 v/v) afforded product **S10** (547 mg, 54%) as a colorless oil.



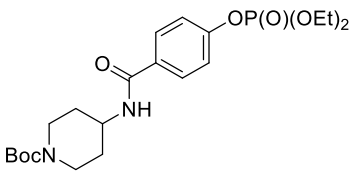
^{1}H NMR (500 MHz, $CDCl_3$): 7.51 (2 H, d, *J* = 8.5 Hz), 7.23 (2 H, d, *J* = 8.3 Hz), 4.47–3.96 (4 H, m), 3.61 (2 H, t, *J* = 7.0 Hz), 3.41 (2 H, t, *J* = 6.6 Hz), 1.94 (2 H, dt, *J* = 13.4, 6.6 Hz), 1.86 (2 H, dt, *J* = 13.0, 6.4 Hz), 1.34 (6 H, t, *J* = 7.0 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 169.1, 152.1 (d, *J* = 6.7 Hz), 134.2, 129.3, 120.1 (d, *J* = 5.2 Hz), 65.1 (d, *J* = 6.2 Hz), 50.0, 46.6, 26.8, 24.8, 16.4 (d, *J* = 6.7 Hz) ppm. – ^{31}P NMR (202 Hz, $CDCl_3$): −6.6 ppm. – IR: 2983, 1709, 1607, 1509, 1442, 1366, 1269, 1224, 1167, 1301, 967 cm^{-1}. – HRMS: calcd for $C_{15}H_{23}NO_5P$: 328.1308, found 328.1309 [M+H$^+$].

tert-Butyl 4-(4-((diethoxyphosphoryl)oxy)benzamido)piperidine-1-carboxylate (S11)



S11

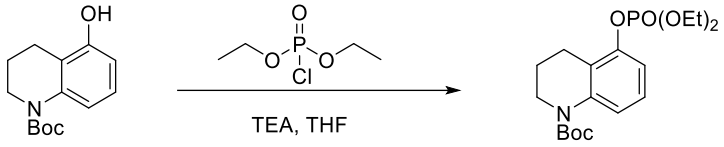
The general procedure GP7 was followed with (*tert*-butyl 4-(4-hydroxybenzamido)piperidine-1-carboxylate (991 mg, 3.1 mmol), triethylamine (0.55 mL, 3.85 mmol), diethyl chlorophosphate (0.48 mL, 3.85 mmol) and THF (20 mL). The mixture was stirred at room temperature overnight. Purification flash chromatography on silica gel (EtOAc/hexane, 1 : 1 v/v) afforded product **S11** (835 mg, 59%) as a colorless oil.



^{1}H NMR (500 MHz, $CDCl_3$): 7.77 (2 H, d, *J* = 8.7 Hz), 7.17 (2 H, dd, *J* = 8.7, 1.0 Hz), 6.97 (1 H, d, *J* = 7.9 Hz), 4.24–4.15 (4 H, m), 4.09–3.97 (3 H, m), 2.81 (2 H, s), 1.89 (2 H, brs), 1.41 (9 H, s), 1.39–1.32 (2 H, m), 1.30 (6 H, td, *J* = 7.1, 1.1 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 166.0, 154.7, 152.92, 152.87, 131.4, 129.1, 119.73, 119.69, 79.6, 64.9 (d, *J* = 6.3 Hz), 47.3, 42.8, 31.8, 28.4, 16.0 (d, *J* = 6.7 Hz) ppm. – ^{31}P NMR (202 Hz, $CDCl_3$): −7.1 ppm. – IR: 2980, 1640, 1605,

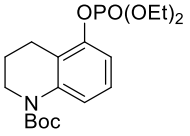
1542, 1500, 1478, 1427, 1366, 1327, 1271, 1235, 1166, 1100, 1028, 963, 936 cm^{-1}. – HRMS: calcd for $C_{31}H_{34}N_2O_7P$: 457.2098, found 457.2100 [$M+H^+$].

tert-Butyl 5-((diethoxyphosphoryl)oxy)-3,4-dihydroquinoline-1(2*H*)-carboxylate (S12)



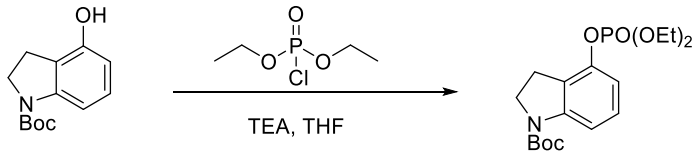
S12

The general procedure GP7 was followed with *tert*-butyl 5-hydroxy-3,4-dihydroquinoline-1(2*H*)-carboxylate (772 mg, 3.1 mmol), triethylamine (0.55 mL, 3.85 mmol), diethyl chlorophosphate (0.48 mL, 3.85 mmol) and THF (10 mL). The mixture was stirred at room temperature overnight. Purification flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afforded product **S12** (721 mg, 61%) as a colorless oil.



^{1}H NMR (500 MHz, $CDCl_3$): 7.59 (1 H, d, *J* = 9.3 Hz), 7.13–6.70 (2 H, m), 4.26–4.12 (4 H, m), 3.70–3.63 (2 H, m), 2.73 (2 H, t, *J* = 6.6 Hz), 1.89 (2 H, p, *J* = 6.5 Hz), 1.49 (9 H, s), 1.33 (6 H, td, *J* = 7.1, 1.1 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 154.0, 146.25, 146.19, 135.7, 131.5, 125.4, 119.6, 119.5, 117.39, 117.35, 81.0, 64.6 (d, *J* = 6.0 Hz), 44.6, 28.5, 27.6, 23.4, 16.2 (d, *J* = 6.8 Hz) ppm. – ^{31}P NMR (202 Hz, $CDCl_3$): −6.2 ppm. – IR: 2979, 1694, 1495, 1455, 1367, 1337, 1252, 1158, 1139, 1029, 975, 915 cm^{-1}. – HRMS: calcd for $C_{18}H_{32}N_2O_6P$: 403.1992, found 403.1990 [$M+NH_4^+$].

tert-Butyl 4-((diethoxyphosphoryl)oxy)indoline-1-carboxylate (S13)



S13

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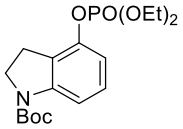
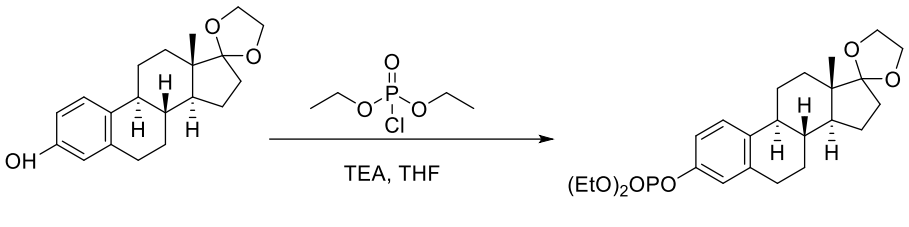
The general procedure GP7 was followed with *tert*-butyl 4-hydroxyindoline-1-carboxylate (728 mg, 3.1 mmol), triethylamine (0.55 mL, 3.85 mmol), diethyl chlorophosphate (0.48 mL, 3.85 mmol) and THF (10 mL). The mixture was stirred at room temperature overnight. Purification flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afforded product **S13** (782 mg, 68%) as a colorless oil.



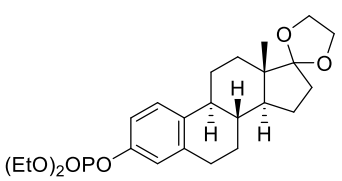
^{1}H NMR (500 MHz, $CDCl_3$): 7.72 (1 H, s), 7.12 (1 H, t, *J* = 8.1 Hz), 6.85 (1 H, d, *J* = 8.2 Hz), 4.27–4.13 (4 H, m), 3.99 (2 H, t, *J* = 8.9 Hz), 3.14 (2 H, t, *J* = 8.7 Hz), 1.55 (9 H, s), 1.35 (6 H, td, *J* = 7.0, 1.0 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 152.5, 147.1, 129.0, 113.7, 111.7, 64.8 (d, *J* = 6.2 Hz), 48.0, 29.8, 28.6, 24.7, 16.3 (d, *J* = 6.7 Hz) ppm. – ^{31}P NMR (202 Hz, $CDCl_3$): −6.0 ppm. – IR: 2979, 1699, 1614, 1466, 1388, 1337, 1266, 1238, 1164, 1142, 1031, 974 cm^{-1}. – HRMS: calcd for $C_{17}H_{30}N_2O_6P$: 389.1836, found 389.1836 [M+NH_4^+].

Diethyl ((8*R*,9*S*,13*S*,14*S*)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolan]-3-yl) phosphate (S14)



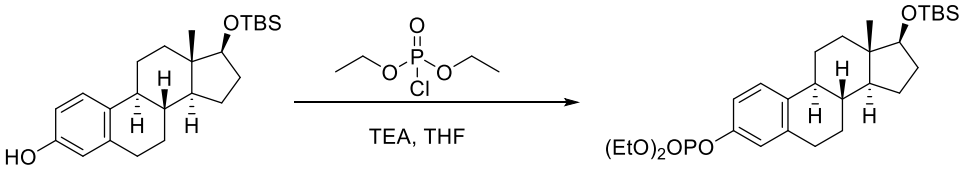
S14

The general procedure GP7 was followed with (8*R*,9*S*,13*S*,14*S*)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolan]-3-ol (973 mg, 3.1 mmol), triethylamine (0.55 mL, 3.85 mmol), diethyl chlorophosphate (0.48 mL, 3.85 mmol) and THF (15 mL). The mixture was stirred at room temperature overnight. Purification flash chromatography on silica gel (EtOAc/hexane, 2 : 3 v/v) afforded product **S14** (990 mg, 71%) as a colorless oil.



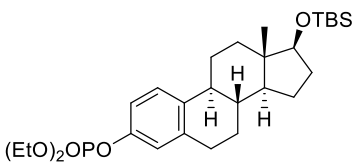
$[\alpha]_D$ = +73 (*c* 0.23M, $CHCl_3$). – ^1H NMR (500 MHz, $CDCl_3$): 7.22 (1 H, d, *J* = 8.5 Hz), 6.96 (1 H, d, *J* = 8.5 Hz), 6.92 (1 H, s), 4.37–4.14 (4 H, m), 4.01–3.77 (4 H, m), 2.84 (2 H, dd, *J* = 8.4, 4.1 Hz), 2.36–2.27 (1 H, m), 2.23 (1 H, td, *J* = 10.2, 4.1 Hz, 1H), 2.07–1.99 (1 H, m), 1.93–1.71 (4 H, m), 1.67–1.59 (1 H, m), 1.57–1.34 (5 H, m), 1.35 (6 H, t, *J* = 7.1 Hz), 0.88 (3 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 148.65, 148.59, 138.7, 137.3, 126.7, 119.99, 119.95, 119.5, 117.1, 117.0, 65.4, 64.6 (d, *J* = 6.0 Hz), 64.5, 49.5, 46.2, 43.8, 38.9, 34.4, 30.8, 29.7, 26.9, 26.1, 22.5, 16.2 (d, *J* = 6.7 Hz), 14.4 ppm. – ^{31}P NMR (202 Hz, $CDCl_3$): −6.1 ppm. – IR: 2936, 1607, 1580, 1494, 1456, 1379, 1273, 1232, 1156, 1104, 1029, 973 cm^{-1}. – HRMS: calcd for $C_{24}H_{36}O_6P$: 451.2244, found 451.2240 [$M+H^+$].

(8*R*,9*S*,13*S*,14*S*,17*S*)-17-((*tert*-Butyldimethylsilyl)oxy)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl diethyl phosphate (S15)



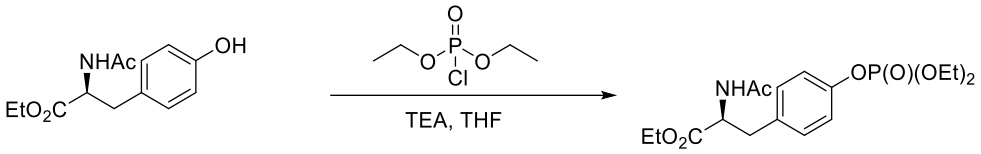
S15

The general procedure GP7 was followed with (8*R*,9*S*,13*S*,14*S*,17*S*)-17-((*tert*-butyldimethylsilyl)oxy)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-ol (1.20 g, 3.1 mmol), triethylamine (0.55 mL, 3.85 mmol), diethyl chlorophosphate (0.48 mL, 3.85 mmol) and THF (20 mL). The mixture was stirred at room temperature overnight. Purification flash chromatography on silica gel (EtOAc/hexane, 1 : 4 v/v) afforded product **S15** (1.05 g, 65%) as a colorless oil.



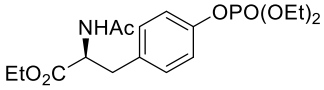
$[\alpha]_D$ = +46 (*c* 0.41M, $CHCl_3$). – ^{1}H NMR (500 MHz, $CDCl_3$): 7.21 (1 H, d, *J* = 8.6 Hz), 6.95 (1 H, dd, *J* = 8.6, 2.7 Hz), 6.91 (1 H, s), 4.31–4.07 (4 H, m), 3.63 (1 H, t, *J* = 8.3 Hz), 2.83 (2 H, dd, *J* = 10.9, 4.9 Hz), 2.25 (1 H, dd, *J* = 17.2, 3.7 Hz), 2.20–2.11 (1 H, m), 1.97–1.81 (3 H, m), 1.69–1.59 (1 H, m), 1.54–1.43 (2 H, m), 1.42–1.25 (8 H, m), 1.23–1.17 (1 H, m), 1.16–1.08 (1 H, m), 0.88 (9 H, s), 0.73 (3 H, s), 0.03 (3 H, s), 0.01 (3 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 148.53, 148.48, 138.6, 137.3, 126.6, 119.88, 119.85, 117.00, 116.96, 81.8, 77.4, 64.4 (d, *J* = 6.0 Hz), 49.7, 44.2, 43.6, 38.6, 37.2, 31.0, 29.7, 27.1, 26.3, 25.9, 23.3, 18.1, 16.2 (d, *J* = 6.6 Hz), 11.4, −4.4, −4.8 ppm. – ^{31}P NMR (202 Hz, $CDCl_3$): −6.1 ppm. – IR: 2928, 1608, 1495, 1472, 1389, 1297, 1248, 1140, 1096, 1061, 1031, 1006, 974, 889 cm^{-1}. – HRMS: calcd for $C_{28}H_{48}O_5PSi$: 523.3003, found 523.3004 [$M+H^+$].

Ethyl (*S*)-2-acetamido-3-(4-((diethoxyphosphoryl)oxy)phenyl)propanoate (S16)



S16

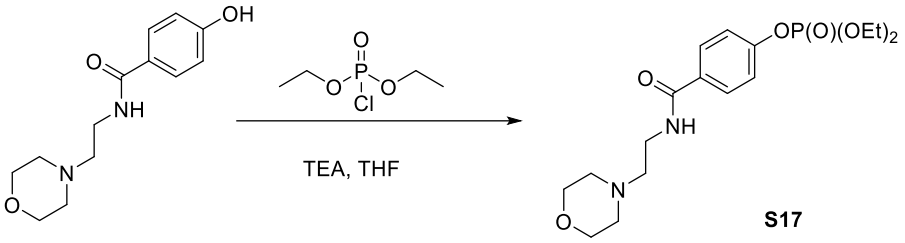
The general procedure GP7 was followed with ethyl acetyl-*L*-tyrosinate (778 mg, 0.2 mmol), triethylamine (0.55 mL, 3.85 mmol), diethyl chlorophosphate (0.48 mL, 3.85 mmol) and THF (12 mL). The mixture was stirred at room temperature overnight. Purification flash chromatography on silica gel (EtOAc/DCM, 3 : 2 v/v) afforded product **S17** (732 mg, 61%) as a colorless oil.



$[\alpha]_D$ = +60 (*c* 0.12M, $CHCl_3$). – ^{1}H NMR (500 MHz, $CDCl_3$): 7.10 (2 H, d, *J* = 8.2 Hz), 7.05 (2 H, d, *J* = 8.6 Hz), 6.14 (1 H, d, *J* = 7.6 Hz), 4.78 (1 H, dt, *J* = 7.9, 5.9 Hz), 4.29–3.87 (6 H, m), 3.05 (2 H, qd, *J* = 14.0, 6.0 Hz), 1.94 (3 H, s), 1.31 (6 H, t, *J* = 7.1 Hz), 1.20 (3 H, t, *J* = 7.2 Hz) ppm. – ^{13}C

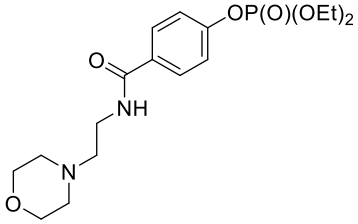
NMR (125 MHz, $CDCl_3$): 171.8, 170.0, 150.1 (d, *J* = 7.0 Hz), 133.1, 130.8, 120.3 (d, *J* = 4.9 Hz), 64.9 (d, *J* = 5.9 Hz), 61.8, 53.5, 37.4, 23.4, 16.4 (d, *J* = 6.9 Hz), 14.4 ppm. – ^{31}P NMR (202 Hz, $CDCl_3$): −6.4 ppm. – IR: 3373, 2988, 1729, 1651, 1557, 1508, 1445, 1374, 1255, 1217, 1167, 1029, 970 cm^{-1}. – HRMS: calcd for $C_{17}H_{27}NO_7P$: 388.1520, found 388.1522 [$M+H^+$].

Diethyl (4-((2-morpholinoethyl)carbamoyl)phenyl) phosphate (S17)



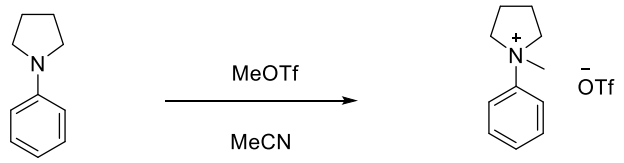
S17

The general procedure GP7 was followed with 4-hydroxy-N-(2-morpholinoethyl)benzamide (775 mg, 3.1 mmol), triethylamine (0.55 mL, 3.85 mmol), diethyl chlorophosphate (0.48 mL, 3.85 mmol) and THF (15 mL). The mixture was stirred at room temperature overnight. Purification flash chromatography on silica gel (MeOH/DCM, 1 : 19 v/v) afforded product **S17** (177 mg, 60%) as a colorless oil.



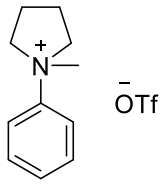
^1H NMR (500 MHz, $CDCl_3$): 7.76 (2 H, d, *J* = 8.6 Hz), 7.27 (2 H, d, *J* = 8.9 Hz), 6.77 (1 H, s), 4.21 (4 H, ddt, *J* = 11.3, 6.8, 3.6 Hz), 3.71 (4 H, t, *J* = 4.6 Hz), 3.53 (2 H, q, *J* = 5.6 Hz), 2.59 (2 H, t, *J* = 6.0 Hz), 2.49 (4 H s), 1.35 (6 H, t, *J* = 7.1 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 166.3, 153.0 (d, *J* = 6.5 Hz), 131.2, 128.6, 119.9 (d, *J* = 5.2 Hz), 66.8, 64.7 (d, *J* = 5.9 Hz), 56.7, 54.0, 35.9, 16.0 (d, *J* = 6.6 Hz) ppm. – ^{31}P NMR (202 Hz, $CDCl_3$): –6.7 ppm. – IR: 3389, 2985, 1636, 1604, 1552, 1500, 1446, 1262, 1220, 1166, 1113, 1024, 964, 936 cm^{-1}. – HRMS: calcd for $C_{17}H_{28}N_2O_6P$: 387.1679, found 387.1673 [$M+H^+$].

1-Methyl-1-phenylpyrrolidin-1-ium trifluoromethanesulfonate (S18)



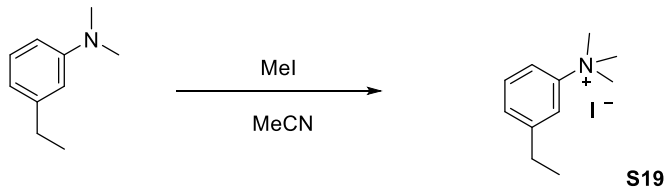
S18

To a solution 1-phenylpyrrolidine (294 mg, 2 mmol) in CH_3CN (5 mL) was added MeOTf (394 mg, 2.4 mmol). The mixture was stirred for 2 h at room temperature, and then concentrated and washed with diethyl ether to afford the desired product **S18** (498 mg, 80%) as a brown liquid.



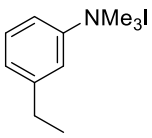
^{1}H NMR (500 MHz, CD_3CN): 7.71 (2 H, d, *J* = 7.7 Hz), 7.66–7.54 (3 H, m), 4.15 (2 H, ddd, *J* = 7.0, 4.8, 2.7 Hz), 3.90 (2 H, dt, *J* = 12.2, 6.5 Hz), 3.34 (3 H, s), 2.29 (4 H, ddd, *J* = 13.3, 7.0, 4.2 Hz) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 131.3, 122.8 (q, *J* = 111.8 Hz), 121.8, 120.7, 66.9, 55.6, 21.4 ppm. – ^{19}F NMR (470.5 Hz, $CDCl_3$): −79.3 ppm. – IR: 3509, 1640, 1596, 1497, 1475, 1456, 1247, 1224, 1156, 1027, 1009, 933, 876 cm^{-1}. – HRMS: calcd for $C_{13}H_{16}F_6NO_6S_2$: 460.0329, found 460.0311 [M+$CF_3O_3S^-$].

3-Ethyl-*N*,*N*,*N*-trimethylbenzenaminium (S19)



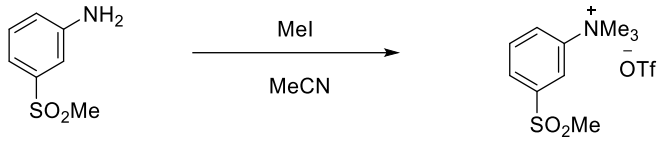
S19

According to a literature procedure, [10] to a solution of 3-ethyl-*N*,*N*-dimethylaniline (447 mg, 3 mmol) in CH_3CN (5 mL) was added CH_3I (1.28 g, 9 mmol). The solution was stirred for 8 h at 90 °C in a screw-capped vial. At the conclusion of the reaction, diethyl ether was added (40 mL), the precipitate was isolated by filtration, washed with ethyl ether, and the residual solvent was removed in vacuo to afford the desired product **S19** (856 mg, 98%) as a colorless solid.



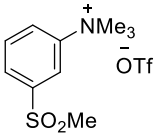
M.p.: > 200 °C. – ^{1}H NMR (500 MHz, CD_3CN): 7.76 (1 H, s), 7.66 (1 H, dd, *J* = 8.4, 2.7 Hz), 7.51 (1 H, t, *J* = 8.0 Hz), 7.42 (1 H, d, *J* = 7.6 Hz), 3.63 (9 H, s), 2.75 (2 H, q, *J* = 7.6 Hz), 1.25 (3 H, t, *J* = 7.6 Hz) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 148.3, 131.0, 130.8, 120.7, 118.1, 58.0, 29.3, 15.8 ppm. – IR: 3004, 1748, 1716, 1614, 1588, 1492, 1473, 1456, 1375, 1338, 1247, 1208, 1181, 1096, 955, 883 cm^{-1}. – HRMS: calcd for $C_{11}H_{18}I_2N$: 417.9534, found 417.9520 [M+I^-].

N,N,N-Trimethyl-3-(methylsulfonyl)benzenaminium trifluoromethanesulfonate (S20)



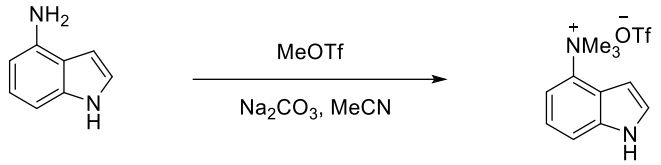
S20

To a solution of 3-(methylsulfonyl)aniline (353 mg, 2 mmol) in CH_3CN (5 mL) was added MeOTf (1.05 g, 6.4 mmol) and Na_2CO_3 (636 mg, 6 mmol). The mixture was stirred for 2 h at room temperature, and then filter through celite® pad, concentrated and washed with diethyl ether to afford the desired product **S20** (566 mg, 78%) as a brown oil.



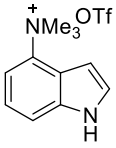
^{1}H NMR (500 MHz, CD_3CN): 8.27 (1 H, dd, *J* = 2.4, 1.4 Hz), 8.16 (1 H, dd, *J* = 8.5, 2.7 Hz), 8.13 (1 H, d, *J* = 8.2 Hz), 7.89 (1 H, t, *J* = 8.2 Hz), 3.63 (9 H, s), 3.16 (3 H, s) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 148.0, 143.8, 132.8, 130.3, 126.6, 120.5 (t, *J* = 320.3 Hz), 120.4, 58.0, 44.2 ppm. – ^{19}F NMR (470.5 Hz, CD_3CN): −79.3 ppm. – IR: 3405, 1635, 1489, 1435, 1310, 1250, 1226, 1157, 1099, 1029, 958 cm^{-1}. – HRMS: calcd for $C_{12}H_{16}F_6NO_8S_3$: 511.9948, found 511.9953 [M+$CF_3O_3S^-$].

N,N,N-Trimethyl-1*H*-indol-4-aminium trifluoromethanesulfonate (S21)



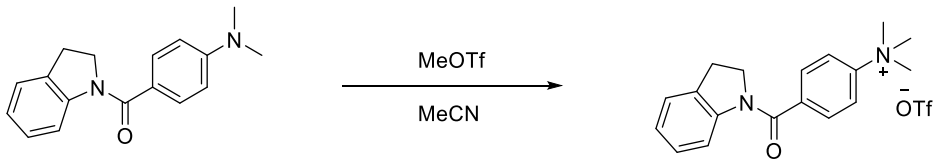
S21

To a solution of 1*H*-indol-4-amine (264 mg, 2 mmol) in CH_3CN (5 mL) was added MeOTf (1.05 g, 6.4 mmol) and Na_2CO_3 (636 mg, 6 mmol). The mixture was stirred for 2 h at room temperature, and then filter through celite® pad, concentrated and washed with diethyl ether to afford the desired product **S21** (389 mg, 60%) as a colorless solid.



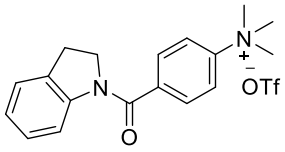
M.p.: > 200 °C. – ^{1}H NMR (500 MHz, CD_3CN): 10.47 (1 H, s), 7.71 (1 H, d, *J* = 8.2 Hz), 7.53 (1 H, t, *J* = 3.0 Hz), 7.37 (1 H, d, *J* = 8.0 Hz), 7.23 (1 H, t, *J* = 8.1 Hz), 6.79 (1 H, s), 3.69 (9 H, s) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 139.2, 138.7, 128.1, 121.6, 121.3 (q, *J* = 319.4 Hz), 118.4, 115.6, 111.2, 100.4, 56.4 ppm. – ^{19}F NMR (470.5 Hz, CD_3CN): –79.2 ppm. – IR: 3493, 1627, 1493, 1342, 1247, 1227, 1168, 1029, 981, 944, 896 cm^{-1}. – HRMS: calcd for $C_{13}H_{15}F_6N_2O_6S_2$: 473.0281, found 473.0292 [M+$CF_3O_3S^-$].

4-(Indoline-1-carbonyl)-*N,N,N*-trimethylbenzenaminium trifluoromethanesulfonate (S22)



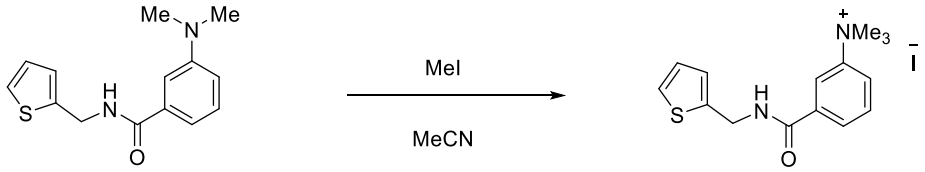
S22

To a solution of (4-(dimethylamino)phenyl)(indolin-1-yl)methanone (532 mg, 2 mmol) in CH_3CN (5 mL) was added MeOTf (394 mg, 2.4 mmol). The mixture was stirred for 2 h at room temperature, and then concentrated and washed with diethyl ether to afford the desired product **S22** (817 mg, 95%) as a colorless solid.



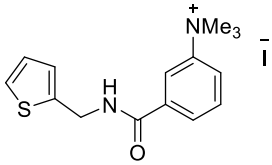
M.p.: > 200 °C. – ^{1}H NMR (500 MHz, CD_3CN): 8.16 (1 H, brs), 7.91 (2 H, d, *J* = 9.0 Hz), 7.78 (2 H, d, *J* = 7.9 Hz), 7.29 (2 H, d, *J* = 7.4 Hz), 7.24 (1 H, s), 7.09 (1 H, s), 3.96 (2 H, brs), 3.61 (9 H, s), 3.14 (2 H, t, *J* = 8.3 Hz) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 167.8, 148.4, 140.5, 129.7, 127.9, 126.0, 125.2, 121.6, 51.5, 28.8 ppm. – ^{19}F NMR (470.5 Hz, CD_3CN): −78.7 ppm. – IR: 1723, 1641, 1596, 1499, 1482, 1463, 1399, 1352, 1257, 1226, 1150, 1119, 1071, 1029, 943 cm^{-1}. – HRMS: calcd for $C_{20}H_{21}F_6N_2O_7S_2$: 579.0700, found 579.0683 [M+$CF_3O_3S^-$].

N,N,N-Trimethyl-3-((thiophen-2-ylmethyl)carbamoyl)benzenaminium iodide (S23)



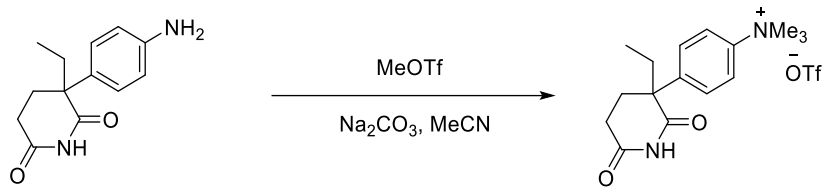
S23

To a solution of 3-(dimethylamino)-*N*-(thiophen-2-ylmethyl)benzamide (520 mg, 2 mmol) in CH_3CN (5 mL) was added MeI (1.2 g, 8 mmol). The mixture was stirred overnight at 80 °C, and then concentrated and washed with diethyl ether to afford the desired product **S23** (788 mg, 98%) as a colorless solid.

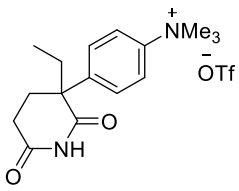


M.p.: 161−164 °C. – ^{1}H NMR (500 MHz, CD_3CN): 8.47 (2 H, s), 8.07 (1 H, d, *J* = 7.8 Hz), 7.95 (1 H, dd, *J* = 8.4, 2.5 Hz), 7.70 (1 H, t, *J* = 8.1 Hz), 7.27 (1 H, d, *J* = 6.1 Hz), 7.09 (1 H, d, *J* = 2.6 Hz), 6.98–6.90 (1 H, m), 4.73 (2 H, d, *J* = 6.0 Hz), 3.65 (9 H, s) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 165.5, 143.0, 137.4, 131.6, 130.4, 127.7, 127.0, 126.0, 123.8, 120.5, 58.2, 38.7 ppm. – IR: 3253, 1709, 1647, 1581, 1529, 1487, 1418, 1355, 1303, 1270, 1218, 1143, 1089, 1041, 950, 935 cm^{-1}. – HRMS: calcd for $C_{15}H_{18}N_2OSI$: 401.0190, found 401.0178 [M+H^+].

4-(3-Ethyl-2,6-dioxopiperidin-3-yl)-*N,N,N*-trimethylbenzenaminium trifluoromethanesulfonate (S24)

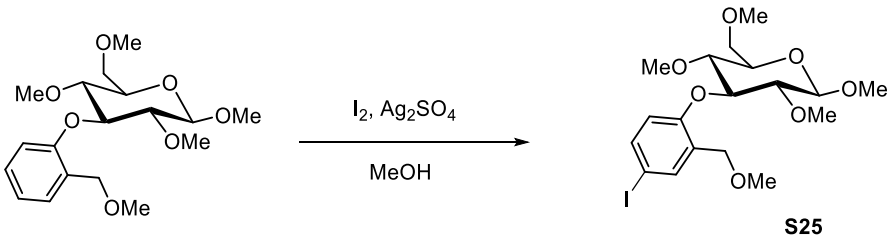


To a solution of 3-(4-aminophenyl)-3-ethylpiperidine-2,6-dione (464 mg, 2 mmol) in CH_3CN (5 mL) was added MeOTf (1.05 g, 6.4 mmol) and Na_2CO_3 (636 mg, 6 mmol). The mixture was stirred for 2 h at room temperature, and then filter through celite® pad, concentrated and washed with diethyl ether to afford the desired product **S24** (678 mg, 80%) as a colorless solid.



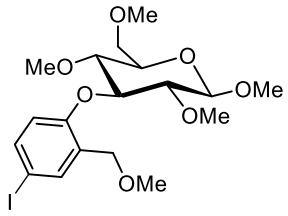
M.p.: 96–99 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 8.85 (1 H, s), 7.77 (2 H, d, *J* = 9.2 Hz), 7.55 (2 H, d, *J* = 9.1 Hz), 3.53 (9 H, s), 2.65–2.47 (1 H, m), 2.46–2.38 (2 H, m), 2.33–2.14 (2 H, m), 2.00 (1 H, dt, *J* = 14.9, 7.4 Hz), 0.83 (3 H, t, *J* = 7.4 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 175.8, 173.1, 143.7, 129.5, 121.8, 121.3, 57.9, 51.6, 32.7, 29.7, 27.6, 9.1 ppm. – ^{19}F NMR (470.5 Hz, CD_3CN): –79.4 ppm. – IR: 2974, 1717, 1684, 1647, 1602, 1510, 1496, 1457, 1354, 1259, 1231, 1195, 1170, 1030 cm^{-1}. – HRMS: calcd for $C_{17}H_{22}F_3N_2O_5S$: 423.1207, found 423.1192 [$M-H^+$].

(2*R*,3*R*,4*S*,5*R*,6*R*)-4-(4-Iodo-2-(methoxymethyl)phenoxy)-2,3,5-trimethoxy-6-(methoxymethyl)tetrahydro-2*H*-pyran (S25)



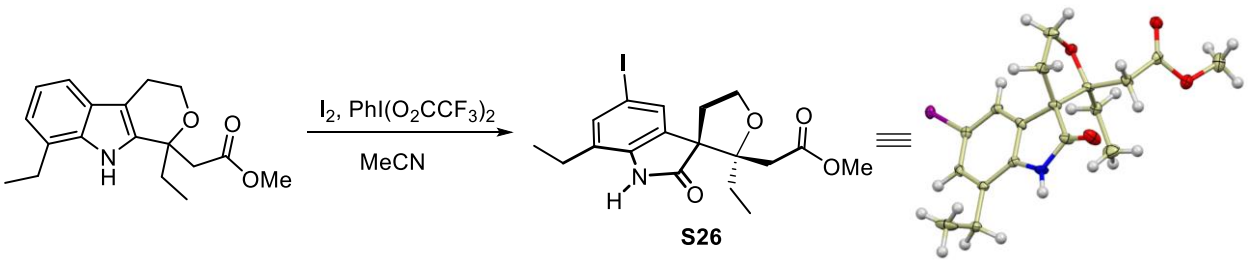
According to a literature procedure,[11] a suspension of (2*R*,3*R*,4*S*,5*R*,6*R*)-2,3,5-trimethoxy-6-(methoxymethyl)-4-(2-(methoxymethyl)phenoxy)tetrahydro-2*H*-pyran

(356 mg, 1.0 mmol), iodine (330 mg, 1.05 mmol) and silver sulfate (328 mg, 1.05 mmol) in methanol was stirred at rt for 1 h and then the solid filtrated off. The filtrate was treated with saturated aqueous sodium sulfite solution until the violet color disappeared and then concentrated under reduced pressure. The resulting residue was extracted with dichloromethane (20 mL) and the organic phase washed with water (2 × 10 mL) and brine (10 mL), and dried over sodium sulfate. Upon removal of the solvent under reduced pressure, compound **S25** was obtained as a colorless solid (429 mg, 89%).



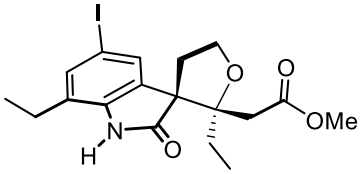
$[\alpha]_D = -39$ (*c* 0.14M, $CHCl_3$). – m.p.: 80–83 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 7.69 (1 H, s), 7.51 (1 H, d, *J* = 8.6 Hz), 6.78 (1 H, d, *J* = 8.6 Hz), 4.75 (1 H, d, *J* = 7.1 Hz), 4.61–4.25 (2 H, m), 3.65 (7 H, d, *J* = 8.9 Hz), 3.55 (4 H, d, *J* = 8.0 Hz), 3.39–3.33 (7 H, m), 3.30–3.19 (3 H, m) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 154.6, 137.4, 137.0, 130.7, 117.3, 101.3, 86.7, 85.8, 83.6, 79.2, 75.0, 71.2, 68.7, 61.1, 60.9, 60.6, 59.5, 58.7 ppm. – IR: 2979, 2939, 1742, 1720, 1609, 1419, 1345, 1288, 1225, 1135, 1093, 1065, 991 cm^{-1}. – HRMS: calcd for $C_{18}H_{31}INO_7$: 500.1140, found 500.1138 [$M+NH_4^+$].

Methyl 2-((2*S*,3*R*)-2,7'-diethyl-5'-iodo-2'-oxo-4,5-dihydro-2*H*-spiro[furan-3,3'-indolin]-2-yl)acetate (S26)



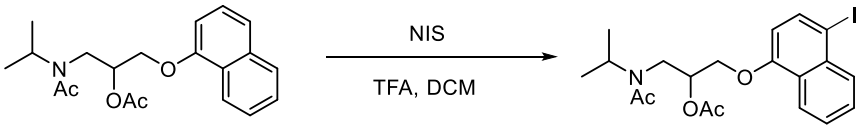
According to literature procedure, [12] methyl 2-(1,8-diethyl-1,3,4,9-tetrahydropyrano[3,4-*b*]indol-1-yl)acetate (903 mg, 3 mmol) and iodine (915 mg, 3.6 mmol) were dissolved in anhydrous CH_3CN (50 mL). $PhI(O_2CCF_3)_2$ (3.1 g, 7.42 mmol) in CH_3CN (60 mL) was

added dropwise to the above solution at room temperature. The reaction mixture stirred at room temperature overnight. The reaction mixture was quenched with 0.1M NaOH and then partition between diethyl ether and H_2O. The combined organic layers were washed with brine, dried, filtered and concentrated. The resulting crude mixture was purified by flash column chromatography on silica gel (EtOAc/hexane, 1 : 6 v/v) to afford the desired product **S26** (1.1 g, 88%) as a colorless liquid.



$[\alpha]_D$ = +35 (*c* 0.10M, $CHCl_3$). – ^{1}H NMR (500 MHz, $CDCl_3$): 8.80 (1 H, s), 7.43 (2 H, s), 4.33 (1 H, td, *J* = 9.5, 4.2 Hz), 4.17 (1 H, q, *J* = 8.7 Hz), 3.65 (3 H, s), 3.05 (1 H, d, *J* = 14.4 Hz), 2.87 (1 H, d, *J* = 14.4 Hz), 2.80–2.72 (1 H, m), 2.56 (2 H, q, *J* = 7.6 Hz), 2.18 (1 H, ddd, *J* = 12.9, 8.7, 4.2 Hz), 1.90 (1 H, dq, *J* = 15.0, 7.6 Hz), 1.51 (1 H, dq, *J* = 14.2, 7.3 Hz), 1.23 (3 H, t, *J* = 7.6 Hz), 0.61 (3 H, t, *J* = 7.5 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 178.7, 171.1, 137.8, 136.6, 134.1, 131.4, 127.9, 88.5, 85.9, 64.5, 59.3, 51.7, 38.4, 36.5, 27.4, 23.9, 14.0, 8.4 ppm. – IR: 2984, 1756, 1628, 1598, 1459, 1433, 1378, 1332, 1259, 1230, 1121, 1051, 988, 899 cm^{-1}. – HRMS: calcd for $C_{18}H_{23}INO_4$: 444.0666, found 444.0671 [$M+H^+$].

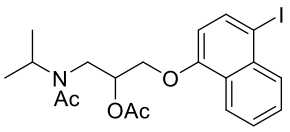
1-((4-Iodonaphthalen-1-yl)oxy)-3-(*N*-isopropylacetamido)propan-2-yl acetate (S27)



S27

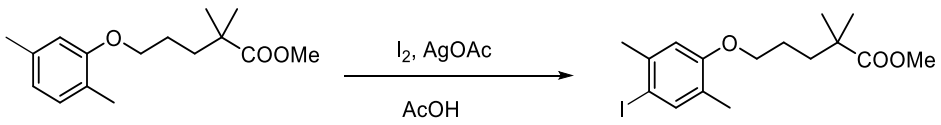
According to literature procedure, [13] 1-(*N*-isopropylacetamido)-3-(naphthalen-1-yloxy)propan-2-yl acetate (0.86 g, 2.5 mmol) was dissolved in anhydrous CH_3CN (10 mL), followed by cooling to 0 °C. Trifluoroacetic acid (0.06 mL, 0.3 equiv.) was then added slowly. Subsequently, a solution of *N*-iodosuccinimide (675 mg, 3.0 mmol) in CH_3CN (8 mL), was added dropwise to the initial solution over a period of 30 minutes, after which point the reaction was warmed to room temperature and stirred overnight. The reaction

was concentrated then diluted with dichloromethane and neutralized with concentrated ammonium hydroxide. The reaction mixture was then extracted with dichloromethane (4 x 25 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated. The resulting crude mixture was purified by flash column chromatography on silica gel (EtOAc/hexane, 5 : 1 v/v) to afford the desired product **S27** (915 mg, 78%)as a brown solid.



M.p.: 79–81 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 8.17 (1 H, d, *J* = 8.3 Hz), 8.01 (1 H, d, *J* = 8.4 Hz), 7.92 (1 H, d, *J* = 8.1 Hz), 7.61–7.54 (1 H, m), 7.51 (1 H, t, *J* = 7.6 Hz), 6.59 (1 H, d, *J* = 8.2 Hz), 5.69–5.52 (1 H, m), 4.38–4.07 (2 H, m), 4.13–4.00 (1 H, m), 3.83 (1 H, dd, *J* = 14.3, 5.6 Hz), 3.37 (1 H, dd, *J* = 14.3, 6.7 Hz), 2.44–1.94 (6 H, m), 1.53–1.05 (6 H, m) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 171.6, 170.6, 155.2, 137.0, 136.8, 134.8, 132.2, 131.9, 128.5, 128.3, 126.7, 126.6, 126.3, 122.5, 122.0, 106.8, 106.6, 88.8, 71.6, 70.9, 68.8, 67.3, 49.7, 47.4, 45.6, 41.5, 29.7, 22.9, 22.3, 21.9, 21.3, 21.1, 20.8, 20.4 ppm. – IR: 2979, 1732, 1622, 1590, 1453, 1419, 1366, 1342, 1259, 1235, 1126, 1058, 982, 896 cm^{-1}. – HRMS: calcd for $C_{20}H_{25}INO_4$: 470.0823, found 470.0818 [$M+H^+$].

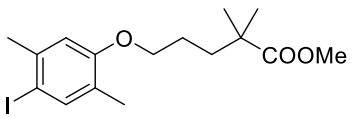
Methyl 5-(4-iodo-2,5-dimethylphenoxy)-2,2-dimethylpentanoate (S28)



S28

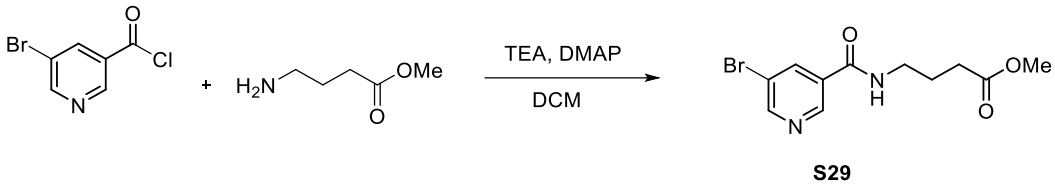
Methyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (1.32 g, 5 mmol) was added to a mixture of iodine (1.27 g, 5 mmol) and silver acetate (0.83 g, 5mmol) in acetic acid (15 mL) at room temperature. The reaction mixture stirred at room temperature overnight. The reaction mixture was quenched with 0.1M NaOH and then partition between diethyl ether and H_2O. The combined organic layers were washed with brine, dried, filtered and concentrated. The resulting crude mixture was purified by flash column chromatography

on silica gel (EtOAc/hexane, 1 : 6 v/v) to afford the desired product **S28** (1.76 g, 90%) as a brown liquid.



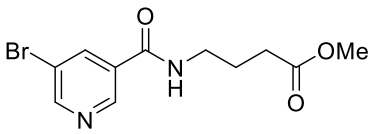
^{1}H NMR (500 MHz, $CDCl_3$): 7.51 (1 H, s), 6.67 (1 H, s), 3.89 (2 H, t, *J* = 5.6 Hz), 3.66 (3 H, s), 2.37 (3 H, s), 2.13 (3 H, s), 1.86–1.56 (4 H, m), 1.22 (6 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 178.3, 157.4, 140.0, 139.4, 126.6, 112.8, 89.1, 68.1, 51.8, 42.2, 37.1, 28.1, 25.3, 25.2, 15.3 ppm. – IR: 1728, 1607, 1493, 1471, 1360, 1312, 1245, 1197, 1140, 1087, 1048, 1031, 1020, 963 cm^{-1}. – HRMS: calcd for $C_{16}H_{24}IO_3$: 391.0765, found 391.0767 [$M+H^+$].

Methyl 4-(5-bromonicotinamido)butanoate (S29)



S29

According to literature procedure,[14] 5-bromonicotinoyl chloride (660 mg, 3 mmol, 1.5 equiv.) was dissolved in DCM (10 mL) and added to a mixture of methyl 4-aminobutanoate (234 mg, 2 mmol), DMAP (24 mg, 0.2 mmol, 0.1 equiv.) and Et_3N (303 mg, 3 mmol, 1.5 equiv.) in DCM (10 mL). The reaction was allowed to stirred overnight at room temperature. Then the mixture was quenched upon addition of 15 mL water and extracted with DCM (3 x 30 mL). The organic phases were combined and concentrated under reduced pressure and purified by flash chromatography on silica gel (EtOAc/hexane 3 : 1 v/v) afford the desired product **S29** (432 mg, 72%) as a colorless solid.

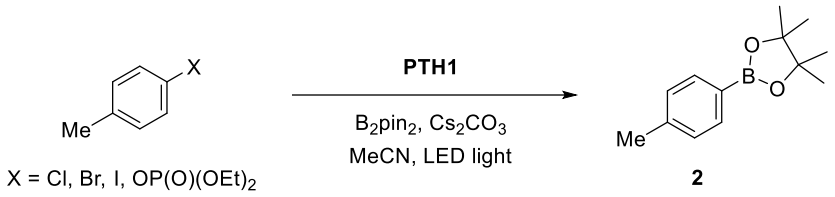


M.p.: 105−108 °C. – ^{1}H NMR (500 MHz, CD_3CN): 8.90 (1 H, s), 8.77 (1 H, d, *J* = 1.8 Hz), 8.28 (1 H, s), 7.05 (1 H, s), 3.69 (3 H, s), 3.52 (2 H, q, *J* = 6.3 Hz), 2.48 (2 H, t, *J* = 6.7 Hz), 1.97 (2 H, p, *J* = 6.7 Hz) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 174.7, 164.3, 153.3, 146.0, 138.0, 131.6, 121.1, 52.1, 40.3, 32.0, 24.1 ppm. – IR: 3390, 1704, 1633, 1588, 1547, 1439, 1365, 1329,

1228, 1175, 1091, 988 cm^{-1}. – HRMS: calcd for $C_{11}H_{14}BrN_2O_3$: 301.0182, found 301.0182 [M+H$^+$].

Borylation products

4,4,5,5-Tetramethyl-2-(*p*-tolyl)-1,3,2-dioxaborolane (2)[15]



From 1-iodo-4-methylbenzene: The general procedure GP1 was followed with 1-iodo-4-methylbenzene (44 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.2 mg, 0.001 mmol, 0.5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **2** (40 mg, 92%) as a colorless oil.

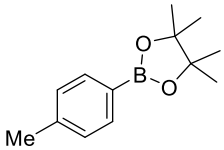
From 1-bromo-4-methylbenzene: The general procedure GP1 was followed with 1-bromo-4-methylbenzene (34 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **2** (30 mg, 69%) as a colorless oil.

From 1-chloro-4-methylbenzene: The general procedure GP1 was followed with 1-chloro-4-methylbenzene (25 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%), H_2O (3.6 mg, 0.2 mmol, 1.0 equiv.) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **2** (31 mg, 80%) as a colorless oil.

From diethyl *p*-tolyl phosphate: The general procedure GP1 was followed with diethyl *p*-tolyl phosphate (46 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 36 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afforded product **2** (36 mg, 83%) as a colorless oil.

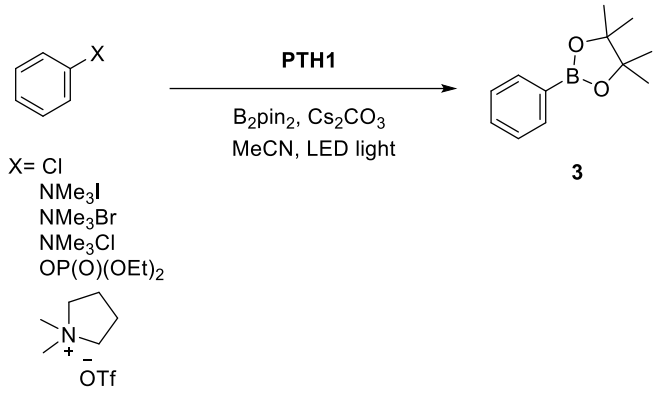
From diethyl *p*-tolyl phosphate with 2 equiv. of B_2pin_2: The general procedure GP1 was followed with diethyl *p*-tolyl phosphate (46 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 36 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afforded product **2** (28 mg, 64%) as a colorless oil.

From diethyl *p*-tolyl phosphate with addition of H_2O: The general procedure GP1 was followed with diethyl *p*-tolyl phosphate (46 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%), H_2O (3.6 mg, 0.2 mmol, 1.0 equiv.) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light at 45 °C for 20 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afforded product **2** (34 mg, 78%) as a colorless oil.



^{1}H NMR (500 MHz, $CDCl_3$): 7.72 (2 H, d, J = 7.7 Hz), 7.20 (2 H, d, J = 7.6 Hz), 2.38 (3 H, s), 1.35 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 141.5, 134.9, 128.6, 83.7, 25.0, 21.9 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.0 ppm. – IR: 2983, 1735, 1446, 1372, 1360, 1235, 1145, 1089, 1044, 938 cm^{-1}.

4,4,5,5-Tetramethyl-2-phenyl-1,3,2-dioxaborolane (3)[15]



From chlorobenzene: The general procedure GP1 was followed with chlorobenzene (22 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%), H_2O (3.6 mg, 0.2 mmol, 1.0 equiv.) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **3** (28 mg, 68%) as a colorless oil.

From *N,N,N*-trimethylbenzenaminium iodide: The general procedure GP1 was followed with *N,N,N*-trimethylbenzenaminium iodide (53 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **3** (36 mg, 88%) as a colorless oil.

From *N,N,N*-trimethylbenzenaminium iodide with 420 nm LED light: The general procedure GP1 was followed with *N,N,N*-trimethylbenzenaminium iodide (53 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 420 nm LED light for 18 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **3** (34 mg, 83%) as a colorless oil.

From *N,N,N*-trimethylbenzenaminium bromide: The general procedure GP1 was followed with *N,N,N*-trimethylbenzenaminium bromide (43 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **3** (31 mg, 76%) as a colorless oil.

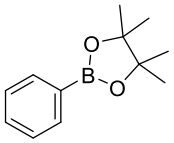
From *N,N,N*-trimethylbenzenaminium chloride: The general procedure GP1 was followed with *N,N,N*-trimethylbenzenaminium chloride (34 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **3** (29 mg, 71%) as a colorless oil.

From 1-methyl-1-phenylpyrrolidin-1-ium((trifluoromethyl)sulfonyl)-λ^1-oxidane: The general procedure GP1 was followed with 1-methyl-1-phenylpyrrolidin-1-ium((trifluoromethyl)sulfonyl)-λ^1-oxidane (62 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **3** (34 mg, 83%) as a colorless oil.

From diethyl phenyl phosphate: The general procedure GP1 was followed with diethyl phenyl phosphate (46 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) and CH_3CN (2 mL). The mixture was irradiated with an 400 m LED light without air flow supply for 36 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **3** (34 mg, 84%) as a colorless oil.

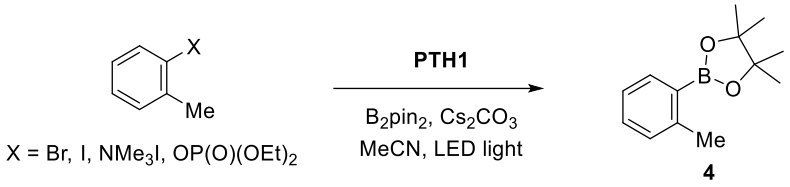
From diethyl phenyl phosphate with 2 equiv. of B_2pin_2: The general procedure GP1 was followed with diethyl phenyl phosphate (46 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0

equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) and CH_3CN (2 mL). The mixture was irradiated with an 400 m LED light without air flow supply for 36 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **3** (31 mg, 80%) as a colorless oil.



^{1}H NMR (500 MHz, $CDCl_3$): 7.82 (2 H, d, *J* = 6.9 Hz), 7.46 (1 H, t, *J* = 7.4 Hz), 7.37 (2 H, t, *J* = 7.4 Hz), 1.35 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 134.9, 131.4, 127.8, 83.9, 25.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.0 ppm. – IR: 2977, 1738, 1604, 1498, 1438, 1358, 1324, 1274, 1216, 1144, 1090, 1027 cm^{-1}.

4,4,5,5-Tetramethyl-2-(*o*-tolyl)-1,3,2-dioxaborolane (4)[15]



From 1-bromo-2-methylbenzene: The general procedure GP1 was followed with 1-bromo-2-methylbenzene (34 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **4** (37 mg, 85%) as a colorless oil.

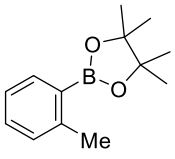
From 1-iodo-2-methylbenzene: The general procedure GP1 was followed with 1-iodo-2-methylbenzene (44 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **4** (38 mg, 87%) as a colorless oil.

From *N,N,N,*2-tetramethylbenzenaminium iodide: The general procedure GP1 was followed with *N,N,N,*2-tetramethylbenzenaminium iodide (56 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **4** (34 mg, 78%) as a colorless oil.

Gram scale from *N,N,N,*2-tetramethylbenzenaminium iodide: According to general procedure GP1 three identical reactions were run with *N,N,N,*2-tetramethylbenzenaminium iodide (0.98 g, 3.5 mmol), B_2pin_2 (2.67 g, 10.5 mmol, 3.0 equiv.), Cs_2CO_3 (3.45 g, 10.5 mmol, 3.0 equiv.), **PTH1** (34.9 mg, 0.175 mmol, 5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 450 nm LED light for 36 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afforded product **4** (1.7 g, 78%) as a colorless solid.

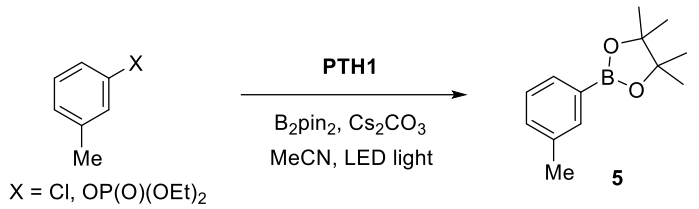
From *N,N,N,*2-tetramethylbenzenaminium iodide with 420 nm LED light: The general procedure GP1 was followed with *N,N,N,*2-tetramethylbenzenaminium iodide (56 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 420 nm LED light for 18 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **4** (39 mg, 89%) as a colorless oil.

From diethyl *o*-tolyl phosphate: The general procedure GP1 was followed with diethyl *o*-tolyl phosphate (49 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%), H_2O (3.6 mg, 0.2 mmol, 1.0 equiv.) and CH_3CN (2 mL). The mixture was irradiated with an 400 m LED light without air flow supply for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **4** (28 mg, 80%) as a colorless oil.



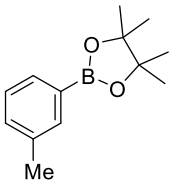
^{1}H NMR (500 MHz, $CDCl_3$): 7.76 (1 H, d, *J* = 7.2 Hz), 7.31 (1 H, t, *J* = 7.3 Hz), 7.16 (2 H, t, *J* = 6.5 Hz), 2.54 (3 H, s), 1.34 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 145.0, 136.0, 130.9, 129.9, 124.8, 83.6, 25.0, 22.4 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.3 ppm. – IR: 2977, 2928, 1601, 1490, 1439, 1379, 1345, 1311, 1273, 1213, 1145, 1072 cm^{-1}.

4,4,5,5-Tetramethyl-2-(*m*-tolyl)-1,3,2-dioxaborolane (5)[15]



From 1-chloro-3-methylbenzene: The general procedure GP1 was followed with 1-chloro-3-methylbenzene (25 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%), H_2O (3.6 mg, 0.2 mmol, 1.0 equiv.) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **5** (32 mg, 77%) as a colorless oil.

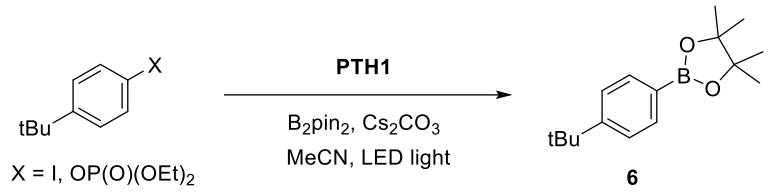
From diethyl *m*-tolyl phosphate: The general procedure GP1 was followed with diethyl *m*-tolyl phosphate (49 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.020 mmol, 10 mol%), H_2O (3.6 mg, 0.2 mmol, 1.0 equiv.) and CH_3CN (2 mL). The mixture was irradiated with an 400 m LED light without air flow supply for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **5** (29 mg, 84%) as a colorless oil.



^{1}H NMR (500 MHz, $CDCl_3$): 7.65 (1 H, s), 7.64–7.59 (1 H, m), 7.31–7.27 (2 H, m), 2.36 (3 H, s), 1.35 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 137.3,

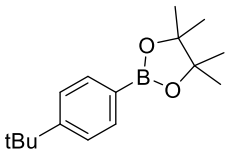
135.5, 132.2, 131.9, 127.8, 83.9, 25.0, 21.4 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.0 ppm. – IR: 2976, 2927, 1738, 1606, 1583, 1416, 1353, 1267, 1207, 112, 1102, 1078 cm^{-1}.

2-(4-(*tert*-Butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6)[15]



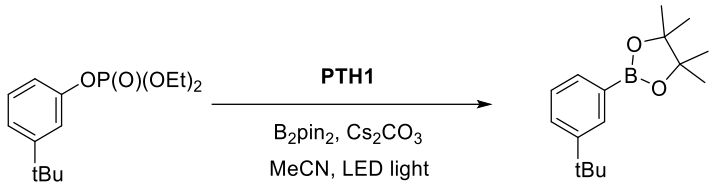
From 1-(*tert*-butyl)-4-iodobenzene: The general procedure GP1 was followed with 1-(*tert*-butyl)-4-iodobenzene (52 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.08 mg, 0.0004 mmol, 0.2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **6** (42 mg, 81%) as a colorless solid.

From 4-(*tert*-butyl)phenyl diethyl phosphate: The general procedure GP1 was followed with 4-(*tert*-butyl)phenyl diethyl phosphate (58 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.020 mmol, 10 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afforded product **6** (31 mg, 60%) as a colorless solid.



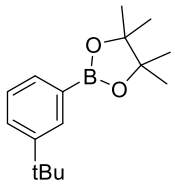
M.p.: 139–141 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 7.77 (2 H, d, J = 8.2 Hz), 7.42 (2 H, d, J = 8.2 Hz), 1.34 (12 H, s), 1.33 (9 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 154.6, 134.8, 124.8, 83.7, 35.0, 31.3, 25.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.0 ppm. – IR: 2964, 1611, 1462, 1400, 1362, 1323, 1271, 1214, 1144, 1118 cm^{-1}.

2-(3-(*tert*-Butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7)[16]



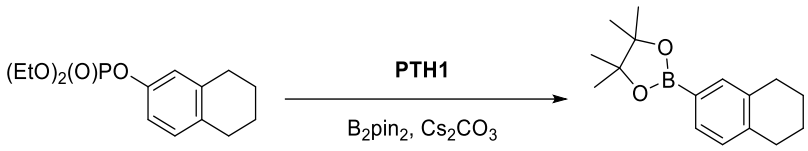
7

The general procedure GP1 was followed with 3-(*tert*-butyl)phenyl diethyl phosphate (58 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.8 mg, 0.024 mmol, 12 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afforded product **7** (30 mg, 57%) as a colorless oil.



^{1}H NMR (500 MHz, $CDCl_3$): 7.86 (1 H, s), 7.66 (1 H, d, *J* = 7.3 Hz), 7.52 (1 H, ddd, *J* = 7.9, 2.2, 1.3 Hz), 7.33 (1 H, t, *J* = 7.6 Hz), 1.37 (21 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 150.3, 132.2, 131.5, 128.5, 127.6, 83.8, 34.8, 31.6, 25.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.1 ppm. – IR: 2965, 1603, 1477, 1414, 1354, 1313, 1260, 1213, 1145, 1102, 1081, 963 cm^{-1}.

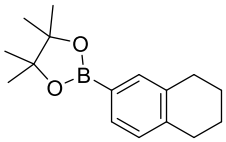
4,4,5,5-Tetramethyl-2-(5,6,7,8-tetrahydronaphthalen-2-yl)-1,3,2-dioxaborolane (8)[17]



8

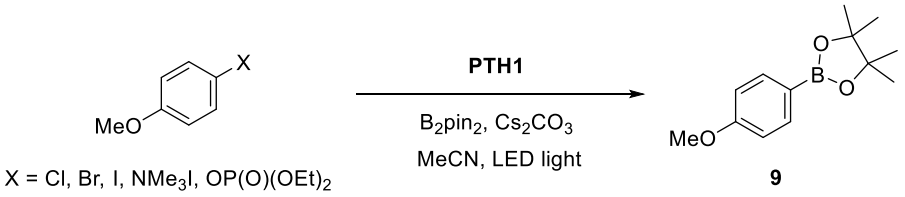
The general procedure GP1 was followed with diethyl (5,6,7,8-tetrahydronaphthalen-2-yl) phosphate (57 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) and CH_3CN (2 mL). The

mixture was irradiated with a 400 nm LED light without air flow supply for 72 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afforded **8** (30 mg, 57%) as a colorless liquid.



^{1}H NMR (500 MHz, $CDCl_3$): 7.54 (1 H, s), 7.52 (1 H, s), 7.08 (1 H, d, *J* = 7.4 Hz), 2.78 (4 H, s), 1.80 (4 H, p, *J* = 3.1 Hz), 1.34 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 140.9, 136.6, 135.8, 131.8, 128.8, 83.7, 29.8, 29.3, 25.0, 23.4, 23.2 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 30.8 ppm. – IR: 1738, 1635, 1612, 1407, 1363, 1350, 1310, 1238, 1183, 1145, 1090, 1045, 964, 910 cm^{-1}.

2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9)[15]



From 1-iodo-4-methoxybenzene: The general procedure GP1 was followed with 1-iodo-4-methoxybenzene (47 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.2 mg, 0.001 mmol, 0.5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **9** (44 mg, 94%) as a colorless oil.

From 1-iodo-4-methoxybenzene with 1.2 equiv. of B_2pin_2: The general procedure GP1 was followed with 1-iodo-4-methoxybenzene (47 mg, 0.2 mmol), B_2pin_2 (61 mg, 0.24 mmol, 1.2 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.2 mg, 0.001 mmol, 0.5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **9** (44 mg, 94%) as a colorless oil.

From 1-bromo-4-methoxybenzene: The general procedure GP1 was followed with 1-bromo-4-methoxybenzene (36 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **9** (42 mg, 90%) as a colorless oil.

From 1-chloro-4-methoxybenzene: The general procedure GP1 was followed with 1-chloro-4-methoxybenzene (28 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (2 mg, 0.01 mmol, 5 mol%), H_2O (3.6 mg, 0.2 mmol, 1.0 equiv.) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **9** (38 mg, 72%) as a colorless oil.

From 4-methoxy-*N,N,N*-trimethylbenzenaminium iodide: The general procedure GP1 was followed with 4-methoxy-*N,N,N*-trimethylbenzenaminium iodide (59 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 16 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **9** (40 mg, 85%) as a colorless oil.

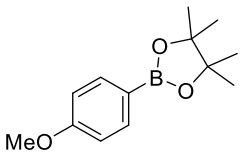
From 4-methoxy-*N,N,N*-trimethylbenzenaminium iodide with 420 nm LED light: The general procedure GP1 was followed with 4-methoxy-*N,N,N*-trimethylbenzenaminium iodide (59 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 420 nm LED light for 18 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **9** (39 mg, 83%) as a colorless oil.

From 4-methoxy-*N,N,N*-trimethylbenzenaminium iodide with 2 equiv. of B_2pin_2: The general procedure GP1 was followed with 4-methoxy-*N,N,N*-trimethylbenzenaminium iodide (59 mg, 0.2 mmol), B_2pin_2 (76 mg, 0.3 mmol, 1.5 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol,

3.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 420 nm LED light for 18 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **9** (34 mg, 73%) as a colorless oil.

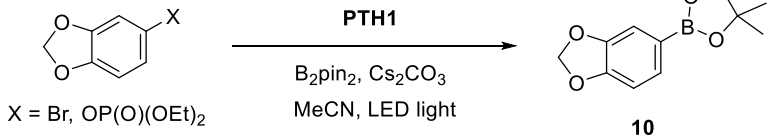
From diethyl (4-methoxyphenyl) phosphate: The general procedure GP1 was followed with diethyl (4-methoxyphenyl) phosphate (52 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.020 mmol, 10 mol%), H_2O (3.6 mg, 0.2 mmol, 1.0 equiv.) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afforded product **9** (34 mg, 72%) as a colorless oil.

From diethyl (4-methoxyphenyl) phosphate with 2 equiv. of B_2pin_2: The general procedure GP1 was followed with diethyl (4-methoxyphenyl) phosphate (52 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.020 mmol, 10 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afforded product **9** (26 mg, 55%) as a colorless oil.



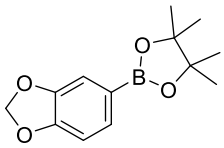
^{1}H NMR (500 MHz, $CDCl_3$): 7.77 (2 H, d, *J* = 8.6 Hz), 6.90 (2 H, d, *J* = 8.6 Hz), 3.83 (3 H, s), 1.34 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 162.3, 136.6, 113.4, 83.6, 55.2, 25.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.0 ppm. – IR: 2983, 1736, 1605, 1446, 1395, 1372, 1360, 1235, 1144, 1091, 1044 cm^{-1}.

2-(Benzo[*d*][1,3]dioxol-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10)[18]



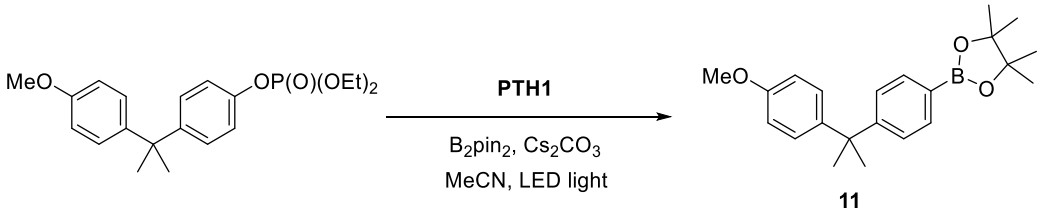
From 5-bromobenzo[*d*][1,3]dioxole: The general procedure GP1 was followed with 5-bromobenzo[*d*][1,3]dioxole (40 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **10** (40 mg, 80%) as a colorless solid.

From benzo[*d*][1,3]dioxol-5-yl diethyl phosphate: The general procedure GP1 was followed with benzo[*d*][1,3]dioxol-5-yl diethyl phosphate (55 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.8 mg, 0.024 mmol, 12 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 36 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afforded product **10** (36 mg, 83%) as a colorless solid.



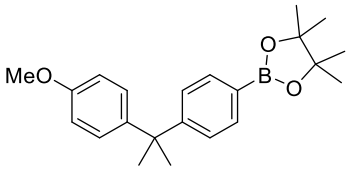
M.p.: 41−43 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 7.36 (1 H, d, *J* = 7.7 Hz), 7.24 (1 H, s), 6.83 (1 H, d, *J* = 7.7 Hz), 5.95 (2 H, s), 1.33 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 150.3, 147.3, 129.9, 114.1, 108.4, 100.8, 83.8, 25.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 30.6 ppm. – IR: 2980, 1710, 1435, 1354, 1236, 1219, 1144, 1091, 1057, 1037, 963 cm^{-1}.

2-(4-(2-(4-Methoxyphenyl)propan-2-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11)



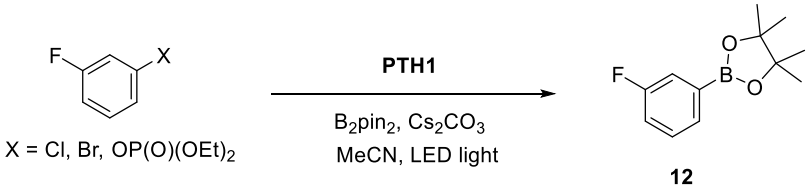
The general procedure GP1 was followed with diethyl (4-(2-(4-methoxyphenyl)propan-2-yl)phenyl) phosphate (76 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3

(197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 72 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afforded **11** (36 mg, 52%) as a colorless solid.



M.p.: 88–90 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 7.75 (2 H, d, *J* = 8.2 Hz), 7.27 (2 H, d, *J* = 8.3 Hz), 7.15 (2 H, d, *J* = 8.8 Hz), 6.82 (2 H, d, *J* = 8.8 Hz), 3.79 (3 H, s), 1.68 (6 H, s), 1.35 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 157.6, 154.4, 142.8, 134.7, 127.9, 126.3, 113.4, 83.8, 55.3, 42.7, 30.9, 25.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 30.9 ppm. – IR: 1609, 1511, 1464, 1397, 1361, 1320, 1258, 1181, 1143, 1117, 1094, 1034, 1020 cm^{-1}. – HRMS: calcd for $C_{22}H_{30}BO_3$: 353.2283, found 353.2284 [M+H$^+$].

2-(3-Fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12)[19]

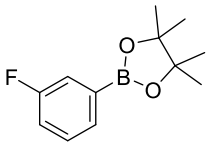


From 1-fluoro-3-bromobenzene: The general procedure GP1 was followed with 1-fluoro-3-bromobenzene (35 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **12** (44 mg, 99%) as a colorless oil.

From 1-fluoro-3-chlorobenzene: The general procedure GP1 was followed with 1-fluoro-3-bromobenzene (35 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (2.0 mg, 0.1 mmol, 5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 72 h.

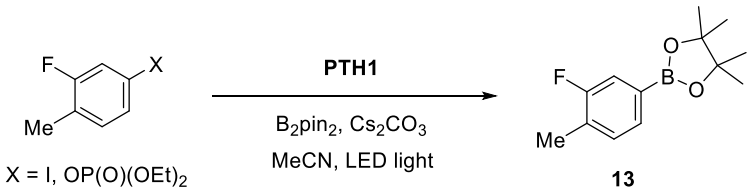
Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **12** (26 mg, 60%) as a colorless oil.

From diethyl (3-fluorophenyl) phosphate: The general procedure GP1 was followed with diethyl (3-fluorophenyl) phosphate (50 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 420 nm LED light without air flow supply for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afforded product **12** (23 mg, 52%) as a colorless oil.



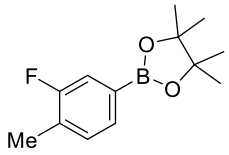
^{1}H NMR (500 MHz, $CDCl_3$): 7.58 (1 H, d, *J* = 7.3 Hz), 7.49 (1 H, dd, *J* = 9.2, 2.5 Hz), 7.34 (1 H, td, *J* = 7.8, 5.5 Hz), 7.22–7.11 (1 H, m), 1.35 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 162.6 (d, *J* = 246.6 Hz), 130.4 (d, *J* = 3.2 Hz), 129.6 (d, *J* = 7.2 Hz), 121.1 (d, *J* = 19.2 Hz), 118.3 (d, *J* = 21.0 Hz), 84.2, 25.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 30.6 ppm. – ^{19}F NMR (470.5 Hz, $CDCl_3$): −114.2 (td, *J* = 9.1, 5.6 Hz) ppm. – IR: 2979, 1580, 1488, 1430, 1380, 1372, 1353, 1324, 1298, 1262, 1206, 1143, 1112, 1091, 1061, 964 cm^{-1}.

2-(3-Fluoro-4-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13)[20]



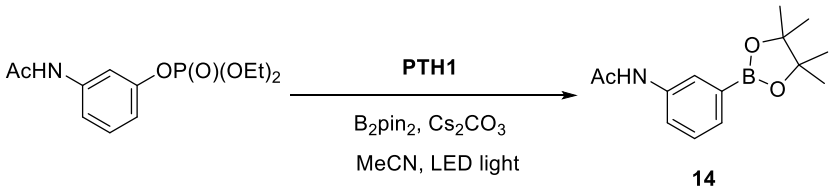
From 2-fluoro-4-iodo-1-methylbenzene: The general procedure GP1 was followed with 2-fluoro-4-iodo-1-methylbenzene (47 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.08 mg, 0.0004 mmol, 0.2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **13** (39 mg, 83%) as a colorless oil.

From diethyl (3-fluoro-4-methylphenyl) phosphate: The general procedure GP1 was followed with diethyl (3-fluoro-4-methylphenyl) phosphate (52 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 420 nm LED light without air flow supply for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afforded product **13** (23.5 mg, 50%) as a colorless oil.

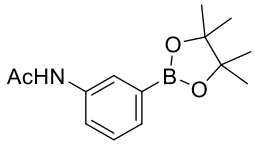


^{1}H NMR (500 MHz, $CDCl_3$): 7.46 (1 H, d, *J* = 7.4 Hz), 7.41 (1 H, d, *J* = 10.1 Hz), 7.18 (1 H, t, *J* = 7.4 Hz), 2.29 (3 H, s), 1.34 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 161.3 (d, *J* = 245.2 Hz), 131.2 (d, *J* = 4.5 Hz), 130.3 (d, *J* = 3.6 Hz), 128.4 (d, *J* = 17.2 Hz), 120.8 (d, *J* = 20.5 Hz), 84.1, 25.0, 14.9 (d, *J* = 3.7 Hz) ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 30.6 ppm. – ^{19}F NMR (470.5 Hz, $CDCl_3$): −119.1 ppm. – IR: 2978, 2929, 1624, 1566, 1511, 1406, 1351, 1319, 1286, 1266, 1217, 1143, 1129, 1076 cm^{-1}.

N-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetamide (14)[21]



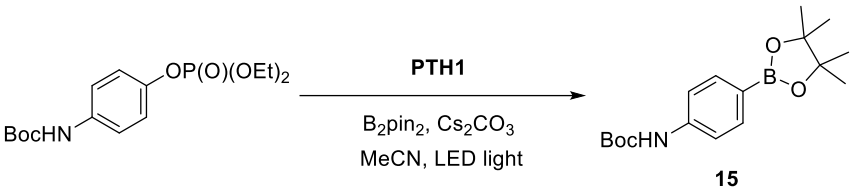
The general procedure GP1 was followed with 3-acetamidophenyl diethyl phosphate (58 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 2 : 3 v/v) afforded product **14** (31 mg, 60%) as a colorless solid.



M.p.: 186–187 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 7.85 (1 H, d, *J* = 7.8 Hz), 7.65 (1 H, s), 7.53 (1 H, d, *J* = 7.3 Hz), 7.43 (1 H, s), 7.33 (1 H, t, *J* = 7.7 Hz), 2.15 (3 H, s), 1.32 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$):

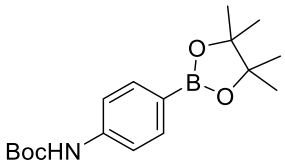
168.6, 137.5, 130.7, 128.7, 126.0, 123.3, 84.0, 25.0, 24.6 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 30.5 ppm. – IR: 2980, 1723, 1625, 1572, 1521, 1399, 1367, 1318, 1269, 1221, 1160, 1144, 1107, 1096, 1021 cm^{-1}.

***tert*-Butyl (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)carbamate (15)** [22]



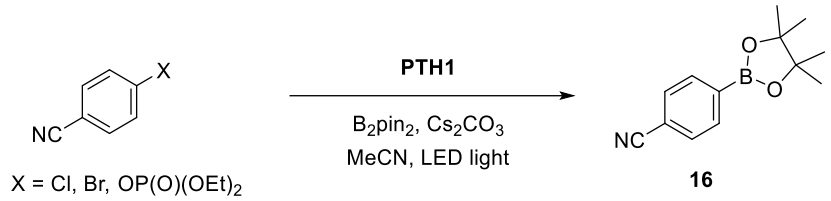
The general procedure GP1 was followed with 3-acetamidophenyl diethyl phosphate (69 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 4 v/v) afforded product **15** (47 mg, 73%) as a colorless solid.

With 2 equiv. of B_2pin_2: The general procedure GP1 was followed with 3-acetamidophenyl diethyl phosphate (69 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 40 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 4 v/v) afforded product **15** (38 mg, 60%) as a colorless solid.



M.p.: 135–137 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 7.73 (2 H, d, J = 8.5 Hz), 7.36 (2 H, d, J = 8.1 Hz), 6.59 (1 H, s), 1.51 (9 H, s), 1.33 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 152.6, 141.2, 136.0, 117.3, 83.8, 80.8, 28.4, 25.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.0 ppm. – IR: 3344, 2977, 1698, 1610, 1587, 1509, 1397, 1357, 1314, 1232, 1139, 1091, 1016, 962 cm^{-1}.

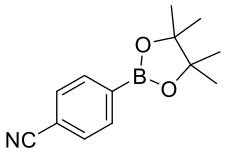
4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (16)[15]



From 4-bromobenzonitrile: The general procedure GP1 was followed with 4-bromobenzonitrile (36 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.4 mg, 0.008 mmol, 1 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **16** (38 mg, 83%) as a colorless solid.

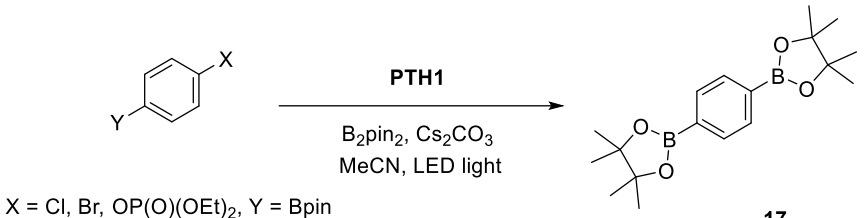
Gram scale from 4-chlorobenzonitrile: According to general procedure GP1 two identical reactions were run with 4-chlorobenzonitrile (550 mg, 4 mmol), B_2pin_2 (2.0 g, 8.0 mmol, 2.0 equiv.), Cs_2CO_3 (2.6 g, 8.0 mmol, 2.0 equiv.), **PTH1** (15.9 mg, 0.08 mmol, 2 mol%) and CH_3CN (40 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **16** (1.2 g, 66%) as a colorless solid.

From 4-cyanophenyl diethyl phosphate: The general procedure GP1 was followed with 4-cyanophenyl diethyl phosphate (51 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 450 nm LED light without air flow supply for 36 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afforded product **16** (31 mg, 68%) as a colorless solid.



M.p.: 96–98 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 7.88 (2 H, d, J = 8.1 Hz), 7.64 (2 H, d, J = 8.2 Hz), 1.35 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 135.2, 131.3, 119.0, 114.7, 84.6, 25.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 30.4 ppm. – IR: 2969, 1612, 1487, 1432, 1364, 1323, 1256, 1220, 1149, 1105, 1089, 968 cm^{-1}.

1,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (17)[15]



17

X = Cl, Br, $OP(O)(OEt)_2$, Y = Bpin
X = Cl, Y= I
X= Br, Y = I
X = Y = I
X= Cl, Y = Br
X = $OP(O)(OEt)_2$, Y = Cl
X = $OP(O)(OEt)_2$, Y = Br
X = Y = NMe_3I
X = NMe_3I, Y = Br

From 2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: The general procedure GP1 was followed with 2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (56 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by Kugelrohr distillation (150 °C, 2 h) according to GP5 afforded boronic ester **17** (61 mg, 92%) as a colorless solid.

From 2-(4-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: The general procedure GP1 was followed with 2-(4-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (48 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by Kugelrohr distillation (150 °C, 2 h) according to GP5 afforded boronic ester **17** (49 mg, 74%) as a colorless solid.

From diethyl (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) phosphate: The general procedure GP1 was followed with diethyl (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) phosphate (71 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0

equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 48 h. Purification by Kugelrohr distillation (150 °C, 2 h) according to GP5 afforded boronic ester **17** (52 mg, 79%) as a colorless solid.

Gram scale from diethyl (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) phosphate: According to general procedure GP1 two identical reactions were run with diethyl (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) phosphate (1.42 g, 4 mmol), B_2pin_2 (3.05 g, 12.0 mmol, 3.0 equiv.), Cs_2CO_3 (3.95 g, 12.0 mmol, 3.0 equiv.), **PTH1** (79.7 mg, 0.4 mmol, 10 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 48 h. Purification by Kugelrohr distillation (150 °C, 3h) according to GP5 afforded boronic ester **17** (1.6 mg, 61%) as a colorless solid.

From 1,4-diiodobenzene: The general procedure GP1 was followed with 1,4-diiodobenzene (66 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), B_2pin_2 (203 mg, 0.8 mmol, 4.0 equiv.), Cs_2CO_3 (263 mg, 0.8 mmol, 4.0 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (4 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by Kugelrohr distillation (150 °C, 2 h) according to GP5 afforded boronic ester **17** (64 mg, 97%) as a colorless solid.

From 1-bromo-4-iodobenzene: The general procedure GP1 was followed with 1-bromo-4-iodobenzene (56 mg, 0.2 mmol), B_2pin_2 (203 mg, 0.8 mmol, 4.0 equiv.), Cs_2CO_3 (263 mg, 0.8 mmol, 4.0 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (4 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by Kugelrohr distillation (150 °C, 2 h) according to GP5 afforded boronic ester **17** (47 mg, 71%) as a colorless solid.

From 1-chloro-4-iodobenzene: The general procedure GP1 was followed with 1-chloro-4-iodobenzene (48 mg, 0.2 mmol), B_2pin_2 (203 mg, 0.8 mmol, 4.0 equiv.), Cs_2CO_3 (263 mg, 0.8 mmol, 4.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (4 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by Kugelrohr

distillation (150 °C, 2 h) according to GP5 afforded boronic ester **17** (53 mg, 80%) as a colorless solid.

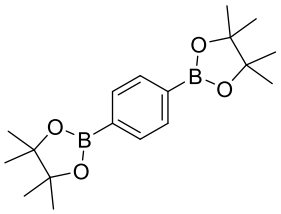
From 1-bromo-4-chlorobenzene: The general procedure GP1 was followed with 1-bromo-4-chlorobenzene (38 mg, 0.2 mmol), B_2pin_2 (203 mg, 0.8 mmol, 4.0 equiv.), Cs_2CO_3 (263 mg, 0.8 mmol, 4.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (4 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by Kugelrohr distillation (150 °C, 2 h) according to GP5 afforded boronic ester **17** (41 mg, 62%) as a colorless solid.

From 4-bromophenyl diethyl phosphate: The general procedure GP1 was followed with 4-bromophenyl diethyl phosphate (62 mg, 0.2 mmol), B_2pin_2 (254 mg, 1.0 mmol, 5.0 equiv.), Cs_2CO_3 (263 mg, 0.8 mmol, 4.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (4.5 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by Kugelrohr distillation (150 °C, 2.5 h) according to GP5 afforded boronic ester **17** (56 mg, 85%) as a colorless solid.

From 4-chlorophenyl diethyl phosphate: The general procedure GP1 was followed with 4-chlorophenyl diethyl phosphate (53 mg, 0.2 mmol), B_2pin_2 (254 mg, 1.0 mmol, 5.0 equiv.), Cs_2CO_3 (329 mg, 1.0 mmol, 5.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (4.5 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by Kugelrohr distillation (150 °C, 2.5 h) according to GP5 afforded boronic ester **17** (46 mg, 70%) as a colorless solid.

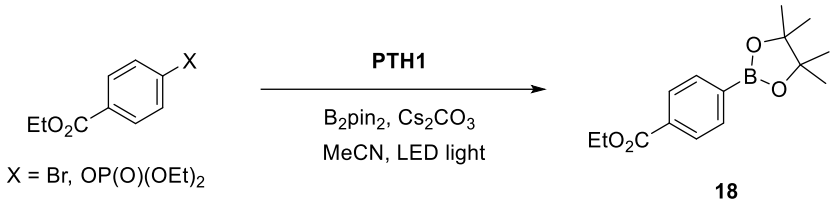
From 4-bromo-*N,N,N*-trimethylbenzenaminium iodide: The general procedure GP1 was followed with 4-bromo-*N,N,N*-trimethylbenzenaminium iodide (68 mg, 0.2 mmol), B_2pin_2 (254 mg, 1.0 mmol, 5.0 equiv.), Cs_2CO_3 (329 mg, 1.0 mmol, 5.0 equiv.), **PTH1** (2.4 mg, 0.012 mmol, 6 mol%) and CH_3CN (4.5 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by Kugelrohr distillation (150 °C, 2 h) according to GP5 afforded boronic ester **17** (58 mg, 88%) as a colorless solid.

From *N*¹,*N*¹,*N*¹,*N*⁴,*N*⁴,*N*⁴-hexamethylbenzene-1,4-diaminium iodide: The general procedure GP1 was followed with *N*¹,*N*¹,*N*¹,*N*⁴,*N*⁴,*N*⁴-hexamethylbenzene-1,4-diaminium iodide (90 mg, 0.2 mmol), B_2pin_2 (203 mg, 0.8 mmol, 4.0 equiv.), Cs_2CO_3 (263 mg, 0.8 mmol, 4.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (4.5 mL). The mixture was irradiated with a 400 nm LED light for 24 h. Purification by Kugelrohr distillation (150 °C, 2.5 h) according to GP5 afforded boronic ester **17** (47 mg, 71%) as a colorless solid.



M.p.: > 220 ^{0}C. – ^{1}H NMR (500 MHz, $CDCl_3$): 7.80 (4 H, s), 1.35 (24 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 134.0, 84.0, 25.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.0 ppm. – IR: 2981, 1732, 1521, 1393, 1372, 1347, 1322, 1237, 1141, 1099, 1044, 1019 cm^{-1}.

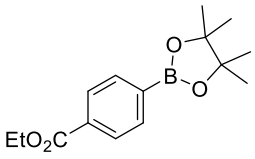
Ethyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (18)[15]



From ethyl 4-bromobenzoate: The general procedure GP1 was followed with ethyl 4-bromobenzoate (45 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **18** (45 mg, 82%) as a colorless solid.

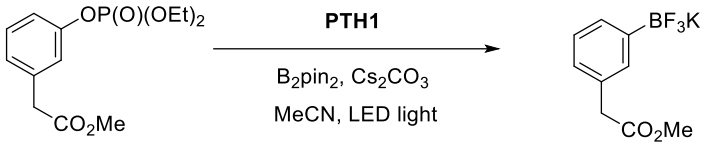
From ethyl 4-((diethoxyphosphoryl)oxy)benzoate: The general procedure GP1 was followed with ethyl 4-((diethoxyphosphoryl)oxy)benzoate (60 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light

without air flow supply for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afforded product **18** (31 mg, 56%) as a colorless solid.



M.p.: 78–80 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 8.02 (2 H, d, *J* = 8.3 Hz), 7.86 (2 H, d, *J* = 8.2 Hz), 4.38 (2 H, q, *J* = 7.1 Hz), 1.40 (3 H, t, *J* = 7.1 Hz), 1.35 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 166.8, 134.8, 132.8, 128.7, 84.3, 61.2, 25.0, 14.5 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.0 ppm. – IR: 2979, 1713, 1614, 1561, 1508, 1398, 1357, 1308, 1266, 1218, 1167, 1143, 1107, 1096, 1021, 962 cm^{-1}.

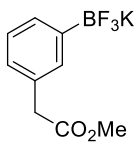
Methyl 2-(3-(trifluoro-λ^4-boraneyl)phenyl)acetate, potassium salt (19)



19

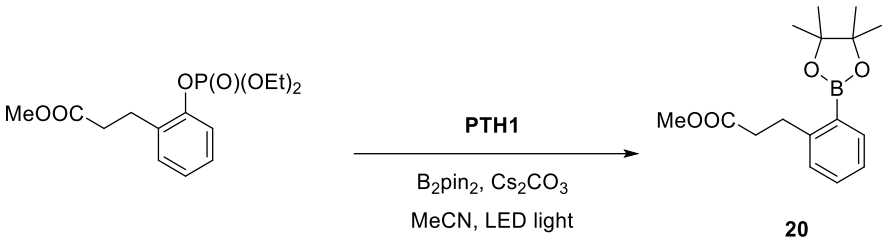
The general procedure GP1 was followed with methyl 2-(3-((diethoxyphosphoryl)oxy)phenyl)acetate (60 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 72 h. Purification by treatment with methylboronic acid and then KHF_2 according to GP4 afforded organotrifluoroborate salt **19** (41 mg, 81%) as a colorless solid.

With 1.5 equiv. of B_2pin_2: The general procedure GP1 was followed with methyl 2-(3-((diethoxyphosphoryl)oxy)phenyl)acetate (60 mg, 0.2 mmol), B_2pin_2 (76 mg, 0.3 mmol, 1.5 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 72 h. Purification by treatment with methylboronic acid and then KHF_2 according to GP4 afforded organotrifluoroborate salt **19** (29 mg, 56%) as a colorless solid.

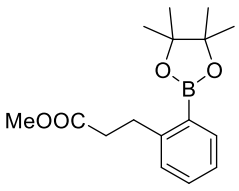


M.p.: > 200 °C. – ^{1}H NMR (500 MHz, CD_3CN): 7.34 (1 H, d, *J* = 7.3 Hz), 7.32 (1 H, s), 7.14 (1 H, t, *J* = 7.4 Hz), 7.02 (1 H, d, *J* = 7.5 Hz), 3.63 (3 H, s), 3.57 (2 H, s) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 173.6, 133.34, 133.29, 130.9, 127.7, 127.4, 52.2, 41.8 ppm. – ^{11}B NMR (160.4 Hz, CD_3CN): 3.6 ppm. – ^{19}F NMR (470.5 Hz, CD_3CN): −142.2 ppm. – IR: 2132, 1720, 1636, 1434, 1329, 1239, 1181, 1158, 1141, 1098, 1022, 998, 947 cm^{-1}. – HRMS: calcd for $C_9H_9BF_3O_2$: 217.0653, found 217.0653 [M−K$^+$].

Methyl 3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propanoate (20)

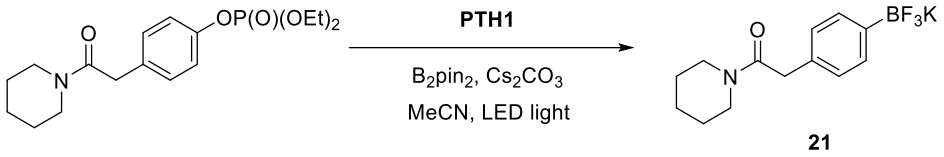


The general procedure GP1 was followed with methyl 3-(2-((diethoxyphosphoryl)oxy)phenyl)propanoate (63 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 72 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 14 v/v) afford product **20** (41 mg, 70%) as a colorless liquid.

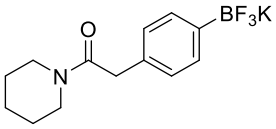


^{1}H NMR (500 MHz, $CDCl_3$): 7.79 (1 H, d, *J* = 7.9 H), 7.35 (1 H, t, *J* = 6.8 Hz), 7.24–7.16 (2 H, m), 3.67 (3 H, s), 3.23–3.12 (2 H, m), 2.63–2.54 (2 H, m), 1.34 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 173.9, 147.7, 136.4, 131.2, 129.4, 125.7, 83.7, 51.6, 37.2, 31.3, 25.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.3 ppm. – IR: 2979, 1739, 1600, 1489, 1443, 1381, 1348, 1315, 1260, 1215, 1145, 1071, 963 cm^{-1}. – HRMS: calcd for $C_{16}H_{24}BO_4$: 291.1762, found 291.1760 [M+H$^+$].

1-(Piperidin-1-yl)-2-(4-(trifluoro-λ⁴-boraneyl)phenyl)ethan-1-one, potassium salt (21)

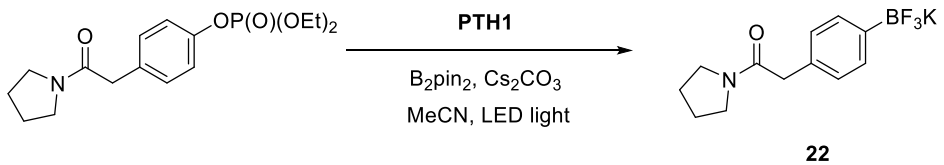


The general procedure GP1 was followed with diethyl (4-(2-oxo-2-(piperidin-1-yl)ethyl)phenyl) phosphate (71 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 72 h. Purification by treatment with methylboronic acid and then KHF_2 according to GP4 afforded organotrifluoroborate salt **21** (50 mg, 80%) as a colorless solid.



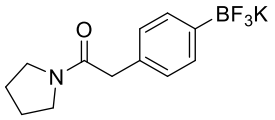
M.p.: > 200 °C. – ^{1}H NMR (500 MHz, CD_3CN): 7.40 (2 H, d, *J* = 7.4 Hz), 7.04 (2 H, d, *J* = 7.4 Hz), 3.62 (2 H, s), 3.44 (4 H, d, *J* = 36.2 Hz), 1.67–1.52 (2 H, m), 1.45 (2 H, s), 1.36 (2 H, s) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 170.6, 134.0, 132.5, 128.0, 47.7, 43.2, 41.2, 26.9, 26.3, 25.0 ppm. – ^{11}B NMR (160.4 Hz, CD_3CN): 3.7 ppm. – ^{19}F NMR (470.5 Hz, CD_3CN): −142.3 ppm. – IR: 3365, 2212, 1834, 1747, 1592, 1473, 1448, 1367, 1253, 1217, 1184, 1138, 957 cm^{-1}. – HRMS: calcd for $C_{13}H_{16}BF_3NO$: 270.1283, found 270.1292 [M−K$^+$].

1-(Pyrrolidin-1-yl)-2-(4-(trifluoro-λ⁴-boraneyl)phenyl)ethan-1-one, potassium salt (22)



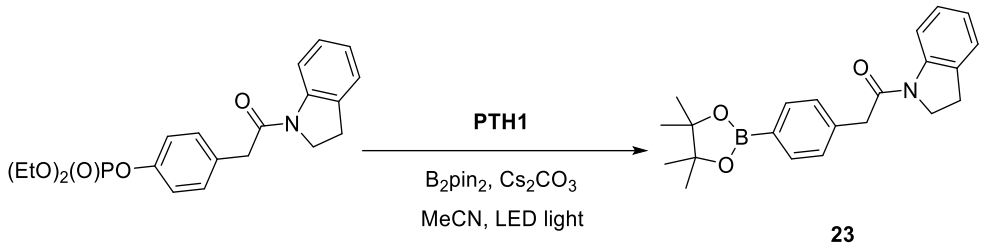
The general procedure GP1 was followed with diethyl (4-(2-oxo-2-(pyrrolidin-1-yl)ethyl)phenyl) phosphate (68 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for

72 h. Purification by treatment with methylboronic acid and then KHF_2 according to GP4 afforded organotrifluoroborate salt **22** (38 mg, 65%) as a colorless solid.

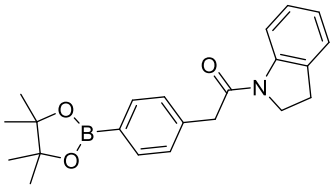


M.p.: > 200 °C. – ^{1}H NMR (500 MHz, CD_3CN): 7.37 (2 H, d, *J* = 7.7 Hz), 7.04 (2 H, d, *J* = 7.5 Hz), 3.54 (2 H, s), 3.44 (2 H, t, *J* = 6.8 Hz), 3.33 (2 H, t, *J* = 6.9 Hz), 1.88 (2 H, p, *J* = 6.6 Hz), 1.79 (2 H, p, *J* = 6.7 Hz) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 170.8, 133.5, 132.4, 128.3, 47.5, 46.4, 42.5, 26.7, 25.0 ppm. – ^{11}B NMR (160.4 Hz, CD_3CN): 3.3 ppm. – ^{19}F NMR (470.5 Hz, CD_3CN): −142.4 ppm. – IR: 3350, 2087, 1664, 1597, 1457, 1398, 1343, 1218, 1184, 1005, 956 cm^{-1}. – HRMS: calcd for $C_{12}H_{14}BF_3ON$: 256.1126, found 256.1130 [M−K$^+$].

1-(Indolin-1-yl)-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (23)



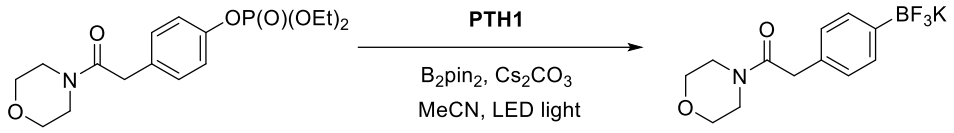
The general procedure GP1 was followed with diethyl (4-(2-(indolin-1-yl)-2-oxoethyl)phenyl) phosphate (78 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 72 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afforded **23** (62 mg, 85%) as a colorless solid.



M.p.: 145−147 °C. − ^{1}H NMR (500 MHz, $CDCl_3$): 8.26 (1 H, d, *J* = 8.1 Hz), 7.79 (2 H, d, *J* = 7.9 Hz), 7.33 (2 H, d, *J* = 7.7 Hz), 7.19 (1 H, t, *J* = 7.8 Hz), 7.15 (1 H, d, *J* = 7.3 Hz), 7.01 (1 H, t, *J* = 7.4 Hz), 4.02 (2 H, t, *J* = 8.5 Hz), 3.83 (2 H, s), 3.13 (2 H, t, *J* = 8.4 Hz), 1.34 (12 H, s) ppm. – ^{13}C NMR

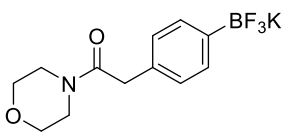
(125 MHz, $CDCl_3$): 169.0, 143.2, 137.5, 135.4, 131.2, 128.5, 127.7, 124.6, 123.9, 117.3, 83.9, 48.3, 44.1, 28.2, 25.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.0 ppm. – IR: 1740, 1620 1597, 1525, 1513, 1489, 1464, 1408, 1312, 1229, 1031, 983 cm^{-1}. – HRMS: calcd for $C_{22}H_{27}BNO_3$: 364.2079, found 364.2083 [$M+H^+$].

1-Morpholino-2-(4-(trifluoro-λ⁴-boraneyl)phenyl)ethan-1-one, potassium salt (24)



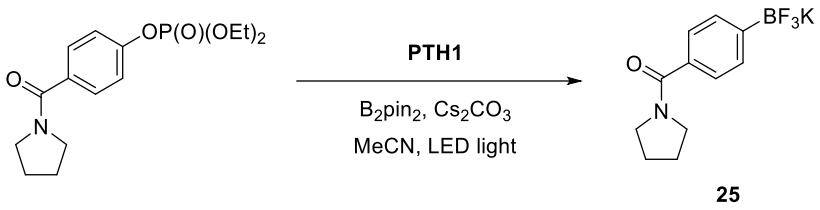
24

The general procedure GP1 was followed with diethyl (4-(2-morpholino-2-oxoethyl)phenyl) phosphate (72 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 72 h. Purification by treatment with methylboronic acid and then KHF_2 according to GP4 afforded organotrifluoroborate salt **24** (43 mg, 70%) as a colorless solid.



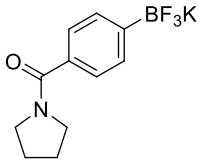
M.p.: > 200 °C. – ^1H NMR (500 MHz, DMSO): 7.33 (2 H, d, *J* = 7.6 Hz), 6.99 (2 H, d, *J* = 7.5 Hz), 3.62 (2 H, s), 3.55 (2 H, t, *J* = 4.8 Hz), 3.49 (2 H, t, *J* = 4.7 Hz), 3.44 (4 H, s) ppm. – ^{13}C NMR (125 MHz, DMSO): 169.8, 131.8, 131.6, 126.7, 66.2, 66.1, 46.2, 41.7, 40.0 ppm. – ^{11}B NMR (160.4 Hz, DMSO): 3.1 ppm. – ^{19}F NMR (470.5 Hz, DMSO): −140.3 ppm. – IR: 3367, 2216, 1823, 1754, 1590, 1456, 1402, 1366, 1256, 1209, 1180, 1129, 950 cm^{-1}. – HRMS: calcd for $C_{12}H_{14}BF_3NO_2$: 272.1075, found 272.1086 [$M-K^+$].

Pyrrolidin-1-yl(4-(trifluoro-λ⁴-boraneyl)phenyl)methanone, potassium salt (25)



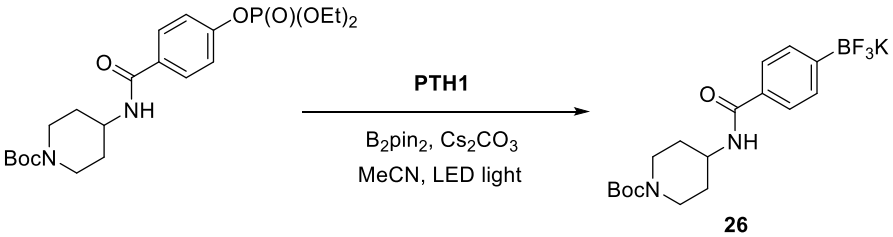
25

The general procedure GP1 was followed with diethyl (4-(pyrrolidine-1-carbonyl)phenyl) phosphate (66 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 72 h. Purification by treatment with methylboronic acid and then KHF_2 according to GP4 afforded organotrifluoroborate salt **25** (35 mg, 62%) as a colorless solid.



M.p.: > 200 °C. – ^{1}H NMR (500 MHz, CD_3CN): 7.48 (2 H, d, *J* = 7.9 Hz), 7.30 (2 H, d, *J* = 7.7 Hz), 3.49 (2 H, t, *J* = 6.9 Hz), 3.41 (2 H, t, *J* = 6.6 Hz), 1.89 (2 H, p, *J* = 6.6 Hz), 1.81 (2 H, p, *J* = 6.4 Hz) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 171.1, 135.7, 131.9, 126.3, 50.2, 46.8, 27.0, 25.0 ppm. – ^{11}B NMR (160.4 Hz, CD_3CN): 3.3 ppm. – ^{19}F NMR (470.5 Hz, CD_3CN): −142.6 ppm. – IR: 3343, 2133, 1987, 1723, 1635, 1581, 1545, 1515, 1456, 1313, 1215, 1152, 956 cm^{-1}. – HRMS: calcd for $C_{11}H_{12}BF_3ON$: 242.0970, found 242.0977 [M–K$^+$].

***tert*-Butyl 4-(4-(trifluoro-l4-boraneyl)benzamido)piperidine-1-carboxylate, potassium salt (26)**



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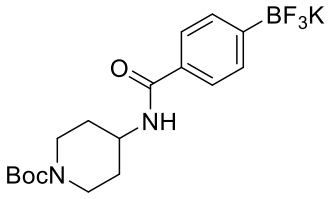
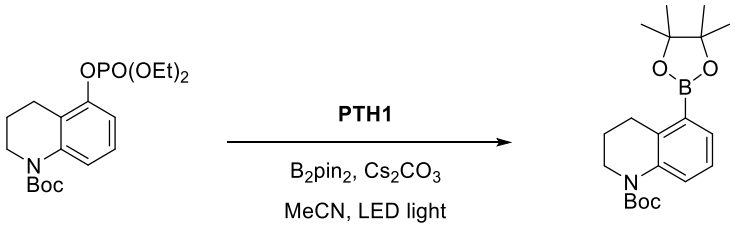
The general procedure GP1 was followed with *tert*-butyl 4-(4-((diethoxyphosphoryl)oxy)benzamido)piperidine-1-carboxylate (91 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 48 h. Purification by treatment with methylboronic acid and then KHF_2 according to GP4 afforded organotrifluoroborate salt **26** (43 mg, 52%) as a colorless solid.



M.p.: > 200 °C. – ^{1}H NMR (500 MHz, DMSO/ CD_3CN): 7.77 (1 H, s), 7.75 (2 H, d, *J* = 7.4 Hz), 7.59 (2 H, d, *J* = 7.5 Hz), 4.23–4.05 (3 H, m), 3.02 (2 H, t, *J* = 12.8 Hz), 1.97 (2 H, dd, *J* = 13.1, 3.7 Hz), 1.67–1.60 (2 H, m), 1.58 (9 H, s) ppm. – ^{13}C NMR (125 MHz, DMSO/CD_3CN): 166.9, 154.1, 131.6, 130.9, 125.0, 78.5, 46.4, 42.6, 31.3, 27.7 ppm. – ^{11}B NMR (160.4 Hz, CD_3CN): 0.83 (q, *J* = 18.3 Hz) ppm. – ^{19}F NMR (470.5 Hz, CD_3CN): −139.2 ppm. – IR: 3372, 2028, 1635, 1541, 1479, 1433, 1367, 1332, 1274, 1240, 1210, 1152, 1075, 973 cm^{-1}. – HRMS: calcd for $C_{17}H_{23}BF_3O_3N_2$: 371.1759, found 371.1767 [M−K$^+$].

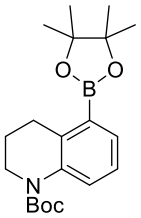
tert-Butyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydroquinoline-1(2*H*)-carboxylate (27)



27

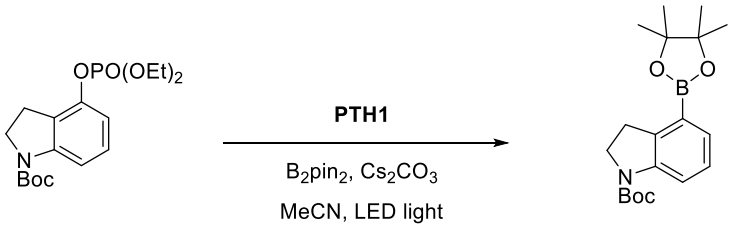
The general procedure GP1 was followed with *tert*-butyl 5-((diethoxyphosphoryl)oxy)-3,4-dihydroquinoline-1(2*H*)-carboxylate (77 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) and

CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 72 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 4 v/v) afford product **27** (47 mg, 65%) as a colorless liquid.

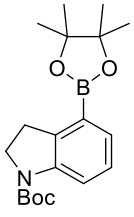


^{1}H NMR (500 MHz, $CDCl_3$): 7.66 (1 H, d, *J* = 8.2 Hz), 7.57 (1 H, d, *J* = 8.3 Hz), 7.53 (1 H, d, *J* = 1.5 Hz), 3.92–3.41 (2 H, m), 2.76 (2 H, t, *J* = 6.6 Hz), 1.91 (2 H, p, *J* = 6.4 Hz), 1.52 (9 H, s), 1.33 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 153.9, 141.6, 135.4, 132.4, 129.1, 123.3, 83.8, 81.1, 45.0, 28.5, 27.6, 25.0, 23.6 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.9 ppm. – IR: 2976, 1698, 1610, 1568, 1418, 1357, 1330, 1295, 1266, 1211, 1145, 1098, 1012 cm^{-1}. – HRMS: calcd for $C_{20}H_{32}BNO_4$: 360.2346, found 360.2344 [M+H$^+$].

***tert*-Butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)indoline-1-carboxylate (28)[23]**



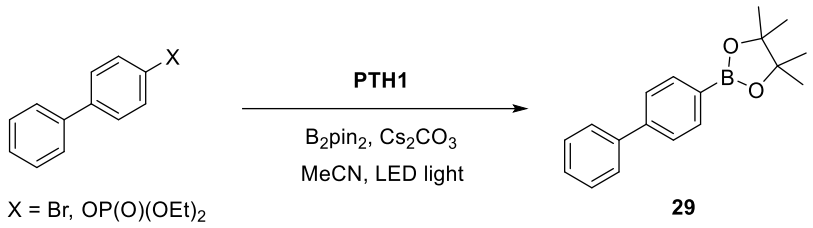
The general procedure GP1 was followed with *tert*-butyl 4-((diethoxyphosphoryl)oxy)indoline-1-carboxylate (74 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 72 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 4 v/v) afford product **28** (35 mg, 50%) as a colorless liquid.



^{1}H NMR (500 MHz, $CDCl_3$): 8.05 (1 H, s), 7.60 (1 H, dd, *J* = 7.4, 1.2 Hz), 7.38 (1 H, t, *J* = 7.7 Hz), 4.18 (2 H, t, *J* = 8.7 Hz), 3.50 (2 H, t, *J* = 8.7 Hz), 1.80 (9 H, s), 1.56 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 152.9, 142.3, 138.8, 129.1,

126.8, 117.5, 83.7, 80.8, 47.8, 28.7, 25.1 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.6 ppm. – IR: 2984, 1736, 1448, 1373, 1236, 1140, 1097, 1044, 917 cm^{-1}.

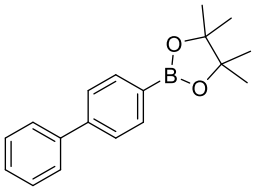
2-([1,1'-Biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (29)[15]



From 4-bromo-1,1'-biphenyl: The general procedure GP1 was followed with 4-bromo-1,1'-biphenyl (47 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.08 mg, 0.0004 mmol, 0.2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **29** (45 mg, 80%) as a colorless oil.

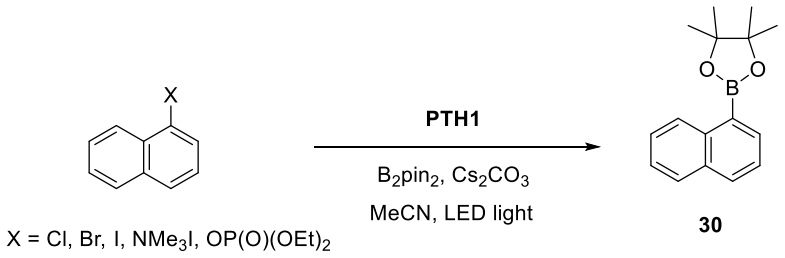
From [1,1'-biphenyl]-4-yl diethyl phosphate: The general procedure GP1 was followed with [1,1'-biphenyl]-4-yl diethyl phosphate (61 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.8 mg, 0.024 mmol, 12 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 36 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afforded product **29** (39 mg, 70%) as a colorless oil.

From [1,1'-biphenyl]-4-yl diethyl phosphate with 2 equiv. of B_2pin_2: The general procedure GP1 was followed with [1,1'-biphenyl]-4-yl diethyl phosphate (61 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.8 mg, 0.024 mmol, 12 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 36 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afforded product **29** (39 mg, 70%) as a colorless oil.



^{1}H NMR (500 MHz, $CDCl_3$): 7.90 (2 H, d, *J* = 8.1 Hz), 7.68–7.59 (4 H, m), 7.45 (2 H, t, *J* = 7.6 Hz), 7.37 (1 H, t, *J* = 7.4 Hz), 1.38 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 144.0, 141.2, 135.4, 128.9, 127.7, 127.4, 126.6, 84.0, 25.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 30.9 ppm. – IR: 2978, 2200, 1735, 1609, 1360, 1321, 1238, 1143, 1093, 1045, 1021, 1008 cm^{-1}.

4,4,5,5-Tetramethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborolane (30)[15]



From 1-iodonaphthalene: The general procedure GP1 was followed with 1-iodonaphthalene (47 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.08 mg, 0.0004 mmol, 0.2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **30** (38 mg, 75%) as a colorless solid.

From 1-bromonaphthalene: The general procedure GP1 was followed with 1-bromonaphthalene (41 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **30** (42 mg, 82%) as a colorless solid.

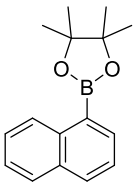
From 1-chloronaphthalene: The general procedure GP1 was followed with 1-chloronaphthalene (32 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The

mixture was irradiated with a 400 nm LED light at 24 °C for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **30** (36 mg, 70%) as a colorless solid.

From *N,N,N*-trimethylnaphthalen-1-aminium iodide: The general procedure GP1 was followed with *N,N,N*-trimethylnaphthalen-1-aminium iodide (62 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 450 nm LED light for 18 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afforded product **30** (43 mg, 85%) as a colorless solid.

Gram scale from *N,N,N*-trimethylnaphthalen-1-aminium iodide: According to general procedure GP1 three identical reactions were run with *N,N,N*-trimethylnaphthalen-1-aminium iodide (1.08 g, 3.5 mmol), B_2pin_2 (2.67 g, 10.5 mmol, 3.0 equiv.), Cs_2CO_3 (3.45 g, 10.5 mmol, 3.0 equiv.), **PTH1** (34.9 mg, 0.175 mmol, 5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 450 nm LED light for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afforded product **30** (1.6 g, 60%) as a colorless solid.

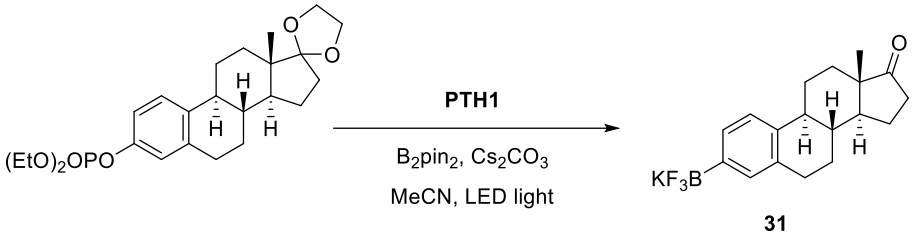
From [1,1'-biphenyl]-4-yl diethyl phosphate: The general procedure GP1 was followed with [1,1'-biphenyl]-4-yl diethyl phosphate (61 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.8 mg, 0.024 mmol, 12 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 450 nm LED light for 72 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afforded product **30** (39 mg, 85%) as a colorless solid.



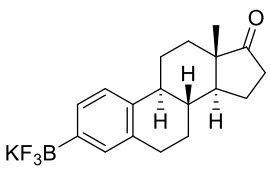
M.p.: 40–43 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 8.80 (1 H, d, *J* = 8.4 Hz), 8.11 (1 H, d, *J* = 6.8 Hz), 7.95 (1 H, d, *J* = 8.2 Hz), 7.85 (1 H, d, *J* = 8.1 Hz), 7.56 (1 H, t, *J* = 7.6 Hz), 7.49 (2 H, t, *J* = 7.4 Hz), 1.45 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 137.1, 135.8, 133.3, 131.7, 128.6, 128.5, 126.5, 125.6, 125.1, 83.8, 25.1 ppm. – ^{11}B NMR

(160.4 Hz, $CDCl_3$): 31.7 ppm. – IR: 3042, 2976, 1713, 1576, 1507, 1462, 1413, 1390, 1335, 1296, 1274, 1255, 1205, 1133, 1023 cm^{-1}.

(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-(trifluoro-l4-boraneyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one, potassium salt (31)

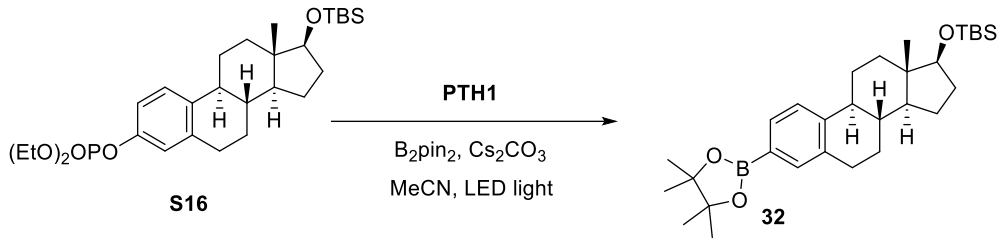


The general procedure GP1 was followed with diethyl ((8*R*,9*S*,13*S*,14*S*)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolan]-3-yl) phosphate (90 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) H_2O (3.6 mg, 0.2 mmol, 1.0 equiv.), and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 72 h. Purification by treatment with methylboronic acid and then KHF_2 according to GP4 afforded organotrifluoroborate salt **31** (37 mg, 52%) as a colorless solid.

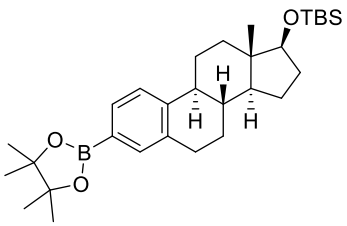


$[\alpha]_D$ = +92 (*c* 0.12M, CH_3CN). − m.p.: > 200 °C. – ^{1}H NMR (500 MHz, CD_3CN): 7.35 (1 H, d, *J* = 7.7 Hz), 7.32 (1 H, s), 7.27 (1 H, d, *J* = 7.7 Hz), 3.15–2.95 (2 H, m), 2.66–2.56 (2 H, m), 2.45 (1 H, td, *J* = 10.8, 4.0 Hz), 2.24–2.17 (3 H, m), 2.06–1.99 (1 H, m), 1.87–1.51 (6 H, m), 1.07 (3 H, s) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 221.3, 137.5, 135.0, 133.2, 129.8, 124.3, 51.3, 48.7, 45.4, 39.4, 36.3, 32.6, 30.2, 27.6, 26.7, 22.2, 14.2 ppm. – ^{11}B NMR (160.4 Hz, CD_3CN): 3.6 ppm. – ^{19}F NMR (470.5 Hz, CD_3CN): −141.7 ppm. – IR: 3420, 2035, 1972, 1724, 1608, 1493, 1456, 1407, 1366, 1217, 1087 cm^{-1}. – HRMS: calcd for $C_{18}H_{21}BF_3O$: 321.1643, found 321.1631 [$M-K^+$].

***tert*-Butyldimethyl(((8*R*,9*S*,13*S*,14*S*,17*S*)-13-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl)oxy)silane (32)**

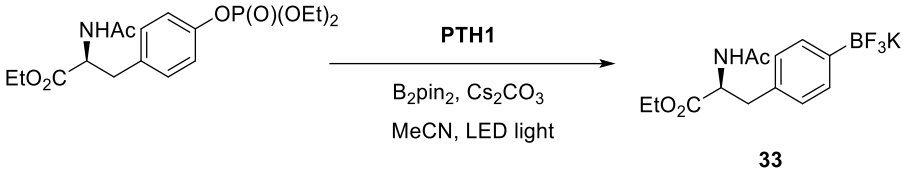


The general procedure GP1 was followed with **S16** (104 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%), H_2O (3.6 mg, 0.2 mmol, 1.0 equiv.), and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 72 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 9 v/v) afford product **32** (41 mg, 70%) as a colorless liquid.



$[\alpha]_D$ = +75 (*c* 0.06M, $CHCl_3$). – ^{1}H NMR (500 MHz, $CDCl_3$): 7.58 (1 H, d, *J* = 6.5 Hz), 7.55 (1 H, s), 7.32 (1 H, d, *J* = 7.8 Hz), 3.65 (1 H, t, *J* = 8.3 Hz), 2.88 (2 H, dd, *J* = 8.9, 4.2 Hz), 2.45–2.11 (2 H, m), 1.99–1.85 (3 H, m), 1.71–1.61 (1 H, m), 1.58–1.35 (3 H, m), 1.34 (12 H, s,), 1.33–1.21 (2 H, m), 1.21–1.10 (2 H, m), 0.90 (9 H, s), 0.74 (3 H, s), 0.04 (3 H, s), 0.03 (3 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 144.2, 136.3, 135.7, 132.1, 125.0, 83.8, 81.9, 50.0, 45.0, 43.7, 38.7, 37.3, 31.1, 29.5, 27.4, 26.2, 26.0, 25.0, 24.9, 23.4, 18.3, 11.5, –4.3, –4.6 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 33.0 ppm. – IR: 2953, 2928, 1610, 1471, 1363, 1351, 1312, 1255, 1145, 1099, 1007, 966, 916 cm^{-1}.– HRMS: calcd for $C_{30}H_{50}BO_3Si$: 497.3617, found 497.3616 [$M+H^+$].

Ethyl (*S*)-2-acetamido-3-(4-(trifluoro-λ⁴-boraneyl)phenyl)propanoate, potassium salt (33)



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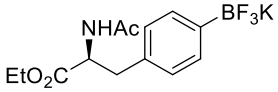
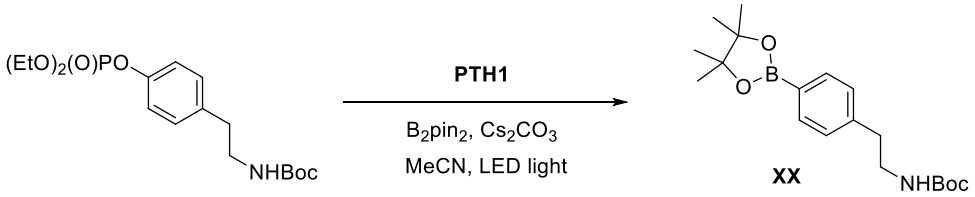
The general procedure GP1 was followed with ethyl (*S*)-2-acetamido-3-(4-((diethoxyphosphoryl)oxy)phenyl)propanoate (78 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light without air flow supply for 72 h. Purification by treatment with methylboronic acid and then KHF_2 according to GP4 afforded organotrifluoroborate salt **33** (38 mg, 56%) as a colorless solid.



$[\alpha]_D$ = +50 (*c* 0.6M, CH_3CN). – M.p.: > 200 °C. – ^{1}H NMR (500 MHz, CD_3CN): 7.40 (2 H, d, *J* = 7.7 Hz), 7.03 (2 H, d, *J* = 7.6 Hz), 6.78 (1 H, d, *J* = 7.8 Hz), 4.56 (1 H, td, *J* = 7.9, 5.7 Hz), 4.11 (2 H, q, *J* = 7.0 Hz), 3.03 (1 H, dd, *J* = 13.8, 5.6 Hz), 2.88 (1 H, dd, *J* = 13.8, 8.0 Hz), 1.84 (3 H, s), 1.21 (3 H, t, *J* = 7.1 Hz) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 172.7, 170.9, 134.8, 132.3, 128.6, 61.8, 55.0, 38.2, 22.7, 14.4 ppm. – ^{11}B NMR (160.4 Hz, CD_3CN): 3.4 ppm. – ^{19}F NMR (470.5 Hz, CD_3CN): −142.0 ppm. – IR: 3370, 2989, 1732, 1649, 1558, 1502, 1441, 1371, 1259, 1219, 1174, 1031, 977 cm^{-1}. – HRMS: calcd for $C_{13}H_{16}BF_3NO_3$: 302.1181, found 302.1190 [M−K$^+$].

***tert*-Butyl (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenethyl)carbamate (34)[24]**



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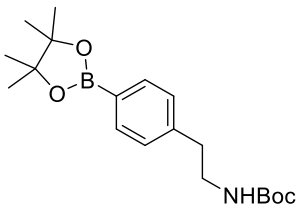
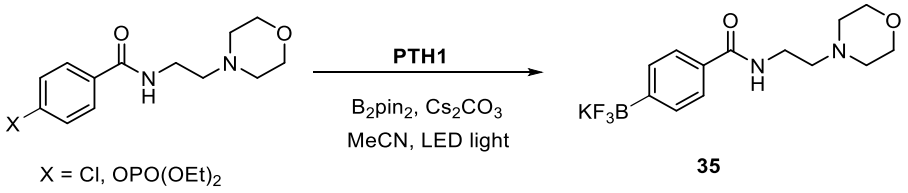
The general procedure GP1 was followed with *tert*-butyl (4-((diethoxyphosphoryl)oxy)phenethyl)carbamate (75 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light with air flow supply off (without air flow supply) for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 14 v/v) afford product **34** (55 mg, 80%) as a colorless liquid.



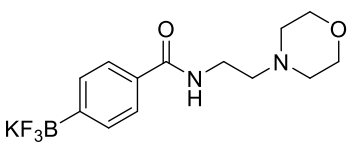
^{1}H NMR (500 MHz, $CDCl_3$): 7.75 (2 H, d, *J* = 7.9 Hz), 7.20 (2 H, d, *J* = 7.7 Hz), 4.55 (1 H, s), 3.37 (2 H, d, *J* = 6.2 Hz), 2.80 (2 H, t, *J* = 6.9 Hz), 1.42 (9 H, s), 1.33 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 156.0, 142.5, 135.2, 128.4, 83.8, 79.3, 41.8, 36.4, 28.5, 25.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 30.9 ppm. – IR: 1977, 1698, 1612, 1518, 1398, 1360, 1318, 1271, 1249, 1215, 1167, 1143, 1089, 1022, 962 cm^{-1}.

N-(2-Morpholinoethyl)-4-(trifluoro-λ^4-boraneyl)benzamide, potassium salt (35)



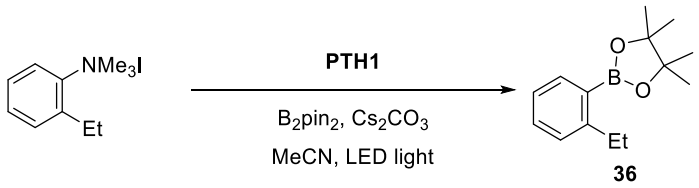
From 4-chloro-*N*-(2-morpholinoethyl)benzamide: The general procedure GP1 was followed with 4-chloro-N-(2-morpholinoethyl)benzamide (54 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by Kugelrohr distillation (145 °C, 1.5 h), followed by treatment with 4.5M KHF_2 (0.12 mL, 0.54 mmol, 2.7 equiv.) and K_2CO_3 according to GP4 afforded organotrifluoroborate salt **35** (44 mg, 66%) as a colorless solid.

From diethyl (4-((2-morpholinoethyl)carbamoyl)phenyl) phosphate: The general procedure GP1 was followed with diethyl (4-((2-morpholinoethyl)carbamoyl)phenyl) phosphate **S28** (78 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) and CH_3CN (2 mL). Purification by Kugelrohr distillation (145 °C, 1.5 h), followed by treatment with 4.5M KHF_2 (0.12 mL, 0.54 mmol, 2.7 equiv.) and K_2CO_3 according to GP4 afforded organotrifluoroborate salt **35** (33 mg, 48%) as a colorless solid.



M.p.: > 200 °C. – ^{1}H NMR (500 MHz, CD_3CN): 7.58 (2 H, d, *J* = 7.8 Hz), 7.51 (2 H, d, *J* = 7.9 Hz), 6.97 (1 H, s), 3.63 (4 H, t, *J* = 4.6 Hz), 3.44 (2 H, q, *J* = 6.2 Hz), 2.52 (2 H, t, *J* = 6.5 Hz), 2.46 (4 H, t, *J* = 4.6 Hz) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 168.7, 132.8, 132.3, 126.0, 67.6, 58.2, 54.3, 37.1 ppm. – ^{11}B NMR (160.4 Hz, CD_3CN): 3.2 ppm. – ^{19}F NMR (470.5 Hz, CD_3CN): −142.7 ppm. – IR: 3382, 1625, 1545, 1450, 1313, 1267, 1208, 1112, 1068, 956 cm^{-1}. – HRMS: calcd for $C_{13}H_{17}BF_3N_2O_2$: 301.1341, found 301.1336 [M−K$^+$].

2-(2-Ethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (36)[25]



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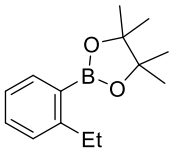
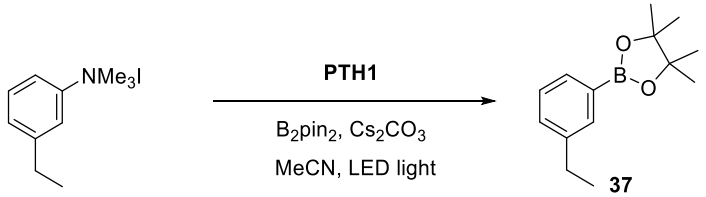
At 400 nm wavelength: The general procedure GP1 was followed with 2-ethyl-*N*,*N*,*N*-trimethylbenzenaminium iodide (58 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **36** (36 mg, 78%) as a colorless oil.

With 420 nm LED light: The general procedure GP1 was followed with 2-ethyl-N,N,N-trimethylbenzenaminium iodide (58 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 420 nm LED light for 18 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **36** (28 mg, 61%) as a colorless oil.

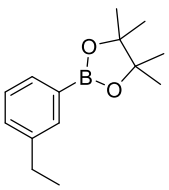


^{1}H NMR (500 MHz, $CDCl_3$): 7.78 (1 H, d, *J* = 7.4 Hz), 7.36 (1 H, t, *J* = 8.2 Hz), 7.22–7.16 (2 H, m), 2.92 (2 H, q, *J* = 7.5 Hz), 1.35 (12 H, s), 1.21 (3 H, t, *J* = 7.5 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 151.6, 136.2, 131.1, 128.5, 125.0, 83.5, 29.0, 25.0, 17.3 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.4 ppm. – IR: 2976, 2929, 2871, 1599, 1488, 1439, 1379, 1346, 1310, 1273, 1259, 1214, 1144, 1125, 1110, 1077, 1030 cm^{-1}.

2-(3-Ethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (37)[16]



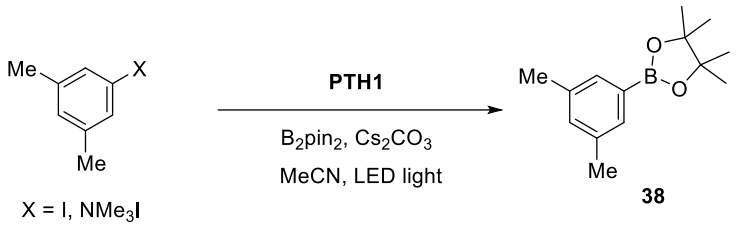
The general procedure GP1 was followed with 3-ethyl-*N*,*N*,*N*-trimethylbenzenaminium iodide (58 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **37** (35 mg, 78%) as a colorless oil.



^{1}H NMR (500 MHz, $CDCl_3$): 7.66 (2 H, s), 7.64 (2 H, dd, *J* = 5.2, 3.4 Hz), 7.33–7.28 (2 H, m), 2.66 (2 H, q, *J* = 7.6 Hz), 1.35 (12 H, s), 1.25 (3 H, t, *J* = 7.6 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 143.6, 134.4, 132.2, 131.0, 127.9, 83.8,

29.0, 25.0, 15.9 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.1 ppm. – IR: 2976, 2930, 1605, 1462, 1388, 1356, 1317, 1273, 1202, 1143, 1110, 1080, 961 cm^{-1}.

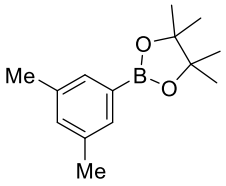
2-(3,5-Dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38)[15]



From 1-iodo-3,5-dimethylbenzene: The general procedure GP1 was followed with 1-iodo-3,5-dimethylbenzene (46 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **38** (30 mg, 66%) as a colorless solid.

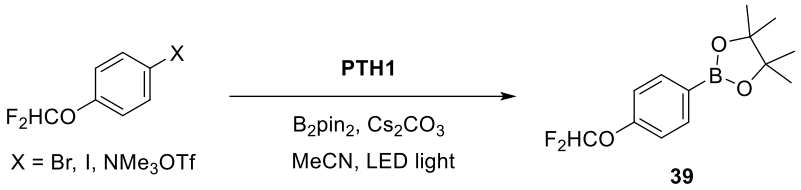
From *N,N,N*,3,5-pentamethylbenzenaminium iodide: The general procedure GP1 was followed with *N,N,N*,3,5-pentamethylbenzenaminium iodide (58 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **38** (41 mg, 90%) as a colorless solid.

From *N,N,N*,3,5-pentamethylbenzenaminium iodide with 420 nm LED light: The general procedure GP1 was followed with *N,N,N*,3,5-pentamethylbenzenaminium iodide (58 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 420 nm LED light for 18 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **38** (36 mg, 78%) as a colorless solid.



M.p.: 82–85 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 7.45 (2 H, s), 7.11 (1 H, s), 2.33 (6 H, s), 1.35 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 137.3, 133.1, 132.5, 83.8, 25.0, 21.3 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.3 ppm. – IR: 3022, 2991, 2976, 2921, 1738, 1600, 1357, 1318, 1260, 1240, 1209, 1139, 1116, 964 cm^{-1}.

2-(4-(Difluoromethoxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (39)[26]



From 1-(difluoromethoxy)-4-iodobenzene: The general procedure GP1 was followed with 1-(difluoromethoxy)-4-iodobenzene (54 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.08 mg, 0.004 mmol, 0.2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **39** (48 mg, 88%) as a colorless oil.

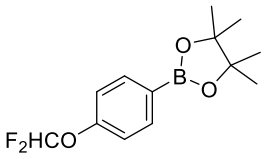
From 1-(difluoromethoxy)-4-iodobenzene with 1.2 equiv. of B_2pin_2: The general procedure GP1 was followed with 1-(difluoromethoxy)-4-iodobenzene (54 mg, 0.2 mmol), B_2pin_2 (61 mg, 0.24 mmol, 1.2 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.08 mg, 0.004 mmol, 0.2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **39** (43 mg, 80%) as a colorless oil.

From 1-(difluoromethoxy)-4-iodobenzene at 420 nm wavelength: The general procedure GP1 was followed with 1-(difluoromethoxy)-4-iodobenzene (54 mg, 0.2 mmol), B_2pin_2 (151 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.04 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 420 nm

LED light for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **39** (46 mg, 85%) as a colorless oil.

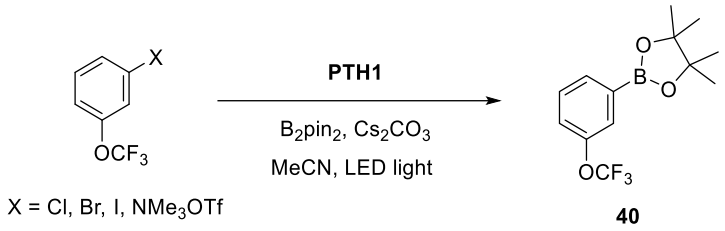
From 1-bromo-4-(difluoromethoxy)benzene: The general procedure GP1 was followed with 1-bromo-4-(difluoromethoxy)benzene (45 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **39** (49 mg, 90%) as a colorless oil.

From 4-(difluoromethoxy)aniline: The general procedure GP6 was followed with 4-(difluoromethoxy)aniline (32 mg, 0.2 mmol), Cs_2CO_3 (132 mg, 0.4 mmol, 2 equiv.), methyl trifluoromethanesulfonate (105 mg, 0.64 mmol, 3.2 equiv.) and CH_3CN (1.5 mL). The mixture was stirred for 20 minutes at room temperature before adding B_2pin_2 (152 mg, 0.6 mmol, 3 equiv.), Cs_2CO_3 (165 mg, 0.5 mmol, 2.5 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (0.5 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **39** (39 mg, 72%) as a colorless oil.



^{1}H NMR (500 MHz, $CDCl_3$): 7.82 (2 H, d, *J* = 8.5 Hz), 7.10 (2 H, d, *J* = 8.5 Hz), 6.54 (1 H, t, *J* = 73.9 Hz), 1.34 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 153.9, 136.8, 118.4, 115.9 (t, *J* = 259.3 Hz), 84.1, 25.0 ppm. –^{11}B NMR (160.4 Hz, $CDCl_3$): 30.6 ppm. – ^{19}F NMR (470.5 Hz, $CDCl_3$): −80.9 (d, *J* = 74.0 Hz) ppm. – IR: 2979, 1606, 1578, 1469, 1399, 1358, 1323, 1270, 1215, 1163, 1127, 1085, 1046 cm^{-1}.

4,4,5,5-Tetramethyl-2-(3-(trifluoromethoxy)phenyl)-1,3,2-dioxaborolane (40)[27]



40

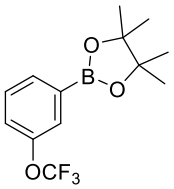
From 1-iodo-3-(trifluoromethoxy)benzene: The general procedure GP1 was followed with 1-iodo-3-(trifluoromethoxy)benzene (58 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.08 mg, 0.0004 mmol, 0.2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 16 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **40** (49 mg, 84%) as a colorless oil.

From 1-bromo-3-(trifluoromethoxy)benzene: The general procedure GP1 was followed with 1-bromo-3-(trifluoromethoxy)benzene (48 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **40** (49 mg, 85%) as a colorless oil.

From 1-chloro-3-(trifluoromethoxy)benzene: The general procedure GP1 was followed with 1-bromo-3-(trifluoromethoxy)benzene (39 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **40** (41 mg, 70%) as a colorless oil.

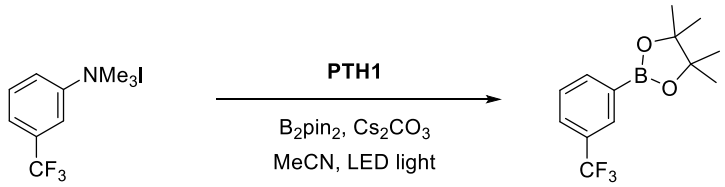
From 3-(trifluoromethoxy)aniline: The general procedure GP6 was followed with 3-(trifluoromethoxy)aniline (36 mg, 0.2 mmol), Cs_2CO_3 (132 mg, 0.4 mmol, 2 equiv.), methyl trifluoromethanesulfonate (105 mg, 0.64 mmol, 3.2 equiv.) and CH_3CN (1.5 mL). The

mixture was stirred for 20 minutes at room temperature before adding B_2pin_2 (152 mg, 0.6 mmol, 3 equiv.), Cs_2CO_3 (165 mg, 0.5 mmol, 2.5 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (0.5 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **40** (42 mg, 73%) as a colorless oil.



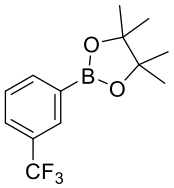
^{1}H NMR (500 MHz, $CDCl_3$): 7.73 (1 H, d, *J* = 7.3 Hz), 7.64 (1 H, s), 7.40 (1 H, t, *J* = 7.8 Hz), 7.30 (1 H, d, *J* = 8.2 Hz), 1.35 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 149.1, 133.2, 129.4, 127.0, 123.9, 120.7 (q, *J* = 256.6 Hz), 84.4, 25.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 30.8 ppm. – ^{19}F NMR (470.5 Hz, $CDCl_3$): −57.7 ppm. – IR: 2980, 1715, 1578, 1428, 1355, 1327, 129, 1158, 1141, 1097, 1071, 1002 cm^{-1}.

4,4,5,5-Tetramethyl-2-(3-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (41)[28]



41

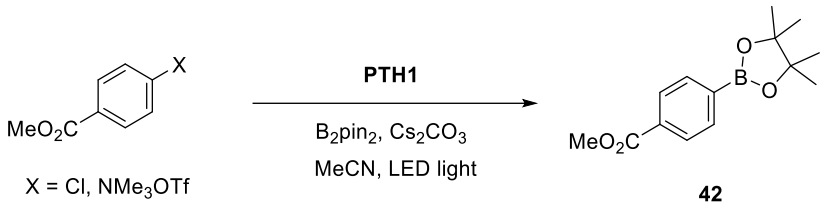
The general procedure GP1 was followed with N,N,N-trimethyl-3-(trifluoromethyl)benzenaminium iodide (66 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **41** (39 mg, 73%) as a colorless oil.



^{1}H NMR (500 MHz, $CDCl_3$): 8.07 (1 H, s), 7.98 (1 H, d, *J* = 7.4 Hz), 7.70 (1 H, d, *J* = 7.8 Hz), 7.48 (1 H, t, *J* = 7.6 Hz), 1.36 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 138.1, 131.5 (q, *J* = 3.5 Hz), 130.2 (q, *J* = 32.3 Hz), 128.2, 127.9 (q, *J* = 3.5 Hz), 124.4 (q, *J* = 271.9 Hz), 84.4, 25.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 30.6

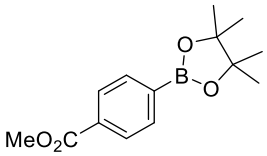
ppm. – ^{19}F NMR (470.5 Hz, $CDCl_3$): −62.6 ppm. – IR: 2979, 2255, 1977, 1739, 1521, 1400, 1362, 1321, 1274, 1242, 1209, 1160, 1141, 1098, 1017 cm^{-1}.

Methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (42)[15]



From methyl 4-chlorobenzoate: The general procedure GP1 was followed with methyl 4-chlorobenzoate (34 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **42** (46 mg, 88%) as a colorless oil.

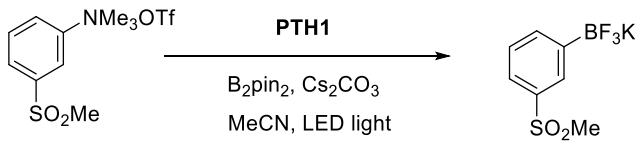
From methyl 4-(dimethylamino)benzoate: The general procedure GP6 was followed with methyl 4-(dimethylamino)benzoate (36 mg, 0.2 mmol), methyl trifluoromethanesulfonate (40 mg, 0.24 mmol, 1.2 equiv.) and CH_3CN (1.5 mL). The mixture was stirred for 20 minutes at room temperature before adding B_2pin_2 (152 mg, 0.6 mmol, 3 equiv.), Cs_2CO_3 (197 mg, 0.3 mmol, 3 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (0.5 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **42** (43 mg, 82%) as a colorless oil.



^{1}H NMR (500 MHz, $CDCl_3$): 8.02 (2 H, d, *J* = 8.2 Hz), 7.86 (2 H, d, *J* = 8.1 Hz), 3.91 (3 H, s), 1.35 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 167.2, 134.8, 132.3, 128.7, 84.3, 52.3, 25.0 ppm. – ^{11}B NMR

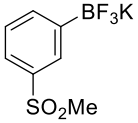
(160.4 Hz, $CDCl_3$): 30.9 ppm. – IR: 2984, 1721, 1561, 1507, 1434, 1359, 1325, 1311, 1275, 1253, 1209, 1190, 1140, 1109, 1097, 1086 cm^{-1}.

Trifluoro(3-(methylsulfonyl)phenyl)-λ⁴-borane, potassium salt (43)[29]



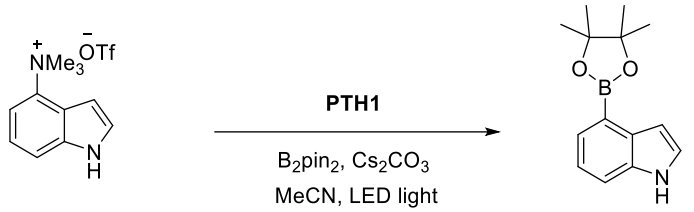
43

The general procedure GP1 was followed with *N,N,N*-trimethyl-3-(methylsulfonyl)benzenaminium trifluoromethanesulfonate (73 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 18 h. The crude mixture was diluted in EtOAc (5 mL) and H_2O (0.5 mL) and added 2-iodoxybenzoic acid (168 mg, 0.6 mmol, 3 equiv.). After heating at 80 ℃ for 2 h, solid precipitated from the solution was filter off. The filtrate was extracted with saturated $NaHCO_3$, brine, filter and concentrated then followed by treatment with KHF_2 according to GP3 afforded organotrifluoroborate salt **43** (36 mg, 68%) as a colorless solid.



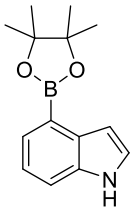
M.p.: > 200 °C. – ^{1}H NMR (500 MHz, $(CD_3)_2CO$): 7.93 (1 H, s), 7.67 (1 H, d, *J* = 7.2 Hz), 7.52 (1 H, d, *J* = 7.7 Hz), 7.24 (1 H, t, *J* = 7.5 Hz), 2.89 (3 H, s) ppm. – ^{13}C NMR (125 MHz, $(CD_3)_2CO$): 140.1, 137.6, 130.7, 127.8, 124.7, 44.6 ppm. – ^{11}B NMR (160.4 Hz, $(CD_3)_2CO$): 3.0 (q, *J* = 48.0, 47.6 Hz) ppm. – ^{19}F NMR (470.5 Hz, $(CD_3)_2CO$): –143.5 (dd, *J* = 93.3, 37.1 Hz) ppm. – IR: 3405, 1635, 4121, 1399, 1284, 1215, 1138, 1088, 974, 904 cm^{-1}. – HRMS: calcd for $C_7H_7BF_3O_2S$: 223.0217, found 223.0224 [$M+H^+$].

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (44)[30]



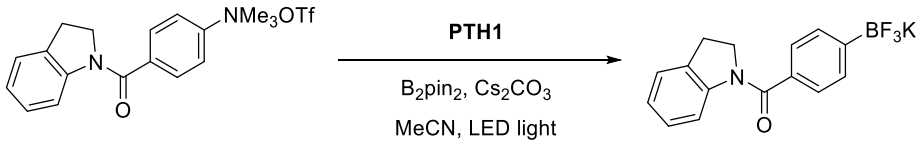
44

The general procedure GP1 was followed with *N,N,N*-trimethyl-1*H*-indol-4-aminium trifluoromethanesulfonate (65 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) and CH_3CN (2.5 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by Prep TLC (EtOAc/hexane, 1 : 5 v/v) afford product **44** (40 mg, 82%) as a colorless solid.



M.p.: 139−141 ^{0}C. – ^{1}H NMR (500 MHz, $CDCl_3$): 8.19 (1 H, s), 7.66 (1 H, d, *J* = 7.0 Hz), 7.50 (1 H, d, *J* = 8.1 Hz), 7.27–7.24 (1 H, m), 7.22 (1 H, dd, *J* = 8.1, 7.1 Hz), 7.07 (1 H, s), 1.41 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 135.3, 132.7, 128.0, 124.7, 121.5, 114.1, 104.7, 83.5, 25.1 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.4 ppm. – IR: 2979, 2926, 1608, 1575, 1507, 1407, 1374, 1338, 1290, 1269, 1167, 1133, 1066, 970, 896 cm^{-1}.

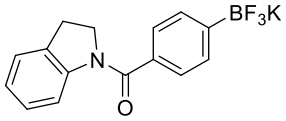
Indolin-1-yl(4-(trifluoro-λ^4-boraneyl)phenyl)methanone, potassium salt (45)



45

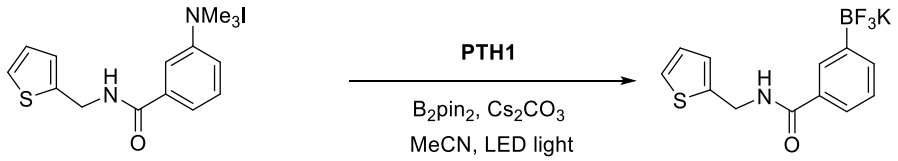
The general procedure GP1 was followed with 4-(indoline-1-carbonyl)-*N,N,N*-trimethylbenzenaminium trifluoromethanesulfonate (86 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol,

10 mol%) and CH_3CN (2.5 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by Prep TLC (EtOAc/hexane, 1 : 6 v/v) then followed by treatment with KHF_2 according to GP3 afforded organotrifluoroborate salt **45** (50 mg, 76%) as a colorless solid.



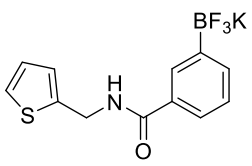
M.p.: > 200 °C. – ^{1}H NMR (500 MHz, CD_3CN): 7.69 (1 H, s), 7.53 (2 H, d, *J* = 7.8 Hz), 7.35 (2 H, d, *J* = 7.6 Hz), 7.24 (1 H, d, *J* = 7.4 Hz), 7.13 (1 H, s), 7.00 (1 H, t, *J* = 7.3 Hz), 4.03 (2 H, t, *J* = 8.3 Hz), 3.07 (2 H, t, *J* = 8.3 Hz) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 171.0, 144.3, 135.4, 133.9, 132.2, 127.7, 126.1, 125.8, 124.3, 51.5, 28.7 ppm. – ^{11}B NMR (160.4 Hz, CD_3CN): 3.0 ppm. – ^{19}F NMR (470.5 Hz, CD_3CN): −142.7 ppm. – IR: 3365, 1747, 1628, 1587, 1523, 1503, 1485, 1463, 1404, 1303, 1228, 1021, 973 cm^{-1}. – HRMS: calcd for $C_{15}H_{12}BF_3NO$: 290.0970, found 290.0964 [$M-K^+$].

N-(Thiophen-2-ylmethyl)-4-(trifluoro-λ⁴-boraneyl)benzamide, potassium salt (46)



46

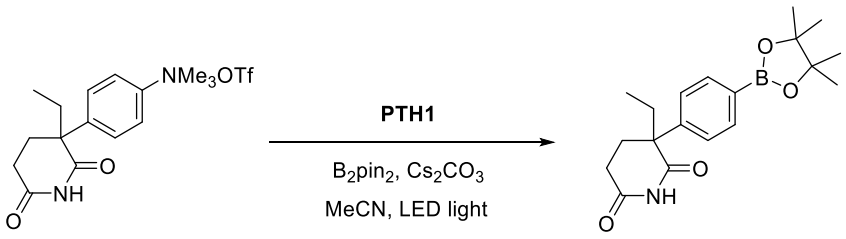
The general procedure GP1 was followed with 4-(indoline-1-carbonyl)-*N*,*N*,*N*-trimethylbenzenaminium iodide (80 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) and CH_3CN (2.5 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by rapid column chromatography then followed by treatment with KHF_2 according to GP3 afforded organotrifluoroborate salt **46** (47 mg, 73%) as a colorless solid.



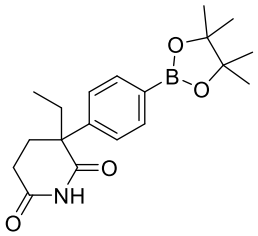
M.p.: > 200 °C. – ^{1}H NMR (500 MHz, CD_3CN): 7.89 (1 H, s), 7.63–7.57 (3 H, m), 7.31–7.23 (2 H, m), 7.00 (1 H, d, *J* = 4.3 Hz), 6.94 (1 H, dd, *J* = 5.1, 3.5 Hz), 4.67 (2 H, d, *J* = 6.1 Hz) ppm. – ^{13}C NMR (125 MHz,

CD_3CN): 169.1, 143.9, 135.6, 133.4, 130.5, 127.7, 127.6, 126.2, 125.6, 38.7 ppm. – ^{11}B NMR (160.4 Hz, CD_3CN): 3.4 ppm. – ^{19}F NMR (470.5 Hz, CD_3CN): −142.6 ppm. – IR: 3336, 1626, 1540, 1482, 1366, 1297, 1216, 1135, 1023, 963 cm^{-1}. – HRMS: calcd for $C_{12}H_{10}BF_3NOS$: 284.0534, found 284.0528 [$M-K^+$].

3-Ethyl-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)piperidine-2,6-dione (47)

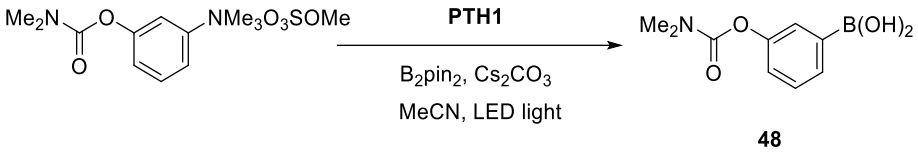


The general procedure GP1 was followed with 4-(3-ethyl-2,6-dioxopiperidin-3-yl)-*N,N,N*-trimethylbenzenaminium trifluoromethanesulfonate (83 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) and CH_3CN (2.5 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by Prep TLC (EtOAc/hexane, 1 : 3 v/v) afford product **47** (56 mg, 84%) as a colorless solid.



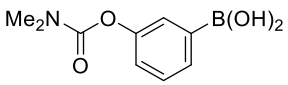
M.p.: 165−168 ^0C. – ^1H NMR (500 MHz, $CDCl_3$): 7.94 (1 H, s), 7.80 (2 H, d, *J* = 8.3 Hz), 7.28 (2 H, d, *J* = 8.3 Hz), 2.65–2.51 (1 H, m), 2.44–2.30 (2 H, m), 2.22 (1 H, td, *J* = 15.3, 14.3, 4.2 Hz), 2.06 (1 H, dq, *J* = 14.8, 7.4 Hz), 1.92 (1 H, dq, *J* = 14.7, 7.4 Hz), 1.34 (12 H, s), 0.87 (3 H, t, *J* = 7.4 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 175.1, 172.3, 142.0, 135.6, 125.6, 84.1, 51.5, 32.9, 29.4, 27.2, 25.0, 9.2 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.2 ppm. – IR: 2974, 1698, 1609, 1558, 1458, 1399, 1359, 1326, 1307, 1264, 1189, 1142, 1095, 1019, 962 cm^{-1}. – HRMS: calcd for $C_{19}H_{27}BNO_4$: 344.2028, found 344.2017 [$M+H^+$].

(3-((Dimethylcarbamoyl)oxy)phenyl)boronic acid (48)



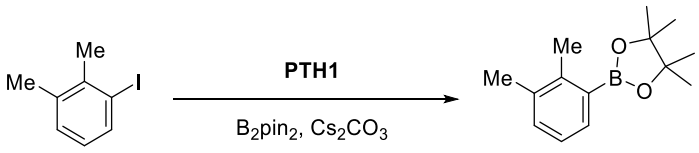
48

The general procedure GP1 was followed with 3-((dimethylcarbamoyl)oxy)-*N*,*N*,*N*-trimethylbenzenaminium methyl sulfate (67 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) and CH_3CN (2.5 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by GP4 afforded boronic acid 48 (31 mg, 74%) as a colorless oil.



^{1}H NMR (500 MHz, CD_3OD): 7.41 (1 H, s), 7.21 (2 H, s), 6.84 (1 H, s), 3.12 (3 H, s), 2.98 (3 H, s) ppm. – ^{13}C NMR (125 MHz, CD_3OD): 157.4, 152.0, 131.3, 128.4, 126.8, 119.4, 36.8, 36.7 ppm. – ^{11}B NMR (160.4 Hz, CD_3OD): 6.4 ppm. – IR: 3362, 2518, 1640, 1449, 1397, 1315, 1206, 1079, 917 cm^{-1}. – HRMS: calcd for $C_9H_{13}BNO_4$: 210.0932, found 210.0932 [$M+H^+$].

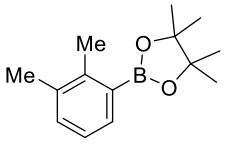
2-(2,3-Dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (49)[20]



49

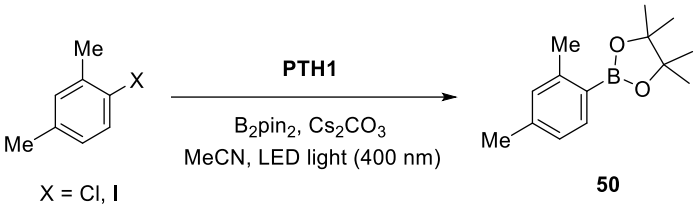
The general procedure GP1 was followed with 1-iodo-2,3-dimethylbenzene (46 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400

nm LED light for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **49** (36 mg, 78%) as a colorless oil.



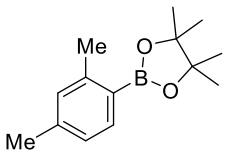
^{1}H NMR (500 MHz, $CDCl_3$): 7.63 (1 H, d, *J* = 7.4 Hz), 7.23 (1 H, d, *J* = 7.3 Hz), 7.11 (1 H, t, *J* = 7.4 Hz), 2.49 (3 H, s), 2.29 (3 H, s), 1.37 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 143.2, 136.6, 133.6, 132.4, 125.0, 83.6, 25.0, 20.6, 18.6 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.6 ppm. – IR: 2976, 2929, 1587, 1427, 1346, 1302, 1272, 1245, 1214, 1136, 1111, 1081, 1032 cm^{-1}.

2-(2,4-Dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (50)[25]



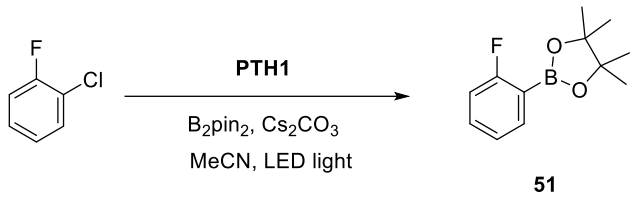
From 1-iodo-2,4-dimethylbenzene: The general procedure GP1 was followed with 1-iodo-2,4-dimethylbenzene (46 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **50** (36 mg, 78%) as a colorless oil.

From 1-chloro-2,4-dimethylbenzene: The general procedure GP1 was followed with 1-chloro-2,4-dimethylbenzene (28 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **50** (33 mg, 72%) as a colorless oil.



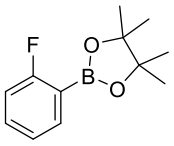
^{1}H NMR (500 MHz, $CDCl_3$): 7.67 (1 H, d, *J* = 7.4 Hz), 7.04–6.96 (2 H, m), 2.52 (3 H, s), 2.32 (3 H, s), 1.34 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 145.1, 141.0, 136.2, 130.9, 125.7, 83.4, 25.0, 22.3, 21.6 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.5 ppm. – IR: 2977, 1714, 1611, 1446, 1404, 1345, 1311, 1273, 1218, 1146, 1133, 1063 cm^{-1}.

2-(2-Fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (51)[19]



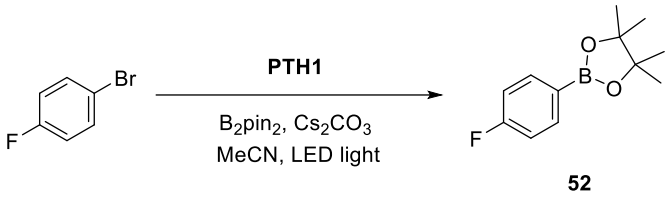
51

The general procedure GP1 was followed with 1-chloro-2-fluorobenzene (26 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **51** (31 mg, 70%) as a colorless oil.



^{1}H NMR (500 MHz, $CDCl_3$): 7.74 (1 H, t, *J* = 6.7 Hz), 7.50–7.33 (1 H, m), 7.13 (1 H, t, *J* = 7.4 Hz), 7.02 (1 H, t, *J* = 8.9 Hz), 1.36 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 167.3 (d, *J* = 250.7 Hz), 137.0 (d, *J* = 8.1 Hz), 133.4 (d, *J* = 8.7 Hz), 123.7 (d, *J* = 3.4 Hz), 115.4 (d, *J* = 24.0 Hz), 84.0, 66.0, 25.0, 15.4 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 30.3 ppm. – ^{19}F NMR (470.5 Hz, $CDCl_3$): 102.64 ppm. – IR: 2979, 1738, 1615, 1573, 1446, 1389, 1355, 1324, 1270, 1240, 1215, 1144, 1113, 1074, 1046, 1030 cm^{-1}.

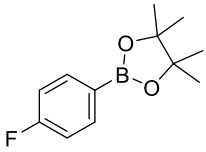
2-(4-Fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (52)[15]



52

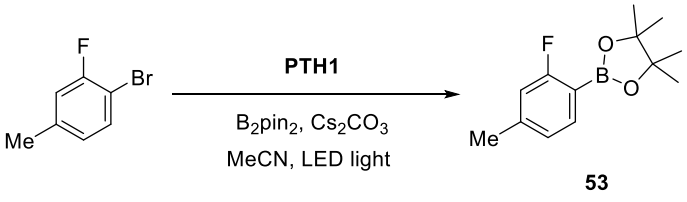
At 400 nm wavelength: The general procedure GP1 was followed with 1-bromo-4-fluorobenzene (35 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **52** (40 mg, 90%) as a colorless oil.

At 420 nm wavelength: The general procedure GP1 was followed with 1-bromo-4-fluorobenzene (35 mg, 0.2 mmol), B_2pin_2 (151 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 36 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **52** (40 mg, 91%) as a colorless oil.



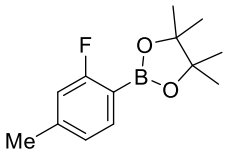
^{1}H NMR (500 MHz, $CDCl_3$): 7.80 (2 H, dd, J = 8.2, 6.3 Hz), 7.05 (2 H, t, J = 8.9 Hz), 1.34 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 165.2 (d, J = 250.3 Hz), 137.1 (d, J = 8.4 Hz), 115.0 (d, J = 20.1 Hz), 84.0, 25.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.1 ppm. – ^{19}F NMR (470.5 Hz, $CDCl_3$): −108.5 ppm. – IR: 2979, 1602, 1514, 1467, 1399, 1360, 1319, 1270, 1221, 1143, 1087, 1017, 962 cm^{-1}.

2-(2-Fluoro-4-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (53)[31]



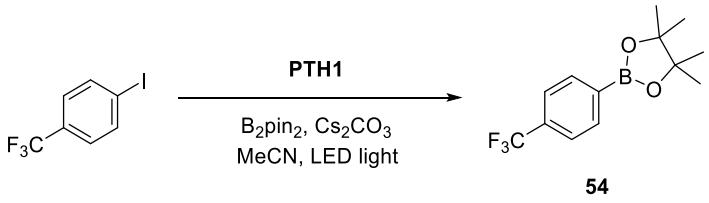
53

The general procedure GP1 was followed with 1-bromo-2-fluoro-4-methylbenzene (38 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **53** (31 mg, 65%) as a colorless oil.



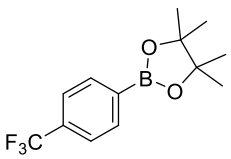
^{1}H NMR (500 MHz, $CDCl_3$): 7.62 (1 H, t, *J* = 7.0 Hz), 6.95 (1 H, d, *J* = 8.1 Hz), 6.85 (1 H, d, *J* = 10.4 Hz), 2.35 (3 H, s), 1.35 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 167.5 (d, *J* = 250.4 Hz), 144.4 (d, *J* = 8.5 Hz), 136.8 (d, *J* = 8.9 Hz), 124.6 (d, *J* = 2.9 Hz), 116.0 (d, *J* = 23.8 Hz), 83.8, 25.0, 21.6 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 30.4 ppm. – ^{19}F NMR (470.5 Hz, $CDCl_3$): −103.8 (dd, *J* = 10.4, 7.0 Hz) ppm. – IR: 2979, 2925, 1715, 1621, 1563, 1410, 1371, 1349, 1326, 1270, 1233, 1213, 1144, 1130, 1065 cm^{-1}.

4,4,5,5-Tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (54)[32]



54

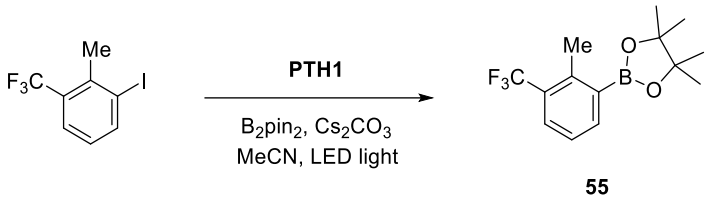
The general procedure GP1 was followed with 1-iodo-4-(trifluoromethyl)benzene (54 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **54** (46 mg, 86%) as a colorless solid.



M.p.: 68–70 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 7.91 (2 H, d, *J* = 7.8 Hz), 7.61 (2 H, d, *J* = 8.1 Hz), 1.36 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 135.2, 133.0 (q, *J* = 32.1 Hz), 124.4 (q, *J* = 3.6 Hz), 124.3 (q, *J* =

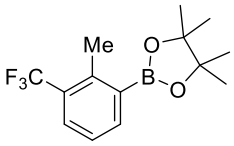
272.3 Hz), 84.4, 25.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 30.8 ppm. – ^{19}F NMR (470.5 Hz, $CDCl_3$): −63.0 ppm. – IR: 2979, 2254, 1974, 1739, 1520, 1401, 1362, 1320, 1272, 1242, 1213, 1158, 1140, 1096, 1017 cm^{-1}.

4,4,5,5-Tetramethyl-2-(2-methyl-3-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (55)



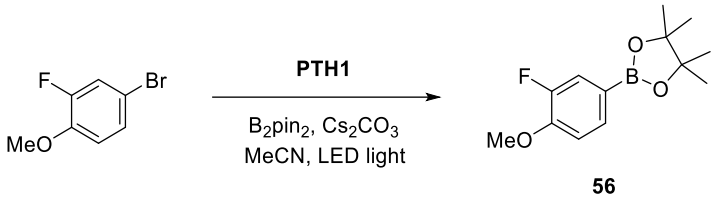
55

The general procedure GP1 was followed with 1-iodo-2-methyl-3-(trifluoromethyl)benzene (57 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.2 mg, 0.001 mmol, 0.5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **55** (44 mg, 77%) as a colorless oil.



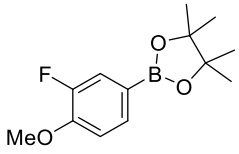
^{1}H NMR (500 MHz, $CDCl_3$): 7.92 (1 H, d, *J* = 7.5 Hz), 7.69 (1 H, d, *J* = 7.8 Hz), 7.26 (1 H, t, *J* = 7.7 Hz), 2.70 (3 H, s), 1.38 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 134.3, 139.2, 129.1 (q, *J* = 28.9 Hz), 128.2 (q, *J* = 6.2 Hz), 125.0 (d, *J* = 274.1 Hz), 124.9, 84.1, 25.0, 18.3 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.4 ppm. – ^{19}F NMR (470.5 Hz, $CDCl_3$): −61.0 ppm. – IR: 2980, 1593, 1445, 1390, 1360, 1307, 1267, 1222, 1169, 1144, 1122, 1075, 1020, 963 cm^{-1}. – HRMS: calcd for $C_{14}H_{19}BF_3O_2$: 287.1425, found 287.1423 [$M+H^+$].

2-(3-Fluoro-4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (56)[33]



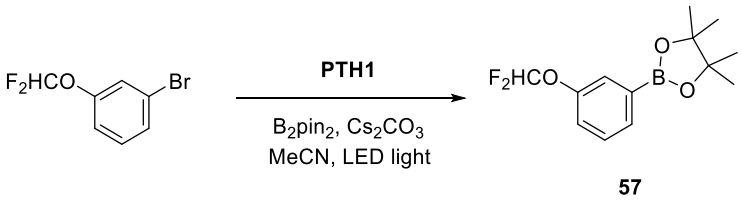
56

The general procedure GP1 was followed with 4-bromo-2-fluoro-1-methoxybenzene (41 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **56** (48 mg, 95%) as a colorless solid.



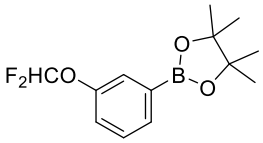
M.p.: 125–128 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 7.53 (1 H, d, *J* = 8.1 Hz), 7.49 (1 H, d, *J* = 11.8 Hz), 6.94 (1 H, t, *J* = 8.1 Hz), 3.90 (3 H, s), 1.33 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 152.2 (d, *J* = 246.1 Hz), 150.4 (d, *J* = 10.4 Hz), 131.6 (d, *J* = 3.7 Hz), 121.8 (d, *J* = 16.3 Hz), 112.7, 84.0, 56.2, 25.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 30.4 ppm. – ^{19}F NMR (470.5 Hz, $CDCl_3$): −137.1 (dd, *J* = 11.8, 8.1 Hz) ppm. – IR: 2986, 1642, 1598, 1432, 1385, 1296, 1208, 1165, 1123 1037 cm^{-1}.

2-(3-(Difluoromethoxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (57)[34]



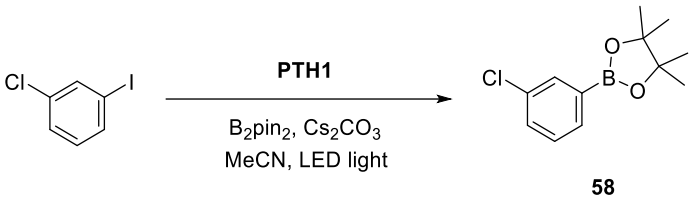
57

The general procedure GP1 was followed with 1-bromo-3-(difluoromethoxy)benzene (45 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **57** (49 mg, 90%) as a colorless liquid.

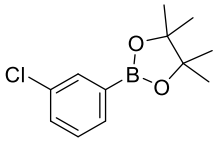


^{1}H NMR (500 MHz, $CDCl_3$): 7.65 (1 H, d, *J* = 7.3 Hz), 7.53 (1 H, d, *J* = 2.2 Hz), 7.37 (1 H, t, *J* = 7.7 Hz), 7.21 (1 H, dd, *J* = 8.1, 2.2 Hz), 6.53 (1 H, t, *J* = 74.2 Hz), 1.35 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 151.1, 131.9, 129.5, 125.2, 122.7, 116.2 (t, *J* = 259.1 Hz), 84.3, 25.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 30.8 ppm. – ^{19}F NMR (470.5 Hz, $CDCl_3$): −80.5 (d, *J* = 74.9 Hz) ppm. – IR: 2980, 1580, 1491, 1430, 1381, 1355, 1325, 1271, 1212, 1129, 1046, 964 cm^{-1}.

2-(3-Chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (58)[15]

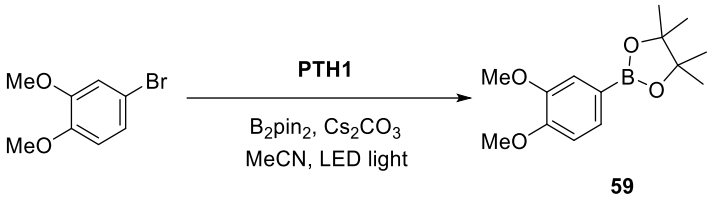


The general procedure GP1 was followed with 1-chloro-3-iodobenzene (47 mg, 0.2 mmol), B_2pin_2 (61 mg, 0.24 mmol, 1.2 equiv.), Cs_2CO_3 (79 mg, 0.24 mmol, 1.2 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **58** (24 mg, 50%) as a colorless oil.



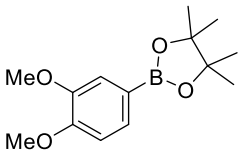
^{1}H NMR (500 MHz, $CDCl_3$): 7.78 (1 H, s), 7.67 (1 H, d, *J* = 7.3 Hz), 7.42 (1 H, dd, *J* = 8.0, 2.2 Hz), 7.30 (1 H, t, *J* = 7.7 Hz), 1.34 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 134.7, 134.2, 132.8, 131.4, 129.3, 84.3, 25.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 30.6 ppm. – IR: 2978, 1715, 1598, 1562, 1479, 1409, 1349, 1321, 1271, 1259, 1216, 1165, 1142, 1106, 1064, 1023 cm^{-1}.

2-(3,4-Dimethoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (59)[35]



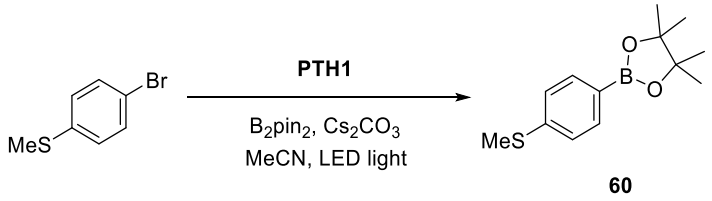
59

The general procedure GP1 was followed with 4-bromo-1,2-dimethoxybenzene (44 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 72 h. The crude mixture was diluted in EtOAc (5 mL) and H_2O (0.5 mL) and added 2-iodoxybenzoic acid (168 mg, 0.6 mmol, 3 equiv.). After heating at at 80 °C for 2 h, solid precipitated from the solution was filter off. The filtrate was extracted with saturated $NaHCO_3$ and brine then filter and concentrated to afford product **59** (46 mg, 86%) as a colorless solid.



M.p.: 66–69 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 7.42 (1 H, d, *J* = 8.0 Hz), 7.28 (1 H, s), 6.87 (1 H, d, *J* = 8.0 Hz), 3.91 (3 H, s), 3.88 (3 H, s), 1.32 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 151.7, 148.4, 128.7, 116.7, 110.6, 83.7, 55.9, 55.8, 24.9 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 30.8 ppm. – IR: 2976, 2837, 1599, 1577, 1518, 1449, 1409, 1351, 1294, 1226, 1175, 1137, 1110, 1095, 1027 cm^{-1}.

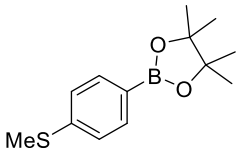
4,4,5,5-Tetramethyl-2-(4-(methylthio)phenyl)-1,3,2-dioxaborolane (60)[36]



60

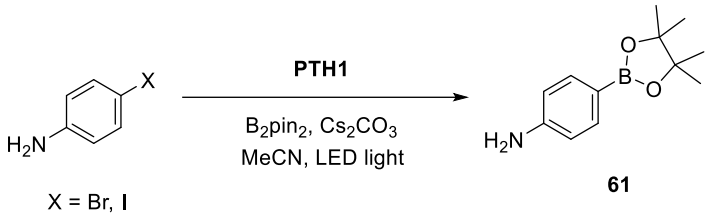
The general procedure GP1 was followed with (4-bromophenyl)(methyl)sulfane (40 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (2 mL). The mixture was irradiated with

a 400 nm LED light for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **60** (43 mg, 85%) as a colorless solid.



M.p.: 28–31 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 7.71 (2 H, d, *J* = 8.1 Hz), 7.23 (2 H, d, *J* = 8.2 Hz), 2.49 (3 H, s), 1.34 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 142.7, 135.2, 125.1, 83.9, 25.0, 15.2 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 30.9 ppm. – IR: 2976, 2922, 1737, 1715, 1545, 1436, 1393, 1355, 1325, 1296, 1271, 1256, 1215, 1100, 1075, 1015, 961 cm^{-1}.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (61)[37]

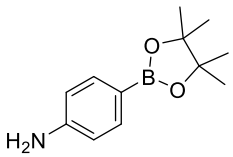


From 4-iodoaniline: The general procedure GP1 was followed with 4-iodoaniline (44 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.2 mg, 0.001 mmol, 0.5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **61** (35 mg, 80%) as a colorless solid.

From 4-bromoaniline: The general procedure GP1 was followed with 4-bromoaniline (34 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **61** (32 mg, 72%) as a colorless solid.

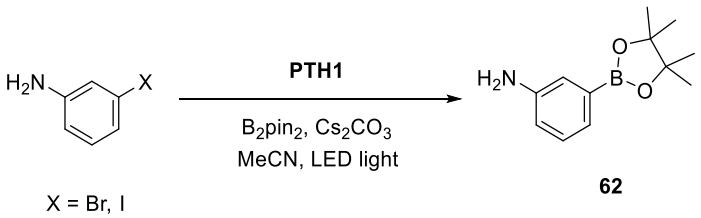
Gram scale from 4-bromoaniline: According to general procedure GP1 two identical reactions were run with 4-bromoaniline (688 mg, 4 mmol), B_2pin_2 (2.0 g, 8.0 mmol, 2.0 equiv.), Cs_2CO_3 (2.6 g, 8.0 mmol, 2.0 equiv.), **PTH1** (8.0 mg, 0.04 mmol, 1 mol%) and

CH_3CN (40 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **61** (1.7 g, 97%) as a colorless solid.



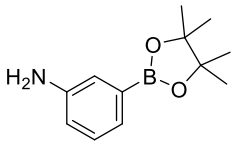
M.p.: 131−134 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 7.63 (2 H, d, *J* = 8.3 Hz), 6.65 (2 H, d, *J* = 8.4 Hz), 3.80 (2 H, brs), 1.33 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 149.4, 136.5, 114.2, 83.4, 25.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 30.8 ppm. – IR: 3448, 3356, 2993, 2975, 2926, 1701, 1626, 1601, 1564, 1470, 1429, 1396, 1351, 1299, 1270, 1140, 1108, 1086 cm^{-1}.

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (62)[38]



From 3-iodoaniline: The general procedure GP1 was followed with 3-iodoaniline (44 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.2 mg, 0.001 mmol, 0.5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **62** (31 mg, 70%) as a colorless solid.

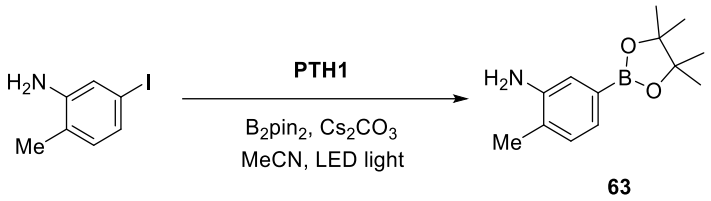
From 3-bromoaniline: The general procedure GP1 was followed with 3-bromoaniline (34 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **62** (29 mg, 65%) as a colorless solid.



M.p.: 65–67 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 7.21 (1 H, d, *J* = 7.2 Hz), 7.17 (1 H, t, *J* = 7.5 Hz), 7.14 (1 H, d, *J* = 2.3 Hz), 6.82–6.74 (1 H, m), 3.60

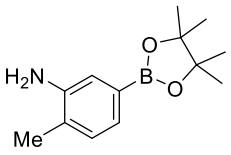
(2 H, brs), 1.34 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 145.9, 128.9, 125.1, 121.3, 118.2, 83.8, 25.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.0 ppm. – IR: 3463, 3374, 3228, 2984, 1709, 1627, 1600, 1492, 1441, 1355, 1319, 1284, 1262, 1210, 1138, 1110, 1075, 991, 965 cm^{-1}.

2-Methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (63)[39]



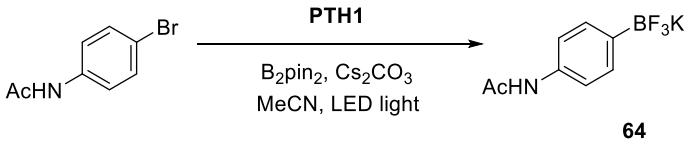
63

The general procedure GP1 was followed with 5-iodo-2-methylaniline (47 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.2 mg, 0.001 mmol, 0.5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **63** (33 mg, 72%) as a colorless liquid.



^{1}H NMR (500 MHz, $CDCl_3$): 7.17 (1 H, d, J = 7.4 Hz), 7.12 (1 H, s), 7.07 (1 H, d, J = 7.3 Hz), 3.57 (2 H, brs), 2.18 (3 H, s), 1.34 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 144.2, 130.1, 126.0, 125.4, 121.2, 83.7, 25.0, 17.7 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.0 ppm. – IR: 3373, 2979, 1708, 1634, 1566, 1416, 1354, 1321, 1260, 1220, 1144, 1092, 995 cm^{-1}.

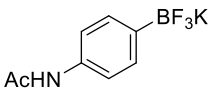
N-(4-(Trifluoro-λ^4-boraneyl)phenyl)acetamide, potassium salt (64)[40]



64

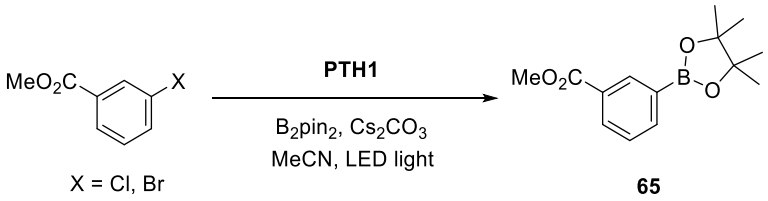
The general procedure GP1 was followed with N-(4-bromophenyl)acetamide (43 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1**

(0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by rapid column chromatography followed by treatment with KHF_2 according to GP3 afforded organotrifluoroborate salt **64** (43 mg, 83%) as a colorless solid.



M.p.: > 200 °C. – ^{1}H NMR (500 MHz, DMSO): 9.58 (1 H, s), 7.27 (2 H, d, J = 7.8 Hz), 7.20 (2 H, d, J = 7.2 Hz), 1.98 (3 H, s) ppm. – ^{13}C NMR (125 MHz, DMSO): 167.7, 136.5, 131.4, 117.6, 24.0 ppm. – ^{11}B NMR (160.4 Hz, DMSO): 3.2 ppm. – ^{19}F NMR (470.5 Hz, DMSO): −142.0 ppm. – IR: 3609, 3232, 1975, 1658, 1601, 1540, 1372, 1322, 1293, 1239, 1213, 1185, 1026, 961 cm^{-1}.

Methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (65)[41]



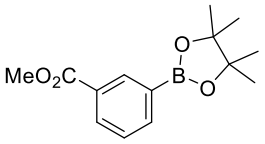
From methyl 3-bromobenzoate: The general procedure GP1 was followed with methyl 3-bromobenzoate (43 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **65** (43 mg, 83%) as a colorless solid.

From methyl 3-chlorobenzoate: The general procedure GP1 was followed with methyl 3-chlorobenzoate (34 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash

chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **65** (43 mg, 82%) as a colorless solid.

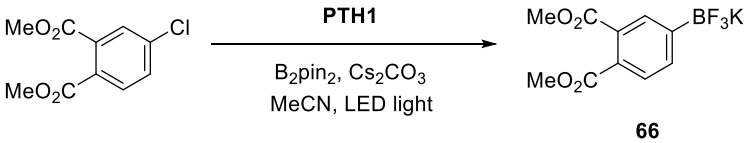
From methyl 3-chlorobenzoate with 1.5 equiv. of B_2pin_2: The general procedure GP1 was followed with methyl 3-chlorobenzoate (34 mg, 0.2 mmol), B_2pin_2 (76 mg, 0.3 mmol, 1.5 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **65** (38 mg, 73%) as a colorless solid.

From methyl 3-chlorobenzoate at 420 nm wavelength: The general procedure GP1 was followed with methyl 3-chlorobenzoate (34 mg, 0.2 mmol), B_2pin_2 (151 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 36 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **65** (42 mg, 81%) as a colorless solid.



M.p.: 65–68 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 8.47 (1 H, s), 8.12 (1 H, d, *J* = 10.9 Hz), 7.98 (1 H, d, *J* = 7.4 Hz), 7.44 (1 H, t, *J* = 7.6 Hz), 3.91 (3 H, s), 1.35 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 167.3, 139.3, 136.0, 132.4, 129.7, 127.9, 84.2, 52.2, 25.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 30.7 ppm. – IR: 2978, 1715, 1605, 1487, 1420, 1358, 1323, 1278, 1219, 1166, 1142, 1091, 1076 cm^{-1}.

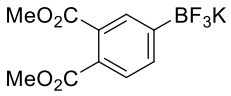
Dimethyl 4-(trifluoro-l4-boraneyl)phthalate, potassium salt (66)



66

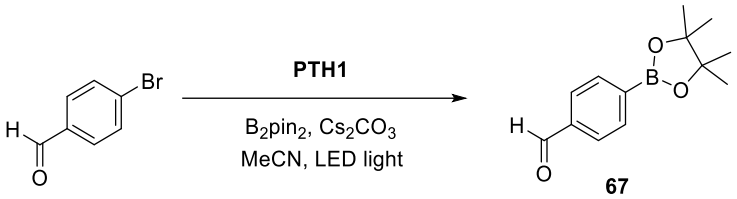
The general procedure GP1 was followed with dimethyl 4-chlorophthalate (46 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1**

(0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by GP2 afforded organotrifluoroborate salt **66** (37 mg, 62%) as a colorless solid.

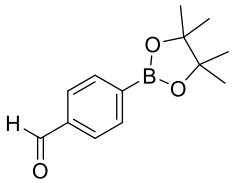


M.p.: > 200 °C. – ^{1}H NMR (500 MHz, CD_3CN): 7.73 (1 H, s), 7.66 (1 H, s), 7.57 (1 H, s), 3.81 (6 H, s) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 170.4, 169.4, 134.8, 132.2, 131.7, 129.6, 128.1, 52.9, 52.8 ppm. – ^{11}B NMR (160.4 Hz, CD_3CN): 2.7 ppm. – ^{19}F NMR (470.5 Hz, $CDCl_3$): 143.6 ppm. – IR: 3405, 2957, 1705, 1639, 1558, 1492, 1439, 1364, 1296, 1208, 1134, 1074, 1000 cm^{-1}. – HRMS: calcd for $C_{10}H_9BF_3O_4$: 261.0546, found 261.0549 [M−K$^+$].

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (67)[42]

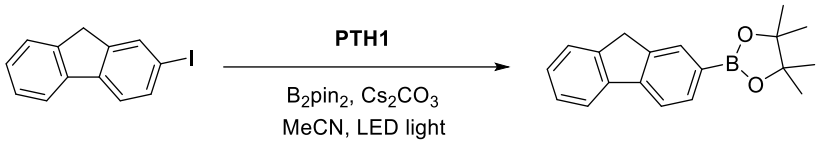


The general procedure GP1 was followed with 4-bromobenzaldehyde (37 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **67** (32 mg, 70%) as a colorless solid.



M.p.: 48–50 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 10.05 (1 H, s), 7.96 (2 H, d, J = 7.9 Hz), 7.86 (2 H, d, J = 7.8 Hz), 1.36 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 192.8, 138.2, 135.4, 128.8, 84.5, 25.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 30.8 ppm. – IR: 3429, 2978, 1704, 1583, 1507, 1382, 1355, 1304, 1271, 1168, 1141, 1084 cm^{-1}.

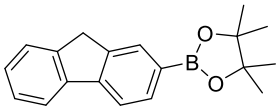
2-(9*H*-Fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (68)[43]



68

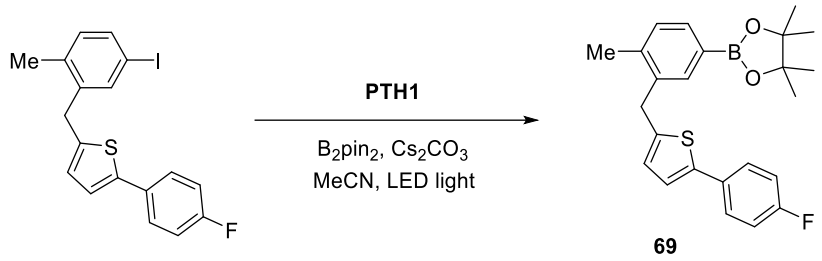
At 400 nm wavelength: The general procedure GP1 was followed with 2-iodo-9H-fluorene (58 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 36 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **68** (46 mg, 80%) as a colorless solid.

At 450 nm wavelength: The general procedure GP1 was followed with 2-iodo-9H-fluorene (58 mg, 0.2 mmol), B_2pin_2 (151 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 450 nm LED light for 36 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **68** (55 mg, 95%) as a colorless solid.



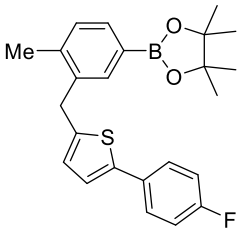
M.p.: 79–81 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 8.02 (1 H, s), 7.88–7.77 (3 H, m), 7.56 (1 H, d, *J* = 7.3 Hz), 7.39 (1 H, t, *J* = 7.4 Hz), 7.34 (1 H, t, *J* = 7.4 Hz), 3.92 (2 H, s), 1.39 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 144.7, 144.0, 142.6, 141.6, 133.5, 131.4, 127.3, 126.9, 125.2, 120.5, 119.4, 83.9, 36.9, 25.1 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.4 ppm. – IR: 3395, 2976, 1712, 1611, 1489, 1459, 1417, 1351, 1315, 1267, 1230, 1142, 1100, 1077, 1003 cm^{-1}.

2-(3-((5-(4-Fluorophenyl)thiophen-2-yl)methyl)-4-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (69)



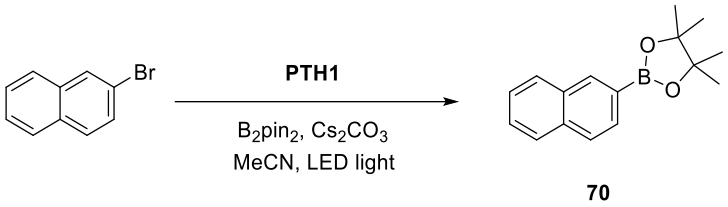
69

The general procedure GP1 was followed with 2-(4-fluorophenyl)-5-(5-iodo-2-methylbenzyl)thiophene (82 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **69** (64 mg, 78%) as a colorless liquid.

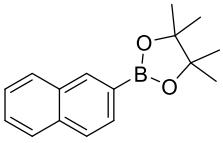


^{1}H NMR (500 MHz, $CDCl_3$): 7.71 (1 H, s), 7.66 (1 H, d, *J* = 7.5 Hz), 7.47 (2 H, dd, *J* = 8.8, 5.3 Hz), 7.21 (1 H, d, *J* = 7.5 Hz), 7.06–6.96 (3 H, m), 6.63 (1 H, d, *J* = 3.6 Hz), 4.15 (2 H, s), 2.34 (3 H, s), 1.36 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 162.2 (d, *J* = 246.4 Hz), 144.0, 141.4, 140.2, 137.5, 136.4, 133.8, 131.0, 130.2, 127.2 (d, *J* = 8.2 Hz), 125.8, 122.7, 115.8 (d, *J* = 21.5 Hz), 83.8, 34.4, 25.0, 19.9 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.5 ppm. – ^{19}F NMR (470.5 Hz, $CDCl_3$): −115.3 ppm. – IR: 2977, 1711, 1610, 1549, 1508, 1410, 1355, 1318, 1273, 1219, 1159, 1144, 1088, 1044 cm^{-1}. – HRMS: calcd for $C_{24}H_{27}BFO_2S$: 409.1803, found 409.1805 [M+H$^+$].

4,4,5,5-Tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane (70)[15]

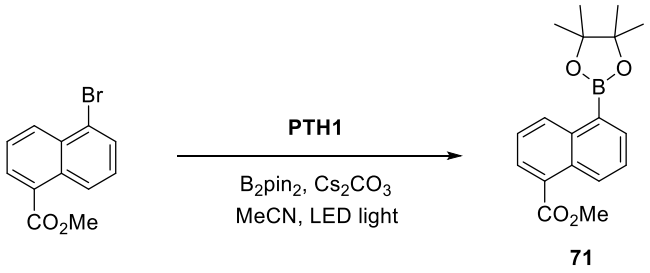


The general procedure GP1 was followed with 2-bromonaphthalene (42 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **70** (29 mg, 57%) as a colorless liquid.



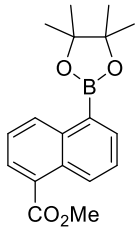
^{1}H NMR (500 MHz, $CDCl_3$): 8.39 (1 H, s), 7.90 (1 H, d, *J* = 7.9 Hz), 7.87–7.82 (3 H, m), 7.57–7.42 (2 H, m), 1.41 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 136.4, 135.2, 133.0, 130.5, 128.8, 127.8, 127.1, 125.9, 84.1, 25.1 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.1 ppm. – IR: 2976, 2928, 1629, 1599, 1474, 1430, 1399, 1382, 1371, 1297, 1271, 1236, 1143 cm^{-1}.

Methyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-naphthoate (71)



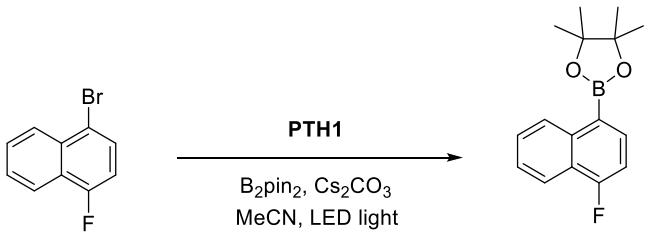
The general procedure GP1 was followed with methyl 5-bromo-1-naphthoate (53 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400

nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **71** (38 mg, 61%) as a colorless solid.



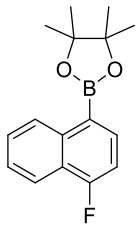
M.p.: 65–68 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 9.01 (2 H, d, *J* = 8.4 Hz), 8.15 (2 H, t, *J* = 6.8 Hz), 7.65–7.49 (2 H, m), 4.00 (3 H, s), 1.43 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 168.4, 137.4, 136.1, 133.8, 131.3, 129.8, 129.2, 127.5, 126.8, 125.0, 84.0, 52.3, 25.1 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 32.0 ppm. – IR: 2980, 1736, 1717, 1511, 1436, 1371, 1371, 1332, 1300, 1236, 1166, 1133, 1044, 970 cm^{-1}. – HRMS: calcd for $C_{18}H_{22}BO_4$: 313.1606, found 313.1607 [M+H$^+$].

2-(4-Fluoronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (72)[44]



72

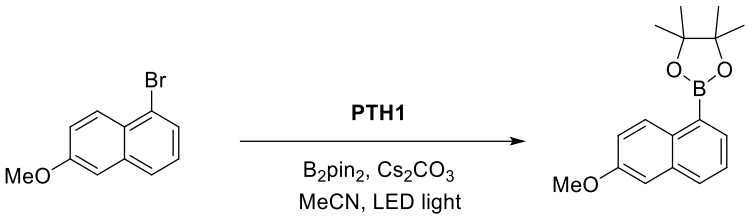
The general procedure GP1 was followed with 1-bromo-4-fluoronaphthalene (45 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **72** (40 mg, 74%) as a colorless liquid.



^{1}H NMR (500 MHz, $CDCl_3$): 8.81 (1 H, d, *J* = 8.4 Hz), 8.13 (1 H, d, *J* = 8.2 Hz), 8.08–8.02 (1 H, m), 7.60 (1 H, t, *J* = 7.1 Hz), 7.54 (1 H, t, *J* = 7.4 Hz), 7.14 (1 H, dd, *J* = 10.4, 7.7 Hz), 1.42 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 161.4 (d, *J* = 256.8 Hz), 138.9 (d, *J* = 4.7 Hz), 136.3 (d, *J* = 8.9 Hz), 128.4 (d, *J* = 3.0 Hz), 127.4, 126.0, 123.7 (d, *J* = 15.1 Hz), 120.7 (d, *J* = 6.3 Hz), 108.9 (d, *J* = 18.9 Hz), 83.9, 25.1

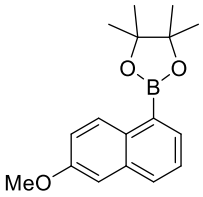
ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.4 ppm. – ^{19}F NMR (470.5 Hz, $CDCl_3$): −118.2 ppm. – IR: 2999, 1709, 1575, 1509, 1427, 1359, 1259, 1220, 1143, 1091, 1049, 1023 cm^{-1}.

2-(6-Methoxynaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (73)[45]



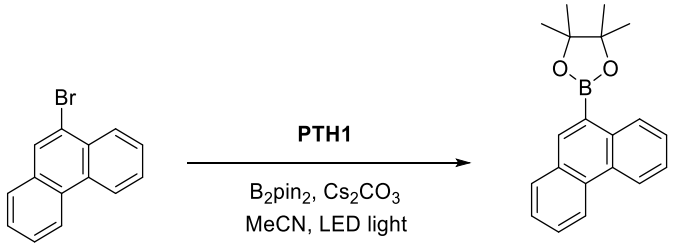
73

The general procedure GP1 was followed with 1-bromo-6-methoxynaphthalene (48 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **73** (34 mg, 60%) as a colorless liquid.



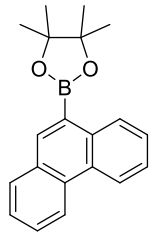
^{1}H NMR (500 MHz, $CDCl_3$): 8.30 (1 H, s), 7.82 (1 H, d, *J* = 8.2 Hz), 7.78 (1 H, d, *J* = 8.6 Hz), 7.72 (1 H, d, *J* = 8.2 Hz), 7.18–7.11 (2 H, m), 3.93 (3 H, s), 1.39 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 158.7, 136.6, 136.1, 131.2, 130.4, 128.5, 126.0, 118.8, 105.8, 83.9, 55.4, 25.1 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.3 ppm. – IR: 3002, 1709, 1626, 1487, 1418, 1358, 1272, 1219, 1144, 1080, 1030 cm^{-1}.

4,4,5,5-Tetramethyl-2-(phenanthren-9-yl)-1,3,2-dioxaborolane (74)[]



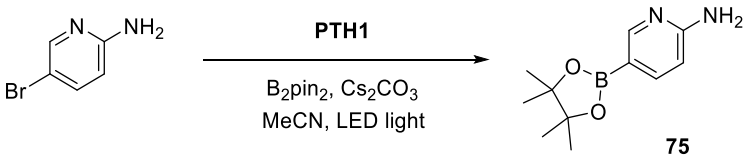
74

The general procedure GP1 was followed with 9-bromophenanthrene (52 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **74** (37 mg, 61%) as a colorless liquid.

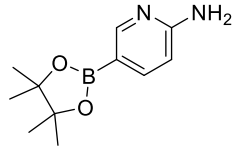


^{1}H NMR (500 MHz, $CDCl_3$): 8.89 (1 H, dd, *J* = 6.7, 2.8 Hz), 8.77–8.66 (2 H, m), 8.45 (1 H, s), 7.98 (1 H, d, *J* = 7.9 Hz), 7.78–7.66 (3 H, m), 7.62 (1 H, t, *J* = 7.4 Hz), 1.49 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 138.3, 134.6, 132.0, 131.1, 130.0, 129.4, 129.2, 127.9, 126.8, 126.6, 126.3, 122.8, 122.6, 84.0, 25.1 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.6 ppm. – IR: 2975, 1713, 1614, 1528, 1445, 1370, 1341, 1306, 1263, 1213, 1133, 1109, 1005, 979 cm^{-1}.

5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pyridin-2-amine (75)[46]

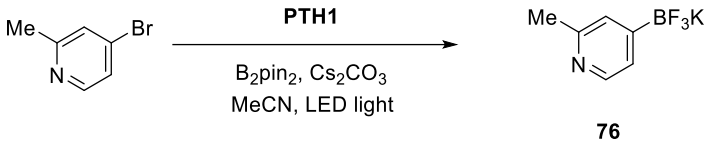


The general procedure GP1 was followed with 5-bromopyridin-2-amine (35 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc) afford product **75** (27 mg, 62%) as a colorless solid.



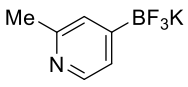
M.p: 132–134 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 8.43 (1 H, s), 7.77 (1 H, d, *J* = 8.2 Hz), 6.44 (1 H, d, *J* = 8.2 Hz), 4.73 (2 H, s), 1.31 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 160.3, 155.4, 144.0, 107.8, 83.7, 25.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.0 ppm. – IR: 3362, 3204, 2978, 1731, 1602, 1557, 1470, 1358, 1299, 1271, 1245, 1139, 1099 cm^{-1}.

2-Methyl-4-(trifluoro-λ⁴-boraneyl)pyridine, potassium salt (76)[47]



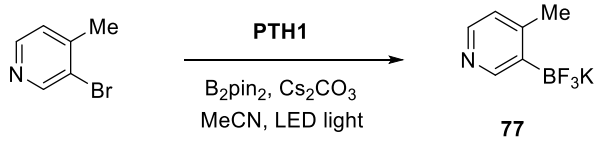
76

The general procedure GP1 was followed with 4-bromo-2-methylpyridine (34 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (79 mg, 0.24 mmol, 1.2 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by treatment with KF, tartaric acid and then K_2CO_3 according to GP2 afforded organotrifluoroborate salt **76** (40 mg, 99%) as a colorless solid.



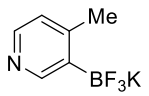
M.p.: > 200 °C. – ^{1}H NMR (500 MHz, CD_3CN): 8.20 (1 H, d, *J* = 4.8 Hz), 7.24 (1 H, s), 7.15 (1 H, d, *J* = 4.6 Hz), 2.41 (3 H, s) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 156.6, 147.8, 127.1, 124.8, 24.3 ppm. – ^{11}B NMR (160.4 Hz, CD_3CN): 2.8 ppm. – ^{19}F NMR (470.5 Hz, CD_3CN): −144.2 (dd, *J* = 99.9, 44.1 Hz) ppm. – IR: 3358, 1634, 1539, 1447, 1384, 1273, 1172, 1007, 977 cm^{-1}.

4-Methyl-3-(trifluoro-λ⁴-boraneyl)pyridine, potassium salt (77)



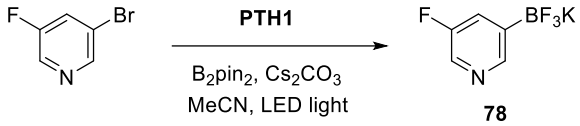
77

The general procedure GP1 was followed with 3-bromo-4-methylpyridine (34 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (79 mg, 0.24 mmol, 1.2 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by GP2 afforded organotrifluoroborate salt **77** (28 mg, 70%) as a colorless solid.

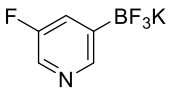


M.p.: > 200 °C. – ^{1}H NMR (500 MHz, CD_3CN): 8.48 (1 H, s), 8.17 (1 H, d, *J* = 5.0 Hz), 6.95 (1 H, d, *J* = 5.0 Hz), 2.36 (3 H, s) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 153.4, 151.4, 147.9, 125.2, 21.3 ppm. – ^{11}B NMR (160.4 Hz, CD_3CN): 3.4 (q, *J* = 44.1 Hz) ppm. – ^{19}F NMR (470.5 Hz, CD_3CN): −140.4 (dd, *J* = 103.3, 45.2 Hz) ppm. – IR: 3382, 1737, 1614, 1476, 1408, 1360, 1294, 1231, 1192, 1128, 957 cm^{-1}. – HRMS: calcd for $C_6H_6BF_3N$: 160.0551, found 160.0549 [M−K$^+$].

3-Fluoro-5-(trifluoro-λ^4-boraneyl)pyridine, potassium salt (78)

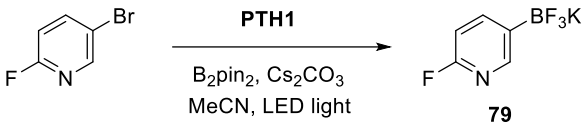


The general procedure GP1 was followed with 3-bromo-5-fluoropyridine (35 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (79 mg, 0.24 mmol, 1.2 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by treatment with KF, tartaric acid and then K_2CO_3 according to GP2 afforded organotrifluoroborate salt **78** (28 mg, 70%) as a colorless solid.

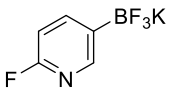


M.p.: > 200 °C. – ^{1}H NMR (500 MHz, CD_3CN): 8.40 (1 H, s), 8.18 (1 H, d, *J* = 2.6 Hz), 7.45 (1 H, d, *J* = 8.9 Hz) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 160.9 (d, *J* = 251.0 Hz), 149.7, 135.3 (d, *J* = 23.1 Hz), 125.5 (d, *J* = 13.7 Hz) ppm. – ^{11}B NMR (160.4 Hz, CD_3CN $_3$): 2.7 (q, *J* = 50.9 Hz) ppm. – ^{19}F NMR (470.5 Hz, CD_3CN): −131.8 (d, *J* = 9.4 Hz), −142.9 (dd, *J* = 99.9, 47.9 Hz) ppm. – IR: 3342, 2138, 1634, 1553, 1407, 1364, 1320, 1258, 1228, 1159, 1078, 1004, 882 cm^{-1}. – HRMS: calcd for $C_5H_3BF_4NK$: 164.0300, found 164.0305 [M−K$^+$].

2-Fluoro-5-(trifluoro-λ⁴-boraneyl)pyridine, potassium salt (79)[48]

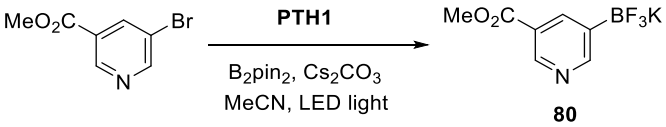


The general procedure GP1 was followed with 5-bromo-2-fluoropyridine (35 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (79 mg, 0.24 mmol, 1.2 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by treatment with KF, tartaric acid and then K_2CO_3 according to GP2 afforded organotrifluoroborate salt **79** (34 mg, 85%) as a colorless solid.

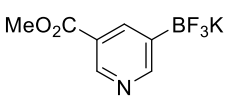


M.p.: > 200 °C. – ^{1}H NMR (500 MHz, CD_3CN): 8.15 (1 H, s), 7.87 (1 H, t, *J* = 8.4 Hz), 6.78 (1 H, dd, *J* = 8.0, 2.0 Hz) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 163.8 (d, *J* = 230.7 Hz), 150.8 (d, *J* = 12.5 Hz), 145.5 (d, *J* = 6.6 Hz), 108.1 (d, *J* = 35.5 Hz) ppm. – ^{11}B NMR (160.4 Hz, CD_3CN): 3.1 (q, *J* = 49.6 Hz) ppm. – ^{19}F NMR (470.5 Hz, CD_3CN): −75.1, −142.8 (dd, *J* = 97.7, 44.5 Hz) ppm. – IR: 3335, 1737, 1638, 1594, 1478, 1347, 1307, 1249, 1204, 1123, 965 cm^{-1}.

Methyl 5-(trifluoro-λ⁴-boraneyl)nicotinate, potassium salt (80)



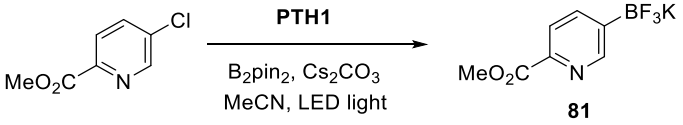
The general procedure GP1 was followed with methyl 5-bromonicotinate (43 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (79 mg, 0.24 mmol, 1.2 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by treatment with KF, tartaric acid and then K_2CO_3 according to GP2 afforded organotrifluoroborate salt **80** (33 mg, 69%) as a colorless solid.



M.p.: > 200 °C. – ^{1}H NMR (500 MHz, DMSO): 8.83 (1 H, s), 8.66 (1 H, s), 8.17 (1 H, s), 3.85 (3 H, s) ppm. – ^{13}C NMR (125 MHz, DMSO): 166.5,

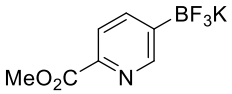
156.5, 147.4, 139.4, 124.1, 52.0 ppm. – ^{11}B NMR (160.4 Hz, DMSO): 2.7 ppm. – ^{19}F NMR (470.5 Hz, DMSO): −139.7 ppm. – IR: 3247, 2575, 2436, 2359, 2340, 1684, 1640, 1585, 1541, 1494, 1366, 1347, 1310, 1231, 1195, 1135, 1078 cm^{-1}. – HRMS: calcd for $C_7H_6BF_3NO_2$: 204.0449, found 204.0449 [M−K$^+$].

Methyl 6-(trifluoro-λ^4-boraneyl)picolinate, potassium salt (81)



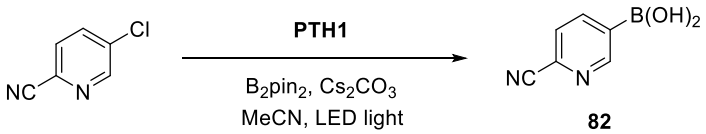
81

The general procedure GP1 was followed with methyl 5-chloropicolinate (34 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (79 mg, 0.24 mmol, 1.2 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by treatment with KF, tartaric acid and then K_2CO_3 according to GP2 afforded organotrifluoroborate salt **81** (22 mg, 44%) as a colorless solid.



M.p.: > 200 °C. – ^{1}H NMR (500 MHz, CD_3CN): 8.73 (1 H, d, *J* = 7.5 Hz), 8.66 (1 H, s), 8.34 (1 H, d, *J* = 7.7 Hz), 4.06 (3 H, s) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 160.6, 151.7, 144.4, 136.9, 126.8, 54.5 ppm. – ^{11}B NMR (160.4 Hz, CD_3CN): 2.7 (q, *J* = 47.0 Hz) ppm. – ^{19}F NMR (470.5 Hz, CD_3CN): −144.3 (dd, *J* = 79.1, 41.3 Hz) ppm. – IR: 1716, 1614, 1562, 1508, 1464, 1398, 1357, 1326, 1265, 1143, 1107, 1096, 1021, 962 cm^{-1}. – HRMS: calcd for $C_7H_6BF_3NO_2$: 204.0449, found 204.0445 [M−K$^+$].

(6-Cyanopyridin-3-yl)boronic acid (82)[49]



82

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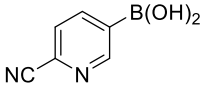
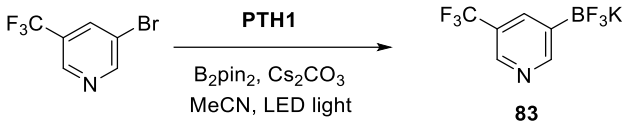
The general procedure GP1 was followed with 5-chloropicolinonitrile (28 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.04 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by treatment with methylboronic acid and then extraction according to GP4 afforded boronic acid **82** (17 mg, 58%) as a colorless oil.

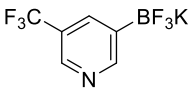


^{1}H NMR (500 MHz, CD_3OD): 8.72 (1 H, s), 8.03 (1 H, d, *J* = 8.3 Hz), 7.65 (1 H, d, *J* = 7.5 Hz) ppm. – ^{13}C NMR (125 MHz, CD_3OD): 156.6, 143.5, 130.4, 128.5, 119.1 ppm. – ^{11}B NMR (160.4 Hz, CD_3OD): 3.9 ppm. – IR: 3339, 2946, 2835, 2497, 2242, 2074, 1646, 1449, 1314, 1204, 1118, 1021 cm^{-1}.

3-(Trifluoro-λ^4-boraneyl)-5-(trifluoromethyl)pyridine, potassium salt (83)[50]

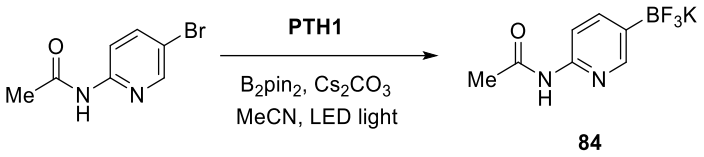


The general procedure GP1 was followed with 3-bromo-5-(trifluoromethyl)pyridine (45 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (79 mg, 0.24 mmol, 1.2 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by treatment with KF, tartaric acid and then K_2CO_3 according to GP2 afforded organotrifluoroborate salt **83** (39 mg, 78%) as a colorless solid.

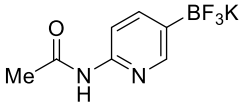


M.p.: > 200 °C. – ^{1}H NMR (500 MHz, CD_3CN): 8.80 (1 H, s), 8.64 (1 H, s), 7.98 (1 H, s) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 150.5, 143.7, 139.8 (d, *J* = 4.5 Hz), 128.3 (q, *J* = 32.4, 31.9 Hz), 124.0 (q, *J* = 271.9 Hz) ppm. – ^{11}B NMR (160.4 Hz, CD_3CN): 2.7 (q, *J* = 49.9 Hz) ppm. – ^{19}F NMR (470.5 Hz, CD_3CN): −63.4, −144.2 (dd, *J* = 89.7, 42.3 Hz) ppm. – IR: 3418, 1738, 1646, 1596, 1344, 1321, 1216, 1175, 1128, 1091 cm^{-1}.

N-(5-(Trifluoro-λ⁴-boraneyl)pyridin-2-yl)acetamide, potassium salt (84)

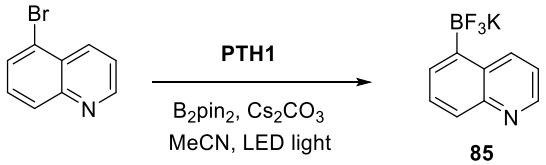


The general procedure GP1 was followed with *N*-(5-bromopyridin-2-yl)acetamide (43 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (79 mg, 0.24 mmol, 1.2 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by treatment with KF, tartaric acid and then K_2CO_3 according to GP2 afforded organotrifluoroborate salt **84** (41 mg, 85%) as a colorless solid.



M.p.: > 200 °C. – ^{1}H NMR (500 MHz, $(CD_3)_2CO$): 8.35 (1 H, s), 8.19 (1 H, d, *J* = 8.1 Hz), 7.57 (1 H, d, *J* = 8.2 Hz), 2.26 (3 H, s) ppm. – ^{13}C NMR (125 MHz, $(CD_3)_2CO$): 171.8, 148.6, 147.5, 144.6, 113.8, 24.2 ppm. – ^{11}B NMR (160.4 Hz, $(CD_3)_2CO$): 2.5 ppm. – ^{19}F NMR (470.5 Hz, $(CD_3)_2CO$): −143.2 ppm. – IR: 3247, 2581, 2441, 1694, 1639, 1585, 1541, 1494, 1366, 1310, 1232, 1194, 1135, 1024, 973 cm^{-1}. – HRMS: calcd for $C_7H_7BF_3N_2O$: 203.0609, found 203.0606 [M−K$^+$].

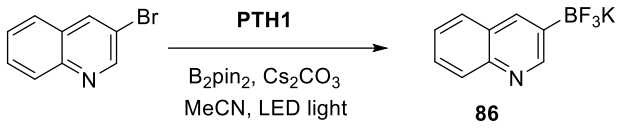
5-(Trifluoro-λ⁴-boraneyl)quinoline, potassium salt (85)[47]



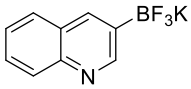
The general procedure GP1 was followed with 5-bromoquinoline (43 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by treatment with KF, tartaric acid and then K_2CO_3 according to GP2 afforded organotrifluoroborate salt **85** (34 mg, 73%) as a colorless solid.

M.p.: > 200 °C. – ^{1}H NMR (500 MHz, CD_3CN): 8.81 (1 H, d, *J* = 8.5 Hz), 8.75 (1 H, dd, *J* = 4.1, 1.7 Hz), 7.81 (1 H, d, *J* = 8.3 Hz), 7.71 (1 H, d, *J* = 6.5 Hz), 7.63–7.52 (1 H, m), 7.34 (1 H, dd, *J* = 8.5, 4.1 Hz) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 149.7, 139.0, 130.01, 129.98, 129.5, 127.7, 120.4 ppm. – ^{11}B NMR (160.4 Hz, CD_3CN): 3.6 (q, *J* = 54.8 Hz) ppm. – ^{19}F NMR (470.5 Hz, CD_3CN): −138.0 (dd, *J* = 103.7, 45.7 Hz) ppm. – IR: 2943, 2357, 2253, 1975, 1632, 1558, 1444, 1374, 1246, 1153, 1037 cm^{-1}.

3-(Trifluoro-λ^4-boraneyl)quinoline, potassium salt (86)[48]

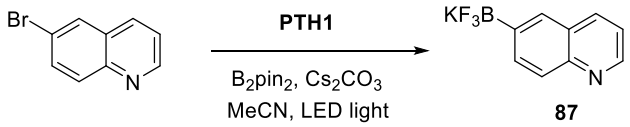


The general procedure GP1 was followed with 3-bromoquinoline (43 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by treatment with KF, tartaric acid and then K_2CO_3 according to GP2 afforded organotrifluoroborate salt **86** (29 mg, 62%) as a colorless solid.

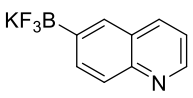


M.p.: > 200 °C. – ^{1}H NMR (500 MHz, CD_3CN): 8.97 (1 H, s), 8.23 (1 H, s), 7.95 (1 H, d, *J* = 8.4 Hz), 7.82 (1 H, d, *J* = 8.1 Hz), 7.59 (1 H, t, *J* = 8.3 Hz), 7.46 (1 H, t, *J* = 7.5 Hz) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 156.2, 148.1, 138.7, 129.5, 129.4, 128.7, 128.4, 126.1 ppm. – ^{11}B NMR (160.4 Hz, CD_3CN): 3.2 (q, *J* = 54.2, 52.8 Hz) ppm. – ^{19}F NMR (470.5 Hz, CD_3CN): -142.0 (q, *J* = 92.1, 34.2 Hz) ppm. – IR: 3020, 1619, 1597, 1571, 1493, 1418, 1354, 1325, 1280, 1173, 1127, 1029, 970 cm^{-1}.

6-(Trifluoro-λ⁴-boraneyl)quinoline, potassium salt (87)[48]

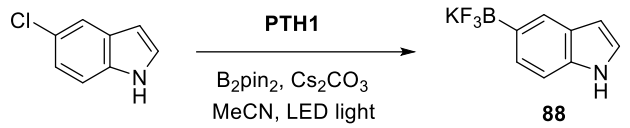


The general procedure GP1 was followed with 6-bromoquinoline (43 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by treatment with KF, tartaric acid and then K_2CO_3 according to GP2 afforded organotrifluoroborate salt **87** (25 mg, 53%) as a colorless solid.

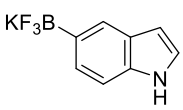


M.p.: > 200 °C. – ^{1}H NMR (500 MHz, CD_3CN): 8.75 (1 H, d, *J* = 5.4 Hz), 8.18 (1 H, d, *J* = 8.2 Hz), 7.92 (1 H, s), 7.86 (2 H, q, *J* = 8.4 Hz), 7.35 (1 H, dd, *J* = 8.2, 4.2 Hz) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 149.7, 148.7, 136.7, 135.0, 130.7, 128.8, 127.5, 121.1 ppm. – ^{11}B NMR (160.4 Hz, CD_3CN): 3.4 (q, *J* = 52.0, 50.9 Hz) ppm. – ^{19}F NMR (470.5 Hz, CD_3CN): −142.7 (dd, *J* = 95.9, 39.0 Hz) ppm. – IR: 3373, 2969, 2231, 1738, 1697, 1621, 1573, 1498, 1457, 1365, 1345, 1309, 1229, 1168, 1120, 992 cm^{-1}.

5-(Trifluoro-λ⁴-boraneyl)-1H-indole, potassium salt (88)[47]

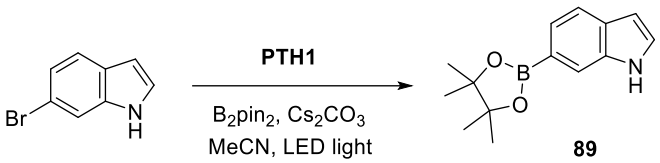


The general procedure GP1 was followed with 5-chloro-1*H*-indole (30 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 72 h at 45 ^{0}C. Purification by rapid chromatography then treatment with KHF_2 and K_2CO_3 accroding to GP4 afforded organotrifluoroborate salt **88** (25 mg, 55%) as a colorless solid.

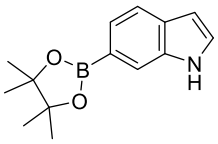


M.p.: > 200 °C. – ^{1}H NMR (500 MHz, CD_3CN): 8.99 (1 H, s), 7.65 (1 H, s), 7.41–7.21 (2 H, m), 7.11 (1 H, t, *J* = 2.7 Hz), 6.54–6.20 (1 H, m) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 136.2, 128.4, 126.6, 124.0, 123.6, 110.3, 102.1 ppm. – ^{11}B NMR (160.4 Hz, CD_3CN): 4.2 ppm. – ^{19}F NMR (470.5 Hz, CD_3CN): −140.6 ppm. – IR: 3355, 1634, 1416, 1342, 1229, 1146, 1096, 986 cm^{-1}.

6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (89)[15]

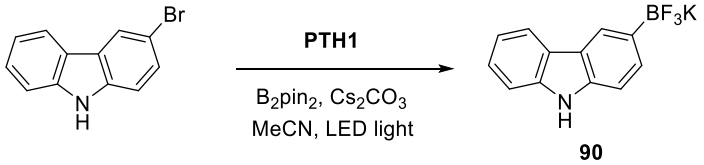


The general procedure GP1 was followed with 6-bromo-1H-indole (39 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **89** (34 mg, 70%) as a colorless liquid.



^{1}H NMR (500 MHz, $CDCl_3$): 8.29 (1 H, s), 7.93 (1 H, s), 7.68 (1 H, d, *J* = 7.1 Hz), 7.59 (1 H, d, *J* = 7.1 Hz), 7.26 (1 H, s), 6.58 (1 H, s), 1.40 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 135.7, 130.5, 125.7, 125.7, 120.2, 118.2, 102.8, 83.7, 25.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.5 ppm. – IR: 2984, 2254, 1736, 1712, 1446, 1372, 1238, 1095, 1044, 916 cm^{-1}.

3-(Trifluoro-λ^4-boraneyl)-9*H*-carbazole, potassium salt (90)



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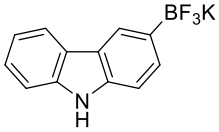
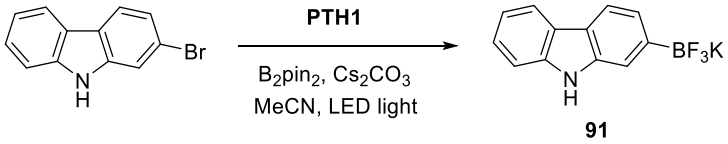
The general procedure GP1 was followed with 3-bromo-9*H*-carbazole (49 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (79 mg, 0.24 mmol, 1.2 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by treatment with KF, tartaric acid and then K_2CO_3 according to GP2 afforded organotrifluoroborate salt **90** (41 mg, 76%) as a colorless solid.

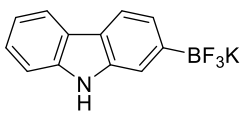


M.p.: > 200 °C. – ^{1}H NMR (500 MHz, CD_3CN): 9.04 (1 H, s), 8.15 (1 H, s), 8.06 (1 H, d, *J* = 7.8 Hz), 7.52 (1 H, d, *J* = 8.0 Hz), 7.43 (1 H, d, *J* = 8.1 Hz), 7.32 (2 H, t, *J* = 7.5 Hz), 7.12 (1 H, t, *J* = 7.9 Hz) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 140.6, 139.9, 130.9, 125.5, 124.6, 123.4, 122.9, 120.7, 119.2, 111.3, 110.0 ppm. – ^{11}B NMR (160.4 Hz, CD_3CN): 4.3 ppm. – ^{19}F NMR (470.5 Hz, CD_3CN): −140.5 ppm. – IR: 3393, 3272, 1737, 1624, 1601, 1459, 1438, 1352, 1243, 1208, 1175, 1127, 1035 cm^{-1}. – HRMS: calcd for $C_{12}H_8BF_3N$: 234.0707, found 237.0705 [M−K$^+$].

2-(Trifluoro-λ^4-boraneyl)-9*H*-carbazole, potassium salt (91)



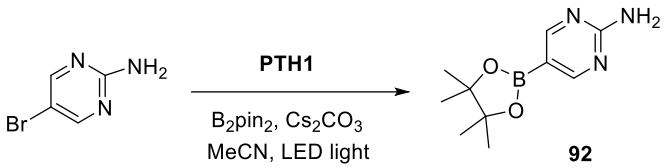
The general procedure GP1 was followed with 2-bromo-9*H*-carbazole (49 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (79 mg, 0.24 mmol, 1.2 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by treatment with KF, tartaric acid and then K_2CO_3 according to GP2 afforded organotrifluoroborate salt **91** (38 mg, 70%) as a colorless solid.



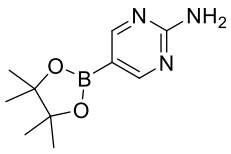
M.p.: > 200 °C. – ^{1}H NMR (500 MHz, CD_3CN): 9.88 (1 H, s), 7.99 (1 H, d, *J* = 7.7 Hz), 7.86 (1 H, d, *J* = 7.7 Hz), 7.65 (1 H, s), 7.40 (2 H, dd, *J* =

7.8, 3.6 Hz), 7.26 (1 H, t, *J* = 8.0 Hz), 7.07 (1 H, t, *J* = 7.4 Hz) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 141.1, 140.8, 124.99, 124.95, 124.3, 121.8, 120.2, 118.8, 118.6, 114.6, 111.3 ppm. – ^{11}B NMR (160.4 Hz, CD_3CN): 4.2 ppm. – ^{19}F NMR (470.5 Hz, CD_3CN): −143.0 ppm. – IR: 3410, 2969, 1737, 1625, 1497, 1458, 1436, 1365, 1324, 1274, 1227, 1216, 1166, 996 cm^{-1}. – HRMS: calcd for $C_{12}H_8BF_3N$: 234.0707, found 237.0705 [M−K$^+$].

5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pyrimidin-2-amine (92)[51]

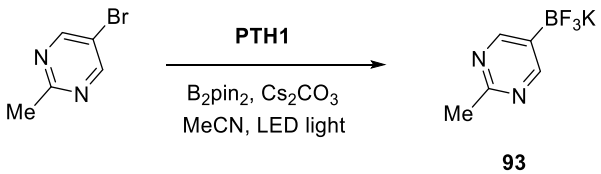


The general procedure GP1 was followed with 5-bromopyrimidin-2-amine (35 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc) afford product **92** (25 mg, 71%) as a colorless solid.



M.p.: 208–210 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 8.59 (2 H, s), 5.38 (2 H, s), 1.32 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 164.7, 164.0, 83.9, 24.8 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 30.5 ppm. – IR: 3426, 3325, 3220, 2974, 2425, 1706, 1647, 1594, 1539, 1506, 1399, 1350, 1298, 1222, 1140, 1119 cm^{-1}.

2-Methyl-5-(trifluoro-λ^4-boraneyl)pyrimidine, potassium salt (93)



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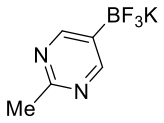
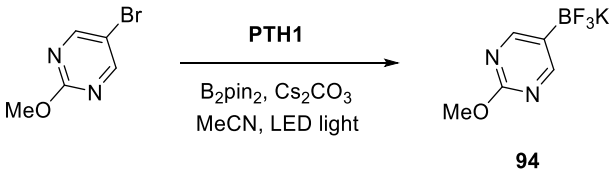
The general procedure GP1 was followed with 5-bromo-2-methylpyrimidine (35 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (79 mg, 0.24 mmol, 1.2 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by treatment with KF, tartaric acid and then K_2CO_3 according to GP2 afforded organotrifluoroborate salt **93** (34 mg, 85%) as a colorless solid.

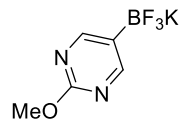


M.p.: > 200 °C. – ^{1}H NMR (500 MHz, $(CD_3)_2CO$): 8.56 (2 H, s), 2.48 (3 H, s) ppm. – ^{13}C NMR (125 MHz, $(CD_3)_2CO$): 165.2, 160.8, 25.8 ppm. – ^{11}B NMR (160.4 Hz, $(CD_3)_2CO$): 2.9 (q, J = 50.1 Hz) ppm. – ^{19}F NMR (470.5 Hz, $(CD_3)_2CO$): −142.8 (dd, J = 96.4, 48.3 Hz) ppm. – IR: 3356, 2947, 2835, 1697, 1368, 1258, 1232, 1111, 1017 cm^{-1}. – HRMS: calcd for $C_5H_5BF_3N_2$: 161.0503, found 161.0500 [M−K$^+$].

2-Methoxy-5-(trifluoro-λ^4-boraneyl)pyrimidine, potassium salt (94)[52]

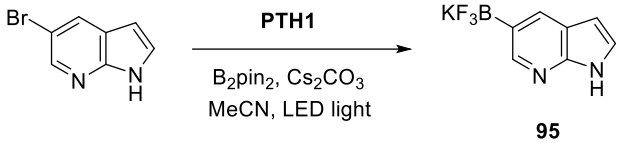


The general procedure GP1 was followed with 5-bromo-2-methoxypyrimidine (38 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (79 mg, 0.24 mmol, 1.2 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 16 h. Purification by treatment with KF, tartaric acid and then K_2CO_3 according to GP2 afforded organotrifluoroborate salt **94** (34 mg, 80%) as a colorless solid.



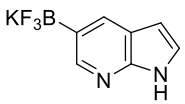
M.p.: > 200 °C. – ^{1}H NMR (500 MHz, CD_3CN): 8.45 (2 H, s), 3.88 (3 H, s) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 165.7, 162.9, 54.4 ppm. – ^{11}B NMR (160.4 Hz, CD_3CN): 2.8 (q, J = 50.5 Hz) ppm. – ^{19}F NMR (470.5 Hz, CD_3CN): −141.9 (dd, J = 96.8, 45.7 Hz) ppm. – IR: 3352, 1748, 1848, 1589, 1474, 1364, 1327, 1226, 1183 cm^{-1}.

5-(Trifluoro-λ⁴-boraneyl)-1*H*-pyrrolo[2,3-*b*]pyridine, potassium salt (95)[47]



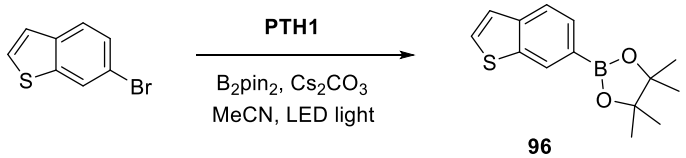
95

The general procedure GP1 was followed with 5-bromo-1*H*-pyrrolo[2,3-*b*]pyridine (40 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (79 mg, 0.24 mmol, 1.2 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 18 h. Purification by treatment with KF, tartaric acid and then K_2CO_3 according to GP2 afforded organotrifluoroborate salt **95** (32 mg, 71%) as a colorless solid.



M.p.: > 200 °C. – ^{1}H NMR (500 MHz, CD_3CN): 8.67 (1 H, s), 8.19 (1 H, s), 7.49 (1 H, d, *J* = 3.6 Hz), 6.73 (1 H, d, *J* = 3.6 Hz) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 143.0, 138.5, 135.4, 128.5, 126.8, 103.5 ppm. – ^{11}B NMR (160.4 Hz, CD_3CN): 2.6 (q, *J* = 47.7 Hz) ppm. – ^{19}F NMR (470.5 Hz, CD_3CN): −142.7 (dd, *J* = 92.0, 41.0 Hz) ppm. – IR: 3295, 2926, 2854, 1735, 1703, 1644, 1601, 1580, 1507, 1409, 1351, 1270, 1234, 1141, 1104, 1020 cm^{-1}.

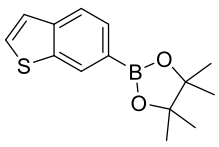
2-(Benzo[*b*]thiophen-6-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (96)[53]



96

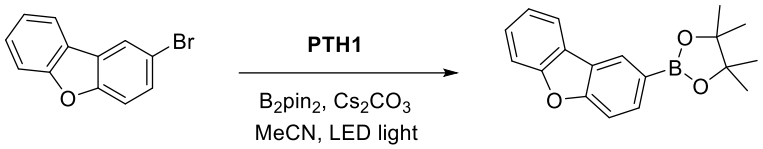
The general procedure GP1 was followed with 6-bromobenzo[*b*]thiophene (43 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400

nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **96** (37 mg, 72%) as a colorless liquid.



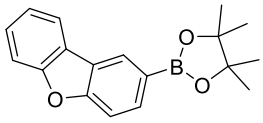
^{1}H NMR (500 MHz, $CDCl_3$): 8.39 (1 H, s), 7.83 (1 H, d, *J* = 7.9 Hz), 7.79 (1 H, d, *J* = 8.0 Hz), 7.52 (1 H, d, *J* = 5.4 Hz), 7.35 (1 H, d, *J* = 5.4 Hz), 1.38 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 141.9, 139.4, 129.9, 129.7, 128.3, 124.0, 123.1, 84.0, 25.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.5 ppm. – IR: 2979, 1709, 1596, 1488, 1417, 1353, 1324, 1285, 1253, 1219, 1143, 1103, 1077, 1047 cm^{-1}.

2-(Dibenzo[*b*,*d*]furan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (97)[54]



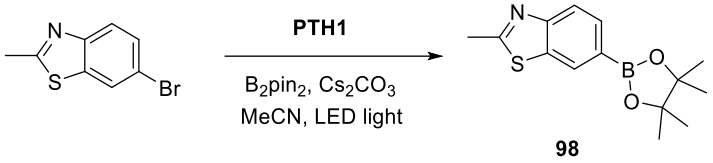
97

The general procedure GP1 was followed with 2-bromodibenzo[*b*,*d*]furan (50 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **97** (47 mg, 80%) as a colorless solid.

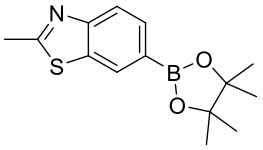


M.p.: 57–59 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 8.47 (1 H, s), 7.98 (1 H, d, *J* = 7.6 Hz), 7.95 (1 H, d, *J* = 8.2 Hz), 7.58 (2 H, d, *J* = 8.2 Hz), 7.51–7.42 (1 H, m), 7.36 (1 H, t, *J* = 7.5 Hz), 1.41 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 158.5, 156.3, 134.0, 127.9, 127.2, 124.2, 124.1, 123.0, 122.8, 120.9, 120.8, 111.8, 111.3, 84.0, 25.1 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.2 ppm. – IR: 3508, 2978, 1710, 1600, 1586, 1450, 1423, 1354, 1336, 1301, 1204, 1143, 1106, 1023, 962 cm^{-1}.

6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*d*]thiazole (98)[55]

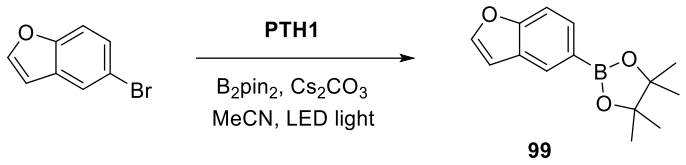


The general procedure GP1 was followed with 6-bromo-2-methylbenzo[*d*]thiazole (46 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **98** (39 mg, 70%) as a colorless solid.

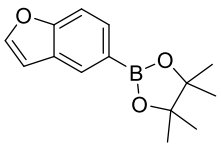


M.p.: 50–52 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 8.38 (1 H, s), 7.81 (1 H, d, *J* = 7.9 Hz), 7.75 (1 H, d, *J* = 8.0 Hz), 2.83 (3 H, s), 1.36 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 166.6, 153.3, 139.0, 130.5, 129.1, 120.9, 84.1, 25.0, 20.3 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.2 ppm. – IR: 2981, 1736, 1602, 1459, 1409, 1372, 1356, 1238, 1167, 1143, 1079, 1045, 964 cm^{-1}.

2-(Benzofuran-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (99)[56]

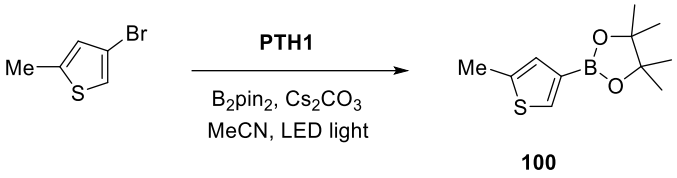


The general procedure GP1 was followed with 5-bromobenzofuran (40 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **99** (28 mg, 57%) as a colorless liquid.



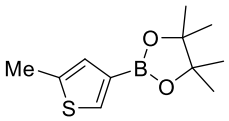
^{1}H NMR (500 MHz, $CDCl_3$): 8.12 (1 H, s), 7.77 (1 H, d, *J* = 8.3 Hz), 7.62 (1 H, d, *J* = 2.2 Hz), 7.51 (1 H, d, *J* = 8.3 Hz), 6.77 (1 H, d, *J* = 2.1 Hz), 1.37 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 157.2, 145.0, 130.9, 128.8, 127.2, 111.0, 106.8, 83.9, 25.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.2 ppm. – IR: 2978, 1610, 1539, 1473, 1431, 1371, 1354, 1288, 1264, 1146, 1129, 1109, 1068, 1029 cm^{-1}.

4,4,5,5-Tetramethyl-2-(5-methylthiophen-3-yl)-1,3,2-dioxaborolane (100)[57]



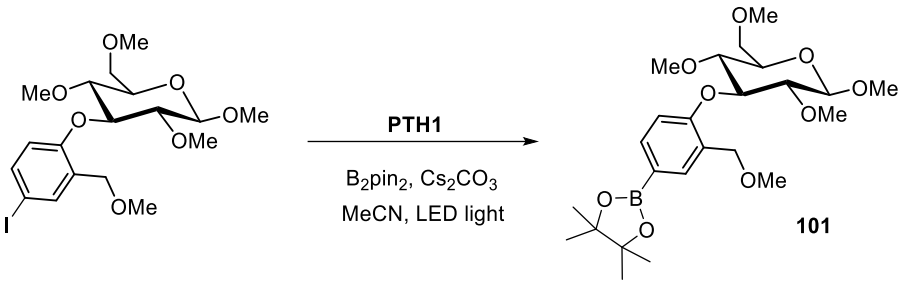
100

The general procedure GP1 was followed with methyl 4-bromo-2-methylthiophene (35 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h at 45 ^{0}C. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **100** (23 mg, 52%) as a colorless liquid.

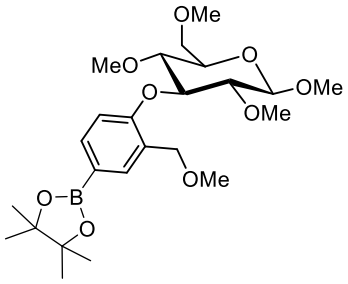


^{1}H NMR (500 MHz, $CDCl_3$): 7.67 (1 H, s), 7.04 (1 H, s), 2.49 (3 H, s), 1.32 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 140.0, 134.9, 130.2, 83.7, 25.0, 14.9 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 28.9 ppm. – IR: 2984, 1731, 1447, 1372, 1236, 1143, 1095, 1044, 916 cm^{-1}.

2-(3-(Methoxymethyl)-4-(((2*R*,3*R*,4*S*,5*R*,6*R*)-2,3,5-trimethoxy-6-(methoxymethyl)tetrahydro-2*H*-pyran-4-yl)oxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (101)

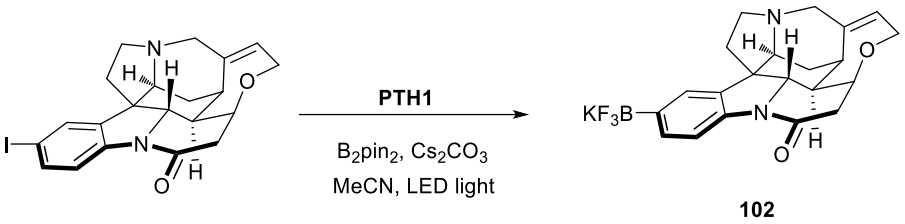


The general procedure GP1 was followed with ((2*R*,3*R*,4*S*,5*R*,6*R*)-4-(4-iodo-2-(methoxymethyl)phenoxy)-2,3,5-trimethoxy-6-(methoxymethyl)tetrahydro-2*H*-pyran (96 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 24 h. Purification by prep TLC (EtOAc/hexane, 1 : 7 v/v) afford product **101** (50 mg, 52%) as a colorless oil.



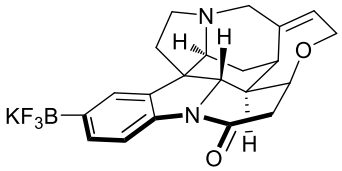
$[\alpha]_D = -55$ (*c* 0.13M, $CHCl_3$). – ^{1}H NMR (500 MHz, $CDCl_3$): 7.82 (1 H, s), 7.69 (1 H, d, *J* = 8.2 Hz), 6.99 (1 H, d, *J* = 8.3 Hz), 4.88 (1 H, d, *J* = 7.5 Hz), 4.57 (1 H, d, *J* = 12.1 Hz), 4.48 (1 H, d, *J* = 12.1 Hz), 3.73–3.59 (8 H, m), 3.56 (4 H, d, *J* = 9.2 Hz), 3.37 (7 H, d, *J* = 11.3 Hz), 3.44–3.12 (2 H, m), 1.32 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 157.5, 136.1, 136.0, 126.8, 114.0, 100.7, 86.7, 83.8, 83.7, 79.2, 75.0, 71.2, 69.4, 61.1, 60.8, 60.6, 59.5, 58.4, 25.01, 24.95 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.7 ppm. – IR: 2977, 2932, 1738, 1714, 1606, 1417, 1355, 1284, 1218, 1132, 1094, 1060, 990 cm^{-1}. – HRMS: calcd for $C_{24}H_{40}BO_9$: 483.2760, found 483.2764 [$M+H^+$].

(4a*R*,4a1*R*,5a*S*,8a*R*,8a1*S*,15a*S*)-10-(Trifluoro-l4-boraneyl)-2,4a,4a1,5,5a,7,8,8a1,15,15a-decahydro-14*H*-4,6-methanoindolo[3,2,1-*ij*]oxepino[2,3,4-de]pyrrolo[2,3-*h*]quinolin-14-one, potassium salt (102)



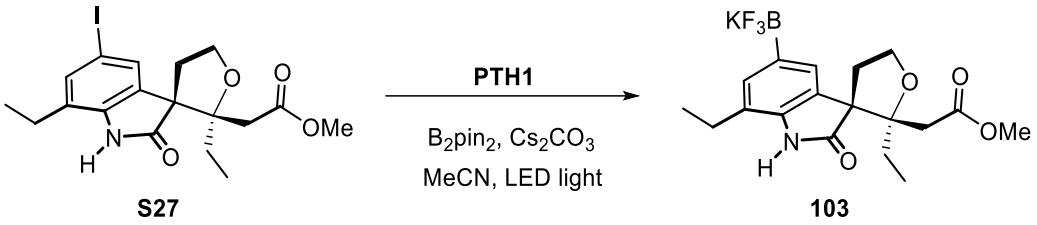
102

The general procedure GP1 was followed with (4a*R*,4a1*R*,5a*S*,8a*R*,8a1*S*,15a*S*)-10-iodo-2,4a,4a1,5,5a,7,8,8a1,15,15a-decahydro-14*H*-4,6-methanoindolo[3,2,1-*ij*]oxepino[2,3,4-de]pyrrolo[2,3-*h*]quinolin-14-one (92 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 24 h. Purification by treatment with methylboronic acid and then KHF_2 and K_2CO_3 according to GP4 afforded organotrifluoroborate salt **102** (44 mg, 50%) as a colorless solid.

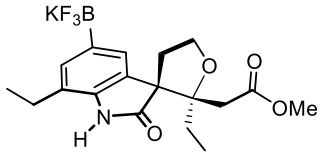


$[\alpha]_D$ = −160 (*c* 0.12M, CH_3CN). − M.p.: > 200 °C. − ^{1}H NMR (500 MHz, CD_3CN): 7.78 (1 H, s), 7.29 (2 H, d, *J* = 7.1 Hz), 5.86 (1 H, t, *J* = 5.5 Hz), 4.26 (1 H, dt, *J* = 8.5, 3.5 Hz), 4.06 (2 H, d, *J* = 6.4 Hz), 3.97–3.87 (1 H, m), 3.77 (1 H, d, *J* = 10.6 Hz), 3.63 (1 H, d, *J* = 14.6 Hz), 3.13 (1 H, t, *J* = 3.4 Hz), 3.10–3.02 (1 H, m), 2.93 (1 H, dd, *J* = 17.1, 8.4 Hz), 2.85–2.71 (1 H, m), 2.66 (1 H, d, *J* = 14.7 Hz), 2.57 (1 H, dd, *J* = 17.1, 3.5 Hz), 2.33–2.28 (1 H, m), 1.85–1.74 (2 H, m), 1.37 (1 H, d, *J* = 16.3 Hz), 1.25 (1 H, dt, *J* = 10.6, 3.4 Hz) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 169.8, 141.9, 141.3, 136.4, 132.1, 127.9, 126.1, 114.9, 78.3, 64.9, 60.8, 60.8, 52.9, 52.8, 50.9, 48.8, 43.4, 42.9, 32.3, 27.4 ppm. – ^{11}B NMR (160.4 Hz, CD_3CN): 3.3 ppm. – ^{19}F NMR (470.5 Hz, $CDCl_3$): −140.5 ppm. – IR: 2944, 22261, 2112, 1645, 1599, 1481, 1423, 1386, 1333, 1306, 1215, 1146, 1104, 1048, 991 cm^{-1}. – HRMS: calcd for $C_{21}H_{21}BF_3N_2O_2$: 401.1654, found 401.1660 [M−K$^+$].

Methyl 2-((2*S*,3*R*)-2,7'-diethyl-2'-oxo-5'-(trifluoro-l4-boraneyl)-4,5-dihydro-2*H*-spiro[furan-3,3'-indolin]-2-yl)acetate, potassium salt (103)

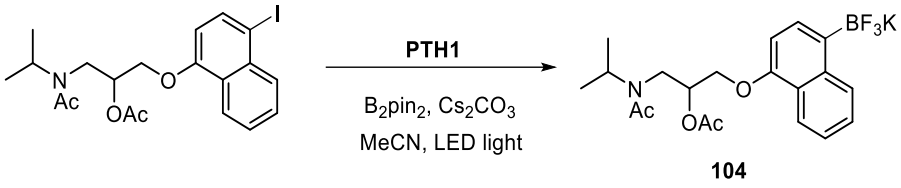


The general procedure GP1 was followed with iodide **S27**, B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by rapid column chromatography followed by treatment with KHF_2 and K_2CO_3 according to GP4 afforded organotrifluoroborate salt **103** (44 mg, 52%) as a colorless solid.

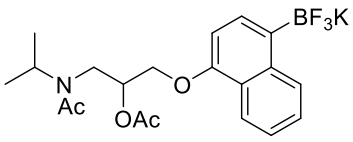


$[\alpha]_D$ = +6.7 (*c* 0.05M, CH_3CN). − m.p.: > 200 °C. – ^{1}H NMR (500 MHz, CD_3CN): 8.24 (1 H, s), 7.14 (1 H, s), 7.13 (1 H, s), 4.21–4.14 (1 H, m), 4.14–4.09 (1 H, m), 3.55 (3 H, s), 2.97 (1 H, dd, *J* = 14.3, 1.2 Hz), 2.75 (1 H, d, *J* = 14.3 Hz), 2.62 (1 H, ddd, *J* = 12.7, 9.8, 7.5 Hz), 2.55 (2 H, qd, *J* = 7.4, 2.1 Hz), 2.10 (1 H, ddd, *J* = 12.8, 8.6, 4.3 Hz), 1.80 (1 H, dq, *J* = 15.2, 7.6 Hz), 1.48 (1 H, dq, *J* = 14.9, 7.4 Hz), 1.16 (3 H, t, *J* = 7.6 Hz), 0.56 (3 H, t, *J* = 7.5 Hz) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 178.5, 170.9, 136.1, 130.6, 129.7, 125.1, 122.9, 87.5, 64.0, 58.2, 51.2, 37.9, 36.3, 26.8, 23.6, 15.1, 8.1 ppm. – ^{11}B NMR (160.4 Hz, CD_3CN): 3.5 ppm. – ^{19}F NMR (470.5 Hz, CD_3CN): −141.4 ppm. – IR: 1695, 1618, 1461, 1434, 1361, 1318, 1276, 1221, 1144, 1009 cm^{-1}. – HRMS: calcd for $C_{18}H_{22}BF_3NO_3$: 384.1599, found 384.1604 [M−K$^+$].

1-(*N*-Isopropylacetamido)-3-((4-(trifluoro-λ⁴-boraneyl)naphthalen-1-yl)oxy)propan-2-yl acetate, potassium salt (104)

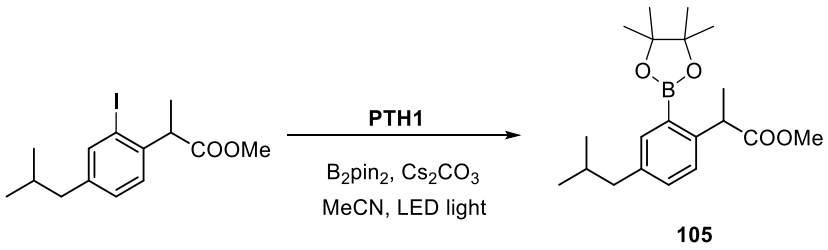


The general procedure GP1 was followed with 1-((4-iodonaphthalen-1-yl)oxy)-3-(*N*-isopropylacetamido)propan-2-yl acetate (90 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by rapid column chromatography followed by treatment with KHF_2 according to GP4 afforded organotrifluoroborate salt **104** (61 mg, 68%) as a colorless solid.



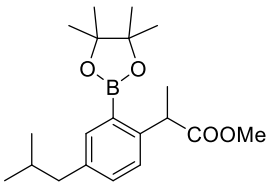
M.p.: > 200 °C. – ^{1}H NMR (500 MHz, CD_3CN): 8.41 (1 H, t, *J* = 7.3 Hz), 8.15 (1 H, d, *J* = 7.6 Hz), 7.57 (1 H, t, *J* = 6.7 Hz), 7.45–7.33 (2 H, m), 6.77 (1 H, dd, *J* = 19.3, 7.5 Hz), 5.71–5.42 (1 H, m), 4.48–4.00 (3 H, m), 3.88–3.27 (2 H, m), 2.47–1.76 (6 H, m), 1.42–1.08 (6 H, m) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 172.2, 171.9, 171.4, 171.2, 153.6, 153.4, 138.7, 138.6, 130.7, 130.6, 129.7, 126.3, 126.2, 125.6, 125.5, 124.7, 124.6, 122.0, 121.8, 105.5, 72.0, 71.4, 68.9, 68.1, 50.2, 48.2, 46.4, 42.1, 23.0, 22.4, 21.7, 21.3, 21.2, 21.0, 20.6, 20.3 ppm. – ^{11}B NMR (160.4 Hz, CD_3CN): 3.9 ppm. – ^{19}F NMR (470.5 Hz, CD_3CN): −138.0 ppm. – IR: 2975, 1738, 1627, 1578, 1508, 1455, 1422, 1371, 1340, 1316, 1236, 1216, 1126, 1053, 1025 cm^{-1}. – HRMS: calcd for $C_{20}H_{24}BF_3NO_4$: 401.1756, found 401.1756 [M–K$^+$].

Methyl 2-(4-isobutyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propanoate (105)



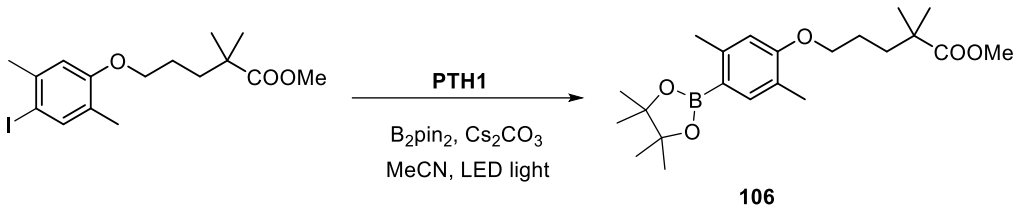
105

The general procedure GP1 was followed with methyl 2-(2-iodo-4-isobutylphenyl)propanoate (69 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **105** (35 mg, 50%) as a colorless liquid.



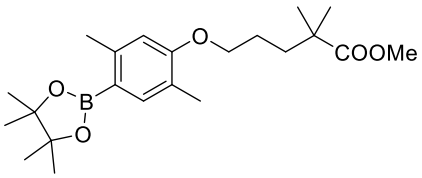
^{1}H NMR (500 MHz, C_6D_6): 8.16 (1 H, s), 7.57 (1 H, d, *J* = 7.9 Hz), 7.21 (1 H, d, *J* = 9.9 Hz), 5.20 (1 H, q, *J* = 7.1 Hz), 3.41 (3 H, s, H), 2.43 (2 H, d, *J* = 7.2 Hz), 1.82 (1 H, dt, *J* = 13.5, 6.8 H), 1.76 (3 H, d, *J* = 7.1 Hz), 1.33 (2 H, d, *J* = 6.0 Hz), 1.22 (12 H, d, *J* = 10.6 Hz), 0.88 (6 H, d, *J* = 6.6 Hz) ppm. – ^{13}C NMR (125 MHz, C_6D_6): 175.6, 145.9, 139.5, 137.8, 132.7, 126.7, 83.6, 51.3, 45.2, 43.4, 30.4, 25.1, 24.9, 22.5, 19.9 ppm. – ^{11}B NMR (160.4 Hz, C_6D_6): 32.0 ppm. – IR: 2976, 2952, 2928, 2868, 1736, 1570, 1463, 1412, 1372, 1347, 1312, 1272, 1251, 1212, 1166, 112, 1110, 1082 cm^{-1}. – HRMS: calcd for $C_{20}H_{32}BO_4$: 347.2388, found 347.2390 [M+H$^+$].

Methyl 5-(2,5-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)-2,2-dimethylpentanoate (106)



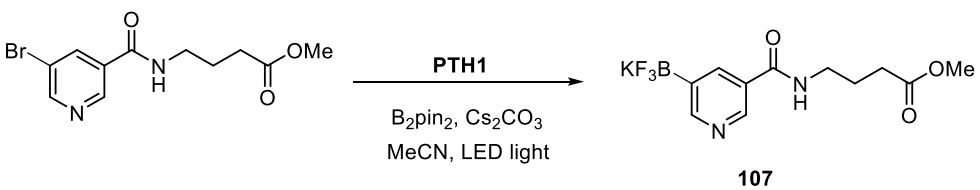
106

The general procedure GP1 was followed with methyl 5-(4-iodo-2,5-dimethylphenoxy)-2,2-dimethylpentanoate (78 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **106** (50 mg, 64%) as a colorless liquid.



^{1}H NMR (500 MHz, $CDCl_3$): 7.54 (1 H, s), 6.59 (1 H, s), 3.95 (2 H, t, *J* = 5.6 Hz), 3.67 (3 H, s), 2.51 (3 H, s), 2.18 (3 H, s), 1.82–1.60 (4 H, m), 1.33 (12 H, s), 1.22 (6 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 178.4, 159.3, 144.8, 138.4, 122.9, 112.6, 83.1, 67.8, 51.8, 42.2, 37.2, 25.3, 25.2, 25.0, 22.4, 15.6 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.8 ppm. – IR: 2975, 1731, 1606, 1568, 1507, 1447, 1389, 1335, 1303, 1273, 1240, 1196, 1137, 1051, 1006, 984 cm^{-1}. – HRMS: calcd for $C_{22}H_{36}BO_5$: 391.2650, found 391.2653 [M+H$^+$].

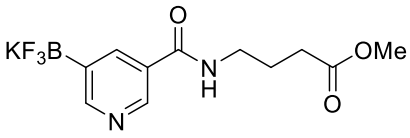
Methyl 4-(5-(trifluoro-l4-boraneyl)nicotinamido)butanoate, potassium salt (107)



107

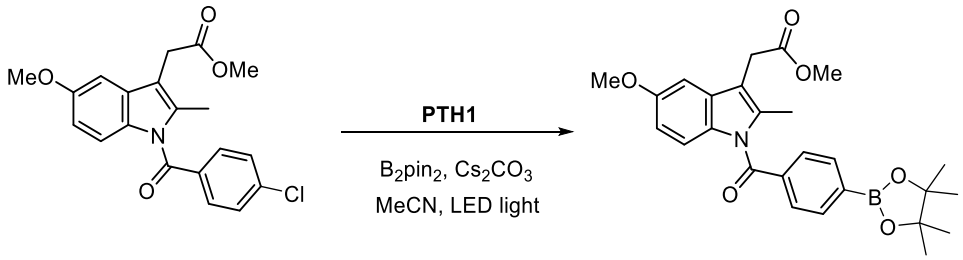
The general procedure GP1 was followed with methyl 4-(5-bromonicotinamido)butanoate (60 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.),

Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (2.5 mL). The mixture was irradiated with a 400 nm LED light for 24 h. Purification by treatment with methylboronic acid and then 4.5M KHF_2 (0.12 mL, 0.54 mmol, 2.7 equiv.) and K_2CO_3 according to GP4 afforded organotrifluoroborate salt **107** (53 mg, 81%) as a colorless solid.

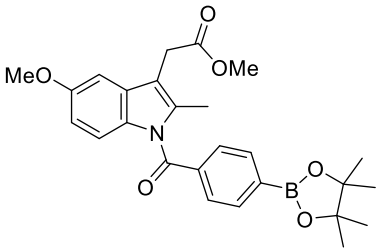


M.p.: > 200 °C. – ^{1}H NMR (500 MHz, CD_3CN): 8.74 (1 H, s), 8.67 (1 H, s), 8.18 (1 H, s), 7.25 (1 H, s), 3.61 (3 H, s), 3.43–3.27 (2 H, m), 2.38 (2 H, t, *J* = 7.4 Hz), 1.85 (2 H, p, *J* = 7.1 Hz) ppm. – ^{13}C NMR (125 MHz, CD_3CN): 174.6, 167.5, 154.7, 146.1, 139.0, 130.2, 52.0, 39.6, 31.9, 25.4 ppm. – ^{11}B NMR (160.4 Hz, CD_3CN): 3.0 ppm. – ^{19}F NMR (470.5 Hz, CD_3CN): −142.0 ppm. – IR: 3264, 1723, 1645, 1585, 1537, 1438, 1417, 1357, 1332, 1305, 1267, 1219, 1173, 977, 902 cm^{-1}. – HRMS: calcd for $C_{11}H_{13}BF_3N_2O_3$: 289.0977, found 289.0979 [M–K$^+$].

Methyl 2-(5-methoxy-2-methyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoyl)-1*H*-indol-3-yl)acetate (108)[55]

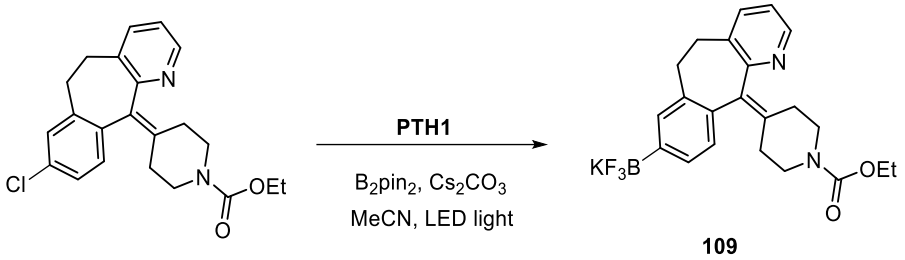


The general procedure GP1 was followed with methyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (74 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by prep TLC (EtOAc/hexane, 1 : 2 v/v) afforded **108** (59 mg, 64%) as a colorless liquid.

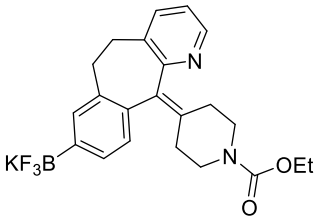


^{1}H NMR (500 MHz, $CDCl_3$): 7.91 (2 H, d, *J* = 7.9 Hz), 7.68 (2 H, d, *J* = 8.0 Hz), 6.95 (1 H, s), 6.89 (1 H, d, *J* = 9.0 Hz), 6.64 (1 H, d, *J* = 6.7 Hz), 3.83 (3 H, s), 3.70 (3 H, s), 3.66 (2 H, s), 2.36 (3 H, s), 1.38 (12 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 171.5, 169.6, 156.1, 138.0, 136.2, 135.1, 131.0, 130.7, 129.8, 128.9, 128.7, 115.3, 112.5, 111.7, 111.0, 101.3, 84.5, 55.8, 52.3, 30.3, 25.0, 13.5 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 30.9 ppm. – IR: 2981, 1739, 1709, 1613, 1477, 1436, 1397, 1322, 1267, 1218, 1166, 1142, 1088, 1036 cm^{-1}.

Ethyl 4-(8-(trifluoro-λ^4-boraneyl)-5,6-dihydro-11*H*-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidine-1-carboxylate, potassium salt (109)

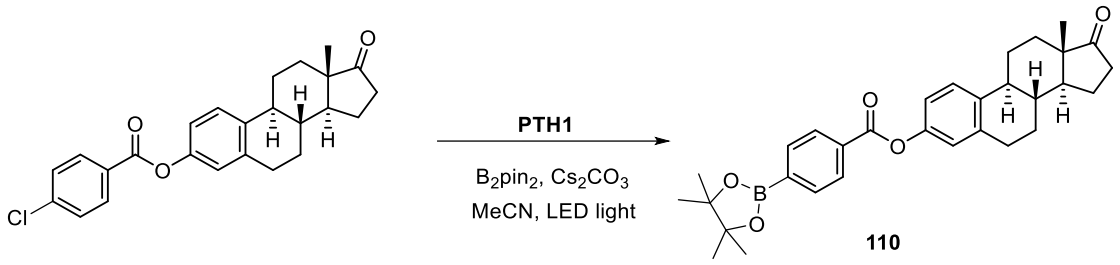


The general procedure GP1 was followed with ethyl 4-(8-chloro-5,6-dihydro-11*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11-ylidene)piperidine-1-carboxylate (76 mg, 0.2 mmol), B_2pin_2 (152 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 72 h at 45 ^{0}C. Purification by rapid column chromatography followed by treatment with KHF_2 and K_2CO_3 according to GP4 afforded organotrifluoroborate salt **109** (56 mg, 62%) as a colorless solid.

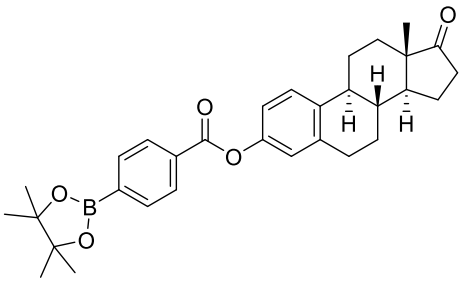


M.p.: > 200 °C. – ^{1}H NMR (500 MHz, CD_3CN): 8.31 (1 H, d, *J* = 4.6 Hz), 7.50 (1 H, d, *J* = 7.6 Hz), 7.24 (1 H, s), 7.19 (1 H, d, *J* = 7.4 Hz), 7.10 (1 H, dd, *J* = 7.6, 4.8 Hz), 6.88 (1 H, d, *J* = 7.4 Hz), 4.07 (2 H, q, *J* = 7.1 Hz), 3.78–3.54 (2 H, m), 3.46–3.29 (2 H, m), 3.26–3.11 (2 H, m), 2.80 (2 H, ddd, *J* = 14.8, 11.2, 8.2 Hz), 2.39–2.29 (2 H, m), 2.17–2.05 (2 H, m), 1.20 (3 H, t, *J* = 7.1 Hz) ppm. – ^{13}C NMR (125 MHz, $(CD_3)_2CO$): 170.9, 159.7, 155.8, 146.9, 137.7, 137.5, 136.8, 135.8, 135.2, 134.9, 133.5, 130.0, 127.9, 122.5, 61.5, 60.5, 45.9, 45.8, 32.8, 32.7, 31.5, 31.4, 15.0 ppm. – ^{11}B NMR (160.4 Hz, $(CD_3)_2CO$): 3.4 ppm. – ^{19}F NMR (470.5 Hz, $(CD_3)_2CO$): −142.6 ppm. – IR: 3501, 2914, 1689, 1436, 1360, 1277, 1227, 1152, 1115, 994 cm^{-1}. – HRMS: calcd for $C_{22}H_{23}BF_3N_2O_2$: 415.1810, found 415.1815 [$M-K^+$].

(8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (110)

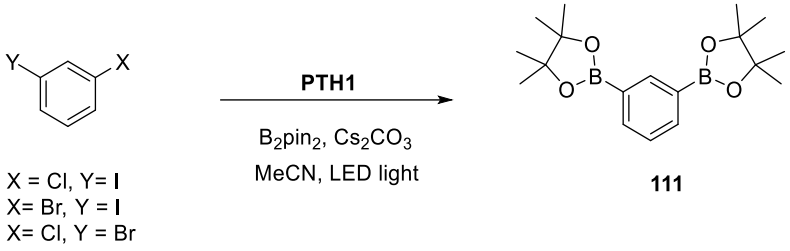


The general procedure GP1 was followed with (8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl 4-chlorobenzoate (81 mg, 0.2 mmol), B_2pin_2 (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afford product **110** (47 mg, 47%) as a colorless oil.



$[\alpha]_D$ = +103 (*c* 0.14M, $CHCl_3$). – M.p.: > 200 °C. – ^1H NMR (500 MHz, $CDCl_3$): 8.16 (2 H, d, *J* = 8.0 Hz), 7.93 (2 H, d, *J* = 7.9 Hz), 7.33 (1 H, d, *J* = 8.5 Hz), 6.99 (1 H, d, *J* = 8.4 Hz), 6.95 (1 H, s), 3.13–2.79 (2 H, m), 2.51 (1 H, dd, *J* = 19.0, 8.7 Hz), 2.43 (1 H, d, *J* = 13.6 Hz), 2.32 (1 H, t, *J* = 10.4 Hz), 2.22–1.89 (4 H, m), 1.81–1.43 (3 H, m), 1.37 (12 H, s), 1.26 (3 H, s), 0.92 (3 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 220.9, 165.6, 148.9, 138.2, 137.6, 134.9, 131.9, 129.2, 126.6, 121.8, 119.0, 84.5, 50.6, 48.1, 44.30, 38.1, 36.0, 31.7, 29.5, 26.5, 25.9, 25.1, 25.0, 21.7, 14.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 30.6 ppm. – IR: 3449, 3970, 2928, 1735, 1611, 1509, 1492, 1454, 1398, 1359, 1260, 1219, 1177, 1144, 1090, 1065, 1018 cm^{-1}. – HRMS: calcd for $C_{31}H_{37}BKO_5$: 539.2371, found 539.2354 [$M+K^+$].

1,3-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (111)[58]

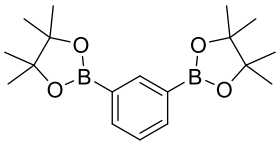


From 1-bromo-3-iodobenzene: The general procedure GP1 was followed with 1-bromo-3-iodobenzene (56 mg, 0.2 mmol), B_2pin_2 (203 mg, 0.8 mmol, 4.0 equiv.), Cs_2CO_3 (263 mg, 0.8 mmol, 4.0 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (4 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by Kugelrohr distillation (150 °C, 2 h) according to GP5 afforded boronic ester **111** (37 mg, 56%) as a colorless solid.

From 1-chloro-3-iodobenzene: The general procedure GP1 was followed with 1-chloro-3-iodobenzene (48 mg, 0.2 mmol), B_2pin_2 (203 mg, 0.8 mmol, 4.0 equiv.), Cs_2CO_3 (263 mg, 0.8 mmol, 4.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (4 mL). The

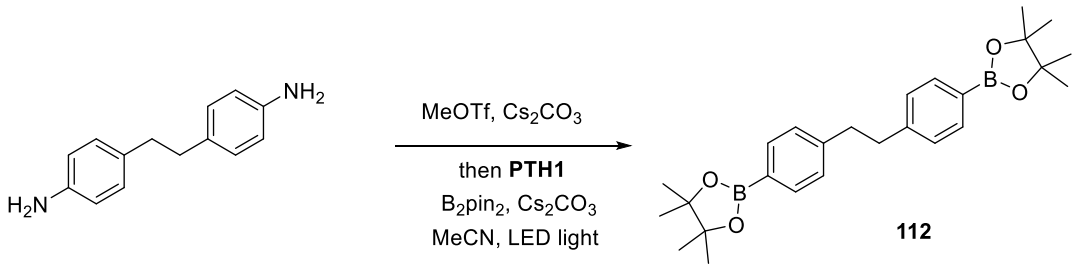
mixture was irradiated with a 400 nm LED light for 48 h. Purification by Kugelrohr distillation (150 °C, 2 h) according to GP5 afforded boronic ester **111** (45 mg, 68%) as a colorless solid.

From 1-bromo-3-chlorobenzene: The general procedure GP1 was followed with 1-bromo-3-chlorobenzene (38 mg, 0.2 mmol), B_2pin_2 (203 mg, 0.8 mmol, 4.0 equiv.), Cs_2CO_3 (263 mg, 0.8 mmol, 4.0 equiv.), **PTH1** (0.8 mg, 0.004 mmol, 2 mol%) and CH_3CN (4 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by Kugelrohr distillation (150 °C, 2 h) according to GP5 afforded boronic ester **111** (37 mg, 56%) as a brown solid.



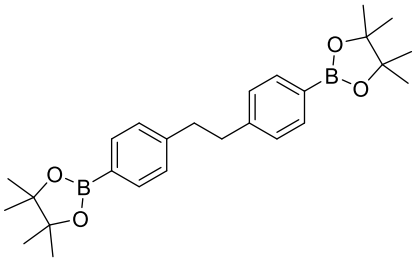
M.p.: 119–122 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 8.28 (1 H, s), 7.90 (2 H, d, *J* = 7.4 Hz), 7.37 (1 H, t, *J* = 7.4 Hz), 1.34 (24 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 141.4, 137.8, 127.2, 83.9, 25.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.2 ppm. – IR: 2977, 2930, 1739, 1601, 1578, 1483, 1369, 1328, 1305, 1270, 1241, 1213, 1140, 1110, 1088, 1078, 1047 cm^{-1}.

1,2-Bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethane (112)[59]



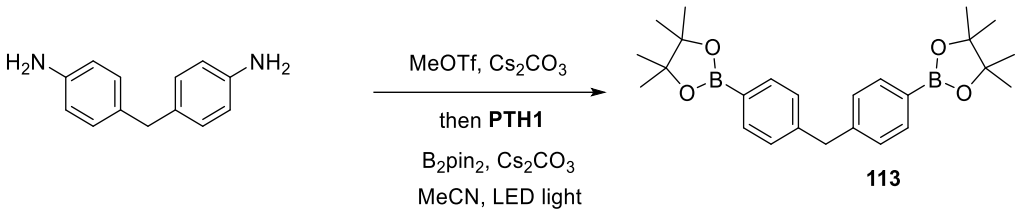
The general procedure GP6 was followed with 4,4'-(ethane-1,2-diyl)dianiline (42 mg, 0.2 mmol), Cs_2CO_3 (263 mg, 0.8 mmol, 4 equiv.), methyl trifluoromethanesulfonate (210 mg, 1.28 mmol, 6.4 equiv.) and CH_3CN (3 mL). The mixture was stirred for 20 minutes at room temperature before adding B_2pin_2 (305 mg, 1.2 mmol, 6 equiv.), Cs_2CO_3 (329 mg, 1.0 mmol, 5.0 equiv.), **PTH1** (4.0 mg, 0.02 mmol, 10 mol%) and CH_3CN (2 mL). The mixture was

irradiated with a 400 nm LED light for 36 h. Purification by Kugelrohr distillation (150 °C, 2 h) according to GP5 afforded boronic ester **112** (62 mg, 71%) as a brown solid.

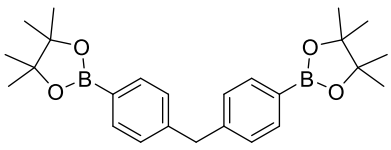


M.p.: > 200 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 7.72 (4 H, d, *J* = 7.9 Hz), 7.19 (4 H, d, *J* = 7.9 Hz), 2.93 (4 H, s), 1.34 (24 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 145.2, 135.0, 128.1, 83.8, 38.1, 25.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 30.6 ppm. – IR: 2976, 1610, 1516, 1456, 1397, 1356, 1316, 1270, 1164, 1140, 1087, 1031, 962 cm^{-1}.

Bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methane (113)[60]

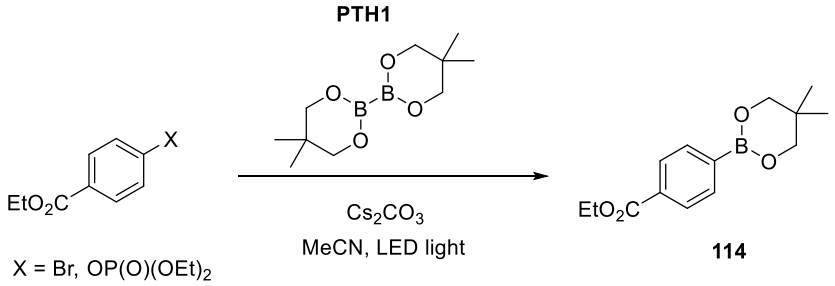


The general procedure GP6 was followed with 4,4'-methylenedianiline (40 mg, 0.2 mmol), Cs_2CO_3 (263 mg, 0.8 mmol, 4 equiv.), methyl trifluoromethanesulfonate (210 mg, 1.28 mmol, 6.4 equiv.) and CH_3CN (3 mL). The mixture was stirred for 20 minutes at room temperature before adding B_2pin_2 (305 mg, 1.2 mmol, 6 equiv.), Cs_2CO_3 (329 mg, 1.0 mmol, 5.0 equiv.), **PTH1** (3.2 mg, 0.016 mmol, 8 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 420 nm LED light for 36 h. Purification by Kugelrohr distillation (150 °C, 2 h) according to GP5 afforded boronic ester **113** (75 mg, 89%) as a brown solid.



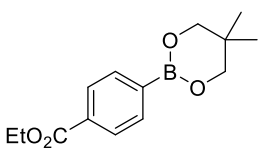
M.p.: > 200 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 7.73 (4 H, d, *J* = 7.8 Hz), 7.19 (4 H, d, *J* = 7.8 Hz), 4.01 (2 H, s), 1.33 (24 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 144.2, 135.2, 128.6, 83.8, 42.4, 25.0 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 31.0 ppm. – IR: 2977, 1608, 1514, 1567, 1397, 1356, 1322, 1271, 1213, 1141, 1105, 1087, 1029, 1020, 963 cm^{-1}.

Ethyl 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoate (114)[61]



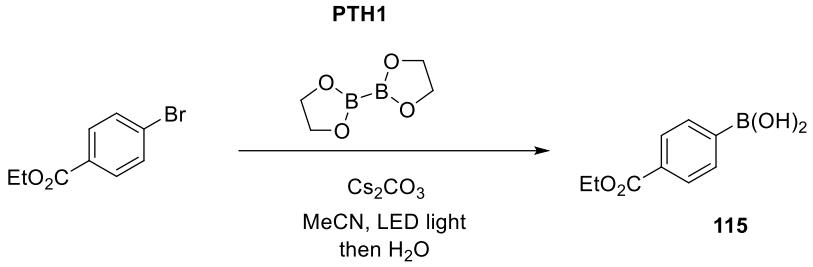
From ethyl 4-bromobenzoate: The general procedure GP1 was followed with ethyl 4-bromobenzoate (45 mg, 0.2 mmol), 5,5,5',5'-tetramethyl-2,2'-bi(1,3,2-dioxaborinane) (90 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **114** (43 mg, 82%) as a colorless solid.

From ethyl 4-((diethoxyphosphoryl)oxy)benzoate: The general procedure GP1 was followed with ethyl 4-((diethoxyphosphoryl)oxy)benzoate (60 mg, 0.2 mmol), 5,5,5',5'-tetramethyl-2,2'-bi(1,3,2-dioxaborinane) (135 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afforded product **114** (31 mg, 60%) as a colorless solid.

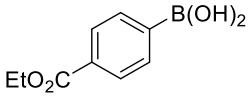


M.p.: 91–93 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 8.01 (2 H, d, *J* = 8.2 Hz), 7.86 (2 H, d, *J* = 8.2 Hz), 4.38 (2 H, q, *J* = 7.1 Hz), 3.78 (4 H, s), 1.40 (3 H, t, *J* = 7.1 Hz), 1.03 (6 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 167.0, 133.9, 132.3, 128.6, 72.5, 61.1, 32.0, 22.0, 14.5 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 26.6 ppm. – IR: 2958, 1704, 1580, 1506, 1478, 1446, 1369, 1317, 1306, 1264, 1248, 1176, 1128, 1105, 1097, 1018 cm^{-1}.

(4-(Ethoxycarbonyl)phenyl)boronic acid (115)[62]

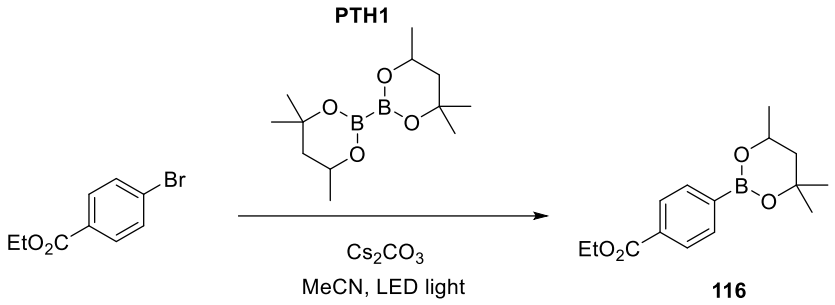


The general procedure GP1 was followed with ethyl 4-bromobenzoate (45 mg, 0.2 mmol), 2,2'-bi(1,3,2-dioxaborolane) (57 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. H_2O (4 mL) was added and the reaction mixture was stirred for 30 minutes at room temperature, then added a mixture of 1M aqueous solution of fructose (5 mL) and 1M aqueous solution of sodium carbonate (5 mL). Ethyl acetate (15 mL) was added, and the organic portion was separated and discarded. The aqueous phase was acidified to pH 2 using 2M aqueous solution of hydrochloric acid, then extracted with ethyl acetate (4 × 10 mL). The combined organic portions as dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure to yield the desired boronic acid **115** (28 mg, 73%) as a colorless oil.

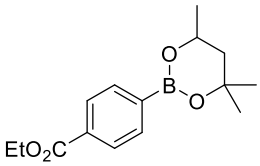


^{1}H NMR (500 MHz, CD_3OD): 7.91 (2 H, d, *J* = 7.8 Hz), 7.73 (2 H, s), 4.34 (2 H, q, *J* = 7.1 Hz), 3.67 (2 H, s), 1.37 (3 H, t, *J* = 7.1 Hz) ppm. – ^{13}C NMR (125 MHz, CD_3OD): 168.7, 134.5, 129.0, 64.5, 61.9, 14.5 ppm. – ^{11}B NMR (160.4 Hz, CD_3OD): 22.3 ppm. – IR: 2970, 2919, 2871, 1719, 1614, 1509, 1401, 1362, 1310, 1287, 1237, 1208, 1178, 1096, 1077, 1021, 987 cm^{-1}.

Ethyl 4-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)benzoate (116)[63]

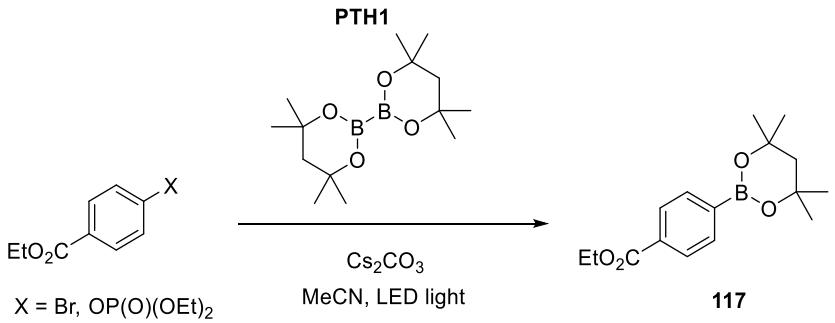


The general procedure GP1 was followed with ethyl 4-bromobenzoate (45 mg, 0.2 mmol), 4,4,4',4',6,6'-hexamethyl-2,2'-bi(1,3,2-dioxaborinane) (101 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **116** (40 mg, 72%) as a colorless oil.



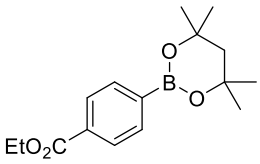
^{1}H NMR (500 MHz, $CDCl_3$): 8.01 (2 H, d, *J* = 8.1 Hz), 7.88 (2 H, d, *J* = 8.1 Hz), 4.6–4.13 (3 H, m), 1.90 (1 H, dd, *J* = 13.9, 2.9 Hz), 1.73–1.55 (1 H, m), 1.43–1.37 (12 H, m) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 167.1, 133.8, 132.0, 128.5, 71.5, 65.3, 61.0, 46.1, 31.4, 28.3, 23.3, 14.5 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 26.7 ppm. – IR: 2918, 1718, 1614, 1510, 1401, 1263, 1267, 1237, 1108, 1096, 1021, 883 cm^{-1}.

Ethyl 4-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)benzoate (117)



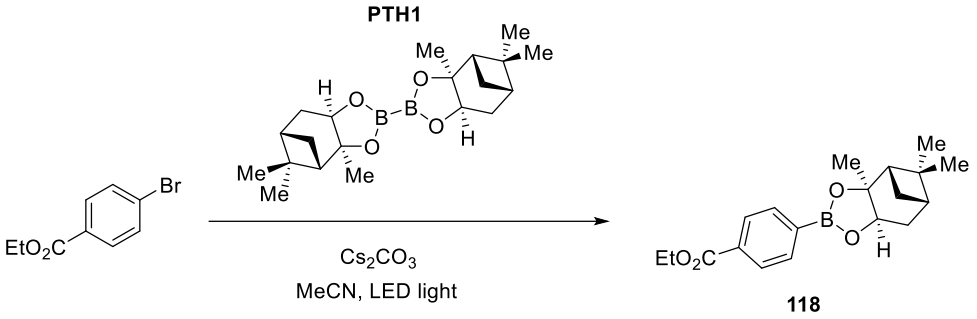
From ethyl 4-bromobenzoate: The general procedure GP1 was followed with ethyl 4-bromobenzoate (45 mg, 0.2 mmol), 4,4,4',4',6,6,6',6'-octamethyl-2,2'-bi(1,3,2-dioxaborinane) (112 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **117** (52 mg, 90%) as a colorless solid.

From ethyl 4-((diethoxyphosphoryl)oxy)benzoate: The general procedure GP1 was followed with ethyl 4-((diethoxyphosphoryl)oxy)benzoate (60 mg, 0.2 mmol), 4,4,4',4',6,6,6',6'-octamethyl-2,2'-bi(1,3,2-dioxaborinane) (168 mg, 0.6 mmol, 3.0 equiv.), Cs_2CO_3 (197 mg, 0.6 mmol, 3.0 equiv.), **PTH1** (2.0 mg, 0.01 mmol, 5 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 48 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 19 v/v) afforded product **117** (31 mg, 53%) as a colorless solid.

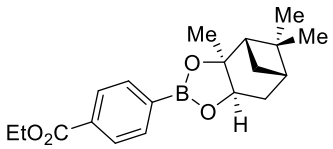


M.p.: 42−45 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 7.99 (2 H, d, *J* = 8.2 Hz), 7.88 (2 H, d, *J* = 8.1 Hz), 4.38 (2 H, q, *J* = 7.1 Hz), 1.93 (2 H, s), 1.43 (12 H, s), 1.40 (3 H, t, *J* = 7.1 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 167.1, 133.8, 131.9, 128.4, 71.3, 61.0, 49.1, 31.9, 14.5 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 26.6 ppm. – IR: 2972, 2935, 1715, 1561, 1506, 1432, 1355, 1329, 1302, 1265, 1207, 1137, 1095, 1020 cm^{-1}. – HRMS: calcd for $C_{16}H_{24}BO_4$: 291.1762, found 291.1765 [M+H$^+$].

Ethyl 4-((3a*S*,4*S*,6*S*,7a*R*)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[*d*][1,3,2]dioxaborol-2-yl)benzoate (118)



The general procedure GP1 was followed with ethyl 4-bromobenzoate (45 mg, 0.2 mmol), bis((+)-pinanediolato)diboron (143 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (132 mg, 0.4 mmol, 2.0 equiv.), **PTH1** (0.4 mg, 0.002 mmol, 1 mol%) and CH_3CN (2 mL). The mixture was irradiated with a 400 nm LED light for 24 h. Purification by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) afford product **118** (50 mg, 76%) as a colorless oil.



^{1}H NMR (500 MHz, $CDCl_3$): 8.02 (2 H, d, *J* = 8.2 Hz), 7.87 (2 H, d, *J* = 8.1 Hz), 4.46 (1 H, dd, *J* = 8.7, 1.7 Hz), 4.38 (2 H, q, *J* = 7.1 Hz), 2.47–2.37 (1 H, m), 2.24 (1 H, dtd, *J* = 11.1, 6.0, 2.1 Hz), 2.15 (1 H, t, *J* = 5.5 Hz), 2.04–1.83 (2 H, m), 1.49 (3 H, s), 1.39 (3 H, t, *J* = 7.1 Hz), 1.31 (3 H, s), 1.19 (1 H, d, *J* = 10.9 Hz), 0.89 (3 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 166.8, 134.8, 132.8, 128.7, 86.8, 78.6, 61.2, 51.5, 39.6, 38.4, 35.6, 28.8, 27.2, 26.6, 24.2, 14.5 ppm. – ^{11}B NMR (160.4 Hz, $CDCl_3$): 30.4 ppm. – IR: 2974, 1715, 1560, 1507, 1401, 1313, 1227, 1199, 1139, 1108, 1094, 1021 cm^{-1}. – HRMS: calcd for $C_{19}H_{26}BO_4$: 329.1919, found 329.1920 [$M+H^+$].

Computational Data

1. Software

All geometry optimizations, vertical excitations, vibrational frequency calculations, and IRCs were conducted using the Gaussian 16 program.[64] Calculations were performed using the Stampede2 supercomputer at the Texas Advanced Computing Center (TACC) hosted by the University of Texas in Austin, Texas.[65] General day-to-day visualization and monitoring of calculations was performed with Chemcraft.[66] Final images of minima and transition state geometries were rendered using CYLview.[67] Spin density images were generated from the optimized .chk files (converted to .fchk) with the Gaussian Cubegen utility (with spin=SCF and npts = 300). VMD was used to render the final images from the .cube files with an isovalue of 0.02 au for radical species.[68]

2. Details of calculations

Geometries of ground state minima and transition states were optimized without constraints using the M06-2X functional[69] with the def2-SVP[70-71] basis set in the SMD solvation model[72] using the "acetonitrile" keyword. This combination of functional and basis set was chosen for its accuracy in reproducing experimental values for electronic and excited state transitions in a benchmarking study of different methodologies. Two experimental values were used as benchmarking criteria for selection of an appropriate computational method: the $E_{0\text{-}0}$ for the first singlet excited state of **PTH1** and the redox potential of ground state **PTH1** (**PTH1** to **PTH1**$^{\bullet+}$). Empirical dispersion was then included in the form of the D3 model developed by Grimme[73] to account for the long-range noncovalent interactions present in several intermediate species. Convergence criteria for the calculations were set to "tight" and an ultrafine grid was selected. Frequency calculations were performed on the resultant geometries to verify the nature of the isolated stationary points. Geometries with zero imaginary frequencies were

deemed minima whereas those with exactly one imaginary frequency along the chemical path of interest were deemed transition states. IRC calculations were performed to further corroborate that the located transition states connected reactants to products. The ground state encounter complex of **PTH1** and carbonate dianion was optimized separately using the B3LYP functional[74-77] and 6-31+G(d) basis set.[78] A subsequent single-point calculation was performed on the optimized geometry at the M06-2X D3 / def2-SVP / SMD (MeCN) level to verify that the geometry corresponded to a minimum on the M06-2X surface. TD-DFT calculations (vertical excitation of 10 excited states, optimization, and frequency analysis) were all conducted at the M06-2X / def2-SVP / SMD (MeCN) level of theory. The D3 empirical dispersion correction was omitted in TD-DFT calculations as corrections for noncovalent forces were parameterized for ground state species and may introduce inaccuracies in excited state geometries.[79-81]

3. Marcus theory-based estimation of activation barrier for stepwise and concerted dissociative PCET of photocatalyst complex 123(S1) and phosphate ester 124

Activation barriers for stepwise and concerted dissociative proton-coupled electron transfer (PCET) were calculated using Marcus-Hush theory[82] in conjunction with the Savéant model.[83,84]

$$\Delta G_{PCET}{}^{\ddagger} = \Delta G_0{}^{\ddagger}\left(1 + \frac{\Delta G_r}{4\Delta G_0{}^{\ddagger}}\right)^2 \quad (1)$$

The intrinsic barrier, $\Delta G_0{}^{\ddagger}$, is estimated by calculating λ, the sum of internal and solvent reorganization energies:

$$\Delta G_0{}^{\ddagger} = \frac{\lambda}{4} = \frac{\lambda_i + \lambda_0}{4} = \frac{\lambda_i + \lambda_0}{4} \quad (2)$$

Internal Reorganization Energy

The internal reorganization energy, λ_i, is calculated using the Savéant model[83,84] as:

$$\lambda_i = \frac{\lambda_i^R + \lambda_i^P}{2} \quad (3)$$

Where λ_i^R and λ_i^P are the difference between distorted (those of products for reactants and those of reactants for products) and equilibrium geometries for reactants and products, respectively.

Solvent Reorganization Energy

The solvent reorganization energy, λ_0, is separated into two components, one related to electron transfer (4) and the other related to proton transfer (5):[83,84]

$$\lambda_s^{ET} = \left(332\frac{kcal}{mol}\right)\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R_{12}}\right)\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right) \quad (4)$$

$$\lambda_s^{PT} = \frac{1}{4\pi\varepsilon_0}\left(\frac{\varepsilon_s - 1}{2\varepsilon_s + 1} - \frac{\varepsilon_{op} - 1}{\varepsilon_{op} + 1}\right)\frac{(\mu_R - \mu_P)^2}{a^3} \quad (5)$$

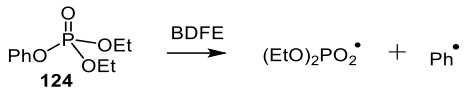
Where a_1 and a_2 are the radii of the donor and acceptor species and R_{12} is the inter-center distance. ε_{op} is the square of the refractive index and ε_s the dielectric constant, both in reference to acetonitrile. a is the total radius of the encounter complex (11.2 Å). μ_R and μ_P are reactant and product dielectric constants, respectively.

Contribution of BDFE

In the case of the concerted dissociative process, the intrinsic barrier also contains a contribution from the bond dissociation free energy of the acceptor species:

$$\Delta G_0^{\ddagger} = \frac{\lambda_i + \lambda_0 + BDFE}{4} \quad (6)$$

The BDFE is calculated for:



(7)

Table S3. Stepwise and Concerted dissociative PCET values [a]

	a_1, Å	a_2, Å	ε_{op}	ε	λ_i	λ_{ET}	λ_{PT}	BDFE	ΔG_r	$\Delta G_{PCET}^{\ddagger}$
Stepwise	5.64	5.74	1.81	35.69	33.99	15.33	1.25	–	−29.93	2.11
Concerted	5.64	5.74	1.81	35.69	33.99	15.33	1.25	99.76	−41.2	19.81

[a] a_1 is the radius of the donor species, a_2 the radius of the acceptor species; ε_{op} is the square of the refractive index of acetonitrile, ε_s the dielectric constant of acetonitrile; λ_i is the internal reorganization energy, λ_0 is the solvent reorganization energy; BDFE the bond dissociation free energy of **124** along the C–O bond, ΔG_r the Gibbs free energy of the stepwise and concerted processes, and $\Delta G_{ET}^{\ddagger}$ is the calculated activation barrier of the electron transfer processes. λ and free energy entries are expressed in kcal/mol.

The calculations suggest that the stepwise process has a substantially lower activation barrier than the concerted dissociative process, indicating that the reaction likely proceeds by the stepwise mechanism.

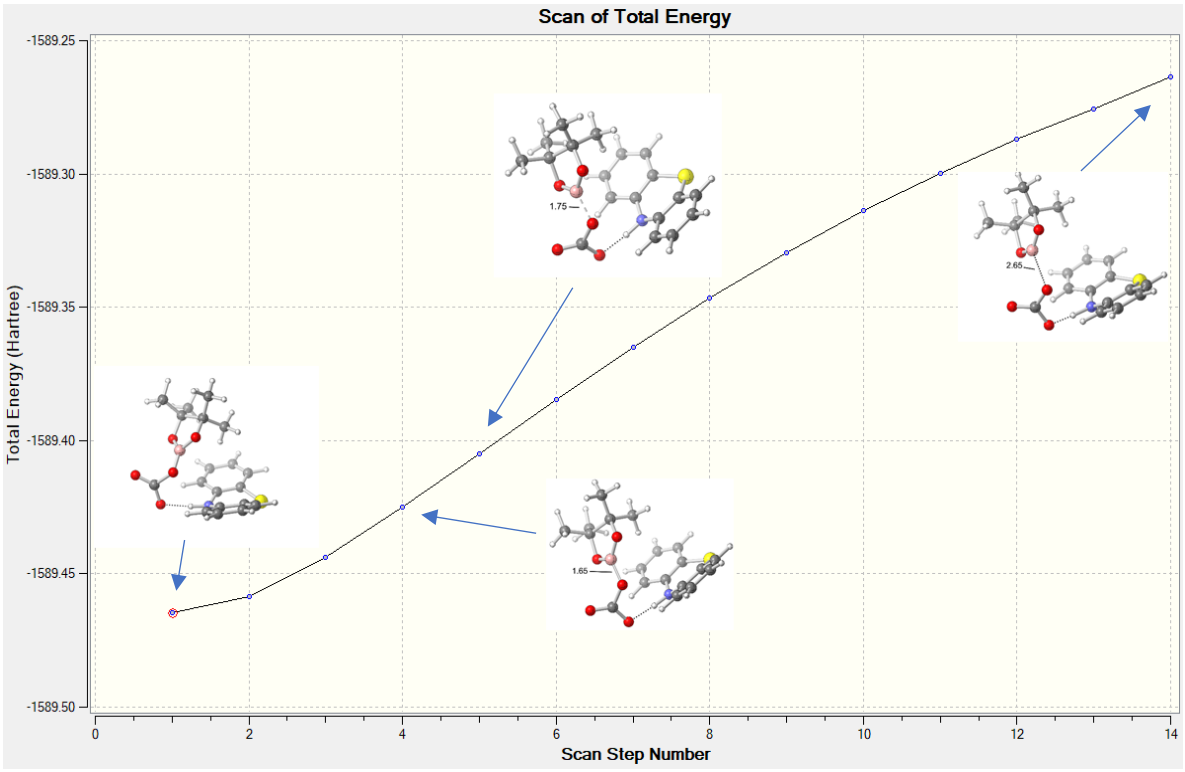
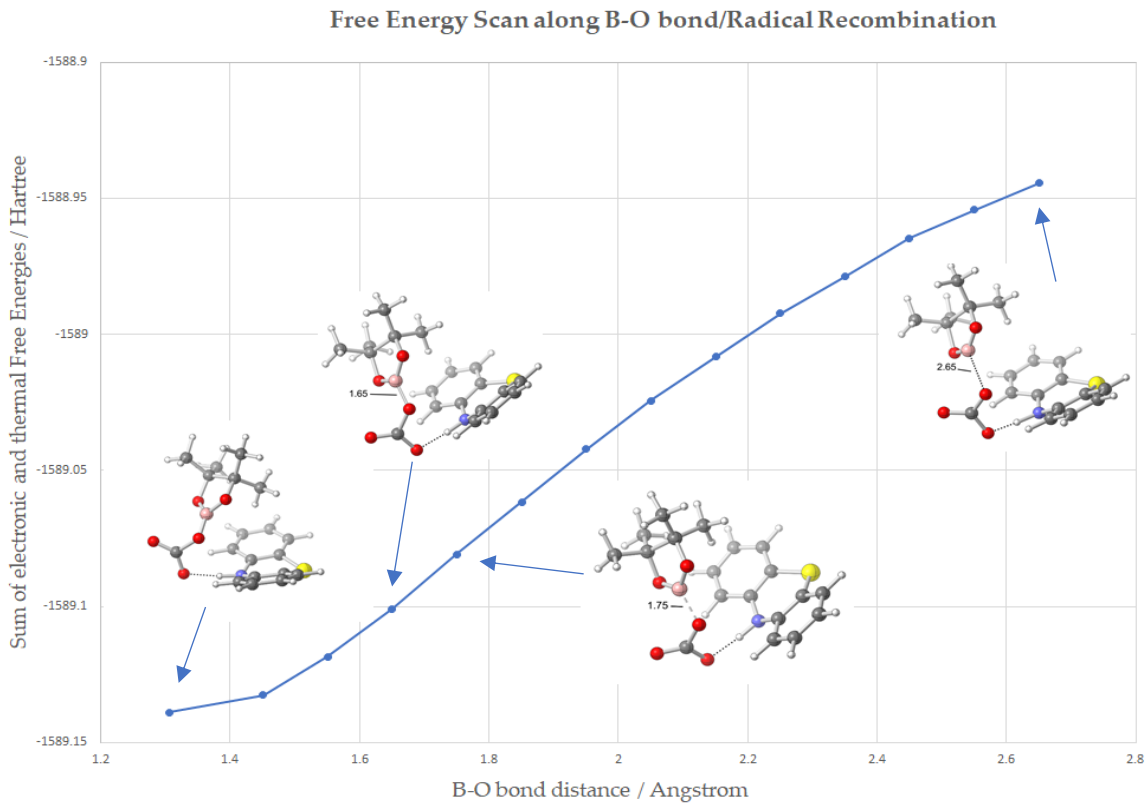


Figure S6. Relaxed PES Scan of 125 + Bpin Radical → 126. A relaxed scan of the B–O bond length was conducted at the uM06-2X D3 / def2-SVP / SMD (MeCN) level of theory to probe for the presence of a barrier to radical recombination. Scanning began from the optimized bond distance from structure **126** (1.3504 Å). An interval of 0.1 Å was selected for the scan, and 14 geometries were obtained. The final B–O bond distance was 2.6504 Å. Cleavage of the bond occurred between points 4 and 5, corresponding to distances of 1.6504 Å and 1.7504 Å, respectively.



FES Scan of 125 + Bpin Radical → 126

Figure S7. FES Scan of 125 + Bpin Radical → 126. Single point calculations were conducted at each of the optimized sub-geometries of the relaxed PES scan of the B–O bond length in order to further investigate the energetics of the radical recombination step. The FES scan indicates that the radical recombination proceeds without a barrier.

Optimized Geometries (M06-2X D3 / Def2-SVP / SMD (MeCN))

123 – GS PTH Carbonate Dianion

pth-carb-m062x-sp3.log

m062x/def2svp

E(RM062X) = -1178.64707046

Zero-point correction= 0.194806 (Hartree/Particle)

Thermal correction to Energy= 0.209419

Thermal correction to Enthalpy= 0.210363

Thermal correction to Gibbs Free Energy= 0.151993

Sum of electronic and ZPE= -1178.452264

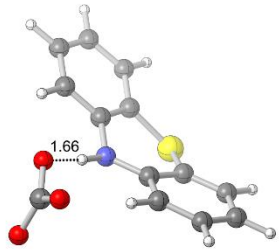
Sum of electronic and thermal Energies= -1178.437651

Sum of electronic and thermal Enthalpies= -1178.436707

Sum of electronic and thermal Free Energies= -1178.495077

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	131.413	56.071	122.85

Optimized Cartesian Coordinates:



Charge = -2 Multiplicity = 1

C -7.74513 0.28405 -0.10309

C -6.59283 0.65286 -0.80004

C -5.97697 1.89746 -0.56284

C -6.54606 2.75427 0.40316

C -7.67626 2.36222 1.12639

C -8.28995 1.13072 0.86911

C -4.1646 4.0846 0.20706

C -3.85017 3.08317 -0.73653

C -2.5057 2.93321 -1.13052

H -2.25078 2.15644 -1.84845

C -1.51451 3.76639 -0.60741

C -1.83222 4.7431 0.34311

C -3.16151 4.88816 0.75653

H -8.20977 -0.67653 -0.31321

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H -6.15173 -0.00859 -1.54122

H -8.08987 3.03053 1.87832

H -9.17945 0.84158 1.42255

H -0.48588 3.63917 -0.93669

H -1.06065 5.38456 0.76059

H -3.42404 5.64316 1.49417

S -5.88088 4.40401 0.60661

N -4.83361 2.25436 -1.27854

H -4.48712 1.5189 -1.95373

C -3.01155 0.48974 -3.78752

O -3.23808 1.14457 -4.88084

O -1.82906 0.04902 -3.49902

O -4.00467 0.27224 -2.94471

123 – No D3 – S1 PTH Carbonate Dianion

pth-carb-m062x-es1-freq.log

m062x/def2svp

E(RM062X) = -1178.62515762

Zero-point correction= 0.189937 (Hartree/Particle)

Thermal correction to Energy= 0.205988

Thermal correction to Enthalpy= 0.206932

Thermal correction to Gibbs Free Energy= 0.143838

Sum of electronic and ZPE= -1178.346557

Sum of electronic and thermal Energies= -1178.330505

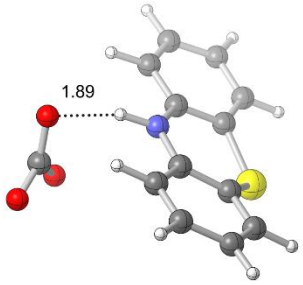
Sum of electronic and thermal Enthalpies= -1178.329561

Sum of electronic and thermal Free Energies= -1178.392656

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	129.259	59.531	132.793

Optimized Cartesian Coordinates:

Charge = -2 Multiplicity = 1



C -7.85577 0.29893 -0.21085

C -6.55663 0.45731 -0.66657

C -5.79933 1.61719 -0.36677

C -6.45625 2.67731 0.35659

C -7.75741 2.48818 0.82023

C -8.47078 1.31123 0.57102

C -4.01216 3.92193 0.21326

C -3.60283 2.73574 -0.50301

C -2.25131 2.64498 -0.91241

H -1.94832 1.76693 -1.48855

C -1.32427 3.62502 -0.58957

C -1.7163 4.76013 0.17472

C -3.05762 4.8843 0.54527

H -8.4023 -0.6135 -0.45932

H -6.08371 -0.32137 -1.27228

H -8.23374 3.30552 1.37207

H -9.48064 1.1841 0.96235

H -0.29027 3.51406 -0.92284

H -0.99065 5.52017 0.46655

H -3.38912 5.77337 1.09262

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S -5.73782 4.29853 0.3843

N -4.48065 1.70071 -0.73506

H -4.1376 0.95964 -1.34709

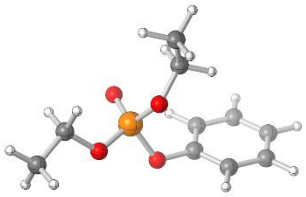
C -3.46333 1.02938 -3.62979

O -4.58282 1.64461 -3.75448

O -2.52381 1.47765 -4.32266

O -3.3876 0.06132 -2.83449

124 - $PhPO_4Et_2$



phpo4-ethyl-m062x-svp-d3.log

m062x/def2svp

E(RM062X) = -1031.51618321

Zero-point correction= 0.244947 (Hartree/Particle)

Thermal correction to Energy= 0.261100

Thermal correction to Enthalpy= 0.262044

Thermal correction to Gibbs Free Energy= 0.197139

Sum of electronic and ZPE= -1031.271236

Sum of electronic and thermal Energies= -1031.255084

Sum of electronic and thermal Enthalpies= -1031.254139

Sum of electronic and thermal Free Energies= -1031.319045

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	163.842	57.719	136.605

C,0,-1.2184557593,2.0235133426,0.4602261088

C,0,0.1718398217,2.1127263034,0.4029693304

C,0,0.7535460914,3.2181804067,-0.2136752009

C,0,-0.0236593986,4.2300814854,-0.7765203205

C,0,-1.4136013244,4.1248815589,-0.7167011372

C,0,-2.0130985387,3.0257083073,-0.1003328781

H,0,-1.6824831589,1.161914395,0.9432258202

H,0,0.8140342239,1.3395290203,0.82689589

H,0,0.4662393239,5.0801111603,-1.2532295998

H,0,-2.0299023049,4.9119866588,-1.1544554318

H,0,-3.1005228116,2.9498075799,-0.0555338146

O,0,2.1360913619,3.2950178652,-0.2502222405

P,0,2.8689013883,3.2477615834,-1.6894607677

O,0,2.6878498568,4.4398434838,-2.5430859499

O,0,4.3335829473,2.930141306,-1.1758966251

O,0,2.3772837899,1.8800744092,-2.3452331652

C,0,5.4132184506,2.8975975958,-2.1314816472

H,0,5.231631276,2.072736861,-2.8378765951

H,0,5.4159883445,3.84337751,-2.6932429933

C,0,1.4090111696,1.8342683751,-3.4120578481

H,0,0.4461767057,1.5365842227,-2.9704661509

H,0,1.301663547,2.8406038624,-3.8409730658

C,0,6.7020973913,2.6981894529,-1.3762314509

H,0,6.6794362186,1.7531240807,-0.8161360035

H,0,7.5421395299,2.6664583281,-2.0834307471

H,0,6.867741938,3.524820295,-0.6714776344

C,0,1.8706376635,0.8403288297,-4.4489934639

H,0,1.1213024969,0.7664036613,-5.2494191669

H,0,2.8253083009,1.1589428917,-4.8913073501

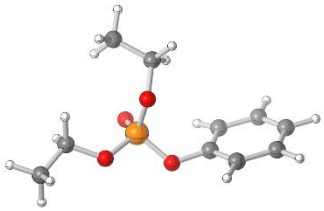
H,0,2.001915309,-0.1546274028,-4.0010807609

$124^{\cdot-}$ – $PhPO_4Et_2$ Radical Anion

phpo4-radan-ethyl-m062x-svp-d3.log

um062x/def2svp

E(UM062X) = -1031.55118740



Zero-point correction= 0.238592 (Hartree/Particle)

Thermal correction to Energy= 0.255234

Thermal correction to Enthalpy= 0.256179

Thermal correction to Gibbs Free Energy= 0.192034

Sum of electronic and ZPE= -1031.312595

Sum of electronic and thermal Energies= -1031.295953

Sum of electronic and thermal Enthalpies= -1031.295009

Sum of electronic and thermal Free Energies= -1031.359153

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	160.162	61.169	135.003

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C,0,0.1394539474,2.4578936492,0.7523094475

C,0,0.6621334308,3.2794106917,-0.2210468714

C,0,-0.1106815312,4.0697080394,-1.0964419262

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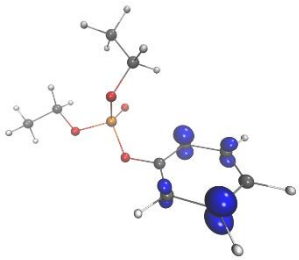
C,0,-2.0987833815,3.2098795702,0.0772737747



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H,0,0.3756898542,4.7842817474,-1.7597877527

H,0,-2.2047986906,4.6248513766,-1.5420118277

H,0,-3.1876746606,3.1894405675,0.1981903036

O,0,2.0639865489,3.3208471449,-0.3306335884

P,0,2.771330719,3.1023369358,-1.7465565117

O,0,2.7537717585,4.2152719362,-2.7229582544

O,0,4.2162974009,2.6998260719,-1.1992775503

O,0,2.1693921449,1.7297376431,-2.309664743

C,0,5.278647353,2.529801544,-2.1490159326

H,0,5.0342951804,1.682905534,-2.8107948038

H,0,5.3555953936,3.437723993,-2.7664192562

C,0,1.451272489,1.6838596161,-3.5536482481

H,0,0.7685349162,0.8285283639,-3.4660087367

H,0,0.8471113645,2.5970070571,-3.6569615101

C,0,6.5563596226,2.2712106193,-1.3900108609

H,0,7.3868581059,2.1338031278,-2.0960275416

H,0,6.7916590095,3.1197745019,-0.7324002481

H,0,6.4643873658,1.3640503569,-0.7765707844

C,0,2.398495285,1.5172985771,-4.7194518577

H,0,1.829237644,1.4390063243,-5.6567963739

H,0,3.0682924396,2.3866436165,-4.7906234336

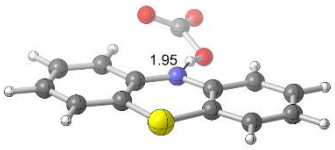
H,0,3.0029863137,0.6061283752,-4.6028377668

125 – PTH Carbonate Radical Anion

pth-carb-radan-d3.log

um062x/def2svp

E(UM062X) = -1178.55201795



Zero-point correction= 0.196358 (Hartree/Particle)

Thermal correction to Energy= 0.211209

Thermal correction to Enthalpy= 0.212153

Thermal correction to Gibbs Free Energy= 0.151775

Sum of electronic and ZPE= -1178.355660

Sum of electronic and thermal Energies= -1178.340809

Sum of electronic and thermal Enthalpies= -1178.339865

Sum of electronic and thermal Free Energies= -1178.400243

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	132.536	56.028	127.077

C,0,-7.5192345013,0.0270289214,-0.1731334887

C,0,-6.1445330345,0.1366644466,-0.1891101096

C,0,-5.4992258642,1.4028253103,-0.101880221

C,0,-6.3302825042,2.5549134195,-0.0002954119

C,0,-7.7267888803,2.43160739,0.0156681721

C,0,-8.319037501,1.180148907,-0.0689928846

C,0,-3.9438391923,3.8607737159,0.0773690316

C,0,-3.4129713951,2.5429849054,-0.0215132052

C,0,-1.996435727,2.3978860025,-0.0179262022

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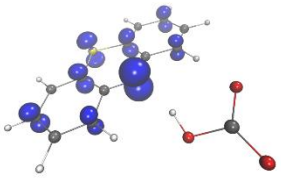

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C,0,-1.1699585373,3.5002964639,0.0647189723

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C,0,-3.0915832901,4.9706007137,0.1590641275

H,0,-7.9873794933,-0.9561067452,-0.2406762307

H,0,-5.4983704993,-0.739750935,-0.2718917295

H,0,-8.3456848256,3.3283182941,0.0948580525

H,0,-9.4064685931,1.0958489712,-0.0549387594

H,0,-0.0866583938,3.3681500379,0.0667412873

H,0,-1.0609510675,5.6652538503,0.2134502962

H,0,-3.5182587043,5.9736057354,0.2302102573

S,0,-5.6633560595,4.1657160402,0.0983724557

N,0,-4.1445206187,1.40601502,-0.1192695611

H,0,-3.334488455,-0.2898516352,-0.645617508

C,0,-1.9247854785,-1.5955169834,-0.4953331666

O,0,-1.6077519827,-2.7577223698,-0.7648270366

O,0,-1.2786745746,-0.7214332806,0.1233162961

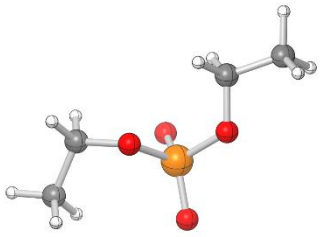
O,0,-3.1780718886,-1.2039564164,-0.9534045958

$(EtO)_2PO_2^-$ Anion

po4-ethyl-m062x-svp-d3.log

m062x/def2svp

E(RM062X) = -800.258747681



Zero-point correction= 0.151669 (Hartree/Particle)

Thermal correction to Energy= 0.162463

Thermal correction to Enthalpy= 0.163408

Thermal correction to Gibbs Free Energy= 0.113729

Sum of electronic and ZPE= -800.107078

Sum of electronic and thermal Energies= -800.096284

Sum of electronic and thermal Enthalpies= -800.095340

Sum of electronic and thermal Free Energies= -800.145018

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	101.947	37.409	104.556

P,0,-0.2716810669,1.471527536,-0.1811703296

O,0,0.3084922984,2.5350549608,-1.2920078853

O,0,0.4896264612,2.1247985321,1.1428637757

C,0,-0.078484948,3.8906797718,-1.1924165275

H,0,0.4886163509,4.3798790338,-0.3806214921

H,0,-1.1475489215,3.9516966663,-0.9278479778

C,0,-0.0876422681,1.9114709049,2.4134386771

H,0,0.4297203815,2.5844626893,3.1151051901

H,0,-1.1525403229,2.1983570388,2.3911663565

O,0,-1.7506253752,1.6636163055,0.0010762598

O,0,0.3204553131,0.1384377439,-0.5083547679

C,0,0.1841477044,4.5814206814,-2.5128414037

H,0,-0.4010818062,4.1095895498,-3.3156826192

H,0,-0.0933952187,5.6438090937,-2.4556685039

H,0,1.2495039096,4.5143071414,-2.7782111859

C,0,0.0523208107,0.4706356164,2.8737618552

H,0,-0.3296687322,0.3506017884,3.8984441869

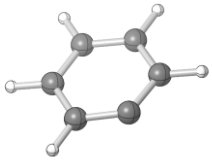
H,0,-0.5094664975,-0.2029831752,2.2102698825

H,0,1.1088863774,0.1644139908,2.854232376

Ph Radical

bs1-m062x-svp-d3.log

m062x/def2svp



E(UM062X) = -231.292276445

Zero-point correction= 0.088207 (Hartree/Particle)

Thermal correction to Energy= 0.092539

Thermal correction to Enthalpy= 0.093484

Thermal correction to Gibbs Free Energy= 0.060180

Sum of electronic and ZPE= -231.204069

Sum of electronic and thermal Energies= -231.199737

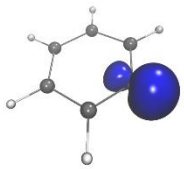
Sum of electronic and thermal Enthalpies= -231.198793

Sum of electronic and thermal Free Energies= -231.232096

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	58.069	16.59	70.093

C,0,-1.1690430004,1.5763795043,0.0000579303

C,0,0.2074202481,1.645185124,0.0004539033



C,0,0.9552964943,2.8028365046,-0.0000477203

C,0,0.2433438048,4.0110269428,-0.0010409058

C,0,-1.1539030901,4.0032821732,-0.0014839703

C,0,-1.859227298,2.7971118981,-0.0009381379

H,0,-1.7083585718,0.6264044143,0.0004976274

H,0,2.0477122107,2.7946235271,0.0003020802

H,0,0.7863512772,4.958572321,-0.0014764712

H,0,-1.6997320762,4.9482813828,-0.0022641763

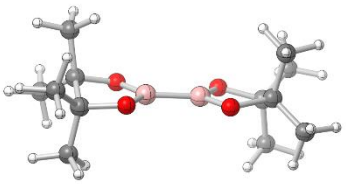
H,0,-2.9513846056,2.8009274667,-0.0012861594

B_2Bin_2

bpin-dimer-m062x-svp-d3.log

m062x/def2svp

E(RM062X) = -821.592421021



Zero-point correction= 0.364062 (Hartree/Particle)

Thermal correction to Energy= 0.383506

Thermal correction to Enthalpy= 0.384450

Thermal correction to Gibbs Free Energy= 0.317458

Sum of electronic and ZPE= -821.228359

Sum of electronic and thermal Energies= -821.208915

Sum of electronic and thermal Enthalpies= -821.207971

Sum of electronic and thermal Free Energies= -821.274963

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	240.654	77.579	140.997

C,0,-0.7710452149,0.9069844962,0.137298704

C,0,0.4506126119,1.6626869088,0.7589906498

B,0,-1.1357419687,3.1533625426,0.0937041206

C,0,-3.18058289,6.2409746464,-1.2169652824

C,0,-2.6082065493,6.7953531583,0.1301582641

B,0,-1.9175105788,4.6502315829,-0.1896455351

O,0,-0.0820540303,2.9921266798,0.9541579251

O,0,-1.4918956215,1.9778123601,-0.5128859009

O,0,-2.9356463069,4.8222517287,-1.0898646261

O,0,-1.5977567298,5.8148045772,0.4572227952

C,0,-1.9625650155,8.165490592,0.0283399532

H,0,-2.6958253726,8.9083179134,-0.3189802111

H,0,-1.6012788854,8.4765848144,1.0191121549

H,0,-1.1104850192,8.1586545878,-0.6630301935

C,0,-2.3960743,6.719674473,-2.4345478398

H,0,-2.7141960415,6.1384960049,-3.3117274549

H,0,-2.5806561868,7.7841064445,-2.6356482858

H,0,-1.3156688444,6.56904164,-2.2936312511

C,0,-4.6665752906,6.476595534,-1.4192880856

H,0,-4.9756442174,6.0624751269,-2.3898306736

H,0,-5.2612890702,5.9942400586,-0.6333357272

H,0,-4.8860211233,7.55452912,-1.4200001716

C,0,-3.6313438837,6.7727762472,1.2614000111

H,0,-3.1143926739,6.9734759441,2.210570911

H,0,-4.4045155926,7.540127287,1.1166669479

H,0,-4.1191000715,5.7896337925,1.3347457535

C,0,0.9249949751,1.1120948812,2.0918059895

H,0,1.2437384566,0.0650741994,1.981031227

H,0,1.7856371678,1.6974940205,2.4461542244

H,0,0.1358841782,1.1638114367,2.8525175219

C,0,1.6219102188,1.7919556165,-0.2097848457

H,0,2.3508298609,2.5004654302,0.208684353

H,0,2.122727843,0.8258661197,-0.3627366612

H,0,1.288394714,2.1752146828,-1.1853583118

C,0,-0.407098507,-0.1489029705,-0.890916404

H,0,0.2259464005,-0.9242300057,-0.434582868

H,0,-1.3228269953,-0.6291933995,-1.2646989209

H,0,0.1267507254,0.2871674661,-1.7446902234

C,0,-1.7038270074,0.3211677691,1.1927150784

H,0,-2.6311750071,-0.0071929243,0.7021622372

H,0,-1.2482295517,-0.5448709075,1.6926746582

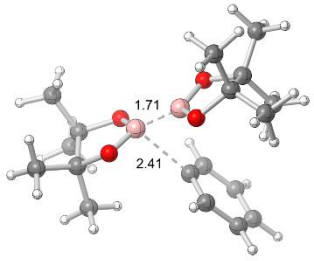
H,0,-1.9626459949,1.0722707073,1.9534561237

TS2

bpin-tsr-d3-b.log

um062x/def2svp

E(UM062X) = -1052.89818321



Zero-point correction= 0.452459 (Hartree/Particle)

Thermal correction to Energy= 0.477327

Thermal correction to Enthalpy= 0.478271

Thermal correction to Gibbs Free Energy= 0.398142

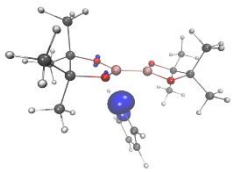
Sum of electronic and ZPE= -1052.445724

Sum of electronic and thermal Energies= -1052.420856

Sum of electronic and thermal Enthalpies= -1052.419912

Sum of electronic and thermal Free Energies= -1052.500041

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	299.527	98.321	168.646



C,0,-0.8361279076,0.7393120807,0.2251669163

C,0,0.3383786059,1.4231603744,1.0066447393

B,0,-1.0285275454,3.0091239034,0.1020308298

C,0,-2.9836607304,6.1330569988,-1.2608241896

C,0,-2.386790026,6.6983940929,0.0735237142

B,0,-1.7661145161,4.5240217579,-0.207994585

O,0,-0.1150153709,2.790021034,1.106818593

O,0,-1.3900802775,1.8385063547,-0.5275610336

O,0,-2.7882978905,4.7105485448,-1.1038860516

O,0,-1.4193767979,5.6879161669,0.4311460969

C,0,-1.6800959661,8.0351065804,-0.0675737469

H,0,-2.3777598954,8.8009655313,-0.4375067912

H,0,-1.3043109788,8.3578500442,0.9140951501

H,0,-0.8290295703,7.968210368,-0.7575762982

C,0,-2.1945151638,6.5648144954,-2.4940509672

H,0,-2.5373610568,5.9760401652,-3.3573962544

H,0,-2.3537842876,7.6299326412,-2.7135872841

H,0,-1.1162803181,6.3890147072,-2.3621610544

C,0,-4.4625250752,6.4132106782,-1.4610132002

H,0,-4.7895262057,5.9878653732,-2.4208196489

H,0,-5.068501892,5.9677085211,-0.6620140036

H,0,-4.6473254364,7.4973379416,-1.4849031041

C,0,-3.41030412,6.7549546158,1.203113843

H,0,-2.8850152337,6.9635957691,2.1460220397

H,0,-4.1510481795,7.5488632843,1.0338182877

H,0,-3.9380837738,5.7955746895,1.3071012442

C,0,0.5707898981,0.874617268,2.4038650781

H,0,0.8175541052,-0.1964222248,2.3589352069

H,0,1.4156722223,1.4025301158,2.8692673026

H,0,-0.3125799686,1.0086868664,3.0408303553

C,0,1.6473764066,1.4312521152,0.2224765756

H,0,2.3550313085,2.10891641,0.7220533633

H,0,2.0931967418,0.4273382187,0.1849350227

H,0,1.4963772018,1.7883386613,-0.8062056001

C,0,-0.4038786084,-0.3555700328,-0.73432584

H,0,0.1101038912,-1.1619027545,-0.1904736334

H,0,-1.2892053279,-0.7832484394,-1.2266376594

H,0,0.2680298782,0.0328755595,-1.5103486968

C,0,-1.9413977164,0.2305652435,1.1460539424

H,0,-2.8102223797,-0.0498773768,0.5336928093

H,0,-1.6160823108,-0.6519017771,1.7144021304

H,0,-2.2564066128,1.0106798595,1.8546255381

C,0,0.2556016681,4.0401082766,-1.6634012508

C,0,1.1970806953,5.0022636761,-1.3666678097

C,0,1.8491508785,5.5934204042,-2.457308945

C,0,1.5331683082,5.2014898637,-3.7618362962

C,0,0.5726204501,4.2141621814,-3.99830198

C,0,-0.0935590415,3.6078056665,-2.924404391

H,0,1.4110749983,5.3047986686,-0.3393633609

H,0,2.6022824828,6.3652495407,-2.2845344751

H,0,2.0428480414,5.6714481187,-4.6046287206

H,0,0.3350464194,3.9151678432,-5.0215236384

H,0,-0.8574335489,2.8423896187,-3.0777227622

PhBPin

bs3-m062x-svp-d3.log

um062x/def2svp

E(UM062X) = -642.200759529

Zero-point correction= 0.273611 (Hartree/Particle)

Thermal correction to Energy= 0.287786

Thermal correction to Enthalpy= 0.288730

Thermal correction to Gibbs Free Energy= 0.233006

Sum of electronic and ZPE= -641.927148

Sum of electronic and thermal Energies= -641.912974

Sum of electronic and thermal Enthalpies= -641.912030

Sum of electronic and thermal Free Energies= -641.967753

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	180.588	56.753	117.28

C,0,-0.5187898598,0.428764,-1.2314383209

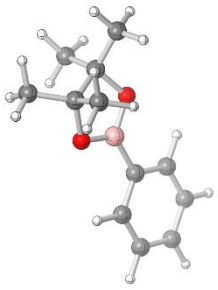
C,0,0.8628771692,0.6181590576,-1.2538038781

C,0,1.5423439746,0.917472131,-0.0707886827

C,0,0.839200344,1.0276511114,1.1310115929

C,0,-0.5426182227,0.8390294303,1.1459316765

C,0,-1.2416120742,0.5364734966,-0.033045582



H,0,-1.0492794838,0.1923552548,-2.1571922226

H,0,1.4131241849,0.5320282308,-2.1927473679

H,0,2.6240190975,1.0657857507,-0.0854814713

H,0,1.3709147914,1.2620189211,2.0552447284

H,0,-1.0923746809,0.9272452646,2.0862856995

B,0,-2.7889038983,0.3231934828,-0.0102255437

O,0,-3.5368885668,0.3583253566,1.1332139489

O,0,-3.5339226204,0.0817331479,-1.1303776848

C,0,-4.8598789368,-0.2922456711,-0.6906378252

C,0,-4.9273458243,0.3548437857,0.7360507294

C,0,-5.8833679218,0.2414365003,-1.6757175894

H,0,-6.9020530565,0.0569114016,-1.3040965515

H,0,-5.75646819,1.3183475553,-1.8435156389

H,0,-5.7700898961,-0.2750651635,-2.6396826589

C,0,-4.9017079699,-1.8161484791,-0.649621378

H,0,-5.9029531325,-2.1807837826,-0.3816323279

H,0,-4.6440365196,-2.2040089657,-1.64535569

H,0,-4.1757394381,-2.2136910387,0.0749721956

C,0,-5.7358882911,-0.4330589128,1.7500659817

H,0,-6.7772781498,-0.5345207992,1.4108773148

H,0,-5.3154903326,-1.4339339993,1.9098407749

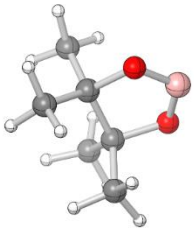
H,0,-5.7380604498,0.0993663222,2.7120119371

C,0,-5.384305283,1.8093361658,0.7021391981

H,0,-4.8170510659,2.3858085995,-0.043487612

H,0,-6.4547998983,1.8857368309,0.4667829087

H,0,-5.2115164117,2.2577975032,1.6907404085



Bpin Radical

bpin-r-d3.log

um062x/def2svp

E(UM062X) = -410.711637141

Zero-point correction= 0.180108 (Hartree/Particle)

Thermal correction to Energy= 0.189334

Thermal correction to Enthalpy= 0.190278

Thermal correction to Gibbs Free Energy= 0.146735

Sum of electronic and ZPE= -410.531529

Sum of electronic and thermal Energies= -410.522303

Sum of electronic and thermal Enthalpies= -410.521359

Sum of electronic and thermal Free Energies= -410.564902

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	118.809	36.907	91.643

B,0,-2.8012464607,0.3228812205,-0.0093187202

O,0,-3.520119024,0.3638110967,1.1338043155

O,0,-3.5159705117,0.0831030395,-1.130393053

C,0,-4.8602115397,-0.2911252444,-0.6906883375

C,0,-4.9280865995,0.3540203711,0.736433462

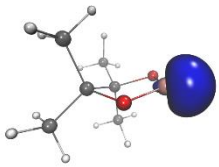
C,0,-5.8708348029,0.2549088596,-1.6799463522

H,0,-6.8924252776,0.0742705003,-1.3140781535

H,0,-5.7371144962,1.3318432751,-1.8409736459

H,0,-5.7553165634,-0.2584387336,-2.6450744427

C,0,-4.9036163441,-1.8133490712,-0.6597663316



H,0,-5.9081262317,-2.1743008394,-0.398726892

H,0,-4.6440120335,-2.1954037953,-1.6569850486

H,0,-4.1829677095,-2.218171617,0.0655831858

C,0,-5.7206465804,-0.4428886504,1.7537553643

H,0,-6.7633183501,-0.5496343386,1.4197282604

H,0,-5.293294465,-1.441651662,1.9069074063

H,0,-5.7208187547,0.087153324,2.7167557533

C,0,-5.3872058563,1.8060381128,0.712186883

H,0,-4.826957243,2.3884437012,-0.0336098018

H,0,-6.4594557804,1.8768988133,0.4827691738

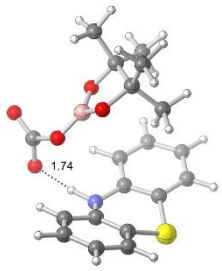
H,0,-5.2123030156,2.2497257378,1.7023031146

126 - PTH-Carbonate-Bpin Anion

pth-bpin-co3-an-d3.log

um062x/def2svp

E(UM062X) = -1589.46468018



Zero-point correction= 0.380708 (Hartree/Particle)

Thermal correction to Energy= 0.405456

Thermal correction to Enthalpy= 0.406400

Thermal correction to Gibbs Free Energy= 0.325720

Sum of electronic and ZPE= -1589.083972

Sum of electronic and thermal Energies= -1589.059225

Sum of electronic and thermal Enthalpies= -1589.058280

Sum of electronic and thermal Free Energies= -1589.138960

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	254.427	96.347	169.805

B,0,-2.5166430844,-2.9667308129,0.2763775762

O,0,-1.1426723585,-2.965464795,0.2717597974

O,0,-3.0527938258,-2.8545223133,-0.9872397976

C,0,-1.9736579059,-2.4904935624,-1.8660517508

C,0,-0.7241968249,-3.0540995867,-1.1031019418

C,0,-2.2089081717,-3.1011786476,-3.2351887498

H,0,-1.3443673442,-2.9187699705,-3.8905485244

H,0,-2.3814903645,-4.1829311255,-3.1679205562

H,0,-3.0932517356,-2.6385032062,-3.6970193504

C,0,-1.9605467012,-0.9673530959,-1.9484984263

H,0,-1.2072127291,-0.6034768525,-2.6616383727

H,0,-2.9521537014,-0.6207230901,-2.275466608

H,0,-1.7512331587,-0.5336607051,-0.9594692999

C,0,0.5460606251,-2.244857491,-1.2936227473

H,0,0.8270684942,-2.2158702639,-2.3568611537

H,0,0.421372829,-1.2162189189,-0.9309029704

H,0,1.3687500541,-2.7121173284,-0.7329431876

C,0,-0.4703262201,-4.527631641,-1.4052349171

H,0,-1.3936575618,-5.115795091,-1.2958990744

H,0,-0.0806698557,-4.6693748228,-2.4229984899

H,0,0.2705399465,-4.9127580939,-0.6901440726

O,0,-3.3093971277,-3.0181832711,1.3683434101

C,0,-2.8099955155,-3.3274733717,2.6724788147

O,0,-3.0751585489,-2.438266673,3.5047785465

O,0,-2.2505207109,-4.4040490158,2.7946510905

C,0,-0.4484813096,0.6374892812,1.2060167365

C,0,-1.5444662624,0.0058930774,1.7904417202

C,0,-2.8505470004,0.4445755925,1.520187638

C,0,-3.0276392394,1.5165552968,0.6239006744

C,0,-1.9283405371,2.1202488291,0.0142135005

C,0,-0.6322775099,1.6923171017,0.310669735

C,0,-5.6171935423,0.7030931499,0.604968328

C,0,-5.1693475528,-0.2756403171,1.5112337182

C,0,-6.0016966092,-1.3740379604,1.7777590442

H,0,-5.6349478738,-2.1373468499,2.4664245037

C,0,-7.2498121649,-1.4826937961,1.1703554997

C,0,-7.6802749073,-0.5167622443,0.2585316464

C,0,-6.8531852687,0.5701625943,-0.0283928247

H,0,0.5583248785,0.2887183163,1.443645678

H,0,-1.416443048,-0.8348937769,2.4749459288

H,0,-2.0914869044,2.9420245488,-0.6867394355

H,0,0.2234005488,2.1818030121,-0.1563859364

H,0,-7.8849058444,-2.3397630427,1.4018967785

H,0,-8.6524878573,-0.6049492738,-0.2280240162

H,0,-7.1736839672,1.33578413,-0.7384744547

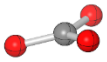
S,0,-4.656740129,2.1814048346,0.3678120353

N,0,-3.9295997663,-0.1825101071,2.12936527

H,0,-3.6656576354,-1.0179136505,2.6916719877

CO_3^{2-} Dianion

co3-m062x-svp-d3.log



m062x/def2svp

E(RM062X) = -263.662862590

Zero-point correction= 0.014869 (Hartree/Particle)

Thermal correction to Energy= 0.018013

Thermal correction to Enthalpy= 0.018958

Thermal correction to Gibbs Free Energy= -0.010647

Sum of electronic and ZPE= -263.647993

Sum of electronic and thermal Energies= -263.644849

Sum of electronic and thermal Enthalpies= -263.643905

Sum of electronic and thermal Free Energies= -263.673509

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	11.304	8.512	62.307

C,0,-0.4373532547,1.4219037928,-0.0000053644

O,0,0.2077196174,2.5401156892,0.0000017699

O,0,0.2077196208,0.3036918982,0.0000017699

O,0,-1.7282742235,1.4219037908,0.0000018247

$PinBOCO_2^-$ Anion

bs8-m062x-svp-d3.log

m062x/def2svp

E(RM062X) = -674.493993392

Zero-point correction= 0.198858 (Hartree/Particle)

Thermal correction to Energy= 0.211977

Thermal correction to Enthalpy= 0.212921

Thermal correction to Gibbs Free Energy= 0.159071

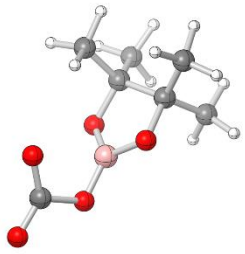
Sum of electronic and ZPE= -674.295135

Sum of electronic and thermal Energies= -674.282017

Sum of electronic and thermal Enthalpies= -674.281073

Sum of electronic and thermal Free Energies= -674.334922

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	133.017	49.475	113.336



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O,0,-3.6295825971,0.6632682532,-1.1183081516

C,0,-4.8571024385,0.0038802614,-0.7662407321

C,0,-4.8734851632,0.150519731,0.795439461

C,0,-6.0158180262,0.6832230167,-1.4748794657

H,0,-6.9750221971,0.2670329628,-1.1326670769

H,0,-6.0135346981,1.7655685362,-1.2935549736

H,0,-5.9356000544,0.5148777366,-2.5587845877

C,0,-4.737821101,-1.4493428598,-1.2165082274

H,0,-5.6710873559,-2.0034525662,-1.0433119804

H,0,-4.5151325619,-1.4687508987,-2.2930602064

H,0,-3.9209253432,-1.960430915,-0.6857080873

C,0,-5.537708033,-0.9990206176,1.5313480409

H,0,-6.5902219748,-1.0946917497,1.2254882981

H,0,-5.0248883713,-1.9500368207,1.3382483387

H,0,-5.5116035106,-0.8071642346,2.6139530675

C,0,-5.4572255783,1.486614052,1.2476938354

H,0,-4.963536667,2.3170680974,0.7229923783

H,0,-6.5418373739,1.5345935602,1.0769992941

H,0,-5.2670739722,1.6056496922,2.3243335394

O,0,-1.4929726002,0.9991422112,-0.0298780029

C,0,-1.2663841472,2.3569030614,0.3668279189

O,0,-0.0897125021,2.6874533283,0.4241619384

O,0,-2.3173977805,2.9840240018,0.5839766246

X-Ray Crystallographic Data

Methyl 2-((2*S*,3*R*)-2,7'-diethyl-5'-iodo-2'-oxo-4,5-dihydro-2*H*-spiro[furan-3,3'-indolin]-2-yl)acetate (S27)

CCDC 1959507

Bond precision: C–C = 0.0051 Å Wavelength = 0.71073

Cell: a = 14.7645(4) b = 7.7901(2) c = 16.2371(4)

α = 90 β = 107.458(2) γ = 90

Temperature: 100 K

	Calculated	Reported
Volume	1781.52(8)	1781.52(8)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	$C_{18}H_{22}INO_4$	$C_{18}H_{22}INO_4$
Sum formula	$C_{18}H_{22}INO_4$	$C_{18}H_{22}INO_4$
M_r	443.27	443.26
D_x,g cm^{-3}	1.653	1.653
Z	4	4
Mu (mm^{-1})	1.819	1.819
F000	888.0	888.0
F000'	886.48	
h,k,l_{max}	17,9,19	17,9,19
N_{ref}	3318	3318
T_{min},T_{max}	0.419,0.549	0.901,1.000
T_{min}'	0.387	

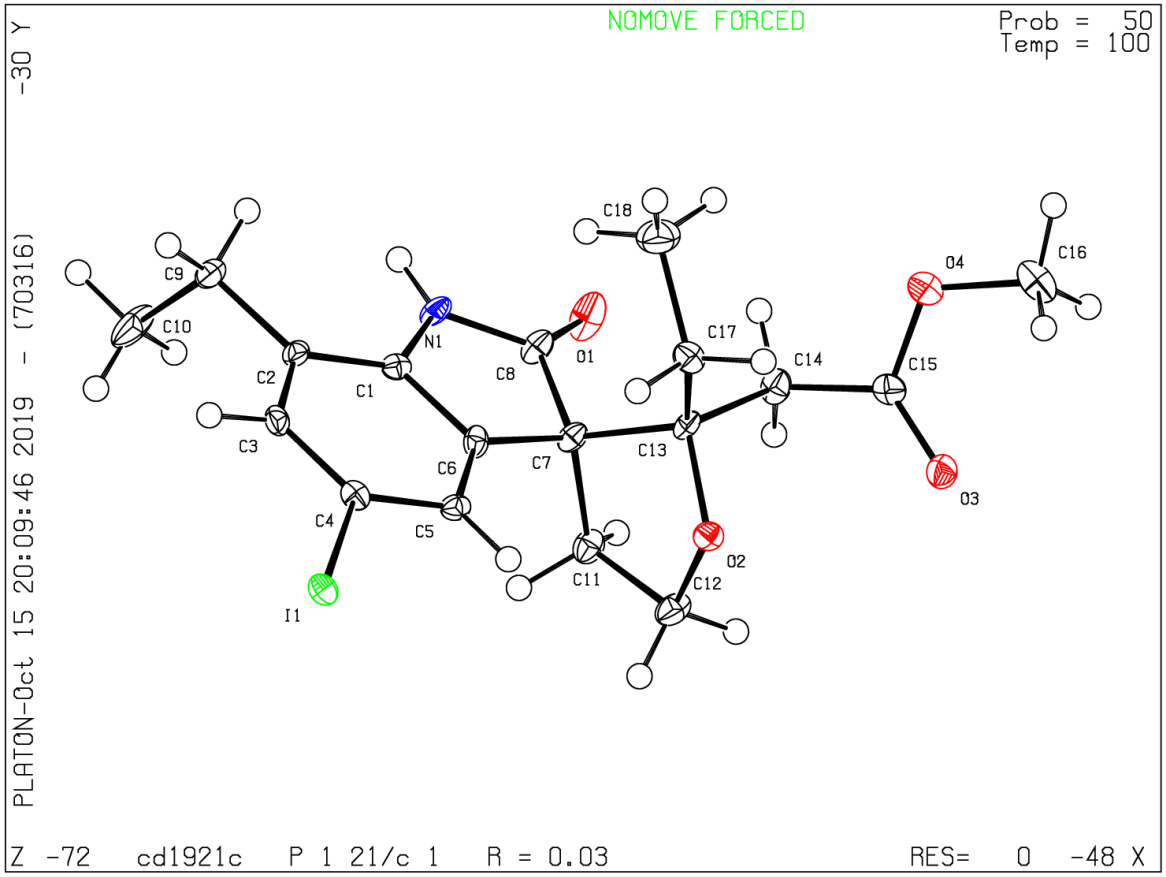
Correction method= # Reported T Limits: T_{min}=0.901 T_{max}=1.000

AbsCorr = MULTI-SCAN

Data completeness= 1.000 Theta(max)= 25.490

R(reflections)= 0.0336(3312) wR2(reflections)= 0.0920(3318)

S = 1.100 N_{par}= 220



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2-(4-(2-(4-Methoxyphenyl)propan-2-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11)

CCDC 1959288

Bond precision: C–C = 0.0030 Å Wavelength = 0.71073

Cell: a = 25.9588(8) b = 6.6139(2) c = 11.2968(3)

α = 90 β = 92.514(2) γ = 90

Temperature: 98 K

	Calculated	Reported
Volume	1937.67(10)	1937.67(10)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	$C_{22}H_{29}BO_3$	$C_{22}H_{29}BO_3$
Sum formula	$C_{22}H_{29}BO_3$	$C_{22}H_{29}BO_3$
M_r	352.26	352.26
D_x,g cm^{-3}	1.207	1.208
Z	4	4
Mu (mm^{-1})	0.077	0.077
F000	760.0	760.0
F000'	760.33	
h,k,l_{max}	30,7,13	30,7,13
N_{ref}	3429	3427
T_{min},T_{max}	0.982,0.996	0.736,1.000
T_{min}'	0.962	

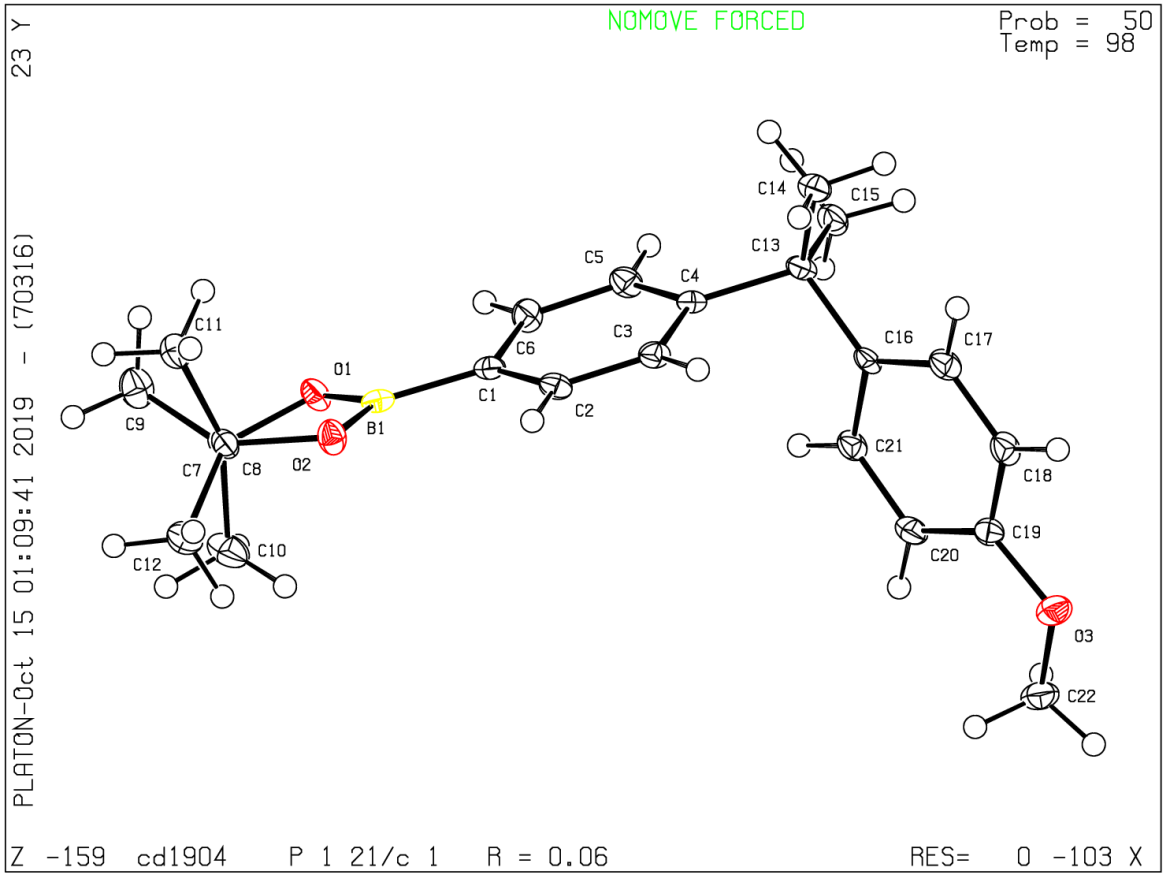
Correction method= # Reported T Limits: T_{min}=0.736 T_{max}=1.000

AbsCorr = MULTI-SCAN

Data completeness= 0.999 Theta(max)= 25.050

R(reflections)= 0.0624(3337) wR2(reflections)= 0.1244(3427)

S = 1.064 N_{par}= 242



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tert-Butyl (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)carbamate (15)

CCDC 1959289

Bond precision: C–C = 0.0031 Å Wavelength = 0.71073

Cell: a = 10.0080(3) b = 19.8705(8) c = 9.1491(2)

α = 90 β = 90 γ = 90

Temperature: 100 K

	Calculated	Reported
Volume	1819.43(10)	1819.43(10)
Space group	P n a 21	P n a 21
Hall group	P 2c -2n	P 2c -2n
Moiety formula	$C_{17}H_{26}BNO_4$	$C_{17}H_{26}BNO_4$
Sum formula	$C_{17}H_{26}BNO_4$	$C_{17}H_{26}BNO_4$
M_r	319.20	319.20
D_x,g cm^{-3}	1.165	1.165
Z	4	4
Mu (mm^{-1})	0.081	0.081
F000	688.0	688.0
F000'	688.33	
h,k,l_{max}	12,24,11	12,24,11
N_{ref}	3591 [1915]	3561
T_{min},T_{max}	0.984,0.998	0.870,1.000
T_{min}'	0.970	

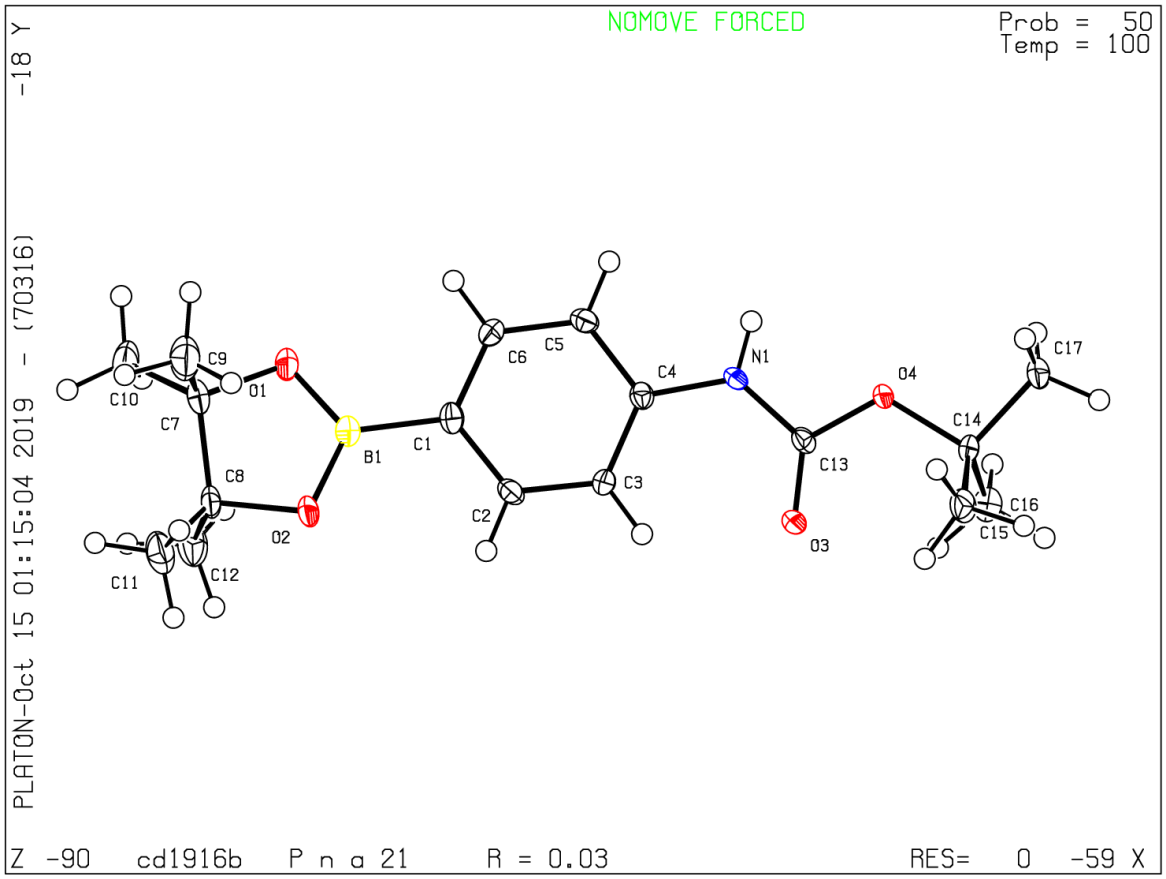
Correction method= # Reported T Limits: T_{min}=0.870 T_{max}=1.000

AbsCorr = MULTI-SCAN

Data completeness= 1.86/0.99 Theta(max)= 25.998

R(reflections)= 0.0347(3472) wR2(reflections)= 0.0792(3561)

S = 1.090 N_{par}= 218



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1-(Indolin-1-yl)-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one

(23)

CCDC 1959498

Bond precision: C–C = 0.0020 Å Wavelength = 0.71073

Cell: a = 9.1074(6) b = 10.4748(6) c = 11.1129(7)

α = 90.070(5) β = 103.031(5) γ = 112.623(6)

Temperature: 97 K

	Calculated	Reported
Volume	948.81(11)	948.81(11)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	$C_{22}H_{26}BNO_3$	$C_{22}H_{26}BNO_3$
Sum formula	$C_{22}H_{26}BNO_3$	$C_{22}H_{26}BNO_3$
M_r	363.25	363.25
D_x,g cm^{-3}	1.271	1.271
Z	2	2
Mu (mm^{-1})	0.083	0.083
F000	388.0	388.0
F000'	388.17	
h,k,l_{max}	11,12,13	11,12,13
N_{ref}	3731	3729
T_{min},T_{max}	0.980,0.986	0.972,1.000
T_{min}'	0.973	

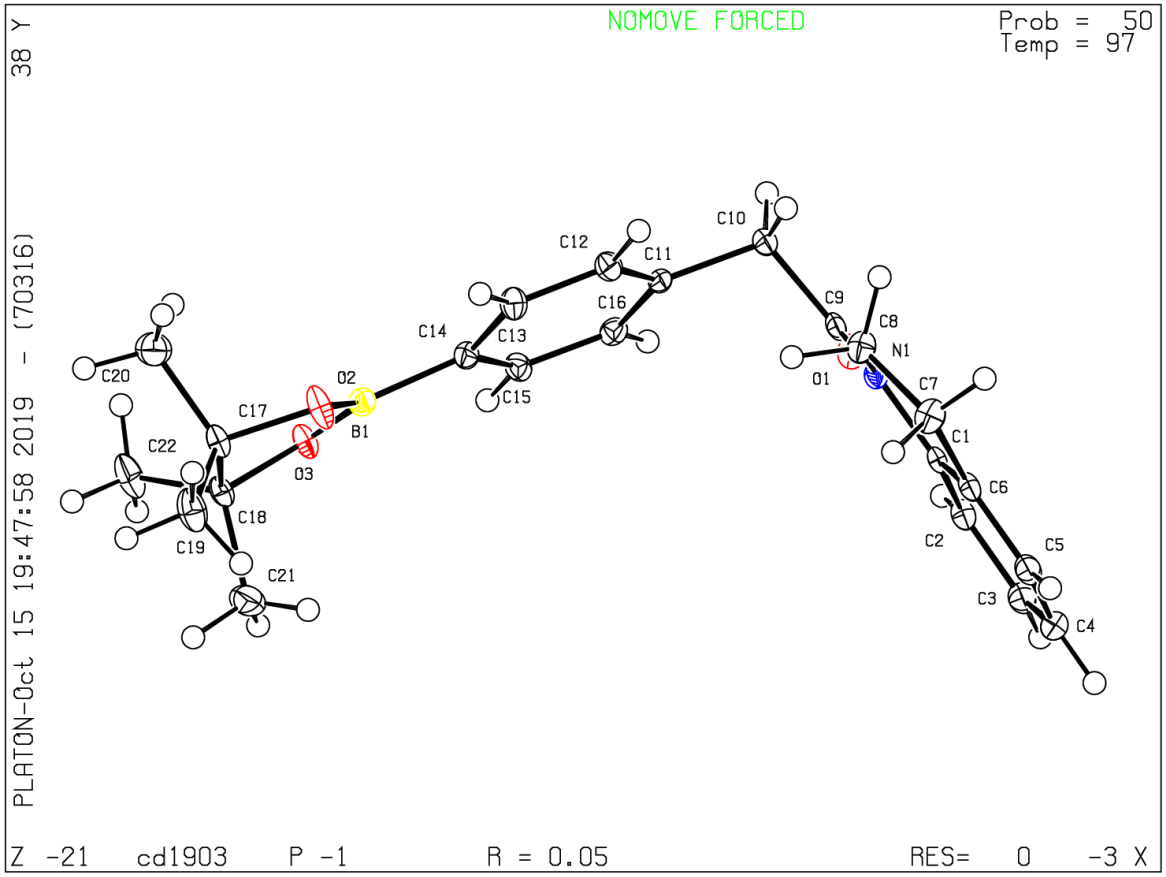
Correction method= # Reported T Limits: T_{min}=0.972 T_{max}=1.000

AbsCorr = MULTI-SCAN

Data completeness= 0.999 Theta(max)= 25.997

R(reflections)= 0.0474(3684) wR2(reflections)= 0.0998(3729)

S = 1.006 N_{par}= 248



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Trifluoro(3-(methylsulfonyl)phenyl)-λ^4-borane, potassium salt (43)

CCDC 1946411

Bond precision: C–C = 0.0028 Å Wavelength = 0.71073

Cell: a = 13.0091(8) b = 6.6126(3) c = 12.8870(7)

α = 90 β = 114.410(7) γ = 90

Temperature: 100 K

	Calculated	Reported
Volume	1009.50(11)	1009.50(11)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	$C_7H_7BF_3KO_2S$	$C_7H_7BF_3KO_2S$
Sum formula	$C_7H_7BF_3KO_2S$	$C_7H_7BF_3KO_2S$
M_r	262.10	262.10
D_x,g cm^{-3}	1.724	1.725
Z	4	4
Mu (mm^{-1})	0.750	0.750
F000	528.0	528.0
F000'	529.65	
h,k,l_{max}	16,8,16	16,8,16
N_{ref}	2065	2061
T_{min},T_{max}	0.921,0.969	0.709,1.000
T_{min}'	0.829	

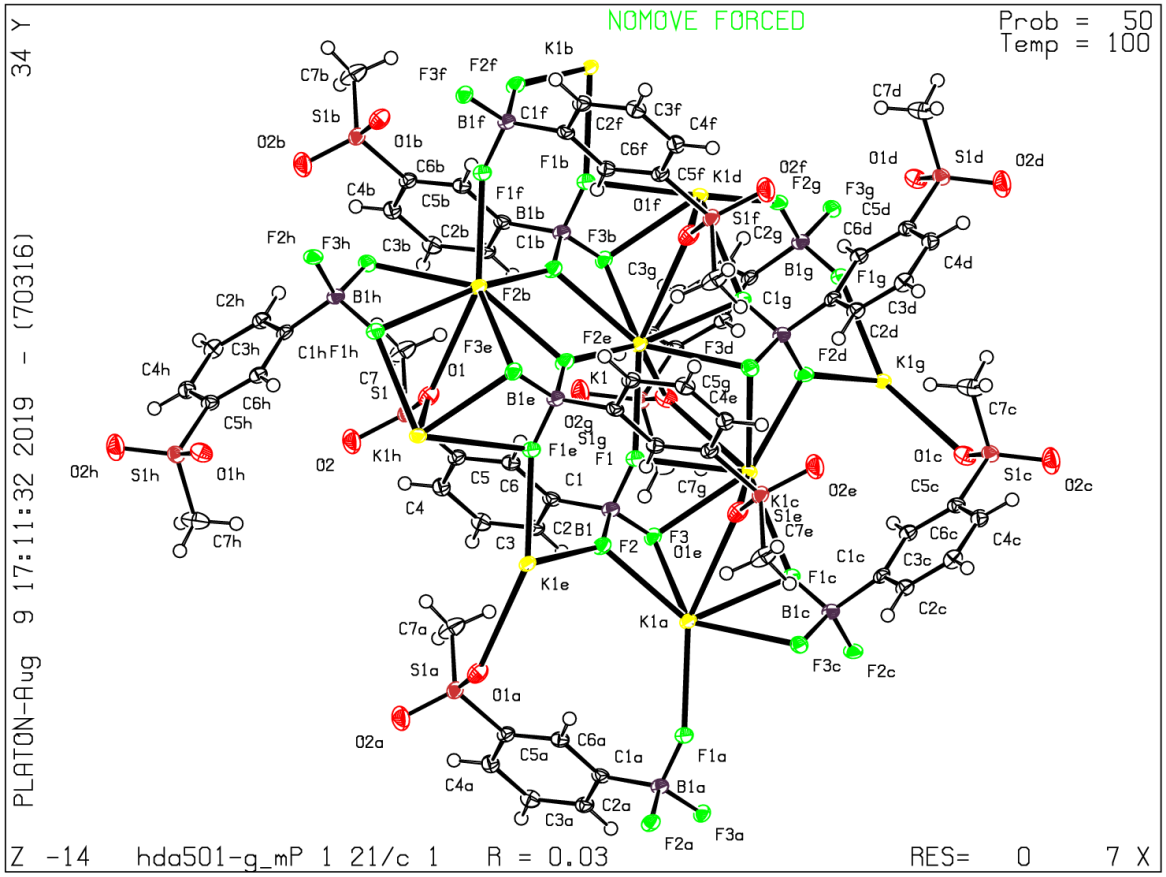
Correction method = # Reported T Limits: T_{min} = 0.709 T_{max} = 1.000

AbsCorr = MULTI-SCAN

Data completeness = 0.998 Theta(max) = 26.369

R(reflections) = 0.0262(1833) wR2(reflections) = 0.0662(2061)

S = 1.037 N_{par} = 137



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4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (44)

CCDC 1959497

Bond precision: C–C = 0.0020 Å Wavelength = 0.71073

Cell: a = 20.3444(5) b = 9.5619(2) c = 13.8608(3)

α = 90 β = 103.721(2) γ = 90

Temperature: 98 K

	Calculated	Reported
Volume	2619.41(10)	2619.41(10)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	$C_{14}H_{18}BNO_2$	$C_{14}H_{18}BNO_2$
Sum formula	$C_{14}H_{18}BNO_2$	$C_{14}H_{18}BNO_2$
M_r	243.10	243.10
D_x,g cm^{-3}	1.233	1.233
Z	8	8
Mu (mm^{-1})	0.080	0.080
F000	1040.0	1040.0
F000'	1040.44	
h,k,l_{max}	25,11,17	25,11,17
N_{ref}	5152	5148
T_{min},T_{max}	0.969,0.990	0.971,1.000
T_{min}'	0.969	

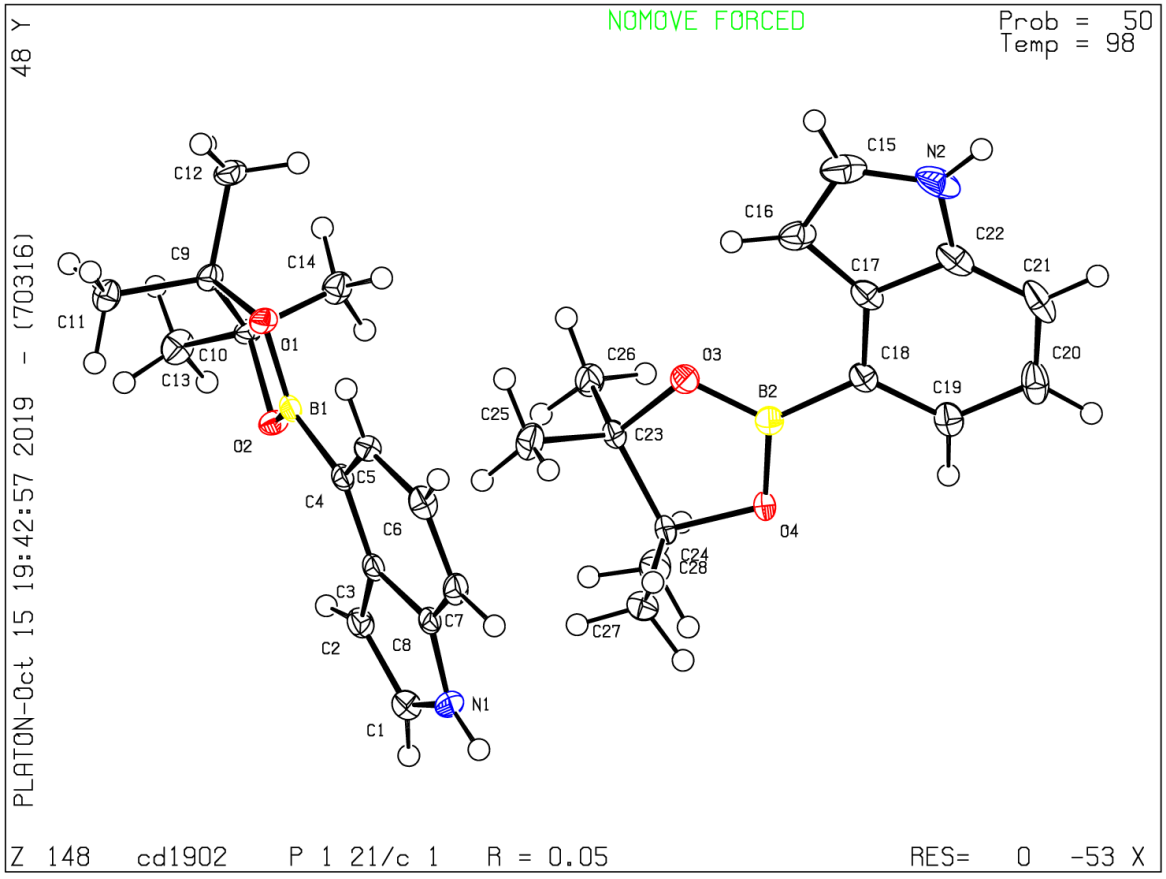
Correction method= # Reported T Limits: T_{min}=0.971 T_{max}=1.000

AbsCorr = MULTI-SCAN

Data completeness= 0.999 Theta(max)= 25.998

R(reflections)= 0.0488(5080) wR2(reflections)= 0.1049(5148)

S = 1.069 N_{par}= 339



Indolin-1-yl(4-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)phenyl)methanone (45-Bpin)

CCDC 1946412

Bond precision: C–C = 0.0021 Å Wavelength = 0.71073

Cell: a = 7.9153(2) b = 9.4724(2) c = 12.8773(2)

α = 100.926(2) β = 101.026(2) γ = 94.341(2)

Temperature: 98 K

	Calculated	Reported
Volume	924.20(4)	924.20(3)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	$C_{21}H_{24}BNO_3$	$C_{21}H_{24}BNO_3$
Sum formula	$C_{21}H_{24}BNO_3$	$C_{21}H_{24}BNO_3$
M_r	349.22	349.22
D_x,g cm^{-3}	1.255	1.255
Z	2	2
Mu (mm^{-1})	0.082	0.082
F000	372.0	372.0
F000'	372.16	
h,k,l_{max}	9,11,15	9,11,15
N_{ref}	3451	3446
T_{min},T_{max}	0.973,0.986	0.991,1.000
T_{min}'	0.973	

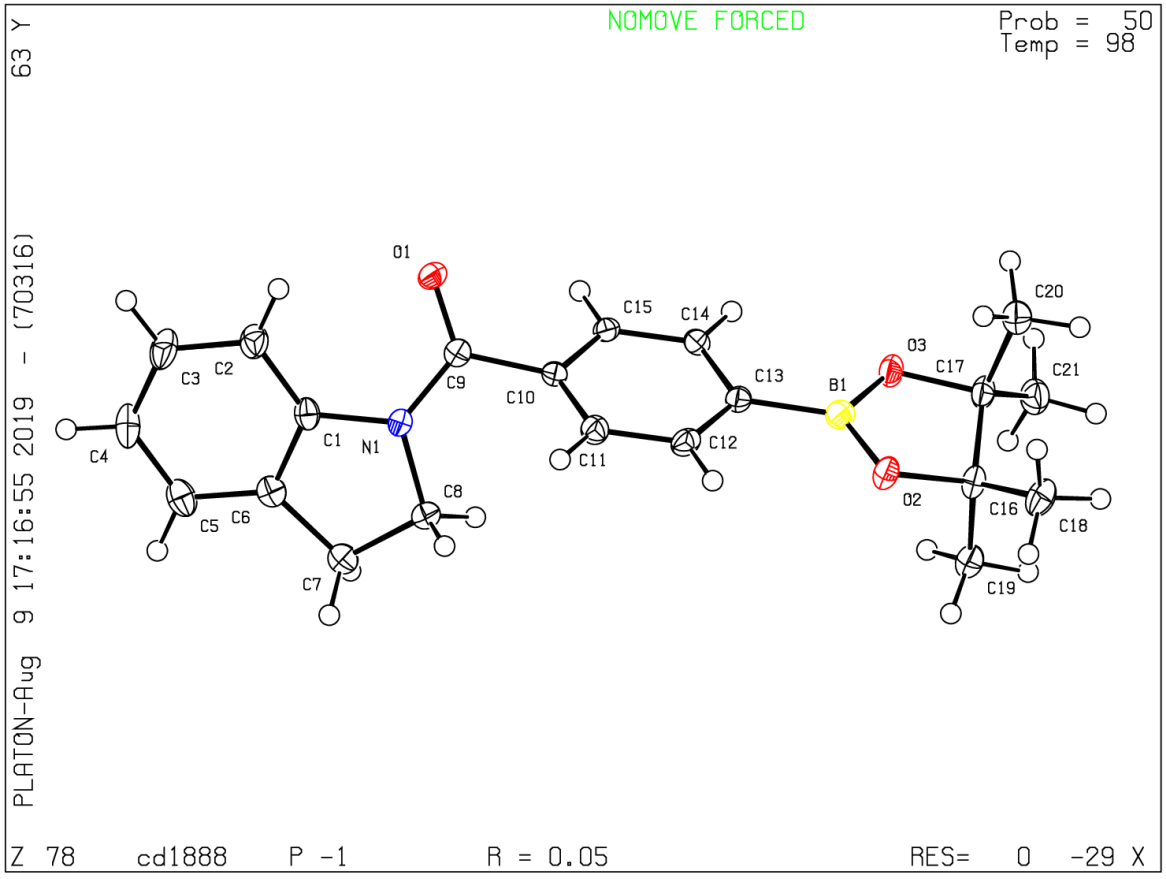
Correction method = # Reported T Limits: T_{min} = 0.991 T_{max} = 1.000

AbsCorr = MULTI-SCAN

Data completeness = 0.999 Theta(max) = 25.500

R(reflections) = 0.0458(3414) wR2(reflections) = 0.1055(3446)

S = 1.055 N_{par} = 239



3-Ethyl-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)piperidine-2,6-dione

(47)

CCDC 1946413

Bond precision: C–C = 0.0053 Å Wavelength = 0.71073

Cell: a = 27.1253(12) b = 6.6649(2) c = 12.1310(6)

$\alpha = 90$ $\beta = 119.012(6)$ $\gamma = 90$

Temperature: 98 K

	Calculated	Reported
Volume	1917.93(18)	1917.93(17)
Space group	C 2	C 1 2 1
Hall group	C 2y	C 2y
Moiety formula	$C_{19}H_{26}BNO_4$	$C_{19}H_{26}BNO_4$
Sum formula	$C_{19}H_{26}BNO_4$	$C_{19}H_{26}BNO_4$
M_r	343.22	343.22
D_x,g cm^{-3}	1.189	1.189
Z	4	4
Mu (mm^{-1})	0.082	0.082
F000	736.0	736.0
F000'	736.35	
h,k,l_{max}	32,8,14	32,8,14
N_{ref}	3552 [1940]	3535
T_{min},T_{max}	0.978,0.986	0.876,1.000
T_{min}'	0.973	

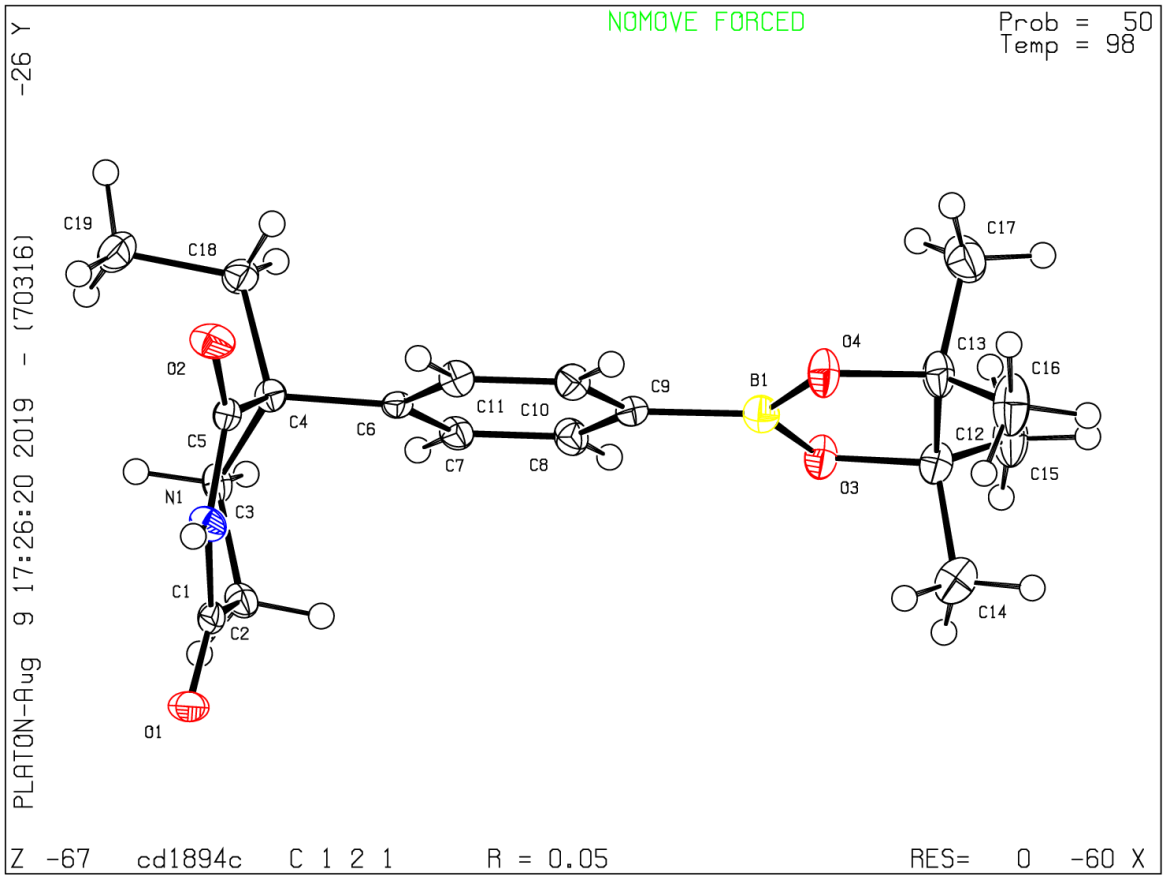
Correction method = # Reported T Limits: T_{min} = 0.876 T_{max} = 1.000

AbsCorr = MULTI-SCAN

Data completeness = 1.82/1.00 Theta(max) = 25.492

R(reflections) = 0.0460(3502) wR2(reflections) = 0.1275(3535)

S = 1.076 N_{par} = 234



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2-(2-Fluoro-4-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (53)

CCDC 1959499

Bond precision: C–C = 0.0020 Å Wavelength = 0.71073

Cell: a = 13.7679(4) b = 7.5766(2) c = 12.4291(3)

α = 90 β = 92.295(2) γ = 90

Temperature: 98 K

	Calculated	Reported
Volume	1295.49(6)	1295.49(6)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	$C_{13}H_{18}BFO_2$	$C_{13}H_{18}BFO_2$
Sum formula	$C_{13}H_{18}BFO_2$	$C_{13}H_{18}BFO_2$
M_r	236.08	236.08
D_x,g cm^{-3}	1.210	1.210
Z	4	4
Mu (mm^{-1})	0.088	0.088
F000	504.0	504.0
F000'	504.27	
h,k,l_{max}	16,9,15	16,9,15
N_{ref}	2544	2544
T_{min},T_{max}	0.982,0.997	0.984,1.000
T_{min}'	0.959	

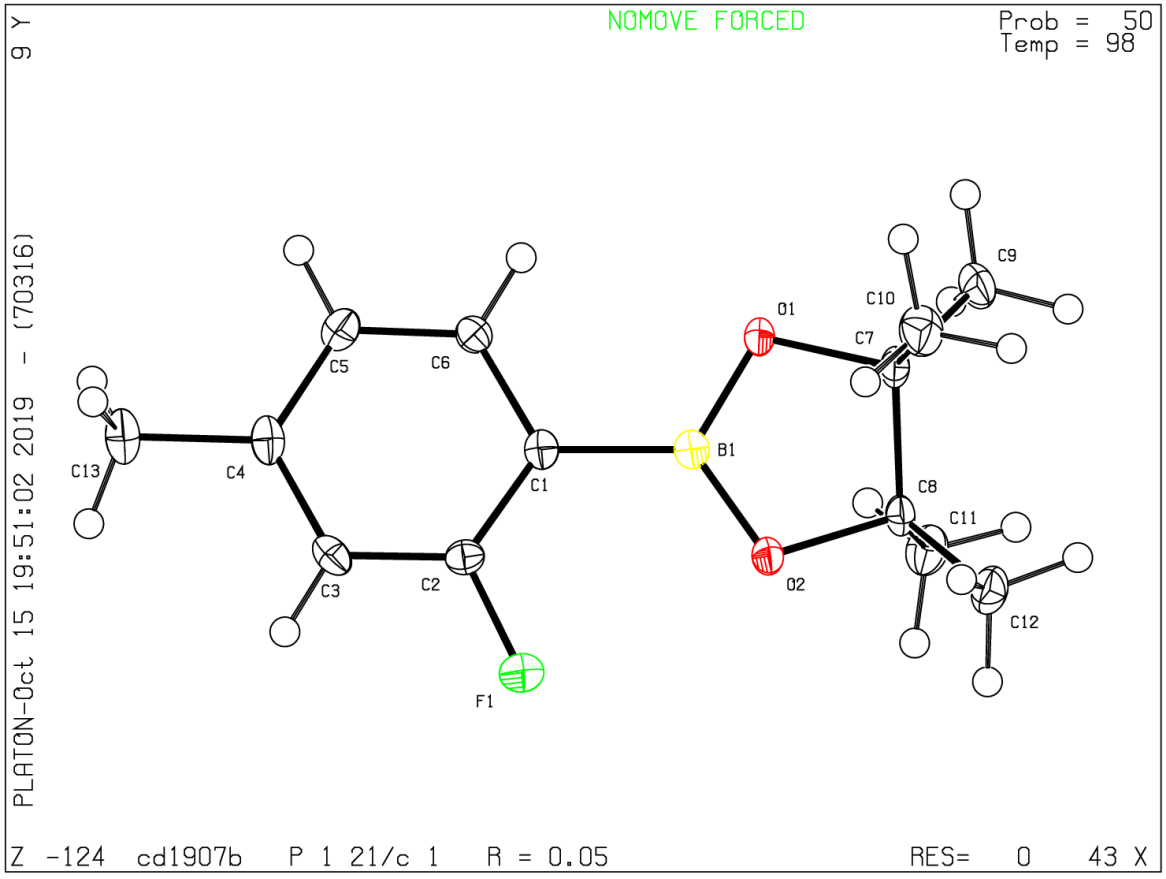
Correction method= # Reported T Limits: T_{min}=0.984 T_{max}=1.000

AbsCorr = MULTI-SCAN

Data completeness= 1.000 Theta(max)= 25.999

R(reflections)= 0.0493(2515) wR2(reflections)= 0.1179(2544)

S = 1.071 N_{par}= 159



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4,4,5,5-Tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (54)

CCDC 1946414

Bond precision: C–C = 0.0057 Å Wavelength = 0.71073

Cell: a = 8.4082(5) b = 8.7515(5) c = 10.3759(3)

α = 107.497(4) β = 105.684(4) γ = 97.298(5)

Temperature: 98 K

	Calculated	Reported
Volume	682.79(7)	682.79(6)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	$C_{13}H_{16}BF_3O_2$	$C_{13}H_{16}BF_3O_2$
Sum formula	$C_{13}H_{16}BF_3O_2$	$C_{13}H_{16}BF_3O_2$
M_r	272.07	272.07
D_x,g cm^{-3}	1.323	1.323
Z	2	2
Mu (mm^{-1})	0.113	0.113
F000	284.0	284.0
F000'	284.20	
h,k,l_{max}	10,10,12	10,10,12
N_{ref}	2424	4483
T_{min},T_{max}	0.980,0.989	0.981,1.000
T_{min}'	0.972	

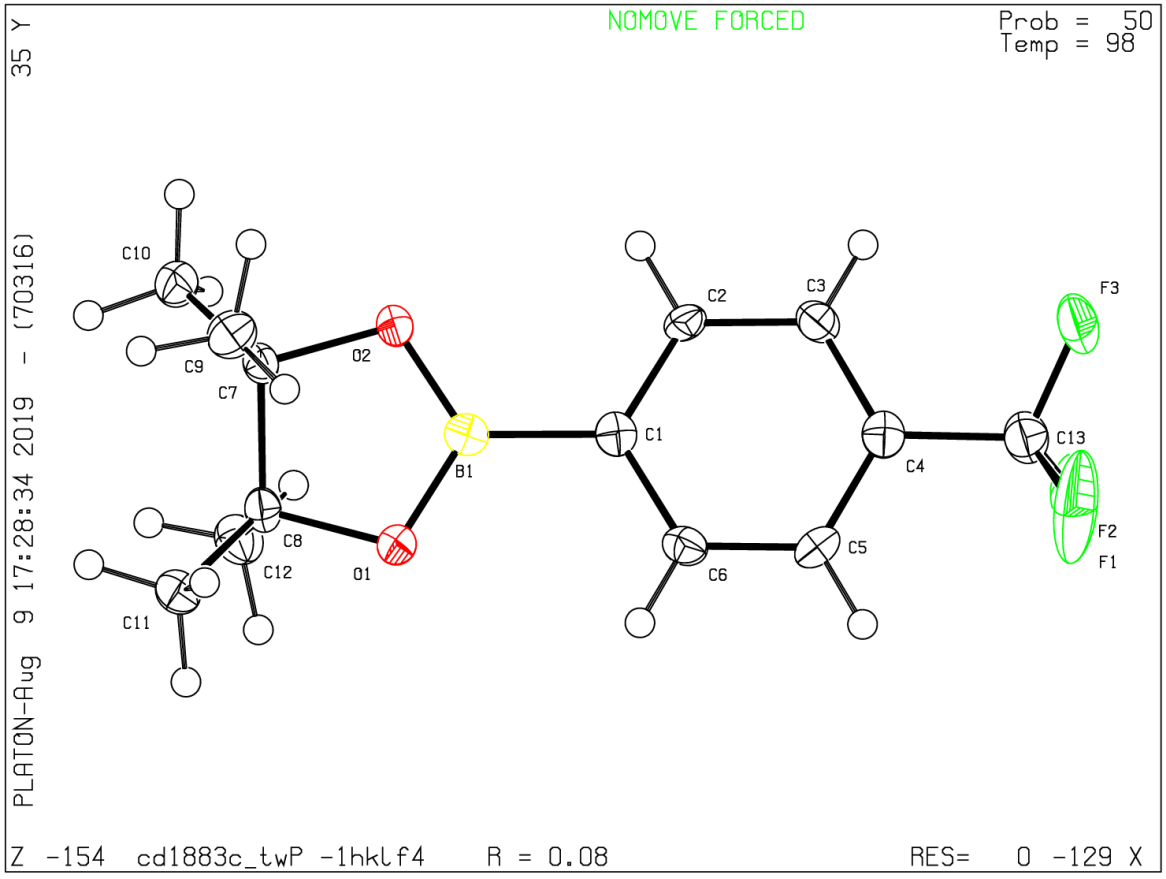
Correction method = # Reported T Limits: T_{min} = 0.981 T_{max} = 1.000

AbsCorr = MULTI-SCAN

Data completeness = 1.849 Theta(max) = 25.049

R(reflections) = 0.0758(3779) wR2(reflections) = 0.1491(4483)

S = 1.091 N_{par} = 176



2-(3-Fluoro-4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (56)

CCDC 1946415

Bond precision: C–C = 0.0018 Å Wavelength = 0.71073

Cell: a = 6.7381(2) b = 12.3279(4) c = 15.8619(5)

α = 90 β = 96.910(3) γ = 90

Temperature: 98 K

	Calculated	Reported
Volume	1308.02(7)	1308.02(7)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	$C_{13}H_{18}BFO_3$	$C_{13}H_{18}BFO_3$
Sum formula	$C_{13}H_{18}BFO_3$	$C_{13}H_{18}BFO_3$
M_r	252.08	252.08
D_x,g cm^{-3}	1.280	1.280
Z	4	4
Mu (mm^{-1})	0.097	0.097
F000	536.0	536.0
F000'	536.31	
h,k,l_{max}	8,15,19	8,15,19
N_{ref}	2584	2583
T_{min},T_{max}	0.980,0.995	0.947,1.000
T_{min}'	0.968	

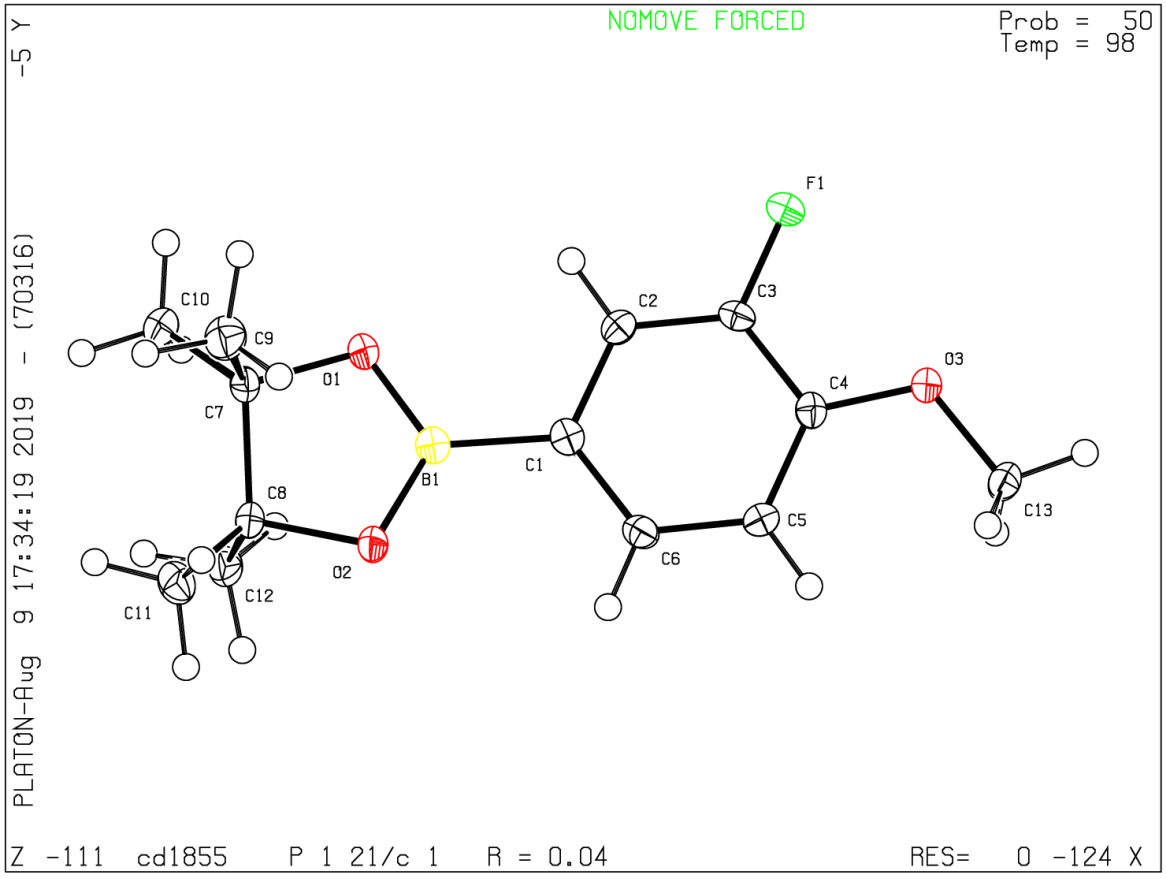
Correction method = # Reported T Limits: T_{min} = 0.947 T_{max} = 1.000

AbsCorr = MULTI-SCAN

Data completeness = 1.000 Theta(max) = 26.000

R(reflections) = 0.0407(2568) wR2(reflections) = 0.0953(2583)

S = 1.072 N_{par} = 168



2-(3,4-Dimethoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (59)

CCDC 1946416

Bond precision: C—C = 0.0020 Å Wavelength = 0.71073

Cell: a = 17.8482(4) b = 7.0235(2) c = 22.7583(6)

α = 90 β = 90 γ = 90

Temperature: 98 K

	Calculated	Reported
Volume	2852.91(13)	2852.91(13)
Space group	P b c a	P b c a
Hall group	-P 2ac 2ab	-P 2ac 2ab
Moiety formula	$C_{14}H_{21}BO_4$	$C_{14}H_{21}BO_4$
Sum formula	$C_{14}H_{21}BO_4$	$C_{14}H_{21}BO_4$
M_r	264.12	264.12
D_x,g cm^{-3}	1.230	1.230
Z	8	8
Mu (mm^{-1})	0.087	0.087
F000	1136.0	1136.0
F000'	1136.59	
h,k,l_{max}	22,8,28	22,8,28
N_{ref}	2804	2802
T_{min},T_{max}	0.962,0.994	0.950,1.000
T_{min}'	0.960	

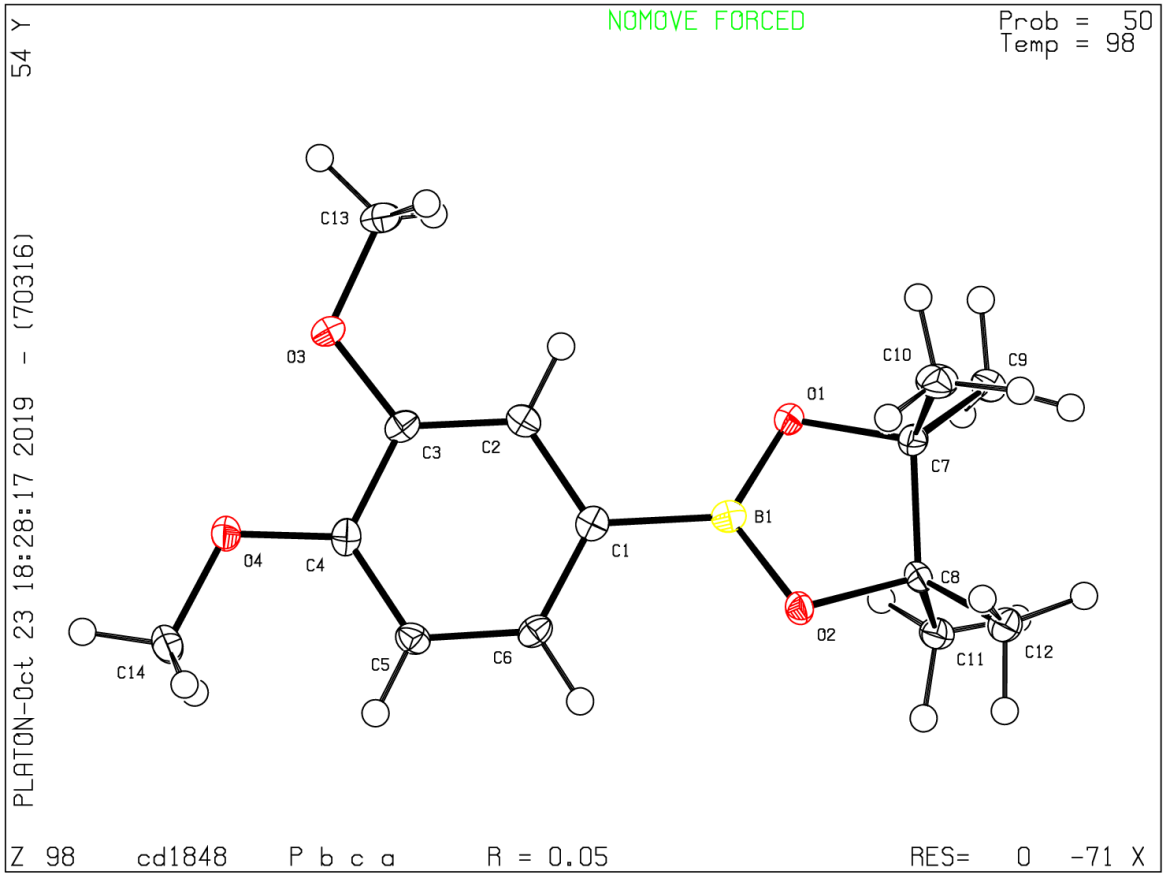
Correction method= # Reported T Limits: T_{min} = 0.950 T_{max} = 1.000

AbsCorr = MULTI-SCAN

Data completeness = 0.999 Theta(max) = 25.992

R(reflections) = 0.0476(2765) wR2(reflections) = 0.1072(2802)

S = 1.070 Npar= 178



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4,4,5,5-Tetramethyl-2-(4-(methylthio)phenyl)-1,3,2-dioxaborolane (60)

CCDC 1946417

Bond precision: C–C = 0.0025 Å Wavelength = 0.71073

Cell: a = 9.4792(2) b = 11.0501(2) c = 13.2369(3)

α = 90 β = 90 γ = 90

Temperature: 98 K

	Calculated	Reported
Volume	1386.51(5)	1386.51(5)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	$C_{13}H_{19}BO_2S$	$C_{13}H_{19}BO_2S$
Sum formula	$C_{13}H_{19}BO_2S$	$C_{13}H_{19}BO_2S$
M_r	250.15	250.15
D_x,g cm^{-3}	1.198	1.198
Z	4	4
Mu (mm^{-1})	0.221	0.221
F000	536.0	536.0
F000'	536.70	
h,k,l_{max}	11,13,16	11,13,16
N_{ref}	2725 [1577]	2724
T_{min},T_{max}	0.941,0.972	0.963,1.000
T_{min}'	0.930	

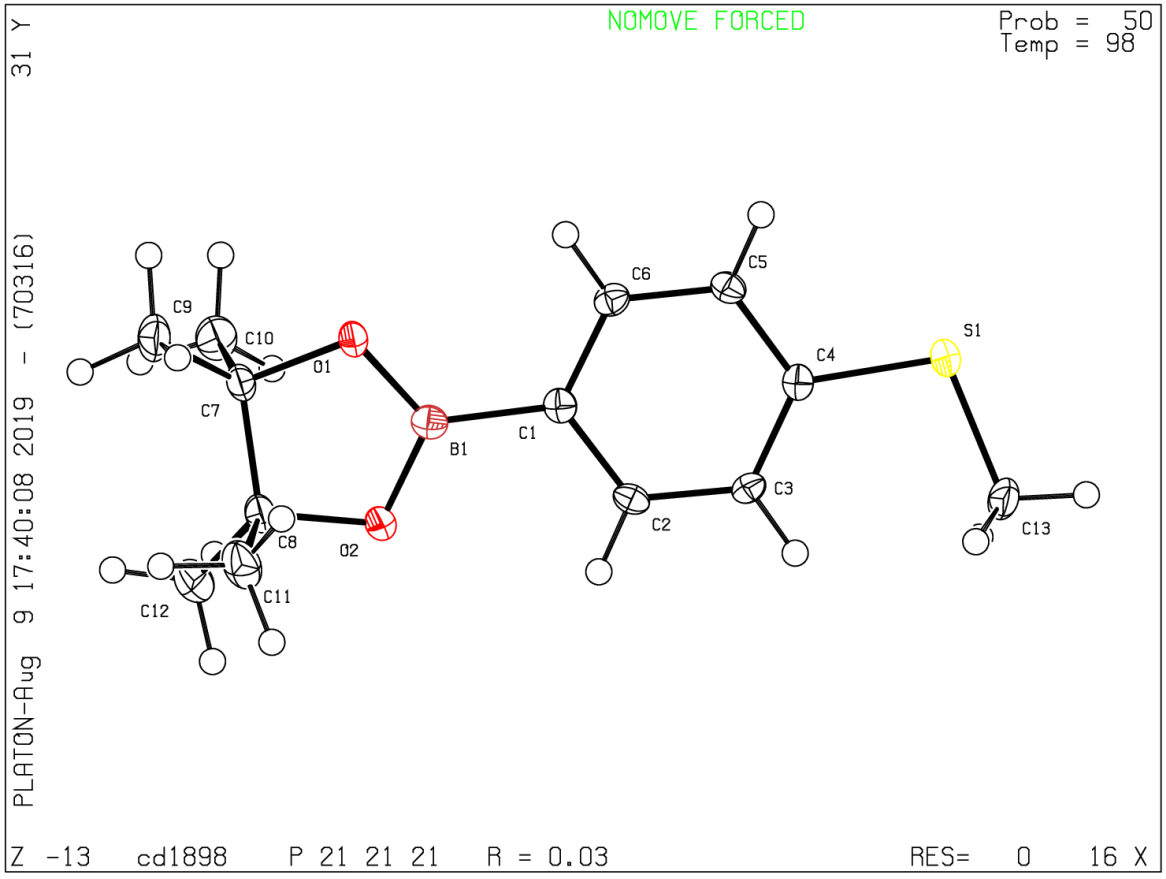
Correction method = # Reported T Limits: T_{min} = 0.963 T_{max} = 1.000

AbsCorr = MULTI-SCAN

Data completeness = 1.73/1.00 Theta(max) = 25.990

R(reflections) = 0.0252(2706) wR2(reflections) = 0.0667(2724)

S = 1.015 N_{par} = 159



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Methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (65)

CCDC 1946418

Bond precision: C–C = 0.0030 Å Wavelength = 0.71073

Cell: a = 10.2772(4) b = 6.1873(2) c = 11.9566(5)

α = 90 β = 113.206(4) γ = 90

Temperature: 98 K

	Calculated	Reported
Volume	698.79(5)	698.78(5)
Space group	P 21	P 1 21 1
Hall group	P 2yb	P 2yb
Moiety formula	$C_{14}H_{19}BO_4$	$C_{14}H_{19}BO_4$
Sum formula	$C_{14}H_{19}BO_4$	$C_{14}H_{19}BO_4$
M_r	262.10	262.10
D_x,g cm^{-3}	1.246	1.246
Z	2	2
Mu (mm^{-1})	0.089	0.089
F000	280.0	280.0
F000'	280.15	
h,k,l_{max}	12,7,14	12,7,14
N_{ref}	2746 [1507]	2744
T_{min},T_{max}	0.971,0.991	0.976,1.000
T_{min}'	0.971	

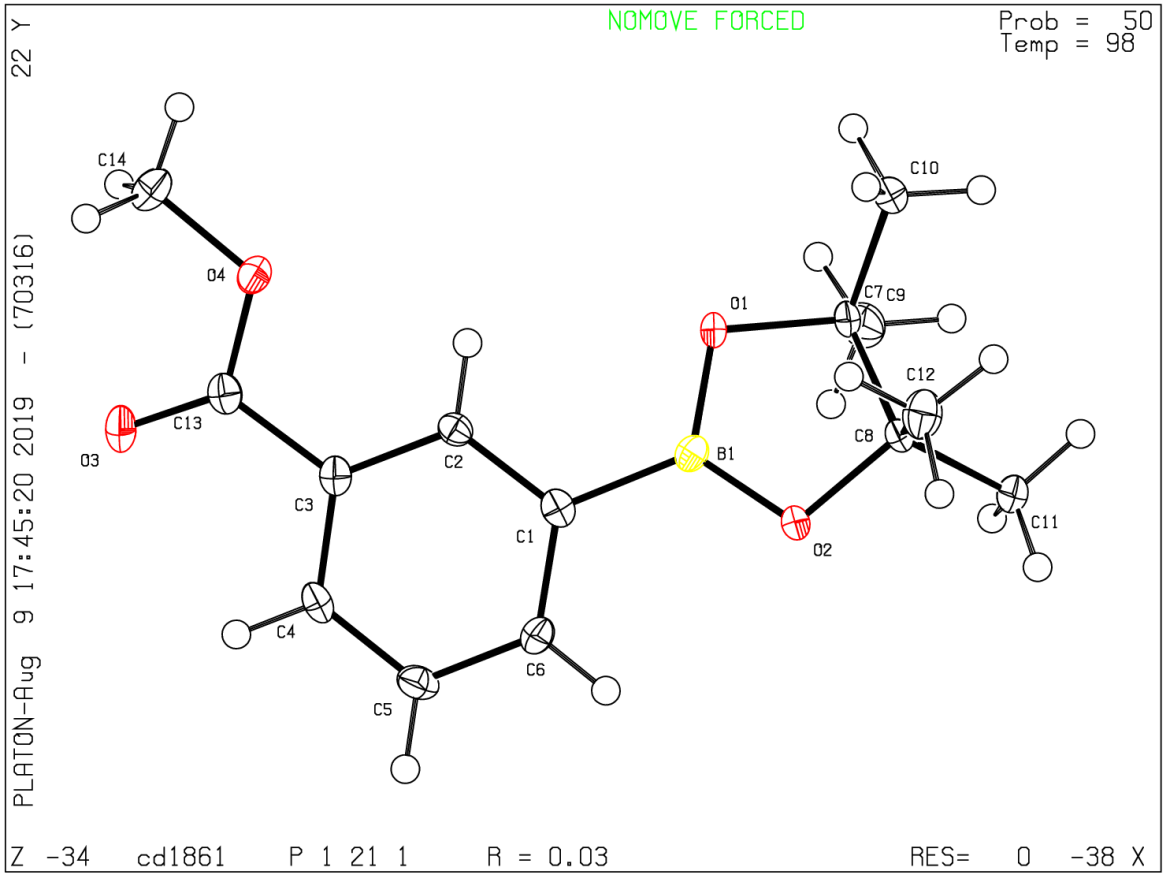
Correction method = # Reported T Limits: T_{min} = 0.976 T_{max} = 1.000

AbsCorr = MULTI-SCAN

Data completeness = 1.82/1.00 Theta(max) = 25.992

R(reflections) = 0.0286(2726) wR2(reflections) = 0.0664(2744)

S = 1.006 N_{par} = 177



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Dimethyl 4-(trifluoro-l4-boraneyl)phthalate, potassium salt (66)

CCDC 1959500

Bond precision: C–C = 0.0034 Å Wavelength = 0.71073

Cell: a = 8.0689(2) b = 19.1049(5) c = 8.6490(2)

α = 90 β = 90 γ = 90

Temperature: 100 K

	Calculated	Reported
Volume	1333.29(6)	1333.29(6)
Space group	P c a 21	P c a 21
Hall group	P 2c -2ac	P 2c -2ac
Moiety formula	$C_{10}H_{11}BF_3KO_5$	$C_{10}H_{11}BF_3KO_5$
Sum formula	$C_{10}H_{11}BF_3KO_5$	$C_{10}H_{11}BF_3KO_5$
M_r	318.10	318.10
D_x,g cm^{-3}	1.585	1.585
Z	4	4
Mu (mm^{-1})	0.449	0.449
F000	648.0	648.0
F000'	649.30	
h,k,l_{max}	9,23,10	9,23,10
N_{ref}	2486 [1338]	2404
T_{min},T_{max}	0.824,0.969	0.968,1.000
T_{min}'	0.824	

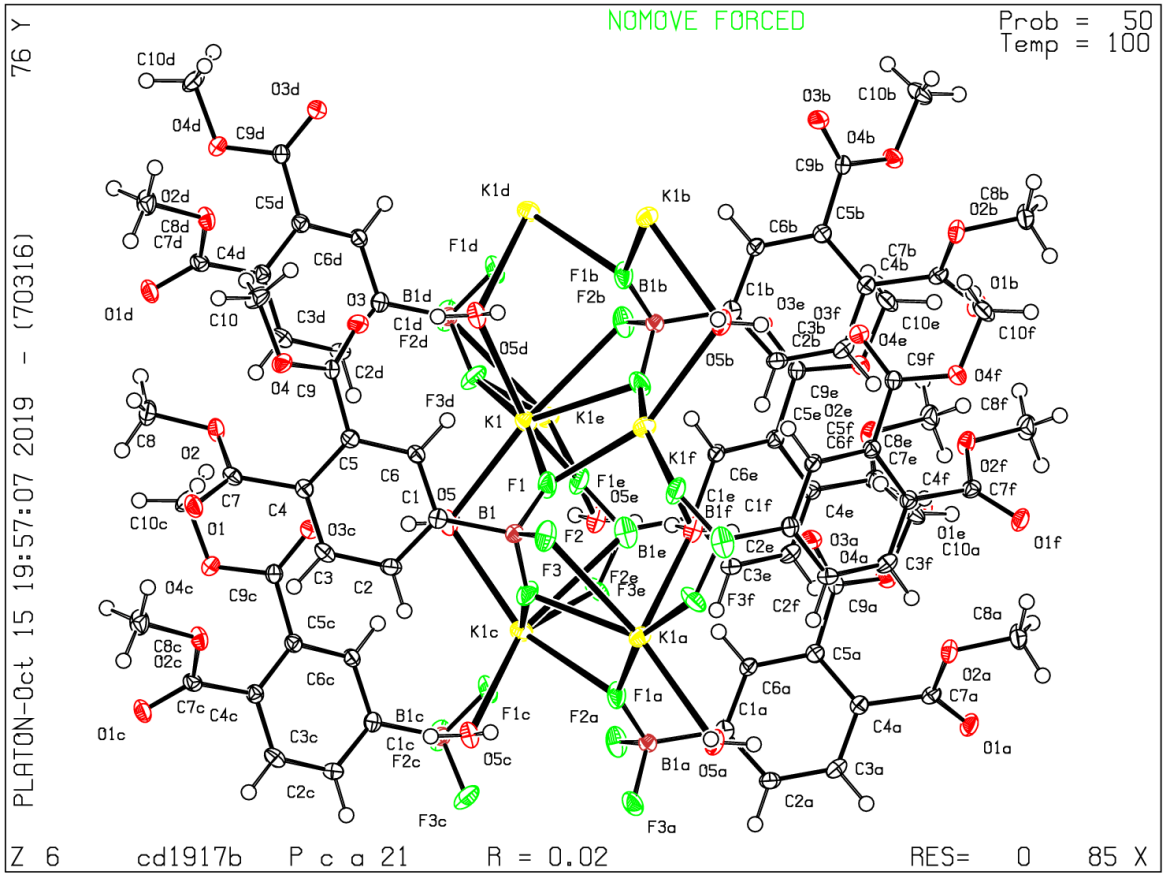
Correction method= # Reported T Limits: T_{min}=0.968 T_{max}=1.000

AbsCorr = MULTI-SCAN

Data completeness= 1.80/0.97 Theta(max)= 25.500

R(reflections)= 0.0221(2393) wR2(reflections)= 0.0593(2404)

S = 1.089 N_{par}= 191



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2-(6-Methoxynaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (73)

CCDC 1959501

Bond precision: C–C = 0.0031 Å Wavelength = 0.71073

Cell: a = 10.5926(2) b = 21.6904(3) c = 14.3419(2)

α = 90 β = 107.969(2) γ = 90

Temperature: 98 K

	Calculated	Reported
Volume	3134.44(9)	3134.44(9)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	$C_{17}H_{21}BO_3$	$C_{17}H_{21}BO_3$
Sum formula	$C_{17}H_{21}BO_3$	$C_{17}H_{21}BO_3$
M_r	284.15	284.15
D_x,g cm^{-3}	1.204	1.204
Z	8	8
Mu (mm^{-1})	0.080	0.080
F000	1216.0	1216.0
F000'	1216.57	
h,k,l_{max}	12,25,17	12,25,17
N_{ref}	5549	5545
T_{min},T_{max}	0.972,0.986	0.991,1.000
T_{min}'	0.969	

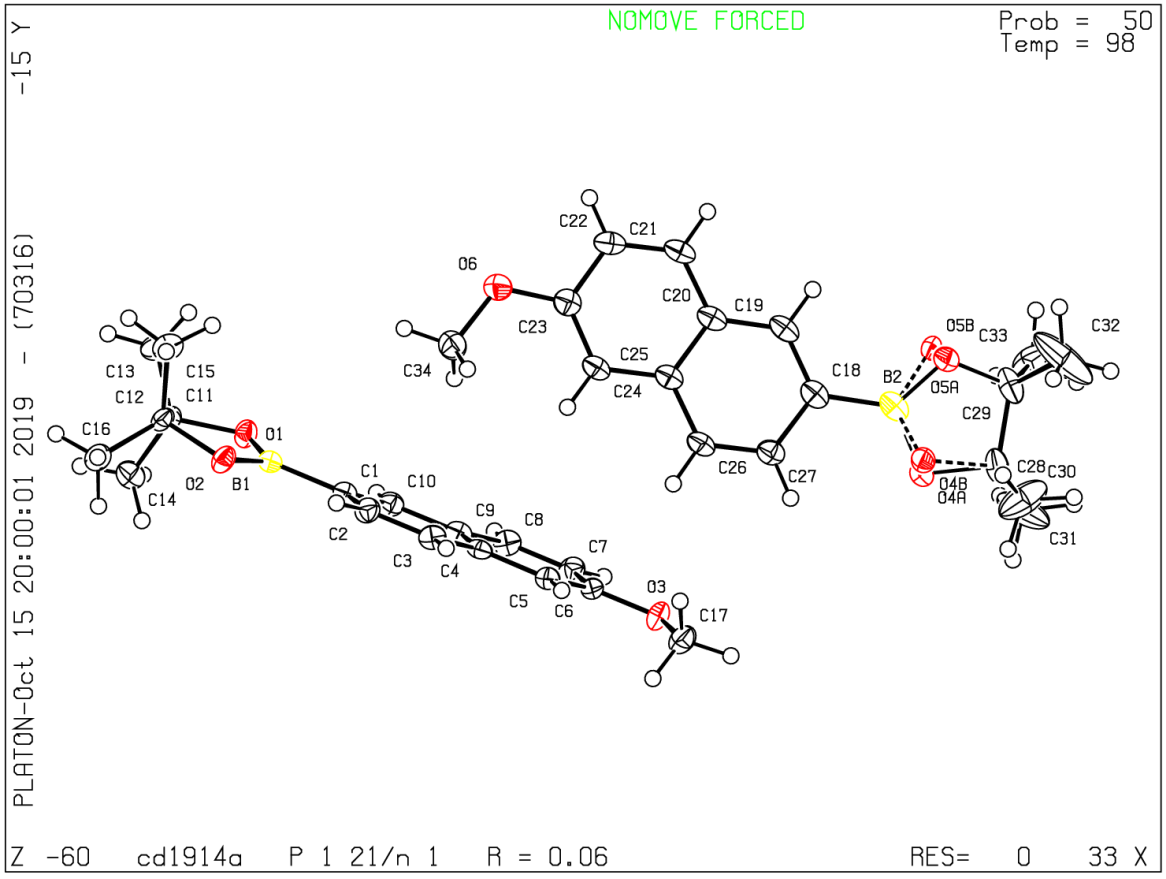
Correction method= # Reported T Limits: T_{min}=0.991 T_{max}=1.000

AbsCorr = MULTI-SCAN

Data completeness= 0.999 Theta(max)= 25.050

R(reflections)= 0.0588(5250) wR2(reflections)= 0.1243(5545)

S = 1.069 N_{par}= 407



4,4,5,5-Tetramethyl-2-(phenanthren-9-yl)-1,3,2-dioxaborolane (74)

CCDC 1959505

Bond precision: C–C = 0.0056 Å Wavelength = 0.71073

Cell: a = 10.1479(2) b = 10.5387(3) c = 31.4024(7)

α = 90 β = 90 γ = 90

Temperature: 100 K

	Calculated	Reported
Volume	3358.35(14)	3358.35(14)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	$C_{20}H_{21}BO_2$	$C_{20}H_{21}BO_2$
Sum formula	$C_{20}H_{21}BO_2$	$C_{20}H_{21}BO_2$
M_r	304.18	304.18
D_x,g cm^{-3}	1.203	1.203
Z	8	8
Mu (mm^{-1})	0.075	0.075
F000	1296.0	1296.0
F000'	1296.55	
h,k,l_{max}	12,12,38	12,13,38
N_{ref}	6584 [3725]	6582
T_{min},T_{max}	0.976,0.980	0.359,1.000
T_{min}'	0.976	

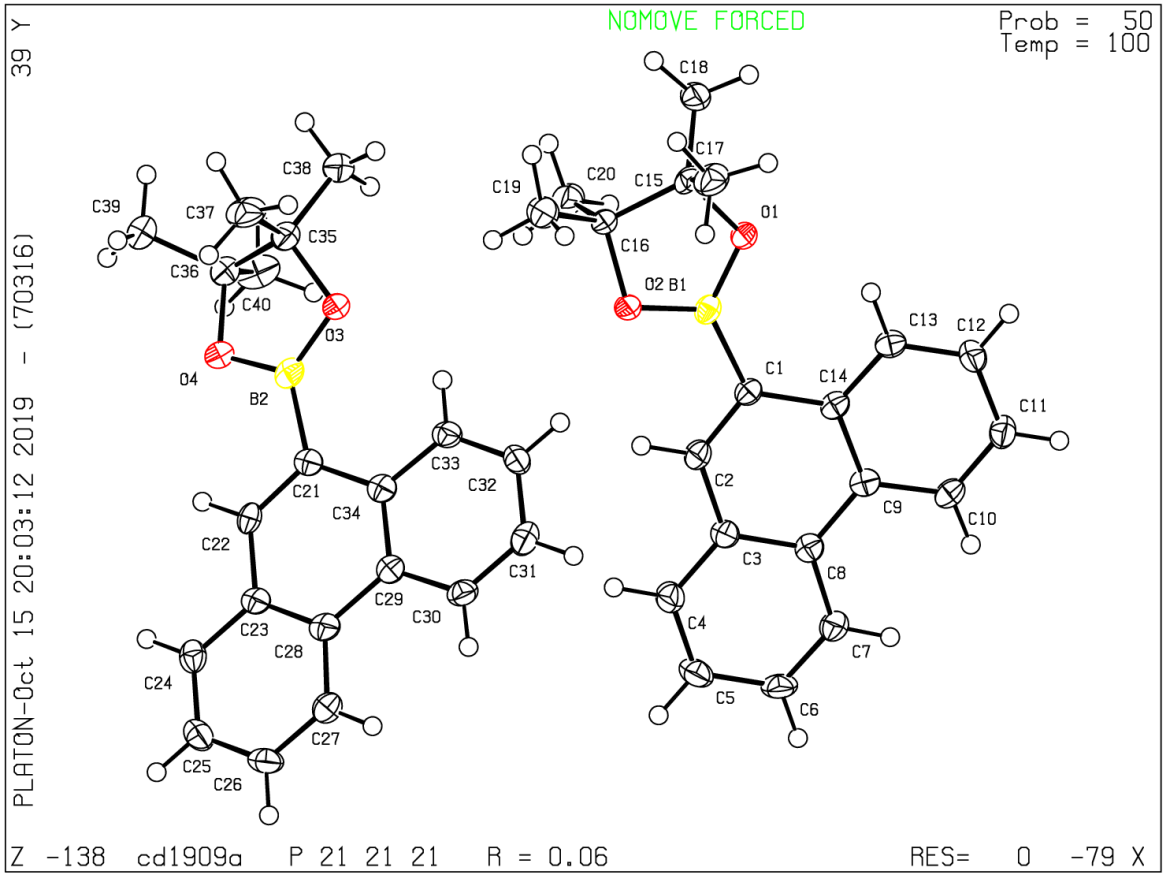
Correction method= # Reported T Limits: T_{min}=0.359 T_{max}=1.000

AbsCorr = MULTI-SCAN

Data completeness= 1.77/1.00 Theta(max)= 25.995

R(reflections)= 0.0644(6331) wR2(reflections)= 0.1366(6582)

S = 1.086 N_{par}= 423



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2-Methyl-4-(trifluoro-λ⁴-boraneyl)pyridine, potassium salt (76-H)

CCDC 1946419

Bond precision: C–C = 0.0017 Å Wavelength = 0.71073

Cell: a = 7.5748(2) b = 7.5235(2) c = 13.5891(4)

α = 90 β = 91.676(3) γ = 90

Temperature: 98 K

	Calculated	Reported
Volume	774.10(4)	774.10(4)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	$C_6H_7BF_3N$, H_2O	$C_6H_7BF_3N$, H_2O
Sum formula	$C_6H_9BF_3NO$	$C_6H_9BF_3NO$
M_r	178.95	178.95
D_x,g cm^{-3}	1.536	1.535
Z	4	4
Mu (mm^{-1})	0.149	0.149
F000	368.0	368.0
F000'	368.30	
h,k,l_{max}	9,9,17	9,9,17
N_{ref}	1605	1606
T_{min},T_{max}	0.970,0.985	0.937,1.000
T_{min}'	0.938	

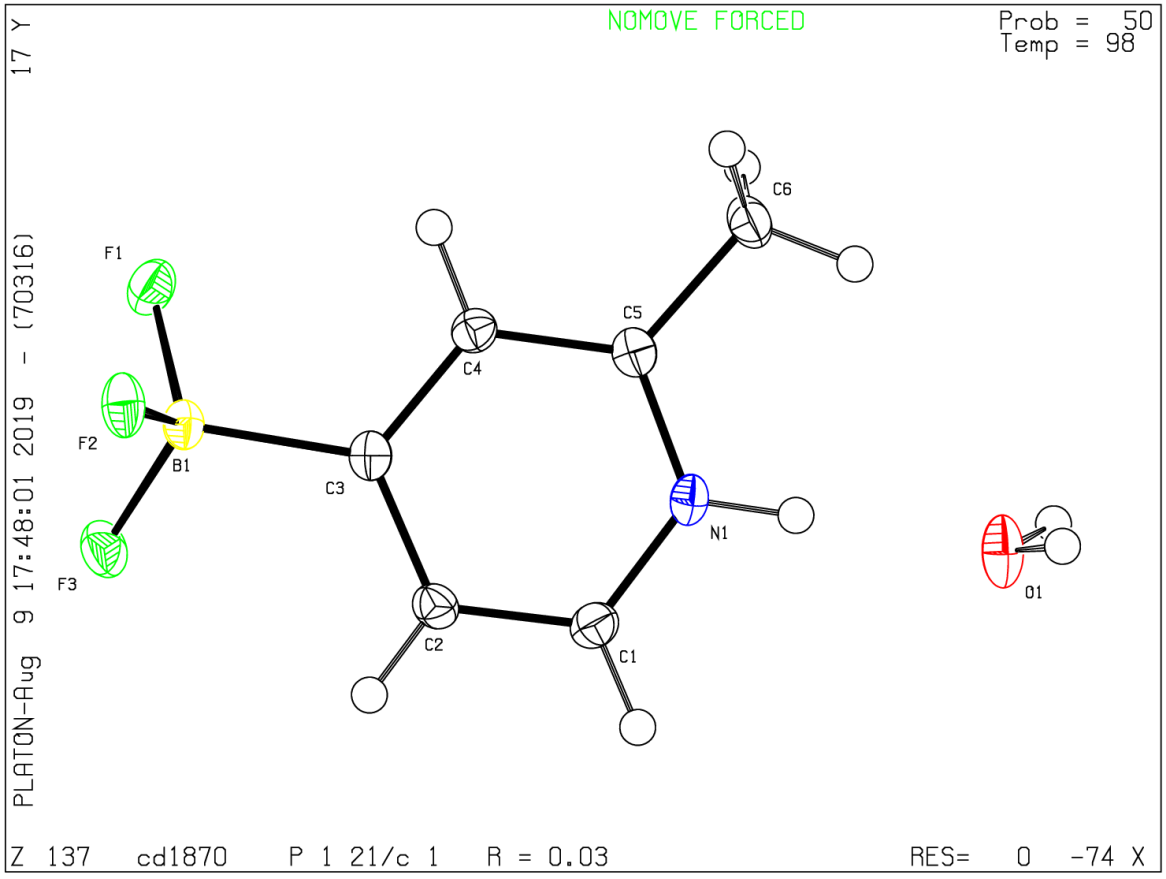
Correction method = # Reported T Limits: T_{min} = 0.937 T_{max} = 1.000

AbsCorr = MULTI-SCAN

Data completeness = 1.001 Theta(max) = 26.486

R(reflections) = 0.0343(1590) wR2(reflections) = 0.0866(1606)

S = 1.050 N_{par} = 119



3-Fluoro-5-(trifluoro-λ⁴-boraneyl)pyridine, potassium salt (78)

CCDC 1946420

Bond precision: C–C = 0.0027 Å Wavelength = 0.71073

Cell: a = 8.5562(3) b = 13.8694(6) c = 6.9835(3)

α = 90 β = 90 γ = 90

Temperature: 98 K

	Calculated	Reported
Volume	828.73(6)	828.73(6)
Space group	P b c m	P b c m
Hall group	-P 2c 2b	-P 2c 2b
Moiety formula	$C_5H_5BF_4KNO$	$0.25(C_{20}H_{20}B_4F_{16}K_4N_4O_4)$
Sum formula	$C_5H_5BF_4KNO$	$C_5H_5BF_4KNO$
M_r	221.01	221.01
D_x,g cm^{-3}	1.771	1.771
Z	4	4
Mu (mm^{-1})	0.664	0.664
F000	440.0	440.0
F000'	441.16	
h,k,l_{max}	10,16,8	10,16,8
N_{ref}	843	843
T_{min},T_{max}	0.833,0.893	0.941,1.000
T_{min}'	0.737	

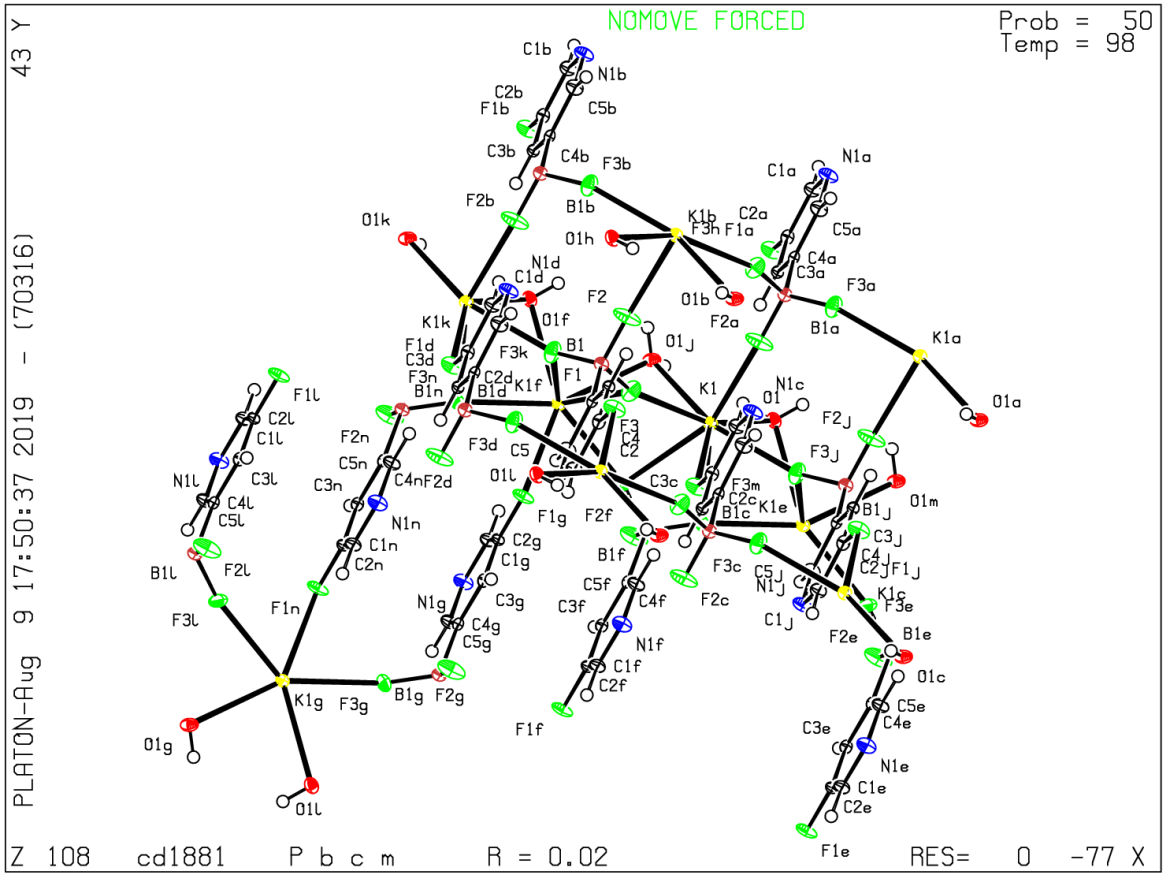
Correction method = # Reported T Limits: T_{min} = 0.941 T_{max} = 1.000

AbsCorr = MULTI-SCAN

Data completeness = 1.000 Theta(max) = 25.499

R(reflections) = 0.0229(843) wR2(reflections) = 0.0634(843)

S = 1.031 N_{par} = 78



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(8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (110)

CCDC 1946421

Bond precision: C–C = 0.0045 Å Wavelength = 0.71073

Cell: a = 9.4219(3) b = 11.3625(3) c = 16.4678(4)

α = 104.315(2) β = 92.465(2) γ = 114.483(3)

Temperature: 98 K

	Calculated	Reported
Volume	1533.35(9)	1533.34(8)
Space group	P 1	P 1
Hall group	P 1	P 1
Moiety formula	$C_{31}H_{37}BO_5$, $CHCl_3$	$C_{31}H_{37}BO_5$, $CHCl_3$
Sum formula	$C_{32}H_{38}BCl_3O_5$	$C_{32}H_{38}BCl_3O_5$
M_r	619.78	619.78
D_x,g cm^{-3}	1.342	1.342
Z	2	2
Mu (mm^{-1})	0.338	0.338
F000	652.0	652.0
F000'	653.15	
h,k,l_{max}	11,14,20	11,14,20
N_{ref}	12052 [6026]	11851
T_{min},T_{max}	0.875,0.977	0.981,1.000
T_{min}'	0.865	

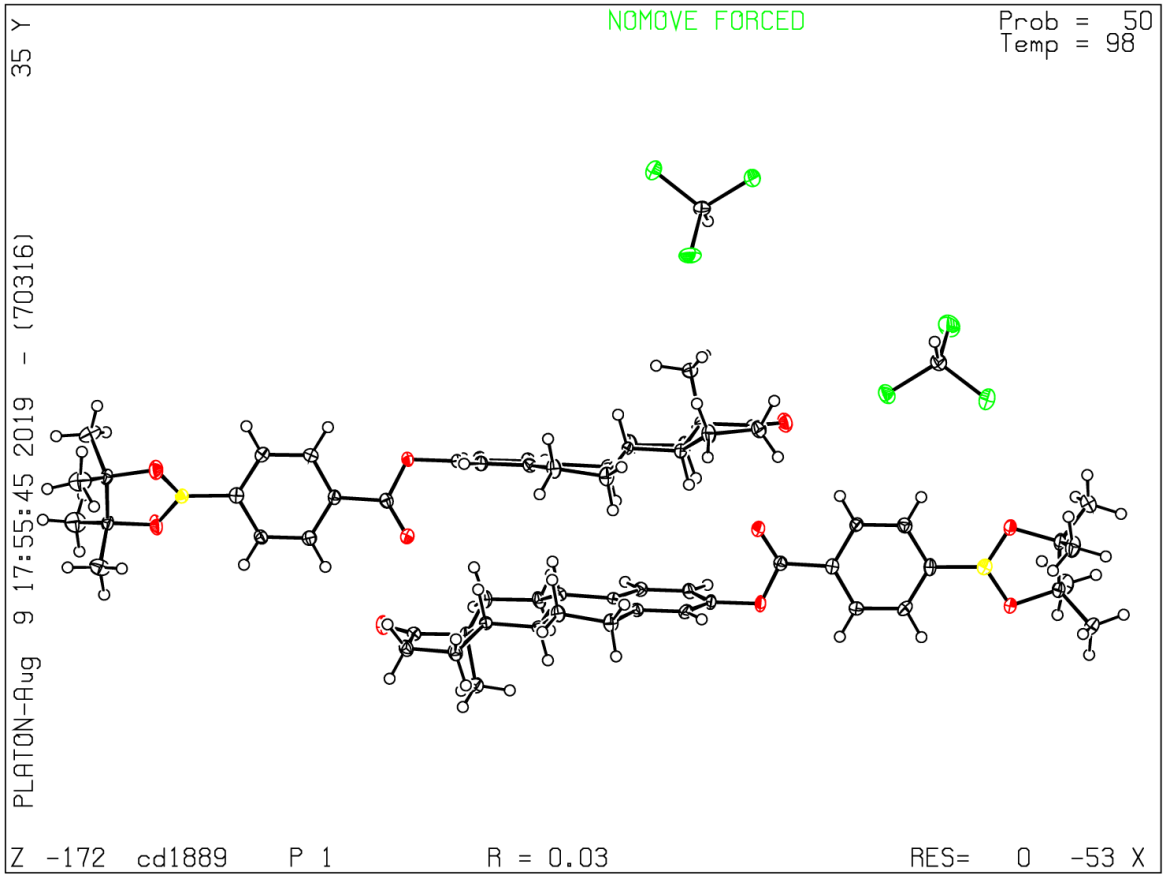
Correction method = # Reported T Limits: T_{min} = 0.981 T_{max} = 1.000

AbsCorr = MULTI-SCAN

Data completeness = 1.97/0.98 Theta(max) = 25.999

R(reflections) = 0.0342(11638) wR2(reflections) = 0.0861(11851)

S = 1.023 N_{par} = 749



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Bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methane (112)

CCDC 1959506

Bond precision: C–C = 0.0030 Å Wavelength = 0.71073

Cell: a = 17.2944(14) b = 6.5162(4) c = 11.3970(8)

α = 90 β = 106.818(8) γ = 90

Temperature: 100 K

	Calculated	Reported
Volume	1229.44(16)	1229.44(16)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	$C_{26}H_{36}B_2O_4$	$C_{26}H_{36}B_2O_4$
Sum formula	$C_{26}H_{36}B_2O_4$	$C_{26}H_{36}B_2O_4$
M_r	434.17	434.17
D_x,g cm^{-3}	1.173	1.173
Z	2	2
Mu (mm^{-1})	0.076	0.076
F000	468.0	468.0
F000'	468.21	
h,k,l_{max}	21,8,14	21,8,14
N_{ref}	2405	3644
T_{min},T_{max}	0.979,0.996	0.889,1.000
T_{min}'	0.977	

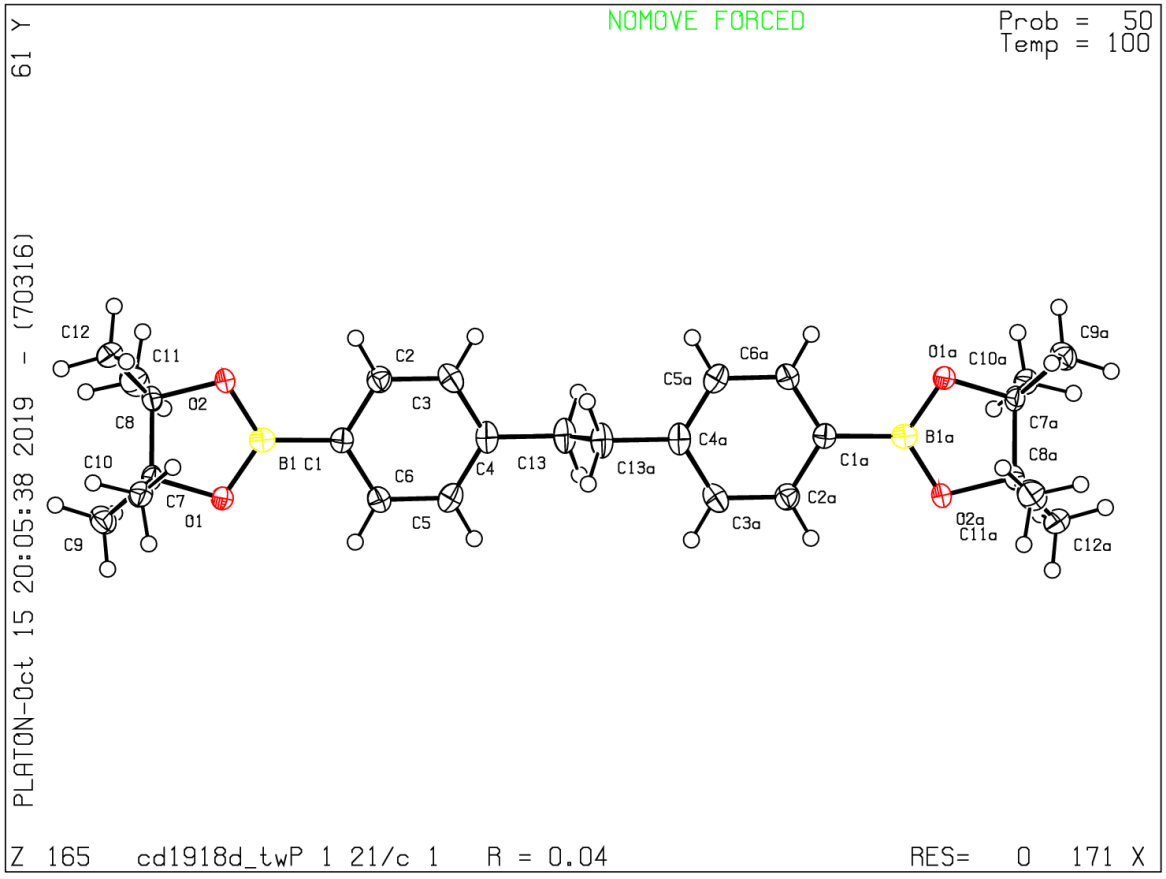
Correction method= # Reported T Limits: T_{min}=0.889 T_{max}=1.000

AbsCorr = MULTI-SCAN

Data completeness= 1.515 Theta(max)= 25.999

R(reflections)= 0.0411(2595) wR2(reflections)= 0.0757(3644)

S = 1.038 N_{par}= 149



Bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methane (113)

CCDC 1946422

Bond precision: C–C = 0.0030 Å Wavelength = 0.71073

Cell: a = 25.3806(6) b = 6.6166(1) c = 31.0990(8)

α = 90 β = 112.921(3) γ = 90

Temperature: 98 K

	Calculated	Reported
Volume	4810.2(2)	4810.2(2)
Space group	I 2/a	I 1 2/a 1
Hall group	-I 2ya	-I 2ya
Moiety formula	$C_{25}H_{34}B_2O_4$	$C_{25}H_{34}B_2O_4$
Sum formula	$C_{25}H_{34}B_2O_4$	$C_{25}H_{34}B_2O_4$
M_r	420.14	420.14
D_x,g cm^{-3}	1.160	1.160
Z	8	8
Mu (mm^{-1})	0.075	0.075
F000	1808.0	1808.0
F000'	1808.80	
h,k,l_{max}	30,7,37	30,7,37
N_{ref}	4253	4247
T_{min},T_{max}	0.976,0.987	0.993,1.000
T_{min}'	0.976	

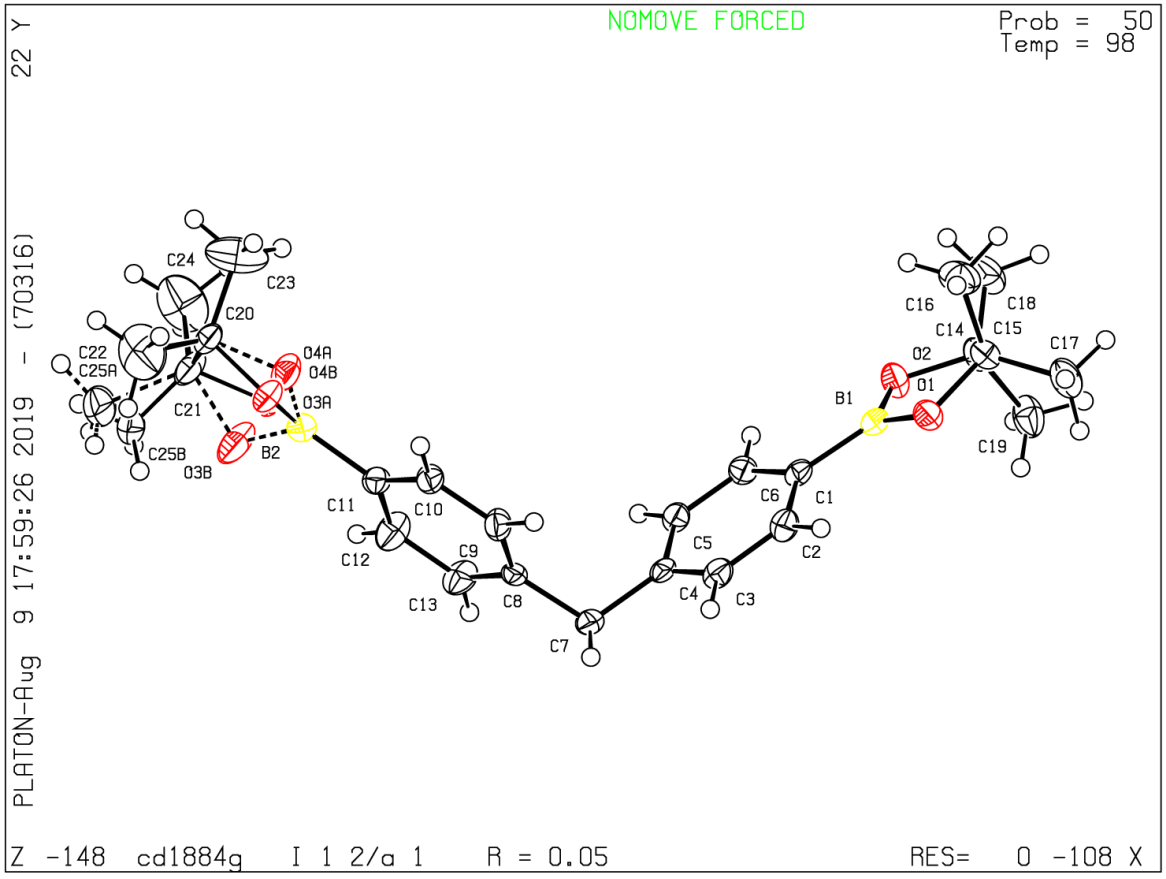
Correction method = # Reported T Limits: T_{min} = 0.993 T_{max} = 1.000

AbsCorr = MULTI-SCAN

Data completeness = 0.999 Theta(max) = 25.049

R(reflections) = 0.0547(4137) wR2(reflections) = 0.1200(4247)

S = 1.072 N_{par} = 316



Ethyl 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoate (114)

CCDC 1946423

Bond precision: C–C = 0.0018 Å Wavelength = 0.71073

Cell: a = 5.8375(2) b = 17.0381(4) c = 13.9958(4)

α = 90 β = 94.048(2) γ = 90

Temperature: 98 K

	Calculated	Reported
Volume	1388.55(7)	1388.55(7)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	$C_{14}H_{19}BO_4$	$C_{14}H_{19}BO_4$
Sum formula	$C_{14}H_{19}BO_4$	$C_{14}H_{19}BO_4$
M_r	262.10	262.10
D_x,g cm^{-3}	1.254	1.254
Z	4	4
Mu (mm^{-1})	0.089	0.089
F000	560.0	560.0
F000'	560.30	
h,k,l_{max}	7,21,17	7,21,17
N_{ref}	2731	2731
T_{min},T_{max}	0.984,0.991	0.958,1.000
T_{min}'	0.974	

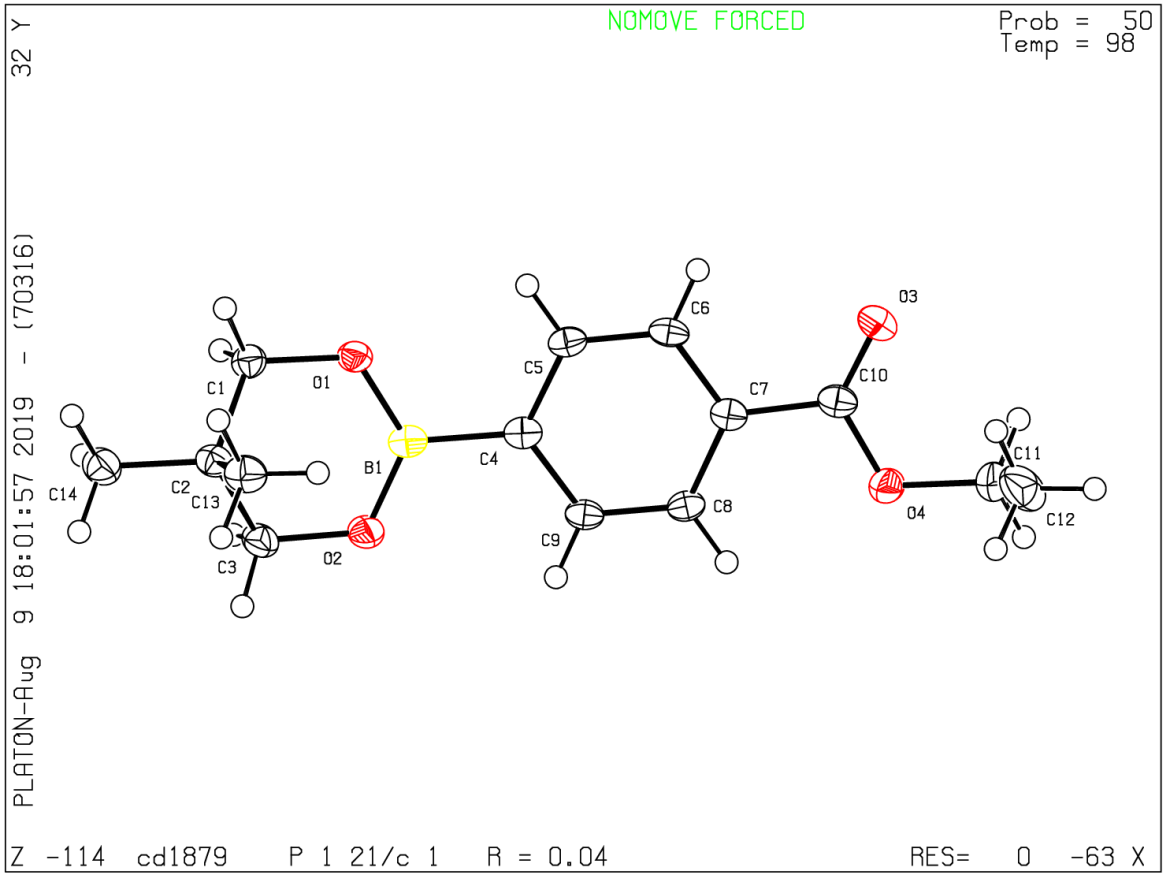
Correction method = # Reported T Limits: T_{min} = 0.958 T_{max} = 1.000

AbsCorr = MULTI-SCAN

Data completeness = 1.000 Theta(max) = 26.000

R(reflections) = 0.0427(2696) wR2(reflections) = 0.1055(2731)

S = 1.019 N_{par} = 175



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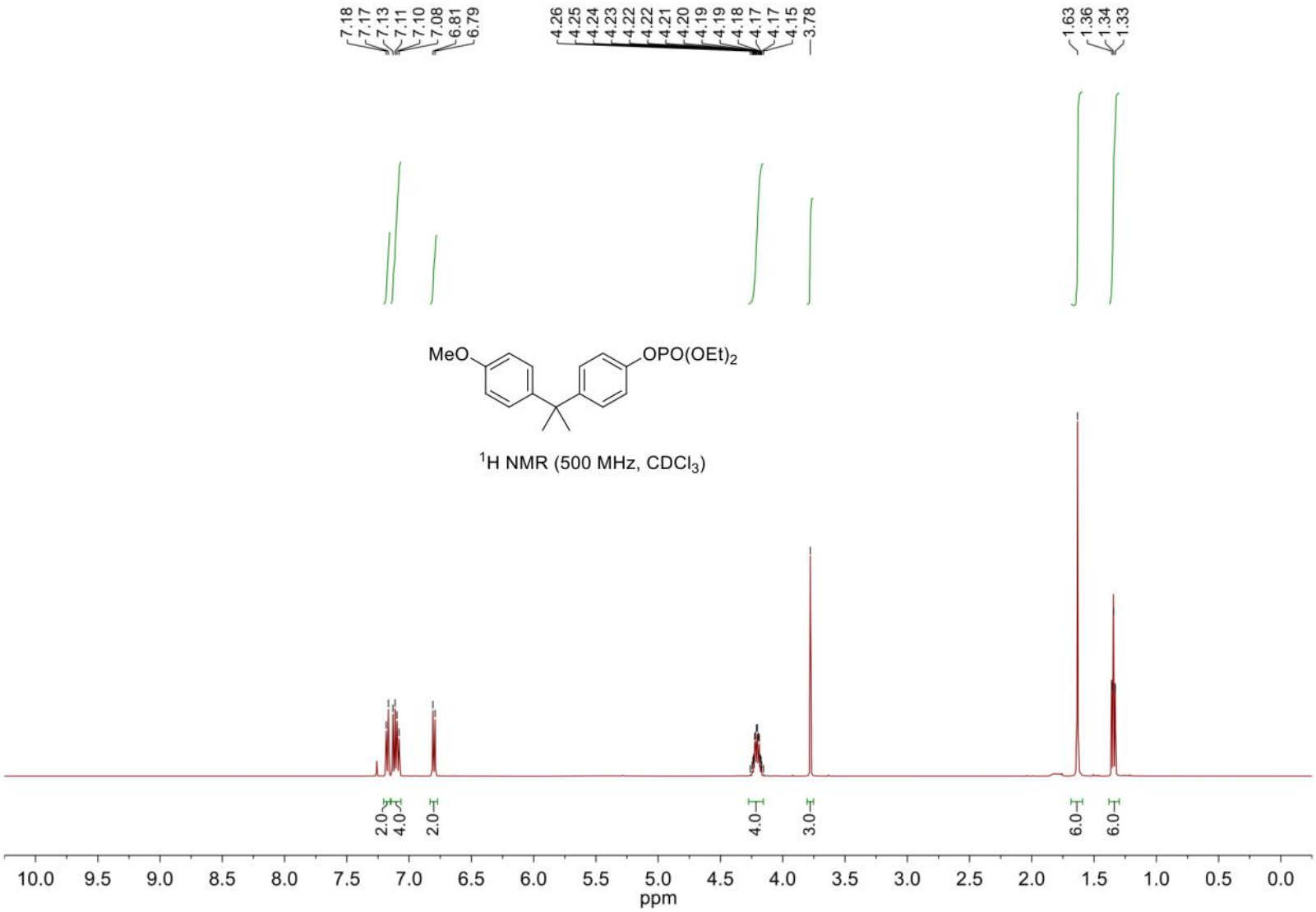
NMR Spectroscopic data

Diethyl (4-(2-(4-methoxyphenyl)propan-2-yl)phenyl) phosphate (S1)



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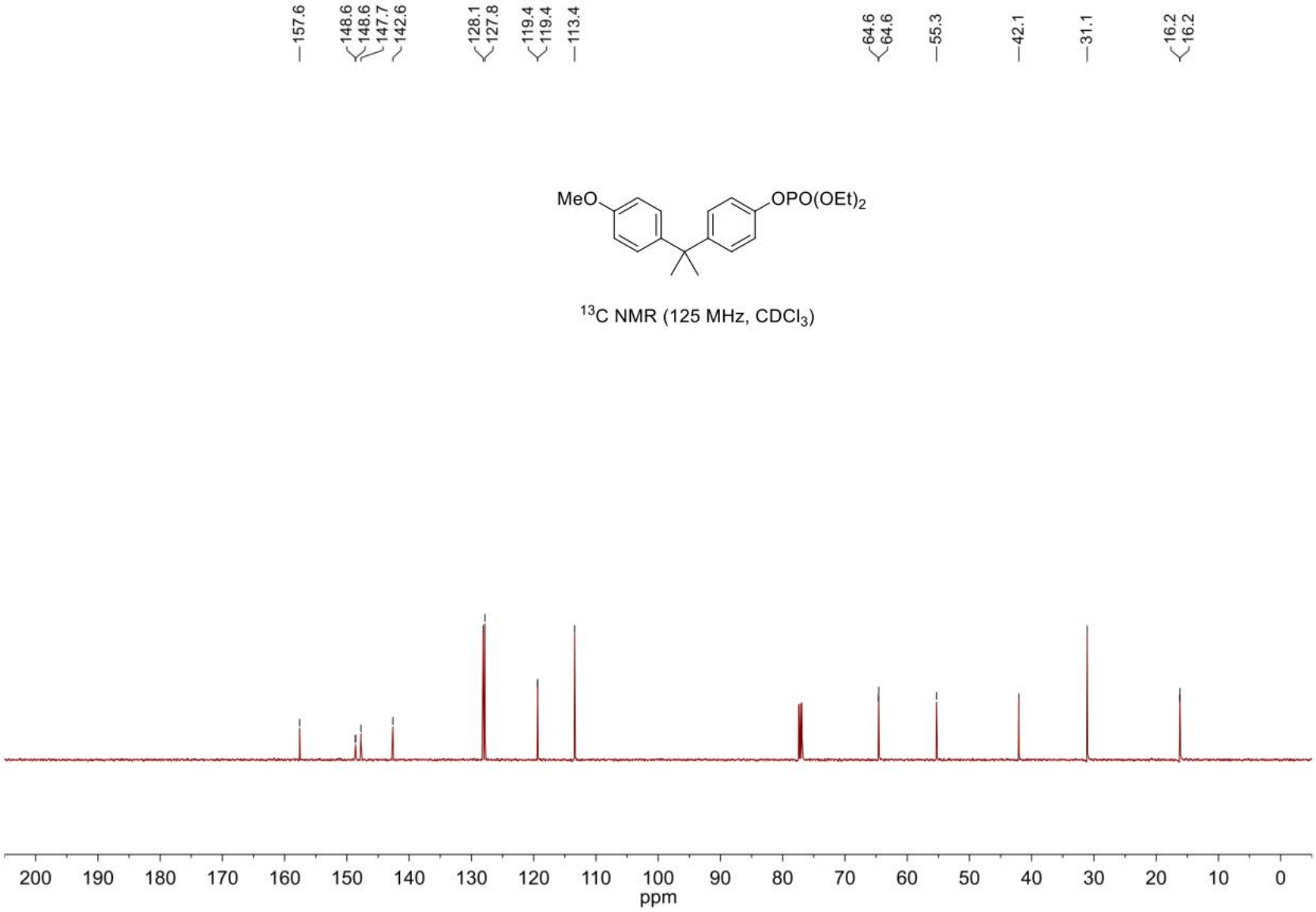
Diethyl (4-(2-(4-methoxyphenyl)propan-2-yl)phenyl) phosphate (S1)



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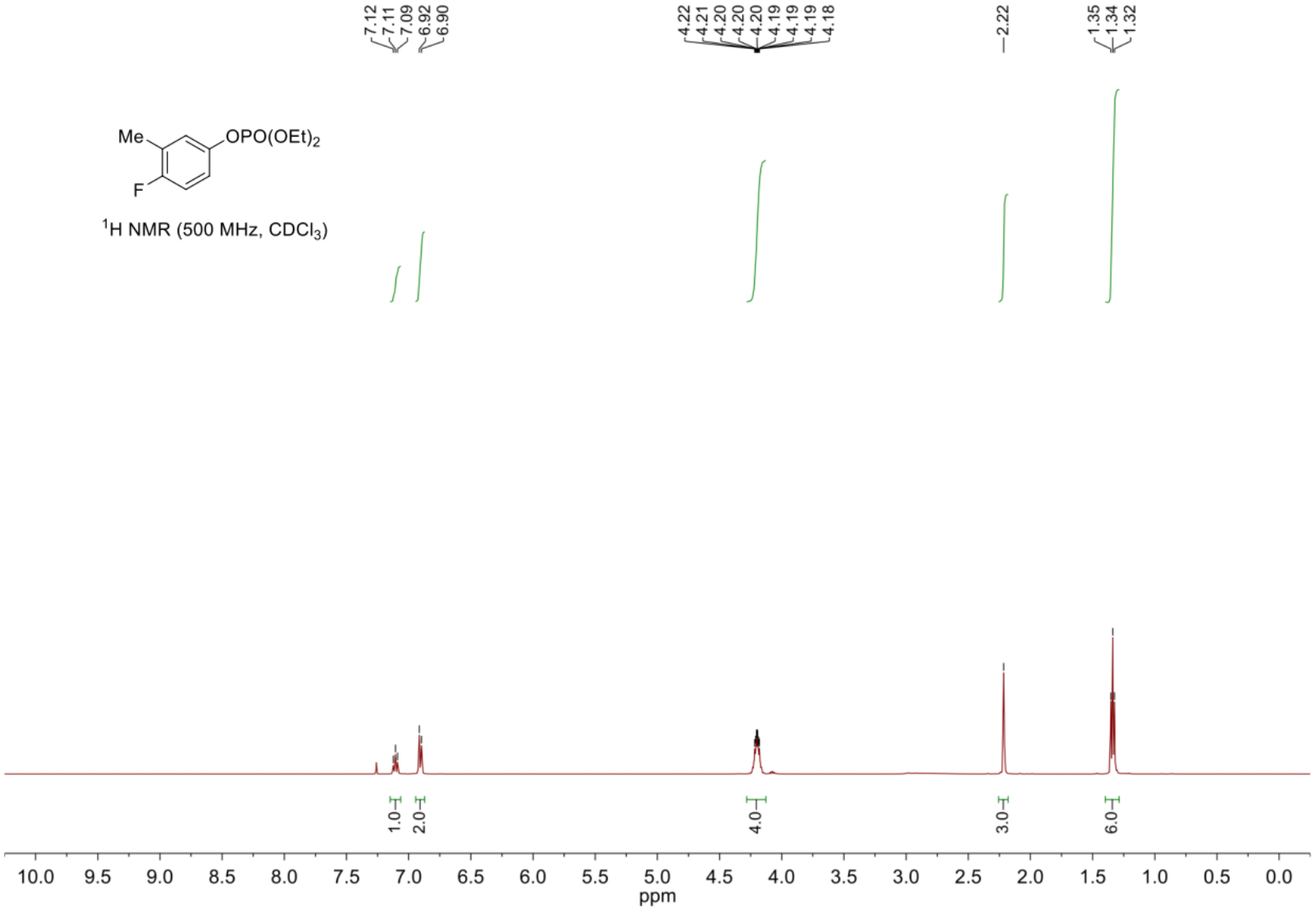
Diethyl (3-fluoro-4-methylphenyl) phosphate (S2)



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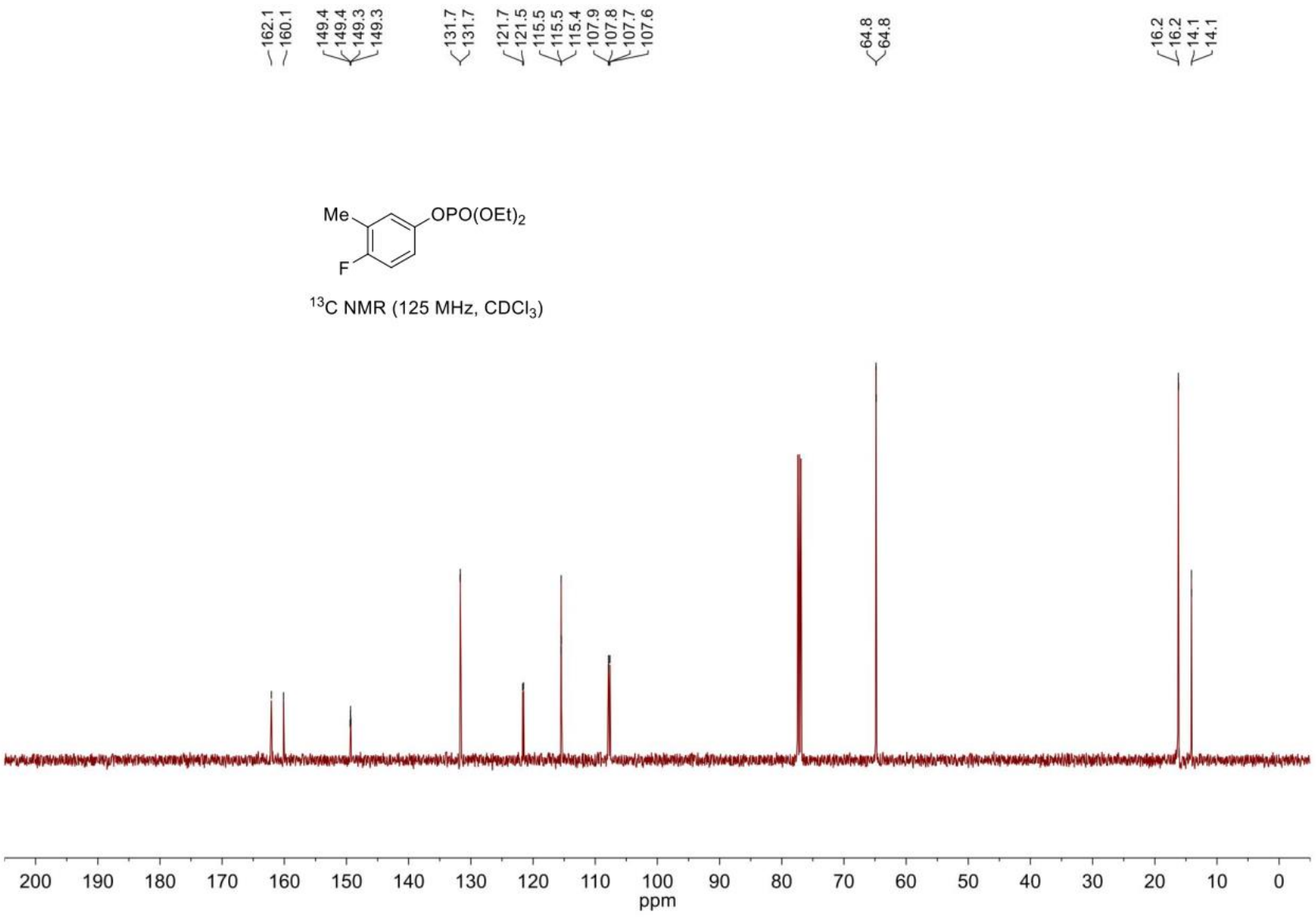
Diethyl (3-fluoro-4-methylphenyl) phosphate (S2)



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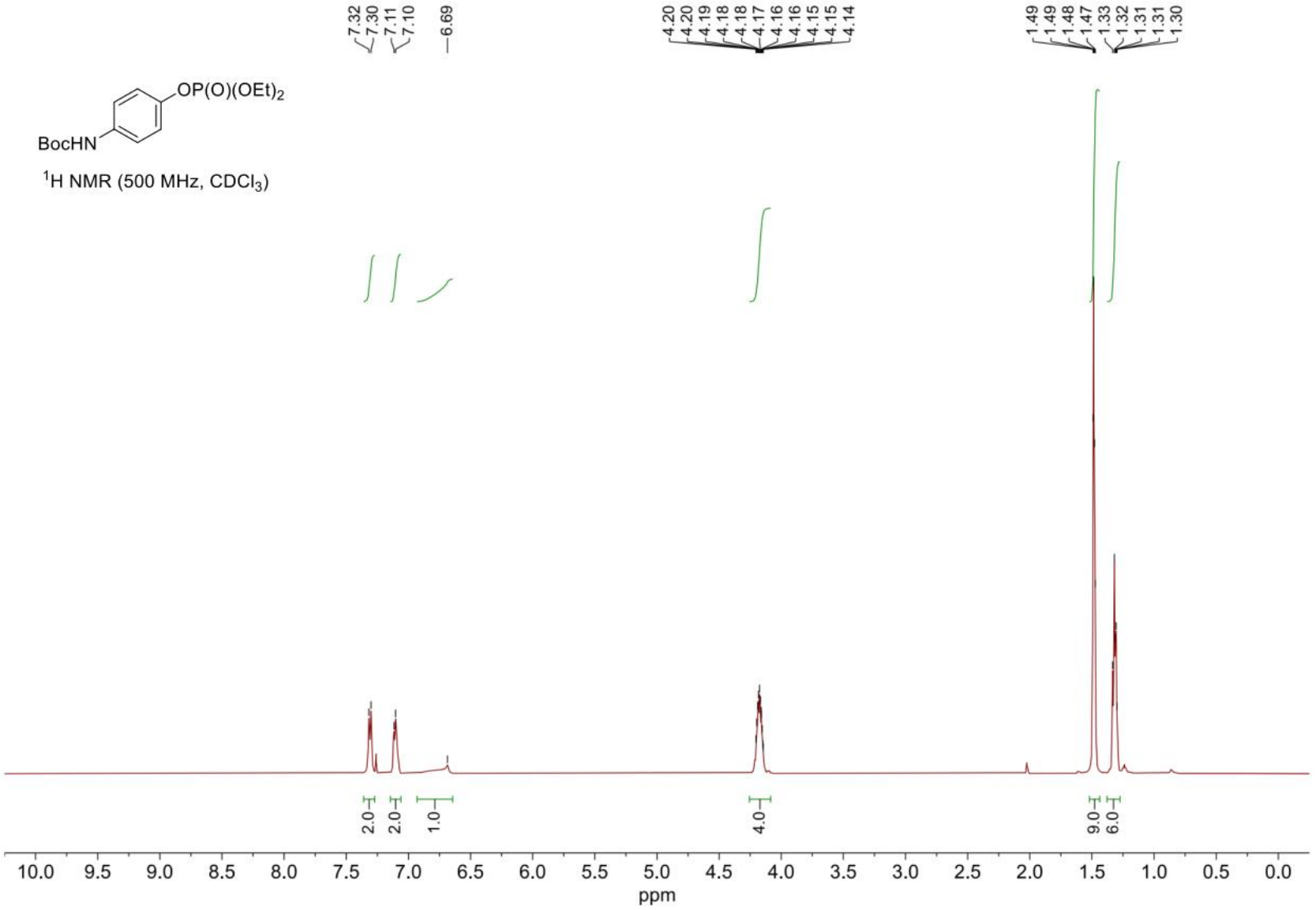
tert-Butyl (4-((diethoxyphosphoryl)oxy)phenyl)carbamate (S122)



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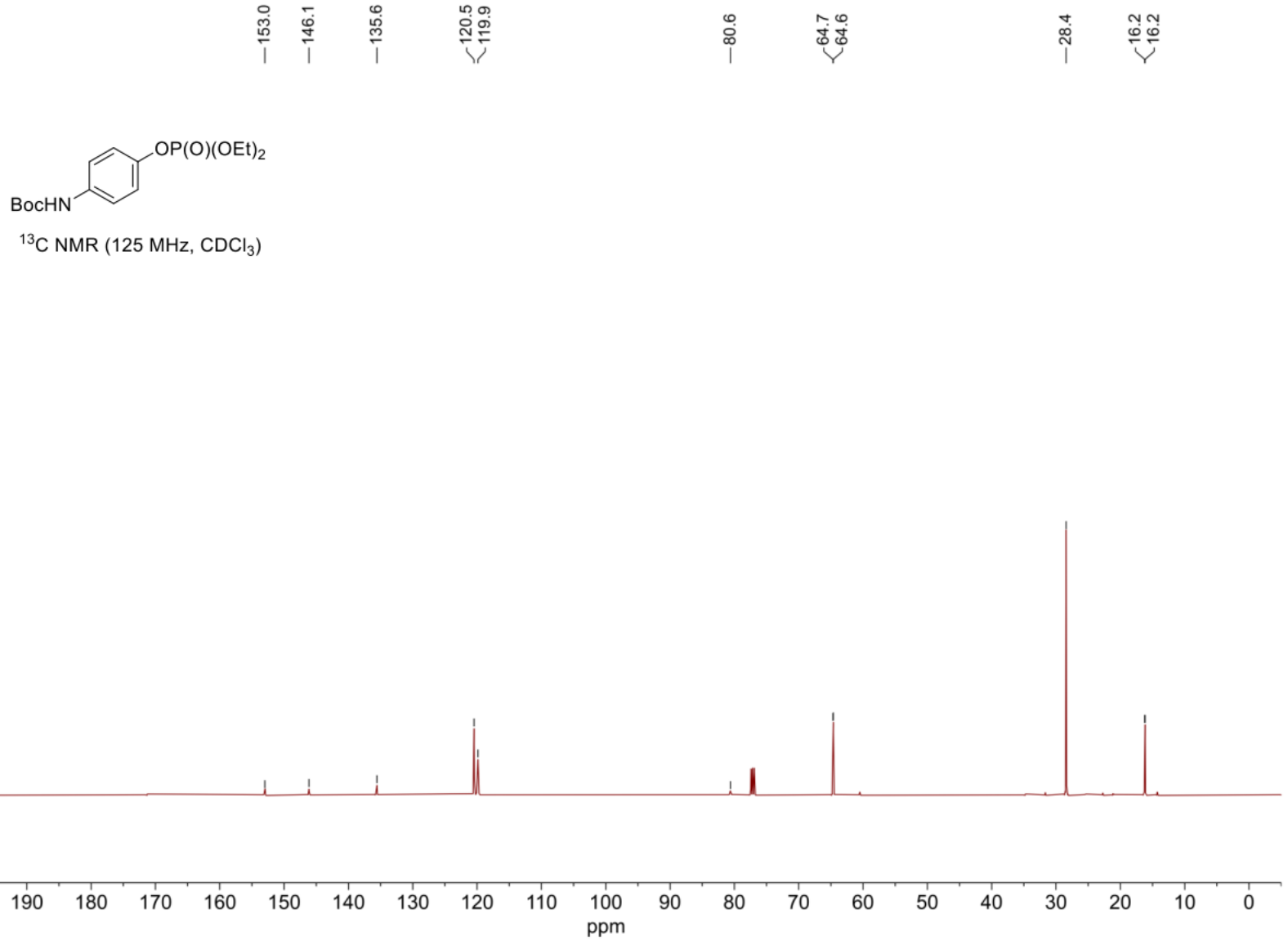
tert-Butyl (4-((diethoxyphosphoryl)oxy)phenyl)carbamate (S122)



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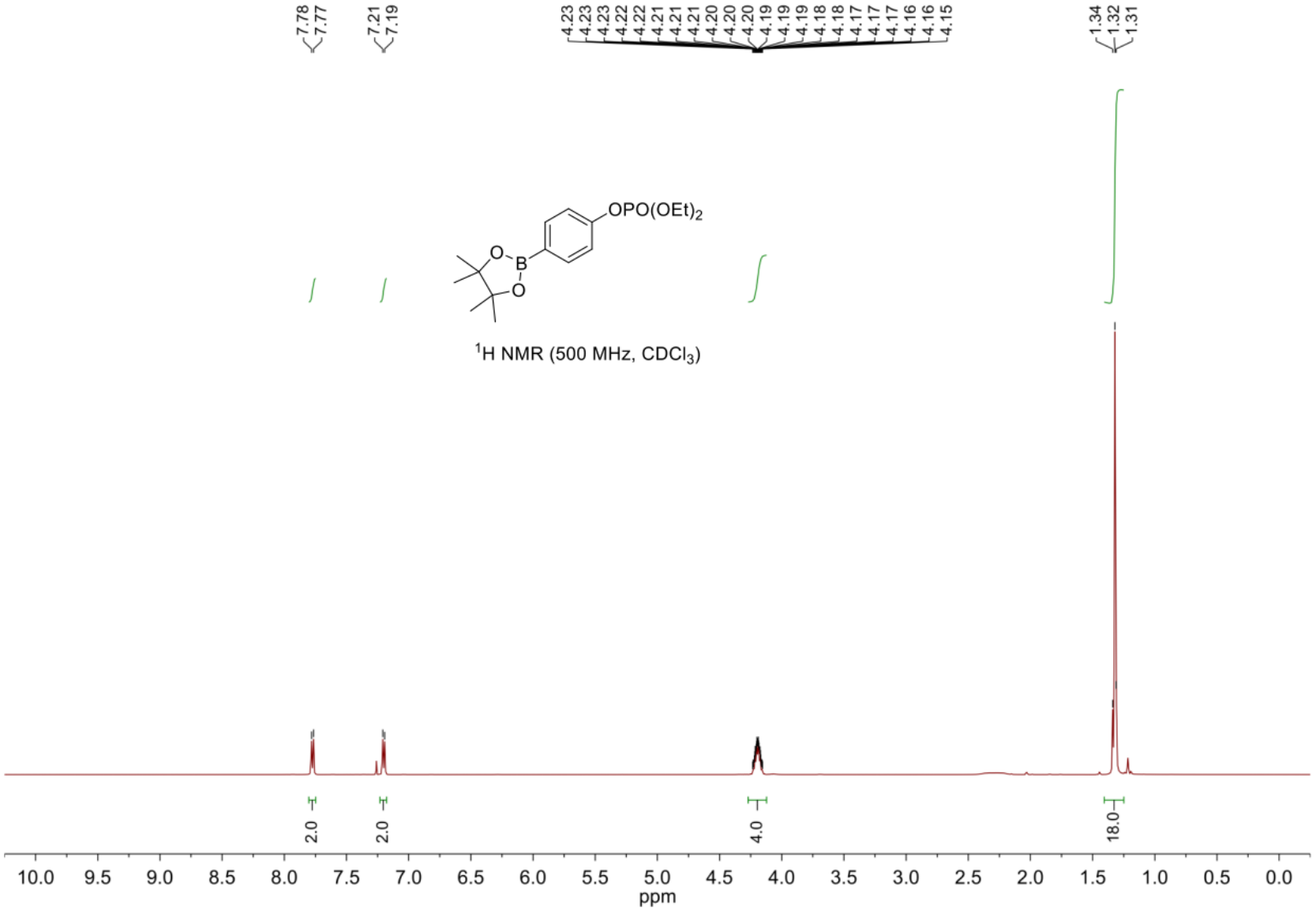
Diethyl (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) phosphate (S3)



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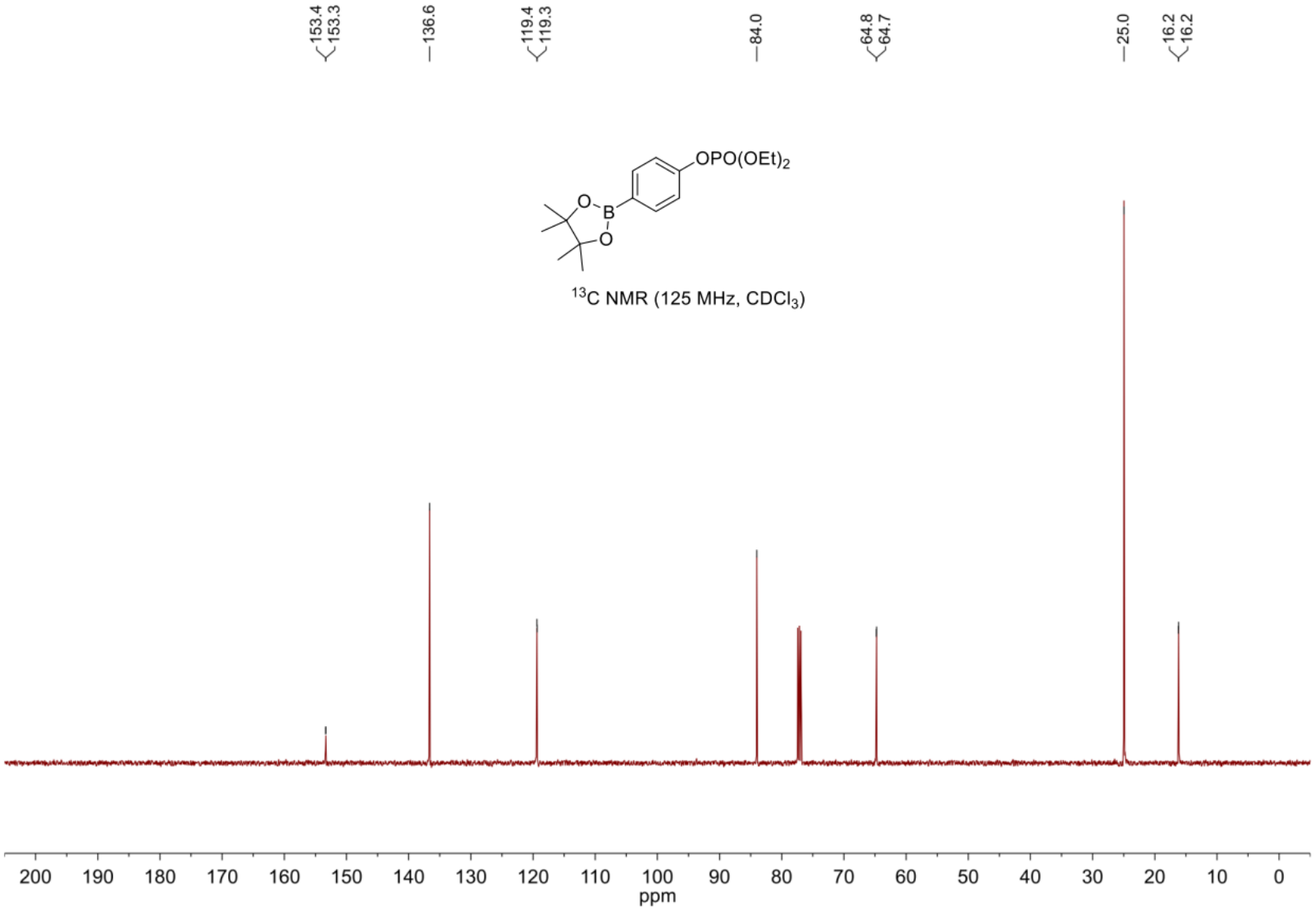
Diethyl (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) phosphate (S3)



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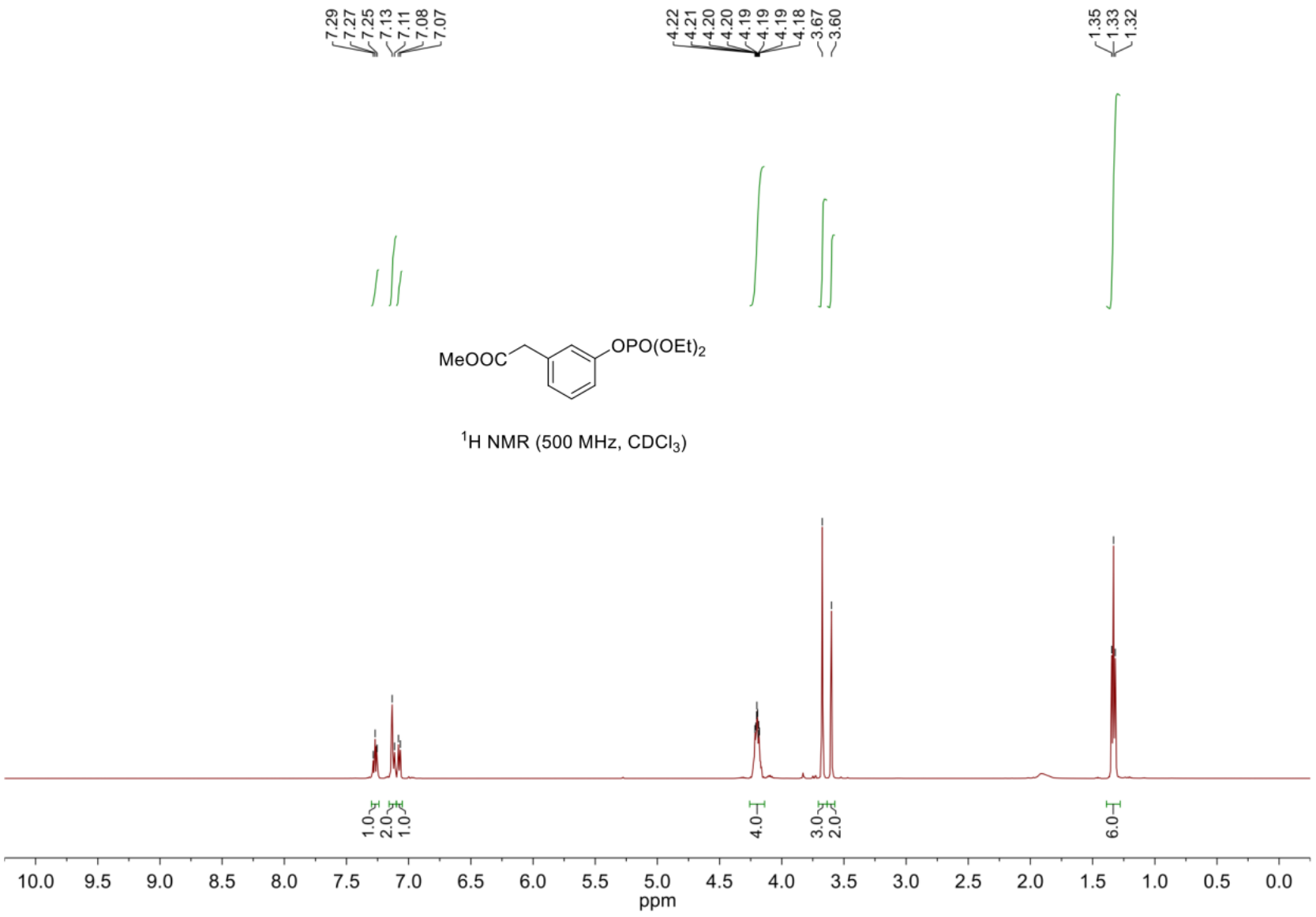
Methyl 2-(3-((diethoxyphosphoryl)oxy)phenyl)acetate (S4)



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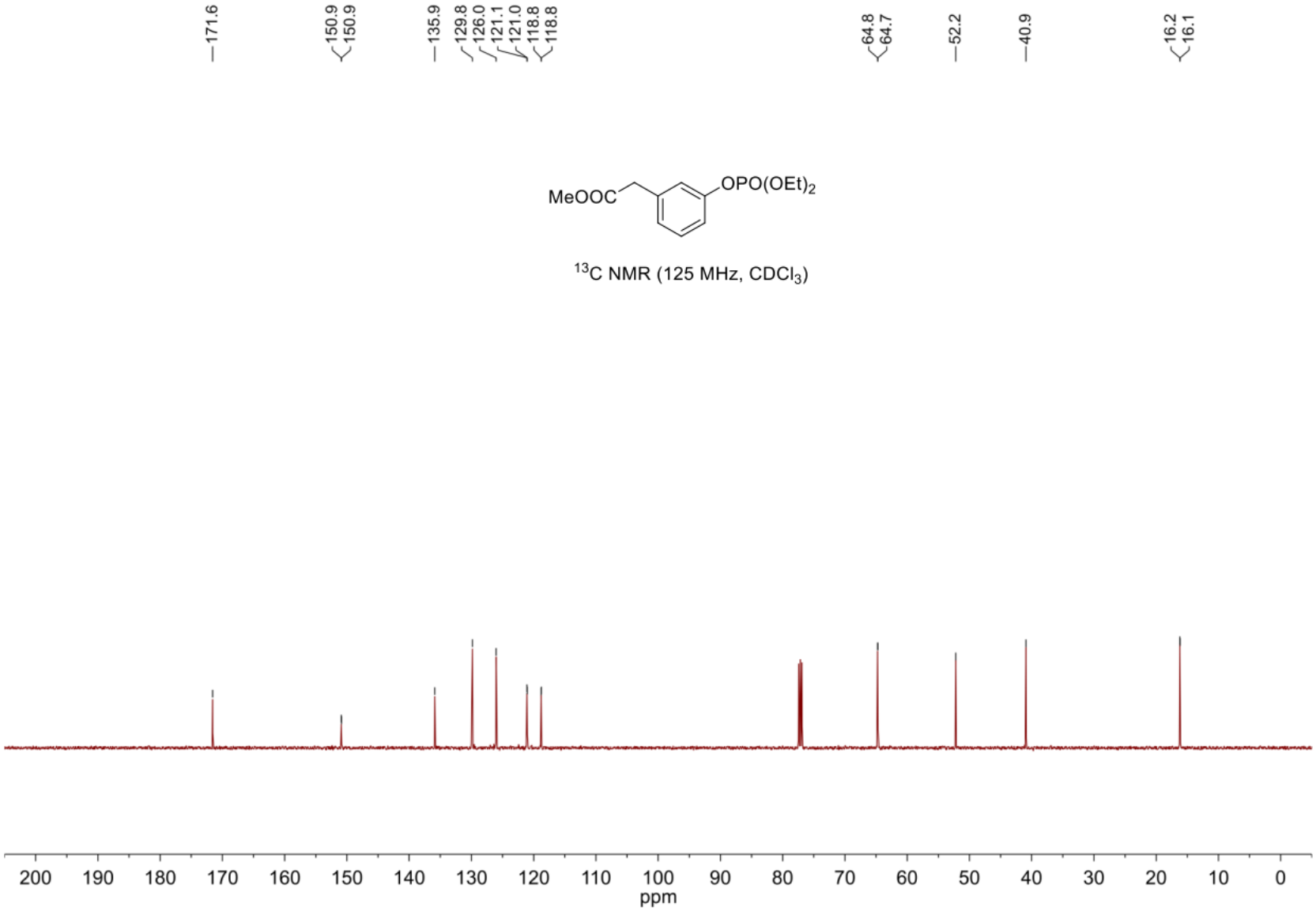
Methyl 2-(3-((diethoxyphosphoryl)oxy)phenyl)acetate (S4)



^{13}C NMR (125 MHz, $CDCl_3$)

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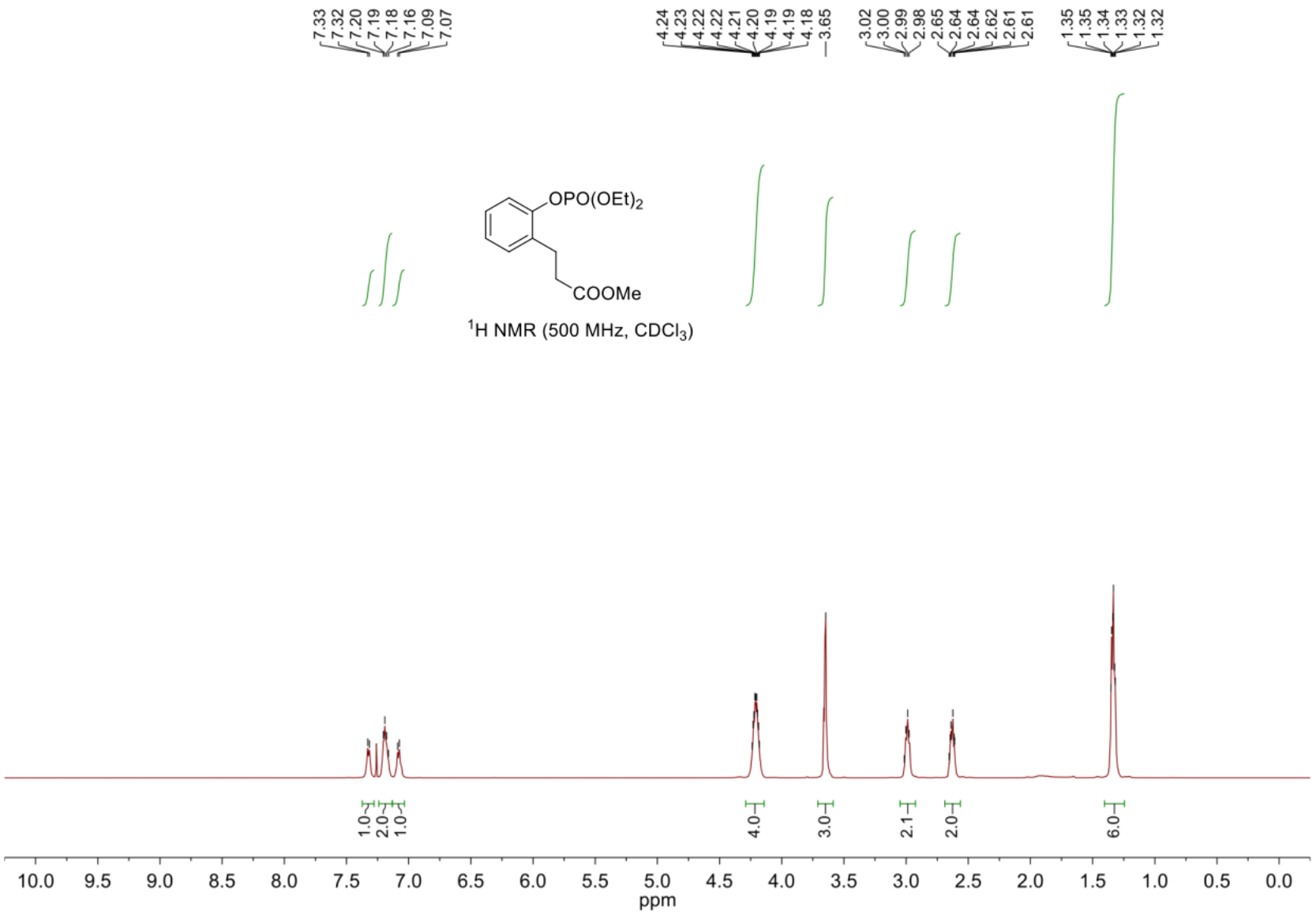
Methyl 3-(2-((diethoxyphosphoryl)oxy)phenyl)propanoate (S5)



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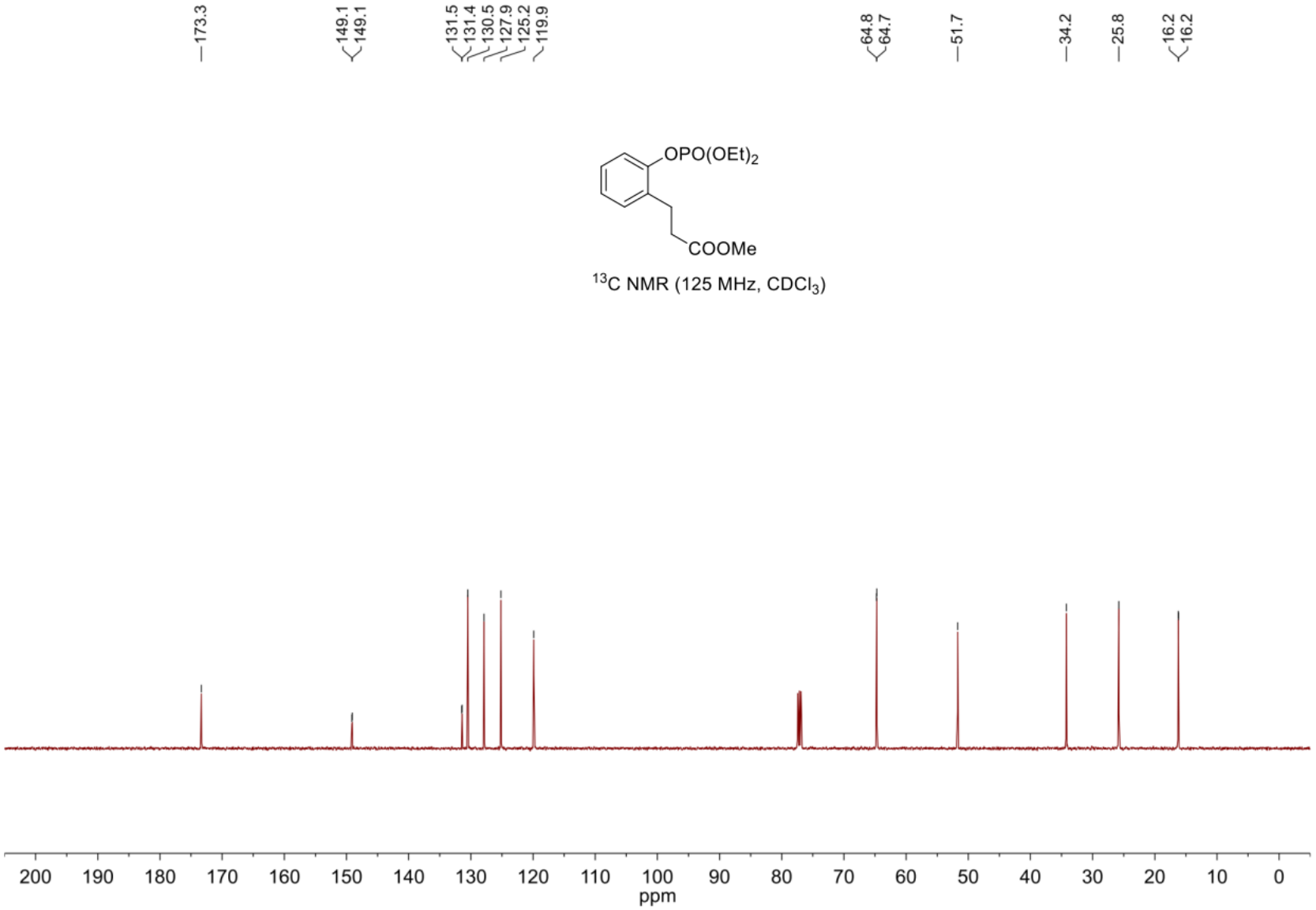
Methyl 3-(2-((diethoxyphosphoryl)oxy)phenyl)propanoate (S5)



^{13}C NMR (125 MHz, $CDCl_3$)

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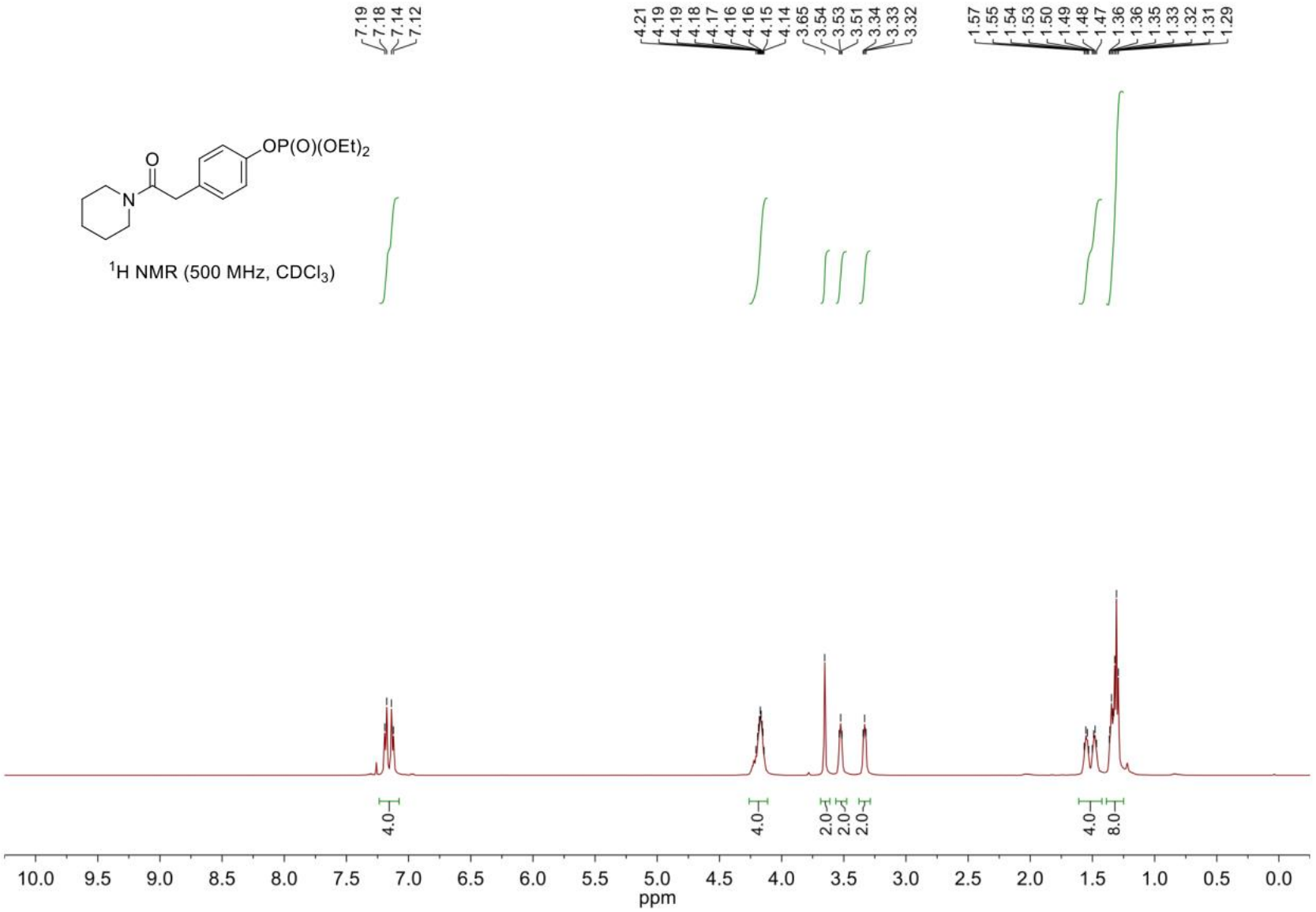
Diethyl (4-(2-oxo-2-(piperidin-1-yl)ethyl)phenyl) phosphate (S6)



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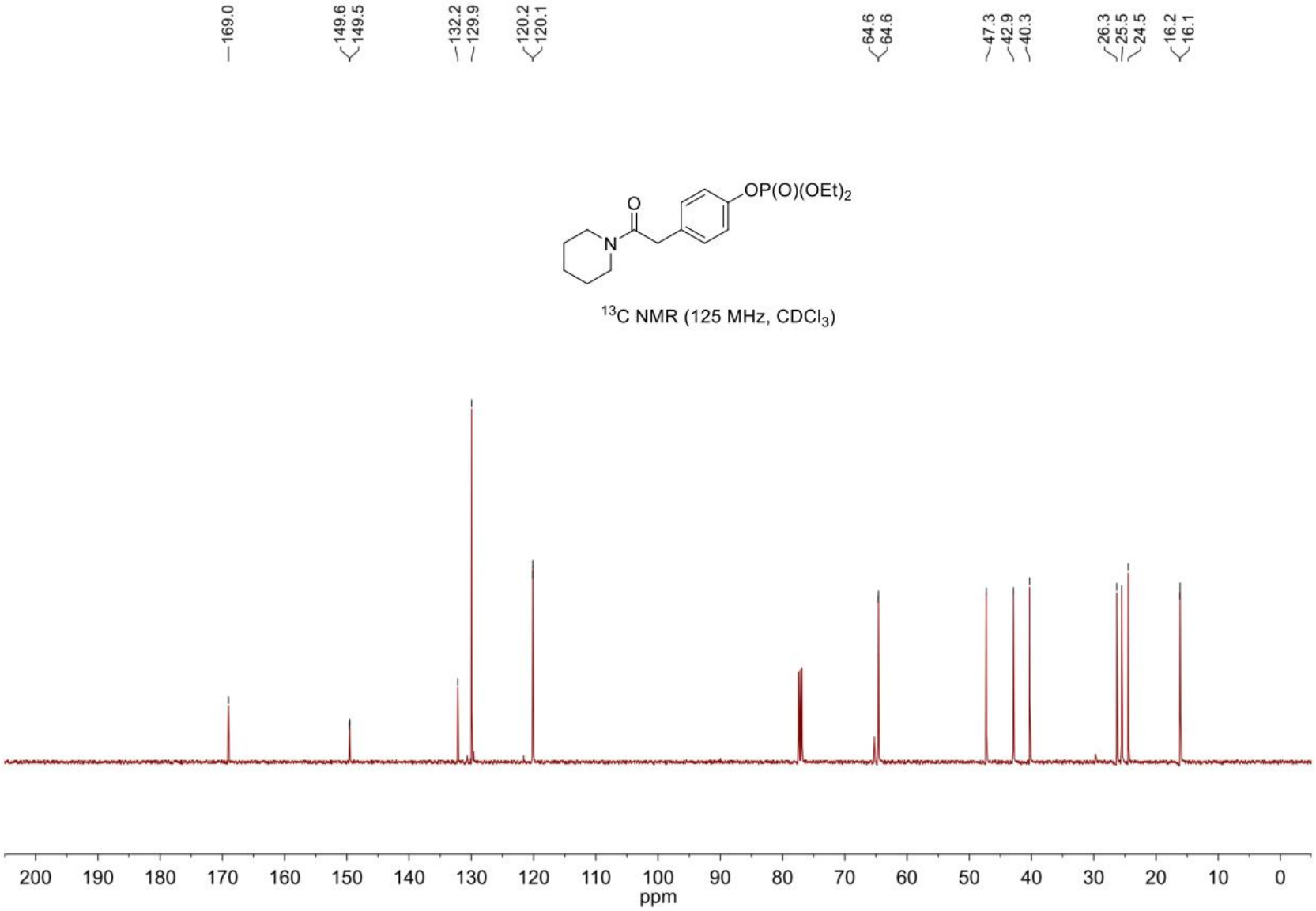
Diethyl (4-(2-oxo-2-(piperidin-1-yl)ethyl)phenyl) phosphate (S6)



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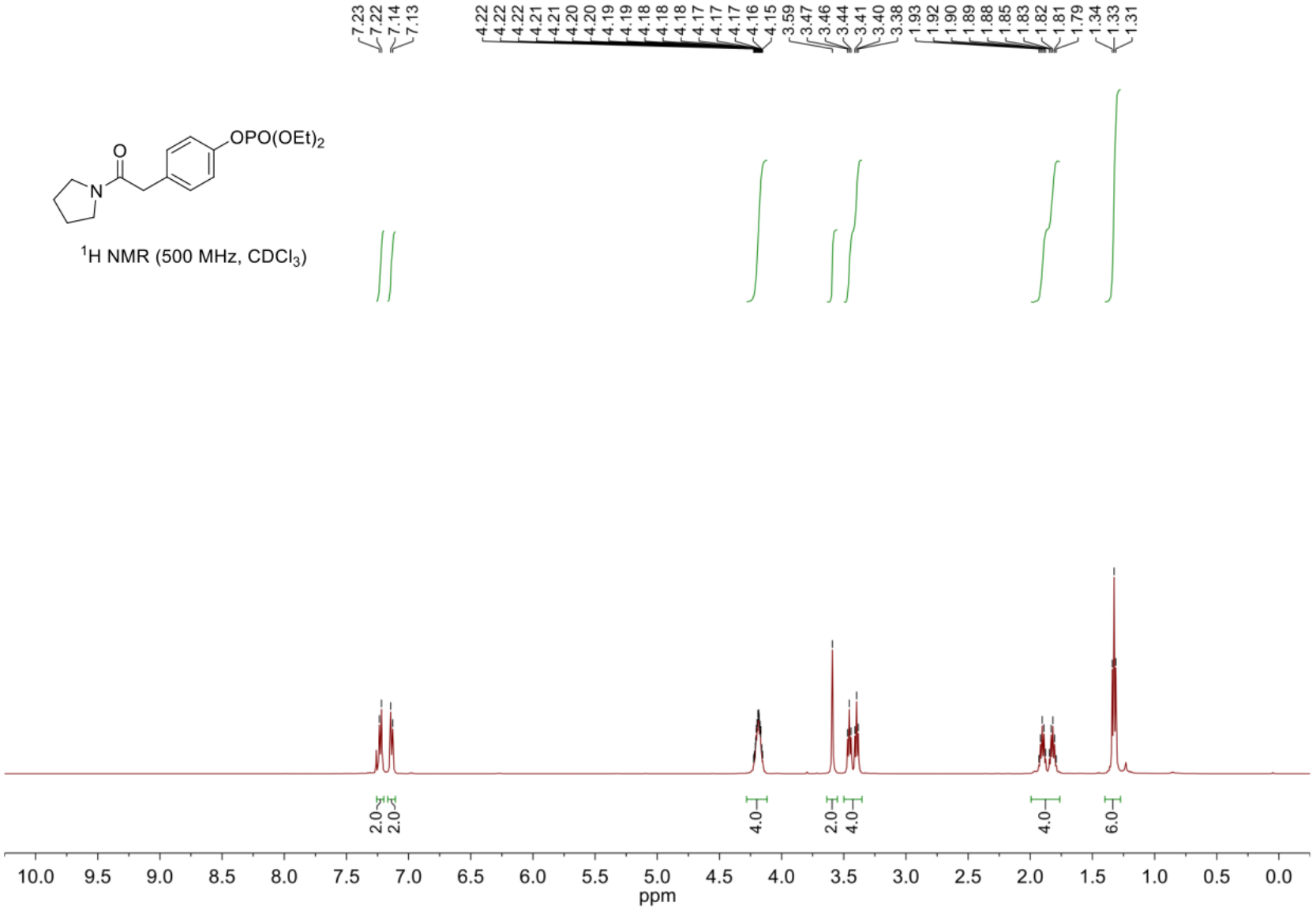
Diethyl (4-(2-oxo-2-(pyrrolidin-1-yl)ethyl)phenyl) phosphate (S7)



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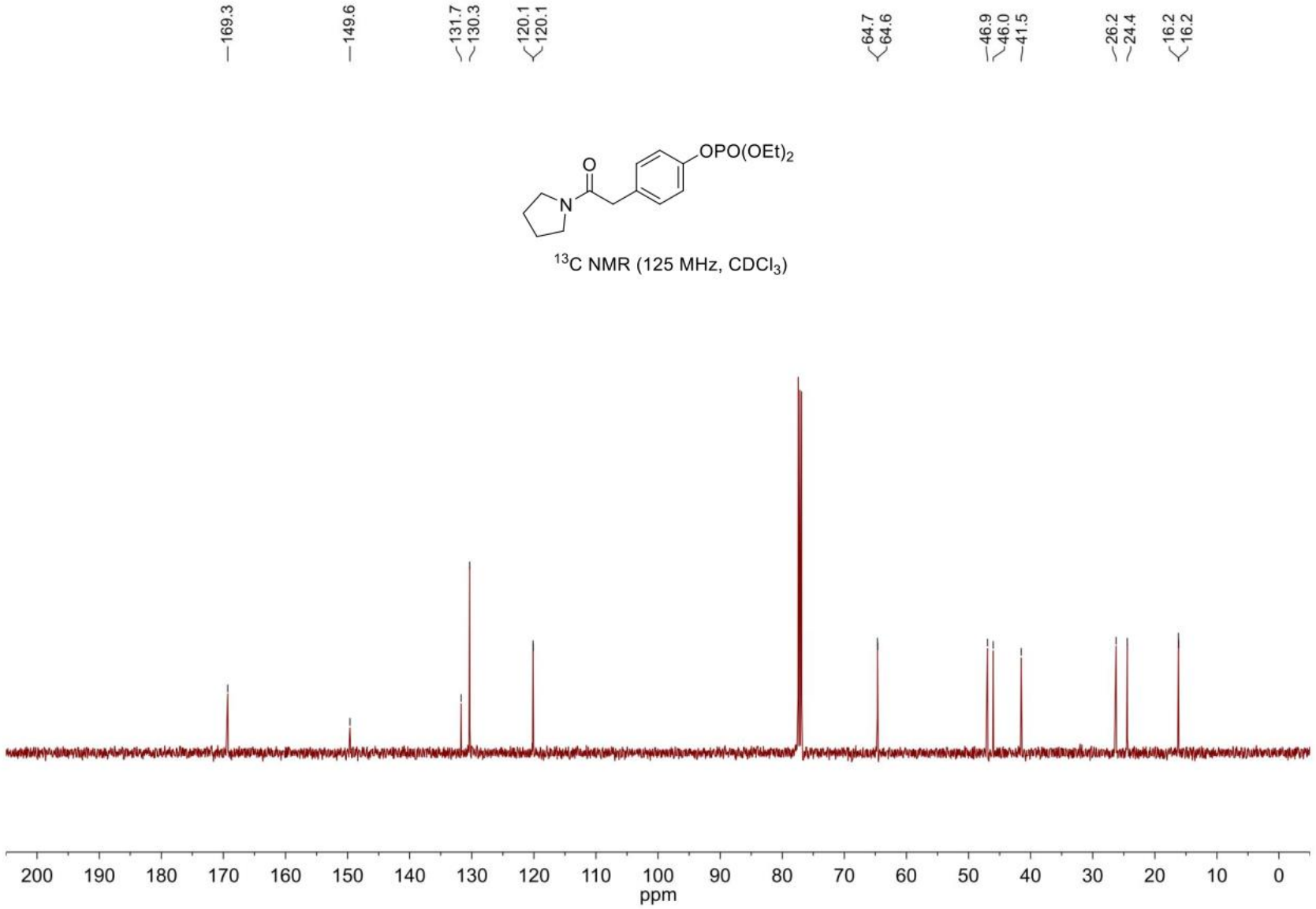
Diethyl (4-(2-oxo-2-(pyrrolidin-1-yl)ethyl)phenyl) phosphate (S7)



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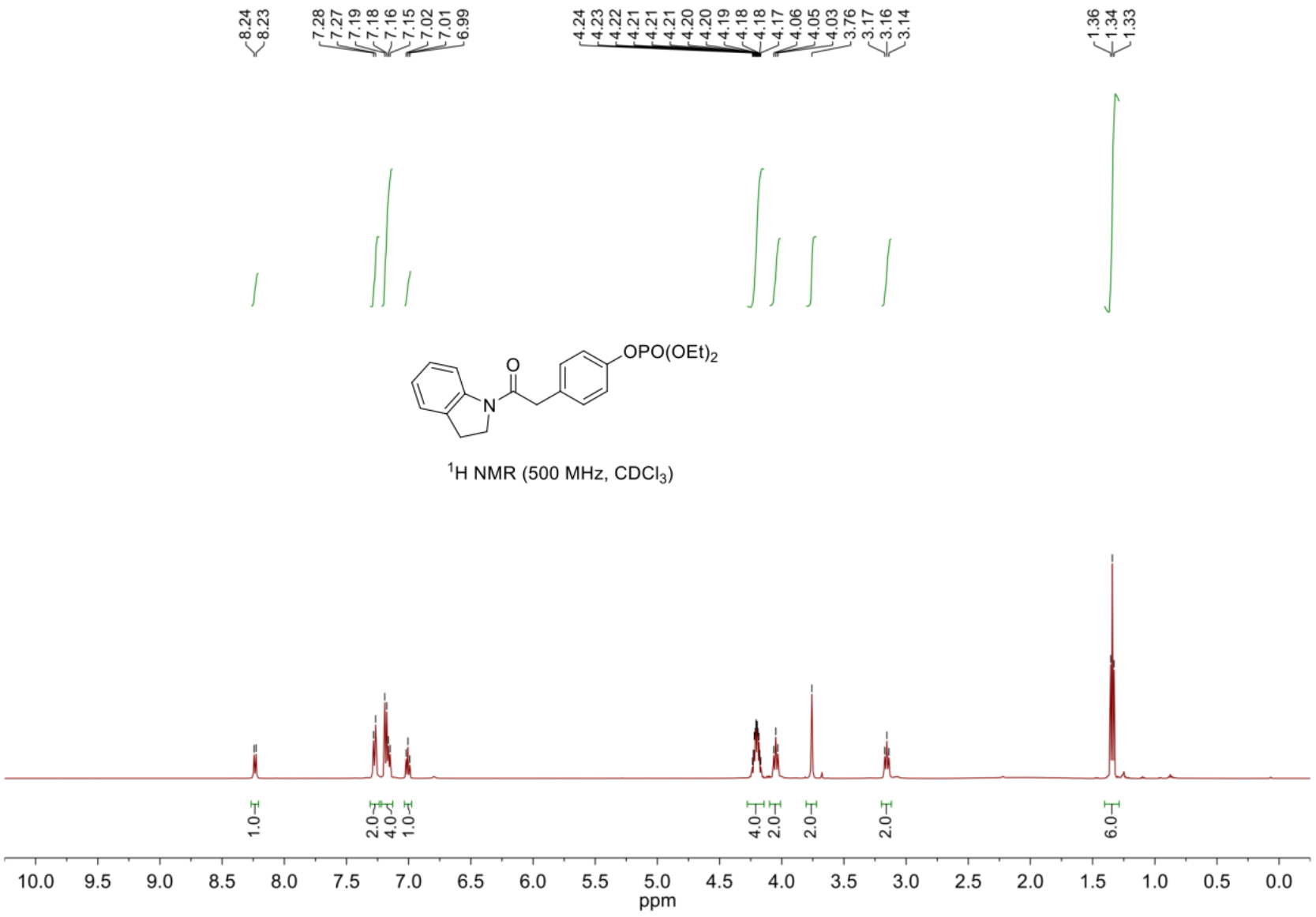
Diethyl (4-(2-(indolin-1-yl)-2-oxoethyl)phenyl) phosphate (S8)



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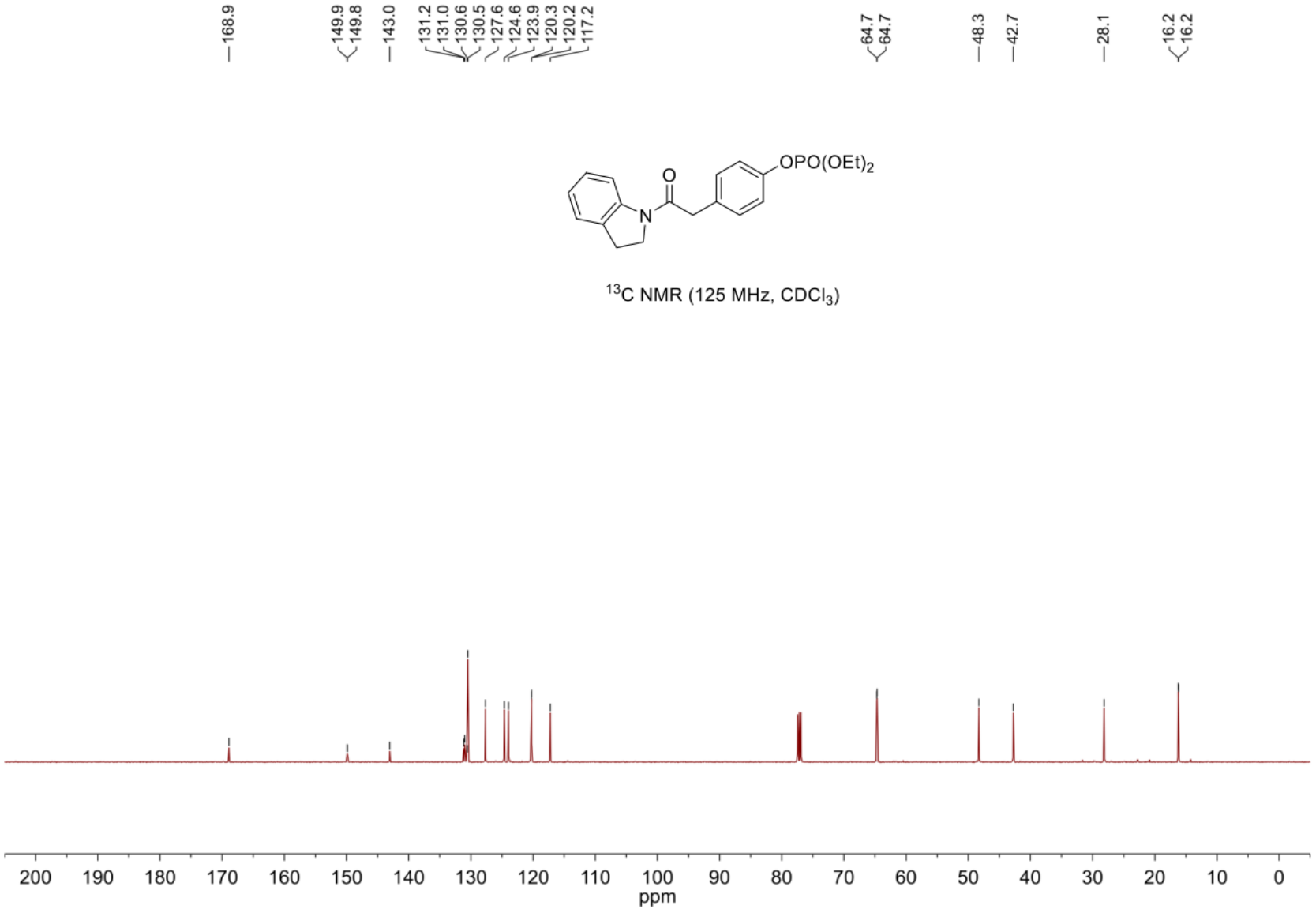
Diethyl (4-(2-(indolin-1-yl)-2-oxoethyl)phenyl) phosphate (S8)



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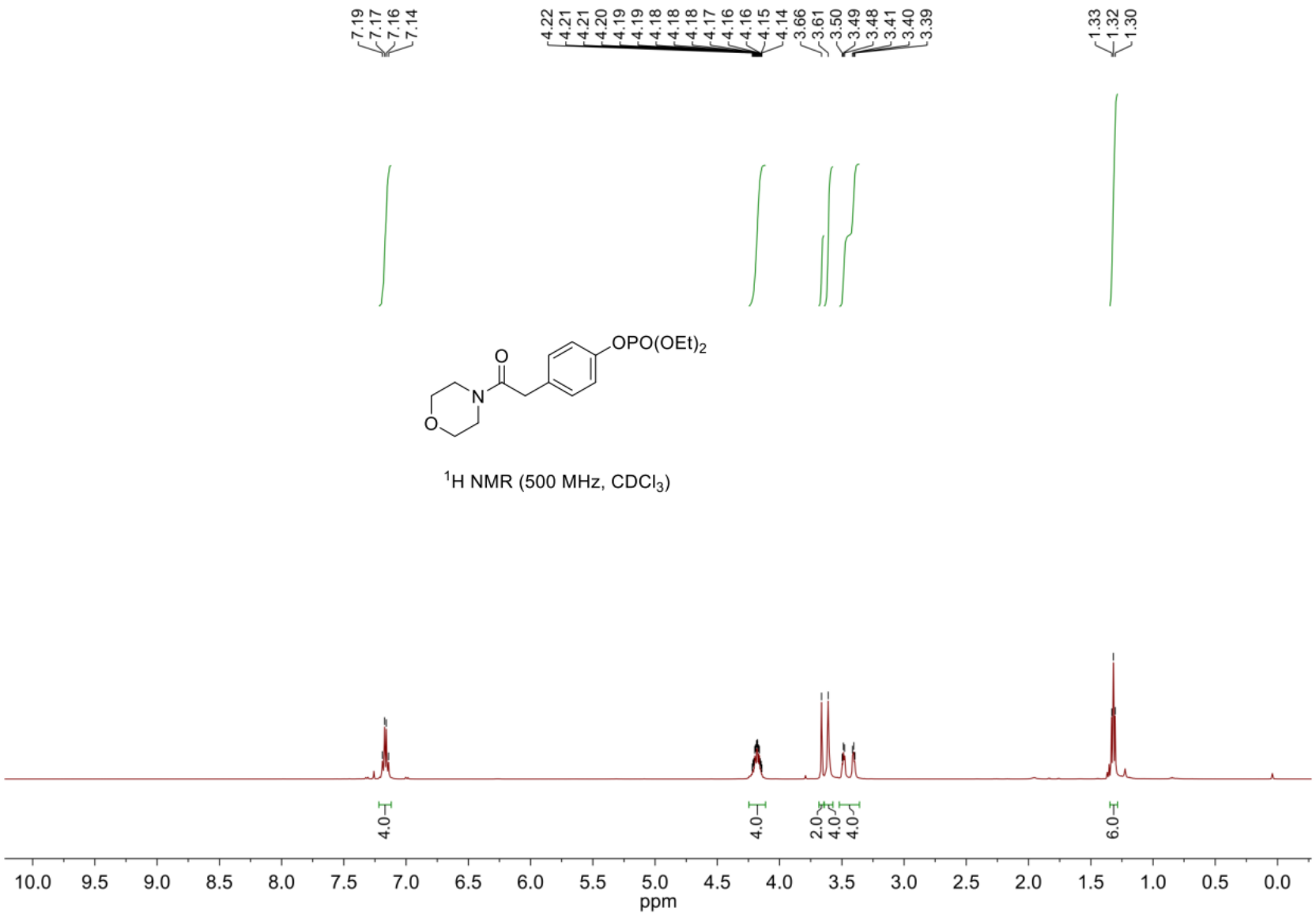
Diethyl (4-(2-morpholino-2-oxoethyl)phenyl) phosphate (S9)



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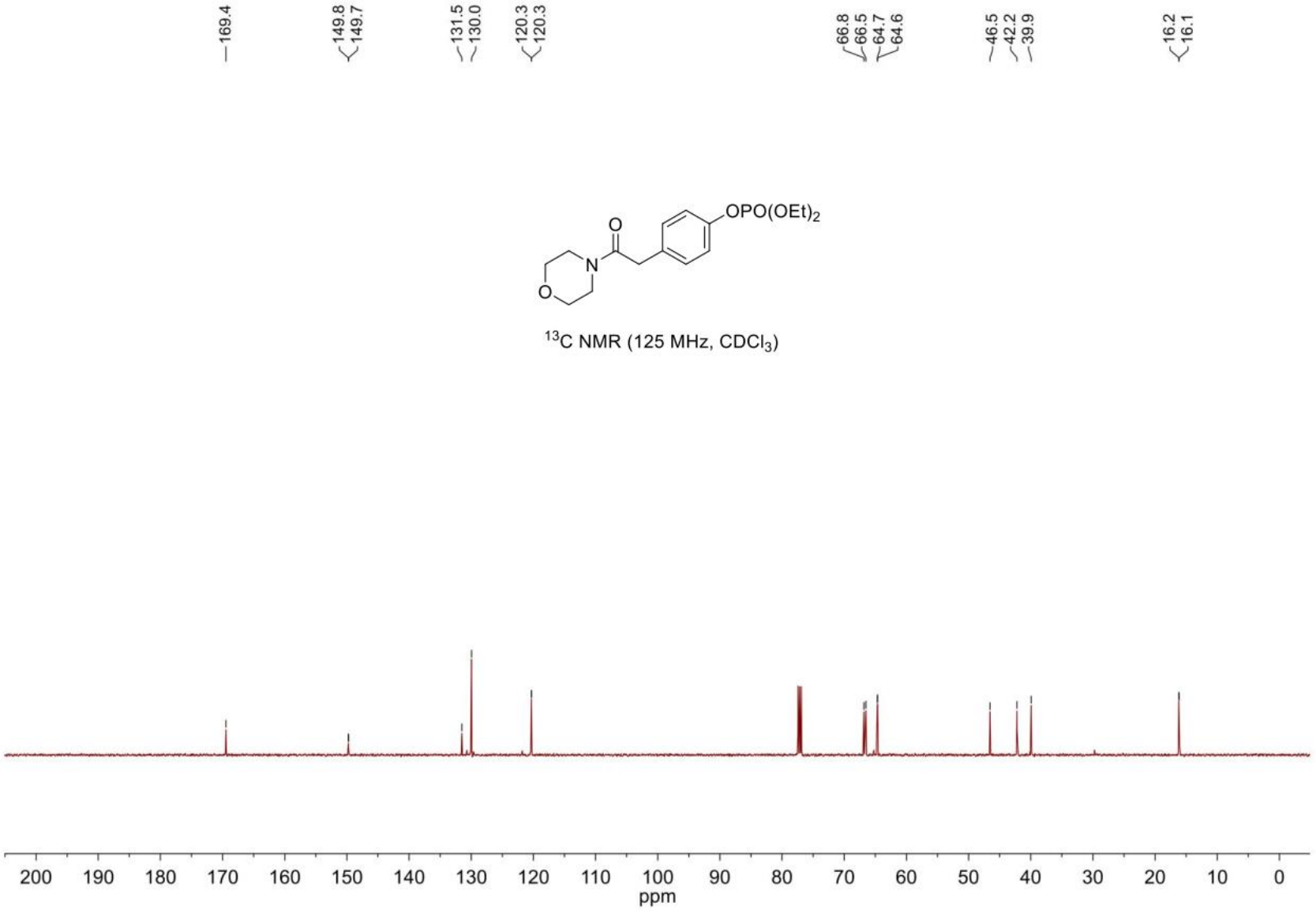
Diethyl (4-(2-morpholino-2-oxoethyl)phenyl) phosphate (S9)



^{13}C NMR (125 MHz, $CDCl_3$)

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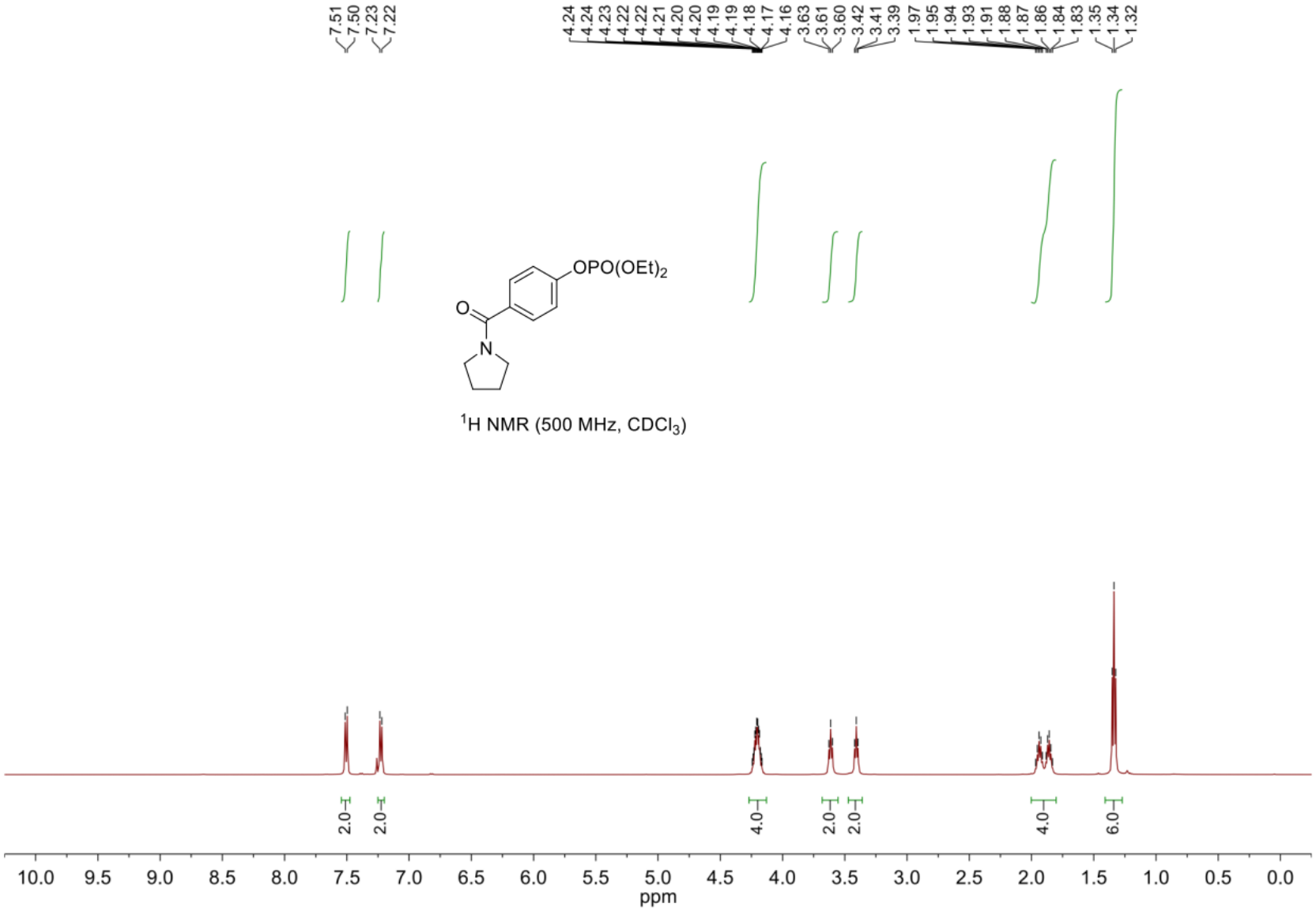
Diethyl (4-(pyrrolidine-1-carbonyl)phenyl) phosphate (S10)



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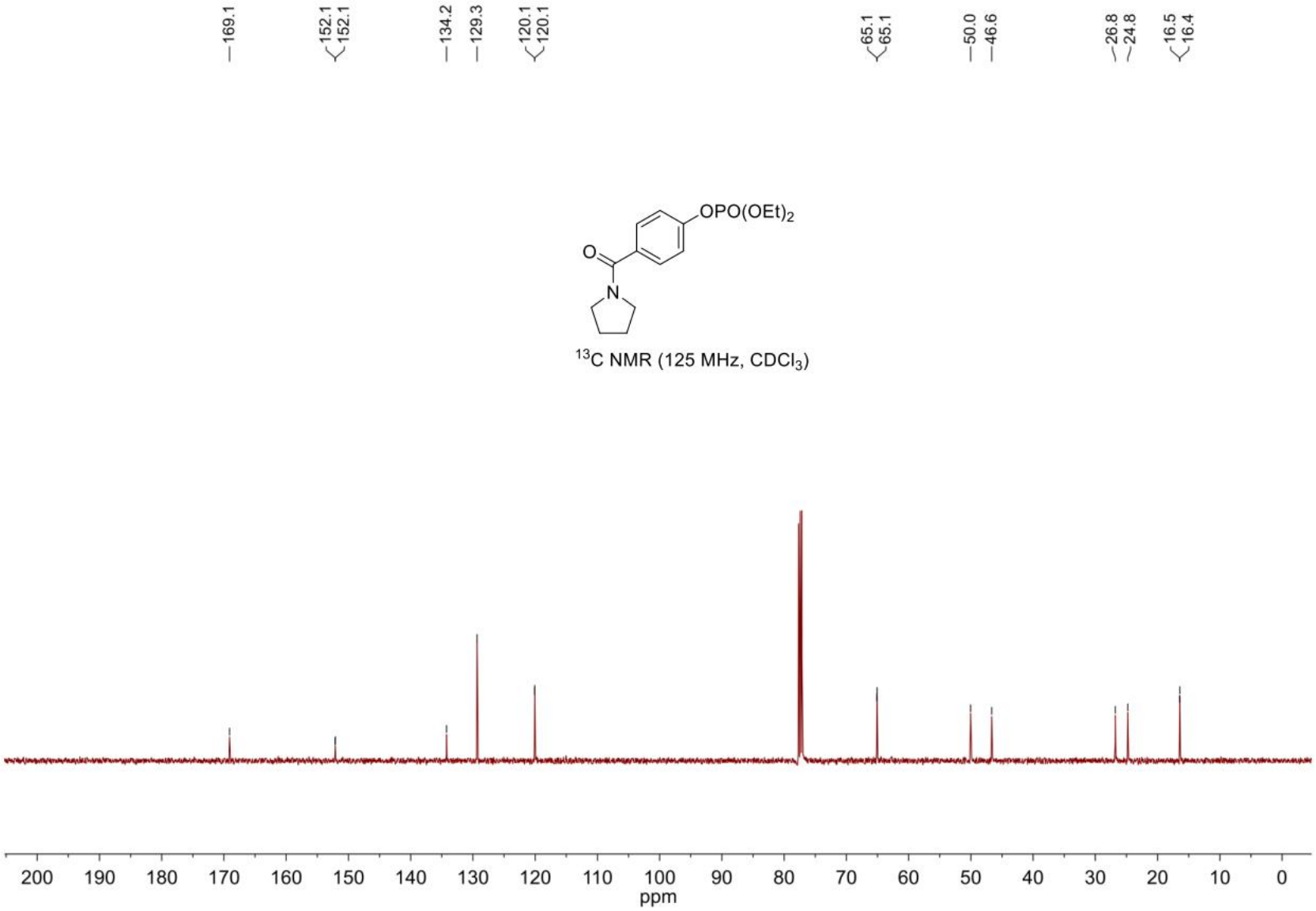
Diethyl (4-(pyrrolidine-1-carbonyl)phenyl) phosphate (S10)



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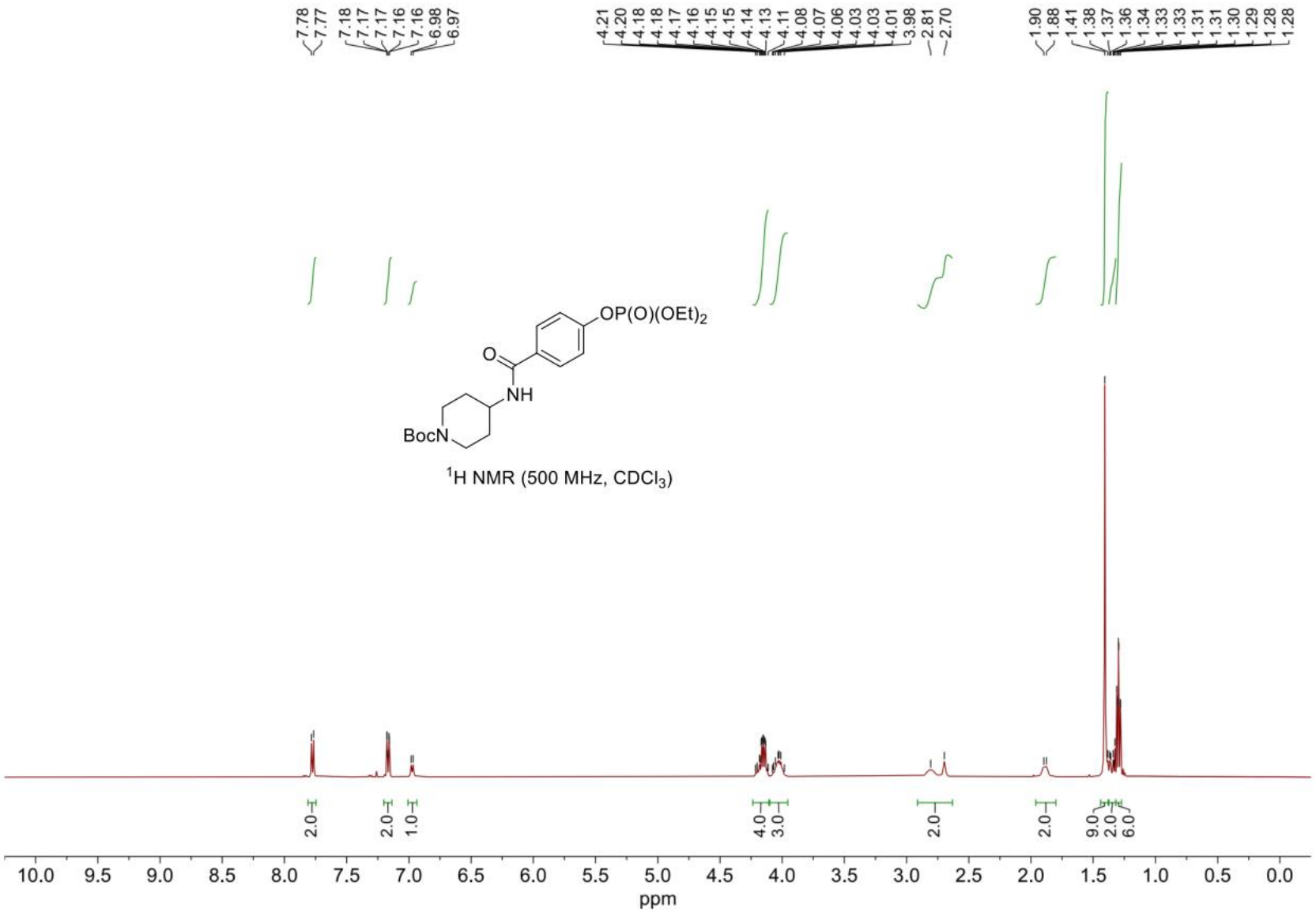
tert-Butyl 4-(4-((diethoxyphosphoryl)oxy)benzamido)piperidine-1-carboxylate (S11)



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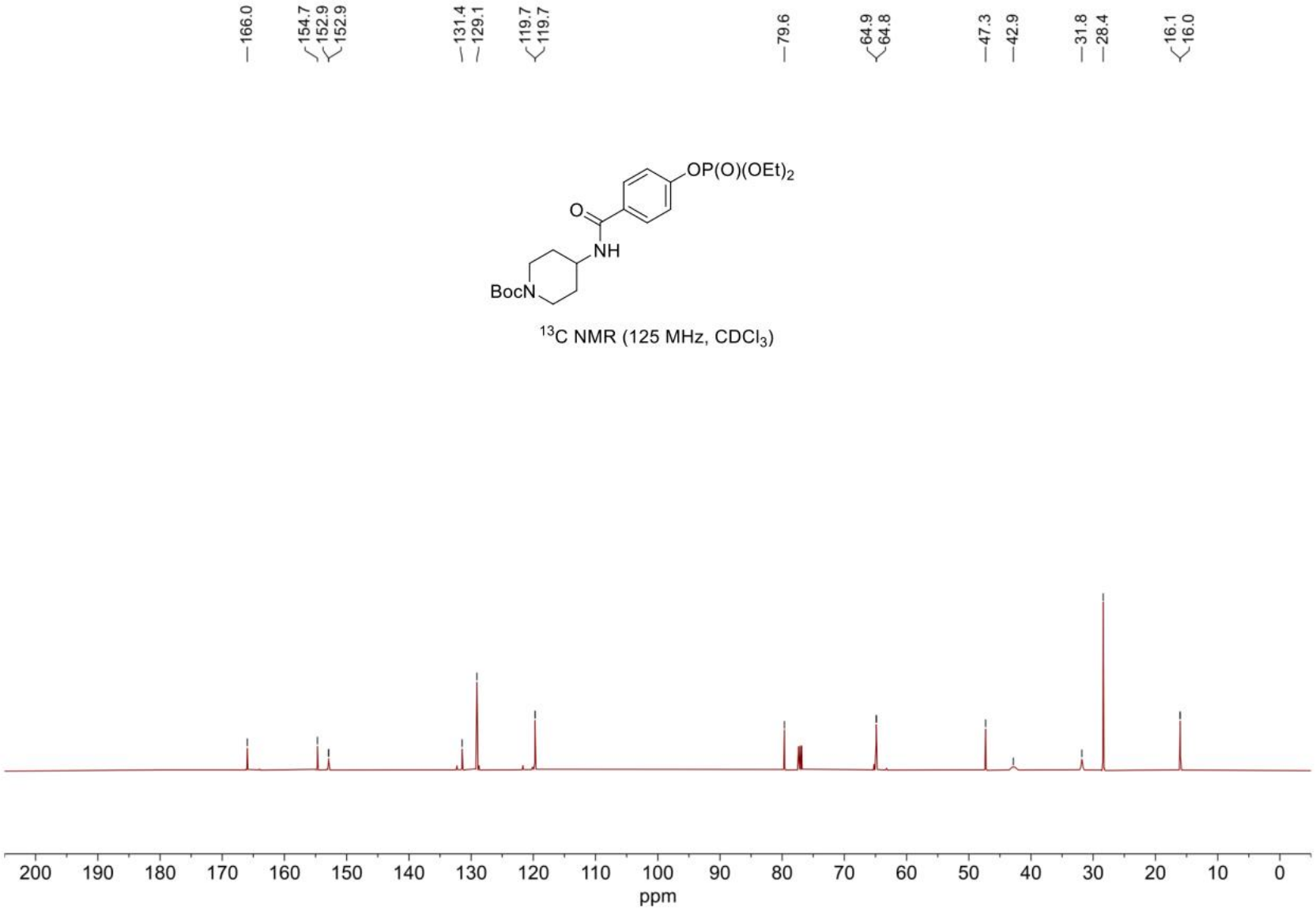
tert-Butyl 4-(4-((diethoxyphosphoryl)oxy)benzamido)piperidine-1-carboxylate (S11)



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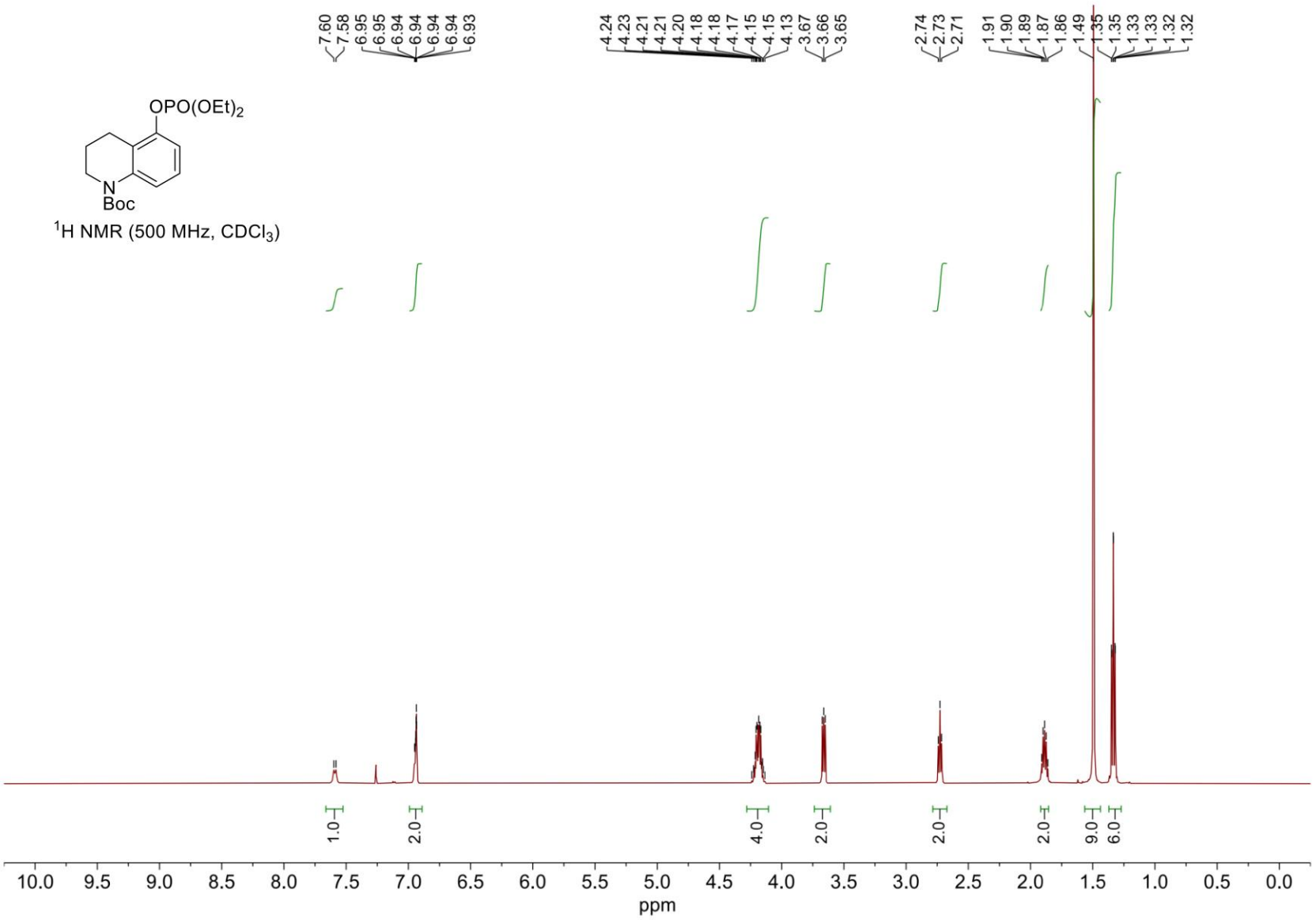
tert-Butyl 5-((diethoxyphosphoryl)oxy)-3,4-dihydroquinoline-1(2*H*)-carboxylate (S12)



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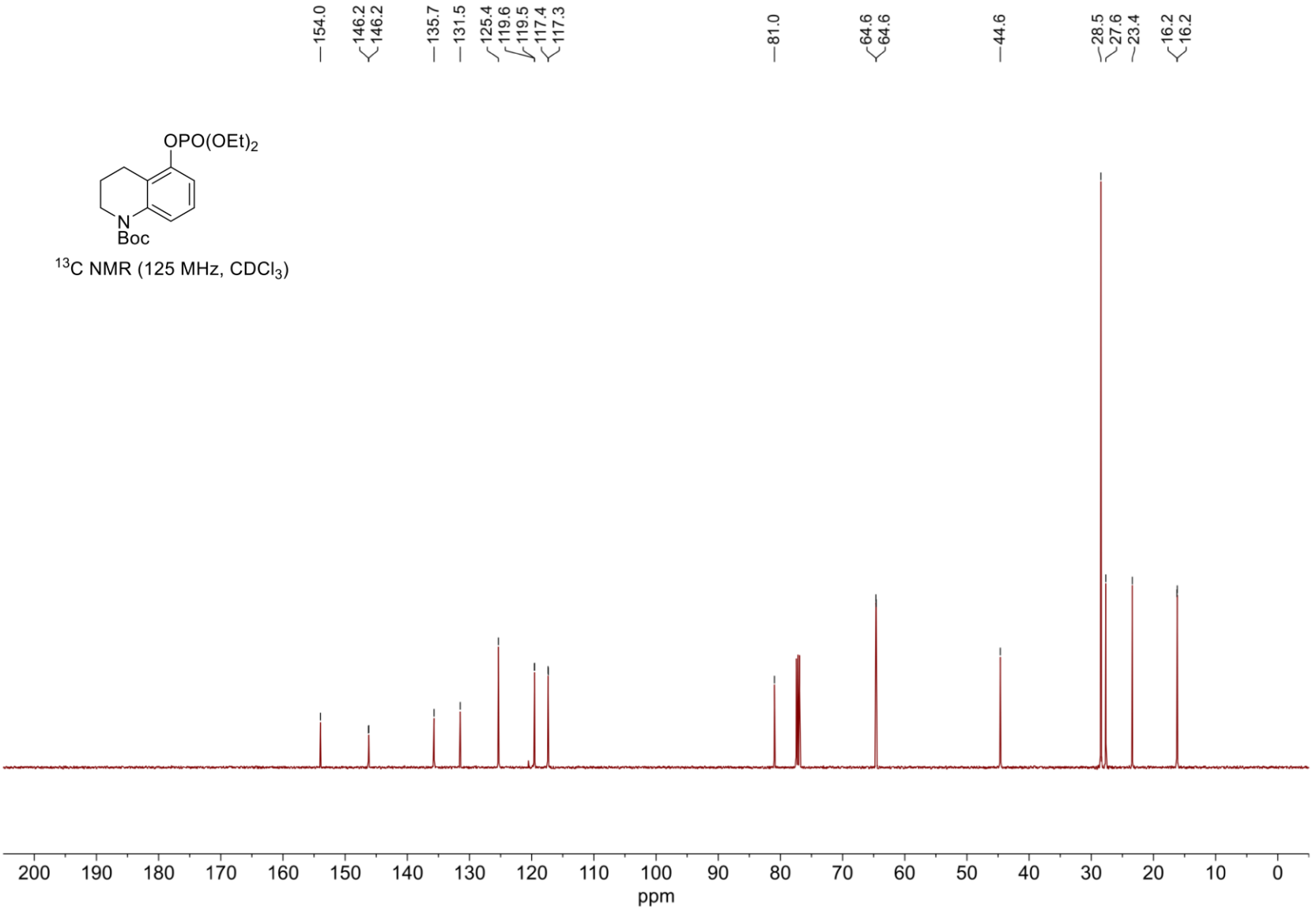
tert-Butyl 5-((diethoxyphosphoryl)oxy)-3,4-dihydroquinoline-1(2*H*)-carboxylate (S12)



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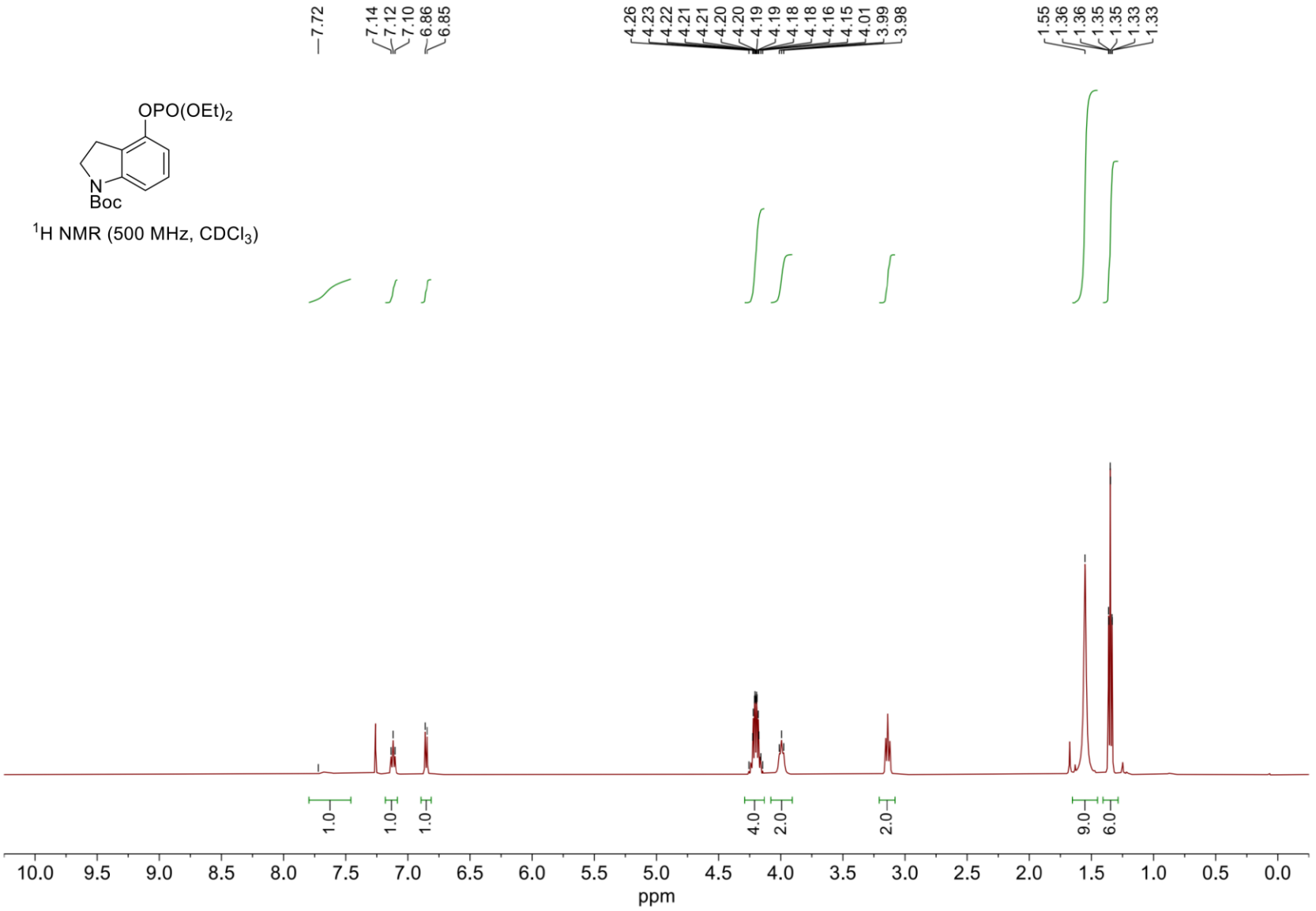
tert-Butyl 4-((diethoxyphosphoryl)oxy)indoline-1-carboxylate (S13)



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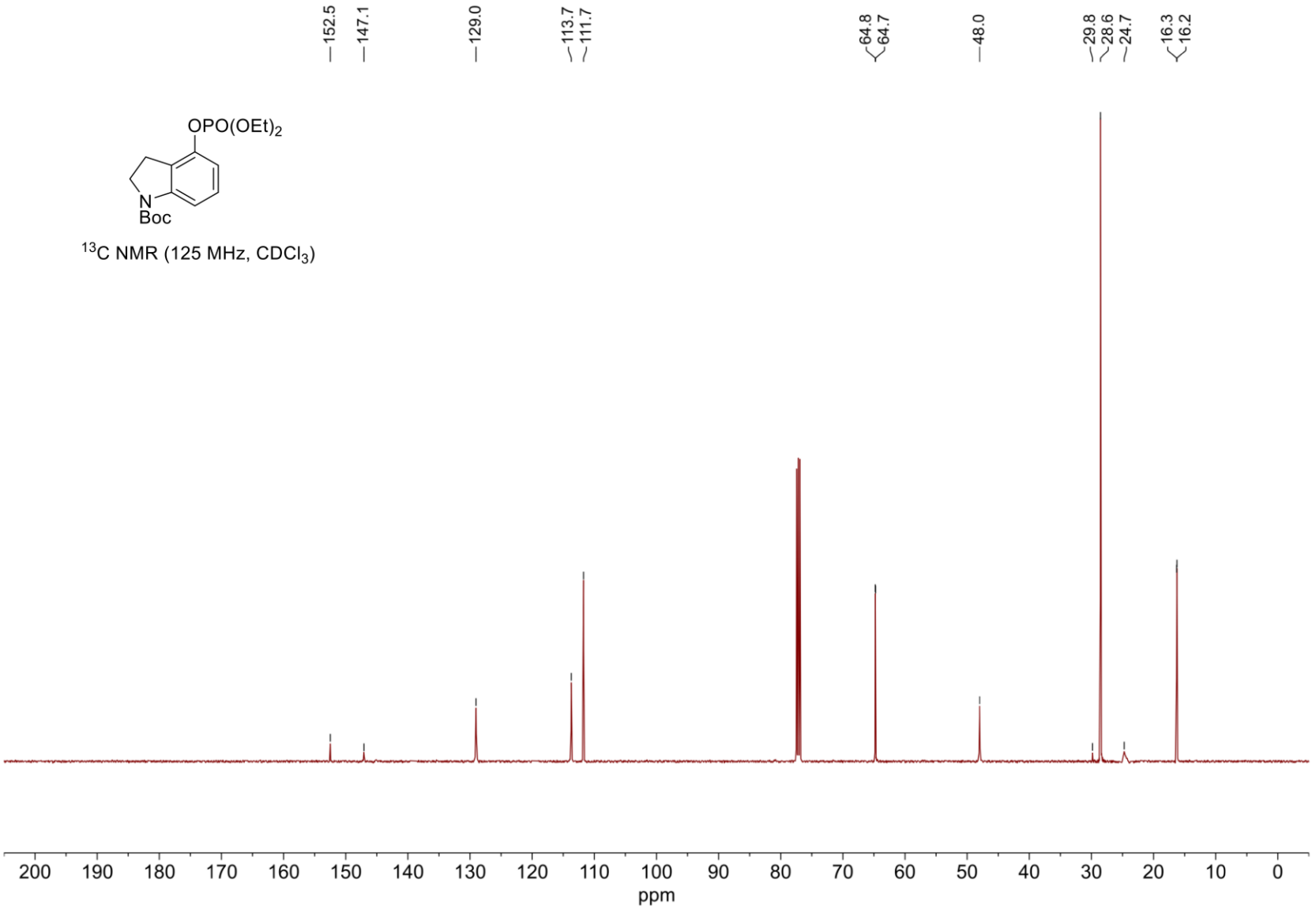
tert-Butyl 4-((diethoxyphosphoryl)oxy)indoline-1-carboxylate (S13)



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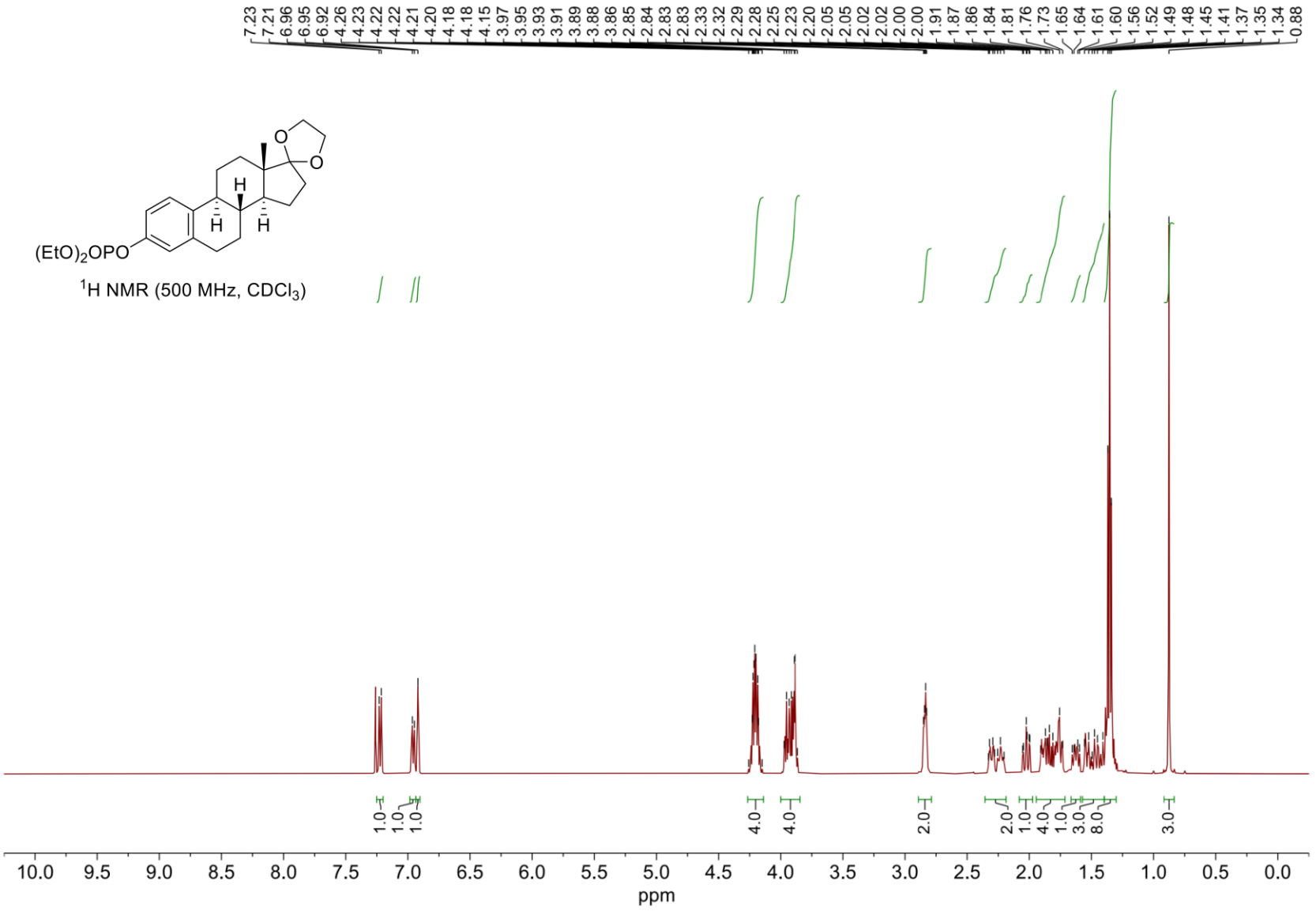
Diethyl ((8*R*,9*S*,13*S*,14*S*)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolan]-3-yl) phosphate (S14)



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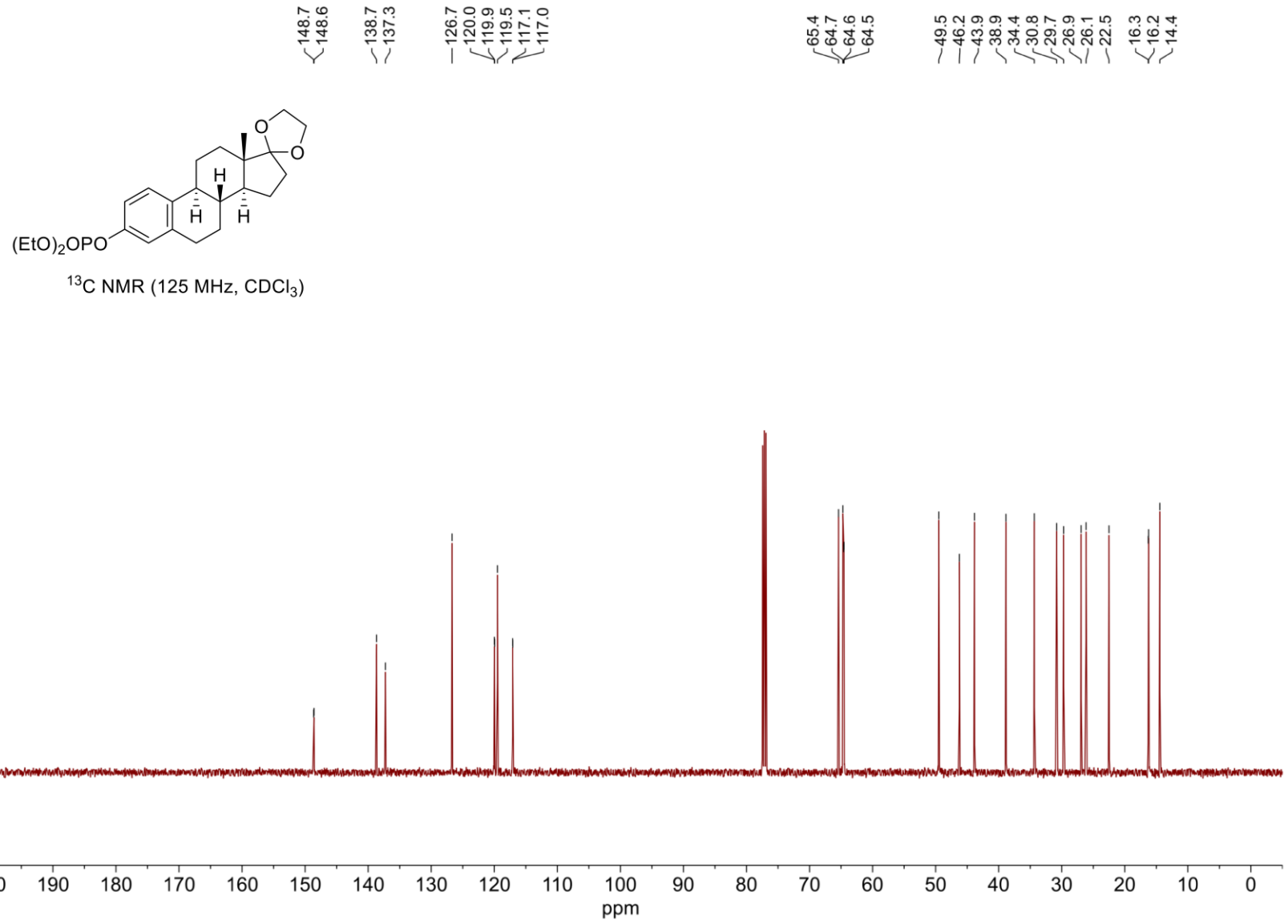
Diethyl ((8*R*,9*S*,13*S*,14*S*)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolan]-3-yl) phosphate (S14)



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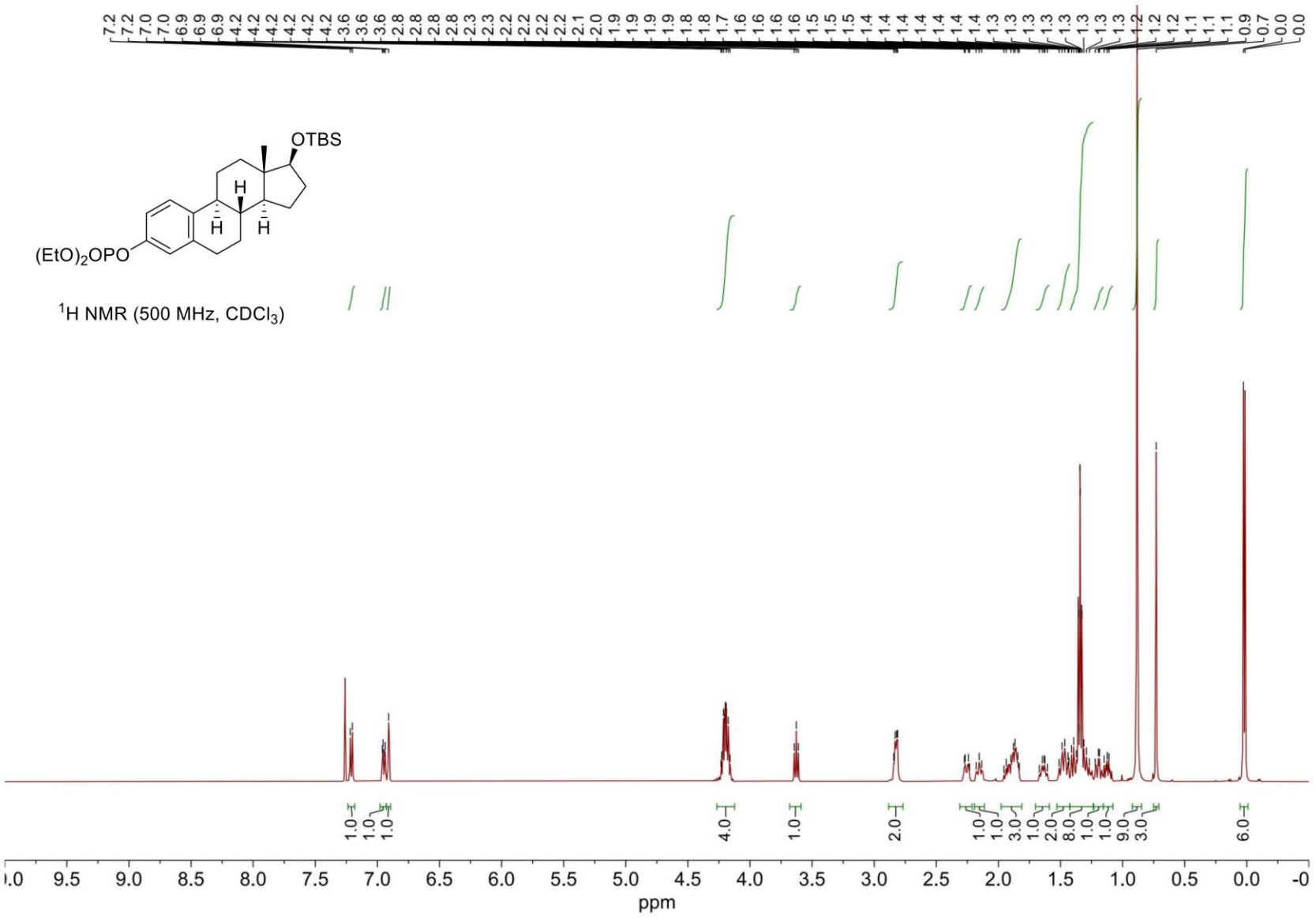
(8*R*,9*S*,13*S*,14*S*,17*S*)-17-((*tert*-Butyldimethylsilyl)oxy)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl diethyl phosphate (S15)



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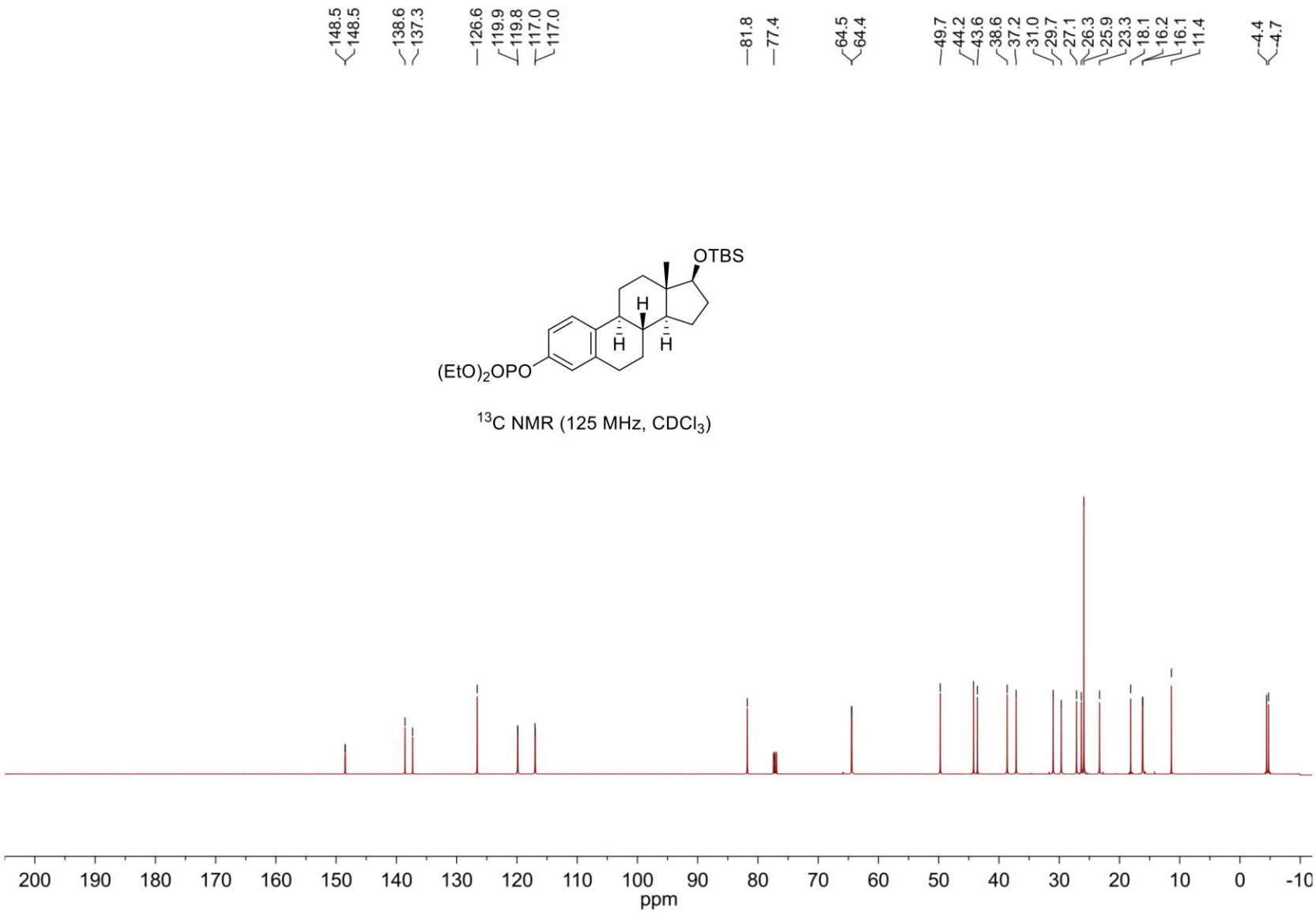
(8*R*,9*S*,13*S*,14*S*,17*S*)-17-((*tert*-Butyldimethylsilyl)oxy)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl diethyl phosphate (S15)



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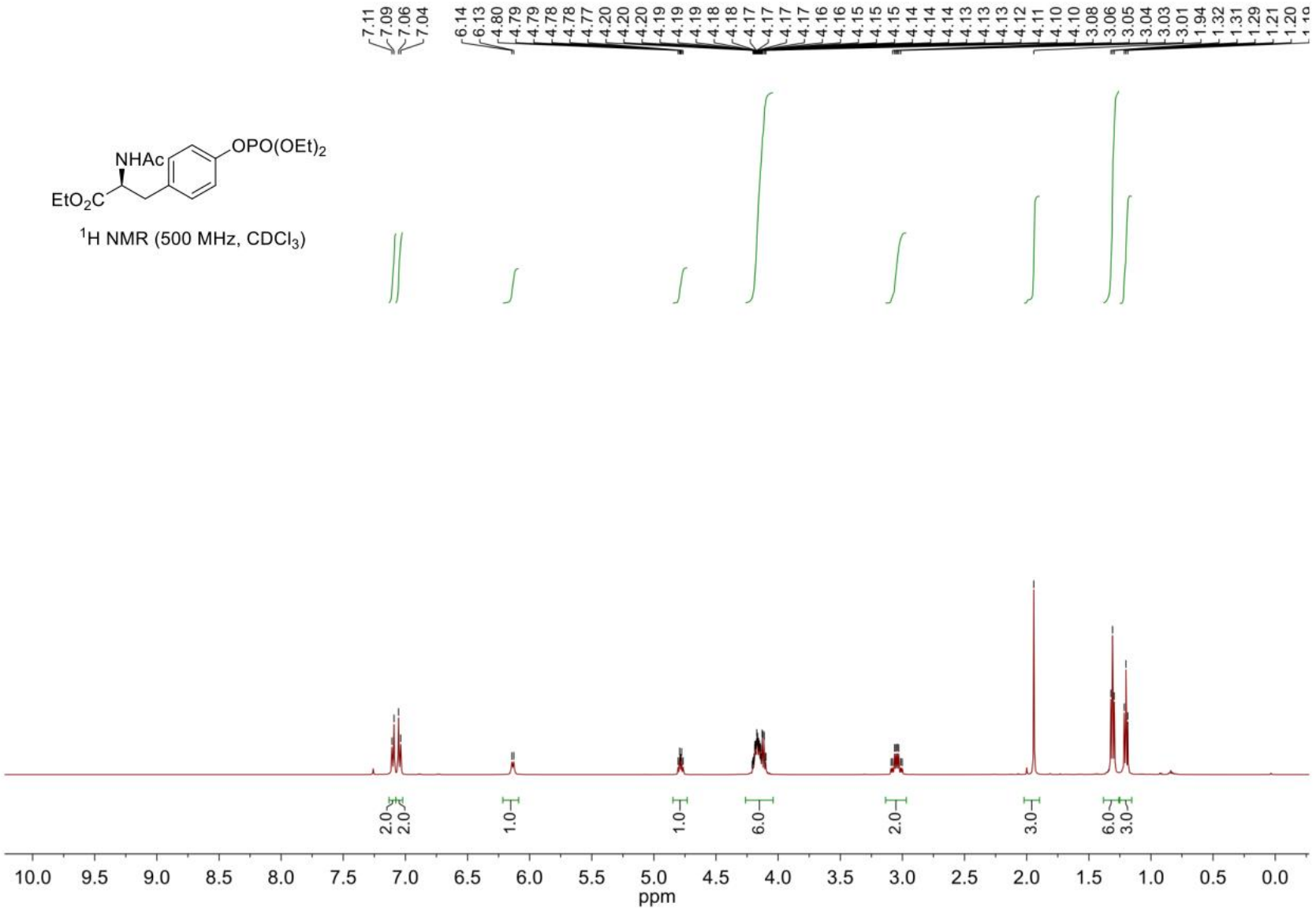
Ethyl (*S*)-2-acetamido-3-(4-((diethoxyphosphoryl)oxy)phenyl)propanoate (S16)



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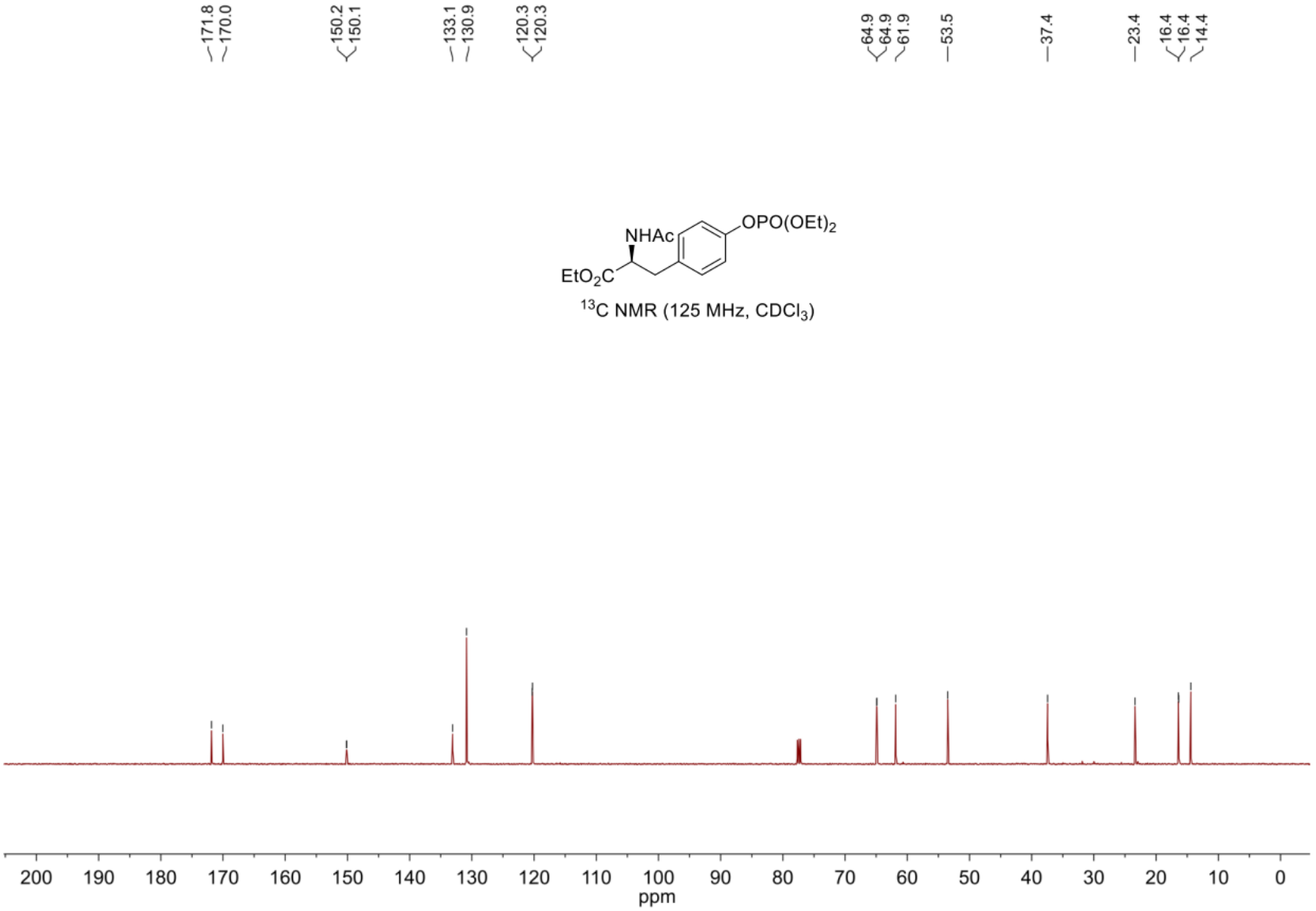
Ethyl (*S*)-2-acetamido-3-(4-((diethoxyphosphoryl)oxy)phenyl)propanoate (S16)



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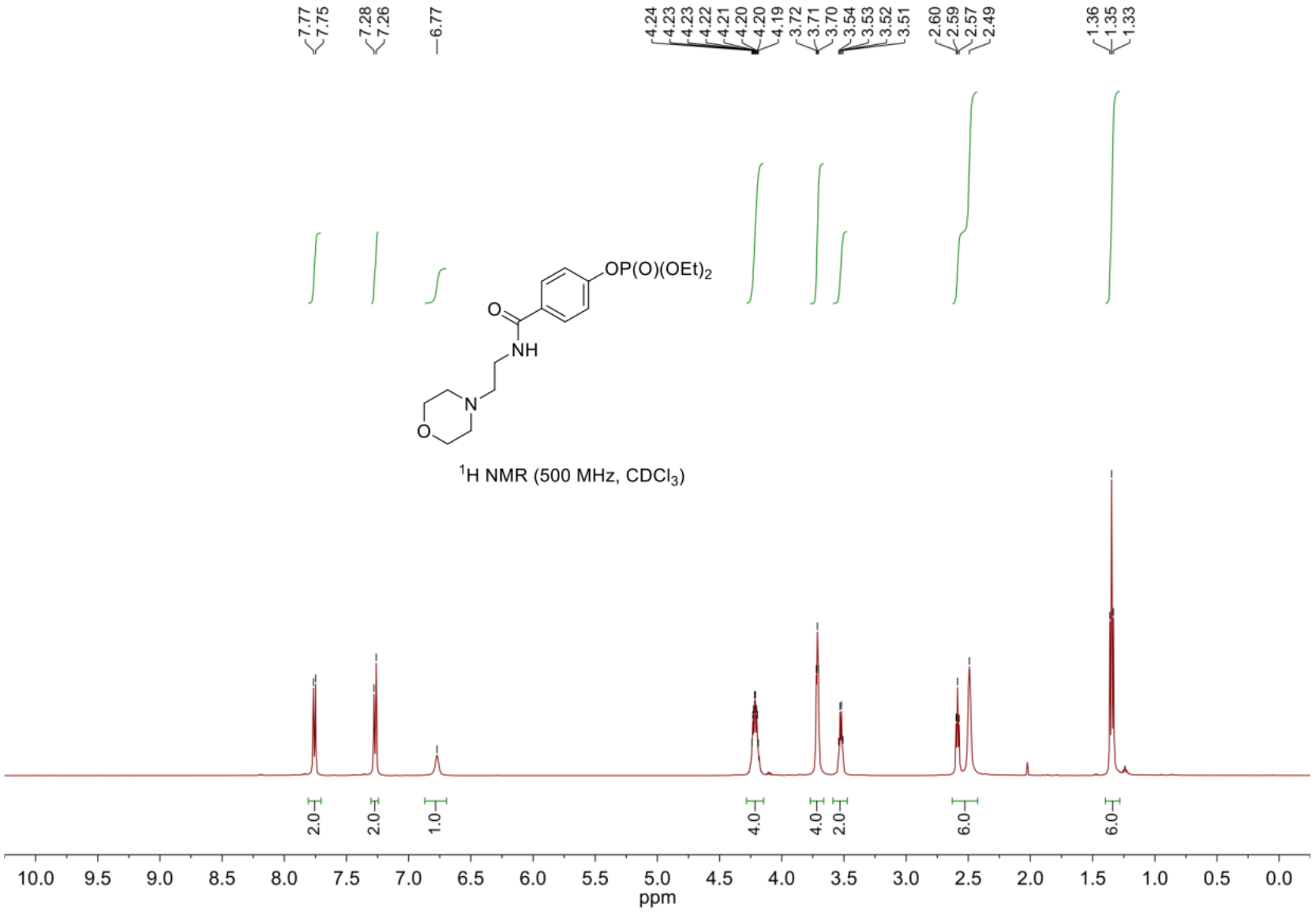
Diethyl (4-((2-morpholinoethyl)carbamoyl)phenyl) phosphate (S17)



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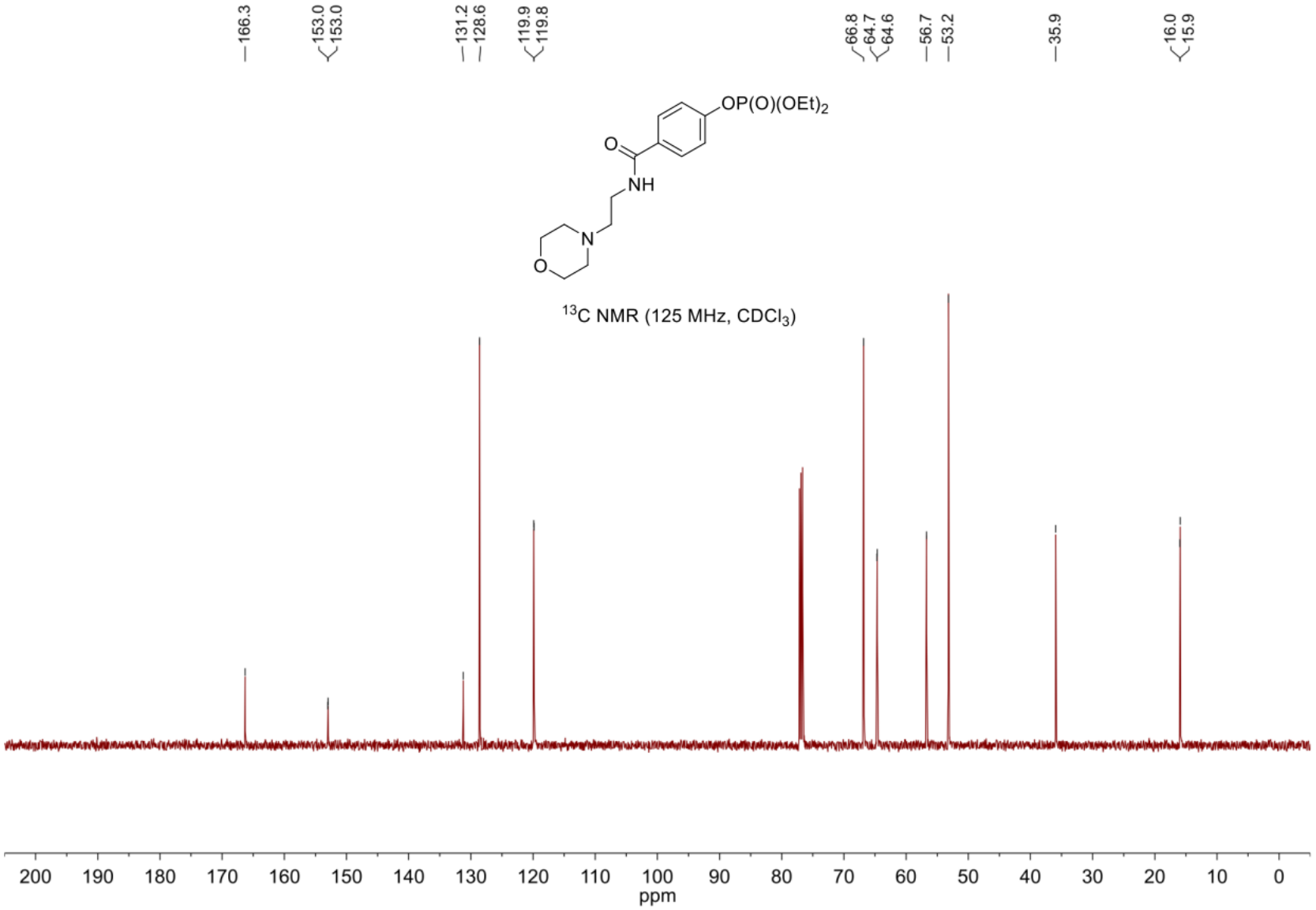
Diethyl (4-((2-morpholinoethyl)carbamoyl)phenyl) phosphate (S17)



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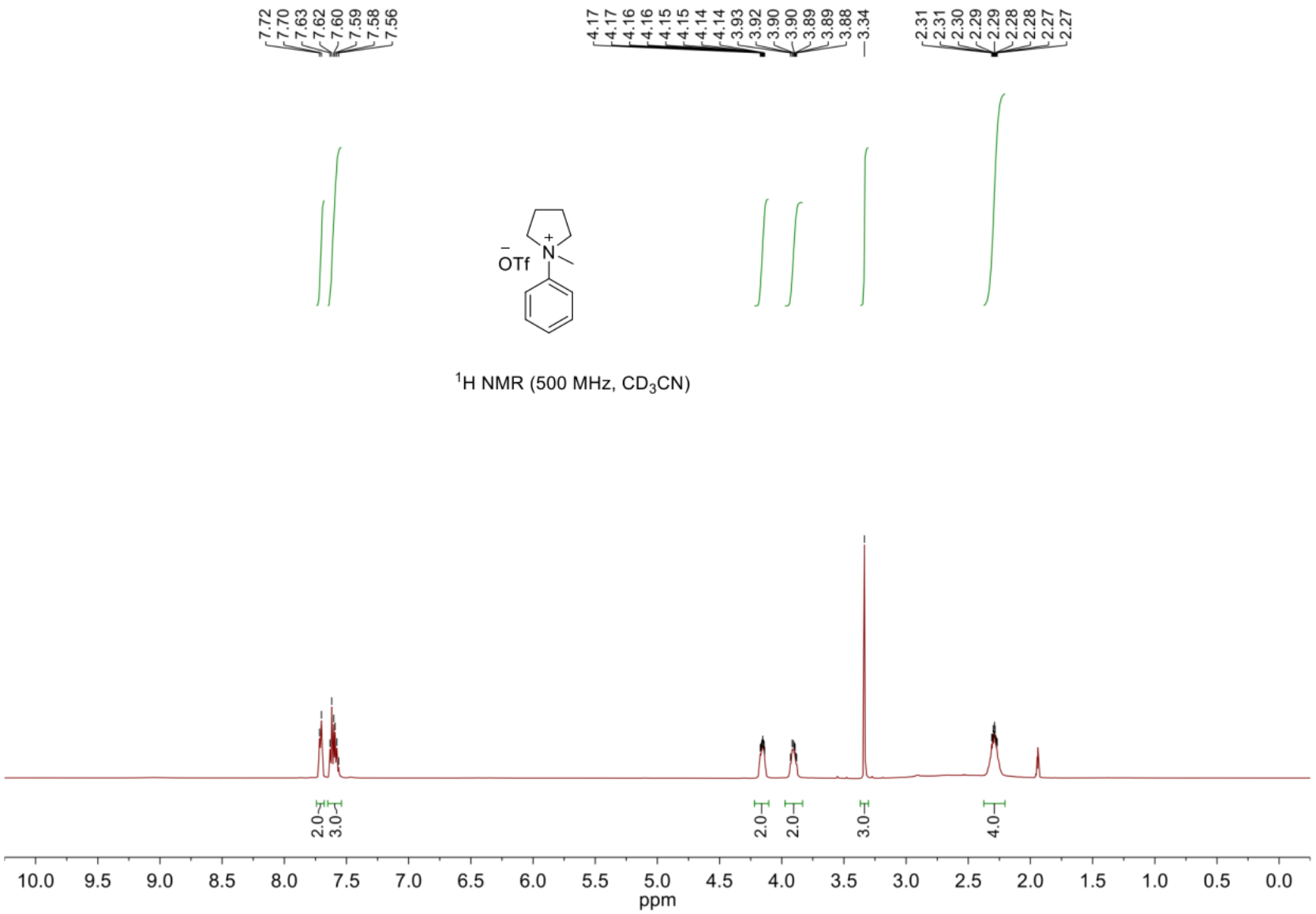
1-Methyl-1-phenylpyrrolidin-1-ium trifluoromethanesulfonate (S18)



^{1}H NMR (500 MHz, CD_3CN)

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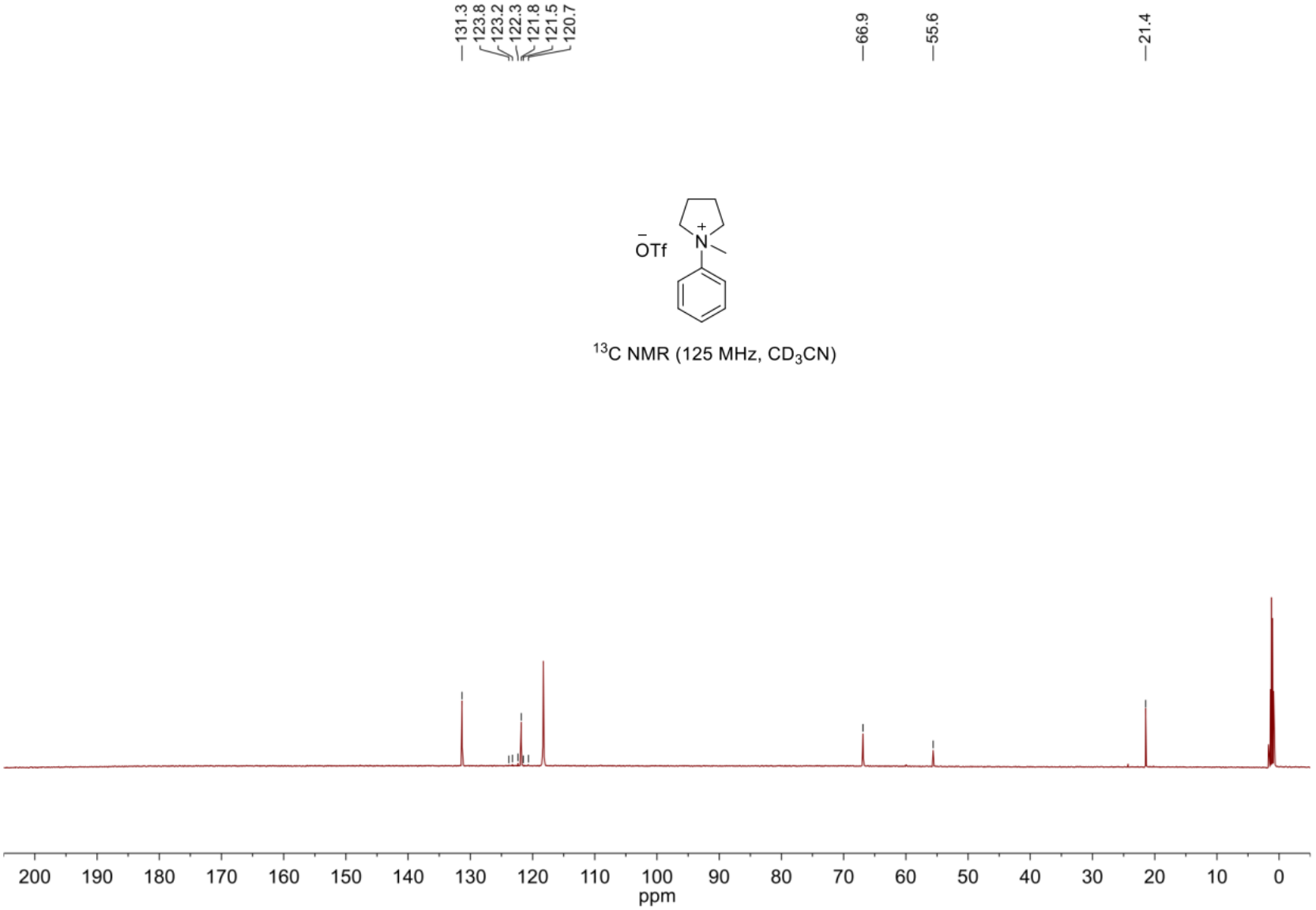
1-Methyl-1-phenylpyrrolidin-1-ium trifluoromethanesulfonate (S18)



^{13}C NMR (125 MHz, CD_3CN)

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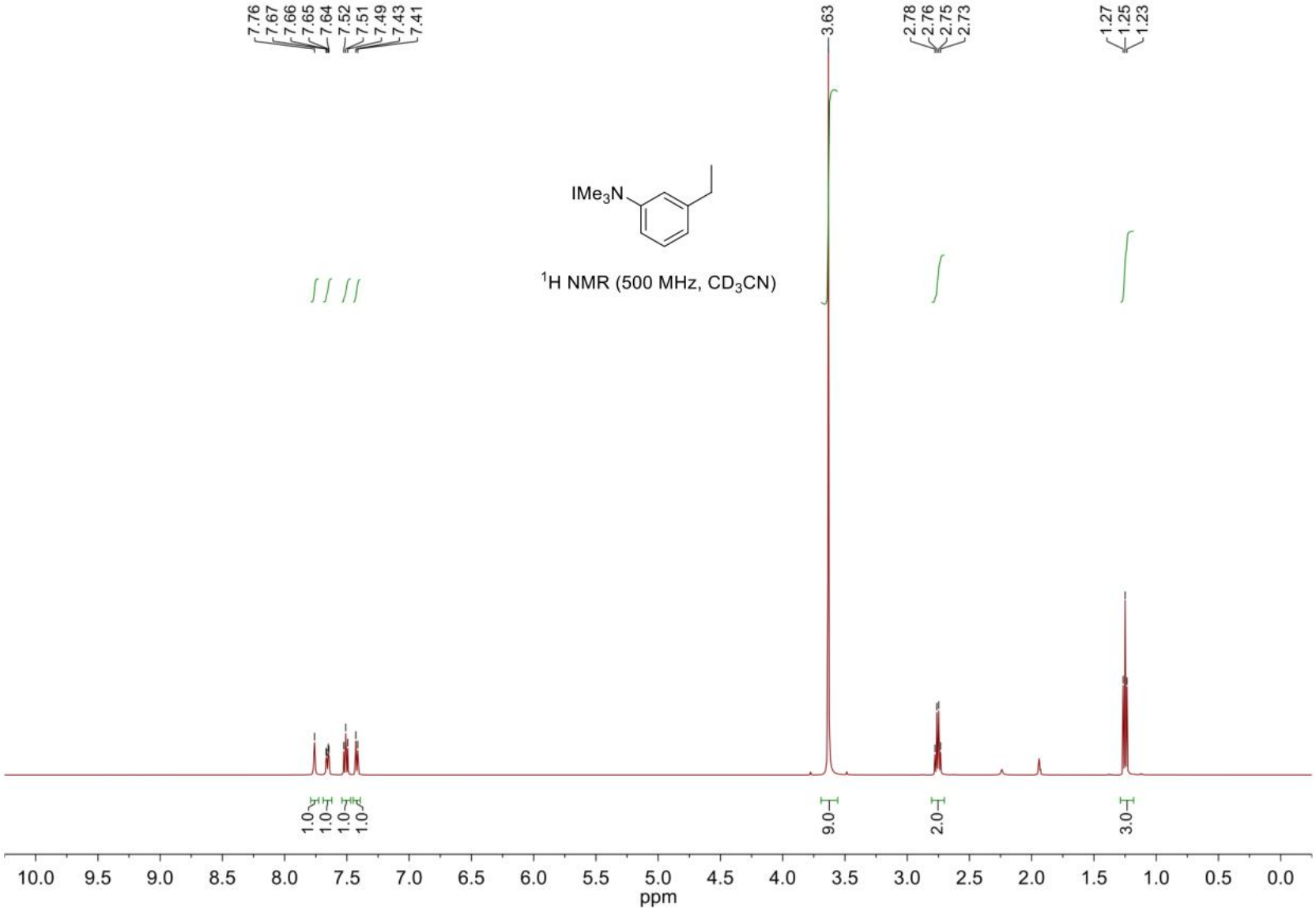
3-Ethyl-*N,N,N*-trimethylbenzenaminium (S19)



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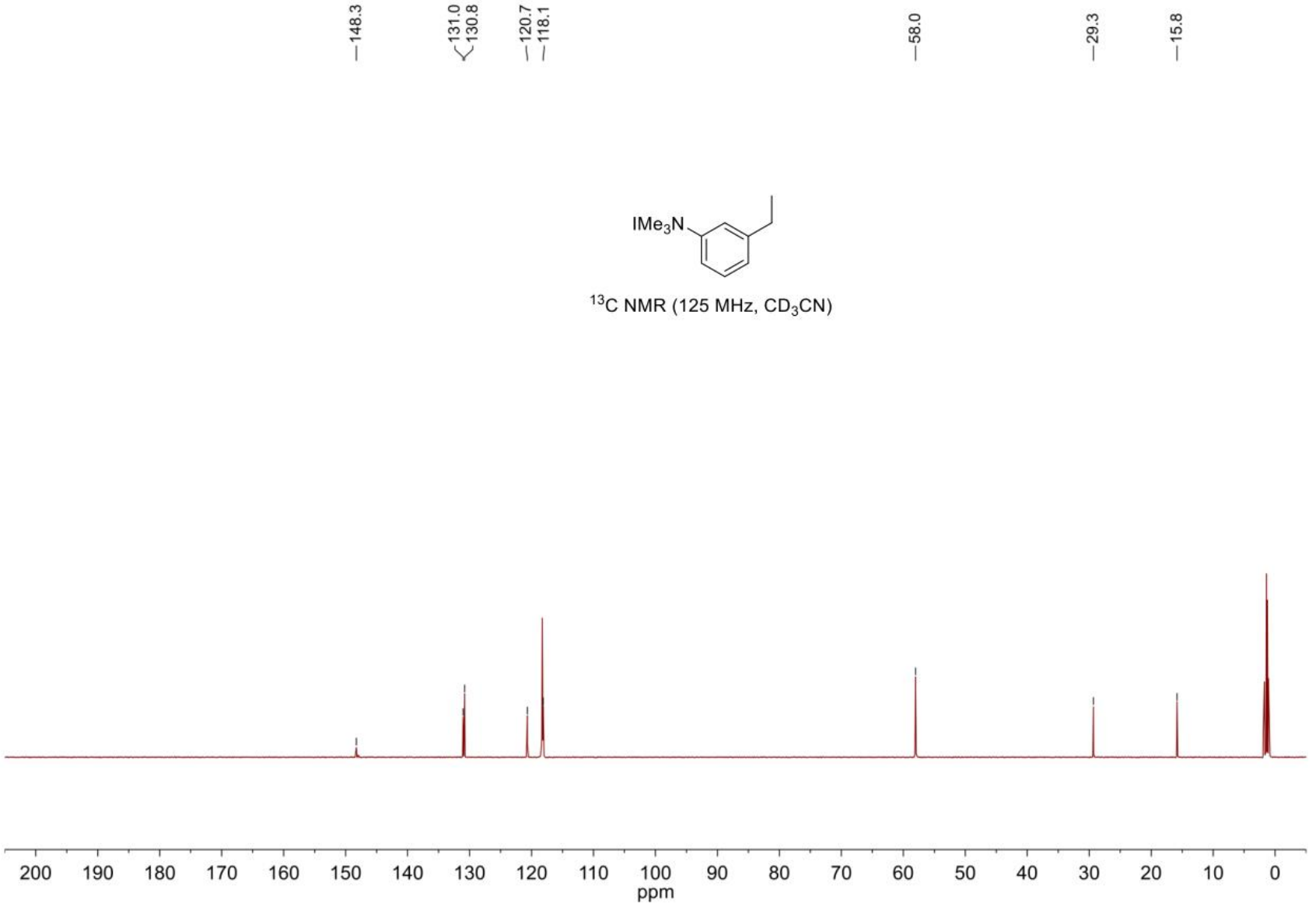
3-Ethyl-*N,N,N*-trimethylbenzenaminium (S19)



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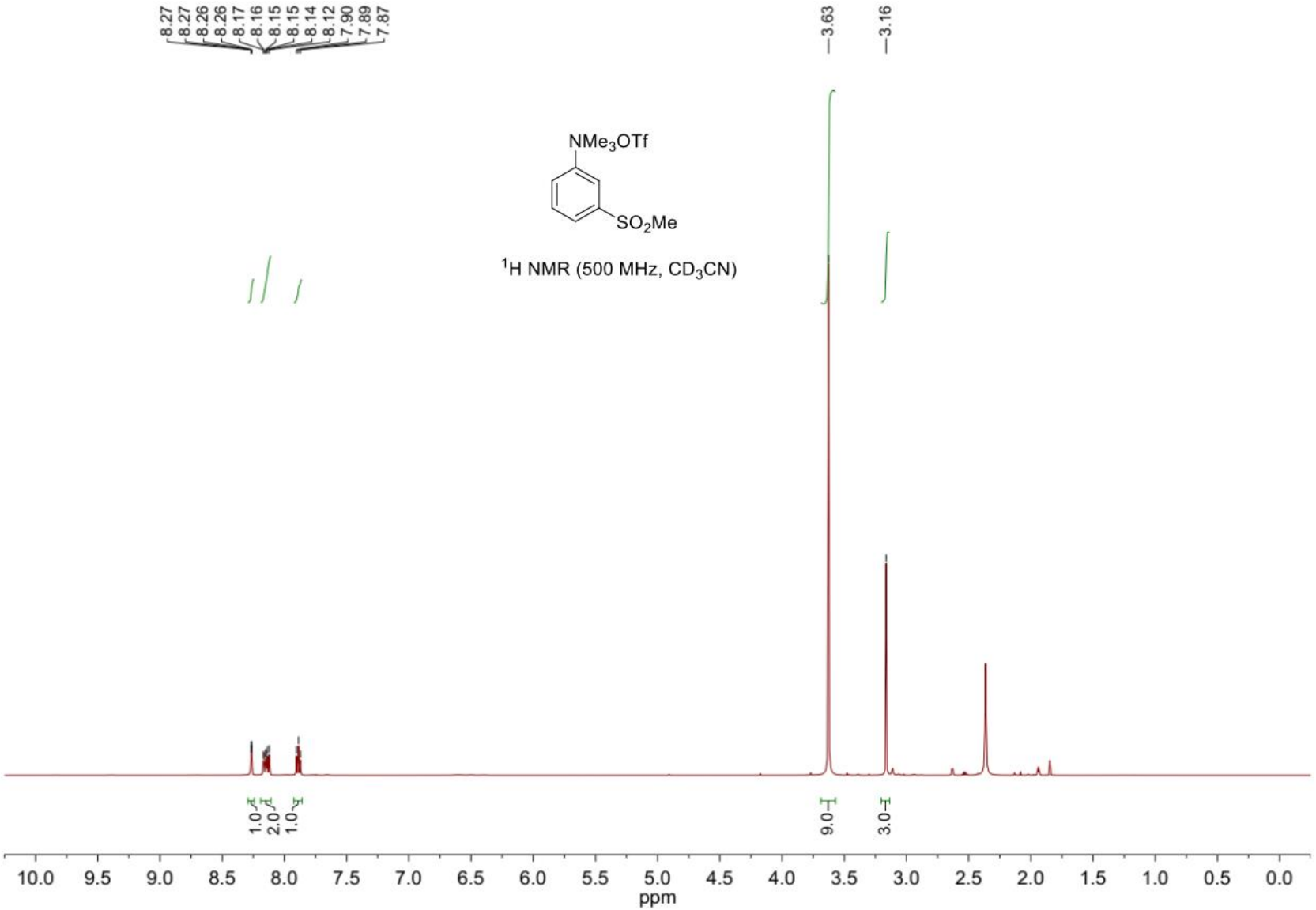
_N,N,N_-Trimethyl-3-(methylsulfonyl)benzenaminium trifluoromethanesulfonate (S20)



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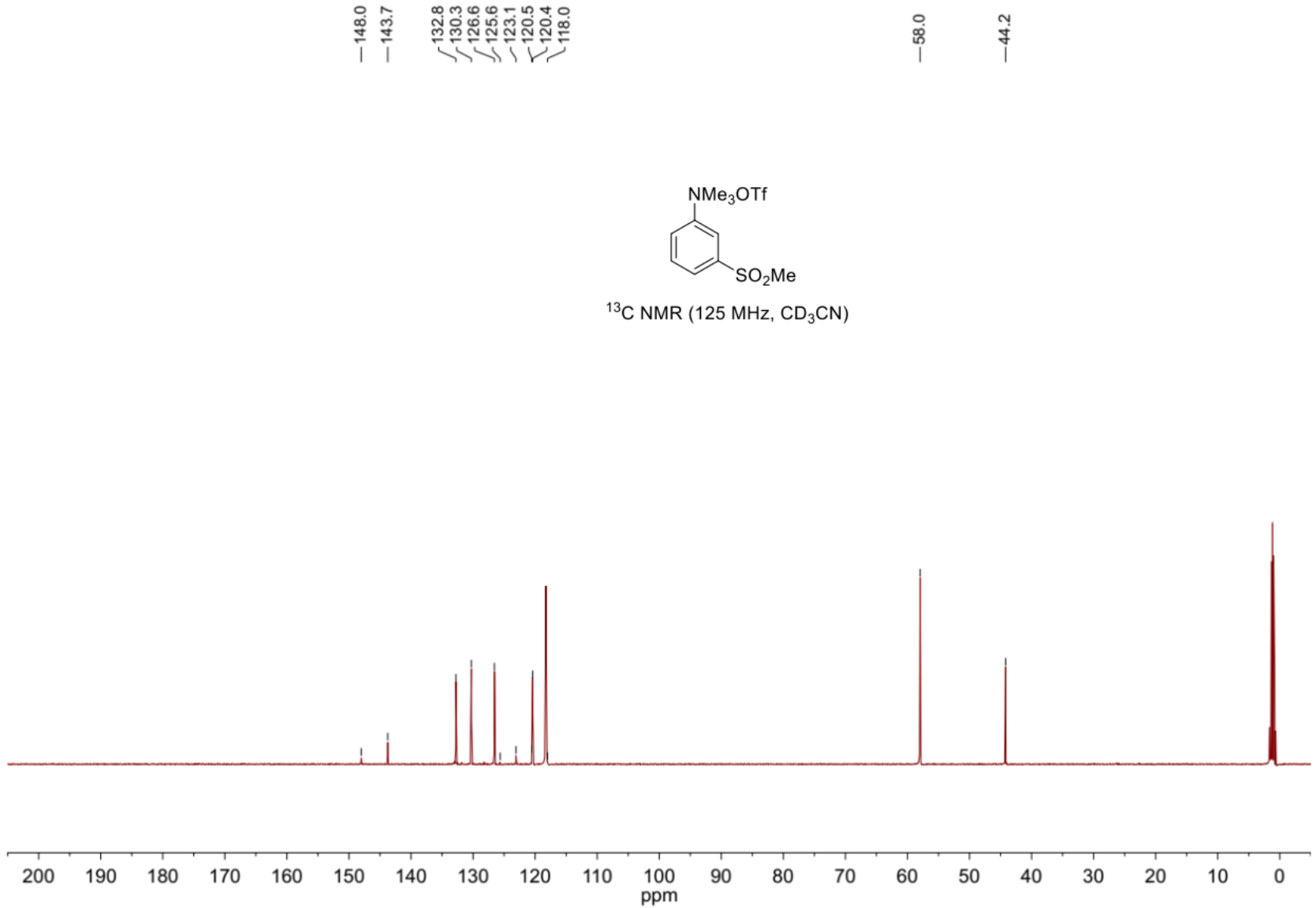
N,N,N-Trimethyl-3-(methylsulfonyl)benzenaminium trifluoromethanesulfonate (S20)



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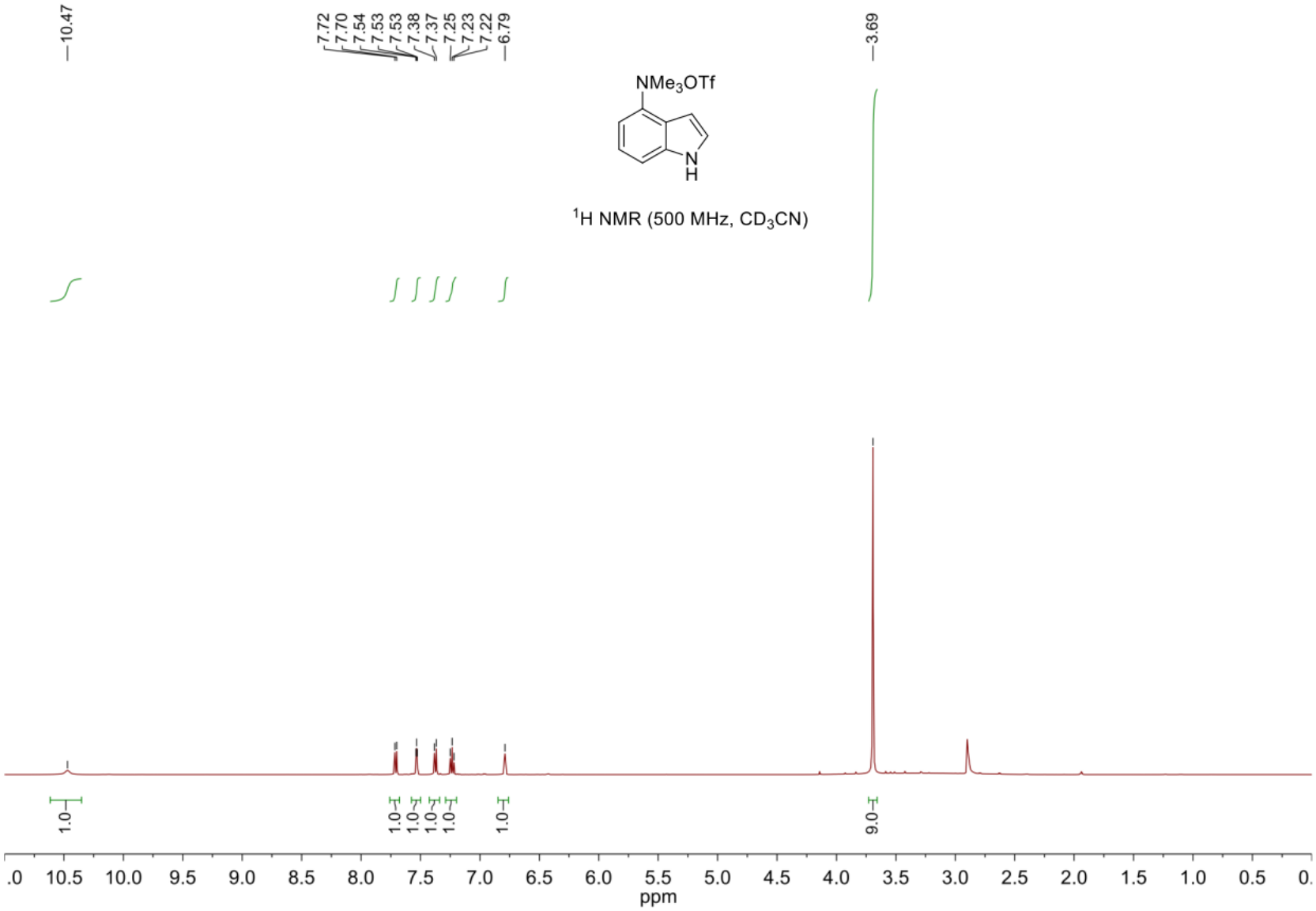
N,N,N-Trimethyl-1*H*-indol-4-aminium trifluoromethanesulfonate (S21)



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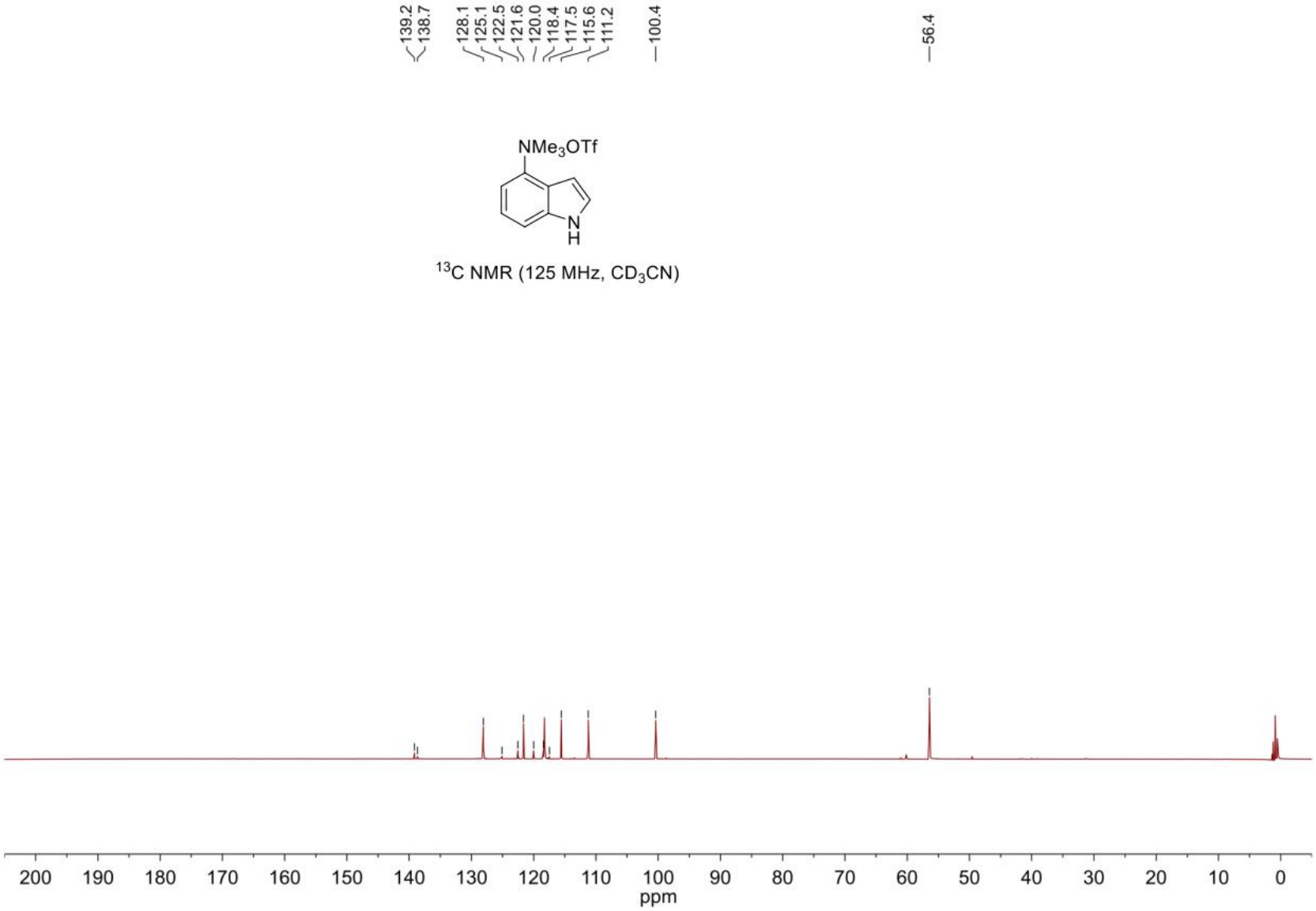
N,N,N-Trimethyl-1*H*-indol-4-aminium trifluoromethanesulfonate (S21)



^{13}C NMR (125 MHz, CD_3CN)

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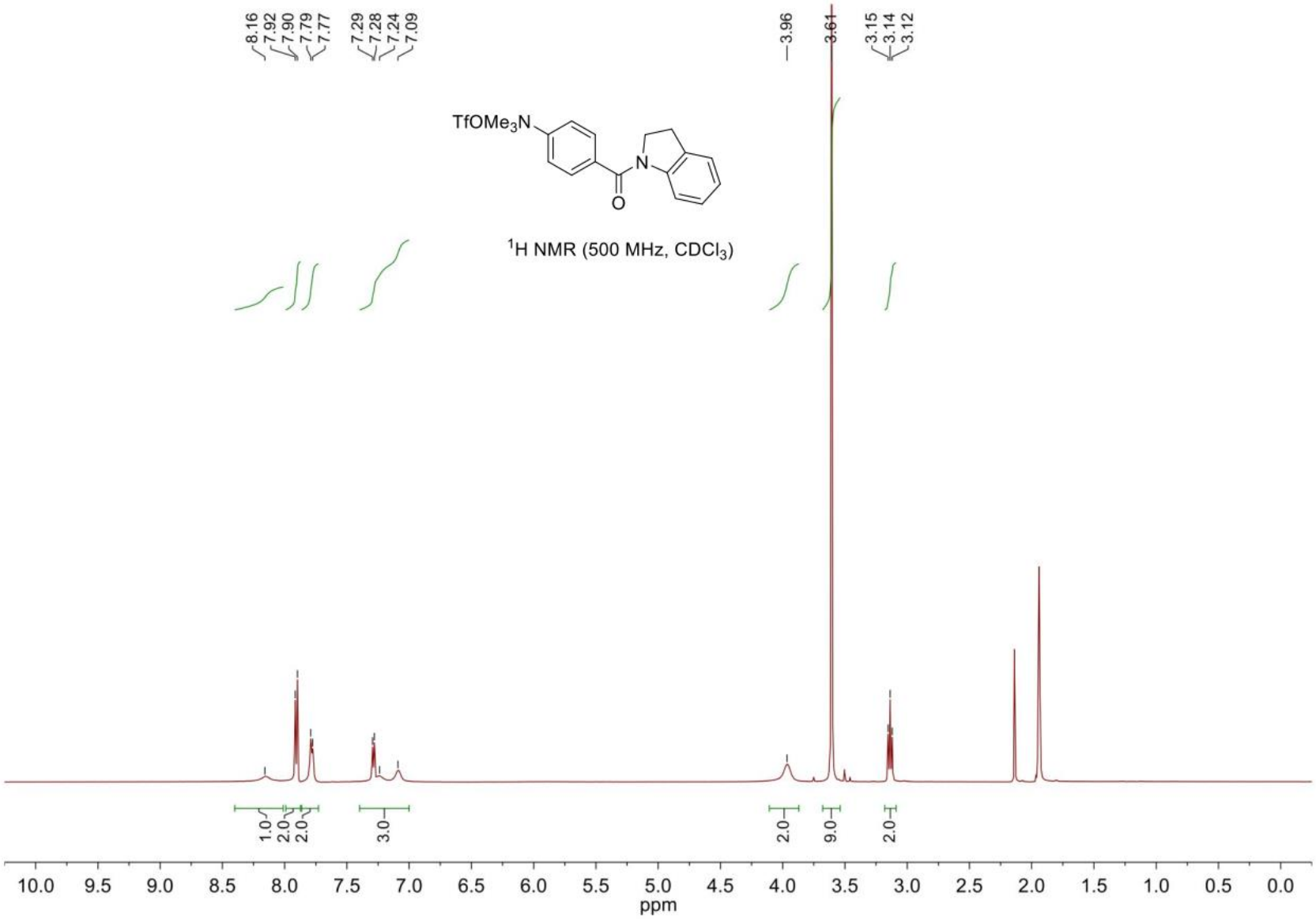
4-(Indoline-1-carbonyl)-*N,N,N*-trimethylbenzenaminium trifluoromethanesulfonate (S22)



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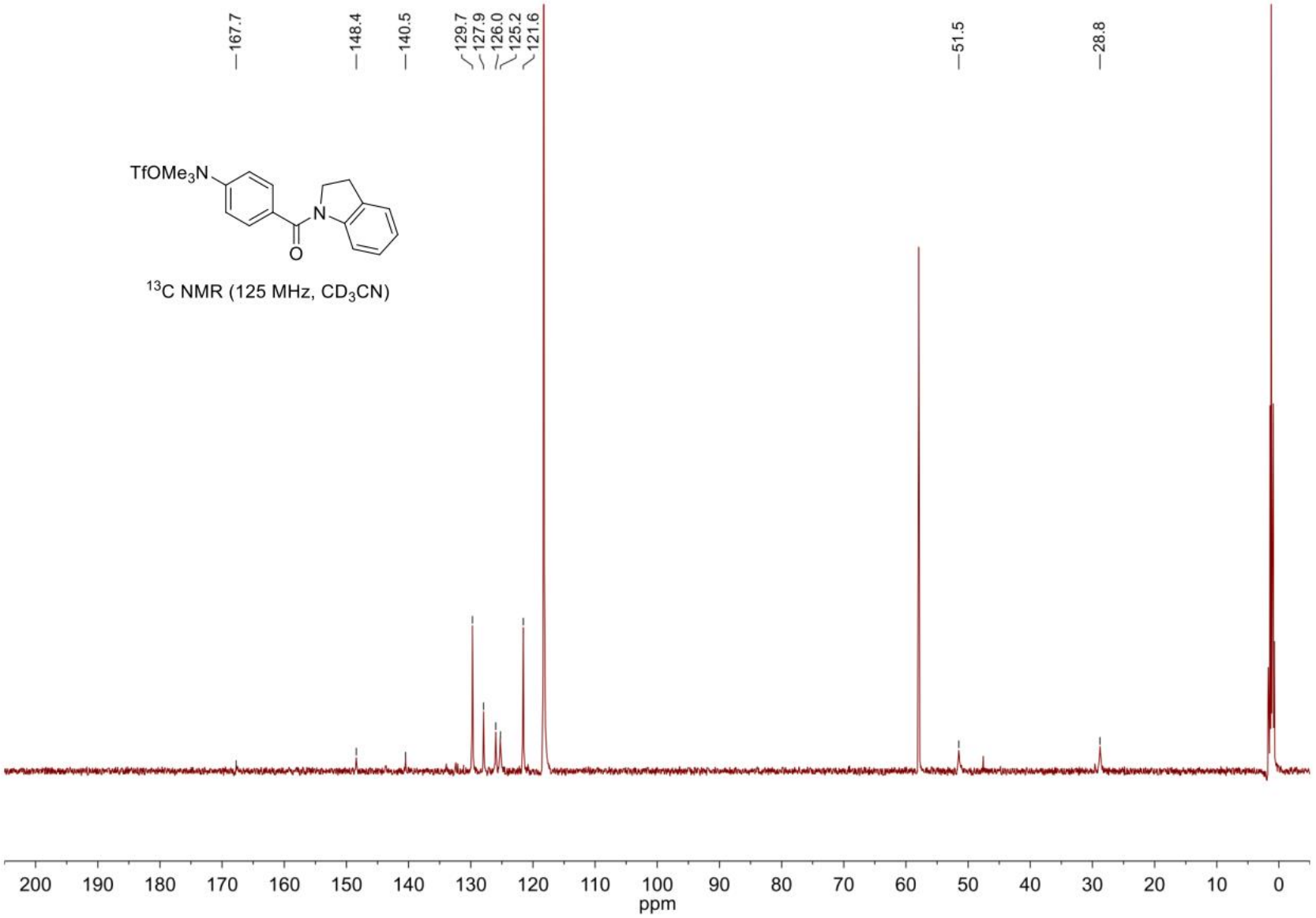
4-(Indoline-1-carbonyl)-*N,N,N*-trimethylbenzenaminium trifluoromethanesulfonate (S22)



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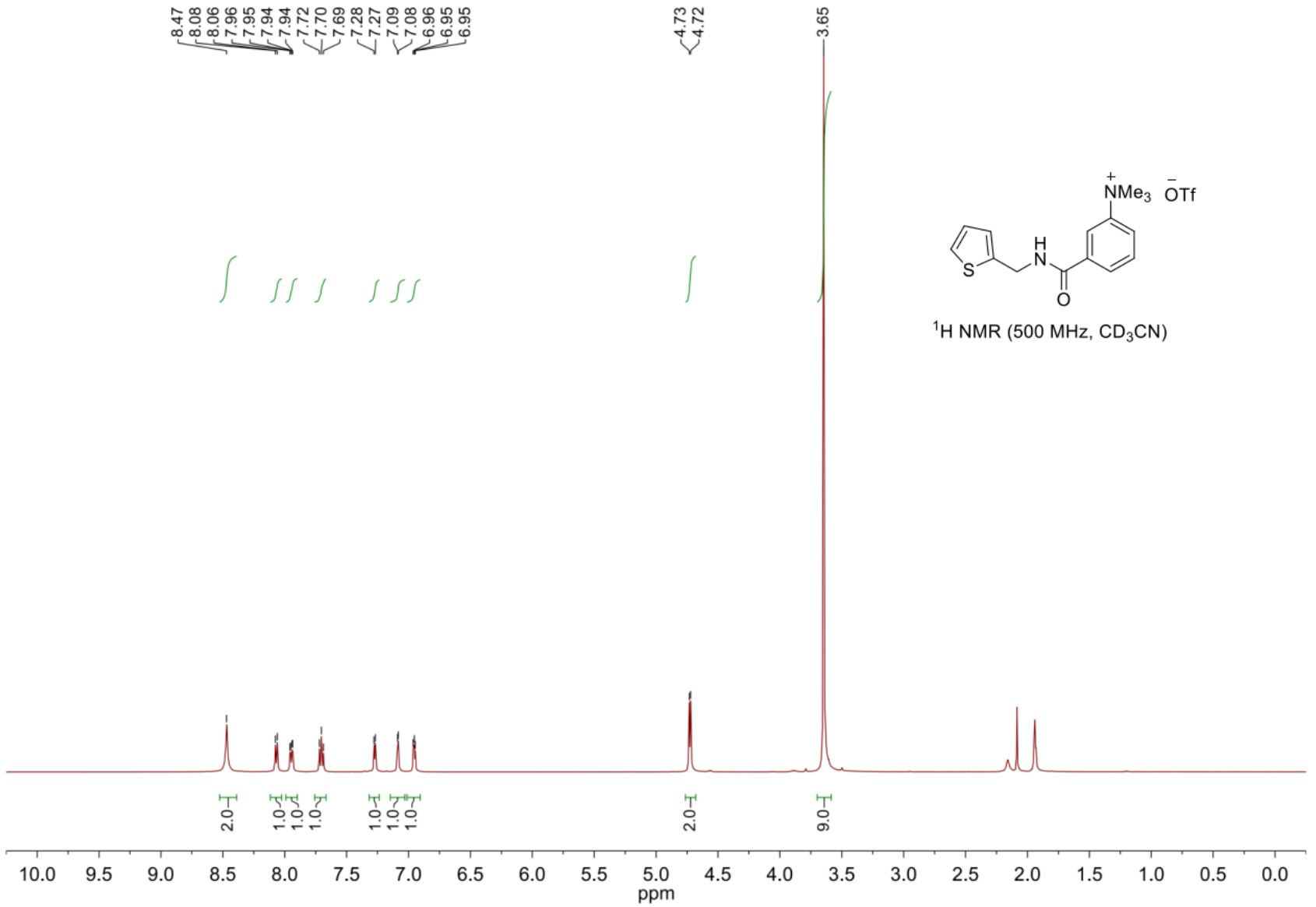
_N,N,N_-Trimethyl-3-((thiophen-2-ylmethyl)carbamoyl)benzenaminium trifluoromethanesulfonate (S23)



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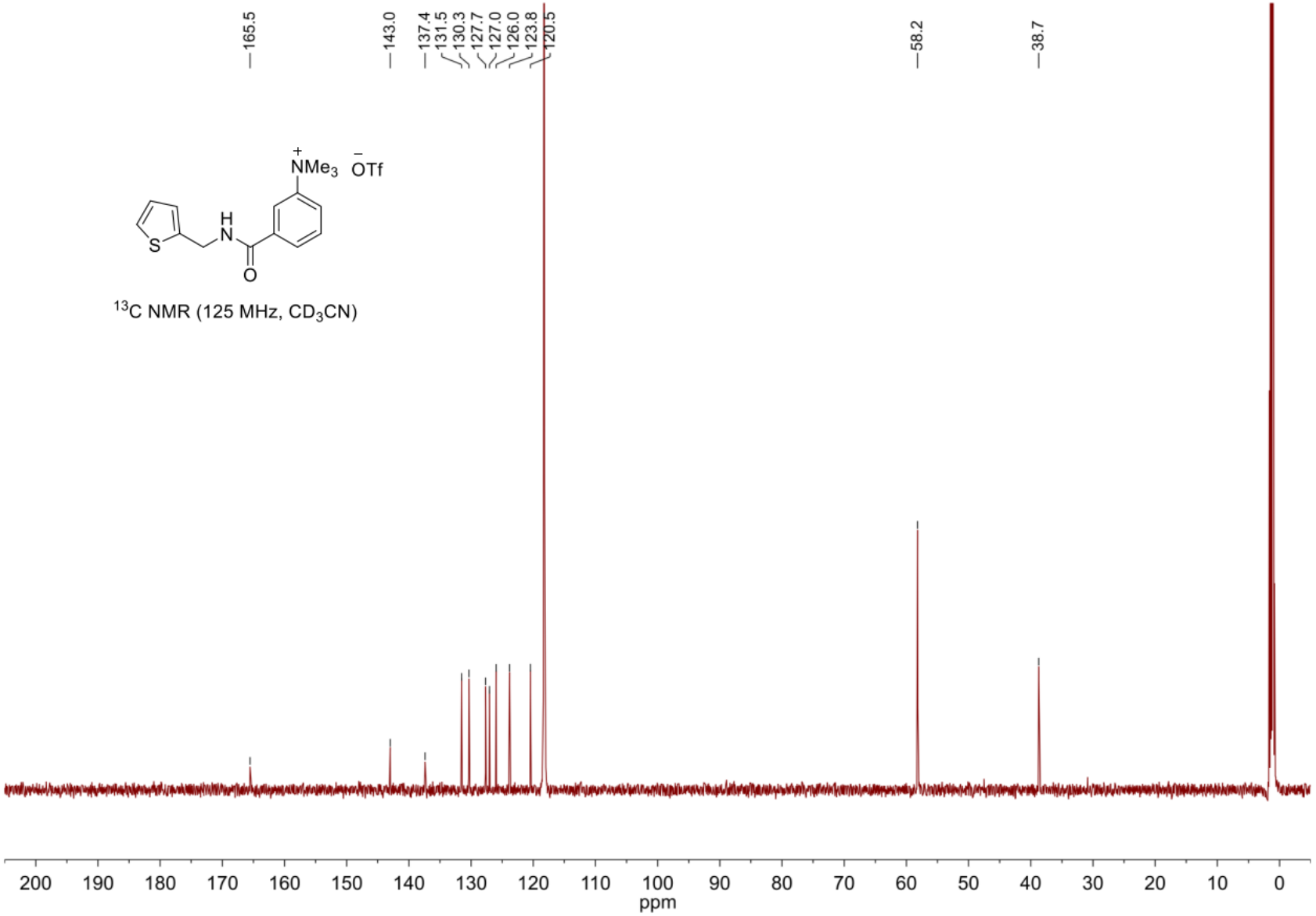
_N,N,N_-Trimethyl-3-((thiophen-2-ylmethyl)carbamoyl)benzenaminium trifluoromethanesulfonate (S23)



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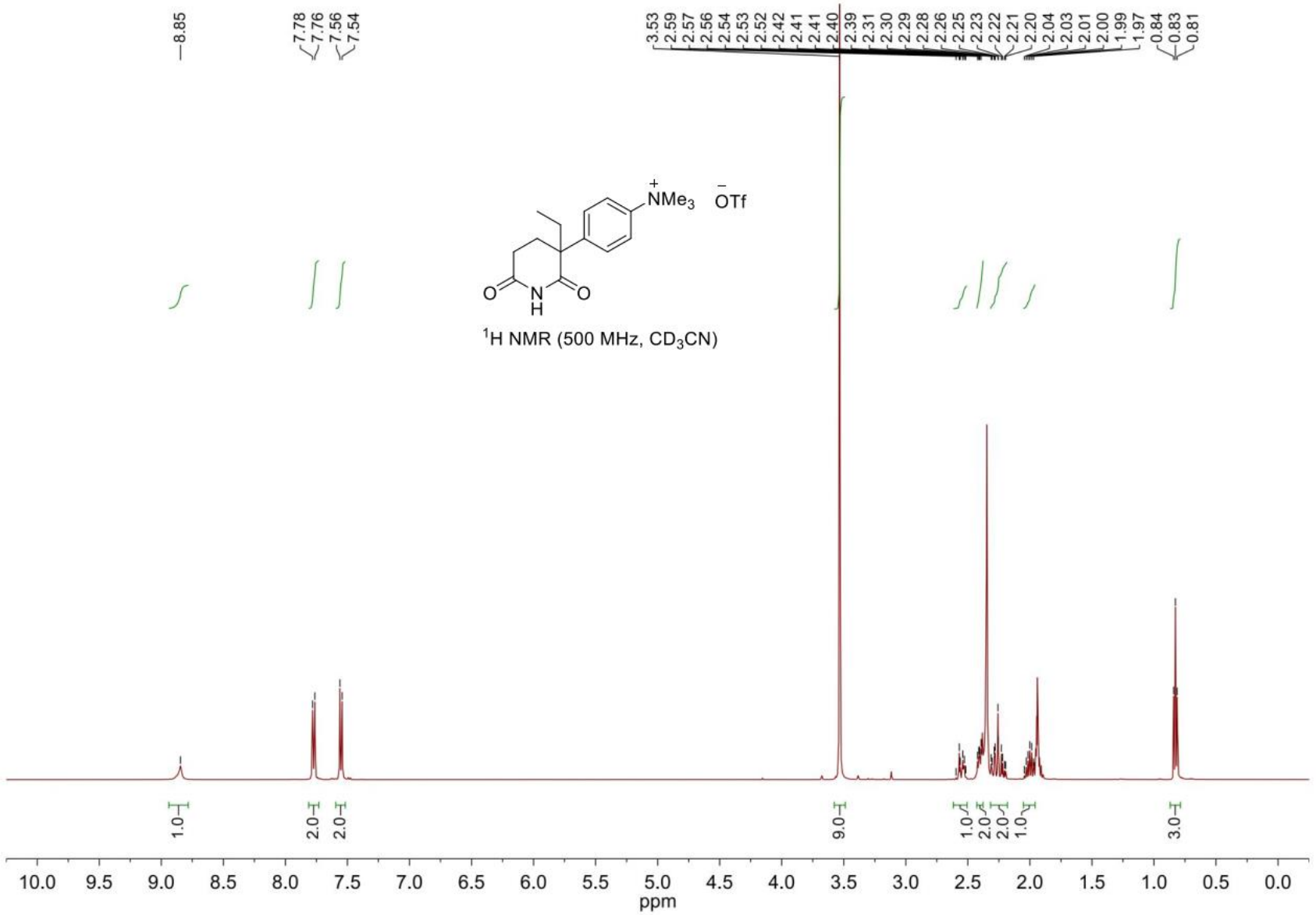
4-(3-Ethyl-2,6-dioxopiperidin-3-yl)-*N,N,N*-trimethylbenzenaminium trifluoromethanesulfonate (S24)



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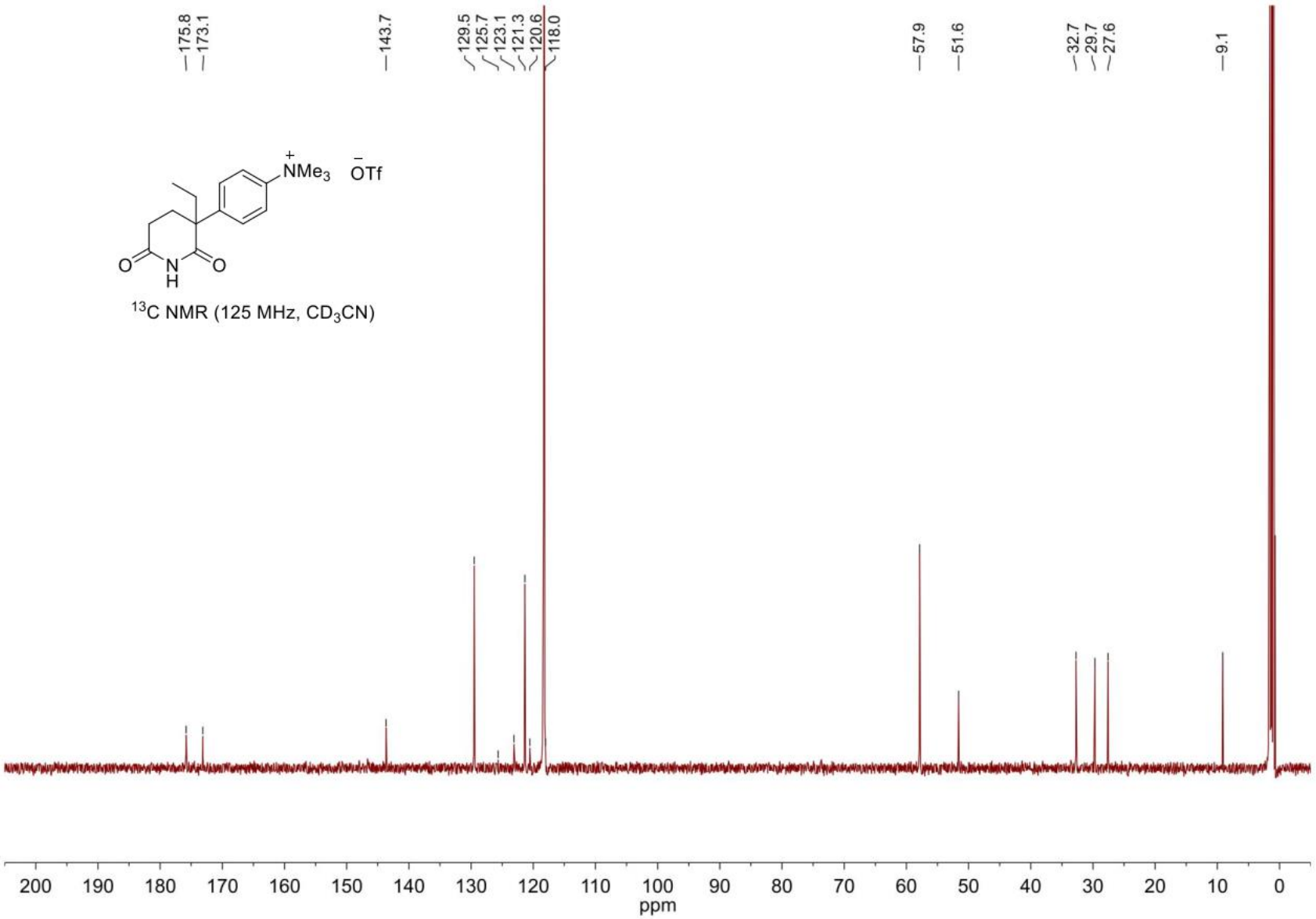
4-(3-Ethyl-2,6-dioxopiperidin-3-yl)-*N,N,N*-trimethylbenzenaminium trifluoromethanesulfonate (S24)



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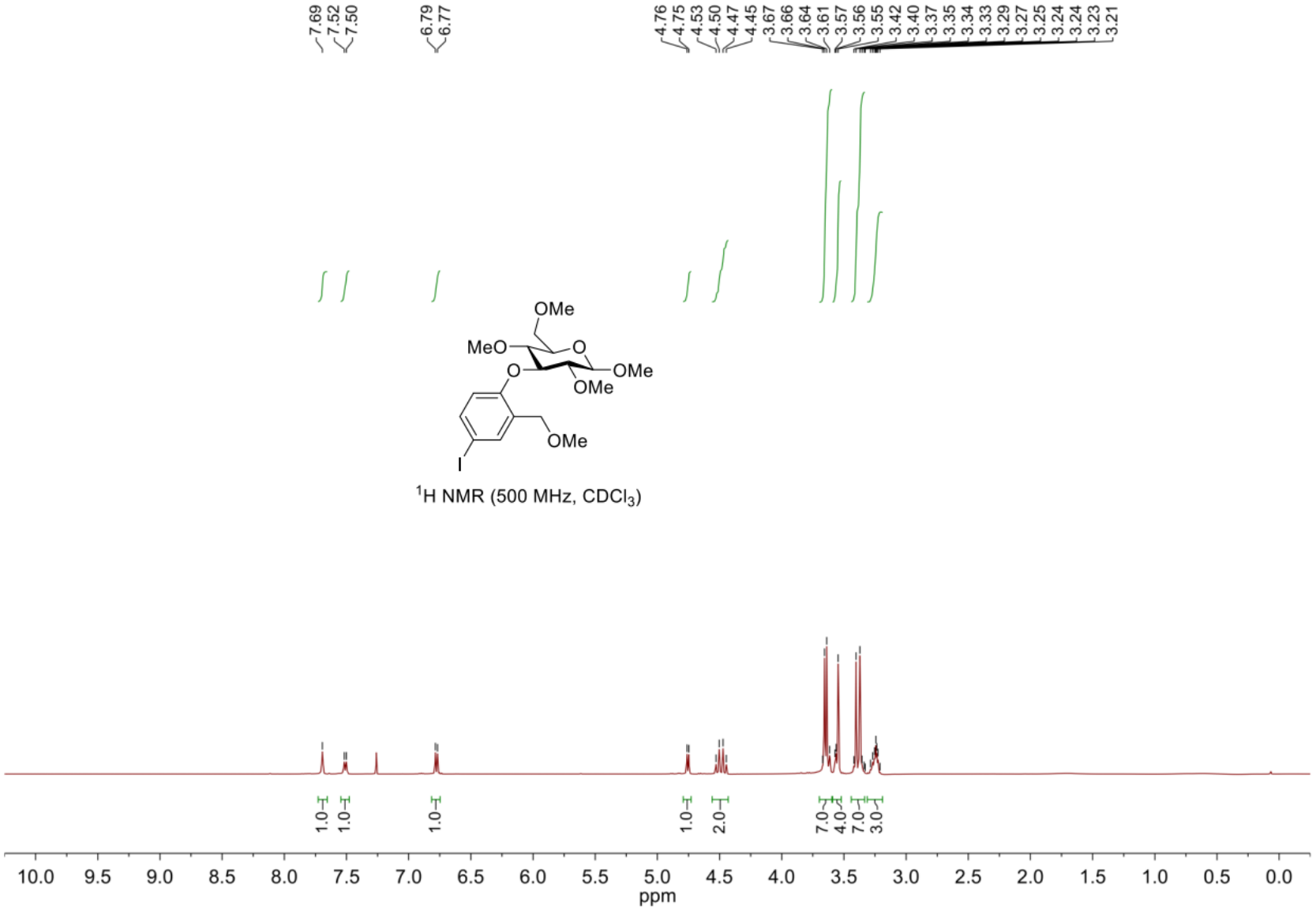
(2*R*,3*R*,4*S*,5*R*,6*R*)-4-(4-Iodo-2-(methoxymethyl)phenoxy)-2,3,5-trimethoxy-6-(methoxymethyl)tetrahydro-2*H*-pyran (S25)



^{1}H NMR (500 MHz, $CDCl_3$)

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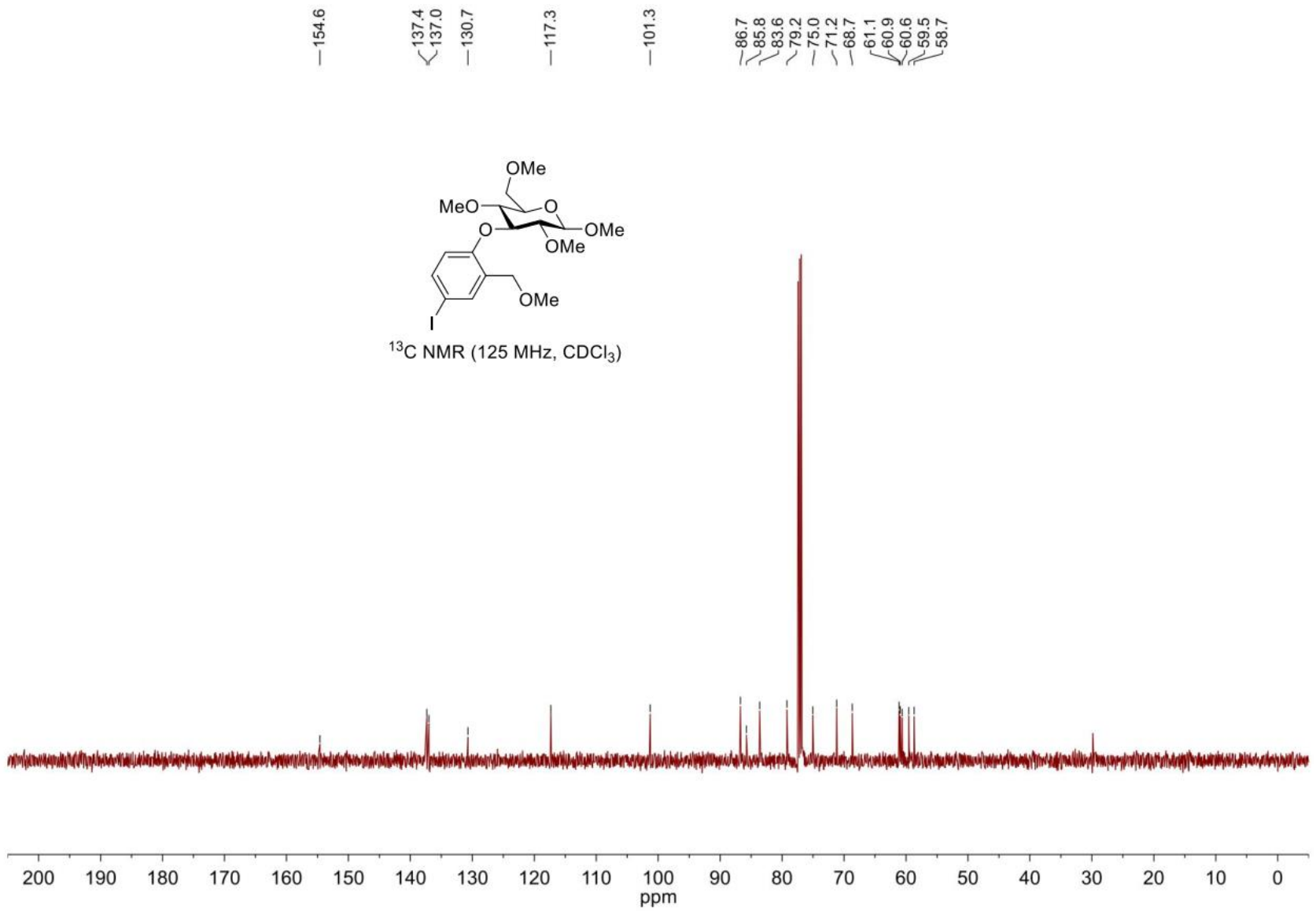
(2*R*,3*R*,4*S*,5*R*,6*R*)-4-(4-Iodo-2-(methoxymethyl)phenoxy)-2,3,5-trimethoxy-6-(methoxymethyl)tetrahydro-2*H*-pyran (S25)



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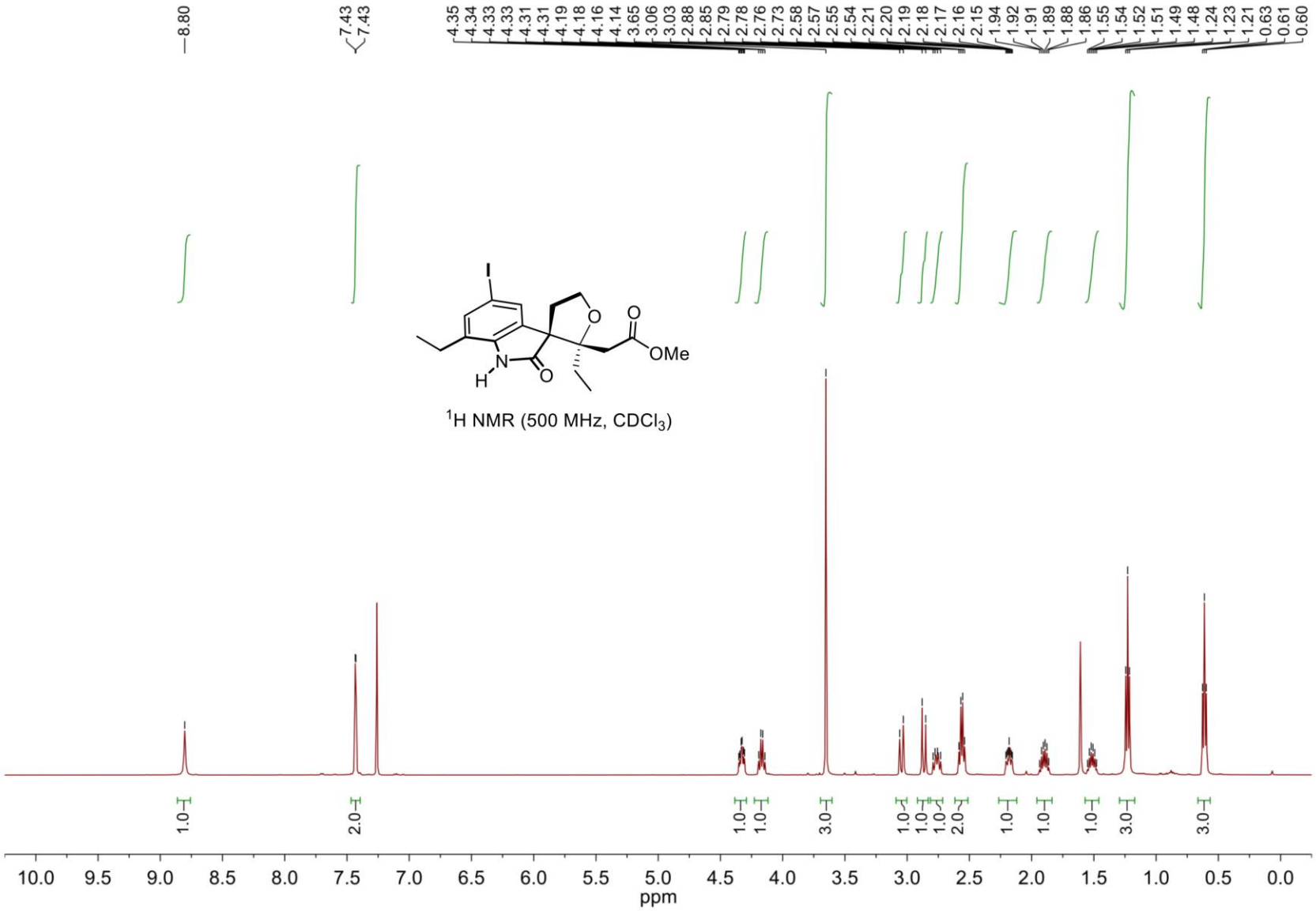
Methyl 2-((2*S*,3*R*)-2,7'-diethyl-5'-iodo-2'-oxo-4,5-dihydro-2*H*-spiro[furan-3,3'-indolin]-2-yl)acetate (S26)



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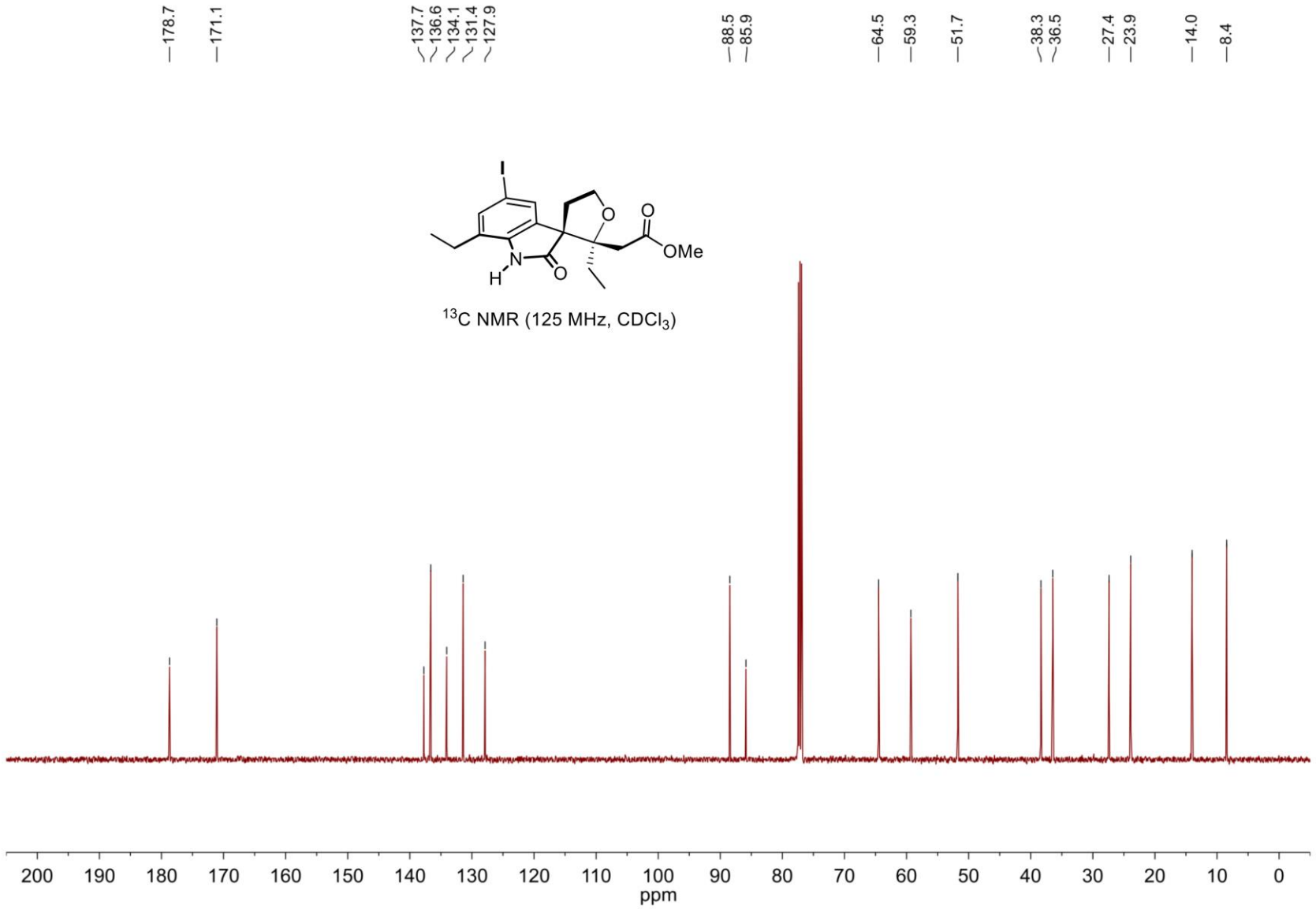
Methyl 2-((2*S*,3*R*)-2,7'-diethyl-5'-iodo-2'-oxo-4,5-dihydro-2*H*-spiro[furan-3,3'-indolin]-2-yl)acetate (S26)



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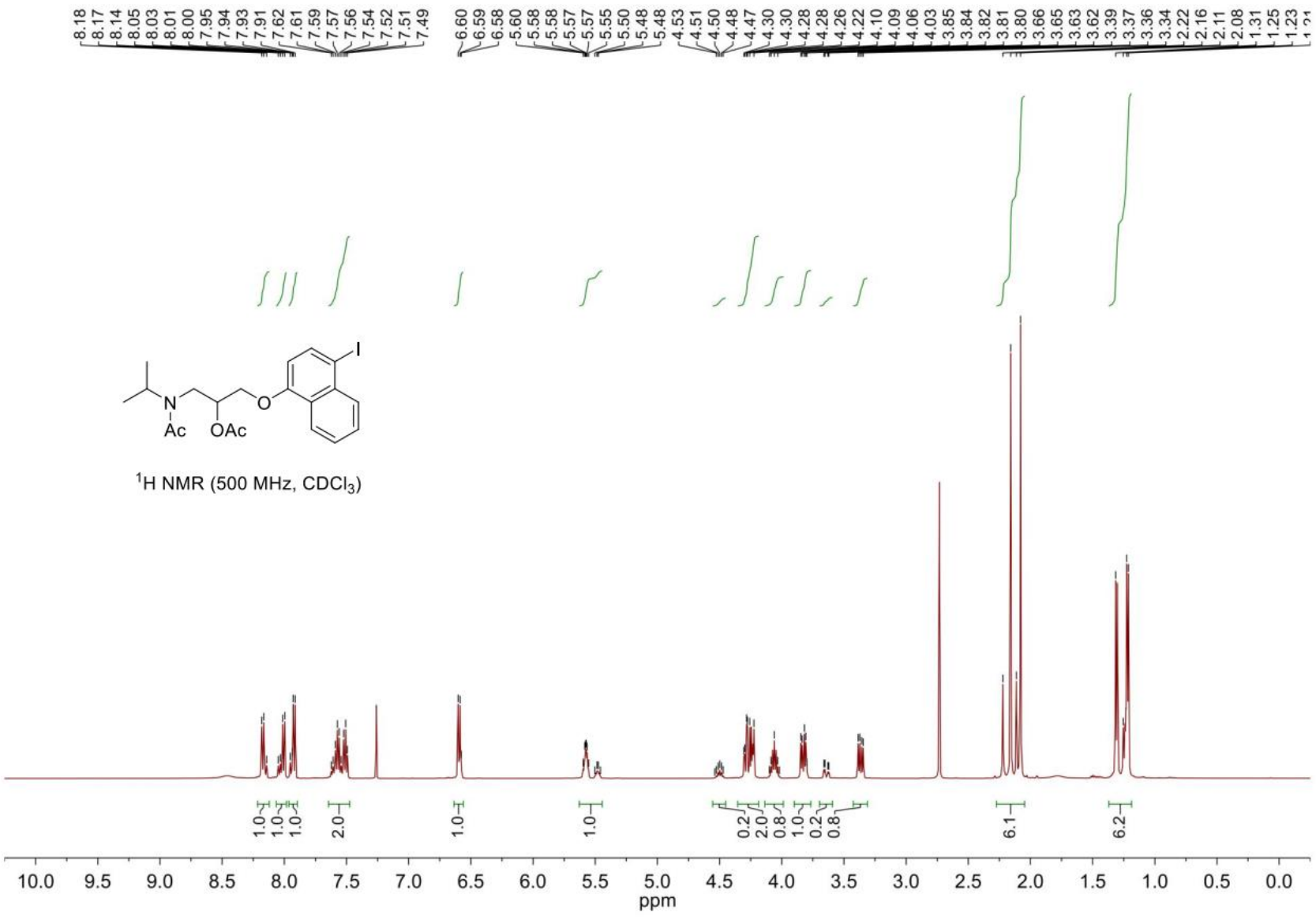
1-((4-Iodonaphthalen-1-yl)oxy)-3-(*N*-isopropylacetamido)propan-2-yl acetate (S27)



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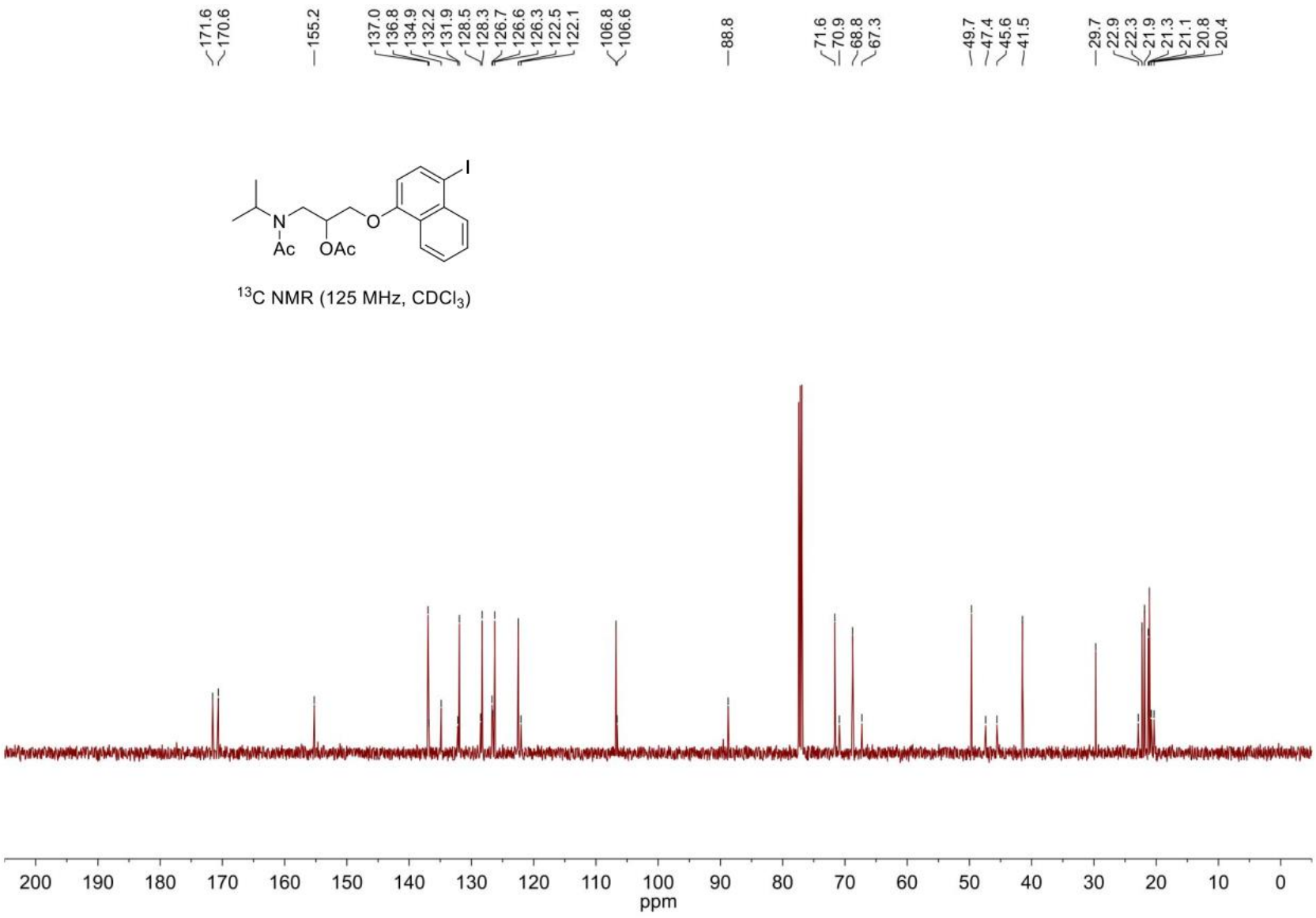
1-((4-Iodonaphthalen-1-yl)oxy)-3-(*N*-isopropylacetamido)propan-2-yl acetate (S27)



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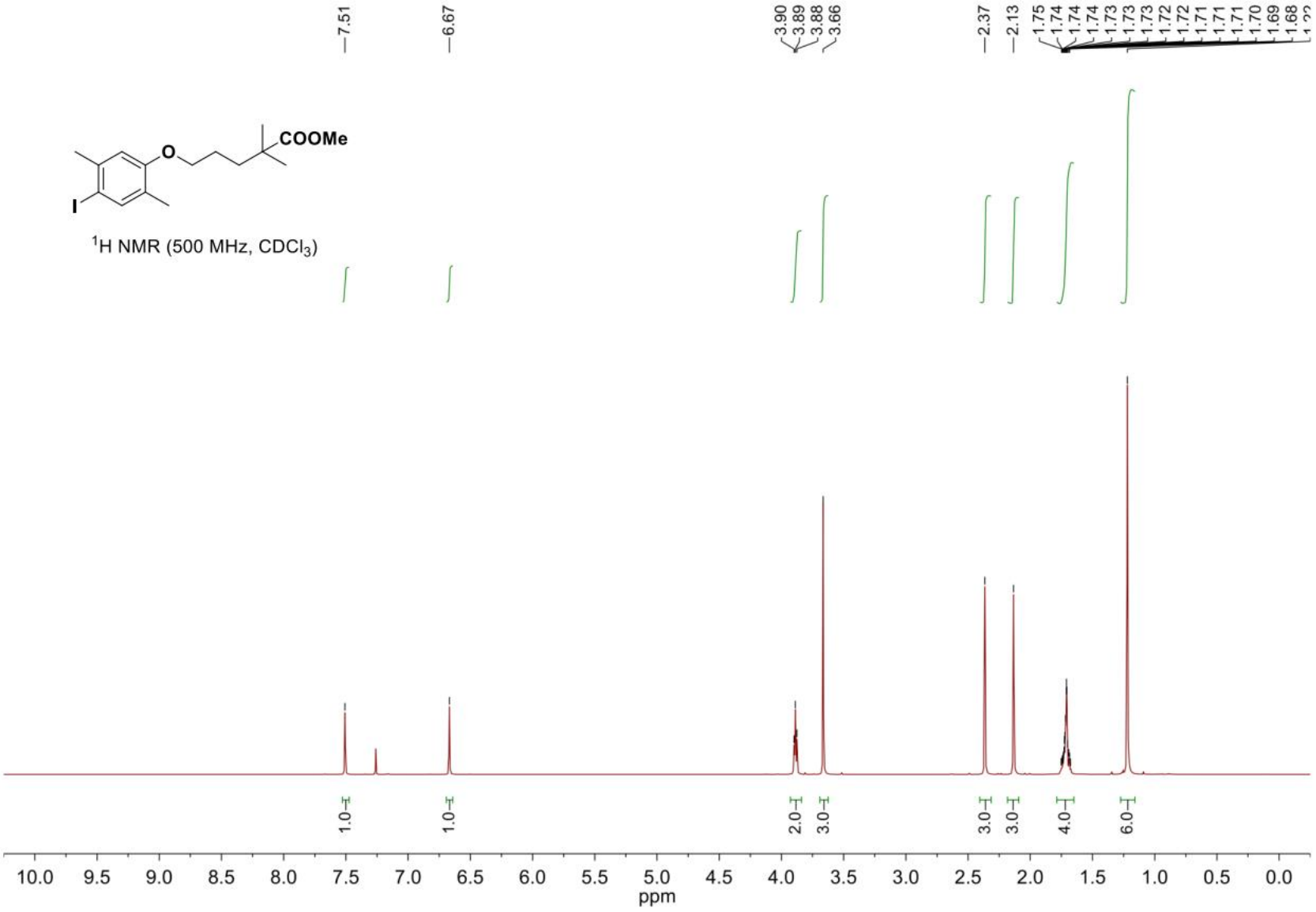
Methyl 5-(4-iodo-2,5-dimethylphenoxy)-2,2-dimethylpentanoate (S28)



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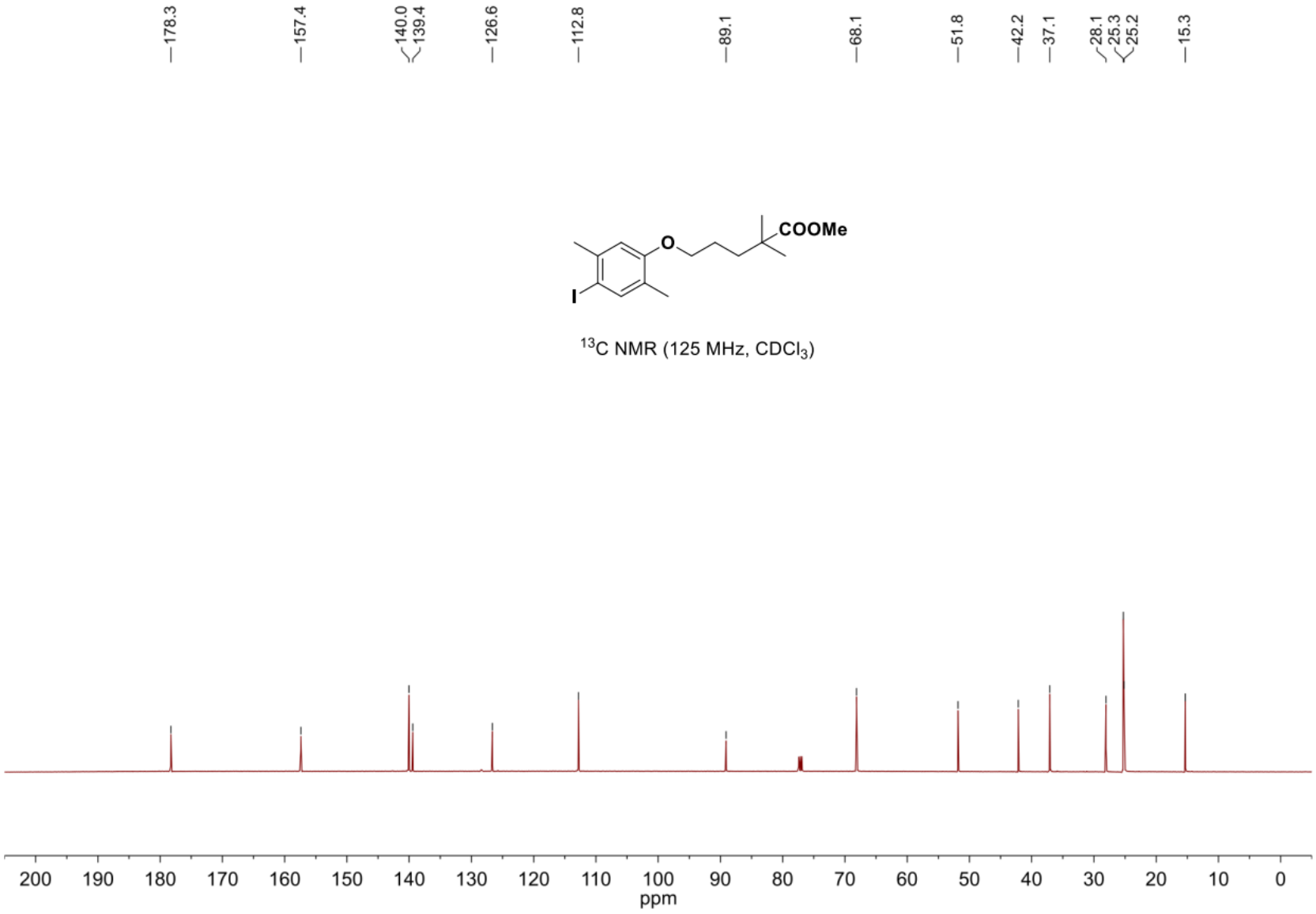
Methyl 5-(4-iodo-2,5-dimethylphenoxy)-2,2-dimethylpentanoate (S28)



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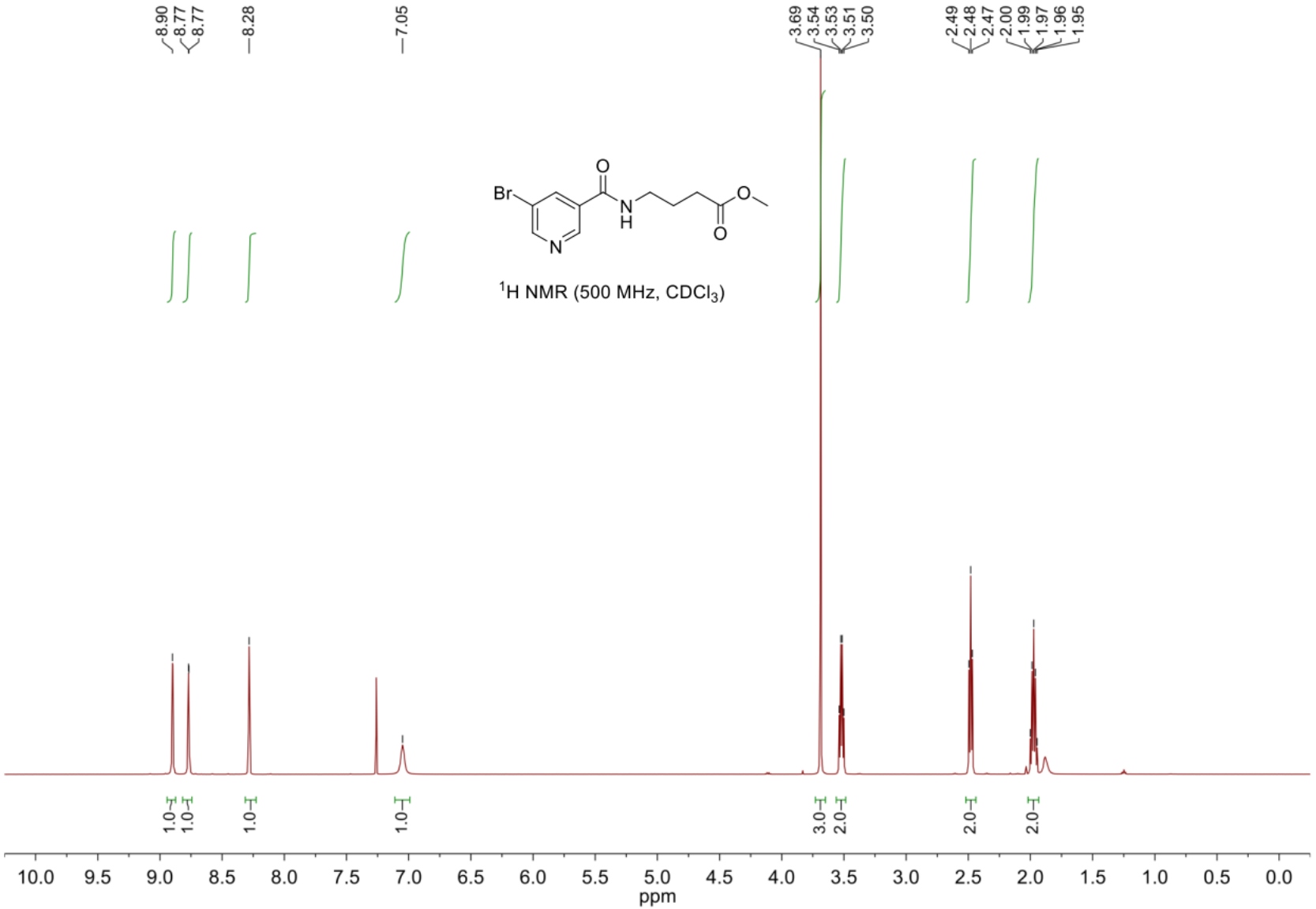
Methyl 4-(5-bromonicotinamido)butanoate (S29)



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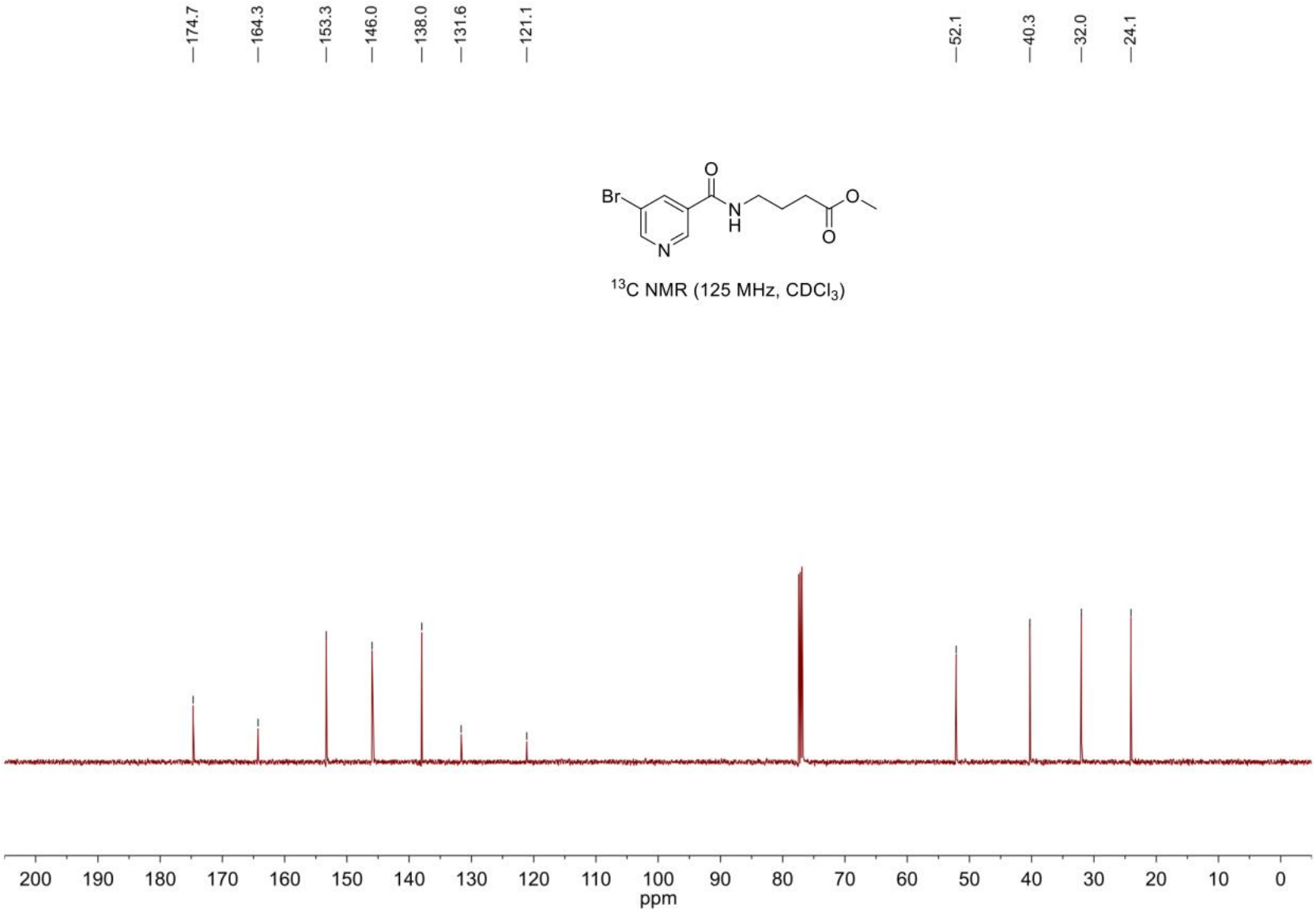
Methyl 4-(5-bromonicotinamido)butanoate (S29)



^{13}C NMR (125 MHz, $CDCl_3$)

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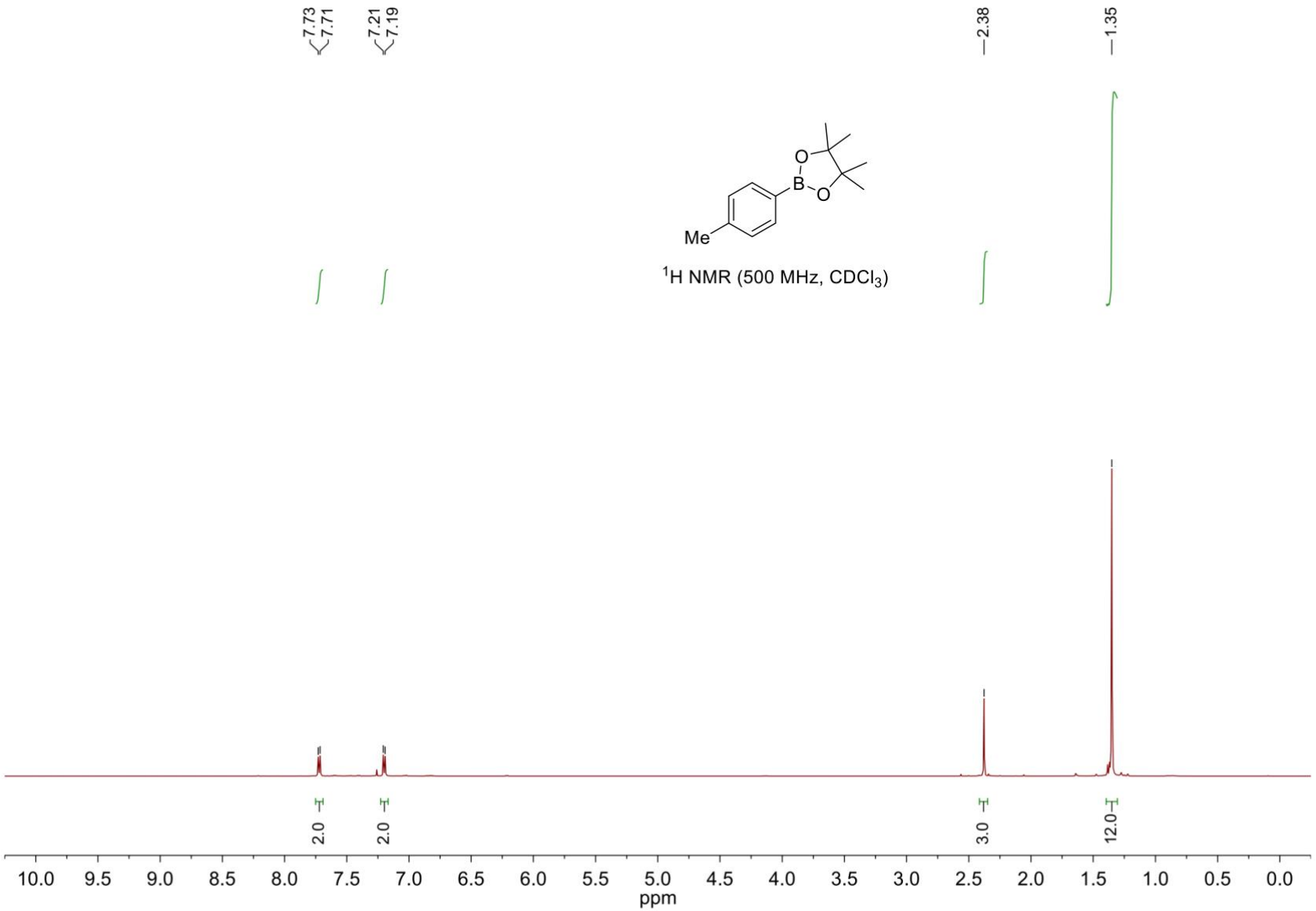
4,4,5,5-Tetramethyl-2-(*p*-tolyl)-1,3,2-dioxaborolane (2)



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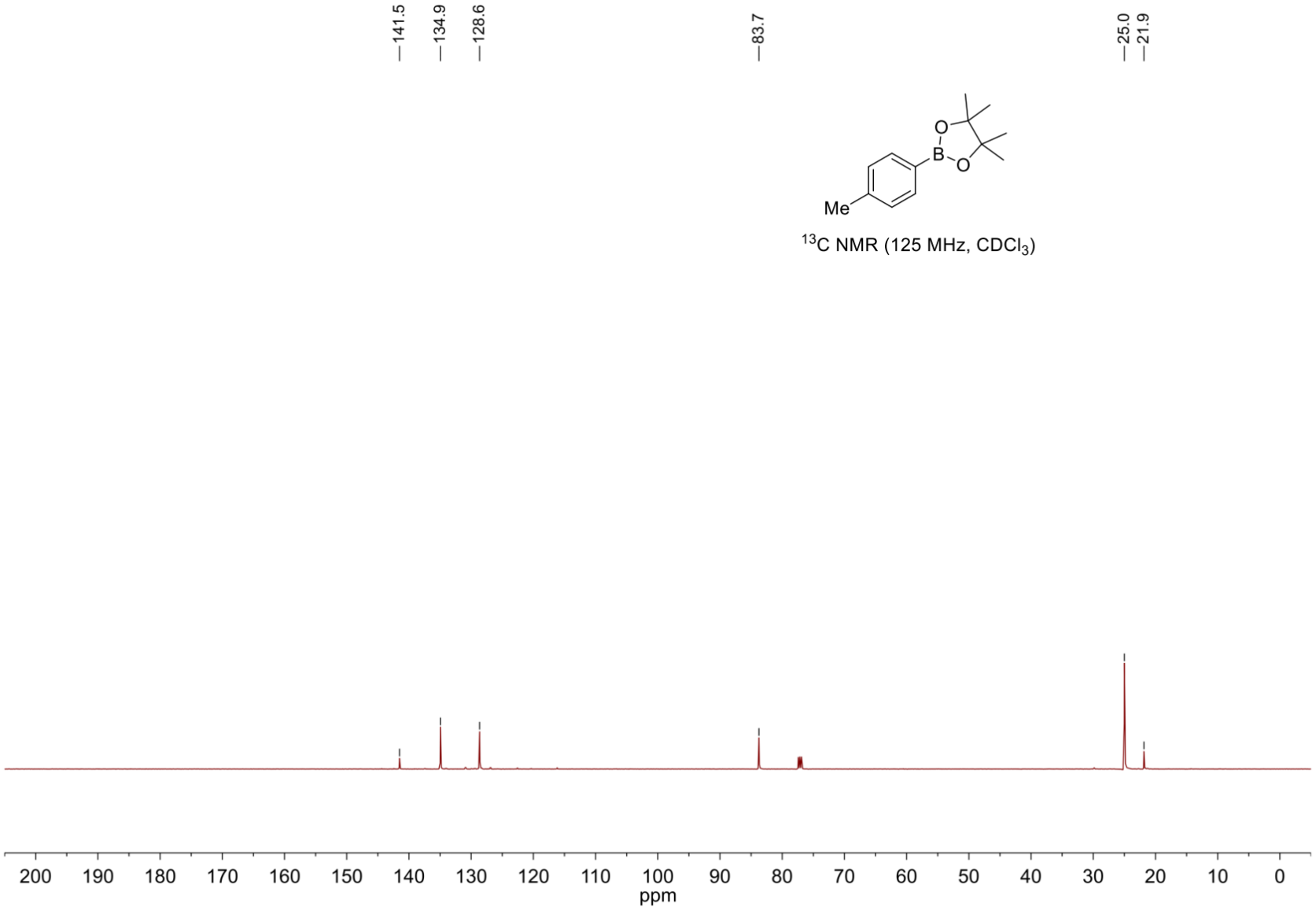
4,4,5,5-Tetramethyl-2-(*p*-tolyl)-1,3,2-dioxaborolane (2)



^{13}C NMR (125 MHz, $CDCl_3$)

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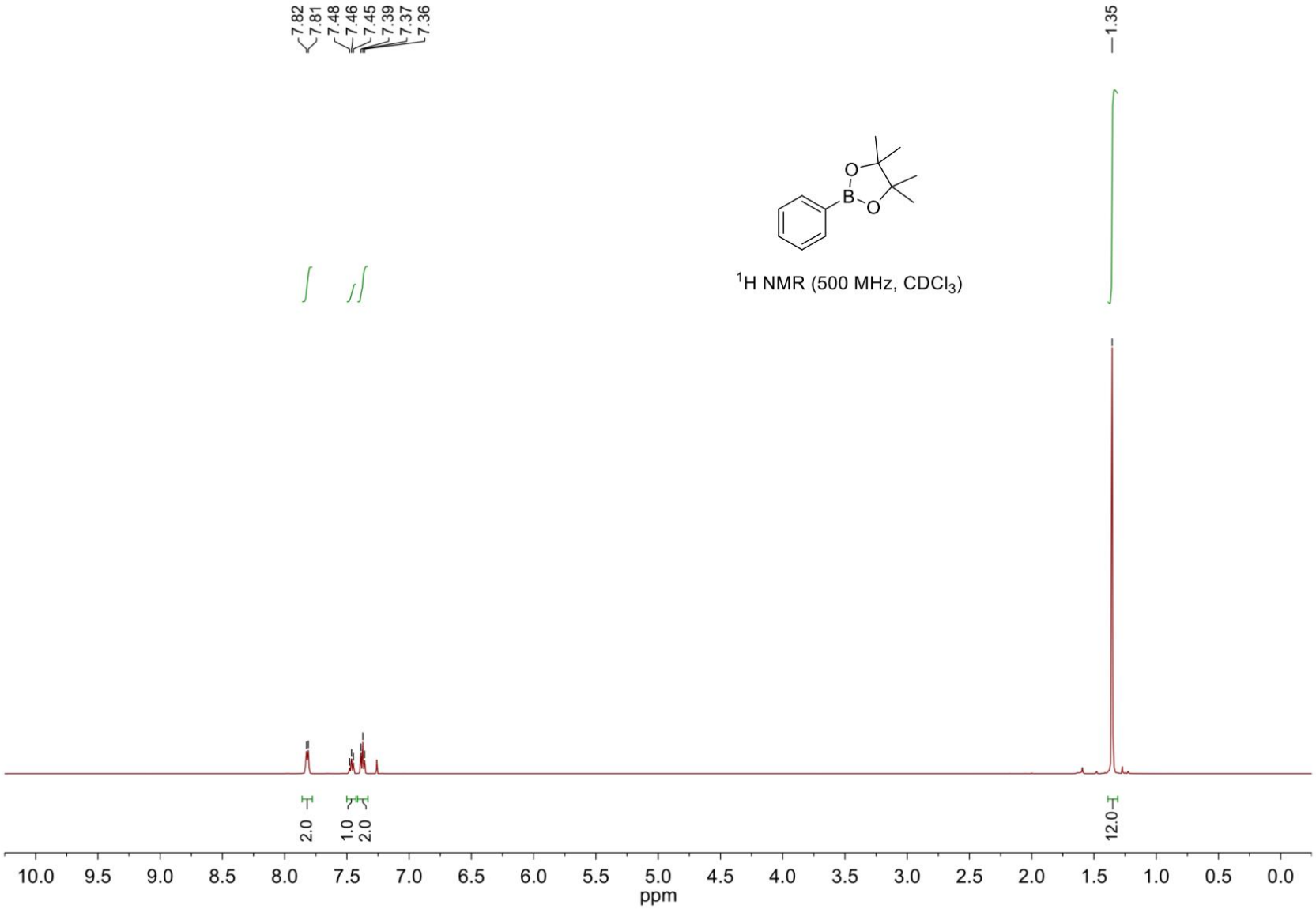
4,4,5,5-Tetramethyl-2-phenyl-1,3,2-dioxaborolane (3)



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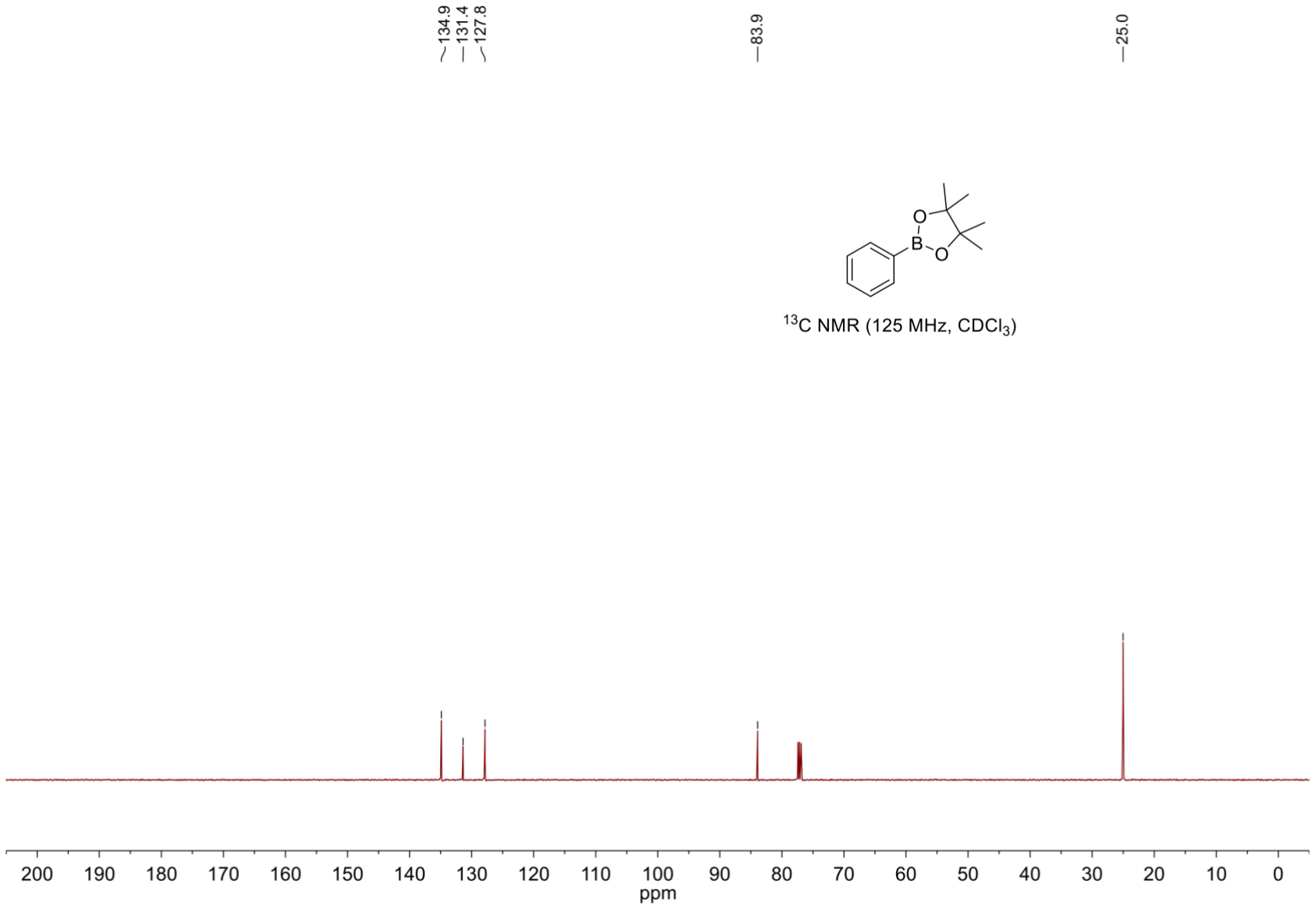
4,4,5,5-Tetramethyl-2-phenyl-1,3,2-dioxaborolane (3)



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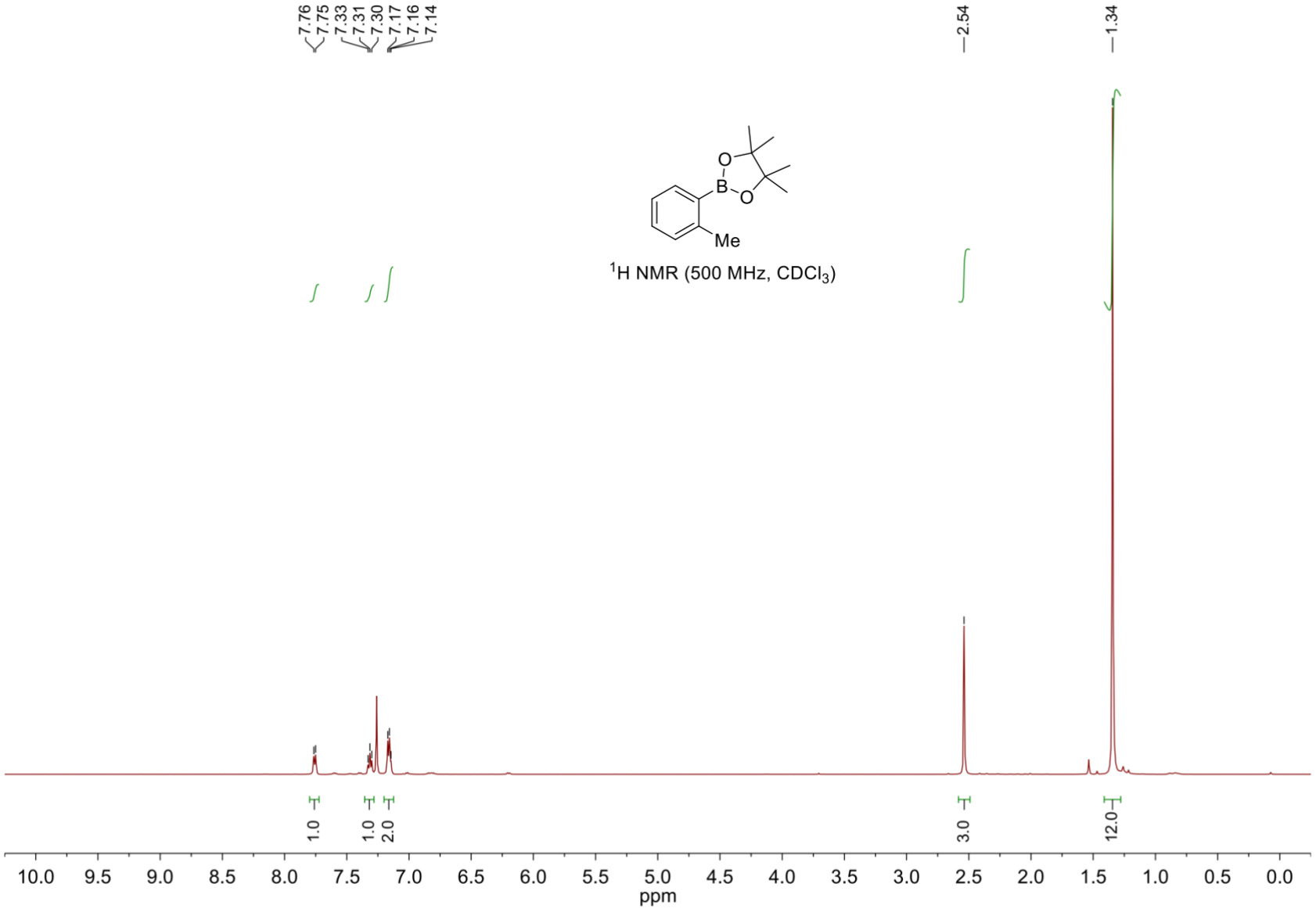
4,4,5,5-Tetramethyl-2-(*o*-tolyl)-1,3,2-dioxaborolane (4)



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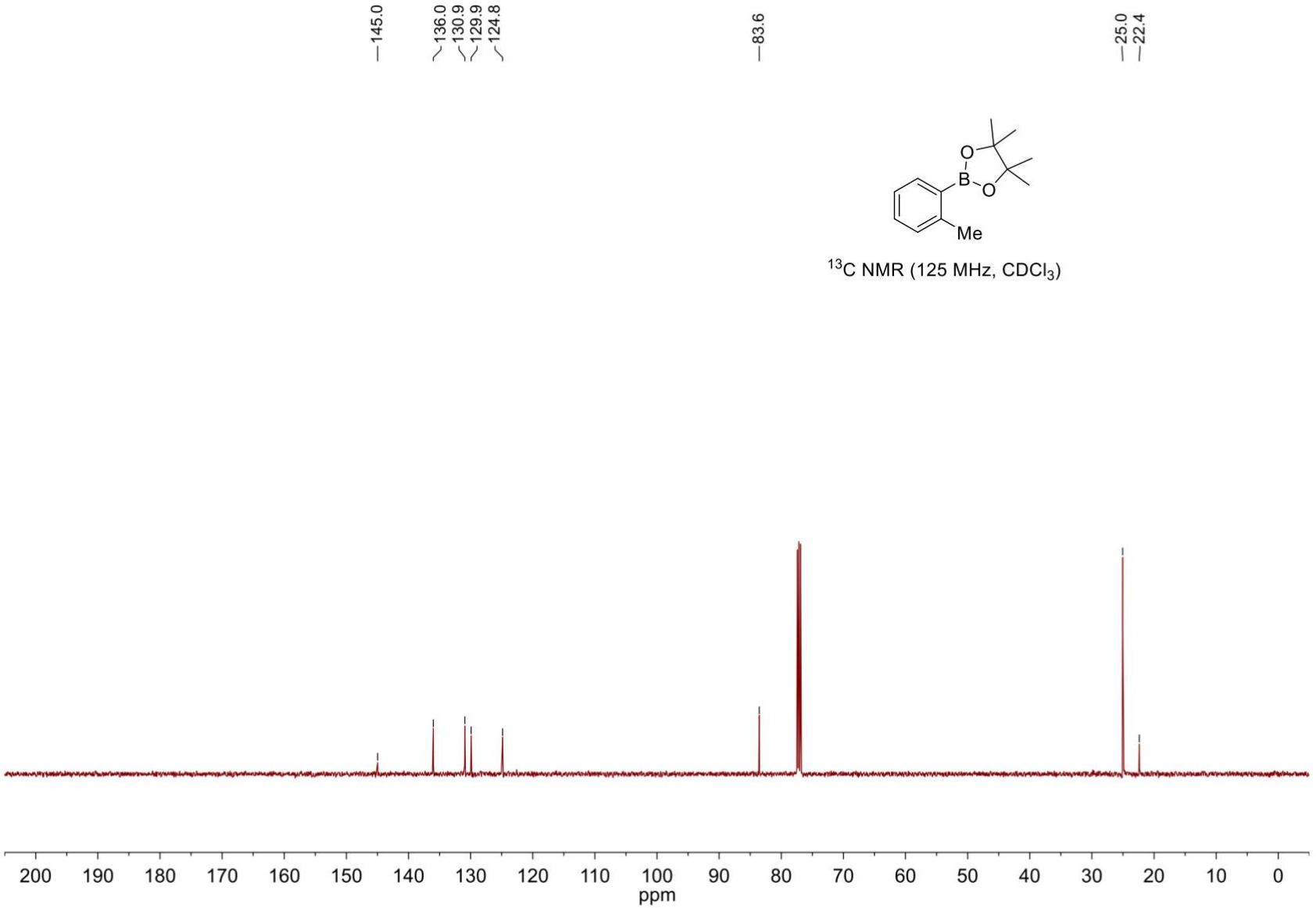
4,4,5,5-Tetramethyl-2-(*o*-tolyl)-1,3,2-dioxaborolane (4)



^{13}C NMR (125 MHz, $CDCl_3$)

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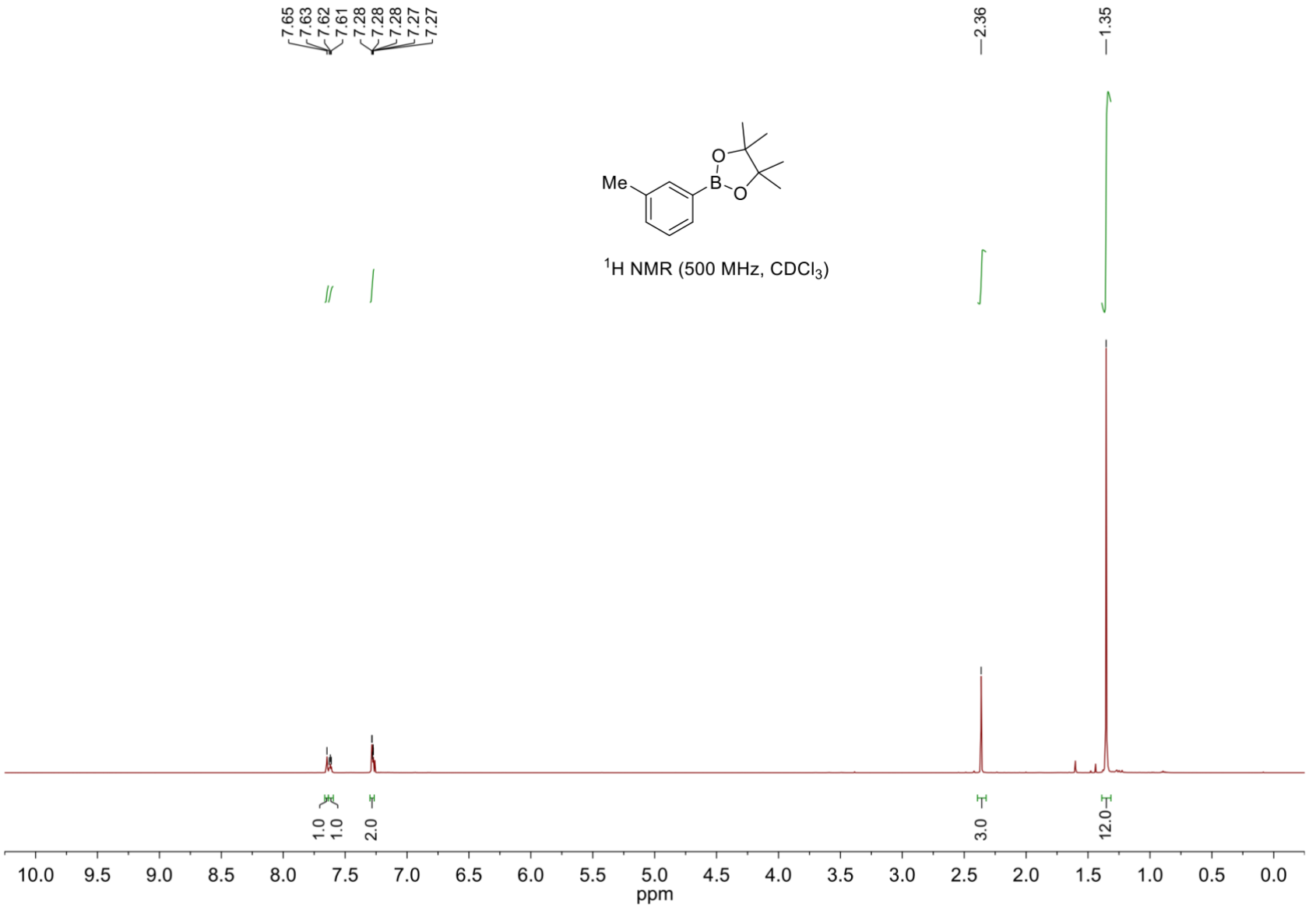
4,4,5,5-Tetramethyl-2-(*m*-tolyl)-1,3,2-dioxaborolane (5)



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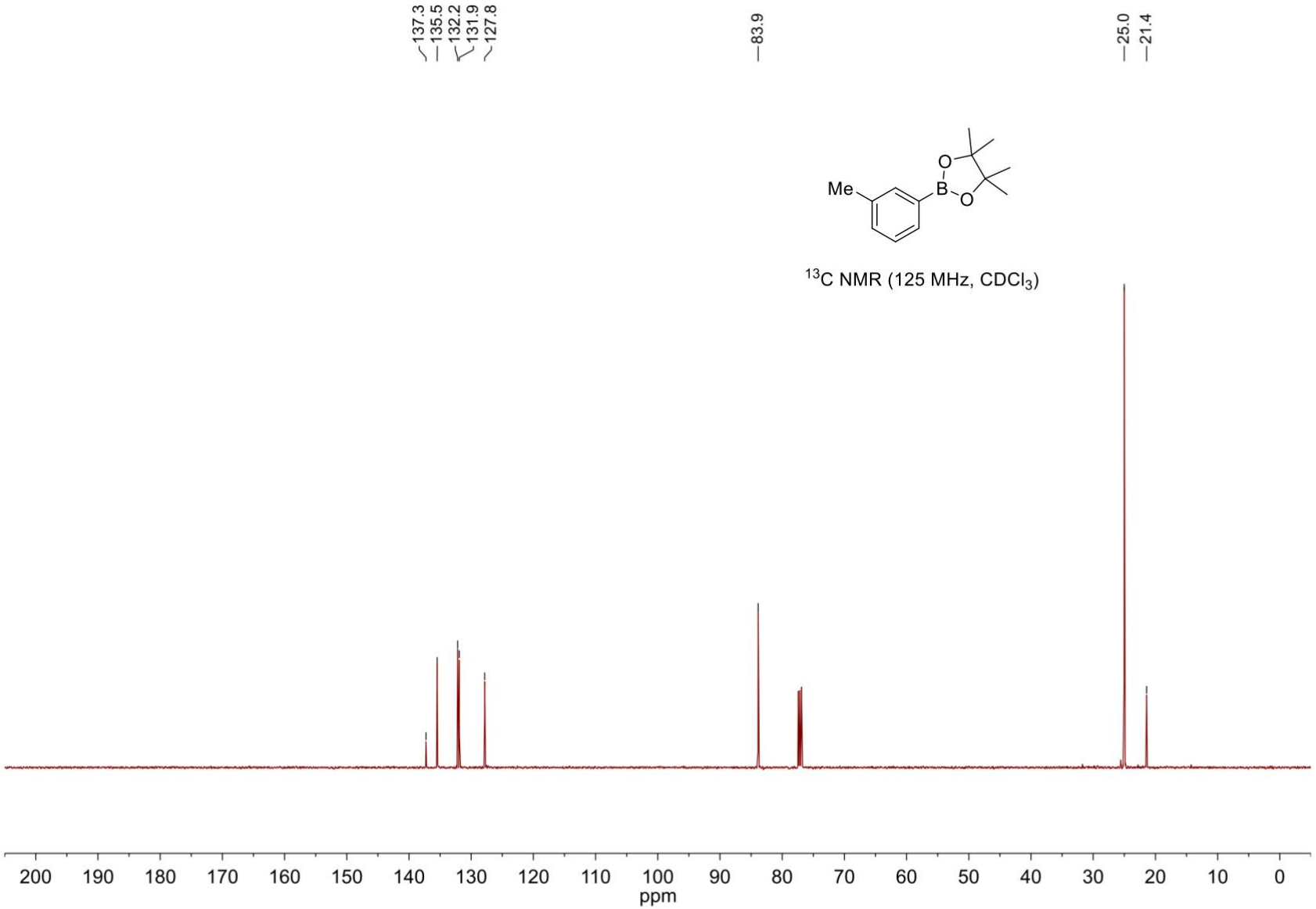
4,4,5,5-Tetramethyl-2-(*m*-tolyl)-1,3,2-dioxaborolane (5)



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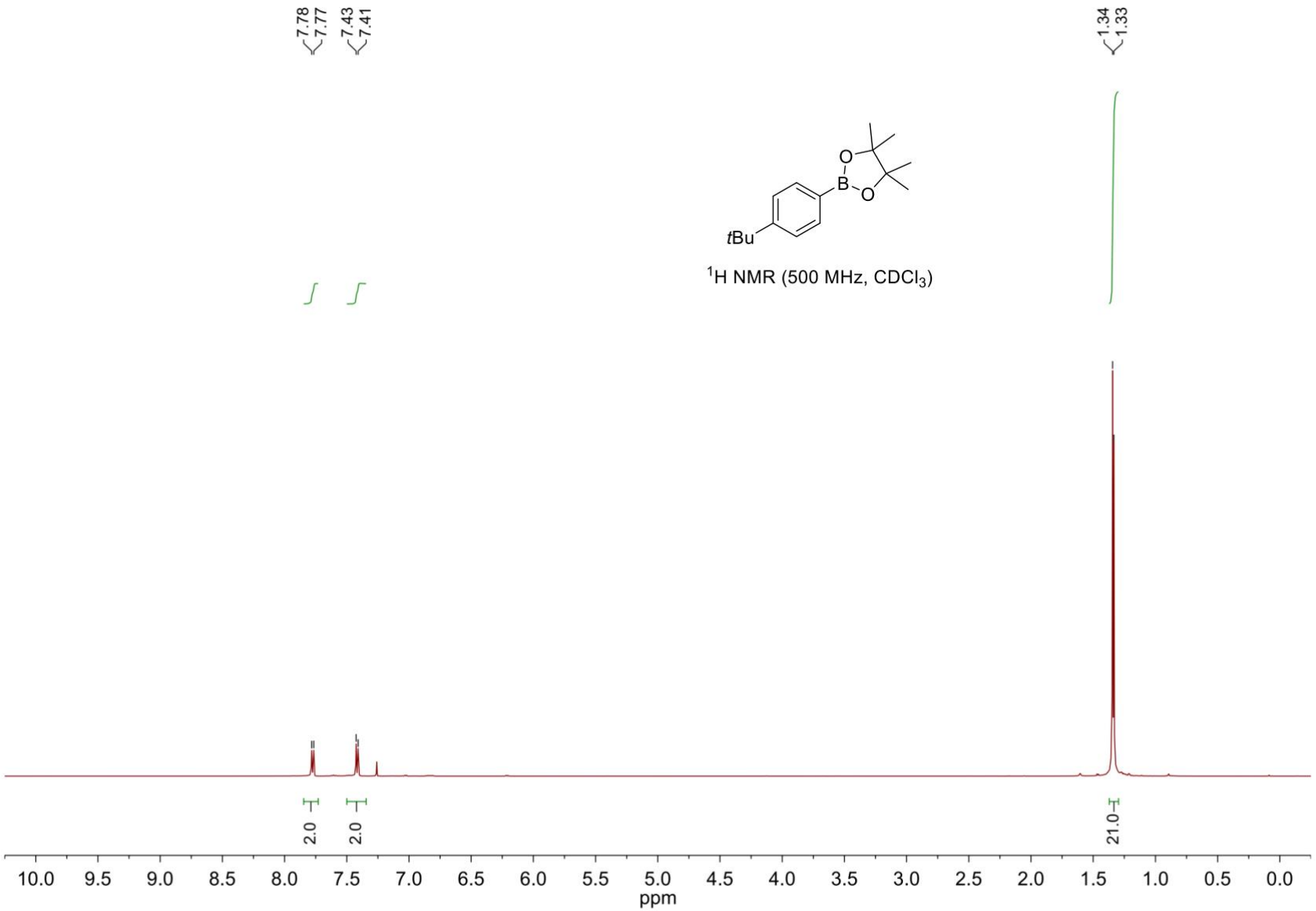
2-(4-(*tert*-Butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6)



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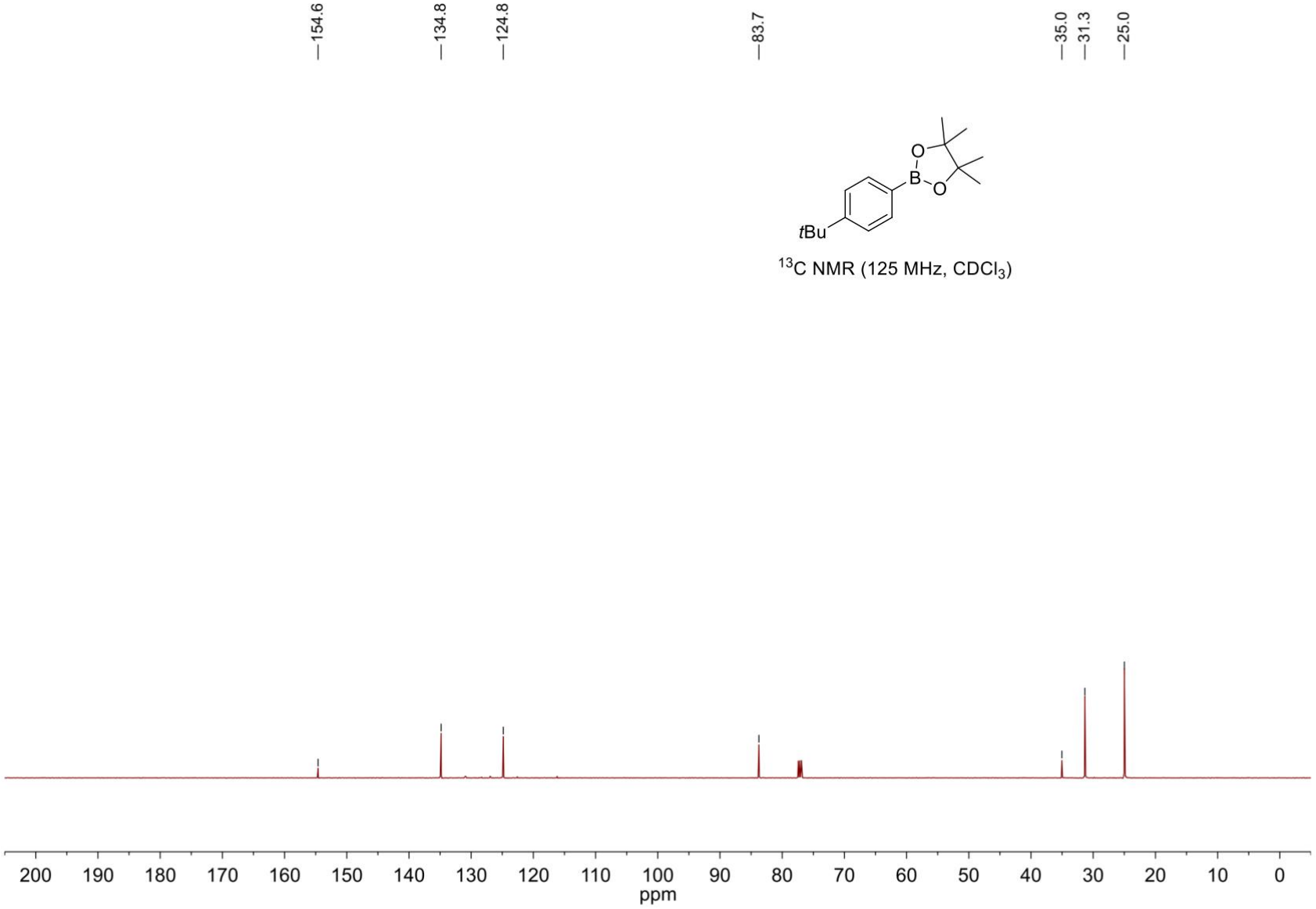
2-(4-(*tert*-Butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6)



^{13}C NMR (125 MHz, $CDCl_3$)

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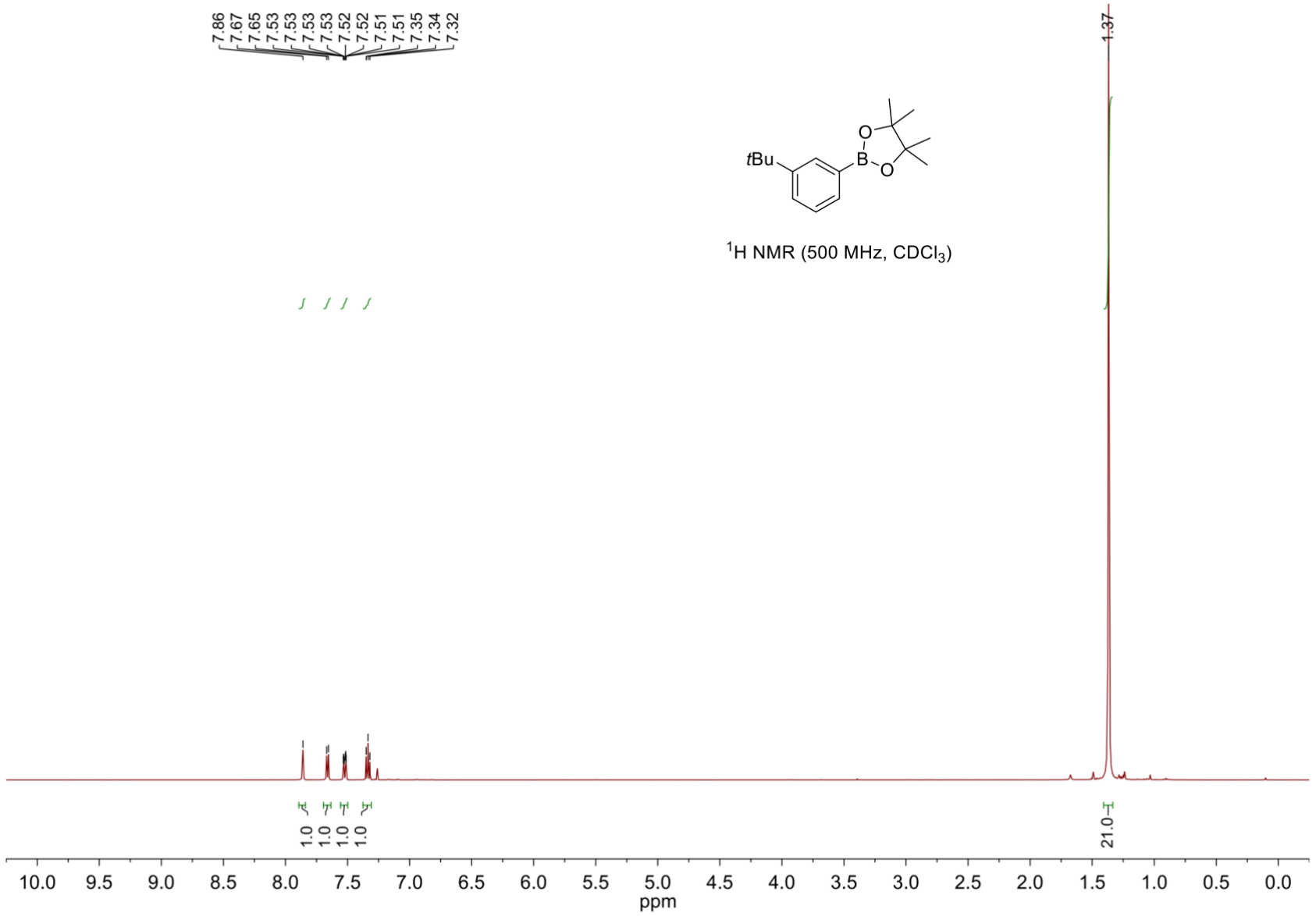
2-(3-(*tert*-Butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7)



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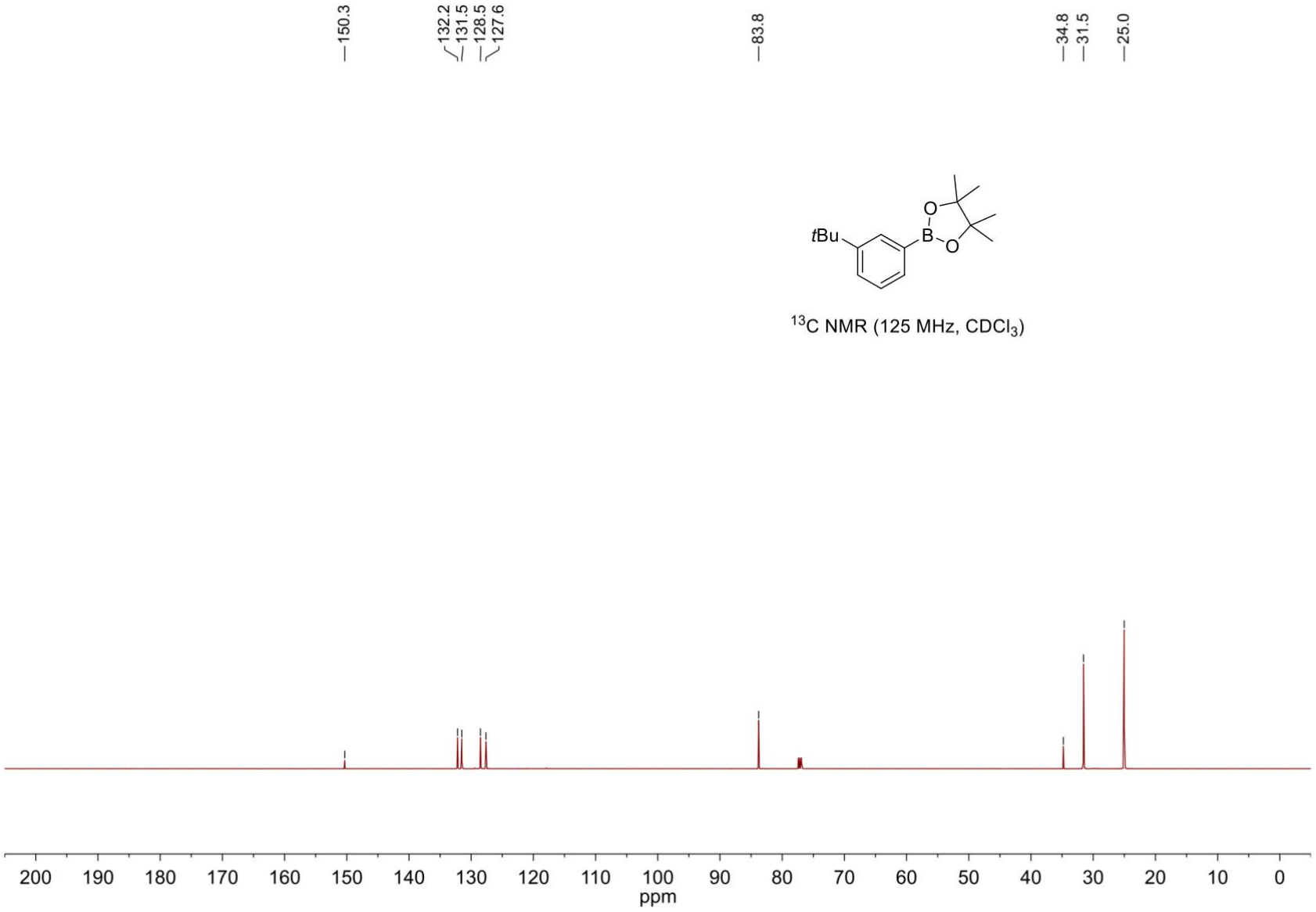
2-(3-(*tert*-Butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7)



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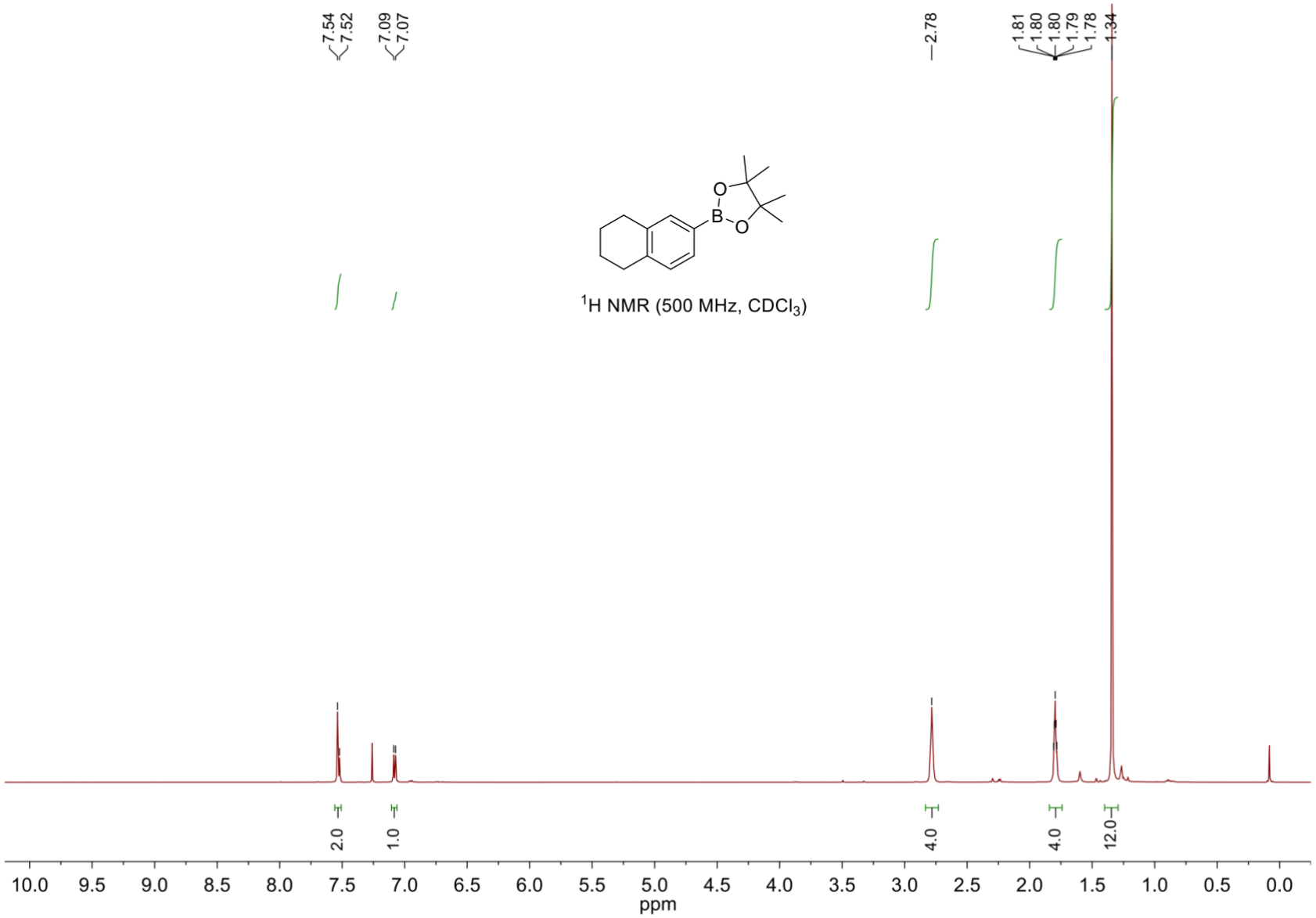
4,4,5,5-Tetramethyl-2-(5,6,7,8-tetrahydronaphthalen-2-yl)-1,3,2-dioxaborolane (8)



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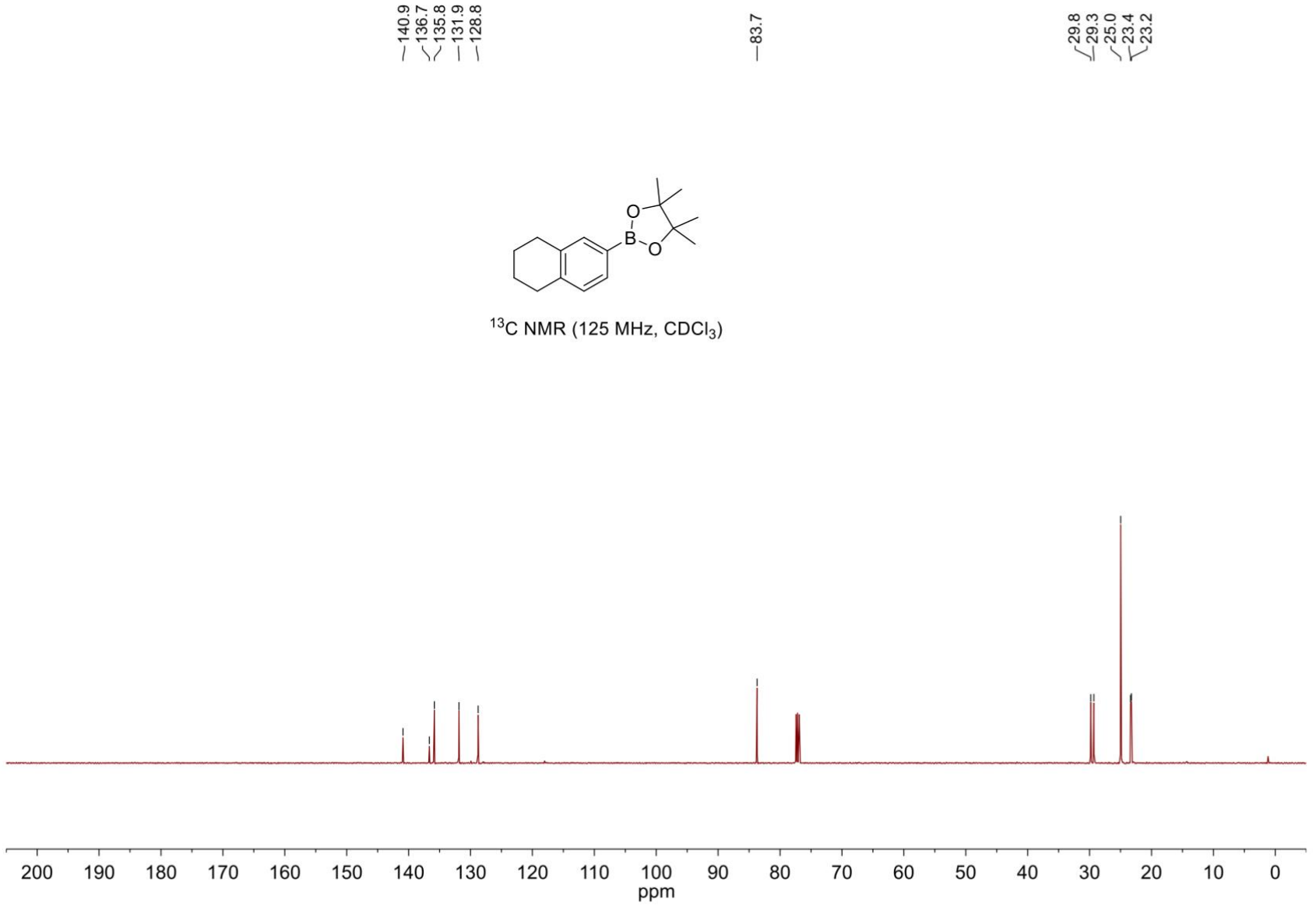
4,4,5,5-Tetramethyl-2-(5,6,7,8-tetrahydronaphthalen-2-yl)-1,3,2-dioxaborolane (8)



^{13}C NMR (125 MHz, $CDCl_3$)

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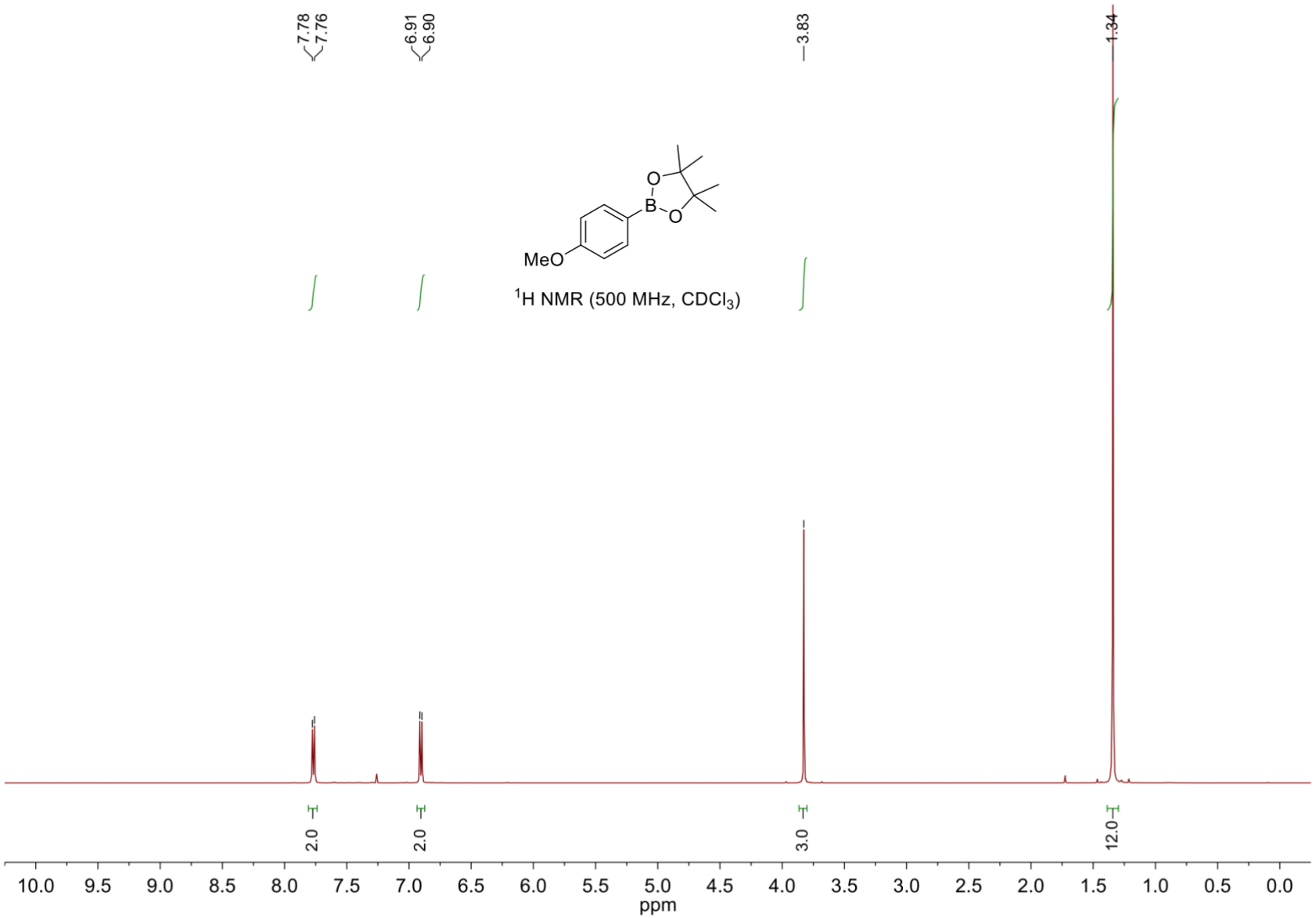
2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9)



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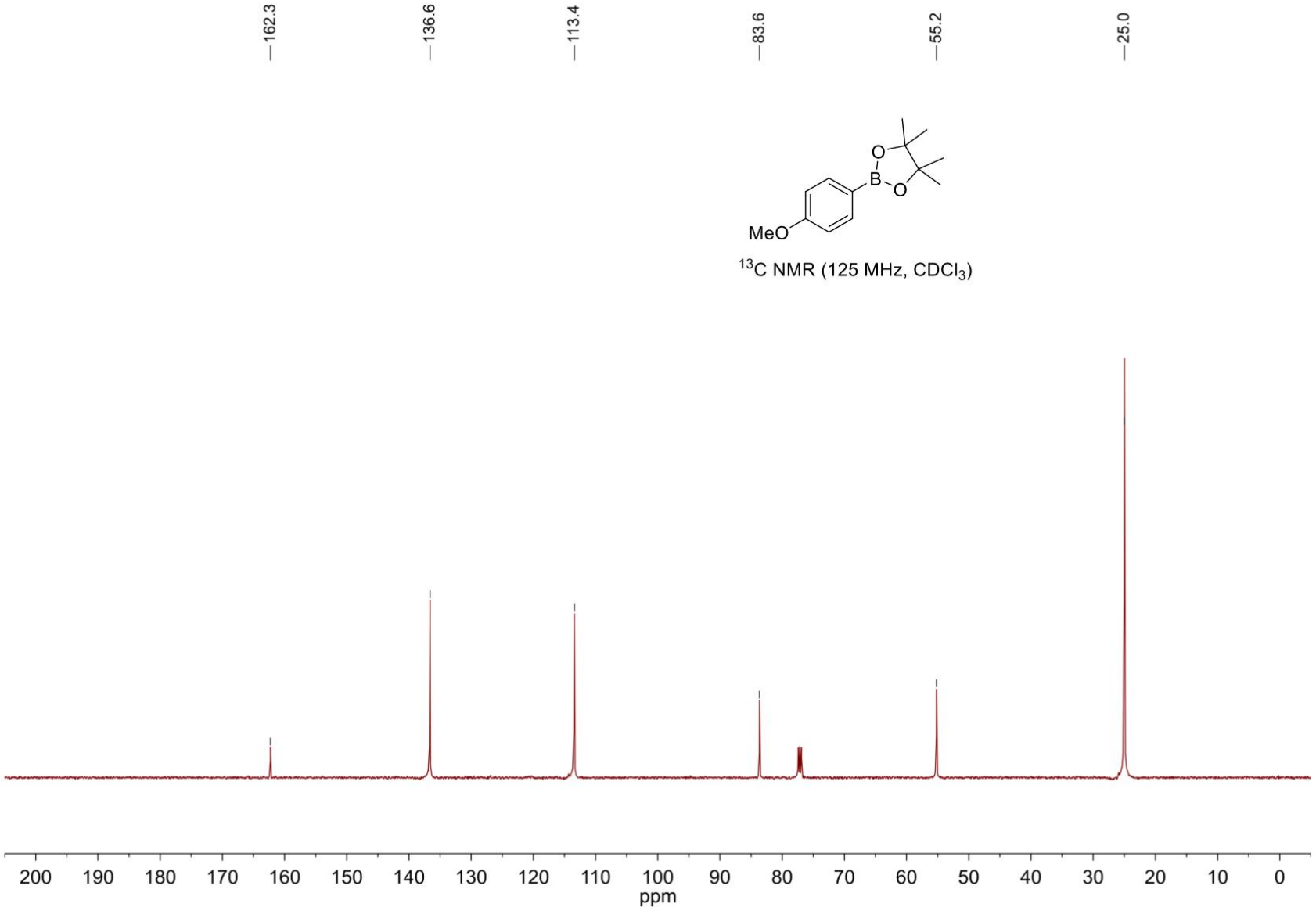
2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9)



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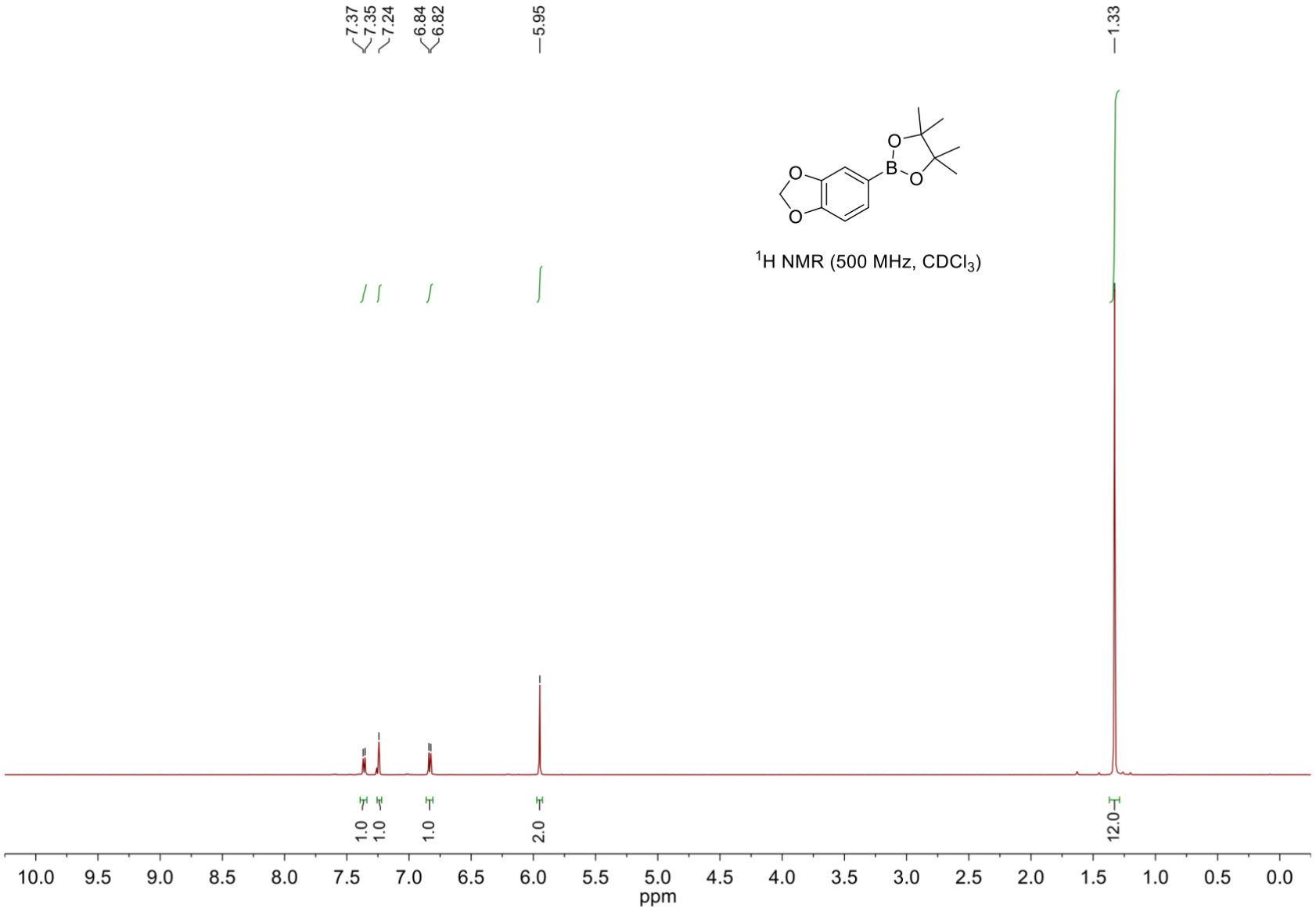
2-(Benzo[d][1,3]dioxol-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10)



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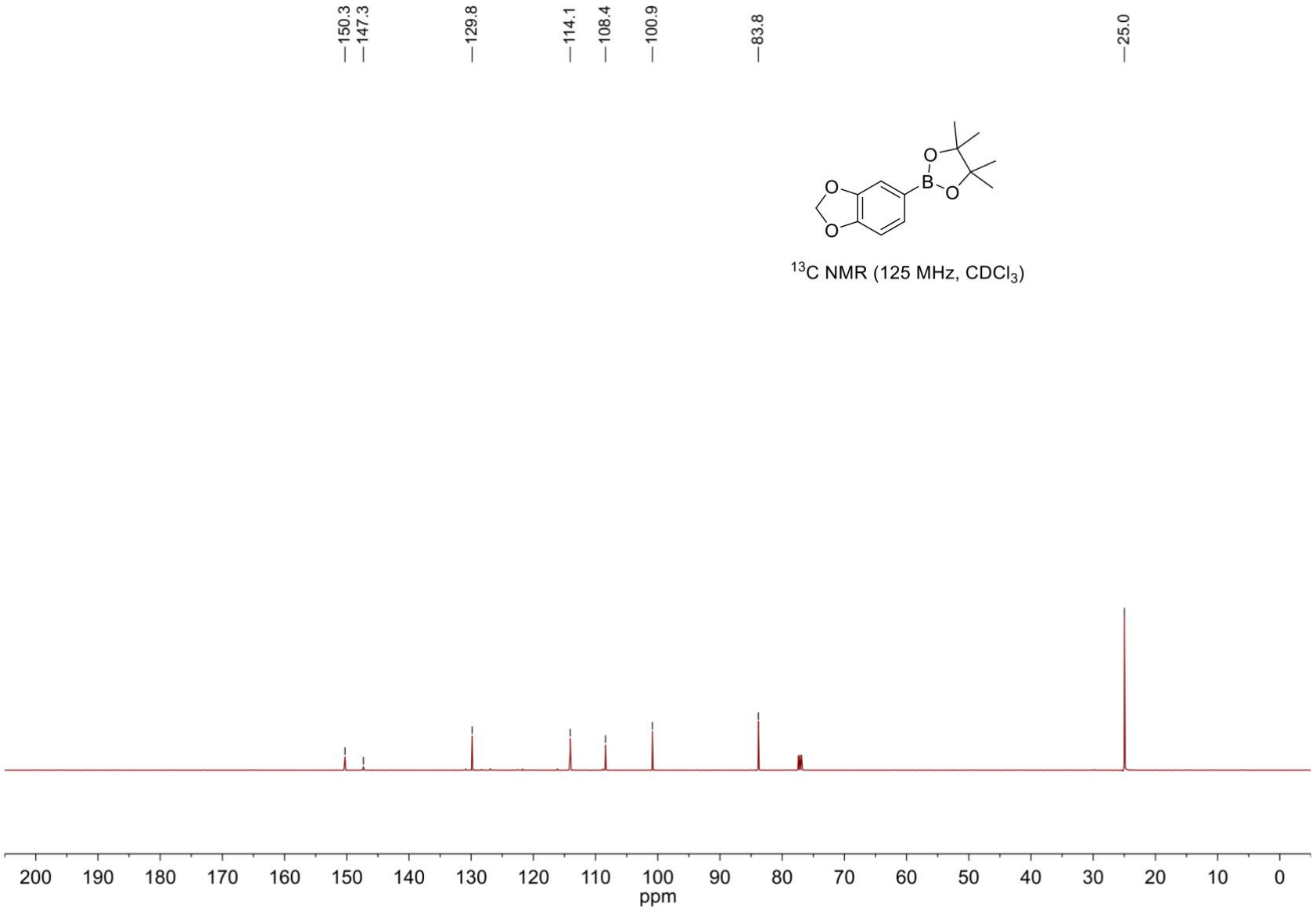
2-(Benzo[d][1,3]dioxol-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10)



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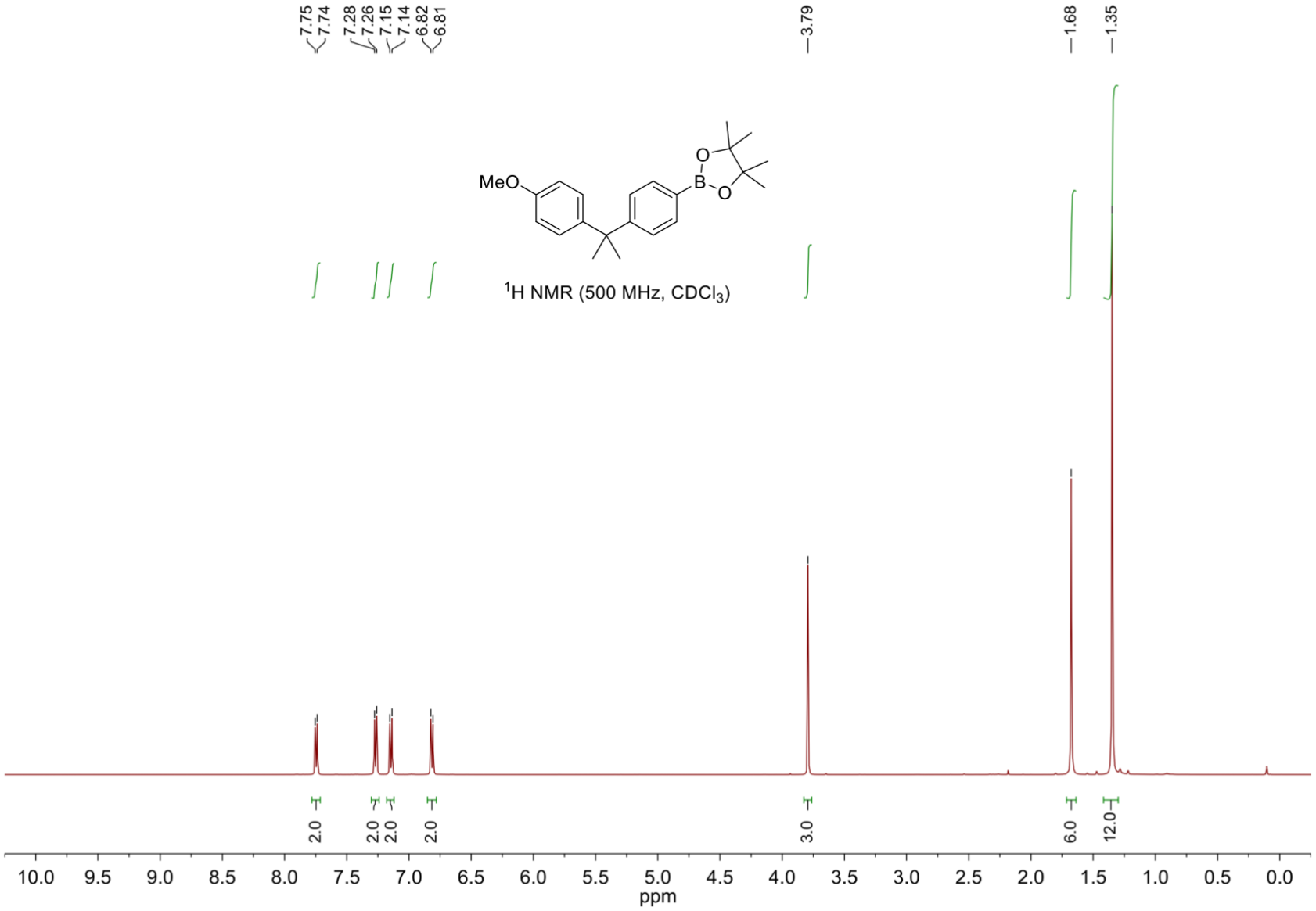
2-(4-(2-(4-Methoxyphenyl)propan-2-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11)



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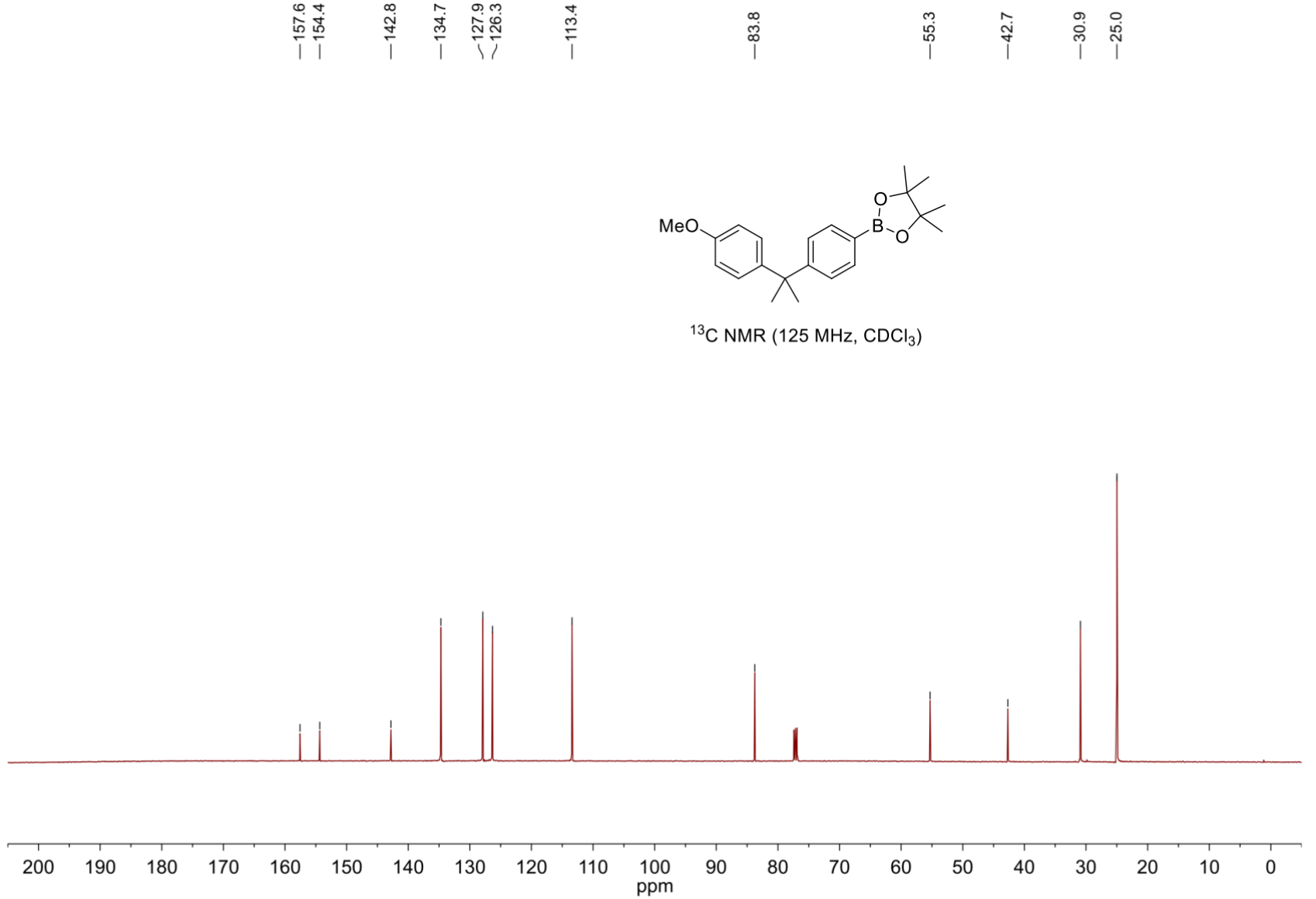
2-(4-(2-(4-Methoxyphenyl)propan-2-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11)



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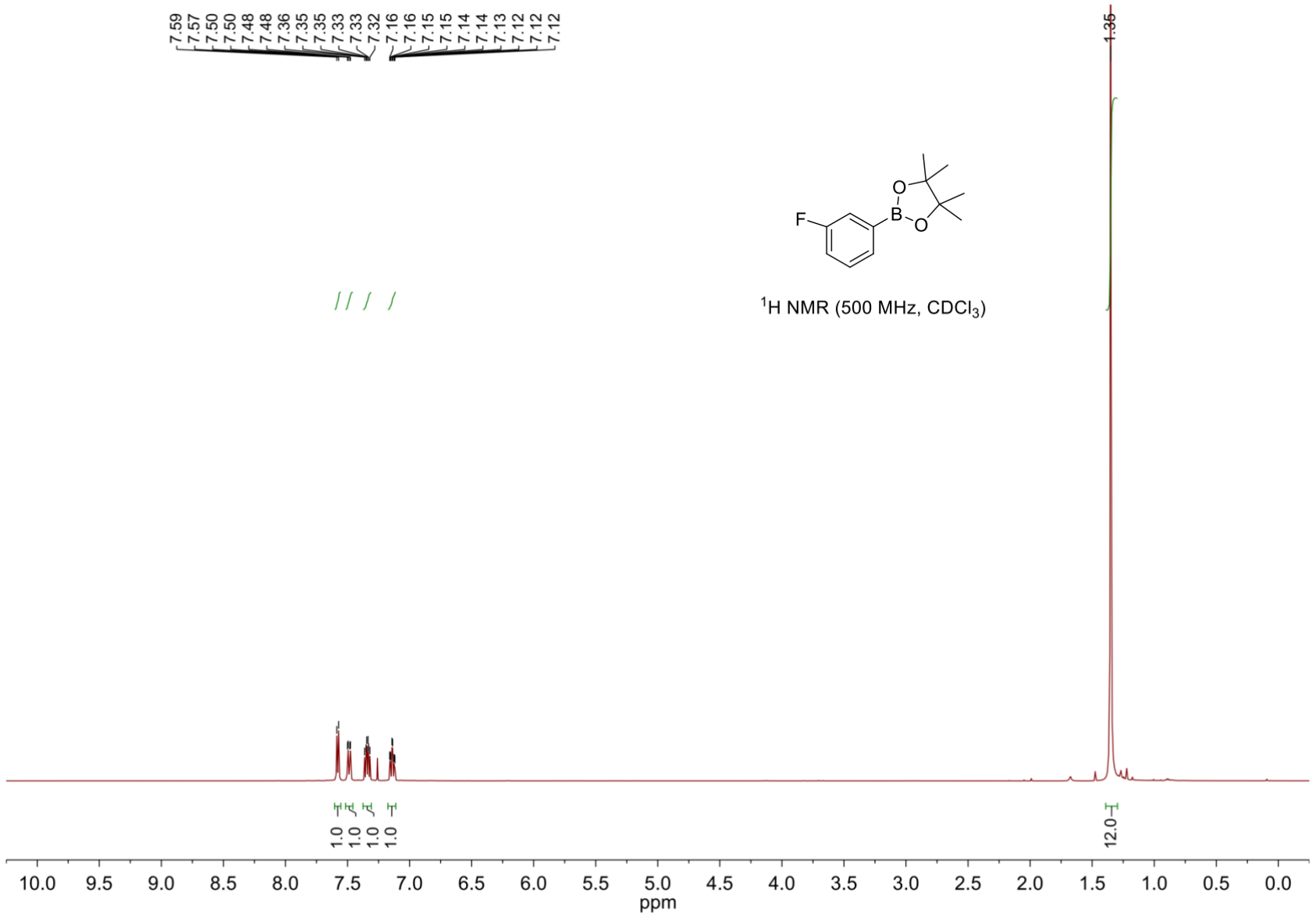
2-(3-Fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12)



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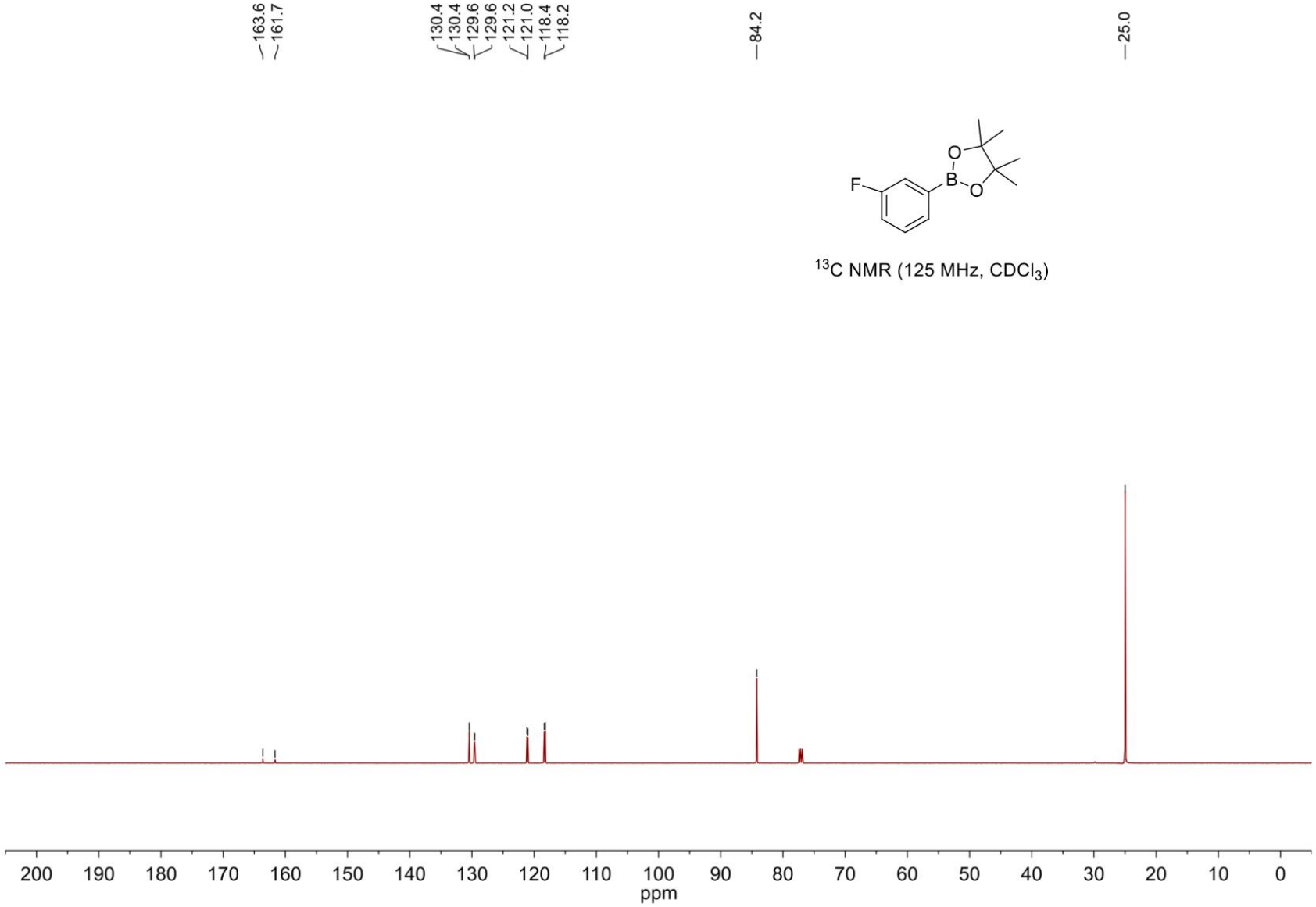
2-(3-Fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12)



^{13}C NMR (125 MHz, $CDCl_3$)

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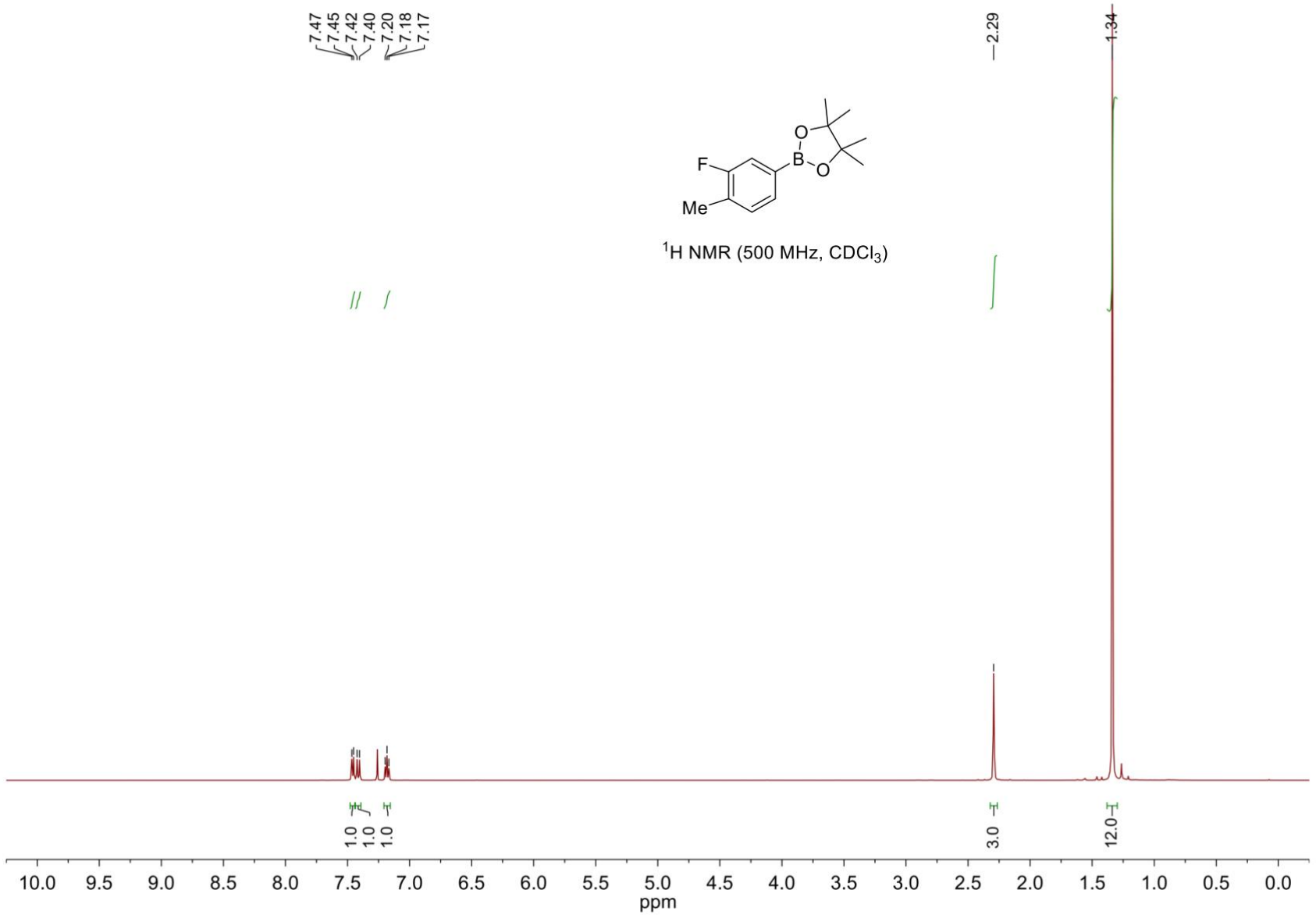
2-(3-Fluoro-4-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13)



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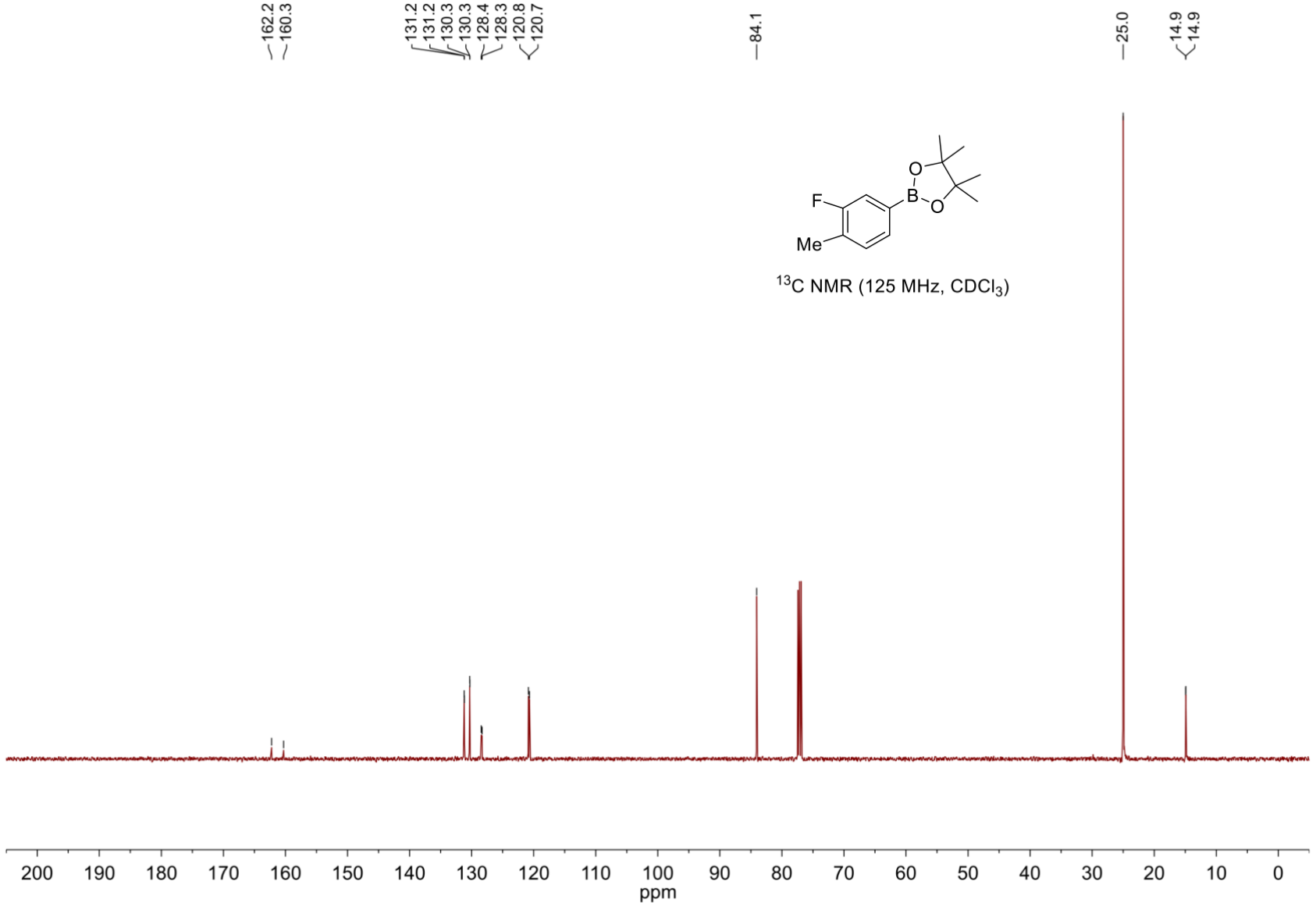
2-(3-Fluoro-4-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13)



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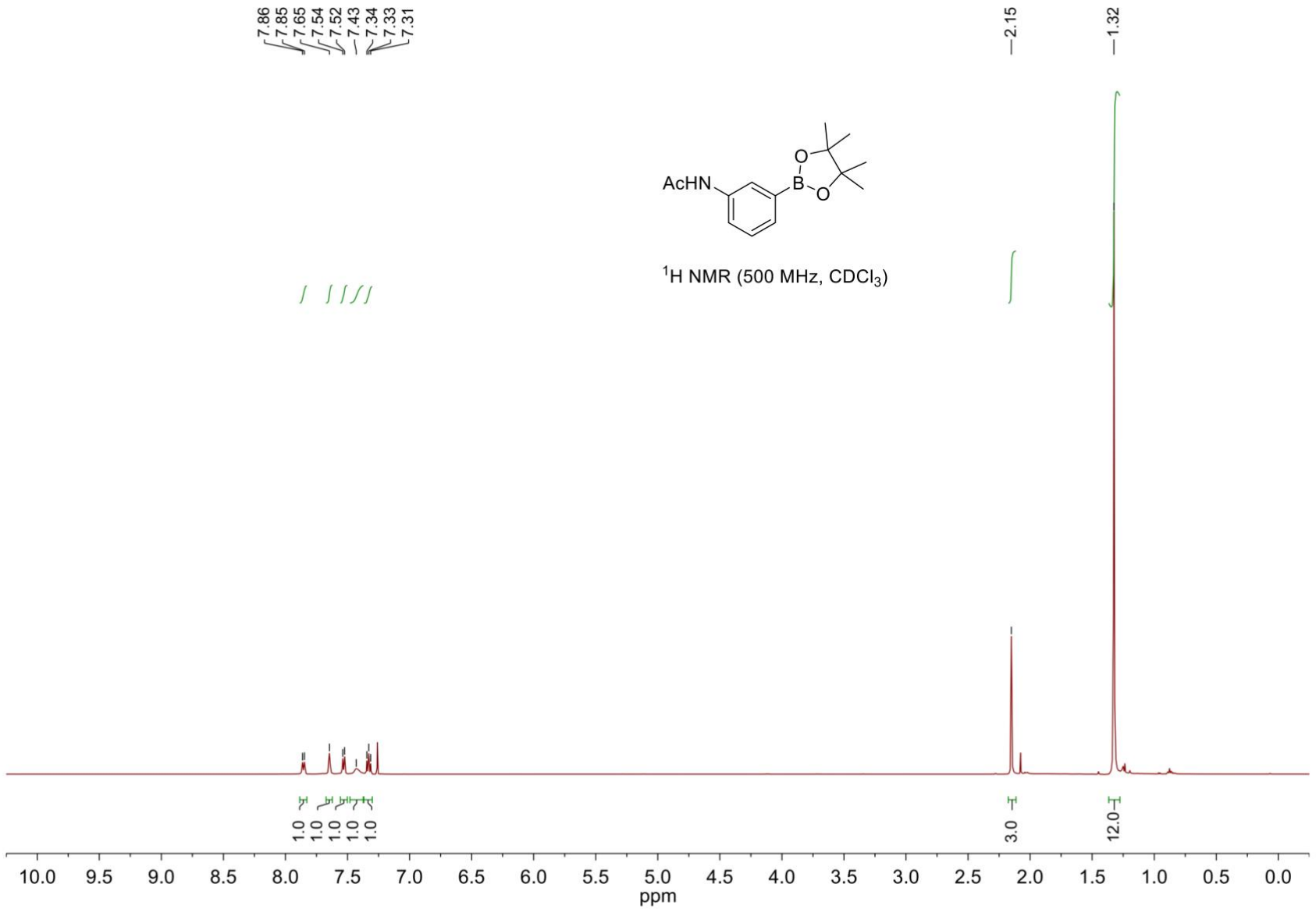
_N_-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetamide (14)



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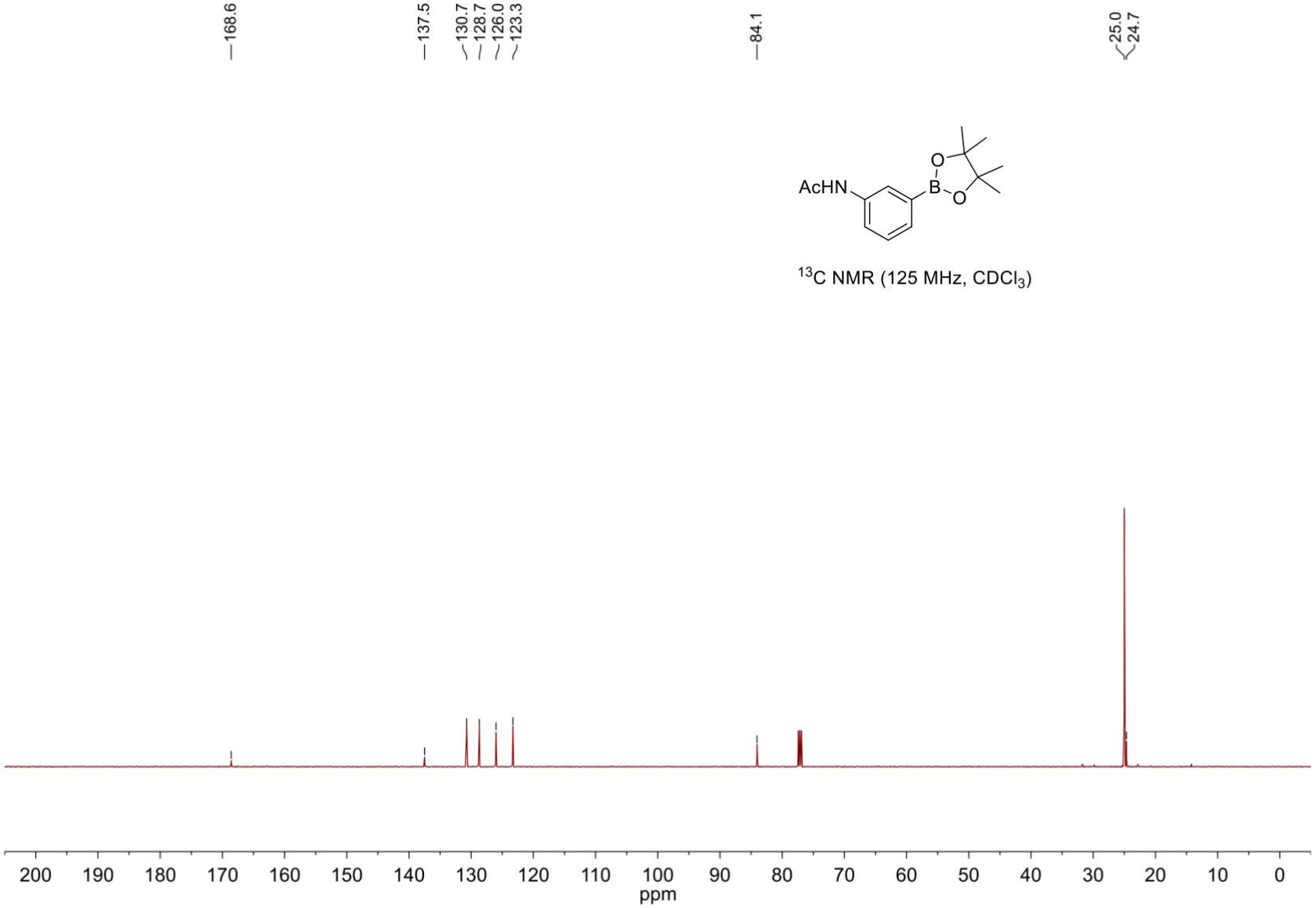
_N_-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetamide (14)



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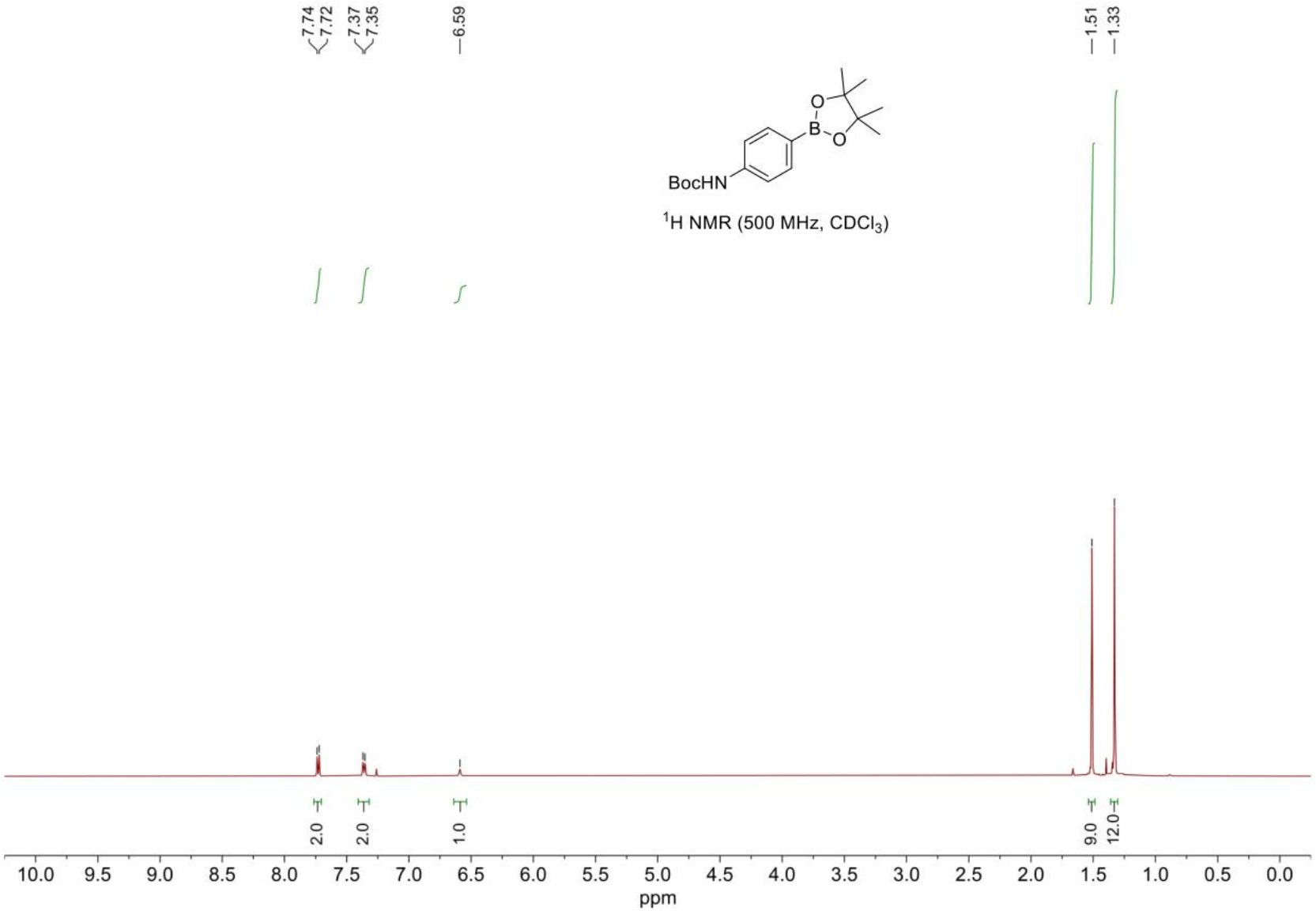
tert-Butyl (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)carbamate (15)



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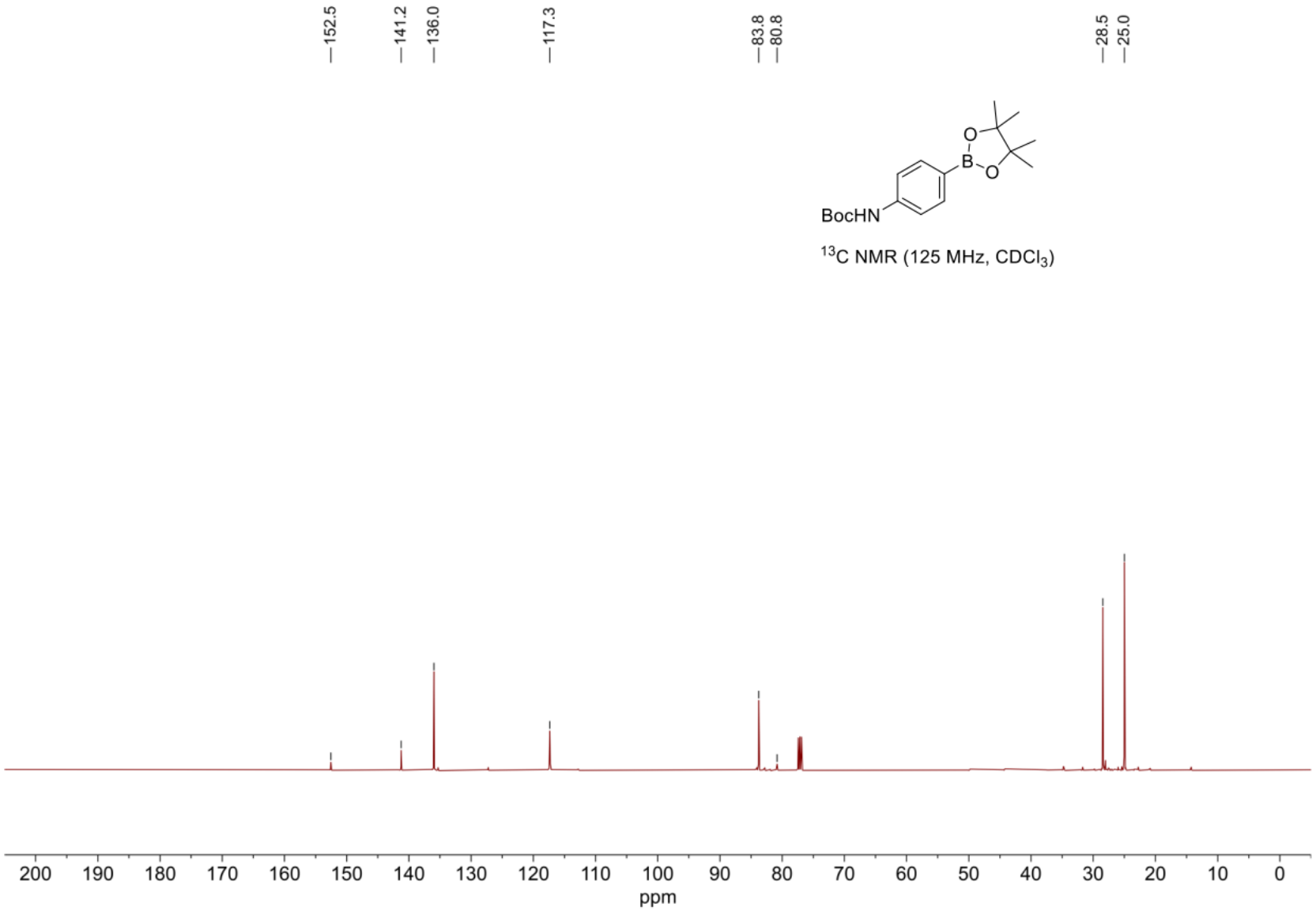
tert-Butyl (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)carbamate (15)



^{13}C NMR (125 MHz, $CDCl_3$)

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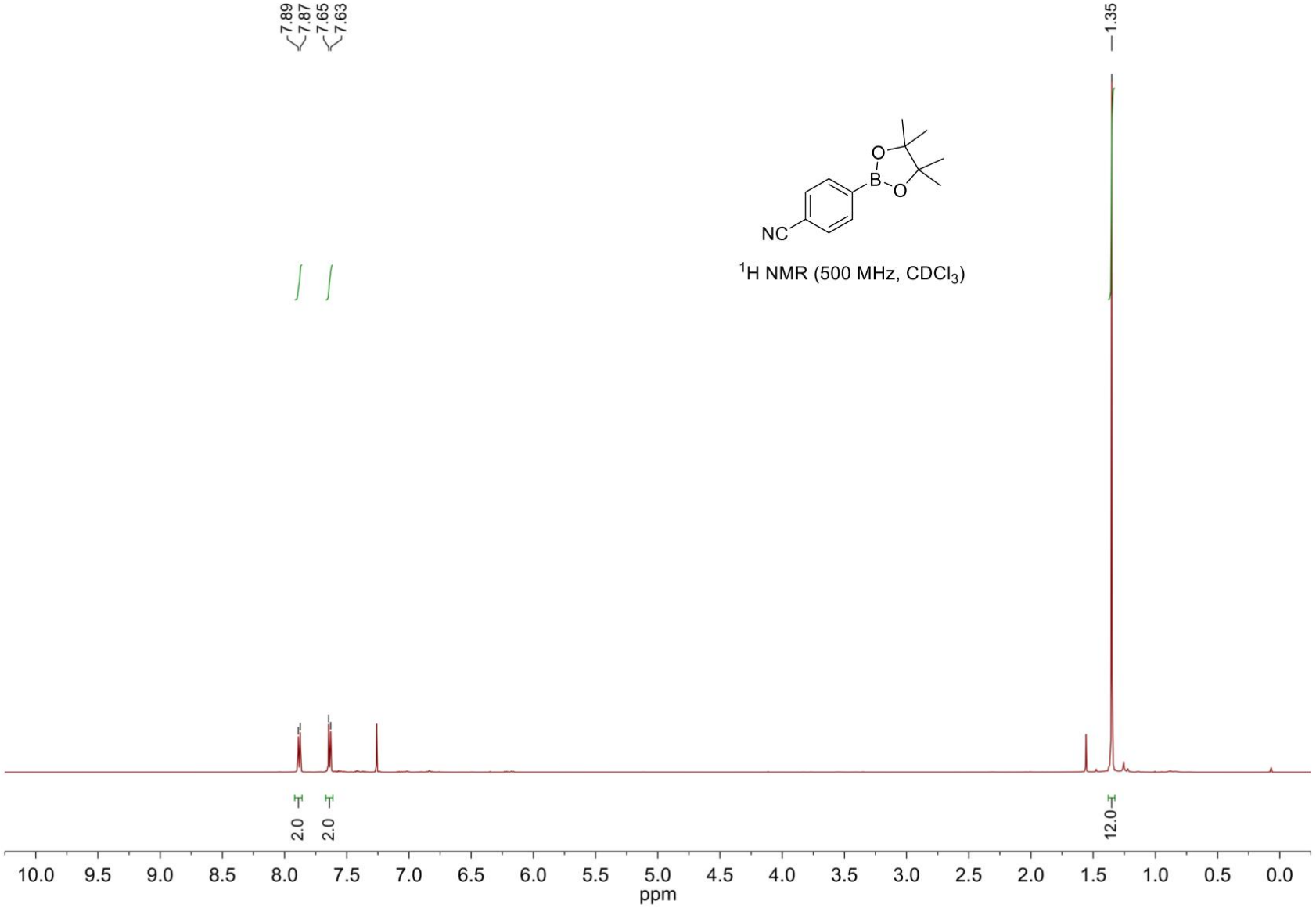
4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (16)



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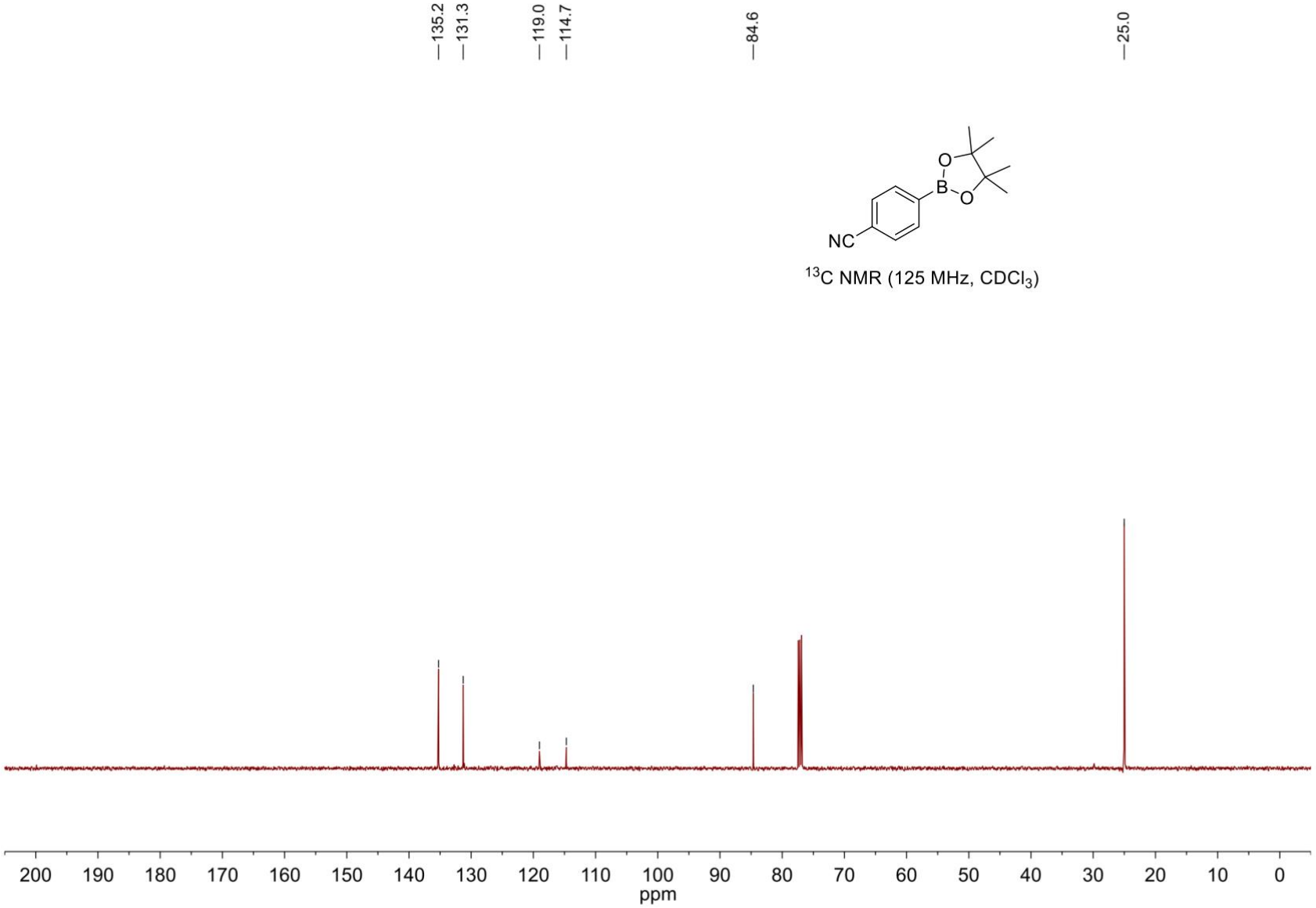
4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (16)



^{13}C NMR (125 MHz, $CDCl_3$)

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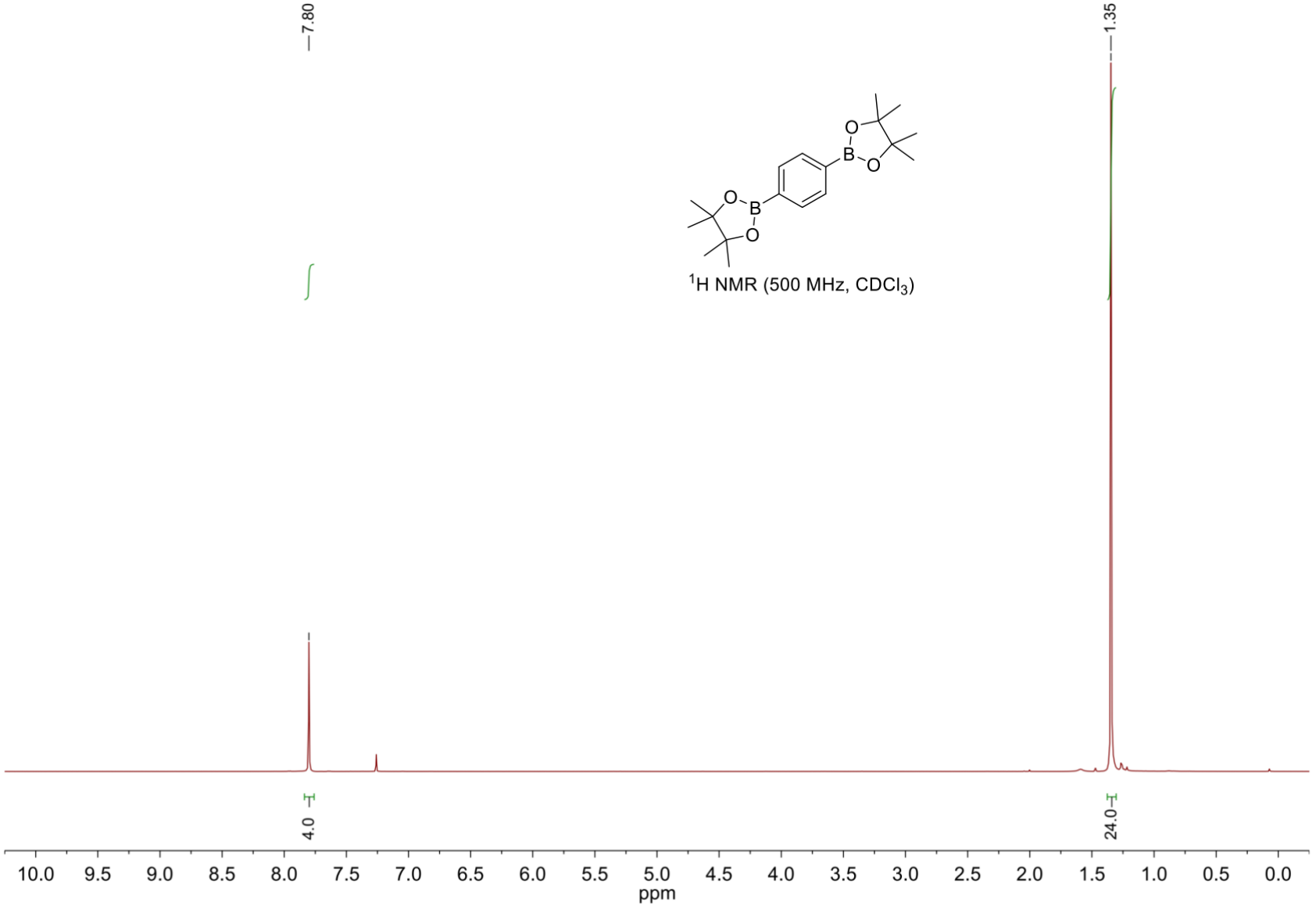
1,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (17)



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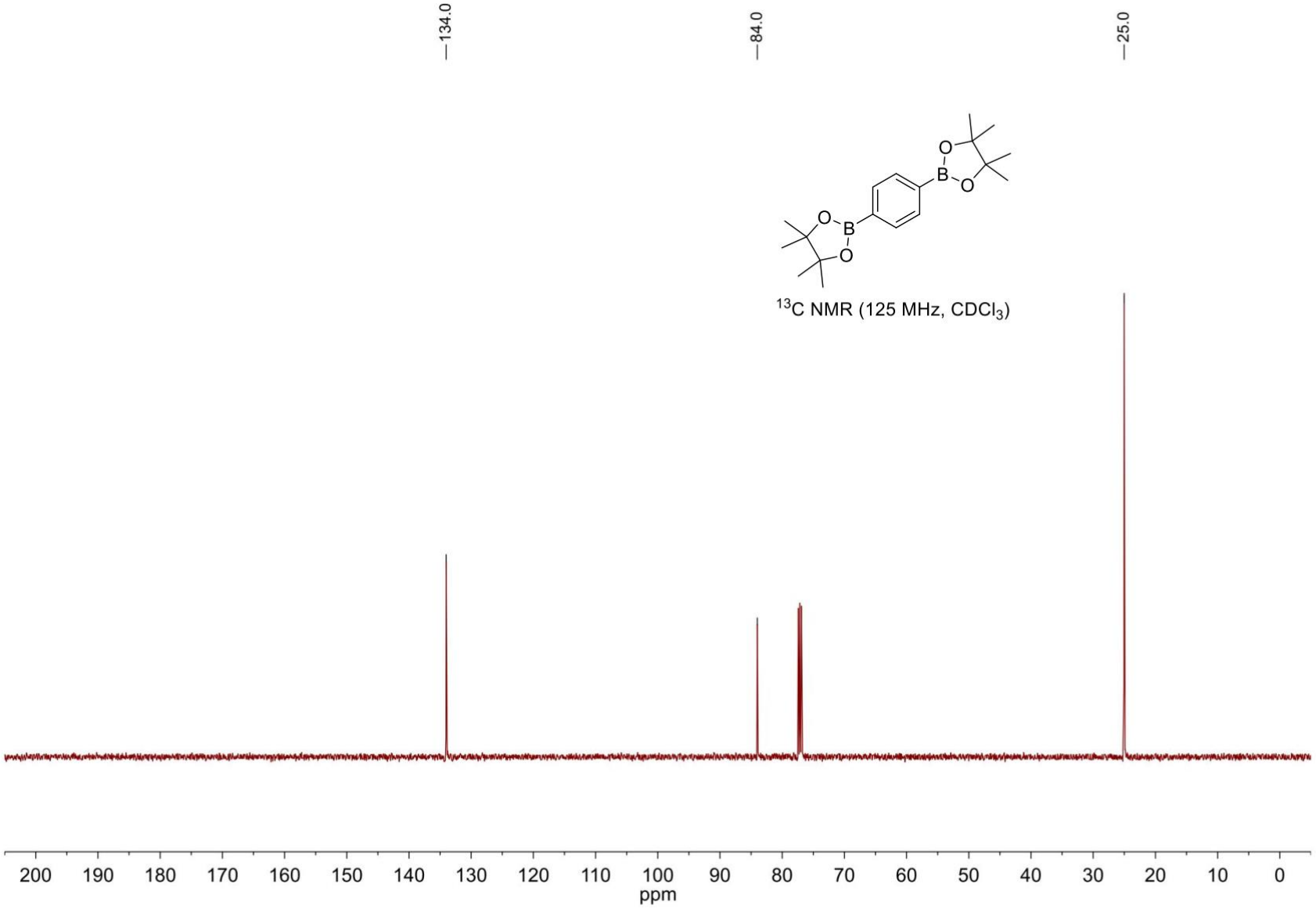
1,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (17)



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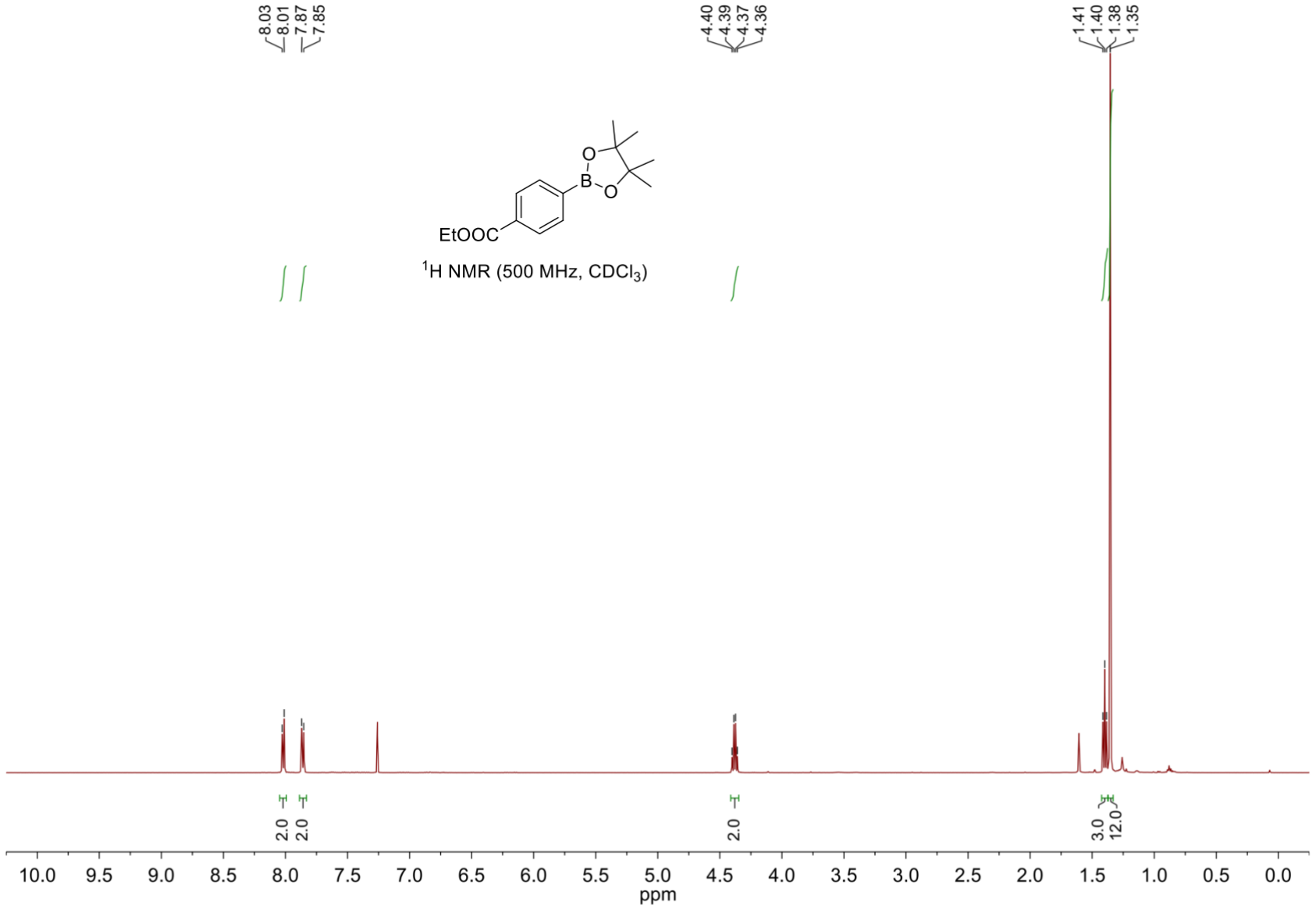
Ethyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (18)



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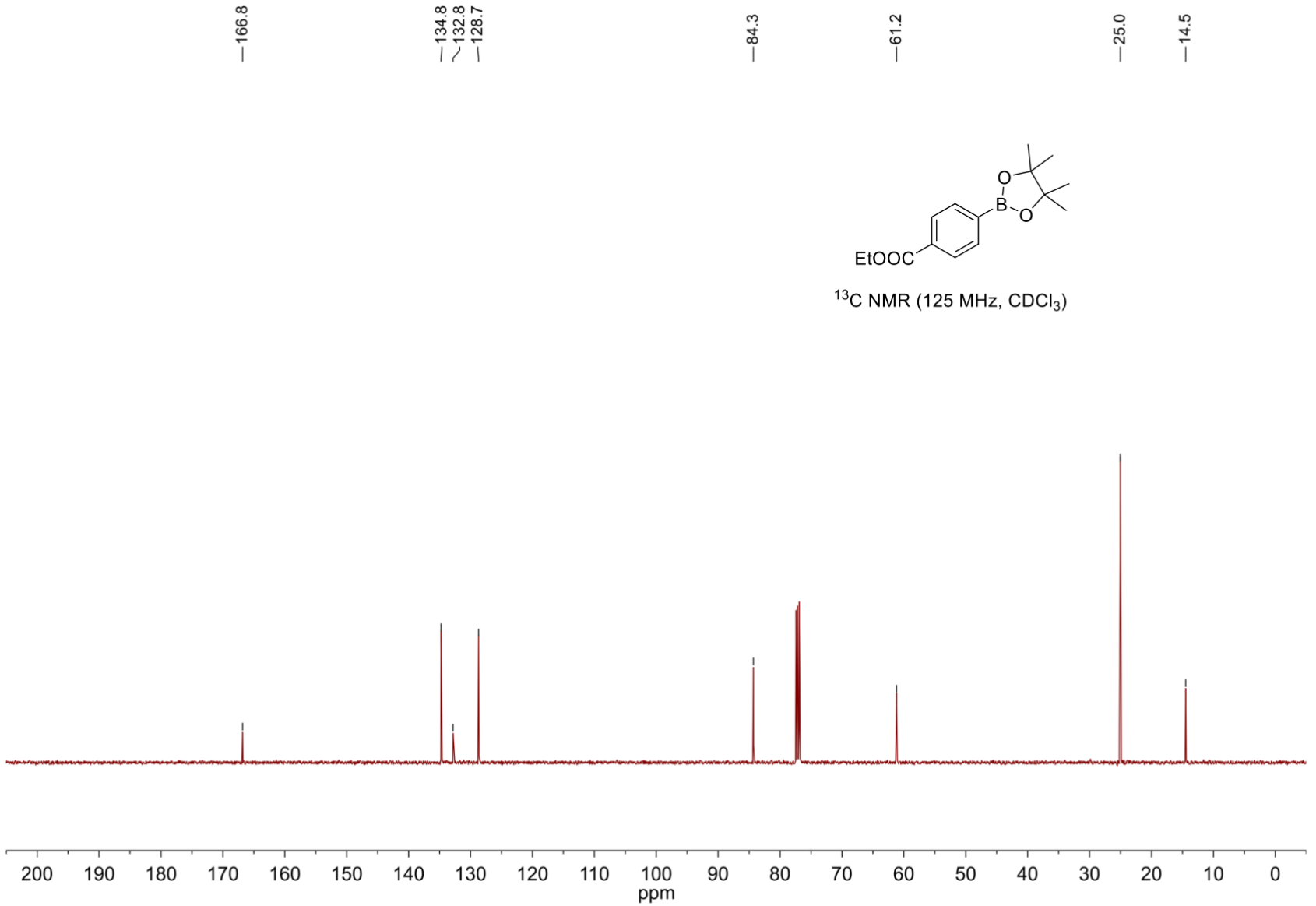
Ethyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (18)



^{13}C NMR (125 MHz, $CDCl_3$)

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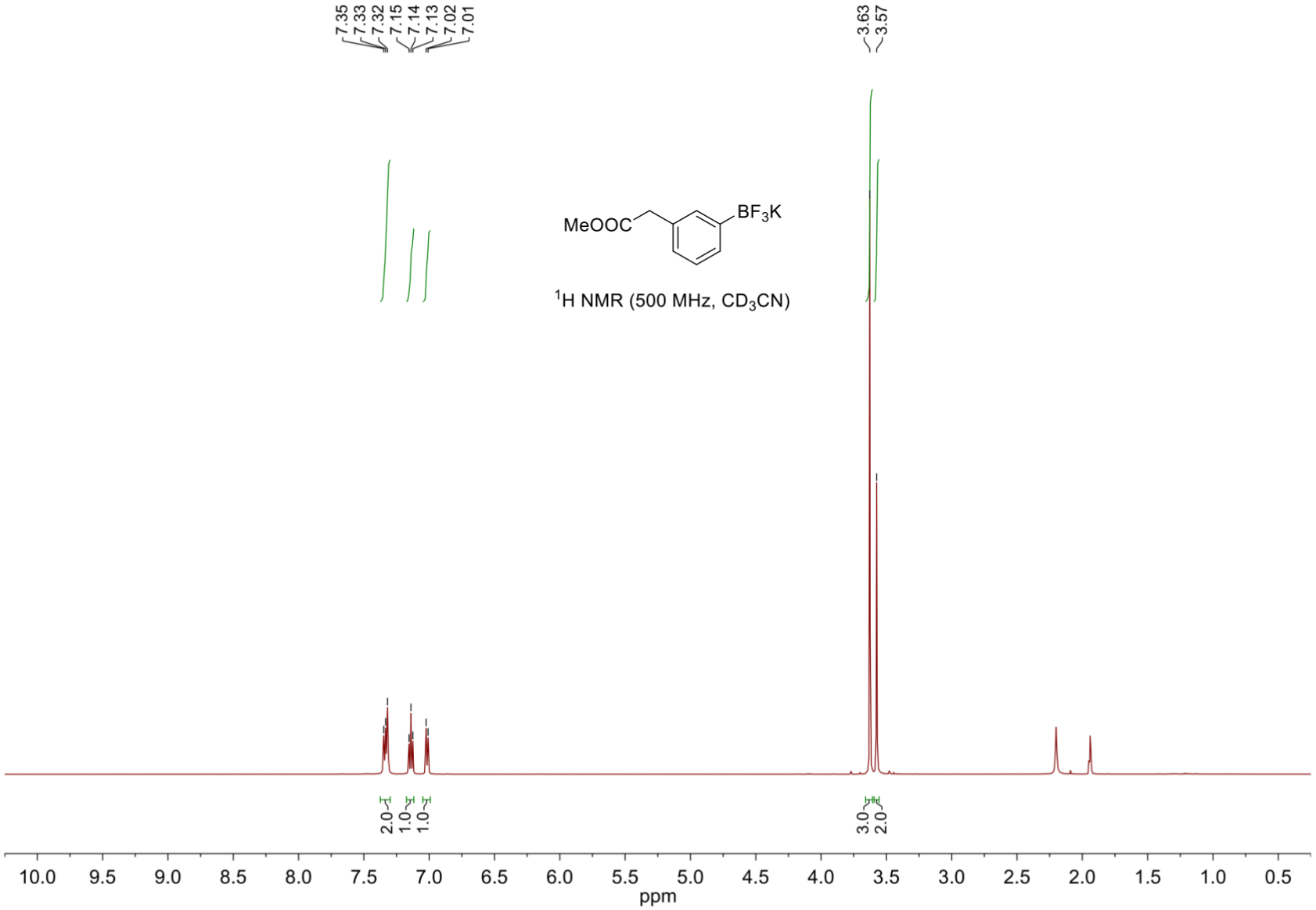
Methyl 2-(3-(trifluoro-λ⁴-boraneyl)phenyl)acetate, potassium salt (19)



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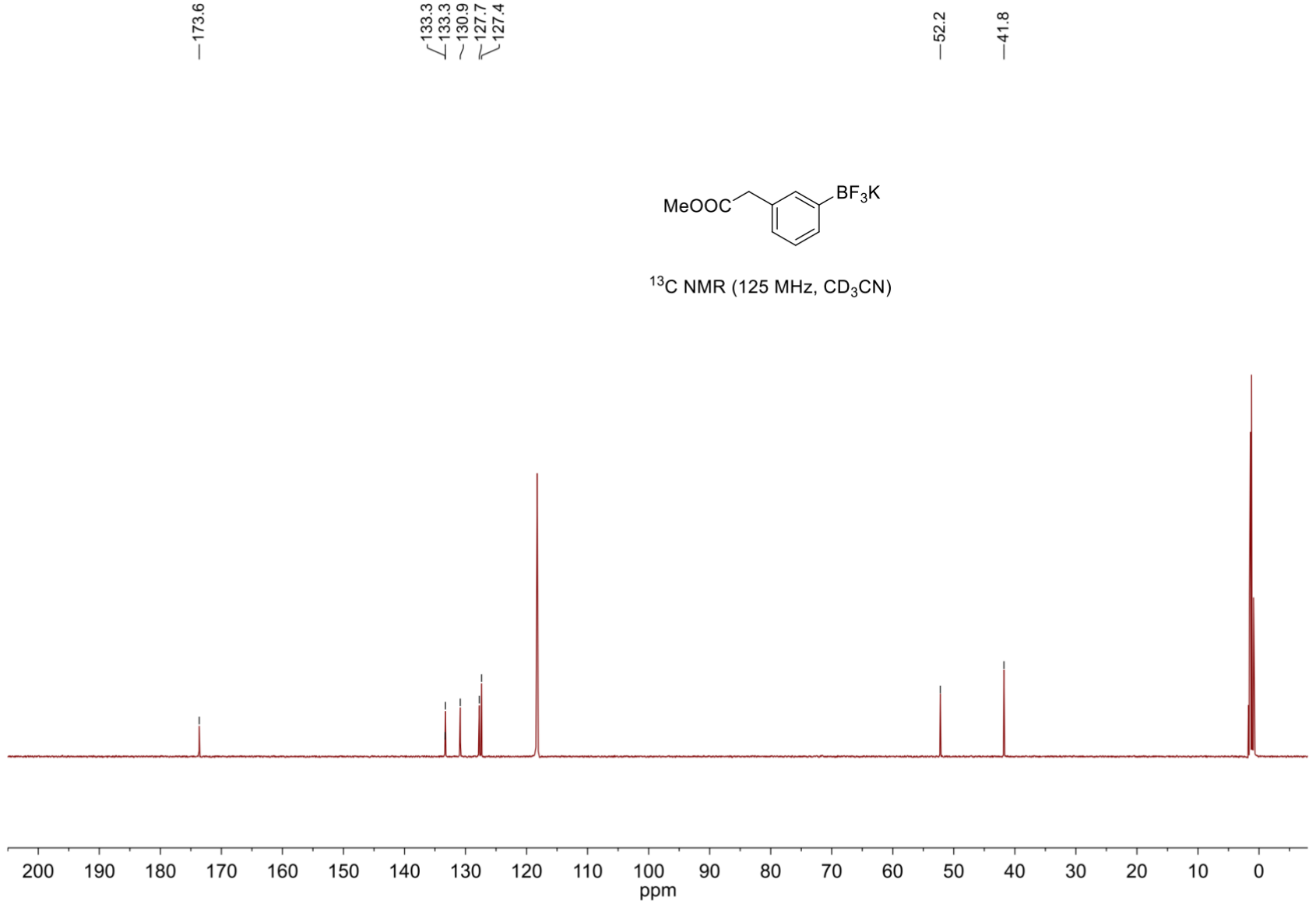
Methyl 2-(3-(trifluoro-λ⁴-boraneyl)phenyl)acetate, potassium salt (19)



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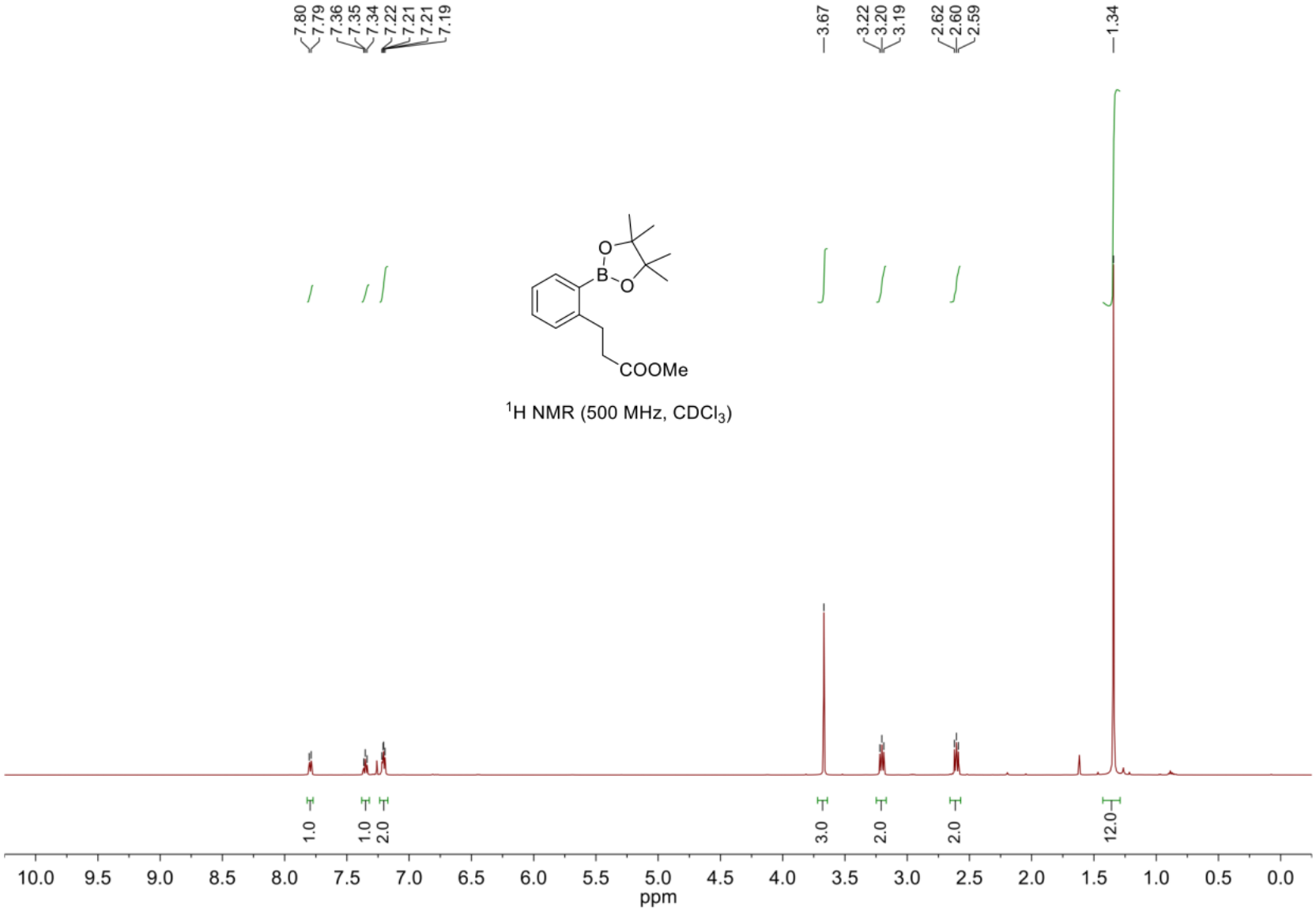
Methyl 3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propanoate (20)



^{1}H NMR (500 MHz, $CDCl_3$)

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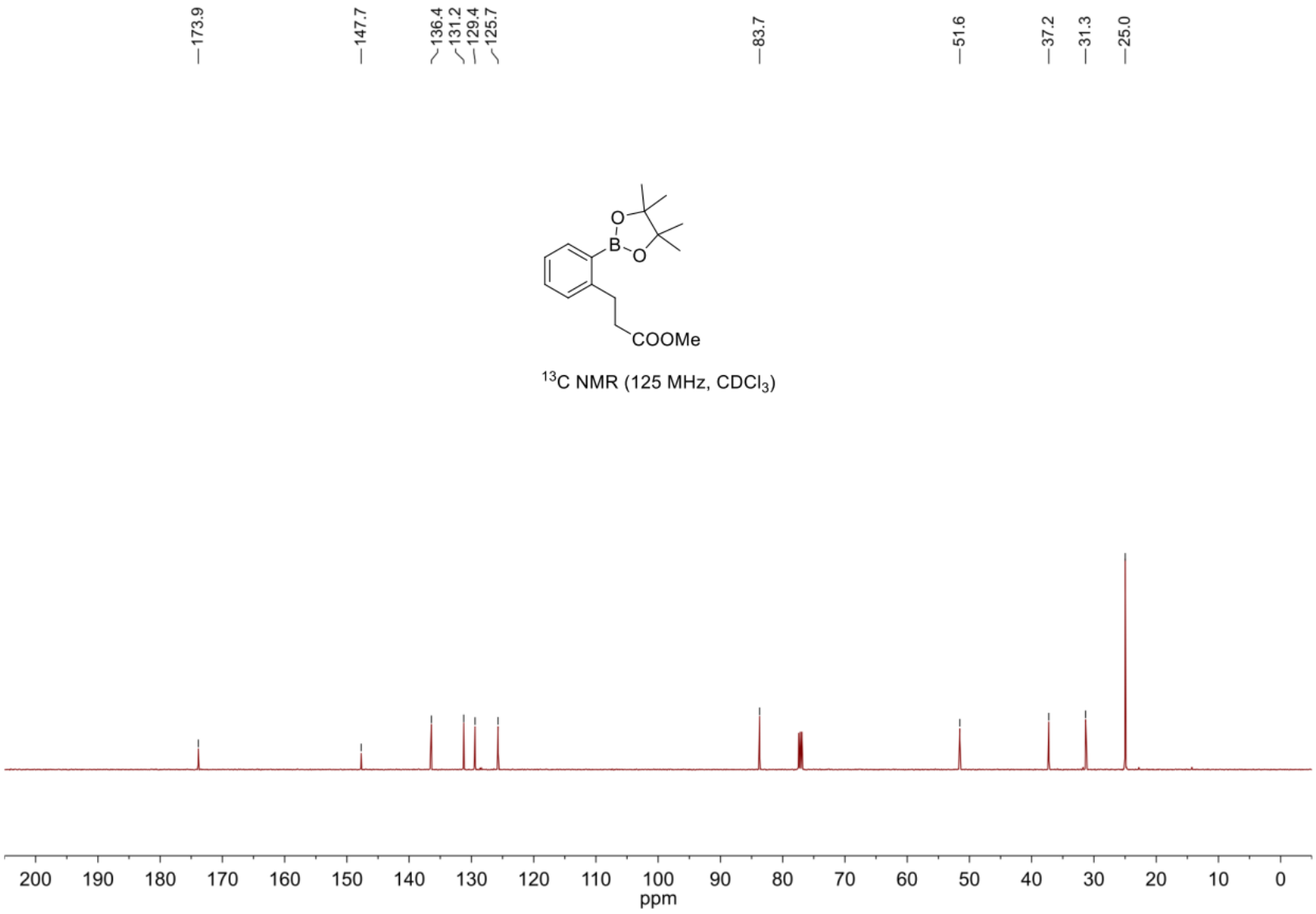
Methyl 3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propanoate (20)



^{13}C NMR (125 MHz, $CDCl_3$)

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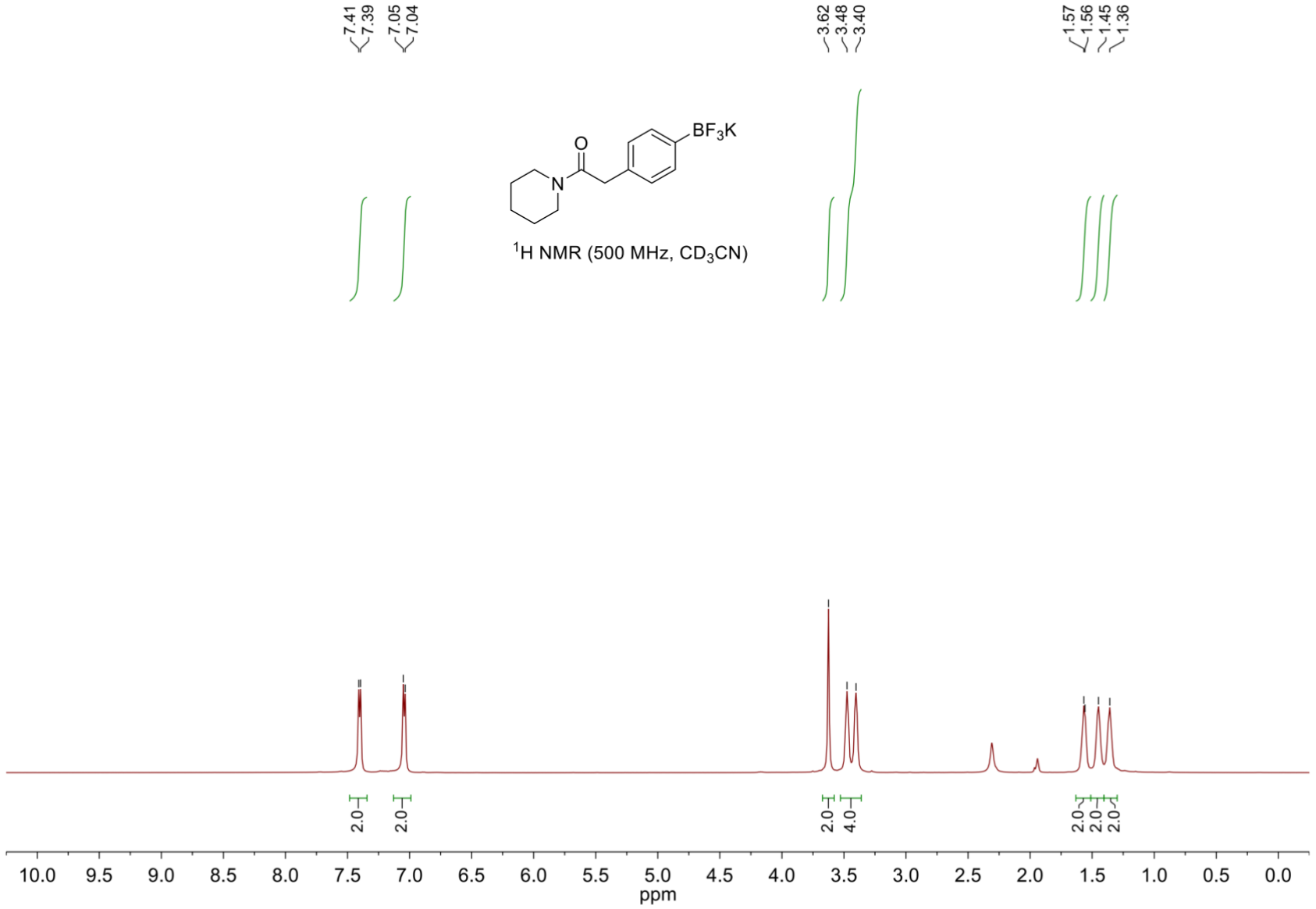
1-(Piperidin-1-yl)-2-(4-(trifluoro-λ⁴-boraneyl)phenyl)ethan-1-one, potassium salt (21)



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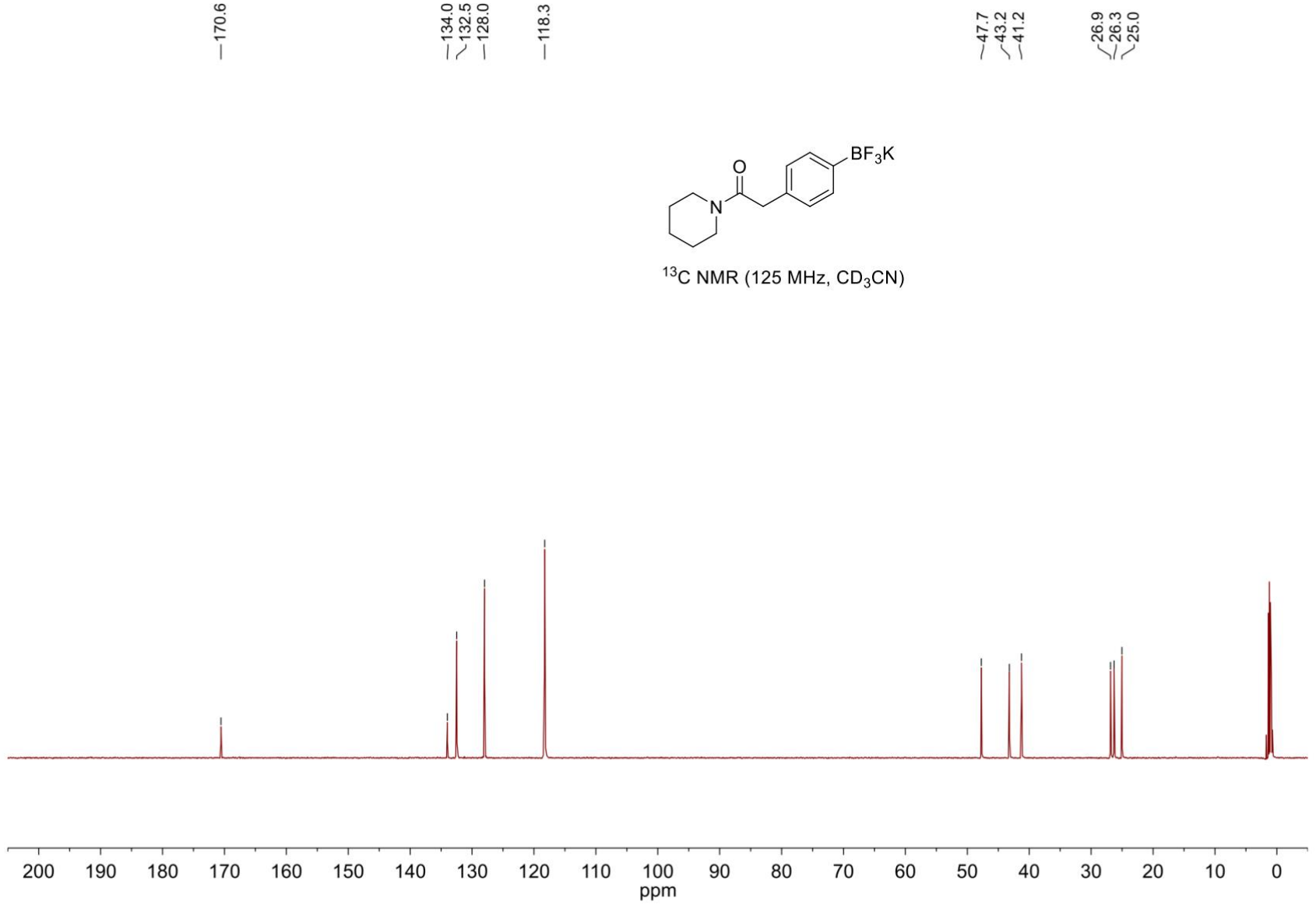
1-(Piperidin-1-yl)-2-(4-(trifluoro-λ⁴-boraneyl)phenyl)ethan-1-one, potassium salt (21)



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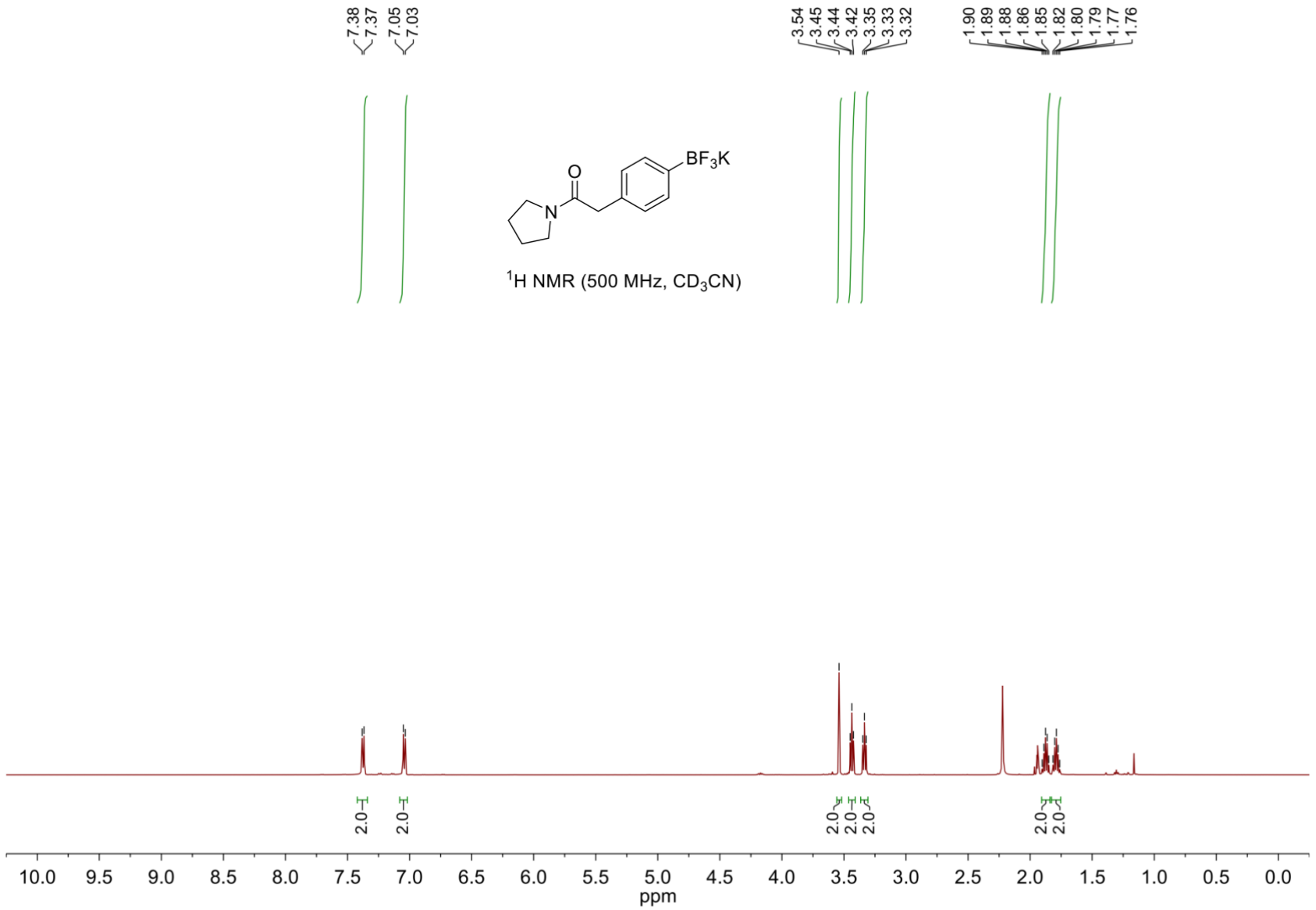
1-(Pyrrolidin-1-yl)-2-(4-(trifluoro-λ⁴-boraneyl)phenyl)ethan-1-one, potassium salt (22)



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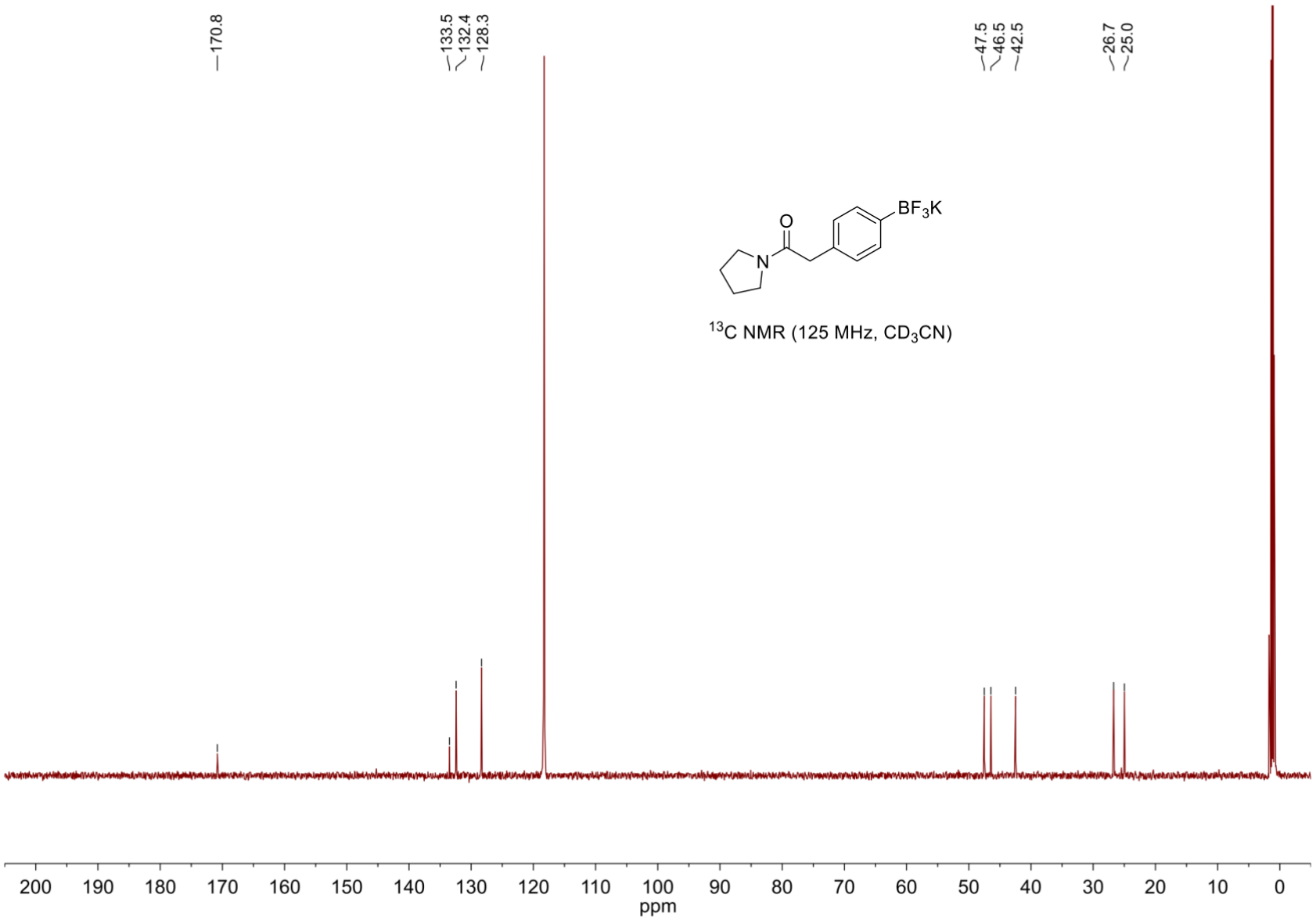
1-(Pyrrolidin-1-yl)-2-(4-(trifluoro-λ⁴-boraneyl)phenyl)ethan-1-one, potassium salt (22)



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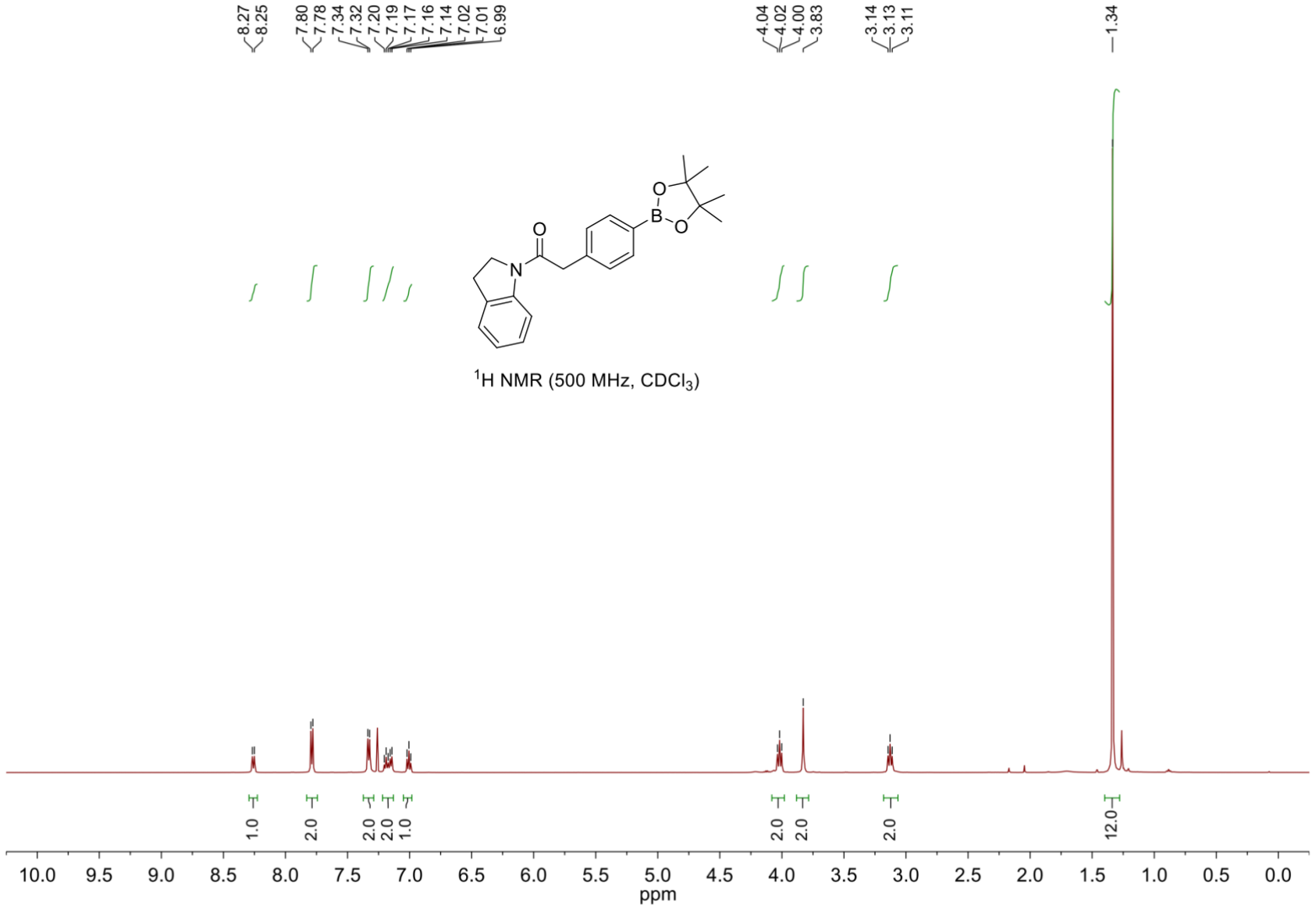
1-(Indolin-1-yl)-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (23)



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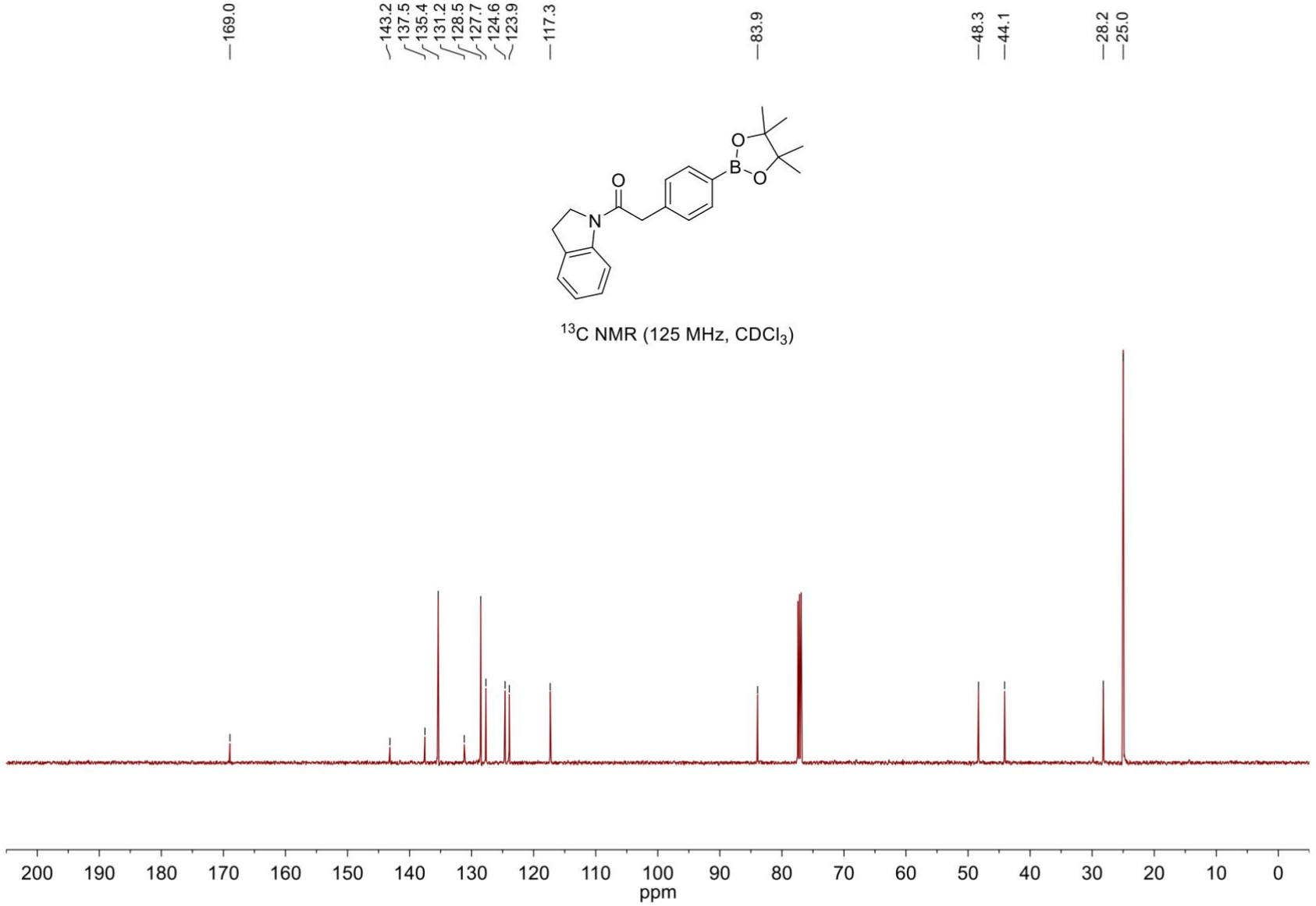
1-(Indolin-1-yl)-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (23)



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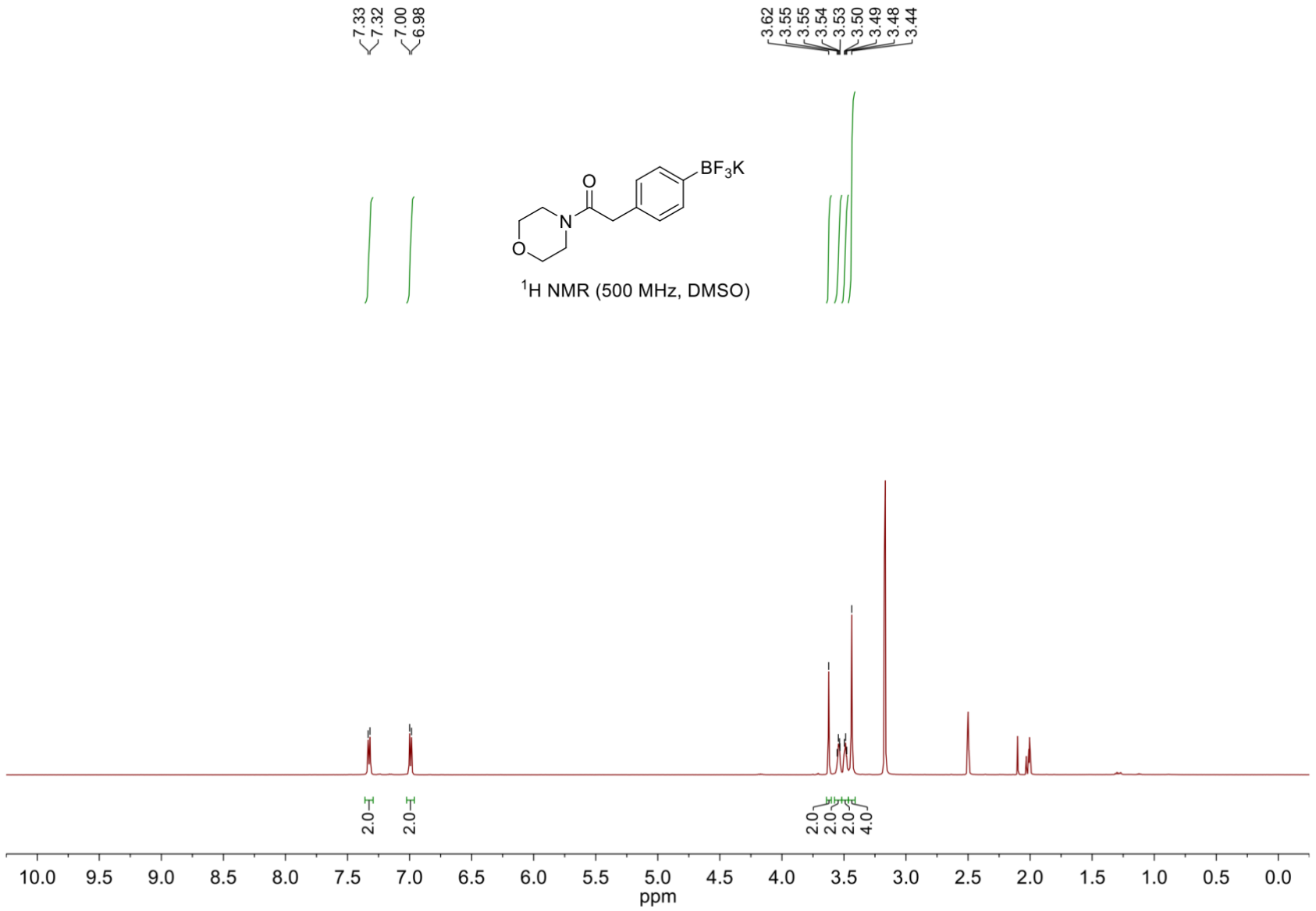
1-Morpholino-2-(4-(trifluoro-λ⁴-boraneyl)phenyl)ethan-1-one, potassium salt (24)



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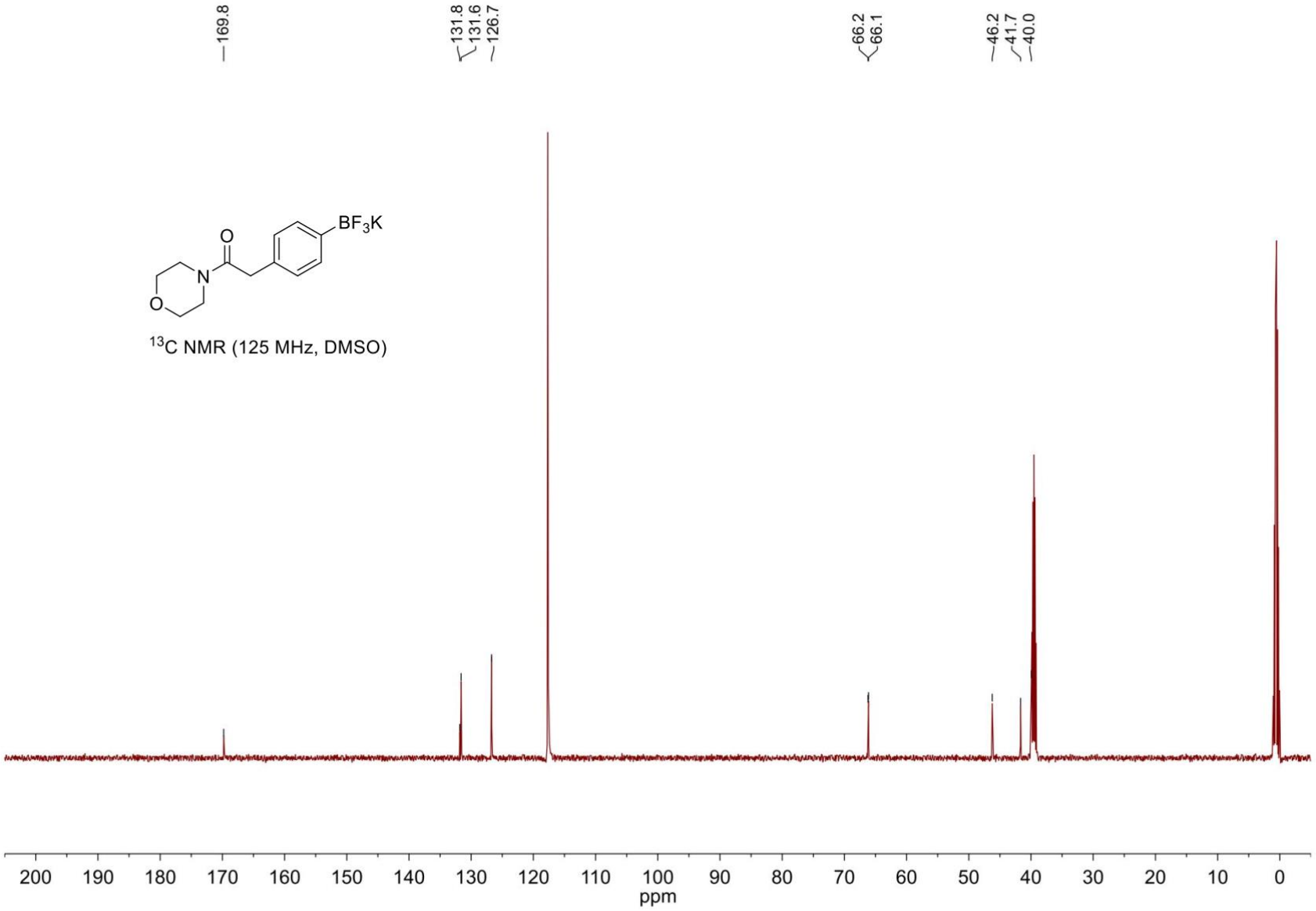
1-Morpholino-2-(4-(trifluoro-λ⁴-boraneyl)phenyl)ethan-1-one, potassium salt (24)



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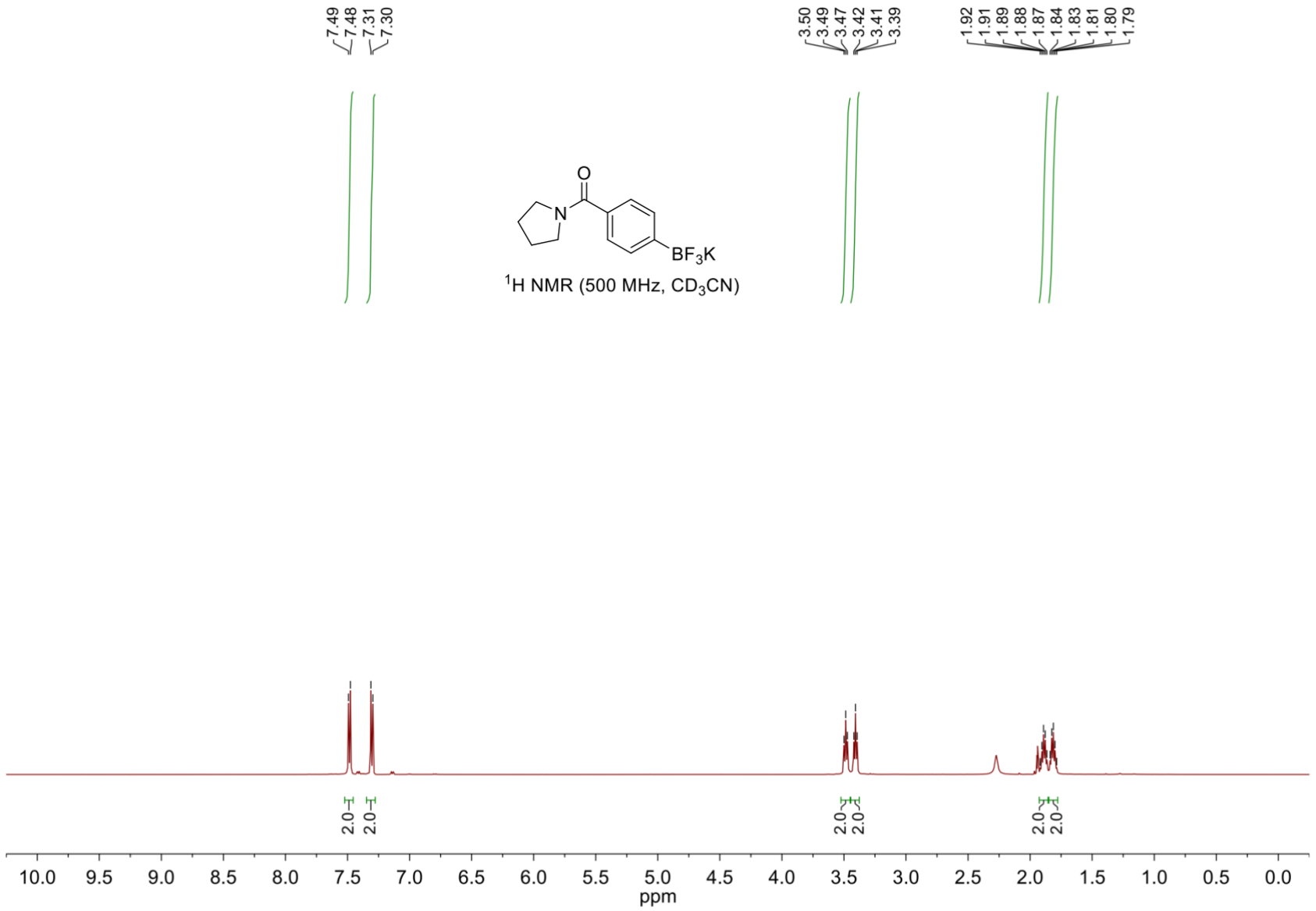
Pyrrolidin-1-yl(4-(trifluoro-λ⁴-boraneyl)phenyl)methanone, potassium salt (25)



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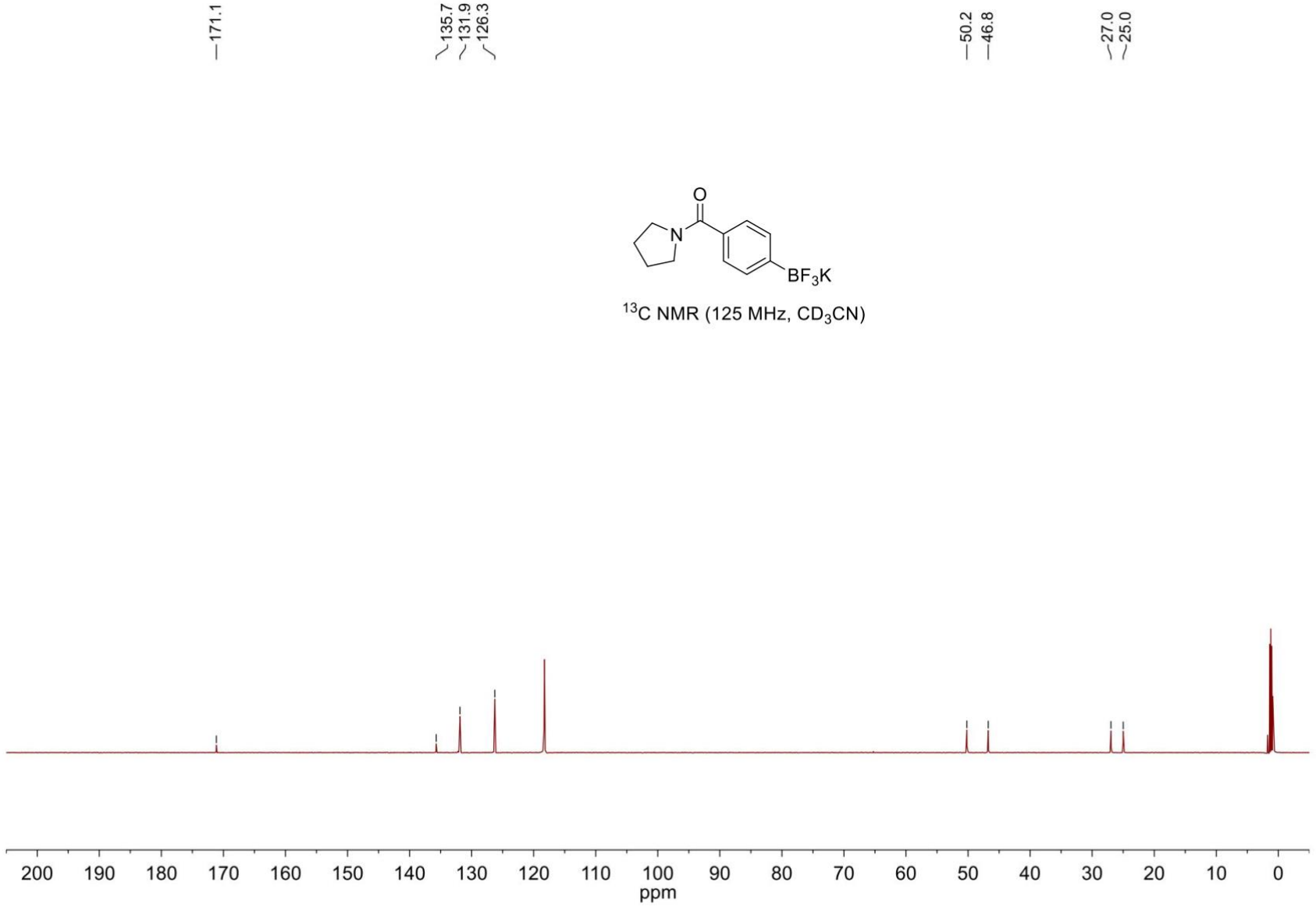
Pyrrolidin-1-yl(4-(trifluoro-λ⁴-boraneyl)phenyl)methanone, potassium salt (25)



^{13}C NMR (125 MHz, CD_3CN)

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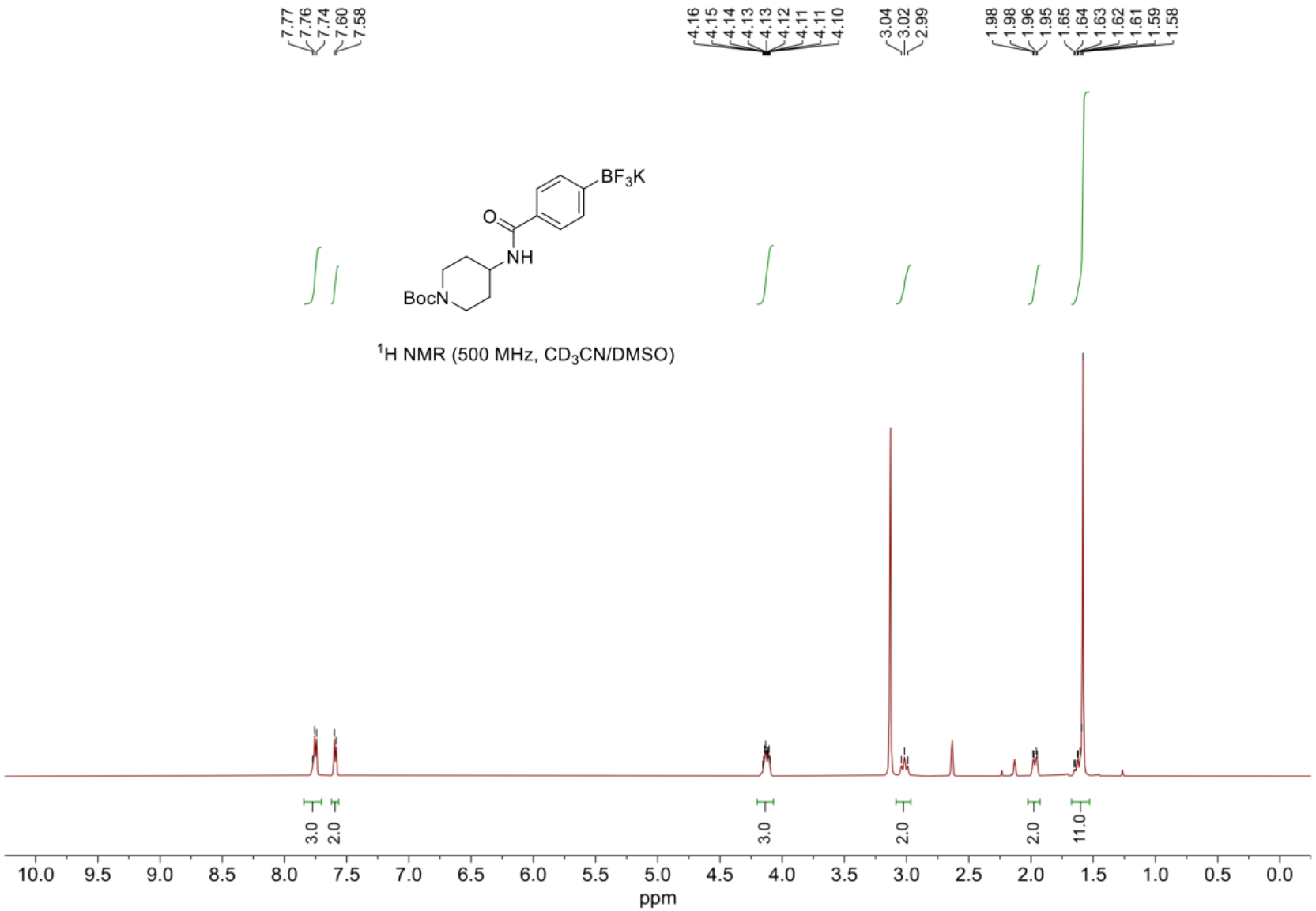
tert-Butyl 4-(4-(trifluoro-l4-boraneyl)benzamido)piperidine-1-carboxylate, potassium salt (26)



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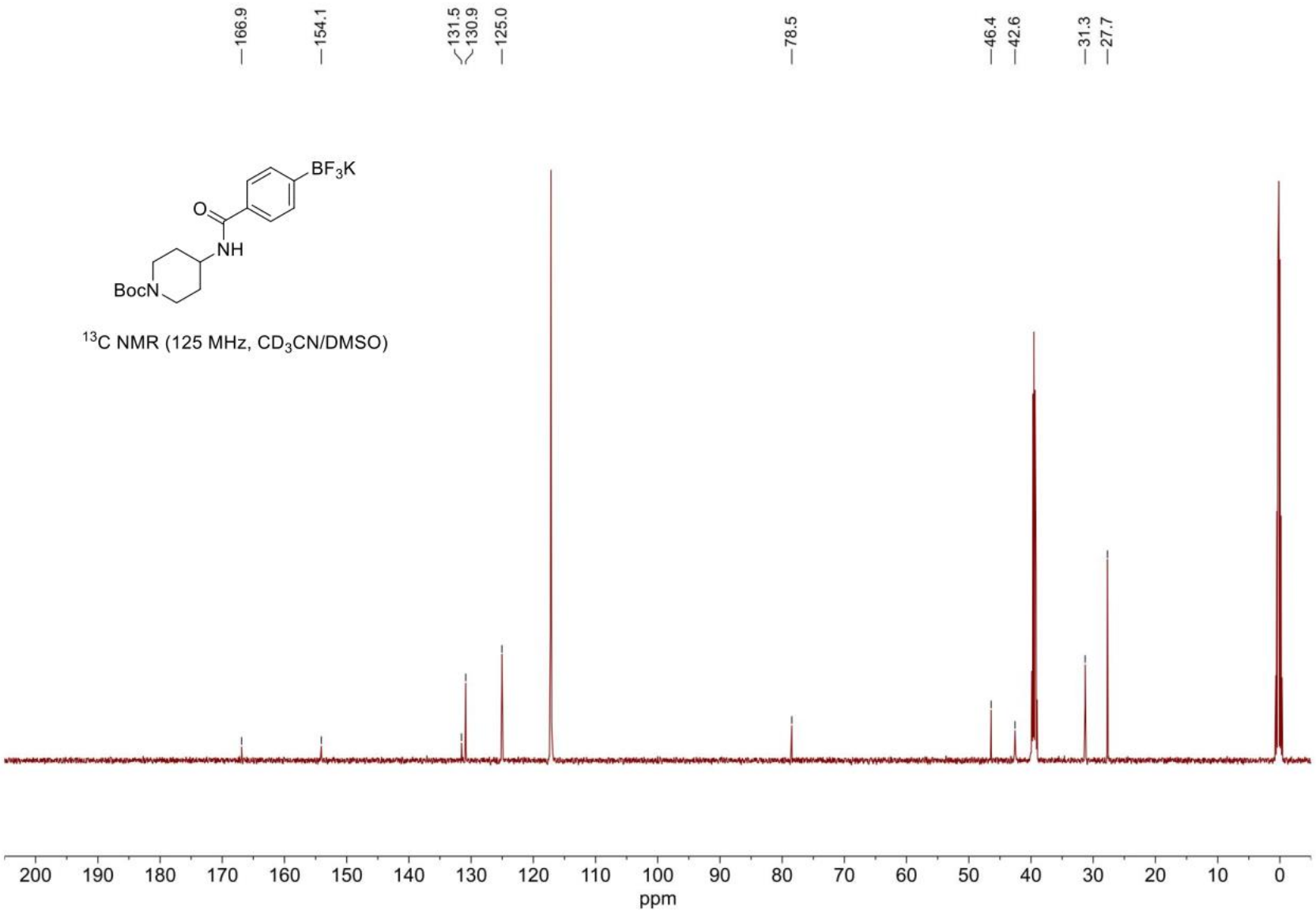
tert-Butyl 4-(4-(trifluoro-l4-boraneyl)benzamido)piperidine-1-carboxylate, potassium salt (26)



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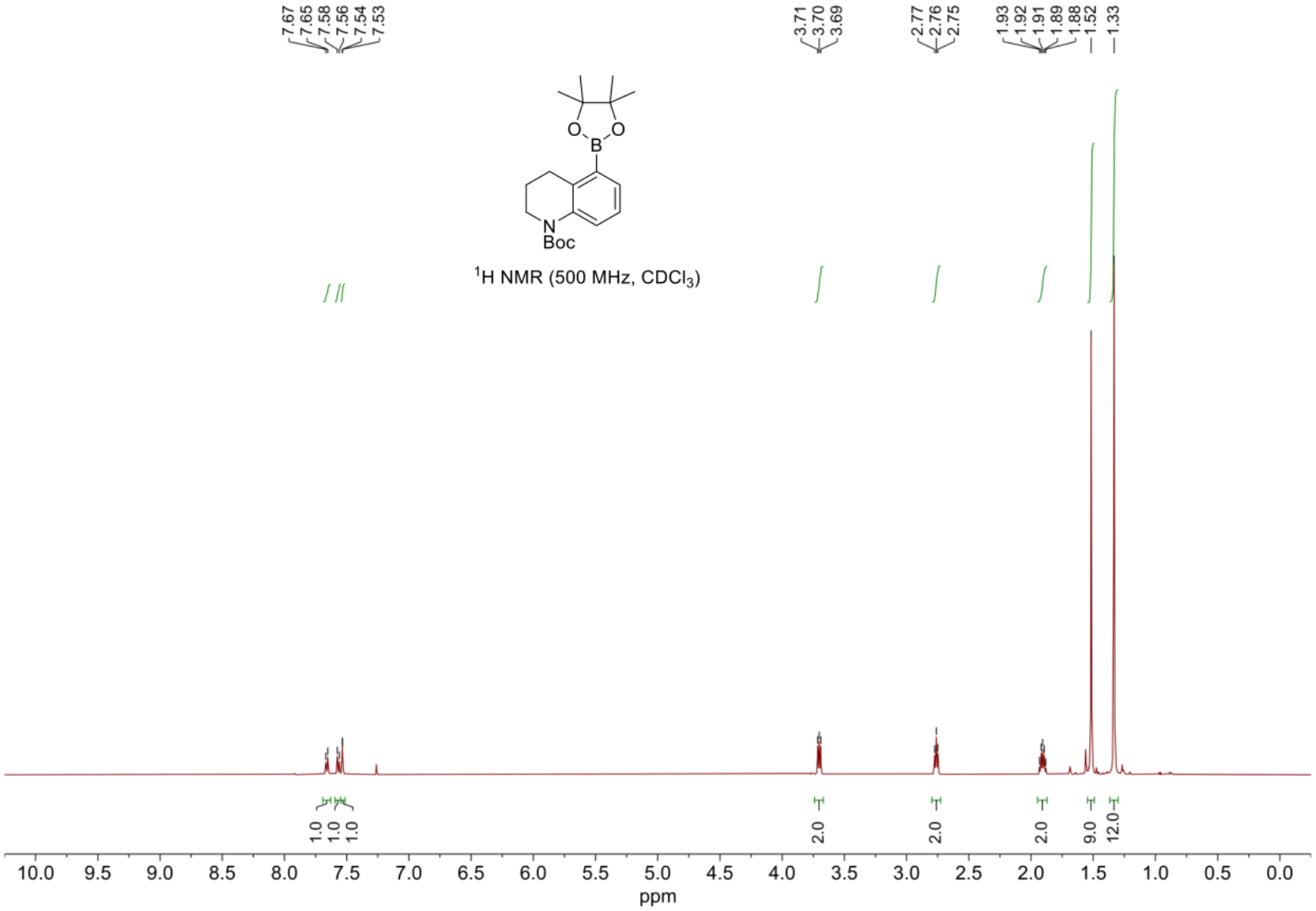
tert-Butyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydroquinoline-1(2*H*)-carboxylate (27)



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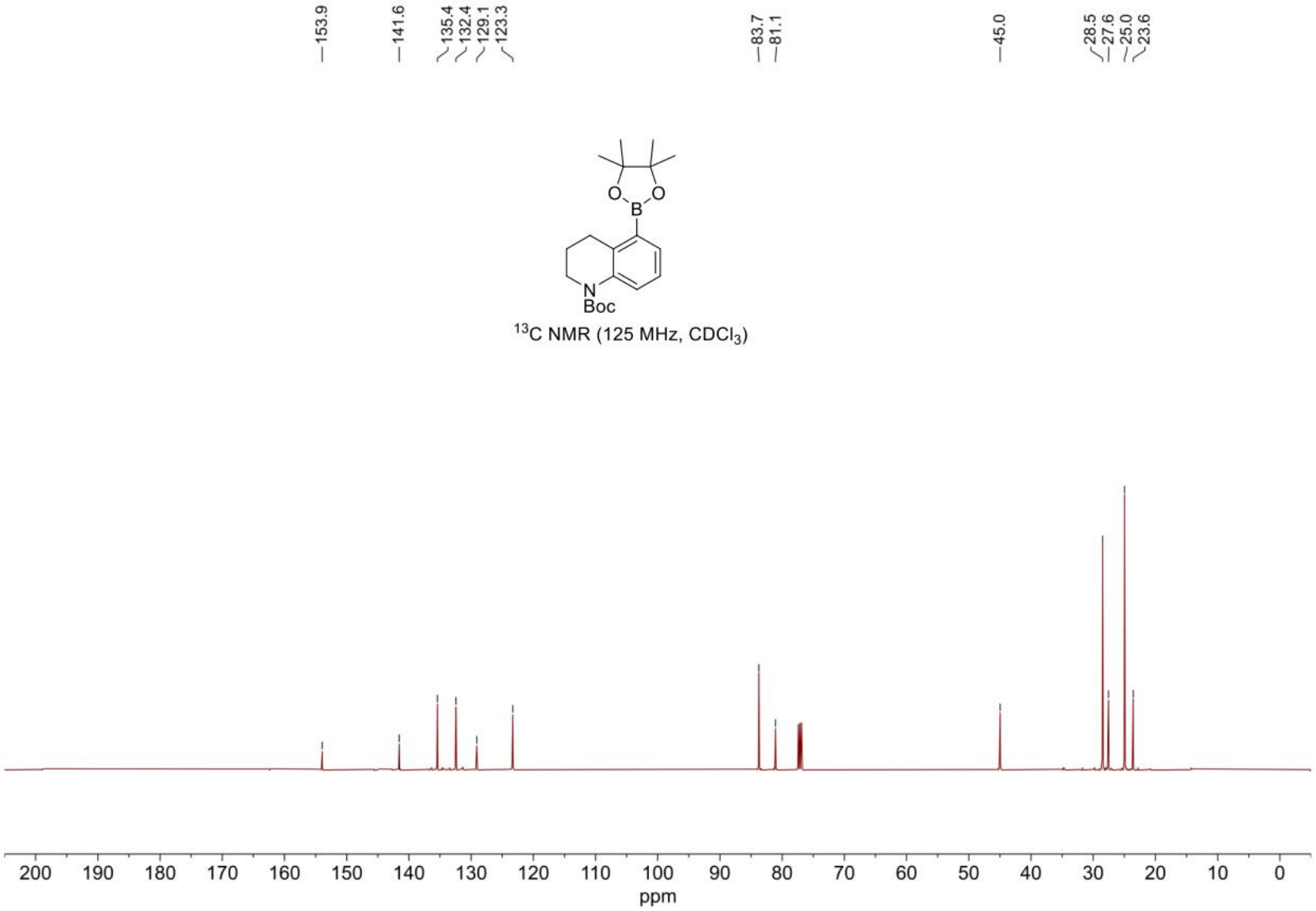
tert-Butyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydroquinoline-1(2*H*)-carboxylate (27)



^{13}C NMR (125 MHz, $CDCl_3$)

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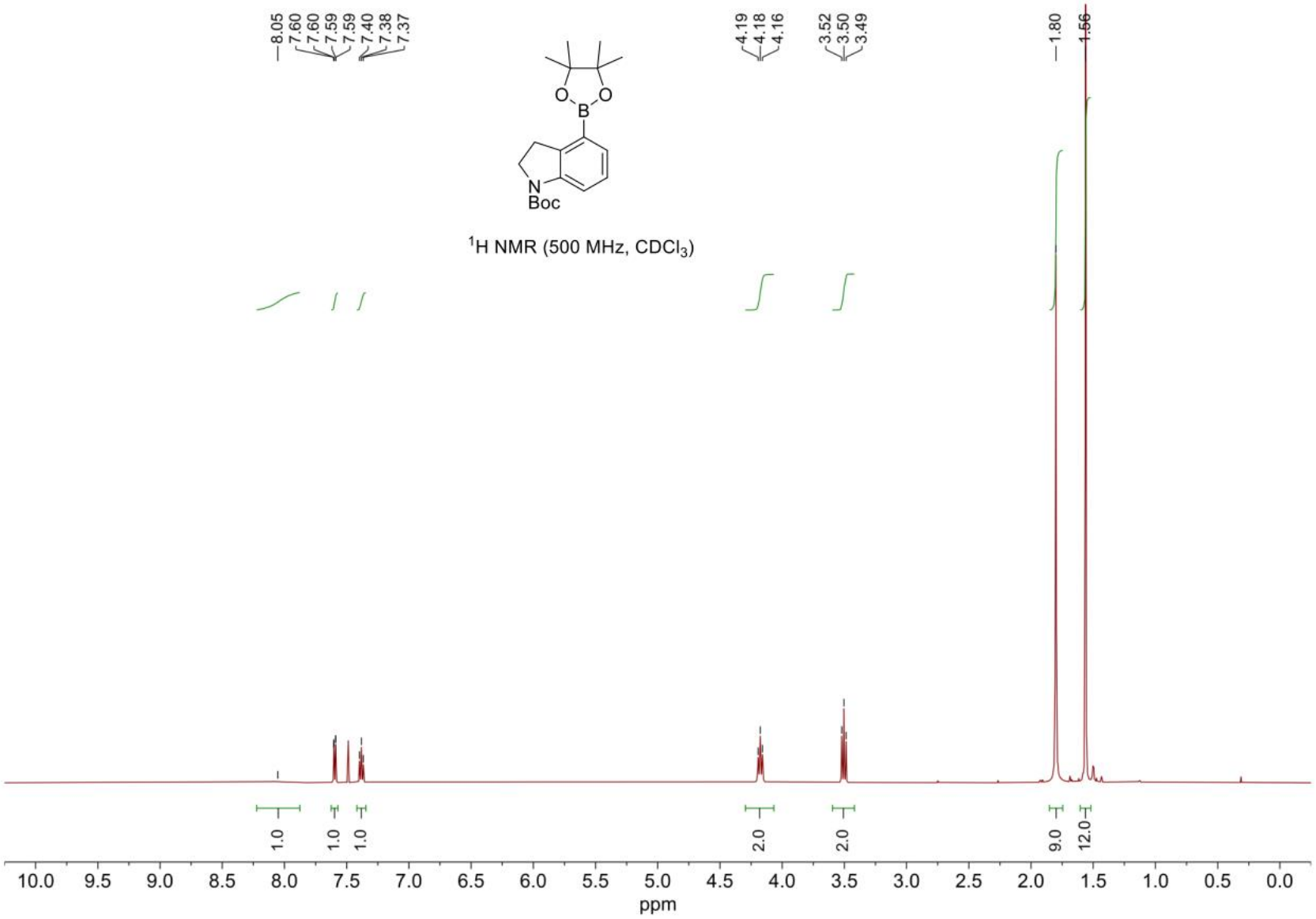
tert-Butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)indoline-1-carboxylate (28)



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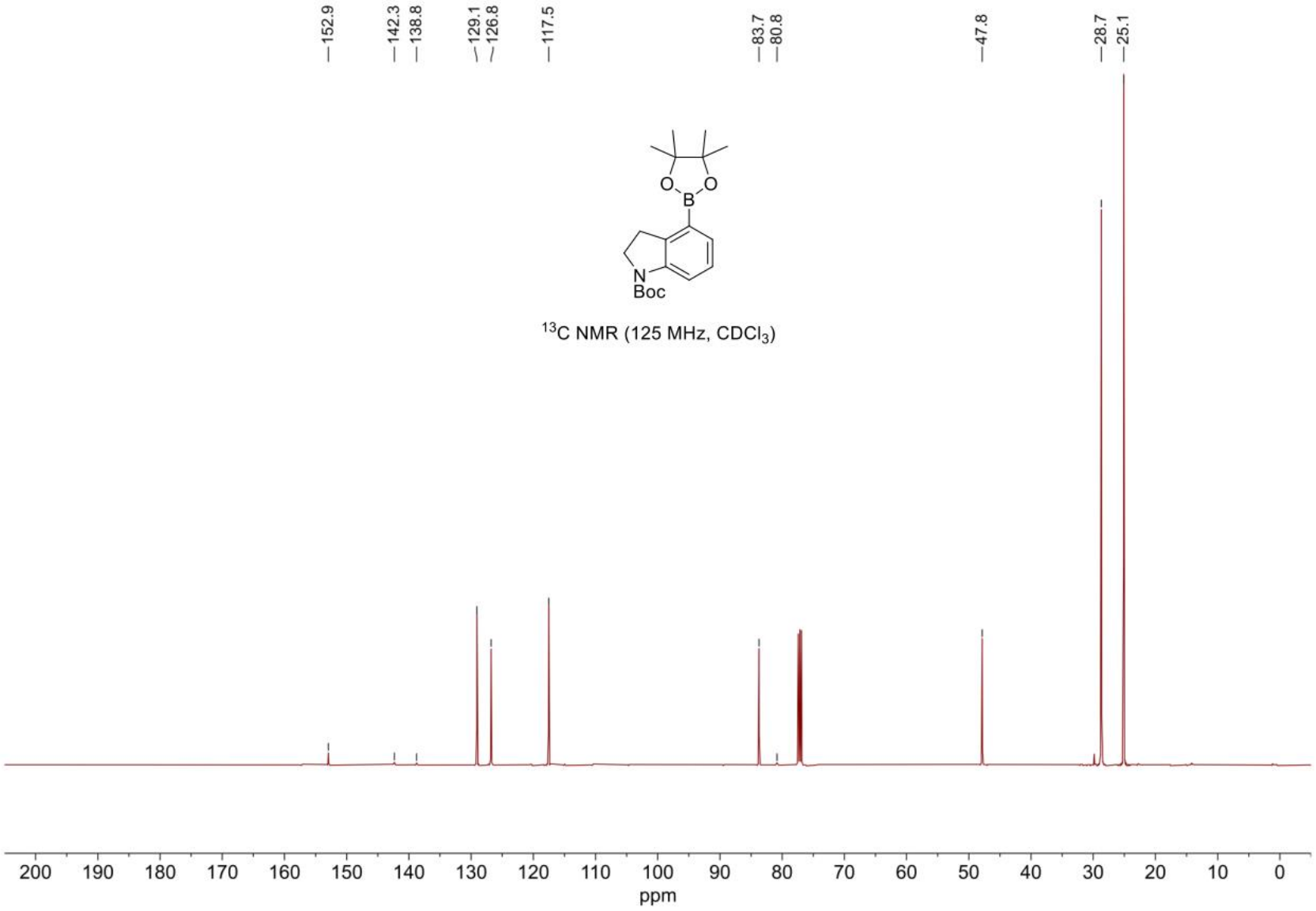
tert-Butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)indoline-1-carboxylate (28)



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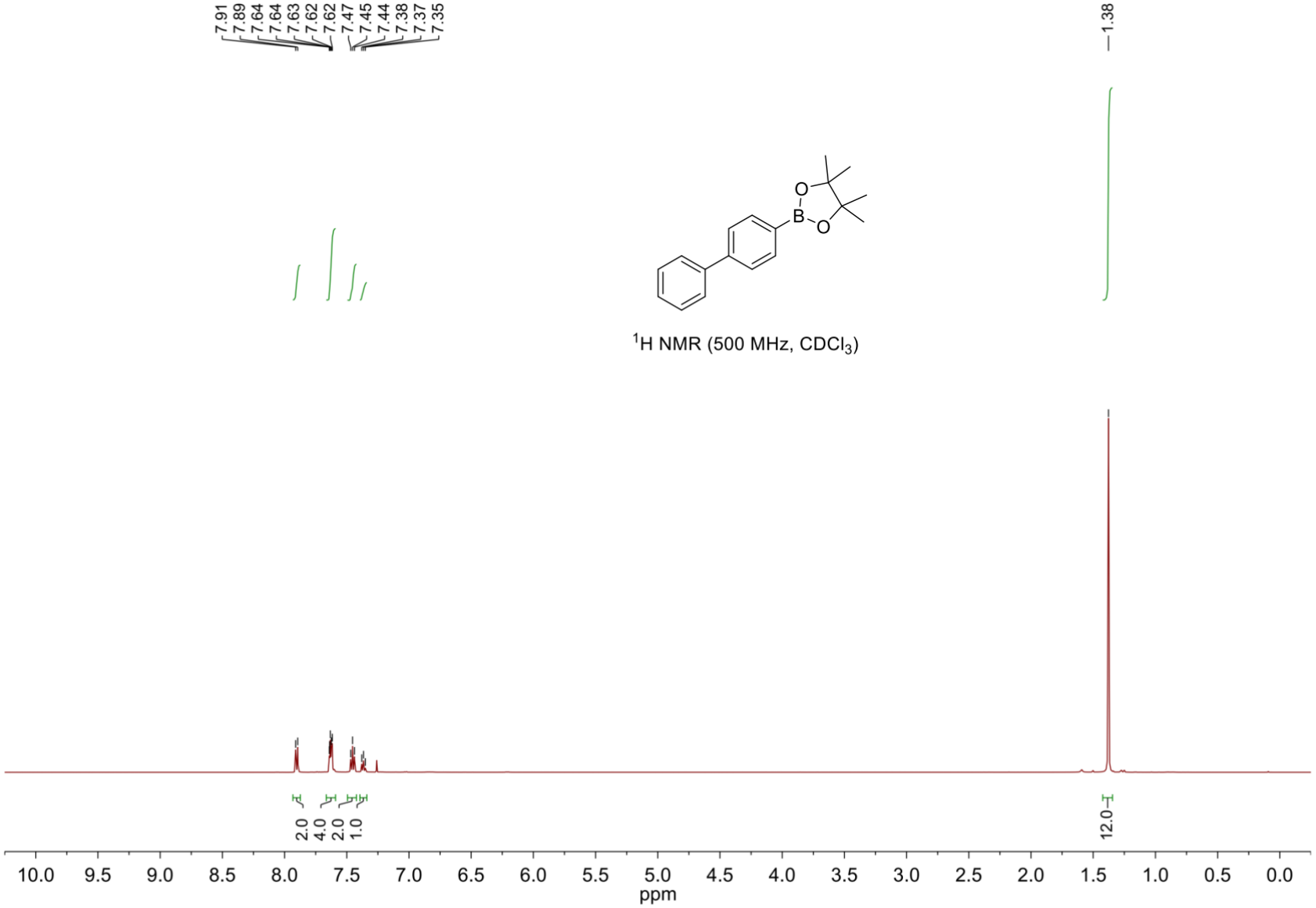
2-([1,1'-Biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (29)



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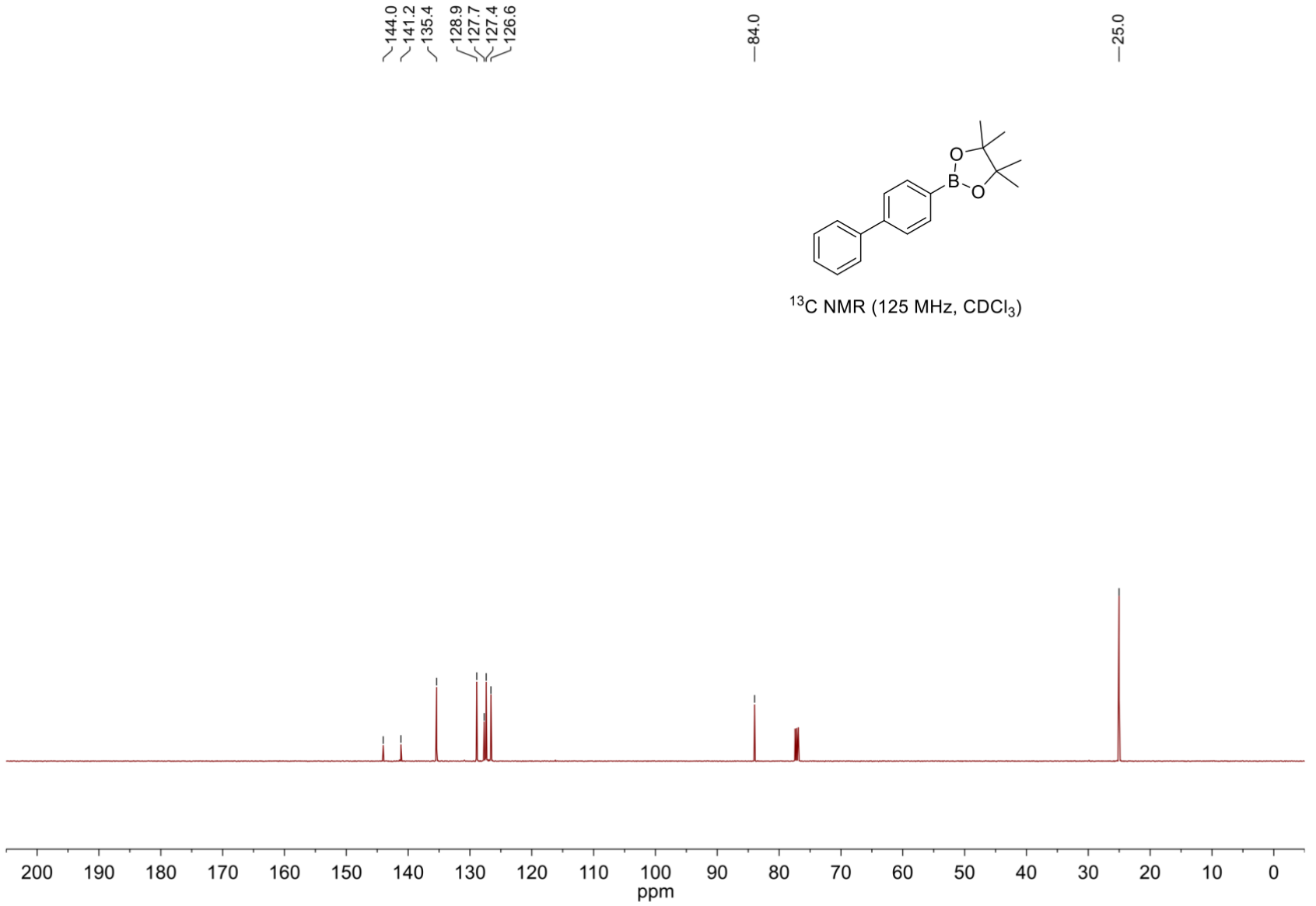
2-([1,1'-Biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (29)



^{13}C NMR (125 MHz, $CDCl_3$)

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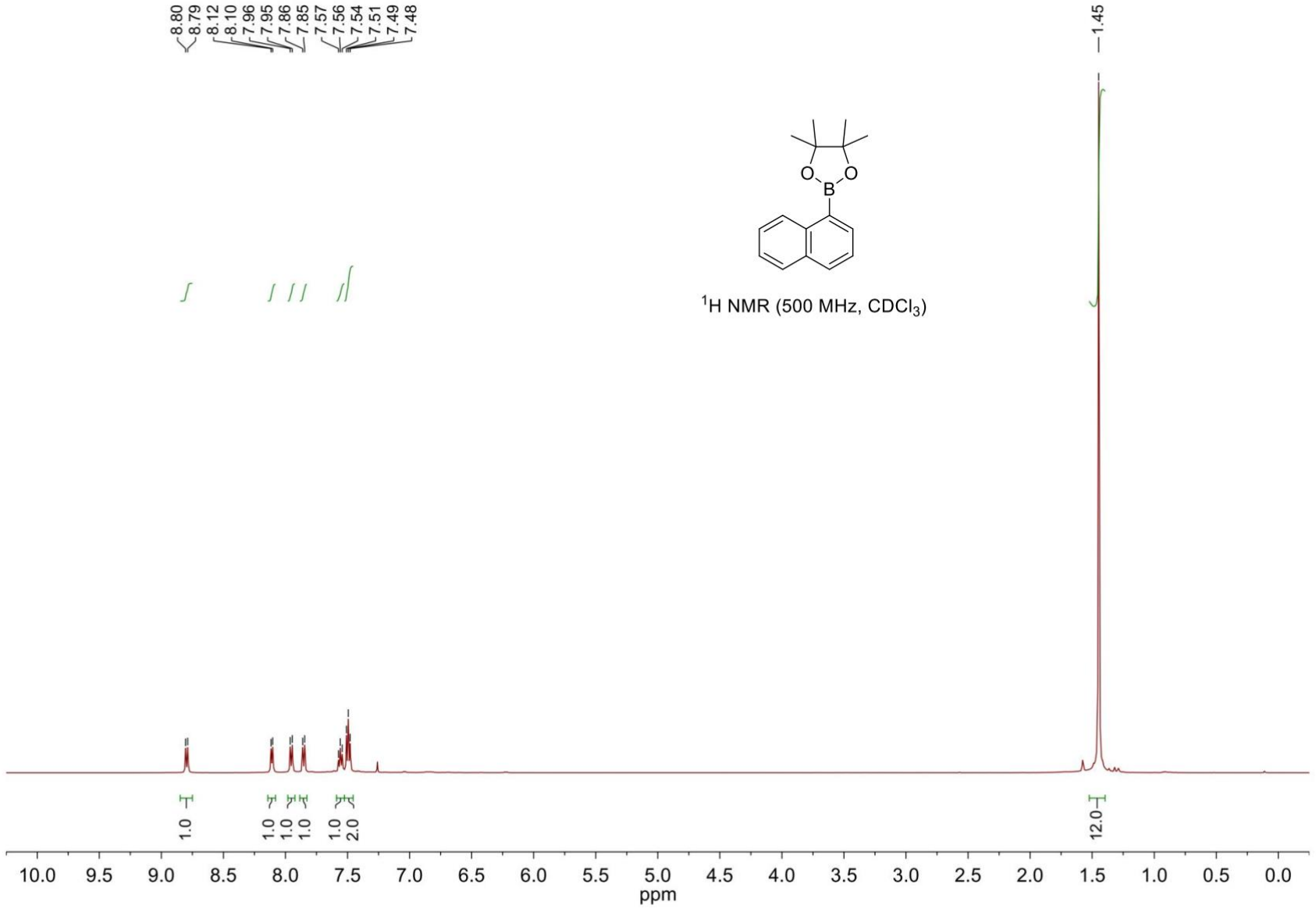
4,4,5,5-Tetramethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborolane (30)



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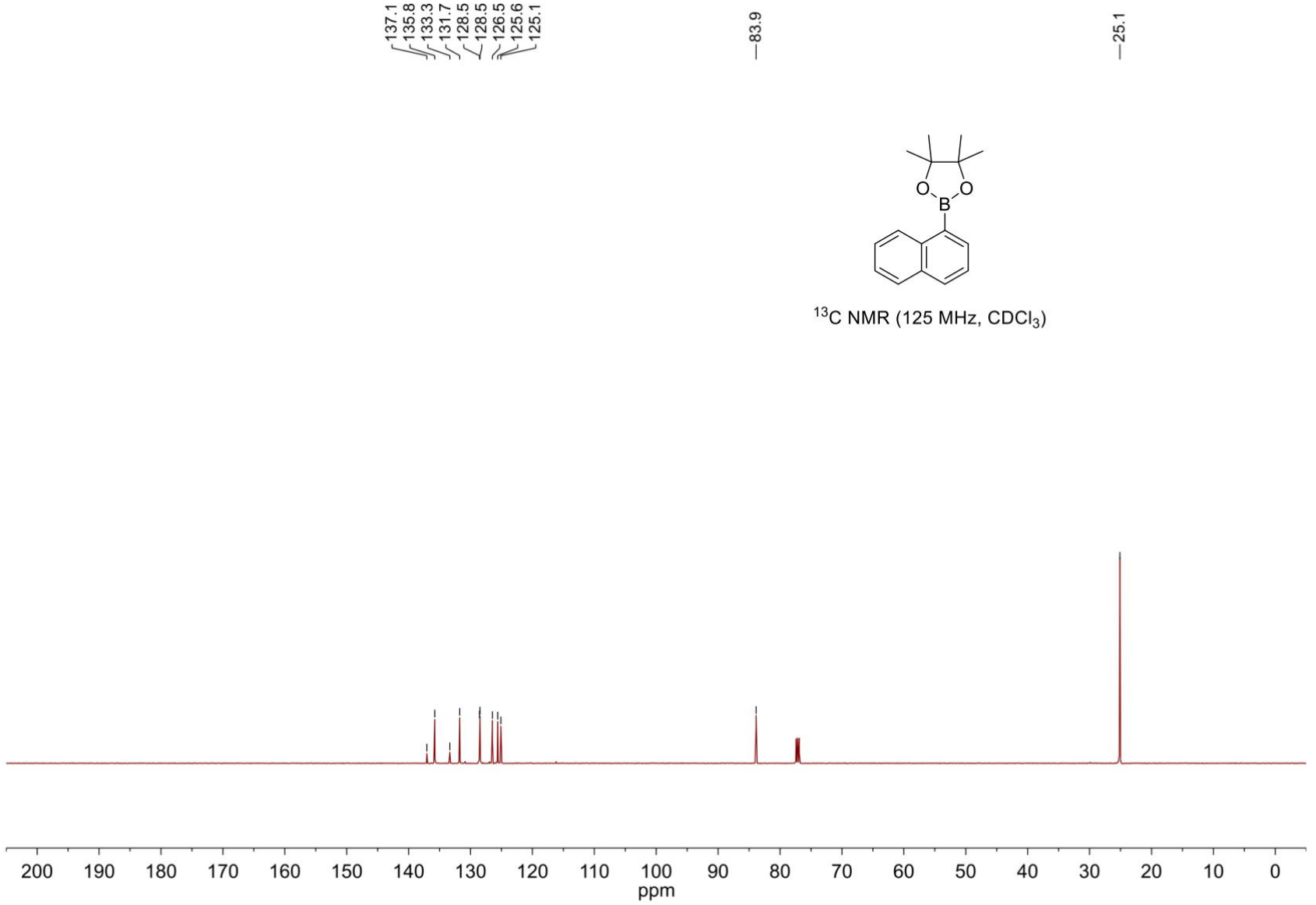
4,4,5,5-Tetramethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborolane (30)



^{13}C NMR (125 MHz, $CDCl_3$)

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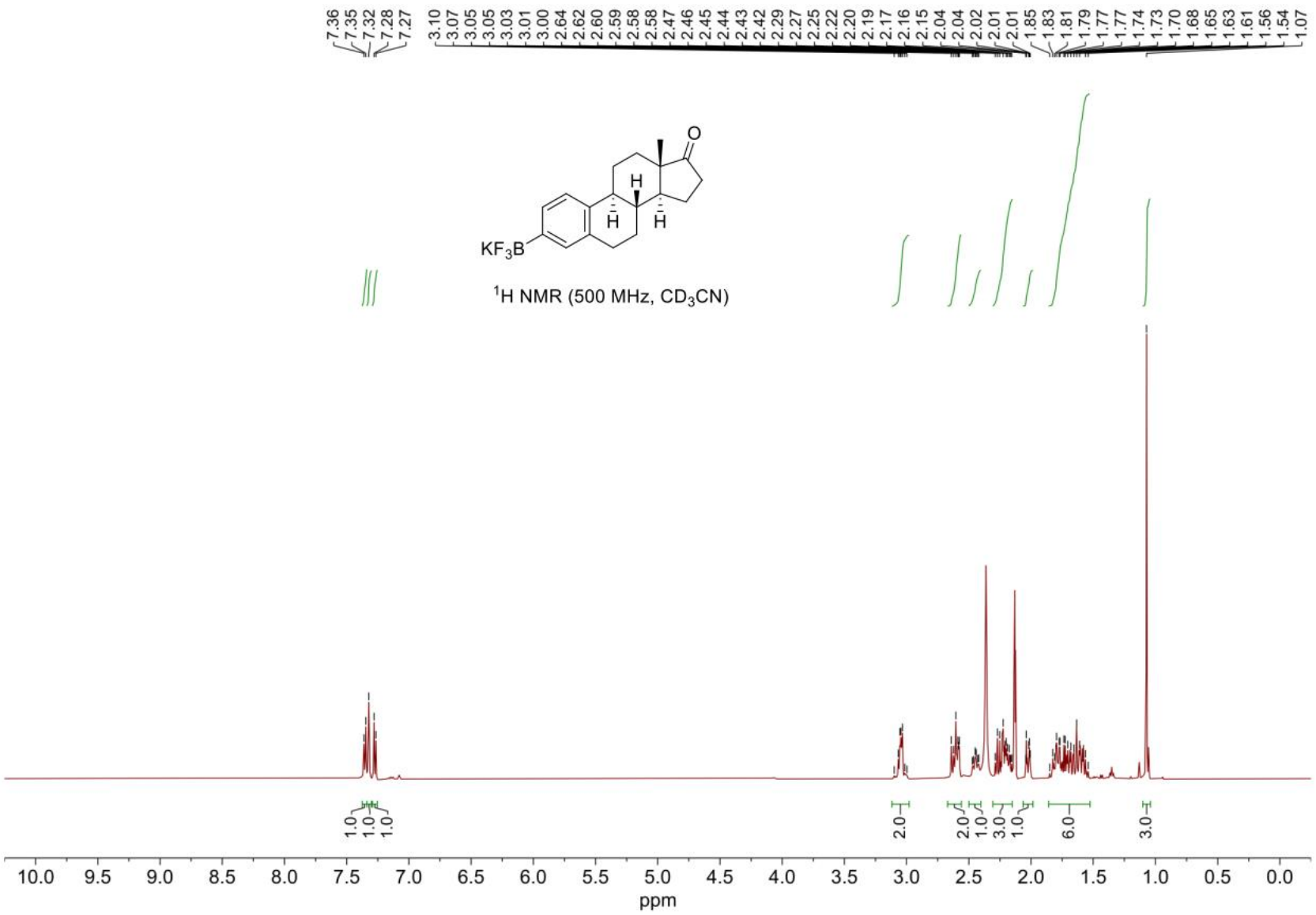
(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-(trifluoro-l4-boraneyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one, potassium salt (31)



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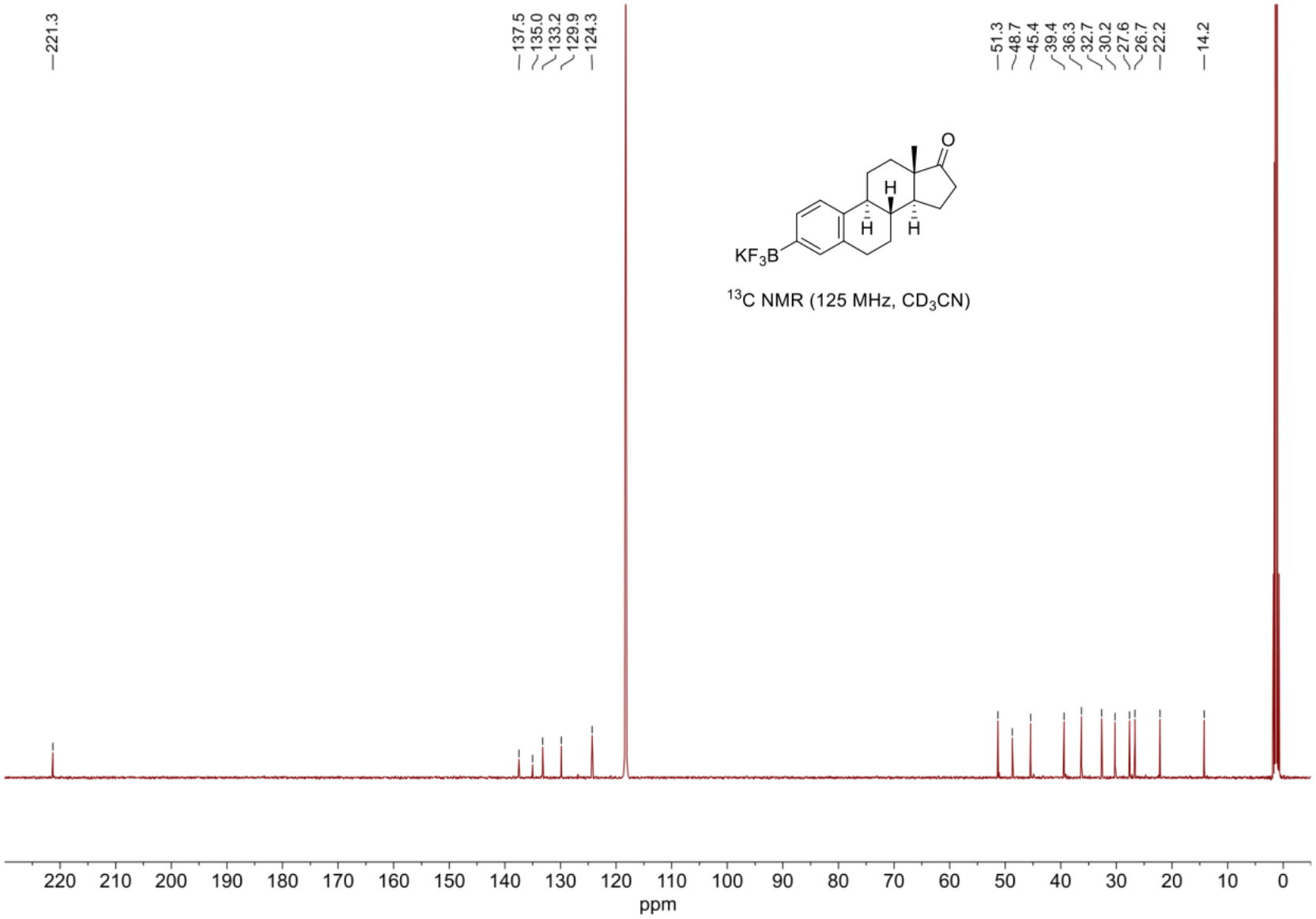
(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-(trifluoro-l4-boraneyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one, potassium salt (31)



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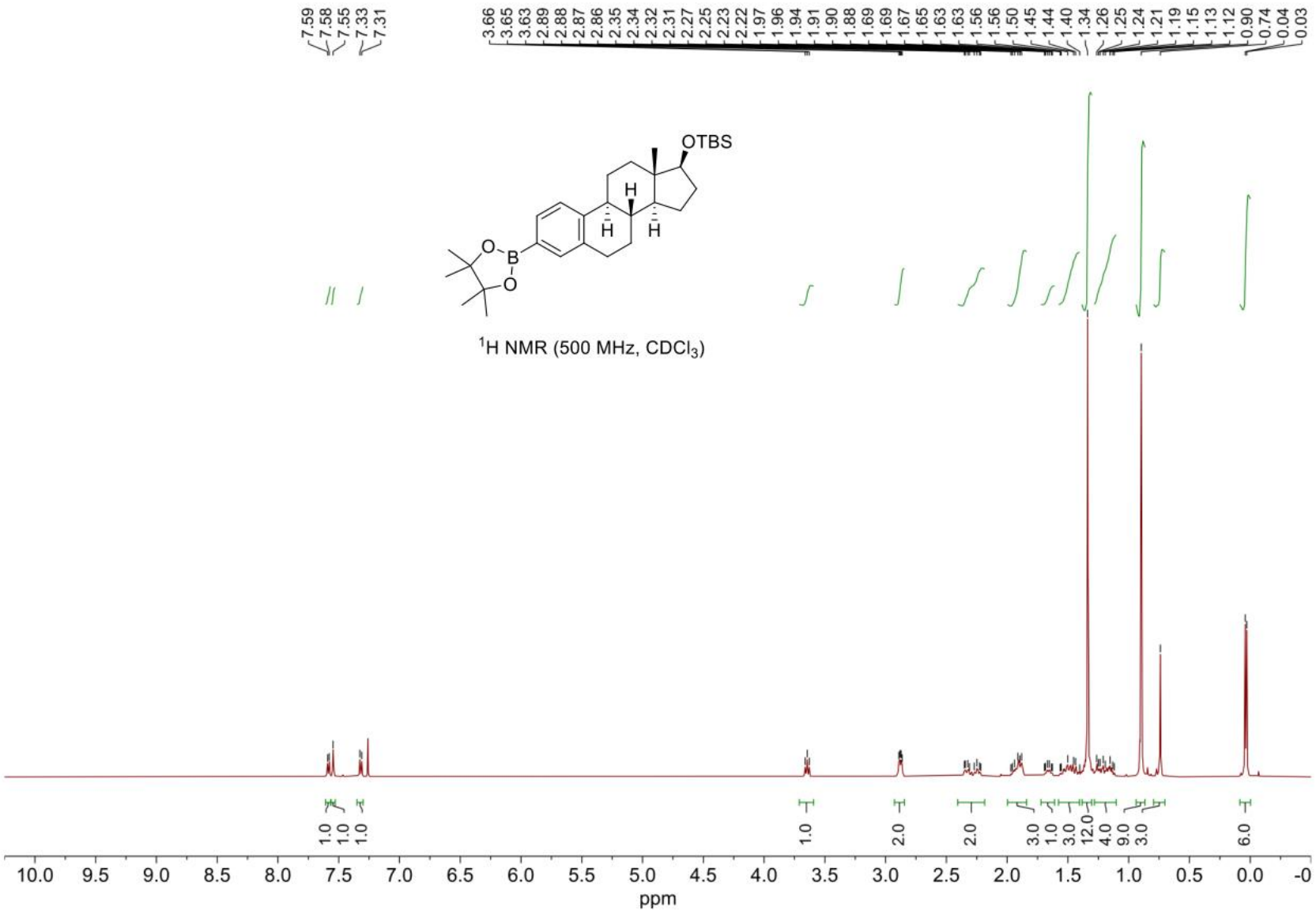
tert-Butyldimethyl(((8*R*,9*S*,13*S*,14*S*,17*S*)-13-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl)oxy)silane (32)



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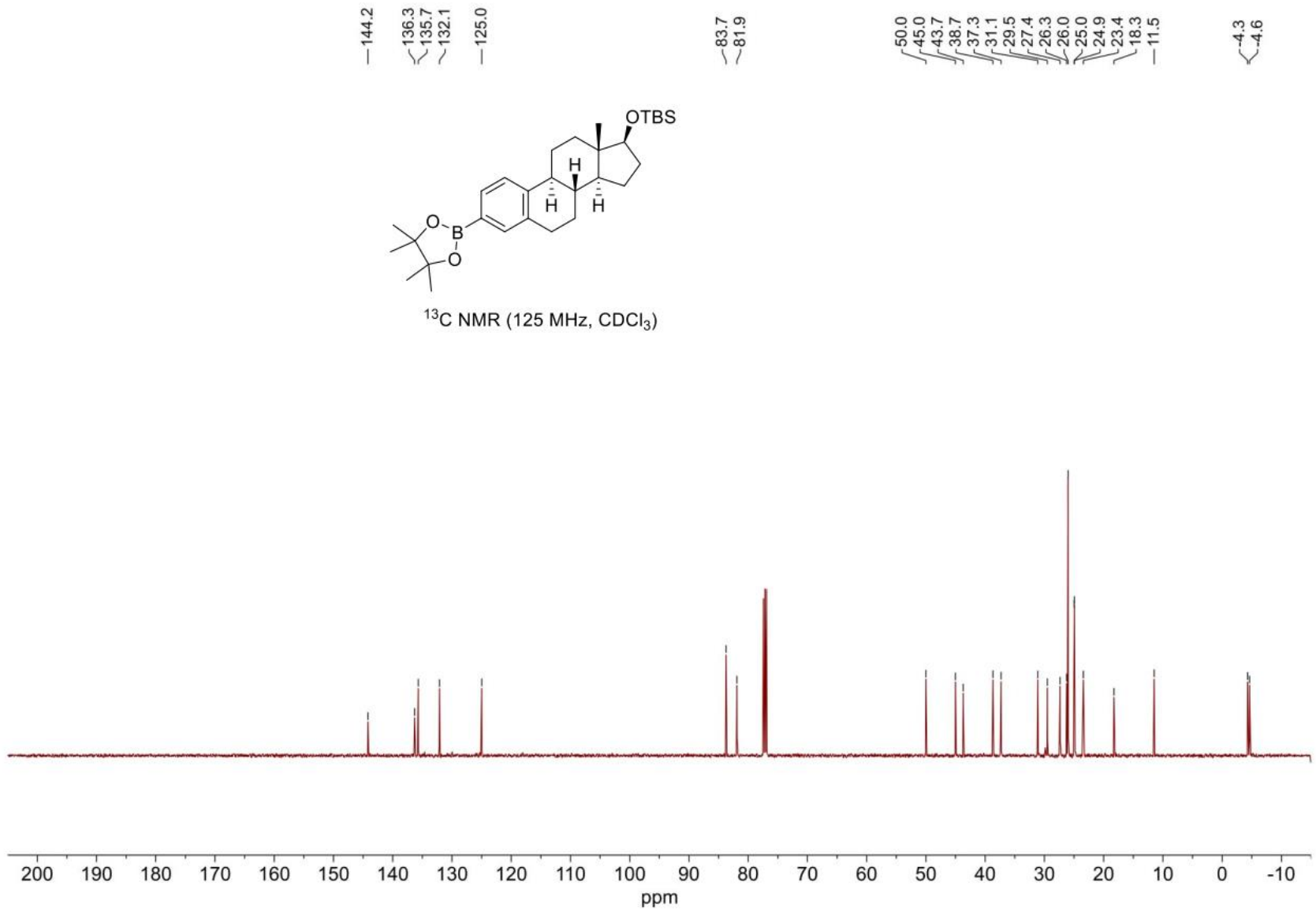
tert-Butyldimethyl(((8*R*,9*S*,13*S*,14*S*,17*S*)-13-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl)oxy)silane (32)



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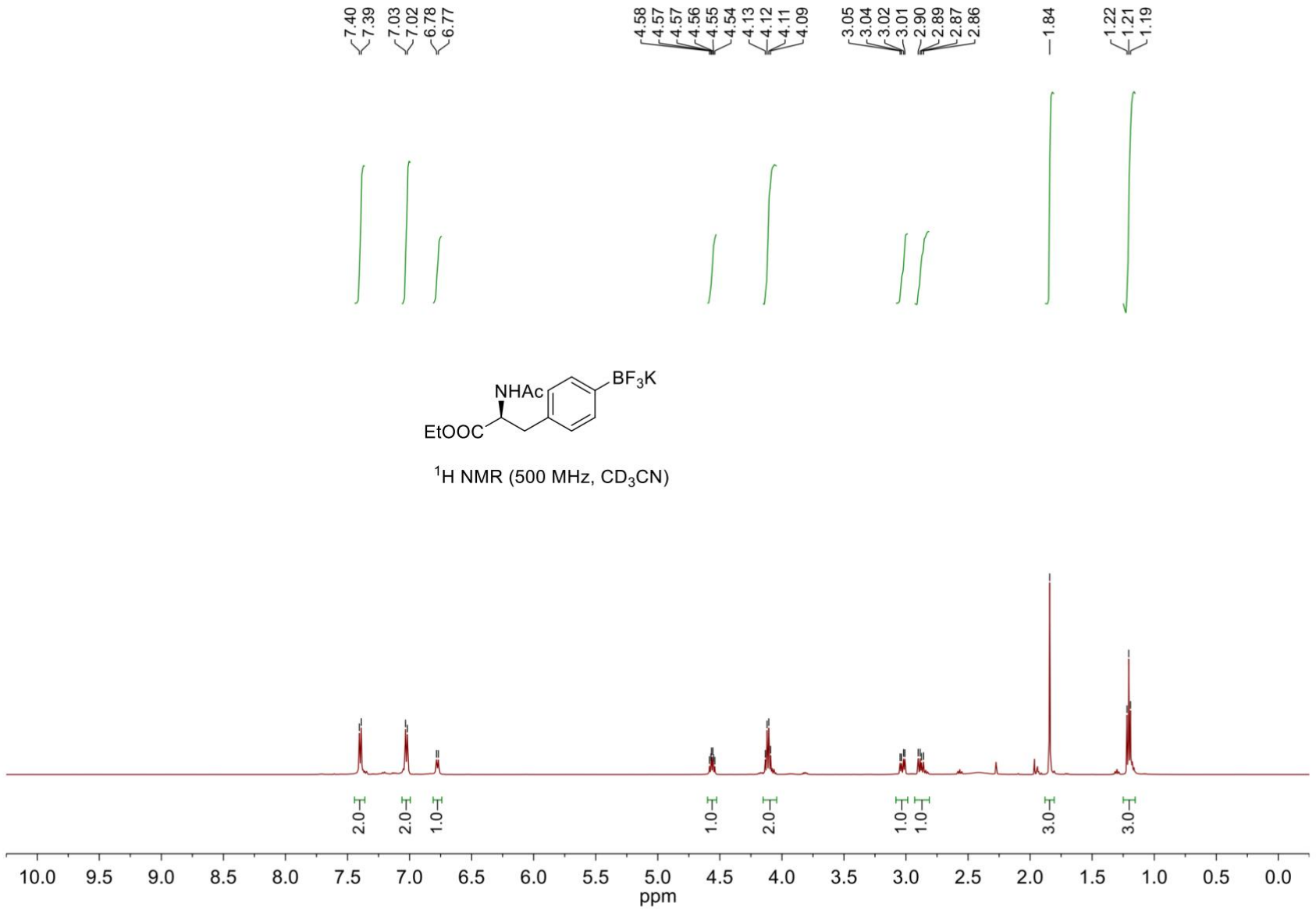
Ethyl (*S*)-2-acetamido-3-(4-(trifluoro-λ⁴-boraneyl)phenyl)propanoate, potassium salt (33)



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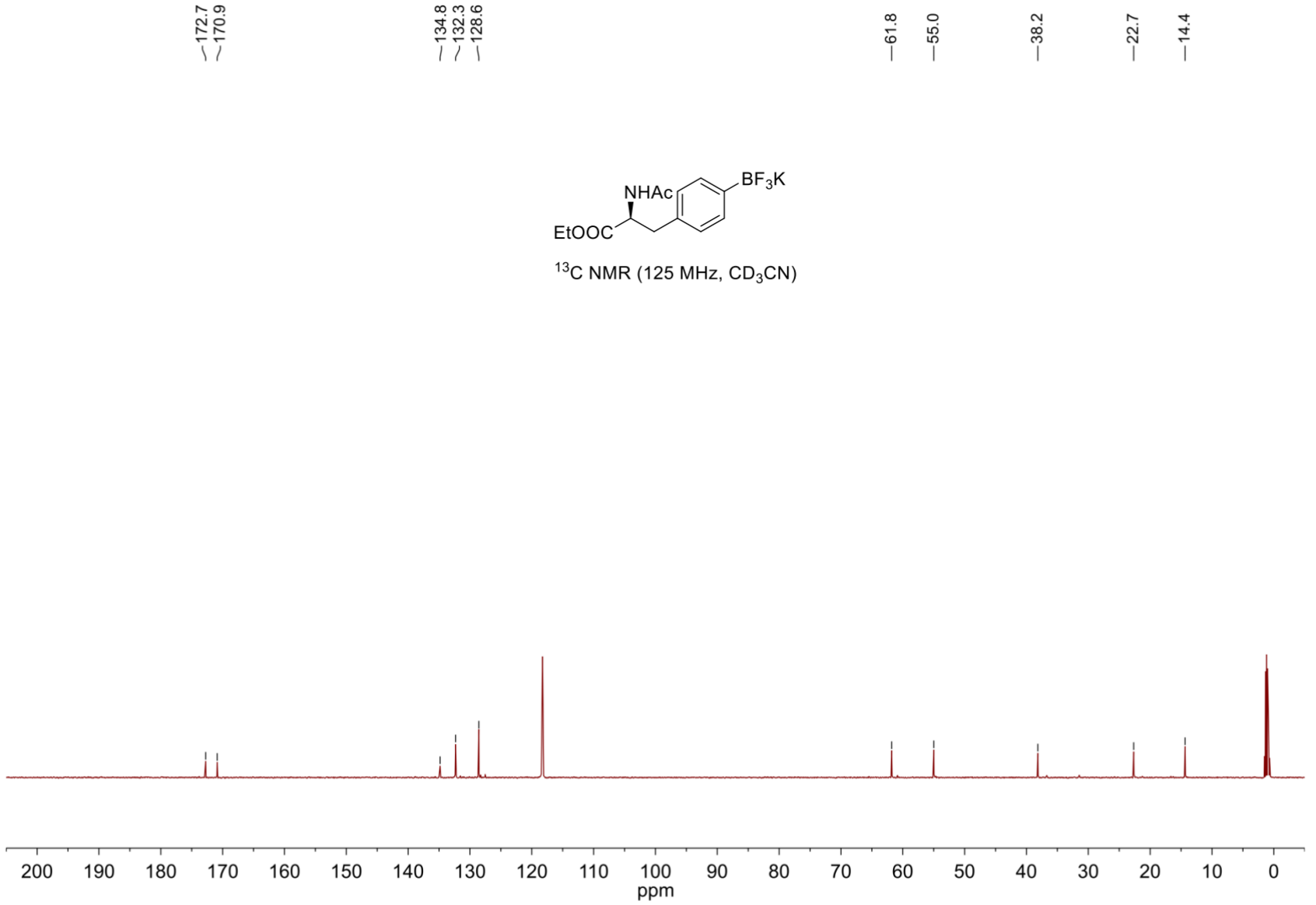
Ethyl (*S*)-2-acetamido-3-(4-(trifluoro-λ⁴-boraneyl)phenyl)propanoate, potassium salt (33)



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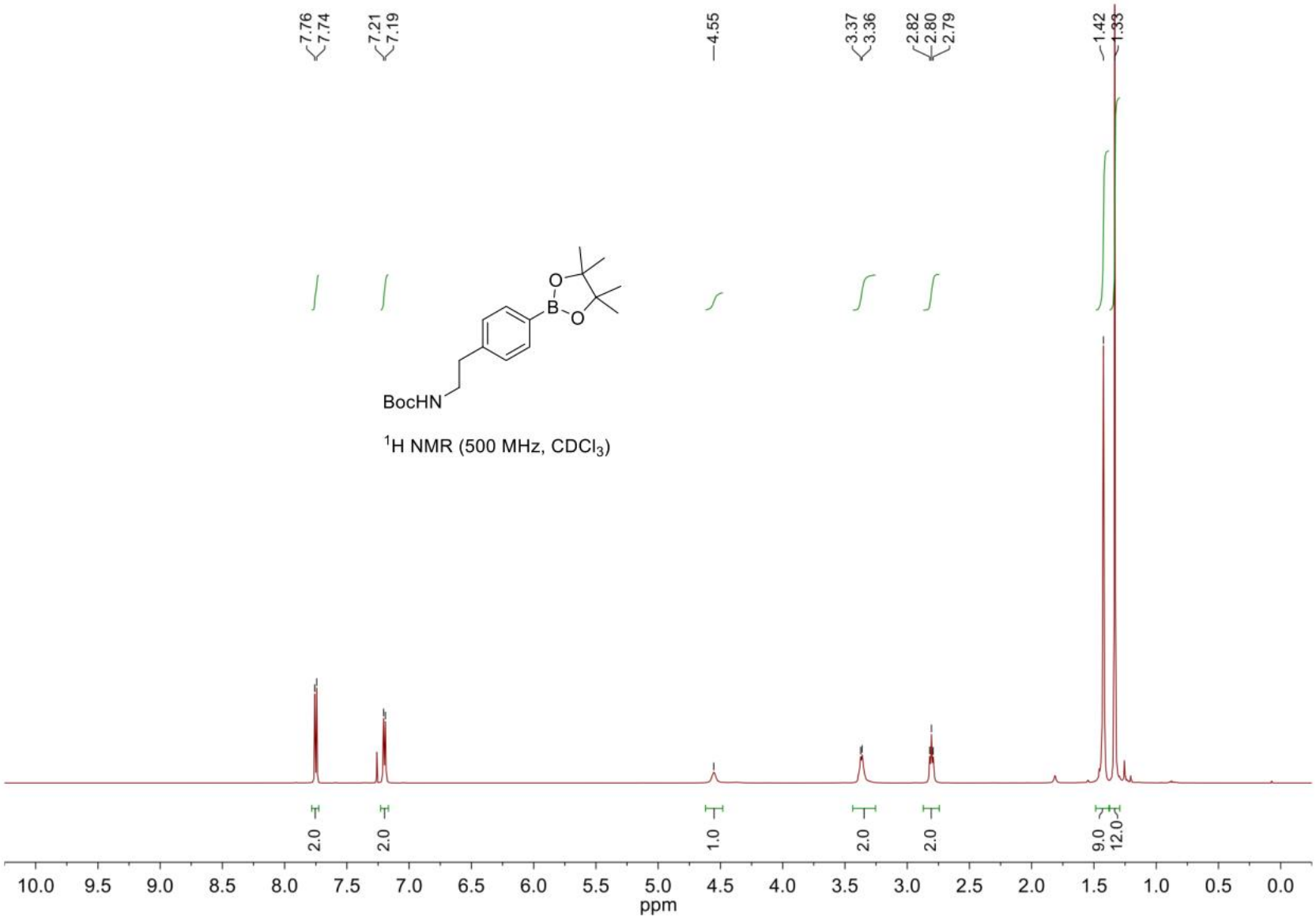
tert-Butyl (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenethyl)carbamate (34)



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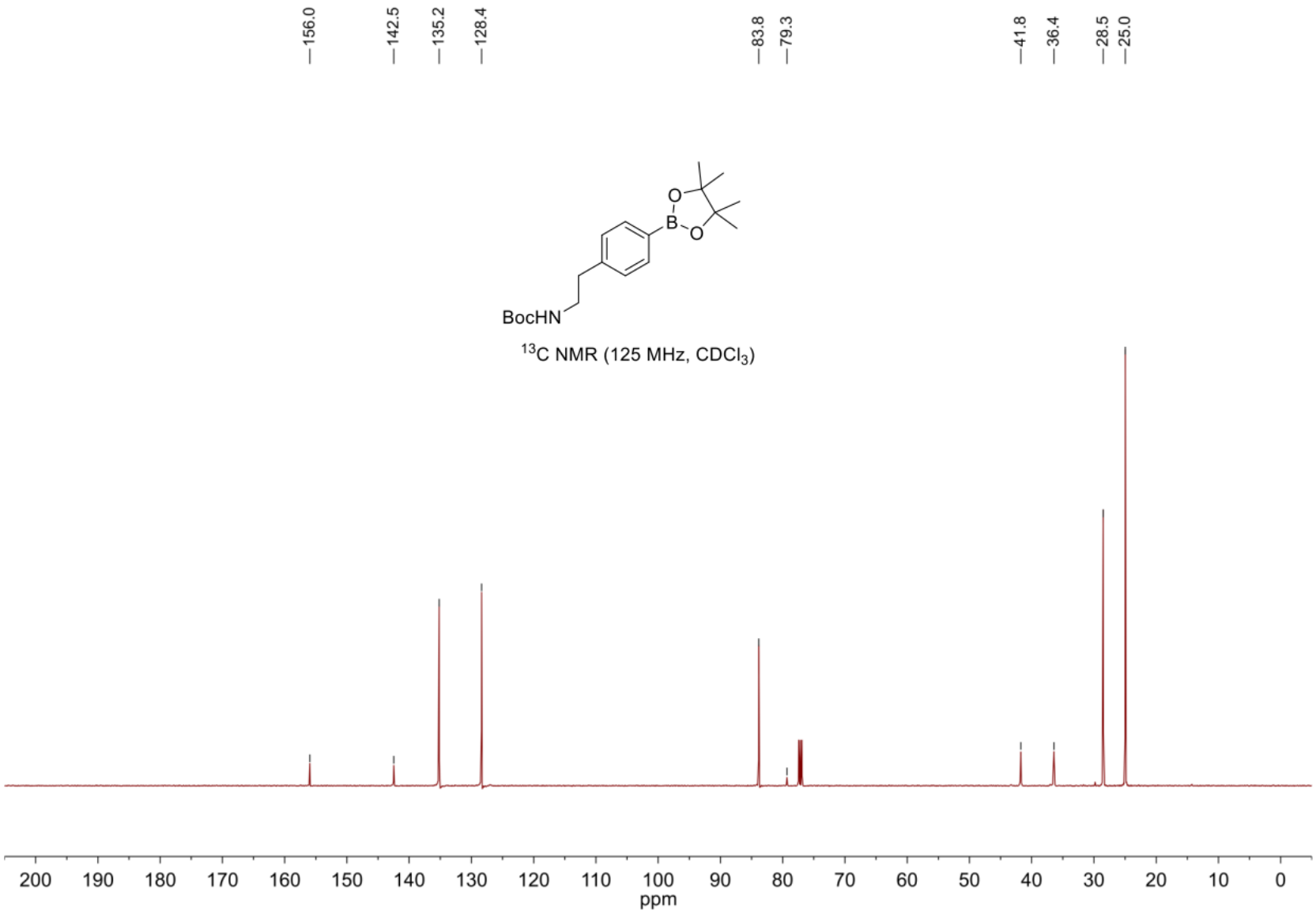
tert-Butyl (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenethyl)carbamate (34)



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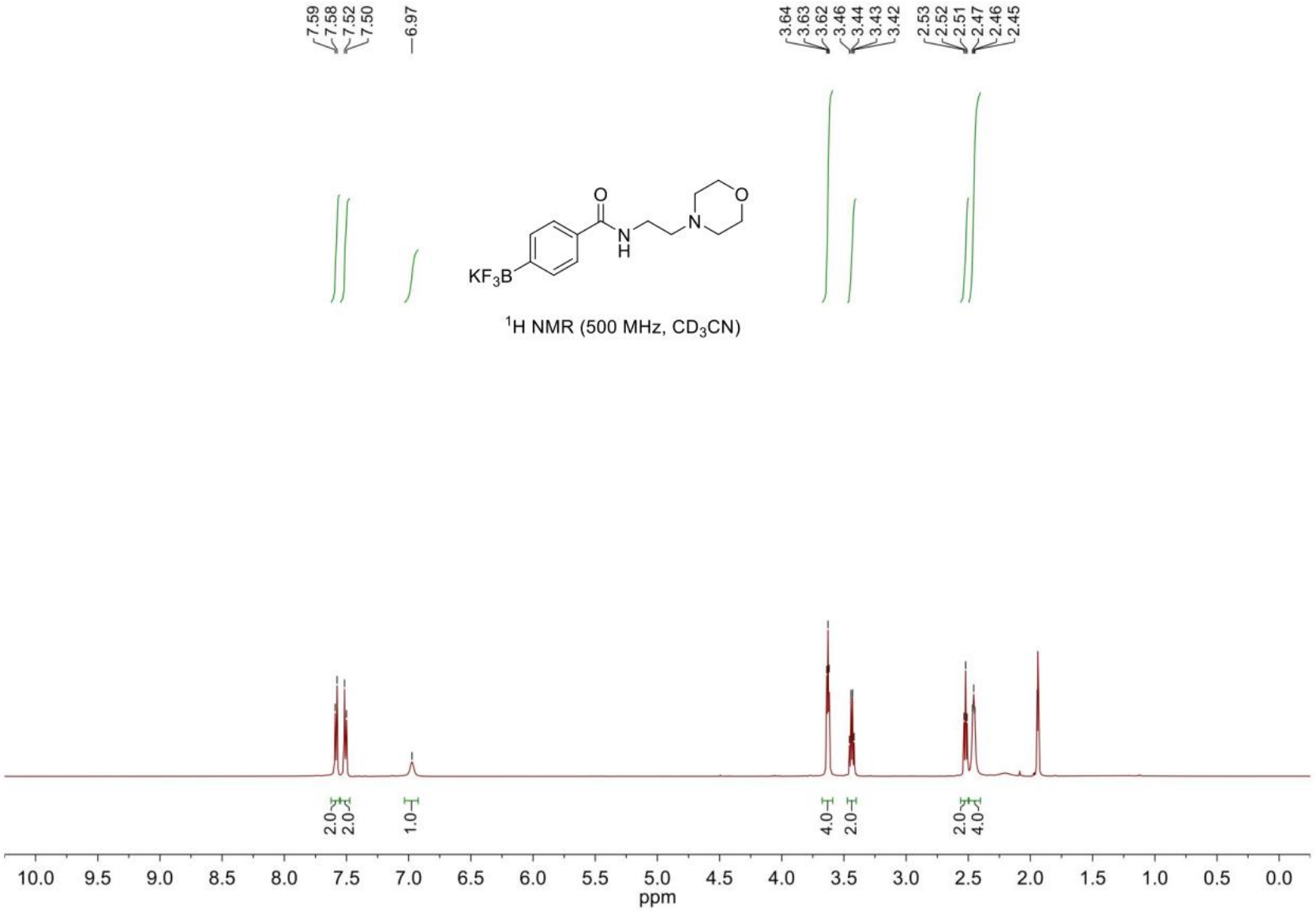
N-(2-Morpholinoethyl)-4-(trifluoro-λ⁴-boraneyl)benzamide, potassium salt (35)



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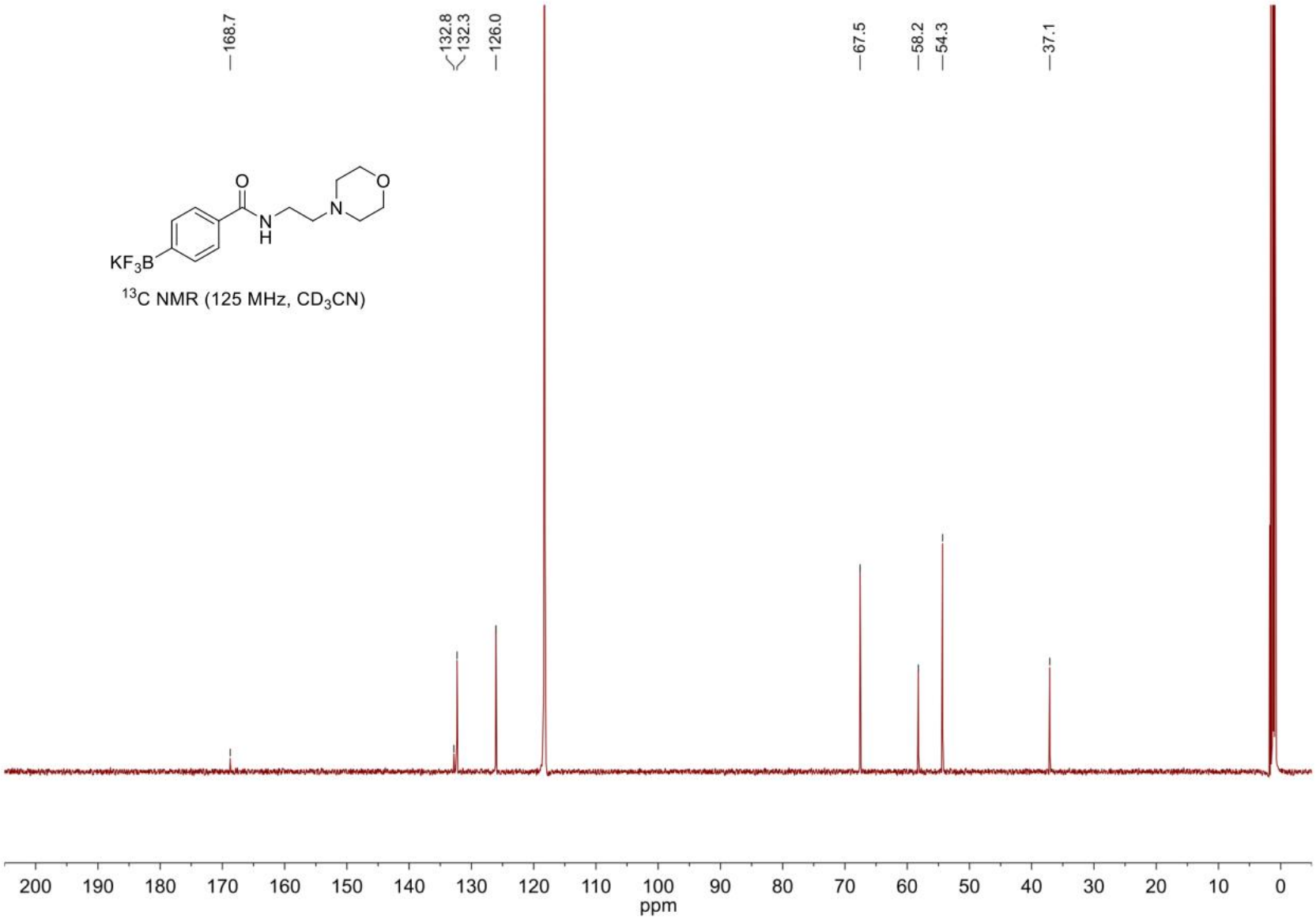
_N_-(2-Morpholinoethyl)-4-(trifluoro-λ⁴-boraneyl)benzamide, potassium salt (35)



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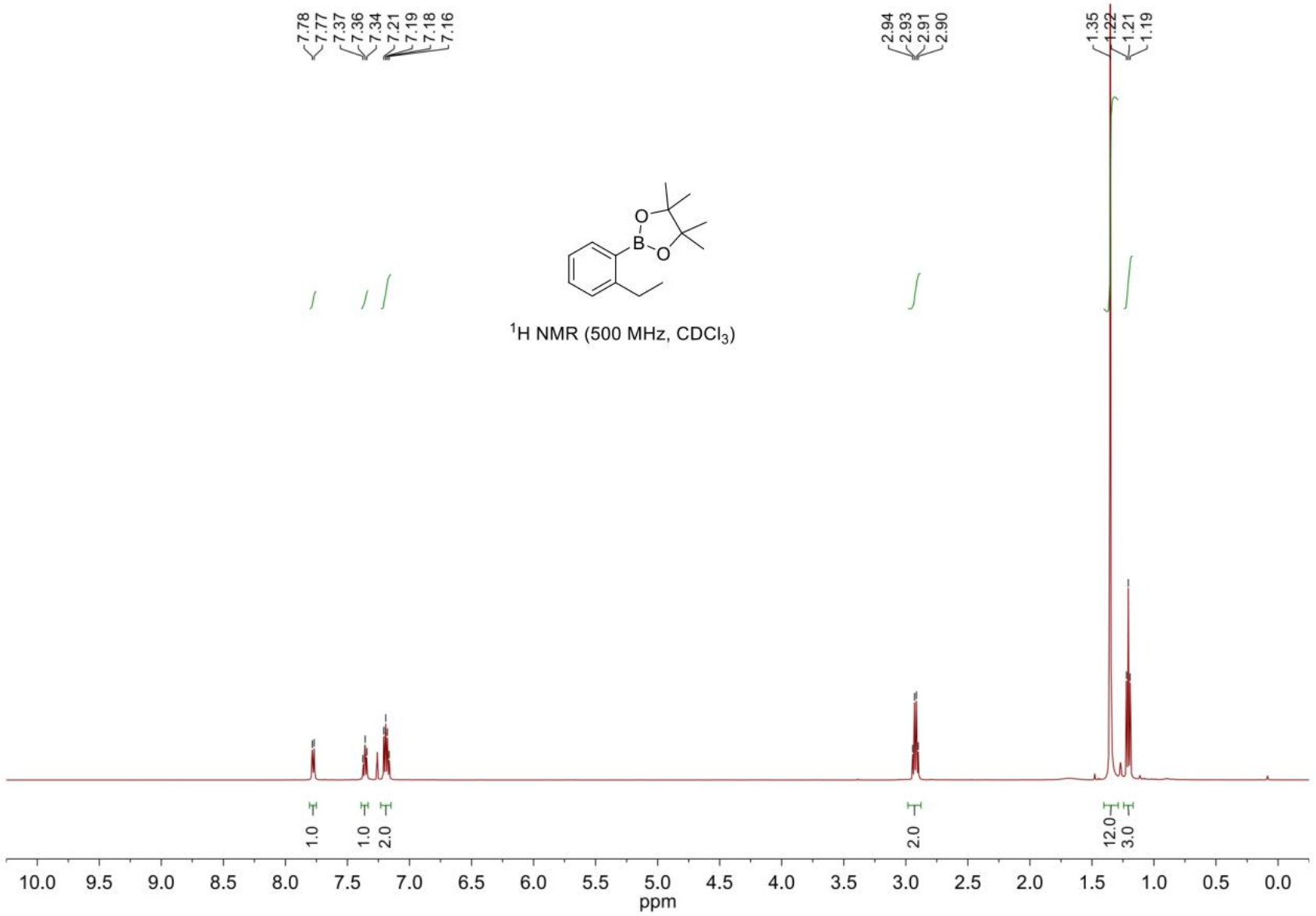
2-(2-Ethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (36)



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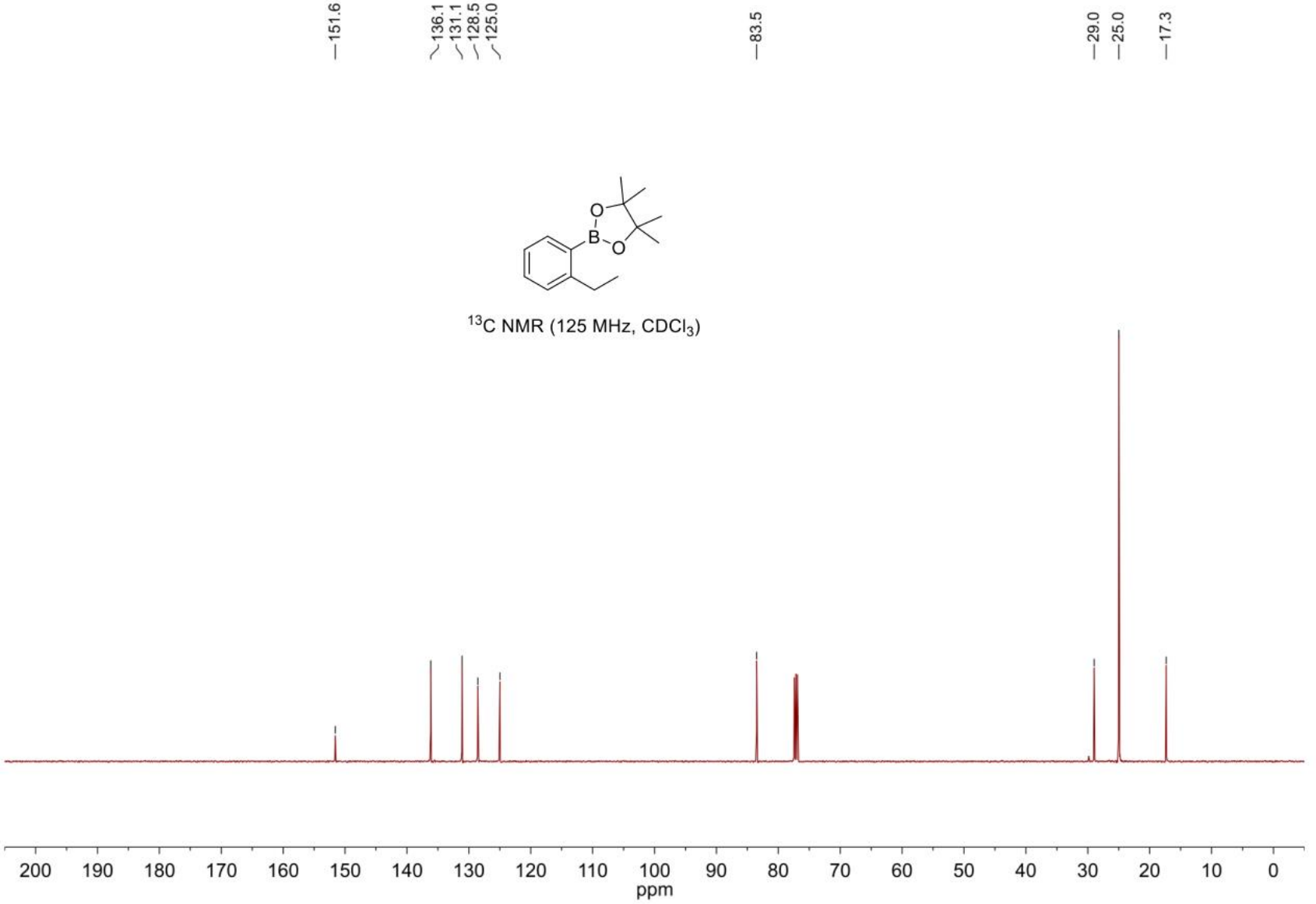
2-(2-Ethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (36)



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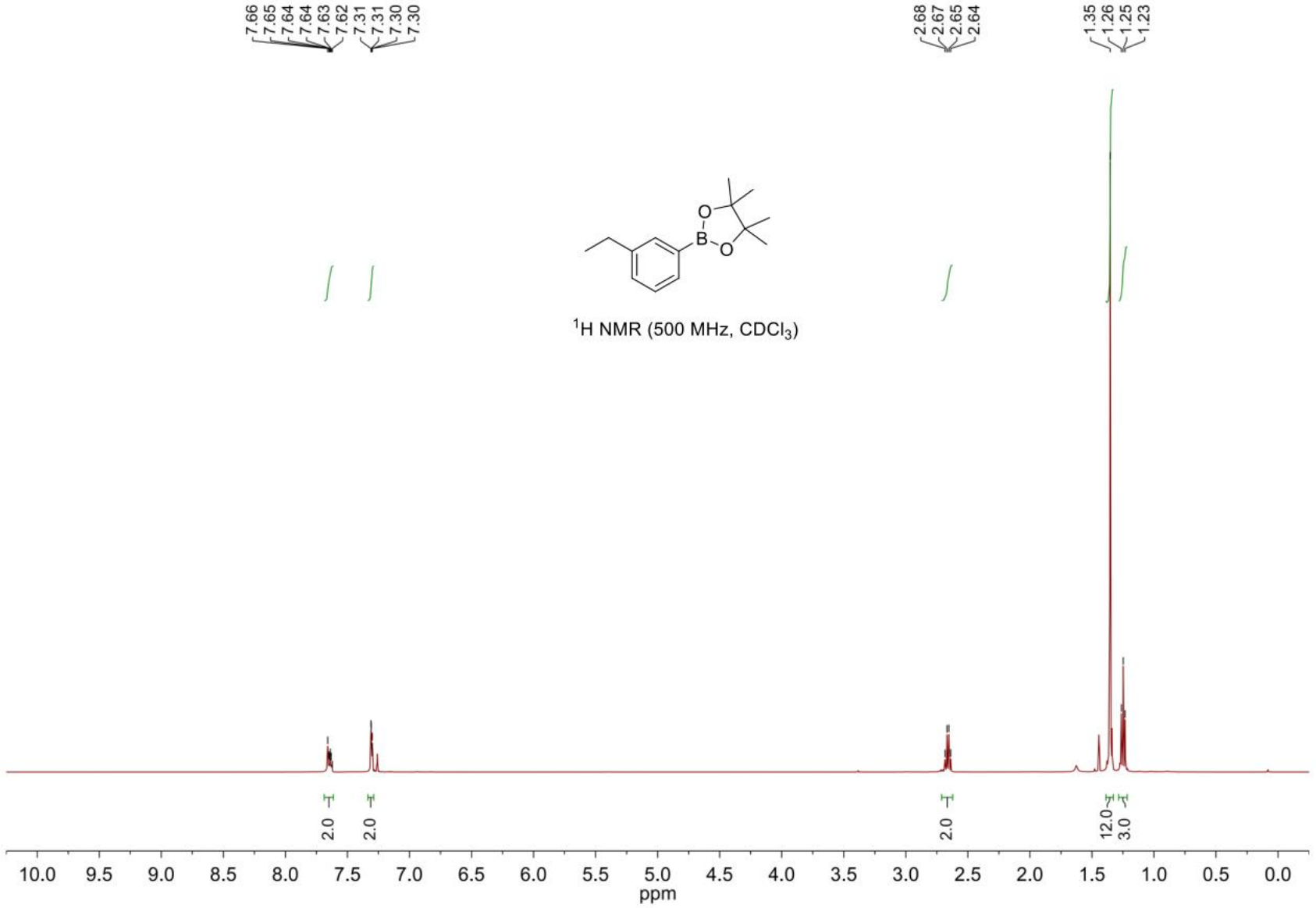
2-(3-Ethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (37)



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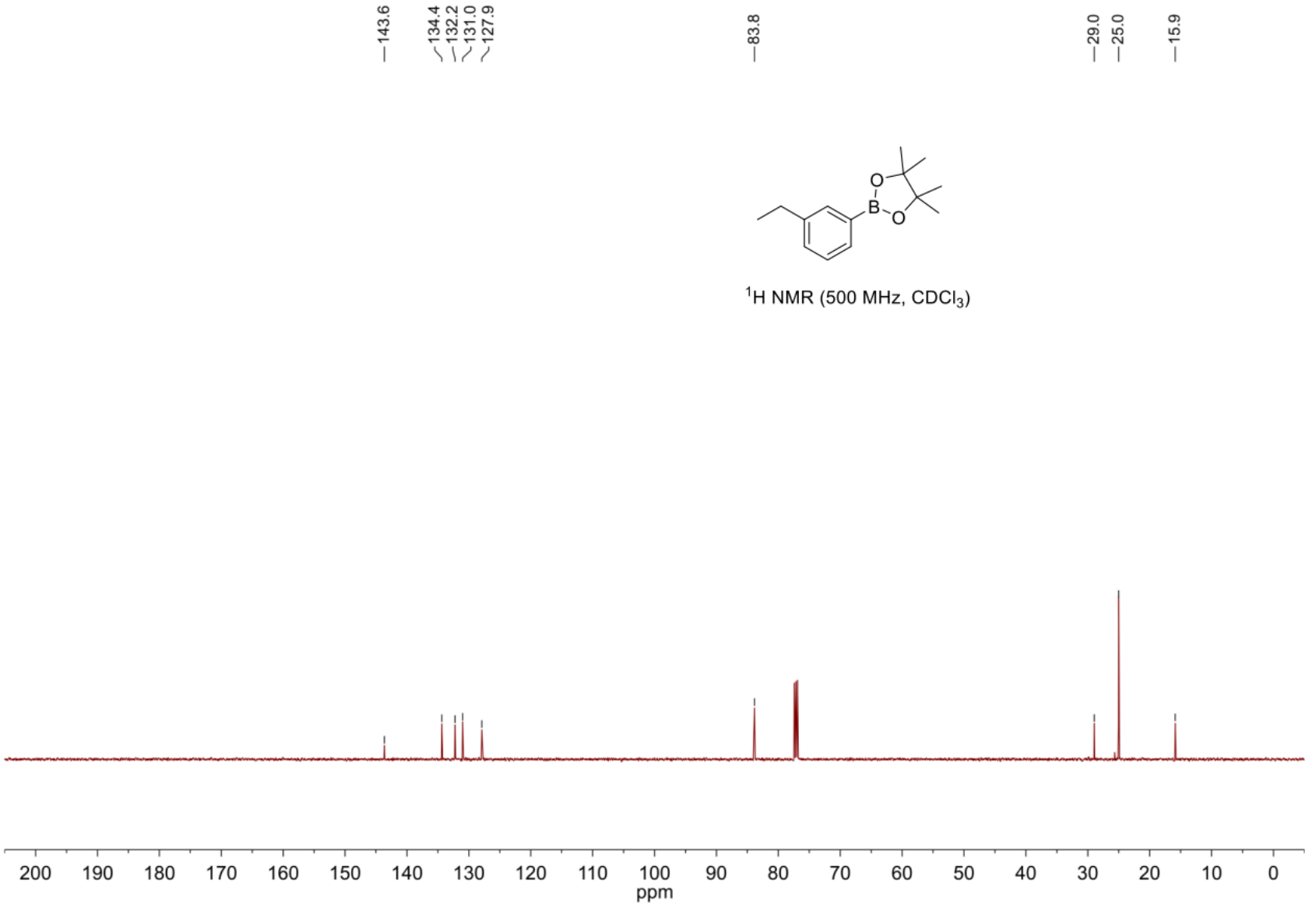
2-(3-Ethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (37)



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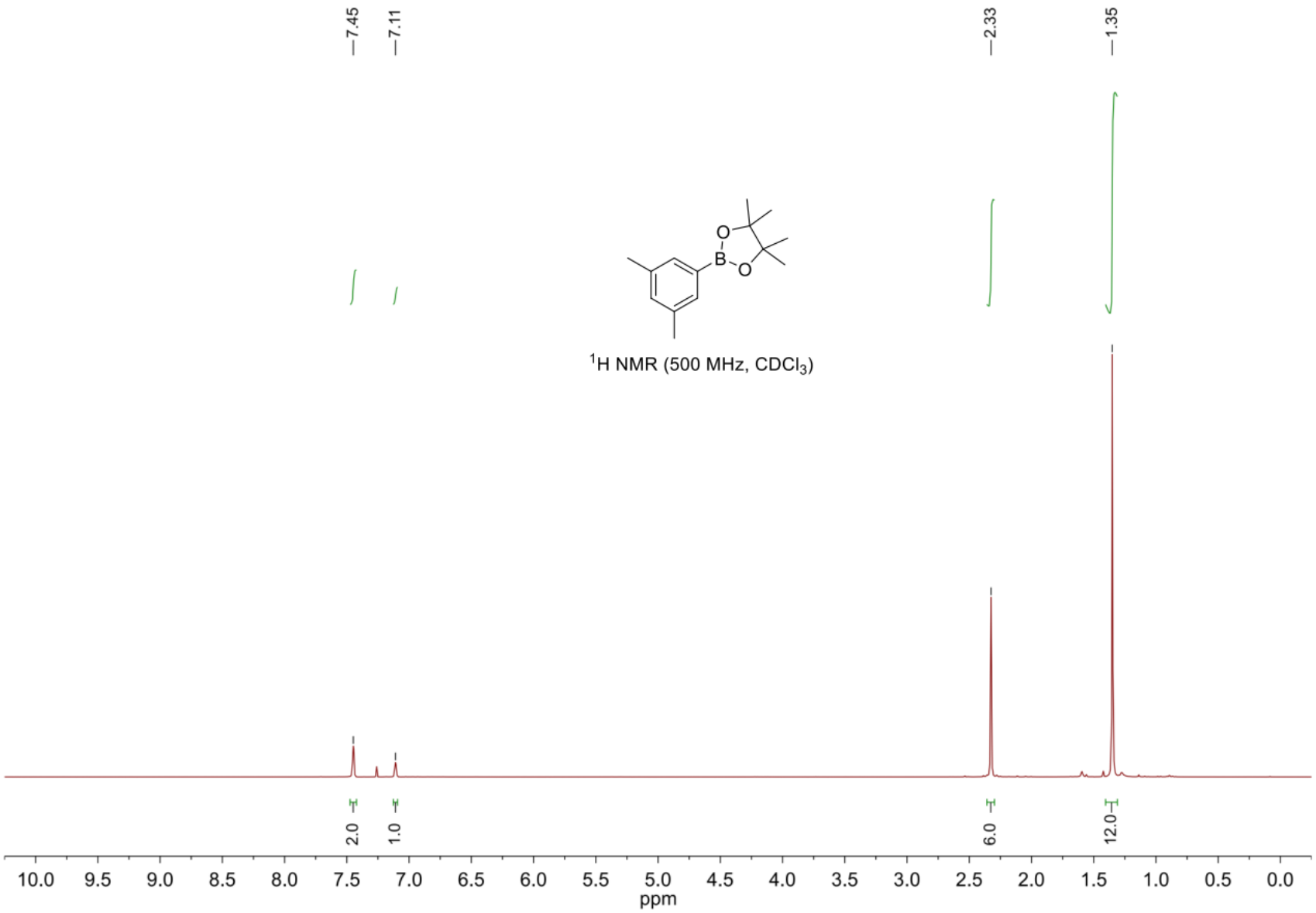
2-(3,5-Dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38)



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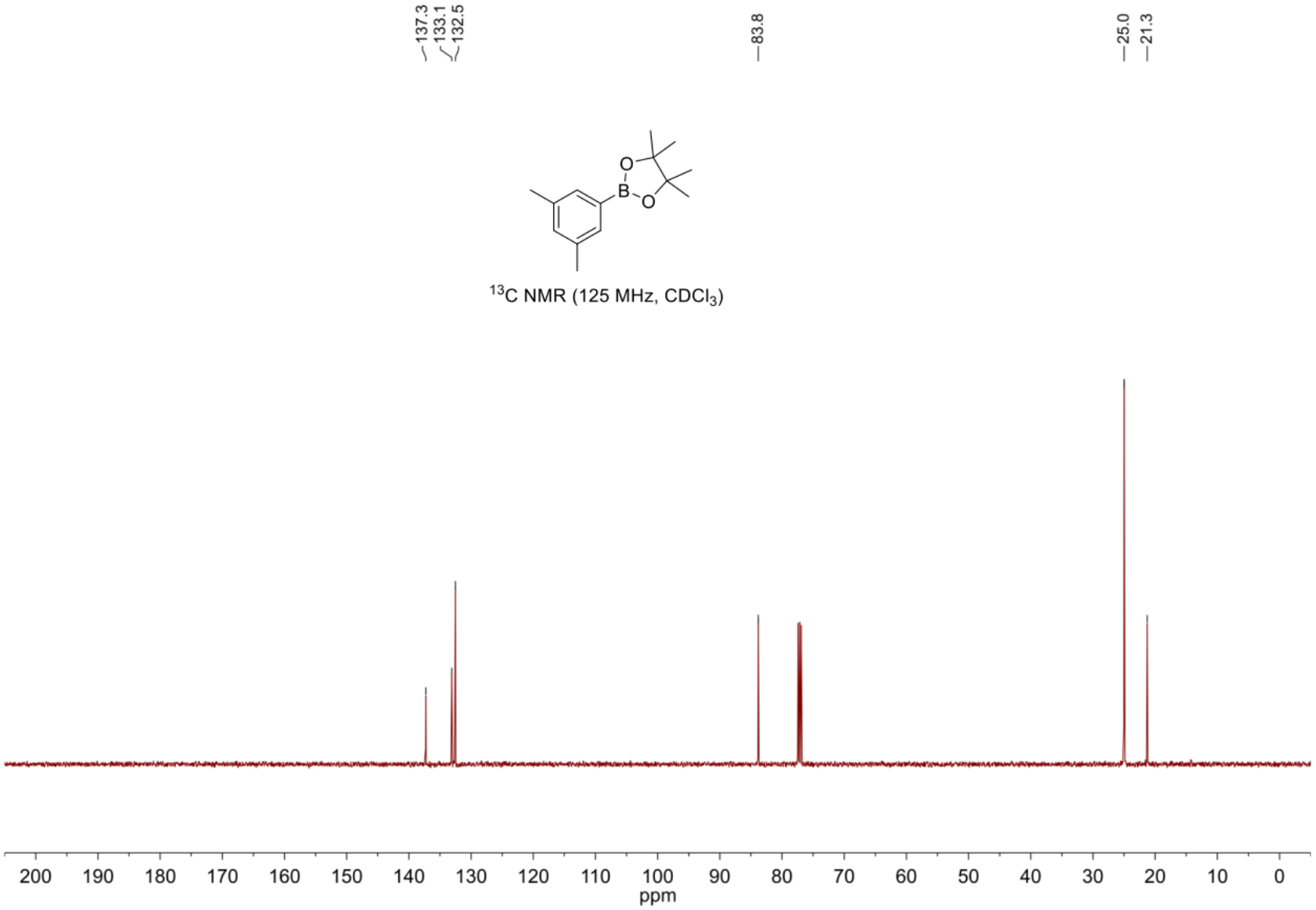
2-(3,5-Dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38)



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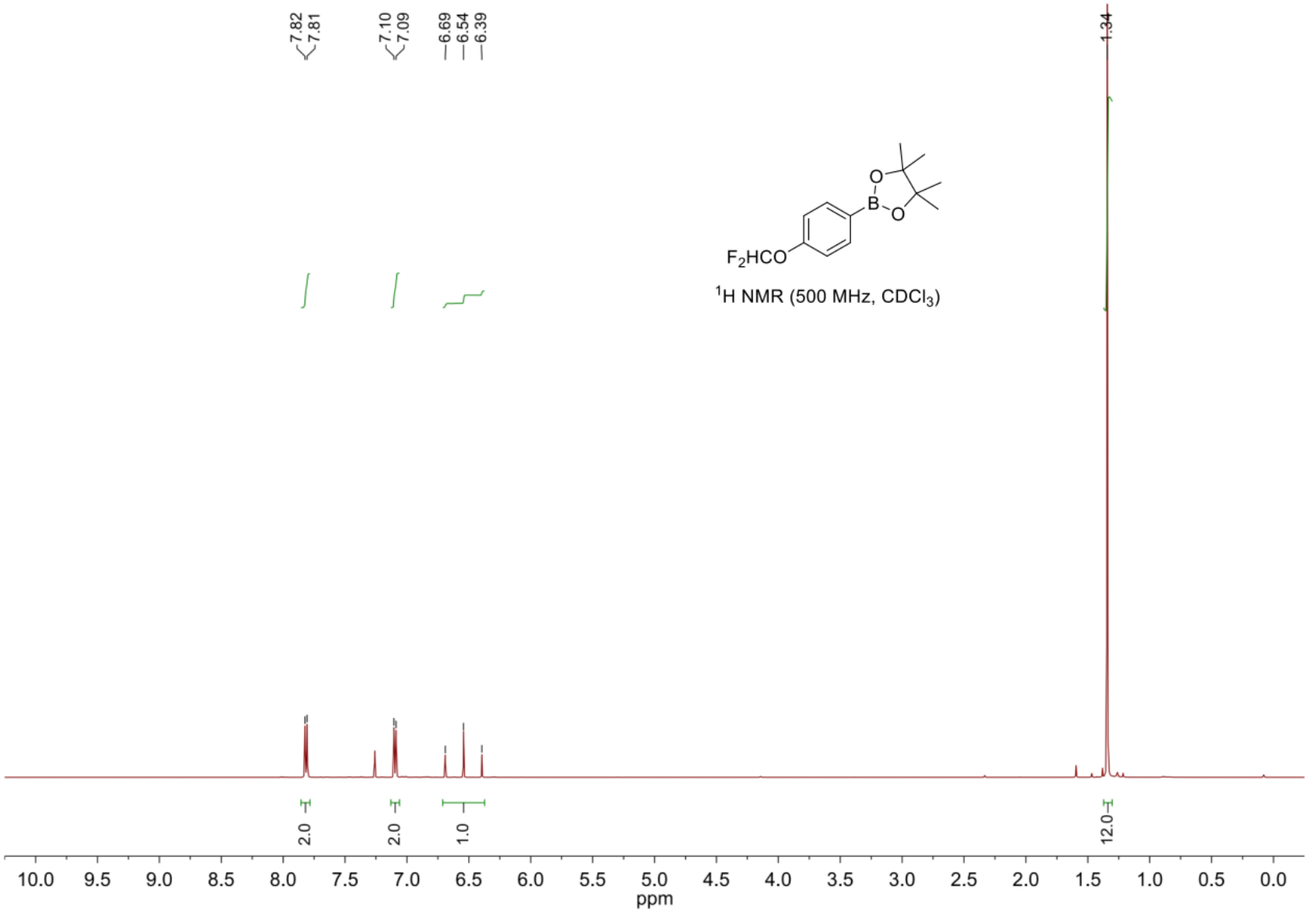
2-(4-(Difluoromethoxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (39)



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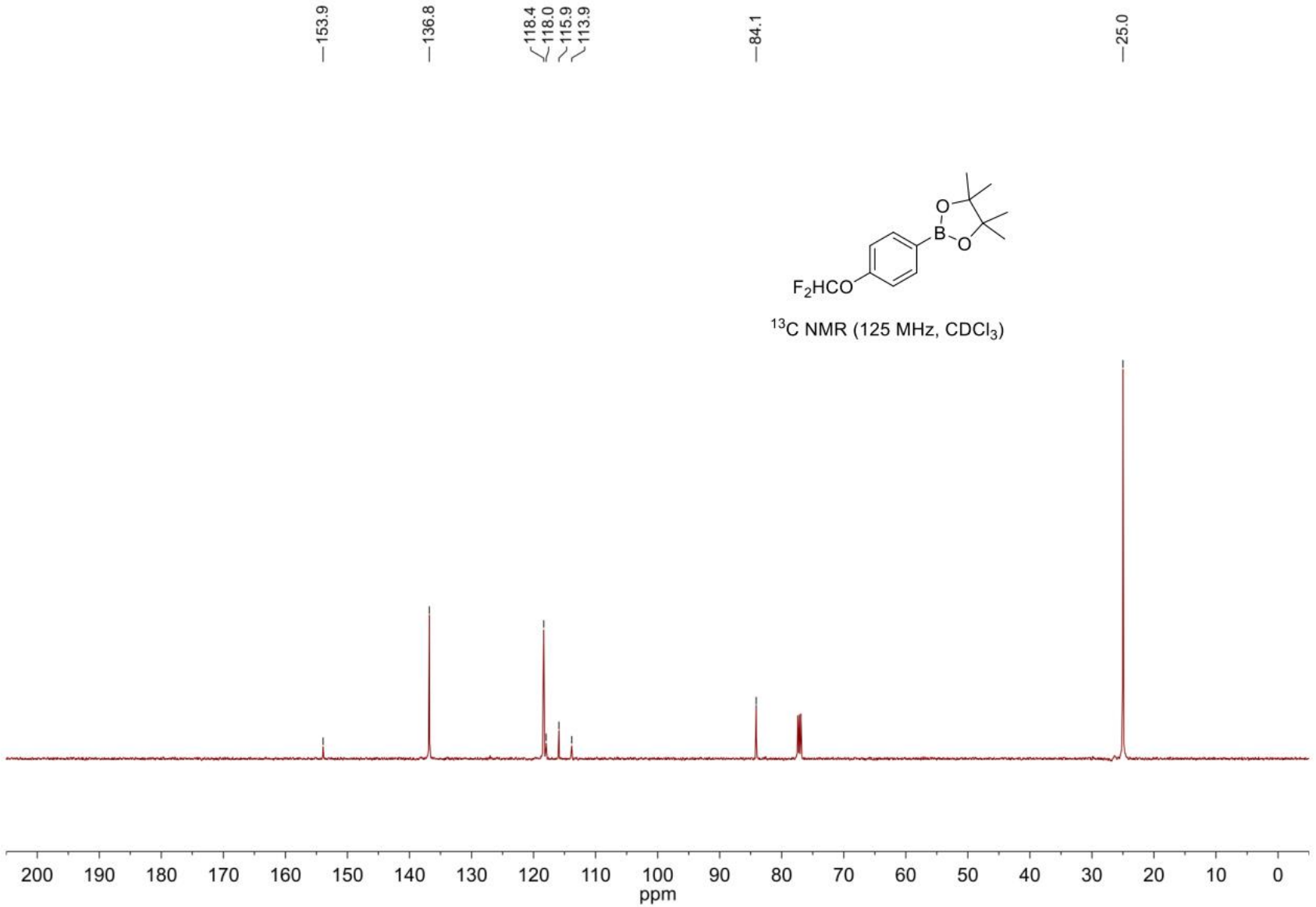
2-(4-(Difluoromethoxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (39)



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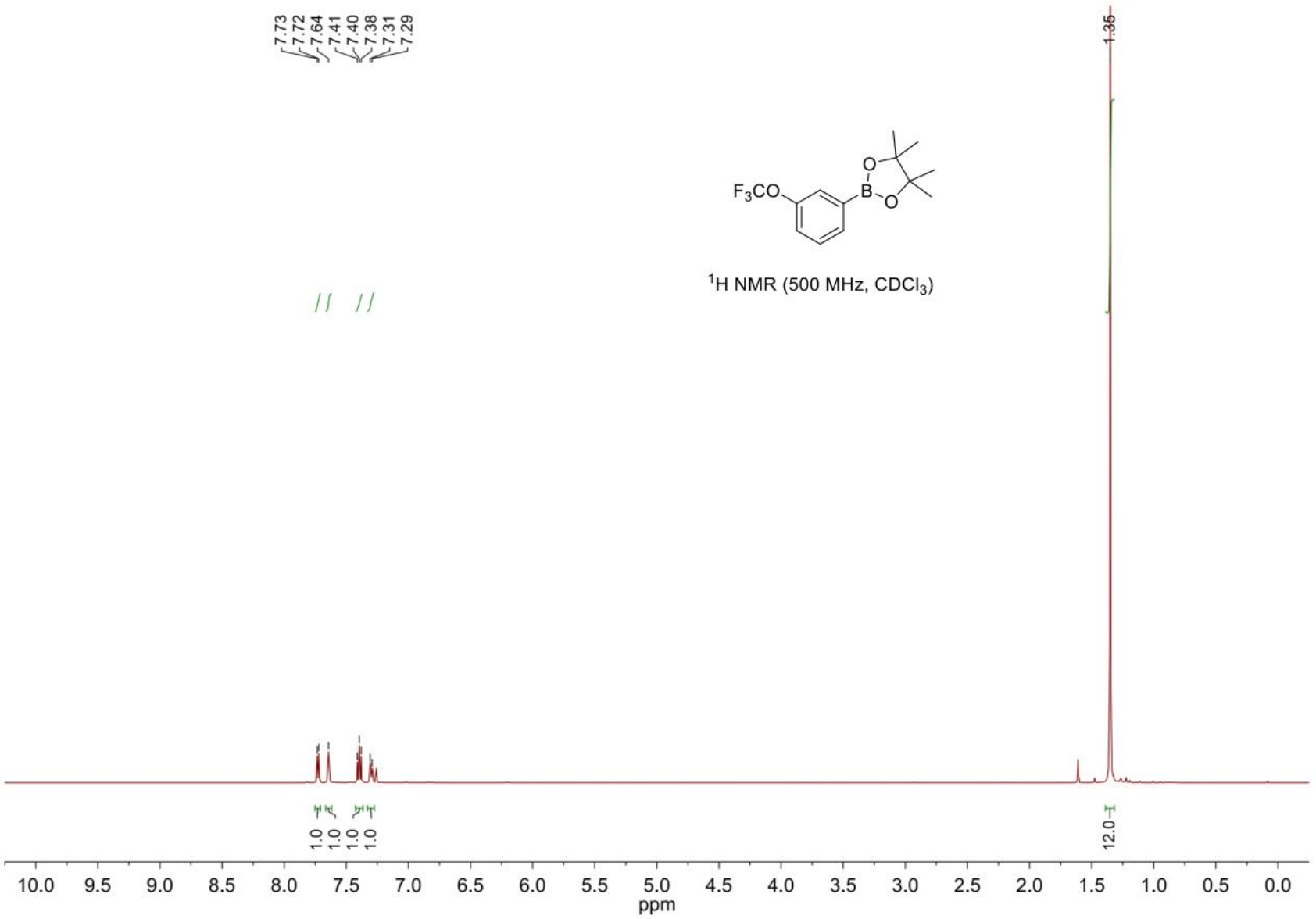
4,4,5,5-Tetramethyl-2-(3-(trifluoromethoxy)phenyl)-1,3,2-dioxaborolane (40)



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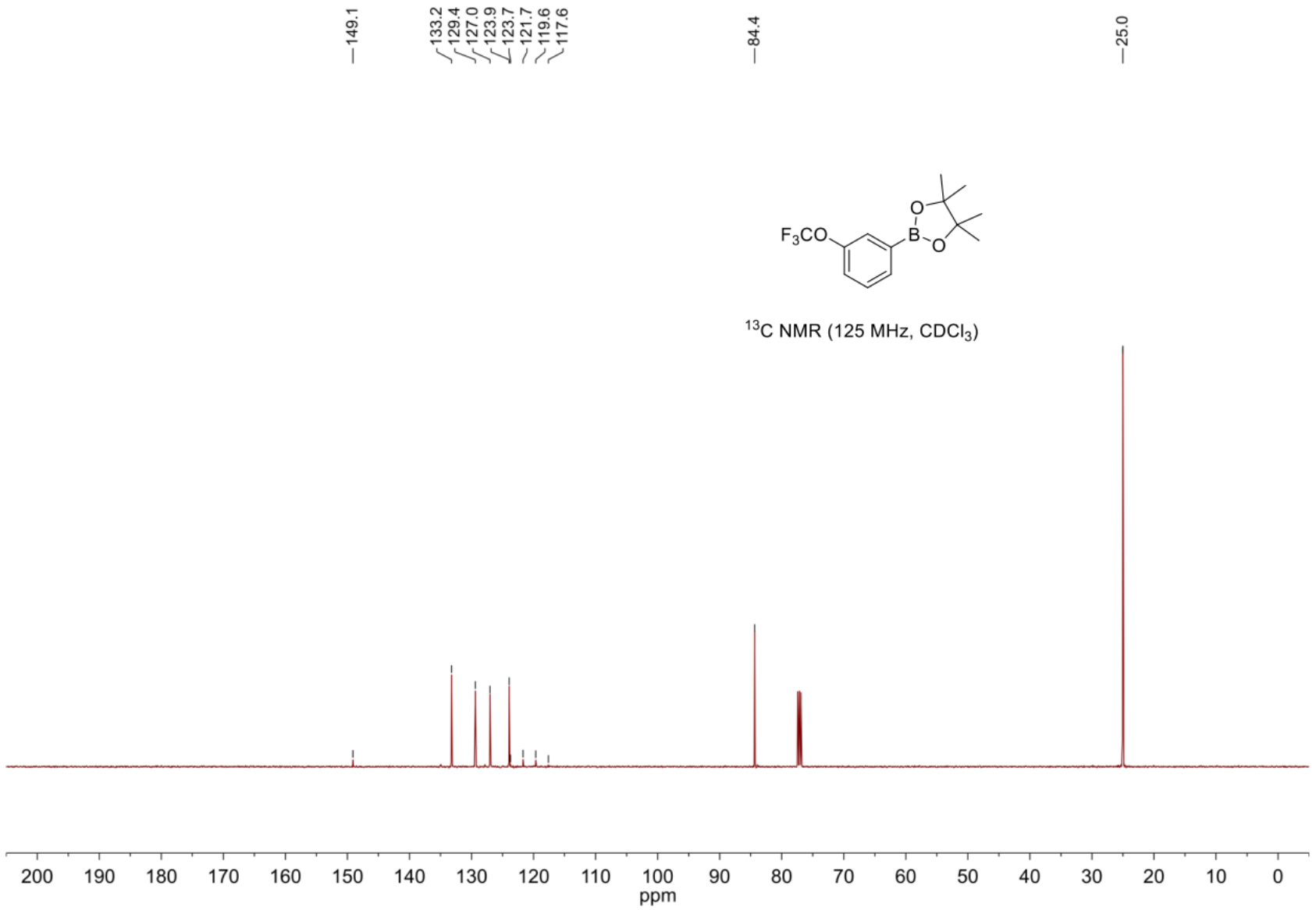
4,4,5,5-Tetramethyl-2-(3-(trifluoromethoxy)phenyl)-1,3,2-dioxaborolane (40)



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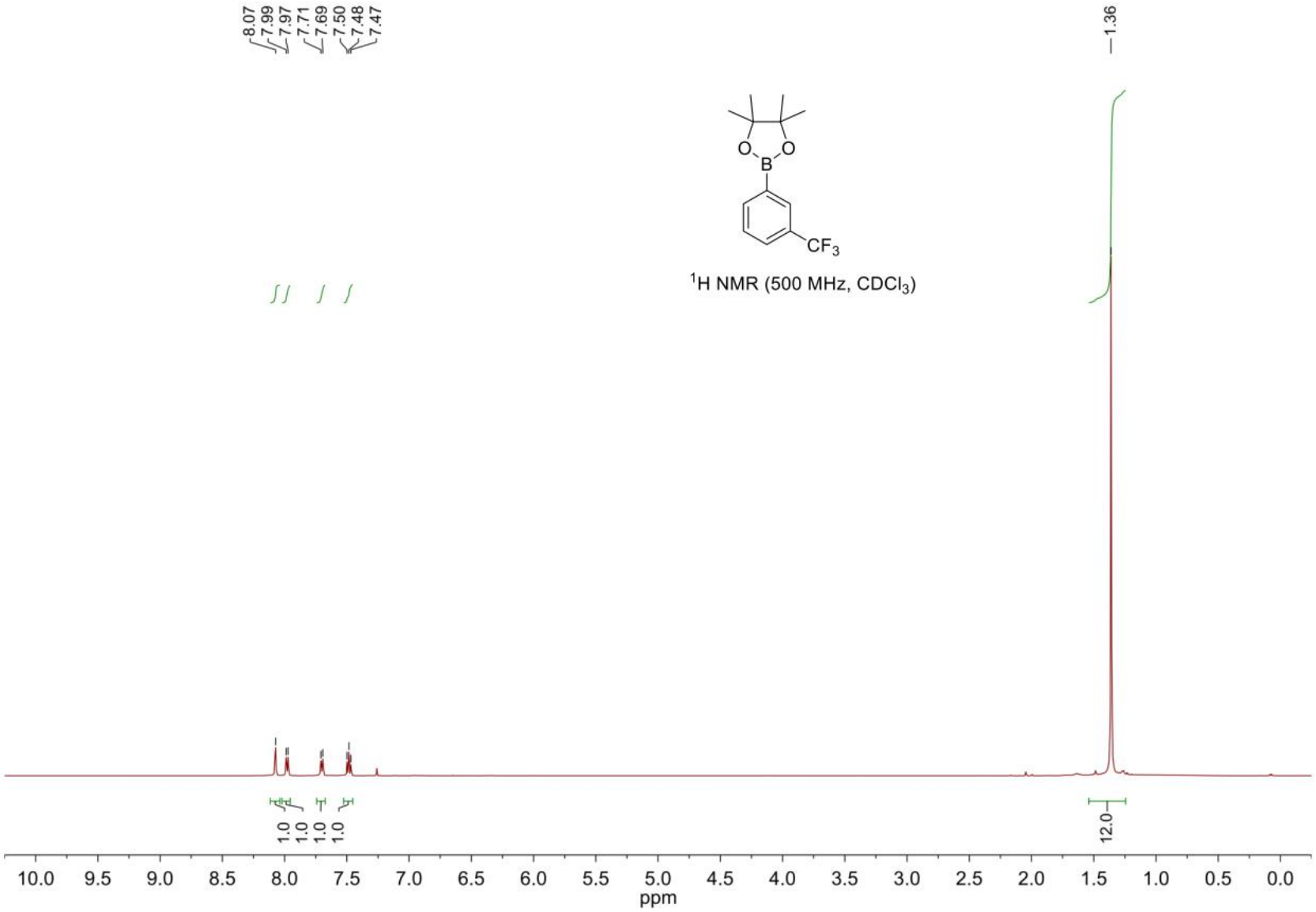
4,4,5,5-Tetramethyl-2-(3-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (41)



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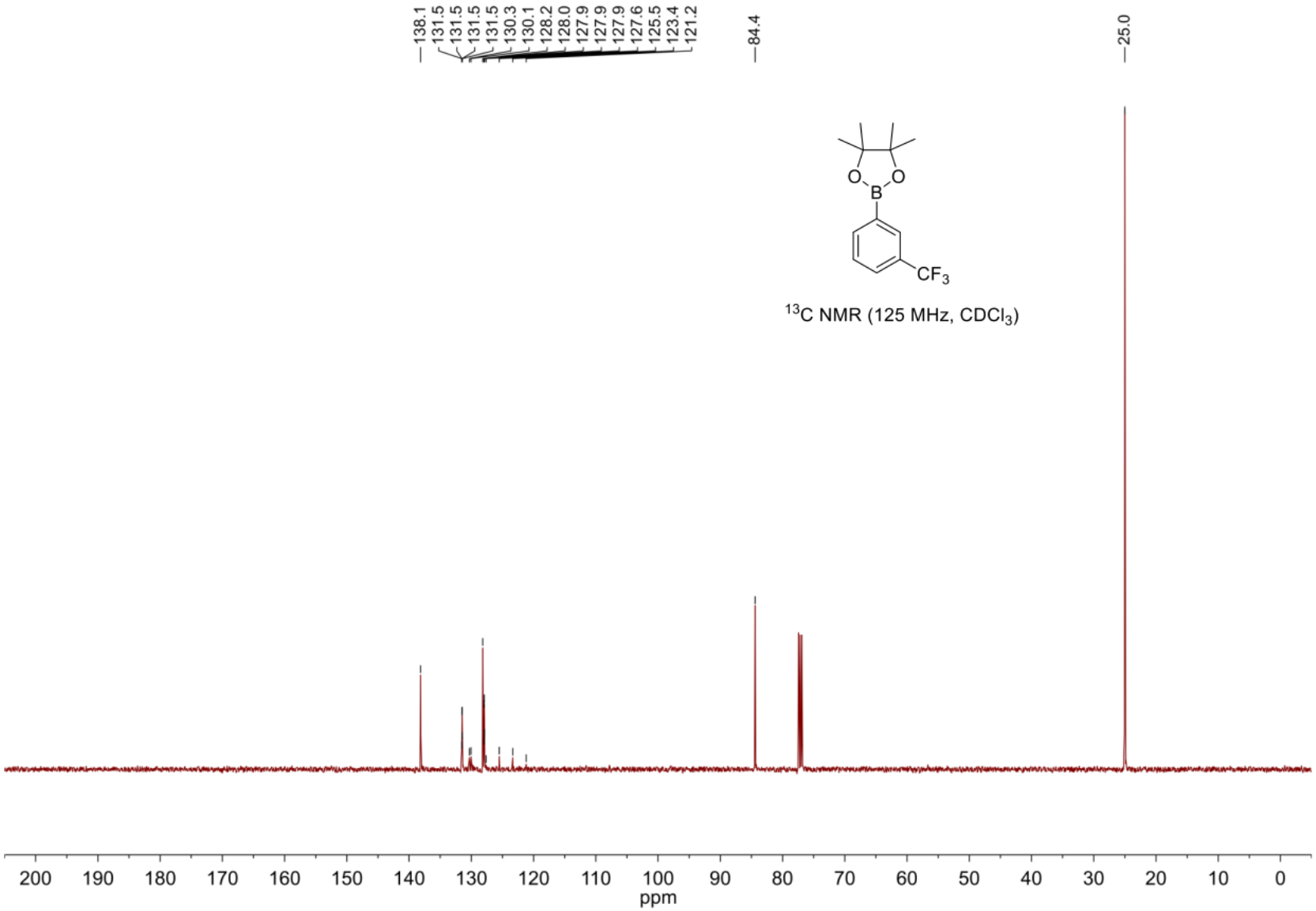
4,4,5,5-Tetramethyl-2-(3-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (41)



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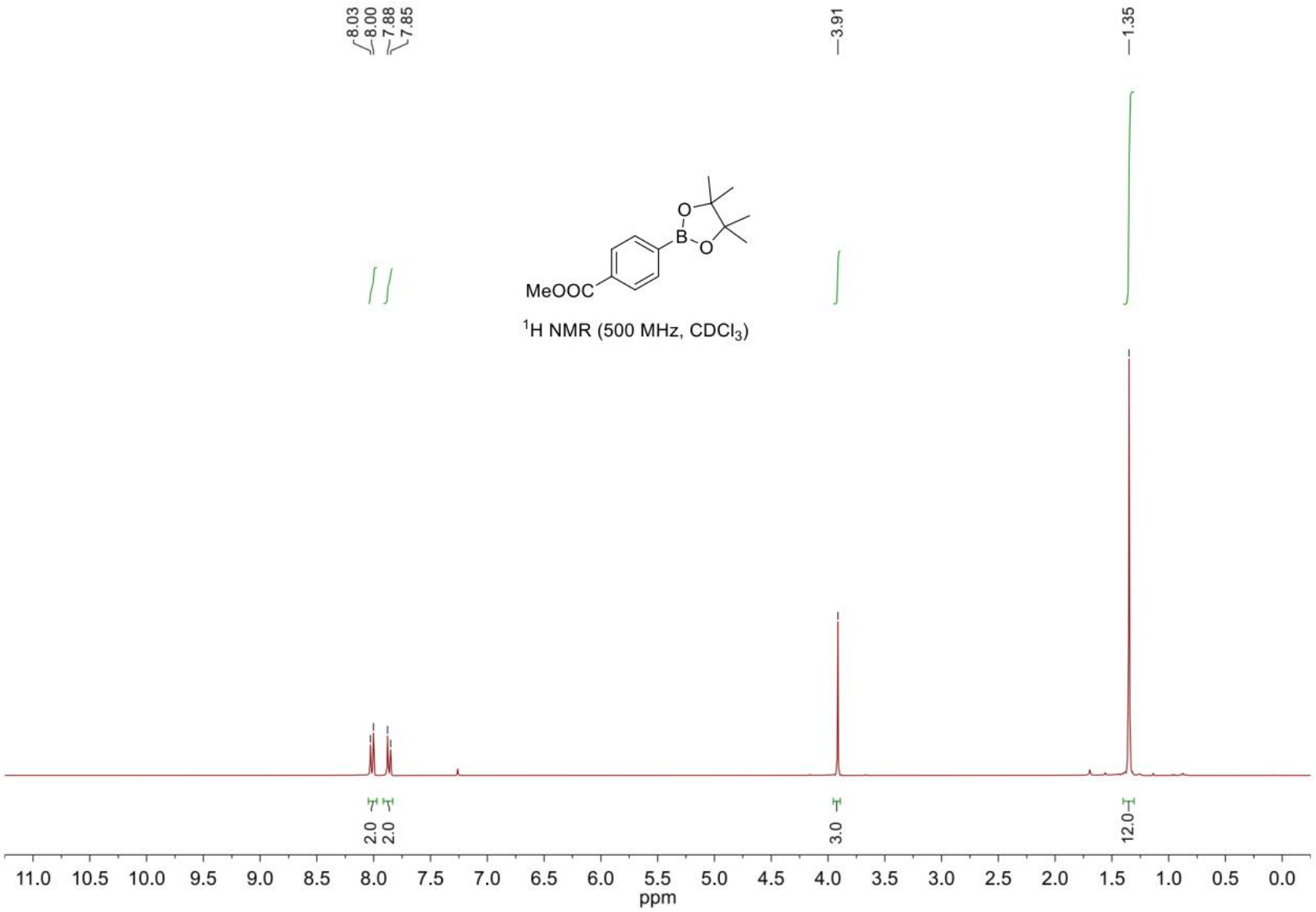
Methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (42)



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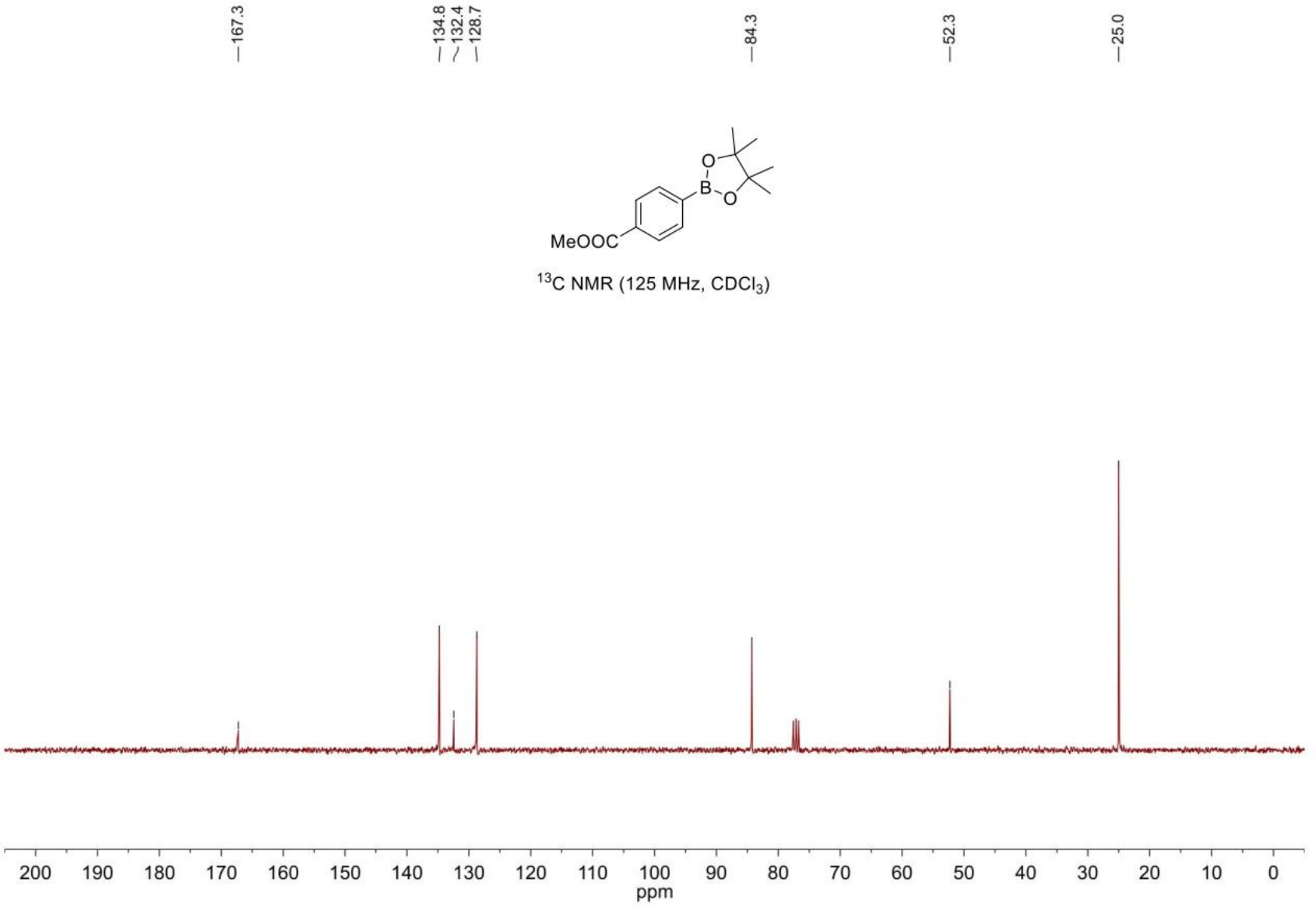
Methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (42)



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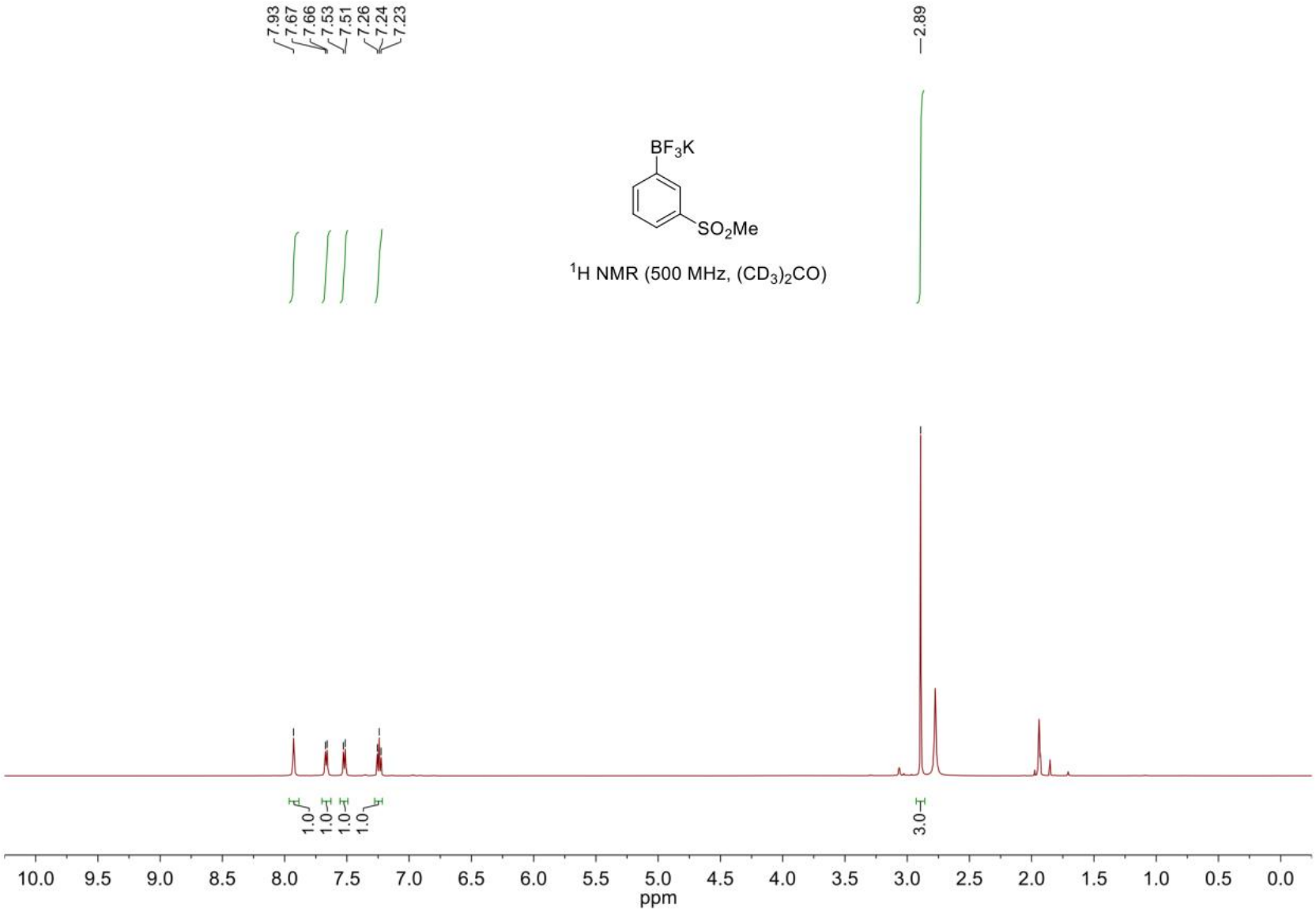
Trifluoro(3-(methylsulfonyl)phenyl)-λ⁴-borane, potassium salt (43)



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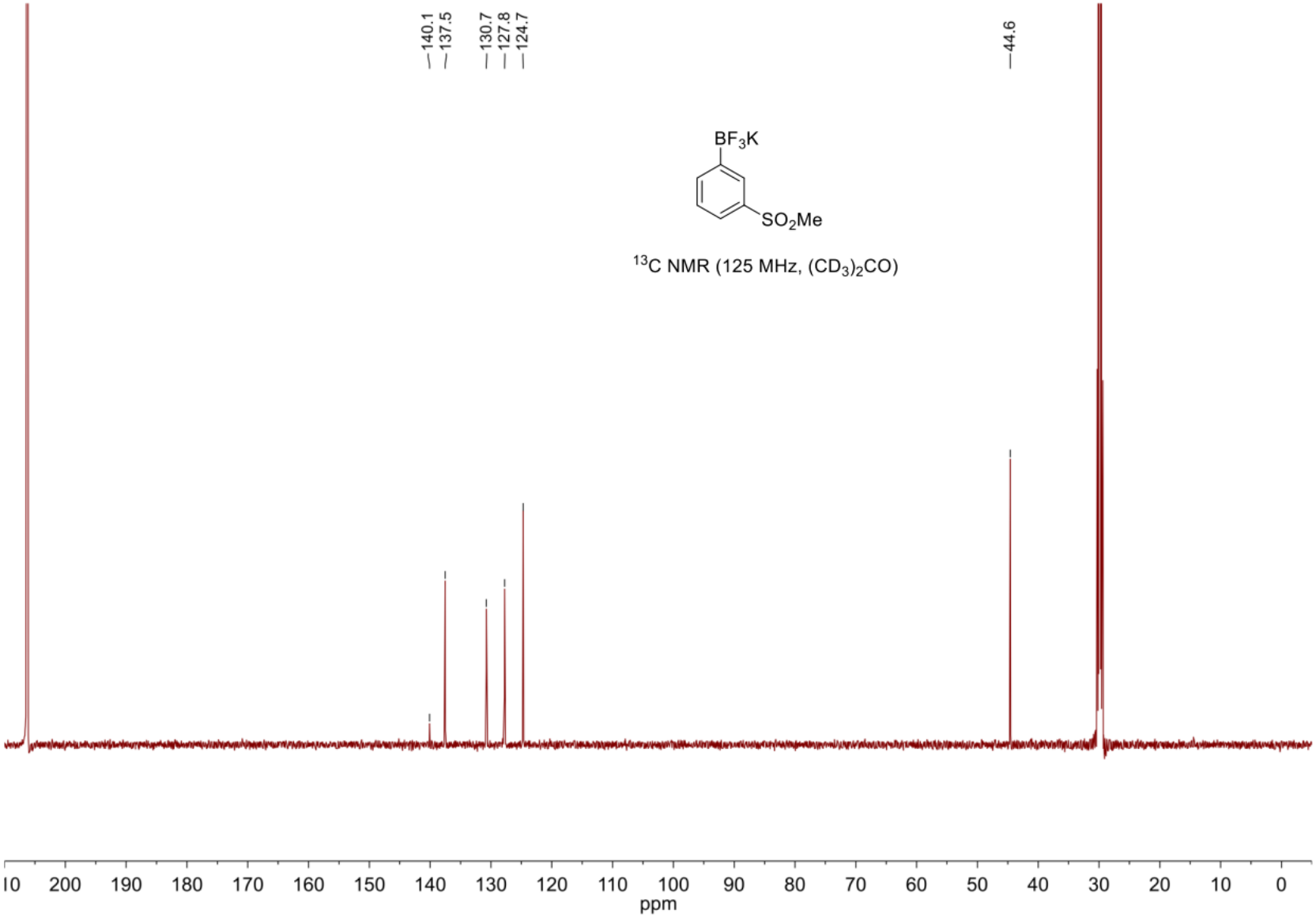
Trifluoro(3-(methylsulfonyl)phenyl)-λ⁴-borane, potassium salt (43)



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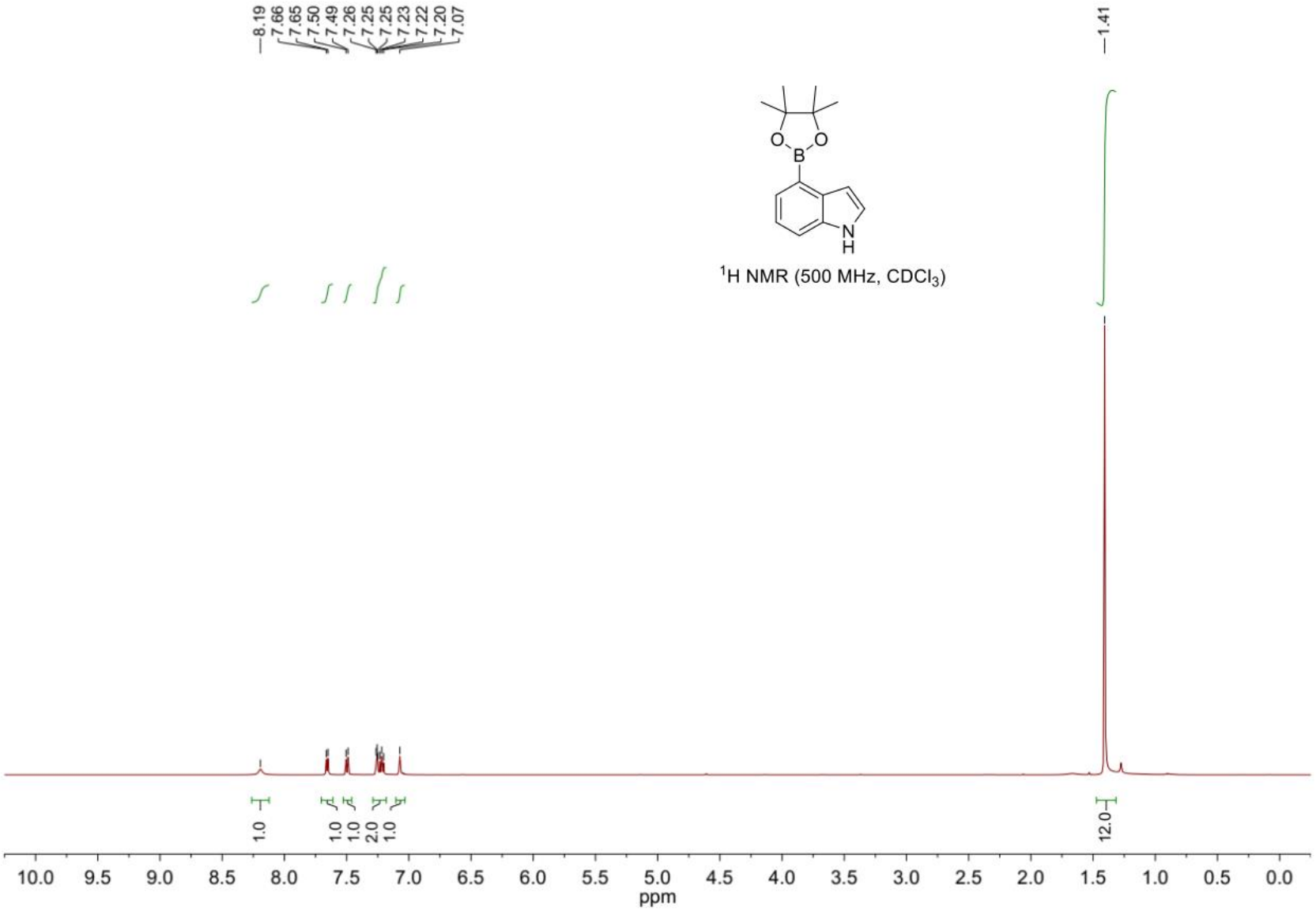
4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (44)



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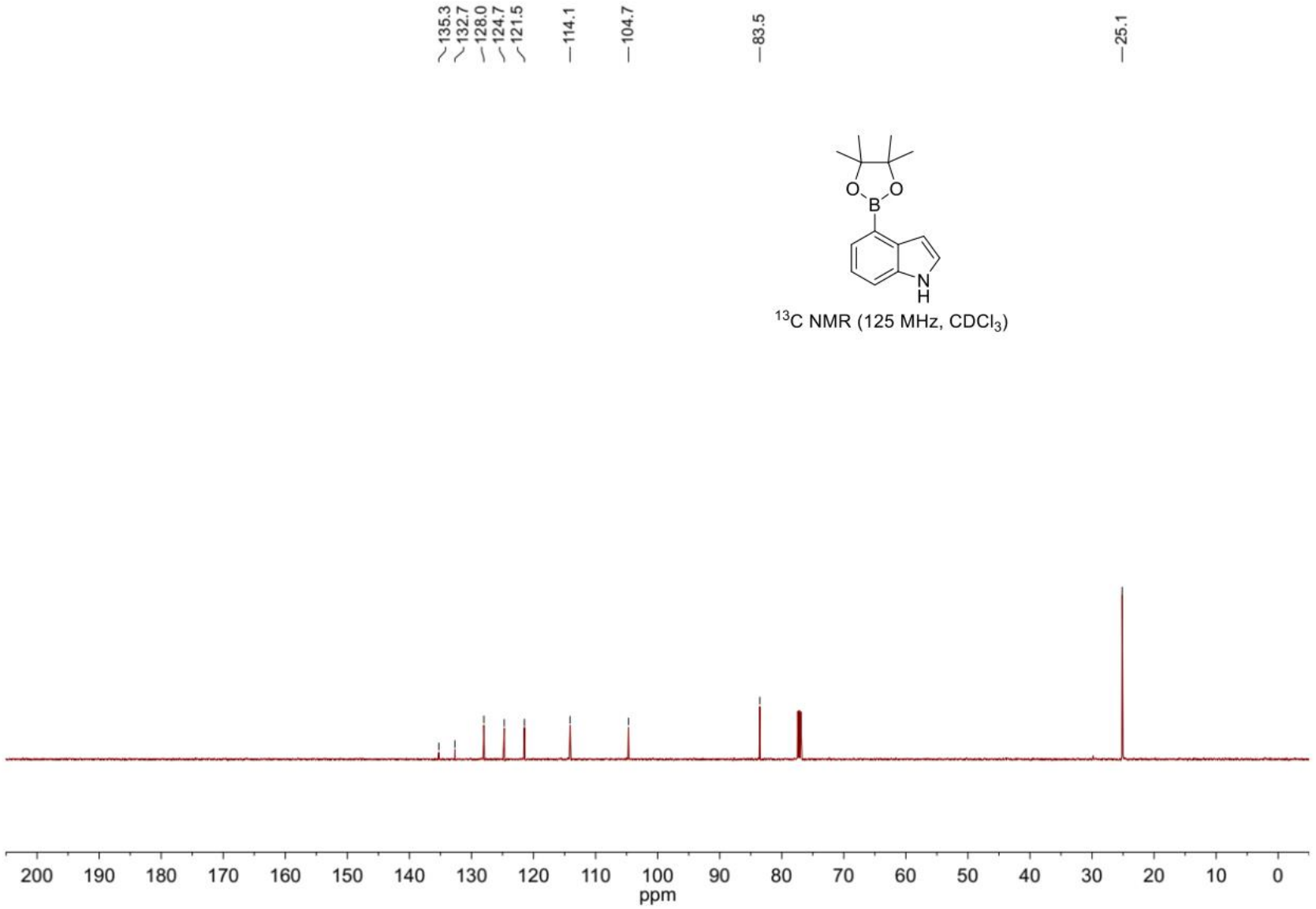
4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (44)



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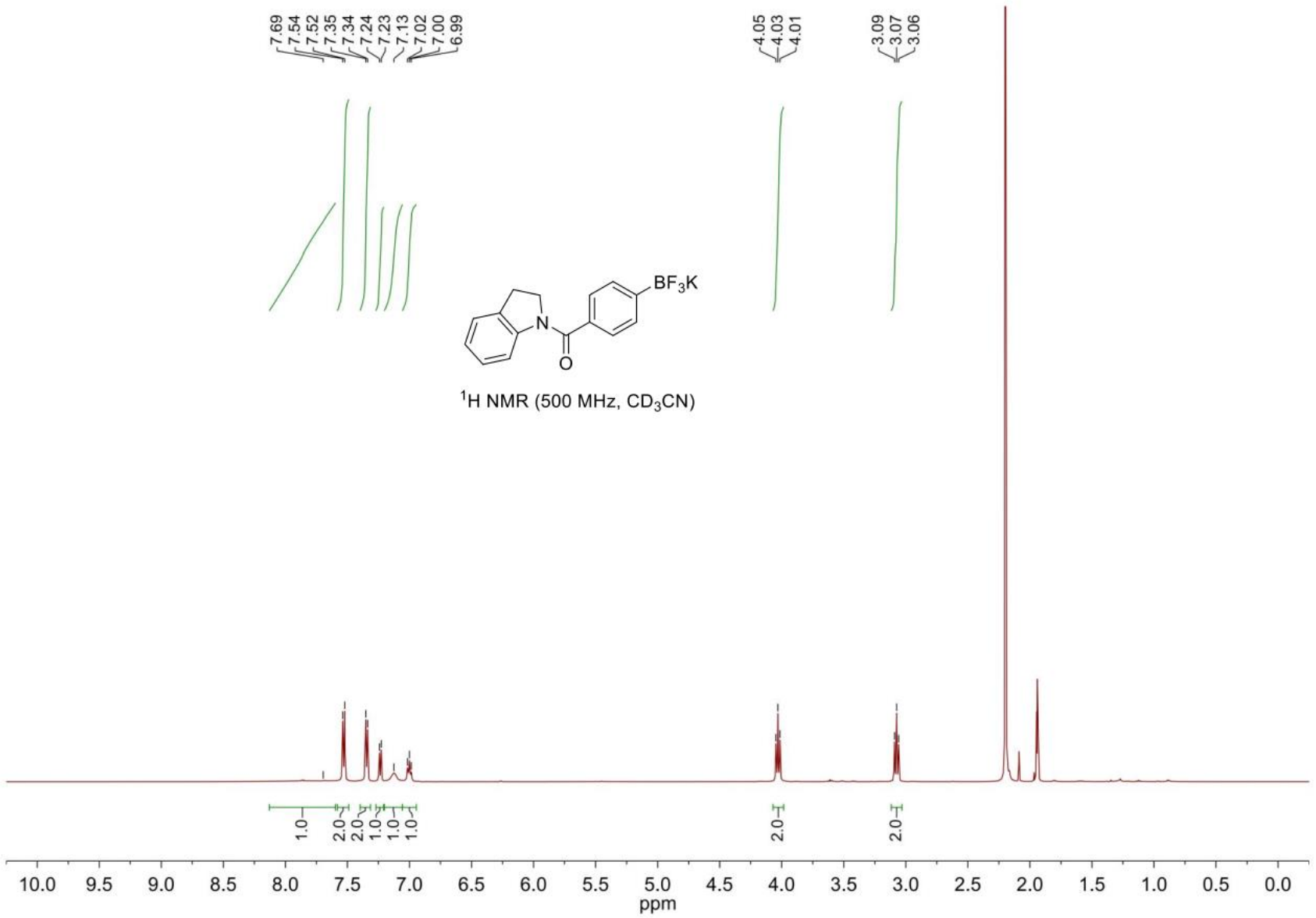
Indolin-1-yl(4-(trifluoro-λ⁴-boraneyl)phenyl)methanone, potassium salt (45)



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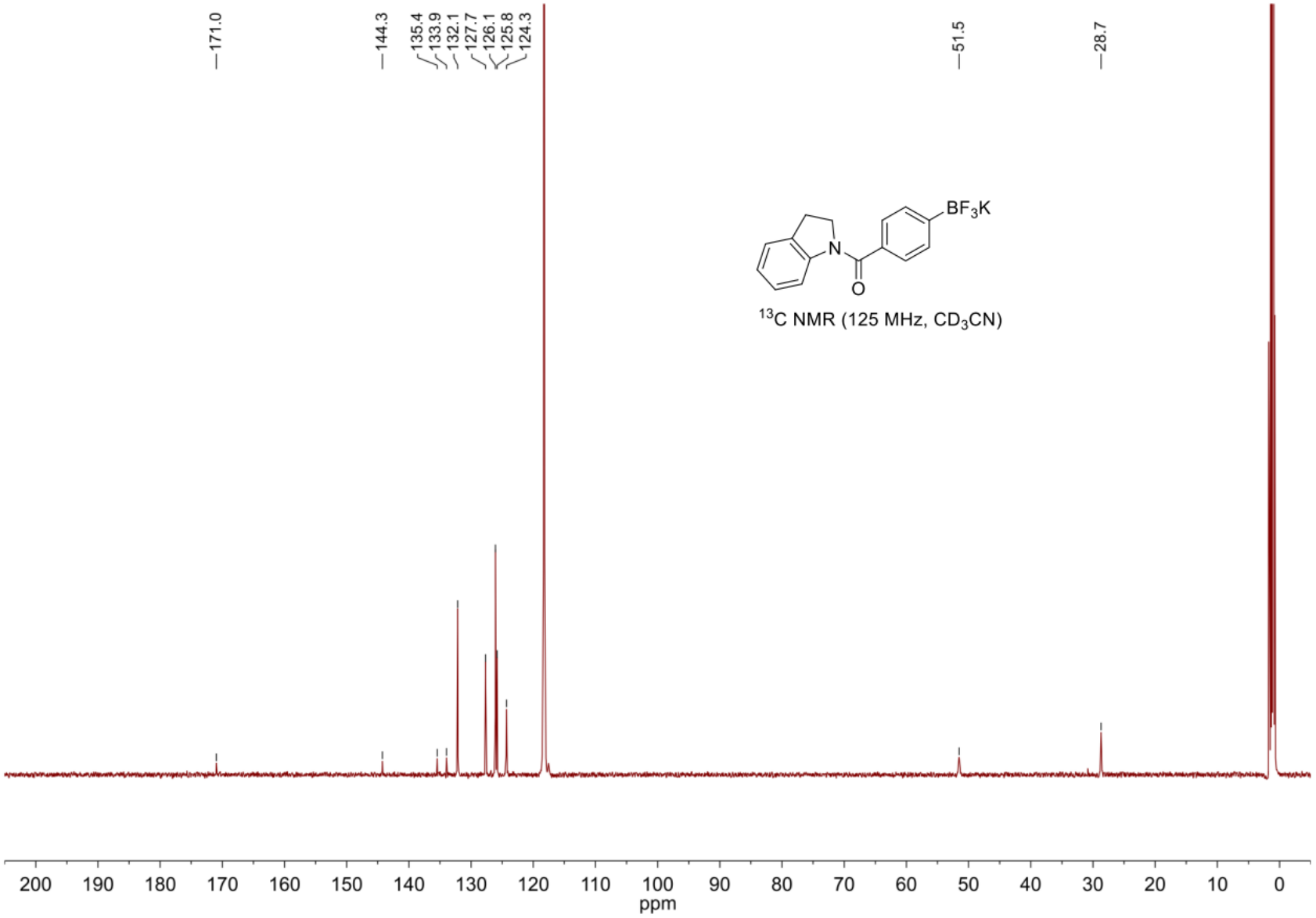
Indolin-1-yl(4-(trifluoro-λ⁴-boraneyl)phenyl)methanone, potassium salt (45)



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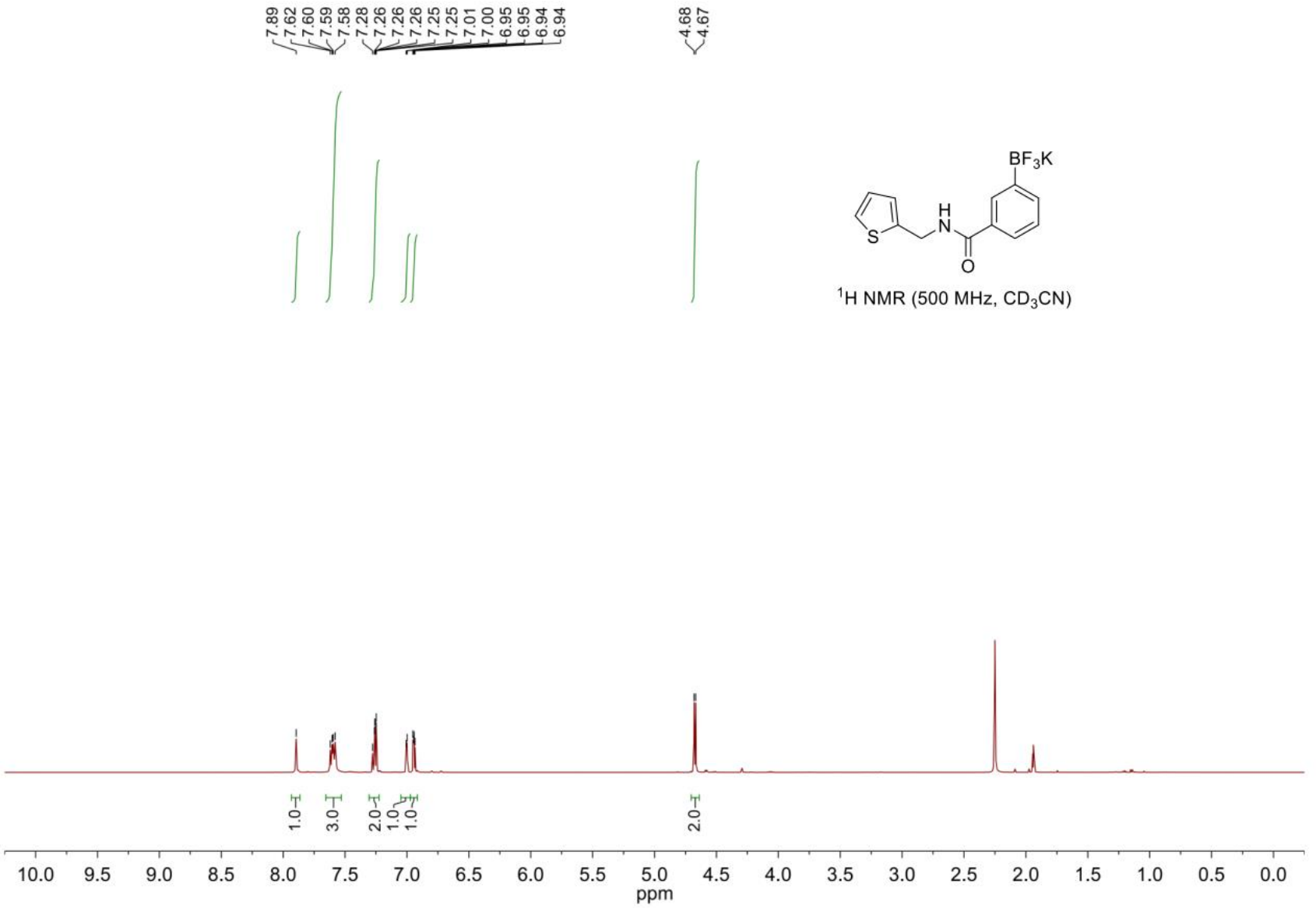
_N_-(Thiophen-2-ylmethyl)-4-(trifluoro-λ⁴-boraneyl)benzamide, potassium salt (46)



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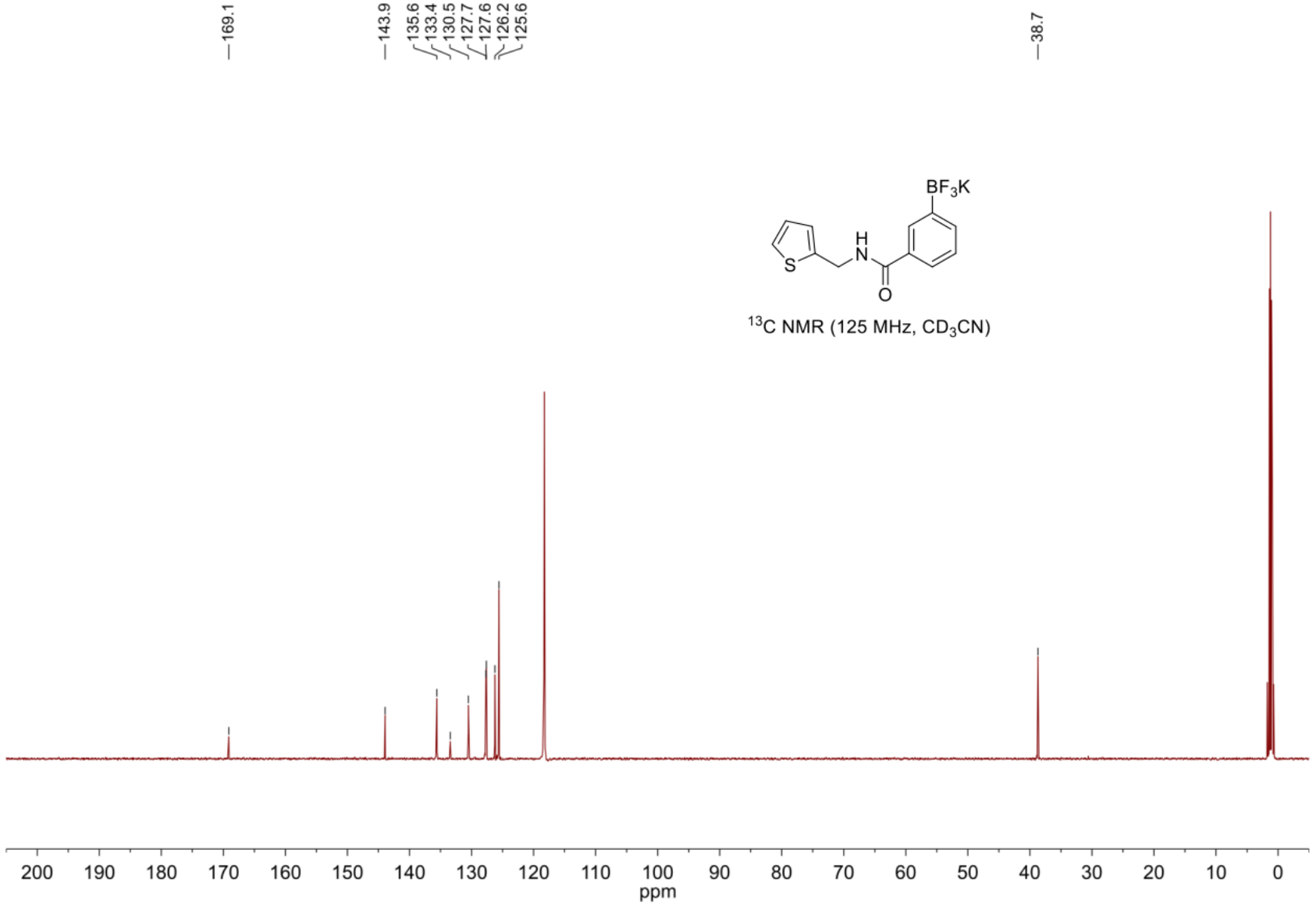
_N_-(Thiophen-2-ylmethyl)-4-(trifluoro-λ⁴-boraneyl)benzamide, potassium salt (46)



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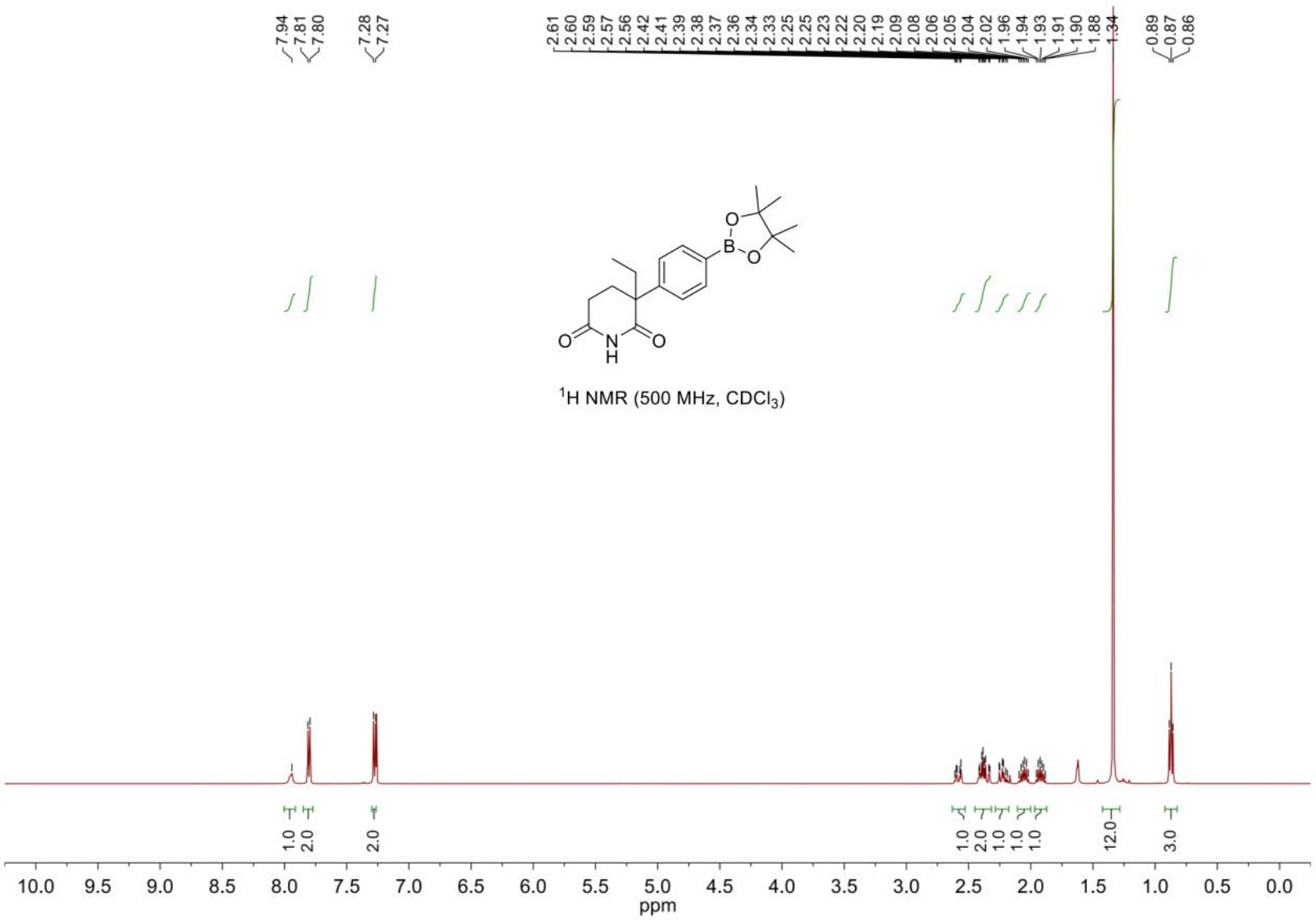
3-Ethyl-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)piperidine-2,6-dione (47)



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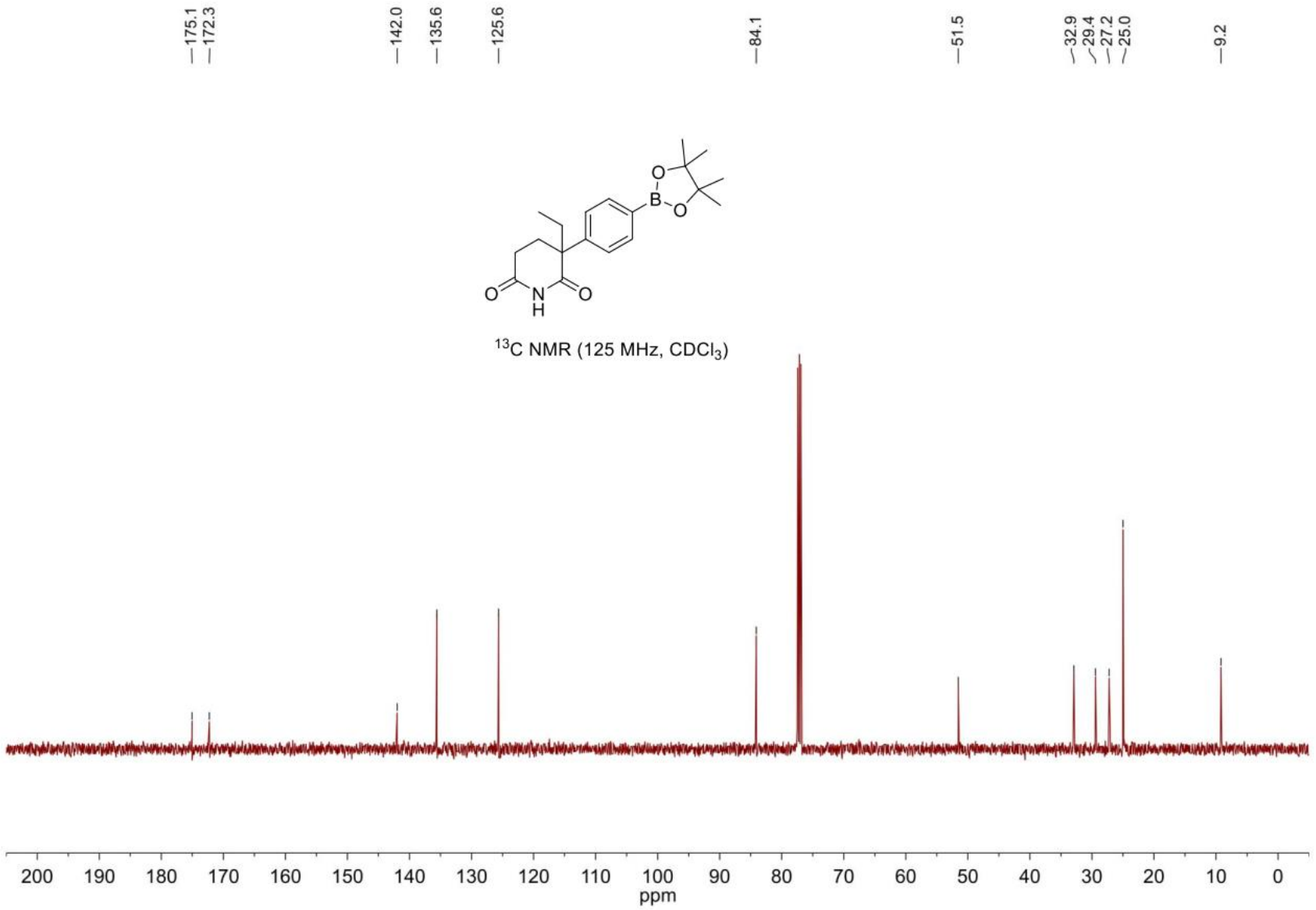
3-Ethyl-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)piperidine-2,6-dione (47)



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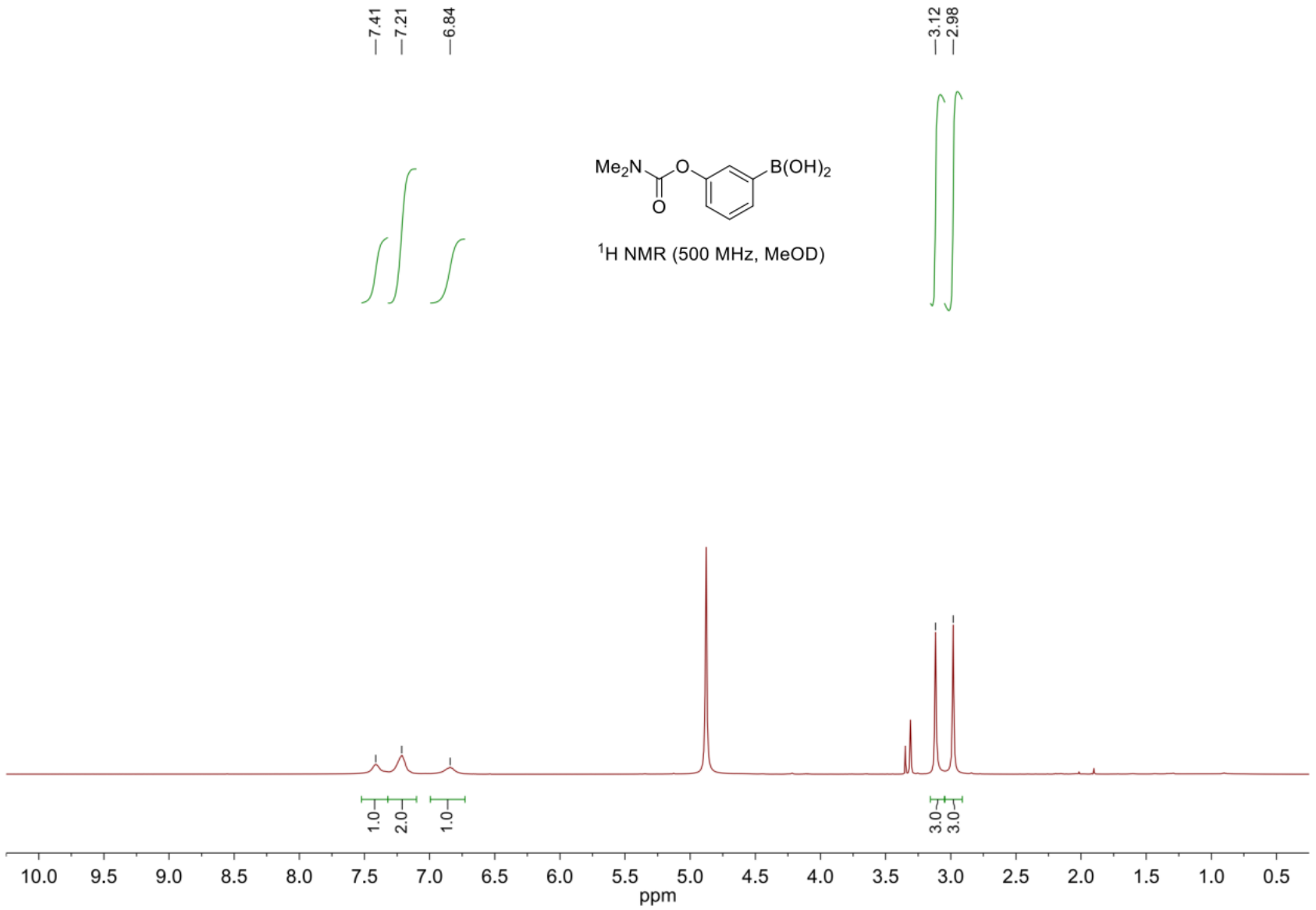
(3-((Dimethylcarbamoyl)oxy)phenyl)boronic acid (48)



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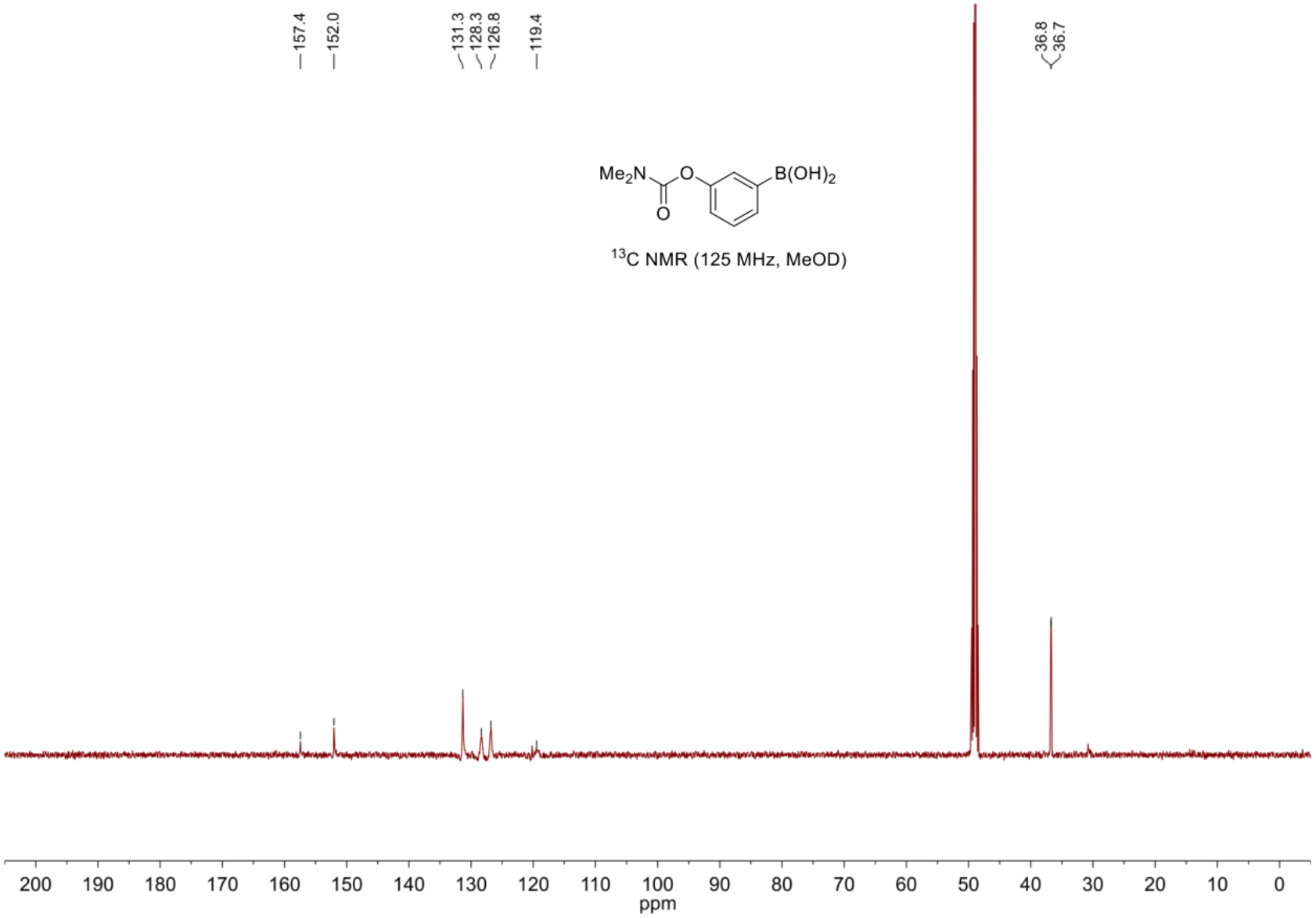
(3-((Dimethylcarbamoyl)oxy)phenyl)boronic acid (48)



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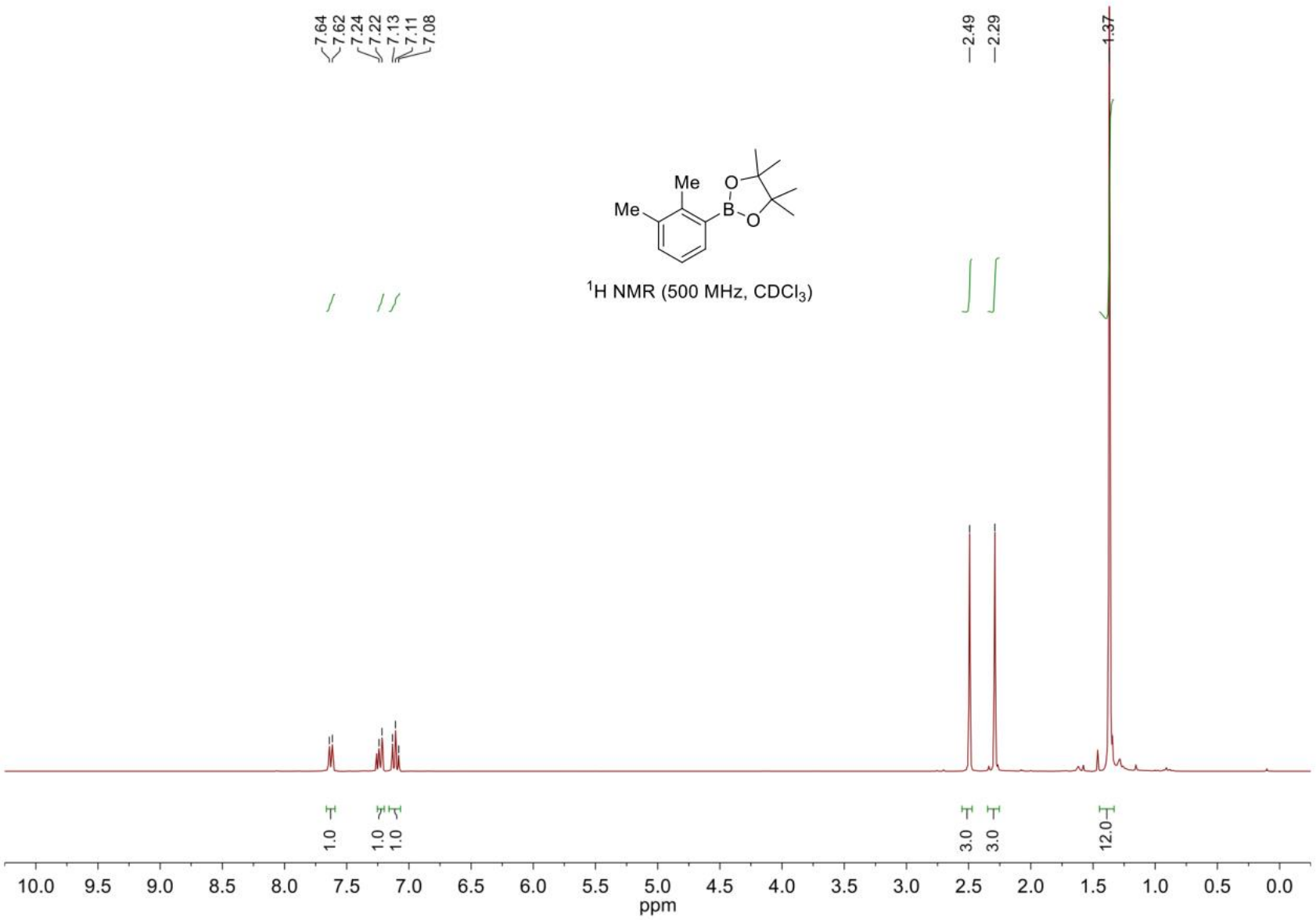
2-(2,3-Dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (49)



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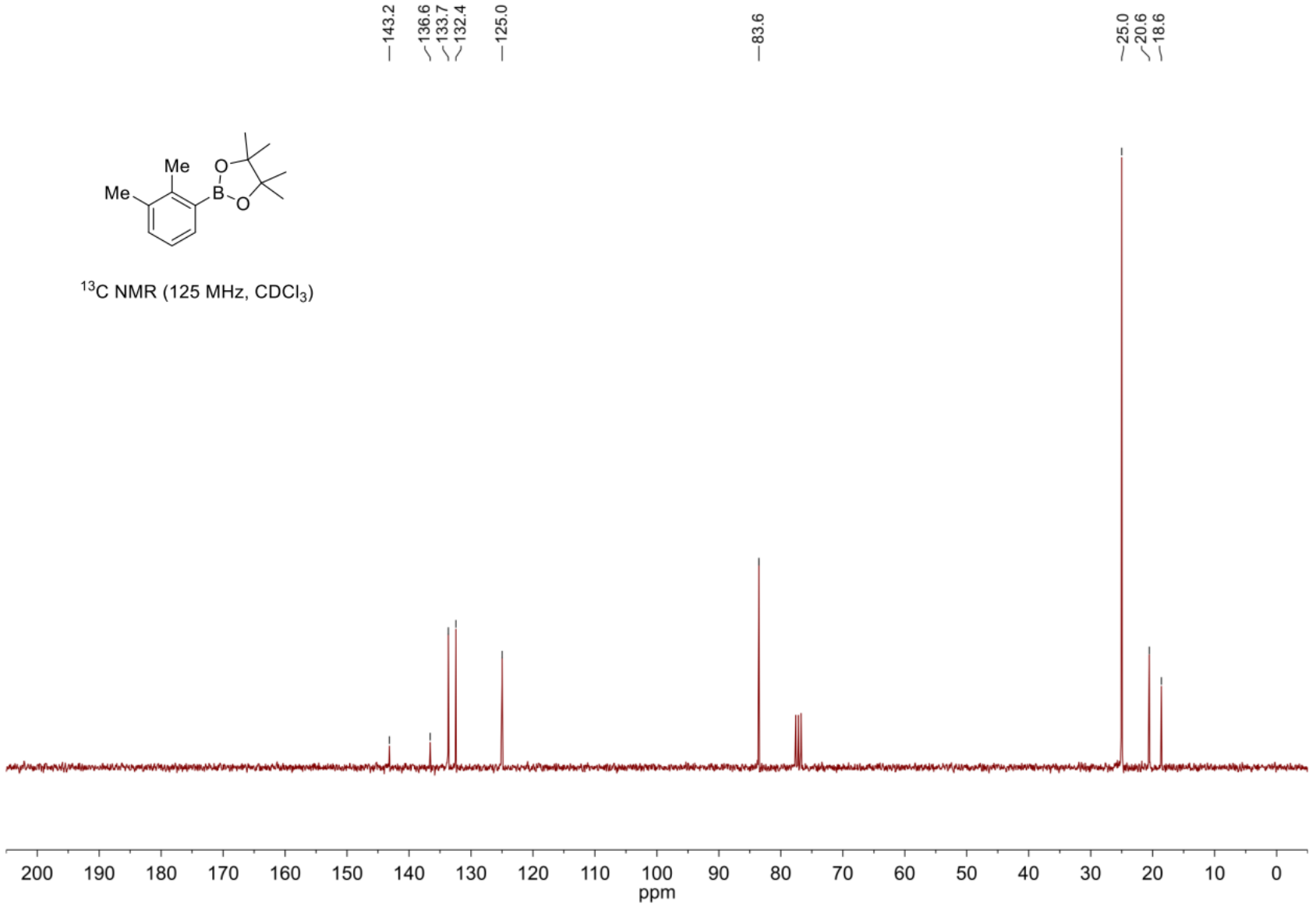
2-(2,3-Dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (49)



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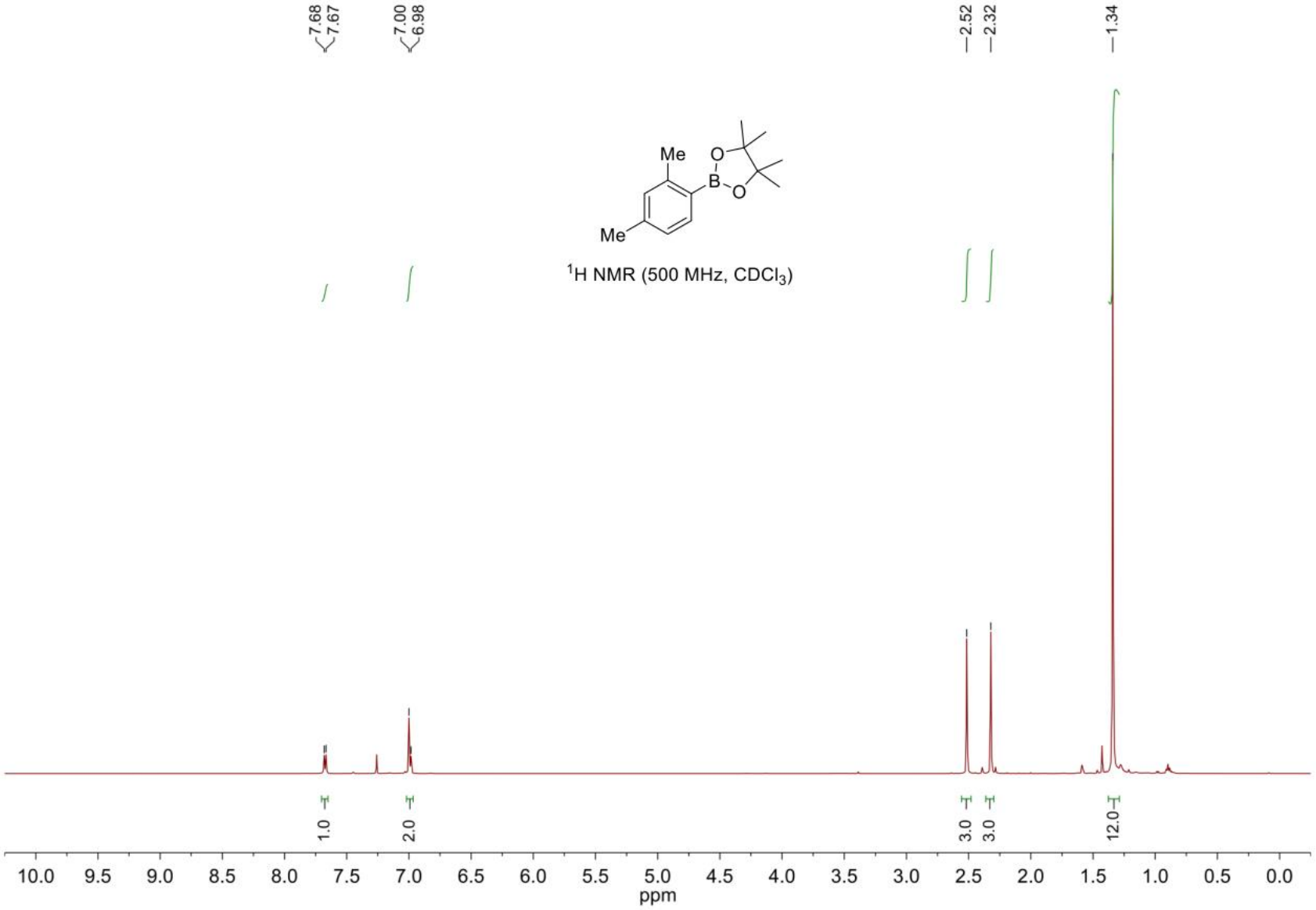
2-(2,4-Dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (50)



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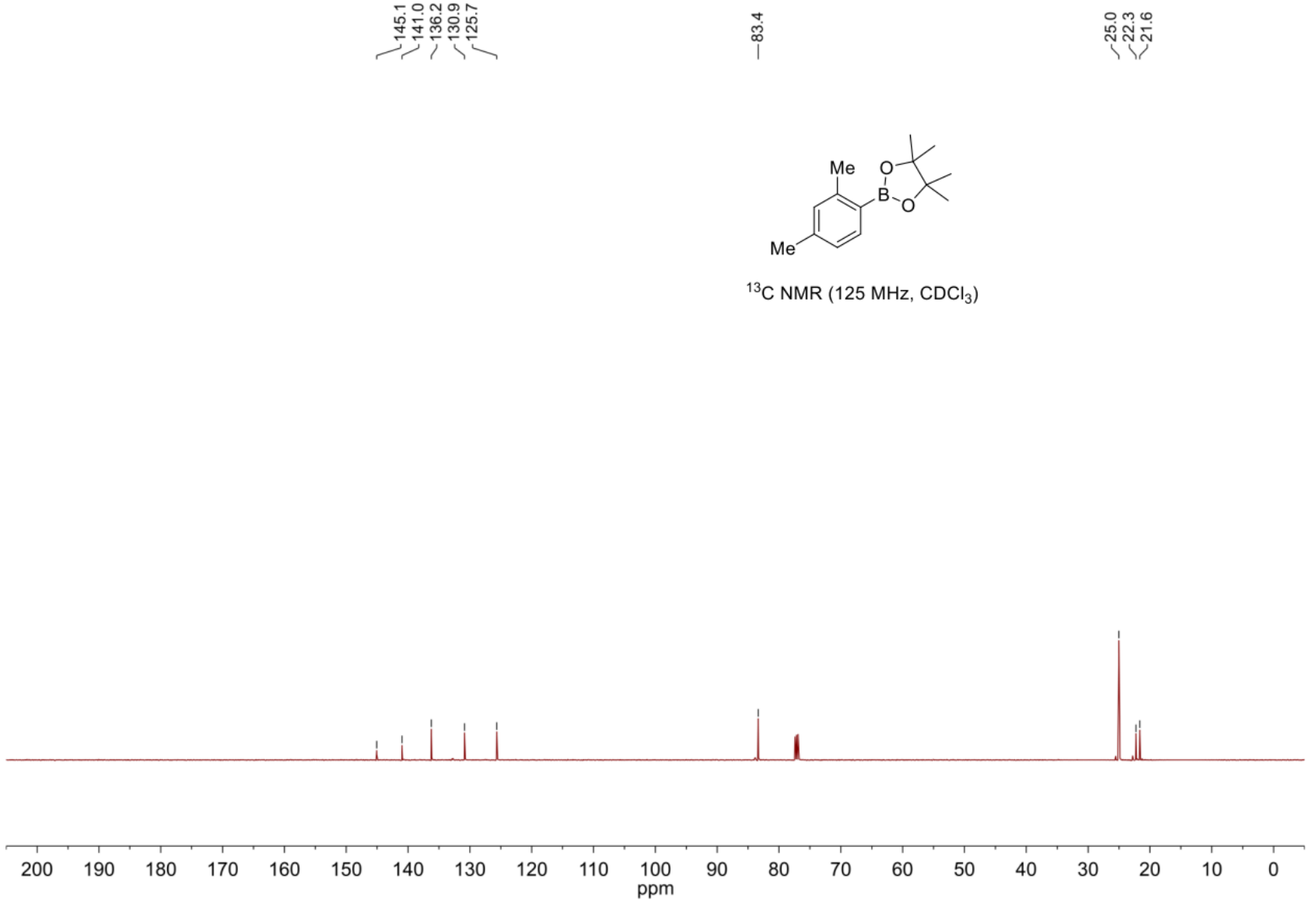
2-(2,4-Dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (50)



^{13}C NMR (125 MHz, $CDCl_3$)

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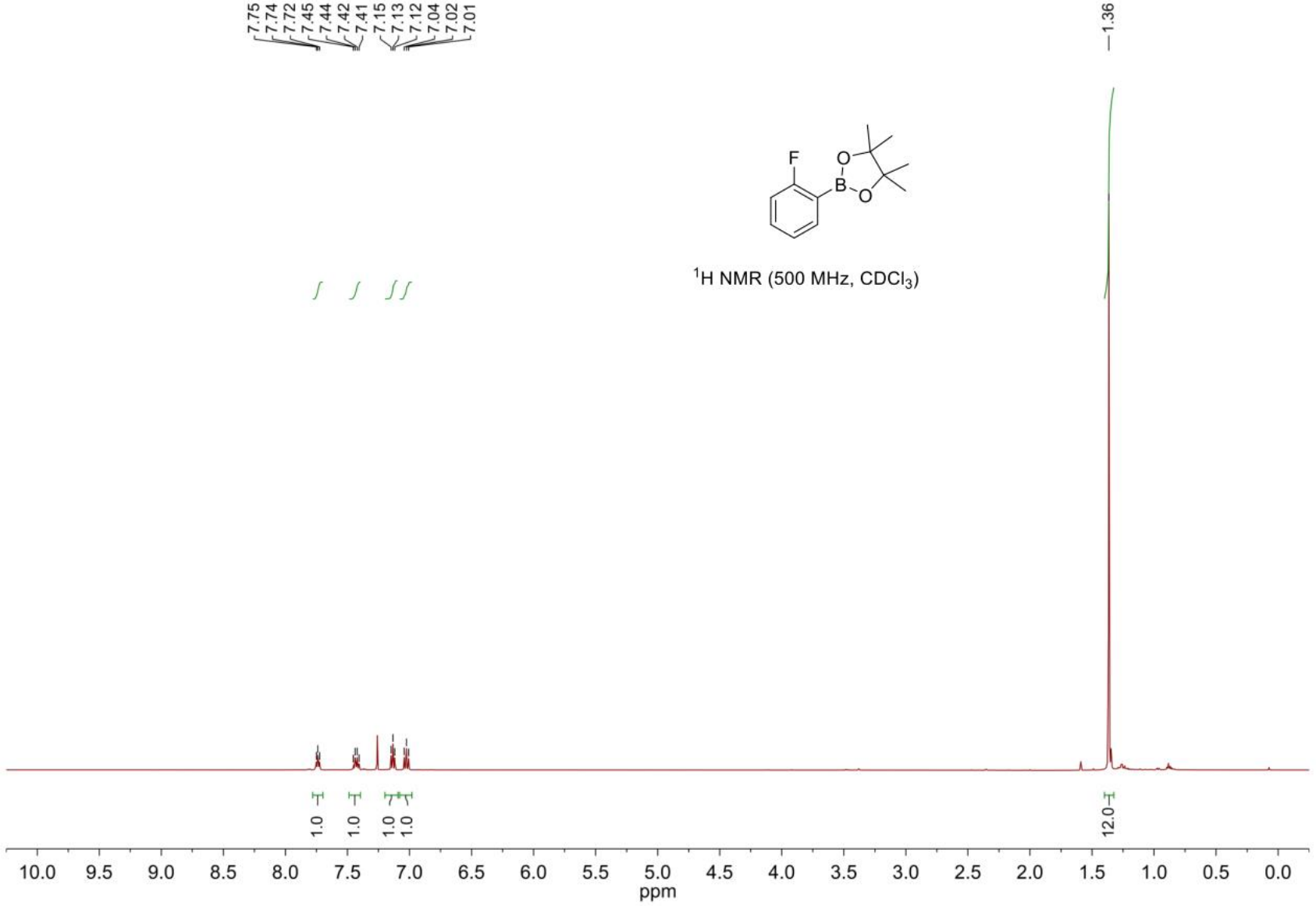
2-(2-Fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (51)



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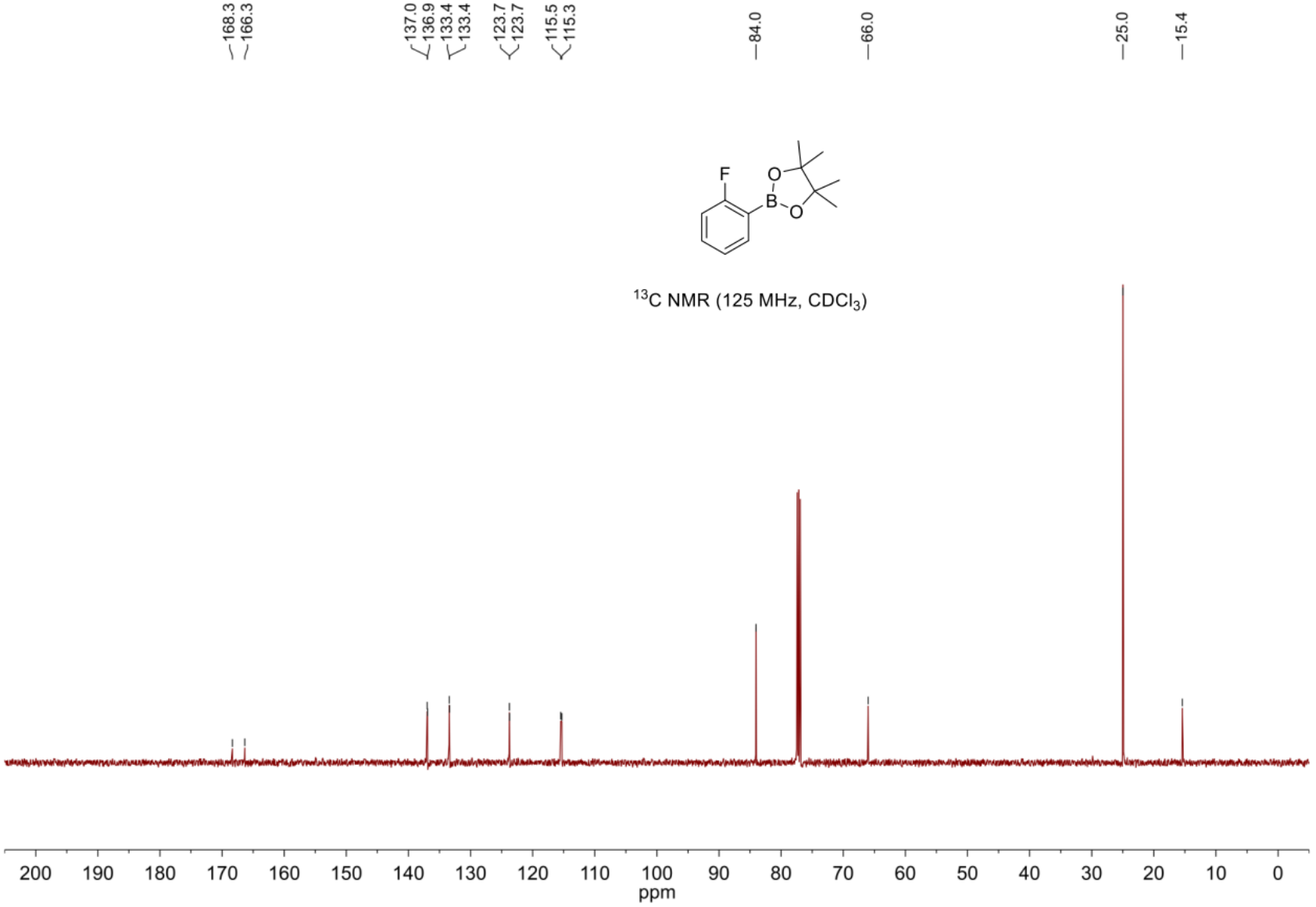
2-(2-Fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (51)



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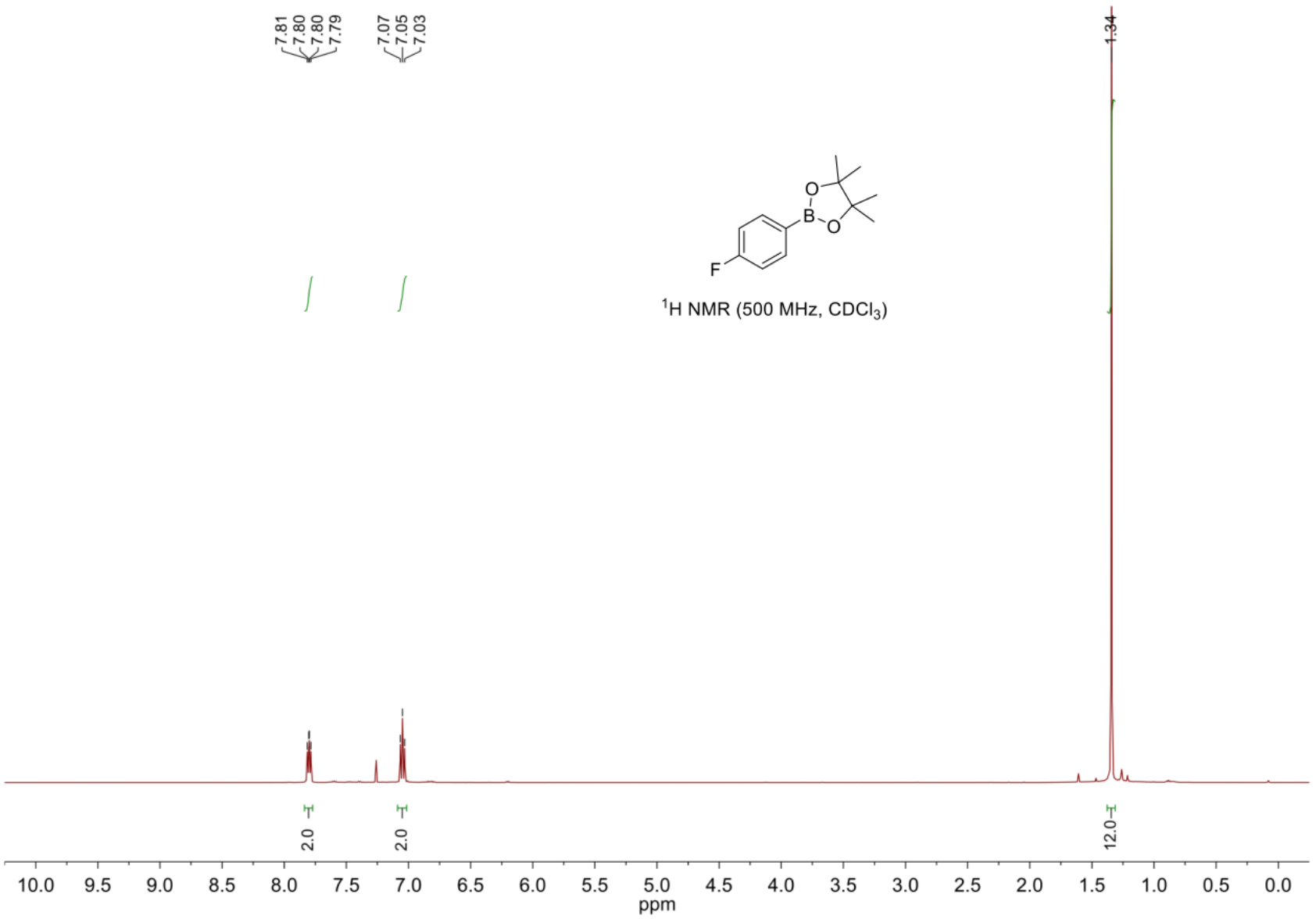
2-(4-Fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (52)



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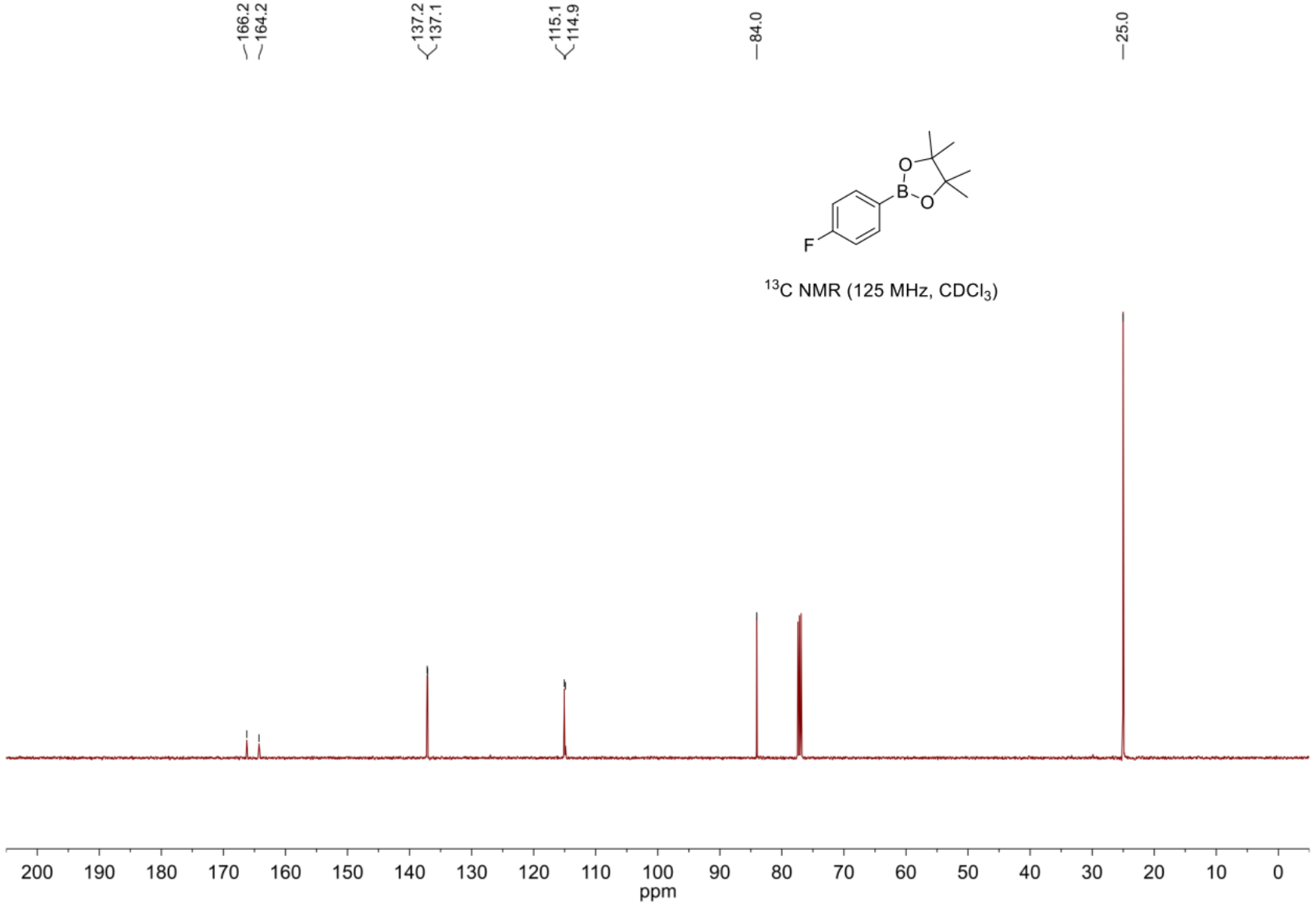
2-(4-Fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (52)



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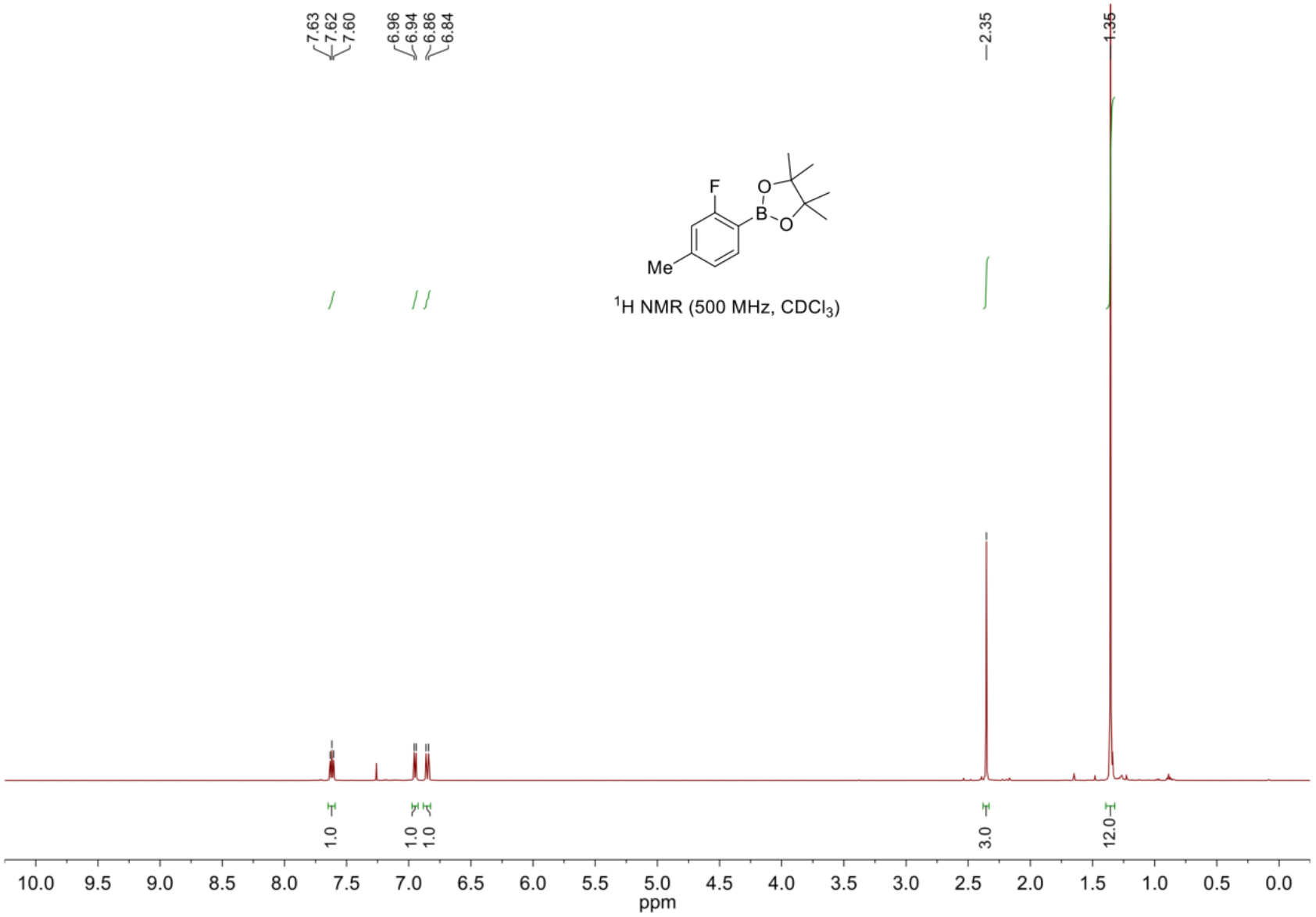
2-(2-Fluoro-4-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (53)



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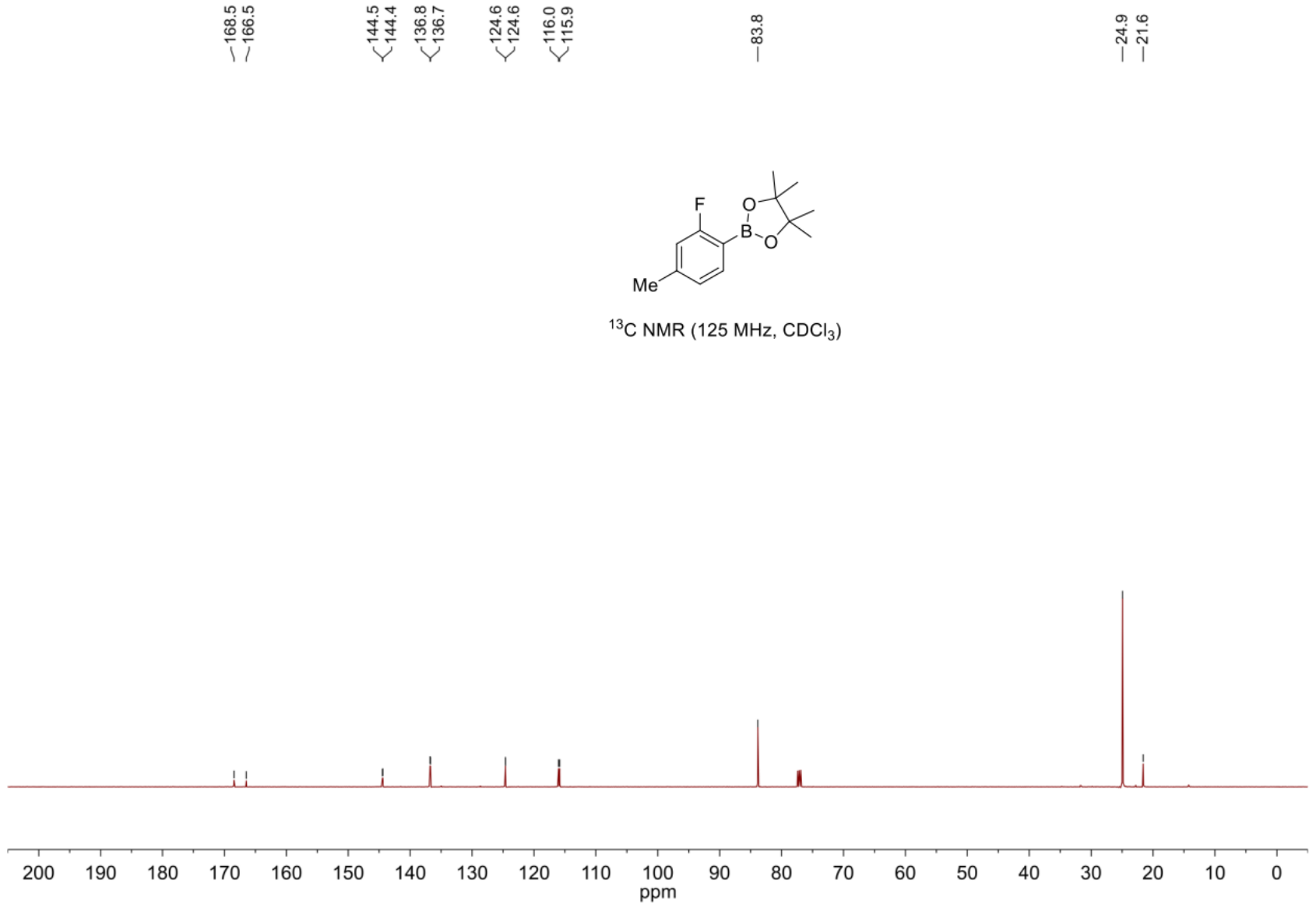
2-(2-Fluoro-4-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (53)



^{13}C NMR (125 MHz, $CDCl_3$)

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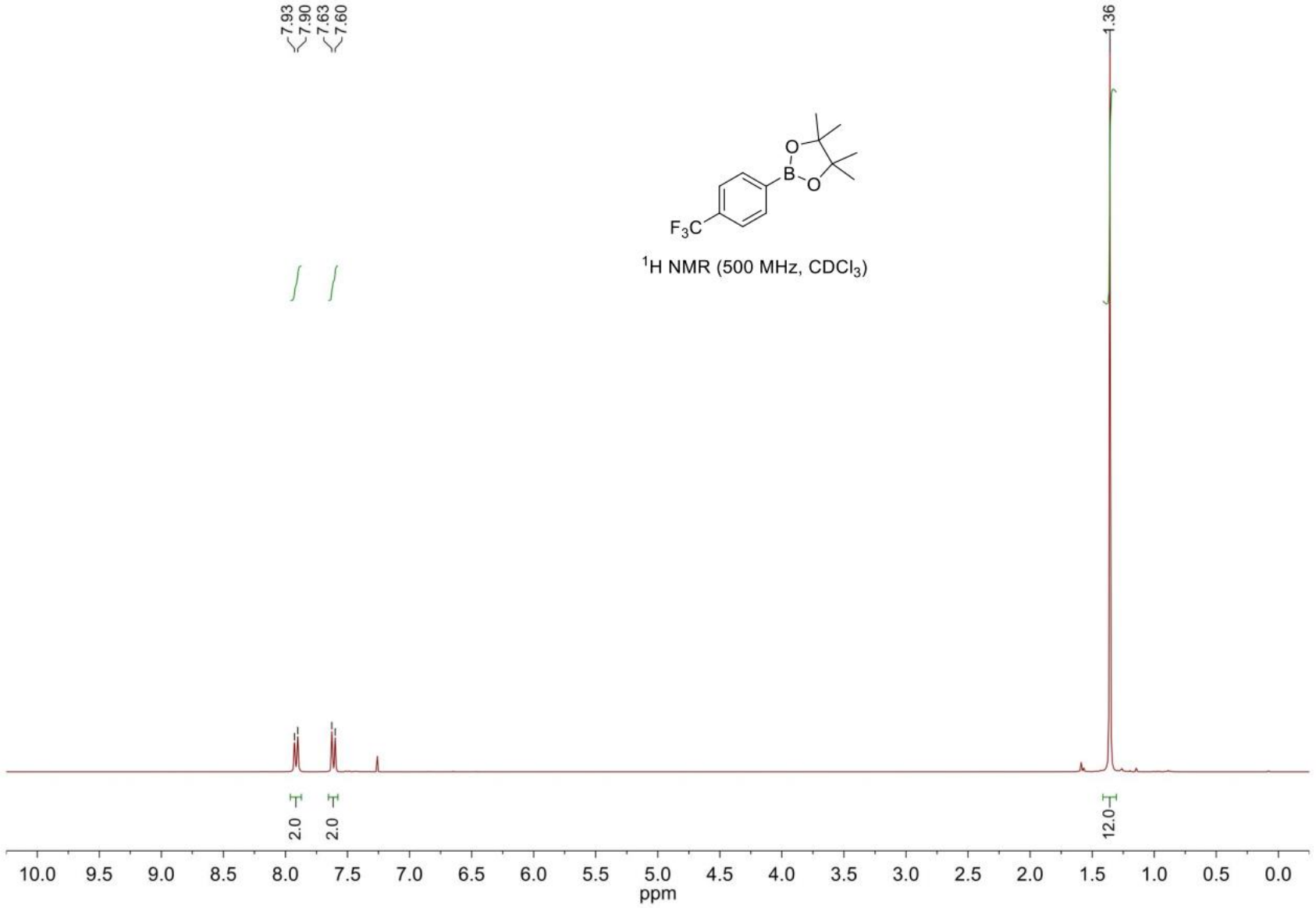
4,4,5,5-Tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (54)



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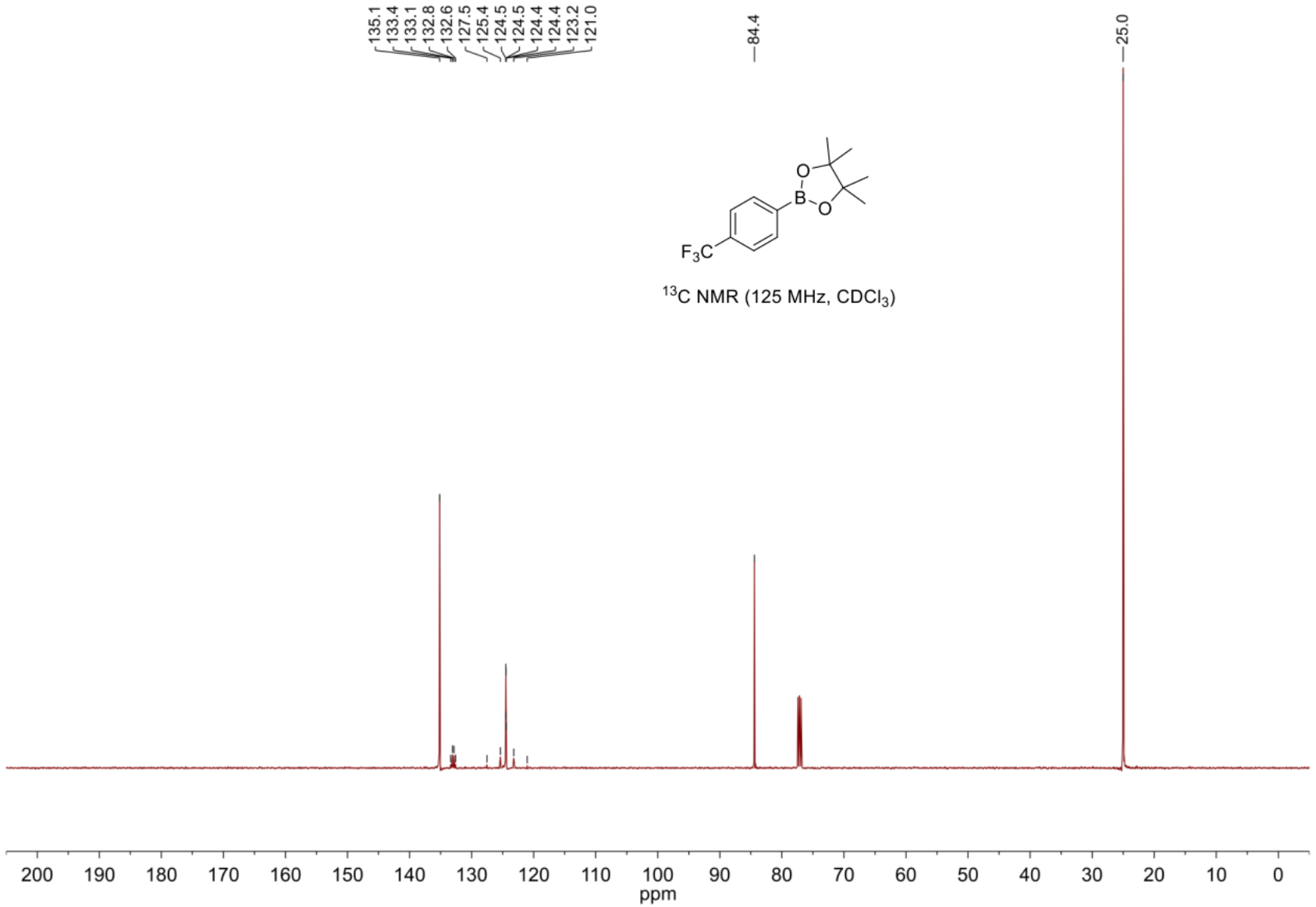
4,4,5,5-Tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (54)



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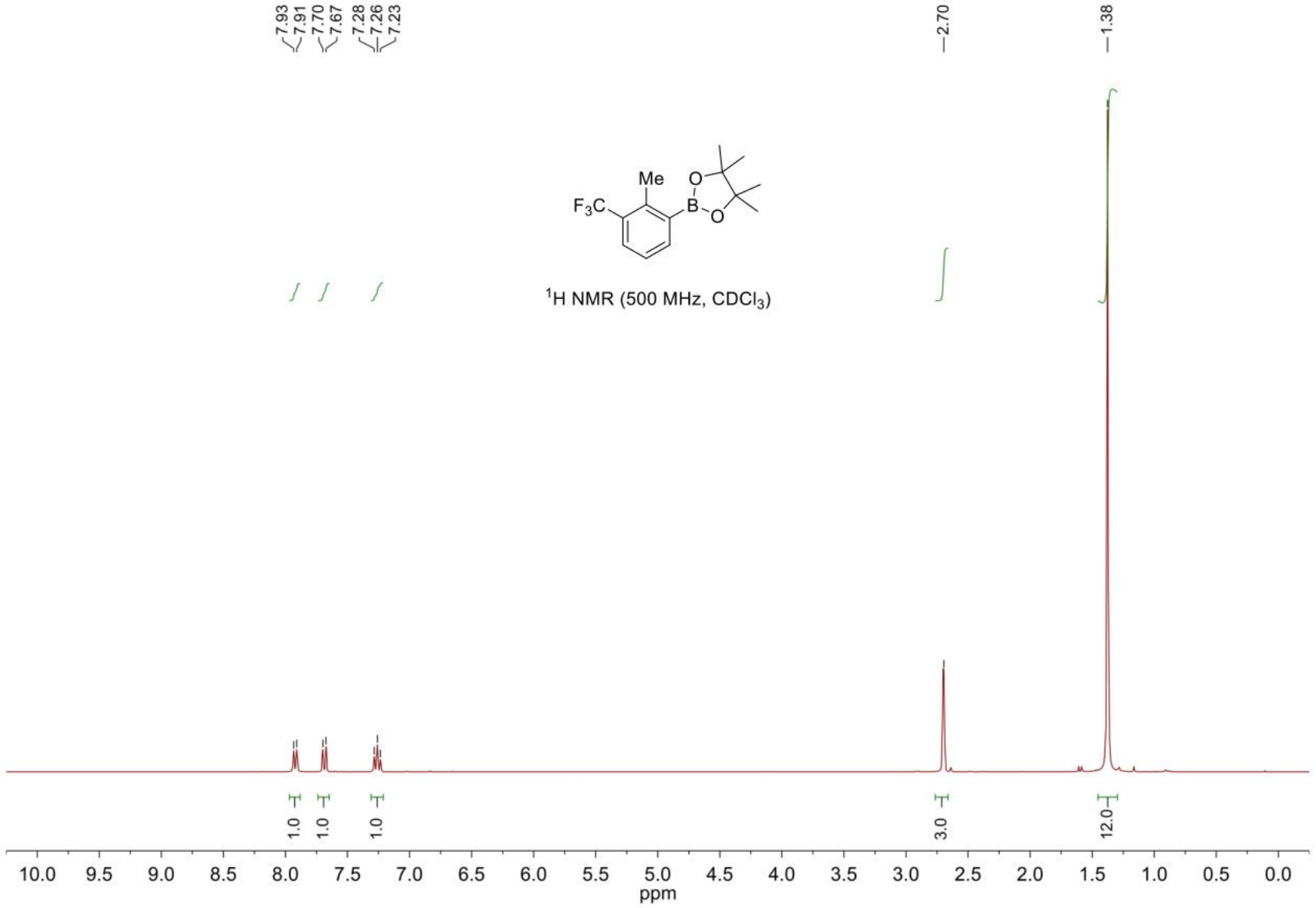
4,4,5,5-Tetramethyl-2-(2-methyl-3-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (55)



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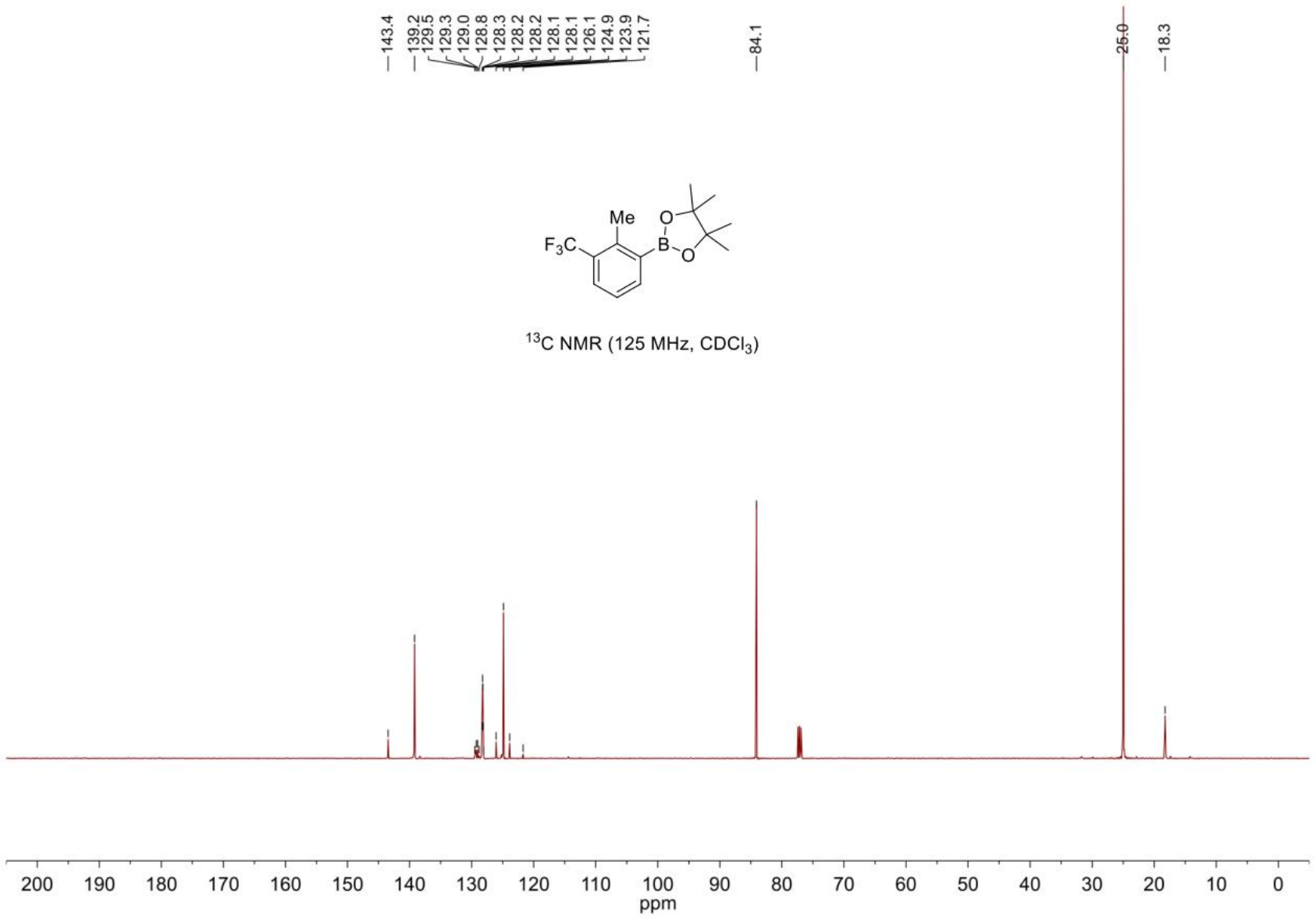
4,4,5,5-Tetramethyl-2-(2-methyl-3-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (55)



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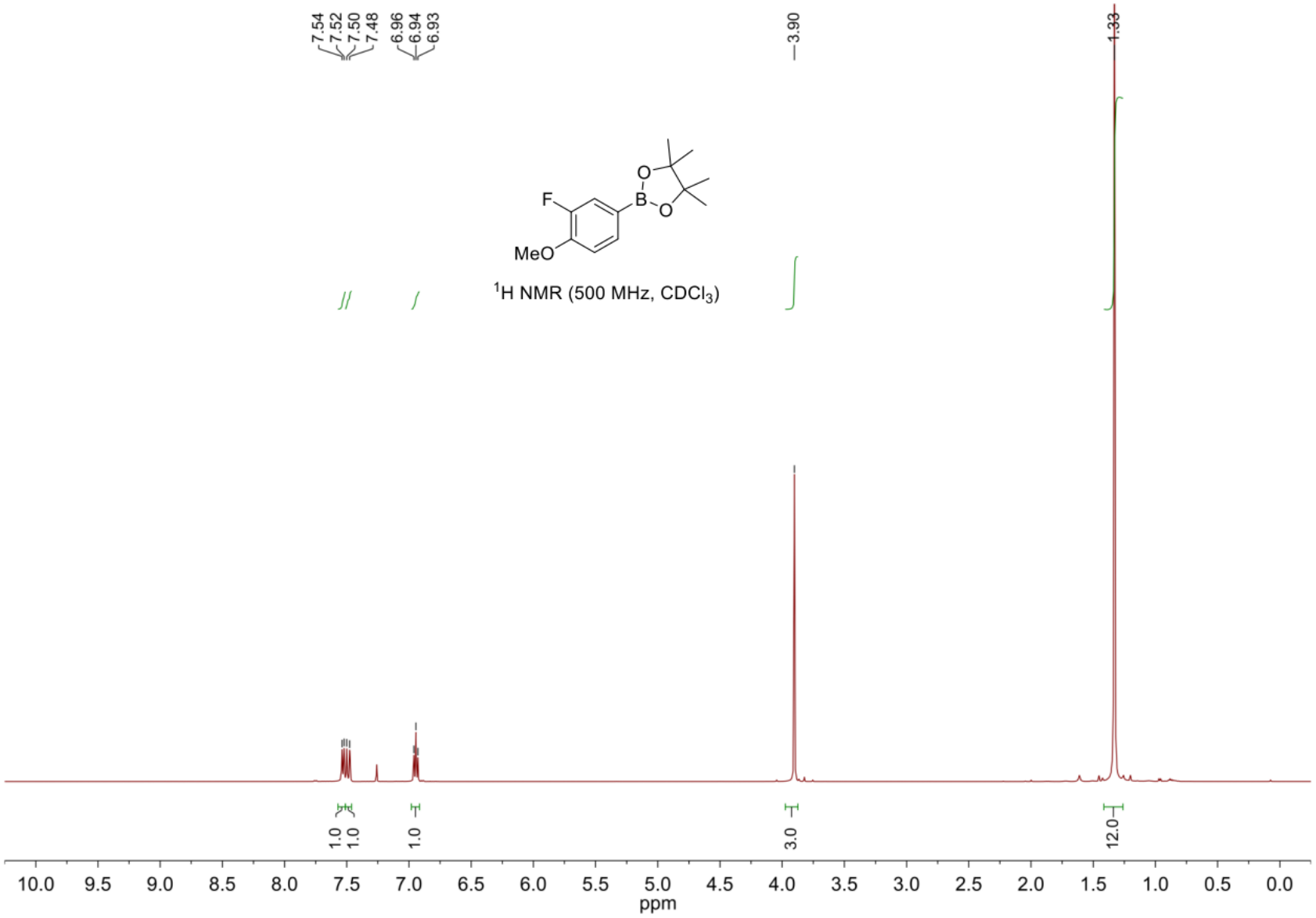
2-(3-Fluoro-4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (56)



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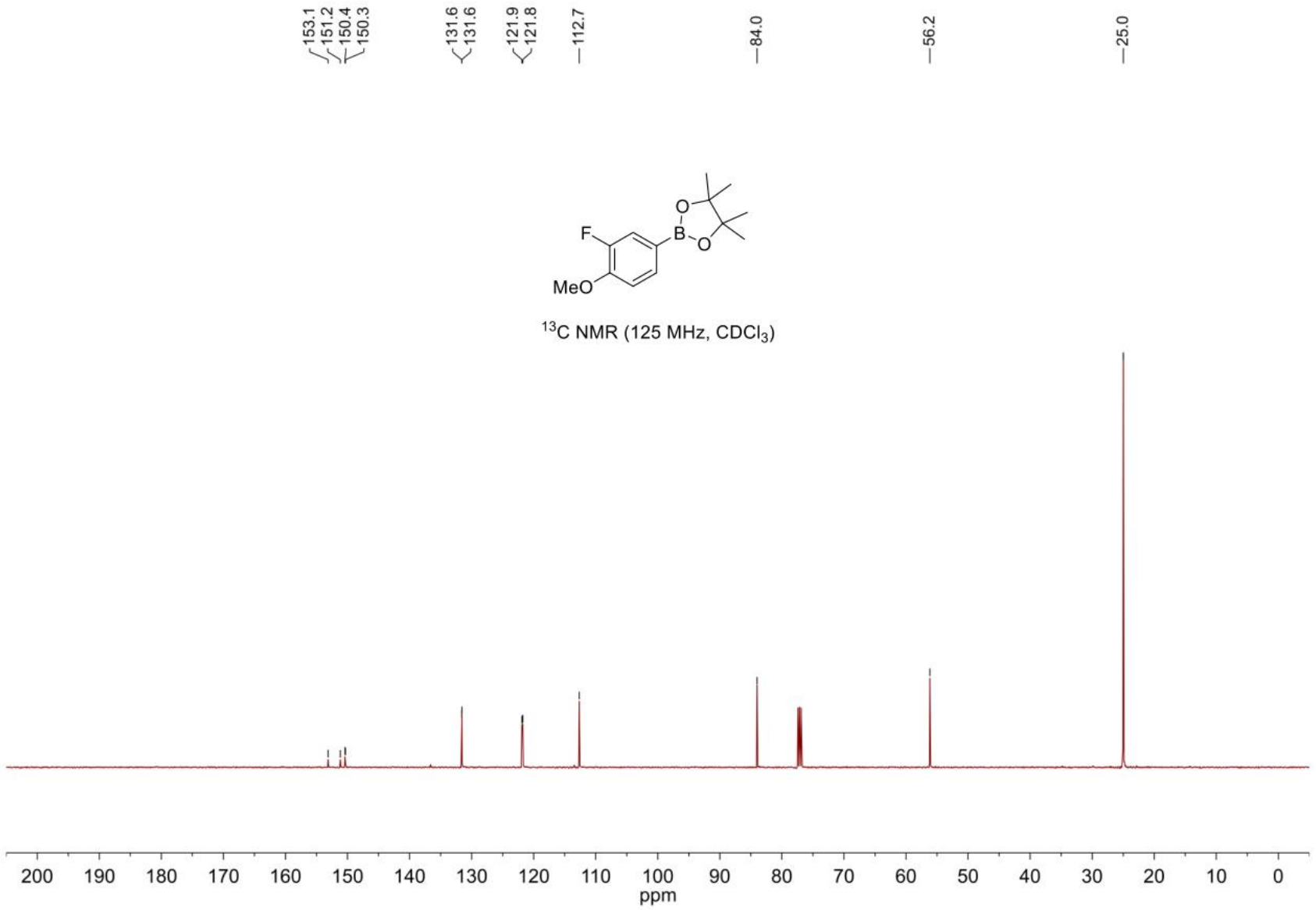
2-(3-Fluoro-4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (56)



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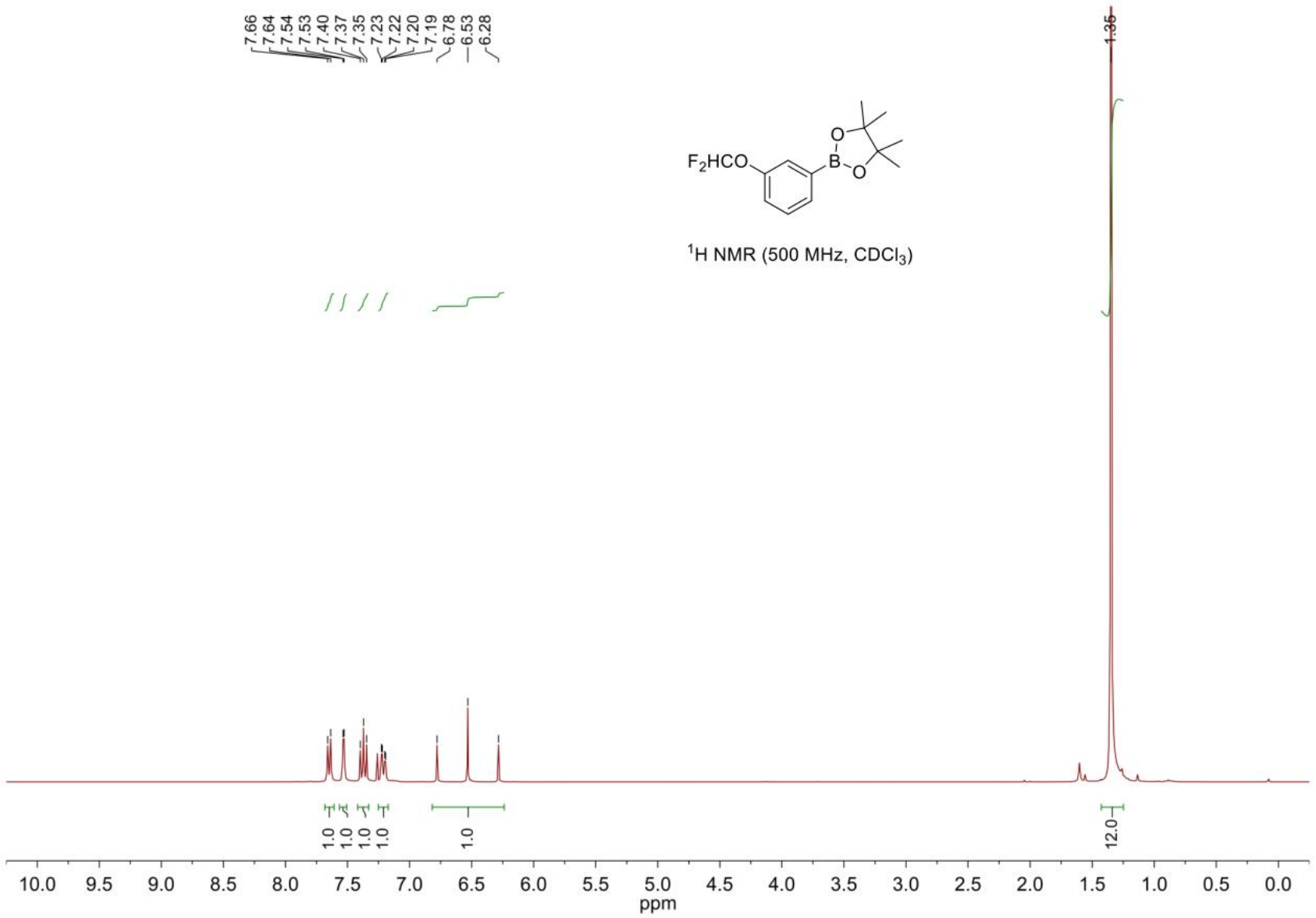
2-(3-(Difluoromethoxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (57)



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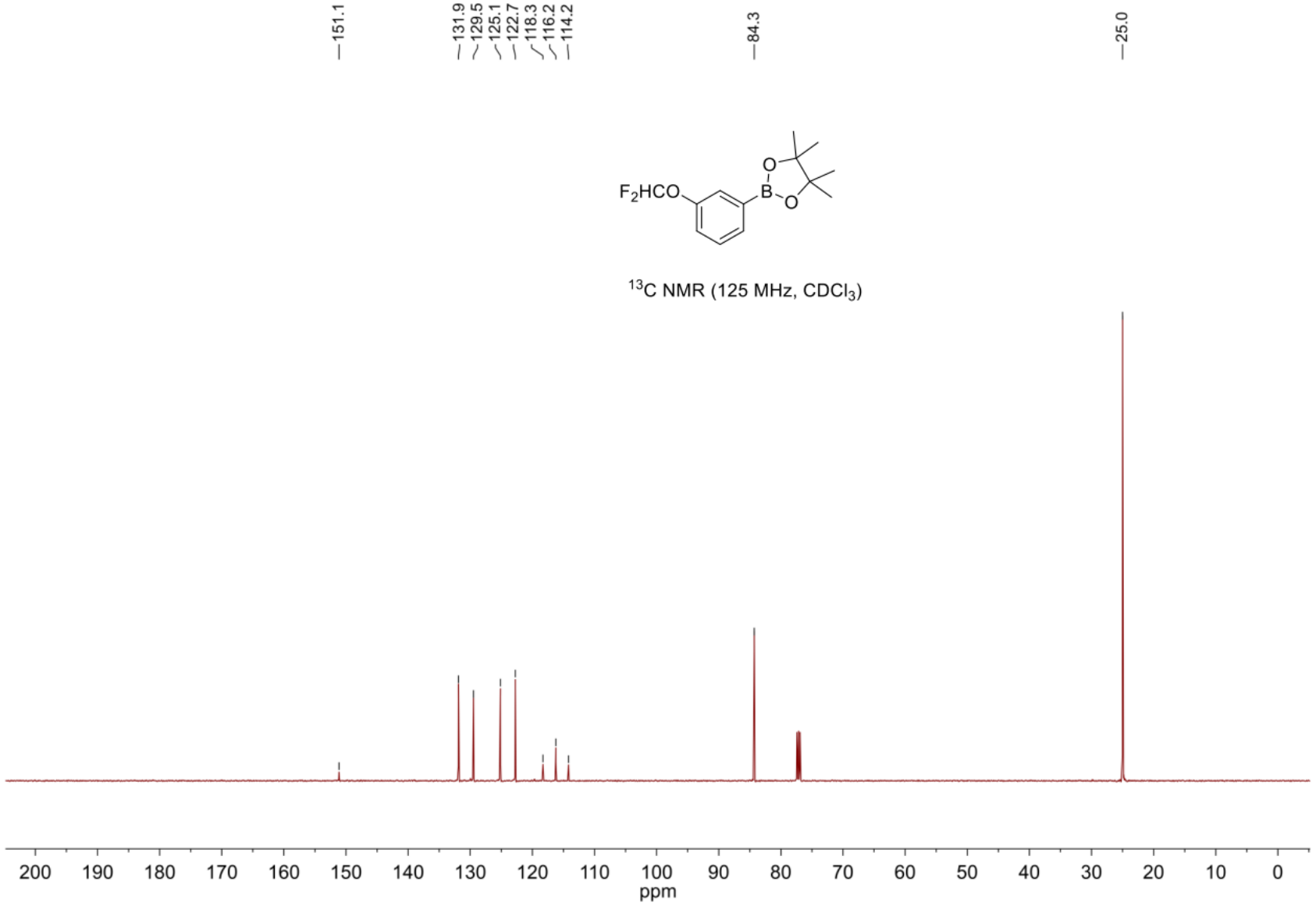
2-(3-(Difluoromethoxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (57)



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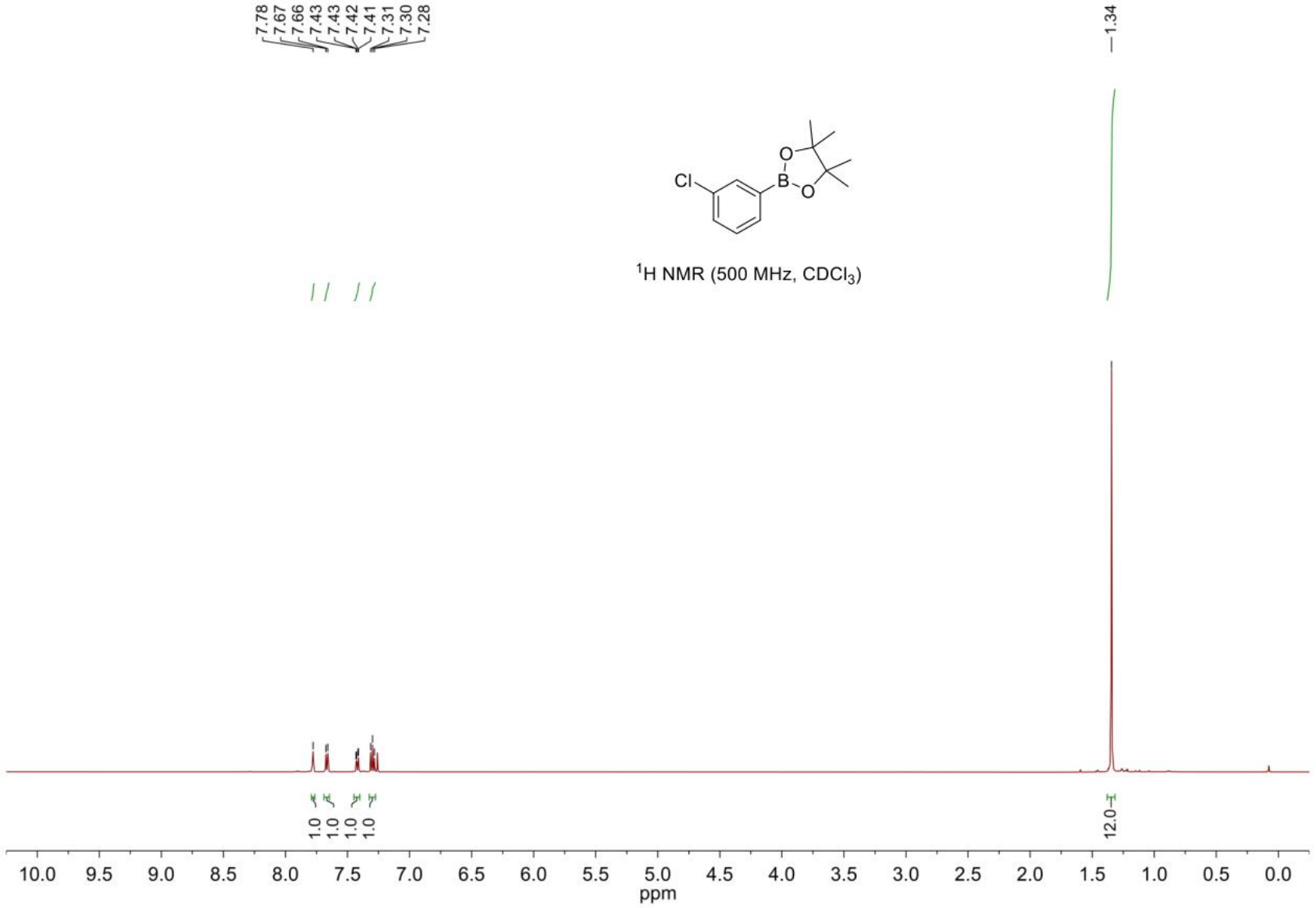
2-(3-Chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (58)



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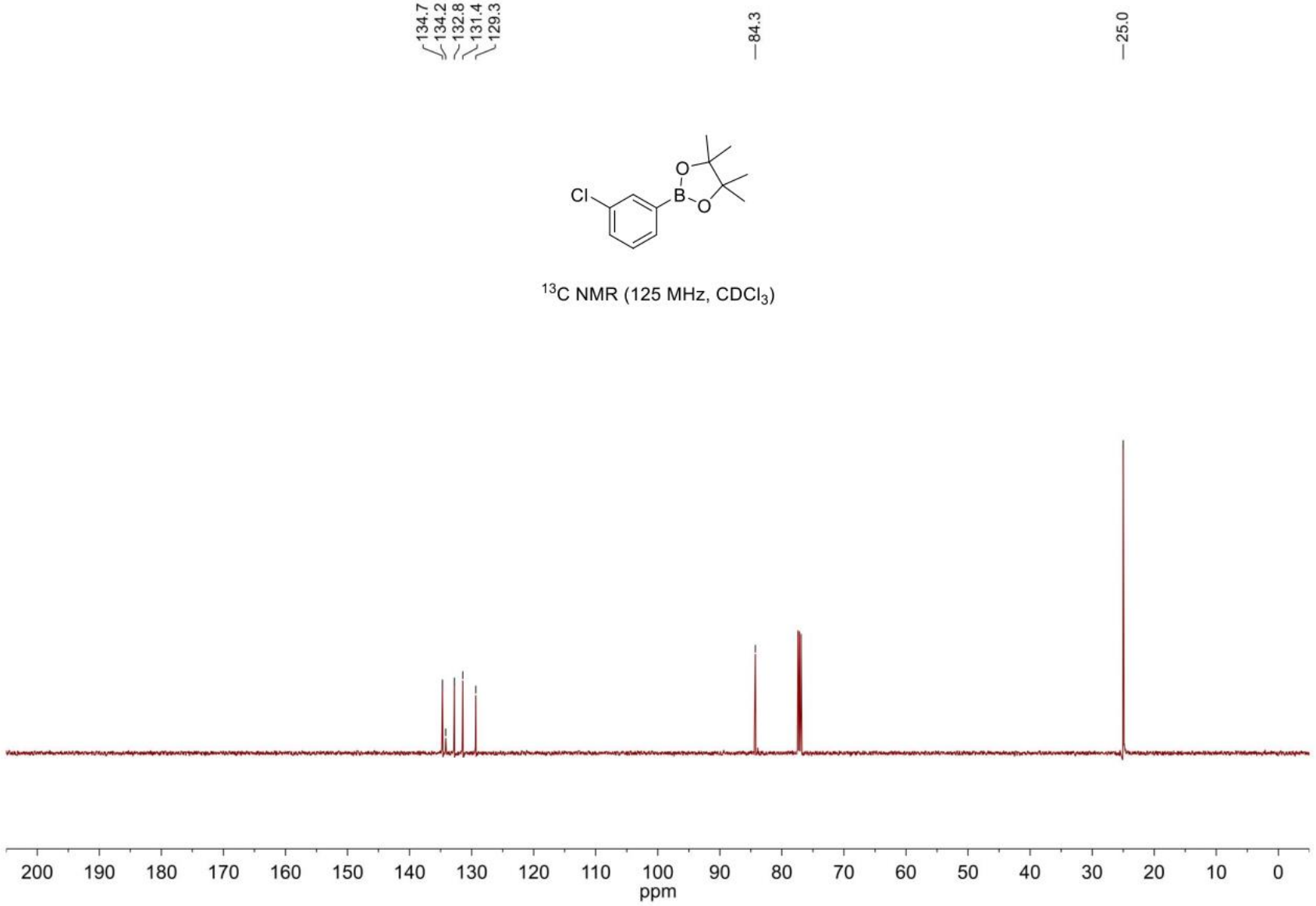
2-(3-Chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (58)



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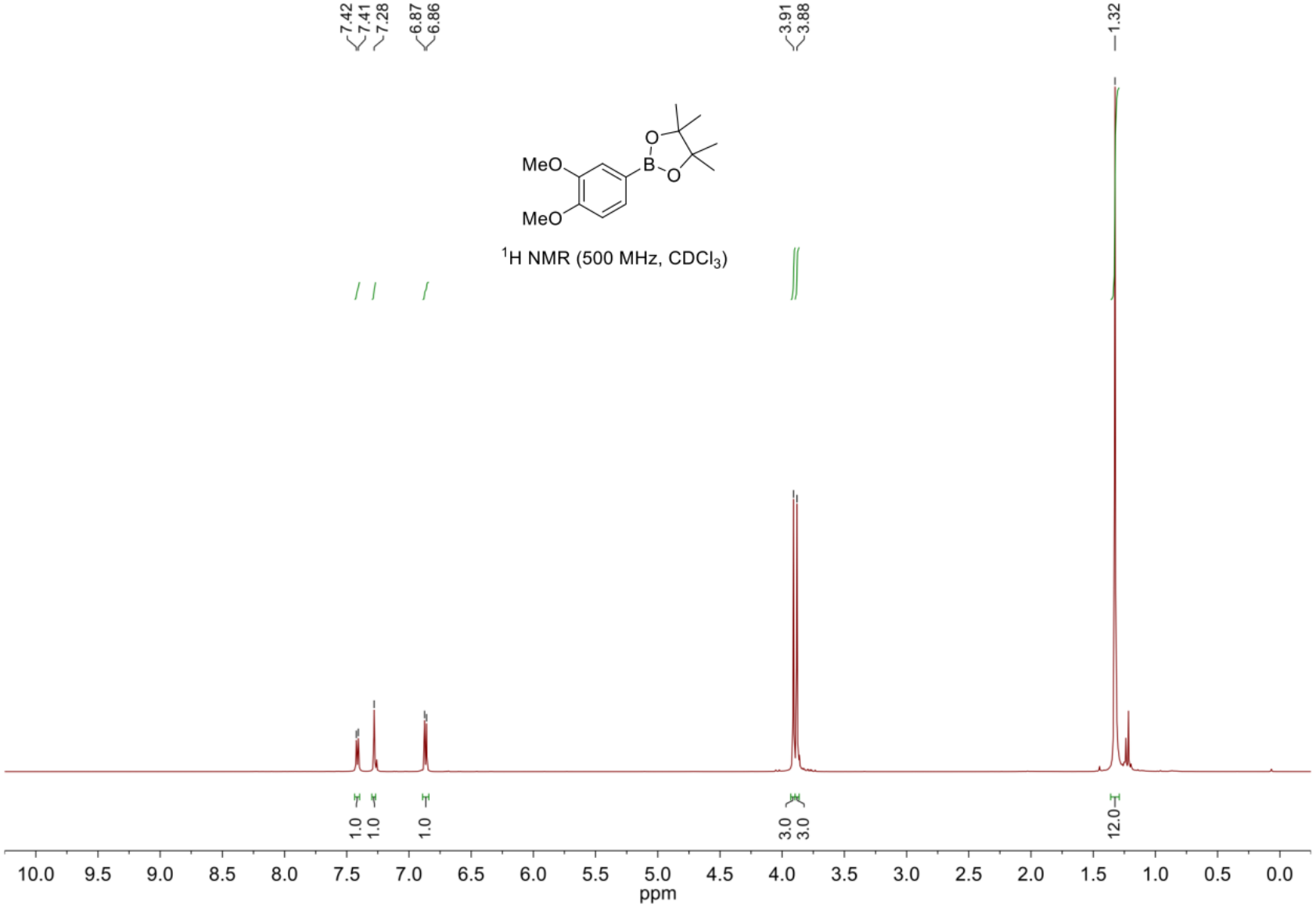
2-(3,4-Dimethoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (59)



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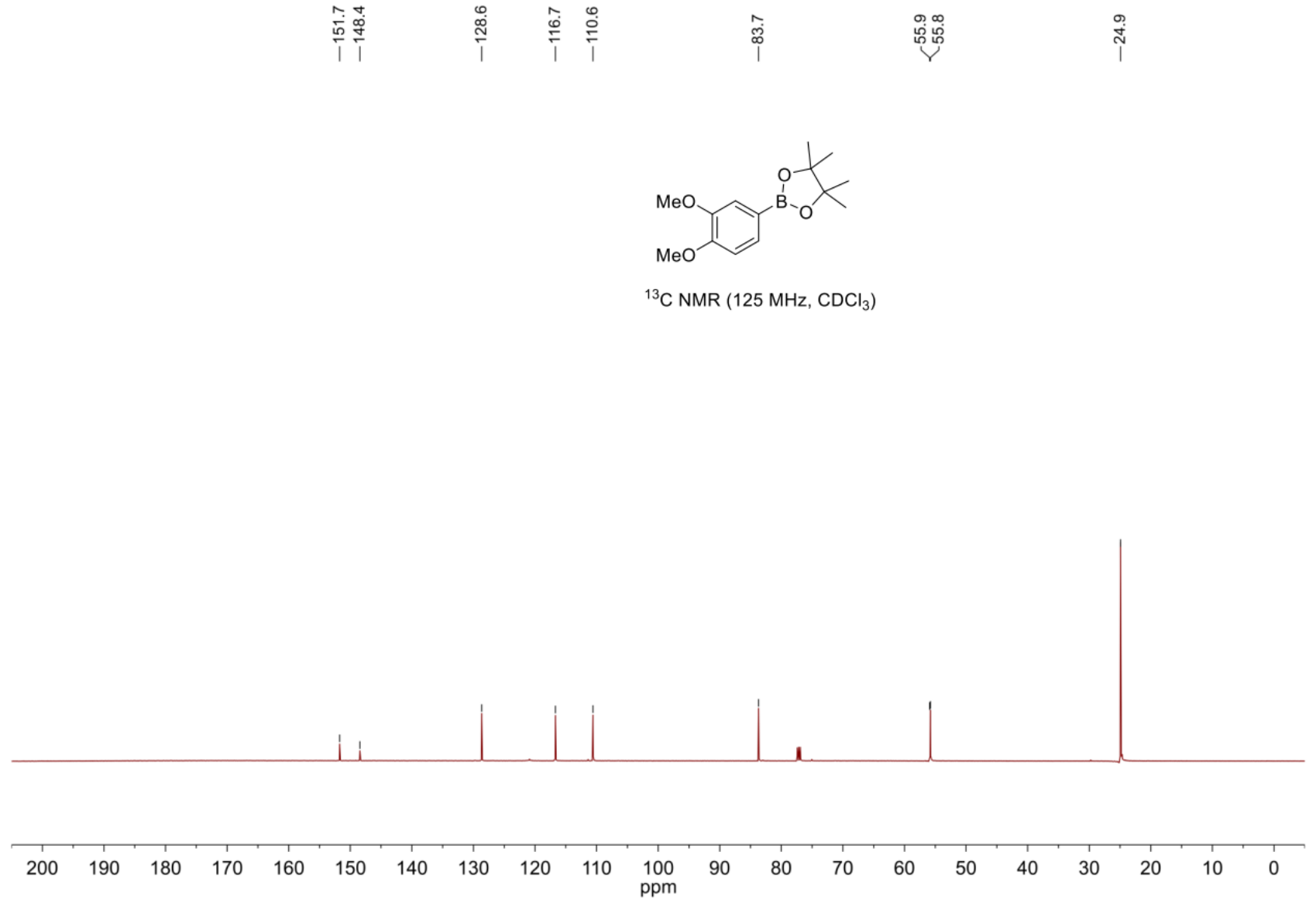
2-(3,4-Dimethoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (59)



^{13}C NMR (125 MHz, $CDCl_3$)

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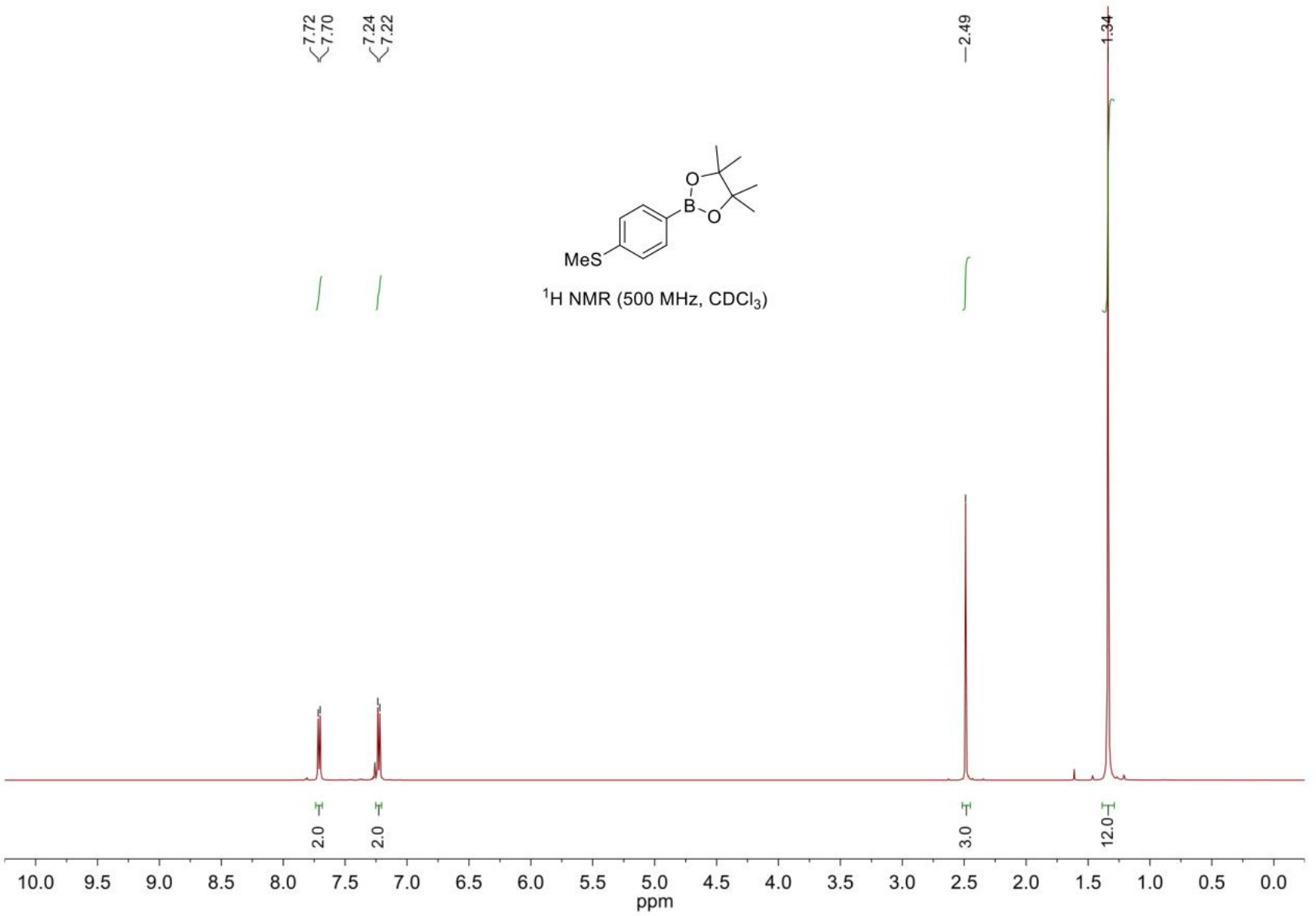
4,4,5,5-Tetramethyl-2-(4-(methylthio)phenyl)-1,3,2-dioxaborolane (60)



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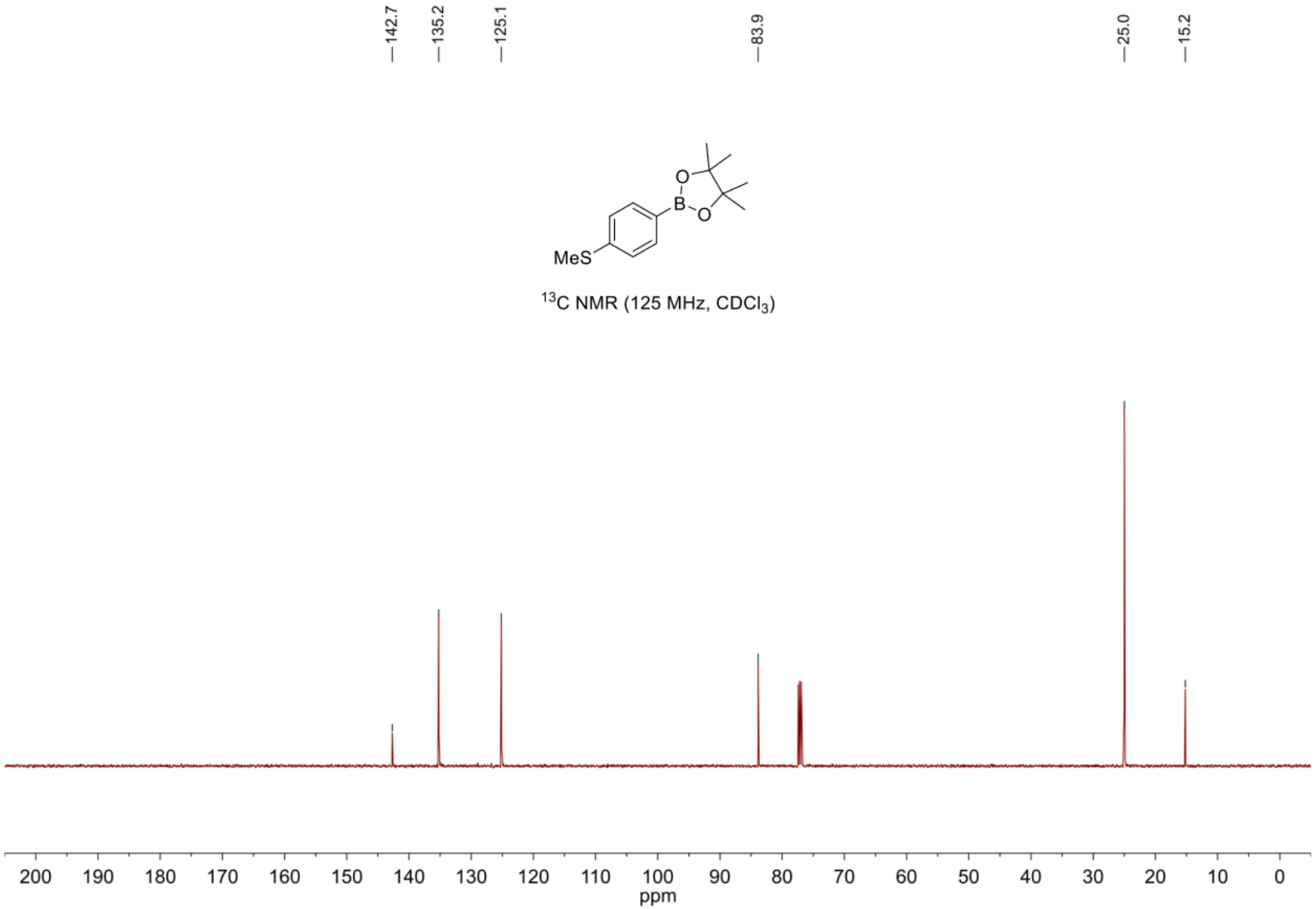
4,4,5,5-Tetramethyl-2-(4-(methylthio)phenyl)-1,3,2-dioxaborolane (60)



^{13}C NMR (125 MHz, $CDCl_3$)

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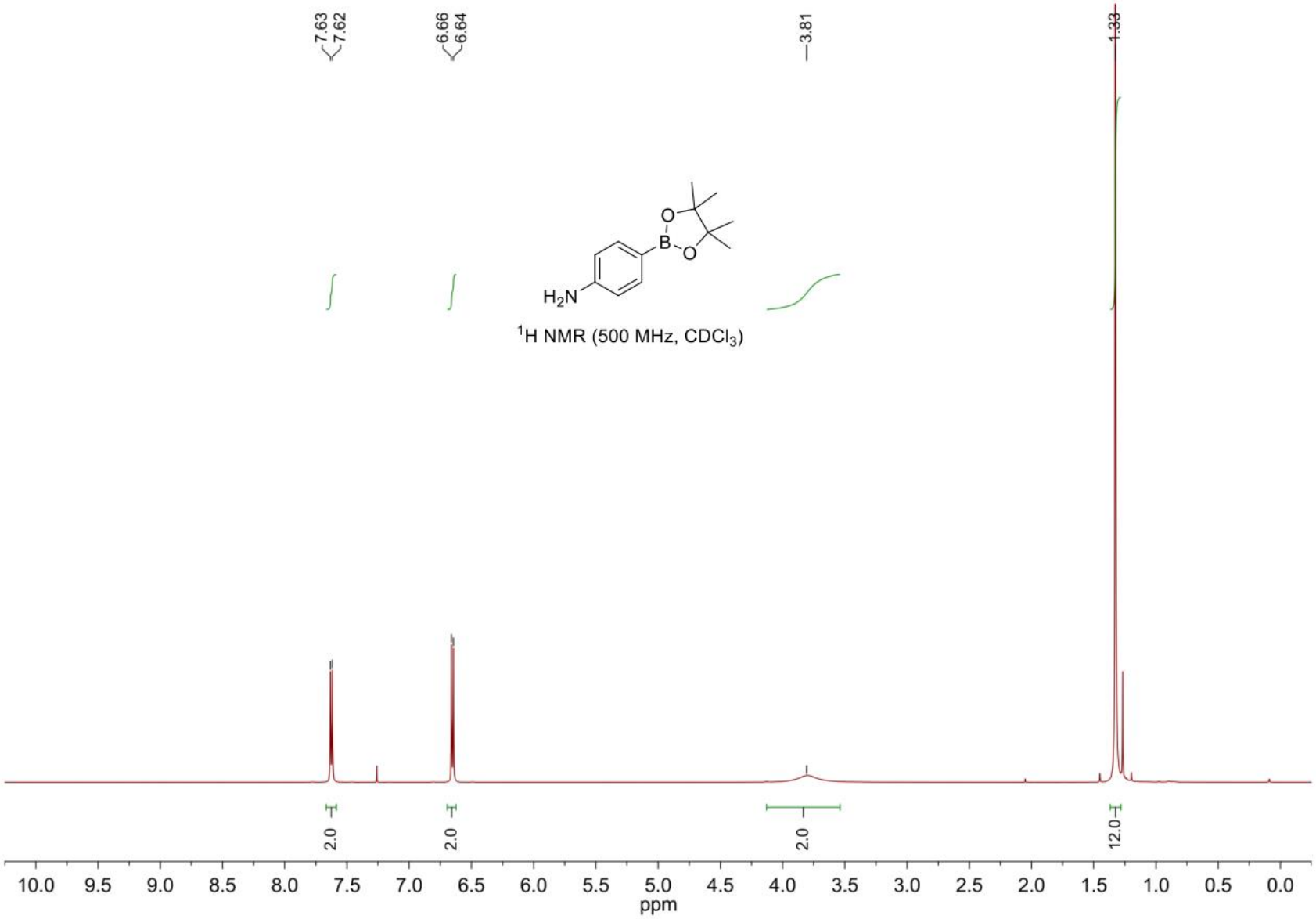
4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (61)



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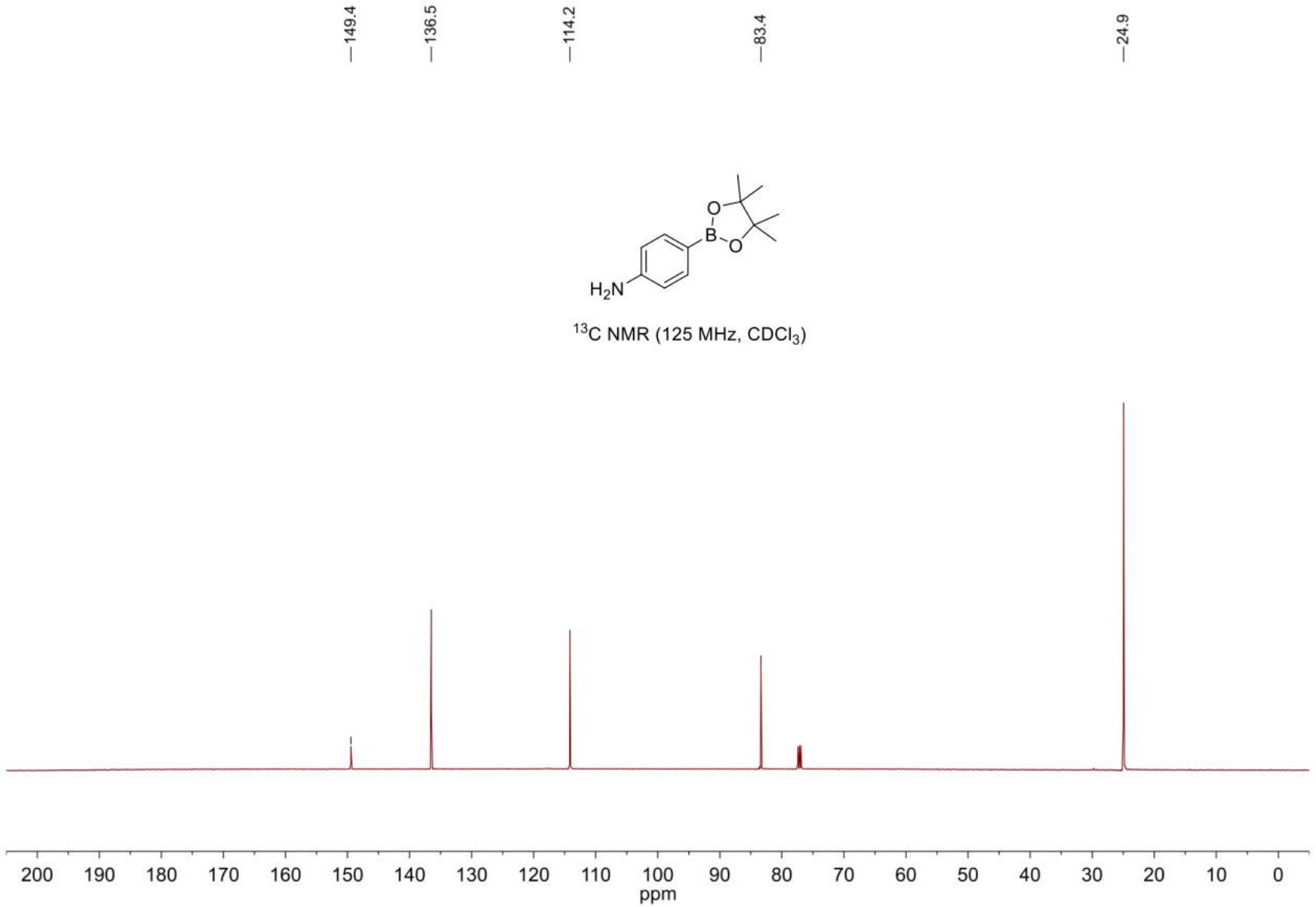
4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (61)



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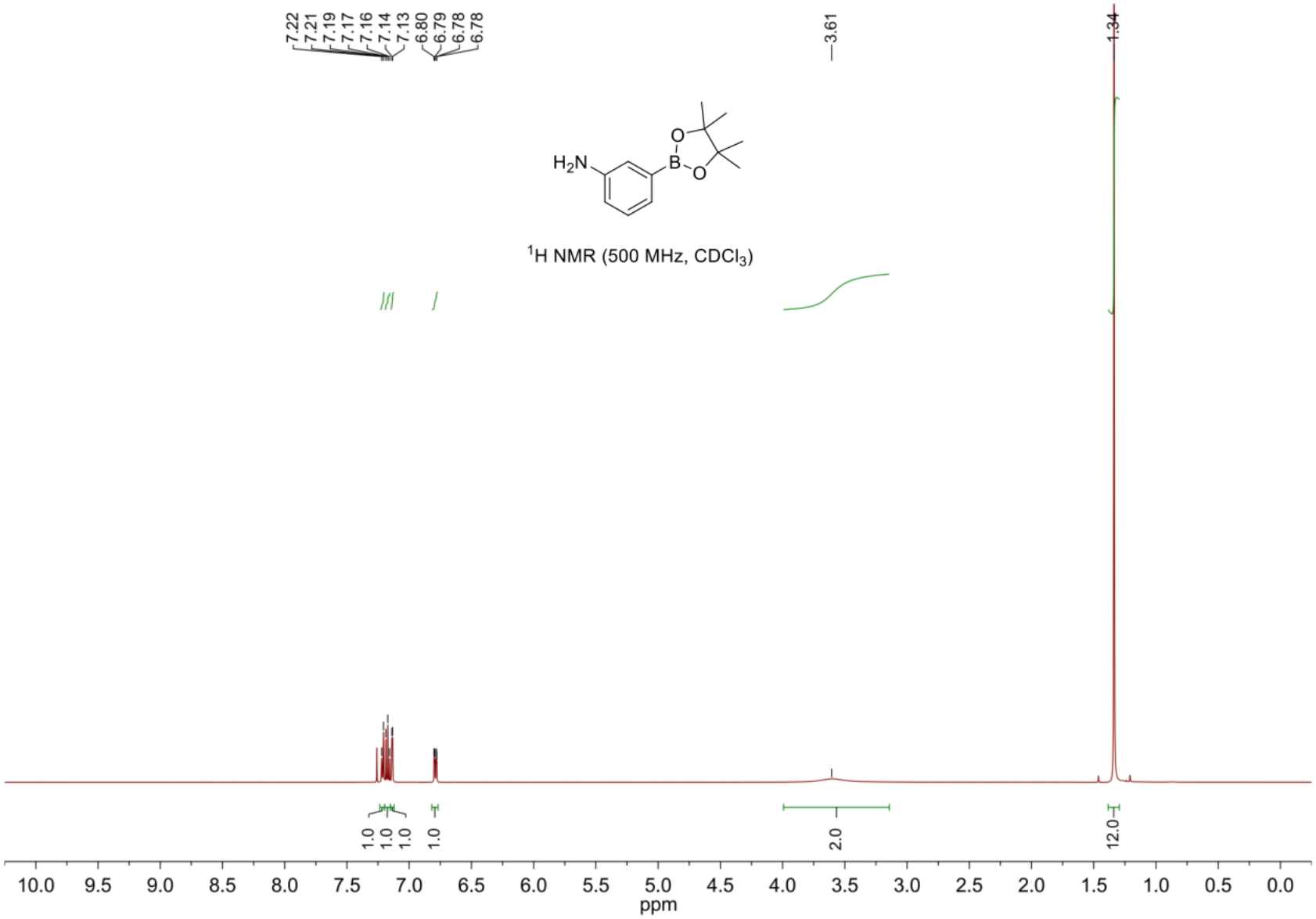
3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (62)



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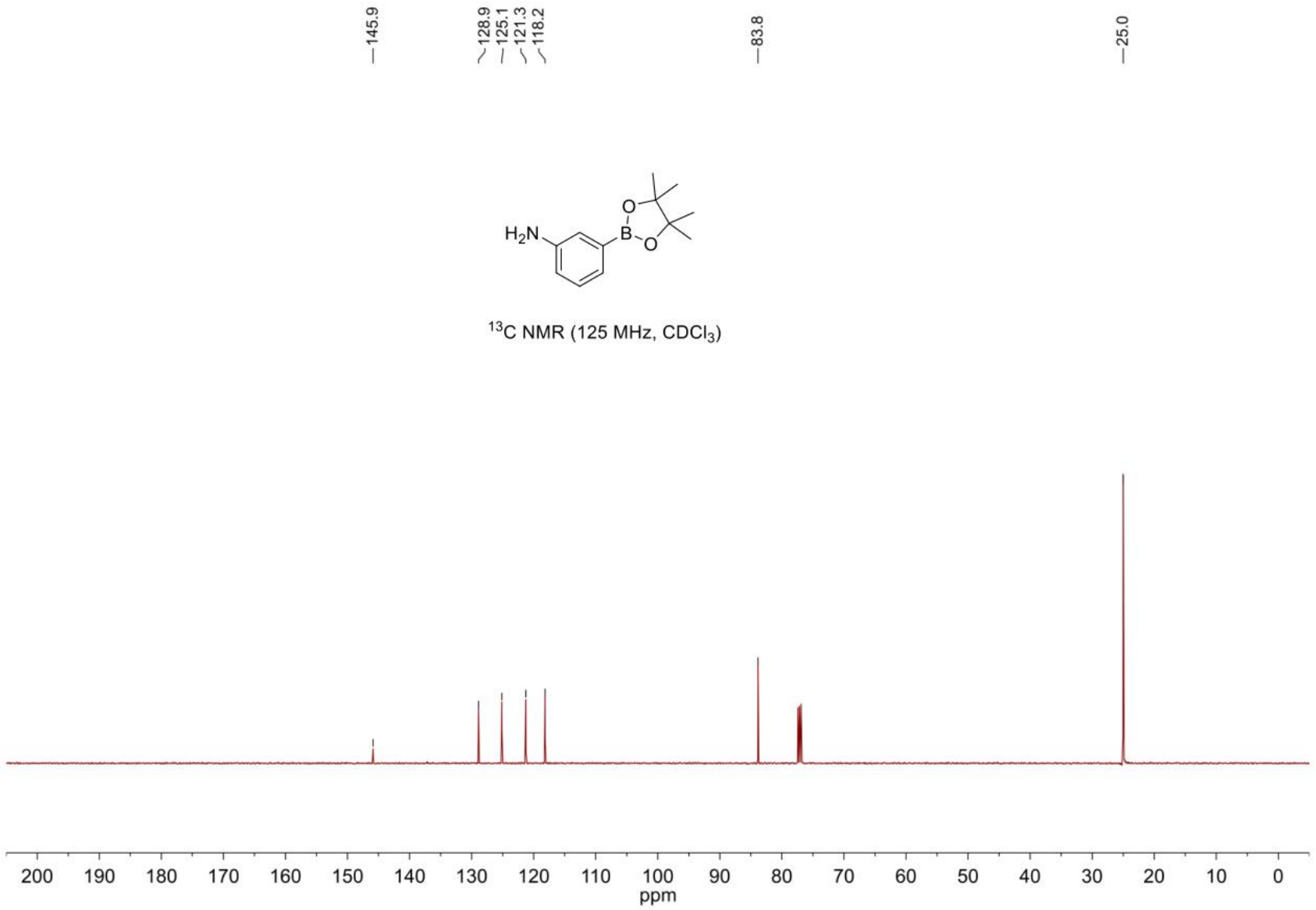
3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (62)



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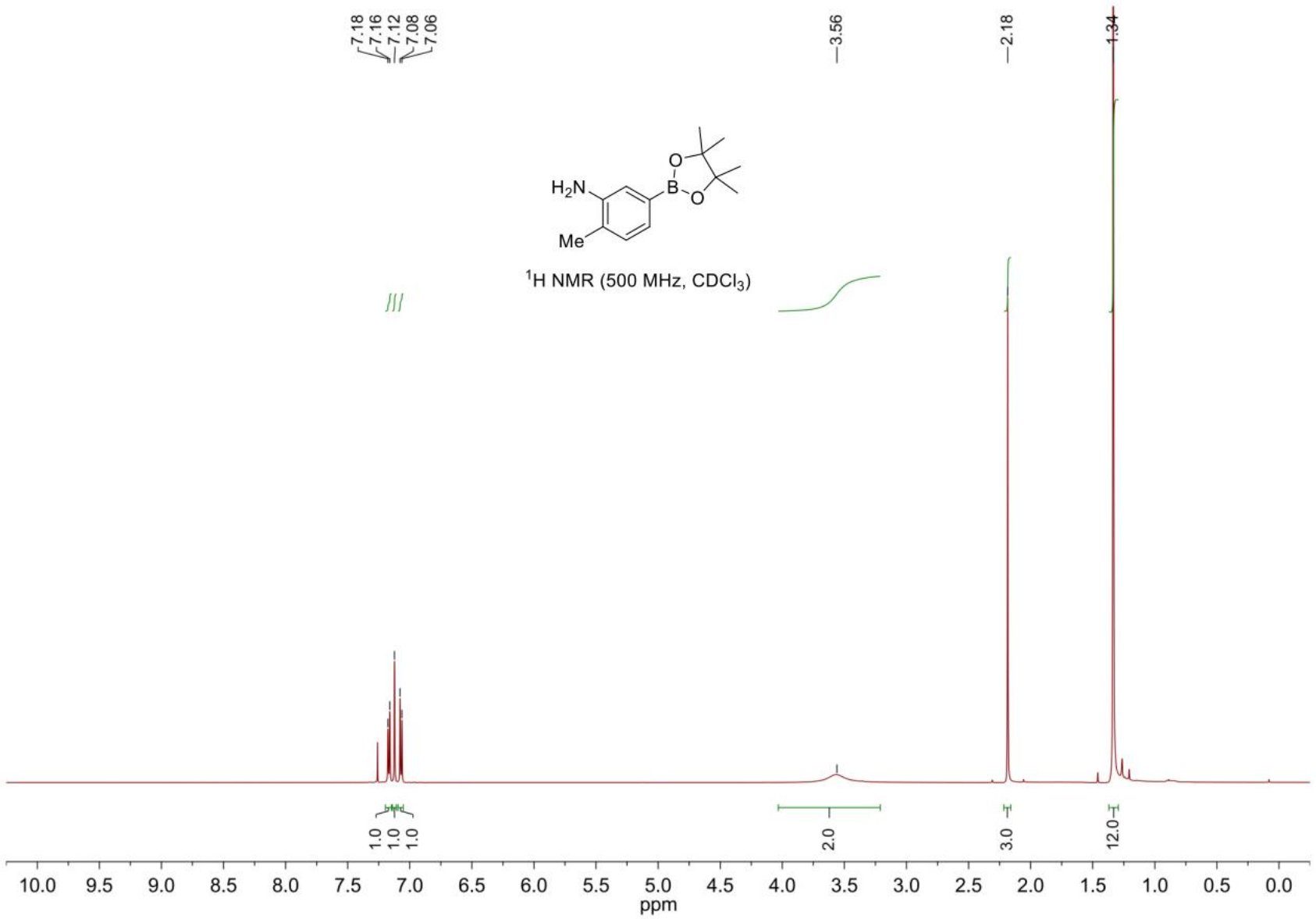
2-Methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (63)



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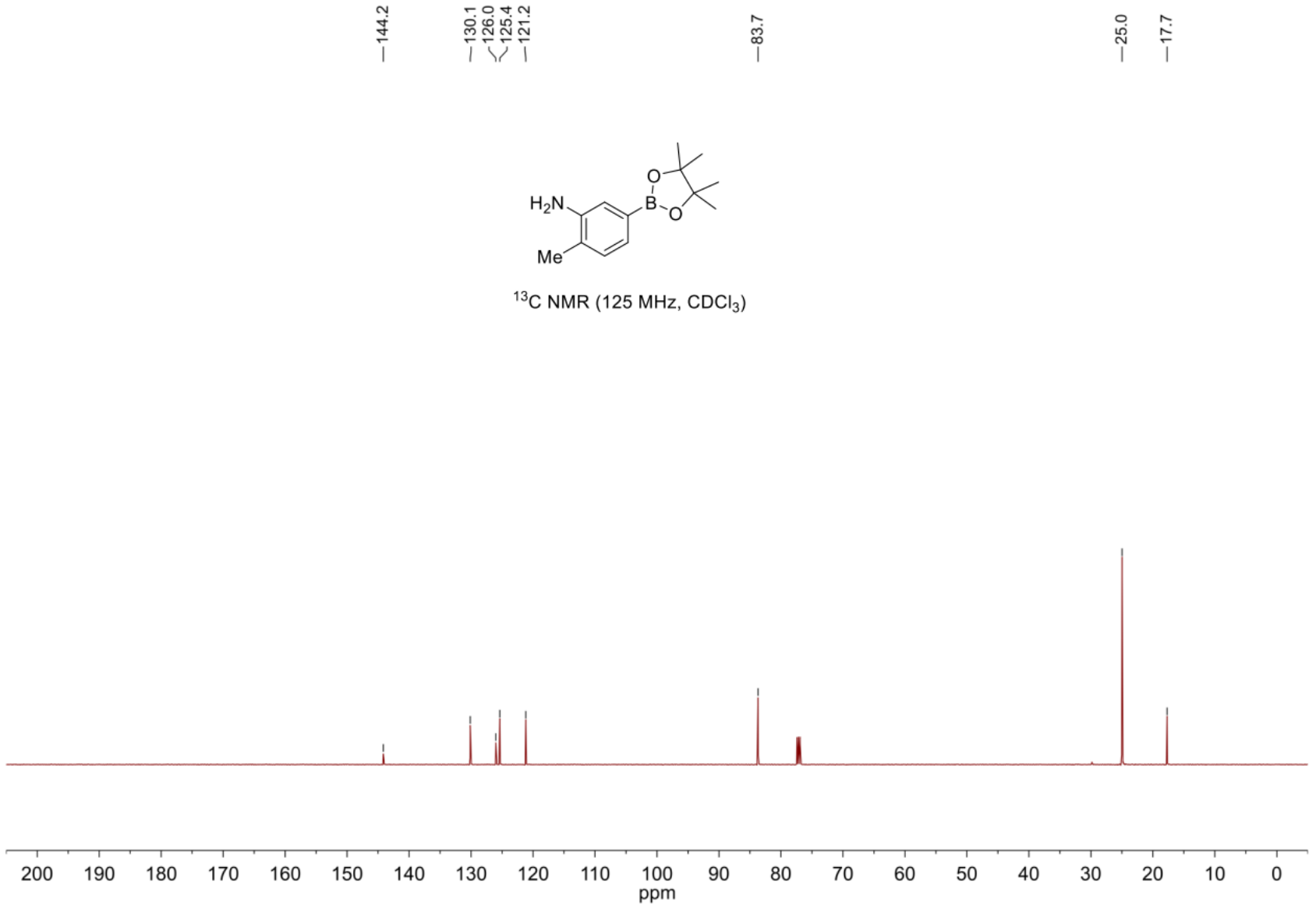
2-Methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (63)



^{13}C NMR (125 MHz, $CDCl_3$)

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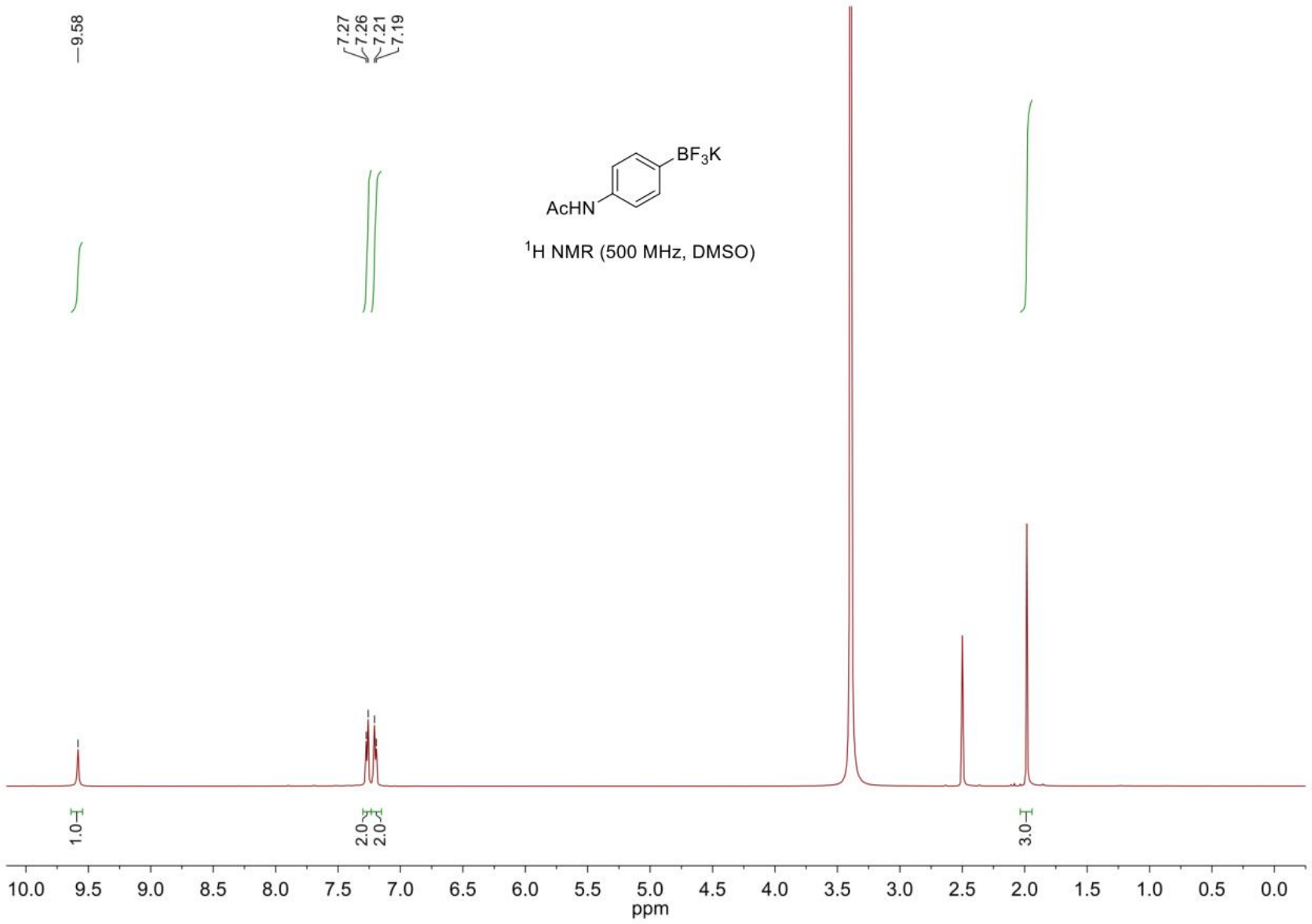
_N_-(4-(trifluoro-λ⁴-boraneyl)phenyl)acetamide, potassium salt (64)



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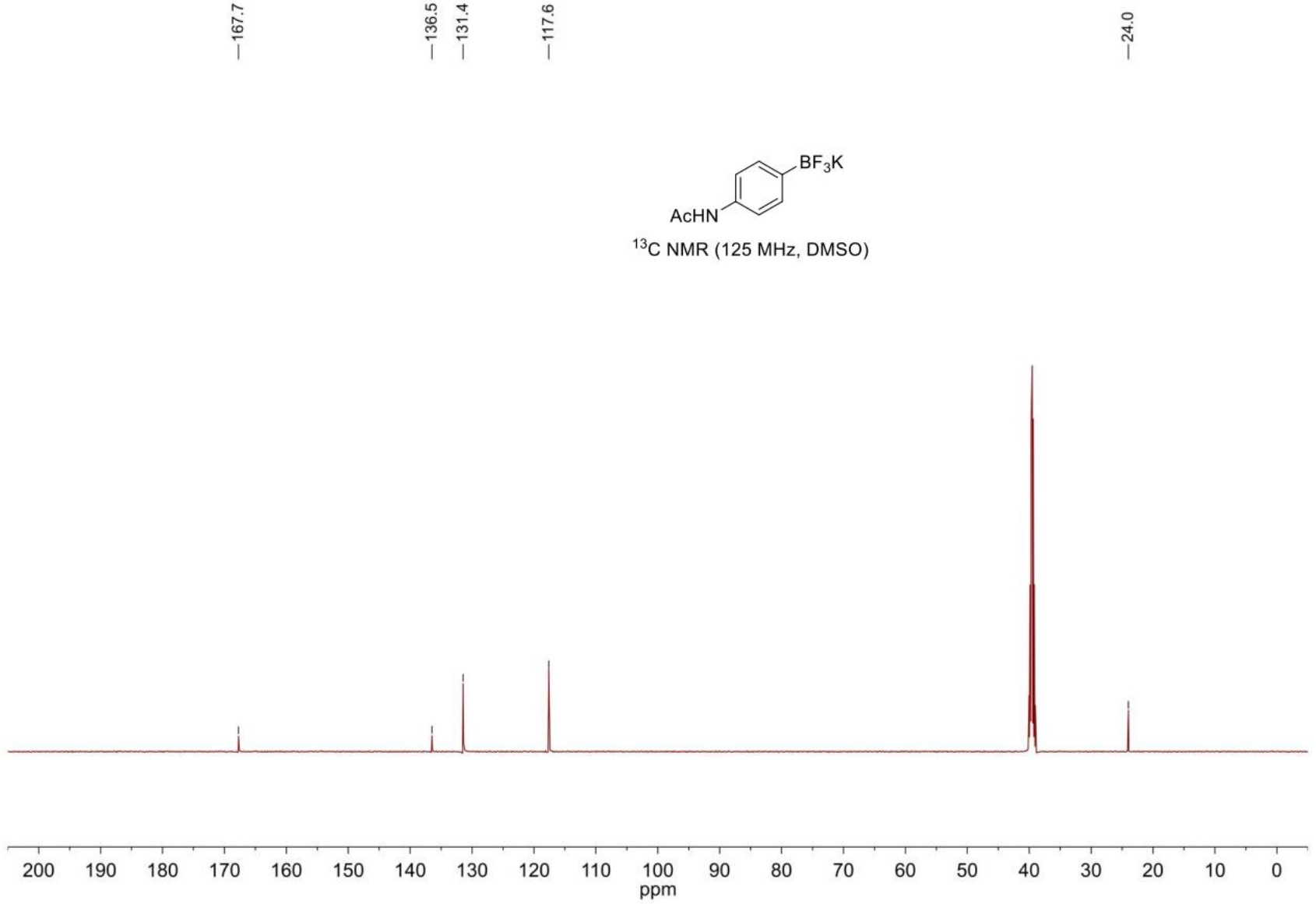
_N_-(4-(trifluoro-λ⁴-boraneyl)phenyl)acetamide, potassium salt (64)



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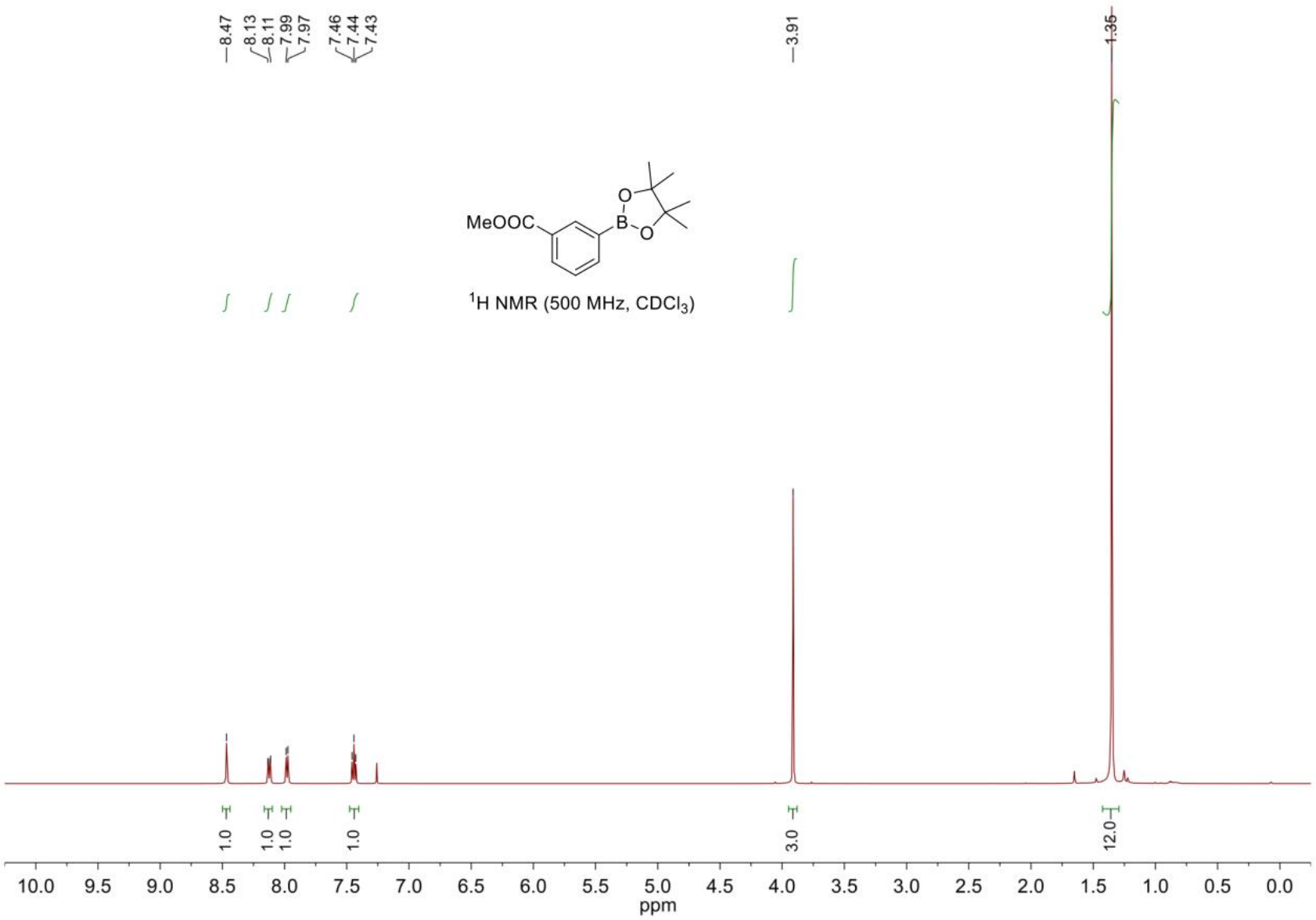
Methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (65)



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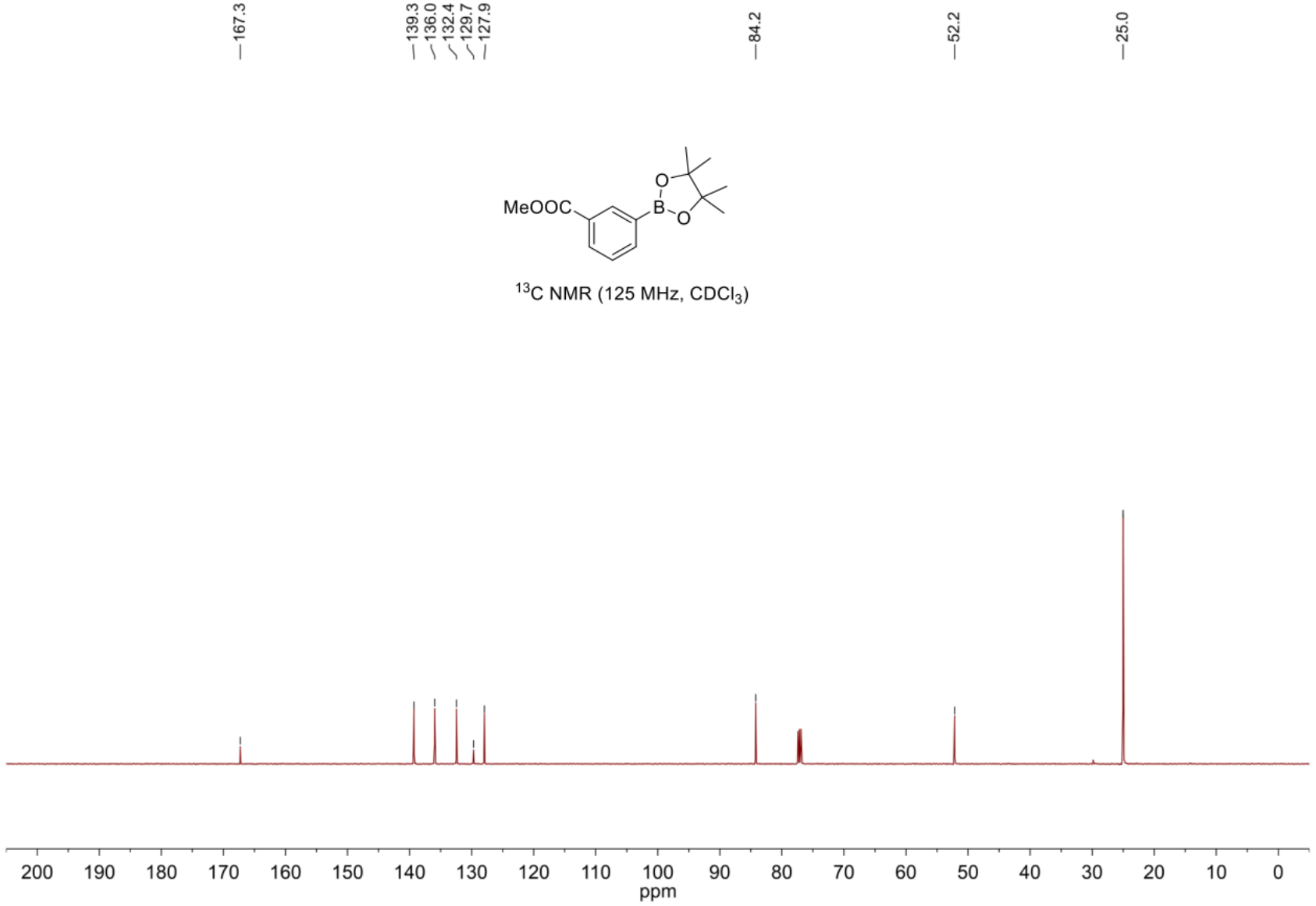
Methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (65)



^{13}C NMR (125 MHz, $CDCl_3$)

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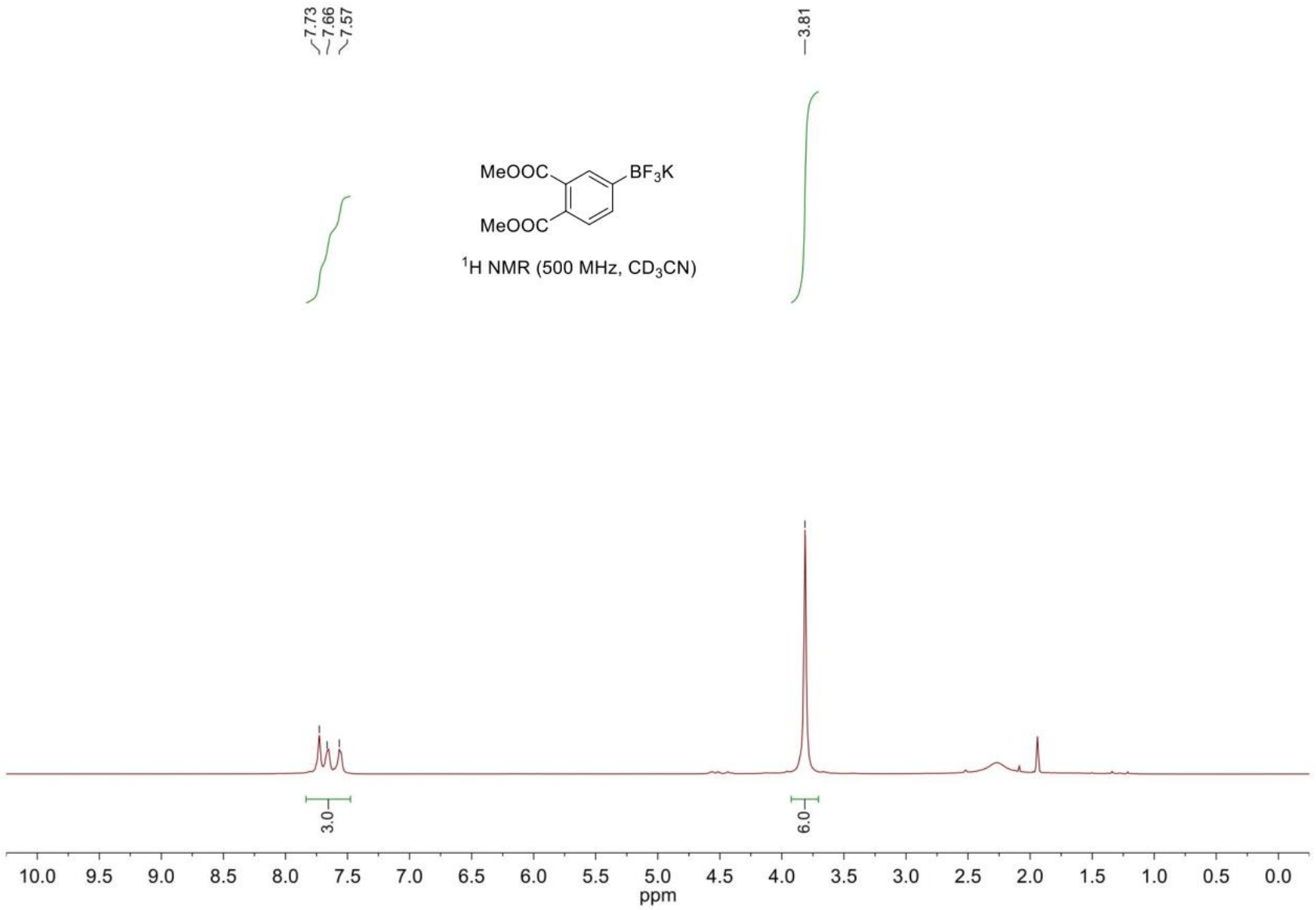
Dimethyl 4-(trifluoro-l4-boraneyl)phthalate, potassium salt (66)



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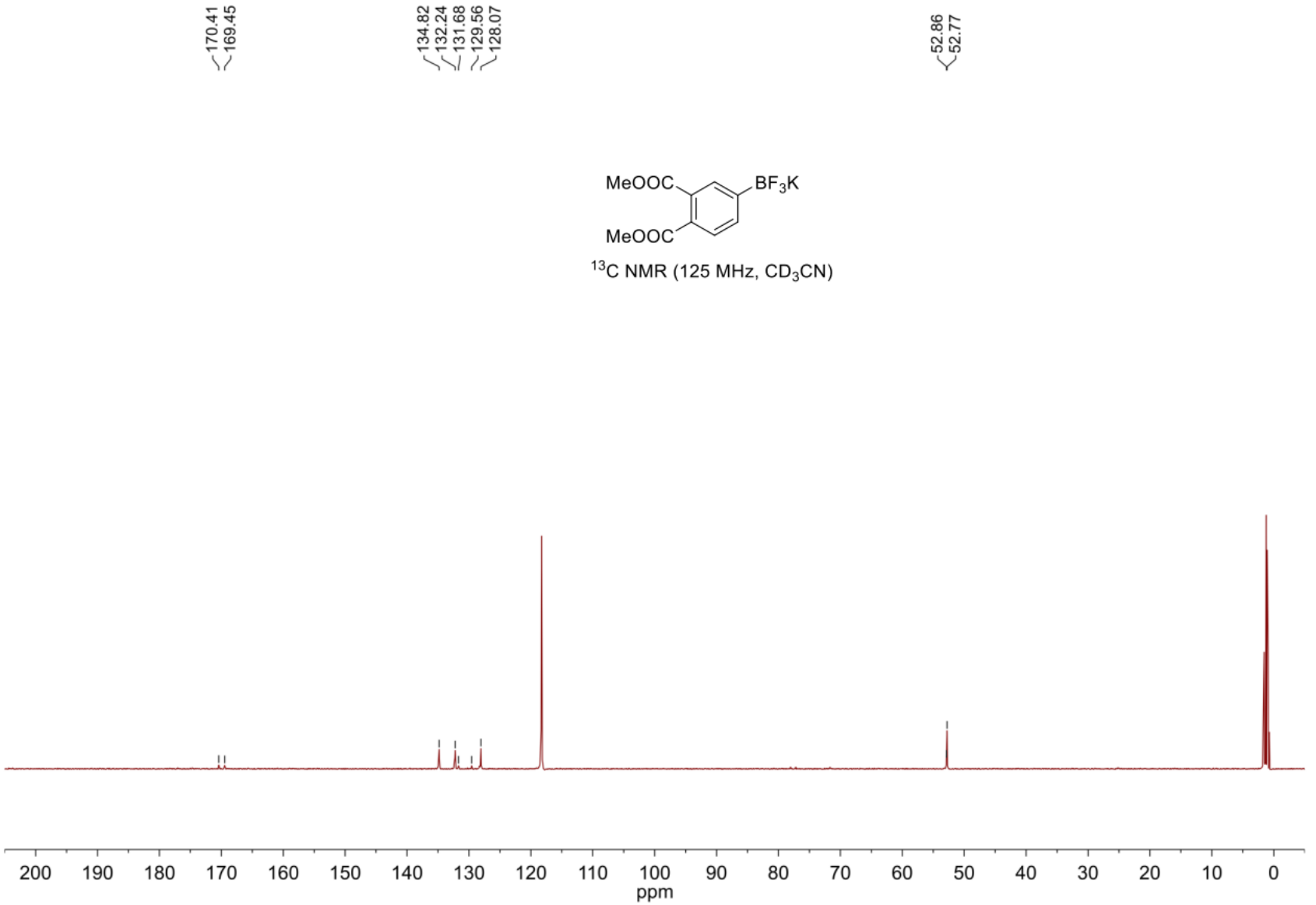
Dimethyl 4-(trifluoro-l4-boraneyl)phthalate, potassium salt (66)



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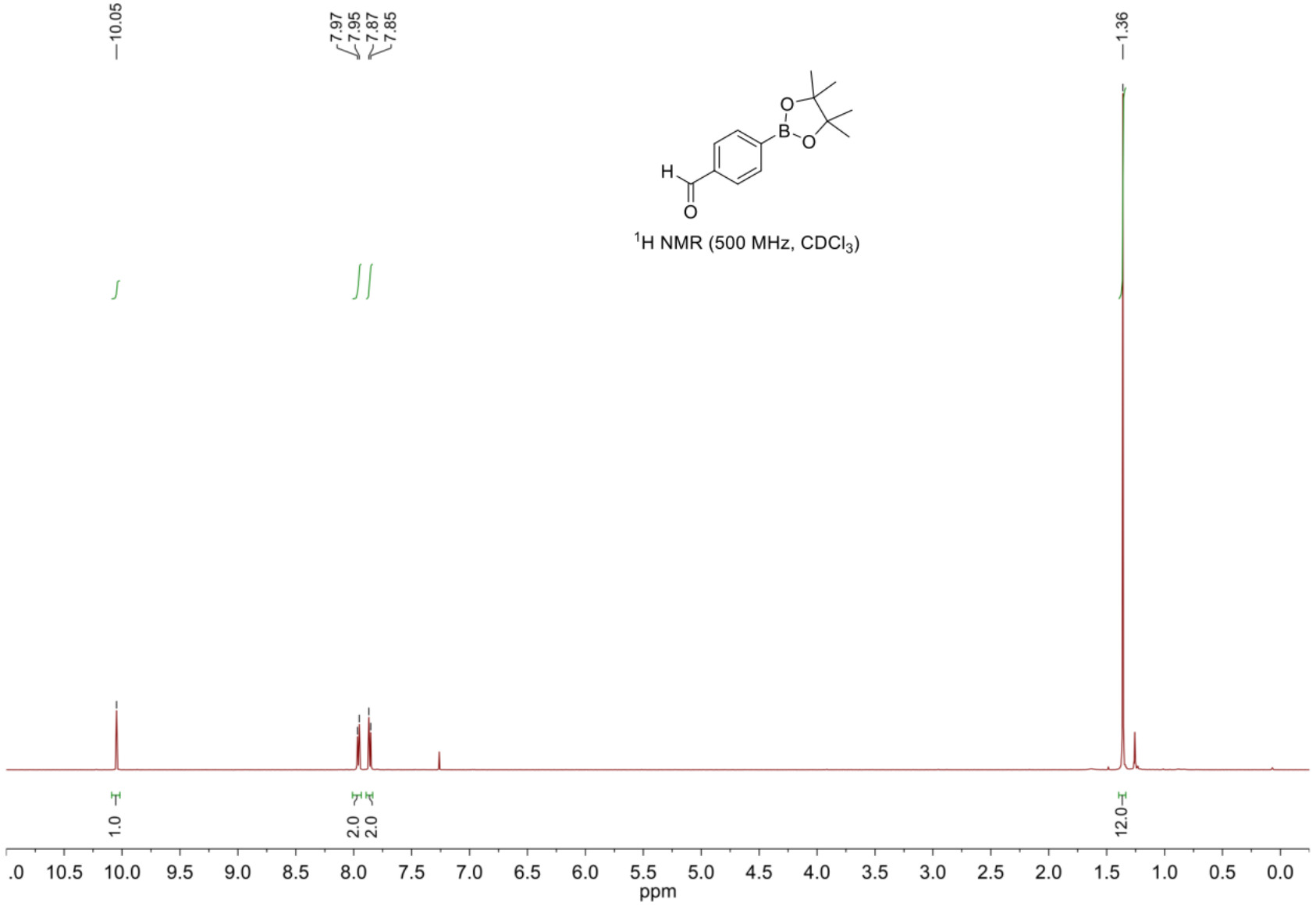
4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (67)



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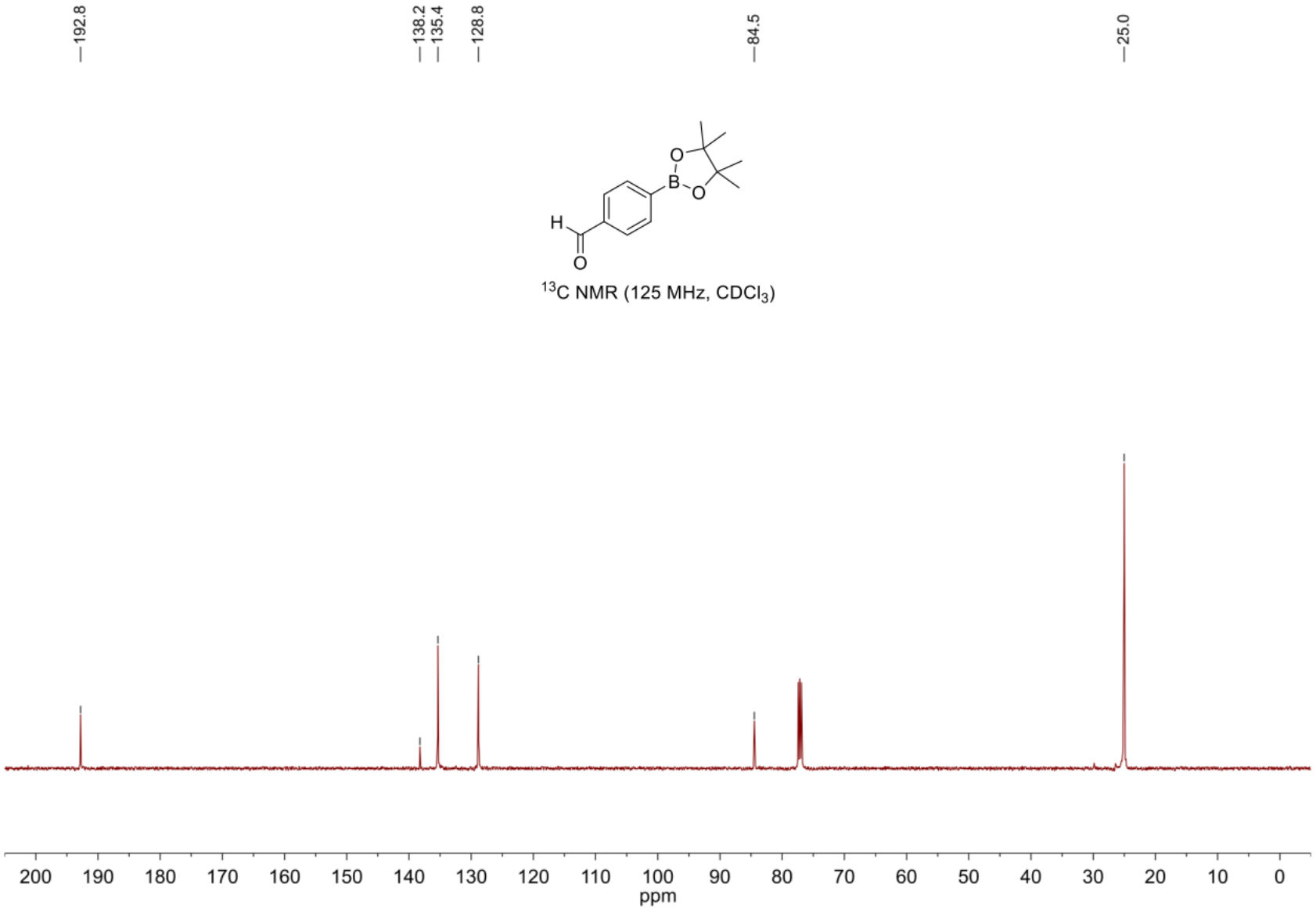
4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (67)



^{13}C NMR (125 MHz, $CDCl_3$)

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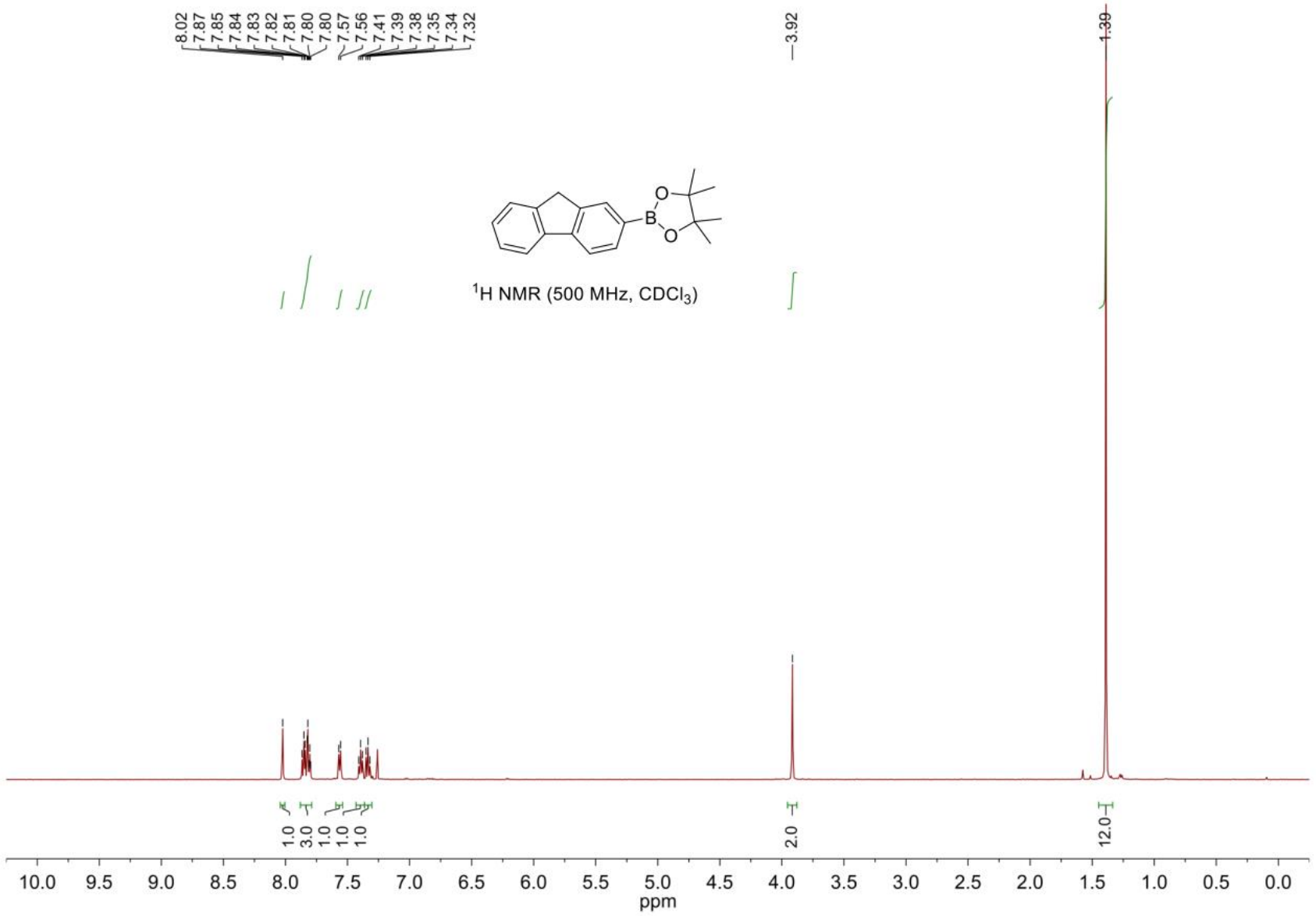
2-(9*H*-Fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (68)



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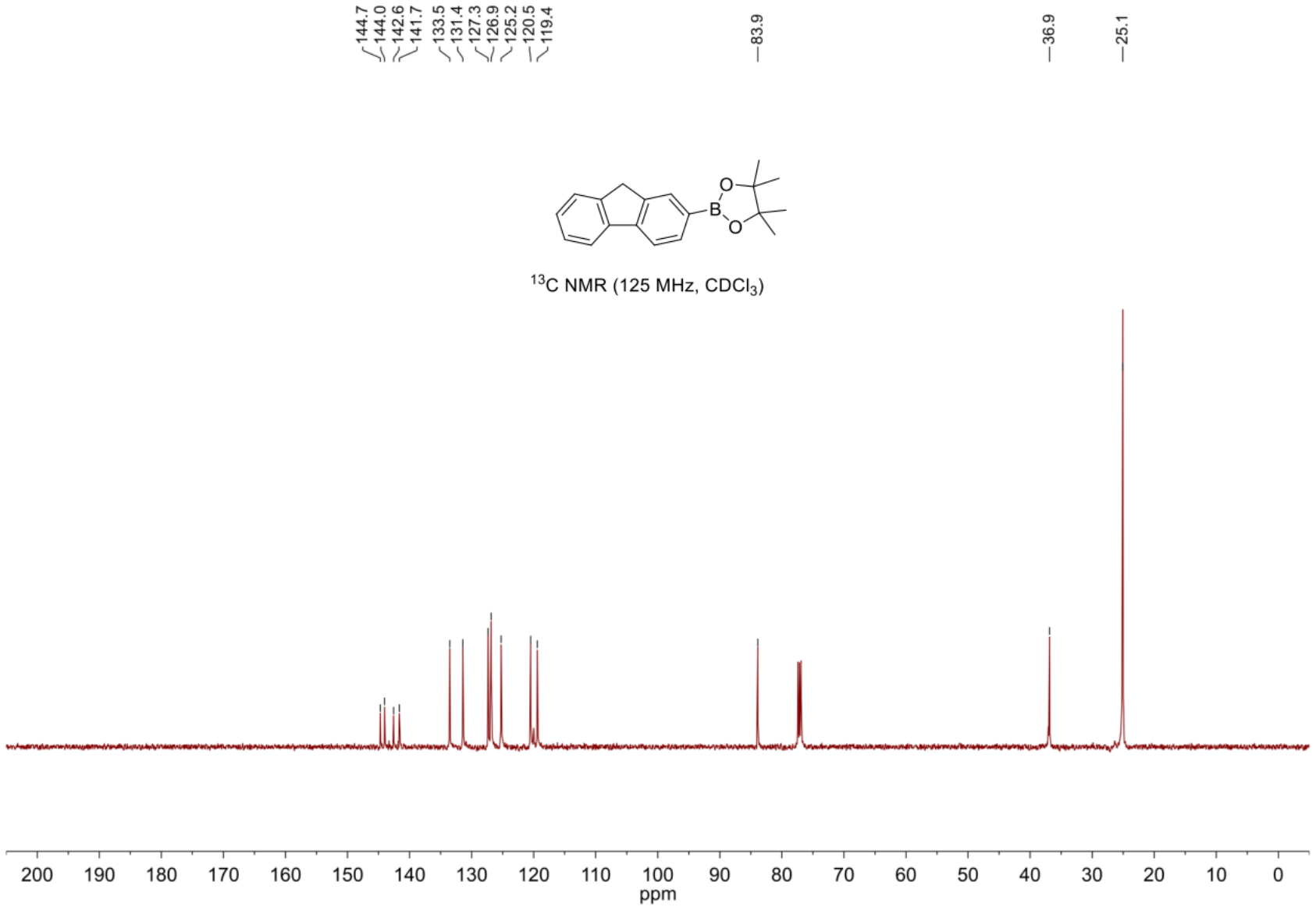
2-(9*H*-Fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (68)



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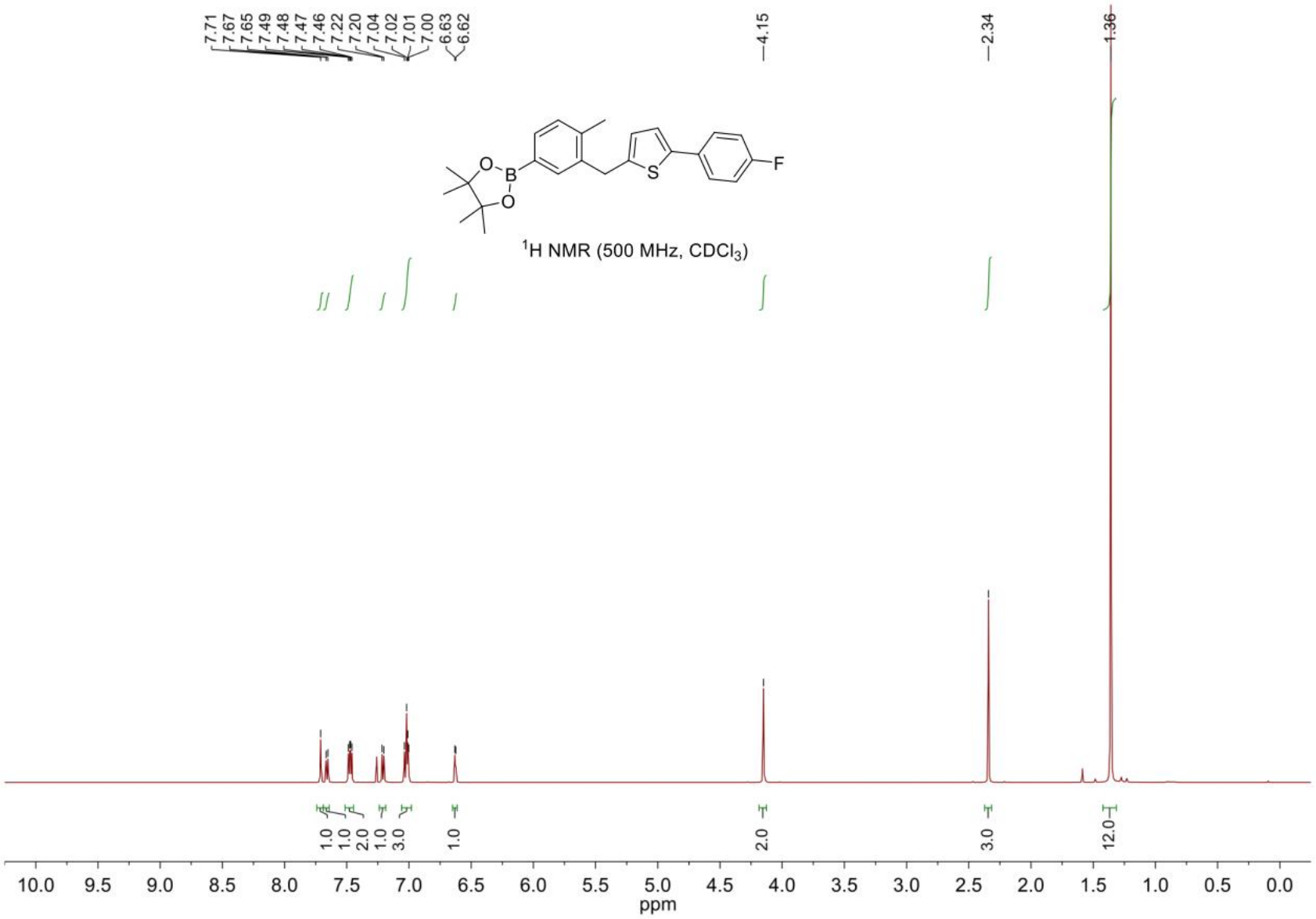
2-(3-((5-(4-Fluorophenyl)thiophen-2-yl)methyl)-4-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (69)



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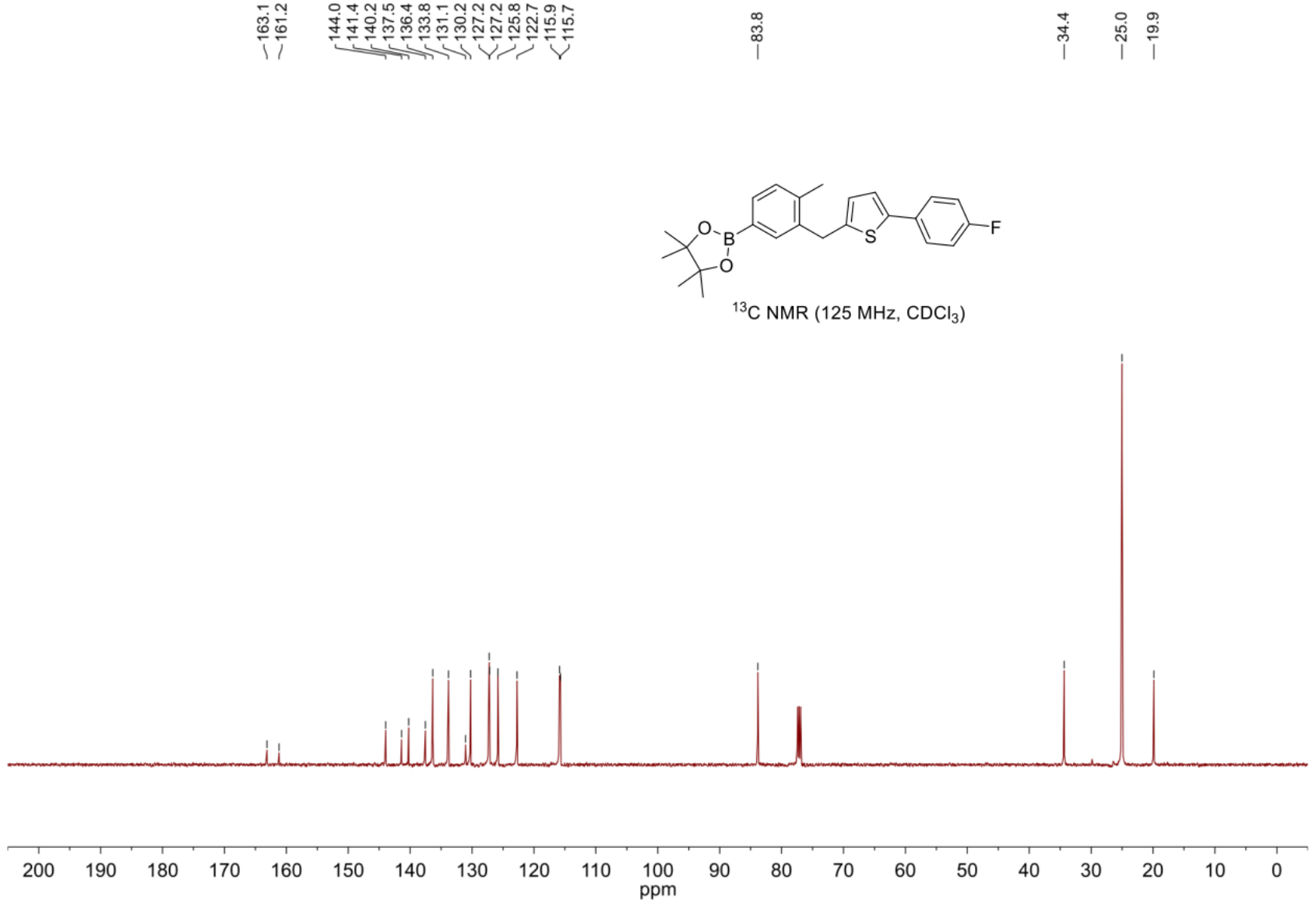
2-(3-((5-(4-Fluorophenyl)thiophen-2-yl)methyl)-4-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (69)



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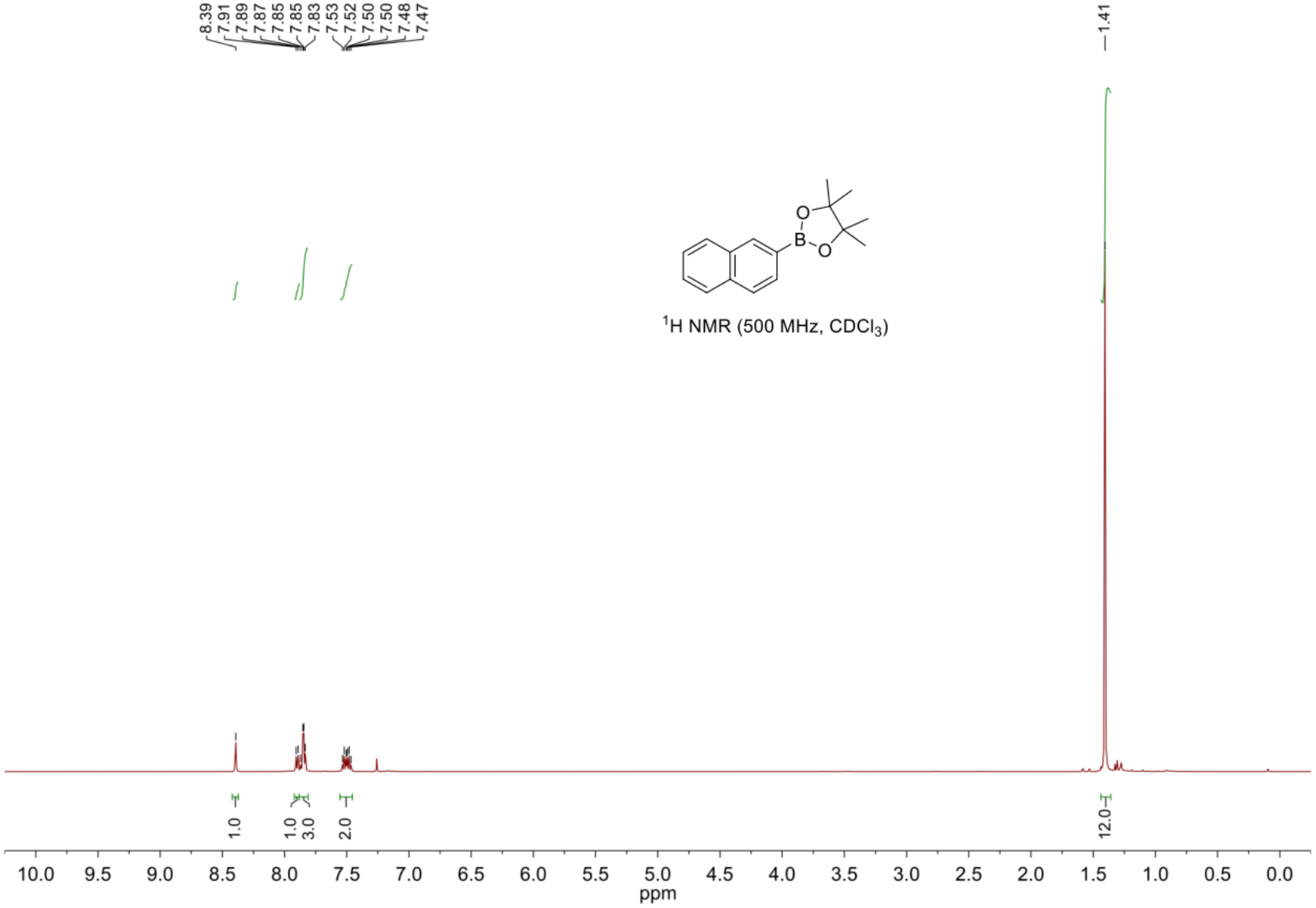
4,4,5,5-Tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane (70)



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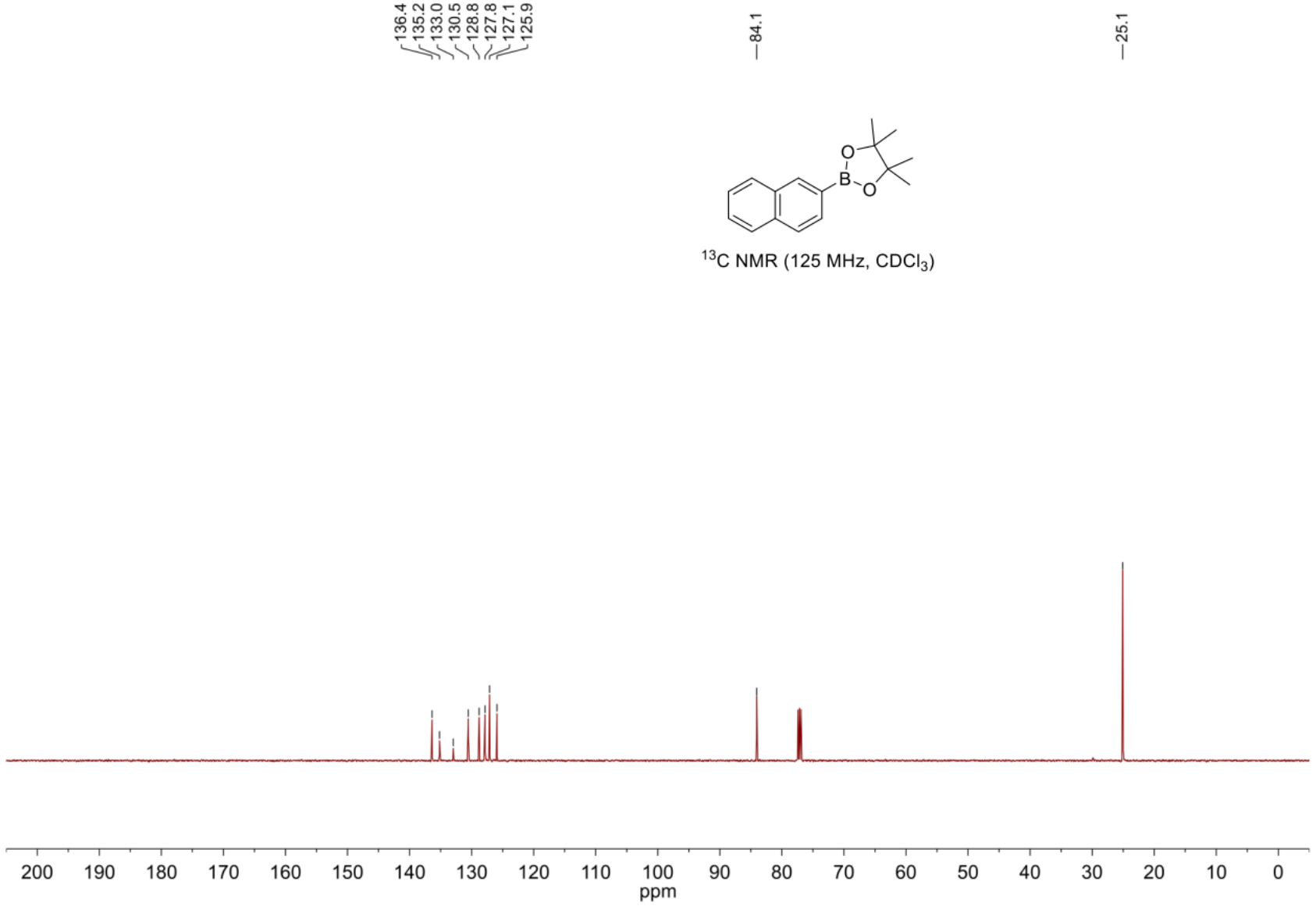
4,4,5,5-Tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane (70)



^{13}C NMR (125 MHz, $CDCl_3$)

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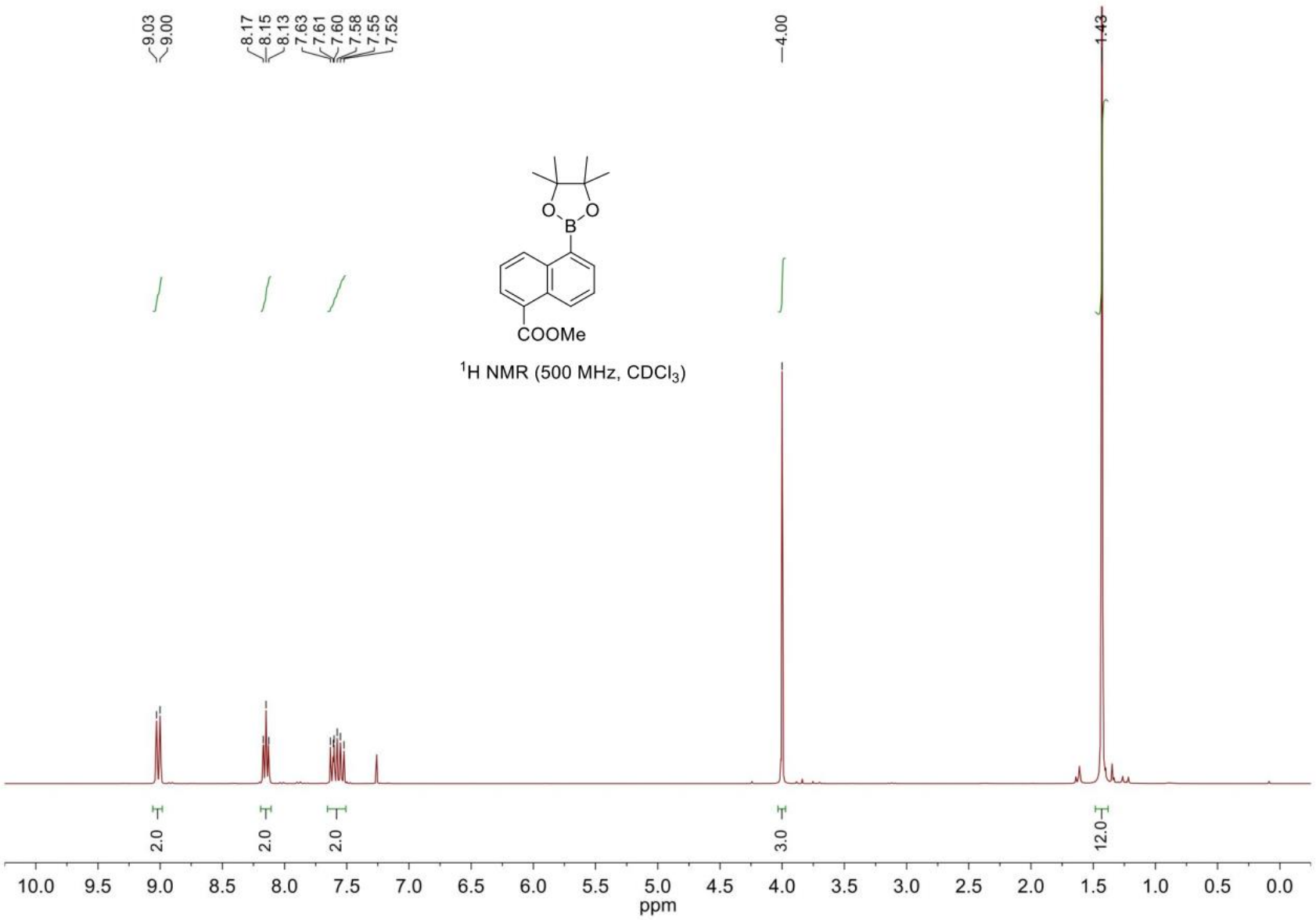
Methyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-naphthoate (71)



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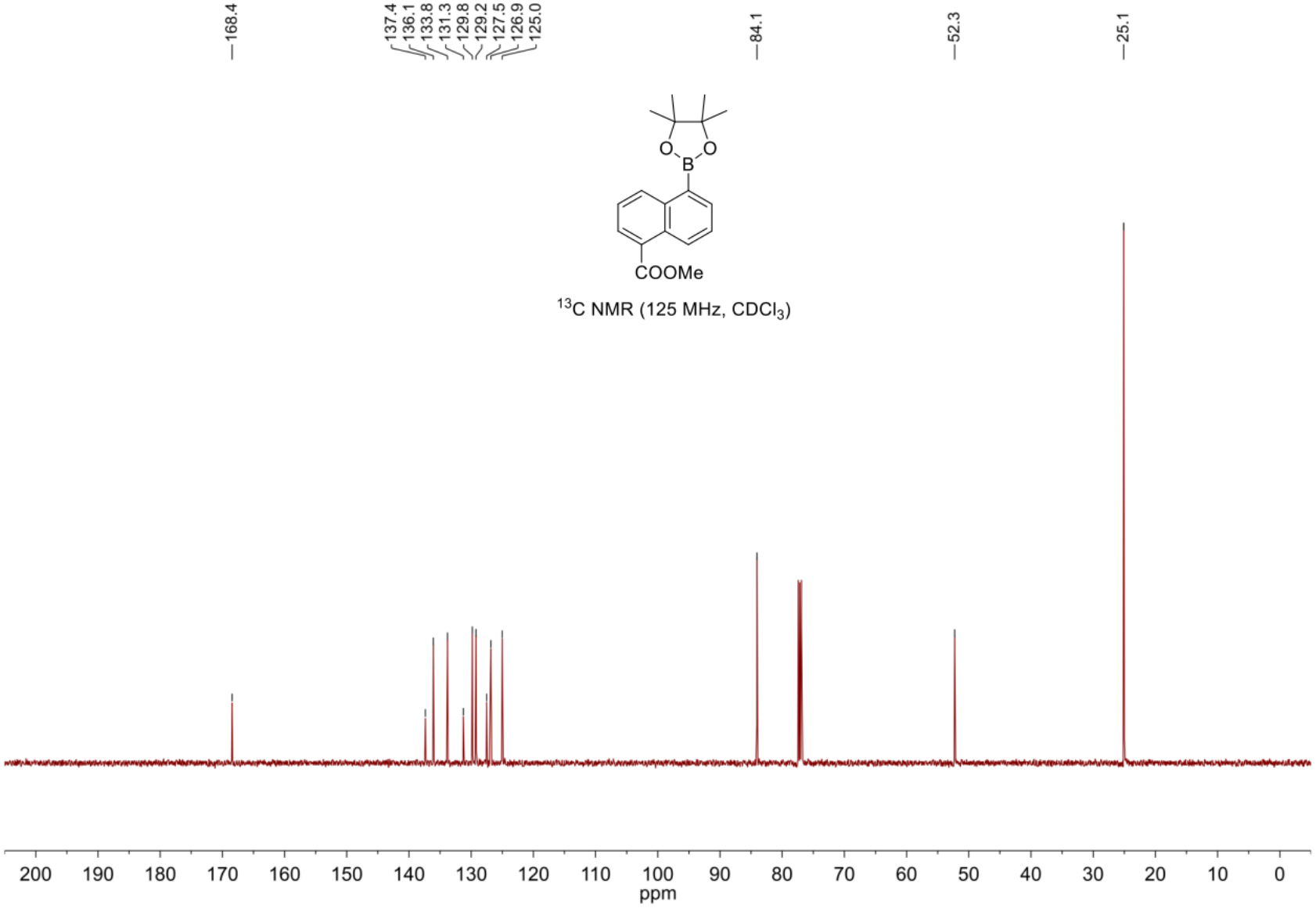
Methyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-naphthoate (71)



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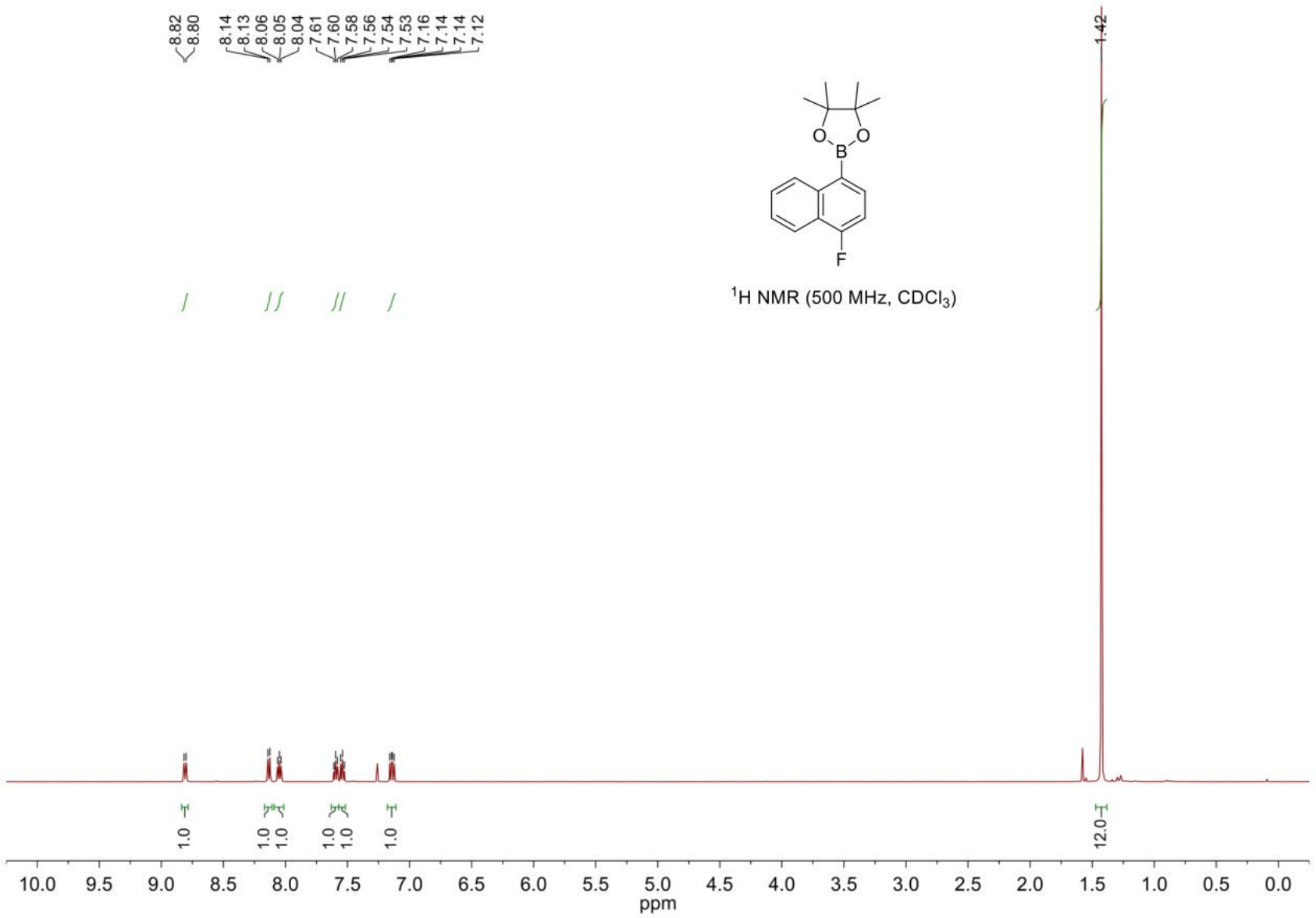
2-(4-Fluoronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (72)



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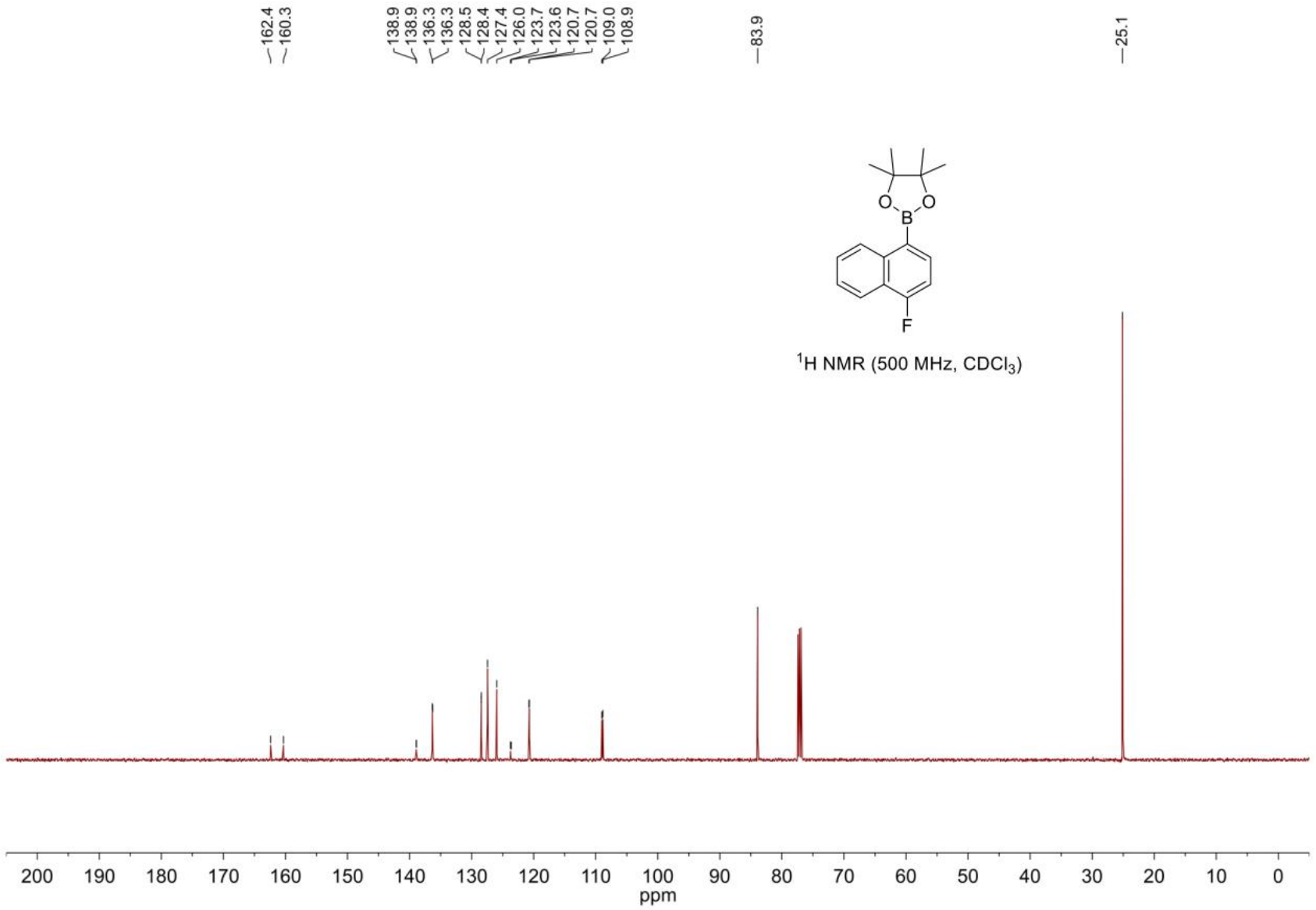
2-(4-Fluoronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (72)



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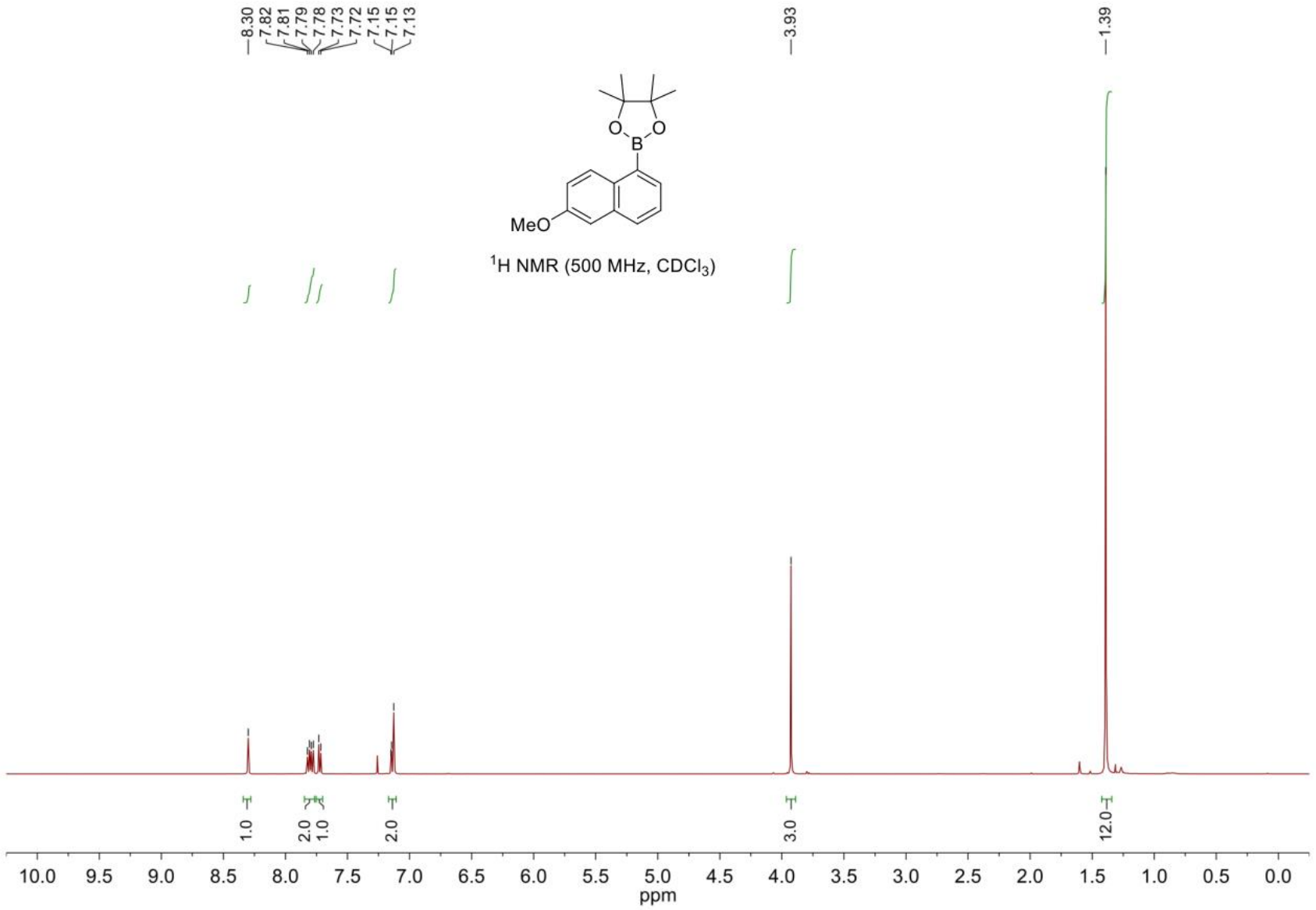
2-(6-Methoxynaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (73)



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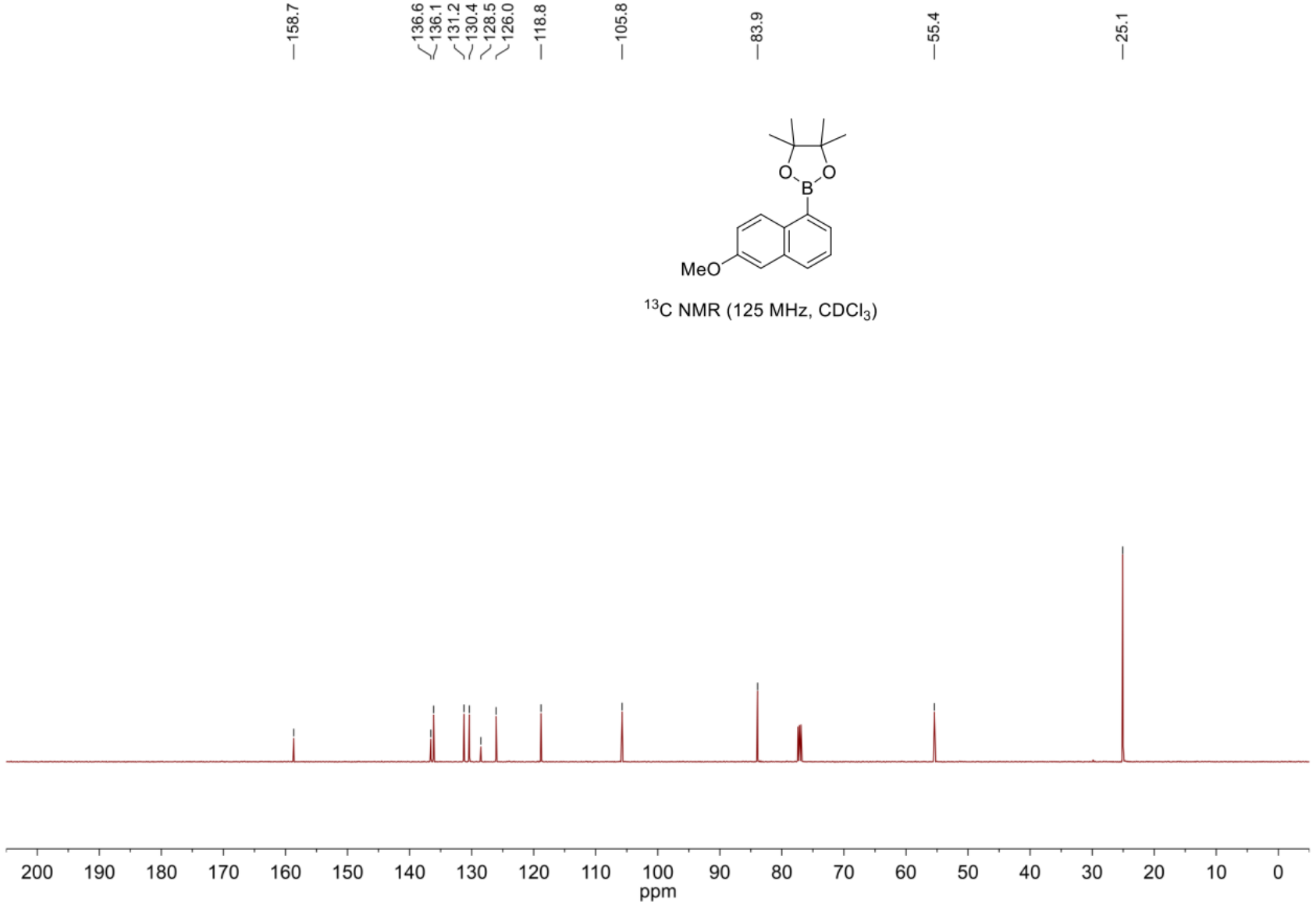
2-(6-Methoxynaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (73)



^{13}C NMR (125 MHz, $CDCl_3$)

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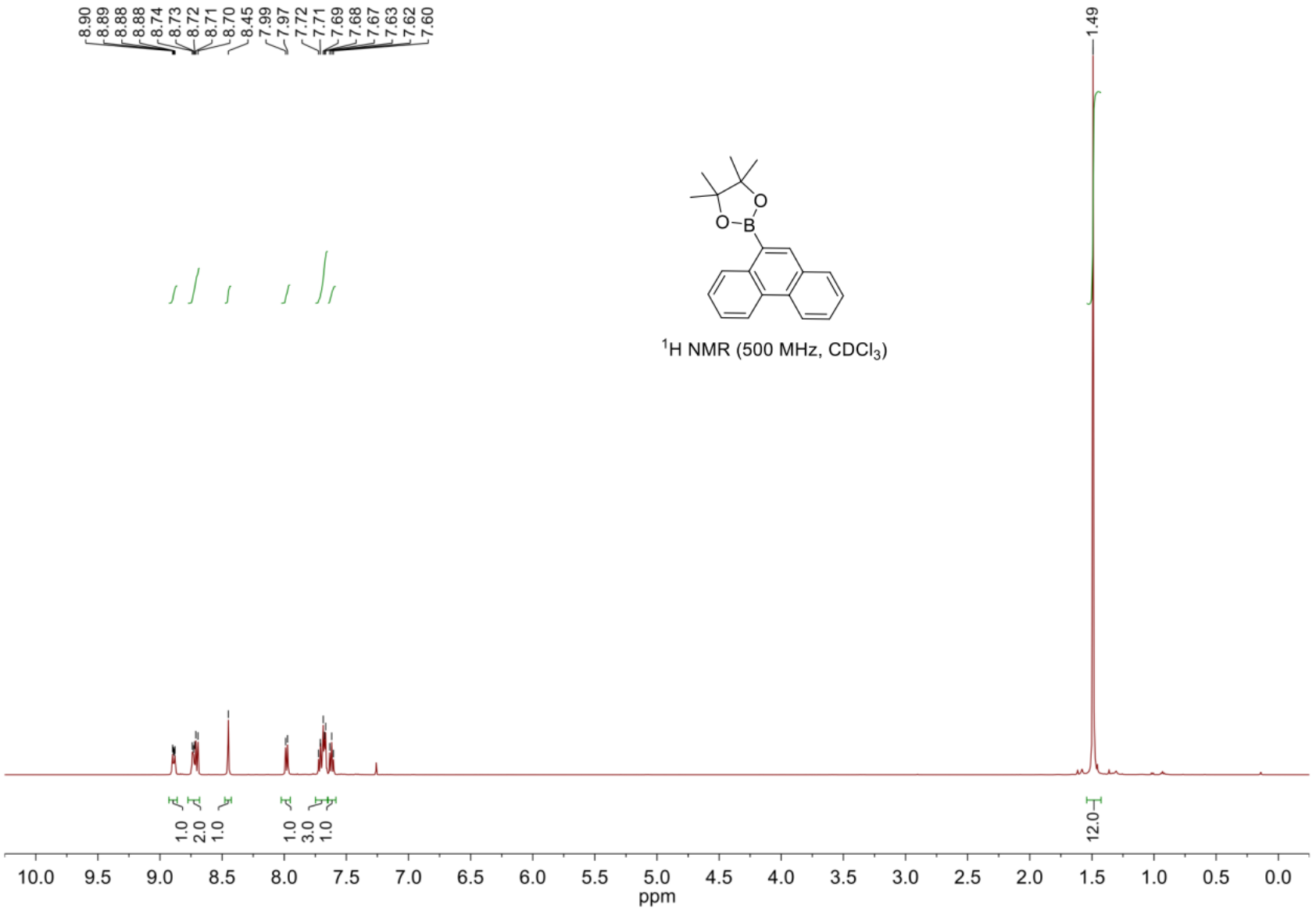
4,4,5,5-Tetramethyl-2-(phenanthren-9-yl)-1,3,2-dioxaborolane (74)



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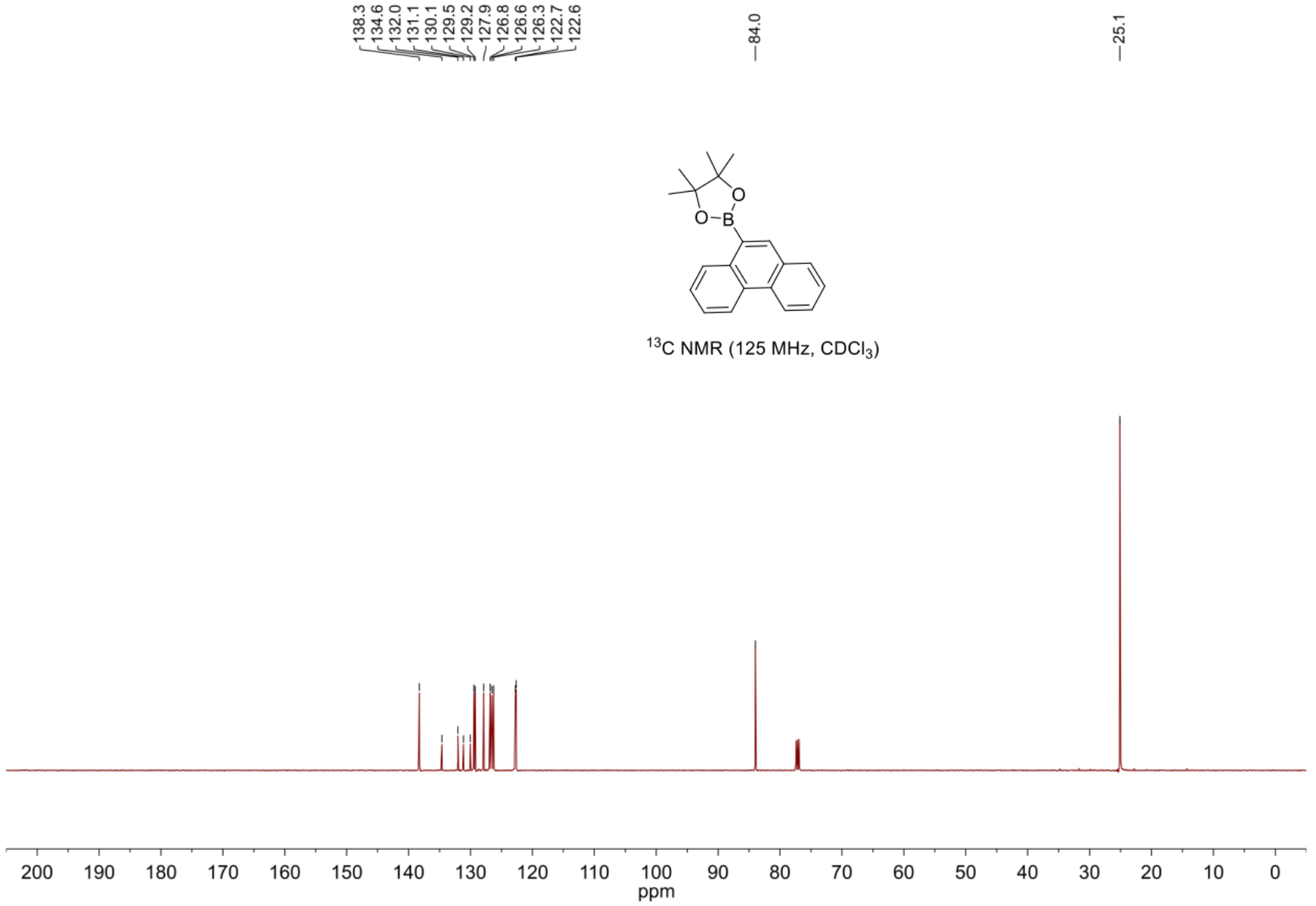
4,4,5,5-Tetramethyl-2-(phenanthren-9-yl)-1,3,2-dioxaborolane (74)



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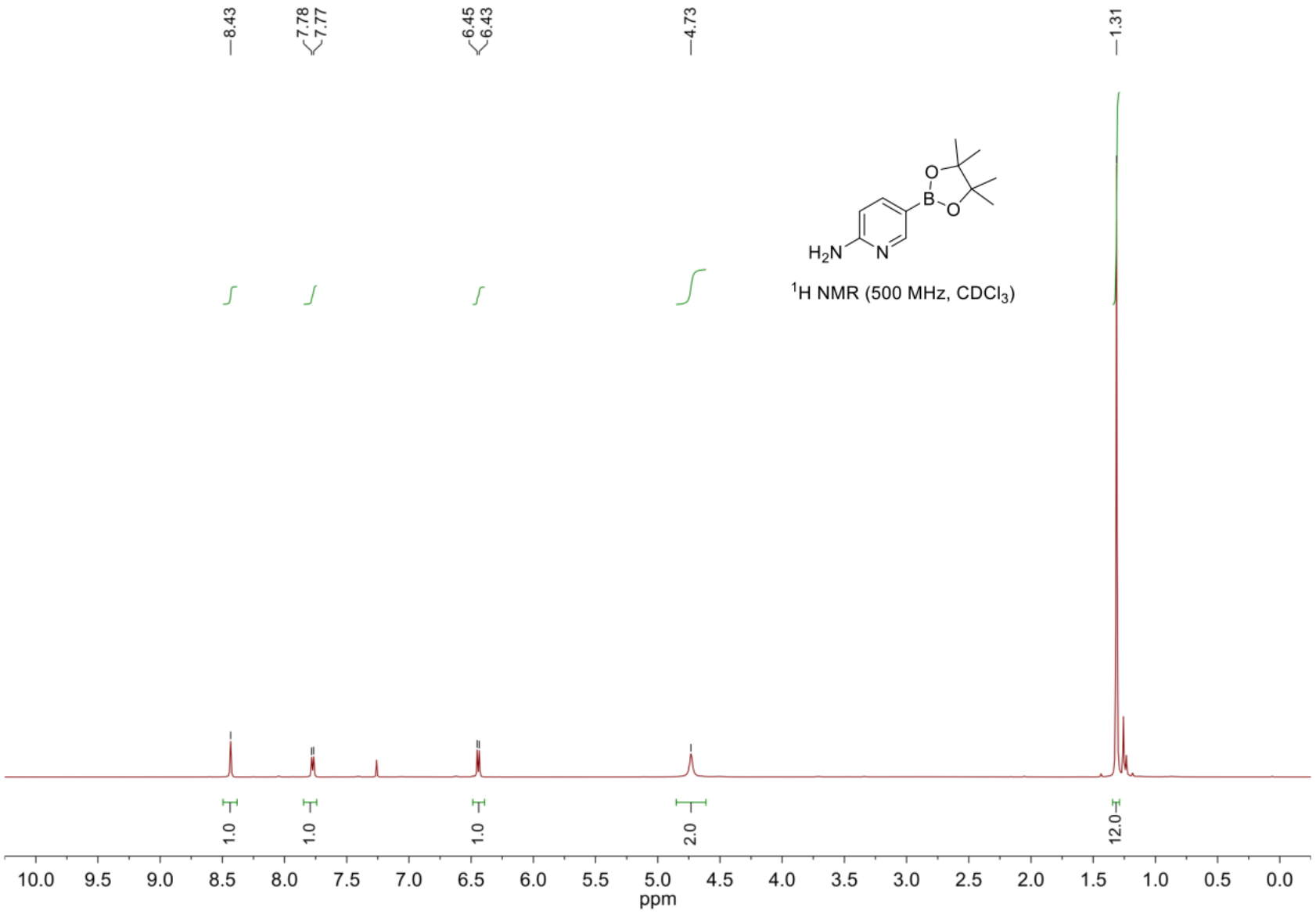
5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pyridin-2-amine (75)



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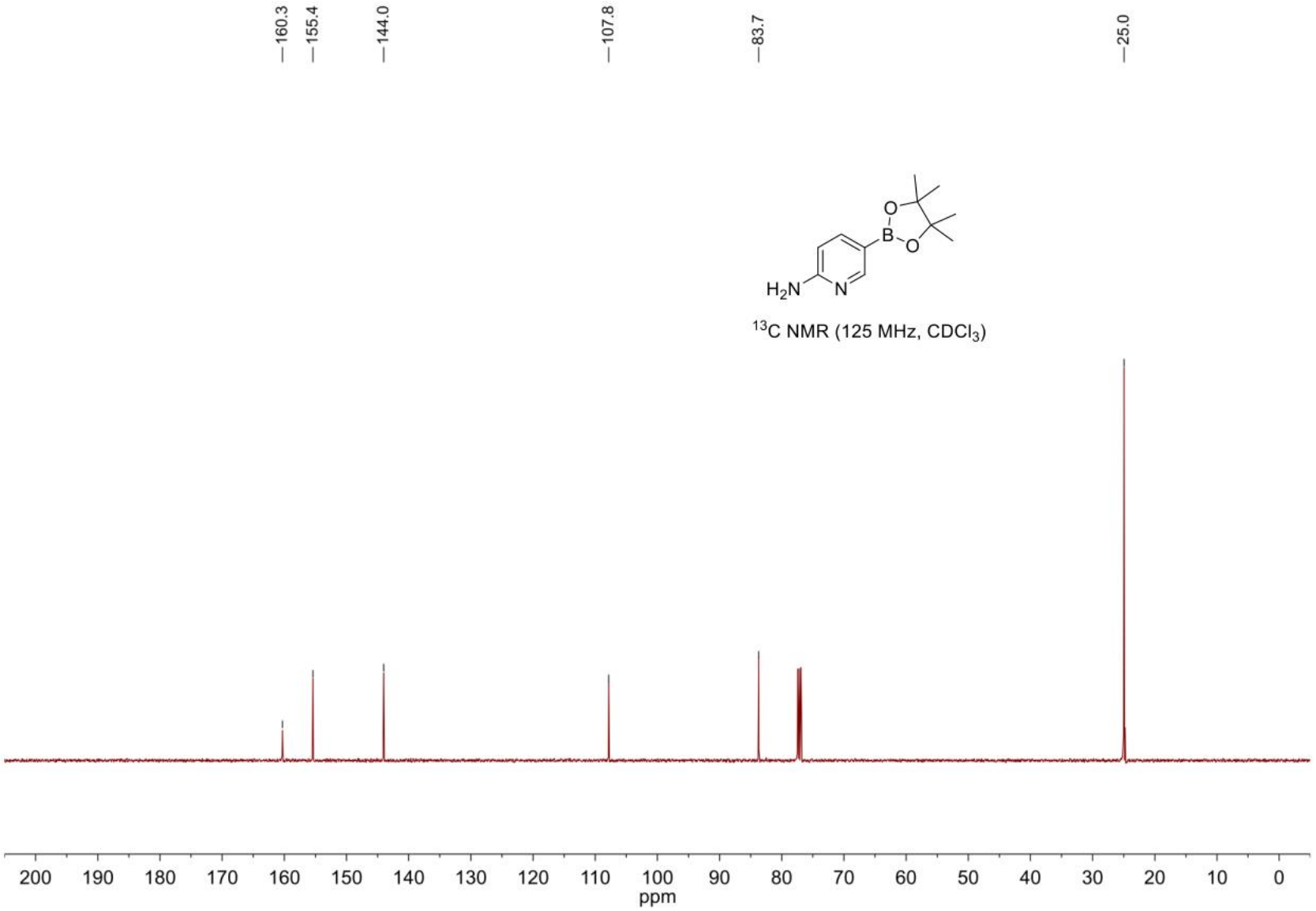
5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pyridin-2-amine (75)



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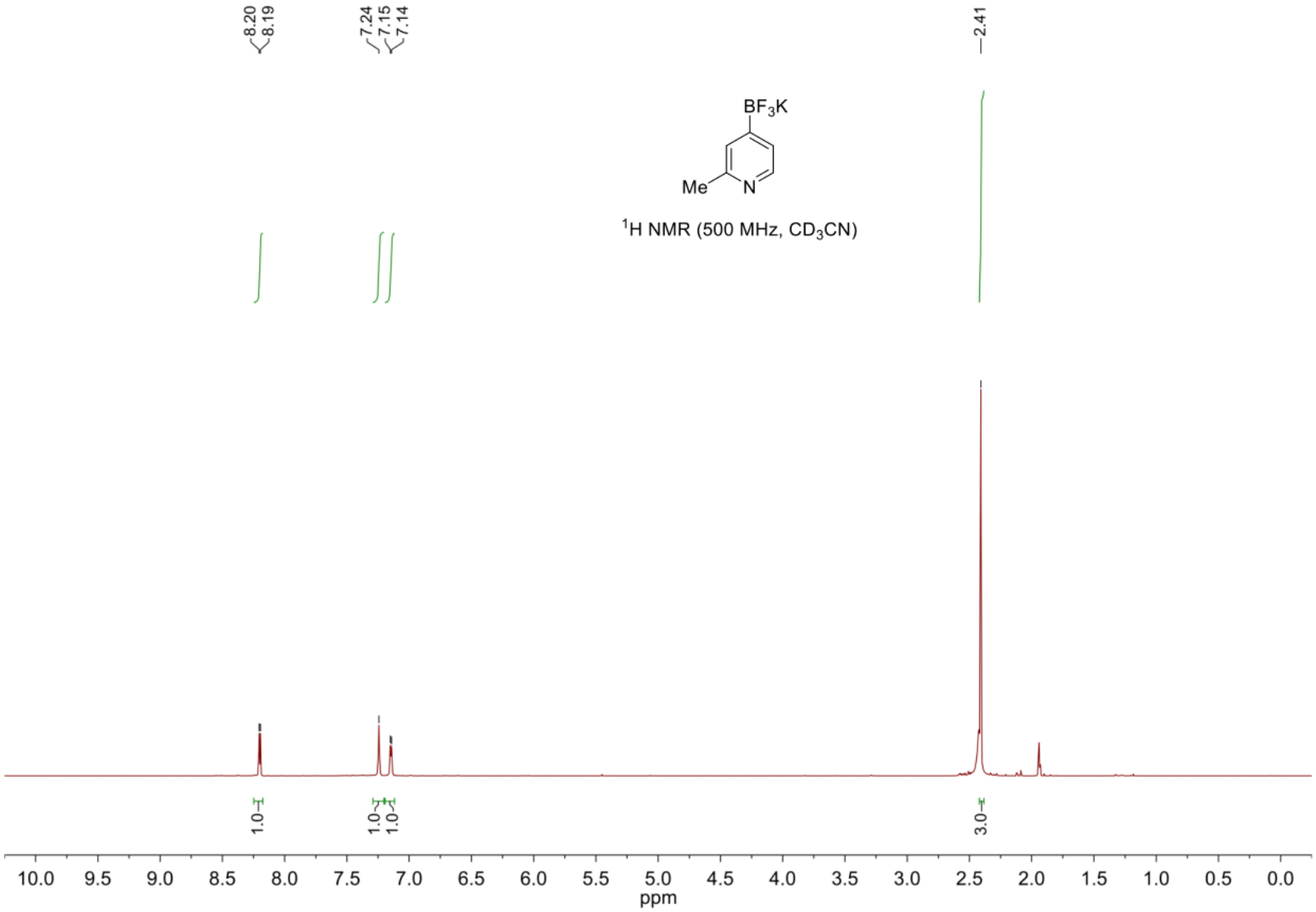
2-Methyl-4-(trifluoro-λ⁴-boraneyl)pyridine, potassium salt (76)



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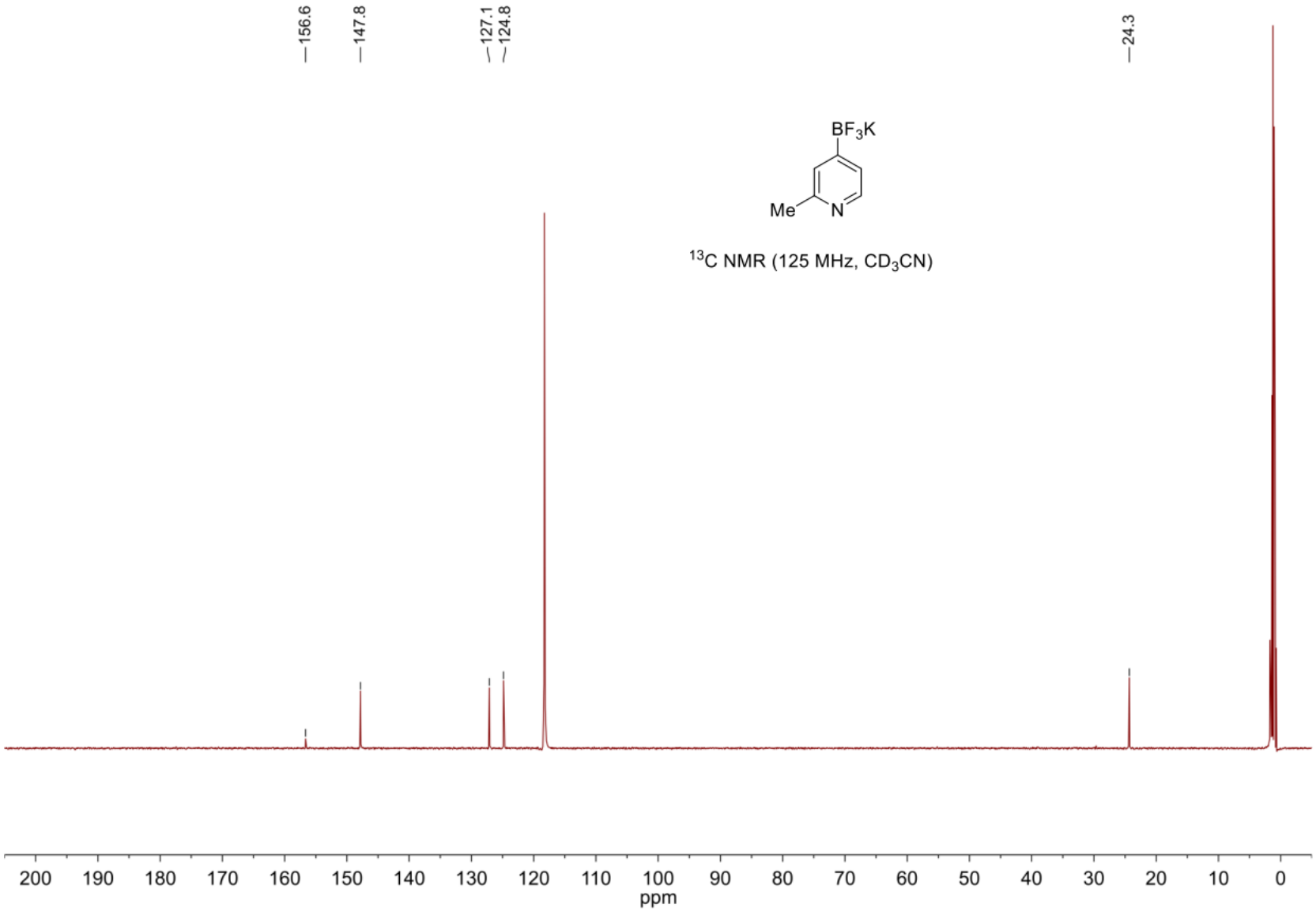
2-Methyl-4-(trifluoro-λ⁴-boraneyl)pyridine, potassium salt (76)



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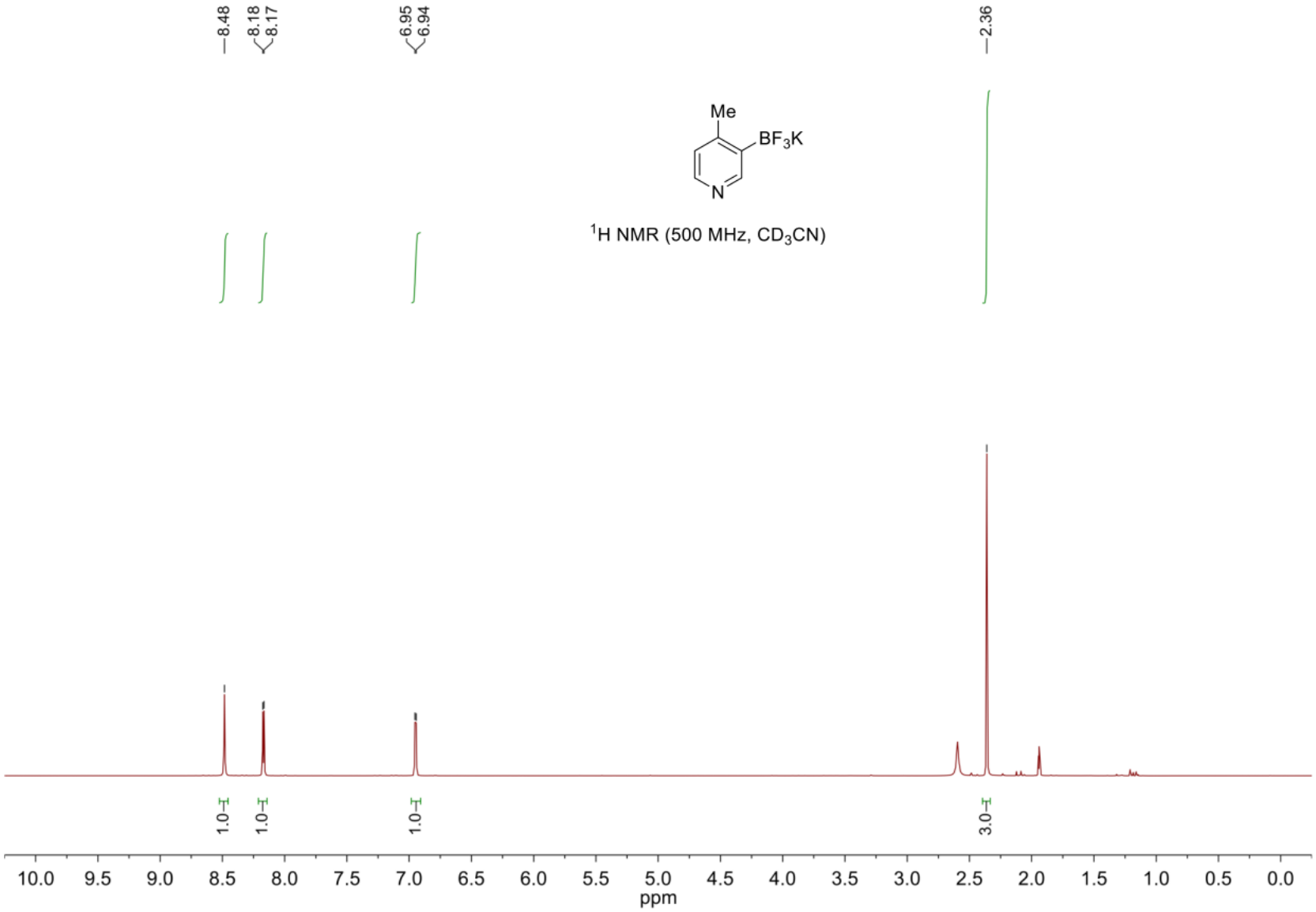
4-Methyl-3-(trifluoro-λ⁴-boraneyl)pyridine, potassium salt (77)



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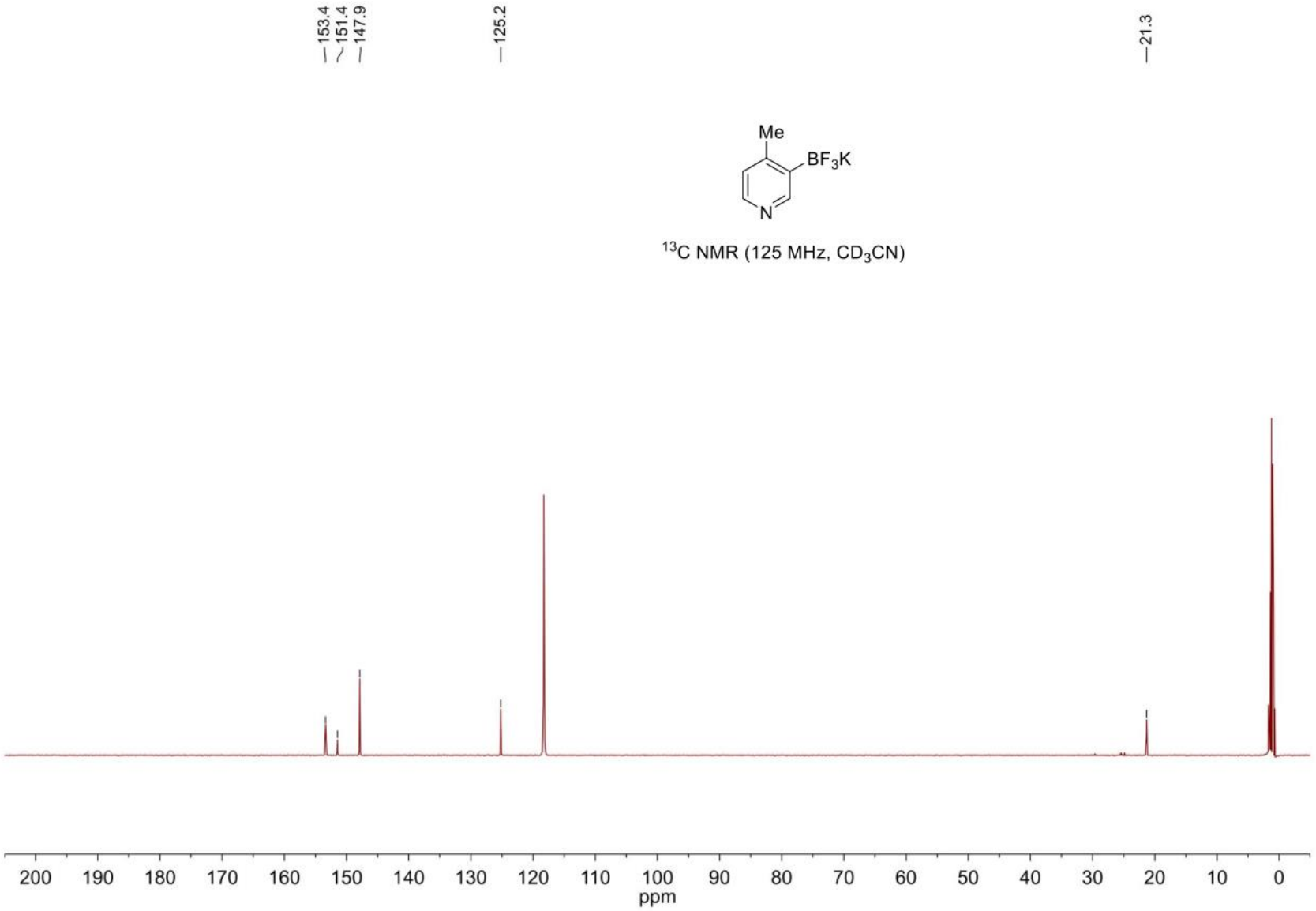
4-Methyl-3-(trifluoro-λ⁴-boraneyl)pyridine, potassium salt (77)



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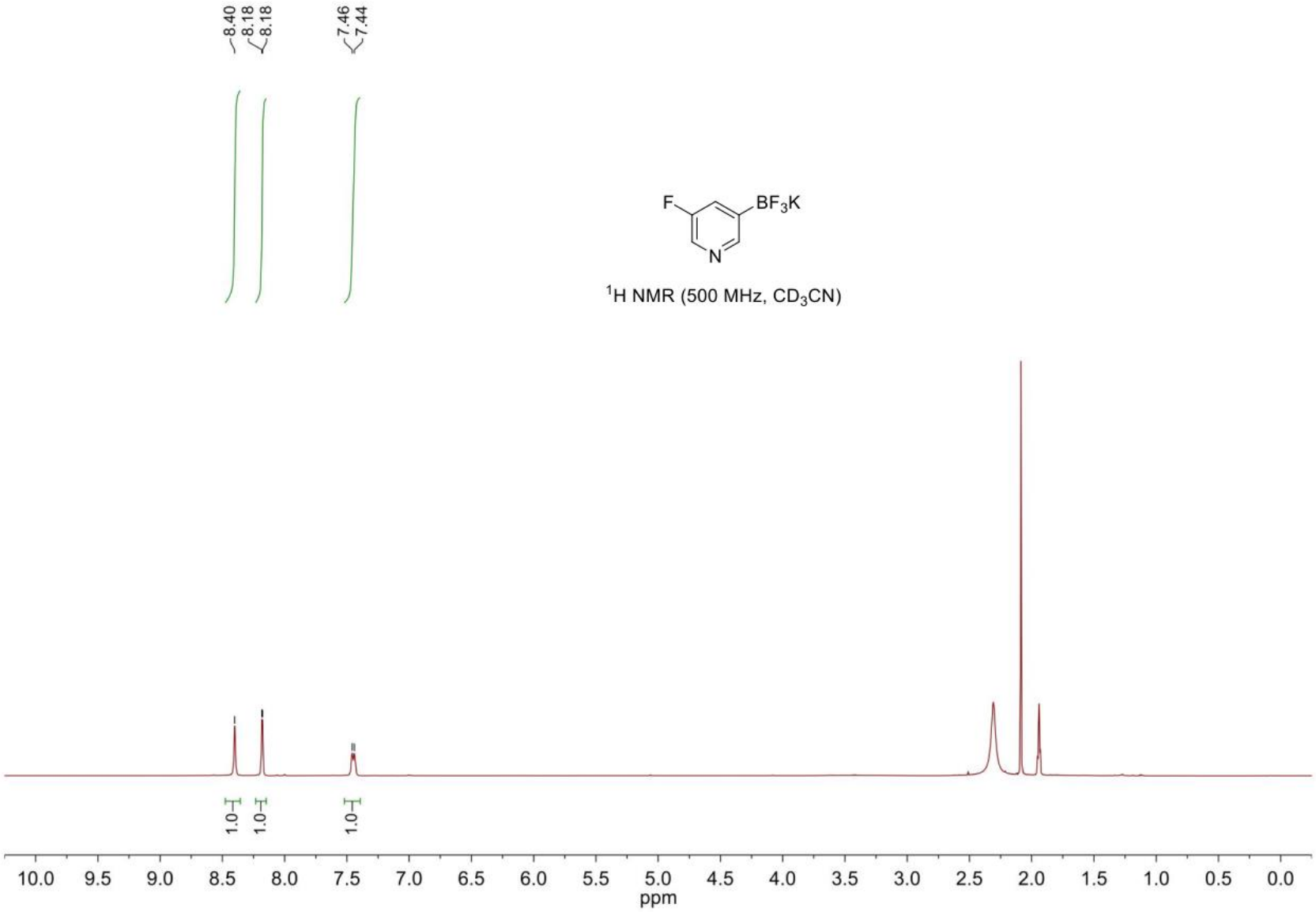
3-Fluoro-5-(trifluoro-λ⁴-boraneyl)pyridine, potassium salt (78)



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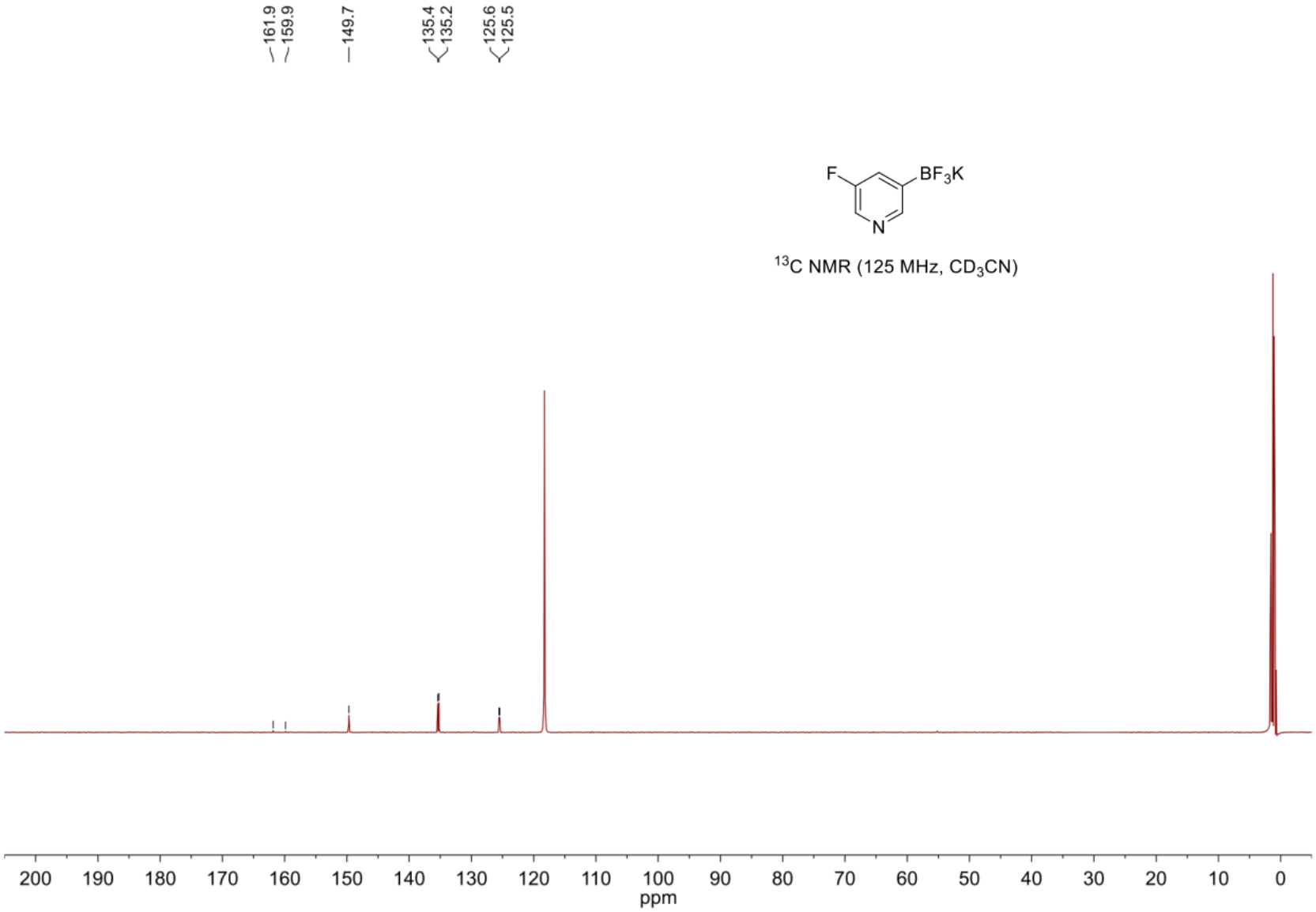
3-Fluoro-5-(trifluoro-λ⁴-boraneyl)pyridine, potassium salt (78)



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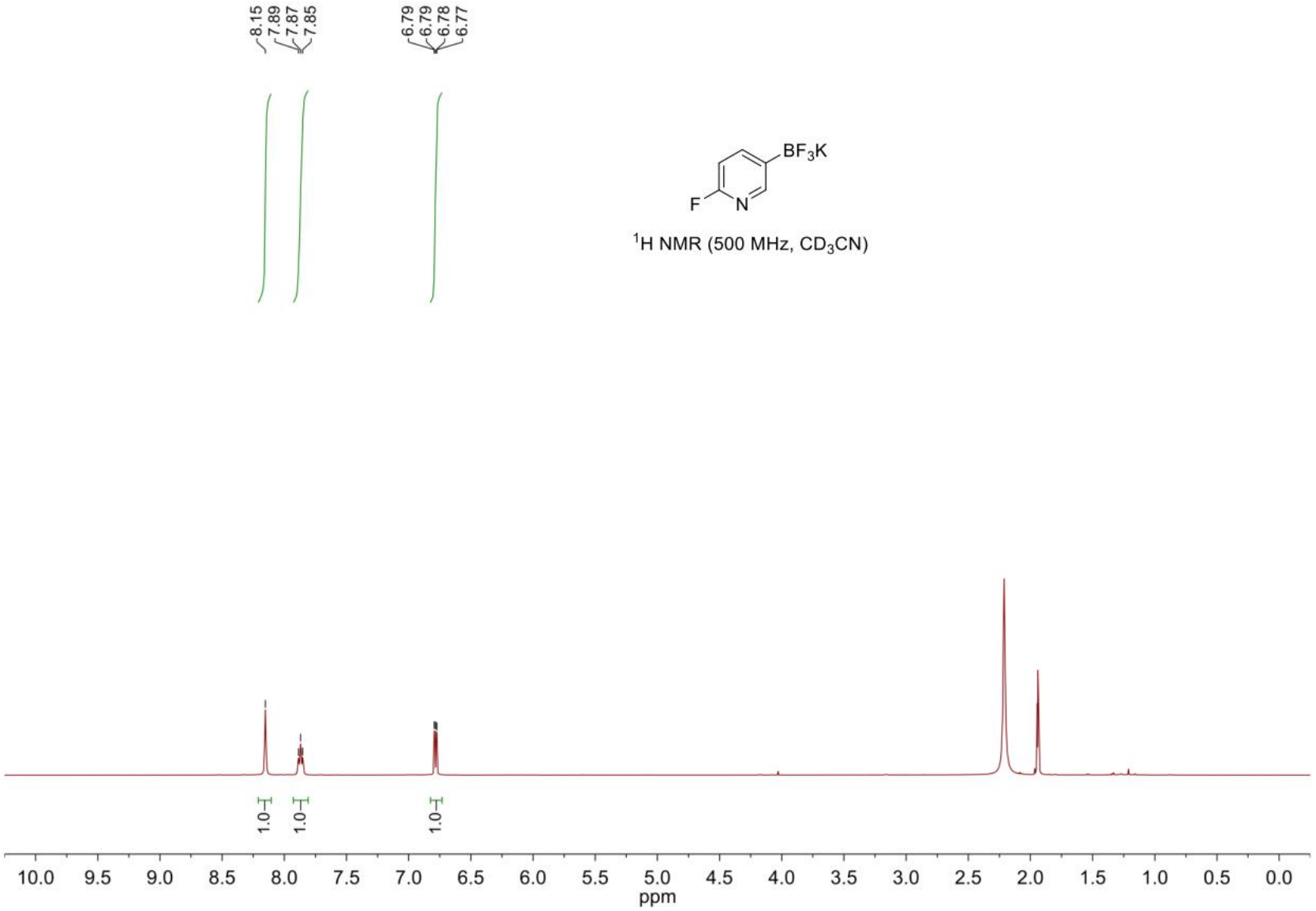
2-Fluoro-5-(trifluoro-λ⁴-boraneyl)pyridine, potassium salt (79)



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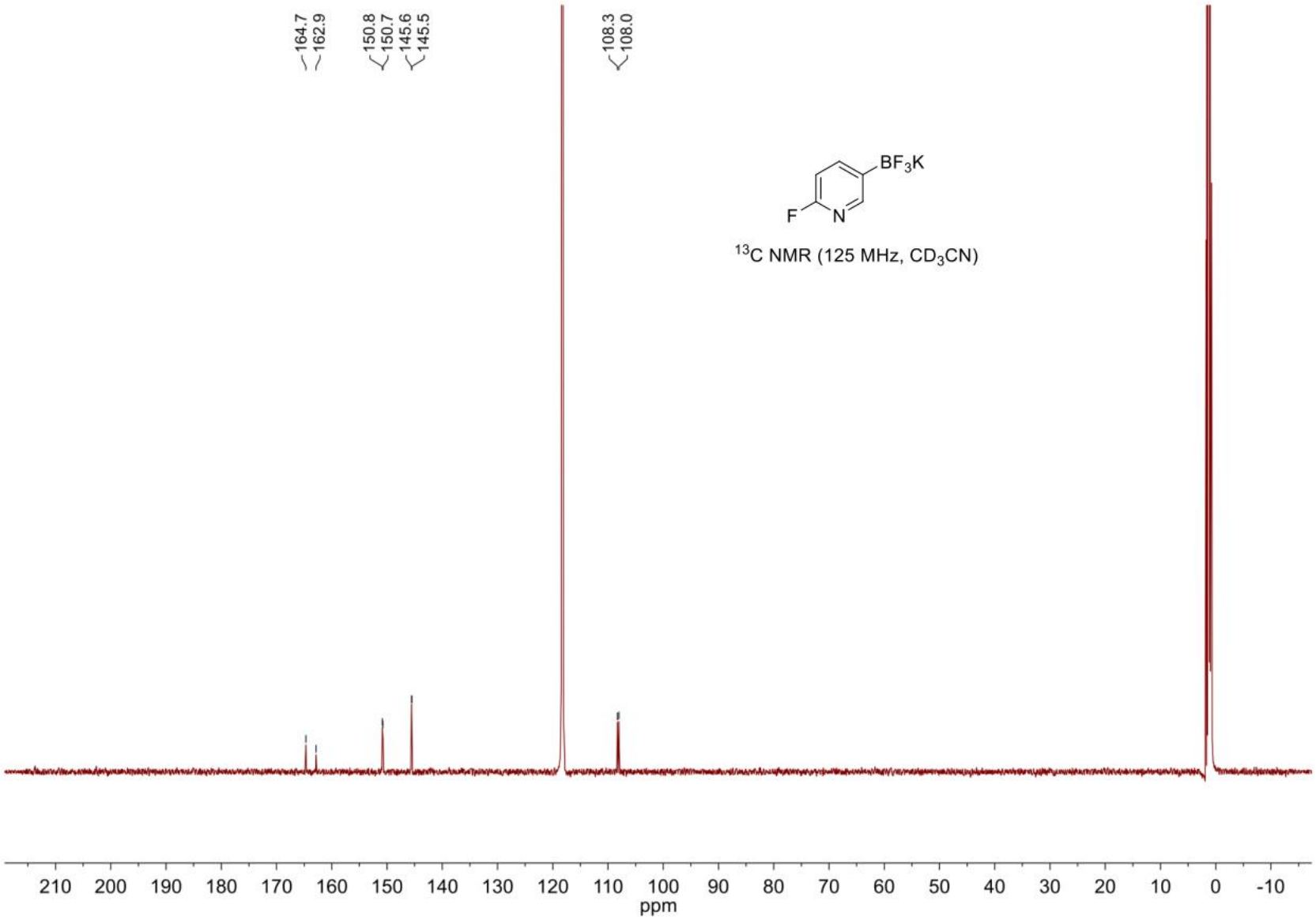
2-Fluoro-5-(trifluoro-λ⁴-boraneyl)pyridine, potassium salt (79)



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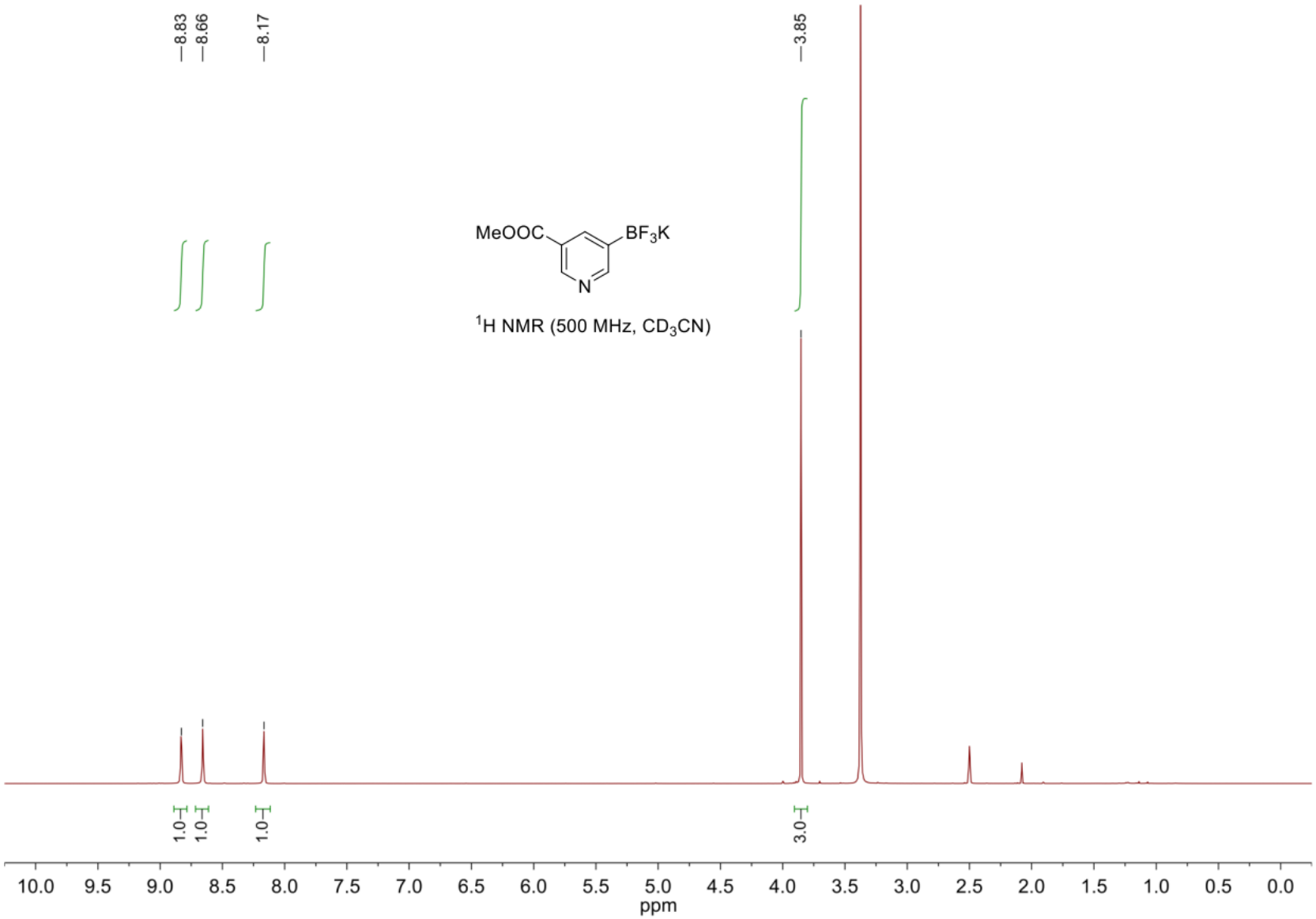
Methyl 5-(trifluoro-λ⁴-boraneyl)nicotinate, potassium salt (80)



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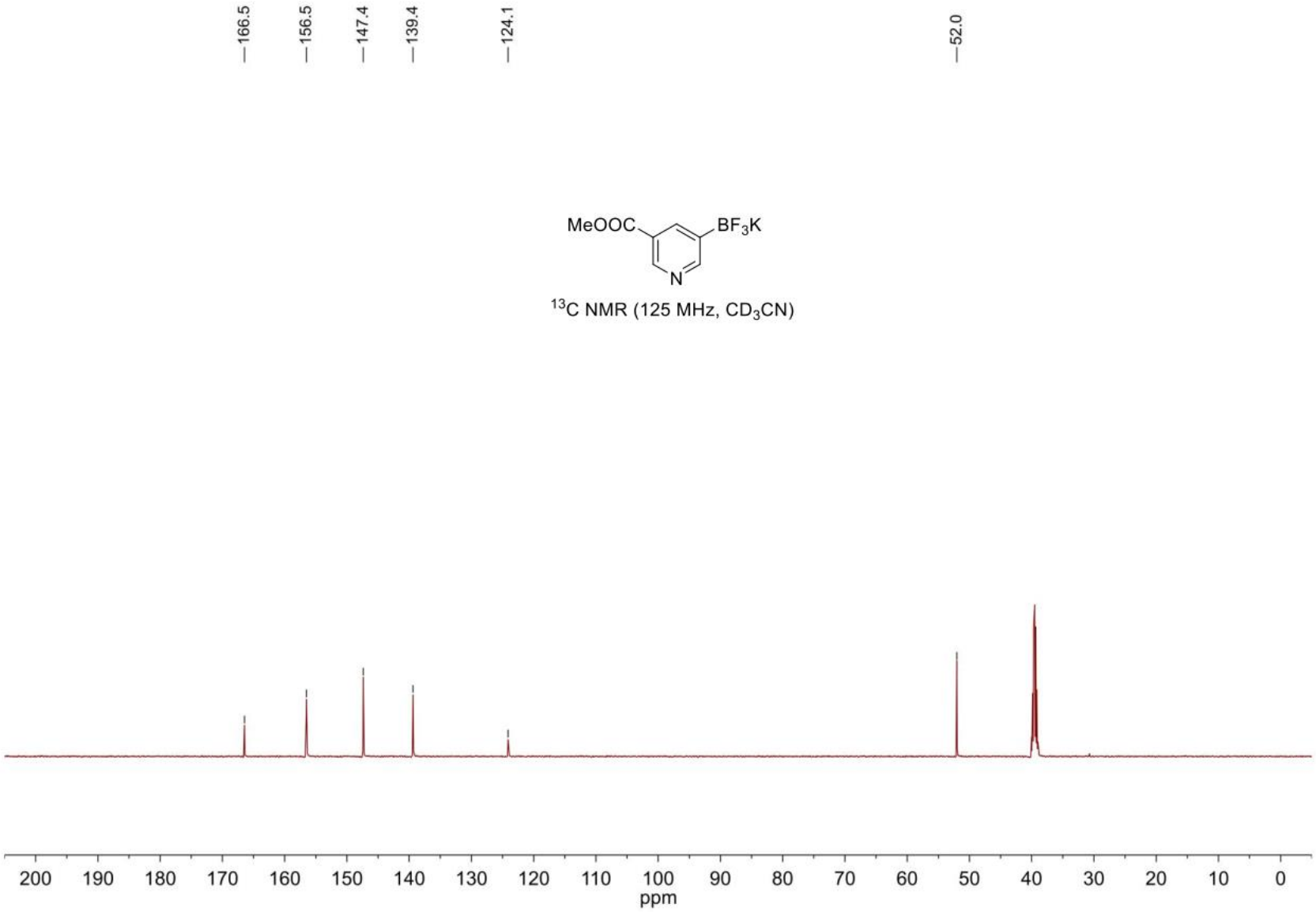
Methyl 5-(trifluoro-λ⁴-boraneyl)nicotinate, potassium salt (80)



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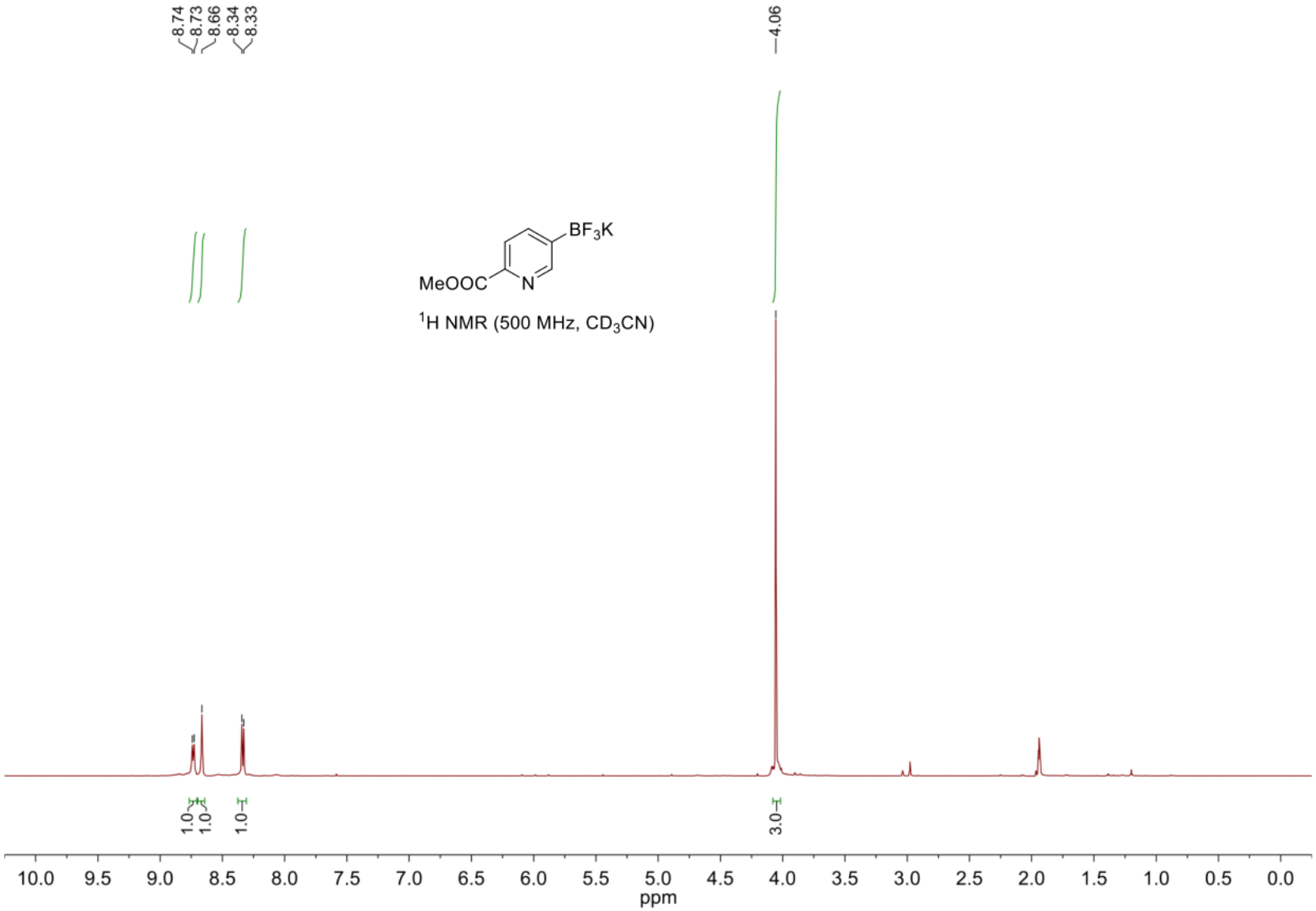
Methyl 6-(trifluoro-λ⁴-boraneyl)picolinate, potassium salt (81)



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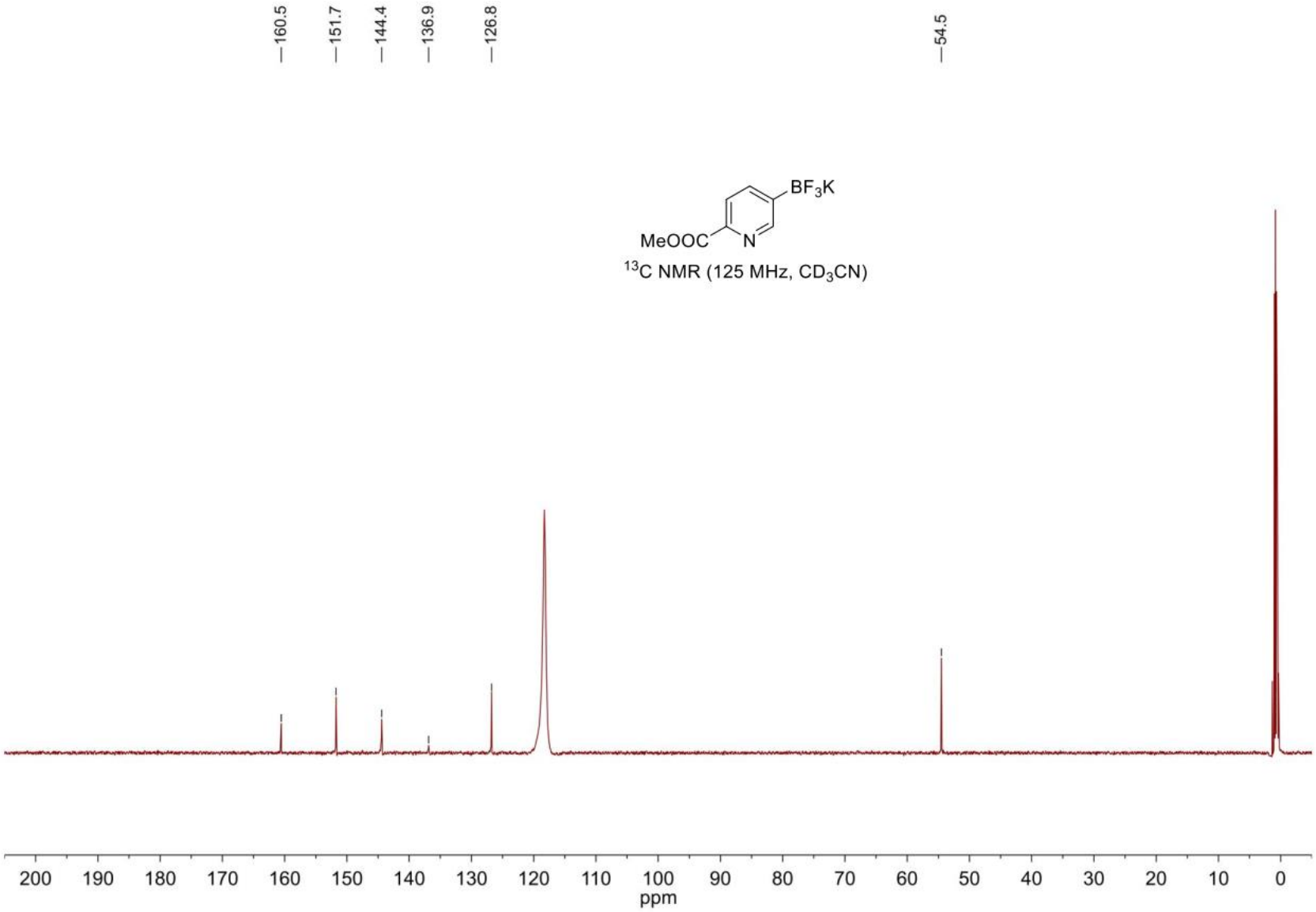
Methyl 6-(trifluoro-λ⁴-boraneyl)picolinate, potassium salt (81)



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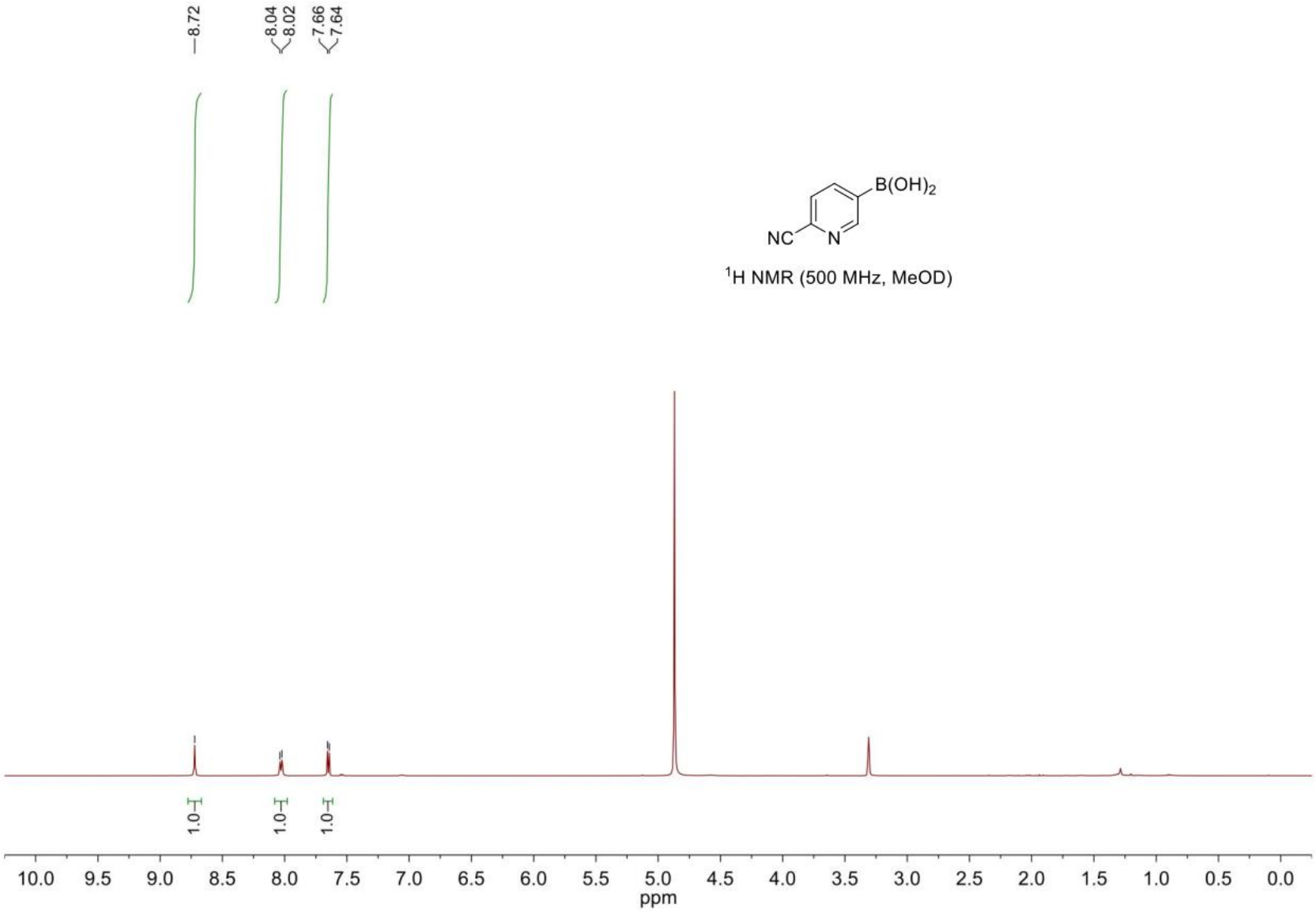
(6-Cyanopyridin-3-yl)boronic acid (82)



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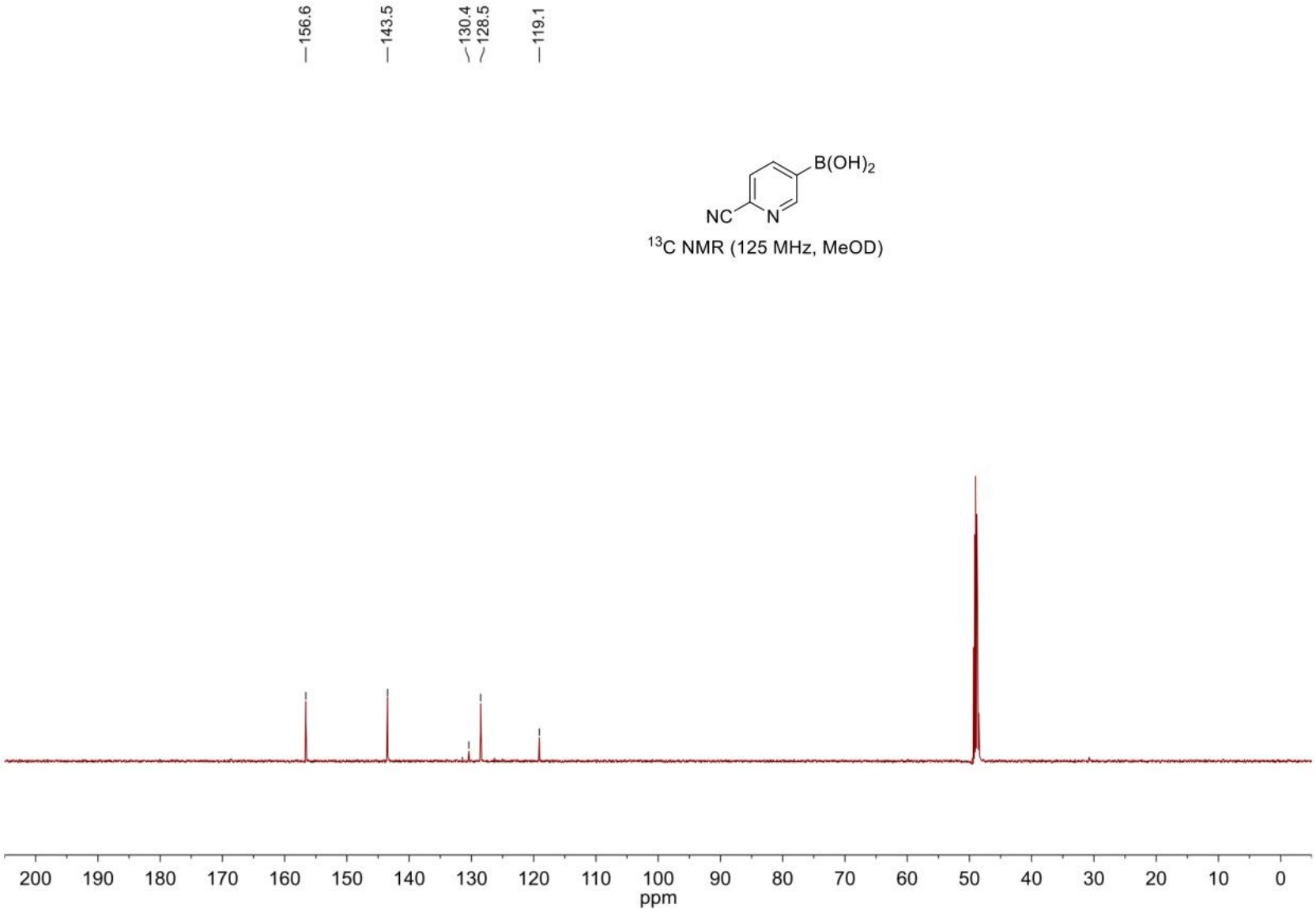
(6-Cyanopyridin-3-yl)boronic acid (82)



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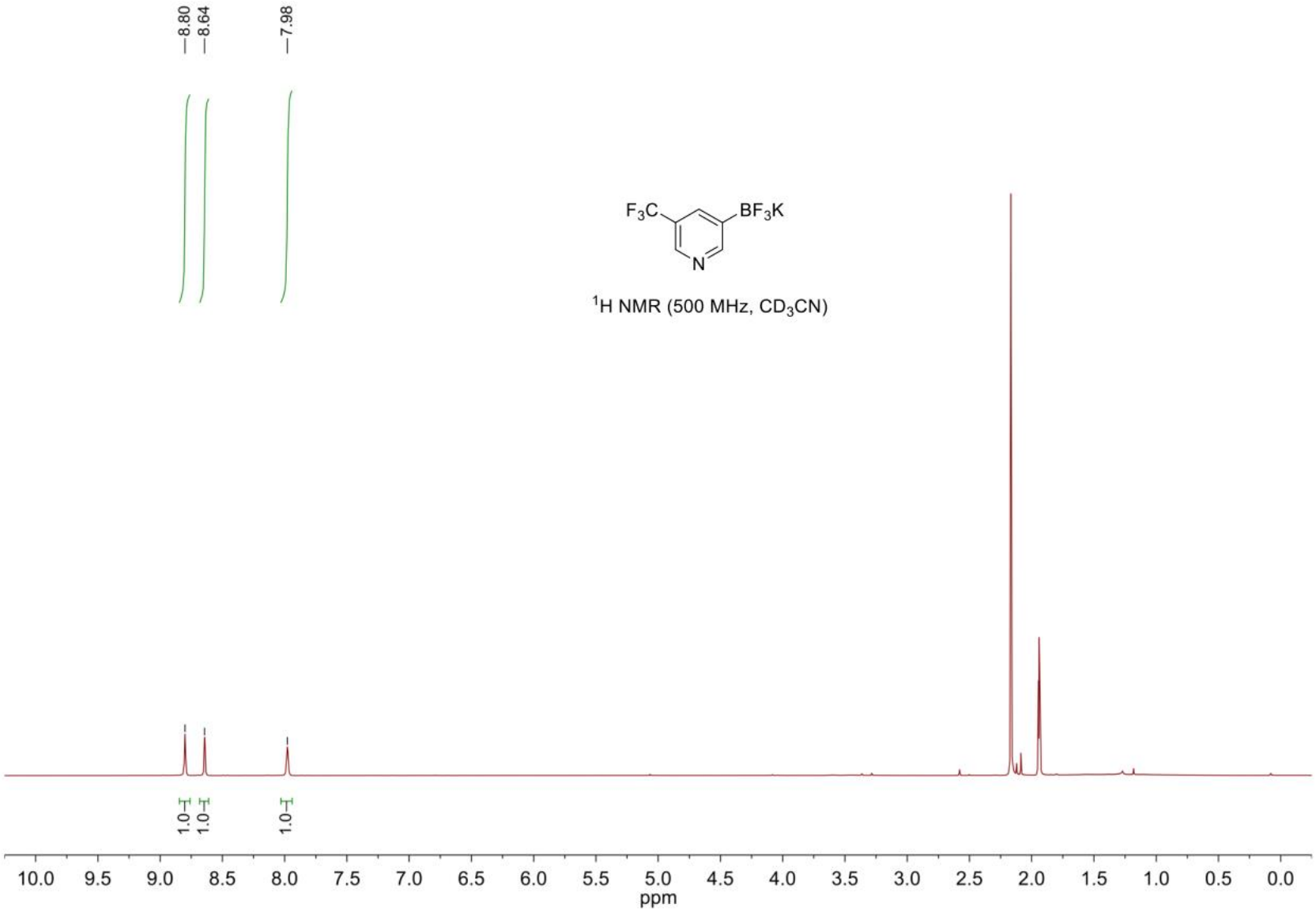
3-(Trifluoro-λ⁴-boraneyl)-5-(trifluoromethyl)pyridine, potassium salt (83)



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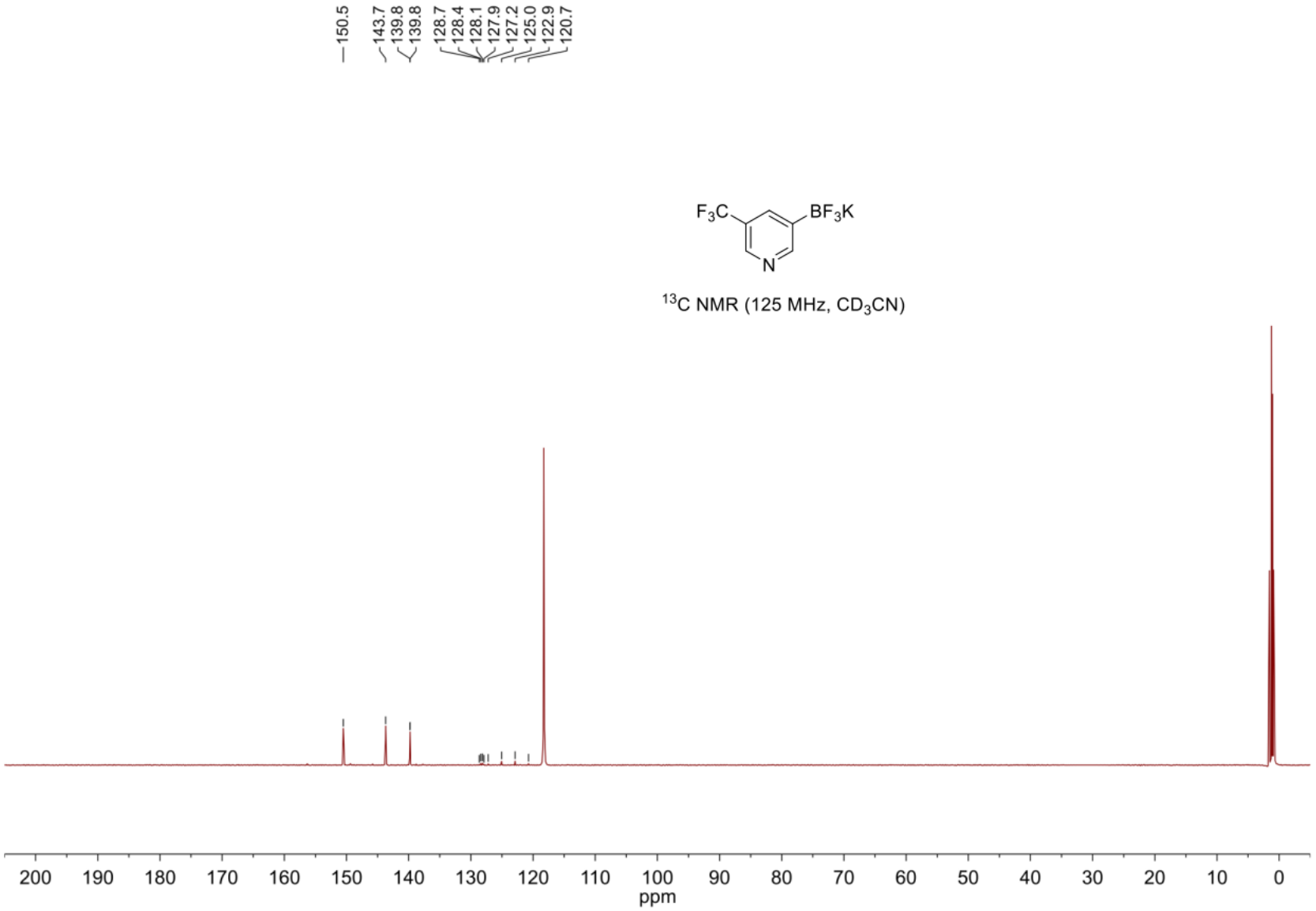
3-(Trifluoro-λ⁴-boraneyl)-5-(trifluoromethyl)pyridine, potassium salt (83)



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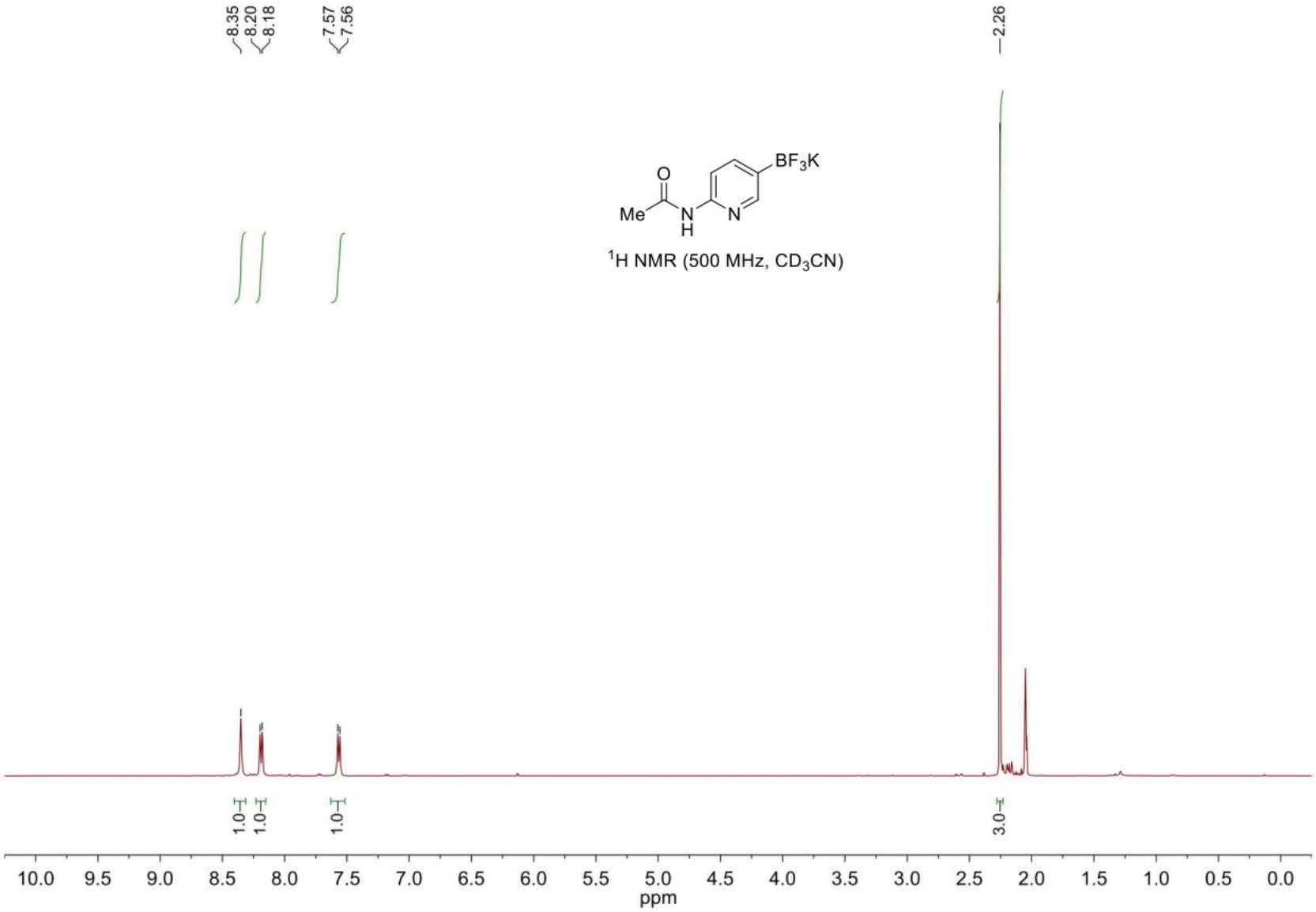
_N_-(5-(Trifluoro-λ⁴-boraneyl)pyridin-2-yl)acetamide, potassium salt (84)



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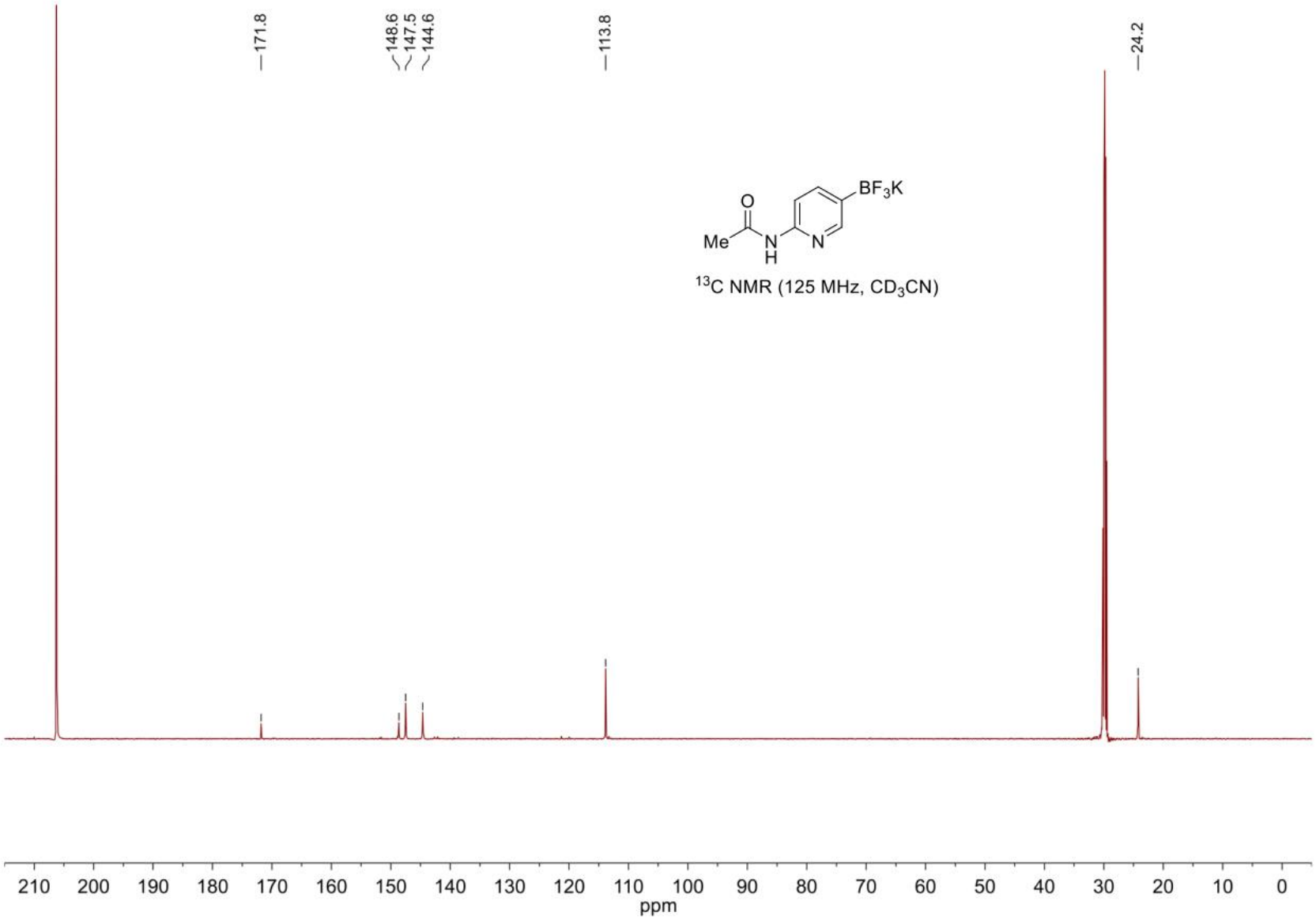
_N_-(5-(Trifluoro-λ⁴-boraneyl)pyridin-2-yl)acetamide, potassium salt (84)



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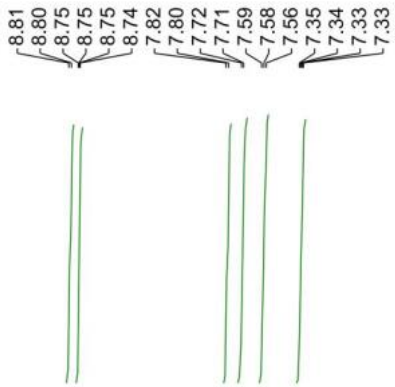
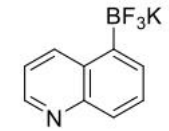
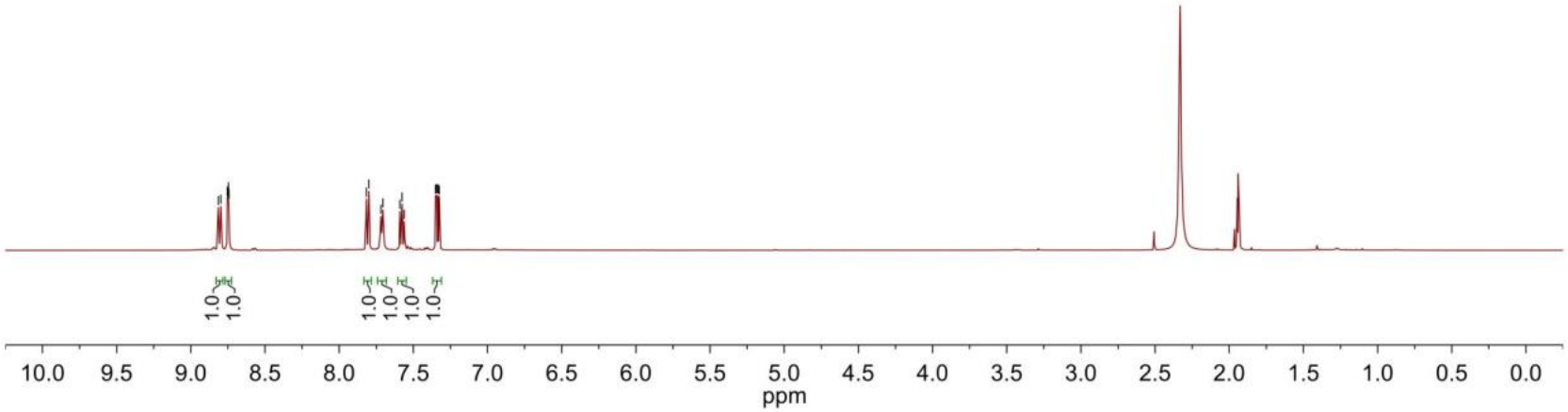
5-(Trifluoro-λ⁴-boraneyl)quinoline, potassium salt (85)





^{1}H NMR (500 MHz, CD_3CN)



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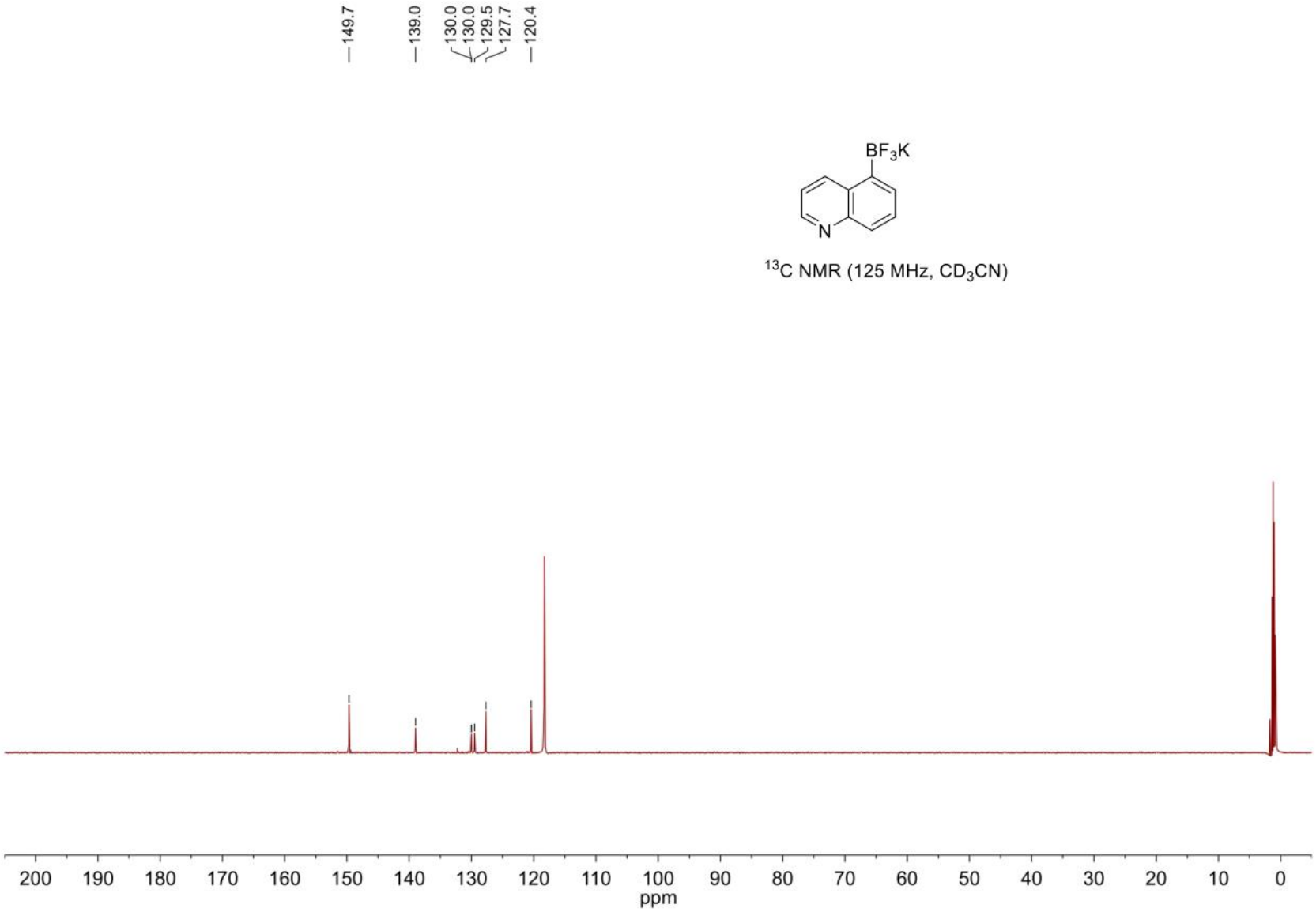
5-(Trifluoro-λ⁴-boraneyl)quinoline, potassium salt (85)



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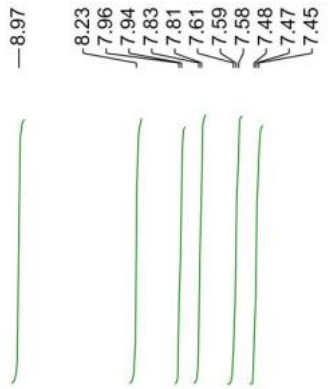
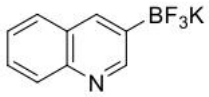
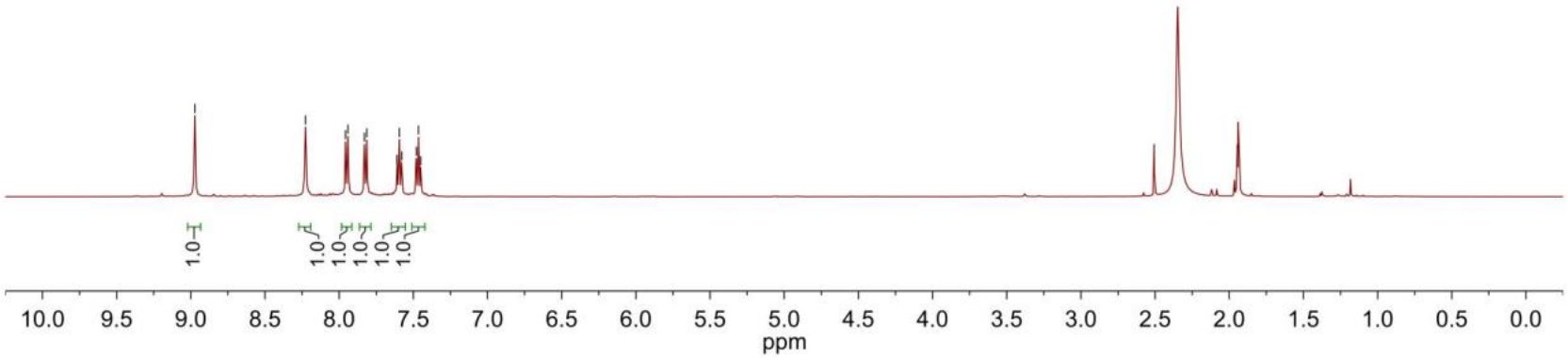
3-(Trifluoro-λ⁴-boraneyl)quinoline, potassium salt (86)





^{1}H NMR (500 MHz, CD_3CN)



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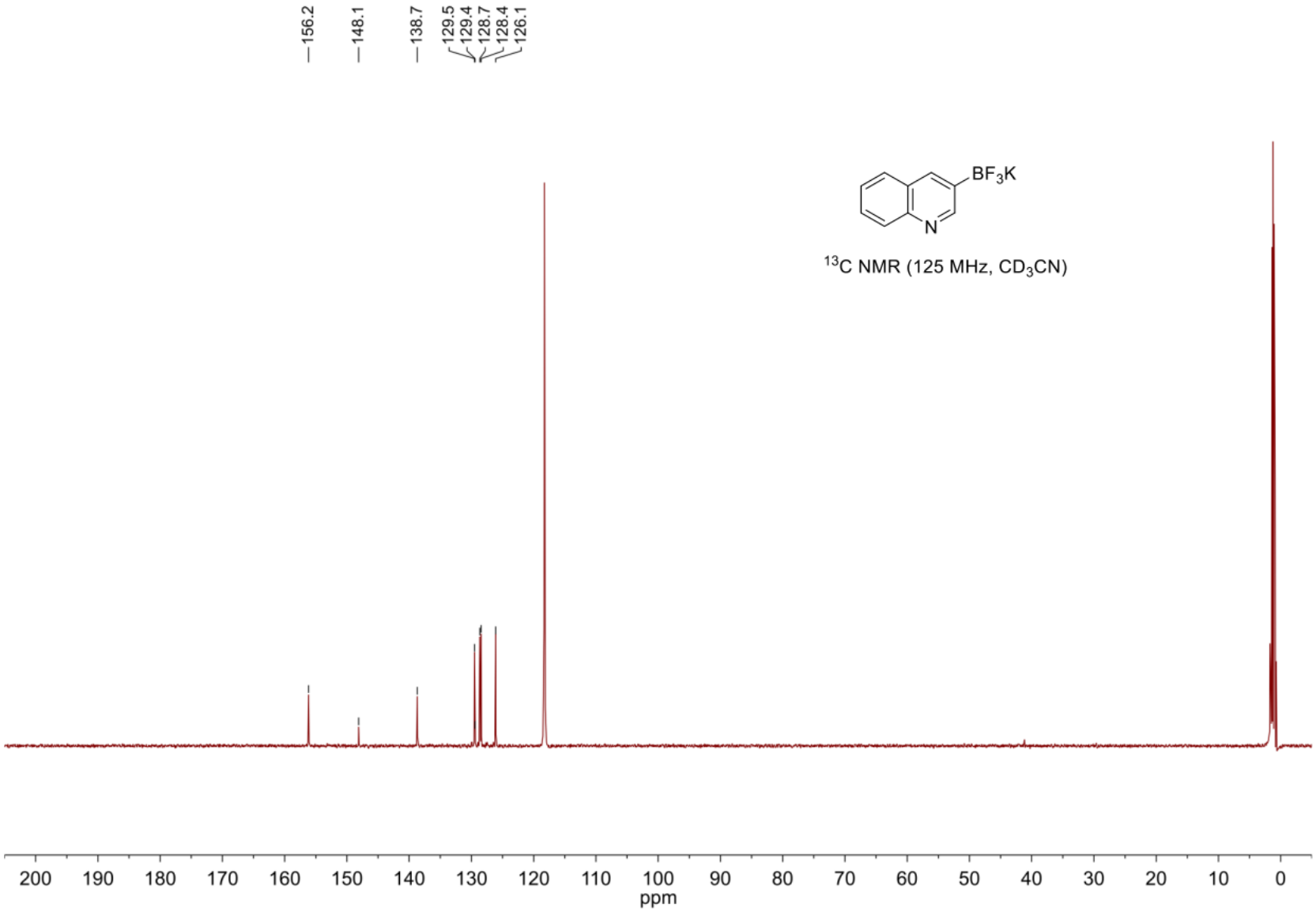
3-(Trifluoro-λ⁴-boraneyl)quinoline, potassium salt (86)



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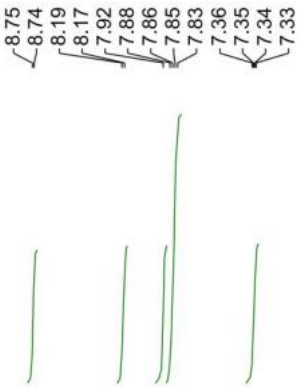
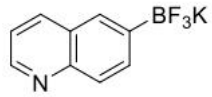
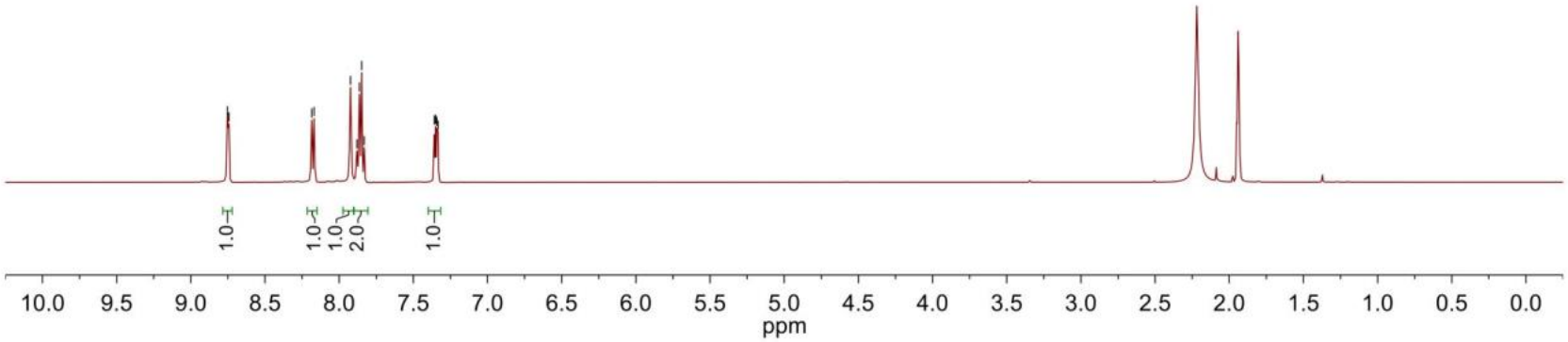
6-(Trifluoro-λ⁴-boraneyl)quinoline, potassium salt (87)





^{1}H NMR (500 MHz, CD_3CN)



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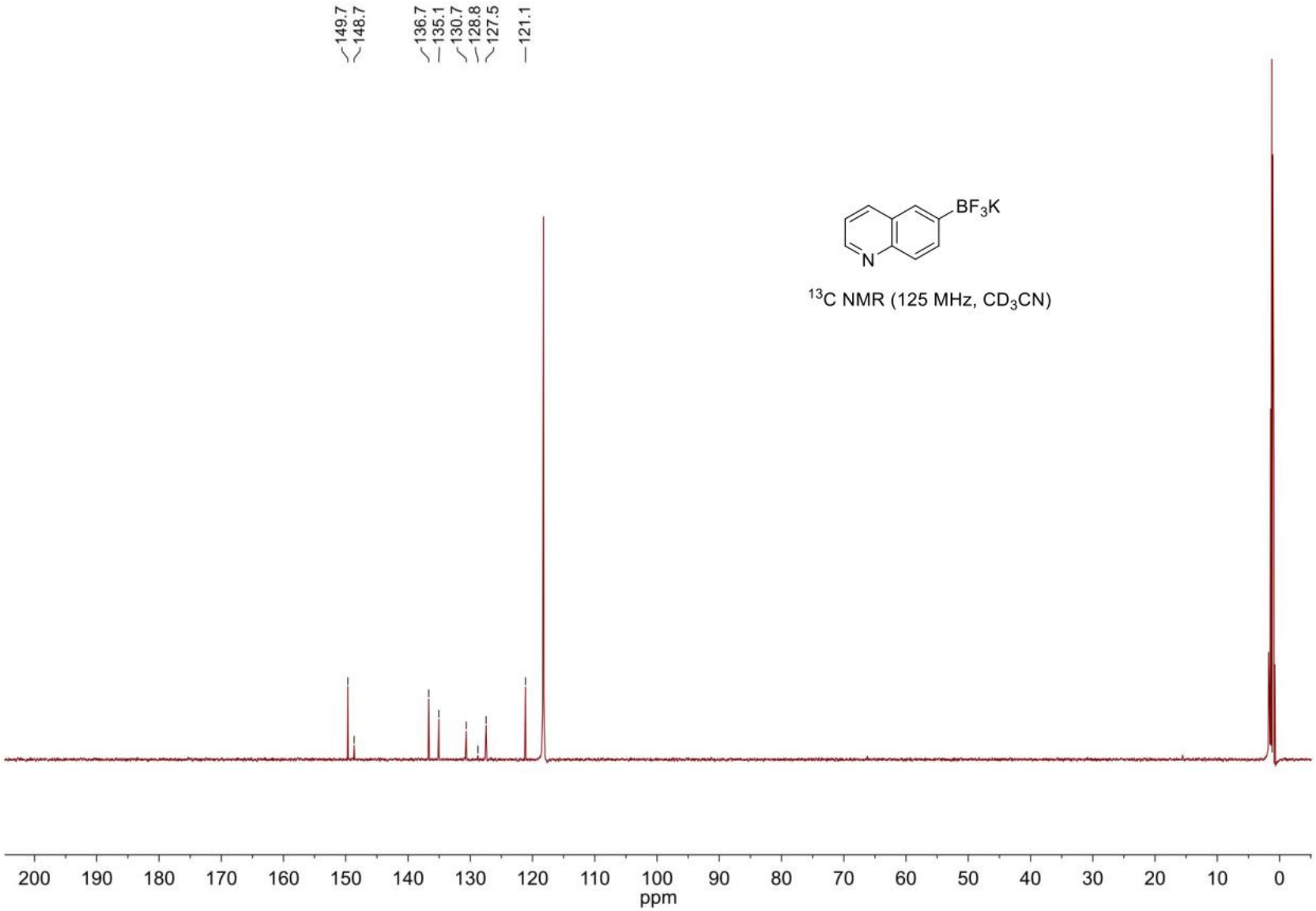
6-(Trifluoro-λ⁴-boraneyl)quinoline, potassium salt (87)



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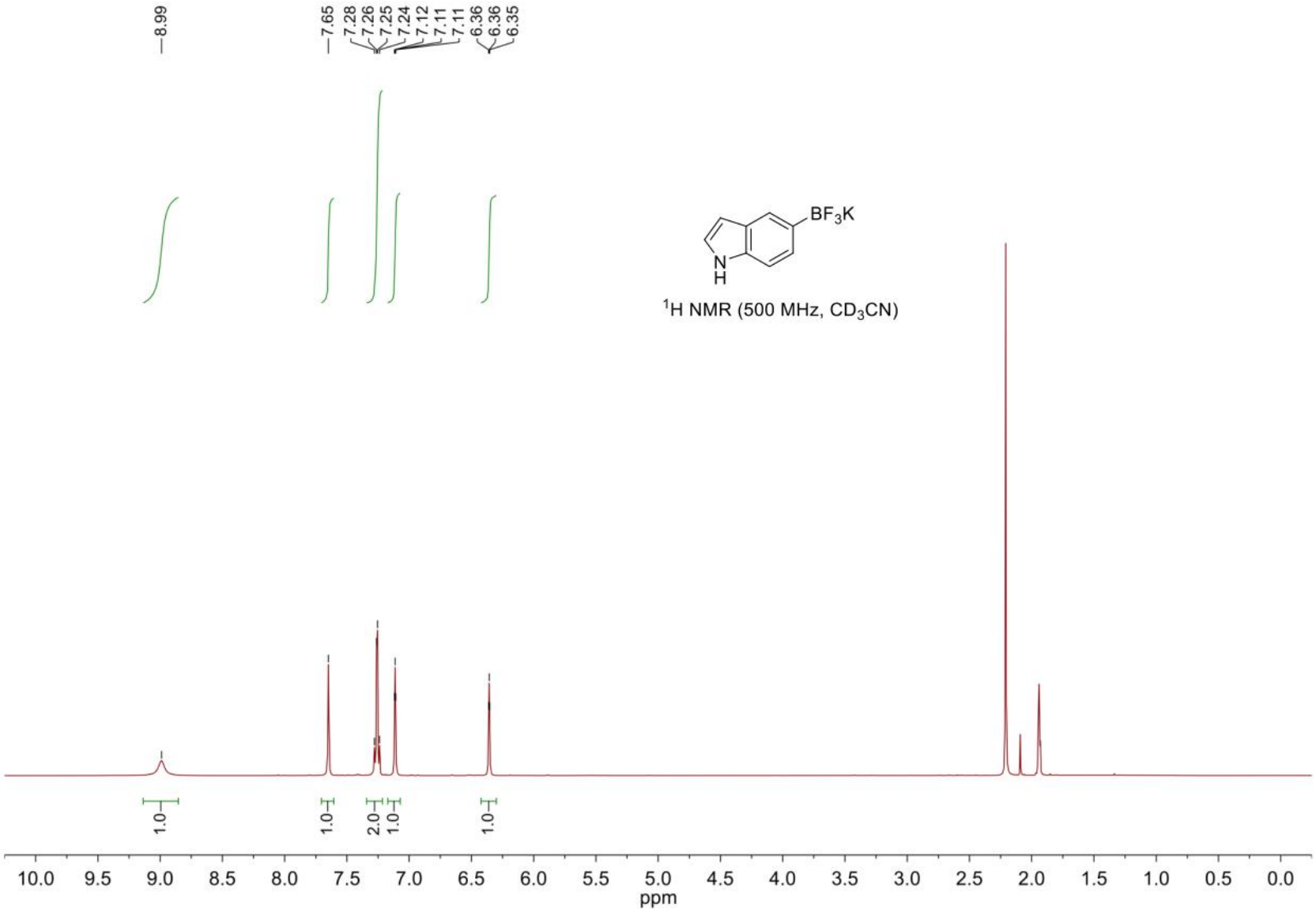
5-(Trifluoro-λ⁴-boraneyl)-1*H*-indole, potassium salt (88)



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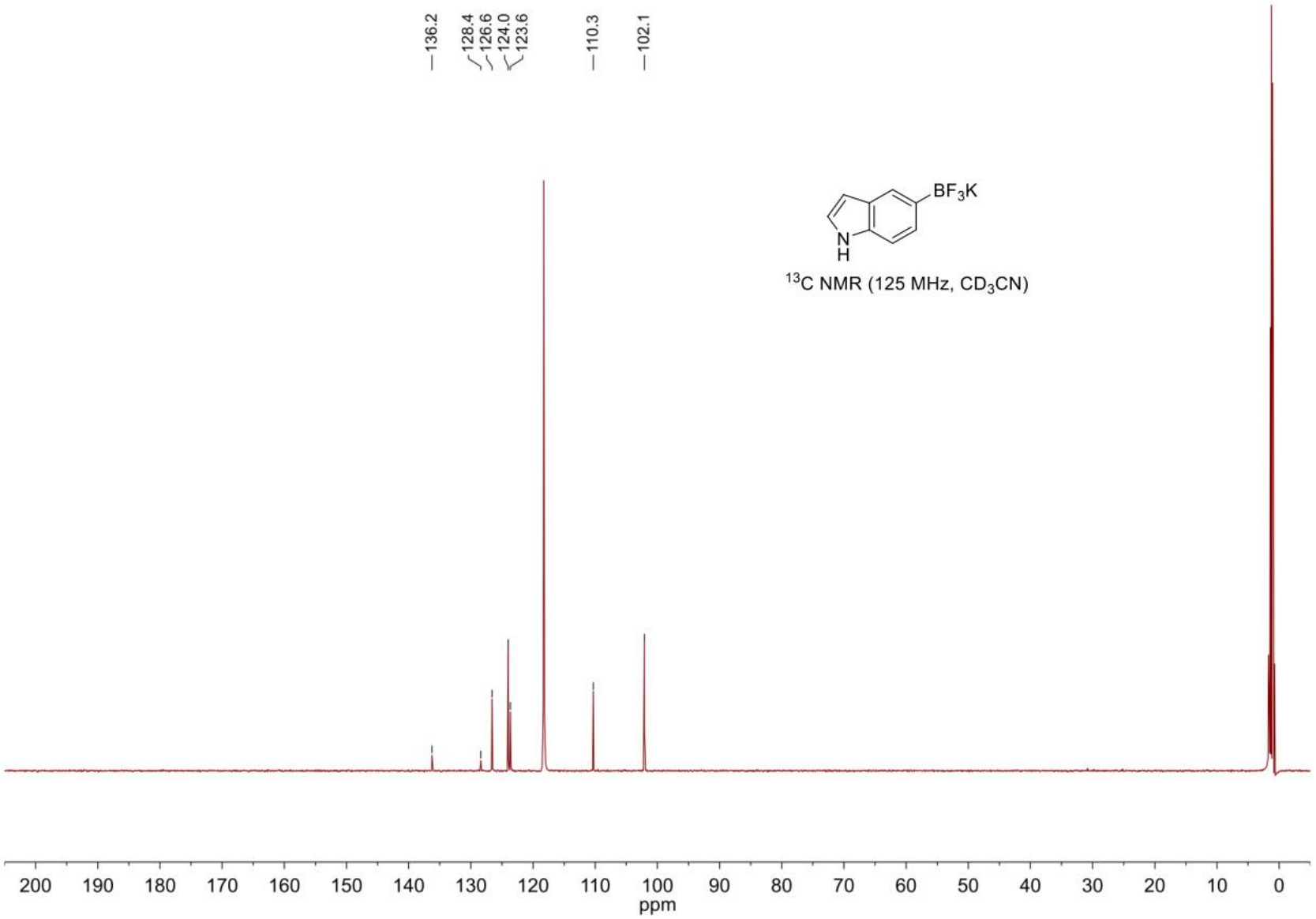
5-(Trifluoro-λ⁴-boraneyl)-1*H*-indole, potassium salt (88)



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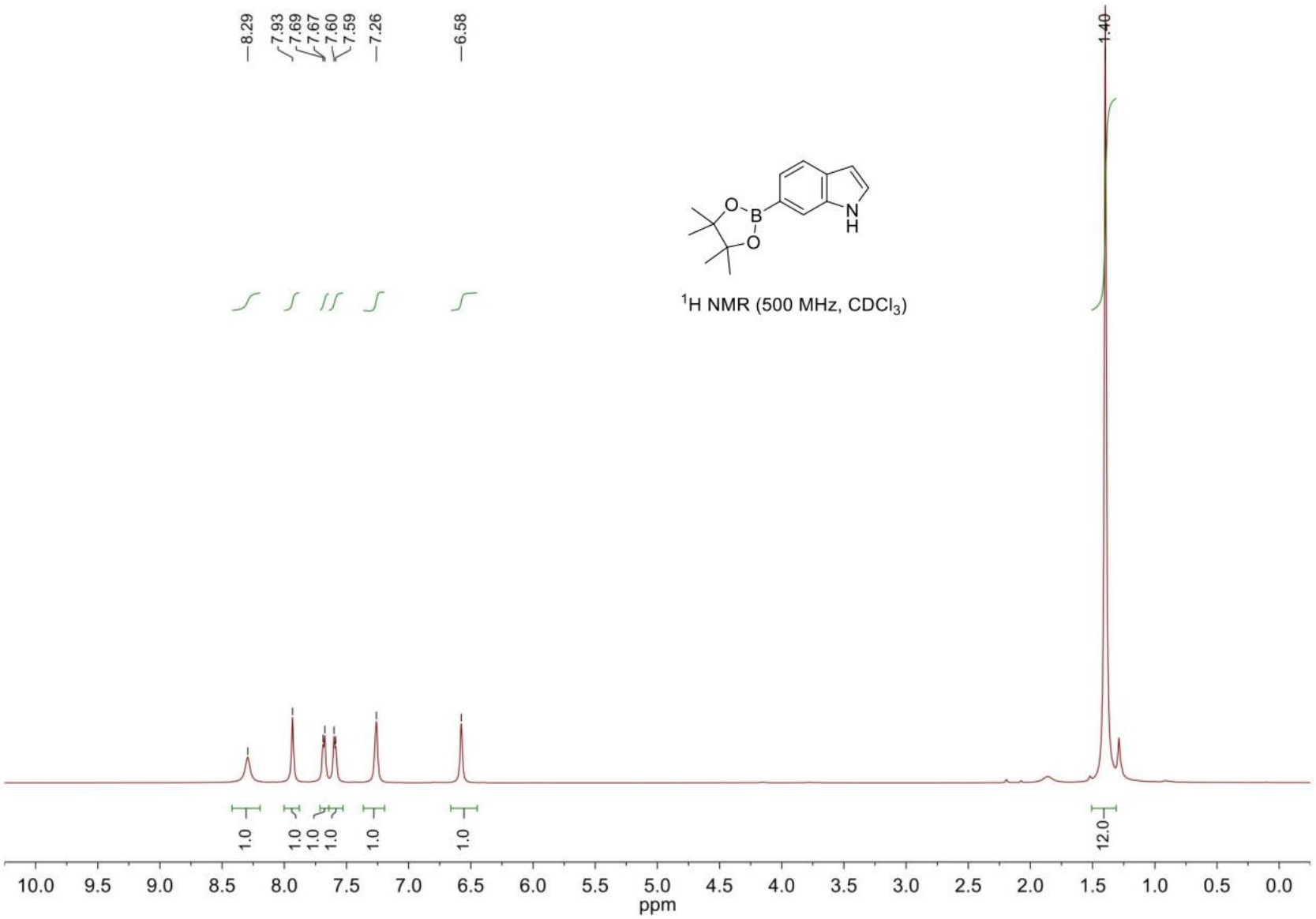
6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (89)



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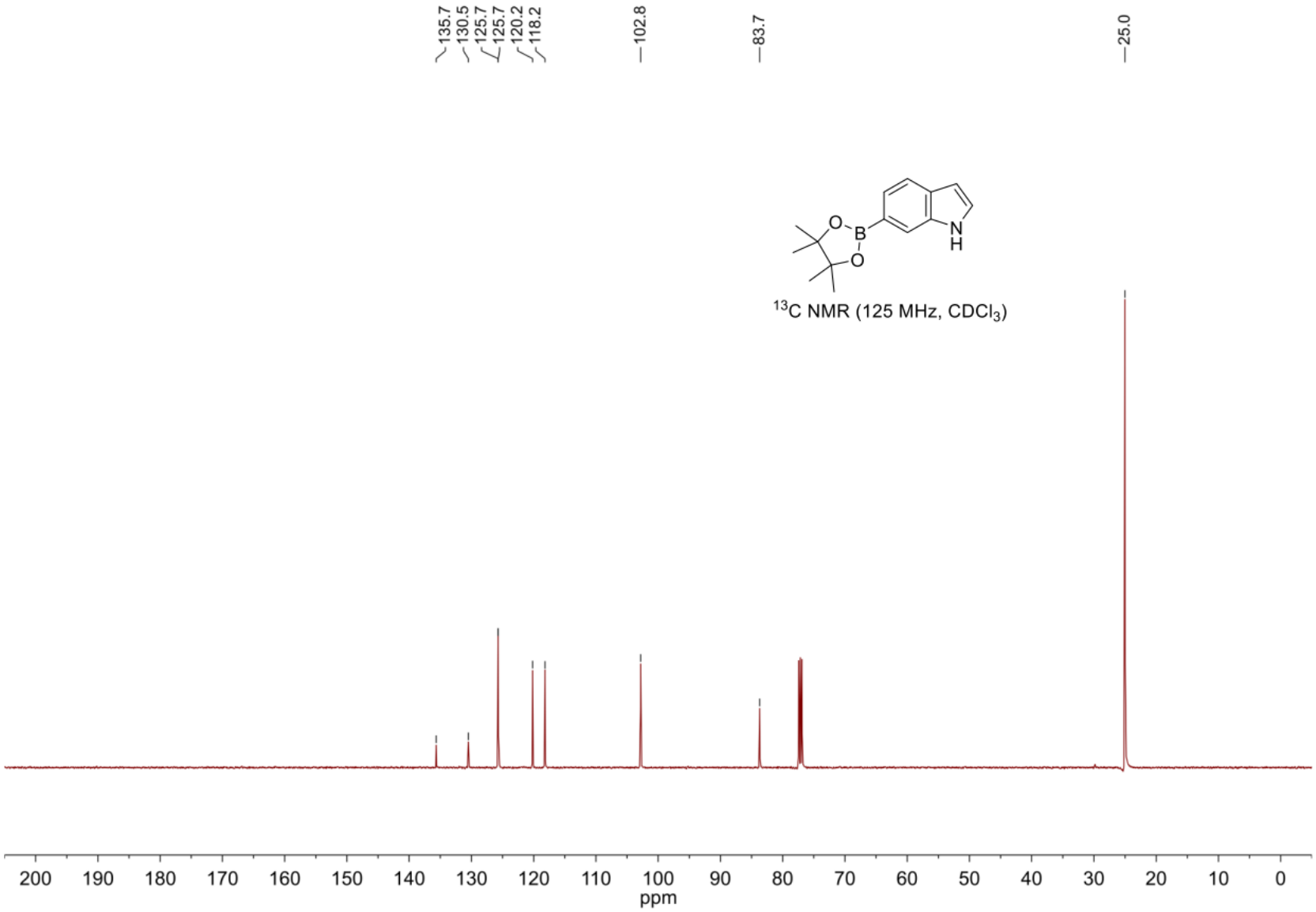
6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (89)



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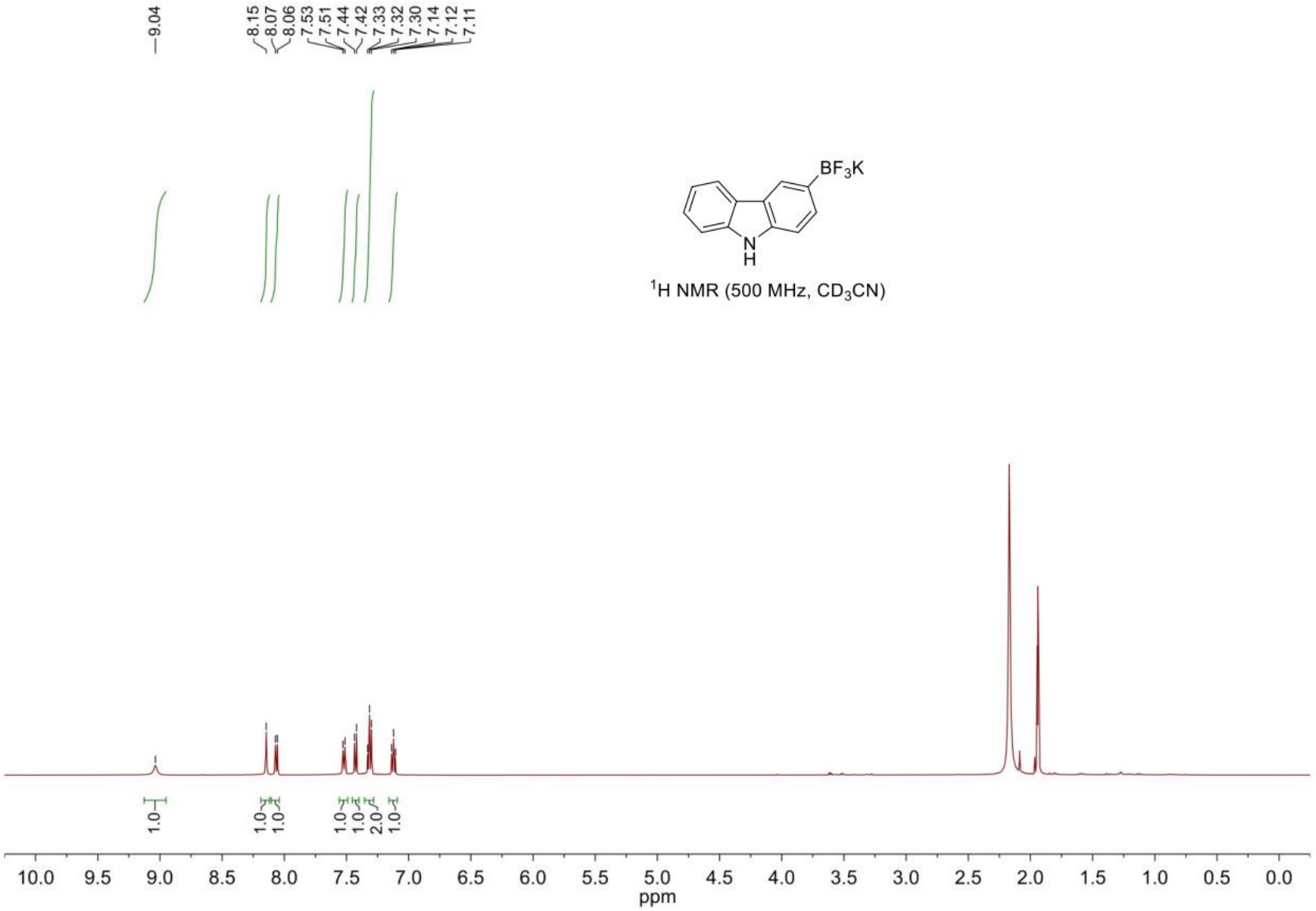
3-(Trifluoro-λ⁴-boraneyl)-9*H*-carbazole, potassium salt (90)



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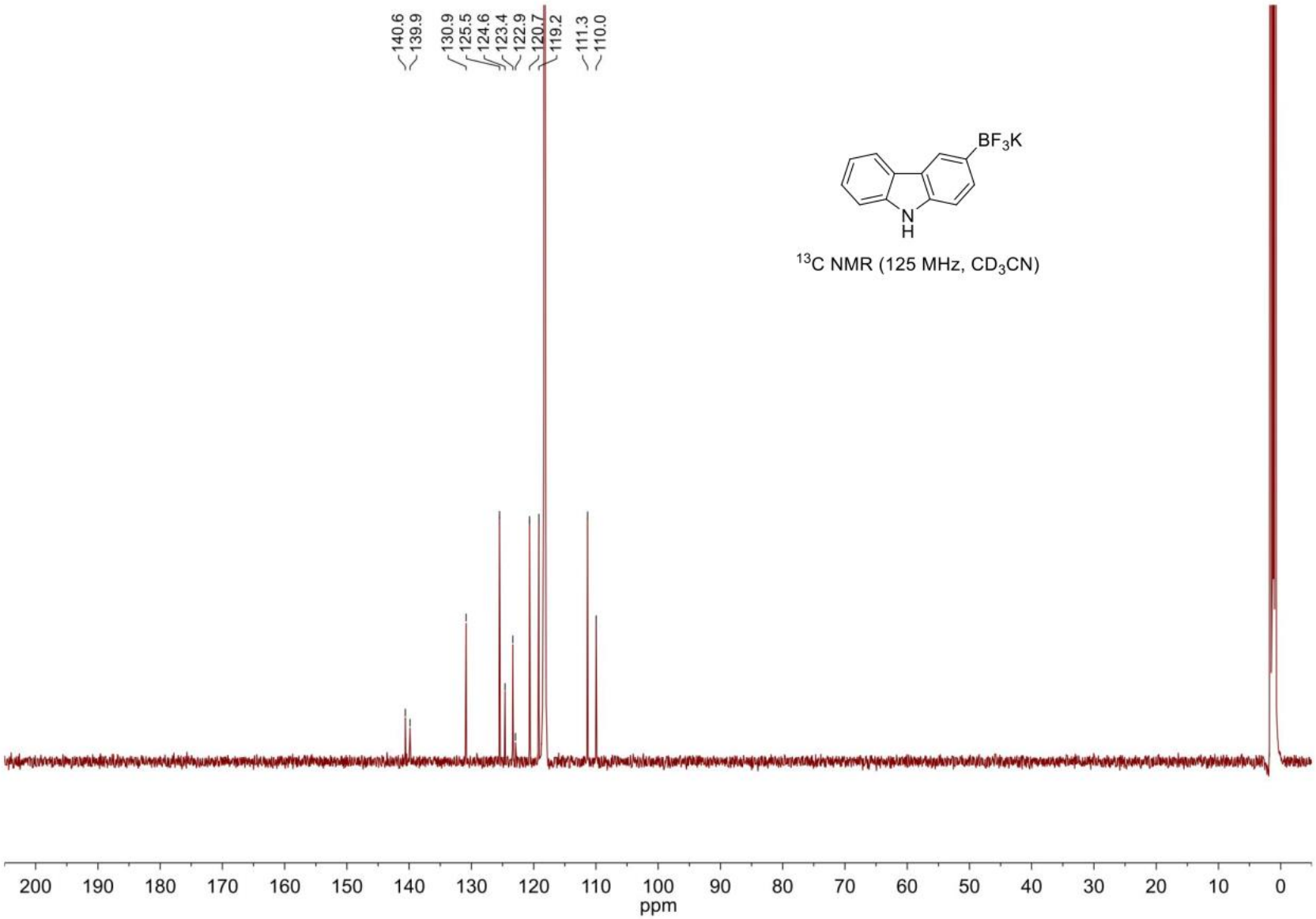
3-(Trifluoro-λ⁴-boraneyl)-9*H*-carbazole, potassium salt (90)



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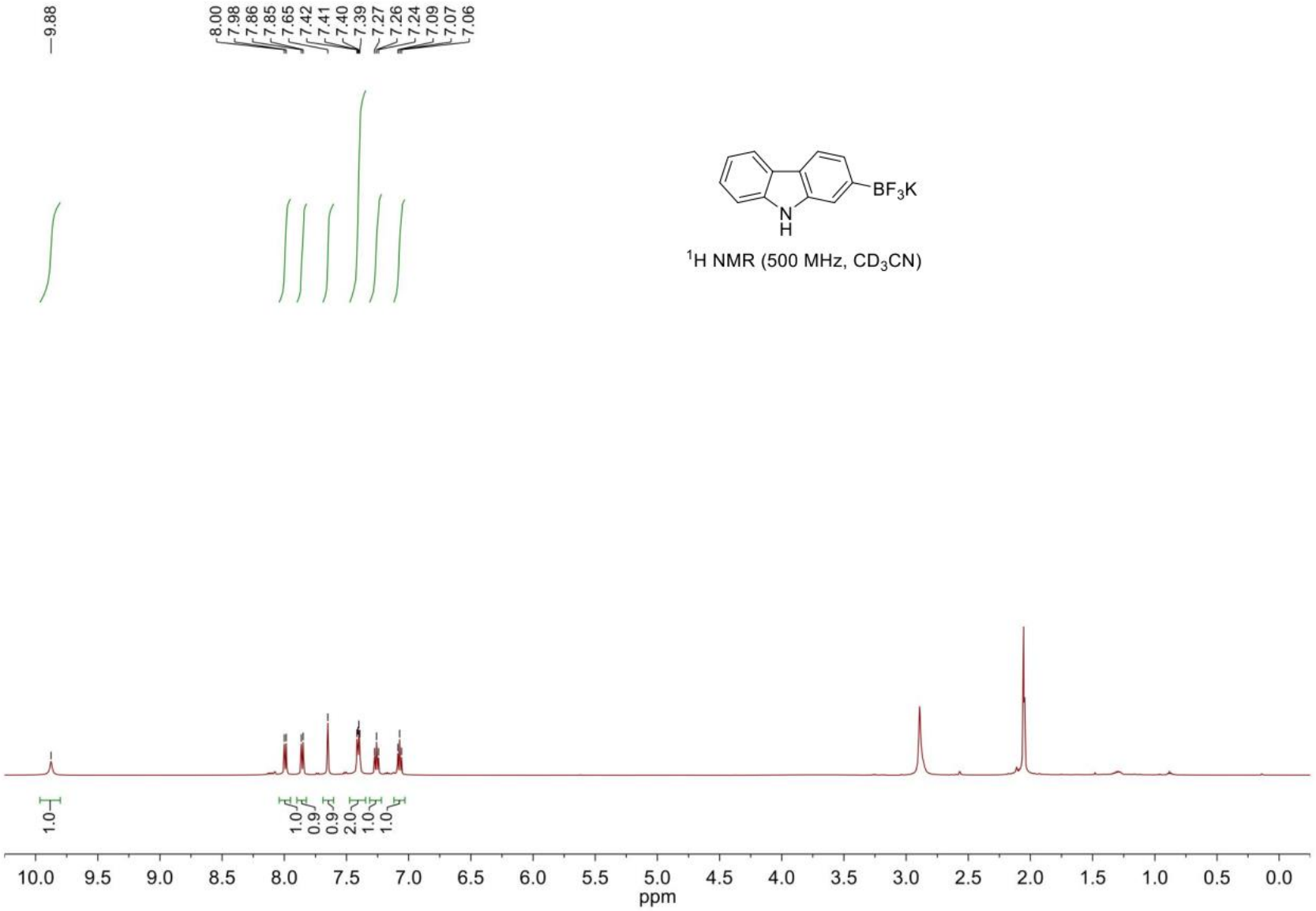
2-(Trifluoro-λ⁴-boraneyl)-9*H*-carbazole, potassium salt (91)



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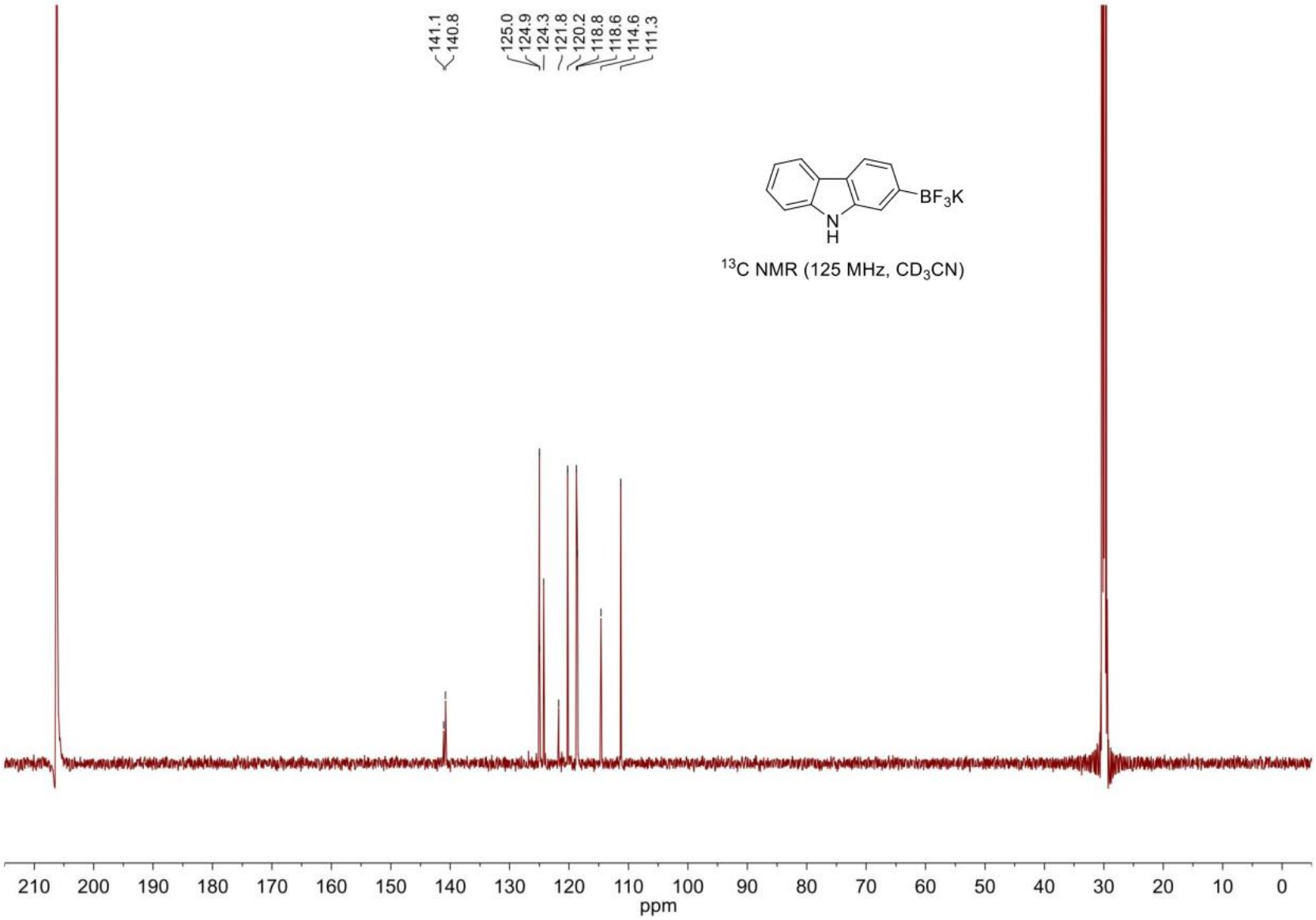
2-(Trifluoro-λ⁴-boraneyl)-9*H*-carbazole, potassium salt (91)



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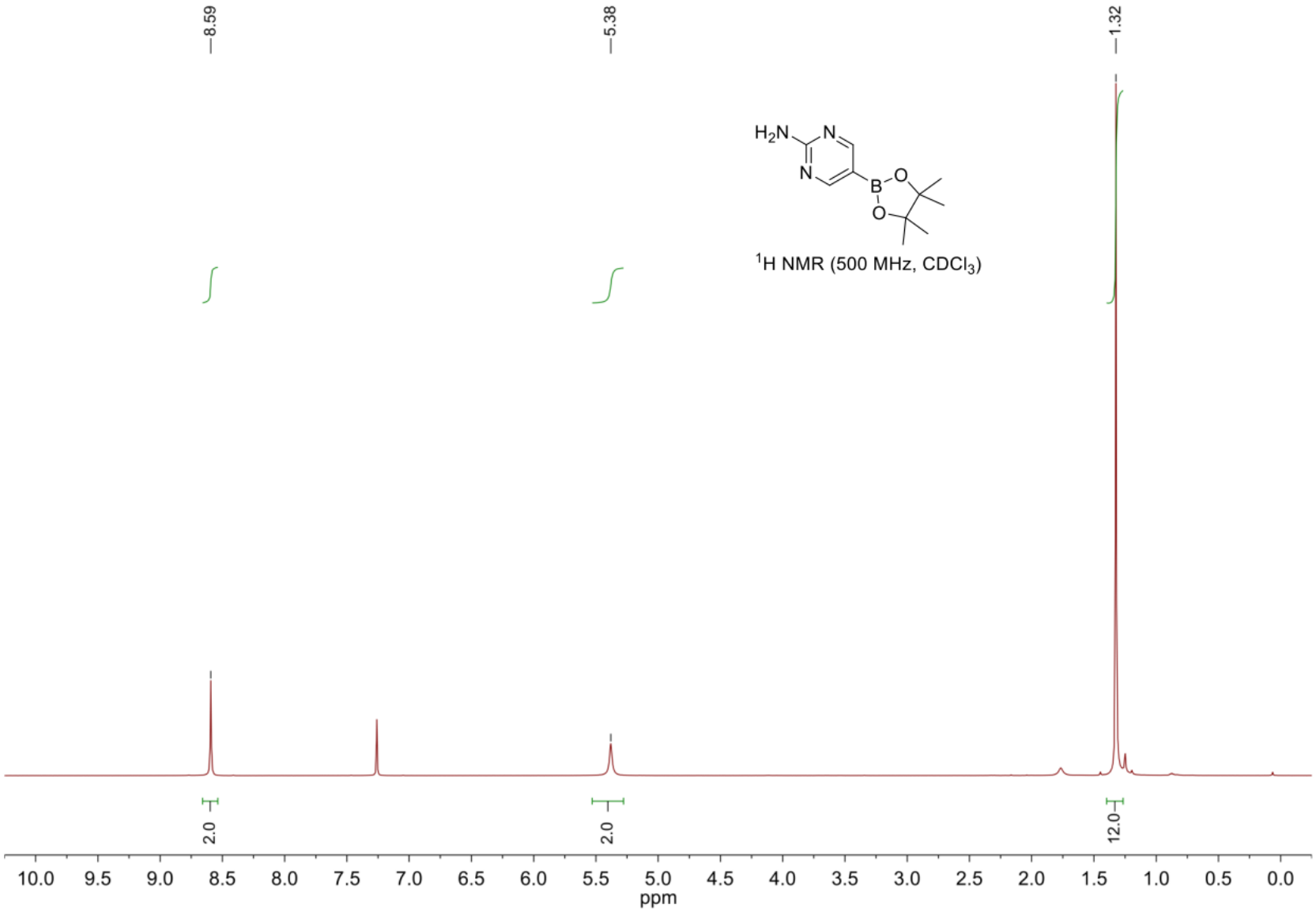
5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pyrimidin-2-amine (92)



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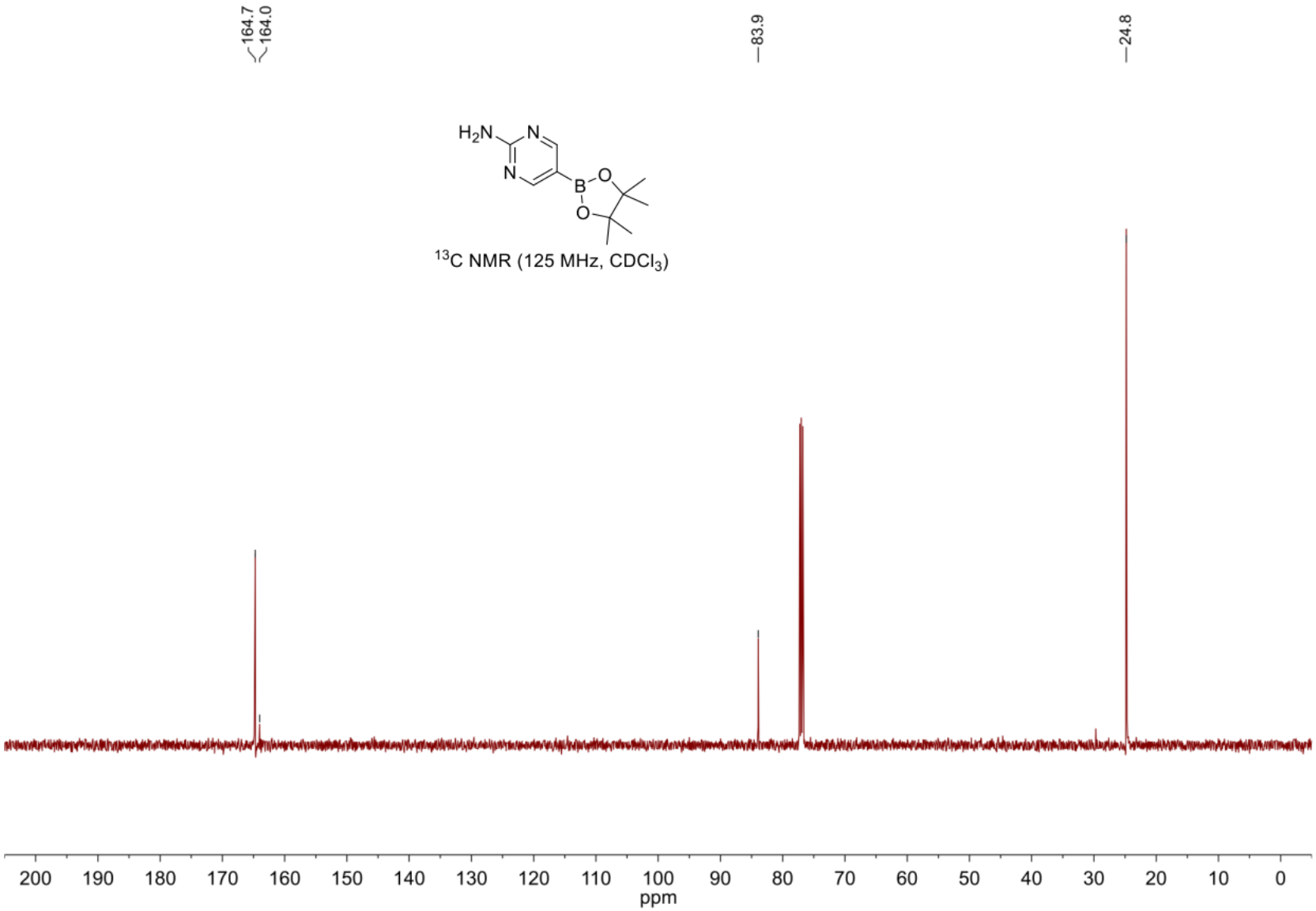
5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pyrimidin-2-amine (92)



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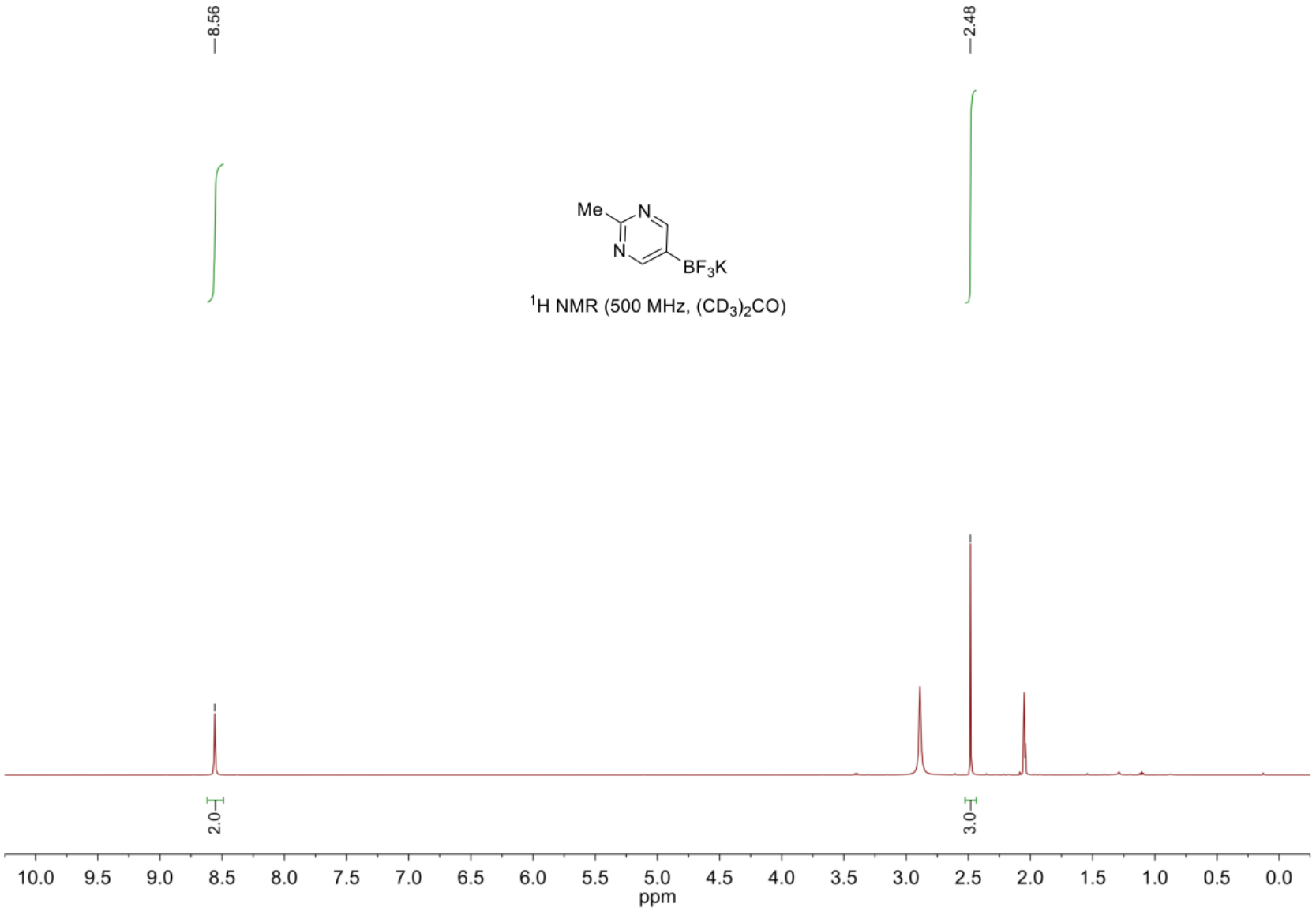
2-Methyl-5-(trifluoro-λ⁴-boraneyl)pyrimidine, potassium salt (93)



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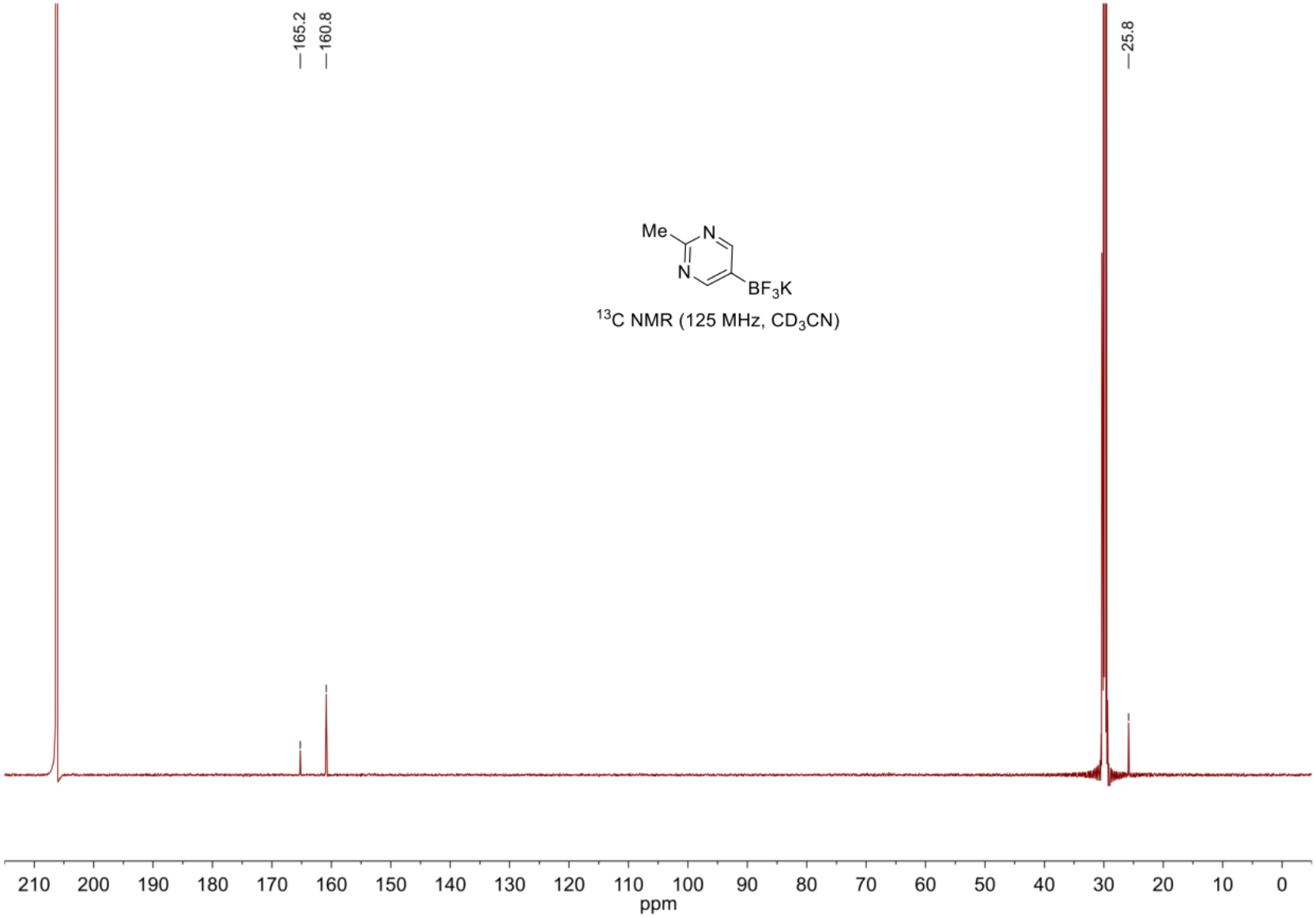
2-Methyl-5-(trifluoro-λ⁴-boraneyl)pyrimidine, potassium salt (93)



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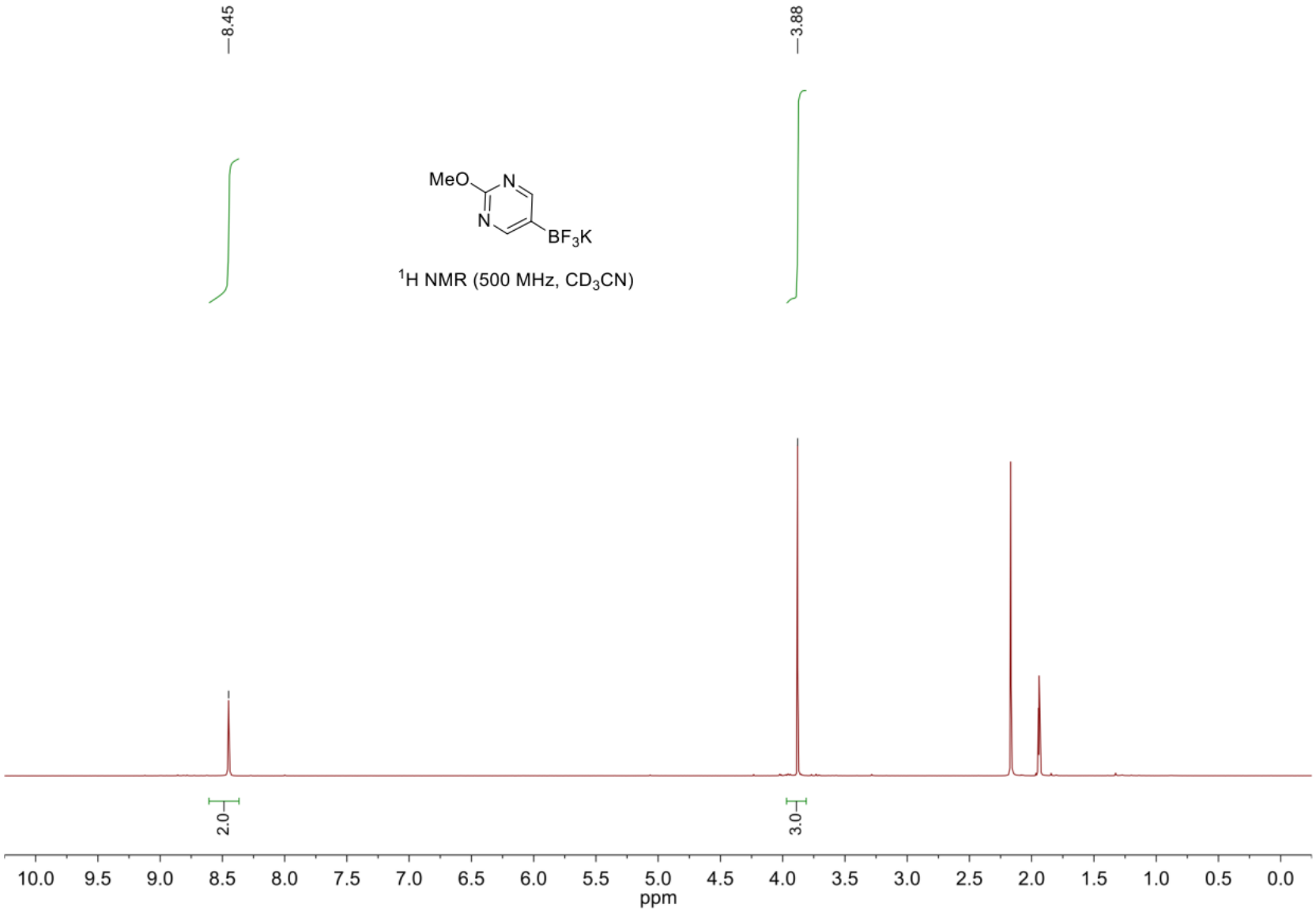
2-Methoxy-5-(trifluoro-λ⁴-boraneyl)pyrimidine, potassium salt (94)



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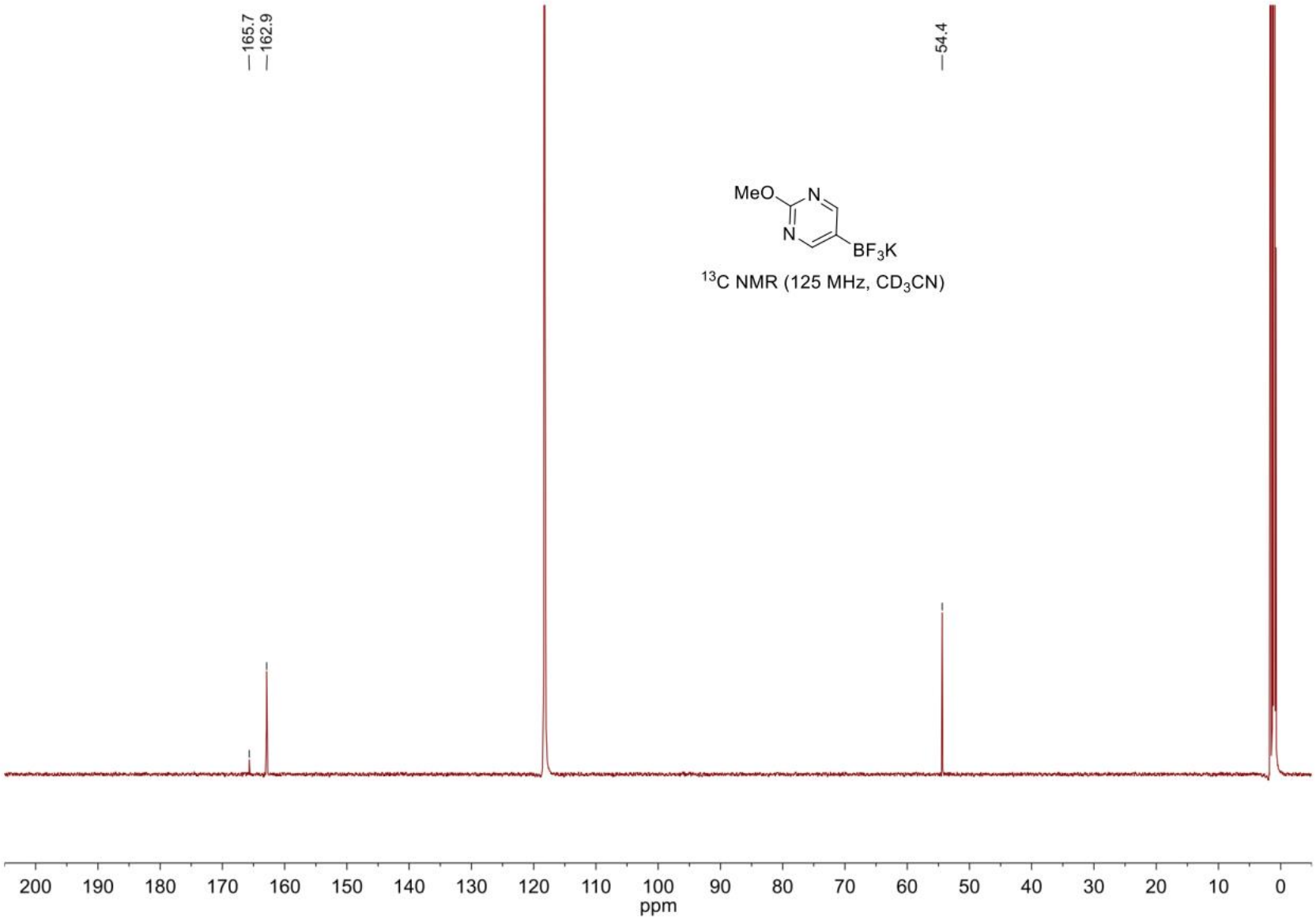
2-Methoxy-5-(trifluoro-λ⁴-boraneyl)pyrimidine, potassium salt (94)



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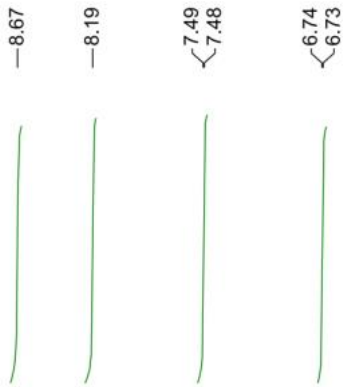
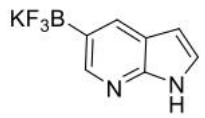
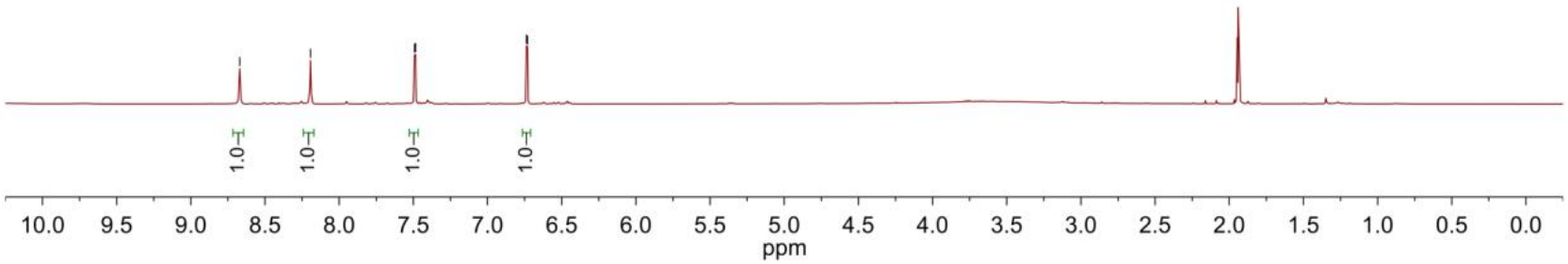
5-(Trifluoro-λ⁴-boraneyl)-1*H*-pyrrolo[2,3-*b*]pyridine, potassium salt (95)





^{1}H NMR (500 MHz, CD_3CN)



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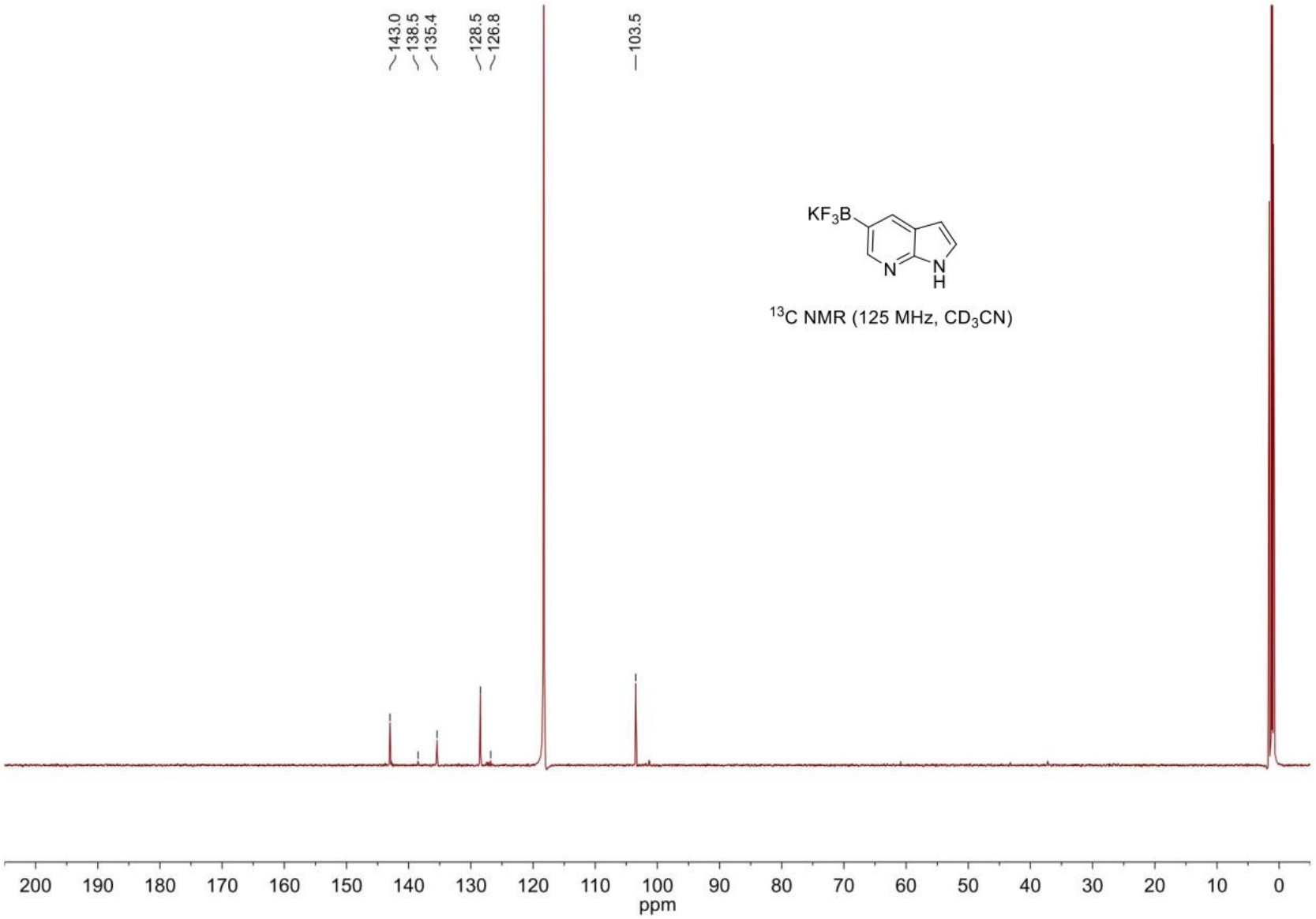
5-(Trifluoro-λ⁴-boraneyl)-1*H*-pyrrolo[2,3-*b*]pyridine, potassium salt (95)



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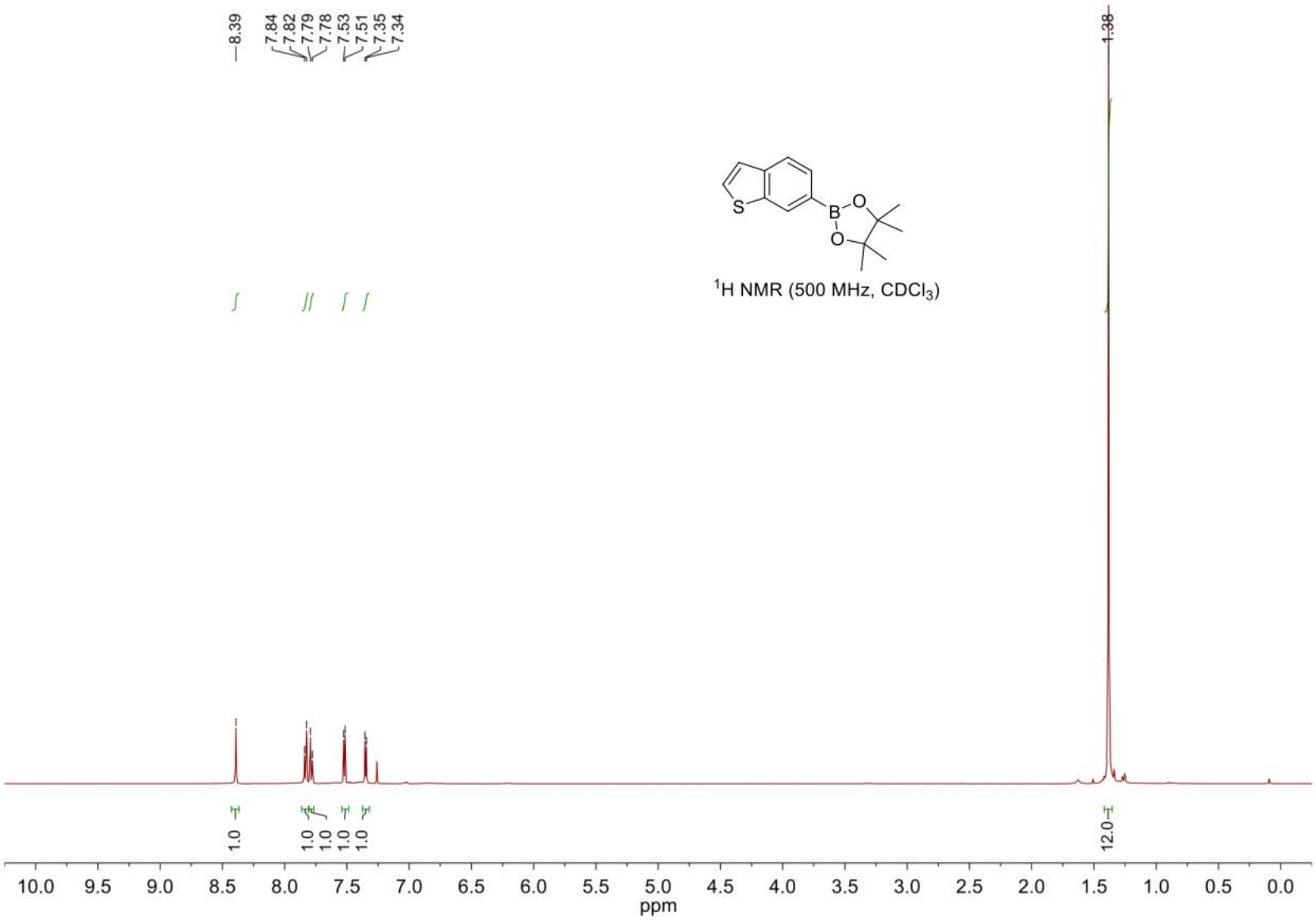
2-(Benzo[*b*]thiophen-6-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (96)



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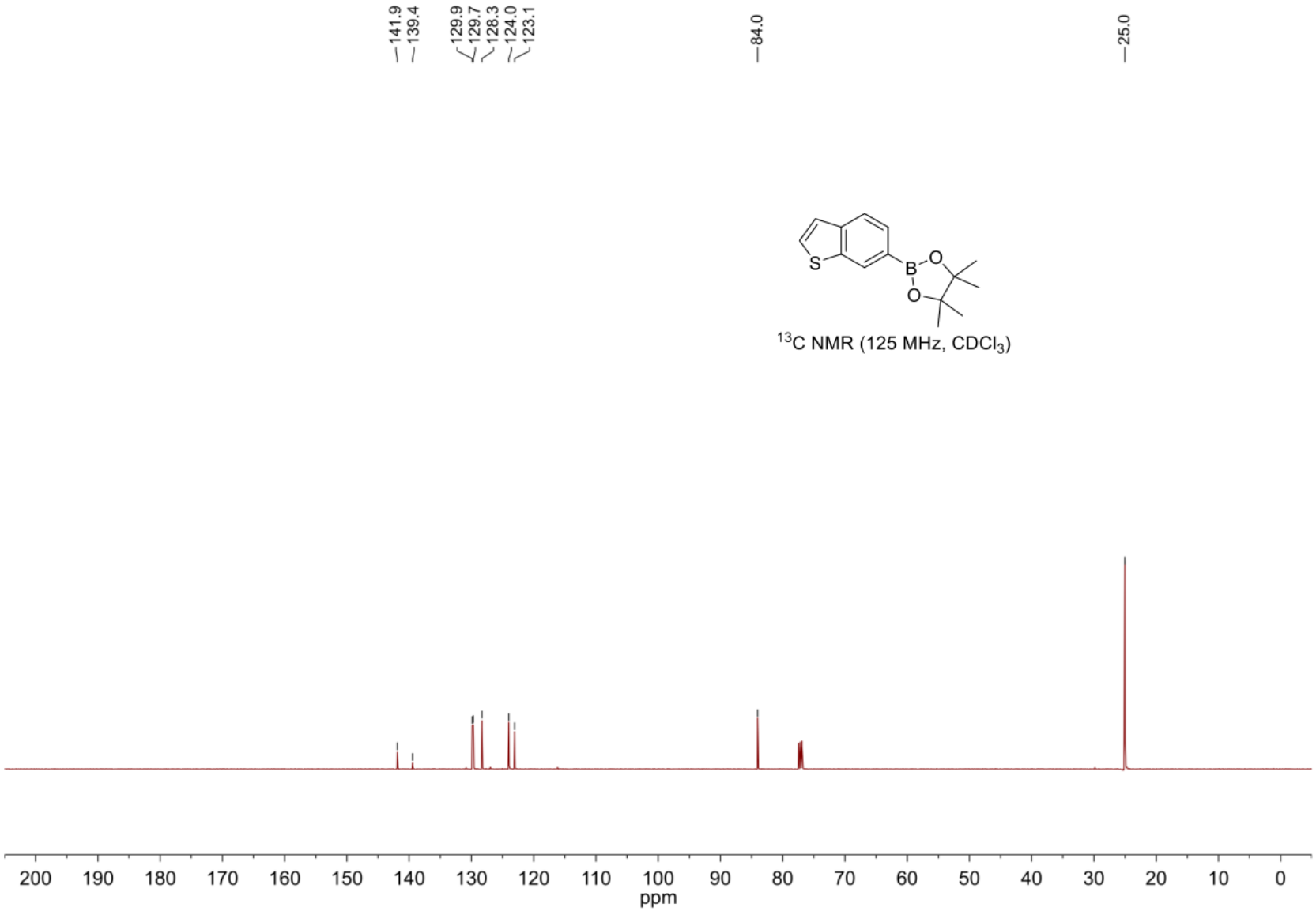
2-(Benzo[*b*]thiophen-6-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (96)



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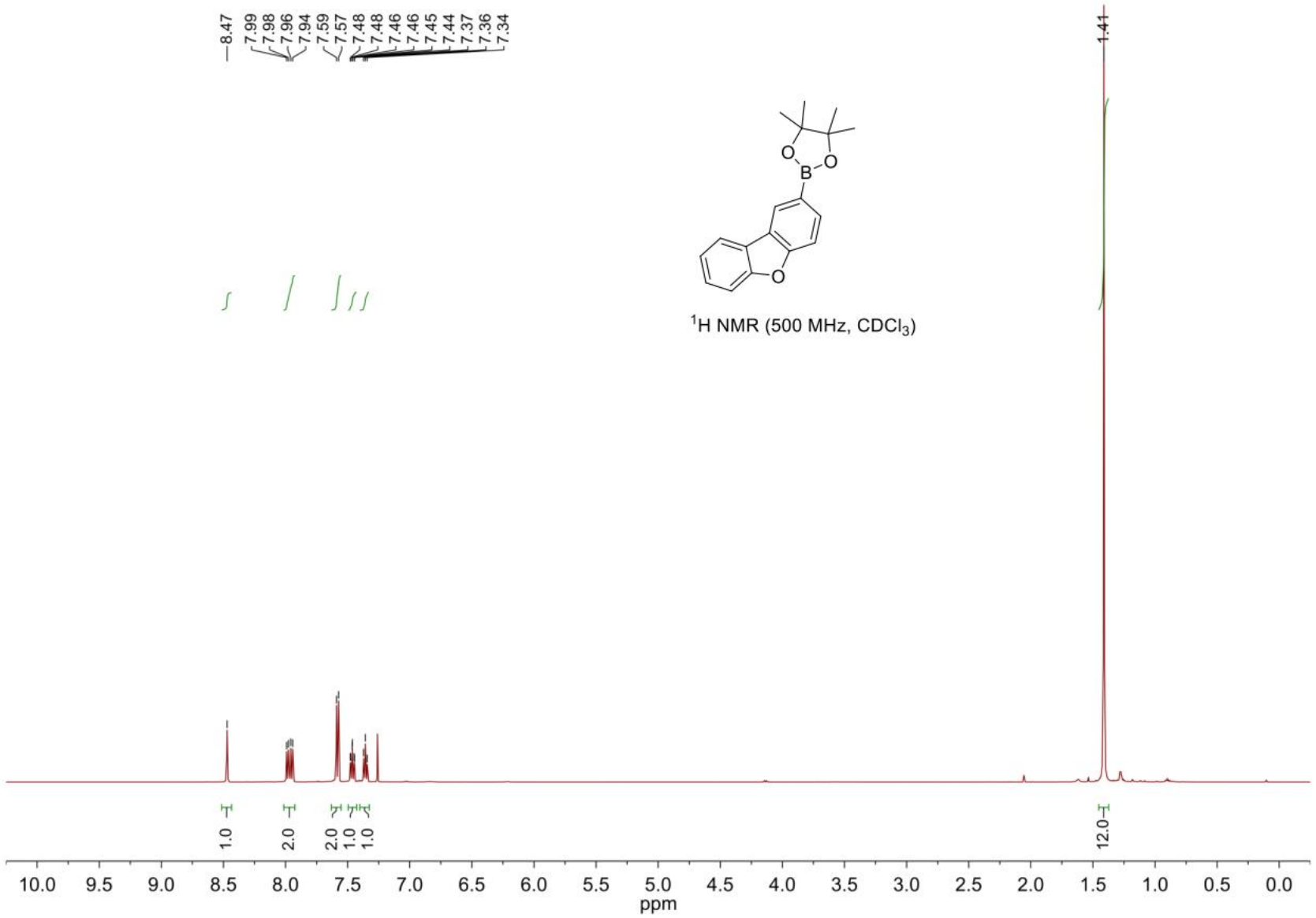
2-(Dibenzo[*b*,*d*]furan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (97)



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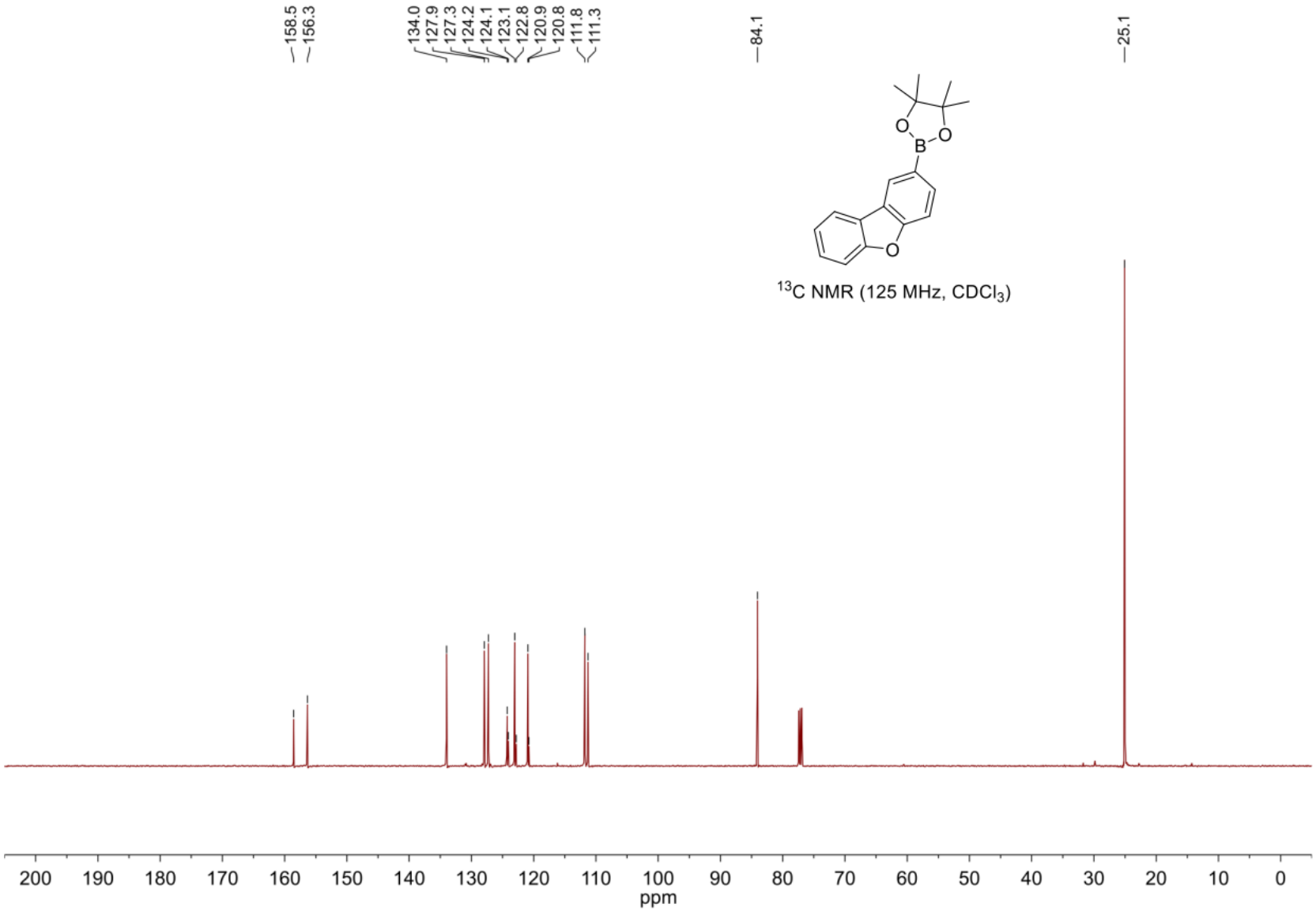
2-(Dibenzo[*b*,*d*]furan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (97)



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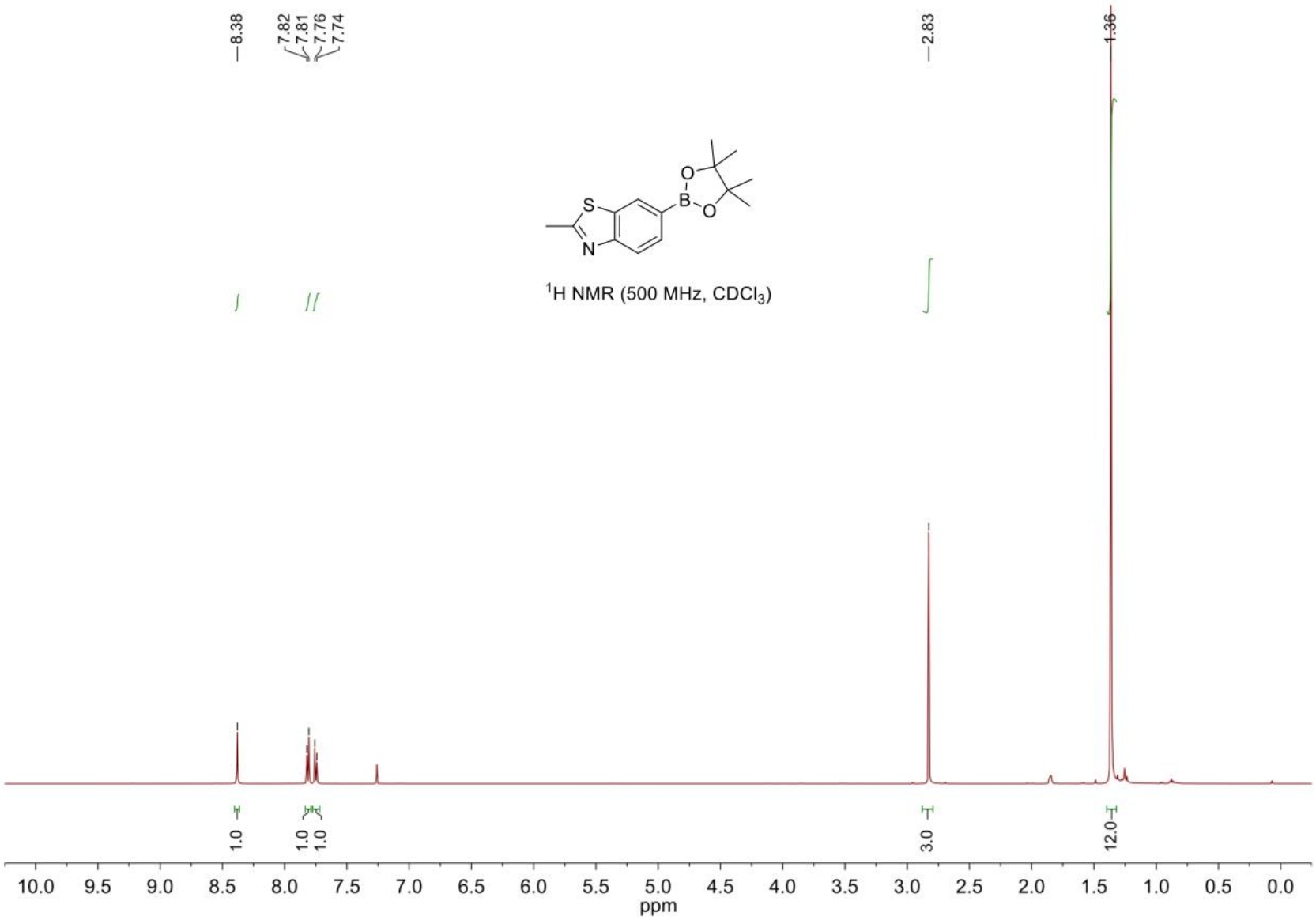
6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*d*]thiazole (98)



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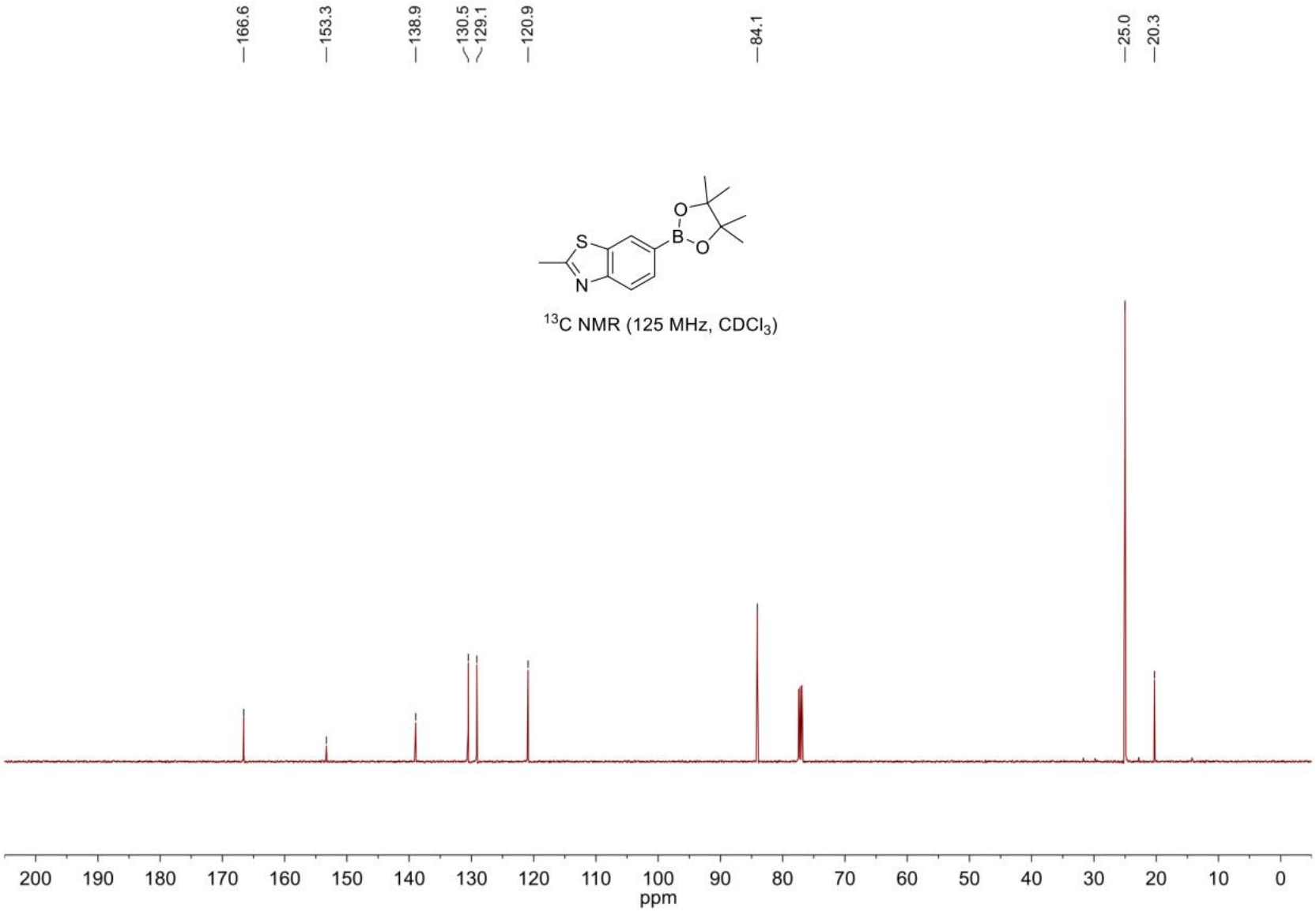
6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*d*]thiazole (98)



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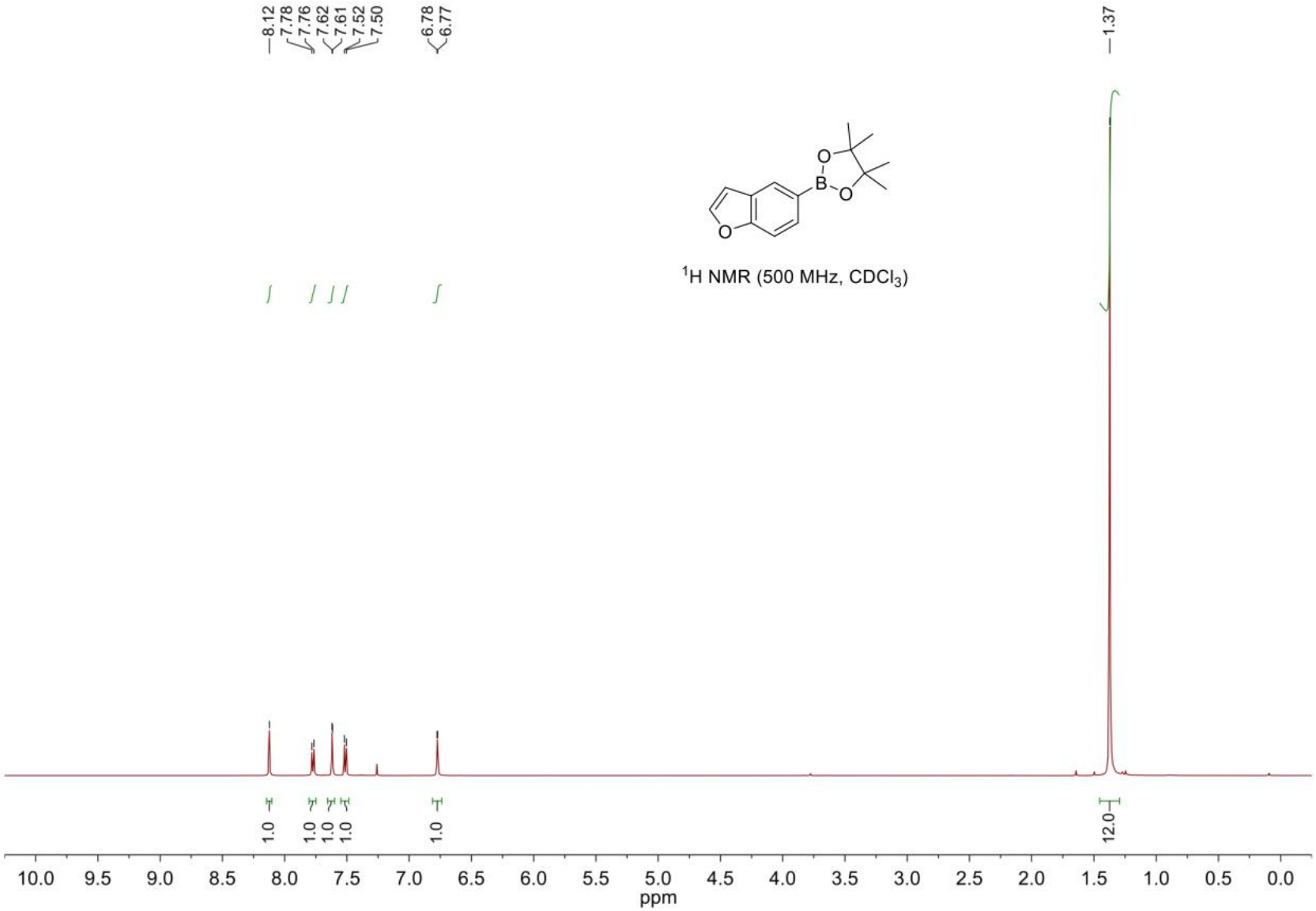
2-(Benzofuran-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (98)



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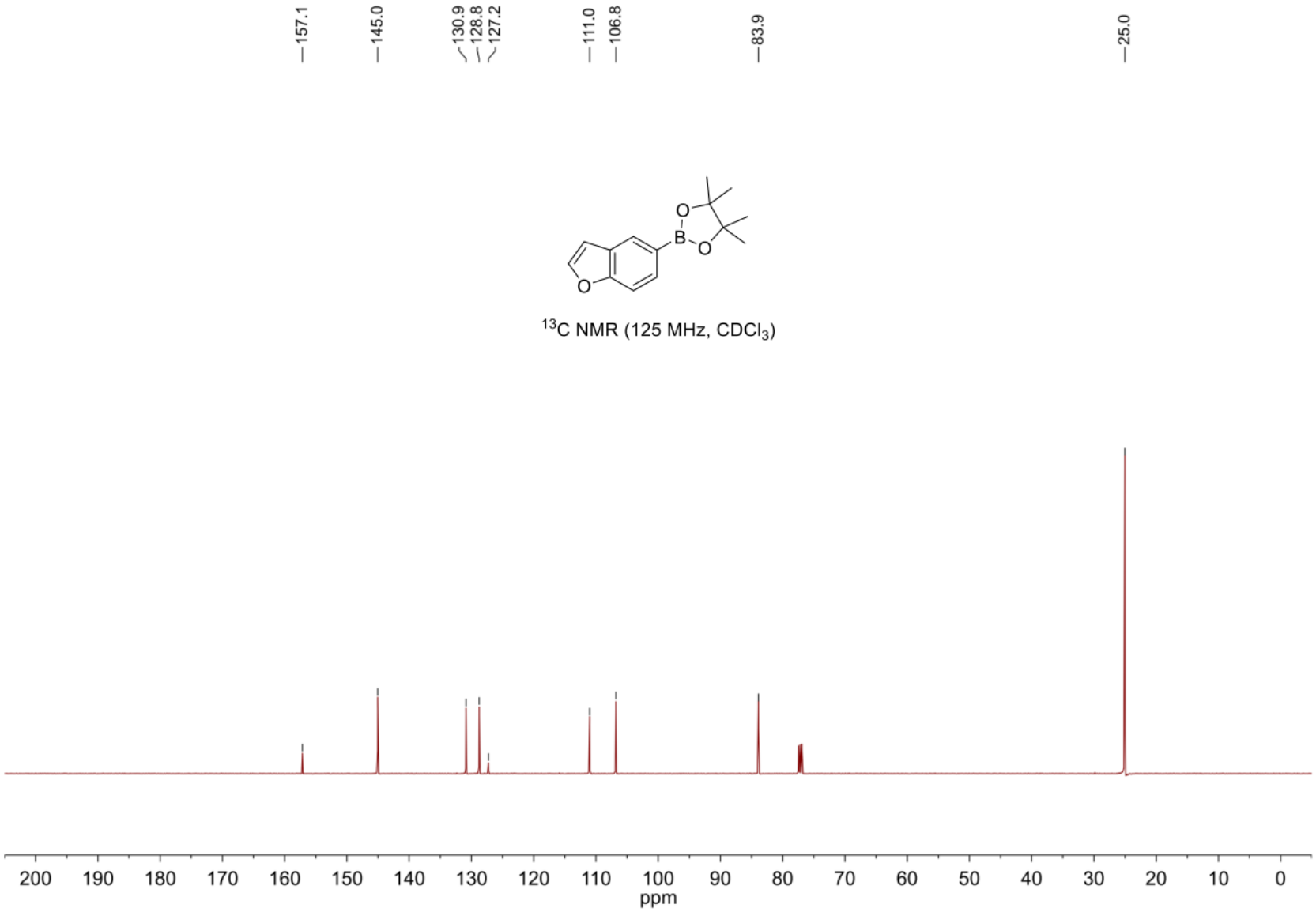
2-(Benzofuran-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (99)



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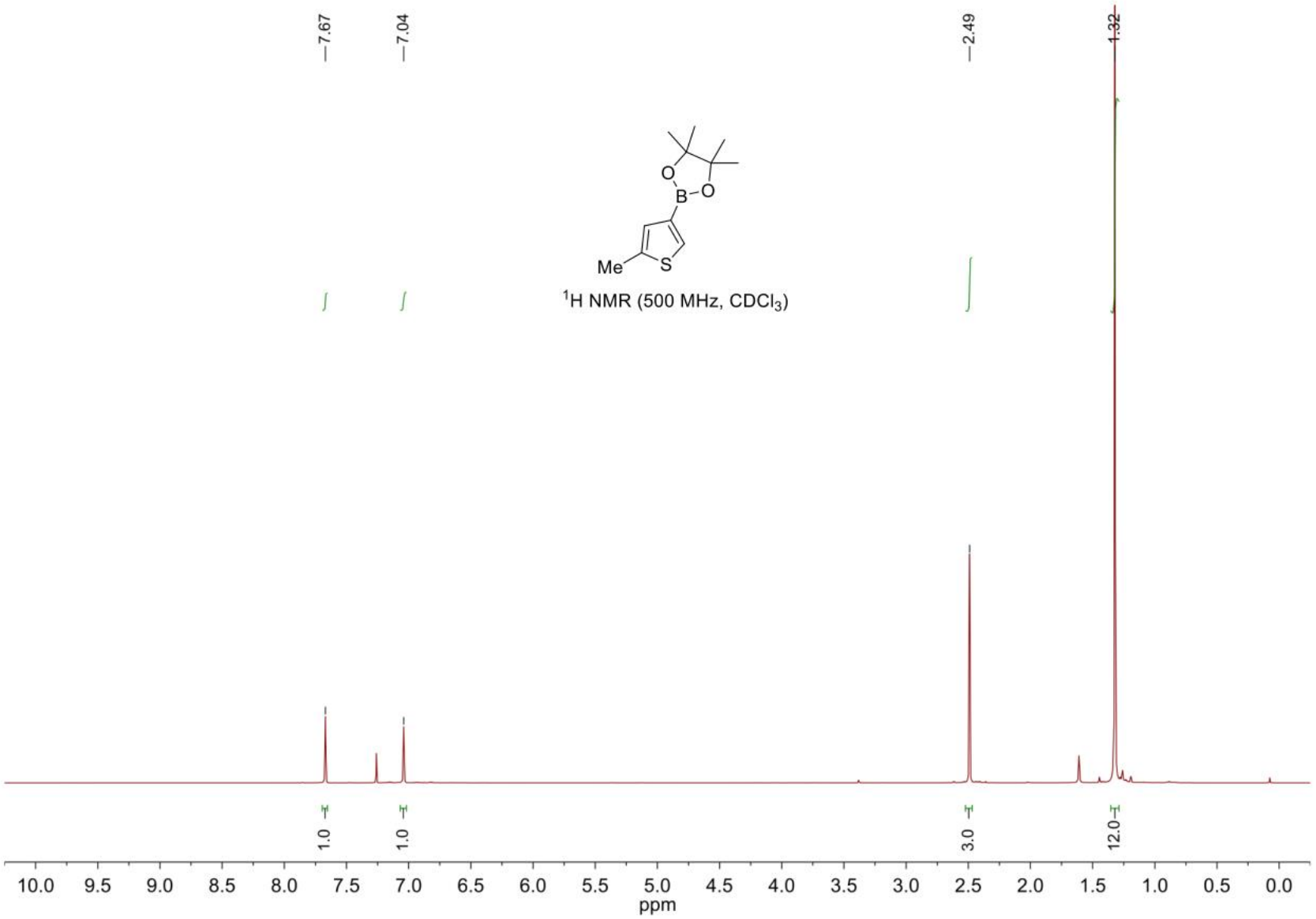
4,4,5,5-Tetramethyl-2-(5-methylthiophen-3-yl)-1,3,2-dioxaborolane (100)



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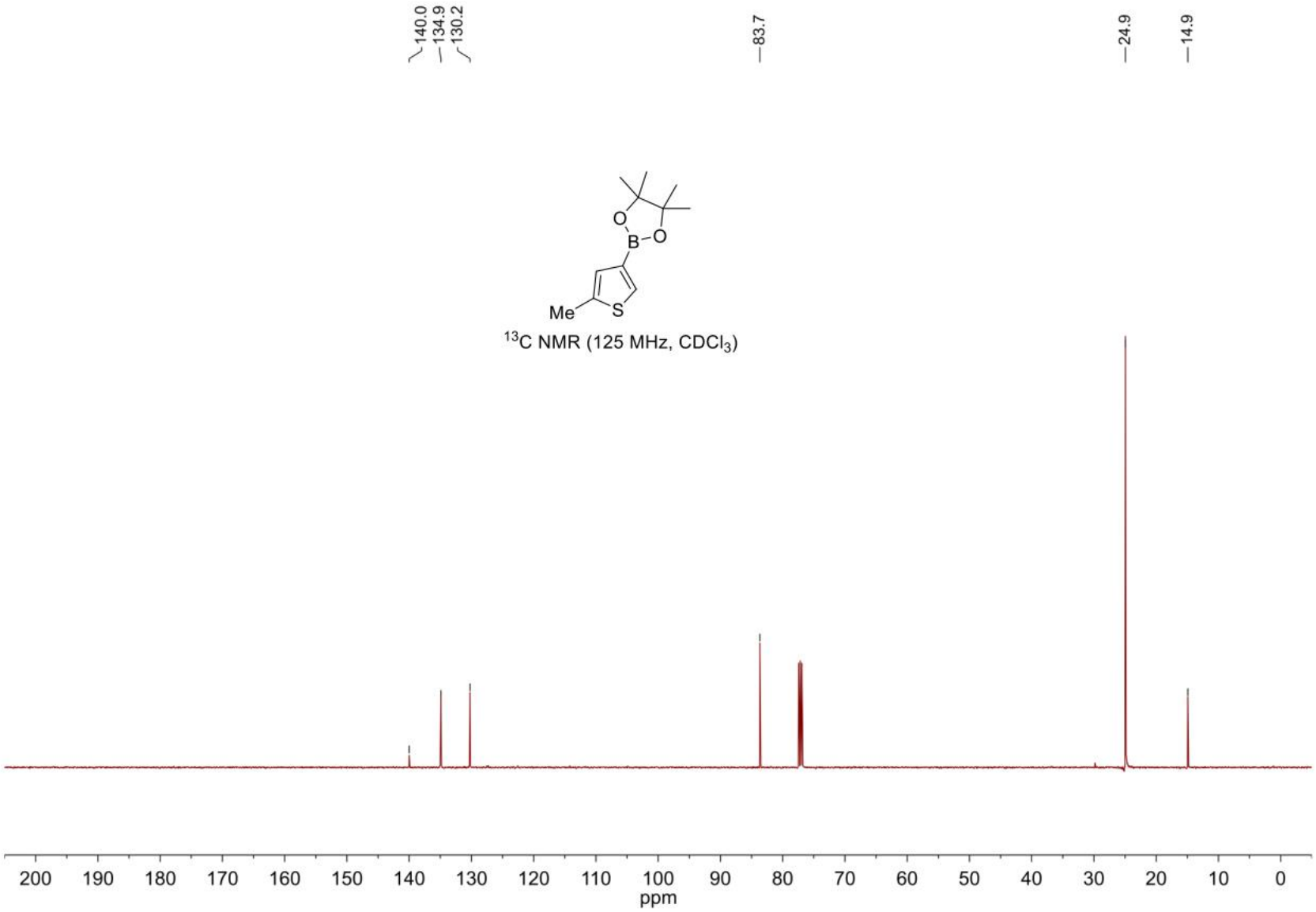
4,4,5,5-Tetramethyl-2-(5-methylthiophen-3-yl)-1,3,2-dioxaborolane (100)



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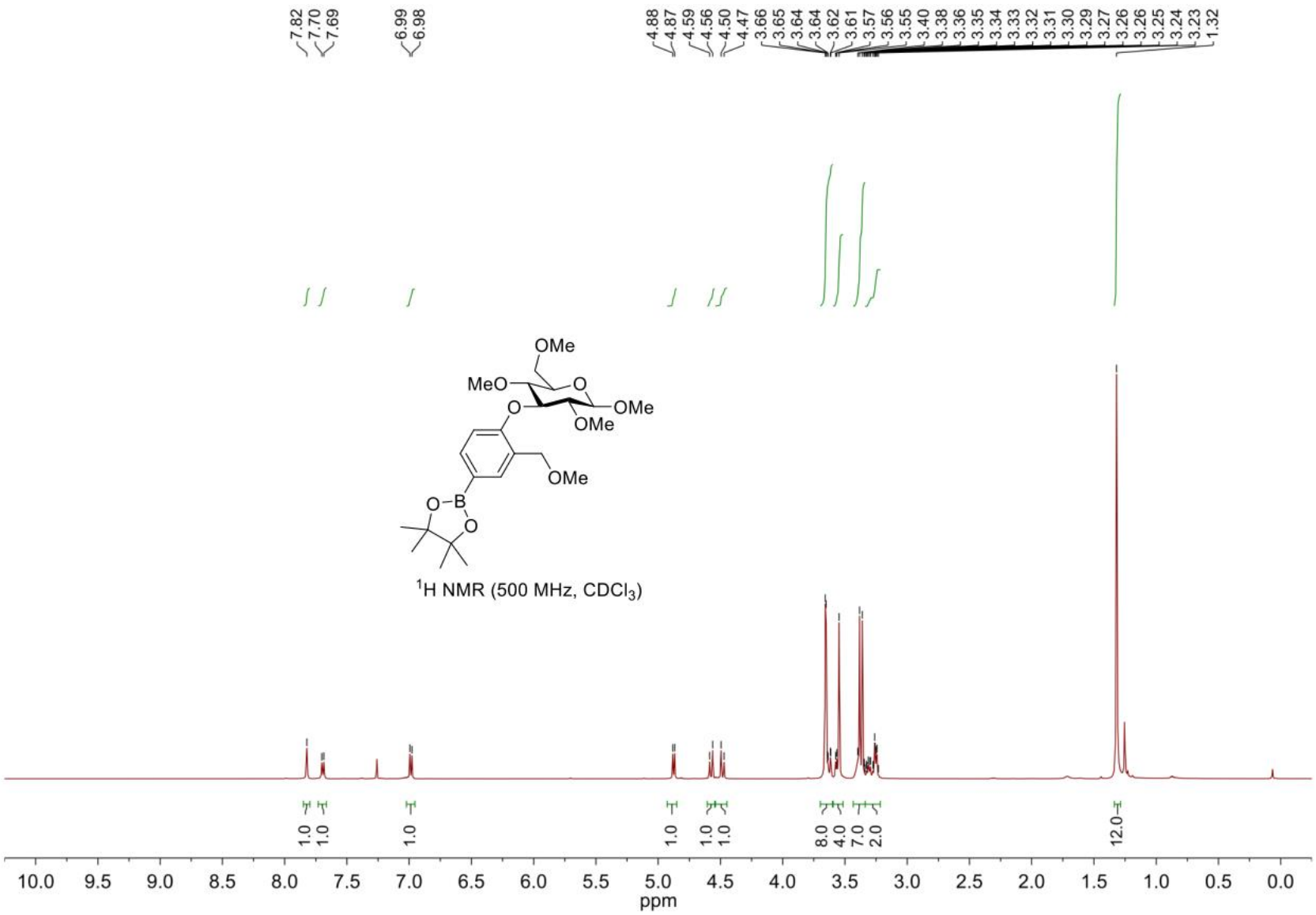
2-(3-(Methoxymethyl)-4-(((2*R*,3*R*,4*S*,5*R*,6*R*)-2,3,5-trimethoxy-6-(methoxymethyl)tetrahydro-2*H*-pyran-4-yl)oxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (101)



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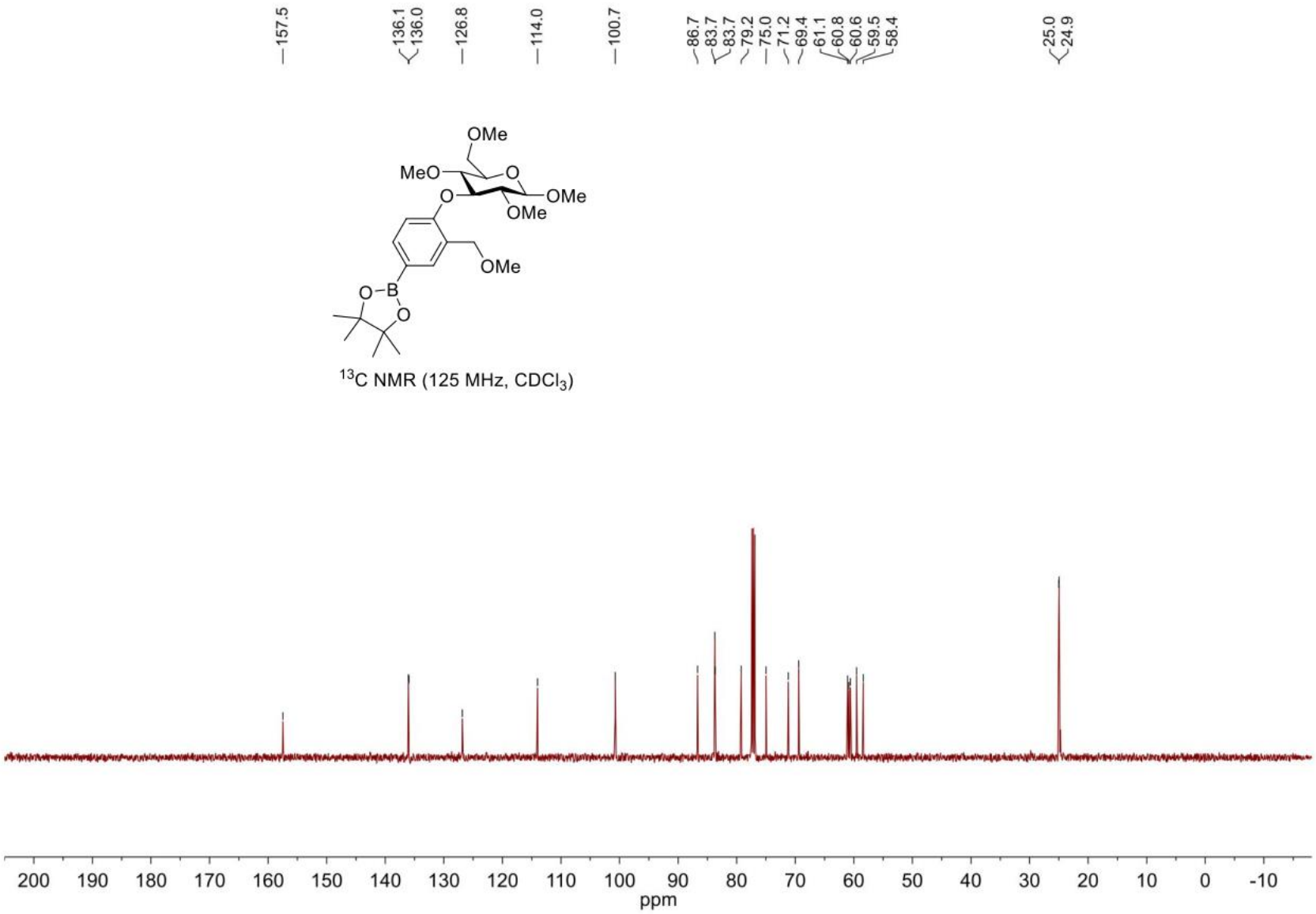
2-(3-(Methoxymethyl)-4-(((2*R*,3*R*,4*S*,5*R*,6*R*)-2,3,5-trimethoxy-6-(methoxymethyl)tetrahydro-2*H*-pyran-4-yl)oxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (101)



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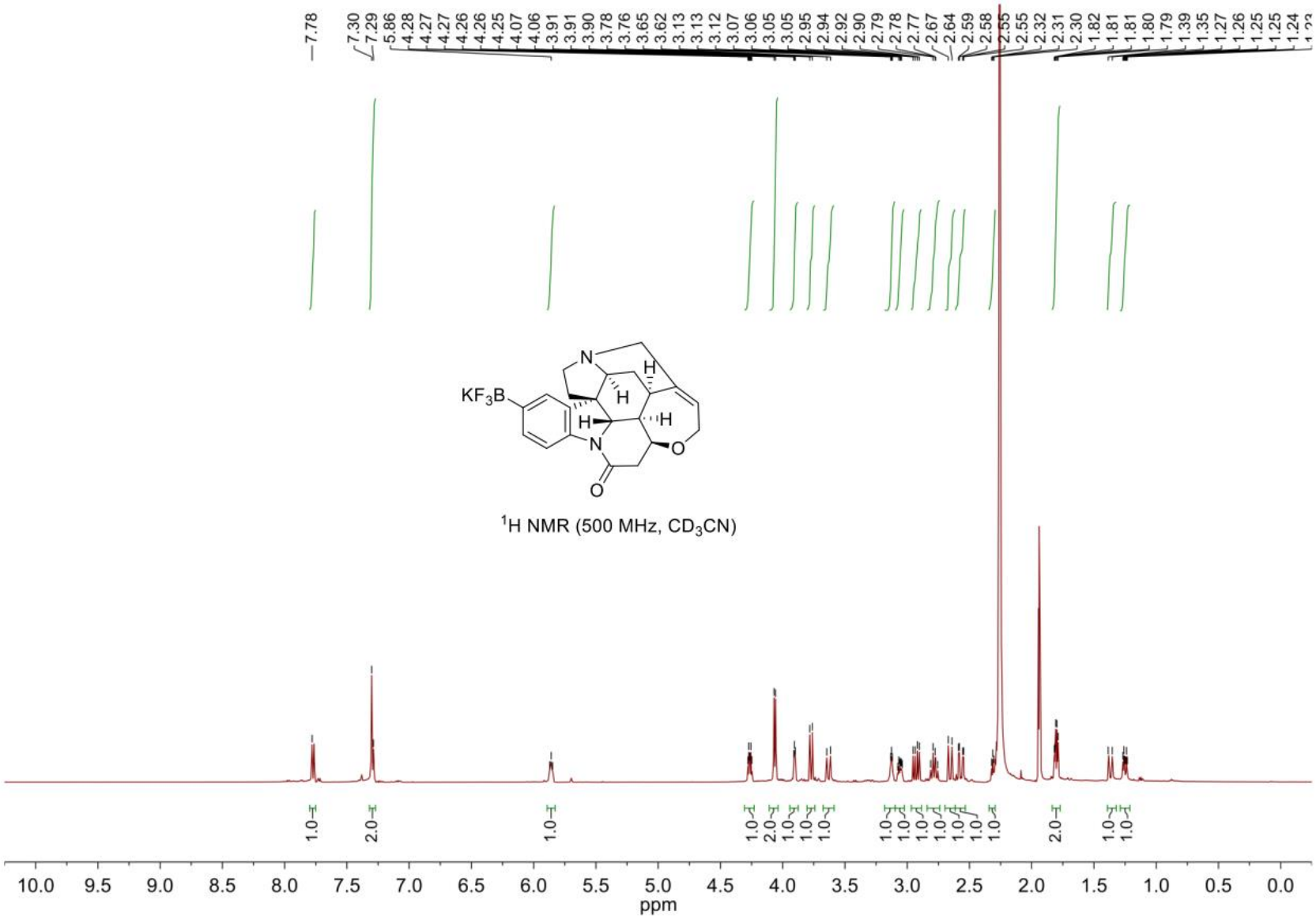
(4a*R*,4a1*R*,5a*S*,8a*R*,8a1*S*,15a*S*)-10-(Trifluoro-l4-boraneyl)-2,4a,4a1,5,5a,7,8,8a1,15,15a-decahydro-14*H*-4,6-methanoindolo[3,2,1-*ij*]oxepino[2,3,4-de]pyrrolo[2,3-*h*]quinolin-14-one, potassium salt (102)



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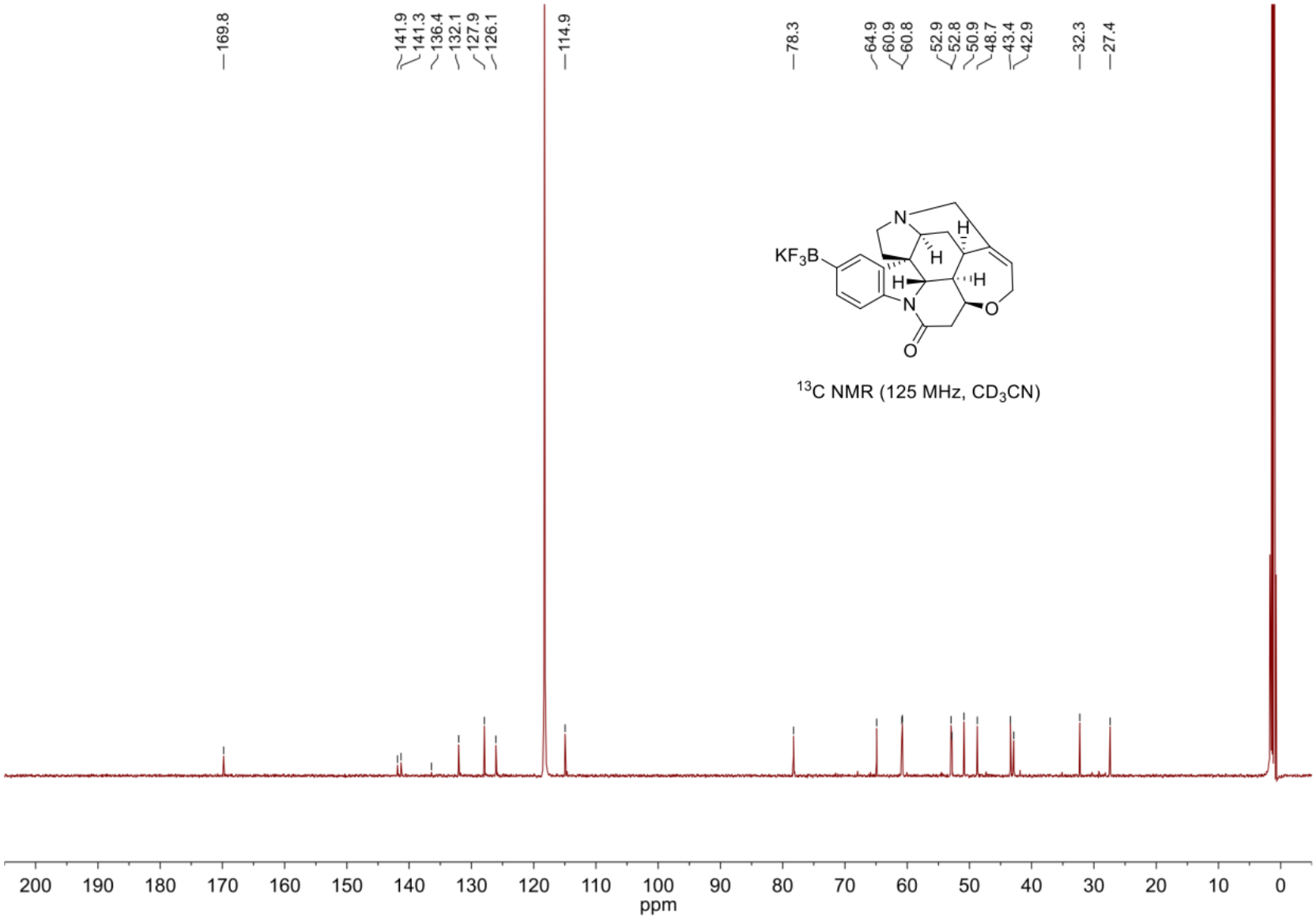
(4a*R*,4a1*R*,5a*S*,8a*R*,8a1*S*,15a*S*)-10-(Trifluoro-l4-boraneyl)-2,4a,4a1,5,5a,7,8,8a1,15,15a-decahydro-14*H*-4,6-methanoindolo[3,2,1-*ij*]oxepino[2,3,4-de]pyrrolo[2,3-*h*]quinolin-14-one, potassium salt (102)



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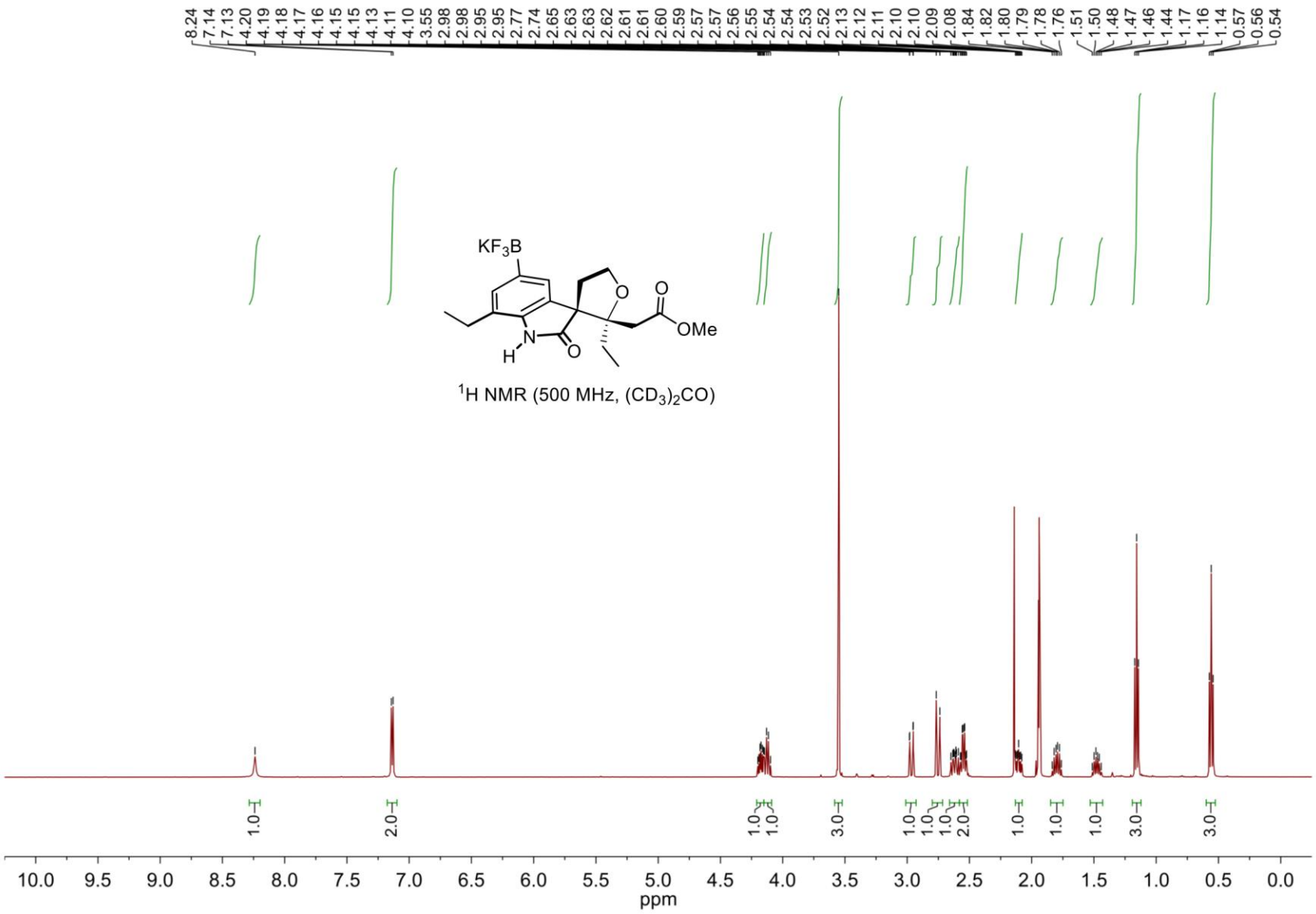
Methyl 2-((2*S*,3*R*)-2,7'-diethyl-2'-oxo-5'-(trifluoro-l4-boraneyl)-4,5-dihydro-2*H*-spiro[furan-3,3'-indolin]-2-yl)acetate, potassium salt (103)



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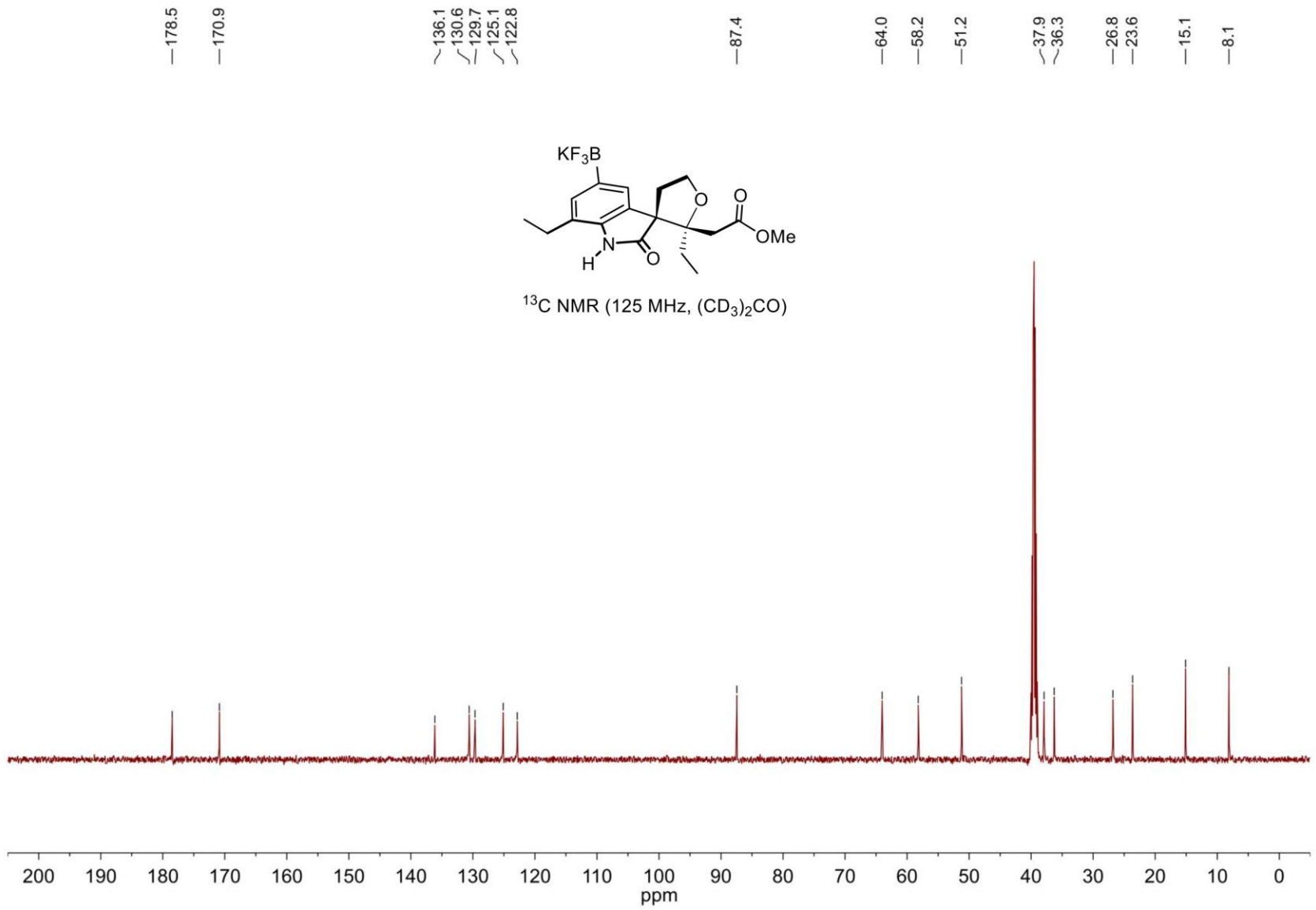
Methyl 2-((2*S*,3*R*)-2,7'-diethyl-2'-oxo-5'-(trifluoro-l4-boraneyl)-4,5-dihydro-2*H*-spiro[furan-3,3'-indolin]-2-yl)acetate, potassium salt (103)



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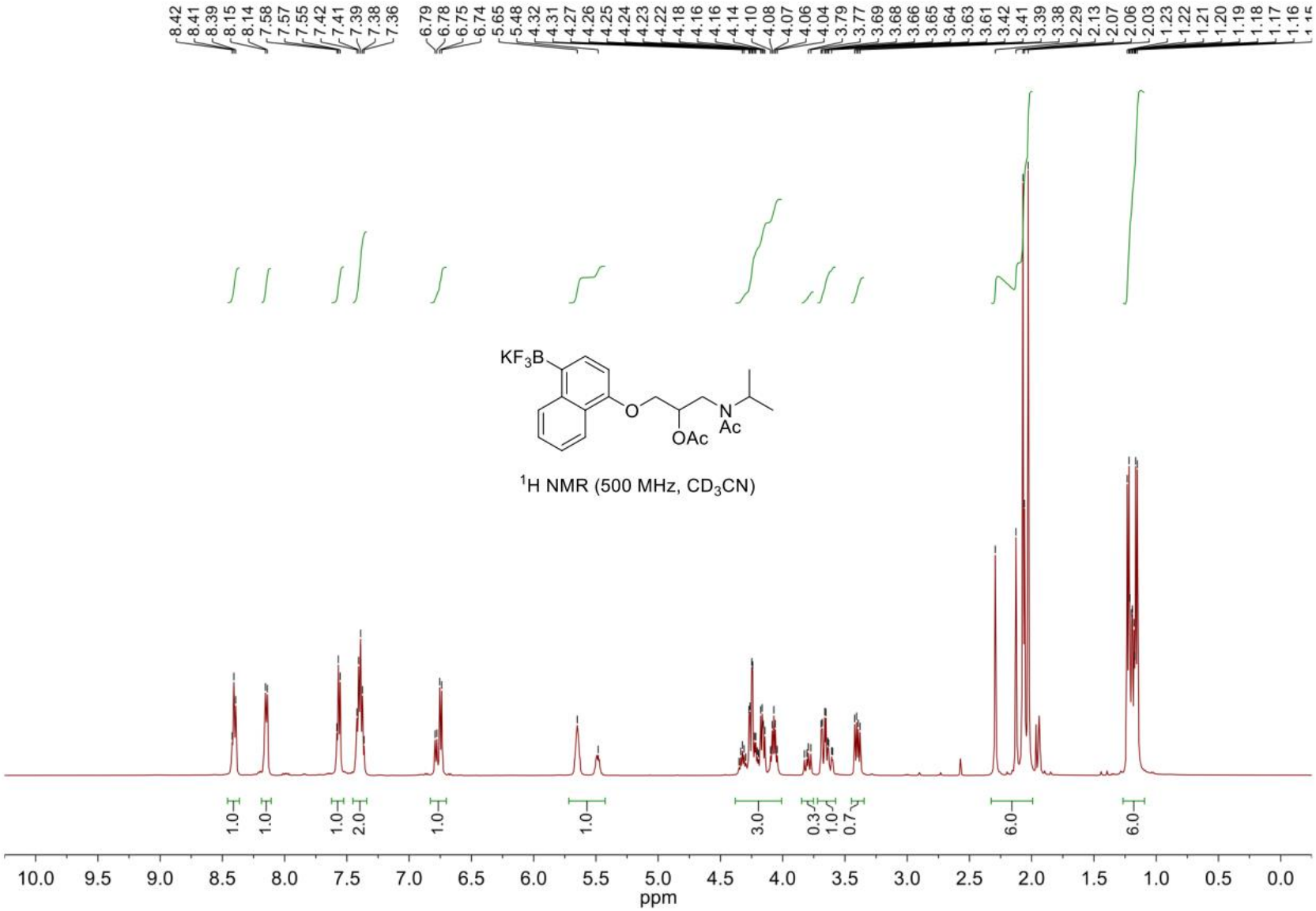
1-(*N*-Isopropylacetamido)-3-((4-(trifluoro-λ⁴-boraneyl)naphthalen-1-yl)oxy)propan-2-yl acetate, potassium salt (104)



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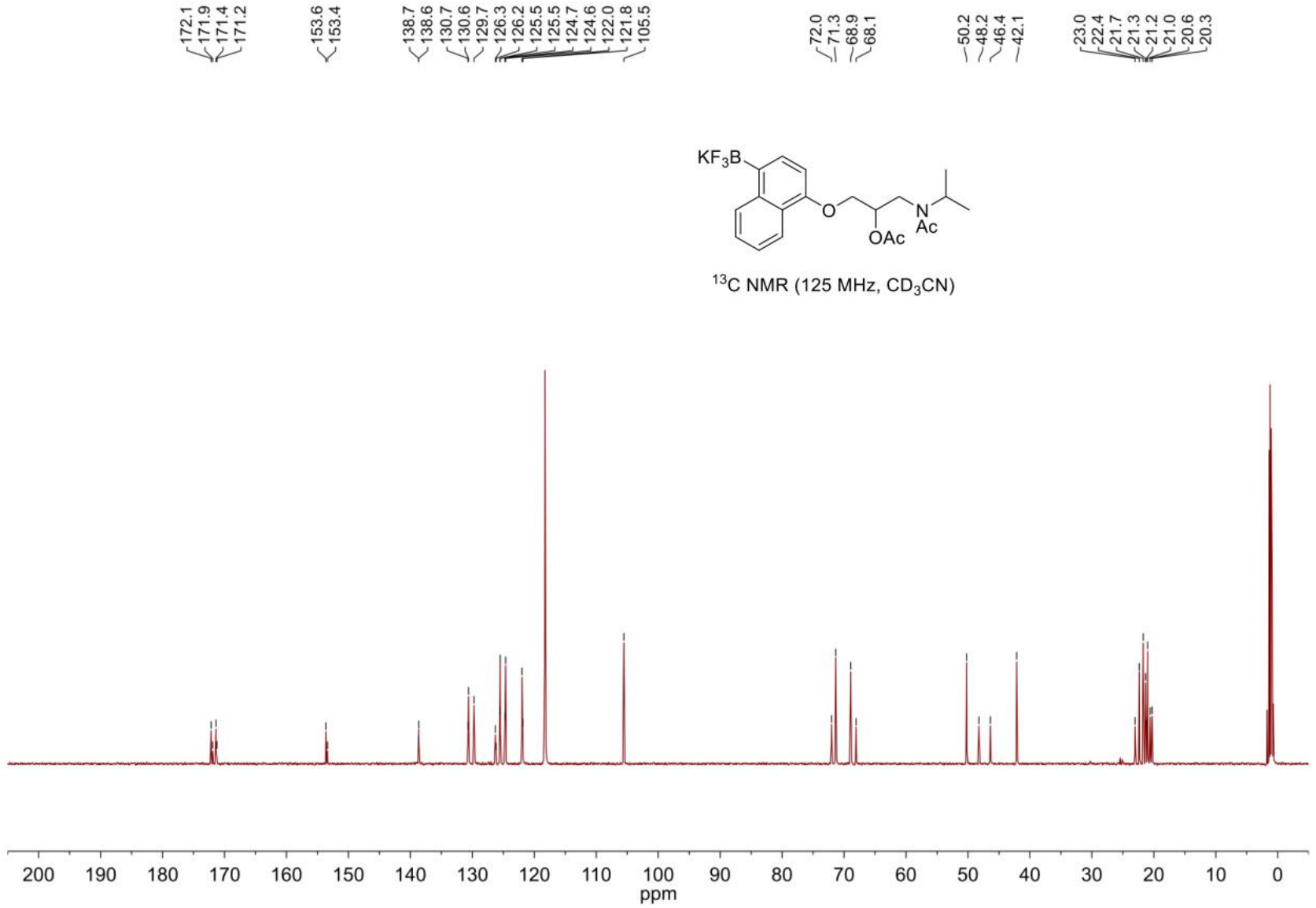
1-(*N*-Isopropylacetamido)-3-((4-(trifluoro-λ⁴-boraneyl)naphthalen-1-yl)oxy)propan-2-yl acetate, potassium salt (104)



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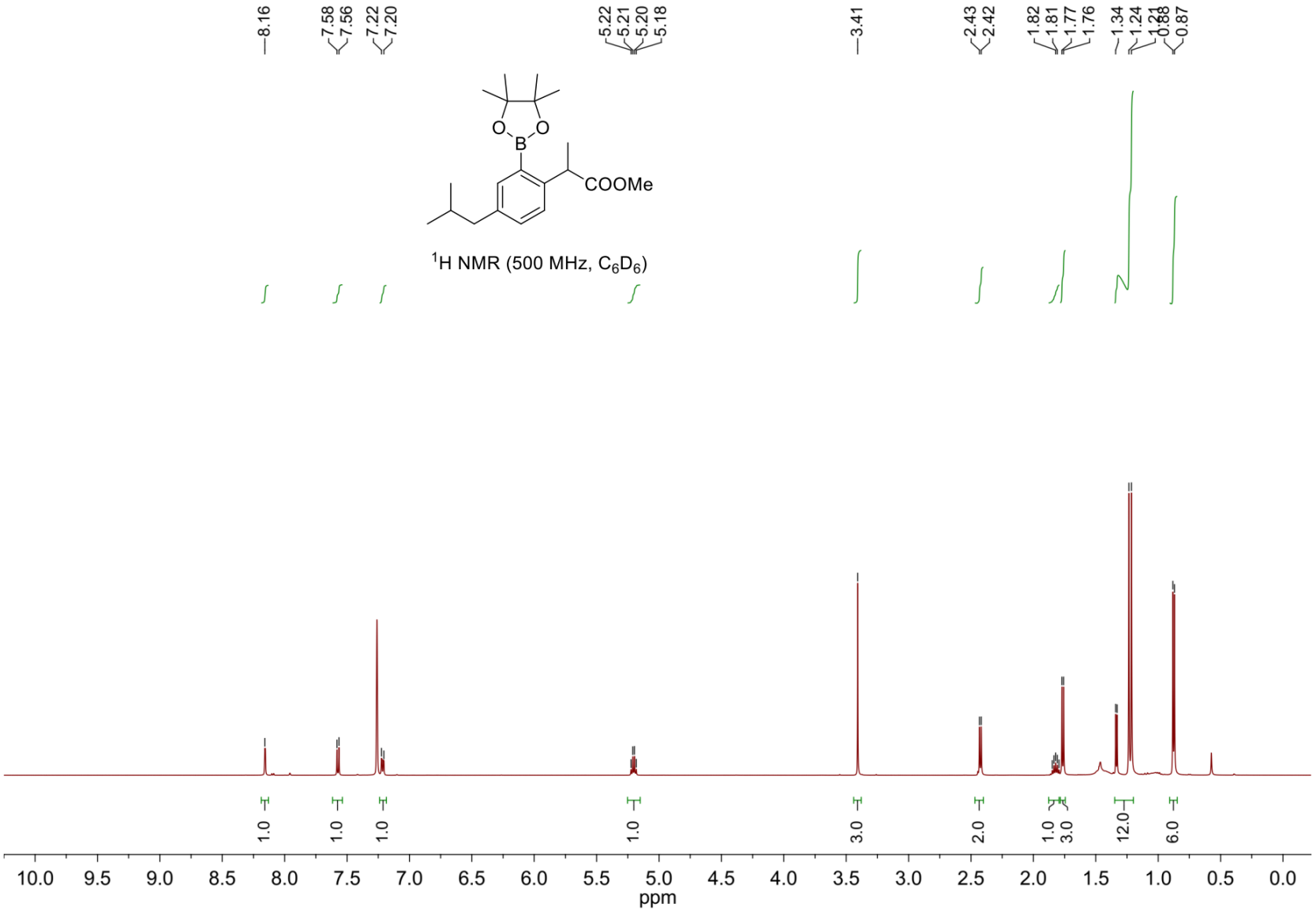
Methyl 2-(4-isobutyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propanoate (105)



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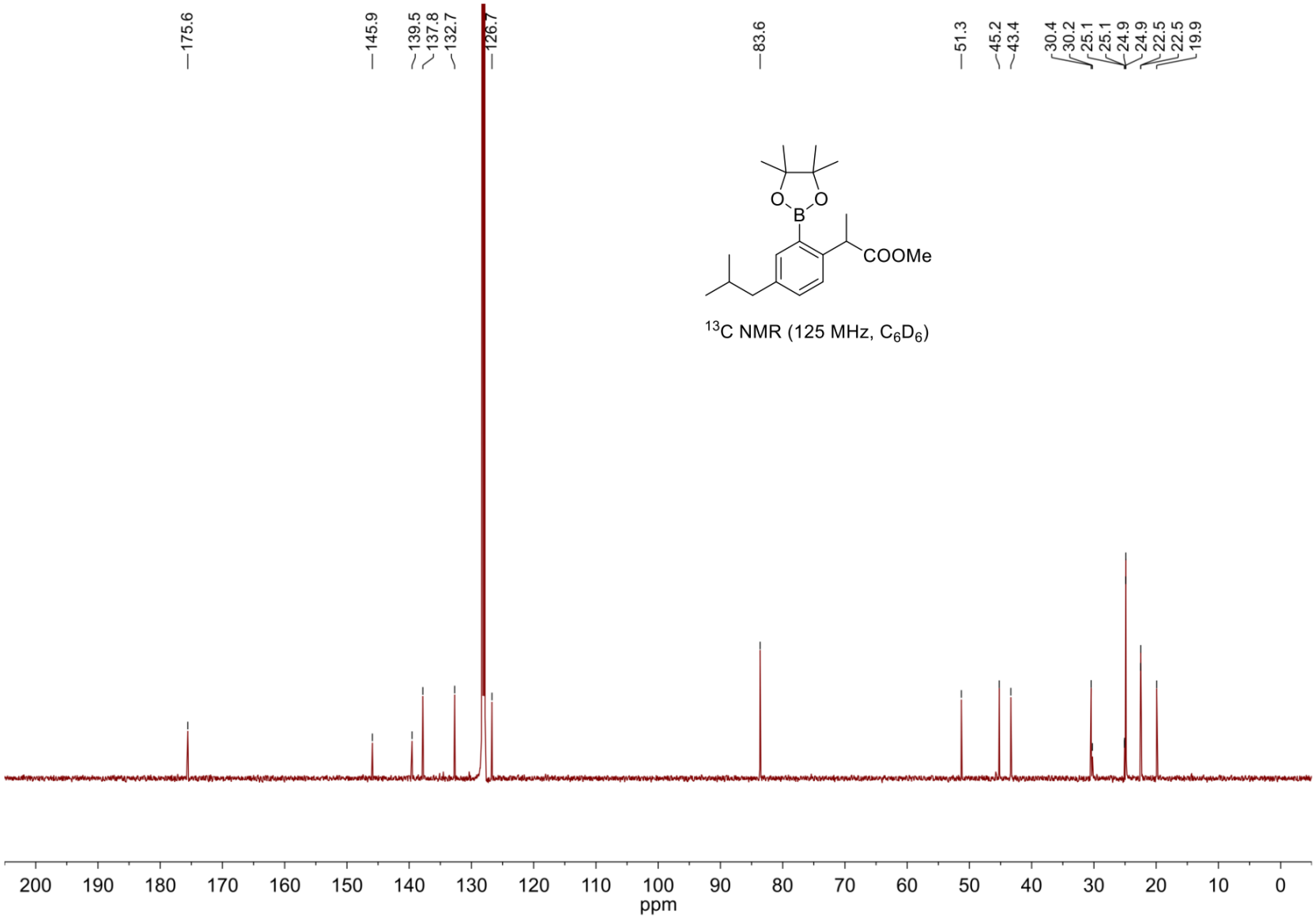
Methyl 2-(4-isobutyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propanoate (105)



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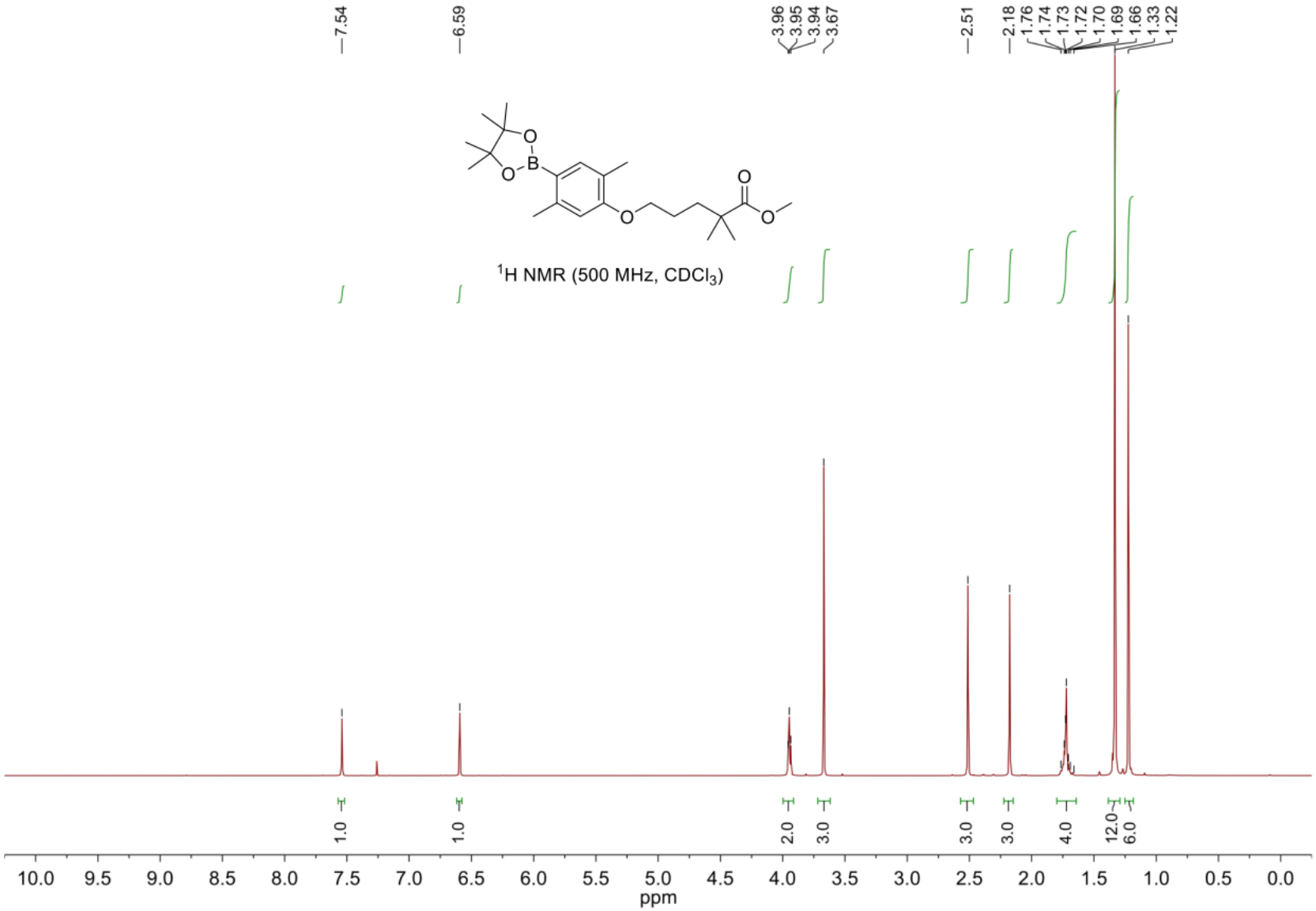
Methyl 5-(2,5-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)-2,2-dimethylpentanoate (106)



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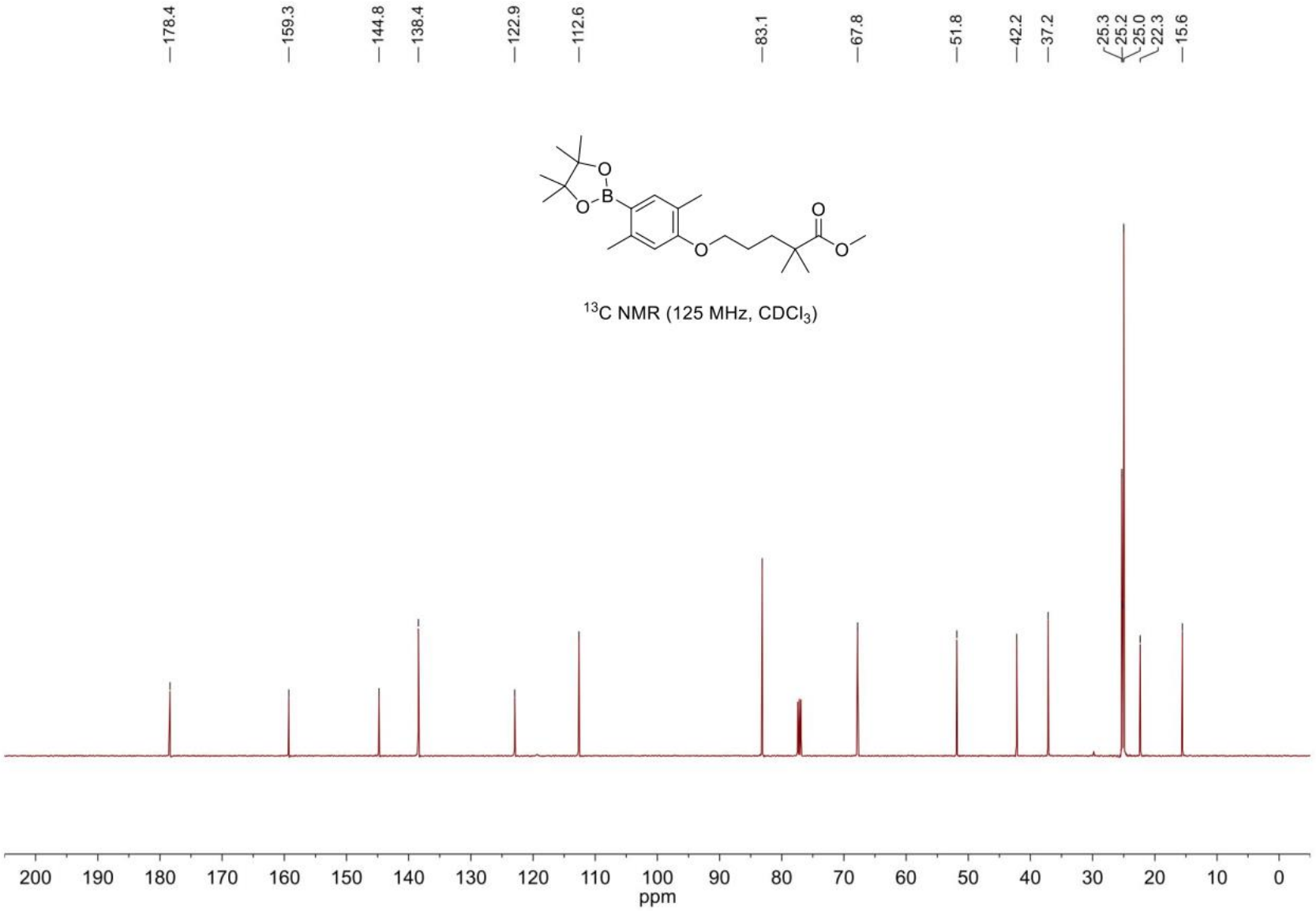
Methyl 5-(2,5-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)-2,2-dimethylpentanoate (106)



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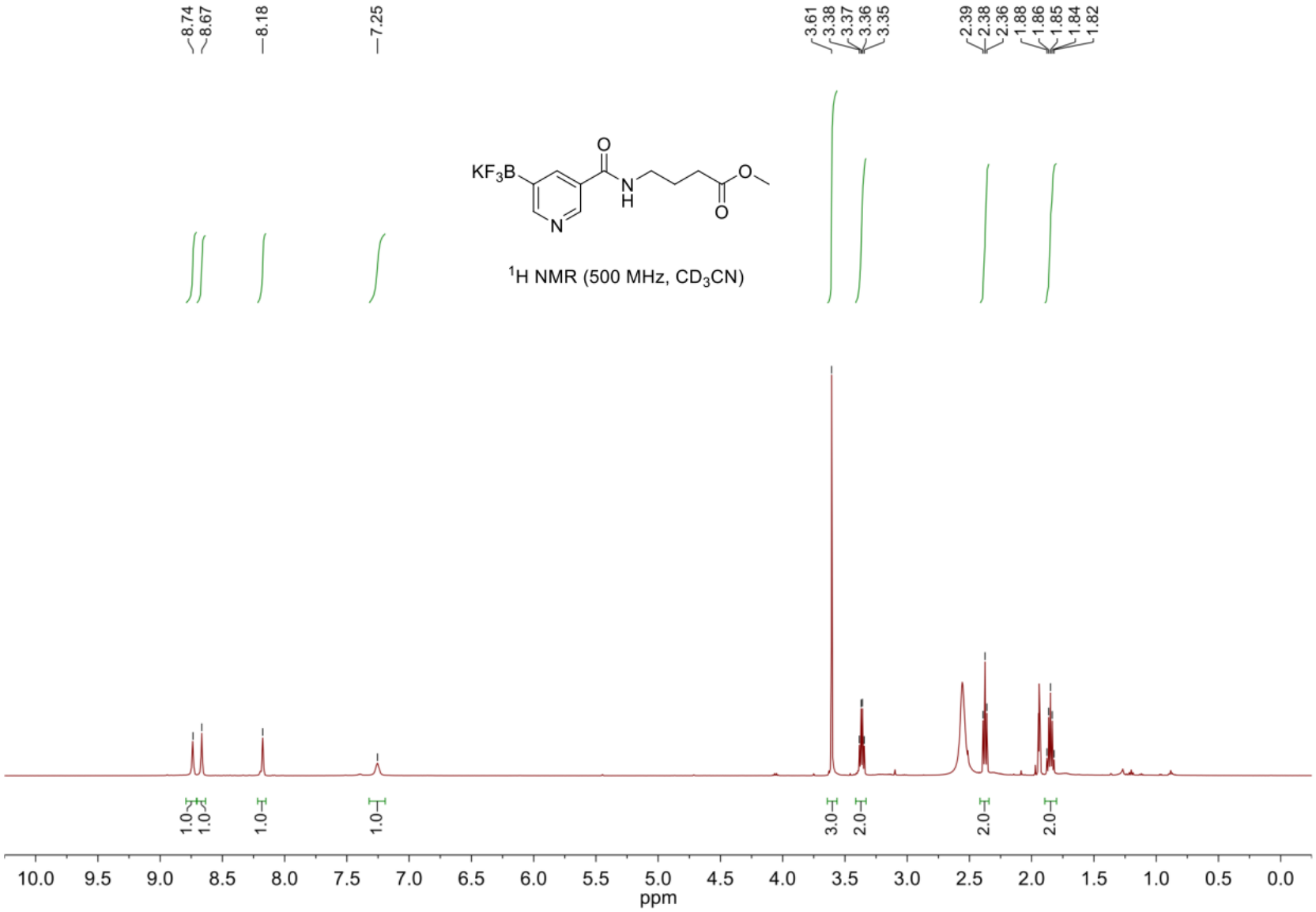
Methyl 4-(5-(trifluoro-l4-boraneyl)nicotinamido)butanoate, potassium salt (107)



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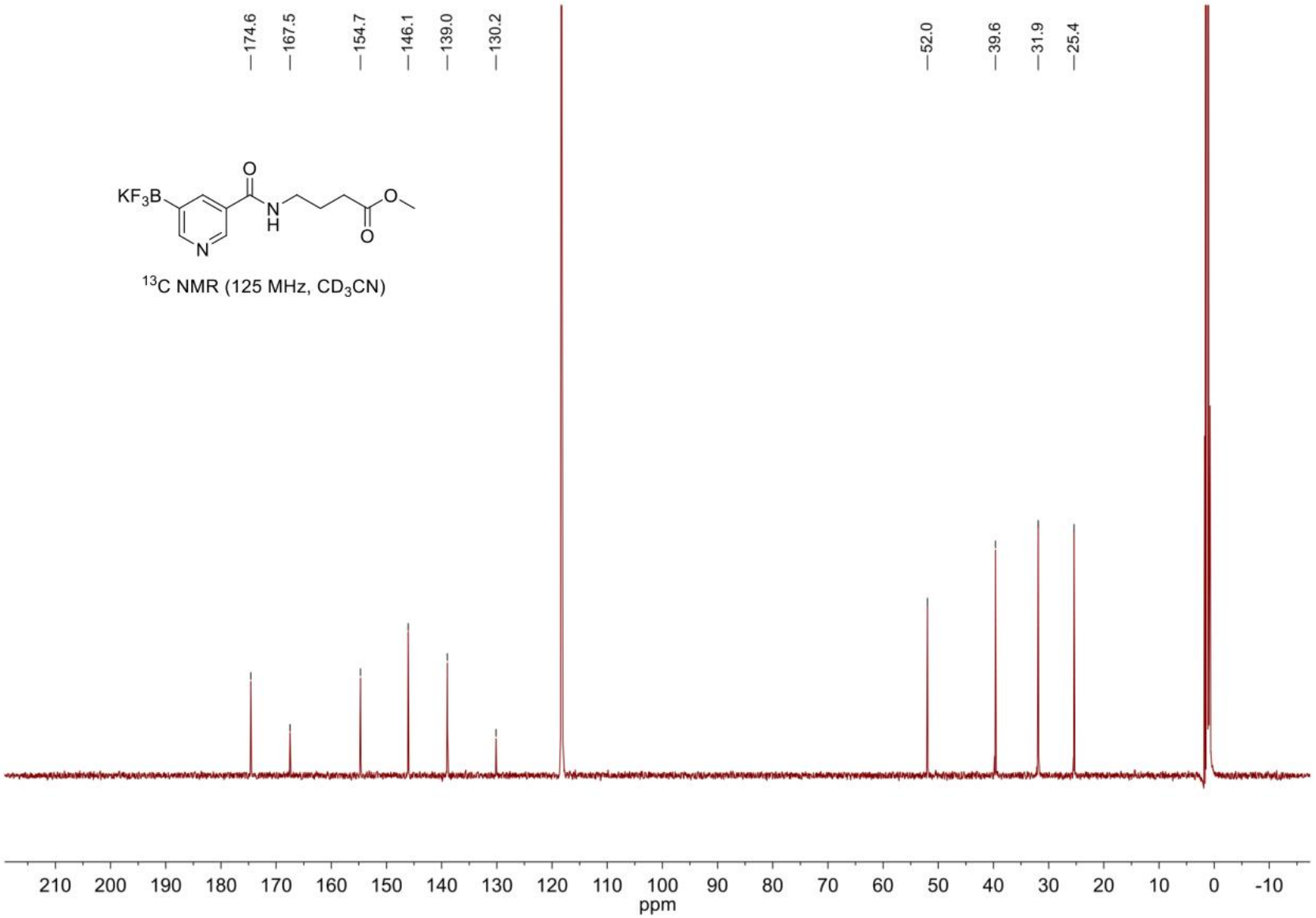
Methyl 4-(5-(trifluoro-l4-boraneyl)nicotinamido)butanoate, potassium salt (107)



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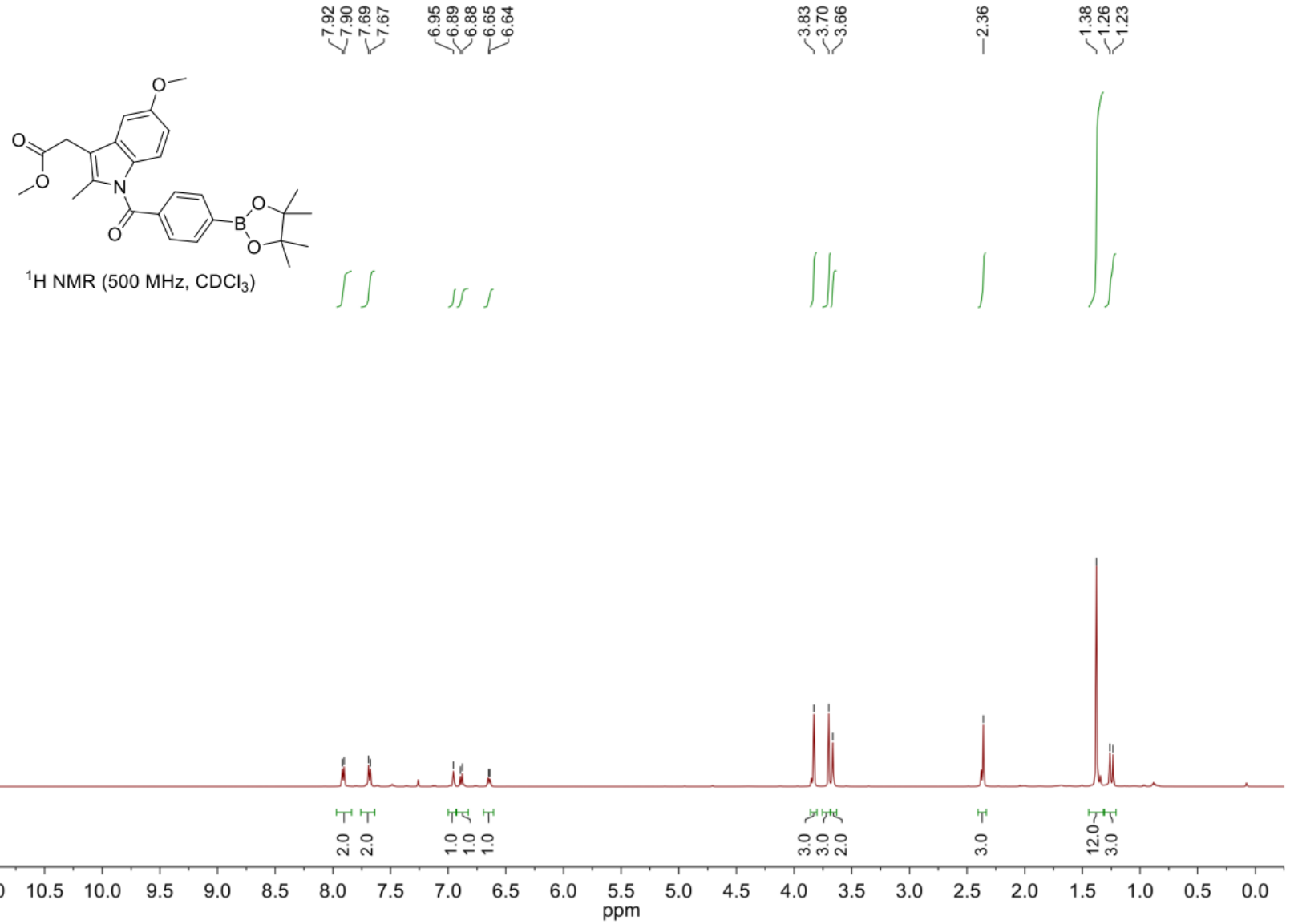
Methyl 2-(5-methoxy-2-methyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoyl)-1*H*-indol-3-yl)acetate (108)



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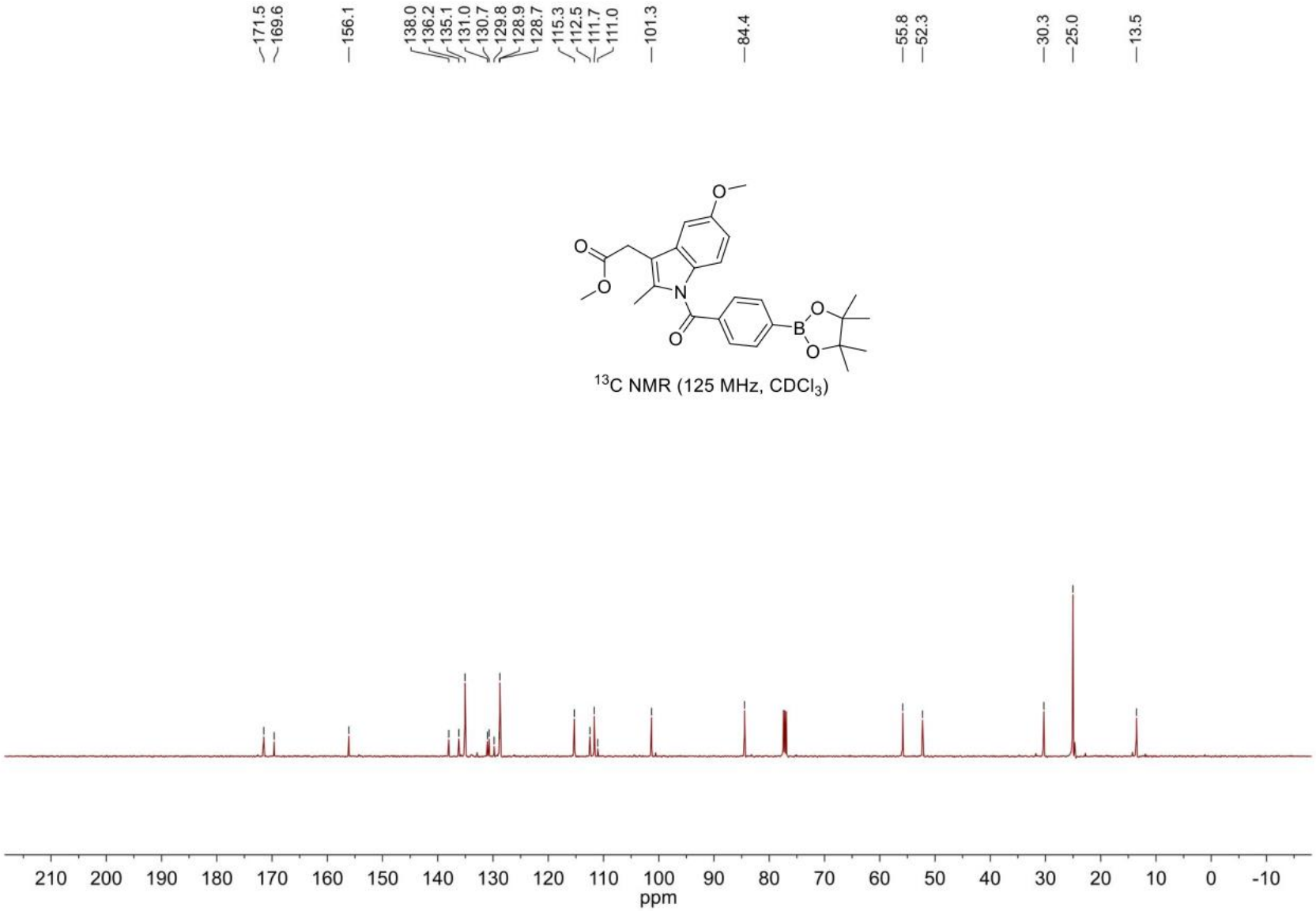
Methyl 2-(5-methoxy-2-methyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoyl)-1*H*-indol-3-yl)acetate (108)



^{13}C NMR (125 MHz, $CDCl_3$)

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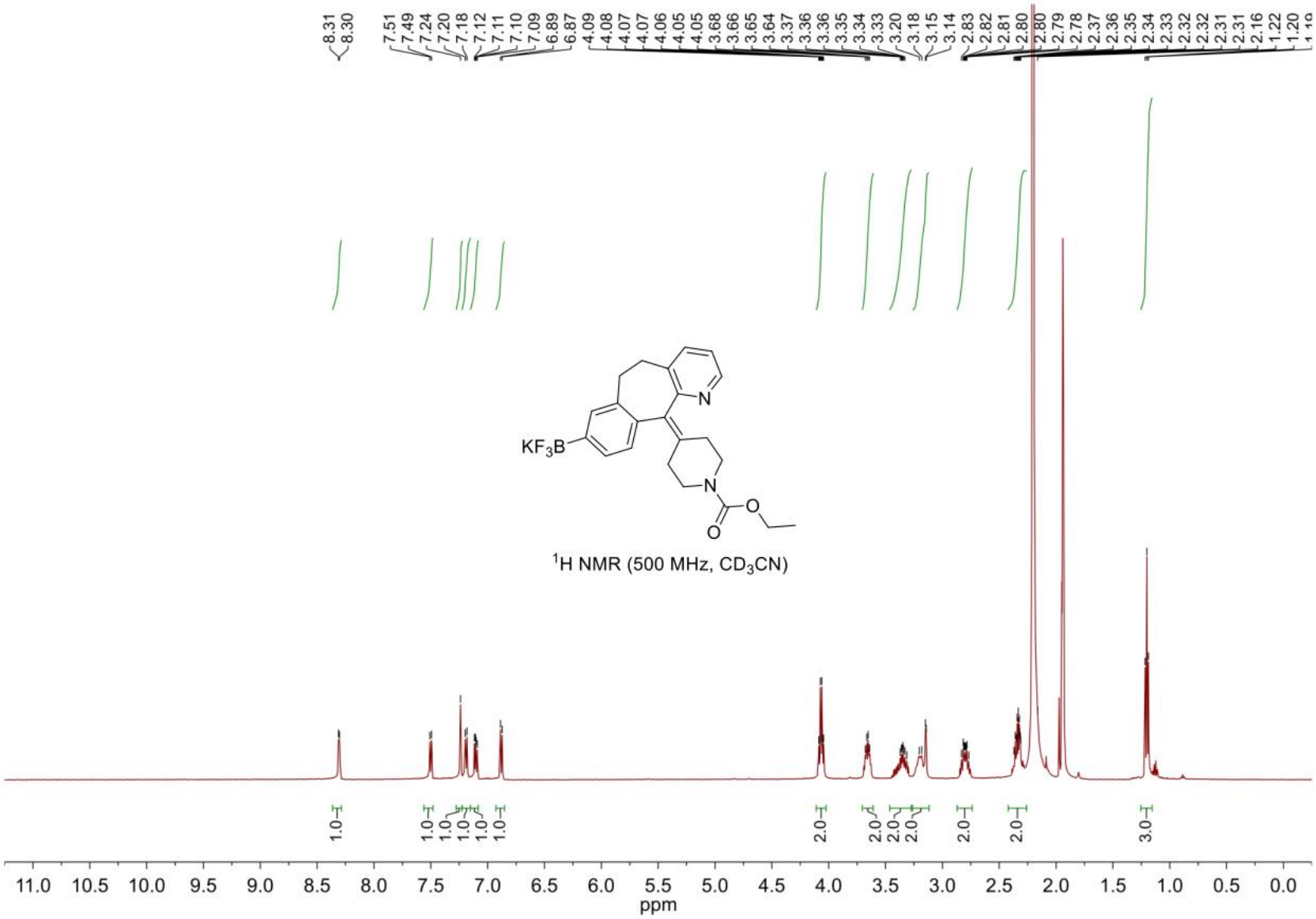
Ethyl 4-(8-(trifluoro-λ⁴-boraneyl)-5,6-dihydro-11*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11-ylidene)piperidine-1-carboxylate, potassium salt (109)



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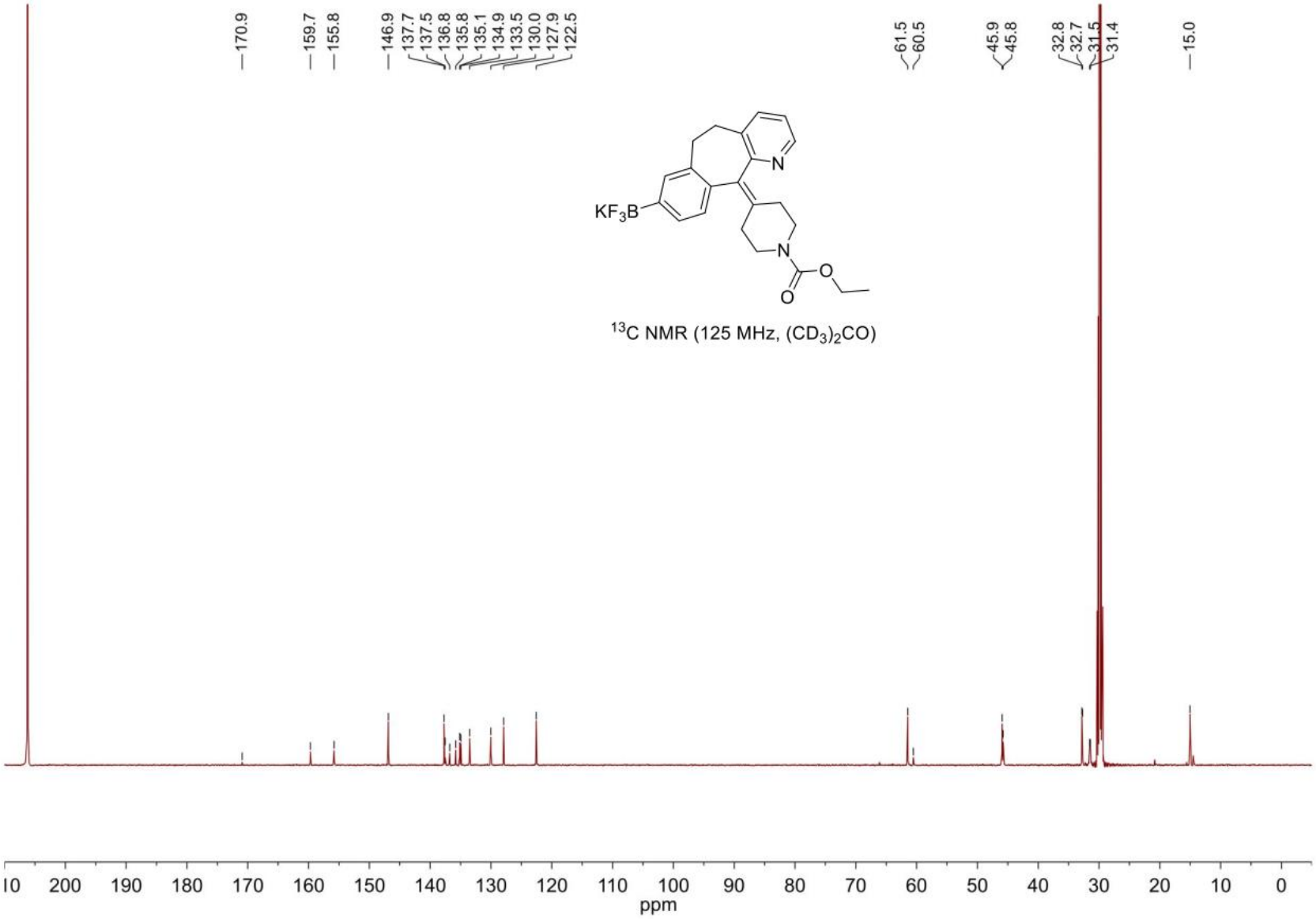
Ethyl 4-(8-(trifluoro-λ⁴-boraneyl)-5,6-dihydro-11*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11-ylidene)piperidine-1-carboxylate, potassium salt (109)



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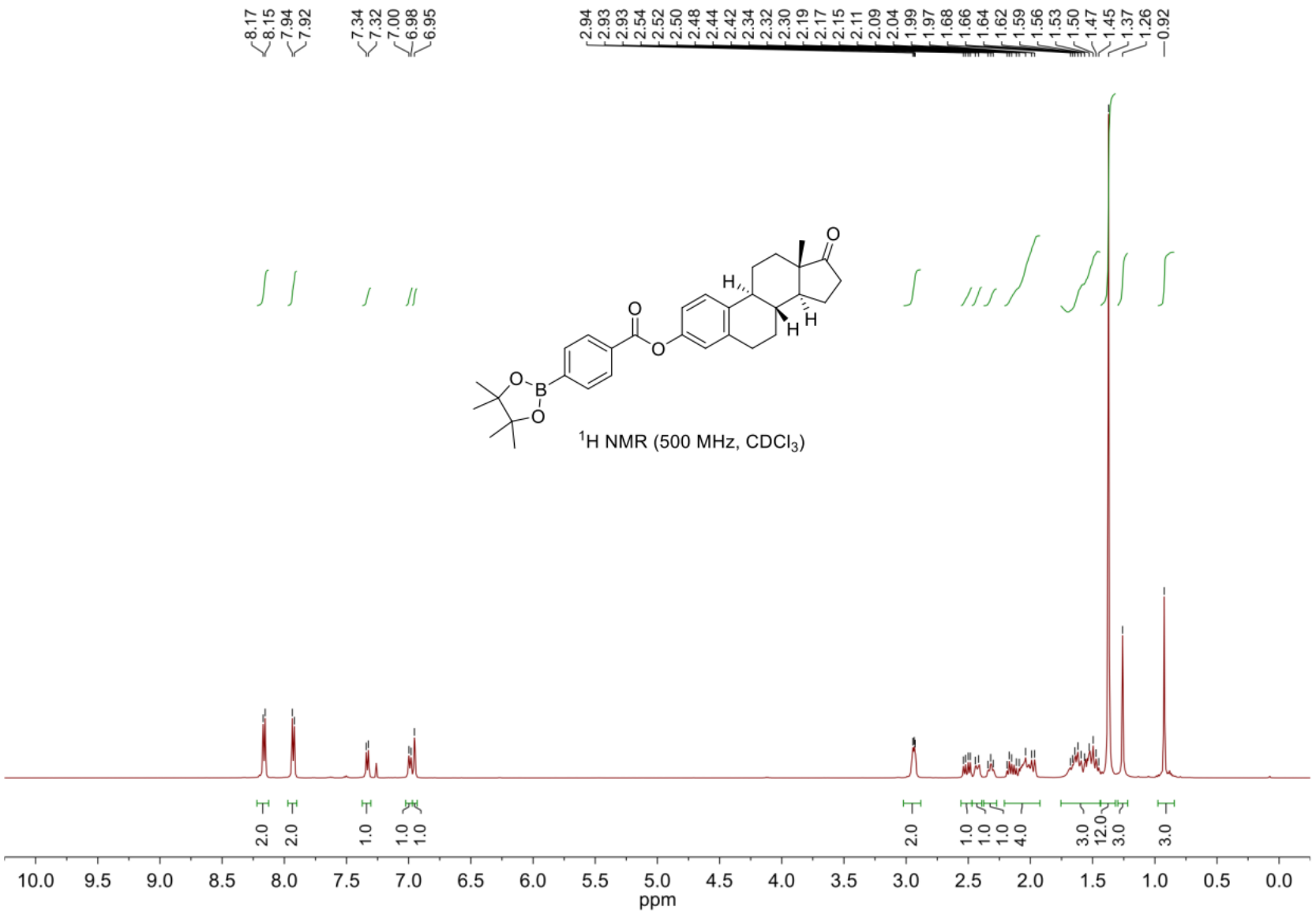
(8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (110)



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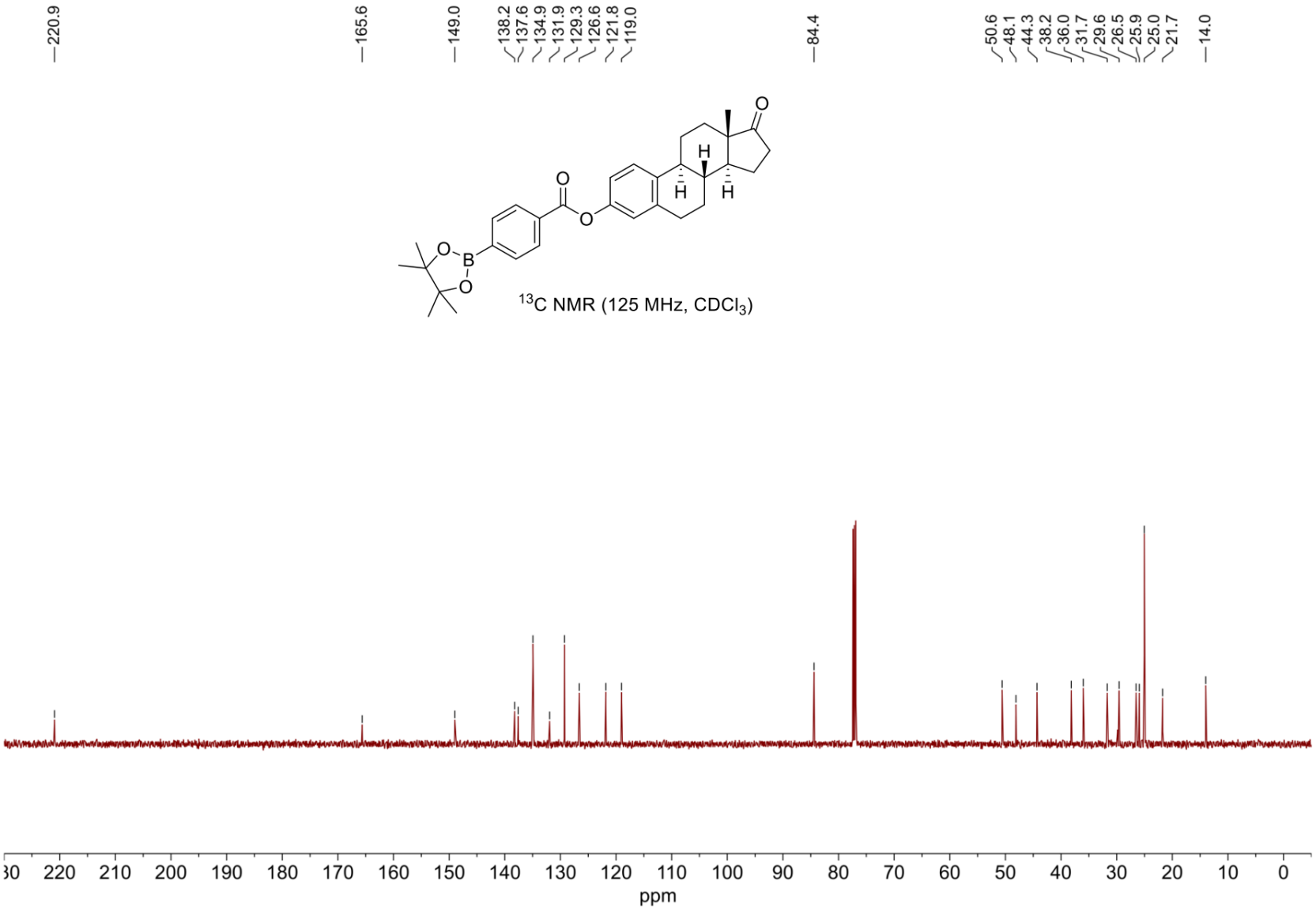
(8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (110)



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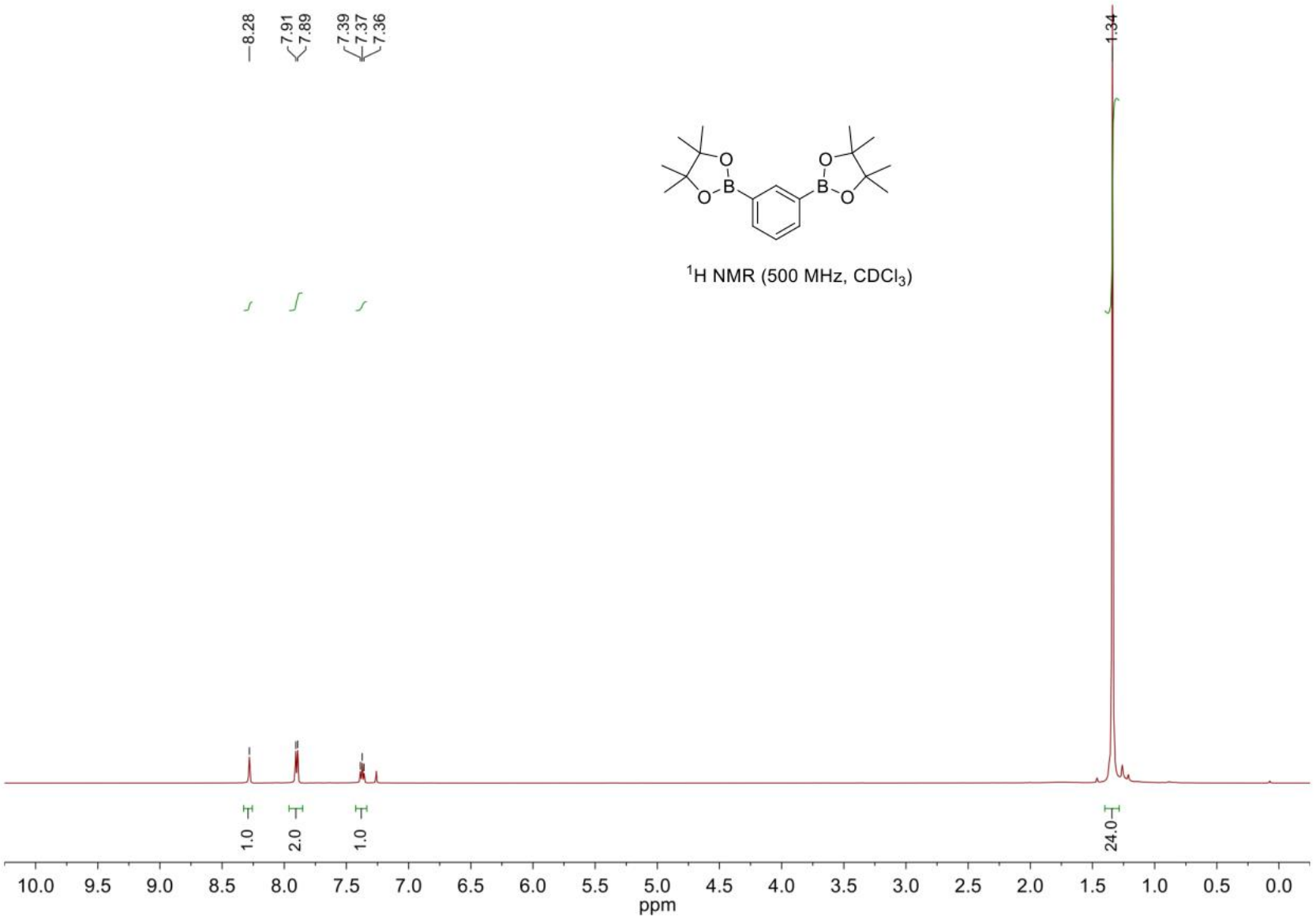
1,3-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (111)



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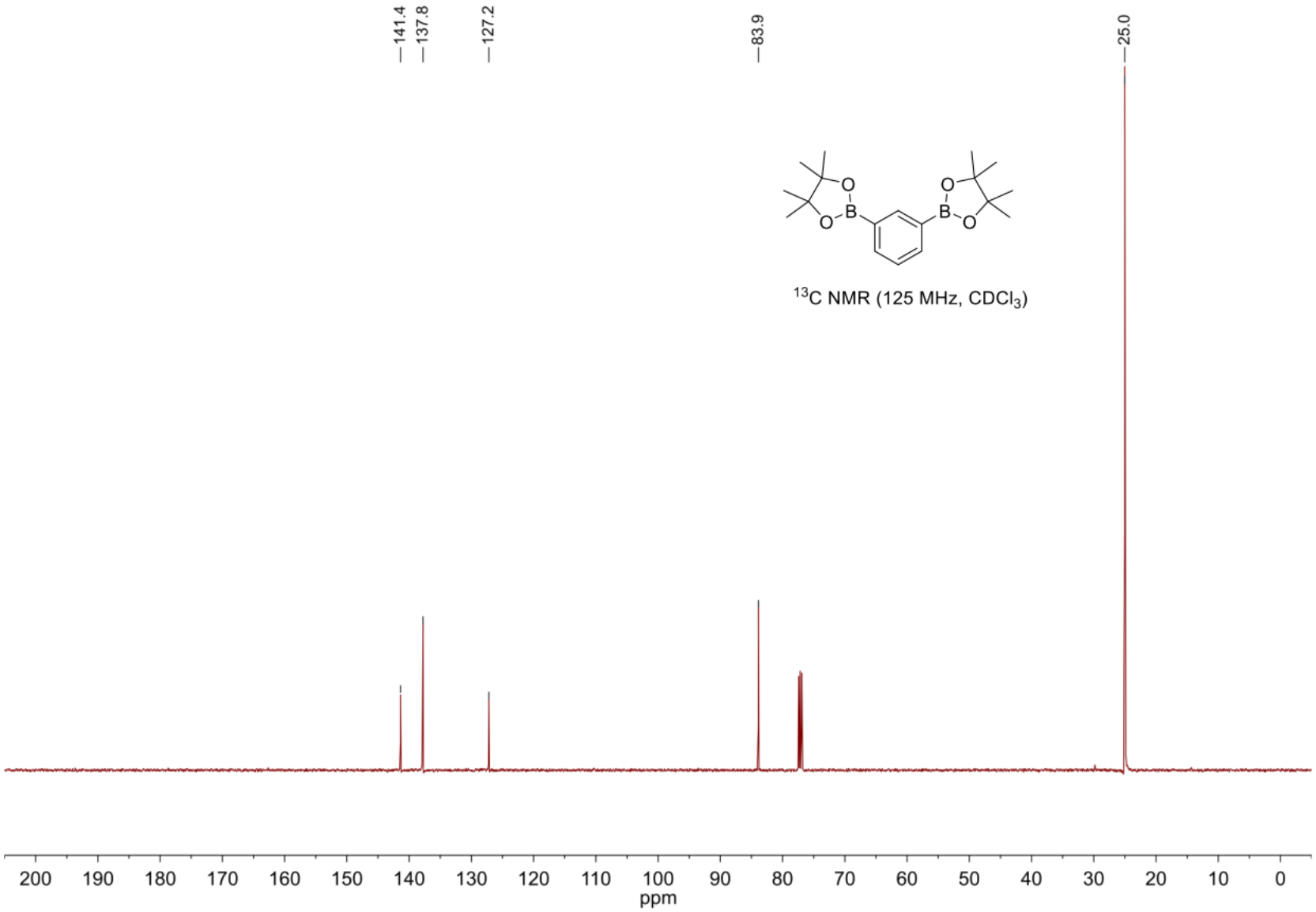
1,3-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (111)



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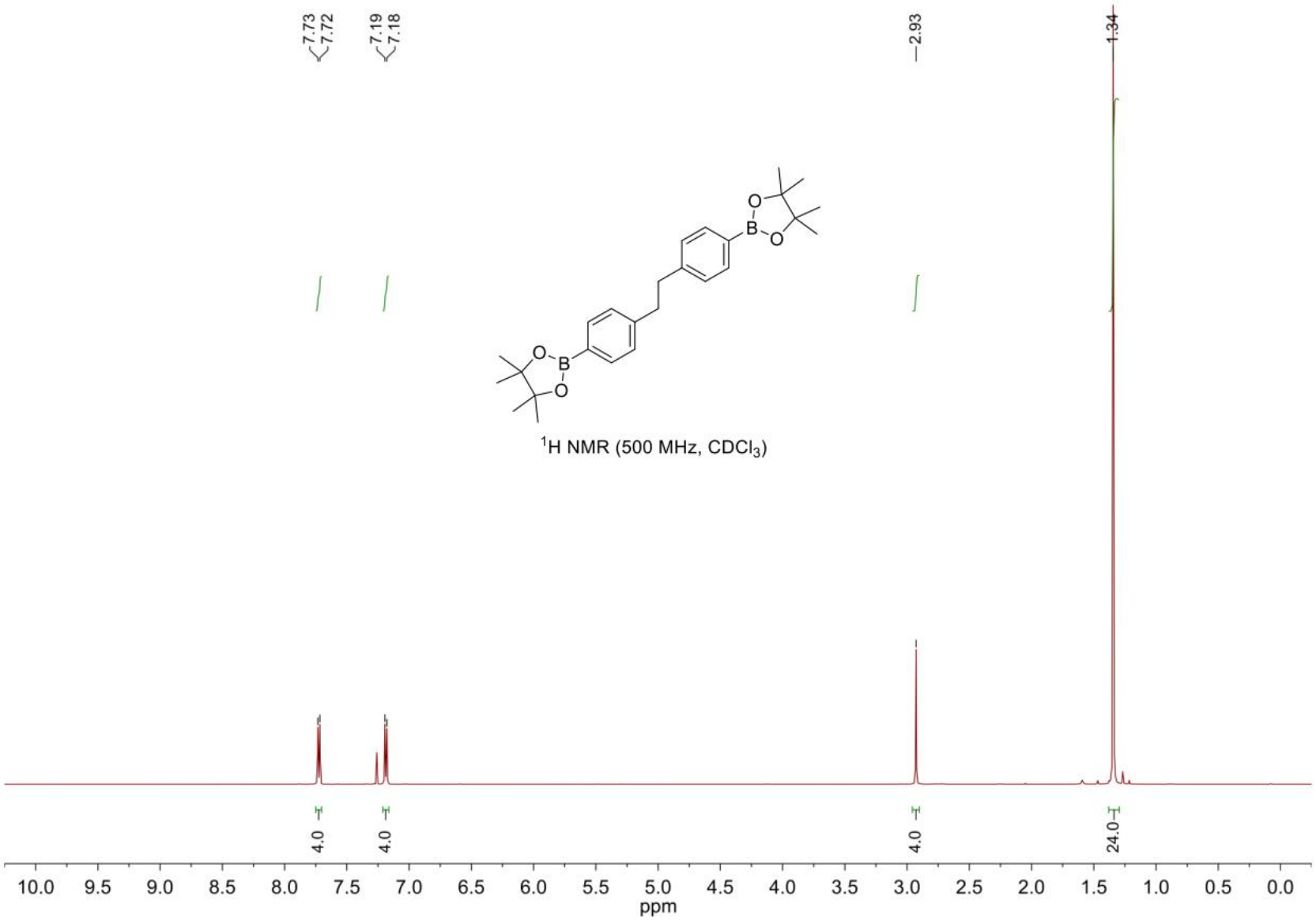
Bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methane (112)



^{1}H NMR (500 MHz, $CDCl_3$)

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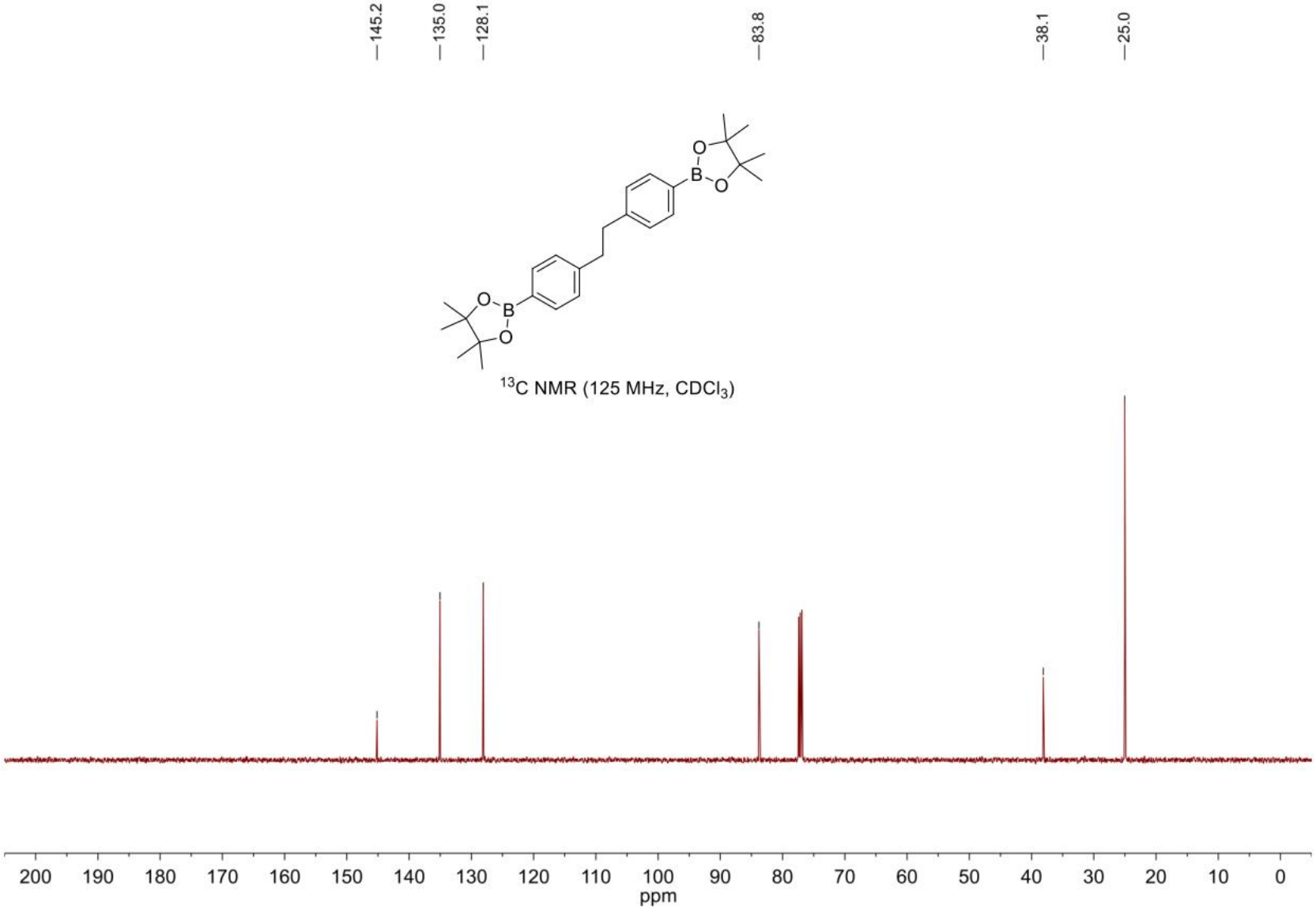
Bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methane (112)



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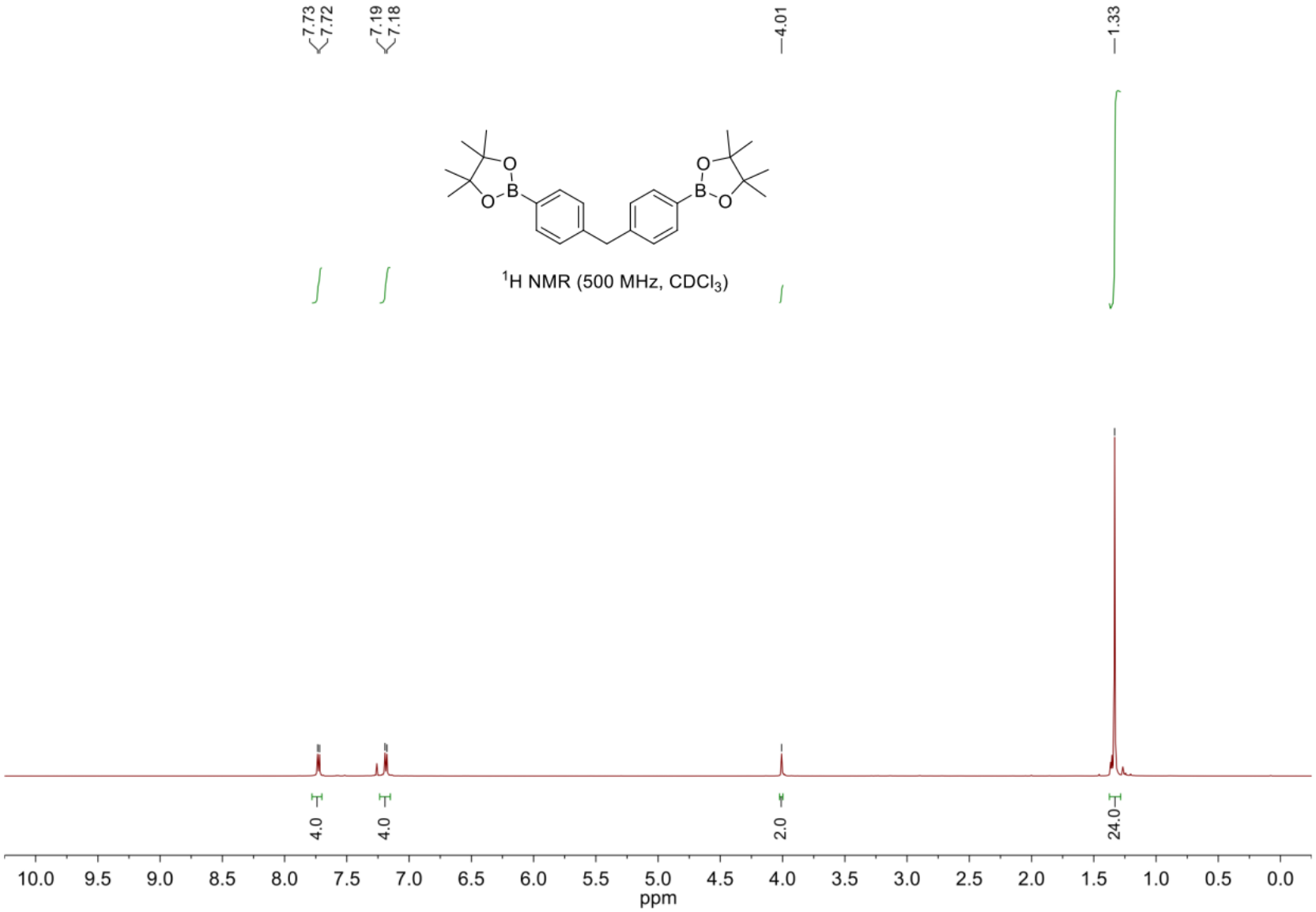
1,2-Bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethane (113)



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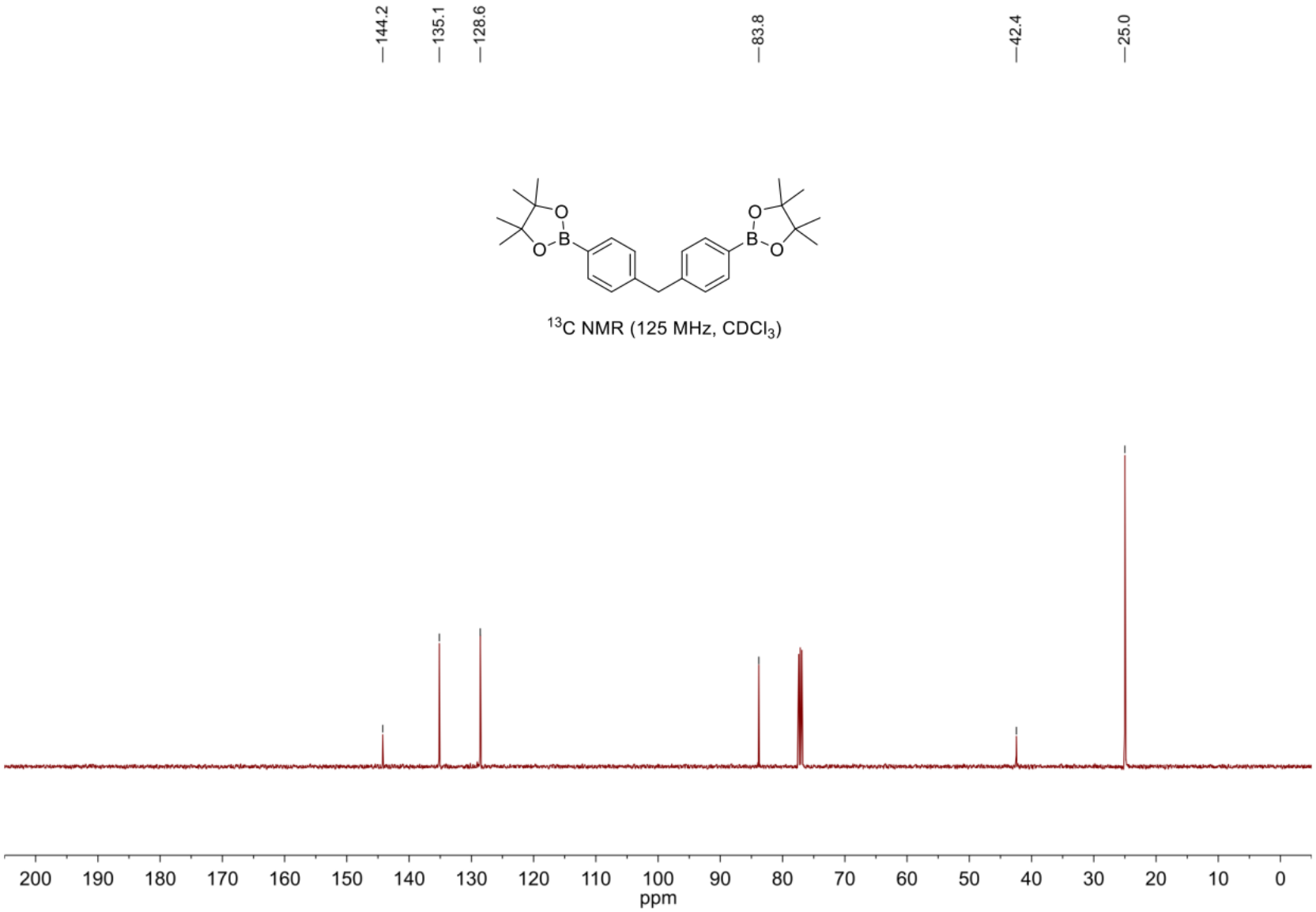
1,2-Bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethane (113)



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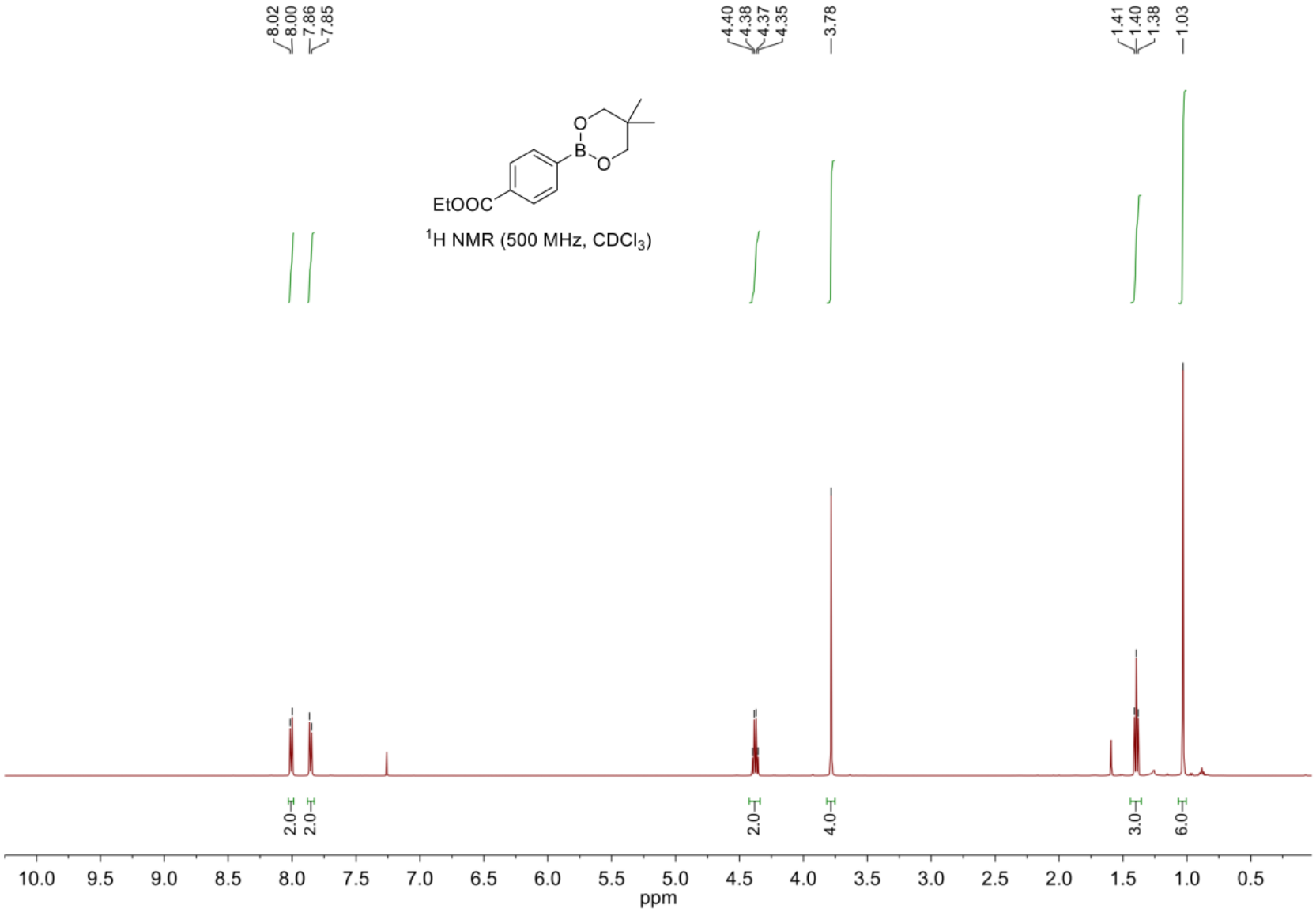
Ethyl 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoate (114)



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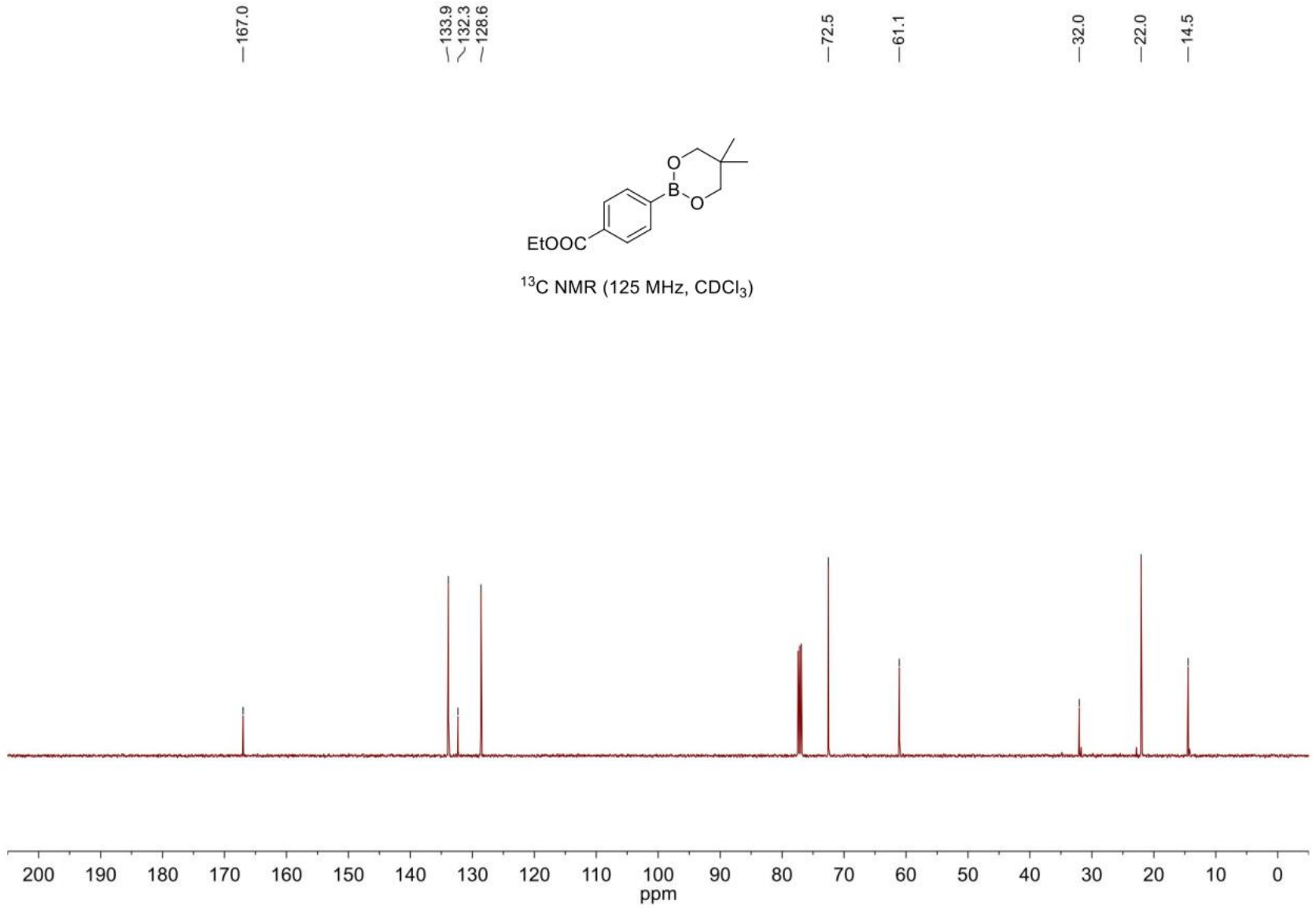
Ethyl 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoate (114)



^{13}C NMR (125 MHz, $CDCl_3$)

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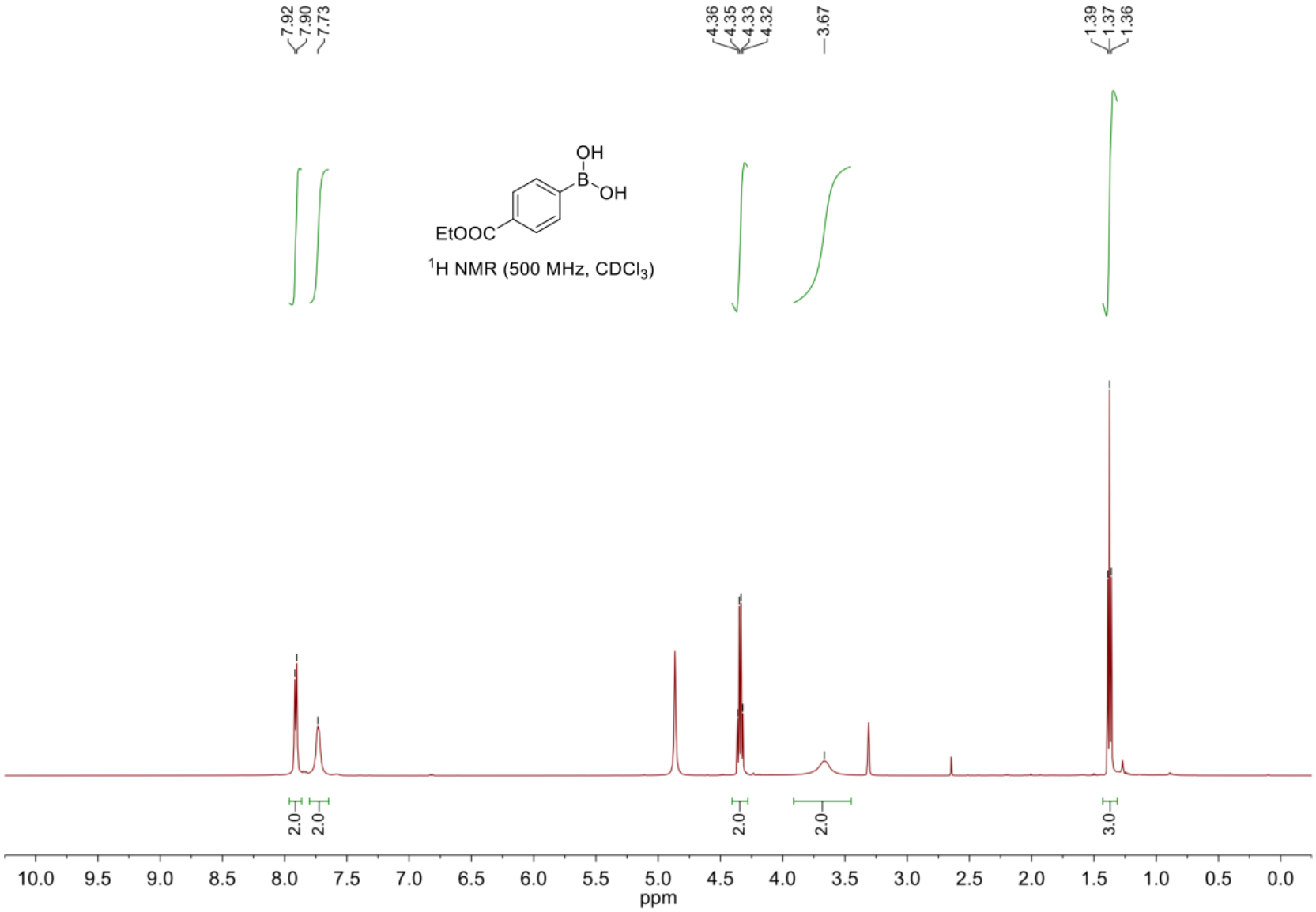
(4-(Ethoxycarbonyl)phenyl)boronic acid (115)



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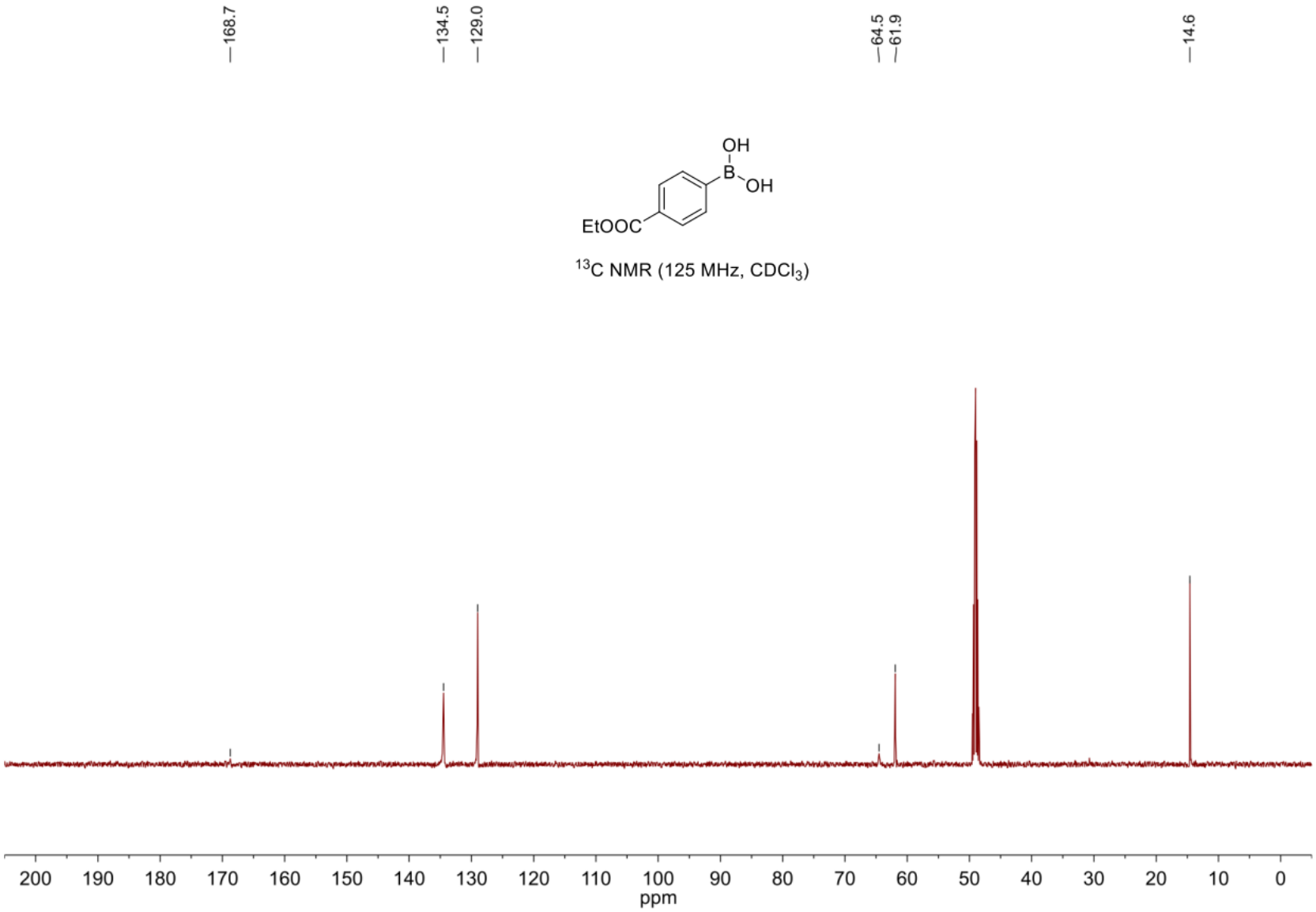
(4-(Ethoxycarbonyl)phenyl)boronic acid (115)



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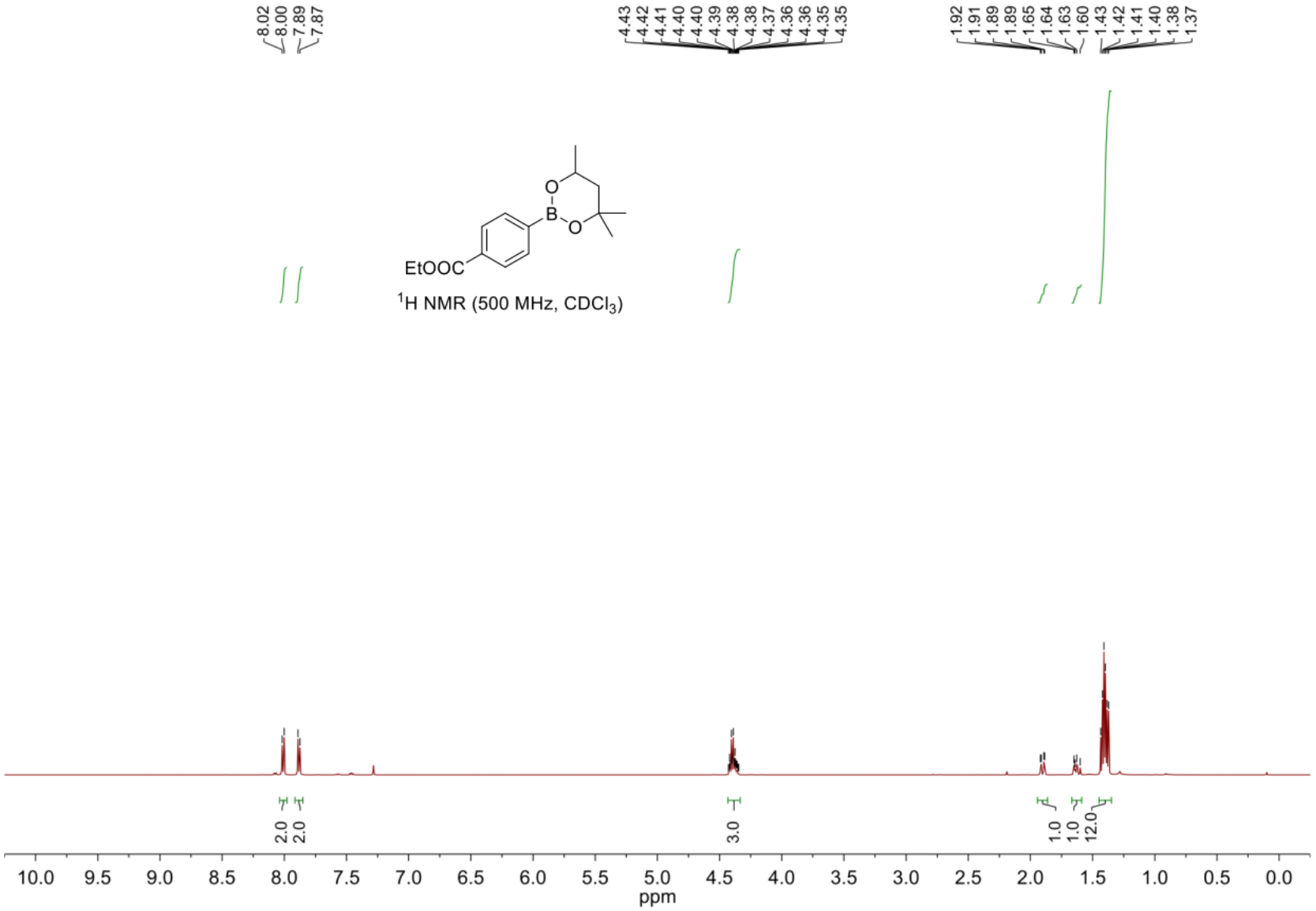
Ethyl 4-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)benzoate (116)



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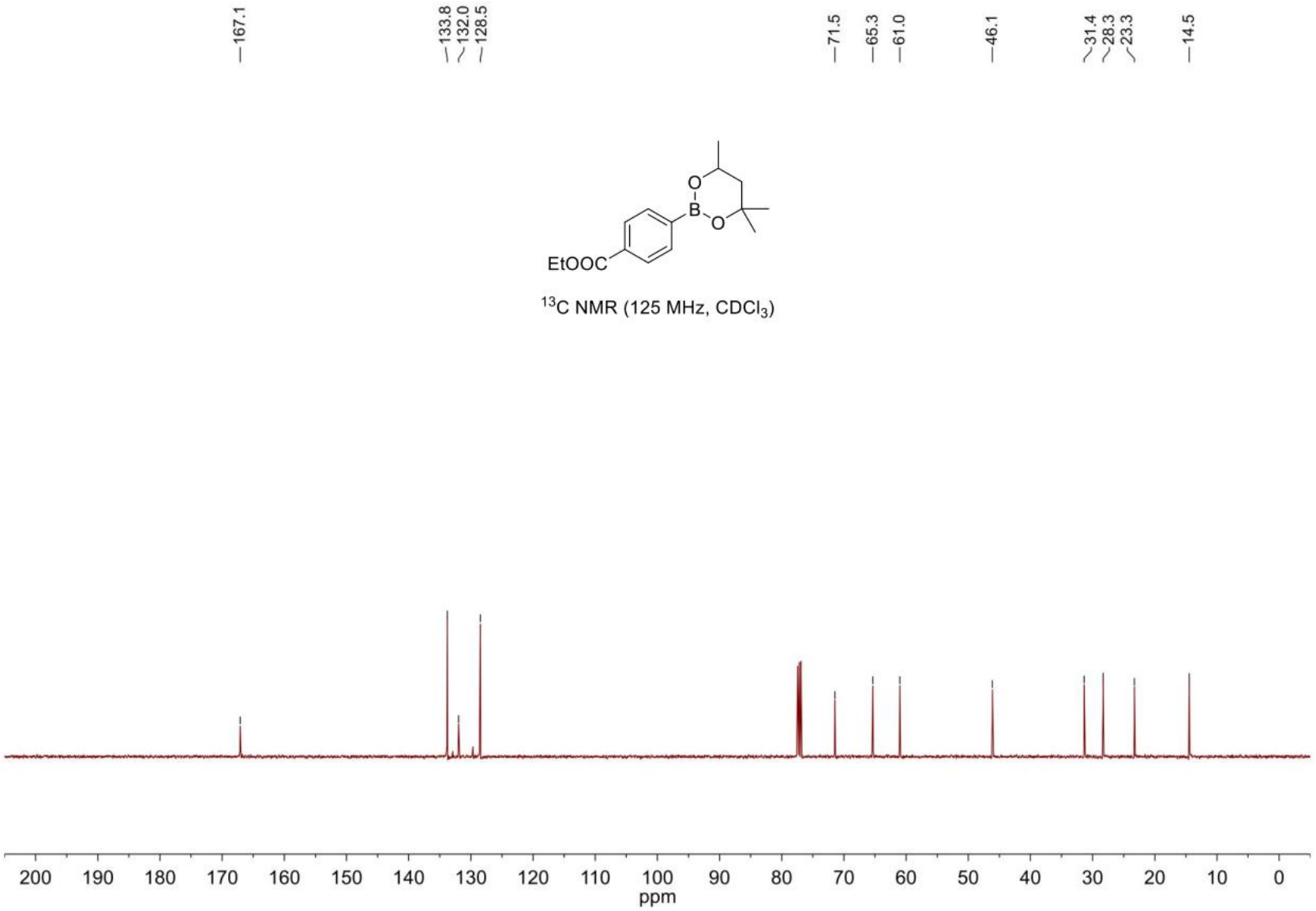
Ethyl 4-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)benzoate (116)



^{13}C NMR (125 MHz, $CDCl_3$)

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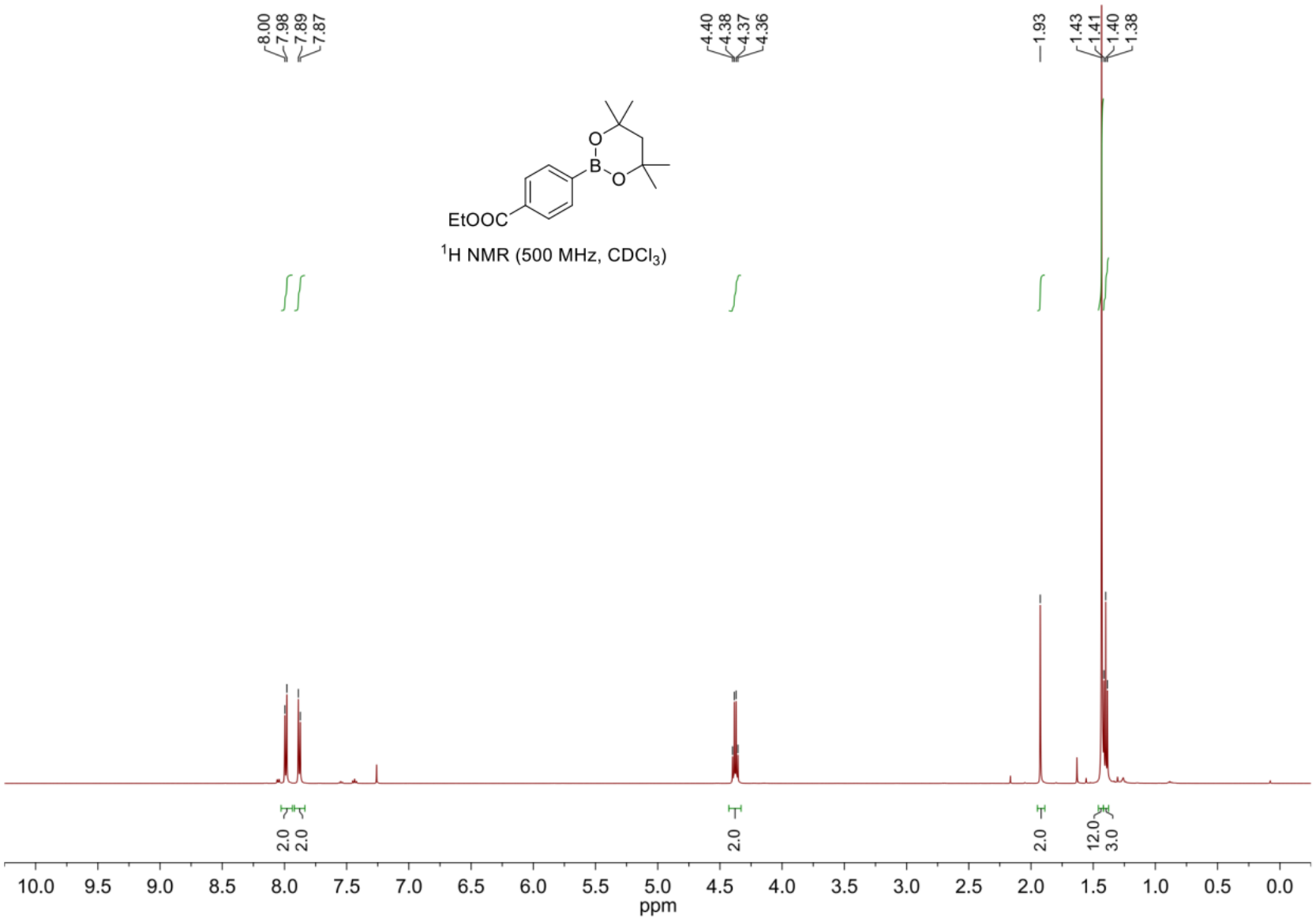
Ethyl 4-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)benzoate (117)



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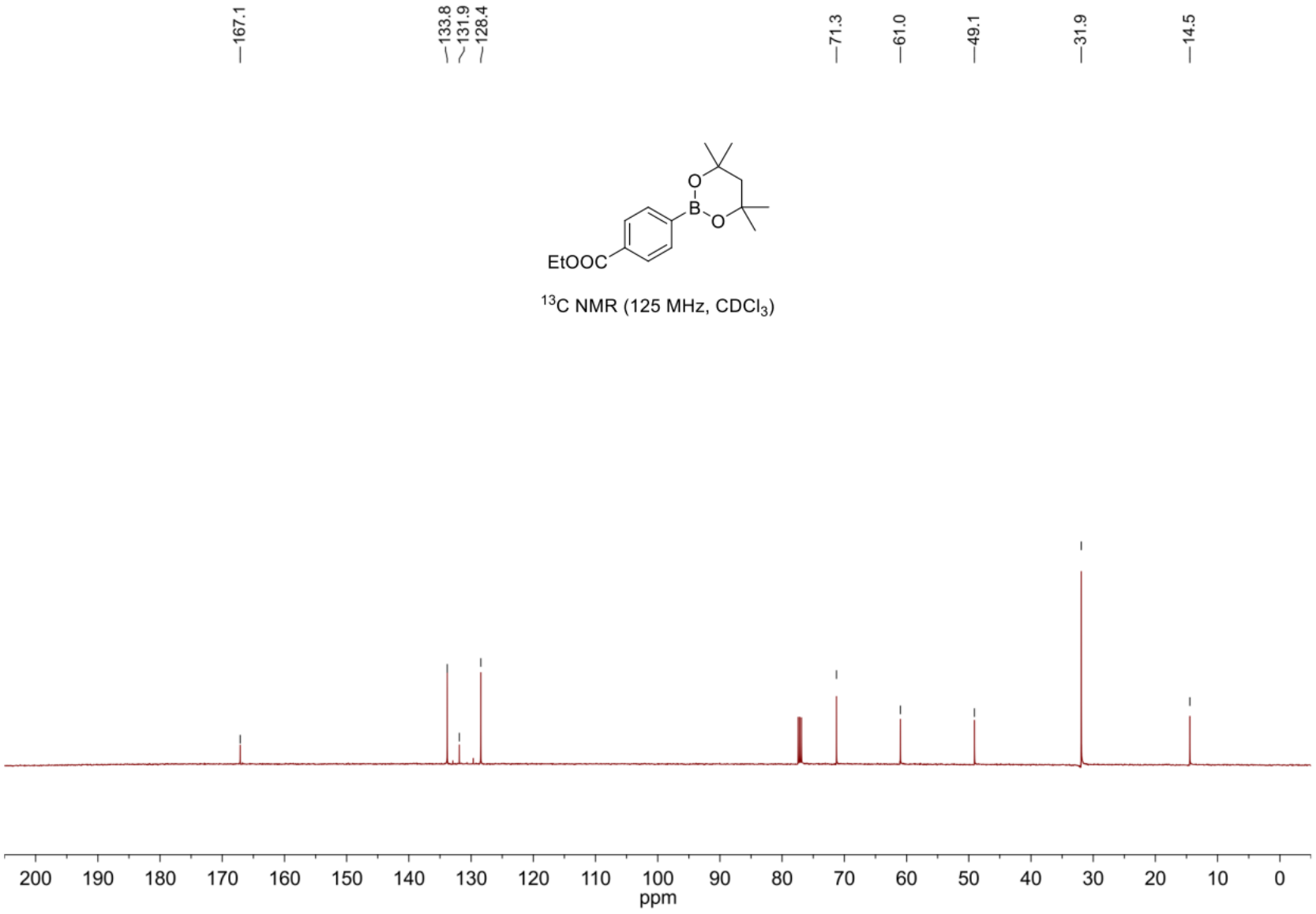
Ethyl 4-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)benzoate (117)



^{13}C NMR (125 MHz, $CDCl_3$)

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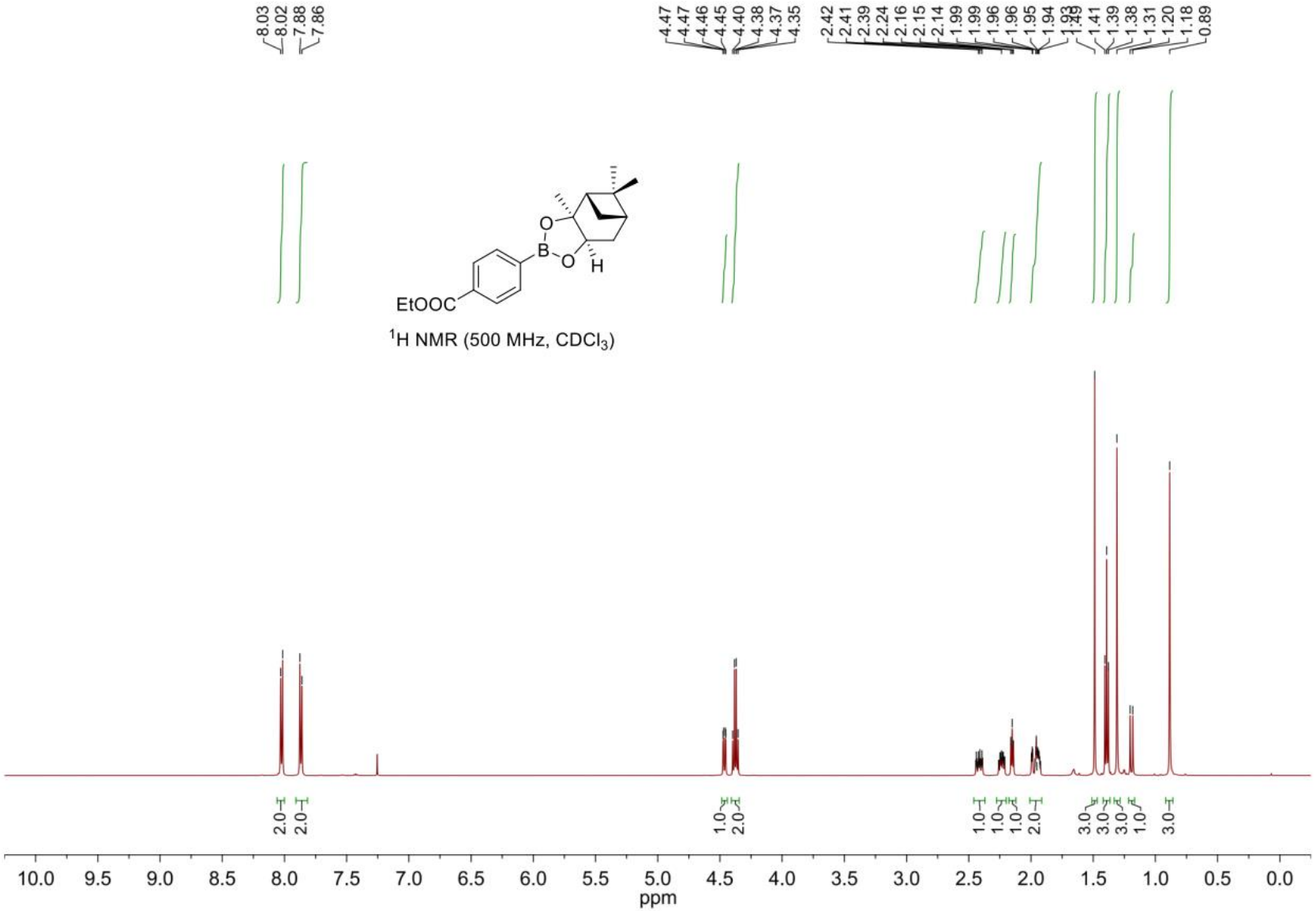
Ethyl 4-((3a*S*,4*S*,6*S*,7a*R*)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[*d*][1,3,2]dioxaborol-2-yl)benzoate (118)



^{1}H NMR (500 MHz, $CDCl_3$)

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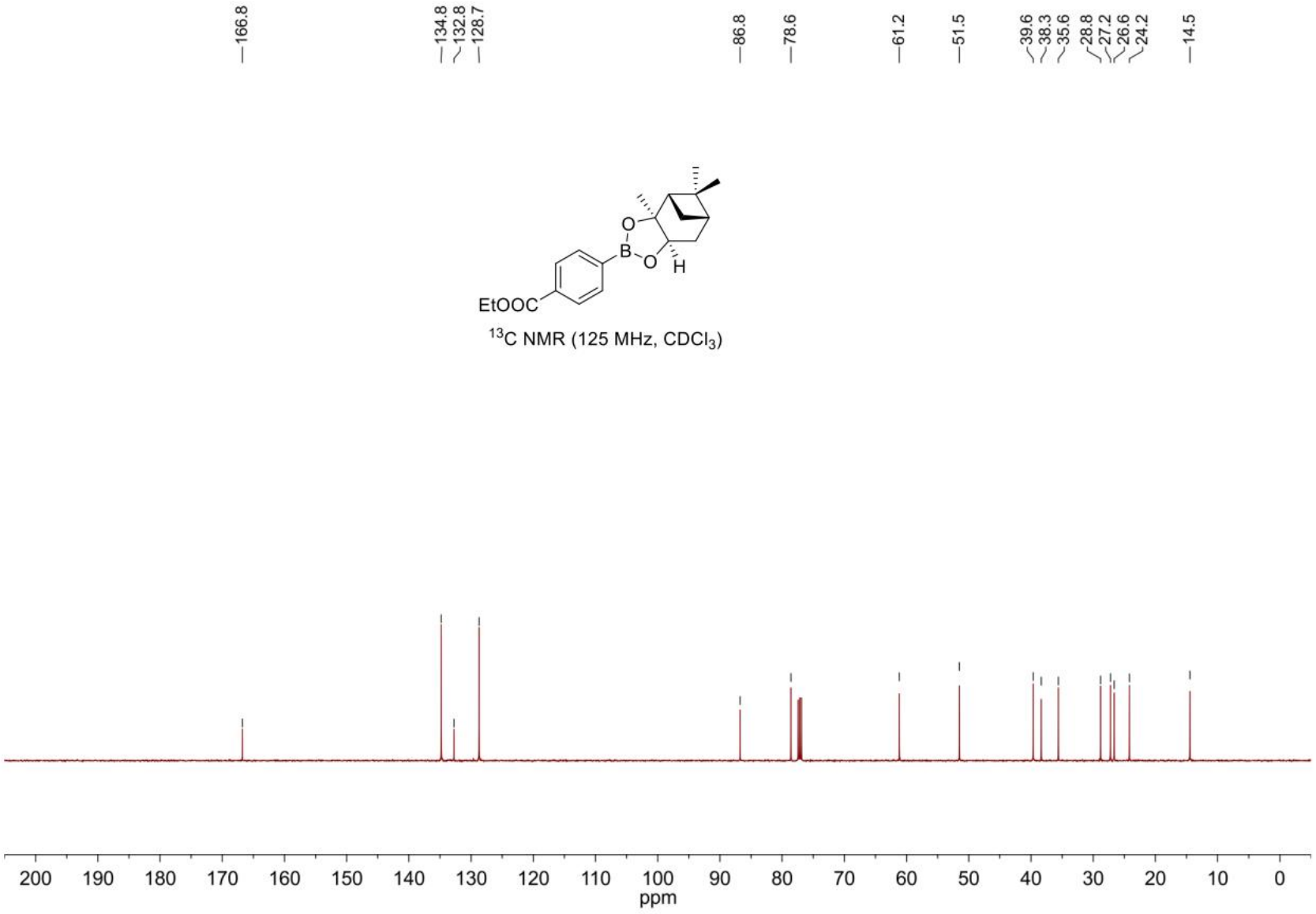
Ethyl 4-((3a*S*,4*S*,6*S*,7a*R*)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[*d*][1,3,2]dioxaborol-2-yl)benzoate (118)



^{13}C NMR (125 MHz, $CDCl_3$)

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References

[1] Cuthbertson , T. J.; Ibanez , M.; Rijnbrand , C. A.; Jackson, A. J.; Mittapalli, G. K.; Zhao, F.; Macdonald, J. E.; Wong-Staal , F. Hepatitis c virus entry inhibitors. PCT Int. Appl. 2008021745, 2008.

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