Exploiting the sp^2 character of bicyclo[1.1.1]pentyl radicals in the transition-metal-free multi-component difunctionalization of [1.1.1]propellane

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SUPPLEMENTARY MATERIALS

Table of Contents

1. General Considerations

1.1 Methods

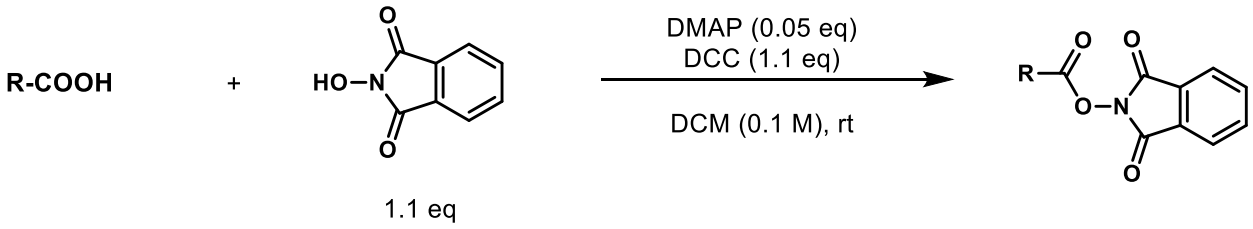
All chemical transformations requiring inert atmospheric conditions or vacuum distillation utilized Schlenk line techniques with a 4- or 5-port dual-bank manifold. Purple light irradiation was accomplished via Kessil PR160L 390 nm lamp set to full intensity (~352 mW/cm^2). The setup was described in a previous report.[1] Blue light irradiation was accomplished using Kessil H150-Blue LED lamps (456 nm, 34 W High Luminous DEX 2100 LEDs) that were each placed 1.5 inches away from reaction vessels with two fans to ensure the reactions remained at room temperature (rt). 10 W blue LED irradiation was accomplished via the LED reactor described in a previous report.[2] CFL irradiation is accomplished via a 26 W CFL (GE FLE26HT3/2/D). Unless otherwise noted, benchtop photo reactions were performed in 4 mL Chemglass vials (1-dram, 15 x 45 mm, 13-425 Green Open Top Cap, TFE Septa, part number: CG-4909-04) or 8 mL Chemglass vials (2-dram, 17 x 60 mm, 15-425 Green Open Top Cap, TFE Septa, part number: CG-4909-03). NMR Spectra (^{1}H, ^{13}C{1H}, ^{19}F{1H}, ^{11}B{1H}) were performed at 300 K. ^{1}H NMR spectra were referenced to residual non-deuterated chloroform (δ 7.26) in $CDCl_3$, residual DMSO-*d*$_5$ (δ 2.50 ppm) in DMSO-*d*$_6$. ^{13}C NMR spectra were referenced to $CDCl_3$ (δ 77.2 ppm), DMSO-*d*$_6$ (δ 39.5 ppm), and acetone-*d*$_6$ (δ 206.2 ppm). Data is presented as follow: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant *J* (Hz), and integration. Reactions were monitored by LC-MS, GC-MS, ^{1}H NMR, and/or TLC using silica gel F254 plates (60 Å porosity, 250 µm thickness). TLC analysis was performed using EtOAc/hexanes or CH_2Cl_2/MeOH as the eluent and developed using permanganate stain, CAM (cerium ammonium molybdate) stain and/or UV light in 254 nm and/or 365 nm wavelengths. Flash chromatography was accomplished using an automated flash chromatography system [with a UV detector monitoring at 254 nm, 280 nm, and an evaporative light scattering detector (ELSD)] with RediSep® R_f silica gel disposable flash columns (60 Å porosity, 40-60 µm) or RediSep R_f Gold® silica gel disposable flash columns (60 Å porosity, 20-40 µm). Accurate mass measurement analyses were conducted using electron ionization (EI) or electrospray ionization (ESI). The signals were mass measured (TOF) against an internal lock mass reference of perfluorotributylamine (PFTBA) for EI-GCMS, and leucine enkephalin for ESI-LCMS. The utilized software calibrates the instruments and reports measurements by use of neutral atomic masses. The mass of the electron is not included. IR spectra were recorded on a Perkin Elmer Spectrum Two FT-IR using either neat oil or solid products. Melting points (°C) are uncorrected.

1.2 Chemicals

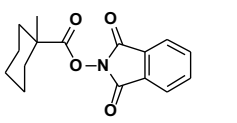
All reagents were purchased and used as received from suppliers unless otherwise noted. Tetrahydrofuran (THF), CH_2Cl_2, and Et_2O were dried by passing through alumina cartridges in a solvent purification system. Other dried solvents were purchased from commercial sources and used as received. Deuterated NMR solvents were purchased and stored over 4Å molecular sieves (MS). Carboxylic acids and organohalides were purchased from commercial sources unless otherwise noted. Me_2PhSi-Bpin (CAS: 185990-03-8) is purchased from TCI or prepared following literature[3] and stored in glovebox.

2. Preparation of Starting Materials

2.1 General Procedure for Preparing Redox Active Ester (General Procedure A – GP-A)



Redox active esters were prepared based on published procedures: to a round bottom flask were added *N*-hydroxyphthalimide (1.1 equiv), DMAP (0.05 equiv), carboxylic acid (1 equiv, if solid, otherwise added after the addition of the solvent CH_2Cl_2). CH_2Cl_2 (0.1 M) was added to the round bottom flask followed by DCC (1.1 equiv). The reaction mixture was stirred at rt. When judged complete by TLC, the reaction mixture was then filtered through a pad of Celite® and concentrated *in vacuo*. The product was purified by flash-column chromatography or recrystallization.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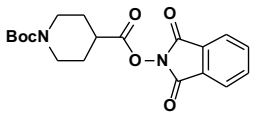

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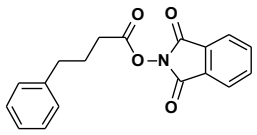
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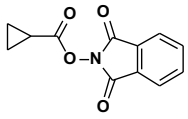
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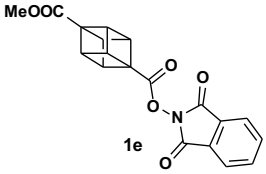

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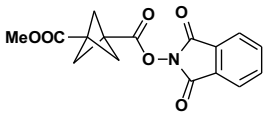

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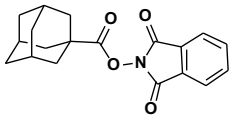
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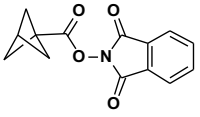
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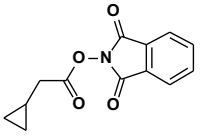
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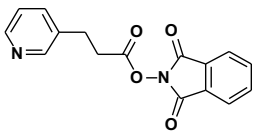
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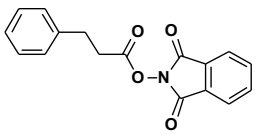
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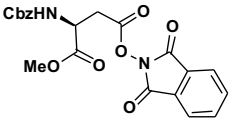

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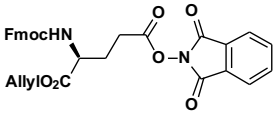

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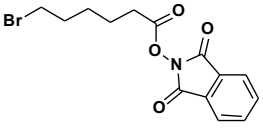

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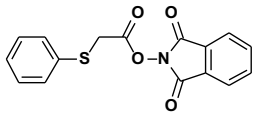
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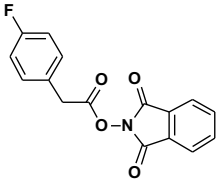

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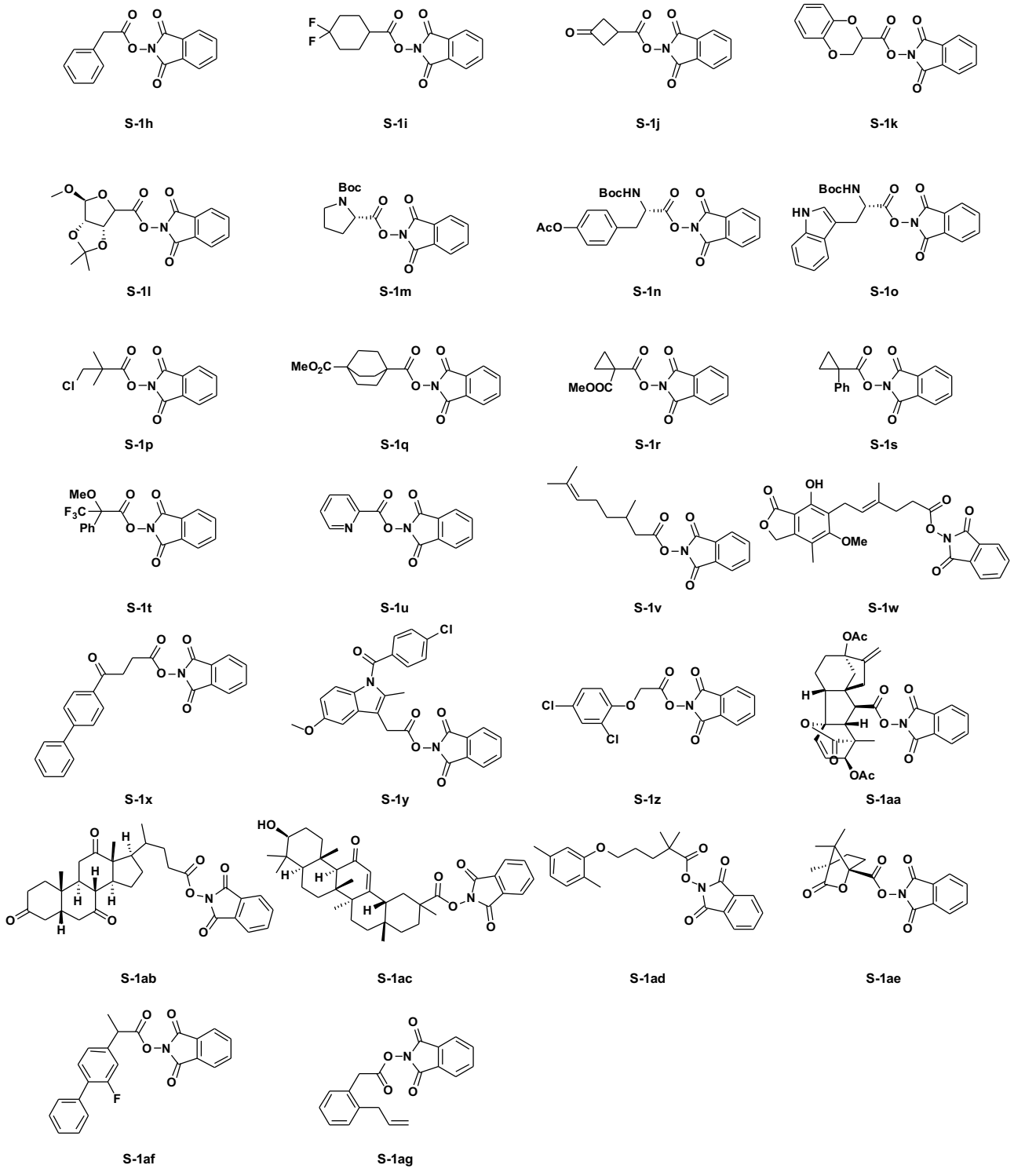
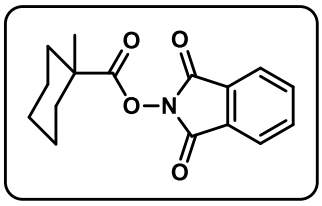


Figure S1. Scope of RAEs used in this study

Characterization Data of Redox-active Esters



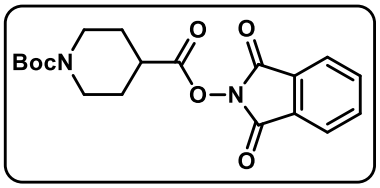
1,3-Dioxoisoindolin-2-yl 1-Methylcyclohexane-1-carboxylate (**1a**, 14.1 mmol scale, 3.7 g, 91%).

Prepared following **GP-A** and purified by column chromatography (5% EtOAc/hexanes). The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 – 7.85 (m, 2H), 7.80 – 7.75 (m, 2H), 2.29 – 2.18 (m, 2H), 1.72 – 1.61 (m, 3H), 1.61 – 1.52 (m, 2H), 1.42 (s, 3H), 1.41 – 1.34 (m, 2H), 1.34 – 1.21 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.8, 162.4, 134.8, 129.2, 124.0, 43.3, 35.8, 26.8, 25.6, 23.2.

The spectra are in accordance with the previous report.[4]



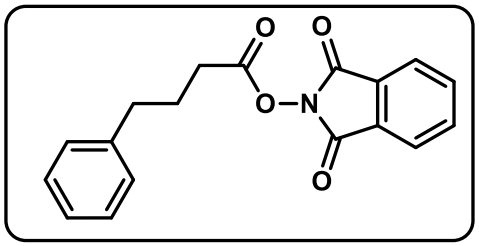
1-(*tert*-Butyl) 4-(1,3-Dioxoisoindolin-2-yl) Piperidine-1,4-dicarboxylate (**1b**, 5.0 mmol scale, 1.6 g, 87%).

Prepared following **GP-A** and purified by recrystallization with EtOH. The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.78 (dd, *J* = 5.5, 3.1 Hz, 2H), 4.02 (s, 1H), 3.03 – 2.96 (m, 2H), 2.94 – 2.86 (m, 1H), 2.09 – 2.01 (m, 2H), 1.89 – 1.79 (m, 2H), 1.45 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.7, 162.0, 154.7, 134.9, 129.0, 124.1, 79.9, 77.4, 77.2, 77.0, 42.9, 38.7, 28.5, 27.9.

The spectra are in accordance with the previous report.[5]



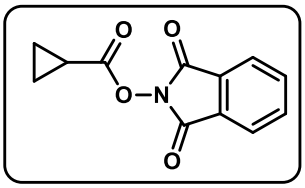
1,3-Dioxoisoindolin-2-yl 4-Phenylbutanoate (**1c**, 5.0 mmol scale, 1.2 g, 58%).

Prepared following **GP-A** and purified by column chromatography (15% EtOAc/hexanes). The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.79 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.26 – 7.21 (m, 3H), 2.79 (t, *J* = 7.6 Hz, 2H), 2.69 (t, *J* = 7.3 Hz, 2H), 2.13 (p, *J* = 7.4 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.5, 162.1, 140.7, 134.8, 129.0, 128.6, 128.6, 126.3, 124.0, 34.7, 30.3, 26.4.

The spectra are in accordance with the previous report.[6]



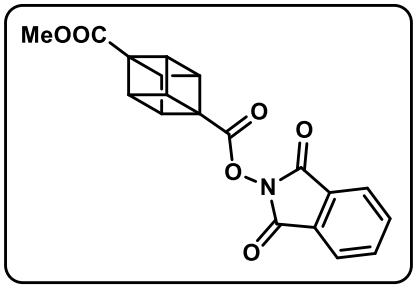
1,3-Dioxoisoindolin-2-yl Cyclopropanecarboxylate (**1d**, 11.6 mmol scale, 2.5 g, 92%).

Prepared following **GP-A** and purified by recrystallization with EtOH. The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.77 (dd, *J* = 5.5, 3.1 Hz, 2H), 1.95 (tt, *J* = 8.3, 4.6 Hz, 1H), 1.28 – 1.23 (m, 2H), 1.21 – 1.14 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.3, 162.1, 134.8, 129.0, 124.3, 10.7, 10.4.

The spectra are in accordance with the previous report.[7]



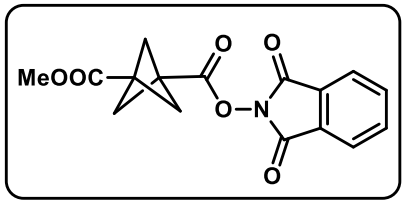
1-(1,3-Dioxoisoindolin-2-yl) 4-Methyl-cubane-1,4-dicarboxylate (**1e**, 1.0 mmol scale, 0.35 g, 58%).

Prepared following **GP-A** and purified by column chromatography (30% EtOAc/hexanes). The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.79 (dd, *J* = 5.5, 3.1 Hz, 2H), 4.49 (dd, *J* = 5.6, 4.0 Hz, 3H), 4.36 (dd, *J* = 5.7, 4.0 Hz, 3H), 3.73 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.6, 167.1, 162.2, 134.9, 129.1, 124.1, 55.9, 53.1, 51.9, 47.8, 47.8, 47.7.

The spectra are in accordance with the previous report.[8]



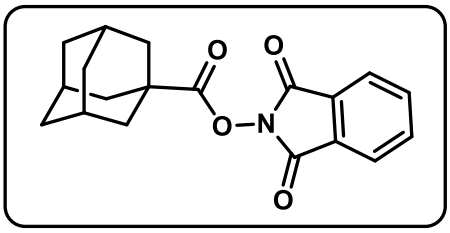
1-(1,3-Dioxoisoindolin-2-yl) 3-Methyl Bicyclo[1.1.1]pentane-1,3-dicarboxylate (**1f**, 11.8 mmol scale, 2.5 g, 68%).

Prepared following **GP-A** and purified by recrystallization with EtOH. The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 – 7.86 (m, 2H), 7.82 – 7.76 (m, 2H), 3.72 (s, 3H), 2.55 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 164.8, 161.8, 135.0, 129.0, 124.2, 53.7, 52.1, 38.7, 35.5.

The spectra are in accordance with the previous report.[8]



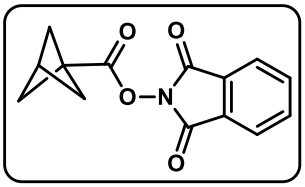
1,3-Dioxoisoindolin-2-yl Adamantane-1-carboxylate (**1g**, 27.7 mmol scale, 8.5 g, 94%).

Prepared following **GP-A** and purified by recrystallization with EtOH. The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.77 (dd, *J* = 5.5, 3.1 Hz, 2H), 2.13 (d, *J* = 2.9 Hz, 6H), 2.11 – 2.08 (m, 3H), 1.77 (t, *J* = 2.8 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.4, 162.3, 134.7, 129.2, 123.9, 40.6, 38.6, 36.3, 27.8.

The spectra are in accordance with the previous report.[6]



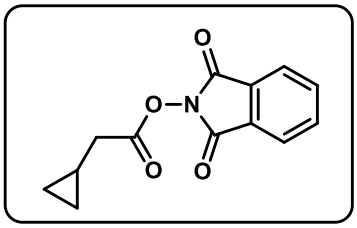
1,3-Dioxoisoindolin-2-yl Bicyclo[1.1.1]pentane-1-carboxylate (**1h**, 30.0 mmol scale, 7.7 g, >99%).

Prepared following **GP-A** and purified by filtering through a 60 g SiO_2 plug using DCM as the eluent. The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.77 (dd, *J* = 5.5, 3.1 Hz, 2H), 2.55 (s, 1H), 2.32 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.7, 162.0, 134.8, 129.1, 124.0, 52.5, 40.0, 29.3.

The spectra are in accordance with the previous report.[9]



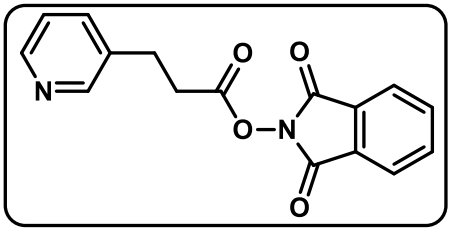
1,3-Dioxoisoindolin-2-yl 2-Cyclopropylacetate (**1i**, 2.0 mmol scale, 0.35 g, 71%).

Prepared following **GP-A** and purified by column chromatography (10% EtOAc/hexanes). The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.78 (dd, *J* = 5.5, 3.1 Hz, 2H), 2.58 (d, *J* = 7.1 Hz, 2H), 1.28 – 1.09 (m, 1H), 0.78 – 0.59 (m, 2H), 0.32 (dt, *J* = 6.1, 4.8 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.1, 162.1, 134.9, 129.1, 124.1, 36.2, 6.7, 4.8.

The spectra are in accordance with the previous report.[10]



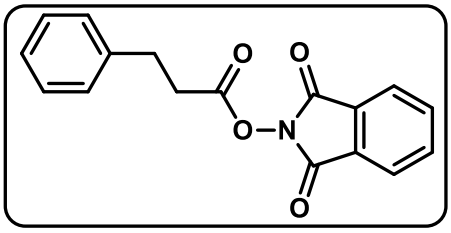
1,3-Dioxoisoindolin-2-yl 3-(Pyridin-3-yl)propanoate (**S-1a**, 3.0 mmol scale, 0.42 g, 47%).

Prepared following **GP-A** and purified by quickly filtering through a 20 g SiO_2 plug using EtOAc (100 mL) as eluent. The product was obtained as a pale-yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.57 – 8.54 (m, 1H), 8.52 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.89 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.83 – 7.77 (m, 2H), 7.62 (ddt, *J* = 7.8, 2.3, 1.1 Hz, 1H), 7.31 – 7.27 (m, 1H), 3.12 (t, *J* = 7.6 Hz, 2H), 3.01 (ddd, *J* = 8.0, 6.8, 0.8 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.7, 162.0, 150.0, 148.5, 136.1, 135.0, 134.7, 129.0, 124.2, 123.8, 32.5, 27.9.

The spectra are in accordance with the previous report.[9]



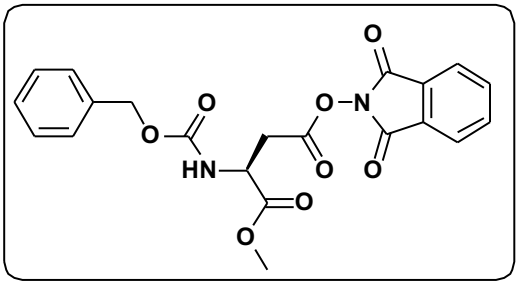
1,3-Dioxoisoindolin-2-yl 3-Phenylpropanoate (**S-1b**, 6.7 mmol scale, 1.7 g, 88%).

Prepared following **GP-A** and purified by recrystallization with EtOH. The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 – 7.86 (m, 2H), 7.80 – 7.77 (m, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.24 (m, 3H), 3.13 (t, *J* = 7.8 Hz, 2H), 3.01 (t, *J* = 7.8 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.9, 161.9, 139.2, 134.8, 128.9, 128.7, 128.3, 126.7, 123.9, 32.7, 30.5.

The spectra are in accordance with the previous report.[11]



4-(1,3-Dioxoisoindolin-2-yl) 1-Methyl ((Benzyloxy)carbonyl)-*L*-aspartate (**S-1c**, 5.3 mmol scale, 1.2 g, 53%).

Prepared following **GP-A** and purified by column chromatography (60% EtOAc/hexanes). The product was obtained as a white solid.

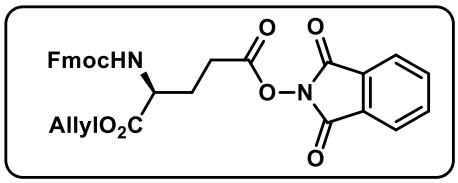
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.85 – 7.77 (m, 2H), 7.43 – 7.34 (m, 4H), 7.34 – 7.28 (m, 1H), 5.83 (d, *J* = 8.0 Hz, 1H), 5.37 – 4.89 (m, 2H), 4.80 (dt, *J* = 8.7, 4.8 Hz, 1H), 3.82 (s, 3H), 3.38 (dd, *J* = 16.9, 4.7 Hz, 1H), 3.28 (dd, *J* = 16.9, 5.1 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.2, 167.4, 161.7, 156.0, 136.2, 135.1, 129.0, 128.7, 128.4, 128.3, 124.3, 67.5, 53.4, 50.4, 34.3.

FT-IR (cm^{-1}, neat, ATR) 3374, 2954, 1818, 1789, 1744, 1524, 1467, 1346, 1218, 1187, 1083, 971, 878, 697, 519.

HRMS (ESI-TOF) calcd for ($C_{21}H_{18}N_2O_8Na$) $[M+Na]^+$ 449.0961, found 449.0967.

Melting point: 129 – 131 °C.



1-Allyl 5-(1,3-Dioxoisoindolin-2-yl) (((9*H*-fluoren-9-yl)methoxy)carbonyl)-*L*-glutamate (**S-1d**, 4.7 mmol scale, 2.40 g, 91%).

Prepared following **GP-A** and purified by column chromatography (20% EtOAc/hexanes). The product was obtained as a white solid.

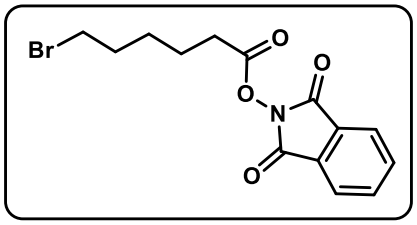
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.82 – 7.75 (m, 4H), 7.62 (t, *J* = 8.1 Hz, 2H), 7.40 (t, *J* = 8.2 Hz, 2H), 7.31 (td, *J* = 7.5, 1.2 Hz, 2H), 5.93 (ddt, *J* = 16.6, 11.2, 5.8 Hz, 1H), 5.52 (d, *J* = 8.3 Hz, 1H), 5.36 (d, *J* = 17.1 Hz, 1H), 5.29 (dd, *J* = 10.0, 0.8 Hz, 1H), 4.68 (d, *J* = 5.9 Hz, 2H), 4.57 – 4.47 (m, 2H), 4.43 – 4.36 (m, 1H), 4.23 (t, *J* = 6.7 Hz, 1H), 2.86 – 2.66 (m, 2H), 2.49 – 2.36 (m, 1H), 2.24 – 2.13 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.2, 169.0, 161.9, 156.1, 143.9, 141.5, 134.9, 131.3, 129.0, 127.9, 127.2, 125.3, 125.2, 124.2, 120.1, 119.6, 67.3, 66.6, 53.3, 47.3, 27.7.

FT-IR (cm^{-1}, neat, ATR) 1782, 1744, 1694, 1526, 1357, 1292, 1193, 1119, 1103, 1083, 1001, 963, 935, 906, 876, 759, 738, 693.

HRMS (ESI-TOF) calcd for ($C_{31}H_{26}N_2NaO_8$) $[M+Na]^+$ 577.1587, found 577.1592.

Melting point: 139 – 142 °C.



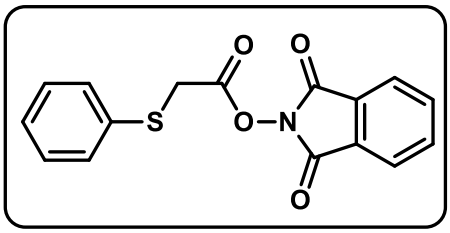
1,3-Dioxoisoindolin-2-yl 6-Bromohexanoate (**S-1e**, 5.1 mmol scale, 1.1 g, 65%).

Prepared following **GP-A** and purified by recrystallization with EtOH. The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 – 7.85 (m, 2H), 7.82 – 7.75 (m, 2H), 3.43 (t, *J* = 6.7 Hz, 2H), 2.69 (t, *J* = 7.4 Hz, 2H), 1.99 – 1.87 (m, 2H), 1.87 – 1.76 (m, 2H), 1.67 – 1.50 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.5, 162.1, 134.9, 129.1, 124.1, 33.3, 32.4, 31.0, 27.5, 24.0.

The spectra are in accordance with the previous report.[12]



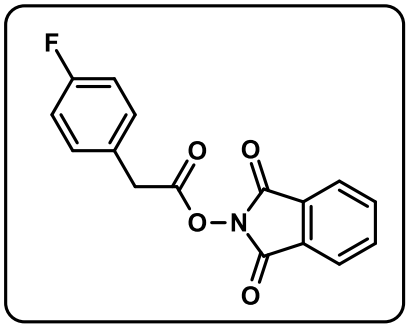
1,3-Dioxoisoindolin-2-yl 2-(Phenylthio)acetate (**S-1f**, 29.7 mmol scale, 7.8 g, 84%).

Prepared following **GP-A** and purified by recrystallization with EtOH. The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.78 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.59 – 7.55 (m, 2H), 7.38 – 7.34 (m, 2H), 7.33 – 7.29 (m, 1H), 3.89 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.4 , 161.7, 134.9, 133.4, 132.0, 129.4, 128.9, 128.3, 124.1, 34.6.

The spectra are in accordance with the previous report.[9]



1,3-Dioxoisoindolin-2-yl 2-(4-Fluorophenyl)acetate (**S-1g**, 6.5 mmol scale, 1.5 g, 77%).

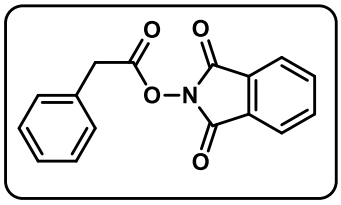
Prepared following **GP-A** and purified by recrystallization with EtOH. The product was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.82 – 7.76 (m, 2H), 7.39 – 7.33 (m, 2H), 7.11 – 7.03 (m, 2H), 3.97 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.7, 162.5 (d, *J* = 246.7 Hz), 161.9, 134.9, 131.1 (d, *J* = 8.2 Hz), 129.0, 127.4, 124.2, 115.9 (d, *J* = 21.7 Hz), 37.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.5.

The spectra are in accordance with the previous report.[13]



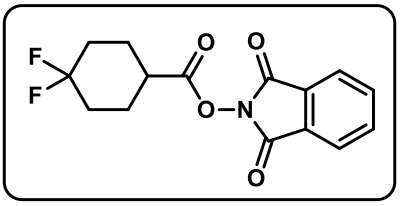
1,3-Dioxoisoindolin-2-yl 2-Phenylacetate (**S-1h**, 7.3 mmol scale, 1.8 g, 88%).

Prepared following **GP-A** and purified by recrystallization with EtOH. The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 – 7.82 (m, 2H), 7.79 – 7.74 (m, 2H), 7.42 – 7.36 (m, 4H), 7.36 – 7.30 (m, 1H), 4.00 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.8, 161.9, 134.9, 131.6, 129.4, 129.0, 127.9, 124.1, 37.8.

The spectra are in accordance with the previous report.[9]



1,3-Dioxoisoindolin-2-yl 4,4-Difluorocyclohexane-1-carboxylate (**S-1i**, 6.1 mmol scale, 1.7 g, 92%).

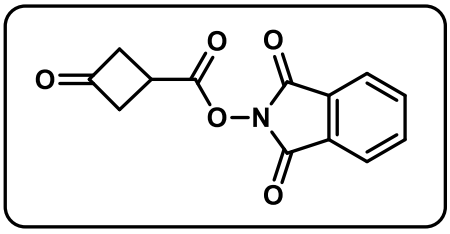
Prepared following **GP-A** and purified by recrystallization with EtOH. The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.79 (dd, *J* = 5.5, 3.1 Hz, 2H), 2.88 (ddt, *J* = 13.0, 9.0, 3.8 Hz, 1H), 2.23 – 2.13 (m, 4H), 2.08 (tdd, *J* = 13.6, 9.2, 5.2 Hz, 2H), 1.96 – 1.84 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.5, 162.0, 134.9, 129.0, 124.1, 122.3 (t, J = 241.3 Hz), 37.9, 32.1 (t, *J* = 24.8 Hz), 25.1 (t, *J* = 5.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -95.76 (d, *J* = 238.1 Hz), -98.48 (d, *J* = 238.5 Hz).

The spectra are in accordance with the previous report.[9]



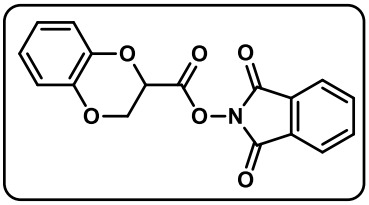
1,3-Dioxoisoindolin-2-yl 3-Oxocyclobutane-1-carboxylate (**S-1j**, 3.0 mmol scale, 0.65 g, 84%).

Prepared following **GP-A** and purified by recrystallization with EtOH. The product was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 5.5, 3.2 Hz, 2H), 7.78 (dd, *J* = 5.5, 3.1 Hz, 2H), 3.65 – 3.59 (m, 3H), 3.51 (ddt, *J* = 14.5, 8.9, 3.5 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 201.3, 170.6, 161.6, 134.9, 128.7, 124.0, 52.1, 24.9.

The spectra are in accordance with the previous report.[5]



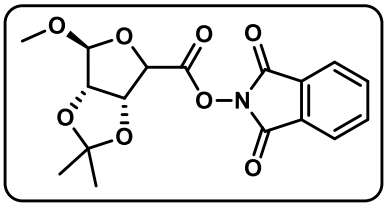
1,3-Dioxoisoindolin-2-yl 2,3-Dihydrobenzo[*b*][1,4]dioxine-2-carboxylate (**S-1k**, 8.3 mmol scale, 2.5 g, 91%).

Prepared following **GP-A** and purified by recrystallization with EtOH. The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.80 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.06 – 6.99 (m, 1H), 6.98 – 6.93 (m, 1H), 6.94 – 6.82 (m, 2H), 5.27 (dd, *J* = 4.8, 2.8 Hz, 1H), 4.61 (dd, *J* = 11.6, 4.7 Hz, 1H), 4.56 (dd, *J* = 11.6, 2.8 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.9, 161.5, 142.9, 141.8, 135.2, 128.9, 124.4, 122.6, 117.8, 117.6, 70.8, 64.9.

The spectra are in accordance with the previous report.[14]



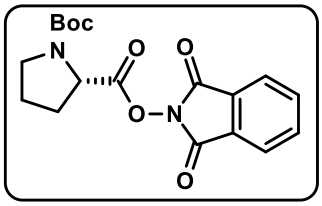
1,3-Dioxoisoindolin-2-yl (3*aR*,6*S*,6*aS*)-6-Methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3] dioxole-4-carboxylate (**S-1l**, 1.8 mmol scale, 0.41 g, 62%).

Prepared following **GP-A** and purified by column chromatography (30% EtOAc/hexanes). The product was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.83 – 7.77 (m, 2H), 5.36 (dd, *J* = 5.8, 1.2 Hz, 1H), 5.14 (s, 1H), 5.01 (t, *J* = 0.9 Hz, 1H), 4.67 (dd, *J* = 5.8, 0.7 Hz, 1H), 3.50 (s, 3H), 1.53 – 1.49 (m, 3H), 1.38 – 1.32 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 161.5, 135.0, 129.0, 124.2, 113.4, 109.9, 84.3, 82.4, 82.2, 56.2, 26.6, 25.2.

The spectra are in accordance with the previous report.[15]



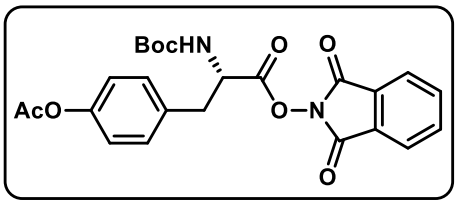
1-(*tert*-butyl) 2-(1,3-dioxoisoindolin-2-yl) (*S*)-pyrrolidine-1,2-dicarboxylate (**S-1m**, 23 mmol scale, 6.9 g, 82%).

Prepared following **GP-A** and purified by recrystallization with EtOH. The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 – 7.83 (m, 2H), 7.83 – 7.72 (m, 2H), 4.73 – 4.55 (m, 1H), 3.69 – 3.54 (m, 1H), 3.54 – 3.39 (m, 1H), 2.53 – 2.39 (m, 1H), 2.39 – 2.32 (m, 1H), 2.16 – 2.04 (m, 1H), 2.04 – 1.92 (m, 1H), 1.56 – 1.43 (m, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.8, 169.5, 161.8, 161.7, 154.2, 153.6, 134.9, 134.8, 129.1, 124.1, 124.0, 81.3, 80.5, 57.3, 57.2, 46.6, 46.4, 31.6, 30.4, 28.5, 28.2, 24.6, 23.7.

The spectra are in accordance with the previous report.[8]



1,3-Dioxoisoindolin-2-yl (*S*)-3-(4-Acetoxyphenyl)-2-((*tert*-butoxycarbonyl)amino)propanoate (**S-1n**, 2.0 mmol scale, 651 mg, 71%).

Prepared following **GP-A** and purified by column chromatography (20% EtOAc/hexanes). The product was obtained as a white solid.

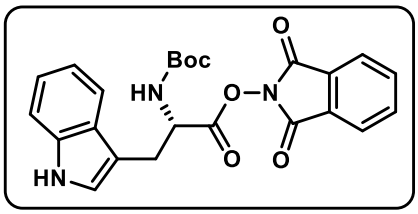
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 5.5, 3.2 Hz, 2H), 7.80 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 5.05 – 4.94 (m, 1H), 4.78 (br, 1H), 3.41 – 3.13 (m, 2H), 2.29 (s, 3H), 1.44 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.5, 168.6, 161.6, 154.8, 150.1, 135.0, 132.4, 130.9, 128.9, 124.2, 121.9, 80.8, 52.7, 37.7, 28.4, 21.4.

FT-IR (cm^{-1}, neat, ATR) 1785, 1746, 1702, 1493, 1367, 1250, 1213, 1203, 1170, 1130, 1056, 1016, 973, 920, 876, 843, 746.

HRMS (ESI-TOF) calcd for ($C_{24}H_{24}N_2NaO_8$) $[M+Na]^+$ 491.1430, found 491.1417.

Melting point: 155 – 156 °C.



1,3-Dioxoisoindolin-2-yl (*tert*-Butoxycarbonyl)-*L*-tryptophanate (**S-1o**, 3.3 mmol scale, 876 mg, 59%).

Prepared following **GP-A** and purified by recrystallization ($CHCl_3$-MeOH). The product was obtained as a yellow solid.

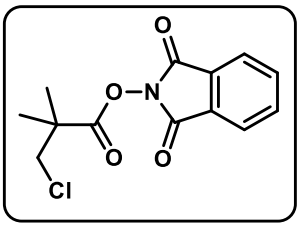
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.91 – 7.88 (m, 2H), 7.82 – 7.78 (m, 2H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.42 (s, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 5.15 – 5.12 (m, 1H), 5.04 (d, *J* = 8.8 Hz, 1H), 3.58 (dd, *J* = 15.0, 5.8 Hz, 1H), 3.47 (dd, *J* = 15.0, 4.5 Hz, 1H), 1.44 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) 169.0, 161.8, 155.0, 136.2, 135.0, 129.0, 128.3, 124.3, 124.2, 122.4, 120.0, 118.9, 111.4, 108.9, 80.6, 53.4, 28.5, 28.2.

FT-IR (cm^{-1}, neat, ATR) 3413, 2979, 1817, 1788, 1742, 1707, 1502, 1458, 1368, 1252, 1186, 1164, 1052, 975, 911, 878, 783, 739, 697, 518.

HRMS (ESI-TOF) calcd for ($C_{24}H_{23}N_3O_6Na$) $[M+Na]^+$ 472.1485, found 472.1489.

Melting point: 180 – 182 °C.



1,3-Dioxoisoindolin-2-yl 3-Chloro-2,2-dimethylpropanoate (**S-1p**, 7.3 mmol scale, 1.31 g, 65%).

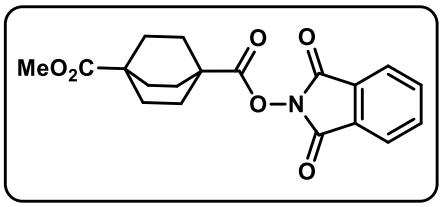
Prepared following **GP-A** and purified by filtering through a 30 g SiO_2 plug using DCM as eluent (125 mL). The product was obtained as a colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.79 (dd, *J* = 5.5, 3.1 Hz, 2H), 3.76 (s, 2H), 1.53 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.6, 161.9, 135.0, 129.1, 124.1, 50.9, 44.6, 23.4.

FT-IR (cm^{-1}, neat, ATR) 1810, 1785, 1739, 1468, 1370, 1290, 1186. 1160, 1130, 1055, 1019, 977, 964, 878, 859, 816, 786, 759, 659, 518.

HRMS (ESI-TOF) calcd for ($C_{13}H_{12}ClNO_4Na$) $[M+Na]^+$ 304.0353, found 304.0349.



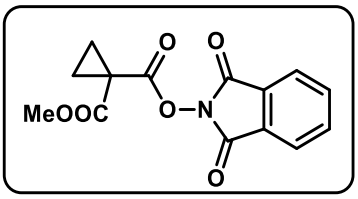
1-(1,3-Dioxoisoindolin-2-yl) 4-Methyl Bicyclo[2.2.2]octane-1,4-dicarboxylate (**S-1q**, 3.0 mmol scale, 0.99 g, 92%).

Prepared following **GP-A** and purified by column chromatography (20% EtOAc/hexanes). The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 2H), 7.80 – 7.75 (m, 2H), 3.67 (s, 3H), 2.11 – 2.00 (m, 6H), 1.95 – 1.83 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 177.5, 173.4, 162.1, 134.8, 129.1, 124.0, 52.0, 38.6, 38.5, 27.8, 27.6.

The spectra are in accordance with the previous report.[16]



1-(1,3-Dioxoisoindolin-2-yl) 1-Methyl Cyclopropane-1,1-dicarboxylate (**S-1r**, 2.0 mmol scale, 460 mg, 79%).

Prepared following **GP-A** and purified by column chromatography (20% EtOAc/hexanes). The product was obtained as a white solid.

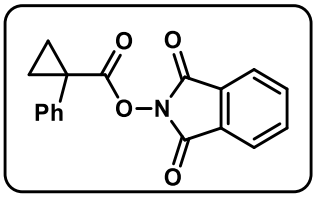
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.79 (dd, *J* = 5.5, 3.1 Hz, 2H), 3.83 (s, 3H), 1.83 (td, *J* = 6.2, 2.5 Hz, 2H), 1.77 (td, *J* = 6.3, 2.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 166.2, 161.8, 134.9, 129.0, 124.1, 53.2, 26.1, 19.0.

FT-IR (cm^{-1}, neat, ATR) 1785, 1738, 1347, 1188, 1021, 936, 875, 698, 517.

HRMS (ESI-TOF) calcd for ($C_{14}H_{11}NNaO_6$) $[M+Na]^+$ 312.0484, found 312.0475.

Melting point: 102 – 103 °C.



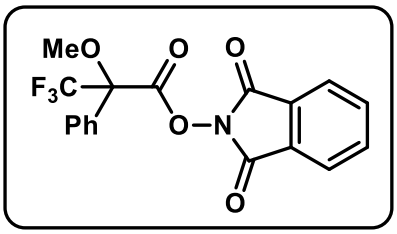
1,3-Dioxoisoindolin-2-yl 1-Phenylcyclopropane-1-carboxylate (**S-1s**, **6.2 mmol scale, 1.3 g, 70%).**

Prepared following **GP-A** and purified by column chromatography (5% EtOAc/hexanes). The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.74 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.55 – 7.48 (m, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.33 – 7.22 (m, 1H), 1.91 (q, *J* = 4.3 Hz, 2H), 1.49 (q, *J* = 4.3 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.2, 162.0, 137.1, 134.8, 130.7, 129.0, 128.6, 128.1, 124.0, 27.4, 18.8.

The spectra are in accordance with the previous report.[8]



1,3-Dioxoisoindolin-2-yl 3,3,3-Trifluoro-2-methoxy-2-phenylpropanoate (**S-1t**, 1.5 mmol scale, 0.29 g, 51%).

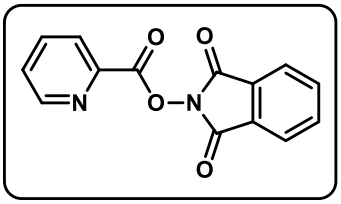
The praparation of compound **S-1aa** is adapted from the report of Doyle *et al*.[9] To a 25 mL flask with a stir bar was charged α-methoxy-α-trifluoromethylphenylacetic acid (351 mg, 1.5 mmol, 1 equiv), DMF (11.0 mg, 0.15 mmol, 0.1 equiv) and oxalyl chloride (222 mg, 2.6 mmol, 1.75 equiv). Then 8 mL of DCM was added, followed by *N*-hydroxyphthalimide (269 mg, 1.7 mmol, 1.1 equiv) and NEt_3 (167 mg, 1.7 mmol, 1.1 equiv). The reaction was allowed to run overnight and then concentrated under reduced pressure. The crude was purifies by SiO_2 column chromatophrapgy (10% EtOAc/hexanes). The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.82 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.74 – 7.71 (m, 2H), 7.52 – 7.47 (m, 3H), 3.82 (d, *J* = 1.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.9, 161.4, 135.2, 131.0, 130.4, 128.9, 128.7, 127.6, 124.3, 122.8 (q, *J* = 289.0 Hz), 85.0(q, *J* = 29.5 Hz), 56.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -72.3.

The spectra are in accordance with the previous report.[17]



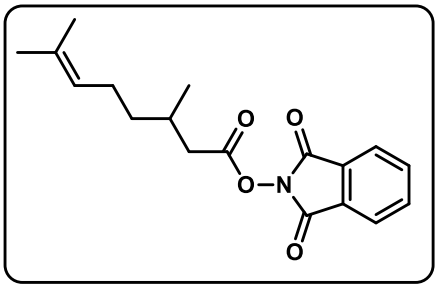
1,3-Dioxoisoindolin-2-yl Picolinate (**S-1u**, 20 mmol scale, 4.8 g, 90%).

Prepared following **GP-A** and purified by recrystallization with EtOH. The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.88 – 8.83 (m, 1H), 8.27 – 8.22 (m, 1H), 7.96 – 7.89 (m, 3H), 7.84 – 7.78 (m, 2H), 7.64 – 7.59 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.8, 161.5, 150.6, 144.4, 137.5, 135.0, 129.1, 128.6, 126.8, 124.2.

The spectra are in accordance with the previous report.[18]



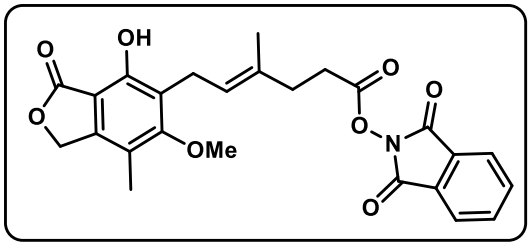
1,3-Dioxoisoindolin-2-yl 3,7-Dimethyloct-6-enoate (**S-1v**, 3.0 mmol scale, 0.7 g, 74%).

Prepared following **GP-A** and purified by column chromatography (20% EtOAc/hexanes). The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 – 7.82 (m, 2H), 7.80 – 7.74 (m, 2H), 5.14 – 5.04 (m, 1H), 2.66 (dd, *J* = 15.0, 5.7 Hz, 1H), 2.45 (dd, *J* = 15.0, 8.3 Hz, 1H), 2.14 – 1.95 (m, 3H), 1.67 (s, 3H), 1.60 (s, 3H), 1.52 – 1.42 (m, 1H), 1.40 – 1.28 (m, 1H), 1.08 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.1, 162.1, 134.8, 132.0, 129.0, 124.0, 124.0, 38.3, 36.6, 30.3, 25.8, 25.4, 19.5, 17.8.

The spectra are in accordance with the previous report.[12]



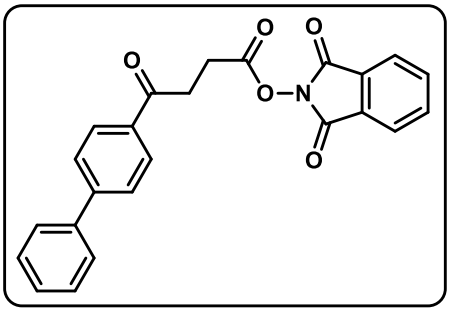
1,3-Dioxoisoindolin-2-yl (*E*)-6-(4-Hydroxy-6-methoxy-7-methyl-3-oxo-1,3-dihydroisobenzofuran-5-yl)-4-methylhex-4-enoate (**S-1w**, 3.1 mmol scale, 0.58 g, 40%).

Prepared following **GP-A** and purified by recrystallization with EtOH. The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.78 (dd, *J* = 5.5, 3.1 Hz, 2H), 5.34 (t, *J* = 7.0 Hz, 1H), 5.19 (s, 2H), 4.36 (br, 1H), 3.77 (s, 3H), 3.42 (d, *J* = 7.1 Hz, 2H), 2.76 (t, *J* = 7.8 Hz, 2H), 2.45 (t, *J* = 7.9 Hz, 2H), 2.15 (s, 3H), 1.85 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.1, 169.4, 163.9, 162.1, 153.9, 144.2, 134.9, 133.2, 129.1, 124.1, 124.0, 122.1, 116.9, 106.6, 70.2, 61.2, 34.2, 34.0, 22.8, 16.3, 11.8.

The spectra are in accordance with the previous report.[19]



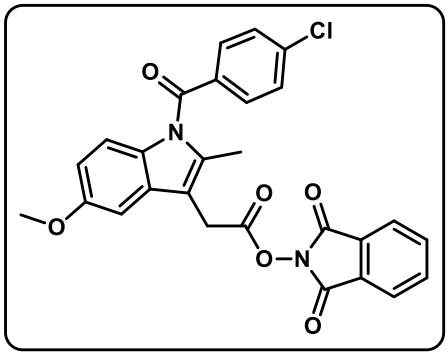
1,3-Dioxoisoindolin-2-yl 4-([1,1'-Biphenyl]-4-yl)-4-oxobutanoate (**S-1x**, 3.0 mmol scale, 1.4 g, 85%).

Prepared following **GP-A** and purified by recrystallization with EtOH. The product was obtained as a purple solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 – 8.04 (m, 2H), 7.89 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.79 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.67 – 7.60 (m, 2H), 7.53 – 7.45 (m, 2H), 7.43 – 7.38 (m, 1H), 3.50 (t, *J* = 6.9 Hz, 2H), 3.18 (t, *J* = 6.9 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.2, 169.5, 162.0, 146.3, 139.9, 135.0, 134.9, 129.1, 129.1, 128.9, 128.5, 127.5, 127.5, 124.2, 33.4, 25.7.

The spectra are in accordance with the previous report.[9]



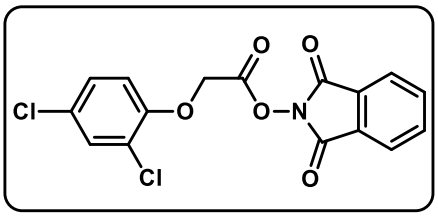
1,3-Dioxoisoindolin-2-yl 2-(1-(4-Chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (**S-1y**, 5.0 mmol scale, 2.1 g, 53%).

Prepared following **GP-A** and purified by recrystallization with EtOH. The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (dt, *J* = 7.6, 3.8 Hz, 2H), 7.79 (dd, *J* = 5.6, 3.1 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.50 – 7.46 (m, 2H), 7.03 (d, *J* = 2.5 Hz, 1H), 6.93 (d, *J* = 9.0 Hz, 1H), 6.71 (dd, *J* = 9.0, 2.5 Hz, 1H), 4.04 (s, 2H), 3.89 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.5, 167.2, 162.0, 156.4, 139.6, 136.6, 135.0, 133.9, 131.5, 130.9, 130.1, 129.4, 129.1, 124.2, 115.2, 112.7, 110.4, 100.8, 55.9, 27.3, 13.6.

The spectra are in accordance with the previous report.[10]



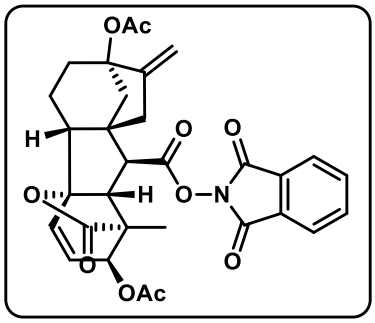
1,3-Dioxoisoindolin-2-yl 2-(2,4-Dichlorophenoxy)acetate (**S-1z**, 2.0 mmol scale, 0.47 g, 64%).

Prepared following **GP-A** and purified by recrystallization with EtOH. The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 – 7.85 (m, 2H), 7.84 – 7.74 (m, 2H), 7.41 (d, *J* = 2.5 Hz, 1H), 7.24 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 5.10 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.1, 161.6, 152.0, 135.2, 130.7, 128.9, 128.3, 128.0, 124.8, 124.3, 115.7, 64.8.

The spectra are in accordance with the previous report.[20]



(1*S*,2*S*,4*aR*,4*bR*,7*S*,9*aS*,10*S*,10*aR*)-10-(((1,3-Dioxoisoindolin-2-yl)oxy)carbonyl)-1-methyl-8-methylene-13-oxo-1,2,5,6,8,9,10,10*a*-octahydro-4*a*,1-(epoxymethano)-7,9a-methanobenzo[*a*]azulene-2,7(4*bH*)-diyl Diacetate (**S-1aa**, 5.8 mmol scale, 1.7 g, 52% over two steps).

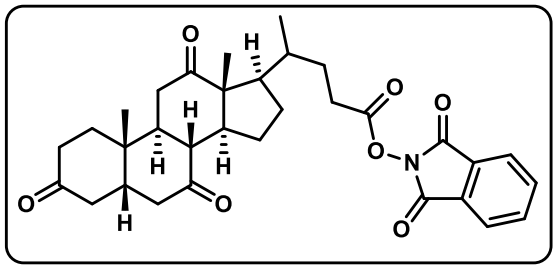
The praparation of compound **S-1aa** is adapted from the report of Aggarwal *et al*.[9] To a solution of Gibberellic acid (2.0 g, 5.8 mmol, 1.0 equiv), acetic anhydride (7.1 g, 69.3 mmol, 12 equiv) and DMAP (70.5 mg, 0.58 mmol, 0.1 equiv) in anhydrous DCM (100 mL) at room temperature was slowly added pyridine (9.1 g, 115.5 mmol, 20 equiv) over 5 min. The reaction mixture was monitored by LC-MS and was found completed after 24 h. The reaction mixture was quench with water (100 mL) and extracted with DCM (50mL×2). The combined organic layers was washed with satd $NaHCO_3$ (50mL×2) and brine (50mL). The organic phas was dried over Na_2SO_4, filtered and concentrated under reduced pressure to give a foam-like powder. (**Note**: it is very important to make sure the mixture is completely dry as the remaining acetic acid could interfere with the phthalimide ester formation). The crude material was directly used in the preparation of the phthalimide ester following **GP-A** and purified by recrystallization using EtOH.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.82 (dd, *J* = 5.5, 3.1 Hz, 2H), 6.41 (d, *J* = 9.3 Hz, 1H), 5.92 (dd, *J* = 9.3, 3.8 Hz, 1H), 5.39 (d, *J* = 3.8 Hz, 1H), 5.29 – 5.26 (m, 1H), 5.12 – 5.09 (m, 1H), 3.40 (d, *J* = 11.1 Hz, 1H), 3.16 (d, *J* = 11.1 Hz, 1H), 2.92 (dt, *J* = 15.1, 3.1

Hz, 1H), 2.53 – 2.44 (m, 3H), 2.28 – 2.23 (m, 1H), 2.12 (d, *J* = 3.7 Hz, 1H), 2.11 (s, 3H), 2.07 (s, 3H), 2.04 (d, *J* = 4.7 Hz, 1H), 1.85 (td, *J* = 11.7, 7.5 Hz, 1H), 1.79 – 1.73 (m, 1H), 1.33 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 176.6, 170.1, 168.8, 161.8, 153.2, 135.1, 134.1, 129.6, 129.0, 124.3, 108.9, 89.9, 84.0, 70.2, 54.2, 52.3, 51.6, 51.5, 48.2, 42.4, 39.9, 36.3, 22.2, 20.9, 17.1, 14.5.

The spectra are in accordance with the previous report.[9]



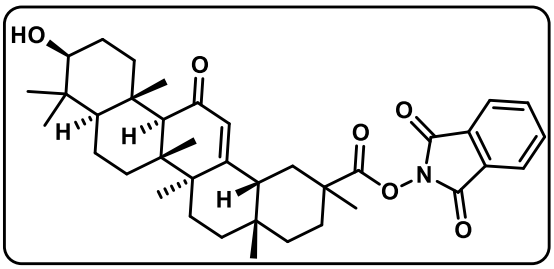
1,3-Dioxoisoindolin-2-yl 4-((5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-Dimethyl-3,7,12-trioxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoate (**S-1ab**, 4.0 mmol scale, 1.6 g, 72%).

Prepared following **GP-A** and purified by column chromatography (60% EtOAc/hexanes). The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.72 (dd, *J* = 5.5, 3.0 Hz, 2H), 2.88 – 2.76 (m, 3H), 2.69 (ddd, *J* = 16.0, 8.6, 5.1 Hz, 1H), 2.57 (dt, *J* = 16.2, 8.2 Hz, 1H), 2.32 – 2.19 (m, 4H), 2.19 – 2.12 (m, 2H), 2.11 – 2.06 (m, 2H), 2.02 – 1.93 (m, 4H), 1.93 – 1.86 (m, 1H), 1.80 (td, *J* = 11.5, 7.1 Hz, 1H), 1.55 (td, *J* = 14.5, 4.6 Hz, 1H), 1.50 – 1.43 (m, 1H), 1.42 – 1.35 (m, 1H), 1.34 (s, 3H), 1.27 – 1.16 (m, 2H), 1.05 (s, 3H), 0.85 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 212.1, 209.2, 208.8, 170.0, 162.1, 134.9, 129.1, 124.1, 57.1, 51.9, 49.2, 47.0, 45.8, 45.7, 45.1, 43.0, 38.8, 36.7, 36.2, 35.4, 34.1, 30.5, 28.6, 27.8, 25.3, 22.1, 18.7, 12.0.

The spectra are in accordance with the previous report.[10]



1,3-Dioxoisoindolin-2-yl (4*aS*,6*aS*,6*bR*,8*aR*,10*S*,12*aS*,12*bR*,14*bR*)-10-Hydroxy-2,4*a*,6*a*,6*b*,9,9,12*a*-heptamethyl-13-oxo-1,2,3,4,4*a*,5,6,6*a*,6*b*,7,8,8*a*,9,10,11,12,12*a*,12*b*,13,14*b*-icosahydropicene-2-carboxylate (**S-1ac**, 3.2 mmol scale, 1.0 g, 52%).

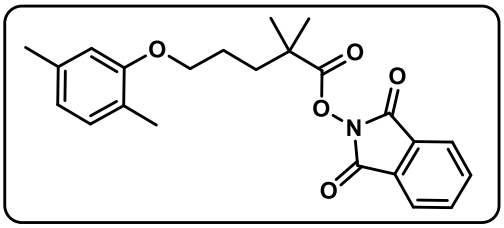
Prepared following **GP-A** and purified by recrystallization with EtOH. The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.79 (dd, *J* = 5.5, 3.1 Hz, 2H), 5.76 (s, 1H), 3.22 (dd, *J* = 11.3, 5.0 Hz, 1H), 2.78 (dt, *J* = 13.6, 3.6 Hz, 1H), 2.46 (ddd, *J* = 13.7, 4.3,

1.7 Hz, 1H), 2.33 (s, 1H), 2.14 (dq, *J* = 13.0, 2.9 Hz, 1H), 2.10 – 2.01 (m, 2H), 1.87 (td, *J* = 13.7, 4.9 Hz, 1H), 1.79 (t, *J* = 13.7 Hz, 1H), 1.69 – 1.57 (m, 6H), 1.55 – 1.47 (m, 1H), 1.47 – 1.44 (m, 1H), 1.43 (s, 3H), 1.42 – 1.39 (m, 1H), 1.38 (s, 3H), 1.31 (s, 1H), 1.24 – 1.18 (m, 1H), 1.14 (s, 3H), 1.12 (s, 3H), 1.07 (ddt, *J* = 13.8, 4.7, 2.2 Hz, 1H), 1.00 (s, 3H), 0.99 – 0.94 (m, 1H), 0.91 (s, 3H), 0.80 (s, 3H), 0.70 (dd, *J* = 11.8, 1.9 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 200.2, 172.8, 168.5, 162.3, 134.9, 129.2, 129.1, 124.1, 78.9, 62.0, 55.1, 47.9, 45.5, 44.1, 43.3, 41.4, 39.3, 37.4, 37.3, 33.0, 32.0, 31.6, 28.5, 28.3, 28.1, 27.5, 26.7, 26.6, 23.7, 18.9, 17.7, 16.5, 15.8.

The spectra are in accordance with the previous report.[21]



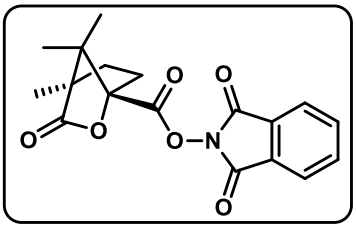
1,3-Dioxoisoindolin-2-yl 5-(2,5-Dimethylphenoxy)-2,2-dimethylpentanoate (**S-1ad**, 4.0 mmol scale, 0.9 g, 57%).

Prepared following **GP-A** and purified by recrystallization with EtOH. The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.79 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.69 – 6.64 (m, 2H), 4.02 (t, *J* = 5.2 Hz, 2H), 2.32 (s, 3H), 2.20 (s, 3H), 2.03 – 1.85 (m, 4H), 1.46 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.9, 162.2, 157.1, 136.6, 134.8, 130.4, 129.2, 124.0, 123.8, 120.9, 112.1, 67.9, 42.1, 37.5, 25.3, 25.2, 21.6, 15.9.

The spectra are in accordance with the previous report.[21]



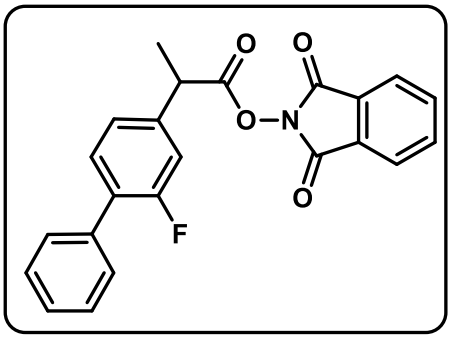
1,3-Dioxoisoindolin-2-yl (1*S*,4*R*)-4,7,7-Trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylate (**S-1ae**, 2.6 mmol scale, 0.39 g, 43%).

Prepared following **GP-A** and purified by column chromatography (50% EtOAc/hexanes). The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.82 (dd, *J* = 5.5, 3.1 Hz, 2H), 2.61 (ddd, *J* = 13.5, 10.8, 4.2 Hz, 1H), 2.29 (ddd, *J* = 13.7, 9.3, 4.6 Hz, 1H), 2.02 (ddd, *J* = 13.1, 10.8, 4.6 Hz, 1H), 1.79 (ddd, *J* = 13.4, 9.3, 4.2 Hz, 1H), 1.19 (s, 3H), 1.18 (s, 3H), 1.17 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 177.3, 164.4, 161.5, 135.2, 129.0, 124.3, 90.0, 55.7, 54.9, 31.0, 29.0, 16.7, 16.6, 10.0.

The spectra are in accordance with the previous report.[21]



1,3-Dioxoisoindolin-2-yl 2-(2-Fluoro-[1,1'-biphenyl]-4-yl)propanoate (**S-1af**, 1.5 mmol scale, 0.43 g, 73%).

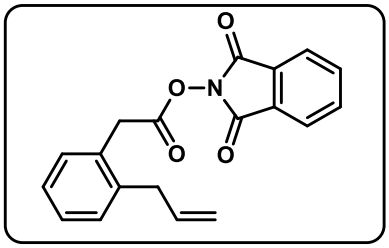
Prepared following **GP-A** and purified by column chromatography (20% EtOAc/hexanes). The product was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dt, *J* = 7.7, 3.8 Hz, 2H), 7.78 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.57 (dt, *J* = 8.1, 1.5 Hz, 2H), 7.47 (dt, *J* = 15.6, 7.9 Hz, 3H), 7.40 – 7.36 (m, 1H), 7.28 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.26 – 7.23 (m, 1H), 4.17 (q, *J* = 7.2 Hz, 1H), 1.73 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.4, 161.9, 159.9 (d, *J* = 248.9 Hz), 139.6 (d, *J* = 7.8 Hz), 135.4, 134.9, 131.3 (d, *J* = 3.3 Hz), 129.1 (d, *J* = 2.9 Hz), 129.0, 128.7, 128.6, 127.9, 124.1, 123.7 (d, *J* = 3.4 Hz), 115.6 (d, J = 24.3 Hz), 42.5, 19.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.9.

The spectra are in accordance with the previous report.[22]



1,3-Dioxoisoindolin-2-yl 2-(2-Allylphenyl)acetate (**S-1ag,** 0.8 mmol scale, 224 mg, 88%).

The 2-allylphenyl acetic acid was prepared in 3 steps starting from the commercially available 2-bromophenyl acetic acid following a procedure from the literature.[23] The corresponding redox active ester was prepared following **GP-A** and purified by column chromatography (20% EtOAc/hexanes). The desired product was obtained as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.79 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.35 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.31 – 7.23 (m, 3H), 5.99 (ddt, *J* = 16.5, 10.1, 6.2 Hz, 1H), 5.14 (dd, *J* = 10.1, 1.7 Hz, 1H), 5.07 (dd, *J* = 17.2, 1.8 Hz, 1H), 4.02 (s, 2H), 3.49 (d, *J* = 6.0 Hz, 2H).

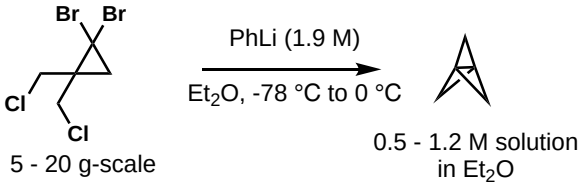
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 162.0, 138.7, 136.2, 134.9, 130.8, 130.5, 130.3, 129.1, 128.5, 127.1, 124.1, 116.7, 37.6, 35.3.

FT-IR (cm^{-1}, neat, ATR) 1815, 1785, 1745, 1359, 1345, 1184, 1137, 1080, 1058, 968, 932, 875, 843, 790, 768, 739, 693.

HRMS (ESI-TOF) calcd for ($C_{19}H_{15}NNaO_4$) $[M+Na]^+$ 344.0899, found 344.0896.

Melting point: 82 – 83 °C.

2.2 General Procedure for Propellane Synthesis



The procedure was adapted from the report of the Baran group.[24] To an appropriately-sized round bottom flask was added 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane (5.0 g, 16.8 mmol) and Et_2O (10-12 mL) under inert atmosphere. Once dissolved, the reaction was cooled to -78 °C in a dry ice-acetone bath. The reaction turned into a slurry at -78 °C. To the light brown slurry was added PhLi (20 mL, 38.0 mmol, 2.3 equiv, 1.9 M soln in *n*-Bu_2O) dropwise over 10 to 15 min. The reaction was then stirred at -78 °C for another 30 min and then was allowed to warm to 0 °C using an ice-water bath. After 2 h, the reaction turned into a dark-brown slurry, which indicates the reaction is finished. The product propellane is co-distilled with Et_2O by house vacuum (*ca.* 4 Torr) as a clear, colorless solution. The receiving flask was submerged in a -78 °C bath or liquid nitrogen bath.

Figure S2. Distillation set-up

Figure S3. Solution of propellane in Et_2O

Determination of the Concentration of Propellane:

In an NMR tube was added 0.100 mmol of 1,3,5-trimethoxybenzene and an appropriate amount of $CDCl_3$. Then 100 μL of the [1.1.1]propellane solution was added into the NMR tube, and the ratio of 1,3,5-trimethoxybenzene:propellane was used to calculate the concentration of [1.1.1]propellane.

*Integration of 3 aromatic protons on 1,3,5-trimethoxybenzene (~6.1 ppm) is set to 1 and the 6 [1.1.1]propellane protons are integrated at ~2.0 ppm.

$$c(propellane) = \frac{Int\ (propellane) \times 0.1mmol \times 3}{6 \times 0.1mL} = Int\ (propellane) \times 0.5\ M$$

Sample calculation:

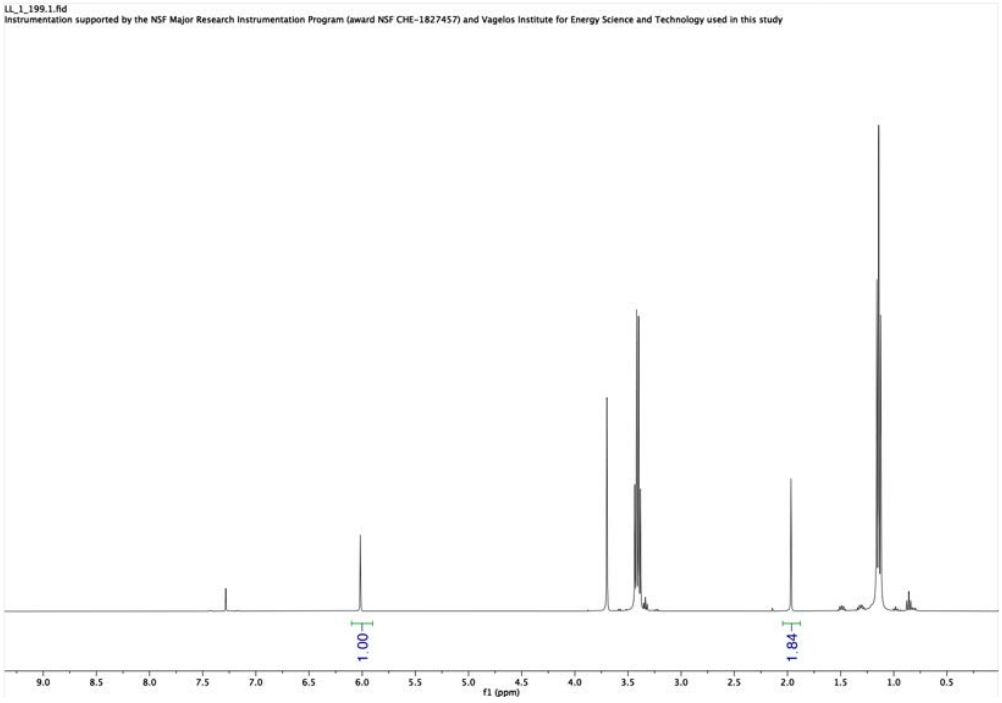


Figure S4. ^{1}H NMR spectrum for the propellane solution with 1,3,5-trimethoxybenzene in $CDCl_3$

$$c(propellane) = Int\ (propellane) \times 0.5\ M = 1.84 \times 0.5\ M = 0.9\ M$$

Note

1. The quality of starting materials are important to achieve a high concentration of [1.1.1]propellane. We observed lower concentrations (0.5 - 0.7 M) when we used a poor quality of tetrahalide and PhLi. The tetrahalide should be a white or light-yellow powder instead of a yellow, chunky solid. Typically, we purchased tetrahalide from Chemscene and PhLi from Sigma-Aldrich.

2. The use of ether solvent (Et_2O and *n*-Bu_2O) proved to be crucial for the formation of propellane.

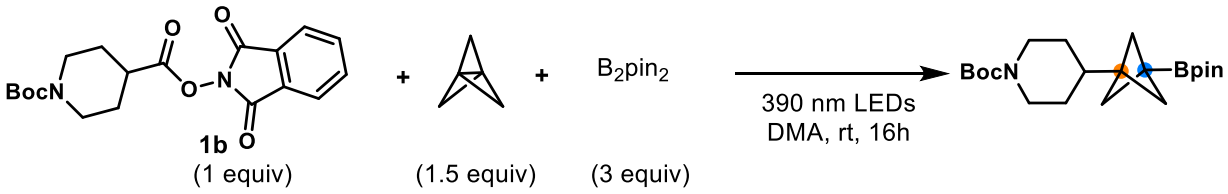
3. The vacuum for distillation is also important: the vacuum should not be too strong because it will lead to loss of product. Careful control while opening the vacuum valve and use of a larger reaction flask are helpful because the reaction mixture tends to bump a lot because of the presence of solids. In the picture, we set up a 20 g scale reaction with a 500 mL round-bottom flask. During co-distillation, the reaction mixture was stirred in a room temperature water bath.

4. Propellane is stable at least for months when stored in Et_2O at < -20 °C. It is semi-stable at room temperature only for a short amount of time (10 - 20 min), as we observed significant polymerization after 2 h at rt.

3. Extended Optimizations and Control Studies

3.1 Optimization and Control Studies with RAE

The optimization of the multicomponent reaction was achieved using RAE **1b** as the model substrate.



Optimization procedure:

The proper amount of radical precursor (0.3 mmol, 1 equiv) was added to an 8 mL sealable vial. Dry B_2pin_2 (or another borylation reagent) was added along with any other additives. Degassed solvent was then added followed by [1.1.1]propellane. The tube was sealed with Parafilm® and irradiated for 16 h under the indicated wavelength at 1 inch distance. The reaction temperature was maintained at rt by two fans. The mixture was then partitioned between Et_2O (50 mL) and brine (25 mL). The organic layer was washed two more times with brine (25 mL each), dried ($MgSO_4$), filtered, and dried under vacuum. LC-MS analysis was performed at this stage by adding 20 μL of the reaction mixture in 1 mL of MeCN. If product was detected, the crude was then purified by flash column chromatography (30% EtOAc in hexanes).

Table S1: Reaction scheme and deviations from the standard conditions.

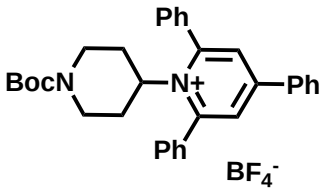
Deviation from standard conditions	% Yield (NMR yield)
None	89
Katritzky salt (1 equiv) instead of **1b**	traces
N-Boc-4-bromopiperidine **2a** (1 equiv) instead of **1b**	0
$B_2(OH)_4$ (1.2 equiv) instead of B_2pin_2*	64 (84)
$B_2(OH)_4$ (3 equiv) instead of B_2pin_2*	(81)
B_2cat_2 (3 equiv) instead of B_2pin_2**	10
Me_2PhSi-Bpin **3b** (3 equiv) instead of B_2pin_2	40
456 nm instead of 390 nm	30
1.2 equiv of B_2pin_2 instead of 3 equiv	60
No precautions (adding 4 equiv of H_2O, under air)	62
with 4-CzIPN (2 mol %) at 456 nm	42

DMF instead of DMA	(58)
MeCN instead of DMA	(59)
THF instead of DMA	(26)
MeOH instead of DMA	(26)
Freeze-pump-thaw (3 cycles)	(82)
No light	0
No light, 60 °C	0

Yields indicated between parentheses were measured by ^{1}H NMR using 1,3,5-trimethoxybenzene as a standard.

*After completion, pinacol (4 equiv) and $MgSO_4$ (10 equiv) were added, and the reaction was vigorously stirred for another 16 h. The product was isolated as the pinacol boronate. The yield indicated is over these two steps.

**After completion, pinacol (10 equiv) and NEt_3 (3 mL) were added, and the reaction was stirred vigorously for another 1 h. The product was isolated as the pinacol boronate. The yield indicated is over these two steps.



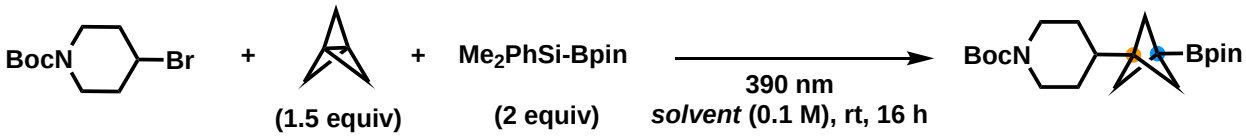
Katritzky salt

Notes

- Completion of this specific reaction is reached after 6 h but all reactions were left for 16 h as the reaction time for other substrates varies.
- Anhydrous solvent and air-free condition are not mandatory and will result in only a slight decrease of the yield.

3.2 Optimization and Control Studies with Organohalides

The optimization of the multicomponent reaction was achieved using 4-bromo-*N*-Boc-piperidine **2a** as the model substrate.



Optimization general procedure:

The proper amount of radical precursor (0.1 mmol, 1 equiv) was added to a 4 mL sealable vial followed by the base (0.05 – 0.1 mmol, 0.5 – 1 equiv), if required. The borylation reagent was added, followed by solvent (0.1 M) and [1.1.1]propellane (0.15 mmol, 1.5 equiv). The tube was sealed with Parafilm® and irradiated for 16 h under the indicated wavelength at 1 inch distance. The reaction temperature was maintained at rt by two fans. LCMS analysis was performed at this stage by adding 20 μL of the reaction mixture in 1 mL of MeCN. The yield was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.

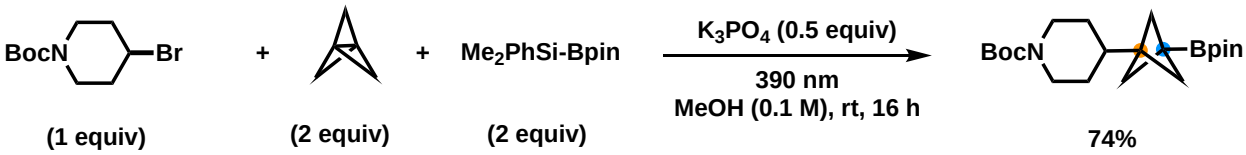
Table S2: Solvent screen

Deviations from standard conditions	
Solvent	**% NMR Yield**
THF	30
Et_2O	35
MeOH	0
MeOH *	60
EtOH *	45
i-PrOH *	40
n-BuOH *	30
t-BuOH *	42
acetone	trace
MeCN	trace
toluene	trace
DMA	trace
DMSO	trace
DMF	trace
CH_2Cl_2	20
1,4-dioxane	20
CPME	18
MTBE	35
DME	15

cyclohexane	23
EtOAc	23
TFT	trace
xylenes	9
$CHCl_3$	0
DCE	20

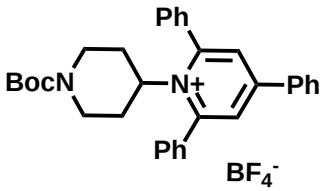
* 1 equiv of K_2CO_3 was added.

Table S3



Deviation from standard conditions	% NMR yield
None	66
N-Boc-4-iodopiperidine **2b** instead of **2a**	72
Katritzky salt (1 equiv) instead of **2a**	27
1b instead of **2a**	<20
3 equiv of [1.1.1]propellane instead of 2 equiv	35
1.5 equiv of [1.1.1]propellane instead of 2 equiv	50
3 equiv of Me_2PhSi-Bpin instead of 2 equiv	17
1 equiv of K_3PO_4 instead of 0.5 equiv	56
Cs_2CO_3 (0.5 equiv) instead of K_3PO_4	37
K_2CO_3 (0.5 equiv) instead of K_3PO_4	58
DIPEA (0.5 equiv) instead of K_3PO_4	42
TMEDA (0.5 equiv) instead of K_3PO_4	35
Ph_3Si-Bpin (2 equiv) instead of Me_2PhSi-Bpin	12
B_2pin_2 (3 equiv) instead of Me_2PhSi-Bpin	8
i-PrOH (0.1 M) instead of MeOH	56
Et_2O (0.1 M) instead of MeOH (w/o base)	32
10 W blue LED	0
34 W Kessil blue LED	27
Freeze-pump-thaw (4 cycles)	58

No base	0
No light	8
No light at 60 °C	trace



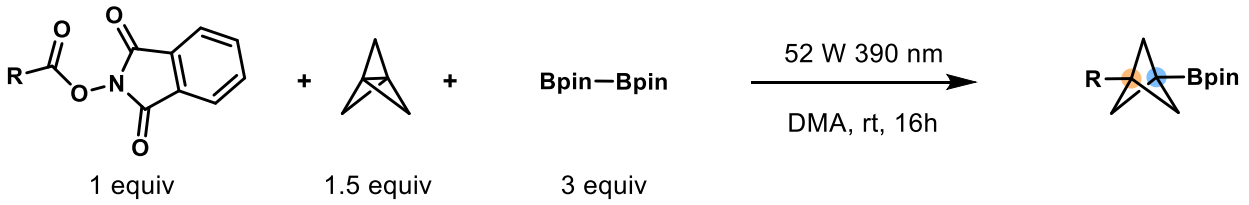
Katritzky salt

Notes

- Increasing or decreasing the amount of base, [1.1.1]propellane, or borylation reagent led to a lower yield
- Anhydrous solvent and air-free condition are not mandatory.

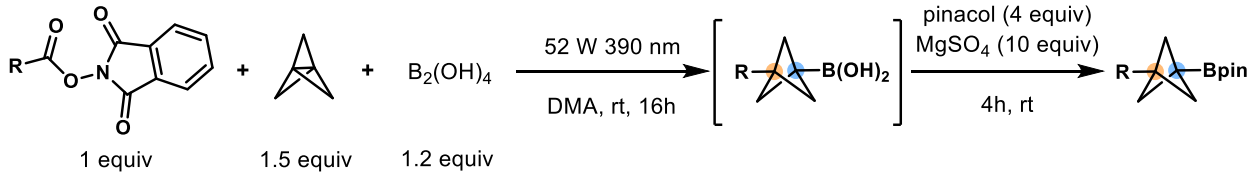
4. Procedures for Reactions

General Procedure for Three-component Borylation with RAE (General Procedure B – GP-B)



To an 8 mL reaction vial equipped with a stirrer bar was added RAE (0.3 mmol, 1 equiv) followed by dry B_2pin_2 (228.5 mg, 0.9 mmol, 3 equiv). The reaction vessel was sealed with a cap containing a TFE-lined silicone septum and then was evacuated and backfilled with argon three times. When done, degassed DMA (3 mL, 0.1 M) was added. Next, freshly prepared and titrated [1.1.1]propellane (0.45 mmol, 1.5 equiv, 0.8 – 1.3 M solution in Et_2O) was then added, and the vial was quickly sealed with Parafilm®. The reaction mixture was then irradiated under vigorous stirring at 52 W 390 nm using a Kessil lamp at 1 inch distance for 16 h. Room temperature was maintained by the use of two fans. When judged complete (*Note:* after completion, the reaction mixture is generally orange), the mixture was then partitioned between Et_2O (10 mL) and satd aq NH_4Cl (10 mL). The organic layer was washed two more times with brine (10 mL × 2), dried ($MgSO_4$), filtered, and further dried under vacuum. The crude mixture was then purified by SiO_2 flash column chromatography.

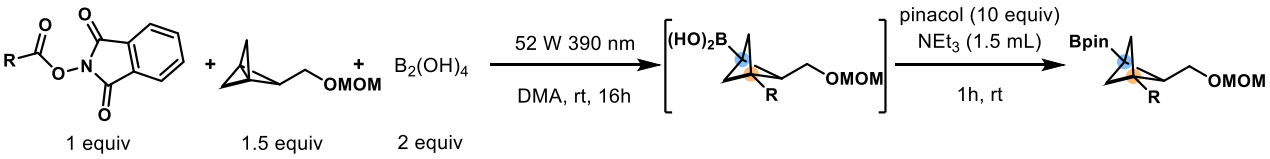
General Procedure for BCP Boronic Acid Preparation with RAE (General Procedure C – GP-C)



To an 8 mL reaction vial equipped with a stirrer bar was added RAE (0.3 mmol, 1 equiv) followed by dry $B_2(OH)_4$ (32.3 mg, 0.36 mmol, 1.2 equiv). The reaction vessel was sealed with a cap containing a TFE-lined silicone septum and then was evacuated and backfilled with argon three times. When done, degassed DMA (3 mL, 0.1 M) was added. Next, freshly prepared and titrated [1.1.1]propellane (0.45 mmol, 1.5 equiv, 0.8 – 1.3 M solution in Et_2O) was then added, and the vial was quickly sealed with Parafilm®. The reaction mixture was then irradiated under vigorous stirring at 52 W 390 nm using a Kessil lamp at 1 inch distance for 16 h. Room temperature was maintained by the use of two fans. When judged complete after 16 h (*Note:* after completion, the reaction mixture remains transparent in most cases, which is different from using B_2pin_2), pinacol (141.8 mg, 1.2 mmol, 4 equiv) and $MgSO_4$ (361.2 mg, 3 mmol, 10 equiv) were added to the reaction mixture, and the reaction mixture was allowed to stirred at rt for 4 h. The mixture was

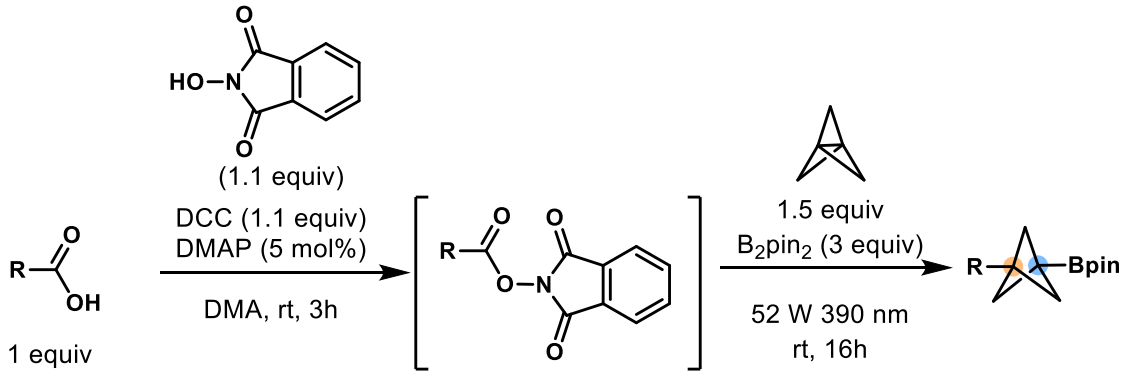
then partitioned between Et_2O (10 mL) and satd aq NH_4Cl (10 mL). The organic layer was washed two more times with brine (10 mL × 2), dried ($MgSO_4$), filtered, and further dried under vacuum. The crude mixture was then purified by SiO_2 flash column chromatography.

General Procedure for the Preparation of 1,2,3-Substituted BCPs (General Procedure D – GP-D)



The C_2-substituted [1.1.1]propellane is prepared according to report from the Baran group.[25] The [1.1.1]propellane was dissolved in DMA to a 0.3 M solution. To a 4 mL reaction vial equipped with a stirrer bar was added RAE (0.2 mmol, 1 equiv) followed by dry $B_2(OH)_4$ (35.9 mg, 0.4 mmol, 2.0 equiv). The reaction vessel was sealed with a cap containing a TFE-lined silicone septum and then was evacuated and backfilled with argon three times. When done, C_2-substituted [1.1.1]propellane stock solution (1 mL) was added and then degassed DMA (1 mL) was added. The vial was quickly sealed with Parafilm®. The reaction mixture was then irradiated under vigorous stirring at 52 W 390 nm using a Kessil lamp at 1 inch distance for 16 h. Room temperature was maintained by the use of two fans. When judged complete after 16 h, pinacol (236.4 mg, 2 mmol, 10 equiv) and NEt_3 (1 mL) were added to the reaction mixture, and the reaction mixture was allowed to stirred at rt for 1 h. The mixture was then partitioned between Et_2O (10 mL) and satd aq NH_4Cl (10 mL). The organic layer was washed two more times with brine (10 mL × 2), dried ($MgSO_4$), filtered, and further dried under vacuum. The crude mixture was then purified by SiO_2 flash column chromatography.

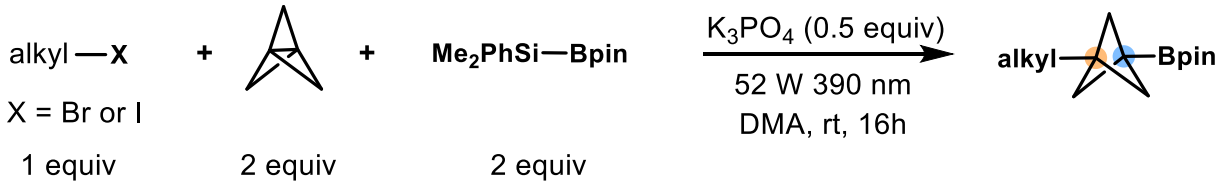
General Procedure for Three-component Borylation with RAE generated *in situ* (General Procedure E – GP-E)



To an 8 mL reaction vial equipped with a stirrer bar was added the carboxylic acid (0.3 mmol, 1 equiv), *N*-hydroxyphthalimide (53.8 mg, 0.33 mol, 1.1 equiv), DMAP (1.8 mg, 0.015 mmol, 5 mol %)

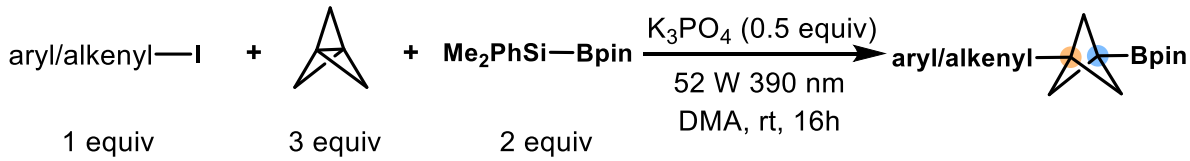
and DMA (3 mL, 0.1 M). The reaction vessel was sealed with a cap containing a TFE-lined silicone septum and was allowed to stir at rt for 3 h. When judged complete by TLC, dry B_2pin_2 (228.5 mg, 0.9 mmol, 3 equiv) and [1.1.1]propellane (0.45 mmol, 1.5 equiv, 0.8 – 1.3 M soln in Et_2O) was then added. The headspace of the reaction vessel was sparged with argon for 10 s and sealed again with the cap and Parafilm®. The reaction mixture was then irradiated under vigorous stirring at 52 W 390 nm using a Kessil lamp at 1 inch distance for 16 h. Room temperature was maintained by the use of two fans. When judged complete (*Note:* after completion, the reaction mixture is generally orange), the mixture was then partitioned between Et_2O (10 mL) and satd aq NH_4Cl (10 mL). The organic layer was washed two more times with brine (10 mL × 2), dried ($MgSO_4$), filtered, and further dried under vacuum. The crude mixture was then purified by SiO_2 flash column chromatography.

General Procedure for Three-component Borylation with Alkyl Halides (General Procedure F – GP-F)



To an 8 mL reaction vial equipped with a stirrer bar was added alkyl halide (0.3 mmol, 1 equiv) and K_3PO_4 (31.8 mg, 0.15 mmol, 0.5 equiv). The vial was then transferred to a nitrogen-filled glovebox. Me_2PhSi-Bpin (157.3 mg, 0.6 mmol, 2 equiv) was added, and then the vial was sealed with a cap containing a TFE-lined silicone septum and transferred out of the glovebox. MeOH (3 mL, 0.1 M) was added. Next, [1.1.1]propellane (0.6 mmol, 2.0 equiv, 0.8 – 1.3 M solution in Et_2O) was added, and the vial was quickly sealed with Parafilm®. The reaction mixture was then irradiated under vigorous stirring at 52 W 390 nm using a Kessil lamp at 1 inch distance for 16 h. Room temperature was maintained by the use of two fans. When judged complete, the crude material was passed through a pad of Celite® and eluted with another 10 mL of acetone. The filtrate was concentrated under reduced pressure and purified by SiO_2 column chromatography.

General Procedure for Three-component Borylation with Aryl/alkenyl Iodides (General Procedure G – GP-G)



To an 8 mL reaction vial equipped with a stirrer bar was added aryl/alkenyl halide (0.3 mmol, 1 equiv) and K_3PO_4 (31.8 mg, 0.15 mmol, 0.5 equiv). The vial was then transferred to a nitrogen-filled glovebox. Me_2PhSi-Bpin (157.3 mg, 0.6 mmol, 2 equiv) was added, and then the vial was sealed with a cap containing a TFE-lined silicone septum and transferred out of the glovebox. MeOH (3 mL, 0.1 M) was added. Next, [1.1.1]propellane (0.9 mmol, 3.0 equiv, 0.8 – 1.3 M soln in Et_2O) was added, and the vial was quickly sealed with Parafilm®. The reaction mixture was then irradiated under vigorous stirring at 52 W 390 nm using a Kessil lamp at 1 inch distance for 16 h.

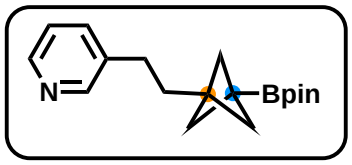
Room temperature was maintained by the use of two fans. When judged complete, the crude material was passed through a pad of Celite® and eluted with another 10 mL of acetone. The filtrate was concentrated under reduced pressure and purified by C18 column chromatography.

Note:

1. In ^{13}C NMR, the carbon directly attached to the boron atom was not detected because of quadrupolar broadening.

2. The purification of the boronate material is generally done by solid-loading the crude material with Celite® and then purify using an automated instrument for column chromatopraphy. The silica-gel chromatography is generally done within 15 minutes, and we observed no or slightly decreased yields (<10%) comparing with NMR yields. However, we noticed significant decrease in yields after running the column for >30 min and complete protodeborylation of products on column after 1 h. In some cases of aryl- and vinyl-substituted BCPs, reverse-phase (C18) chromatography provides quick and simple separations of products but resulted in more product loss (10-20%), probably because of limited solubility of some products in water-MeCN eluent.

3. BCP boronates are stable under proper storage (4 ºC, sealed in Ar environment). No decomposition is observed for products that are under proper storage for over 6 months. The boronate is not sensitive to light but could be sensitive to air. We noticed that slow oxidation of boronate to alcohol is possible when the boronate was in solution without Parafilm®. In those cases, significant oxidation was observed (30-50% of product) over the timescale of months.



3-(2-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)ethyl)pyridine (**4a**, 36.1 mg, 40%).

Prepared following **GP-B** and purified by column chromatography (45% EtOAc/hexanes). The product was obtained as a pale-yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 – 8.37 (m, 2H), 7.49 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.18 (dd, *J* = 7.9, 4.8 Hz, 1H), 2.59 – 2.52 (m, 2H), 1.74 (s, 6H), 1.71 – 1.64 (m, 2H), 1.22 (s, 12H).

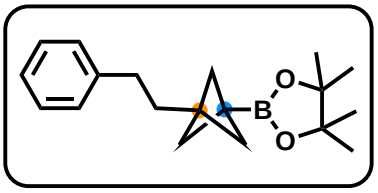
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 147.0, 138.0, 136.0, 123.4, 83.4, 75.1, 51.5, 45.7, 34.4, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.3.

FT-IR (cm^{-1}, neat, ATR) 2959, 2905, 2865, 1727, 1575, 1510, 1478, 1435, 1405, 1371, 1347, 1309, 1197, 1144, 1033, 1006, 855, 805, 714.

HRMS (ESI-TOF) calcd for ($C_{18}H_{27}BNO_2$) $[M+H]^+$ 300.2135, found 300.2133.

Melting point: 69.2 – 70.6 °C.



4,4,5,5-Tetramethyl-2-(3-phenethylbicyclo[1.1.1]pentan-1-yl)-1,3,2-dioxaborolane (**4b**, 41.0 mg, 46%).

Prepared following **GP-B** and purified by column chromatography (25% EtOAc/hexanes). The product was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.22 (m, 2H), 7.20 – 7.13 (m, 3H), 2.59 – 2.52 (m, 2H), 1.76 (s, 6H), 1.72 – 1.66 (m, 2H), 1.24 (s, 12H).

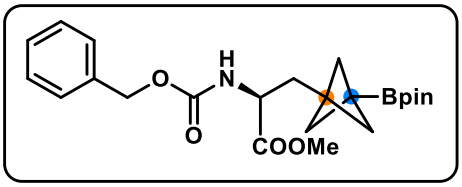
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 128.4, 128.3, 125.6, 83.3, 51.5, 50.2, 48.8, 46.1, 34.9, 32.6, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.6.

FT-IR (cm^{-1}, neat, ATR) 2969, 1454, 1257, 699.

HRMS (EI-TOF) calcd for ($C_{18}H_{24}BNO_2$) $[M-CH_3]^+$ 283.1869, found 283.1884.

Melting point: 90 - 91 °C.



Methyl (*S*)-2-(((Benzyloxy)carbonyl)amino)-3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)propanoate (**4c**, 92.9 mg, 72%).

Prepared following **GP-B** and purified by column chromatography (35% EtOAc/hexanes). The product was obtained as a colorless oil.

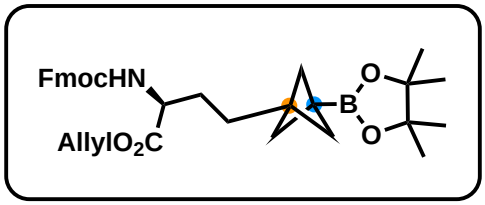
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 5H), 5.20 (d, *J* = 8.3 Hz, 1H), 5.10 (s, 2H), 4.36 (td, *J* = 7.8, 4.6 Hz, 1H), 3.72 (s, 3H), 1.94 (dd, *J* = 14.7, 4.6 Hz, 1H), 1.80 (s, 6H), 1.80 – 1.73 (m, 1H), 1.22 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.1, 155.8, 136.5, 128.7, 128.3, 128.2, 83.5, 67.1, 52.6, 52.5, 52.4, 43.2, 35.4, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.0.

FT-IR (cm^{-1}, neat, ATR) 3342, 2961, 2925, 2869, 1725, 1511, 1436, 1405, 1372, 1346, 1310, 1261, 1201, 1168, 1144, 1045, 855, 739, 698, 666.

HRMS (ESI-TOF) calcd for ($C_{23}H_{32}BNO_6Na$) $[M+Na]^+$ 452.2220, found 452.2225.



Allyl (*S*)-2-((((9*H*-Fluoren-9-yl)methoxy)carbonyl)amino)-4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)butanoate(**4d**, 82.0 mg, 48%).

Prepared following **GP-B** and purified by column chromatography (40% EtOAc/hexanes). The product was obtained as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 2H), 7.63 – 7.55 (m, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 5.90 (ddt, *J* = 16.6, 11.0, 5.8 Hz, 1H), 5.33 (d, *J* = 17.1 Hz, 1H), 5.26 (d, *J* = 10.8 Hz, 2H), 4.63 (dt, *J* = 13.5, 6.4 Hz, 2H), 4.40 (d, *J* = 7.2 Hz, 3H), 4.22 (t, *J* = 7.0 Hz, 1H), 1.75 (s, 6H), 1.60 (tt, *J* = 13.0, 6.2 Hz, 1H), 1.39 (tt, *J* = 13.4, 8.7 Hz, 2H), 1.23 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 156.0, 144.0, 143.8, 141.4, 131.6, 127.8, 127.2, 125.2, 120.1, 120.08, 118.9, 83.4, 67.0, 66.0, 54.0, 51.3, 47.3, 45.2, 29.5, 28.8, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$) δ 31.2.

FT-IR (cm^{-1}, neat, ATR) 2956, 1708, 1511, 1449, 1391, 1380, 1371, 1341, 1307, 1249, 1196, 1166, 1142, 1050, 1032, 987, 854, 758, 738.

HRMS (ESI-TOF) calcd for ($C_{33}H_{40}BNaNO_6$) $[M+Na]^+$ 580.2846, found 580.2859.

2-(3-(5-Bromopentyl)bicyclo[1.1.1]pentan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4e**, 78.1 mg, 76%).

Prepared following **GP-B** and purified by column chromatography (10% EtOAc/hexanes). The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.37 (t, *J* = 6.9 Hz, 2H), 1.86 – 1.78 (m, 2H), 1.71 (s, 6H), 1.43 – 1.35 (m, 2H), 1.34 – 1.27 (m, 2H), 1.23 – 1.19 (m, 2H), 1.22 (s, 12H).

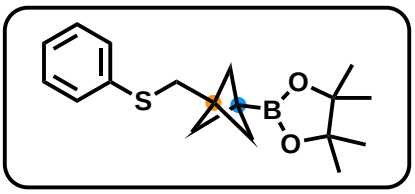
^{13}C NMR (151 MHz, $CDCl_3$) δ 83.3, 51.6, 46.2, 34.1, 33.1, 33.0, 28.5, 25.4, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.2.

FT-IR (cm^{-1}, neat, ATR) 2958, 2929, 2905, 2865, 1435, 1404, 1390, 1379, 1371, 1345, 1307, 1275, 1213, 1196, 1166, 1144, 1111, 1035, 855, 666.

HRMS (EI-TOF) calcd for ($C_{15}H_{25}BBrO_2$) $[M\text{-}CH_3]^+$ 327.1131, found 327.1107.

Melting point: 41 - 42 °C.



4,4,5,5-Tetramethyl-2-(3-((phenylthio)methyl)bicyclo[1.1.1]pentan-1-yl)-1,3,2-dioxaboro lane (**4f**, 57.0 mg, 60%).

Prepared following **GP-B** and purified by column chromatography (20% EtOAc/hexanes). The product was obtained as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 2H), 7.26 – 7.20 (m, 2H), 7.14 – 7.09 (m, 1H), 2.97 (s, 2H), 1.82 (s, 6H), 1.21 (s, 12H).

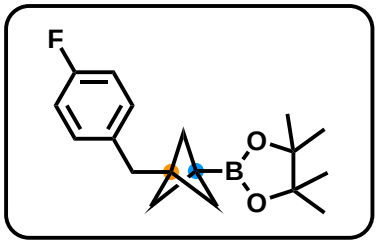
^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2, 128.8, 128.6, 125.5, 83.4, 51.9, 44.4, 36.3, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.3.

FT-IR (cm^{-1}, neat, ATR) 2973, 2906, 2869, 1480, 1437, 1403, 1390, 1379, 1371, 1310, 1242, 1197, 1166, 1143, 1032, 855, 738, 690.

HRMS (EI-TOF) calcd for ($C_{18}H_{25}BNO_2S$) $[M]^+$ 316.1668, found 316.1661.

Melting point: 63 – 64 °C.



2-(3-(4-Fluorobenzyl)bicyclo[1.1.1]pentan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4g**, 41.0 mg, 45%).

Prepared following **GP-B** *with the following modification*: 3 equiv of [1.1.1.]propellane was used. The compound was purified by column chromatography (10% EtOAc/hexanes). The product was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 – 6.97 (m, 2H), 6.96 – 6.90 (m, 2H), 2.62 (s, 2H), 1.69 (s, 6H), 1.20 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4 (d, *J* = 242.9 Hz), 135.1 (d, *J* = 3.2 Hz), 130.3 (d, *J* = 7.9 Hz), 114.9 (d, *J* = 21.1 Hz), 83.3, 51.3, 45.8, 39.3, 24.8.

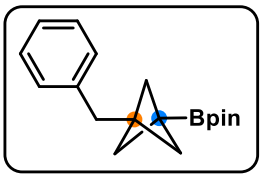
^{19}F NMR (376 MHz, $CDCl_3$) δ -118.30.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.1.

FT-IR (cm^{-1}, neat, ATR) 2975, 1509, 1474, 1372, 1329, 1274, 1251, 1144, 1086, 1009, 981, 850, 839, 793, 750, 697, 673.

HRMS (EI-TOF) calcd for ($C_{18}H_{24}BFO_2$) $[M]^+$ 302.1853, found 302.1848.

Melting point: 90 °C.



2-(3-Benzylbicyclo[1.1.1]pentan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4h**)

Prepared following **GP-B** and purified by column chromatography (5% EtOAc/hexanes). The product was obtained as a white solid. (18.0 mg, 21%)

Prepared following **GP-B** *with the following modification*: 3 equiv of [1.1.1.]propellane was used. The compound was purified by column chromatography (5% EtOAc/hexanes). The product was obtained as a white solid. (30.4 mg, 36%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.22 (m, 2H), 7.18 – 7.13 (m, 1H), 7.08 – 7.03 (m, 2H), 2.65 (s, 2H), 1.70 (s, 6H), 1.20 (s, 12H).

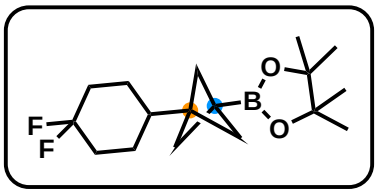
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.5, 129.1, 128.2, 125.7, 83.3, 51.4, 45.9, 40.8, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.4.

FT-IR (cm^{-1}, neat, ATR) 2970, 2906, 2867, 1494, 1434, 1402, 1371, 1350, 1311, 1195, 1168, 1141, 1030, 961, 855, 761, 705, 687, 667, 480.

HRMS (EI-TOF) calcd for ($C_{18}H_{25}BO_2$) $[M]^+$ 284.1948, found 283.1968.

Melting point: 105 - 108 °C.



2-(3-(4,4-Difluorocyclohexyl)bicyclo[1.1.1]pentan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4i**, 54.0 mg, 58%).

Prepared following **GP-B** and purified by column chromatography (20% EtOAc/hexanes). The product was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.15 – 1.99 (m, 2H), 1.70 (s, 6H), 1.68 – 1.53 (m, 4H), 1.41 – 1.13 (m, 15H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 123.7 (dd, *J* = 241.8, 239.5 Hz), 83.2, 49.3, 48.4 (d, *J* = 2.9 Hz), 37.4 (d, *J* = 1.5 Hz), 33.3 (dd, *J* = 25.5, 22.2 Hz), 25.1 (d, *J* = 9.8 Hz), 24.7.

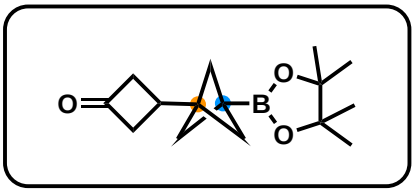
^{11}B NMR (128 MHz, $CDCl_3$) δ 29.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -91.18 (d, *J* = 234.6 Hz), -102.04 (d, *J* = 234.6 Hz).

FT-IR (cm^{-1}, neat, ATR) 2957, 2866, 1433, 1401, 1392, 1373, 1355, 1314, 1272, 1196, 1168, 1143, 1107, 1088, 1042, 1018, 950, 929, 854, 665.

HRMS (EI-TOF) calcd for ($C_{17}H_{26}BFO_2$) $[M\text{-}HF]^+$ 292.2010, found 292.1990.

Melting point: 134 – 136 °C.



3-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)cyclobutan-1-one (4j, 41.0 mg, 52%).

Prepared following **GP-B** and purified by column chromatography (30% EtOAc/hexanes). The product was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.03 – 2.92 (m, 2H), 2.83 – 2.73 (m, 2H), 2.40 (tt, *J* = 9.0, 6.3 Hz, 1H), 1.78 (s, 6H), 1.23 (s, 12H).

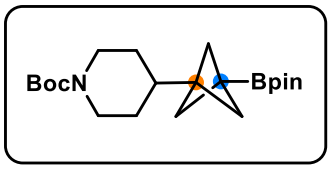
^{13}C NMR (101 MHz, $CDCl_3$) δ 207.9, 83.5, 49.24, 49.21, 47.6, 25.2, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.1.

FT-IR (cm^{-1}, neat, ATR) 2978, 2959, 2865, 1773, 1505, 1438, 1408, 1372, 1351, 1318, 1279, 1203, 1168, 1144, 1125, 1107, 1050, 964, 857.

HRMS (EI-TOF) calcd for ($C_{15}H_{23}BO_3$) $[M]^+$ 262.1740, found 262.1757.

Melting point: 129 – 131 °C.



***tert*-Butyl 4-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)piperidine-1-carboxylate** (**4k**)

Prepared following **GP-B** and purified by column chromatography (30% EtOAc/hexanes). The product was obtained as a white solid. (100.1 mg, 89%).

Prepared following **GP-C** and purified by column chromatography (30% EtOAc/hexanes). The product was obtained as a white solid (73 mg, 64%).

Prepared following **GP-E** and purified by column chromatography (30% EtOAc/hexanes). The product was obtained as a white solid (76 mg, 67%).

Prepared following **GP-F** and purified by column chromatography (30% EtOAc/hexanes). The product was obtained as a white solid (58.4 mg, 52%).

Prepared following **GP-F** *with the following modification:* the corresponding organoiodide was used. The compound was purified by column chromatography (30% EtOAc/hexanes). The product was obtained as a white solid (73 mg, 65%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.10 (br, 2H), 2.60 (br, 2H), 1.69 (s, 6H), 1.53 – 1.48 (m, 2H), 1.44 (s, 9H), 1.32 (tt, *J* = 11.9, 3.5 Hz, 1H), 1.22 (s, 12H), 1.06 – 0.98 (m, 2H).

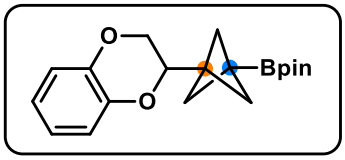
^{13}C NMR (151 MHz, $CDCl_3$) δ 155.1, 83.4, 79.3, 49.2, 48.9, 44.0, 37.8, 28.7, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.3.

FT-IR (cm^{-1}, neat, ATR) 2974, 2929, 1692, 1404, 1390, 1379, 1308, 1274, 1234, 1197, 1169, 1143, 1096, 1008, 995, 978, 855.

HRMS (ESI-TOF) calcd for ($C_{21}H_{37}BNO_4$) $[M+H]^+$ 378.2816, found 378.2802.

Melting point: 93 - 94 °C.



2-(3-(2,3-Dihydrobenzo[*b*][1,4]dioxin-2-yl)bicyclo[1.1.1]pentan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4l**, 61.7 mg, 63%)

Prepared following **GP-B** and purified by column chromatography (30% EtOAc/hexanes). The product was obtained as a colorless oil.

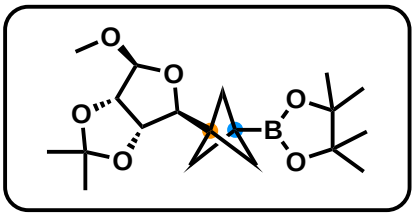
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.89 – 6.85 (m, 1H), 6.85 – 6.69 (m, 3H), 4.18 (dd, *J* = 11.2, 2.3 Hz, 1H), 3.94 (dd, *J* = 7.5, 2.3 Hz, 1H), 3.88 (dd, *J* = 11.1, 7.5 Hz, 1H), 2.00 – 1.80 (m, 6H), 1.23 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.8, 143.4, 121.5, 121.2, 117.4, 117.0, 83.6, 71.8, 65.8, 50.2, 44.0, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.1.

FT-IR (cm^{-1}, neat, ATR) 2975, 2874, 1495, 1467, 1438, 1408, 1391, 1380, 1372, 1348, 1312, 1271, 1259, 1203, 1167, 1144, 1087, 1044, 855, 748.

HRMS (EI-TOF) calcd for ($C_{19}H_{25}BO_4$) $[M]^+$ 328.1846, found 328.1862.



2-(3-((3a*S*,4*S*,6*S*,6a*S*)-6-Methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)bicyclo[1.1.1]pentan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4m**, 64.0 mg, 58%).

Prepared following **GP-B** and purified by column chromatography (25% EtOAc/hexanes). The product was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.90 (s, 1H), 4.59 (dd, *J* = 6.0, 1.4 Hz, 1H), 4.48 (d, *J* = 6.0 Hz, 1H), 4.05 (d, *J* = 1.3 Hz, 1H), 3.34 (s, 3H), 1.80 (s, 6H), 1.45 (s, 3H), 1.30 (s, 3H), 1.22 (s, 12H).

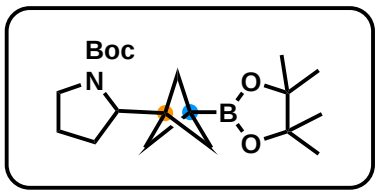
^{13}C NMR (101 MHz, $CDCl_3$) δ 112.3, 109.5, 87.5, 86.1, 83.5, 81.4, 55.0, 50.1, 45.8, 26.8, 25.4, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.4.

FT-IR (cm^{-1}, neat, ATR) 2977, 2913, 1518, 1473, 1454, 1373, 1332, 1254, 1203, 1145, 1105, 1090, 1063, 1030, 1009, 982, 928, 868, 851, 673.

HRMS (EI-TOF) calcd for ($C_{18}H_{28}BO_6$) $[M\text{-}CH_3]^+$ 351.1979, found 351.1982.

Melting point: 68 – 70 °C.



***tert*-Butyl 2-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)pyrrolidine-1-carboxylate** (**4n**, 73.0 mg, 67%).

Prepared following **GP-B** and purified by column chromatography (35% EtOAc/hexanes). The product was obtained as a white waxy solid.

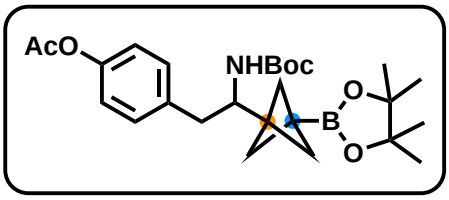
^{1}H NMR (600 MHz, $CDCl_3$) δ (mixture of rotamers) δ 3.79 – 3.62 (m, 1H), 3.35 – 3.31 (m, 2H), 1.86 – 1.76 (m, 4H), 1.76 (s, 6H), 1.45 (s, 9H), 1.22 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (mixture of rotamers) δ 155.2, 83.5, 79.1, 57.7, 50.4, 47.9, 46.3, 28.7, 28.1, 24.9, 23.3.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.4

FT-IR (cm^{-1}, neat, ATR) 2975, 2874, 1693, 1517, 1475, 1454, 1390, 1367, 1331, 1254, 1163, 1009, 982, 951, 926, 851, 773, 674.

HRMS (EI-TOF) calcd for ($C_{16}H_{25}BNO_4$) $[M\text{-}t\text{-}Bu]^+$ 306.1877, found 306.1863.



4-(2-((*tert*-Butoxycarbonyl)amino)-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)ethyl)phenylacetate (**4o**, 86 mg, 61%).

Prepared following **GP-B** and purified by column chromatography (40% EtOAc/hexanes). The product was obtained as a colorless oil.

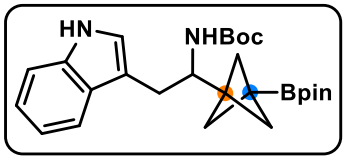
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 4.27 (d, *J* = 9.3 Hz, 1H), 3.86 – 3.77 (m, 1H), 2.73 (dd, *J* = 14.4, 6.1 Hz, 1H), 2.54 (dd, *J* = 14.4, 8.6 Hz, 1H), 2.26 (s, 3H), 1.79 – 1.68 (m, 6H), 1.35 (s, 9H), 1.21 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 155.6, 149.1, 136.2, 130.1, 121.3, 83.5, 79.1, 52.0, 49.6, 47.7, 37.6, 28.4, 24.8, 21.2.

^{11}B NMR (128 MHz, $CDCl_3$) δ 31.6.

FT-IR (cm^{-1}, neat, ATR) 2976, 2871, 1762, 1698, 1507, 1435, 1403, 1391, 1367, 1308, 1196, 1165, 1143, 1044, 1019, 911, 854, 729.

HRMS (ESI-TOF) calcd for ($C_{26}H_{38}BNaNO_6$) $[M+Na]^+$ 494.2690, found 494.2668.



***tert*-Butyl (2-(1*H*-Indol-3-yl)-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)ethyl)carbamate** (**4p**, 113.4 mg, 84%).

Prepared following **GP-B** and purified by column chromatography (45% EtOAc/hexanes). The product was obtained as a colorless oil.

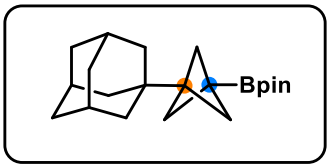
^{1}H NMR (600 MHz, $CDCl_3$) (mixture of rotamers) δ 8.32 (s, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.98 (s, 1H), 4.43 (d, *J* = 9.3 Hz, 1H), 4.14 – 3.61 (m, 1H), 2.89 (dd, *J* = 15.3, 5.7 Hz, 1H), 2.76 – 2.50 (m, 1H), 1.78 (q, *J* = 9.7 Hz, 6H), 1.37 (s, 9H), 1.23 (d, *J* = 2.9 Hz, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) (mixture of rotamers) δ 155.9, 136.3, 128.0, 122.3, 121.8, 119.2, 118.9, 112.5, 111.2, 83.5, 83.0, 75.2, 51.3, 49.6, 48.1, 28.5, 25.0, 24.9, 24.7.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.4.

FT-IR (cm^{-1}, neat, ATR) 3337, 2976, 1690, 1511, 1457, 1436, 1403, 1391, 1366, 1307, 1248, 1197, 1167, 1143, 1110, 1045, 1027, 951, 855, 740, 666.

HRMS (ESI-TOF) calcd for ($C_{26}H_{37}BN_2O_4Na$) $[M+Na]^+$ 475.2744, found 475.2756.



2-(3-(Adamantan-1-yl)bicyclo[1.1.1]pentan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4q**, 70.2 mg, 89%).

Prepared following **GP-B** and purified by column chromatography (30% EtOAc/hexanes). The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.93 – 1.90 (m, 3H), 1.66 (d, *J* = 12.5 Hz, 3H), 1.64 (s, 6H), 1.57 (d, *J* = 10.5 Hz, 3H), 1.36 (s, 6H), 1.23 (s, 12H).

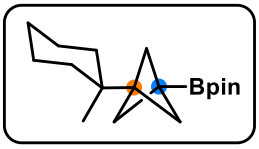
^{13}C NMR (151 MHz, $CDCl_3$) δ 83.1, 46.7, 38.3, 37.8, 37.0, 31.6, 28.2, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.3.

FT-IR (cm^{-1}, neat, ATR) 2963, 2903, 2869, 2848, 1474, 1448, 1372, 1330, 1287, 1253, 1212, 1198, 1146, 1009, 982, 952, 852, 698, 674.

HRMS (ESI-TOF) calcd for ($C_{21}H_{34}BO_3$) $[M+H]^+$ 329.2652, found 329.2635.

Melting point: 93 - 95 °C.



4,4,5,5-Tetramethyl-2-(3-(1-methylcyclohexyl)bicyclo[1.1.1]pentan-1-yl)-1,3,2-dioxaborolane (**4r**)

Prepared following **GP-B** and purified by column chromatography (10% EtOAc/hexanes). The product was obtained as a colorless oil (45.2 mg, 52%).

Prepared following **GP-C** and purified by column chromatography (10% EtOAc/hexanes). The product was obtained as a colorless oil (59.3 mg, 68%).

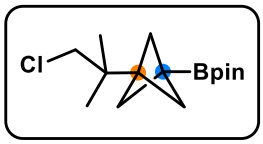
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.67 (s, 6H), 1.58 – 1.51 (m, 1H), 1.51 – 1.43 (m, 2H), 1.38 – 1.28 (m, 2H), 1.22 (s, 12H), 1.17 – 1.11 (m, 4H), 1.09 (dt, *J* = 12.3, 3.9 Hz, 1H), 0.75 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 83.3, 54.6, 47.5, 33.2, 32.3, 26.6, 24.9, 22.2, 19.3.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.0.

FT-IR (cm^{-1}, neat, ATR) 2972, 2925, 2869, 1707, 1515, 1474, 1373, 1328, 1264, 1246, 1218, 1200, 1145, 1009, 982, 952, 851, 698, 674.

HRMS (EI-TOF) calcd for ($C_{17}H_{28}BO_2$) $[M-CH_3]^+$ 275.2182, found 275.2186.



2-(3-(1-Chloro-2-methylpropan-2-yl)bicyclo[1.1.1]pentan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4s**, 51.0 mg, 60%).

Prepared following **GP-B** and purified by column chromatography (15% EtOAc/hexanes). The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.33 (s, 2H), 1.75 (s, 6H), 1.22 (s, 12H), 0.87 (s, 6H).

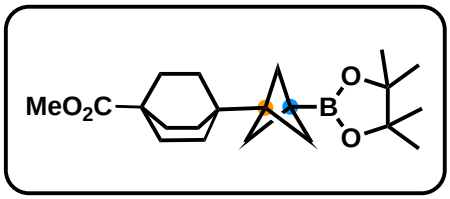
^{13}C NMR (151 MHz, $CDCl_3$) δ 83.5, 54.1, 48.5, 35.3, 25.2, 24.9, 21.3.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.6.

FT-IR (cm^{-1}, neat, ATR) 2964, 2869, 1466, 1437, 1402, 1390, 1380, 1372, 1352, 1314, 1204, 1167, 1140, 1014, 996, 963, 855, 822, 717, 667.

HRMS (EI-TOF) calcd for ($C_{14}H_{23}BClO_2$) $[M\text{-}CH_3]^+$ 269.1480, found 269.1485.

Melting point: 89 - 91 °C.



Methyl 4-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)bicyclo[2.2.2]octane-1-carboxylate (**4t**, 55.0 mg, 51%).

Prepared following **GP-C** and purified by column chromatography (20% EtOAc/hexanes). The product was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.62 (s, 3H), 1.73 – 1.66 (m, 6H), 1.59 (dd, *J* = 10.3, 5.0 Hz, 6H), 1.30 (s, 6H), 1.21 (s, 12H).

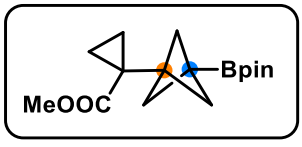
^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 83.3, 51.7, 47.6, 38.9, 30.2, 28.3, 26.6, 26.5, 24.9, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$) δ 31.8.

FT-IR (cm^{-1}, neat, ATR) 2954, 2862, 1722, 1508, 1438, 1408, 1372, 1350, 1311, 1236, 1199, 1145, 1073, 1018, 964, 856, 666.

HRMS (ESI-TOF) calcd for ($C_{21}H_{34}BNO_4$) $[M+H]^+$ 361.2550, found 361.2545.

Melting point: 160 – 163 °C.



Methyl 1-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)cyclopropane-1-carboxylate (**4u**)

Prepared following **GP-B** *with the following modification:* 3 equiv of [1.1.1.]propellane were used. The compound was purified by column chromatography (10% EtOAc/hexanes). The product was obtained as a white solid (36 mg, 41%).

Prepared following **GP-F** and purified by column chromatography (10% EtOAc/hexanes). The product was obtained as a white solid (42 mg, 50%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.64 (s, 3H), 1.82 (s, 6H), 1.23 (s, 12H), 1.05 (q, *J* = 3.8 Hz, 2H), 0.73 (q, *J* = 3.8 Hz, 2H).

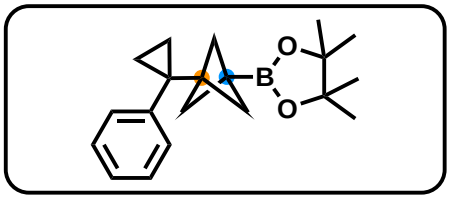
^{13}C NMR (151 MHz, $CDCl_3$) δ 175.4, 83.4, 51.7, 50.6, 45.3, 24.9, 24.3, 13.4.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.7.

FT-IR (cm^{-1}, neat, ATR) 2979, 2955, 2908, 2870, 1714, 1406, 1311, 1214, 1196, 1139, 665.

HRMS (ESI-TOF) calcd for ($C_{16}H_{26}BO_4$) $[M+H]^+$ 293.1924, found 293.1934.

Melting point 110 - 113 °C.



4,4,5,5-Tetramethyl-2-(3-(1-phenylcyclopropyl)bicyclo[1.1.1]pentan-1-yl)-1,3,2-dioxaborolane (**4v**, 39.0 mg, 42%).

Prepared following **GP-B** *with the following modification*: 3 equiv of [1.1.1.]propellane were used. The compound was purified by column chromatography (20% EtOAc/hexanes). The product was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.22 (m, 4H), 7.19 – 7.13 (m, 1H), 1.61 (s, 6H), 1.20 (s, 12H), 0.72 (td, *J* = 6.6, 2.1 Hz, 2H), 0.66 (td, *J* = 5.6, 2.5 Hz, 2H).

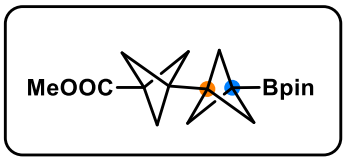
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 130.1, 127.9, 126.1, 83.3, 49.7, 49.6, 27.9, 24.8, 9.4.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.6.

FT-IR (cm^{-1}, neat, ATR) 2974, 2870, 1780, 1475, 1445, 1372, 1329, 1209, 1166, 1144, 1076, 1009, 981, 952, 851, 761, 743, 700.

HRMS (EI-TOF) calcd for ($C_{20}H_{27}BO_2$) $[M]^+$ 310.2104, found 310.2107.

Melting point: 103 °C.



Methyl 3'-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1'-bi(bicyclo[1.1.1]pentane)]-3-carboxylate (**4w**, 41.3 mg, 43%)

Prepared following **GP-B** *with the following modifications*: 3 equiv of [1.1.1.]propellane and 1.2 equiv of B_2pin_2 were used. The compound was purified by C18 column chromatography (80% MeCN/H_2O). The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.64 (s, 3H), 1.84 (s, 6H), 1.72 (s, 6H), 1.22 (s, 12H).

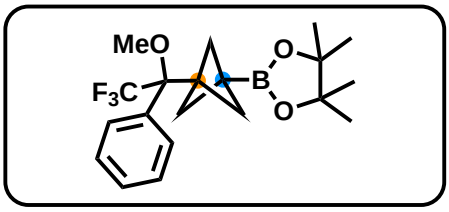
^{13}C NMR (151 MHz, $CDCl_3$) δ 171.3, 83.5, 51.7, 50.4, 50.2, 44.9, 40.0, 36.7, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.0.

FT-IR (cm^{-1}, neat, ATR) 2960, 2907, 2873, 1725, 1504, 1441, 1418, 1380, 1349, 1311, 1219, 1203, 1140, 1113, 1055, 971, 857, 790, 666.

HRMS (EI-TOF) calcd for ($C_{17}H_{24}BO_4$) $[M\text{-}CH_3]^+$ 303.1768, found 303.1750.

Melting point: 179 - 182 °C.



4,4,5,5-Tetramethyl-2-(3-(2,2,2-trifluoro-1-methoxy-1-phenylethyl)bicyclo[1.1.1]pentan-1-yl)-1,3,2-dioxaborolane (**4x**, 47 mg, 41%).

Prepared following **GP-B** *with the following modification*: 3 equiv of [1.1.1.]propellane were used. The compound was purified by column chromatography (15% EtOAc/hexanes). The product was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 5H), 3.31 (d, *J* = 1.7 Hz, 3H), 1.92 – 1.75 (m, 6H), 1.19 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 133.9, 128.2, 128.1, 127.2 (d, *J* = 2.2 Hz), 126.8 (q, *J* = 295.8 Hz), 83.5, 81.4 (q, *J* = 25.3 Hz), 54.0, 50.4, 50.2, 47.9 (d, *J* = 82.6 Hz), 24.8.

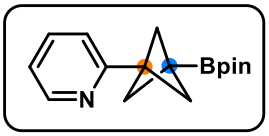
^{11}B NMR (128 MHz, $CDCl_3$) δ 30.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.89.

FT-IR (cm^{-1}, neat, ATR) 2978, 1437, 1405, 1314, 1205, 1168, 1143, 1106, 964, 854, 728.

HRMS (EI-TOF) calcd for ($C_{20}H_{26}BF_3O_3$) $[M]^+$ 382.1927, found 382.1931.

Melting point: 113 – 115 °C.



2-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)pyridine (**4y**, 33.7 mg, 41%).

Prepared following **GP-B** *with the following modification*: 3 equiv of [1.1.1]propellane were used. The compound was purified by column chromatography (55% EtOAc/hexanes). The product was obtained as a white solid.

Prepared following **GP-F** *with the following modification*: 1.5 equiv of [1.1.1]propellane were used. The compound was purified by C18 column chromatography (65% MeCN/H_2O). The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.55 (d, *J* = 5.2 Hz, 1H), 7.63 – 7.59 (m, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.14 – 7.09 (m, 1H), 2.25 (s, 6H), 1.27 (s, 12H).

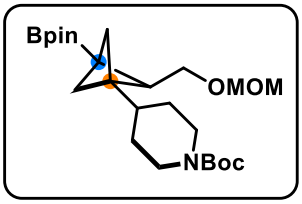
^{13}C NMR (151 MHz, $CDCl_3$) δ 160.3, 149.3, 136.5, 121.7, 120.5, 83.6, 53.0, 48.0, 25.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.9.

FT-IR (cm^{-1}, neat, ATR) 2974, 2911, 2871, 1592, 1567, 1512, 1474, 1430, 1407, 1373, 1314, 1209, 1146, 1121, 1005, 972, 854, 811, 762, 666.

HRMS (ESI-TOF) calcd for ($C_{16}H_{23}BNO_2$) $[M+H]^+$ 272.1822, found 272.1808.

Melting point: 137 - 139 °C.



***tert*-Butyl 4-(2-((Methoxymethoxy)methyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)piperidine-1-carboxylate** (**4z**, 43.2 mg, 48%).

Prepared following **GP-D** and purified by column chromatography (45% EtOAc/hexanes). The product was obtained as a colorless oil.

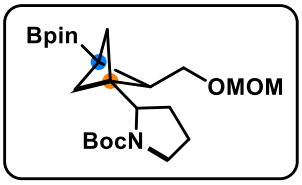
^{1}H NMR (600 MHz, $CDCl_3$)) δ 4.61 (s, 2H), 4.10 (br, *J* = 23.7 Hz, 2H), 3.70 (d, *J* = 7.1 Hz, 2H), 3.36 (s, 3H), 2.57 (br, 2H), 2.40 (q, *J* = 6.9 Hz, 1H), 2.21 (dd, *J* = 9.9, 3.2 Hz, 1H), 1.69 (dd, *J* = 6.4, 3.2 Hz, 1H), 1.65 (d, *J* = 1.9 Hz, 1H), 1.57 (dd, *J* = 9.9, 1.9 Hz, 1H), 1.54 – 1.49 (m, 2H), 1.44 (s, 9H), 1.38 – 1.32 (m, 1H), 1.21 (s, 12H), 1.06 – 0.99 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.0, 96.7, 83.4, 79.4, 64.9, 60.3, 55.3, 50.9, 48.5, 44.1, 37.3, 28.7, 28.1, 24.9, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.7.

FT-IR (cm^{-1}, neat, ATR) 2976, 2928, 1692, 1416, 1389, 1366, 1310, 1274, 1234, 1214, 1193, 1169, 1144, 1107, 1044, 982, 949, 918, 872, 856.

HRMS (ESI-TOF) calcd for ($C_{24}H_{43}BNO_6$) $[M+H]^+$ 452.3183, found 452.3172.



***tert*-Butyl 2-(2-((Methoxymethoxy)methyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)pyrrolidine-1-carboxylate** (**4aa**, 33.6 mg, 38%).

Prepared following **GP-D** and purified by column chromatography (50% EtOAc/hexanes). The product was obtained as a colorless oil.

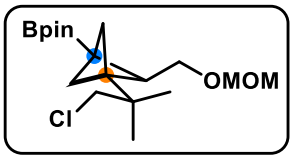
^{1}H NMR (600 MHz, $CDCl_3$) (1:1 mixture of diastereomers and mixture of rotamers) δ 4.60 (s, 2H), 3.77 – 3.70 (m, 2H), 3.68 – 3.62 (m, 1H), 3.35 (s, 3H), 3.27 – 3.24 (m, 2H), 2.53 – 2.39 (m, 1H), 2.35 – 2.25 (m, 1H), 1.78 – 1.74 (m, 5H), 1.70 (s, 1H), 1.67 – 1.58 (m, 1H), 1.46 (s, 9H), 1.21 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) (1:1 mixture of diastereomers and mixture of rotamers) δ 155.2, 155.1, 96.7, 96.6, 83.5, 79.4, 79.3, 64.8, 64.6, 61.1, 60.8, 60.4, 57.7, 57.3, 56.7, 55.3, 55.2, 50.4, 49.8, 49.7, 49.2, 46.6, 46.4, 46.3, 45.9, 45.6, 28.7, 24.9, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.6.

FT-IR (cm^{-1}, neat, ATR) 2975, 2930, 2887, 1693, 1389, 1366, 1311, 1254, 1196, 1165, 1145, 1108, 1045, 950, 917, 856, 771, 667, 579

HRMS (ESI-TOF) calcd for ($C_{23}H_{41}BNO_6$) $[M+H]^+$ 438.3027, found 438.3020.



2-(3-(1-Chloro-2-methylpropan-2-yl)-2-((methoxymethoxy)methyl)bicyclo[1.1.1]pentan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4ab**, 27.1 mg, 38%).

Prepared following **GP-D** and purified by C18 column chromatography (90% MeCN/H_2O). The product was obtained as a colorless oil. *C18 silica gel chromatography was used due to difficult separation between the product and B_2pin_2.

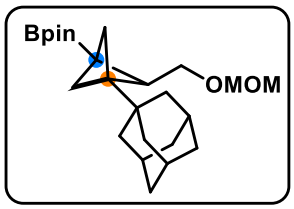
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.62 (s, 2H), 3.77 – 3.65 (m, 2H), 3.37 (s, 3H), 3.35 (s, 2H), 2.48 (q, *J* = 6.9 Hz, 1H), 2.29 (dd, *J* = 9.9, 3.3 Hz, 1H), 1.75 (dd, *J* = 6.3, 3.3 Hz, 1H), 1.71 (d, *J* = 2.0 Hz, 1H), 1.64 (dd, *J* = 9.9, 1.9 Hz, 1H), 1.21 (s, 12H), 0.87 (d, *J* = 4.4 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 96.8, 83.5, 65.1, 60.6, 55.5, 54.1, 53.7, 48.1, 43.6, 35.8, 24.9, 24.8, 21.7, 21.6.

^{11}B NMR (128 MHz, $CDCl_3$) 29.9

FT-IR (cm^{-1}, neat, ATR) 2974, 2931, 2891, 1468, 1438, 1402, 1389, 1372, 1313, 1214, 1199, 1144, 1107, 1045, 997, 949, 918, 855, 824, 719

HRMS (ESI-TOF) calcd for ($C_{18}H_{33}BClO_4$) $[M+H]^+$ 359.2160, found 359.2167.



2-(3-(Adamantan-1-yl)-2-((methoxymethoxy)methyl)bicyclo[1.1.1]pentan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4ac**, 18.5 mg, 23%).

Prepared following **GP-D** and purified by C18 column chromatography (100% MeCN). The product was obtained as a colorless oil. *C18 silica gel chromatography was used due to difficult separation between the product and B_2pin_2.

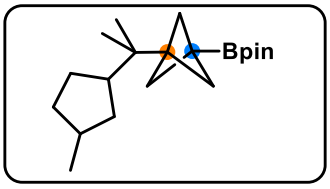
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.67 – 4.53 (m, 2H), 3.71 (dd, *J* = 7.3, 2.9 Hz, 2H), 3.37 (s, 3H), 2.43 (dt, *J* = 8.2, 6.4 Hz, 1H), 2.20 (dd, *J* = 9.9, 3.2 Hz, 1H), 1.90 (s, 3H), 1.65 (d, *J* = 12.3 Hz, 3H), 1.63 – 1.61 (m, 1H), 1.59 (d, *J* = 1.6 Hz, 1H), 1.56 (d, *J* = 11.9 Hz, 3H), 1.52 (dd, *J* = 9.9, 1.8 Hz, 1H), 1.35 (s, 6H), 1.22 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 96.6, 83.3, 65.3, 59.7, 55.6, 55.3, 46.3, 41.3, 38.5, 37.2, 32.4, 28.4, 24.9, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.2.

FT-IR (cm^{-1}, neat, ATR) 2976, 2903, 2847, 1438, 1415, 1389, 1309, 1214, 1195, 1146, 1107, 1079, 1050, 918, 857, 669

HRMS (ESI-TOF) calcd for ($C_{24}H_{39}BO_4Na$) $[M+Na]^+$ 425.2839, found 425.2843.



4,4,5,5-Tetramethyl-2-(3-(2-(3-methylcyclopentyl)propan-2-yl)bicyclo[1.1.1]pentan-1-yl)-1,3,2-dioxaborolane (**4ad**, 80.7 mg, 85%).

Prepared following **GP-B** *using RAE* **S-1v** and purified by column chromatography (10% EtOAc/hexanes). The product was obtained as a colorless oil.

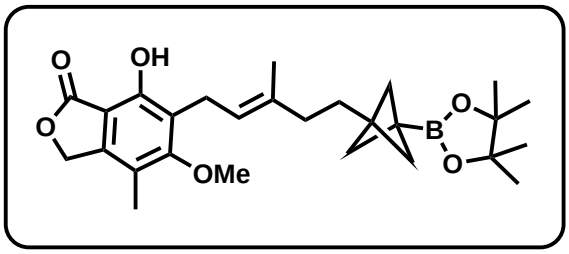
^{1}H NMR (600 MHz, $CDCl_3$) (1.3:1 mixture of diastereomers) δ 1.88 (tt, *J* = 10.0, 7.8 Hz, 0.57H), 1.84 – 1.75 (m, 1.43H), 1.73 – 1.66 (m, 1.43H), 1.71 (s, 6H), 1.66 – 1.57 (m, 0.57H), 1.57 – 1.47 (m, 1H), 1.41 – 1.34 (m, 0.43H), 1.28 – 1.18 (m, 1.13H), 1.22 (s, 12H), 1.12 (ddd, *J* = 13.0, 9.6, 7.0 Hz, 0.57H), 1.04 – 0.94 (m, 0.87H), 0.93 (d, *J* = 6.5 Hz, 1.3H), 0.91 (d, *J* = 6.7 Hz, 1.7H), 0.68 (s, 1.3H), 0.68 (s, 1.3H), 0.67 (s, 1.7H), 0.67 (s, 1.7H).

^{13}C NMR (151 MHz, $CDCl_3$) (1.3:1 mixture of diastereomers) δ 83.2, 54.5, 54.5, 49.1, 47.1, 45.6, 38.0, 36.0, 35.4, 34.9, 34.8, 34.7, 34.4, 34.3, 28.8, 27.1, 24.9, 21.4, 21.3, 21.2, 20.7, 20.2, 20.1.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.1.

FT-IR (cm^{-1}, neat, ATR) 2961, 2870, 1778, 1724, 1474, 1455, 1372, 1362, 1328, 1260, 1205, 1145, 1009, 982, 952, 927, 851, 698, 673.

HRMS (EI-TOF) calcd for ($C_{19}H_{32}BO_2$) $[M\text{-}CH_3]^+$ 303.2495, found 303.2506.



(*E*)-7-Hydroxy-5-methoxy-4-methyl-6-(3-methyl-5-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)pent-2-en-1-yl)isobenzofuran-1(3*H*)-one (**4ae**, 59.0 mg, 43%).

Prepared following **GP-B** and purified by column chromatography (40% EtOAc/hexanes). The product was obtained as a colorless oil.

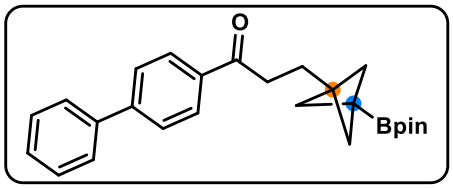
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 5.18 (s, 2H), 5.16 (dt, *J* = 5.5, 1.3 Hz, 1H), 3.75 (s, 3H), 3.36 (d, *J* = 6.9 Hz, 2H), 2.13 (s, 3H), 1.88 (dd, *J* = 10.3, 6.3 Hz, 2H), 1.75 (d, *J* = 1.3 Hz, 3H), 1.69 (s, 6H), 1.43 – 1.37 (m, 2H), 1.21 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 163.8, 153.8, 143.9, 136.3, 122.7, 121.4, 116.8, 106.4, 83.3, 70.1, 61.1, 51.4, 46.1, 36.1, 31.6, 25.0, 24.8, 22.7, 16.4, 11.7.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.6.

FT-IR (cm^{-1}, neat, ATR) 2975, 1733, 1472, 1451, 1409, 1370, 1328, 1273, 1251, 1219, 1195, 1141, 1100, 1078, 1030, 1008, 981, 968, 851.

HRMS (ESI-TOF) calcd for ($C_{27}H_{37}BNaO_4$) $[M+Na]^+$ 491.2581, found 491.2595.



1-([1,1'-Biphenyl]-4-yl)-3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)propan-1-one (**4af**, 66.3 mg, 55%).

Prepared following **GP-B** and purified by column chromatography (20% EtOAc/hexanes). The product was obtained as a white solid (86.1 mg, 71%).

Prepared following **GP-C** and purified by column chromatography (20% EtOAc/hexanes). The product was obtained as a white solid (66.3 mg, 55%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 – 7.99 (m, 2H), 7.70 – 7.65 (m, 2H), 7.65 – 7.60 (m, 2H), 7.50 – 7.44 (m, 2H), 7.43 – 7.37 (m, 1H), 2.92 (t, *J* = 7.3 Hz, 2H), 1.83 (t, *J* = 7.6 Hz, 2H), 1.79 (s, 6H), 1.23 (s, 12H).

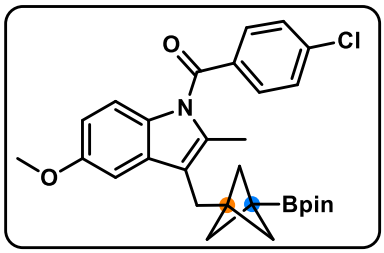
^{13}C NMR (151 MHz, $CDCl_3$) δ 200.0, 145.7, 140.1, 136.0, 129.1, 128.8, 128.3, 127.4, 127.4, 83.4, 51.4, 45.6, 35.4, 28.0, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.3.

FT-IR (cm^{-1}, neat, ATR) 2961, 2905, 2867, 1682, 1604, 1511, 1435, 1404, 1371, 1343, 1308, 1198, 1145, 1034, 1005, 856, 765, 750, 696, 666.

HRMS (ESI-TOF) calcd for ($C_{26}H_{32}BO_3$) $[M+H]^+$ 403.2445, found 403.2430.

Melting point: 99 - 100 °C.



(4-Chlorophenyl)(5-methoxy-2-methyl-3-((3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1*H*-indol-1-yl)methanone (**4ag**, 62.0 mg, 41%).

Prepared following **GP-B** *with the following modification*: 3 equiv of [1.1.1.]propellane were used. The compound was purified by C18 column chromatography (95% MeCN/H_2O). The product was obtained as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 9.0 Hz, 1H), 6.85 (d, *J* = 2.5 Hz, 1H), 6.63 (dd, *J* = 9.0, 2.6 Hz, 1H), 3.82 (s, 3H), 2.72 (s, 2H), 2.24 (s, 3H), 1.76 (s, 6H), 1.19 (s, 12H).

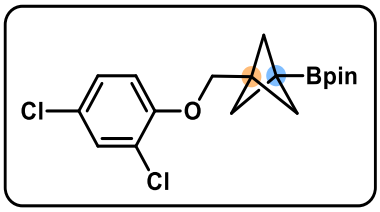
^{13}C NMR (151 MHz, $CDCl_3$) δ 168.5, 156.0, 139.0, 134.6, 134.3, 131.9, 131.2, 131.1, 129.2, 117.8, 115.0, 111.2, 101.8, 83.4, 55.8, 52.0, 45.6, 28.6, 24.9, 13.5.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.0.

FT-IR (cm^{-1}, neat, ATR) 2955, 2861, 1678, 1477, 1455, 1434, 1400, 1370, 1355, 1310, 1289, 1248, 1213, 1195, 1143, 1088, 1064, 923, 854, 835, 753, 730.

HRMS (ESI-TOF) calcd for ($C_{29}H_{34}BClNO_4$) $[M+H]^+$ 506.2269, found 506.2255.

Melting point: 149 - 150 °C.



2-(3-((2,4-Dichlorophenoxy)methyl)bicyclo[1.1.1]pentan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4ah,** 53.6 mg, 48%).

Prepared following **GP-B** *with the following modification*: 3 equiv of [1.1.1.]propellane were used. The compound was purified by column chromatography (20% EtOAc/hexanes). The product was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 2.6 Hz, 1H), 7.12 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.77 (d, *J* = 8.8 Hz, 1H), 3.89 (s, 2H), 1.94 (s, 6H), 1.24 (s, 12H).

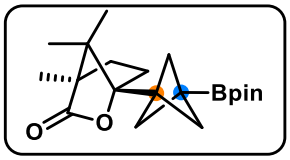
^{13}C NMR (151 MHz, $CDCl_3$) δ 153.6, 130.0, 127.5, 125.5, 124.0, 114.3, 83.6, 69.8, 51.0, 43.5, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.7.

FT-IR (cm^{-1}, neat, ATR) 2975, 2910, 2873, 1483, 1410, 1379, 1312, 1201, 1144, 855, 665.

HRMS (EI-TOF) calcd for ($C_{18}H_{23}BCl_2O_3$) $[M]^+$ 368.1117, found 368.1110.

Melting point 141 - 142 °C.



(1R,4R)-4,7,7-Trimethyl-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1] pentan-1-yl)-2-oxabicyclo[2.2.1]heptan-3-one (**4ai**).

Prepared following **GP-B** and purified by column chromatography (25% EtOAc/hexanes). The product was obtained as a white solid (35.2 mg, 34%).

Prepared following **GP-C** and purified by column chromatography (25% EtOAc/hexanes). The product was obtained as a white solid (22.2 mg, 21%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.06 – 1.98 (m, 6H), 1.92 (ddd, *J* = 13.9, 10.0, 4.0 Hz, 1H), 1.67 (dddd, *J* = 28.4, 13.4, 9.8, 4.4 Hz, 2H), 1.55 (ddd, *J* = 12.0, 8.7, 4.1 Hz, 1H), 1.22 (s, 12H), 1.01 (s, 3H), 0.95 (s, 3H), 0.89 (s, 3H).

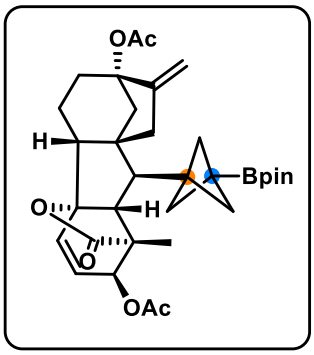
^{13}C NMR (151 MHz, $CDCl_3$) δ 180.9, 92.0, 83.6, 54.9, 52.3, 51.3, 43.9, 28.9, 28.7, 24.9, 17.2, 16.9, 9.8.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.0.

FT-IR (cm^{-1}, neat, ATR) 2972, 2912, 2876, 1772, 1443, 1414, 1393, 1372, 1356, 1316, 1273, 1211, 1168, 1144, 1117, 1075, 1021969, 910, 855.

HRMS (ESI-TOF) calcd for ($C_{20}H_{32}BO_4$) $[M+H]^+$ 347.2434, found 347.2411.

Melting point: 169 - 171 °C.



(1*S*,2*S*,4a*R*,4b*R*,7*S*,9a*R*,10*R*,10a*R*)-1-Methyl-8-methylene-13-oxo-10-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)-1,2,5,6,8,9,10,10a-octahydro-4a,1-(epoxymethano)-7,9a-methanobenzo[*a*]azulene-2,7(4b*H*)-diyl diacetate (**4aj**).

Prepared following **GP-B** and purified by column chromatography (40% EtOAc/hexanes). The product was obtained as a white solid. (111.9 mg, 60%).

Prepared following **GP-C** and purified by column chromatography (40% EtOAc/hexanes). The product was obtained as a white solid. (95.2 mg, 55%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.40 (dd, *J* = 9.2, 0.8 Hz, 1H), 5.79 (dd, *J* = 9.2, 3.7 Hz, 1H), 5.32 (dd, *J* = 3.7, 0.8 Hz, 1H), 4.97 (d, *J* = 2.0 Hz, 2H), 3.10 (dt, *J* = 15.1, 3.1 Hz, 1H), 2.61 (d, *J* = 8.4 Hz, 1H), 2.35 (dd, *J* = 10.6, 2.5 Hz, 1H), 2.27 – 2.21 (m, 1H), 2.12 (s, 3H), 2.09 – 2.06 (m, 1H), 1.97 (s, 3H), 1.96 (dd, *J* = 9.6, 2.1 Hz, 3H), 1.94 – 1.90 (m, 1H), 1.87 (dd, *J* = 9.7, 2.1 Hz, 3H), 1.83 (d, *J* = 8.5 Hz, 2H), 1.80 – 1.76 (m, 2H), 1.73 – 1.66 (m, 1H), 1.22 (s, 12H), 1.19 (s, 3H).

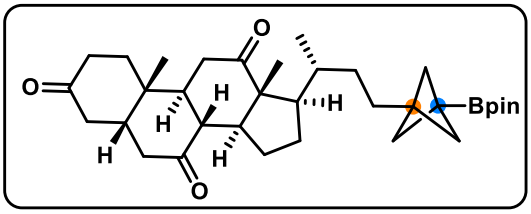
^{13}C NMR (151 MHz, $CDCl_3$) δ 177.9, 170.1, 169.7, 152.1, 134.9, 129.0, 106.2, 90.6, 84.3, 83.6, 71.9, 54.5, 53.1, 52.1, 52.0, 48.6, 47.4, 45.8, 44.5, 42.8, 36.8, 24.9, 24.9, 22.3, 21.1, 17.7, 15.5.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.8.

FT-IR (cm^{-1}, neat, ATR) 2972, 2912, 2876, 1772, 1443, 1414, 1393, 1372, 1356, 1316, 1273, 1211, 1168, 1144, 1117, 1075, 1021, 969, 910, 855.

HRMS (ESI-TOF) calcd for ($C_{33}H_{43}BO_8Na$) $[M+Na]^+$ 601.2949, found 601.2958.

Melting point: 242 - 243 °C.



(5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)butan-2-yl)dodecahydro-3*H*-cyclopenta[*a*]phenanthrene-3,7,12(2*H*,4*H*)-trione (**4ak**).

Prepared following **GP-B** and purified by column chromatography (70% EtOAc/hexanes). The product was obtained as a white solid (99.5 mg, 60%).

Prepared following **GP-C** and purified by column chromatography (70% EtOAc/hexanes). The product was obtained as a white solid (96.2 mg, 58%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.94 – 2.86 (m, 2H), 2.85 – 2.75 (m, 1H), 2.37 – 2.26 (m, 2H), 2.24 – 2.19 (m, 2H), 2.17 – 2.12 (m, 2H), 2.10 – 2.06 (m, 2H), 2.04 – 1.91 (m, 4H), 1.80 (td, *J* = 11.5, 7.5 Hz, 1H), 1.68 (s, 6H), 1.61 – 1.53 (m, 3H), 1.37 (s, 3H), 1.25 – 1.22 (m, 5H), 1.20 (s, 12H), 1.03 (s, 3H), 0.76 (d, *J* = 6.4 Hz, 3H).

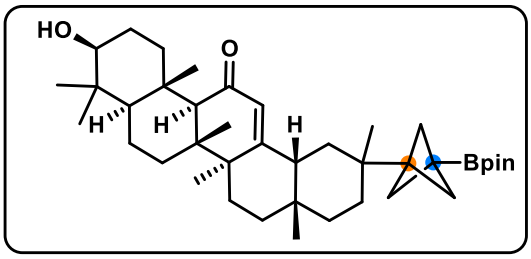
^{13}C NMR (101 MHz, $CDCl_3$) δ 212.3, 209.3, 209.0, 83.3, 57.0, 51.9, 51.4, 50.3, 49.1, 47.0, 45.7, 45.1, 42.9, 38.8, 36.6, 36.1, 35.9, 35.4, 31.6, 29.9, 27.9, 25.3, 25.0, 24.9, 22.0, 19.0, 12.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.0.

FT-IR (cm^{-1}, neat, ATR) 2962, 2868, 1707, 1448, 1404, 1380, 1335, 1305, 1272, 1251, 1195, 1167, 1144, 1121, 1008, 912, 852, 729, 674, 647.

HRMS (ESI-TOF) calcd for ($C_{34}H_{51}BO_5Na$) $[M+Na]^+$ 573.3727, found 573.3719.

Melting point:174 - 175 °C.



(4a*R*,6a*S*,6b*R*,8a*R*,10*S*,12a*S*,12b*R*,14b*R*)-10-Hydroxy-2,4a,6a,6b,9,9,12a-heptamethyl-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)-1,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,14b-octadecahydropicen-13(2*H*)-one (**4al**).

Prepared following **GP-B** and purified by column chromatography (45% EtOAc/hexanes). The product was obtained as a white solid (107.8 mg, 58%).

Prepared following **GP-C** and purified by column chromatography (45% EtOAc/hexanes). The product was obtained as a white solid (100.8 mg, 54%).

^{1}H NMR (600 MHz, $CDCl_3$) (2.1:1 mixture of diastereomers) δ 5.59 (s, 0.67H), 5.55 (s, 0.32H), 3.21 (ddd, *J* = 11.3, 8.8, 5.0 Hz, 1H), 2.80 – 2.75 (m, 1H), 2.31 (d, *J* = 2.3 Hz, 1H), 2.24 – 2.17 (m, 0.54H), 2.08 – 2.02 (m, 0.28H), 1.97 (td, *J* = 13.7, 4.3 Hz, 1H), 1.80 (s, 4H), 1.83 – 1.74 (m, 2H), 1.65 (s, 2H), 1.64 – 1.55 (m, 5H), 1.52 – 1.44 (m, 2H), 1.43 – 1.35 (m, 4H), 1.31 (s, 3H), 1.33 – 1.24 (m, 2H), 1.22 (s, 12H), 1.11 (s, 6H), 0.99 (s, 3H), 0.97 – 0.93 (m, 1H), 0.78 (s, 6H), 0.70 (s, 3H), 0.69 – 0.62 (m, 1H).

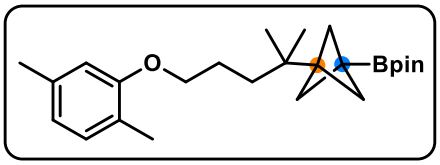
^{13}C NMR (151 MHz, $CDCl_3$) (2.1:1 mixture of diastereomers) δ 200.5, 200.3, 170.9, 170.5, 134.4, 128.3, 123.7, 83.4, 83.4, 78.9, 78.9, 61.9, 61.9, 55.1, 55.1, 54.1, 54.0, 52.2, 50.4, 47.7, 47.1, 47.1, 45.6, 45.4, 43.6, 43.4, 41.2, 39.3, 39.3, 38.7, 37.3, 37.2, 36.9, 36.0, 33.2, 33.2, 33.0, 32.9, 32.6, 32.2, 30.2, 29.4, 28.9, 28.4, 28.3, 27.8, 27.7, 27.5, 27.2, 26.5, 26.4, 24.9, 23.4, 23.3, 18.9, 18.9, 17.6, 17.6, 16.6, 16.5, 15.8.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.9.

FT-IR (cm^{-1}, neat, ATR) 2954, 2867, 1651, 1454, 1402, 1390, 1372, 1307, 1202, 1167, 1142, 1039, 1008, 994, 908, 854, 728, 688, 667, 647.

HRMS (ESI-TOF) calcd for ($C_{40}H_{64}BO_4$) $[M+H]^+$ 619.4898, found 619.4904.

Melting point: 205 - 207 °C.



2-(3-(5-(2,5-Dimethylphenoxy)-2-methylpentan-2-yl)bicyclo[1.1.1]pentan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4am**).

Prepared following **GP-B** and purified by column chromatography (20% EtOAc/hexanes). The product was obtained as a white solid (96.1 mg, 80%).

Prepared following **GP-C** and purified by column chromatography (20% EtOAc/hexanes). The product was obtained as a white solid (98.2 mg, 82%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.02 (d, *J* = 7.7 Hz, 1H), 6.67 (d, *J* = 7.3 Hz, 1H), 6.64 (s, 1H), 3.91 (t, J = 6.6 Hz, 2H), 2.33 (s, 3H), 2.19 (s, 3H), 1.80 – 1.73 (m, 2H), 1.75 (s, 6H), 1.35 – 1.30 (m, 2H), 1.26 (s, 12H), 0.81 (s, 6H).

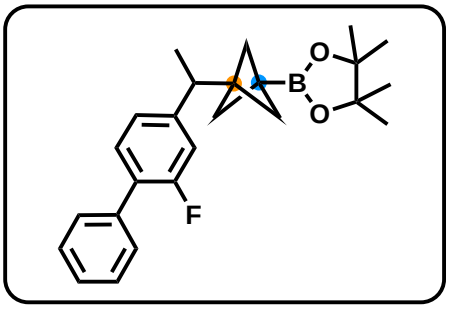
^{13}C NMR (151 MHz, $CDCl_3$) δ 157.3, 136.5, 130.4, 123.8, 120.7, 112.2, 83.3, 68.9, 54.1, 48.1, 34.8, 32.5, 24.9, 24.9, 22.7, 21.6, 15.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 31.0.

FT-IR (cm^{-1}, neat, ATR) 2957, 2867, 1509, 1437, 1403, 1390, 1379, 1371, 1307, 1284, 1264, 1214, 1202, 1141, 1130, 1043, 1011, 994, 855, 802.

HRMS (ESI-TOF) calcd for ($C_{25}H_{40}BO_3$) $[M+H]^+$ 399.3071, found 399.3065.

Melting point: 116 - 117 °C.



2-(3-(1-(2-Fluoro-[1,1'-biphenyl]-4-yl)ethyl)bicyclo[1.1.1]pentan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4an**, 41.0 mg, 35%).

Prepared following **GP-B** *with the following modification*: 3 equiv of [1.1.1.]propellane were used. The compound was purified by column chromatography (10% EtOAc/hexanes). The product was obtained as a colorless, waxy solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dt, *J* = 8.1, 1.5 Hz, 2H), 7.46 – 7.40 (m, 2H), 7.37 – 7.29 (m, 2H), 6.95 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.90 (dd, *J* = 12.0, 1.7 Hz, 1H), 2.78 (q, *J* = 7.1 Hz, 1H), 1.70 (s, 6H), 1.25 – 1.19 (m, 15H).

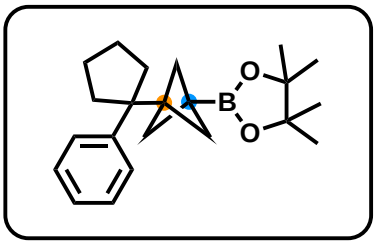
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7 (d, *J* = 247.0 Hz), 146.0 (d, *J* = 7.2 Hz), 136.1, 130.2 (d, *J* = 4.0 Hz), 129.1, 128.5, 127.4, 126.4 (d, *J* = 13.5 Hz), 123.6 (d, *J* = 3.1 Hz), 114.9 (d, *J* = 22.6 Hz), 83.4, 49.5, 49.4, 41.8, 24.9, 16.2.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -119.00.

FT-IR (cm^{-1}, neat, ATR) 2964, 2906, 2869, 1483, 1415, 1372, 1330, 1266, 1249, 1197, 1143, 1126, 911, 870, 851, 832, 766, 725, 697.

HRMS (EI-TOF) calcd for ($C_{25}H_{30}BFO_2$) $[M]^+$ 392.2323, found 392.2324.



4,4,5,5-Tetramethyl-2-(3-(1-phenylcyclopentyl)bicyclo[1.1.1]pentan-1-yl)-1,3,2-dioxaborolane (**4ao**, 38.0 mg, 37%).

Prepared following **GP-E** and purified by column chromatography (10% EtOAc/hexanes). The product was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.4 Hz, 2H), 7.13 (d, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 7.4 Hz, 2H), 2.31 (d, *J* = 10.6 Hz, 1H), 2.24 – 2.12 (m, 1H), 2.07 – 1.95 (m, 1H), 1.75 – 1.65 (m, 6H), 1.60 – 1.55 (m, 1H), 1.50 – 1.30 (m, 3H), 1.19 (s, 12H), 0.93 – 0.83 (m, 1H).

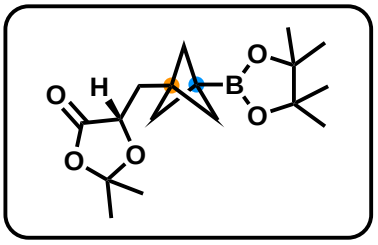
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 128.5, 127.8, 125.6, 83.3, 55.3, 51.3, 42.2, 32.9, 32.3, 26.1, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.9.

FT-IR (cm^{-1}, neat, ATR) 2958, 2906, 2868, 1509, 1450, 1402, 1371, 1309, 1250, 1196, 1144, 1111, 1033, 983, 960, 853, 763, 705, 667.

HRMS (EI-TOF) calcd for ($C_{22}H_{31}BO_2$) $[M]^+$ 338.2417, found 338.2442.

Melting point: 104 – 105 °C.



(*S*)-2,2-Dimethyl-5-((3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,3-dioxolan-4-one (**4ap**, 51 mg, 53%).

Prepared following **GP-E** and purified by column chromatography (20% EtOAc/hexanes). The product was obtained as a colorless oil.

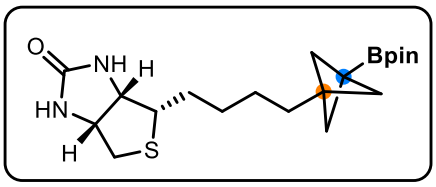
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.35 (dd, *J* = 8.3, 3.4 Hz, 1H), 1.98 (dd, *J* = 14.9, 3.5 Hz, 1H), 1.88 – 1.83 (m, 6H), 1.77 (dd, *J* = 14.9, 8.3 Hz, 1H), 1.60 (s, 3H), 1.51 (s, 3H), 1.22 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 110.6, 83.4, 72.9, 52.4, 43.1, 34.9, 27.4, 25.6, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 32.6.

FT-IR (cm^{-1}, neat, ATR) 2975, 2910, 2872, 1725, 1474, 1448, 1373, 1331, 1251, 1142, 1009, 981, 952, 904, 851, 726, 683.

HRMS (ESI-TOF) calcd for ($C_{17}H_{28}BO_5$) $[M+H]^+$ 323.2030, found 323.2011.



(3aS,4S,6aR)-4-(4-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)butyl)tetrahydro-1*H*-thieno[3,4-*d*]imidazol-2(3*H*)-one (**4aq,** 51.8 mg, 44%).

Prepared following **GP-E** and purified by column chromatography (70% MeCN/H_2O). The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.11 (s, 1H), 5.07 (s, 1H), 4.50 (dd, *J* = 7.8, 4.8 Hz, 1H), 4.32 – 4.28 (m, 1H), 3.19 – 3.11 (m, 1H), 2.92 (dd, *J* = 12.8, 5.0 Hz, 1H), 2.72 (d, *J* = 12.8 Hz, 1H), 1.72 (s, 6H), 1.67 – 1.61 (m, 2H), 1.44 – 1.28 (m, 6H), 1.23 (s, 12H).

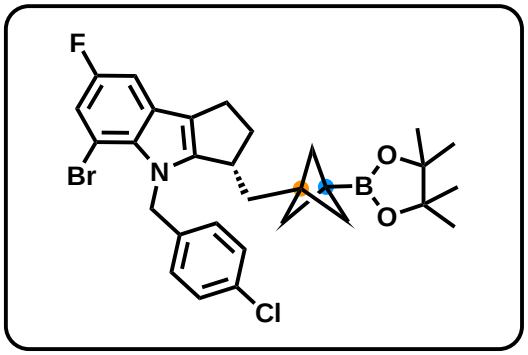
^{13}C NMR (151 MHz, $CDCl_3$) δ 163.3, 83.4, 62.1, 60.3, 55.7, 51.6, 46.2, 40.7, 33.1, 29.4, 28.8, 26.2, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.1.

FT-IR (cm^{-1}, neat, ATR) 3211, 2958, 2924, 2866, 1697, 1471, 1434, 1405, 1379, 1372, 1306, 1270, 1251, 1196, 1166, 1145, 1110, 856, 732, 666.

HRMS (ESI-TOF) calcd for ($C_{20}H_{34}BN_2O_3S$) $[M+H]^+$ 393.2383, found 393.2362.

Melting point: 119 - 120 °C.



(*R*)-5-Bromo-4-(4-chlorobenzyl)-7-fluoro-3-((3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,2,3,4-tetrahydrocyclopenta[*b*]indole (**4ar**, 74 mg, 42%).

Prepared following **GP-E** and purified by column chromatography (5% EtOAc/hexanes). The product was obtained as a white crystalline solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 – 7.21 (m, 2H), 7.02 (ddd, *J* = 12.2, 8.8, 2.5 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 5.86 (d, *J* = 17.1 Hz, 1H), 5.36 (d, *J* = 17.2 Hz, 1H), 3.01 (t, *J* = 9.5 Hz, 1H), 2.82 (ddd, *J* = 14.4, 5.6, 3.7 Hz, 1H), 2.73 – 2.68 (m, 1H), 2.66 – 2.60 (m, 1H), 2.18 (tdd, *J* = 9.5, 6.5, 3.3 Hz, 1H), 1.80 – 1.70 (m, 6H), 1.60 (dd, *J* = 14.5, 2.2 Hz, 2H), 1.47 (dd, *J* = 14.4, 10.1 Hz, 1H), 1.22 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.0 (d, *J* = 238.7 Hz), 152.8, 138.0, 134.2, 133.1, 128.9, 127.4 (d, *J* = 9.9 Hz), 127.2, 119.3 (d, *J* = 4.7 Hz), 114.0 (d, *J* = 28.5 Hz), 103.5 (d, *J* = 22.4 Hz), 103.1 (d, *J* = 12.0 Hz), 83.4, 52.3, 48.5, 45.1, 37.6, 36.7, 35.1, 24.9, 23.2.

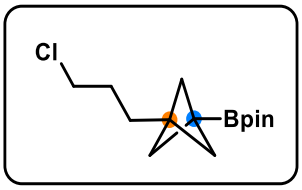
^{11}B NMR (128 MHz, $CDCl_3$) δ 32.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -123.85.

FT-IR (cm^{-1}, neat, ATR) 2959, 2904, 2865, 1583, 1486, 1448, 1404, 1371, 1347, 1310, 1198, 1176, 1143, 1093, 1033, 1014, 964, 854, 809.

HRMS (ESI-TOF) calcd for ($C_{30}H_{34}BBrClFNO_2$) $[M+H]^+$ 584.1539, found 584.1552.

Melting point: 147 – 149 °C.



2-(3-(3-Chloropropyl)bicyclo[1.1.1]pentan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5a**, 42.3 mg, 52%).

Prepared following **GP-F** and purified by column chromatography (10% EtOAc/hexanes). The product was obtained as a clear oil.

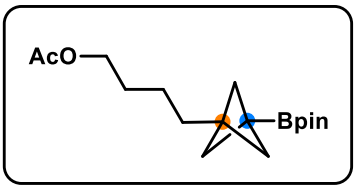
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.51 (t, *J* = 6.8 Hz, 2H), 1.75 (s, 6H), 1.74 – 1.65 (m, 2H), 1.52 – 1.42 (m, 2H), 1.23 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 83.4, 51.5, 45.5, 45.4, 30.7, 29.7, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.0.

FT-IR (cm^{-1}, neat, ATR) 2958, 2905, 2868, 1512, 1436, 1405, 1390, 1379, 1372, 1346, 1309, 1275, 1198, 1166, 1145, 1111, 1034, 960, 856, 666.

HRMS (ESI-TOF) calcd for ($C_{14}H_{25}BClO_2$) $[M+H]^+$ 271.1636, found 271.1624.



4-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)butyl Acetate (**5b**, 42.5 mg, 46%).

Prepared following **GP-F** and purified by column chromatography (10% EtOAc/hexanes). The product was obtained as a clear oil.

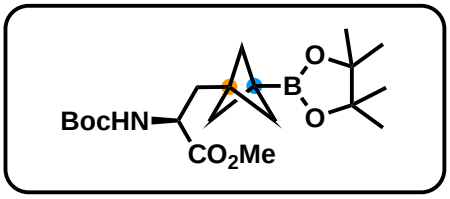
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.03 (t, *J* = 6.8 Hz, 2H), 2.04 (s, 3H), 1.73 (s, 6H), 1.63 – 1.57 (m, 2H), 1.36 – 1.32 (m, 2H), 1.30 – 1.25 (m, 2H), 1.23 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.4, 83.3, 64.8, 51.5, 46.1, 32.9, 28.9, 24.9, 22.7, 21.2.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.1.

FT-IR (cm^{-1}, neat, ATR) 2958, 2867, 1741, 1512, 1436, 1406, 1371, 1309, 1244, 1197, 1145, 1031, 856, 666.

HRMS (ESI-TOF) calcd for ($C_{17}H_{29}BO_4Na$) $[M+Na]^+$ 331.2057, found 331.2074.



Methyl (*S*)-2-((*tert*-Butoxycarbonyl)amino)-3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)propanoate (**5c**, 50.0 mg, 42 %).

Prepared following **GP-F** and purified by column chromatography (50% EtOAc/hexanes). The product was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.94 (d, *J* = 8.2 Hz, 1H), 4.25 (td, *J* = 7.7, 4.6 Hz, 1H), 3.70 (s, 3H), 1.90 (dd, *J* = 14.6, 4.8 Hz, 1H), 1.80 (s, 6H), 1.76 – 1.68 (m, 1H), 1.42 (s, 9H), 1.20 (s, 12H).

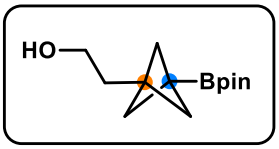
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 155.2, 83.4, 79.8, 52.3, 52.3, 52.1, 43.2, 35.2, 28.4, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.8.

FT-IR (cm^{-1}, neat, ATR) 2975, 1744, 1715, 1510, 1435, 1404, 1391, 1366, 1308, 1249, 1199, 1162, 1144, 1111, 1045, 1032, 995, 855, 732.

HRMS (ESI-TOF) calcd for ($C_{20}H_{34}BNaNO_6$) $[M+Na]^+$ 418.2377, found 418.2317.

Melting point: 107 – 108 °C.



2-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)ethan-1-ol (**5d**, 32.9 mg, 46%).

Prepared following **GP-F** and purified by column chromatography (20% EtOAc/hexanes). The product was obtained as a clear oil.

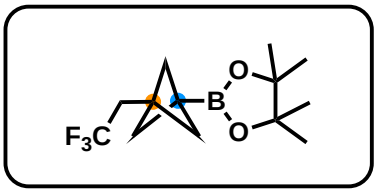
^{1}H NMR (600 MHz, $CDCl_3$) δ 3.64 (t, *J* = 6.8 Hz, 2H), 1.80 (s, 6H), 1.63 (t, *J* = 6.8 Hz, 2H), 1.22 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 83.4, 77.4, 77.2, 77.0, 61.2, 52.1, 43.9, 36.2, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.8.

FT-IR (cm^{-1}, neat, ATR) 3375, 2959, 2905, 2867, 1512, 1471, 1435, 1404, 1379, 1372, 1343, 1306, 1197, 1167, 1144, 1110, 1037, 978, 961, 855, 666.

HRMS (ESI-TOF) calcd for ($C_{13}H_{24}BO_3$) $[M+H]^+$ 239.1819, found 239.1835.



4,4,5,5-Tetramethyl-2-(3-(2,2,2-trifluoroethyl)bicyclo[1.1.1]pentan-1-yl)-1,3,2-dioxaborolane (**5e**, 42.1 mg, 51%).

Prepared following **GP-F** and purified by column chromatography (5% EtOAc/hexanes). The product was obtained as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.25 – 2.14 (m, 2H), 1.95 (s, 6H), 1.25 (s, 12H).

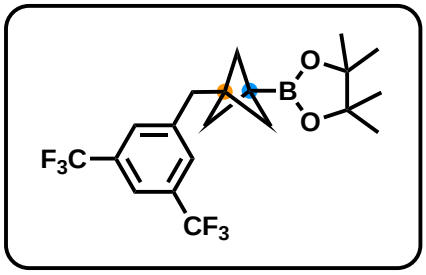
^{13}C NMR (151 MHz, $CDCl_3$) δ 126.5 (q, *J* = 277.4 Hz), 83.5, 52.7, 50.2, 39.1, 37.2 (q, *J* = 27.4 Hz), 24.8.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -64.1.

FT-IR (cm^{-1}, neat, ATR) 2967, 2854, 1463.

HRMS (EI-TOF) calcd for ($C_{13}H_{20}BF_3O_2$) $[M]^+$ 276.1508, found 276.1528.



2-(3-(3,5-Bis(trifluoromethyl)benzyl)bicyclo[1.1.1]pentan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5f**, 43.3 mg, 34%).

Prepared following **GP-F** and purified by column chromatography (5% EtOAc/hexanes). The product was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.50 (s, 2H), 2.79 (s, 2H), 1.71 (s, 6H), 1.19 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 131.5 (q, *J* = 33.1 Hz), 129.1 (d, *J* = 3.8 Hz), 123.6 (d, *J* = 272.5 Hz), 119.9 (p, *J* = 3.9 Hz), 83.5, 51.3, 45.0, 40.4, 24.8.

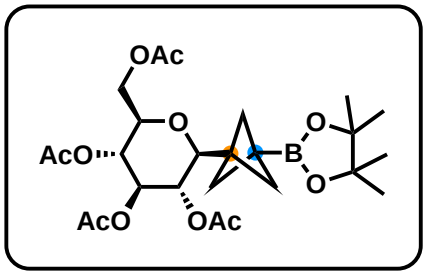
^{11}B NMR (128 MHz, $CDCl_3$) δ 30.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.9.

FT-IR (cm^{-1}, neat, ATR) 2965, 2871, 1436, 1404, 1391, 1375, 1349, 1331, 1276, 1198, 1169, 1130, 1029, 921, 893, 855, 842, 708, 682.

HRMS (EI-TOF) calcd for ($C_{20}H_{23}BF_5O_4$) $[M\text{-}F]^+$ 401.1711, found 401.1721.

Melting point: 66 – 67°C.



(2*R*,3*R*,4*R*,5*S*,6*S*)-2-(Acetoxymethyl)-6-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)tetrahydro-2H-pyran-3,4,5-triyl Triacetate (**5g**, 93 mg, 59%).

Prepared following **GP-F** and purified by column chromatography (30% EtOAc/hexanes). The product was obtained as a colorless oil.

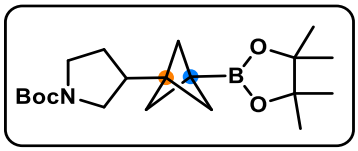
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.48 (t, *J* = 9.5 Hz, 1H), 5.03 (dd, *J* = 10.0, 6.2 Hz, 1H), 4.92 (t, *J* = 9.2 Hz, 1H), 4.18 – 4.01 (m, 3H), 3.97 (d, *J* = 6.2 Hz, 1H), 2.15 – 1.97 (m, 18H), 1.23 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 170.2, 169.9, 169.7, 83.7, 71.3, 71.2, 70.6, 70.3, 69.0, 62.7, 53.3, 50.1, 45.0, 24.9, 20.9, 20.9, 20.8, 20.8.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.3.

FT-IR (cm^{-1}, neat, ATR) 2975, 2874, 1745, 1438, 1369, 1312, 1208, 1157, 1142, 1097, 1085, 1032, 955, 913, 854, 730, 666, 599.

HRMS (ESI-TOF) calcd for ($C_{25}H_{37}BNaNO_{11}$) $[M+Na]^+$ 547.2320, found 547.2329.



***tert*-Butyl 3-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)pyrrolidine-1-carboxylate** (**5h**, 48.1 mg, 44%).

Prepared following **GP-F** and purified by column chromatography (10% EtOAc/hexanes). The product was obtained as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.43 – 3.35 (m, 1H), 3.35 – 3.28 (m, 1H), 3.28 – 3.16 (m, 1H), 3.02 (t, *J* = 8.9 Hz, 1H), 2.15 – 2.05 (m, 1H), 1.85 – 1.77 (m, 1H), 1.75 (d, *J* =1.6 Hz, 6H), 1.65 – 1.56 (m, 1H), 1.45 (s, 9H), 1.23 (s, 12H).

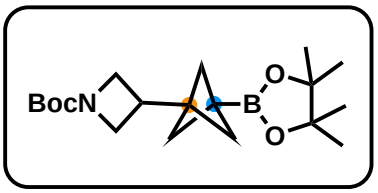
^{13}C NMR (151 MHz, $CDCl_3$) δ 154.8, 83.5, 79.1, 50.0, 48.1, 46.5, 45.8, 40.1, 28.7, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.3.

FT-IR (cm^{-1}, neat, ATR) 2975, 1698, 1401, 1311, 1202, 1169, 1145, 1112.

HRMS (EI-TOF) calcd for ($C_{16}H_{26}BNO_4$) $[M-C(CH_3)_3+H]^+$ 307.1955, found 307.1974.

Melting point: 125 - 127 °C.



***tert*-Butyl 3-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)azetidine-1-carboxylate** (**5i**, 43 mg, 41%).

Prepared following **GP-F** and purified by column chromatography (20% EtOAc/hexanes). The product was obtained as a colorless oil.

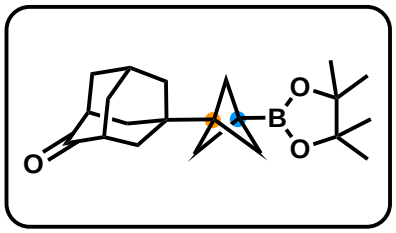
^{1}H NMR (600 MHz, $CDCl_3$) δ 3.84 (t, *J* = 8.4 Hz, 2H), 3.60 (dd, *J* = 8.4, 5.5 Hz, 2H), 2.44 (tt, *J* = 8.4, 5.4 Hz, 1H), 1.77 (s, 6H), 1.42 (s, 9H), 1.23 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 83.5, 79.3, 50.2, 49.1, 46.6, 46.2, 30.3, 28.5, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.3.

FT-IR (cm^{-1}, neat, ATR) 2963, 2907, 2872, 1702, 1512, 1479, 1436, 1390, 1367, 1346, 1310, 1255, 1201, 1165, 1141, 1060, 963, 855, 773.

HRMS (EI-TOF) calcd for ($C_{15}H_{24}BNO_4$) $[M-t\text{-}Bu]^+$ 293.1798, found 293.1801.



(1*R*,3*S*,5*S*,7*S*)-5-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)adamantan-2-one (**5j**, 42 mg, 41%).

Prepared following **GP-F** and purified by column chromatography (60% EtOAc/hexanes). The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.49 (t, *J* = 2.9 Hz, 2H), 2.11 – 2.09 (m , 1H), 1.92 (t, *J* = 2.9 Hz, 4H), 1.74 – 1.70 (m, 2H), 1.67 (s, 6H), 1.64 (t, *J* = 1.6 Hz, 1H), 1.61 (d, *J* = 3.2 Hz, 2H), 1.22 (s, 12H).

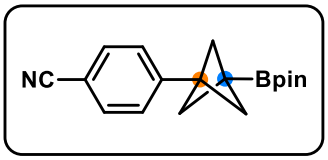
^{13}C NMR (101 MHz, $CDCl_3$) δ 218.9, 83.3, 51.7, 47.1, 46.1, 39.6, 38.7, 36.9, 31.9, 27.5, 24.7.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.9.

FT-IR (cm^{-1}, neat, ATR) 2957, 2917, 2855, 1721, 1510, 1438, 1404, 1371, 1349, 1311, 1251, 1201, 1166, 1145, 1111, 1083, 1058, 988, 855.

HRMS (ESI-TOF) calcd for ($C_{21}H_{31}BO_3$) $[M+H]^+$ 342.2366, found 342.2372.

Melting point: 155 – 158 °C.



4-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)benzonitrile (**5k**, 60.6 mg, 68%).

Prepared following **GP-G** *with the following modification*: 1.5 equiv of [1.1.1]propellane was used. The compound was purified by column chromatography (50% CH_2Cl_2/hexanes). The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.3 Hz, 2H), 2.17 (s, 6H), 1.26 (s, 12H).

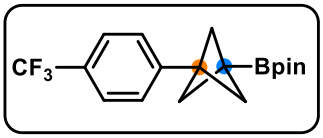
^{13}C NMR (151 MHz, $CDCl_3$) δ 147.2, 132.2, 126.8, 119.3, 110.2, 83.7, 53.2, 47.1, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 31.0.

FT-IR (cm^{-1}, neat, ATR) 2975, 2227, 1607, 1434, 1403, 1382, 1373, 1357, 1321, 1272, 1208, 1168, 1146, 1105, 970, 853, 833, 790, 664, 563.

HRMS (EI-TOF) calcd for ($C_{18}H_{22}BNO_2$) $[M]^+$ 295.1744, found 295.1735.

Melting point: 178 - 180 °C.



4,4,5,5-Tetramethyl-2-(3-(4-(trifluoromethyl)phenyl)bicyclo[1.1.1]pentan-1-yl)-1,3,2-dioxaborolane (**5l**, 47.9 mg, 47%).

Prepared following **GP-G** *with the following modification*: 1.5 equiv of [1.1.1]propellane were used. The compound was purified by C18 column chromatography (85% MeCN/H_2O). The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 2.19 (s, 6H), 1.27 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 146.0, 128.8 (q, *J* = 32.2 Hz), 126.3, 125.2 (q, *J* = 3.8 Hz), 124.5 (q, *J* = 271.9 Hz), 83.7, 53.2, 47.1, 25.0.

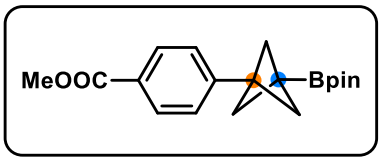
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.4.

FT-IR (cm^{-1}, neat, ATR) 2965, 1439, 1410, 1391, 1383, 1373, 1352, 1324, 1210, 1160, 1141, 1114, 1066, 1016, 970, 849, 833, 791, 666, 600.

HRMS (EI-TOF) calcd for ($C_{17}H_{19}BF_3O_2$) $[M\text{-}CH_3]^+$ 323.1430, found 323.1419.

Melting point: 136 - 138 °C.



Methyl 4-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)benzoate (**5m**, 51.7 mg, 53%).

Prepared following **GP-G** and purified by C18 column chromatography (85% MeCN/H_2O). The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 3.89 (s, 3H), 2.18 (s, 6H), 1.27 (s, 12H).

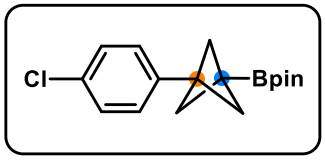
^{13}C NMR (151 MHz, $CDCl_3$) δ 167.3, 147.2, 129.7, 128.3, 126.0, 83.7, 53.2, 52.2, 47.4, 25.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.5.

FT-IR (cm^{-1}, neat, ATR) 2970, 2872, 1721, 1610, 1568, 1437, 1411, 1349, 1309, 1277, 1210, 1144, 1098, 1019, 969856, 823, 761, 703, 666.

HRMS (ESI-TOF) calcd for ($C_{19}H_{26}BO_4$) $[M+H]^+$ 329.1924, found 329.1906.

Melting point: 135 - 137 °C.



2-(3-(4-Chlorophenyl)bicyclo[1.1.1]pentan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5n**, 43.7 mg, 48%).

Prepared following **GP-G** and purified by C18 column chromatography (90% MeCN/H_2O). The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 2.14 (s, 6H), 1.26 (s, 12H).

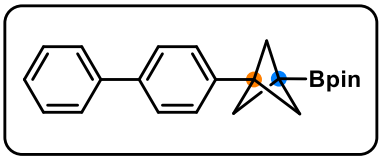
^{13}C NMR (151 MHz, $CDCl_3$) δ 140.8, 132.3, 128.4, 127.4, 83.6, 53.2, 47.0, 25.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.9.

FT-IR (cm^{-1}, neat, ATR) 2967, 2870, 1488, 1436, 1407, 1380, 1349, 1313, 1209, 1144, 1087, 1014, 969, 854, 788, 726, 666, 517.

HRMS (EI-TOF) calcd for ($C_{17}H_{22}BClO_2$) $[M]^+$ 304.1401, found 304.1403.

Melting point: 130 - 131 °C.



2-(3-([1,1'-Biphenyl]-4-yl)bicyclo[1.1.1]pentan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5o**, 54.9 mg, 53%).

Prepared following **GP-G** and purified by column chromatography (15% EtOAc/hexanes). The product was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.5 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.27 – 7.18 (m, 2H), 2.16 (s, 6H), 1.23 (s, 12H).

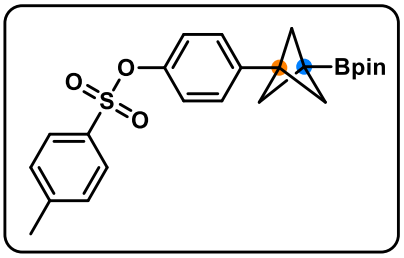
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 139.6, 128.9, 127.3, 127.3, 127.1, 126.4, 83.6, 53.3, 47.4, 25.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.8.

FT-IR (cm^{-1}, neat, ATR) 3043, 2965, 2907, 2869, 1487, 1438, 1408, 1390, 1310, 1208, 1144, 1107, 969, 855, 760, 726, 697, 666, 566.

HRMS (EI-TOF) calcd for ($C_{23}H_{27}BO_2$) $[M]^+$ 346.2104, found 346.2084.

Melting point: 135 - 137 °C.



4-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)phenyl 4-Methylbenzenesulfonate (**5p**, 50.5 mg, 38%).

Prepared following **GP-G** and purified by C18 column chromatography (65% MeCN/H_2O). The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.87 (d, *J* = 8.2 Hz, 2H), 2.45 (s, 3H), 2.12 (s, 6H), 1.25 (s, 12H).

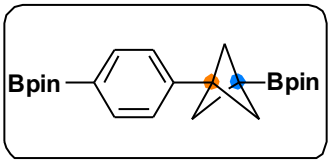
^{13}C NMR (151 MHz, $CDCl_3$) δ 148.3, 145.4, 141.3, 132.8, 129.9, 128.7, 127.2, 122.1, 83.6, 53.2, 46.9, 24.9, 21.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.9.

FT-IR (cm^{-1}, neat, ATR) 2969, 1497, 1437, 1407, 1392, 1372, 1311, 1209, 1197, 1175, 1146, 1094, 864, 815, 795, 748, 723, 667, 570, 552.

HRMS (EI-TOF) calcd for ($C_{24}H_{29}BO_5S$) $[M]^+$ 440.1829, found 440.1820.

Melting point: 176 - 177 °C.



4,4,5,5-Tetramethyl-2-(4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)phenyl)-1,3,2-dioxaborolane (**5q**, 50.7 mg, 43%).

Prepared following **GP-G** and purified by C18 column chromatography (85% MeCN/H_2O). The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 7.7 Hz, 2H), 2.16 (s, 6H), 1.33 (s, 12H), 1.26 (s, 12H).

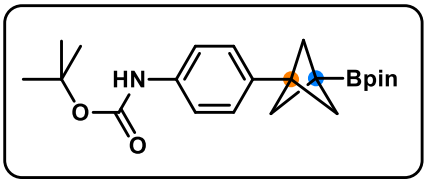
^{13}C NMR (151 MHz, $CDCl_3$) δ 145.2, 134.7, 125.1, 83.7, 83.4, 53.0, 47.5, 24.8, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.6.

FT-IR (cm^{-1}, neat, ATR) 2976, 2870, 1611, 1522, 1439, 1396, 1359, 1316, 1267, 1210, 1143, 1113, 1085, 1020, 962, 854, 830, 740, 657, 578

HRMS (EI-TOF) calcd for ($C_{23}H_{34}B_2O_4$) $[M]^+$ 396.2643, found 396.2640.

Melting point: 214 - 216 °C.



***tert*-Butyl (4-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)phenyl)carbamate** (**5r**, 48.3 mg, 42%).

Prepared following **GP-G** and purified by C18 column chromatography (85% MeCN/H_2O). The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.4 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.43 (br, 1H), 2.13 (s, 6H), 1.50 (s, 9H), 1.26 (s, 12H).

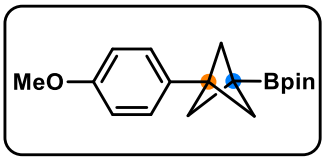
^{13}C NMR (151 MHz, $CDCl_3$) δ 152.9, 137.3, 136.8, 126.5, 118.6, 83.6, 53.3, 47.2, 28.5, 25.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.9.

FT-IR (cm^{-1}, neat, ATR) 3337, 2976, 2869, 1728, 1708, 1594, 1529, 1508, 1438, 1407, 1392, 1368, 1312, 1232, 1208, 1162, 1105, 1052, 1027, 969, 855.

HRMS (ESI-TOF) calcd for ($C_{24}H_{35}BN_2O_4Na$) $[M+Na+CH_3CN]^+$ 449.2592, found 449.2596.

Melting point: 208 - 210 °C.



2-(3-(4-Methoxyphenyl)bicyclo[1.1.1]pentan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5s**, 30.3 mg, 34%).

Prepared following **GP-G** and purified by C18 column chromatography (80% MeCN/H_2O). The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.1 Hz, 2H), 6.83 (d, *J* = 8.0 Hz, 2H), 3.78 (s, 3H), 2.14 (s, 6H), 1.27 (s, 12H).

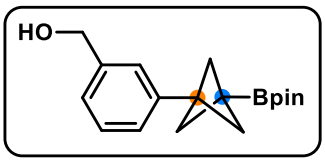
^{13}C NMR (151 MHz, $CDCl_3$) δ 158.4, 134.9, 127.0, 113.7, 83.5, 55.5, 53.3, 47.1, 25.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ 31.3.

FT-IR (cm^{-1}, neat, ATR) 2962, 2907, 2869, 1611, 1503, 1437, 1407, 1311, 1246, 1208, 1172, 1145, 1105, 1036, 969, 856, 831, 792, 666, 602.

HRMS (EI-TOF) calcd for ($C_{18}H_{25}BO_3$) $[M]^+$ 300.1897, found 300.1907.

Melting point: 110 - 112 °C.



(3-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)phenyl)methanol (**5t**, 28.7 mg, 32%).

Prepared following **GP-G** and purified by C18 column chromatography (80% MeCN/H_2O). The product was obtained as a pale-yellow oil.

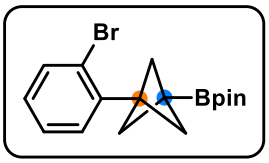
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.7 Hz, 1H), 7.20 (d, *J* = 3.8 Hz, 2H), 7.14 (d, *J* = 7.7 Hz, 1H), 4.68 (s, 2H), 2.17 (s, 6H), 1.27 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 142.7, 140.9, 128.6, 125.3, 125.3, 124.5, 83.6, 53.2, 47.4, 25.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ 31.5.

FT-IR (cm^{-1}, neat, ATR) 3413, 2965, 2907, 2868, 1512, 1435, 1406, 1373, 1344, 1310, 1212, 1167, 1144, 1106, 1021, 855, 806, 776, 703, 666.

HRMS (EI-TOF) calcd for ($C_{18}H_{25}BO_3$) $[M]^+$ 300.1897, found 300.1909.



2-(3-(2-Bromophenyl)bicyclo[1.1.1]pentan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5u**, 56.4 mg, 54%).

Prepared following **GP-G** and purified by C18 column chromatography (90% MeCN/H_2O). The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.9 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 7.8 Hz, 1H), 2.38 (s, 6H), 1.27 (s, 12H).

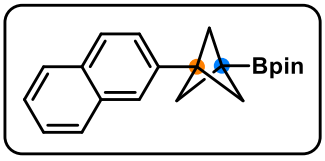
^{13}C NMR (151 MHz, $CDCl_3$) δ 140.1, 133.5, 129.4, 128.4, 127.2, 122.6, 83.6, 53.3, 49.2, 25.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.7.

FT-IR (cm^{-1}, neat, ATR) 2977, 2910, 2872, 1510, 1469, 1435, 1407, 1372, 1312, 1209, 1144, 1114, 1027, 969, 854, 749, 697, 667.

HRMS (EI-TOF) calcd for ($C_{16}H_{19}BBrO_2$) $[M\text{-}CH_3]^+$ 333.0661, found 333.0660.

Melting point: 106 - 108 °C.



4,4,5,5-Tetramethyl-2-(3-(naphthalen-2-yl)bicyclo[1.1.1]pentan-1-yl)-1,3,2-dioxaborolane (**5v**, 44.2 mg, 46%).

Prepared following **GP-G** and purified by C18 column chromatography (85% MeCN/H_2O). The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 – 7.41 (m, 4H), 7.09 (dt, *J* = 20.1, 7.2 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 1H), 1.92 (s, 6H), 0.95 (s, 12H).

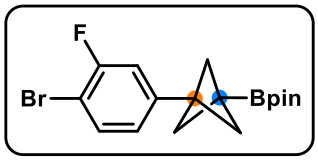
^{13}C NMR (151 MHz, $CDCl_3$) δ 139.8, 133.5, 132.4, 127.9, 127.8, 127.8, 126.2, 125.5, 124.4, 124.2, 83.6, 53.3, 47.8, 25.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.6.

FT-IR (cm^{-1}, neat, ATR) 2967, 2868, 1505, 1436, 1407, 1391, 1380, 1372, 1348, 1311, 1207, 1167, 1144, 1090, 855, 820, 794, 744, 666, 476.

HRMS (EI-TOF) calcd for ($C_{21}H_{25}BO_2$) $[M]^+$ 320.1948, found 320.1951.

Melting point: 131 - 132 °C.



2-(3-(4-Bromo-3-fluorophenyl)bicyclo[1.1.1]pentan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5w**, 41.4 mg, 38%)

Prepared following **GP-G** and purified by C18 column chromatography (85% MeCN/H_2O). The product was obtained as a pale-yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 8.1, 7.0 Hz, 1H), 6.92 (dd, *J* = 9.3, 1.9 Hz, 1H), 6.84 (dd, *J* = 8.1, 1.9 Hz, 1H), 2.14 (s, 6H), 1.26 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.1 (d, *J* = 247.7 Hz), 144.2 (d, *J* = 6.0 Hz), 133.3, 122.9 (d, *J* = 3.3 Hz), 114.2 (d, *J* = 21.5 Hz), 106.8 (d, *J* = 21.1 Hz), 83.7, 53.2, 46.7, 25.0.

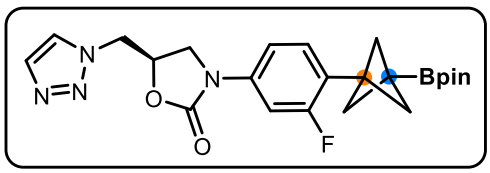
^{19}F NMR (376 MHz, $CDCl_3$) δ -108.1.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.3.

FT-IR (cm^{-1}, neat, ATR) 2975, 2871, 1575, 1481, 1439, 1412, 1314, 1219, 1201, 1144, 1038, 856, 666.

HRMS (EI-TOF) calcd for ($C_{17}H_{21}BBrFO_2$) $[M]^+$ 366.0802, found 366.0801.

Melting point: 73 - 74 °C.



(*R*)-5-((1*H*-1,2,3-Triazol-1-yl)methyl)-3-(3-fluoro-4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxa borolan -2-yl)bicyclo[1.1.1]pentan-1-yl)phenyl)oxazolidin-2-one (**5x**, 26.7 mg, 20%).

Prepared following **GP-G** *with the following modification*: 2:1 MeOH-acetone (0.1 M) mixed solvent was used. The compound was purified by C18 column chromatography (65% MeCN/H_2O). The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.74 (s, 1H), 7.18 (dd, *J* = 12.0, 2.2 Hz, 1H), 7.03 (t, *J* = 8.3 Hz, 1H), 6.97 (dd, *J* = 8.3, 2.3 Hz, 1H), 5.10 – 4.99 (m, 1H), 4.86 – 4.71 (m, 2H), 4.12 (t, *J* = 9.1 Hz, 1H), 3.88 (dd, *J* = 9.4, 6.1 Hz, 1H), 2.22 (s, 6H), 1.26 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.9 (d, *J* = 247.5 Hz), 153.3, 137.2 (d, *J* = 10.6 Hz), 134.7, 129.2 (d, *J* = 6.8 Hz), 125.3 (d, *J* = 17.8 Hz), 125.2, 113.4 (d, *J* = 3.4 Hz), 106.4 (d, *J* = 27.2 Hz), 83.6, 70.5, 53.7, 53.3, 52.2, 47.4, 24.9.

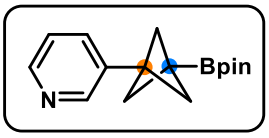
^{19}F NMR (376 MHz, $CDCl_3$) δ -114.5.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.1.

FT-IR (cm^{-1}, neat, ATR) 2973, 2909, 2872, 1739, 1628, 1576, 1505, 1486, 1414, 1311, 1214, 1200, 1146, 1116, 1043, 972, 856, 808, 753, 666.

HRMS (ESI-TOF) calcd for ($C_{23}H_{29}BFN_4O_4$) $[M+H]^+$ 455.2266, found 455.2267.

Melting point: 179 - 182 °C.



3-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)pyridine (**5y**, 39.4 mg, 48%).

Prepared following **GP-G** *with the following modification*: 1.5 equiv of [1.1.1]propellane were used. The compound was purified by C18 column chromatography (65% MeCN/H_2O). The product was obtained as a yellow oil.

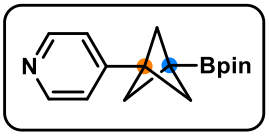
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.44 (s, 2H), 7.50 (d, *J* = 7.3 Hz, 1H), 7.22 (dd, *J* = 7.8, 4.8 Hz, 1H), 2.20 (s, 6H), 1.26 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.5, 147.4, 137.4, 133.9, 123.3, 83.7, 53.2, 45.4, 25.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.2.

FT-IR (cm^{-1}, neat, ATR) 2966, 2908, 2866, 1478, 1408, 1380, 1316, 1272, 1212, 1194, 1145, 1113, 1062, 1030, 969, 854, 815, 785, 713, 666.

HRMS (ESI-TOF) calcd for ($C_{16}H_{23}BNO_2$) $[M+H]^+$ 272.1822, found 272.1825.



4-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)pyridine (**5z**, 35.2 mg, 43%).

Prepared following **GP-G** *with the following modification*: 1.5 equiv of [1.1.1]propellane were used. The compound was purified by C18 column chromatography (65% MeCN/Water). The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.51 (d, *J* = 6.0 Hz, 2H), 7.11 (d, *J* = 6.0 Hz, 2H), 2.18 (s, 6H), 1.27 (s, 12H).

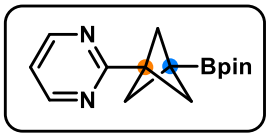
^{13}C NMR (151 MHz, $CDCl_3$) δ 150.6, 149.3, 121.3, 83.8, 53.0, 46.4, 25.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ 31.0.

FT-IR (cm^{-1}, neat, ATR) 2961, 2864, 1625, 1409, 1213, 1156, 1112, 106, 970, 787.

HRMS (ESI-TOF) calcd for ($C_{16}H_{23}BNO_2$) $[M+H]^+$ 272.1822, found 272.1818.

Melting point: 237 - 239 °C.



2-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)pyrimidine (**5aa**, 54.3 mg, 67%).

Prepared following **GP-G** *with the following modification*: 1.5 equiv of [1.1.1]propellane were used. The compound was purified by C18 column chromatography (50% MeCN/H_2O). The product was obtained as a pale-yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.9 Hz, 2H), 7.12 (t, *J* = 4.9 Hz, 1H), 2.32 (s, 6H), 1.27 (s, 12H).

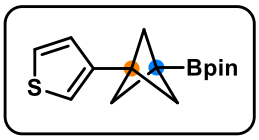
^{13}C NMR (151 MHz, $CDCl_3$) δ 168.0, 157.2, 119.1, 83.7, 53.0, 48.3, 25.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.5.

FT-IR (cm^{-1}, neat, ATR) 2976, 2917, 2873, 1559, 1424, 1400, 1314, 1211, 1167, 1140, 1007, 976, 854, 772, 716, 666, 633.

HRMS (ESI-TOF) calcd for ($C_{15}H_{22}BN_2O_2$) $[M+H]^+$ 273.1774, found 273.1775.

Melting point: 144 - 146 °C.



4,4,5,5-Tetramethyl-2-(3-(thiophen-3-yl)bicyclo[1.1.1]pentan-1-yl)-1,3,2-dioxaborolane (**5ab**, 27.9 mg, 34%).

Prepared following **GP-G** and purified by C18 column chromatography (100% MeCN). The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 – 7.20 (m, 1H), 6.97 – 6.93 (m, 2H), 2.16 (s, 6H), 1.26 (s, 12H).

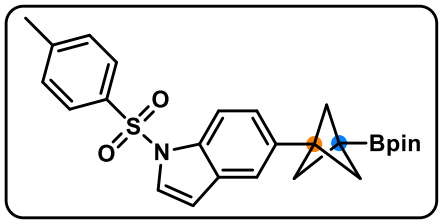
^{13}C NMR (151 MHz, $CDCl_3$) δ 144.4, 126.5, 125.6, 120.2, 83.6, 54.0, 44.0, 25.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.3.

FT-IR (cm^{-1}, neat, ATR) 2962, 2907, 2868, 1438, 1418, 1401, 1372, 1349, 1316, 1213, 1197, 1167, 1142, 1095, 1070, 854, 809, 770, 638.

HRMS (EI-TOF) calcd for ($C_{15}H_{21}BO_2S$) $[M]^+$ 276.1355, found 276.1360.

Melting point: 119 °C.



5-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)-1-tosyl-1*H*-indole (**5ac**, 53.0 mg, 38%).

Prepared following **GP-G** and purified by C18 column chromatography (75% MeCN/H_2O). The product was obtained as a red solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 3.8 Hz, 1H), 7.32 (s, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 1H), 6.60 (d, *J* = 3.6 Hz, 1H), 2.32 (s, 3H), 2.16 (s, 6H), 1.27 (s, 12H).

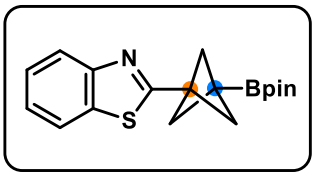
^{13}C NMR (151 MHz, $CDCl_3$) δ 145.0, 137.7, 135.5, 133.8, 130.9, 130.0, 127.0, 126.8, 122.8, 118.4, 113.3, 109.1, 83.6, 53.4, 52.4, 25.0, 21.7.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.3.

FT-IR (cm^{-1}, neat, ATR) 2965, 1460, 1437, 1407, 1371, 1310, 1247, 1210, 1190, 1168, 1132, 1094, 1078, 854, 813, 725, 707, 666, 588, 540.

HRMS (ESI-TOF) calcd for ($C_{26}H_{31}BNO_4S$) $[M+H]^+$ 464.2067, found 464.2047.

Melting point: 133 - 135 °C.



2-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)benzo[*d*]thiazole (**5ad**, 29.5 mg, 30%).

Prepared following **GP-G** and purified by C18 column chromatography (85% MeCN/H_2O). The product was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 8.3 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.5 Hz, 1H), 2.32 (s, 6H), 1.20 (s, 12H).

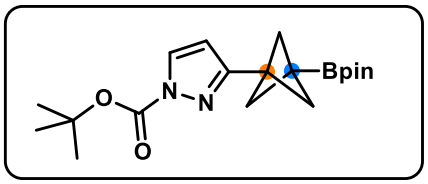
^{13}C NMR (151 MHz, $CDCl_3$) δ 170.9, 153.8, 135.4, 126.2, 125.1, 123.2, 121.8, 83.8, 54.4, 44.7, 25.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.5.

FT-IR (cm^{-1}, neat, ATR) 2976, 2909, 2873, 1499, 1436, 1404, 1391, 1372, 1315, 1267, 1242, 1209, 1143, 1017, 930, 891, 854, 759, 730.

HRMS (ESI-TOF) calcd for ($C_{18}H_{23}BNO_2S$) $[M+H]^+$ 328.1543, found 328.1544.

Melting point: 157 - 159 °C.



***tert*-Butyl 3-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)-1*H*-pyrazole-1-carboxylate** (**5ae**, 26.7 mg, 25%).

Prepared following **GP-G** and purified by C18 column chromatography (75% MeCN/H_2O). The product was obtained as a colorless oil.

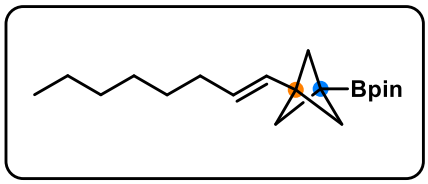
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 2.8 Hz, 1H), 6.18 (d, *J* = 2.8 Hz, 1H), 2.23 (s, 6H), 1.61 (s, 9H), 1.25 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.4, 147.7, 131.3, 107.2, 85.2, 83.6, 53.6, 49.8, 28.1, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.2.

FT-IR (cm^{-1}, neat, ATR) 2975, 2914, 2871, 1770, 1745, 1512, 1397, 1371, 1353, 1296, 1255, 1215, 1199, 1142, 1049, 960, 854, 842, 768, 666.

HRMS (ESI-TOF) calcd for ($C_{19}H_{30}BN_2O_4$) $[M+H]^+$ 361.2299, found 361.2288.



4,4,5,5-Tetramethyl-2-(3-(oct-1-en-1-yl)bicyclo[1.1.1]pentan-1-yl)-1,3,2-dioxaborolane (1:1 mixture of E/Z isomers, **5af**, 29.0 mg, 32%).

Prepared following **GP-G** and purified by C18 column chromatography (100% MeCN). The product was obtained as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.44 (d, *J* = 15.6 Hz, 0.5H), 5.41 – 5.28 (m, 1H), 5.23 (d, *J* = 11.3 Hz, 0.5H), 2.12 (q, *J* = 7.0 Hz, 1H), 2.04 (s, 3H), 1.96 (q, *J* = 6.8 Hz, 1H), 1.87 (s, 3H), 1.38 – 1.25 (m, 8H), 1.23 (s, 12H), 0.87 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 132.5, 131.2, 130.6, 129.3, 83.4, 83.4, 54.9, 52.9, 46.5, 45.2, 32.4, 32.0, 31.9, 30.3, 29.4, 29.2, 29.1, 27.3, 24.9, 22.8, 22.8, 14.3, 14.3.

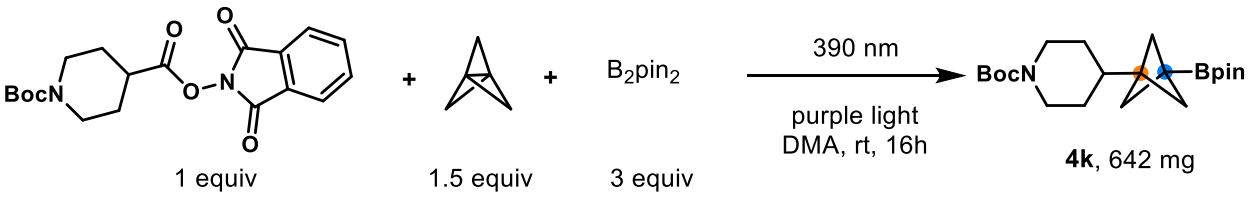
^{11}B NMR (128 MHz, $CDCl_3$) δ 30.2.

FT-IR (cm^{-1}, neat, ATR) 2960, 2926, 2868, 1509, 1438, 1406, 1379, 1372, 1345, 1309, 1200, 1145, 1111, 1040, 962, 856, 666.

HRMS (EI-TOF) calcd for ($C_{19}H_{33}BO_2$) $[M]^+$ 304.2574, found 304.2587.

5. Procedure for Gram-Scale Synthesis of BCP Bpin

5.1 Three-component Borylation with RAE



To a 120 mL ACE pressure tube containing an appropriately-sized stirrer bar was added RAE **1b** (1.00 g, 2.7 mmol, 1 equiv) followed by dry B_2pin_2 (2.03 g, 8.0 mmol, 3 equiv). DMA (27 mL) was then added to allow the solid materials to dissolve. Once dissolved, [1.1.1]propellane (4.01 mL, 4.0 mmol, 1.5 equiv, 1.0 M solution in Et_2O) was added quickly. The reaction vessel was sparged with argon for 30 s and then sealed with a threaded cap. The reaction mixture was placed between two 52 W 390 nm Kessil LED lamps at 100% power facing each other or between four 52 W 390 nm Kessil® LED lamps at 50% power. The lamps were placed 1 inch from the reaction vessel. The reaction was then irradiated under vigorous stirring for 16 h. Room temperature was maintained by the use of two fans. When judged complete (*Note:* after completion, the reaction mixture is generally orange), the mixture was then partitioned between Et_2O (50 mL) and satd aq NH_4Cl (50 mL). The organic layer was washed two more times with brine (30 mL × 2), dried ($MgSO_4$), filtered, and further dried under vacuum. The crude mixture was then purified by SiO_2 flash column chromatography. (642 mg, 64%)

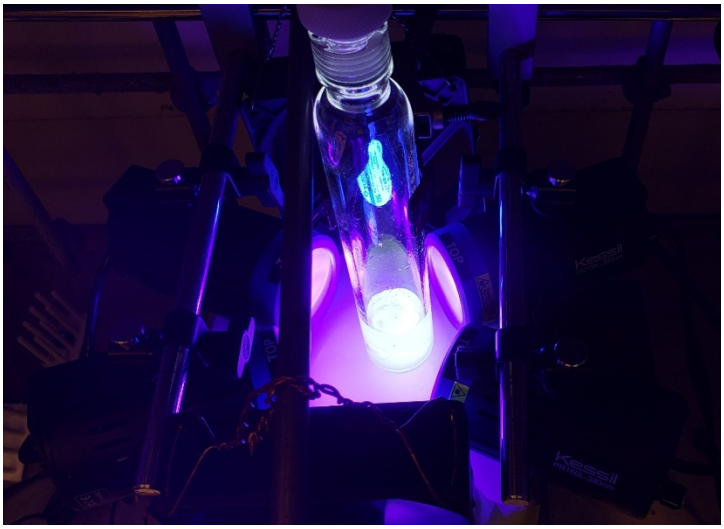
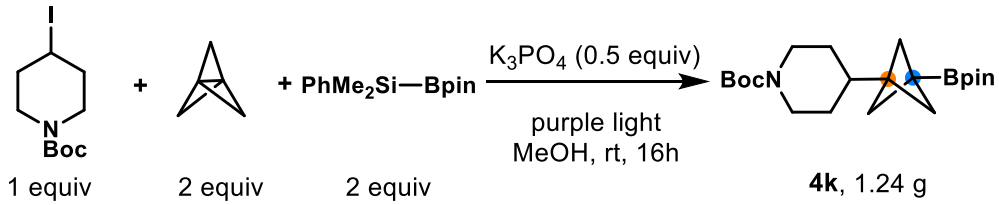


Figure S5. Gram-scale synthesis using 4 Kessil® LEDs at 50% power with 2 fans facing each other for cooling

Figure S6. Gram-scale synthesis using 2 Kessil® LEDs at 100% power with 2 fans facing each other for cooling

5.2 Three-component Borylation with an Organo Iodide



To a 120 mL ACE pressure tube containing an appropriately-sized stirrer bar was added *N*-Boc-4-iodopiperidine **2b** (1.50 g, 4.82 mmol, 1 equiv) followed by powder K_3PO_4 (512 g, 2.41 mmol, 0.5 equiv). The reaction vessel was capped with a rubber septum and then was evacuated and backfilled with nitrogen three times. Dry MeOH (30 mL) was then added to the reaction vessel followed by $PhMe_2Si$-Bpin (2.53 g, 9.64 mmol, 2.0 equiv). Lastly, [1.1.1]propellane (9.6 mL, 9.6 mmol, 2 equiv, 1.0 M solution in Et_2O) was added quickly. The reaction vessel was sparged with argon for 30 s and then sealed with a threaded cap. The reaction mixture was placed between four 52 W 390 nm Kessil LED lamps at 100% power. The lamps were placed 1 inch from the reaction vessel. The reaction was then irradiated under vigorous stirring for 16 h. Room temperature was maintained by the use of two fans. When judged complete after 16 h, the mixture was dried under vacuum. The crude mixture was then purified by SiO_2 flash column chromatography. (1.24 g, 68%)

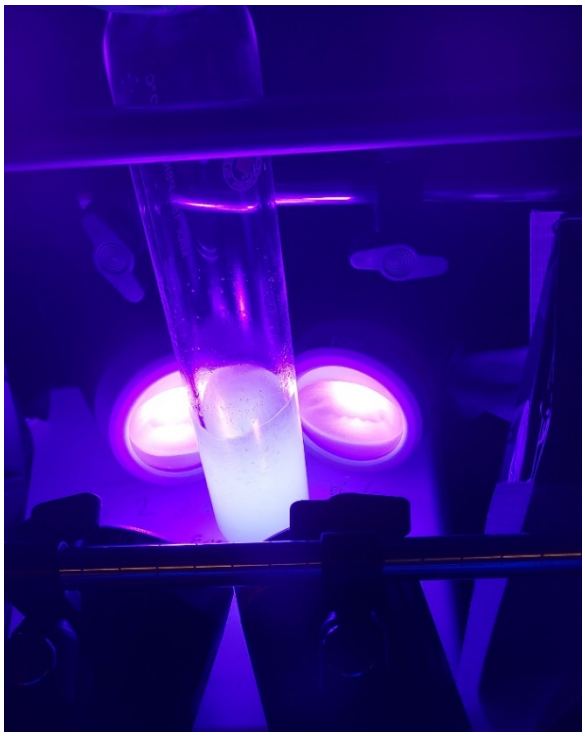
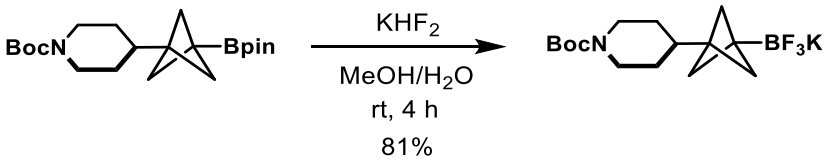


Figure S7. Gram-scale synthesis using 4 Kessil® LEDs at 100% power with 2 fans facing each other for cooling

6. Synthesis and Characterization of BCP Trifluoroborate 6

6.1 Synthesis of Organotrifluoroborate 6 from 4k



***tert*-Butyl 4-(3-(Trifluoro-l4-boraneyl)bicyclo[1.1.1]pentan-1-yl)piperidine-1-carboxylate, Potassium Salt 6** was prepared based on modified literature procedures.[26,27] To a stirred soln of boronate ester **4k** (377 mg, 1 mmol) in 5 mL of MeOH was added KHF_2 (1 mL of 4.5 M satd aq soln, 9 mmol, 4.5 equiv) dropwise. The reaction mixture was stirred at rt. After 4 h, the solvents were removed under vacuum. The residue was redissolved in a mixture of MeOH/H_2O (3:2, 10 mL). Volatile materials were removed by evaporation *in vacuo*. The solubilization/evaporation cycle was repeated 10 times to remove all the pinacol. The residue was triturated with acetone (4 mL). The liquid was collected by filtration. The inorganic salt residue was washed with acetone three times (3 X 1 mL). The combined liquid phases were evaporated to afford product (290 mg, 81%) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 3.93 (d, J = 12.9 Hz, 2H), 2.69 – 2.53 (m, 2H), 1.43 (d, J = 13.2 Hz, 2H), 1.38 (d, J = 1.4 Hz, 9H), 1.25 – 1.17 (m, 1H), 1.15 (s, 6H), 0.83 (qd, J = 12.7, 4.3 Hz, 2H).

^{13}C NMR (101 MHz, acetone-d_6) δ 154.9, 78.9, 47.6, 47.6, 45.8, 44.5, 39.0, 28.9, 28.4.

^{19}F NMR (376 MHz, DMSO-d_6) δ -142.2.

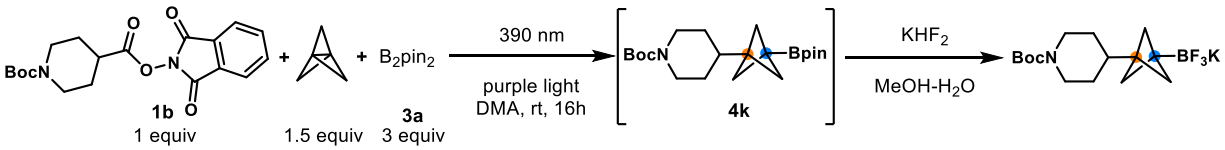
^{11}B NMR (128 MHz, Acetone-d_6) δ 2.3.

FT-IR (cm^{-1}, neat, ATR) 2923, 2905, 2855, 1682, 1428, 1336, 1237, 1156, 1130, 1109, 1017, 934.

HRMS (ESI-TOF) calcd for ($C_{15}H_{24}BF_3NO_2$) $[M-K]^-$ 318.1852, found 318.1879.

Melting point: 234 °C (decomposes).

6.2 Telescoped Gram-Scale Synthesis of BCP BF_3K (6)



To a 120 mL ACE pressure tube with an appropriately-sized stirrer bar was added RAE **1b** (2.00 g, 5.3 mmol, 1 equiv) followed by dry B_2pin_2 (4.07 g, 16.0 mmol, 3 equiv). DMA (30 mL) was then added to allow the solid materials dissolve. Once dissolved, [1.1.1]propellane (8.01 mL, 8.0 mmol, 1.5 equiv, 1.0 M solution in Et_2O) was added quickly. The reaction vessel was sparged with argon for 30 s and then sealed with a threaded cap. The reaction mixture was placed between two 52

W 390 nm Kessil LED lamps at 100% power facing each other. The lamps were placed 1 inch from the reaction vessel. The reaction was then irradiated with vigorous stirring for 16 h. Room temperature was maintained by the use of two fans. After 16 h, the mixture was then partitioned between Et_2O (50 mL) and satd aq NH_4Cl (100 mL). The aq phase was washed with Et_2O (50 mL × 2), and the combined organic layers were washed with brine (50 mL), and then passed through a plug of silica. The filtrate was then concentrated under reduced pressure and further dried under vacuum. The crude, pale-yellow solid material was dissolved in MeOH (40 mL)/H_2O (20 mL), and then KHF_2 (30 mL, 135 mmol, 25.5 equiv, 4.5 M aq soln) was added dropwise at ambient temperature. The reaction mixture was stirred vigorously at rt for 3 h. After 3 h, the solvents were evaporated to dryness under reduced pressure. The resulting crude material was extracted with hot acetone (3×50 mL), followed by filtration. The combined filtrates were concentrated and then triturated with approximately 100 mL of Et_2O. The resultant precipitate was collected by vacuum filtration and dried under vacuum to afford BCP BF_3K (**6**) as a brown solid (1.08 g, 57%). Characterization data matched the data reported in **6.1**.

6.3 Cyclic Voltammogram of BCP BF_3K (6)

Cyclic voltammetry was conducted on a CH Instruments 600E Series Electrochemical Analyzer. Voltammograms were recorded using a glassy carbon working electrode, a platinum counter electrode, and a silver reference electrode in a 0.1 M [$^nBu_4N$][ClO_4] supporting electrolyte MeCN solution, with ferrocene as an internal reference ($E^0_{1/2}$ = + 0.40 V vs SCE). Cyclic voltammograms were recorded with a step potential of 0.001 V at a scan rate of 0.2 V/s.

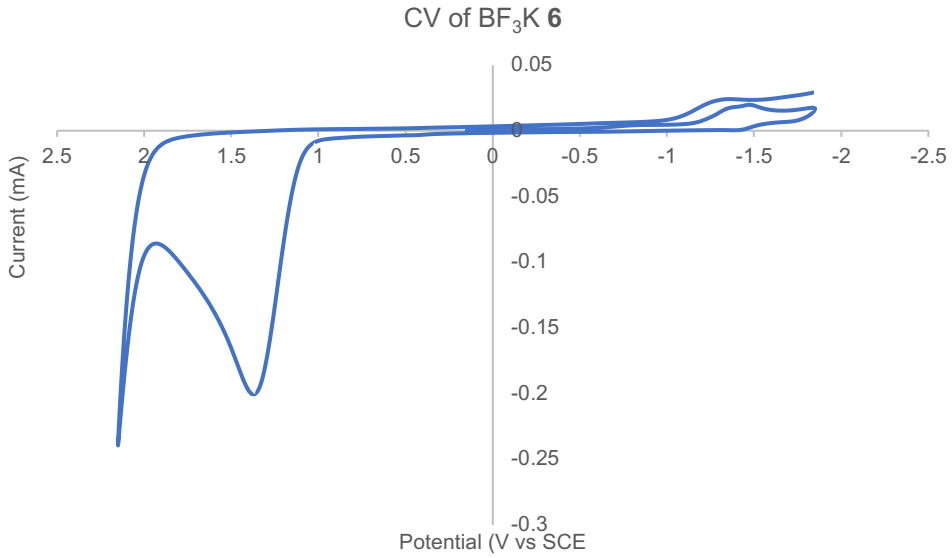
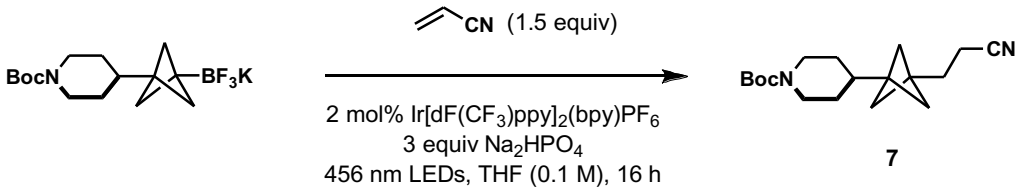


Figure S8. Cyclic voltammetry study on compound **6**

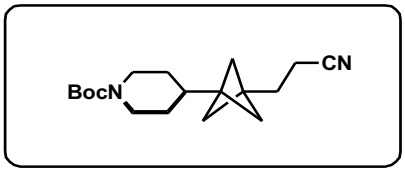
Based on the CV result, the oxidation potential of BCP BF_3K **6** is +1.36 V vs SCE.

7. Post-functionalizations

i) Hydro-alkylation with Acrylonitrile



In a sealable tube was added $Ir[dF(CF_3)ppy]_2(bpy)PF_6$ (4.3 mg, 0.0043 mmol, 0.02 equiv), BCP BF_3K **6** (71.5 mg, 0.2 mmol, 1 equiv), acrylonitrile (31.8 mg, 39.5 μL, 0.6 mmol, 3 equiv), Na_2HPO_4 (85.2 mg, 0.600 mmol, 3 equiv), and THF (2 mL). The mixture was irradiated with a 34 W blue LED for 16 h. Solvent was removed *in vacuo*, and the crude material was purified by column chromatography (25% EtOAc/hexanes). The product was obtained as a colorless oil. *(***7**, 38.0 mg, 77%)



tert-Butyl 4-(3-(2-Cyanoethyl)bicyclo[1.1.1]pentan-1-yl)piperidine-1-carboxylate

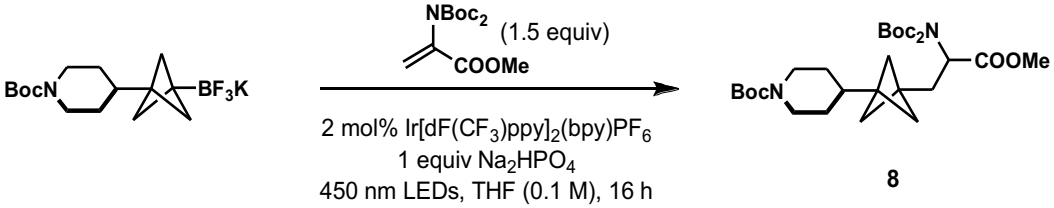
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.10 (d, *J* = 12.7 Hz, 2H), 2.62 (t, *J* = 12.9 Hz, 2H), 2.27 (t, *J* = 7.3 Hz, 2H), 1.81 (t, *J* = 7.3 Hz, 2H), 1.55 - 1.52 (m, 2H), 1.51 (s, 6H), 1.49 – 1.45 (m, 1H), 1.44 (s, 9H), 1.04 (qd, *J* = 12.6, 4.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 120.0, 79.4, 47.9, 43.8, 42.8, 37.8, 36.5, 28.6, 28.4, 27.8, 14.6.

FT-IR (cm^{-1}, neat, ATR) 2962, 2928, 2865, 1687, 1478, 1422, 1365, 1324, 1289, 1255, 1234, 1173, 1149, 1112,1093, 1013, 984, 871.

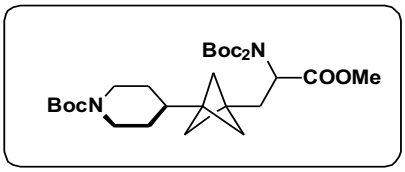
HRMS (ESI-TOF) calcd for ($C_{18}H_{28}NaN_2O_2$) $[M+Na]^+$ 327.2048, found 327.2047.

ii) Hydro-alkylation with Dehydroalanine



In a sealable tube was added $Ir[dF(CF_3)ppy]_2(bpy)PF_6$ (4.3 mg, 0.0043 mmol, 0.02 equiv), BF_3K **6** (71.5 mg, 0.2 mmol, 1 equiv), methyl 2-(bis(*tert*-butoxycarbonyl)amino)acrylate (39.5 μL, 0.6 mmol, 3 equiv) and Na_2HPO_4 (28.4 mg, 0.200 mmol, 1 equiv) in THF (2 mL). The mixture was

irradiated with blue LEDs for 16 h. Solvent was removed *in vacuo*, and the crude was purified by column chromatography (25% EtOAc/hexanes). The product was obtained as a colorless oil (**8**, 54.7 mg, 48%).



***tert*-Butyl 4-(3-(2-(bis(tert-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)bicyclo[1.1.1] pentan-1-yl)piperidine-1-carboxylate**

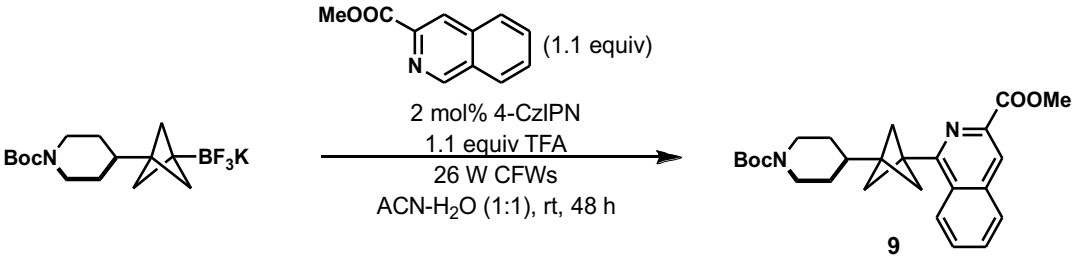
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.91 (dd, *J* = 9.8, 4.5 Hz, 1H), 4.09 (s, 2H), 3.69 (s, 3H), 2.61 (s, 2H), 2.29 (dd, *J* = 15.1, 4.6 Hz, 1H), 2.07 (dd, *J* = 15.1, 9.8 Hz, 1H), 1.53-1.47 (m, 20H), 1.46 (d, *J* = 1.9 Hz, 6H), 1.44 (s, 9H), 1.42-1.37 (m, 1H), 1.07 – 0.96 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.7, 155.0, 152.1, 83.1, 79.3, 56.7, 52.3, 48.6, 43.8, 43.0, 36.8, 36.7, 32.0, 28.6, 28.5, 28.2.

FT-IR (cm^{-1}, neat, ATR) 2976, 2932, 2865, 1747, 1695, 1423, 1366, 1273, 1234, 1173, 1152, 1128, 1035, 942, 873, 850, 811, 769.

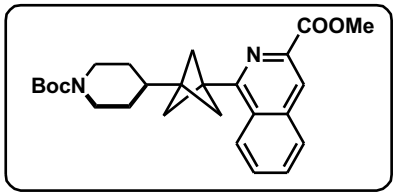
HRMS (ESI-TOF) calcd for ($C_{29}H_{48}NaN_2O_8$) $[M+Na]^+$ 575.3308, found 575.3291.

iii) Minisci reaction



9

Following the reported procedure in the literature[28]: In a scintillation vial were added to a soln of methyl isoquinoline-3-carboxylate (20.6 mg, 0.110 mmol, 1.1 equiv) in $MeCN/H_2O$ (1 mL, 1:1) trifluoroacetic acid (8 μL, 0.11 mmol, 1.1 equiv) followed by 4-CzIPN (4.0 mg, 0.005 mmol, 0.05 equiv), $K_2S_2O_8$ (54 mg, 0.200 mmol, 2 equiv) and compound **6** (35.7 mg, 0.100 mmol, 1 equiv). The mixture was allowed to stir at rt under the irradiation of a compact fluorescent light bulb (24 W CFL). After 48 h, a satd aq soln of $NaHCO_3$ was added, and the mixture was extracted with CH_2Cl_2. The organic layer was dried (Na_2SO_4) and filtered, and the solvent was removed *in vacuo.* The crude material was purified by column chromatography (40% EtOAc/hexanes). The product was obtained as a colorless oil. (**9**, 13 mg, 30%)



Methyl 1-(3-(1-(*tert*-Butoxycarbonyl)piperidin-4-yl)bicyclo[1.1.1]pentan-1-yl)isoquinoline-3-carboxylate

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 8.0 Hz, 1H), 8.45 (s, 1H), 7.95 (d, *J* = 7.7 Hz, 1H), 7.77 – 7.68 (m, 2H), 4.19 (d, *J* = 12.5 Hz, 2H), 4.02 (s, 3H), 2.71 (t, *J* = 13.0 Hz, 2H), 2.31 (s, 6H), 1.75 – 1.65 (m, 3H), 1.47 (s, 9H), 1.21 (dd, *J* = 12.5, 4.3 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.5, 159.2, 154.9, 140.6, 136.0, 130.3, 128.9, 128.8, 128.7, 126.2, 123.3, 79.3, 52.7, 51.5, 43.7, 42.9, 36.4, 28.4, 28.3. (1C missing)

FT-IR (cm^{-1}, neat, ATR) 1737, 1717, 1685, 1445, 1423, 1392, 1296, 1274, 1232, 1202, 1171, 1146, 1096, 993, 793, 775, 749, 734.

HRMS (ESI-TOF) calcd for ($C_{26}H_{33}N_2O_4$) $[M+H]^+$ 437.2440, found 437.2421.

iv) Photoredox Chan-Lam C-N Coupling

Reaction Optimizations and Control Experiments

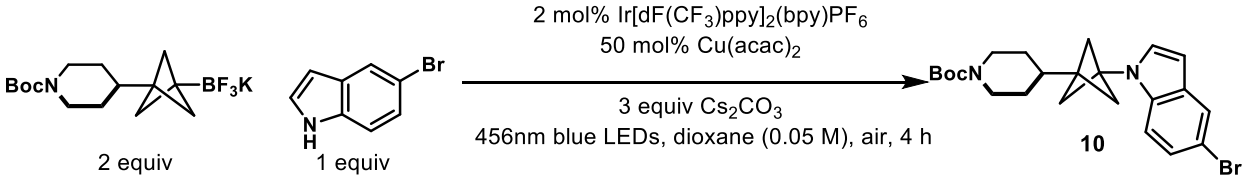
To an 8 mL reaction vial equipped with a stirrer bar was added **6** (35.7 mg, 0.1 mmol, 2 equiv), 5-bromo-1*H*-indole (9.8 mg, 0.05 mmol, 1 equiv), $Ir[dF(CF_3)ppy]_2(bpy)PF_6$ (1.0 mg, 0.001 mmol, 2 mol%), $Cu(acac)_2$ (6.5 mg, 0.025 mmol, 50 mol%), base (0.15 mmol, 3 equiv) and dioxane (1 mL, 0.1 M). The vial was then sealed with a cap containing a TFE-lined silicone septum with an 18 G needle as air inlet. The reaction mixture was then irradiated under vigorous stirring at 34 W 456 nm using a Kessil lamp at 1 inch distance for 4 h. Room temperature was maintained by the use of fans. When judged complete the crude mixture had turned into a dark color, and the crude material was passed through a pad of Celite® and eluted with another 10 mL of acetone. The filtrate was concentrated under reduced pressure and purified by SiO_2 column chromatography.

Table S4: Reaction optimizations of the photoredox Chan-Lam coupling

Entry	Base	Yield (%)
1	TMG	23
2	BTMG	16
3	Cs_2CO_3	83
*Derivation from **Entry 3***		
4	No light	0
5	No [Ir] catalyst	0

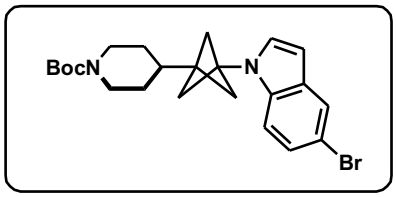
*TMG = 1,1,3,3-tetramethylguanidine
BTMG = 2-*tert*-butyl-1,1,3,3-tetramethylguanidine

Procedure for Chan-Lam C-N Coupling



To an 8 mL reaction vial equipped with a stirrer bar was added **6** (35.7 mg, 0.1 mmol, 2 equiv), 5-bromo-1*H*-indole (9.8 mg, 0.05 mmol, 1 equiv), $Ir[dF(CF_3)ppy]_2(bpy)PF_6$ (1.0 mg, 0.001 mmol, 2 mol %), $Cu(acac)_2$ (6.5 mg, 0.025 mmol, 50 mol %), Cs_2CO_3 (48.9 mg, 0.15 mmol, 3 equiv) and dioxane (1 mL, 0.1 M). The vial was then sealed with a cap containing a TFE-lined silicone septum with an 18 G needle as an air inlet. The reaction mixture was then irradiated under vigorous stirring at 34 W 456 nm using a Kessil lamp at 1 inch distance for 4 h. Room temperature was maintained by the use of fans. When judged complete, the crude mixture had turned into a dark color, and the crude material was passed through a pad of Celite® and eluted with another 10 mL of acetone. The filtrate was concentrated under reduced pressure and purified by SiO_2 column chromatography. (**10**,18.5 mg, 83%)

Note: The surface area and the head space in the reaction vial are important for maintaining good reaction efficiency for this heterogeneous reaction. In this case, the 8 mL reaction vial is optimal for performing reaction at 0.05 mmol scale, and performing a larger scale in this vial resulted in dramatically reduced yield.



tert-Butyl 4-(3-(5-Bromo-1*H*-indol-1-yl)bicyclo[1.1.1]pentan-1-yl)piperidine-1-carboxylate

Purified by SiO_2 column chromatography (10% EtOAc/hexanes). The product was obtained as a colorless oil.

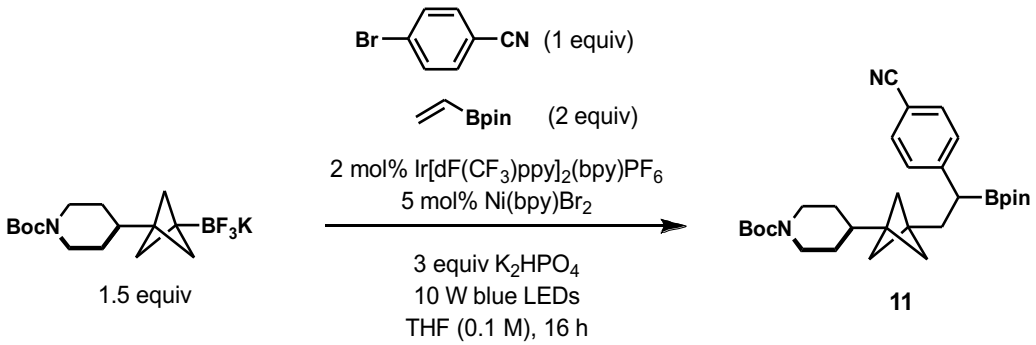
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 1.9 Hz, 1H), 7.37 (d, *J* = 8.7 Hz, 1H), 7.25 (d, *J* = 1.9 Hz, 1H), 7.04 (d, *J* = 3.2 Hz, 1H), 6.39 (d, *J* = 3.2 Hz, 1H), 4.18 (br, 2H), 2.69 (br, 2H), 2.20 (s, 6H), 1.75 – 1.69 (m, 1H), 1.69 – 1.63 (m, 2H), 1.47 (s, 9H), 1.21 – 1.14 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.0, 134.6, 131.1, 127.5, 124.6, 123.6, 113.1, 112.4, 101.1, 79.6, 51.1, 49.7, 43.8, 40.1, 35.4, 28.7.

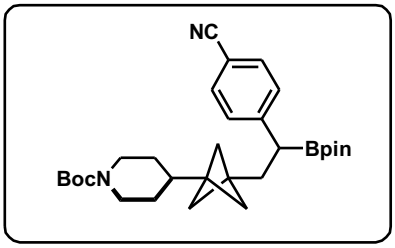
FT-IR (cm^{-1}, neat, ATR) 2974, 2916, 2872, 1689, 1518, 1460, 1424, 1391, 1365, 1323, 1291, 1276, 1236, 1215, 1173, 1155, 1096, 884, 755, 719.

HRMS (ESI-TOF) calcd for ($C_{23}H_{30}BrN_2O_2$) $[M+H]^+$ 445.1491, found 445.1475.

v) Dicarbofunctionalization of Alkene



Following the reported procedure in the literature[29]: in a scintillation vial, under inert atmosphere was added $Ni(bpy)Br_2$ (4.1 mg, 0.011 mmol, 0.05 equiv), $Ir[dF(CF_3)ppy_2(bpy)]PF_6$ (4.4 mg, 0.004 mmol, 0.02 equiv), BCP BF_3K **6** (118 mg, 0.33 mmol, 1.5 equiv), 4-bromobenzonitrile (40.0 mg, 0.220 mmol, 1 equiv) and dried K_2HPO_4 (115 mg, 0.660 mmol, 3 equiv). The vial was evacuated and backfilled with argon three times. Distilled THF (2 mL) was added followed by vinyl-Bpin (67.8 mg, 75 μL, 0.440 mmol, 2 equiv). The reaction vessel was sealed and irradiated with blue LEDs for 16 h. The solvent was then removed under vacuum, and the crude product was purified by column chromatography (20% EtOAc/hexanes). The product was obtained as a colorless oil *(***11**, 45.0 mg, 41%).



tert-Butyl 4-(3-(2-(4-Cyanophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) ethyl)bicyclo[1.1.1]pentan-1-yl)piperidine-1-carboxylate

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 4.08 (t, *J* = 7.0 Hz, 2H), 2.60 (d, *J* = 16.6 Hz, 2H), 2.41 (t, *J* = 7.6 Hz, 1H), 2.07 (dd, *J* = 14.1, 8.0 Hz, 1H), 1.83 (dd, *J* = 14.0, 7.3 Hz, 1H), 1.65 (d, *J* = 9.1 Hz, 1H), 1.43 (s, 9H), 1.35 – 1.27 (m, 6H), 1.24 (t, *J* = 1.9 Hz, 2H), 1.14 (d, *J* = 7.1 Hz, 12H), 0.99 (dt, *J* = 12.7, 6.3 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.0, 149.8, 132.1, 128.9, 119.5, 108.9, 83.8, 79.3, 48.4, 42.8, 39.0, 36.6, 33.7, 28.6, 28.5, 24.7, 24.7.

^{11}B NMR (128 MHz, $CDCl_3$) δ 31.3.

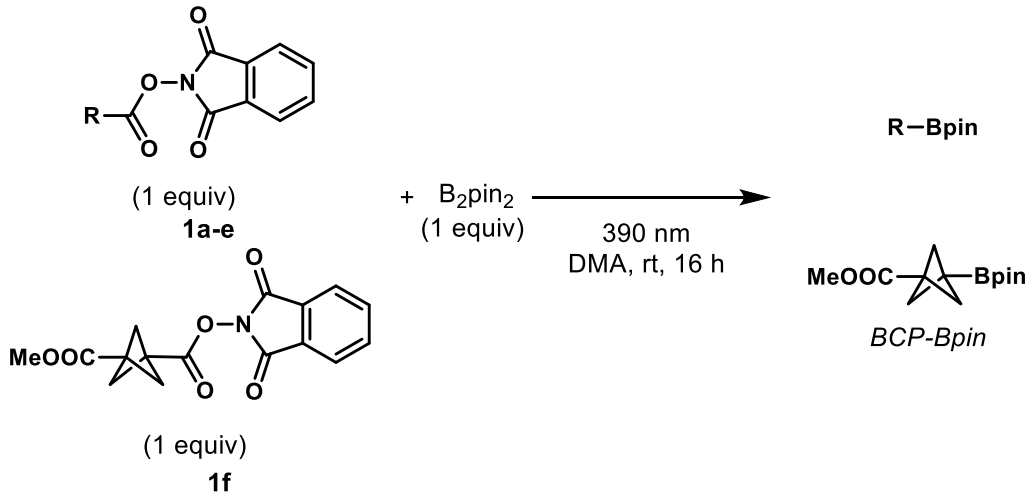
FT-IR (cm^{-1}, neat, ATR) 2974, 2863, 2227, 1691, 1606, 1423, 1365, 1329, 1236, 1170, 1145, 825.

HRMS (ESI-TOF) calcd for ($C_{30}H_{44}BN_2O_4$) $[M+H]^+$ 507.3394, found 507.3387.

8. Mechanistic Investigations

8.1 Studies of Radicals with Varied *s* Character

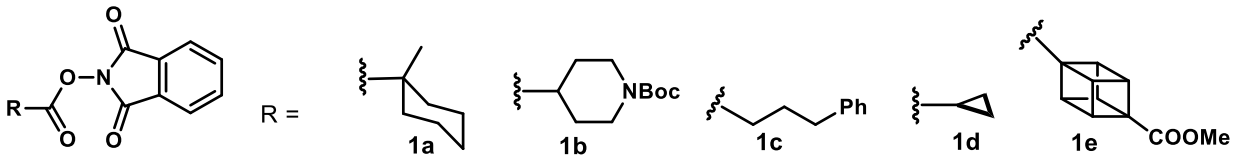
8.1.1 Competition Experiments of Radicals with B_2pin_2



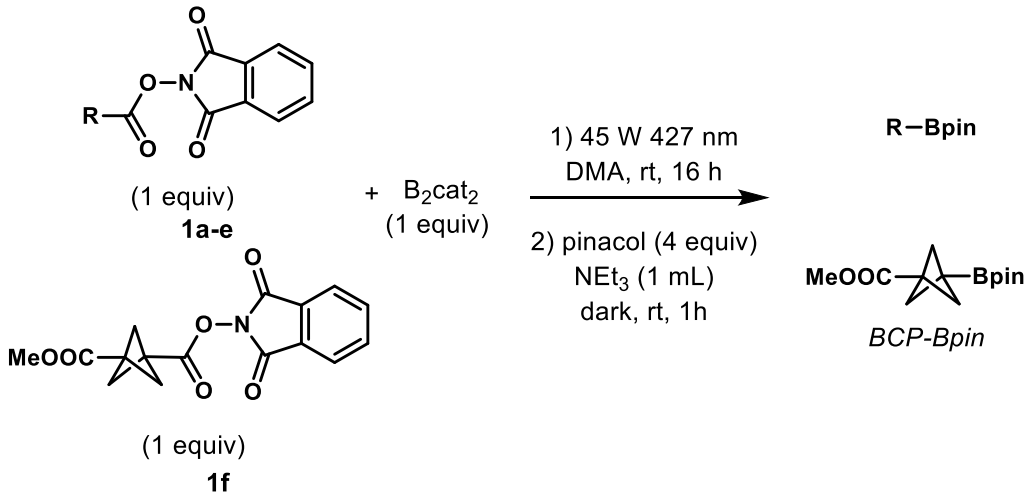
To a 4 mL reaction vial equipped with a stirrer bar was added RAE (**1a/b/c/d/e**) (0.1 mmol, 1 equiv), RAE **1f** (25.4 mg, 0.1 mmol, 1 equiv) and dry B_2pin_2 (25.4 mg, 0.1 mmol, 1 equiv). The reaction vessel was sealed with a cap containing a TFE-lined silicone septum and then was evacuated and backfilled with argon three times. When done, degassed DMA (1 mL, 0.1 M) was added, and then the vial was quickly sealed with Parafilm®. The reaction mixture was then irradiated under vigorous stirring at one 52 W 390 nm using a Kessil lamp at 1 inch distance for 16 h. Room temperature was maintained by the use of two fans. After 16 h, the mixture was partitioned between Et_2O (10 mL) and satd aq NH_4Cl (10 mL). The organic layer was washed two more times with brine (10 mL × 2), dried ($MgSO_4$), filtered, and further dried under vacuum. The yield of each product as well as the remaining starting materials (RSM) was determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard.

Table S5. Competition Experiment Data with B_2pin_2

	R-Bpin/%	RSM **1a**/%	BCP-Bpin/%	RSM **1f**/%
RAE **1a**	0	46.5	30.5	3.5
RAE **1b**	0	67.5	24.3	10.5
RAE **1c**	11.3	21.8	35.5	4.3
RAE **1d**	22.5	0	22.2	2.8
RAE **1e**	50.8	12.8	20.0	9.8



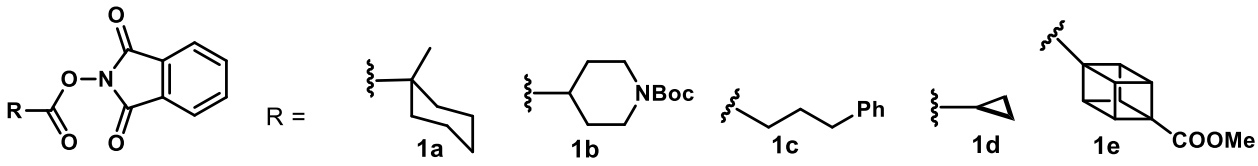
8.1.2 Competition Experiments of Radicals with B_2cat_2



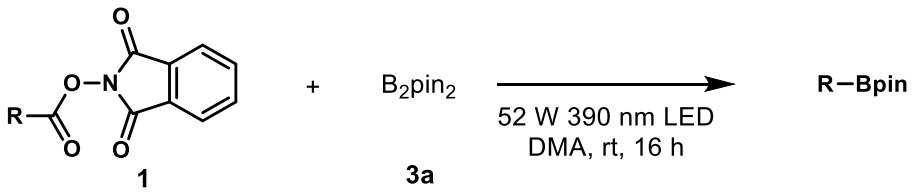
To a 4 mL reaction vial equipped with a stirrer bar was added RAE (**1a/b/c/d/e**) (0.1 mmol, 1 equiv), RAE **1f** (25.4 mg, 0.1 mmol, 1 equiv) and dry B_2cat_2 (23.8 mg, 0.1 mmol, 1 equiv). The reaction vessel was sealed with a cap containing a TFE-lined silicone septum and then was evacuated and backfilled with argon three times. When done, degassed DMA (1 mL, 0.1 M) was added, and then the vial was quickly sealed with Parafilm®. The reaction mixture was then irradiated under vigorous stirring at one 45 W 427 nm using a Kessil lamp at 1 inch distance for 16 h. Room temperature was maintained by the use of two fans. After 16 h, the mixture was added pinacol (47.2 mg, 0.4 mmol, 4 equiv) and NEt_3 (1 mL). The mixture was allowed to stir under dark for 1 h. It was then partitioned between Et_2O (10 mL) and satd aq NH_4Cl (10 mL). The organic layer was washed two more times with brine (10 mL × 2), dried ($MgSO_4$), filtered, and further dried under vacuum. The yield of each product as well as the remaining starting materials (RSM) was determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard.

Table S6. Competition Experiment Data with B_2cat_2

	R-Bpin/%	RSM **1a**/%	BCP-Bpin/%	RSM **1f**/%
RAE **1a**	0	0	19.8	1.5
RAE **1b**	0	9.0	34.5	0.5
RAE **1c**	7.0	8.3	20.0	1.3
RAE **1d**	7.5	0	4.0	1.8
RAE **1e**	34.0	4.0	18.3	1.5



8.1.3 Reactivity of Radicals with B_2pin_2



To a 4 mL reaction vial equipped with a stirrer bar was added RAE **1** (0.1 mmol, 1 equiv) followed by dry B_2pin_2 (76.1 mg, 0.3 mmol, 3 equiv). The reaction vessel was sealed with a cap containing a TFE-lined silicone septum and then was evacuated and backfilled with argon three times. When done, degassed DMA (1 mL, 0.1 M) was added, and then the vial was quickly sealed with Parafilm®. The reaction mixture was then irradiated under vigorous stirring at 52 W 390 nm using a Kessil lamp at 1 inch distance for 16 h. Room temperature was maintained by the use of two fans. After 16 h, the mixture was partitioned between Et_2O (10 mL) and satd aq NH_4Cl (10 mL). The organic layer was washed two more times with brine (10 mL × 2), dried ($MgSO_4$), filtered, and further dried under vacuum. The yield was determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard.

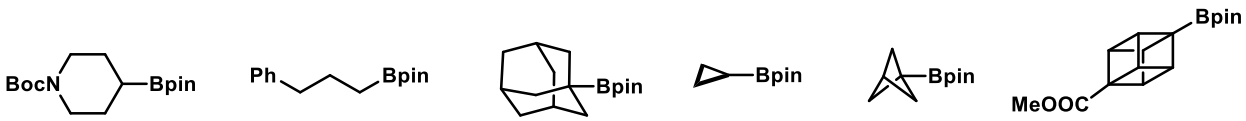


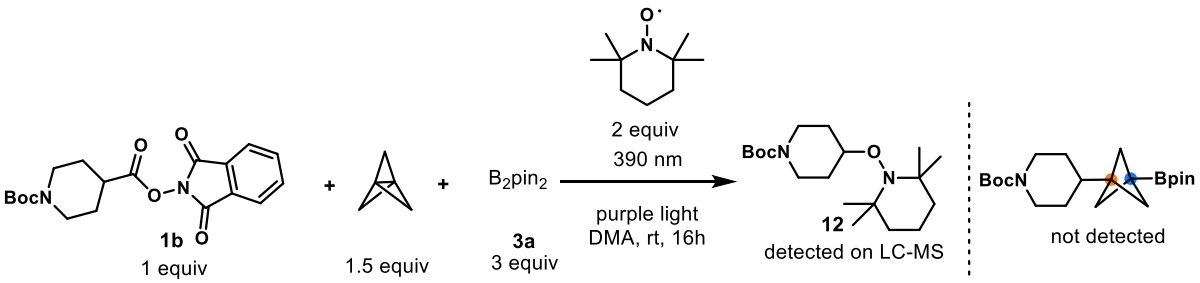
Figure S9. Reactivity studies of radicals bearing different s character with Bpin acceptor

For radicals with little to no angle strain, the reactivity shows a similar trend to that demonstrated in Li's work,[11] with diminished yields mainly due to a difference in solvents. When the angle strain significantly increased, the efficiency of borylation increased by the degree of angle strain. The results here demonstrated that a higher *s* character in the radical center induced by angle strain can lead to more favorable borylation with B_2pin_2.

8.2 TEMPO-trapping Experiments

8.2.1 With RAE:

A TEMPO trapping experiment was carried out using RAE **1b** by following **GP-B**, with the addition of 2 equiv of TEMPO. After 16 h, the reaction was analyzed by LC-MS, and only *N*-Boc-piperidine-TEMPO adduct **12** was found while BCP Bpin **4k** was not present.



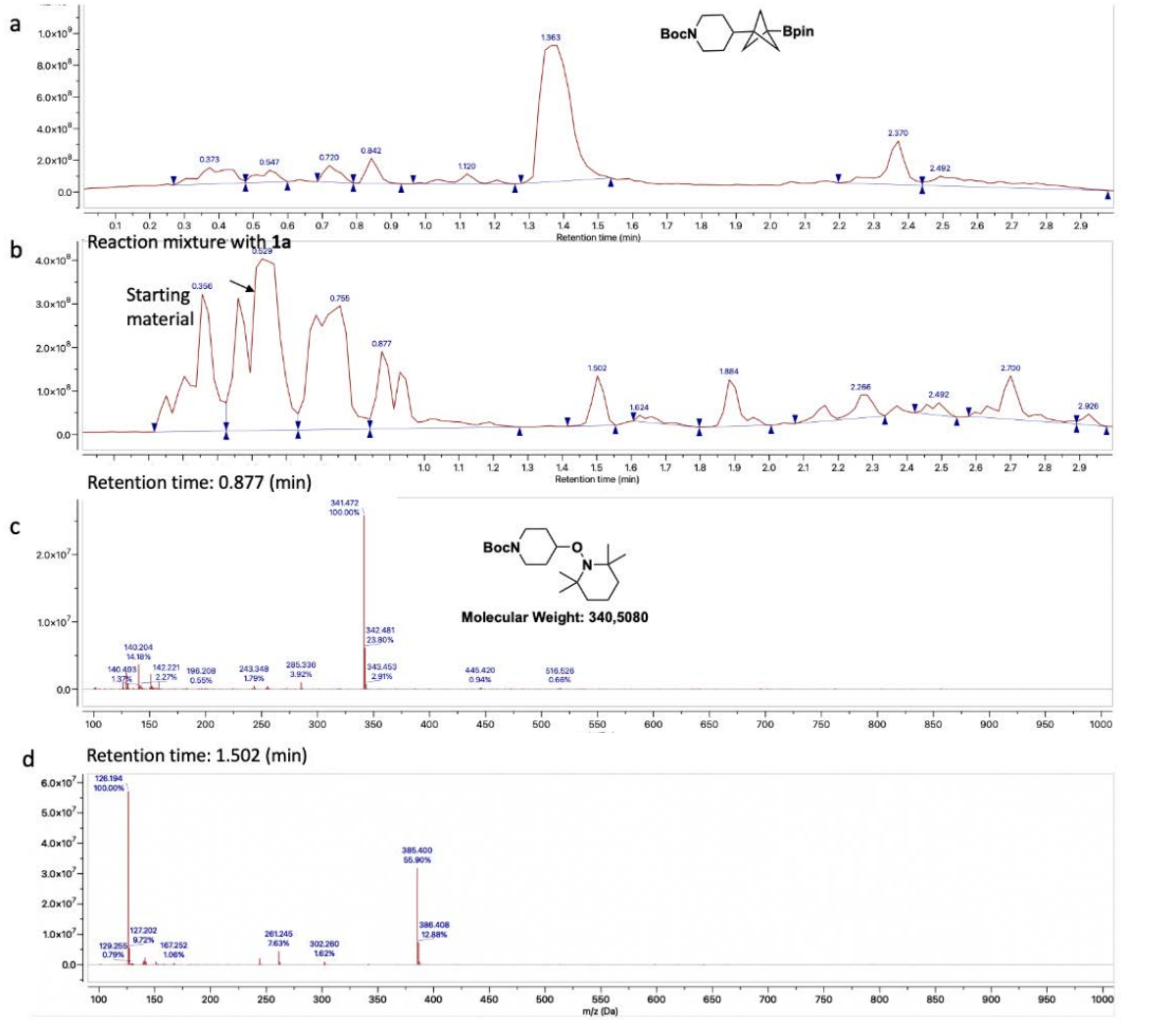
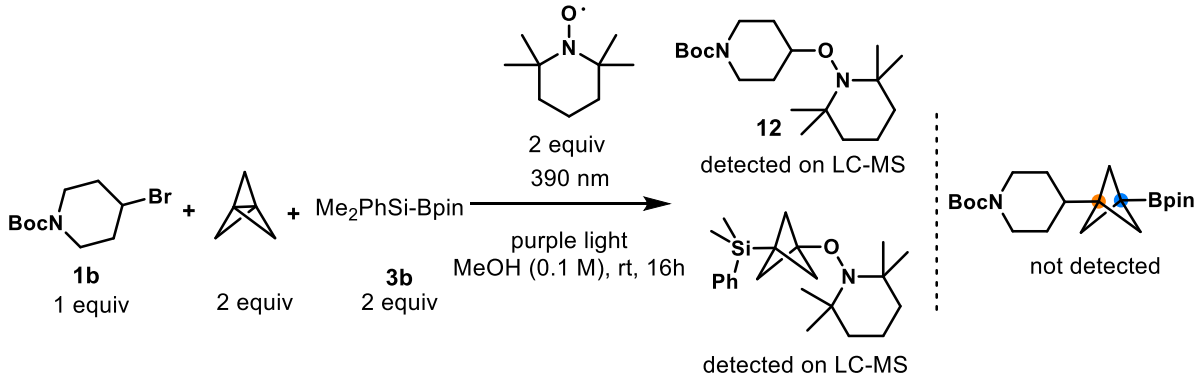


Figure S10. a) MS ES+ TIC spectra of **4k;** b) MS ES+ TIC spectra of the crude mixture with TEMPO showing no formation of product and remaining starting material; c) MS ES+ at 0.877 min, mass detected

341.472, $[M+H]^+$ calculated: 341.516 d) MS ES+ at 1.502 min, the mass does not correspond to the mass of **4k**

8.2.2 With organohalide:

A TEMPO trapping experiment was carried out using RAE **1b** by following **GP-E**, with the addition of 2 equiv of TEMPO. After 16 h, the reaction was analyzed by LC-MS, and only *N*-Boc-piperidine-TEMPO adducts werefound while BCP-Bpin **4k** was not found.



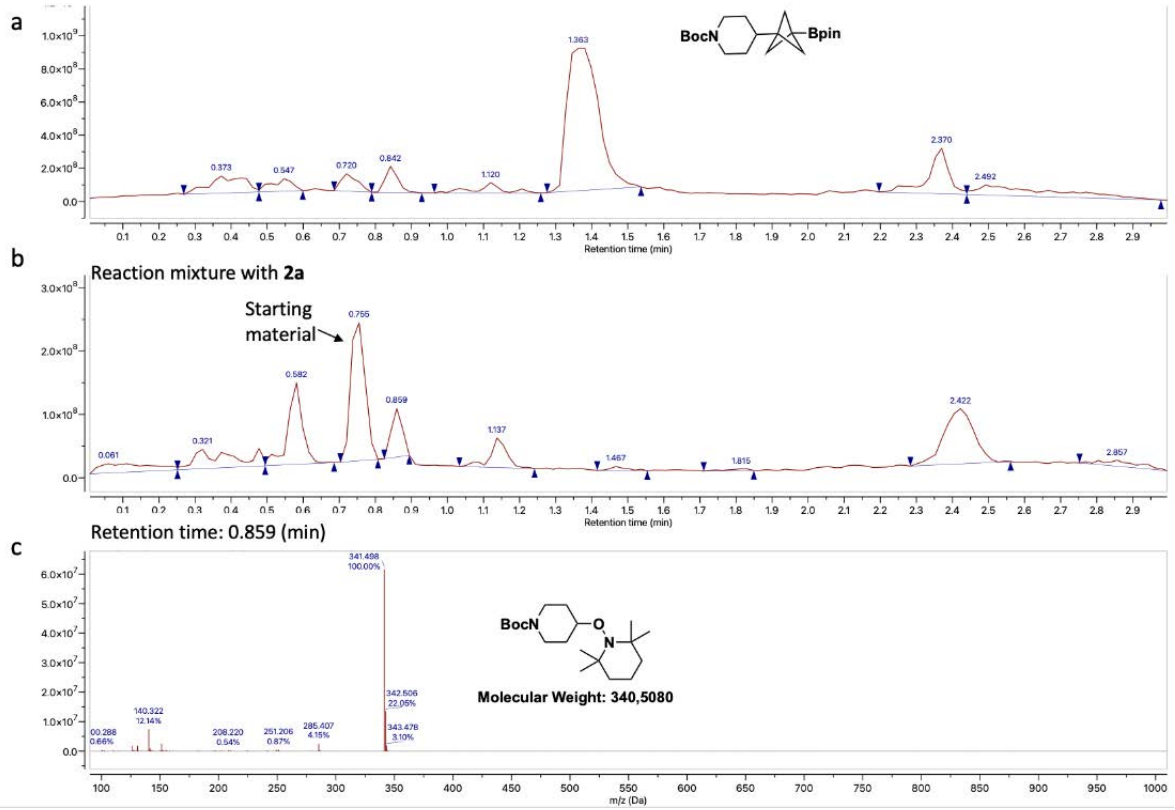


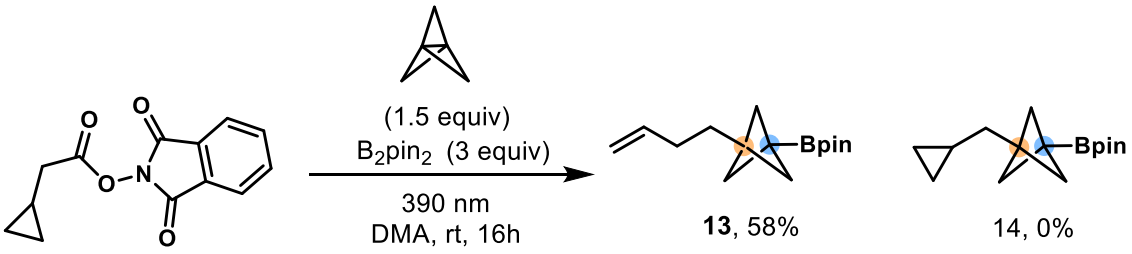
Figure S11. a) MS ES+ TIC spectra of **4j;** b) MS ES+ TIC spectra of the crude mixture with TEMPO showing no formation of product and remaining starting material; c) MS ES+ at 0.859 min, mass detected 341.496, $[M+H]^+$ calculated: 341.516

8.3 Radical Clock Experiments

8.3.1 Radical Clock Experiments with RAE

To study the rate of addition of the alkyl radical to propellane, two redox active ester radical clocks were synthesized from the corresponding carboxylic acids.

Radical ring opening

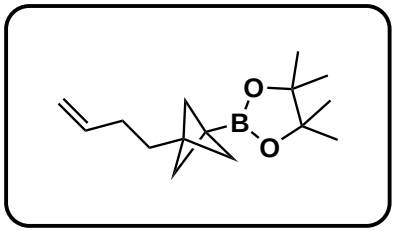


1 equiv

13, 58%

14, 0%

Radical clock experiment with RAE **1i** followed **GP-B**. Only ring-opened product **13** was found.



2-(3-(But-3-en-1-yl)bicyclo[1.1.1]pentan-1-yl)-4,4,5-trimethyl-1,3,2-dioxaborolane (**13**, 43.0 mg, 58%).

Prepared following **GP-B** and purified by column chromatography (10% EtOAc/hexanes). The product was obtained as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.87 – 5.74 (m, 1H), 4.98 (dt, *J* = 17.1, 2.0 Hz, 1H), 4.90 (d, *J* = 10.2 Hz, 1H), 1.98 (q, *J* = 7.4 Hz, 2H), 1.74 (s, 6H), 1.42 (td, *J* = 7.7, 1.5 Hz, 2H), 1.25 – 1.19 (m, 12H).

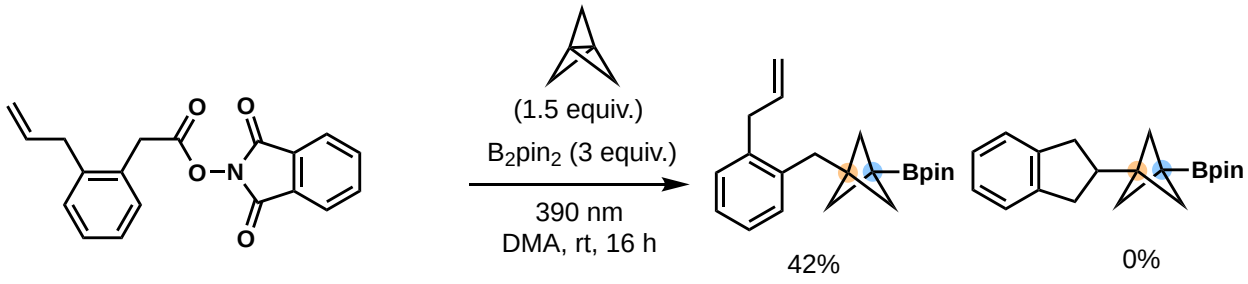
^{13}C NMR (151 MHz, $CDCl_3$) δ 139.3, 114.1, 83.3, 51.6, 46.1, 32.5, 30.6, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.3.

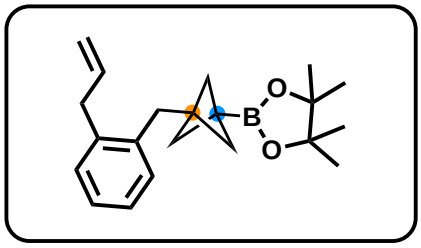
FT-IR (cm^{-1}, neat, ATR) 2977, 2868, 1778, 1475, 1452, 1372, 1328, 1251, 1217, 1167, 1144, 1083, 1009, 981, 952, 925, 851, 697, 673.

HRMS (EI-TOF) calcd for ($C_{14}H_{22}BO_2$) $[M\text{-}CH_3]^+$ 233.1713, found 233.1724.

Radical cyclization



Radical clock experiment with RAE **S-1ag** followed **GP-B**. Only ring-opened product was found.



2-(3-(2-Allylbenzyl)bicyclo[1.1.1]pentan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**S-4a**, 41.0 mg, 42%).

Prepared following **GP-B** and purified by column chromatography (5% EtOAc/hexanes). The product was obtained as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 – 7.09 (m, 3H), 7.03 – 7.00 (m, 1H), 5.93 (ddt, *J* = 16.7, 10.1, 6.4 Hz, 1H), 5.06 – 5.02 (m, 1H), 4.98 (dt, *J* = 17.1, 1.8 Hz, 1H), 3.37 – 3.33 (m, 2H), 2.71 (s, 2H), 1.71 (s, 6H), 1.20 (s, 12H).

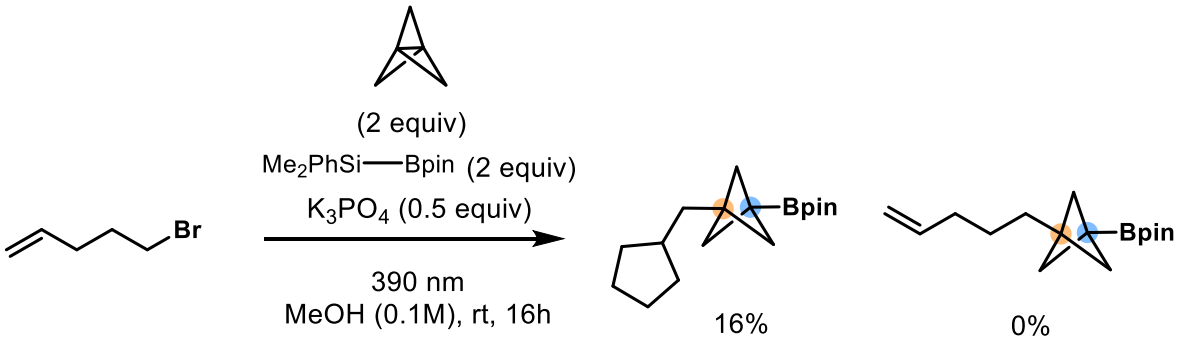
^{13}C NMR (151 MHz, $CDCl_3$) δ 137.8, 137.5, 130.4, 129.4, 126.1, 126.1, 115.7, 83.3, 51.7, 45.9, 37.1, 37.0, 24.8. 1C missing

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.1.

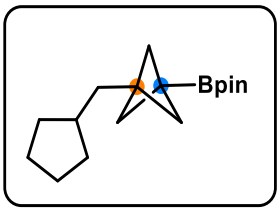
FT-IR (cm^{-1}, neat, ATR) 2972, 2905, 2868, 1475, 1450, 1372, 1328, 1273, 1251, 1216, 1193, 1166, 1144, 1079, 1008, 981, 913, 851, 754, 672.

HRMS (EI-TOF) calcd for ($C_{21}H_{29}BO_2$) $[M]^+$ 324.2261, found 324.2282.

8.3.2 Radical Clock Experiment with Organohalide



Radical clock experiment with the organobromide followed **GP-F**. Only 5-exo-trig cyclized product **15** was found.



2-(3-(Cyclopentylmethyl)bicyclo[1.1.1]pentan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**15**, 14.4 mg, 16%).

Prepared following **GP-F** and purified by column chromatography (5% EtOAc/hexanes). The product was obtained as a clear oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 – 1.70 (m, 9H), 1.58 – 1.51 (m, 2H), 1.50 – 1.42 (m, 2H), 1.35 (d, *J* = 5.9 Hz, 2H), 1.23 (s, 12H), 1.09 – 0.96 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 83.3, 52.4, 46.5, 40.2, 37.8, 33.4, 25.5, 24.9.

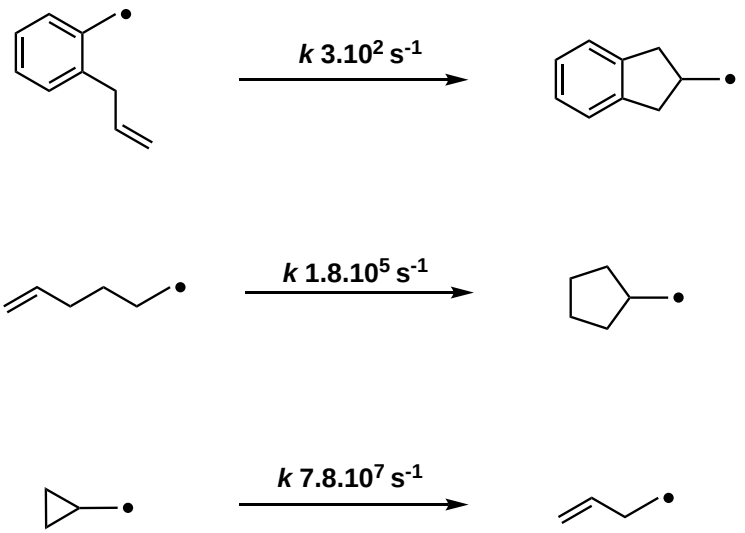
^{11}B NMR (128 MHz, $CDCl_3$) δ 30.3.

FT-IR (cm^{-1}, neat, ATR) 2954, 2904, 2866, 1511, 1435, 1405, 1390, 1379, 1371, 1345, 1307, 1275, 1197, 1166, 1145, 1111, 1033, 960, 856, 666.

HRMS (EI-TOF) calcd for ($C_{17}H_{26}BO_2$) $[M\text{-}CH_3]^+$ 261.2026, found 261.2005.

Comments:

These experiments, along with the 5-exo-trig cyclization result of **4ad**, gave us useful information about the rate of addition of alkyl radical to [1.1.1]propellane.



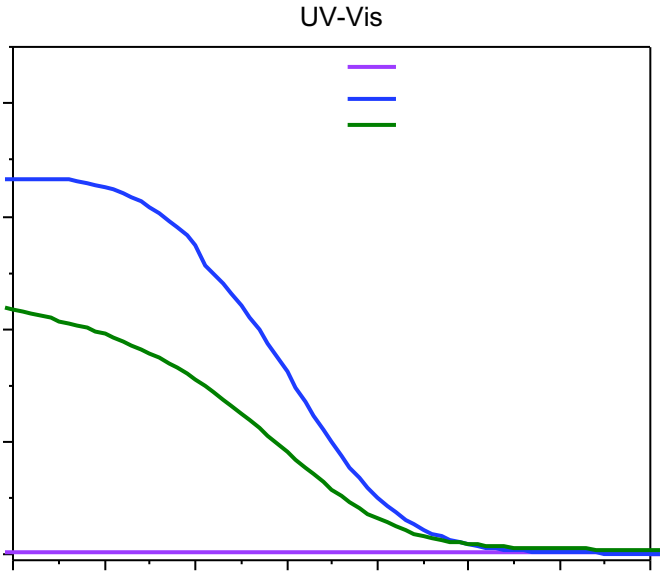
Scheme S1. Values for the radical clock used in our experiments[30]

Given the above values (Scheme S1), the bimolecular process of radical addition onto [1.1.1]propellane appears to be faster than the unimolecular cyclization of the benzylic radical but slower than the cyclization of the hexenyl radical and ring-opening of cyclopropylmethyl radical. The addition to [1.1.1]propellane is comparable to radical additions to substituted alkenes at room temperature.

8.4 UV-vis Studies

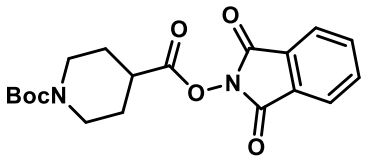
UV/vis Absorption spectra were measured in a 1 cm quartz cuvette using a JASCO-V-650 spectrophotometer. Absorption spectra of individual reaction components and mixtures thereof were recorded at 20 °C in the range of 300-700 nm [temperature controlled by a Peltier (Koolance liquid cooling system)].

8.4.1 For the RAEs:

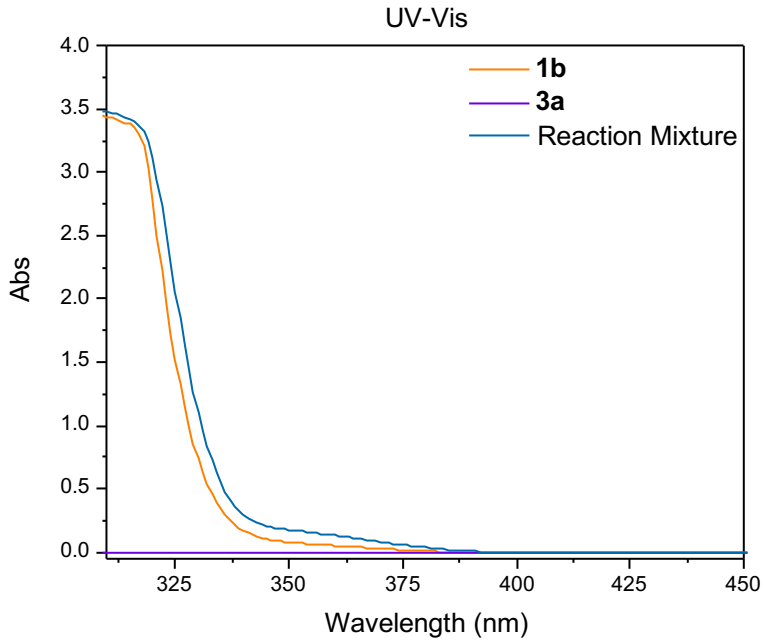


The stock solutions were prepared as following:

- 0.1 M RAE **1b** in DMA/Et_2O (10:1) mixture
- 0.3 M B_2pin_2 **3a** in DMA/Et_2O (10:1) mixture
- Solution of **1b** (0.1 M) and **3a** (0.3 M) in DMA/Et_2O (10:1) mixture

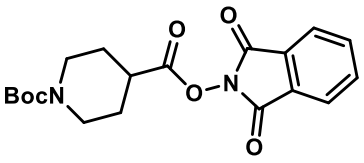


1b

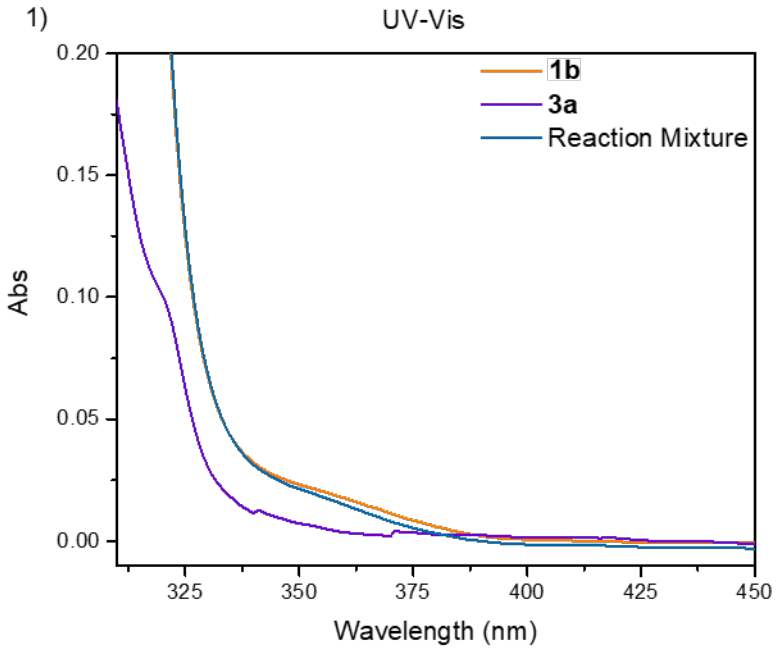


The stock solutions were prepared as following:

- 0.01 M RAE **1b** in DMA/Et_2O (10:1) mixture
- 0.03 M B_2pin_2 **3a** in DMA/Et_2O (10:1) mixture
- Solution of **1a** (0.01 M) and **3a** (0.03 M) in DMA/Et_2O (10:1) mixture



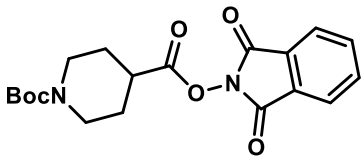
1b



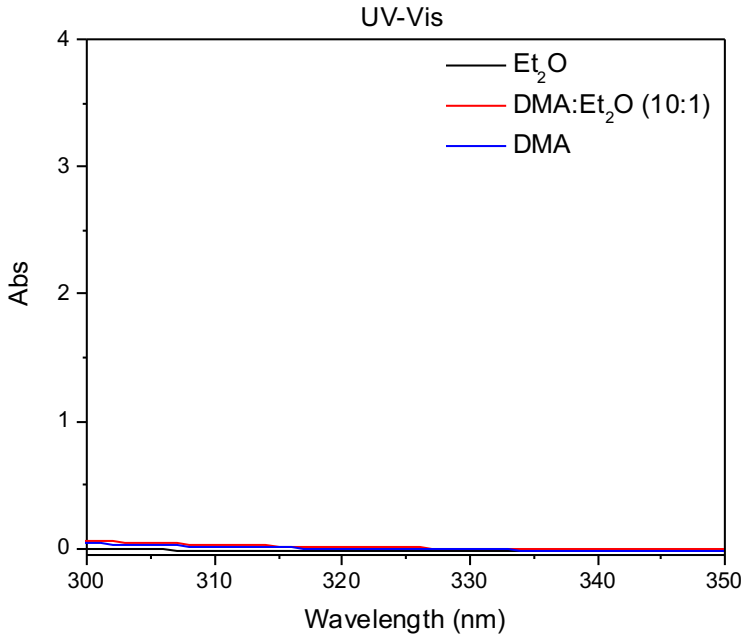
The stock solutions were prepared as following:

- 0.001 M RAE **1b** in DMA/Et_2O (10:1) mixture
- 0.003 M B_2pin_2 **3a** in DMA/Et_2O (10:1) mixture
- Solution of **1a** (0.001 M) and **3a** (0.003 M) in DMA/Et_2O (10:1) mixture

*Due to the high molar absorptivity of RAE **1b**, all experiments used diluted solutions to avoid saturation of UV-vis signals.



1b

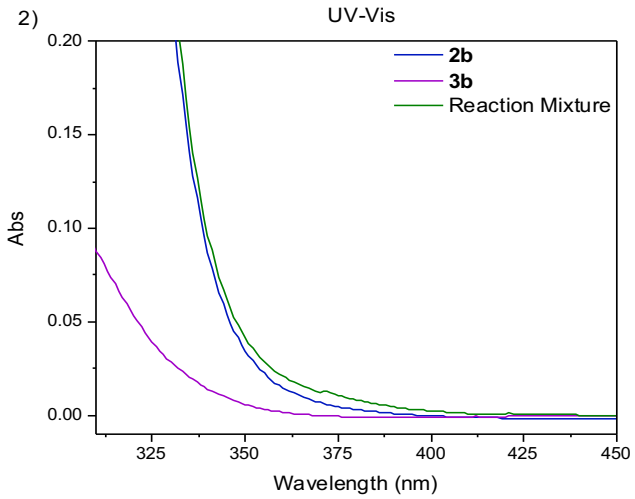


The stock solutions were prepared as following:

- Pure Et_2O
- 10:1 DMA:Et_2O
- Pure DMA

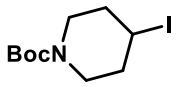
The solvents show no noticeable absorption comparing with the absorption of the reaction mixture.

8.4.2 For the alkyl halides:



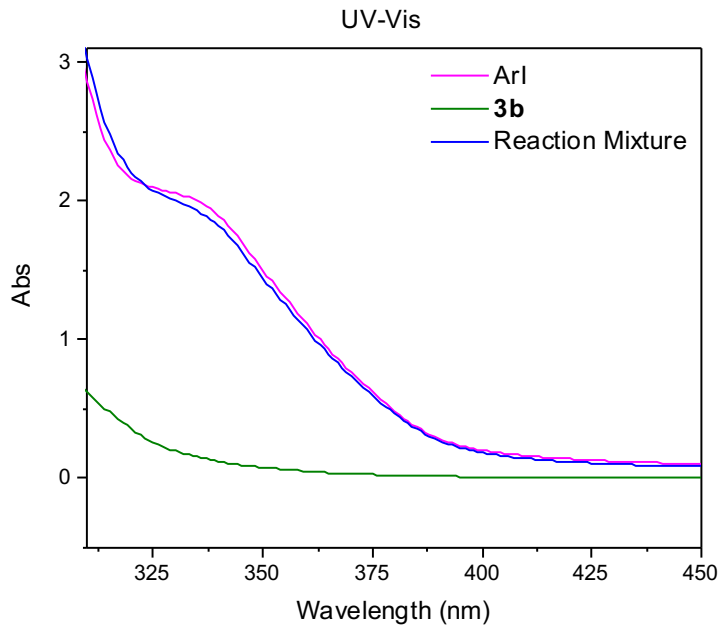
The stock solutions were prepared as following:

- 0.1 M **2b** in MeOH/Et_2O (10:1) mixture
- 0.2 M Me_2PhSiBpin **3b** in MeOH/Et_2O (10:1) mixture
- Solution of **2b** (0.1 M) and **3b** (0.2 M) in MeOH/Et_2O (10:1) mixture



2b

8.4.3 For the aryl halides:

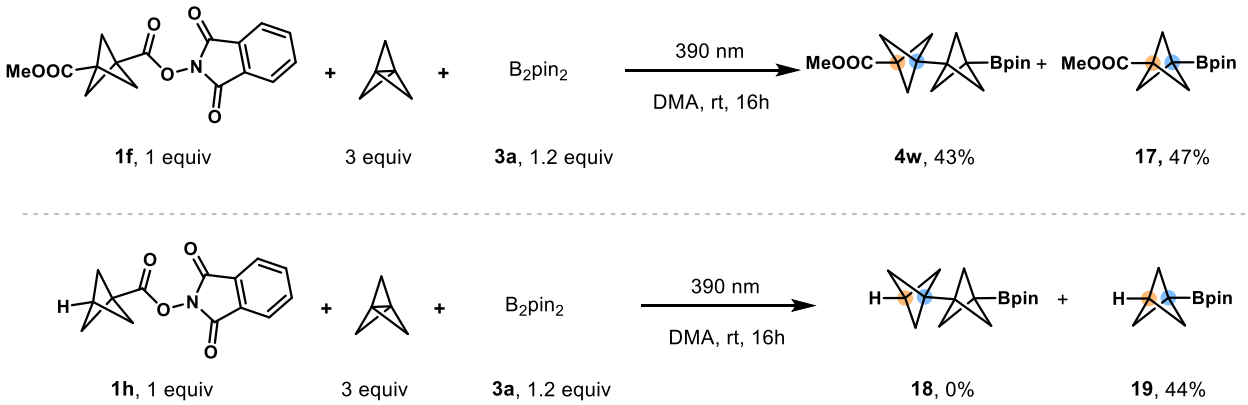


- 1 M 4-iodobenzonitrile (ArI) in MeOH/Et_2O (10:1) mixture
- 2 M $PhMe_2SiBpin$ **3b** in MeOH/Et_2O (10:1) mixture
- Solution of 4-iodobenzonitrile (ArI) (1 M) and **3b** (2 M) in MeOH/Et_2O (10:1) mixture

*Et_2O were added to maintain the dielectric constant of the reaction mixtures.

*Because of the low molar absorptivity of the aryl iodide, all experiments used concentrated solutions to obtain better UV-vis signals.

8.5 Influence of Through-space Interactions on Chemoselectivity



To a 4 mL reaction vial equipped with a stirrer bar was added BCP RAE (0.3 mmol, 1 equiv) followed by dry B_2pin_2 (91.4 mg, 0.36 mmol, 1.2 equiv). The reaction vessel was sealed with a cap containing a TFE-lined silicone septum and then was evacuated and backfilled with argon three times. When done, degassed DMA (3 mL, 0.1 M) was added, and [1.1.1]propellane (0.75 mL, 0.9 mmol, 3 equiv, 1.2 M solution in Et_2O) was added quickly. The vial was quickly sealed with Parafilm®. The reaction mixture was then irradiated under vigorous stirring at 52 W 390 nm using a Kessil lamp at 1 inch distance for 16 h. Room temperature was maintained by the use of two fans. After 16 h, the mixture was partitioned between Et_2O (10 mL) and satd aq NH_4Cl (10 mL). The organic layer was washed two more times with brine (10 mL × 2), dried ($MgSO_4$), filtered, and further dried under vacuum. The NMR yields of **17**, **18** and **19** are determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. **4w** was isolated by C18 chromatography.

Note:

1. The stoichiometry of [1.1.1]propellane and B_2pin_2 were modified to increase the yield of **4w**.
2. In ^1H NMR, only [1.1.1]propellane monomer and dimer [2]staffane were observed.

Results show that the electronic properties of substituents on the BCP radicals have a profound impact on the chemoselectivity of BCP radical borylation vs. oligomerization. In both cases, only monomer and dimer were observed, with no other oligomer noticeable by ^1H NMR. We reason that the C_1 substituent on the BCP radical affects the C_1-C_3 distance,[31] which ultimately affects the electrophilicity through transannular effect and the geometry and hybridization of the BCP radical. Further investigations are necessary to elucidate the reason behind this observation. We hypothesize that when C_1 is an electron-withdrawing group, the BCP radical is more electrophilic by the transannular interaction and we think the increased electrophilicity in BCP radical leads to favorable addition to the electron-rich [1.1.1]propellane. Once the [2]staffanyl radical is formed, the electron-withdrawing group has less influence on the radical because of the elongated distance, and [2]staffanyl radical would not tend to add to another [1.1.1]propellane but forms [2]staffanyl Bpin as the product.

8.6 Kinetic Studies

Because there is no pre-added Lewis base other than solvent DMA when use B_2pin_2 **3a** as boron reagent, the species serving as a Lewis base in the reaction mixture was uncertain at first. In control experiments (Table S1.), we have shown that DMA-boryl radical is not an on-cycle species because non-amide type solvents also give product formation, and the reaction cannot be carried out under thermal conditions. We propose that the phthalimide anion, derived from the reaction by-product, is the Lewis base promoting the reaction. Kinetic studies on the effect of phthalimide anion were conducted:

Procedure:

To a 4 mL reaction vial equipped with a stirrer bar was added RAE **1b** (37.4 mg, 0.1 mmol, 1.0 equiv), B_2pin_2 **3a** (76.2 mg, 0.3 mmol, 3 equiv), and potassium phthalimide (KPhth). The reaction vessel was sealed with a cap containing a TFE-lined silicone septum and then was evacuated and backfilled with argon three times. Once done, dry DMA (1 mL) was added, followed by [1.1.1]propellane (0.15 mmol, 1.5 equiv). The vessel was sealed with Parafilm® and placed in a sonicator for 1 min to make a suspension. It was then irradiated with a 52 W 390 nm LED for specific amounts of time at a distance of ~2 cm. The reaction was maintained at room temperature via two fans. Once done, the vessel was removed from the light source, and the NMR internal standard 1,3,5-trimethoxybenzene (0.05 mmol, 8.4 mg) was added. The reaction mixture was poured into 10 mL of satd aq NH_4Cl. The aq phase was extracted with Et_2O (2 x 5 mL) and the combined organic layers were dried by a plug of Na_2SO_4. The dried organic solution was concentrated under reduced pressure, and the yield of product is determined by ^1H NMR against 1,3,5-trimethoxybenzene. Each data point represents the average of two parallel runs.

Table S7. Data of initial product formation over time

KPhth/mol% / time/min / yield/%	0	5	10	20
5	0			
10	1	9	25	31
20	4			
25	12			
30	20	35	49	67

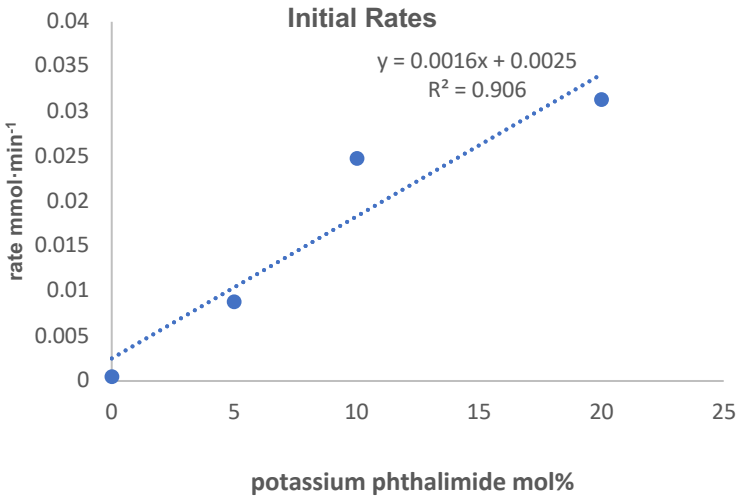


Figure S12. Plot of initial rates vs. the amount of potassium phthalimide indicates the participation of phthalimide in this multi-component borylation

Results:

Initial rates are calculated based on < 30% product formation. Linear regression shows that the initial rates have a positive correlation with the amount of phthalimide anion in the reaction mixture. Because the rate enhancement by the phthalimide anion is very significant, we propose that phthalimide anion, which can exist in equilibrium with adventitious water, can serve as the Lewis base to stabilize boryl radical and sustain the chain propagation.

8.7 ^{11}B NMR Studies

^{11}B NMR studies with B_2pin_2 (0.1 M) suggest that there is no noticeable interaction between B_2pin_2 and DMA (Figure S13i), because the ^{11}B signal is identical to the control (Figure S13ii). Adding RAE **1b** (0.1 M), which makes a 1:1 ratio of B_2pin_2 **3a** and **1b** in DMA, also did not lead to a noticeable change in the ^{11}B NMR signal (Figure S13iii). This suggests that under the reaction conditions, there is no interaction between B_2pin_2 and **1b**, which confirms the UV-Vis studies that there is no EDA complex formation between B_2pin_2 and **1b**. To confirm our proposed idea that the phthalimide anion could serve as a base to form ate complex with B_2pin_2, a 0.1 M B_2pin_2 solution in DMA with 10 mol% of potassium phthalimide was prepared, and a sharp peak was found at 6.9 ppm with slight peak broadening at ~35 ppm (Figure S13iv), suggesting the formation of phthalimide- B_2pin_2 ate complex.

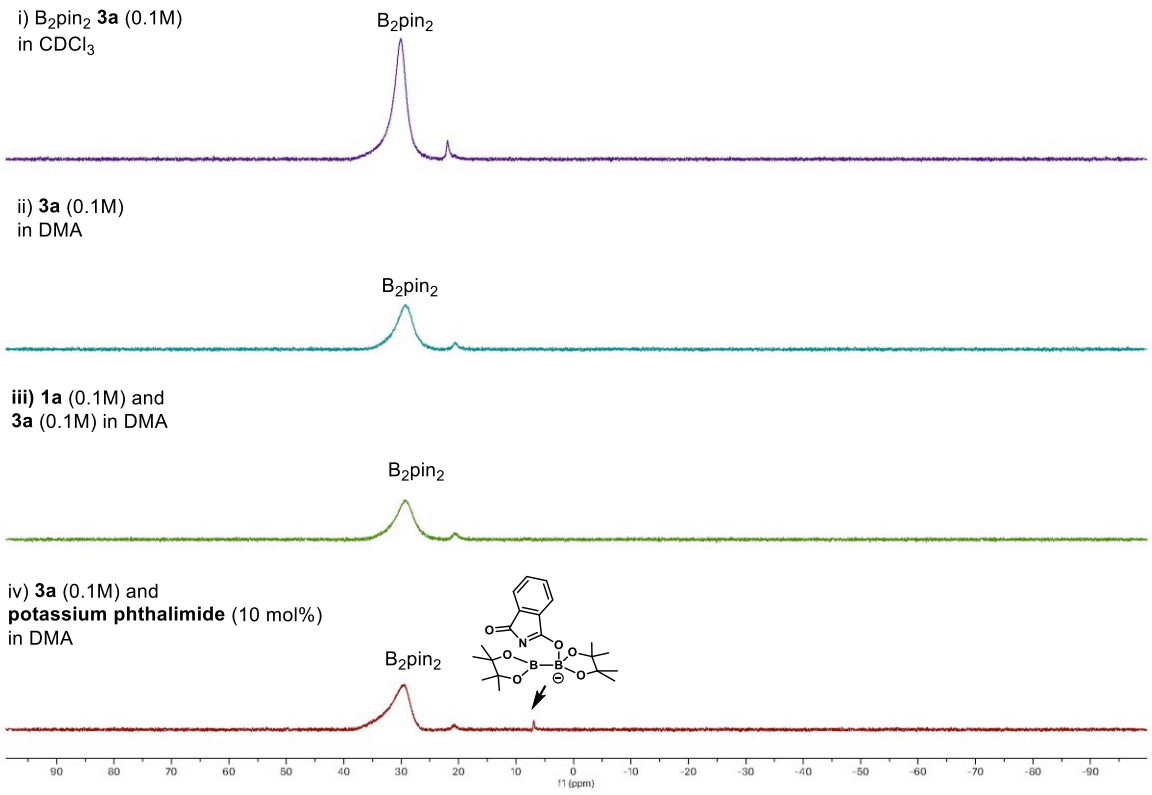


Figure S13. ^{11}B NMR data with RAE and B_2pin_2

*The small sharp peaks at ~20 ppm are assigned to HO-Bpin, which is probably formed by air oxidation of B_2pin_2 during sample preparations since the peaks are in all cases.

*For ii, iii and iv, 10% of $CDCl_3$ was added for lock and shim.

^{11}B NMR studies with $Me_2PhSiBpin$ **3b** (0.1 M) give a similar result. There is no noticeable interaction between **3b** and MeOH (Figure S14i) because the ^{11}B signal is identical to the control (Figure S14ii). Addition of alkyl iodide **2b** does not lead to a change in ^{11}B NMR signal (Figure S14iii). This suggests that under the reaction condition, there is no interaction between **3b** and

2b, which confirms the UV-Vis studies that there is no EDA complex formation between **3b** and **2b**. Lastly, adding 100 mol % of K_3PO_4 to 0.1 M **3b** in MeOH (0.1 M) results in a change in the ^{11}B NMR signal by forming sharp peaks at 4.9 ppm and 2.4 ppm (Figure S14iv). This is indicative of ate complexes of **3b**. The two peaks are likely to be K_3PO_4-**3b** and MeOK-**3b** (small amount of methoxides are from deprotonation of MeOH by K_3PO_4). Because control studies suggest the ate complex cannot reduce organohalides in the reaction (Table S3), these ate-complexes are likely to be off-cycle species.

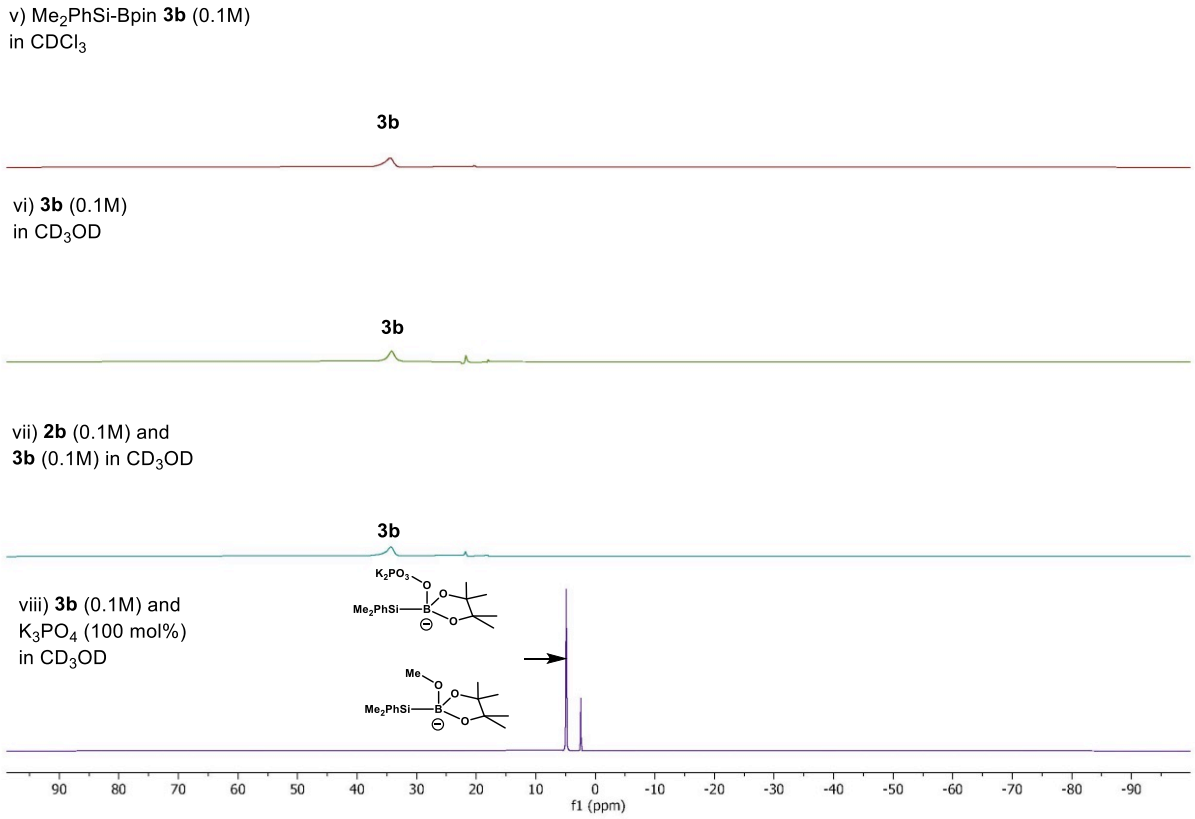


Figure S14. ^{11}B NMR data with organohalide and boronate **3b**

*The small sharp peaks at ~20 ppm are assigned to HO-Bpin, which is probably formed by air oxidation of B_2pin_2 during sample preparations because the peaks are in all samples.

8.8 Determinations of Quantum Yields

Photon flux measurement:

We determined the photon flux of a 52 W PR160 390nm Kessil lamp by standard ferrioxalate actinometry following a procedure reported in the literature[32]:

- 0.15 M ferrioxalate solution: dissolving 1.811 g of potassium ferrioxalate trihydrate in 0.05 M H_2SO_4 by using a 25.0 mL volumetric flask. During the preparation, the flask was protected from light using aluminum foil, and the solution was stored in the dark.
- Buffer solution: dissolving 28.5 mg phenanthroline hydrate and 5.855 g of sodium acetate in 0.5 M H_2SO_4 by using a 25.0 mL volumetric flask.

Determination of the absorbance of the irradiated solution:

A vial containing 3 mL of the ferrioxalate solution was irradiated by a 52 W 390 nm Kessil LED for 60 seconds at 1 inch distance. After, 1 mL of this solution was taken to a vial covered with aluminum foil containing 1 mL of the buffer solution and 4 mL of distilled water. The mixture was stirred in the dark for 1 h to allow complexation. The absorbance of the solution was measured at 510 nm.

Determination of the absorbance of the non-irradiated solution:

In a vial protected from light covered with aluminum foil was added 1 mL of the ferrioxalate solution, 1 mL of the buffer solution, and 4 mL of H_2O. The mixture was stirred in the dark for 1 h. The absorbance of the solution was measured at 510 nm.

Absorbance curves

To ensure reproducibility, the experiment has was carried out in quadruplicate.

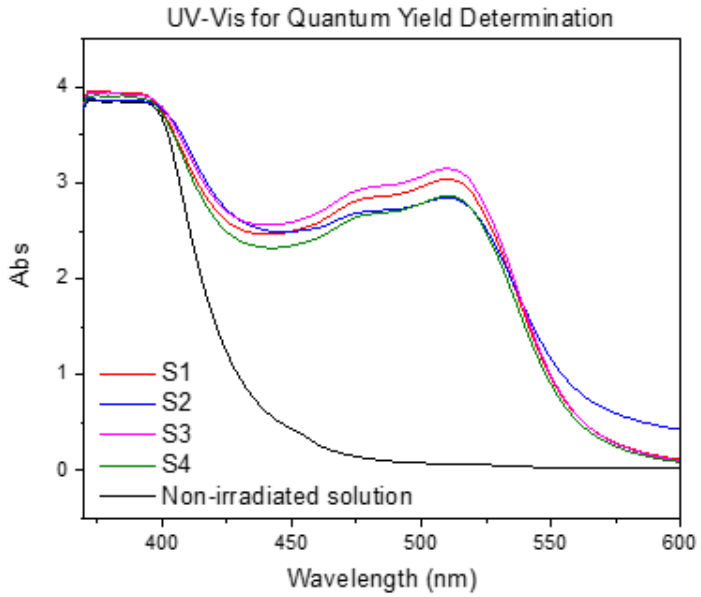


Figure S15. Absorbance curves of the 4 irradiated solution and of the non-irradiated solution

Photon flux determination

$$mol\ (Fe^{2+}) = \frac{V \times \Delta A}{l \times \varepsilon} = \frac{0.006L \times 3 \times 2.91}{1cm \times 11000L \times mol^{-1} \times cm^{-1}} = 4.76 \times 10^{-6}\ mol$$

$$Photon\ flux = \frac{mol\ (Fe^{2+})}{\phi \times t \times f} = \frac{4.76 \times 10^{-6}\ mol}{1.13 \times 60s \times 1} = 7.02 \times 10^{-8}\ einstein\ s^{-1}$$

V is the total volume of the solution; l is the path length (1 cm); ΔA the difference of absorbance between the irradiated sample and non-irradiated sample at 510 nm; ε the molar absorptivity at 510 nm ($11000L \times mol^{-1} \times cm^{-1}$); ϕ is the quantum yield of the ferrioxalate actinometer at 390 nm (ϕ = 1.13); t is the time of irradiation and f = 1 – 10^{-Abs} is the fraction of light absorbed at 390 nm (~1 since abs > 3.5).

Quantum yield of the reactions

The quantum yields of the reaction were determined using the following equation:

$$\phi = \frac{mol\ product}{photon\ flux \times t \times f}$$

Determination of the reaction quantum yield with RAE 1b:

To a 4 mL reaction vial equipped with a stirrer bar was added RAE (95 mg, 0.255 mmol, 1 equiv) followed by dry B_2pin_2 (194 mg, 0.765 mmol, 3 equiv). The reaction vessel was sealed with a cap containing a TFE-lined silicone septum and then was evacuated and backfilled with argon three times. When done, degassed DMA (2.5 mL) was added. Next, freshly prepared and titrated [1.1.1]propellane (425 μL, 0.383 mmol, 1.5 equiv, 0.9 M solution in Et_2O) was then added, and the vial was quickly sealed with Parafilm®. The reaction mixture was then irradiated under vigorous stirring at 52 W 390 nm using the same Kessil lamp for photon flux measurement at 1 inch distance for specific time. Room temperature was maintained by the use of two fans. When the desired reaction time was reached, 1,3,5-trimethoxybenzene was added to the reaction mixture as the internal standard. The mixture was then partitioned between Et_2O (10 mL) and satd aq NH_4Cl (10 mL). The organic layer was dried ($MgSO_4$), filtered, and further dried under vacuum. The product yield was determined by ^1H NMR usinge 1,3,5-trimethoxybenzene as an internal standard. Each time point was run in triplicate.

* Quantum yield Φ is calculated based on conversion from 20 – 30 min as there is an induction period in the first 20 min.

For RAE **1b**, the abs of the reaction mixture is 0.36, so f is calculated as the following:

$$f = 1 - 10^{-Abs} = 0.56$$

$$\phi = \frac{mol\ product}{photon\ flux \times t \times f} = \frac{0.000255mol \times 0.169\ (yield)}{7.02 \times 10^{-8} einstein\ s^{-1} \times 600s \times 0.56} = 1.82$$

Determination of the reaction quantum yield with an aryl iodide:

To a 4 mL reaction vial equipped with a stirrer bar was added 4-iodobenzonitrile (45.8 mg, 0.2 mmol, 1 equiv) followed by K_3PO_4 (21.2 mg, 0.1 mmol, 0.5 equiv) and Me_2PhSi-Bpin (104.9 mg, 0.4 mmol, 2 equiv). The reaction vessel was sealed with a cap containing a TFE-lined silicone septum and then was evacuated and backfilled with argon three times. When done, degassed MeOH (2 mL) was added. Next, freshly prepared and titrated [1.1.1]propellane (1.0 mL, 0.6 mmol, 3 equiv, 0.6 M solution in Et_2O) was then added, and the vial was quickly sealed with Parafilm®. The reaction mixture was then irradiated under vigorous stirring at 52 W 390 nm LED using the same Kessil lamp for photon flux measurement at 1 inch distance for specific time. Room temperature was maintained by the use of two fans. When the desired reaction time was reached, 1,3,5-trimethoxybenzene was added to the reaction mixture as the internal standard. The mixture was then passed through a plug of Celite® and concentrated under reduced pressure. The product yield was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. Each time point was run in triplicate.

* Quantum yield Φ is calculated based on conversion from the first 30 min.

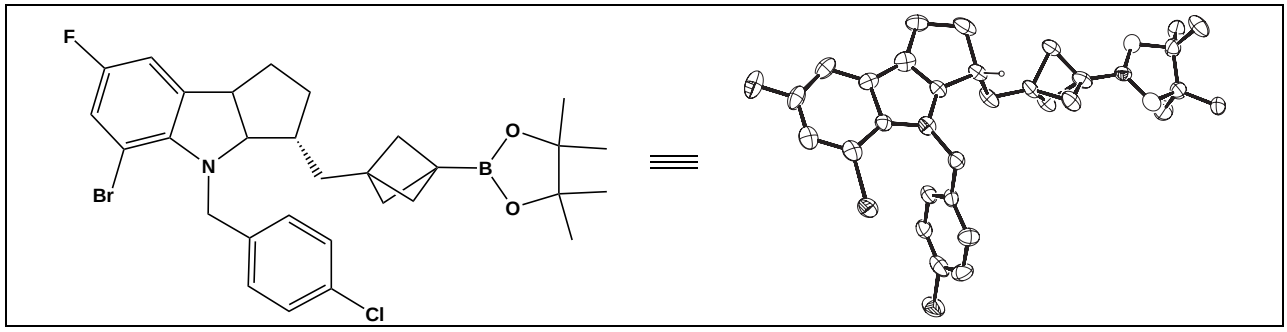
For 4-iodobenzonitrile, the abs of the reaction mixture is 0.0276, so f is calculated as the following:

$$f = 1 - 10^{-Abs} = 0.0615$$

$$\phi = \frac{mol\ product}{photon\ flux \times t \times f} = \frac{0.000200mol \times 0.343\ (yield)}{7.02 \times 10^{-8} einstein\ s^{-1} \times 1800s \times 0.0615} = 8.83$$

9. X-ray Structure Determination of Compound 4ar

A crystal of **4ar** suitable for X-ray diffraction was obtained as following: 30 mg of **4ar** were solubilized in 1 mL of chloroform in a 20 mL scintillation vial and the solution was allowed to slowly evaporate at 25 °C for 2 days.



Compound **4ar**, $C_{30}H_{33}BBrClFNO_2$, crystallizes in the triclinic space group P1 with a=9.4324(3)Å, b=13.5284(4)Å, c=23.6555(4)Å, α=97.609(2)°, β=91.972(2)°, γ=110.314(3)°, V=2795.39(14)Å^3, Z=4, and d_{calc}=1.389 g/cm^3. X-ray intensity data were collected on a Rigaku XtaLAB Synergy-S diffractometer[33] equipped with an HPC area detector (HyPix-6000HE) and employing confocal multilayer optic-monochromated Cu-Kα radiation (λ=1.54184 Å) at a temperature of 100K. Preliminary indexing was performed from a series of sixty 0.5° rotation frames with exposures of 0.25 seconds for θ = ±47.291° and 1 second for θ = 107.75°. A total of 14936 frames (127 runs) were collected employing ω scans with a crystal to detector distance of 40.0 mm, rotation widths of 0.5° and exposures of 1 second for θ = ±42.644°, 42°, 46°, 54°, 58°, 62°, and -66° and 3 seconds for θ = -70°, -74°, -78°, -82°, -86°, -90°, and 111.75°.

The crystal grew as a non-merohedral twin. The Ewald Explorer extension in CrysAlisPro[34] was used to index the diffraction images and to determine the twinning mechanism. The crystal was twinned by a rotation of 180° about the 100 real direction. Rotation frames were integrated using CrysAlisPro[34], producing a listing of unaveraged F^2 and σ(F^2) values. A total of 120127 reflections were measured over the ranges 7.052 ≤ 2θ ≤ 136.77°, -11 ≤ h ≤ 11, -16 ≤ k ≤ 16, -28 ≤ l ≤ 28 yielding 33731 unique reflections (R_{int} = 0.099). The intensity data were corrected for Lorentz and polarization effects and for absorption using SCALE3 ABSPACK[35] (minimum and maximum transmission 0.7621, 1.0000). The structure was solved ƒby direct methods - SHELXT[36]. The asymmetric unit consists of four molecules of the title compound. Refinement was by full-matrix least squares based on F^2 using SHELXL[37]. All reflections were used during refinement. The weighting scheme used was $w=1/[\sigma^2(F_o^2)+ (0.1862P)^2 + 4.1814P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0906 and wR2=0.2510 for 30822 observed reflections for which F > 4σ(F) and R1=0.0993 and wR2=0.2709 and GOF =1.039 for all 33731 unique, non-zero reflections and 1425 variables. The maximum Δ/σ in the final cycle of least squares was 0.004 and the two most prominent peaks in the final difference Fourier were +1.97 and -0.97 e/Å^3. The twinning parameter refined to a value of 0.4209(18).

Table S8 lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in Tables S9 and S10. Anisotropic thermal parameters are in Table S11. Tables S12 and S13 list bond distances and bond angles. Figure S16 is an ORTEP representation of the molecule with 50% probability thermal ellipsoids displayed.

***Author Note on *Alert level B* in the CheckCIF Report:**

PLAT341_ALERT_3_B Low Bond Precision on C-C Bonds ..... 0.02577 Ang.

Author Response: **This alert is generated due to low quality data and the Bpin disorder.**

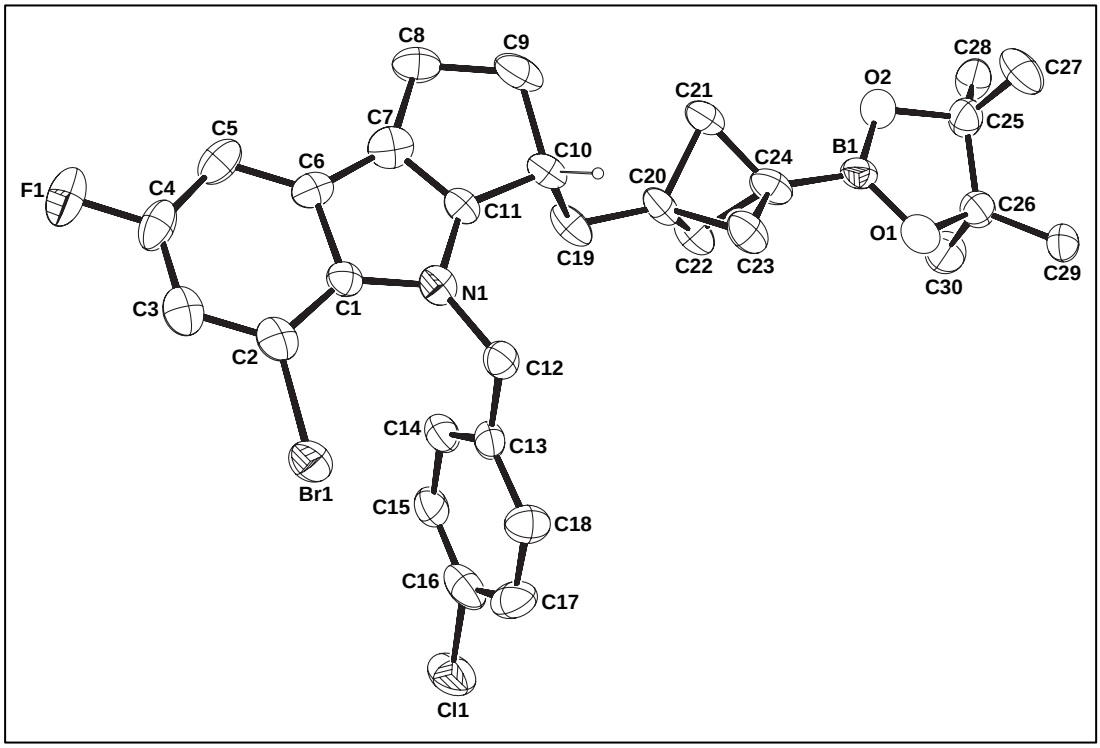


Figure S16. ORTEP drawing of molecule no. 1 with 50% thermal ellipsoids.

Table S8. Summary of Structure Determination of Compound 4ar

Empirical formula	$C_{30}H_{33}BBrClFNO_2$
CCDC	2105768
Formula weight	584.74
Diffractometer	Rigaku XtaLAB Synergy-S (HyPix-6000HE)
Temperature/K	100
Crystal system	triclinic
Space group	P1
a	9.4324(3)Å
b	13.5284(4)Å
c	23.6555(4)Å
α	97.609(2)°
β	91.972(2)°
γ	110.314(3)°
Volume	2795.39(14)Å^3
Z	4
d_{calc}	1.389 g/cm^3
μ	3.159 mm^{-1}
F(000)	1208.0
Crystal size, mm	0.16 × 0.13 × 0.04
2θ range for data collection	7.052 - 136.77°
Index ranges	-11 ≤ h ≤ 11, -16 ≤ k ≤ 16, -28 ≤ l ≤ 28
Reflections collected	120127
Independent reflections	33731[R(int) = 0.099]
Data/restraints/parameters	33731/267/1425
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0906, wR_2 = 0.2510
Final R indexes [all data]	R_1 = 0.0993, wR_2 = 0.2709
Largest diff. peak/hole	1.97/-0.97 eÅ^{-3}
Flack parameter	0.01(2)

Table S9. Refined Positional Parameters for Compound 4ar

Atom	*x*	*y*	*z*	U(eq)
Br1	0.7981(2)	0.23683(16)	0.56854(8)	0.0699(5)
Cl1	1.2596(7)	0.6087(6)	0.4705(2)	0.096(2)
F1	0.3196(12)	0.2616(10)	0.6574(6)	0.085(3)
O1	1.8183(16)	0.7959(12)	0.8669(5)	0.070(3)
O2	1.7069(15)	0.8565(12)	0.9384(5)	0.070(3)
N1	0.9405(16)	0.3936(10)	0.6986(5)	0.048(3)
C1	0.7883(17)	0.3537(12)	0.6789(5)	0.045(3)
C2	0.703(2)	0.2889(14)	0.6284(7)	0.057(4)
C3	0.547(2)	0.2610(15)	0.6215(9)	0.063(4)
C4	0.4727(19)	0.2928(16)	0.6635(10)	0.066(5)
C5	0.546(2)	0.3608(16)	0.7157(9)	0.067(5)
C6	0.704(2)	0.3893(13)	0.7227(7)	0.050(4)
C7	0.815(2)	0.4504(15)	0.7682(8)	0.064(4)
C8	0.829(2)	0.5184(16)	0.8258(7)	0.066(5)
C9	0.992(3)	0.5330(19)	0.8474(7)	0.078(6)
C10	1.083(2)	0.5164(13)	0.7955(6)	0.053(3)
C11	0.9529(18)	0.4522(13)	0.7517(6)	0.049(3)
C12	1.0663(19)	0.3769(13)	0.6710(6)	0.051(3)
C13	1.1167(16)	0.4383(14)	0.6226(6)	0.050(3)
C14	1.0765(19)	0.5285(15)	0.6149(7)	0.057(4)
C15	1.120(2)	0.5763(17)	0.5678(7)	0.063(4)
C16	1.203(3)	0.5438(19)	0.5289(8)	0.077(6)
C17	1.250(2)	0.462(2)	0.5355(9)	0.078(6)
C18	1.205(2)	0.4070(16)	0.5836(8)	0.064(4)
C19	1.189(2)	0.6159(14)	0.7739(7)	0.066(5)
C20	1.336(2)	0.6651(14)	0.8101(6)	0.057(4)
C21	1.366(2)	0.6985(15)	0.8770(6)	0.058(4)
C22	1.453(2)	0.7772(15)	0.8072(8)	0.068(5)
C23	1.466(2)	0.6251(14)	0.8143(8)	0.064(5)
C24	1.526(2)	0.7342(15)	0.8540(7)	0.063(4)
C25	1.871(2)	0.8942(17)	0.9586(8)	0.067(5)
C26	1.941(2)	0.8837(17)	0.9031(8)	0.064(4)
C27	1.887(3)	0.810(2)	0.9946(9)	0.086(7)
C28	1.916(2)	1.0002(16)	0.9942(9)	0.068(5)
C29	2.081(2)	0.8556(18)	0.9023(8)	0.068(5)
C30	1.971(3)	0.985(2)	0.8735(11)	0.087(7)
B1	1.686(2)	0.7967(16)	0.8888(7)	0.053(4)
Br1'	1.75049(16)	0.21419(12)	0.08065(6)	0.0553(4)
Cl1'	1.5558(6)	0.5365(4)	-0.05019(17)	0.0679(11)
F1'	2.2621(10)	0.2767(8)	0.1896(4)	0.056(2)

O1'	1.2865(16)	0.8014(12)	0.3865(7)	0.080(4)
O2'	1.5236(17)	0.9141(13)	0.4159(7)	0.083(4)
N1'	1.7673(13)	0.4020(11)	0.1959(5)	0.043(3)
C1'	1.8798(15)	0.3572(12)	0.1875(5)	0.040(3)
C2'	1.8966(19)	0.2847(13)	0.1448(7)	0.052(4)
C3'	2.0256(18)	0.2557(14)	0.1442(7)	0.052(3)
C4'	2.1401(16)	0.3075(14)	0.1891(7)	0.048(3)
C5'	2.1332(18)	0.3834(14)	0.2324(7)	0.051(3)
C6'	2.0048(15)	0.4105(12)	0.2313(6)	0.043(3)
C7'	1.9560(16)	0.4860(12)	0.2660(6)	0.044(3)
C8'	2.018(2)	0.5779(15)	0.3162(6)	0.057(4)
C9'	1.8751(18)	0.6042(15)	0.3277(7)	0.054(4)
C10'	1.7652(17)	0.5682(13)	0.2710(6)	0.048(3)
C11'	1.8183(15)	0.4820(13)	0.2442(6)	0.043(3)
C12'	1.6165(15)	0.3661(13)	0.1679(6)	0.043(3)
C13'	1.6048(16)	0.4162(12)	0.1159(5)	0.041(3)
C14'	1.4654(17)	0.3772(13)	0.0825(6)	0.047(3)
C15'	1.4483(18)	0.4144(13)	0.0314(6)	0.051(3)
C16'	1.5735(17)	0.4918(13)	0.0152(6)	0.048(3)
C17'	1.7119(19)	0.5337(14)	0.0482(7)	0.055(4)
C18'	1.7280(18)	0.4968(13)	0.0992(7)	0.054(4)
C19'	1.6011(19)	0.5423(13)	0.2795(7)	0.052(3)
C20'	1.5628(17)	0.6307(12)	0.3127(6)	0.045(3)
C21'	1.5916(18)	0.6725(13)	0.3778(6)	0.053(3)
C22'	1.395(2)	0.6253(13)	0.3179(7)	0.054(3)
C23'	1.605(2)	0.7477(14)	0.3040(7)	0.060(4)
C24'	1.4963(17)	0.7316(13)	0.3540(6)	0.049(3)
C25'	1.428(2)	0.9622(15)	0.4464(8)	0.061(4)
C26'	1.265(2)	0.8930(16)	0.4186(7)	0.062(4)
C27'	1.485(3)	1.0781(19)	0.4381(14)	0.093(7)
C28'	1.457(3)	0.958(3)	0.5086(10)	0.118(12)
C29'	1.210(3)	0.947(2)	0.3750(11)	0.101(8)
C30'	1.151(3)	0.855(2)	0.4603(12)	0.097(8)
B1'	1.434(2)	0.8176(15)	0.3864(7)	0.048(4)
Br2	-0.0674(2)	0.30677(17)	0.95621(8)	0.0751(6)
Cl2	-0.6706(6)	0.0045(5)	1.0512(2)	0.0825(15)
F2	0.3616(11)	0.3246(8)	0.8278(4)	0.063(2)
O3	-1.072(2)	-0.2570(18)	0.5842(8)	0.068(4)
O3*	-1.086(4)	-0.305(3)	0.6097(17)	0.058(6)
O4	-1.1886(19)	-0.2136(15)	0.6614(8)	0.063(4)
O4*	-1.190(4)	-0.183(3)	0.6324(19)	0.059(6)
N2	-0.2610(16)	0.1759(11)	0.8276(5)	0.052(3)
C31	-0.100(2)	0.2244(13)	0.8354(6)	0.054(4)

C32	0.001(2)	0.2804(15)	0.8824(6)	0.060(4)
C33	0.150(2)	0.3135(15)	0.8784(7)	0.063(4)
C34	0.207(2)	0.2906(13)	0.8301(6)	0.055(4)
C35	0.1202(19)	0.2266(14)	0.7808(7)	0.054(4)
C36	-0.0397(18)	0.1932(12)	0.7862(5)	0.045(3)
C37	-0.1712(18)	0.1249(12)	0.7464(6)	0.046(3)
C38	-0.206(2)	0.0532(16)	0.6899(7)	0.061(4)
C39	-0.378(2)	0.0214(14)	0.6809(6)	0.057(4)
C40	-0.4392(17)	0.0389(13)	0.7415(6)	0.047(3)
C41	-0.2954(16)	0.1181(12)	0.7743(6)	0.046(3)
C42	-0.364(2)	0.2184(13)	0.8580(6)	0.052(3)
C43	-0.4430(18)	0.1583(13)	0.9038(6)	0.049(3)
C44	-0.4204(19)	0.0709(13)	0.9175(6)	0.052(3)
C45	-0.4935(19)	0.0206(15)	0.9633(8)	0.060(4)
C46	-0.587(2)	0.0619(16)	0.9919(6)	0.058(4)
C47	-0.615(3)	0.1486(16)	0.9780(7)	0.070(5)
C48	-0.545(2)	0.1947(15)	0.9328(7)	0.062(4)
C49	-0.582(2)	0.0635(14)	0.7416(6)	0.054(4)
C50	-0.723(2)	-0.0177(13)	0.7073(6)	0.050(3)
C51	-0.7489(19)	-0.0632(14)	0.6431(7)	0.057(4)
C52	-0.877(2)	-0.0077(14)	0.7026(7)	0.056(4)
C53	-0.8048(19)	-0.1358(13)	0.7177(6)	0.054(3)
C54	-0.9013(18)	-0.1209(12)	0.6673(6)	0.048(3)
C55	-1.235(3)	-0.3011(17)	0.5666(9)	0.067(4)
C55*	-1.237(5)	-0.351(3)	0.5789(19)	0.063(6)
C56	-1.300(2)	-0.3046(17)	0.6254(9)	0.061(4)
C56*	-1.317(5)	-0.276(4)	0.604(2)	0.066(6)
C57	-1.270(3)	-0.412(2)	0.5307(13)	0.070(6)
C57*	-1.294(6)	-0.473(4)	0.576(3)	0.067(10)
C58	-1.276(3)	-0.224(2)	0.5325(12)	0.078(7)
C58*	-1.197(9)	-0.342(7)	0.516(2)	0.081(11)
C59	-1.317(3)	-0.408(2)	0.6489(14)	0.077(6)
C59*	-1.395(9)	-0.325(6)	0.656(3)	0.084(11)
C60	-1.453(3)	-0.287(2)	0.6248(12)	0.062(5)
C60*	-1.435(7)	-0.237(6)	0.578(3)	0.088(13)
B2	-1.058(2)	-0.2013(14)	0.6364(6)	0.054(4)
Br2'	1.8815(2)	1.38518(15)	0.42888(8)	0.0681(5)
Cl2'	2.0228(8)	1.0498(6)	0.55849(19)	0.0932(19)
F2'	1.3493(12)	1.3148(11)	0.3351(6)	0.081(3)
O3'	2.0858(19)	0.6804(12)	0.0909(6)	0.085(5)
O4'	2.3124(18)	0.7851(13)	0.1374(7)	0.091(5)
N2'	1.8446(16)	1.1947(11)	0.3109(5)	0.049(3)
C31'	1.7312(17)	1.2339(15)	0.3257(7)	0.051(4)

C32'	1.7225(18)	1.3111(13)	0.3704(6)	0.049(3)
C33'	1.588(2)	1.3330(15)	0.3712(9)	0.064(4)
C34'	1.473(2)	1.2858(17)	0.3325(9)	0.067(5)
C35'	1.4736(19)	1.2096(16)	0.2883(8)	0.060(4)
C36'	1.6049(19)	1.1816(14)	0.2843(7)	0.052(4)
C37'	1.6449(19)	1.1084(14)	0.2464(7)	0.053(4)
C38'	1.588(2)	1.0306(17)	0.1944(8)	0.067(5)
C39'	1.713(2)	0.9845(16)	0.1858(7)	0.062(4)
C40'	1.8567(19)	1.0517(13)	0.2256(6)	0.052(3)
C41'	1.7903(19)	1.1199(13)	0.2628(7)	0.051(3)
C42'	1.9975(18)	1.2277(14)	0.3407(7)	0.052(4)
C43'	1.9984(19)	1.1753(15)	0.3932(6)	0.053(4)
C44'	2.130(2)	1.2158(16)	0.4320(7)	0.063(4)
C45'	2.140(2)	1.1777(18)	0.4803(7)	0.068(5)
C46'	2.013(2)	1.0952(17)	0.4935(6)	0.065(5)
C47'	1.882(2)	1.0509(19)	0.4581(7)	0.067(5)
C48'	1.8777(18)	1.0925(14)	0.4057(6)	0.053(3)
C49'	1.9288(19)	0.9849(13)	0.2546(6)	0.053(3)
C50'	1.994(2)	0.9188(13)	0.2141(7)	0.056(4)
C51'	1.912(3)	0.8215(16)	0.1673(7)	0.068(5)
C52'	2.097(3)	0.8558(18)	0.2316(8)	0.075(5)
C53'	2.111(3)	0.9611(15)	0.1682(8)	0.074(5)
C54'	2.082(2)	0.8373(13)	0.1645(6)	0.054(4)
C55'	2.187(2)	0.6258(16)	0.0717(7)	0.065(4)
C56'	2.347(3)	0.7024(16)	0.1010(8)	0.073(5)
C57'	2.178(4)	0.605(2)	0.0081(8)	0.129(13)
C58'	2.134(3)	0.518(2)	0.0923(13)	0.095(8)
C59'	2.454(3)	0.761(2)	0.0577(9)	0.090(7)
C60'	2.437(5)	0.658(2)	0.1355(13)	0.144(16)
B2'	2.164(3)	0.7687(16)	0.1311(8)	0.060(5)

Table S10. Positional Parameters for Hydrogens in Compound 4ar

Atom	*x*	*y*	*z*	U(eq)
H3	0.491899	0.219261	0.586956	0.076
H5	0.490629	0.385081	0.743725	0.08
H8a	0.754106	0.480888	0.85114	0.079
H8b	0.8185	0.587406	0.821793	0.079
H9a	0.989338	0.48076	0.873297	0.093
H9b	1.04218	0.605581	0.869135	0.093
H10	1.142653	0.470949	0.804368	0.064
H12a	1.037529	0.299943	0.656363	0.061
H12b	1.153439	0.396697	0.700136	0.061
H14	1.020739	0.554654	0.641957	0.069
H15	1.090375	0.634793	0.562053	0.076
H17	1.311673	0.440729	0.508882	0.094
H18	1.236534	0.348852	0.588717	0.077
H19a	1.208515	0.596167	0.733957	0.079
H19b	1.137727	0.668746	0.77411	0.079
H21a	1.332122	0.75649	0.893716	0.07
H21b	1.343655	0.639275	0.899776	0.07
H22a	1.420927	0.838033	0.820999	0.082
H22b	1.504008	0.785497	0.771438	0.082
H23a	1.517714	0.620435	0.778998	0.077
H23b	1.446548	0.561674	0.833666	0.077
H27a	1.993053	0.829502	1.009037	0.129
H27b	1.852809	0.739667	0.970626	0.129
H27c	1.823986	0.807168	1.027001	0.129
H28a	2.013038	1.015561	1.016313	0.102
H28b	1.838063	1.000782	1.020498	0.102
H28c	1.926578	1.054607	0.969522	0.102
H29a	2.118388	0.858918	0.864157	0.102
H29b	2.057125	0.783211	0.911277	0.102
H29c	2.159164	0.906178	0.930779	0.102
H30a	2.039593	1.048088	0.899121	0.13
H30b	1.875051	0.995069	0.865039	0.13
H30c	2.018295	0.976292	0.837771	0.13
H3'	2.035371	0.203797	0.114914	0.062
H5'	2.213253	0.415967	0.261942	0.061
H8'a	2.100318	0.639354	0.30522	0.069
H8'b	2.056247	0.554796	0.349801	0.069
H9'a	1.903085	0.681794	0.340192	0.065
H9'b	1.823528	0.5664	0.358481	0.065
H10'	1.796294	0.627476	0.247575	0.057

H12c	1.5479	0.381912	0.19552	0.052
H12d	1.580966	0.287779	0.156528	0.052
H14'	1.381204	0.324646	0.094934	0.056
H15'	1.354209	0.387508	0.00853	0.061
H17'	1.795017	0.587403	0.035955	0.066
H18'	1.821436	0.52585	0.122482	0.065
H19c	1.566958	0.479461	0.299572	0.062
H19d	1.543123	0.522003	0.241452	0.062
H21c	1.541011	0.620531	0.403095	0.063
H21d	1.697673	0.716648	0.391996	0.063
H22c	1.340469	0.630636	0.282672	0.065
H22d	1.332096	0.570345	0.339471	0.065
H23c	1.563154	0.759854	0.267592	0.072
H23d	1.711723	0.794322	0.314833	0.072
H27d	1.470723	1.082793	0.397497	0.139
H27e	1.593501	1.110689	0.451116	0.139
H27f	1.428895	1.11598	0.460447	0.139
H28d	1.394034	0.989723	0.531154	0.177
H28e	1.564406	0.998125	0.520934	0.177
H28f	1.432027	0.88367	0.51431	0.177
H29d	1.17943	1.003423	0.39477	0.152
H29e	1.123412	0.894089	0.350796	0.152
H29f	1.292445	0.977429	0.351224	0.152
H30d	1.186096	0.814098	0.485245	0.145
H30e	1.053507	0.808853	0.439581	0.145
H30f	1.137752	0.916038	0.483589	0.145
H33	0.217332	0.354107	0.910844	0.076
H35	0.162858	0.207298	0.747163	0.065
H38a	-0.176369	-0.009712	0.691685	0.073
H38b	-0.154923	0.091632	0.659217	0.073
H39a	-0.424262	-0.054421	0.663168	0.068
H39b	-0.404098	0.065658	0.65516	0.068
H40	-0.461266	-0.029179	0.757463	0.056
H42a	-0.441763	0.220657	0.829624	0.062
H42b	-0.30544	0.292817	0.875726	0.062
H44	-0.355332	0.042676	0.896526	0.062
H45	-0.477096	-0.040467	0.973351	0.072
H47	-0.680591	0.176263	0.99891	0.083
H48	-0.568019	0.25266	0.921272	0.074
H49a	-0.561158	0.132154	0.72716	0.064
H49b	-0.605922	0.074413	0.781859	0.064
H51a	-0.690092	-0.108492	0.629671	0.068
H51b	-0.751299	-0.012611	0.616751	0.068

H52a	-0.886232	0.046764	0.679962	0.067
H52b	-0.928492	-0.00803	0.738391	0.067
H53a	-0.749557	-0.185254	0.708229	0.065
H53b	-0.853253	-0.144573	0.754114	0.065
H57a	-1.229234	-0.402936	0.493325	0.106
H57b	-1.379627	-0.449617	0.525287	0.106
H57c	-1.221881	-0.45252	0.55066	0.106
H57d	-1.216833	-0.500366	0.561097	0.101
H57e	-1.388261	-0.505645	0.551557	0.101
H57f	-1.311622	-0.490582	0.615038	0.101
H58a	-1.286356	-0.165625	0.559019	0.117
H58b	-1.372011	-0.262681	0.509041	0.117
H58c	-1.195455	-0.195573	0.507603	0.117
H58d	-1.229485	-0.287399	0.50296	0.122
H58e	-1.249987	-0.411079	0.492094	0.122
H58f	-1.087555	-0.323041	0.514781	0.122
H59a	-1.234423	-0.432412	0.637592	0.116
H59b	-1.414728	-0.463245	0.633326	0.116
H59c	-1.314396	-0.395461	0.690754	0.116
H59d	-1.482938	-0.388821	0.642241	0.127
H59e	-1.32257	-0.34311	0.67948	0.127
H59f	-1.427567	-0.27221	0.67933	0.127
H60a	-1.486114	-0.283548	0.66361	0.093
H60b	-1.529695	-0.345399	0.599352	0.093
H60c	-1.44107	-0.219119	0.610916	0.093
H60d	-1.418697	-0.164148	0.596951	0.132
H60e	-1.536946	-0.284118	0.583588	0.132
H60f	-1.423302	-0.236469	0.537133	0.132
H33'	1.579751	1.384464	0.401091	0.077
H35'	1.388337	1.176348	0.26099	0.071
H38c	1.573412	1.06541	0.161474	0.08
H38d	1.490778	0.974599	0.199484	0.08
H39c	1.737851	0.982959	0.145484	0.074
H39d	1.676916	0.91031	0.194037	0.074
H40'	1.93275	1.097706	0.202717	0.063
H42c	2.037145	1.306089	0.352163	0.062
H42d	2.066037	1.209209	0.31395	0.062
H44'	2.215402	1.272361	0.423129	0.075
H45'	2.229914	1.205819	0.50535	0.082
H47'	1.797084	0.995072	0.467943	0.081
H48'	1.789964	1.062119	0.37935	0.063
H49c	2.010984	1.032961	0.283243	0.064
H49d	1.851453	0.936569	0.275399	0.064

H51c	1.849098	0.755725	0.181241	0.081
H51d	1.862742	0.83646	0.133574	0.081
H52c	2.198584	0.899864	0.250393	0.09
H52d	2.046053	0.792429	0.249934	0.09
H53c	2.070794	0.982827	0.134549	0.089
H53d	2.21345	1.010632	0.183726	0.089
H57g	2.0861	0.543934	-0.006235	0.193
H57h	2.267435	0.588928	-0.003967	0.193
H57i	2.175696	0.668045	-0.007274	0.193
H58g	2.142237	0.528395	0.134239	0.142
H58h	2.197828	0.477557	0.078217	0.142
H58i	2.028352	0.478014	0.077658	0.142
H59g	2.551219	0.808016	0.077976	0.135
H59h	2.406527	0.804146	0.039132	0.135
H59i	2.470705	0.708771	0.028562	0.135
H60g	2.433738	0.589448	0.115225	0.216
H60h	2.394881	0.648541	0.17252	0.216
H60i	2.542642	0.707798	0.141809	0.216

Table S11. Refined Thermal Parameters (U's) for Compound 4ar

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	0.0678(10)	0.0740(12)	0.0533(9)	-0.0110(8)	-0.0042(7)	0.0154(9)
Cl1	0.087(4)	0.119(5)	0.059(2)	0.032(3)	0.007(2)	-0.002(3)
F1	0.046(5)	0.078(8)	0.133(10)	0.031(7)	0.008(6)	0.018(5)
O1	0.081(9)	0.074(9)	0.054(6)	-0.009(6)	-0.008(6)	0.034(7)
O2	0.064(7)	0.083(9)	0.062(7)	-0.008(6)	-0.005(5)	0.032(7)
N1	0.062(7)	0.035(6)	0.053(6)	0.009(5)	-0.002(5)	0.024(6)
C1	0.053(8)	0.045(8)	0.042(6)	0.013(6)	0.003(6)	0.023(7)
C2	0.07(1)	0.047(9)	0.059(8)	0.029(7)	0.000(7)	0.021(8)
C3	0.066(10)	0.049(10)	0.075(11)	0.022(8)	-0.007(8)	0.018(8)
C4	0.045(8)	0.062(11)	0.103(14)	0.034(10)	0.012(9)	0.028(8)
C5	0.056(10)	0.059(11)	0.095(13)	0.016(9)	0.025(9)	0.031(9)
C6	0.063(9)	0.044(8)	0.058(8)	0.023(7)	0.020(7)	0.030(7)
C7	0.080(12)	0.047(9)	0.072(10)	0.011(8)	0.014(9)	0.031(9)
C8	0.091(13)	0.058(11)	0.055(9)	0.007(7)	0.019(8)	0.032(10)
C9	0.122(18)	0.088(14)	0.041(8)	0.015(8)	0.001(9)	0.058(14)
C10	0.072(10)	0.051(9)	0.038(6)	0.006(6)	-0.004(6)	0.023(8)
C11	0.055(8)	0.049(9)	0.040(6)	0.002(6)	-0.005(6)	0.016(7)
C12	0.057(8)	0.053(9)	0.049(7)	0.003(6)	-0.001(6)	0.030(7)
C13	0.041(7)	0.058(9)	0.049(7)	0.001(6)	-0.007(6)	0.017(7)
C14	0.058(9)	0.064(10)	0.049(8)	0.012(7)	-0.005(6)	0.021(8)
C15	0.060(9)	0.079(13)	0.056(9)	0.020(8)	-0.004(7)	0.028(9)
C16	0.074(12)	0.074(14)	0.056(10)	0.019(9)	-0.018(9)	-0.008(10)
C17	0.058(10)	0.085(15)	0.068(11)	-0.008(10)	0.020(9)	0.001(10)
C18	0.080(12)	0.059(11)	0.059(9)	0.011(8)	0.014(8)	0.031(9)
C19	0.091(13)	0.053(10)	0.048(8)	0.013(7)	-0.018(8)	0.020(9)
C20	0.077(11)	0.058(10)	0.040(7)	0.002(6)	-0.015(7)	0.033(9)
C21	0.084(11)	0.06(1)	0.037(7)	0.004(6)	-0.002(7)	0.037(9)
C22	0.090(13)	0.056(11)	0.056(9)	0.010(8)	-0.015(8)	0.024(9)
C23	0.092(13)	0.05(1)	0.058(9)	0.007(7)	-0.010(8)	0.035(9)
C24	0.092(13)	0.053(10)	0.045(8)	0.002(7)	-0.001(8)	0.031(9)
C25	0.06(1)	0.076(13)	0.064(10)	-0.009(9)	-0.006(8)	0.030(9)
C26	0.070(11)	0.071(12)	0.058(9)	0.001(8)	0.001(8)	0.038(10)
C27	0.101(16)	0.082(15)	0.070(12)	0.035(11)	-0.016(11)	0.020(12)
C28	0.061(10)	0.060(11)	0.078(11)	-0.008(9)	-0.003(8)	0.023(9)
C29	0.066(10)	0.090(14)	0.059(9)	0.006(9)	-0.002(8)	0.046(11)
C30	0.088(14)	0.096(17)	0.096(15)	0.053(13)	0.022(12)	0.042(13)
B1	0.073(11)	0.057(11)	0.042(8)	0.010(7)	0.009(7)	0.037(10)
Br1'	0.0560(9)	0.0631(10)	0.0442(7)	-0.0025(6)	-0.0055(6)	0.0227(8)
Cl1'	0.089(3)	0.065(3)	0.0495(18)	0.0156(17)	-0.0100(18)	0.027(2)
F1'	0.041(4)	0.056(5)	0.076(6)	0.013(4)	0.001(4)	0.025(4)

O1'	0.057(7)	0.063(9)	0.109(11)	-0.025(7)	0.010(7)	0.019(6)
O2'	0.073(9)	0.085(10)	0.089(9)	-0.025(8)	-0.017(7)	0.041(8)
N1'	0.034(5)	0.056(7)	0.042(6)	0.009(5)	-0.004(4)	0.020(5)
C1'	0.038(7)	0.045(8)	0.032(6)	0.004(5)	-0.003(5)	0.010(6)
C2'	0.057(9)	0.049(9)	0.049(8)	0.017(6)	0.003(6)	0.016(7)
C3'	0.048(8)	0.048(9)	0.060(9)	0.011(7)	0.005(6)	0.017(7)
C4'	0.037(7)	0.054(9)	0.062(8)	0.010(7)	0.007(6)	0.026(7)
C5'	0.045(8)	0.051(9)	0.049(7)	0.007(6)	-0.010(6)	0.010(7)
C6'	0.034(6)	0.044(8)	0.046(7)	0.010(6)	-0.002(5)	0.007(6)
C7'	0.040(7)	0.041(8)	0.047(7)	-0.002(6)	0.000(5)	0.014(6)
C8'	0.060(9)	0.058(10)	0.041(7)	-0.011(6)	-0.013(6)	0.015(8)
C9'	0.043(7)	0.067(11)	0.049(8)	0.005(7)	-0.005(6)	0.017(7)
C10'	0.043(7)	0.048(9)	0.053(8)	0.006(6)	0.000(6)	0.018(7)
C11'	0.036(6)	0.055(9)	0.039(6)	0.007(6)	-0.004(5)	0.018(6)
C12'	0.039(7)	0.051(9)	0.039(6)	0.017(6)	0.000(5)	0.013(6)
C13'	0.045(7)	0.045(8)	0.033(6)	0.002(5)	-0.002(5)	0.018(6)
C14'	0.048(7)	0.054(9)	0.039(7)	0.009(6)	-0.001(5)	0.019(7)
C15'	0.060(8)	0.063(9)	0.035(6)	0.006(6)	-0.008(6)	0.030(8)
C16'	0.047(7)	0.056(9)	0.044(7)	0.003(6)	-0.010(5)	0.027(7)
C17'	0.053(8)	0.058(10)	0.053(8)	0.019(7)	-0.002(6)	0.017(7)
C18'	0.056(8)	0.048(9)	0.060(8)	0.010(7)	-0.009(7)	0.021(7)
C19'	0.054(8)	0.043(8)	0.052(8)	-0.006(6)	-0.001(6)	0.015(7)
C20'	0.049(7)	0.047(8)	0.042(6)	0.005(5)	-0.004(5)	0.022(7)
C21'	0.056(8)	0.056(9)	0.045(7)	0.004(6)	0.001(6)	0.022(7)
C22'	0.061(9)	0.048(9)	0.048(7)	-0.003(6)	-0.002(7)	0.019(8)
C23'	0.083(11)	0.052(9)	0.051(8)	0.010(7)	0.011(8)	0.029(9)
C24'	0.051(8)	0.053(9)	0.039(6)	-0.002(6)	-0.004(5)	0.017(7)
C25'	0.06(1)	0.054(10)	0.064(9)	0.005(8)	0.012(7)	0.016(8)
C26'	0.073(11)	0.064(11)	0.050(8)	-0.004(7)	-0.004(7)	0.031(9)
C27'	0.068(12)	0.060(13)	0.15(2)	0.032(14)	0.014(14)	0.020(11)
C28'	0.083(16)	0.16(3)	0.061(12)	-0.022(15)	0.009(11)	-0.012(17)
C29'	0.108(18)	0.098(18)	0.092(15)	0.007(13)	-0.042(14)	0.037(15)
C30'	0.063(12)	0.12(2)	0.104(17)	0.033(15)	0.027(11)	0.014(12)
B1'	0.058(9)	0.042(9)	0.045(8)	-0.001(6)	-0.007(7)	0.023(8)
Br2	0.0763(12)	0.0796(13)	0.0482(9)	-0.0019(8)	0.0049(8)	0.0056(10)
Cl2	0.067(3)	0.114(4)	0.056(2)	0.032(2)	0.0088(19)	0.012(3)
F2	0.054(5)	0.066(6)	0.065(5)	0.017(4)	-0.001(4)	0.013(5)
O3	0.053(7)	0.079(10)	0.065(8)	-0.006(7)	-0.001(7)	0.021(7)
O3*	0.051(10)	0.060(12)	0.063(12)	0.002(10)	-0.003(10)	0.022(10)
O4	0.061(8)	0.061(9)	0.060(8)	-0.005(7)	-0.005(7)	0.018(7)
O4*	0.054(9)	0.059(11)	0.061(11)	-0.006(10)	-0.007(10)	0.022(9)
N2	0.063(8)	0.049(7)	0.041(6)	0.003(5)	0.009(5)	0.015(6)
C31	0.069(10)	0.042(8)	0.050(8)	0.015(6)	0.010(7)	0.013(7)

C32	0.071(10)	0.059(10)	0.037(7)	0.009(6)	0.002(7)	0.008(8)
C33	0.069(10)	0.059(11)	0.044(8)	0.004(7)	-0.005(7)	0.004(8)
C34	0.075(10)	0.046(9)	0.040(7)	0.009(6)	-0.007(7)	0.019(8)
C35	0.061(9)	0.055(10)	0.054(8)	0.009(7)	-0.003(7)	0.028(8)
C36	0.061(8)	0.047(8)	0.028(6)	0.002(5)	-0.005(5)	0.021(7)
C37	0.054(8)	0.043(8)	0.037(6)	-0.002(5)	-0.009(5)	0.018(7)
C38	0.065(10)	0.069(11)	0.048(8)	0.003(7)	-0.008(7)	0.029(9)
C39	0.069(10)	0.056(9)	0.045(7)	-0.012(6)	-0.008(7)	0.030(8)
C40	0.050(8)	0.048(8)	0.043(7)	0.001(6)	-0.003(6)	0.020(7)
C41	0.047(7)	0.047(8)	0.050(7)	0.019(6)	0.010(6)	0.019(6)
C42	0.069(9)	0.043(8)	0.036(6)	0.007(6)	0.014(6)	0.009(7)
C43	0.057(8)	0.049(9)	0.038(6)	0.001(6)	0.000(6)	0.016(7)
C44	0.059(8)	0.045(8)	0.045(7)	0.003(6)	0.001(6)	0.013(7)
C45	0.053(9)	0.06(1)	0.068(10)	0.032(8)	-0.003(7)	0.016(8)
C46	0.054(9)	0.079(12)	0.040(7)	0.003(7)	0.002(6)	0.026(8)
C47	0.087(13)	0.061(11)	0.051(9)	0.004(7)	0.007(8)	0.017(10)
C48	0.072(11)	0.065(11)	0.045(8)	0.007(7)	0.013(7)	0.019(9)
C49	0.072(10)	0.049(9)	0.046(7)	0.012(6)	0.002(7)	0.028(8)
C50	0.067(9)	0.055(9)	0.039(6)	0.001(6)	-0.005(6)	0.039(8)
C51	0.058(9)	0.053(9)	0.058(9)	0.007(7)	-0.009(7)	0.020(7)
C52	0.068(10)	0.055(9)	0.049(8)	0.006(6)	-0.010(7)	0.027(8)
C53	0.066(9)	0.049(9)	0.049(7)	0.002(6)	-0.012(7)	0.025(8)
C54	0.061(8)	0.041(8)	0.046(7)	0.003(6)	-0.010(6)	0.023(7)
C55	0.057(7)	0.068(9)	0.066(8)	-0.002(7)	-0.008(7)	0.017(7)
C55*	0.055(9)	0.063(10)	0.067(10)	0.003(9)	-0.006(9)	0.020(9)
C56	0.056(8)	0.060(9)	0.060(8)	0.004(7)	-0.009(7)	0.016(7)
C56*	0.059(9)	0.065(10)	0.067(10)	-0.005(9)	-0.006(9)	0.017(9)
C57	0.064(12)	0.060(13)	0.077(13)	-0.026(11)	-0.001(10)	0.023(11)
C57*	0.051(17)	0.066(19)	0.09(2)	0.007(18)	-0.007(17)	0.032(16)
C58	0.074(13)	0.084(15)	0.057(11)	0.013(11)	-0.017(10)	0.005(12)
C58*	0.074(17)	0.078(18)	0.069(16)	-0.003(16)	-0.009(16)	0.006(16)
C59	0.074(13)	0.065(13)	0.096(14)	0.036(11)	0.000(11)	0.021(11)
C59*	0.073(17)	0.076(17)	0.082(17)	0.003(16)	0.002(16)	0.003(16)
C60	0.054(11)	0.059(12)	0.074(12)	0.006(10)	-0.008(10)	0.025(10)
C60*	0.06(2)	0.09(2)	0.09(2)	-0.01(2)	-0.021(19)	0.01(2)
B2	0.077(12)	0.051(11)	0.040(8)	0.009(7)	-0.003(7)	0.032(10)
Br2'	0.0699(11)	0.0668(11)	0.068(1)	-0.0039(8)	-0.0153(8)	0.0319(10)
Cl2'	0.136(5)	0.134(5)	0.045(2)	0.019(2)	0.007(2)	0.091(4)
F2'	0.049(5)	0.088(8)	0.116(9)	0.030(7)	0.012(5)	0.032(5)
O3'	0.096(11)	0.069(9)	0.085(9)	-0.022(7)	-0.036(8)	0.040(8)
O4'	0.078(9)	0.072(10)	0.092(10)	-0.044(8)	0.018(8)	0.009(7)
N2'	0.057(7)	0.054(8)	0.036(6)	0.015(5)	-0.003(5)	0.016(6)
C31'	0.050(8)	0.063(10)	0.047(7)	0.033(7)	0.001(6)	0.020(7)

C32'	0.050(8)	0.048(9)	0.045(7)	0.010(6)	-0.001(6)	0.011(7)
C33'	0.073(11)	0.05(1)	0.074(11)	0.025(8)	0.003(9)	0.021(9)
C34'	0.069(11)	0.065(12)	0.075(11)	0.031(10)	0.006(9)	0.025(10)
C35'	0.044(8)	0.072(12)	0.061(9)	0.032(9)	0.000(7)	0.012(8)
C36'	0.056(9)	0.053(10)	0.052(8)	0.020(7)	-0.006(7)	0.021(8)
C37'	0.054(8)	0.053(9)	0.054(8)	0.018(7)	-0.003(6)	0.020(7)
C38'	0.054(9)	0.084(13)	0.066(10)	0.033(9)	-0.001(8)	0.022(9)
C39'	0.058(10)	0.068(11)	0.051(8)	-0.002(7)	-0.006(7)	0.018(9)
C40'	0.058(9)	0.049(9)	0.042(7)	0.010(6)	-0.003(6)	0.008(7)
C41'	0.054(9)	0.043(8)	0.052(8)	0.012(6)	-0.001(6)	0.013(7)
C42'	0.048(8)	0.045(9)	0.056(8)	0.001(7)	-0.012(6)	0.013(7)
C43'	0.062(9)	0.063(10)	0.045(7)	0.007(7)	-0.004(6)	0.035(8)
C44'	0.056(9)	0.064(11)	0.058(9)	-0.013(8)	-0.011(7)	0.019(8)
C45'	0.06(1)	0.095(15)	0.054(9)	-0.005(9)	-0.014(7)	0.041(10)
C46'	0.097(13)	0.095(14)	0.028(6)	-0.003(7)	0.004(7)	0.069(12)
C47'	0.074(11)	0.101(15)	0.054(9)	0.032(9)	0.021(8)	0.055(11)
C48'	0.053(8)	0.067(10)	0.046(7)	0.017(7)	0.009(6)	0.029(8)
C49'	0.061(9)	0.046(8)	0.049(7)	0.010(6)	0.011(6)	0.013(7)
C50'	0.065(9)	0.047(9)	0.054(8)	0.018(7)	0.009(7)	0.011(7)
C51'	0.089(13)	0.059(11)	0.051(8)	0.011(7)	0.009(8)	0.02(1)
C52'	0.098(14)	0.084(14)	0.055(9)	0.010(9)	0.008(9)	0.047(12)
C53'	0.100(15)	0.055(10)	0.058(9)	0.011(8)	0.018(9)	0.012(10)
C54'	0.056(9)	0.051(9)	0.044(7)	0.015(6)	0.008(6)	0.004(7)
C55'	0.085(12)	0.063(11)	0.049(8)	-0.002(7)	-0.005(8)	0.031(10)
C56'	0.095(14)	0.053(11)	0.062(10)	-0.008(8)	0.01(1)	0.021(10)
C57'	0.16(3)	0.12(2)	0.030(9)	-0.01(1)	-0.012(11)	-0.035(18)
C58'	0.080(14)	0.073(15)	0.14(2)	0.054(15)	0.014(14)	0.027(12)
C59'	0.076(13)	0.101(18)	0.070(12)	-0.006(11)	0.015(10)	0.010(12)
C60'	0.21(4)	0.071(17)	0.12(2)	-0.035(15)	-0.10(2)	0.037(19)
B2'	0.083(14)	0.043(10)	0.043(8)	0.006(7)	0.010(8)	0.009(9)

Table S12. Bond Distances in Compound 4ar, Å

Br1-C2	1.888(19)	Cl1-C16	1.73(2)	F1-C4	1.353(19)
O1-C26	1.48(2)	O1-B1	1.37(2)	O2-C25	1.49(2)
O2-B1	1.30(2)	N1-C1	1.38(2)	N1-C11	1.372(19)
N1-C12	1.44(2)	C1-C2	1.42(2)	C1-C6	1.46(2)
C2-C3	1.39(3)	C3-C4	1.34(3)	C4-C5	1.43(3)
C5-C6	1.41(2)	C6-C7	1.42(3)	C7-C8	1.51(3)
C7-C11	1.37(2)	C8-C9	1.54(3)	C9-C10	1.56(3)
C10-C11	1.51(2)	C10-C19	1.53(2)	C12-C13	1.50(2)
C13-C14	1.43(2)	C13-C18	1.39(2)	C14-C15	1.37(2)
C15-C16	1.36(3)	C16-C17	1.36(4)	C17-C18	1.43(3)
C19-C20	1.49(2)	C20-C21	1.58(2)	C20-C22	1.55(3)
C20-C23	1.51(2)	C20-C24	1.90(3)	C21-C24	1.55(3)
C22-C24	1.56(2)	C23-C24	1.55(2)	C24-B1	1.58(3)
C25-C26	1.50(3)	C25-C27	1.55(3)	C25-C28	1.48(3)
C26-C29	1.49(2)	C26-C30	1.57(3)	Br1'-C2'	1.916(16)
Cl1'-C16'	1.756(14)	F1'-C4'	1.353(15)	O1'-C26'	1.45(2)
O1'-B1'	1.33(2)	O2'-C25'	1.45(2)	O2'-B1'	1.36(2)
N1'-C1'	1.400(17)	N1'-C11'	1.408(19)	N1'-C12'	1.439(17)
C1'-C2'	1.37(2)	C1'-C6'	1.454(18)	C2'-C3'	1.40(2)
C3'-C4'	1.41(2)	C4'-C5'	1.37(2)	C5'-C6'	1.38(2)
C6'-C7'	1.43(2)	C7'-C8'	1.54(2)	C7'-C11'	1.361(18)
C8'-C9'	1.54(2)	C9'-C10'	1.58(2)	C10'-C11'	1.50(2)
C10'-C19'	1.49(2)	C12'-C13'	1.499(17)	C13'-C14'	1.40(2)
C13'-C18'	1.40(2)	C14'-C15'	1.394(19)	C15'-C16'	1.39(2)
C16'-C17'	1.39(2)	C17'-C18'	1.39(2)	C19'-C20'	1.50(2)
C20'-C21'	1.547(19)	C20'-C22'	1.566(19)	C20'-C23'	1.54(2)
C20'-C24'	1.87(2)	C21'-C24'	1.53(2)	C22'-C24'	1.54(2)
C23'-C24'	1.58(2)	C24'-B1'	1.60(2)	C25'-C26'	1.56(3)
C25'-C27'	1.51(3)	C25'-C28'	1.50(3)	C26'-C29'	1.51(3)
C26'-C30'	1.49(3)	Br2-C32	1.912(16)	Cl2-C46	1.771(17)
F2-C34	1.37(2)	O3-C55	1.47(2)	O3-B2	1.33(2)
O3*-C55*	1.46(3)	O3*-B2	1.39(3)	O4-C56	1.45(2)
O4-B2	1.36(2)	O4*-C56*	1.47(4)	O4*-B2	1.36(3)
N2-C31	1.43(2)	N2-C41	1.36(2)	N2-C42	1.45(2)
C31-C32	1.38(2)	C31-C36	1.39(2)	C32-C33	1.34(3)
C33-C34	1.32(3)	C34-C35	1.40(2)	C35-C36	1.43(2)
C36-C37	1.473(19)	C37-C38	1.50(2)	C37-C41	1.35(2)
C38-C39	1.52(2)	C39-C40	1.58(2)	C40-C41	1.51(2)
C40-C49	1.49(2)	C42-C43	1.50(2)	C43-C44	1.35(2)
C43-C48	1.39(2)	C44-C45	1.42(2)	C45-C46	1.35(3)
C46-C47	1.37(3)	C47-C48	1.38(2)	C49-C50	1.52(2)

C50-C51	1.54(2)	C50-C52	1.51(2)	C50-C53	1.57(2)
C50-C54	1.90(2)	C51-C54	1.55(2)	C52-C54	1.58(2)
C53-C54	1.553(19)	C54-B2	1.58(2)	C55-C56	1.539(17)
C55-C57	1.539(17)	C55-C58	1.534(18)	C55*-C56*	1.539(19)
C55*-C57*	1.536(19)	C55*-C58*	1.545(19)	C56-C59	1.535(17)
C56-C60	1.547(17)	C56*-C59*	1.549(19)	C56*-C60*	1.535(19)
Br2'-C32'	1.901(16)	Cl2'-C46'	1.741(16)	F2'-C34'	1.35(2)
O3'-C55'	1.45(2)	O3'-B2'	1.38(2)	O4'-C56'	1.46(2)
O4'-B2'	1.34(3)	N2'-C31'	1.38(2)	N2'-C41'	1.37(2)
N2'-C42'	1.475(19)	C31'-C32'	1.41(3)	C31'-C36'	1.42(2)
C32'-C33'	1.40(2)	C33'-C34'	1.31(3)	C34'-C35'	1.37(3)
C35'-C36'	1.42(2)	C36'-C37'	1.41(3)	C37'-C38'	1.46(3)
C37'-C41'	1.36(2)	C38'-C39'	1.52(2)	C39'-C40'	1.54(2)
C40'-C41'	1.50(2)	C40'-C49'	1.52(2)	C42'-C43'	1.51(2)
C43'-C44'	1.42(2)	C43'-C48'	1.37(3)	C44'-C45'	1.32(3)
C45'-C46'	1.40(3)	C46'-C47'	1.37(3)	C47'-C48'	1.43(2)
C49'-C50'	1.51(2)	C50'-C51'	1.55(3)	C50'-C52'	1.58(3)
C50'-C53'	1.59(2)	C50'-C54'	1.91(2)	C51'-C54'	1.54(2)
C52'-C54'	1.57(2)	C53'-C54'	1.59(3)	C54'-B2'	1.55(3)
C55'-C56'	1.58(3)	C55'-C57'	1.49(2)	C55'-C58'	1.52(3)
C56'-C59'	1.56(3)	C56'-C60'	1.47(4)		

Table S13. Bond Angles in Compound 4ar, °

B1-O1-C26	105.7(14)	B1-O2-C25	108.6(15)	C1-N1-C12	128.4(14)
C11-N1-C1	107.2(13)	C11-N1-C12	124.4(14)	N1-C1-C2	134.8(15)
N1-C1-C6	108.2(13)	C2-C1-C6	117.0(15)	C1-C2-Br1	121.3(13)
C3-C2-Br1	117.8(14)	C3-C2-C1	120.9(18)	C4-C3-C2	120.4(19)
F1-C4-C5	116.0(17)	C3-C4-F1	120(2)	C3-C4-C5	124.1(17)
C6-C5-C4	115.6(16)	C5-C6-C1	121.9(16)	C5-C6-C7	132.7(16)
C7-C6-C1	105.4(14)	C6-C7-C8	140.7(18)	C11-C7-C6	107.4(15)
C11-C7-C8	111.7(17)	C7-C8-C9	100.3(15)	C8-C9-C10	109.7(14)
C11-C10-C9	99.2(15)	C11-C10-C19	111.6(12)	C19-C10-C9	117.8(16)
N1-C11-C10	134.5(15)	C7-C11-N1	111.8(15)	C7-C11-C10	113.7(14)
N1-C12-C13	115.0(12)	C14-C13-C12	122.3(14)	C18-C13-C12	119.3(15)
C18-C13-C14	118.4(15)	C15-C14-C13	118.5(17)	C16-C15-C14	122.9(19)
C15-C16-Cl1	121.3(19)	C17-C16-Cl1	117.6(19)	C17-C16-C15	121.0(18)
C16-C17-C18	118.5(18)	C13-C18-C17	120.6(18)	C20-C19-C10	111.7(13)
C19-C20-C21	129.6(17)	C19-C20-C22	124.3(13)	C19-C20-C23	129.0(16)
C19-C20-C24	176.9(14)	C21-C20-C24	52.1(10)	C22-C20-C21	85.3(13)
C22-C20-C24	52.6(10)	C23-C20-C21	85.9(12)	C23-C20-C22	88.6(15)
C23-C20-C24	52.5(10)	C24-C21-C20	74.9(12)	C20-C22-C24	75.5(12)
C20-C23-C24	77.1(13)	C21-C24-C20	53.1(10)	C21-C24-C22	85.6(15)
C21-C24-B1	128.3(13)	C22-C24-C20	51.9(11)	C22-C24-B1	125.2(16)
C23-C24-C20	50.5(10)	C23-C24-C21	85.2(15)	C23-C24-C22	86.6(13)
C23-C24-B1	131.0(16)	B1-C24-C20	177.1(14)	O2-C25-C26	101.3(14)
O2-C25-C27	105.2(17)	C26-C25-C27	109.7(17)	C28-C25-O2	109.8(15)
C28-C25-C26	119.0(19)	C28-C25-C27	110.8(17)	O1-C26-C25	102.6(16)
O1-C26-C29	107.8(15)	O1-C26-C30	106.7(16)	C25-C26-C30	111.6(17)
C29-C26-C25	119.3(15)	C29-C26-C30	108.0(17)	O1-B1-C24	121.6(15)
O2-B1-O1	113.2(18)	O2-B1-C24	125.2(16)	B1'-O1'-C26'	110.0(14)
B1'-O2'-C25'	108.4(16)	C1'-N1'-C11'	107.4(11)	C1'-N1'-C12'	128.5(13)
C11'-N1'-C12'	123.4(12)	N1'-C1'-C6'	109.0(12)	C2'-C1'-N1'	132.4(13)
C2'-C1'-C6'	118.2(13)	C1'-C2'-Br1'	124.1(12)	C1'-C2'-C3'	122.1(14)
C3'-C2'-Br1'	113.8(12)	C2'-C3'-C4'	116.8(14)	F1'-C4'-C3'	116.6(13)
F1'-C4'-C5'	118.9(14)	C5'-C4'-C3'	124.4(13)	C4'-C5'-C6'	117.2(13)
C5'-C6'-C1'	121.2(13)	C5'-C6'-C7'	134.8(13)	C7'-C6'-C1'	104.0(12)
C6'-C7'-C8'	139.3(13)	C11'-C7'-C6'	110.3(12)	C11'-C7'-C8'	110.0(13)
C7'-C8'-C9'	100.4(12)	C8'-C9'-C10'	109.1(12)	C11'-C10'-C9'	97.6(11)
C19'-C10'-C9'	115.3(12)	C19'-C10'-C11'	119.4(13)	N1'-C11'-C10'	134.6(12)
C7'-C11'-N1'	109.2(13)	C7'-C11'-C10'	115.7(13)	N1'-C12'-C13'	114.0(11)
C14'-C13'-C12'	117.6(13)	C18'-C13'-C12'	122.4(12)	C18'-C13'-C14'	120.0(13)
C15'-C14'-C13'	121.1(14)	C16'-C15'-C14'	117.5(13)	C15'-C16'-Cl1'	118.2(10)
C15'-C16'-C17'	122.4(13)	C17'-C16'-Cl1'	119.4(12)	C18'-C17'-C16'	119.8(15)
C17'-C18'-C13'	119.1(14)	C10'-C19'-C20'	115.1(13)	C19'-C20'-C21'	128.9(13)

C19'-C20'-C22'	122.4(13)	C19'-C20'-C23'	129.8(14)	C19'-C20'-C24'	174.6(14)
C21'-C20'-C22'	87.1(11)	C21'-C20'-C24'	52.2(8)	C22'-C20'-C24'	52.4(8)
C23'-C20'-C21'	86.8(12)	C23'-C20'-C22'	88.3(12)	C23'-C20'-C24'	54.1(9)
C24'-C21'-C20'	74.7(10)	C24'-C22'-C20'	74.0(11)	C20'-C23'-C24'	73.7(11)
C21'-C24'-C20'	53.0(8)	C21'-C24'-C22'	88.5(13)	C21'-C24'-C23'	85.9(12)
C21'-C24'-B1'	129.9(12)	C22'-C24'-C20'	53.6(9)	C22'-C24'-C23'	87.8(12)
C22'-C24'-B1'	124.3(13)	C23'-C24'-C20'	52.1(9)	C23'-C24'-B1'	127.0(14)
B1'-C24'-C20'	177.0(11)	O2'-C25'-C26'	103.4(15)	O2'-C25'-C27'	106.1(17)
O2'-C25'-C28'	106(2)	C27'-C25'-C26'	116.2(17)	C28'-C25'-C26'	115.8(17)
C28'-C25'-C27'	108(2)	O1'-C26'-C25'	103.0(14)	O1'-C26'-C29'	105.9(17)
O1'-C26'-C30'	108(2)	C29'-C26'-C25'	111.9(19)	C30'-C26'-C25'	114.6(17)
C30'-C26'-C29'	112(2)	O1'-B1'-O2'	113.2(15)	O1'-B1'-C24'	122.4(14)
O2'-B1'-C24'	124.3(15)	B2-O3-C55	105.7(16)	B2-O3*-C55*	111(3)
B2-O4-C56	104.0(16)	B2-O4*-C56*	113(3)	C31-N2-C42	123.8(14)
C41-N2-C31	106.8(12)	C41-N2-C42	124.0(14)	C32-C31-N2	133.2(15)
C32-C31-C36	117.7(17)	C36-C31-N2	108.5(14)	C31-C32-Br2	121.8(14)
C33-C32-Br2	117.3(12)	C33-C32-C31	120.8(15)	C34-C33-C32	121.0(16)
F2-C34-C35	115.9(14)	C33-C34-F2	119.5(14)	C33-C34-C35	124.5(18)
C34-C35-C36	113.0(15)	C31-C36-C35	122.4(14)	C31-C36-C37	105.8(14)
C35-C36-C37	131.8(13)	C36-C37-C38	139.9(15)	C41-C37-C36	106.5(13)
C41-C37-C38	113.1(14)	C37-C38-C39	101.7(13)	C38-C39-C40	107.9(12)
C41-C40-C39	99.7(12)	C49-C40-C39	116.2(12)	C49-C40-C41	119.8(13)
N2-C41-C40	134.6(13)	C37-C41-N2	112.5(14)	C37-C41-C40	112.6(13)
N2-C42-C43	116.1(14)	C44-C43-C42	123.2(15)	C44-C43-C48	118.9(15)
C48-C43-C42	117.9(15)	C43-C44-C45	120.5(16)	C46-C45-C44	118.4(16)
C45-C46-Cl2	119.0(14)	C45-C46-C47	122.5(16)	C47-C46-Cl2	118.5(13)
C46-C47-C48	118.2(19)	C47-C48-C43	121.4(18)	C40-C49-C50	117.8(13)
C49-C50-C51	129.8(15)	C49-C50-C53	126.1(12)	C49-C50-C54	177.7(13)
C51-C50-C53	86.2(12)	C51-C50-C54	52.3(9)	C52-C50-C49	125.6(13)
C52-C50-C51	87.8(11)	C52-C50-C53	87.7(12)	C52-C50-C54	53.9(9)
C53-C50-C54	52.2(8)	C50-C51-C54	75.7(12)	C50-C52-C54	75.6(11)
C54-C53-C50	74.7(10)	C51-C54-C50	51.9(9)	C51-C54-C52	85.0(13)
C51-C54-C53	86.6(12)	C51-C54-B2	131.1(13)	C52-C54-C50	50.6(8)
C53-C54-C50	53.1(9)	C53-C54-C52	86.0(11)	C53-C54-B2	128.3(13)
B2-C54-C50	175.3(13)	B2-C54-C52	124.8(13)	O3-C55-C56	100.5(16)
O3-C55-C57	107.4(19)	O3-C55-C58	109(2)	C57-C55-C56	114(2)
C58-C55-C56	113(2)	C58-C55-C57	112(2)	O3*-C55*-C56*	103(3)
O3*-C55*-C57*	109(4)	O3*-C55*-C58*	101(4)	C56*-C55*-C58*	115(5)
C57*-C55*-C56*	126(4)	C57*-C55*-C58*	100(5)	O4-C56-C55	103.2(16)
O4-C56-C59	111(2)	O4-C56-C60	107.8(17)	C55-C56-C60	112.3(18)
C59-C56-C55	113(2)	C59-C56-C60	110(2)	O4*-C56*-C55*	103(3)
O4*-C56*-C59*	102(4)	O4*-C56*-C60*	108(4)	C55*-C56*-C59*	106(5)
C60*-C56*-C55*	132(5)	C60*-C56*-C59*	103(5)	O3-B2-O4	115.8(17)

O3-B2-C54	123.6(16)	O3*-B2-C54	126.1(19)	O4-B2-C54	120.5(14)
O4*-B2-O3*	108(2)	O4*-B2-C54	126.1(19)	B2'-O3'-C55'	109.7(17)
B2'-O4'-C56'	110.8(16)	C31'-N2'-C42'	126.8(14)	C41'-N2'-C31'	107.7(14)
C41'-N2'-C42'	125.5(15)	N2'-C31'-C32'	133.0(15)	N2'-C31'-C36'	107.6(16)
C32'-C31'-C36'	119.4(15)	C31'-C32'-Br2'	123.7(12)	C33'-C32'-Br2'	119.0(13)
C33'-C32'-C31'	117.3(15)	C34'-C33'-C32'	123(2)	F2'-C34'-C35'	118.2(18)
C33'-C34'-F2'	119(2)	C33'-C34'-C35'	123(2)	C34'-C35'-C36'	118.3(17)
C35'-C36'-C31'	119.3(16)	C37'-C36'-C31'	106.7(15)	C37'-C36'-C35'	134.0(16)
C36'-C37'-C38'	141.7(16)	C41'-C37'-C36'	107.4(15)	C41'-C37'-C38'	110.7(16)
C37'-C38'-C39'	103.1(14)	C38'-C39'-C40'	110.9(16)	C41'-C40'-C39'	98.5(14)
C41'-C40'-C49'	117.6(12)	C49'-C40'-C39'	113.4(14)	N2'-C41'-C40'	133.9(15)
C37'-C41'-N2'	110.6(16)	C37'-C41'-C40'	115.5(15)	N2'-C42'-C43'	112.6(13)
C44'-C43'-C42'	118.2(17)	C48'-C43'-C42'	123.4(14)	C48'-C43'-C44'	118.4(15)
C45'-C44'-C43'	122.5(19)	C44'-C45'-C46'	118.4(16)	C45'-C46'-Cl2'	118.2(14)
C47'-C46'-Cl2'	118.9(17)	C47'-C46'-C45'	122.8(15)	C46'-C47'-C48'	117.0(19)
C43'-C48'-C47'	120.7(16)	C50'-C49'-C40'	114.2(13)	C49'-C50'-C51'	130.2(16)
C49'-C50'-C52'	126.2(14)	C49'-C50'-C53'	126.5(14)	C49'-C50'-C54'	178.0(15)
C51'-C50'-C52'	86.9(15)	C51'-C50'-C53'	86.1(13)	C51'-C50'-C54'	51.7(10)
C52'-C50'-C53'	86.8(15)	C52'-C50'-C54'	52.3(9)	C53'-C50'-C54'	53.1(10)
C54'-C51'-C50'	76.3(13)	C54'-C52'-C50'	75.0(13)	C54'-C53'-C50'	73.8(12)
C51'-C54'-C50'	51.9(10)	C51'-C54'-C52'	87.3(13)	C51'-C54'-C53'	86.3(14)
C51'-C54'-B2'	131.8(15)	C52'-C54'-C50'	52.7(10)	C52'-C54'-C53'	87.2(13)
C53'-C54'-C50'	53.1(10)	B2'-C54'-C50'	172.9(13)	B2'-C54'-C52'	120.1(15)
B2'-C54'-C53'	129.8(14)	O3'-C55'-C56'	103.7(15)	O3'-C55'-C57'	111(2)
O3'-C55'-C58'	107.7(18)	C57'-C55'-C56'	114.5(19)	C57'-C55'-C58'	107(2)
C58'-C55'-C56'	112.9(17)	O4'-C56'-C55'	103.4(17)	O4'-C56'-C59'	105.4(18)
O4'-C56'-C60'	109(2)	C59'-C56'-C55'	112.7(17)	C60'-C56'-C55'	119(2)
C60'-C56'-C59'	107(3)	O3'-B2'-C54'	122.1(19)	O4'-B2'-O3'	112.0(17)
O4'-B2'-C54'	125.9(16)				

This report has been created with Olex2[38], compiled on 2020.11.12 svn.r5f609507 for OlexSys.

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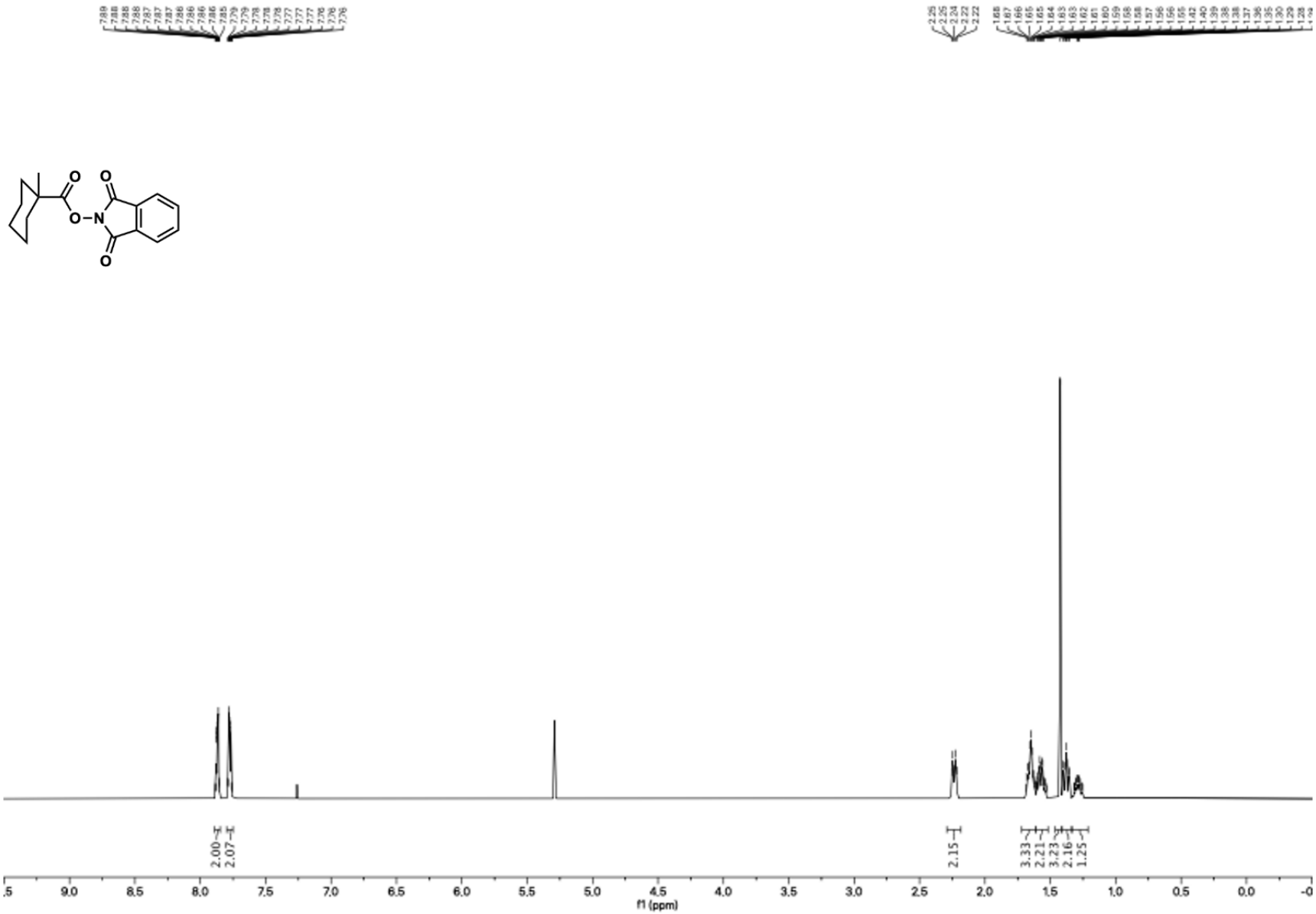
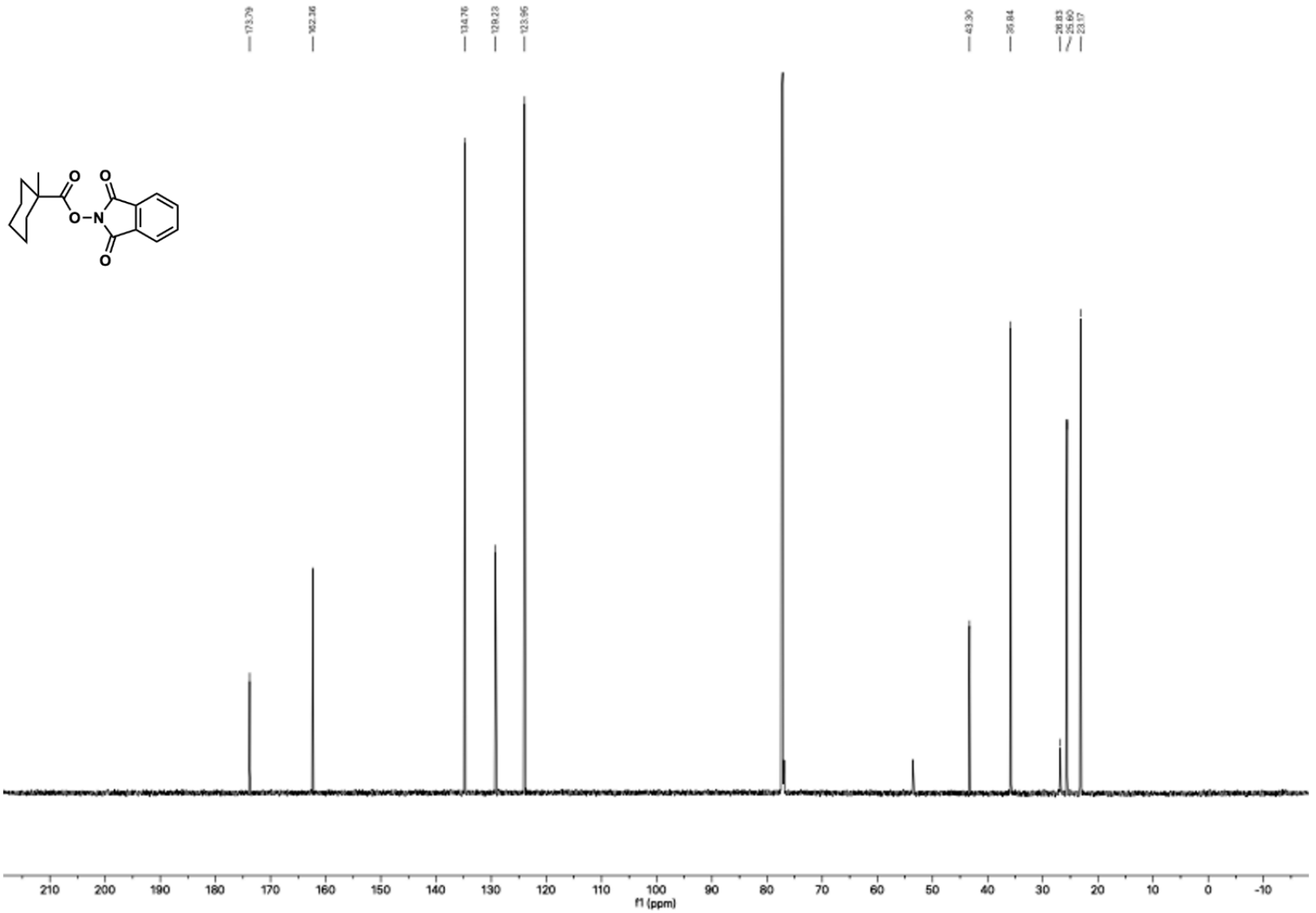
11. NMR Spectra of Synthesized Compounds

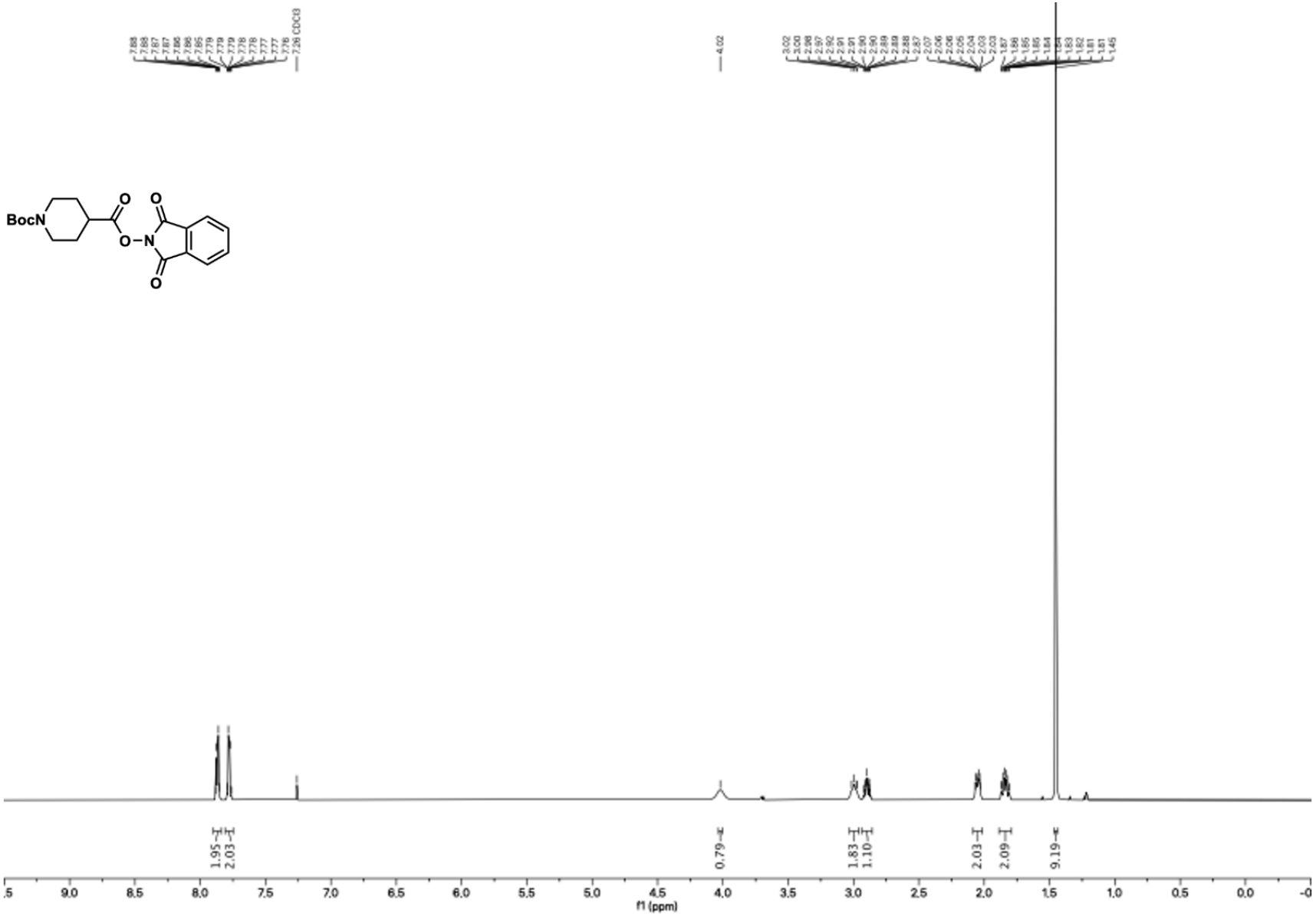
^{1}H NMR (600 MHz, $CDCl_3$) of **1a**



^{13}C NMR (151 MHz, $CDCl_3$) of **1a**



^{1}H NMR (600 MHz, $CDCl_3$) of **1b**



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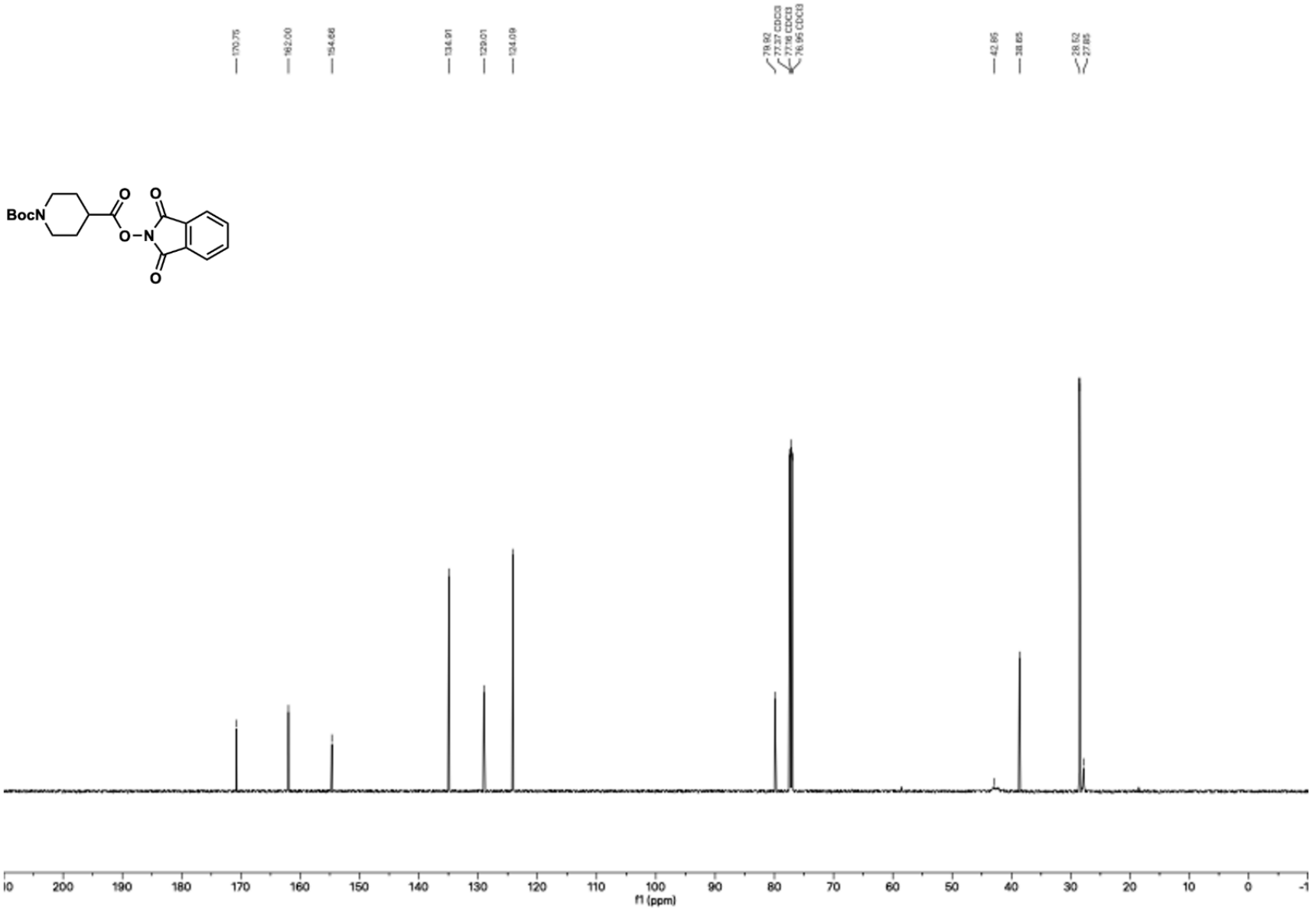

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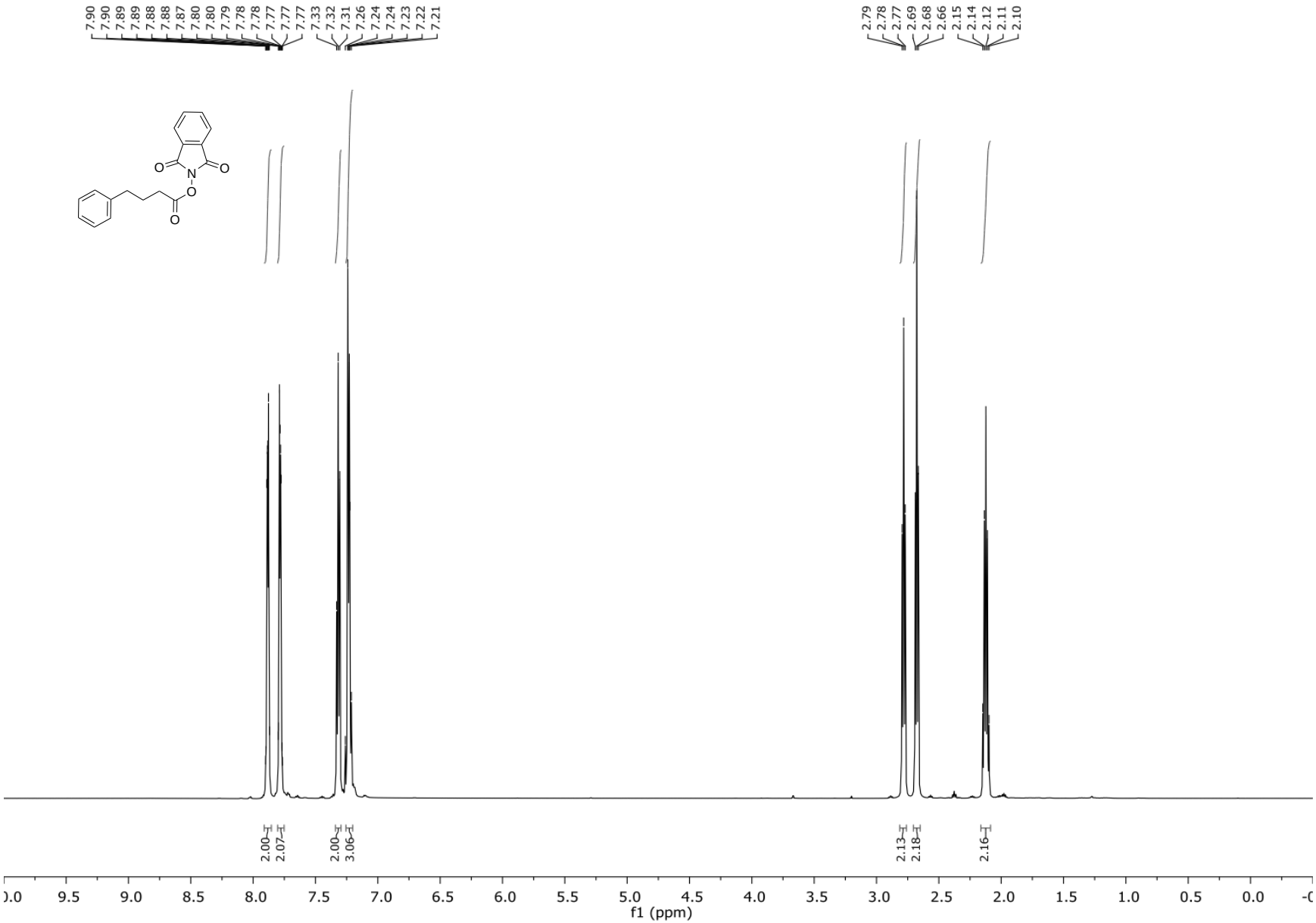

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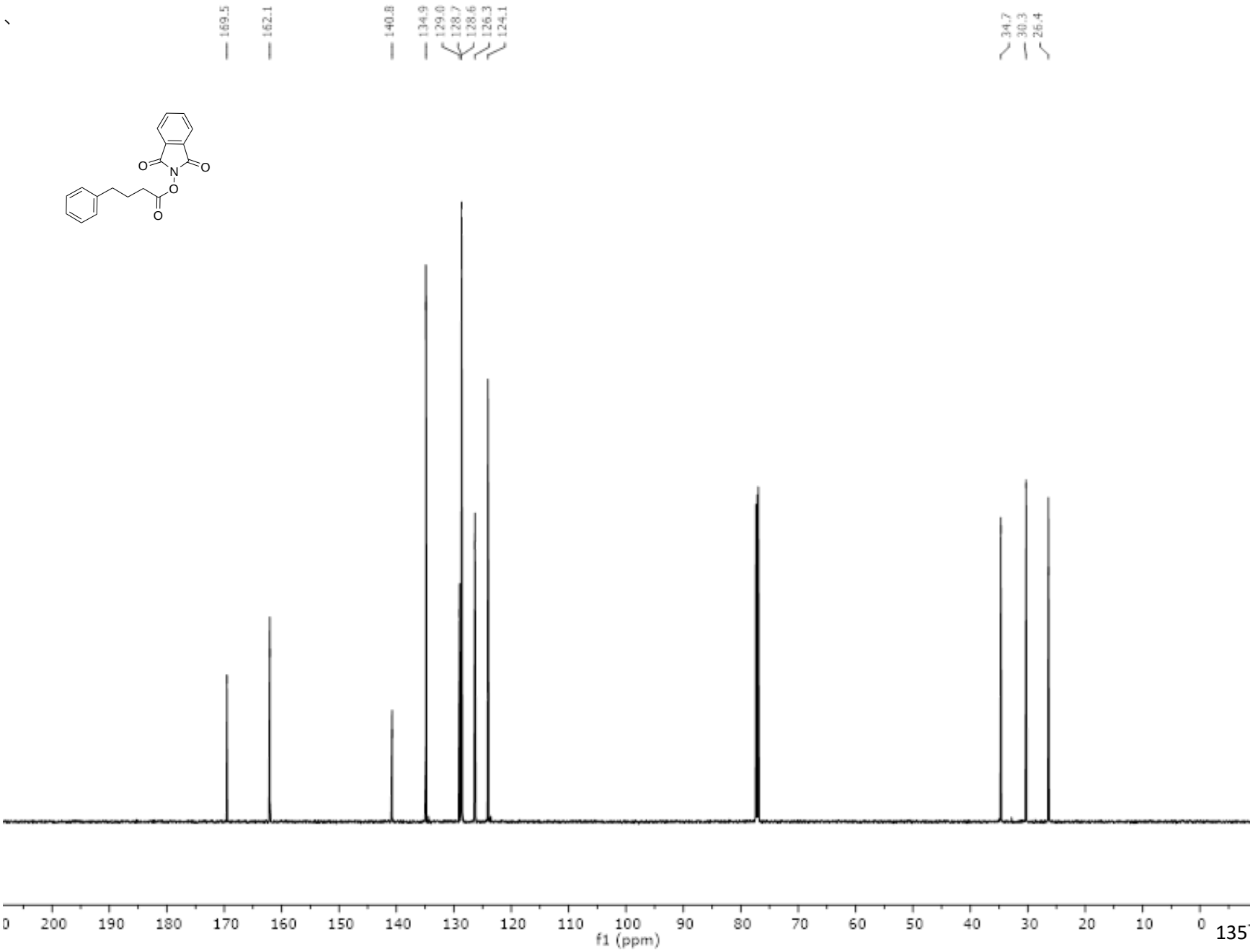

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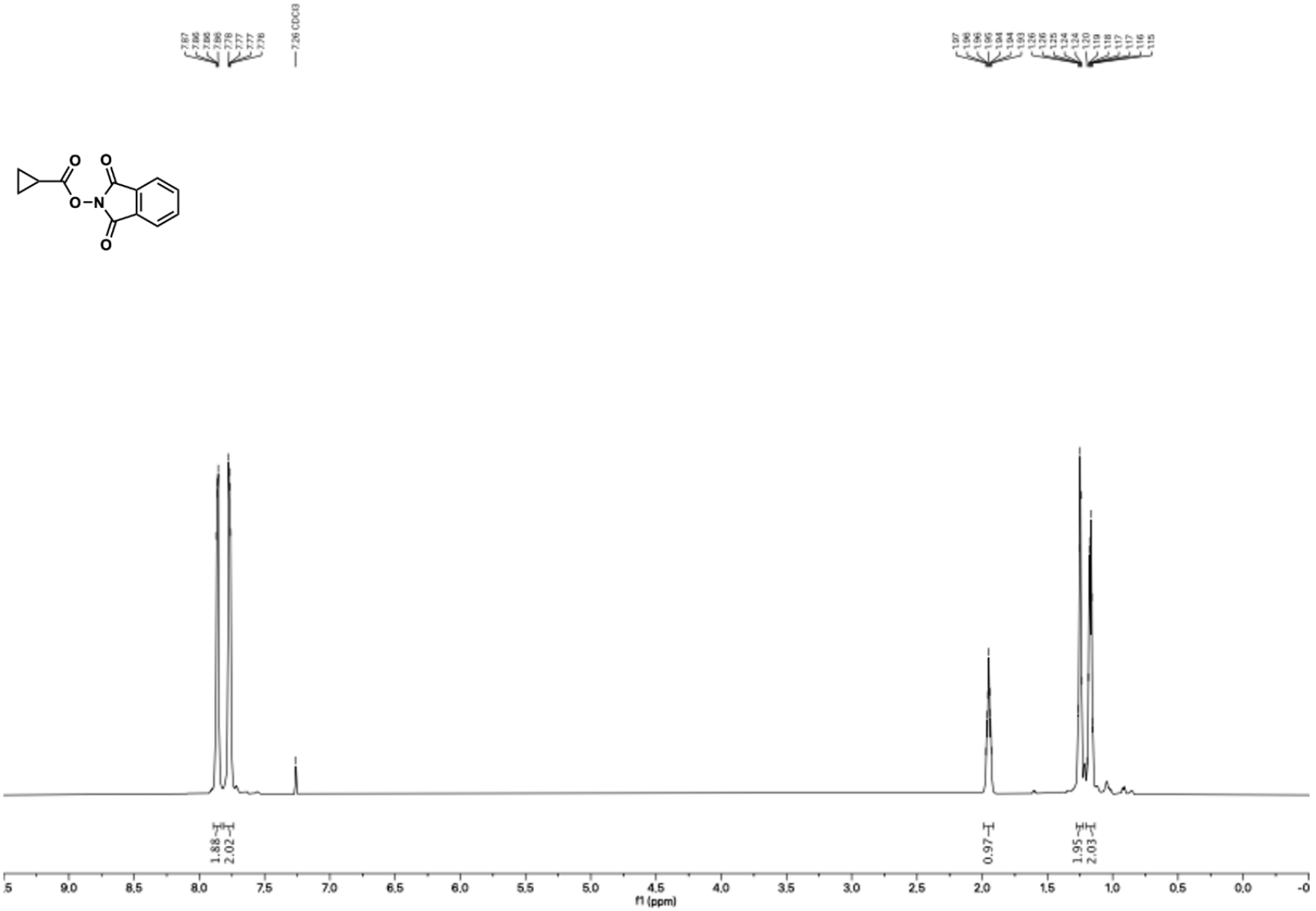

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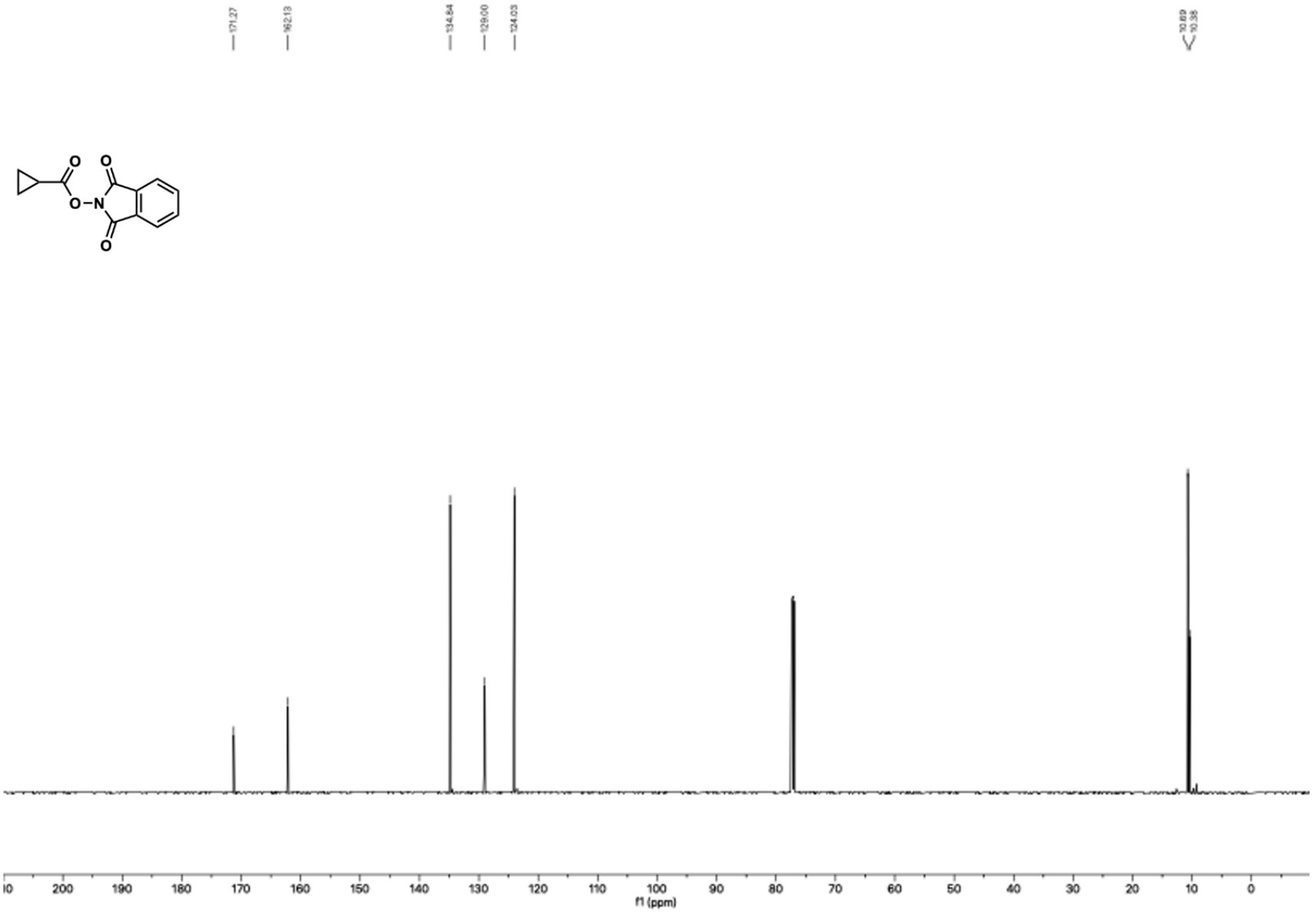

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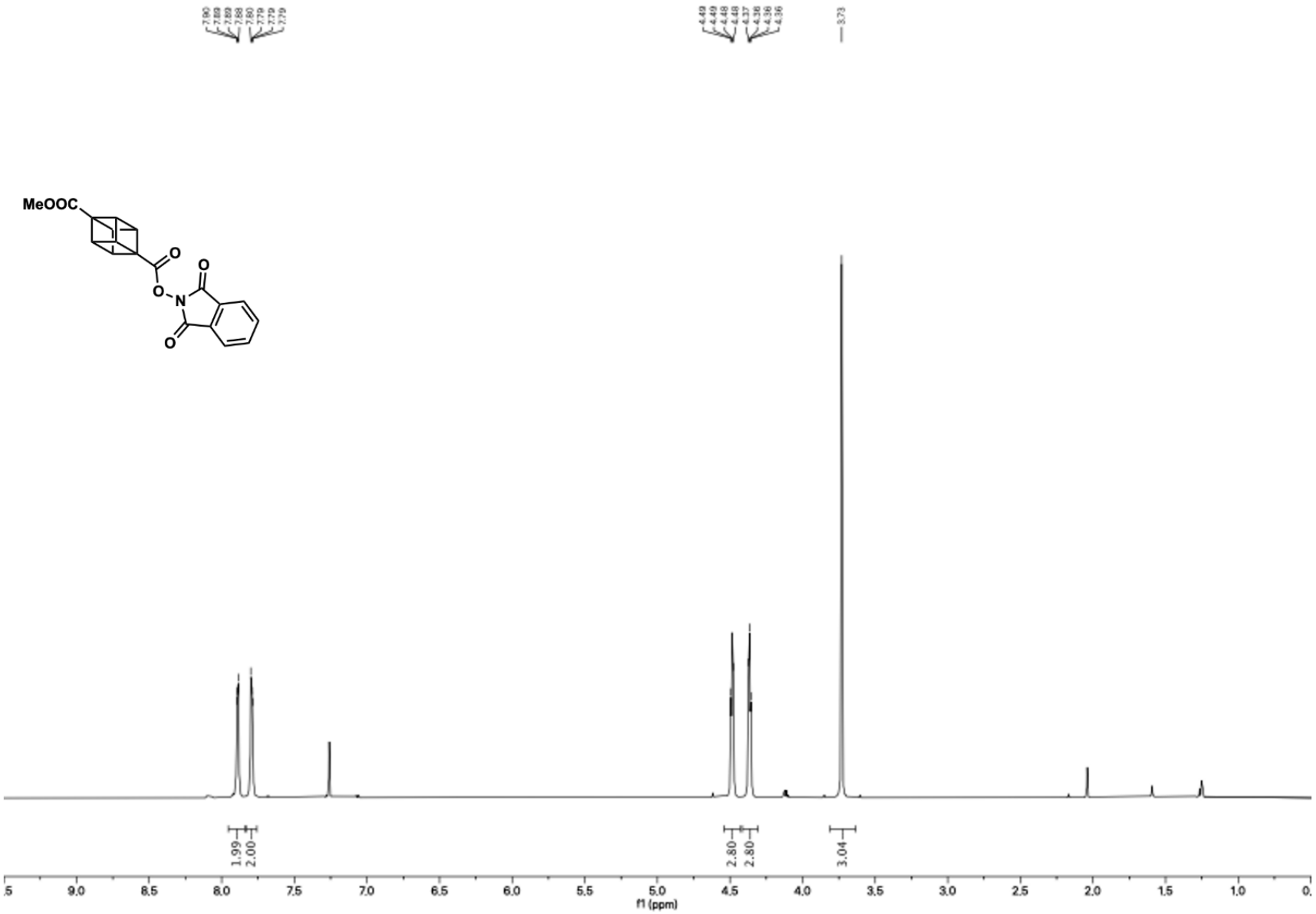

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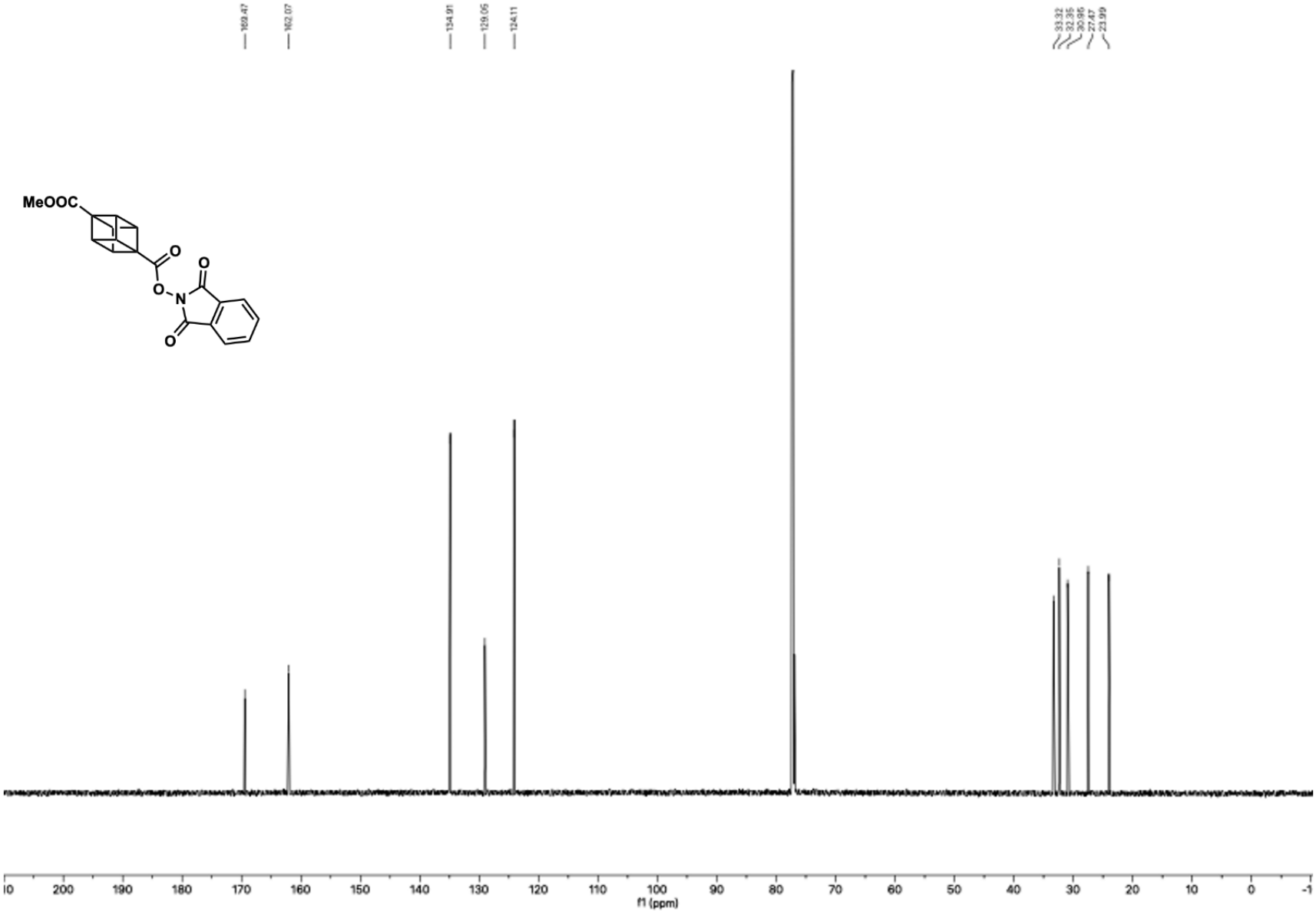
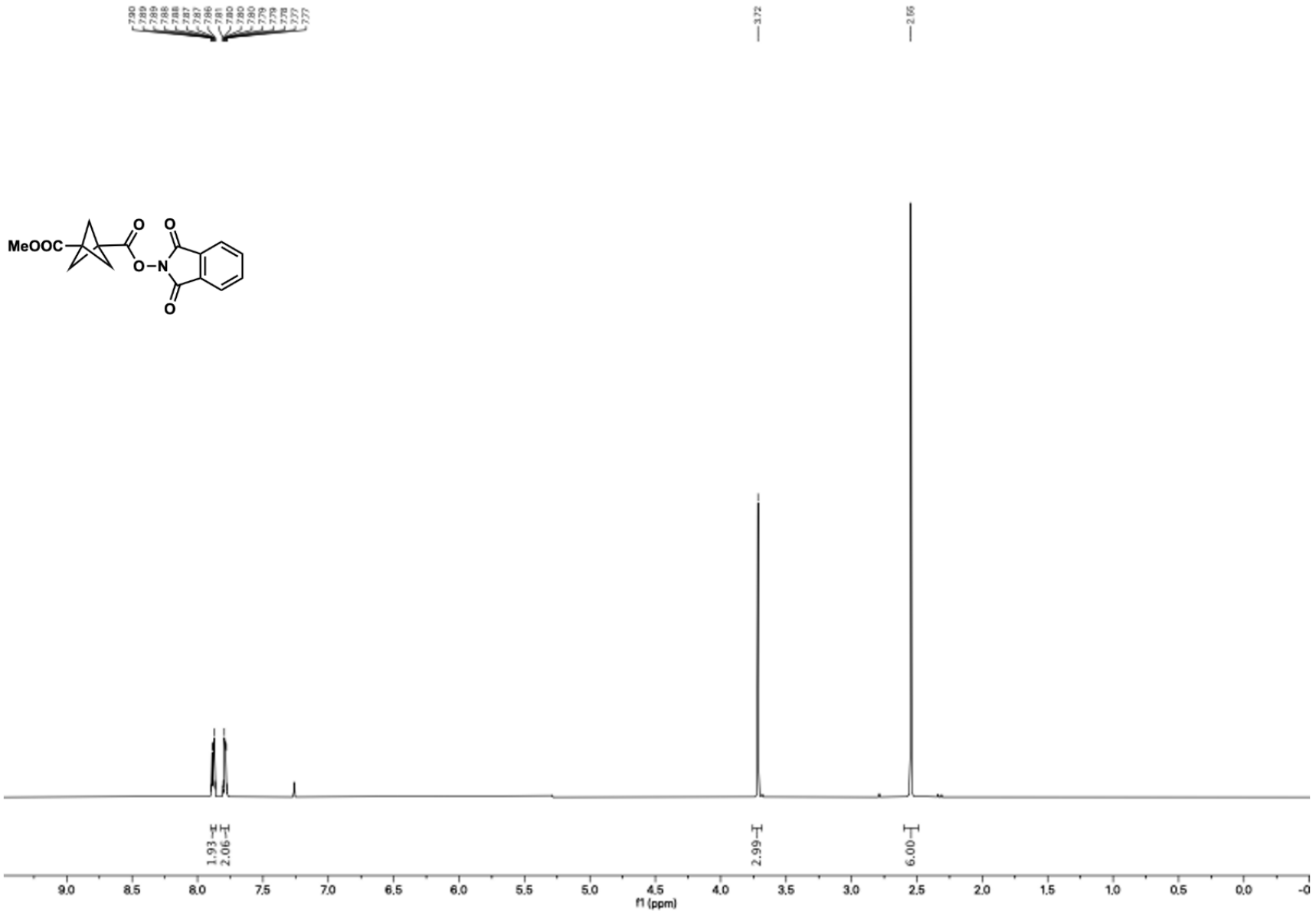


^{1}H NMR (600 MHz, $CDCl_3$) of **1f**



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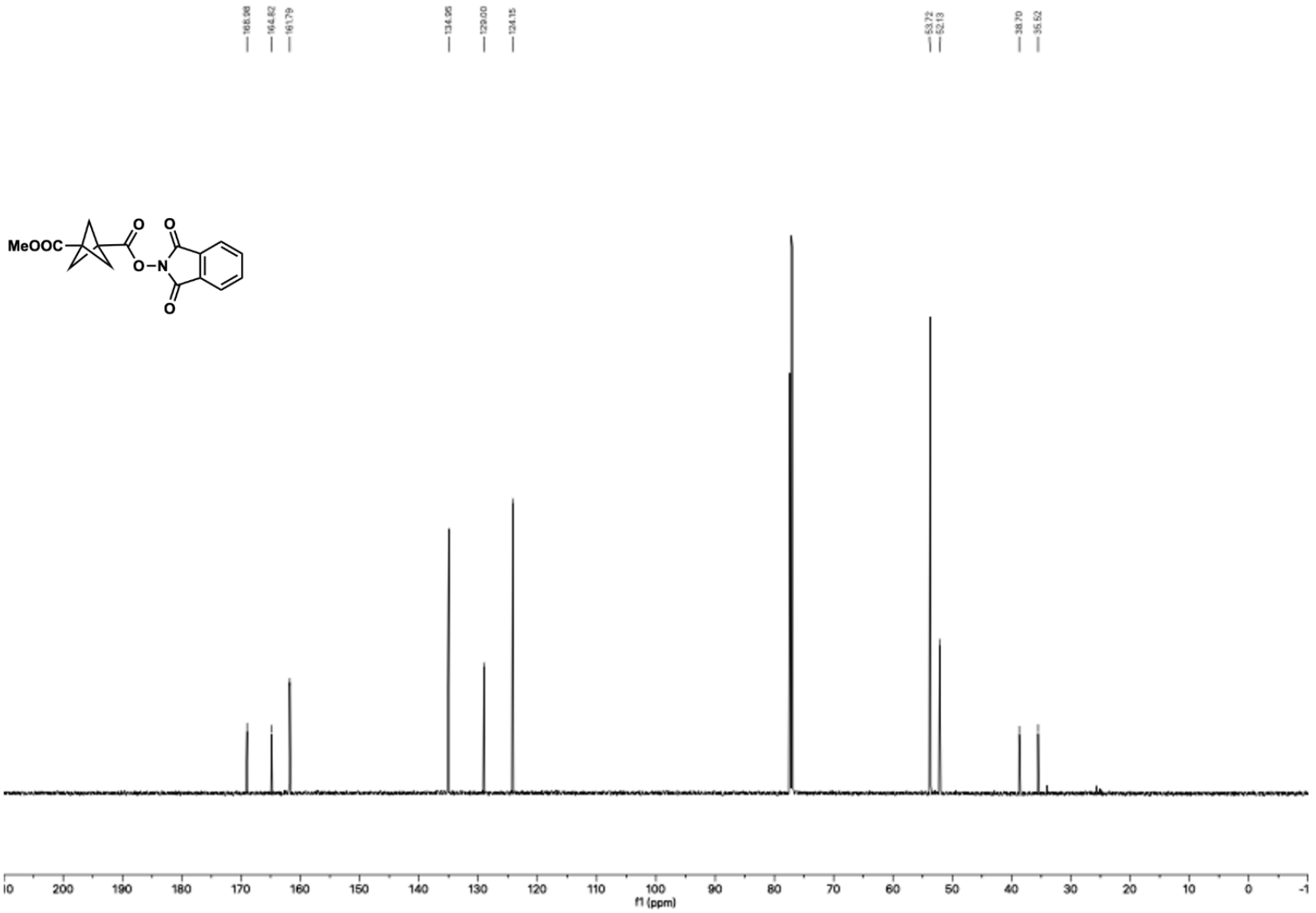

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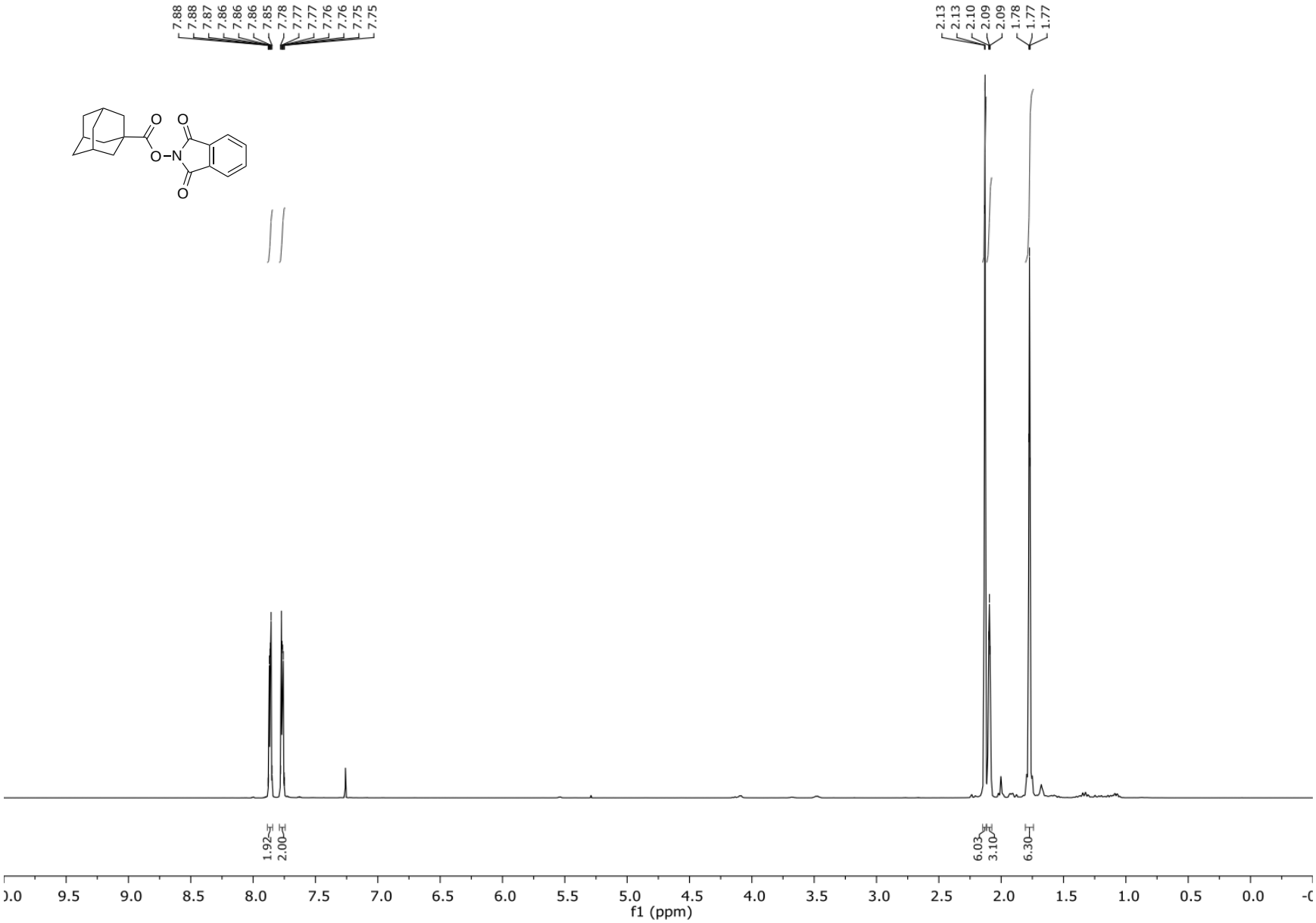

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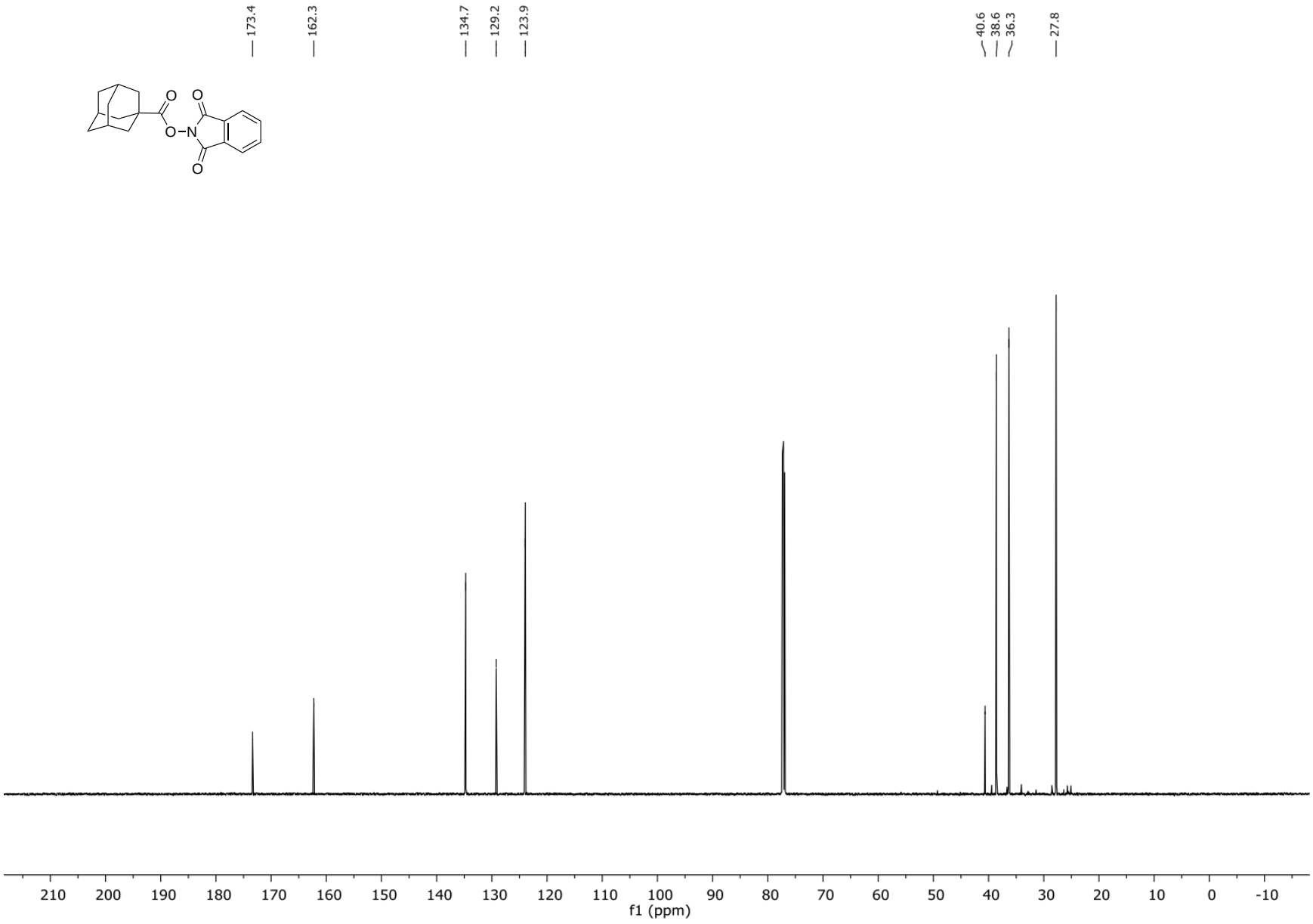

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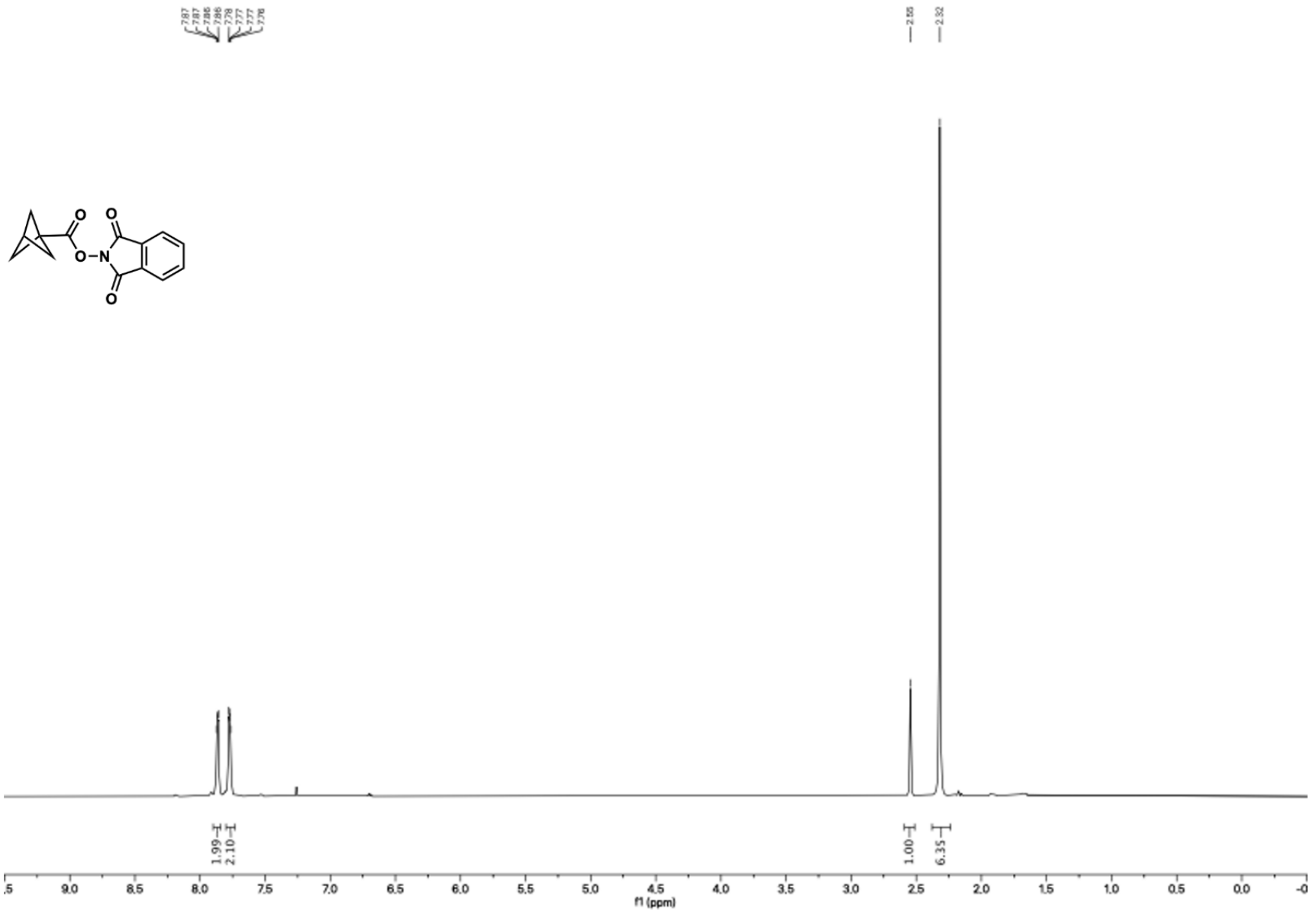

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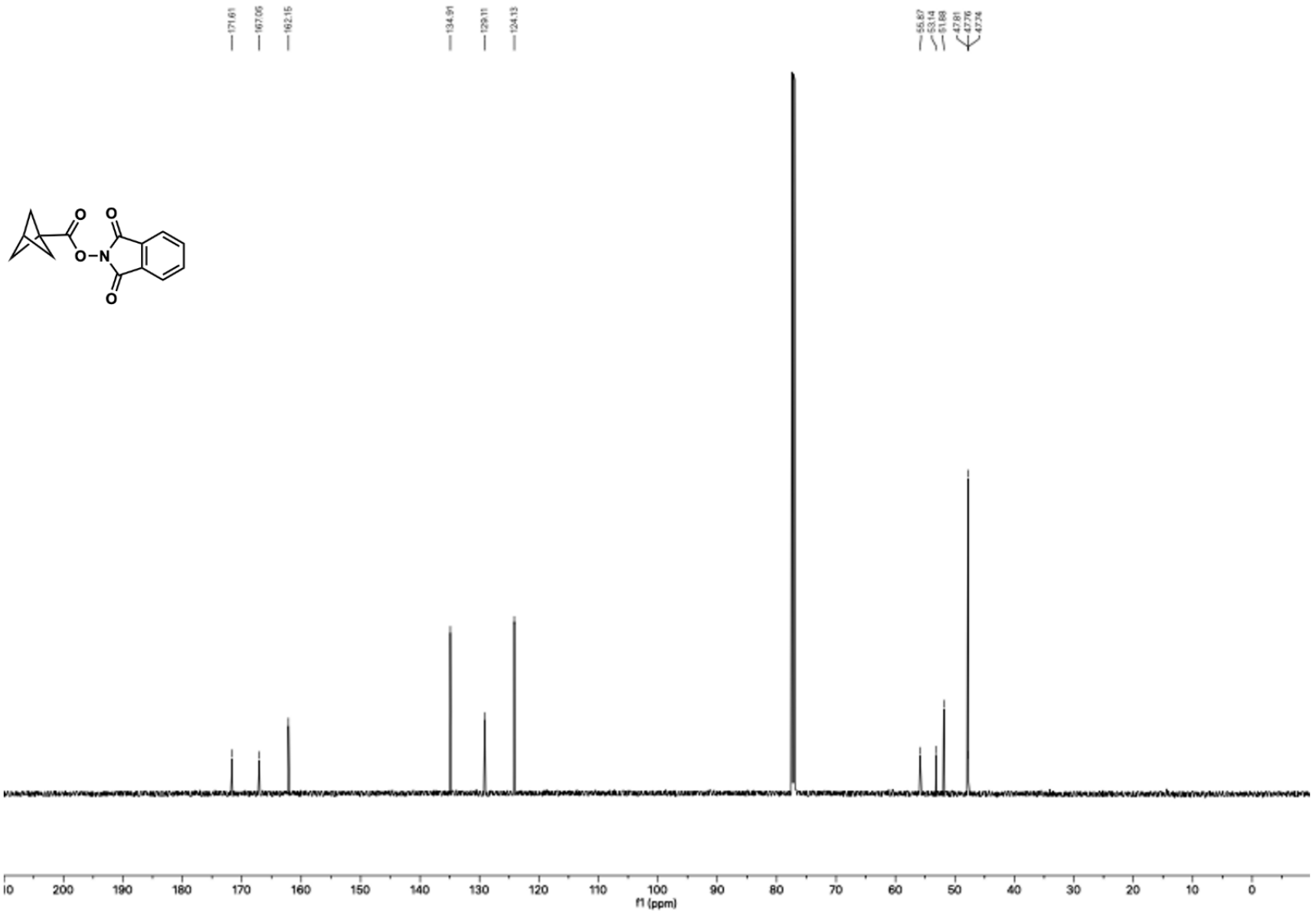

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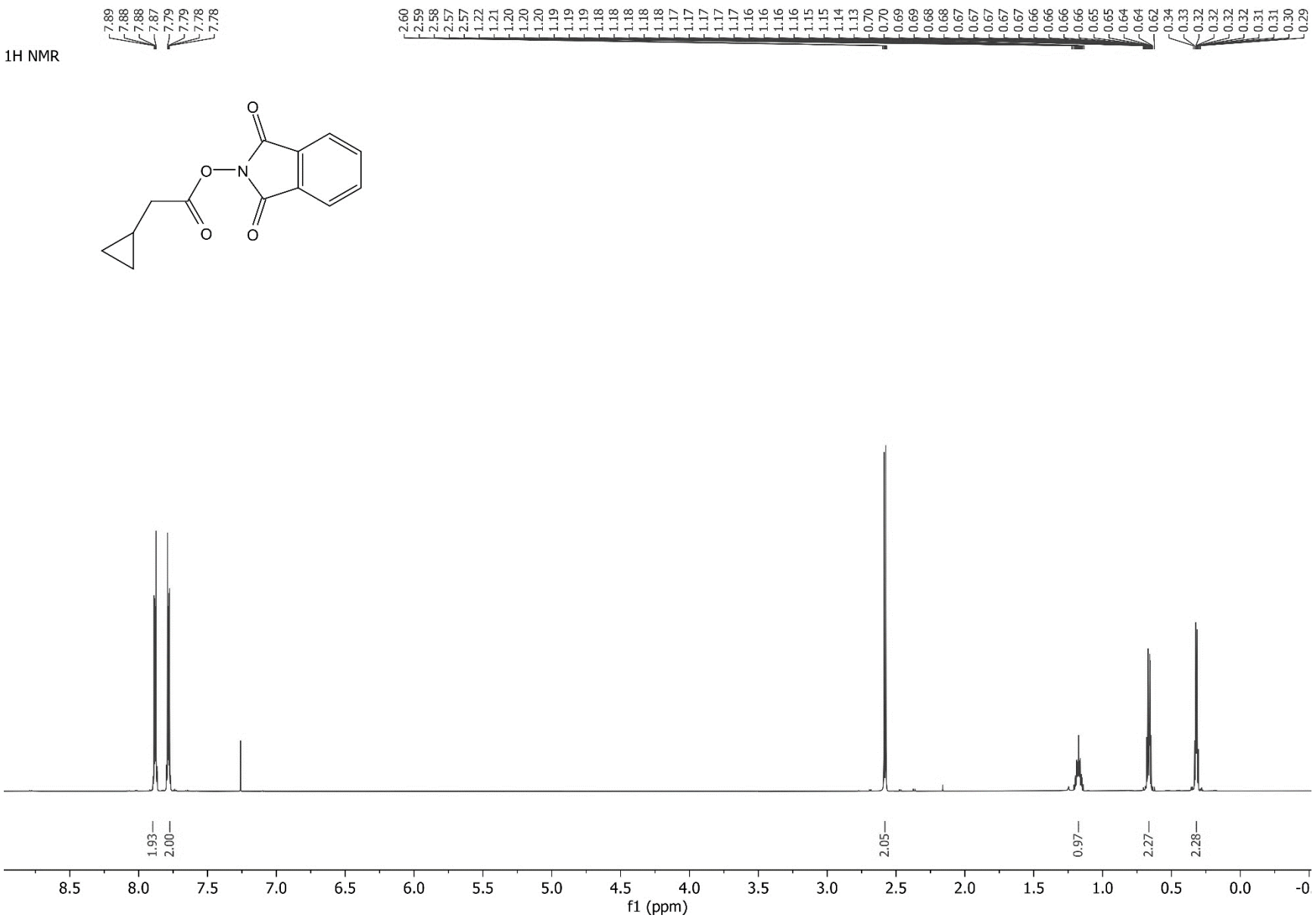
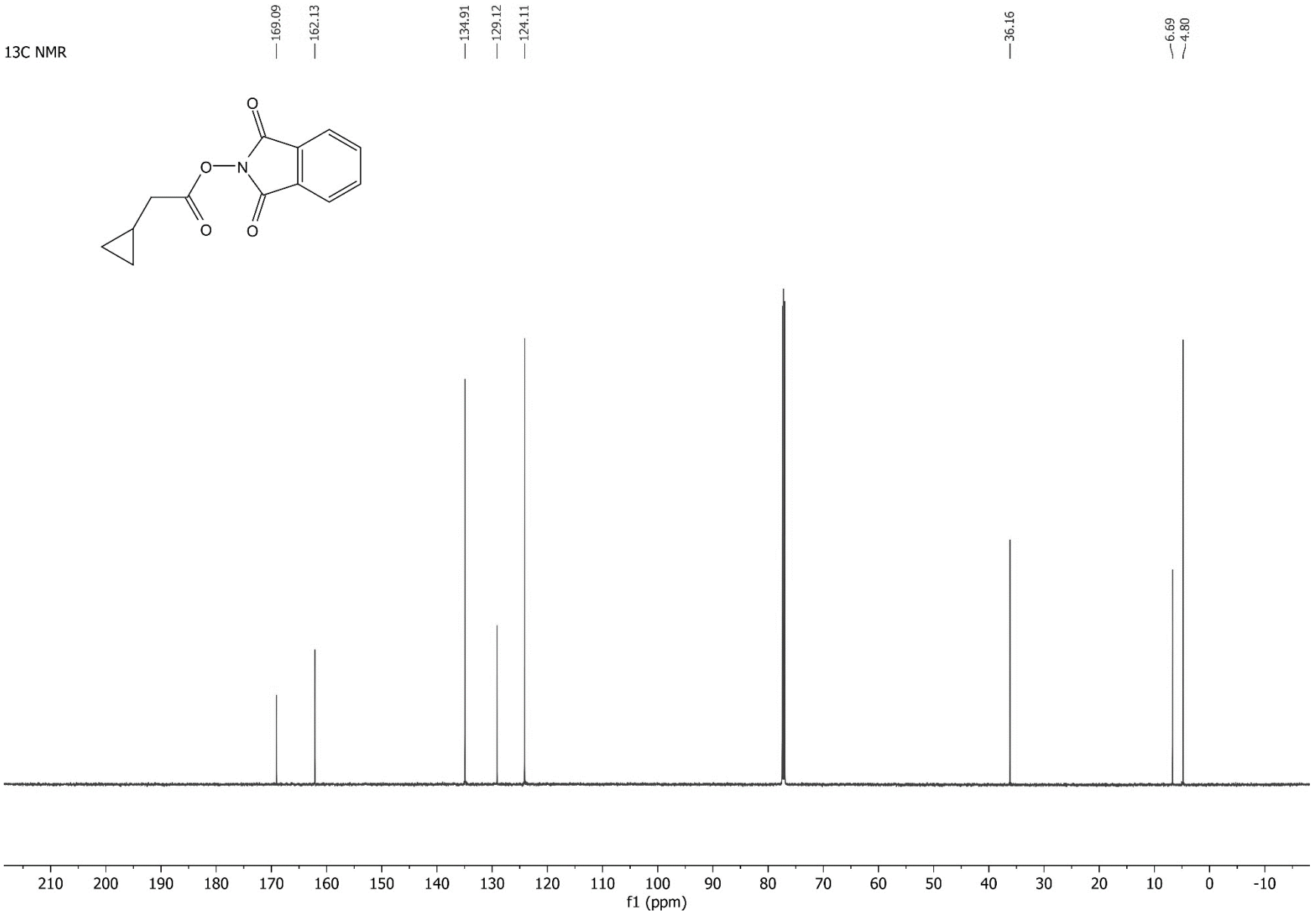
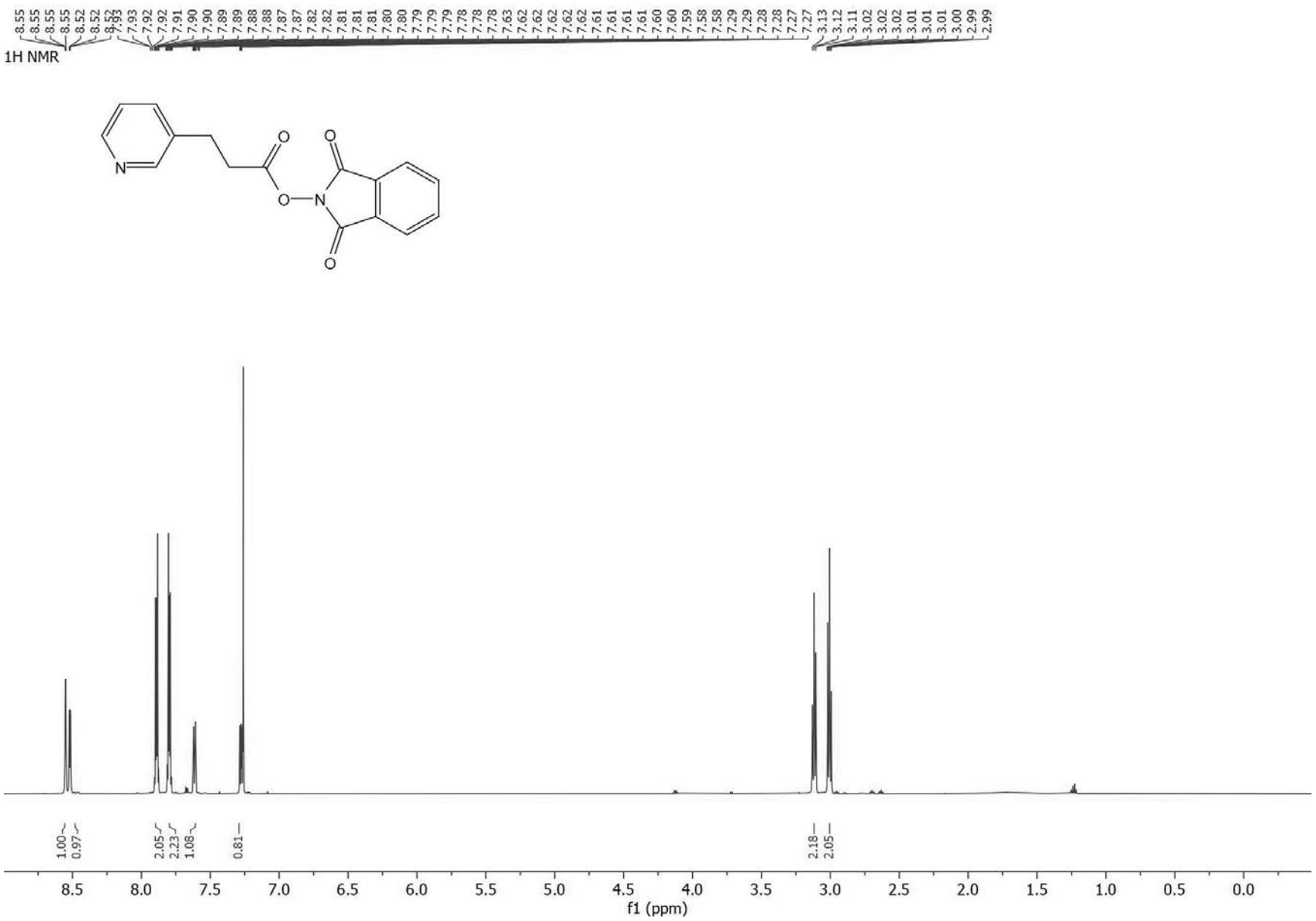


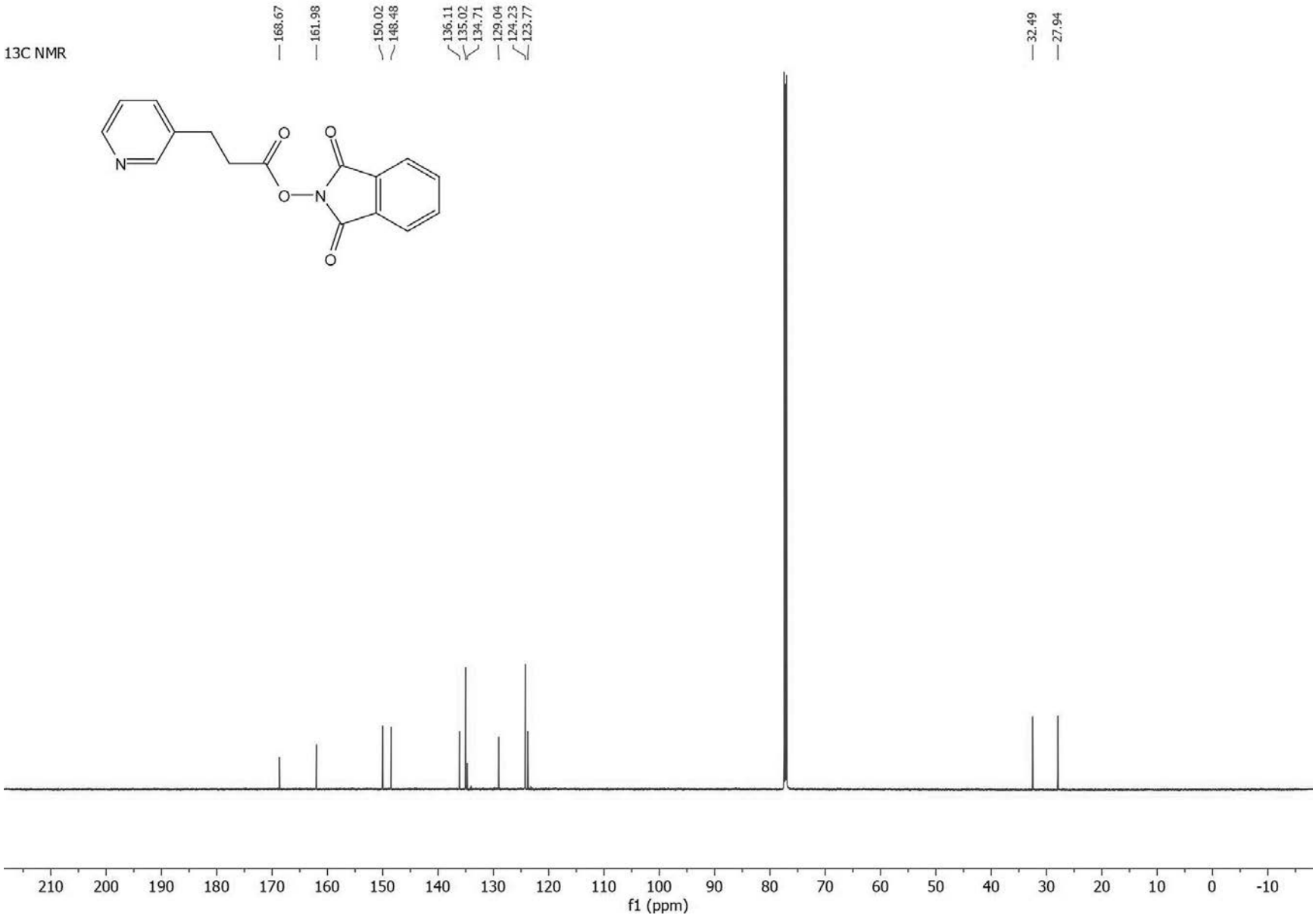
^{13}C NMR (151 MHz, $CDCl_3$) of **1i**



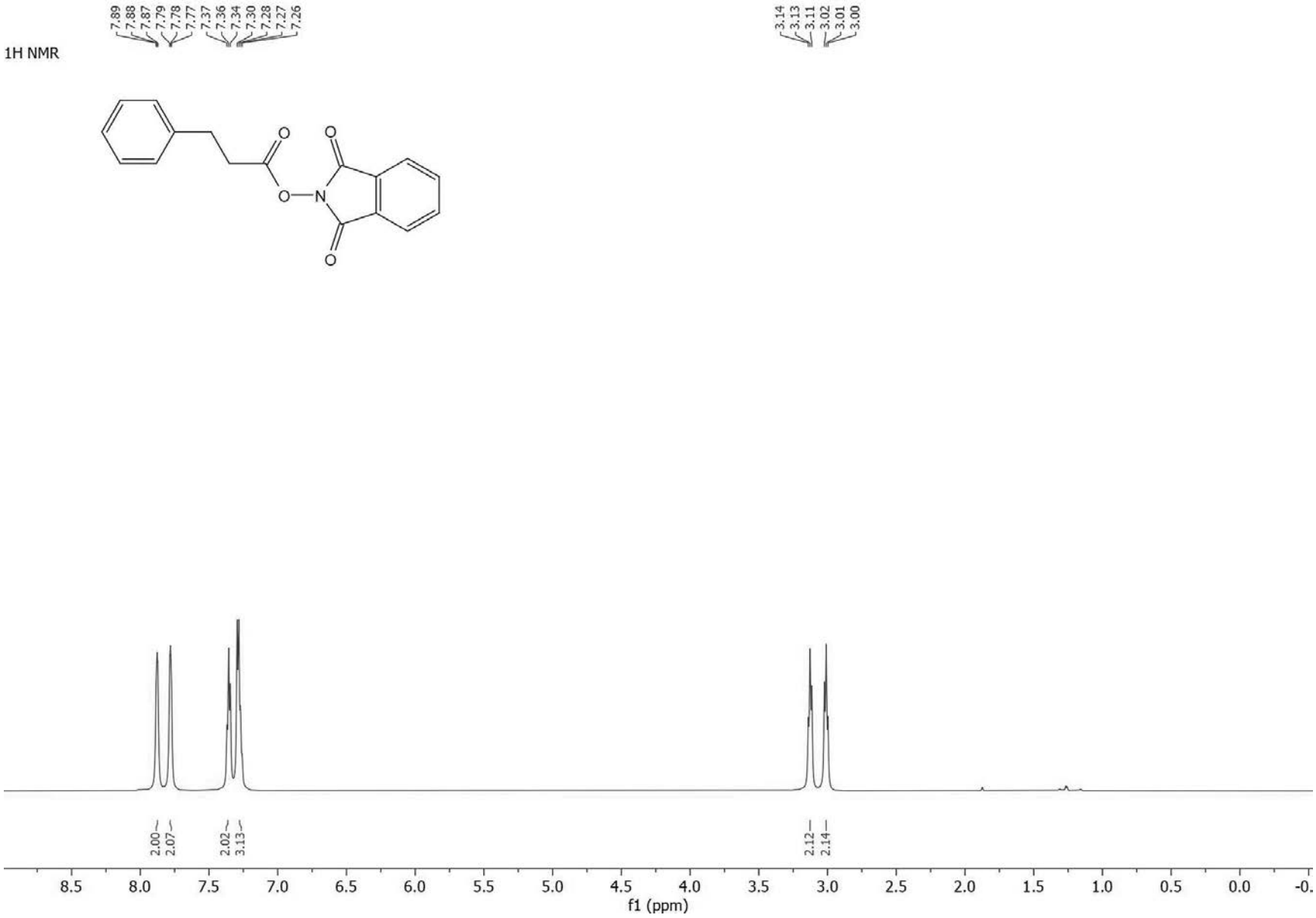
^{1}H NMR (600 MHz, $CDCl_3$) of **S-1a**



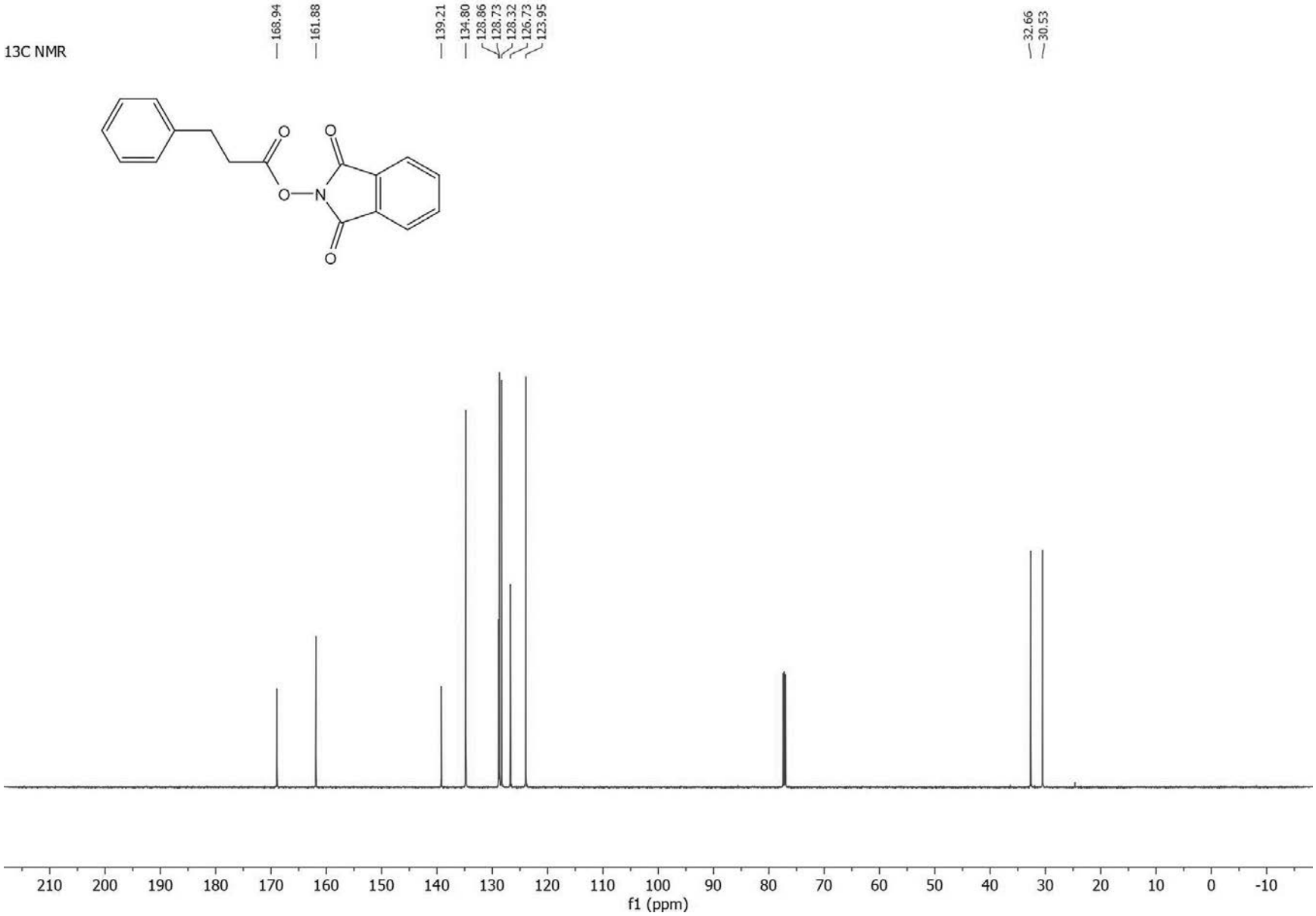
^{13}C NMR (151 MHz, $CDCl_3$) of **S-1a**



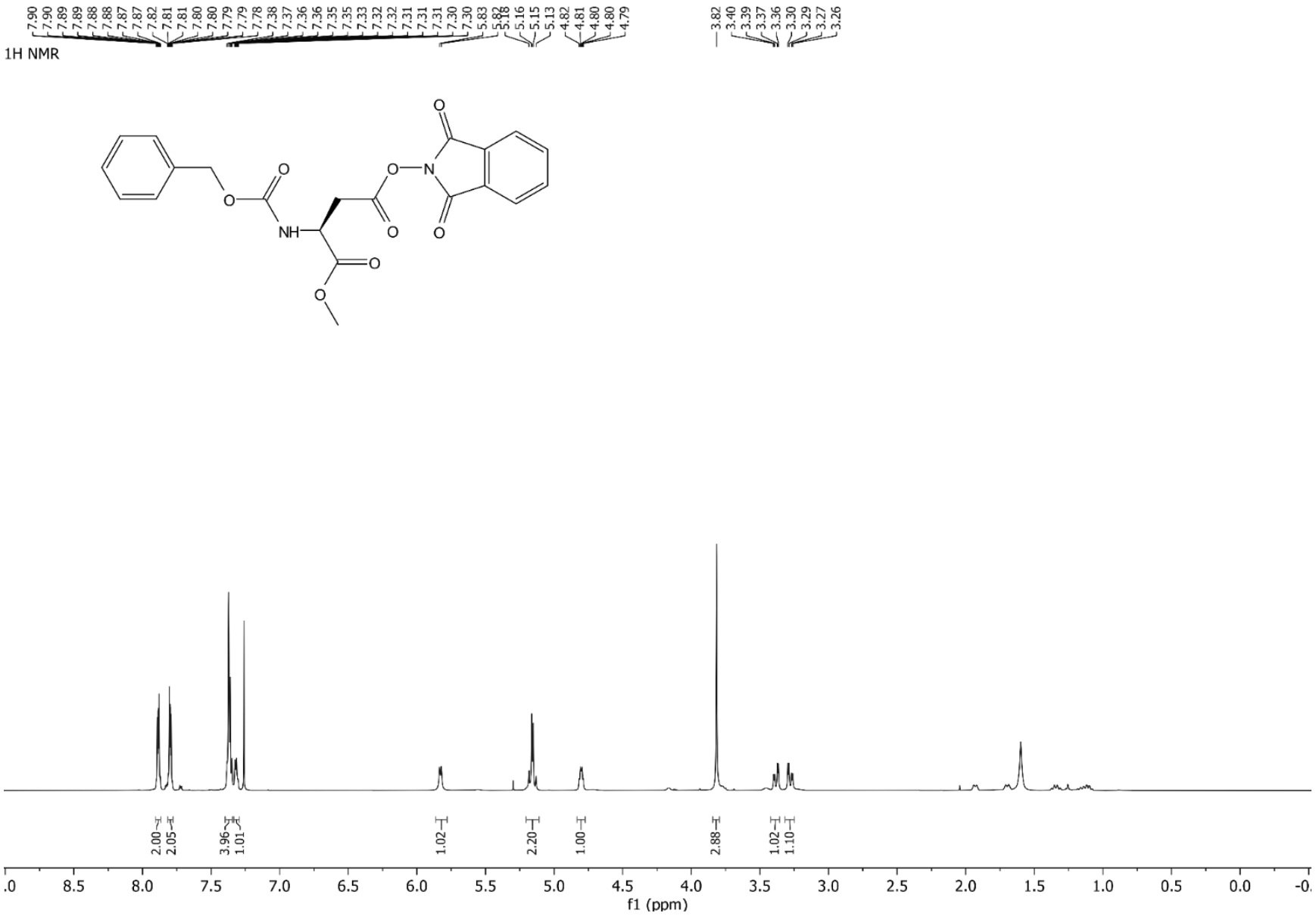
^{1}H NMR (600 MHz, $CDCl_3$) of **S-1b**



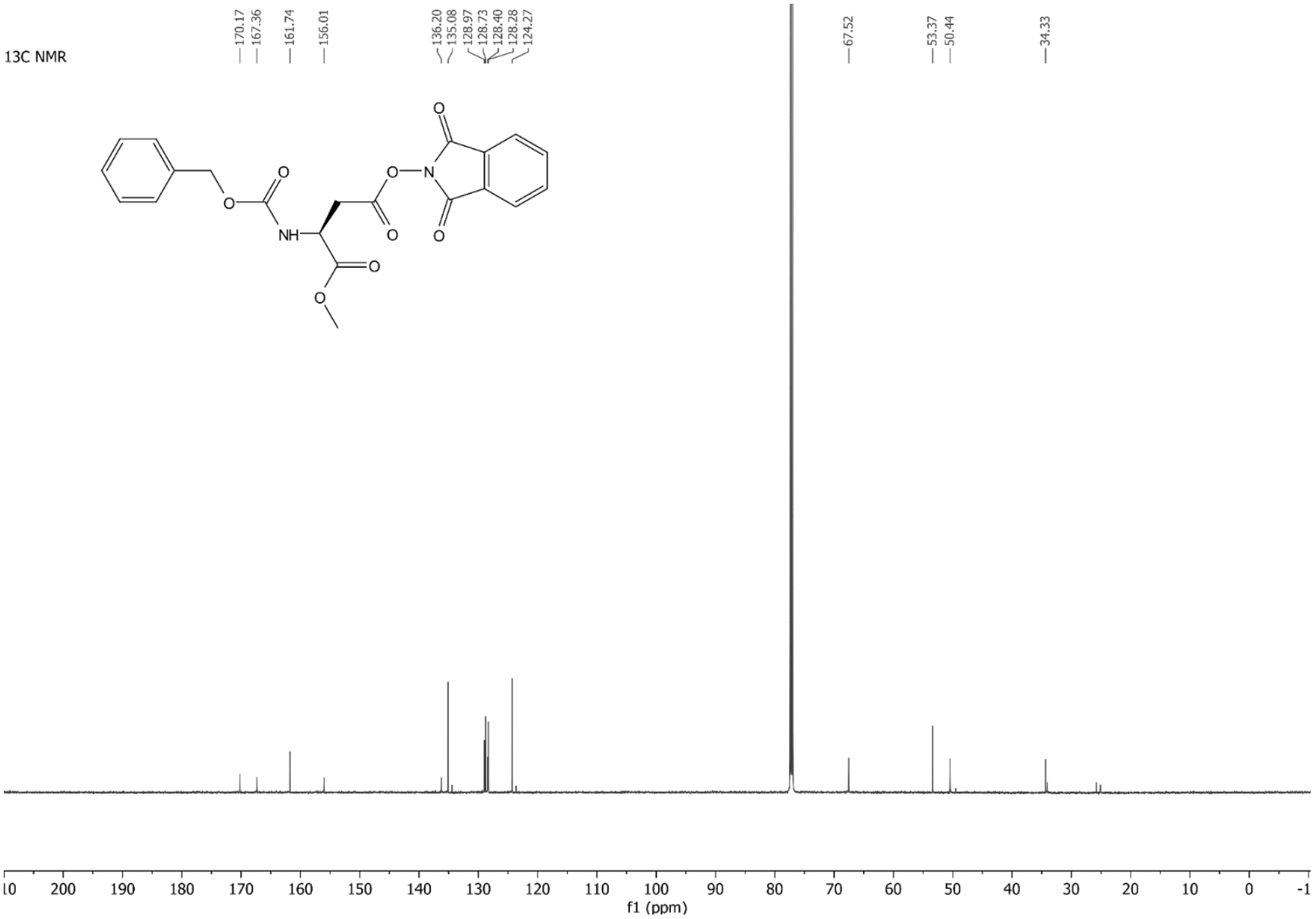
^{13}C NMR (151 MHz, $CDCl_3$) of **S-1b**



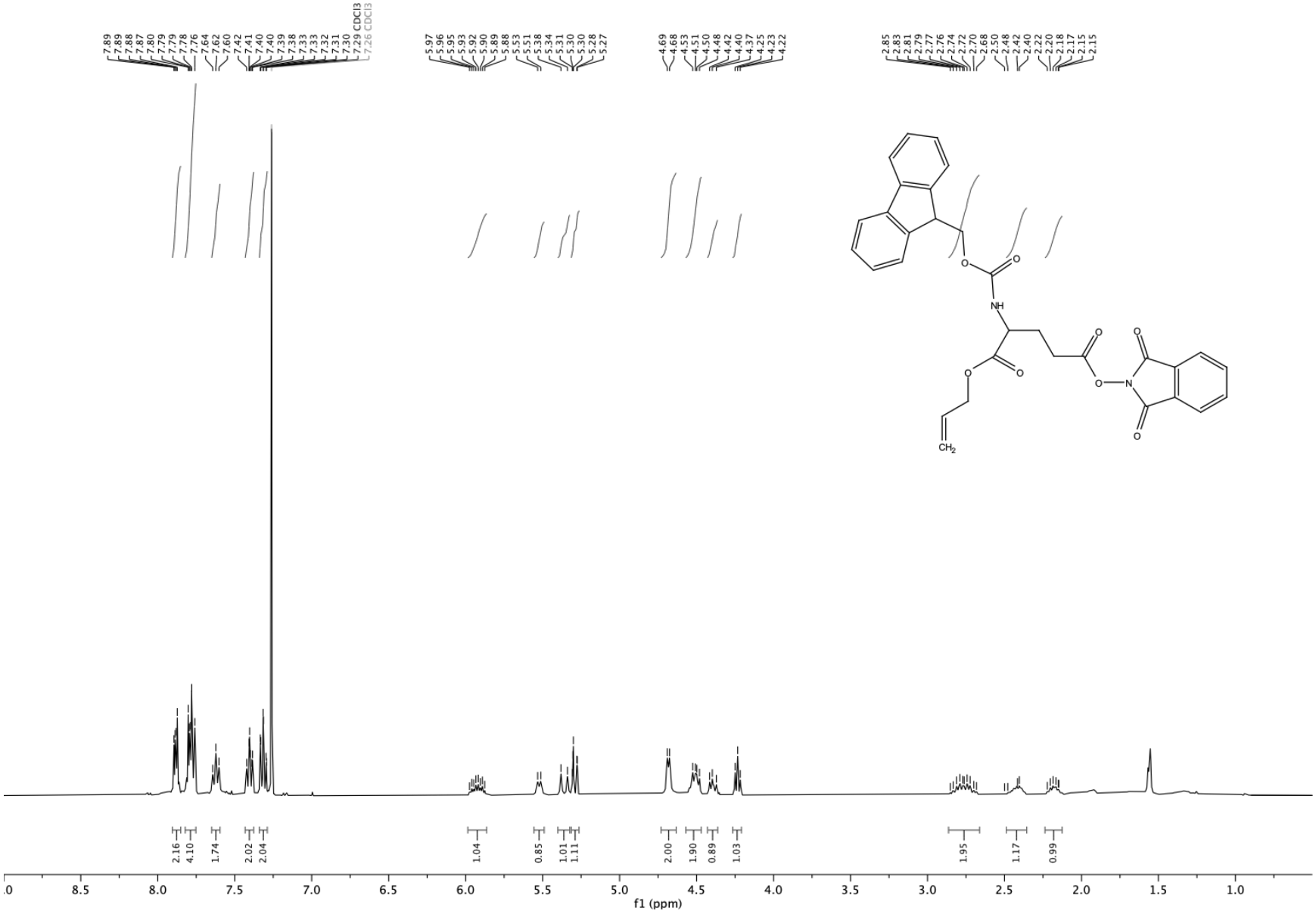
^{1}H NMR (600 MHz, $CDCl_3$) of **S-1c**



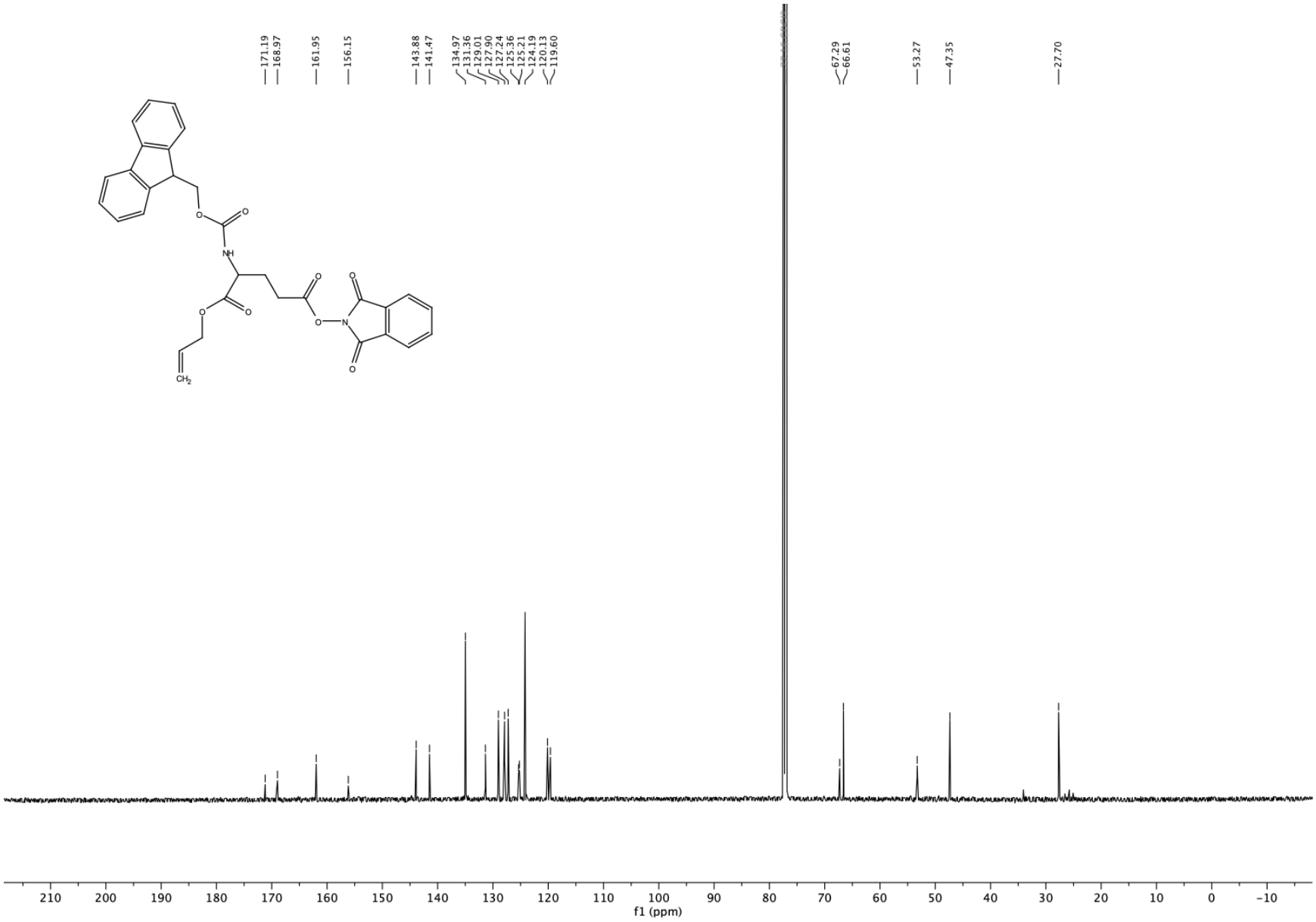
^{13}C NMR (151 MHz, $CDCl_3$) of **S-1c**



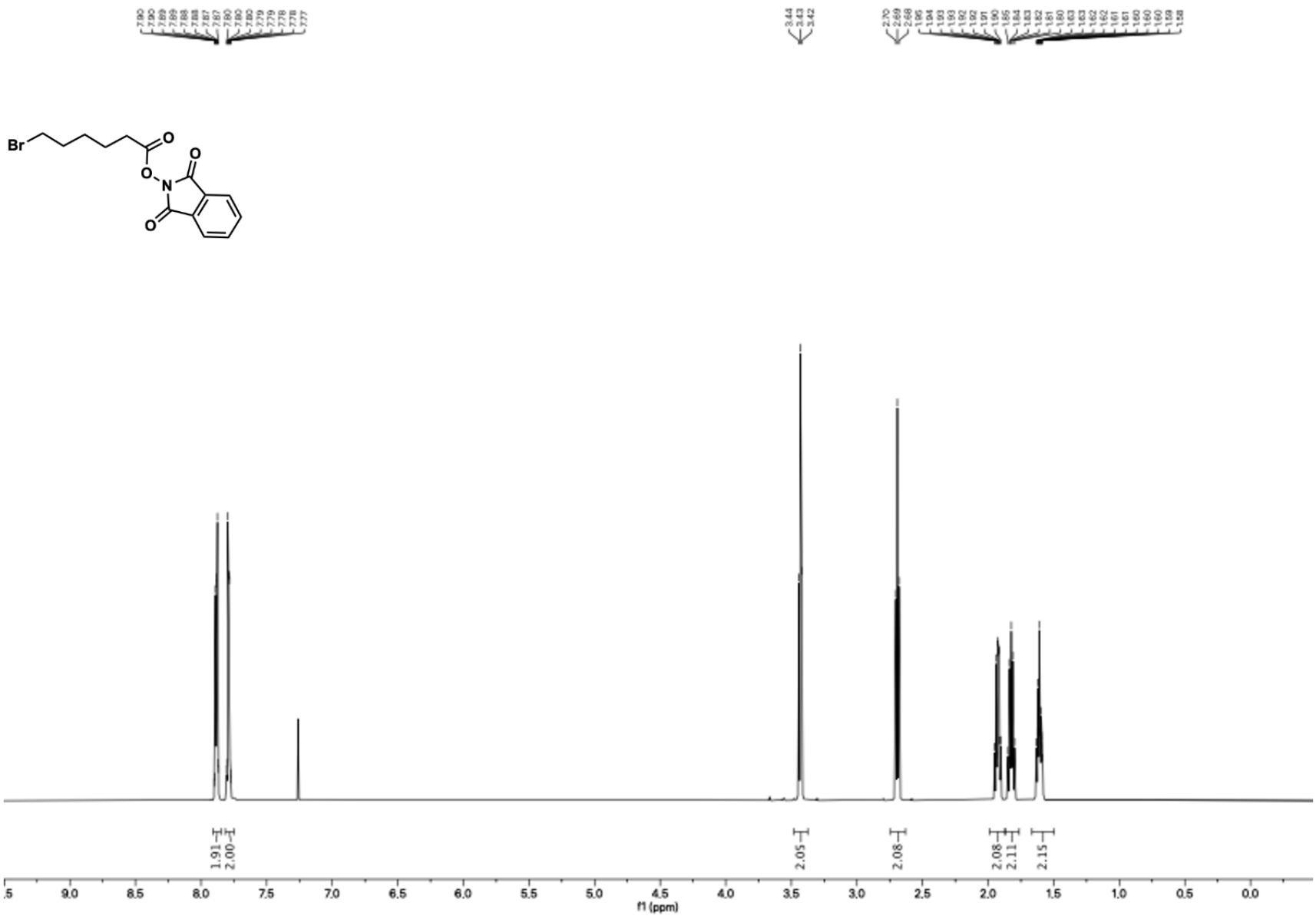
^{1}H NMR (600 MHz, $CDCl_3$) of **S-1d**



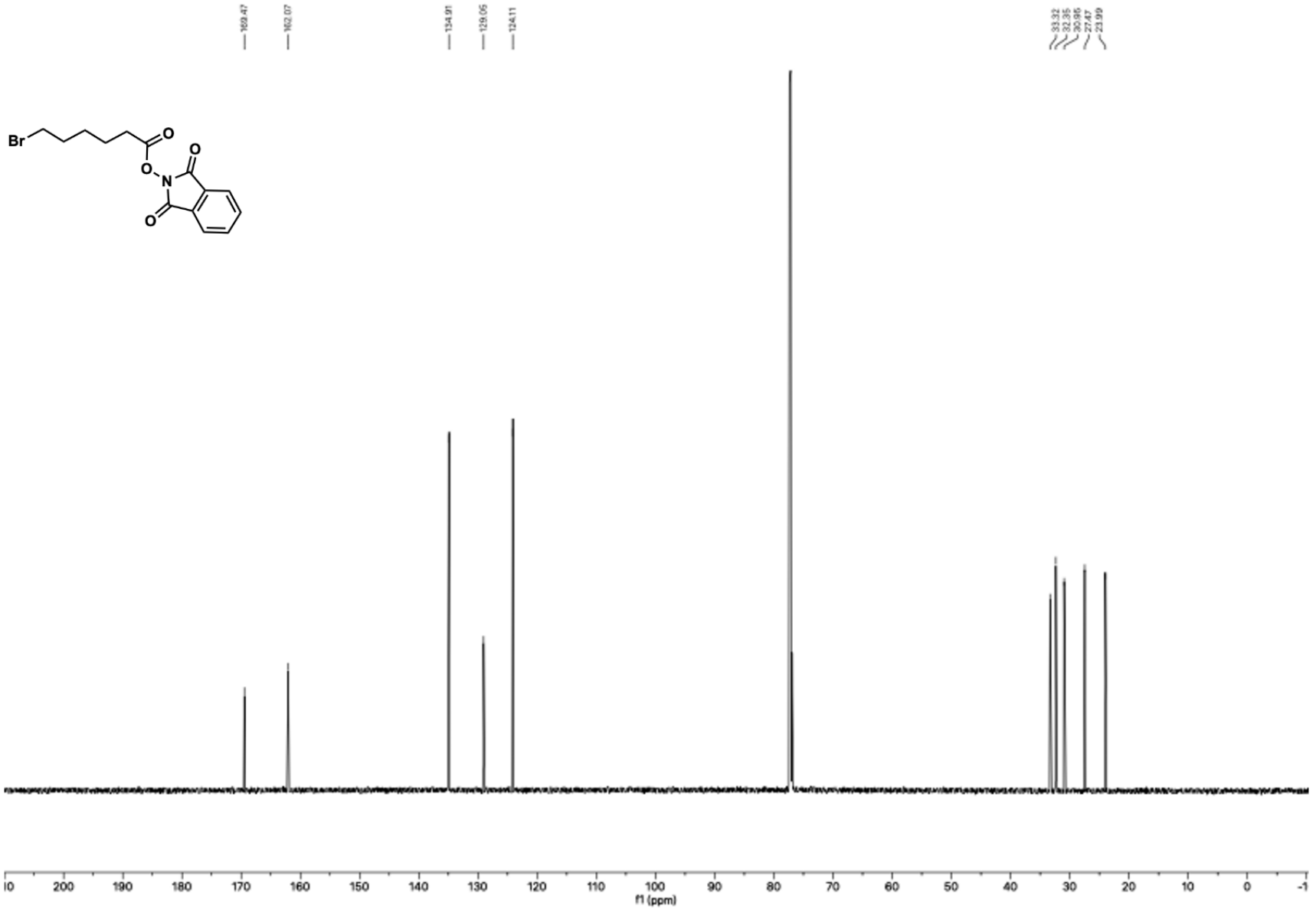
^{13}C NMR (151 MHz, $CDCl_3$) of **S-1d**



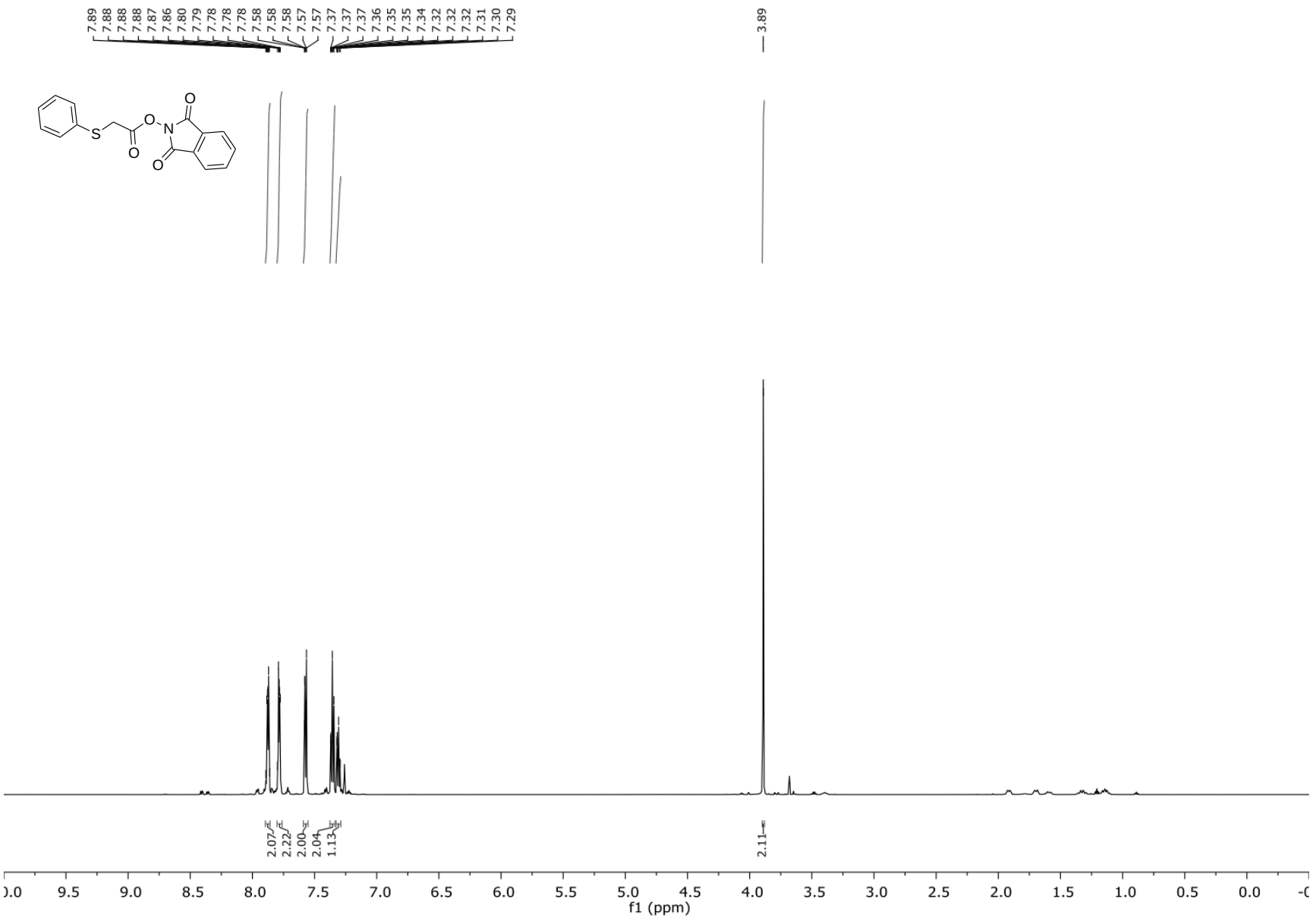
^{1}H NMR (600 MHz, $CDCl_3$) of **S-1e**



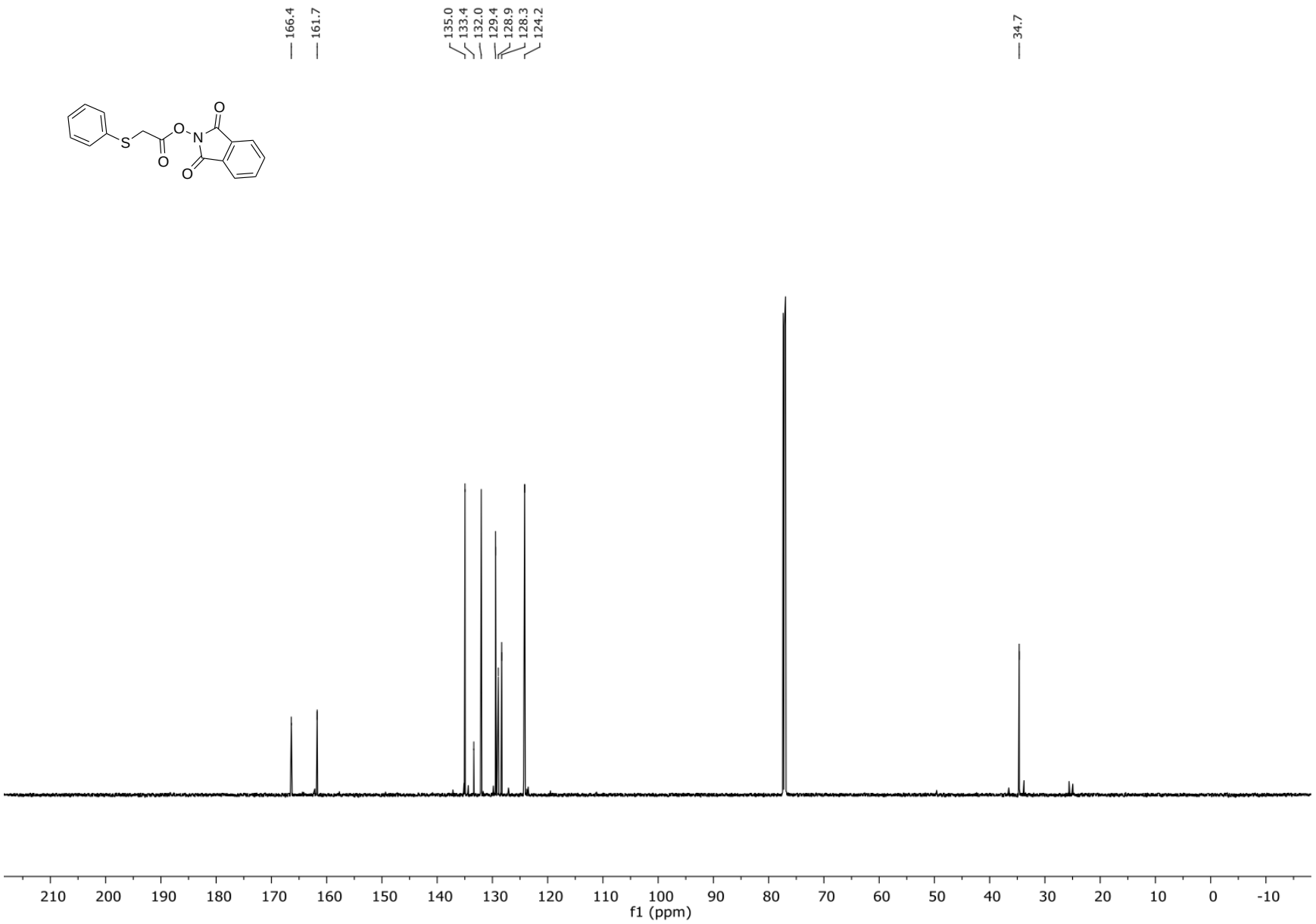
^{13}C NMR (151 MHz, $CDCl_3$) of **S-1e**



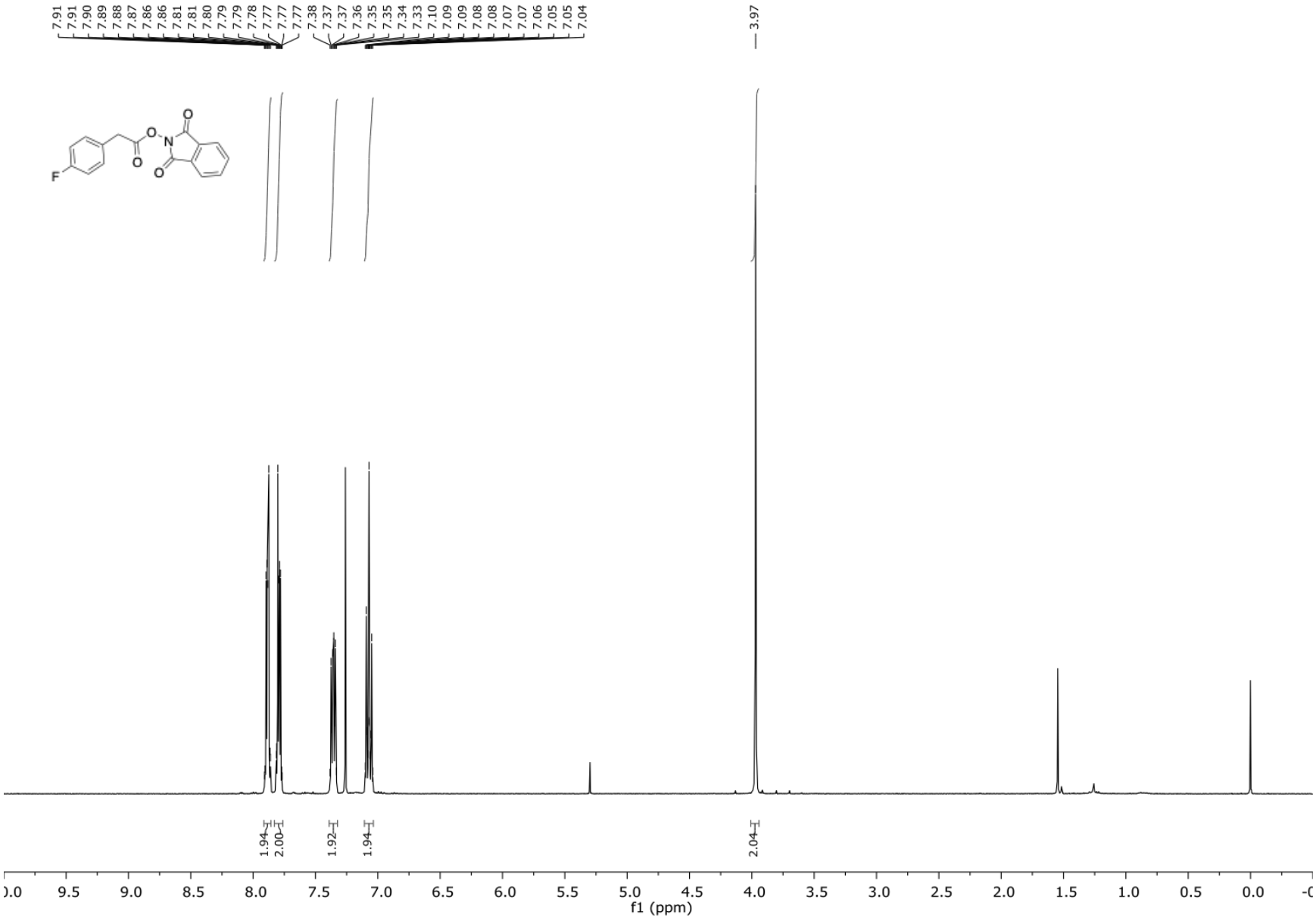
^{1}H NMR (600 MHz, $CDCl_3$) of **S-1f**



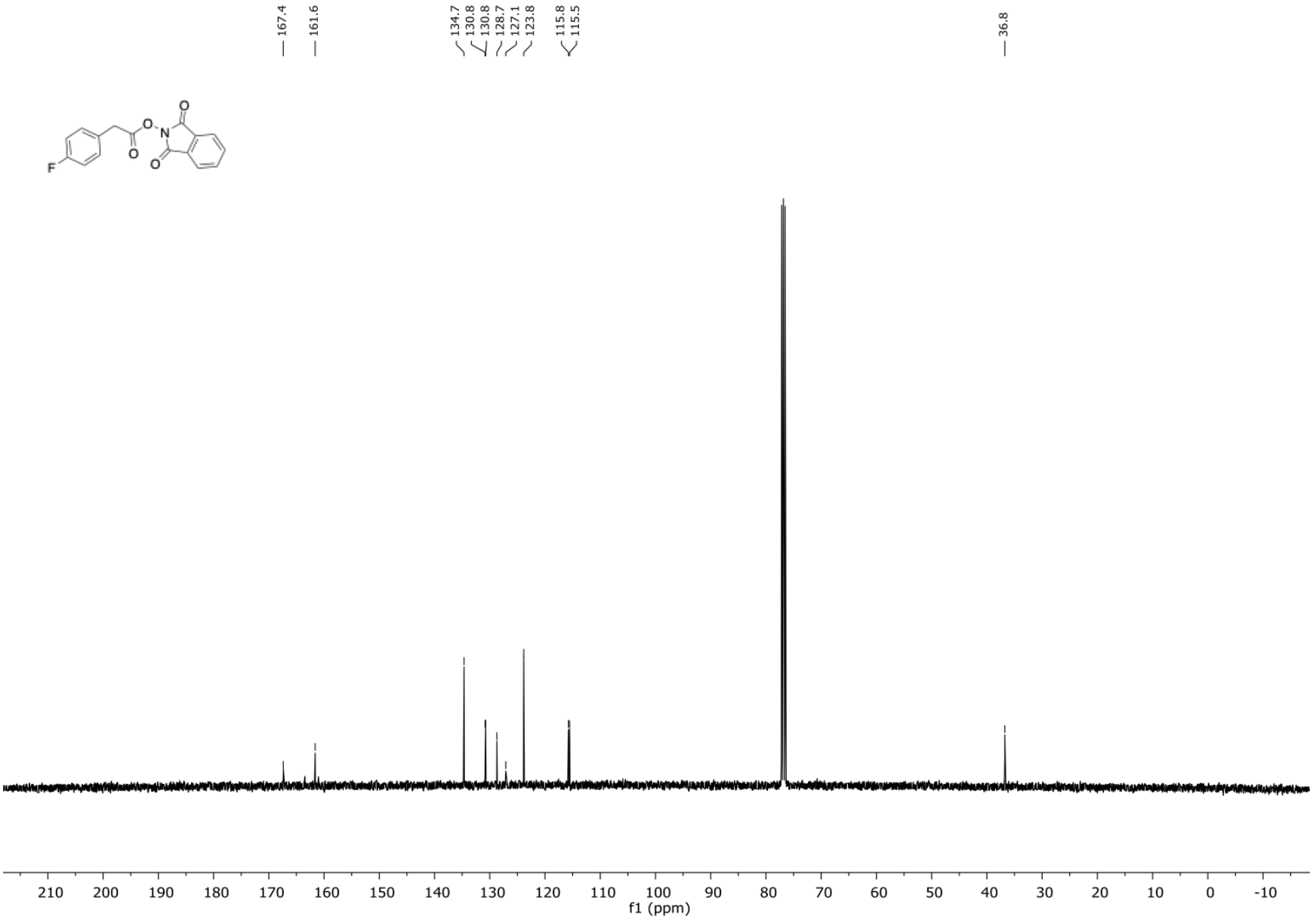
^{13}C NMR (151 MHz, $CDCl_3$) of **S-1f**



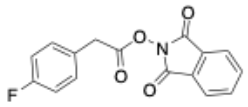
^{1}H NMR (400 MHz, $CDCl_3$) of **S-1g**



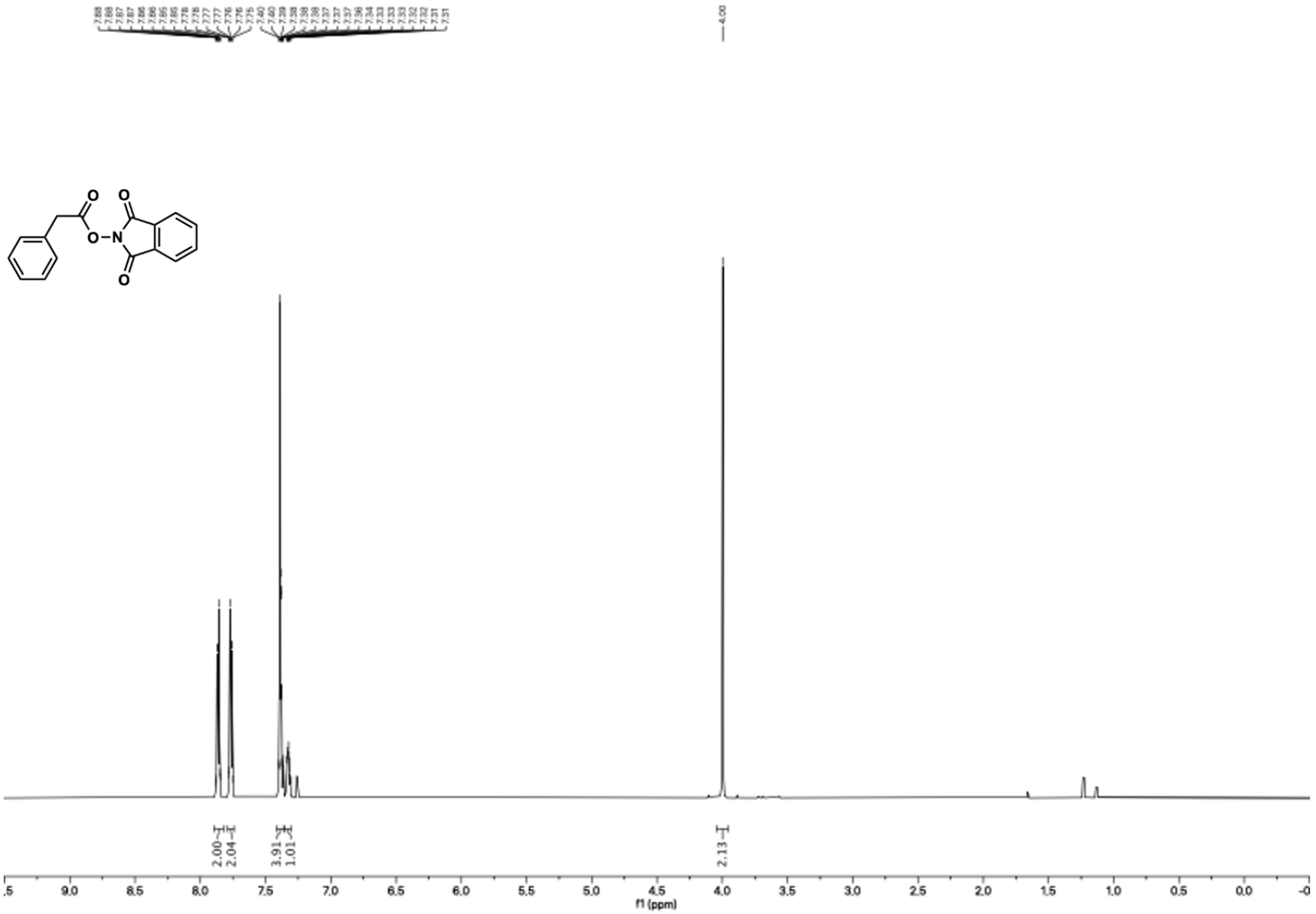
^{13}C NMR (151 MHz, $CDCl_3$) of **S-1g**



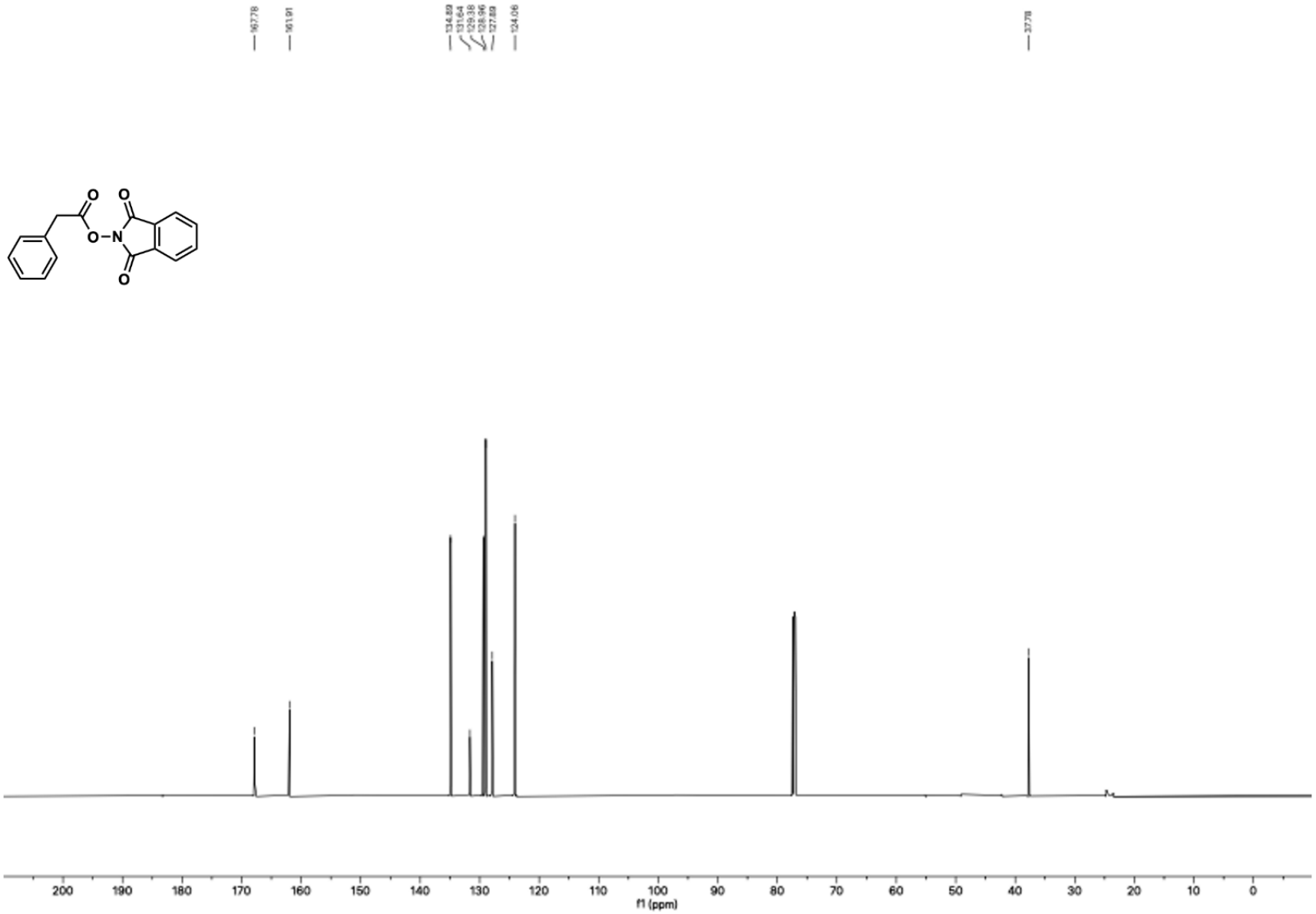
^{19}F NMR (376 MHz, $CDCl_3$) of **S-1g**



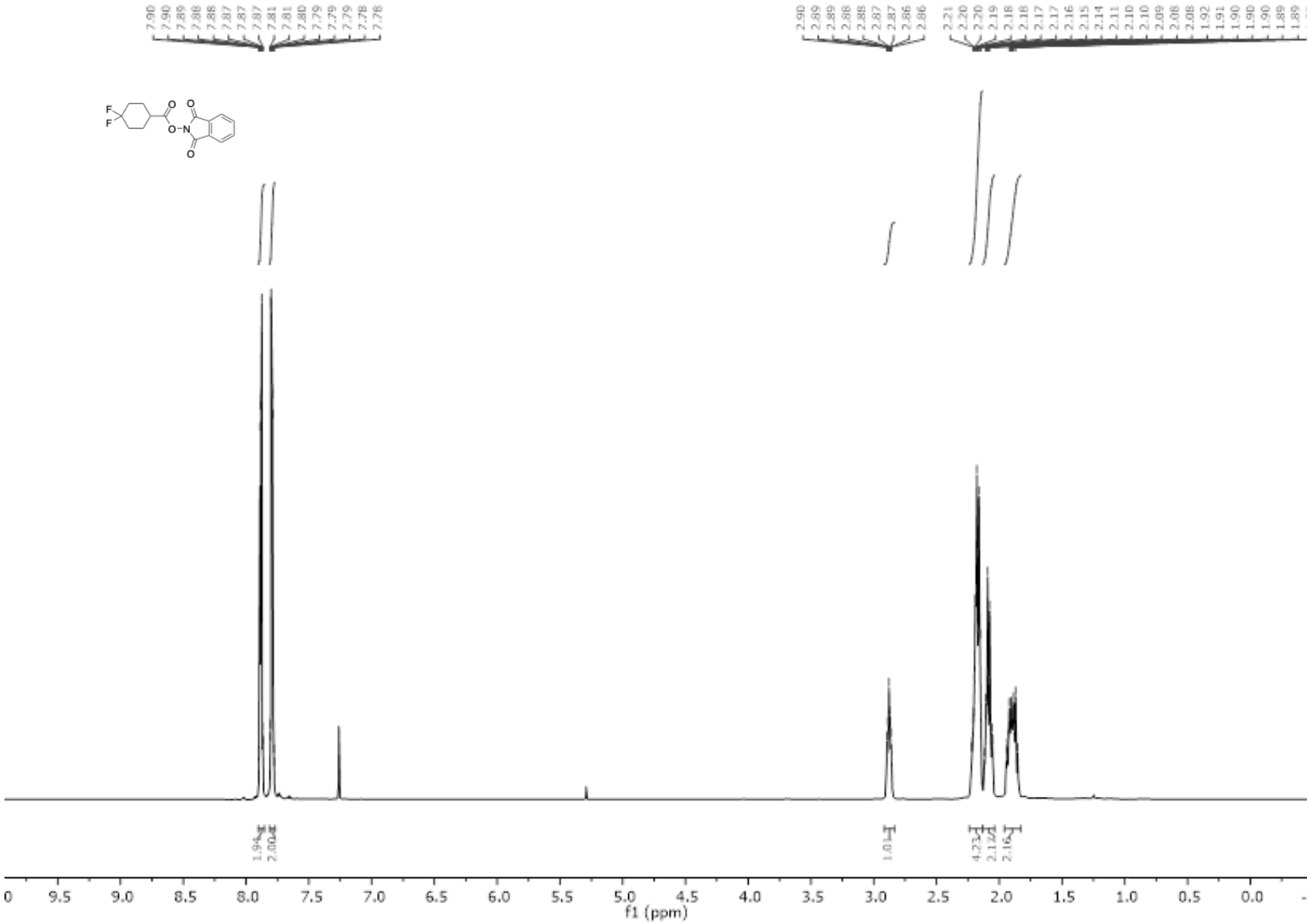
^{1}H NMR (600 MHz, $CDCl_3$) of **S-1h**



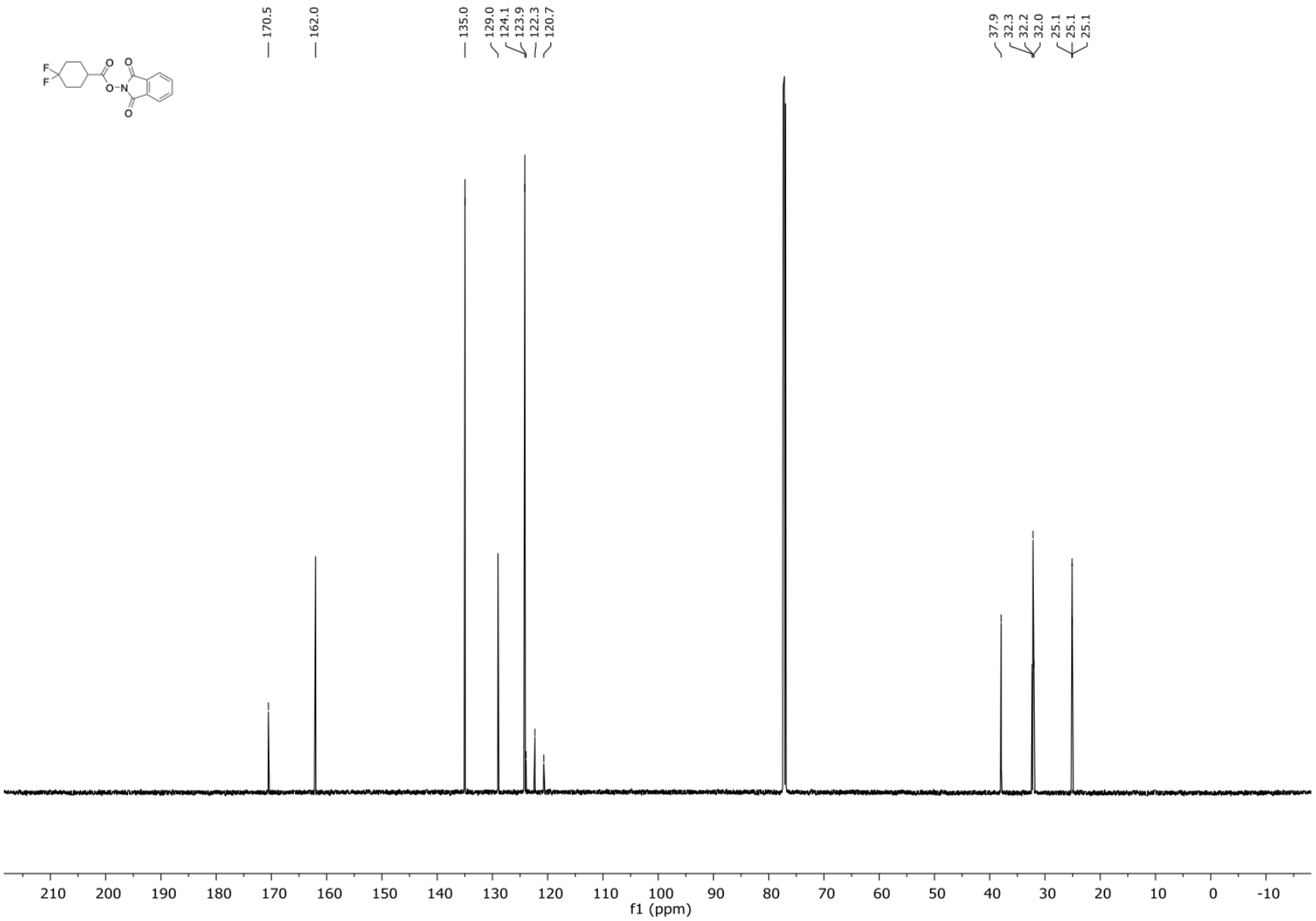
^{13}C NMR (151 MHz, $CDCl_3$) of **S-1h**



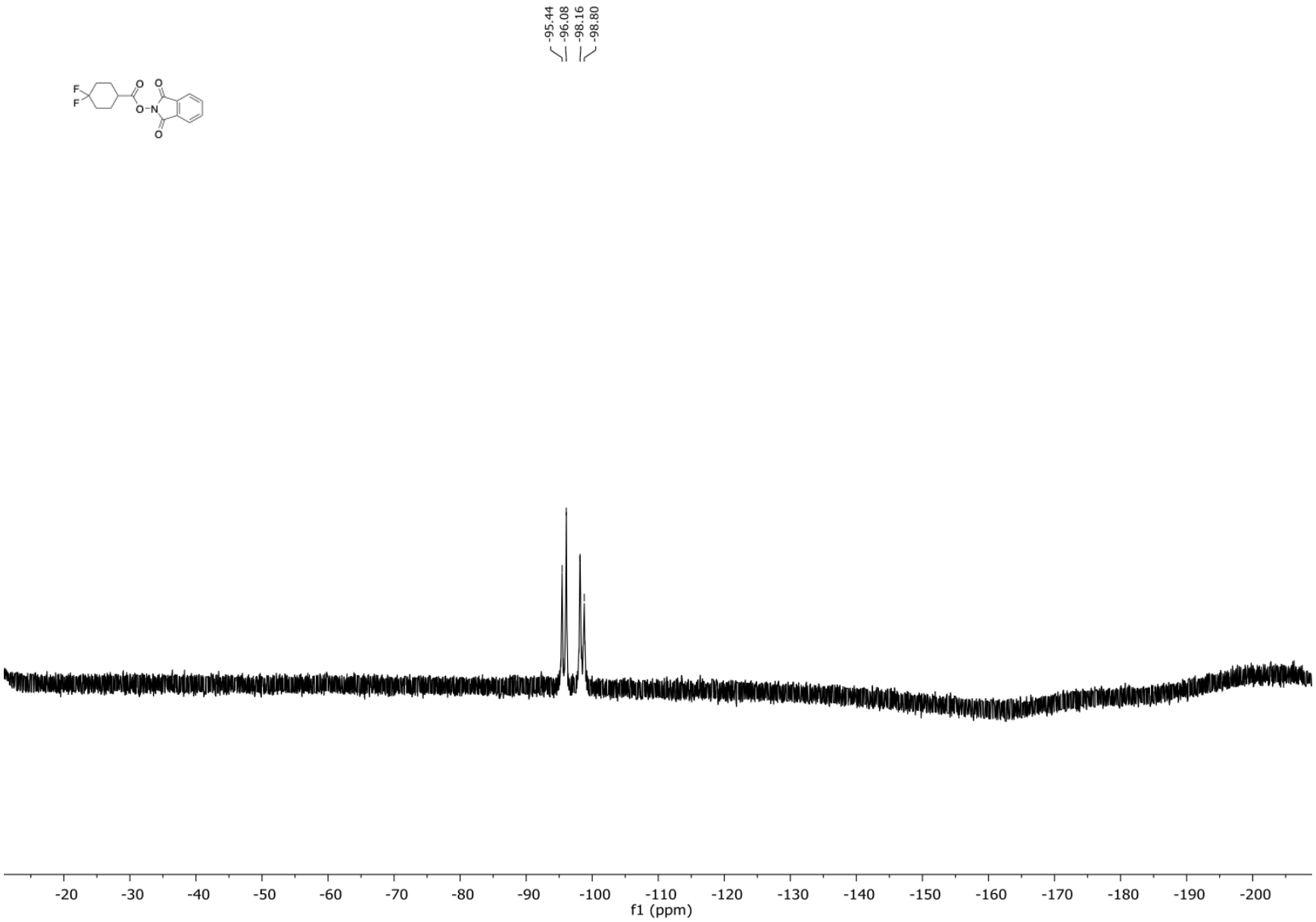
^{1}H NMR (600 MHz, $CDCl_3$) of **S-1i**



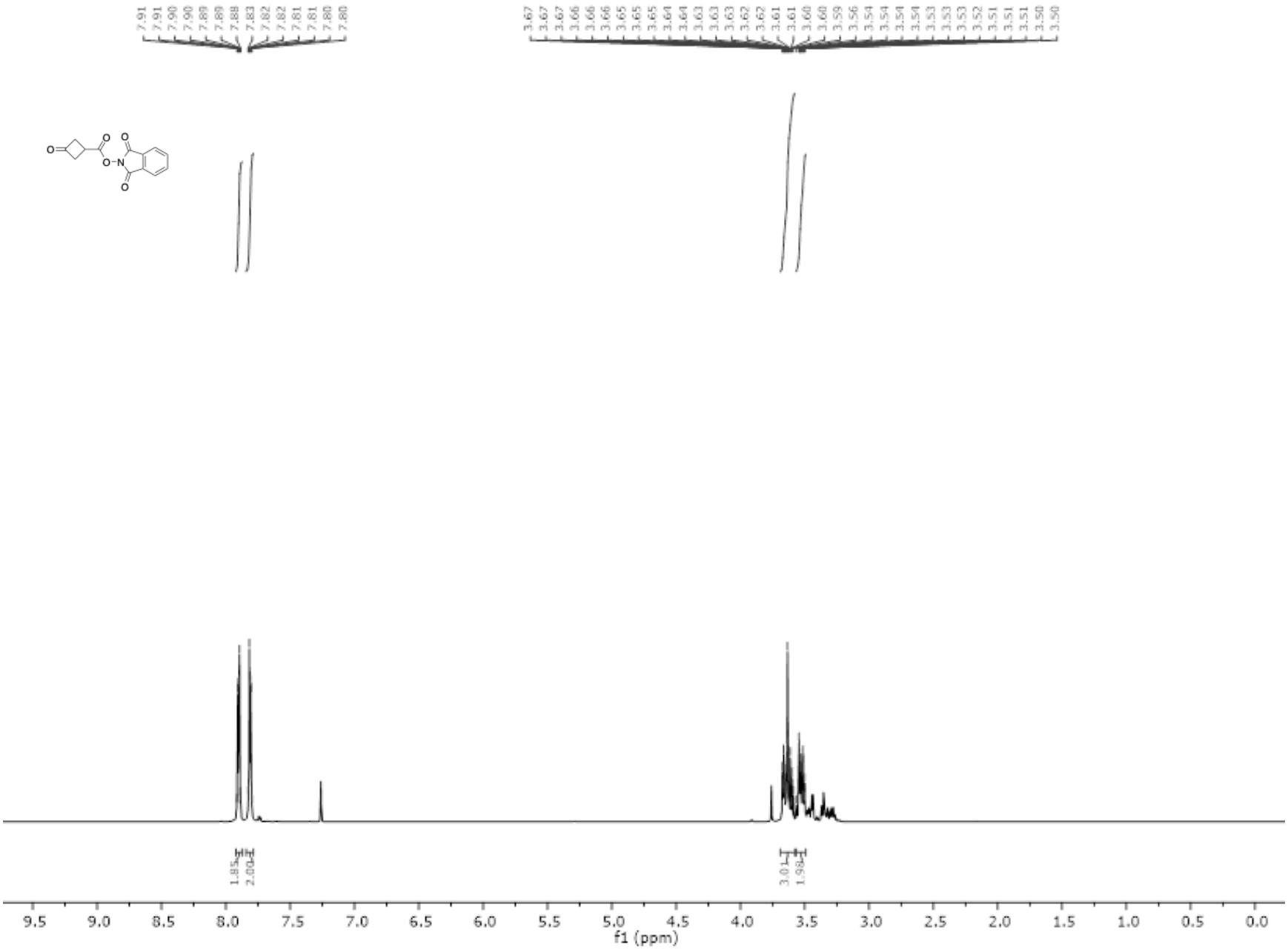
^{13}C NMR (151 MHz, $CDCl_3$) of **S-1i**



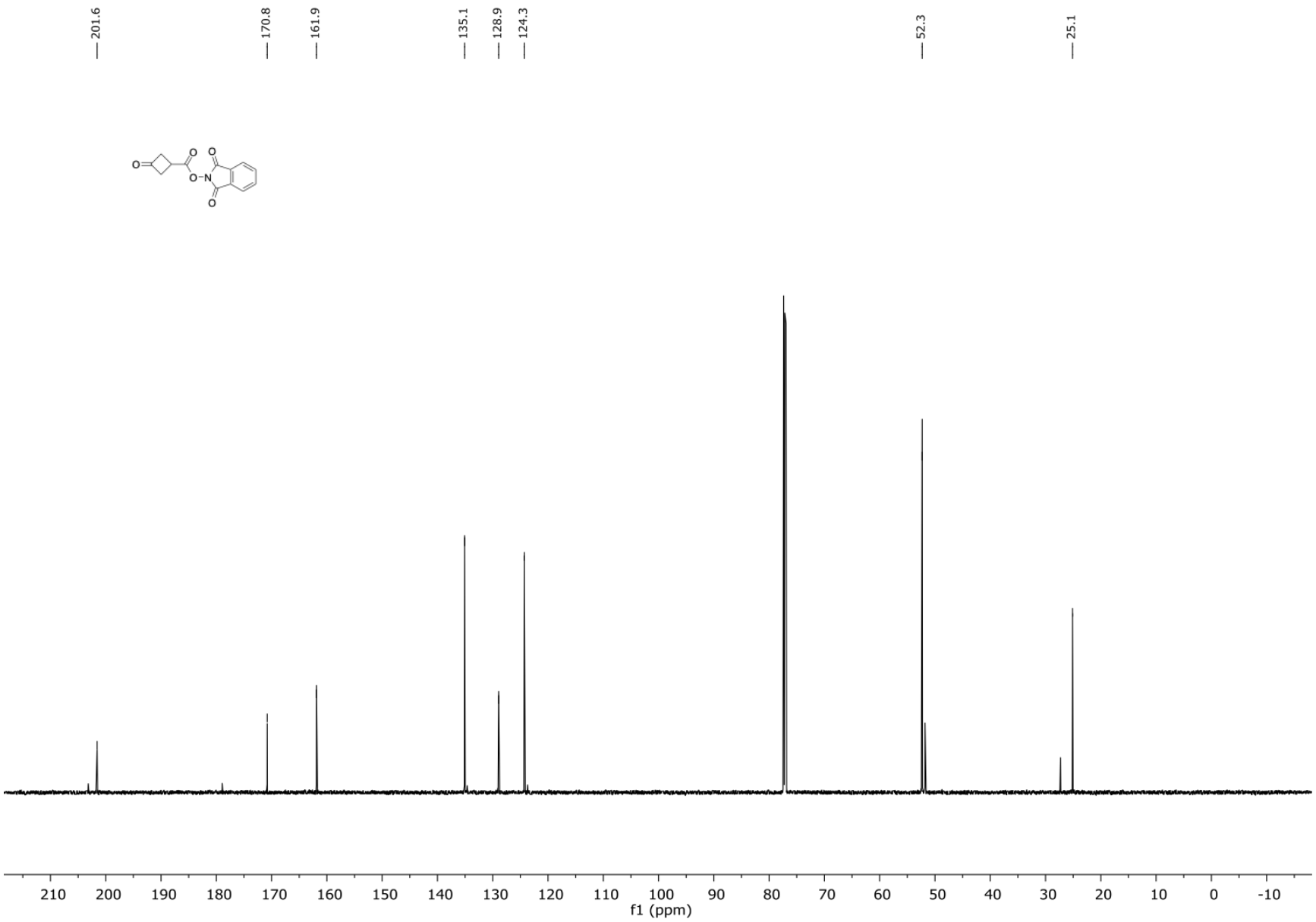
^{19}F NMR (376 MHz, $CDCl_3$) of **S-1i**



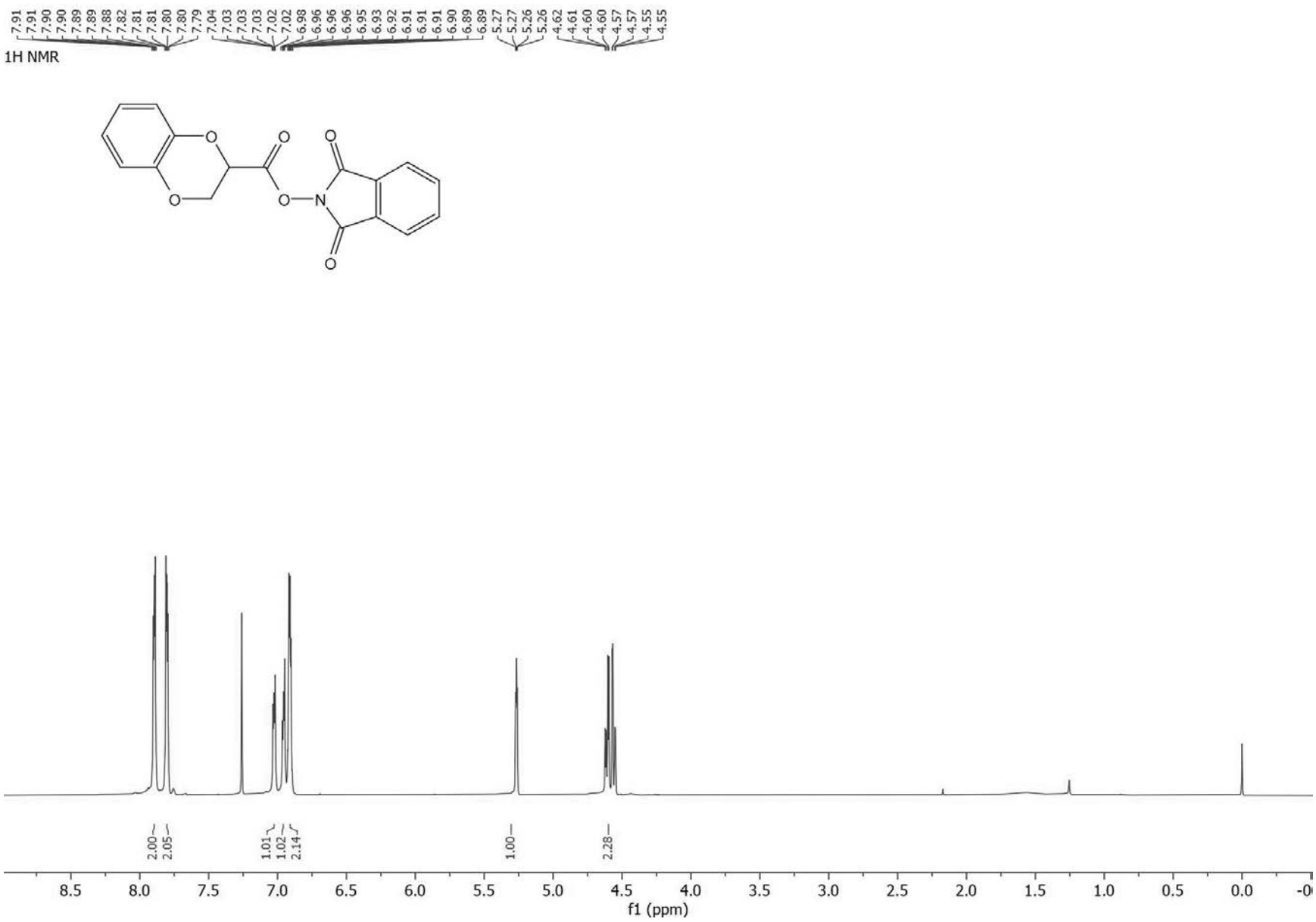
^{1}H NMR (400 MHz, $CDCl_3$) of **S-1j**



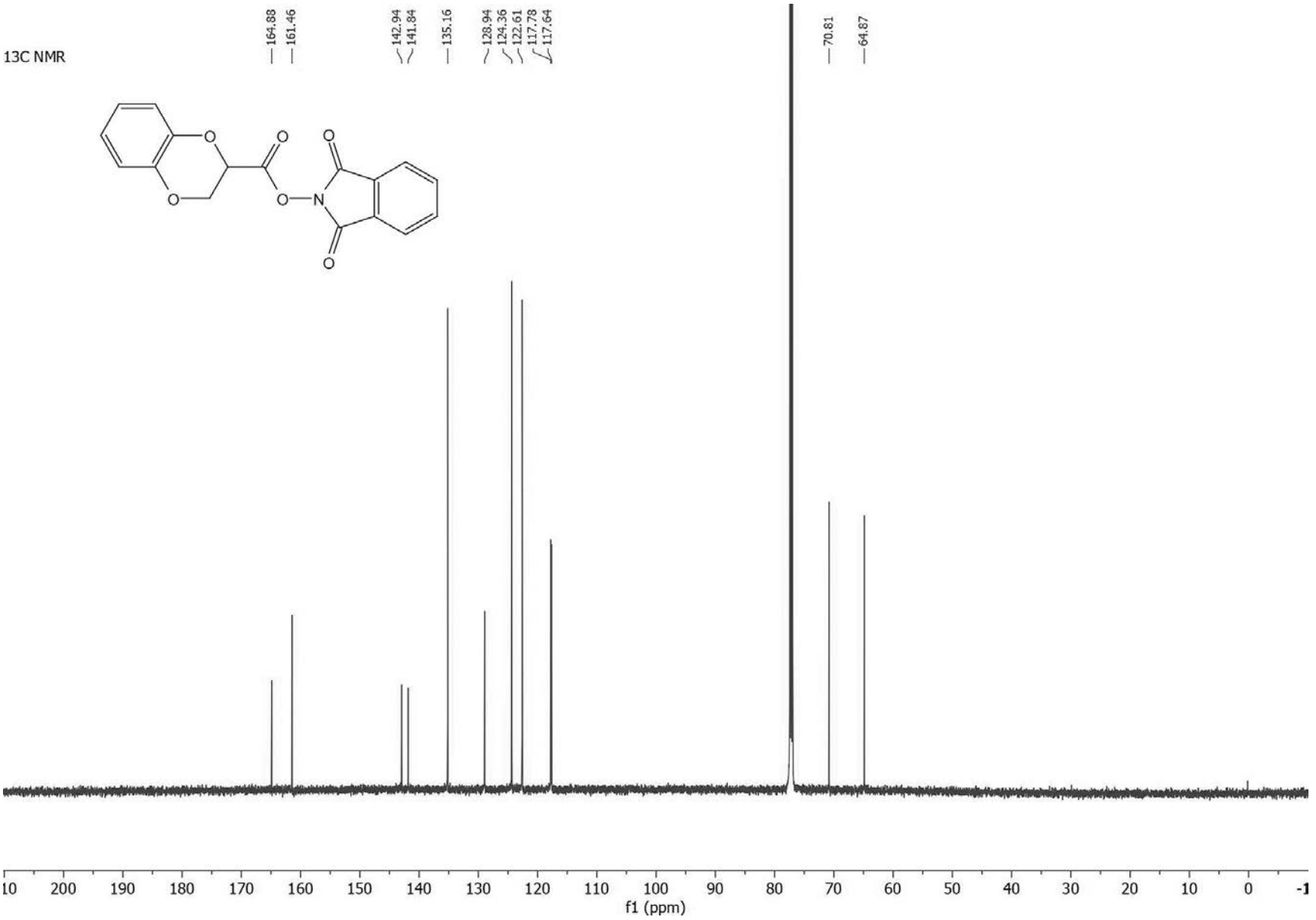
^{13}C NMR (151 MHz, $CDCl_3$) of **S-1j**



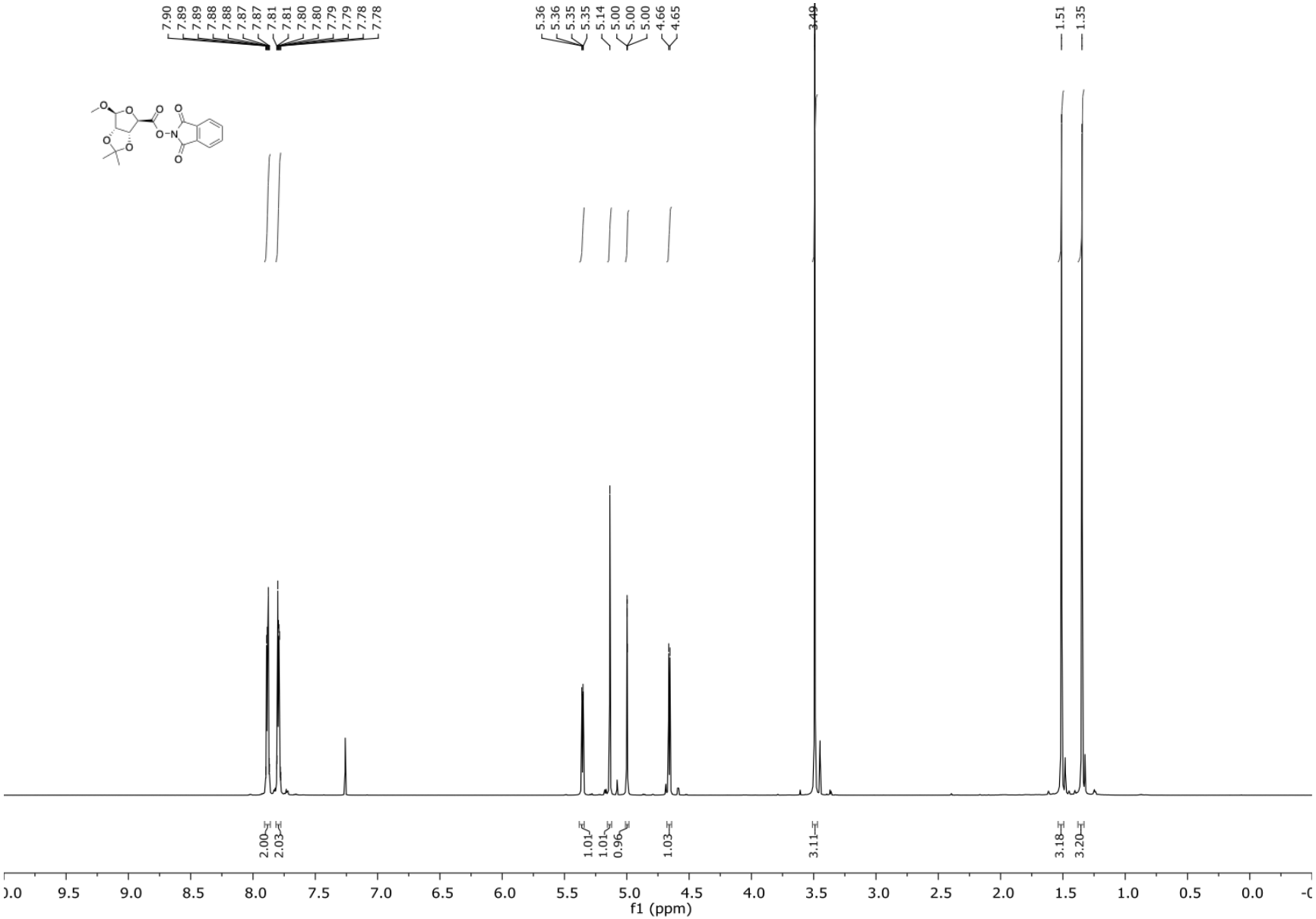
^{1}H NMR (600 MHz, $CDCl_3$) of **S-1k**



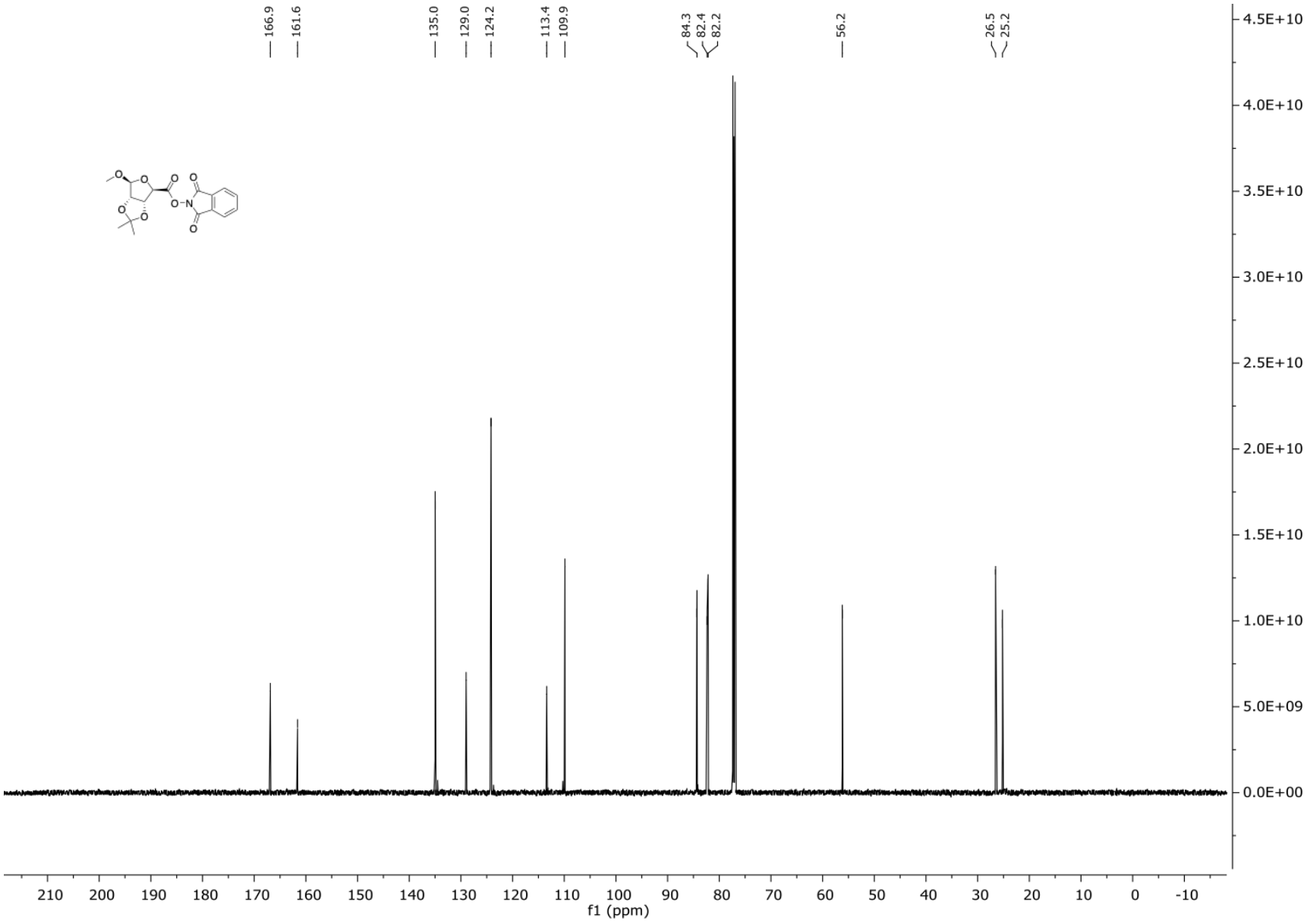
^{13}C NMR (151 MHz, $CDCl_3$) of **S-1k**



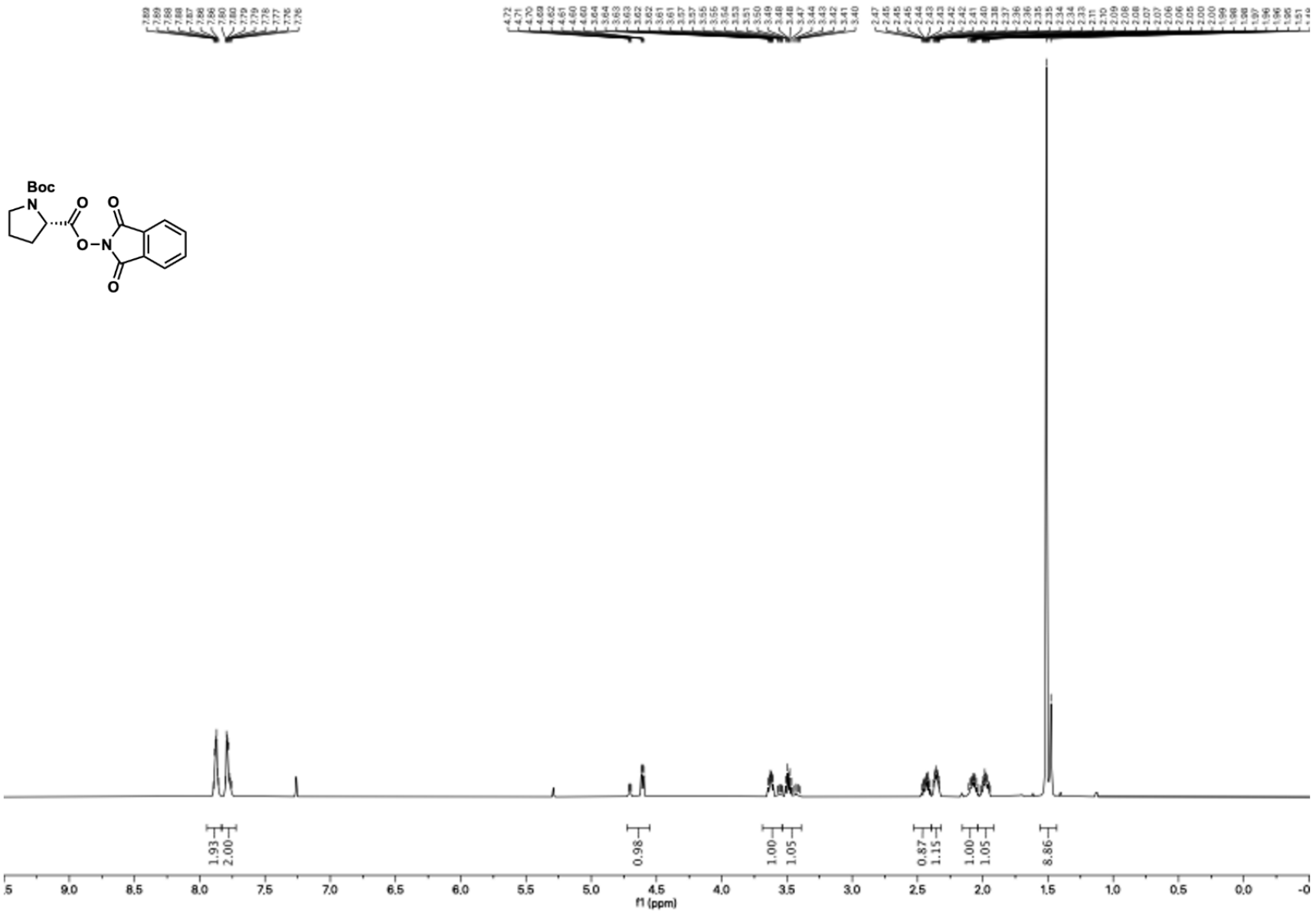
^{1}H NMR (400 MHz, $CDCl_3$) of **S-1l**



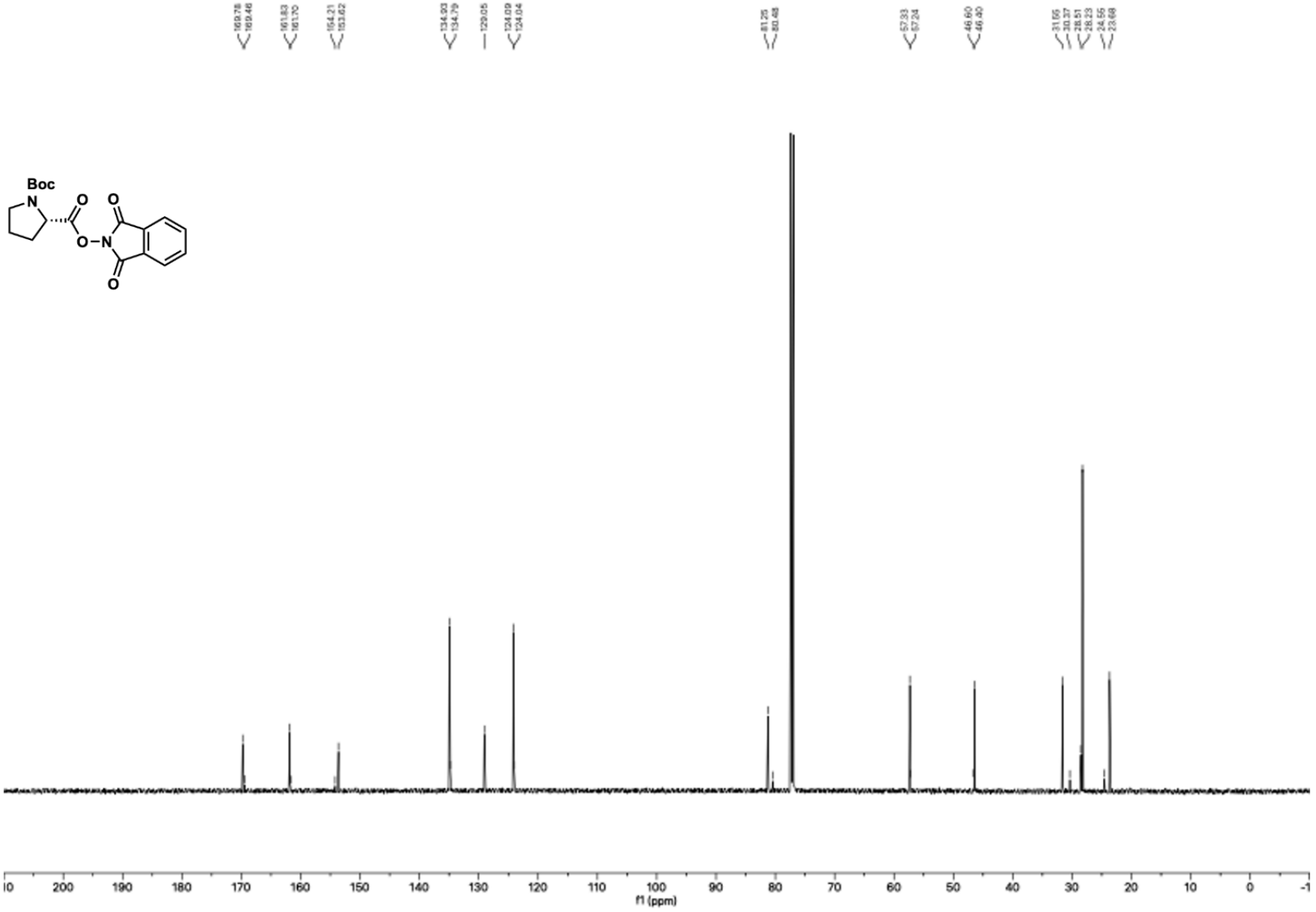
^{13}C NMR (101 MHz, $CDCl_3$) of **S-1l**



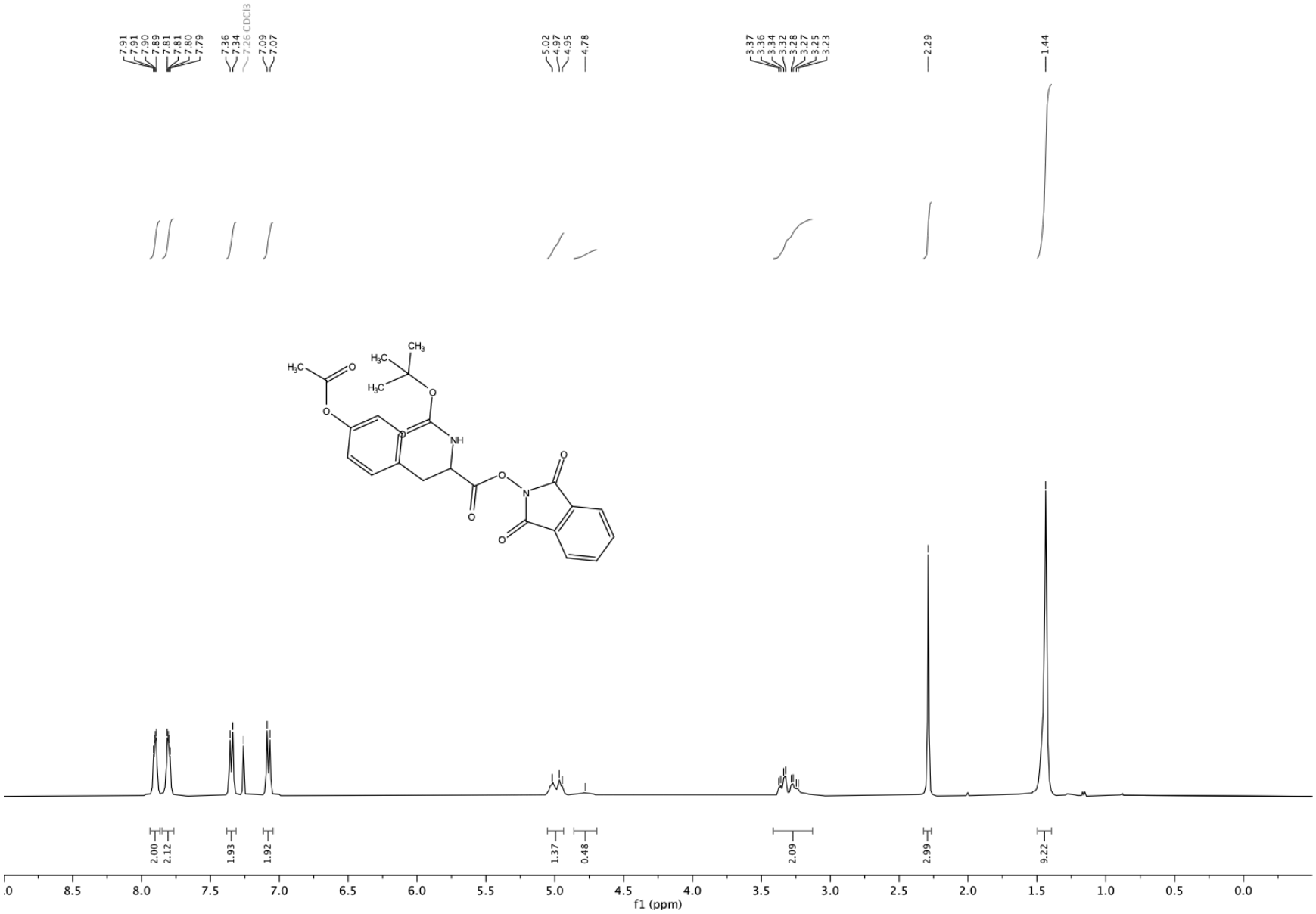
^{1}H NMR (600 MHz, $CDCl_3$) of **S-1m**



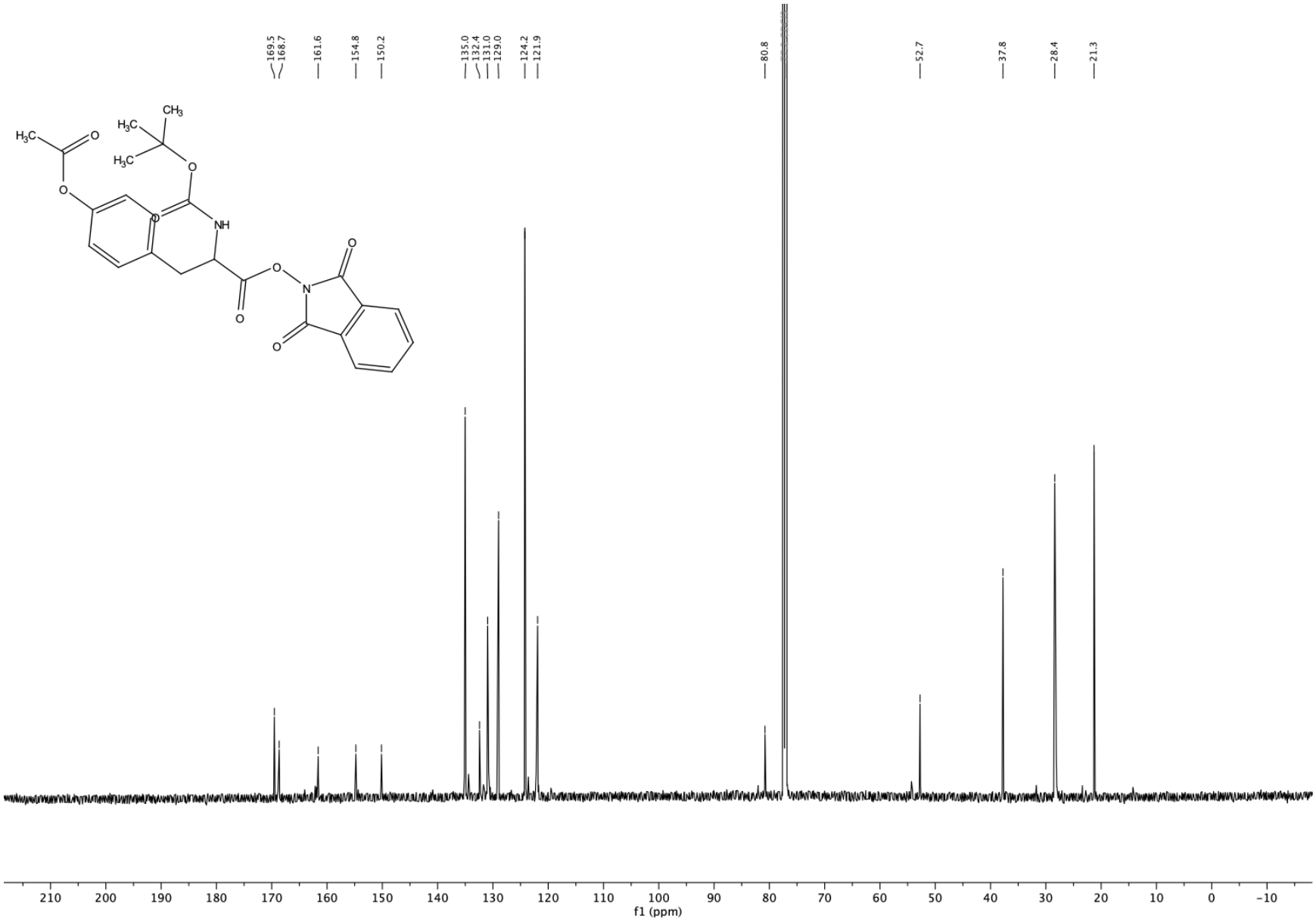
^{13}C NMR (151 MHz, $CDCl_3$) of **S-1m**



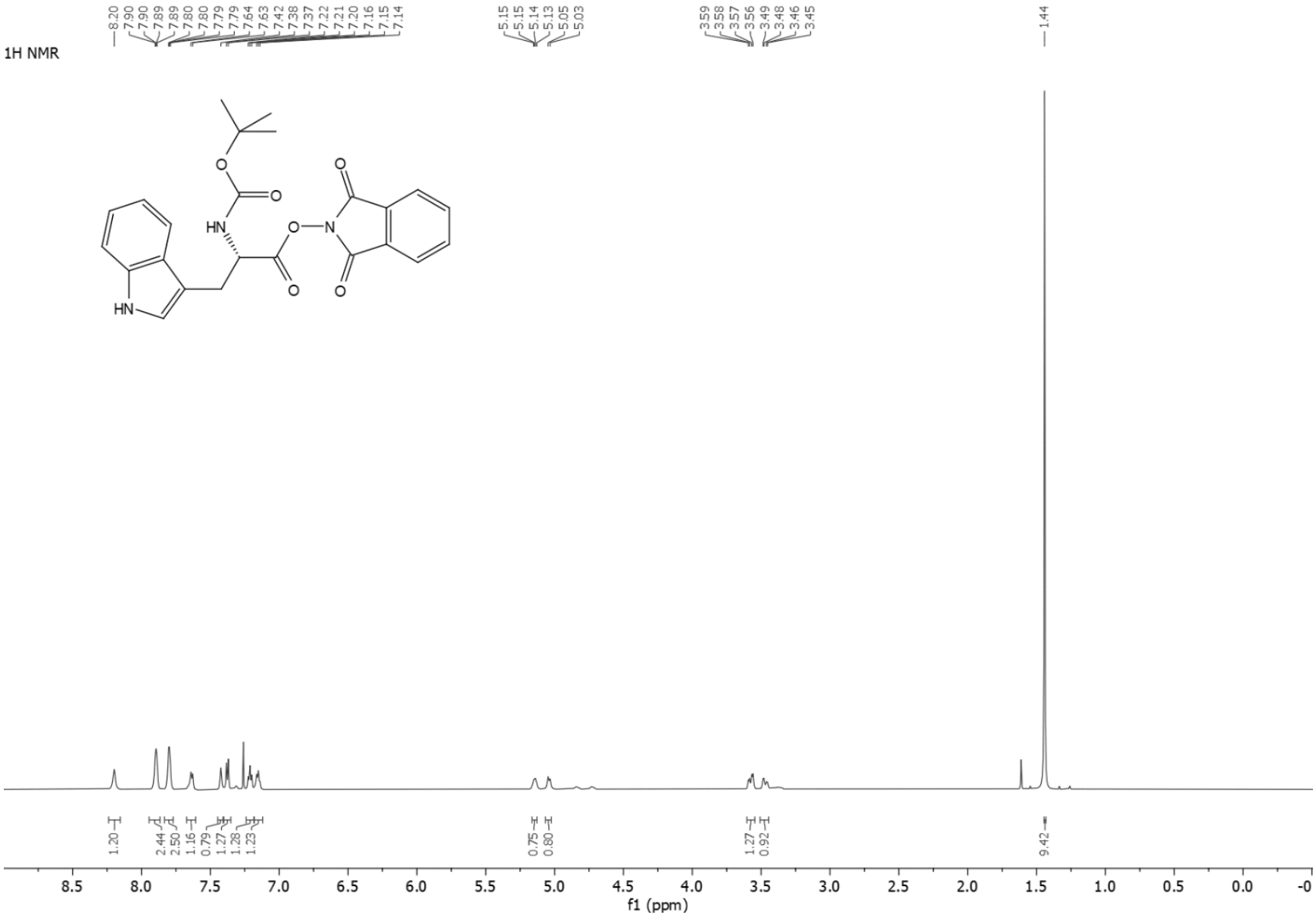
^{1}H NMR (600 MHz, $CDCl_3$) of **S-1n**



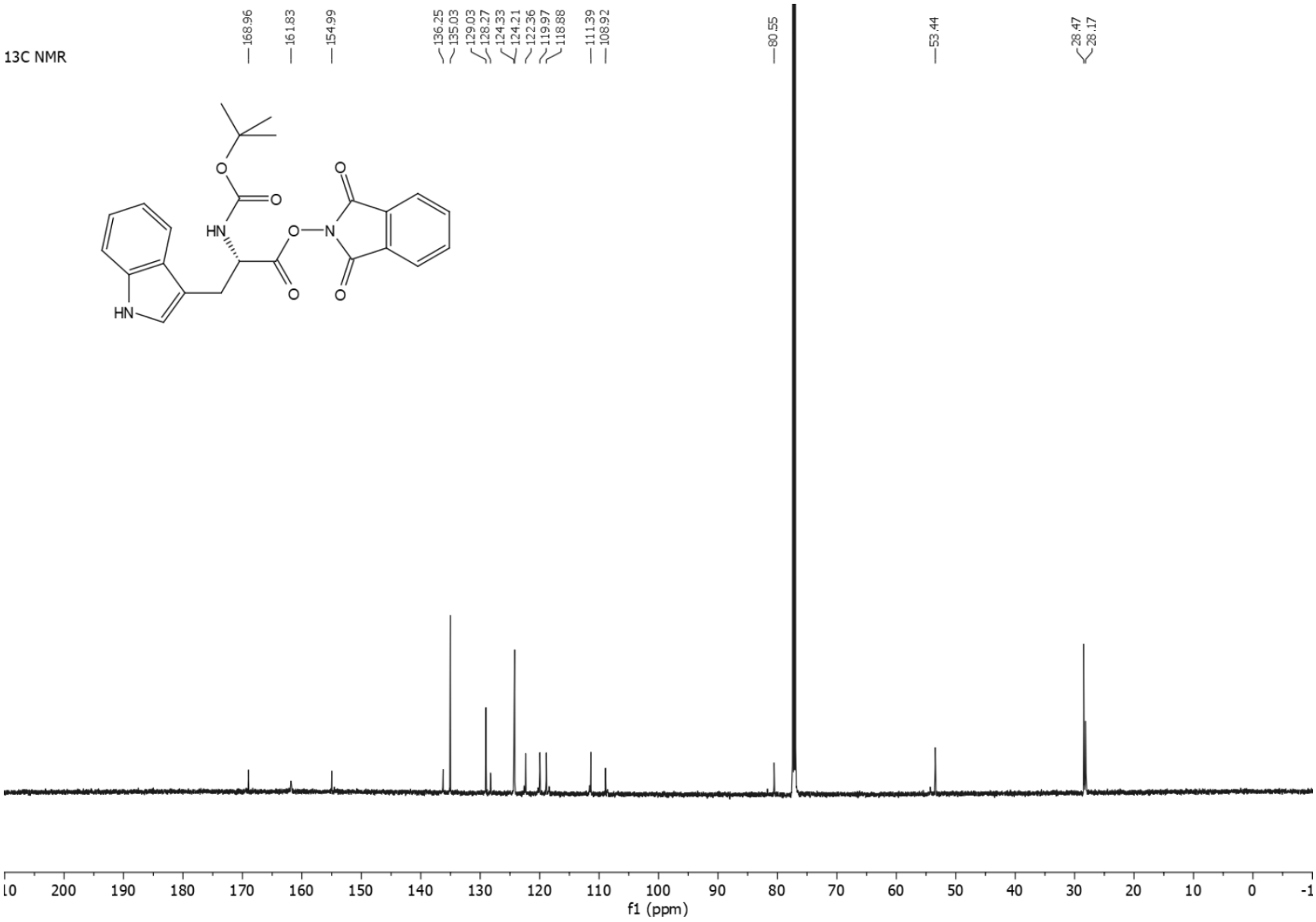
^{13}C NMR (151 MHz, $CDCl_3$) of **S-1n**



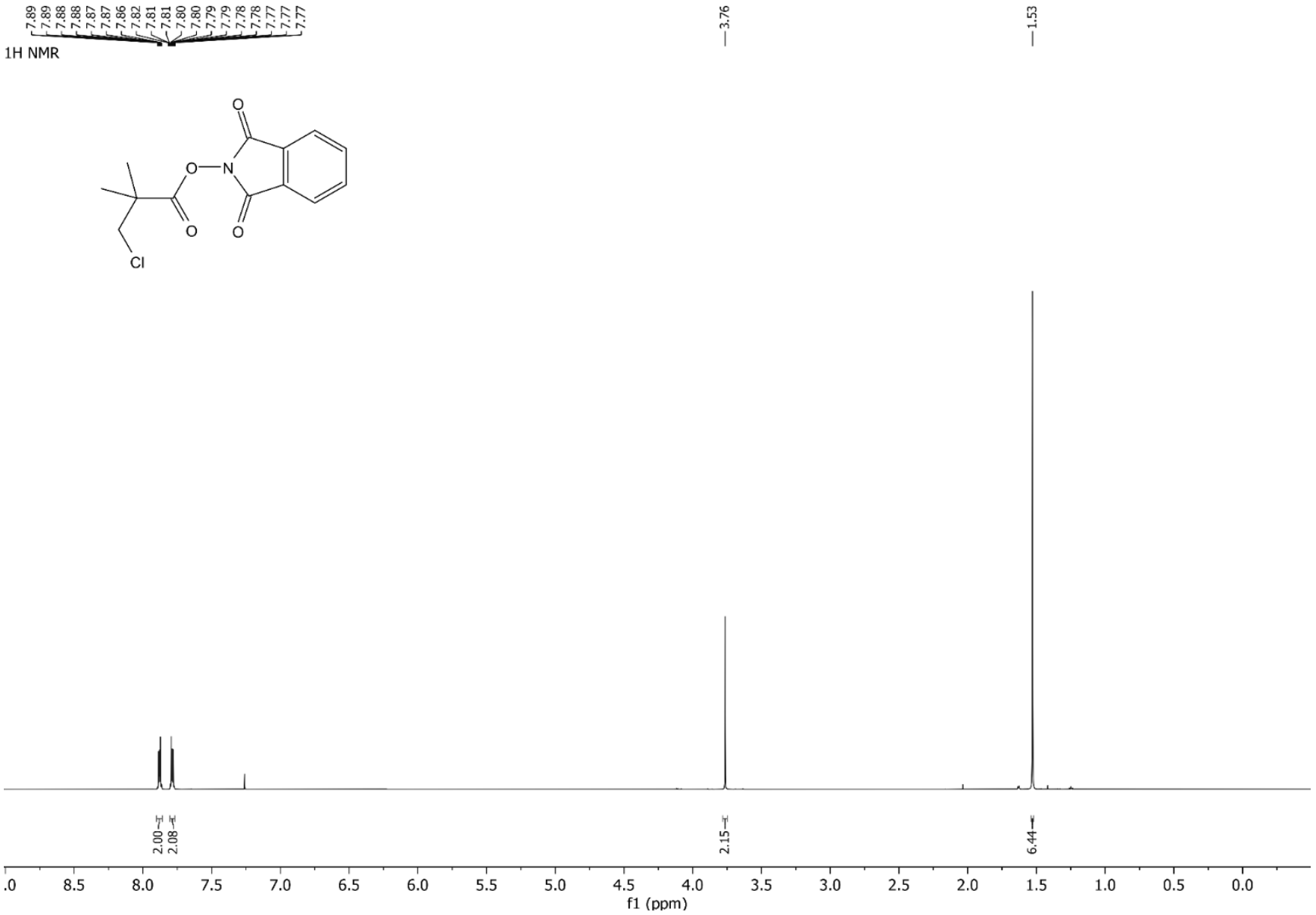
^{1}H NMR (600 MHz, $CDCl_3$) of **S-1o**



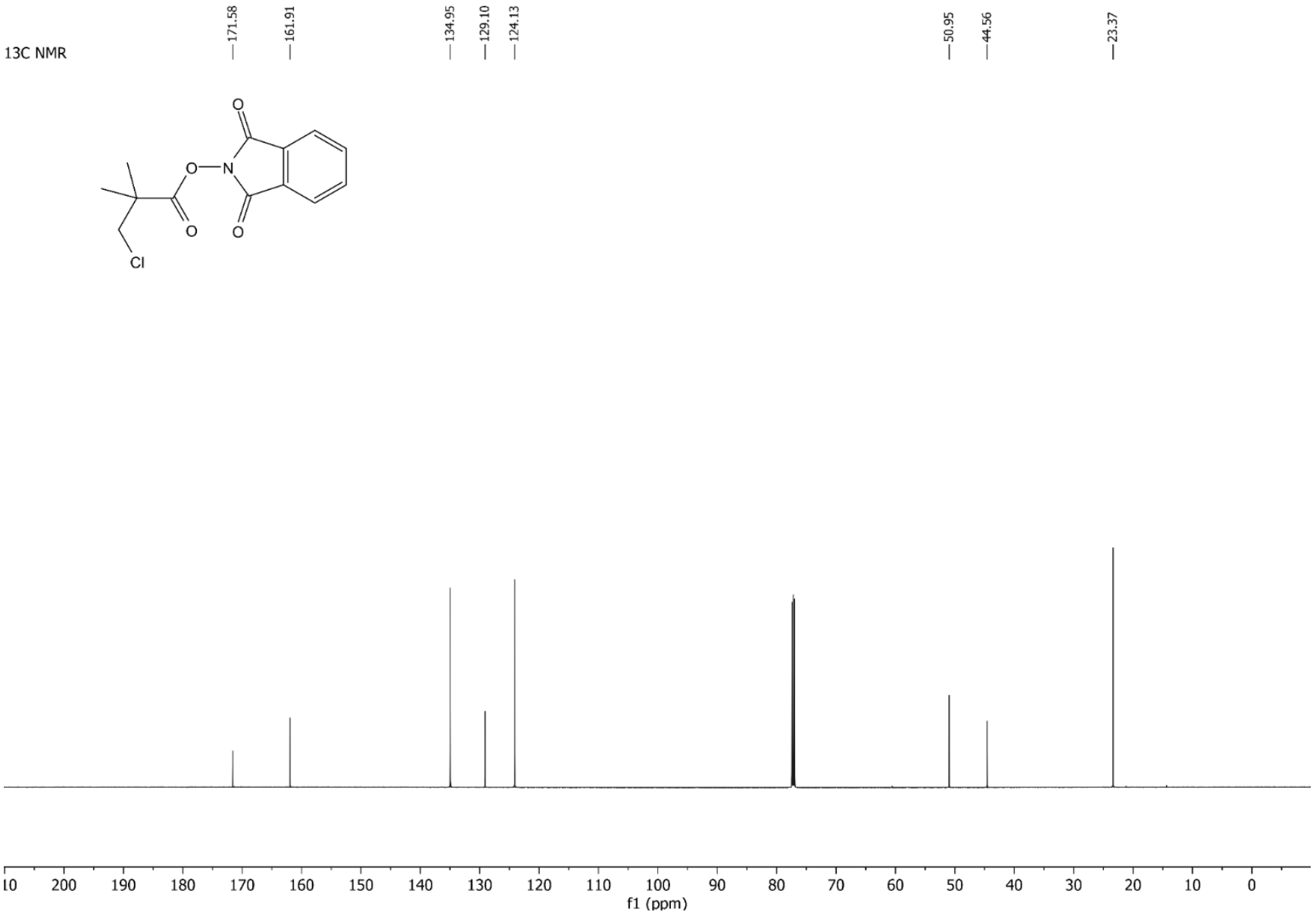
^{13}C NMR (151 MHz, $CDCl_3$) of **S-1o**



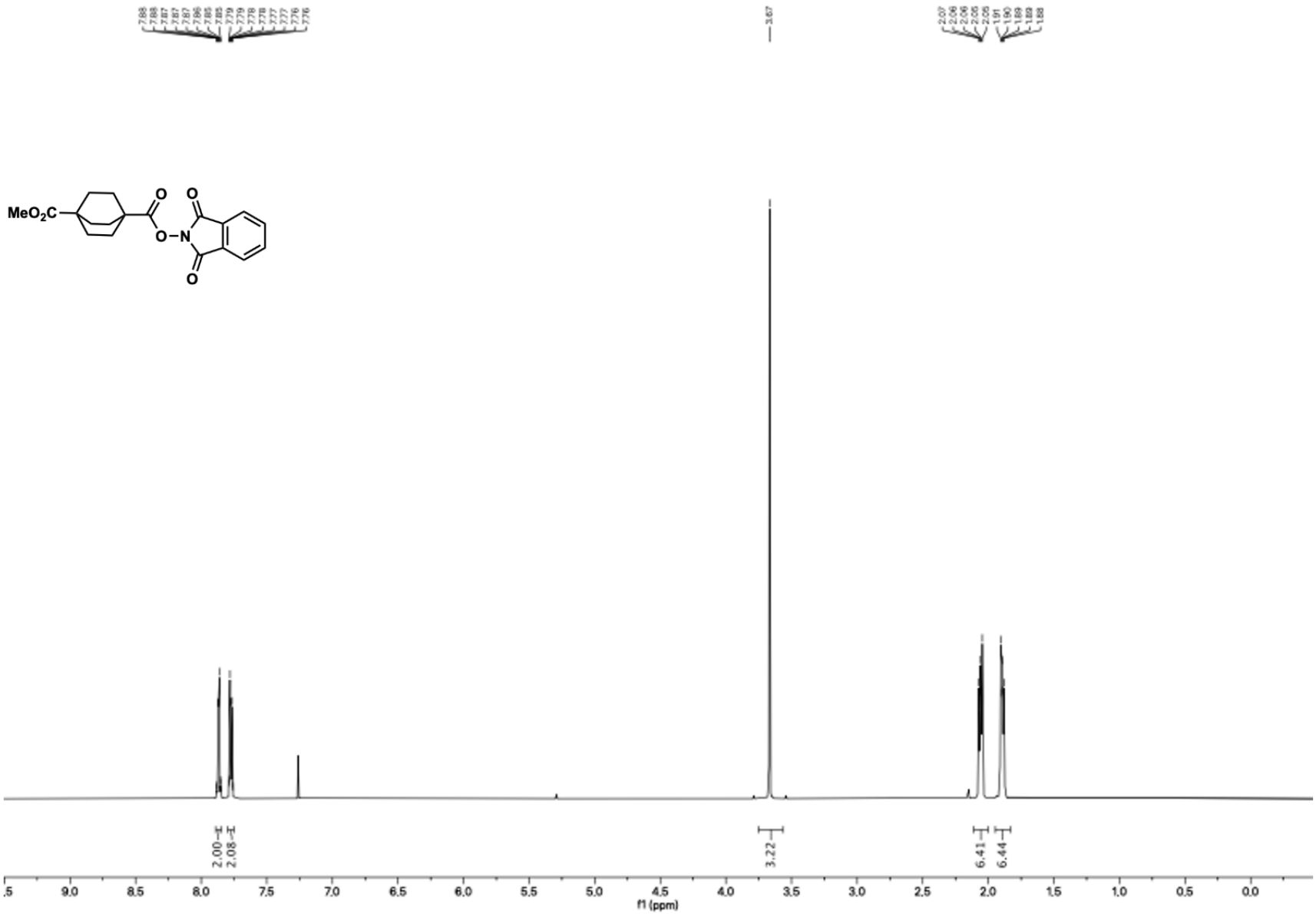
^{1}H NMR (600 MHz, $CDCl_3$) of **S-1p**



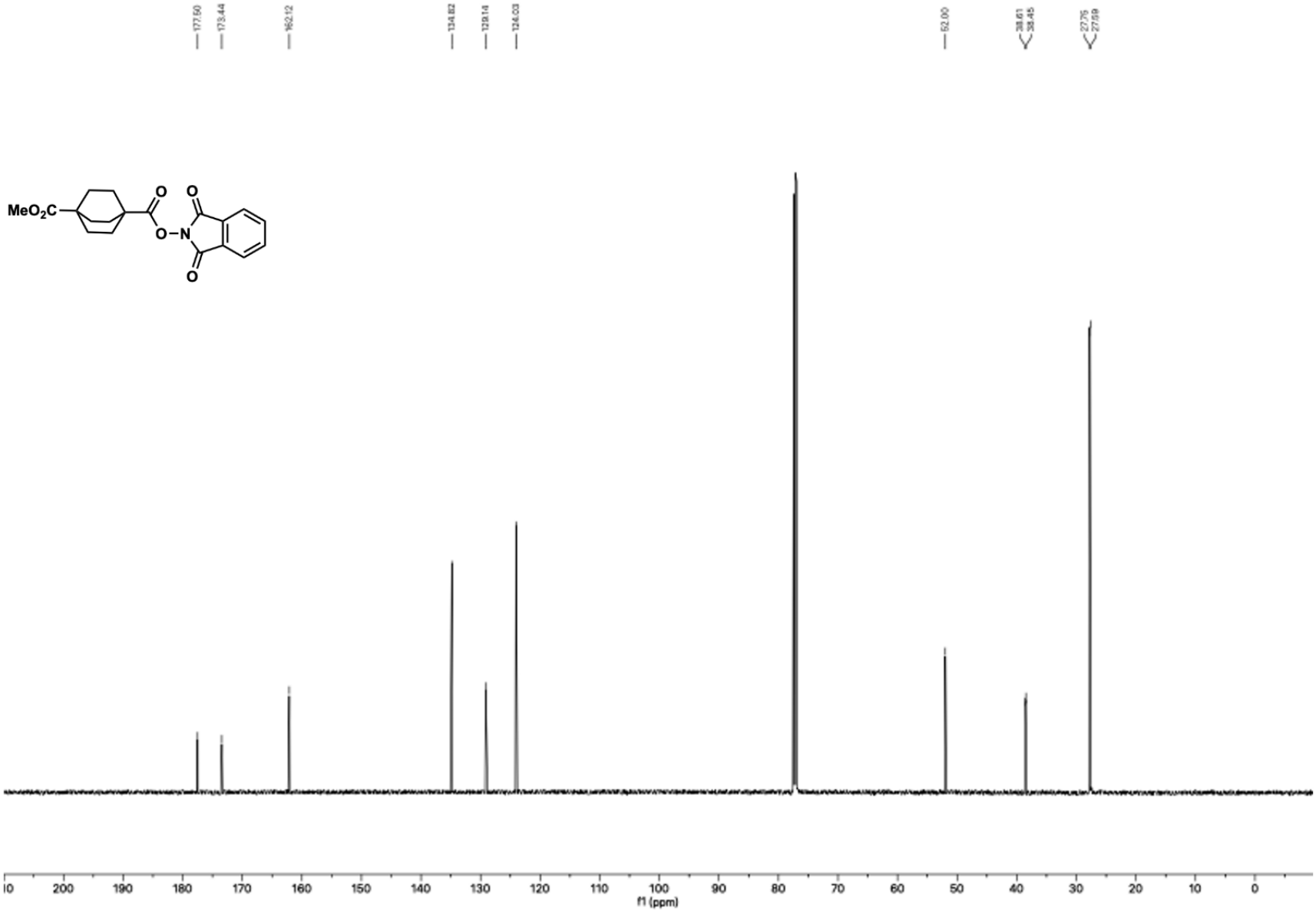
^{13}C NMR (151 MHz, $CDCl_3$) of **S-1p**



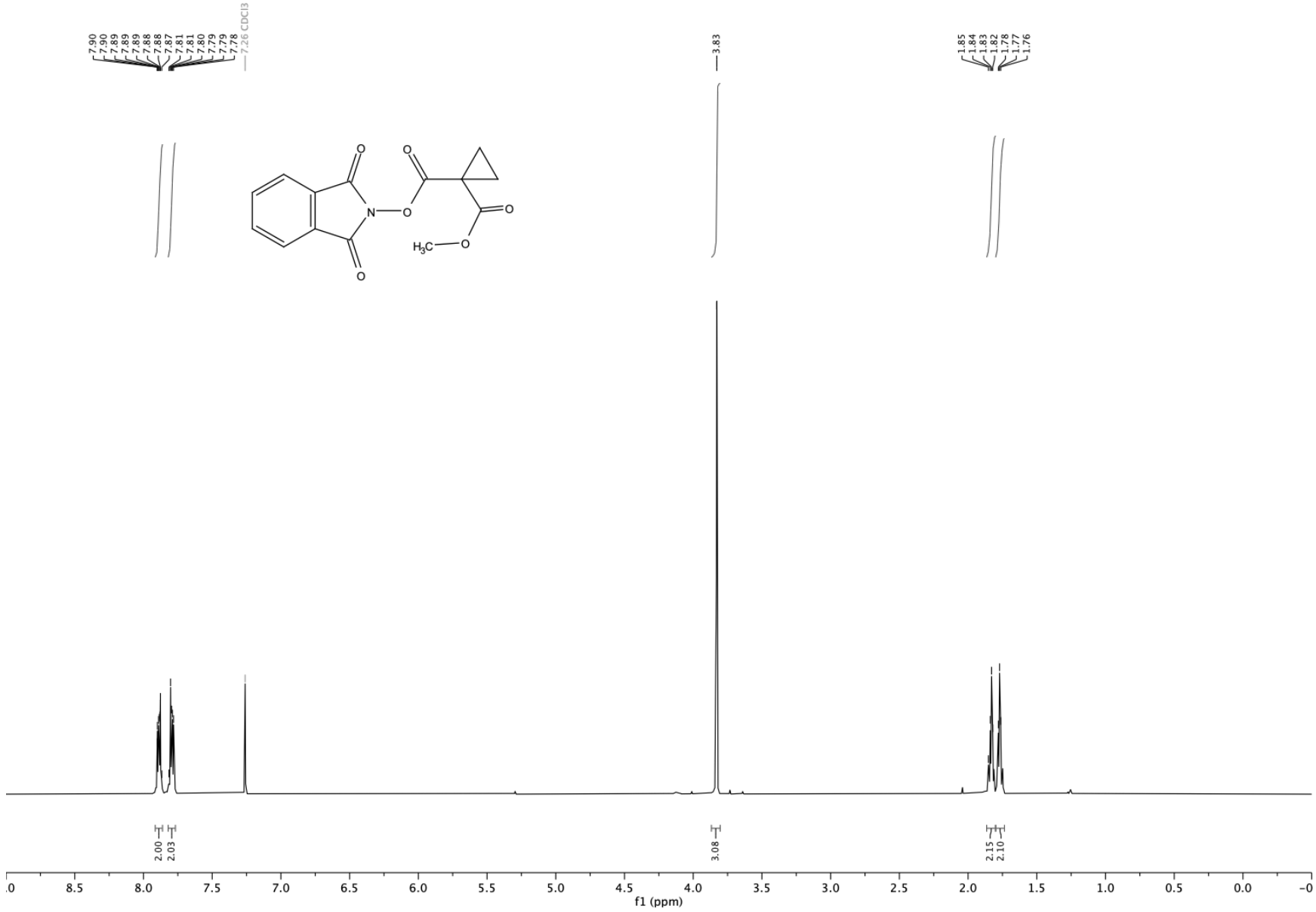
^{1}H NMR (600 MHz, $CDCl_3$) of **S-1q**



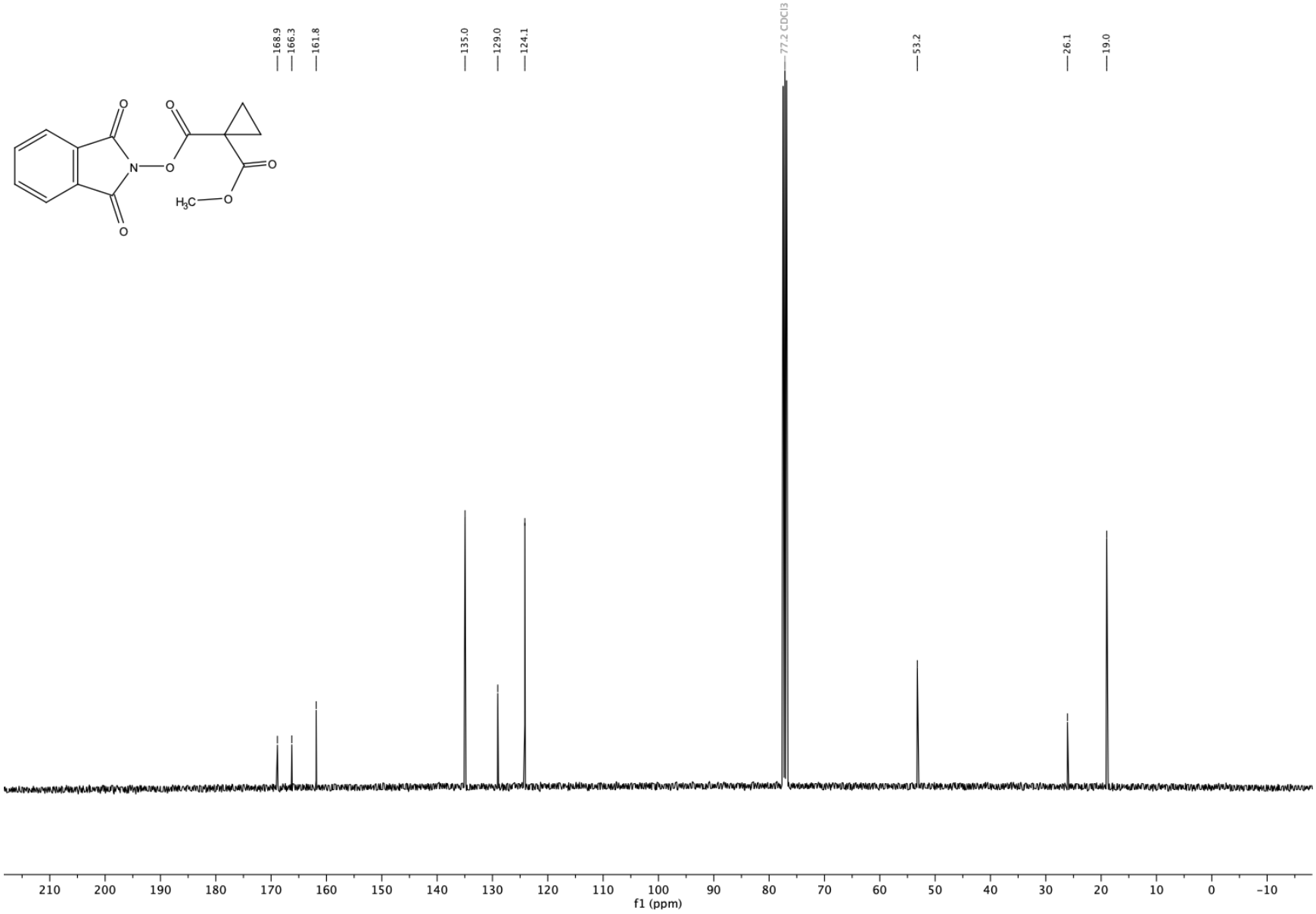
^{13}C NMR (151 MHz, $CDCl_3$) of **S-1q**



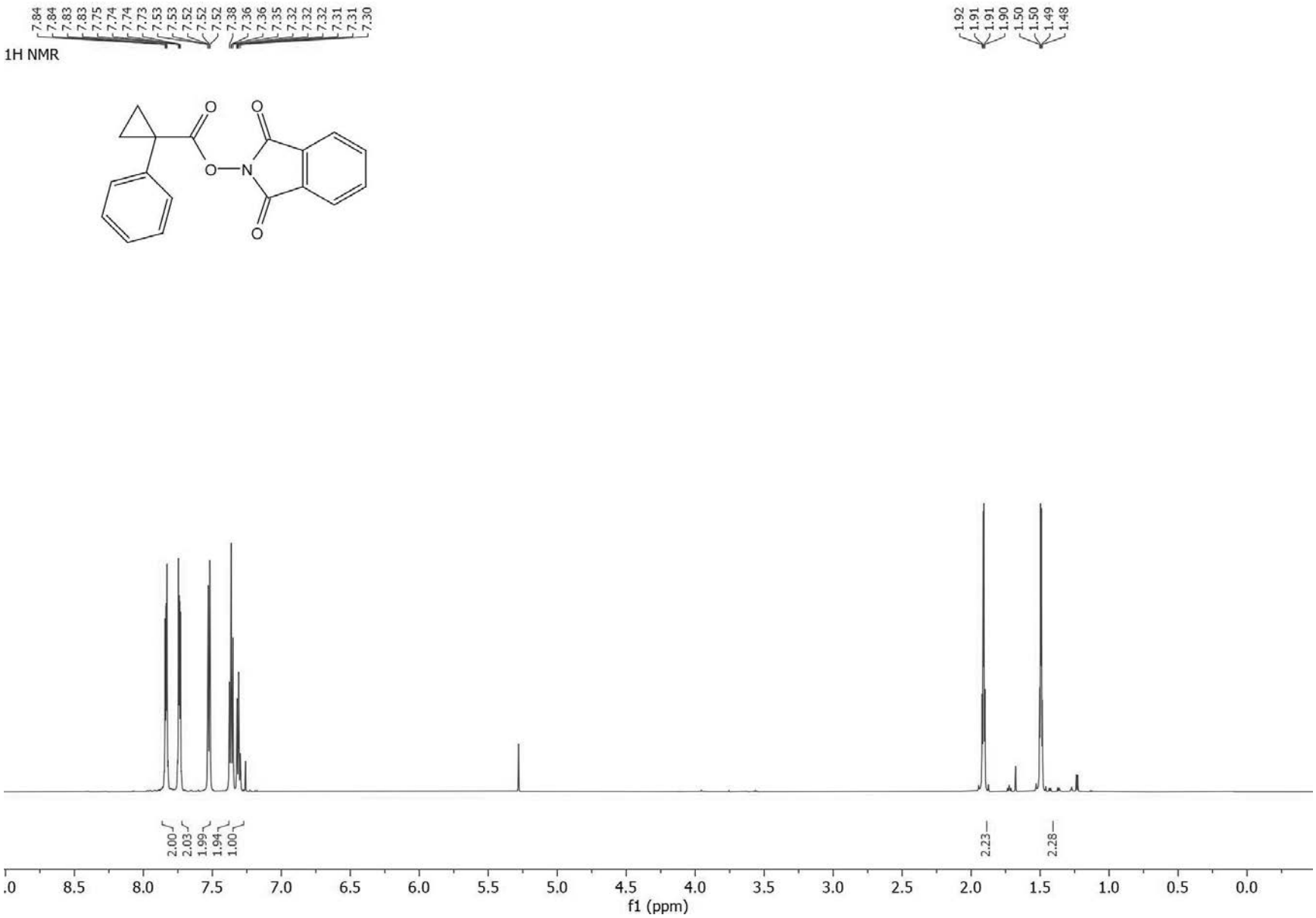
^{1}H NMR (600 MHz, $CDCl_3$) of **S-1r**



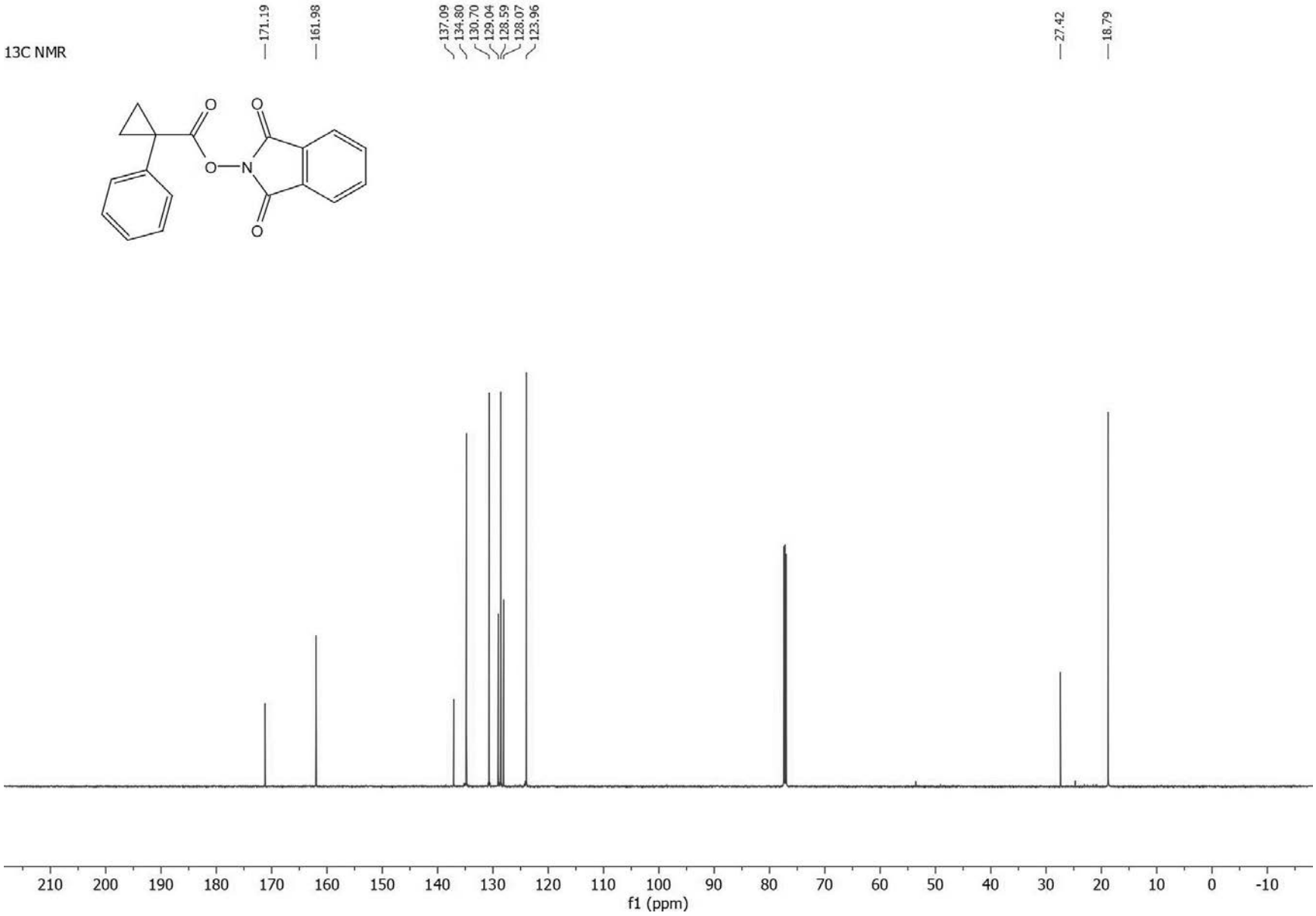
^{13}C NMR (151 MHz, $CDCl_3$) of **S-1r**



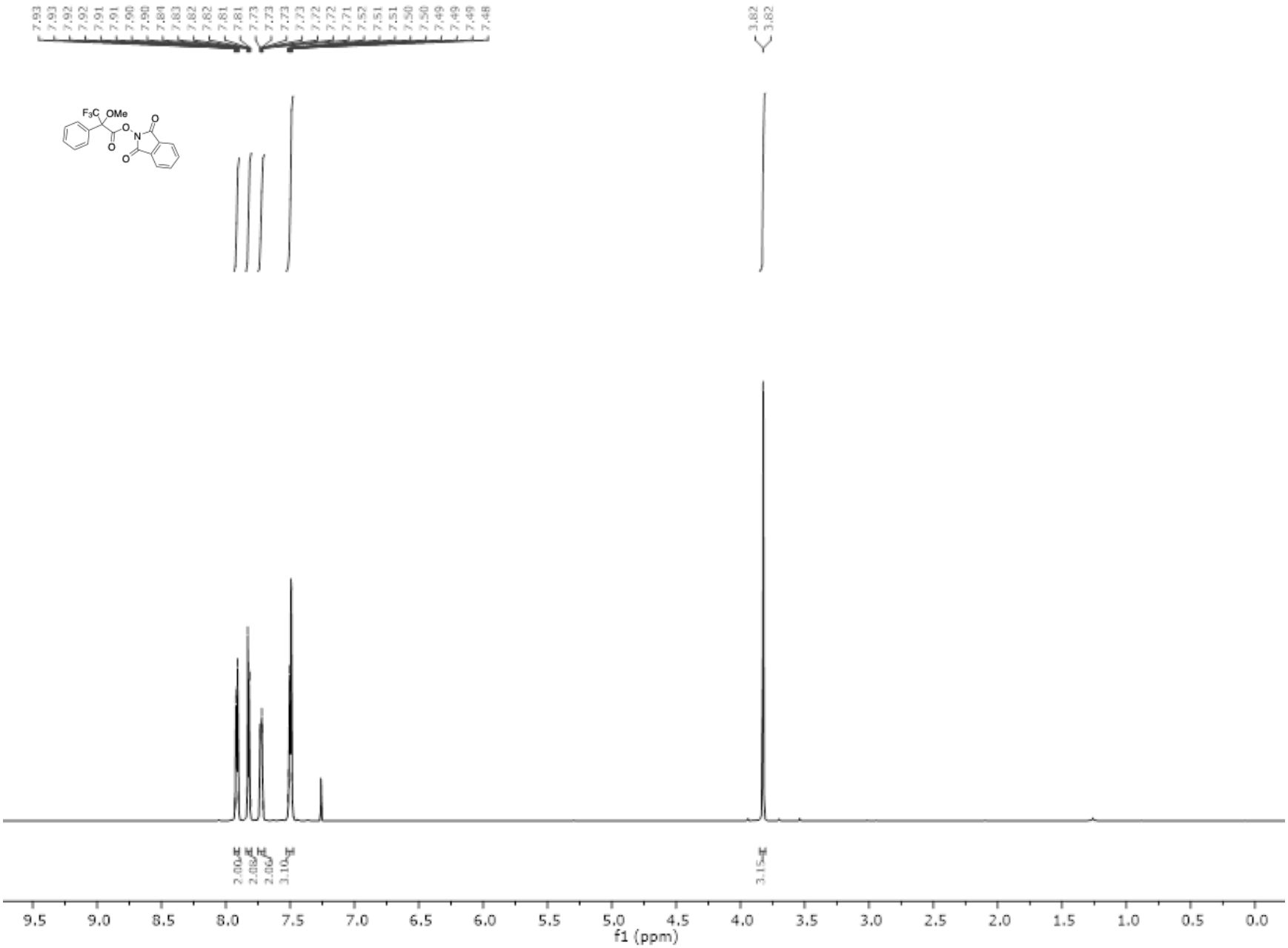
^{1}H NMR (600 MHz, $CDCl_3$) of **S-1s**



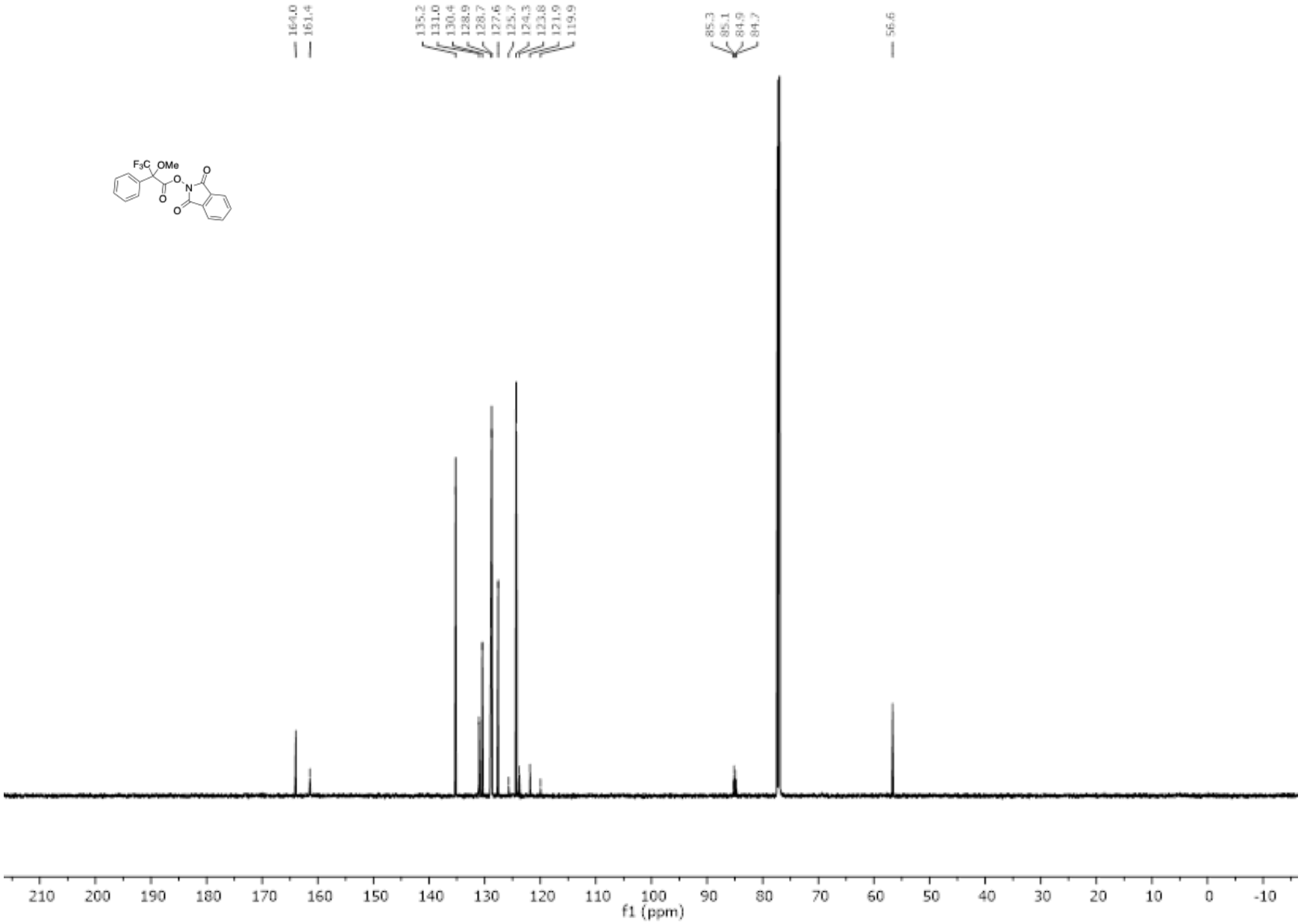
^{13}C NMR (151 MHz, $CDCl_3$) of **S-1s**



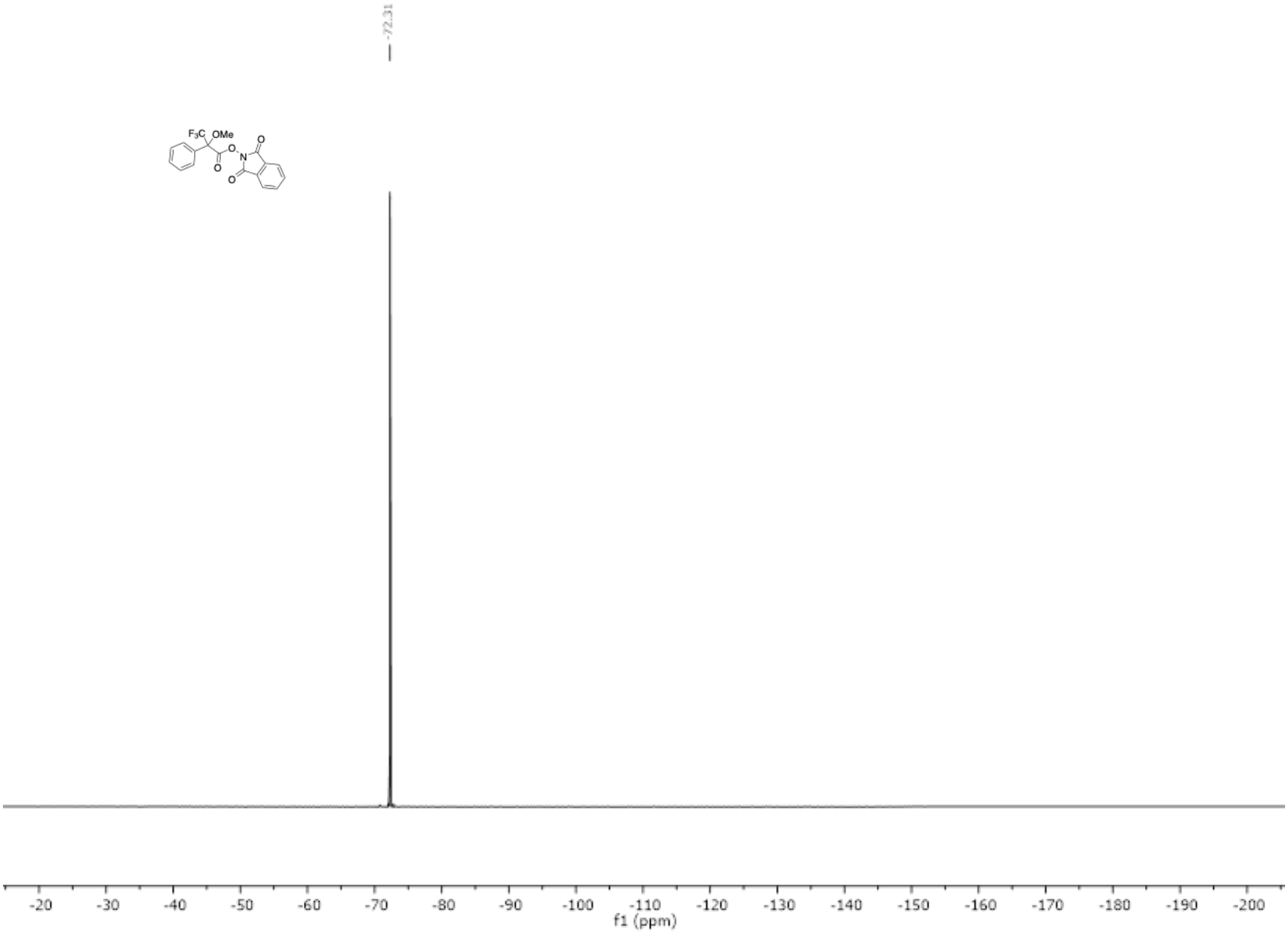
^{1}H NMR (600 MHz, $CDCl_3$) of **S-1t**



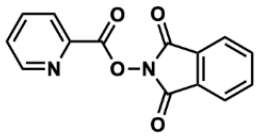
^{13}C NMR (151 MHz, $CDCl_3$) of **S-1t**

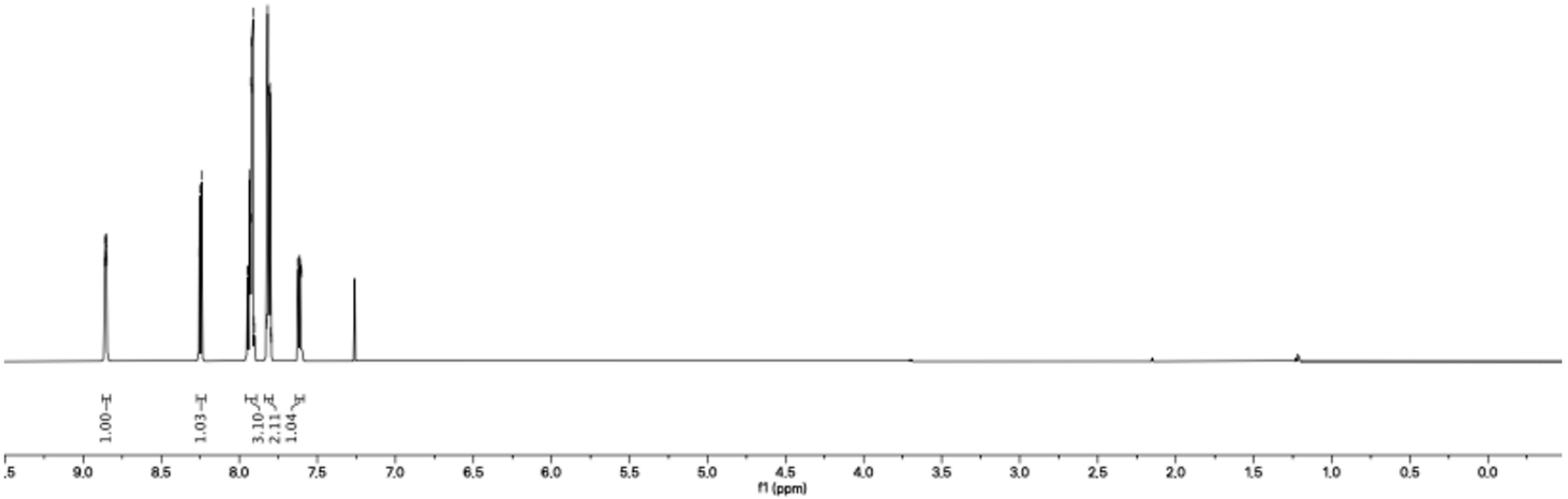


^{19}F NMR (376 MHz, $CDCl_3$) of **S-1t**

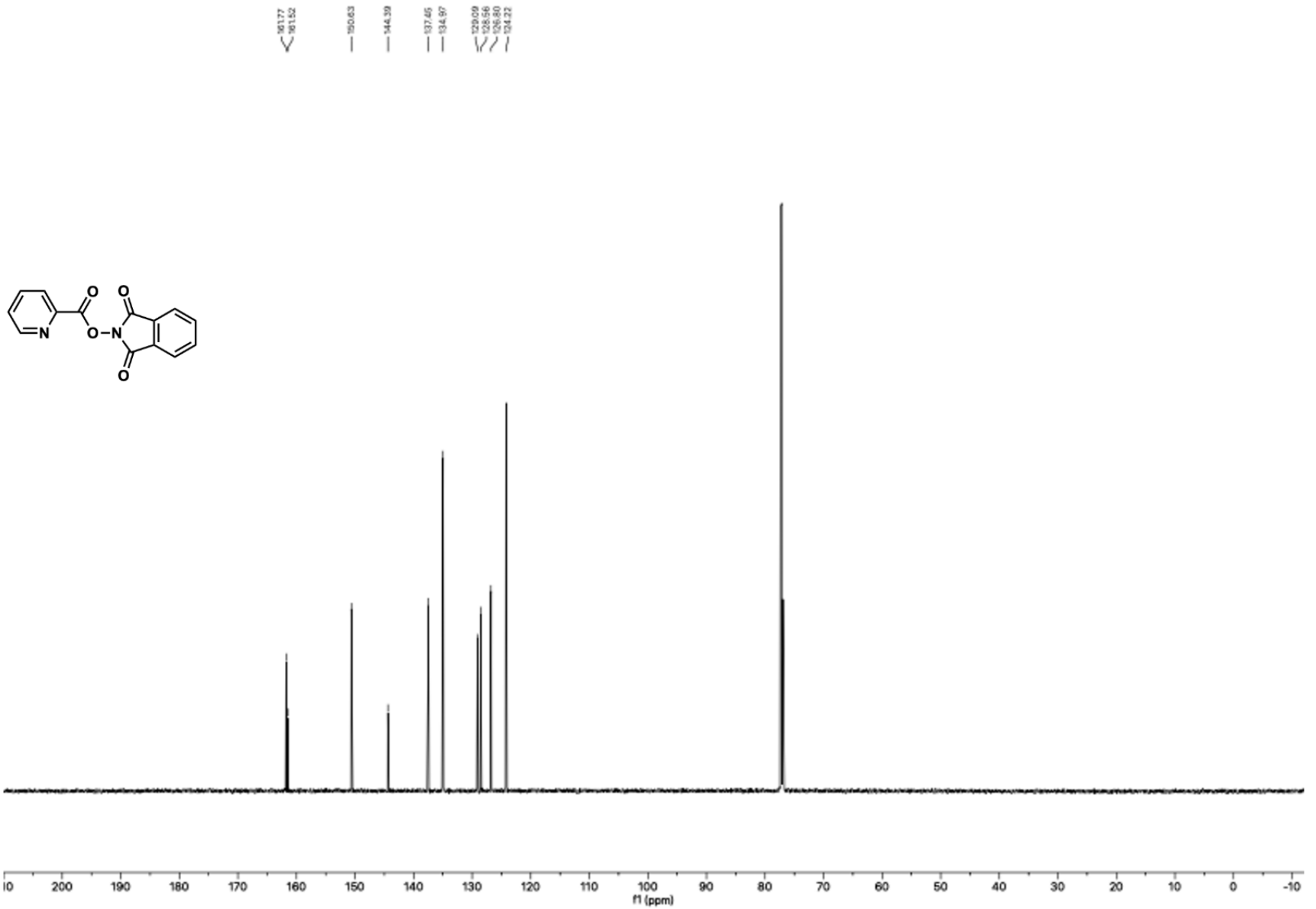


^{1}H NMR (600 MHz, $CDCl_3$) of **S-1u**

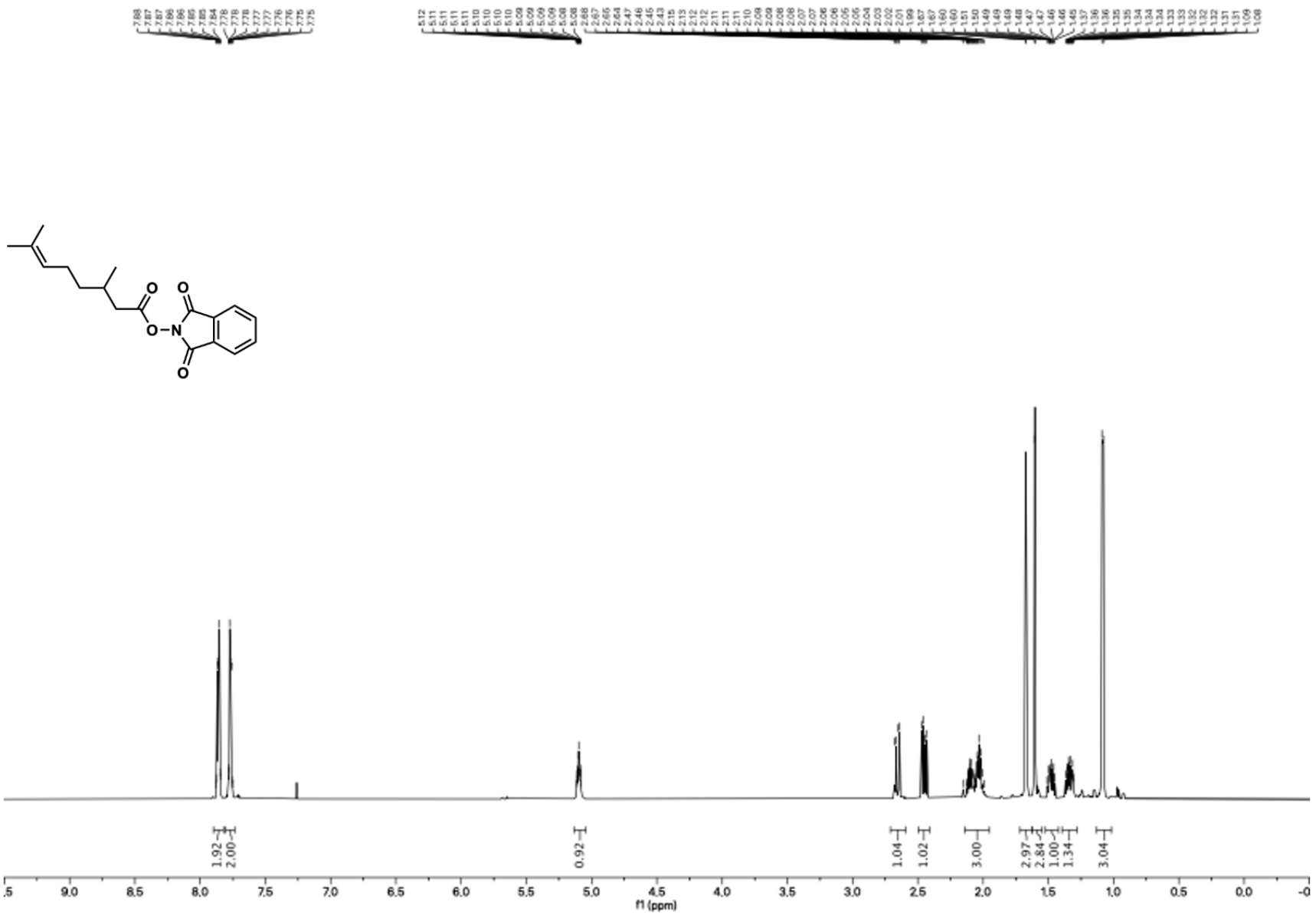




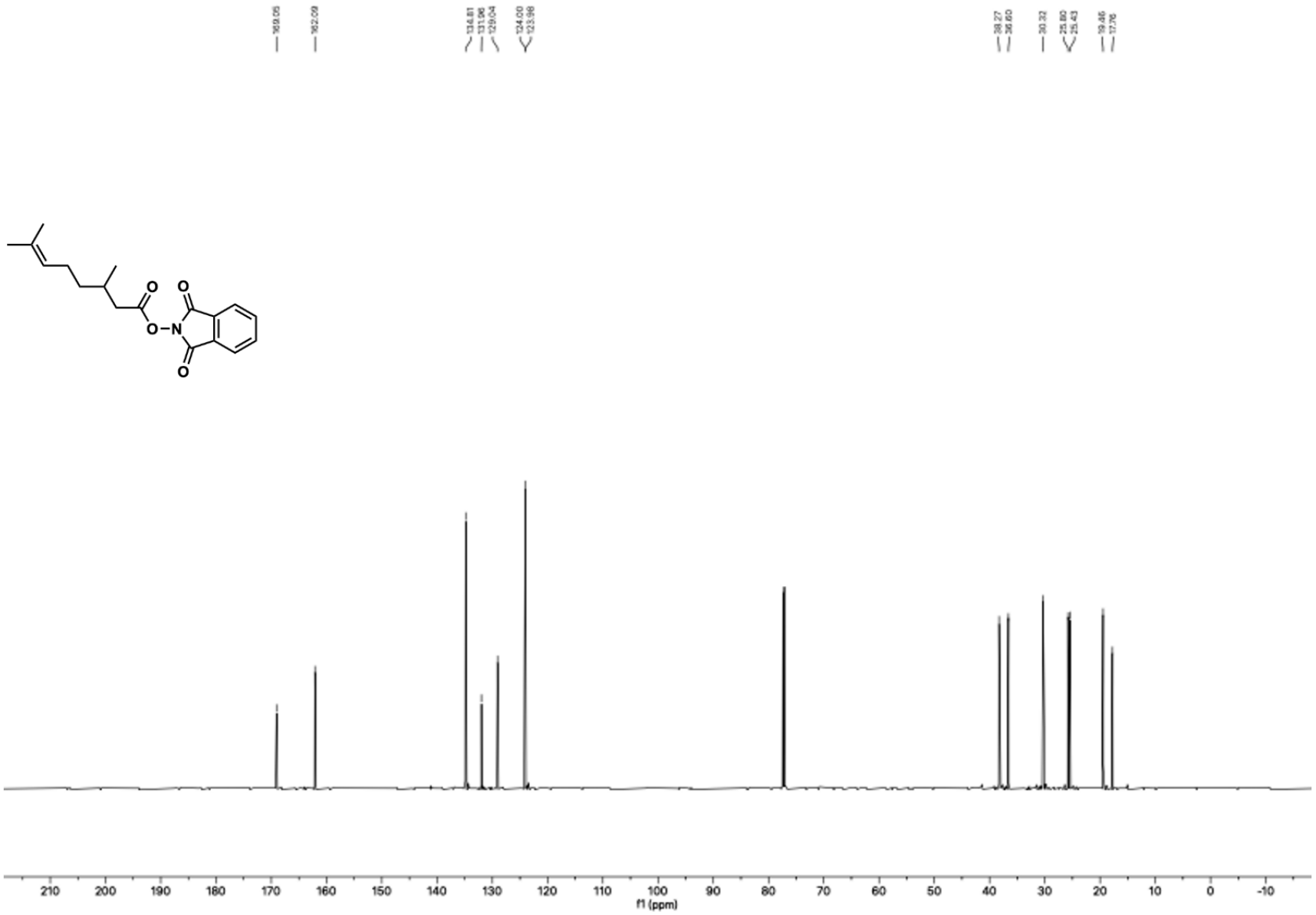
^{13}C NMR (151 MHz, $CDCl_3$) of **S-1u**



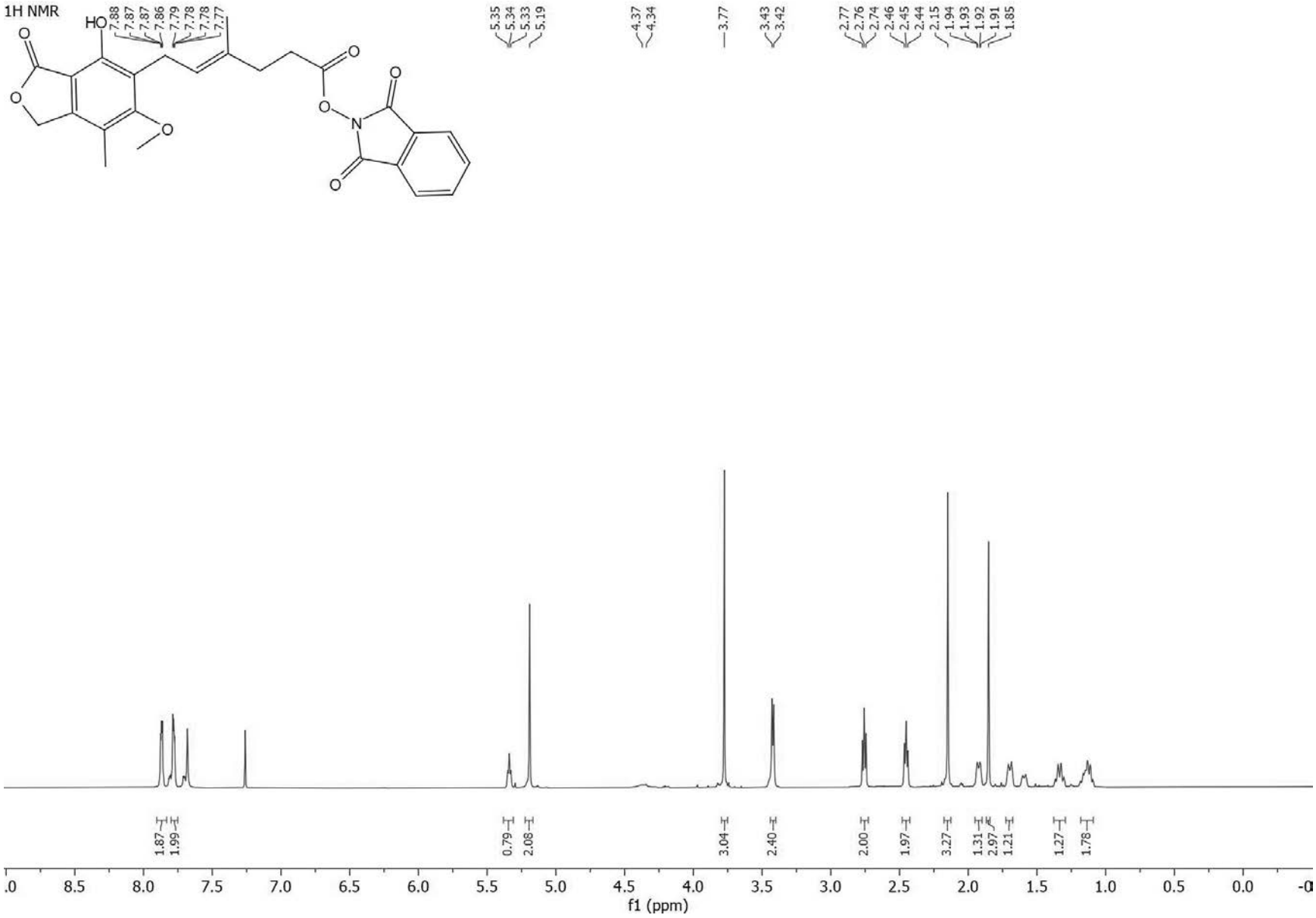
^{1}H NMR (600 MHz, $CDCl_3$) of **S-1v**



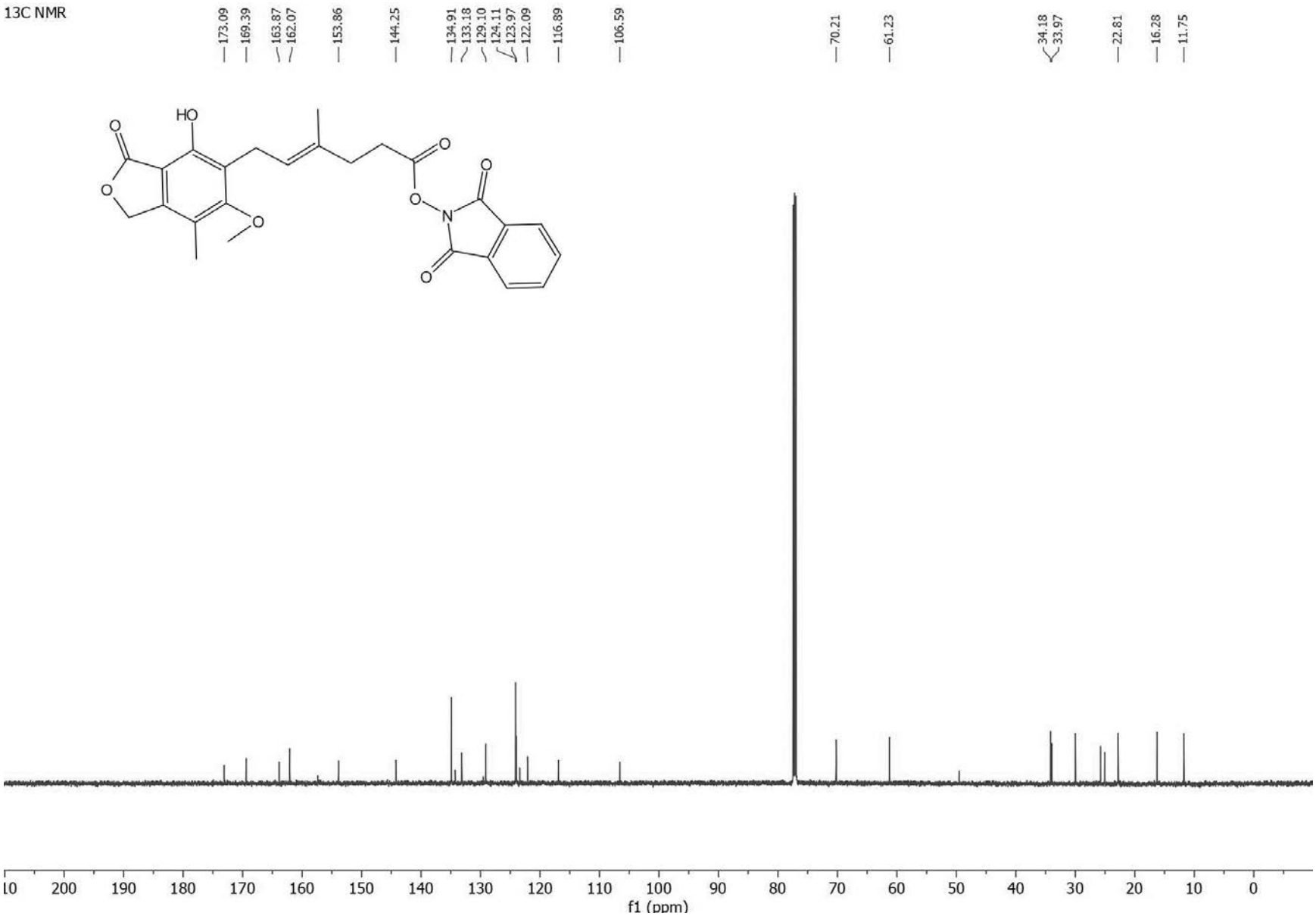
^{13}C NMR (151 MHz, $CDCl_3$) of **S-1v**



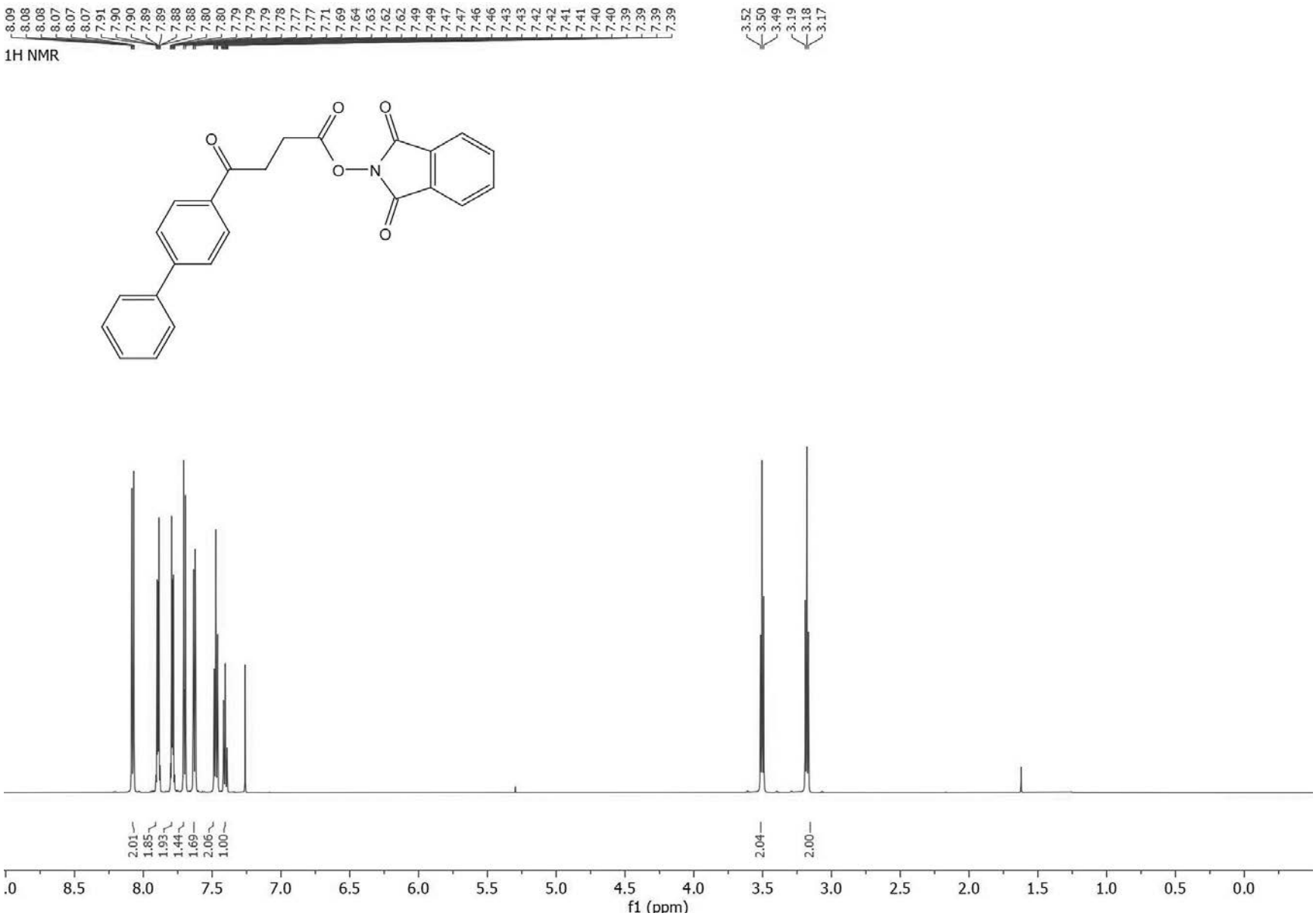
^{1}H NMR (600 MHz, $CDCl_3$) of **S-1w**



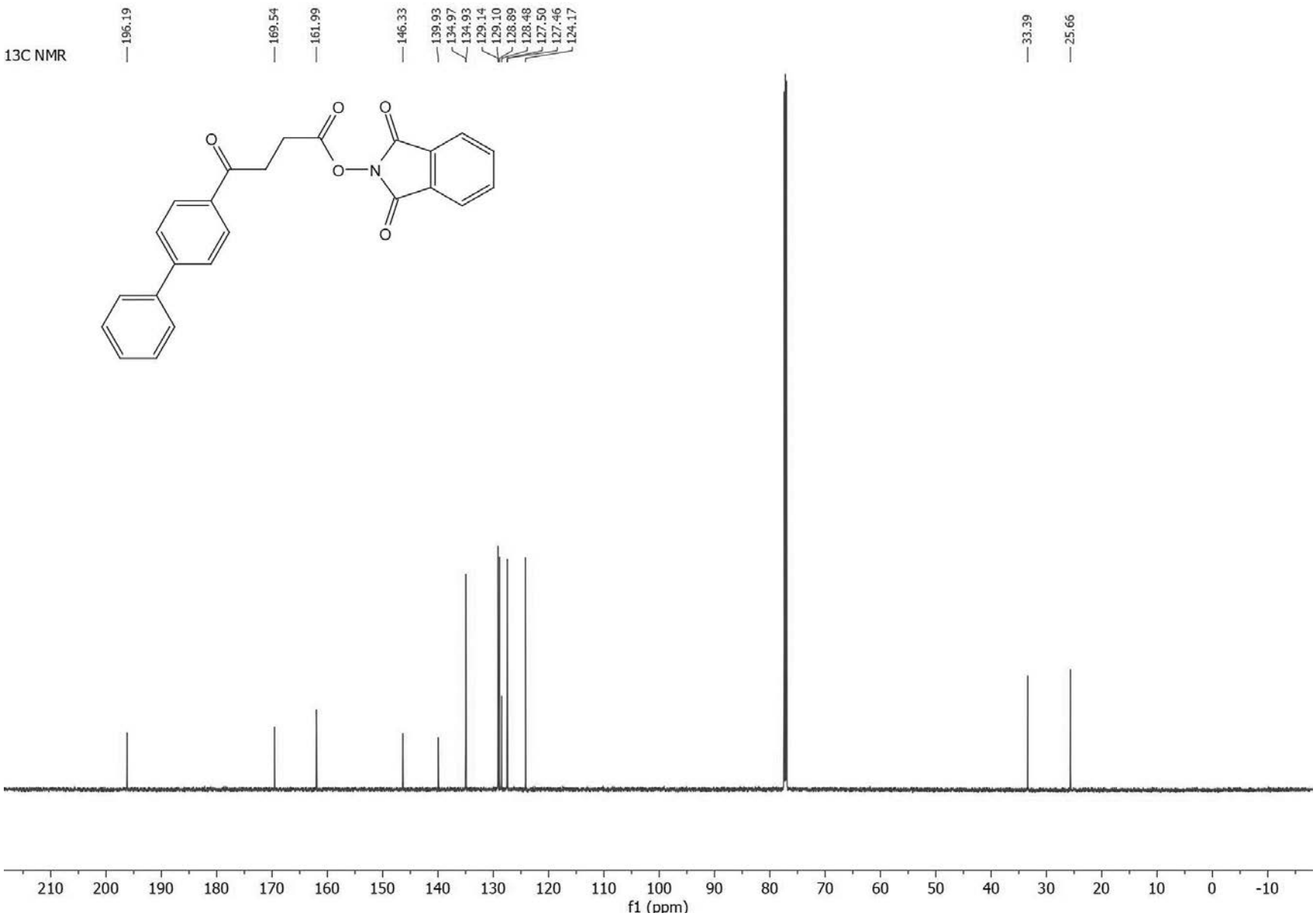
^{13}C NMR (151 MHz, $CDCl_3$) of **S-1w**



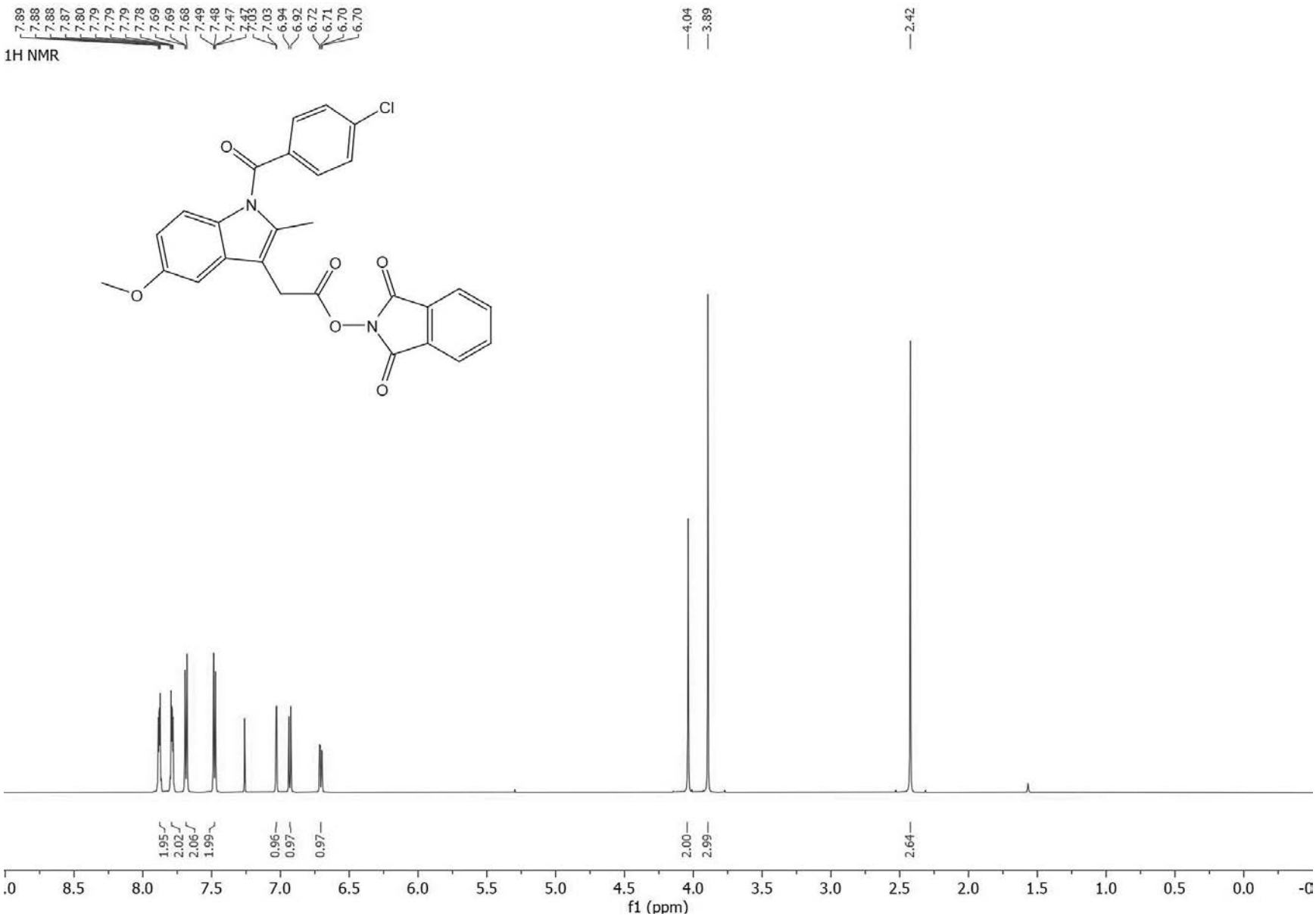
^{1}H NMR (600 MHz, $CDCl_3$) of **S-1x**



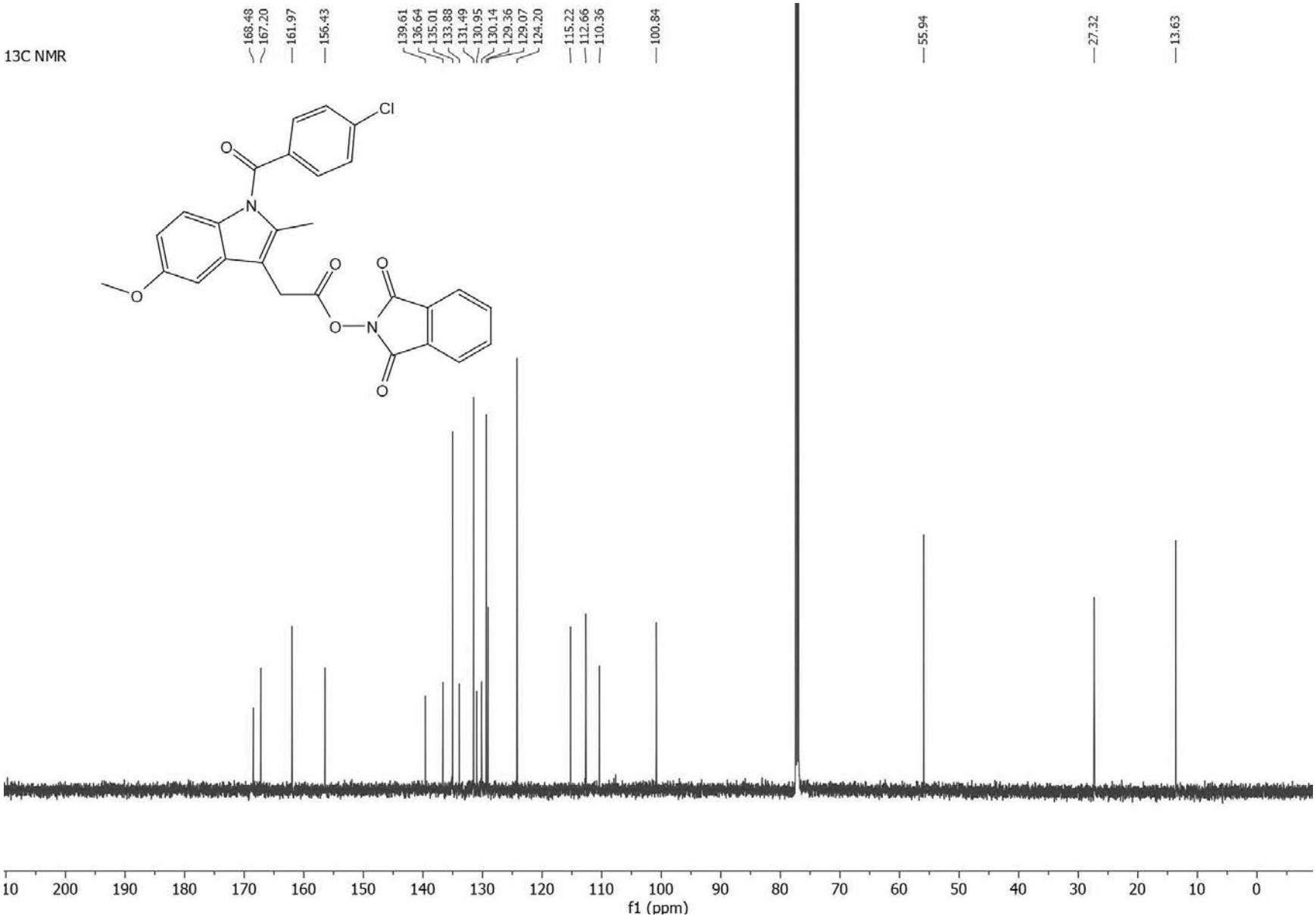
^{13}C NMR (151 MHz, $CDCl_3$) of **S-1x**



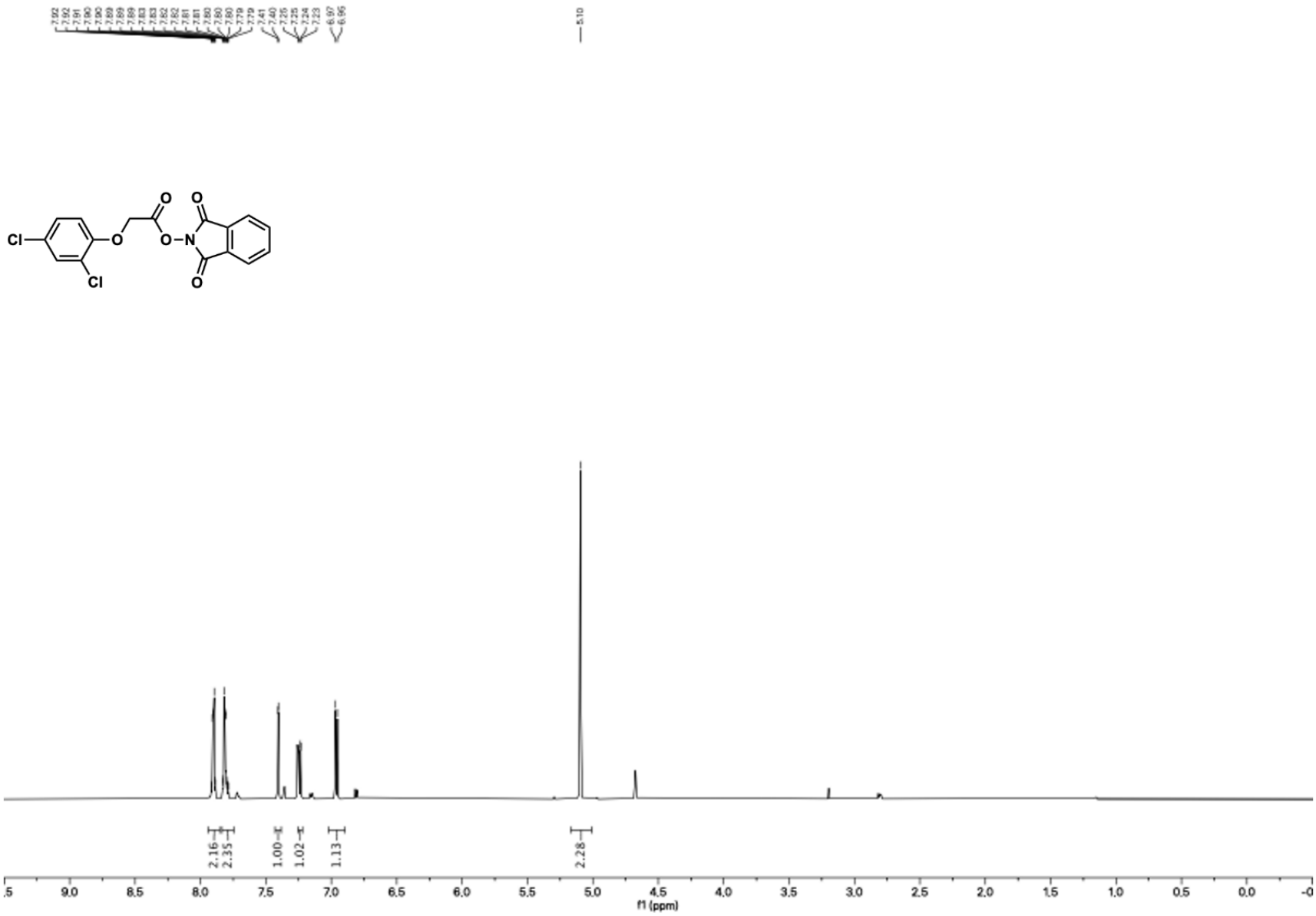
^{1}H NMR (600 MHz, $CDCl_3$) of **S-1y**



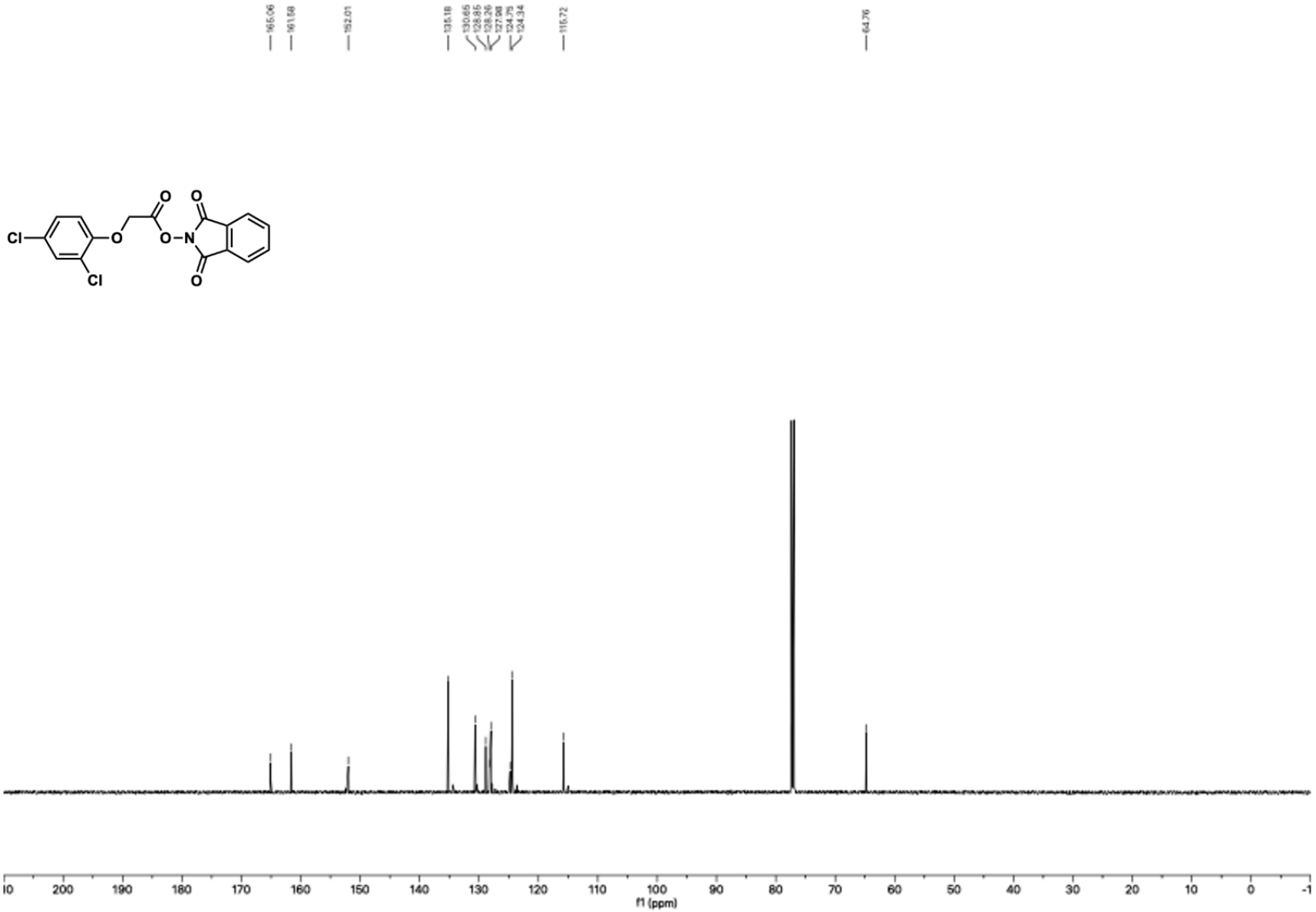
^{13}C NMR (151 MHz, $CDCl_3$) of **S-1y**



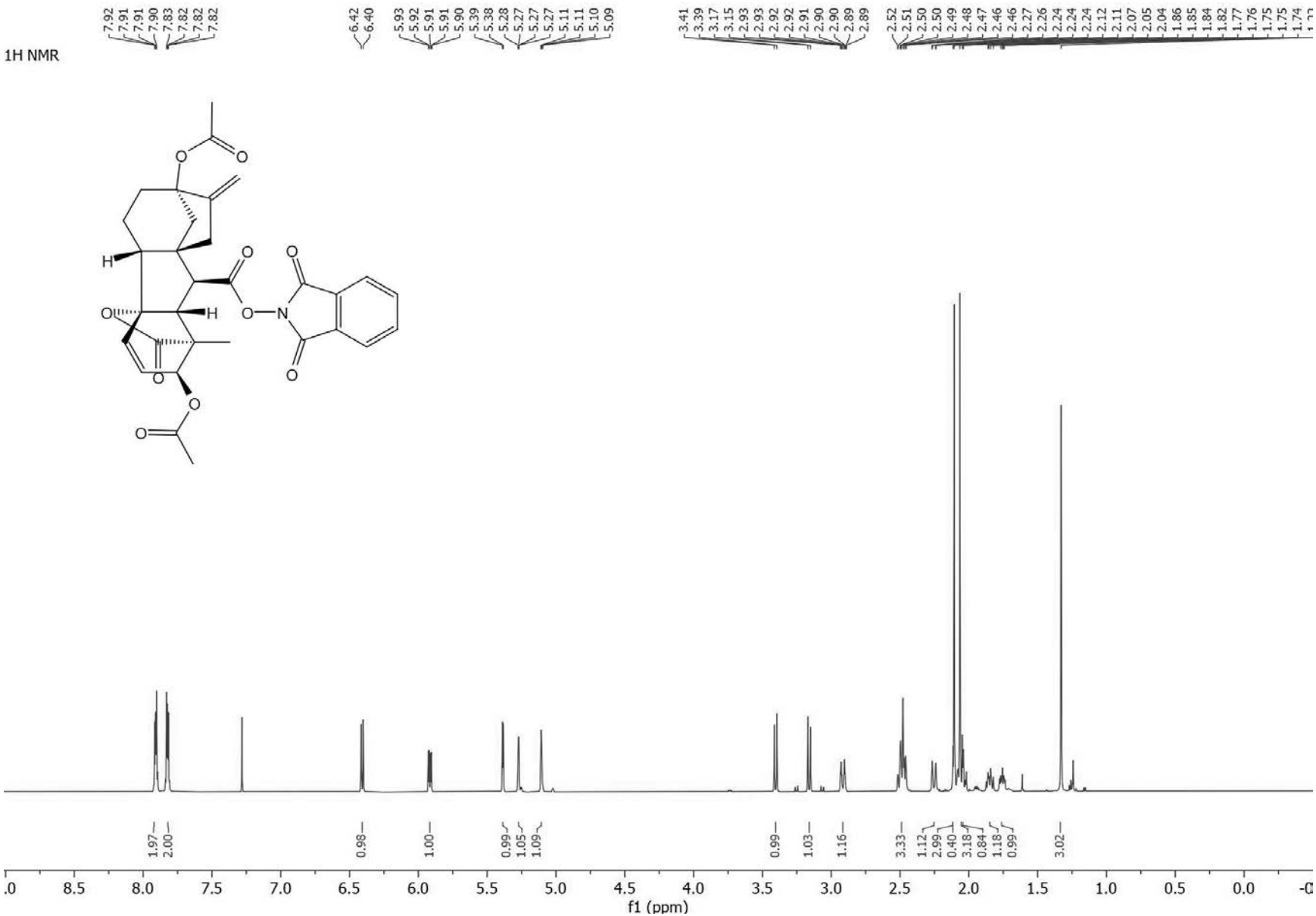
^{1}H NMR (600 MHz, $CDCl_3$) of **S-1z**



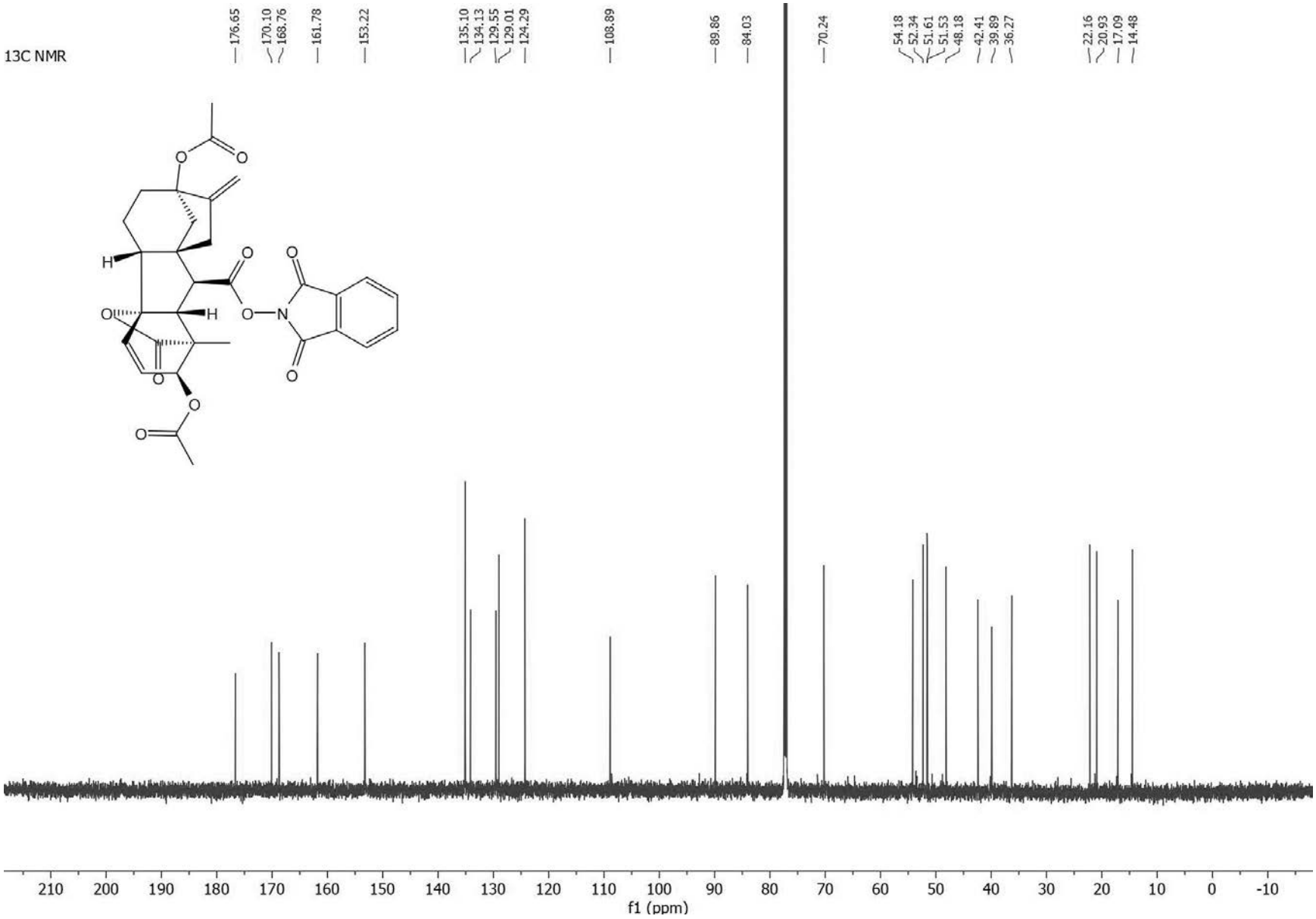
^{13}C NMR (151 MHz, $CDCl_3$) of **S-1z**



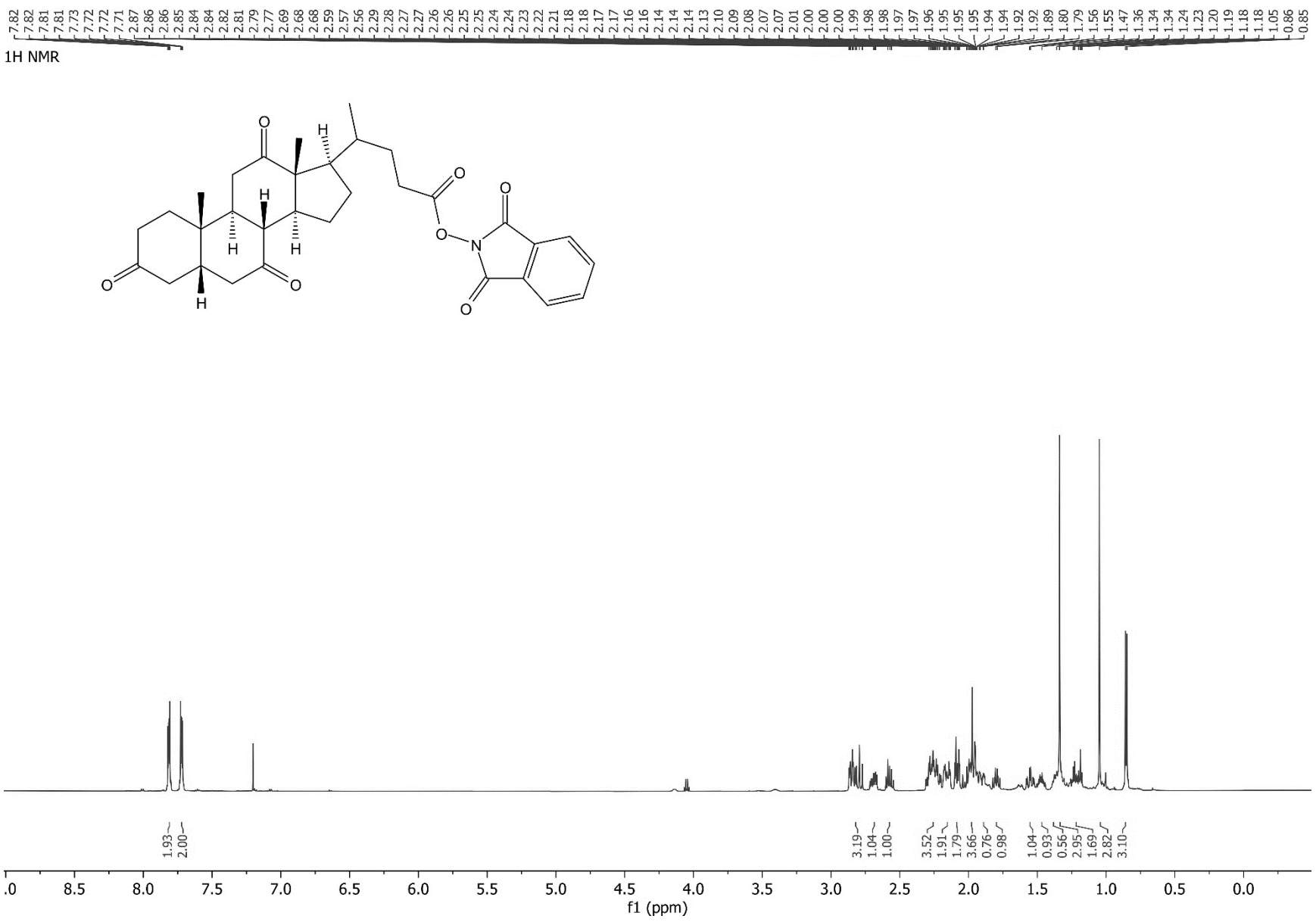
^{1}H NMR (600 MHz, $CDCl_3$) of **S-1aa**



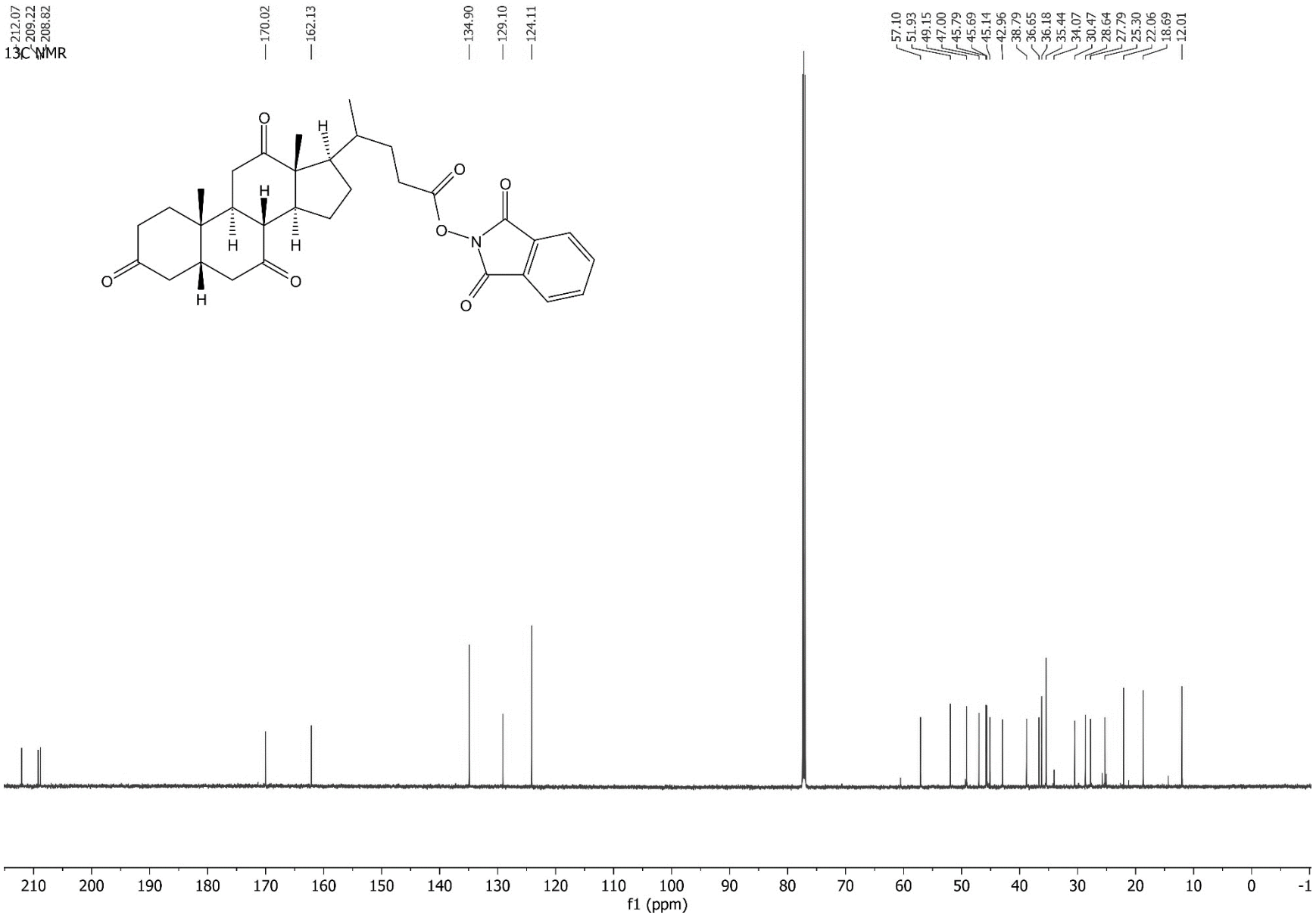
^{13}C NMR (151 MHz, $CDCl_3$) of **S-1aa**



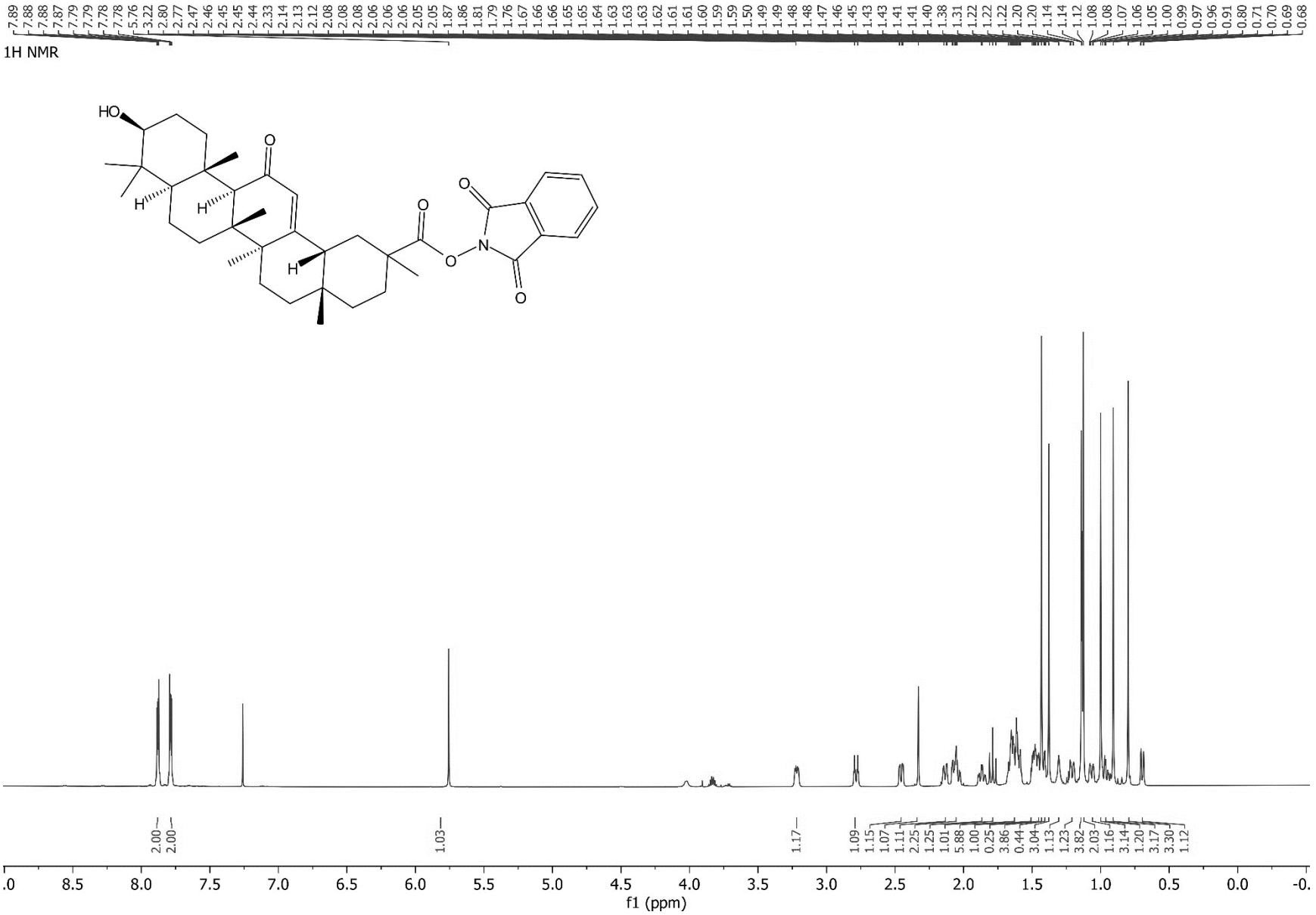
^{1}H NMR (600 MHz, $CDCl_3$) of **S-1ab**



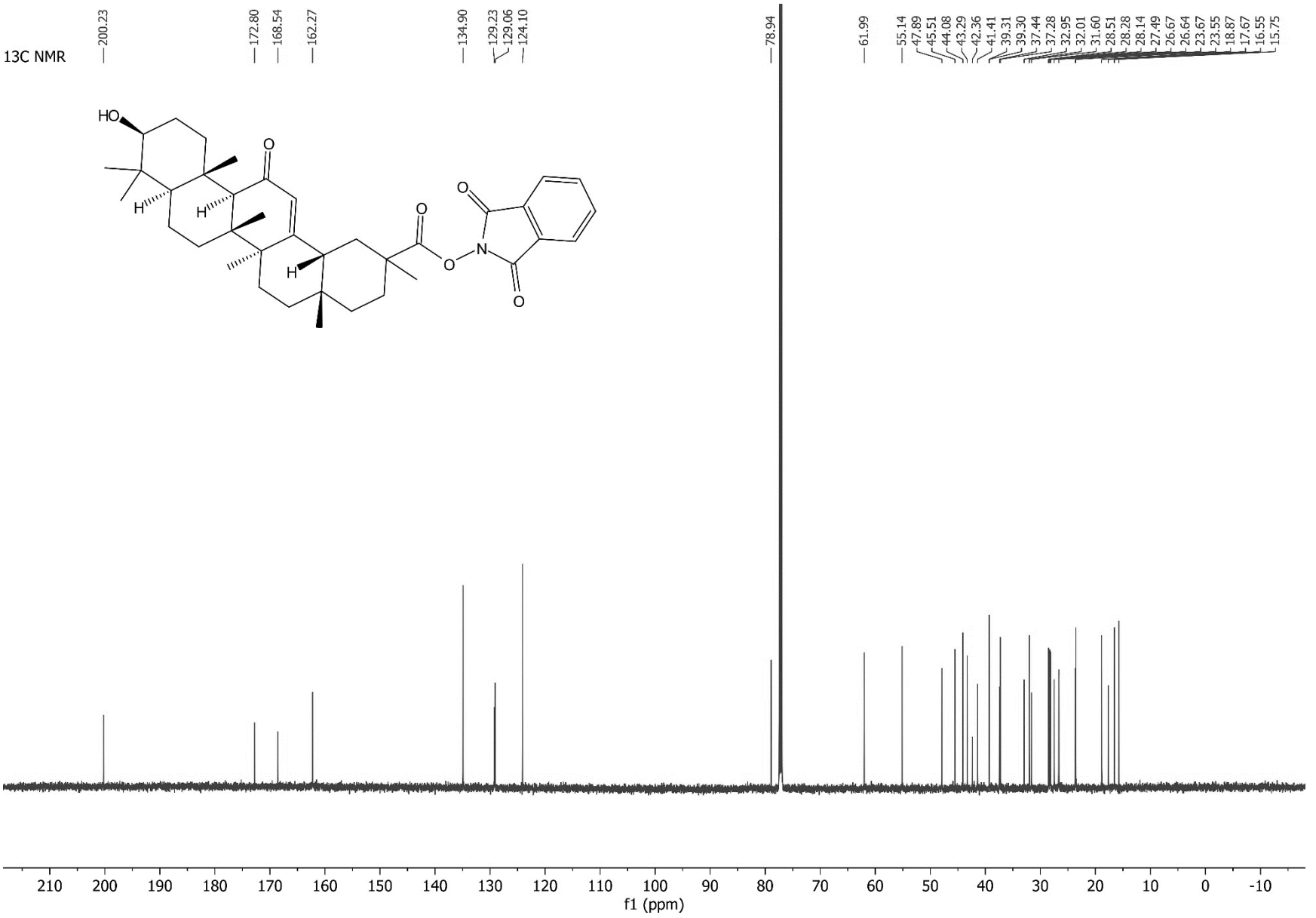
^{13}C NMR (151 MHz, $CDCl_3$) of **S-1ab**



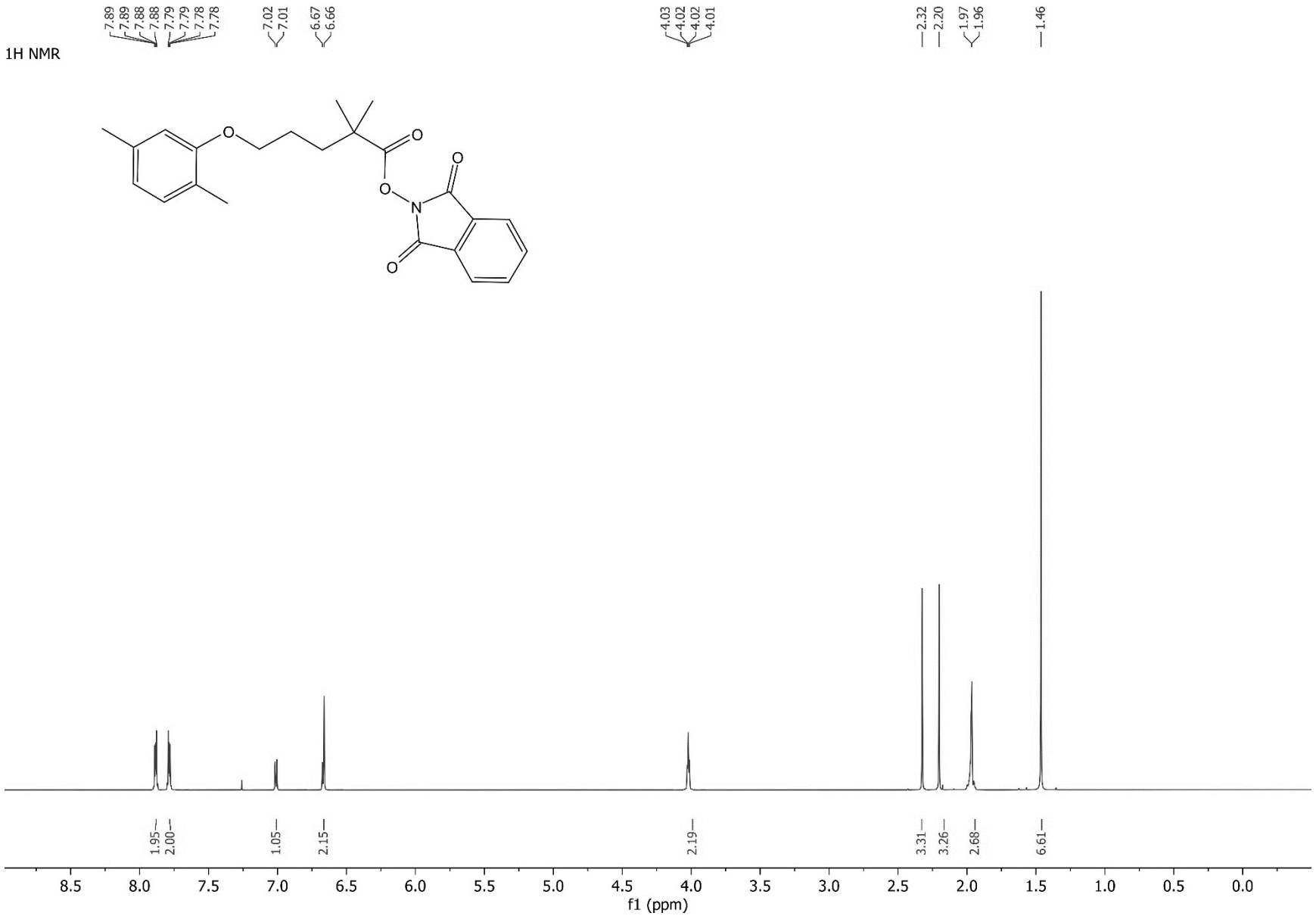
^{1}H NMR (600 MHz, $CDCl_3$) of **S-1ac**



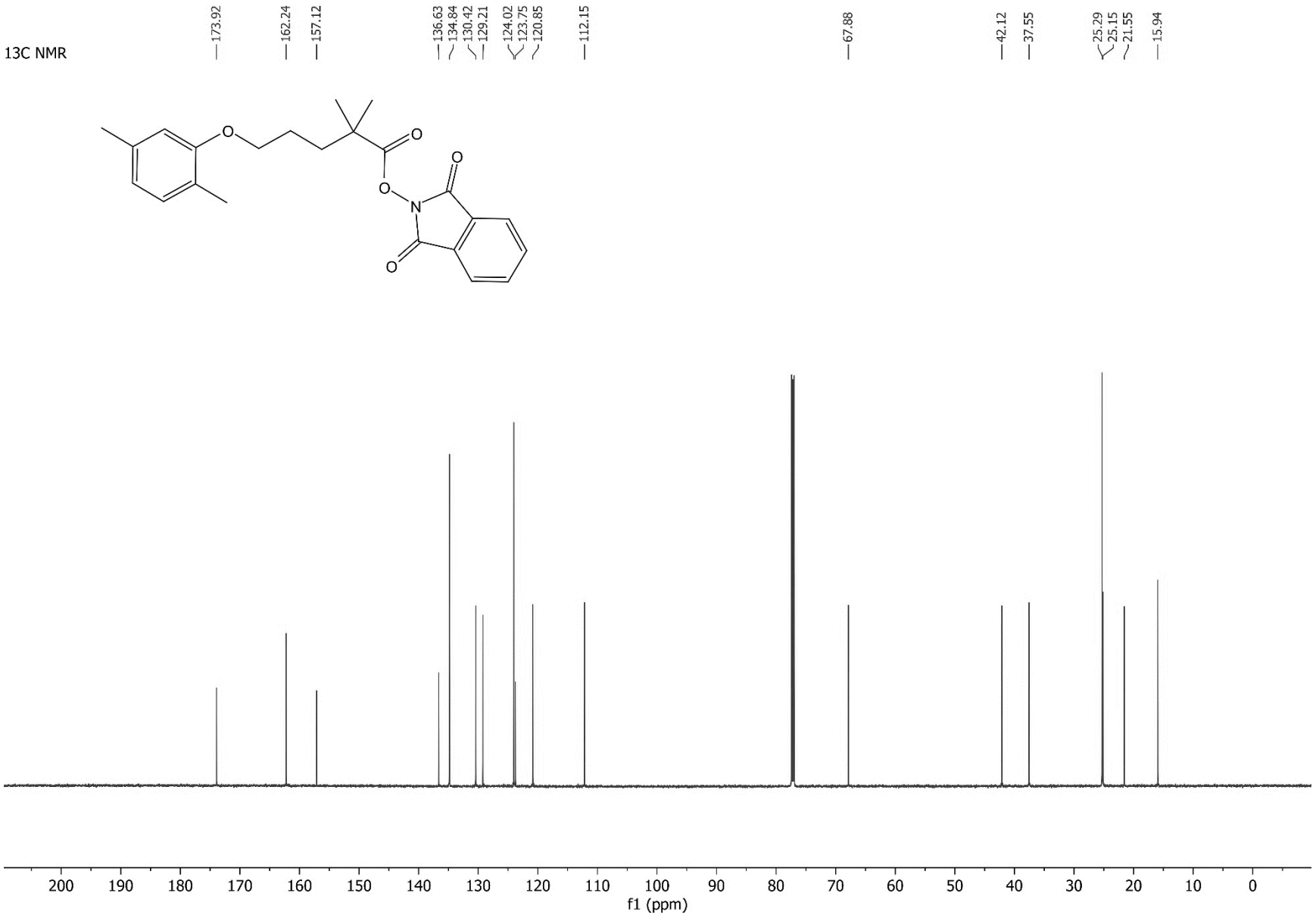
^{13}C NMR (151 MHz, $CDCl_3$) of **S-1ac**



^{1}H NMR (600 MHz, $CDCl_3$) of **S-1ad**

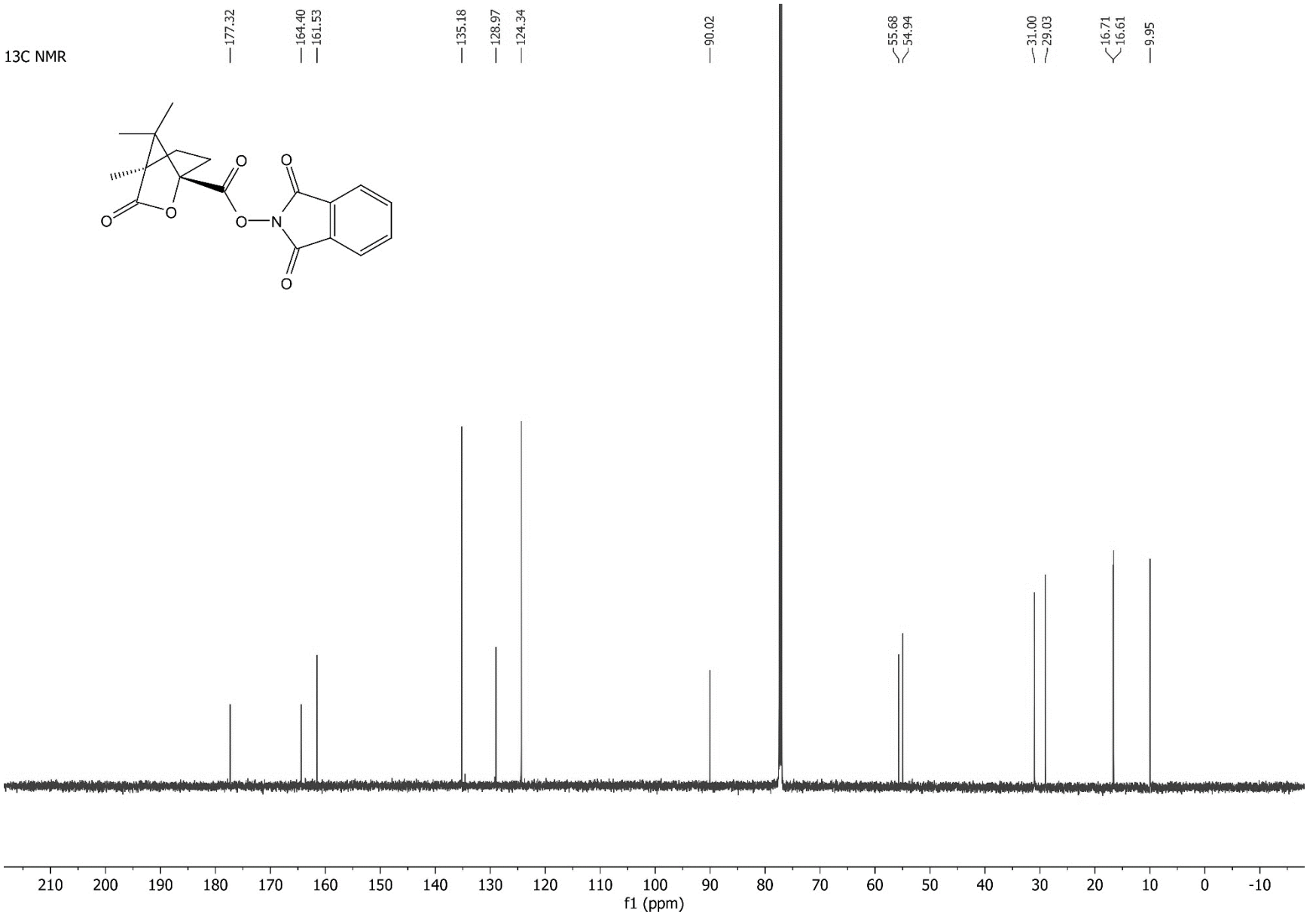


^{13}C NMR (151 MHz, $CDCl_3$) of **S-1ad**

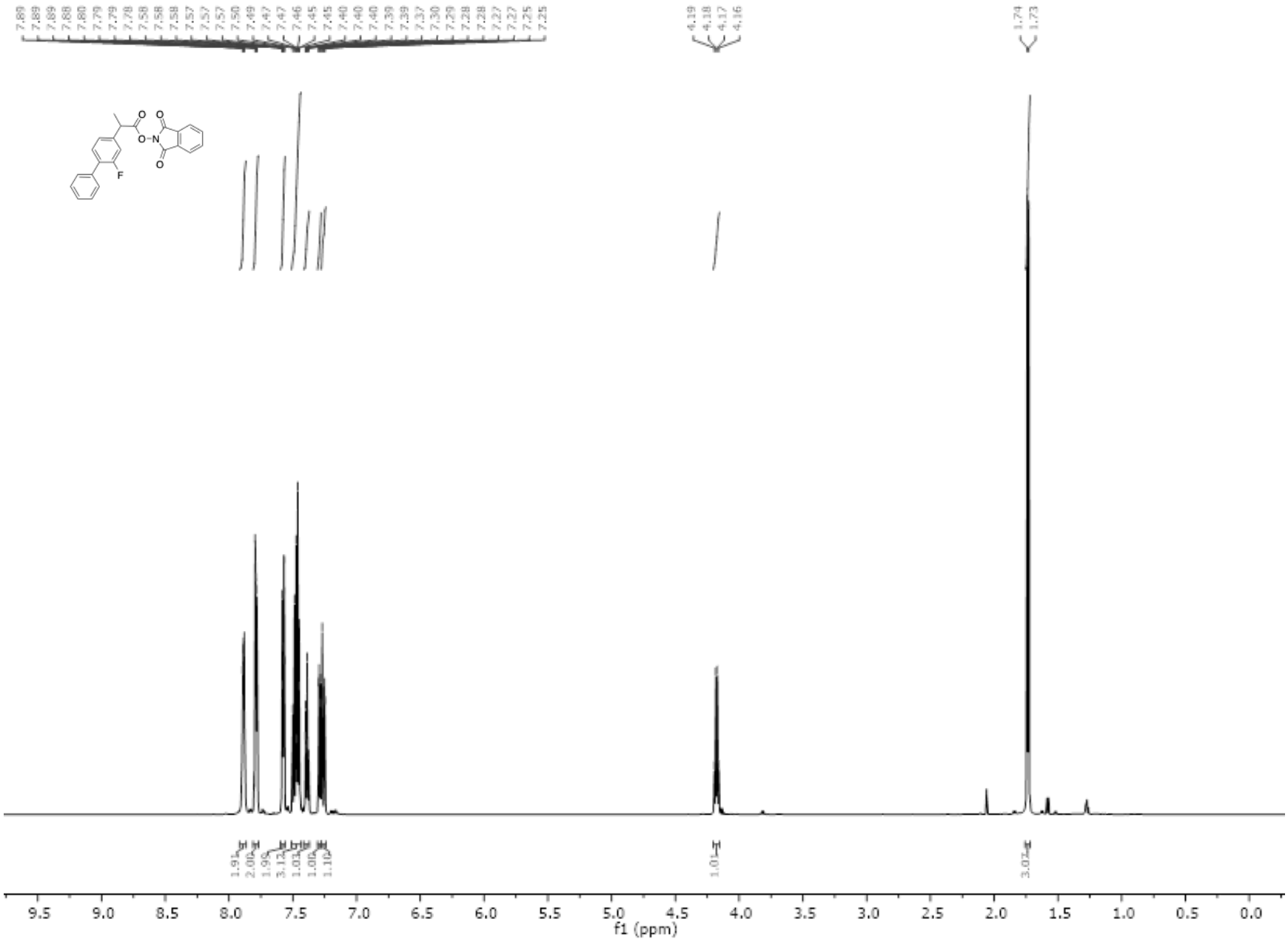


^{1}H NMR (600 MHz, $CDCl_3$) of **S-1ae**

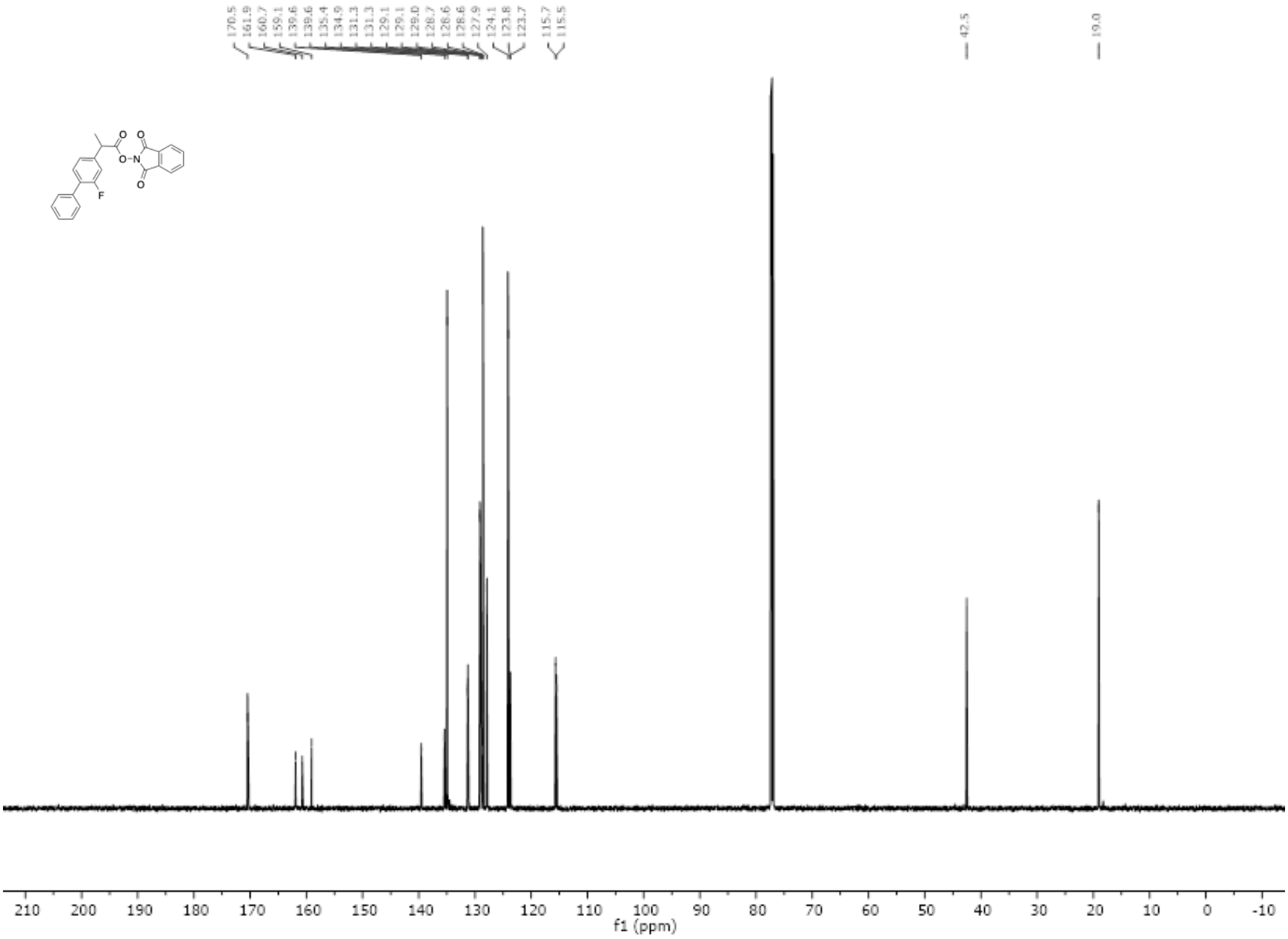
^{13}C NMR (151 MHz, $CDCl_3$) of **S-1ae**



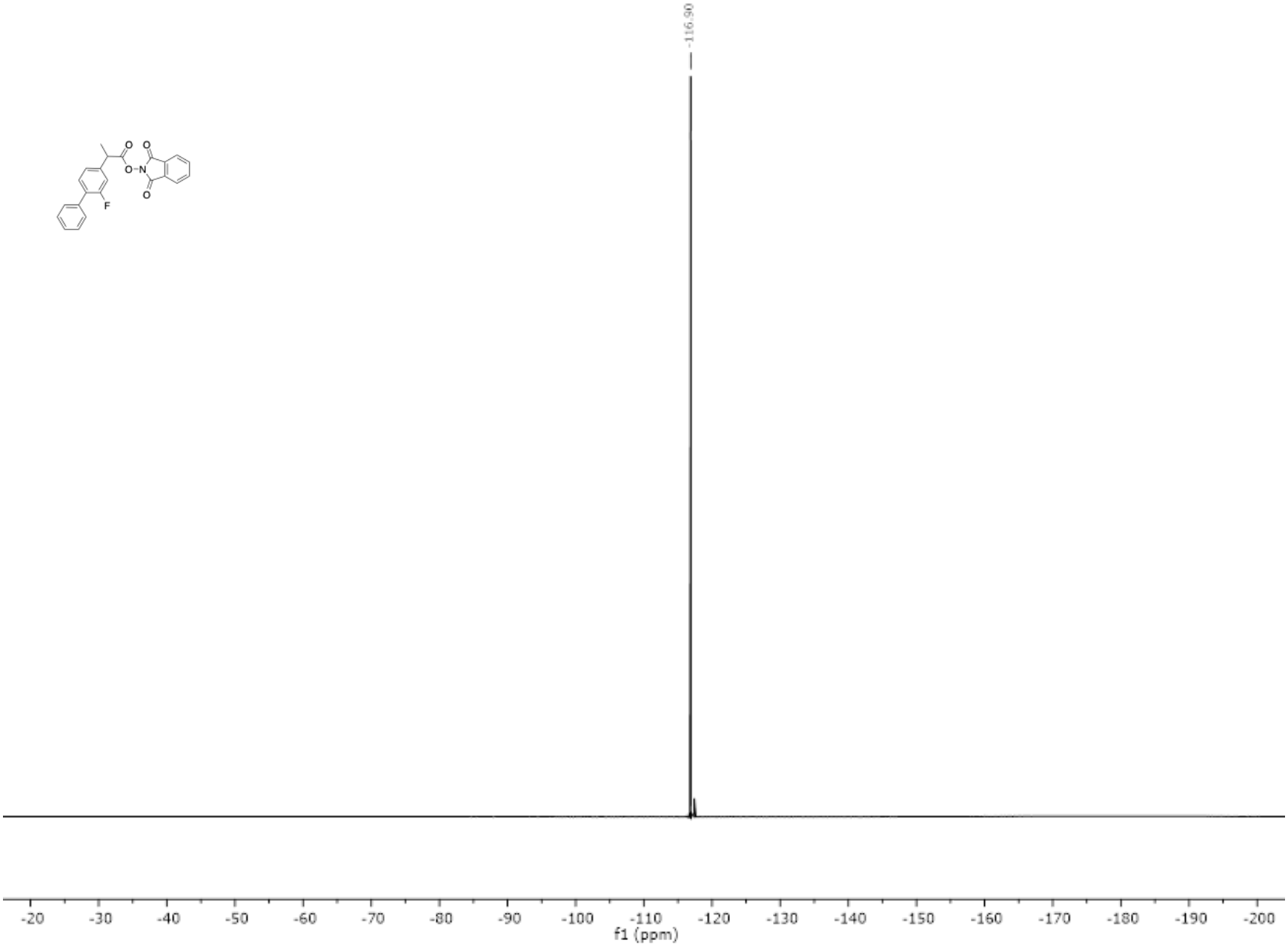
^{1}H NMR (400 MHz, $CDCl_3$) of **S-1af**



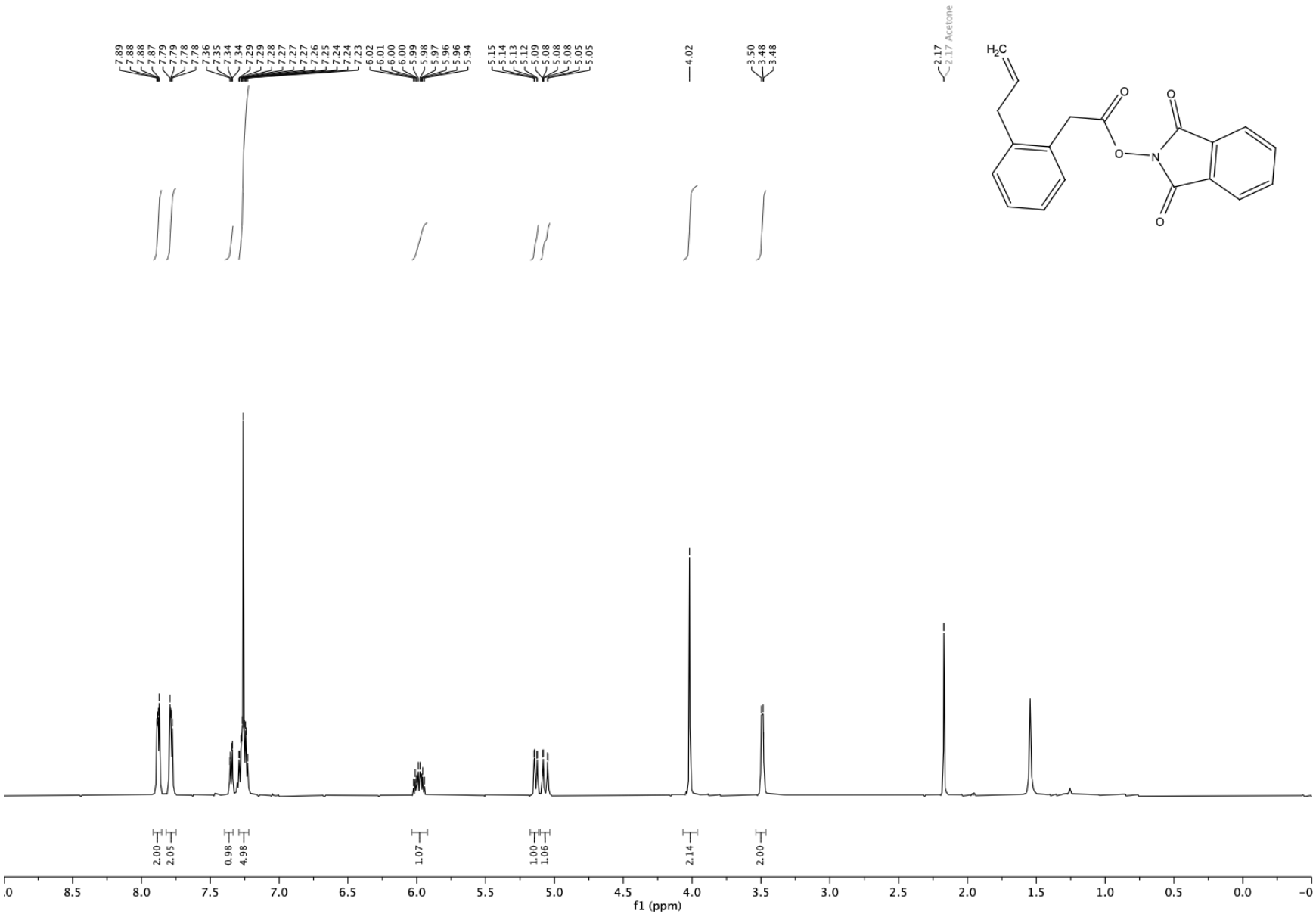
^{13}C NMR (151 MHz, $CDCl_3$) of **S-1af**



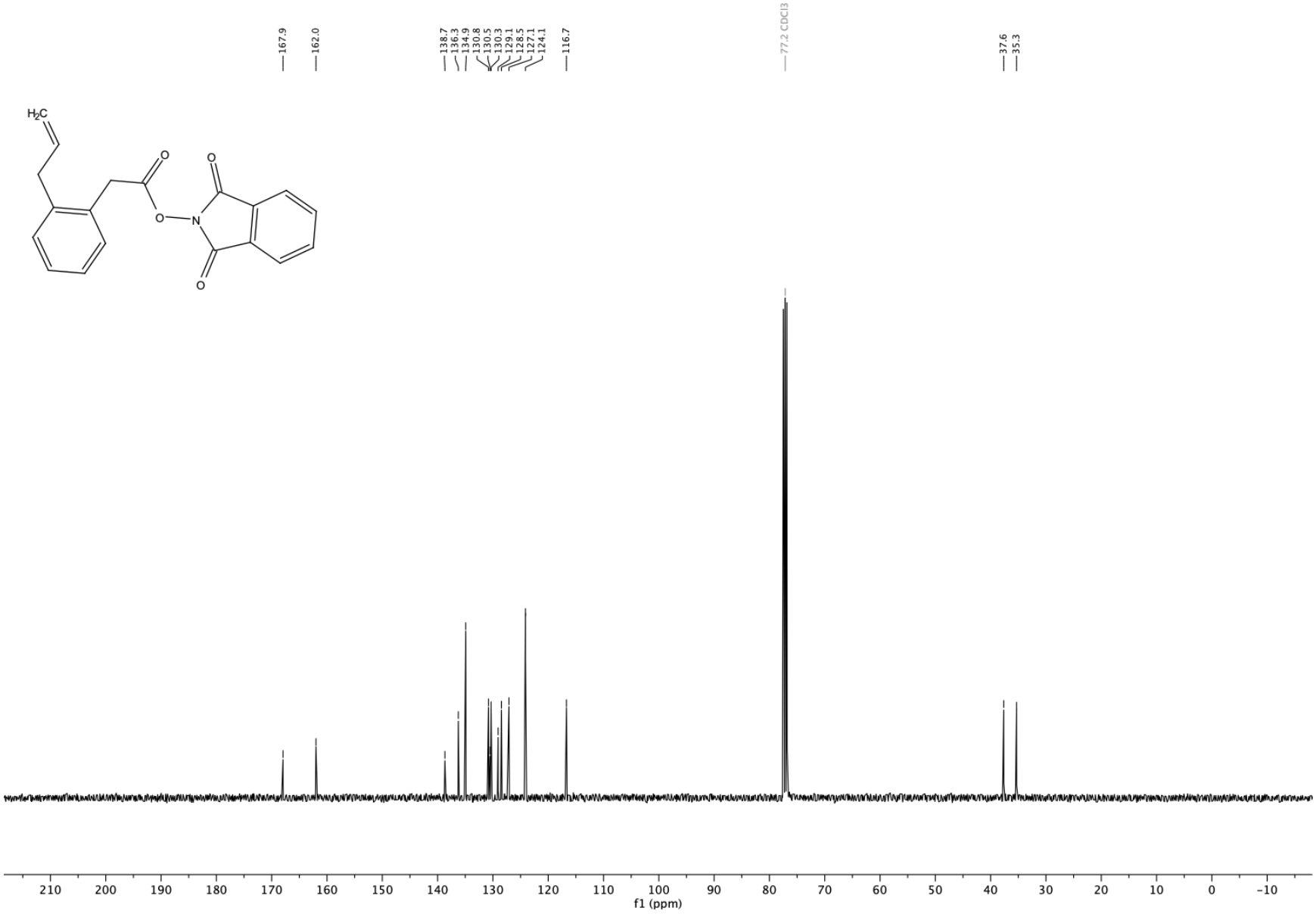
^{19}F NMR (376 MHz, $CDCl_3$) of **S-1af**



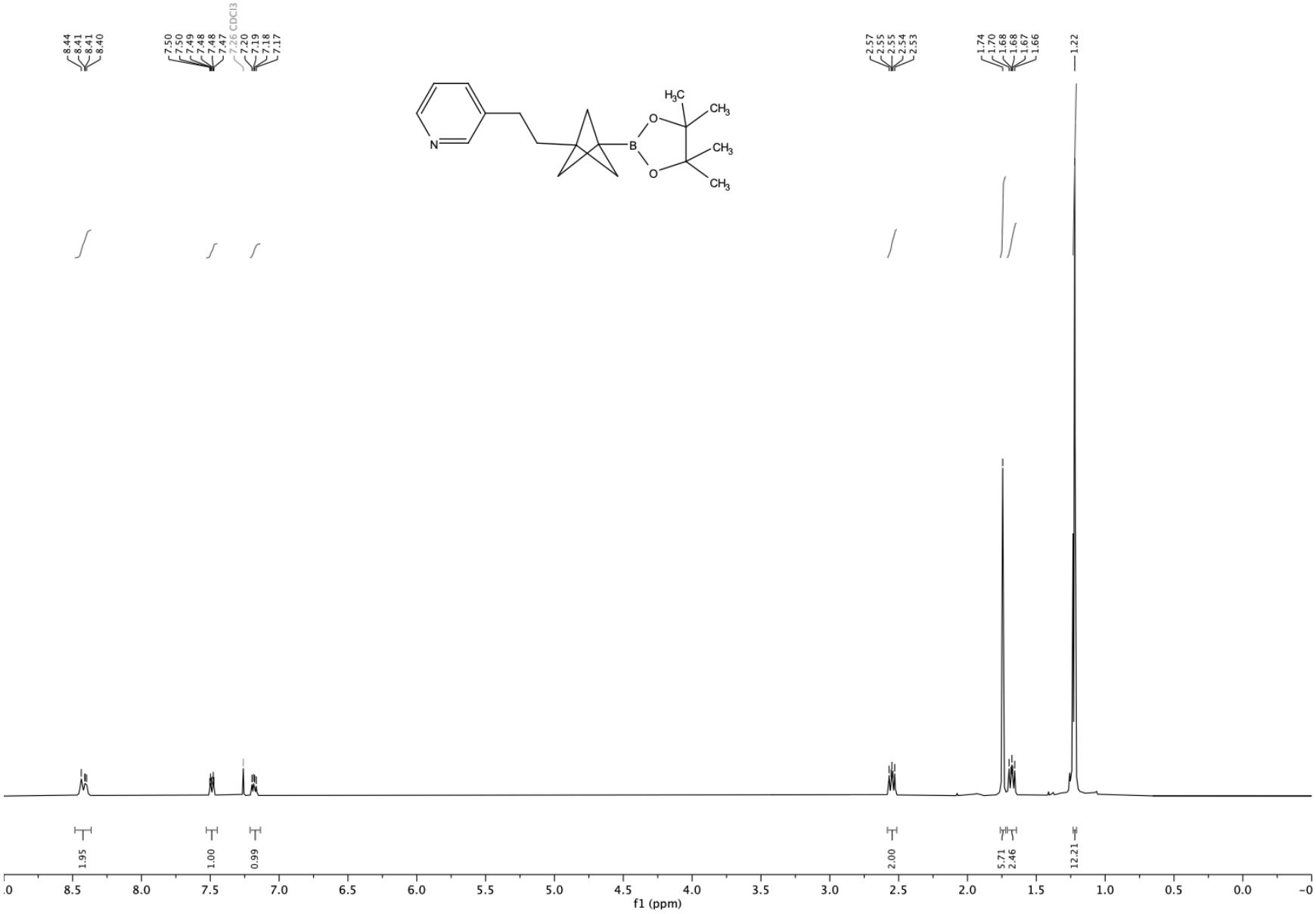
^{1}H NMR (500 MHz, $CDCl_3$) of **S-1ag**



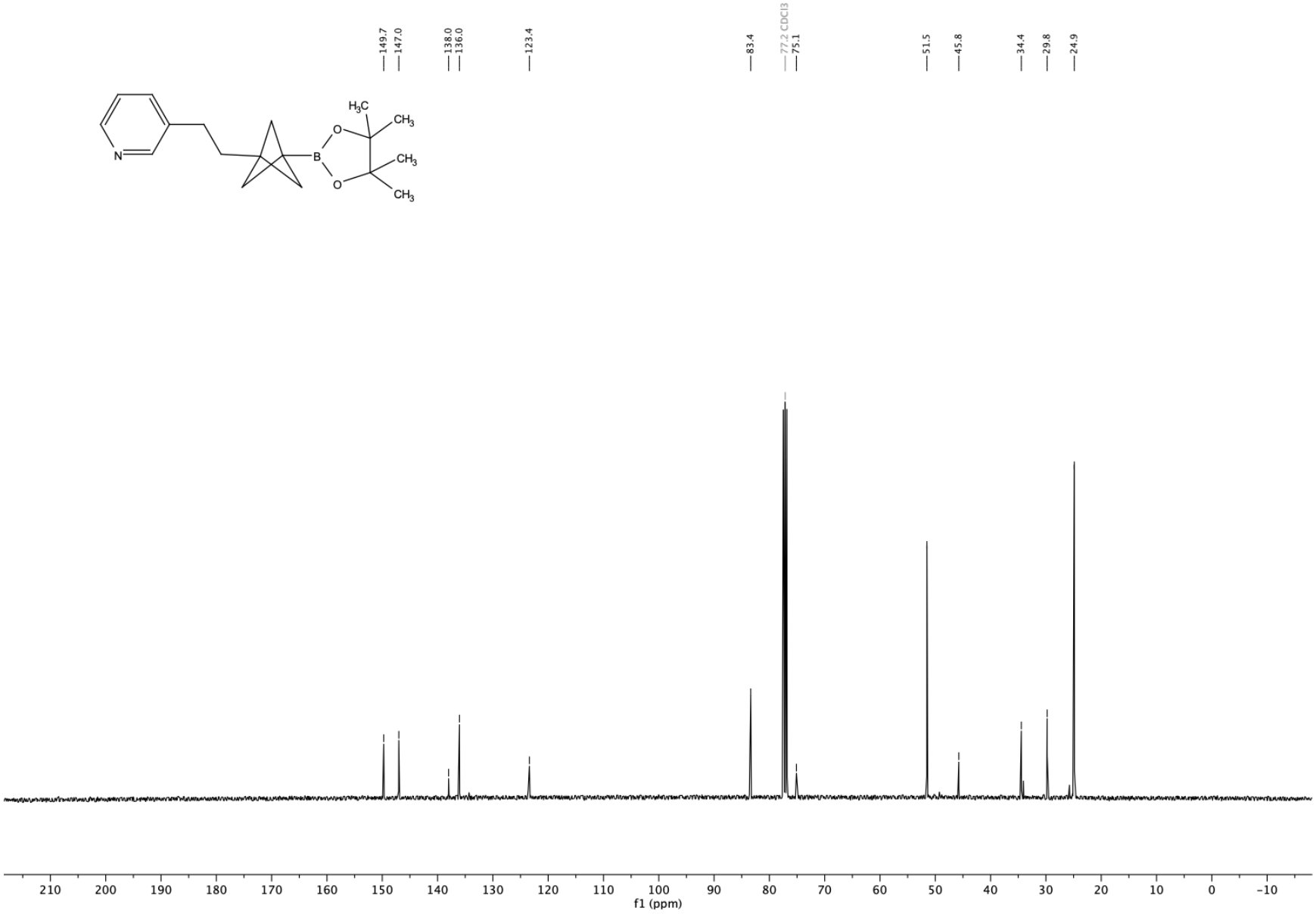
^{13}C NMR (101 MHz, $CDCl_3$) of **S-1ag**



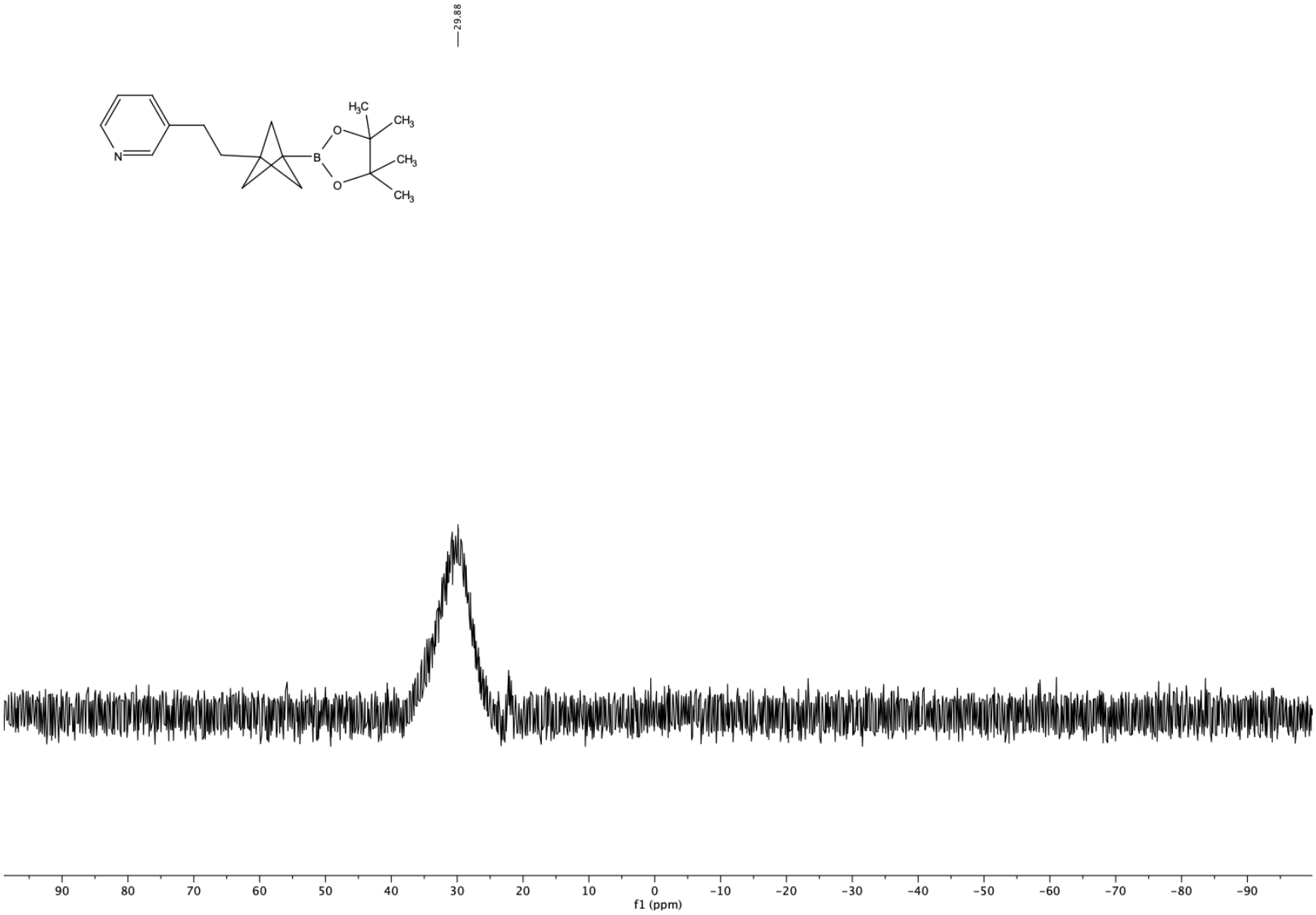
^{1}H NMR (400 MHz, $CDCl_3$) of **4a**



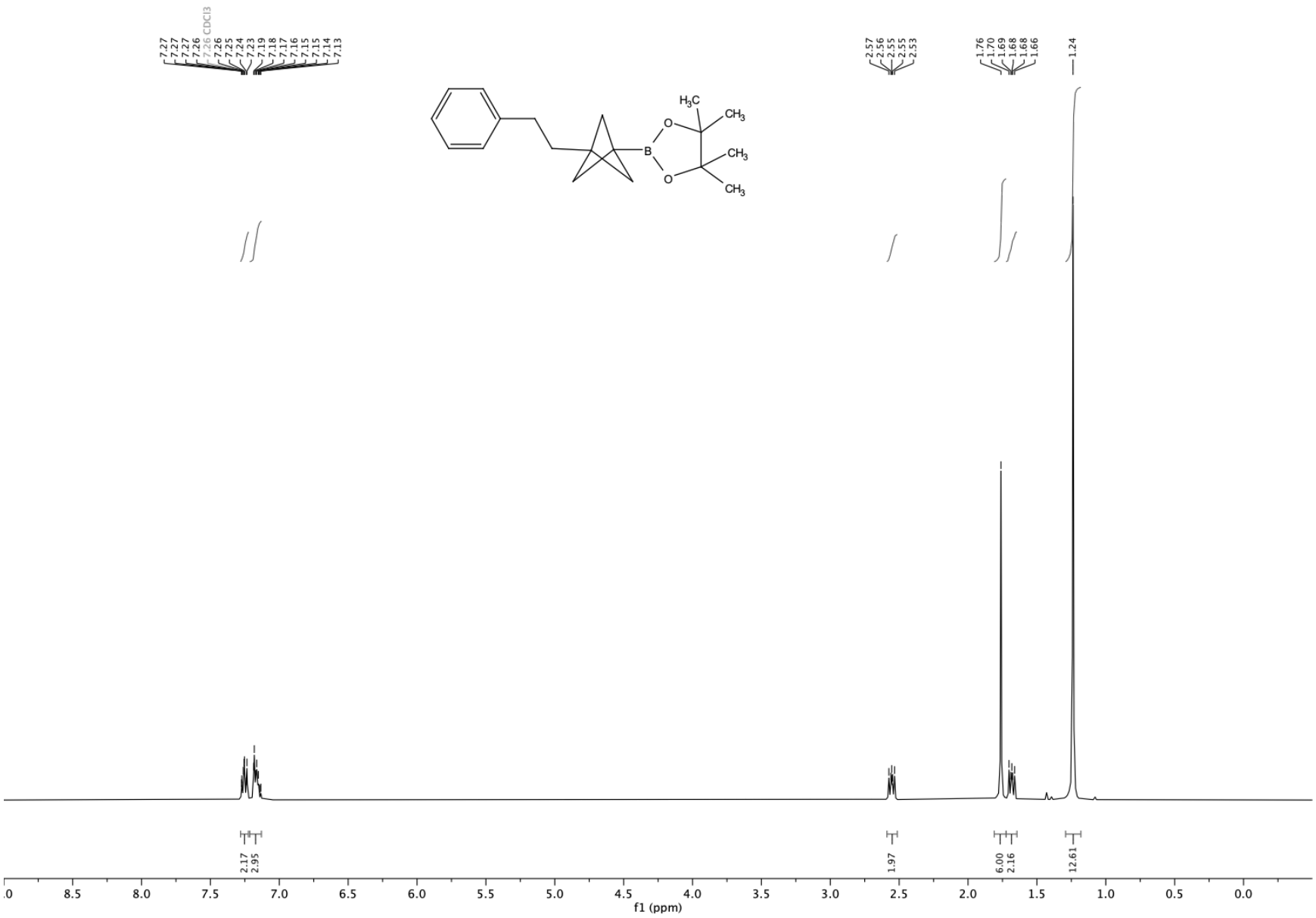
^{13}C NMR (101 MHz, $CDCl_3$) of **4a**



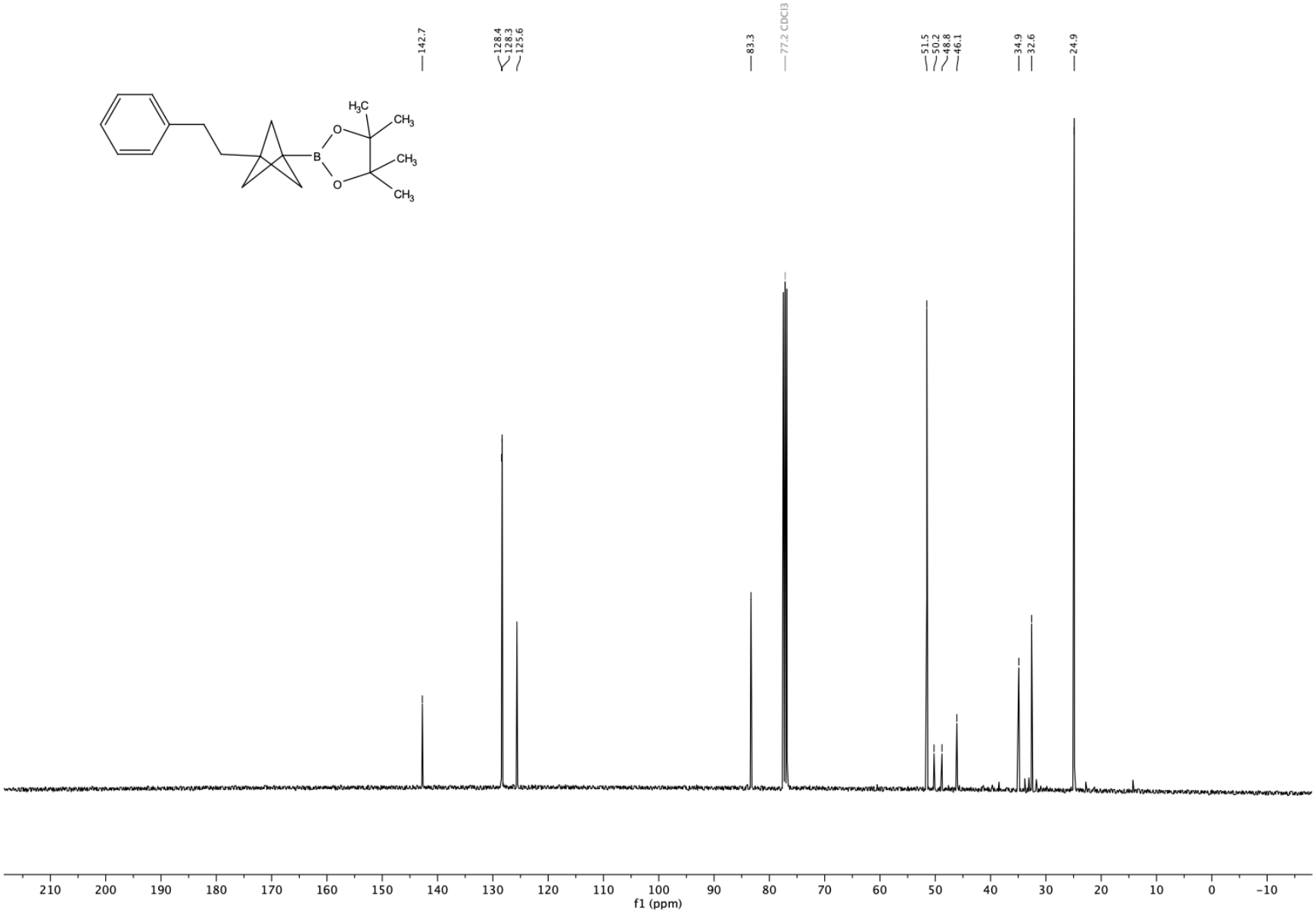
^{11}B NMR (128 MHz, $CDCl_3$) of **4a**



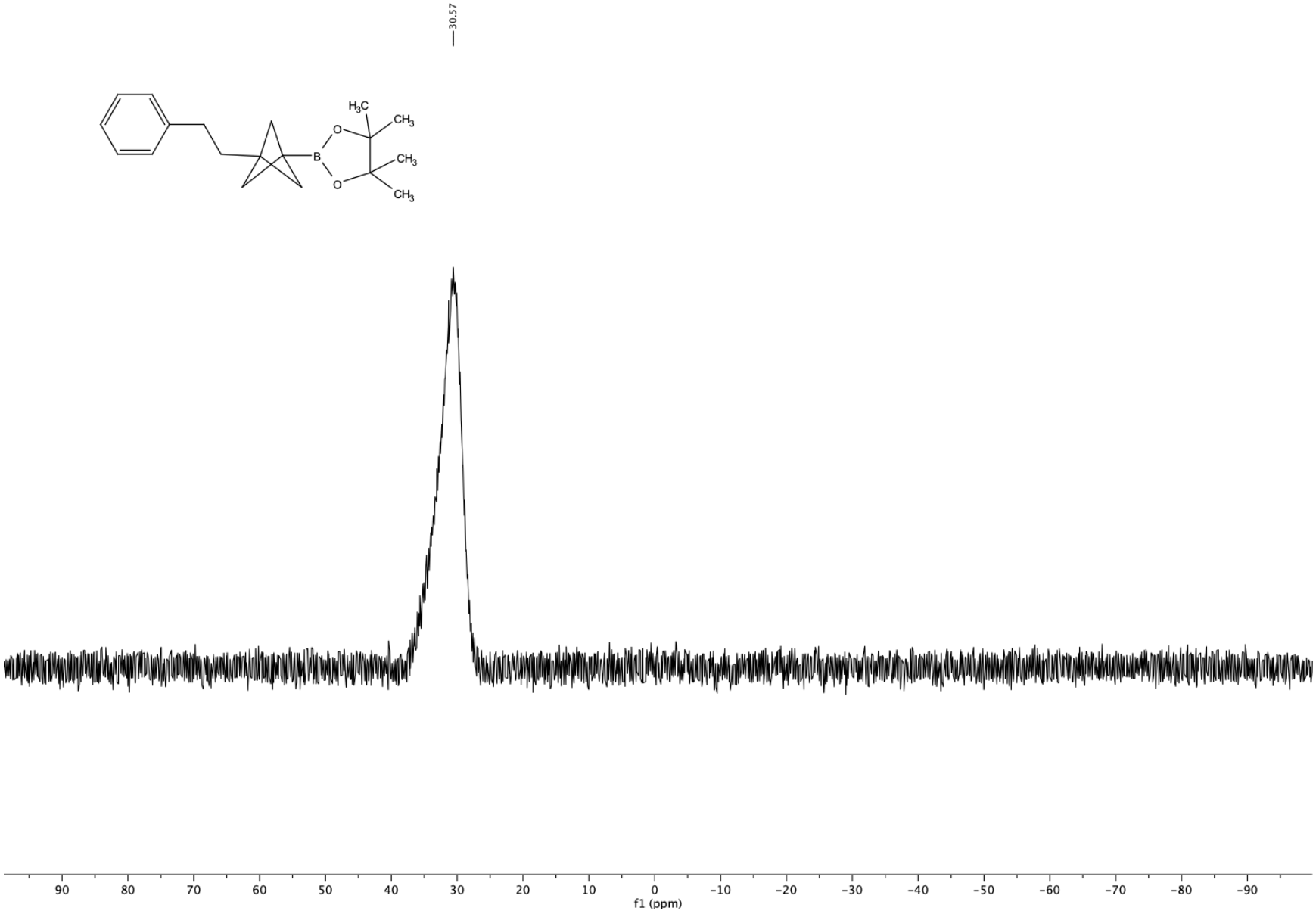
^{1}H NMR (400 MHz, $CDCl_3$) of **4b**



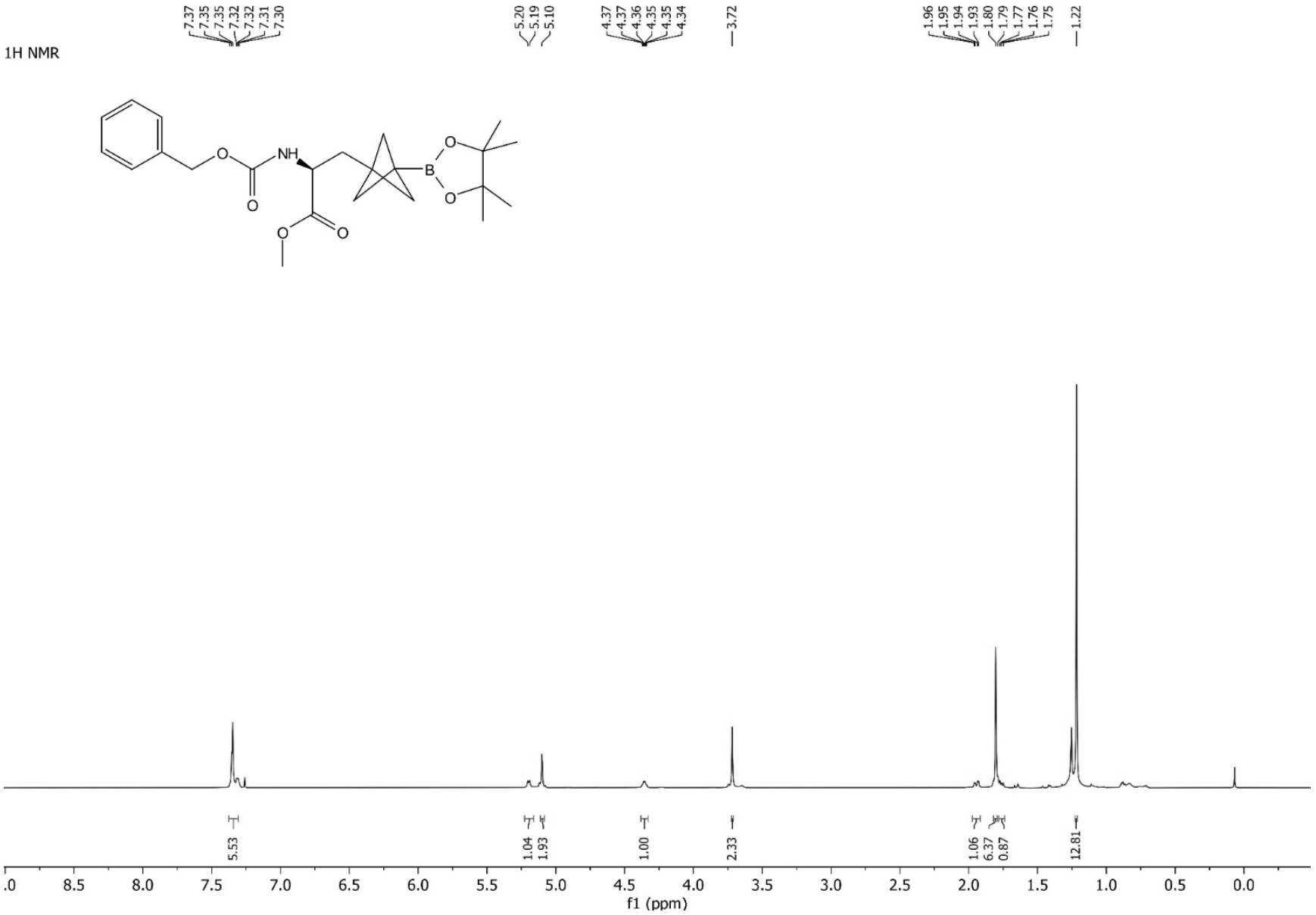
^{13}C NMR (101 MHz, $CDCl_3$) of **4b**



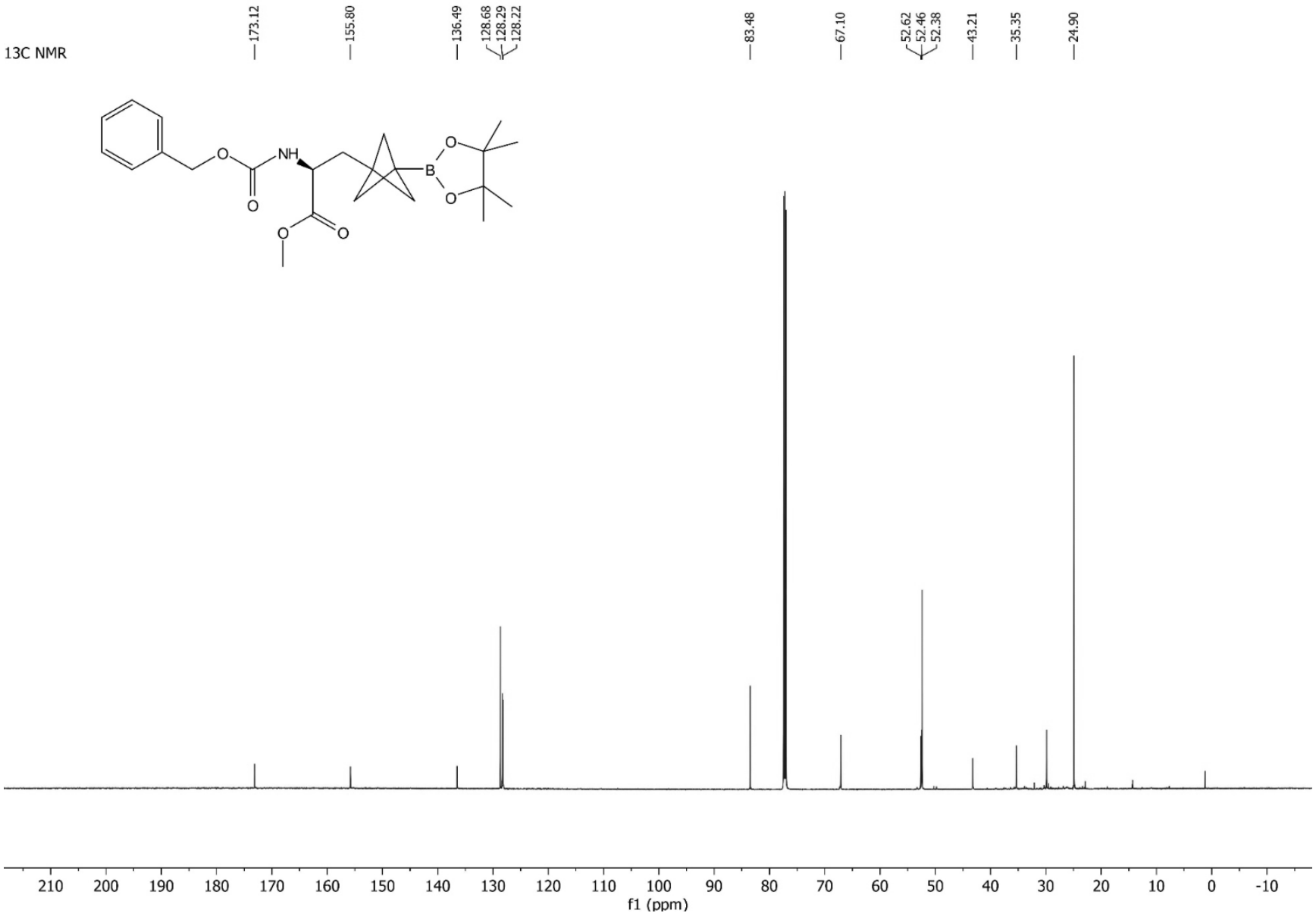
^{11}B NMR (128 MHz, $CDCl_3$) of **4b**



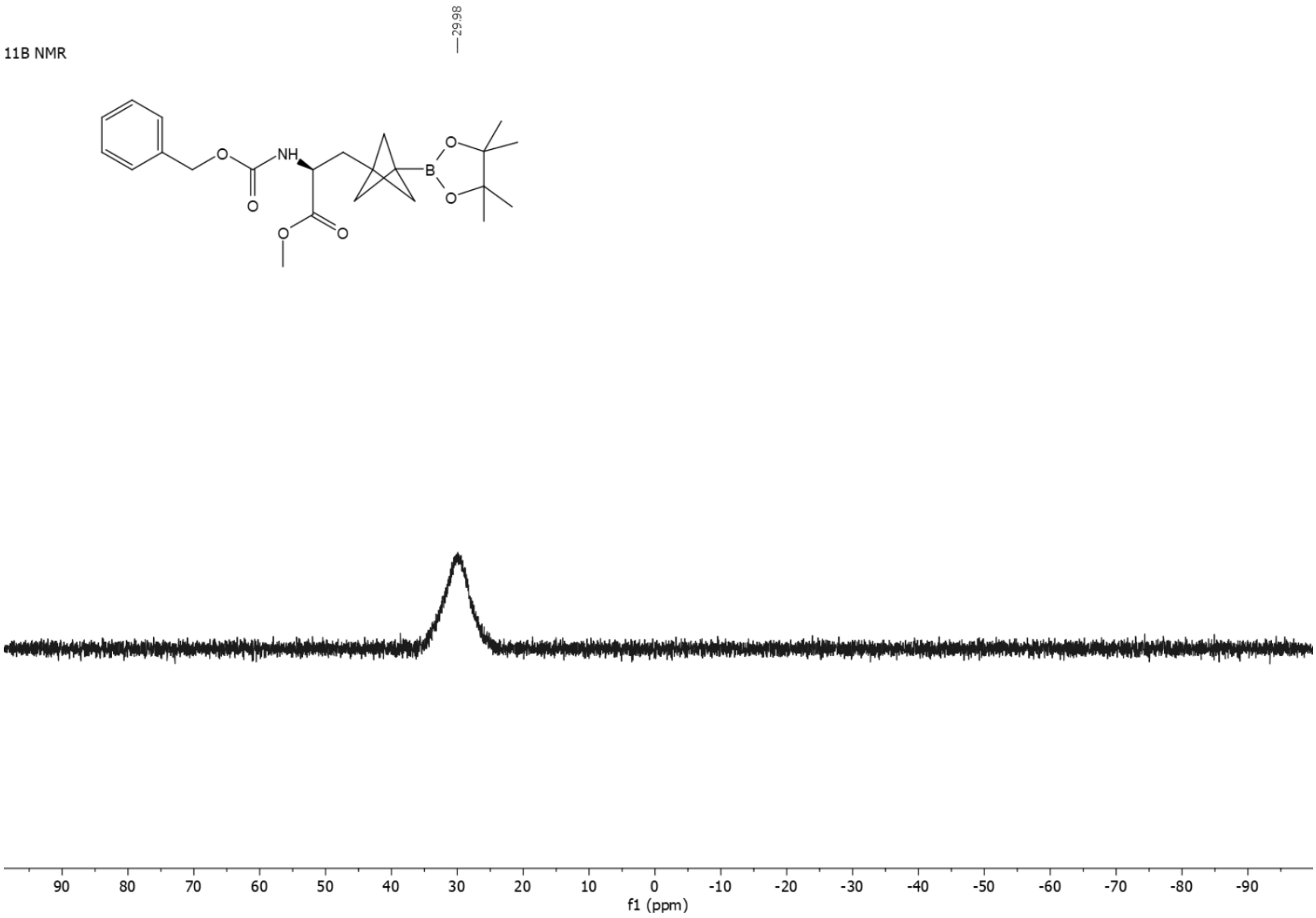
^{1}H NMR (600 MHz, $CDCl_3$) of **4c**



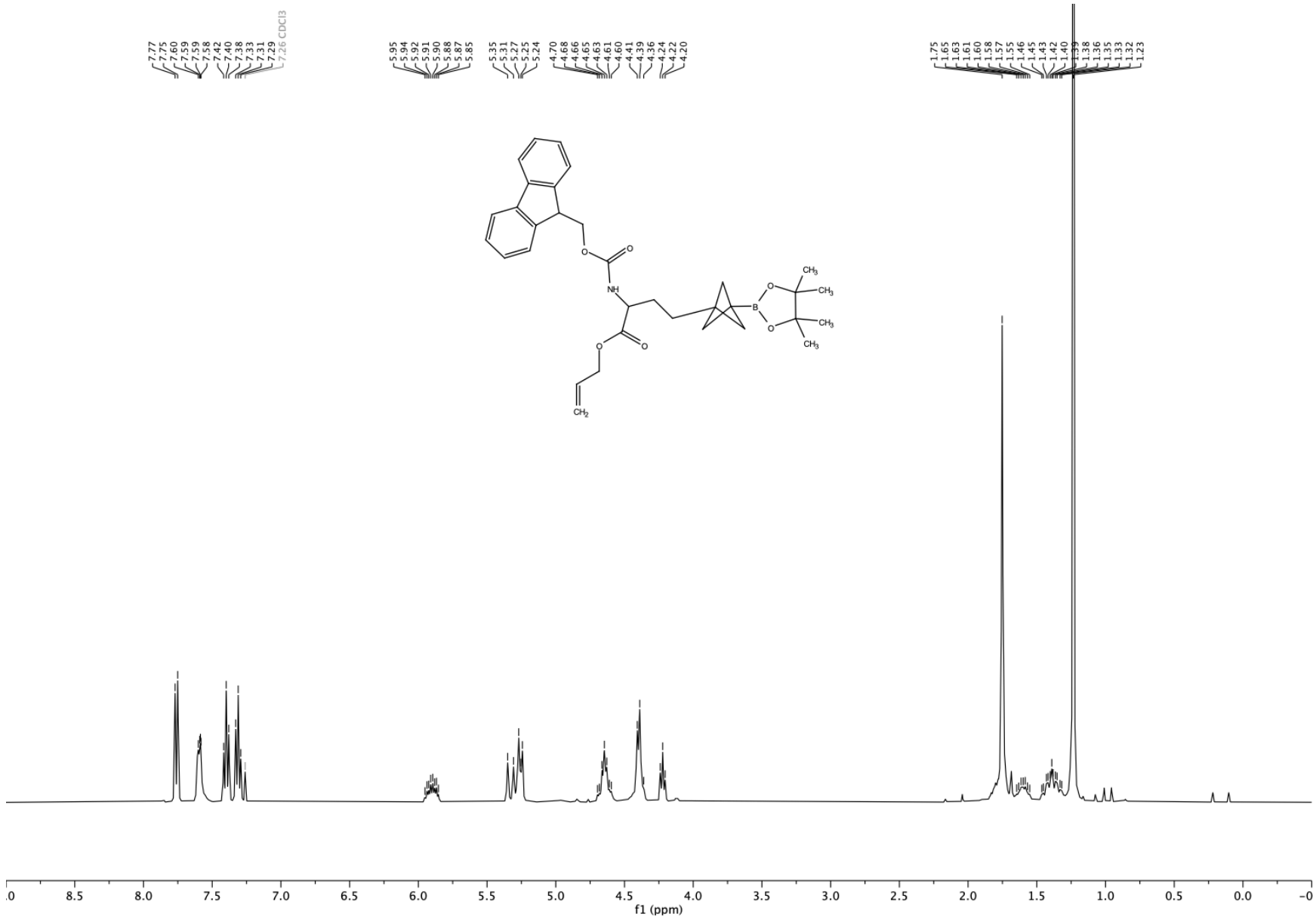
^{13}C NMR (151 MHz, $CDCl_3$) of **4c**



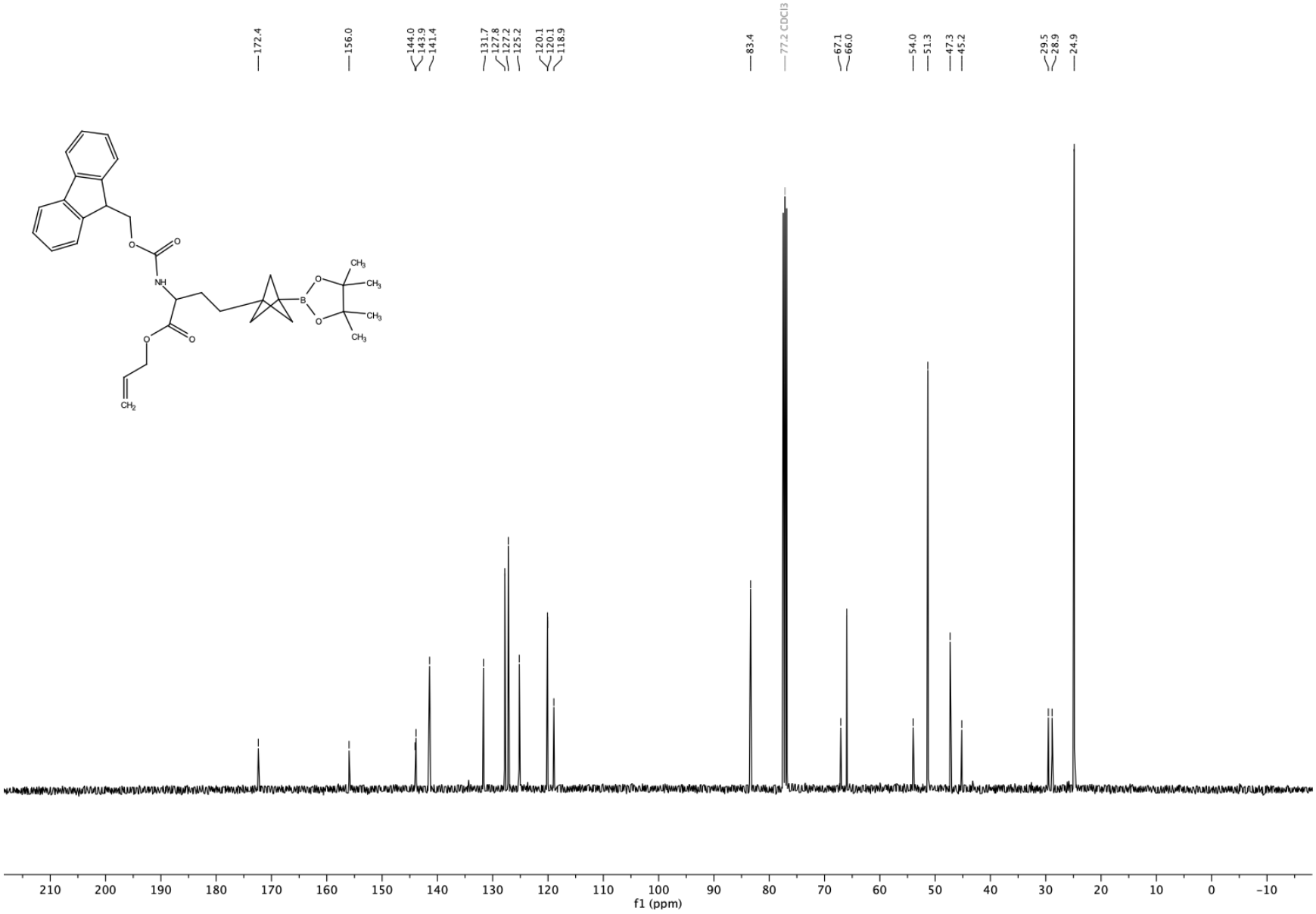
^{11}B NMR (128 MHz, $CDCl_3$) of **4c**



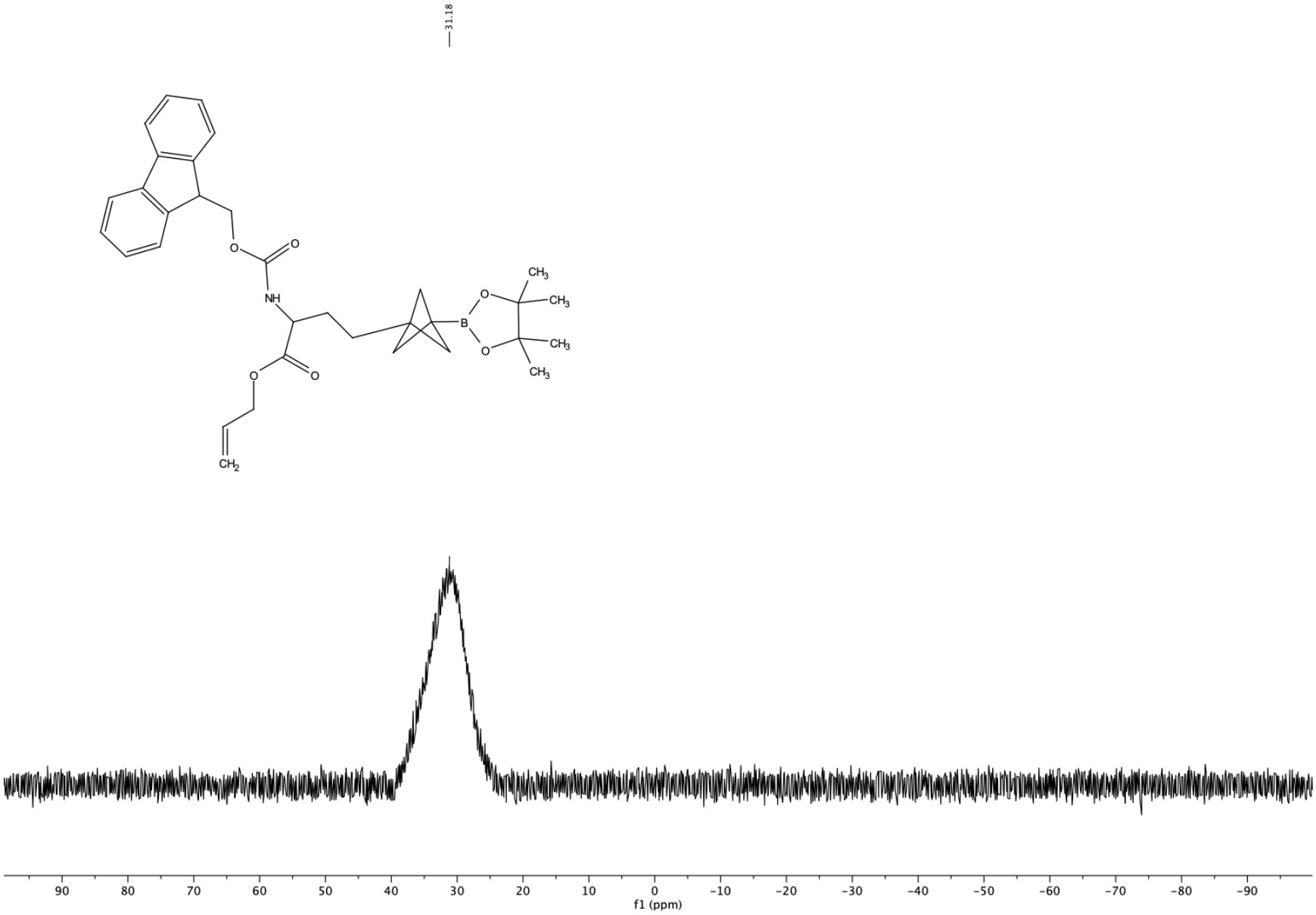
^{1}H NMR (400 MHz, $CDCl_3$) of **4d**



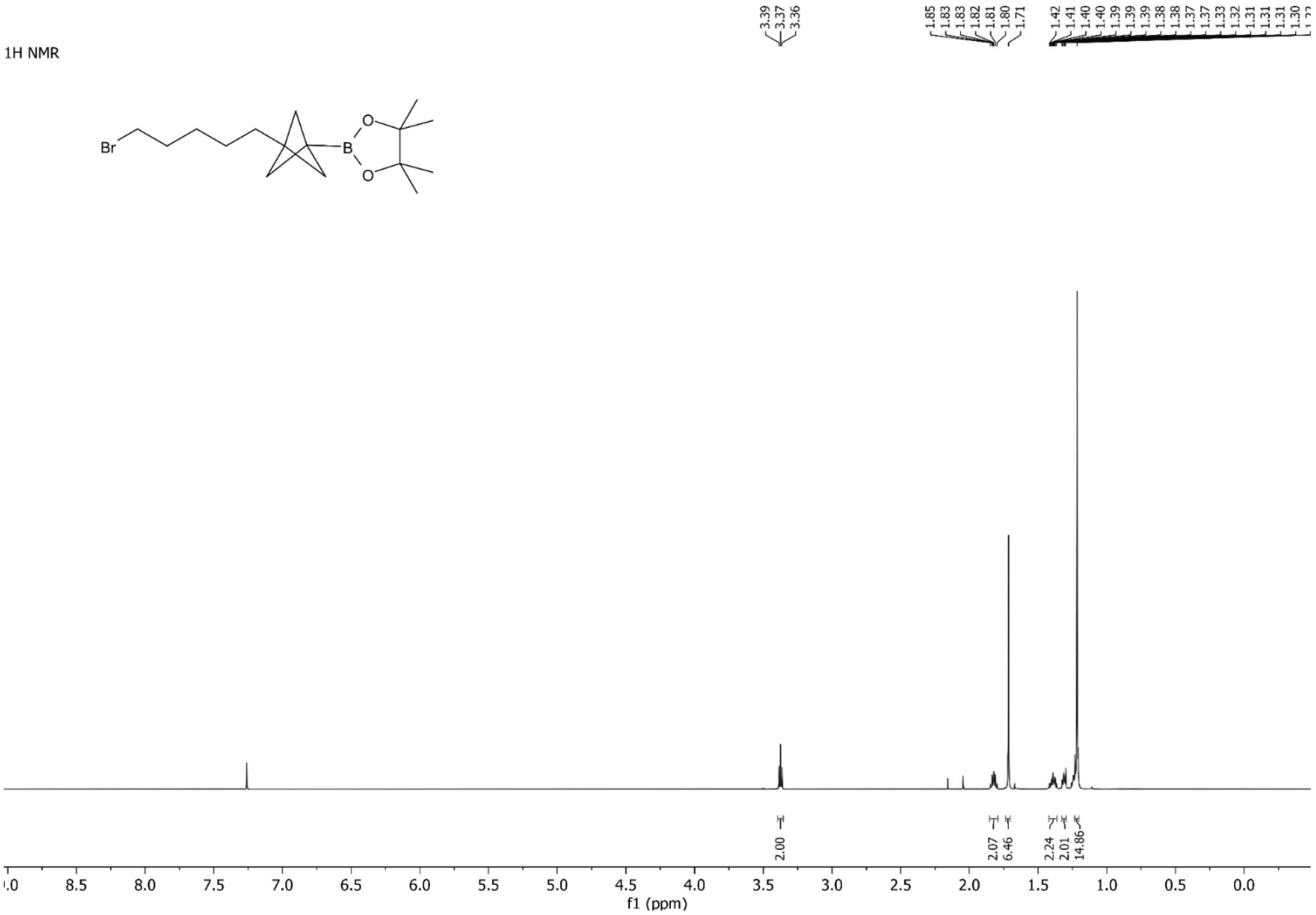
^{13}C NMR (101 MHz, $CDCl_3$) of **4d**



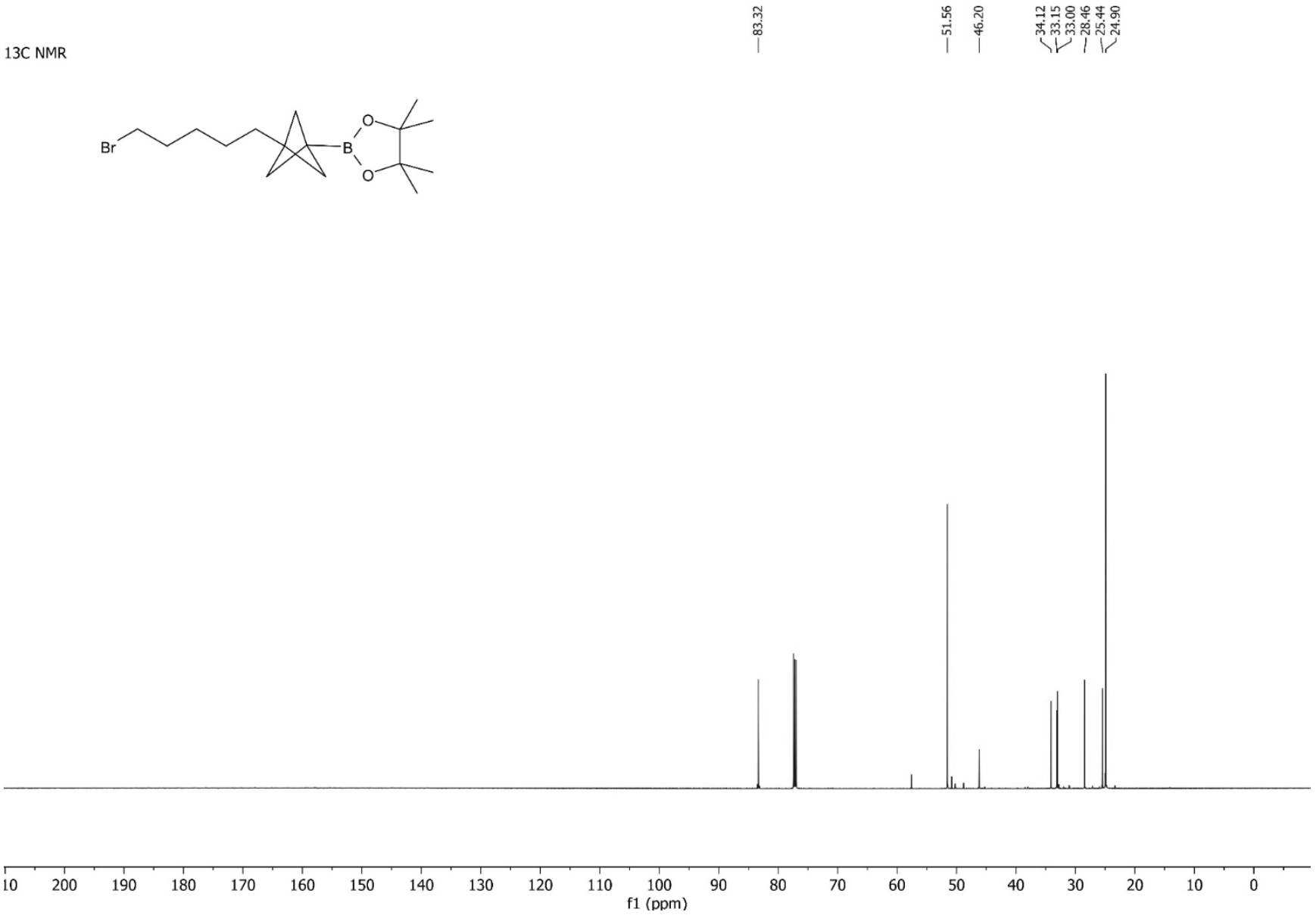
^{11}B NMR (128 MHz, $CDCl_3$) of **4d**



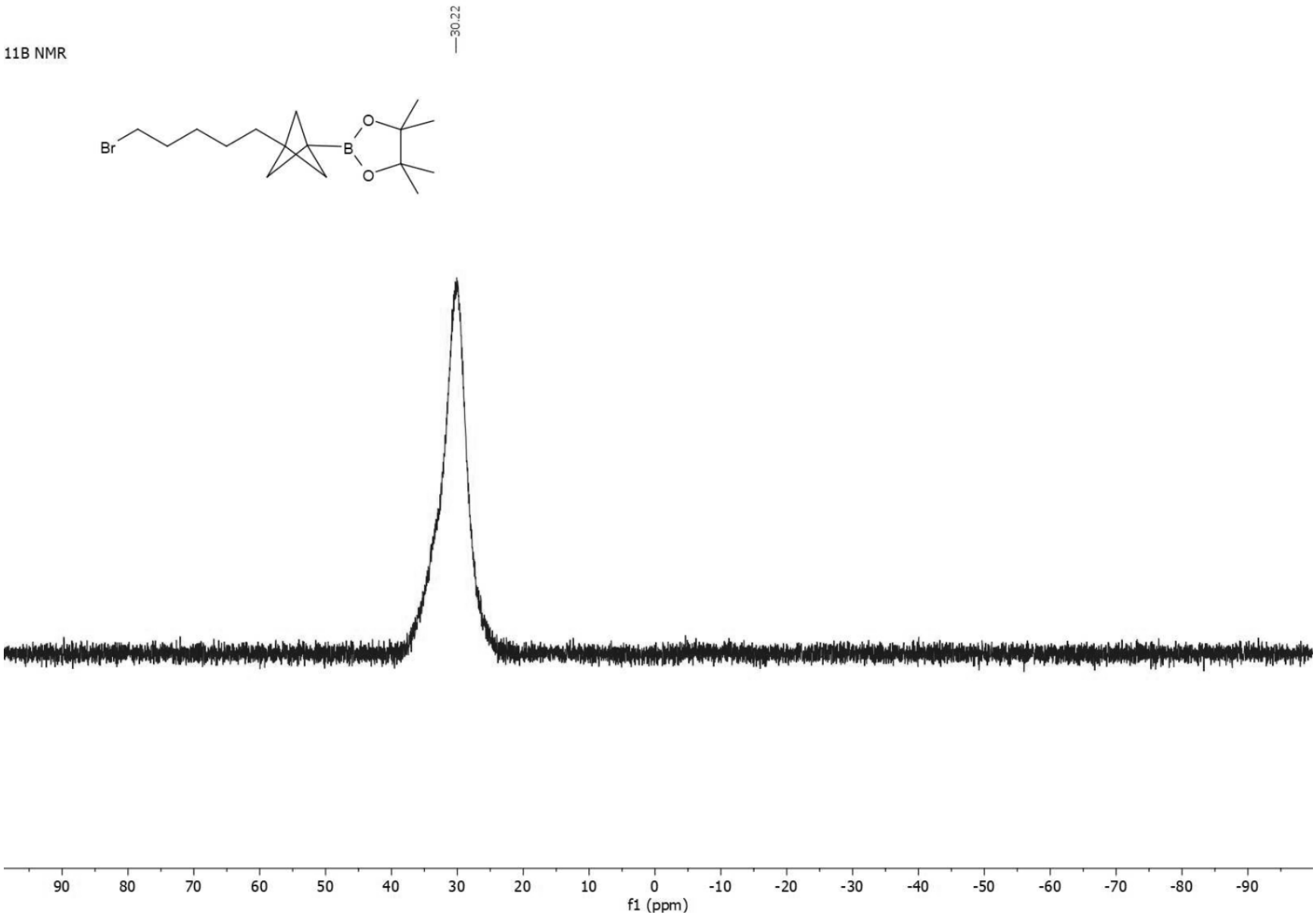
^{1}H NMR (600 MHz, $CDCl_3$) of **4e**



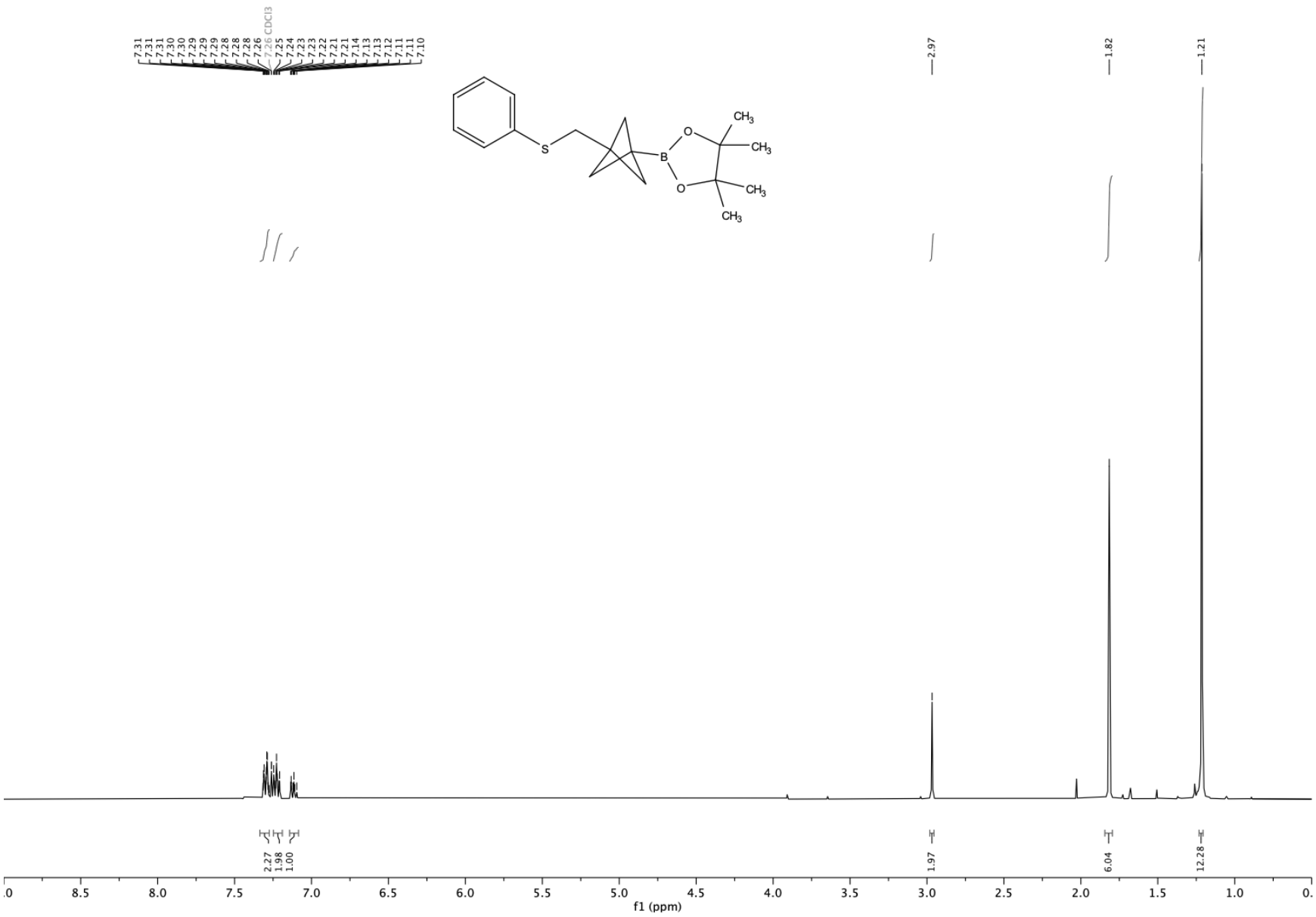
^{13}C NMR (151 MHz, $CDCl_3$) of **4e**



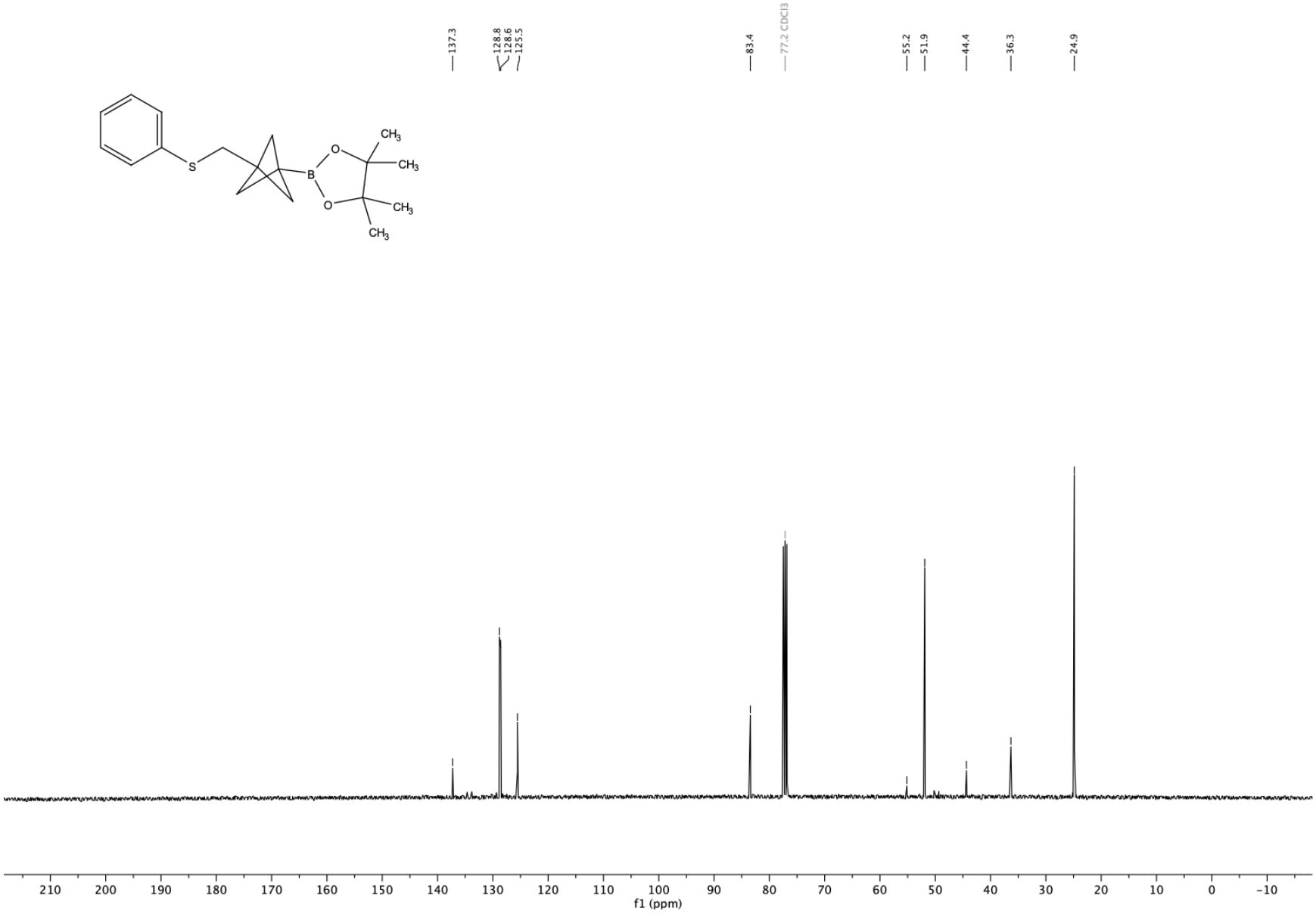
^{11}B NMR (600 MHz, $CDCl_3$) of **4e**



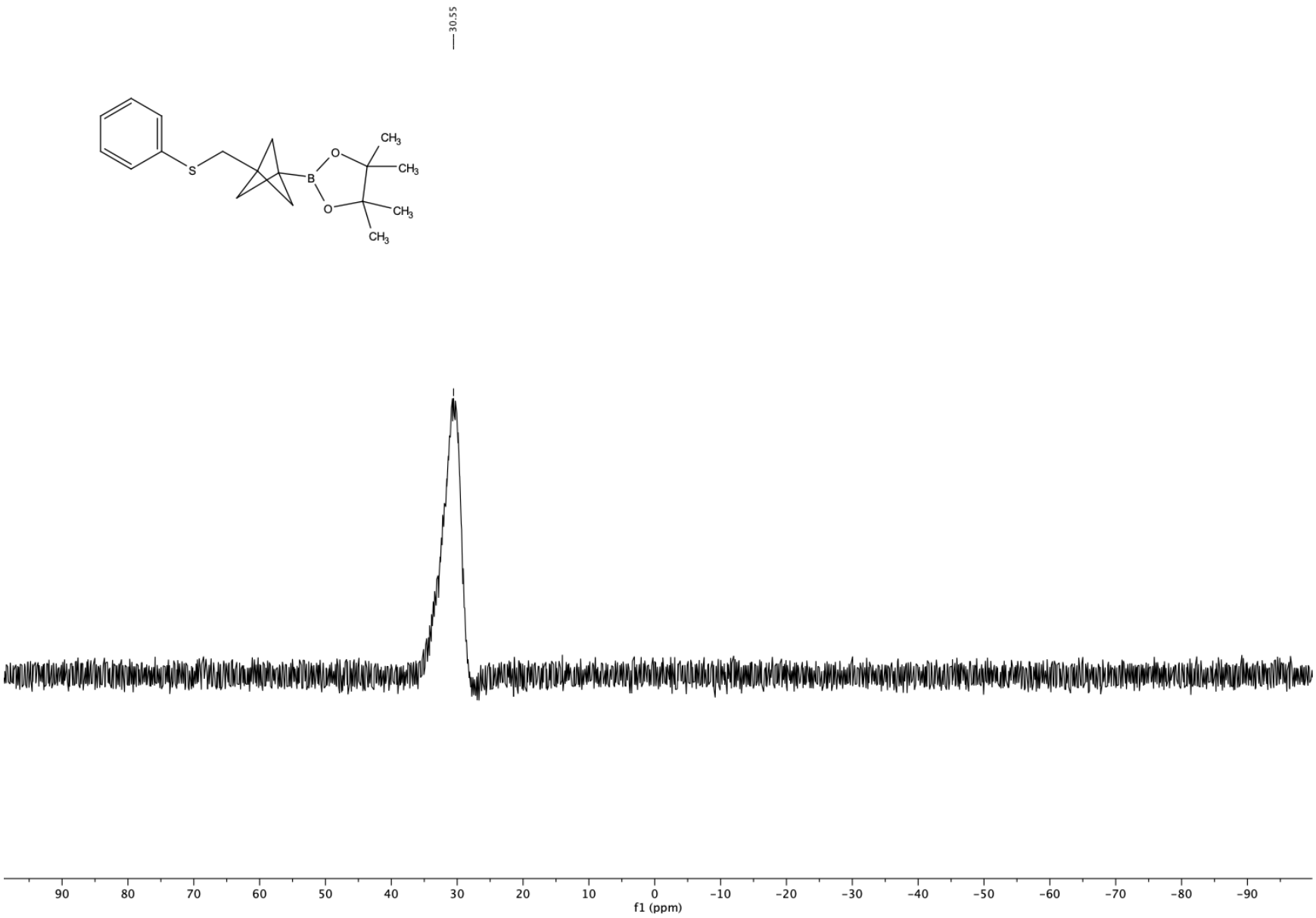
^{1}H NMR (400 MHz, $CDCl_3$) of **4f**



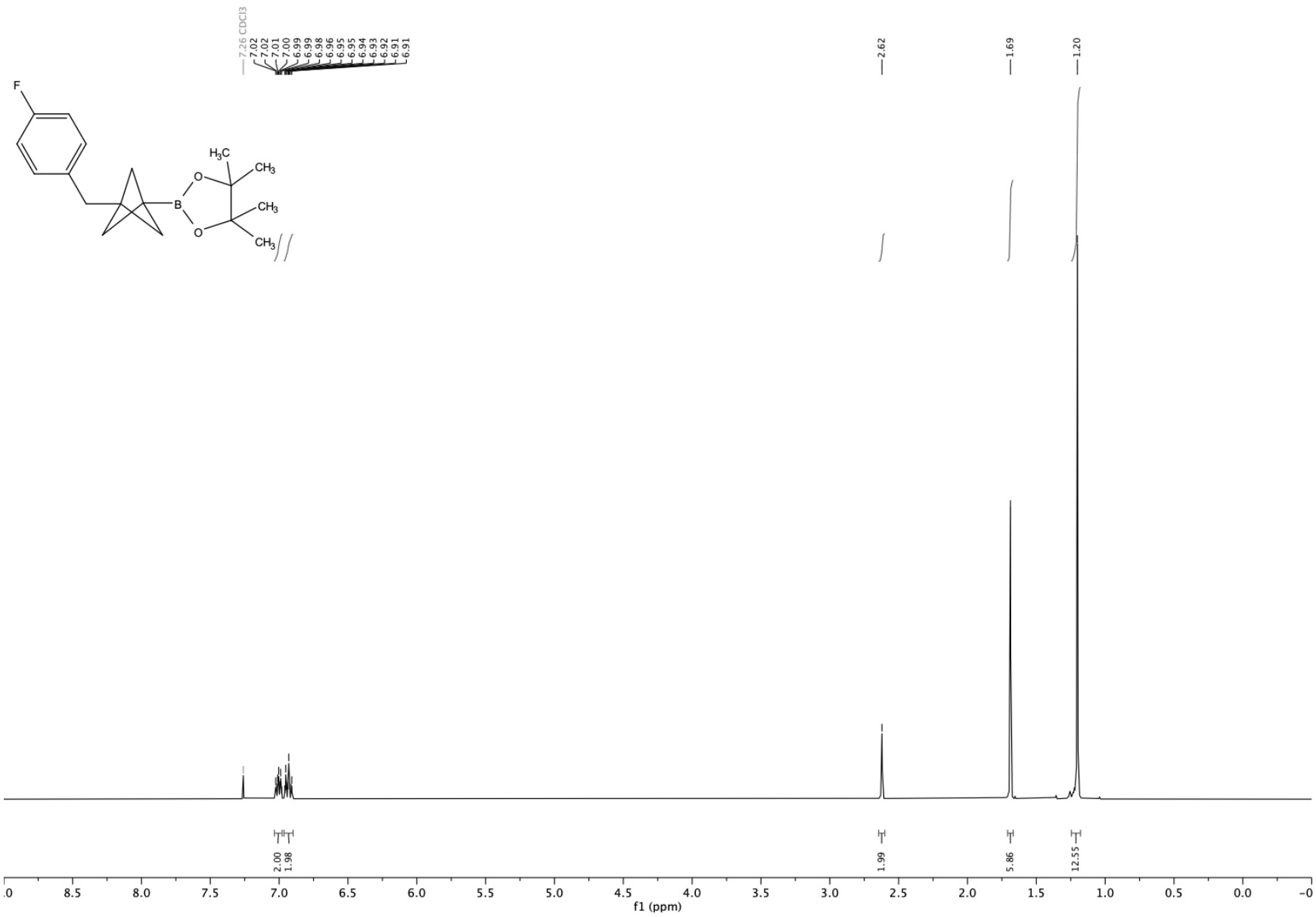
^{13}C NMR (101 MHz, $CDCl_3$) of **4f**



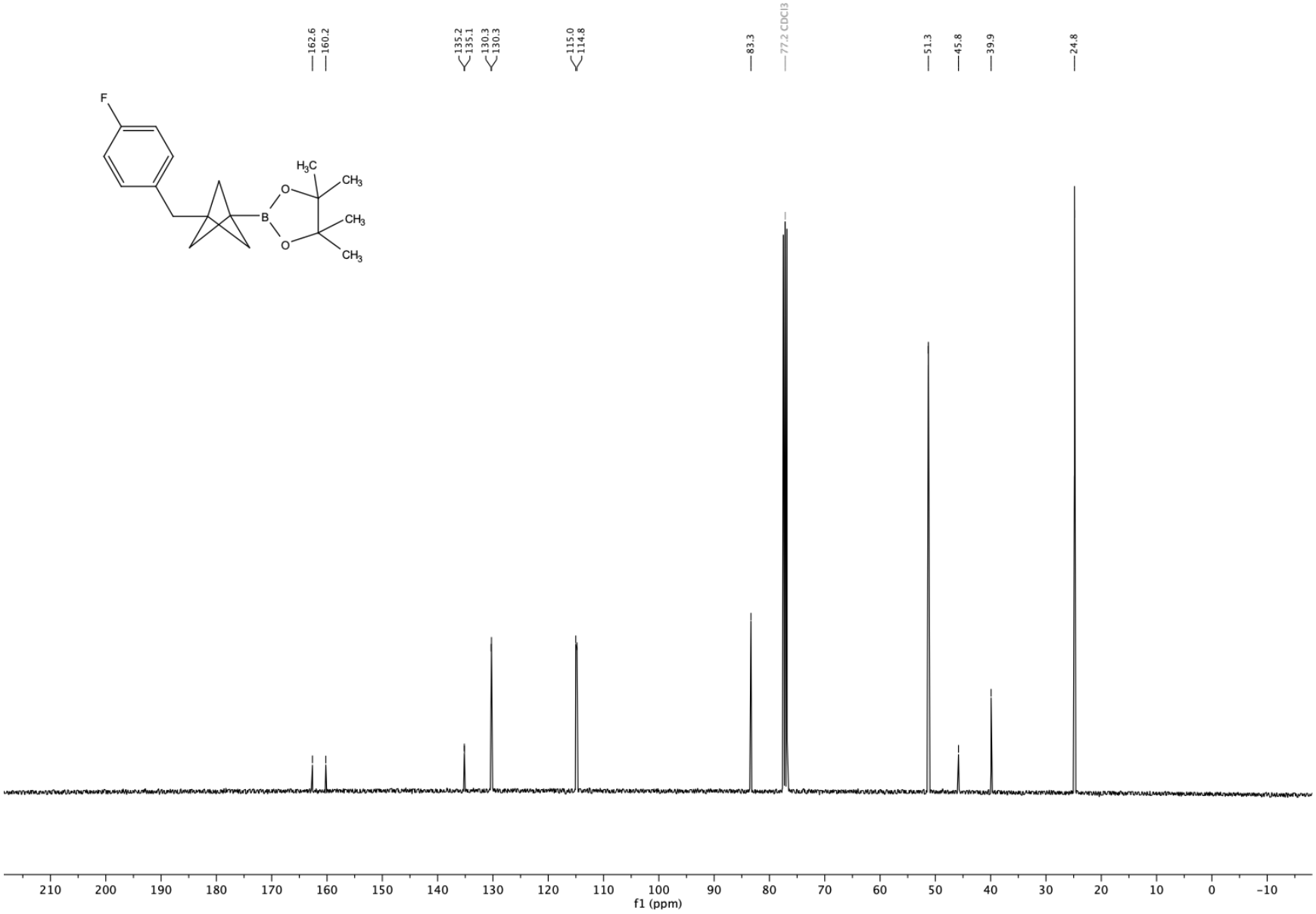
^{11}B NMR (128 MHz, $CDCl_3$) of **4f**



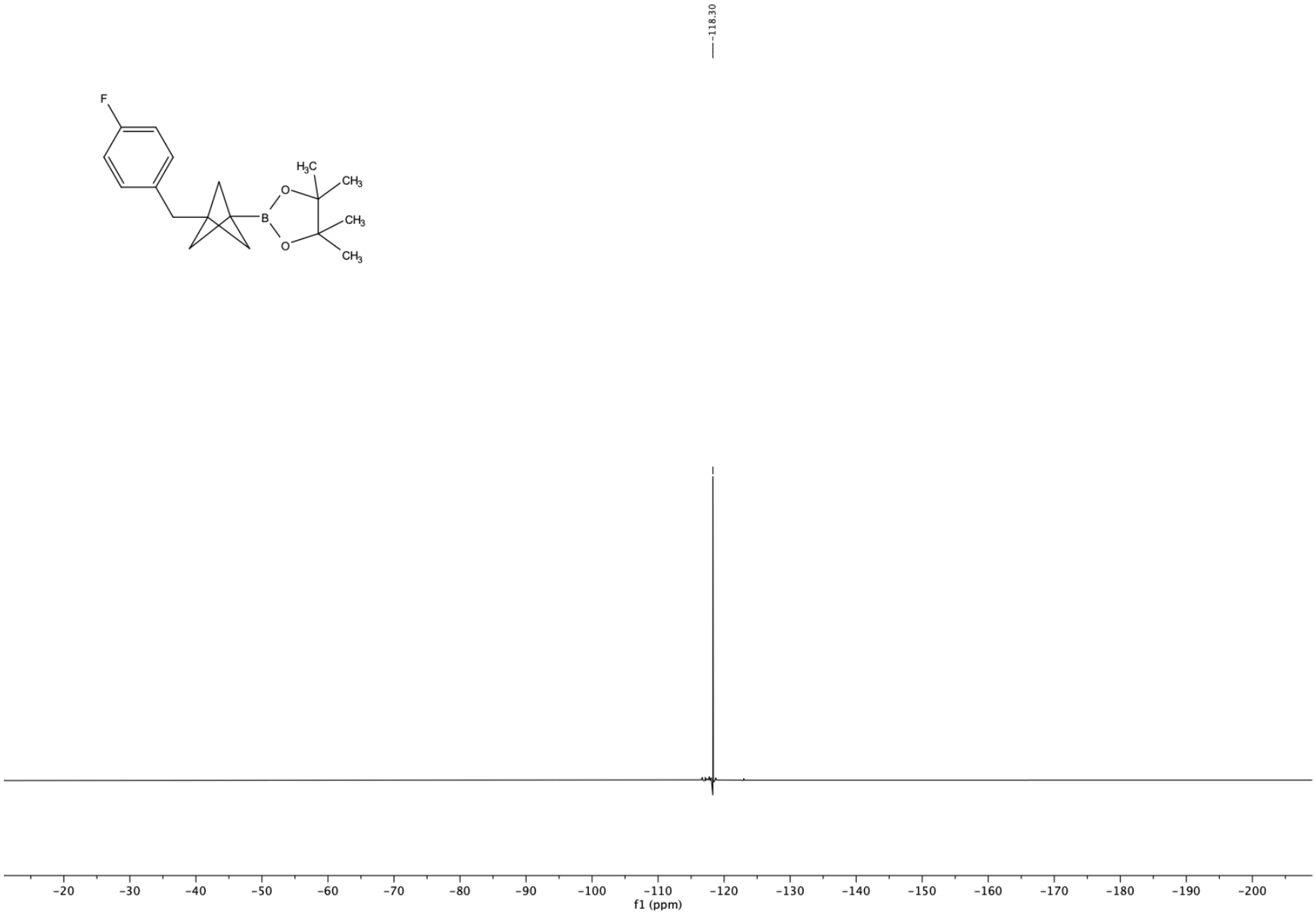
^{1}H NMR (400 MHz, $CDCl_3$) of **4g**



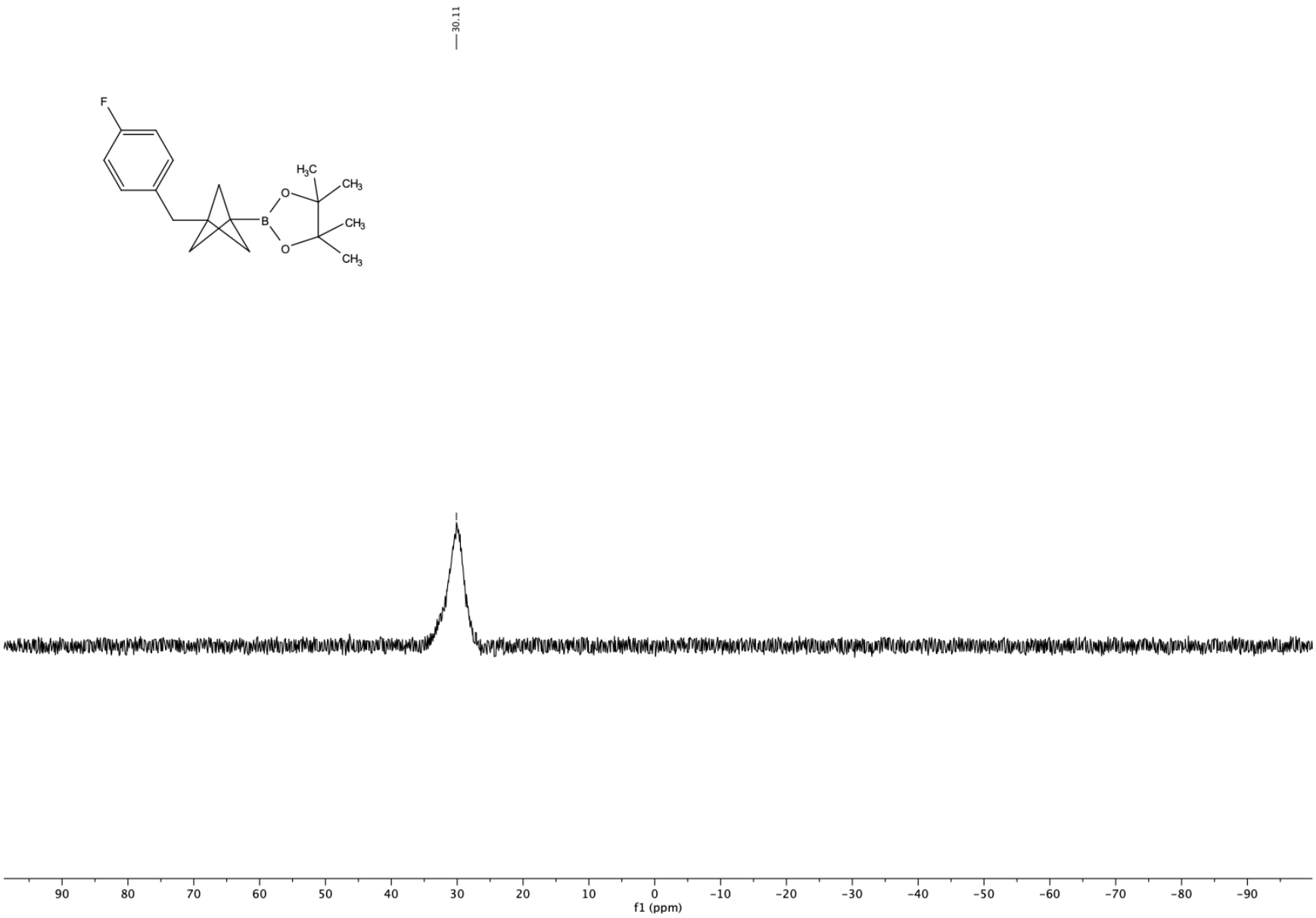
^{13}C NMR (101 MHz, $CDCl_3$) of **4g**



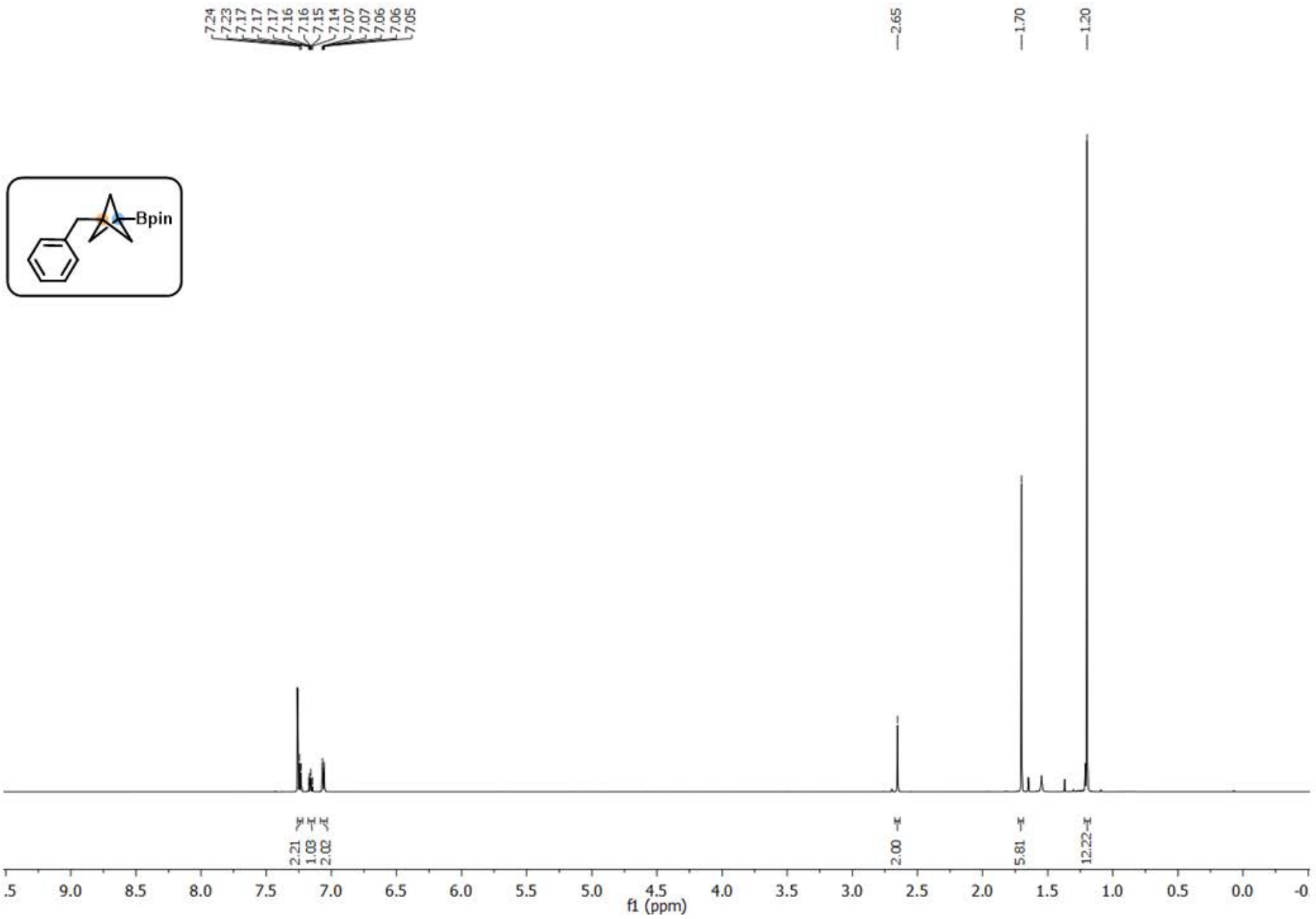
^{19}F NMR (376 MHz, $CDCl_3$) of **4g**



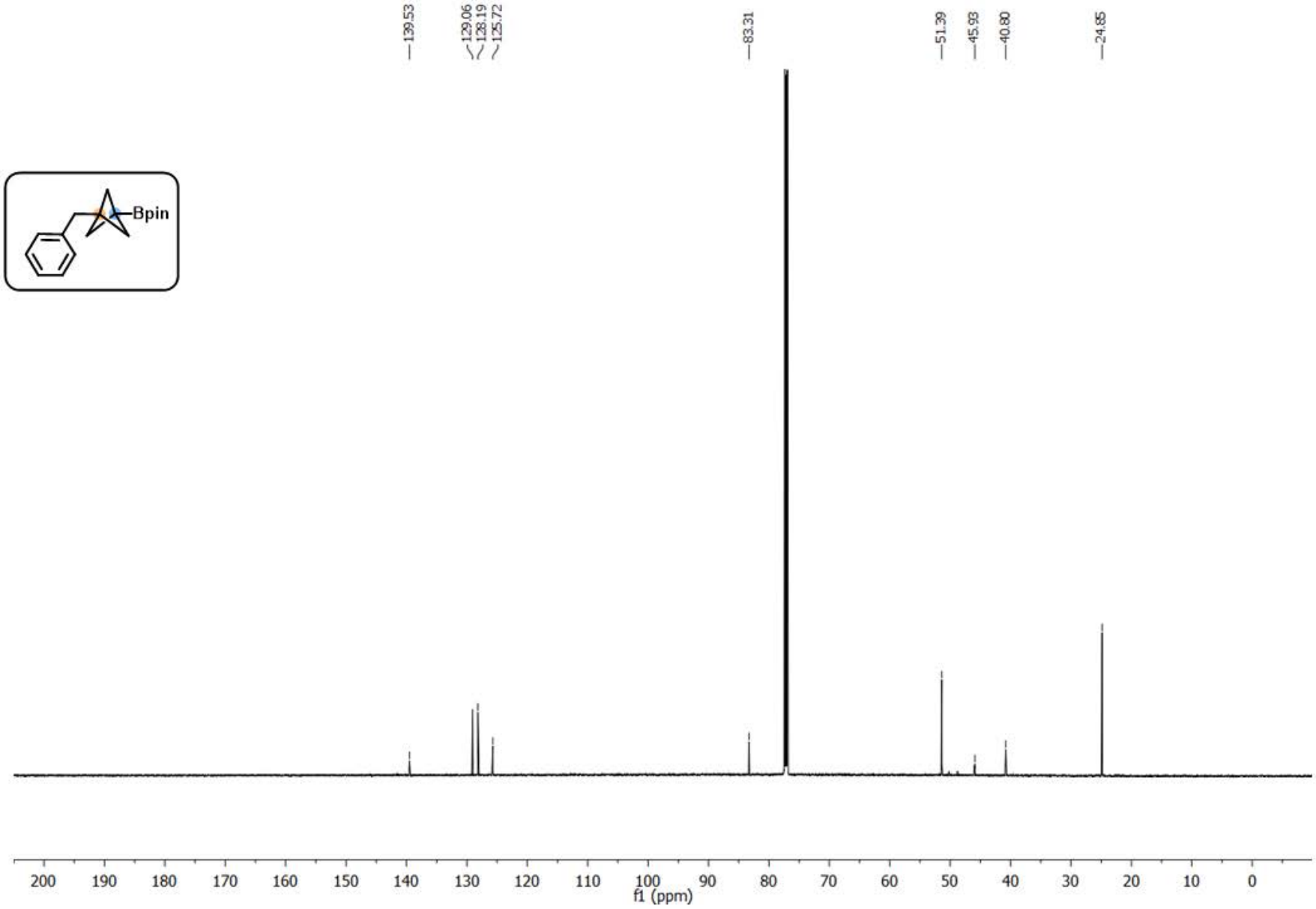
^{11}B NMR (128 MHz, $CDCl_3$) of **4g**



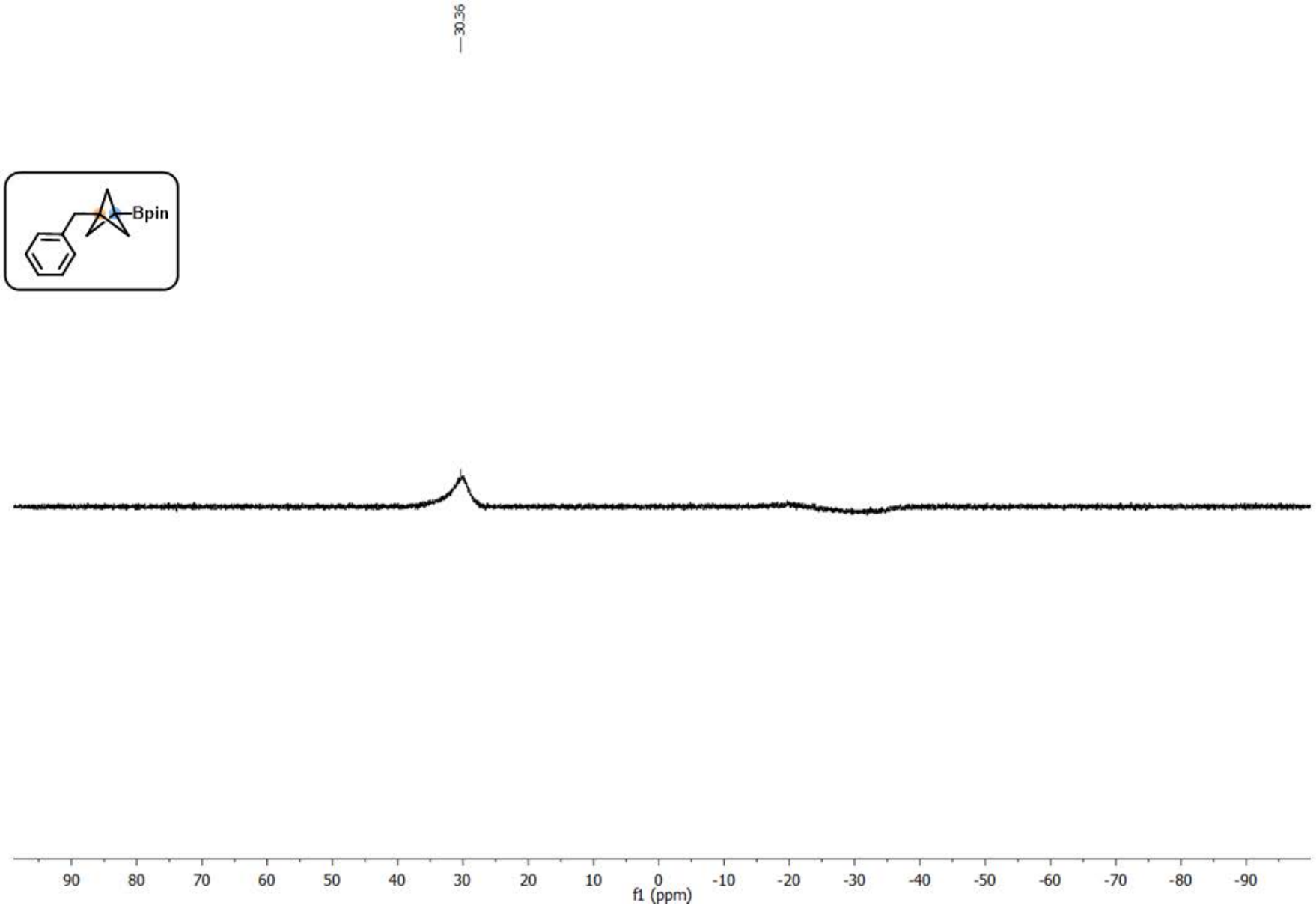
^{1}H NMR (400 MHz, $CDCl_3$) of **4h**



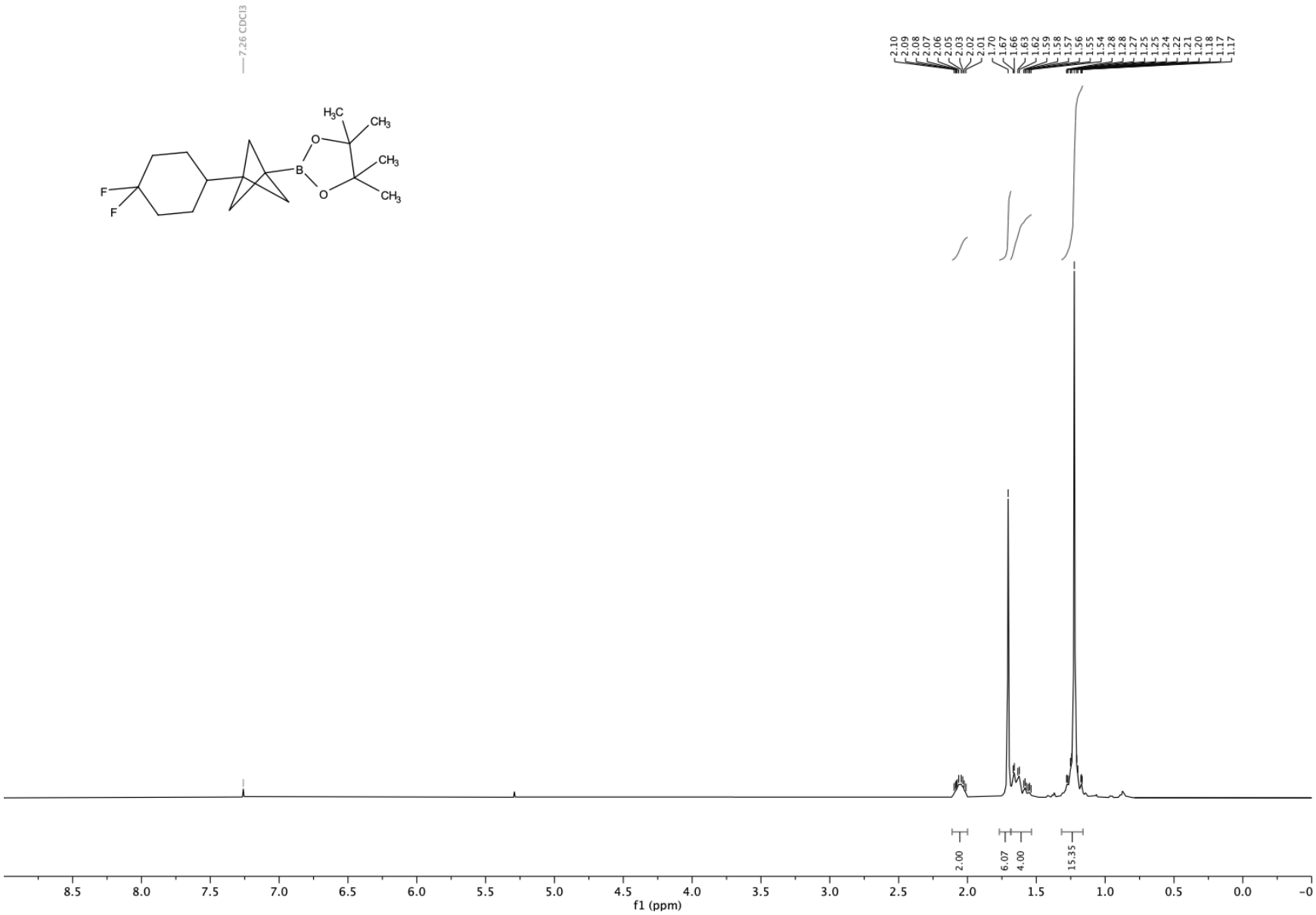
^{13}C NMR (101 MHz, $CDCl_3$) of **4h**



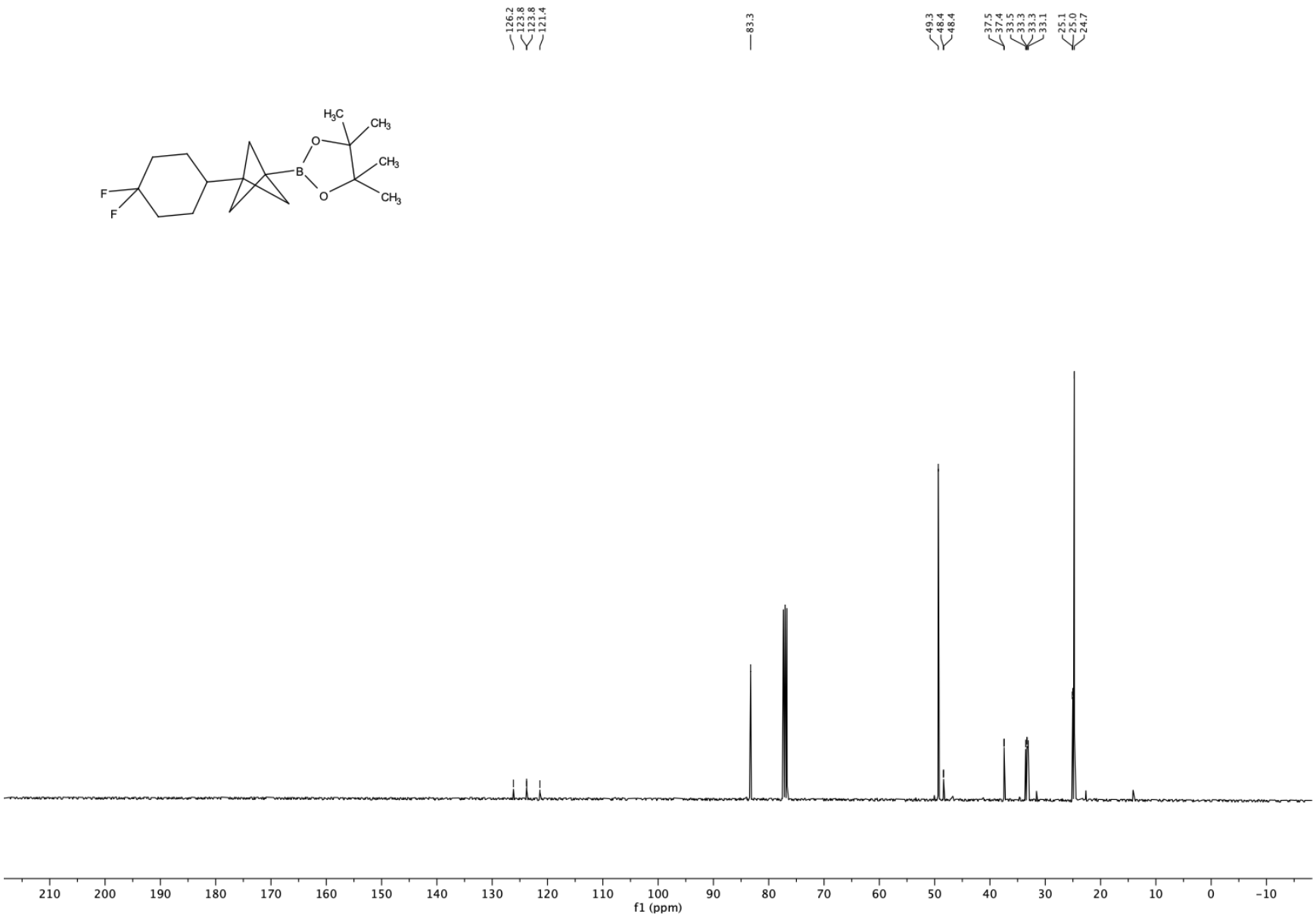
^{11}B NMR (128 MHz, $CDCl_3$) of **4h**



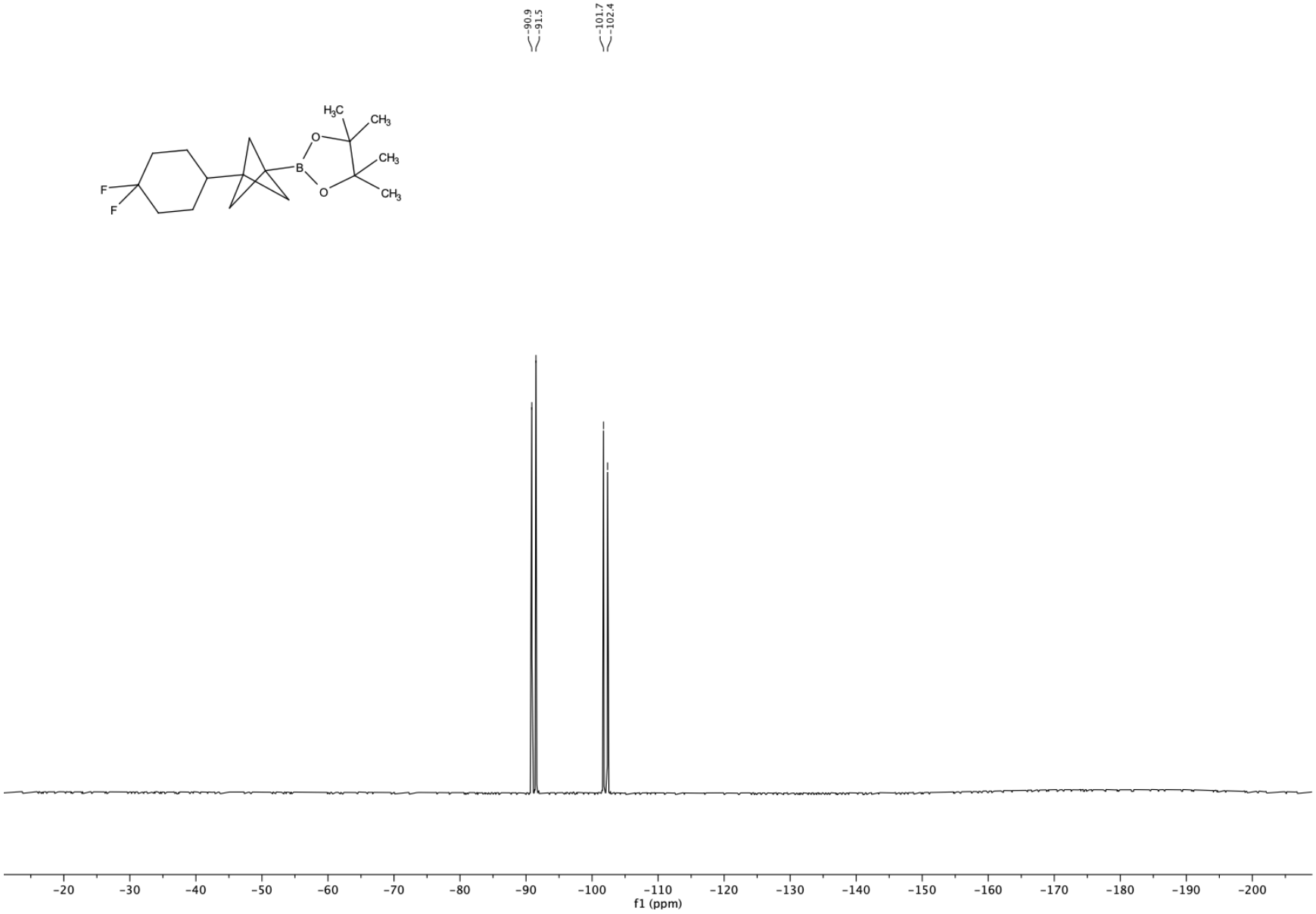
^{1}H NMR (400 MHz, $CDCl_3$) of **4i**



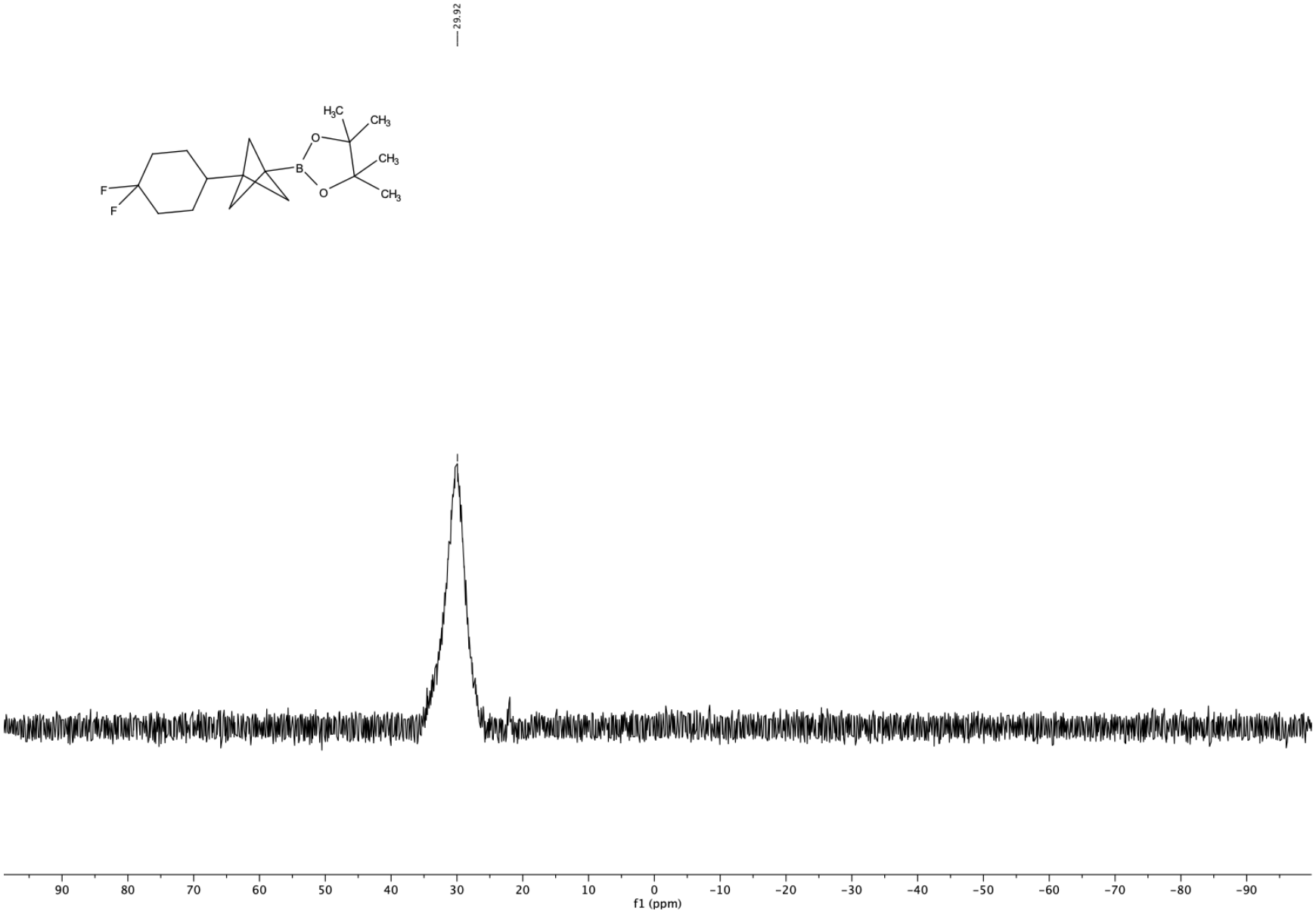
^{13}C NMR (101 MHz, $CDCl_3$) of **4i**



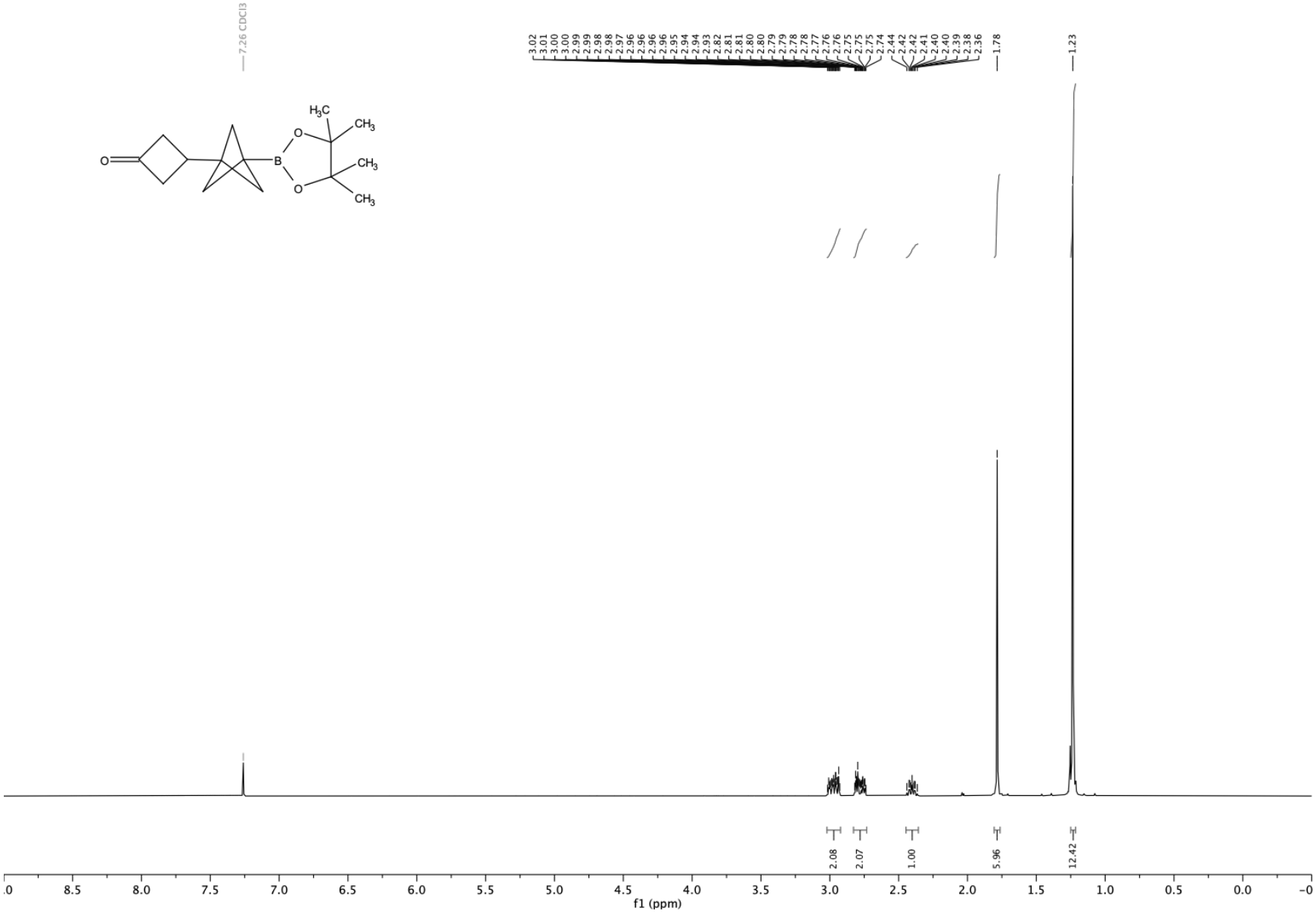
^{19}F NMR (376 MHz, $CDCl_3$) of **4i**



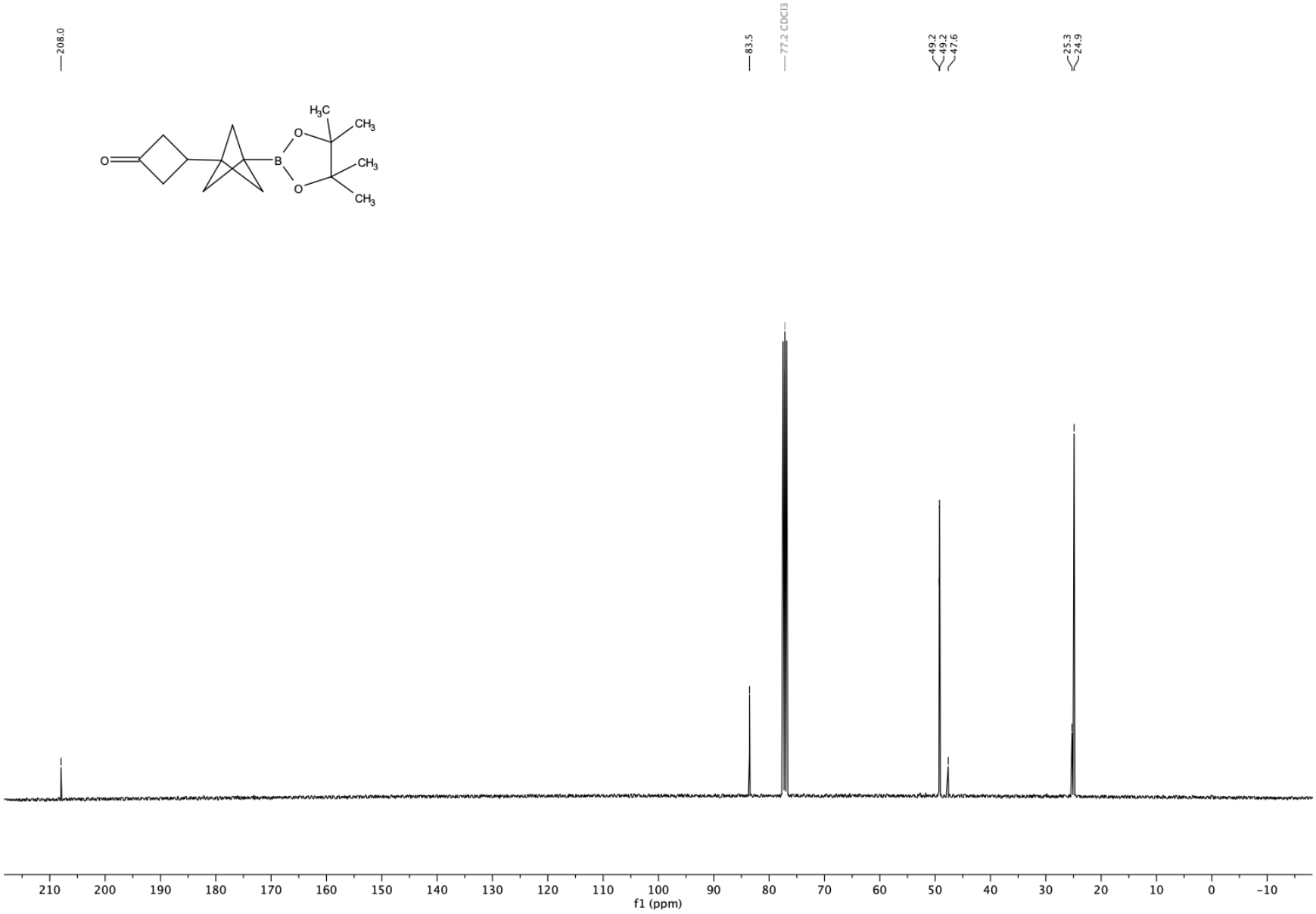
^{11}B NMR (128 MHz, $CDCl_3$) of **4i**



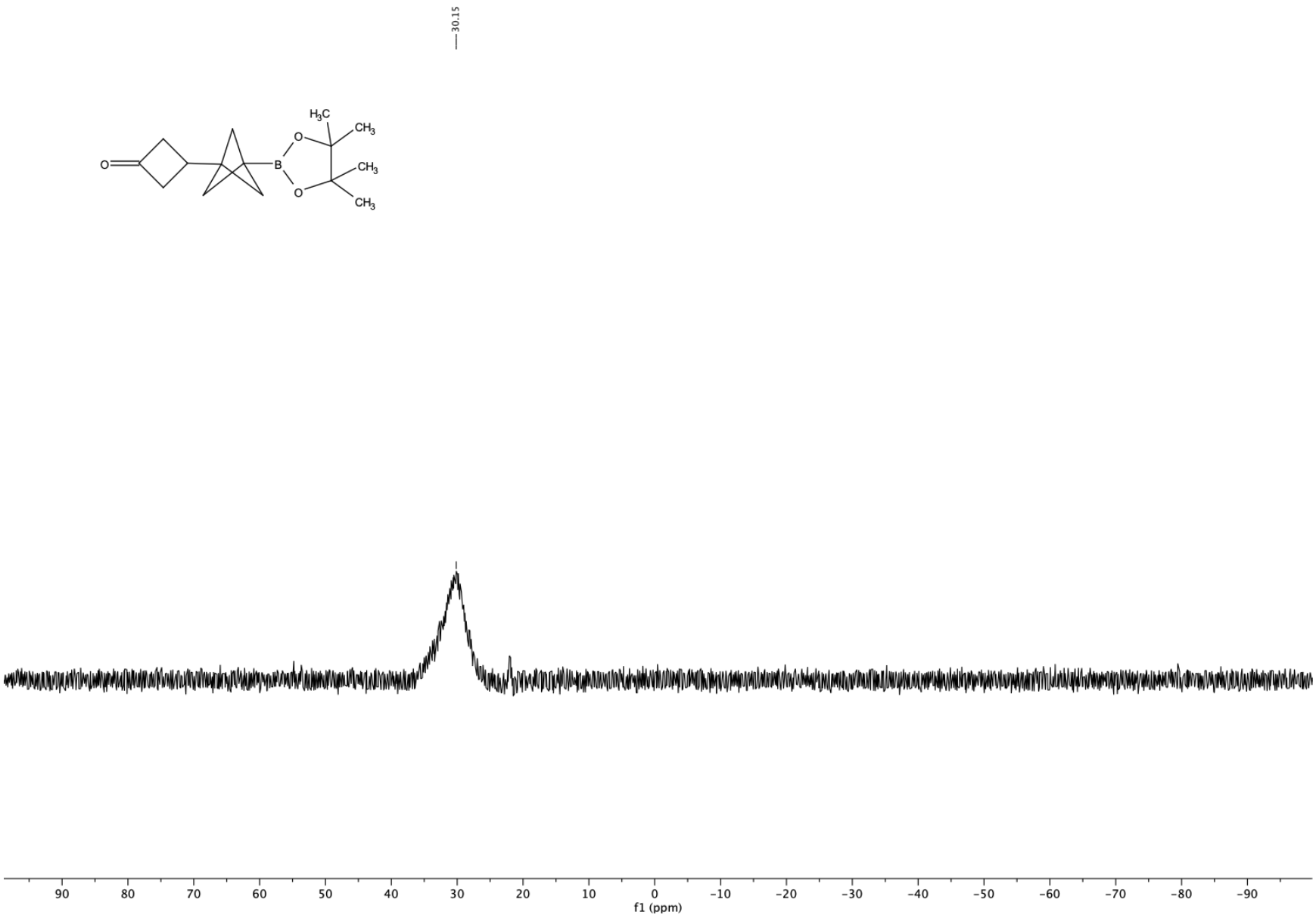
^{1}H NMR (400 MHz, $CDCl_3$) of **4j**



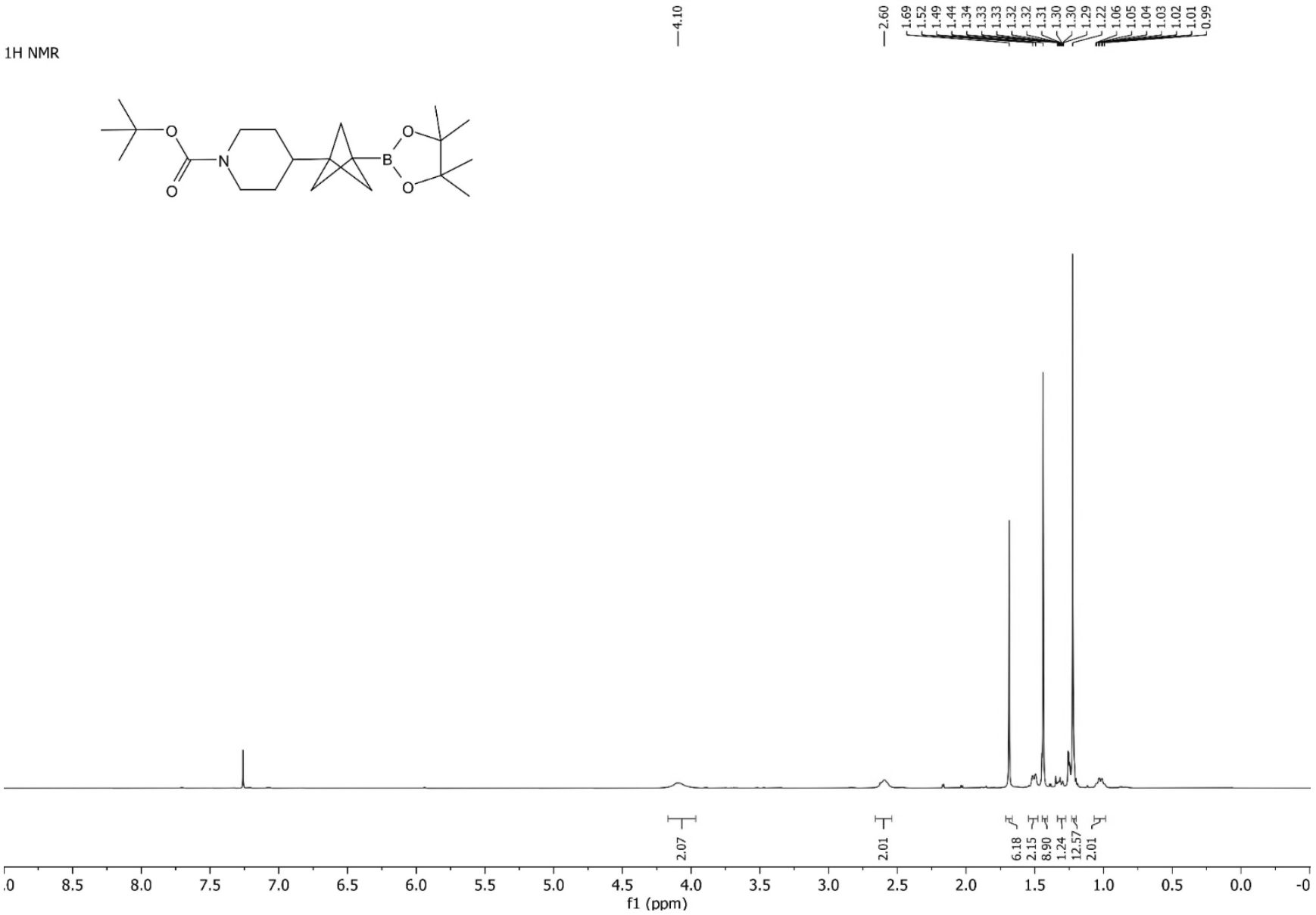
^{13}C NMR (101 MHz, $CDCl_3$) of **4j**



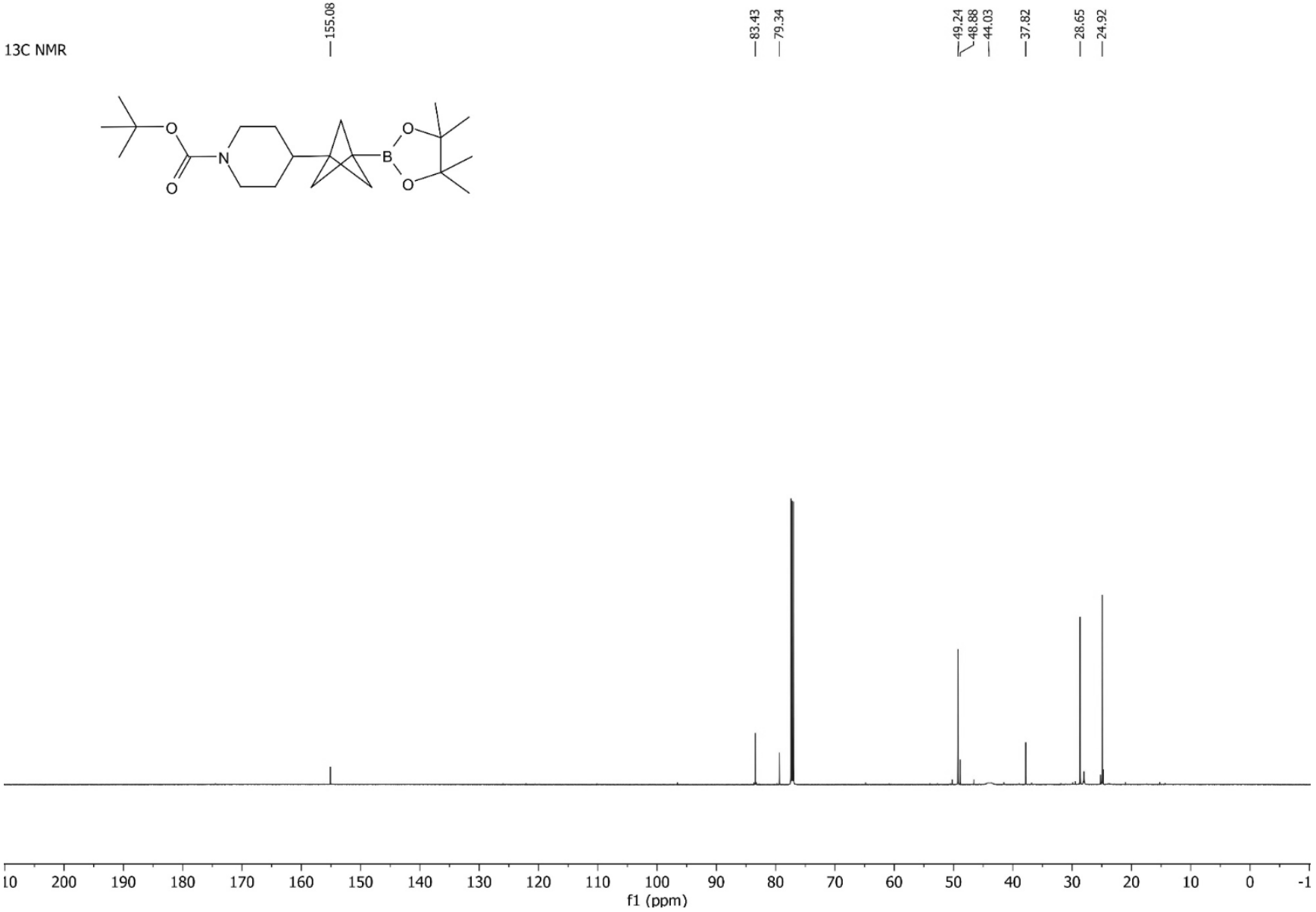
^{11}B NMR (128 MHz, $CDCl_3$) of **4j**



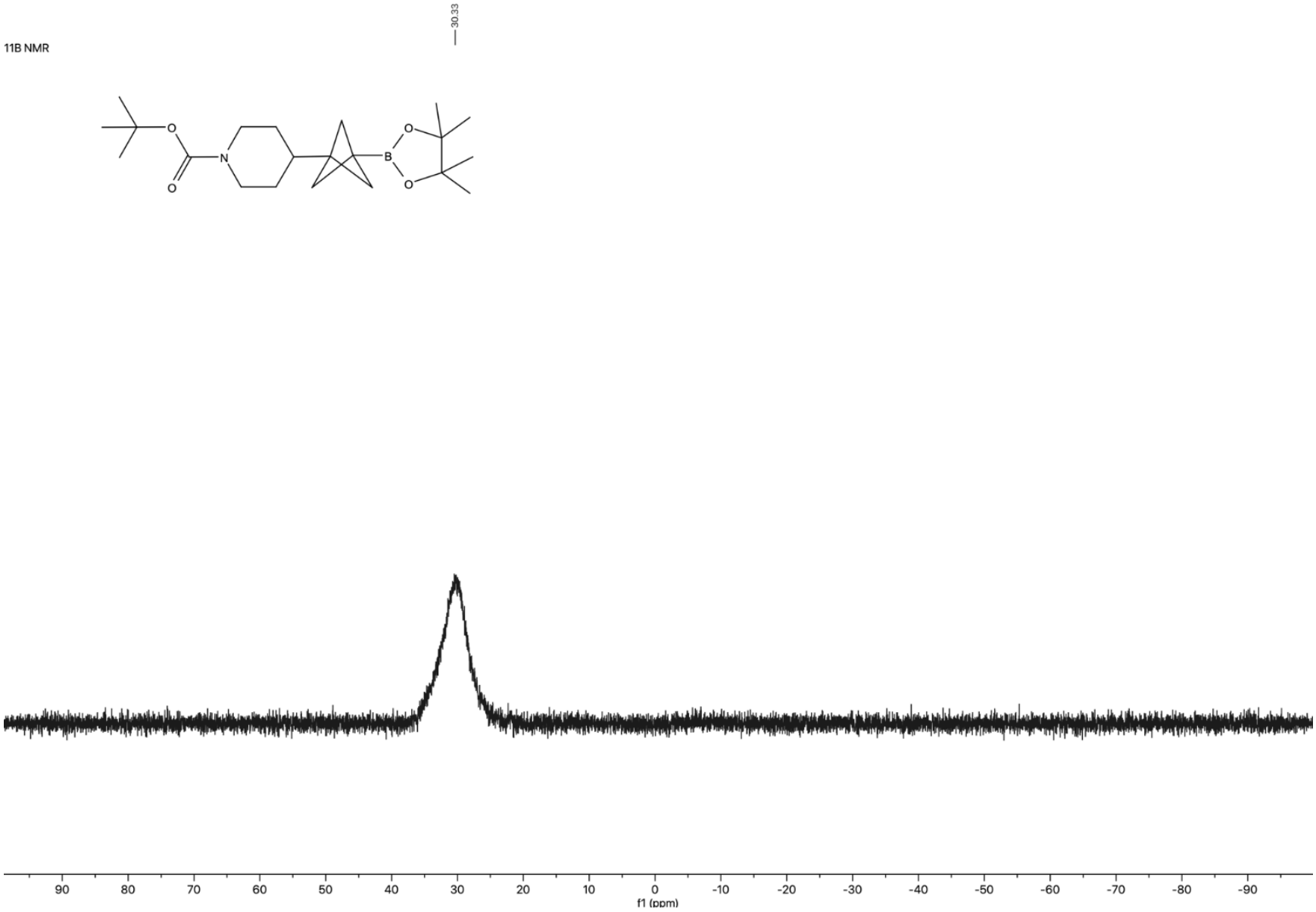
^{1}H NMR (600 MHz, $CDCl_3$) of **4k**



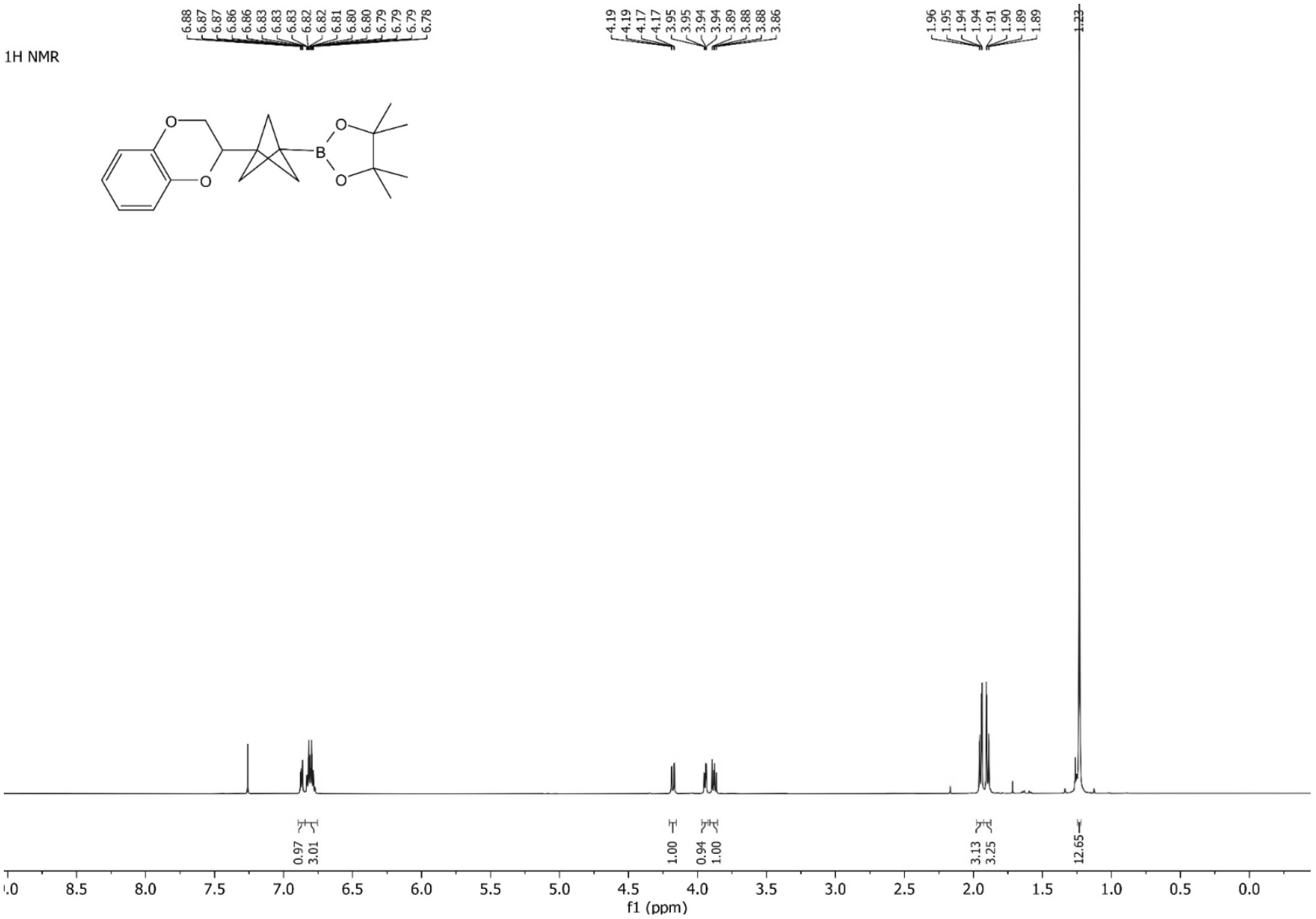
^{13}C NMR (151 MHz, $CDCl_3$) of **4k**



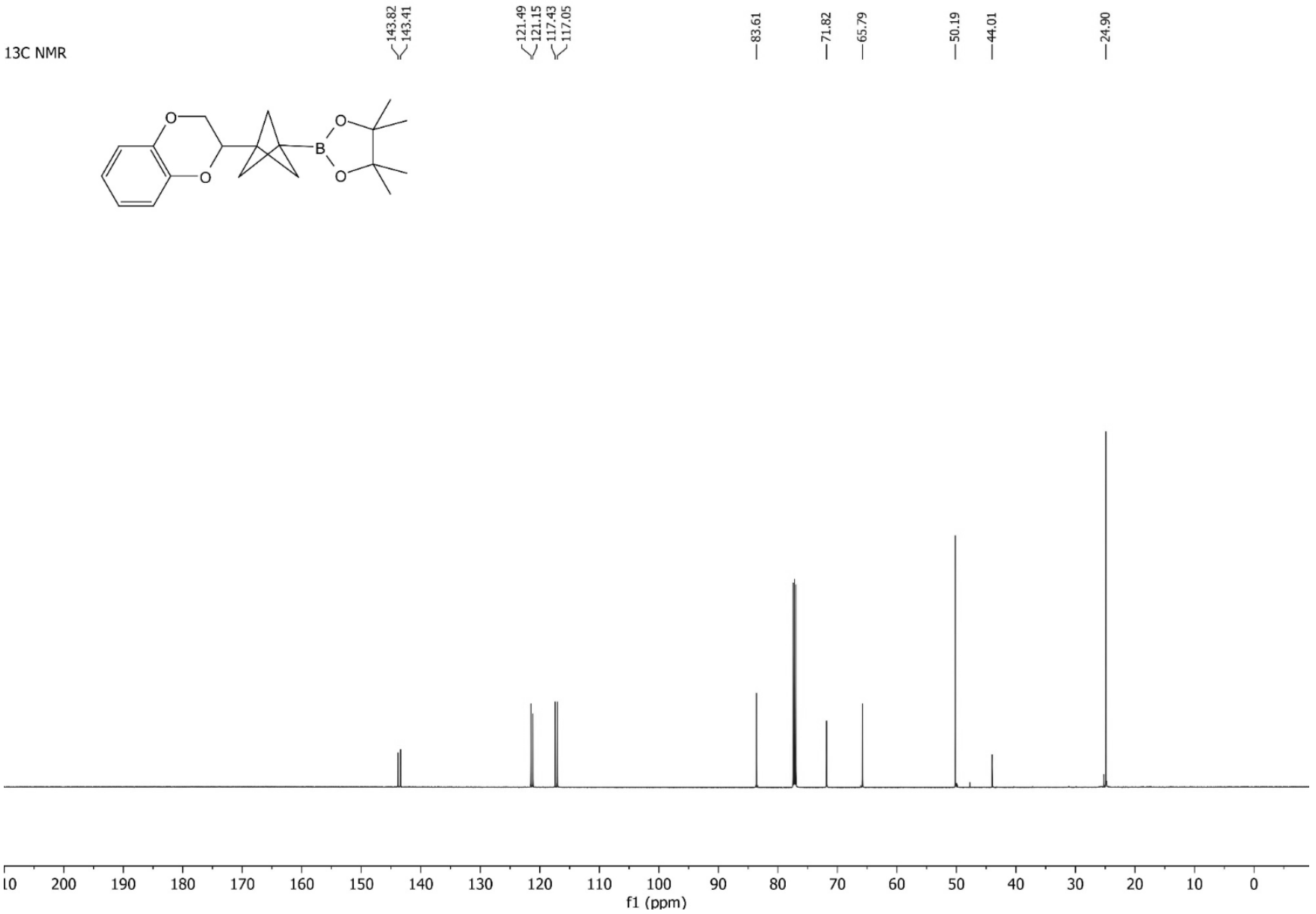
^{11}B NMR (128 MHz, $CDCl_3$) of **4k**



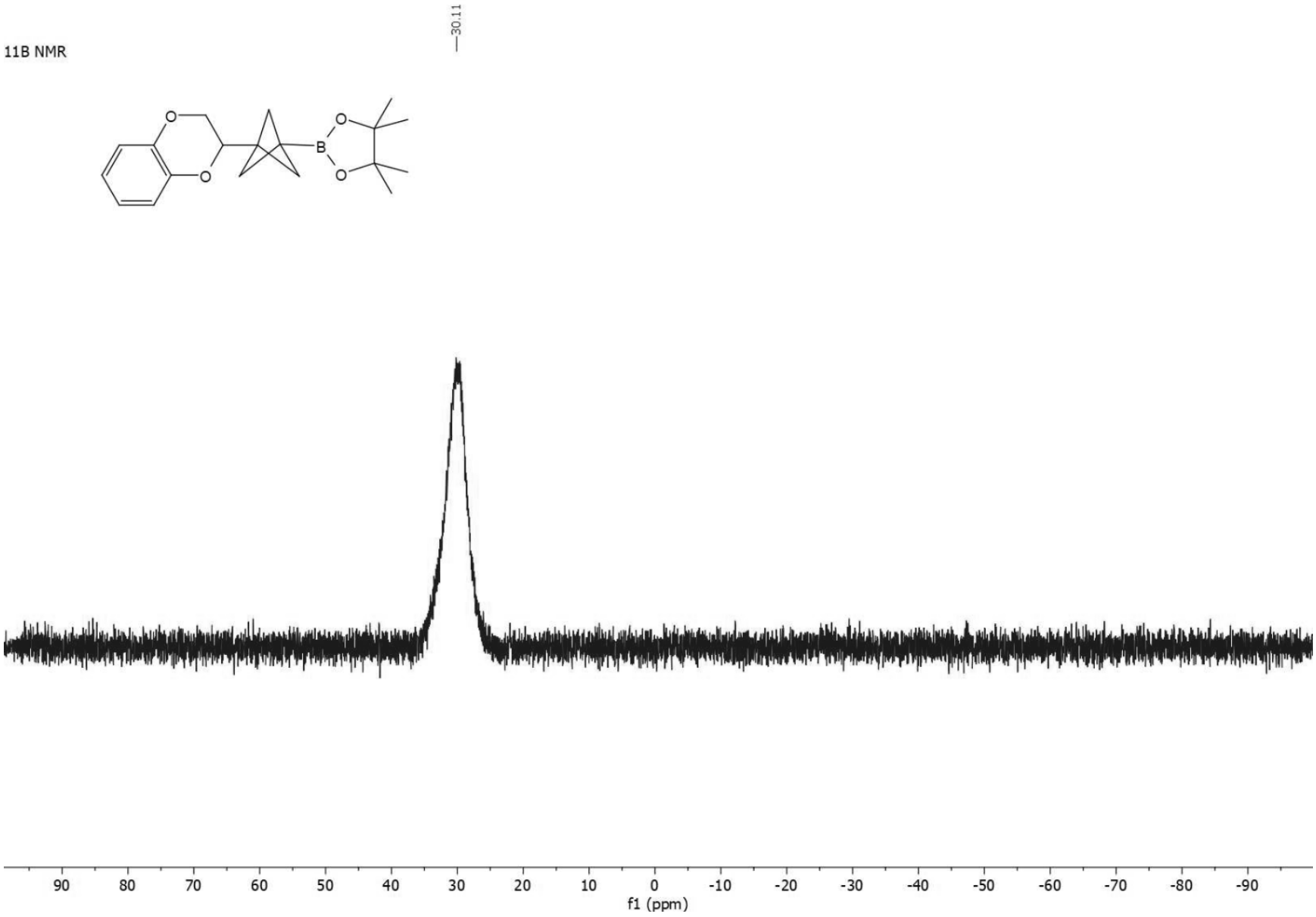
^{1}H NMR (600 MHz, $CDCl_3$) of **4l**



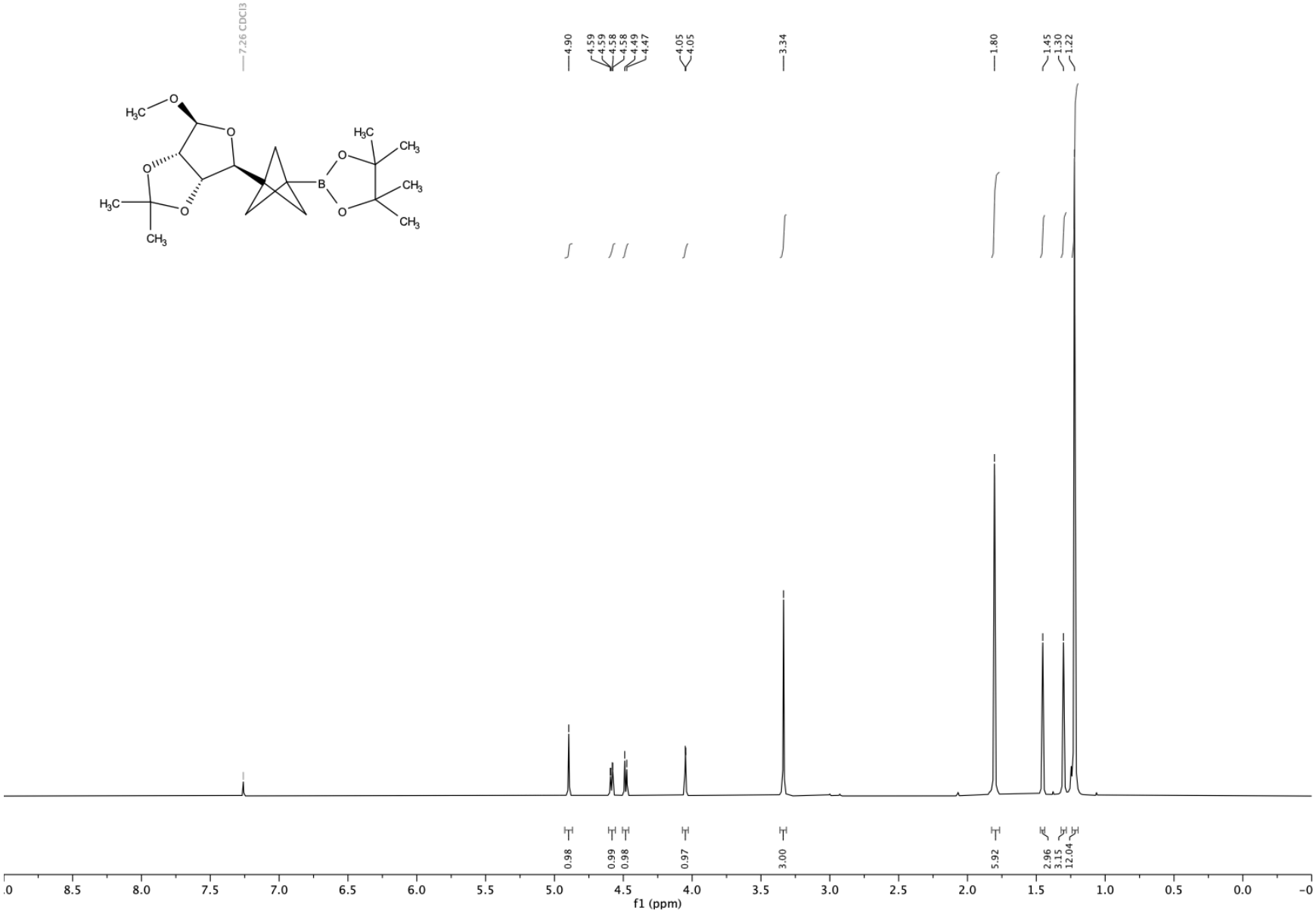
^{13}C NMR (151 MHz, $CDCl_3$) of **4l**



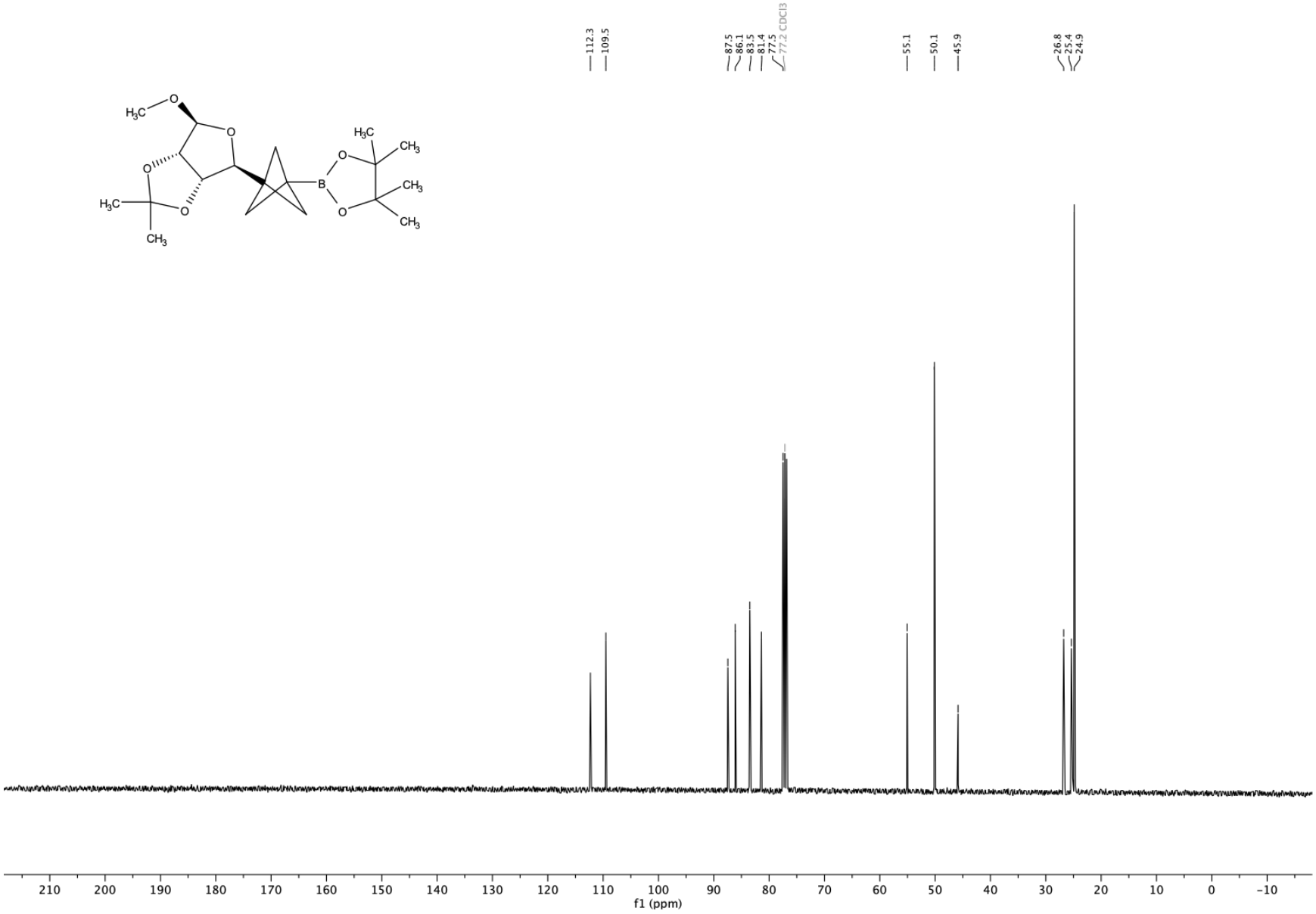
^{11}B NMR (128 MHz, $CDCl_3$) of **4l**



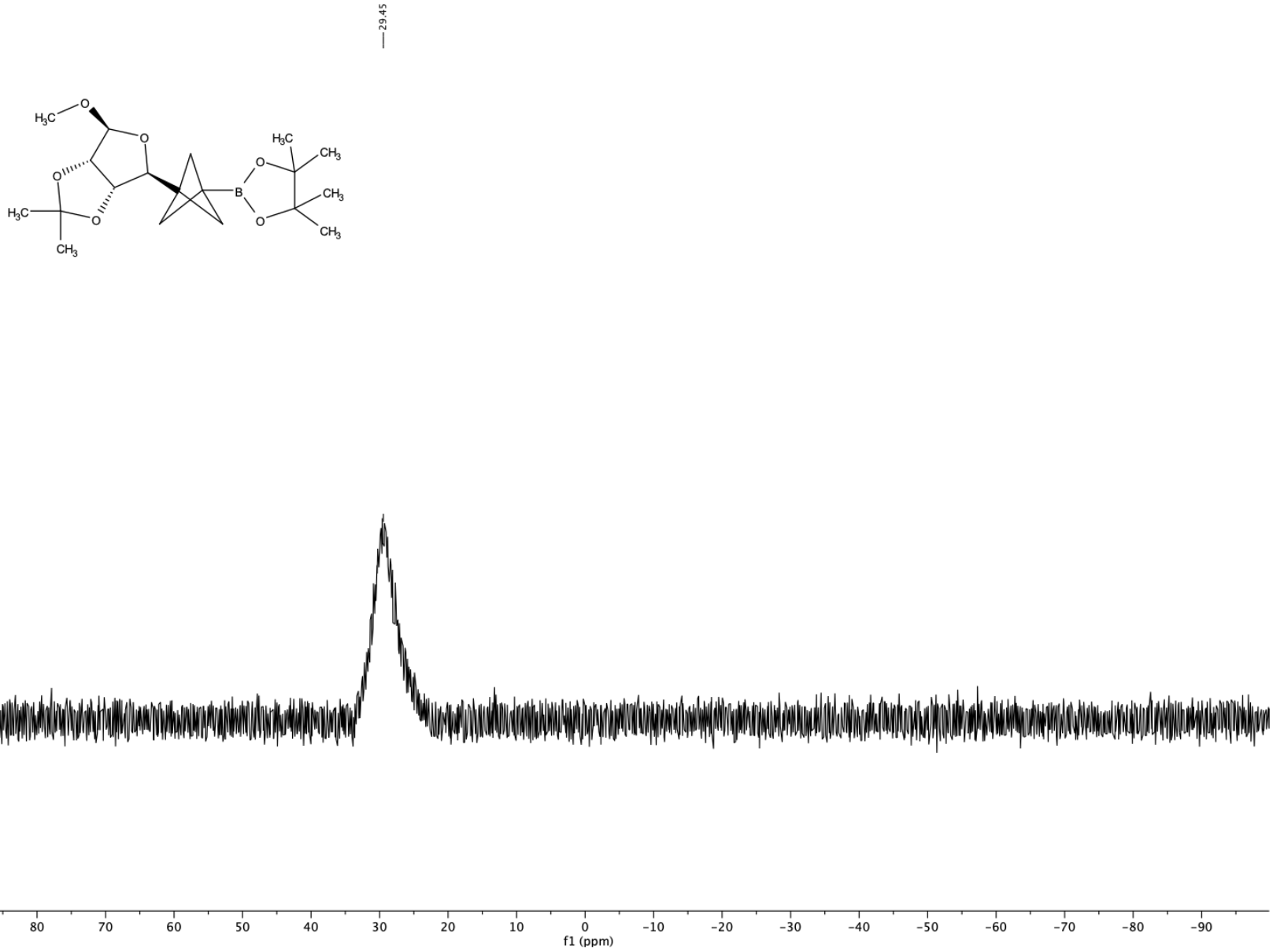
^{1}H NMR (400 MHz, $CDCl_3$) of **4m**



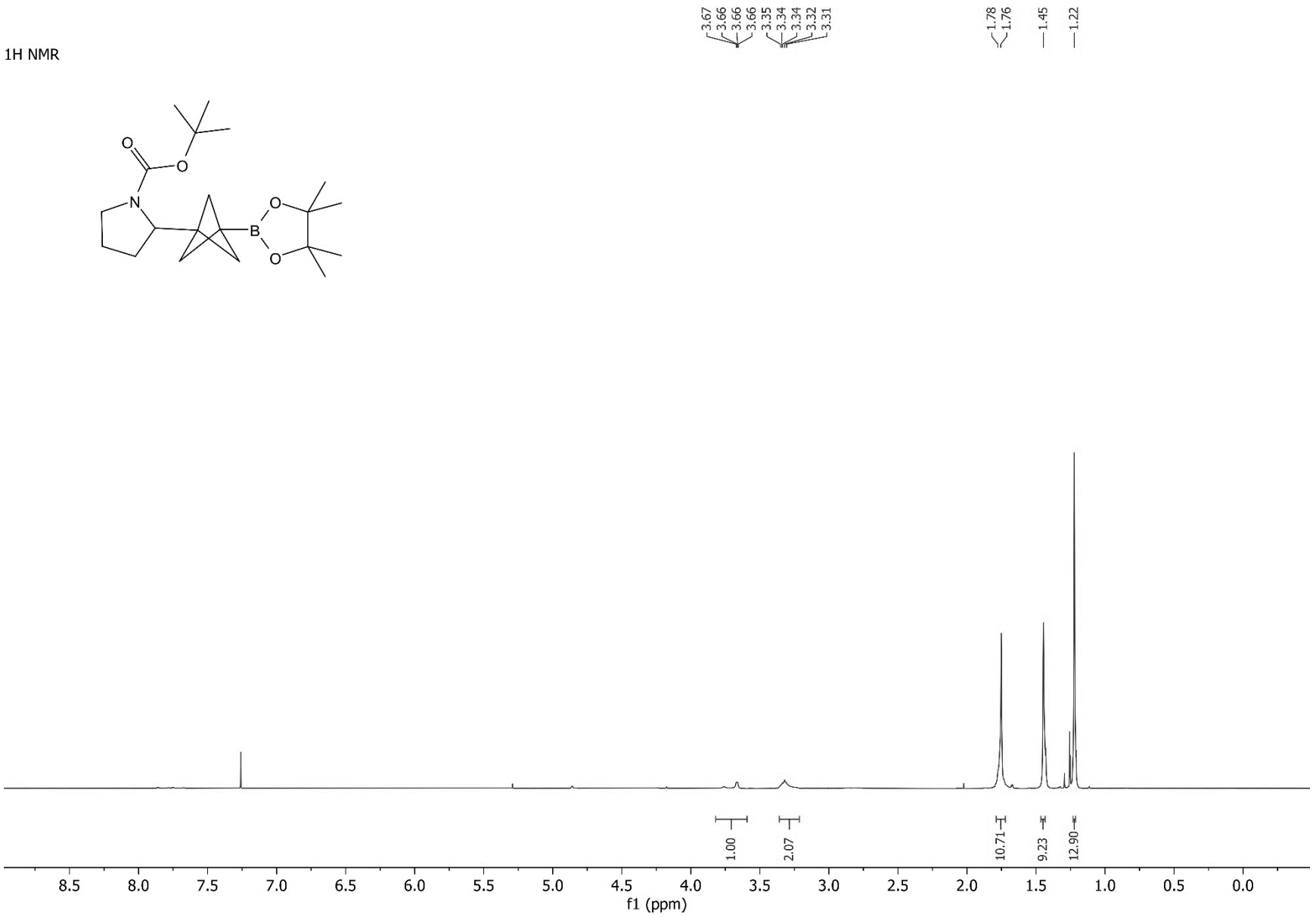
^{13}C NMR (101 MHz, $CDCl_3$) of **4m**



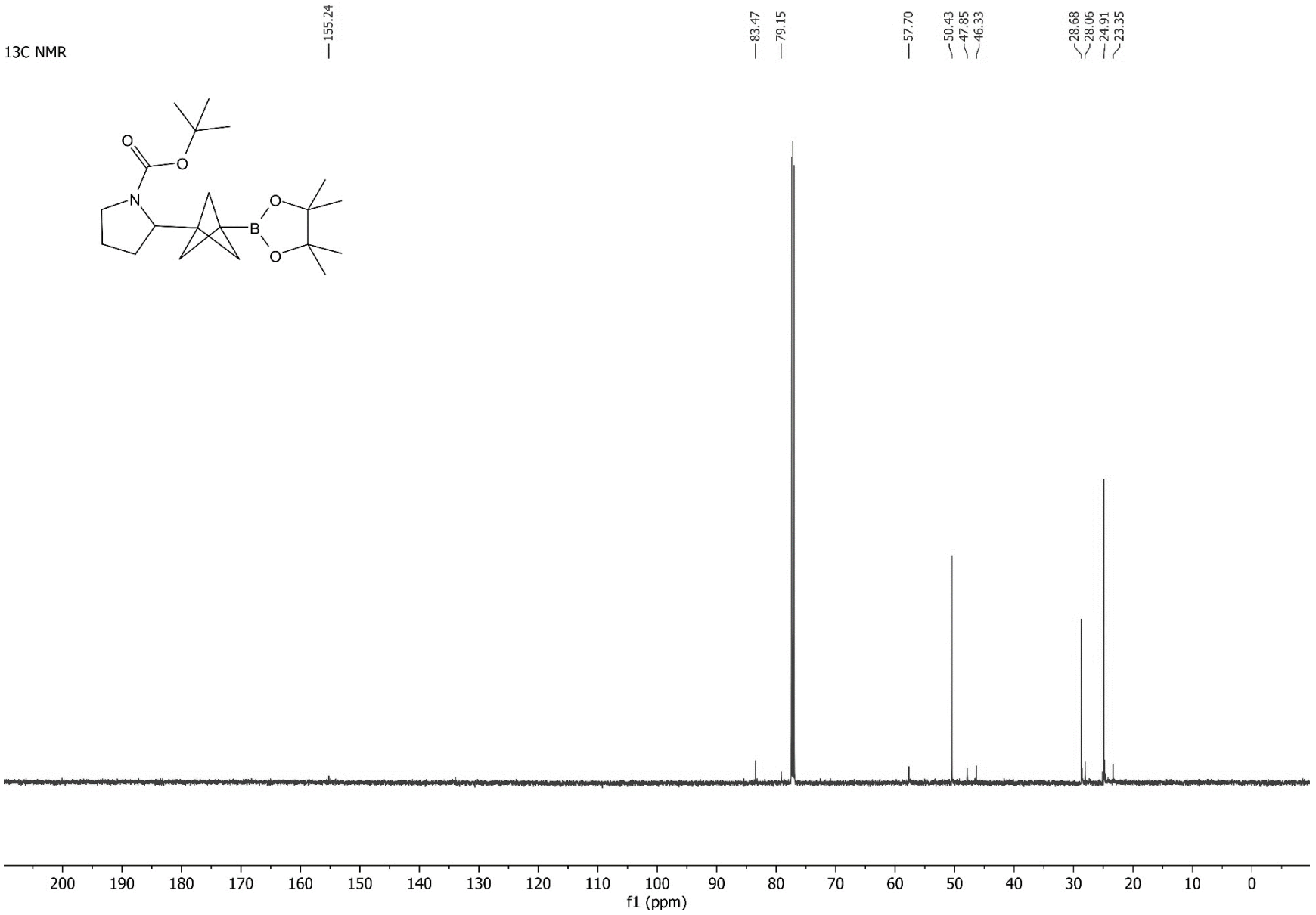
^{11}B NMR (128 MHz, $CDCl_3$) of **4m**



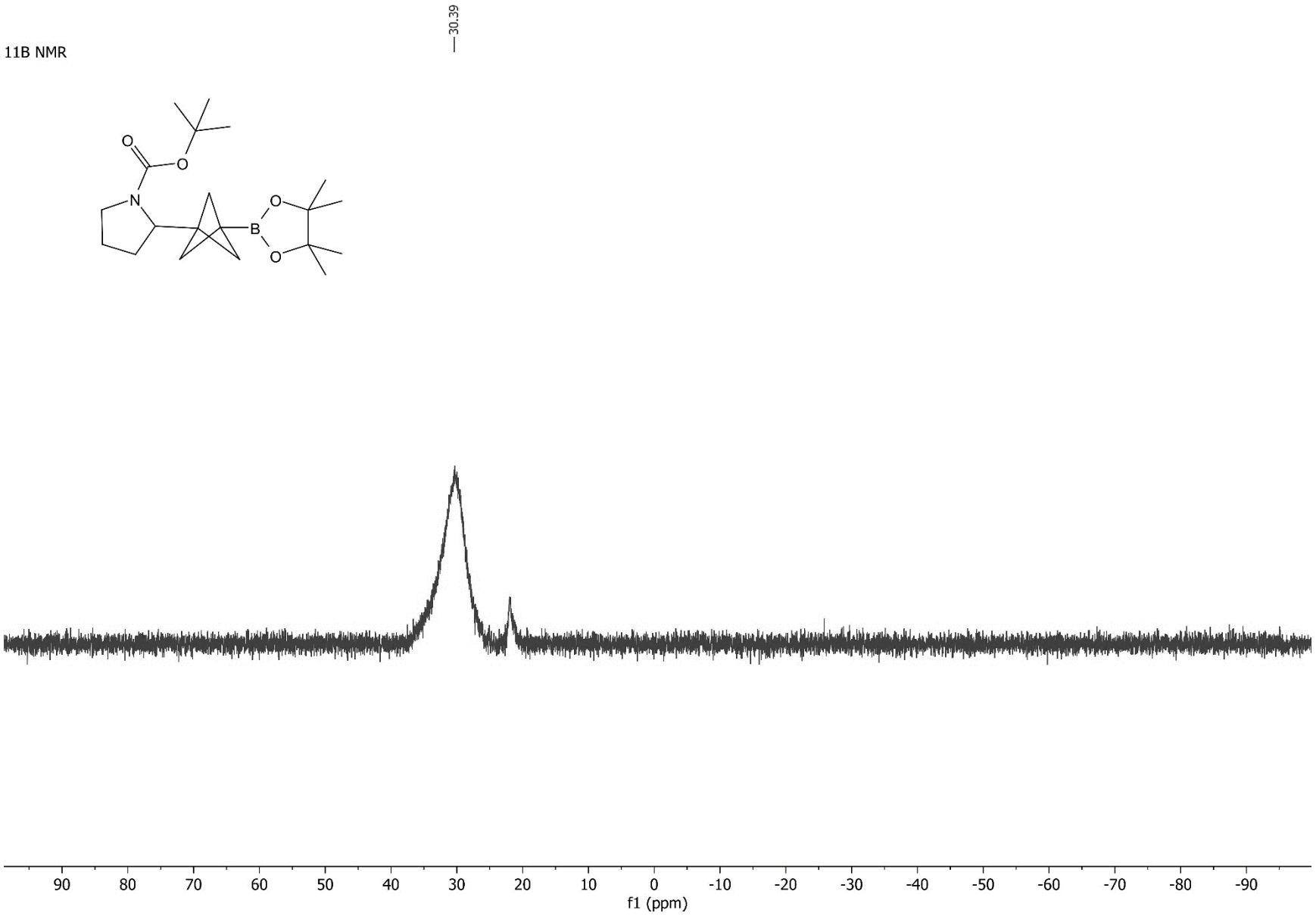
^{1}H NMR (600 MHz, $CDCl_3$) of **4n**



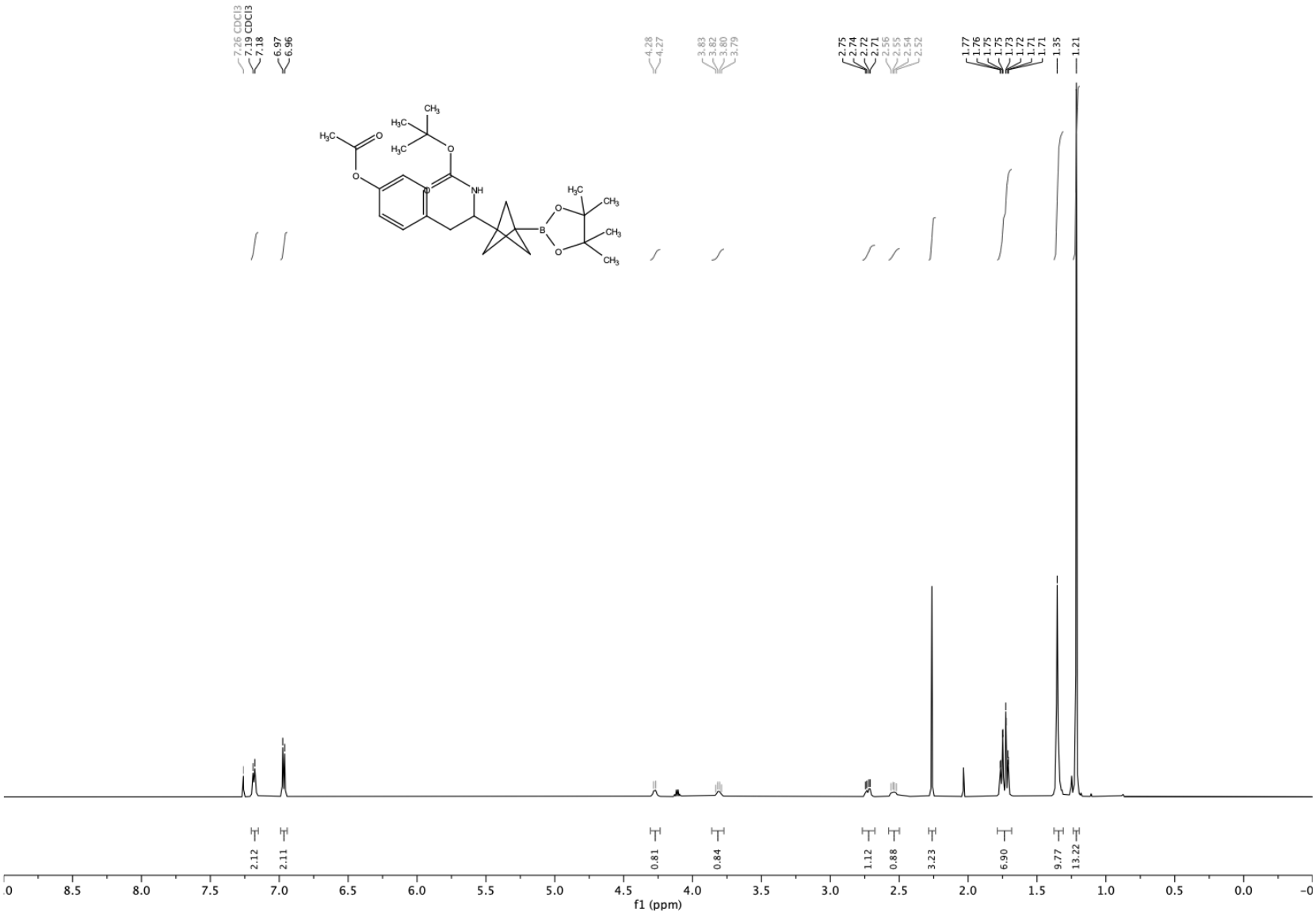
^{13}C NMR (151 MHz, $CDCl_3$) of **4n**



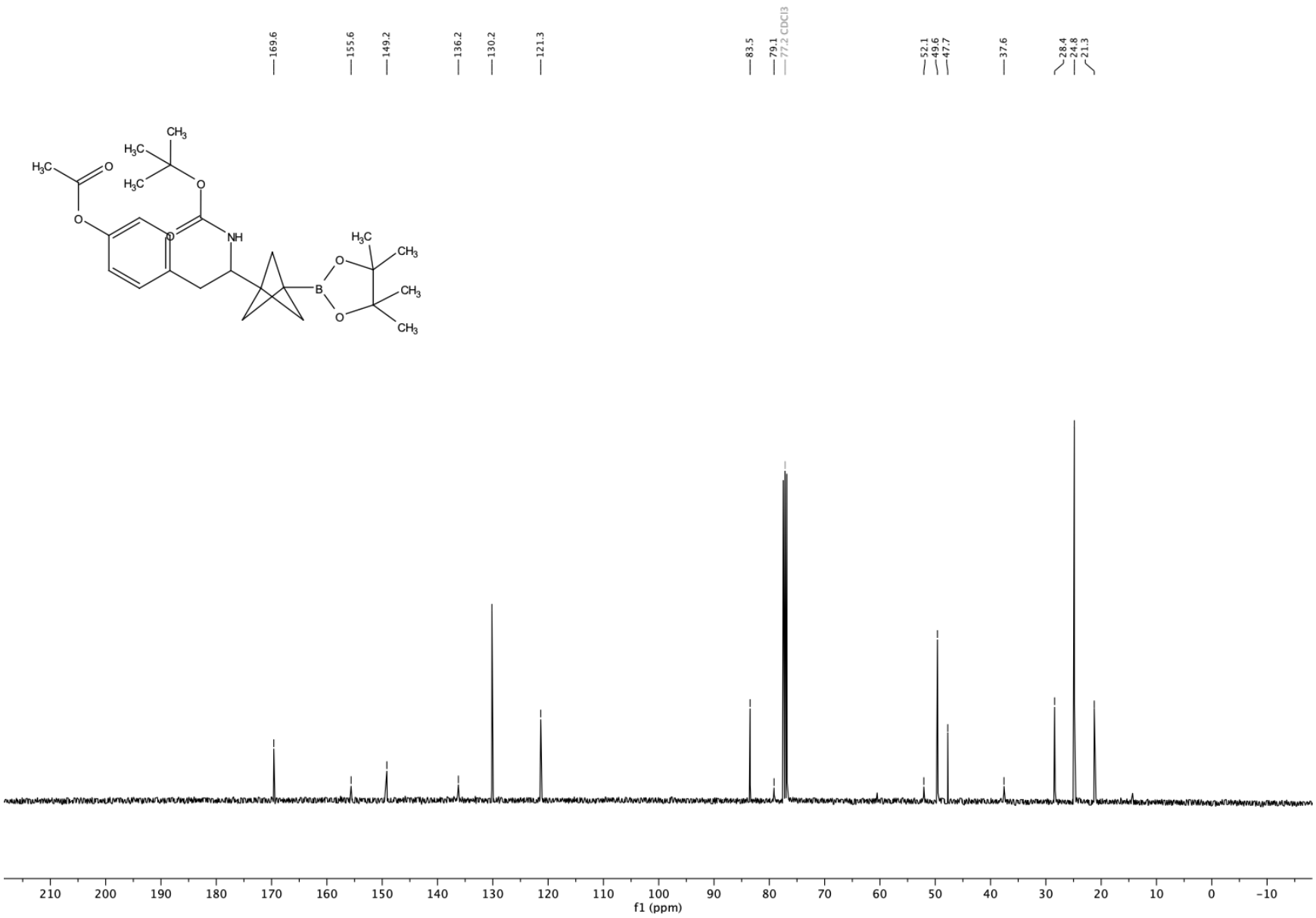
^{11}B NMR (128 MHz, $CDCl_3$) of **4n**



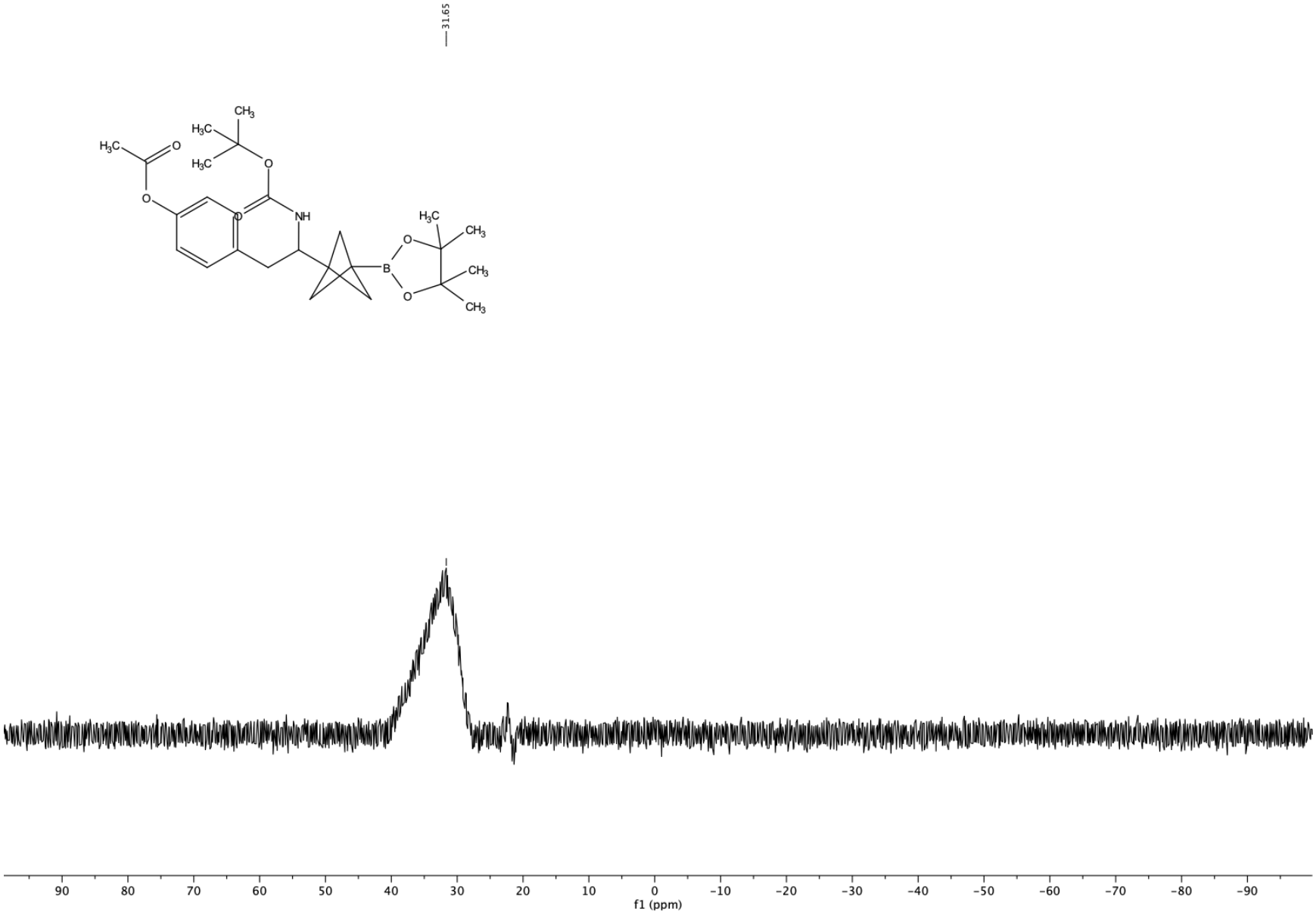
^{1}H NMR (600 MHz, $CDCl_3$) of **4o**



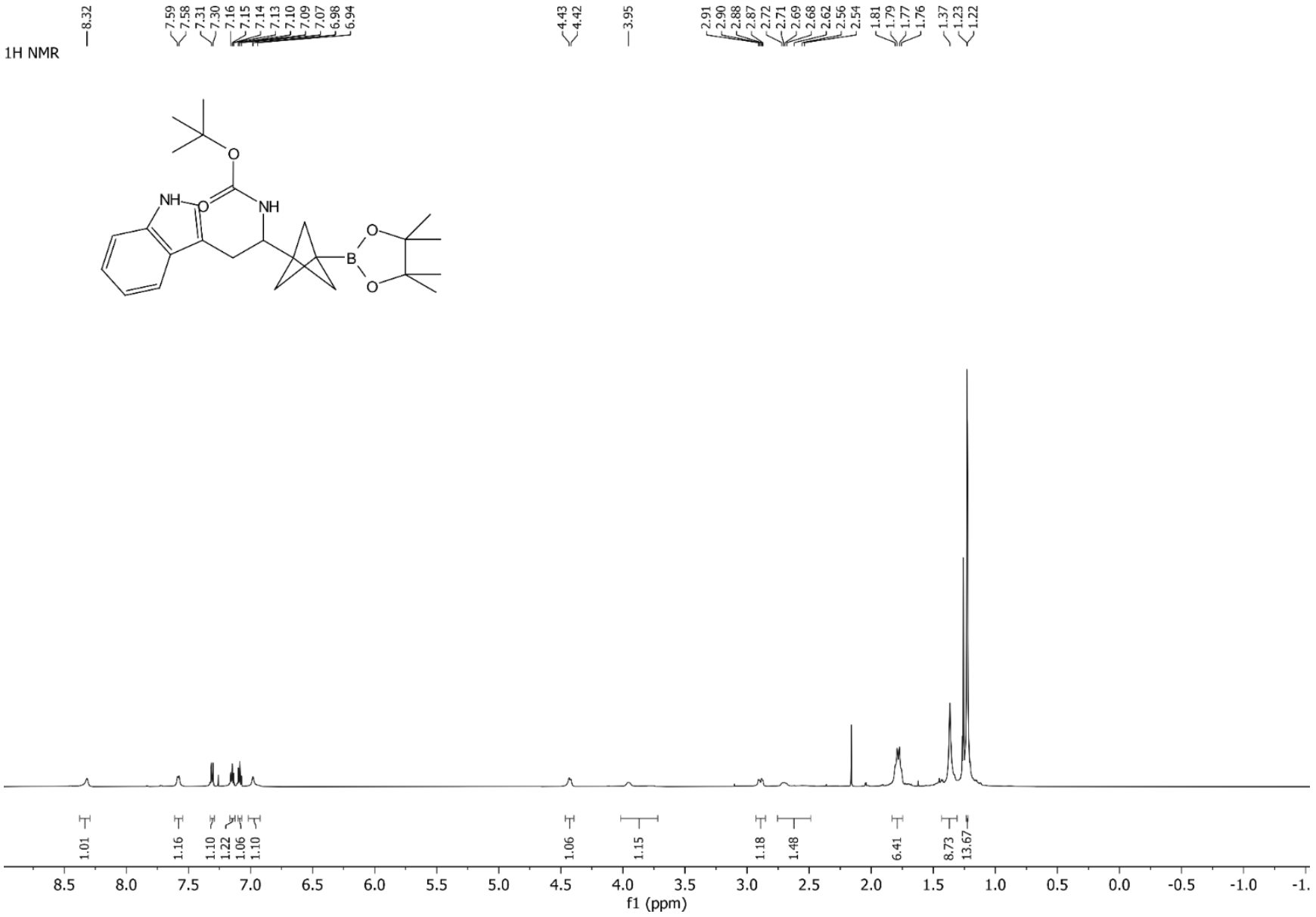
^{13}C NMR (101 MHz, $CDCl_3$) of **4o**



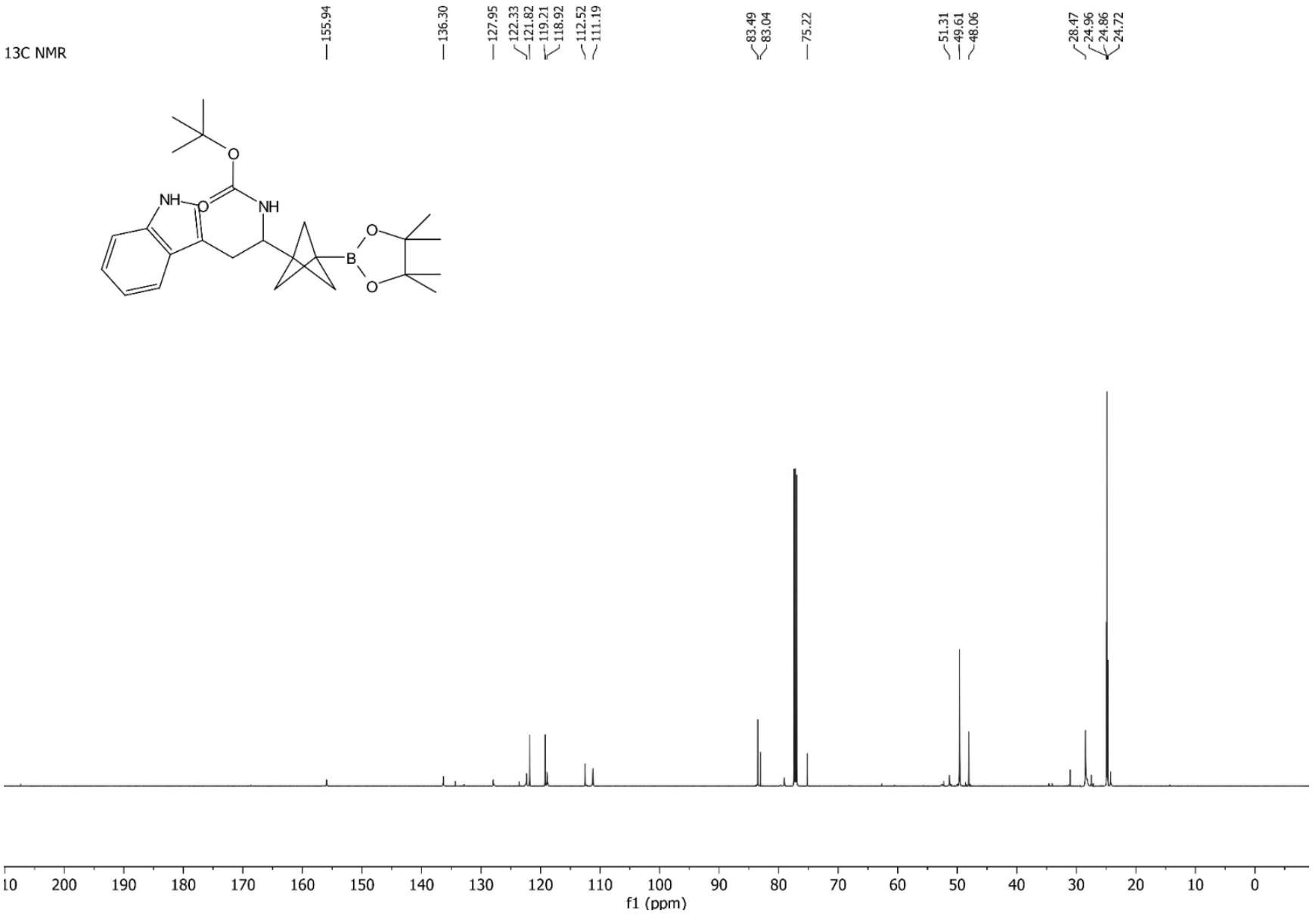
^{11}B NMR (128 MHz, $CDCl_3$) of **4o**



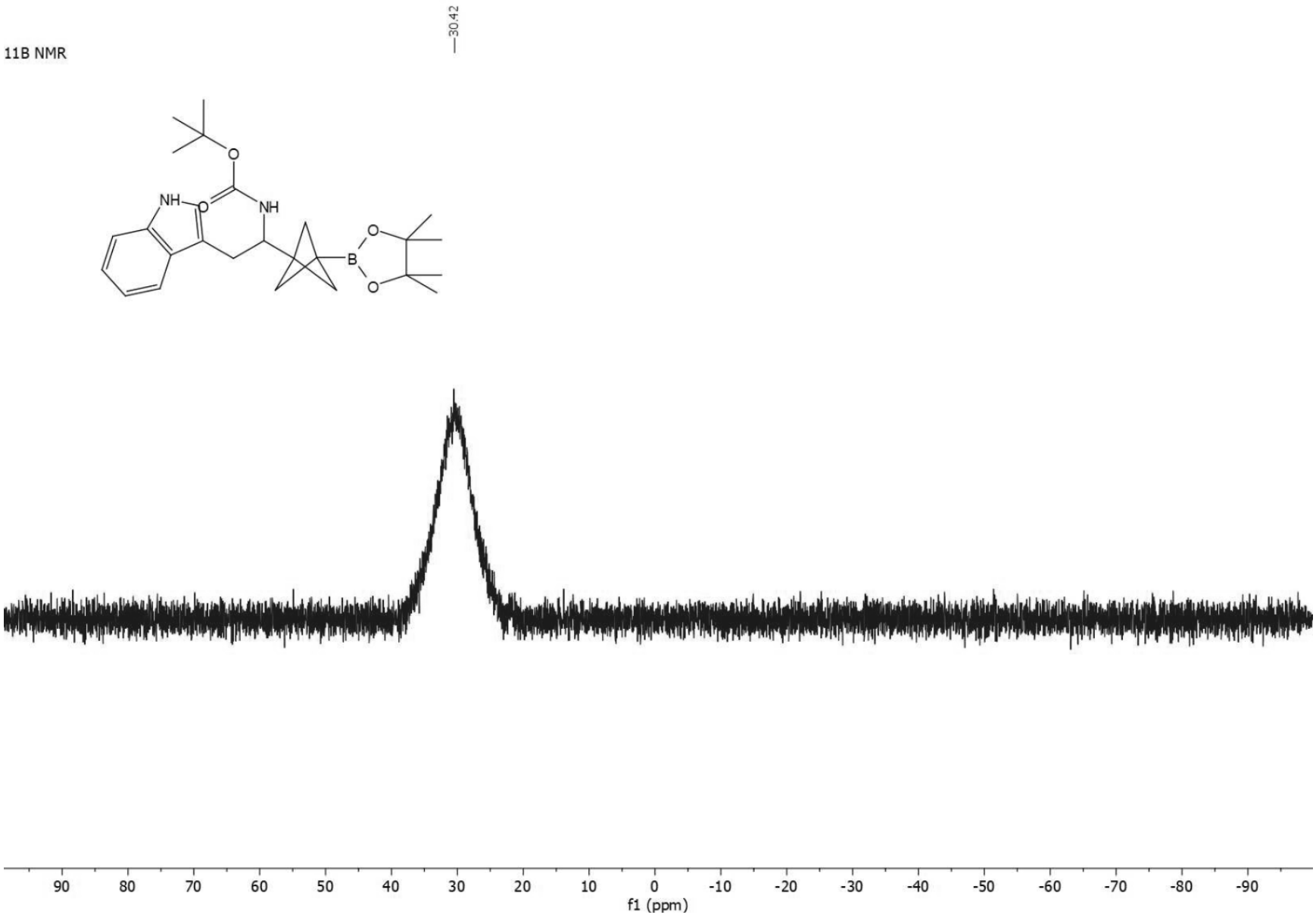
^{1}H NMR (600 MHz, $CDCl_3$) of **4p**



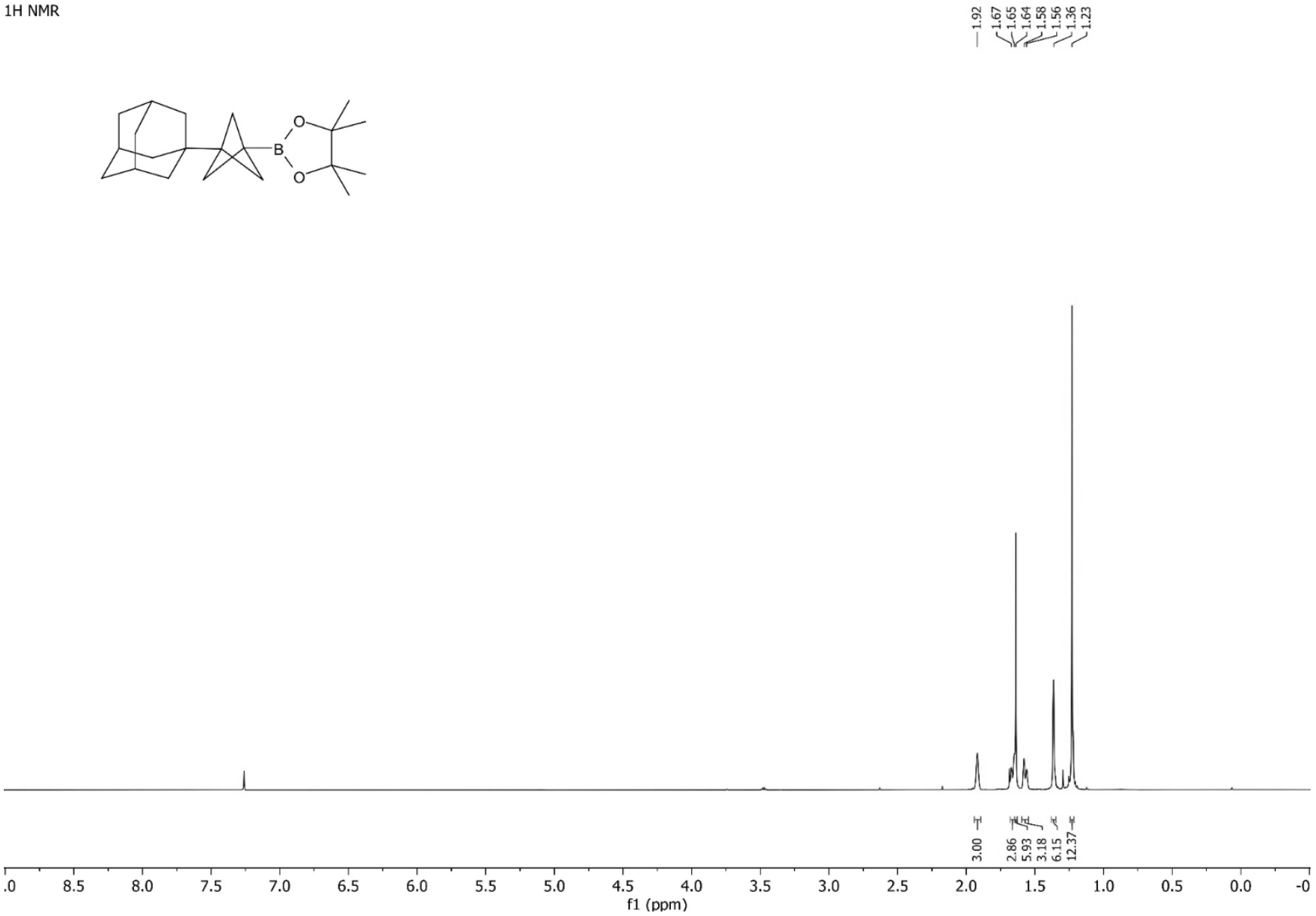
^{13}C NMR (151 MHz, $CDCl_3$) of **4p**



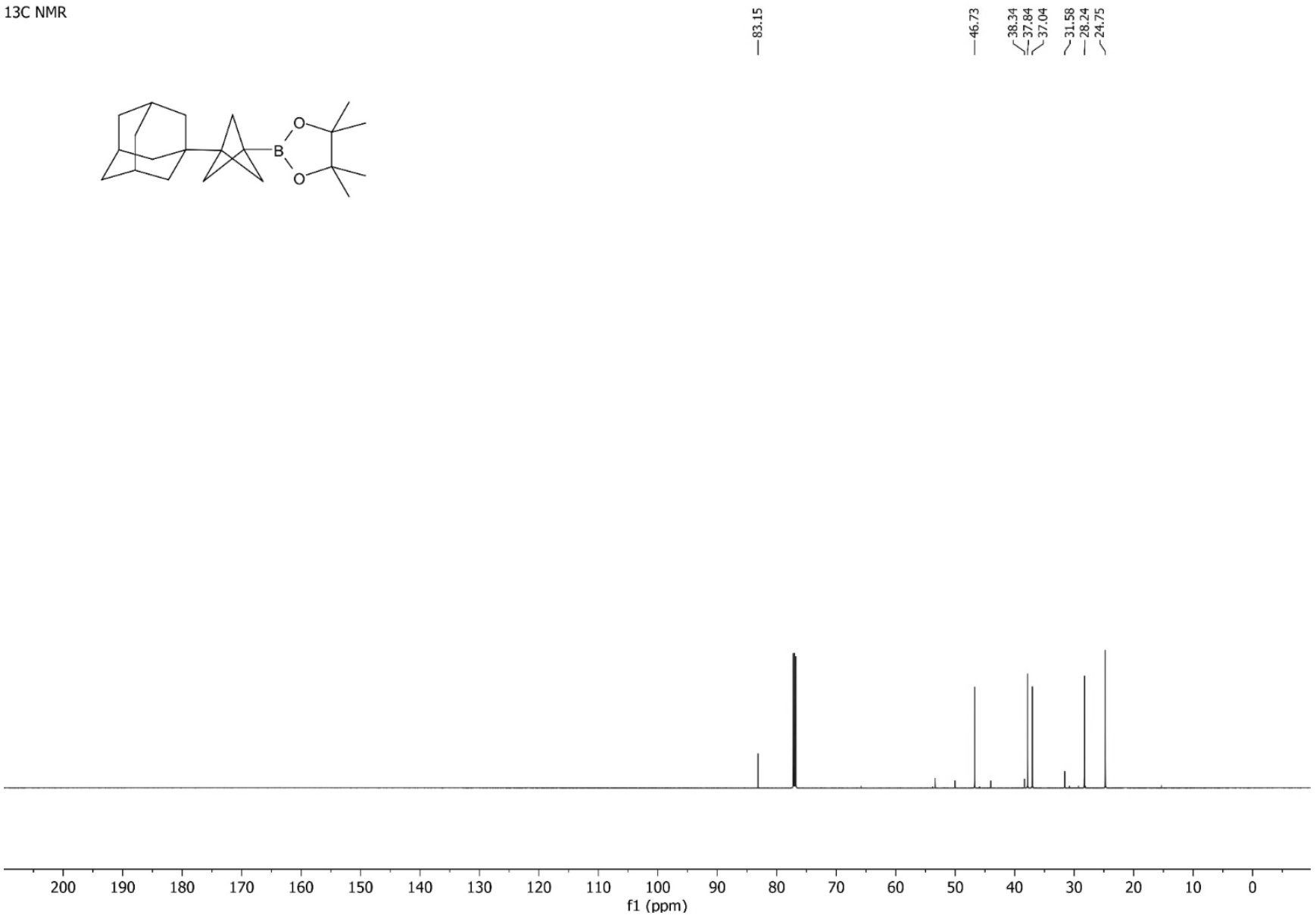
^{11}B NMR (128 MHz, $CDCl_3$) of **4p**



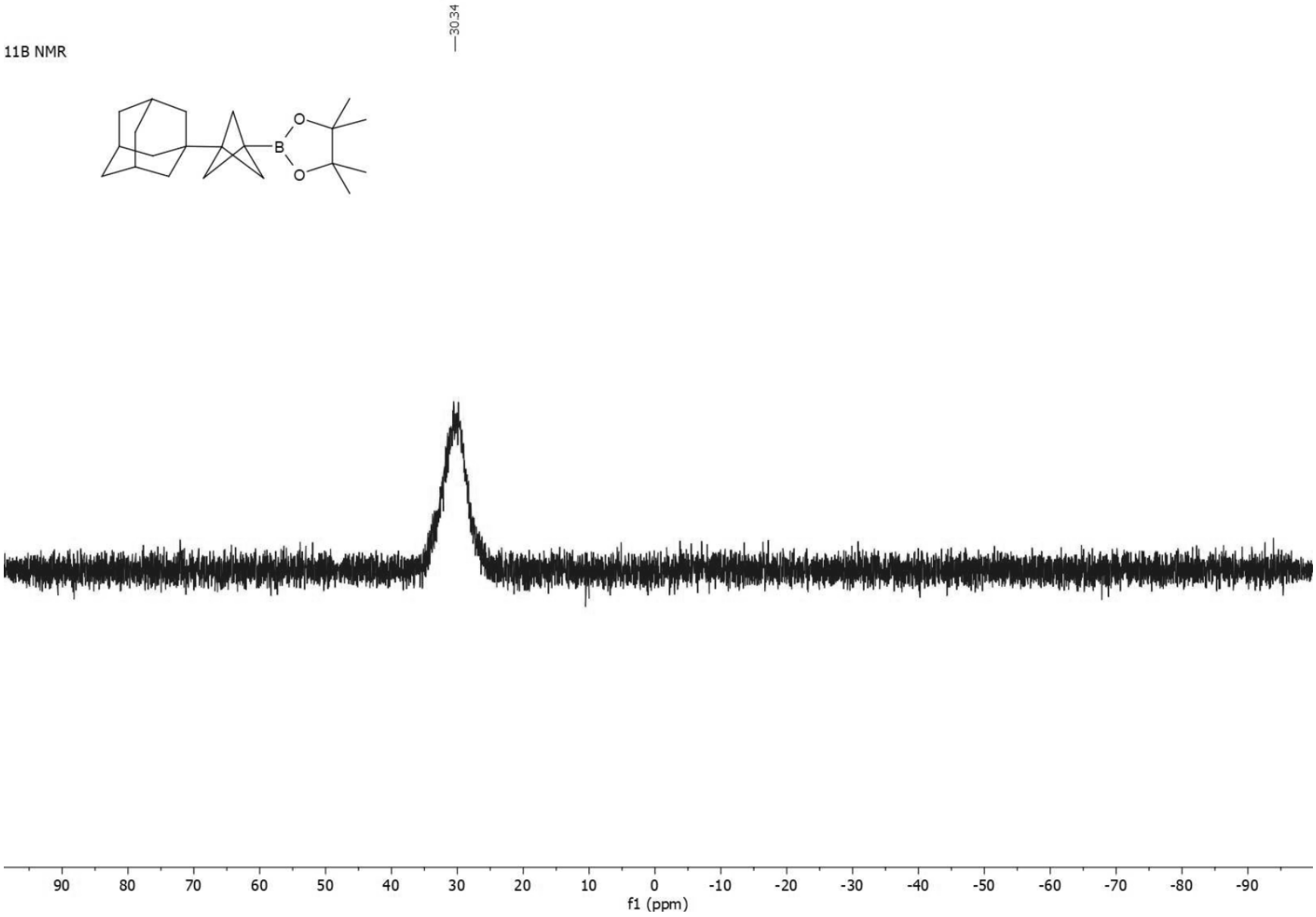
^{1}H NMR (600 MHz, $CDCl_3$) of **4q**



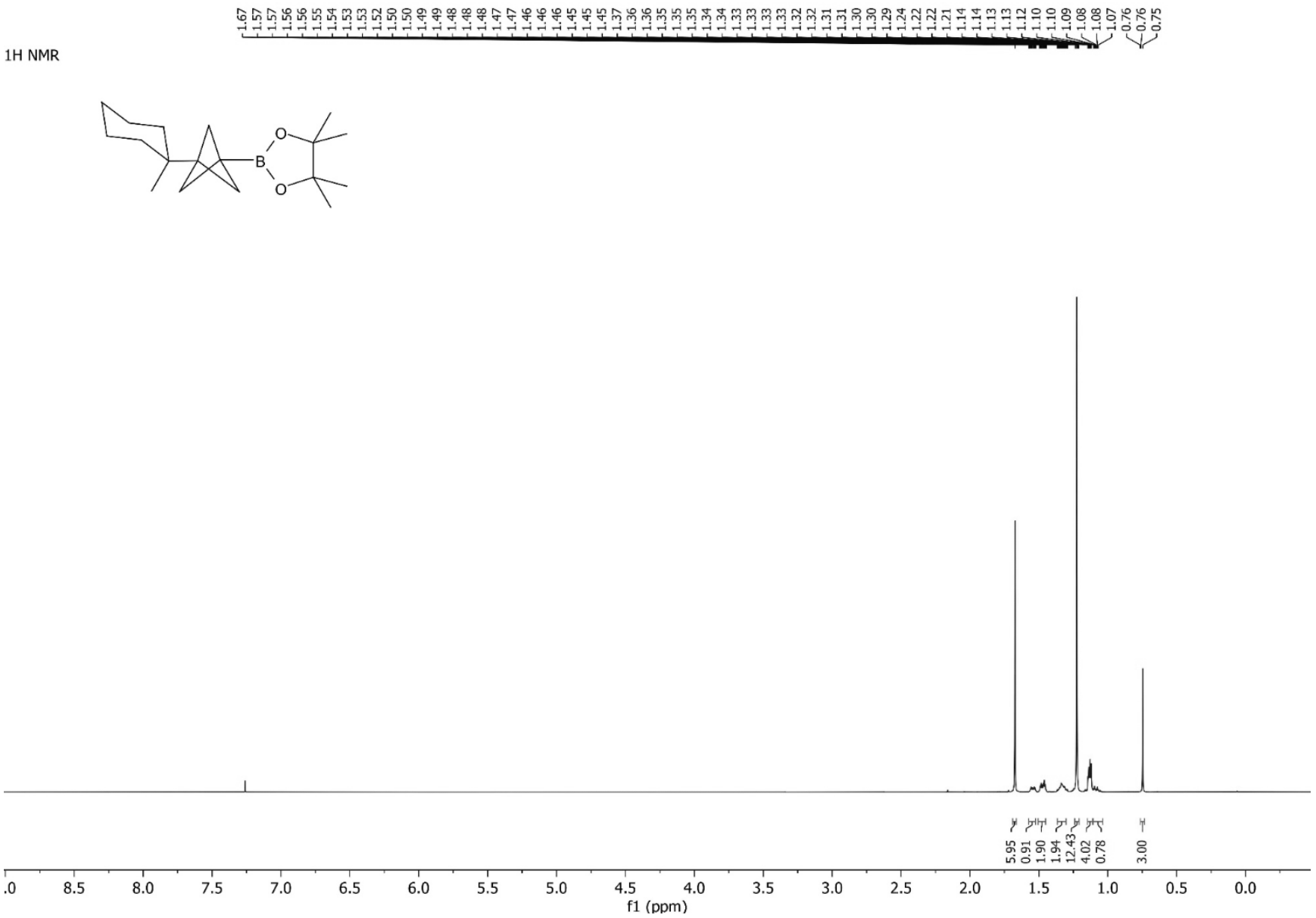
^{13}C NMR (151 MHz, $CDCl_3$) of **4q**



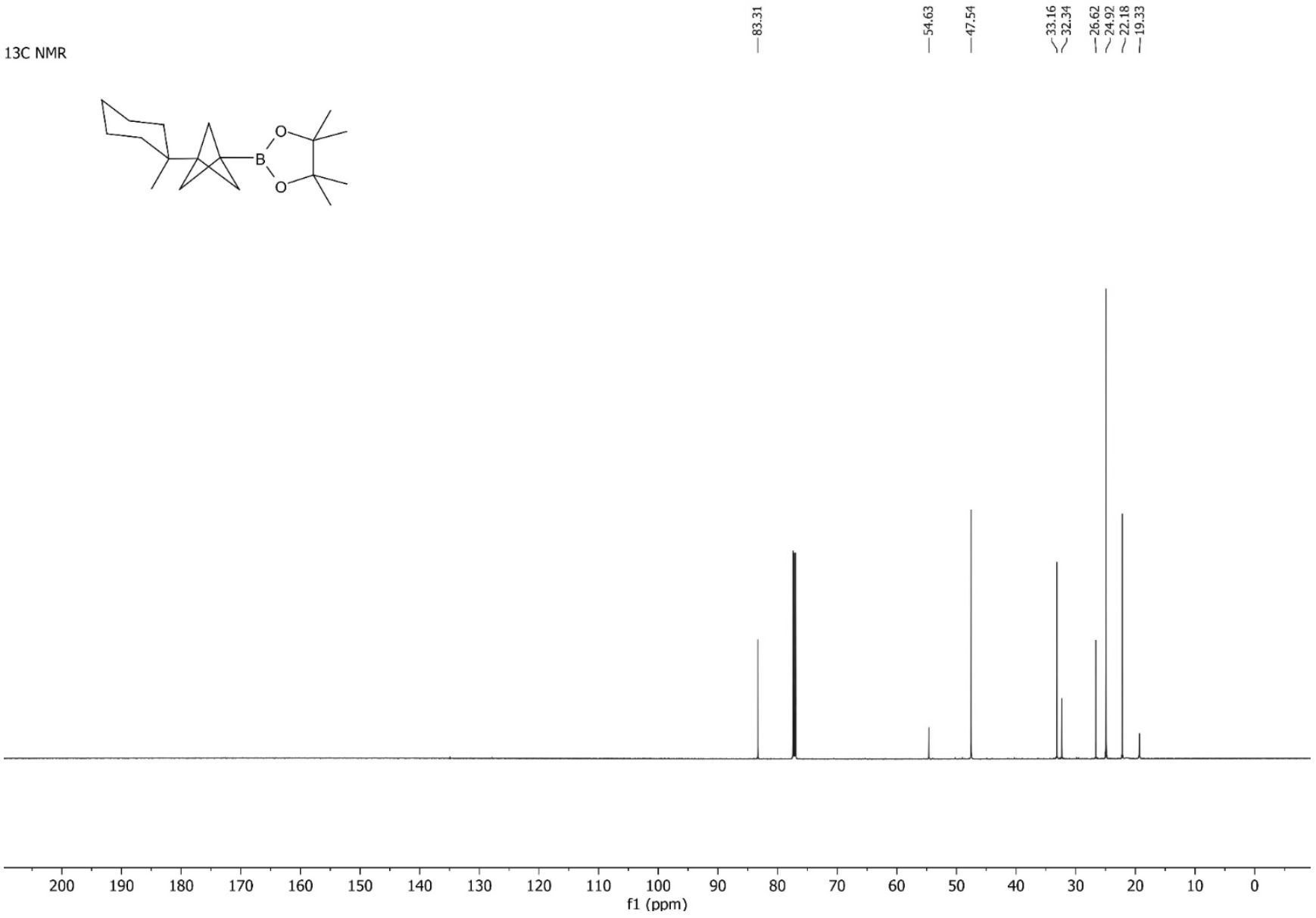
^{11}B NMR (128 MHz, $CDCl_3$) of **4q**



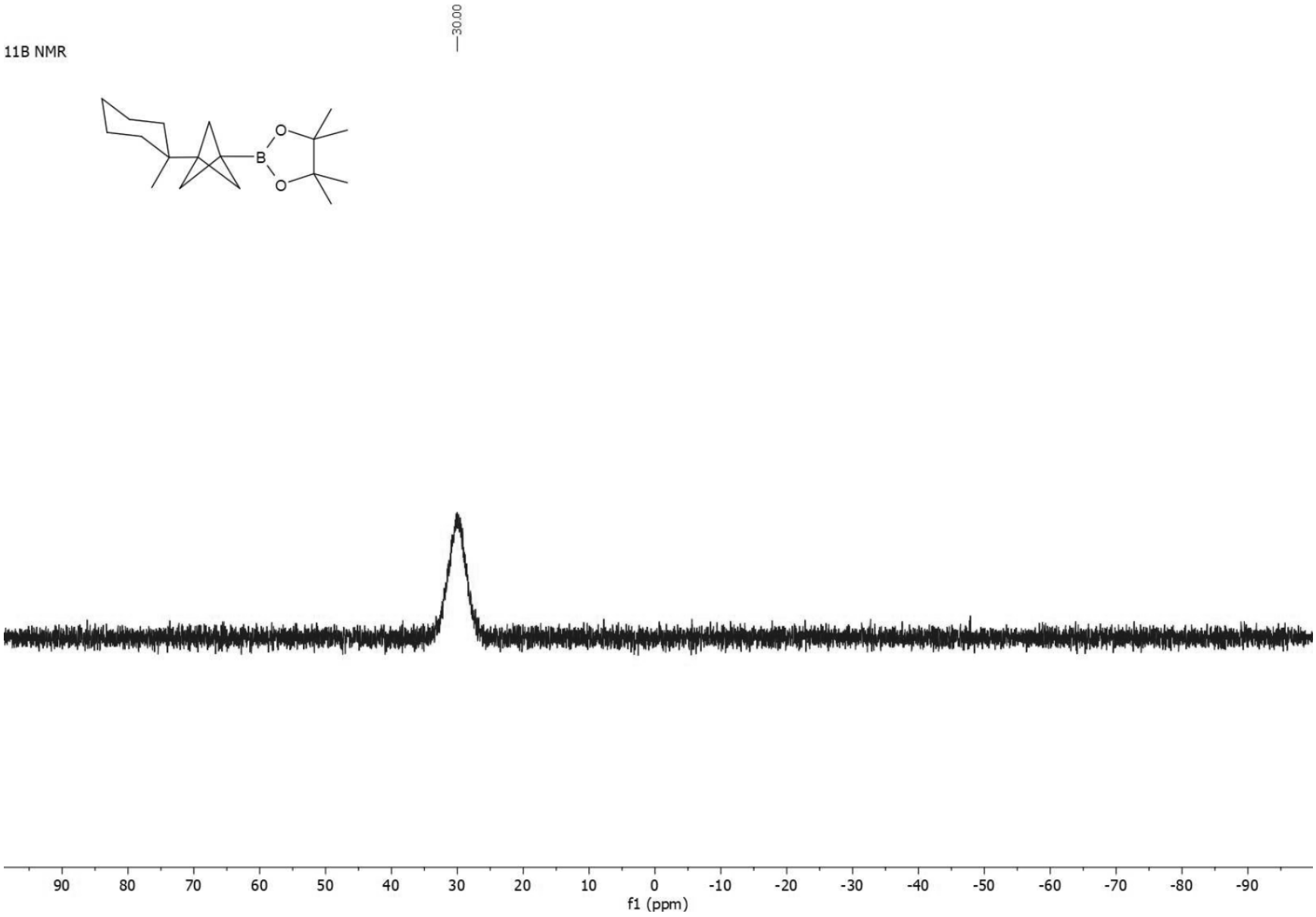
^{1}H NMR (600 MHz, $CDCl_3$) of **4r**



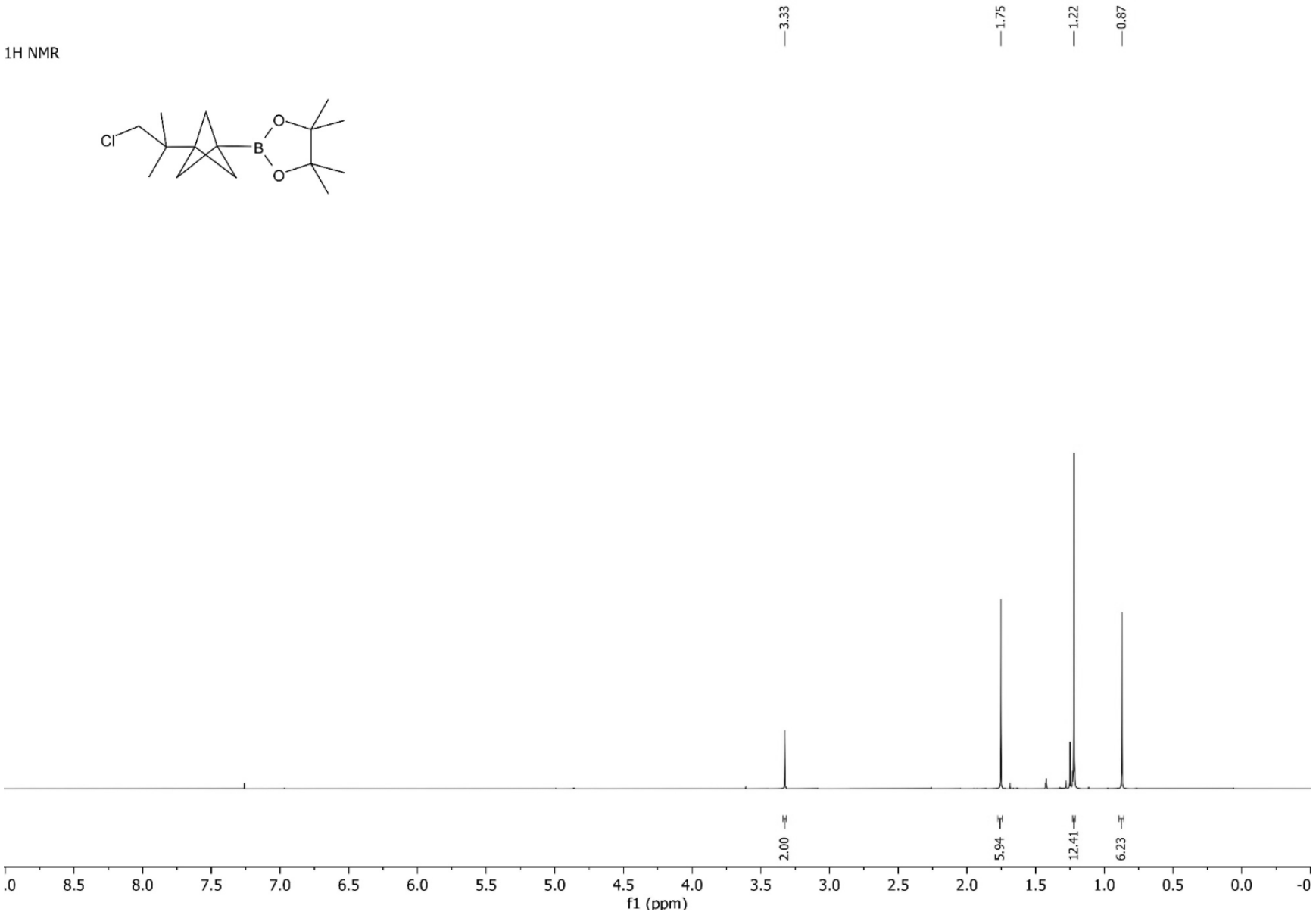
^{13}C NMR (151 MHz, $CDCl_3$) of **4r**



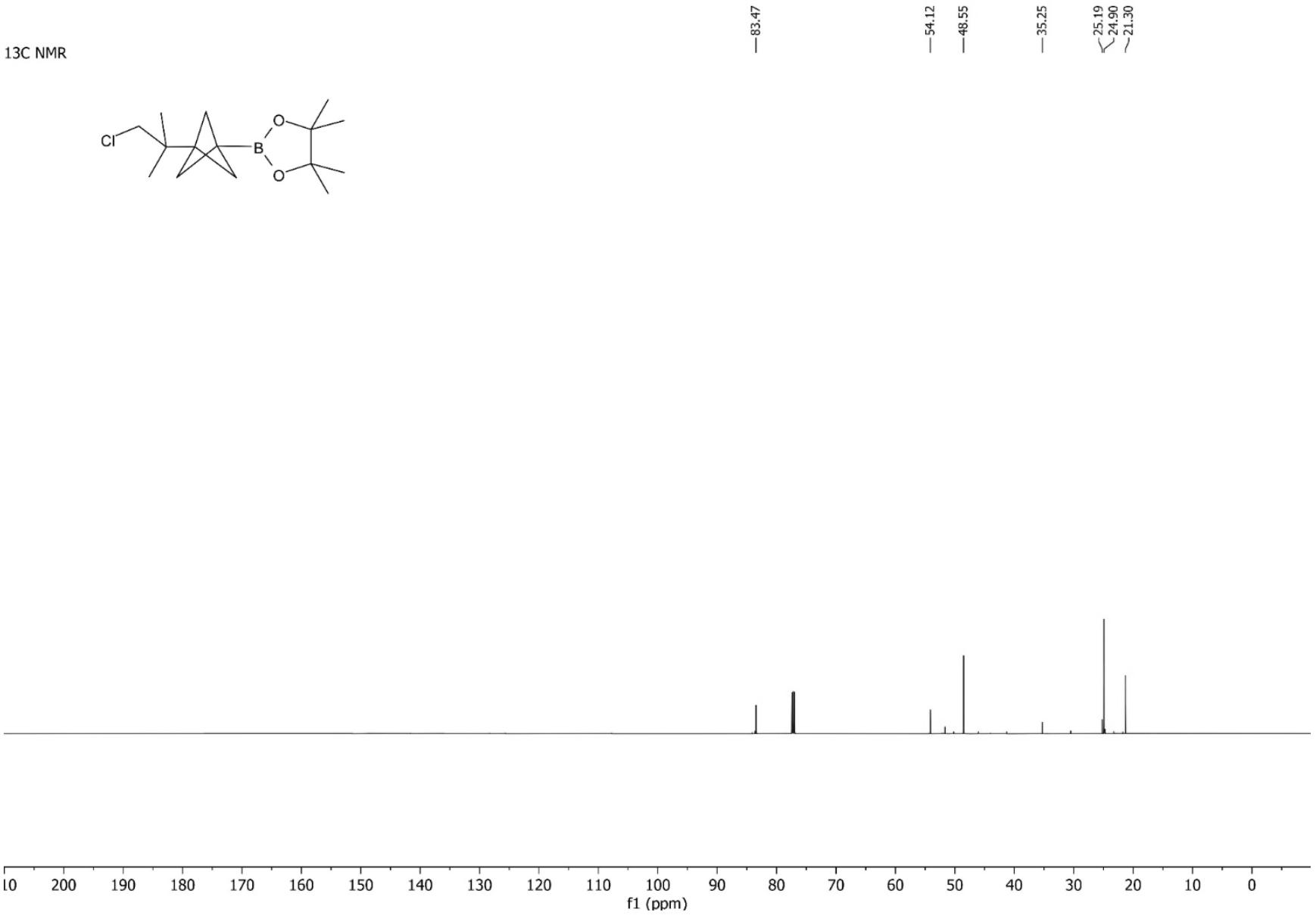
^{11}B NMR (151 MHz, $CDCl_3$) of **4r**



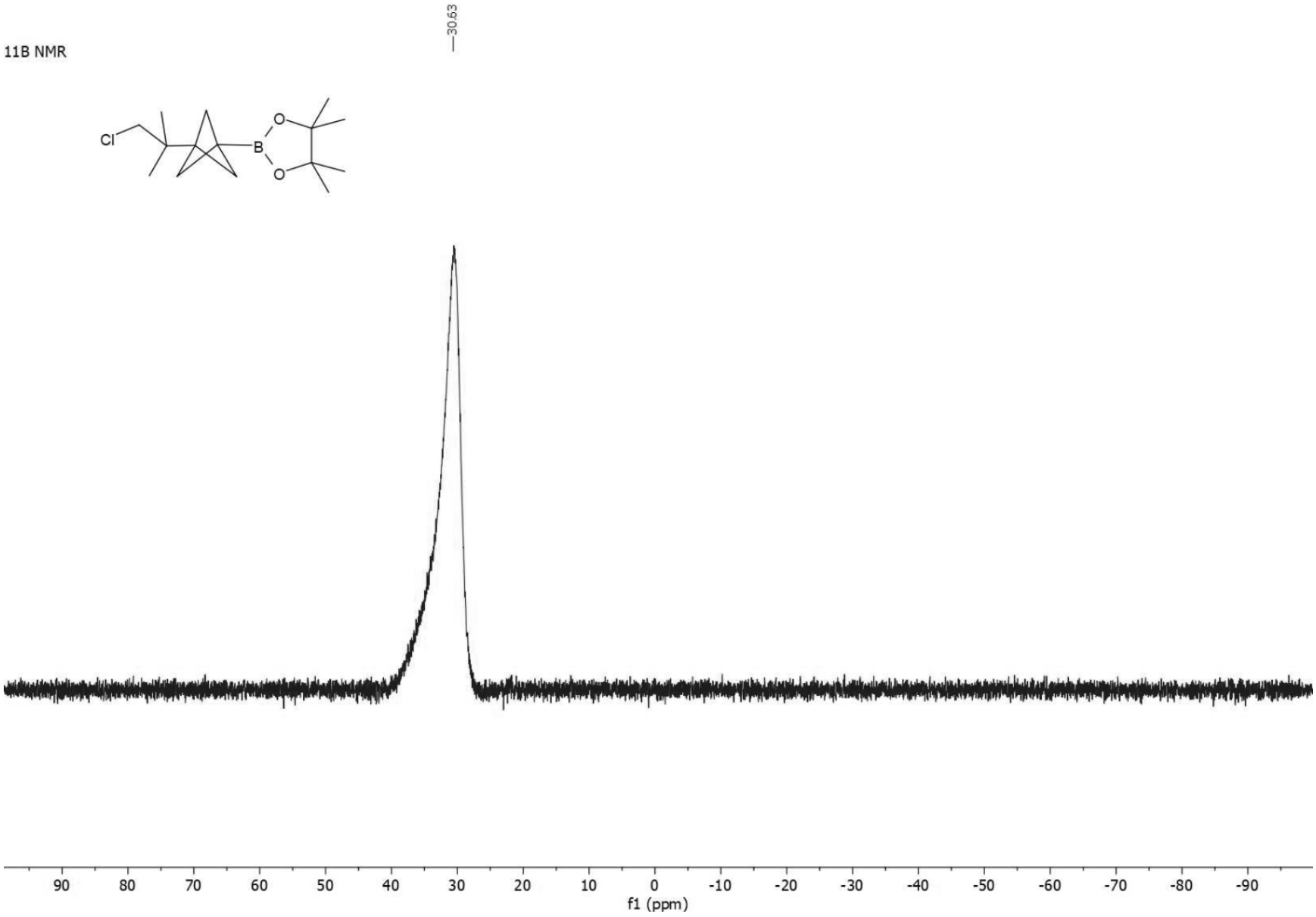
^{1}H NMR (600 MHz, $CDCl_3$) of **4s**



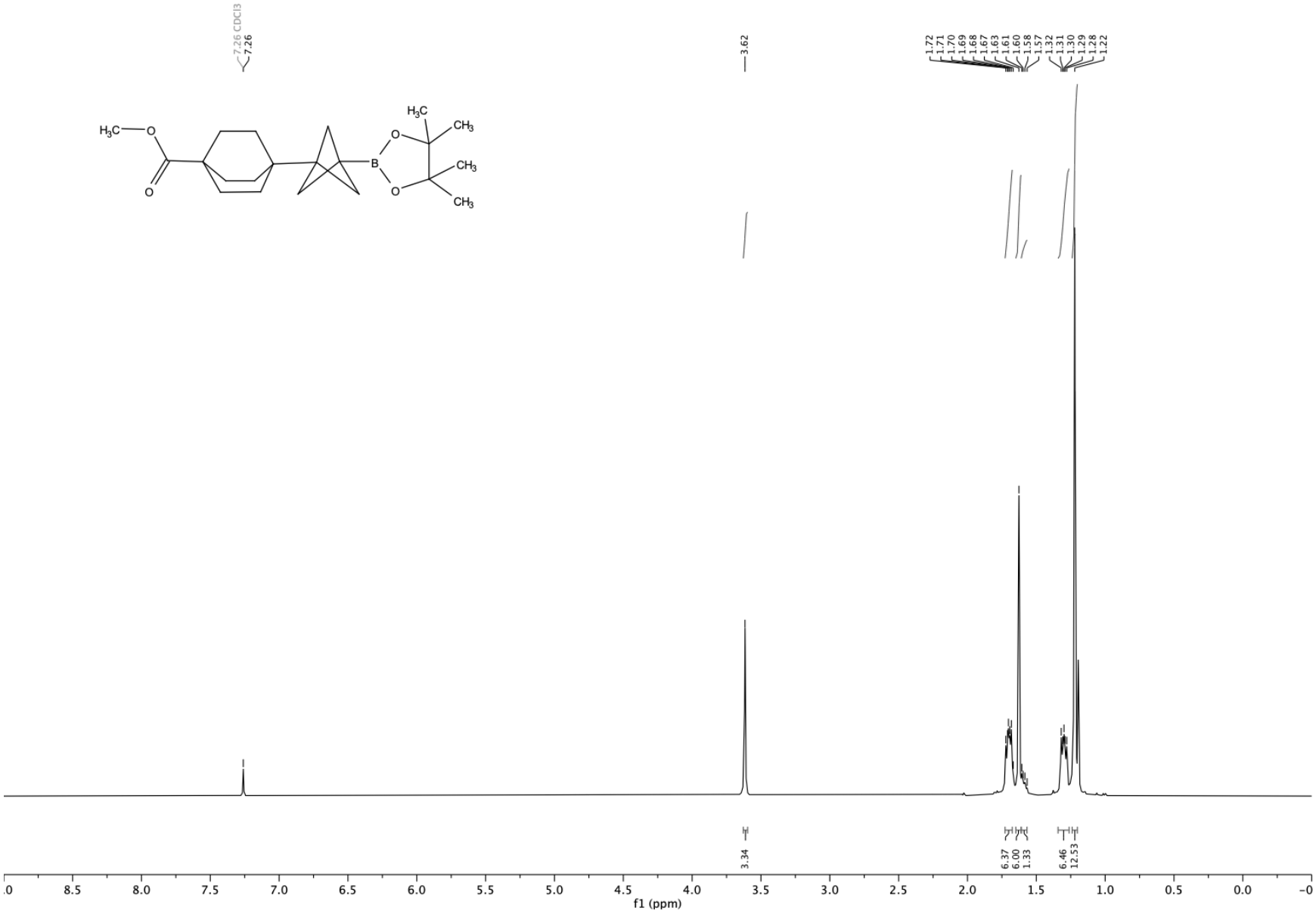
^{13}C NMR (151 MHz, $CDCl_3$) of **4s**



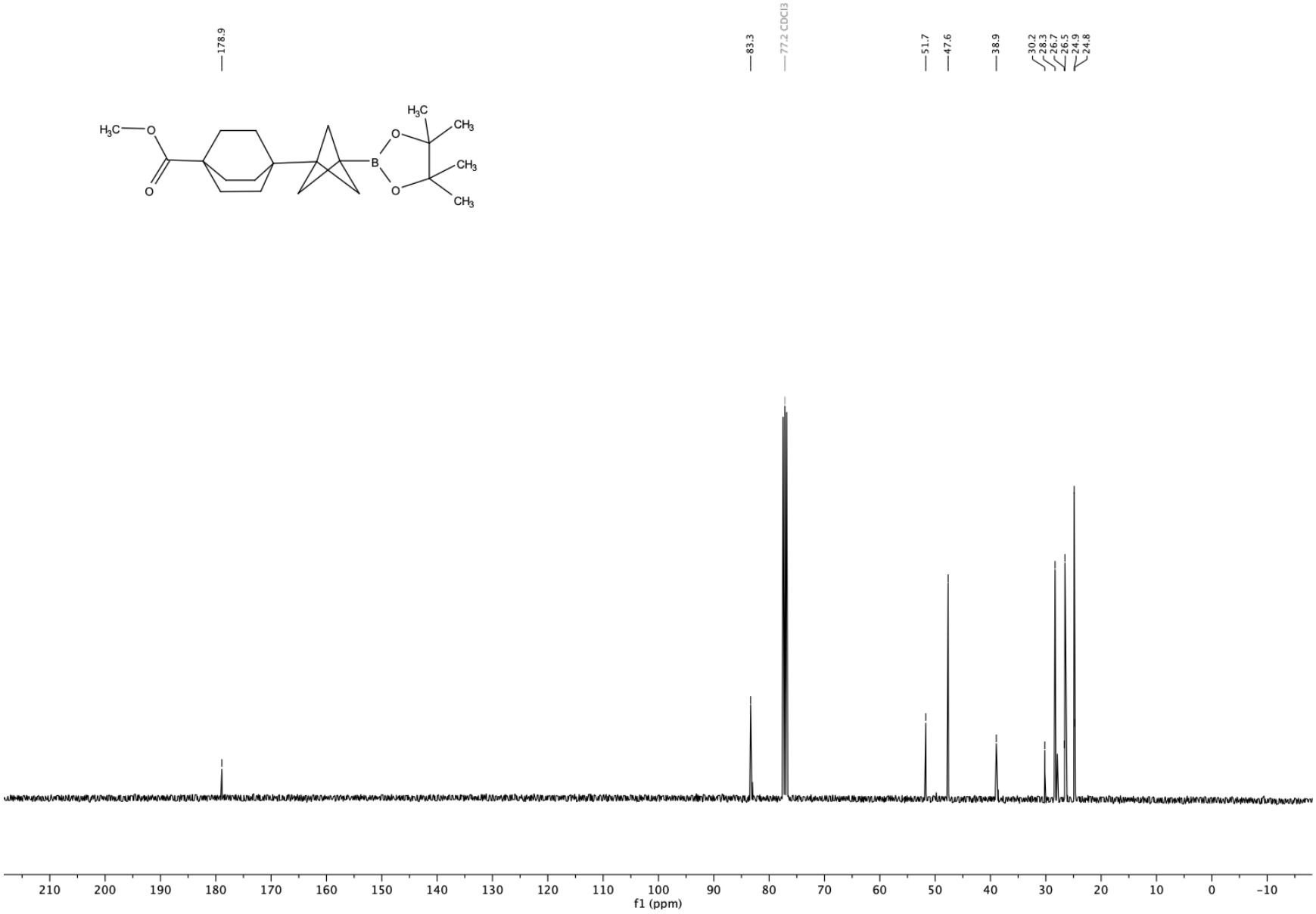
^{11}B NMR (128 MHz, $CDCl_3$) of **4s**



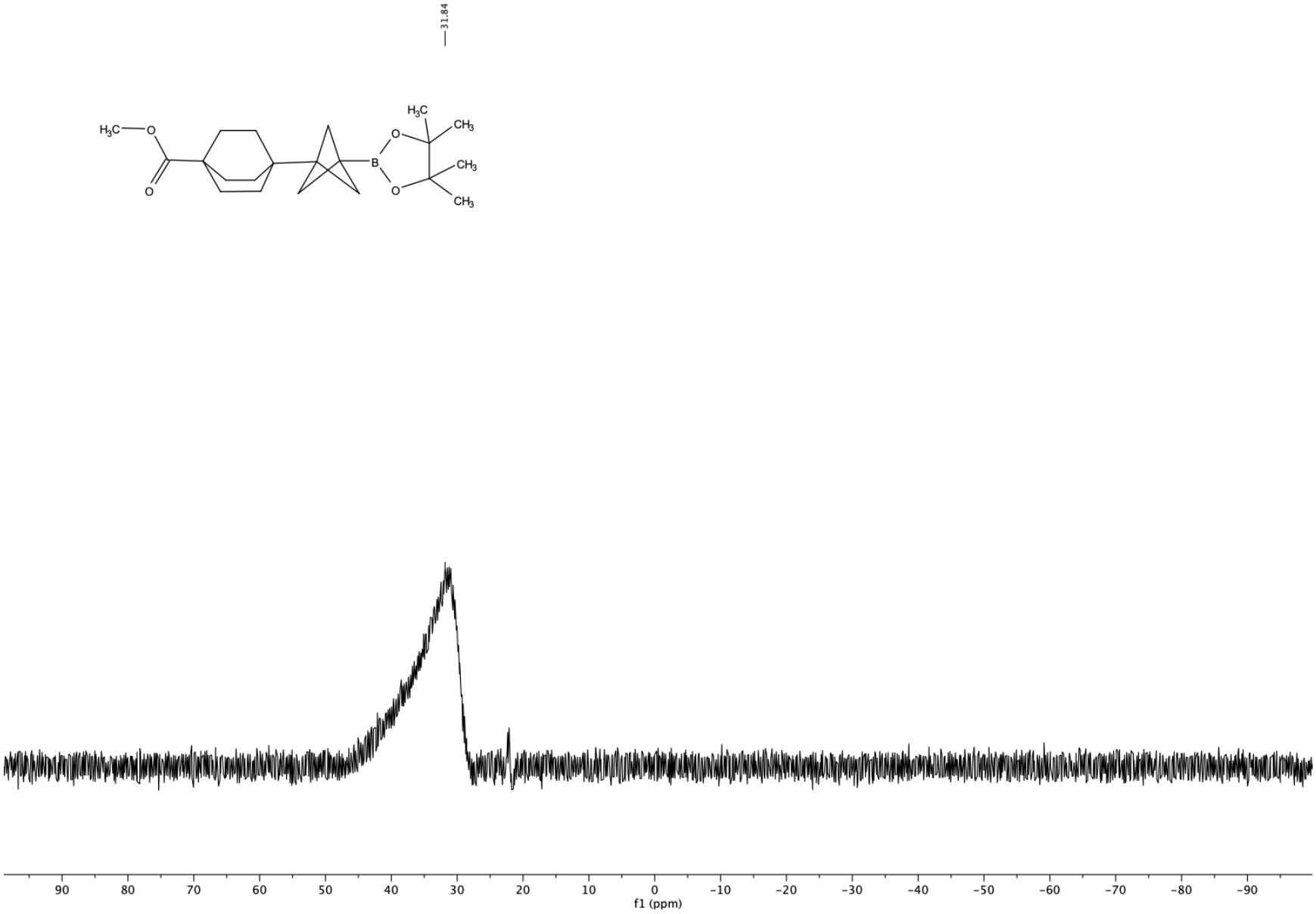
^{1}H NMR (400 MHz, $CDCl_3$) of **4t**



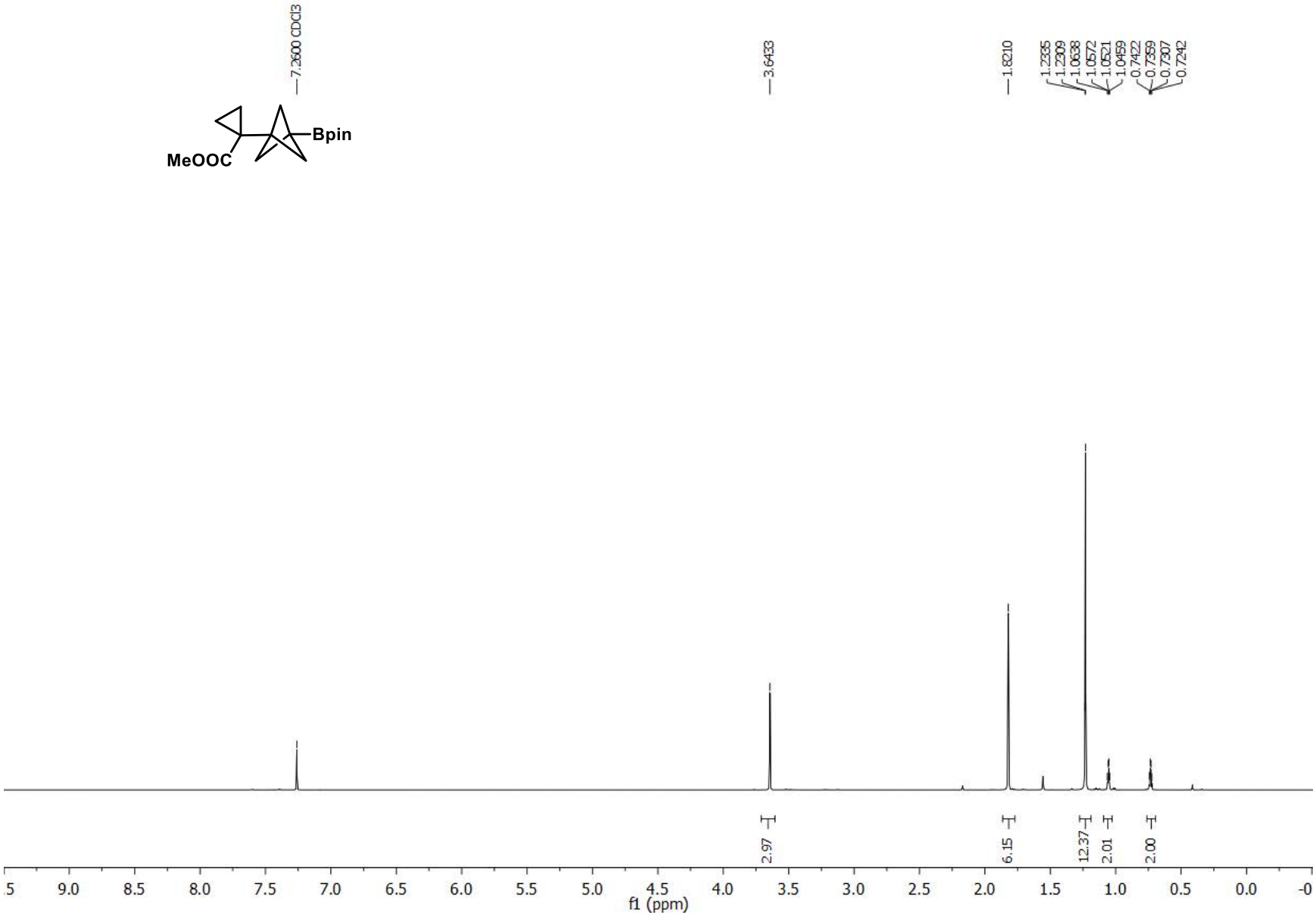
^{13}C NMR (101 MHz, $CDCl_3$) of **4t**



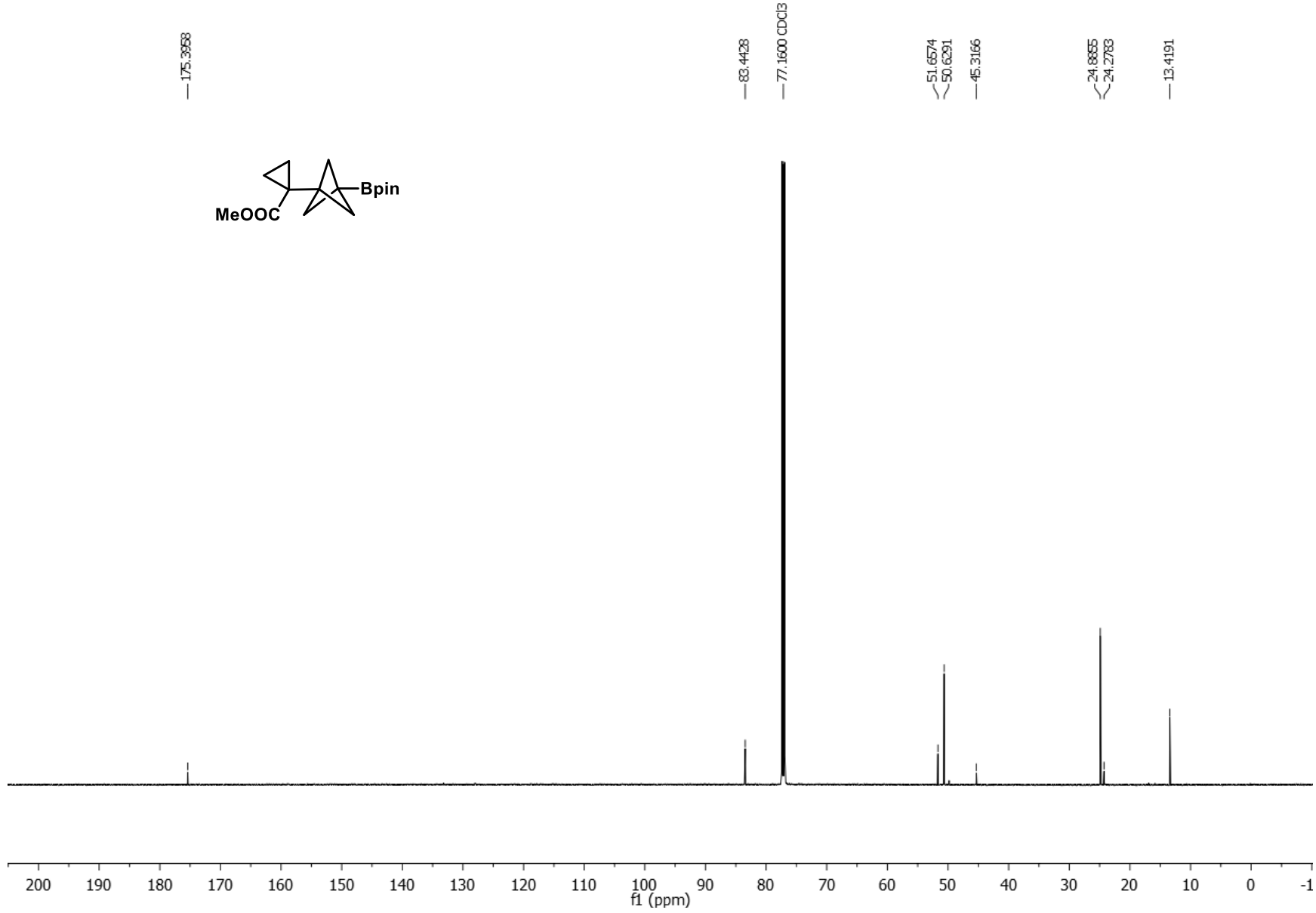
^{11}B NMR (128 MHz, $CDCl_3$) of **4t**



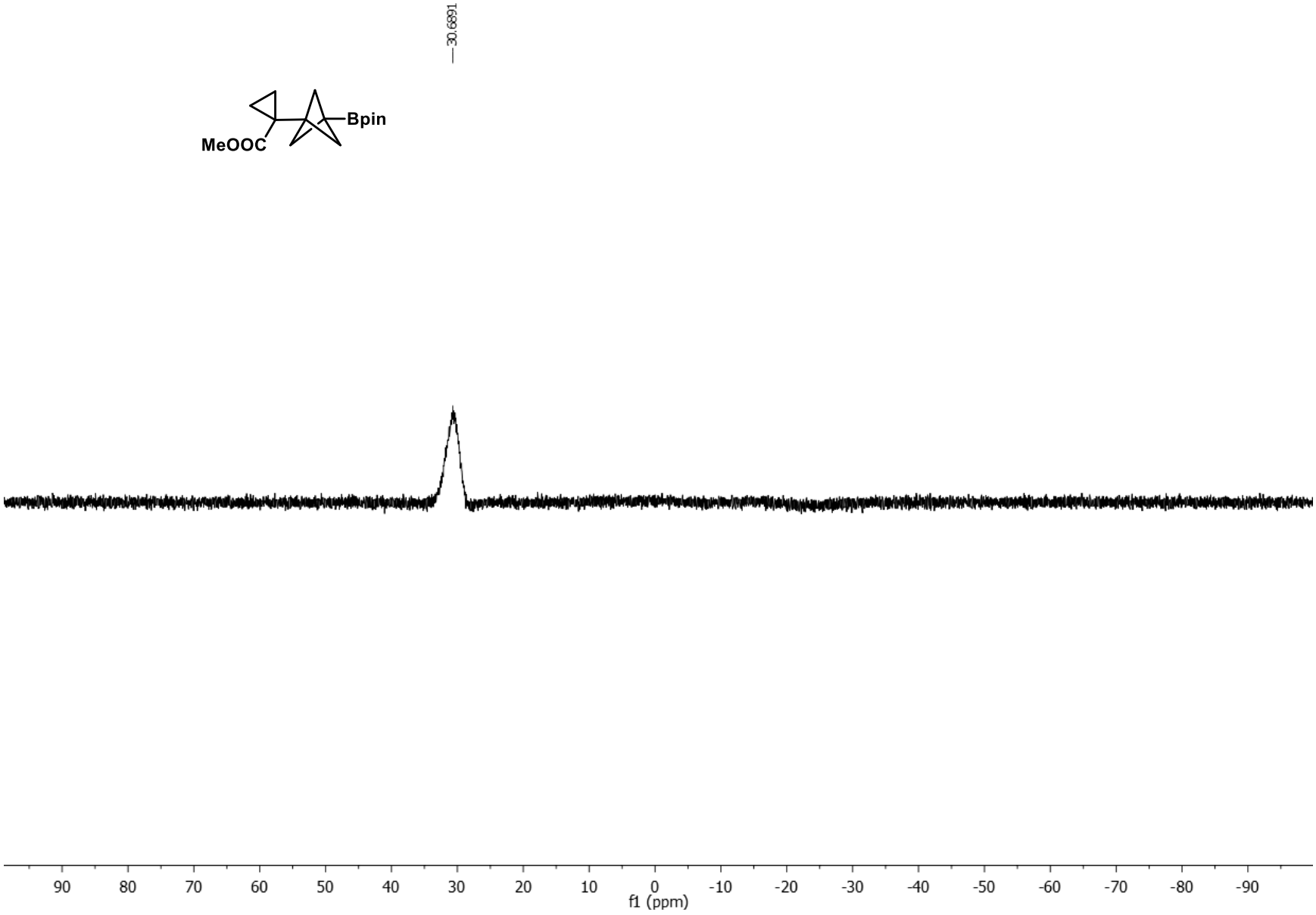
^{1}H NMR (600 MHz, $CDCl_3$) of **4u**



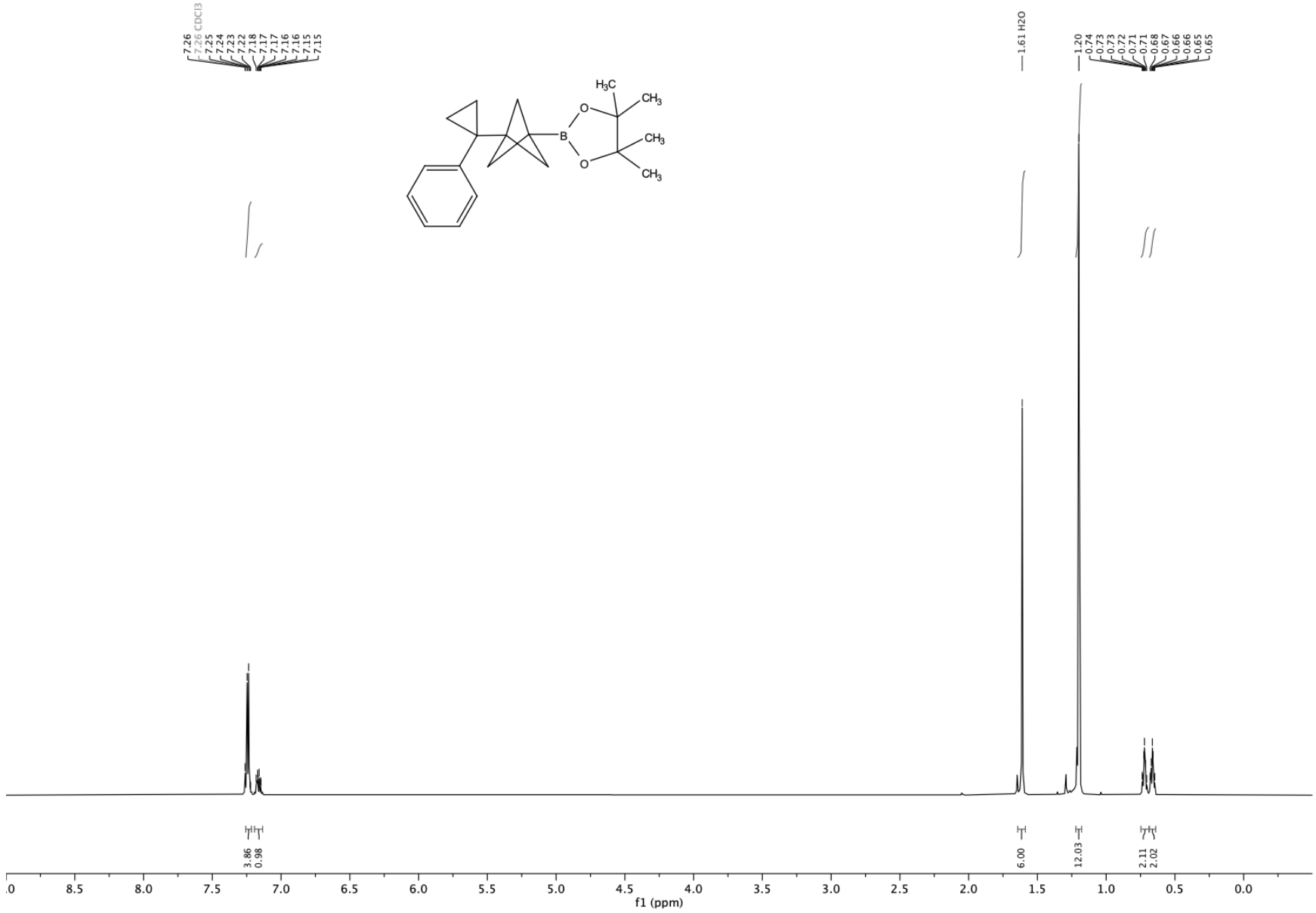
^{13}C NMR (151 MHz, $CDCl_3$) of **4u**



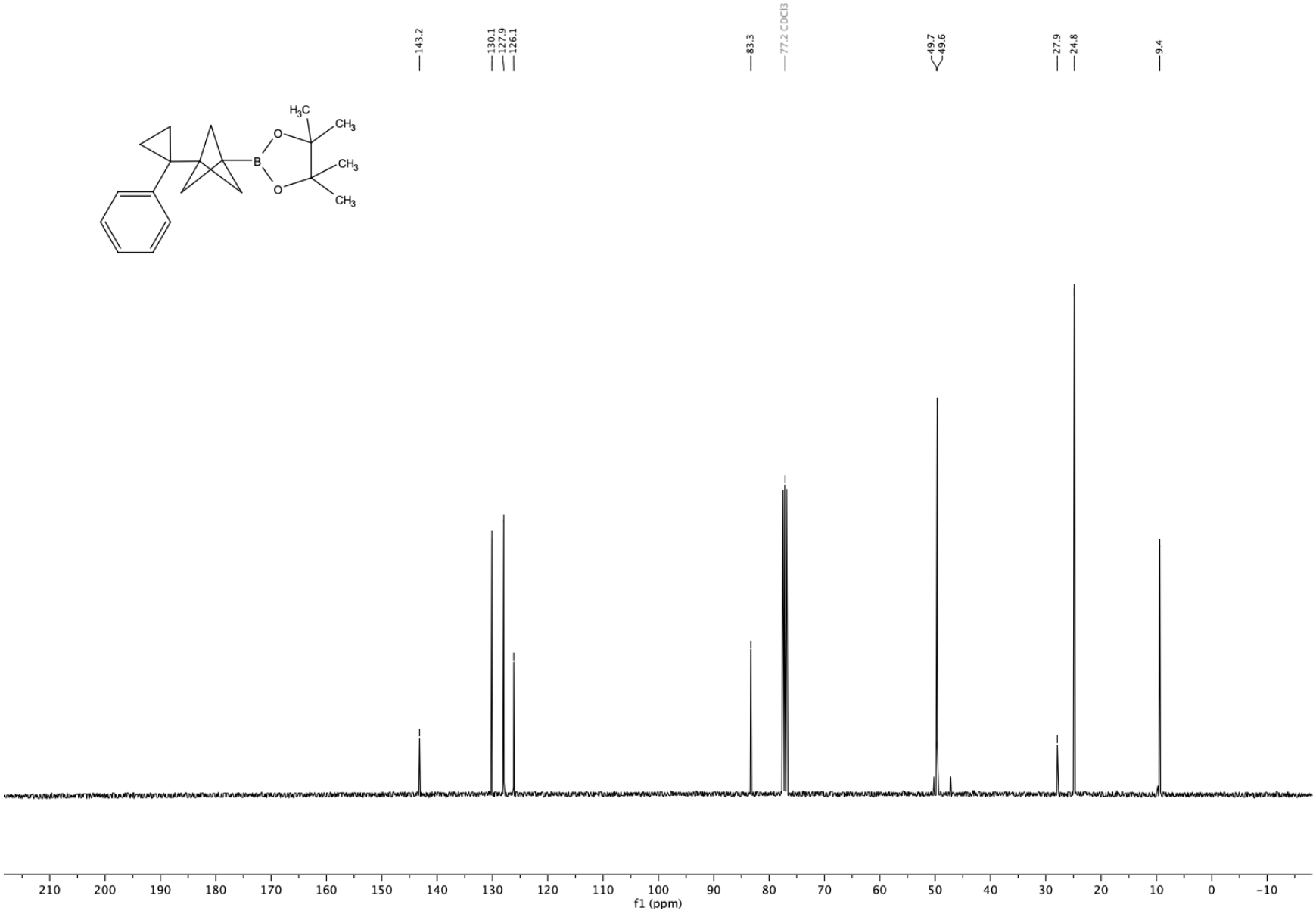
^{11}B NMR (128 MHz, $CDCl_3$) of **4u**



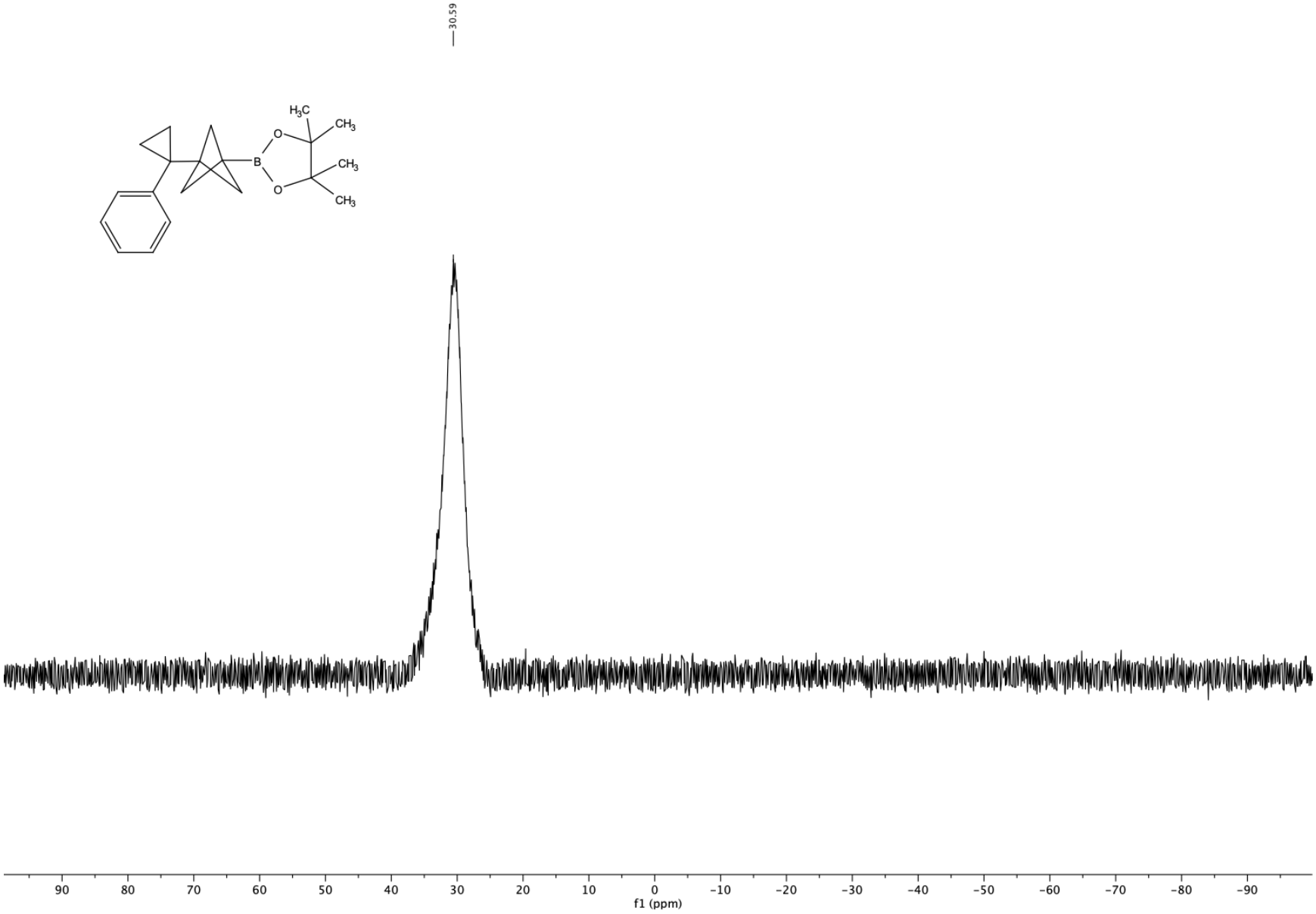
^{1}H NMR (400 MHz, $CDCl_3$) of **4v**



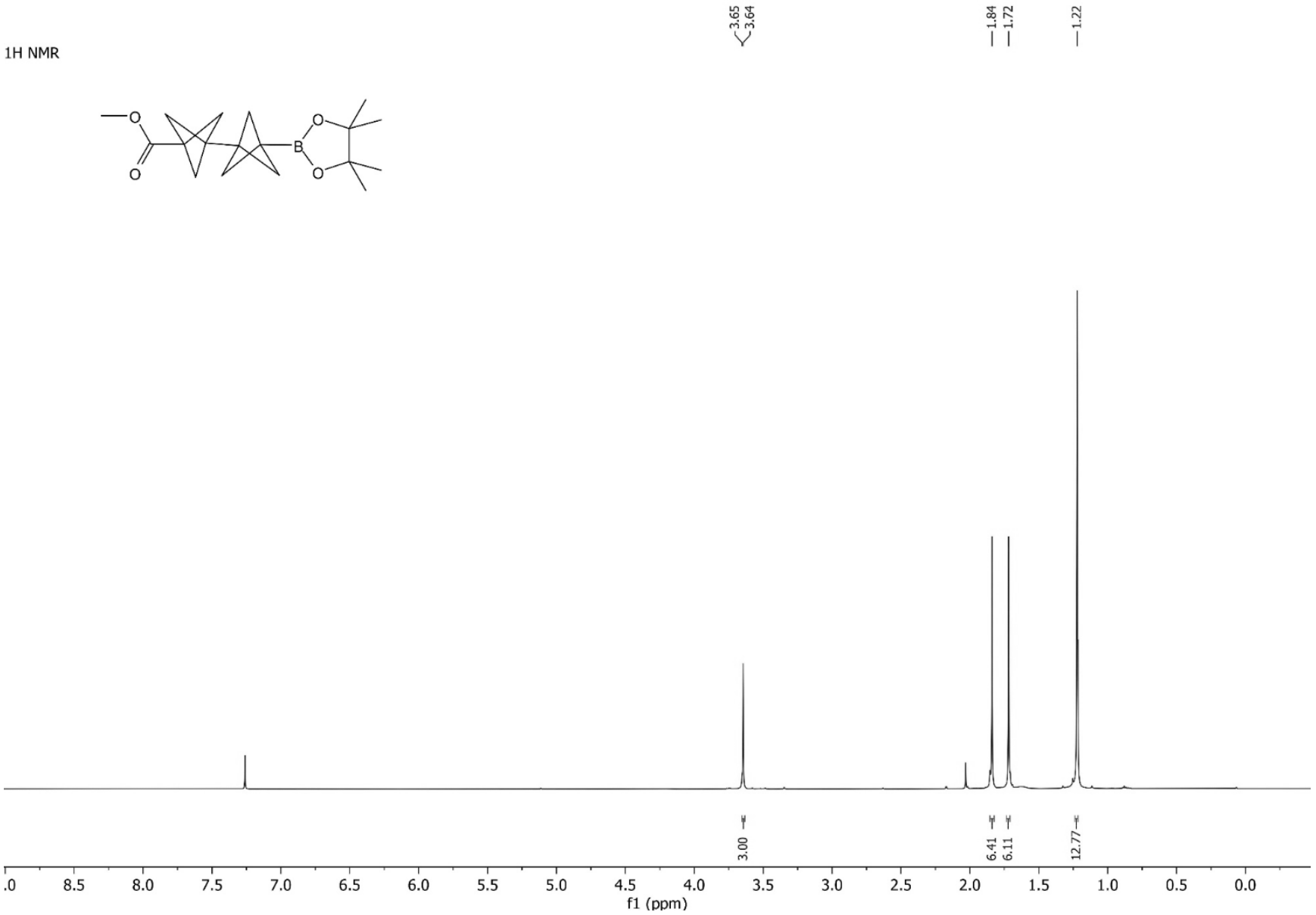
^{13}C NMR (101 MHz, $CDCl_3$) of **4v**



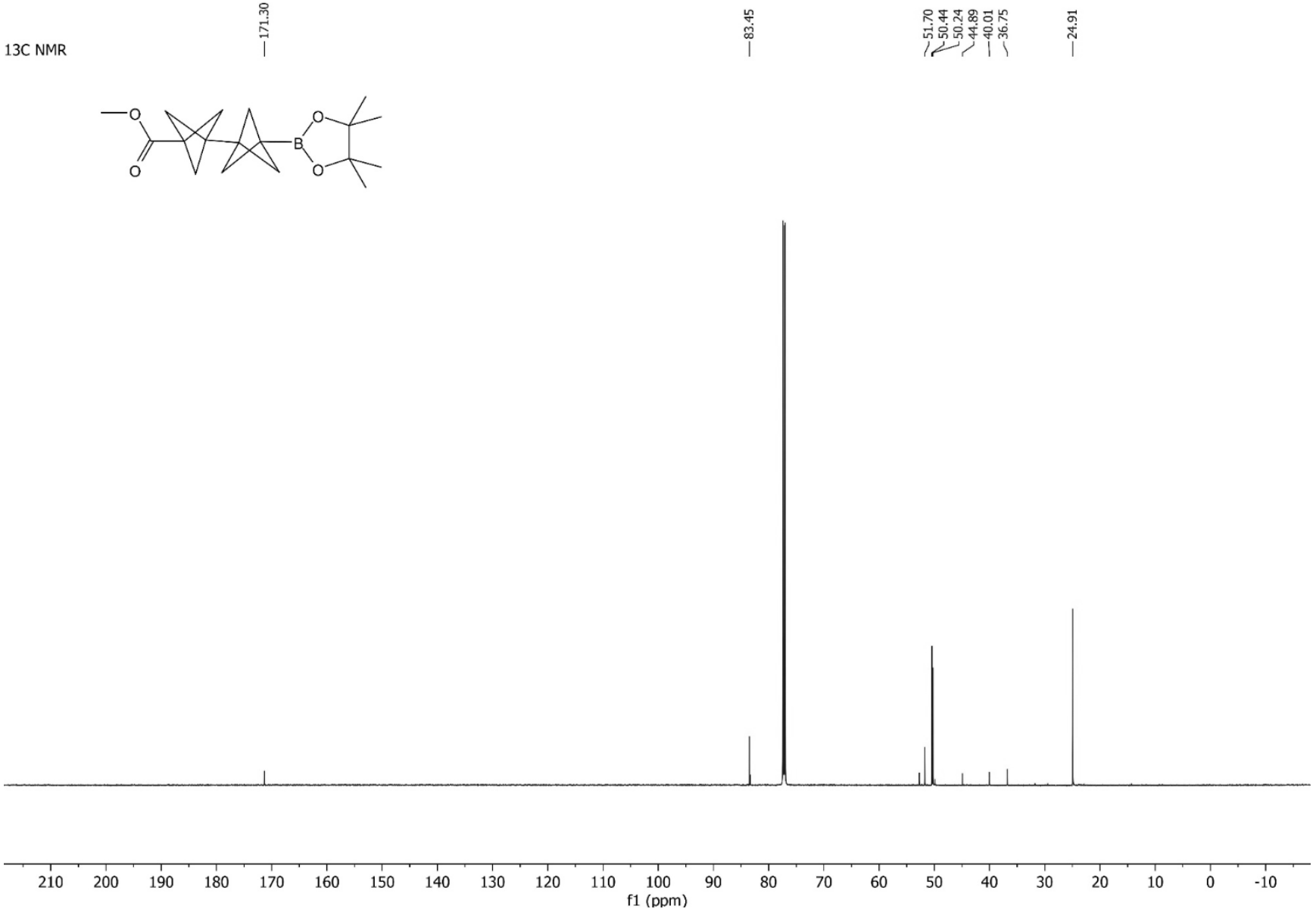
^{11}B NMR (128 MHz, $CDCl_3$) of **4v**



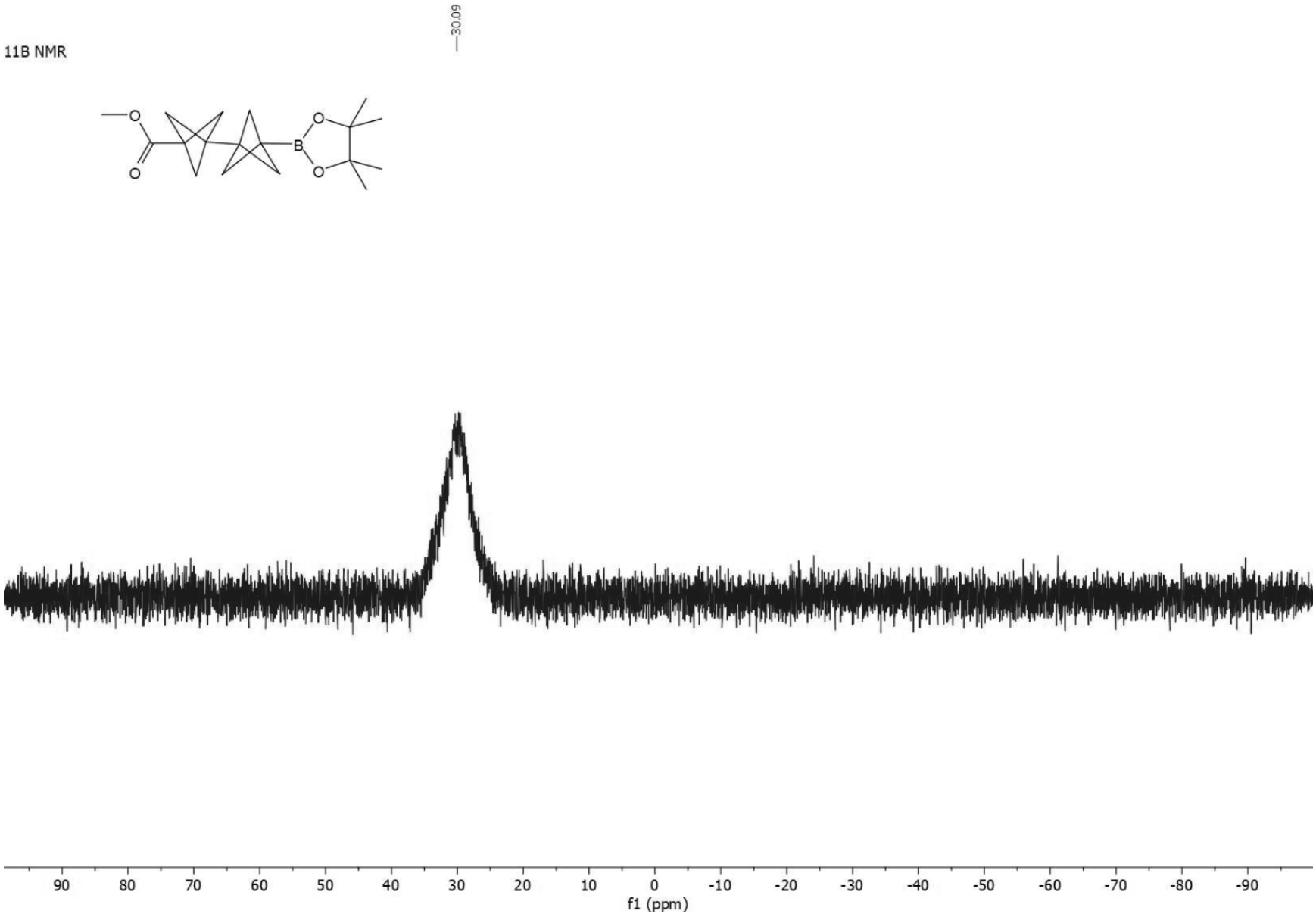
^{1}H NMR (600 MHz, $CDCl_3$) of **4w**



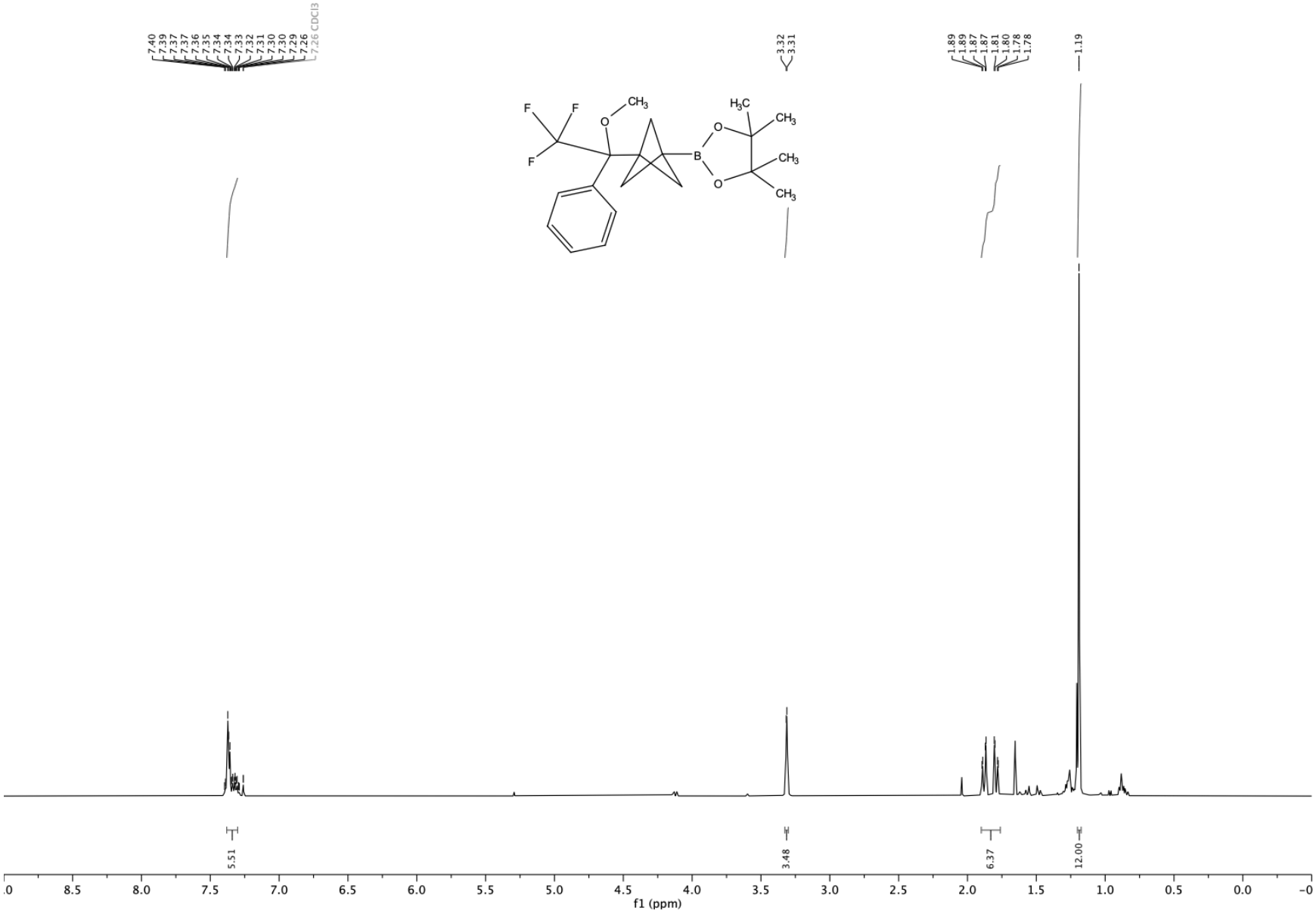
^{13}C NMR (151 MHz, $CDCl_3$) of **4w**



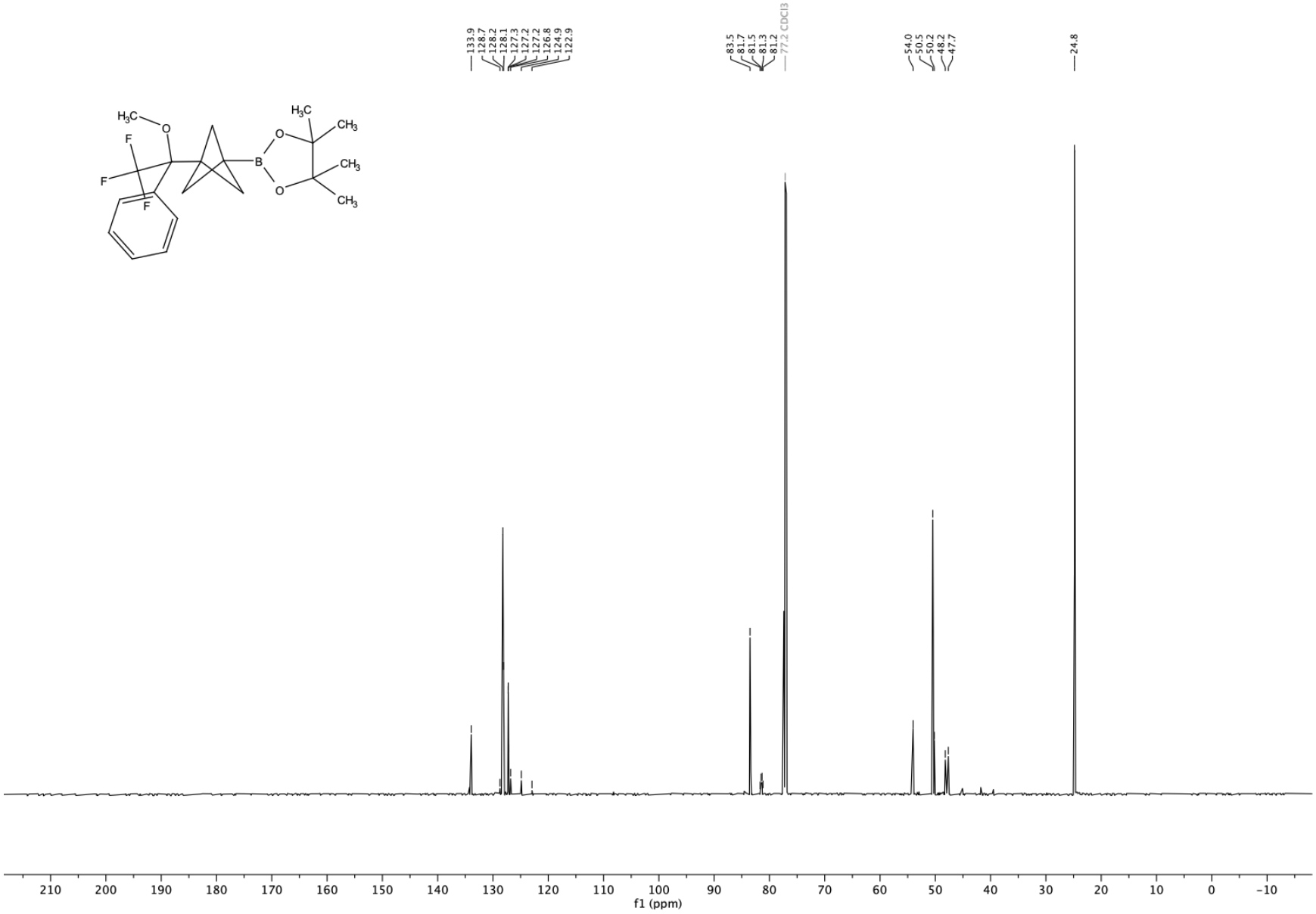
^{11}B NMR (128 MHz, $CDCl_3$) of **4w**



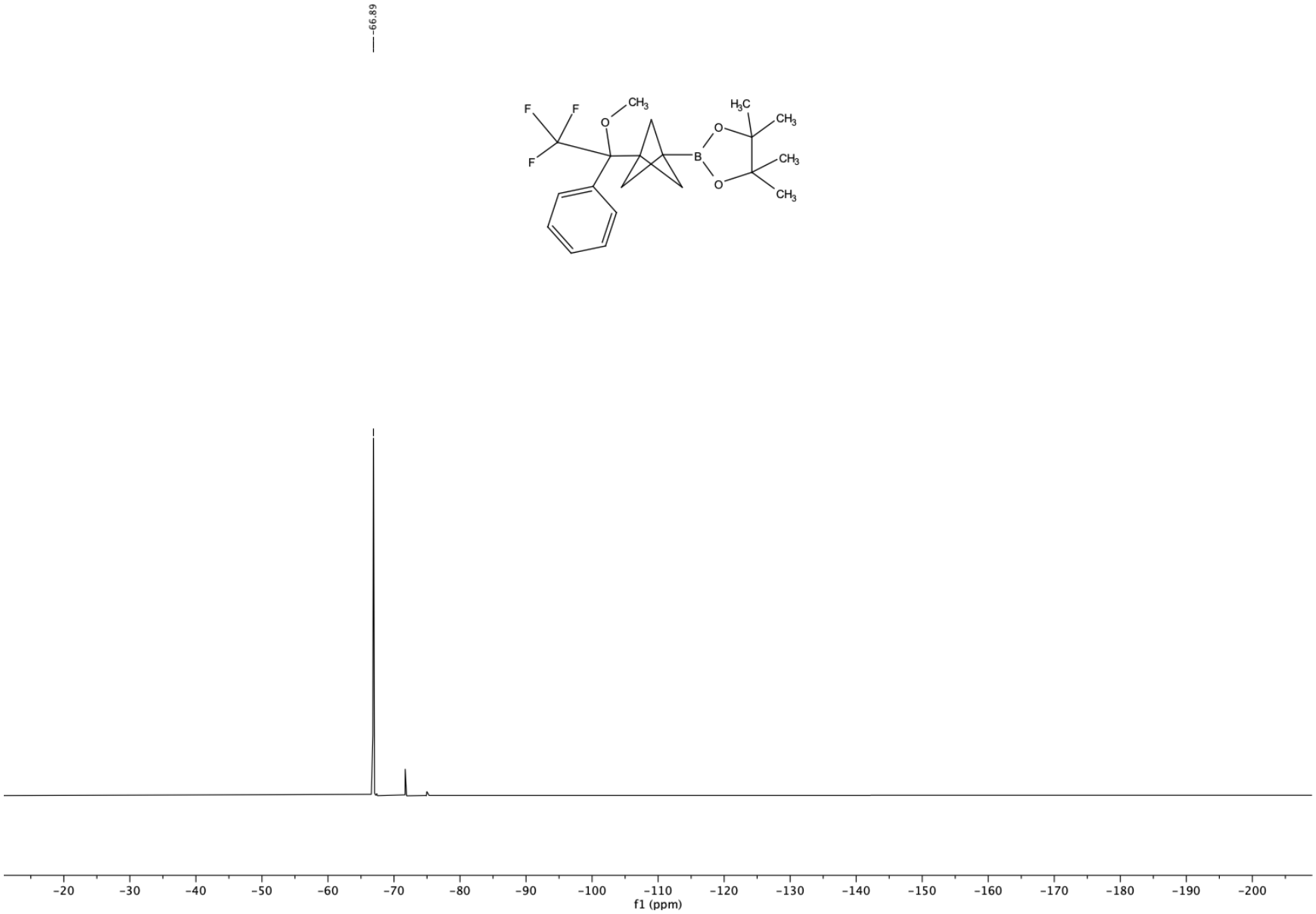
^{1}H NMR (400 MHz, $CDCl_3$) of **4x**



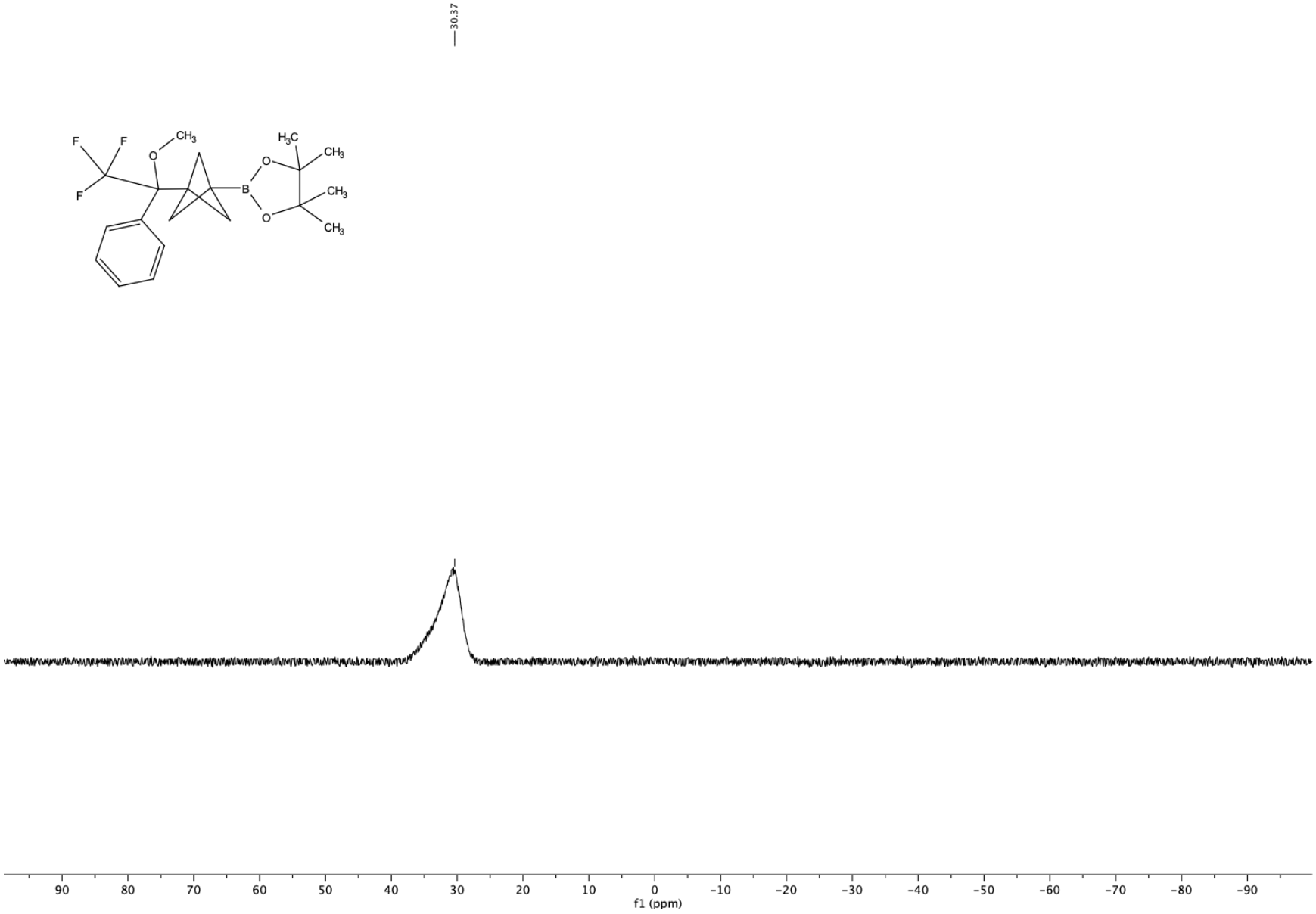
^{13}C NMR (101 MHz, $CDCl_3$) of **4x**



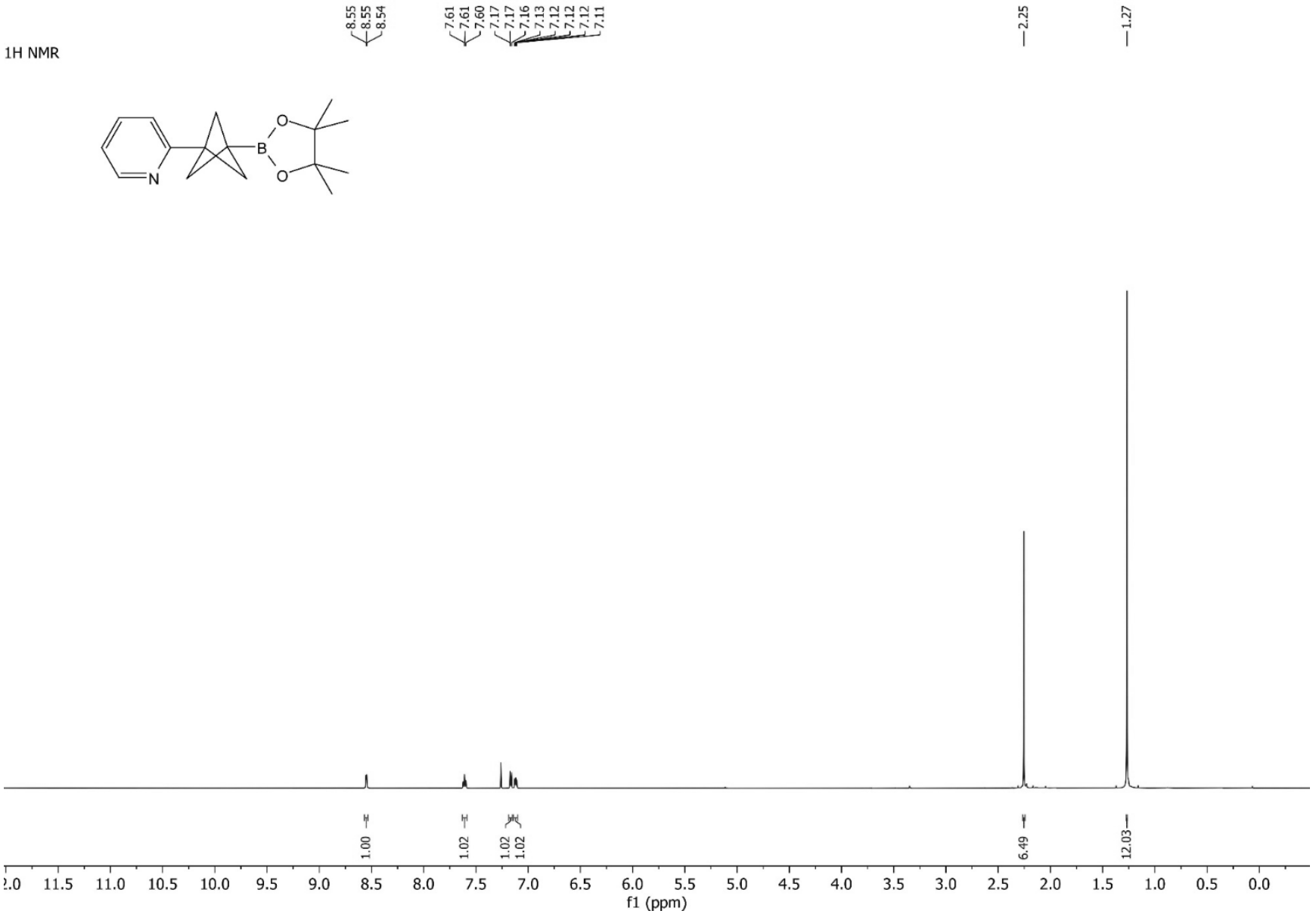
^{19}F NMR (376 MHz, $CDCl_3$) of **4x**



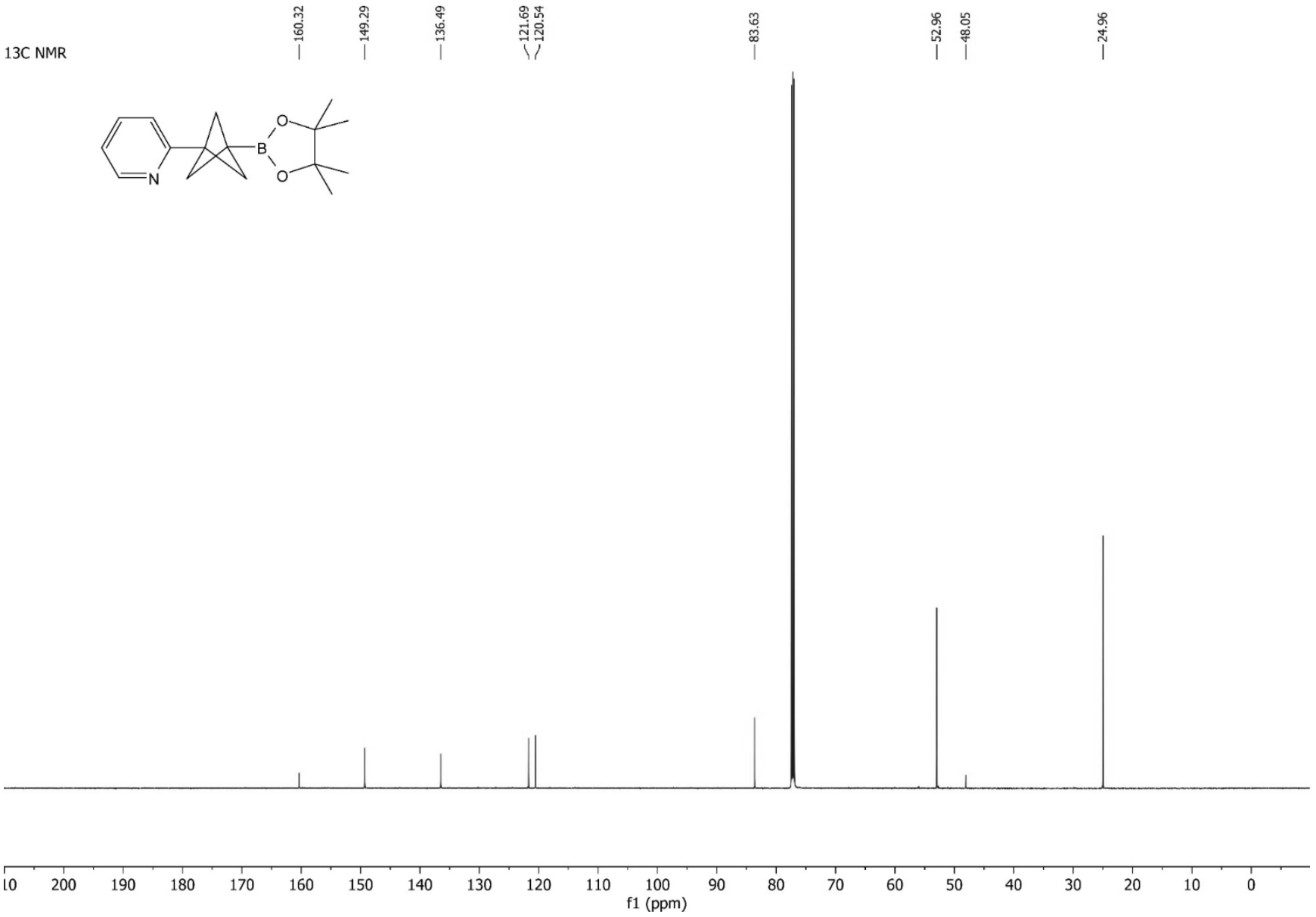
^{11}B NMR (128 MHz, $CDCl_3$) of **4x**



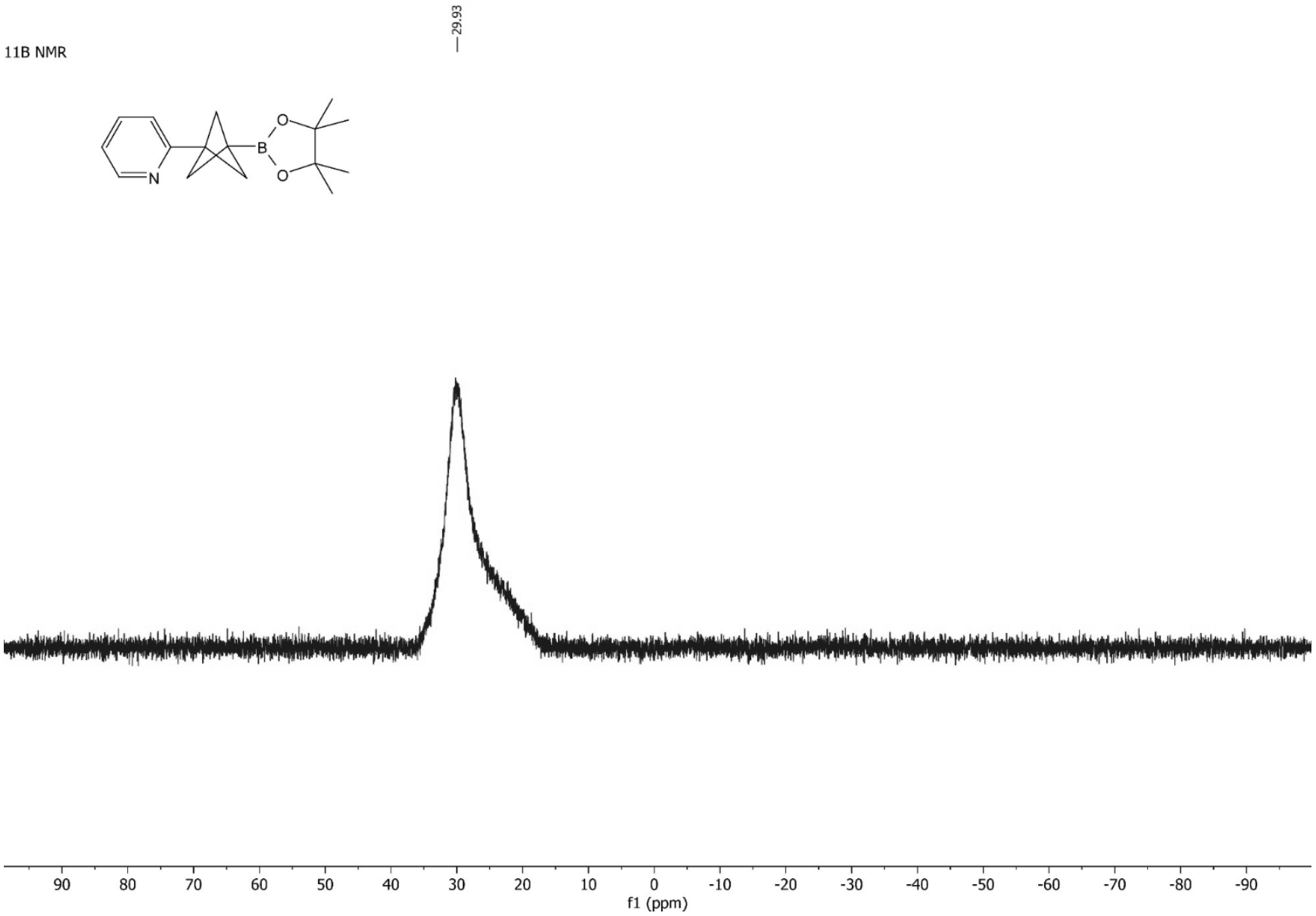
^{1}H NMR (600 MHz, $CDCl_3$) of **4y**



^{13}C NMR (151 MHz, $CDCl_3$) of **4y**

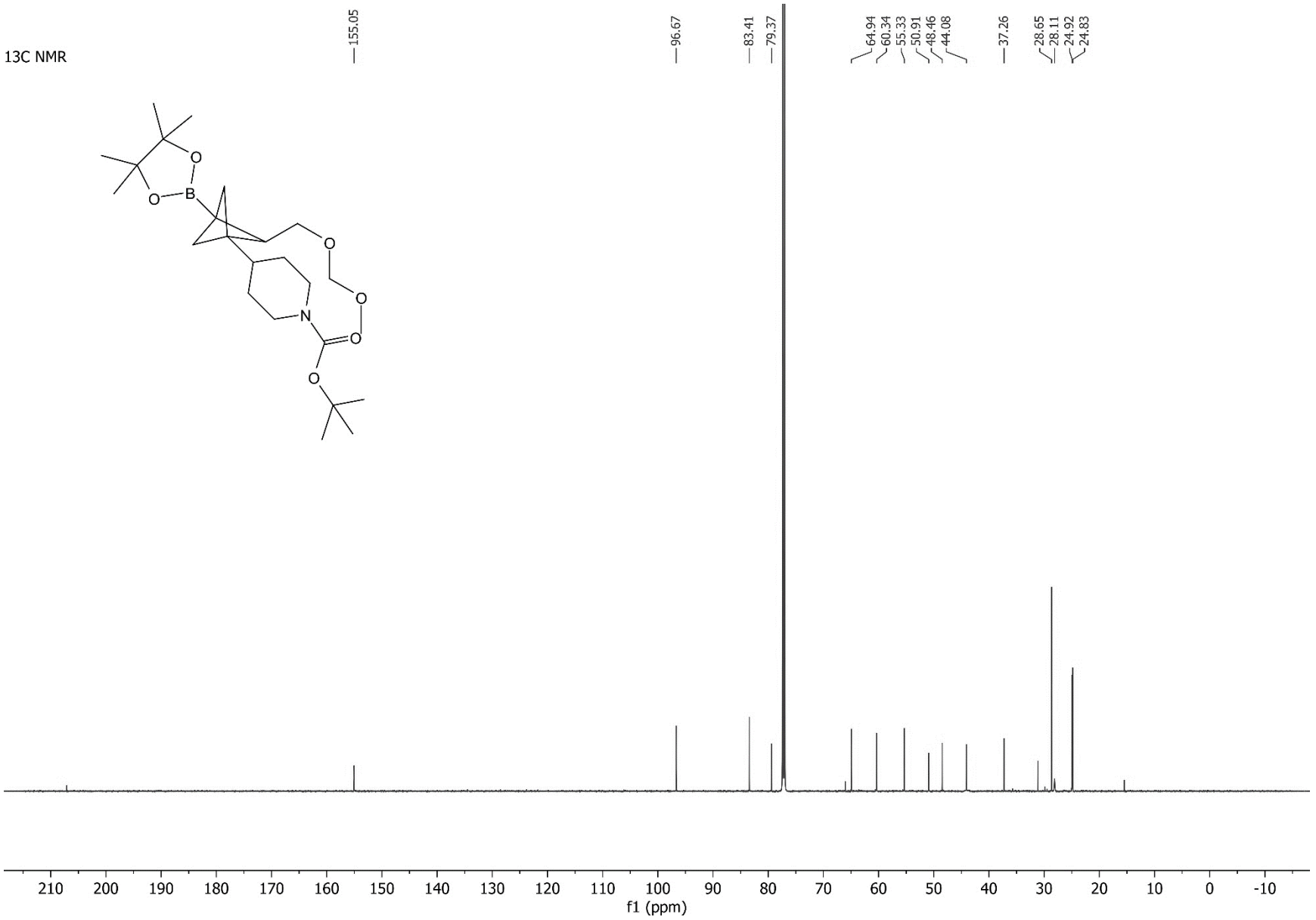


^{11}B NMR (128 MHz, $CDCl_3$) of **4y**

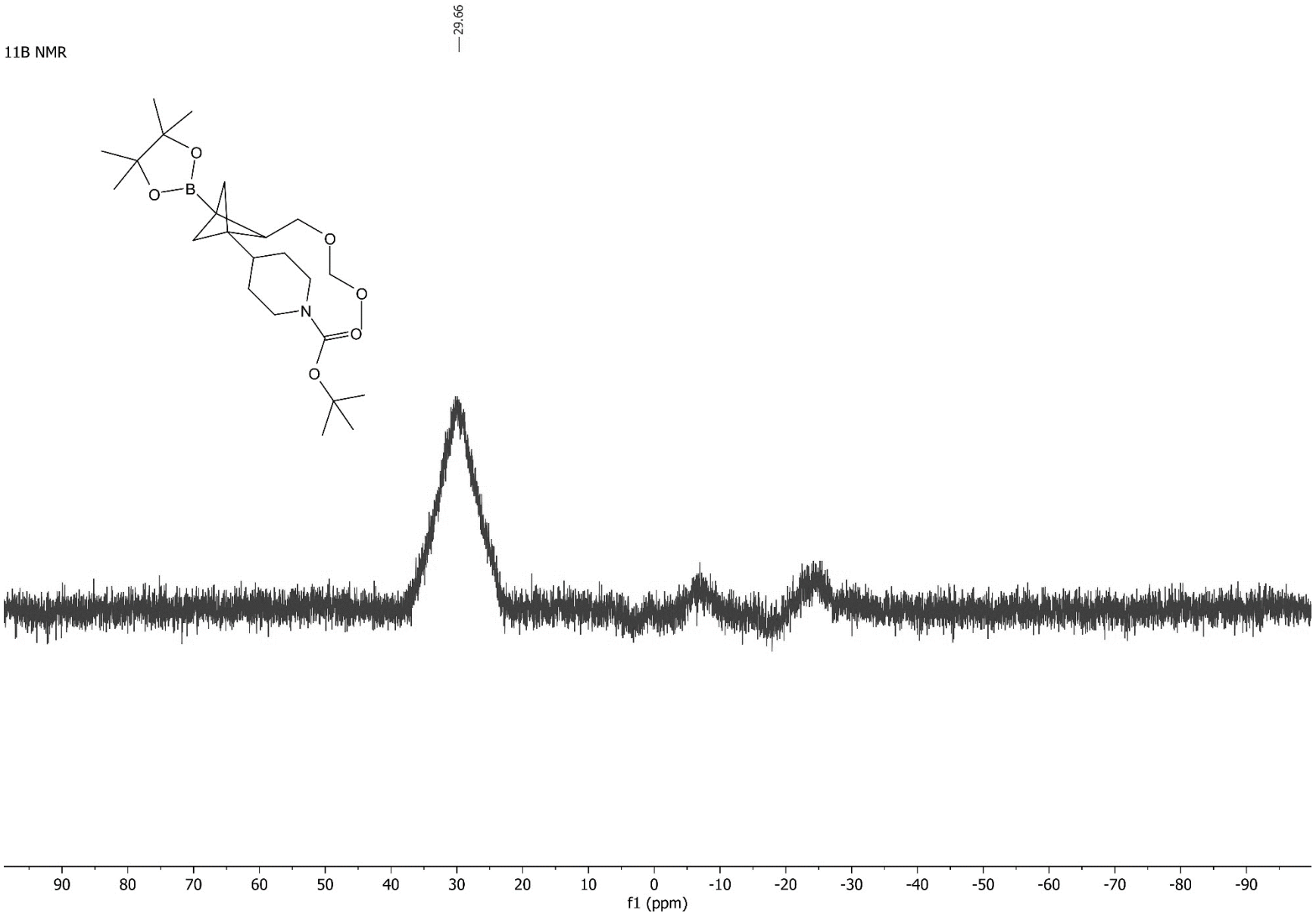


^{1}H NMR (600 MHz, $CDCl_3$) of **4z**

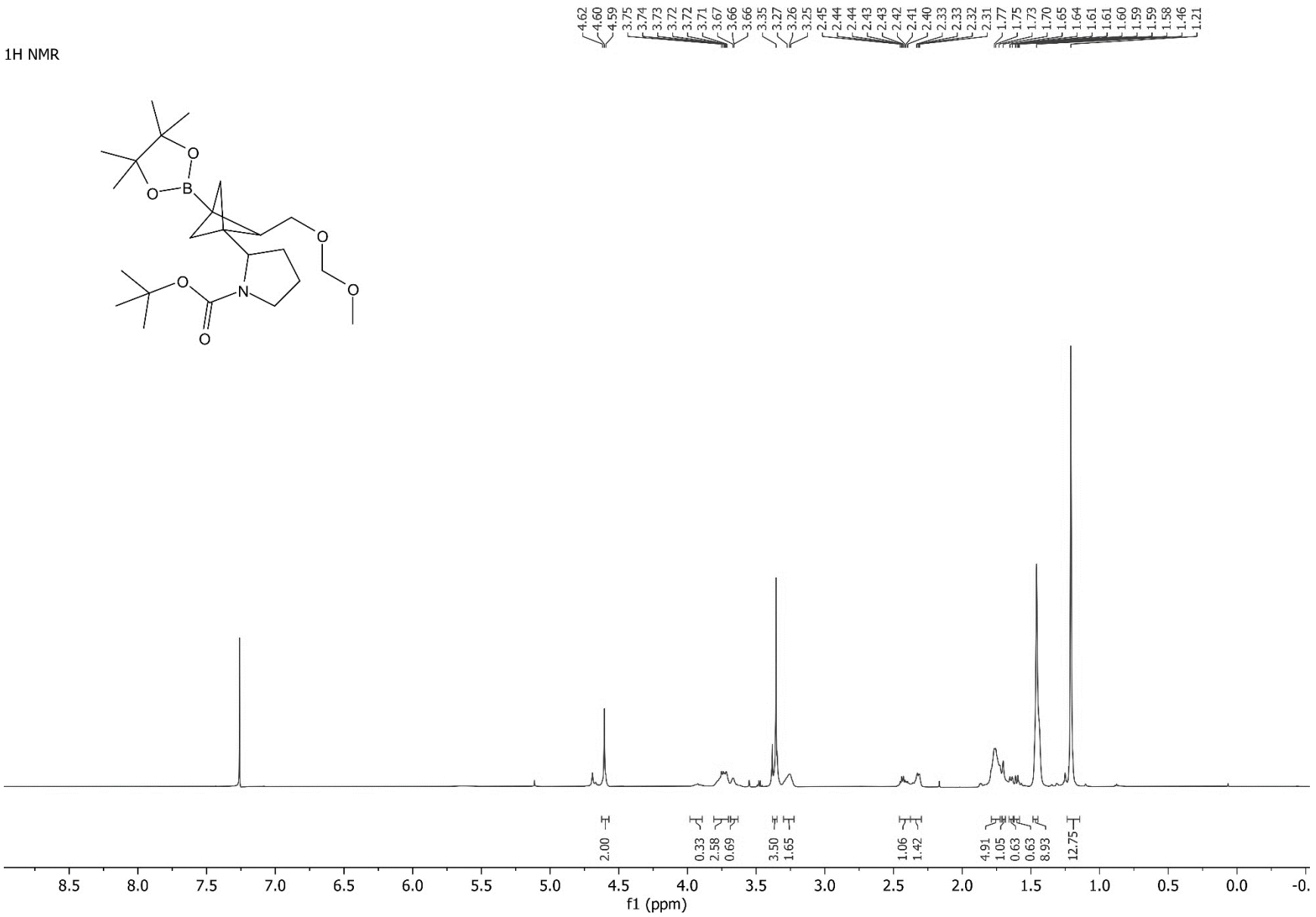
^{13}C NMR (151 MHz, $CDCl_3$) of **4z**



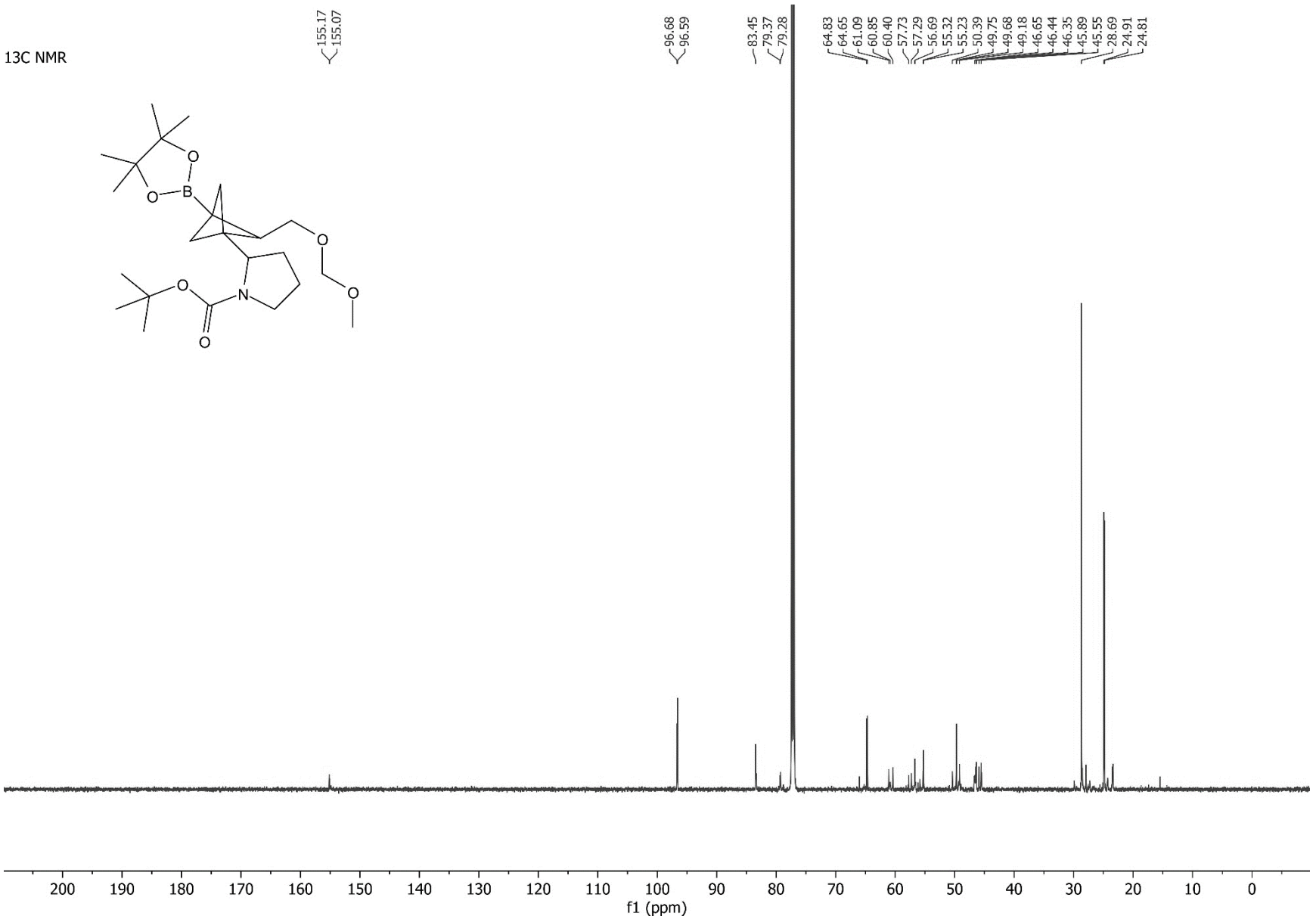
^{11}B NMR (128 MHz, $CDCl_3$) of **4z**



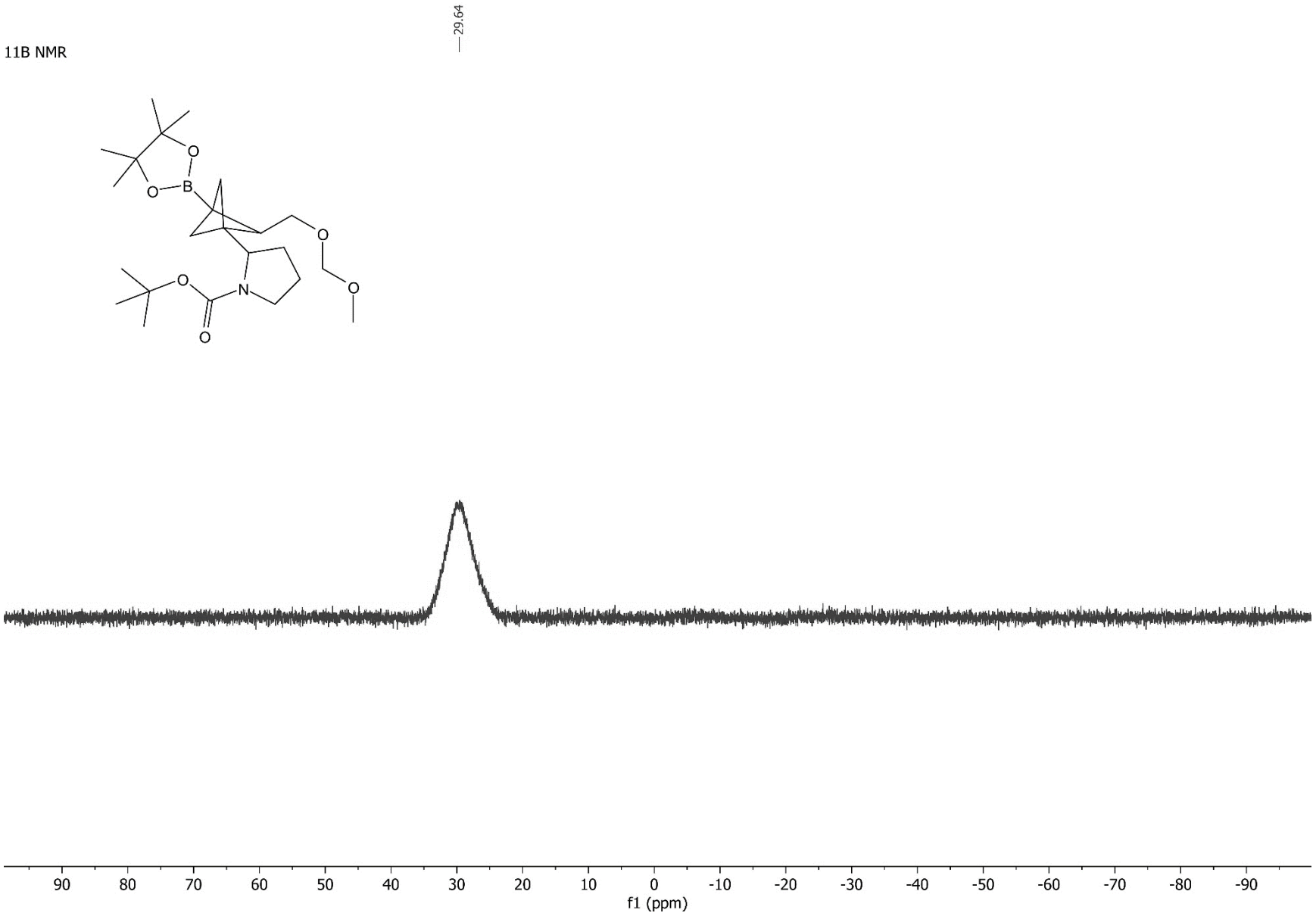
^{1}H NMR (600 MHz, $CDCl_3$) of **4aa**



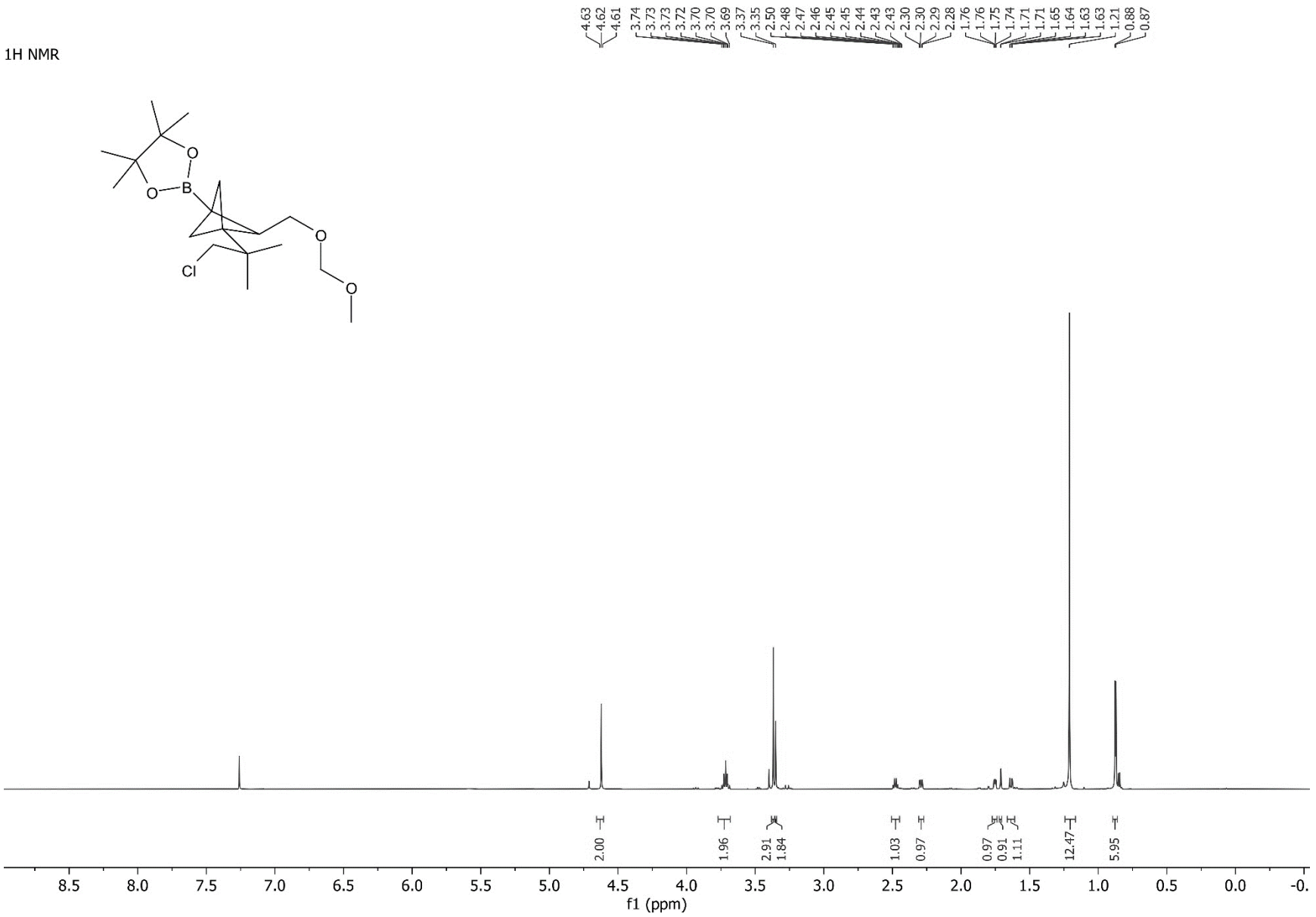
^{13}C NMR (151 MHz, $CDCl_3$) of **4aa**



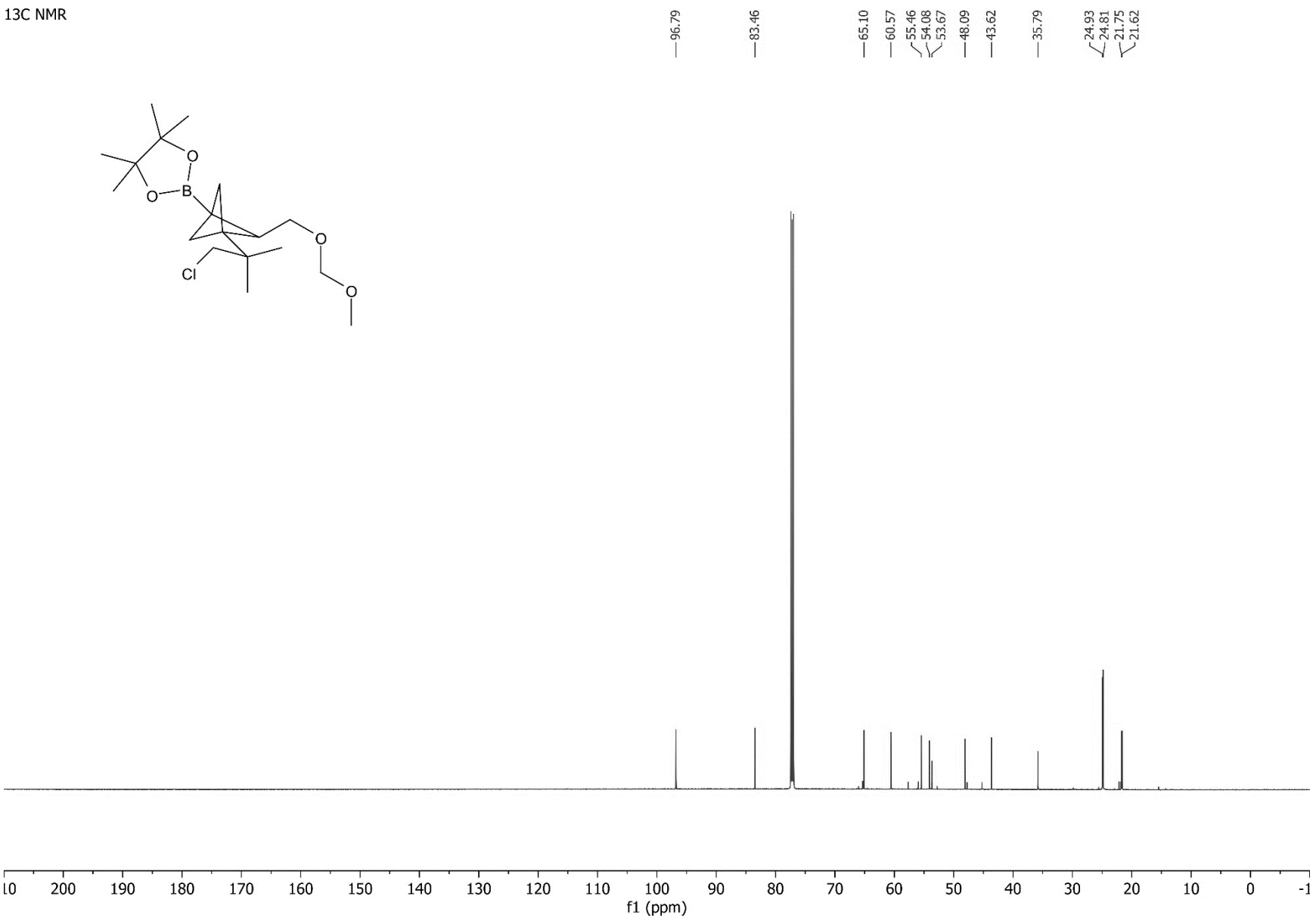
^{11}B NMR (128 MHz, $CDCl_3$) of **4aa**



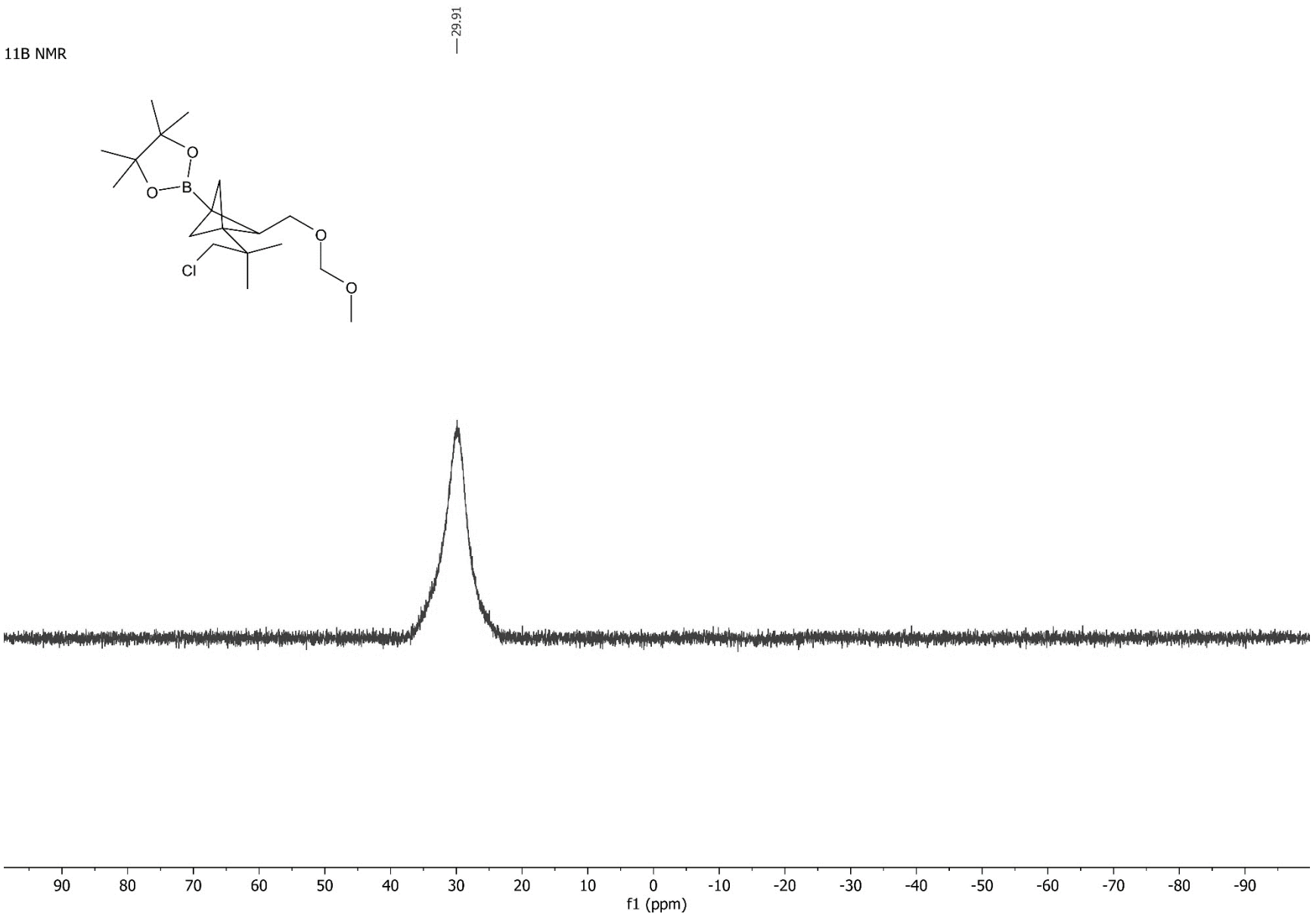
^{1}H NMR (600 MHz, $CDCl_3$) of **4ab**



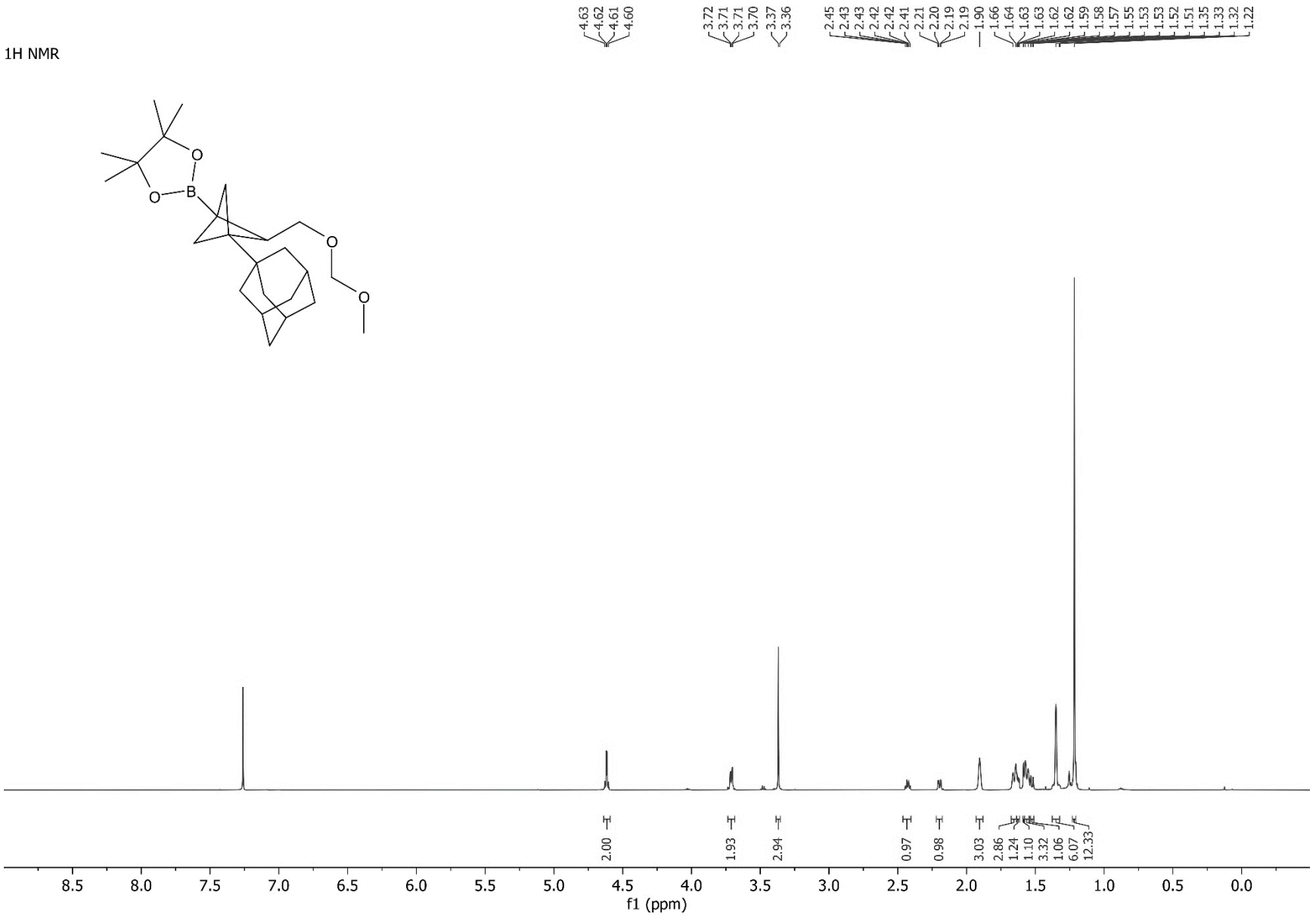
^{13}C NMR (151 MHz, $CDCl_3$) of **4ab**



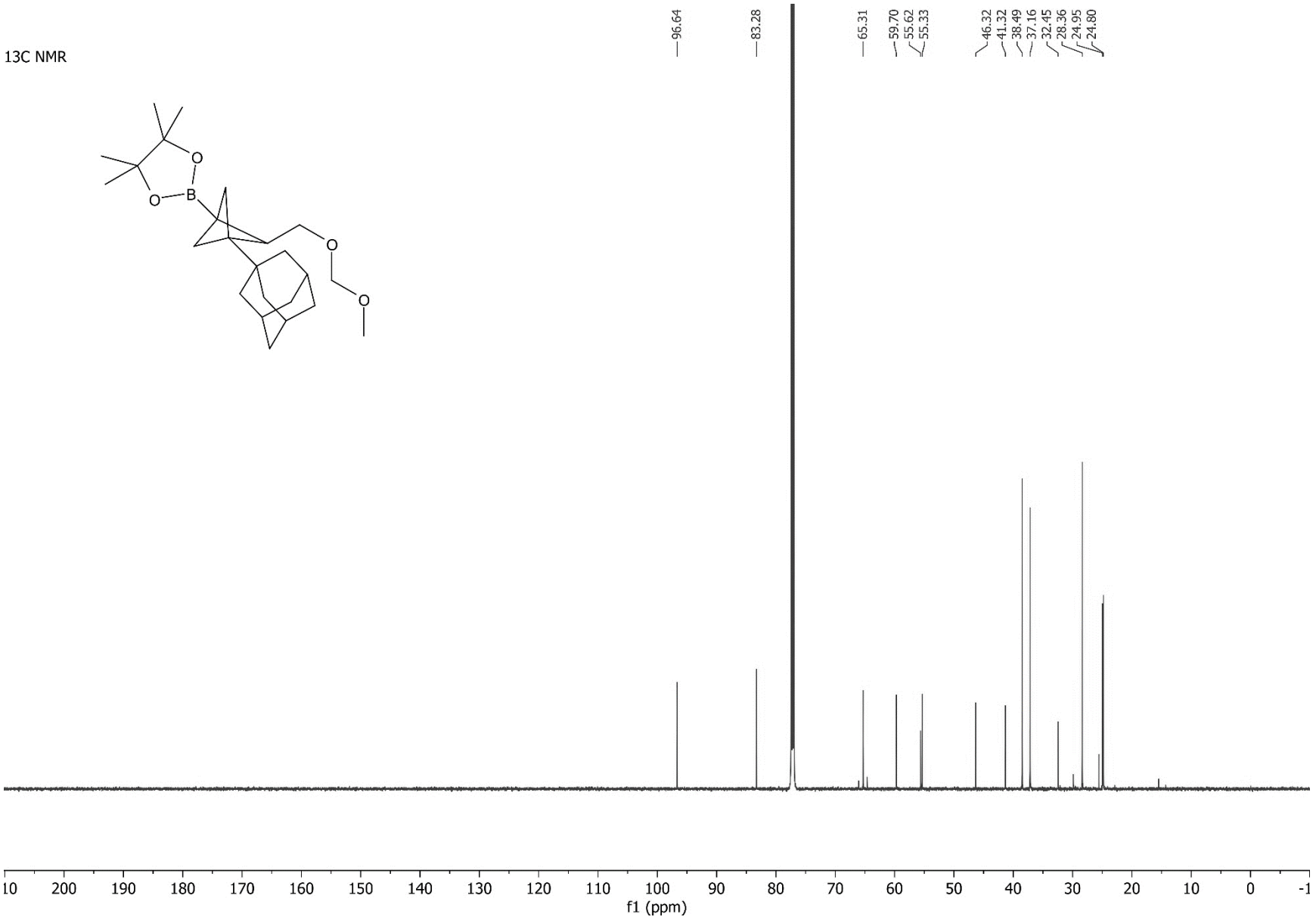
^{11}B NMR (128 MHz, $CDCl_3$) of **4ab**



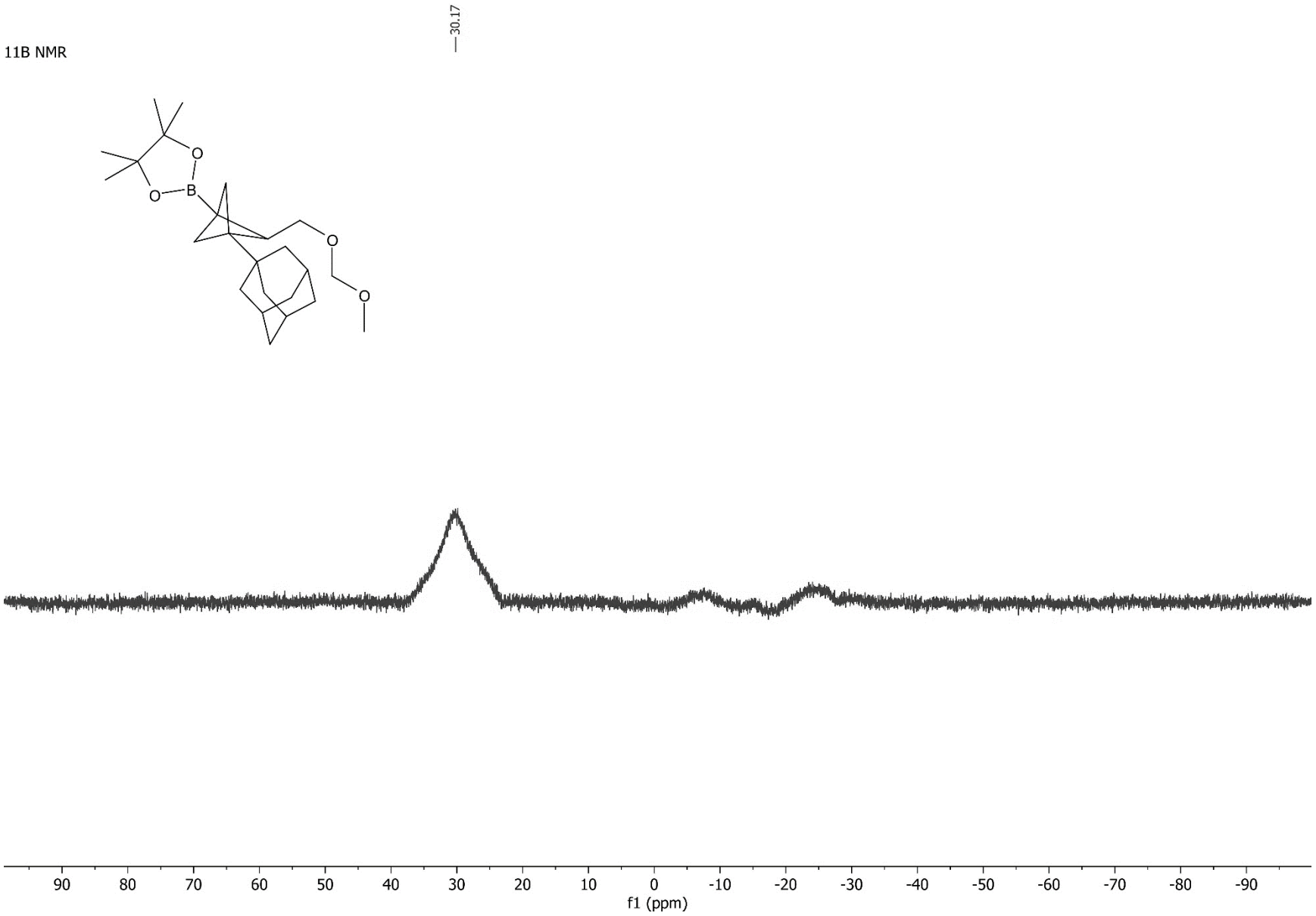
^{1}H NMR (600 MHz, $CDCl_3$) of **4ac**



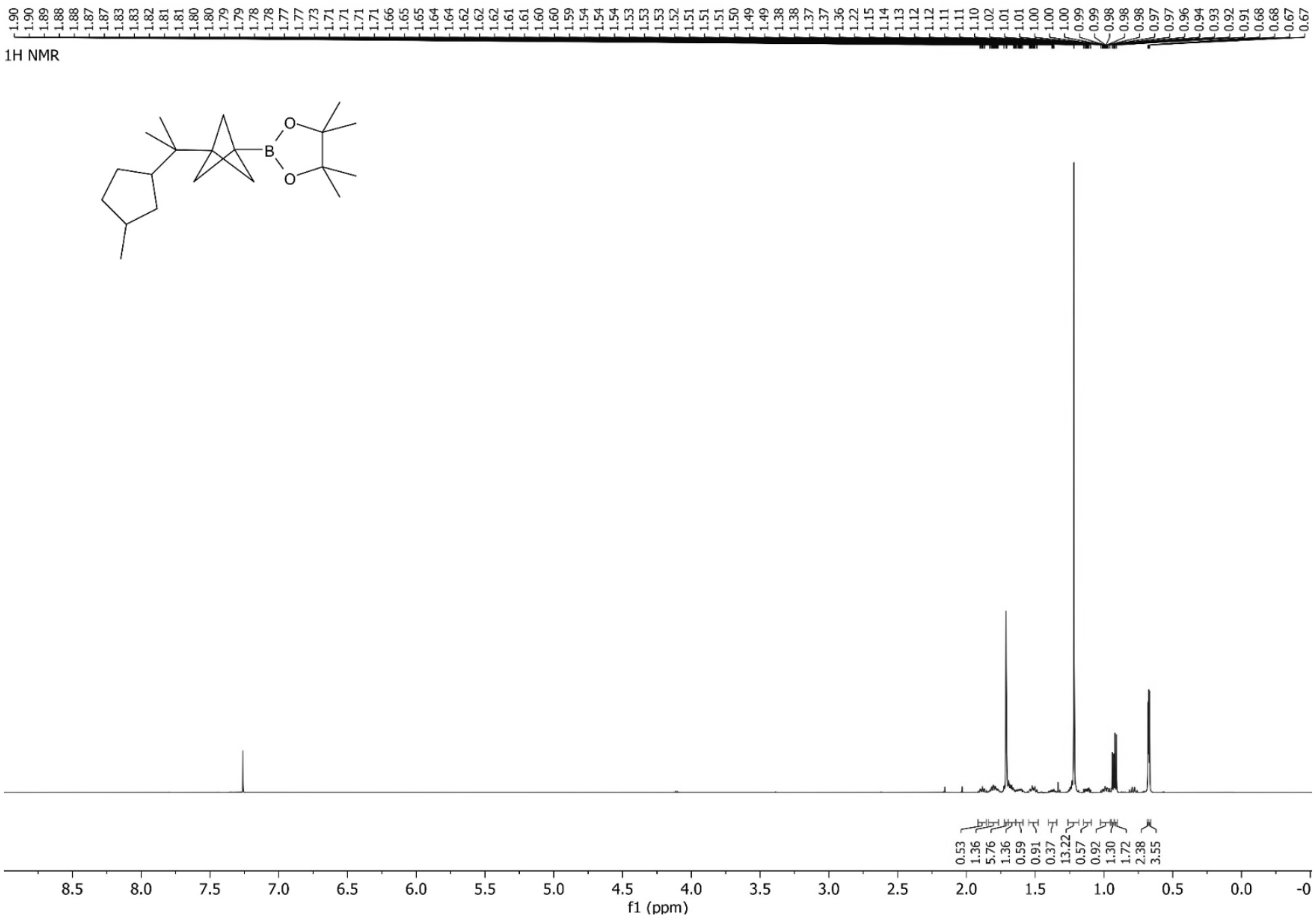
^{13}C NMR (151 MHz, $CDCl_3$) of **4ac**



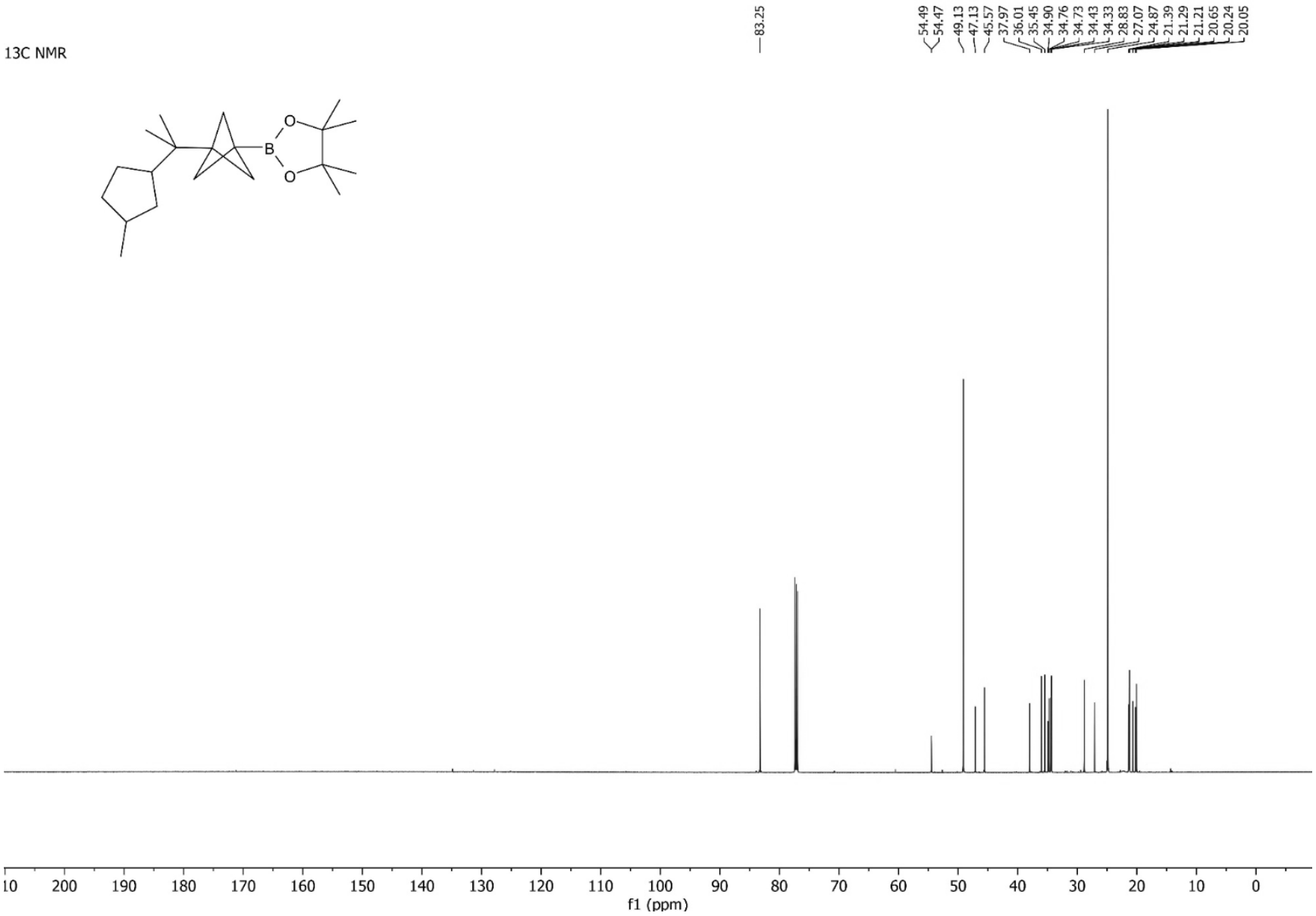
^{11}B NMR (128 MHz, $CDCl_3$) of **4ac**



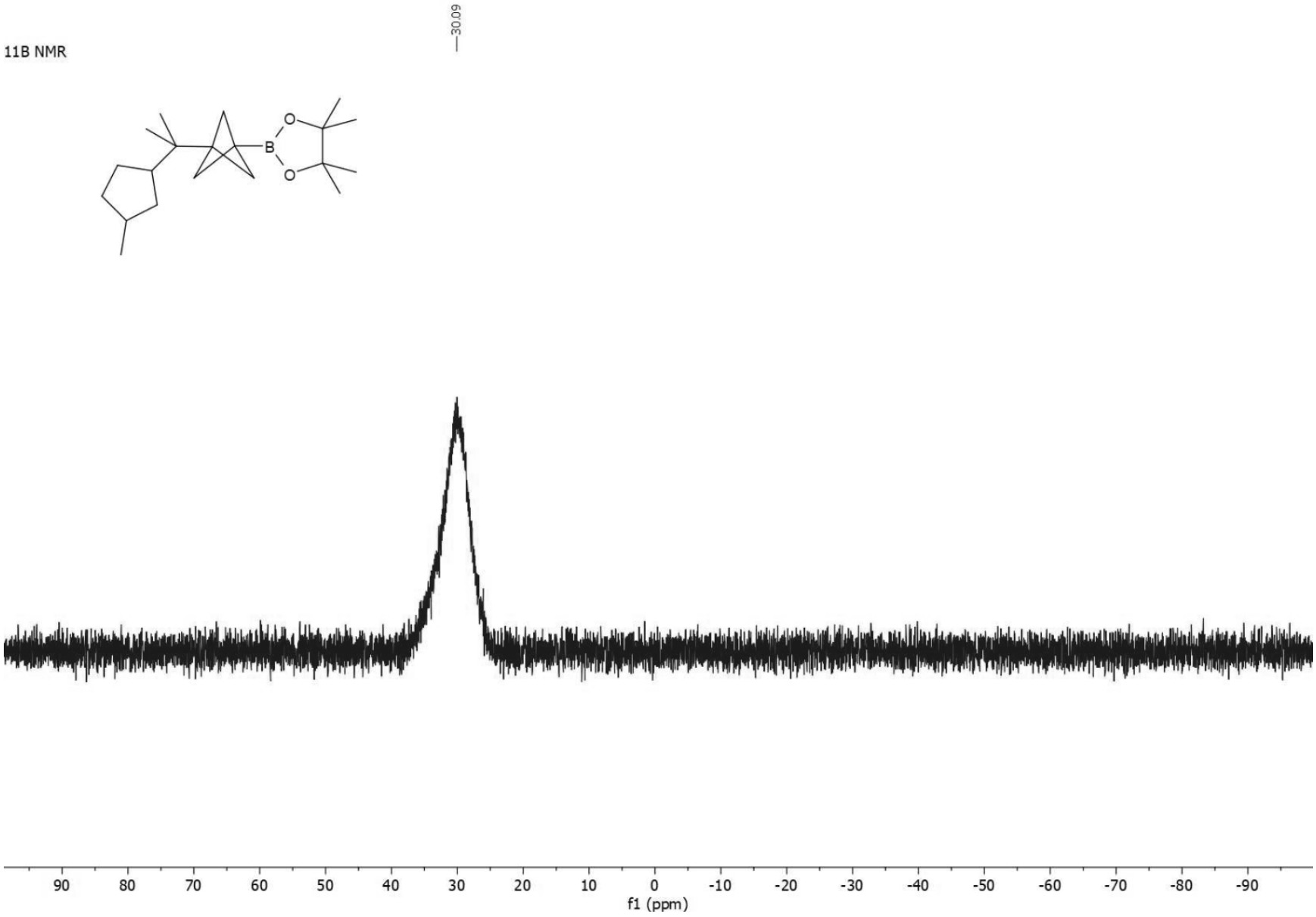
^{1}H NMR (600 MHz, $CDCl_3$) of **4ad**



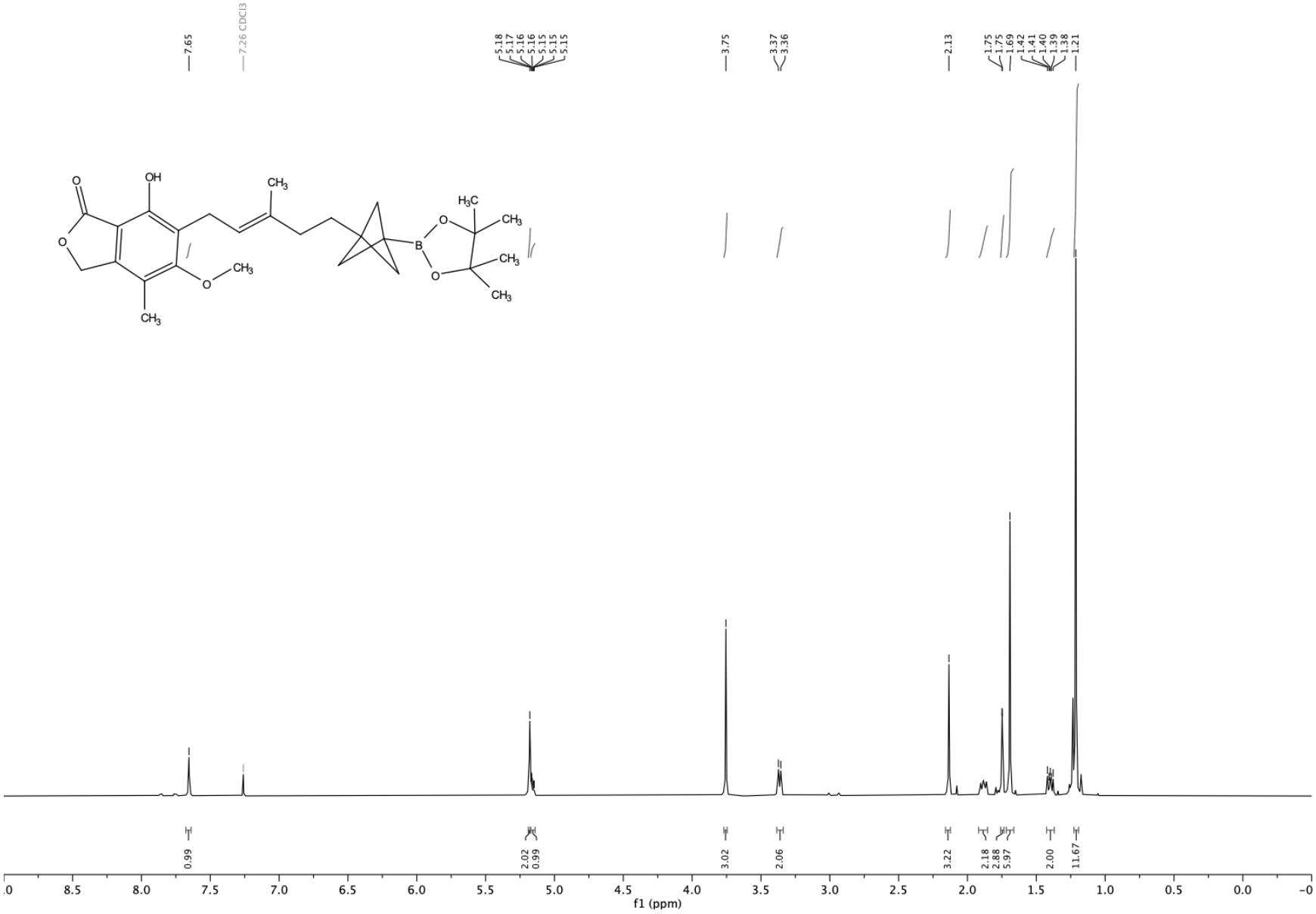
^{13}C NMR (151 MHz, $CDCl_3$) of **4ad**



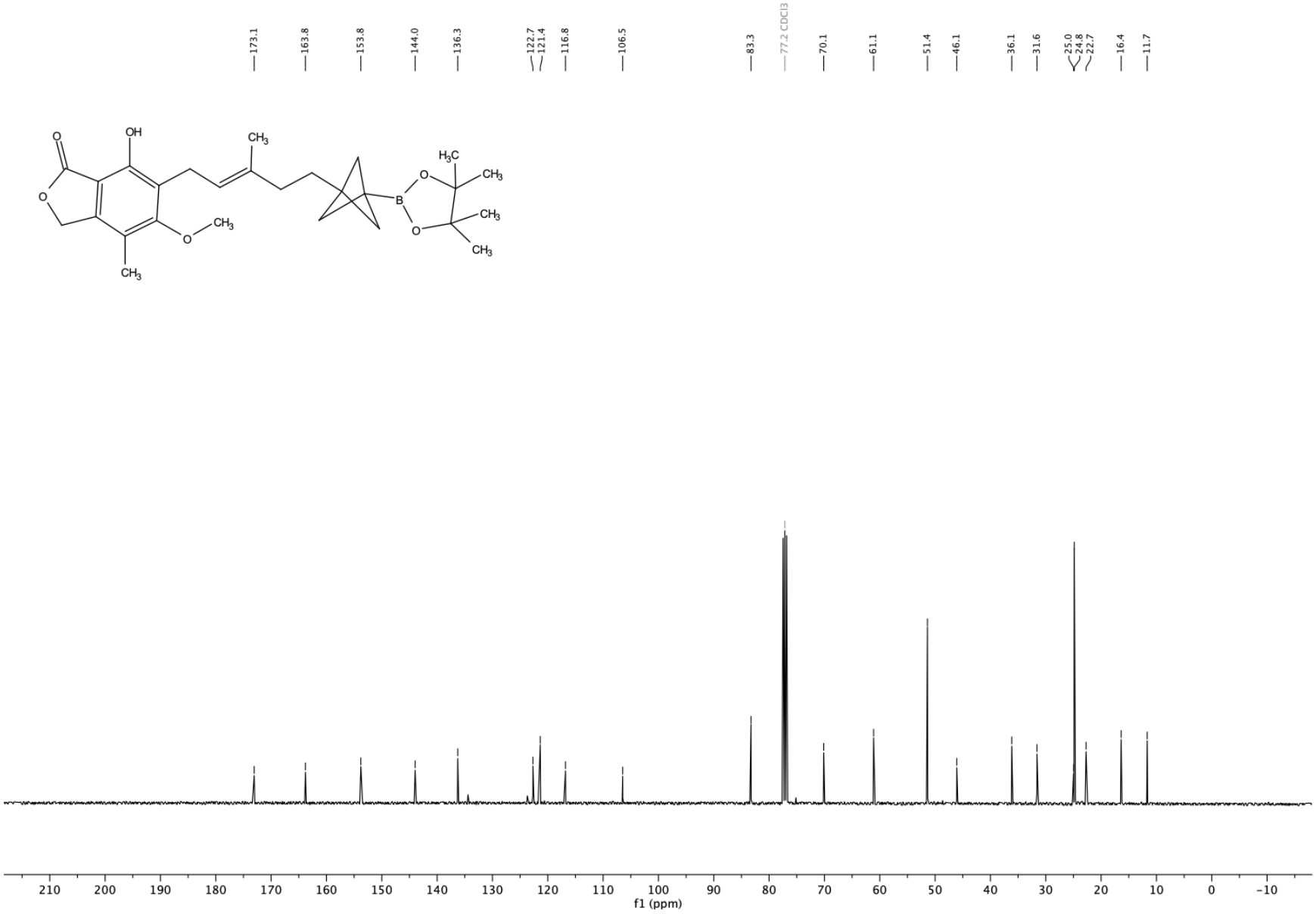
^{11}B NMR (128 MHz, $CDCl_3$) of **4ad**



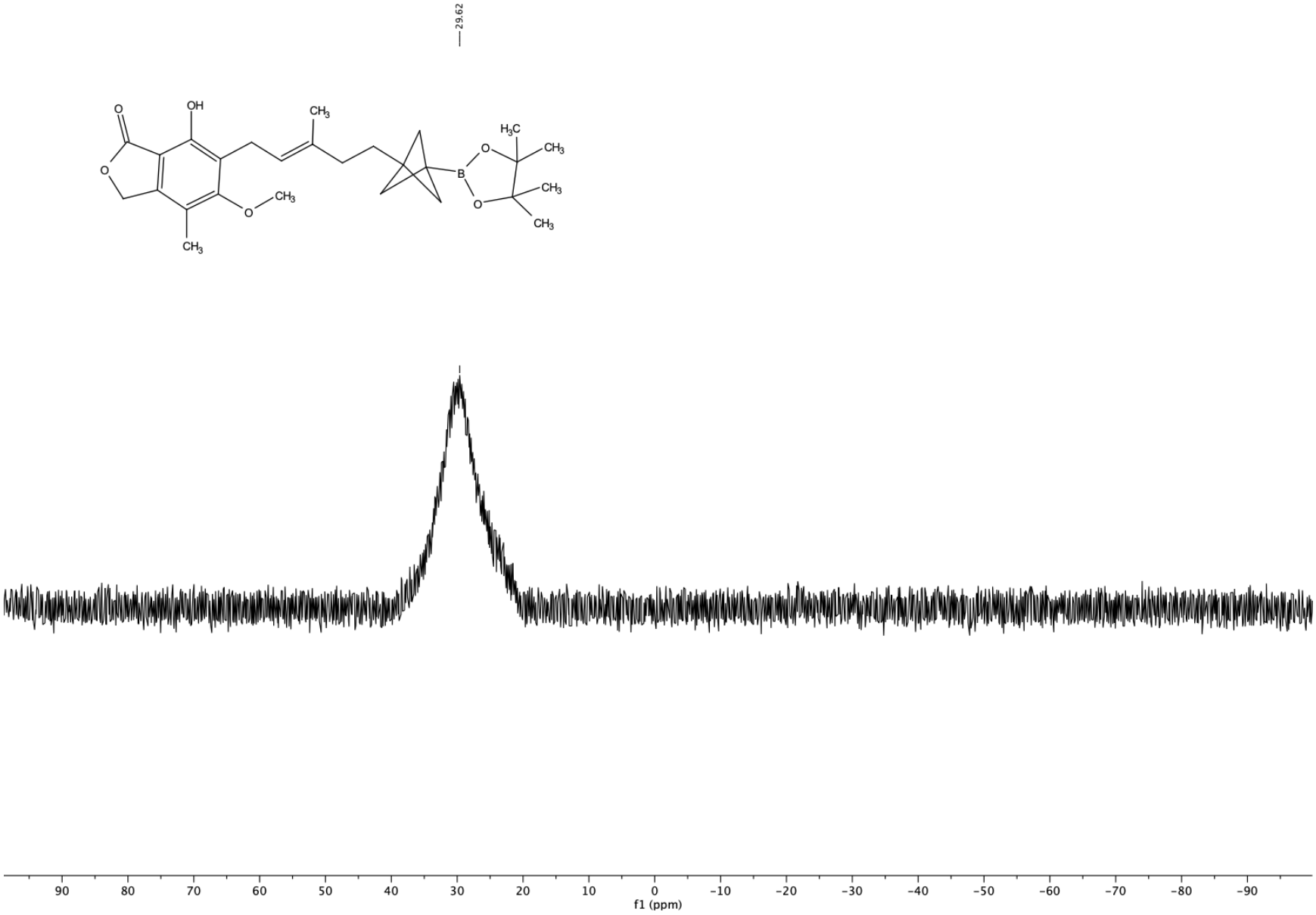
^{1}H NMR (400 MHz, $CDCl_3$) of **4ae**



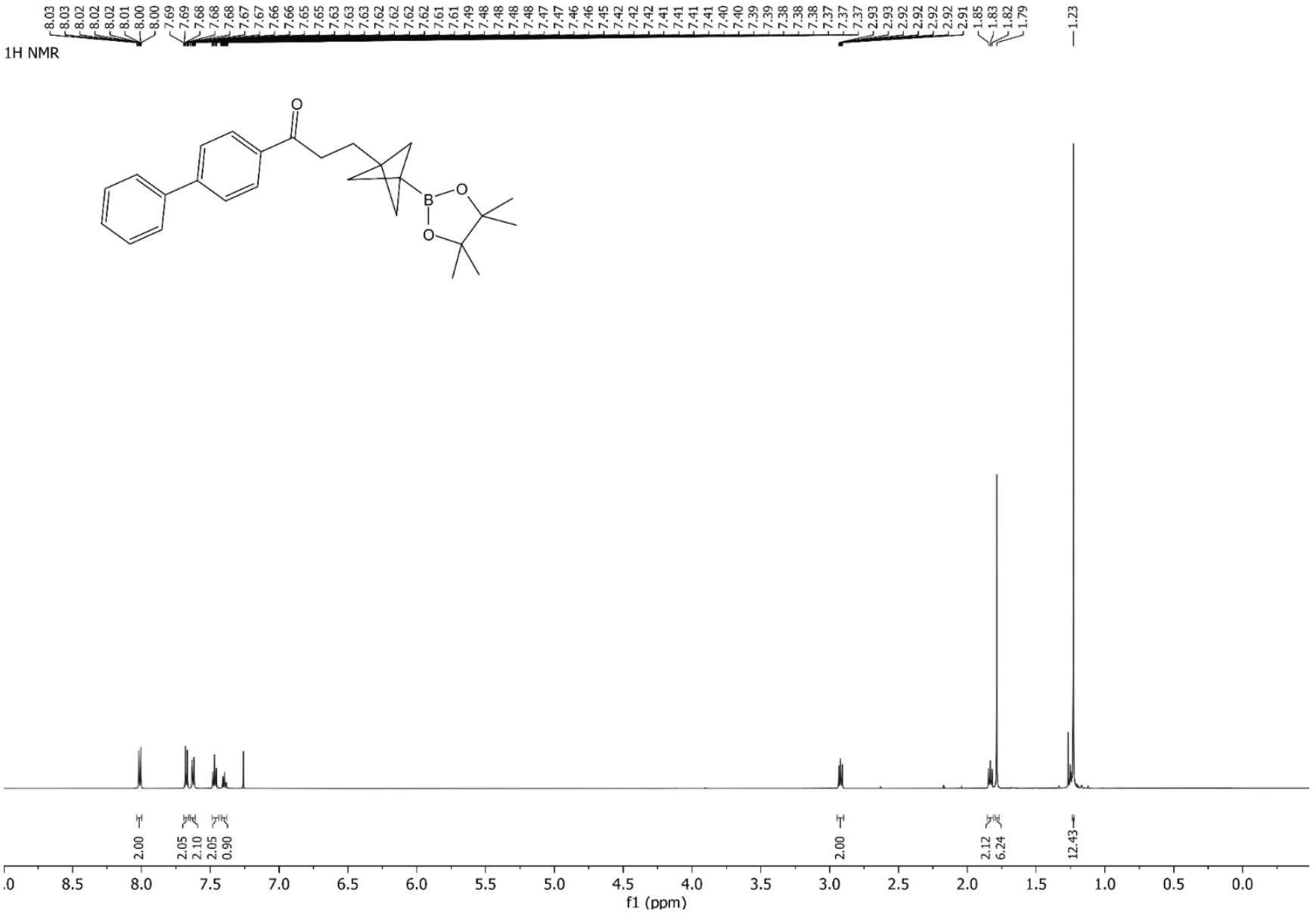
^{13}C NMR (151 MHz, $CDCl_3$) of **4ae**



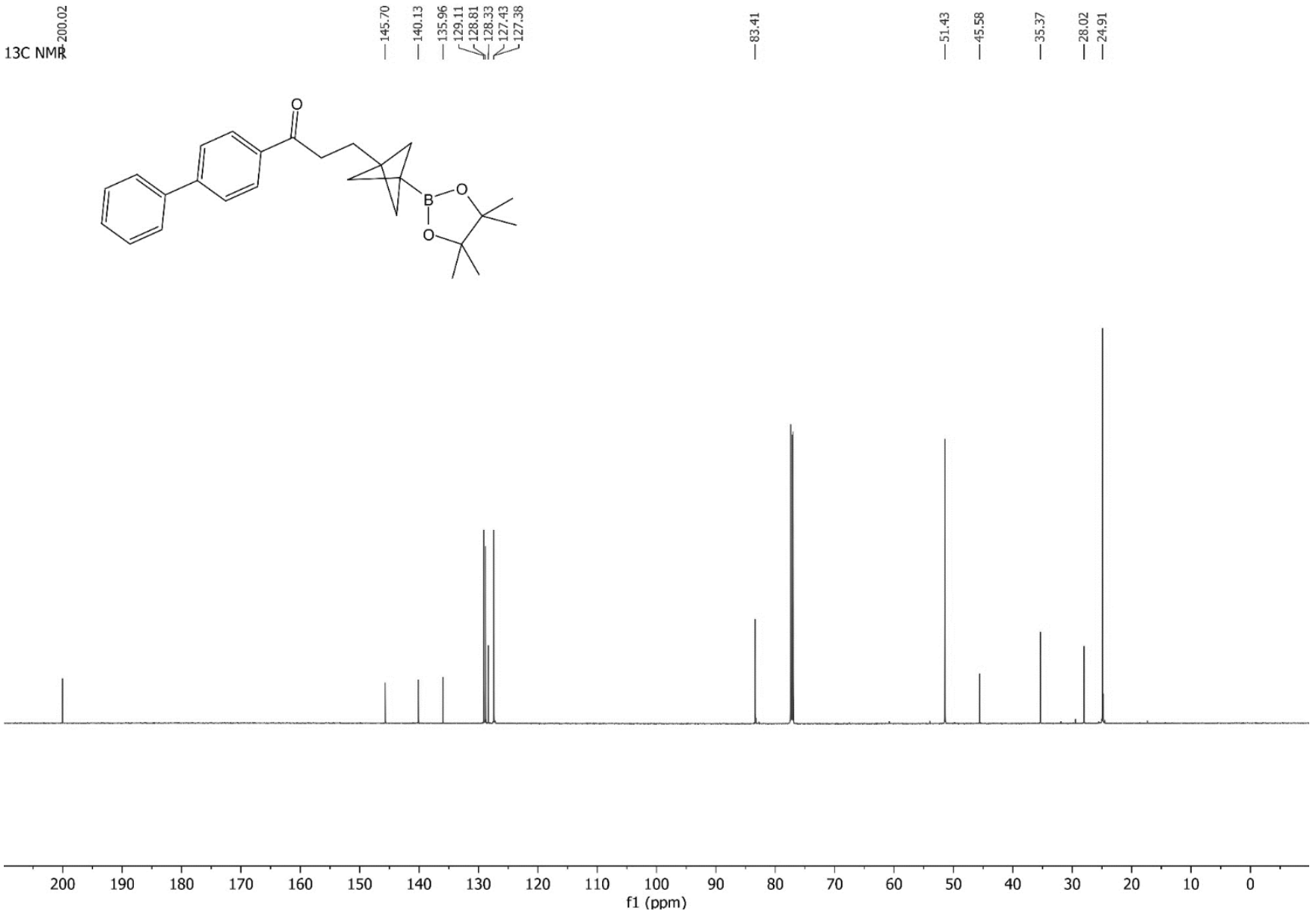
^{11}B NMR (128 MHz, $CDCl_3$) of **4ae**



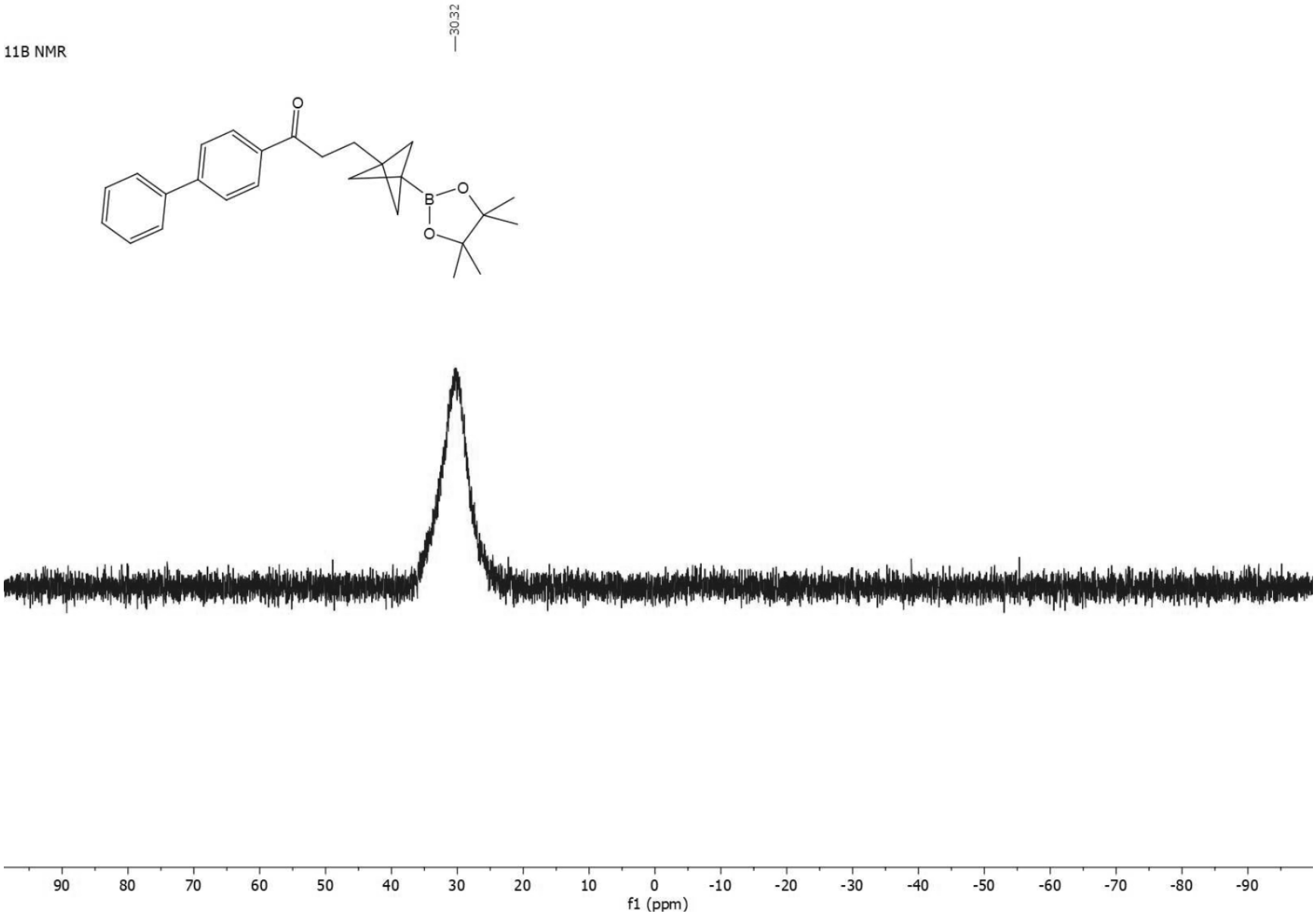
^{1}H NMR (600 MHz, $CDCl_3$) of **4af**



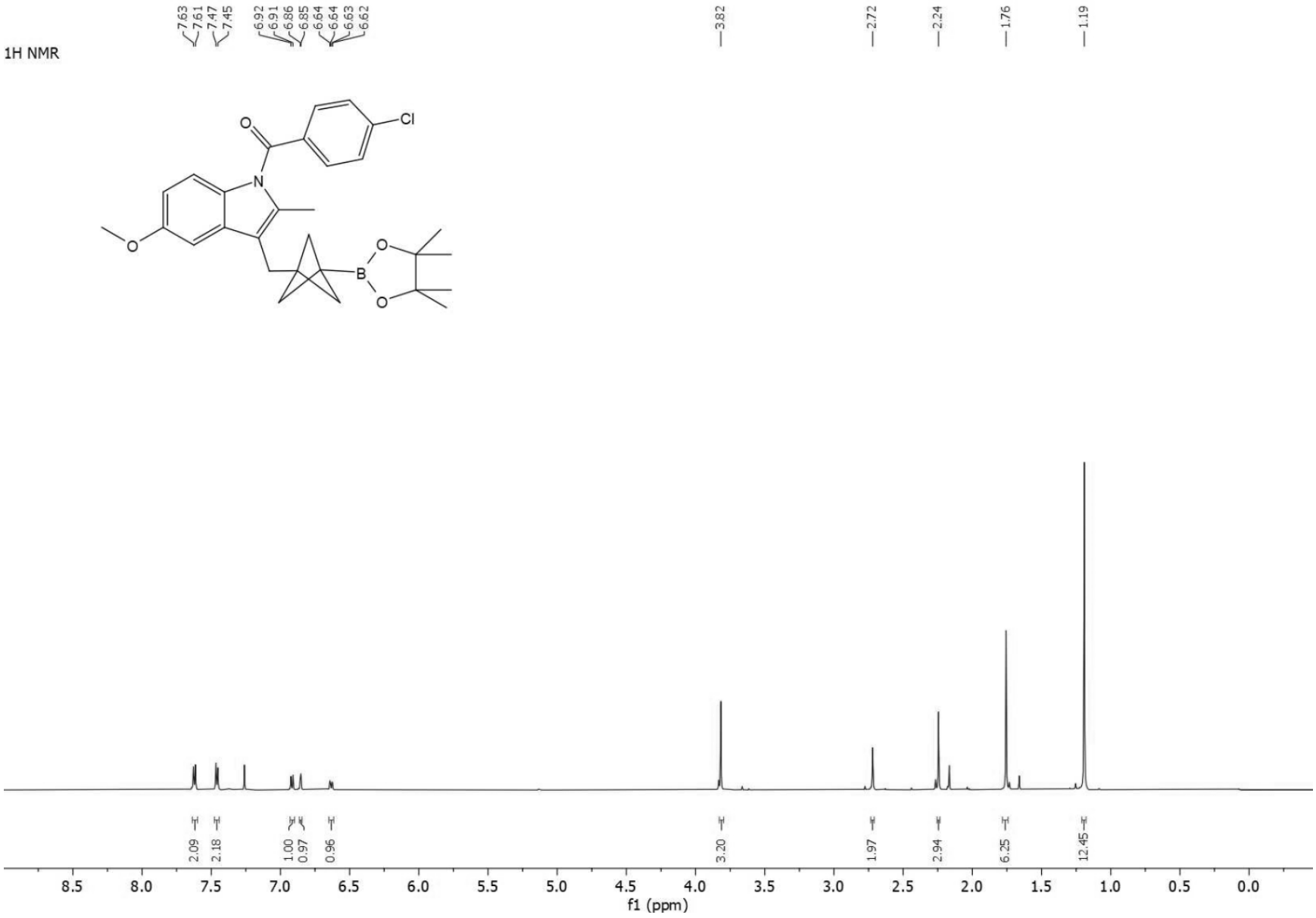
^{13}C NMR (151 MHz, $CDCl_3$) of **4af**



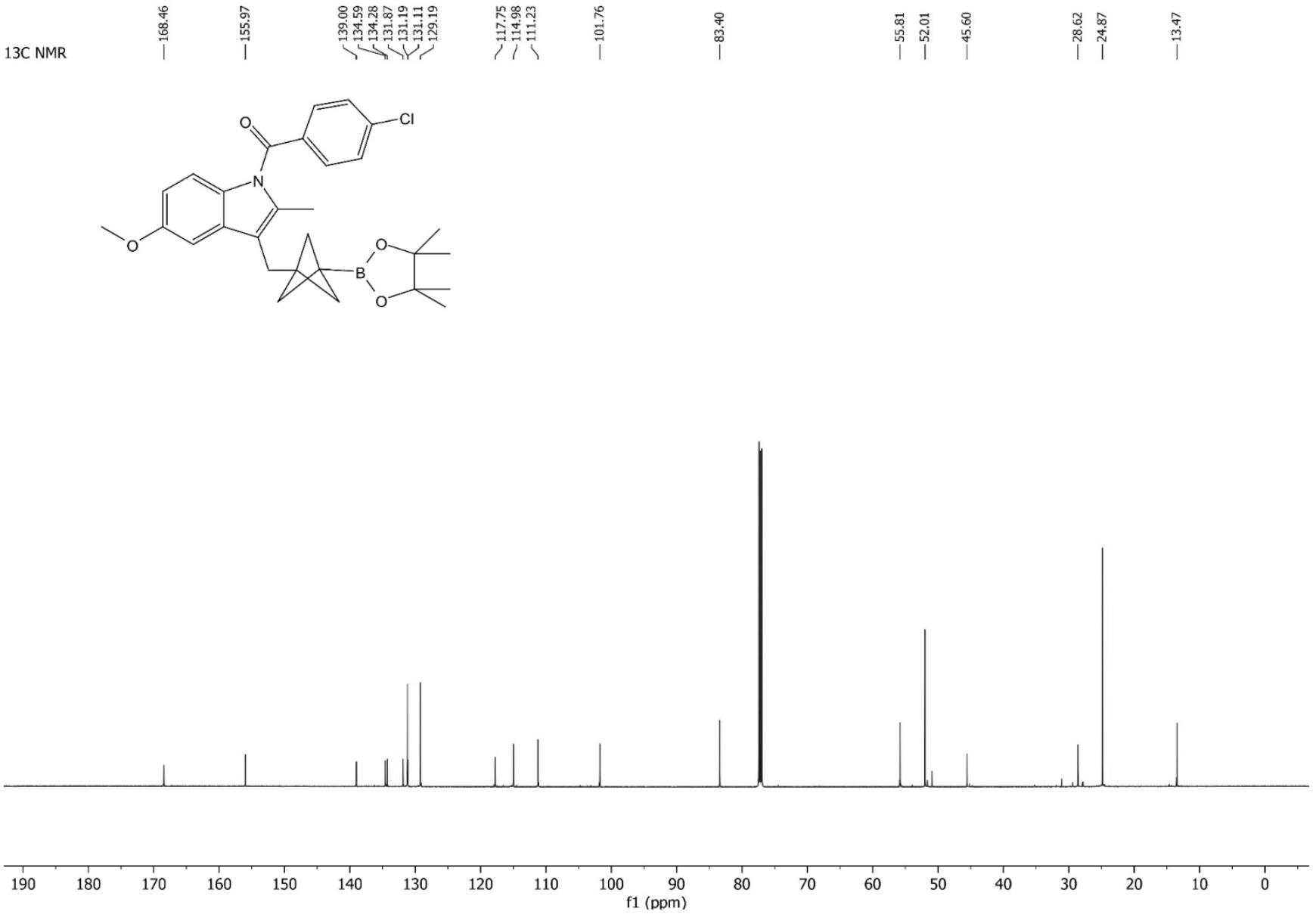
^{11}B NMR (128 MHz, $CDCl_3$) of **4af**



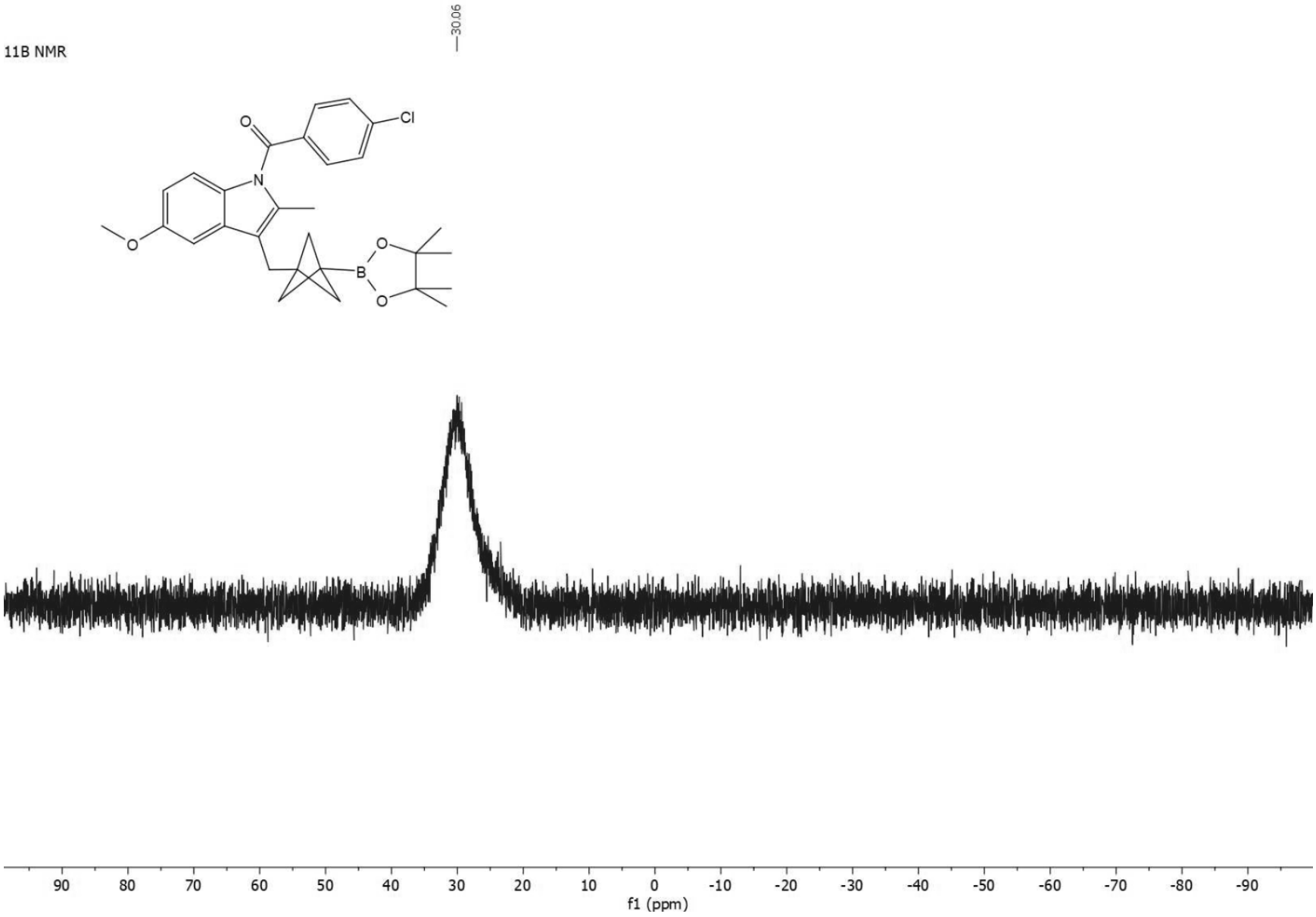
^{1}H NMR (600 MHz, $CDCl_3$) of **4ag**



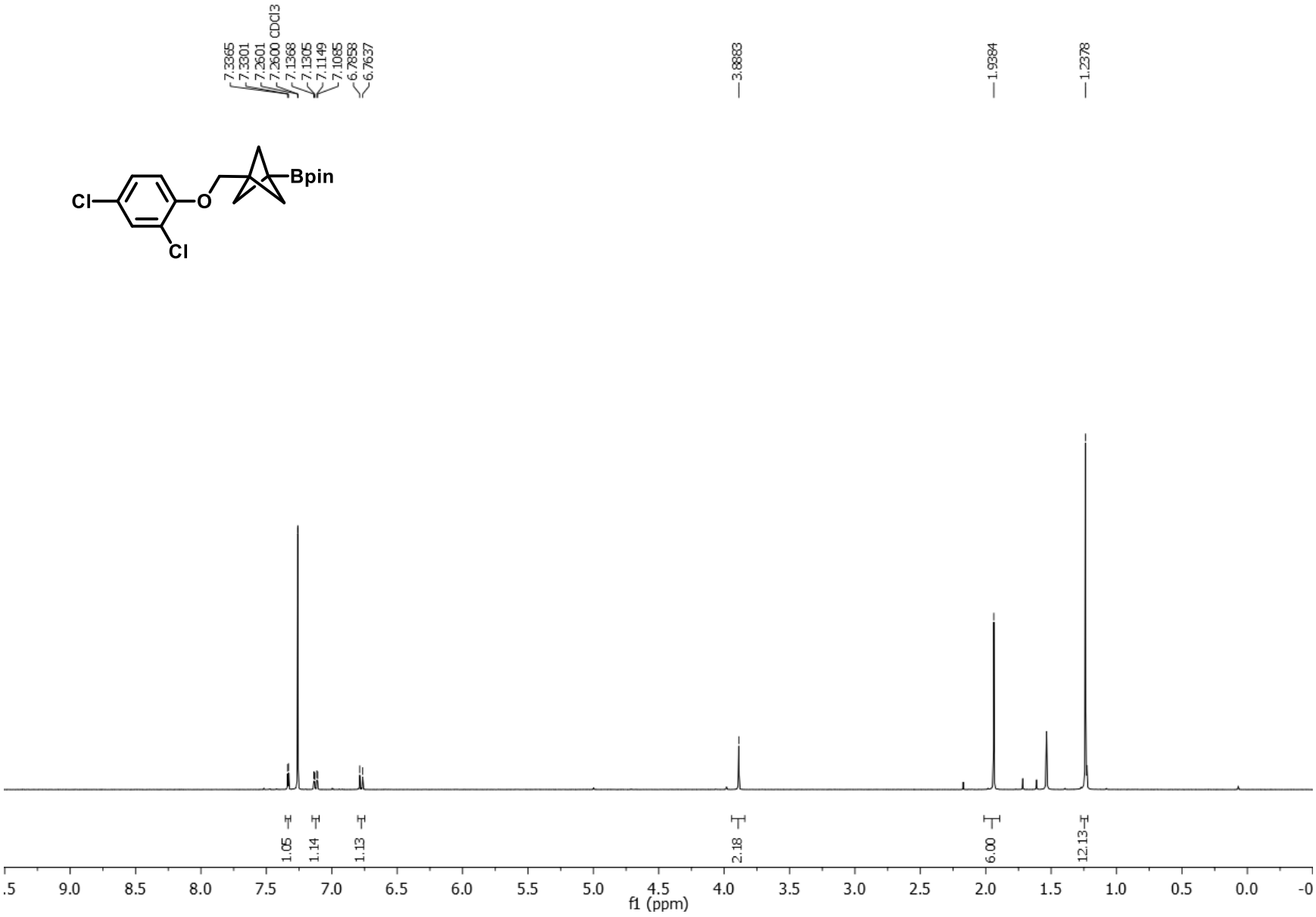
^{13}C NMR (151 MHz, $CDCl_3$) of **4ag**



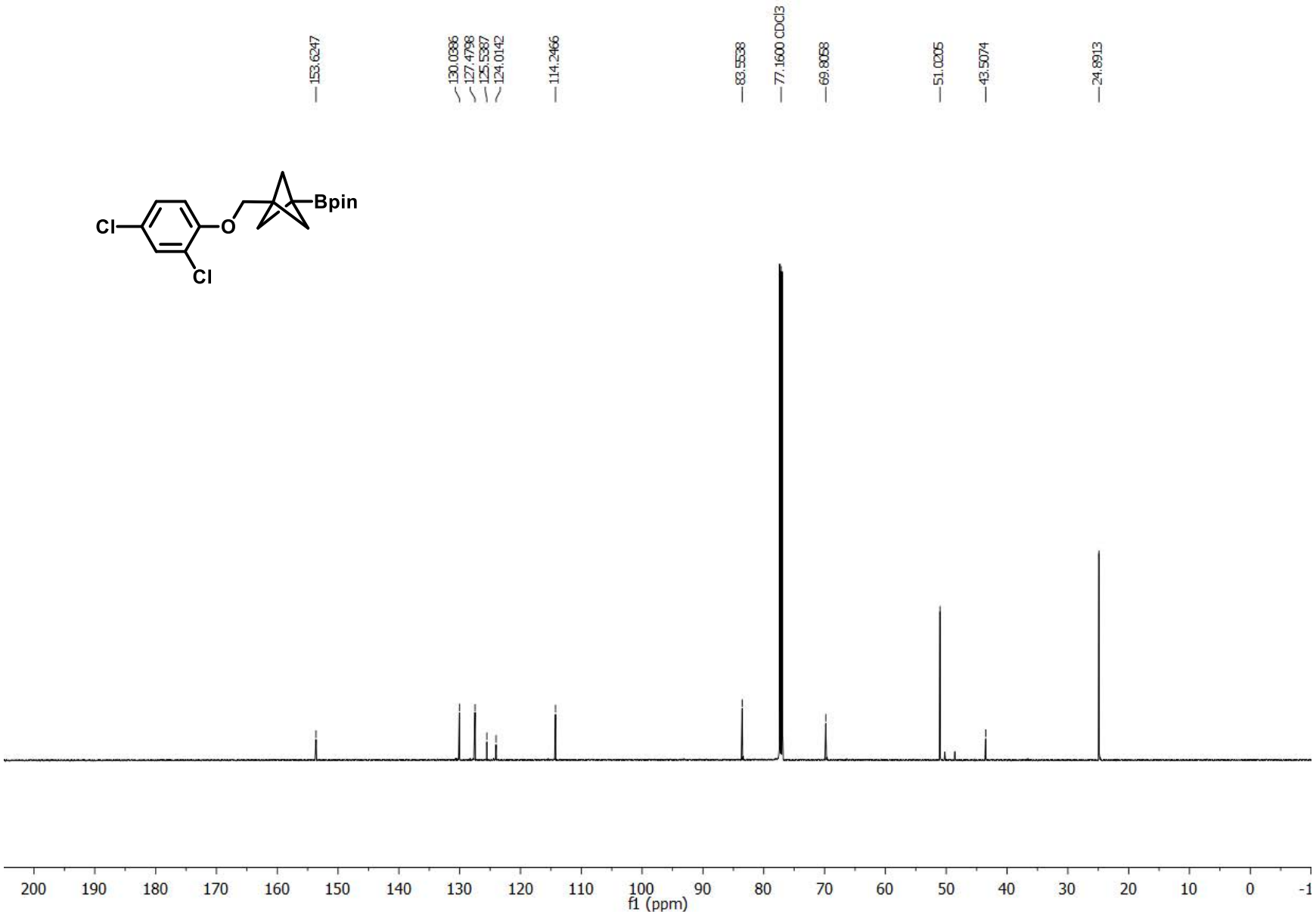
^{11}B NMR (128 MHz, $CDCl_3$) of **4ag**



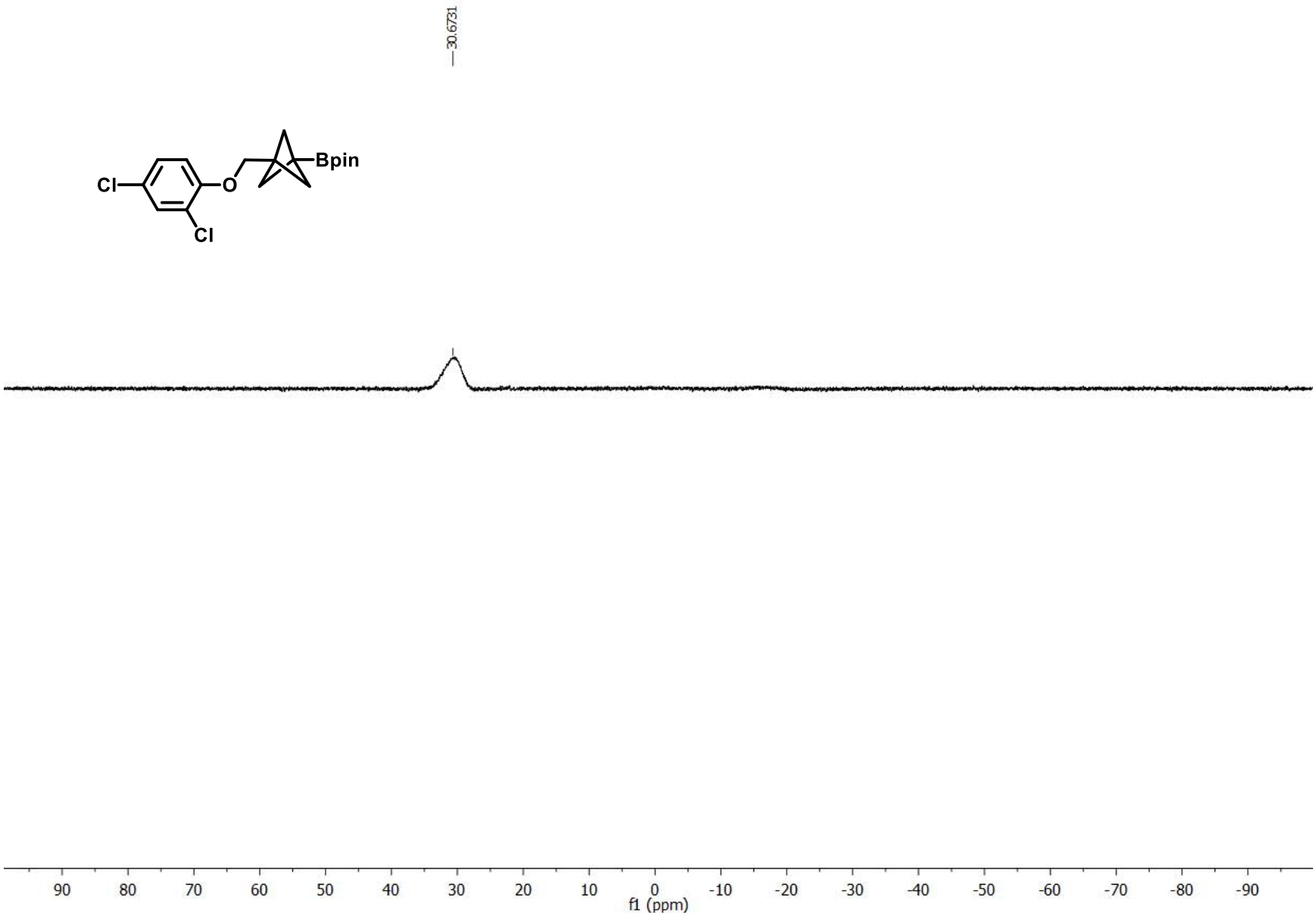
^{1}H NMR (400 MHz, $CDCl_3$) of **4ah**



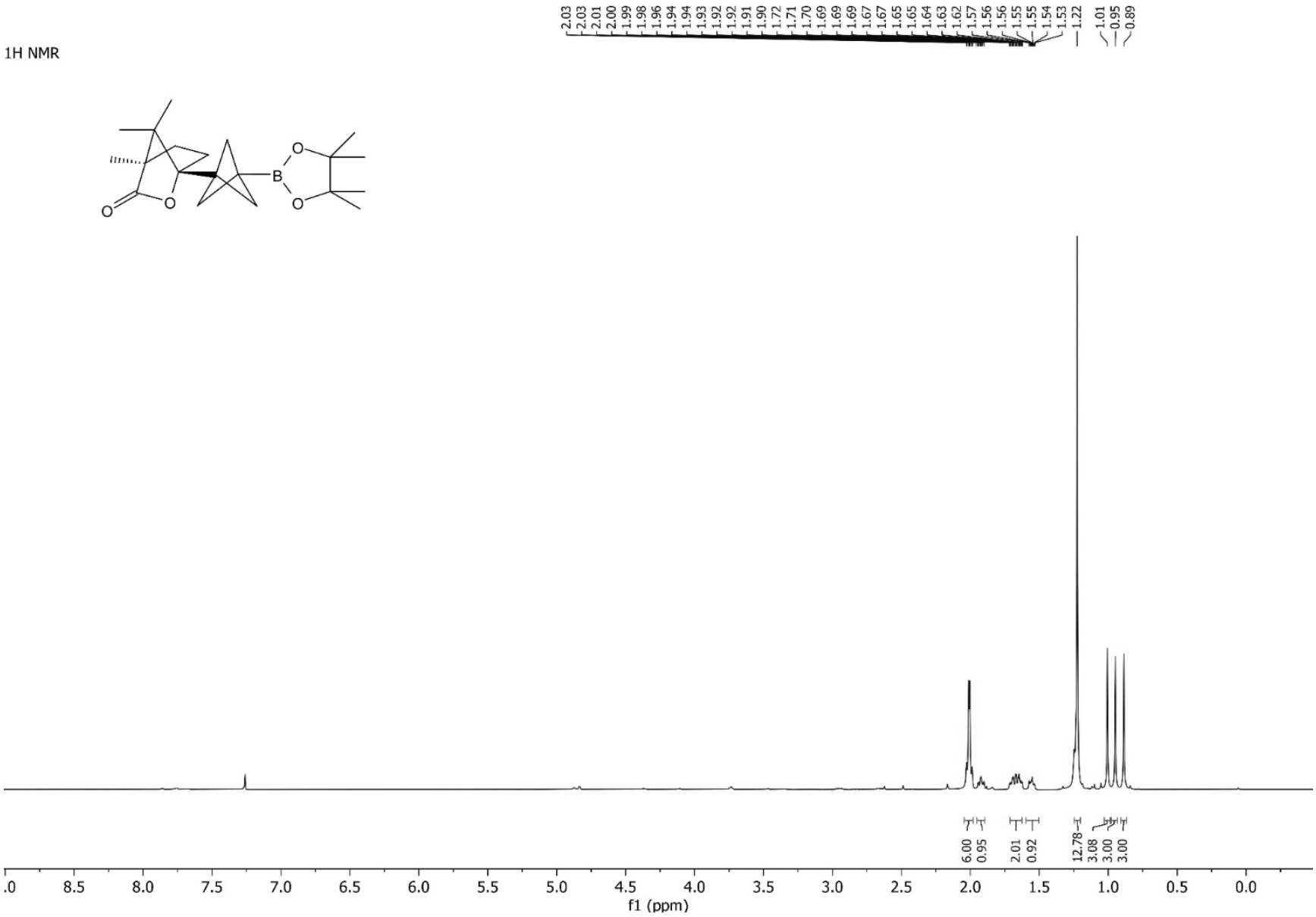
^{13}C NMR (151 MHz, $CDCl_3$) of **4ah**



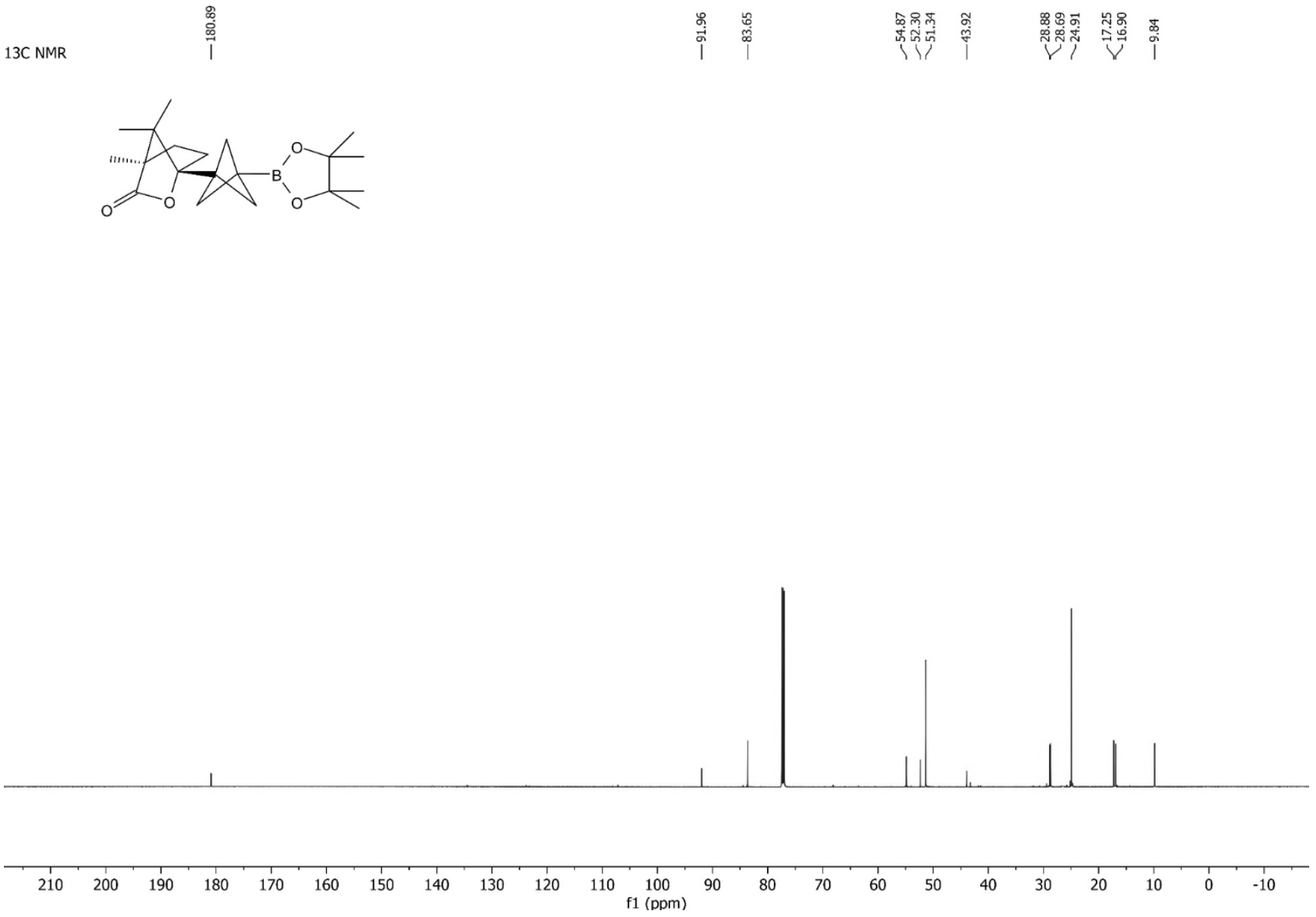
^{11}B NMR (128 MHz, $CDCl_3$) of **4ah**



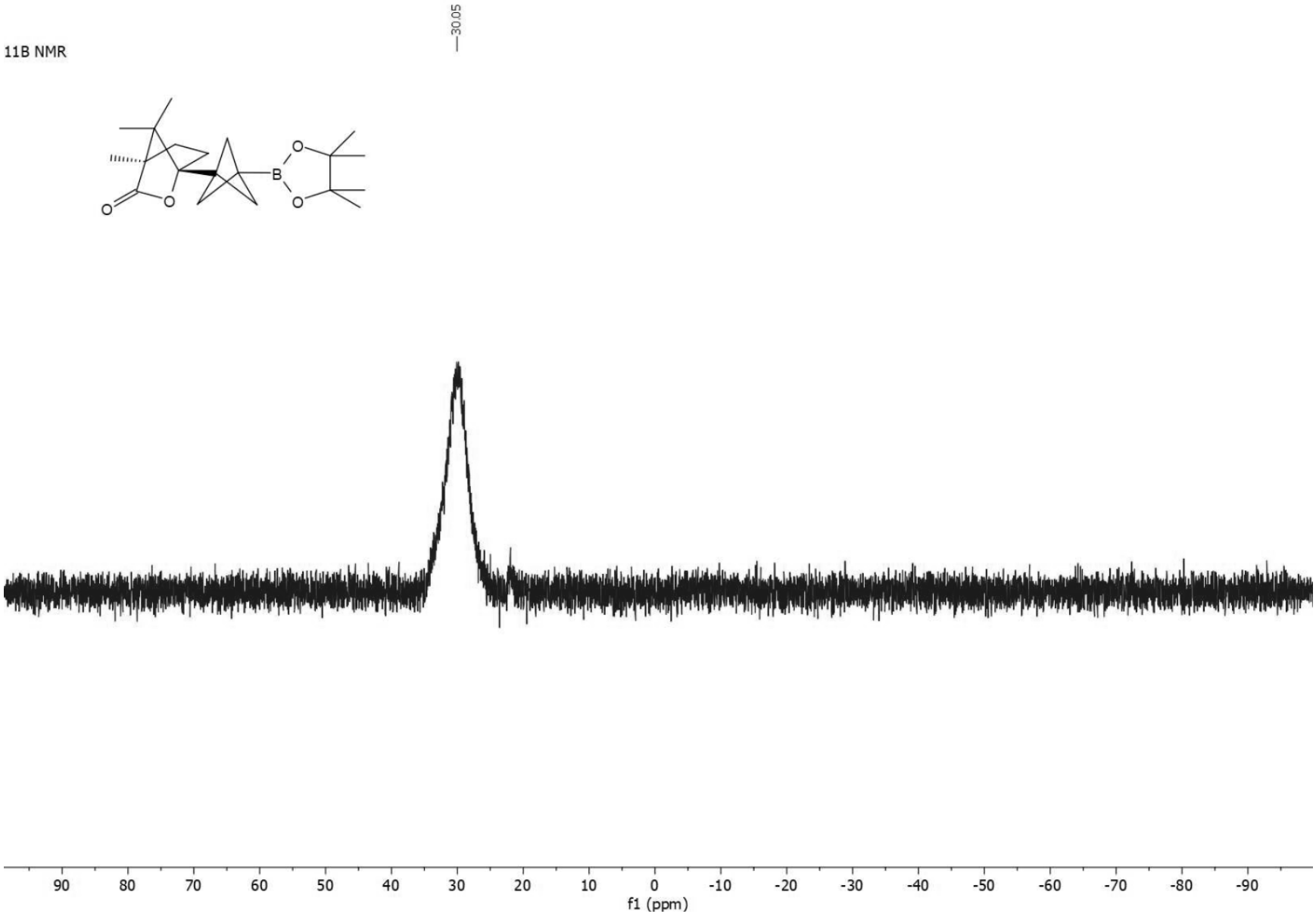
^{1}H NMR (600 MHz, $CDCl_3$) of **4ai**



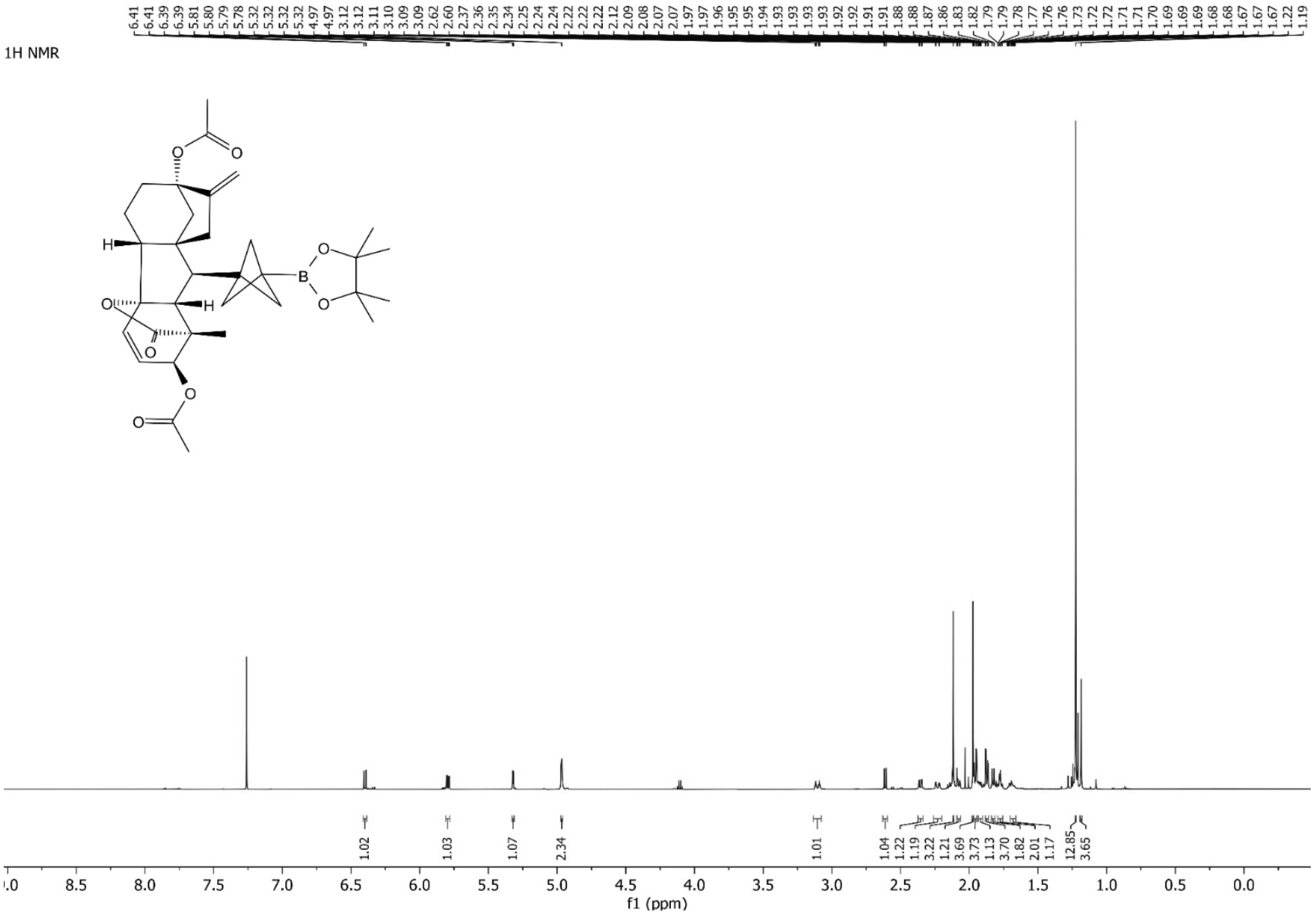
^{13}C NMR (151 MHz, $CDCl_3$) of **4ai**



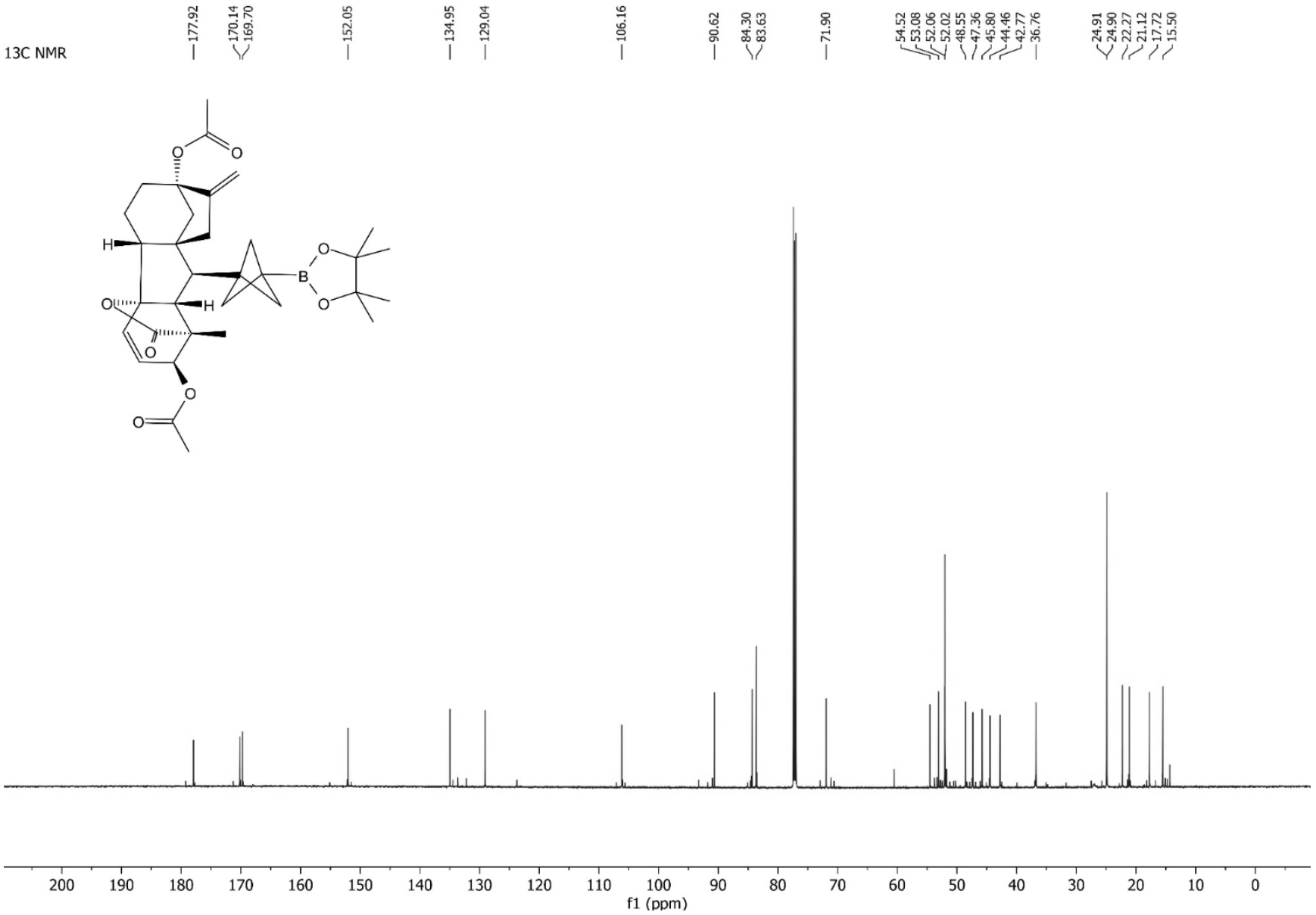
^{11}B NMR (128 MHz, $CDCl_3$) of **4ai**



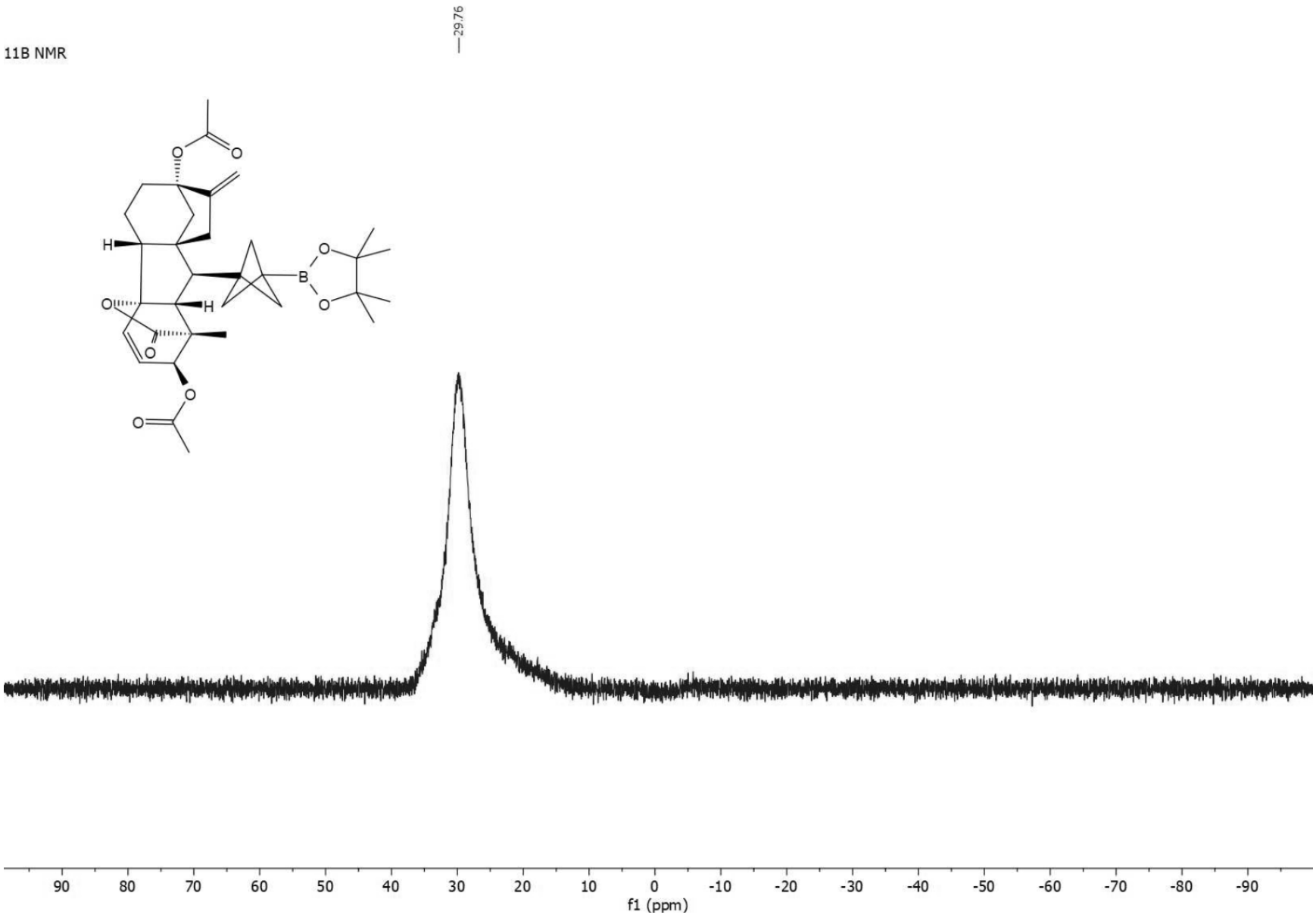
^{1}H NMR (600 MHz, $CDCl_3$) of **4aj**



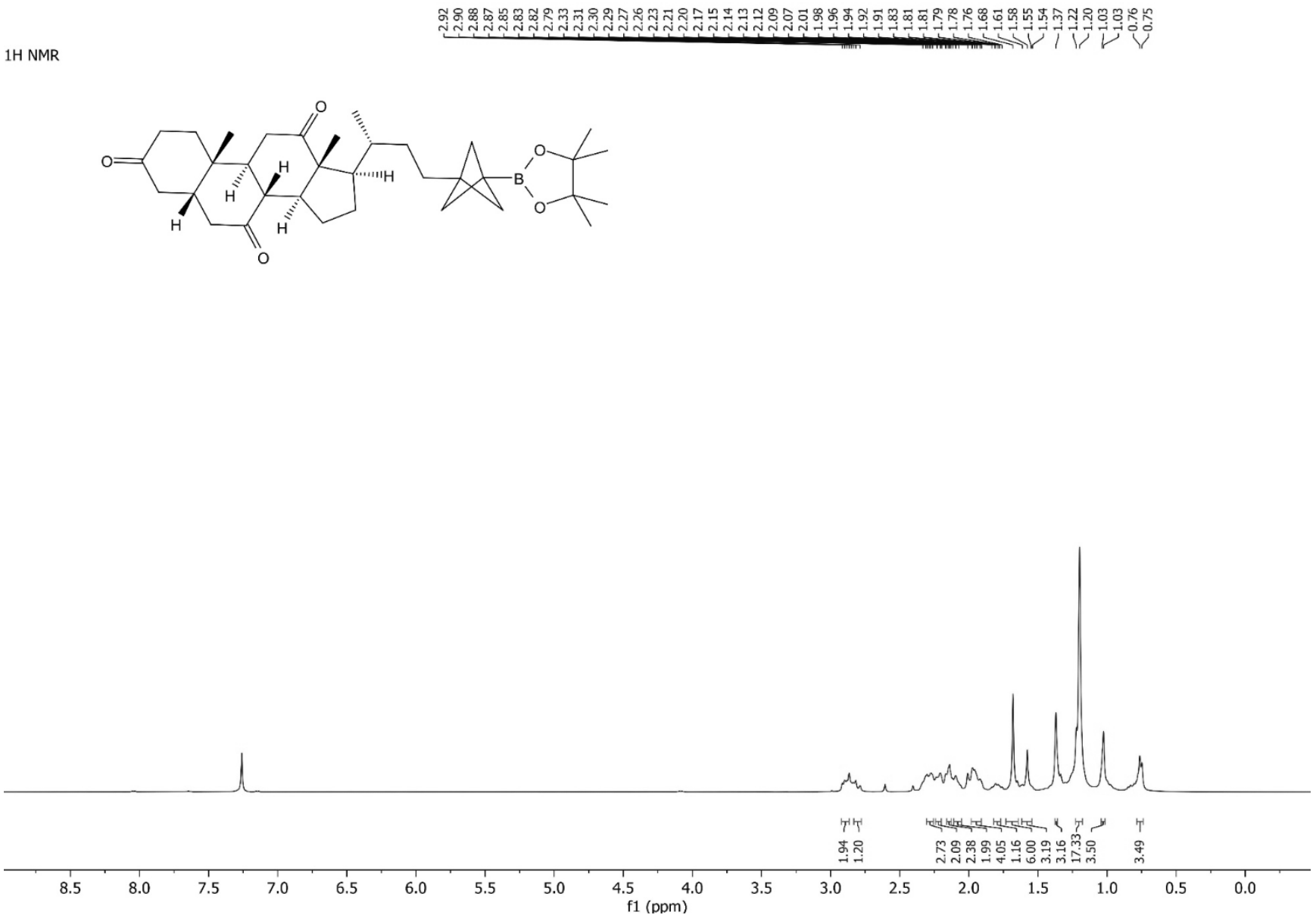
^{13}C NMR (151 MHz, $CDCl_3$) of **4aj**



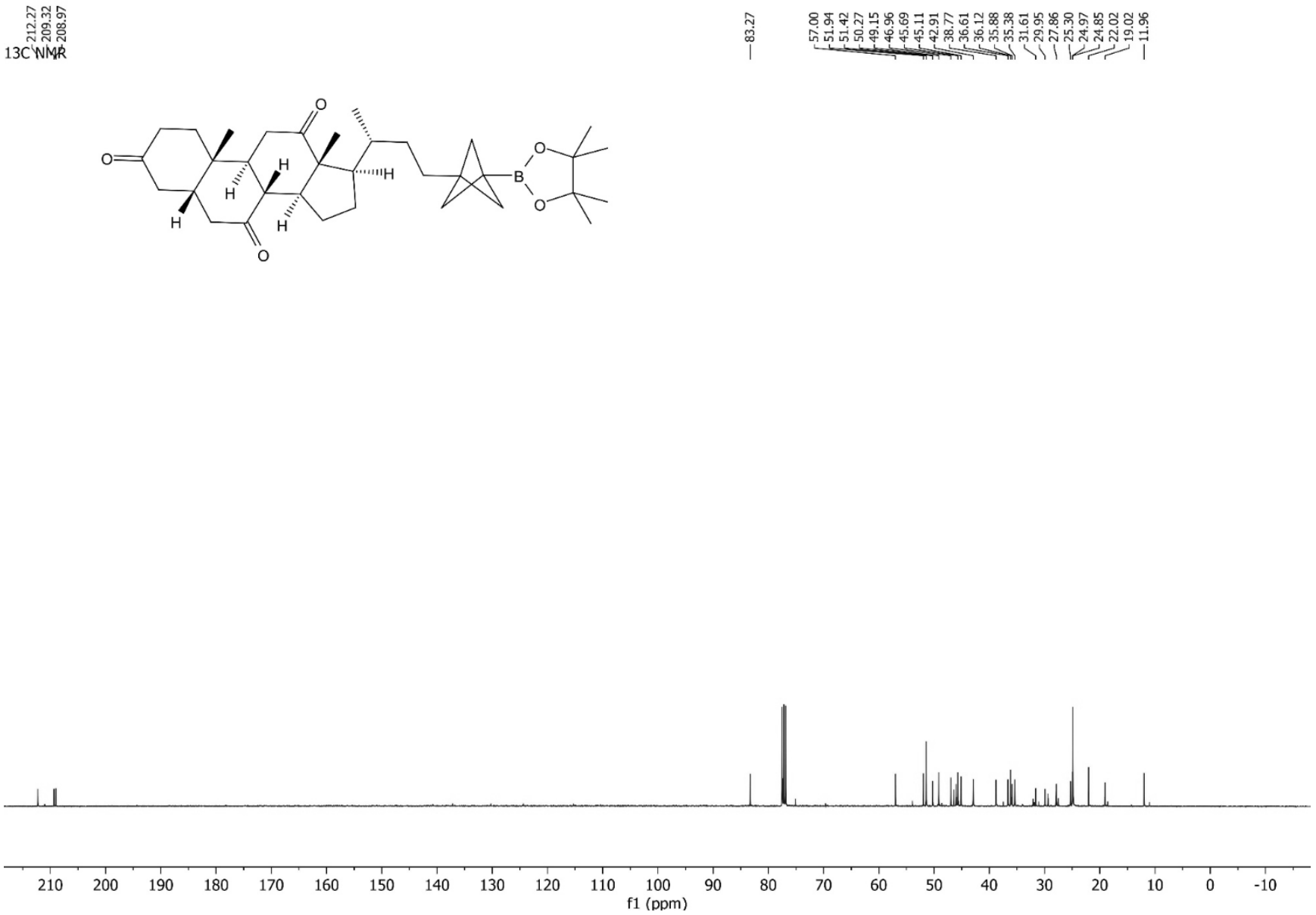
^{11}B NMR (128 MHz, $CDCl_3$) of **4aj**



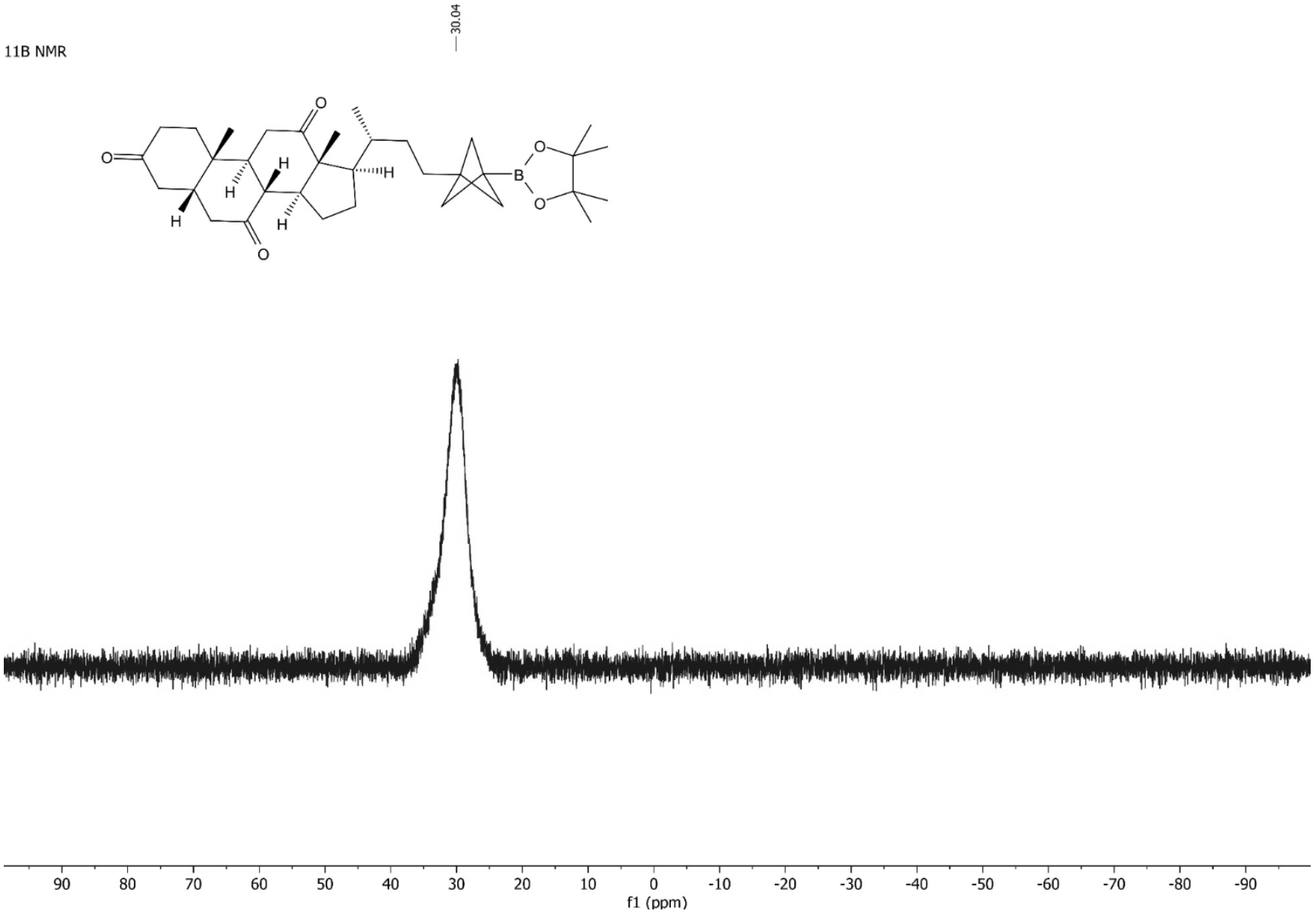
^{1}H NMR (600 MHz, $CDCl_3$) of **4ak**



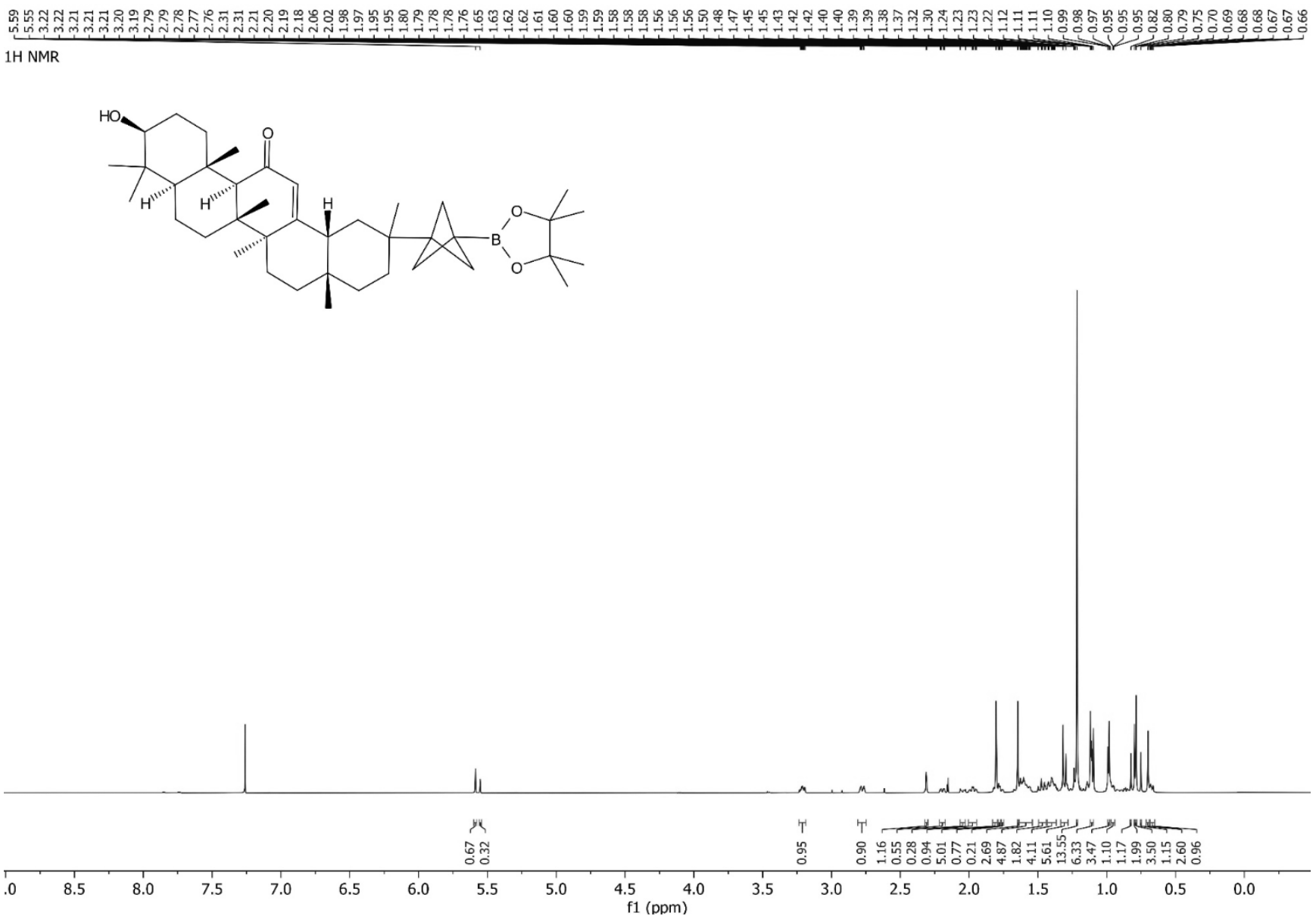
^{13}C NMR (151 MHz, $CDCl_3$) of **4ak**



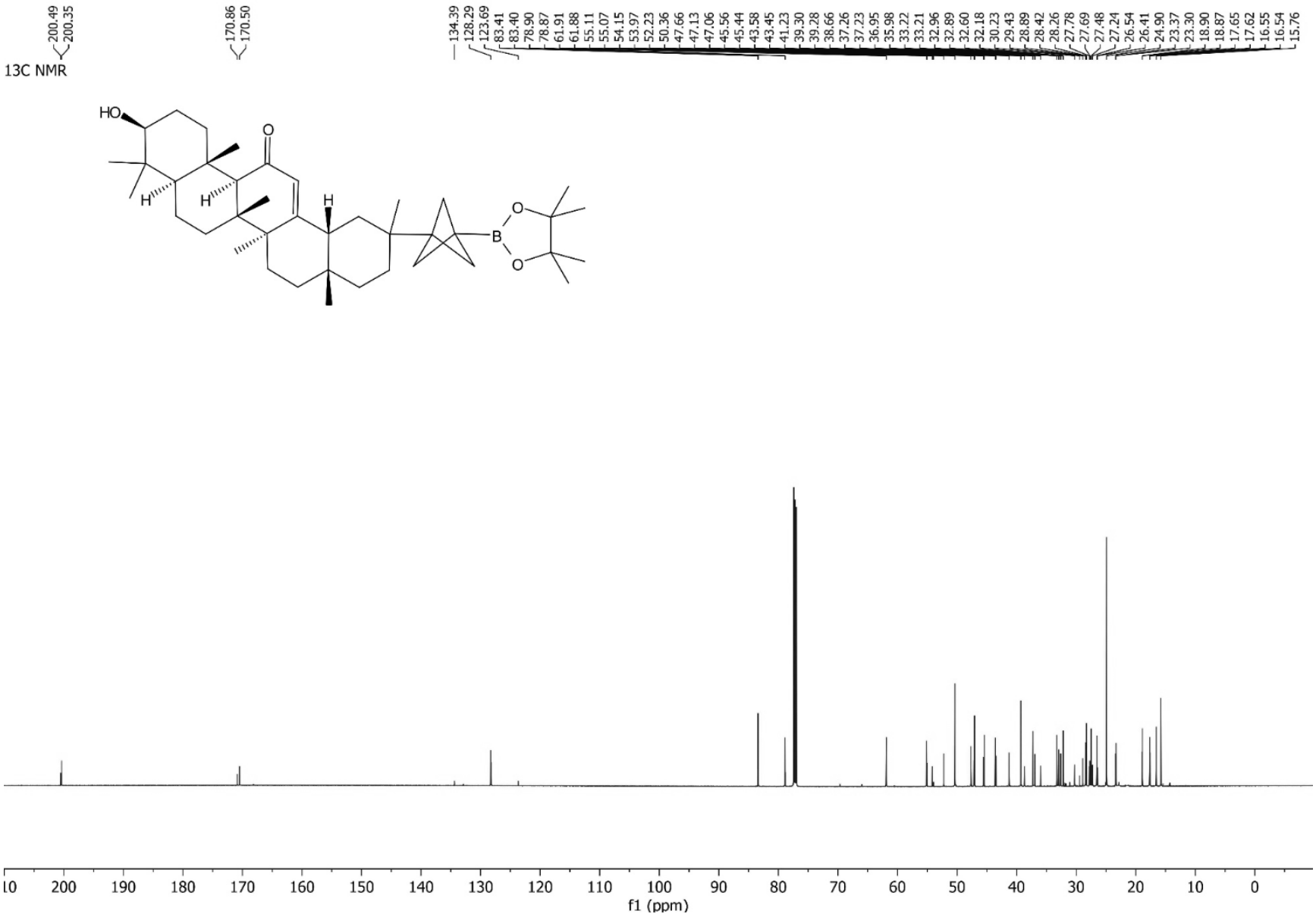
^{11}B NMR (128 MHz, $CDCl_3$) of **4ak**



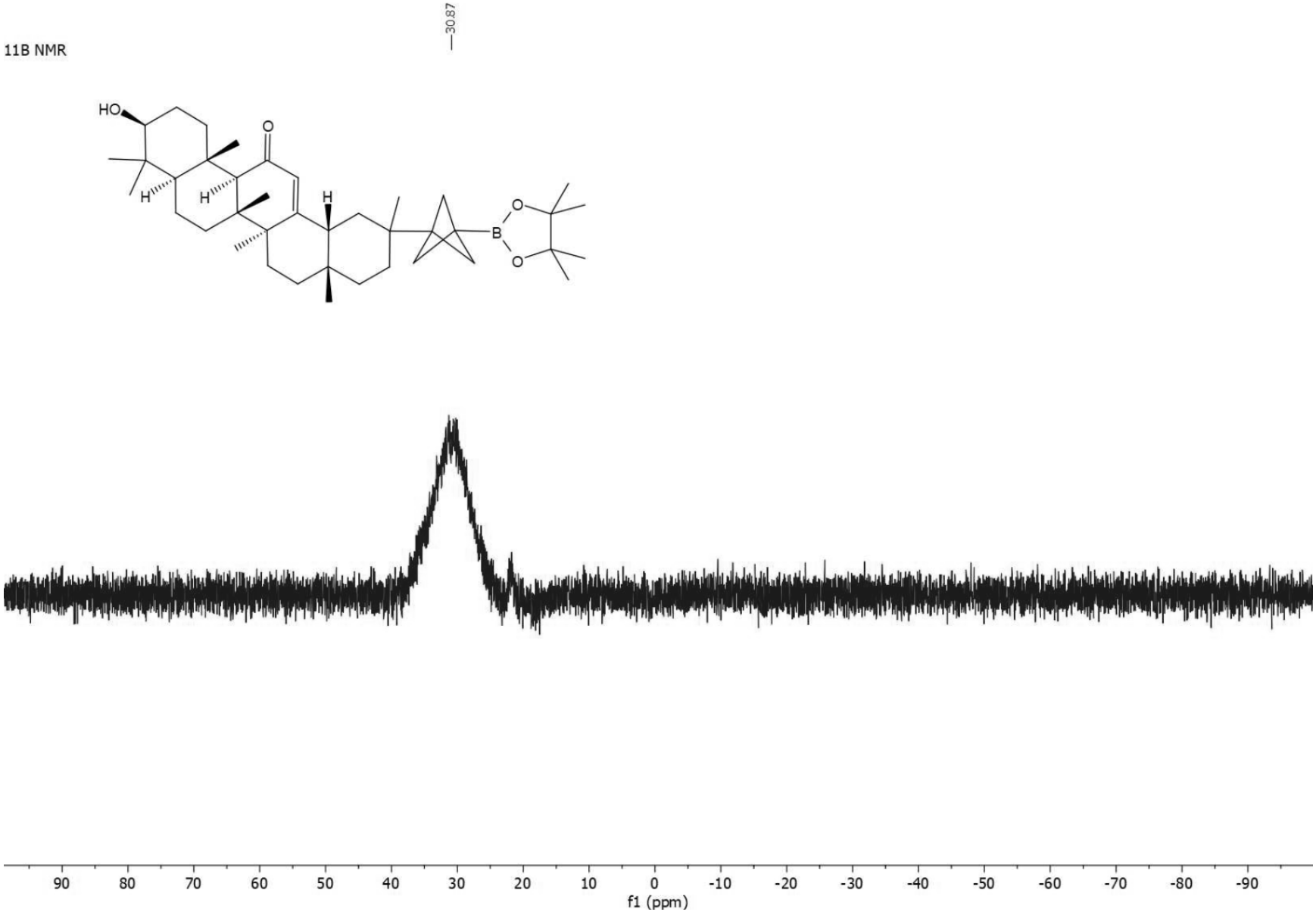
^{1}H NMR (600 MHz, $CDCl_3$) of **4al**



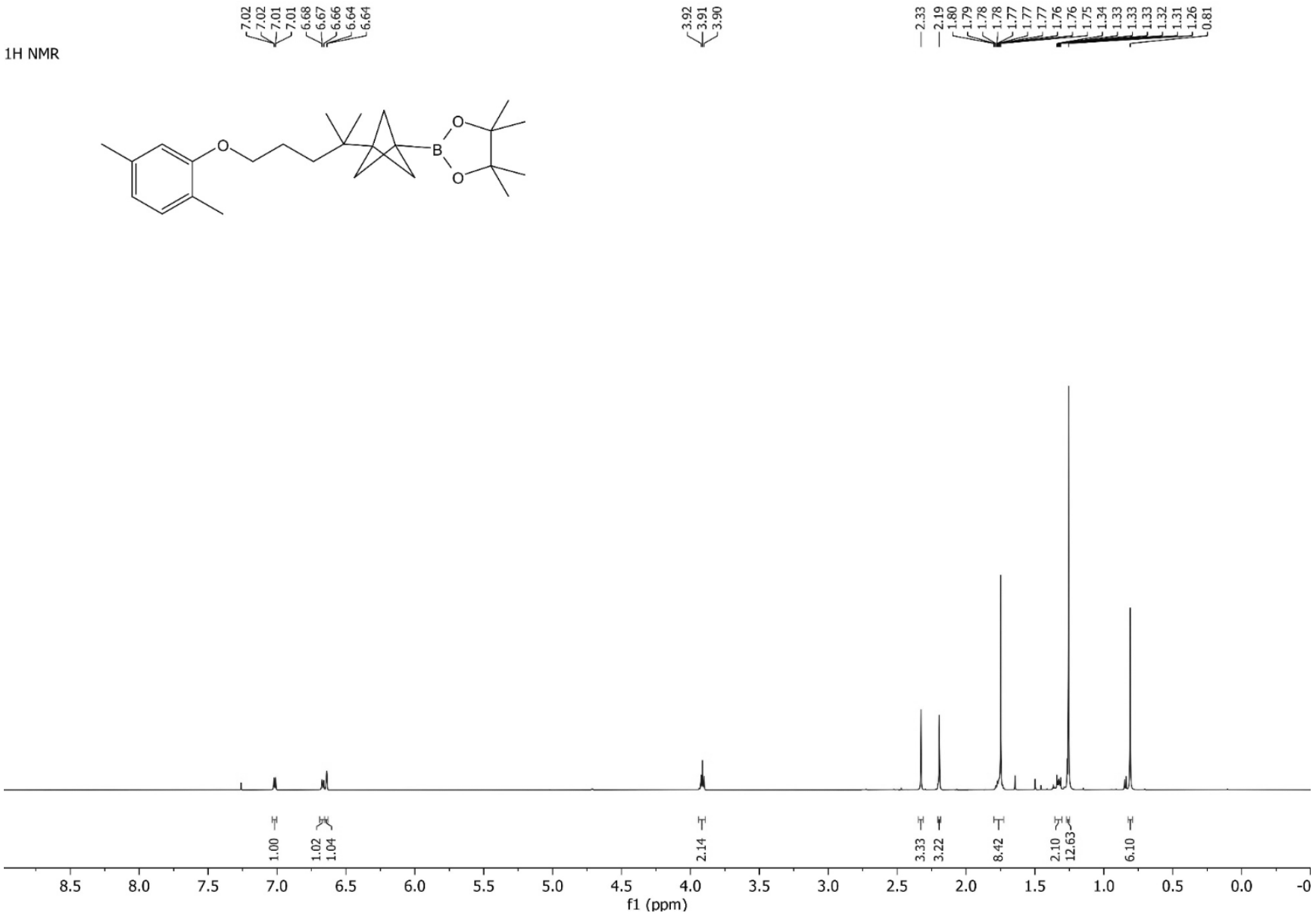
^{13}C NMR (151 MHz, $CDCl_3$) of **4al**



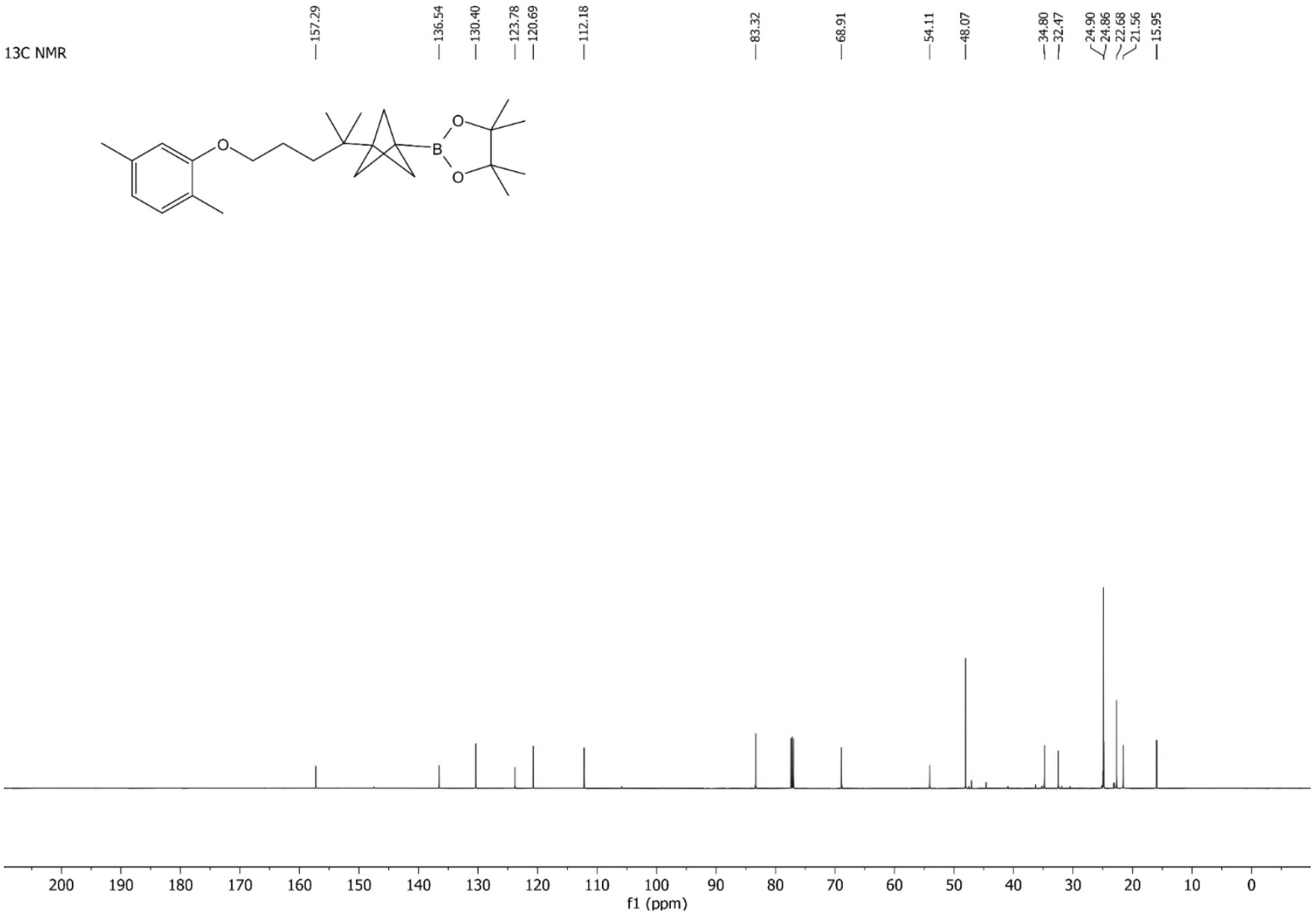
^{11}B NMR (128 MHz, $CDCl_3$) of **4al**



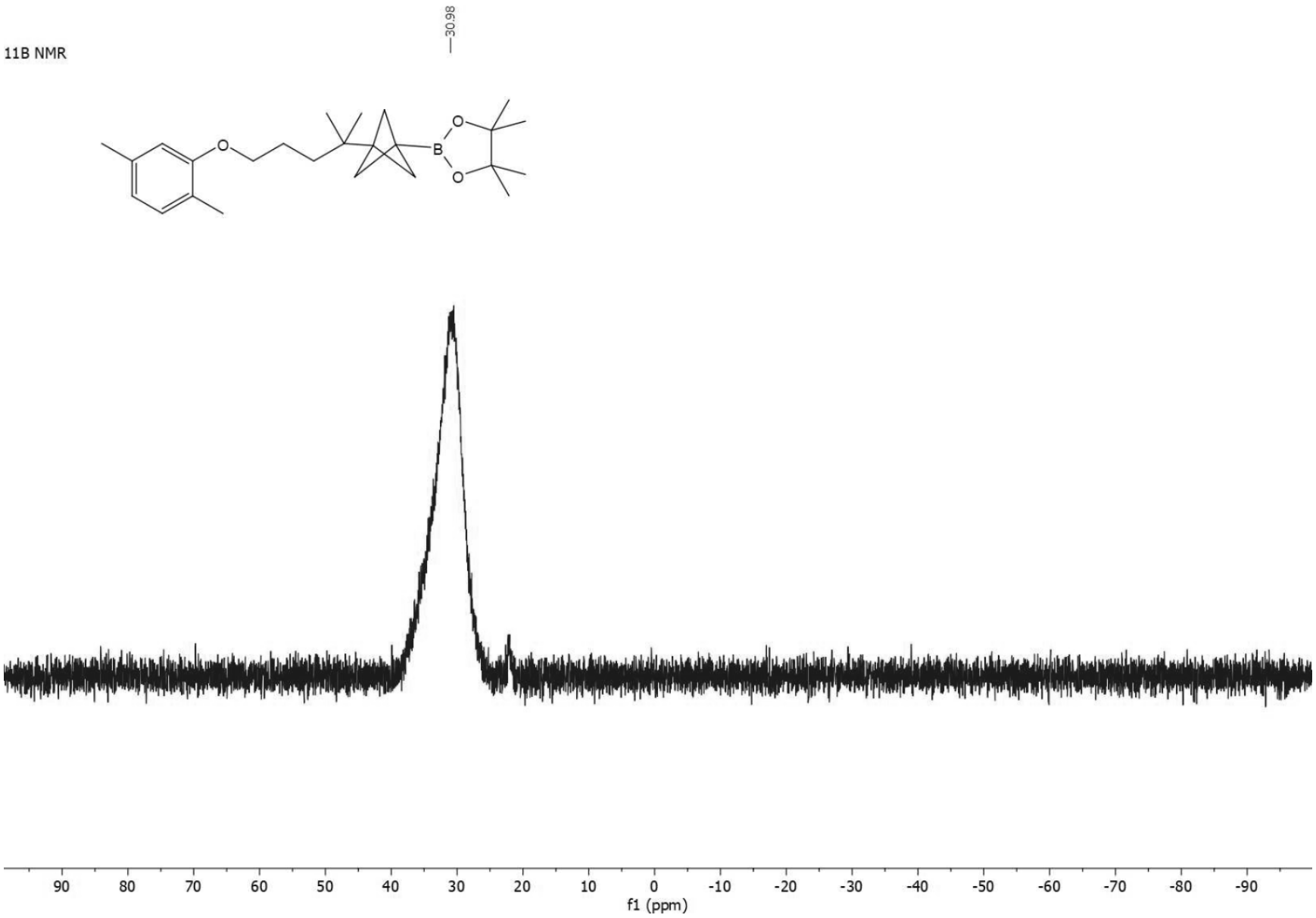
^{1}H NMR (600 MHz, $CDCl_3$) of **4am**



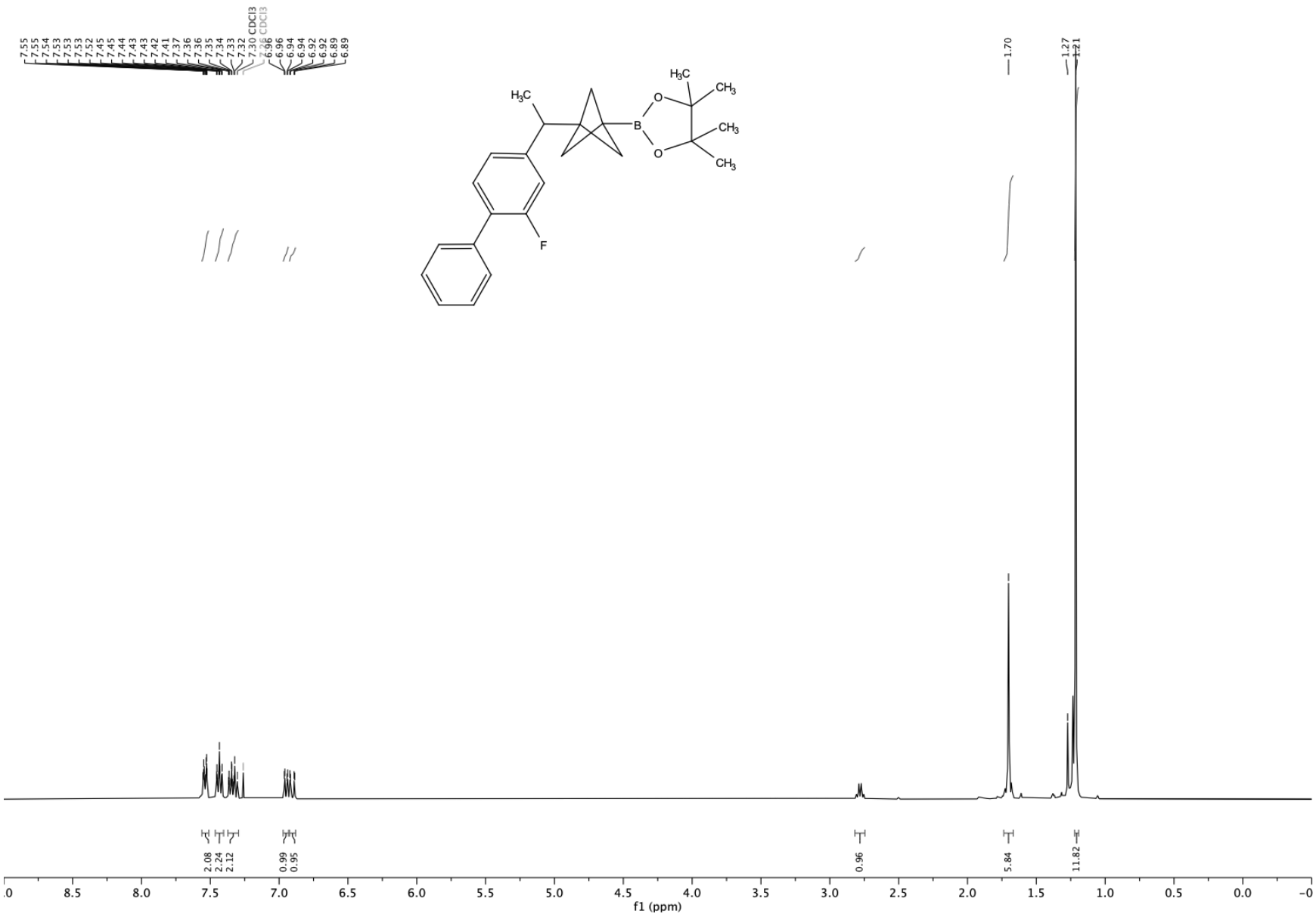
^{13}C NMR (151 MHz, $CDCl_3$) of **4am**



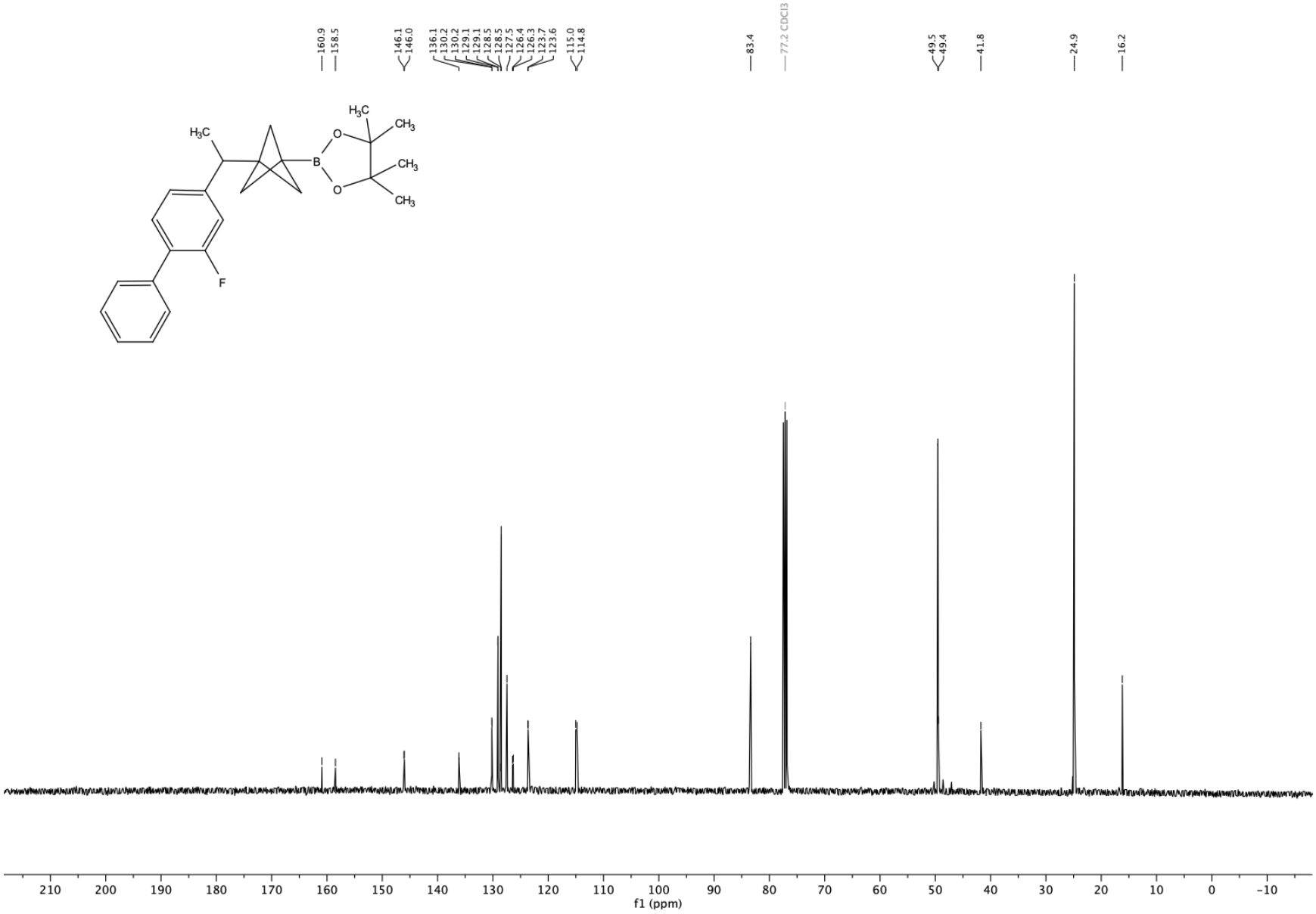
^{11}B NMR (128 MHz, $CDCl_3$) of **4am**



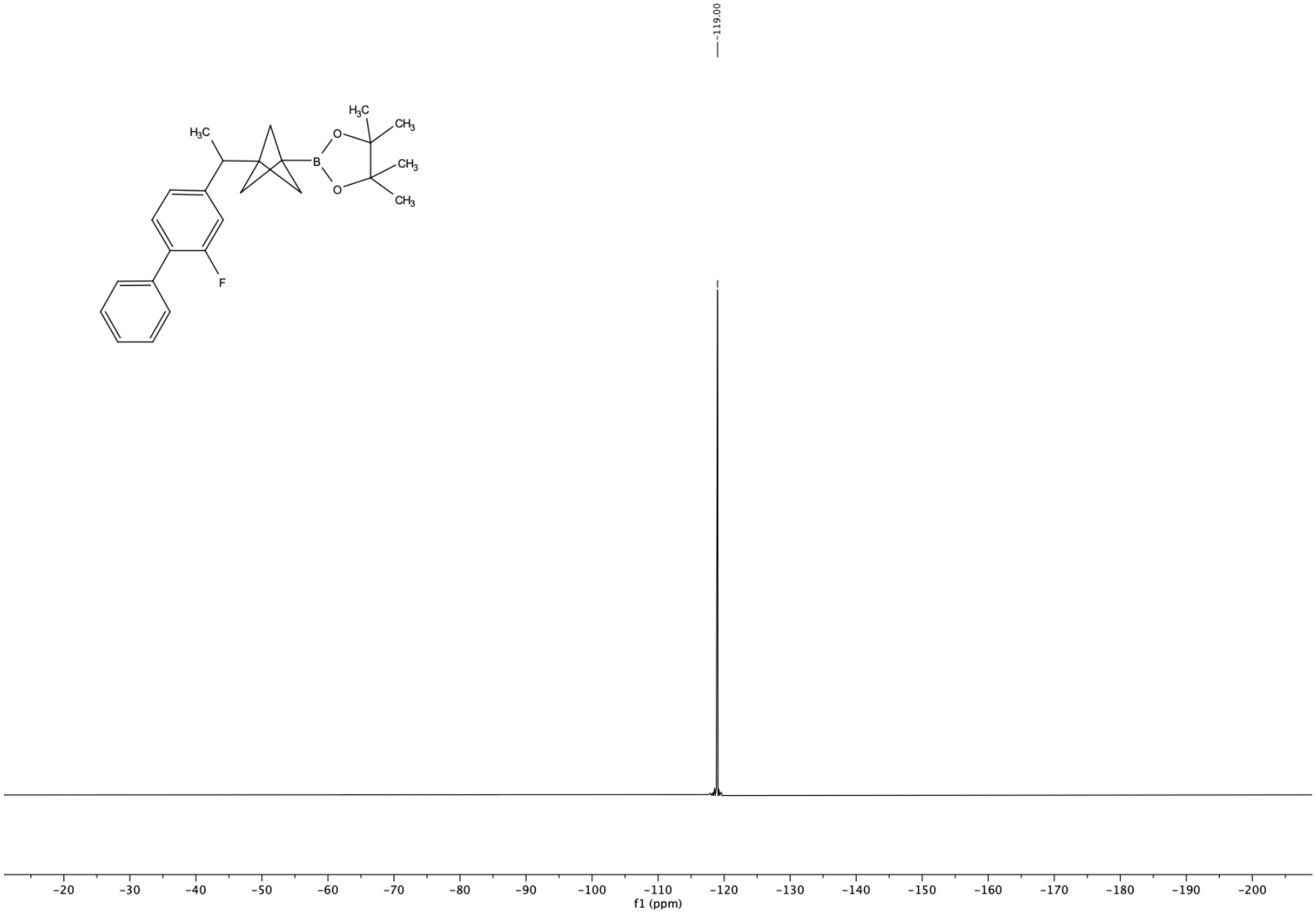
^{1}H NMR (400 MHz, $CDCl_3$) of **4an**



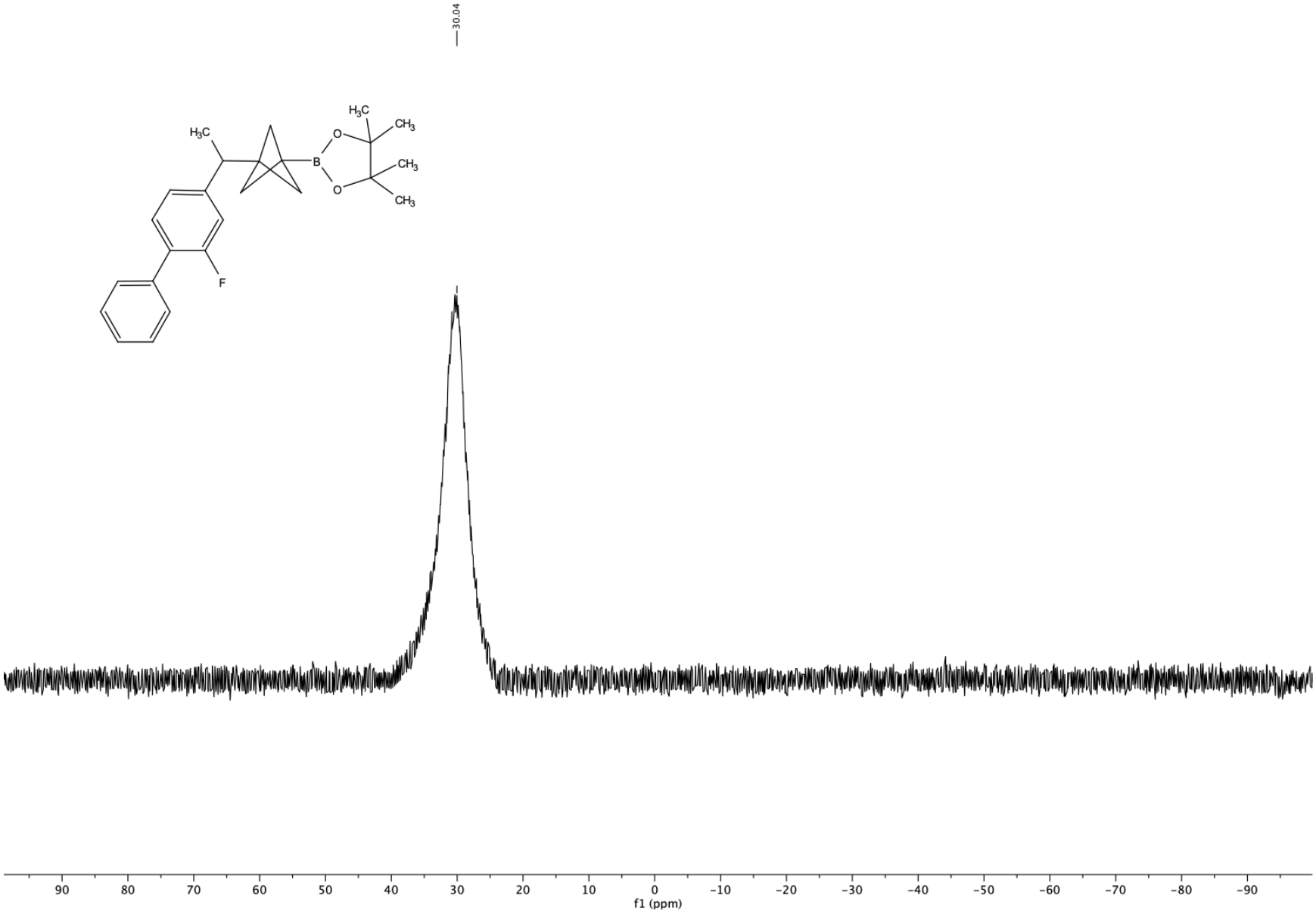
^{13}C NMR (101 MHz, $CDCl_3$) of **4an**



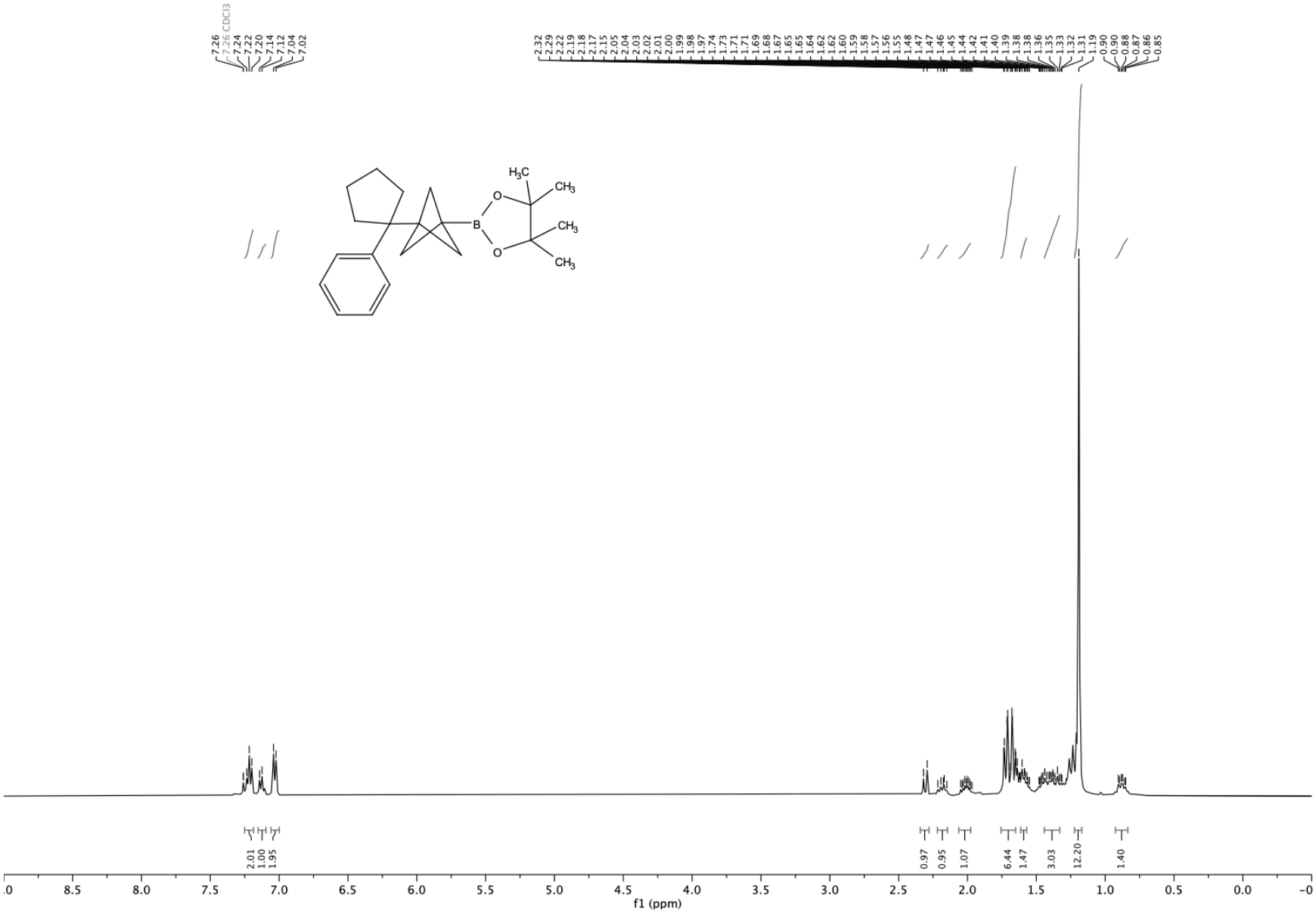
^{19}F NMR (376 MHz, $CDCl_3$) of **4an**



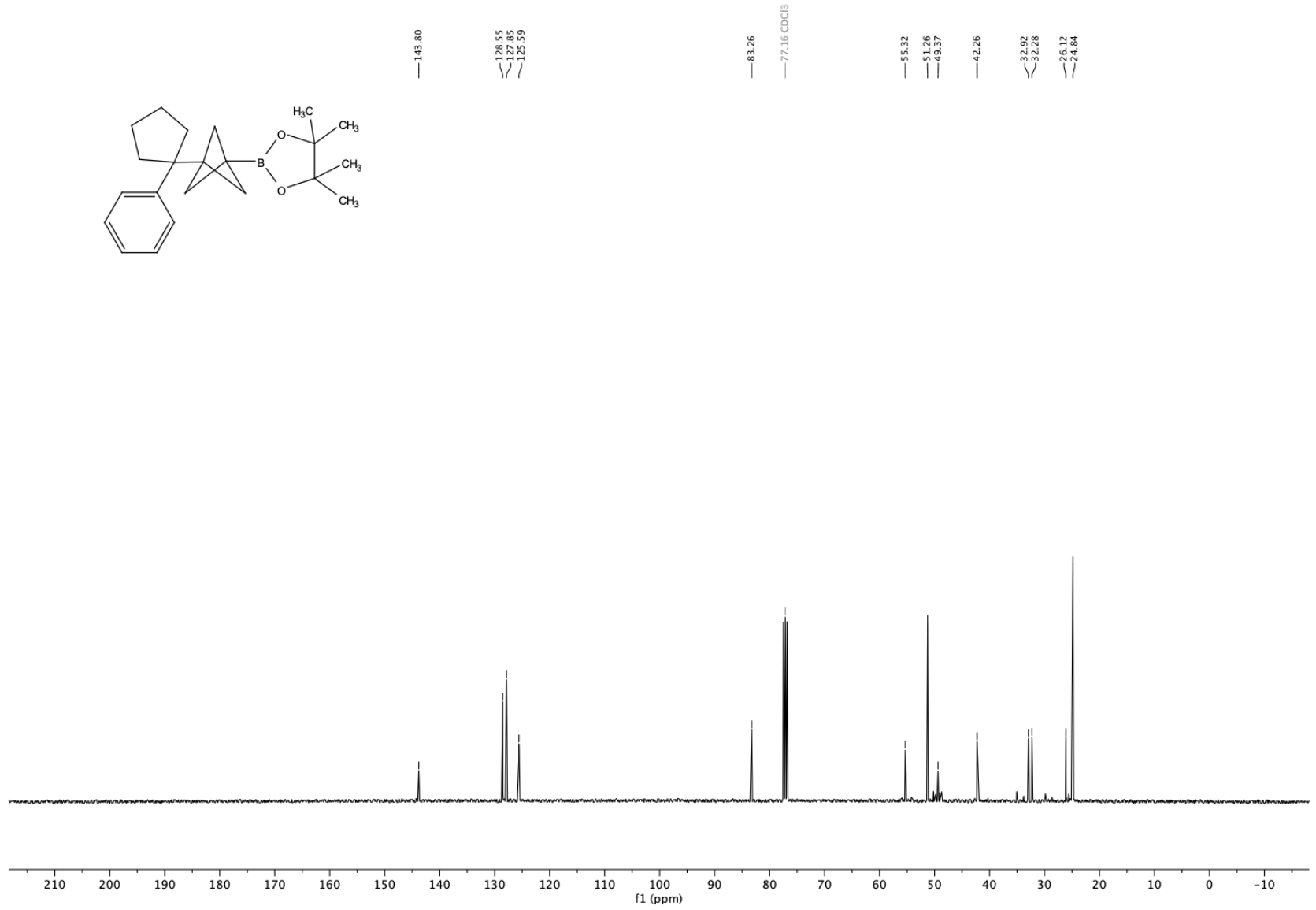
^{11}B NMR (128 MHz, $CDCl_3$) of **4an**



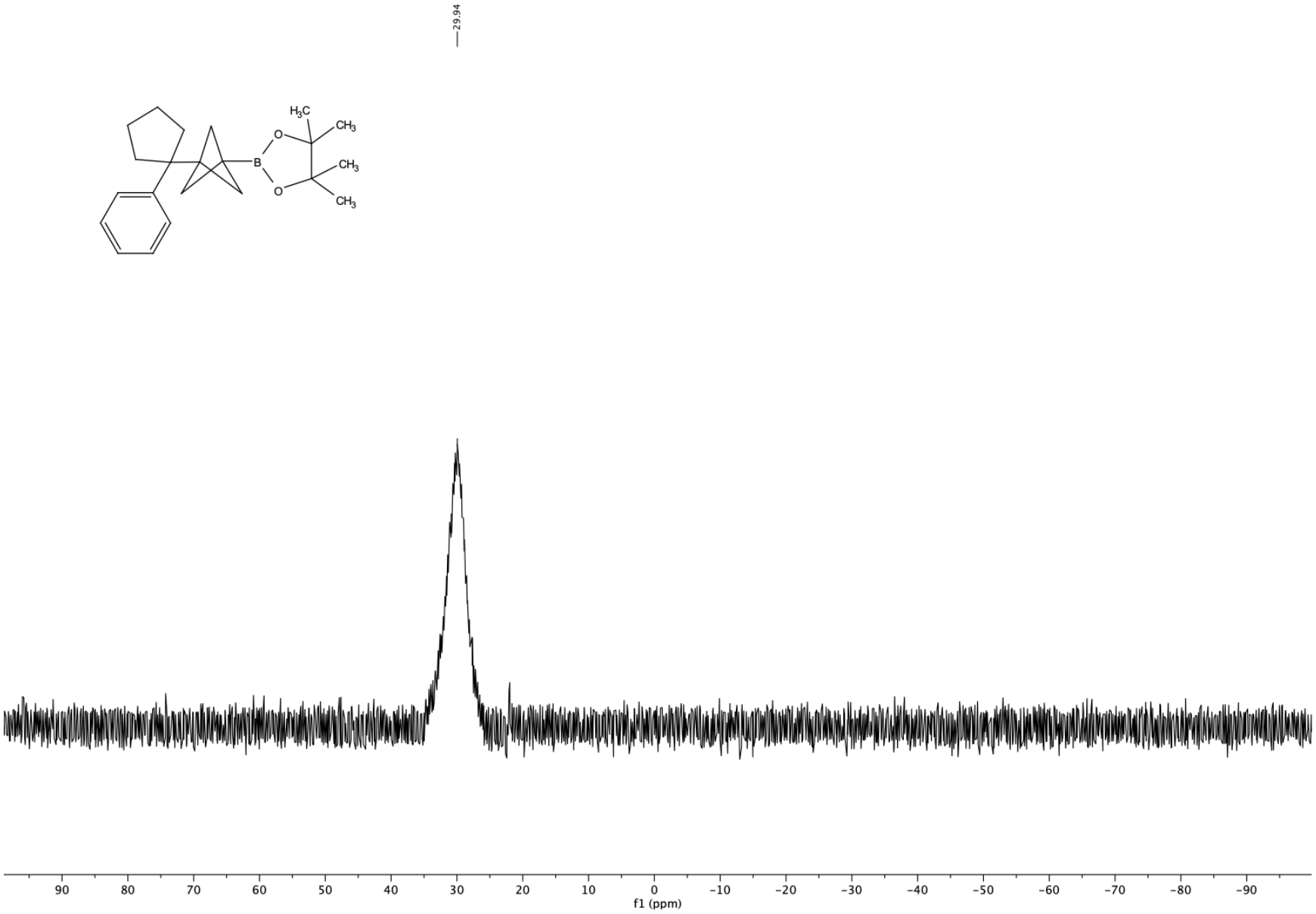
^{1}H NMR (400 MHz, $CDCl_3$) of **4ao**



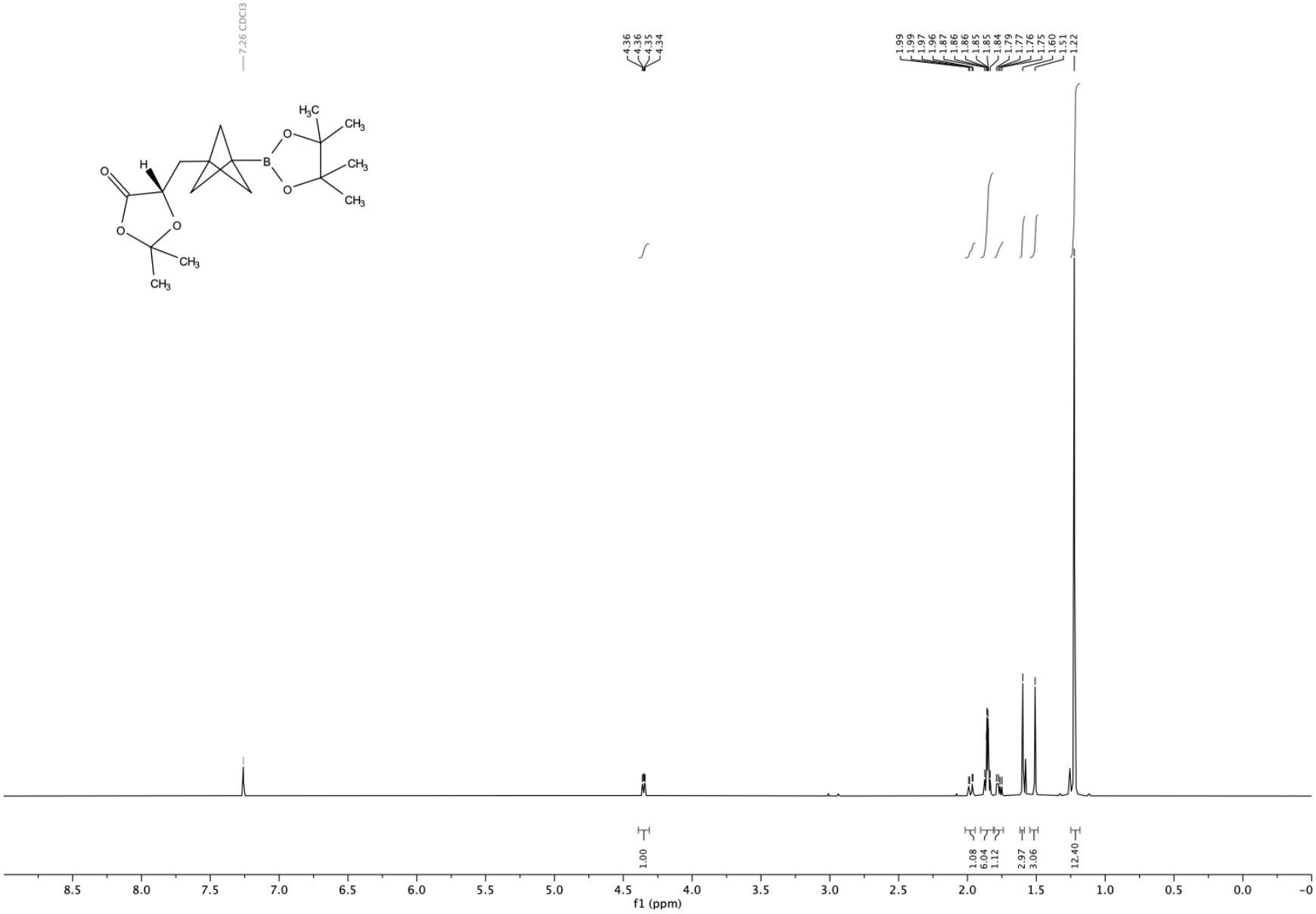
^{13}C NMR (151 MHz, $CDCl_3$) of **4ao**



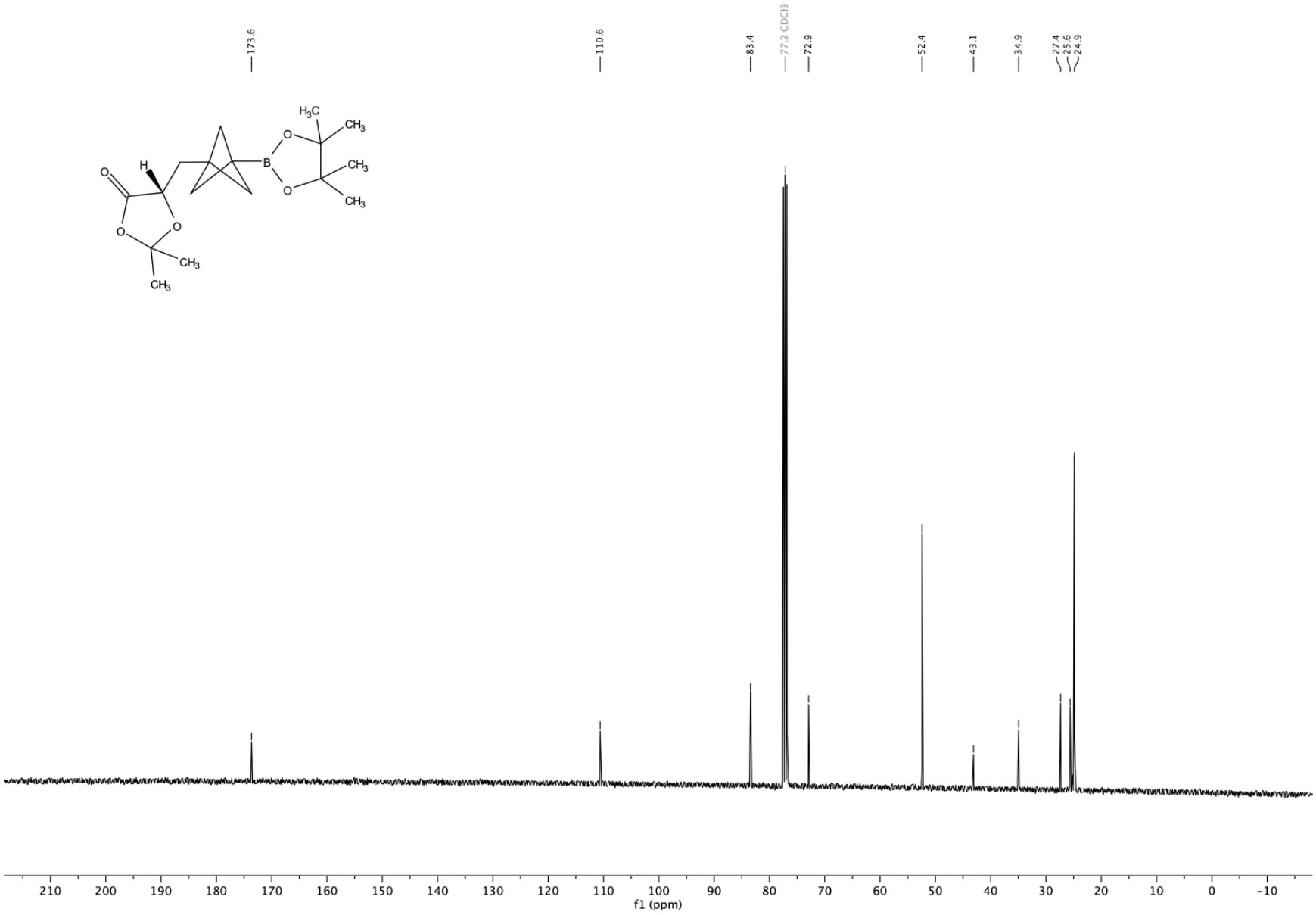
^{11}B NMR (128 MHz, $CDCl_3$) of **4ao**



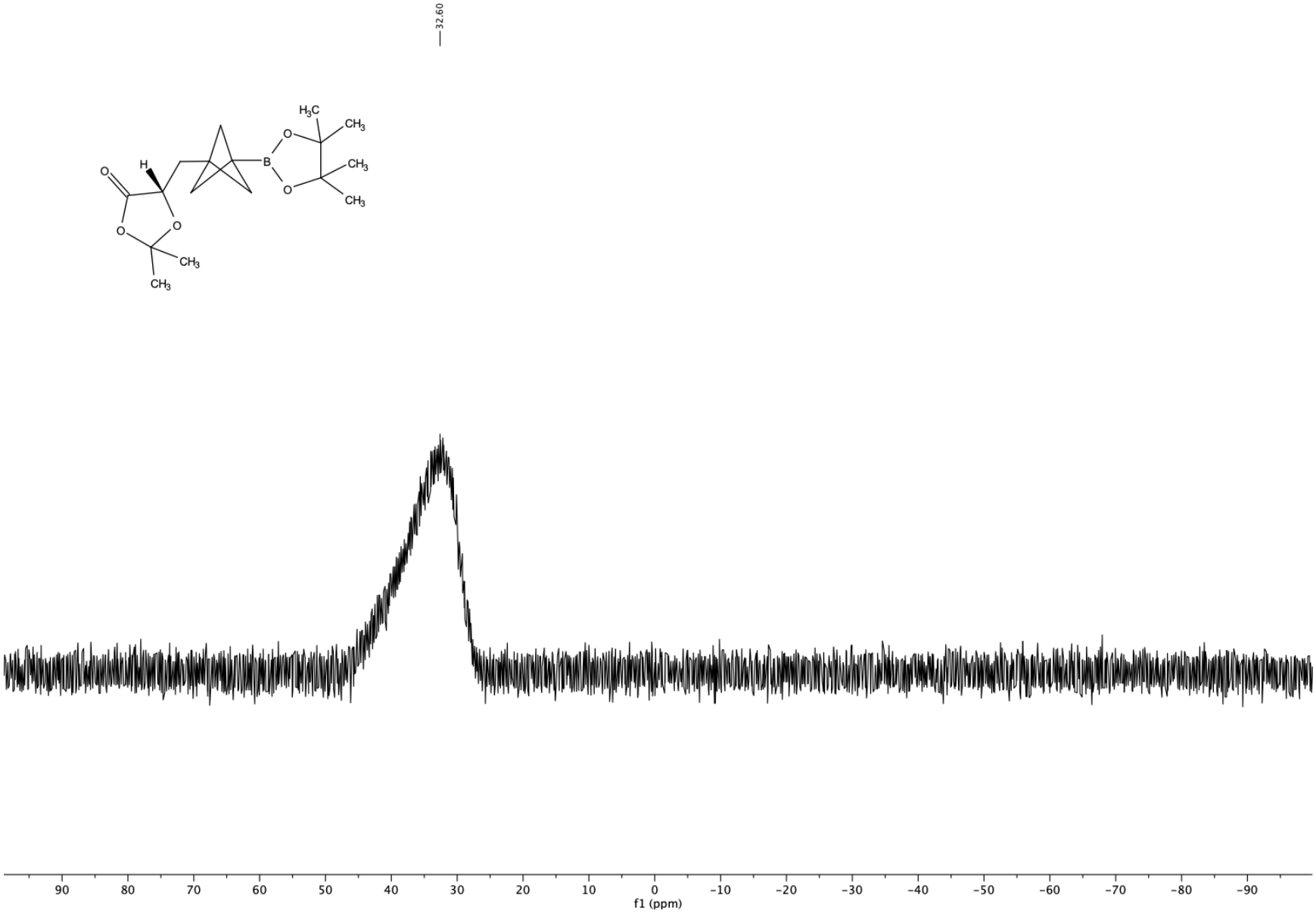
^{1}H NMR (600 MHz, $CDCl_3$) of **4ap**



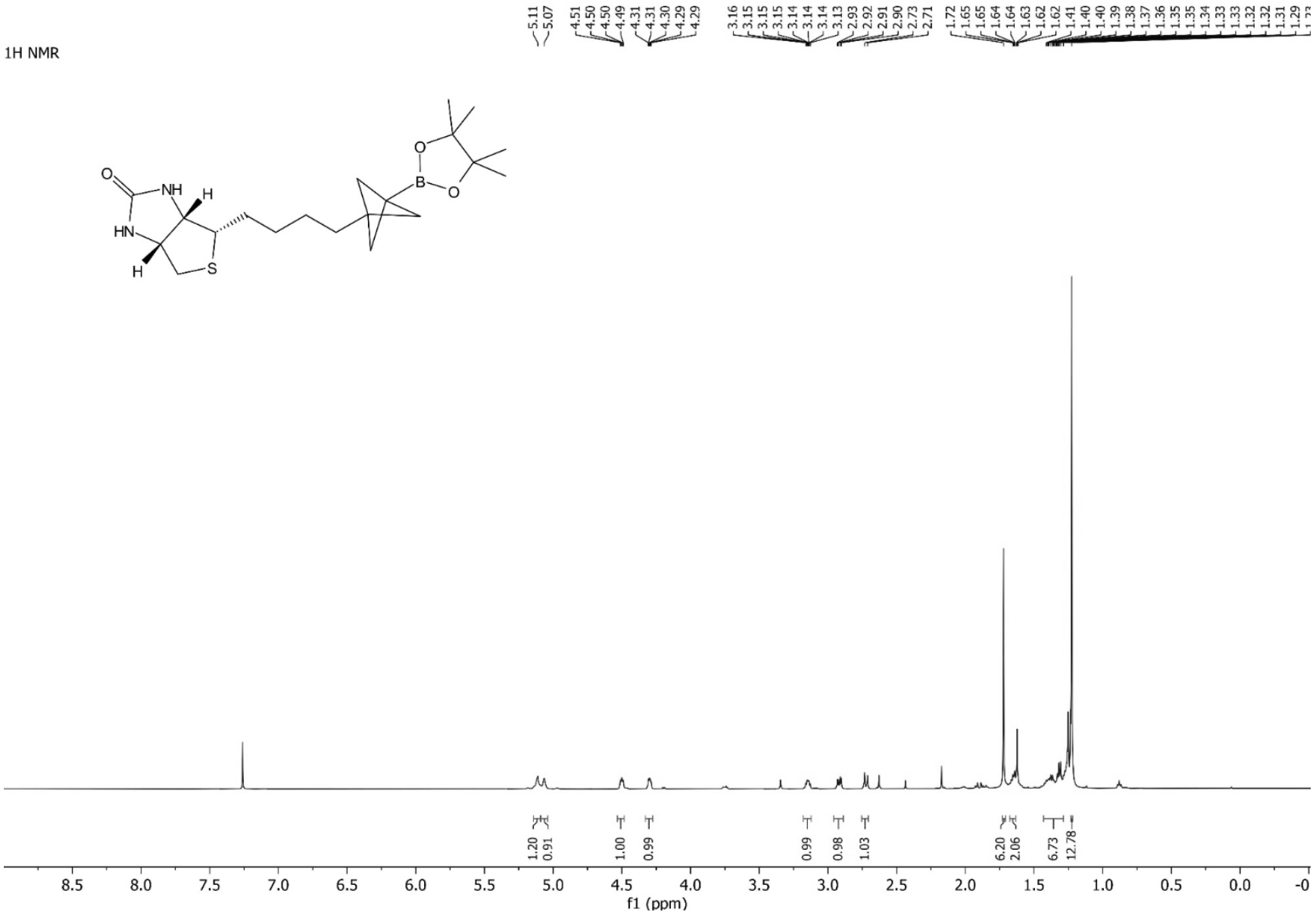
^{13}C NMR (101 MHz, $CDCl_3$) of **4ap**



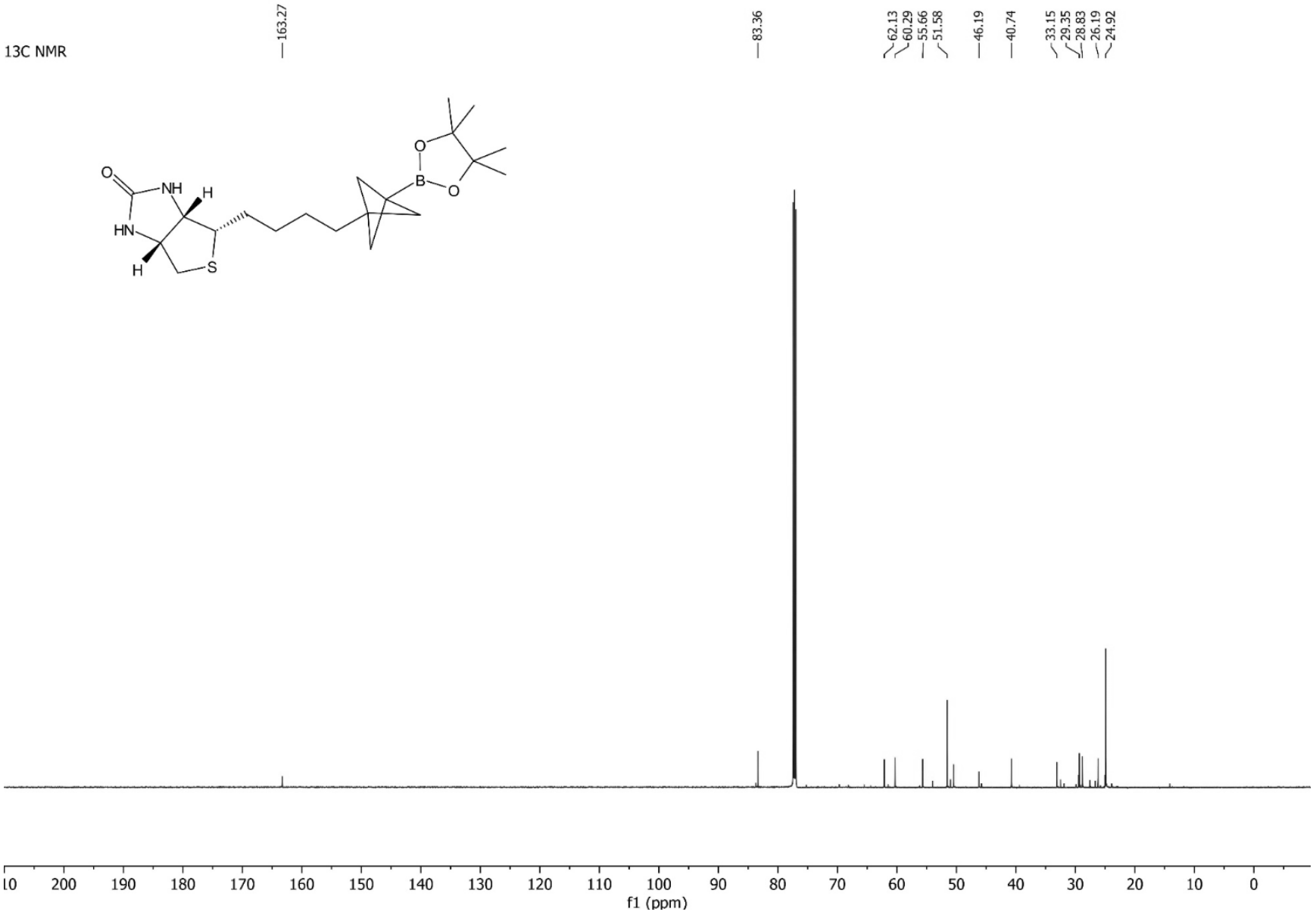
^{11}B NMR (128 MHz, $CDCl_3$) of **4ap**



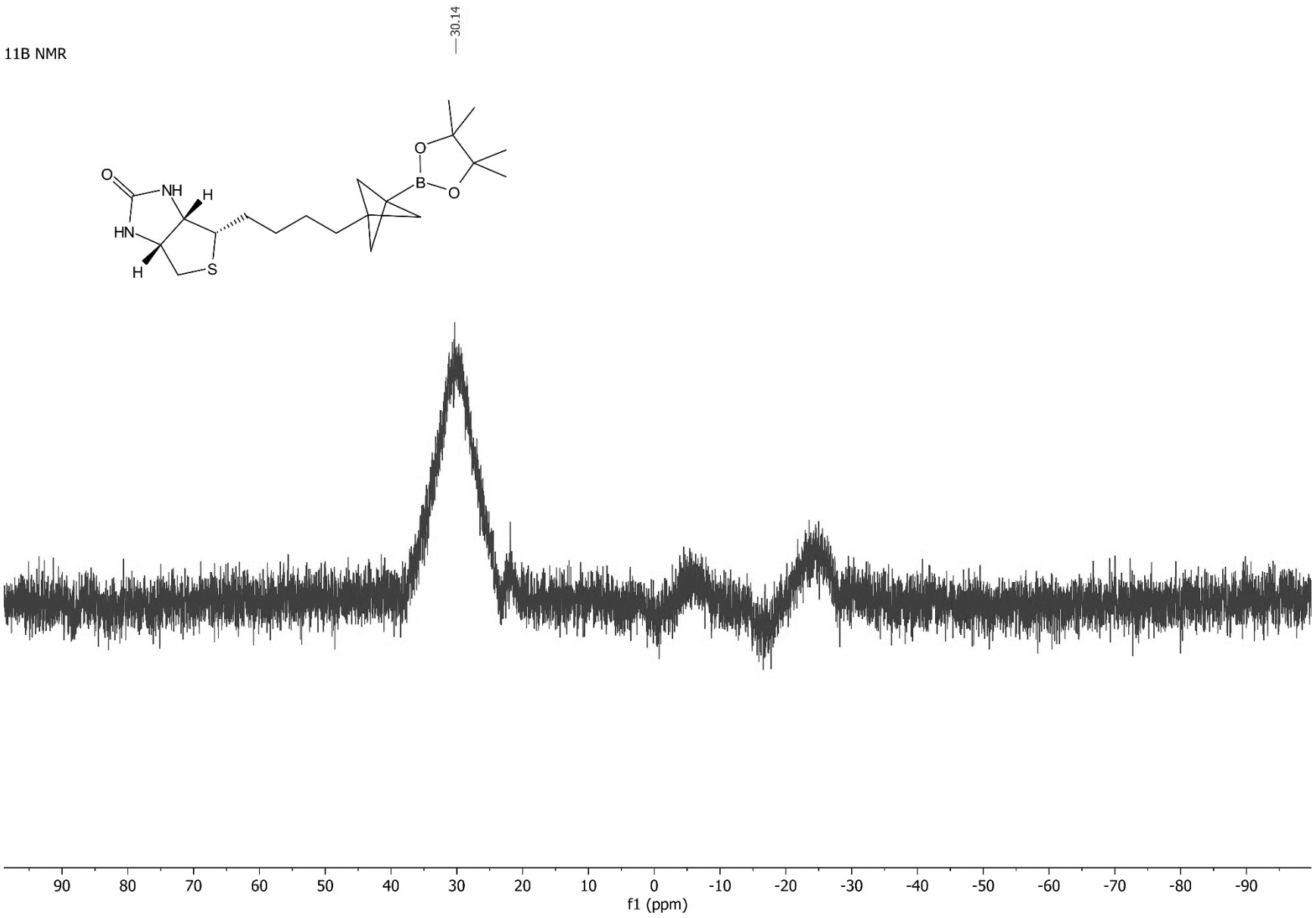
^{1}H NMR (600 MHz, $CDCl_3$) of **4aq**



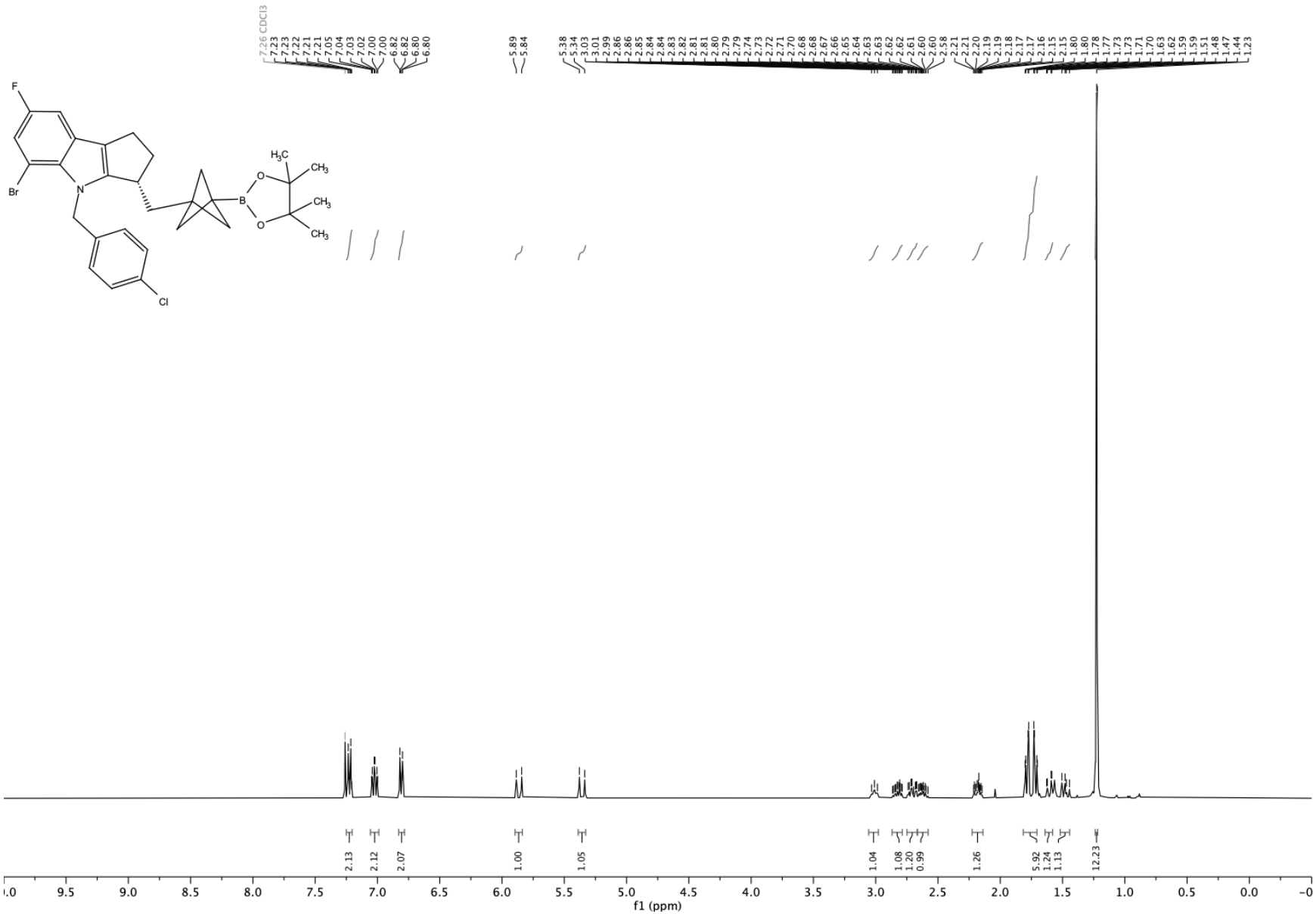
^{11}B NMR (128 MHz, $CDCl_3$) of **4aq**



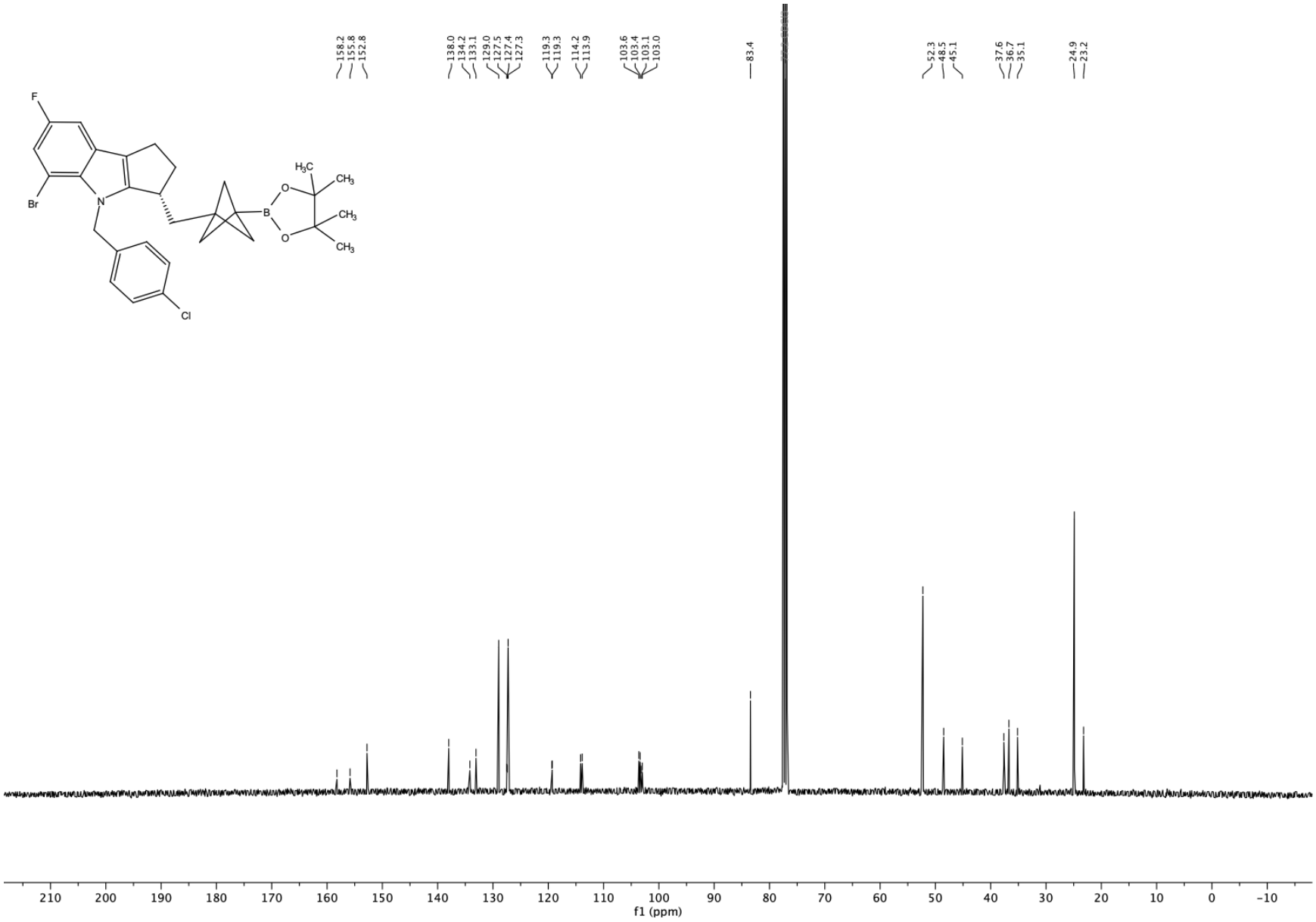
^{13}C NMR (151 MHz, $CDCl_3$) of **4aq**



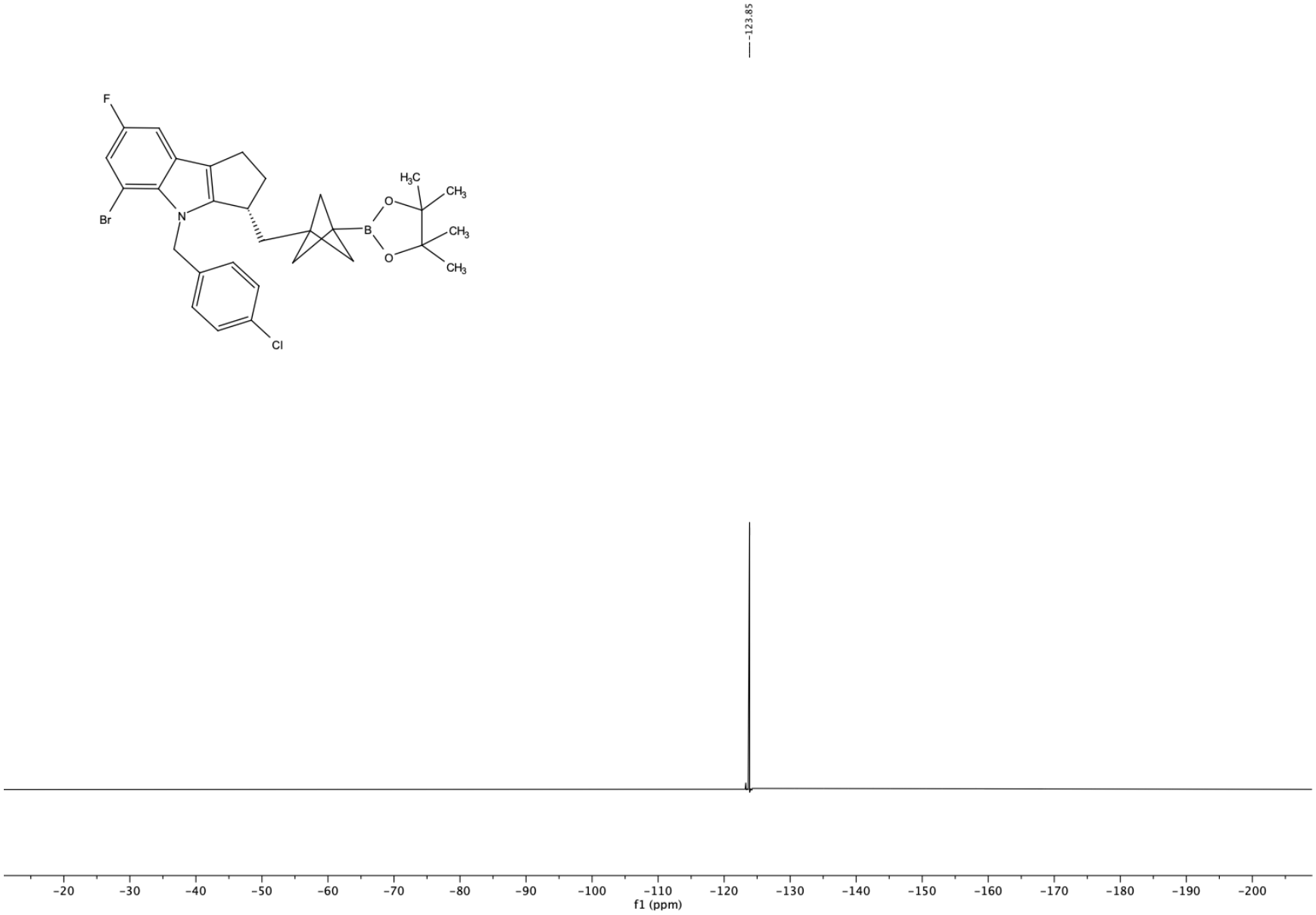
^{1}H NMR (600 MHz, $CDCl_3$) of **4ar**



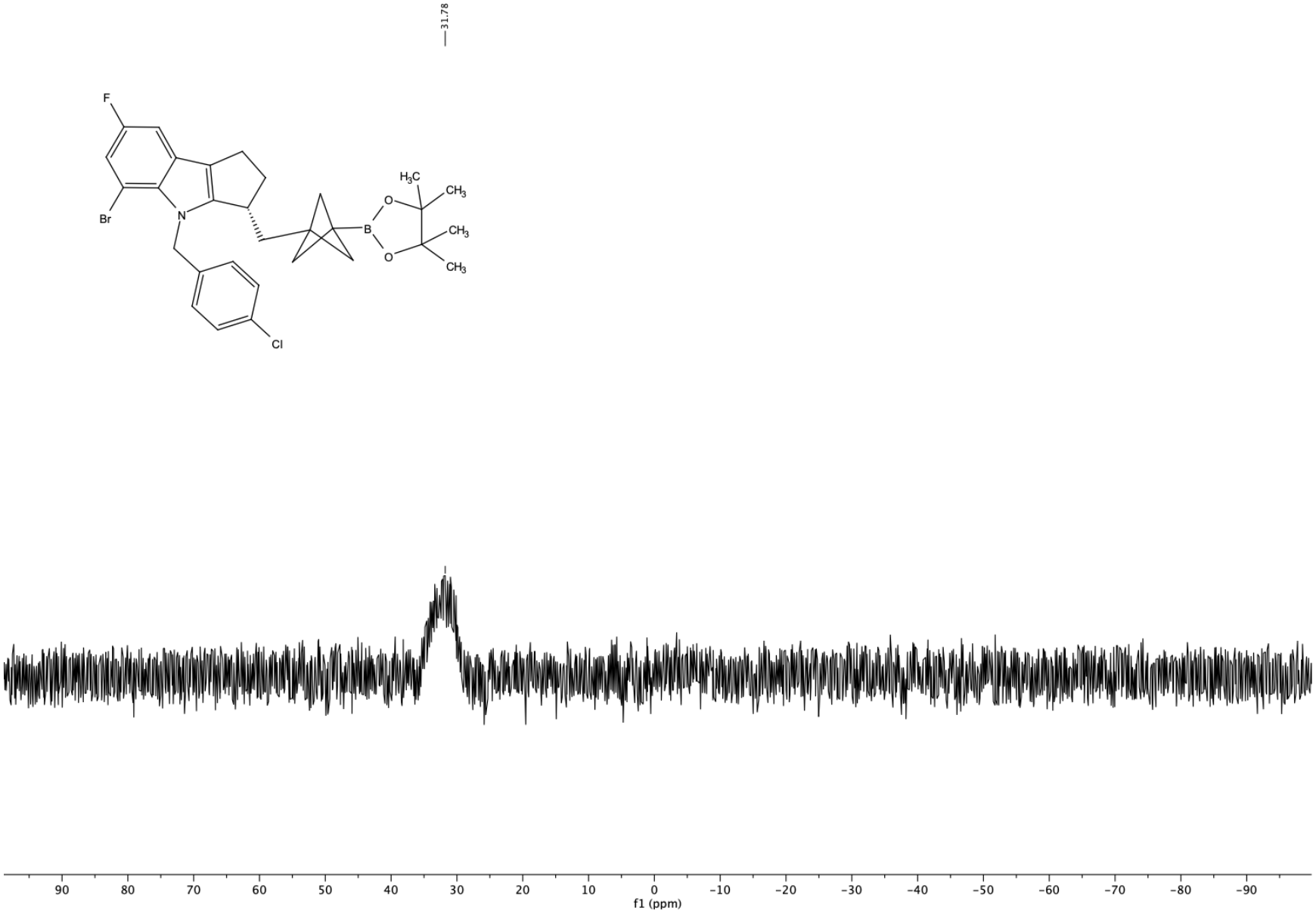
^{13}C NMR (151 MHz, $CDCl_3$) of **4ar**



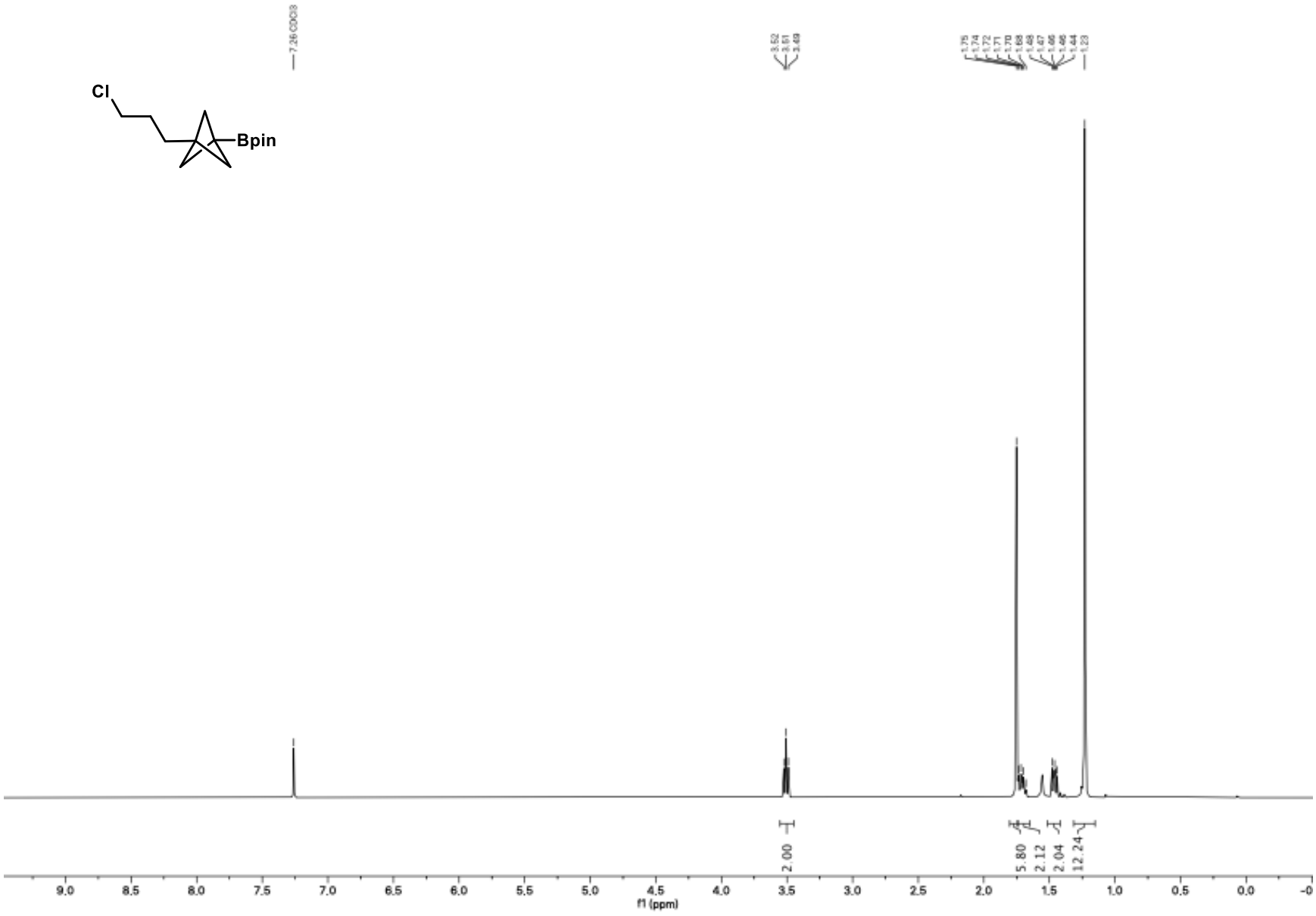
^{19}F NMR (376 MHz, $CDCl_3$) of **4ar**



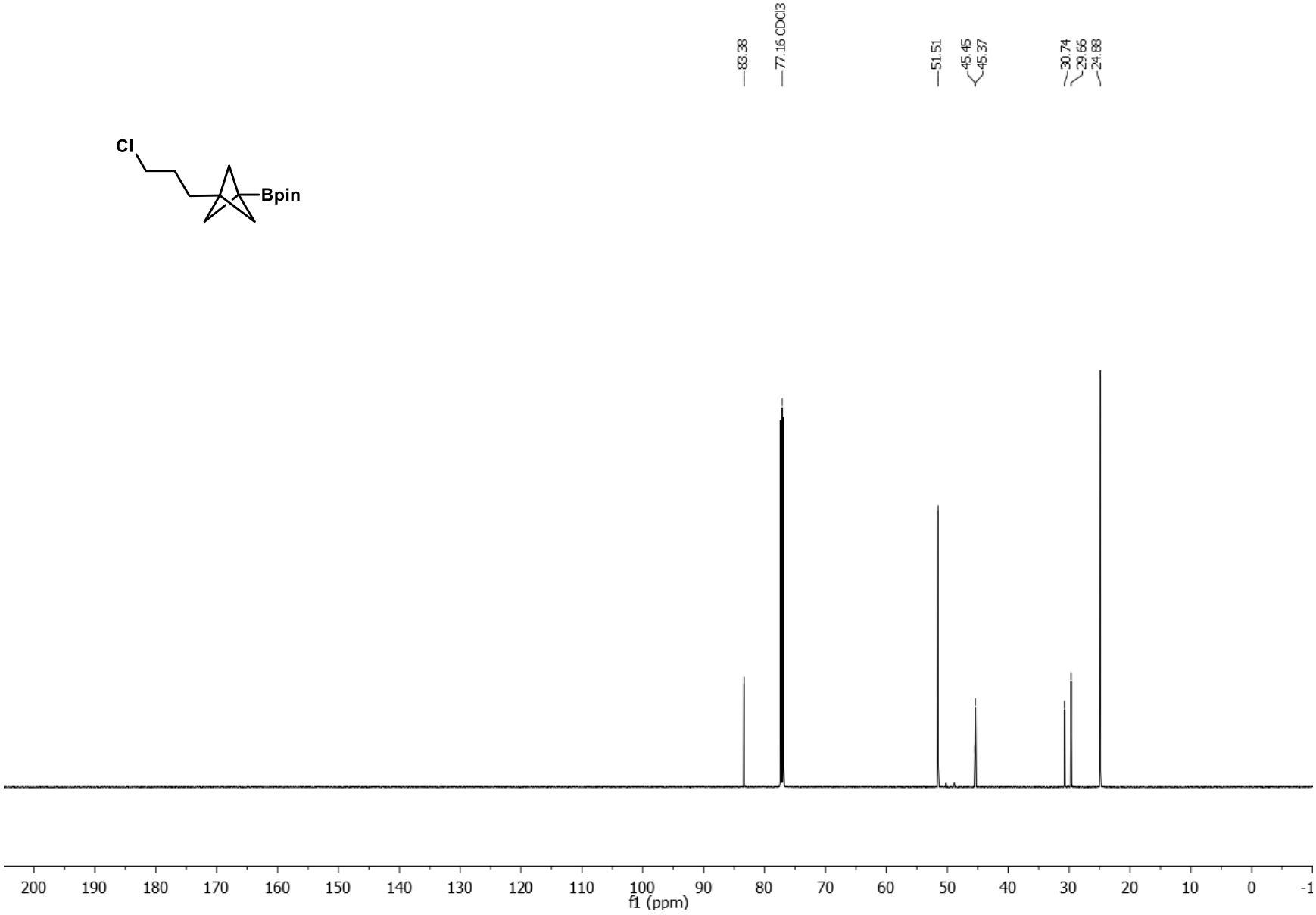
^{11}B NMR (128 MHz, $CDCl_3$) of **4ar**



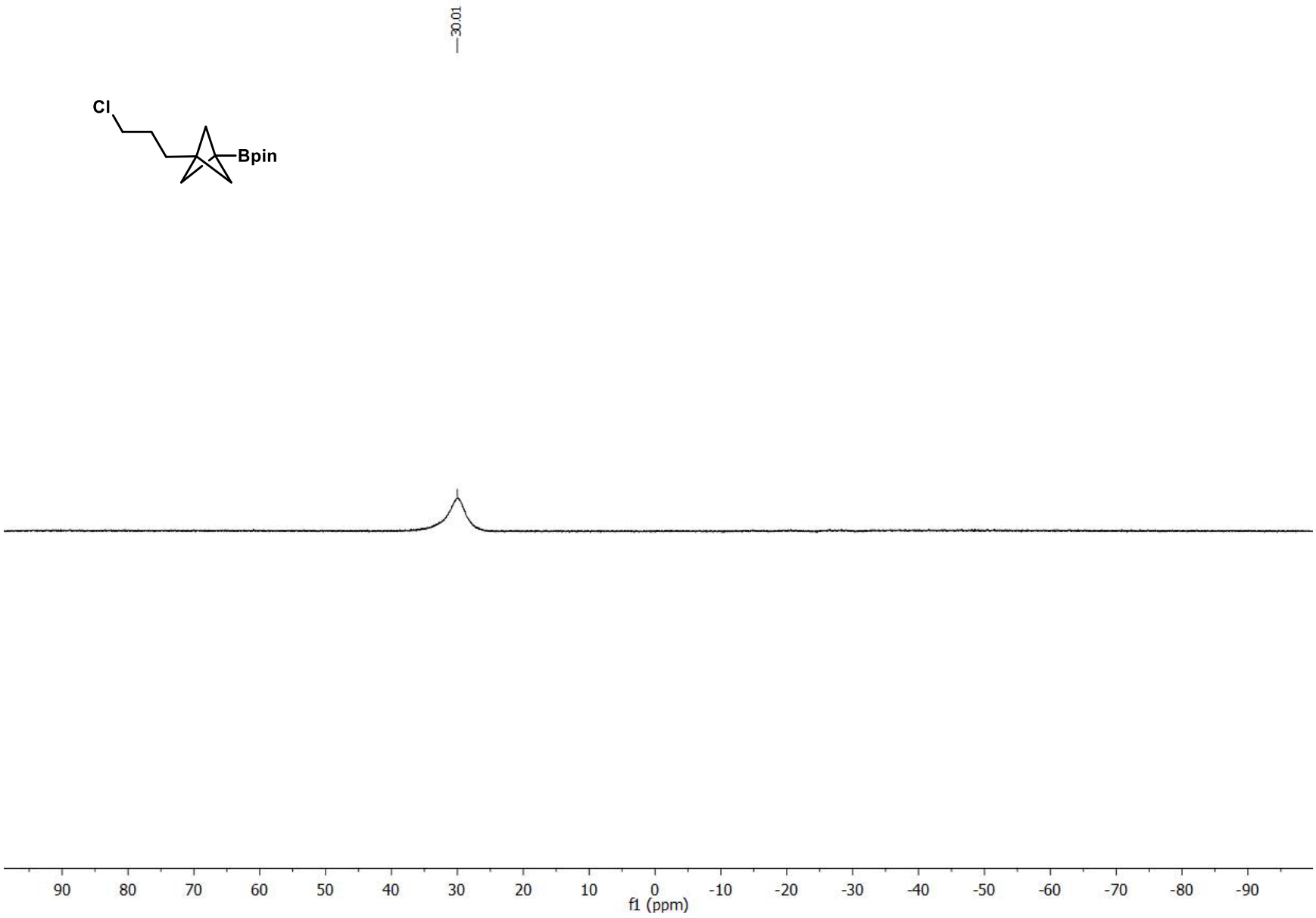
^{1}H NMR (400 MHz, $CDCl_3$) of **5a**



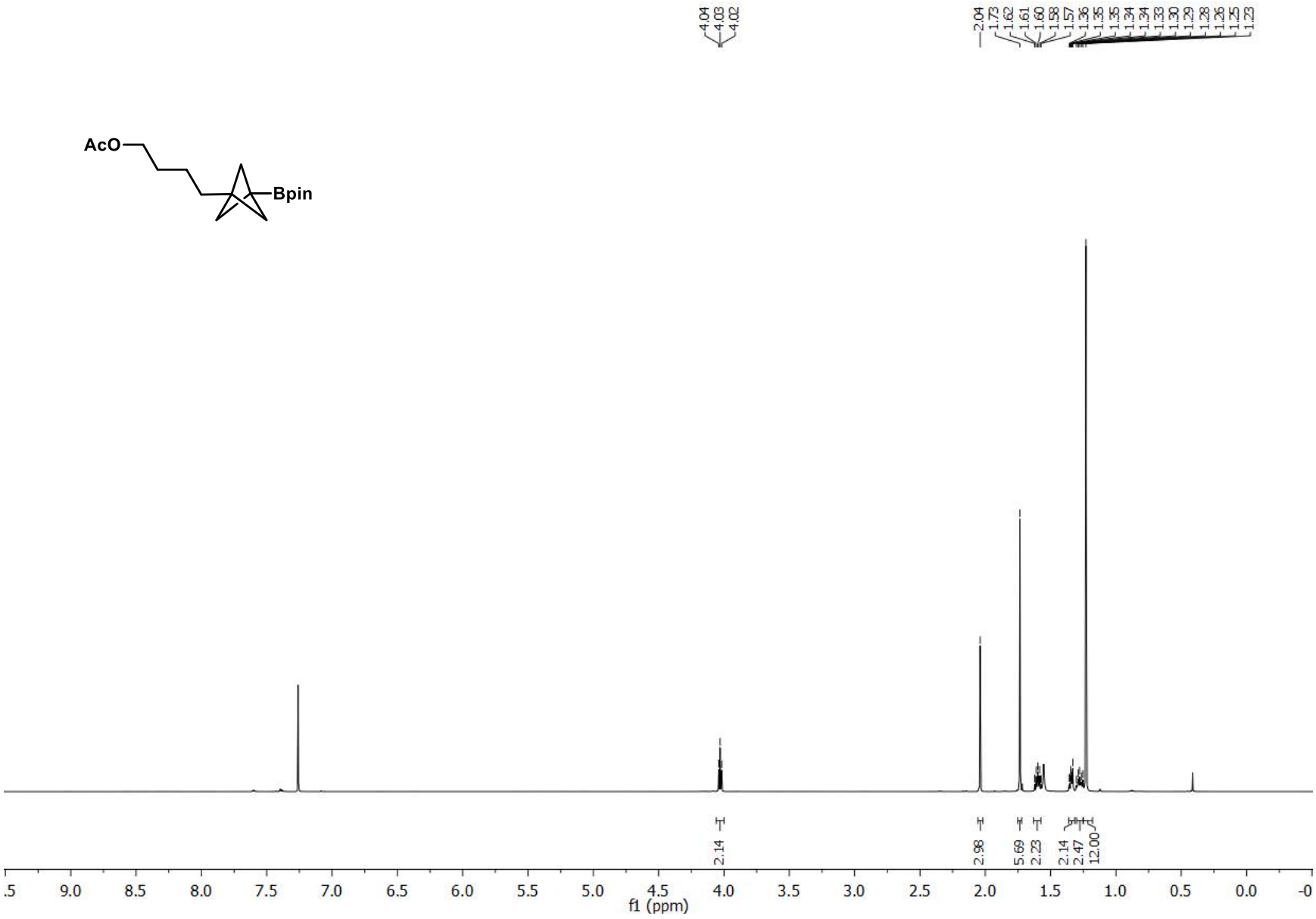
^{13}C NMR (151 MHz, $CDCl_3$) of **5a**



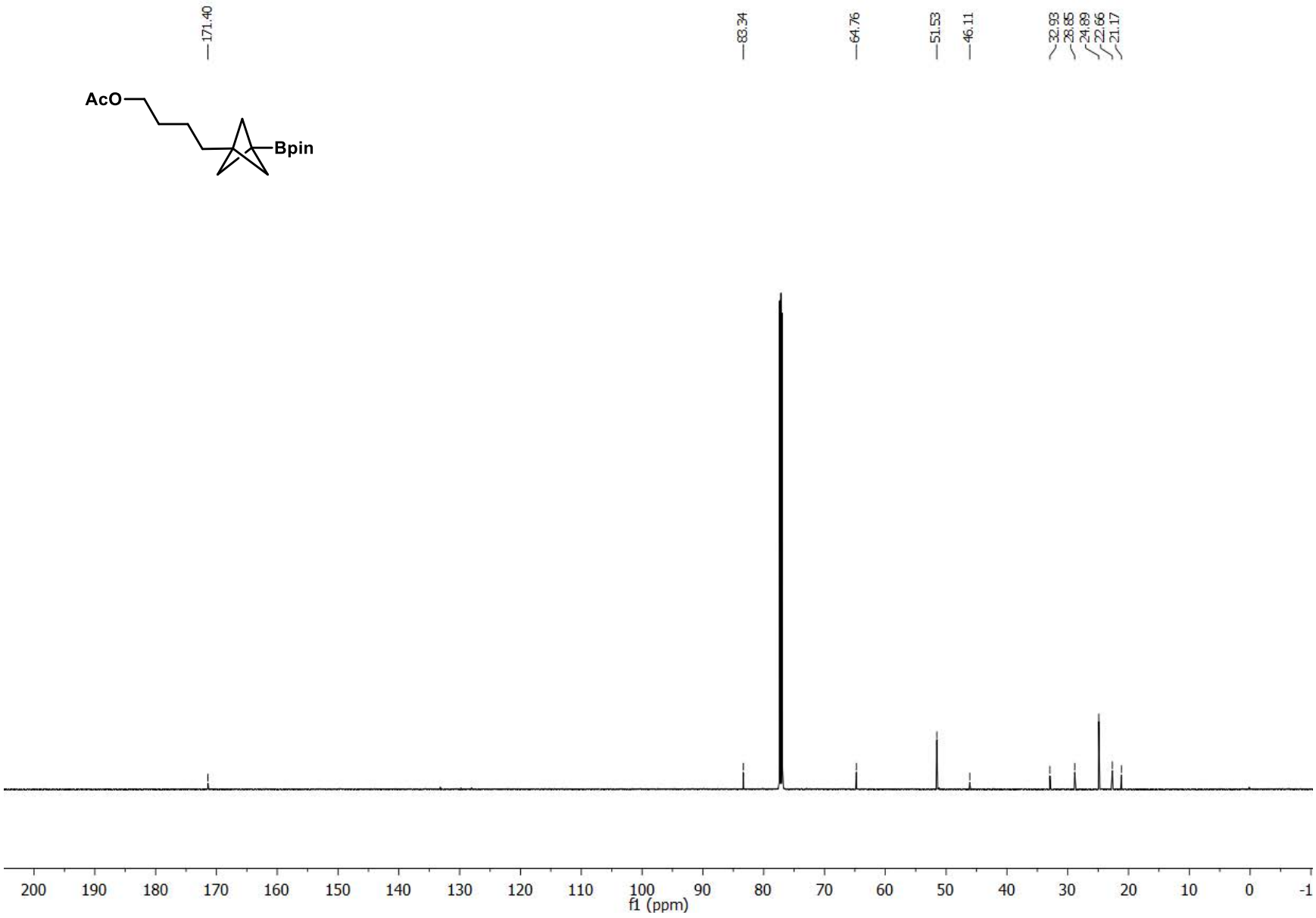
^{11}B NMR (128 MHz, $CDCl_3$) of **5a**



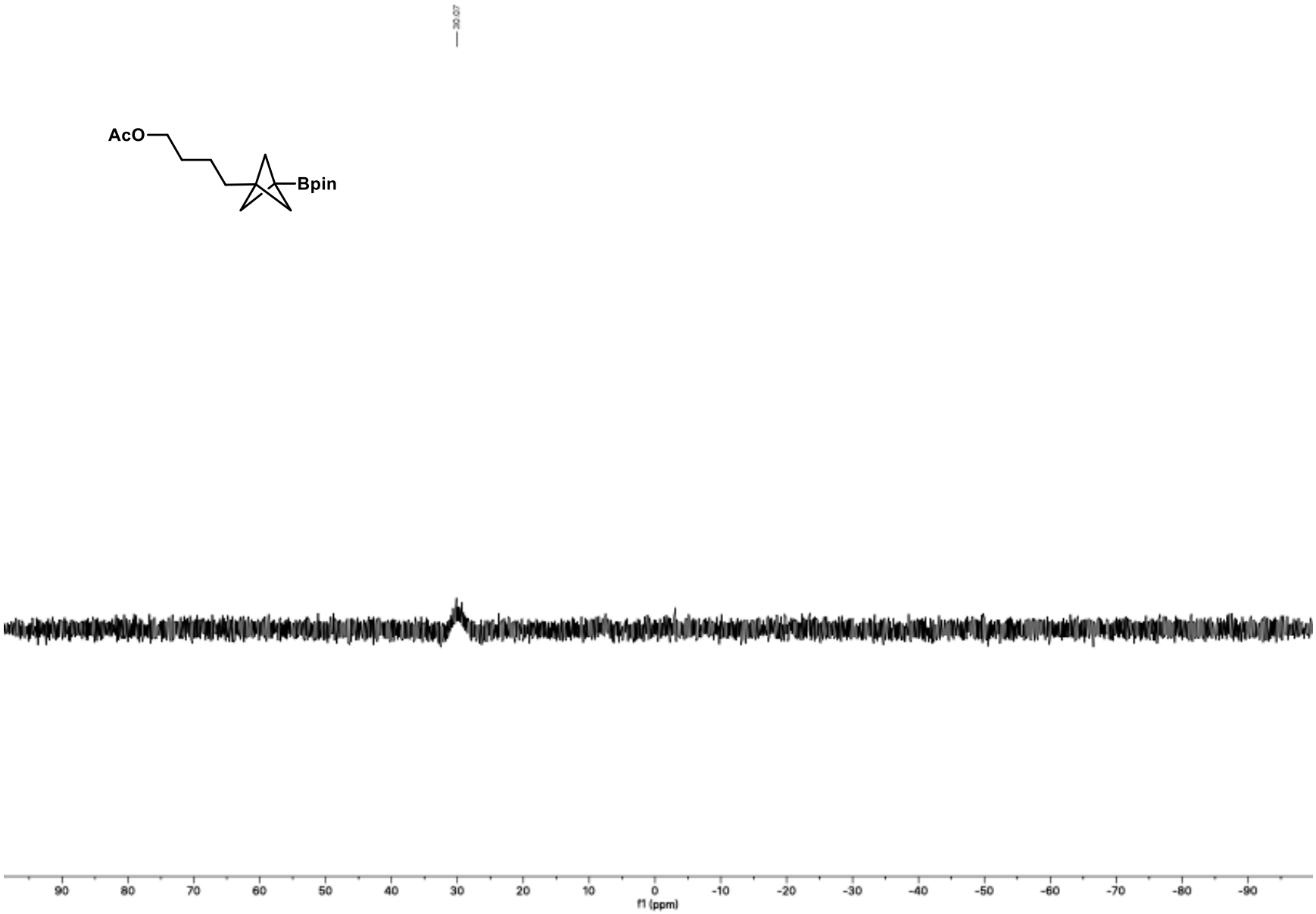
^{1}H NMR (600 MHz, $CDCl_3$) of **5b**



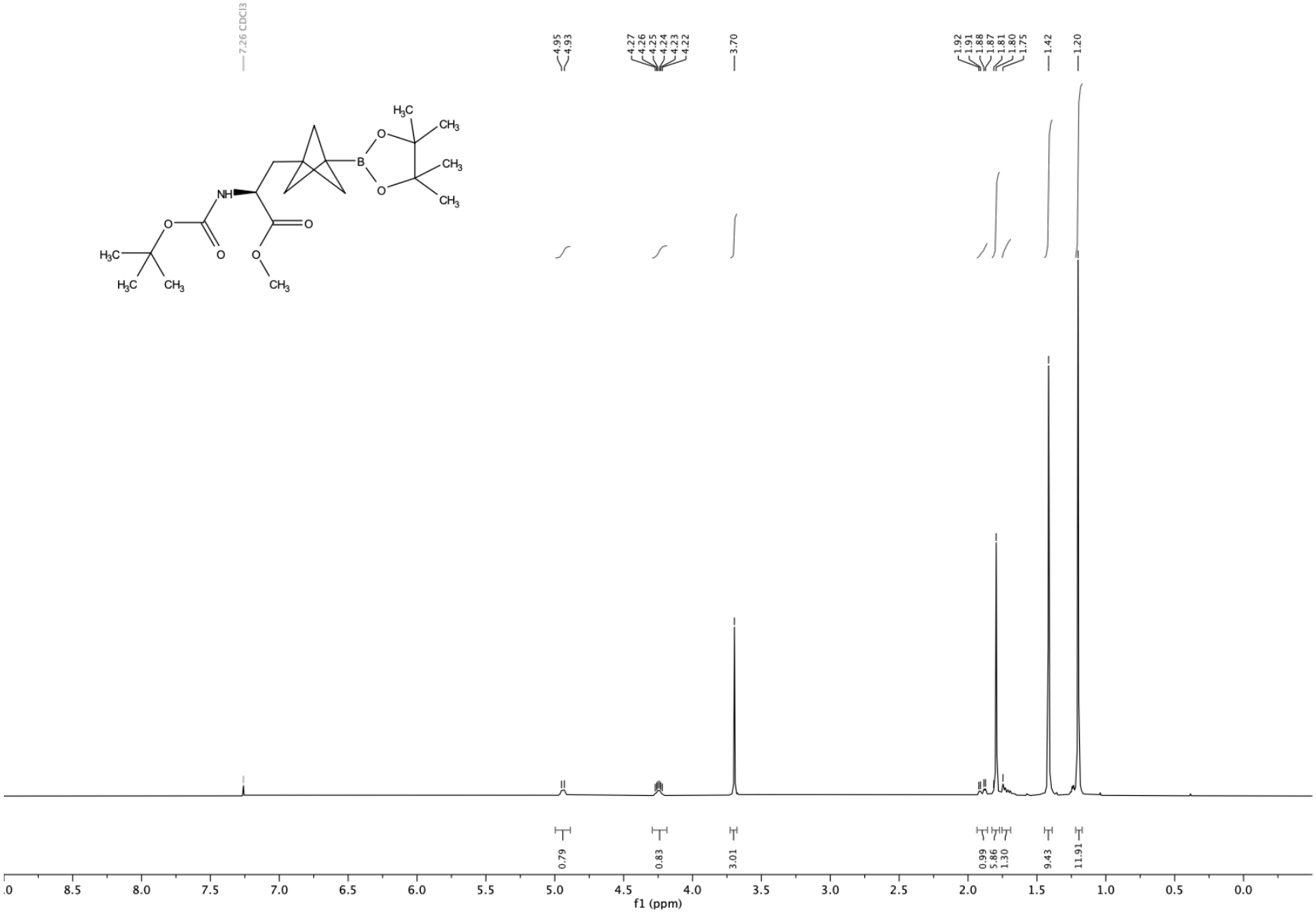
^{13}C NMR (151 MHz, $CDCl_3$) of **5b**



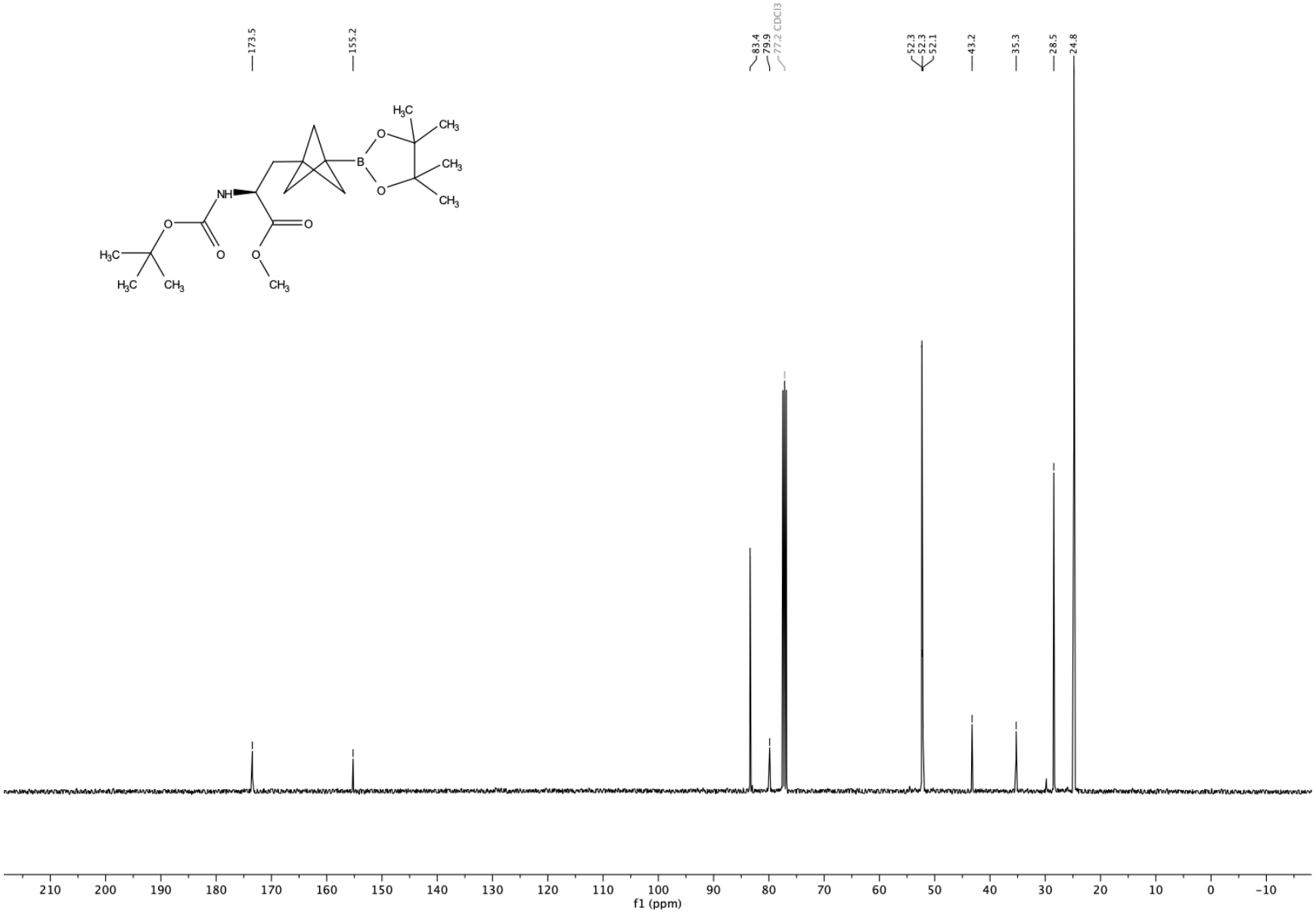
^{11}B NMR (128 MHz, $CDCl_3$) of **5b**



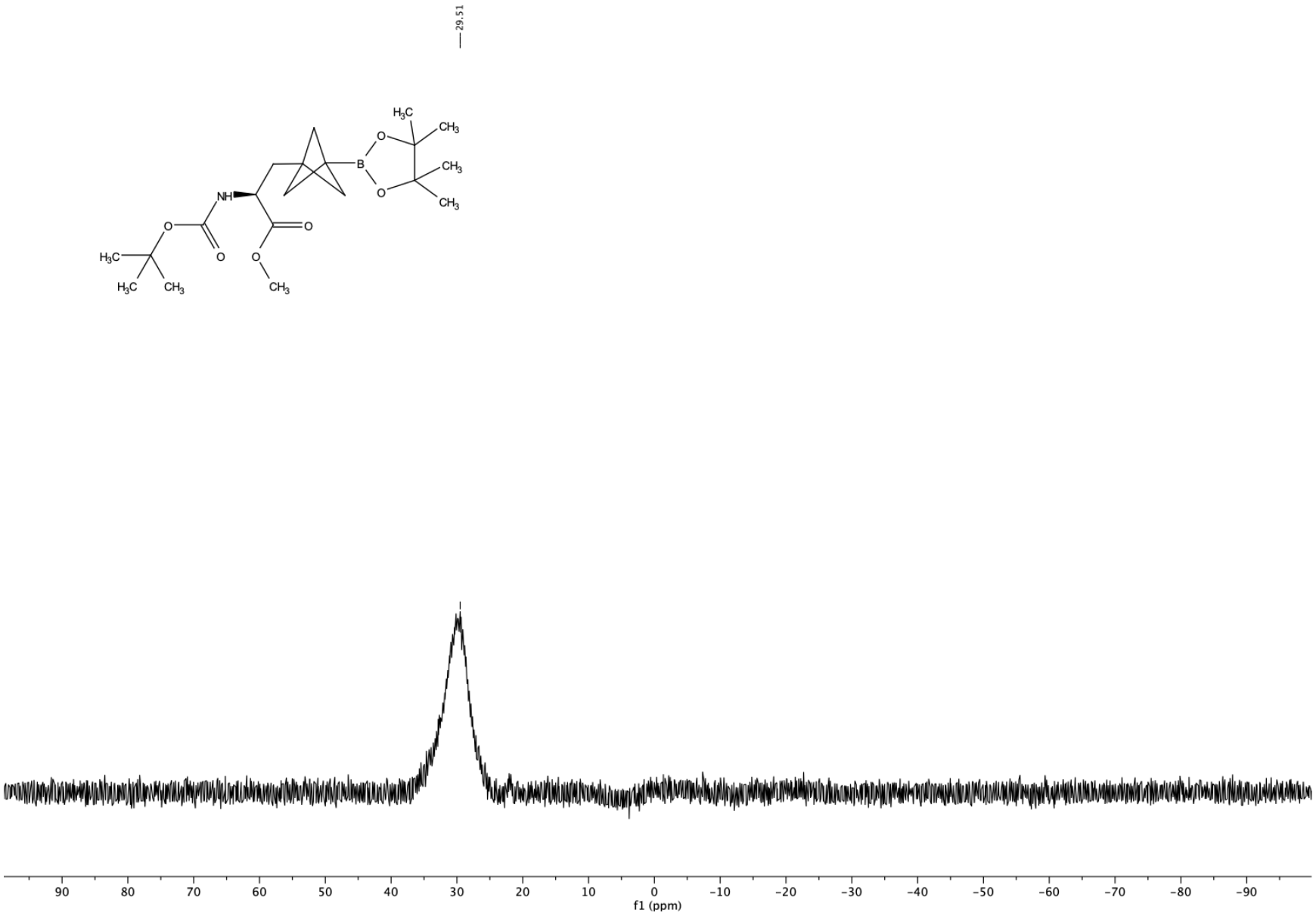
^{1}H NMR (400 MHz, $CDCl_3$) of **5c**



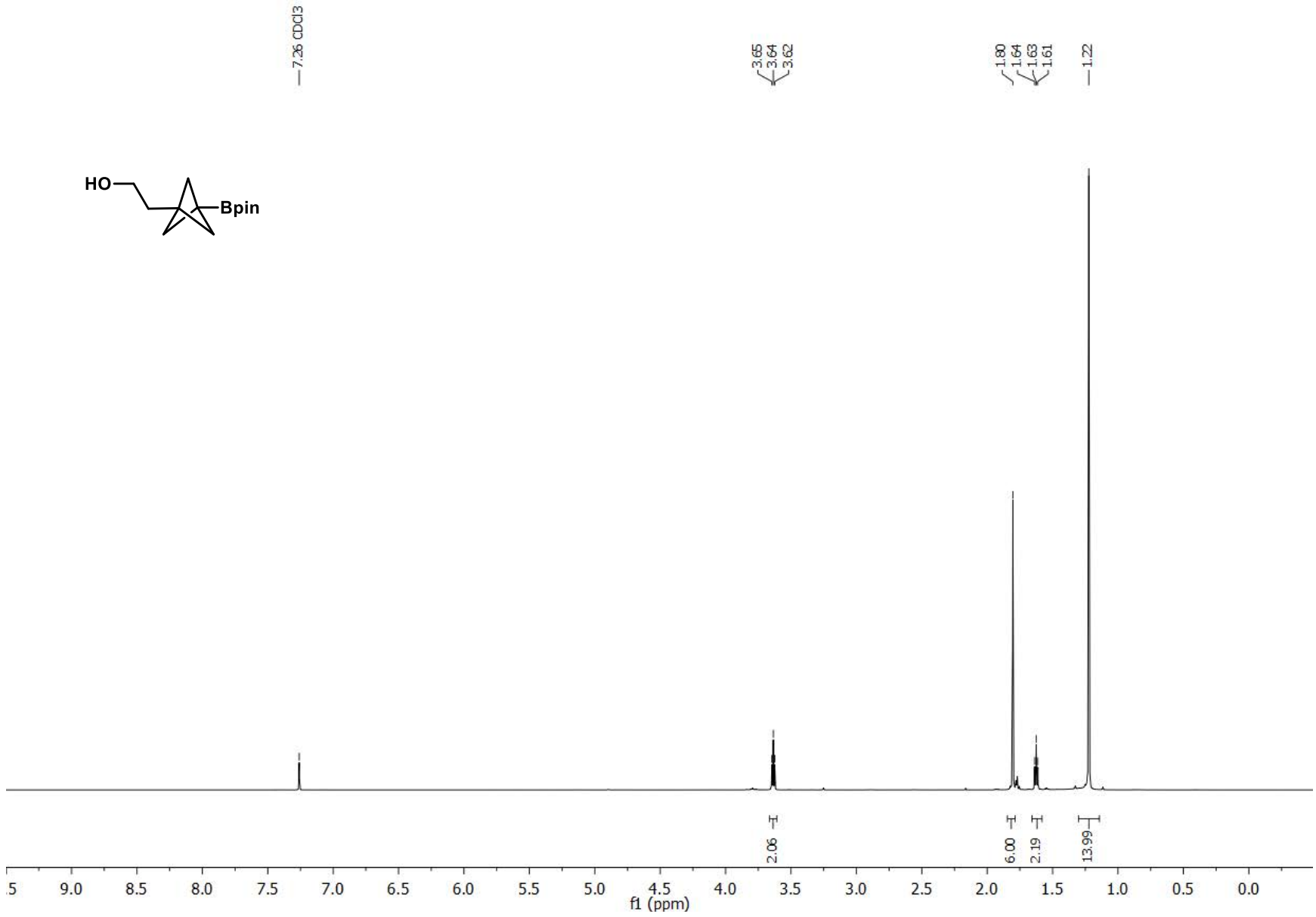
^{13}C NMR (101 MHz, $CDCl_3$) of **5c**



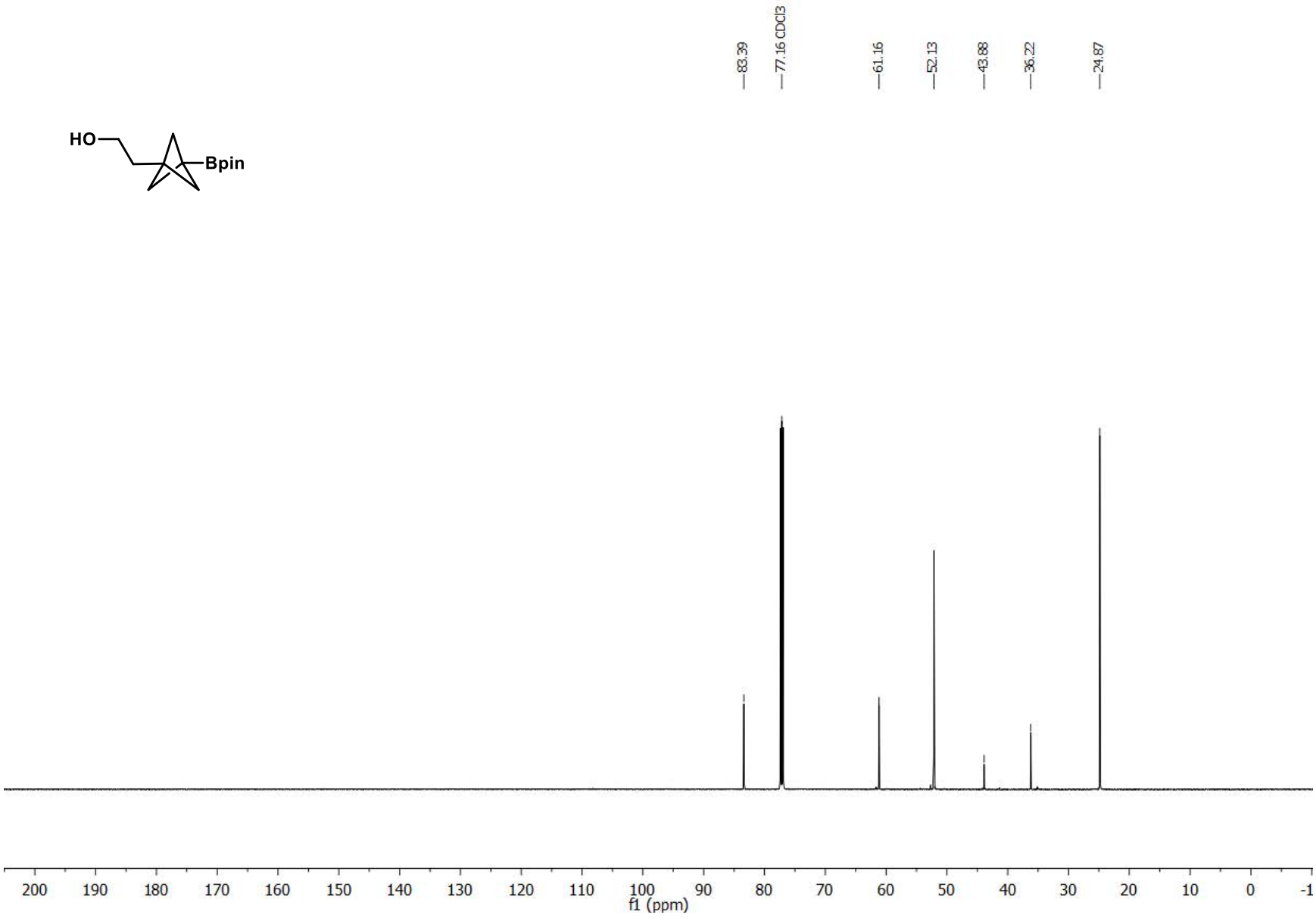
^{11}B NMR (128 MHz, $CDCl_3$) of **5c**



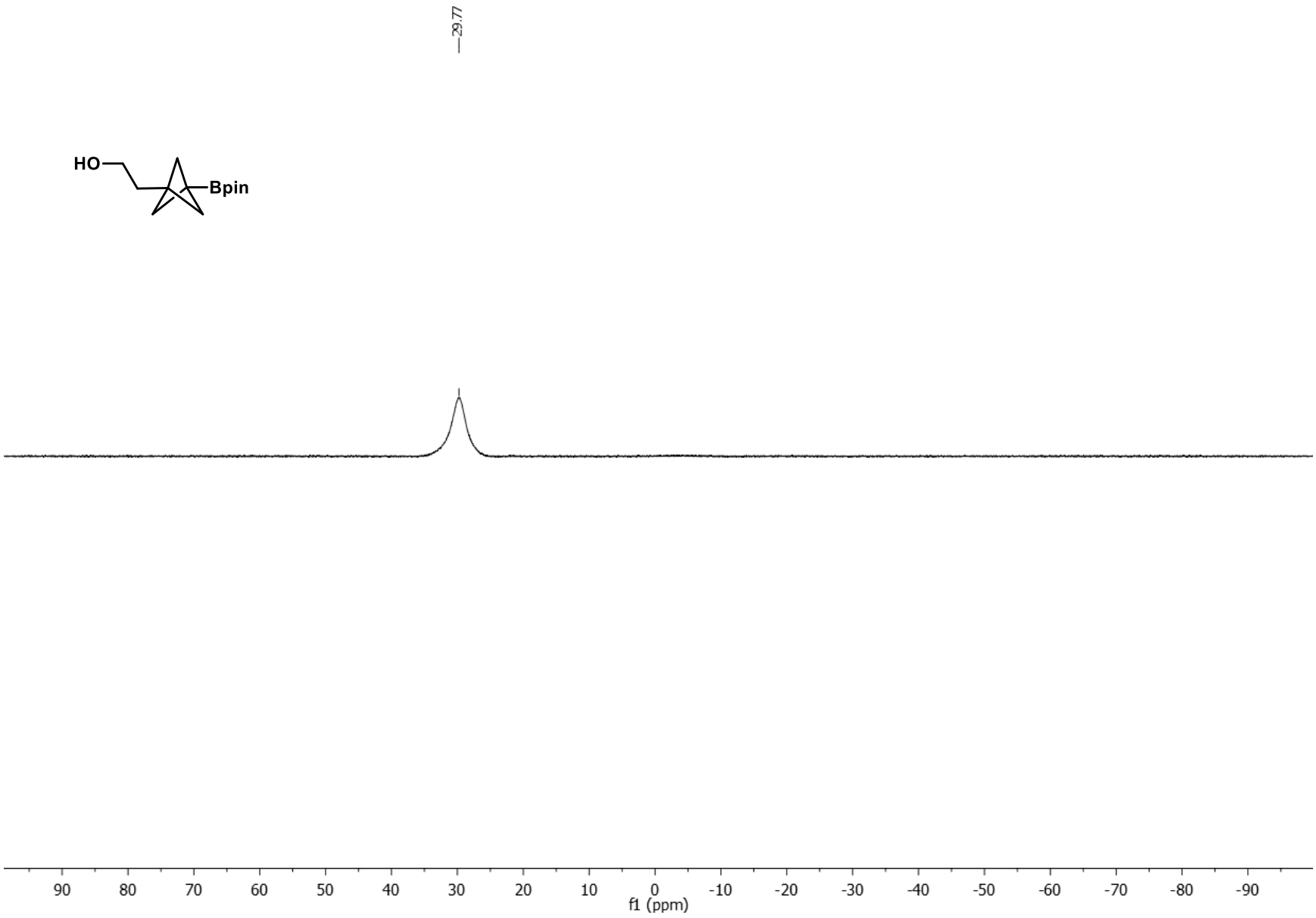
^{1}H NMR (600 MHz, $CDCl_3$) of **5d**



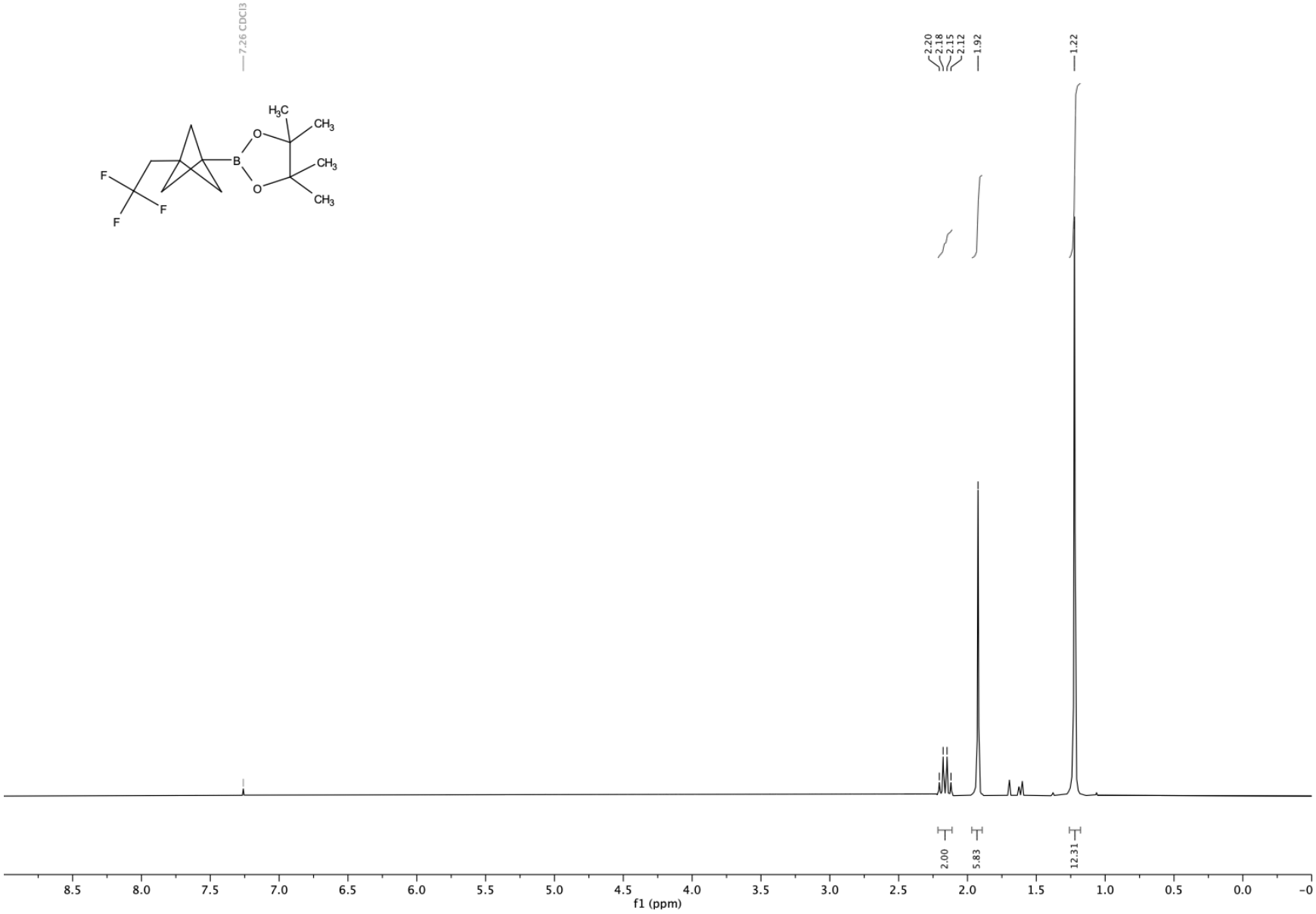
^{13}C NMR (151 MHz, $CDCl_3$) of **5d**



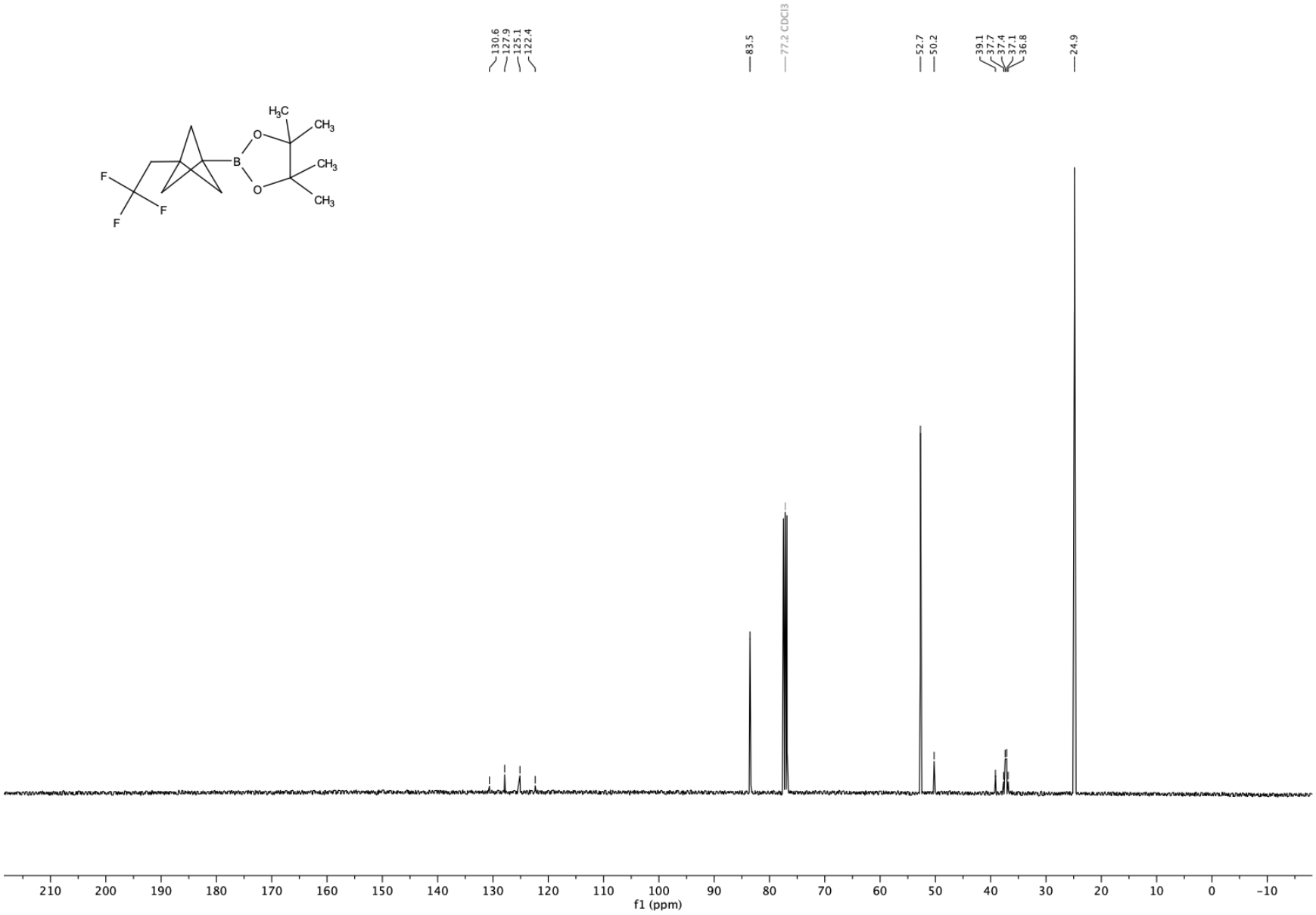
^{11}B NMR (128 MHz, $CDCl_3$) of **5d**



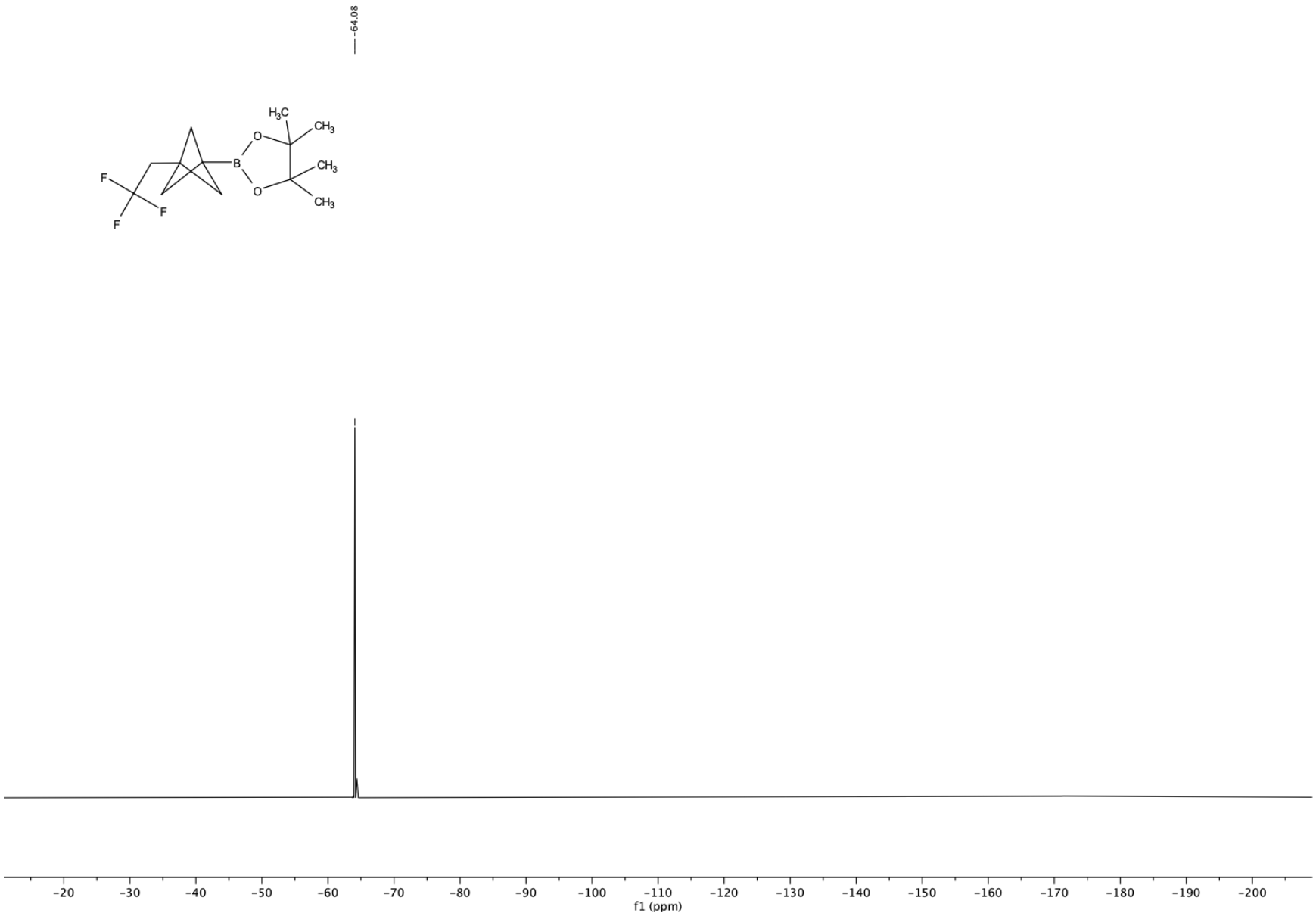
^{1}H NMR (600 MHz, $CDCl_3$) of **5e**



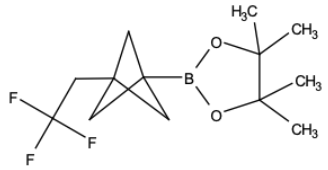
^{13}C NMR (151 MHz, $CDCl_3$) of **5e**



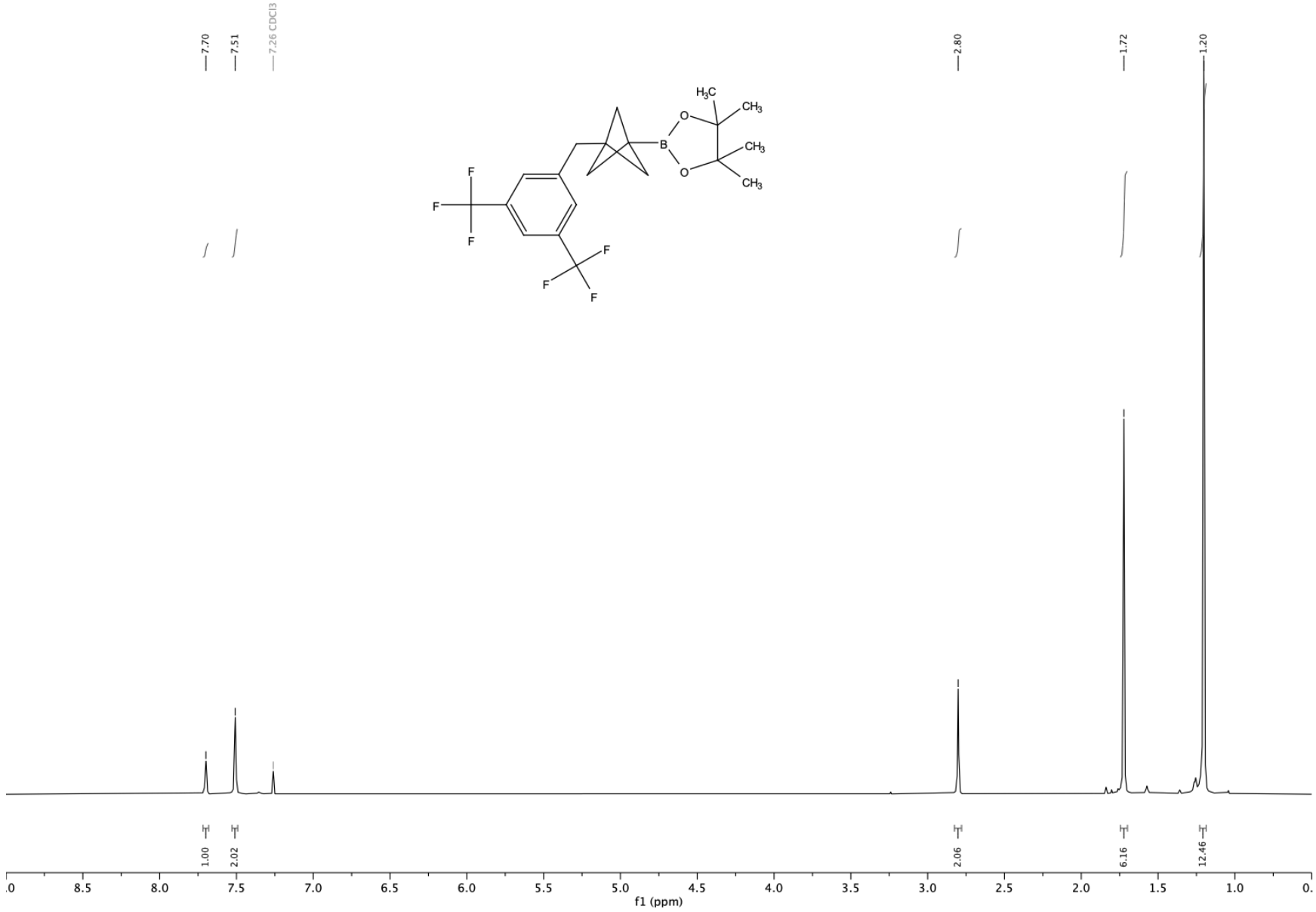
^{19}F NMR (376 MHz, $CDCl_3$) of **5e**



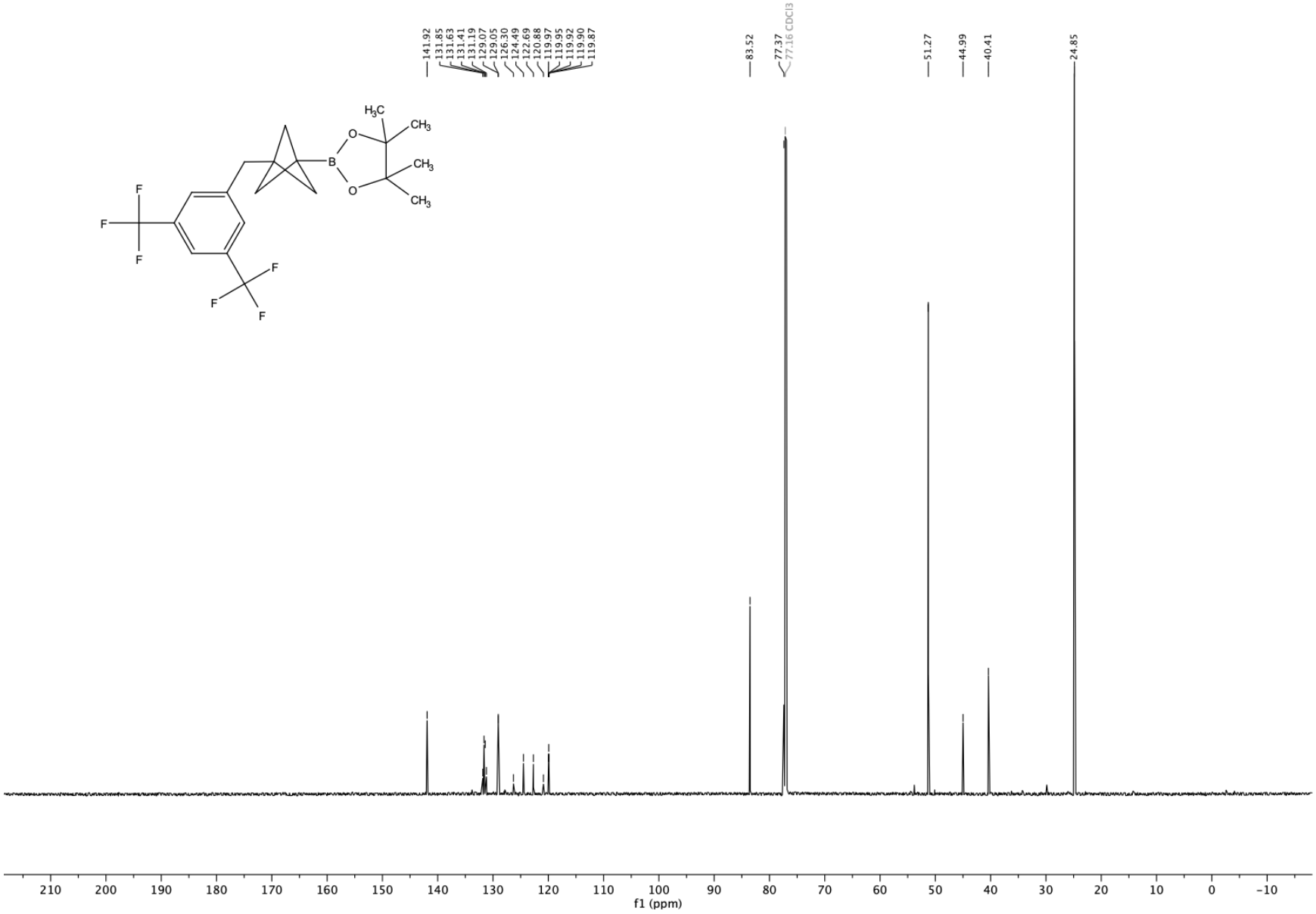
^{11}B NMR (128 MHz, $CDCl_3$) of **5e**



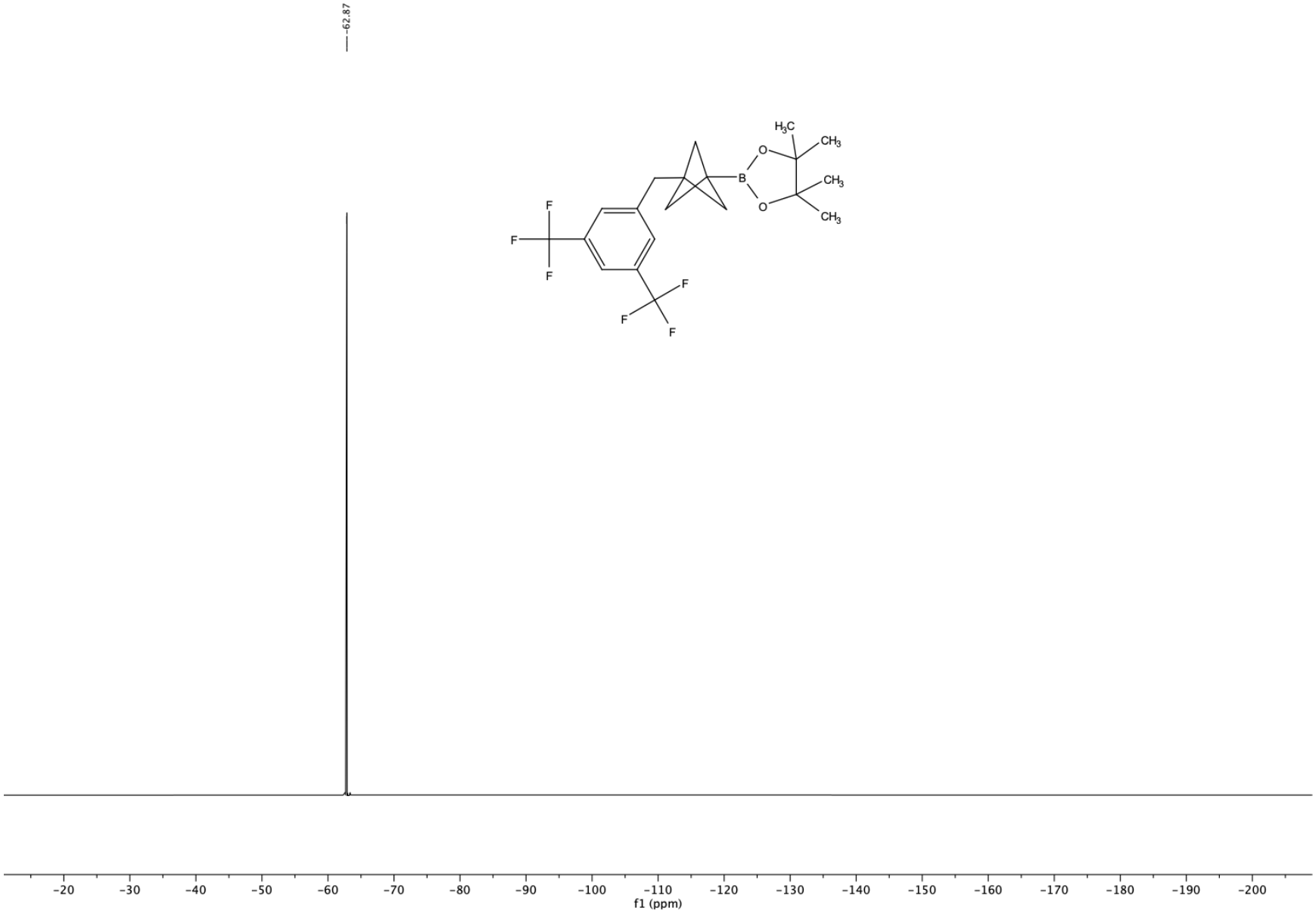
^{1}H NMR (400 MHz, $CDCl_3$) of **5f**



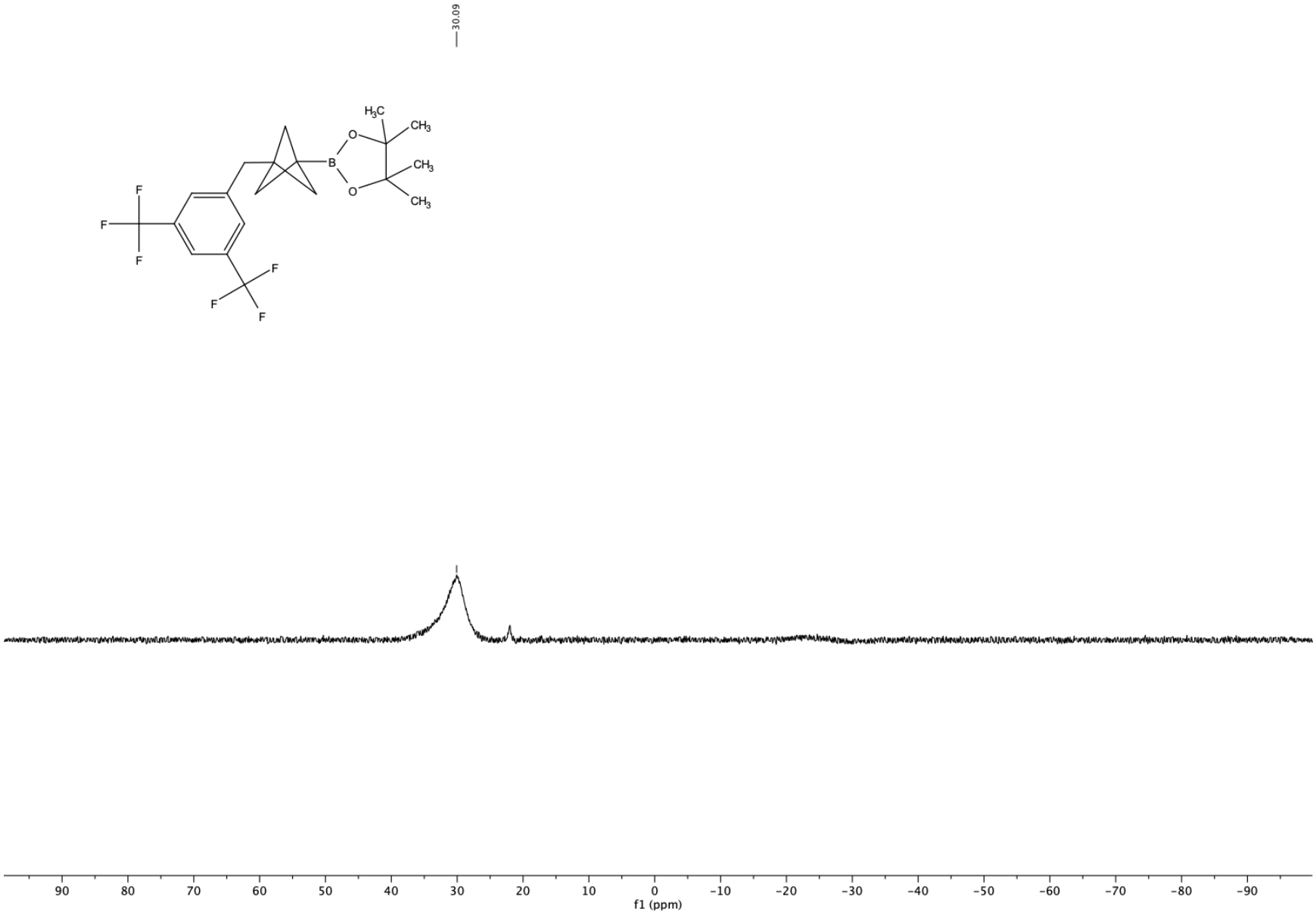
^{13}C NMR (101 MHz, $CDCl_3$) of **5f**



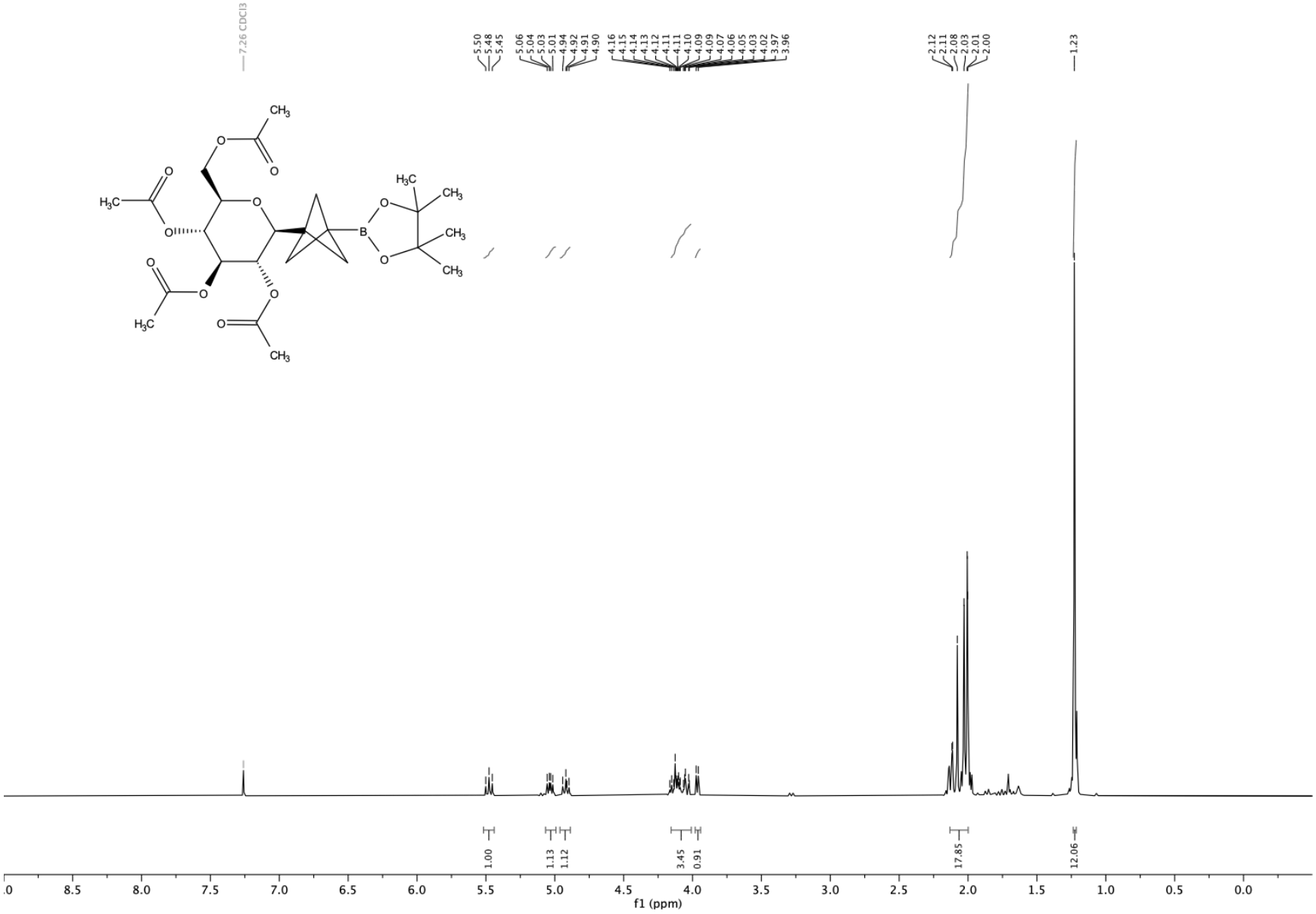
^{19}F NMR (376 MHz, $CDCl_3$) of **5f**



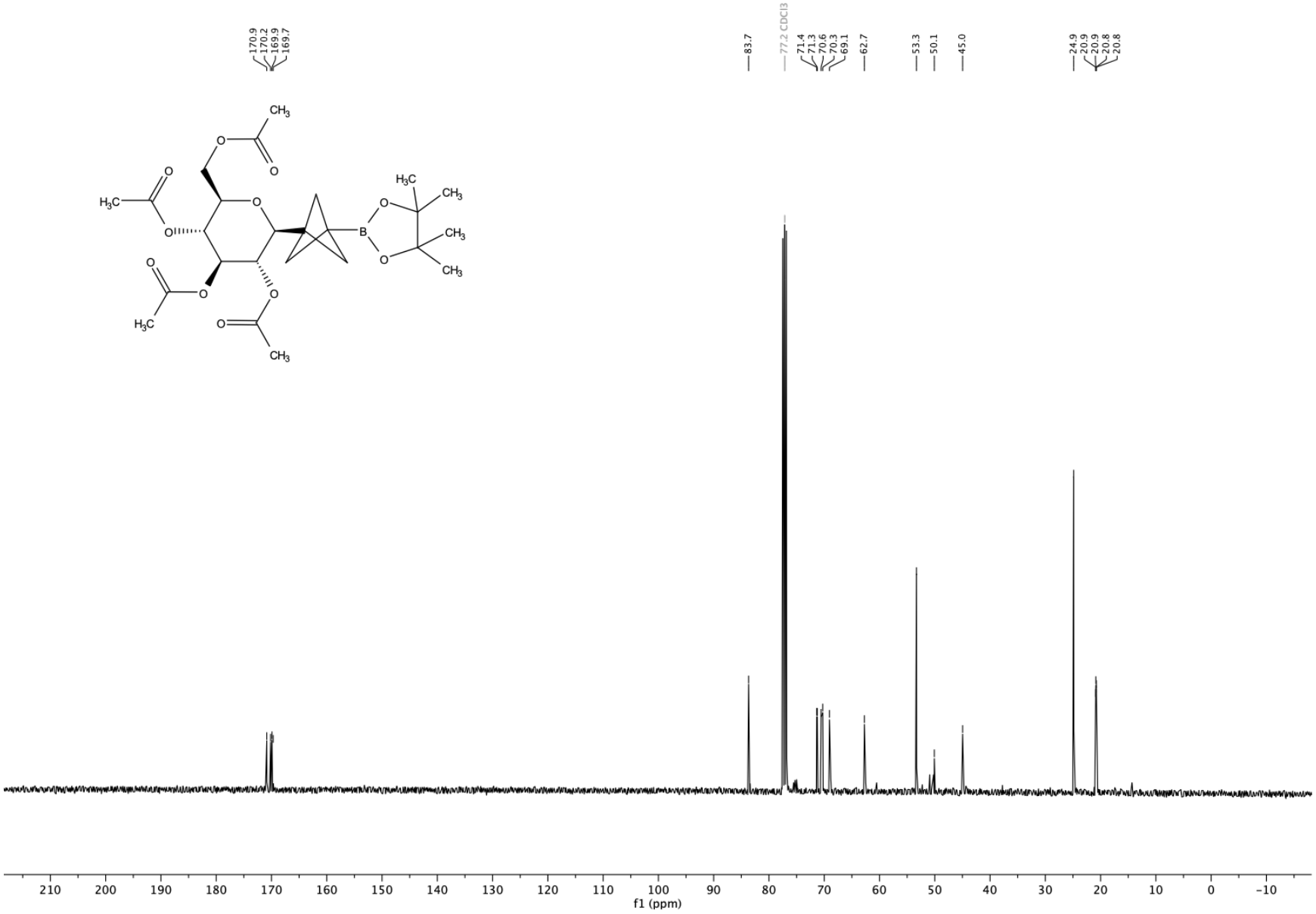
^{11}B NMR (128 MHz, $CDCl_3$) of **5f**



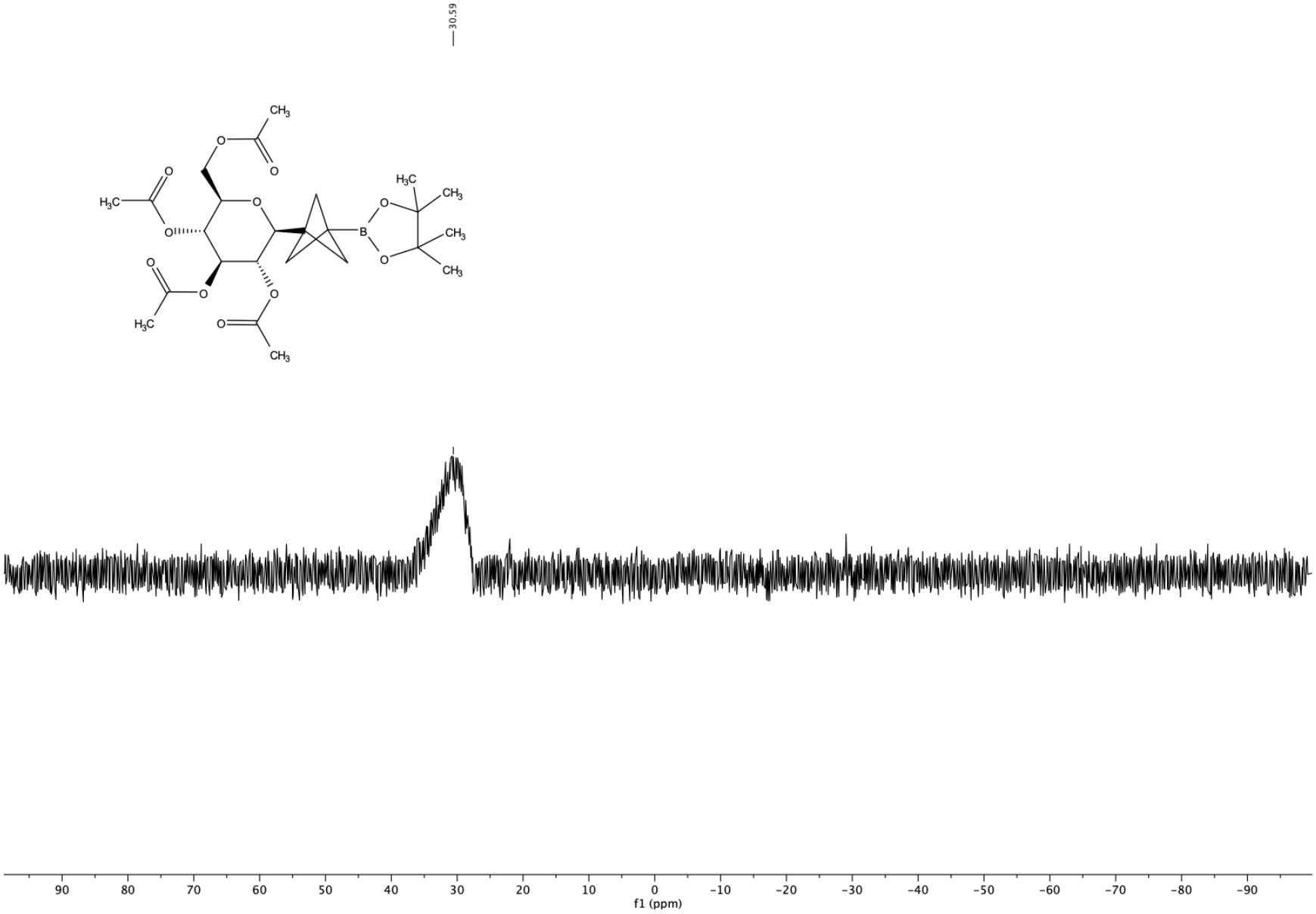
^{1}H NMR (400 MHz, $CDCl_3$) of **5g**



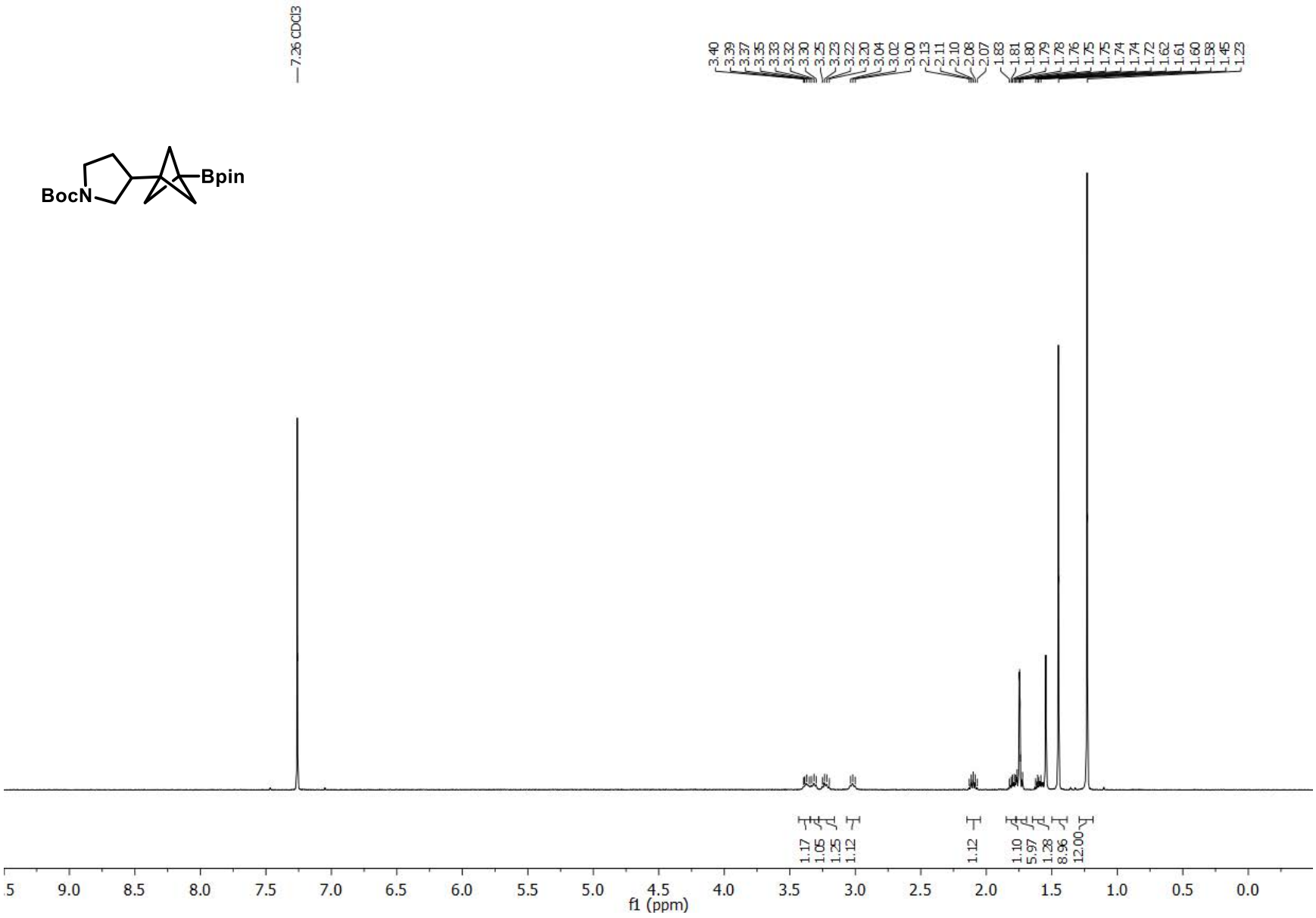
^{13}C NMR (101 MHz, $CDCl_3$) of **5g**



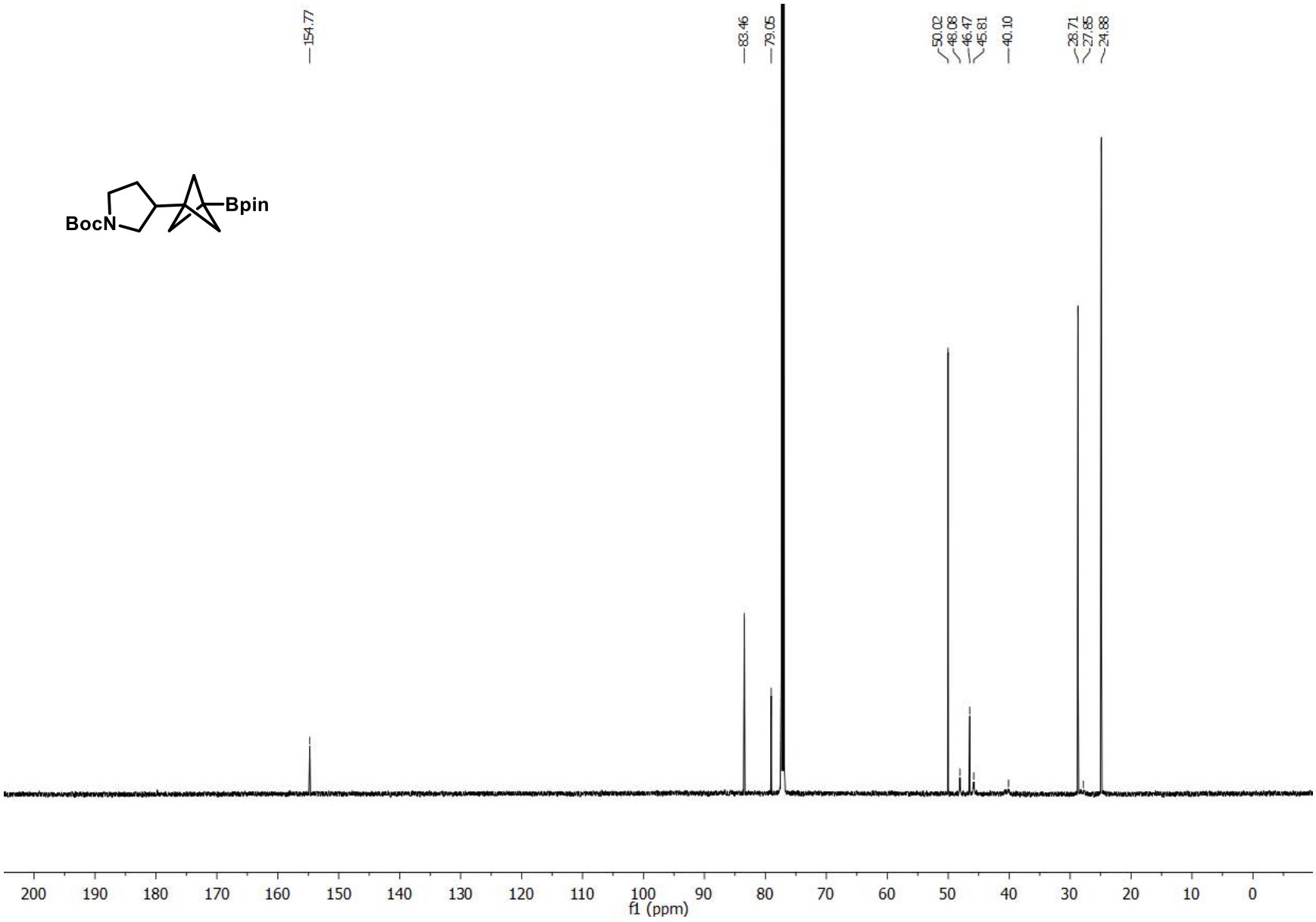
^{11}B NMR (128 MHz, $CDCl_3$) of **5g**



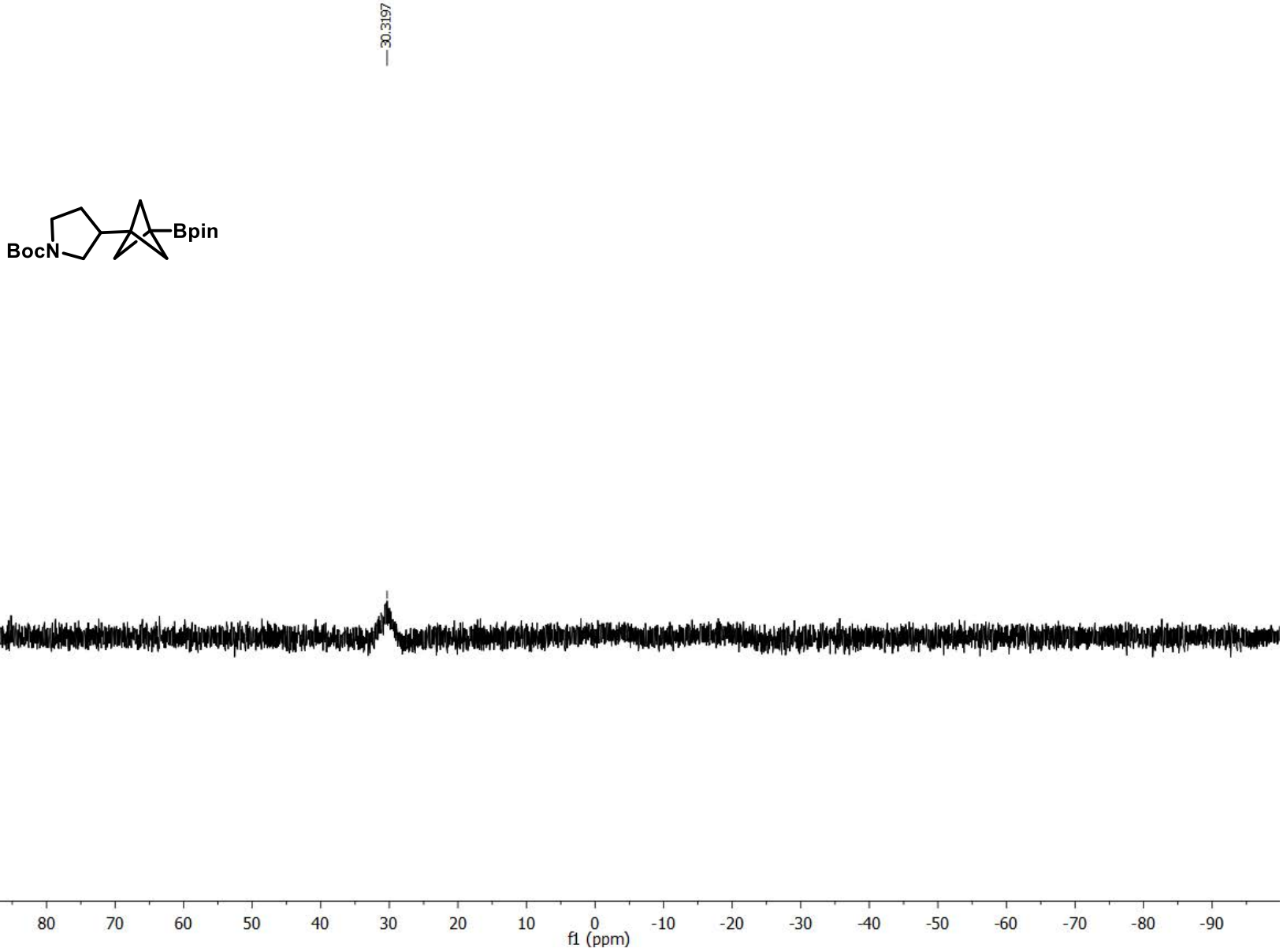
^{1}H NMR (500 MHz, $CDCl_3$) of **5h**



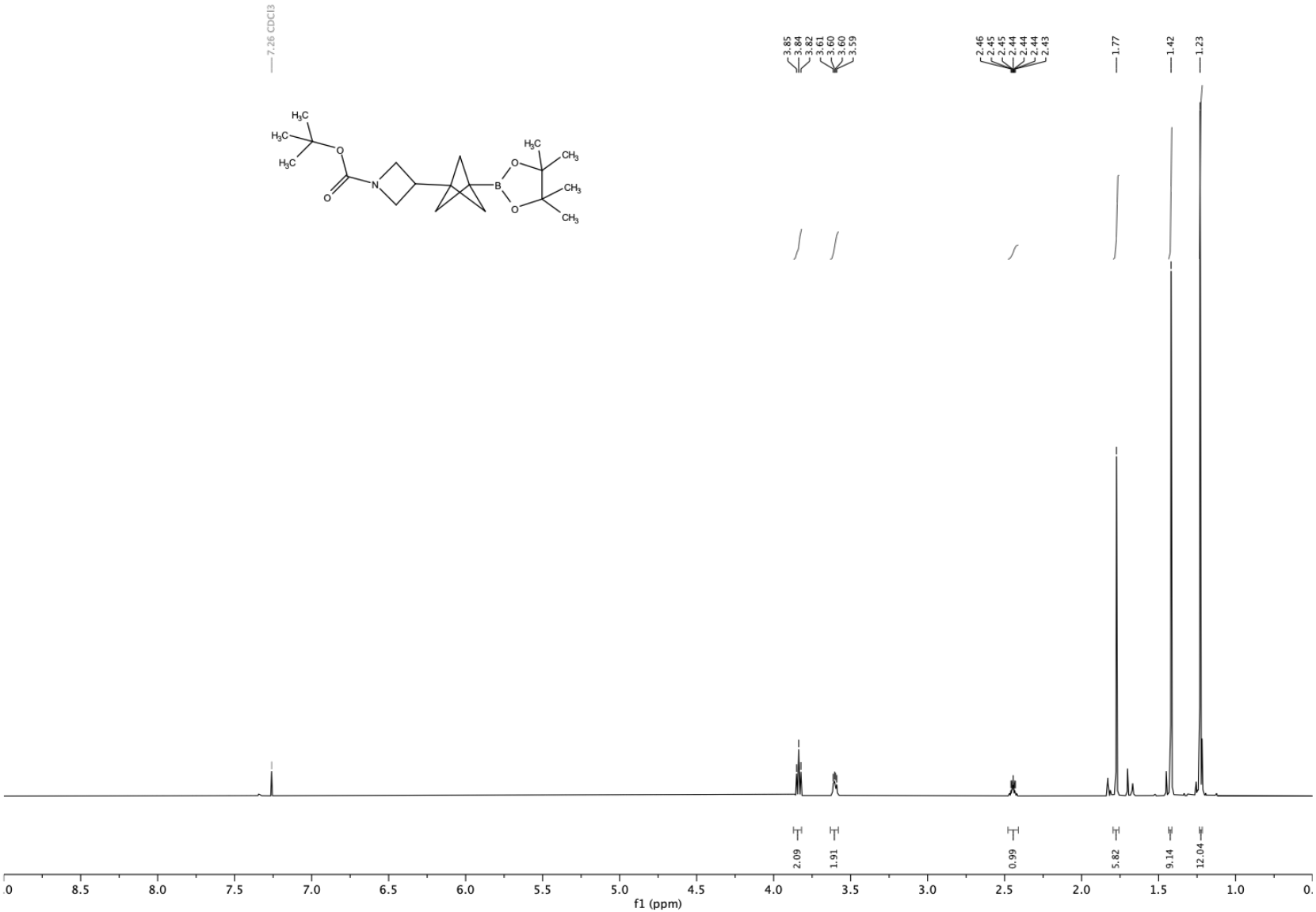
^{13}C NMR (151 MHz, $CDCl_3$) of **5h**



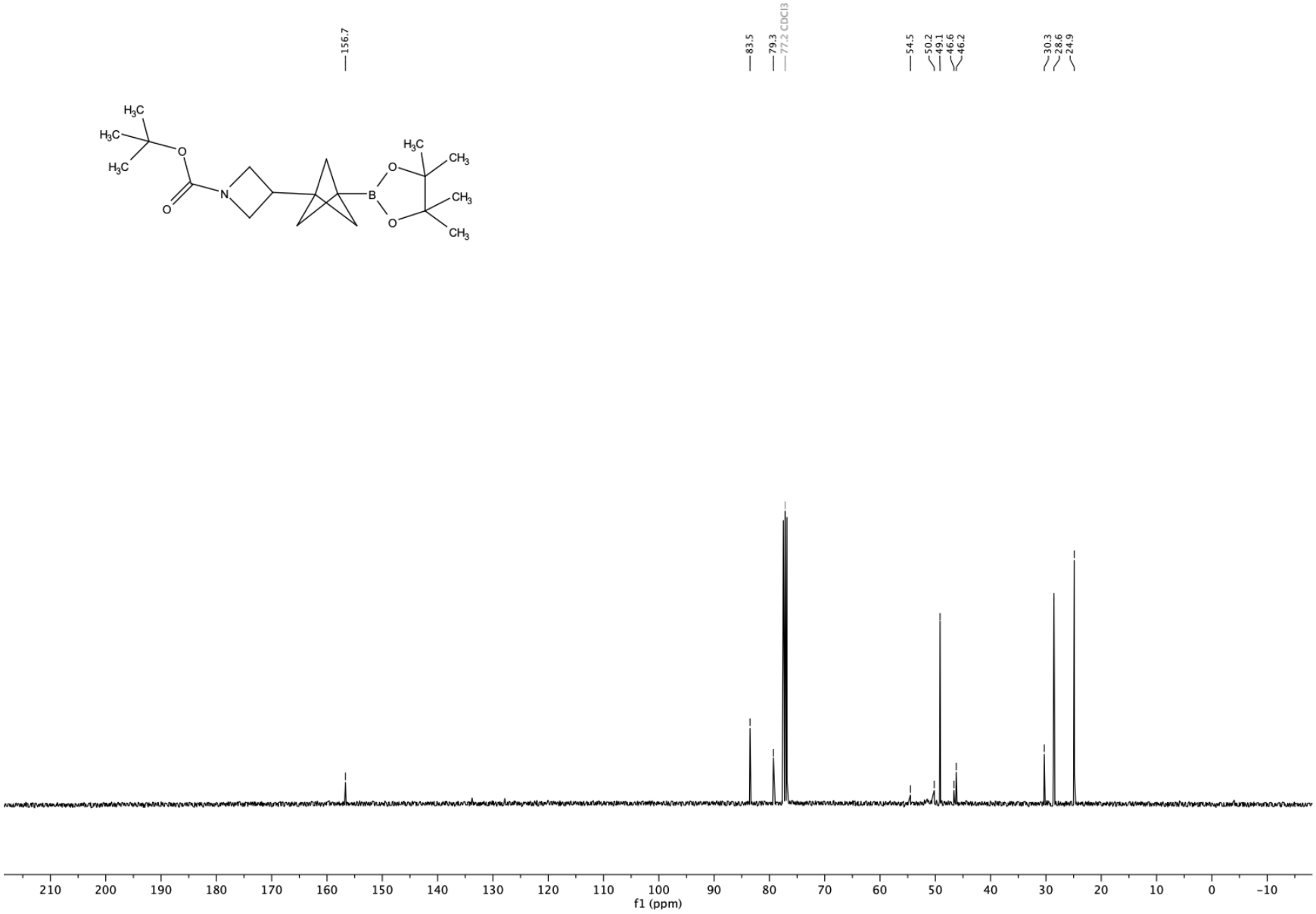
^{11}B NMR (128 MHz, $CDCl_3$) of **5h**



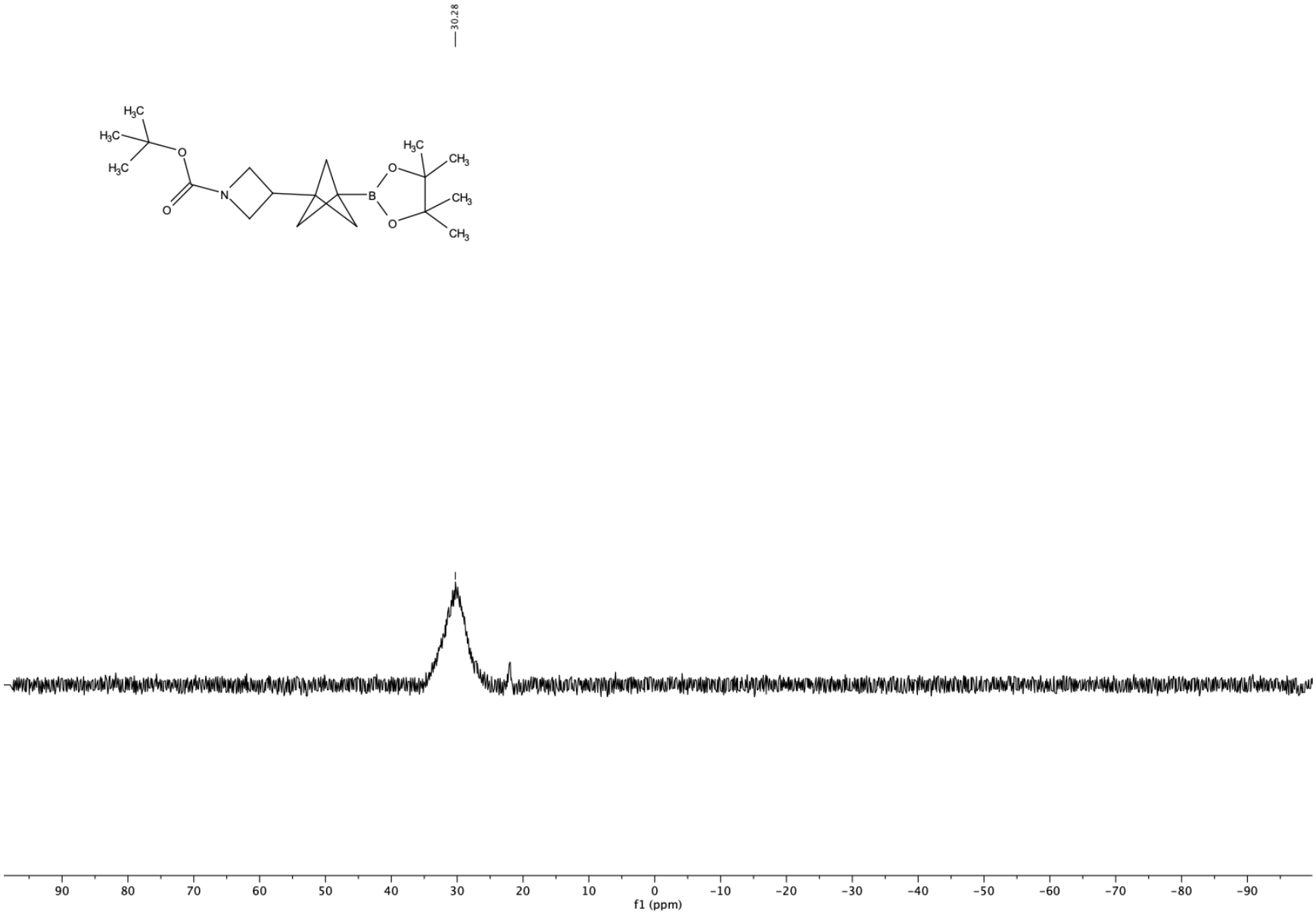
^{1}H NMR (600 MHz, $CDCl_3$) of **5i**



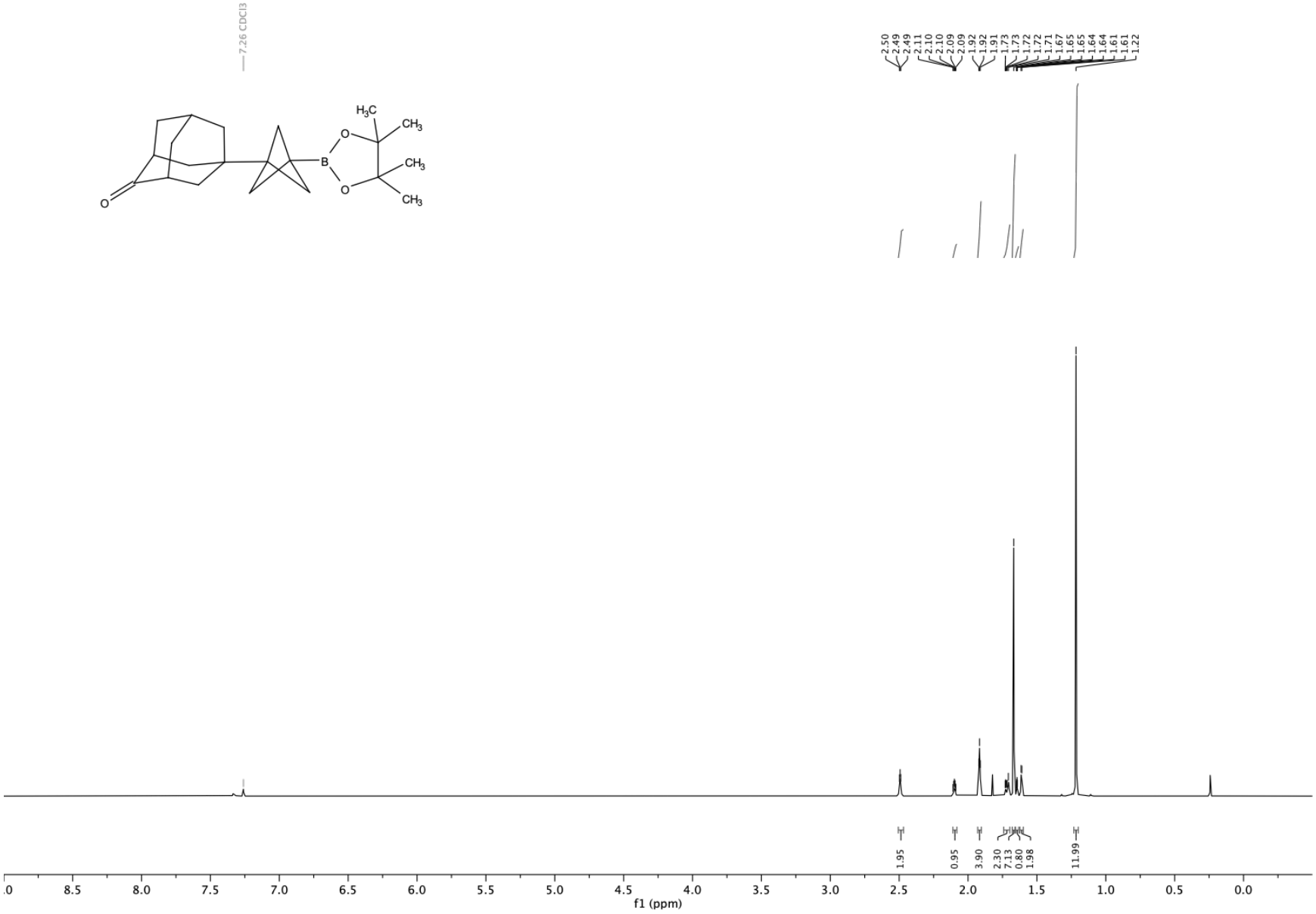
^{13}C NMR (101 MHz, $CDCl_3$) of **5i**



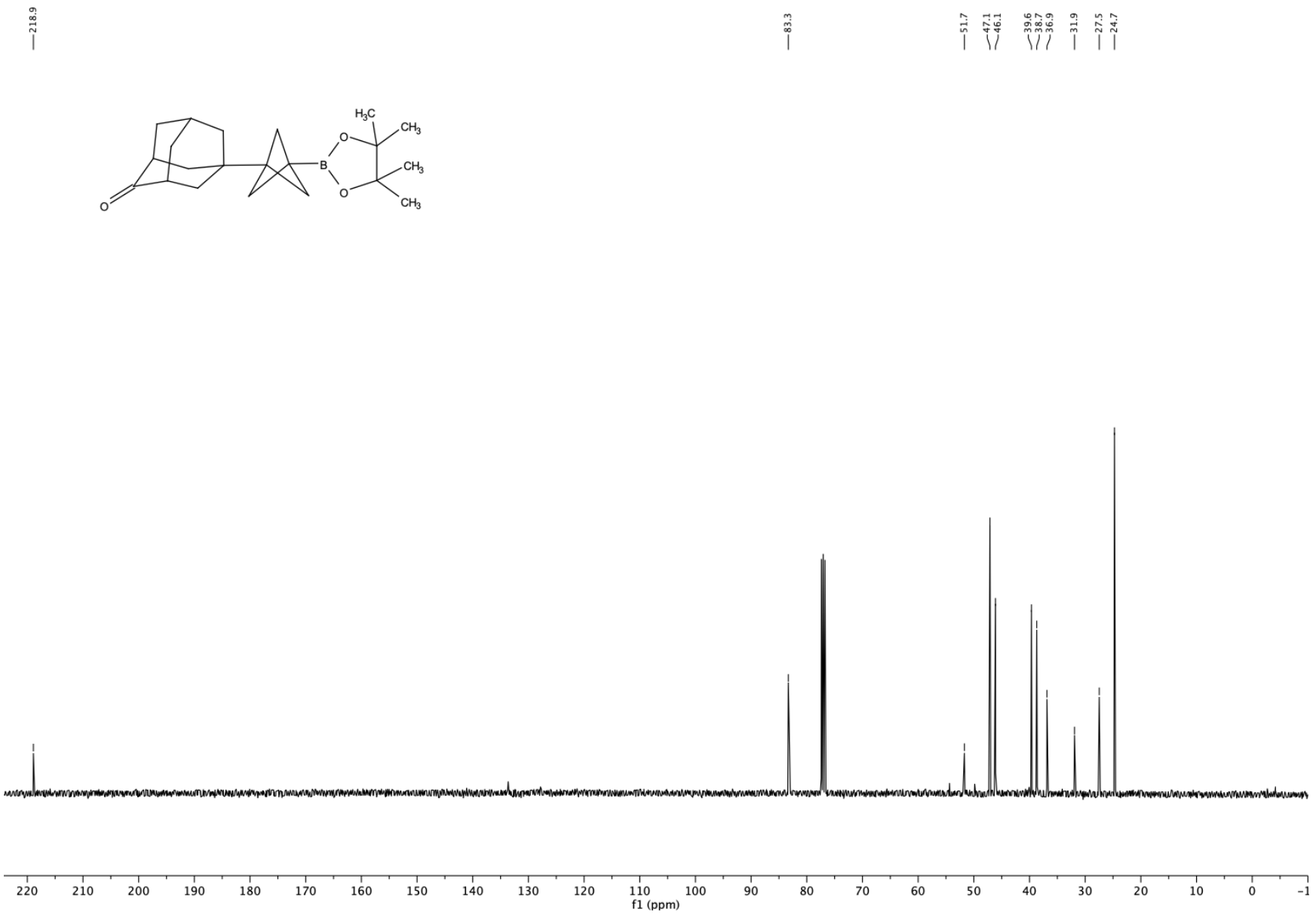
^{11}B NMR (128 MHz, $CDCl_3$) of **5i**



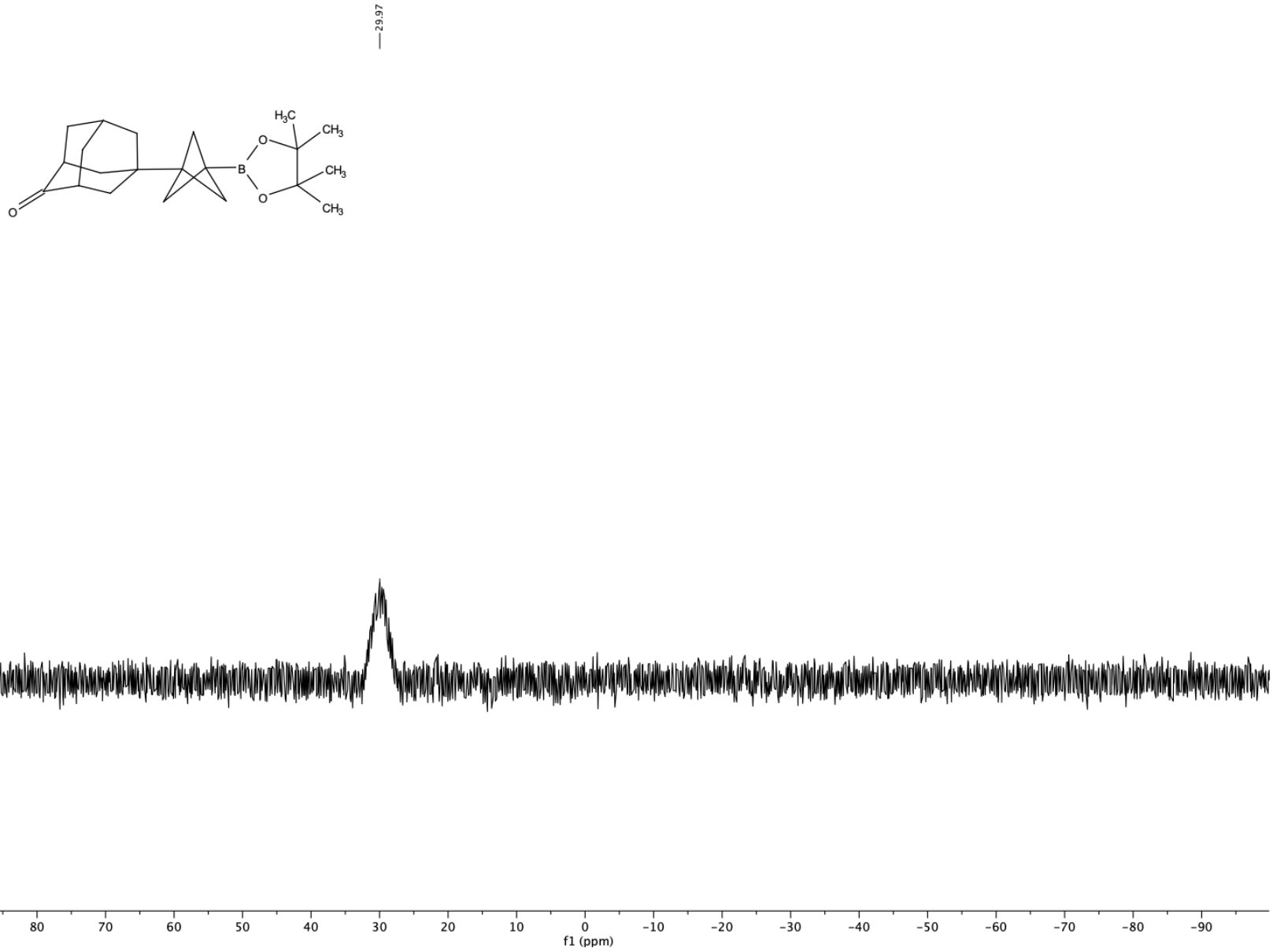
^{1}H NMR (600 MHz, $CDCl_3$) of **5j**



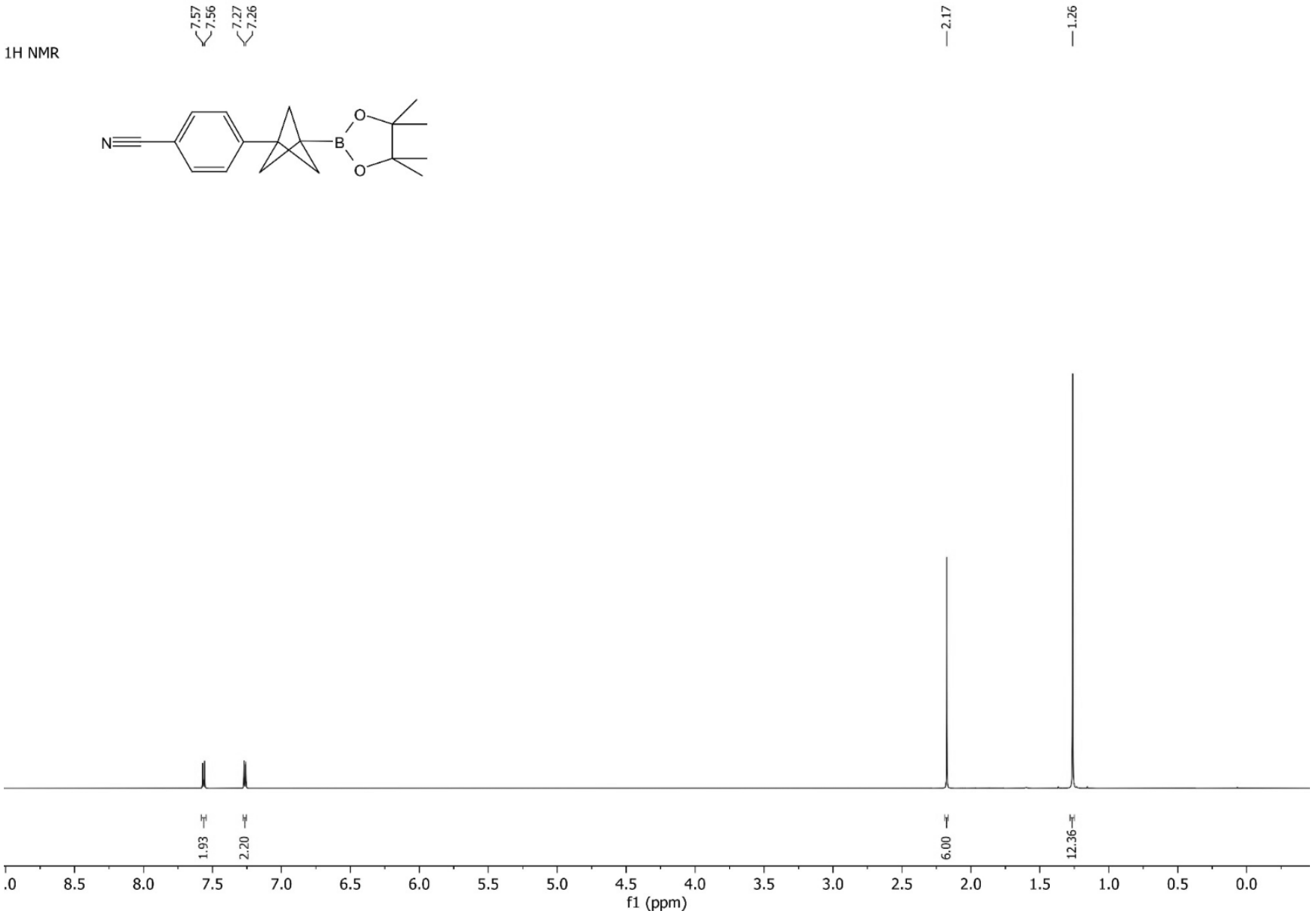
^{13}C NMR (101 MHz, $CDCl_3$) of **5j**



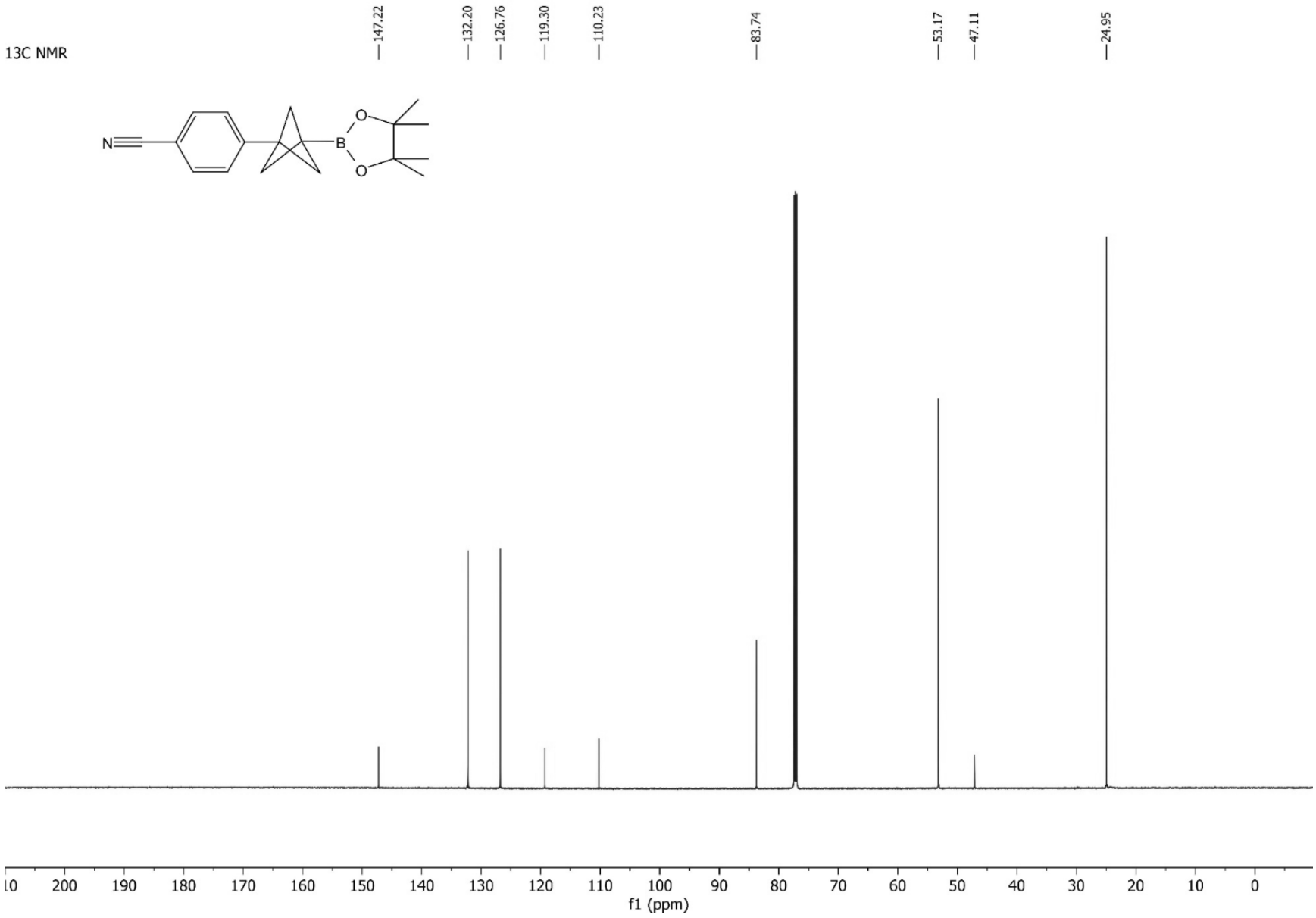
^{11}B NMR (128 MHz, $CDCl_3$) of **5j**



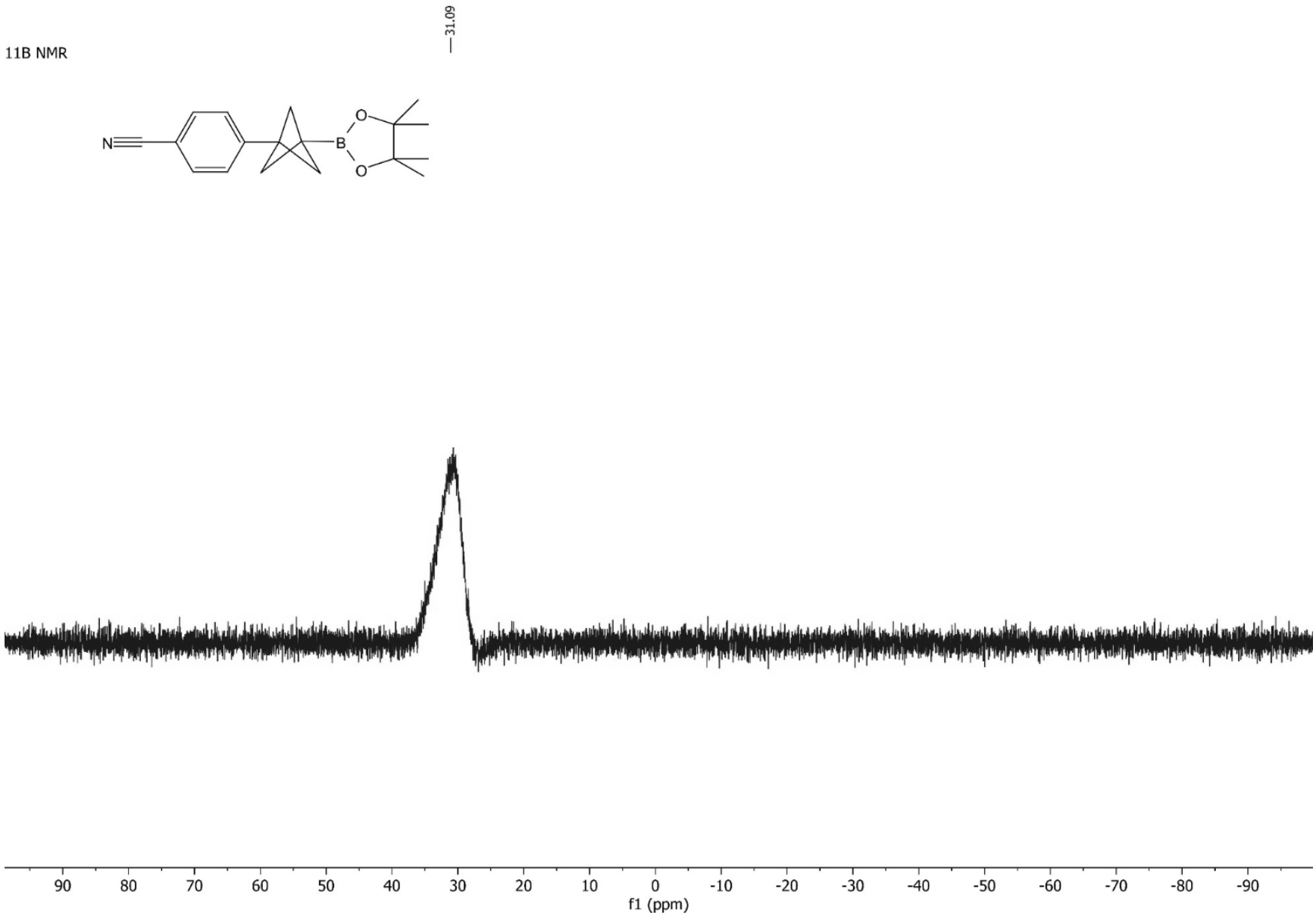
^{1}H NMR (600 MHz, $CDCl_3$) of **5k**



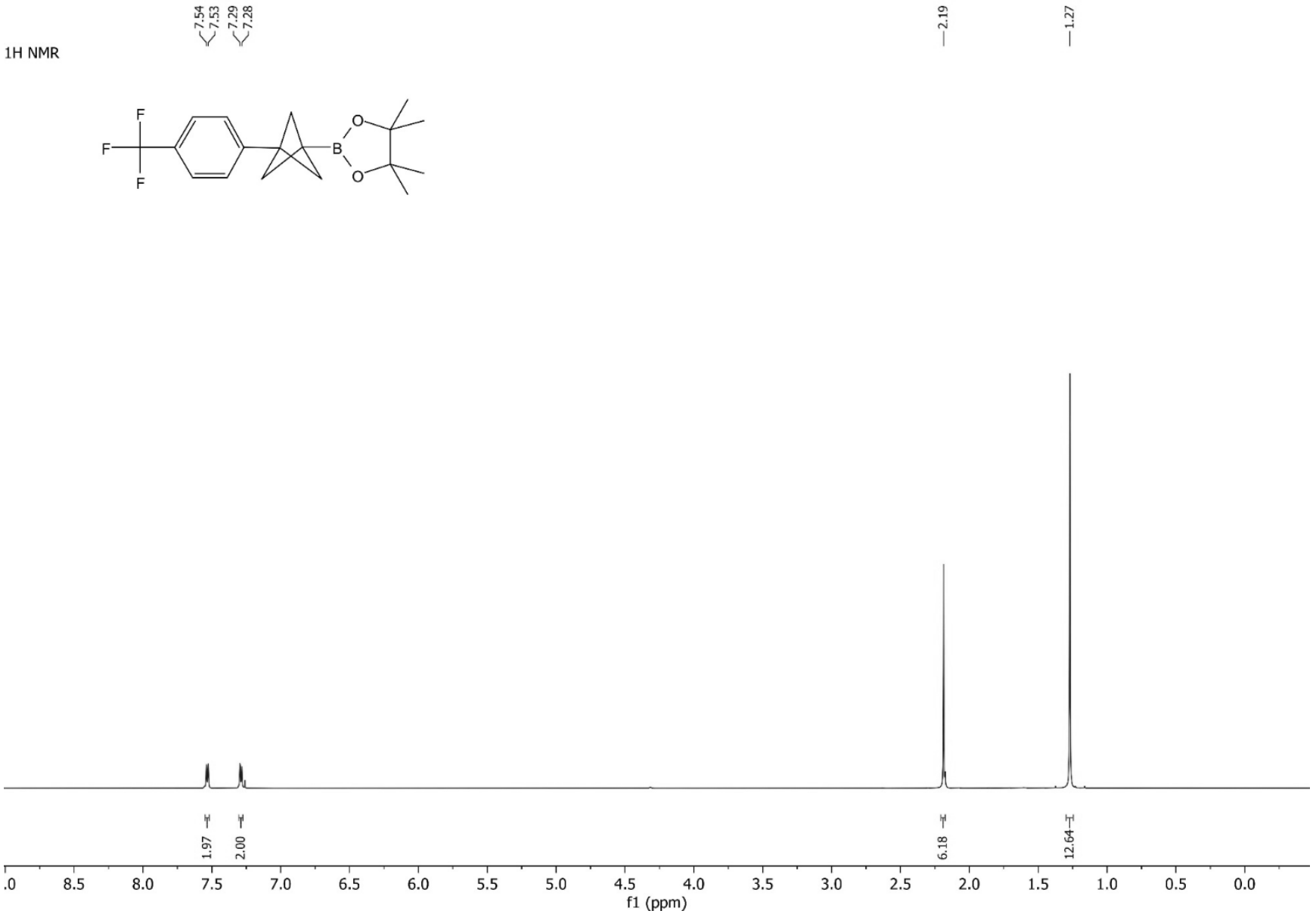
^{13}C NMR (151 MHz, $CDCl_3$) of **5k**



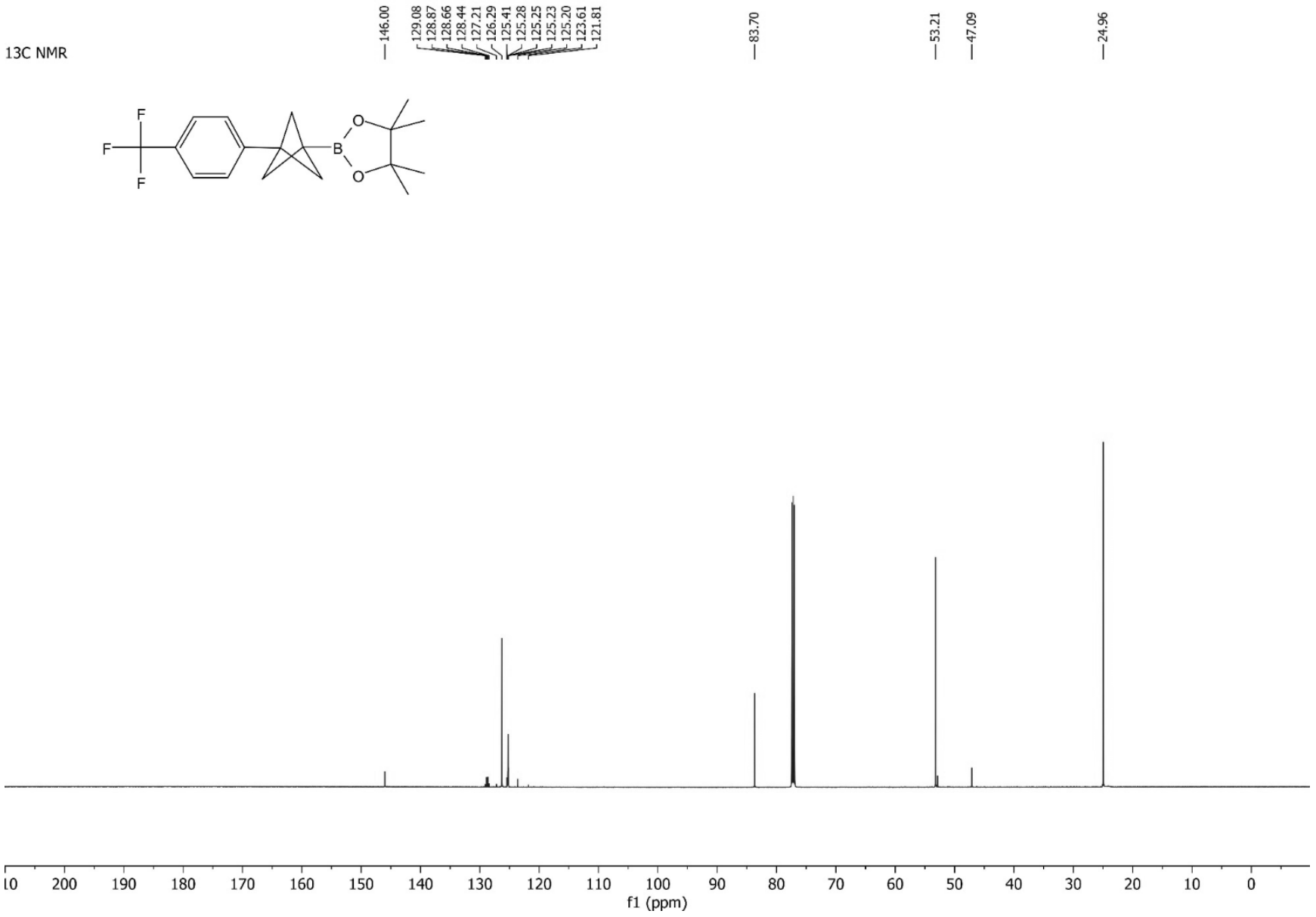
^{11}B NMR (128 MHz, $CDCl_3$) of **5k**



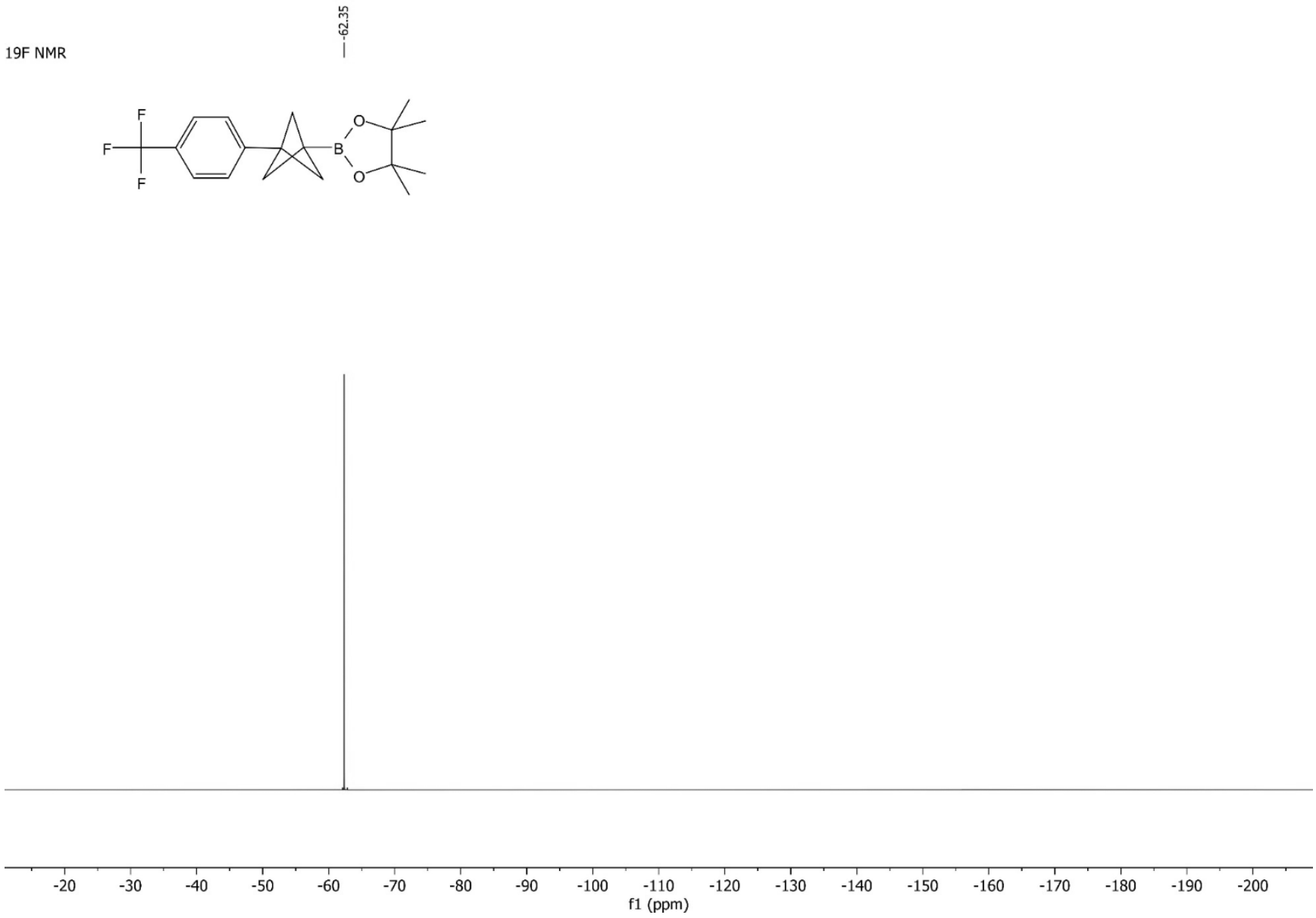
^{1}H NMR (600 MHz, $CDCl_3$) of **5l**



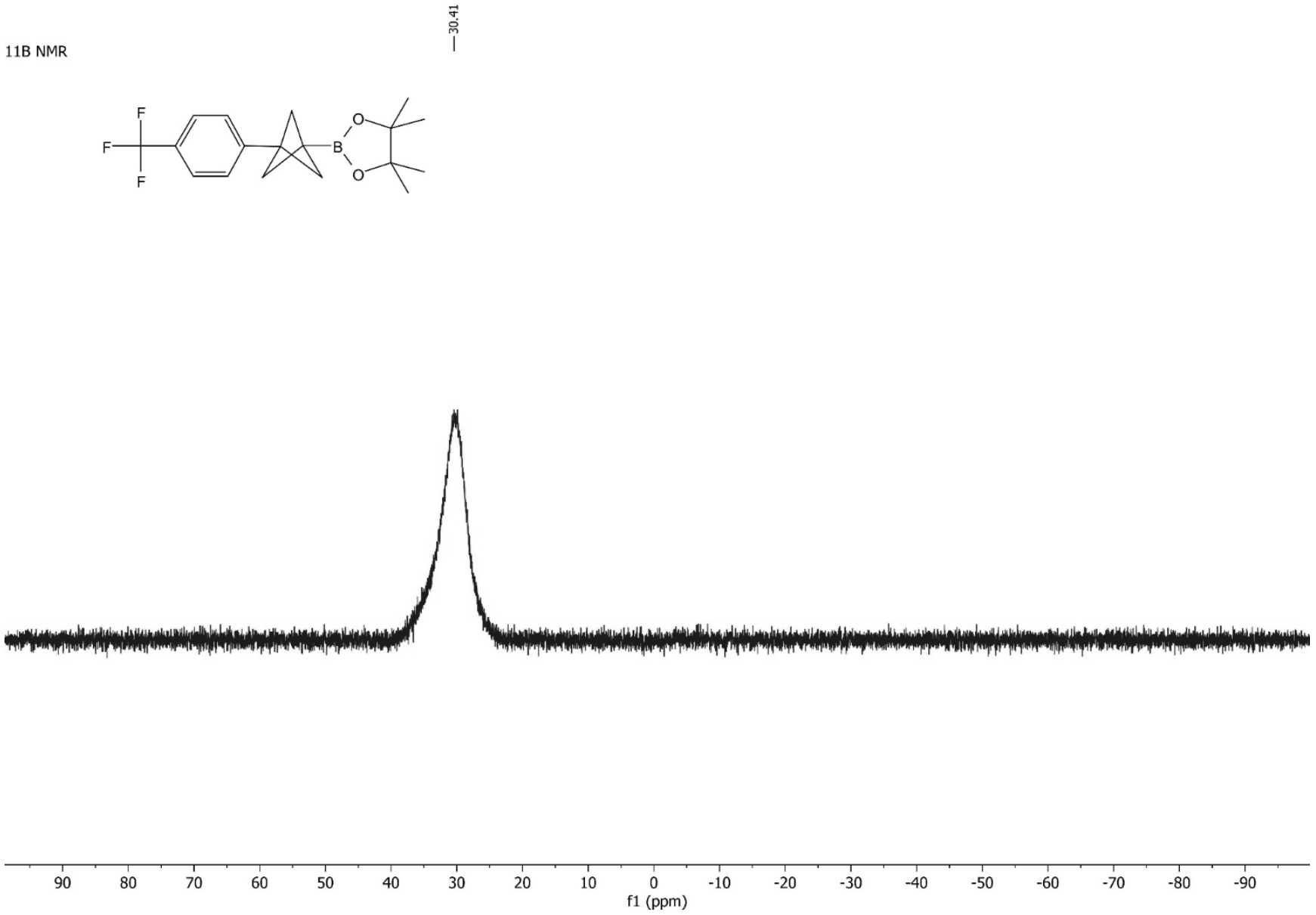
^{13}C NMR (151 MHz, $CDCl_3$) of **5l**



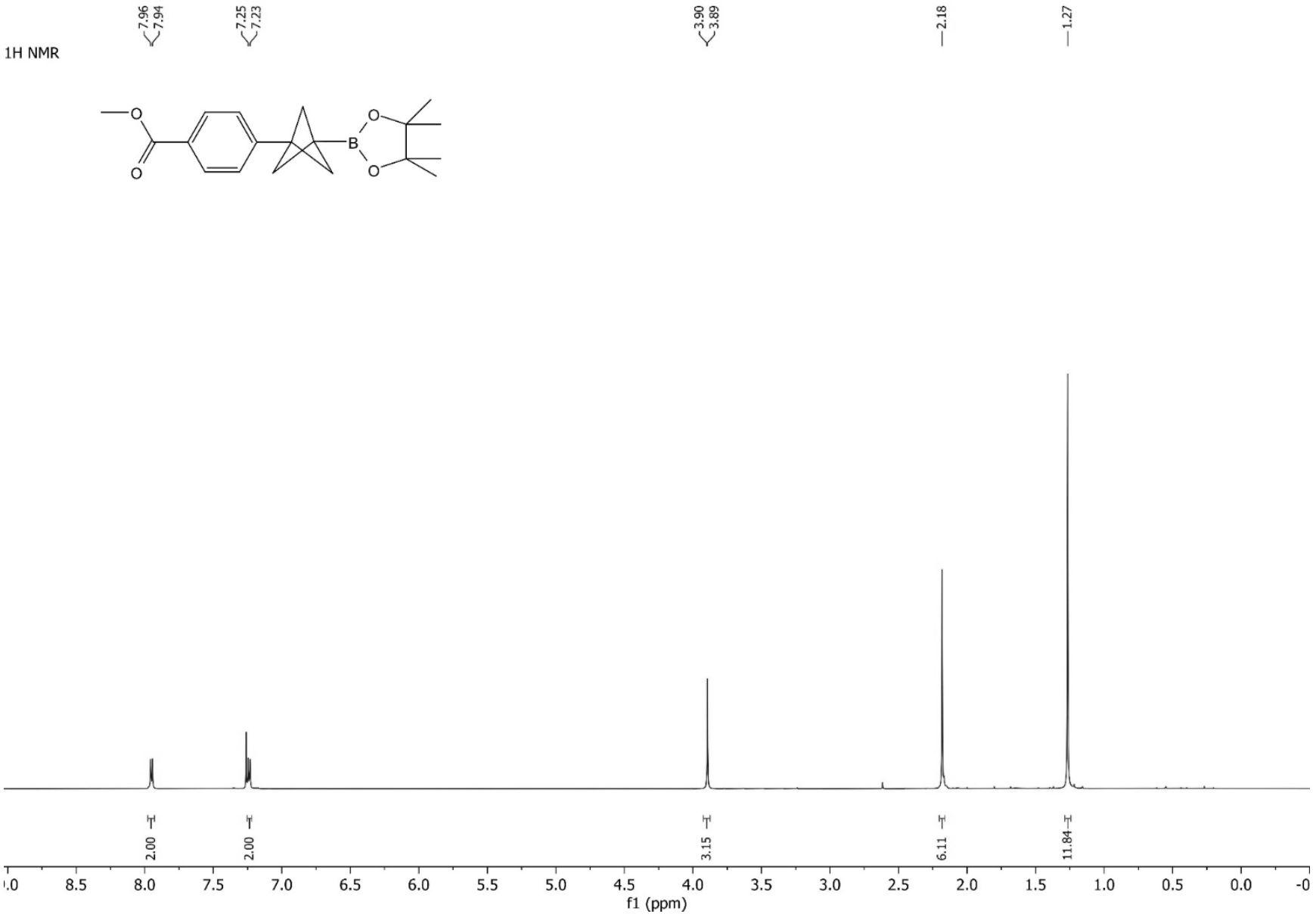
^{19}F NMR (376 MHz, $CDCl_3$) of **5l**



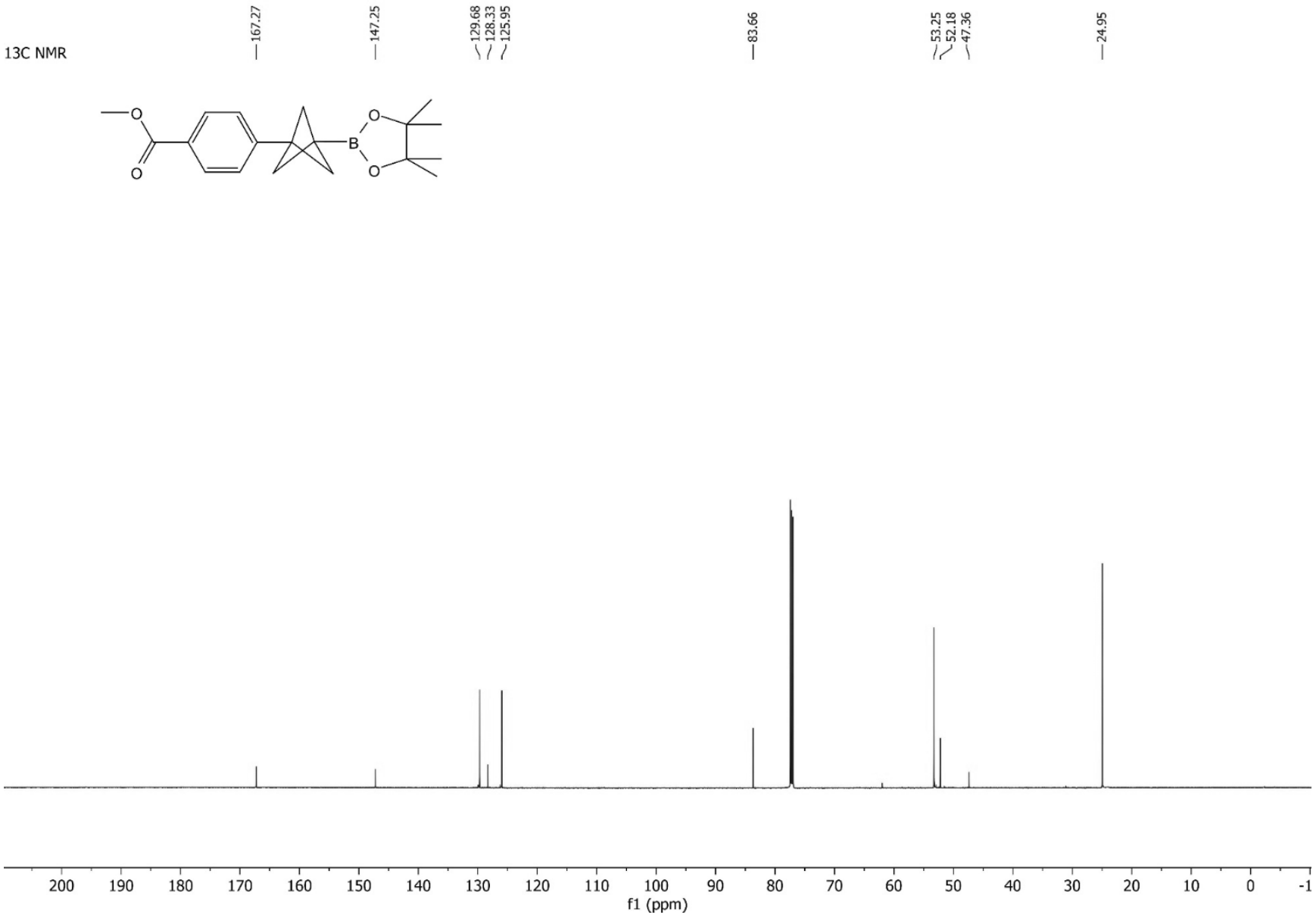
^{11}B NMR (128 MHz, $CDCl_3$) of **5l**



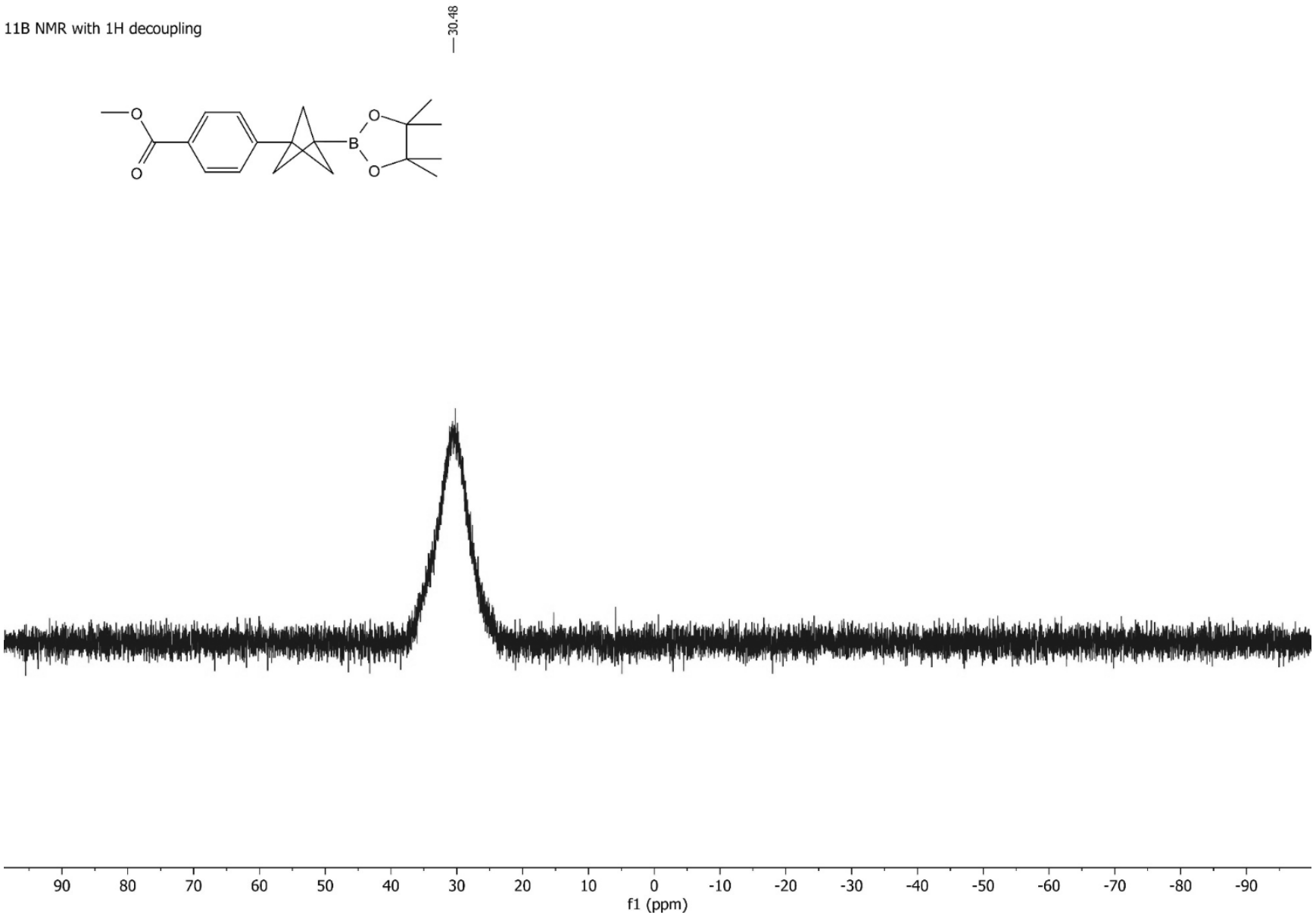
^{1}H NMR (600 MHz, $CDCl_3$) of **5m**



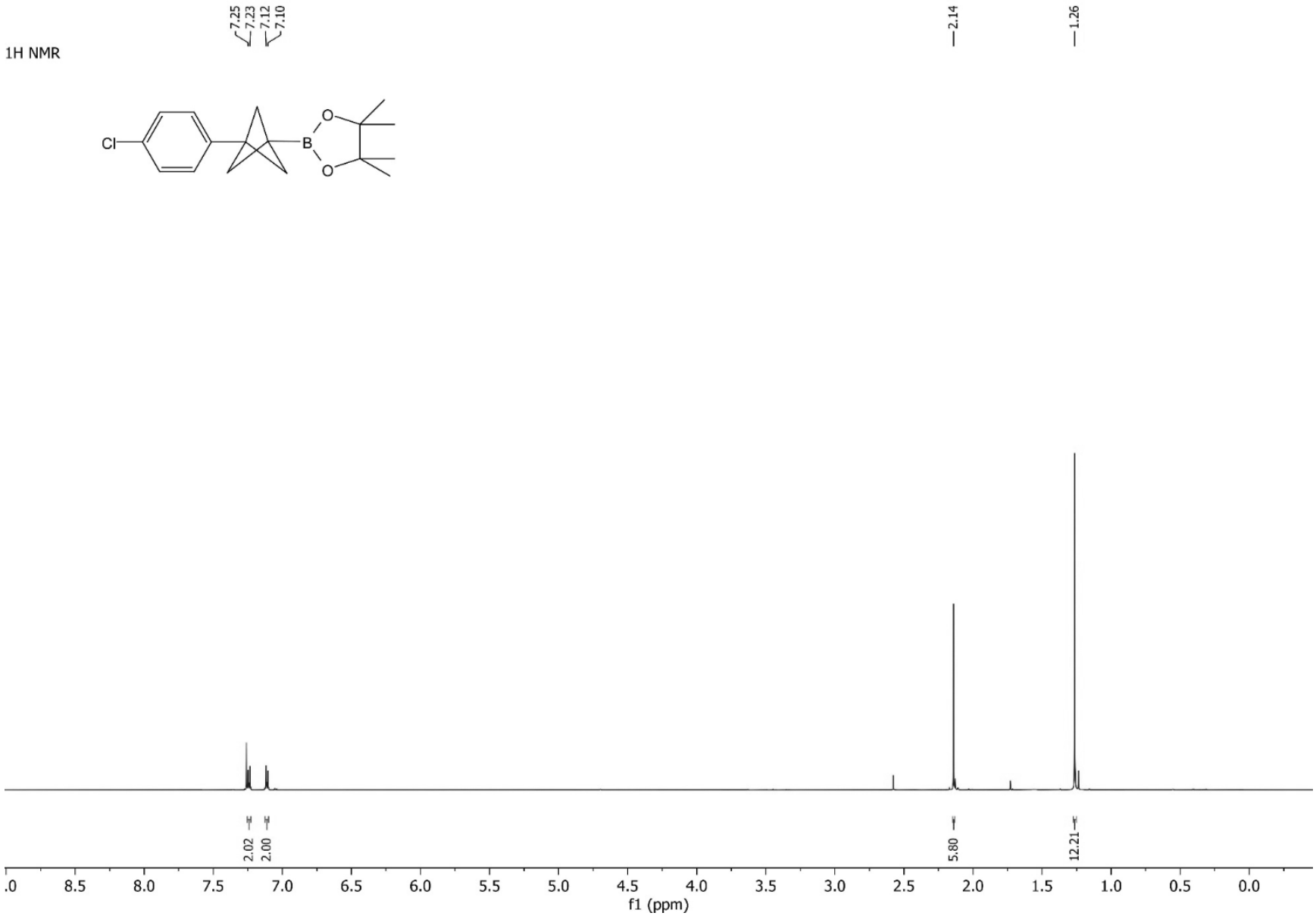
^{13}C NMR (151 MHz, $CDCl_3$) of **5m**



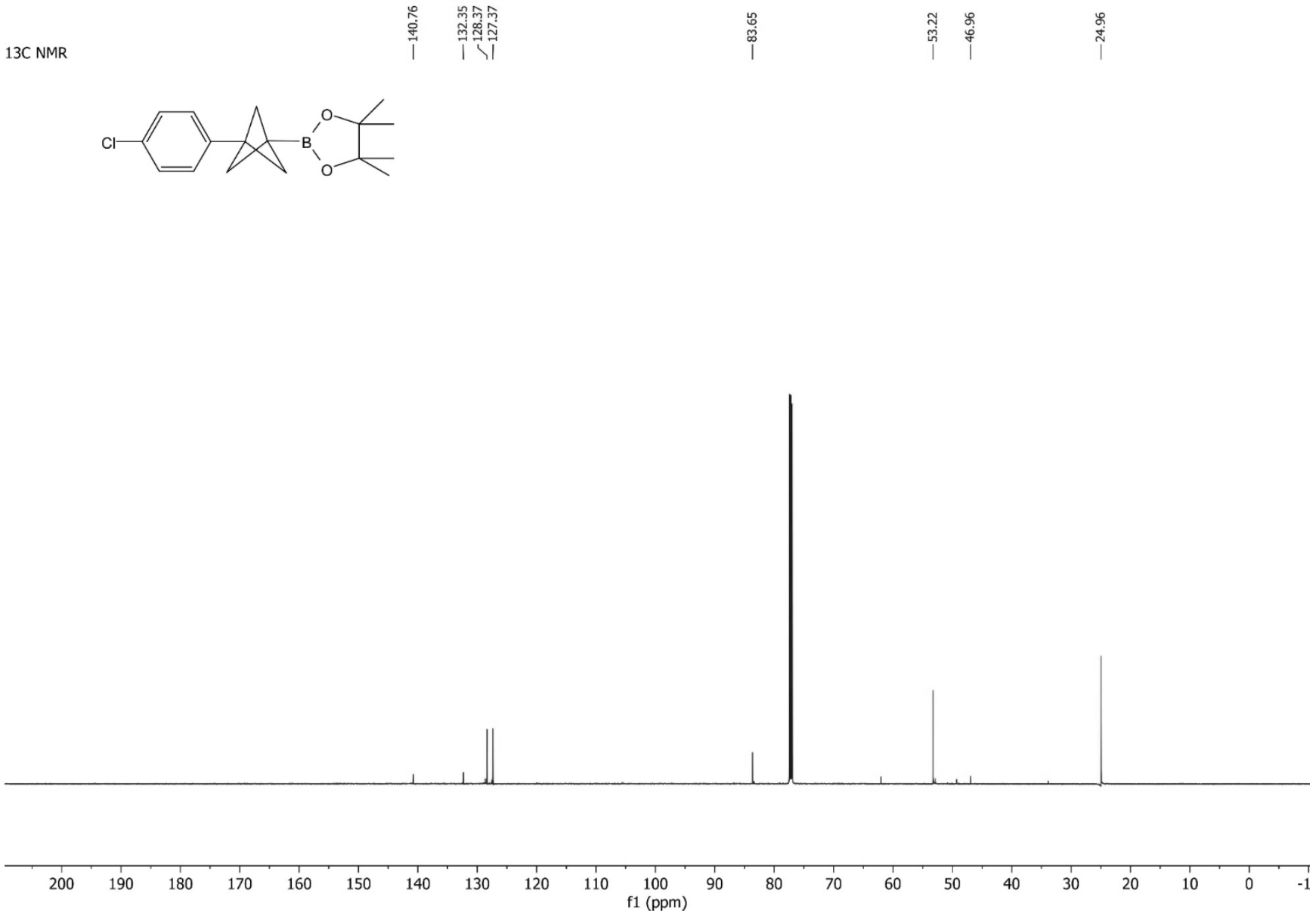
^{11}B NMR (128 MHz, $CDCl_3$) of **5m**



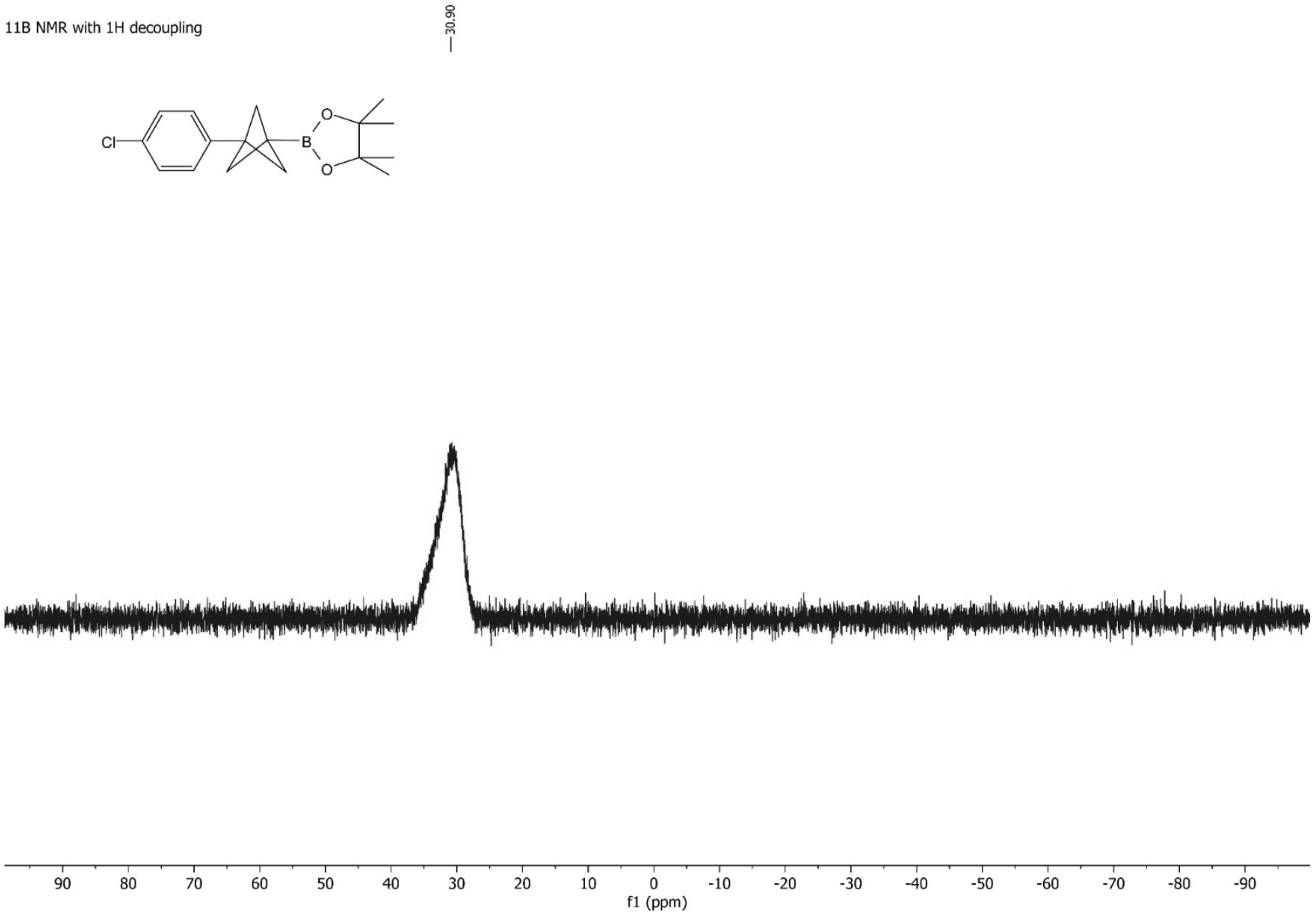
^{1}H NMR (600 MHz, $CDCl_3$) of **5n**



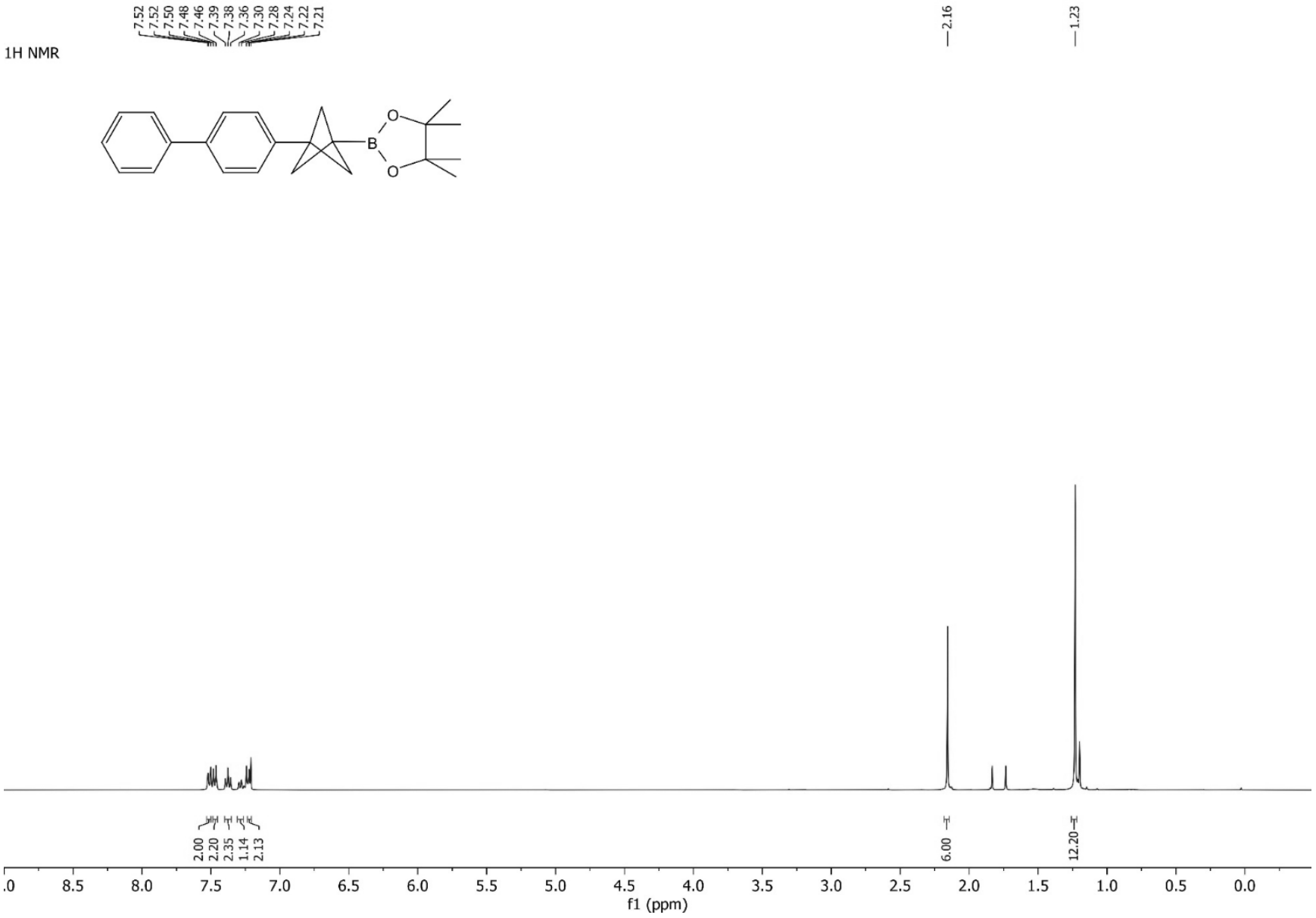
^{13}C NMR (151 MHz, $CDCl_3$) of **5n**



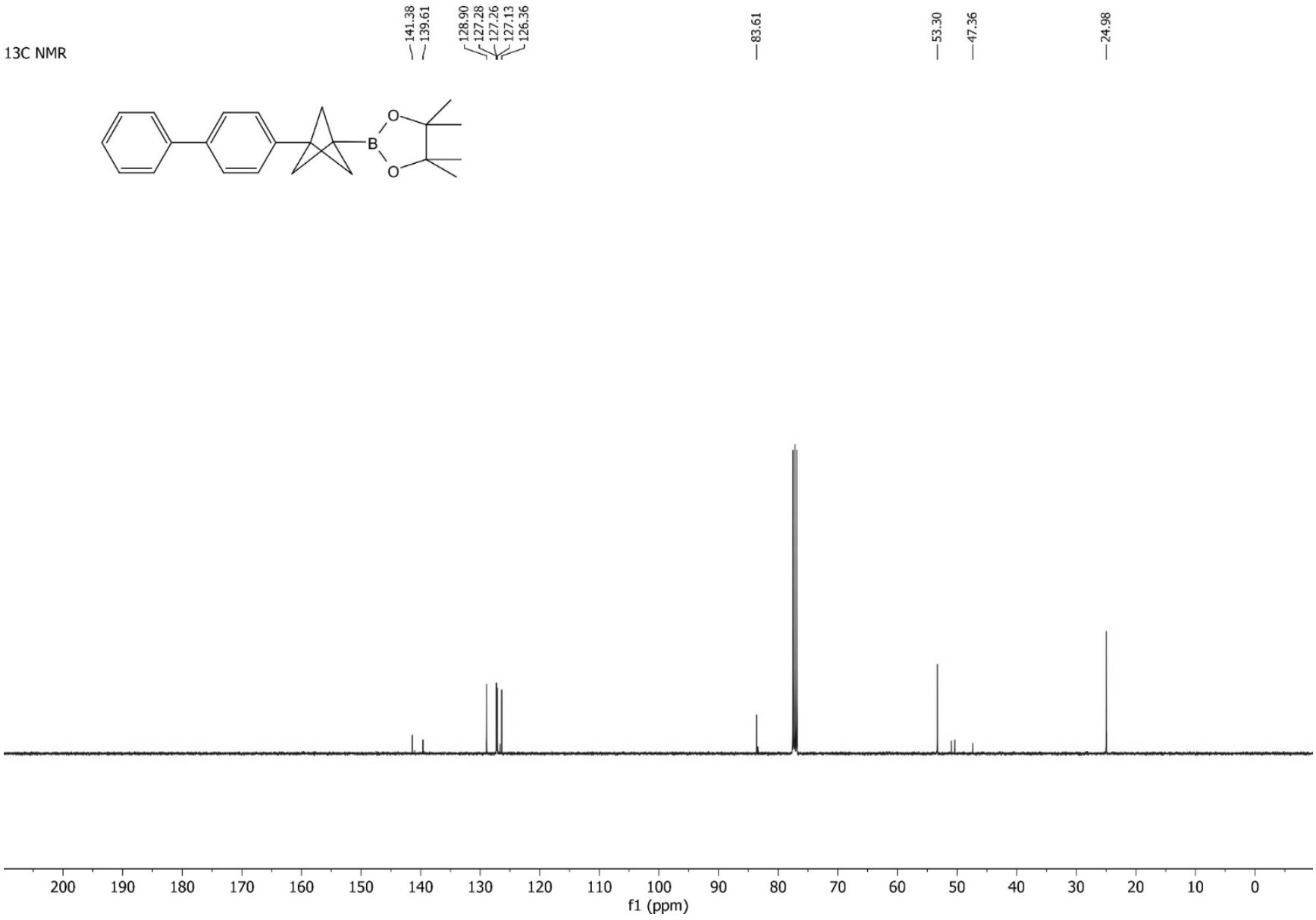
^{11}B NMR (128 MHz, $CDCl_3$) of **5n**



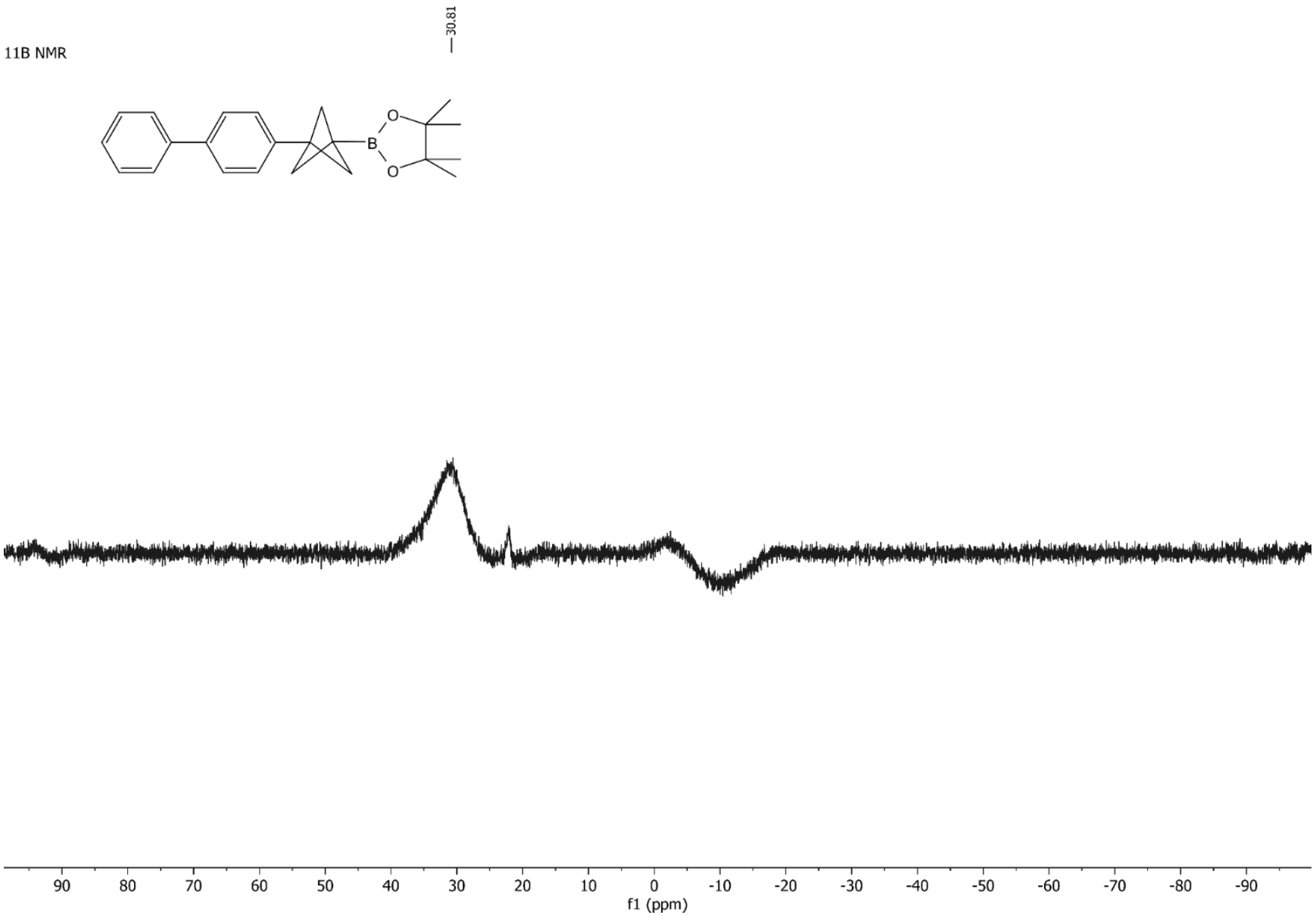
^{1}H NMR (400 MHz, $CDCl_3$) of **5o**



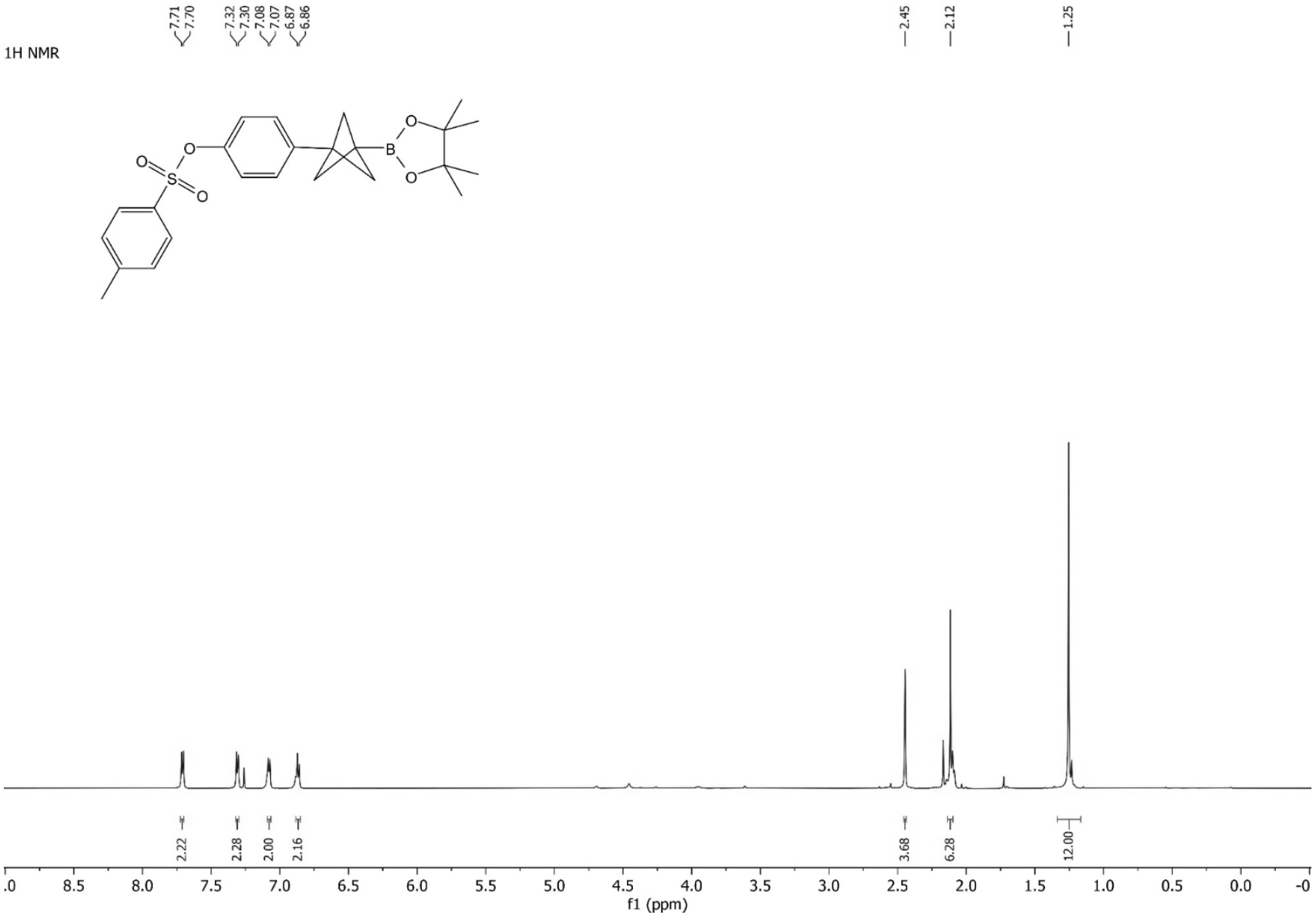
^{13}C NMR (101 MHz, $CDCl_3$) of **5o**



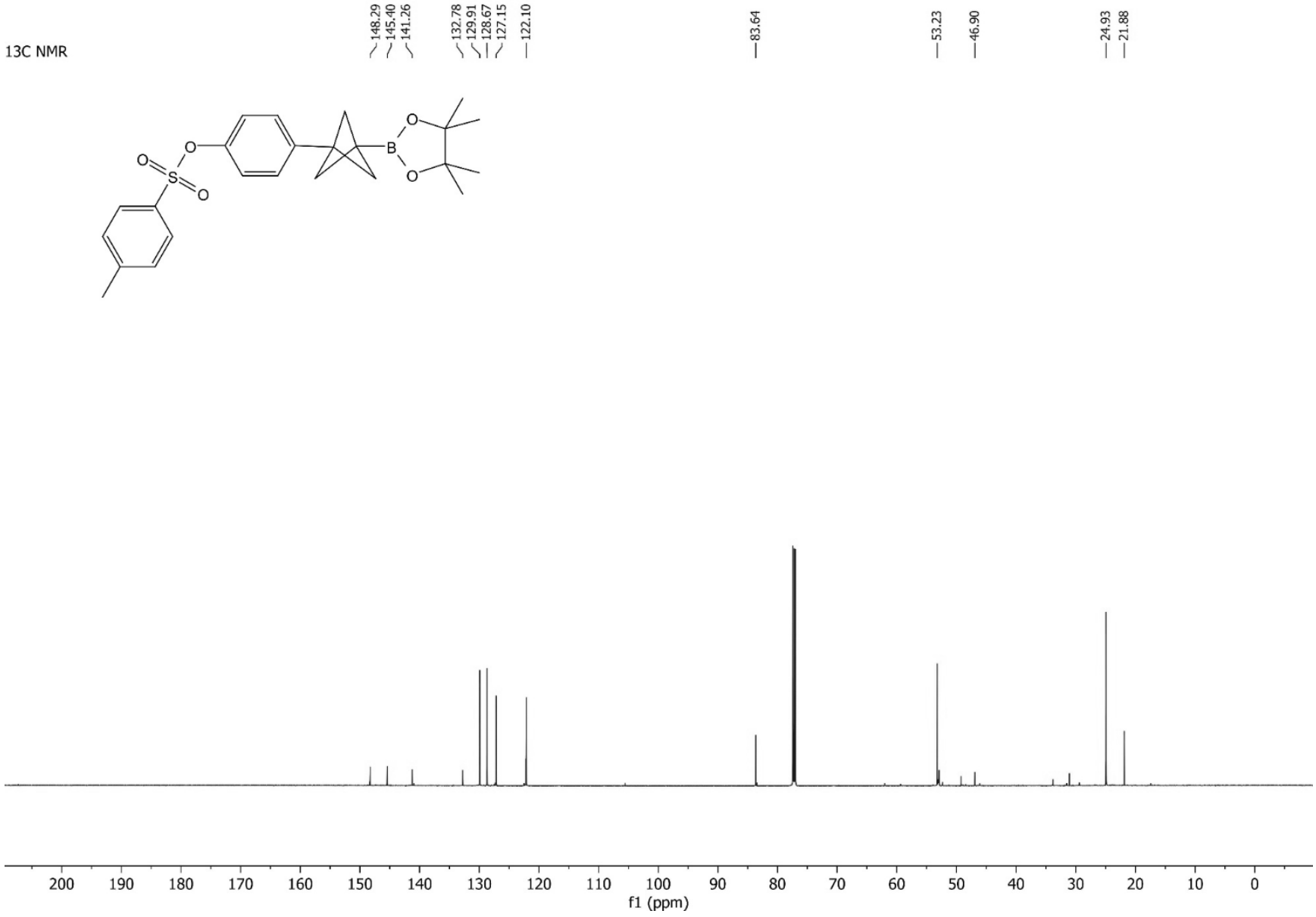
^{11}B NMR (128 MHz, $CDCl_3$) of **5o**



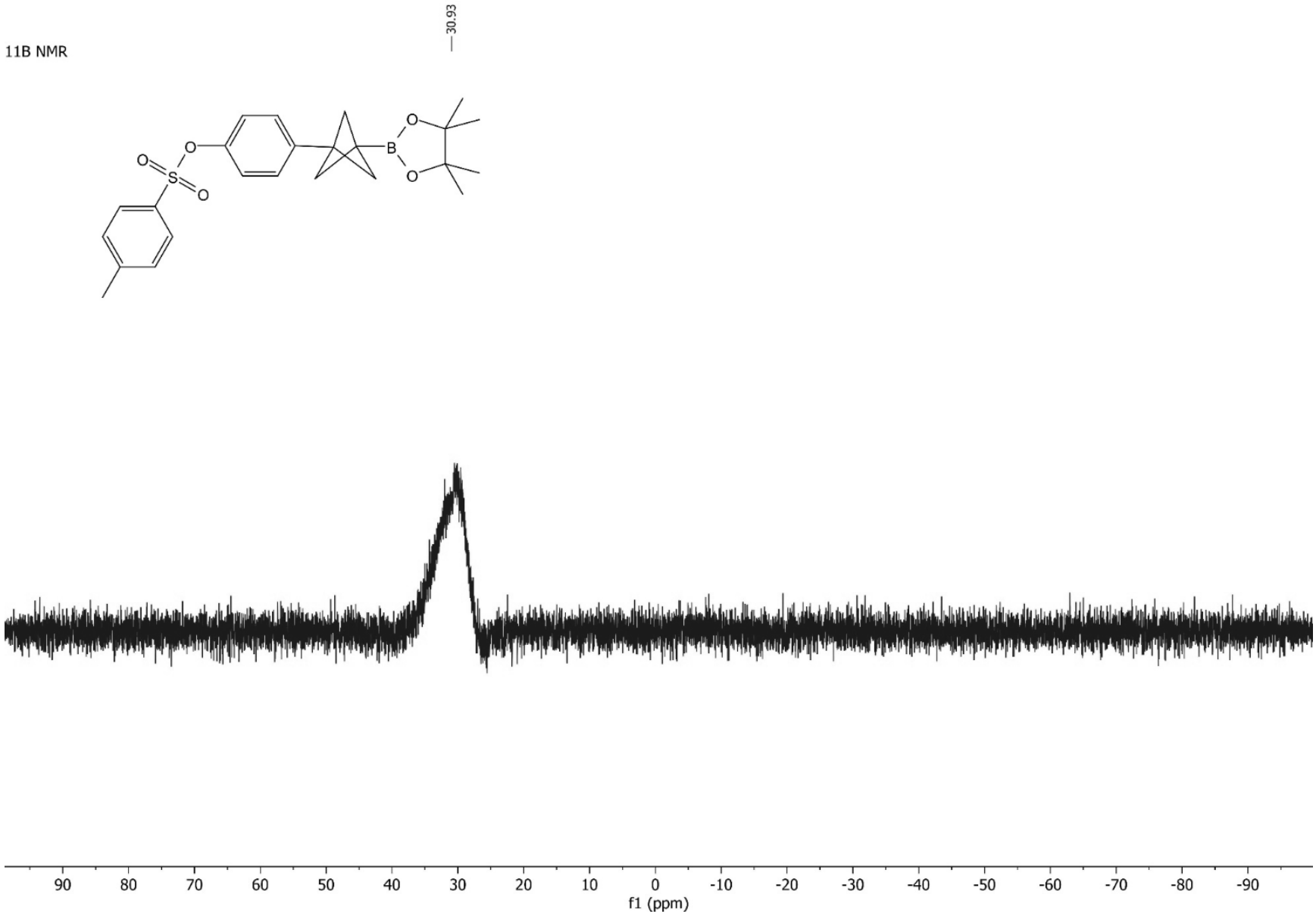
^{1}H NMR (600 MHz, $CDCl_3$) of **5p**



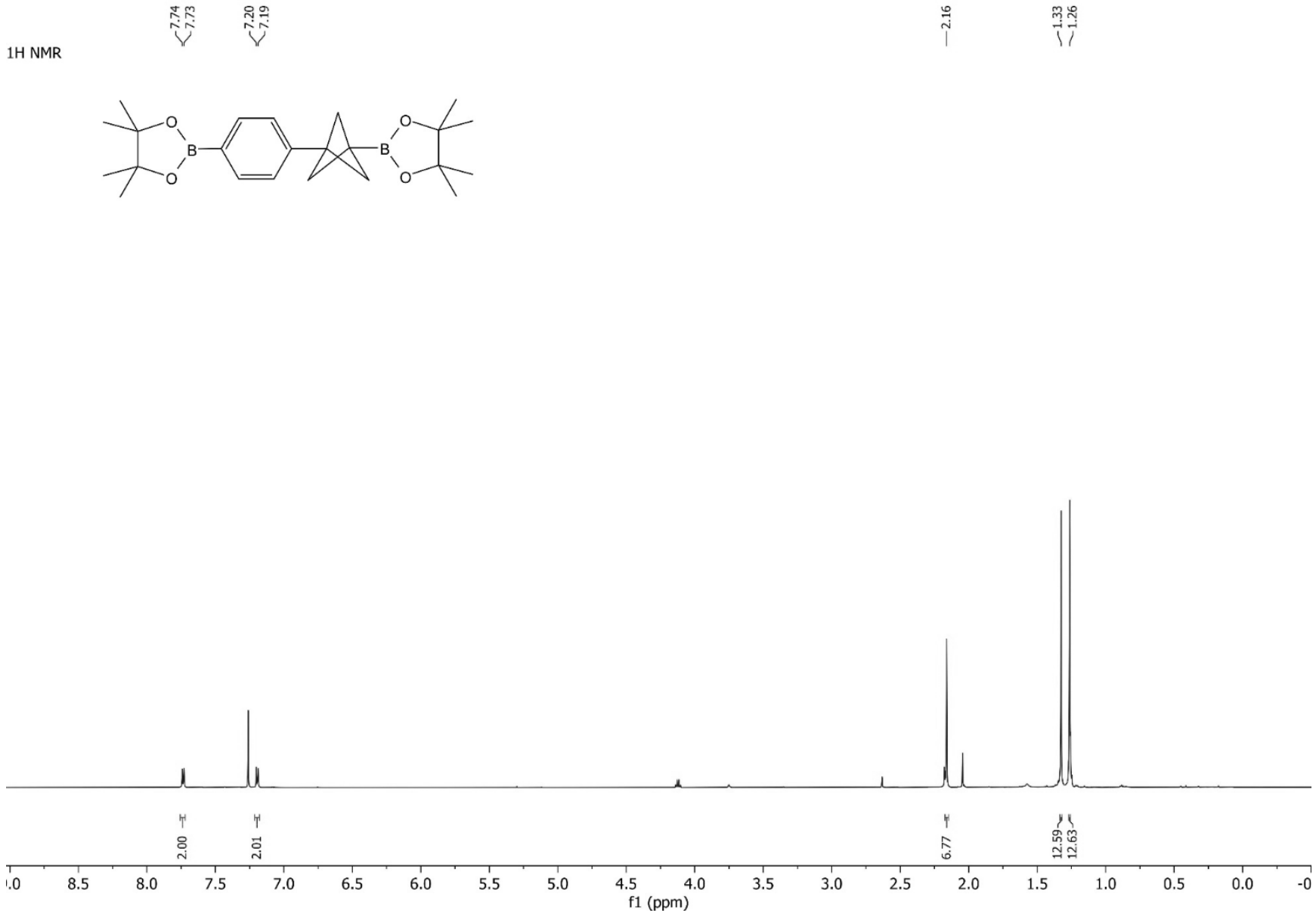
^{13}C NMR (151 MHz, $CDCl_3$) of **5p**



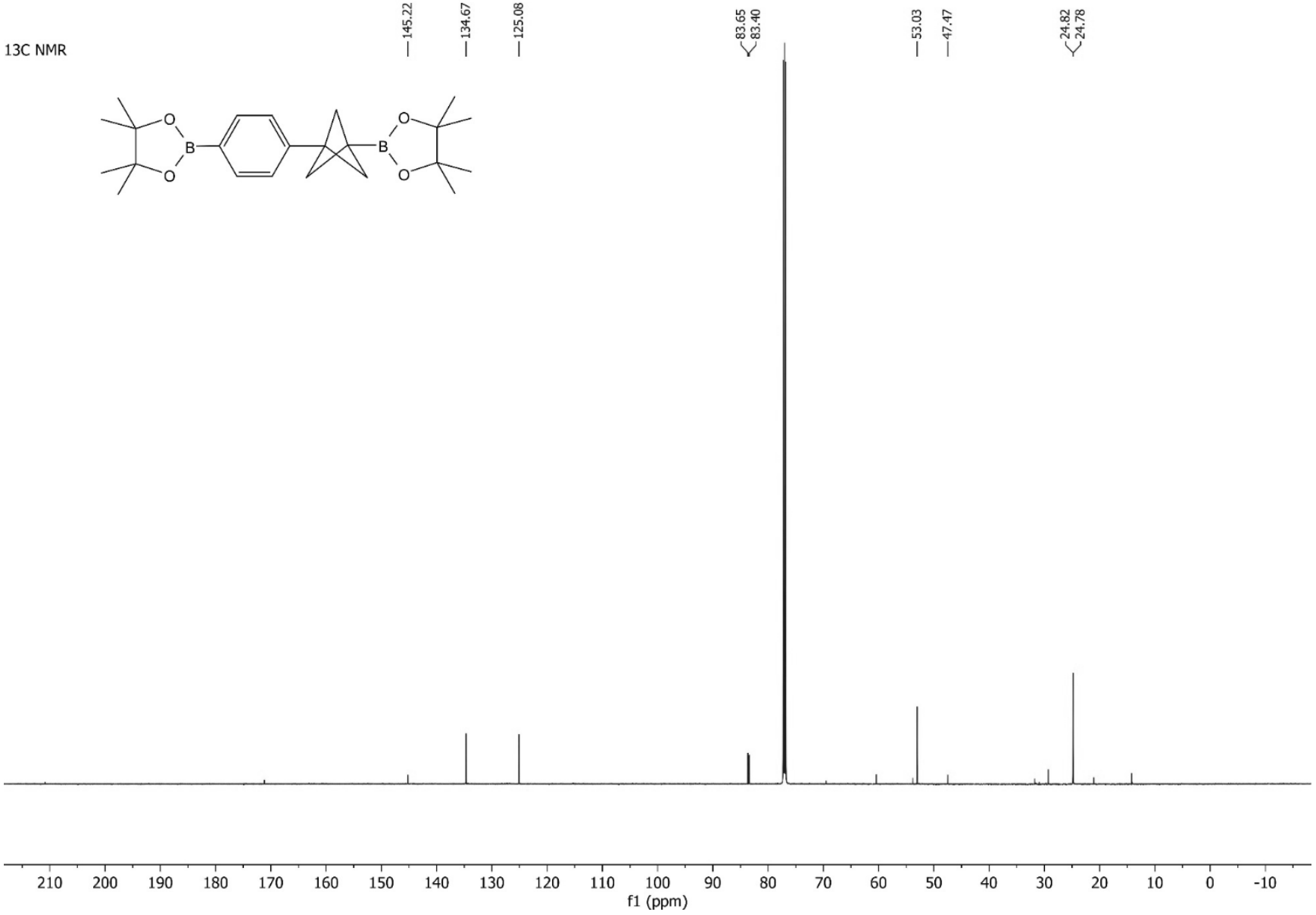
^{11}B NMR (128 MHz, $CDCl_3$) of **5p**



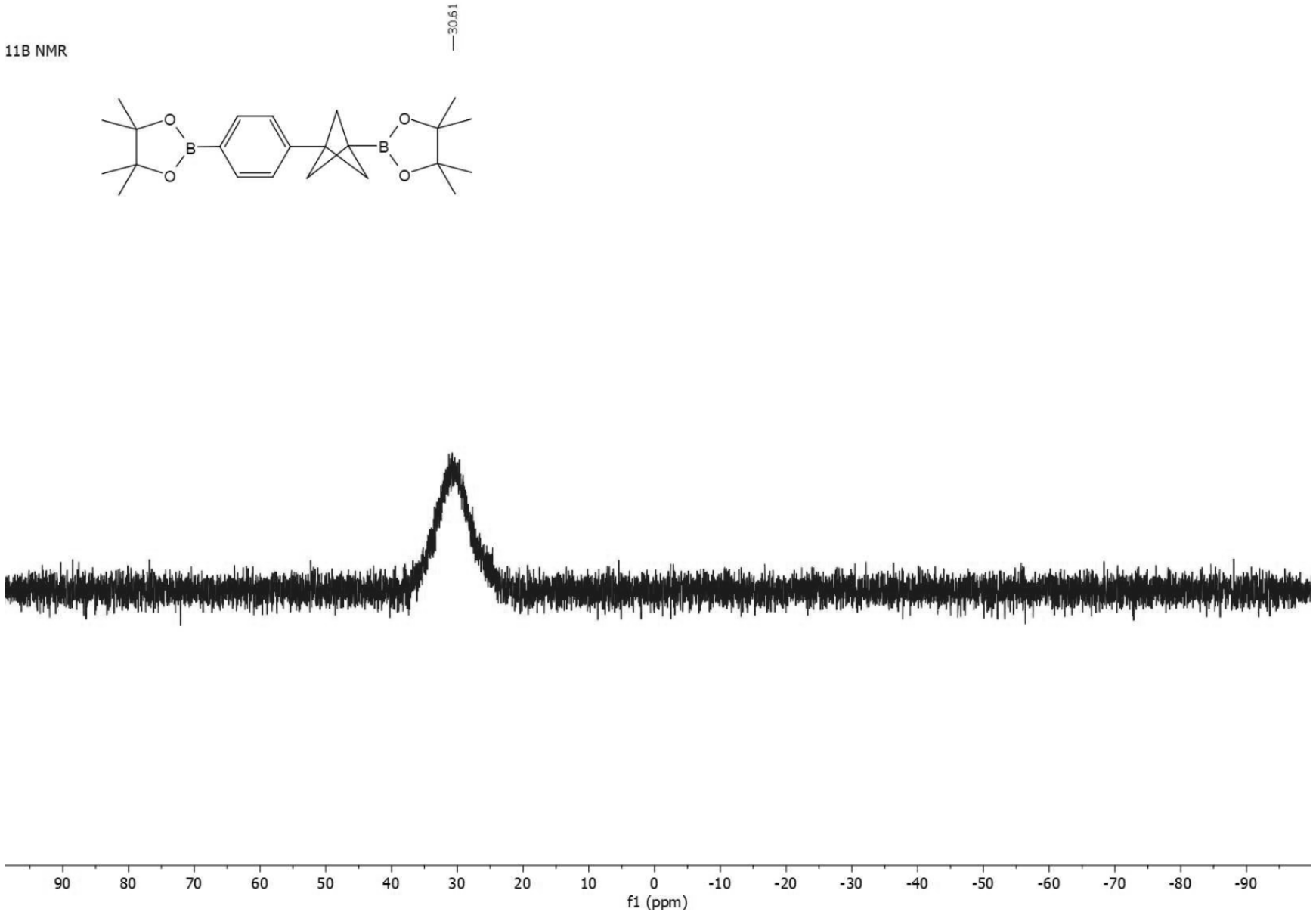
^{1}H NMR (600 MHz, $CDCl_3$) of **5q**



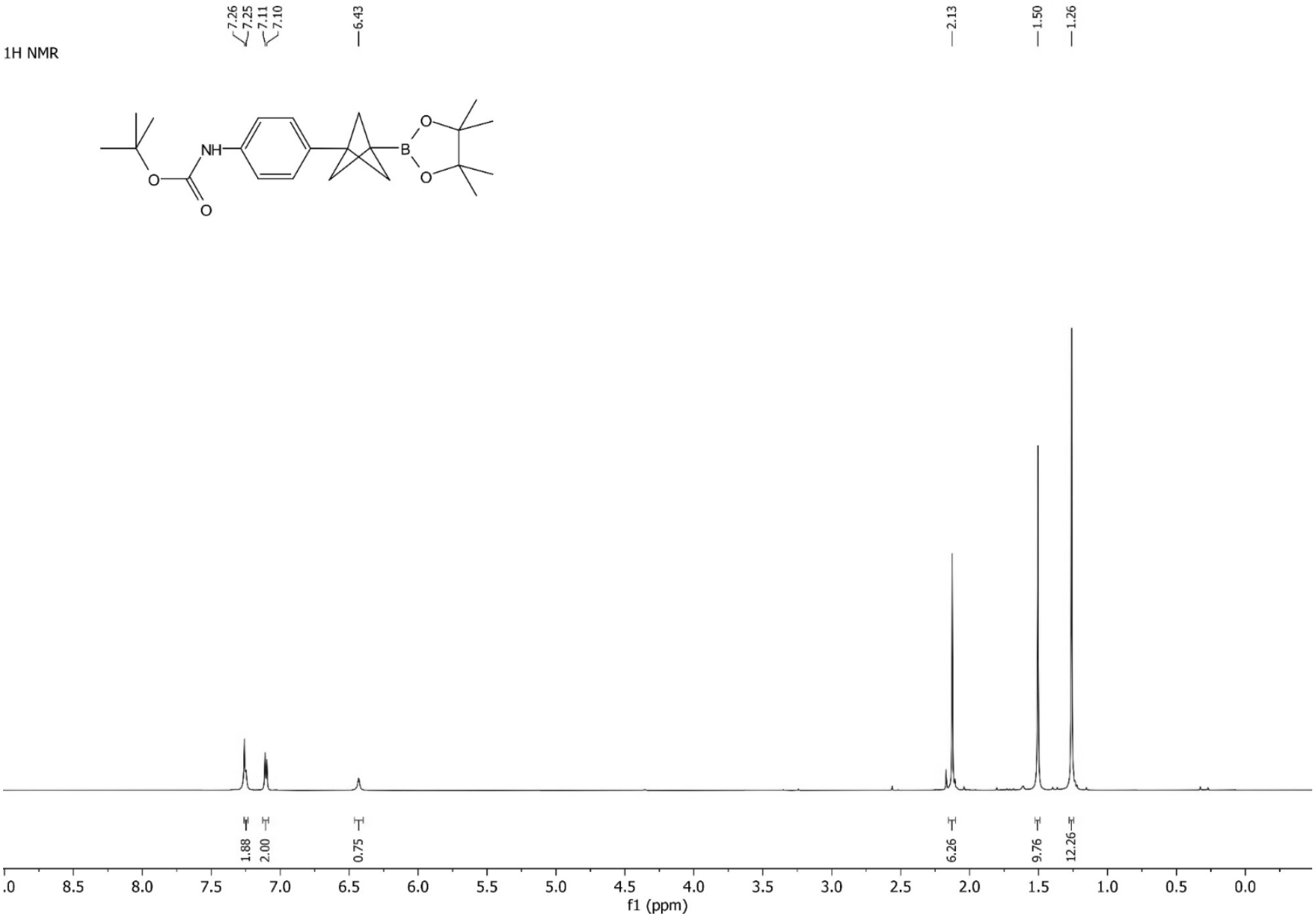
^{13}C NMR (151 MHz, $CDCl_3$) of **5q**



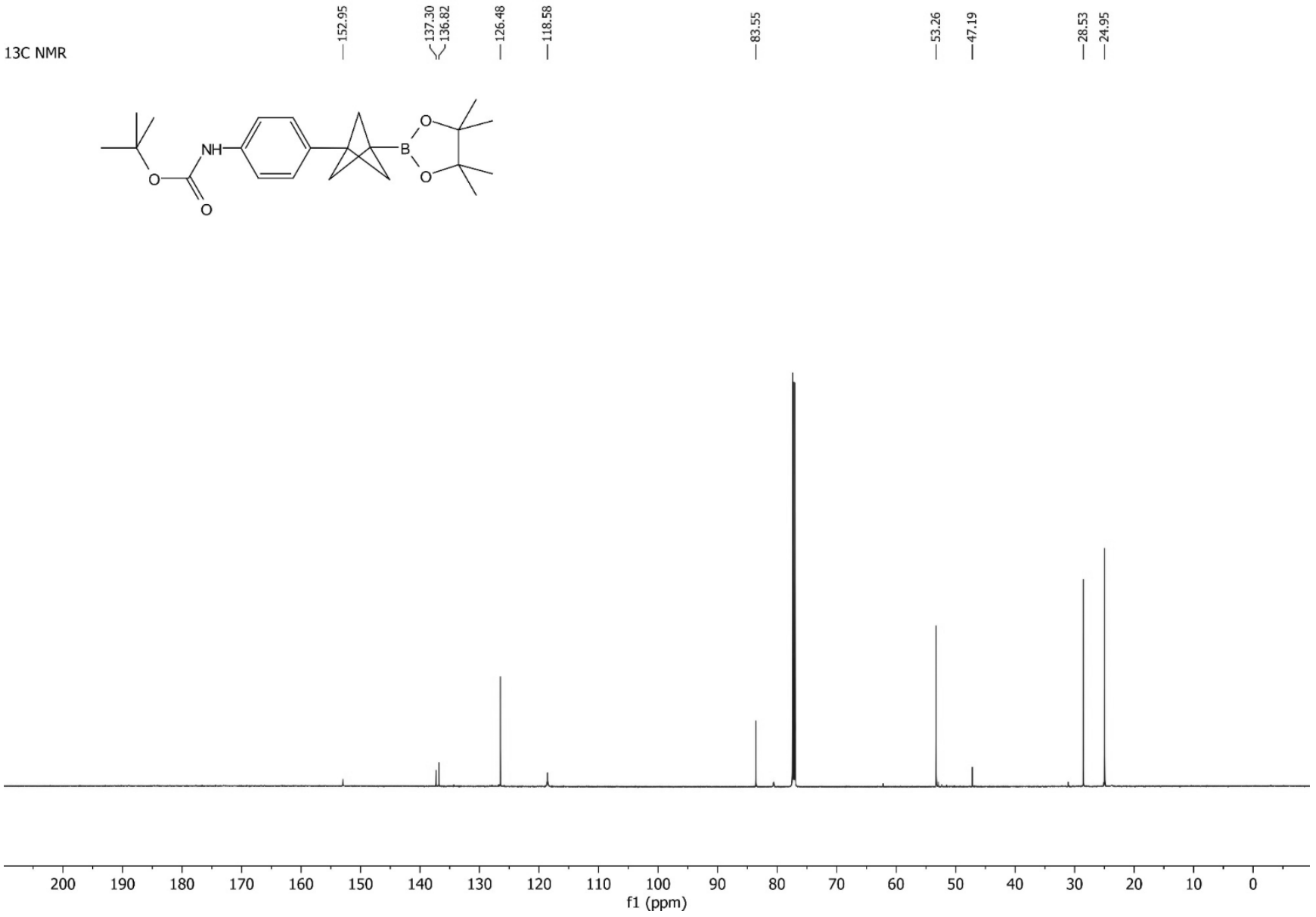
^{11}B NMR (128 MHz, $CDCl_3$) of **5q**



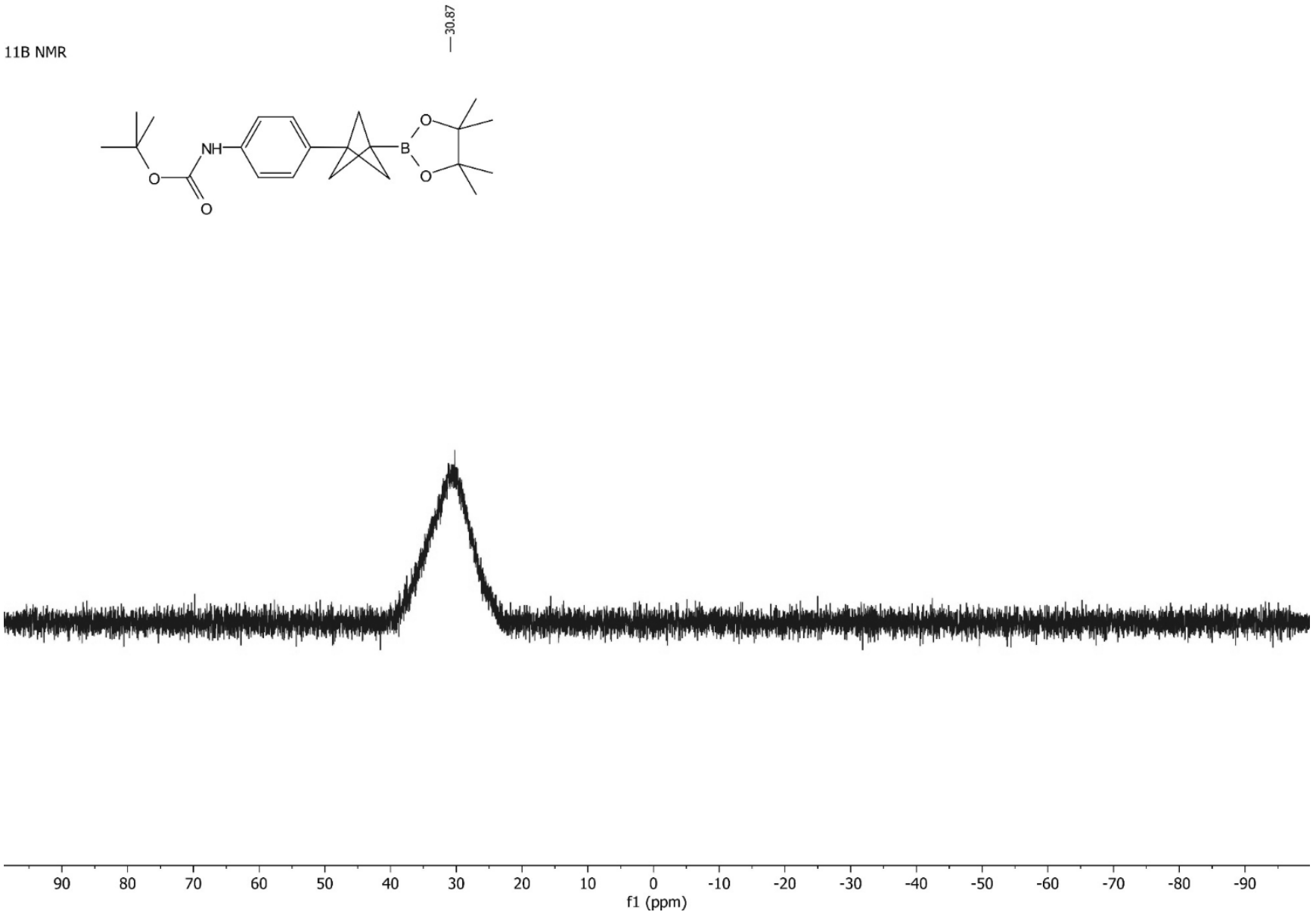
^{1}H NMR (600 MHz, $CDCl_3$) of **5r**



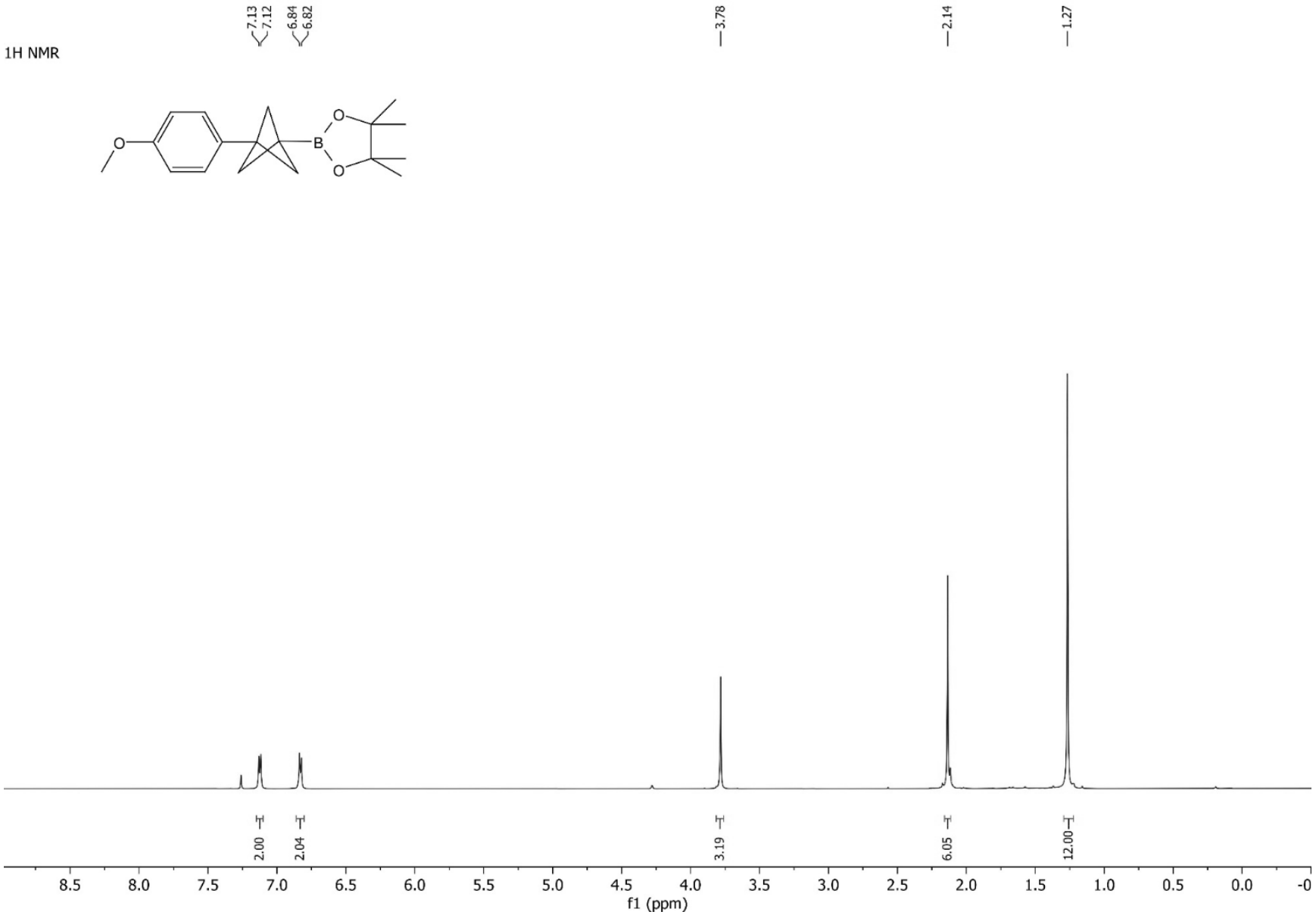
^{13}C NMR (151 MHz, $CDCl_3$) of **5r**



^{11}B NMR (128 MHz, $CDCl_3$) of **5r**



^{1}H NMR (600 MHz, $CDCl_3$) of **5s**



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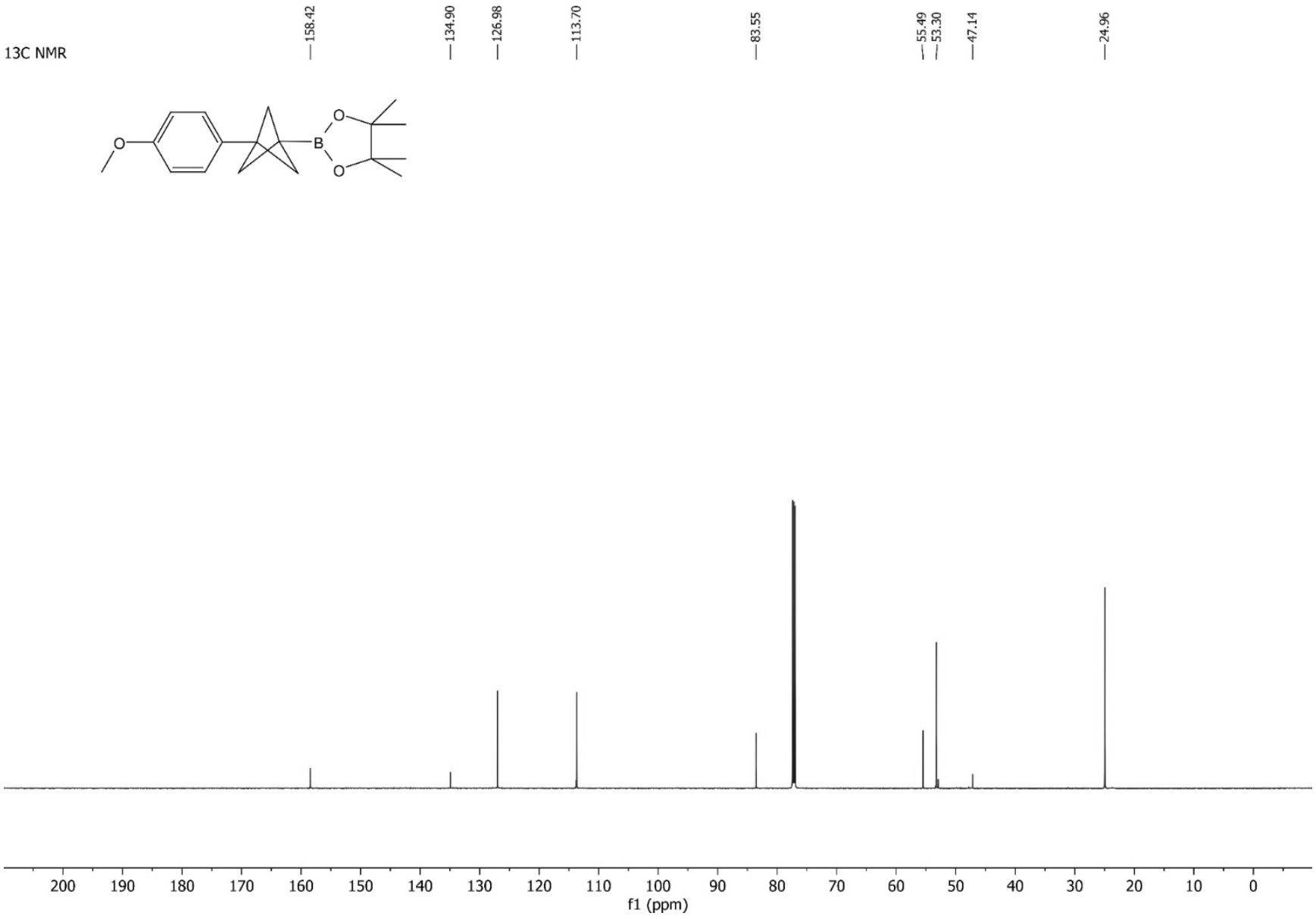

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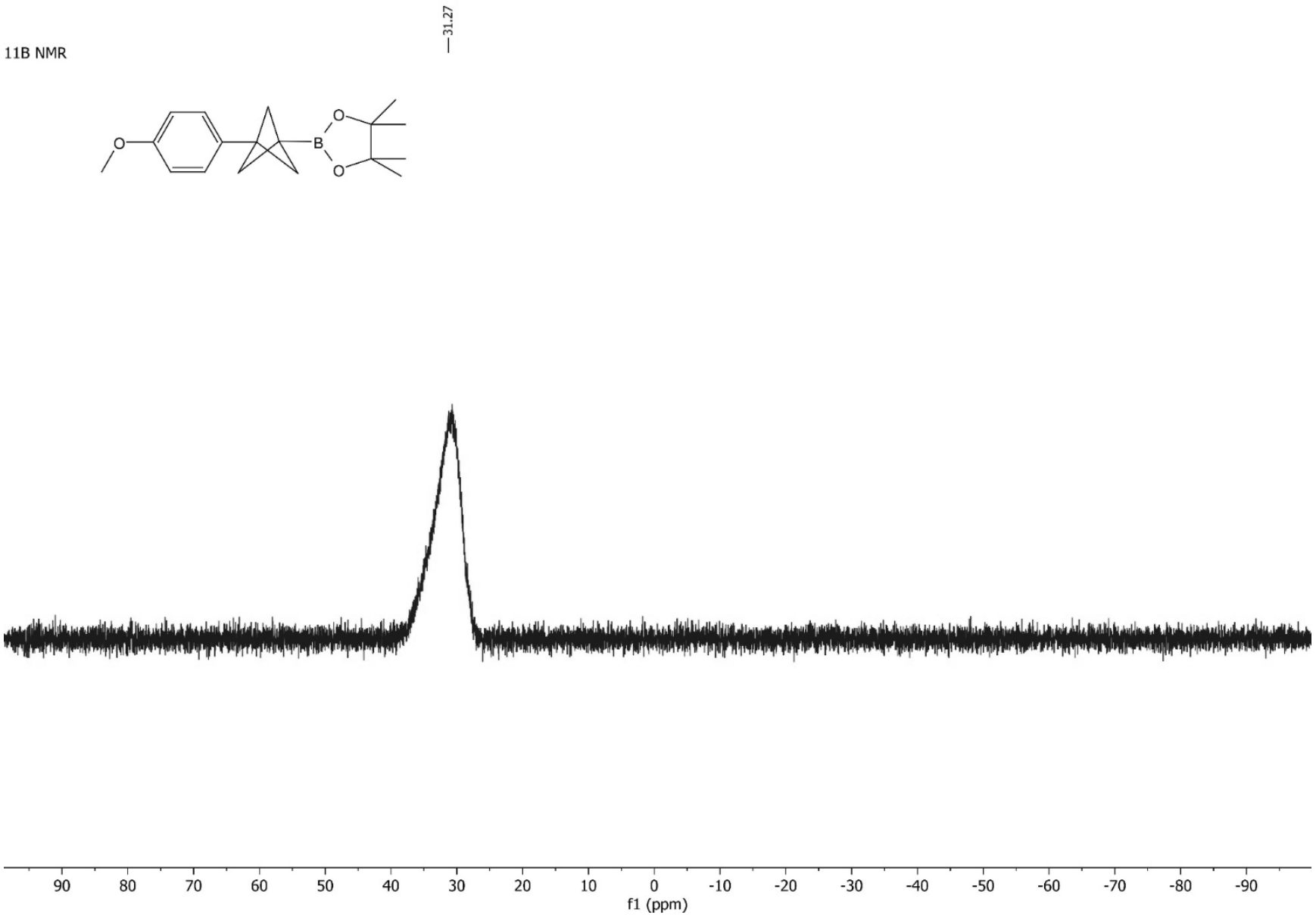
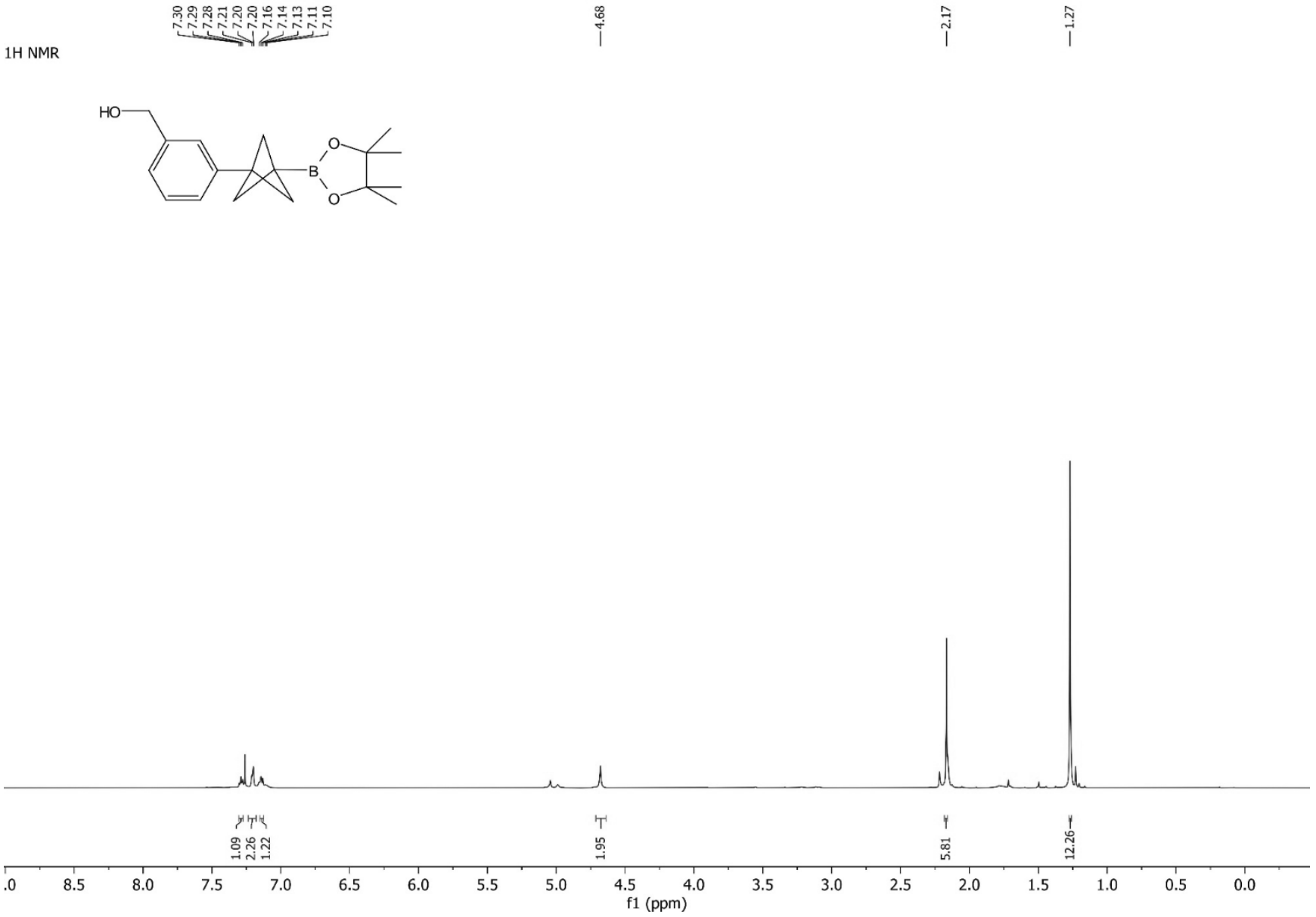
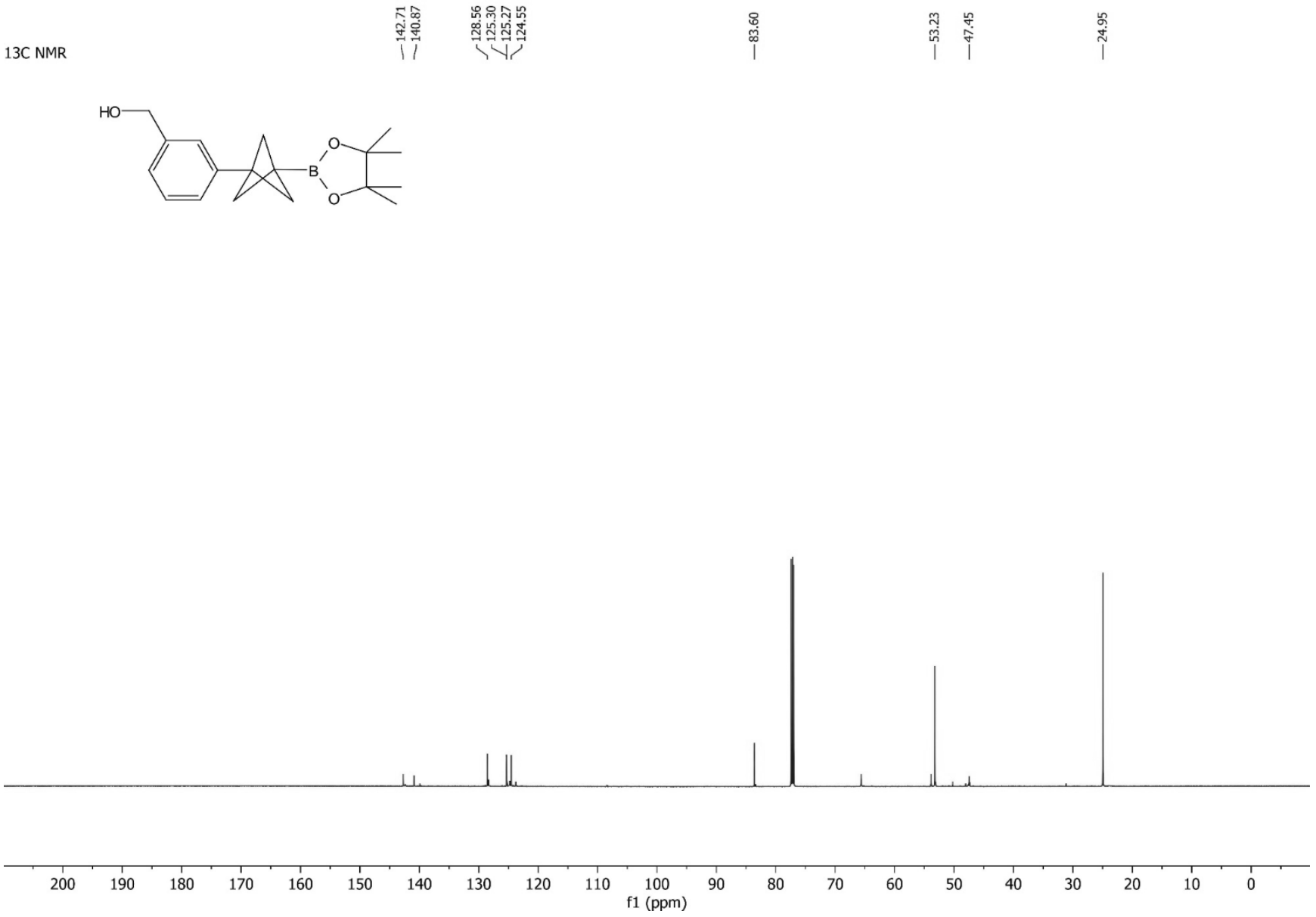


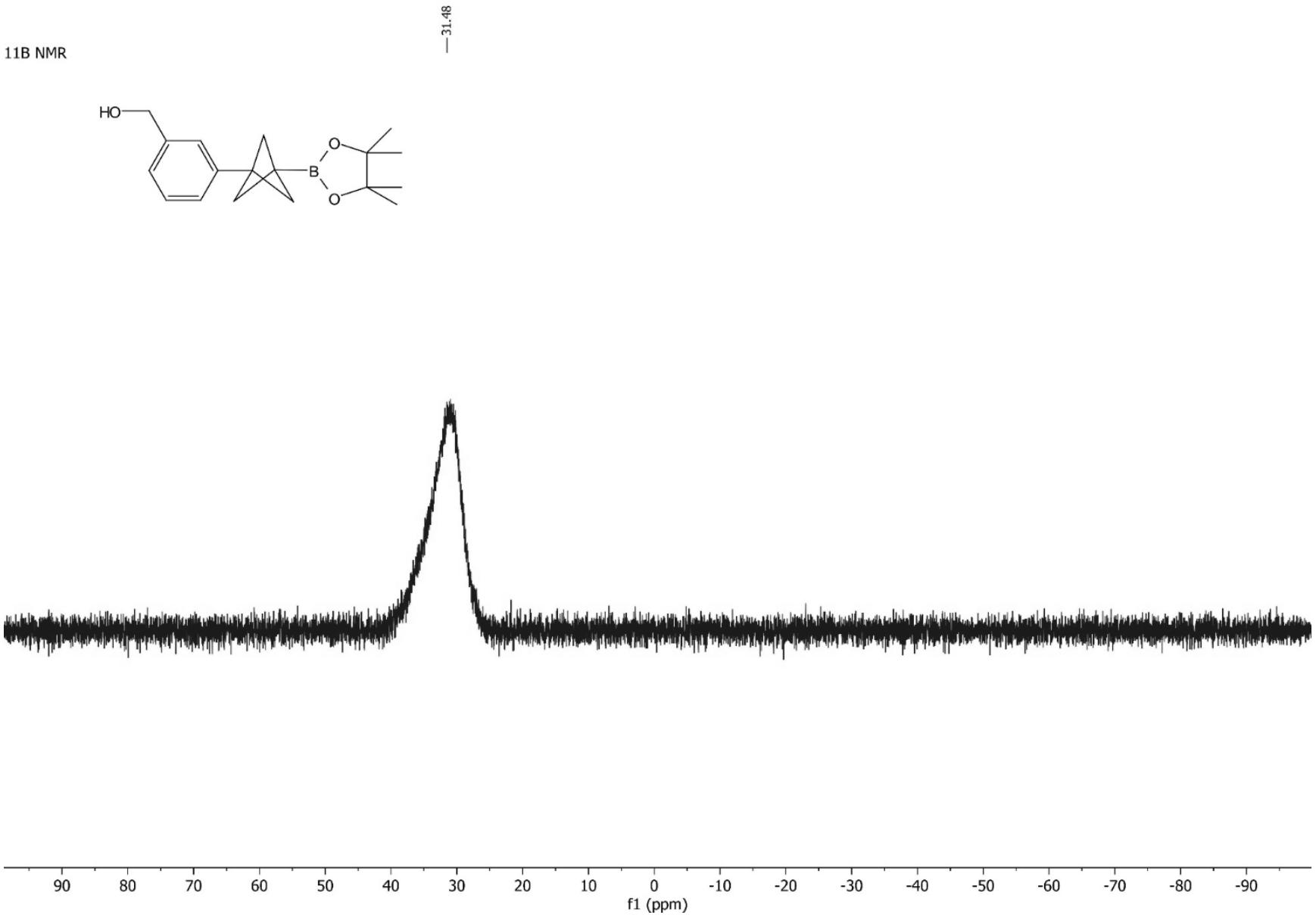
^{1}H NMR (600 MHz, $CDCl_3$) of **5t**



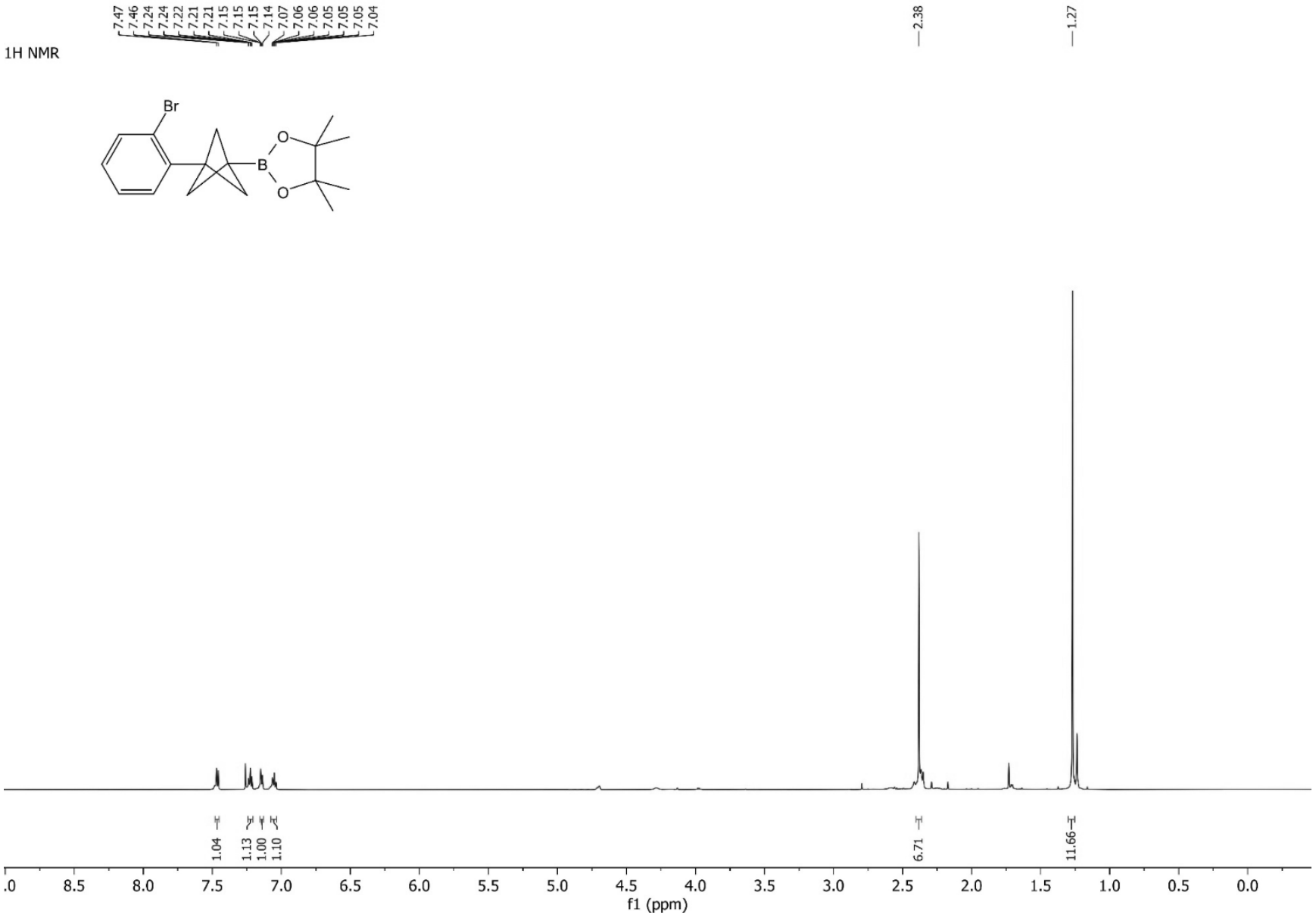
^{13}C NMR (151 MHz, $CDCl_3$) of **5t**



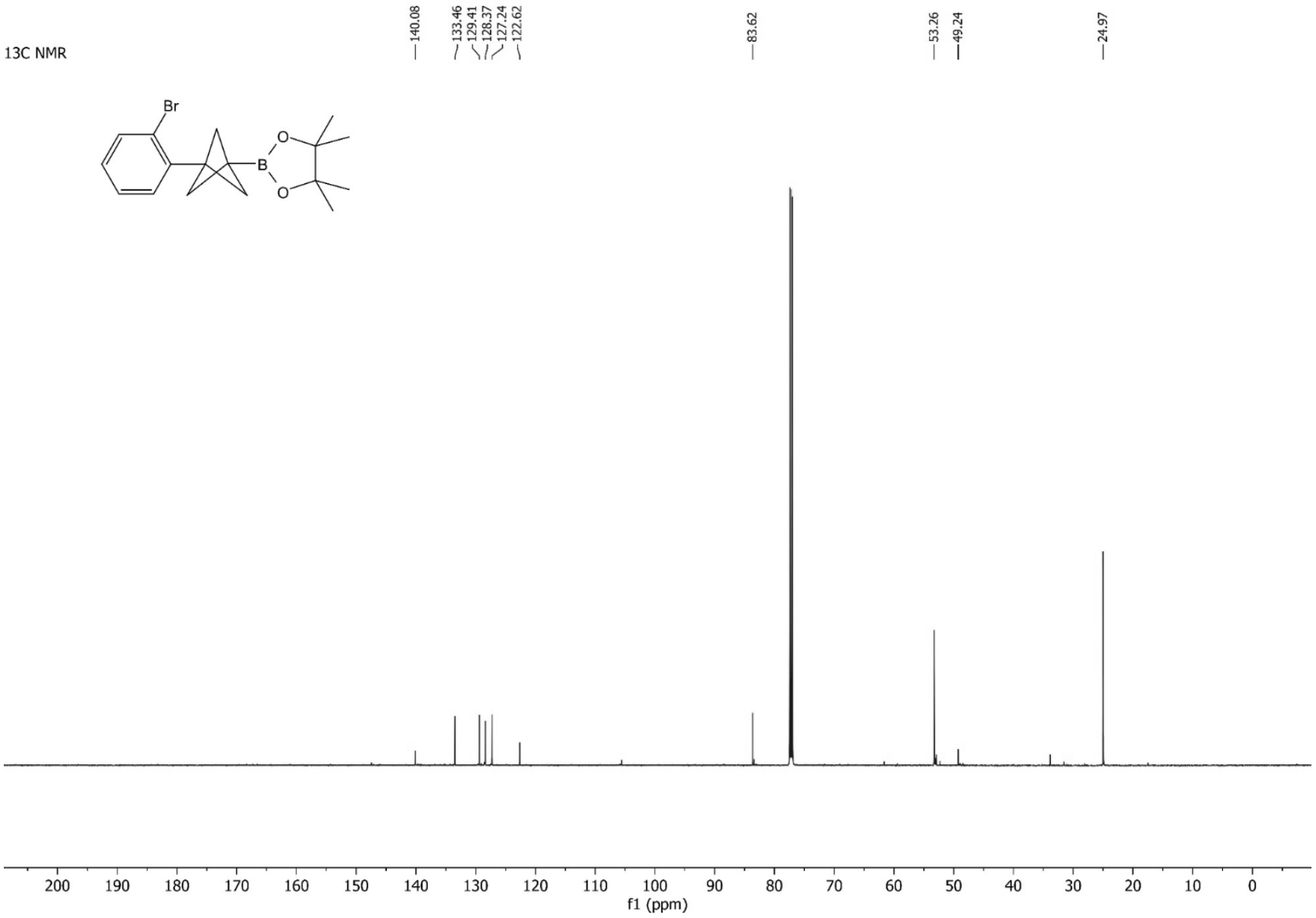
^{11}B NMR (128 MHz, $CDCl_3$) of **5t**



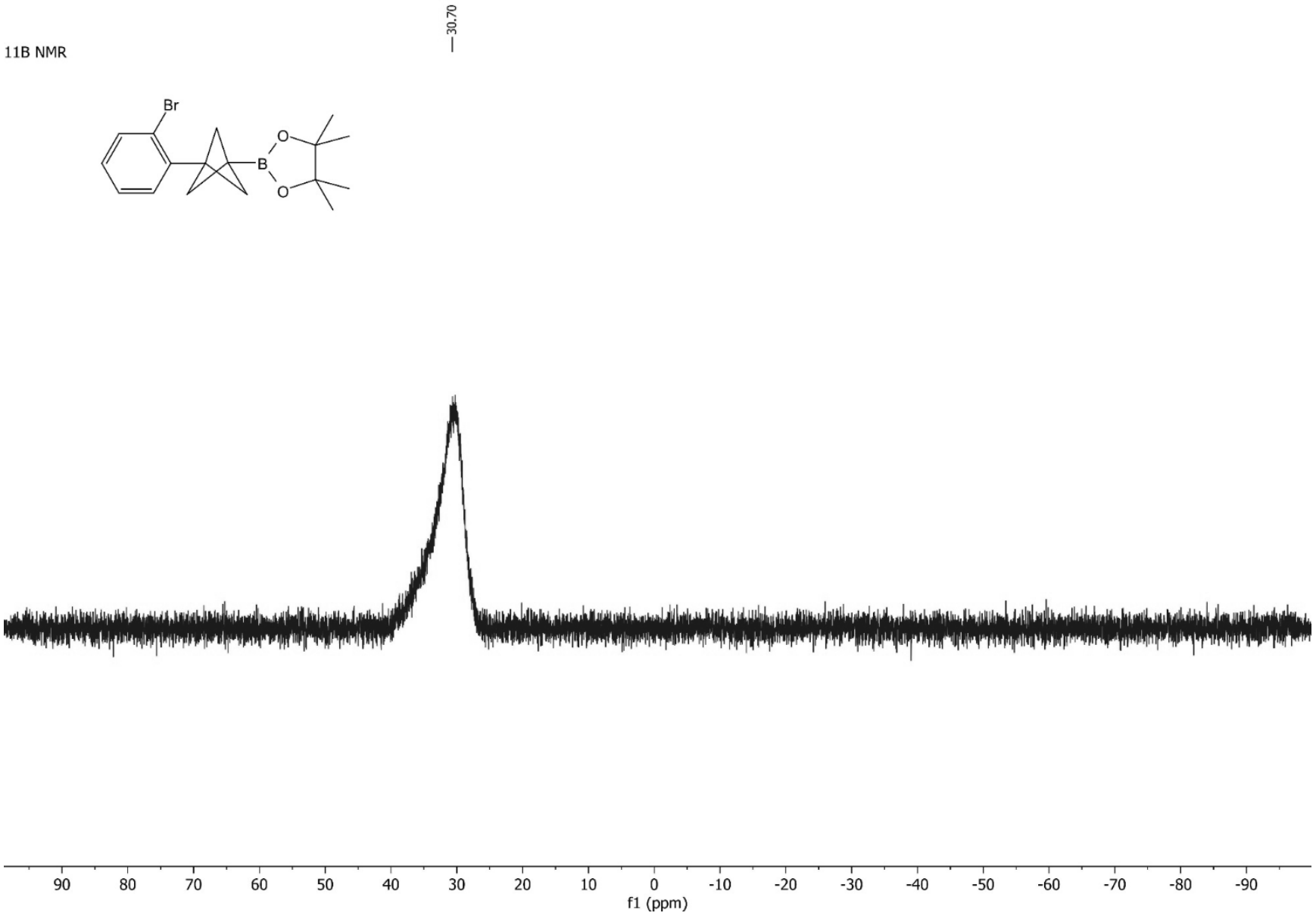
^{1}H NMR (600 MHz, $CDCl_3$) of **5u**



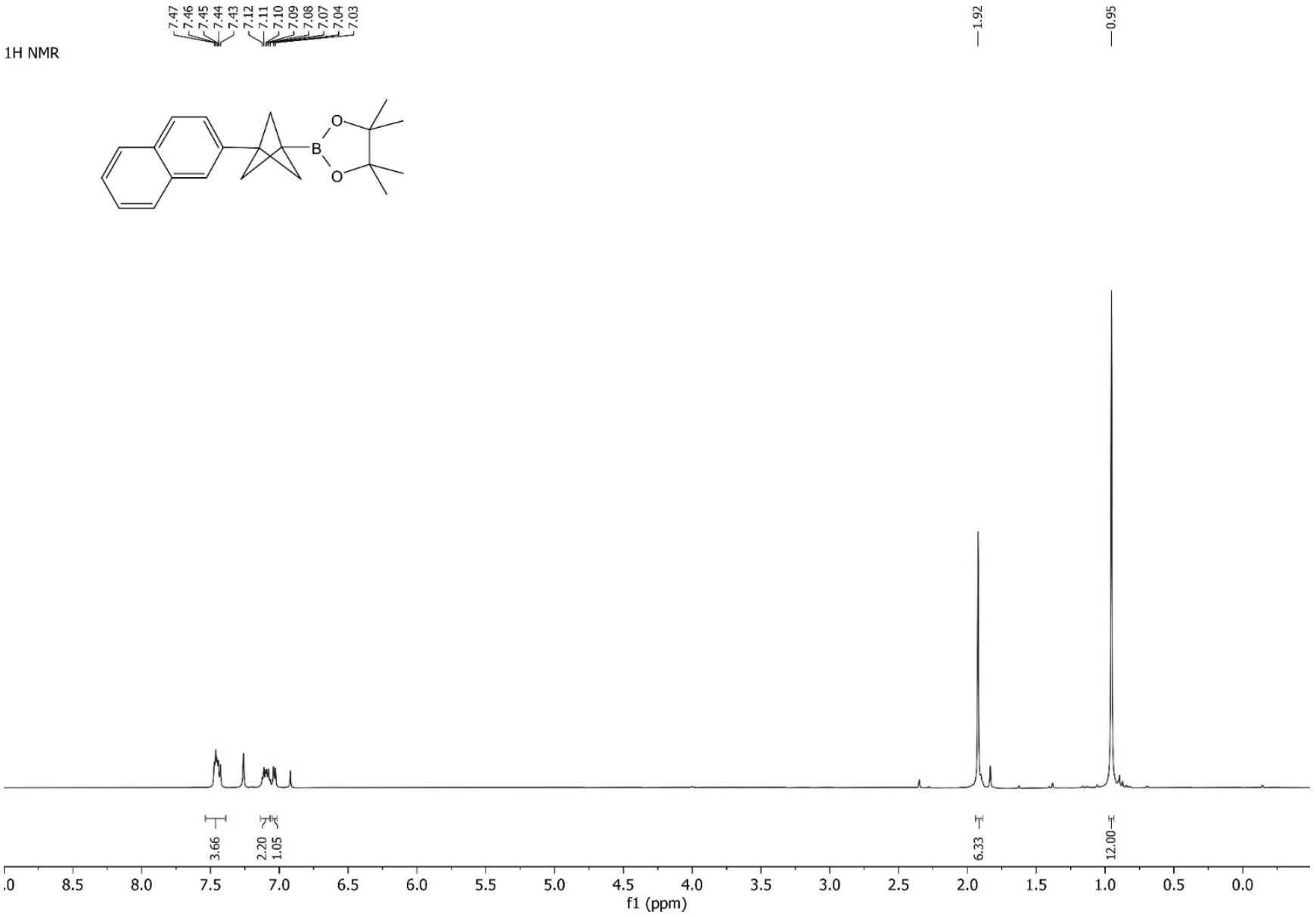
^{13}C NMR (151 MHz, $CDCl_3$) of **5u**



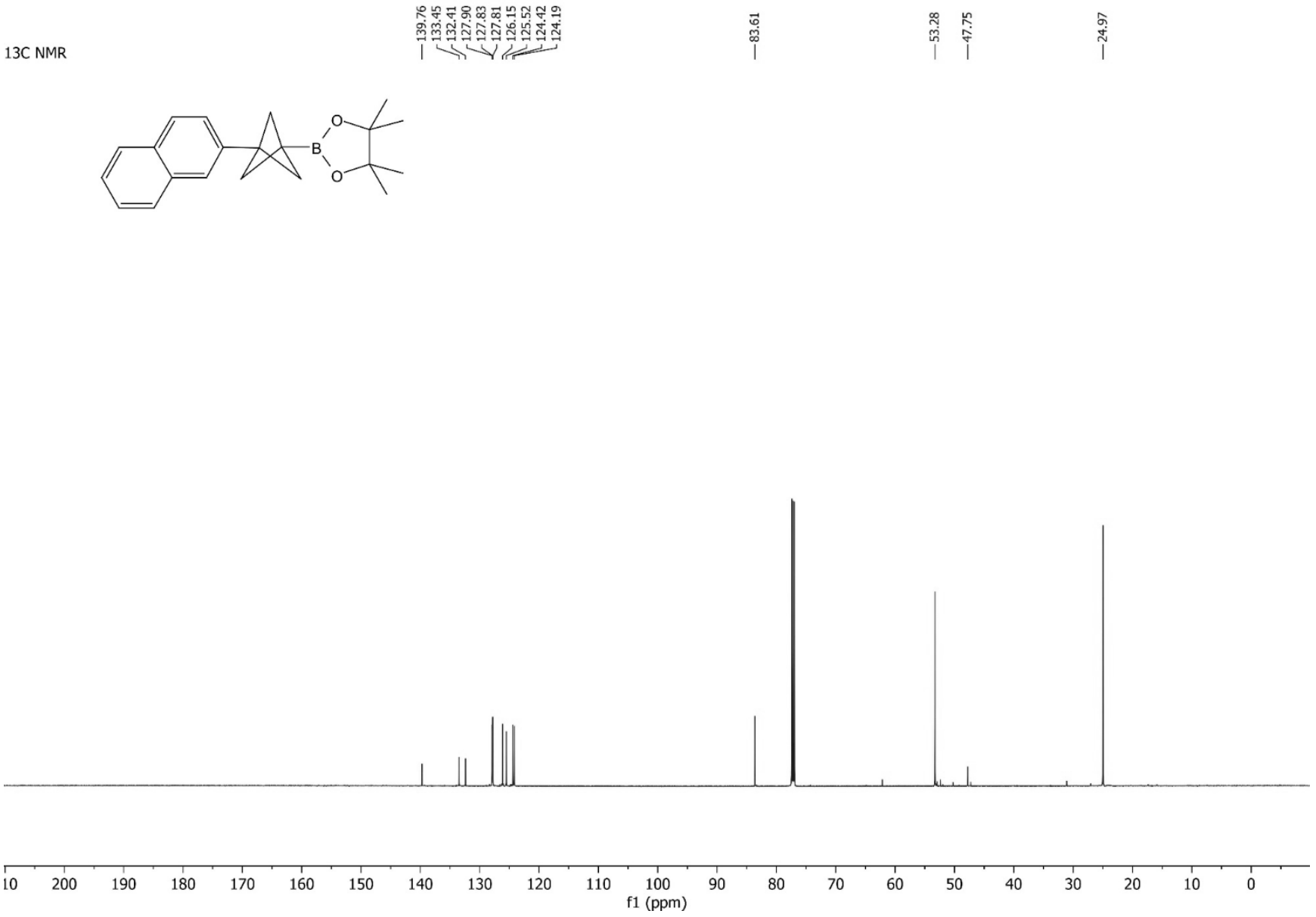
^{11}B NMR (128 MHz, $CDCl_3$) of **5u**



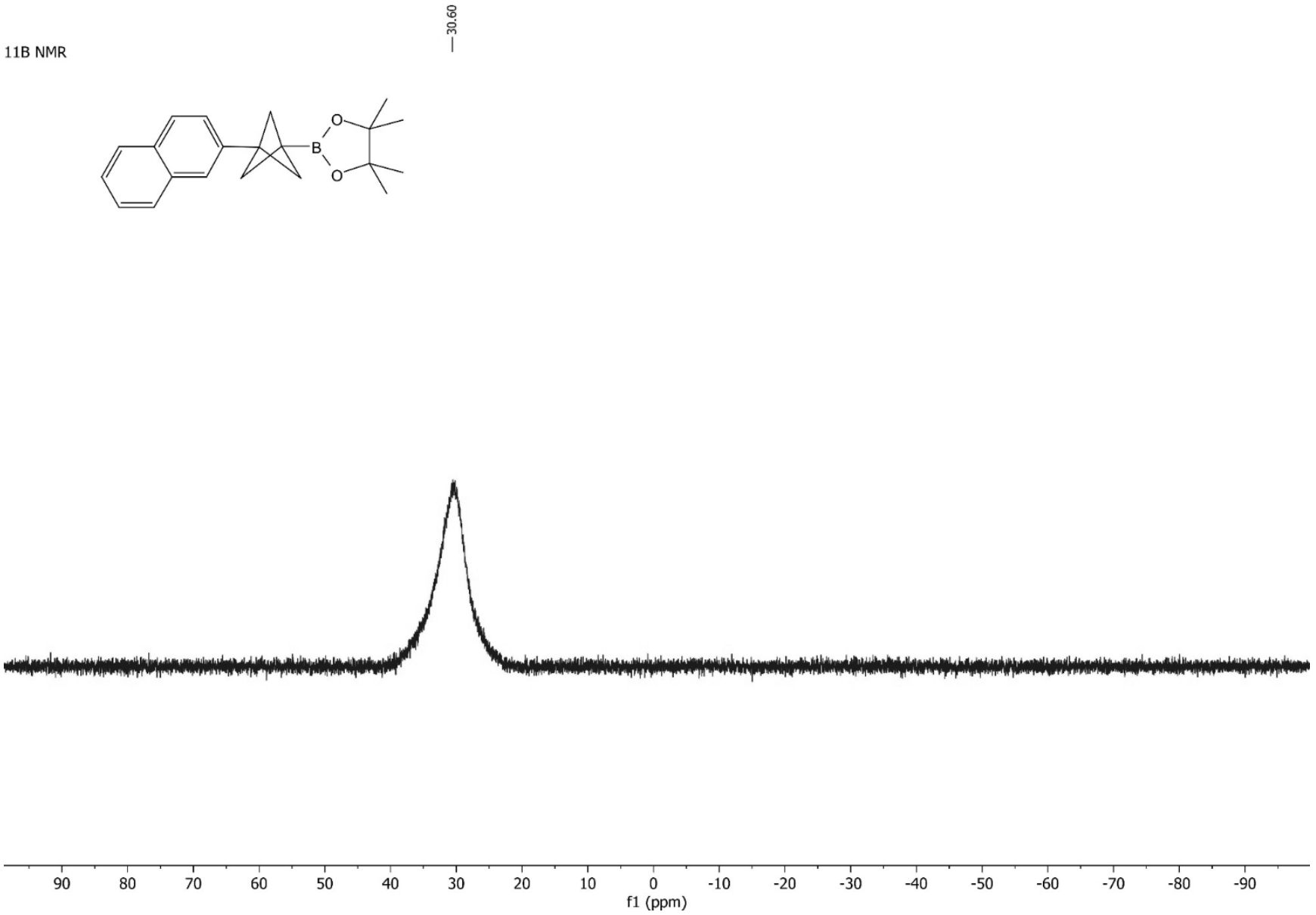
^{1}H NMR (600 MHz, $CDCl_3$) of **5v**



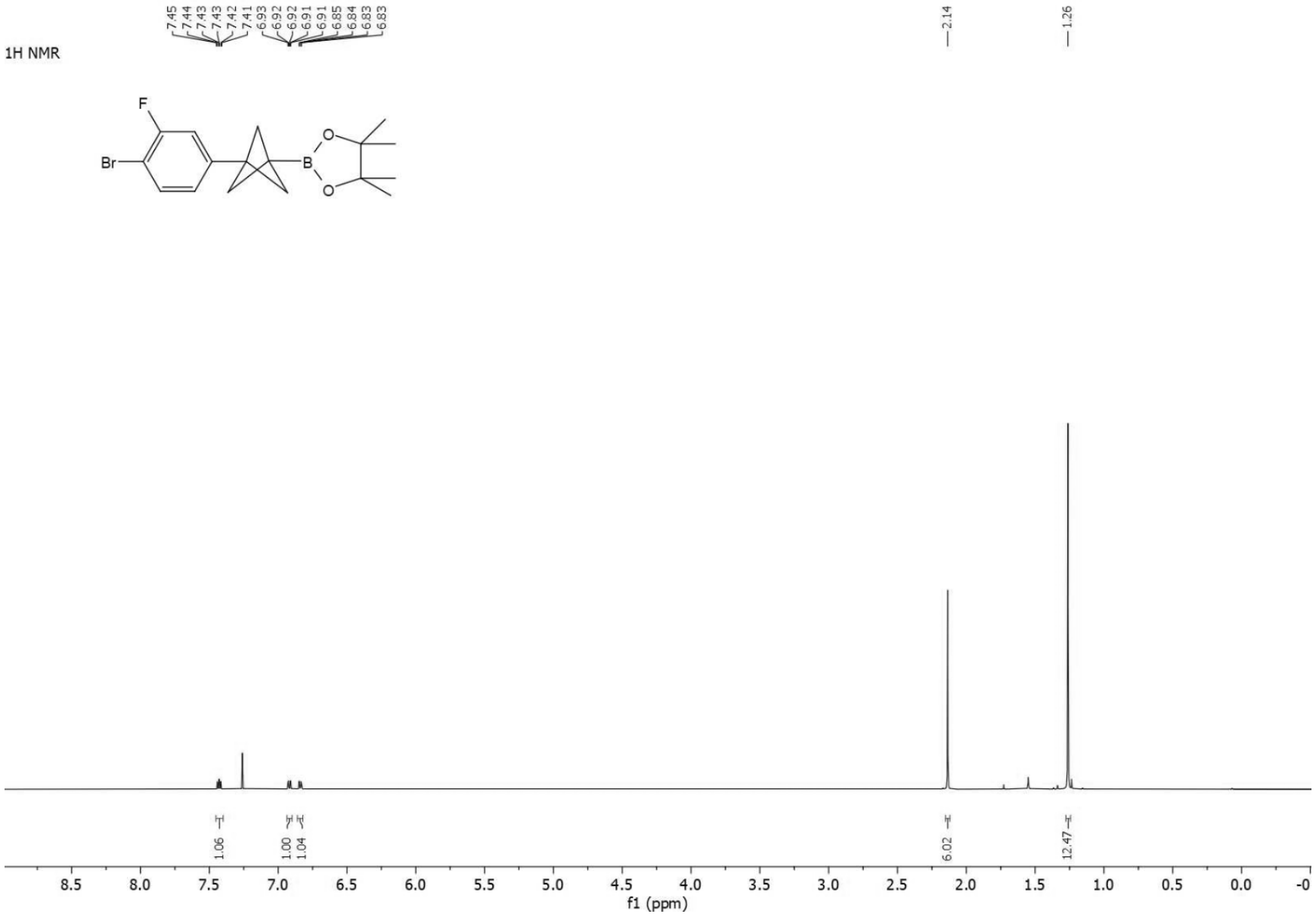
^{13}C NMR (151 MHz, $CDCl_3$) of **5v**



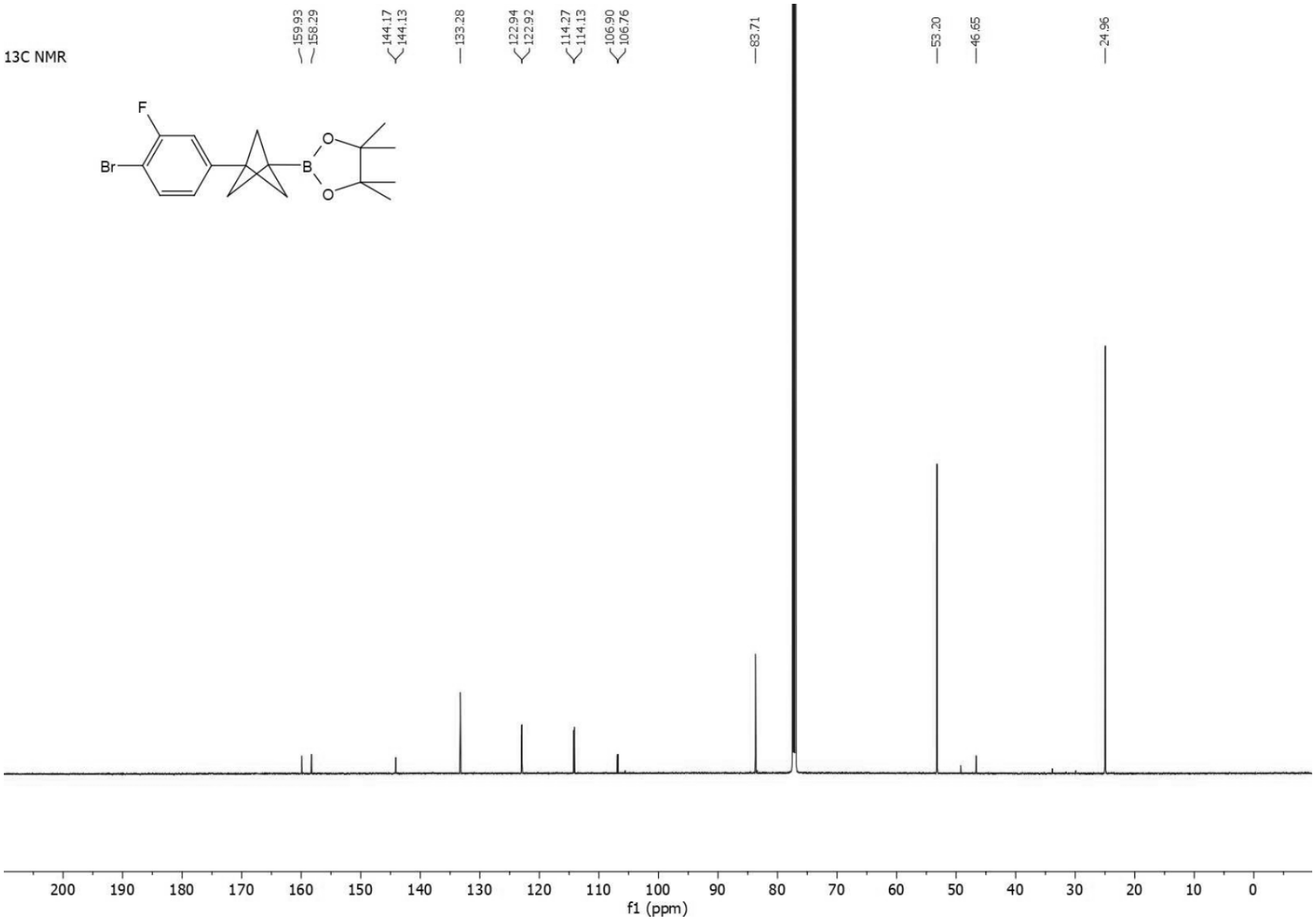
^{11}B NMR (128 MHz, $CDCl_3$) of **5v**



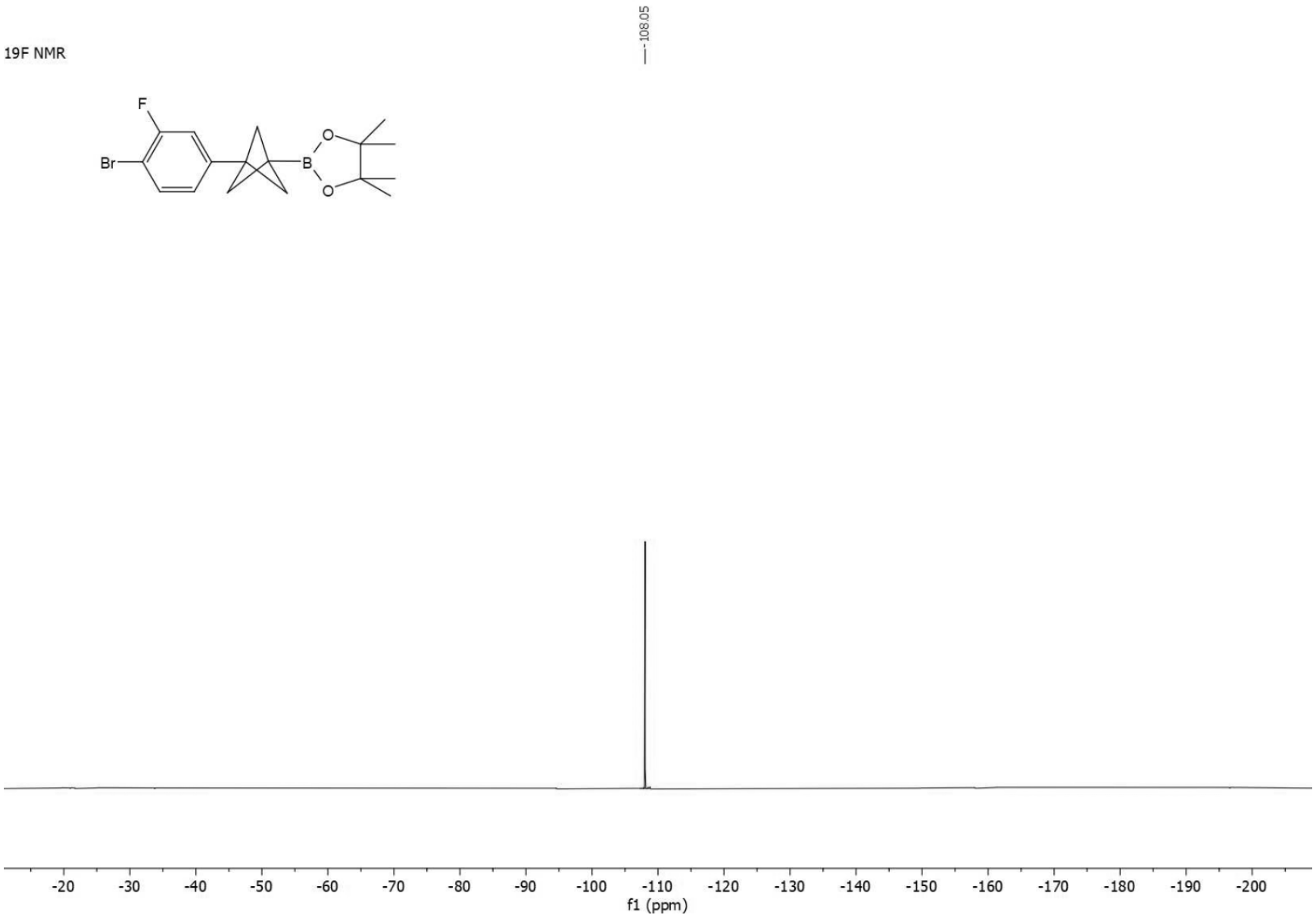
^{1}H NMR (600 MHz, $CDCl_3$) of **5w**



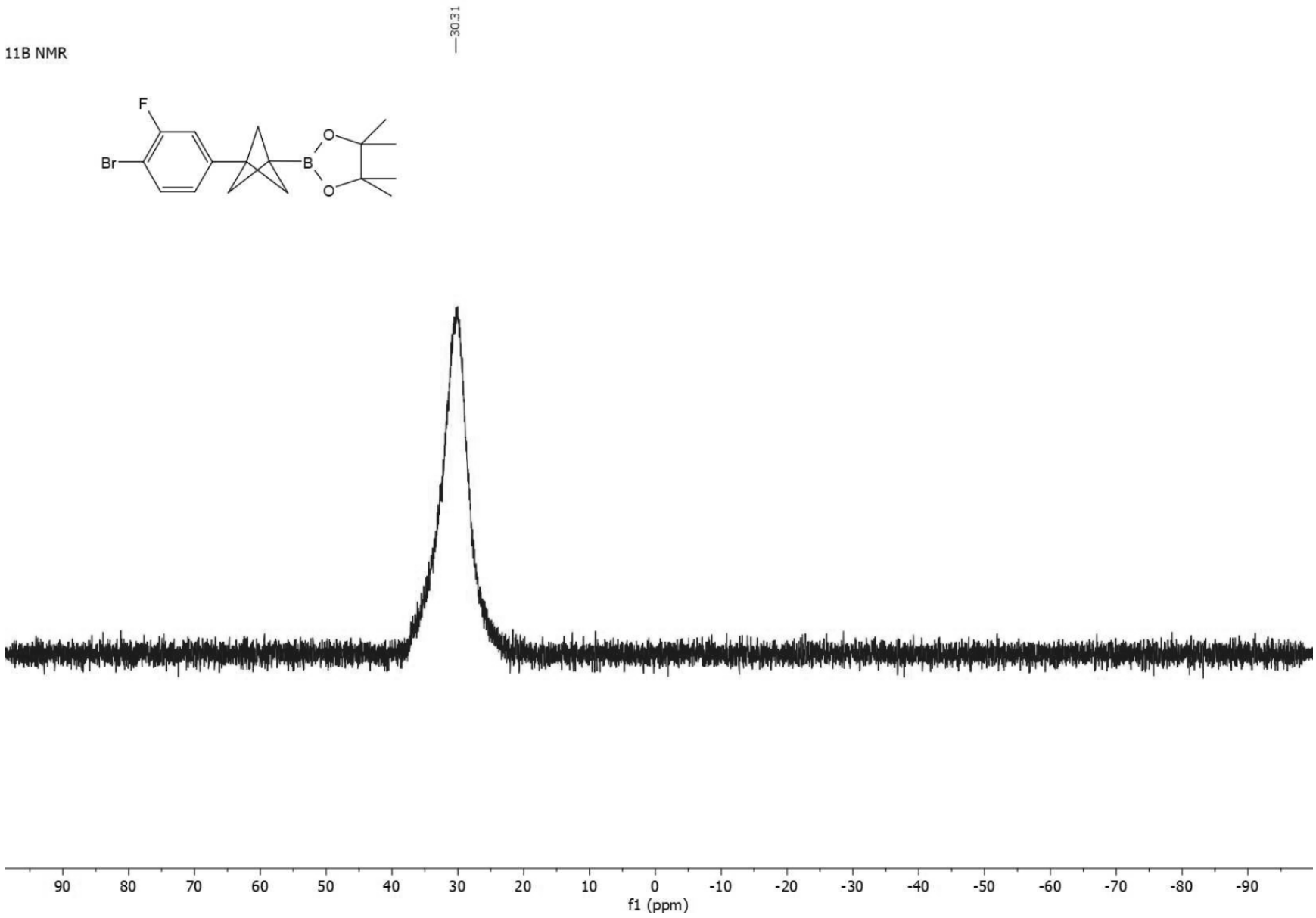
^{13}C NMR (151 MHz, $CDCl_3$) of **5w**



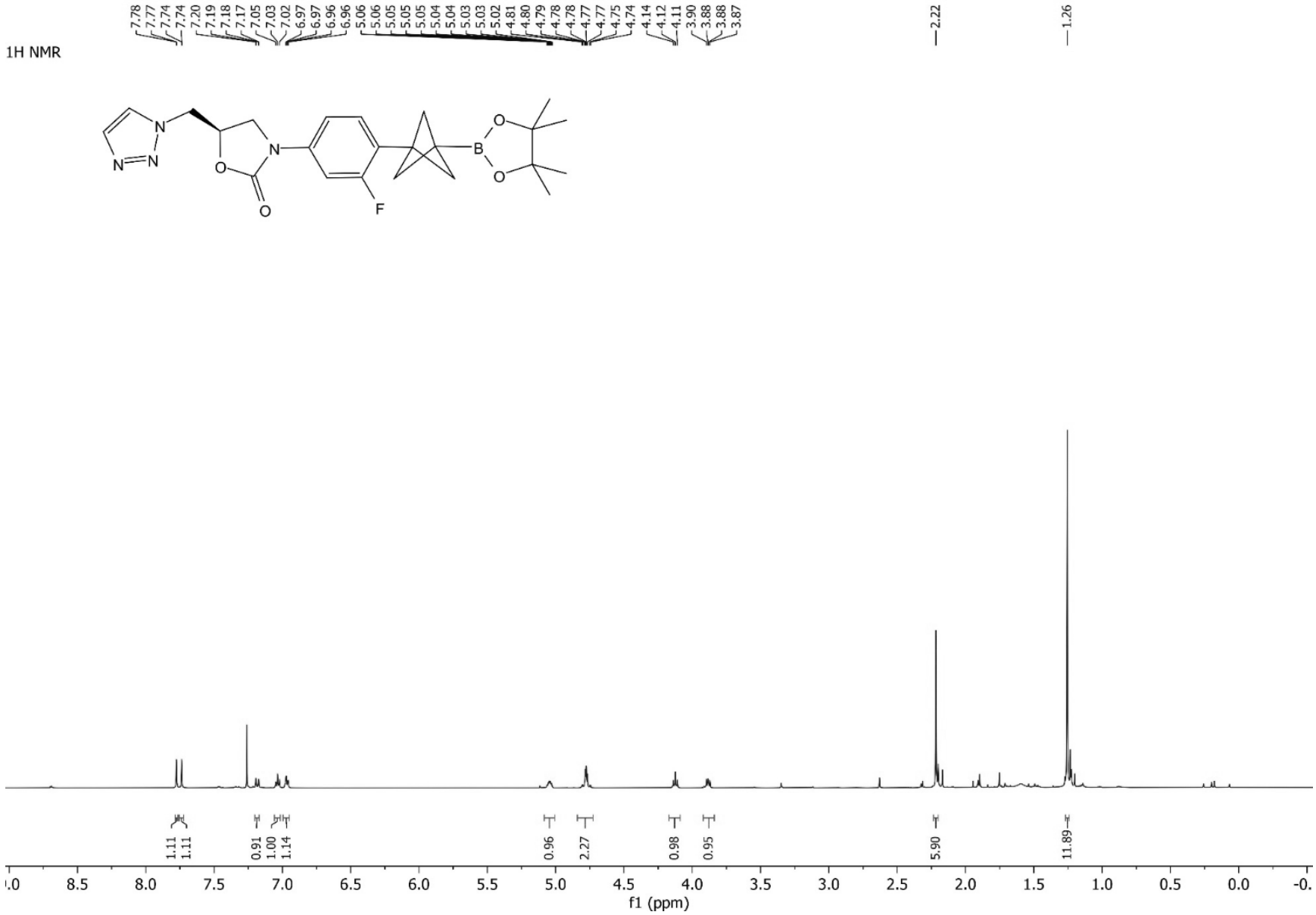
^{19}F NMR (376 MHz, $CDCl_3$) of **5w**



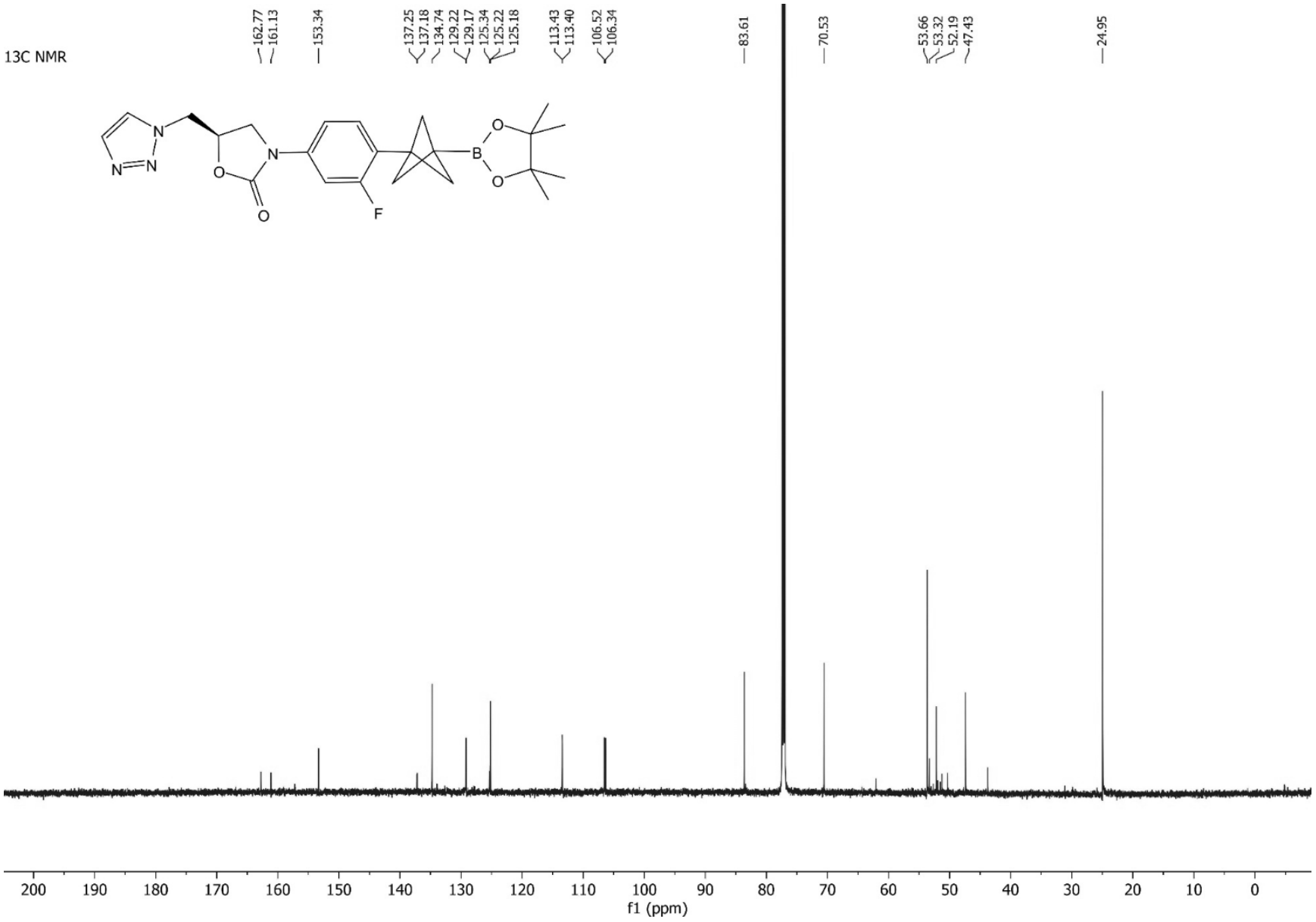
^{11}B NMR (128 MHz, $CDCl_3$) of **5w**



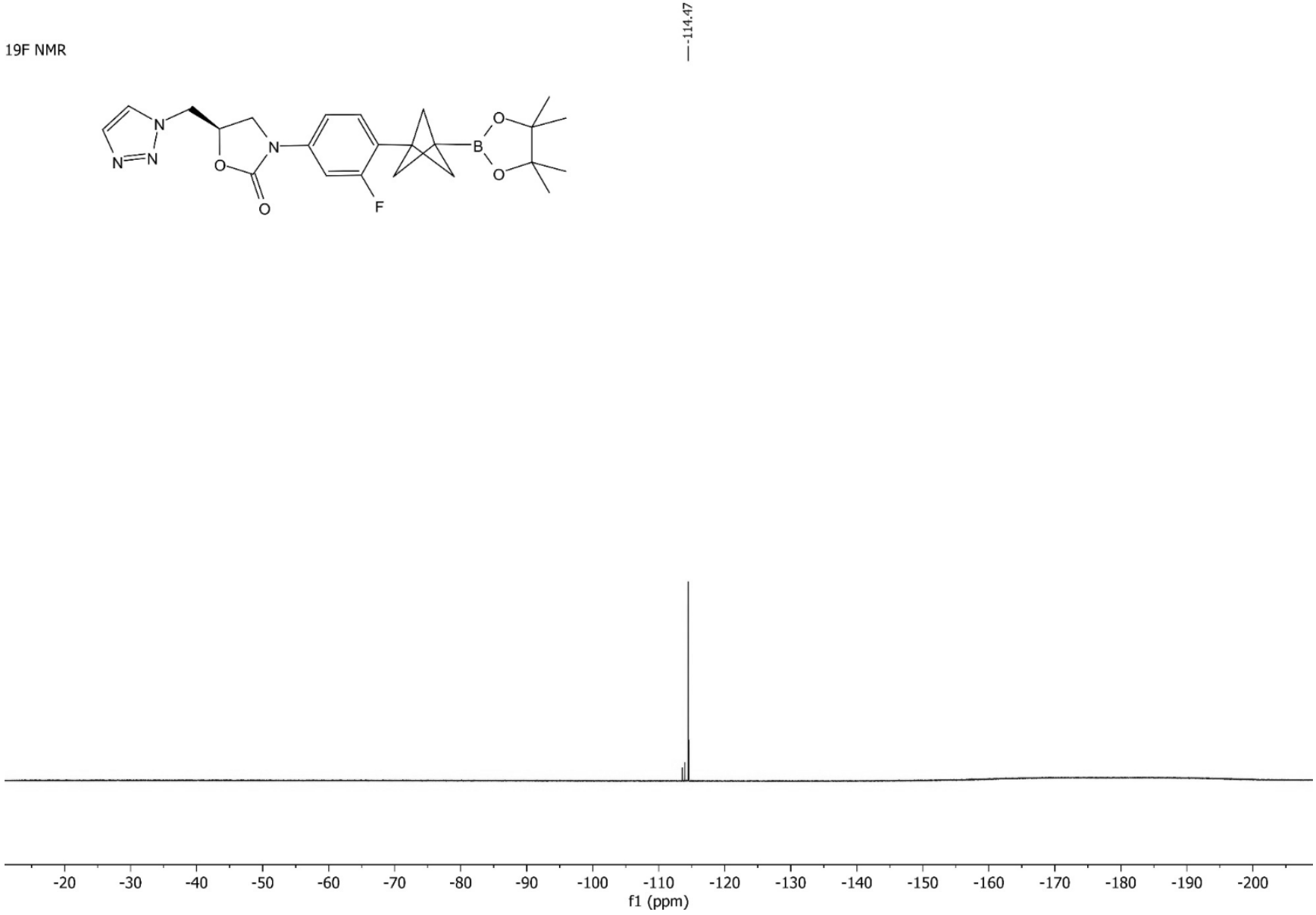
^{1}H NMR (600 MHz, $CDCl_3$) of **5x**



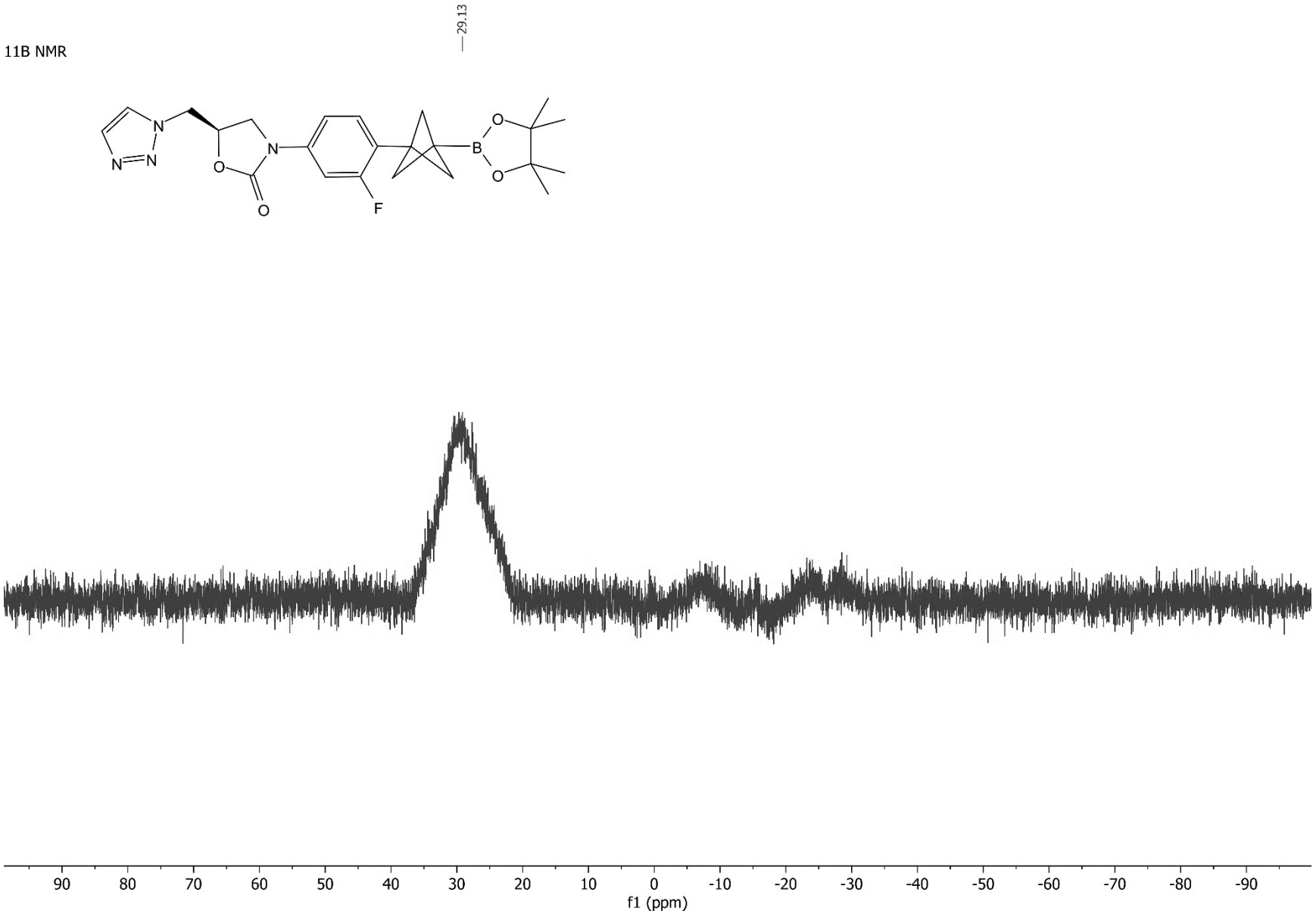
^{13}C NMR (151 MHz, $CDCl_3$) of **5x**



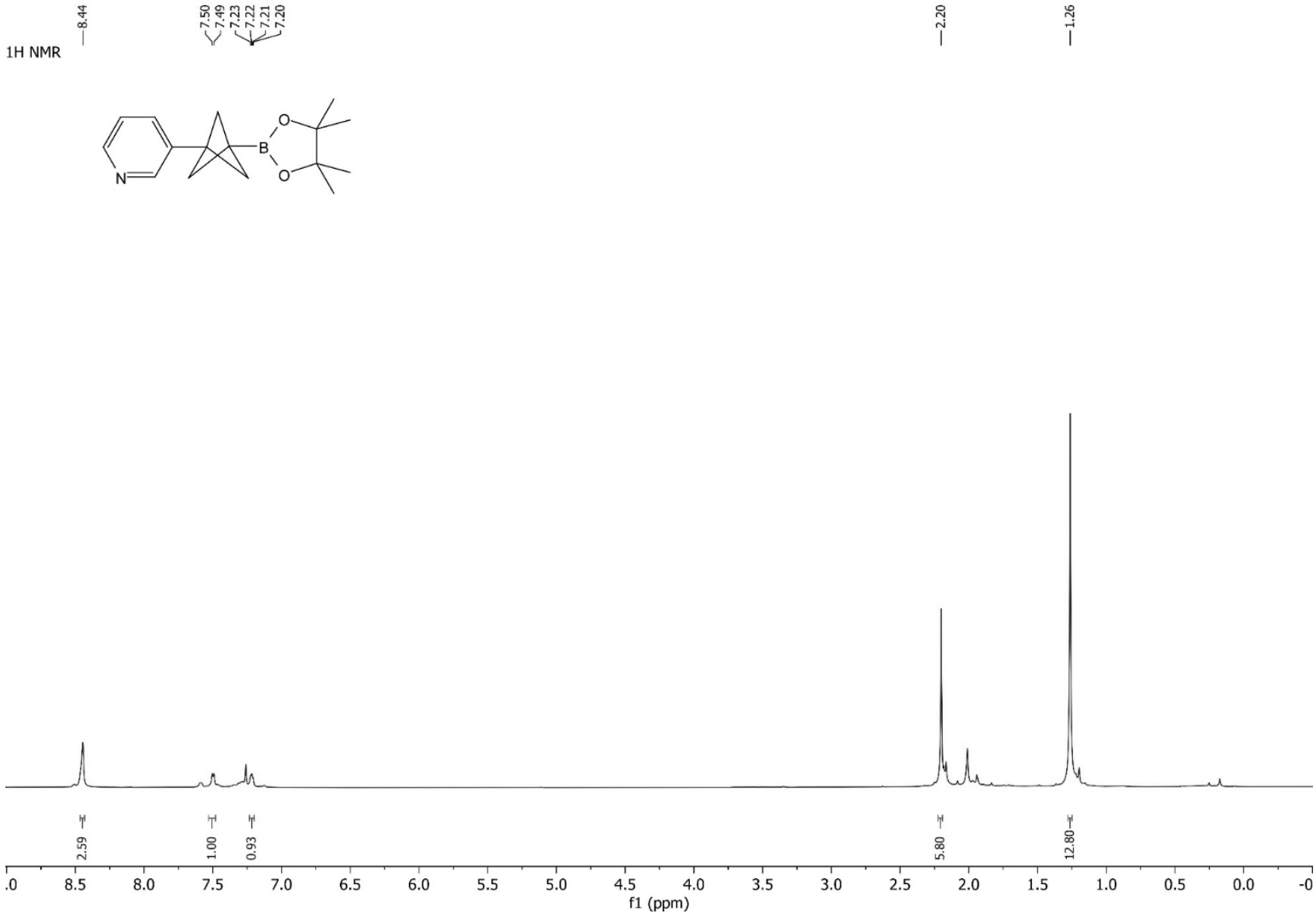
^{19}F NMR (376 MHz, $CDCl_3$) of **5x**



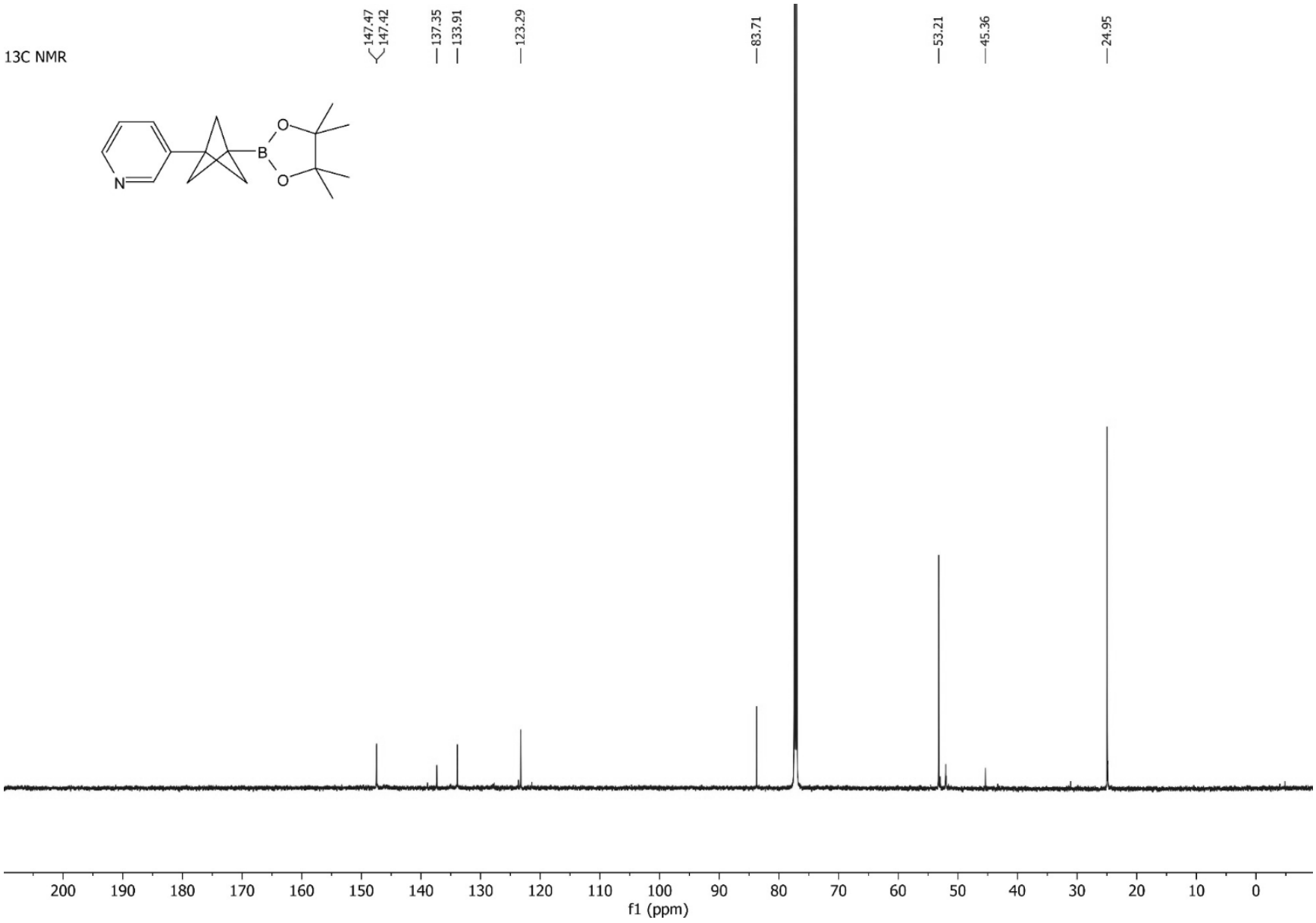
^{11}B NMR (128 MHz, $CDCl_3$) of **5x**



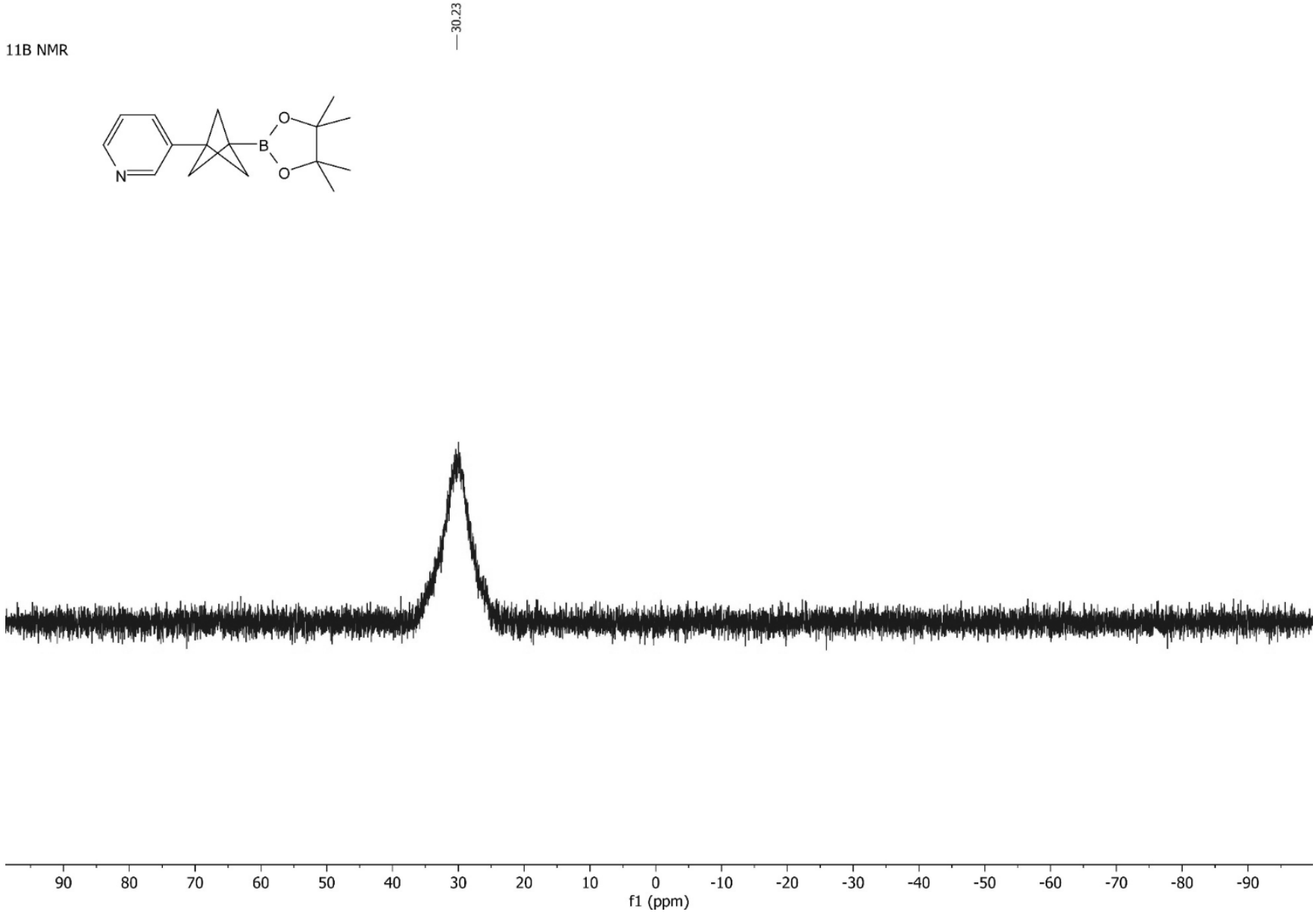
^{1}H NMR (600 MHz, $CDCl_3$) of **5y**



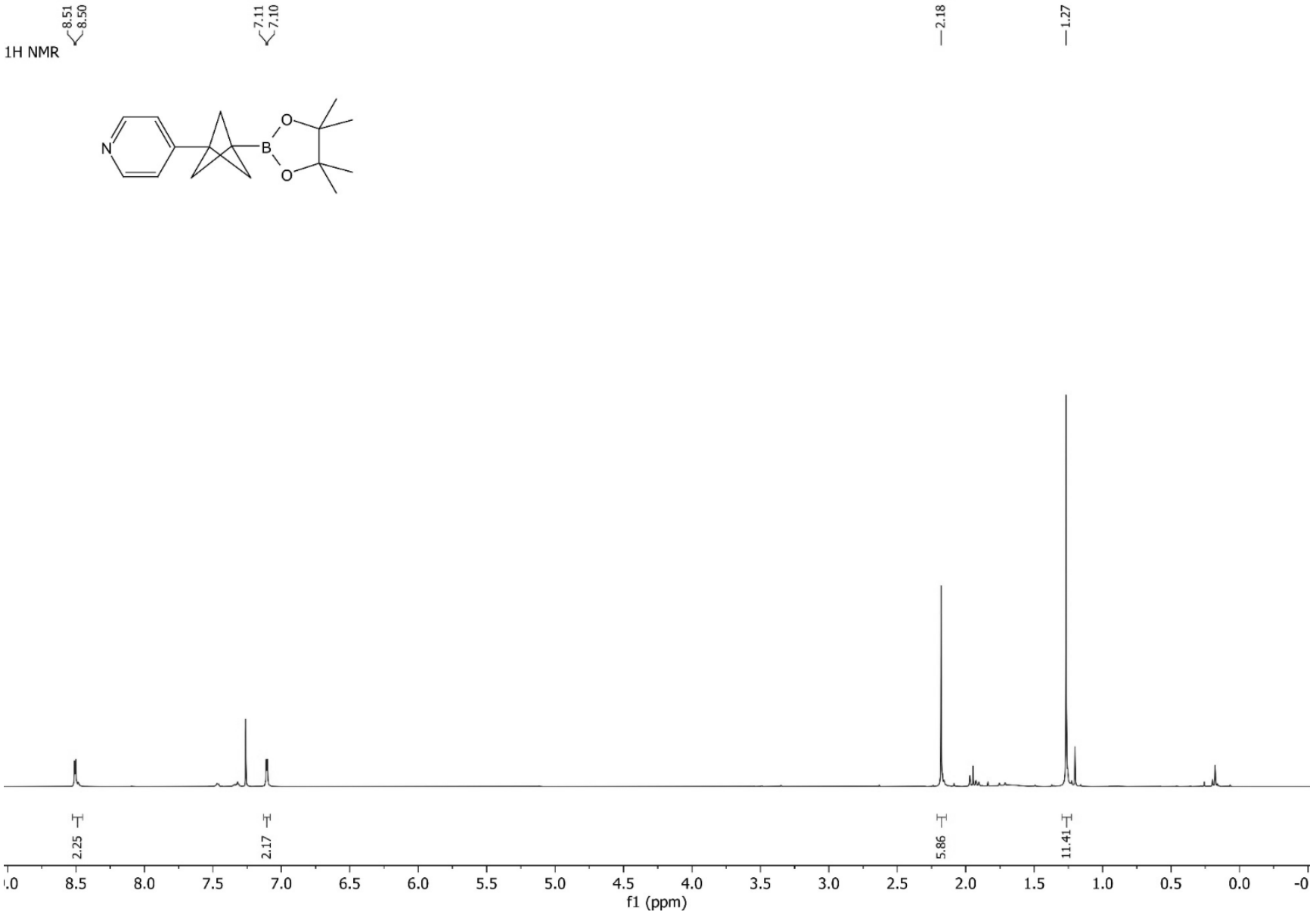
^{13}C NMR (151 MHz, $CDCl_3$) of **5y**



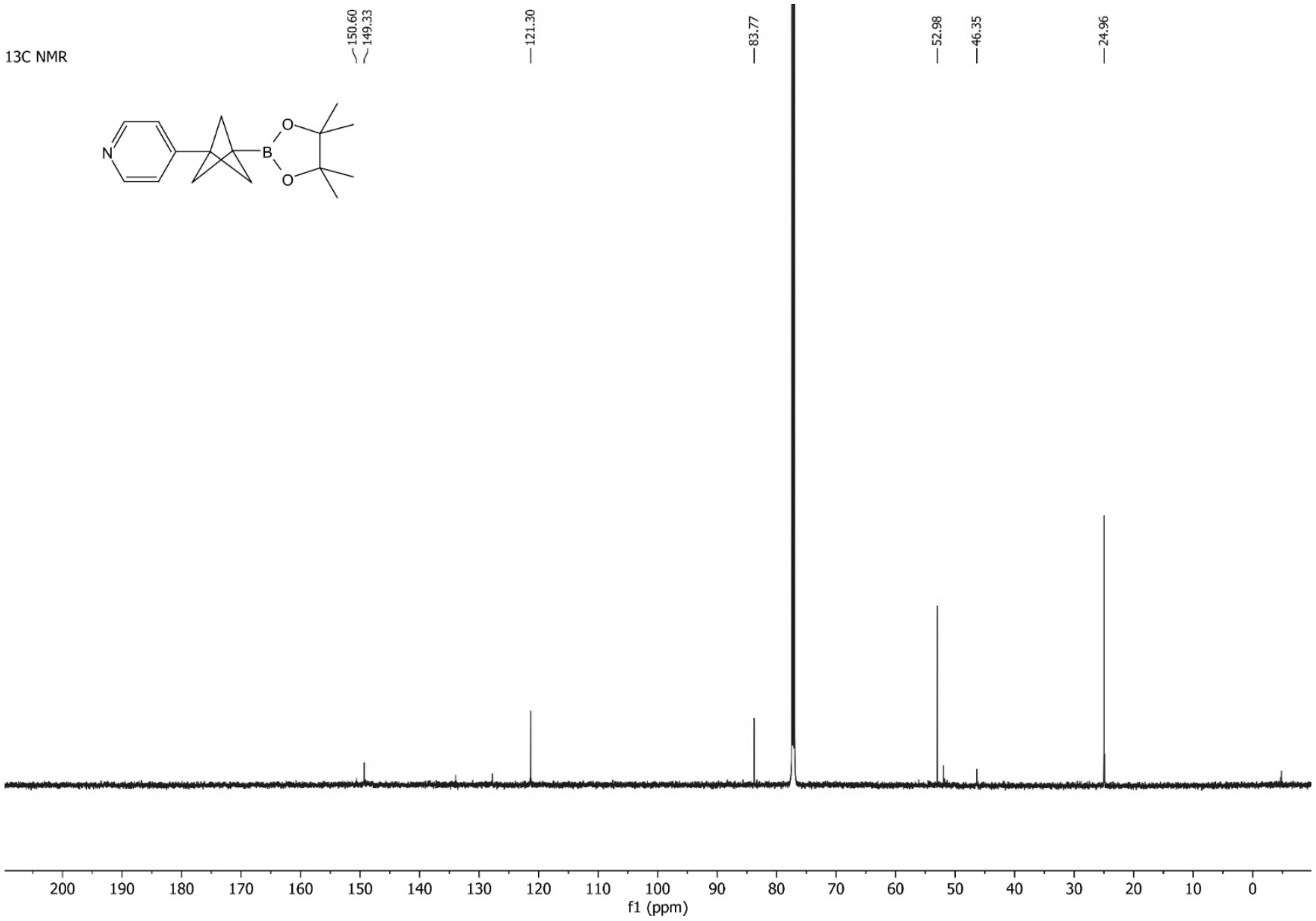
^{11}B NMR (128 MHz, $CDCl_3$) of **5y**



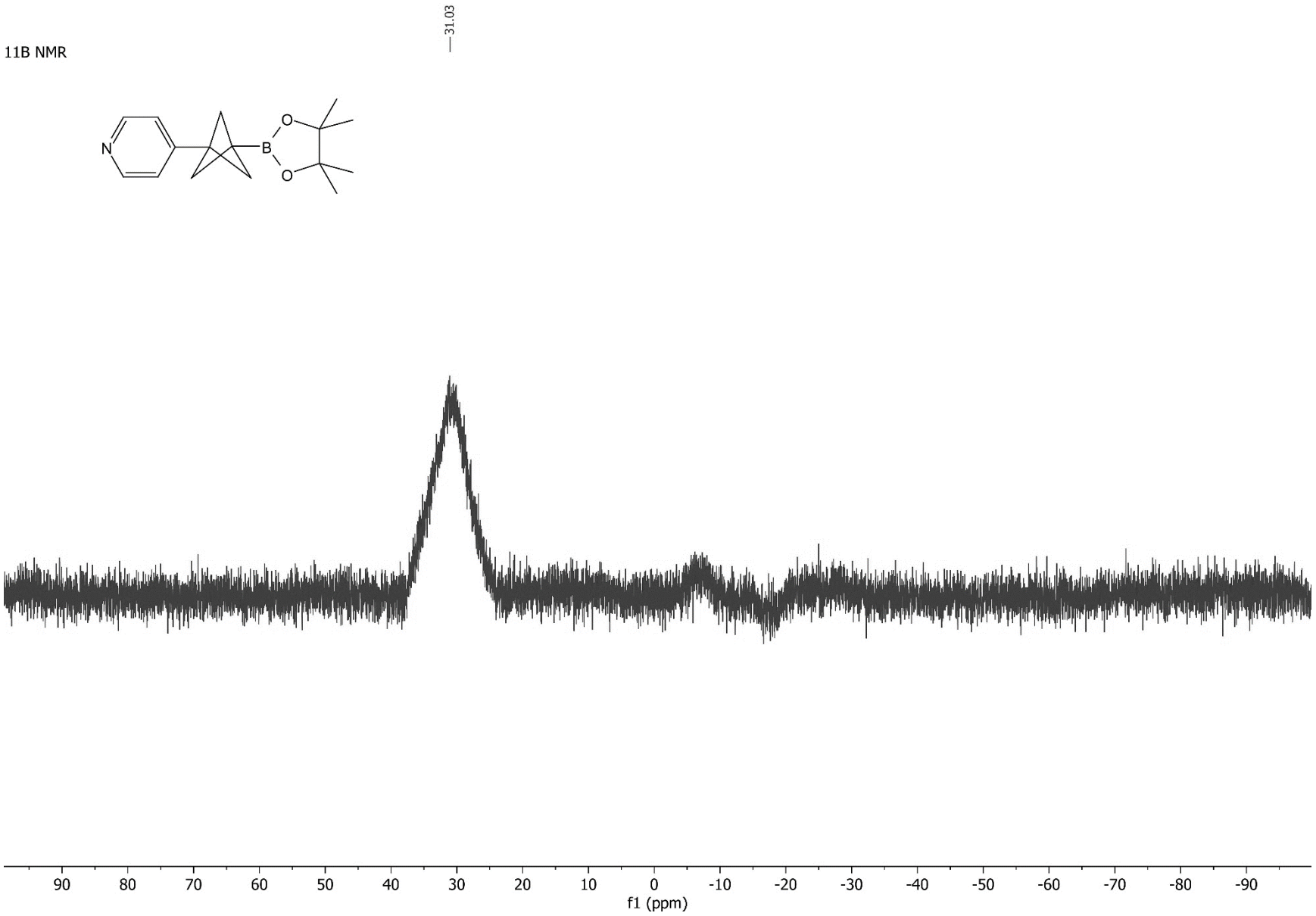
^{1}H NMR (600 MHz, $CDCl_3$) of **5z**



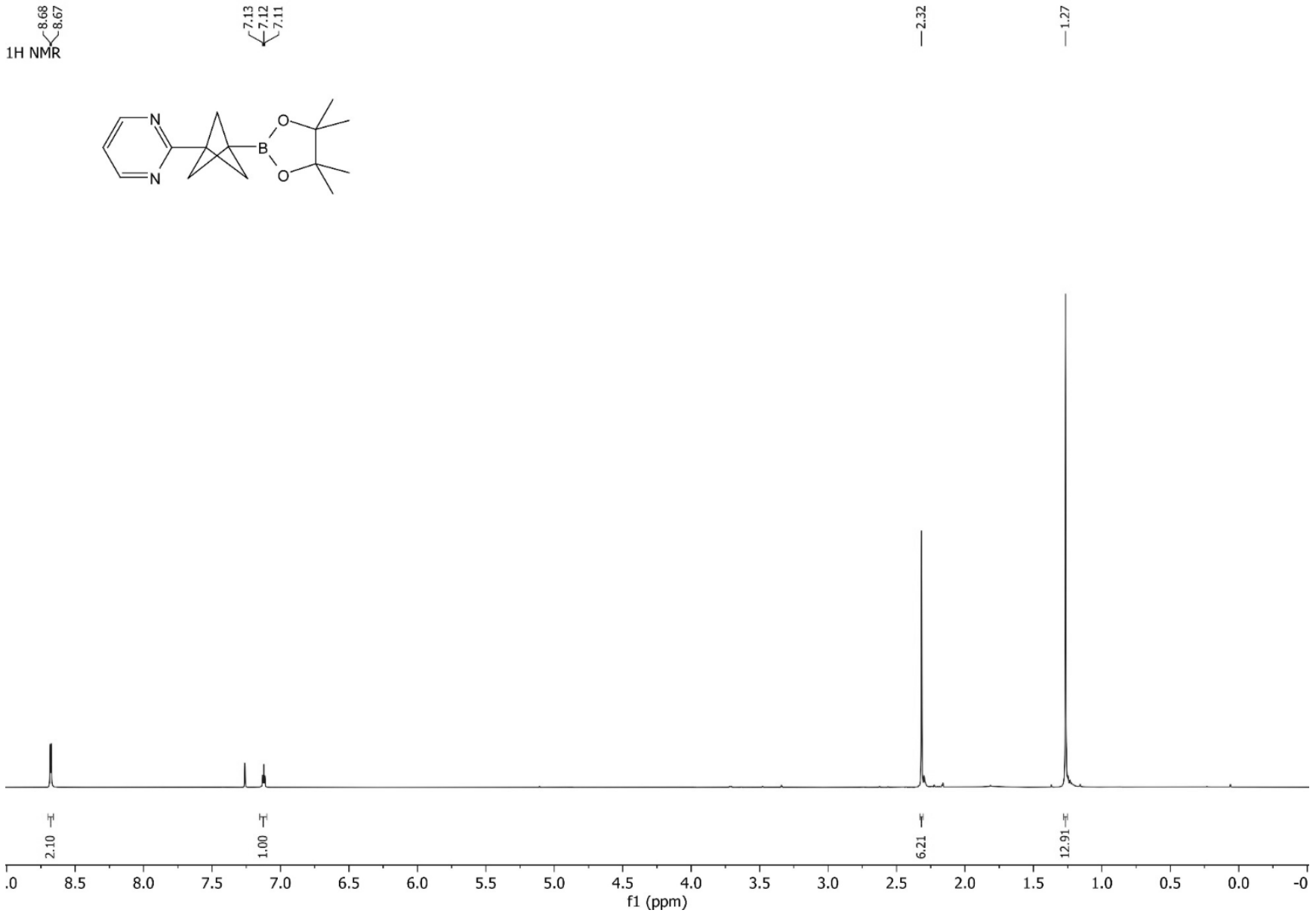
^{13}C NMR (151 MHz, $CDCl_3$) of **5z**



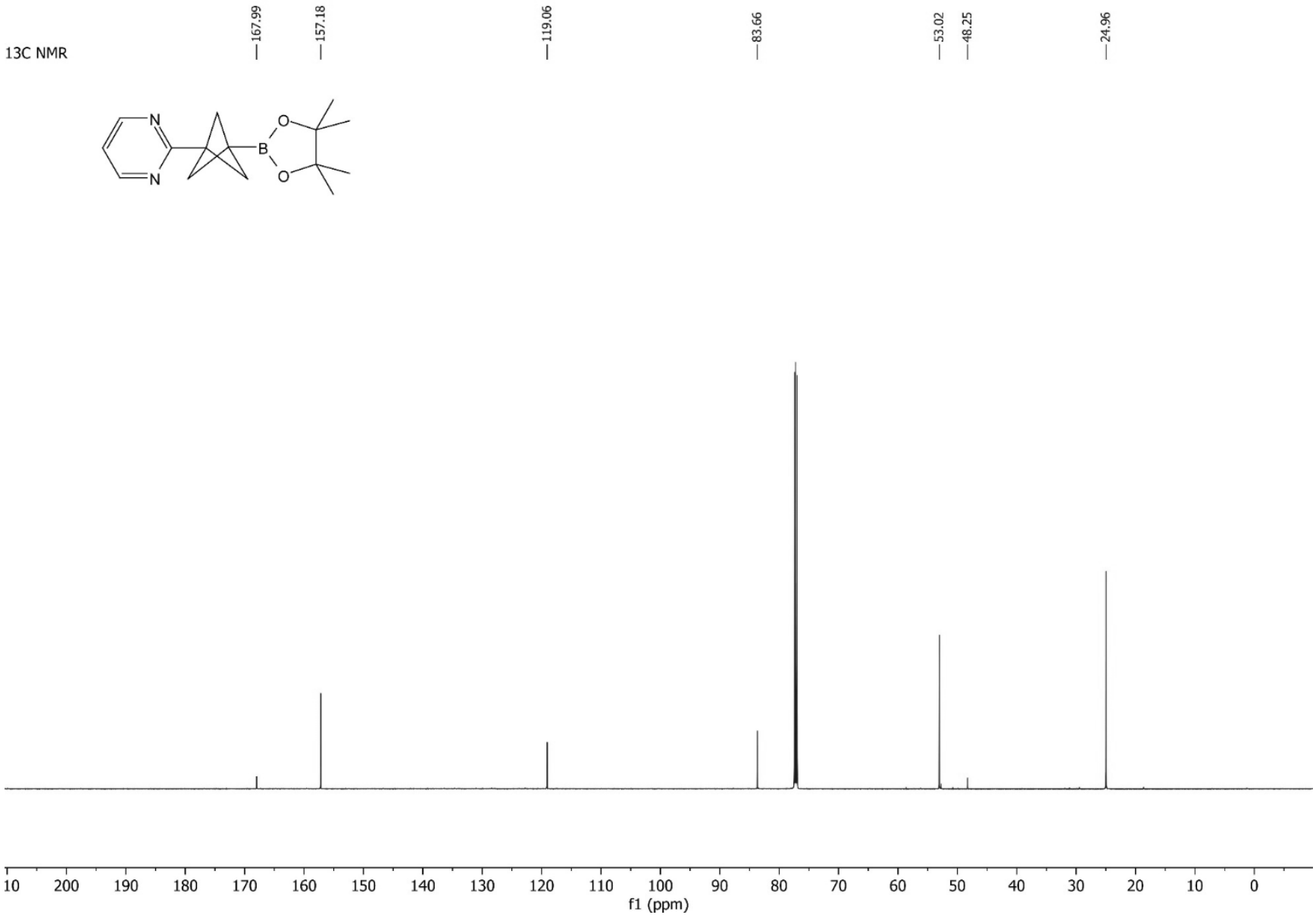
^{11}B NMR (128 MHz, $CDCl_3$) of **5z**



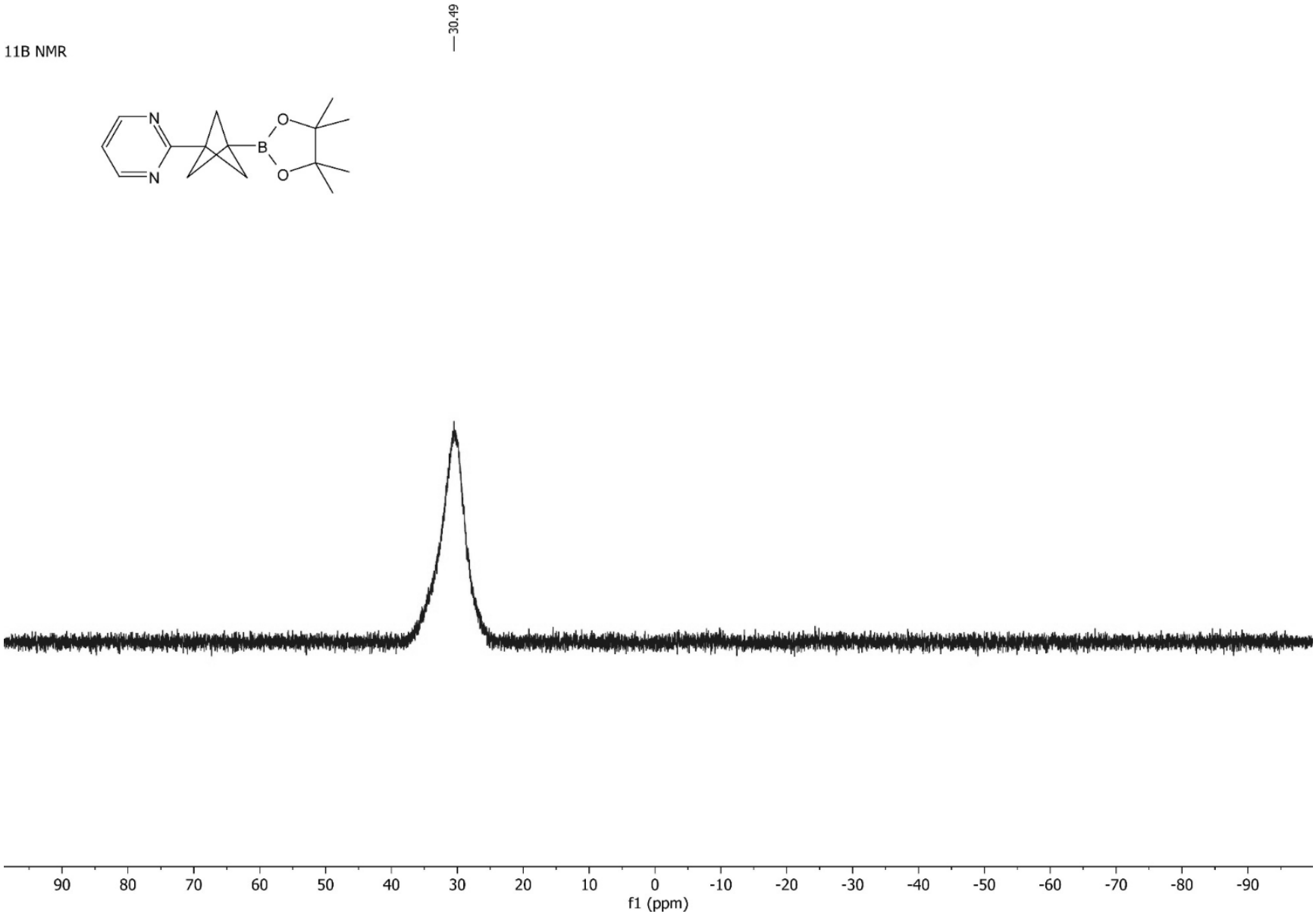
^{1}H NMR (600 MHz, $CDCl_3$) of **5aa**



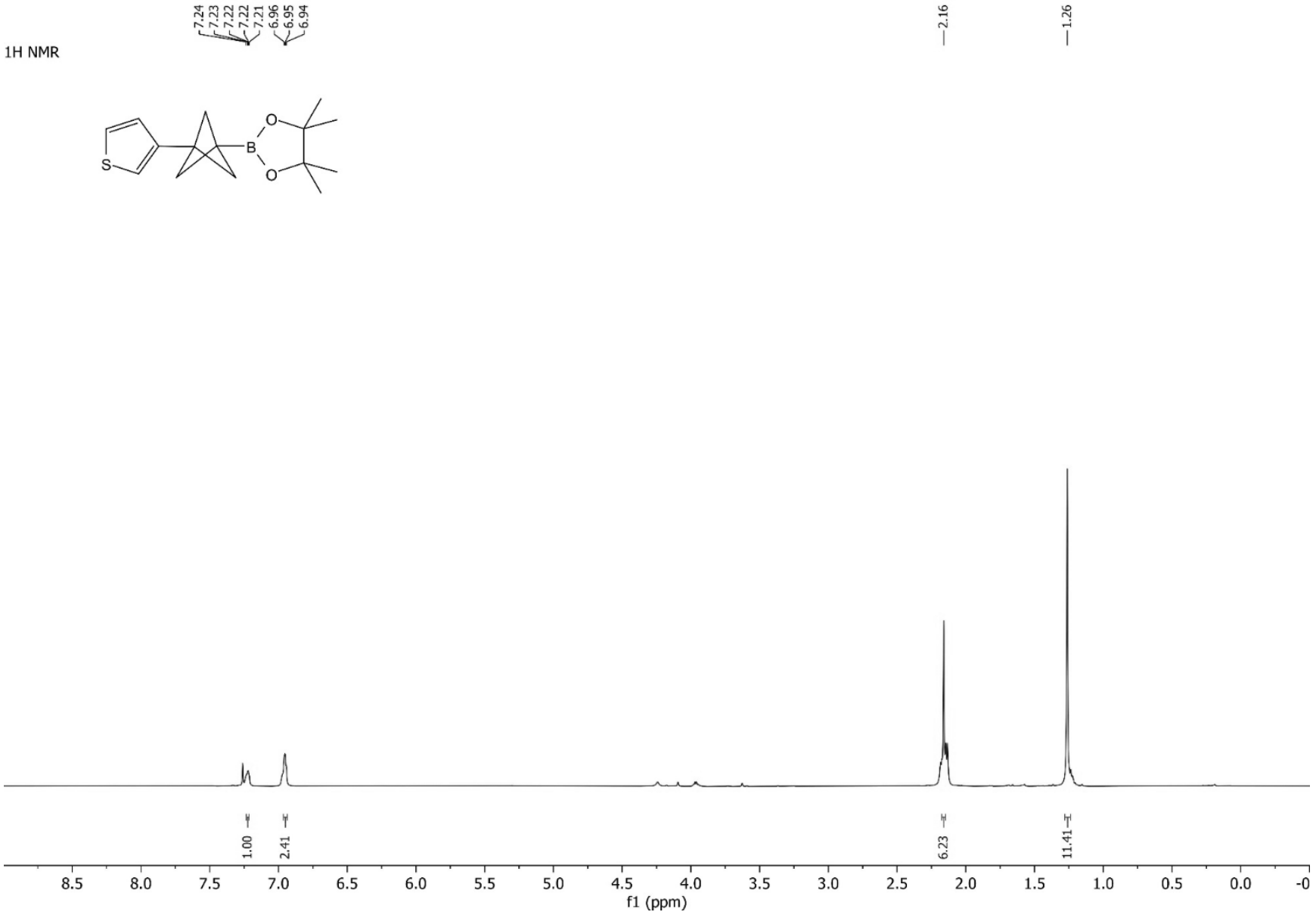
^{13}C NMR (151 MHz, $CDCl_3$) of **5aa**



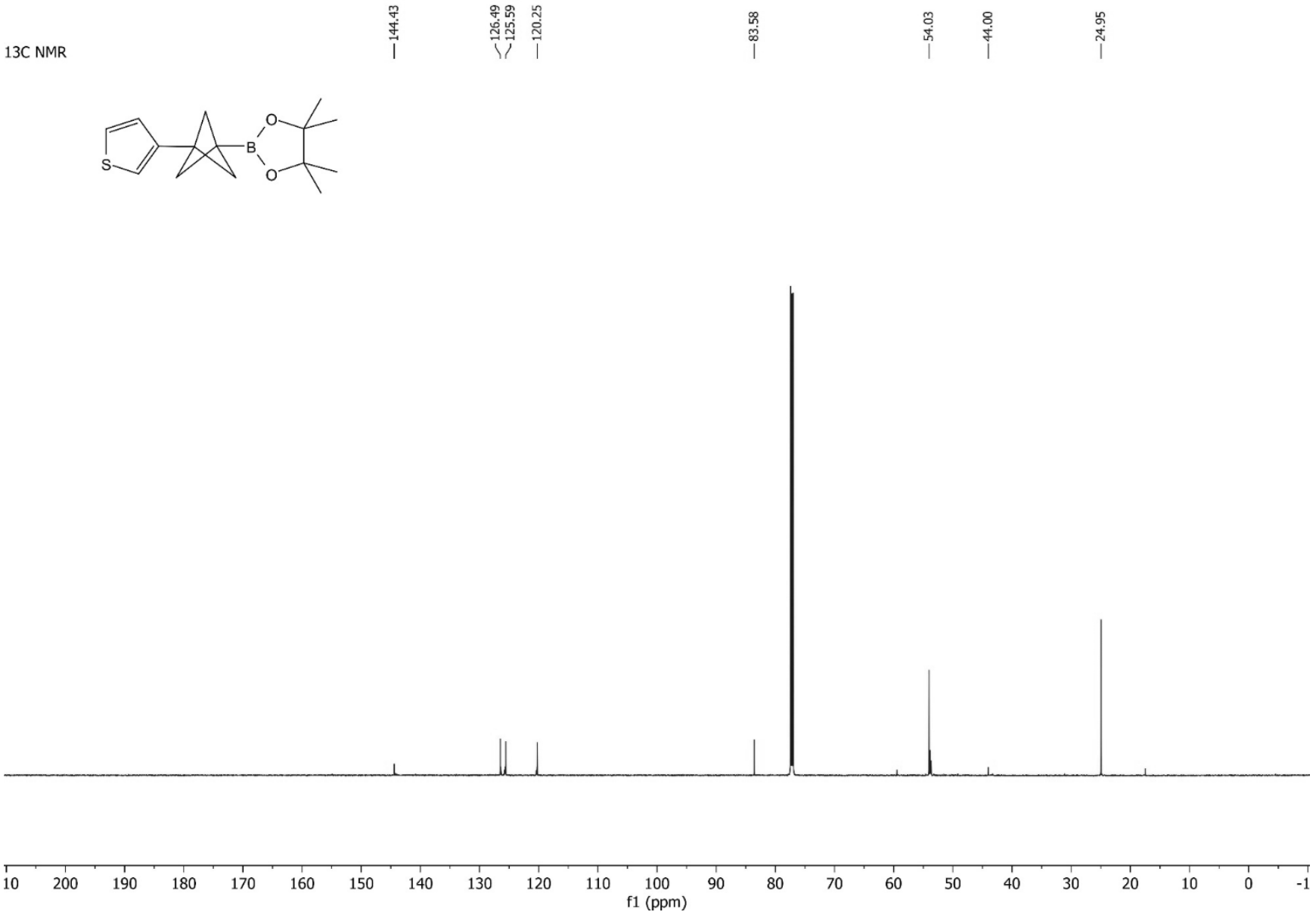
^{11}B NMR (128 MHz, $CDCl_3$) of **5aa**



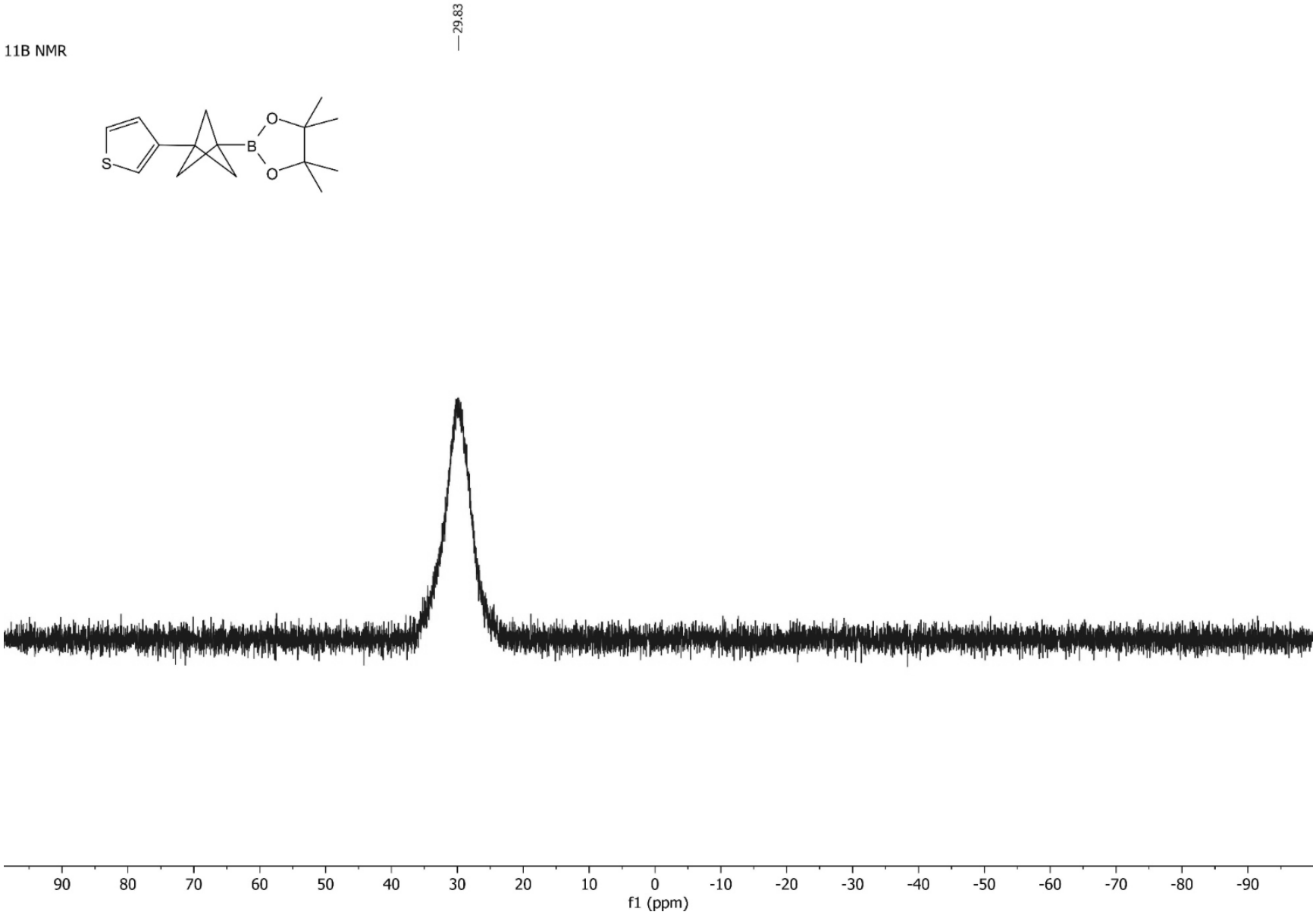
^{1}H NMR (600 MHz, $CDCl_3$) of **5ab**



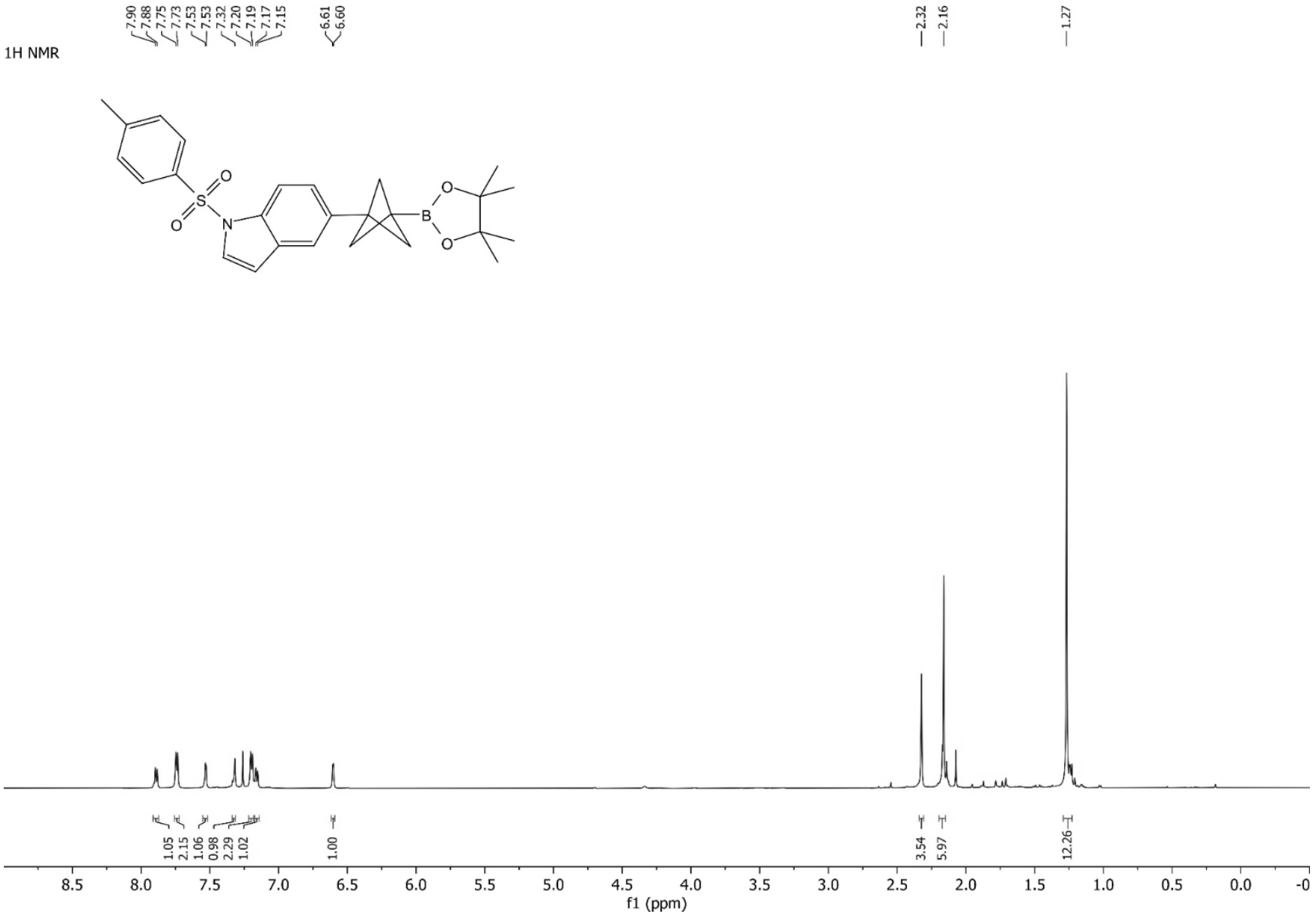
^{13}C NMR (151 MHz, $CDCl_3$) of **5ab**



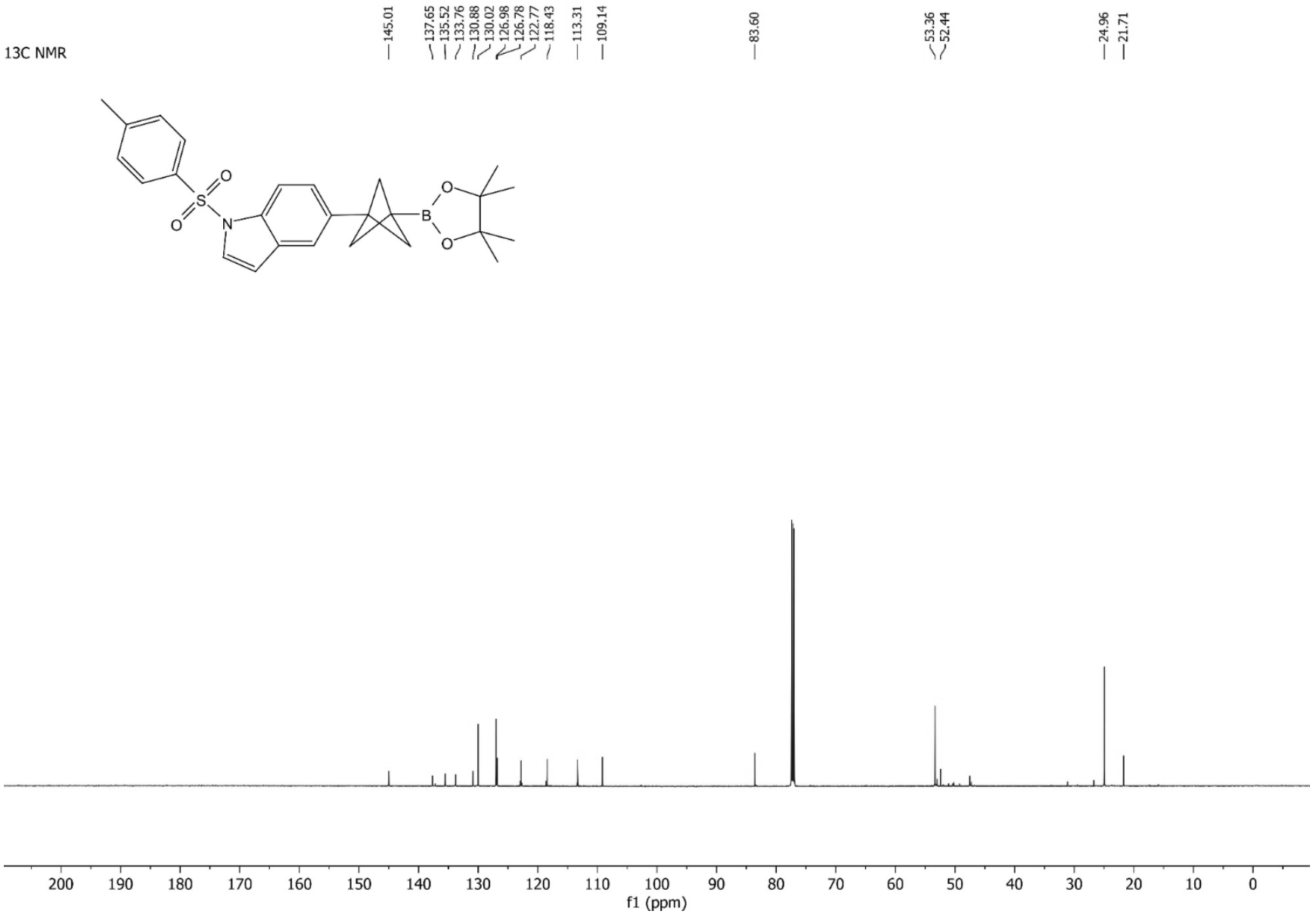
^{11}B NMR (128 MHz, $CDCl_3$) of **5ab**



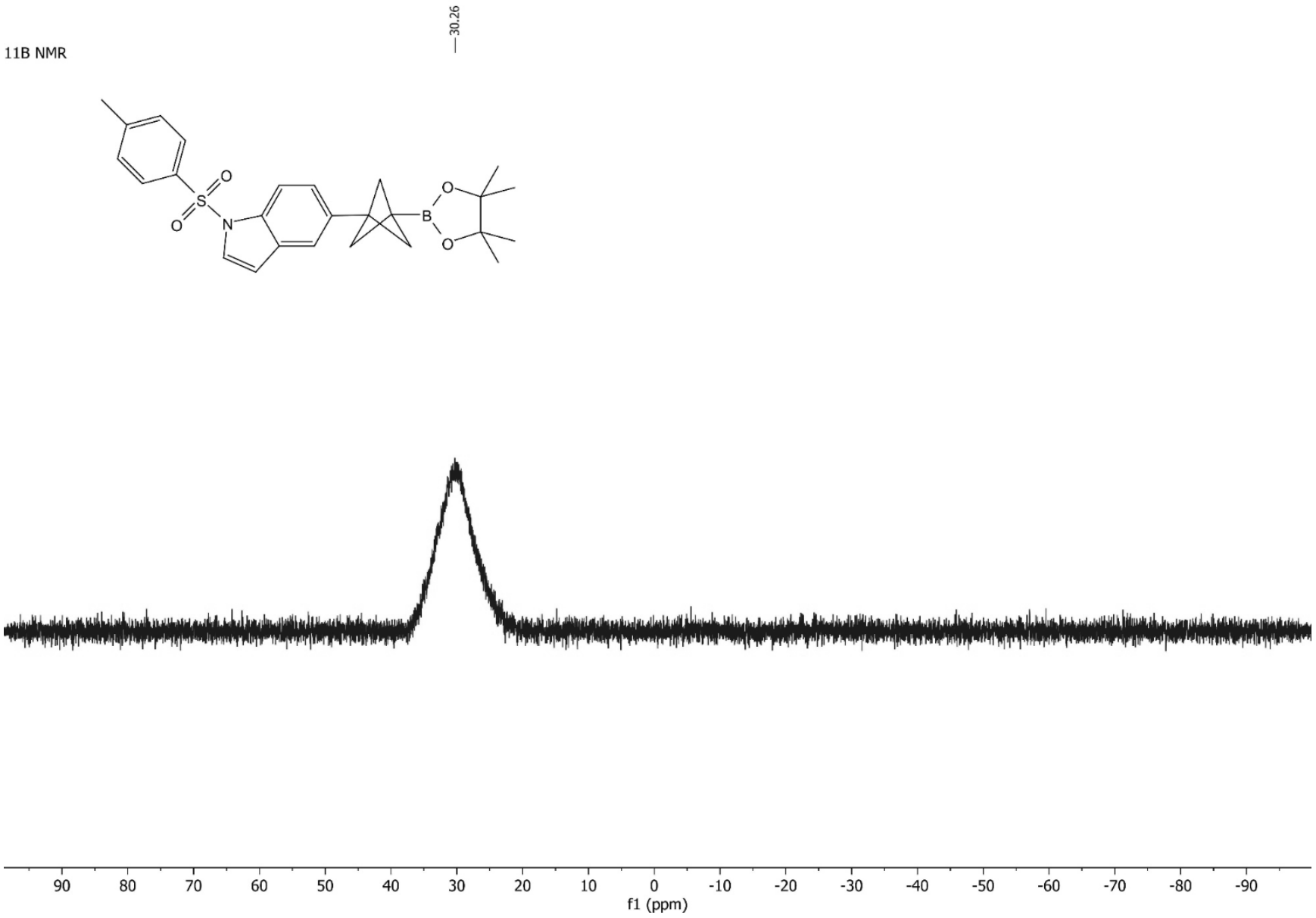
^{1}H NMR (600 MHz, $CDCl_3$) of **5ac**



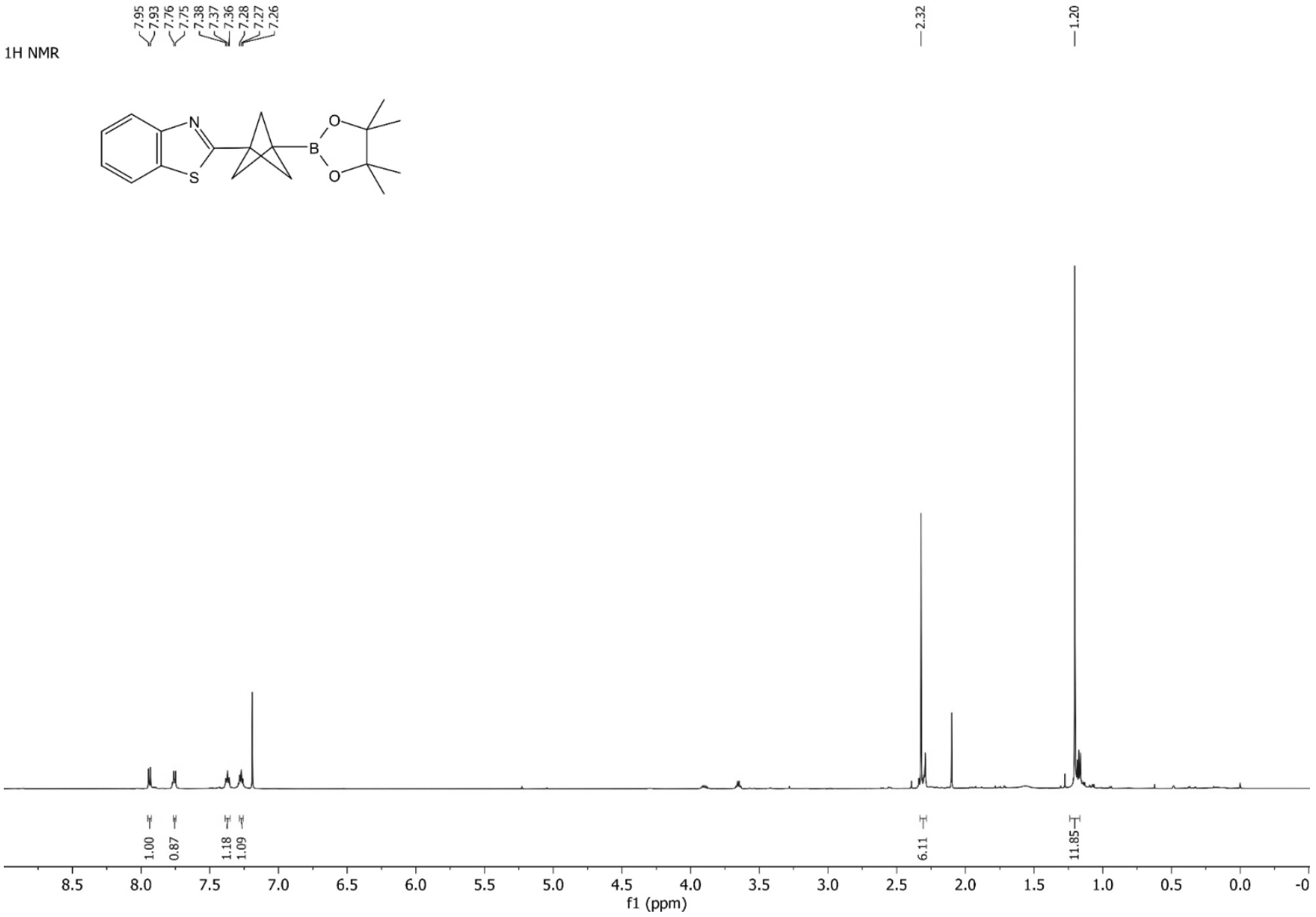
^{13}C NMR (151 MHz, $CDCl_3$) of **5ac**



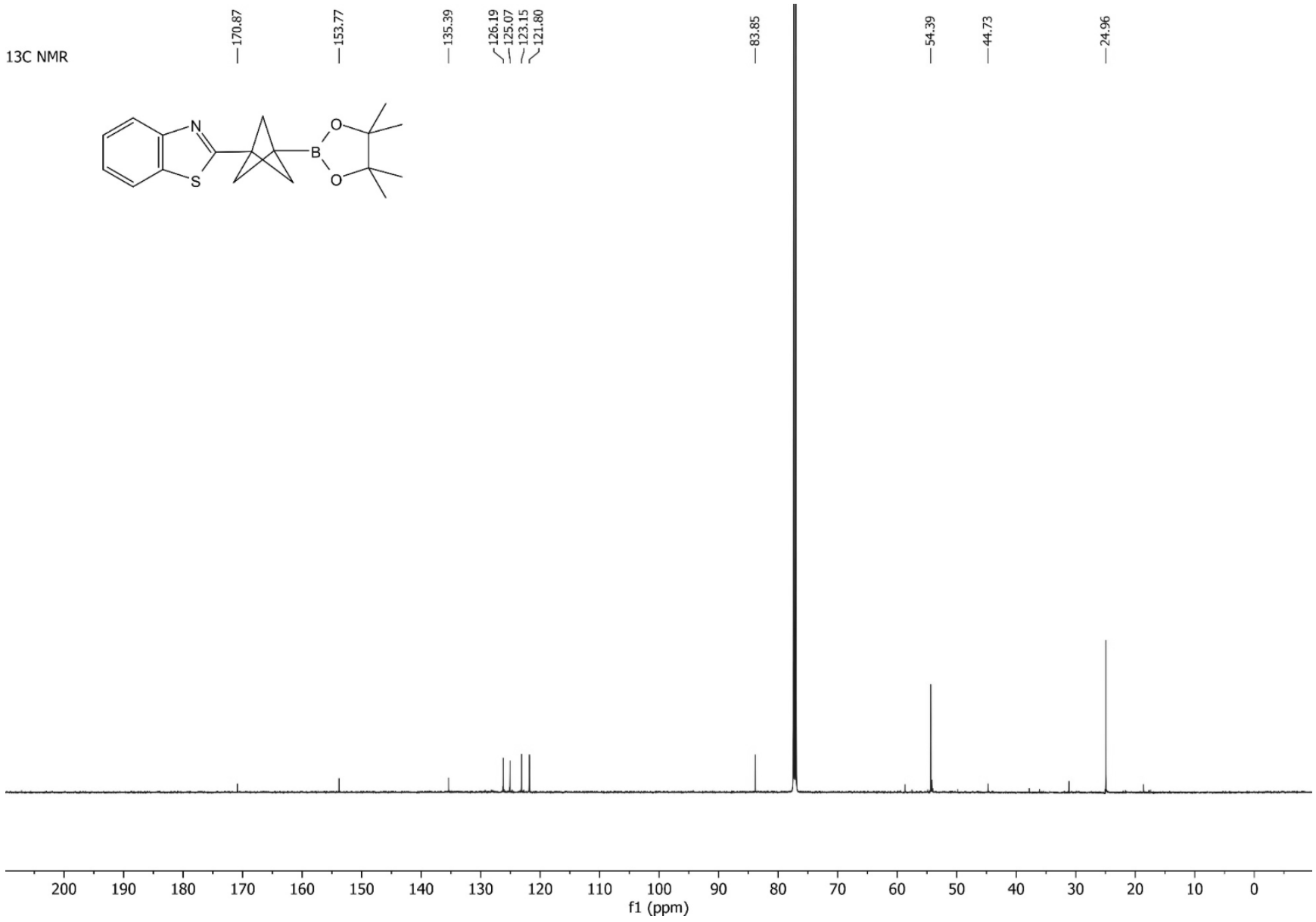
^{11}B NMR (128 MHz, $CDCl_3$) of **5ac**



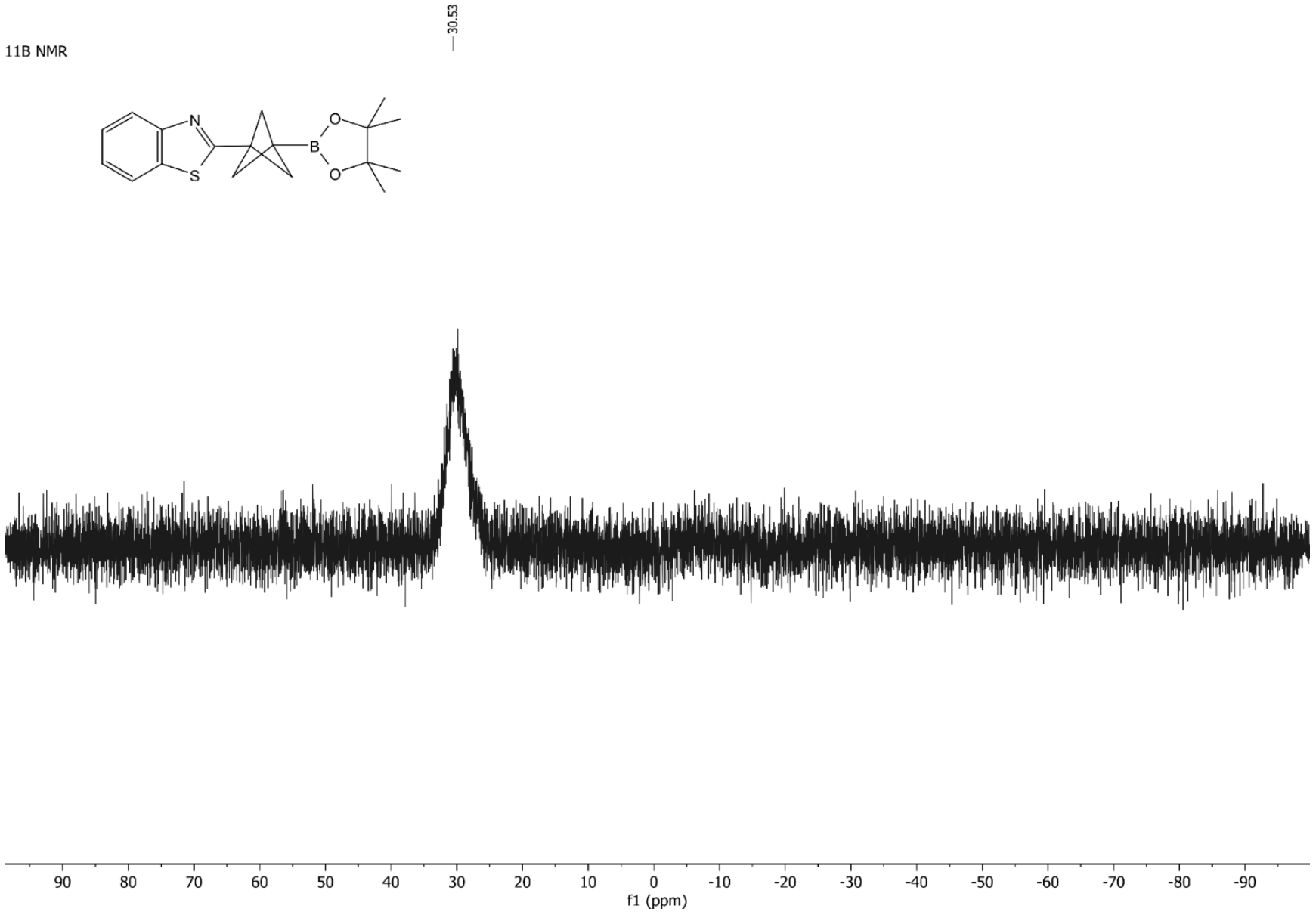
^{1}H NMR (600 MHz, $CDCl_3$) of **5ad**



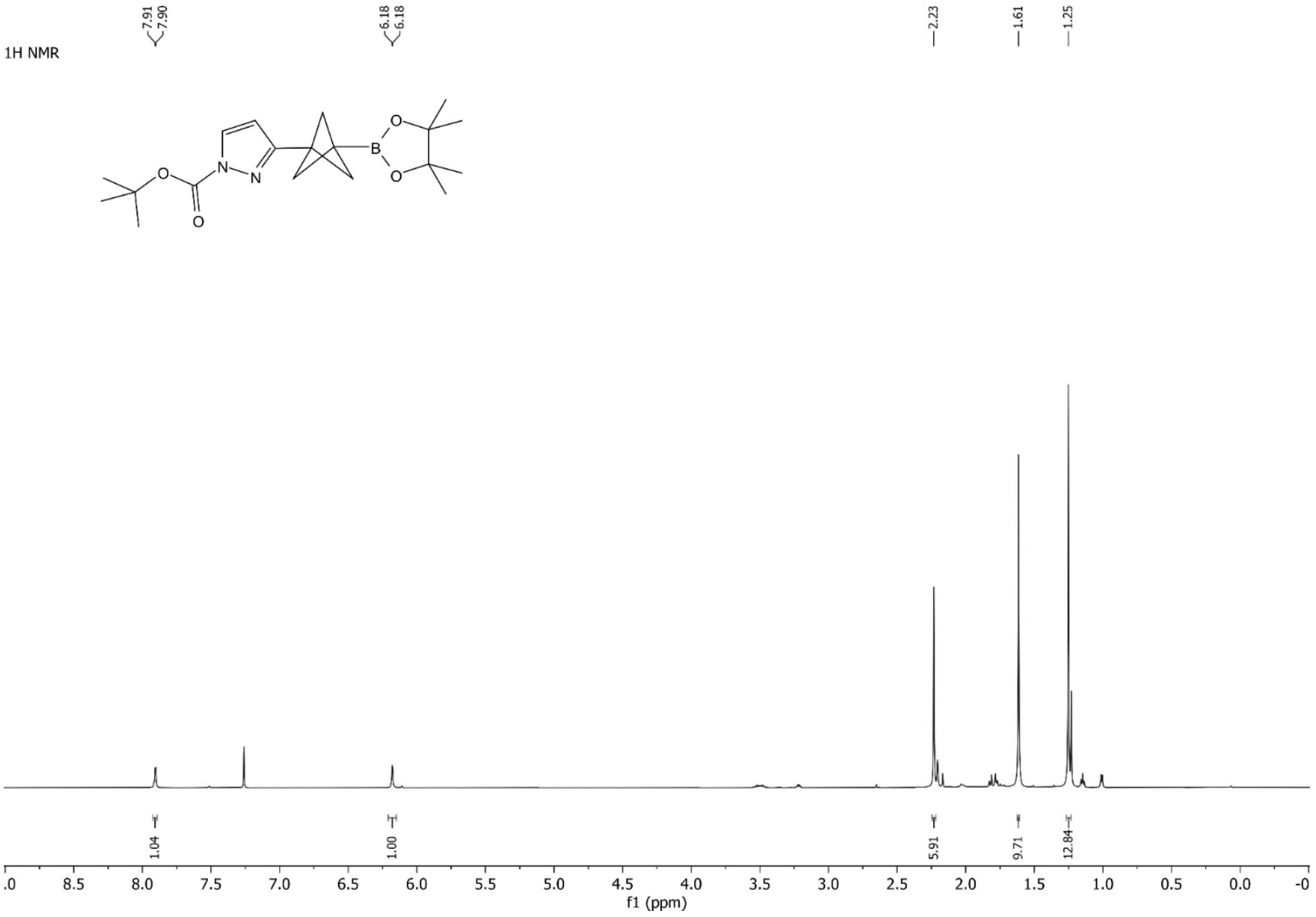
^{13}C NMR (151 MHz, $CDCl_3$) of **5ad**



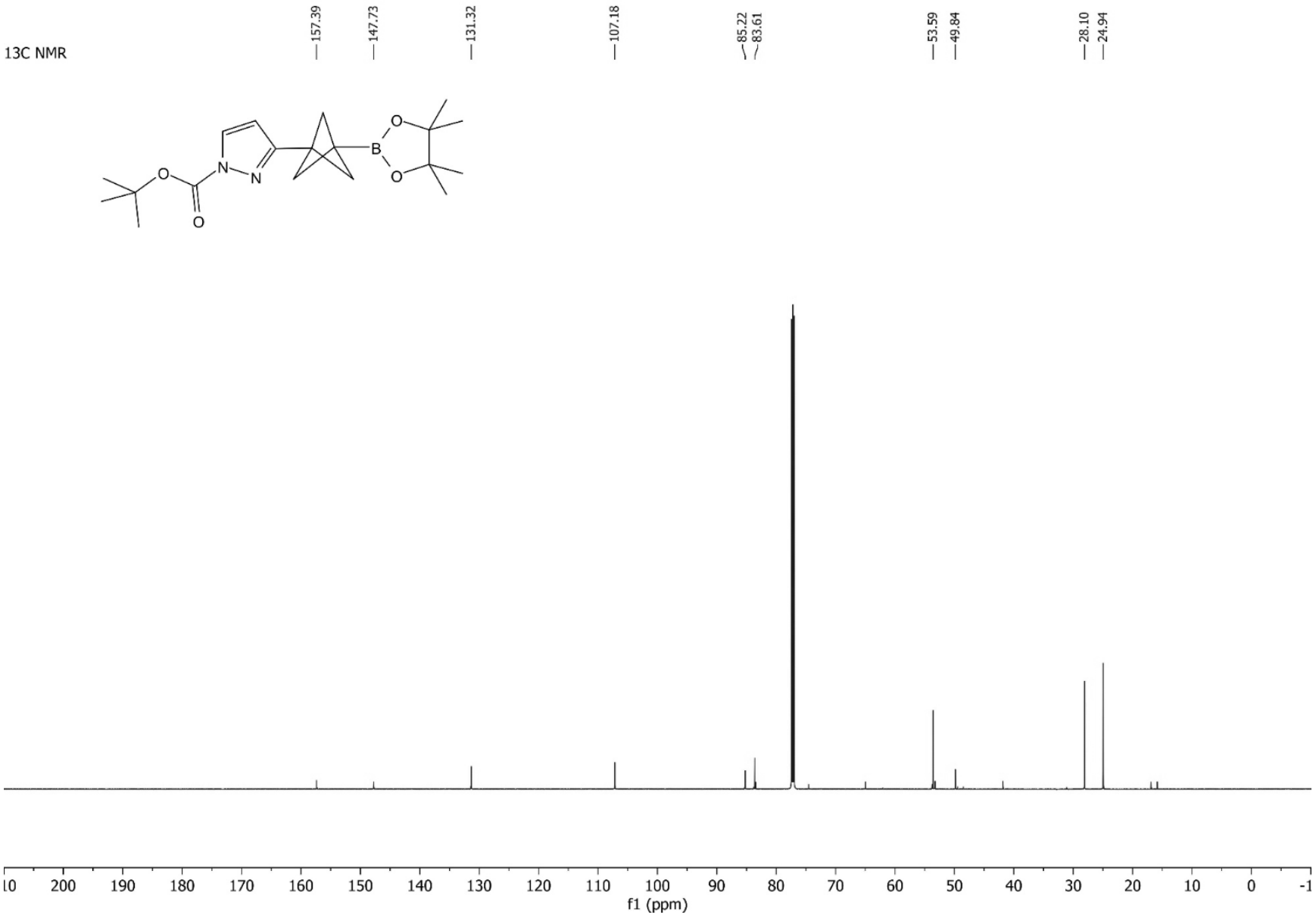
^{11}B NMR (128 MHz, $CDCl_3$) of **5ad**



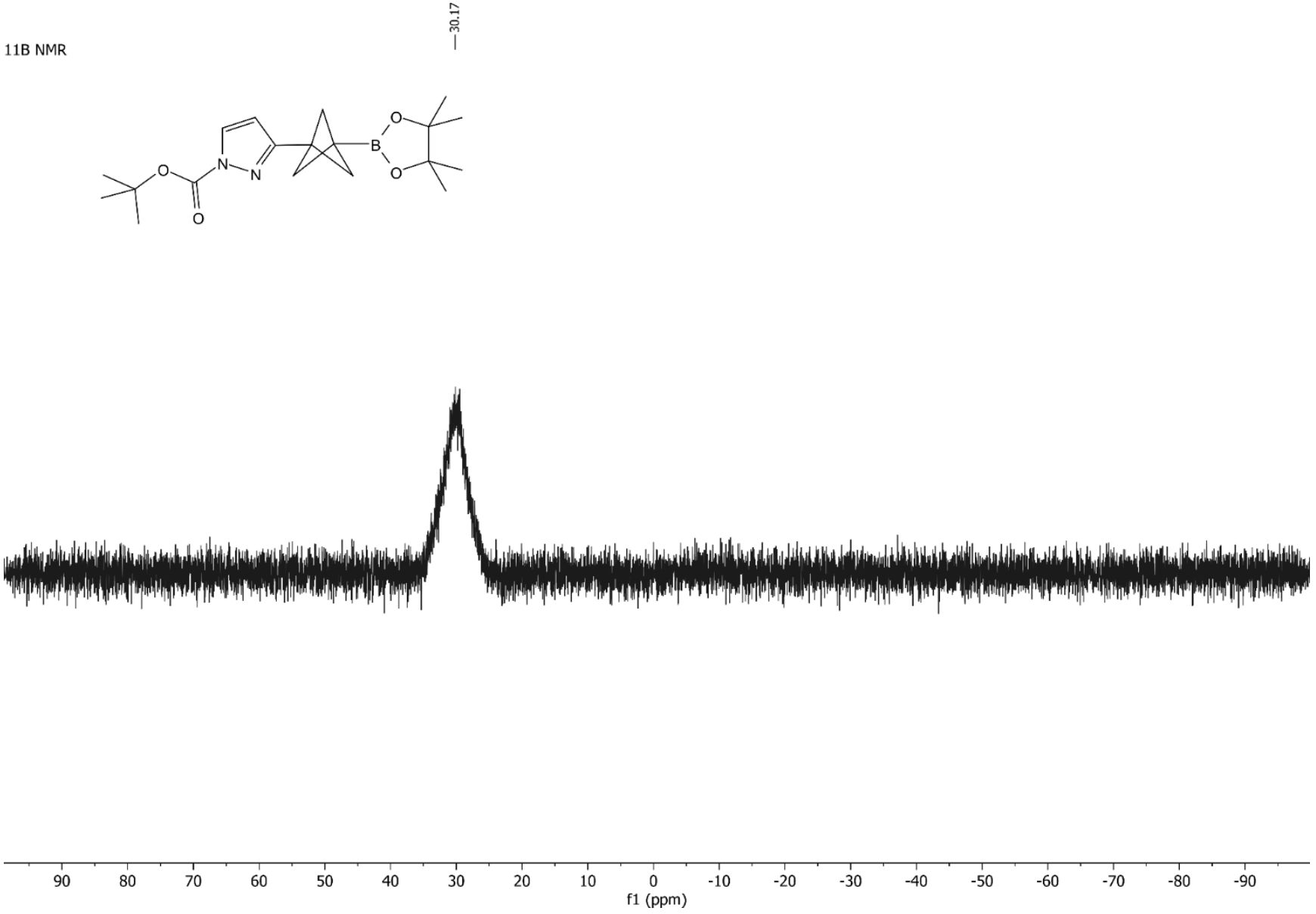
^{1}H NMR (600 MHz, $CDCl_3$) of **5ae**



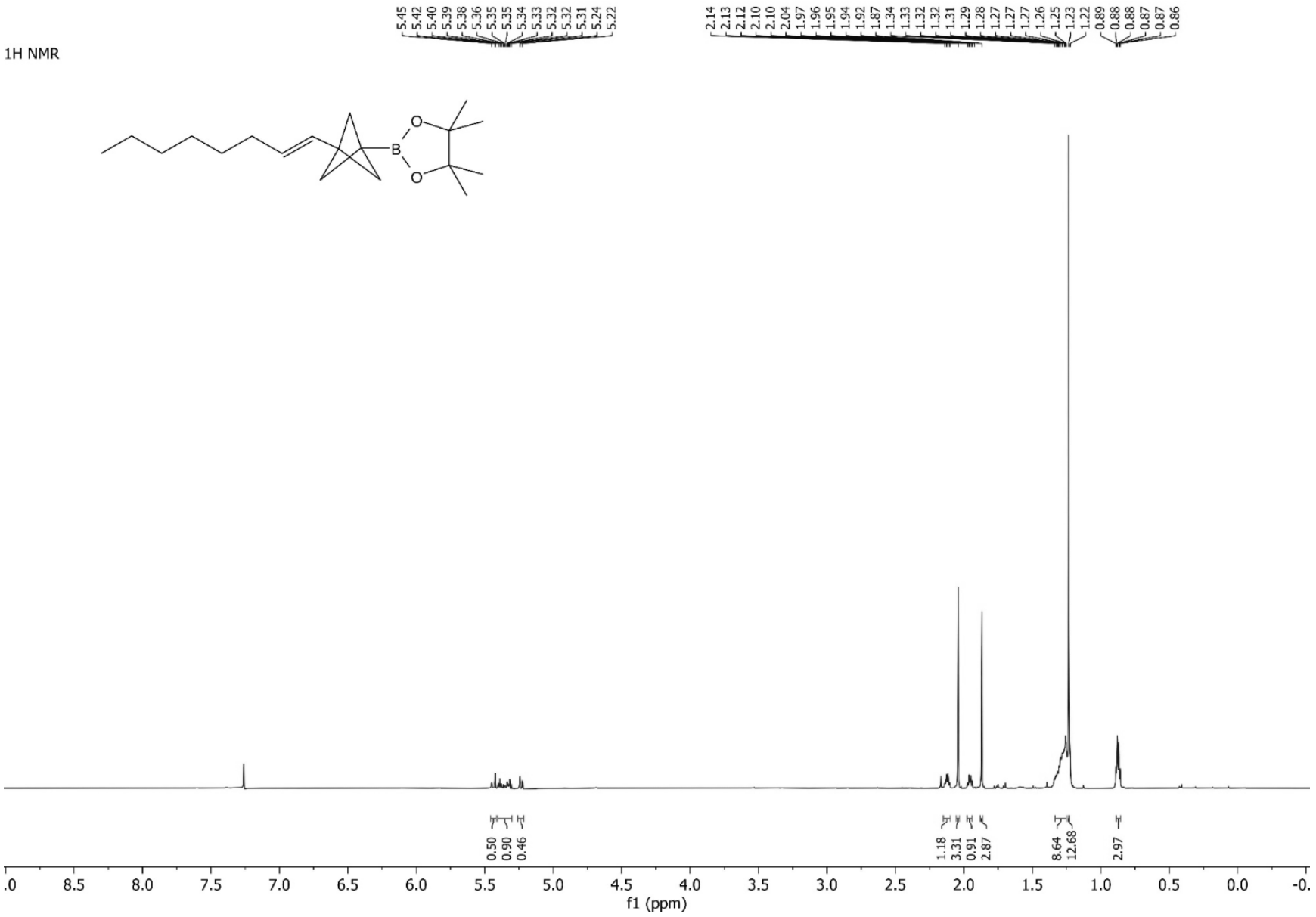
^{13}C NMR (151 MHz, $CDCl_3$) of **5ae**



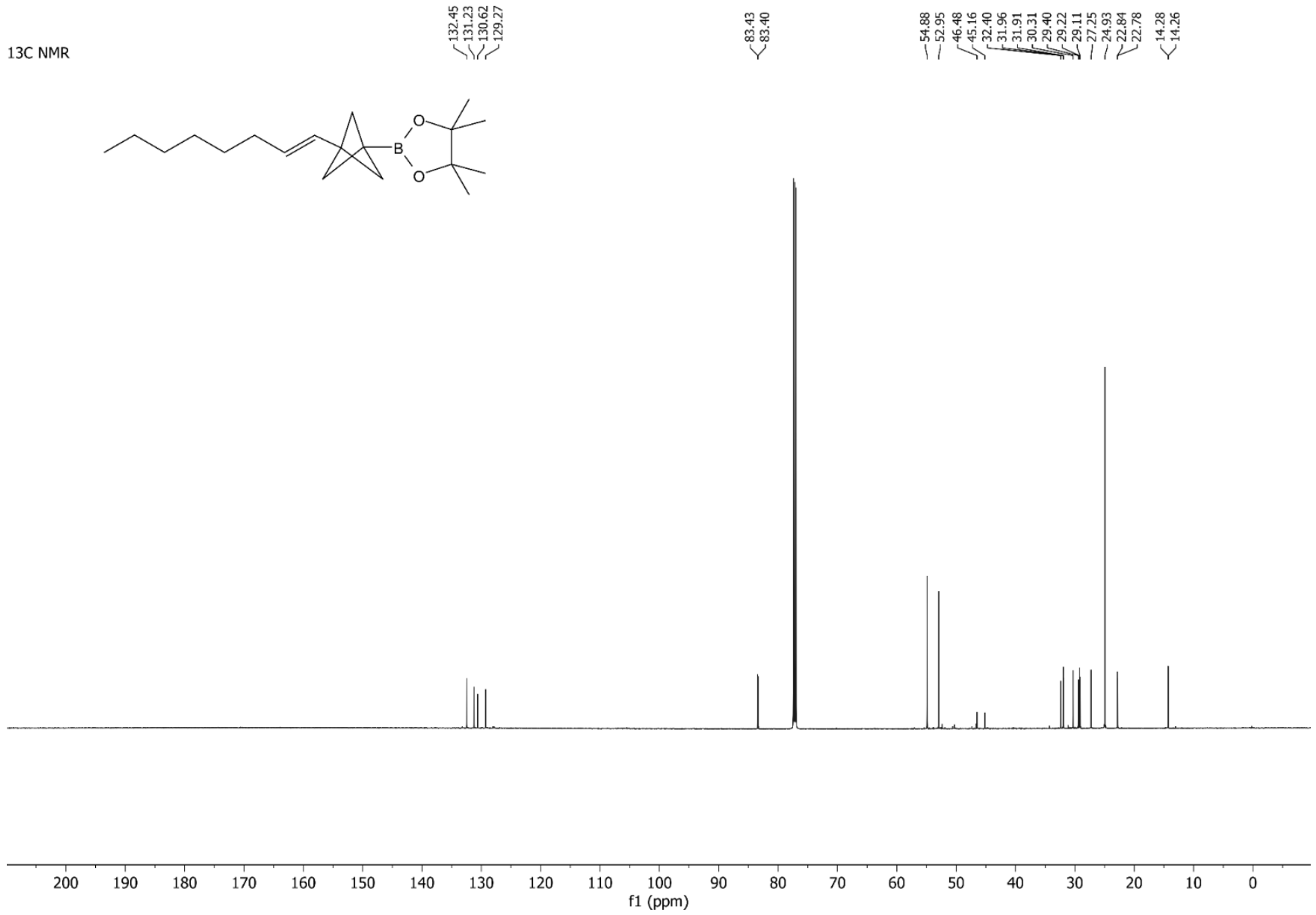
^{11}B NMR (128 MHz, $CDCl_3$) of **5ae**



^{1}H NMR (600 MHz, $CDCl_3$) of **5af**



^{13}C NMR (151 MHz, $CDCl_3$) of **5af**



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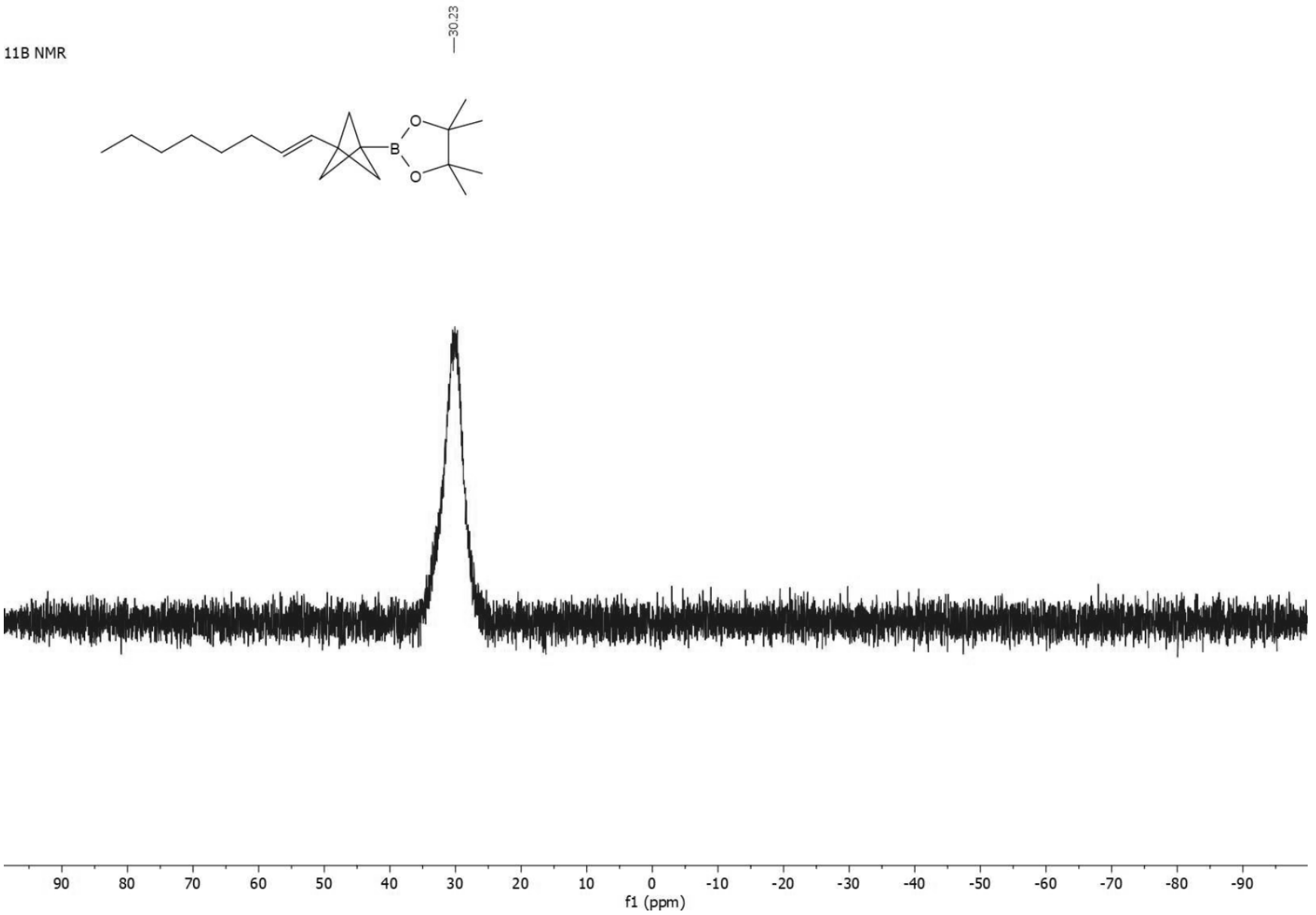
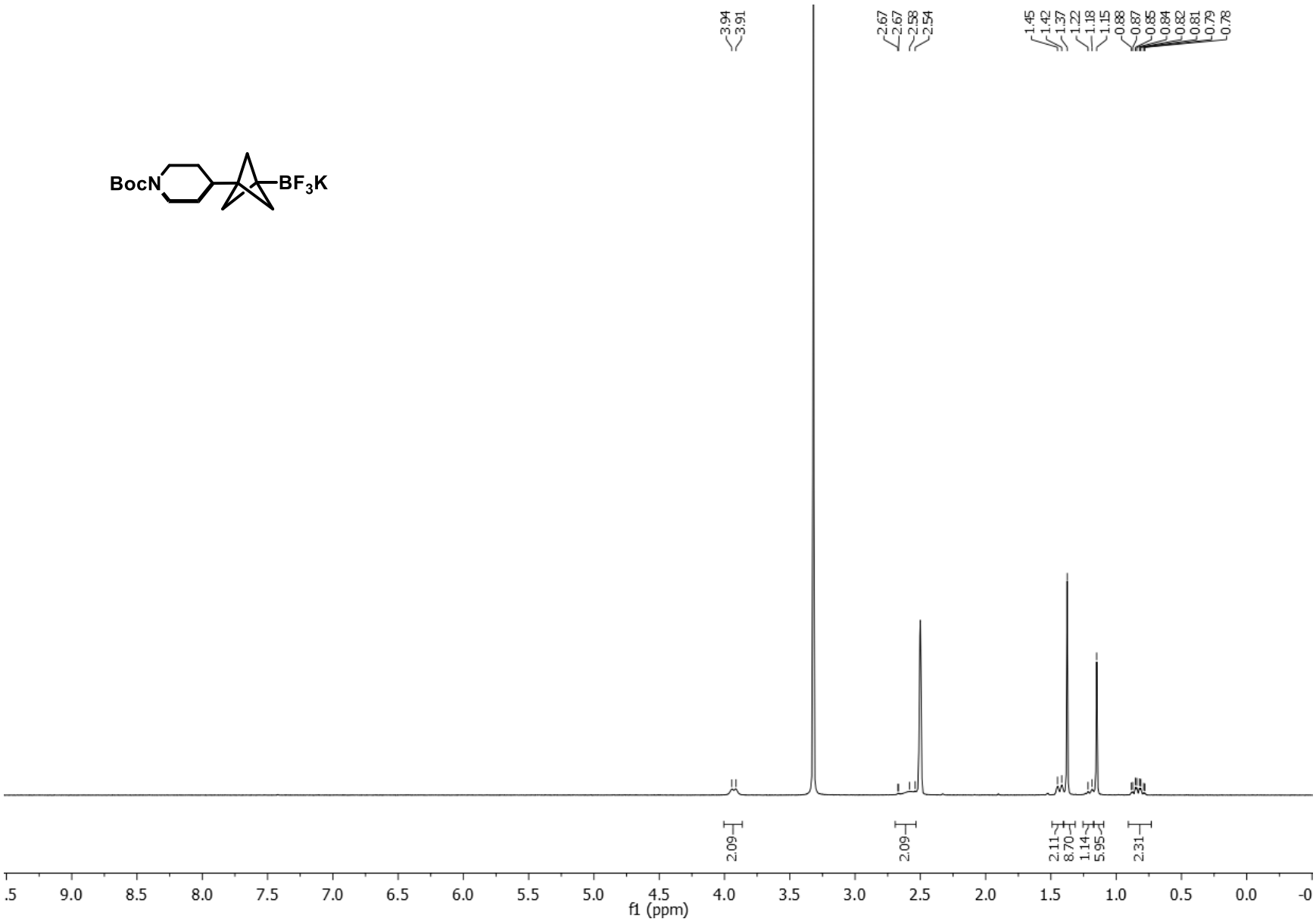
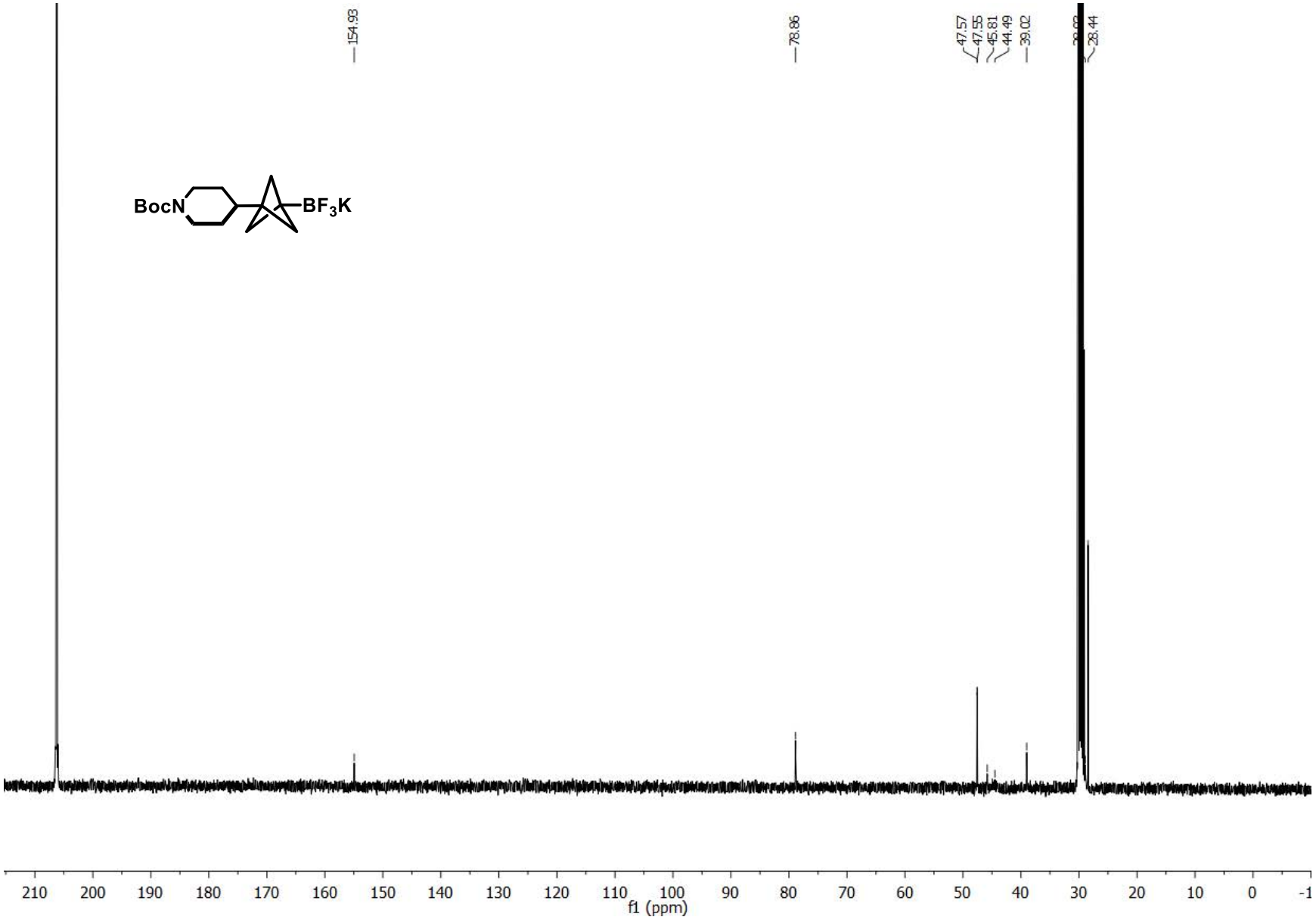


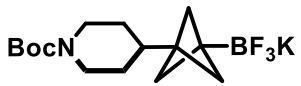
^{1}H NMR (400 MHz, DMSO-d_6) of **6**



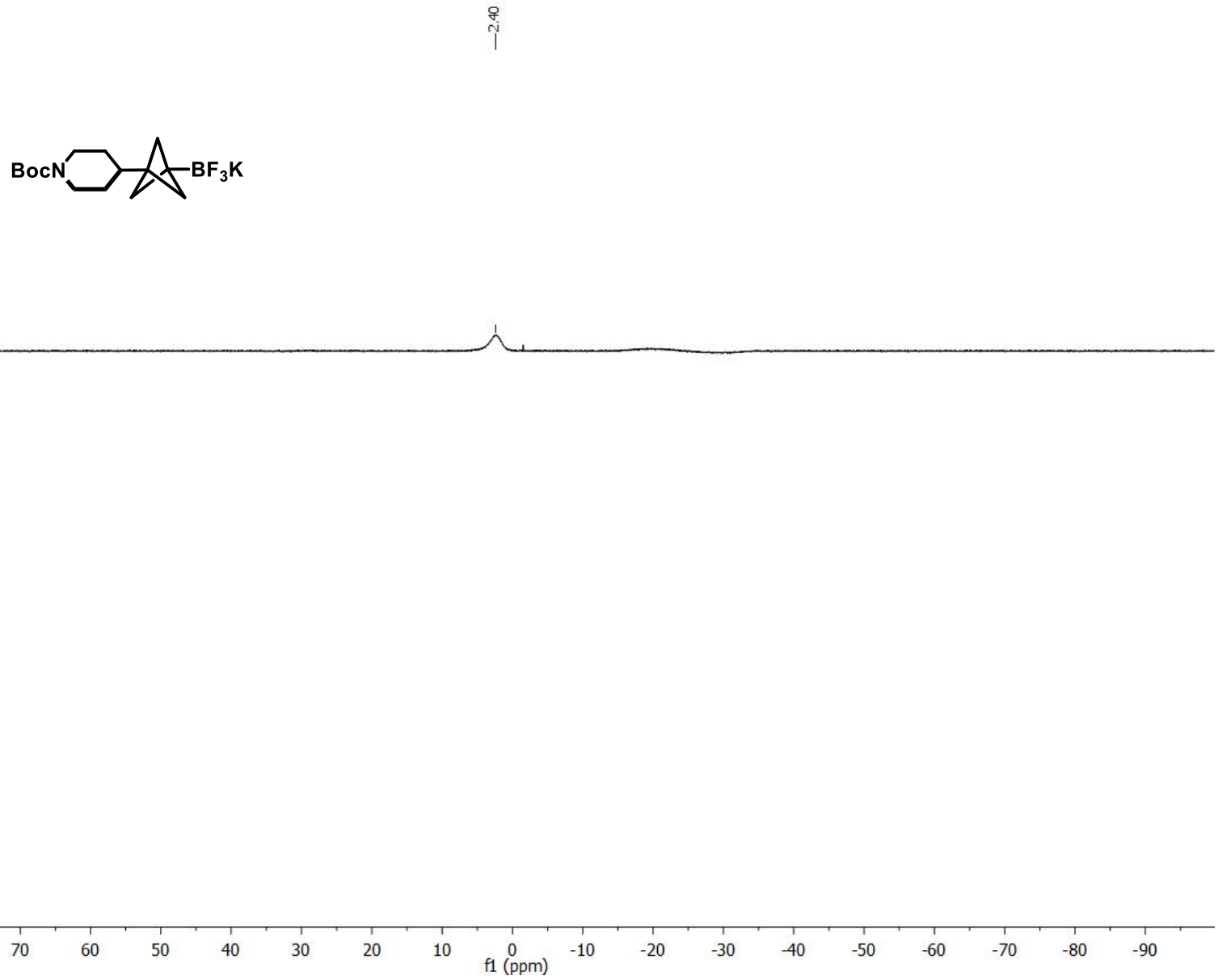
^{13}C NMR (101 MHz, acetone-d_6) of **6**



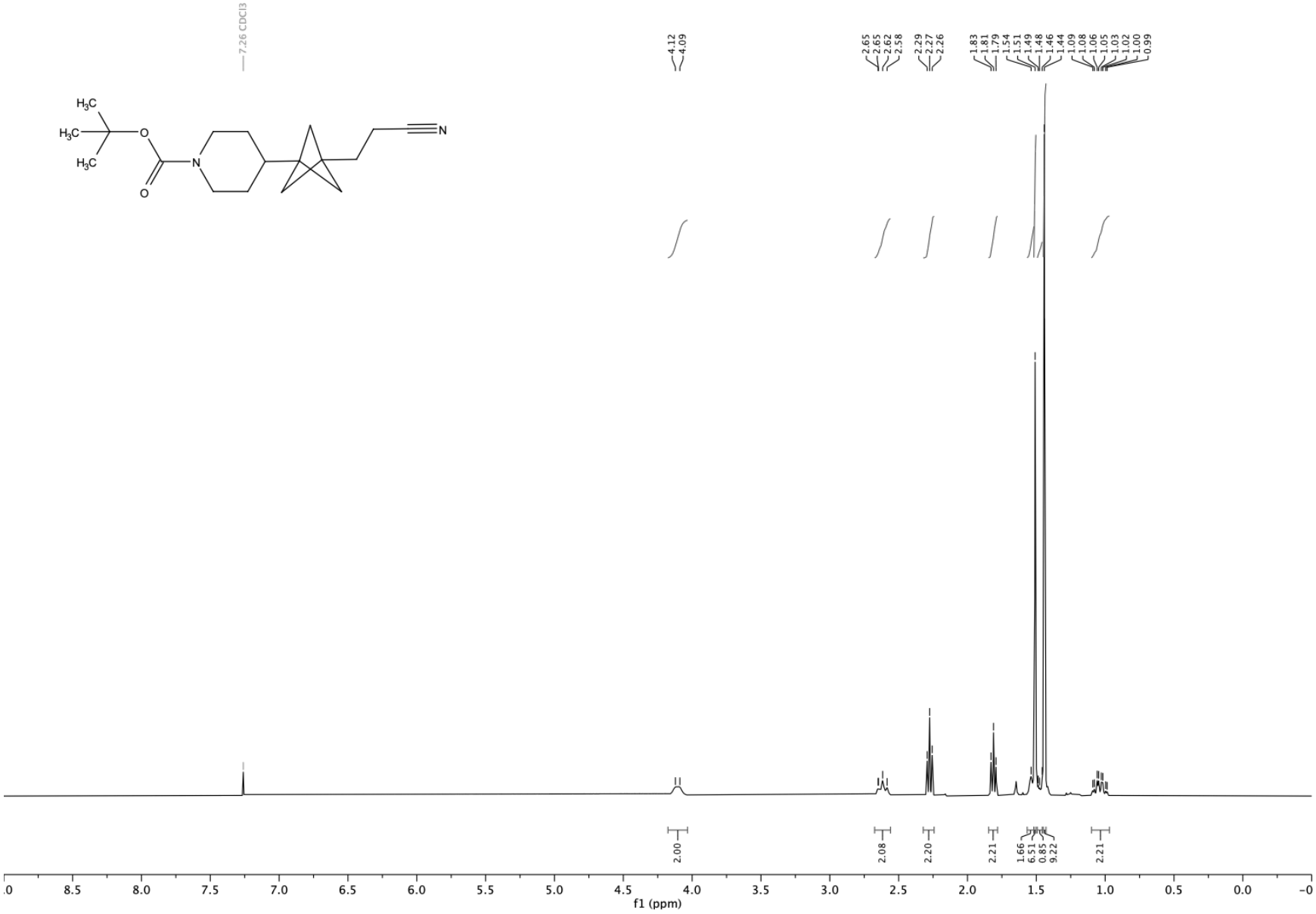
^{19}F NMR (376 MHz, DMSO-d_6) of **6**



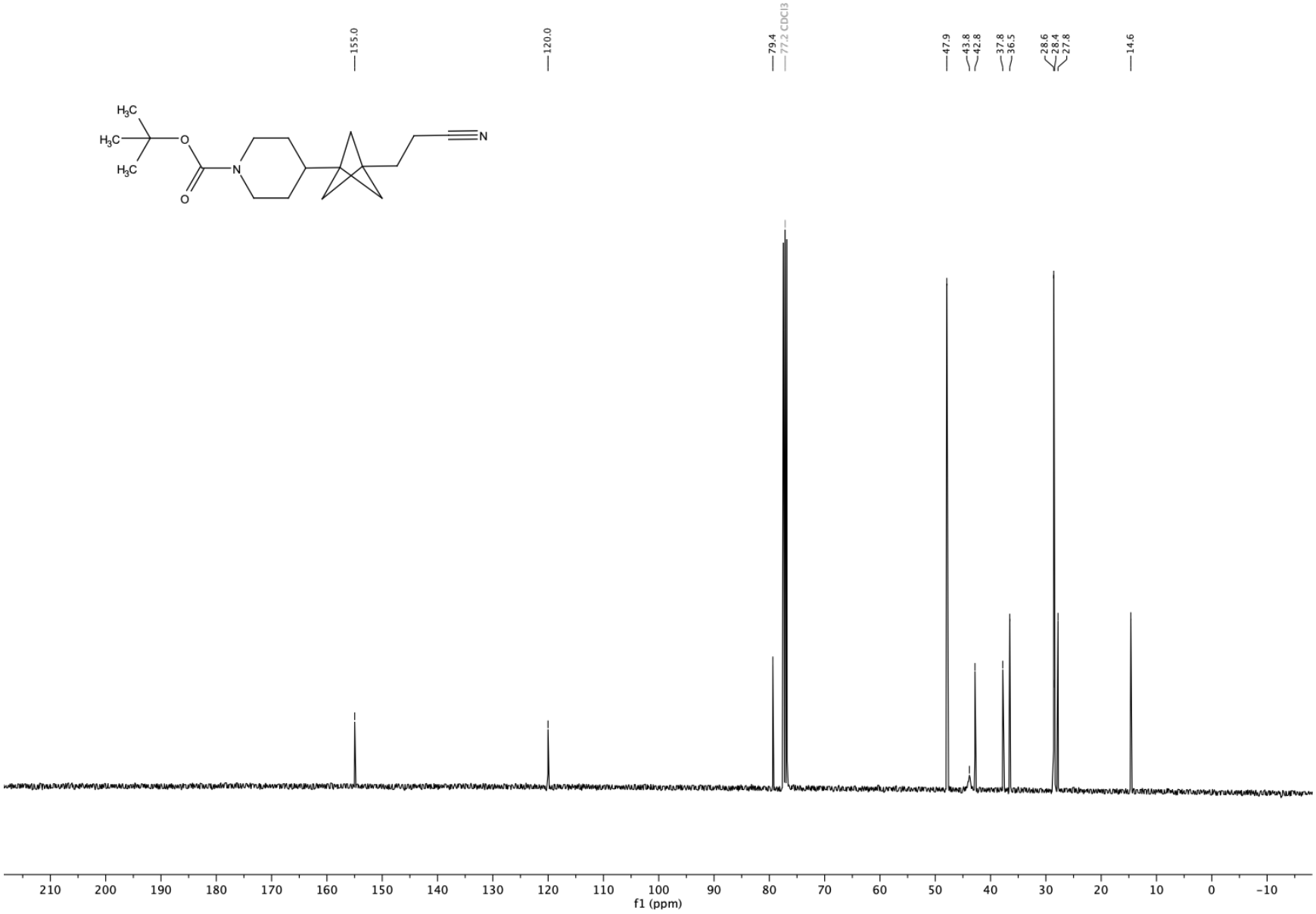
^{11}B NMR (128 MHz, acetone-d_6) of **6**



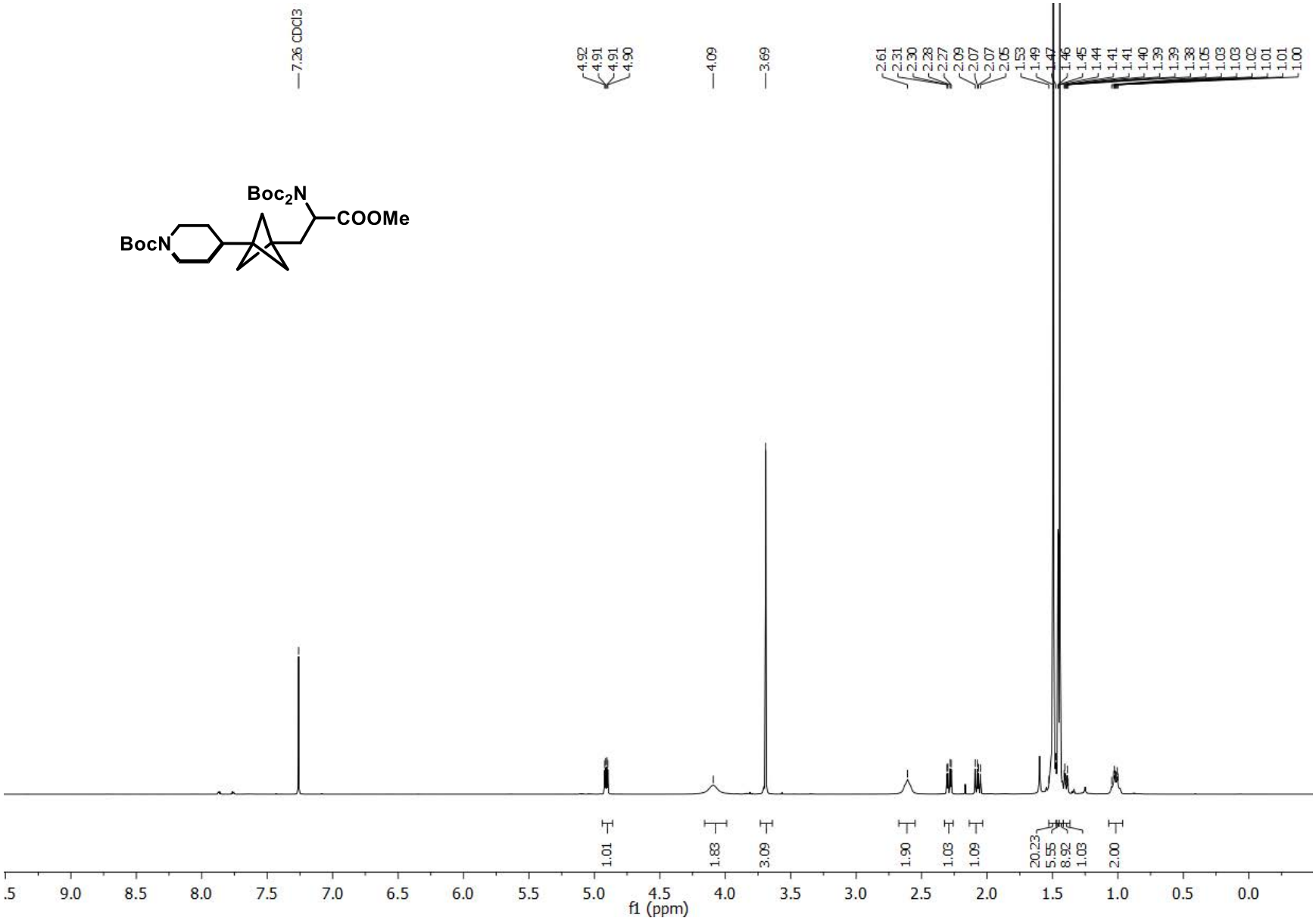
^{1}H NMR (400 MHz, $CDCl_3$) of **7**



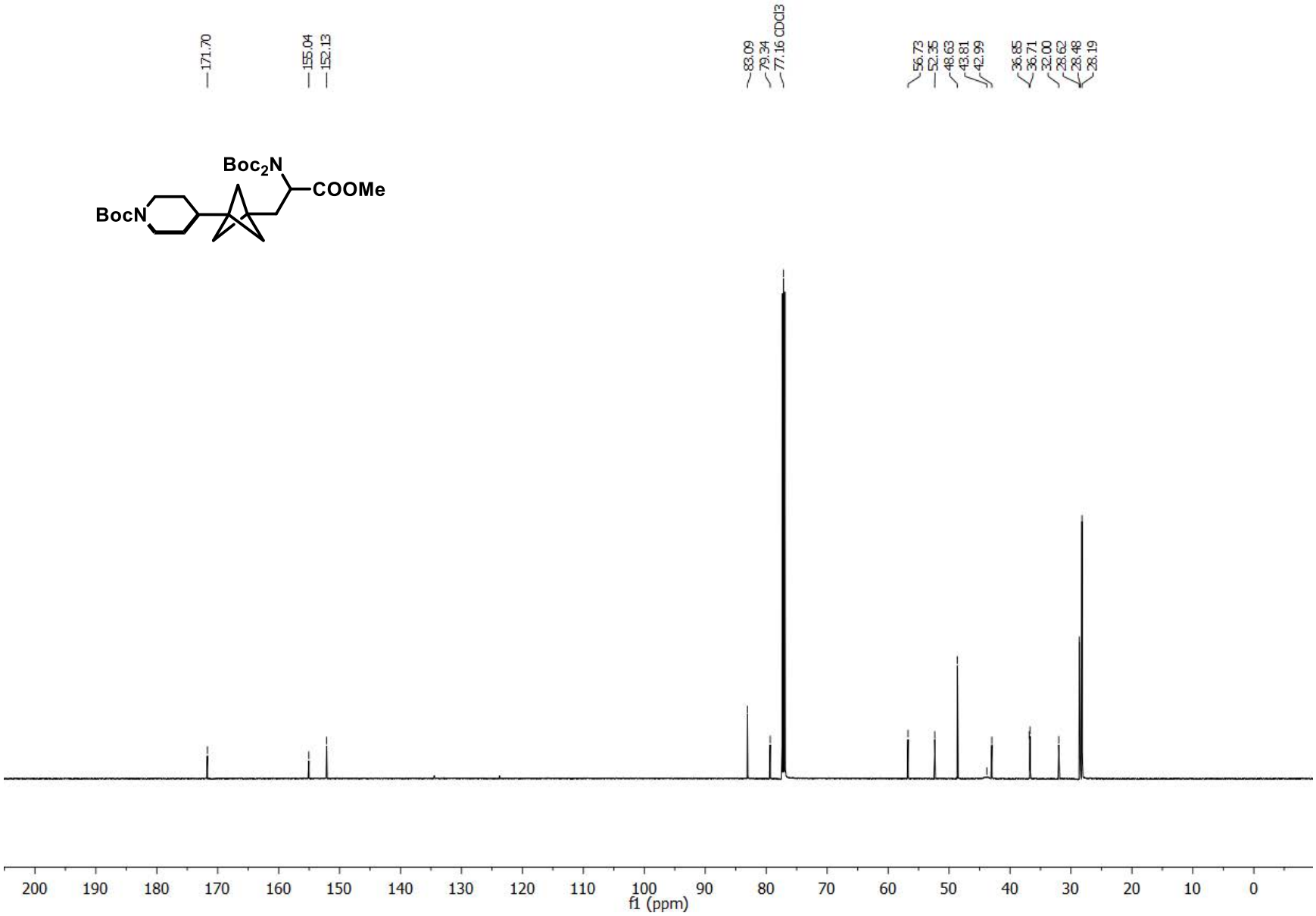
^{13}C NMR (101 MHz, $CDCl_3$) of **7**



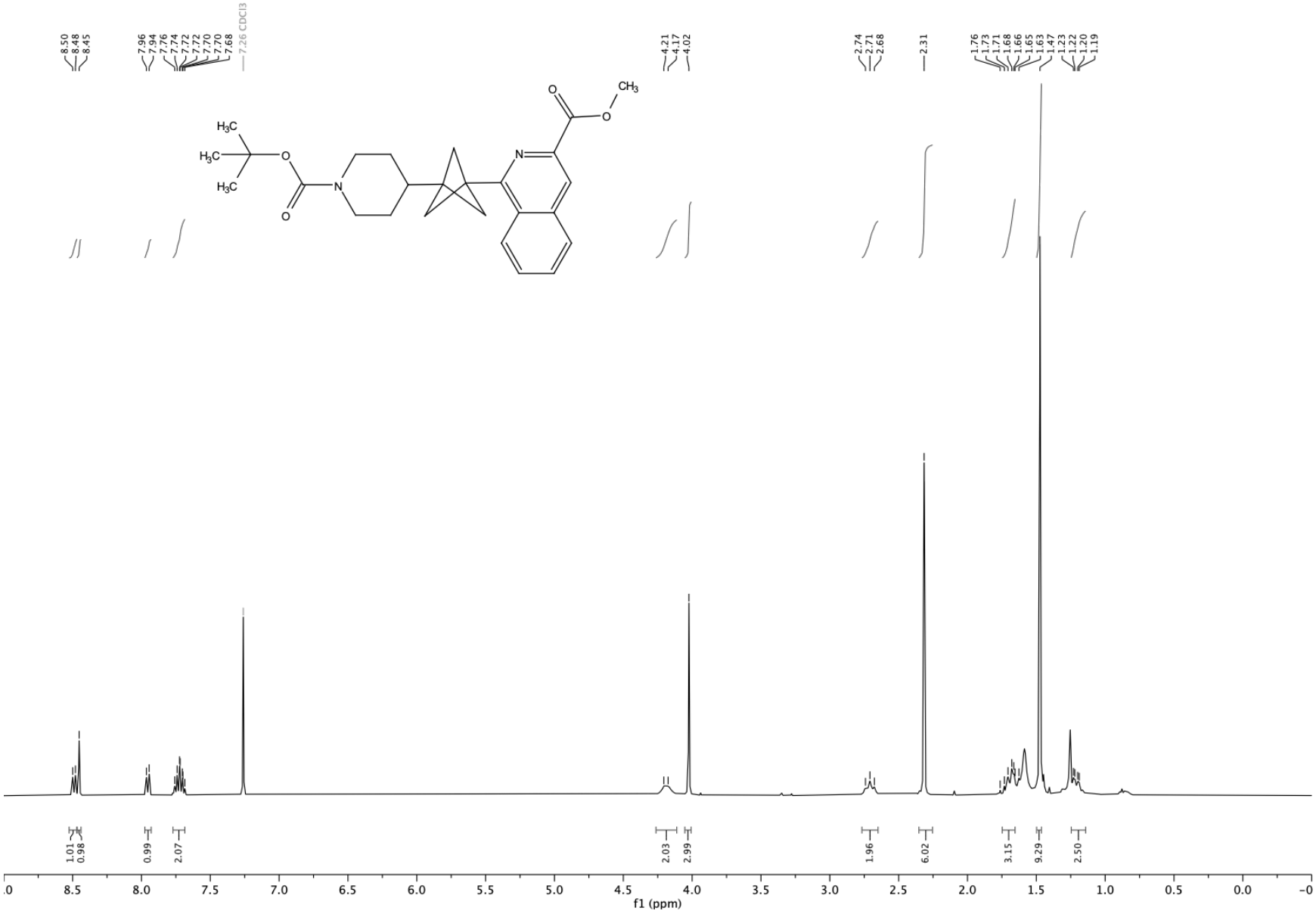
^{1}H NMR (600 MHz, $CDCl_3$) of **8**



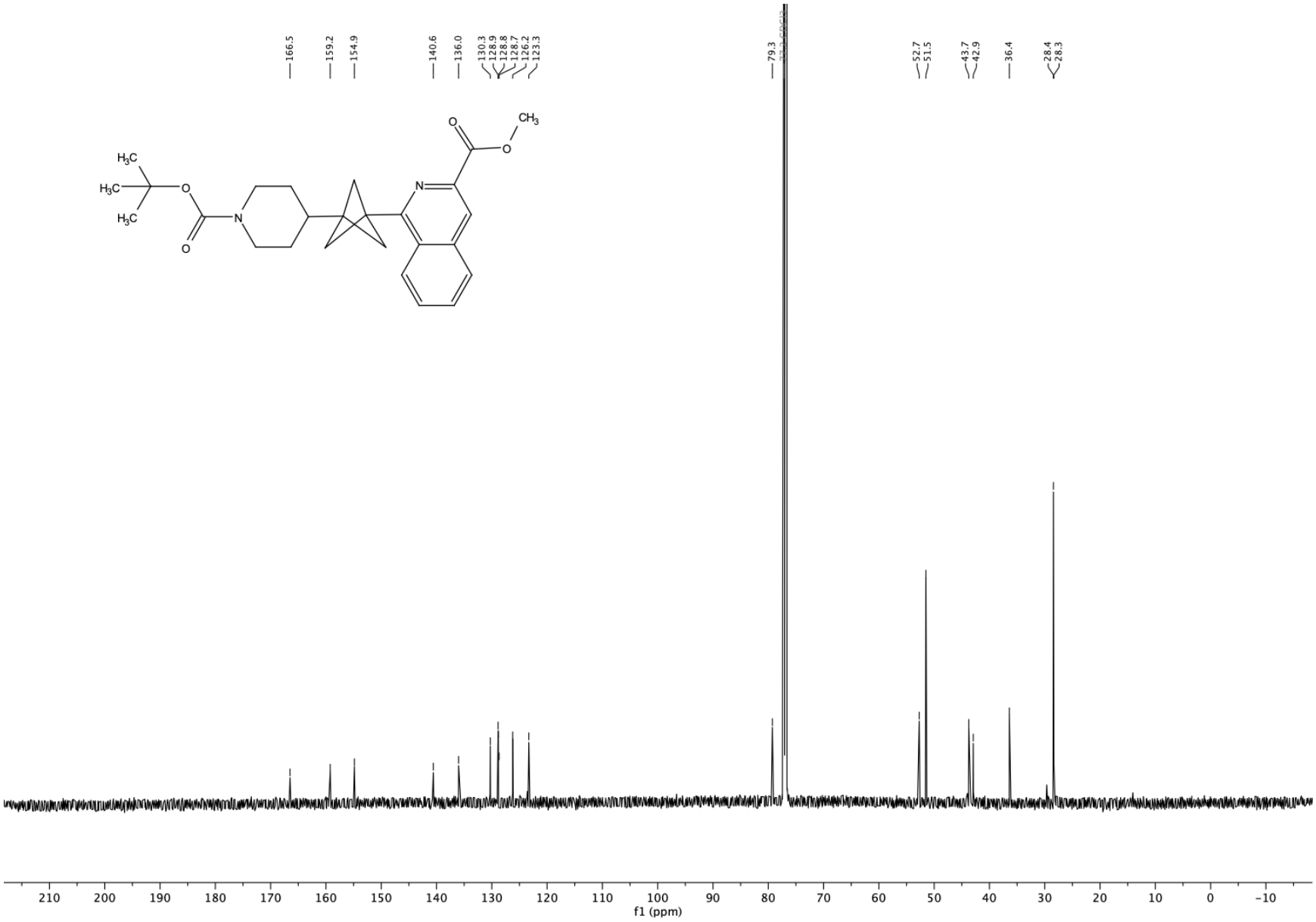
^{13}C NMR (151 MHz, $CDCl_3$) of **8**



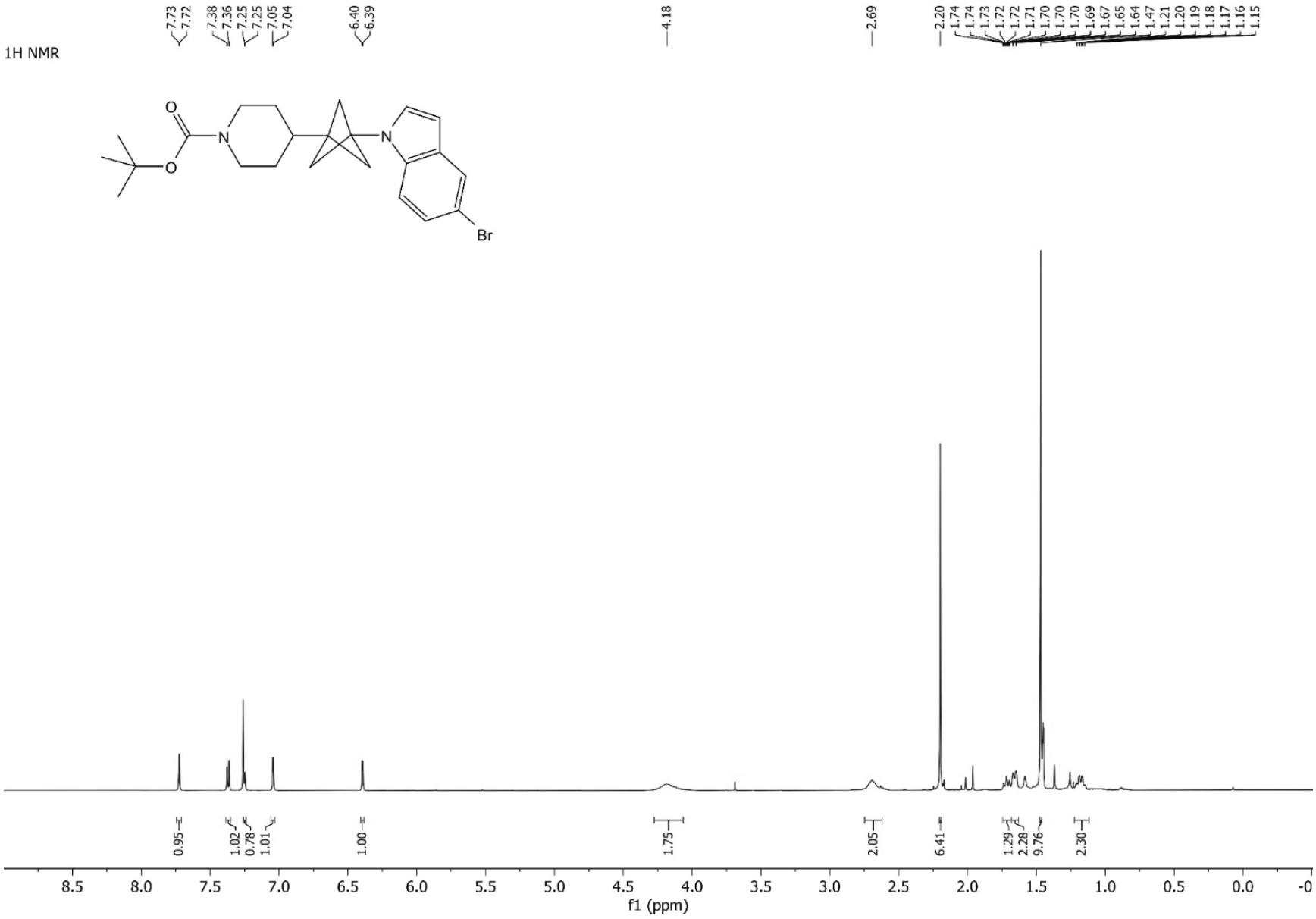
^{1}H NMR (400 MHz, $CDCl_3$) of **9**



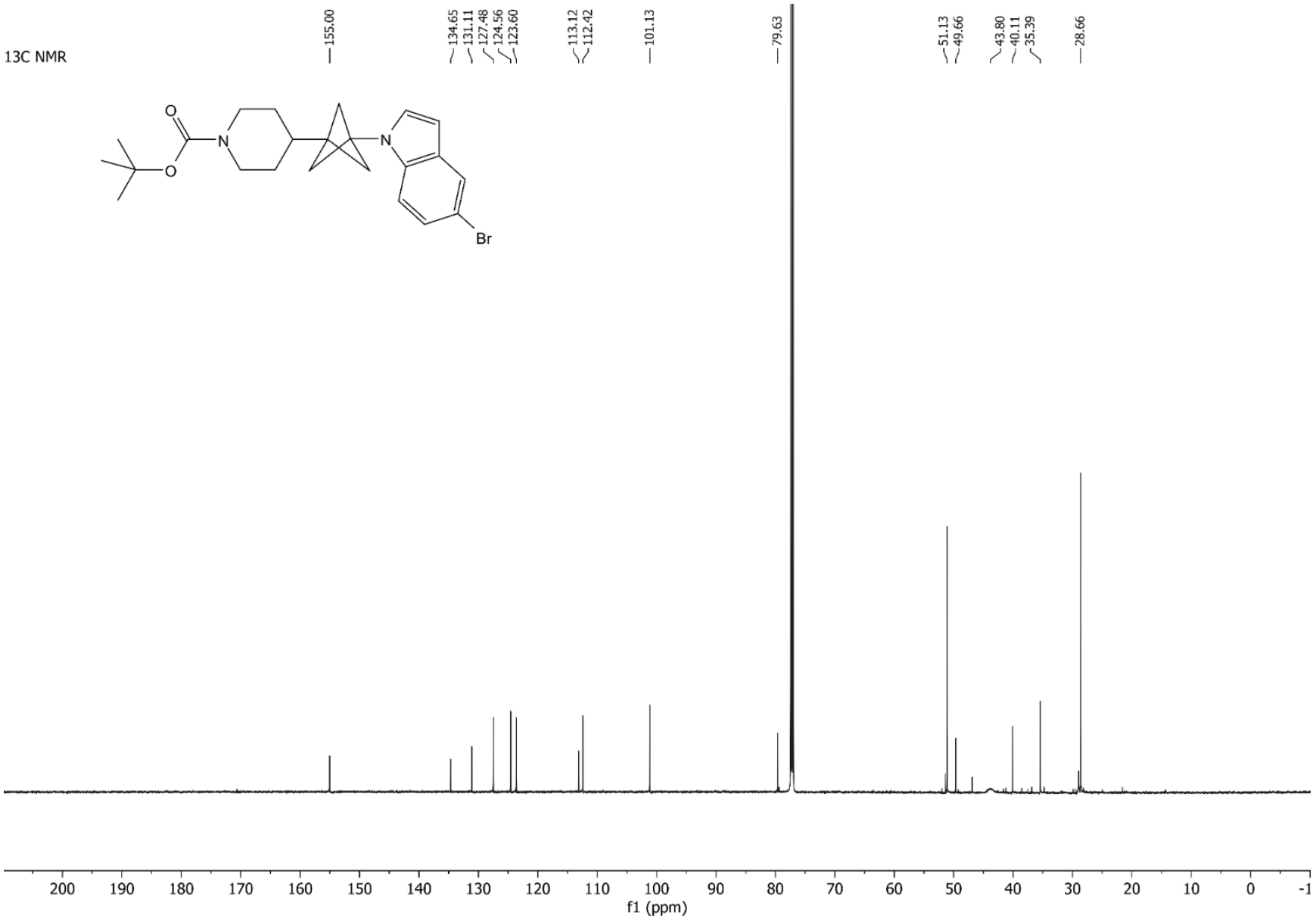
^{13}C NMR (151 MHz, $CDCl_3$) of **9**



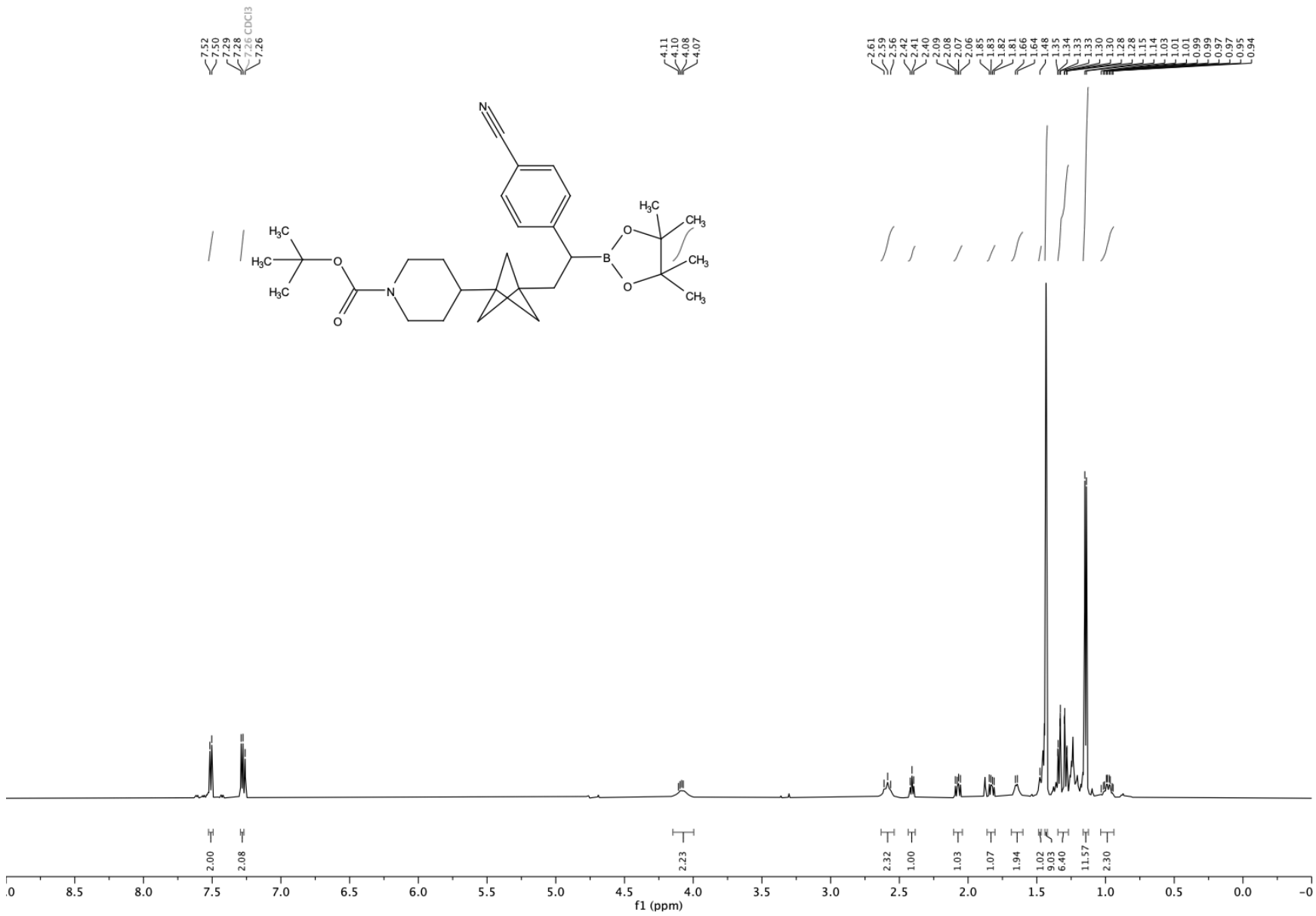
^{1}H NMR (600 MHz, $CDCl_3$) of **10**



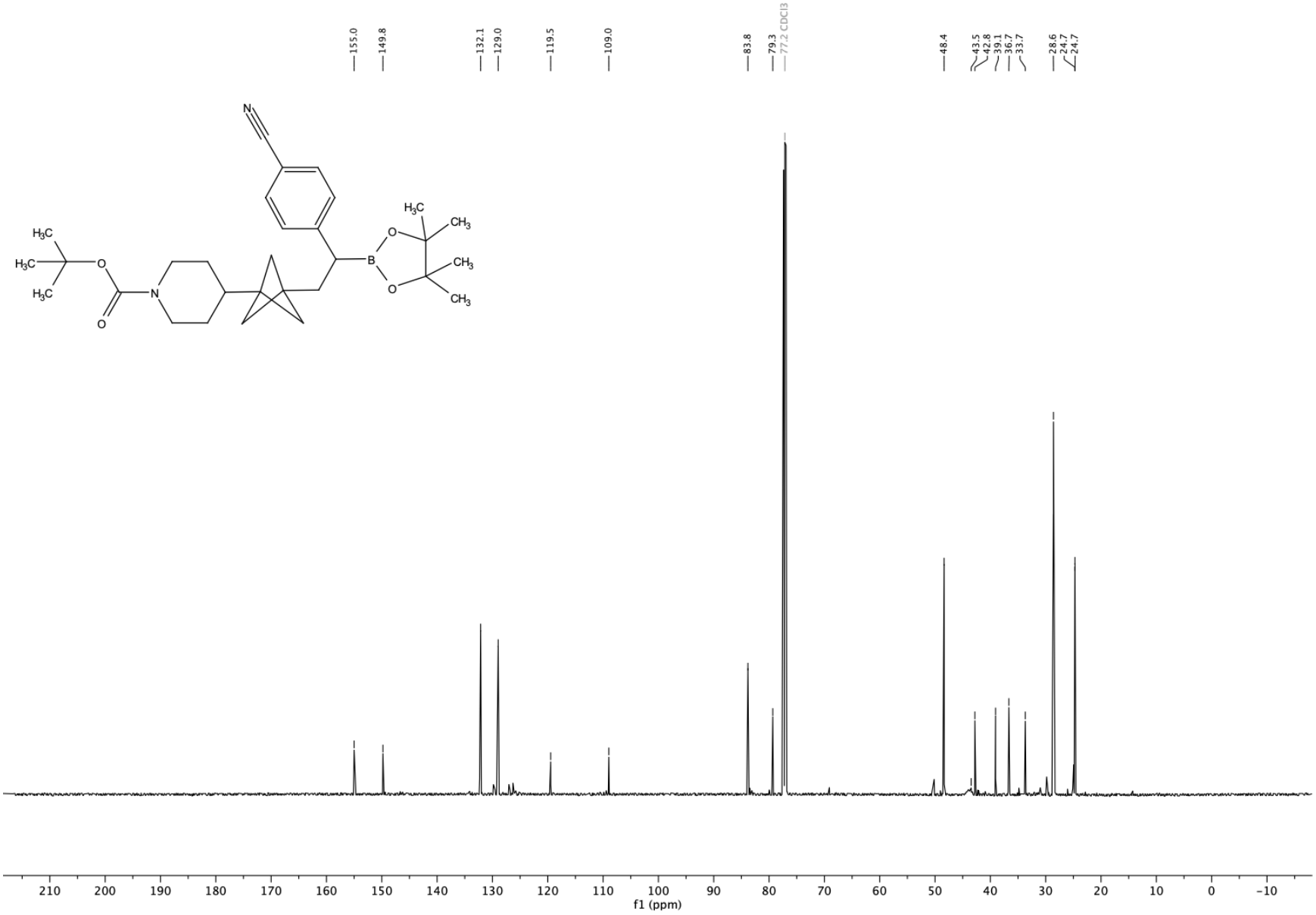
^{13}C NMR (151 MHz, $CDCl_3$) of **10**



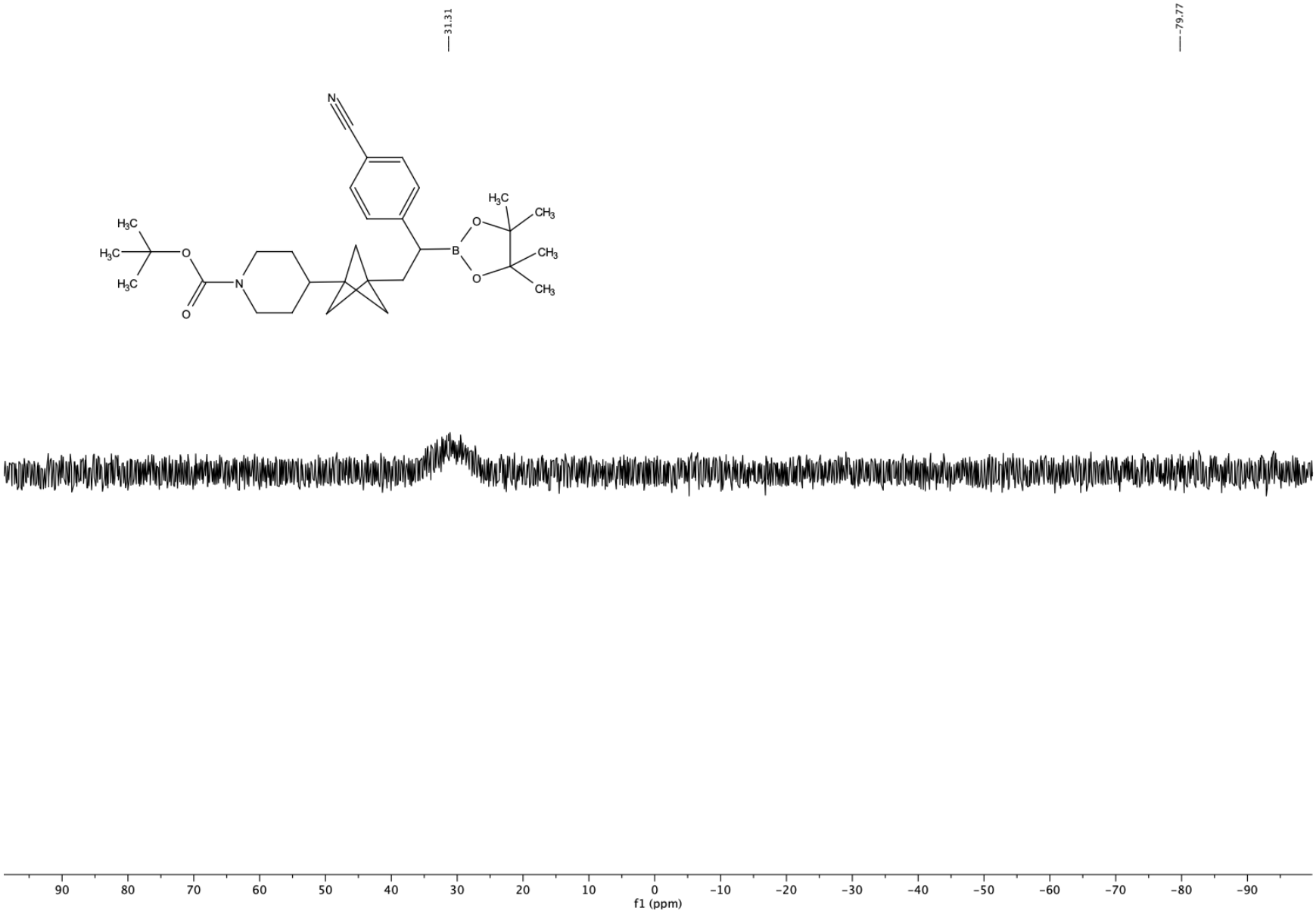
^{1}H NMR (600 MHz, $CDCl_3$) of **11**



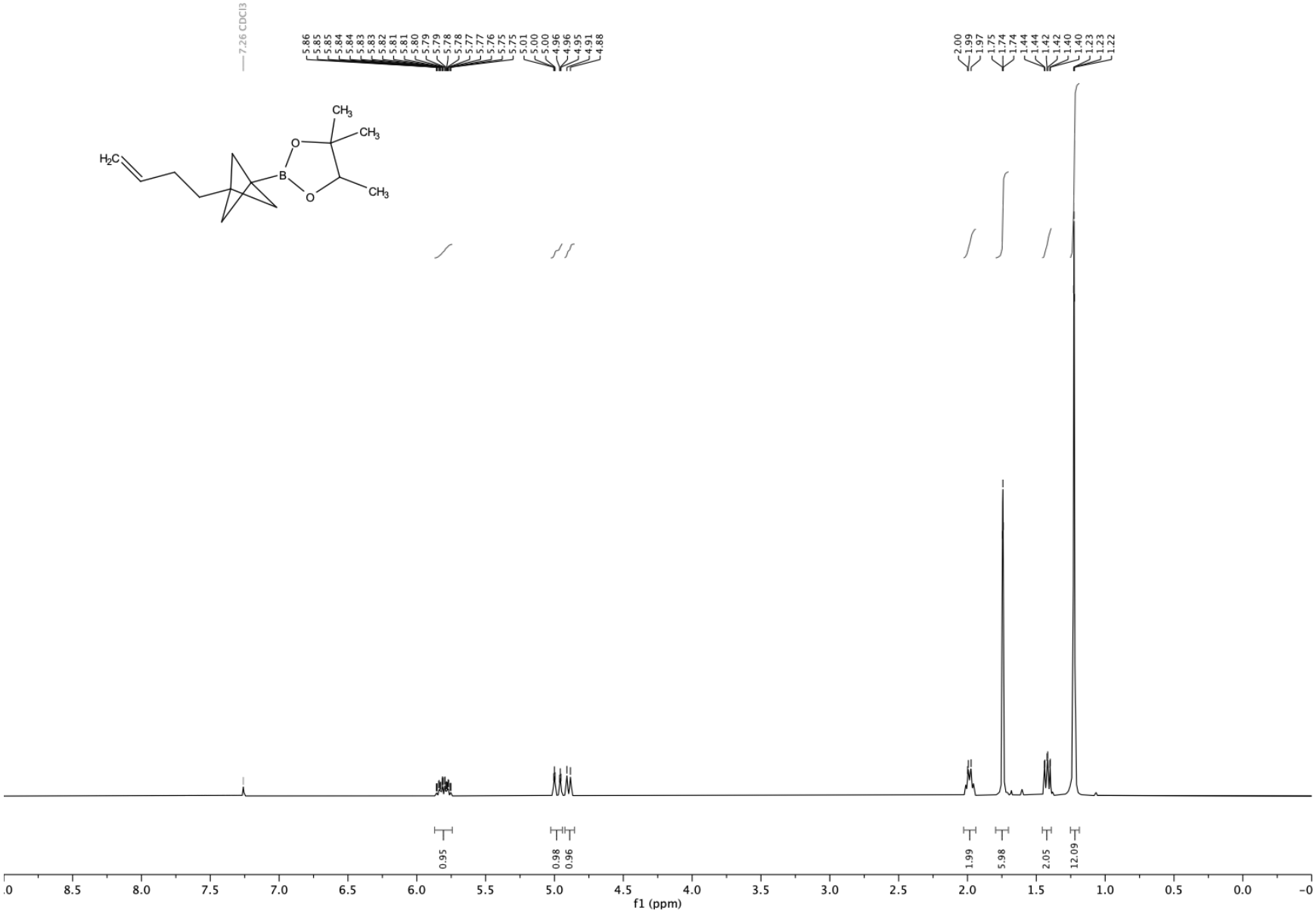
^{13}C NMR (151 MHz, $CDCl_3$) of **11**



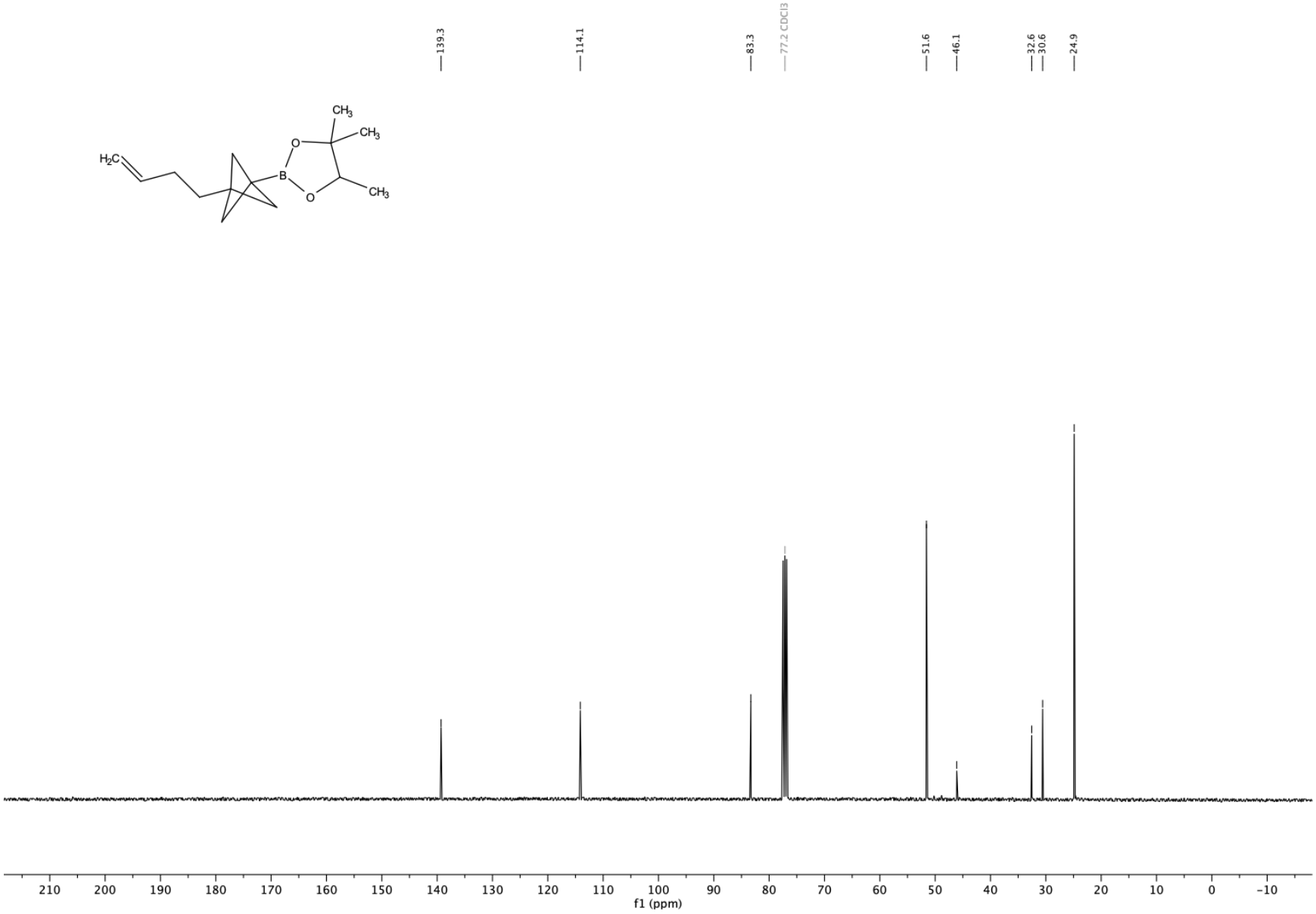
^{11}B NMR (128 MHz, $CDCl_3$) of **11**



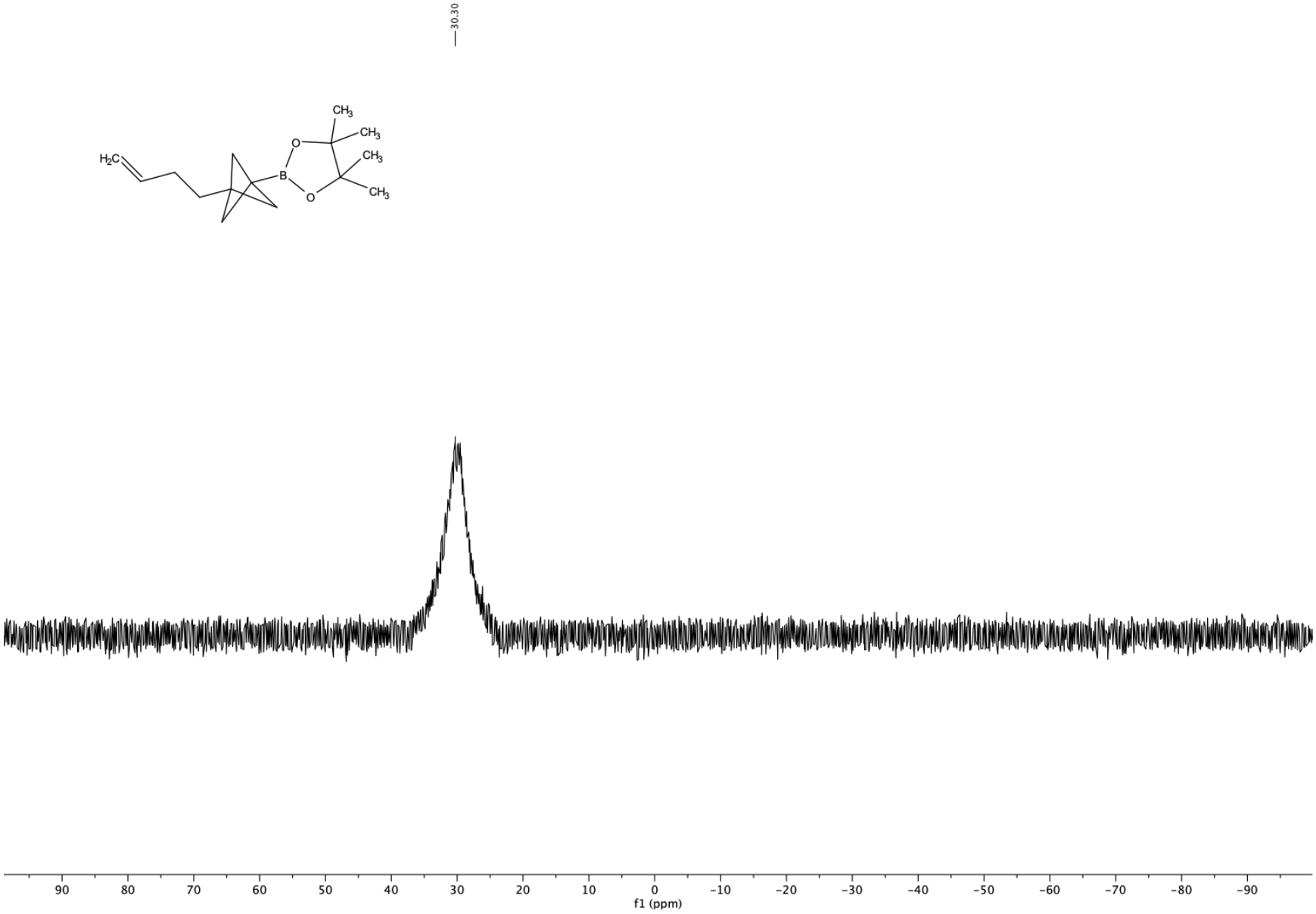
^{1}H NMR (600 MHz, $CDCl_3$) of **13**



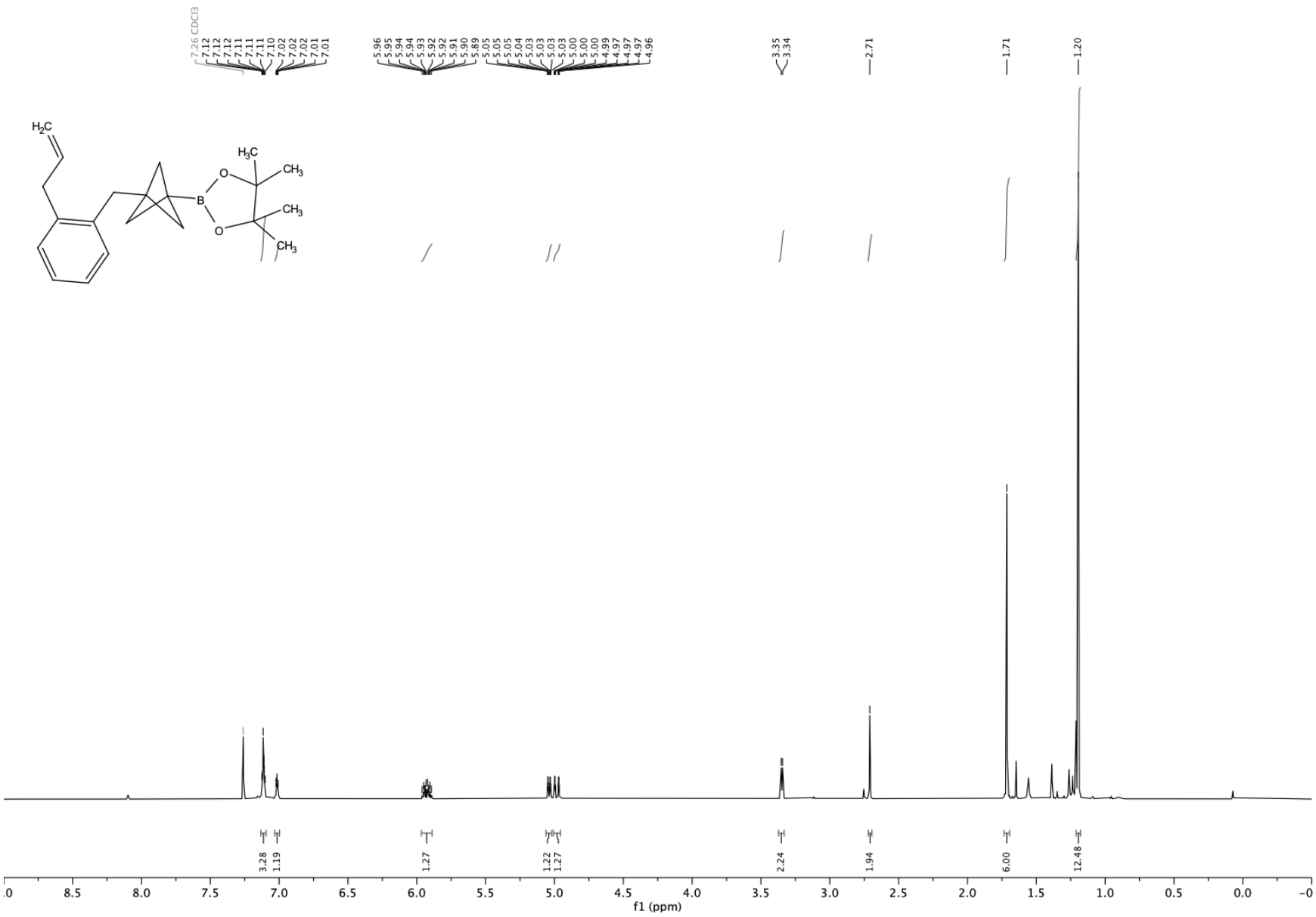
^{13}C NMR (151 MHz, $CDCl_3$) of **13**



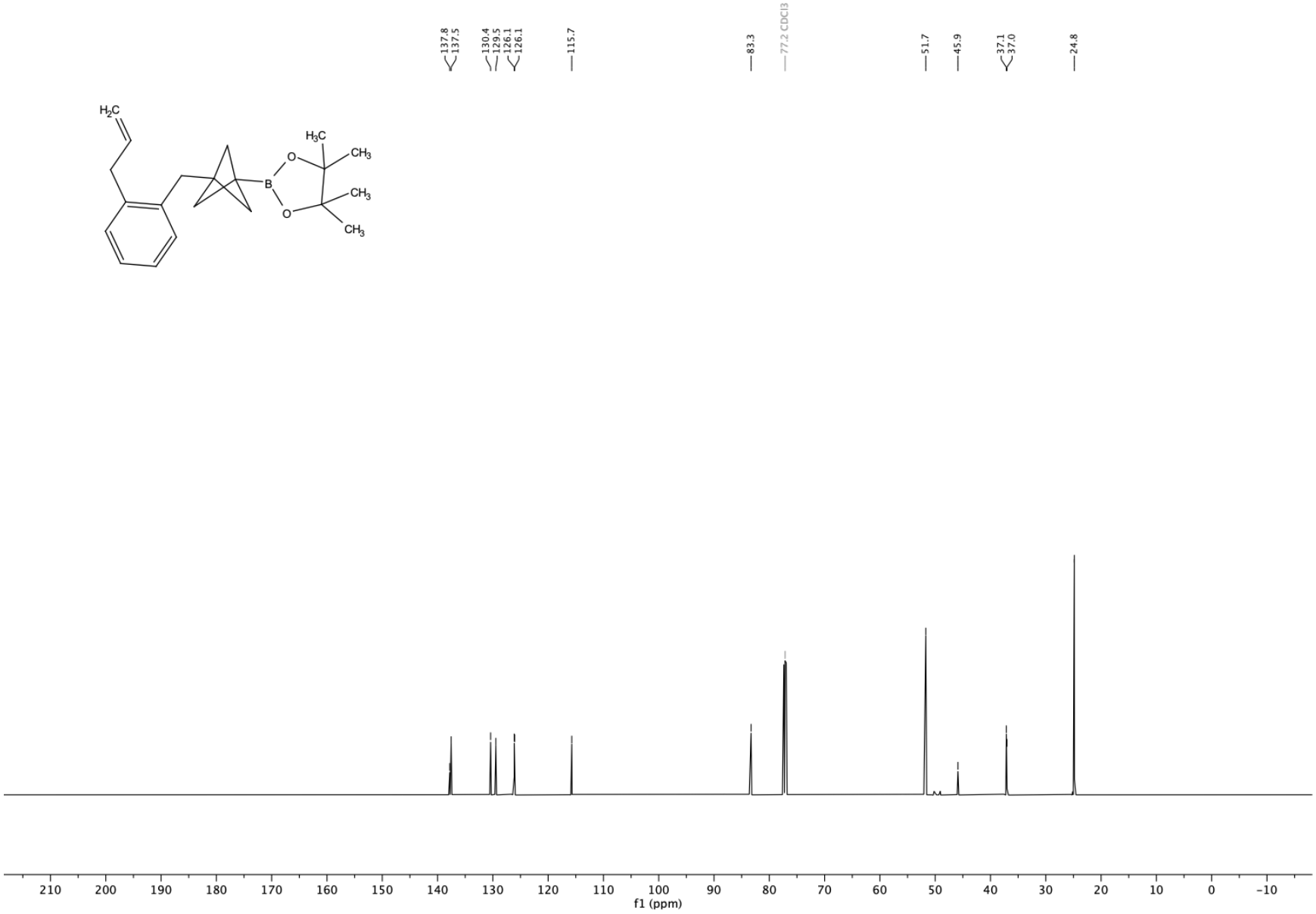
^{11}B NMR (128 MHz, $CDCl_3$) of **13**



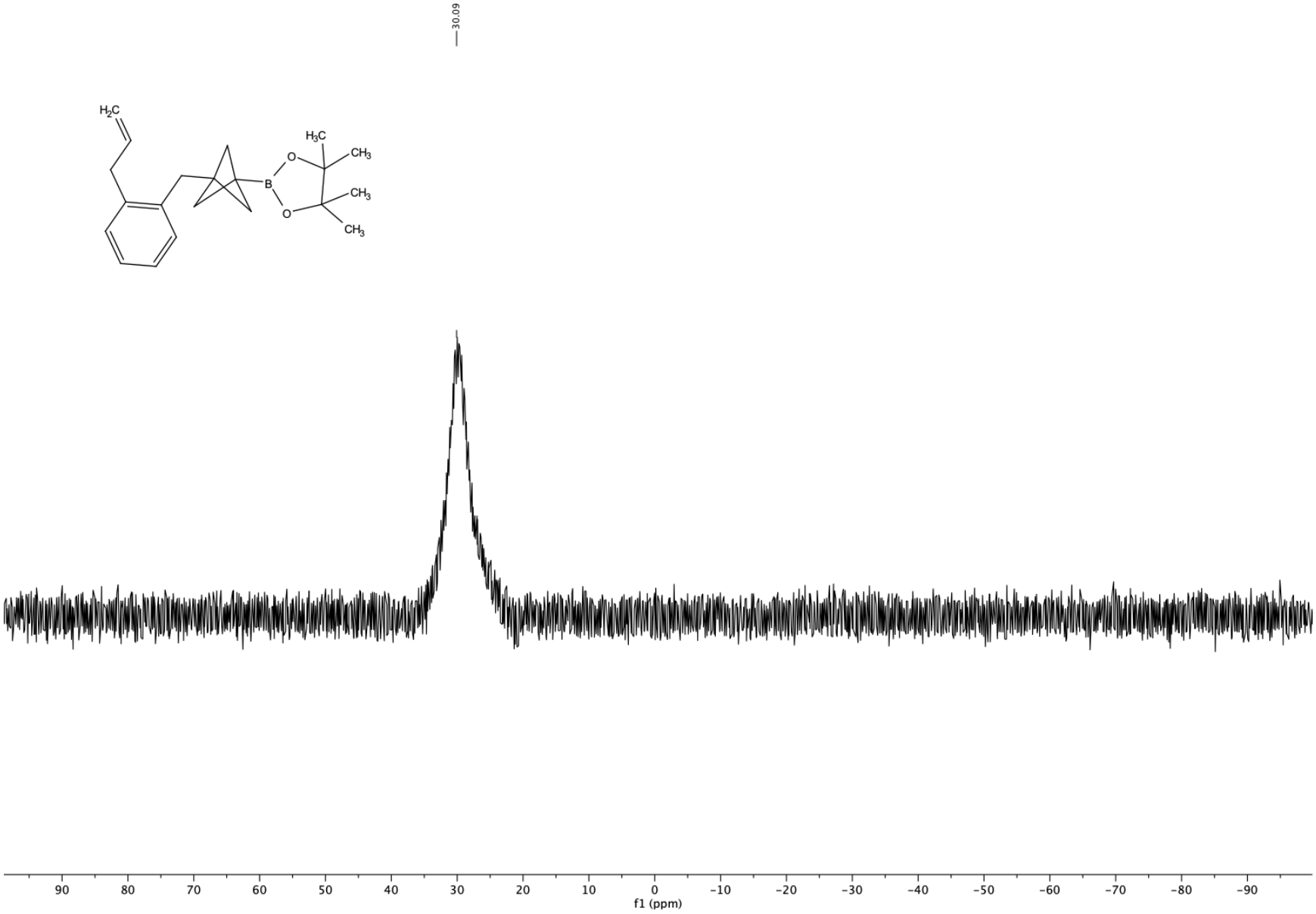
^{1}H NMR (600 MHz, $CDCl_3$) of **S-4a**



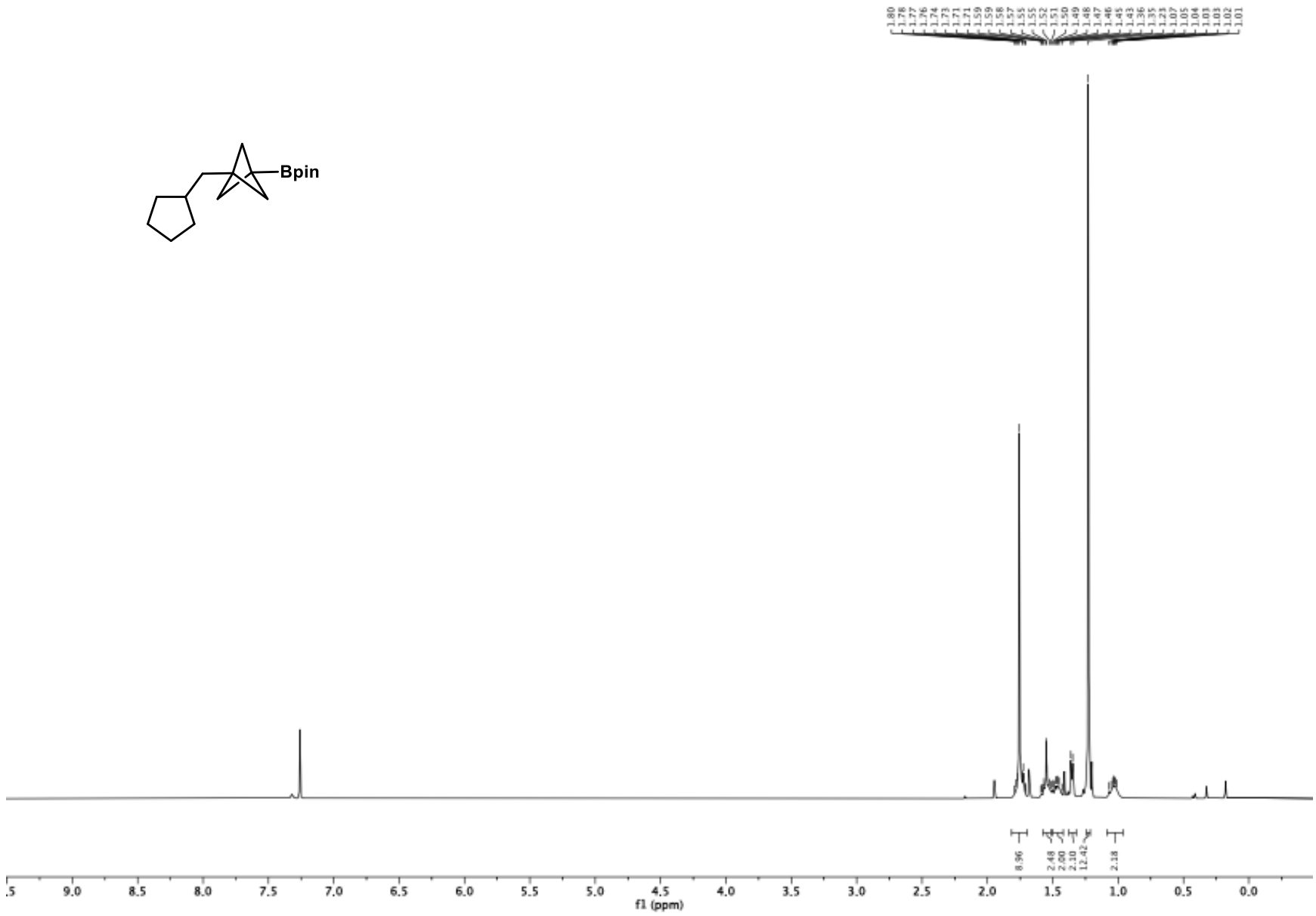
^{13}C NMR (151 MHz, $CDCl_3$) of **S-4a**



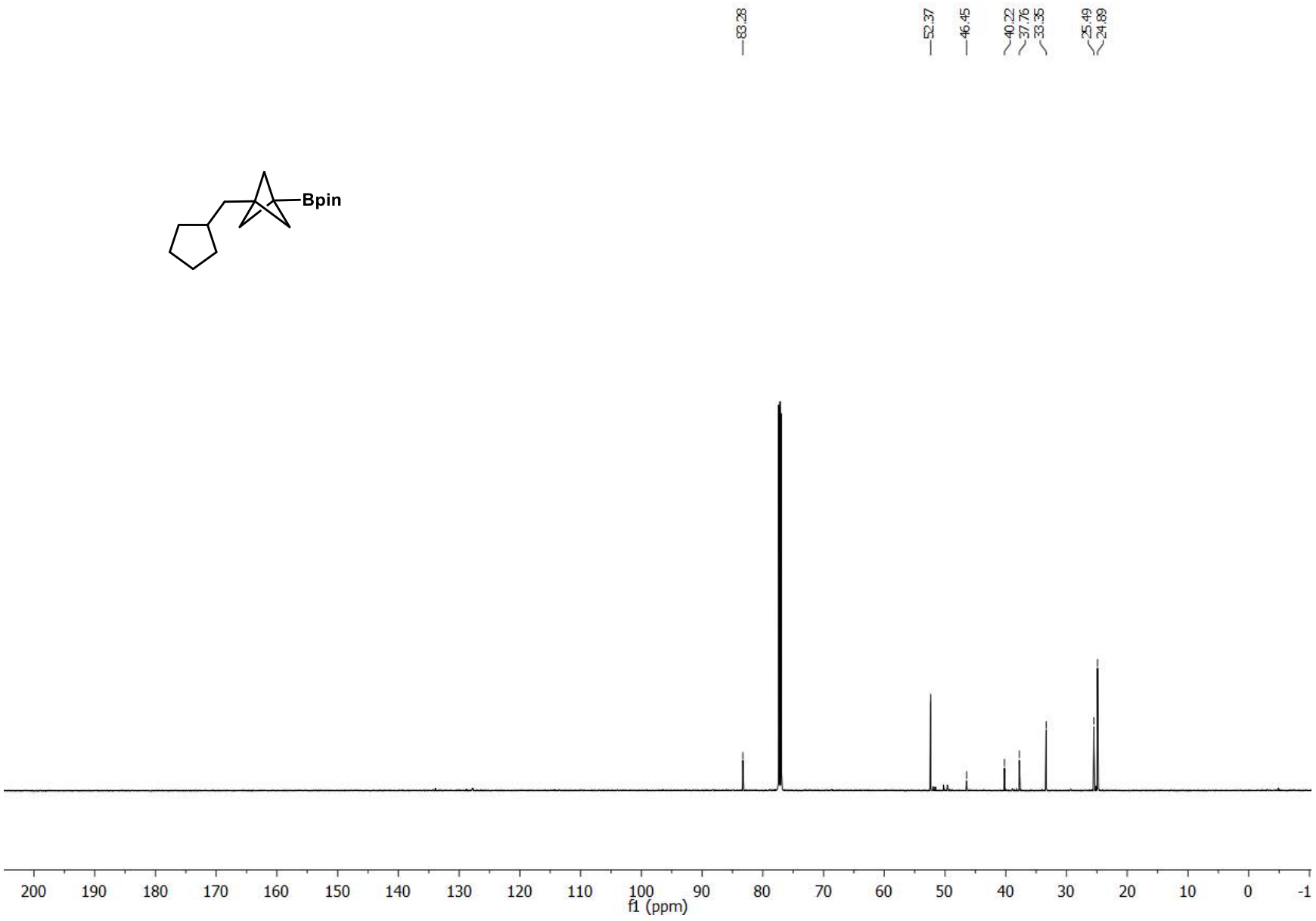
^{11}B NMR (128 MHz, $CDCl_3$) of **S-4a**



^{1}H NMR (400 MHz, $CDCl_3$) of **15**



^{13}C NMR (151 MHz, $CDCl_3$) of **15**



^{11}B NMR (128 MHz, $CDCl_3$) of **15**