

## Supporting Information

for

### Exploiting the Bis-Nucleophilicity of $\alpha$ -Aminoboronates: Copper-Catalyzed, Intramolecular Aminoalkylations of Bromobenzoyl Chlorides

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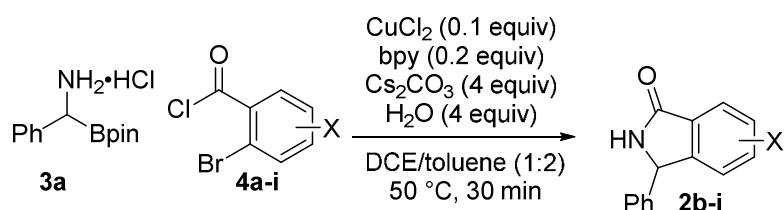
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## General techniques and materials:

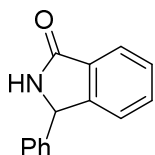
All chemicals unless stated otherwise, were obtained from *Sigma-Aldrich* and used without further purification. All solvents were purchased from *Fisher Scientific* in an HPLC grade and stored over 4Å molecular sieves, and were less than 15 ppm H<sub>2</sub>O by *Karl Fisher* coulometric titration. <sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>19</sup>F NMR spectra were obtained on *Bruker 400 UltraShield™* spectrometer. DMSO-d<sub>6</sub> and CDCl<sub>3</sub> were used as solvents where appropriate. Chemical shifts were referenced relative to the residual protonated solvent for <sup>1</sup>H NMR and to the deuterated solvent for <sup>13</sup>C NMR (DMSO-d<sub>6</sub>: <sup>1</sup>H NMR δ 2.51 ppm, <sup>13</sup>C NMR δ 40.00 ppm, CDCl<sub>3</sub>: <sup>1</sup>H NMR δ 7.26 ppm, <sup>13</sup>C NMR δ 77.06 ppm). Abbreviations used to describe coupling patterns: (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet). Coupling constants (*J*) are reported in Hertz (Hz). HPLC analysis was performed on *Agilent 1100 Series* instrument, with *Ascentis® Express C18* (10 cm x 4.6 mm, 2.7 μm) column. The method was run with acetonitrile and aqueous 0.1% H<sub>3</sub>PO<sub>4</sub> (10% to 95% acetonitrile over 6 minutes, 2 min isocratic hold) as eluents. Flash column chromatography was performed on a *Combiflash® Companion™* instrument, with *RediSep® Rf* 40 gram silica flash column, using toluene and THF (0% to 100% THF over 18 minutes) as eluents. HRMS data was obtained on *Waters Acquity UPLC System* and *Waters Micromass® Q-ToF Premier™* mass spectrometer equipped with *Ascentis® Express C18* (10 cm x 2.1 mm, 2.7 μm) column with 0.1% aqueous formic acid and 0.1% formic acid in acetonitrile as eluents. Gradient was run from 5% to 95% of 0.1% formic acid in acetonitrile over 6 minutes, 2 minutes isocratic hold. LCMS analysis was performed on *Agilent Technologies 1200* equipped with *Ascentis® Express C18* (10 cm x 2.1 mm, 2.7 μm) column with *Agilent Technologies 6150 quadrupole LC/MS* 0.1% aqueous formic acid and 0.1% formic acid in acetonitrile were used as eluents. Gradient was run from 5% to 95% of 0.1% formic acid in acetonitrile over 6 minutes, 2 minutes isocratic hold.



**Synthesis of isoindolinones via *N*-acylation, and Cu catalysed coupling with α-aminoborates 3a and benzoyl chlorides 4a-i (Scheme 3).**

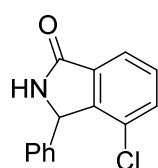
**General procedure for synthesis of isoindolinones 2a-i (General Procedure 1):** Cesium carbonate (1.32 g, 4 mmol, 4 equiv) was placed in a 100 mL round-bottomed flask, put under vacuum and dried with a heat-gun at 200 °C for 10 minutes or until condensation could no longer be observed on sides of the vessel. The flask was back-filled with N<sub>2</sub> and charged with copper(II) chloride (14 mg, 0.1 mmol, 0.1 equiv), bipyridine (31 mg, 0.2 mmol, 0.2 equiv), toluene (24 mL) and DCE (12 mL) to form a brown suspension. The flask was sealed with a rubber septum, put under flow of nitrogen, heated to 50 °C and the mixture was stirred rapidly for 10 minutes. *rac*-Aminoborate 3a (0.27 g, 1 mmol, 1 equiv) and benzoyl chloride

(**4a-i**, 1.25 mmol, 1.25 equiv) were added to the flask, and after 5 minutes water (75  $\mu$ L, 4 mmol, 4 equiv) was added. The mixture was stirred at 50  $^{\circ}$ C under nitrogen for up to 12 hours, or until the reaction was judged complete by HPLC. After cooling to ambient temperature, the slurry was filtered to give a brown solution. This was diluted with DCM, washed sequentially with 10% aq. citric acid and 5% aq. NaHCO<sub>3</sub>, dried over Na<sub>2</sub>SO<sub>4</sub>, then concentrated onto silica gel. The material was purified using flash column chromatography eluting with toluene:THF (0% to 100% THF over 18 minutes). Fractions containing product were combined. The solvent was removed and the material was further dried in a vacuum oven at 50  $^{\circ}$ C to a constant weight to give the isolated isoindolinones **2a-i**.



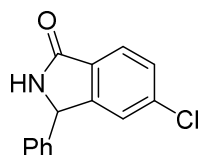
**3-Phenylisoindolin-1-one (2a):** Prepared from **2-bromobenzoyl chloride (4a)**, 0.275 mg 1.25 mmol, 1.25 equiv) using the General Procedure 1. Isolated as a white solid (195 mg, 0.93 mmol, 93%). **HPLC R.t.** = 3.33 min; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.96-7.91 (m, 1H), 7.57-7.47 (m, 2H), 7.42-7.34 (m, 3H), 7.33-7.24 (m, 3H) 6.55 (s, 1H), 5.66 (s, 1H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  170.8 (C) 147.9 (C), 138.4 (C), 132.3 (CH), 130.7 (C), 129.1 (CH), 128.6 (CH), 128.4, (CH) 126.8 (CH), 123.9 (CH), 123.3 (CH), 60.7 (CH); **HRMS** (ESI<sup>+</sup>) calculated for C<sub>14</sub>H<sub>12</sub>NO [M+H]: 210.0919, found: 210.0933.

Starting from (**R**)-**3a** (95:5 e.r.)<sup>1</sup>. General Procedure 1 provided *rac*-**2a** in 70% yield. The enantiomers were distinguished by supercritical fluid chromatography, performed on *Waters Acquity UPC<sup>2</sup>* system equipped with *Chiralpak AD-3* Column (150 cm x 4.6 mm, 3  $\mu$ m) and CO<sub>2</sub>, and methanol with 25 mM Indole-3-butyric acid as eluents. Gradient was run over 10 minutes, with 3.0 mL/min flow rate: 8 minutes CO<sub>2</sub> hold, 1 minute 40% MeOH hold, 1 minute CO<sub>2</sub> hold. **Enantiomer 1 R.t** = 4.755 min; **Enantiomer 2 R.t** = 6.503 min;

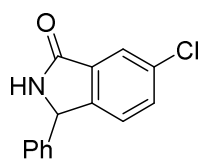


**4-Chloro-3-phenylisoindolin-1-one (2b):** Prepared from **2-bromo-3-chlorobenzoyl chloride (4b)**, 318 mg, 1.25 mmol, 1.25 equiv) using the General Procedure 1. Isolated as a white solid (210 mg, 0.85 mmol, 85% yield). **HPLC R.t.** = 3.79 min; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.85-7.80 (m, 1H), 7.51-7.45 (m, 2H), 7.36-7.29 (m, 3H), 7.27-7.22 (m, 2H), 7.04-6.97 (s, 1H) 5.66 (s, 1H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  169.4 (C), 144.5 (C), 136.1 (C), 133.8 (C), 132.9 (CH) 130.3 (CH), 130.1 (C), 128.8 (CH), 128.7 (CH), 128 (CH), 122.3 (CH), 60.5 (CH); **HRMS** (ESI<sup>+</sup>) calculated for C<sub>14</sub>H<sub>11</sub>(<sup>35</sup>Cl)NO [M+H]: 244.0529, found: 244.0530.

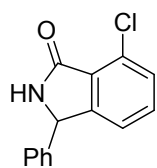
<sup>1</sup> Prepared by borylation of the corresponding (*R*)-tert-butane sulfinylimine, according to the method of Ellman (ref 4).



**5-Chloro-3-phenylisoindolin-1-one (2c):** prepared from **2-bromo-4-chlorobenzoyl chloride (4c, 318 mg, 1.25 mmol, 1.25 equiv)** using the General Procedure: Isolated as a white solid (210 mg, 0.85 mmol, 85% yield). **HPLC R.t.** = 3.95 min; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.85 (d, *J* = 7.8 Hz, 1H), 7.47 (ddd, *J* = 8.1, 1.8, 0.7 Hz, 1H), 7.44-7.35 (m, 3H), 7.31-7.28 (m, 2H), 7.24 (m, 1H), 7.21 (s, 1H), 5.63 (s, 1H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 170 (C), 149.5 (C), 139 (C), 137.6 (C), 129.3 (C), 129.2 (CH), 129.1 (CH), 128.8 (CH), 126.8 (CH), 125.1 (CH), 123.8 (CH), 60.5 (CH); **HRMS** (ESI<sup>+</sup>) calculated for C<sub>14</sub>H<sub>11</sub>(<sup>35</sup>Cl)NO [M+H]: 244.0529, found: 244.0537.

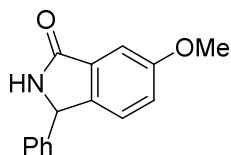


**6-Chloro-3-phenylisoindolin-1-one (2d):** prepared from **2-bromo-5-chlorobenzoyl chloride (4d, 318 mg, 1.25 mmol, 1.25 equiv)** using General Procedure 1. Material isolated as a white solid (min 180 mg, 0.73 mmol, 73% yield). **HPLC R.t.** = 3.94 min; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.89 (d, *J* = 1.8 Hz, 1H) 7.52-7.48 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.41-7.36 (m, 3H), 7.31-3.26 (m, 2H), 7.22-7.17 (d, *J* = 8.1 Hz, 1H), 6.59 (s, 1H), 5.64 (s, 1H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 169.5 (C), 146 (C), 137.7 (C), 134.8 (C), 132.6 (C), 132.5 (CH), 129.2 (CH), 128.8 (CH), 126.8 (CH), 124.7 (CH), 124.0 (CH), 60.5 (CH); **HRMS** (ESI<sup>+</sup>) calculated for C<sub>14</sub>H<sub>11</sub>(<sup>35</sup>Cl)NO [M+H]: 244.0529, found: 244.0542.



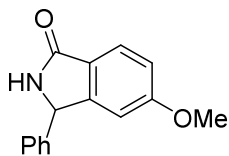
**7-Chloro-3-phenylisoindolin-1-one (2e):** prepared from **2-bromo-6-chlorobenzoyl chloride (4e, 318 mg, 1.25 mmol, 1.25 equiv)** by a modified procedure using CuCl<sub>2</sub> (140 mg, 1.0 mmol, 1.0 equiv) and 2,2'-bipyridine (340 mg, 2.0 mmol, 2.0 equiv) during the catalyst preparation. The crude material isolated after silica gel chromatography was recrystallized from toluene before drying. The remainder of the procedure was identical to the General Procedure 1. Isolated as a white solid (120 mg, 0.49 mmol, 49% yield). **HPLC R.t.** = 3.69 min; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.44-7.35 (m, 5H), 7.32-7.27 (m, 2H), 7.16-7.12 (ddd, *J* = 5.6, 2.9, 0.8 Hz, 1H), 6.96 (s, 1H), 5.60 (s, 1H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 168.7 (C), 150.4 (C), 138.0 (C), 133.1 (CH), 131.6 (C), 130.0 (CH), 129.2 (CH), 128.8 (CH), 126.8 (CH), 122 (CH), 59.7 (CH); **HRMS** (ESI<sup>+</sup>) calculated for C<sub>14</sub>H<sub>11</sub>(<sup>35</sup>Cl)NO [M+H]: 244.0529, found: 244.0538.

**6-Methoxy-3-phenylisoindolin-1-one (2f):** Prepared from **2-bromo-5-methoxybenzoyl chloride (4f, 312 mg, 1.25 mmol, 1.25 equiv)** using General Procedure 1. Isolated as a white solid (200 mg, 0.83 mmol, 83%). **HPLC R.t.** = 3.54 min; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ



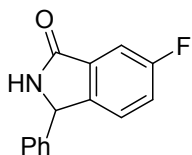
7.50 (s, 1H), 7.39-7.31 (m, 4H), 7.30-7.25 (m, 2H), 7.05-7.16 (m, 2H), 5.59 (s, 1H), 3.87 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  171.2 (C), 160.2 (C), 140.4 (C), 138.7 (C), 132.3 (C), 129 (CH), 128.4 (CH), 126.7 (CH), 124.2 (CH), 120.7 (CH), 106.3 (CH), 60.5 (CH), 55.7 ( $\text{CH}_3$ );

**HRMS** ( $\text{ESI}^+$ ) calculated for  $\text{C}_{15}\text{H}_{14}\text{NO}_2$  [ $\text{M}+\text{H}$ ]: 240.1025, found: 240.1027.



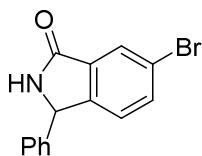
**5-Methoxy-3-phenylisoindolin-1-one (2g)**: prepared from **2-bromo-4-methoxybenzoyl chloride (4g)**, 312 mg, 1.25 mmol, 1.25 equiv) using General Procedure 1. Material isolated as white solid (230 mg, 0.95 mmol, 95% yield). **HPLC R.t.** = 3.53 min;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.81

(d,  $J$  = 8.1 Hz, 1H), 7.42-7.27 (m, 5H), 7.0 (dd,  $J$  = 8.4, 2.5 Hz, 1H), 6.70 (d,  $J$  = 2.5 Hz, 2H), 5.58 (s, 1H), 3.87 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  170.9 (C), 163.4 (C), 150.4 (C), 138.7 (C), 129.1 (CH), 128.5 (CH), 126.9 (CH), 125.2 (CH), 123.4 (C), 115.1 (CH), 108.0 (CH), 60.6 (CH), 55.6 ( $\text{CH}_3$ ); **HRMS** ( $\text{ESI}^+$ ) calculated for  $\text{C}_{15}\text{H}_{14}\text{NO}_2$  [ $\text{M}+\text{H}$ ]: 240.1025, found: 240.1029.



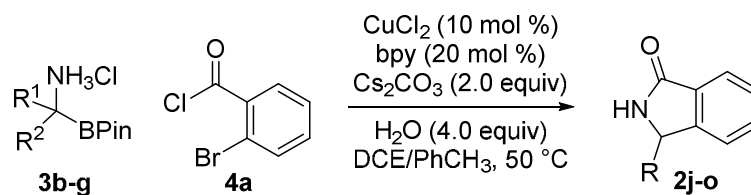
**6-Fluoro-3-phenylisoindolin-1-one (2h)**: prepared from **2-bromo-5-fluorobenzoyl chloride (4h)**, 300 mg, 1.25 mmol, 1.25 equiv) using General Procedure 1. Material isolated as a white solid (180 g, 0.79 mmol, 79%).

**HPLC R.t.** = 3.54 min;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.59-7.54 (m, 1H), 7.41-7.35 (m, 3H), 7.30-7.26 (m, 2H), 7.25-7.20 (m, 2H), 7.01-6.79 (s, 1H), 5.63 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  170 (s, C), 164.2 (d,  $J$  = 250 Hz, C), 143.4 (s, C), 138.0 (s, C), 133.1 (d,  $J$  = 10 Hz, C), 129.2 (s, CH), 128.7 (s, CH), 126.7 (s, CH), 124.9 (d,  $J$  = 10 Hz, CH), 120.0 (d,  $J$  = 20 Hz, CH), 110.6 (d,  $J$  = 20 Hz, CH), 60.6 (s, CH);  $^{19}\text{F}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  -113 (s, 1F); **HRMS** ( $\text{ESI}^+$ ) calculated for  $\text{C}_{14}\text{H}_{11}\text{FNO}$  [ $\text{M}+\text{H}$ ]: 228.0825, found: 228.0828.



**6-Bromo-3-phenylisoindolin-1-one (2i)**: prepared from **2,5-dibromobenzoyl chloride (4i)**, 370 mg, 1.25 mmol, 1.25 equiv) using

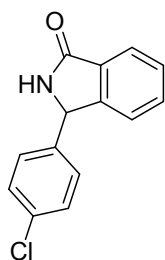
General Procedure 1. Material isolated as a white solid (220 mg, 0.76 mmol, 76% yield). **HPLC R.t.** = 4.04 min;  $^1\text{H}$  NMR (400 MHz, DMSO):  $\delta$  9.24 (s, 1H), 7.85 (d,  $J$  = 1.7 Hz, 1H), 7.75-7.70 (dd,  $J$  = 8.2, 2.1 Hz, 1H), 7.41-7.25 (m, 6H), 5.75 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz, DMSO):  $\delta$  168.5 (C), 147.6 (C), 139.4 (C), 135.1 (CH), 134.3 (C), 129.3 (CH), 128.5 (CH), 127.1 (CH), 126.3 (CH), 126.1 (CH), 121.8 (CH), 59.8 (CH); **HRMS** ( $\text{ESI}^+$ ) calculated for  $\text{C}_{14}\text{H}_{11}(79\text{Br})\text{NO}$  [ $\text{M}+\text{H}$ ]: 288.0024, found: 288.0029.



**Synthesis of isoindolin-1-ones by *N*-acylation and Cu-catalysed coupling with substituted  $\alpha$ -aminoborates 3b-g (Scheme 4):**

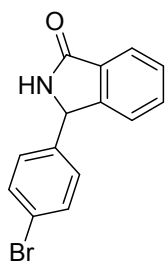
**General procedure for synthesis of isoindolinones 2j-o (General Procedure 2):** General procedure 1 was followed except that the reaction components were  $\alpha$ -aminoborates **3b-g** (1.0 mmol, 1.0 equiv) and 2-bromobenzoyl chloride (0.275 mg, 1.25 mmol, 1.25 equiv).

**3-(4-Chlorophenyl)isoindolin-1-one (2j):** Prepared using General Procedure 2 with **(4-chlorophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methanaminium chloride**



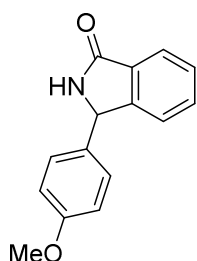
**(3b, 305 mg, 1 mmol, 1 equiv).** Isolated as a white solid (230 mg, 0.73 mmol, 73% yield), **HPLC R.t** = 3.85 min;  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.93-7.88 (m, 1H), 7.59-7.48 (m, 2H), 7.39-7.33 (m, 2H), 7.27-7.21 (m, 3H), 7.09-7.01 (s, 1H), 5.64 (s, 1H);  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  171.0 (C), 147.5 (C), 137 (C), 134.4 (C), 132.4 (CH), 130.7 (C), 129.3 (CH), 128.6 (CH), 128.2 (CH), 123.9 (CH), 123.2 (CH), 60.1 (CH); **HRMS** ( $\text{ESI}^+$ ) calculated for  $\text{C}_{14}\text{H}_{11}(\text{}^{35}\text{Cl})\text{NO}$  [M+H]: 244.0529, found: 244.0529.

**3-(4-Bromophenyl)isoindolin-1-one (2k):** Prepared using General Procedure 2 with **(4-bromophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methanaminium chloride**



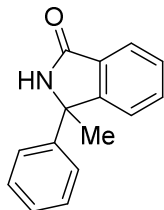
**(3c, 350 mg, 1 mmol, 1 equiv).** Isolated as a white solid (230 mg, 0.79 mmol, 79% yield) **HPLC R.t** = 3.95 min;  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.93-7.88 (m, 1H), 7.58-7.47 (m, 4H), 7.26-7.14 (m, 3H), 7.13-7.06 (s, 1H), 5.62 (s, 1H);  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  171.0 (C), 147.4 (C), 137.5 (C), 132.5 (CH), 132.3 (CH), 130.7 (C), 128.6 (CH), 128.5 (CH), 124 (CH), 123.2 (CH), 122.5 (C), 60.1 (CH); **HRMS** ( $\text{ESI}^+$ ) calculated for  $\text{C}_{14}\text{H}_{11}(79\text{Br})\text{NO}$  [M+H]: 288.0024, found: 288.0024.

**3-(4-Methoxyphenyl)isoindolin-1-one (2l):** Prepared using General Procedure 2 with **(4-methoxyphenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methanaminium chloride** (**3d, 300 mg, 1 mmol, 1 equiv**). Isolated as a bright orange solid (190 mg, 0.79 mmol, 79% yield) **HPLC R.t** = 3.34 min;  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.91-7.84 (d,  $J$  = 7.1 Hz, 1H), 7.70-7.61 (s, 1H), 7.55-7.43 (m, 2H), 7.27-7.22 (d,  $J$  = 7.5 Hz, 1H), 7.22-7.16 (d,  $J$  = 8.7 Hz, 2H), 6.92-6.83 (d,  $J$  = 8.7 Hz, 2H), 5.61 (s, 1H), 3.79 (s, 3H);  **$^{13}\text{C}$**



**NMR** (100 MHz, CDCl<sub>3</sub>): δ 171.4 (C), 159.7 (C), 148.3 (C), 132.2 (CH), 131.0 (C), 130.3 (C), 128.2 (CH), 128.1 (CH), 123.7 (CH), 123.3 (CH), 114.4 (CH), 60.5 (CH), 55.3 (CH<sub>3</sub>); **HRMS** (ESI<sup>+</sup>) calculated for C<sub>15</sub>H<sub>14</sub>NO<sub>2</sub> [M+H]: 240.1025, found: 240.1037.

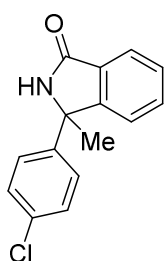
**3-Methyl-3-phenylisoindolin-1-one (2m)**: Prepared using General Procedure 2 with **1-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethanaminium chloride (3e**, 285 mg, 1 mmol, 1 equiv). Isolated as a white solid (200 mg, 0.88 mmol, 88%



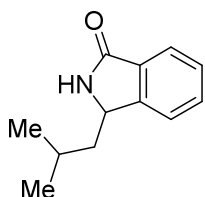
yield) **HPLC R.t.** = 3.50 min; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.96-7.82 (m, 2H), 7.56-7.41 (m, 4H), 7.37-7.24 (m, 2H), 2.01 (m, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 170.5 (C), 153.0 (C), 142.2 (C), 132.4 (CH), 130.2 (C), 128.8 (CH), 128.1 (CH), 127.7 (CH), 125.5 (CH), 124.0 (CH), 122.2 (CH), 63.8 (C), 26.6 (CH<sub>3</sub>); **HRMS** (ESI<sup>+</sup>) calculated for C<sub>15</sub>H<sub>14</sub>NO [M+H]: 224.1075, found:

224.1084

**3-(4-Chlorophenyl)-3-methylisoindolin-1-one (2n)**: Prepared using General Procedure 2 with **1-(4-chlorophenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethanaminium**



**chloride (3f**, 320 mg, 1 mmol, 1 equiv). Isolated as a white solid (220 mg, 0.85 mmol, 85% yield) **HPLC R.t.** = 3.99 min; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.90-7.83 (d, *J* = 6.8 Hz, 1H), 7.61-7.44 (m, 3H), 7.40-7.24 (m, 5H), 2.00 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 170.3 (C), 152.5 (C), 140.8 (C), 133.8 (C), 132.6 (CH), 130.0 (C), 128.9 (CH), 128.4 (CH), 127.0 (CH), 124.1 (CH), 122.0 (CH), 63.3 (C), 26.5 (CH<sub>3</sub>); **HRMS** (ESI<sup>+</sup>) calculated for C<sub>15</sub>H<sub>13</sub>(<sup>35</sup>Cl)NO [M+H]: 258.0686, found: 258.0699.

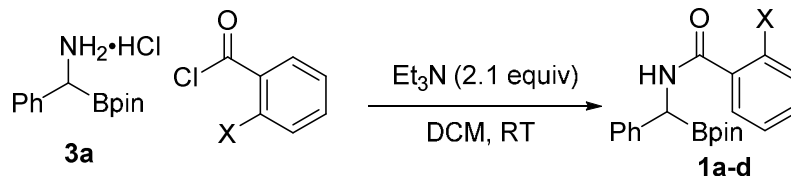


**3-Isobutylisoindolin-1-one (2o)**: Prepared using General Procedure 2 with **3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-**

**aminium chloride (3g**, 250 mg, 1 mmol, 1 equiv). After aqueous workup, the organic stream was concentrated to a residue and the yield was determined by <sup>1</sup>H NMR assay against an internal standard of 1,3,5-trimethoxybenzene and comparison with published data (0.38 mmol, 38%).<sup>2</sup> This was further purified by a flash column chromatography yielding a white solid (60 mg, 0.31 mmol, 31% yield) **HPLC R.t.** = 3.59 min; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.91-7.84 (d, *J* = 7.5 Hz, 1H), 7.63-7.54 (t, *J* = 7.4 Hz, 1H), 7.53-7.40 (q, *J* = 7.4 Hz, 3H), 4.73-4.64 (dd, *J* = 9.4, 4.1 Hz, 1H), 2.02-1.84 (m, 1H), 1.82-1.70 (m, 1H), 1.60-1.48 (m, 1H), 1.15-1.05 (d, *J* = 6.5 Hz, 3H), 1.05-0.93 (d, *J* = 6.5 Hz, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 171.0 (C), 148.3 (C), 131.8 (C), 131.7 (CH), 128.0 (CH), 123.8 (CH), 122.4 (CH), 55.3 (CH), 44.2 (CH<sub>2</sub>), 25.9 (CH),

<sup>2</sup> Ruan, Y.-P., Chen, M.-D., He, M.-Z., Zhou, X., Huang, P.-Q., *Synth. Commun.*, **2004**, 34, 853.

23.5 (CH<sub>3</sub>), 22.0 (CH<sub>3</sub>); **HRMS** (ESI<sup>+</sup>) calculated for C<sub>12</sub>H<sub>16</sub>NO [M+H]: 190.1232, found: 190.1230.



### Synthesis of amidoboronates **1a-d**, (General Procedure 3):

In a 50 mL round-bottomed flask the **phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methanaminium chloride (3a, 1 equiv)** was dissolved in DCM (30 mL) to form a bright-yellow suspension. The reaction vessel was sealed with a rubber septum, put under flow of nitrogen and the mixture was stirred at a room temperature for 10 minutes. Triethylamine (2.1 equiv) was then transferred to the vessel and immediately followed by **2-halobenzoyl chloride** (1.05 equiv). The reaction mixture was stirred for a further 2 minutes, after which it was concentrated to a residue. The residue was dissolved in DCM, washed with 10% aq. citric acid and 5% aq. NaHCO<sub>3</sub> and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated, and dried in a vacuum oven at 50 °C to a constant weight to give the isolated amidoborates **1a-d**, which were used without further purification.

### 2-Bromo-*N*-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide

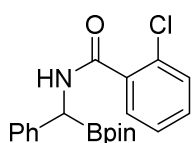
**(1a)**: Prepared using General Procedure 3 with aminoborate **3a** (600 mg, 2.23 mmol, 1 equiv), triethylamine (0.65 mL, 4.67 mmol, 2.1 equiv) and **2-bromobenzoyl chloride** (513 mg, 2.34 mmol, 1.05 equiv). Isolated as a white solid (630 mg, 1.51 mmol, 68% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.02-7.97 (dd, *J* = 7.8 Hz, 1.7 Hz, 1H), 7.79-7.71 (s, 1H), 7.70-7.67 (dd, *J* = 8.0 Hz, 1.3 Hz, 1H), 7.51-7.38 (m, 2H), 7.37-7.32 (m, 4H), 7.27-7.20 (m, 1H), 4.29 (s, 1H), 1.22 (s, 6H), 1.14 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 170.0 (C), 140.0 (C), 140.0 (C), 134.1 (CH), 133.2 (CH), 132.4 (CH), 128.3 (CH), 127.9 (CH), 126.9 (CH), 126.2 (CH), 81.0 (C), 24.9 (CH<sub>3</sub>), 24.7 (CH<sub>3</sub>); **LCMS** (ESI<sup>+</sup>) calculated for C<sub>20</sub>H<sub>24</sub>(<sup>11</sup>B)(<sup>79</sup>Br)NO<sub>3</sub> [M+H]: 416.10 found: 416.0.

### 2-Iodo-*N*-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide (**1b**):

Prepared using General Procedure 3 with aminoborate **3a** (200 mg, 0.74 mmol, 1 equiv), triethylamine (0.22 mL, 1.6 mmol, 2.1 equiv) and **2-iodobenzoyl chloride** (210 mg, 0.8 mmol, 1.05 equiv). Isolated as a yellow solid (205 mg, 0.58 mmol, 86% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.97-7.93 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.73-.67 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.49-7.43 (td, *J* = 7.6 Hz,

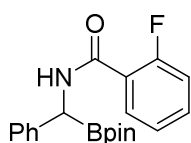
1.1 Hz, 1H), 7.41-7.32 (m, 4H), 7.26-7.11 (m, 3H), 4.35 (s, 1H), 1.22 (s, 1H), 1.17 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  171.1 (C), 140.6 (CH), 139.7 (C), 137.0 (C), 132.4 (CH), 130.4 (CH), 128.4 (CH), 128.3 (CH), 127.1 (CH), 126.4 (CH), 92.7 (C), 82.6 (C), 24.8 ( $\text{CH}_3$ ), 24.7 ( $\text{CH}_3$ ); LCMS ( $\text{ESI}^+$ ) calculated for  $\text{C}_{20}\text{H}_{24}({}^{11}\text{B})({}^{127}\text{I})\text{NO}_3$  [M]: 464.08 found: 464.0.

## 2-Chloro-*N*-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide

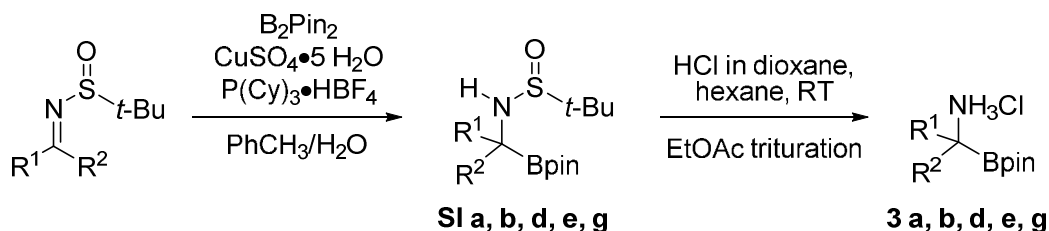


(**1c**): Prepared using General Procedure 3 with aminoborate **3a** (150 mg, 0.56 mmol, 1 equiv), triethylamine (0.16 mL, 1.17 mmol, 2.1 equiv) and **2-chlorobenzoyl chloride** (102 mg, 0.58 mmol, 1.05 equiv). Isolated as a pale-yellow solid (106 mg, 0.29 mmol, 51% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.16-8.10 (d,  $J = 8.9$  Hz, 1H) 8.08-7.98 (s, 1H), 7.59-7.43 (m, 3H), 7.41-7.19 (m, 5H), 4.22 (s, 1H), 1.21 (s, 6H), 1.12 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  169.7 (C), 140.2 (C), 133.62 (CH), 132.94 (CH), 132.14 (C), 132.04 (C), 131.6 (CH), 130.9 (CH), 128.3 (CH), 127.5 (CH), 126.7 (CH), 126.1 (CH), 81.6 (C), 24.9 ( $\text{CH}_3$ ), 24.6 ( $\text{CH}_3$ ); LCMS ( $\text{ESI}^+$ ) calculated for  $\text{C}_{20}\text{H}_{24}({}^{11}\text{B})({}^{35}\text{Cl})\text{NO}_3$  [M+H]: 372.15 found: 372.2.

## 2-Fluoro-*N*-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide



(**1d**): Prepared using General Procedure 3 with aminoborate **3a** (180 mg, 0.67 mmol, 1 equiv), triethylamine (0.2 mL, 1.4 mmol, 2.1 equiv) and **2-fluorobenzoyl chloride** (110 mg, 0.7 mmol, 1.05 equiv). Isolated as a pale-yellow solid (205 mg, 0.58 mmol, 86% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.25-8.19 (td,  $J = 7.8, 1.8$  Hz, 1H), 7.97-7.88 (d,  $J = 10.5$  Hz, 1H), 7.68-7.58 (m, 1H), 7.41-7.27 (m, 5H), 7.26-7.18 (m, 2H), 4.17 (s, 1H), 1.21 (s, 6H), 1.11 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  168.1 (C), 162.9 (C), 160.4 (C), 140.4 (C), 135.7 (CH), 135.5 (CH), 132.8 (CH), 128.2 (CH), 126.75 (CH), 126.0 (CH), 125.2 (CH, d,  $J = 3$  Hz), 116.4 (CH), 116.2 (CH), 81.3 (C), 25.0 ( $\text{CH}_3$ ), 24.6 ( $\text{CH}_3$ );  $^{19}\text{F}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  -111.85 (s, 1F). LCMS ( $\text{ESI}^+$ ) calculated for  $\text{C}_{20}\text{H}_{24}({}^{11}\text{B})\text{FNO}_3$  [M+H]: 356.18 found: 356.2.



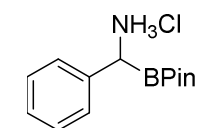
**Synthesis of aminoborates – borylation/deprotection:**

**$\alpha$ -Aminoborates (SI a, b, d, e, g)** are known compounds<sup>3</sup> and have been prepared using a modification of Ellman's method<sup>4</sup> which omits purification by silica gel chromatography.

General method: PCy<sub>3</sub>•HBF<sub>4</sub> (0.012 equiv) was dissolved in toluene (1.3 mL per mmol of sulfinylimine) and stirred rapidly. To the solution were added copper(II) sulfate pentahydrate (0.012 equiv), water (0.45 mL per mmol of sulfinylimine) and benzylamine (0.05 equiv). After stirring the mixture at ambient temperature for 10 minutes, the flask was placed in an ice/water bath and a solution of sulfinylimine (1 equiv) in Toluene (1.3 mL per 1 mmol of sulfinylimine) was added to the catalyst mixture. The B<sub>2</sub>pin<sub>2</sub> (2 equiv) was added in a single portion and the ice/water bath removed. The mixture was stirred for a further 30 minutes after which time a turbid blue/green to dark orange colour change had occurred. The mixture was filtered and the liquours were aezodried with DCM (4x 2.6 mL per mmol of sulfinylimine) using a rotary evaporator with a water bath temperature at 35 °C. The resulting dark brown oil was stirred in cold heptane until a solid precipitated. The resulting sulfinamide was recrystallized from heptane, collected and dried in a vacuum oven at 50 °C overnight. The sulfinamide (1 equiv) was dissolved in hexane (8 mL per mmol of sulfinamide) to form a bright yellow slurry. The solution was stirred rapidly at a room temperature for 10 minutes. After that hydrochloric acid (4M in dioxane, 3 equiv) was added to the vessel. After stirring the mixture for a further 10 minutes any residual solvent was filtered off and the material was washed with hexane and heptane. The product was collected and stirred in ethyl acetate (4 mL per mmol of sulfinamide) at a room temperature overnight. The solvent was filtered off and the material was dried in an oven under vacuum at 50 °C overnight.<sup>5</sup>

**Phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methanaminium chloride (3a):**

Prepared using the general procedure with **2-methyl-N-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)propane-2-sulfinamide** (SI a, 21.15 g, 43.9 mmol, 1 equiv) and hydrochloric acid (4M in dioxane, 33 mL, 132 mmol, 3 equiv). Collected white solid (9.51 g, 35.3 mmol, 80% yield); <sup>1</sup>H NMR (400 MHz, DMSO):  $\delta$  8.77-8.28 (s, 3H), 7.52-7.25 (m, 5H), 3.93 (s, 1H), 1.23 (s, 6H), 1.19 (s, 6H); <sup>13</sup>C NMR (100 MHz, DMSO):  $\delta$  136.0 (C), 129.1 (CH), 128.6 (CH), 128.2 (CH), 85.2 (C), 66.8 (CH), 24.8 (CH<sub>3</sub>), 24.8 (CH<sub>3</sub>);

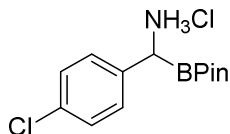


<sup>3</sup> Wen, K., Wang, H., Chen, J., Zhang, H., Cui, X., Wei, C., Fan, E., Sun, Z., *J. Org. Chem.*, **2013**, 78, 3405.

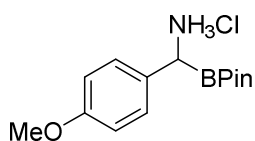
<sup>4</sup> Buesking, A. W., Bacauanu, V., Cai, I., Ellman, J. A., *J. Org. Chem.*, **2013**, 79, 3671.

<sup>5</sup> HRMS/LCMS data were unable to be obtained for aminoboronate salts due to technical issues – spectral data for known compounds matched those previously reported (see ref 3).

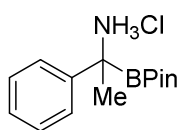
**(4-Chlorophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methanaminium chloride (3b):** Prepared using the general procedure with **N-((4-chlorophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-2-methylpropane-2-sulfinamide (SI b,** 4.12 g, 11.1 mmol, 1 equiv) and hydrochloric acid (4M in dioxane, 8.3 mL, 33.2 mmol, 3 equiv). Collected white solid (1.72 g, 5.66 mmol, 51% yield);  $^1\text{H NMR}$  (400 MHz, DMSO):  $\delta$  8.62 (s, 3H), 7.46 (s, 4H), 3.97 (s, 1H), 1.23 (s, 6H), 1.19 (s, 6H);  $^{13}\text{C NMR}$  (100 MHz, DMSO):  $\delta$  135.2 (C), 132.9 (C), 130.5 (CH), 129.0 (CH), 85.2 (C), 24.9 (CH<sub>3</sub>), 24.8 (CH<sub>3</sub>);



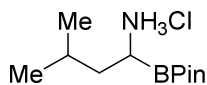
**(4-Methoxyphenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methanaminium chloride (3d):** Prepared using the general procedure with **N-((4-methoxyphenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-2-methylpropane-2-sulfinamide (SI d,** 5.51 g, 15 mmol, 1 equiv) and hydrochloric acid (4M in dioxane, 11.3 mL, 45 mmol, 3 equiv). Collected white solid (1.52 g, 3.12 mmol, 21% yield);  $^1\text{H NMR}$  (400 MHz, DMSO):  $\delta$  8.51 (s, 3H), 7.74-6.82 (dd,  $J = 160$  Hz, 8.8 Hz, 4H), 3.84 (s, 1H), 3.75 (s, 3H), 1.24 (s, 6H), 1.20 (s, 6H);  $^{13}\text{C NMR}$  (100 MHz, DMSO):  $\delta$  159.4 (C), 130.3 (CH), 127.7 (C), 114.5 (CH), 85.1 (C), 55.6 (CH<sub>3</sub>), 24.9 (CH<sub>3</sub>), 24.9 (CH<sub>3</sub>);



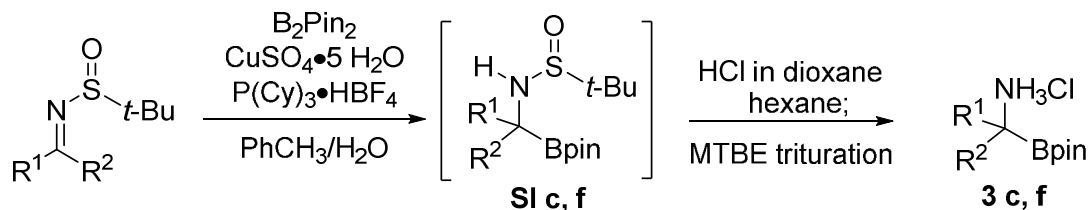
**1-Phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethan-1-aminium chloride (3e):** Prepared using the general procedure with **2-methyl-N-(1-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)propane-2-sulfinamide (SI e,** 3.87 g, 11.0 mmol, 1 equiv) and hydrochloric acid (4M in dioxane, 8.2 mL, 33.0 mmol, 3 equiv). Collected white solid (1.17 g, 7.48 mmol, 68% yield);  $^1\text{H NMR}$  (400 MHz, DMSO):  $\delta$  8.77-8.53 (s, 3H), 7.50-7.37 (m, 5H), 1.69-1.61 (s, 3H), 1.22 (s, 6H), 1.22 (s, 6H);  $^{13}\text{C NMR}$  (100 MHz, DMSO):  $\delta$  140.4 (C), 133.7 (CH), 129.2 (CH), 129.1 (CH), 128.6 (CH), 128.0 (CH), 126.1 (CH), 85.5 (C), 81.8 (CH), 27.2 (CH<sub>3</sub>), 25.0 (CH<sub>3</sub>), 24.7 (CH<sub>3</sub>), 24.4 (CH<sub>3</sub>);



**3-Methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-aminium chloride (3g):** Prepared using the general procedure with **2-methyl-N-(3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)propane-2-sulfinamide (SI g,** 3.71 g, 11.7 mmol, 1 equiv) and hydrochloric acid (4M in dioxane, 8.8 mL, 35.1 mmol, 3 equiv). Collected white solid (2.92 g, 11.7 mmol, 100% yield);  $^1\text{H NMR}$  (400 MHz, DMSO):  $\delta$  8.08-7.93 (s, 3H), 2.73-7.59 (s, 1H), 1.79-1.66 (quint,  $J = 6.6$  Hz, 1H), 1.57-1.39 (m, 2H), 1.25 (s, 6H), 1.25 (s, 6H), 0.90-0.84 (d,  $J = 6.6$  Hz, 6H);  $^{13}\text{C NMR}$



**NMR** (100 MHz, DMSO):  $\delta$  84.9 (C), 38.7 (CH<sub>2</sub>), 25.1 (CH<sub>3</sub>), 24.9 (CH<sub>3</sub>), 22.9 (CH), 24.9 (CH<sub>3</sub>) 22.7 (CH<sub>3</sub>);

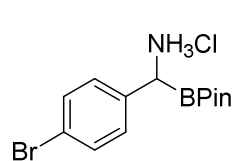


### Synthesis of $\alpha$ -aminoboronates **3c** and **3f** – borylation/deprotection

A modified procedure based on Ellman was used, which omits the silica gel purification of the intermediate boronated sulfinamides. Copper sulfate pentahydrate (125 mg, 0.50 mmol, 2.5 mol%) was dissolved in water (10 mL). To this solution was added PCy<sub>3</sub>•HBF<sub>4</sub> (184 mg, 0.50 mmol, 2.5 mol%), toluene (10 mL), and benzylamine (218  $\mu$ L, 0.1 mmol, 5 mol%). The biphasic mixture was stirred for 15 min at ambient temperature, and a solution of *rac*-sulfinylimine (20.0 mmol, 1.0 equiv) in toluene (100 mL) was added. The flask was immersed in a room temperature water bath, then solid B<sub>2</sub>pin<sub>2</sub> (5.59 g, 22.0 mmol, 1.1 equiv) was added in 3 roughly equal portions 1 min apart. The mixture was stirred at ambient temperature until the blue colour had changed to a dark brown (~15 min), at which point conversion had typically ceased. The resulting slurry was diluted with water (50 mL), filtered, and the layers separated. The brown organic layer was washed with water (2 x 50 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated to give a crude mixture containing primarily boronated sulfinamides. This was taken up in hexane (100 mL) and treated with a solution of HCl in dioxane (4.0M, 12.5 mL, 50.0 mmol, 2.5 equiv), giving a biphasic mixture after 15 min of stirring of ambient temperature. This was concentrated, and the resulting oil sonicated in MTBE (150 mL) until a white solid precipitated. This was filtered, washed with MTBE (50 mL), and dried under vacuum at 50 °C to give the desired  $\alpha$ -aminoboronates.<sup>5</sup>

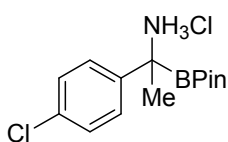
#### (4-Bromophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methanamine hydrochloride (**3c**):

Prepared from (*E*)-*N*-(4-bromobenzylidene)-2-methylpropane-2-sulfinamide (5.76 g, 20 mmol, 1 equiv), and isolated as an off-white solid (2.87 g, 8.2 mmol, 41% yield); <sup>1</sup>H NMR (400 MHz, DMSO):  $\delta$  8.57 (s, 3H), 7.62 (m, 2H), 7.37 (m, 2H), 3.98 (s, 1H), 1.23 (s, 6H), 1.19 (s, 6H); <sup>13</sup>C NMR (100 MHz, DMSO):  $\delta$  135.7 (C), 132.0 (CH), 130.8 (CH), 121.5 (C), 85.3 (C), 24.9 (CH<sub>3</sub>), 24.8 (CH<sub>3</sub>).

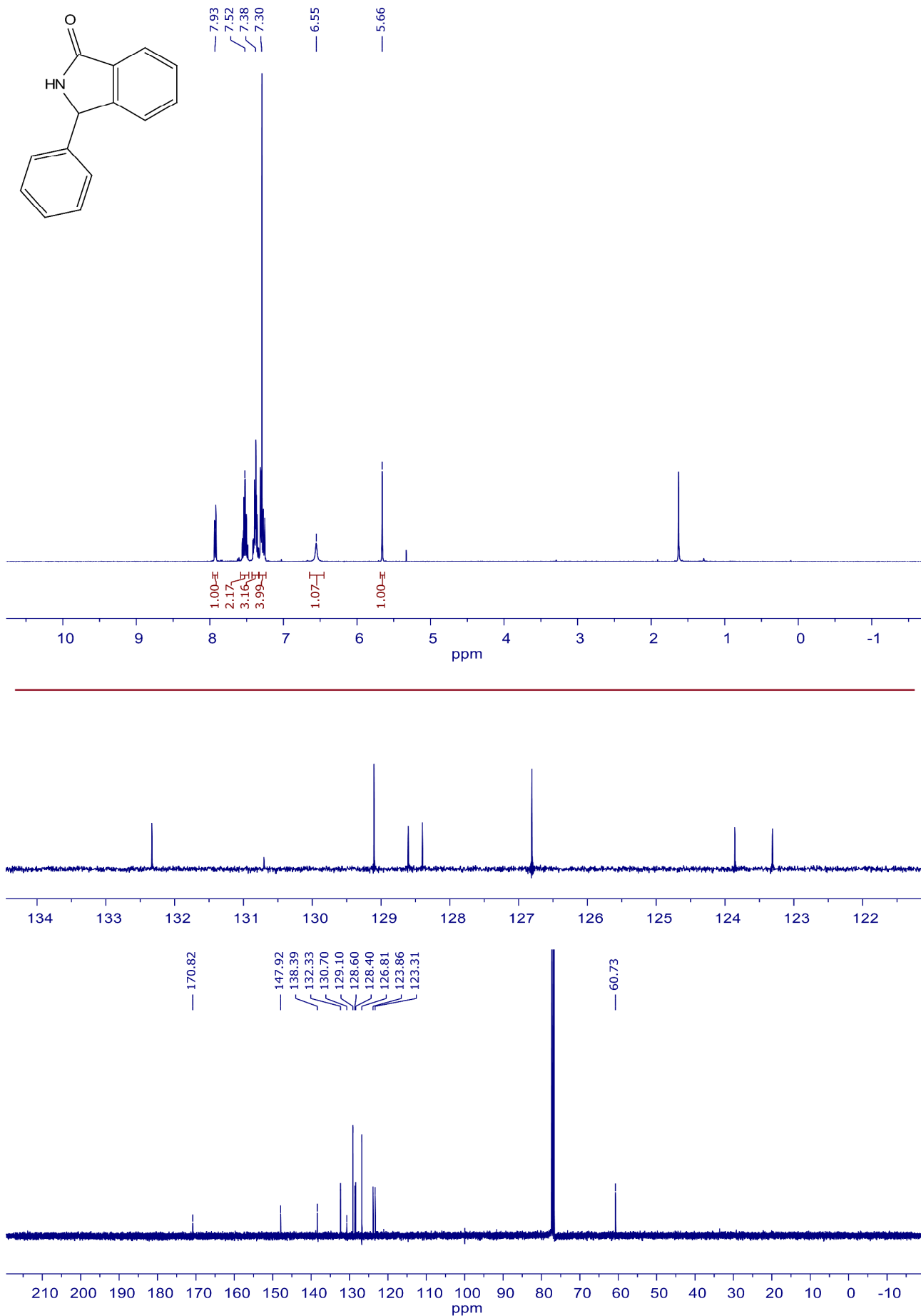


#### 1-(4-Chlorophenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethanamine hydrochloride (**3f**):

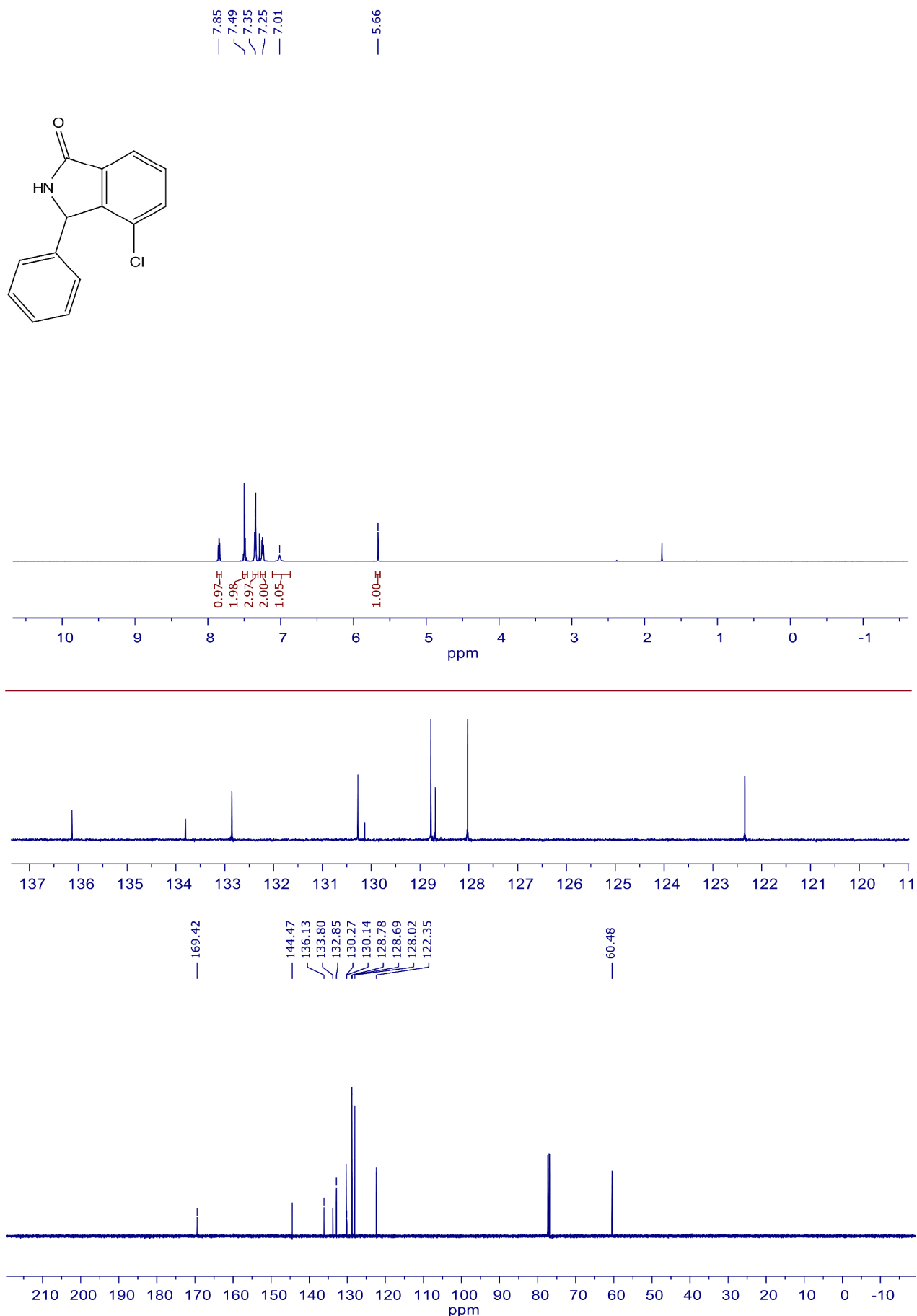
Prepared from (*E*)-*N*-(1-(4-chlorophenyl)ethylidene)-2-methylpropane-2-sulfinamide (5.16 g, 20 mmol, 1 equiv), and isolated



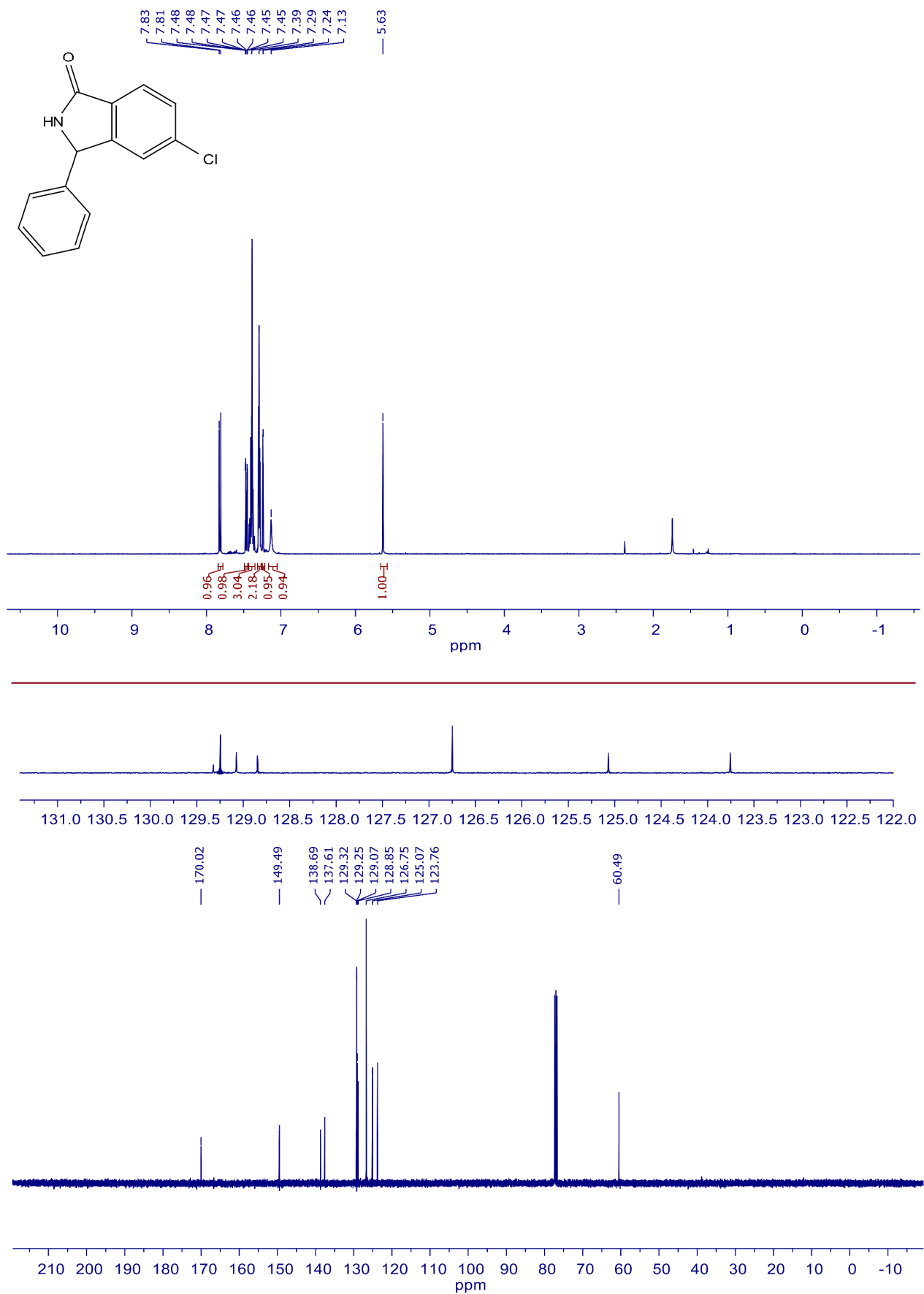
as an off-white solid (1.90 g, 6.0 mmol, 30% yield). **<sup>1</sup>H NMR** (400 MHz, DMSO):  $\delta$  8.92-8.65 (s, 3H), 7.61-7.34 (m, 4H), 1.65 (s, 3H), 1.22 (s, 6H), 1.21 (s, 6H). **<sup>13</sup>C NMR** (100 MHz, DMSO):  $\delta$  139.5 (C), 132.7 (C), 129.0 (CH), 128.2 (CH), 85.6 (C), 24.7 (CH<sub>3</sub>), 24.7 (CH<sub>3</sub>), 22.4 (CH<sub>3</sub>).



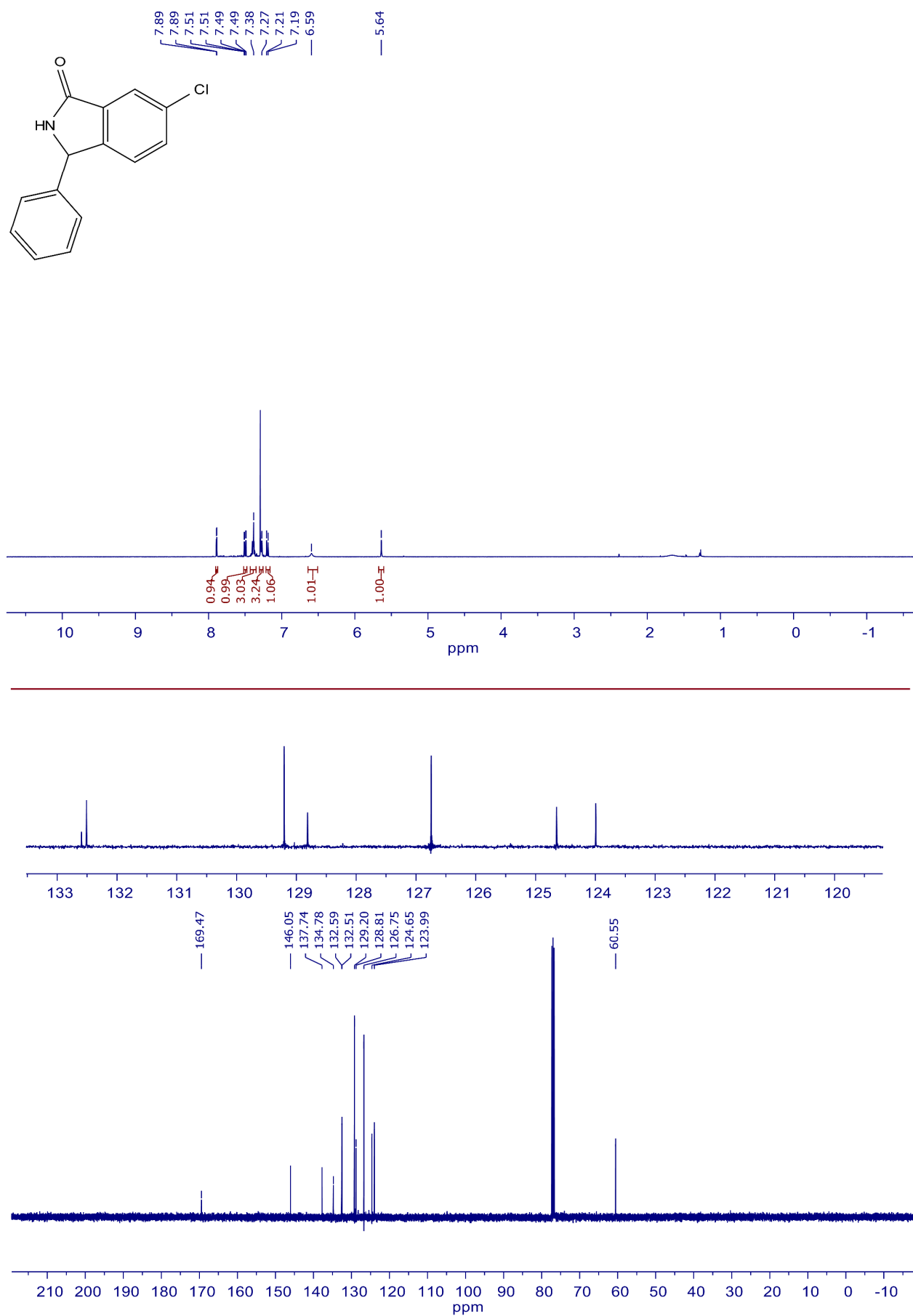
**Figure 1:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) spectrum (top) and  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) spectrum (bottom) of 3-phenylisoindolin-1-one (2a).



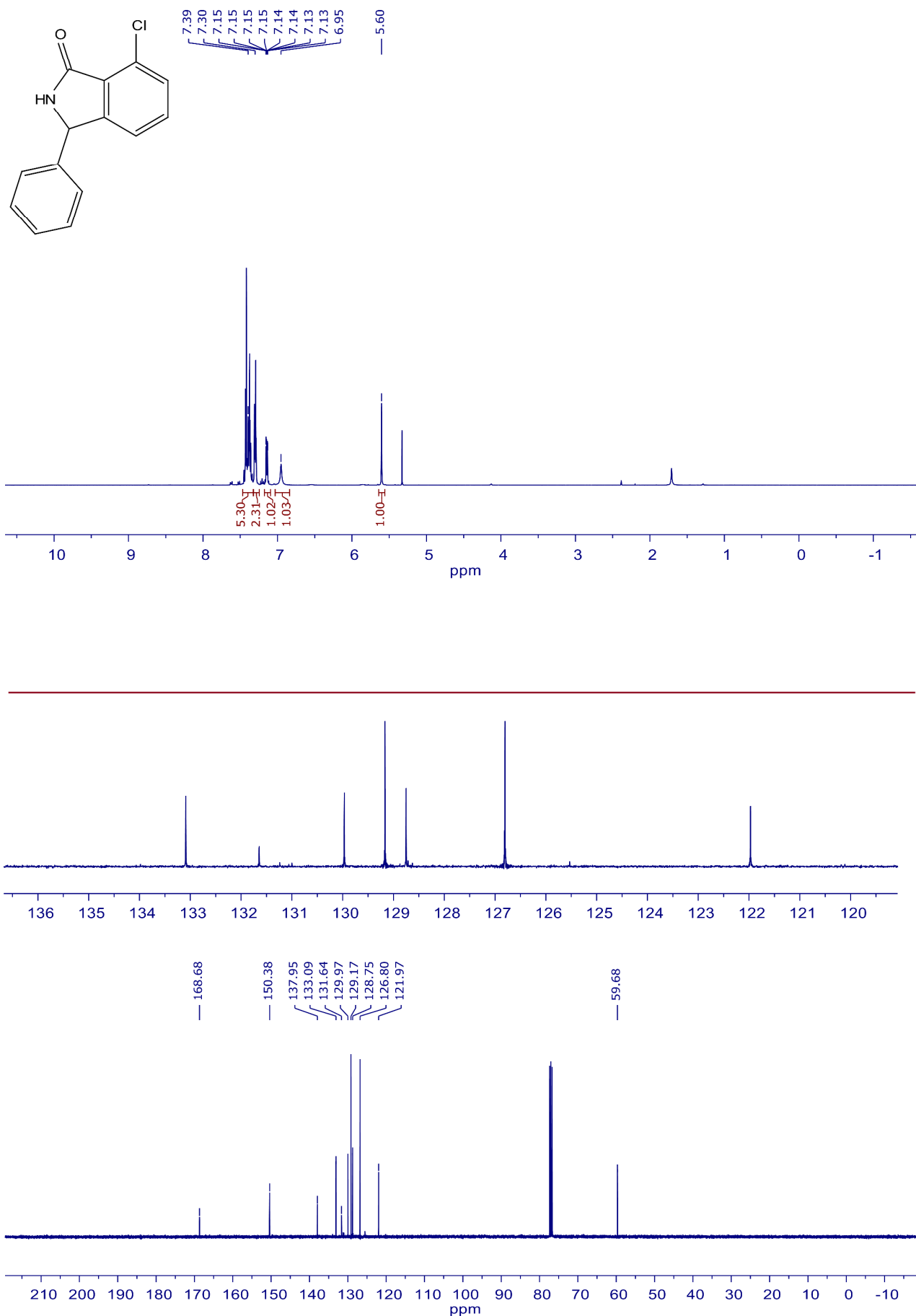
**Figure 2:** <sup>1</sup>H NMR (CDCl<sub>3</sub>) spectrum (top) and <sup>13</sup>C NMR (CDCl<sub>3</sub>) spectrum (bottom) of 4-chloro-3-phenylisoindolin-1-one (2b).



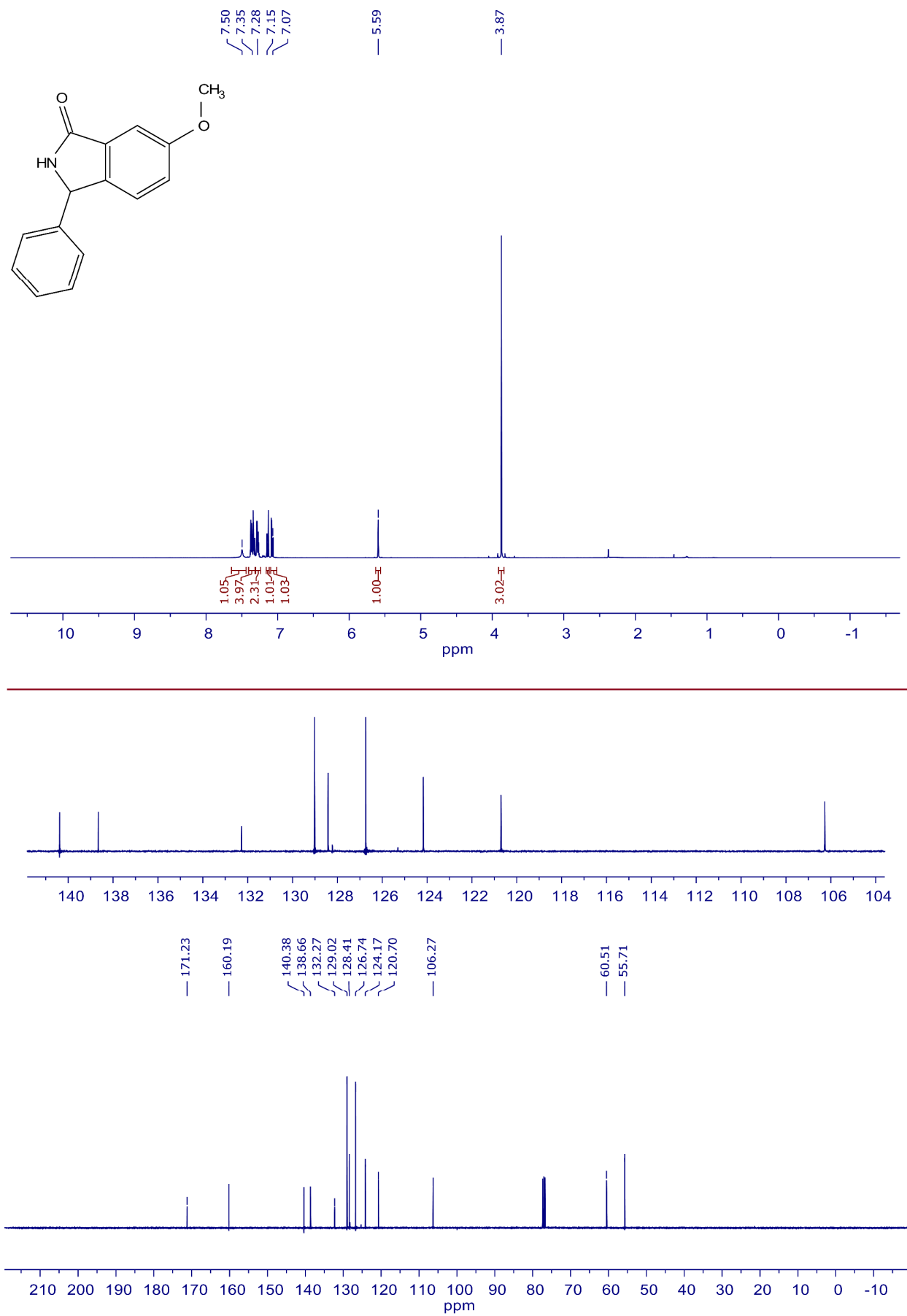
**Figure 3:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum (top) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum (bottom) of 5-chloro-3-phenylisoindolin-1-one (2c).



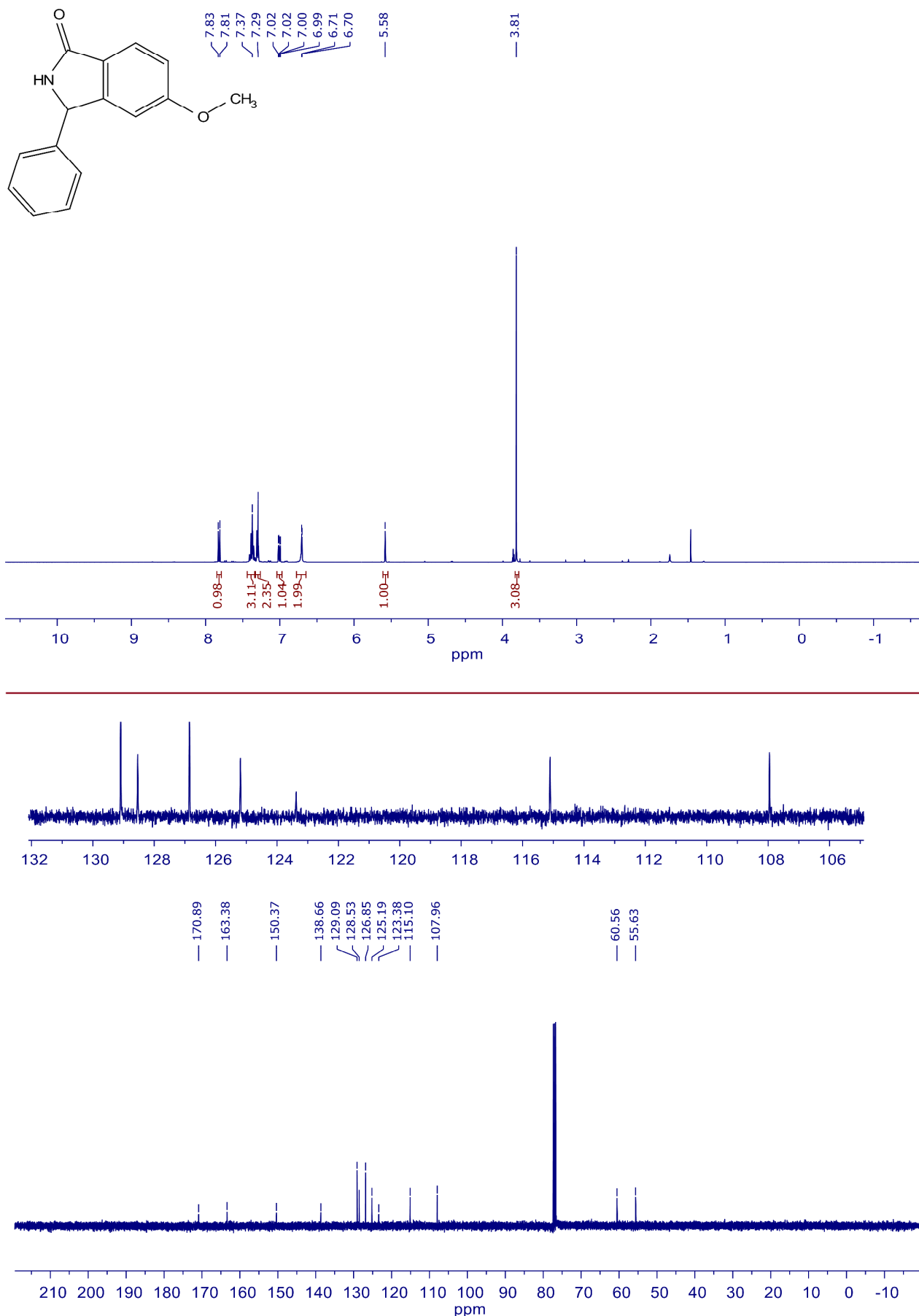
**Figure 4:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum (top) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum (bottom) of 6-chloro-3-phenylisoindolin-1-one (2d).



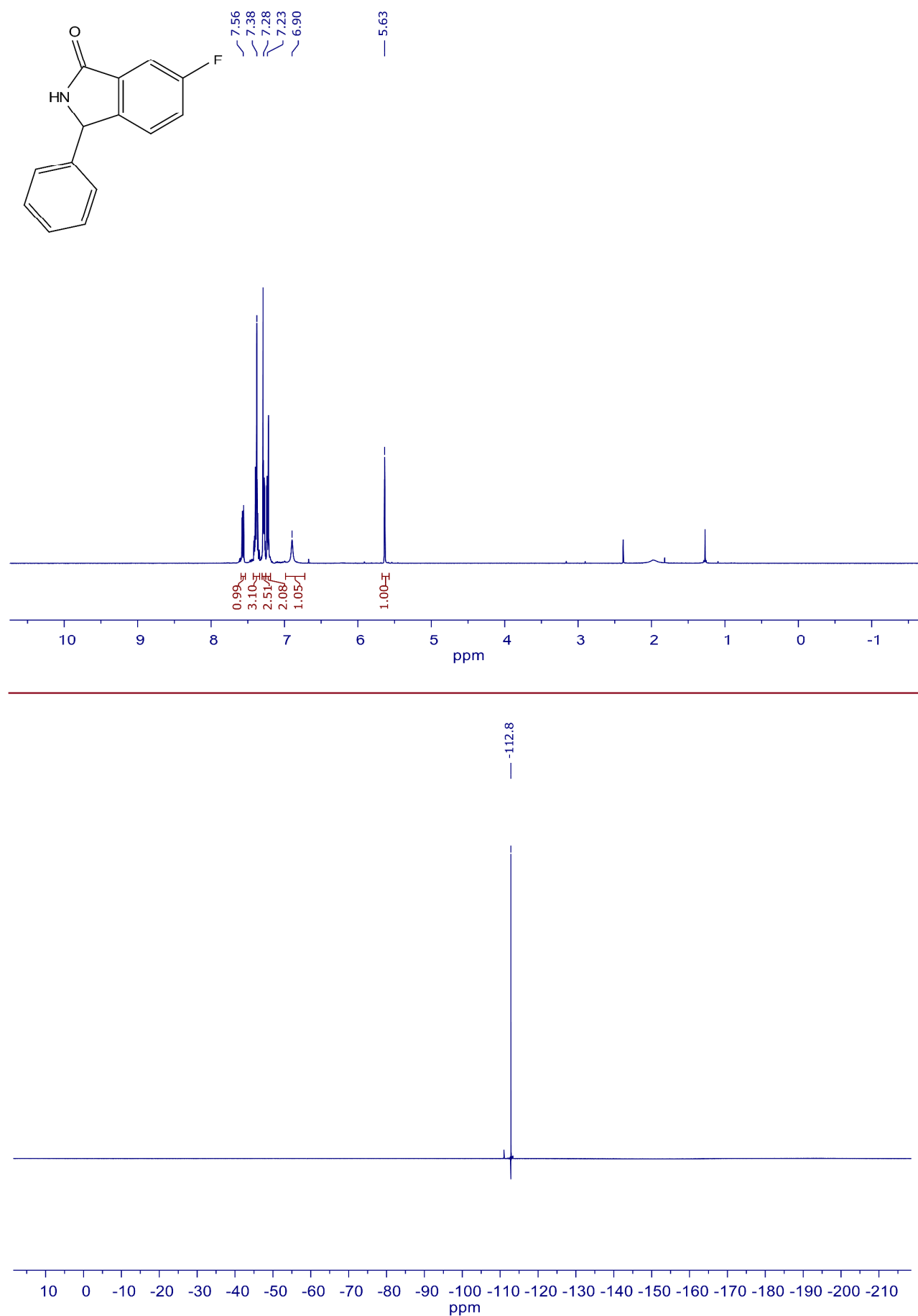
**Figure 5:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum (top) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum (bottom) of 7-chloro-3-phenylisoindolin-1-one (2e).



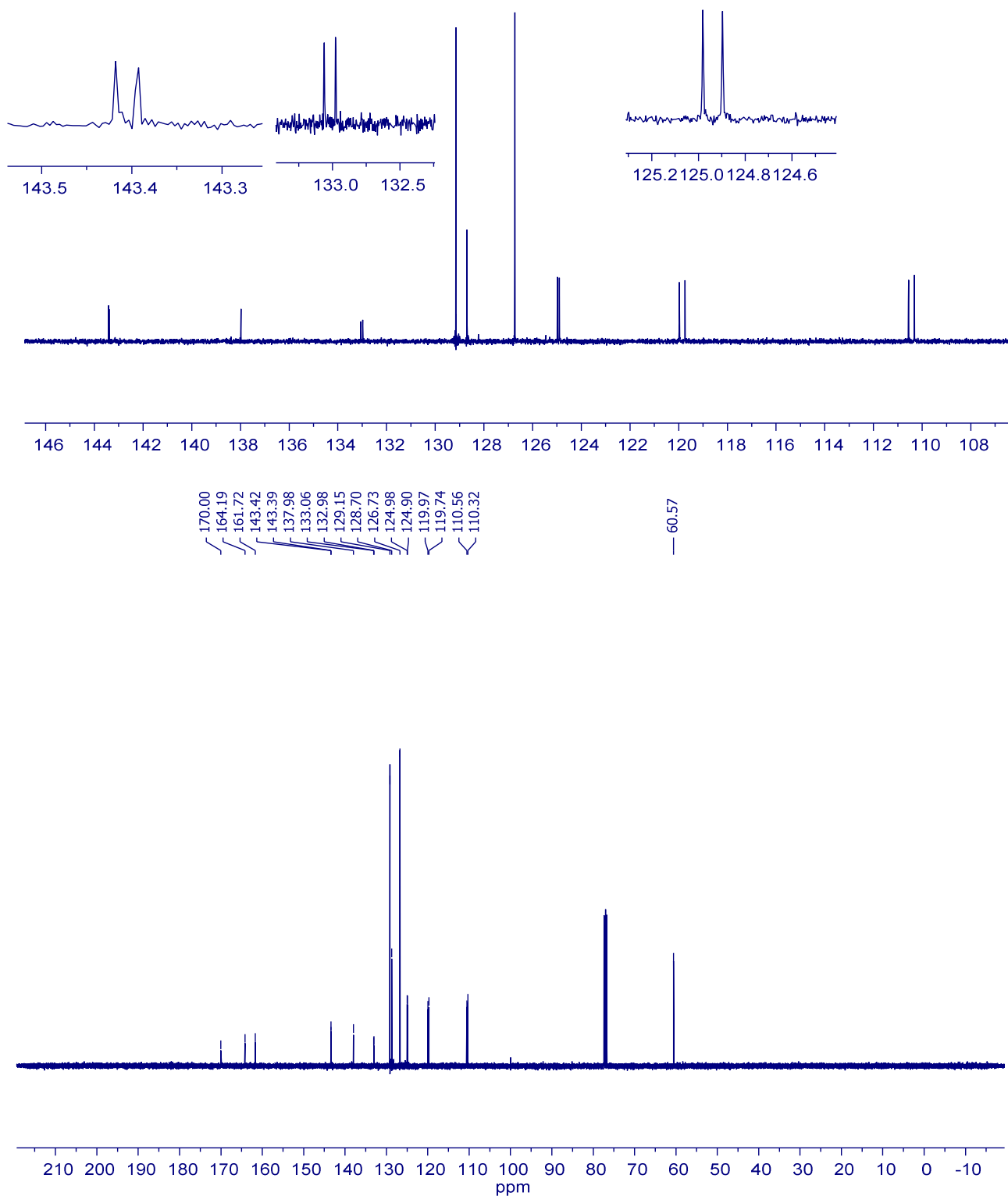
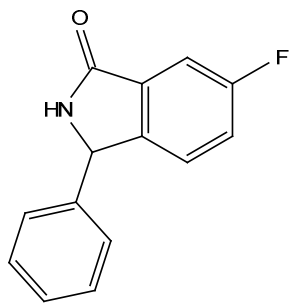
**Figure 6:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum (top) and <sup>13</sup>C NMR (CDCl<sub>3</sub>) spectrum (bottom) of 6-methoxy-3-phenylisoindolin-1-one (2f).



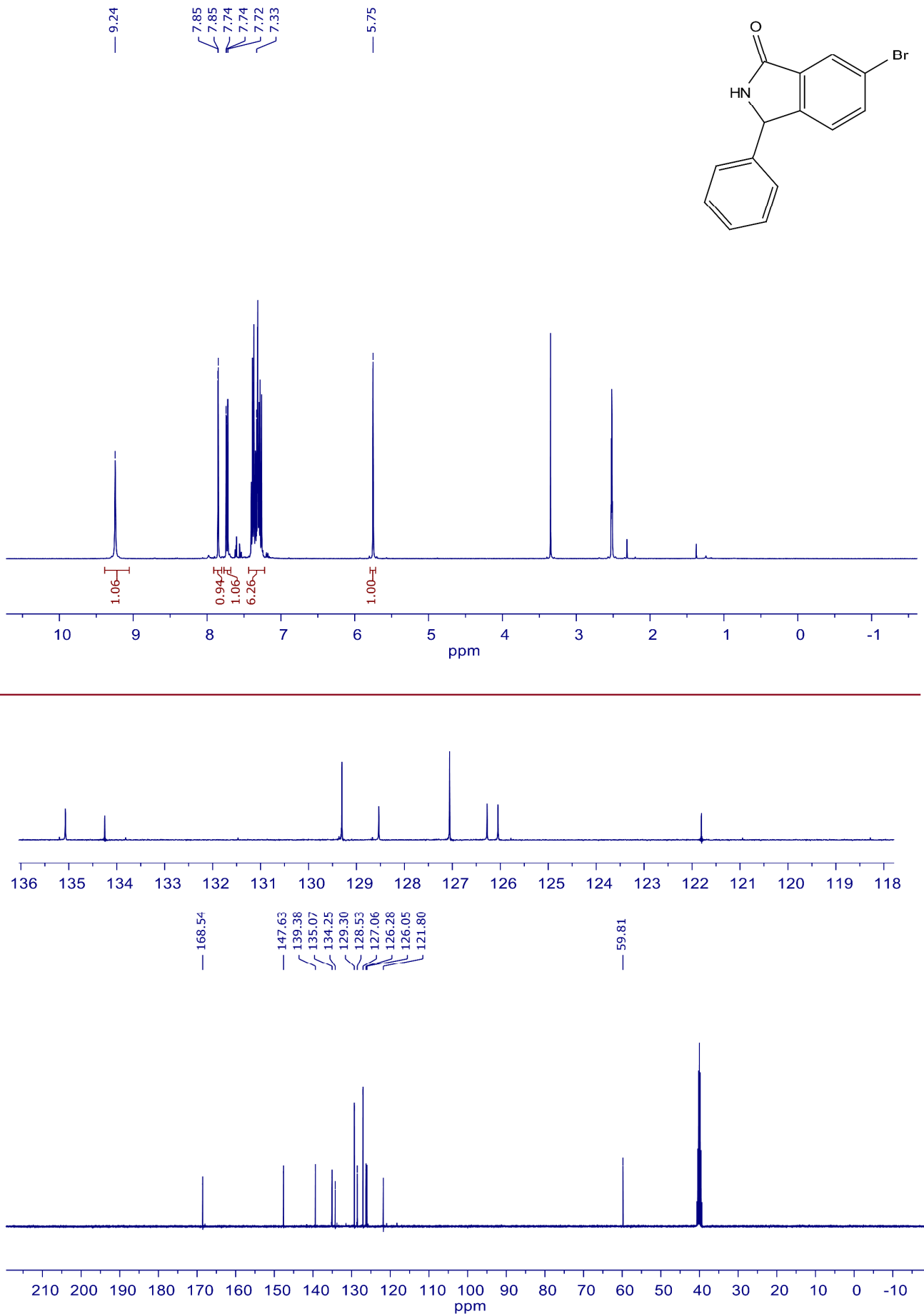
**Figure 7:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum (top) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum (bottom) of 5-methoxy-3-phenylisoindolin-1-one (2g).



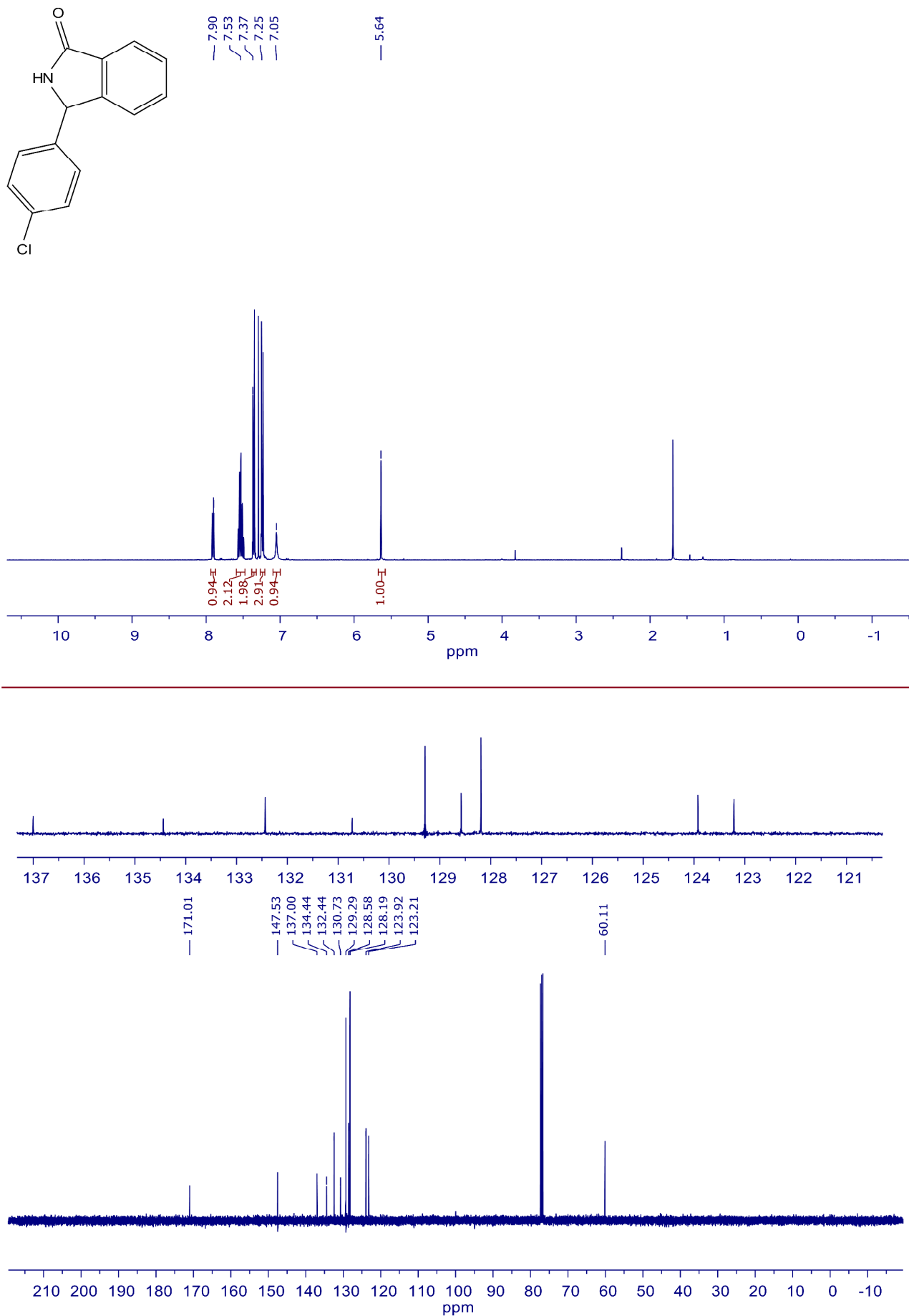
**Figure 8:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum (top) and  $^{19}\text{F}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum (bottom) of **6-fluoro-3-phenylisoindolin-1-one (2h)**.



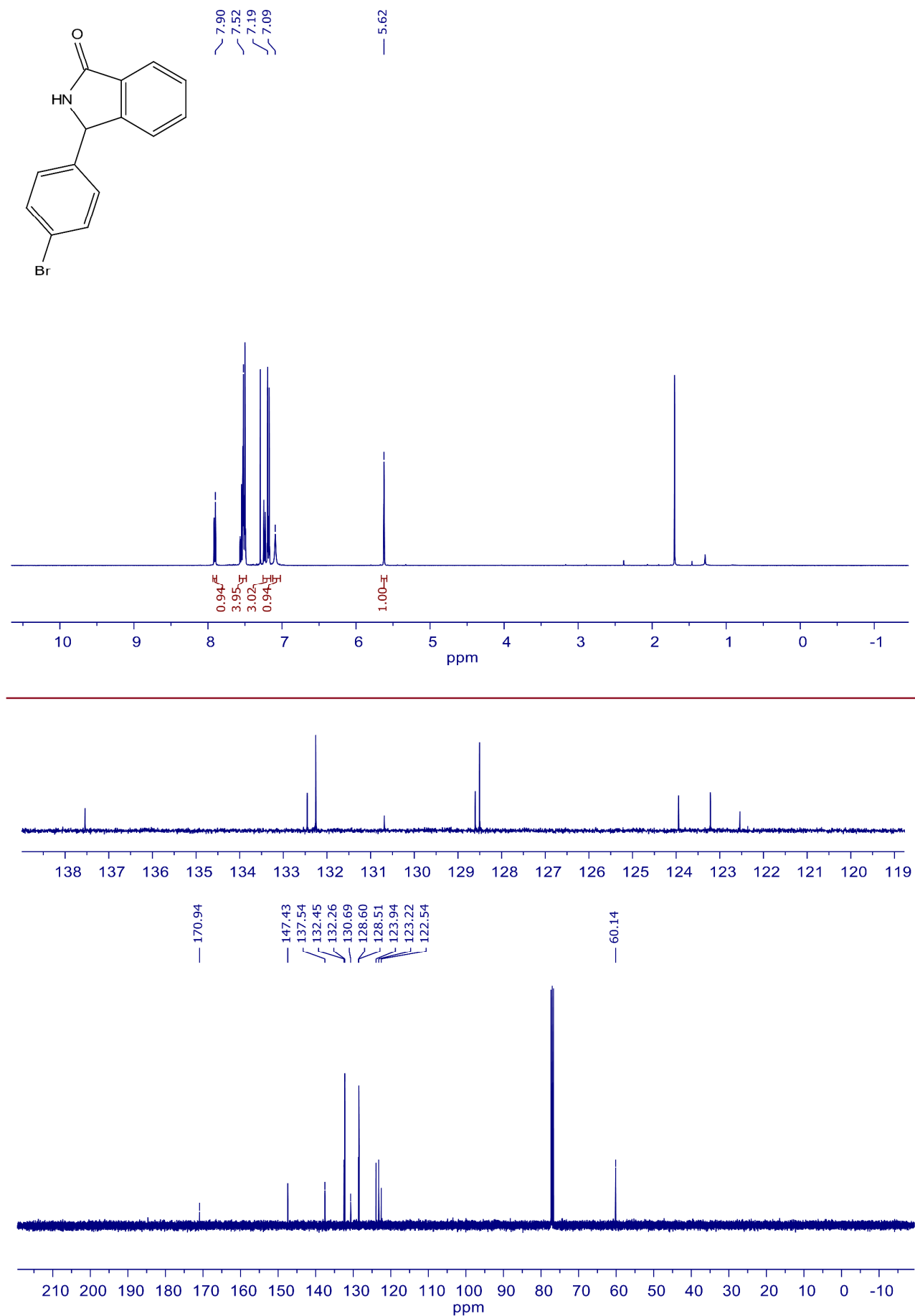
**Figure 9:**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of 6-fluoro-3-phenylisoindolin-1-one (2h).



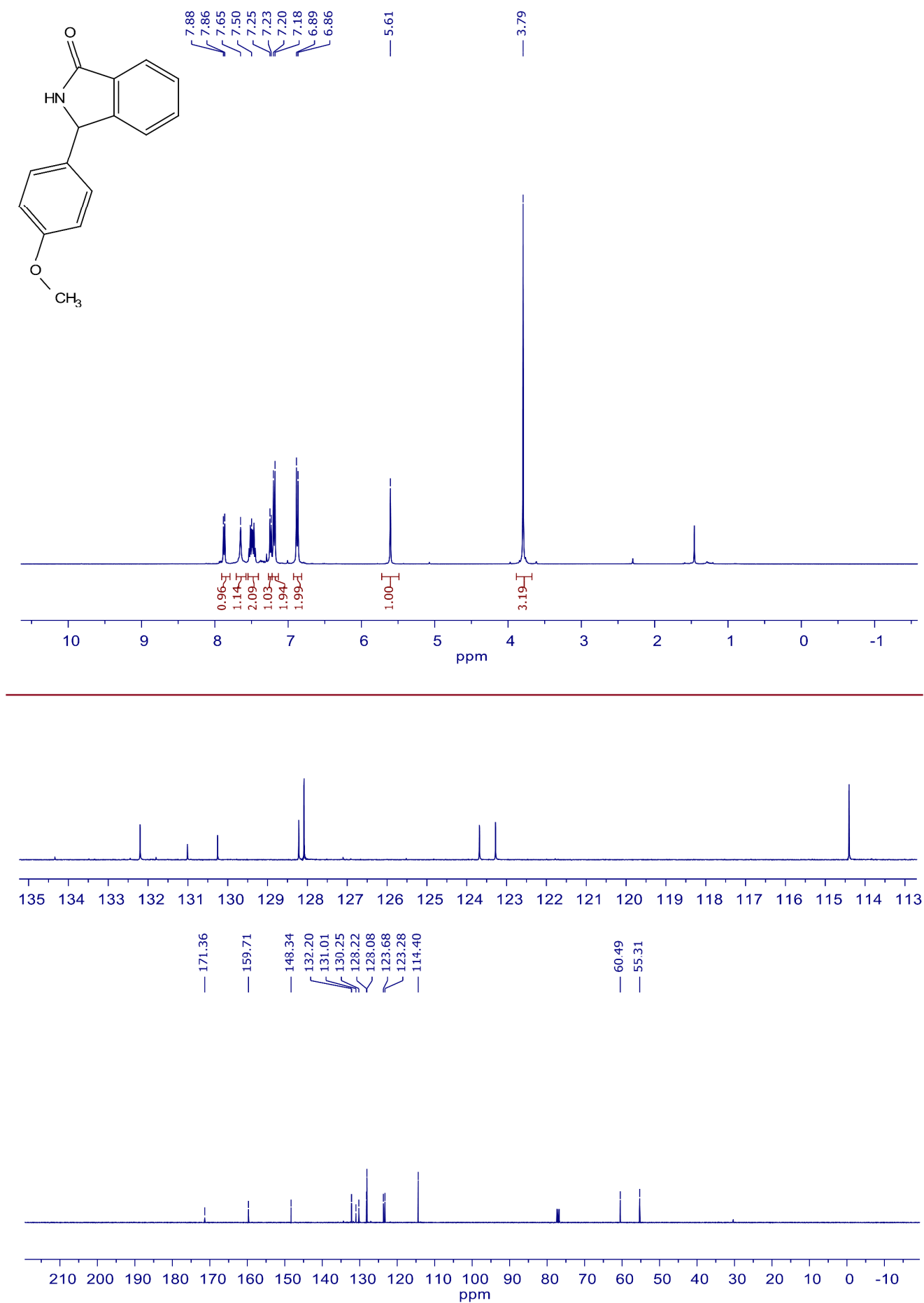
**Figure 10:** <sup>1</sup>H NMR (400 MHz, DMSO) spectrum (top) and <sup>13</sup>C NMR (100 MHz, DMSO) spectrum (bottom) of **6-bromo-3-phenylisoindolin-1-one (2i)**.



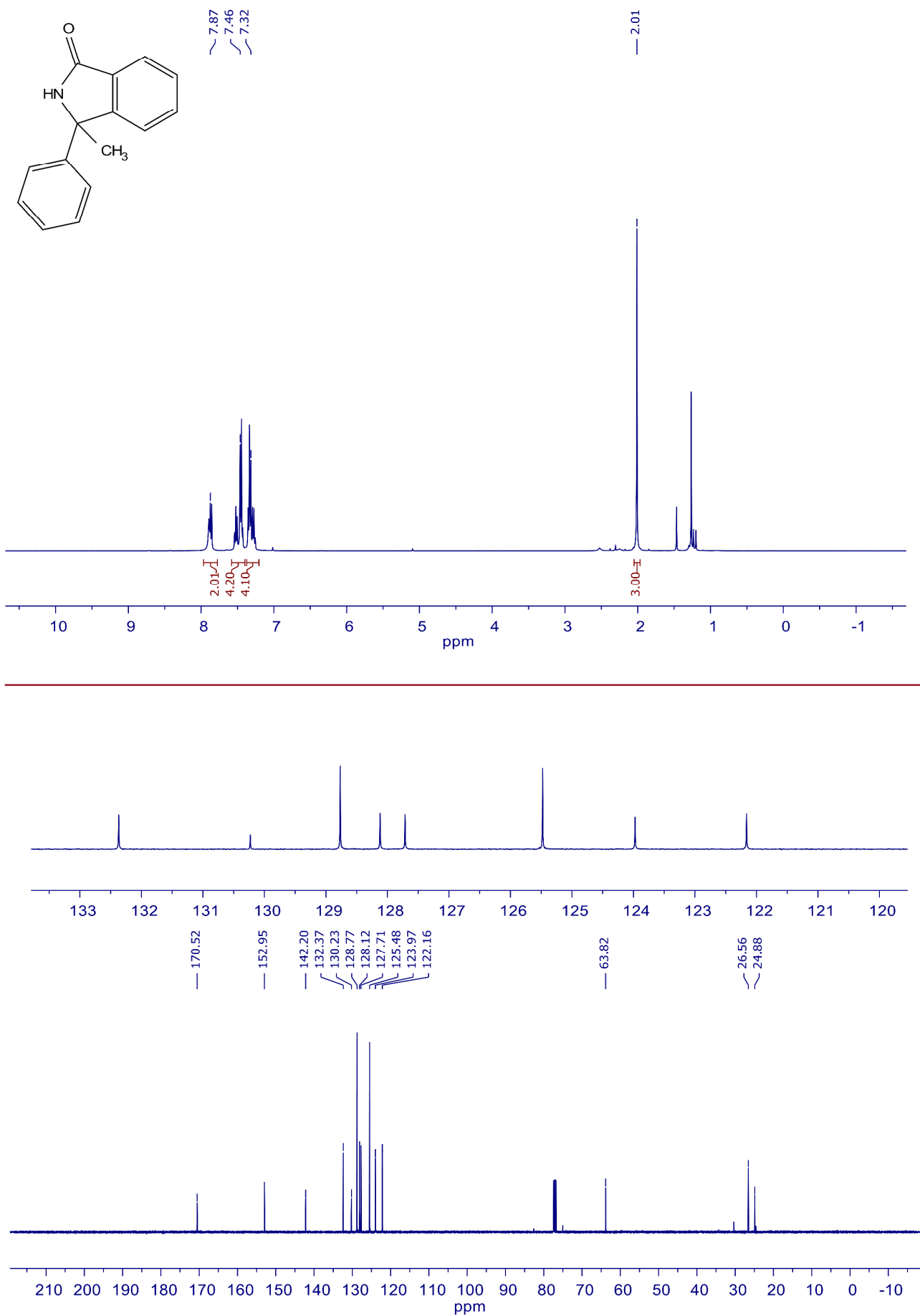
**Figure 11:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum (top) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum (bottom) of 3-(4-chlorophenyl)isoindolin-1-one (2j).



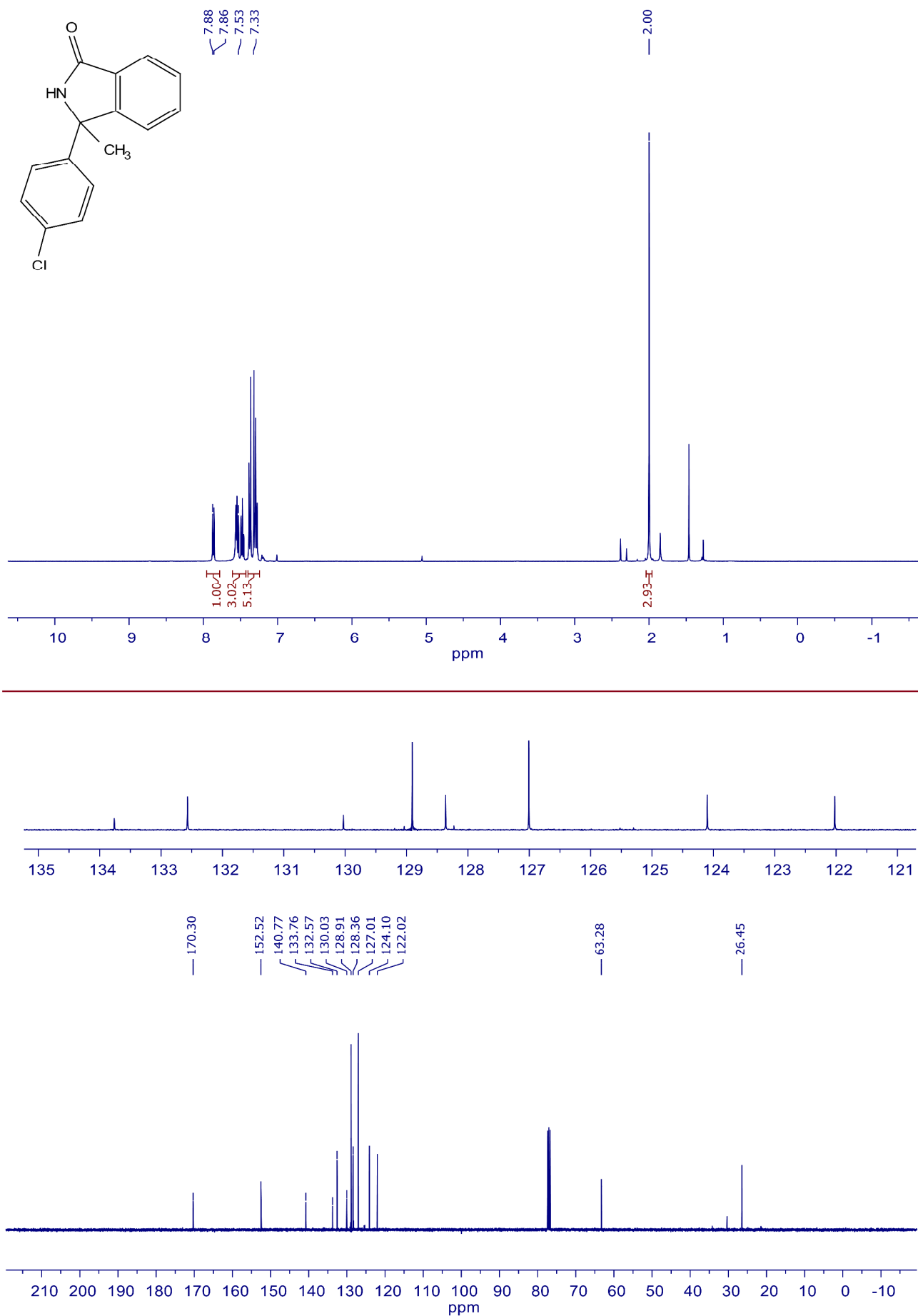
**Figure 12:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum (top) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum (bottom) of 3-(4-bromophenyl)isoindolin-1-one (2k).



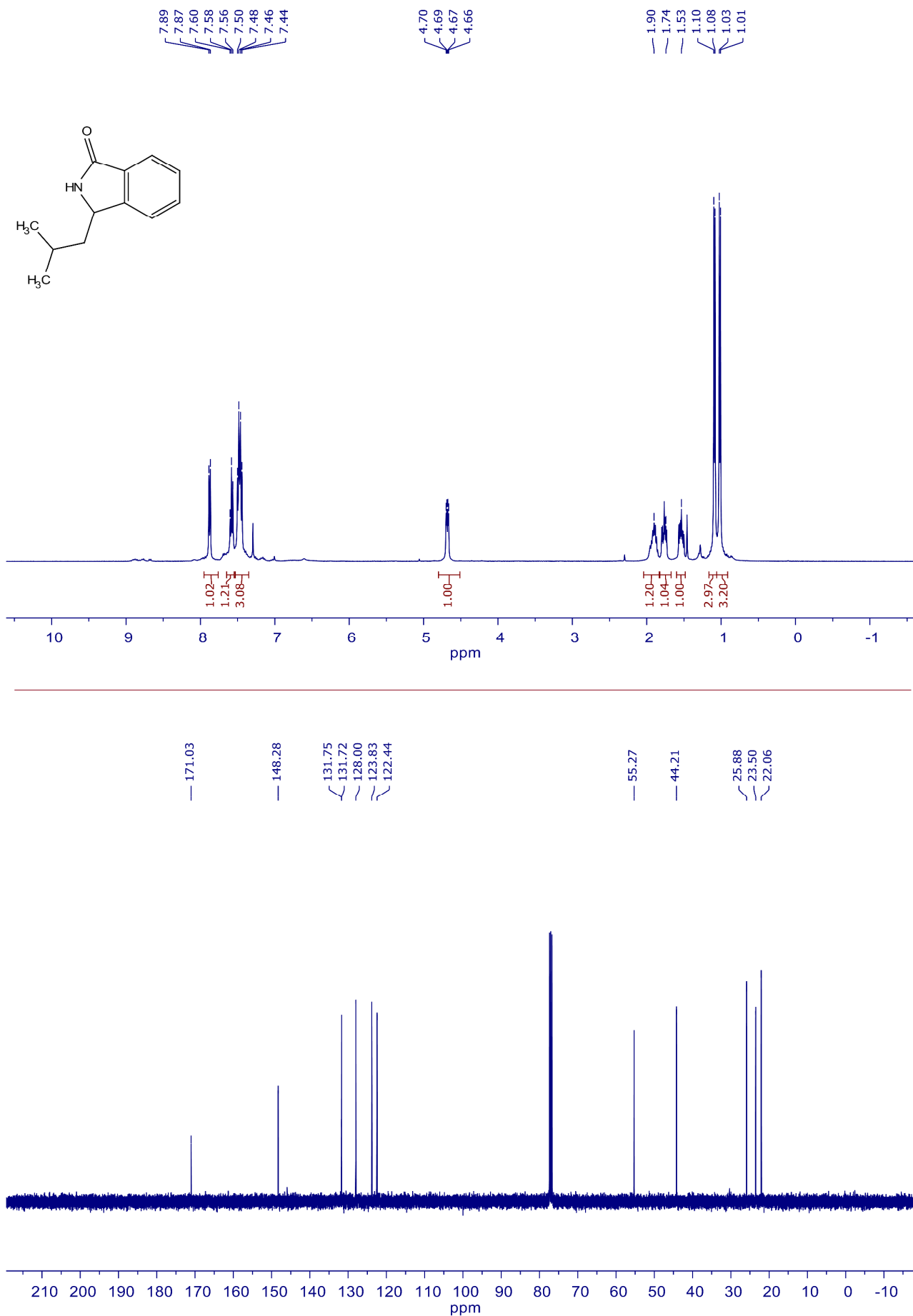
**Figure 13:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum (top) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum (bottom) of 3-(4-methoxyphenyl)isoindolin-1-one (2).



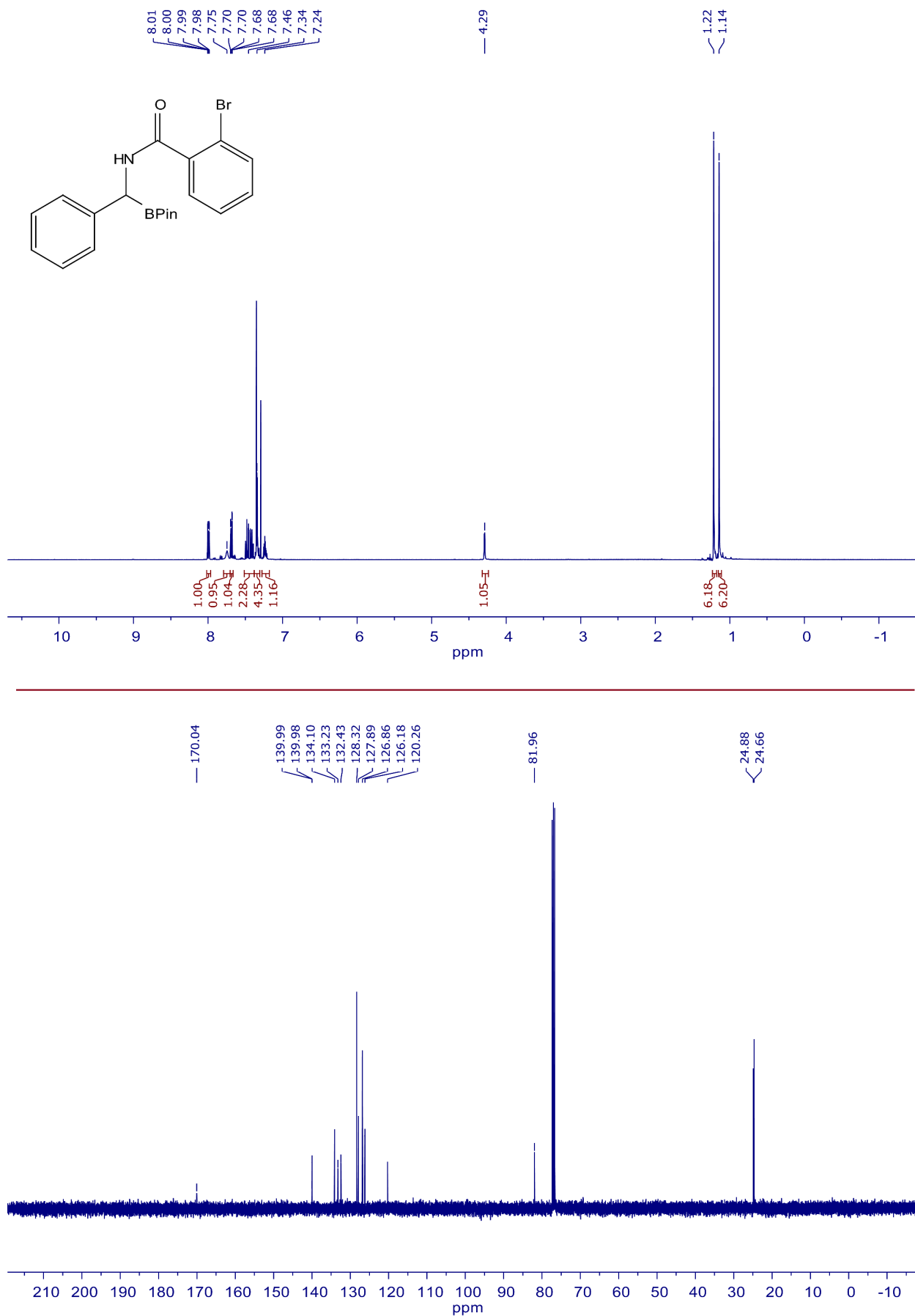
**Figure 14:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum (top) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum (bottom) of 3-methyl-3-phenylisoindolin-1-one (2m).



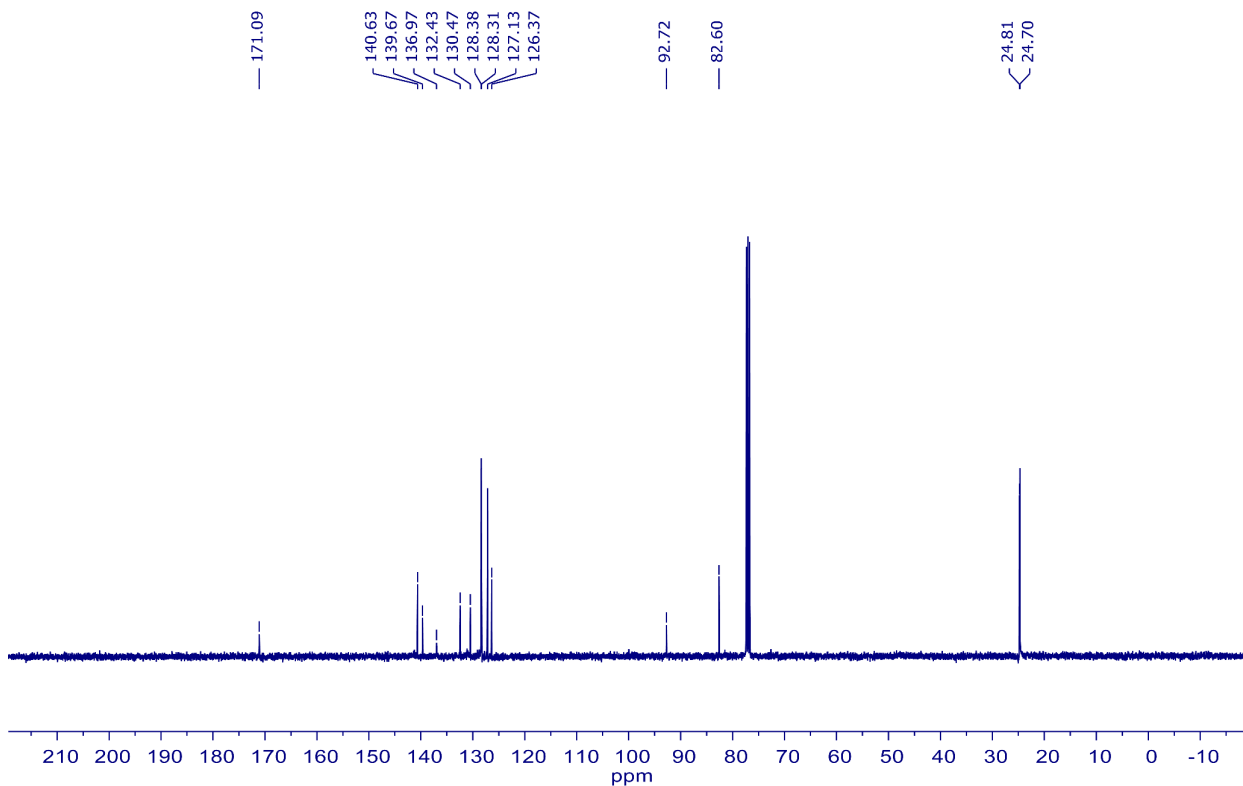
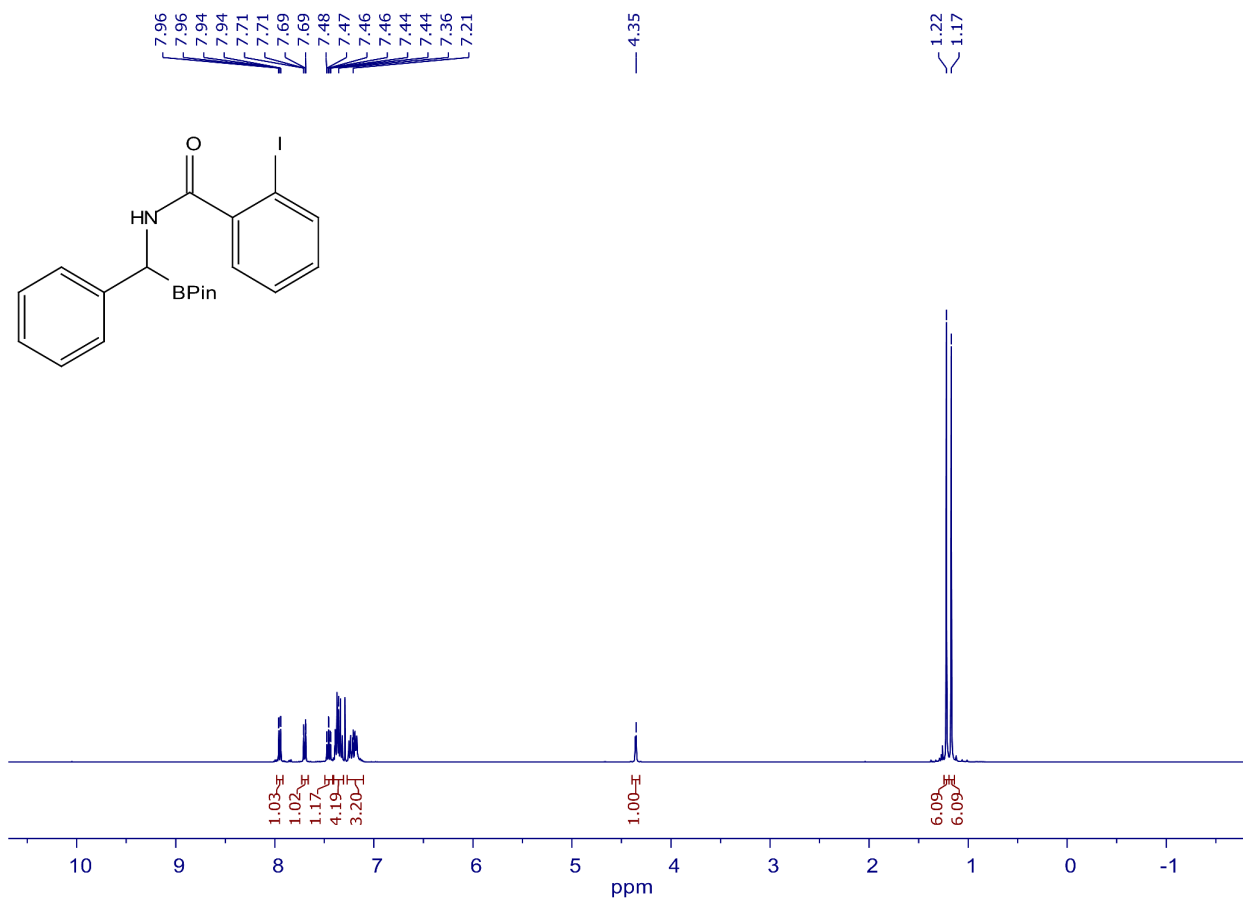
**Figure 15:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum (top) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum (bottom) of 3-(4-chlorophenyl)-3-methylisoindolin-1-one (2n).



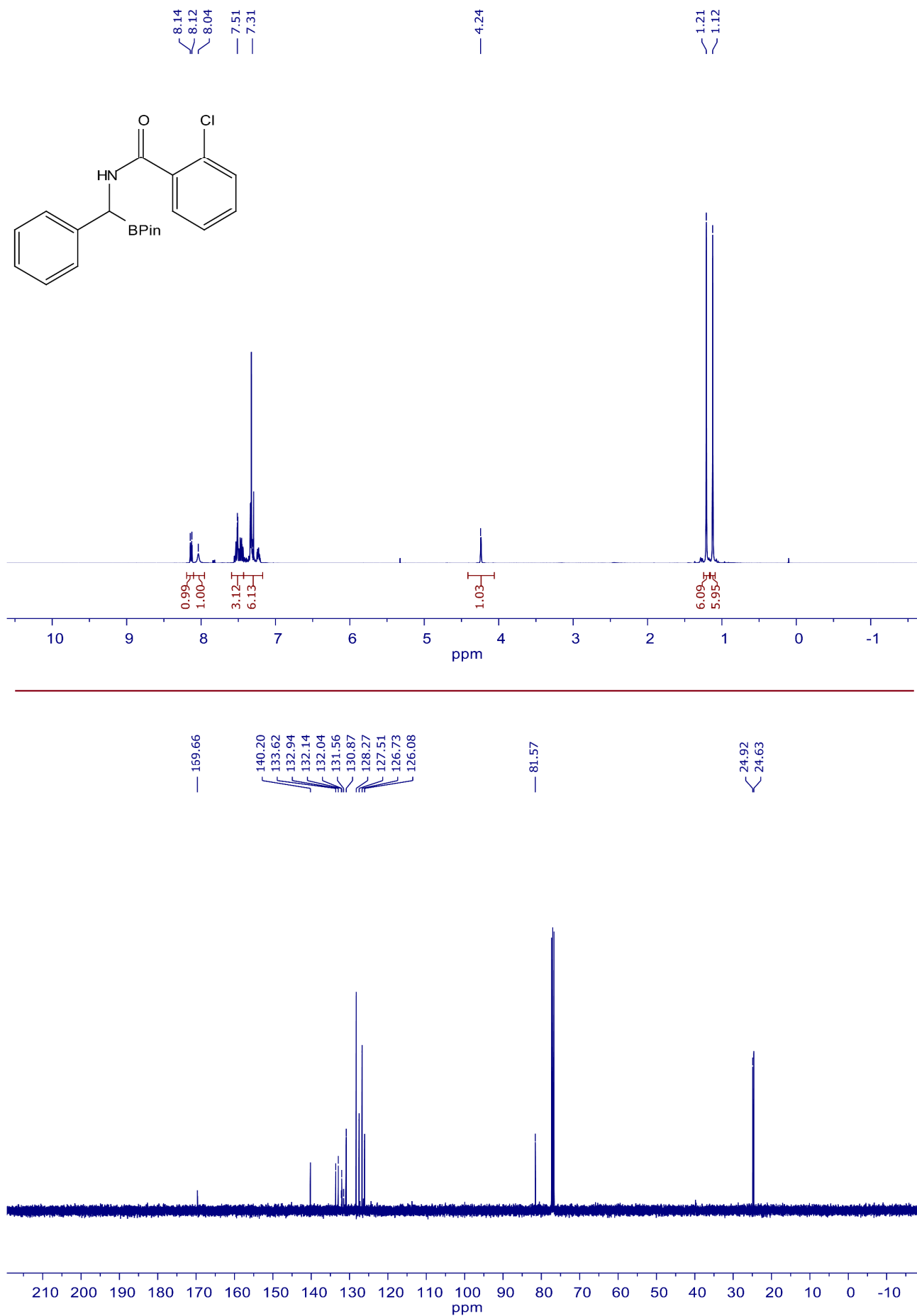
**Figure 16:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum (top) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum (bottom) of **3-Isobutylisoindolin-1-one (2o)**.



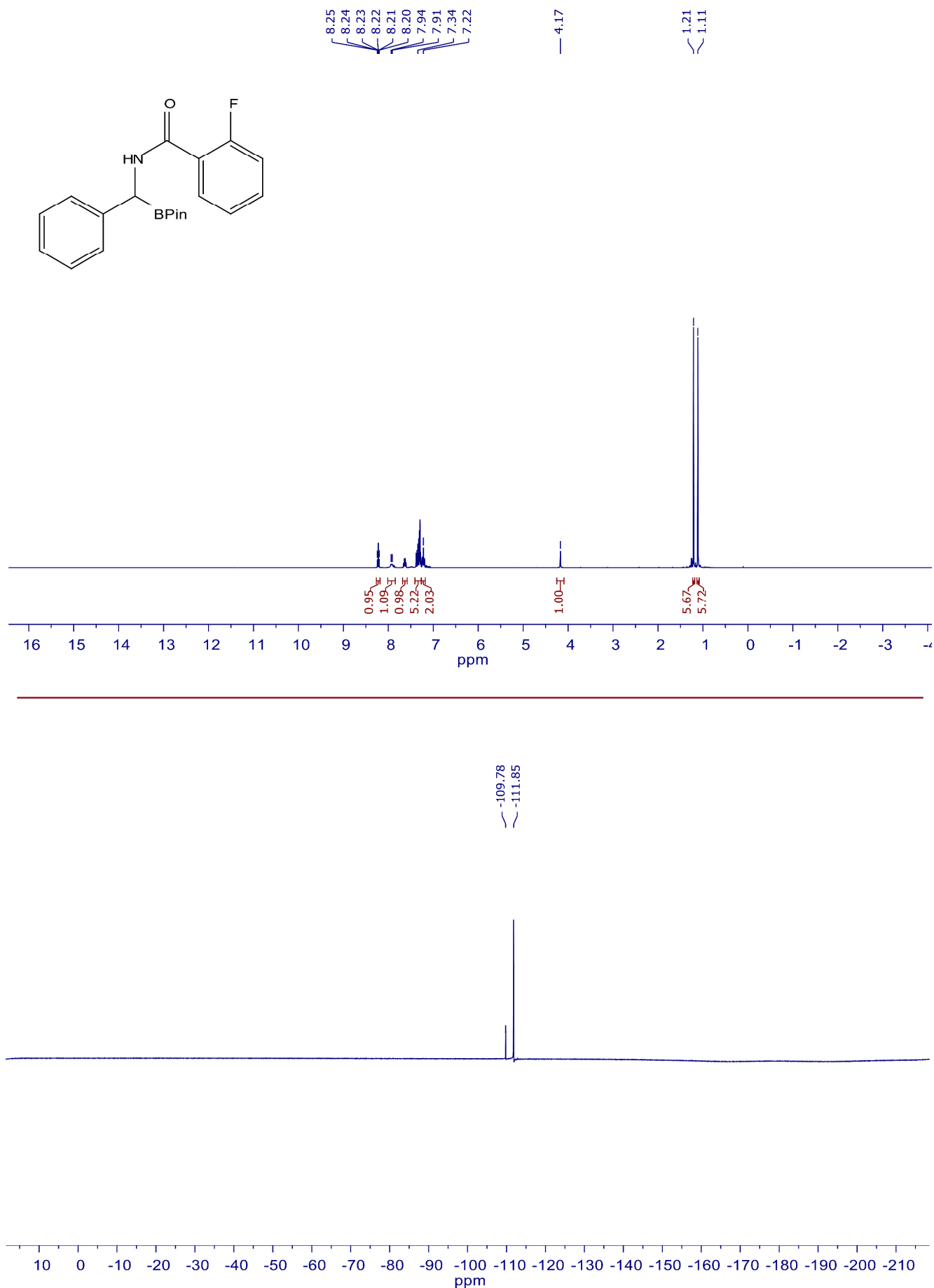
**Figure 17:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum (top) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum (bottom) of 2-bromo-N-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide (1a).



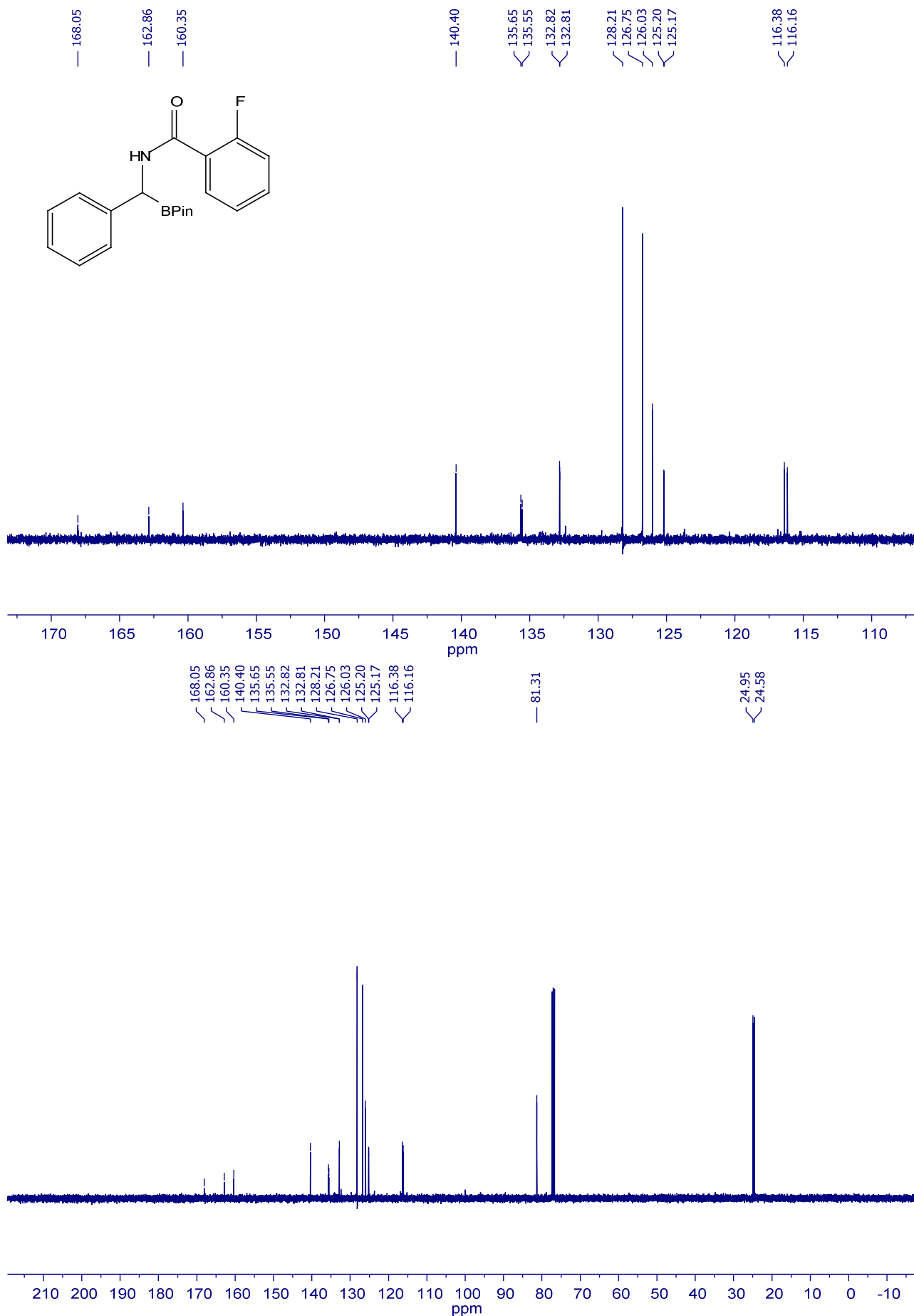
**Figure 18:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum (top) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum (bottom) of 2-iodo-N-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide (1b).



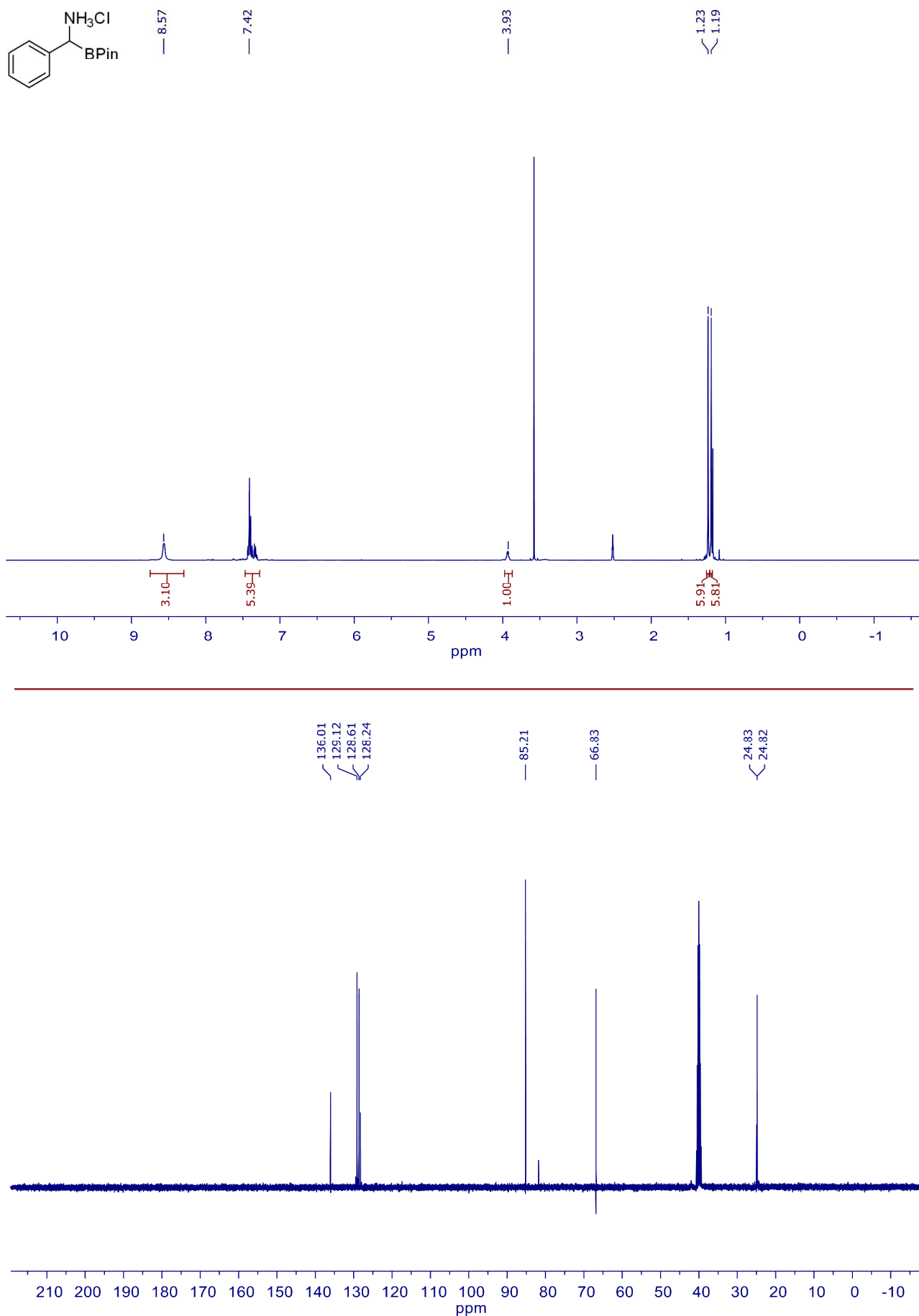
**Figure 19:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum (top) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum (bottom) of 2-chloro-N-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide (1c).



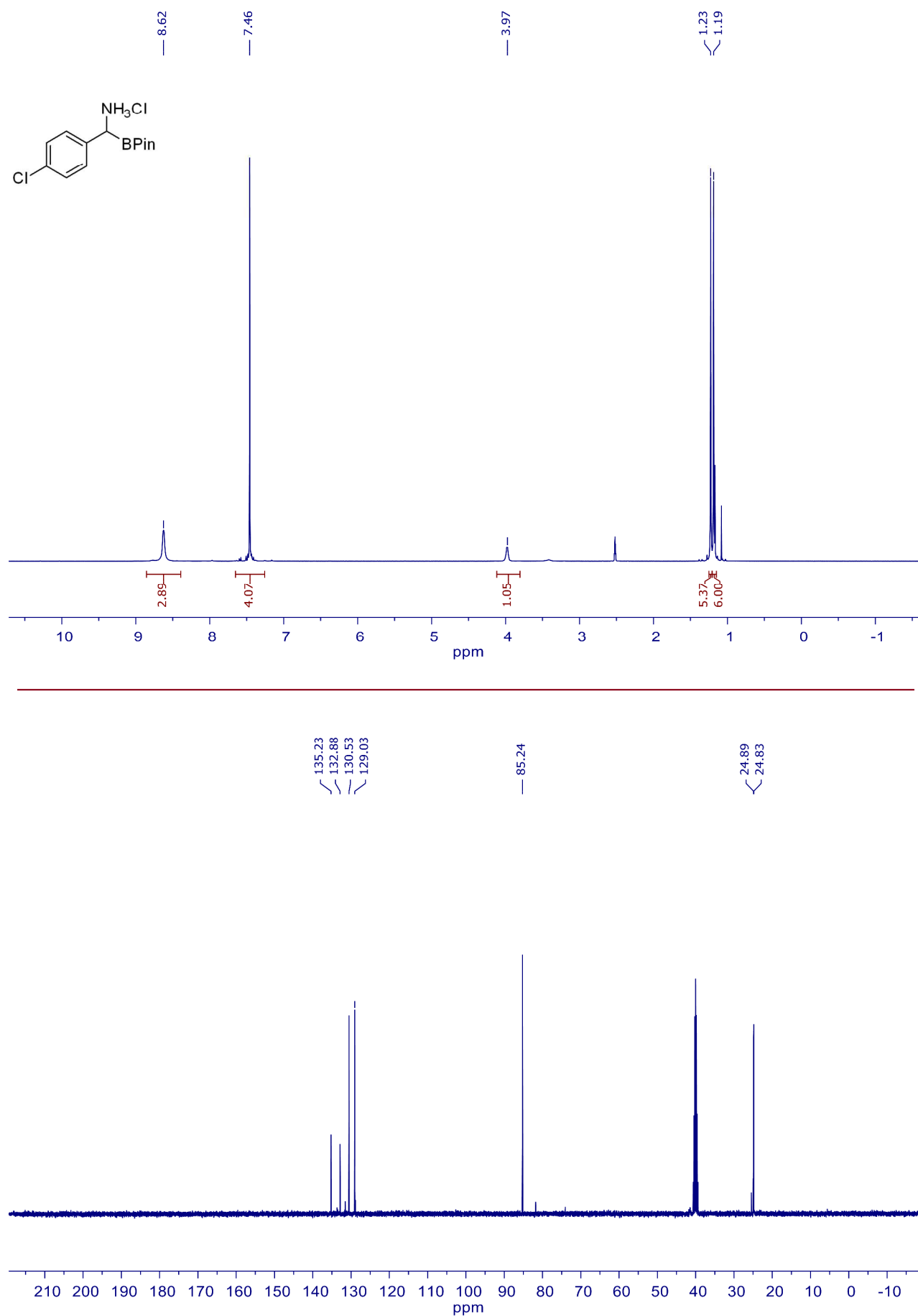
**Figure 20:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum (top) and <sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>) spectrum (bottom) of 2-fluoro-N-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide (1d).



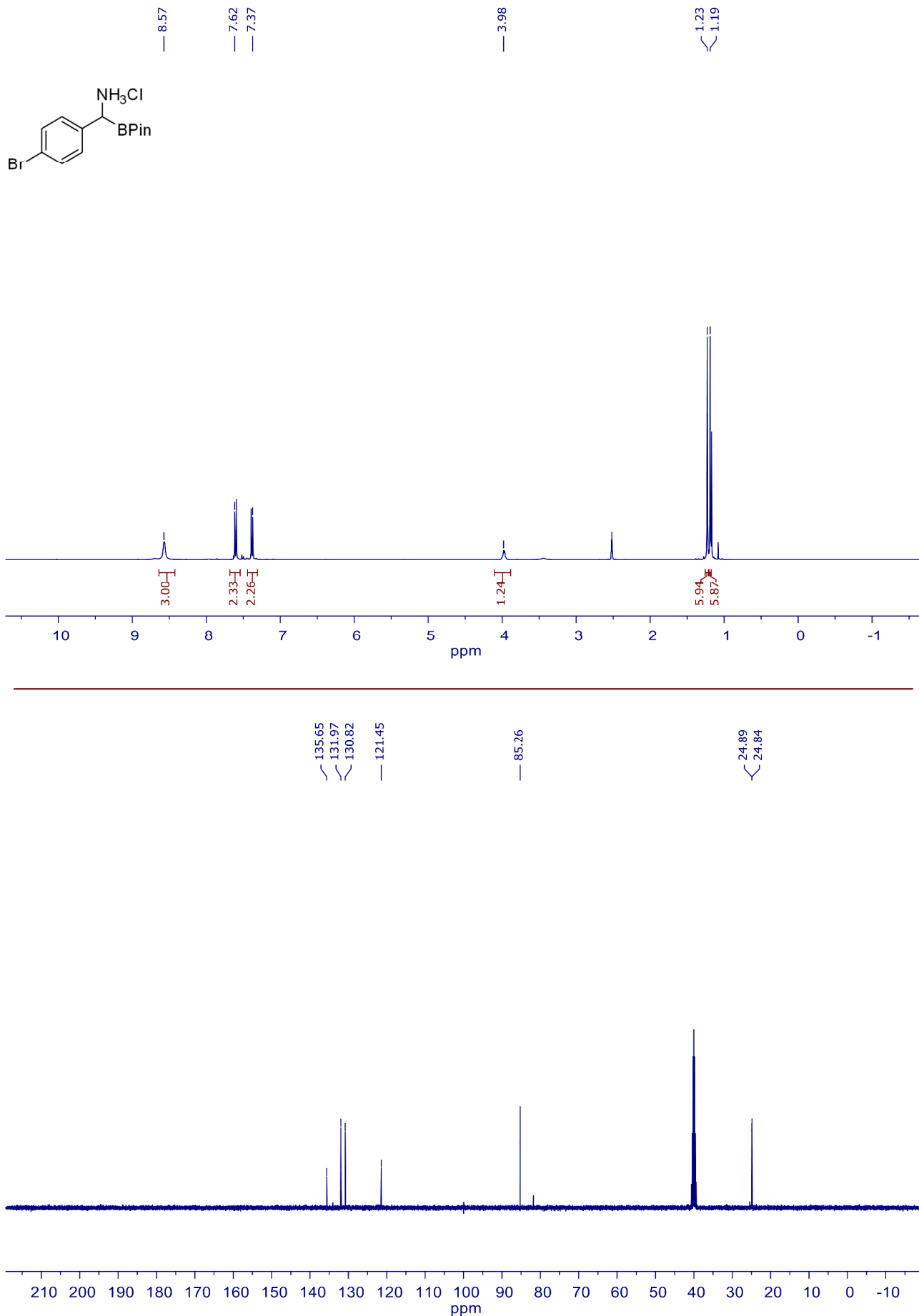
**Figure 21:** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of 2-fluoro-N-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide (1d).



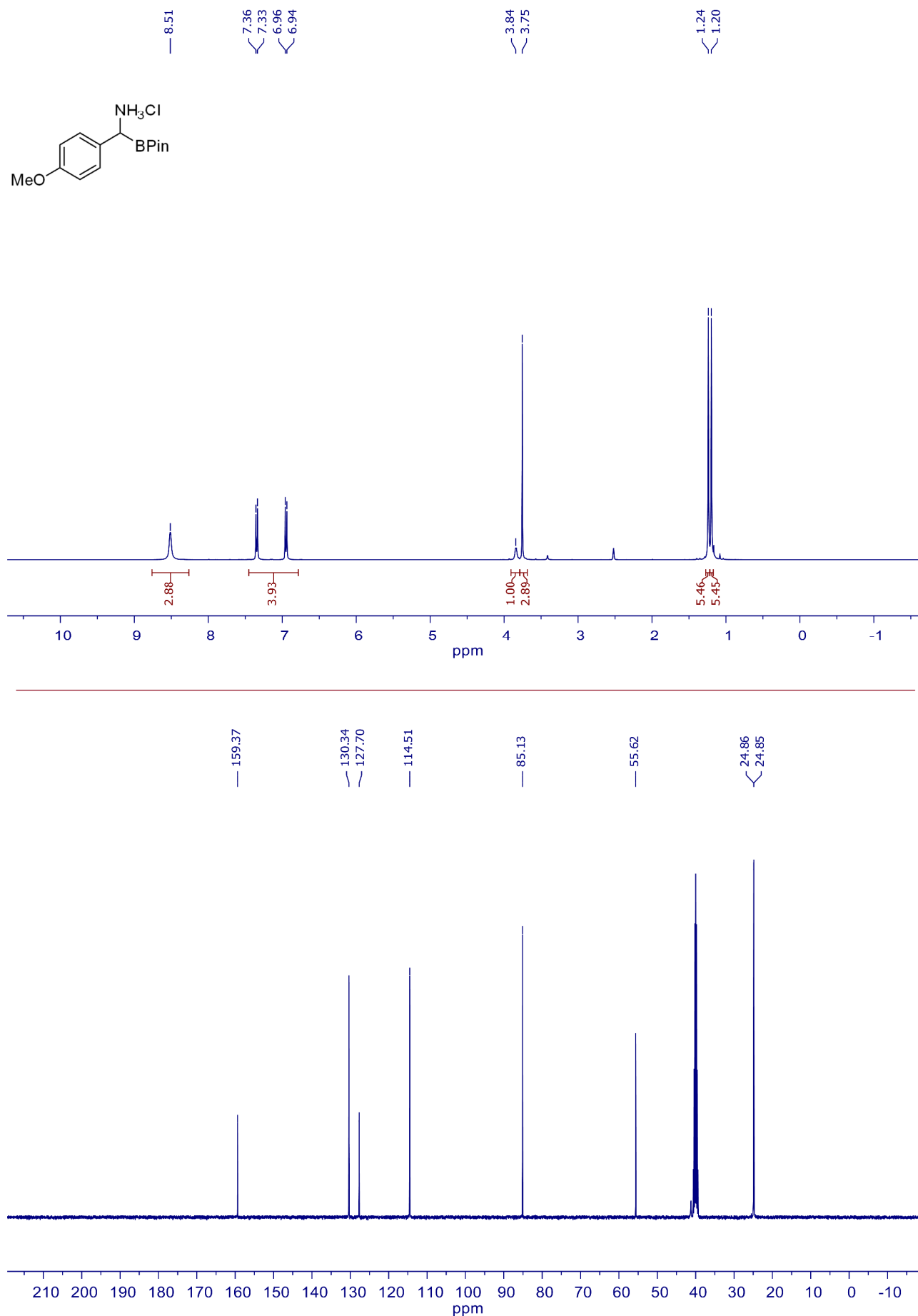
**Figure 22:** <sup>1</sup>H NMR (400 MHz, DMSO) spectrum (top) and <sup>13</sup>C NMR (100 MHz, DMSO) spectrum (bottom) of phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methanaminium chloride (3a).



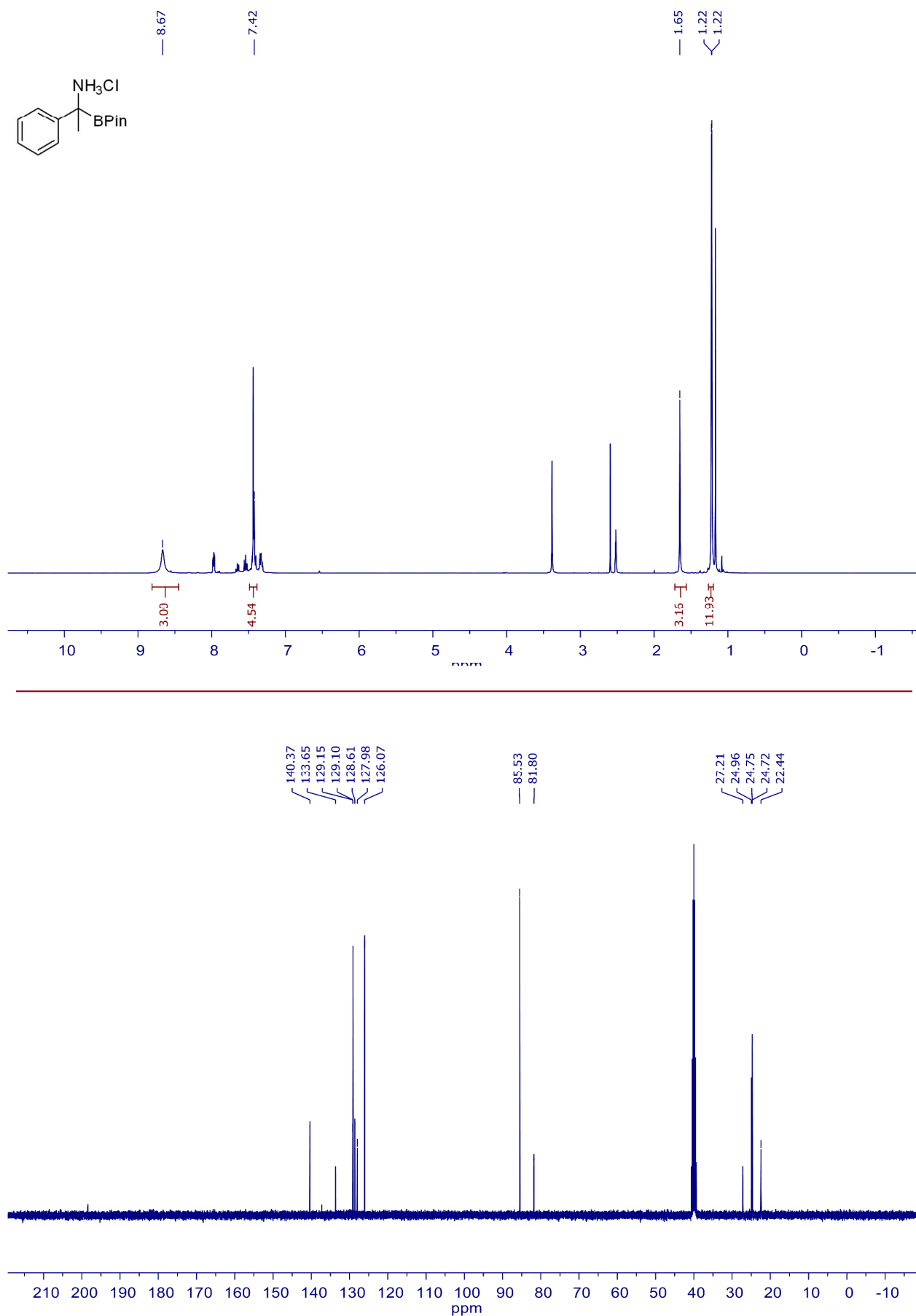
**Figure 23:** <sup>1</sup>H NMR (400 MHz, DMSO) spectrum (top) and <sup>13</sup>C NMR (100 MHz, DMSO) spectrum (bottom) of (4-chlorophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methanaminium chloride (3b).



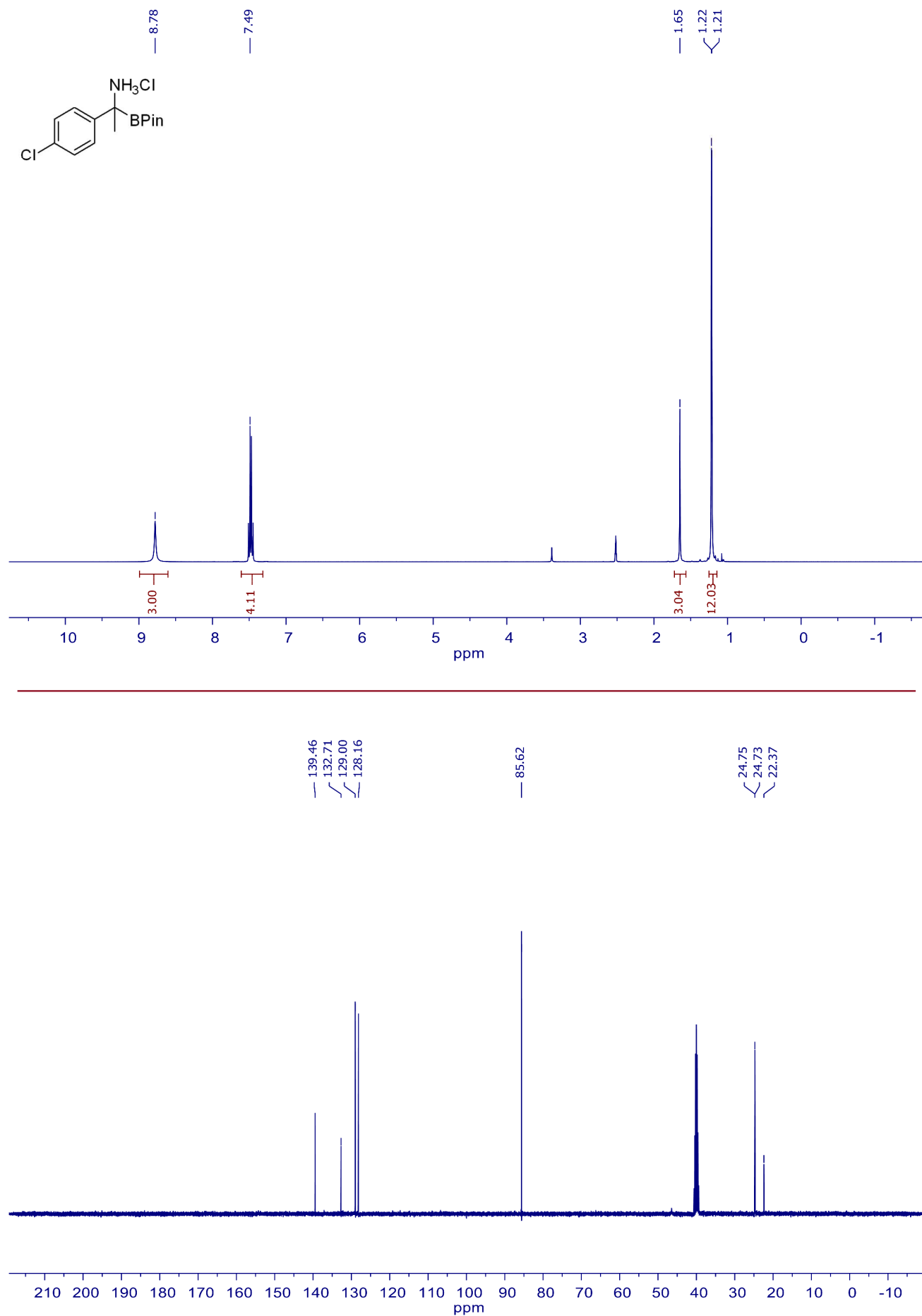
**Figure 24:** <sup>1</sup>H NMR (400 MHz, DMSO) spectrum (top) and <sup>13</sup>C NMR (100 MHz, DMSO) spectrum (bottom) of (4-bromophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methanaminium chloride (3c).



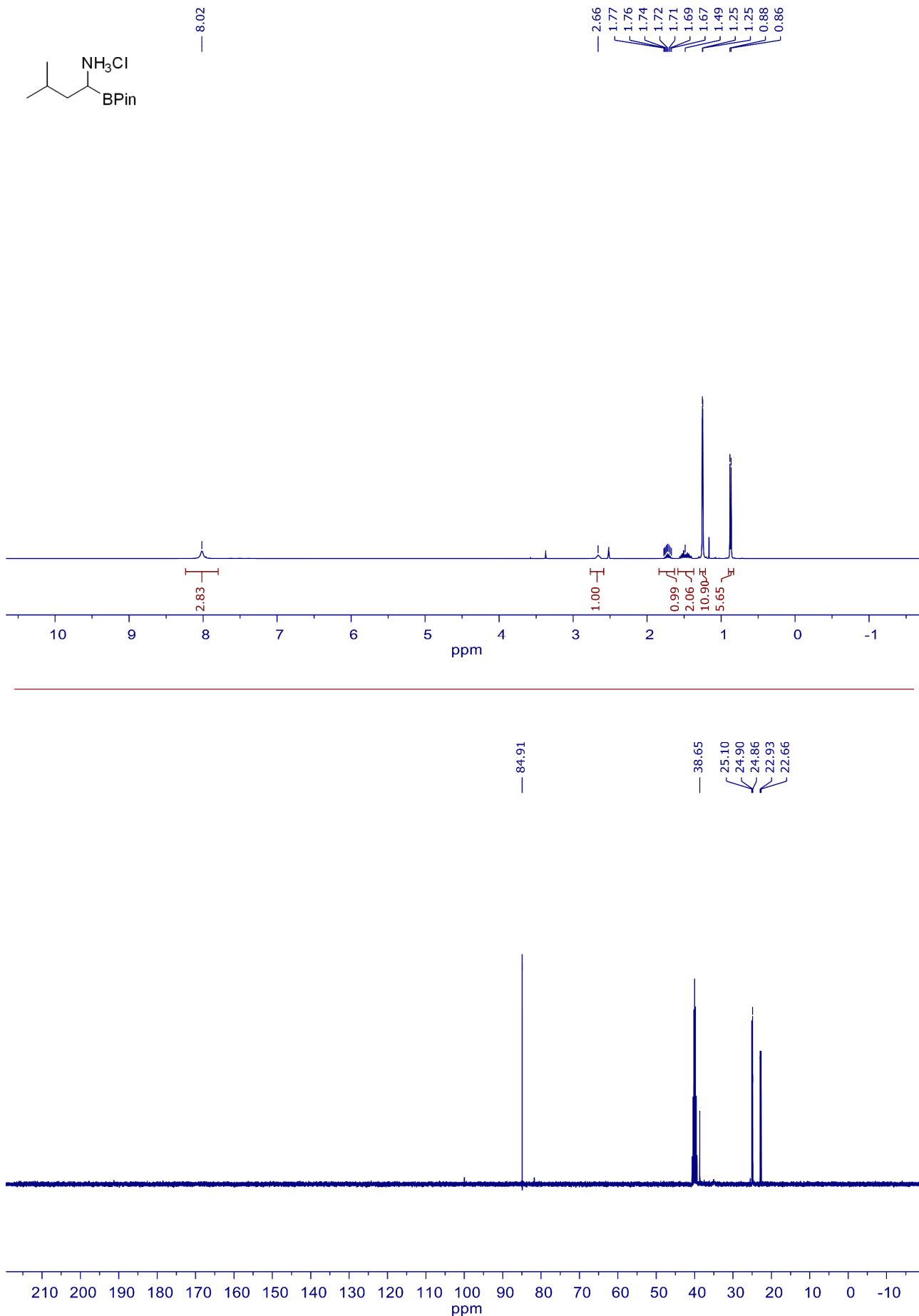
**Figure 25:** <sup>1</sup>H NMR (400 MHz, DMSO) spectrum (top) and <sup>13</sup>C NMR (100 MHz, DMSO) spectrum (bottom) of (4-methoxyphenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methanaminium chloride (3d).



**Figure 26:**  $^1\text{H}$  NMR (400 MHz, DMSO) spectrum (top) and  $^{13}\text{C}$  NMR (100 MHz, DMSO) spectrum (bottom) of 1-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethan-1-aminium chloride (**3e**).



**Figure 27:** <sup>1</sup>H NMR (400 MHz, DMSO) spectrum (top) and <sup>13</sup>C NMR (100 MHz, DMSO) spectrum (bottom) of 1-(4-chlorophenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethanamine hydrochloride (3f).



**Figure 28:** <sup>1</sup>H NMR (400 MHz, DMSO) spectrum (top) and <sup>13</sup>C NMR (100 MHz, DMSO) spectrum (bottom) of 3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-aminium chloride (3g).