

## Ligand-Free Ullmann-Type Arylation of Oxazolidinones by Diaryliodonium

### Salts

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## General information

All reagents and solvents were obtained from commercial sources and used without further purification from freshly opened containers. Amino alcohols **S1a**, **S1b**, **S1c** were obtained from commercial sources, while other amino alcohols was prepared from amino acids (see General procedure **GPI**). Anhydrous solvents were dried and distilled by standard techniques before use. Reactions were monitored with TLC (eluent hexane : EtOAc 3:1). The NMR spectra were recorded on a Bruker Avance 400 at ambient temperature; the residual solvent signal was used as the internal standard. <sup>1</sup>H NMR spectra were recorded at 400 MHz, <sup>13</sup>C NMR spectra were recorded at 100 MHz, and <sup>19</sup>F NMR spectra were recorded at 376 MHz. Chemical shifts are reported in parts per million (ppm).

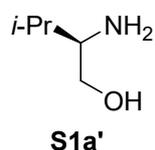
Chiral HPLC analyses were performed using Maestro (Interlab, Russia) chromatograph equipped with a high-pressure quaternary gradient pump, autosampler, column thermostat and UV detector with diode array. Separation of enantiomers was achieved on a Lux Cellulose-1 column (4.6 × 250 mm, 5 μm, Phenomenex, USA) equipped with a pre-column with the same sorbent and thermostatted at 30°C. The elution was carried out in isocratic mode using a mixture of hexane – isopropanol (80:20, v/v); flow rate was 1.5 mL/min.

A sample weighing of 1.3-1.5 mg was dissolved in 1 ml of the mobile phase and analyzed; the injection volume was 5 μl. The detection was done at the wavelengths of 210, 240, 265 and 280 nm, and the full UV spectrum in the range of 210-400 nm was recorded every 2 s. The chromatograph was controlled, data collected and processed using Clarity 8.2 software (DataApex, Prague, Czech Republic).

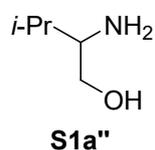
HRMS analysis was performed on a Bruker maXis spectrometer equipped with an electrospray ion source or on a Thermo Scientific DFS (Double Focusing System) with electron ionization (70 eV). The Bruker maXis spectrometer was operated in positive ion mode using an *m/z* range 50–1200. The nebulizer gas flow was 1.0 bar, and the drying gas flow was 4.0 L/min.

## General procedure for the preparation of amino alcohol (GP1)

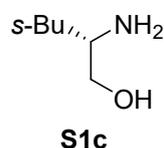
The preparation of amino alcohols was performed according to previous reported methods.<sup>1</sup> A Schlenk flask, fitted with a magnetic stir bar and a reflux condenser, was charged with a suspension of lithium aluminum hydride (2.0 equiv.) in 50 mL of tetrahydrofuran (THF). The mixture was cooled (5–10°C, ice bath) and amino acid (1 equiv.) was added portionwise and reaction was stirred for 1 hour at cooling. Then reaction mixture was warmed to room temperature and then refluxed overnight. The resulting mixture was cooled to 5–10°C on ice bath and treated with aqueous solution of NaOH (2M, 10 mL). The solution was extracted with boiling THF (50 mL), after that organic layers was concentrated in vacuo. Residue was diluted with DCM (50 mL), washed with brine (10 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuo to afford amino alcohol **S1**, which was used for the next step without further purification.



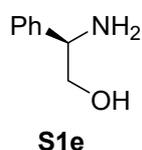
**D-Valinol ((R)-2-amino-3-methylbutan-1-ol, S1a')**.<sup>2</sup> The reaction of D-valine (14 mmol, 1.64 g) according to general procedure **GP1** afforded 0.90 g (63%) of **S1a'** isolated as the colorless oil. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 3.36 (dd, *J* = 10.4, 4.4 Hz, 2H), 3.13 (dd, *J* = 10.4, 7.6 Hz, 1H), 2.40 (dt, *J* = 7.2, 5.1 Hz, 1H), 1.61 – 1.50 (m, 1H), 0.84 (d, *J* = 7.2 Hz, 3H), 0.81 (d, *J* = 6.8 Hz, 3H).



**D,L-Valinol (2-amino-3-methylbutan-1-ol, S1a'')**.<sup>3</sup> The reaction of D,L-valine (21.3 mmol, 2.5 g) according to general procedure **GP1** afforded 1.17 g (11.4 mmol, 54%) of **S1a''** isolated as the colorless oil. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 3.35 (dd, *J* = 10.4, 4.8 Hz, 2H), 3.13 (dd, *J* = 10.4, 7.6 Hz, 1H), 2.40 (dt, *J* = 7.6, 5.1 Hz, 1H), 1.60 – 1.48 (m, 1H), 0.84 (d, *J* = 7.2 Hz, 3H), 0.81 (d, *J* = 6.8 Hz, 3H).



**L-Leucinol ((S)-2-amino-4-methylpentan-1-ol, S1c)**.<sup>4</sup> The reaction of L-Leucine (5 mmol, 0.655 g) according to general procedure **GP1** afforded 0.333 g (2.82 mmol, 56%) of **S1c** isolated as the colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.56 (dd, *J* = 8.8, 4.0 Hz, 1H), 3.22 (dd, *J* = 10.4, 8.0 Hz, 1H), 2.98 – 2.80 (m, 1H), 2.01 – 1.53 (m, 4H), 1.23 – 1.13 (m, 2H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H).

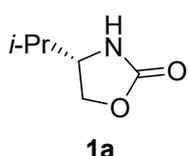


**D-Phenylglycinol ((R)-2-amino-2-phenylethan-1-ol, S1e)**.<sup>5</sup> The reaction of L-phenylglycine (5 mmol, 0.755 g) according to general procedure **GP1** afforded 0.576 g (84%) of **S1e** isolated as the yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.24 – 6.93

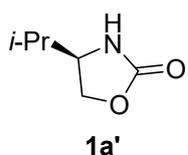
(m, 3H), 3.95 (dd,  $J = 8.4, 4.4$  Hz, 1H), 3.65 (dd,  $J = 10.8, 4.4$  Hz, 1H), 3.46 (dd,  $J = 10.8, 8.4$  Hz, 1H), 2.19 – 1.89 (m, 3H).

## General procedure for the preparation of oxazolidin-2-ones (GP2)

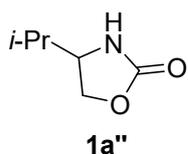
An amino alcohol (3 mmol, 1 equiv.) was dissolved in water (3 mL) in a round bottomed flask. Then, NaHCO<sub>3</sub> (5 mmol, 0.420 g, 1.67 equiv.) was added to reaction flask with subsequent followed by addition of CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The resulting biphasic mixture was vigorously stirred at room temperature before drop wise addition of ethyl chloroformate (3.15 mmol, 0.342 g, 0.3 mL, 1.05 equiv.) . The resulting mixture was stirred at room temperature for 2 hours. After, reaction mixture was concentrated in vacuo and residue was suspended in acetone. Anhydrous MgSO<sub>4</sub> was added to suspension and mixture was filtered and concentrated in vacuo. The crude carbamate was dissolved in acetonitrile and Cs<sub>2</sub>CO<sub>3</sub> (5.0 mmol, 1.625 g, 1.67 equiv.) was added. The reaction mixture was stirred at 90 °C for 4 hours. Then solvent was removed under reduced pressure and product was purified by silica gel column chromatography (eluent hexane : EtOAc, EtOAc 0→50%) or recrystallization (hexane:EtOAc 2:1) to give the desired product.



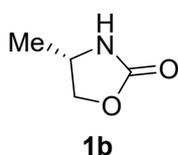
**(S)-4-isopropyl-oxazolidin-2-one (1a).**<sup>6</sup> The reaction of L-valinol (3 mmol, 0.309 g) according to general procedure **GP2** afforded 0.290 g (75 %) of **1a** isolated as the colorless crystalline solid; mp 71–73 °C (lit 72.3 °C).<sup>6</sup> Product was purified by recrystallization. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.90 (brs, 1H), 4.43 (t, *J* = 8.8 Hz, 1H), 4.08 (dd, *J* = 8.8, 6.4 Hz, 1H), 3.62 – 3.57 (m, 1H), 1.73 – 1.68 (m, 1H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H).



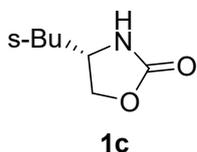
**(R)-4-isopropyl-oxazolidin-2-one (1a').**<sup>7</sup> The reaction of D-valinol (3 mmol, 0.309 g) according to general procedure **GP2** afforded 0.271 g (70 %) of **1a'** isolated as the colorless crystalline solid; mp 70–72 °C (lit 67–70 °C).<sup>7</sup> Product was purified by recrystallization. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.10 (brs, 1H), 4.45 (t, *J* = 8.6 Hz, 1H), 4.11 (dd, *J* = 8.6, 6.2 Hz, 1H), 3.64 – 3.56 (m, 1H), 1.79 – 1.67 (m, 1H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H).



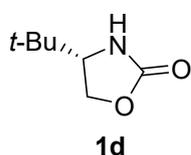
**4-isopropyl-oxazolidin-2-one (1a'').**<sup>8</sup> The reaction of DL-valinol (3 mmol, 0.309 g) according to general procedure **GP2** afforded 0.263 g (68 %) of **1a''** isolated as the colorless crystalline solid; mp 71–73 °C (lit 71–72 °C).<sup>8</sup> Product was purified by recrystallization. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.03 (brs, 1H), 4.45 (t, *J* = 8.6 Hz, 1H), 4.11 (dd, *J* = 8.2, 6.0 Hz, 1H), 3.66 – 3.57 (m, 1H), 1.81 – 1.66 (m, 1H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H).



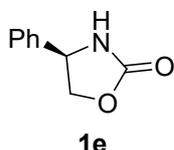
**(S)-4-methyloxazolidin-2-one (1b).**<sup>9</sup> The reaction of L-alaninol (3 mmol, 0.225 g) according to general procedure **GP2** afforded 0.222 g (73 %) of **1b** isolated as the colorless crystalline solid; mp 44–45 °C (lit 45.9 °C).<sup>9</sup> Product was purified by silica gel column chromatography. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.49 (t, *J* = 8.0 Hz, 1H), 4.03 – 3.92 (m, 2H), 1.29 (d, *J* = 6.0 Hz, 3H).



**(S)-4-sec-butyloxazolidin-2-one (1c).**<sup>10</sup> The reaction of L-leucinol (**S1c**, 3 mmol, 0.351 g) according to general procedure **GP2** afforded 0.296 g (69 %) of **1c** isolated as the colorless oil. Product was purified by silica gel column chromatography. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.03 (s, 1H), 4.53 – 4.46 (m, 1H), 4.01 – 3.90 (m, 2H), 1.70 – 1.53 (m, 2H), 1.42 – 1.32 (m, 1H), 0.93 (t, *J* = 6.0 Hz, 6H).



**(S)-4-tert-butyloxazolidin-2-one (1d).**<sup>11</sup> The reaction of L-tert-leucinol (3 mmol, 0.351 g) according to general procedure **GP2** afforded 0.305 g (71 %) of **1d** isolated as colorless crystalline solid; mp 114–115 °C (lit 115–116 °C).<sup>11</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.85 (s, 1H), 4.38 – 4.33 (m, 1H), 4.18 – 4.16 (m, 1H), 3.61 – 3.57 (m, 1H), 0.90 (s, 9H).



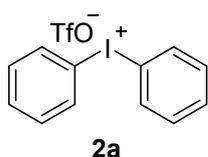
**(R)-4-phenyloxazolidin-2-one (1e).** The reaction of D-phenylglycinol (**S1e**, 3 mmol, 0.411 g) according to general procedure **GP2** afforded 0.332 g (69 %) of **1e** isolated as colorless crystalline solid; mp 127–128 °C (lit 124–126 °C).<sup>12</sup> Product was purified by silica gel column chromatography. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.40 – 7.13 (m, 5H), 4.90 (dd, *J* = 8.8, 6.4 Hz, 1H), 4.62 (d, *J* = 8.8 Hz, 1H), 3.93 (dd, *J* = 8.8, 6.4 Hz, 1H).

## Preparation of diaryliodonium salts

**Preparation of diaryliodonium salts 2b–c (GP3).** Sulfuric acid (2 mL) was added to a stirred mixture of iodine (2.5 mmol, 635 mg), Oxone (10 mmol, 6.17 g) and arene (1.5 mL) in acetonitrile (10 mL). The reaction mixture was stirred overnight and a solution of triflic acid (10 mmol, 0.88 mL) in water (10 mL) was added. Reaction mixture was extracted with DCM (3 × 20 mL) and combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and iodonium salt was isolated by precipitation from hexane (18 mL) and Et<sub>2</sub>O (2 mL) mixture. The product was filtered off, washed with hexane (3 × 5 mL) and dried *in vacuo*.

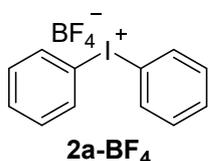
**Preparation of diaryliodonium salts 2d–e (GP4)** is based on the previously reported procedure.<sup>13</sup> Sulfuric acid (2 mL) was added to a stirred mixture of iodoarene (5 mmol), Oxone (5 mmol, 3.08 g) and arene (2 mL) in acetonitrile (10 mL). The reaction mixture was stirred overnight and a solution triflic acid (10 mmol, 0.88 mL) in water (10 mL) was added. The diaryliodonium salt was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL). The combined organic layers were dried with Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under the reduced pressure. A mixture of hexane (18 mL) and Et<sub>2</sub>O (2 mL) was added to the residue. The product was filtered off, washed with hexane (3 × 10 mL) and dried *in vacuo*.

**Preparation of diaryliodonium salts 2h–2o (GP5)** was performed following to the previously reported procedure.<sup>14</sup> Oxone (1.234 g, 2 mmol) and iodoarene (2 mmol) were added to mixture of DCM and TFA (3 mL, 1:1 v/v). The reaction mixture was stirred up to 1 hour at ambient temperature. Reaction was monitored by TLC (eluent Hexane : EtOAc 10:1 v/v), whereupon the solvent was evaporated to dryness at 40 °C, and solid residue was suspended in DCM (25 mL) and stirred for 30 min. The suspension was filtered off and an inorganic residue was washed with 25 mL of DCM. The solvent was removed to 3–5 mL residue in a flask and trifluoroethanol (TFE) (1.5 mL) and 1,3,5-trimethoxybenzene (2.1 mmol, 353 mg) were added to the mixture. After, the stirring was continued for 30 min at ambient temperature. The solvent was evaporated at 40 °C and cold Et<sub>2</sub>O (10 mL) was added to the residue. Product was filtered off and washed with cold Et<sub>2</sub>O (3 × 5 mL). The product was dried *in vacuo* (10 mbar) at ambient temperature.

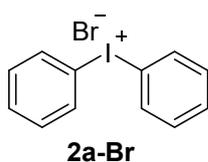


**Diphenyliodonium trifluoromethanesulfonate (2a).**<sup>15,16</sup> Preparation of **2a** is based on the previously reported procedure.<sup>15</sup> Iodobenzene (4.08 g, 20 mmol), benzene (3 mL, 34 mmol) and *m*CPBA (77%, 5.0 g, 22 mmol) dissolved in DCM (50 mL) at 0–5 °C. Then TfOH (3.54 mL, 40 mmol) was added dropwise and reaction mixture was refluxed for 30 min. The resulted solution was concentrated *in vacuo* followed by addition of cold Et<sub>2</sub>O (20 mL). Obtained precipitate was filtered off and washed with cold Et<sub>2</sub>O (3 × 10 mL)

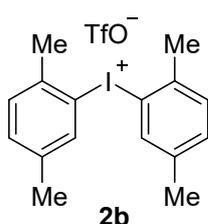
and dried in the air at RT. Product **2a** was isolated in 66% yield (5.634 g) as the colorless crystalline solid; mp 176–177 °C (lit 169–173 °C).<sup>16</sup> <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 8.24 (dd, *J* = 8.4, 0.8 Hz, 4H), 7.67 (t, *J* = 7.4 Hz, 2H), 7.53 (t, *J* = 7.8 Hz, 4H).



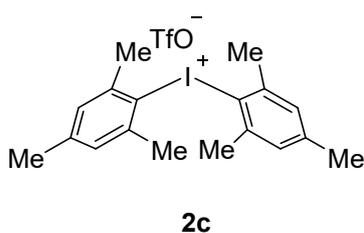
**Diphenyliodonium tetrafluoroborate (2a-BF<sub>4</sub>)**.<sup>17,18</sup> Preparation of **2a-BF<sub>4</sub>** based on the previously reported procedures.<sup>17</sup> BF<sub>3</sub>·Et<sub>2</sub>O (74 μL, 3 mmol) was added to solution of bis(trifluoroacetoxy)iodo]benzene (1.075 g, 2.5 mmol) in DCM (10 ml) at 0–5 °C and stirred for 30 min. Phenylboronic acid (336 mg, 2.75 mmol) was added to reaction mixture and solution was stirred overnight at RT. The resulting solution was concentrated in vacuo followed by addition of cold Et<sub>2</sub>O (10 mL). Obtained precipitate was filtered off and washed with cold Et<sub>2</sub>O (3×5 mL) and dried in the air at RT. Product **2a-BF<sub>4</sub>** was isolated in 65% yield (600 mg) as colorless crystalline solid; mp 118–120 °C (lit 133–135 °C).<sup>18</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.82 (d, *J* = 8.0 Hz, 4H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.8 Hz, 4H).



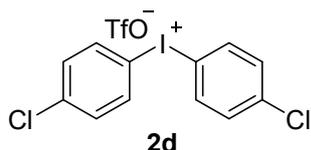
**Diphenyliodonium bromide (2a-Br)**. Preparation of **2a-Br** based on the previously reported procedure. Solution of KBr (595 mg, 5 mmol) in water (5 mL) was added to solution of diphenyliodonium triflate (430 mg, 1 mmol) in MeOH (5 mL) and stirred for 15 min. Obtained precipitate was filtered off and washed with water (3×5 mL) and dried in the air at RT. Product **2a-Br** was isolated in 95% yield (343 mg) as colorless crystalline solid. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.19 (d, *J* = 7.2 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H).



**Bis(2,5-dimethylphenyl)iodonium trifluoromethanesulfonate (2b)**.<sup>16</sup> The reaction of *p*-xylene (12.2 mmol, 1.5 mL), iodine (2.5 mmol, 635 mg), Oxone (5 mmol, 3.08 g), and sulfuric acid (2 mL) accordingly to described procedure **GP3** afforded 1.360 g (56%) of **2b** isolated as the colorless crystalline solid; mp 175–177 °C (lit 168–169 °C).<sup>16</sup> <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.13 (s, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 2.55 (s, 6H), 2.30 (s, 6H).

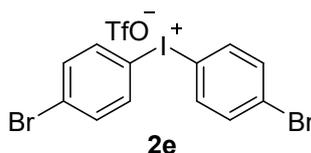


**Dimesityliodonium trifluoromethanesulfonate (2c)**.<sup>16</sup> The reaction of mesitylene (10.8 mmol, 1.5 mL), iodine (2.5 mmol, 635 mg), Oxone (5 mmol, 3.08 g), and sulfuric acid (2 mL) accordingly to described procedure **GP3** afforded 2.163 g (84%) of **2c** isolated as the colorless crystalline solid; mp 189–191 °C (lit 183–186 °C).<sup>16</sup> <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.19 (s, 2H), 2.46 (s, 12H), 2.29 (s, 6H).



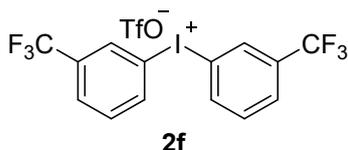
**Bis(4-chlorophenyl)iodonium trifluoromethanesulfonate (2d).**<sup>16</sup>

The reaction of 1-chloro-4-iodobenzene (5 mmol, 1.193 g), chlorobenzene (2 mL), Oxone (5 mmol, 3.08 g), and sulfuric acid (2 mL) accordingly to described procedure **GP4** afforded 1.933 g (77%) of **2d** isolated as the colorless crystalline solid; mp 183–185 °C (lit 183–187 °C).<sup>16</sup> <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.25 (d, *J* = 8.8 Hz, 4H), 7.62 (d, *J* = 8.8 Hz, 1H).



**Bis(4-bromophenyl)iodonium trifluoromethanesulfonate (2e).**<sup>16</sup>

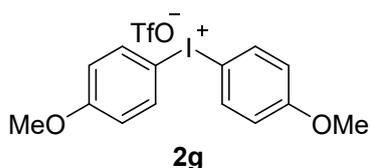
The reaction of 1-bromo-4-iodobenzene (5 mmol, 1.415 g), bromobenzene (2 mL), Oxone (5 mmol, 3.08 g), and sulfuric acid (2 mL) accordingly to described procedure **GP4** afforded 1.930 g (66%) of **2e** isolated as the colorless crystalline solid; mp 181–184 °C (lit 183–188 °C).<sup>16</sup> <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.17 (d, *J* = 8.8 Hz, 4H), 7.75 (d, *J* = 8.8 Hz, 4H).



**Bis(3-(trifluoromethyl)phenyl)iodonium**

**trifluoromethanesulfonate (2d).**<sup>19</sup> Preparation of **2d** is based on the previously reported procedure.<sup>20</sup> Iodine (2.84 mmol, 0.72g) and

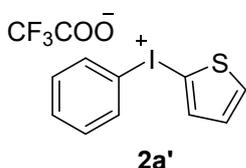
NaIO<sub>4</sub> (4.3 mmol, 0.92 g) were added to the conc. sulfuric acid (10 mL) and stirred at 75°C for 1h. Reaction mixture was cooled with water bath and benzotrifluoride (26 mmol, 3.8 mL) was added dropwise and obtained mixture was stirred overnight at ambient temperature. Next, ice was added to the reaction mixture and after completion of ice melting, aqueous solution of TfOH (20 mmol, 1.77 mL) was added. Resulted mixture was extracted with DCM (3 × 20 mL) and combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. The mixture of hexane (18 mL) and Et<sub>2</sub>O (2 mL) was added to the residue. The product was filtered off and washed with hexane (3 × 10 mL). Product **2f** was dried under vacuo and isolated in 57% yield (3.243 g) as colorless crystalline solid; mp 95–102 °C (lit 90–91 °C).<sup>19</sup> <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.81 (s, 2H), 8.60 (d, *J* = 8.0 Hz, 2H), 8.07 (d, *J* = 7.6 Hz, 2H), 7.79 (t, *J* = 8.0 Hz, 2H).



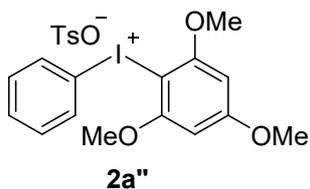
**Bis(4-methoxyphenyl)iodonium trifluoromethanesulfonate (2g).** Preparation of **2d** is based on the previously reported

procedures.<sup>20,21</sup> Iodine (5.7 mmol, 1.45 g) was added to mixture of anisole (20 mmol, 2.2 mL), *m*-CPBA (77%, 14.3 mmol, 3.2 g), *p*-TsOH·H<sub>2</sub>O (19.4 mmol, 3.8 g) in DCM (50 mL). Solution was stirred overnight at room temperature. Then solvent was removed under reduced pressure, residue was precipitated by

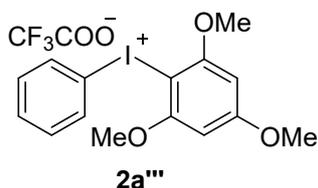
addition of Et<sub>2</sub>O, filtered and washed with Et<sub>2</sub>O (3×15 mL). Obtained iodonium tosylate was dried in the air at room temperature for 4 h and dissolved in DCM (50 mL). The resulted solution was washed with cooled aqueous solution of NaOTf (100 mL) prepared by mixing solutions of NaOH (100 mmol, 4 g in 50 mL of H<sub>2</sub>O) and TfOH (100 mmol, 8.8 mL in 50 mL of H<sub>2</sub>O). Organic layer was dried over MgSO<sub>4</sub> and solvent was removed under reduced pressure. The product was precipitated by Et<sub>2</sub>O, filtered, washed with cold Et<sub>2</sub>O (3×15 mL) and dried in the air at room temperature. Product **2g** was isolated in 66% yield (3.79 g, 7.7 mmol) as the colorless crystalline solid; mp 116–125°C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.13 (d, *J* = 9.2 Hz, 4H), 7.06 (d, *J* = 8.8 Hz, 4H), 3.79 (s, 6H).



**Phenyl(thiophen-2-yl)iodonium trifluoroacetate (2a')**.<sup>22</sup> Compound **2a'** was prepared according previously reported procedure. The thiophene (2.1 mmol, 88 μL) was added to solution of bis(trifluoroacetoxy)iodobenzene (2 mmol, 860 mg) in DCM (5 mL) and reaction mixture was stirred at room temperature for 30 min. Then solvent was removed in vacuo and Et<sub>2</sub>O (15 mL) was added to residue. Product was filtered and dried at room temperature; mp 147–148 °C (lit 152–154 °C). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.25 (d, *J* = 8.0 Hz, 2H), 8.07 (d, *J* = 4.0 Hz, 1H), 7.96 (d, *J* = 4.8 Hz, 1H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.21 – 7.13 (m, 1H).

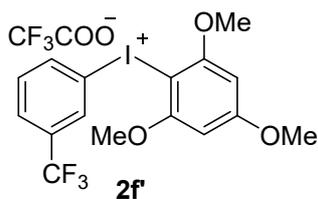


**Phenyl(2,4,6-trimethoxyphenyl)iodonium tosylate (2a'')**<sup>23</sup> was prepared according to the previously reported procedure.<sup>23</sup> *m*CBPA (77%, 2.6 mmol, 588 mg) was added to mixture of iodobenzene (2.5 mmol, 510 mg) and *p*-TsOH·H<sub>2</sub>O (2.62 mmol, 499 mg) in MeCN (5 mL) and reaction mixture was heated at 77 °C for 30 min. Next, 1,3,5-trimethoxybenzene (2.62 mmol, 441 mg) was added and reaction mixture was heated at 77 °C for 5 min. The resulted solution was concentrated in vacuo followed by addition of cold Et<sub>2</sub>O (10 mL). Obtained precipitate was filtered off and washed with cold Et<sub>2</sub>O (3×5 mL) and dried in the air at ambient temperature. Product **2aa''** was isolated in 75% yield (1.02 g) as the colorless crystalline solid; mp 174–176 °C (lit decomp. 167 °C).<sup>23</sup> <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.91 (d, *J* = 7.2 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.47 (m, 4H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.46 (s, 2H), 3.94 (s, 6H), 3.87 (s, 3H), 2.28 (s, 3H).



**Phenyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate (2a''')**.<sup>22,24</sup> Compound **2a'''** was prepared according previously

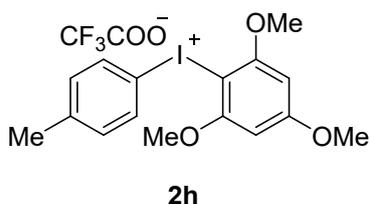
reported procedure. The trimethoxybenzene (10.1 mmol, 1.7 g) was added to solution of bis(trifluoroacetoxy)iodobenzene (10 mmol, 4.3 g) in DCM (50 mL) and reaction mixture was stirred at room temperature for 30 min. Then solvent was removed in vacuo and Et<sub>2</sub>O (50 mL) was added to residue. Product was filtered and dried at room temperature. Product **2a''** was isolated in 83% yield (4.0 g) as the colorless crystalline solid; mp 158–164 °C (lit 153–155 °C).<sup>22</sup> <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.91 (d, *J* = 7.6 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 6.46 (s, 2H), 3.94 (s, 6H), 3.87 (s, 3H).



**(3-(Trifluoromethyl)phenyl)(2,4,6-trimethoxyphenyl)iodonium**

**trifluoroacetate (2f).**<sup>22</sup> The reaction of 3-iodobenzotrifluoride

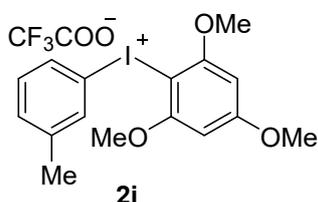
(5 mmol, 1.36 g), and 1,3,5-trimethoxybenzene (5.1 mmol, 2.80 g) accordingly to procedure **GP5** afforded 1.44 g (52%) of **2f** isolated as the colorless crystalline solid; mp 157–158 °C (lit 158–160 °C).<sup>25</sup> <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.33 (s, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.69 (t, *J* = 8.0 Hz, 1H), 6.48 (s, 2H), 3.94 (s, 6H), 3.87 (s, 3H).



***p*-Tolyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate**

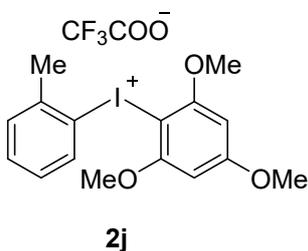
**(2h).**<sup>22,24</sup> The reaction of 1-iodo-4-methylbenzene (5 mmol, 1.09

g), and 1,3,5-trimethoxybenzene (5.1 mmol, 2.80 g) accordingly to procedure afforded **GP5** 1.40 g (58%) of **2h** isolated as the colorless crystalline solid; mp 164–166 °C (lit 163–165 °C).<sup>24</sup> <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.45 (s, 2H), 3.94 (s, 6H), 3.86 (s, 3H), 2.32 (s, 3H).



***m*-Tolyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate (2i).**<sup>26</sup>

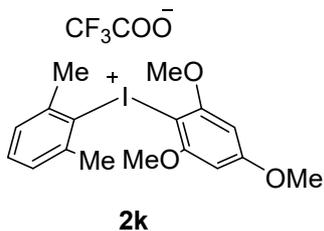
The reaction of 1-iodo-3-methylbenzene (5 mmol, 1.09 g), and 1,3,5-trimethoxybenzene (5.1 mmol, 2.80 g) accordingly to procedure afforded **GP5** 1.60 g (65 %) of **2i** isolated as the colorless crystalline solid; mp 172–173 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.74 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 6.16 (s, 2H), 3.88 (s, 6H), 3.86 (s, 3H), 2.33 (s, 3H).



***o*-Tolyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate (2j).**<sup>26</sup>

The reaction of 1-iodo-2-methylbenzene (5 mmol, 1.09 g), and 1,3,5-trimethoxybenzene (5.1 mmol, 2.80 g) accordingly to procedure afforded **GP5** 1.77 g (71 %) of **2j** isolated as the colorless crystalline

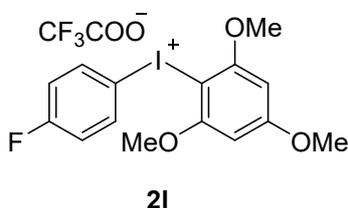
solid; mp 168–169 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.05 (d, *J* = 7.6 Hz, 1H), 7.57 – 7.47 (m, 2H), 7.28 – 7.17 (m, 1H), 6.44 (s, 2H), 3.95 (s, 6H), 3.85 (s, 3H), 2.59 (s, 3H).



**(2,6-Dimethylphenyl)(2,4,6-trimethoxyphenyl)iodonium**

**trifluoroacetate (2k).** The reaction of 2-iodo-1,3-dimethylbenzene (5 mmol, 1.16 g), and 1,3,5-trimethoxybenzene (5.1 mmol, 2.80 g) accordingly to procedure afforded **GP5** 1.55 g (61 %) of **2k** isolated as the colorless crystalline solid; mp 150–151 °C. <sup>1</sup>H NMR (400 MHz,

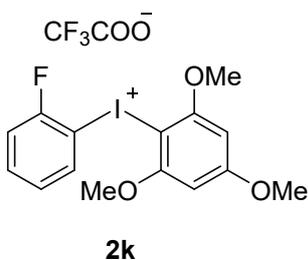
DMSO-*d*<sub>6</sub>) δ 7.40 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 2H), 6.45 (s, 2H), 3.89 (s, 6H), 3.85 (s, 3H), 2.60 (s, 6H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 165.9, 159.6, 157.67 (q, *J* = 30 Hz), 142.0, 132.1, 128.6, 125.4, 117.4 (q, *J* = 299 Hz), 92.2, 84.2, 57.0, 56.2, 25.9.



**(4-Fluorophenyl)(2,4,6-trimethoxyphenyl)iodonium**

**trifluoroacetate (2l).** The reaction of 1-fluoro-4-iodobenzene (5 mmol, 1.11 g), and 1,3,5-trimethoxybenzene (5.1 mmol, 2.80 g) accordingly to procedure afforded **GP5** 1.31 g (52 %) of **2l** isolated

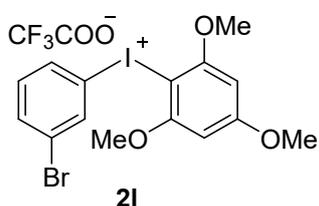
as the colorless crystalline solid; mp 157–160 °C (lit 165–169 °C).<sup>24</sup> <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.97 (dd, *J* = 8.8, 5.2 Hz, 2H), 7.33 (t, *J* = 8.8 Hz, 2H), 6.46 (s, 2H), 3.94 (s, 6H), 3.86 (s, 3H).



**(2-Fluorophenyl)(2,4,6-trimethoxyphenyl)iodonium**

**trifluoroacetate (2m).** The reaction of 1-fluoro-2-iodobenzene (5 mmol, 1.11 g), and 1,3,5-trimethoxybenzene (5.1 mmol, 2.80 g) accordingly to procedure afforded **GP5** 1.71 g (68 %) of **2m** isolated as the colorless crystalline solid; mp 180–181 °C. <sup>1</sup>H NMR (400 MHz,

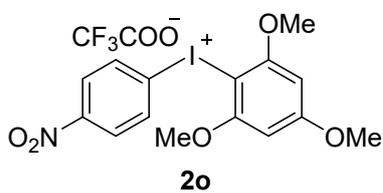
DMSO-*d*<sub>6</sub>) δ 8.09 (t, *J* = 6.6 Hz, 1H), 7.71 – 7.61 (m, 1H), 7.51 (t, *J* = 8.4 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 6.44 (s, 2H), 3.93 (s, 6H), 3.85 (s, 3H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 166.1, 159.38, 159.37 (d, *J* = 249.7 Hz), 157.76 (q, *J* = 30 Hz), 137.2, 134.92 (d, *J* = 8 Hz), 127.25 (d, *J* = 3 Hz), 117.37 (q, *J* = 299 Hz), 116.65 (d, *J* = 22 Hz), 103.69 (d, *J* = 24 Hz), 92.0, 87.6, 57.3, 56.2. <sup>19</sup>F NMR (376 MHz, DMSO-*d*<sub>6</sub>) δ -73.43, -97.90 (dt, *J* = 8.3, 5.8 Hz).



**(3-Bromophenyl)(2,4,6-trimethoxyphenyl)iodonium**

**trifluoroacetate (2n).** The reaction of 1-bromo-3-iodobenzene (5 mmol, 1.42 g), and 1,3,5-trimethoxybenzene (5.1 mmol, 2.80 g) accordingly to procedure afforded **GP5** 1.99 g (71 %) of **2n** isolated as

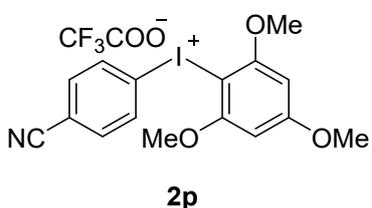
the colorless crystalline solid; mp 147–153 °C (lit. 148–152 °C).<sup>25</sup> <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.15 (s, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 6.48 (s, 2H), 3.95 (s, 9H), 3.87 (s, 4H).



**(4-Nitrophenyl)(2,4,6-trimethoxyphenyl)iodonium**

**trifluoroacetate (2o).**<sup>24,27</sup> The reaction of 1-iodo-4-nitrobenzene (5 mmol, 1.25 g), and 1,3,5-trimethoxybenzene (5.1 mmol, 2.80 g) accordingly to procedure **GP5** afforded 2.01 g (76%) of **2o** as

the beige crystalline solid; mp 152–154 °C (lit 159–161 °C).<sup>25</sup> <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.23 (d, *J* = 8.8 Hz, 2H), 8.14 (d, *J* = 8.8 Hz, 2H), 6.49 (s, 2H), 3.94 (s, 6H), 3.88 (s, 3H).



**(4-Cyanophenyl)(2,4,6-trimethoxyphenyl)iodonium**

**trifluoroacetate (2p).**<sup>24</sup> The reaction of 4-iodobenzonitrile (5 mmol, 1.15 g), and 1,3,5-trimethoxybenzene (5.1 mmol, 2.80 g) accordingly to procedure **GP5** afforded 2.06 g (81%) of **2p** as

isolated as the colorless crystalline solid; mp 174–176 °C (lit 175–176 °C).<sup>25</sup> <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.07 (d, *J* = 8.4 Hz, 2H), 7.92 (d, *J* = 8.4 Hz, 2H), 6.49 (s, 2H), 3.93 (s, 6H), 3.88 (s, 3H).

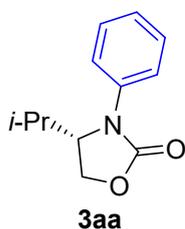
## Preparation of N-aryl oxazolidinones

### General procedure for the preparation of N-aryl oxazolidinones (GP6)

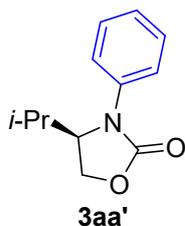
A screw cap vial was charged with mixture of oxazolidinone (**1a-e**, 0.5 mmol), symmetrical diaryliodonium salt (0.75 mmol) and CuI (10 mol%, 9.5 mg) and flashed with argon. Then the solution of triethylamine (0.75 mmol, 104  $\mu$ L) in toluene (5 ml) was added to mixture under argon atmosphere. Resulted mixture was heated at 80 °C for 24 hours. Solvent was removed under reduced pressure and product was purified by silica gel column chromatography (eluent hexane : EtOAc, EtOAc 0 $\rightarrow$ 50%).

### General procedure for the preparation of N-aryl oxazolidinones (GP7)

A screw cap vial was charged with mixture of oxazolidinone (**1a-e**, 0.5 mmol), aryl(2,4,6-trimethoxyphenyl)iodonium salt (0.75 mmol) and CuI (10 mol%, 9.5 mg) and flashed with argon. Then the solution of triethylamine (0.75 mmol, 104  $\mu$ L) in toluene (5 ml) was added to mixture under argon atmosphere. Resulted mixture was heated at 60 °C for 24 hours. Solvent was removed under reduced pressure and product was purified by silica gel column chromatography (eluent hexane : EtOAc, EtOAc 0 $\rightarrow$ 50%).



**(S)-4-isopropyl-3-phenyloxazolidin-2-one (3aa)**.<sup>28,29</sup> The reaction of (*S*)-4-isopropyl-oxazolidin-2-one (**1a**, 0.5 mmol, 65 mg), diphenyliodonium triflate (**2a**, 0.75 mmol, 323 mg) according to general procedure **GP6** afforded 97 mg (94%) of **3aa** isolated as the colorless crystalline solid; mp 88–89 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.45 (d, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 4.48 – 4.36 (m, 2H), 4.29 – 4.18 (m, 1H), 2.19 – 2.05 (m, 1H), 0.90 (d, *J* = 7.2 Hz, 3H), 0.84 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  156.2, 136.8, 129.3, 125.4, 122.4, 62.6, 60.6, 27.7, 17.8, 14.3. HRMS (ESI): *m/z* calcd. for [M+H]<sup>+</sup> C<sub>12</sub>H<sub>16</sub>NO<sub>2</sub><sup>+</sup>: 206.1176, found 206.1179.

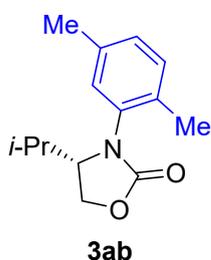


**(R)-4-isopropyl-3-phenyloxazolidin-2-one (3aa')**. The reaction of (*R*)-4-isopropyl-oxazolidin-2-one (**1a'**, 0.5 mmol, 65 mg), diphenyliodonium triflate (0.75 mmol, 323 mg) according to general procedure **GP6** afforded 92 mg (90%) of **3aa'** isolated as the colorless crystalline solid; mp 86–87 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.45 (d, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 4.49 – 4.36 (m, 2H), 4.30 – 4.19 (m, 1H), 2.21 – 2.04 (m, 1H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.85 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  156.2, 136.8, 129.3, 125.5, 122.4, 62.6,

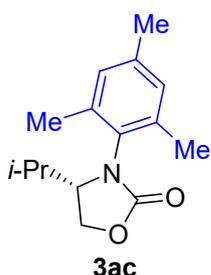
60.6, 27.7, 17.9, 14.3. HRMS (ESI):  $m/z$  calcd. for  $[M+H]^+$   $C_{12}H_{16}NO_2^+$ : 206.1176, found 206.1172.



**4-isopropyl-3-phenyloxazolidin-2-one (3aa).**<sup>28,29</sup> The reaction of 4-isopropyl-oxazolidin-2-one (**1a**, 0.5 mmol, 65 mg), diphenyliodonium triflate (0.75 mmol, 323 mg) according to general procedure **GP6** afforded 98 mg (96%) of **3aa** isolated as the colorless crystalline solid; mp 55–56 °C. <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.45 (d,  $J = 8.4$  Hz, 2H), 7.39 (t,  $J = 7.8$  Hz, 2H), 7.19 (t,  $J = 7.2$  Hz, 1H), 4.49 – 4.36 (m, 2H), 4.31 – 4.19 (m, 1H), 2.20 – 2.05 (m, 1H), 0.90 (d,  $J = 6.8$  Hz, 3H), 0.85 (d,  $J = 6.8$  Hz, 3H). <sup>13</sup>C NMR (100 MHz,  $CDCl_3$ )  $\delta$  156.2, 136.8, 129.3, 125.4, 122.4, 62.6, 60.6, 27.6, 17.8, 14.3. HRMS (ESI):  $m/z$  calcd. for  $[M+H]^+$   $C_{12}H_{16}NO_2^+$ : 206.1176, found 206.1172.

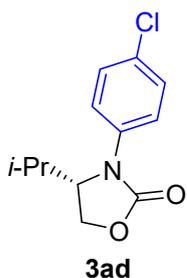


**(S)-3-(2,5-dimethylphenyl)-4-isopropylloxazolidin-2-one (3ab).** The reaction of (*S*)-4-isopropyl-oxazolidin-2-one (**1a**, 0.5 mmol, 65 mg), bis(2,5-dimethylphenyl)iodonium trifluoromethanesulfonate (**2b**, 0.75 mmol, 365 mg) according to general procedure **GP6** afforded 89 mg (76%) of **3ab** isolated as the colorless crystalline solid; mp 89–90 °C. <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.15 (d,  $J = 7.6$  Hz, 1H), 7.10 – 6.98 (m, 2H), 4.45 (t,  $J = 8.8$  Hz, 1H), 4.31 – 4.09 (m, 2H), 2.32 (s, 3H), 2.27 (s, 3H), 1.96 – 1.81 (m, 1H), 0.95 (d,  $J = 6.4$  Hz, 3H), 0.84 (d,  $J = 7.2$  Hz, 3H). <sup>13</sup>C NMR (100 MHz,  $CDCl_3$ )  $\delta$  157.1, 136.6, 135.0, 132.8, 131.5, 129.0, 63.8, 62.5, 28.8, 21.0, 18.4, 17.9, 15.2. HRMS (ESI):  $m/z$  calcd. for  $[M+H]^+$   $C_{14}H_{20}NO_2^+$ : 234.1489, found 234.1489.

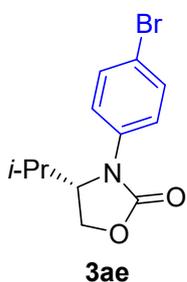


**(S)-4-isopropyl-3-mesityloxazolidin-2-one (3ac).** The reaction of (*S*)-4-isopropyl-oxazolidin-2-one (**1a**, 0.5 mmol, 65 mg), dimesityliodonium trifluoromethanesulfonate (**2c**, 0.75 mmol, 386 mg) according to general procedure **GP6** afforded 38 mg (31%) of **3ac** isolated as the colorless oily liquid. <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ )  $\delta$  6.92 (s, 1H)\*, 6.90 (s, 1H)\*, 4.50 (t,  $J = 8.6$  Hz, 1H), 4.25 (dd,  $J = 9.0, 6.6$  Hz, 1H), 3.99 – 3.89 (m, 1H), 2.29 (s, 3H), 2.27 (s, 3H), 2.23 (s, 3H), 1.90 – 1.78 (m, 1H), 0.96 (d,  $J = 6.4$  Hz, 3H), 0.71 (d,  $J = 6.8$  Hz, 3H). <sup>13</sup>C NMR (100 MHz,  $CDCl_3$ )  $\delta$  157.2, 138.2, 137.8, 135.4, 131.8, 132.0, 129.91, 129.85, , 65.5, 63.1, 30.8, 21.0, 19.6, 18.9, 18.5, 17.0. HRMS (ESI):  $m/z$  calcd. for  $[M+H]^+$   $C_{15}H_{22}NO_2^+$ : 248.1645, found 248.1645.

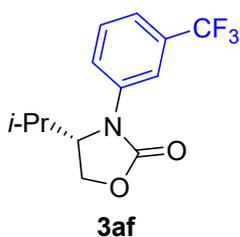
\*The multiplicity related to sterically hindrance of both mesityl group and substituents of oxazolidinones that lead to magnetic inequivalence of H-atoms of mesityl group. Similar phenomenon was observed in <sup>1</sup>H spectrum of 5-isopropyl-1-mesitylpyrrolidin-2-one.<sup>31</sup>



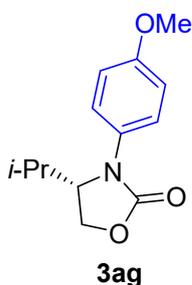
**(S)-3-(4-chlorophenyl)-4-isopropylloxazolidin-2-one (3ad).** The reaction of (*S*)-4-isopropyl-oxazolidin-2-one (**1a**, 0.5 mmol, 65 mg), bis(4-chlorophenyl)iodonium trifluoromethanesulfonate (**2d**, 0.75 mmol, 374 mg) according to general procedure **GP6** afforded 106 mg (88%) of **3ad** isolated as the colorless crystalline solid; mp 97–99 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.41 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 9.2 Hz, 2H), 4.47 – 4.34 (m, 2H), 4.30 – 4.18 (m, 1H), 2.19 – 2.04 (m, 1H), 0.91 (d, *J* = 7.2 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 155.9, 135.5, 130.7, 129.4, 123.4, 62.6, 60.5, 27.6, 17.8, 14.3. HRMS (ESI): *m/z* calcd. for [M+H]<sup>+</sup> C<sub>12</sub>H<sub>15</sub>ClNO<sub>2</sub><sup>+</sup>: 240.0786, found 240.0789.



**(S)-3-(4-Bromophenyl)-4-isopropylloxazolidin-2-one (3ae).** The reaction of (*S*)-4-isopropyl-oxazolidin-2-one (**1a**, 0.5 mmol, 65 mg), bis(4-bromophenyl)iodonium trifluoromethanesulfonate (**2e**, 0.75 mmol, 441 mg) according to general procedure **GP6** afforded 125 mg (87%) of **3ae** isolated as the colorless crystalline solid; mp 99–100 °C (lit 80 °C).<sup>30</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.50 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 2H), 4.46 – 4.35 (m, 2H), 4.29 – 4.19 (m, 1H), 2.19 – 2.05 (m, 1H), 0.91 (d, *J* = 6.8 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 155.8, 136.0, 132.4, 123.6, 118.4, 62.6, 60.4, 27.6, 17.8, 14.3. HRMS (ESI): *m/z* calcd. for [M+H]<sup>+</sup> C<sub>12</sub>H<sub>15</sub>BrNO<sub>2</sub><sup>+</sup>: 284.0281, found 284.0280.

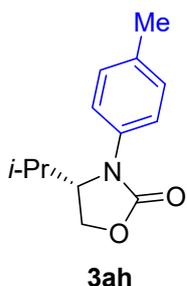


**(S)-4-isopropyl-3-(3-(trifluoromethyl)phenyl)oxazolidin-2-one (3af).** The reaction of (*S*)-4-isopropyl-oxazolidin-2-one (**1a**, 0.5 mmol, 65 mg), bis(3-(trifluoromethyl)phenyl)iodonium trifluoromethanesulfonate (**2f**, 0.75 mmol, 425 mg) according to general procedure **GP6** afforded 99 mg (72%) of **3af** isolated as the oily liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.72 (s, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 4.53 – 4.39 (m, 2H), 4.27 (dd, *J* = 8.1, 3.8 Hz, 1H), 2.13 (pd, *J* = 6.9, 3.3 Hz, 1H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.84 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 155.8, 137.6, 131.2 (q, *J* = 32 Hz), 129.9, 125.0, 123.8 (q, *J* = 4 Hz), 118.3 (q, *J* = 4 Hz), 121.82, 62.7, 60.3, 27.6, 17.8, 14.3. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ –62.66. HRMS (ESI): *m/z* calcd. for [M+Na]<sup>+</sup> C<sub>13</sub>H<sub>14</sub>F<sub>3</sub>NNaO<sub>2</sub><sup>+</sup>: 296.0869, found 296.0867.

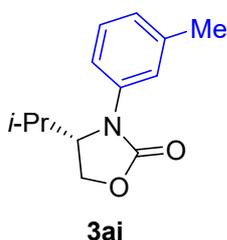


**(S)-4-isopropyl-3-(4-methoxyphenyl)oxazolidin-2-one (3ag).** The reaction of (*S*)-4-isopropyl-oxazolidin-2-one (**1a**, 0.5 mmol, 65 mg), bis(4-methoxyphenyl)iodonium trifluoromethanesulfonate (**2g**, 0.75 mmol, 367 mg)

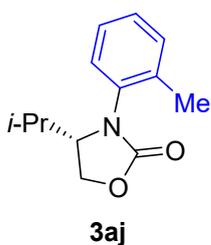
according to general procedure **GP6** afforded 80 mg (68%) of **3ag** isolated as the oily liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 (d,  $J = 8.8$  Hz, 2H), 6.92 (d,  $J = 8.8$  Hz, 2H), 4.41 (t,  $J = 8.6$  Hz, 1H), 4.35 – 4.29 (m, 1H), 4.21 (dd,  $J = 8.4, 4.8$  Hz, 1H), 3.80 (s, 3H), 0.88 (d,  $J = 7.2$  Hz, 3H), 0.86 (d,  $J = 6.8$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.5, 156.7, 129.7, 124.8, 114.6, 62.8, 61.4, 55.6, 27.9, 17.9, 14.5. HRMS (EI):  $m/z$  calcd. for  $[\text{M}]^+ \text{C}_{13}\text{H}_{17}\text{NO}_3^+$ : 235.1203, found 235.1206.



**(S)-4-isopropyl-3-(p-tolyl)oxazolidin-2-one (3ah).** The reaction of (*S*)-4-isopropyl-oxazolidin-2-one (**1a**, 0.5 mmol, 65 mg), *p*-tolyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate (**2h**, 0.75 mmol, 373 mg) according to general procedure **GP7** afforded 52 mg (47%) of **3ah** isolated as the colorless crystalline solid; mp 103–104 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (d,  $J = 8.4$  Hz, 2H), 7.19 (d,  $J = 8.0$  Hz, 2H), 4.46 – 4.33 (m, 2H), 4.28 – 4.16 (m, 1H), 2.34 (s, 3H), 2.16 – 2.02 (m, 1H), 0.89 (d,  $J = 6.8$  Hz, 3H), 0.84 (d,  $J = 6.8$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.4, 135.4, 134.2, 129.9, 122.6, 62.6, 60.9, 27.7, 21.1, 17.9, 14.4. HRMS (ESI):  $m/z$  calcd. for  $[\text{M}+\text{Na}]^+ \text{C}_{13}\text{H}_{17}\text{NNaO}_2^+$ : 242.1151, found 242.1151.

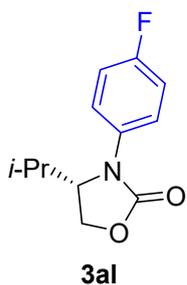


**(S)-4-isopropyl-3-(m-tolyl)oxazolidin-2-one (3ai).** The reaction of (*S*)-4-isopropyl-oxazolidin-2-one (**1a**, 0.5 mmol, 65 mg), *m*-tolyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate (**2i**, 0.75 mmol, 373 mg) according to general procedure **GP7** afforded 68 mg (62%) of **3ai** isolated as colorless oily liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 – 7.25 (m, 2H), 7.21 (d,  $J = 8.4$  Hz, 1H), 7.02 (d,  $J = 7.2$  Hz, 1H), 4.47 – 4.37 (m, 2H), 4.30 – 4.19 (m, 1H), 2.38 (s, 3H), 2.20 – 2.04 (m, 1H), 0.91 (d,  $J = 7.2$  Hz, 3H), 0.86 (d,  $J = 6.8$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.2, 139.3, 136.7, 129.1, 126.4, 123.3, 119.5, 62.6, 60.8, 27.7, 21.7, 17.9, 14.3. HRMS (ESI):  $m/z$  calcd. for  $[\text{M}+\text{Na}]^+ \text{C}_{13}\text{H}_{17}\text{NNaO}_2^+$ : 242.1151, found 242.1151.

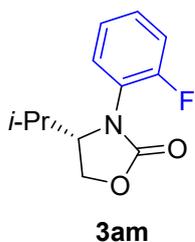


**(S)-4-isopropyl-3-(o-tolyl)oxazolidin-2-one (3aj).** The reaction of (*S*)-4-isopropyl-oxazolidin-2-one (**1a**, 0.5 mmol, 65 mg), *o*-tolyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate (**2j**, 0.75 mmol, 373 mg) according to general procedure **GP7** afforded 41 mg (37%) of **3aj** isolated as colorless oily liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26 – 7.10 (m, 4H), 4.40 (t,  $J = 8.6$  Hz, 1H), 4.24 – 4.05 (m, 2H), 2.26 (s, 3H), 1.90 – 1.73 (m, 1H), 0.88 (d,  $J = 6.8$  Hz, 3H), 0.77 (d,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.0, 136.2, 135.2, 131.8, 128.1,

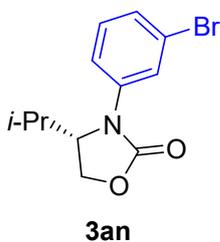
126.9, 63.9, 62.5, 28.9, 18.4, 18.3, 15.3. HRMS (ESI):  $m/z$  calcd. for  $[M+Na]^+ C_{13}H_{17}NNaO_2^+$ : 242.1151, found 242.1150.



**(S)-3-(4-fluorophenyl)-4-isopropylloxazolidin-2-one (3al).** The reaction of (*S*)-4-isopropyl-oxazolidin-2-one (**1a**, 0.5 mmol, 65 mg), (4-fluorophenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate (**2l**, 0.75 mmol, 377 mg) according to general procedure **GP7** afforded 71 mg (63%) of **3al** isolated as the colorless crystalline solid; mp 82–83 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.45 – 7.36 (m, 2H), 7.08 (t,  $J = 8.6$  Hz, 2H), 4.47 – 4.32 (m, 2H), 4.23 (dd,  $J = 8.0, 4.4$  Hz, 1H), 2.13 – 2.00 (m, 1H), 0.90 (d,  $J = 7.2$  Hz, 3H), 0.84 (d,  $J = 6.8$  Hz, 3H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  160.2 (d,  $J = 244$  Hz), 156.3, 132.8 (d,  $J = 3$  Hz), 124.5 (d,  $J = 8.2$  Hz), 116.2 (d,  $J = 23$  Hz), 62.7, 61.0, 27.8, 17.8, 14.4.  $^{19}F$  NMR (376 MHz,  $CDCl_3$ )  $\delta$  –116.39. HRMS (ESI):  $m/z$  calcd. for  $[M+Na]^+ C_{12}H_{14}FNNaO_2^+$ : 246.0901, found 246.0900.

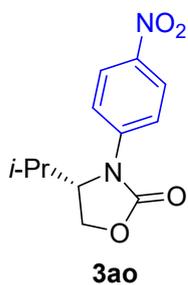


**(S)-3-(2-fluorophenyl)-4-isopropylloxazolidin-2-one (3am).** The reaction of (*S*)-4-isopropyl-oxazolidin-2-one (**1a**, 0.5 mmol, 65 mg), (2-fluorophenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate (**2m**, 0.75 mmol, 377 mg) according to general procedure **GP7** afforded 20 mg (18%) of **3am** isolated as the colorless oily liquid.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.49 (t,  $J = 7.6$  Hz, 1H), 7.33 – 7.26 (m, 1H), 7.24 – 7.10 (m, 2H), 4.48 (t,  $J = 8.6$  Hz, 1H), 4.45 – 4.36 (m, 1H), 4.25 (dd,  $J = 8.4, 5.2$  Hz, 1H), 1.92 – 1.79 (m, 1H), 0.880 (d,  $J = 6.8$ , 3H), 0.877 (d,  $J = 6.8$ , 3H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  157.53 (d,  $J = 249$  Hz), 156.7, 128.8, 128.72 (d,  $J = 6$  Hz), 124.9 (d,  $J = 4$  Hz), 124.3 (d,  $J = 11$  Hz), 116.8 (d,  $J = 20$  Hz), 63.8, 61.4 (d,  $J = 5$  Hz), 28.9, 17.7, 14.8.  $^{19}F$  NMR (376 MHz,  $CDCl_3$ )  $\delta$  –119.99. HRMS (ESI):  $m/z$  calcd. for  $[M+Na]^+ C_{12}H_{14}FNNaO_2^+$ : 246.0901, found 246.0896.

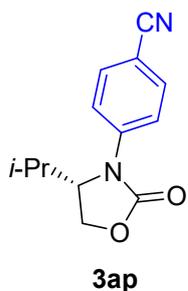


**(S)-3-(3-bromophenyl)-4-isopropylloxazolidin-2-one (3an).**<sup>31</sup> The reaction of (*S*)-4-isopropyl-oxazolidin-2-one (**1a**, 0.5 mmol, 65 mg), (3-bromophenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate (**2n**, 0.75 mmol, 422 mg) according to general procedure **GP7** afforded 60 mg (42%) of **3an** isolated as the colorless oily liquid.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.65 (s, 1H), 7.42 (d,  $J = 8.4$  Hz, 1H), 7.31 (d,  $J = 8.0$  Hz, 1H), 7.25 (t,  $J = 8.0$  Hz, 1H), 4.46 – 4.35 (m, 2H), 4.30 – 4.19 (m, 1H), 2.21 – 2.05 (m, 1H), 0.92 (d,  $J = 7.2$  Hz, 3H), 0.84 (d,  $J = 6.8$  Hz, 3H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  155.7, 138.2, 130.6, 128.3, 124.8, 122.9, 120.5, 62.6, 60.4,

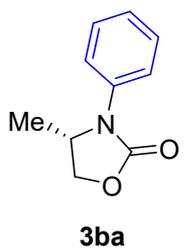
27.6, 17.9, 14.3. HRMS (ESI):  $m/z$  calcd. for  $[M+Na]^+ C_{12}H_{14}BrNNaO_2^+$ : 306.0100, found 306.0091.



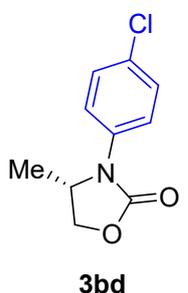
**(S)-4-isopropyl-3-(4-nitrophenyl)oxazolidin-2-one (3ao).** The reaction of (*S*)-4-isopropyl-oxazolidin-2-one (**1a**, 0.5 mmol, 65 mg), (4-nitrophenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate (**2o**, 0.75 mmol, 396 mg) according to general procedure **GP7** afforded 82 mg (65%) of **3ao** isolated as the pale yellow crystalline solid; mp 116 – 118 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.27 (d,  $J = 9.2$  Hz, 2H), 7.72 (d,  $J = 9.2$  Hz, 2H), 4.56 – 4.47 (m, 1H), 4.46 (t,  $J = 8.8$  Hz, 1H), 4.32 (dd,  $J = 8.6, 3.8$  Hz, 1H), 2.32 – 2.19 (m, 1H), 0.98 (d,  $J = 7.2$  Hz, 3H), 0.86 (d,  $J = 6.8$  Hz, 3H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  155.1, 143.9, 142.9, 125.1, 120.2, 62.6, 60.0, 27.6, 17.9, 14.2. HRMS (ESI):  $m/z$  calcd. for  $[M+Na]^+ C_{12}H_{14}N_2NaO_4^+$ : 273.0846, found 273.0846.



**(S)-4-(4-isopropyl-2-oxooxazolidin-3-yl)benzonitrile (3ap).**<sup>32</sup> The reaction of (*S*)-4-isopropyl-oxazolidin-2-one (**1a**, 0.5 mmol, 65 mg), (4-cyanophenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate (**2p**, 0.75 mmol, 297 mg) according to general procedure **GP7** afforded 95 mg (82%) of **3ap** isolated as the colorless oily liquid.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.72 – 7.62 (m, 4H), 4.52 – 4.41 (m, 2H), 4.30 (dd,  $J = 8.1, 3.2$  Hz, 1H), 2.28 – 2.15 (m, 1H), 0.95 (d,  $J = 7.2$  Hz, 3H), 0.84 (d,  $J = 6.8$  Hz, 3H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  155.2, 141.1, 133.4, 120.8, 118.7, 107.9, 62.5, 59.9, 27.6, 17.9, 14.2. HRMS (ESI):  $m/z$  calcd. for  $[M+Na]^+ C_{13}H_{14}N_2NaO_2^+$ : 253.0947, found 253.0947.

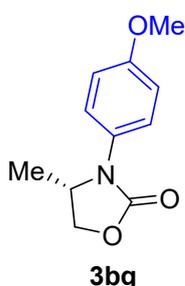


**(S)-4-methyl-3-phenyloxazolidin-2-one (3ba).**<sup>28</sup> The reaction of (*S*)-4-methyloxazolidin-2-one (**1b**, 0.5 mmol, 51 mg), diphenyliodonium triflate (**2a**, 0.75 mmol, 323 mg) according to general procedure **GP6** afforded 81 mg (92%) of **3ba** isolated as the pale yellow oil.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.46 – 7.35 (m, 4H), 7.19 (t,  $J = 6.8$  Hz, 1H), 4.63 – 4.47 (m, 2H), 4.03 (dd,  $J = 7.6, 5.2$  Hz, 1H), 1.33 (d,  $J = 6.0$  Hz, 3H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  155.8, 136.6, 129.3, 125.4, 122.1, 68.8, 52.5, 18.6. HRMS (ESI):  $m/z$  calcd. for  $[M+H]^+ C_{10}H_{12}NO_2^+$ : 178.0863, found 178.0862.



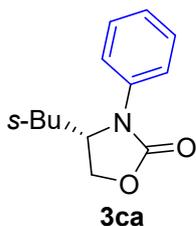
**(S)-3-(4-chlorophenyl)-4-methyloxazolidin-2-one (3bd).**<sup>33</sup> The reaction of (*S*)-4-methyloxazolidin-2-one (**1b**, 0.5 mmol, 51 mg), bis(4-chlorophenyl)iodonium trifluoromethanesulfonate (**2d**, 0.75 mmol, 374 mg) according to general procedure **GP6** afforded 100 mg (94%) of **3bd** isolated as the colorless crystalline

solid; mp 116–118 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.42 – 7.32 (m, 4H), 4.58 (t, *J* = 8.2 Hz, 1H), 4.56 – 4.45 (m, 1H), 4.03 (dd, *J* = 8.4, 5.6 Hz, 1H), 1.34 (d, *J* = 6.0 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 155.6, 135.3, 130.6, 129.4, 123.0, 68.8, 52.3, 18.5. HRMS (ESI): *m/z* calcd. for [M+H]<sup>+</sup> C<sub>10</sub>H<sub>11</sub>ClNO<sub>2</sub><sup>+</sup>: 212.0473, found 212.0473.



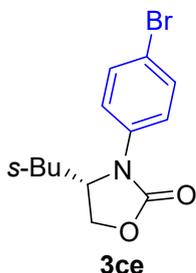
**(S)-3-(4-methoxyphenyl)-4-methyloxazolidin-2-one (3bg).**

The reaction of (*S*)-4-methyloxazolidin-2-one (**1b**, 0.5 mmol, 51 mg), bis(4-methoxyphenyl)iodonium trifluoromethanesulfonate (**2g**, 0.75 mmol, 367 mg) according to general procedure **GP6** afforded 66 mg (64%) of **3bg** isolated as the brown oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.28 (d, *J* = 9.2 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 4.57 (t, *J* = 8.4 Hz, 1H), 4.45 – 4.36 (m, 1H), 4.00 (t, *J* = 8.2, 6.6 Hz, 1H), 3.81 (s, 3H), 1.29 (d, *J* = 6.0 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 157.7, 156.4, 129.3, 124.9, 114.6, 68.9, 55.6, 53.3, 18.7. HRMS (EI): *m/z* calcd. for [M]<sup>+</sup> C<sub>11</sub>H<sub>13</sub>NO<sub>3</sub><sup>+</sup>: 207.0890, found 207.0887.



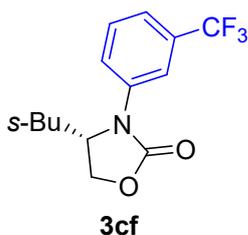
**(S)-4-((R)-sec-butyl)-3-phenyloxazolidin-2-one (3ca).**

The reaction of (*S*)-4-sec-butyloxazolidin-2-one (**1c**, 0.5 mmol, 72 mg), diphenyliodonium triflate (**2a**, 0.75 mmol, 323 mg) according to general procedure **GP6** afforded 72 mg (65%) of **3ca** isolated as colorless oily liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.71 – 7.28 (m, 4H), 7.23 – 7.14 (m, 1H), 4.56 (t, *J* = 8.4 Hz, 1H), 4.50 – 4.39 (m, 1H), 4.13 (dd, *J* = 8.4, 5.6 Hz, 1H), 1.73 – 1.54 (m, 2H), 1.52 – 1.41 (m, 1H), 0.95 (d, *J* = 6.0 Hz, 3H), 0.92 (d, *J* = 6.0 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 155.9, 136.9, 129.3, 125.3, 122.1, 67.8, 55.2, 41.3, 24.8, 23.7, 21.8. HRMS (ESI): *m/z* calcd. for [M+Na]<sup>+</sup> C<sub>13</sub>H<sub>17</sub>NNaO<sub>2</sub><sup>+</sup>: 242.1151, found 242.1148.



**(S)-3-(4-bromophenyl)-4-((R)-sec-butyl)oxazolidin-2-one (3ce).**

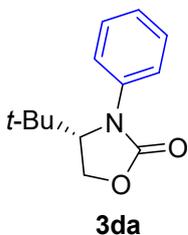
The reaction of (*S*)-4-sec-butyloxazolidin-2-one (**1c**, 0.5 mmol, 72 mg), bis(4-bromophenyl)iodonium trifluoromethanesulfonate (**2e**, 0.75 mmol, 441 mg) according to general procedure **GP6** afforded 102 mg (68%) of **3ce** isolated as colorless crystalline solid; mp 46–47 °C. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 8.8 Hz, 2H), 7.31 (d, *J* = 8.8 Hz, 2H), 4.56 (t, *J* = 8.2 Hz, 1H), 4.46 – 4.34 (m, 1H), 4.13 (dd, *J* = 8.4, 5.2 Hz, 1H), 1.70 – 1.54 (m, 2H), 1.52 – 1.40 (m, 1H), 0.95 (d, *J* = 6.0 Hz, 3H), 0.92 (d, *J* = 6.4 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 155.5, 136.1, 132.4, 123.3, 118.3, 67.7, 55.0, 41.1, 24.8, 23.7, 21.8. HRMS (ESI): *m/z* calcd. for [M+Na]<sup>+</sup> C<sub>13</sub>H<sub>16</sub>BrNNaO<sub>2</sub><sup>+</sup>: 320.0257, found 320.0252.



**(S)-4-((R)-sec-butyl)-3-(3-(trifluoromethyl)phenyl)oxazolidin-2-one**

**(3cf).** The reaction of (*S*)-4-sec-butyloxazolidin-2-one (**1c**, 0.5 mmol, 72 mg), bis(3-(trifluoromethyl)phenyl)iodonium trifluoromethanesulfonate (**2f**, 0.75 mmol, 425 mg) according to general procedure **GP6** afforded 94 mg (65%) of **3cf** isolated as colorless oily liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ

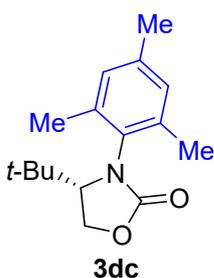
7.69 (d, *J* = 7.7 Hz, 2H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 4.58 (t, *J* = 8.2 Hz, 1H), 4.53 – 4.43 (m, 1H), 4.16 (dd, *J* = 8.2, 5.0 Hz, 1H), 1.72 – 1.57 (m, 2H), 1.56 – 1.44 (m, 1H), 0.97 (d, *J* = 6.0 Hz, 3H), 0.93 (d, *J* = 6.0 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 155.4, 137.6, 131.75 (q, *J* = 32 Hz), 124.4, 123.9 (d, *J* = 271 Hz), 121.57 (q, *J* = 4 Hz), 117.77 (q, *J* = 4 Hz), 67.8, 54.9, 41.1, 24.9, 23.7, 21.8. HRMS (ESI): *m/z* calcd. for [M+H]<sup>+</sup> C<sub>14</sub>H<sub>17</sub>F<sub>3</sub>NO<sub>2</sub><sup>+</sup>: 288.1206, found 288.1209.



**(S)-4-(tert-butyl)-3-phenyloxazolidin-2-one (3da).** The reaction of (*S*)-4-tert-

butyloxazolidin-2-one (**1d**, 0.5 mmol, 72 mg), diphenyliodonium triflate (**2a**, 0.75 mmol, 323 mg) according to general procedure **GP6** afforded 105 mg (95%) of **3da** isolated as the colorless crystalline solid; mp 144–146 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45 – 7.33 (m, 4H), 7.21 (t, *J* = 7.0 Hz, 1H), 4.44 (t, *J* = 9.0 Hz,

1H), 4.32 (dd, *J* = 9.2, 4.0 Hz, 1H), 4.24 (dd, *J* = 8.8, 4.0 Hz, 1H), 0.83 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 157.0, 139.0, 129.2, 126.2, 124.5, 65.3, 64.5, 36.0, 26.0. HRMS (ESI): *m/z* calcd. for [M+H]<sup>+</sup> C<sub>13</sub>H<sub>18</sub>NO<sub>2</sub><sup>+</sup>: 220.1332, found 220.1332.

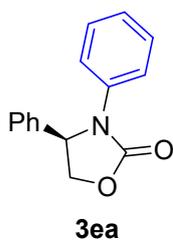


**(S)-4-(tert-butyl)-3-mesityloxazolidin-2-one (3dc).** The reaction of (*S*)-4-tert-

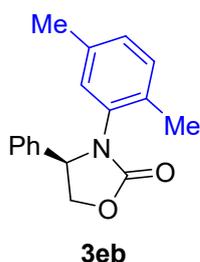
butyloxazolidin-2-one (**1d**, 0.5 mmol, 72 mg), dimesityliodonium trifluoromethanesulfonate (**2c**, 0.75 mmol, 386 mg) according to general procedure **GP6** afforded 34 mg (26%) of **3dc** isolated as the pale yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.91 (s, 1H)\*, 6.86 (s, 1H)\*, 4.48 (t, *J* = 9.0 Hz, 1H), 4.31 (dd, *J* = 9.2, 5.6 Hz, 1H), 3.98 (dd, *J* = 9.2, 5.6 Hz, 1H), 2.37 (s, 3H),

2.26 (s, 6H), 0.85 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 157.7, 137.7, 137.2, 134.1, 133.8, 130.3, 130.0, 129.7, 125.9, 66.1, 65.0, 34.9, 25.7, 21.0, 19.4, 19.1. HRMS (ESI): *m/z* calcd. for [M+H]<sup>+</sup> C<sub>16</sub>H<sub>24</sub>NO<sub>2</sub><sup>+</sup>: 262.1802, found 262.1803.

\*The multiplicity related to sterically hindrance of both mesityl group and substituents of oxazolidinones that lead to magnetic inequivalence of H-atoms of mesityl group. Similar phenomenon was observed in <sup>1</sup>H spectrum of 5-isopropyl-1-mesitylpyrrolidin-2-one.<sup>31</sup>

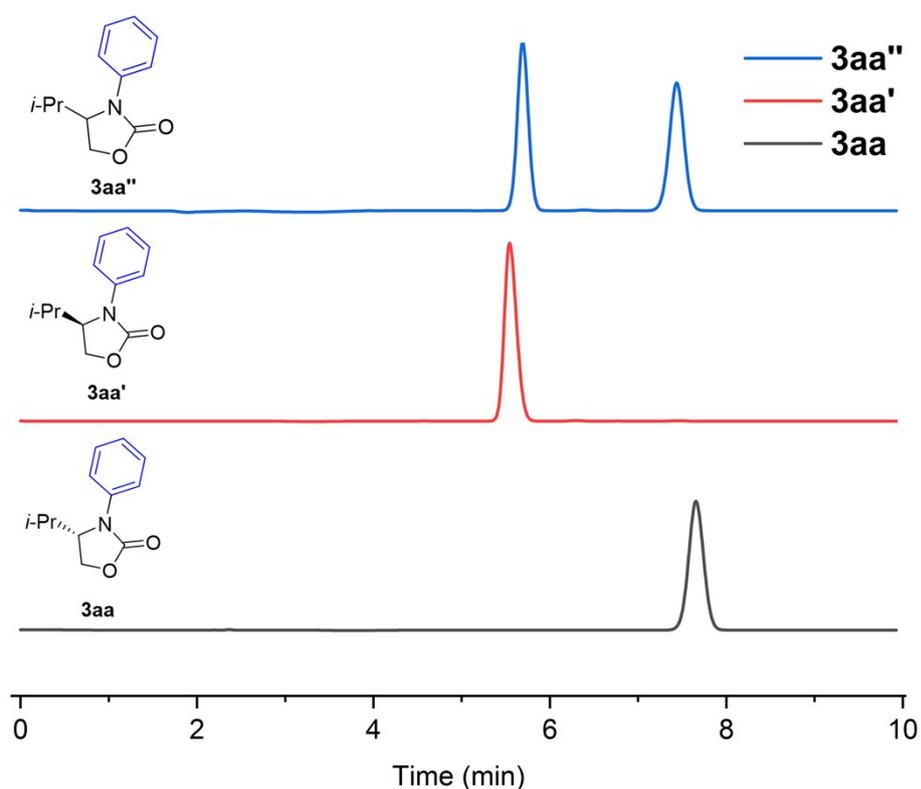


**(R)-3,4-diphenyloxazolidin-2-one (3ea).**<sup>28</sup> The reaction of (*R*)-4-phenyloxazolidin-2-one (**1e**, 0.5 mmol, 72 mg), diphenyliodonium triflate (**2a**, 0.75 mmol, 323 mg) according to general procedure **GP6** afforded 76 mg (63%) of **3ea** isolated as the colorless crystalline solid; mp 128–130 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.46 – 7.24 (m, 9H), 7.09 (t, *J* = 7.4 Hz, 1H), 5.42 (dd, *J* = 8.4, 6.0 Hz, 1H), 4.81 (t, *J* = 8.8 Hz, 1H), 4.23 (t, *J* = 8.4, 6.0 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 156.0, 138.4, 137.2, 129.5, 129.04, 128.96, 126.4, 124.8, 121.0, 69.9, 60.8. HRMS (ESI): *m/z* calcd. for [M+Na]<sup>+</sup> C<sub>15</sub>H<sub>13</sub>NNaO<sub>2</sub><sup>+</sup>: 262.0838, found 262.0840.



**(R)-3-(2,5-dimethylphenyl)-4-phenyloxazolidin-2-one (3eb).** The reaction of (*R*)-4-phenyloxazolidin-2-one (**1e**, 0.5 mmol, 72 mg), bis(2,5-dimethylphenyl)iodonium trifluoromethanesulfonate (**2b**, 0.75 mmol, 365 mg) according to general procedure **GP6** afforded 90 mg (67%) of **3eb** isolated as the colorless oily liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.40 – 7.27 (m, 4H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.77 (s, 1H), 5.21 (t, *J* = 8.0 Hz, 1H), 4.82 (t, *J* = 8.8 Hz, 1H), 4.41 (t, *J* = 8.8, 7.6 Hz, 1H), 2.24 (s, 3H), 2.17 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 156.6, 137.7, 136.4, 134.5, 132.9, 131.2, 129.2, 129.2, 128.9, 127.5, 70.2, 62.9, 20.9, 17.9. HRMS (ESI): *m/z* calcd. for [M+Na]<sup>+</sup> C<sub>17</sub>H<sub>17</sub>NNaO<sub>2</sub><sup>+</sup>: 290.1151, found 290.1147.

## Chiral HPLC analysis of 1aa, 1aa', and 1aa''



**Figure S1.** HPLC chromatograms at 240 nm of **3aa''** (racemic mixture), **3aa'** (D-enantiomer or R-enantiomer), and **3aa** (L-enantiomer or S-enantiomer).

The peak with retention time of 7.4 min corresponds to an enantiomer having a stronger interaction with the chiral sorbent, which causes its broadening and lower intensity if compared to the peak of enantiomer eluting at 5.7 min. Nevertheless, both peaks have the same area values, which confirms the racemic nature of the reaction product. Chromatograms of individual enantiomers exhibit by only one signal corresponding the one of the two peaks of racemic mixture, which prove the chiral selectivity of reaction.

### X-ray structure determinations

Single crystal XRD were measured on SuperNova, Single source at offset/far, HyPix3000 diffractometer (for **3bd** and **3da**) using CuK $\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation; Xcalibur, Eos diffractometer (for **3ah**) using Mo K $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation. Suitable single crystals of compounds **3** were fixed on micro mounts and measured at 100(2) K. Using Olex2,<sup>34</sup> the structure was solved with the ShelXT<sup>35</sup> structure solution program using Intrinsic Phasing and refined with the ShelXL<sup>36</sup> refinement package using Least Squares minimization. Supplementary crystallographic data for this paper have been deposited at Cambridge Crystallographic Data Centre (CCDC numbers 2218690–2218692) and can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Table S1.** Crystal data and structure refinement.

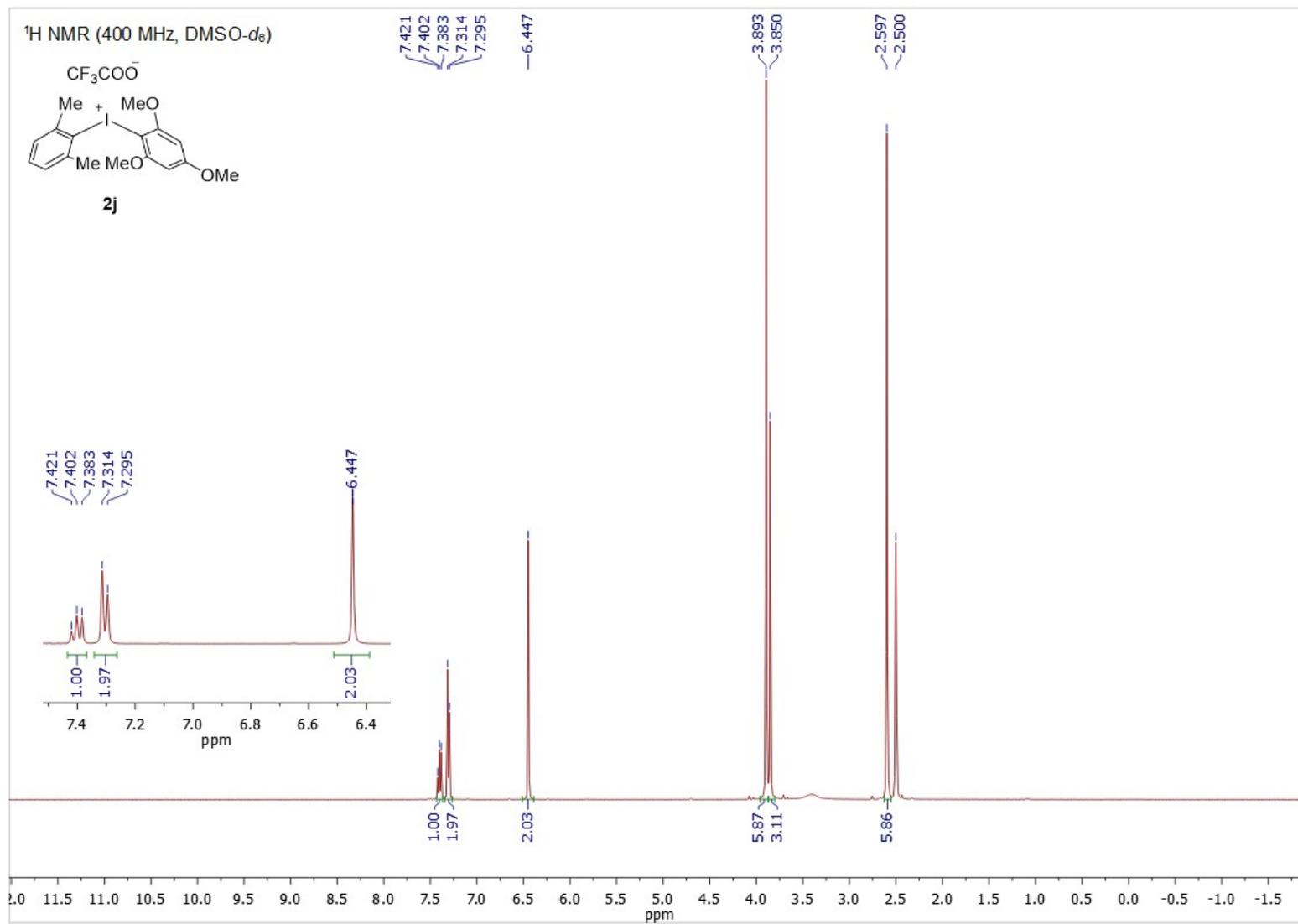
Identification code	<b>3bd</b>	<b>3da</b>	<b>3ah</b>
CCDC number	2218692	2218691	2218690
Empirical formula	C <sub>10</sub> H <sub>10</sub> ClNO <sub>2</sub>	C <sub>13</sub> H <sub>17</sub> NO <sub>2</sub>	C <sub>13</sub> H <sub>17</sub> NO <sub>2</sub>
Formula weight	211.64	219.27	219.27
Temperature/K	100(2)	100(2)	100(2)
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	P2 <sub>1</sub>	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a/Å	5.53040(10)	6.2495(2)	6.5182(2)
b/Å	8.5314(2)	12.5730(3)	12.3029(5)
c/Å	10.1412(2)	15.1106(5)	14.3881(4)
α/°	90	90	90
β/°	93.371(2)	90	90
γ/°	90	90	90
Volume/Å <sup>3</sup>	477.655(17)	1187.31(6)	1153.82(7)
Z	2	4	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.472	1.227	1.262
μ/mm <sup>-1</sup>	3.319	0.661	0.085
F(000)	220.0	472.0	472.0
Crystal size/mm <sup>3</sup>	0.16 × 0.12 × 0.09	0.11 × 0.11 × 0.07	0.17 × 0.15 × 0.1
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Mo Kα (λ = 0.71073)
2θ range for data collection/°	8.734 to 129.734	9.15 to 129.97	5.662 to 51.978
Index ranges	-5 ≤ h ≤ 6, -10 ≤ k ≤ 10, -11 ≤ l ≤ 11	-6 ≤ h ≤ 7, -14 ≤ k ≤ 14, -17 ≤ l ≤ 17	-7 ≤ h ≤ 8, -11 ≤ k ≤ 15, -17 ≤ l ≤ 17
Reflections collected	3560	6810	4051
Independent reflections	1613 [R <sub>int</sub> = 0.0112, R <sub>sigma</sub> = 0.0151]	1980 [R <sub>int</sub> = 0.0553, R <sub>sigma</sub> = 0.0523]	2128 [R <sub>int</sub> = 0.0317, R <sub>sigma</sub> = 0.0446]
Data/restraints/parameters	1613/1/128	1980/0/148	2128/0/148
Goodness-of-fit on F <sup>2</sup>	1.054	1.082	1.048
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0197, wR <sub>2</sub> = 0.0521	R <sub>1</sub> = 0.0405, wR <sub>2</sub> = 0.0944	R <sub>1</sub> = 0.0366, wR <sub>2</sub> = 0.0850
Final R indexes [all data]	R <sub>1</sub> = 0.0199, wR <sub>2</sub> = 0.0523	R <sub>1</sub> = 0.0468, wR <sub>2</sub> = 0.0969	R <sub>1</sub> = 0.0403, wR <sub>2</sub> = 0.0879
Largest diff. peak/hole / e Å <sup>-3</sup>	0.12/-0.21	0.15/-0.17	0.18/-0.20
Flack parameter	-0.014(7)	0.2(2)	1.0(10)

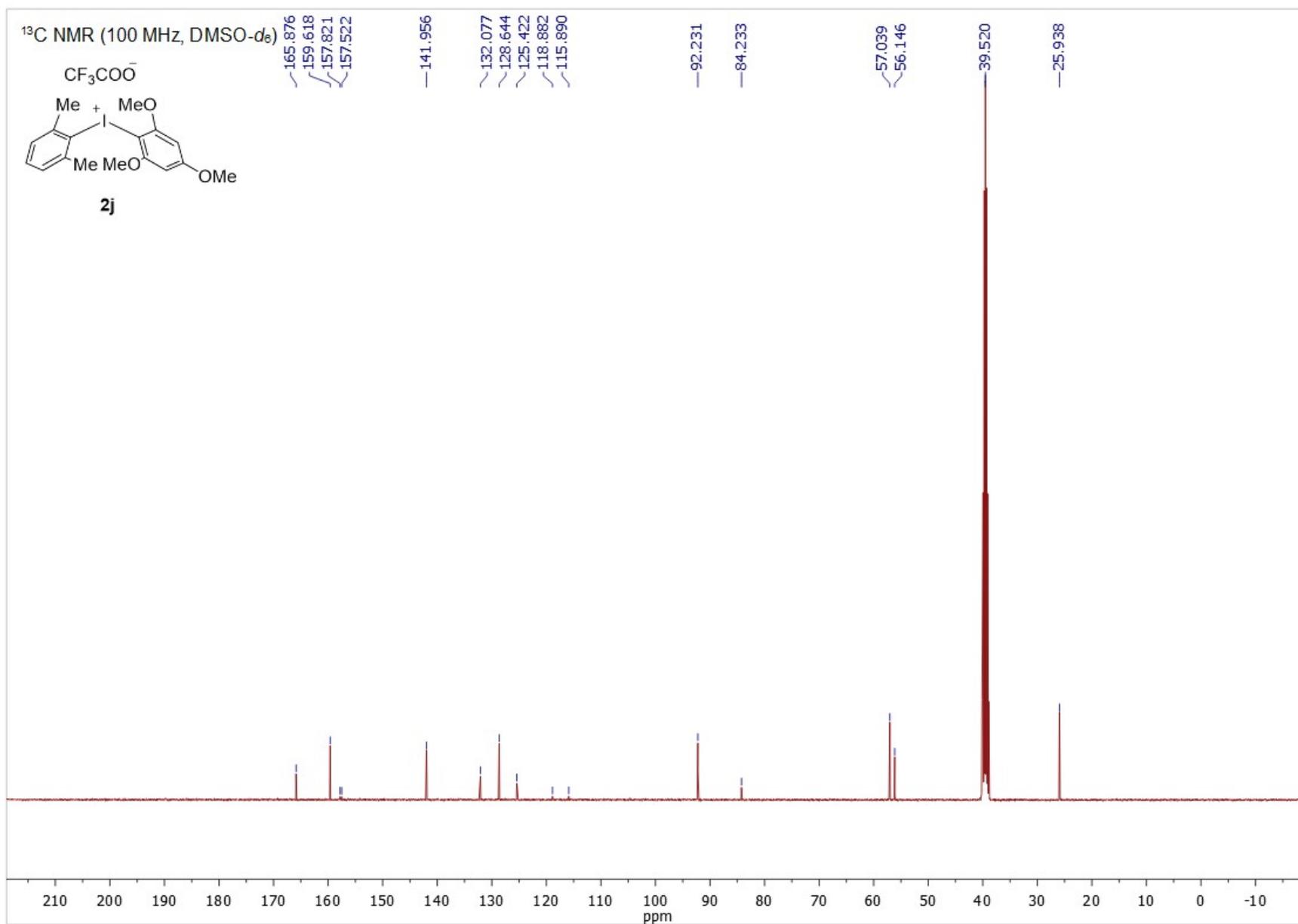
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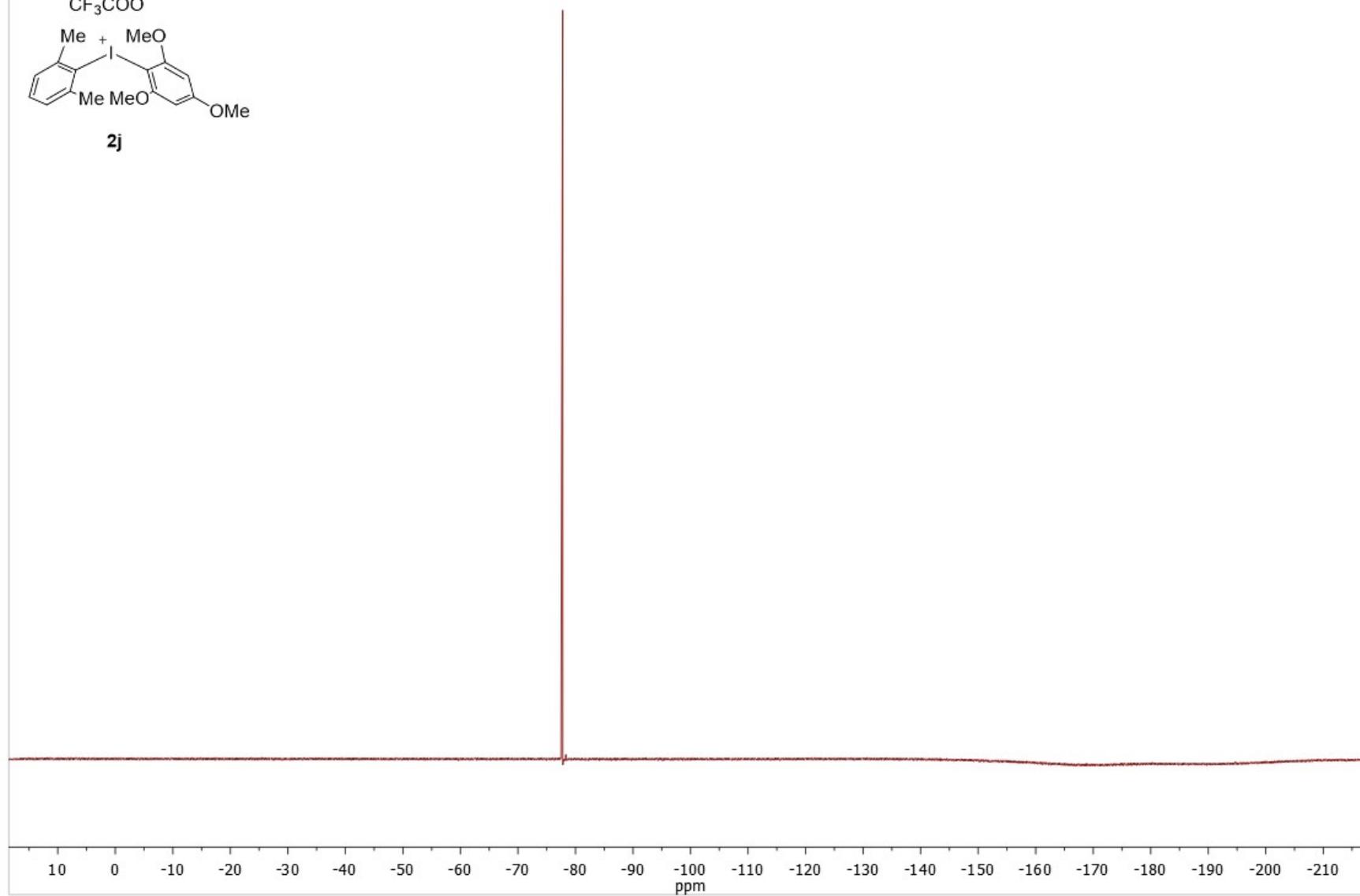
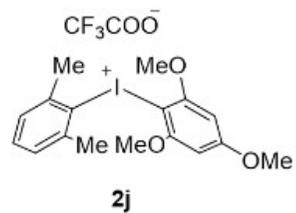
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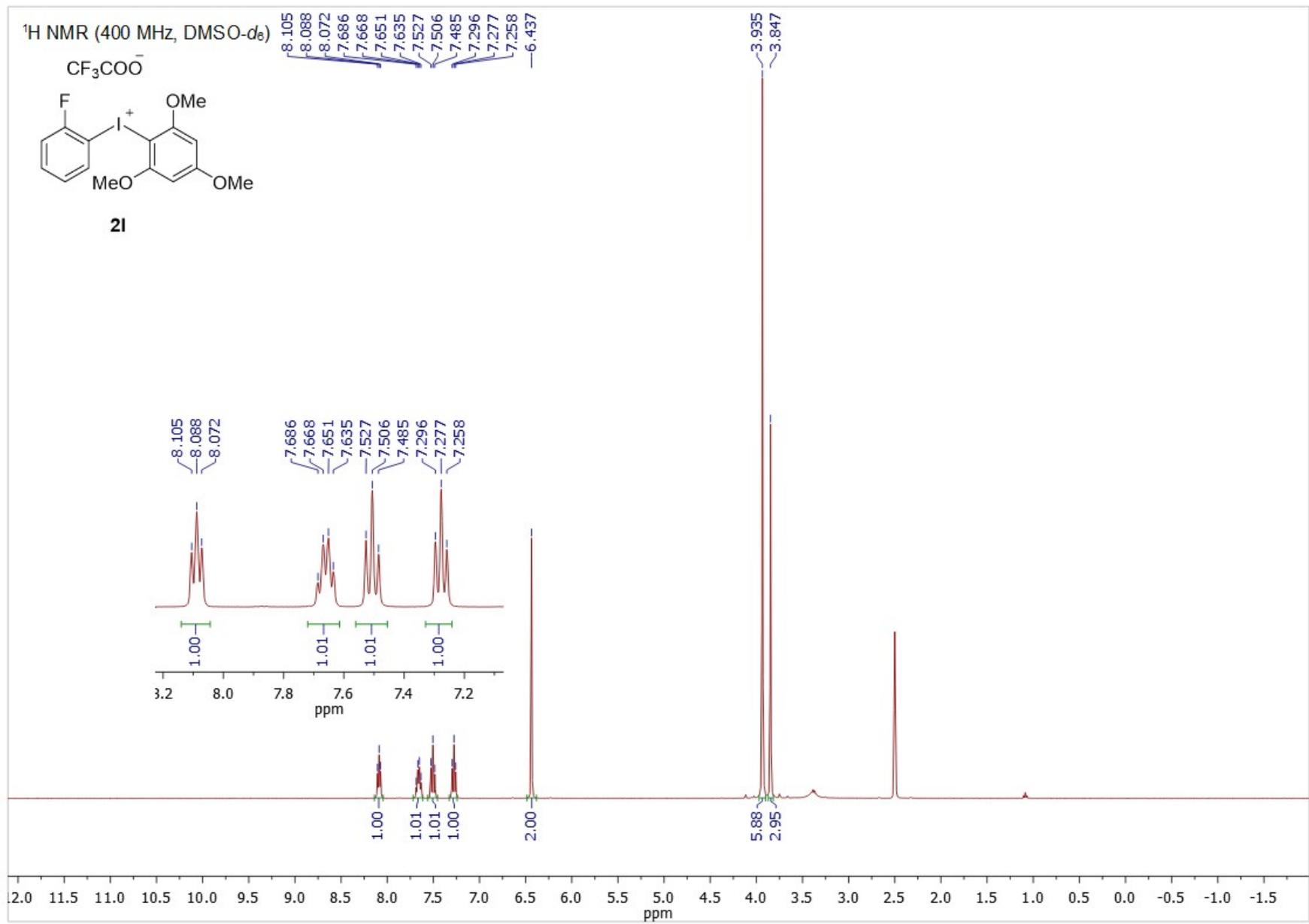
## NMR spectra of 2

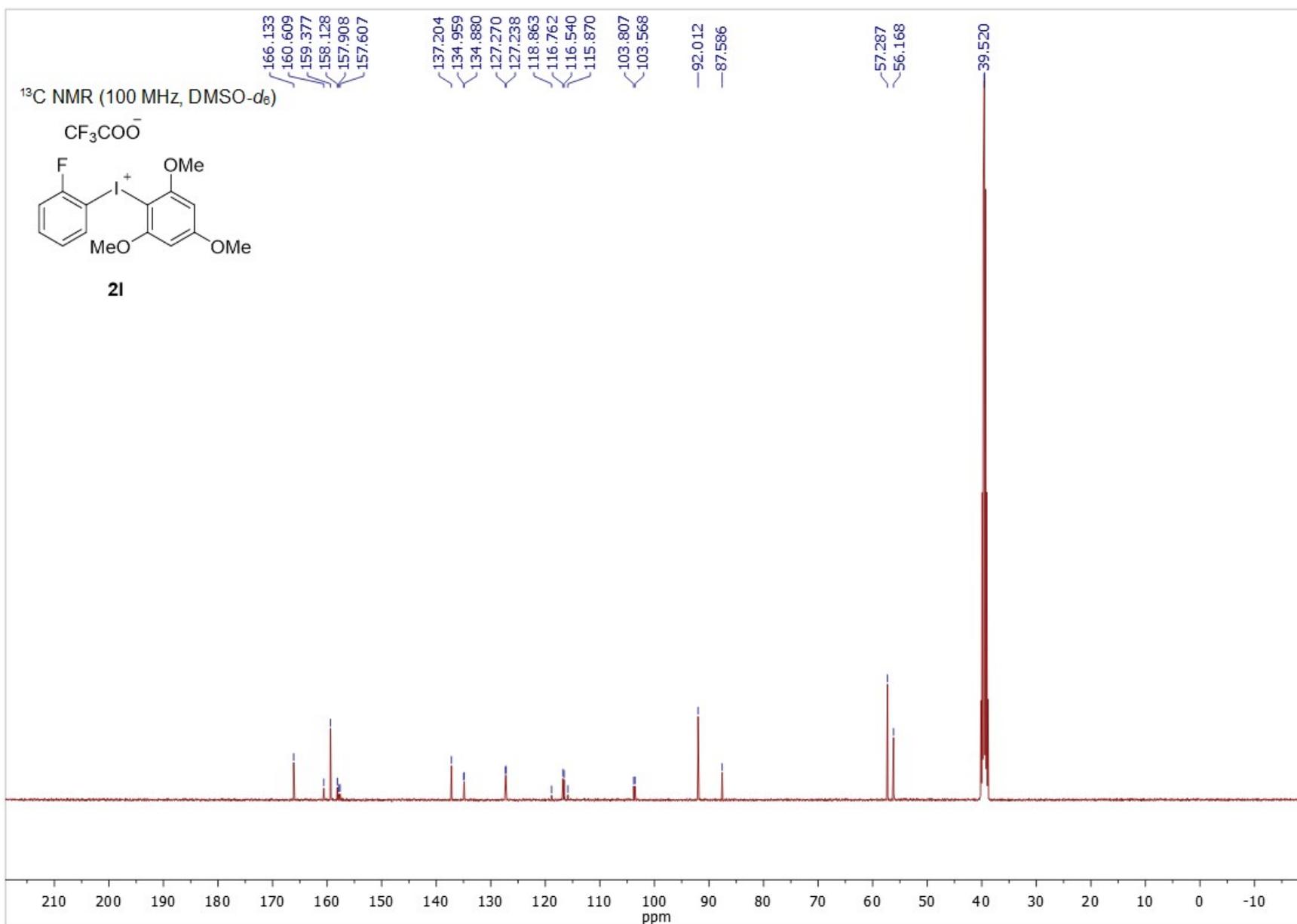




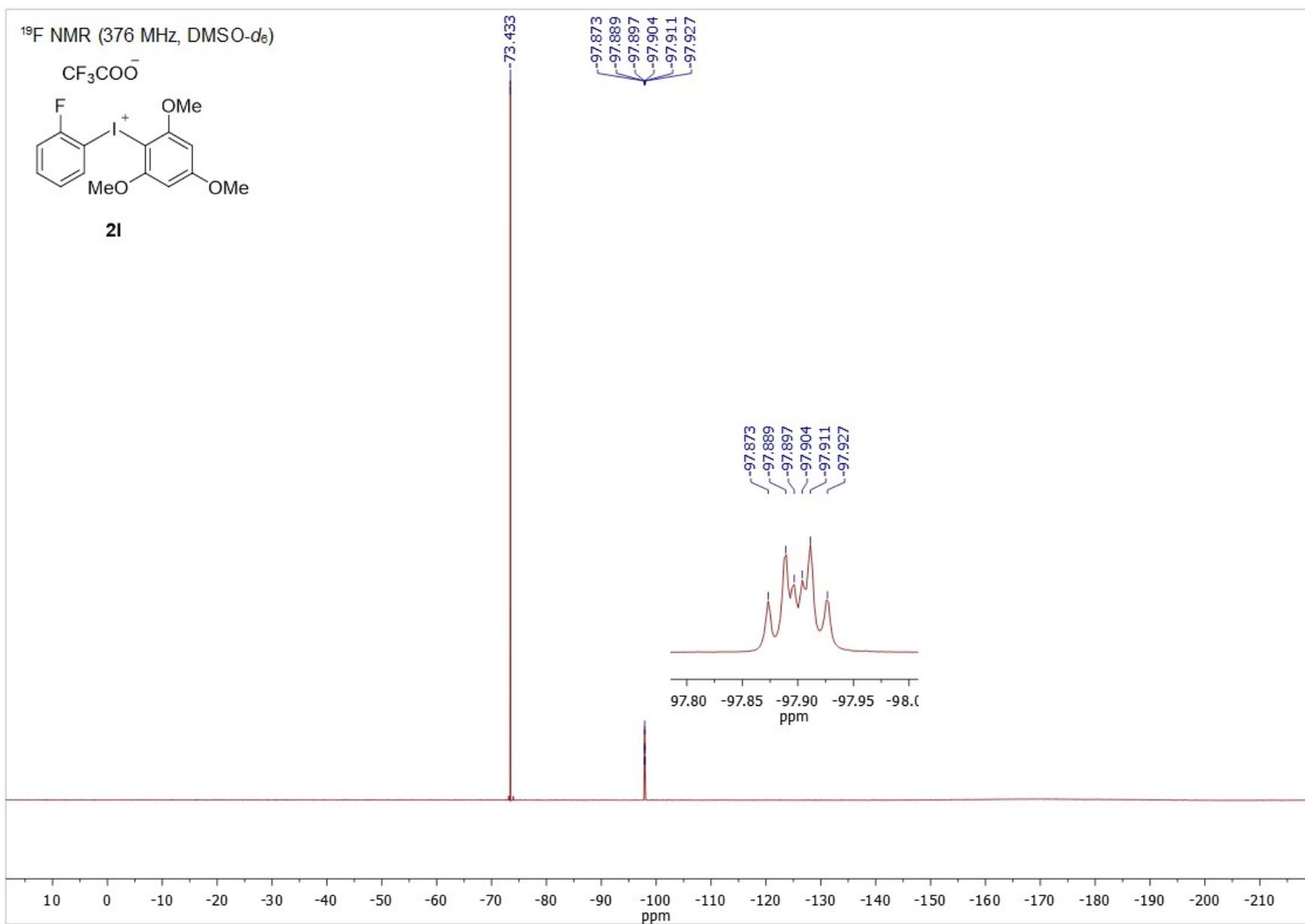
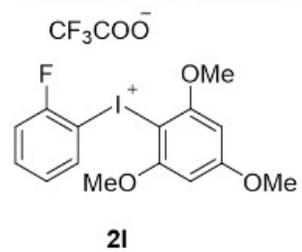
$^{19}\text{F}$  NMR (376 MHz,  $\text{DMSO-}d_6$ )



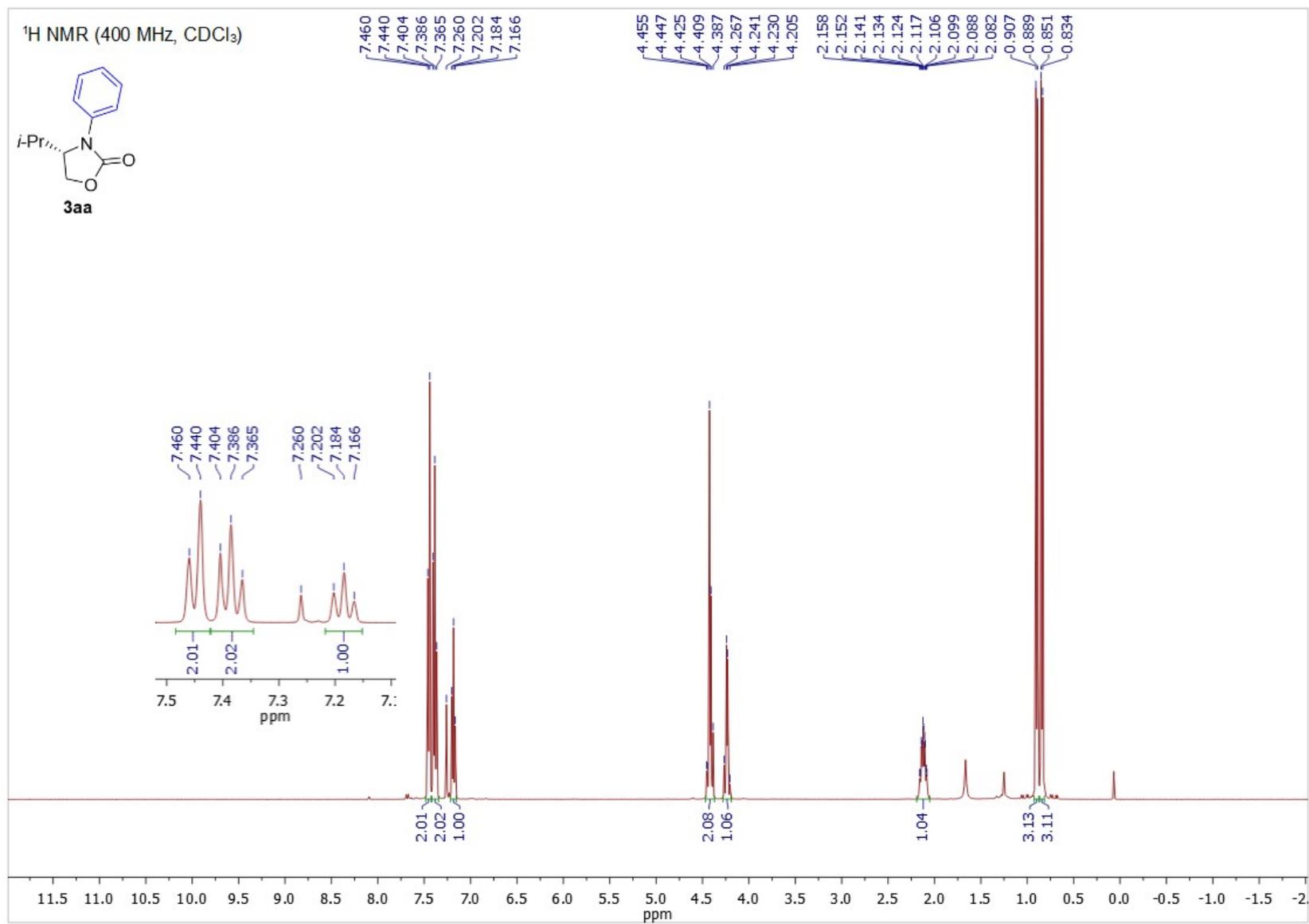


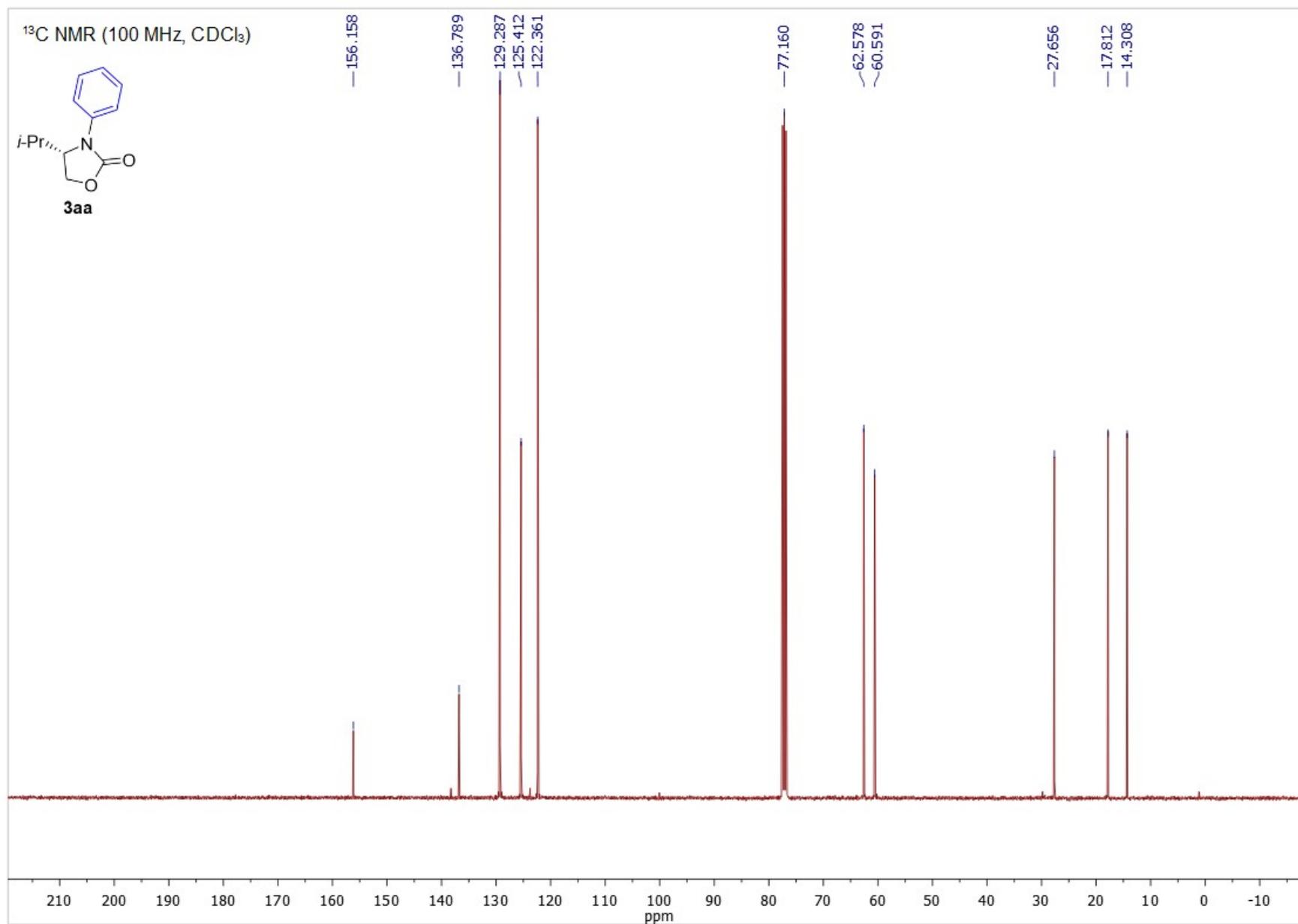


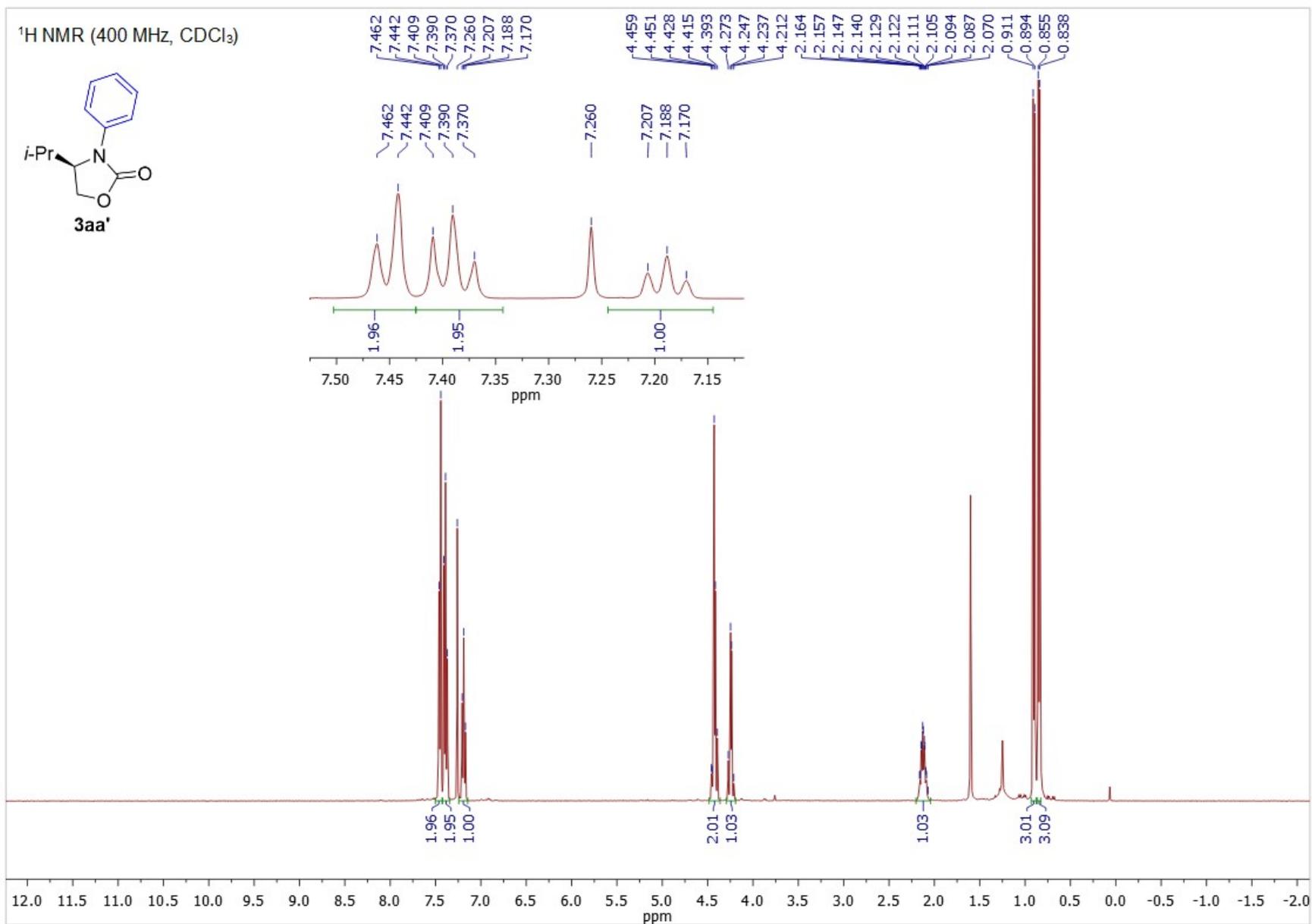
$^{19}\text{F}$  NMR (376 MHz,  $\text{DMSO-}d_6$ )

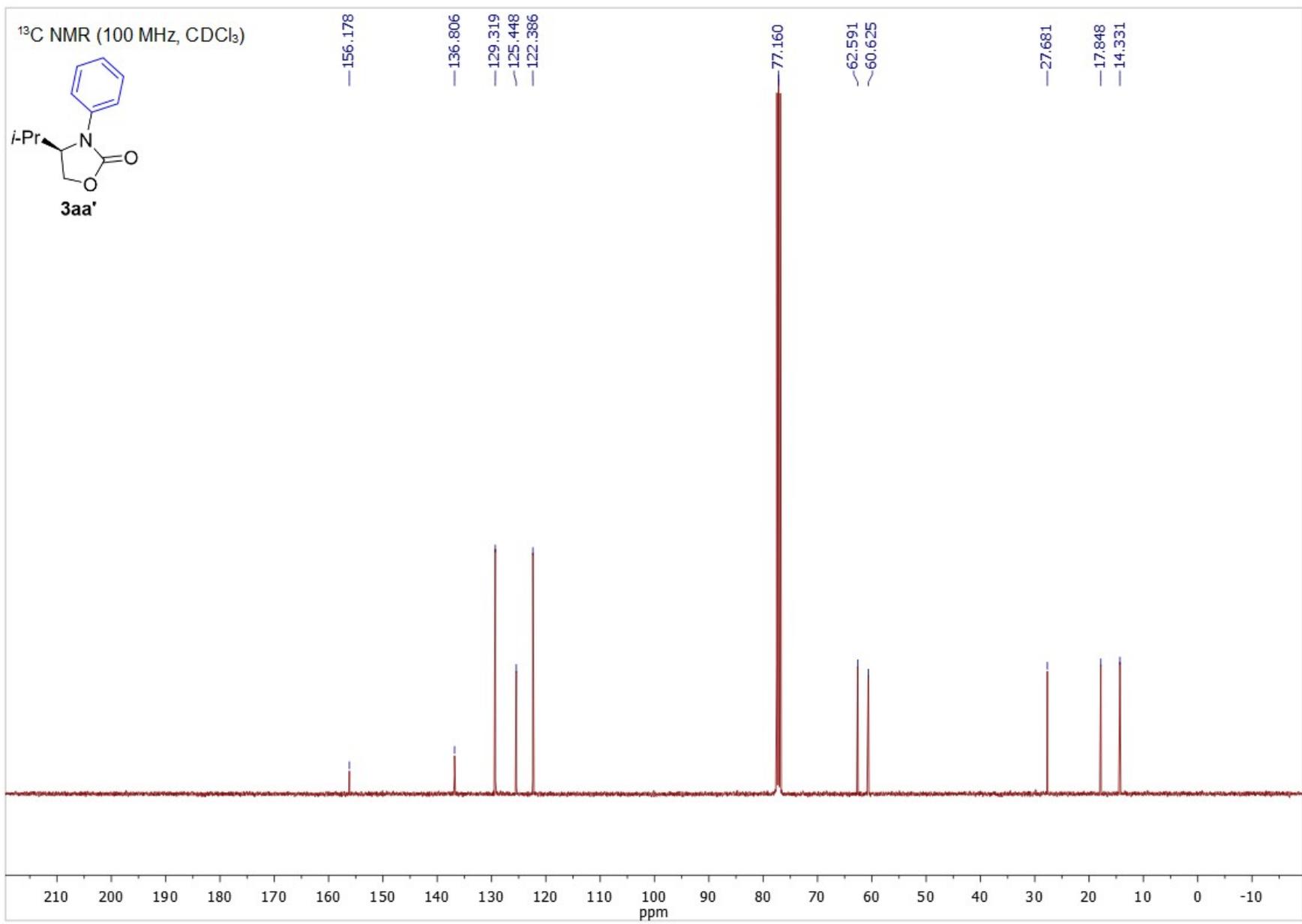


# NMR spectra of 3

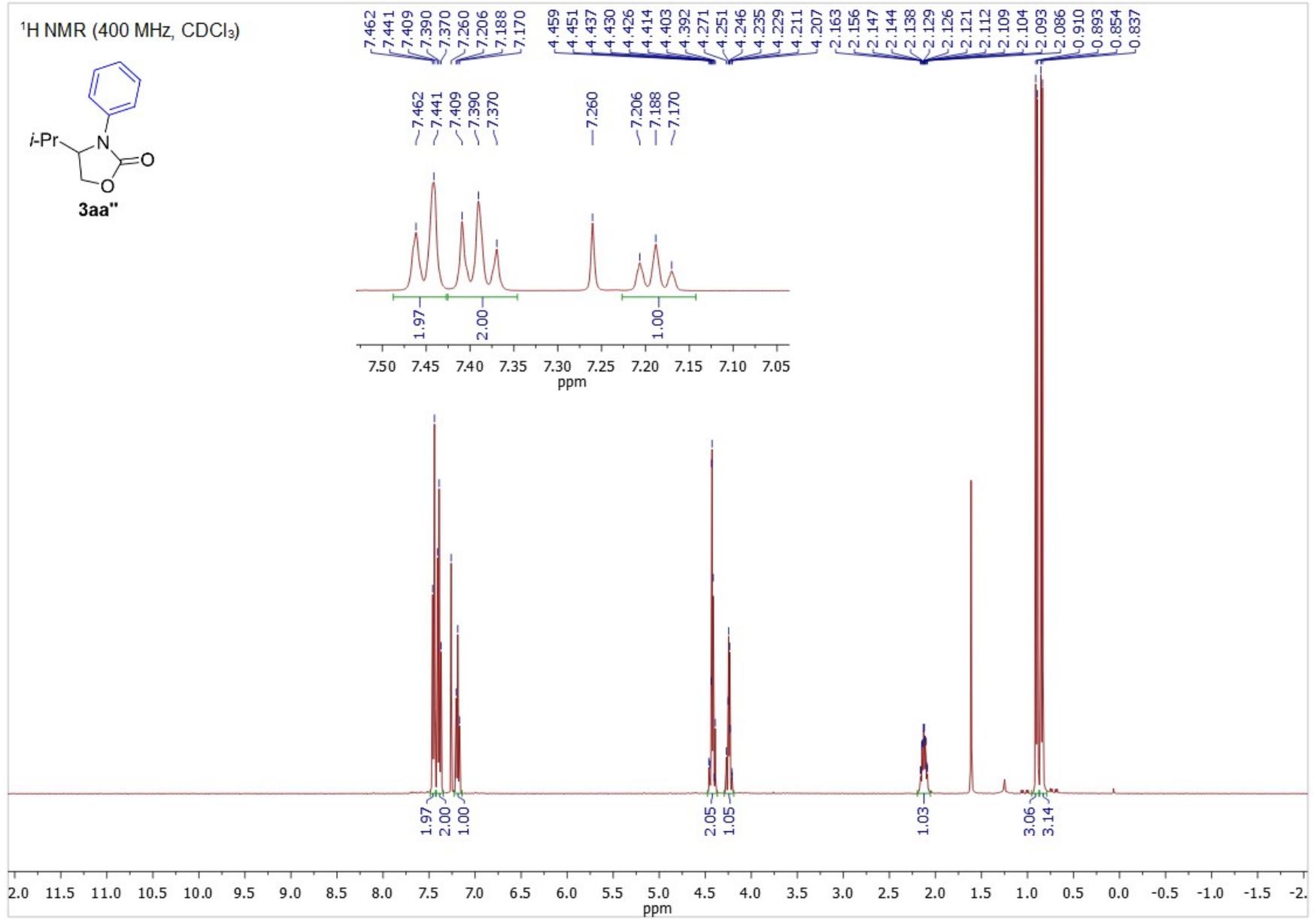
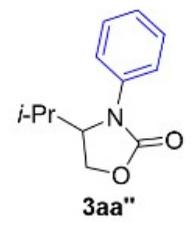


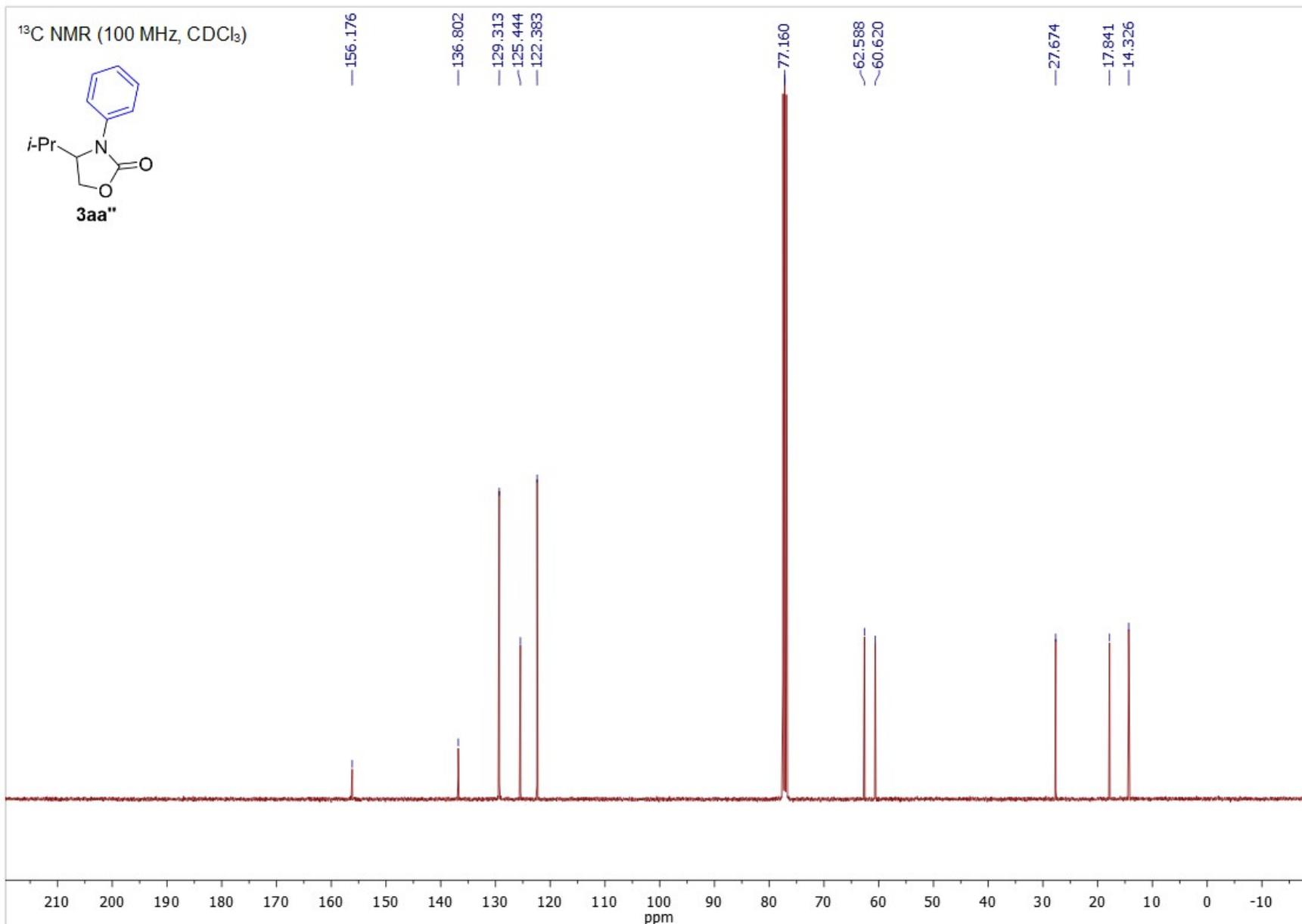




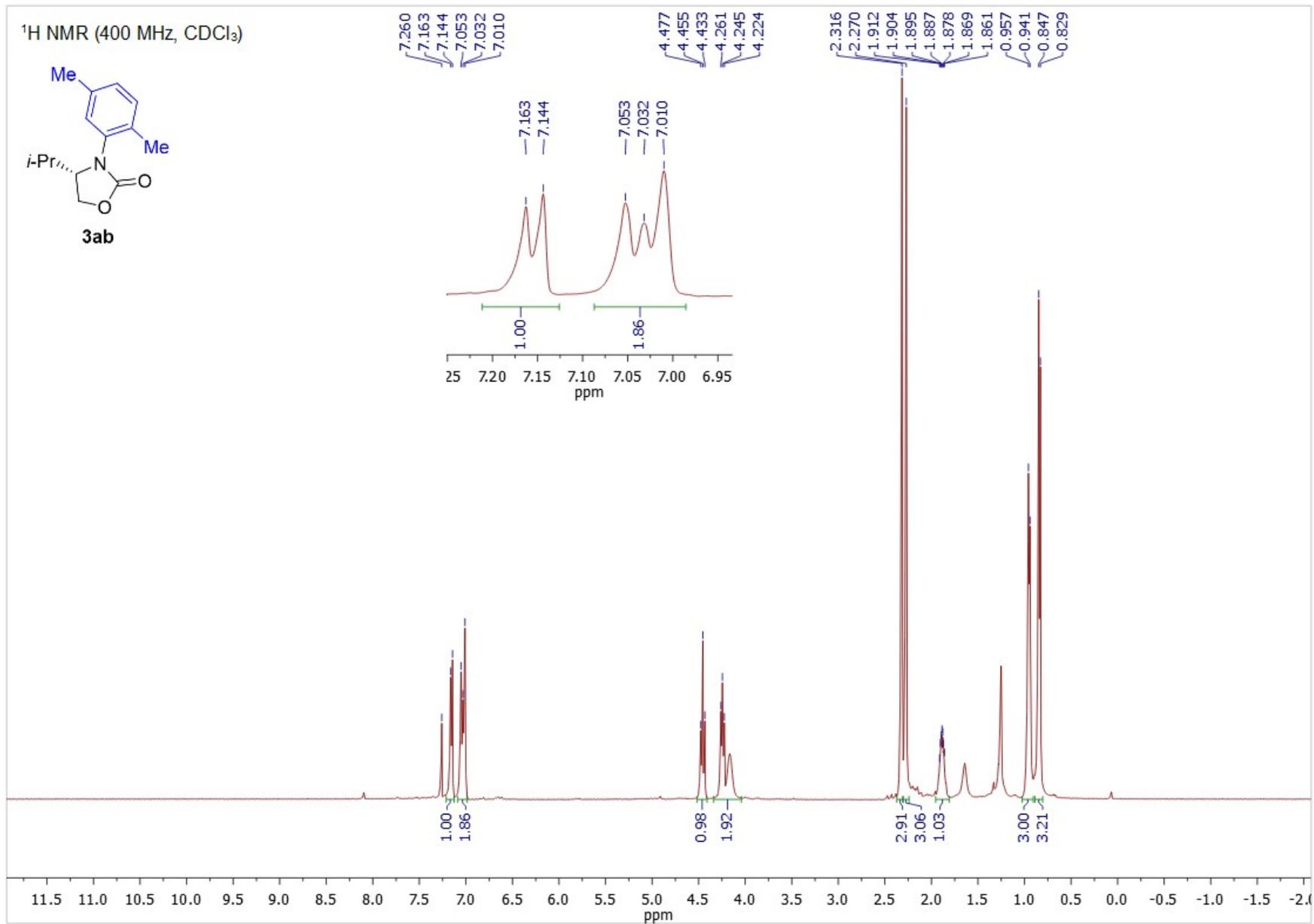
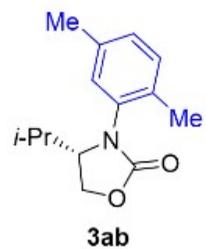


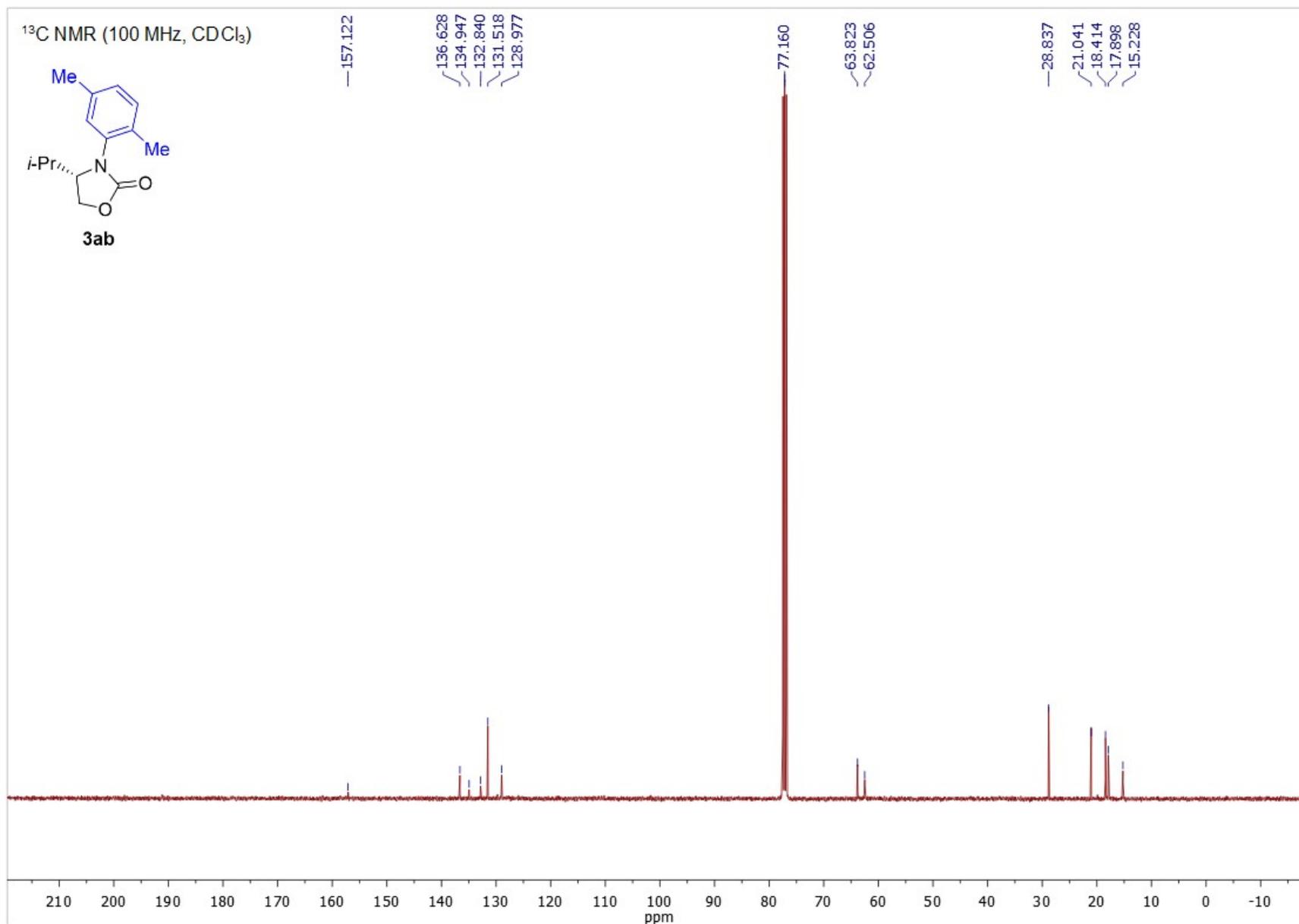
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



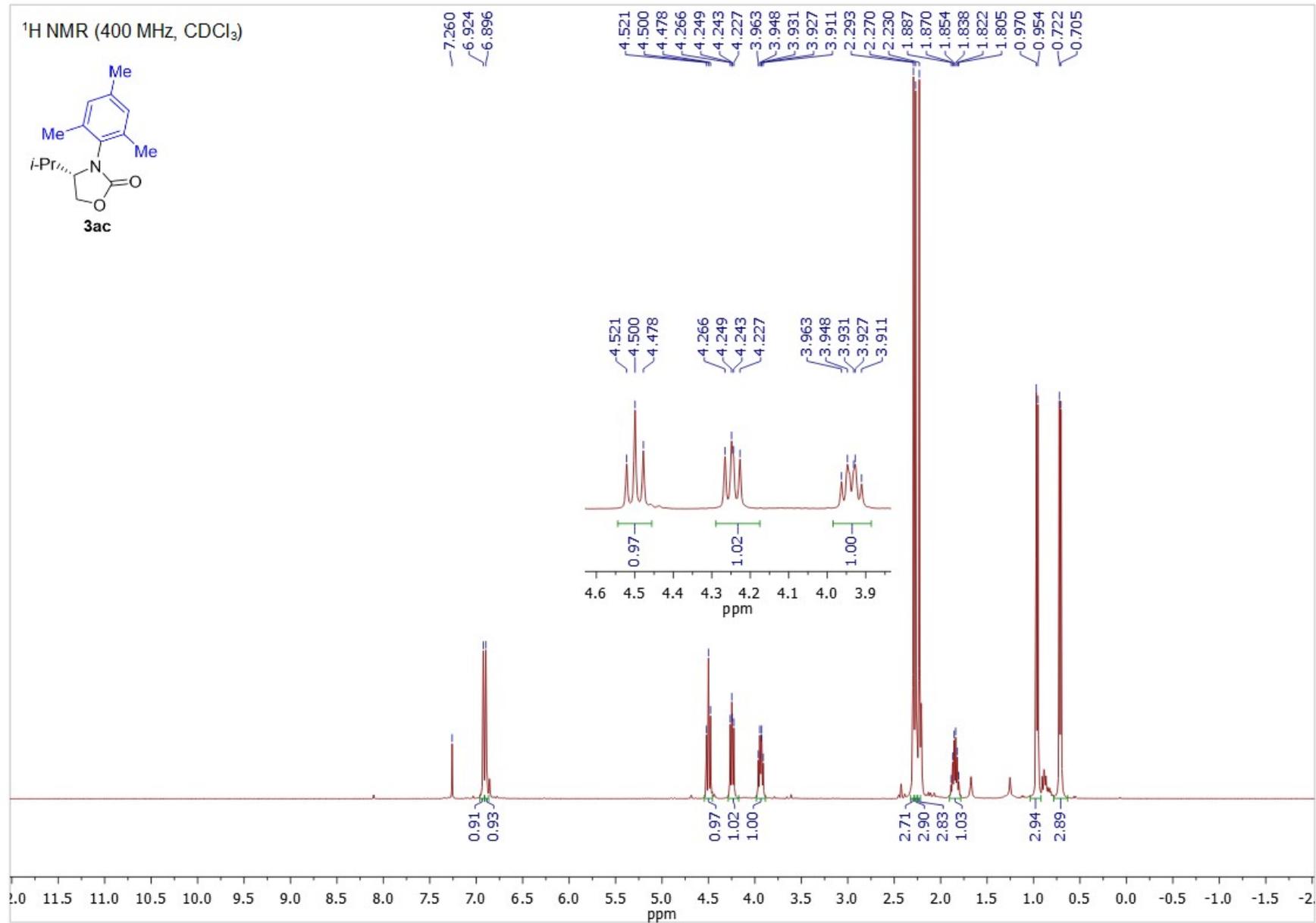
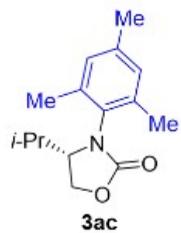


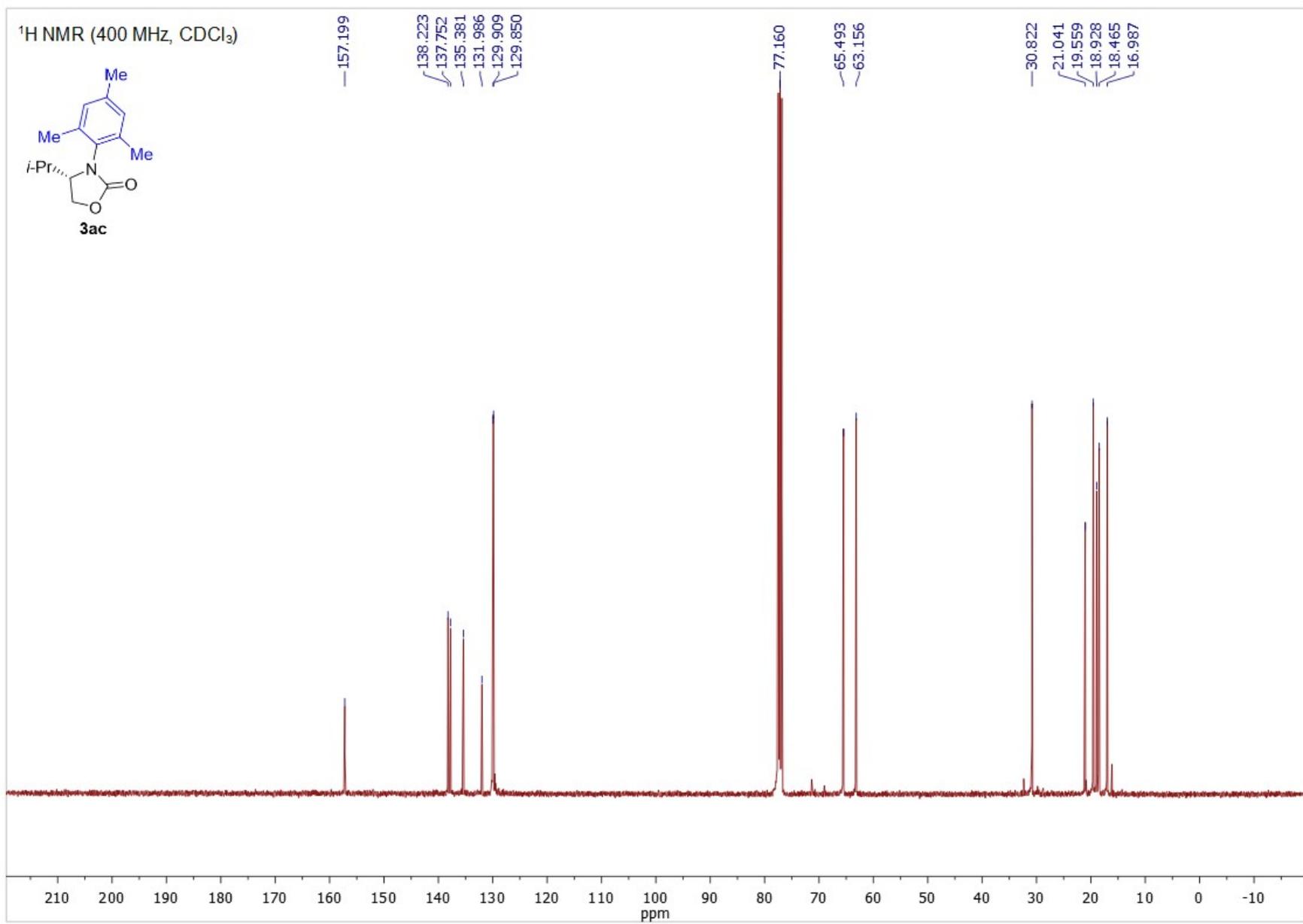
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

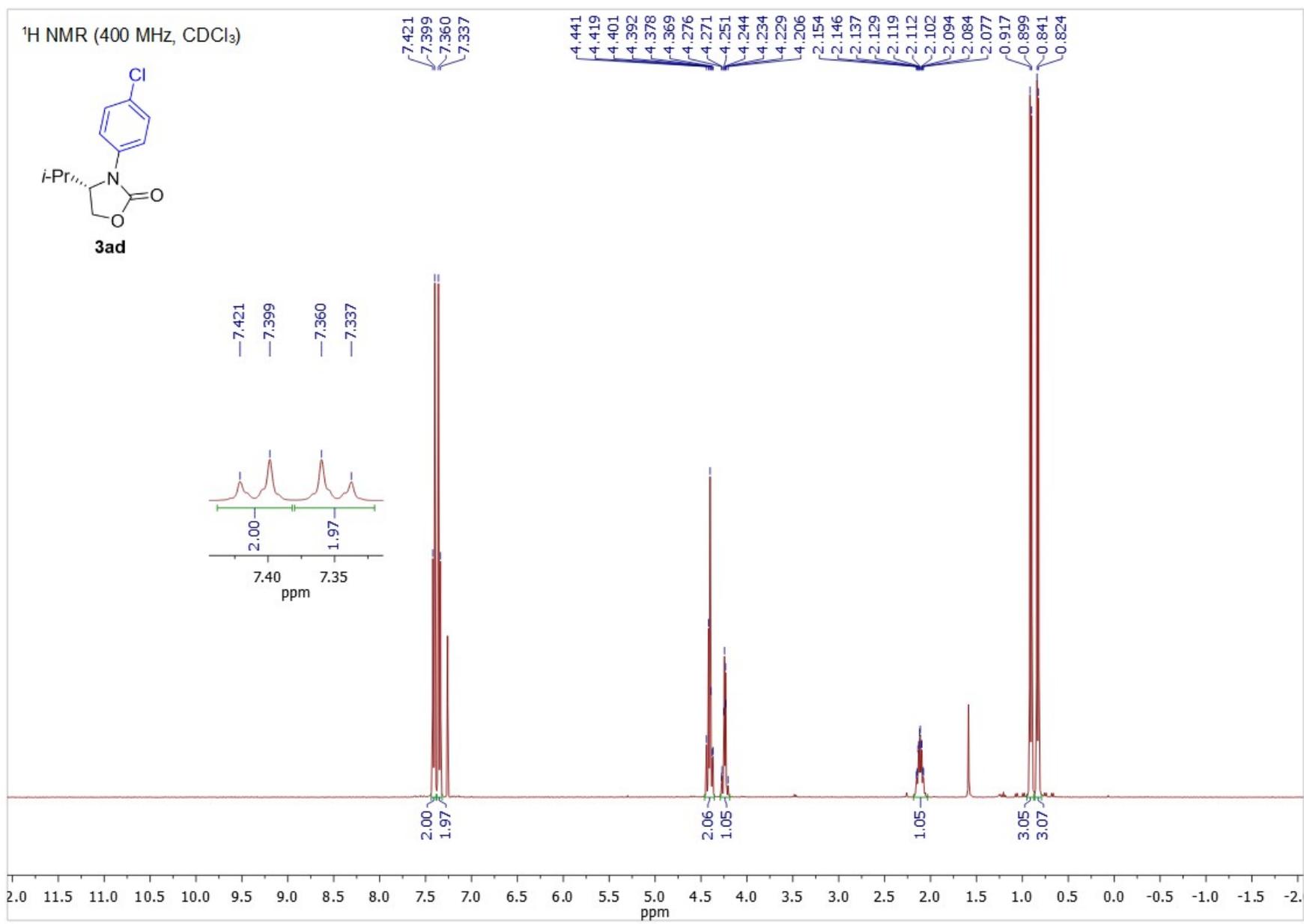


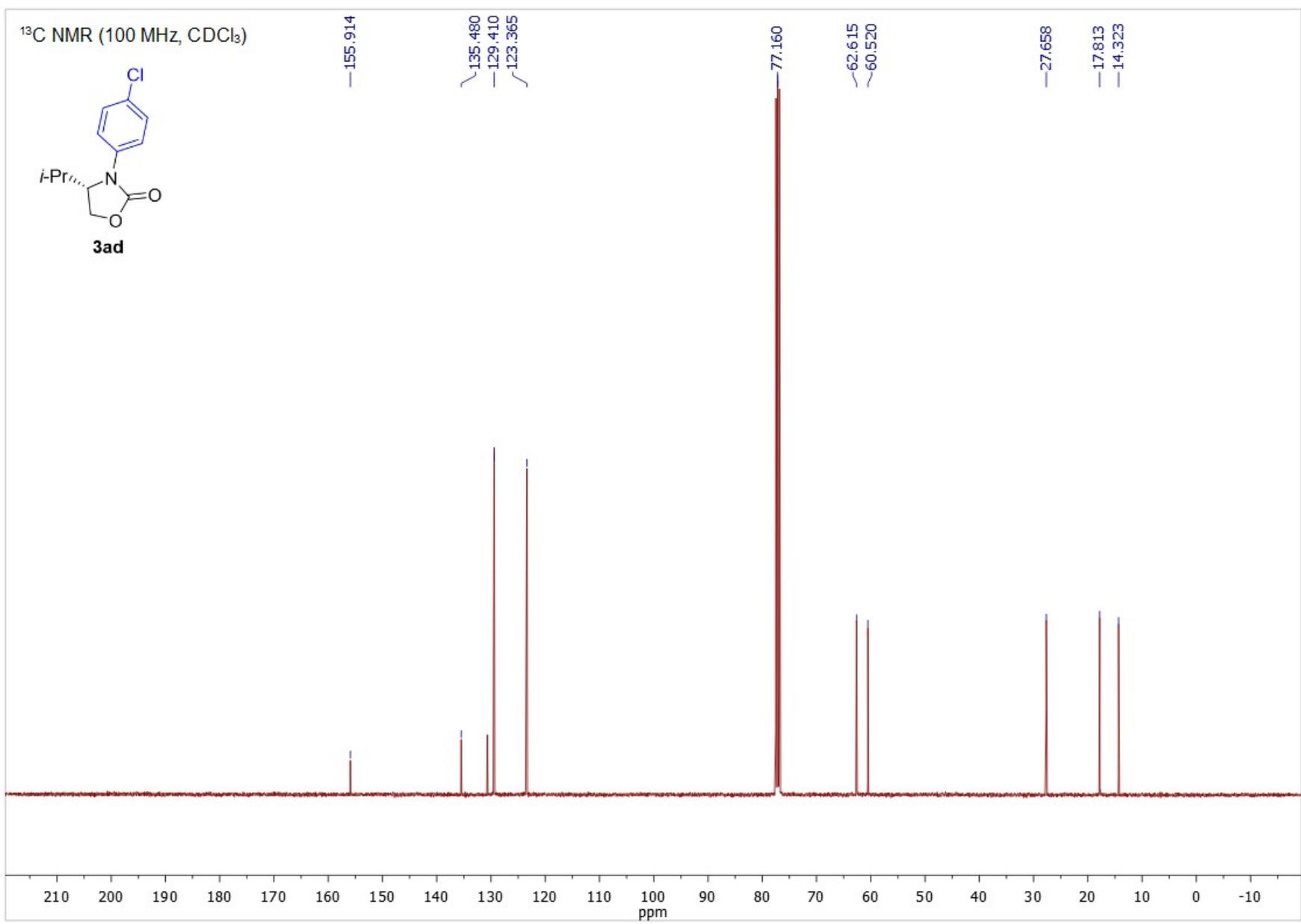


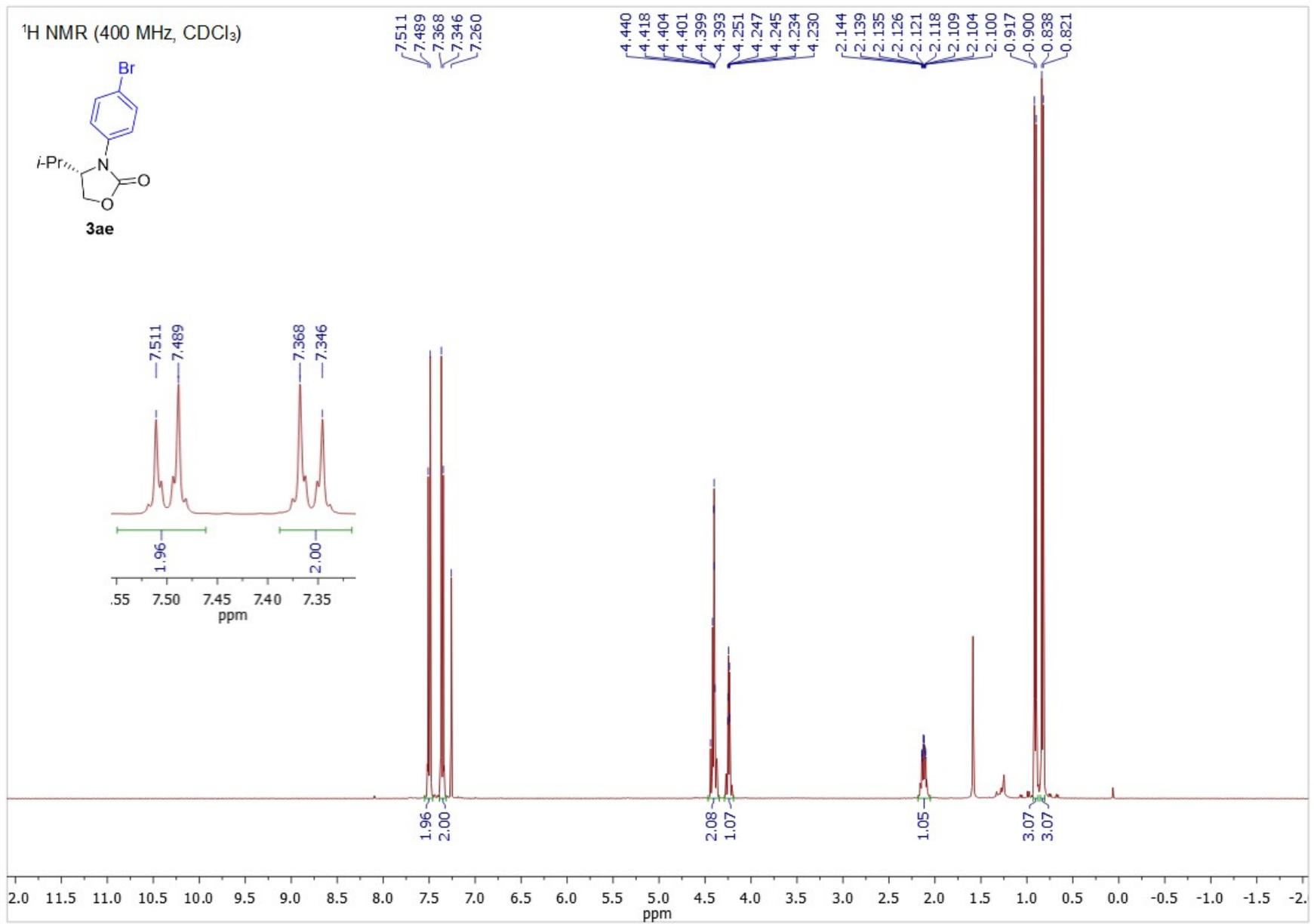
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



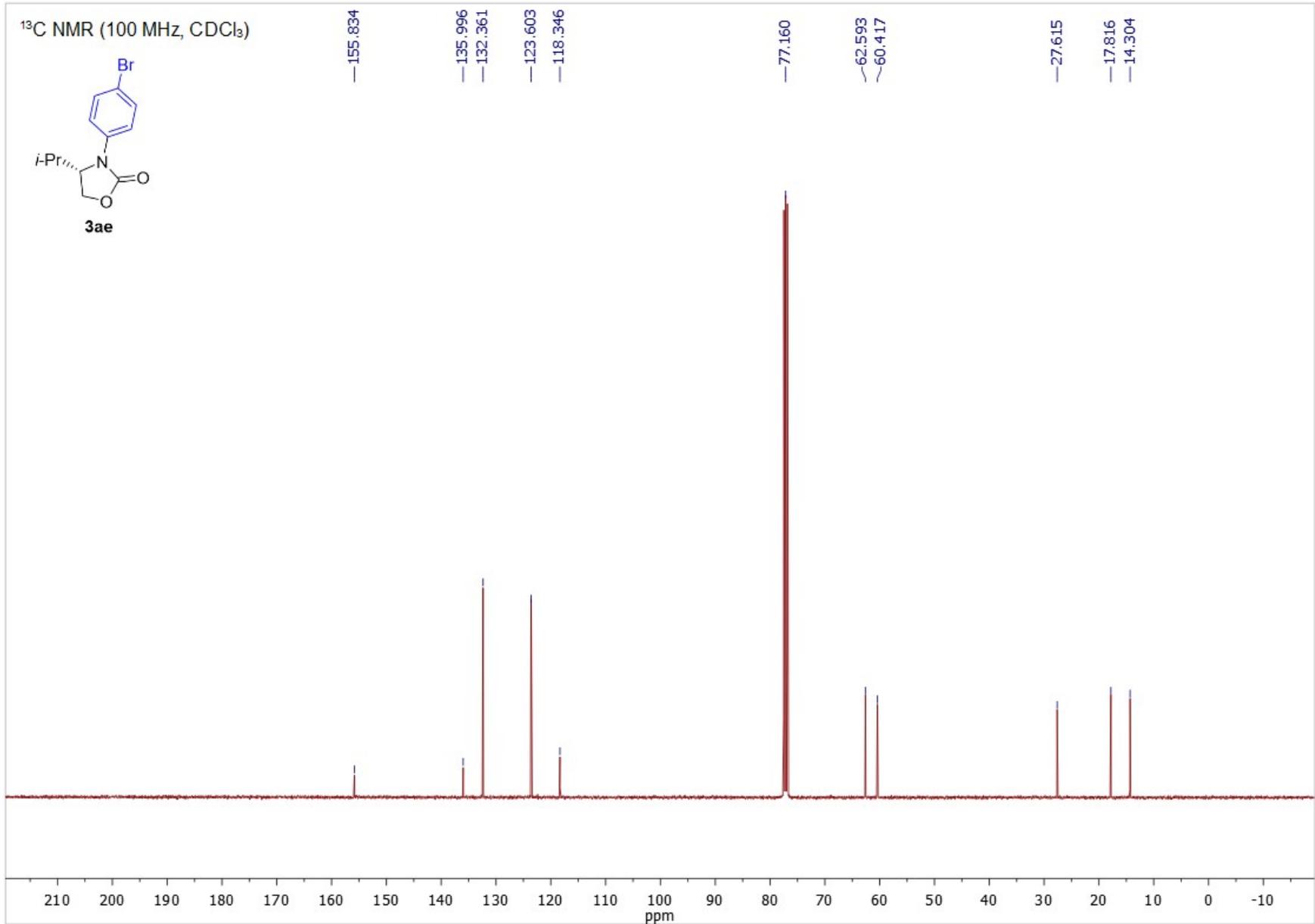
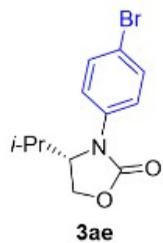


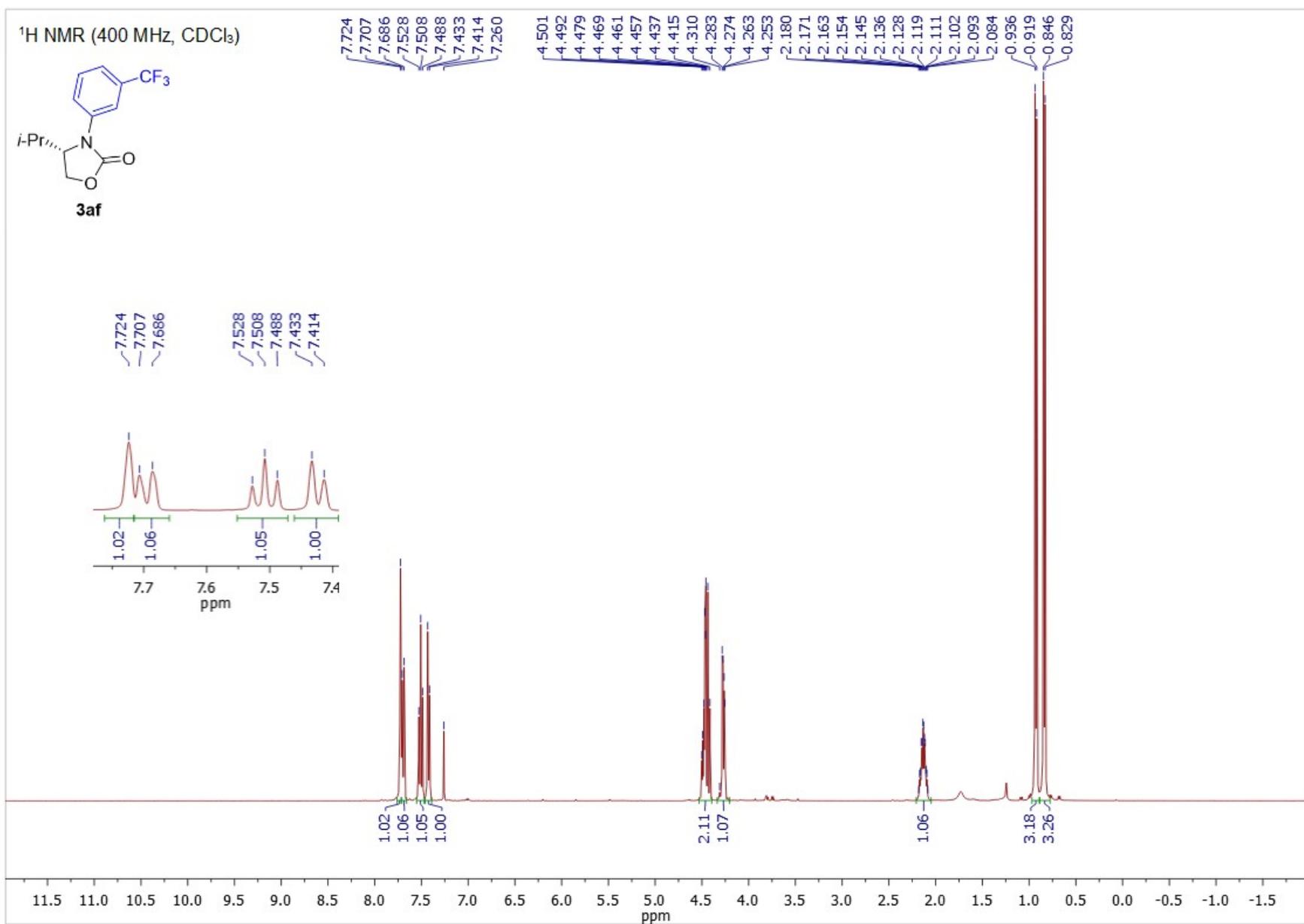




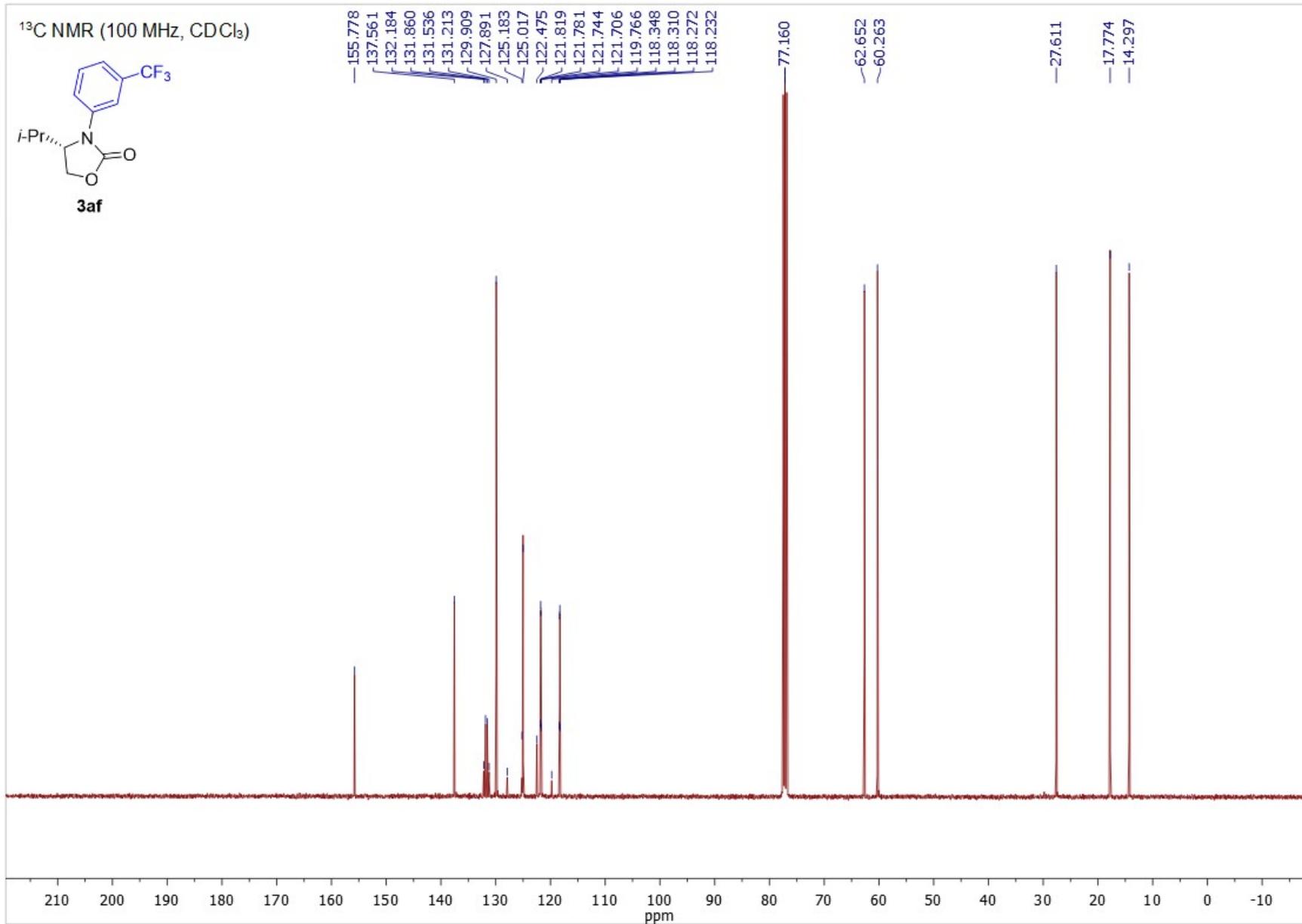


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

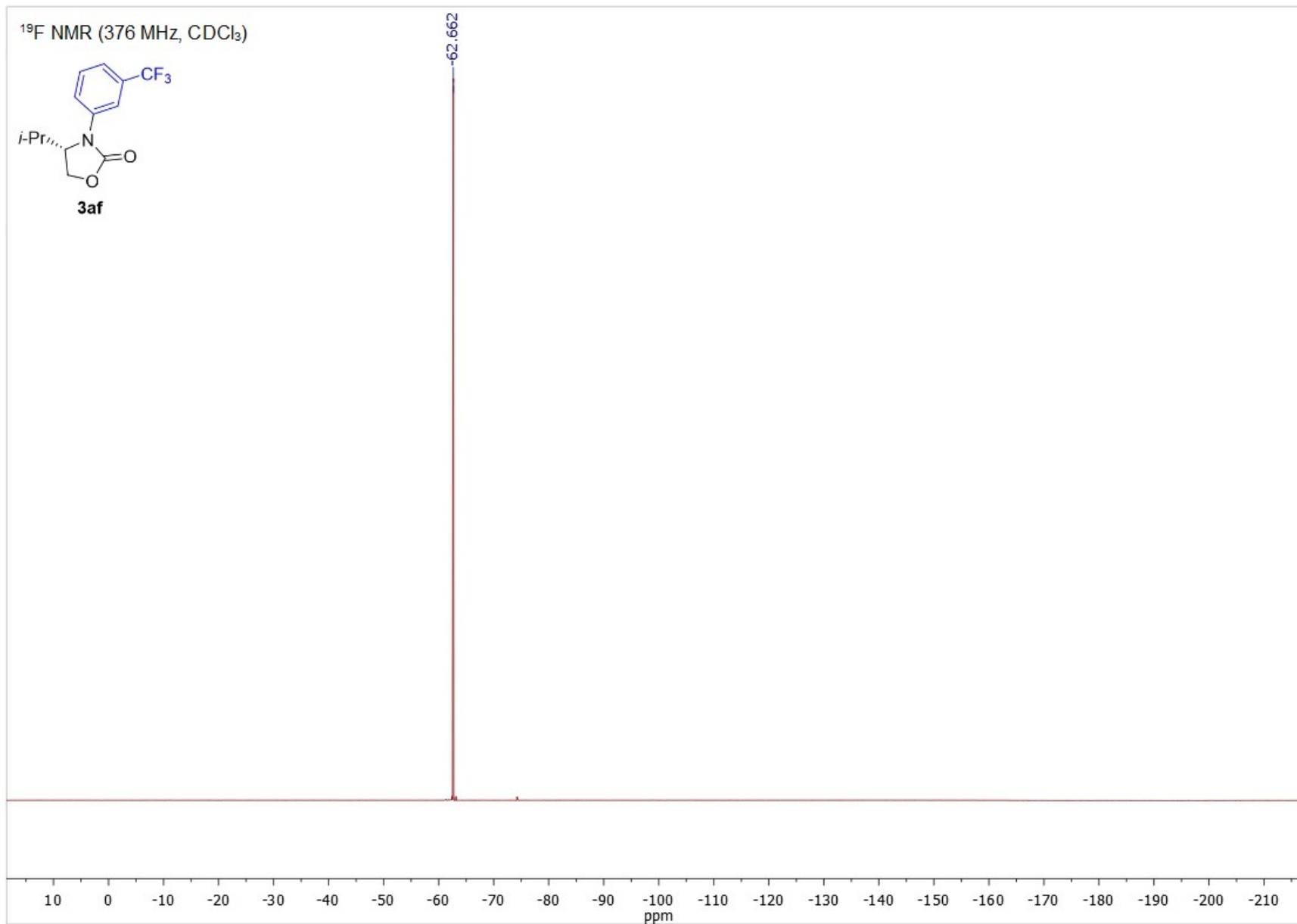


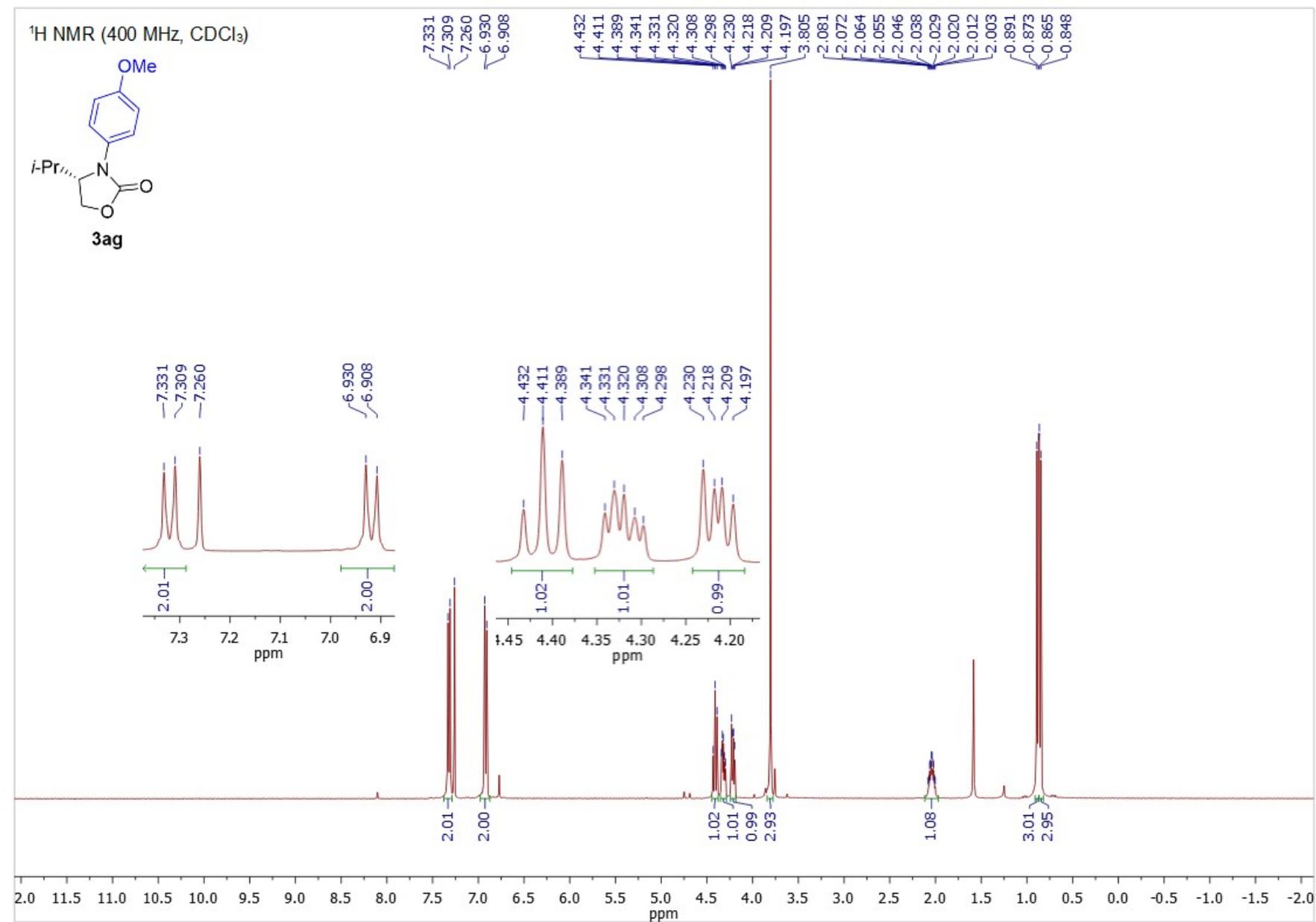


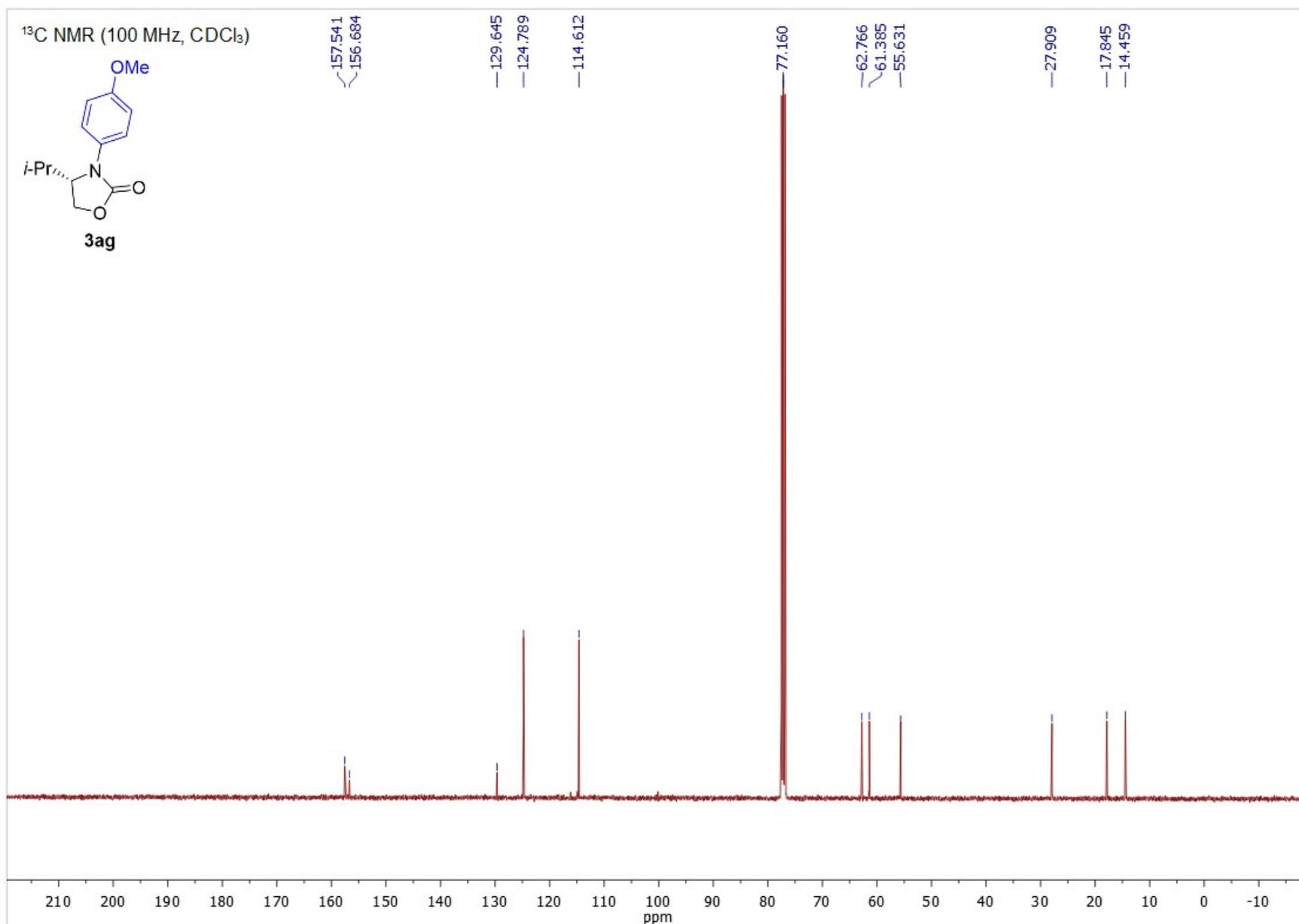
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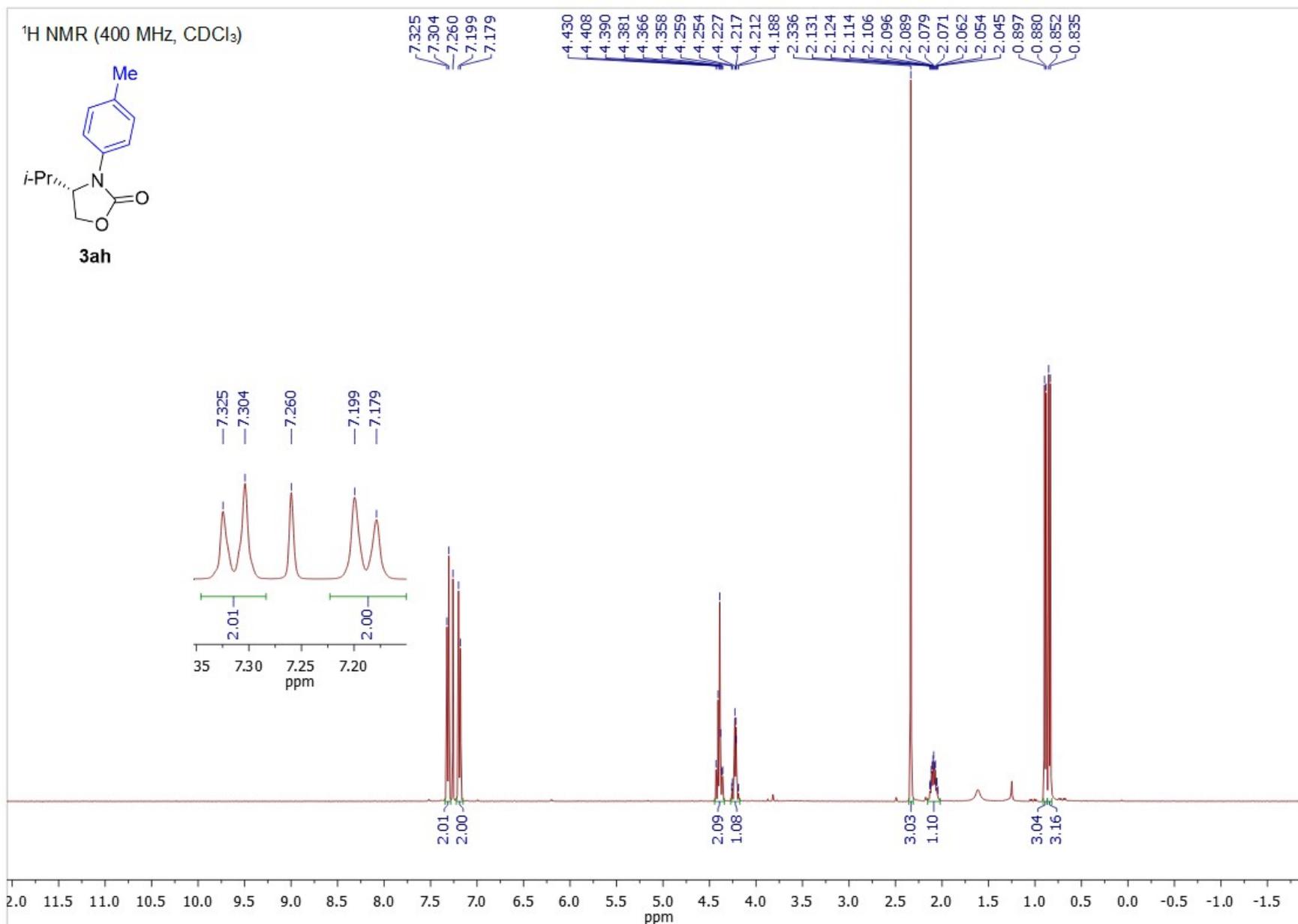


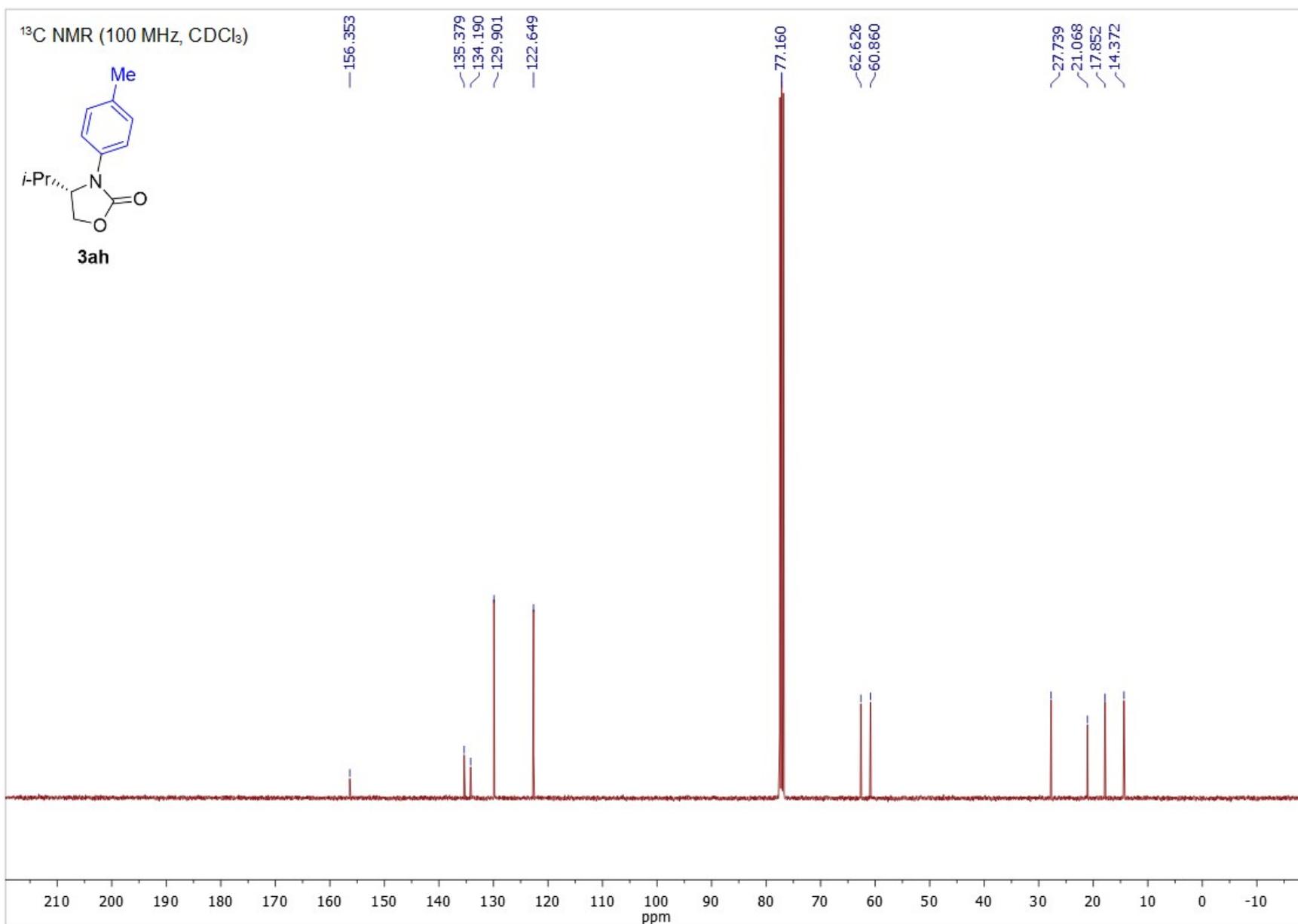
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )

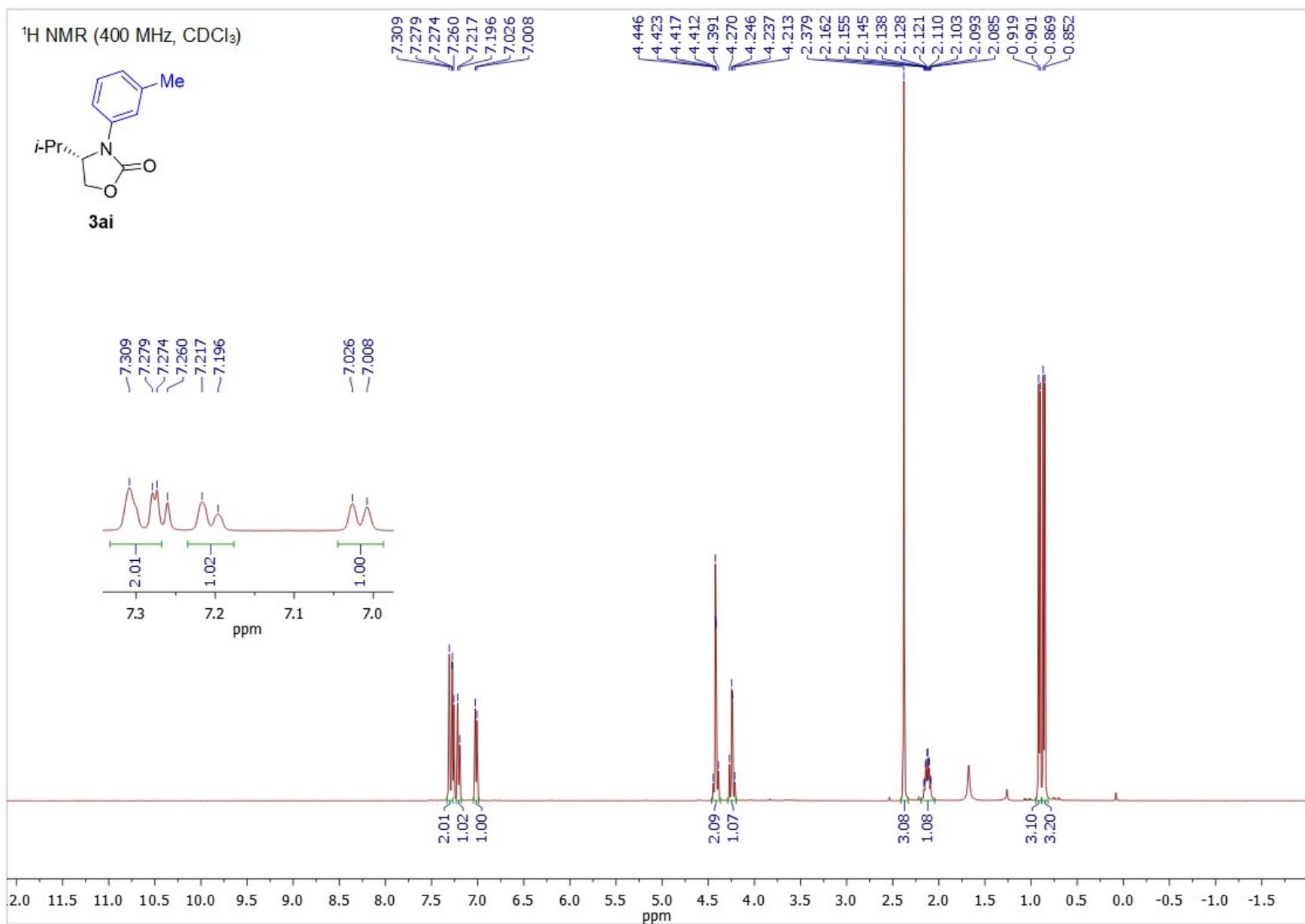




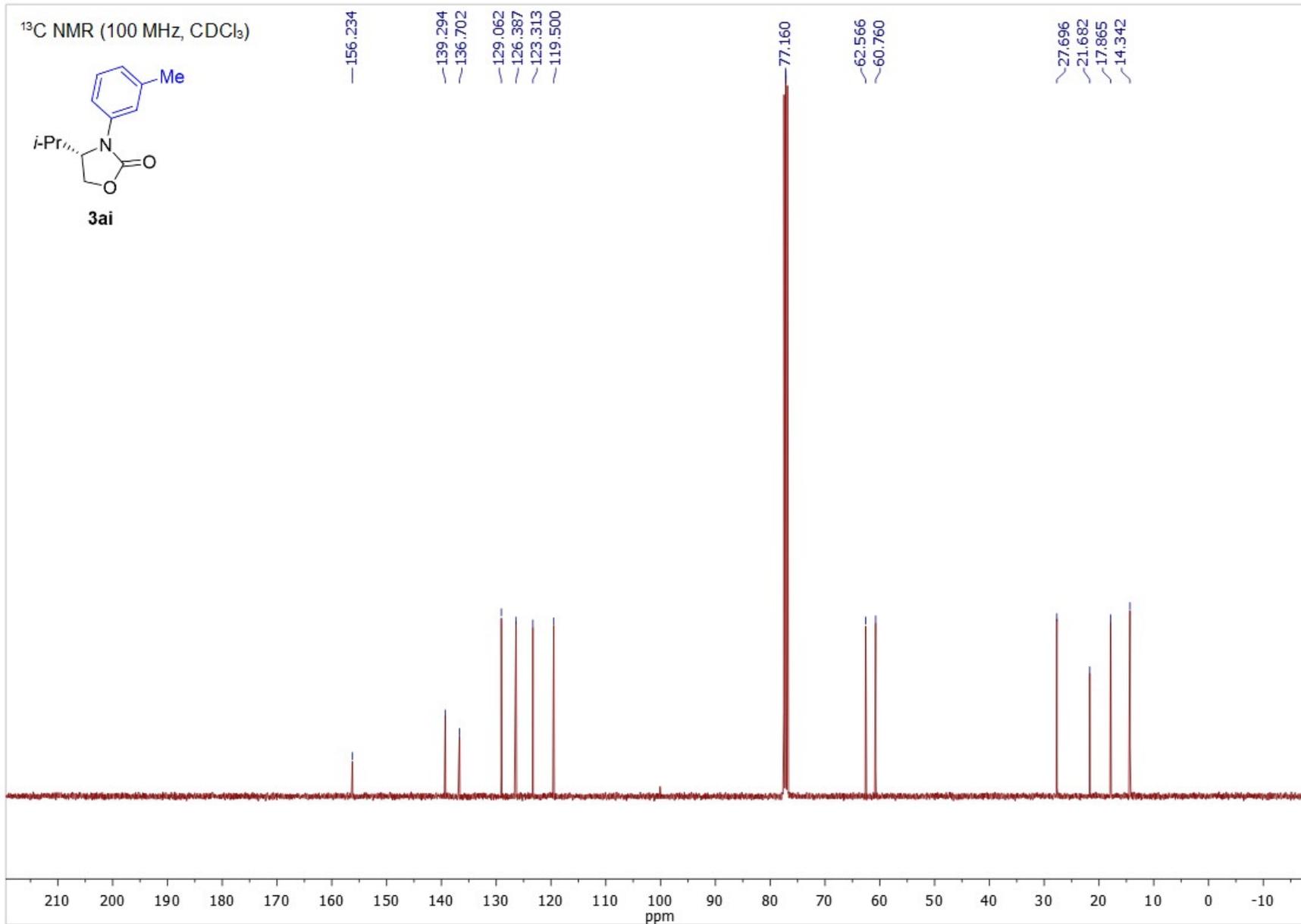


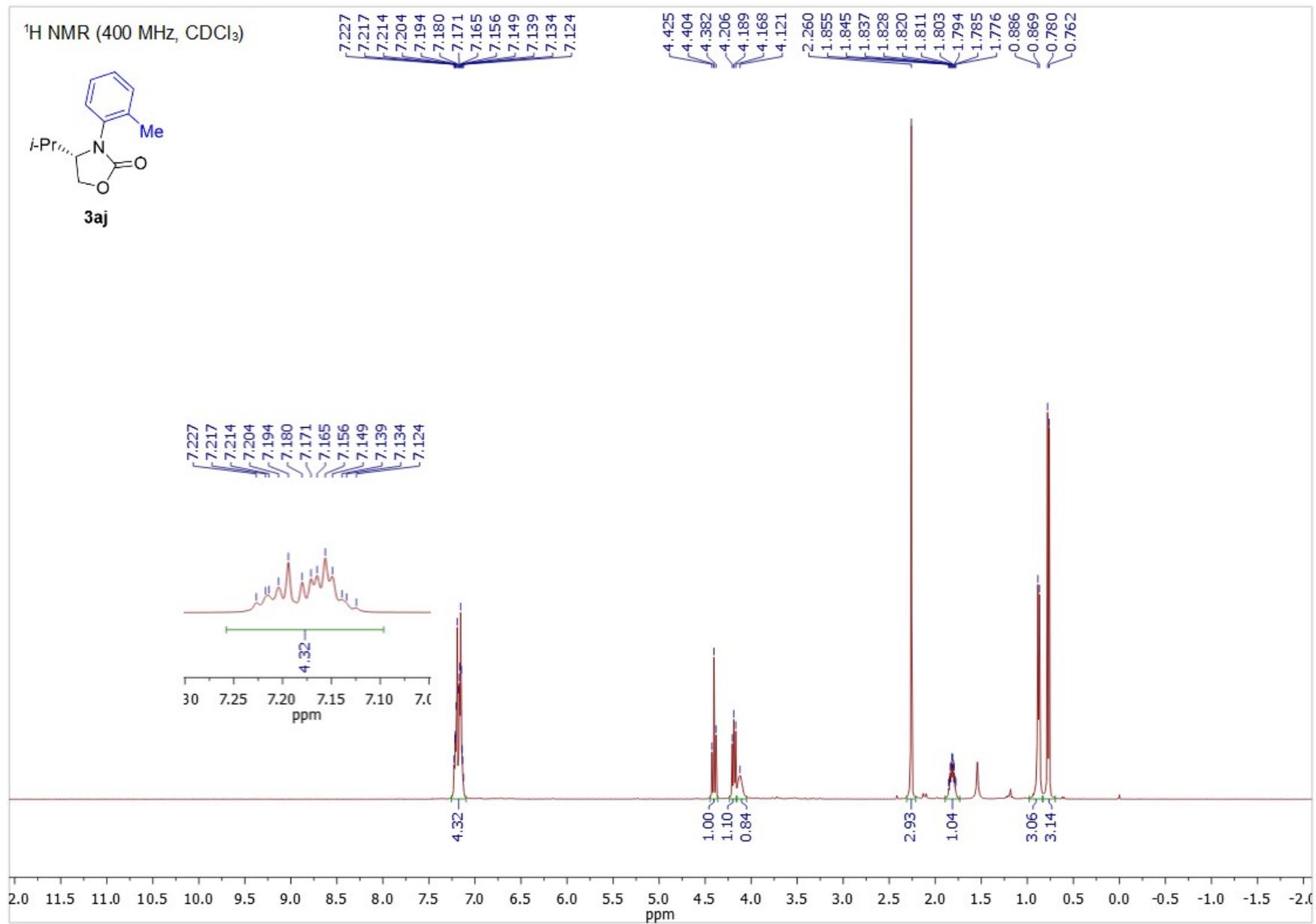


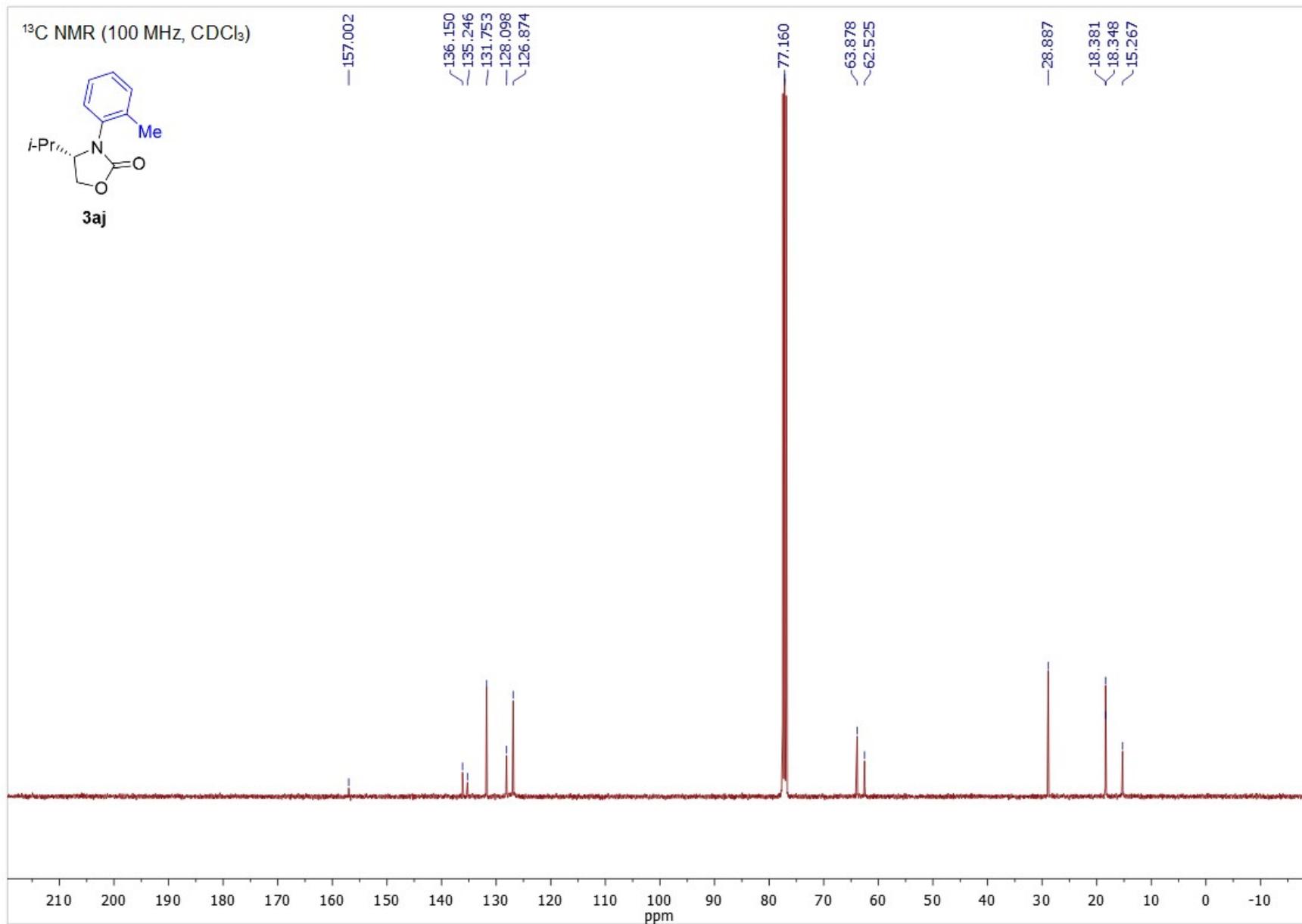


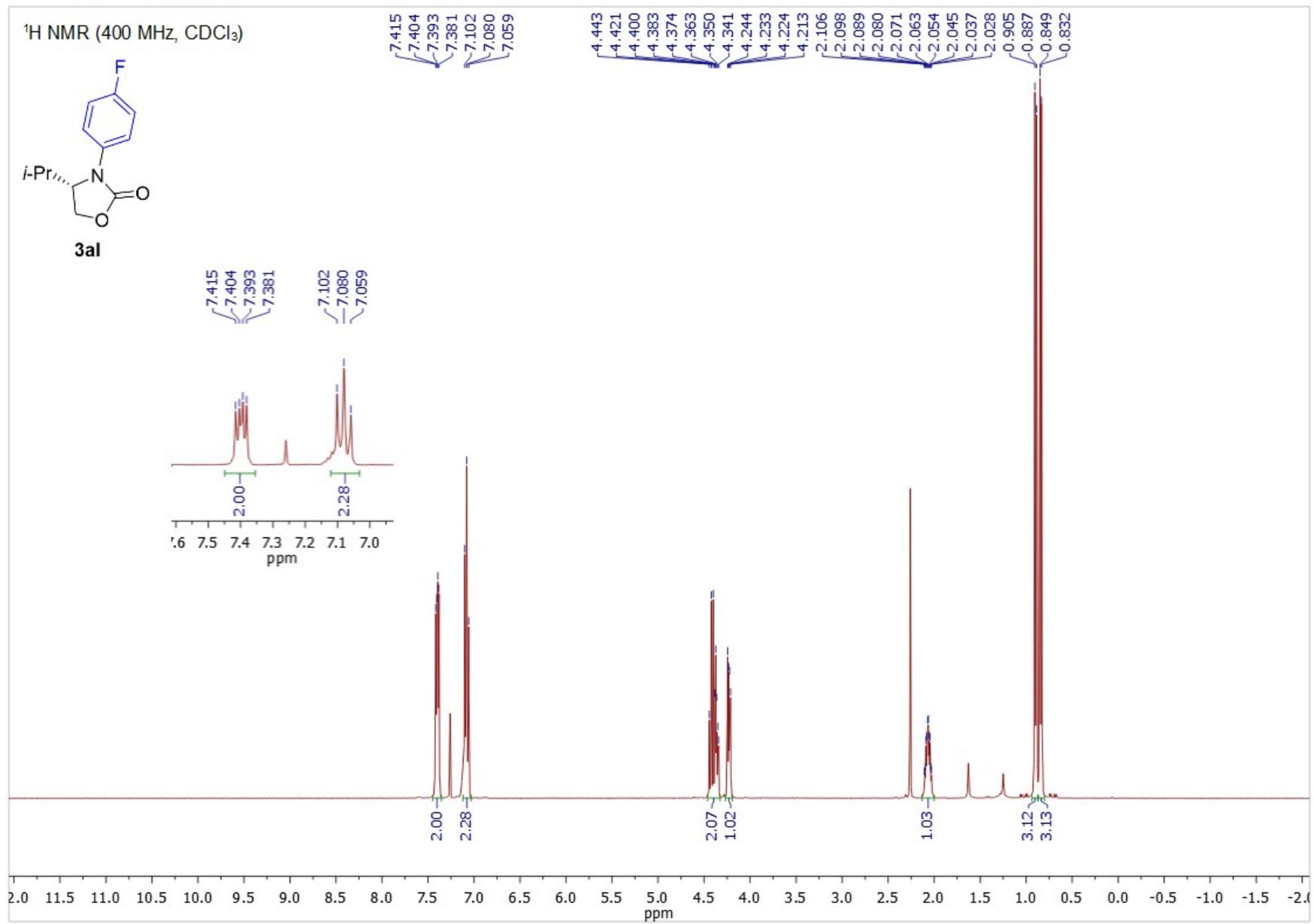


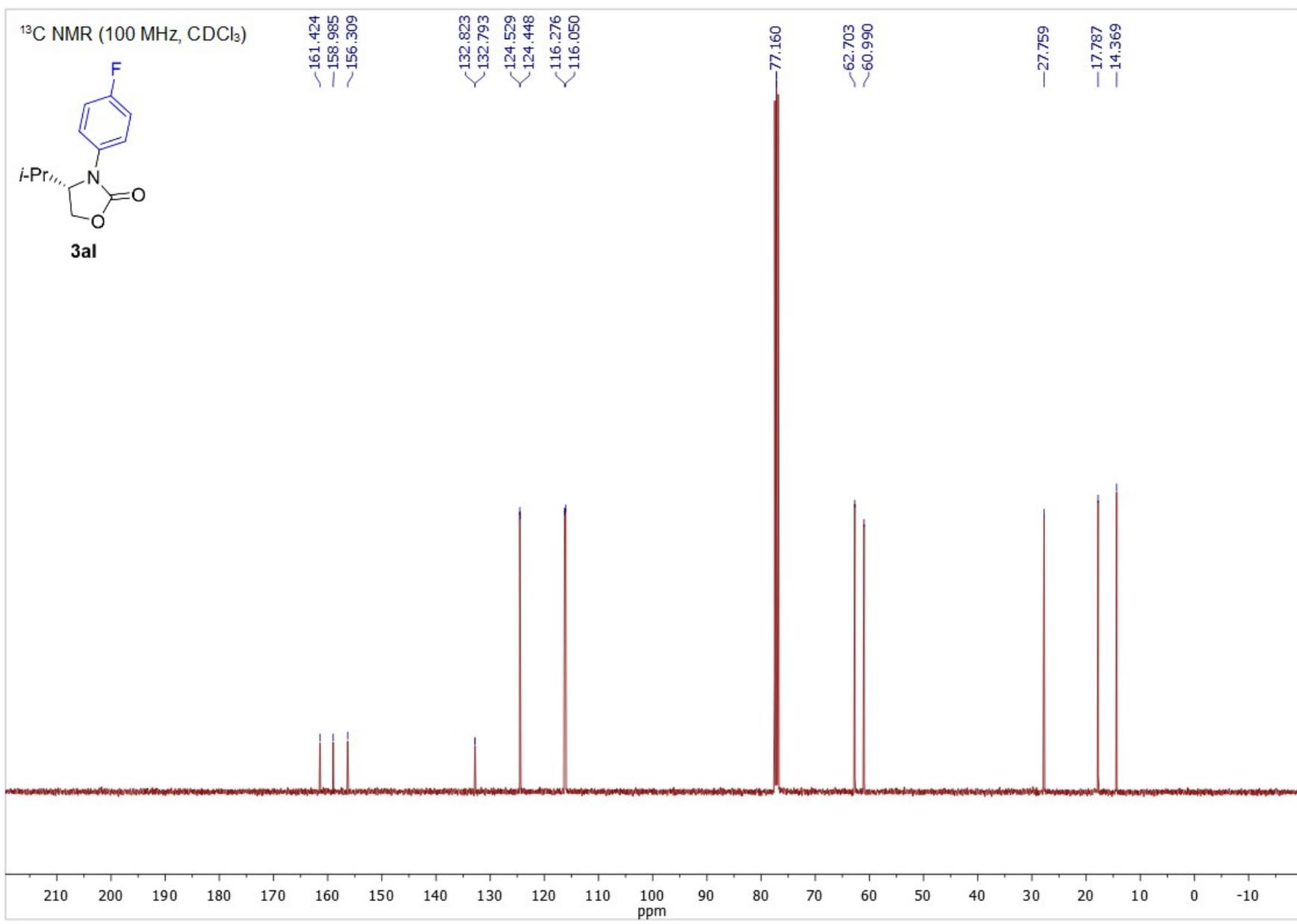
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



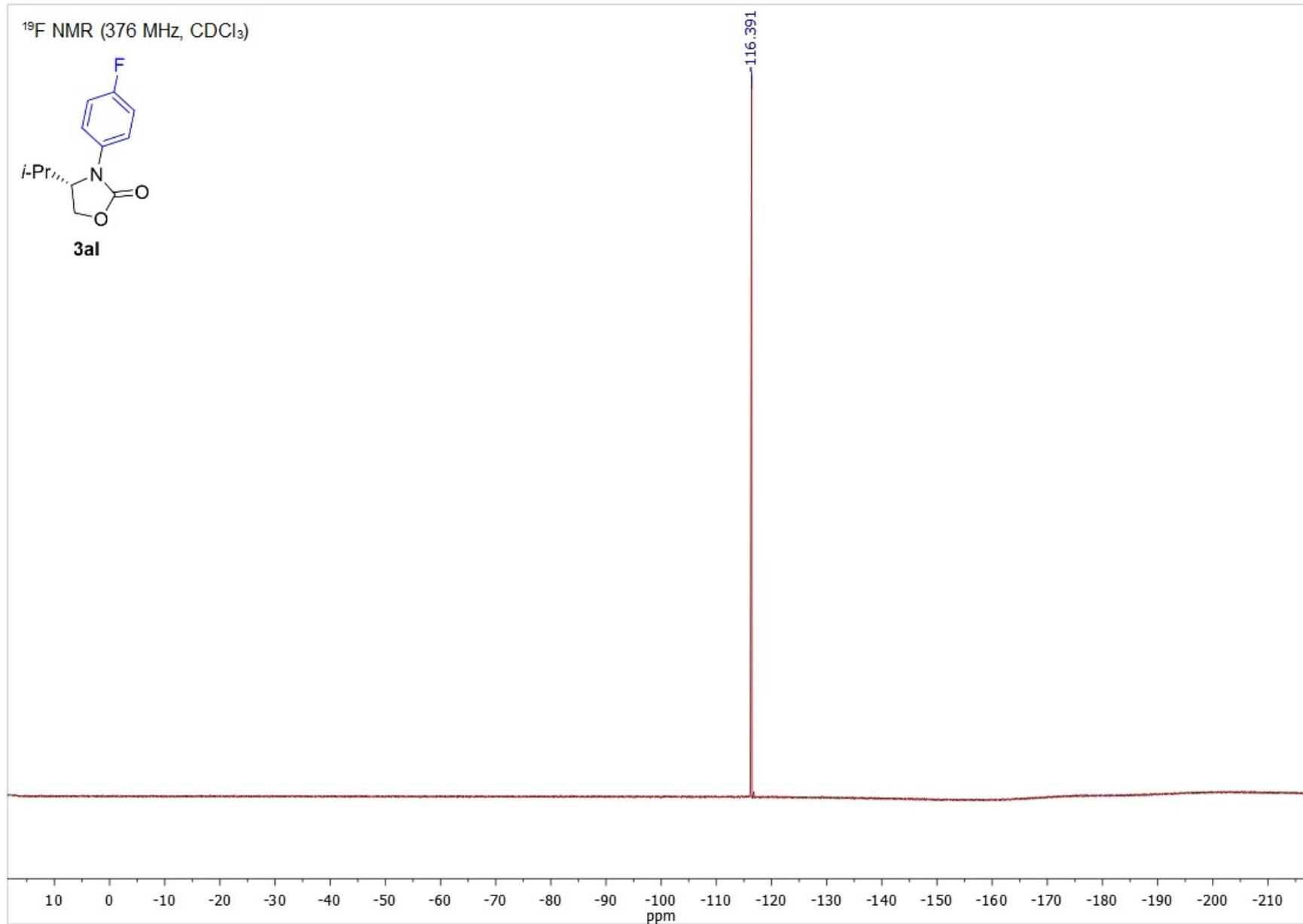
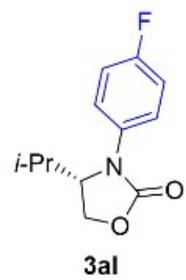


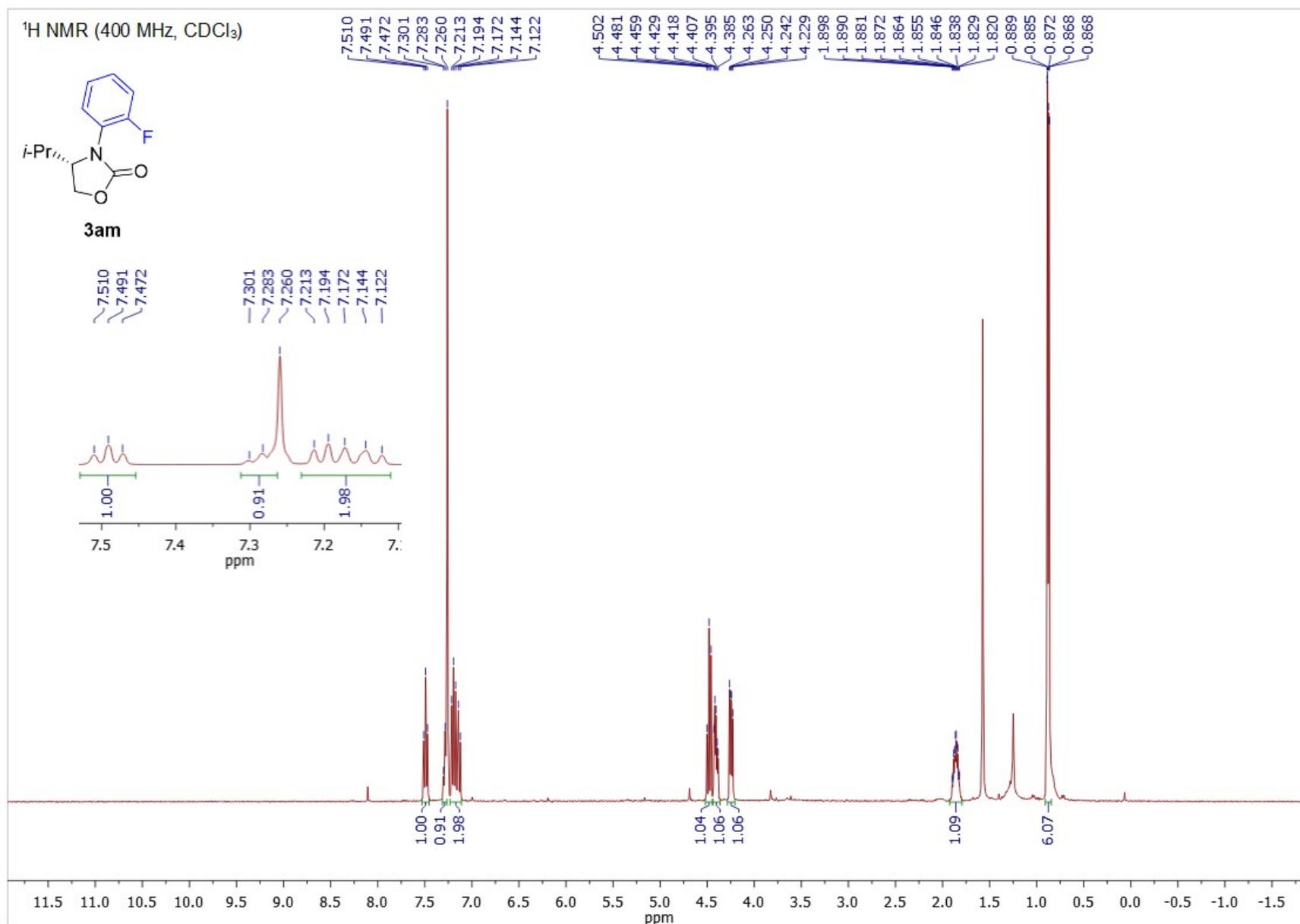






<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)

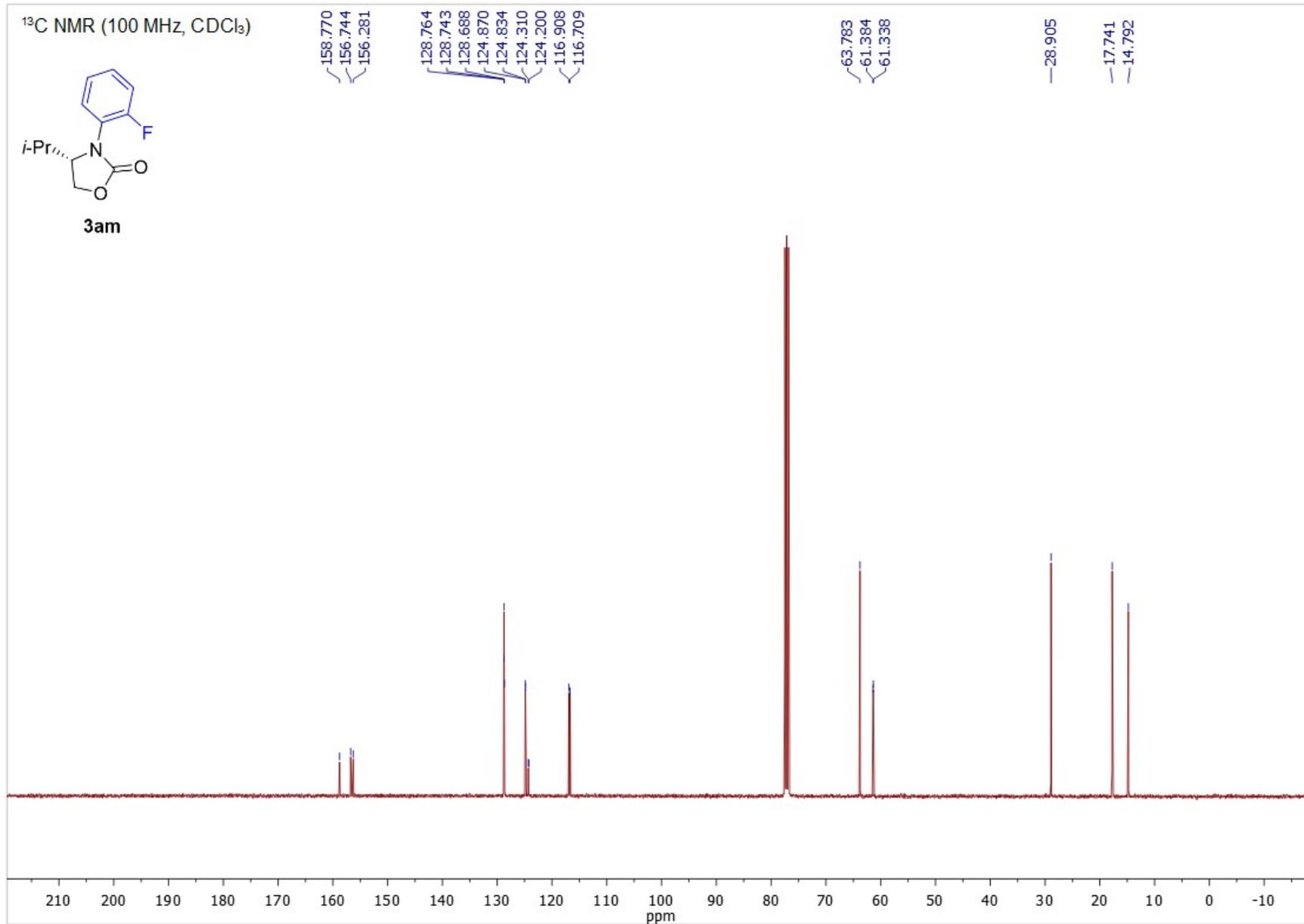




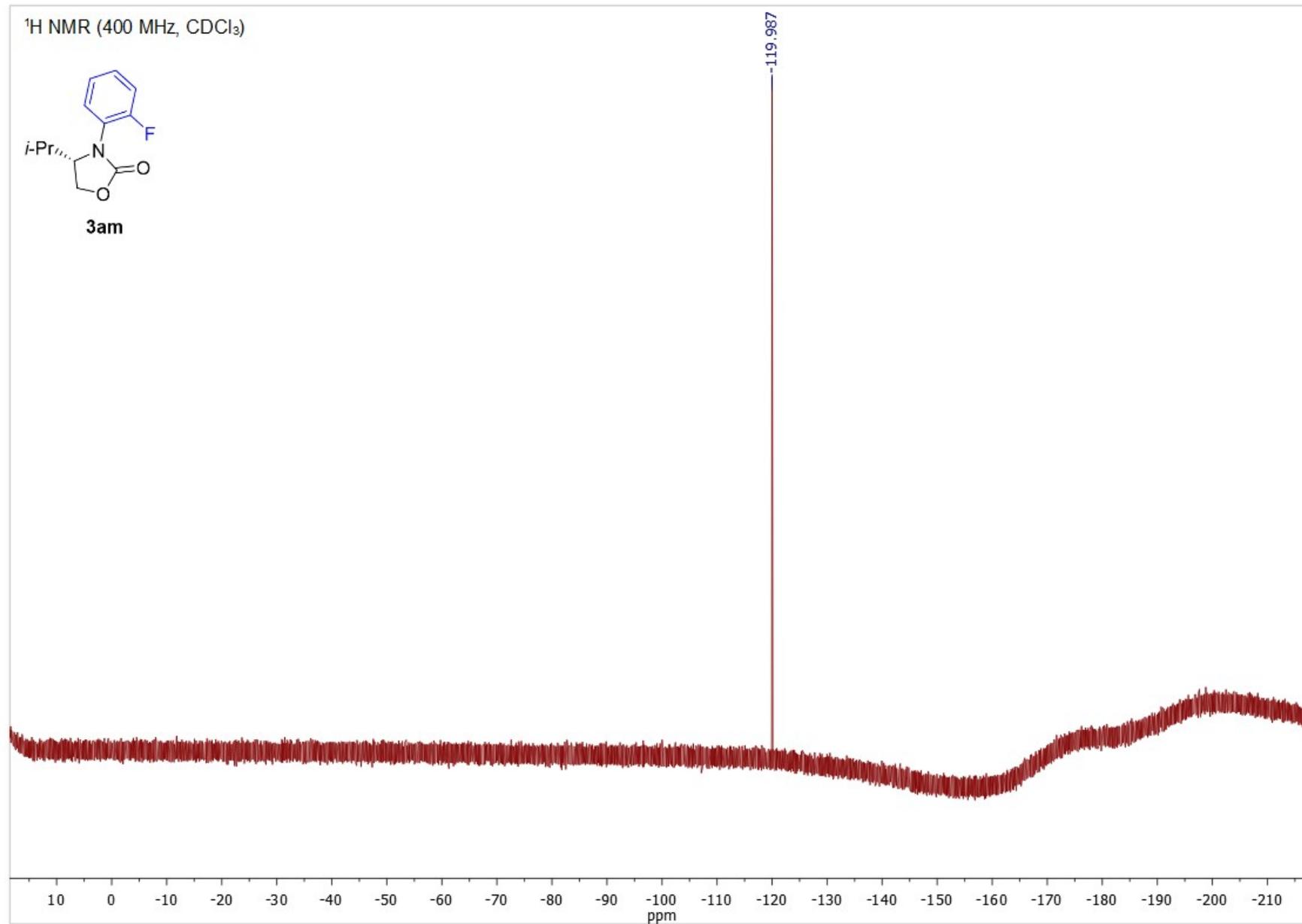
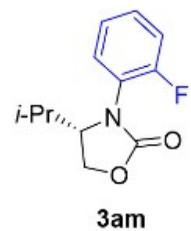
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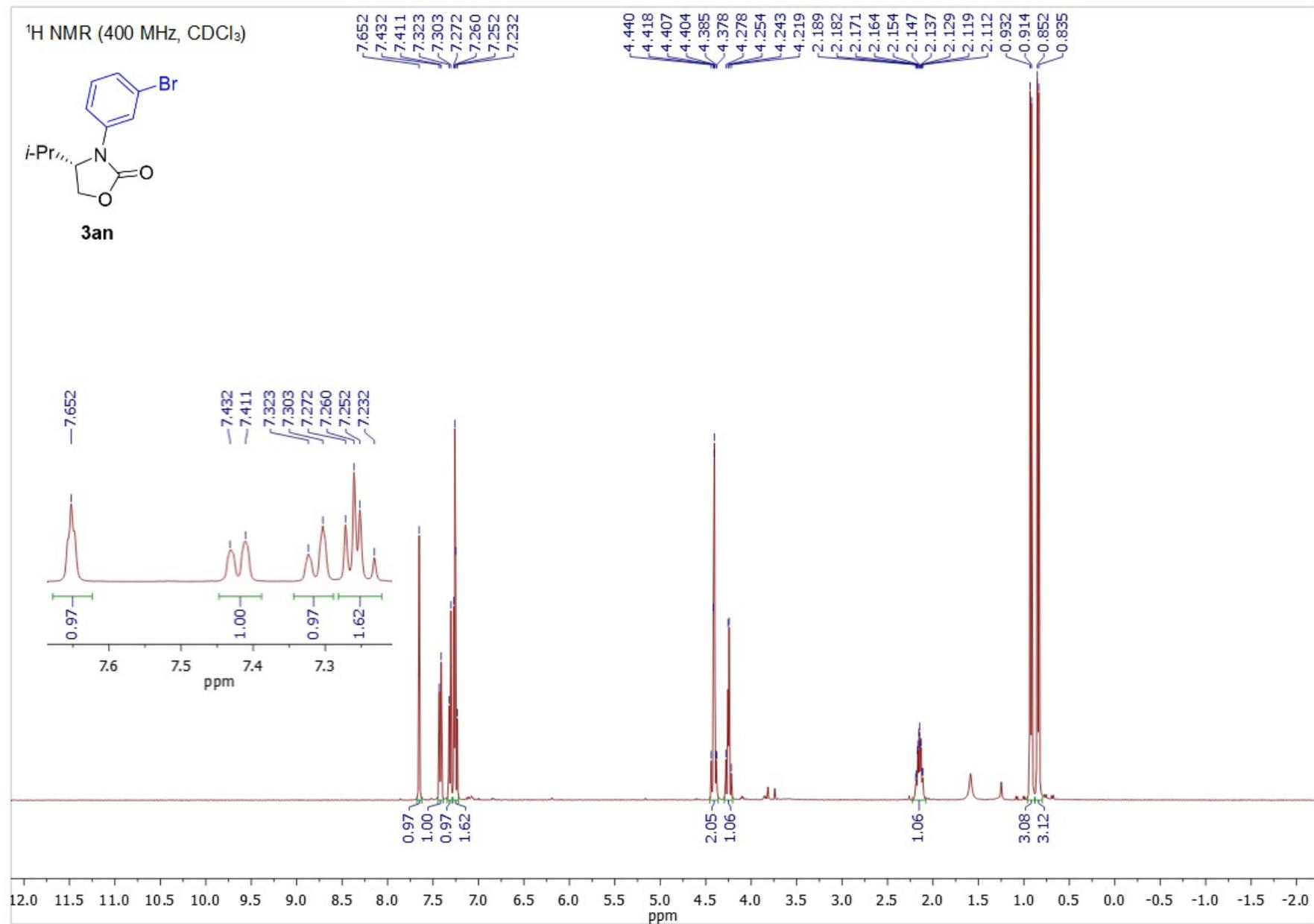


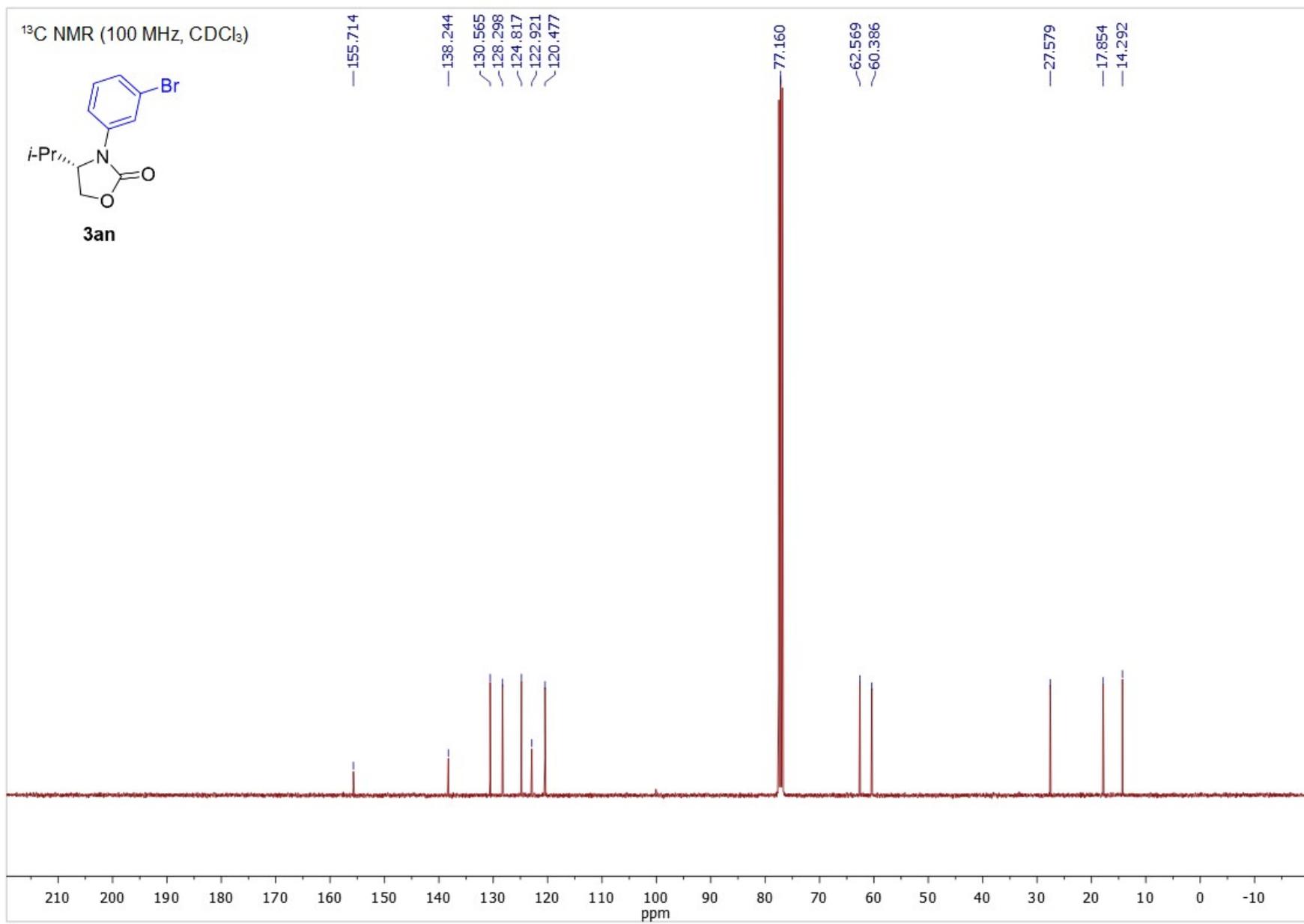
**3am**

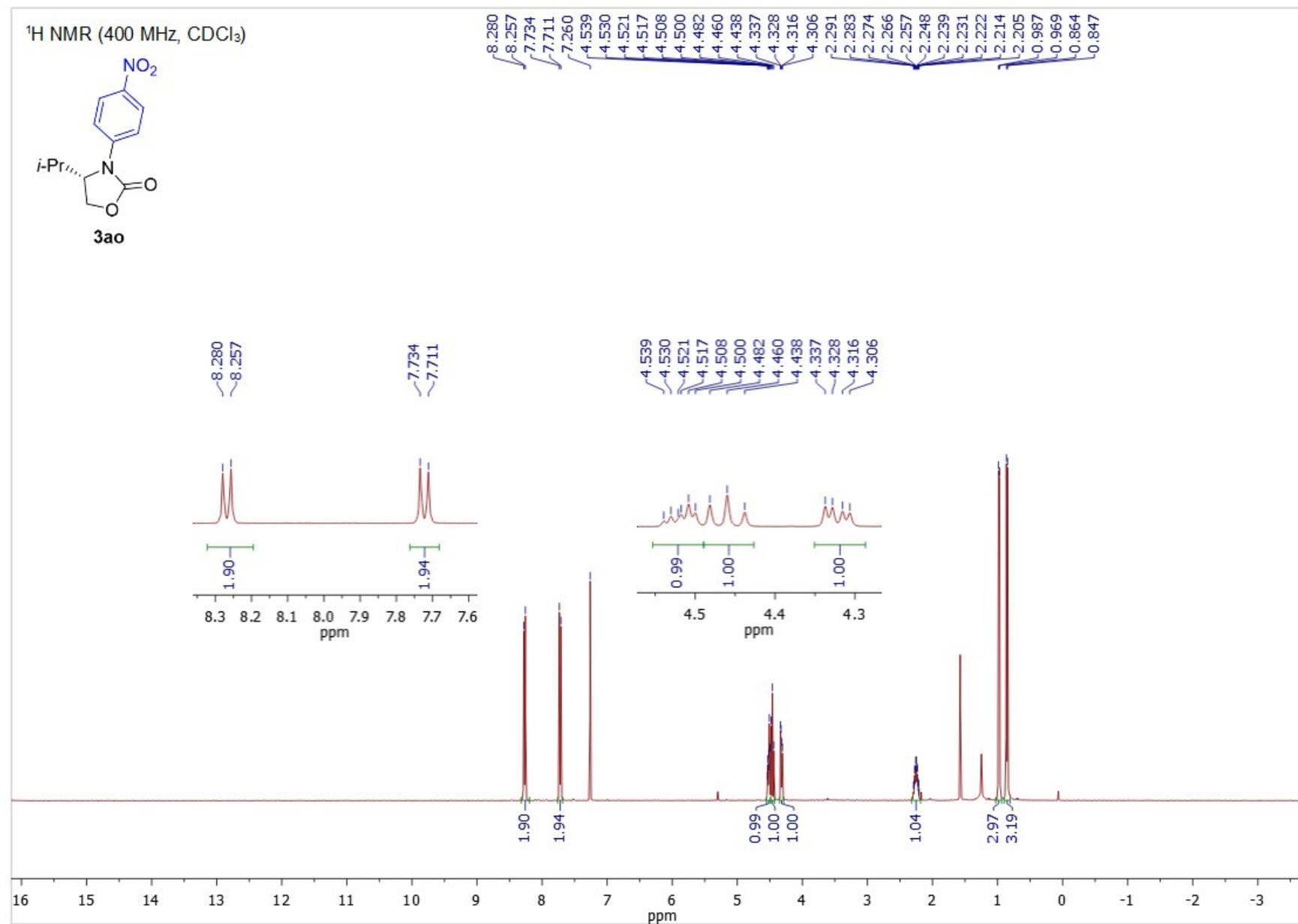


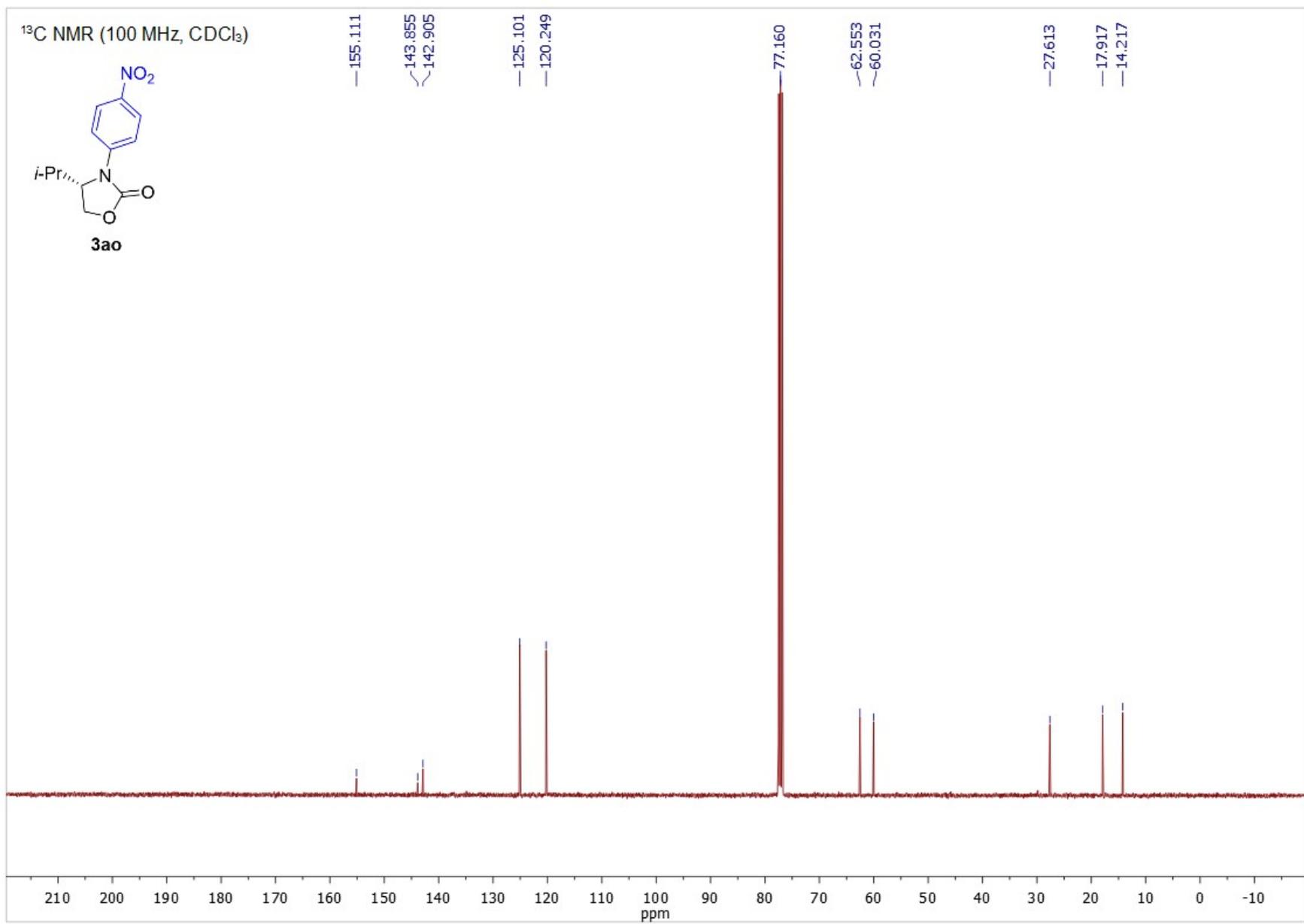
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



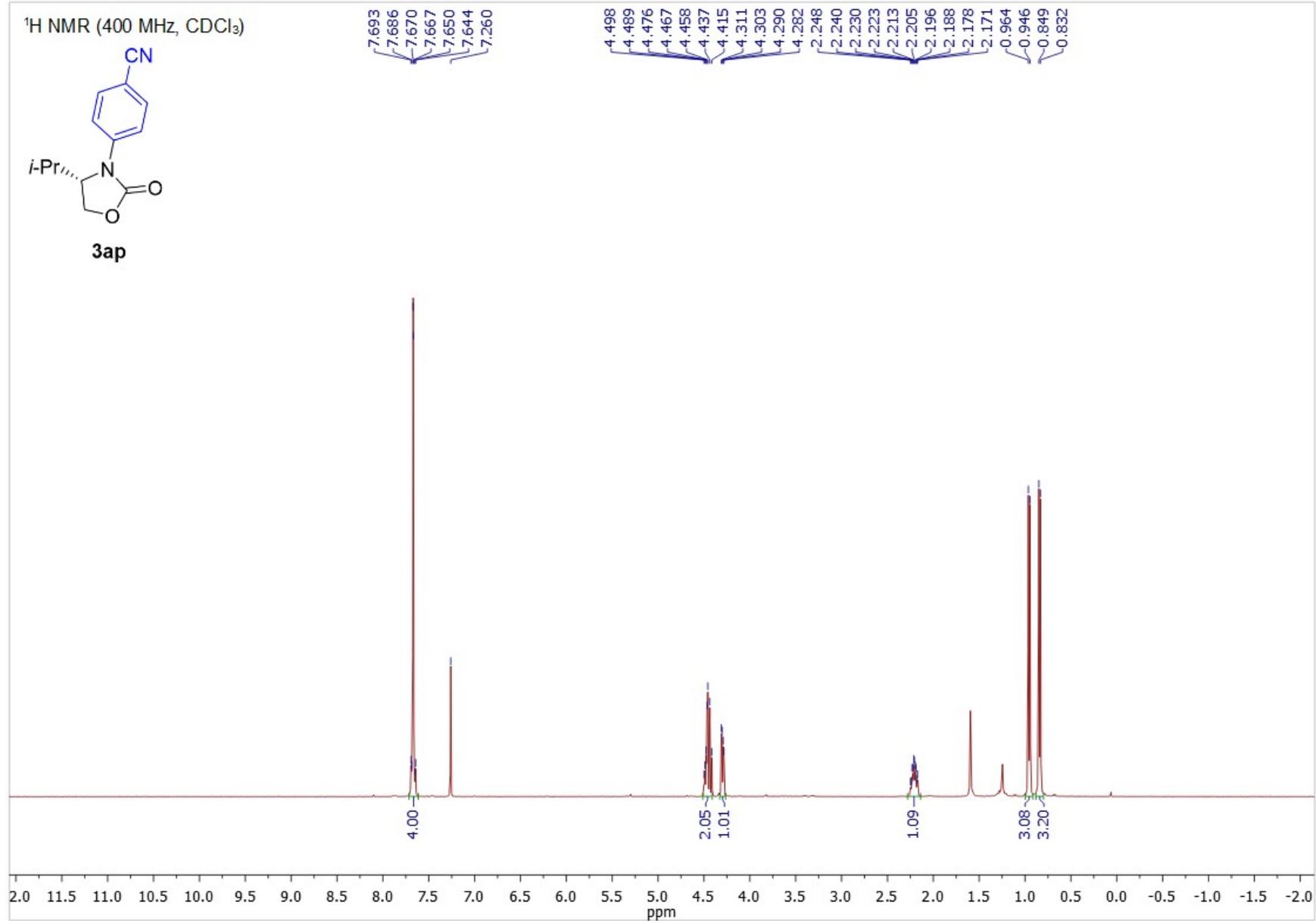
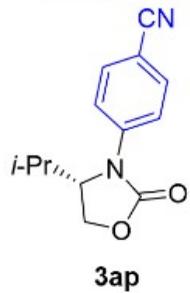




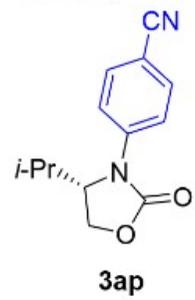




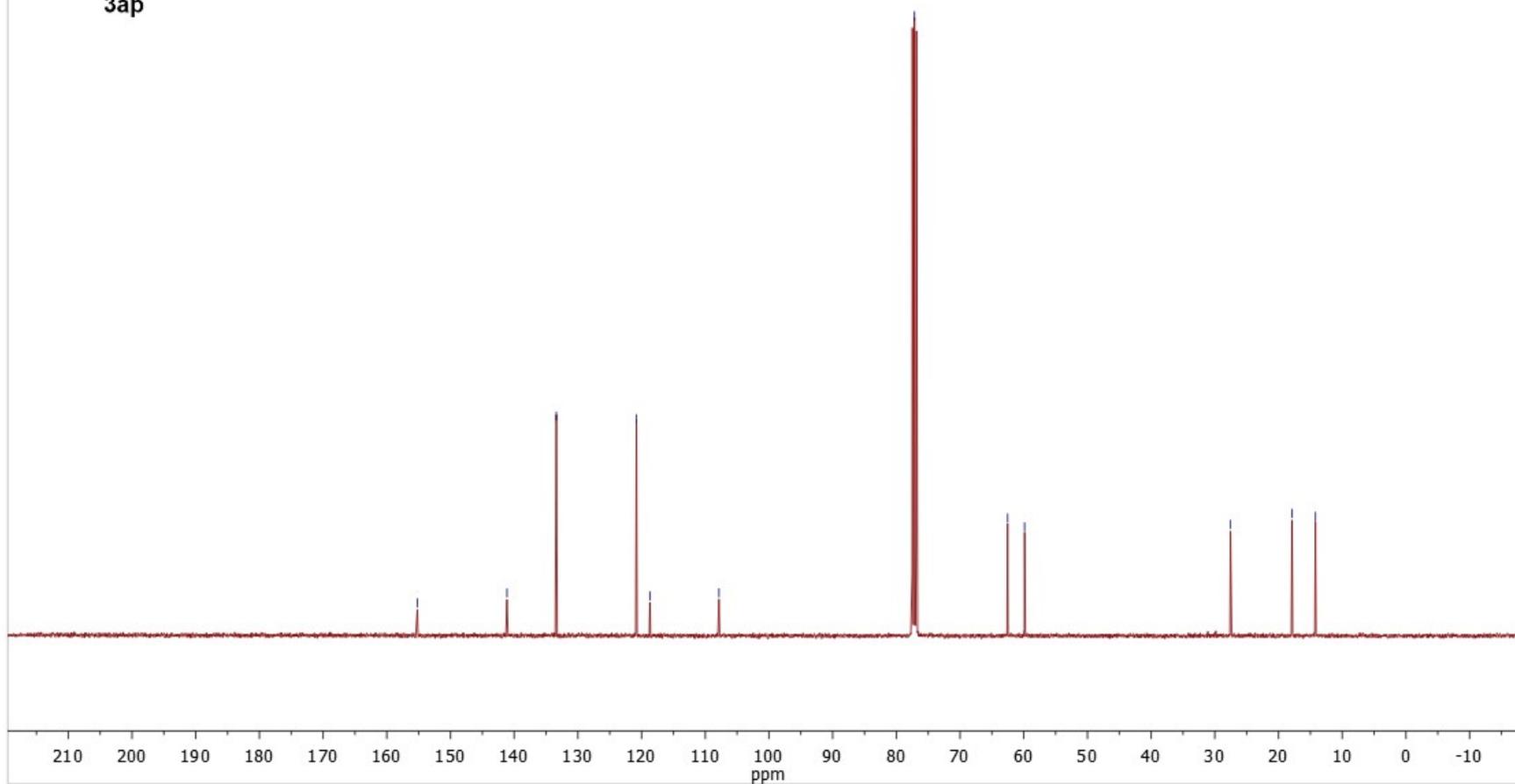
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

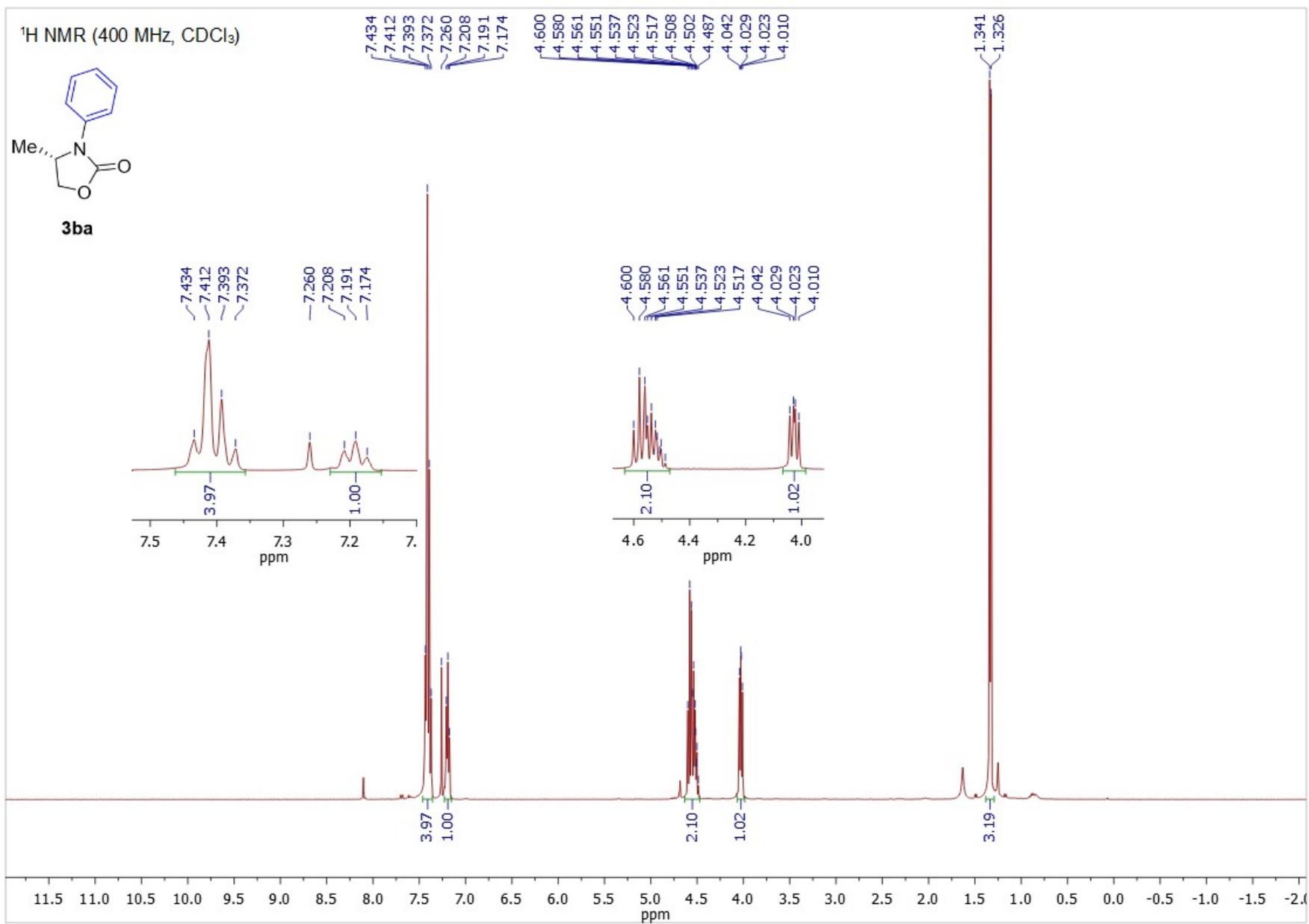


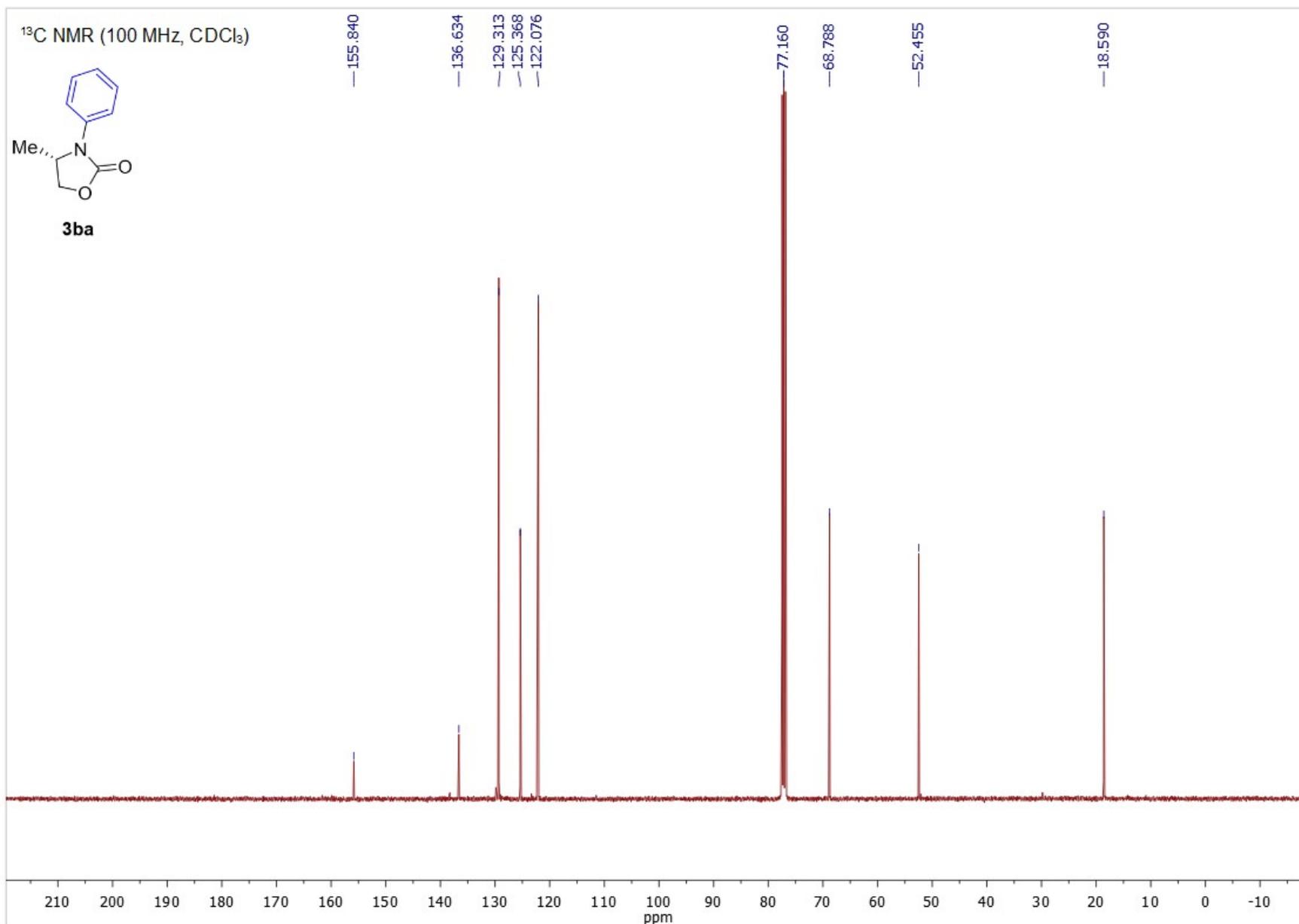
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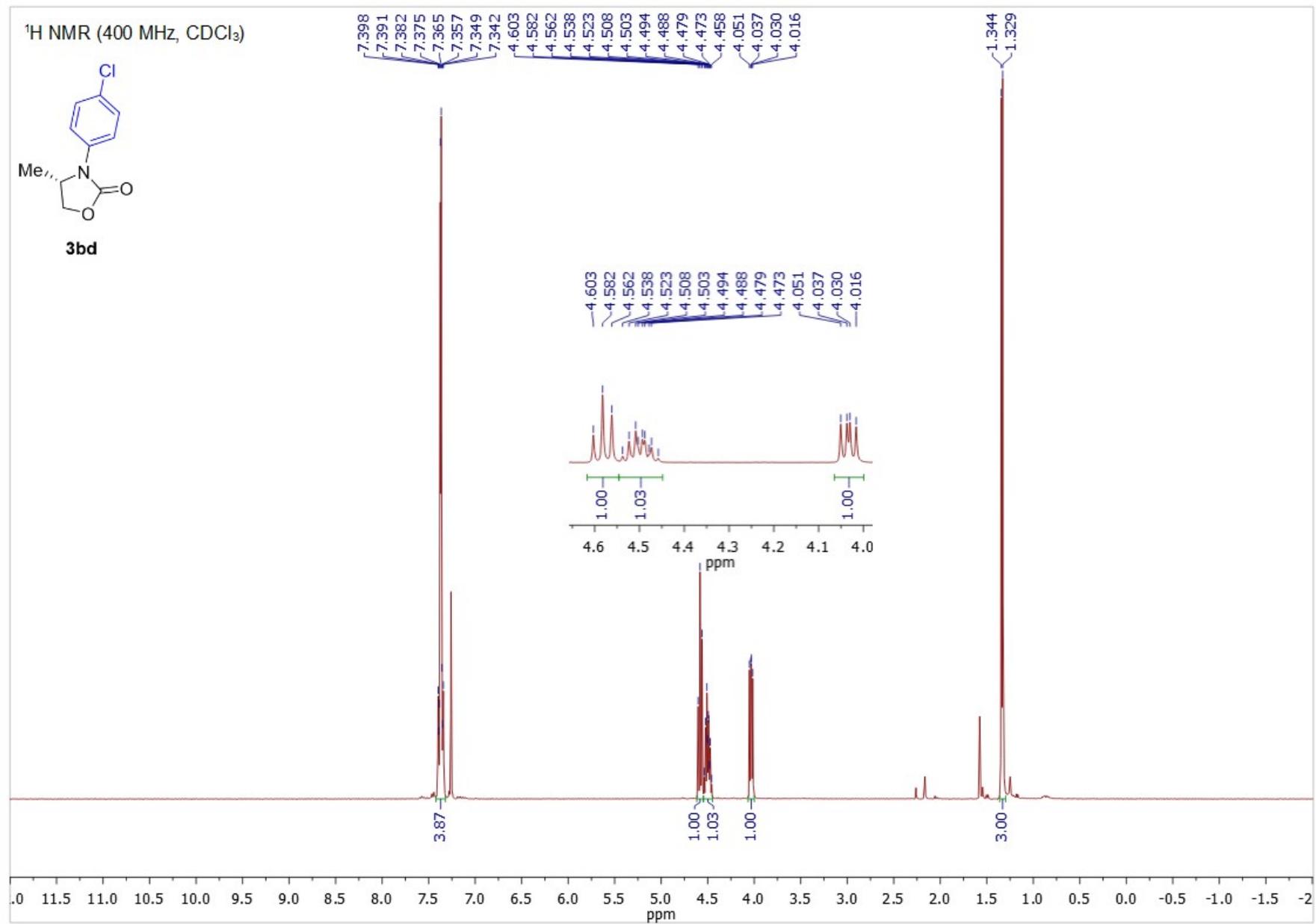


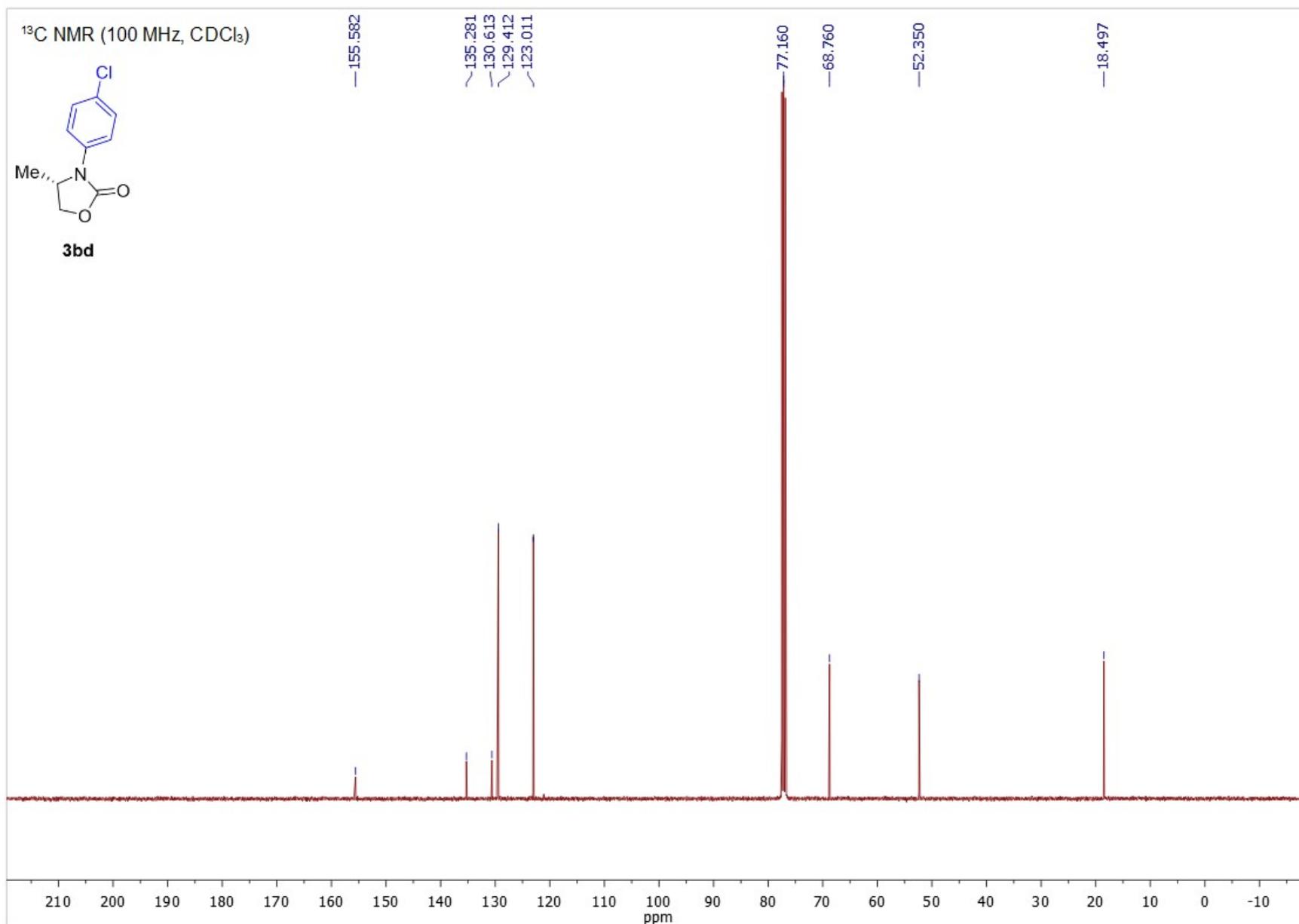
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—141.126  
—133.390  
~120.814  
~118.687  
—107.857  
  
—77.160  
~62.538  
~59.868  
  
—27.550  
—17.877  
—14.211

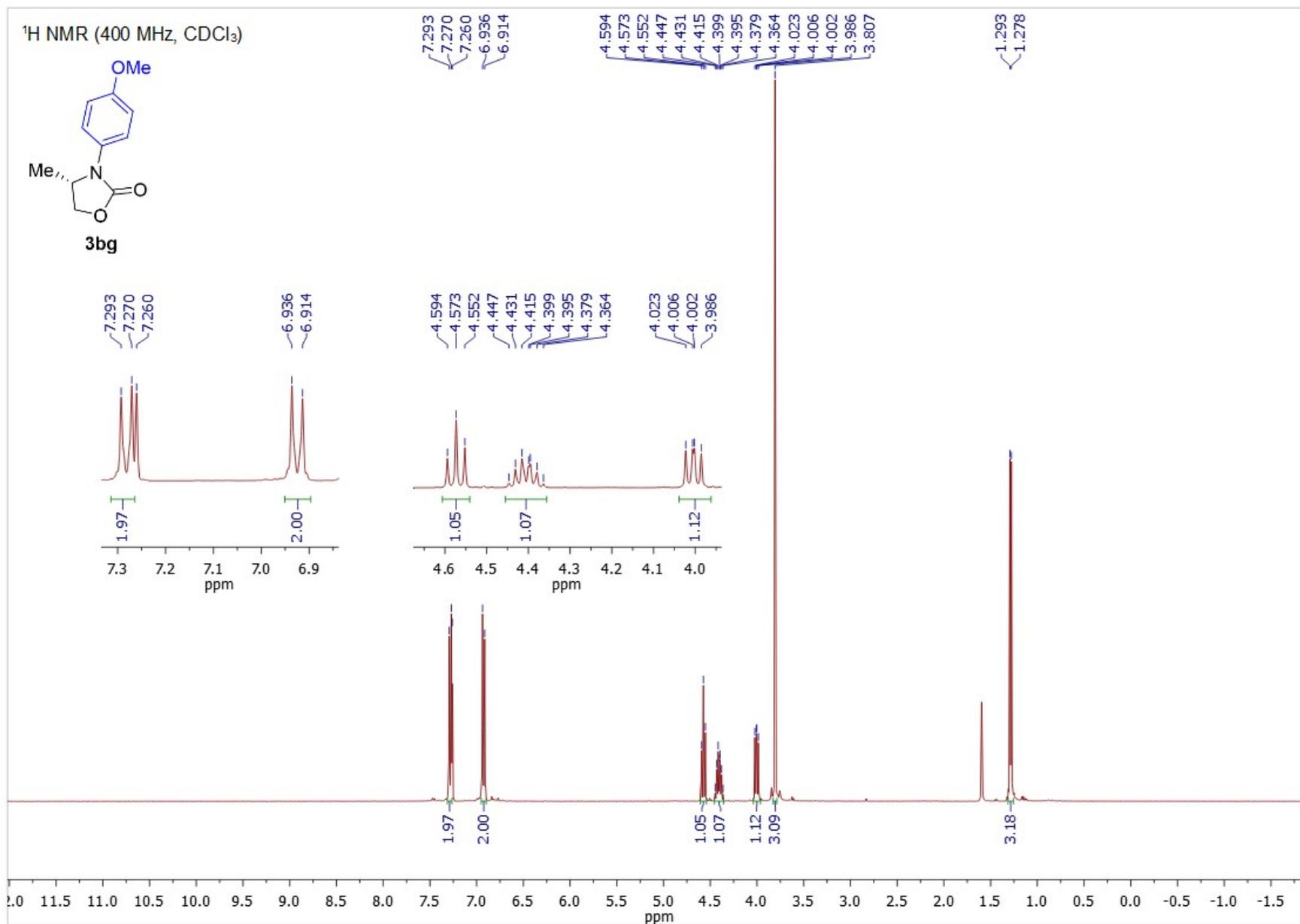




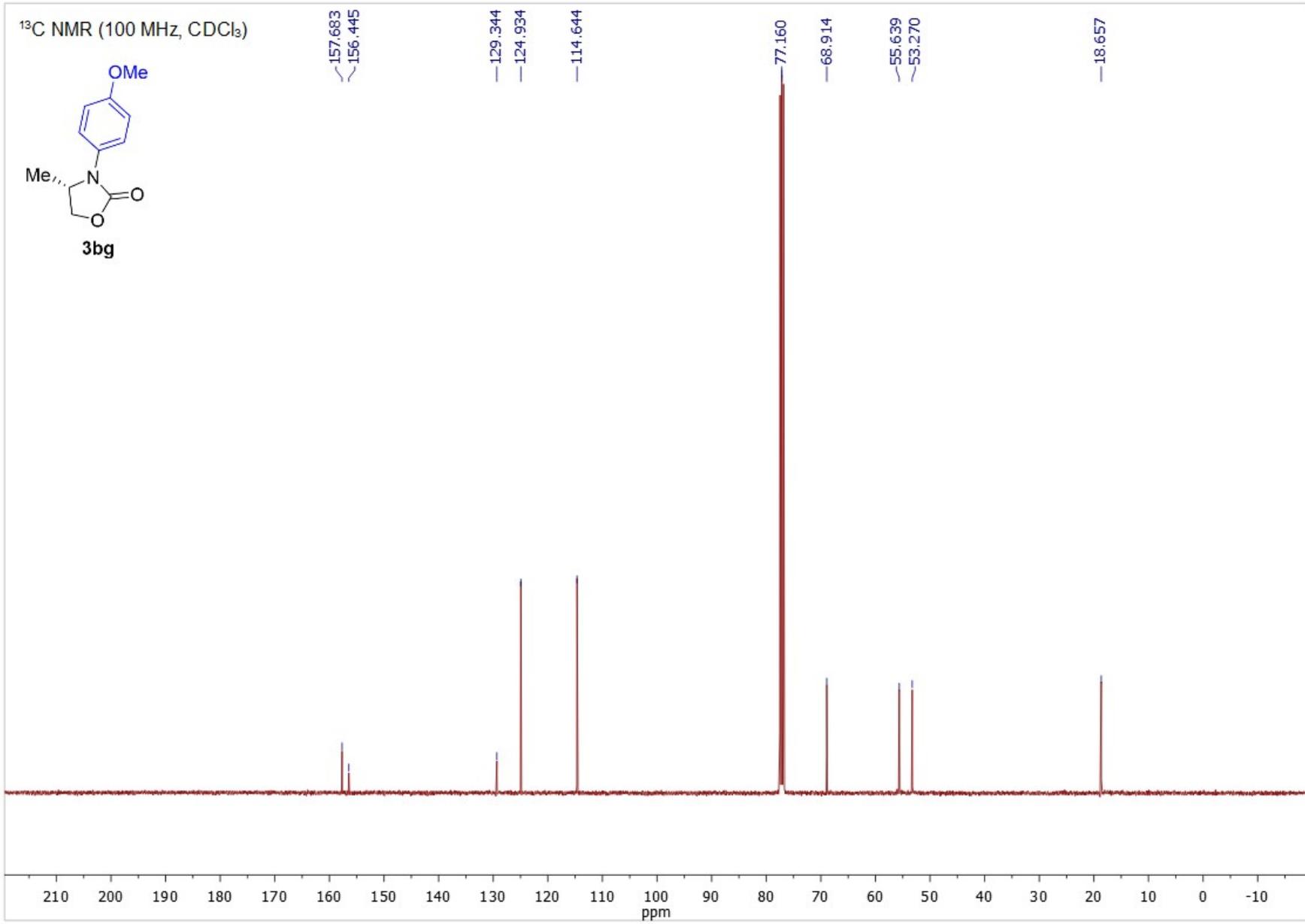
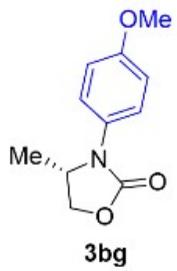


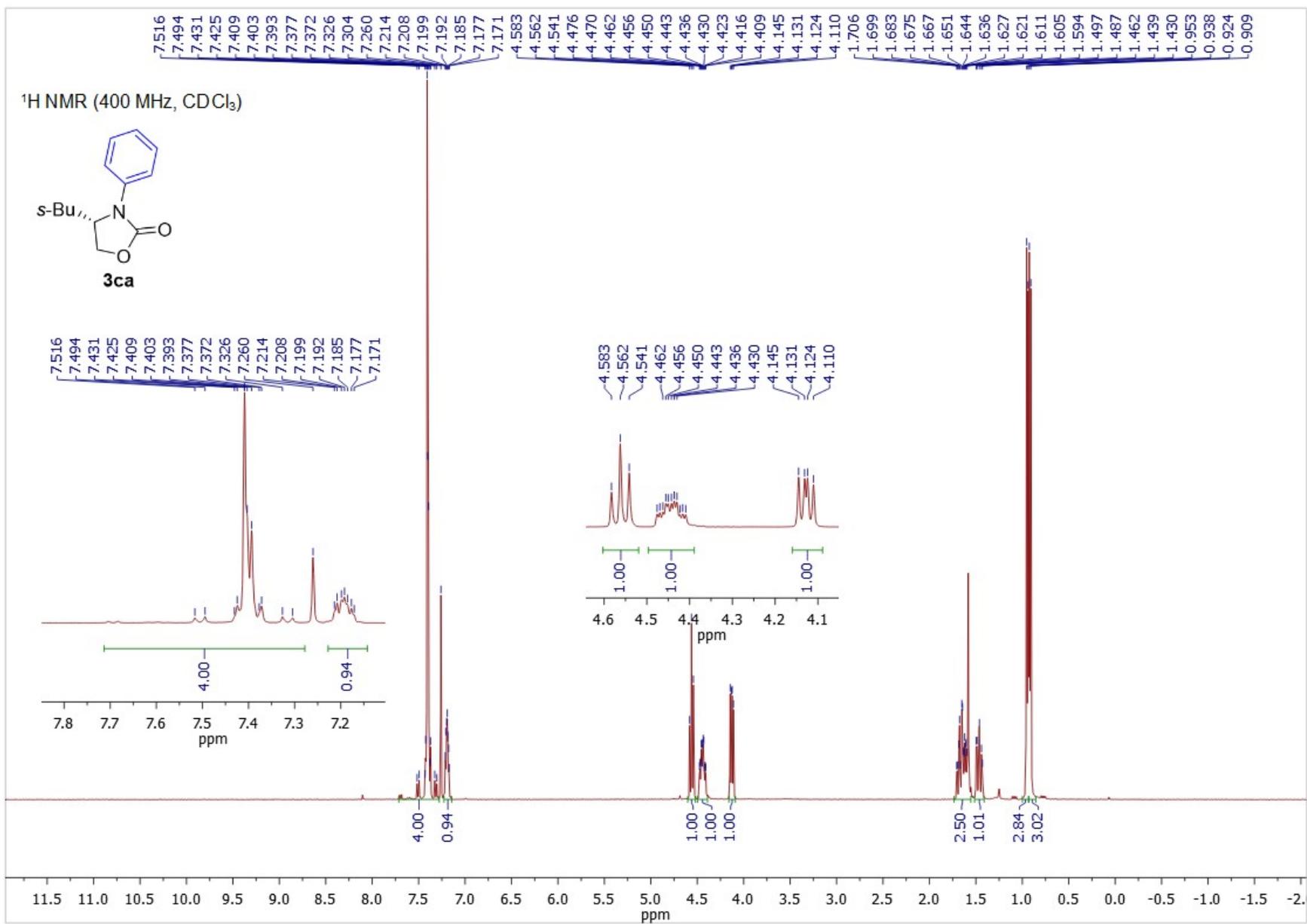


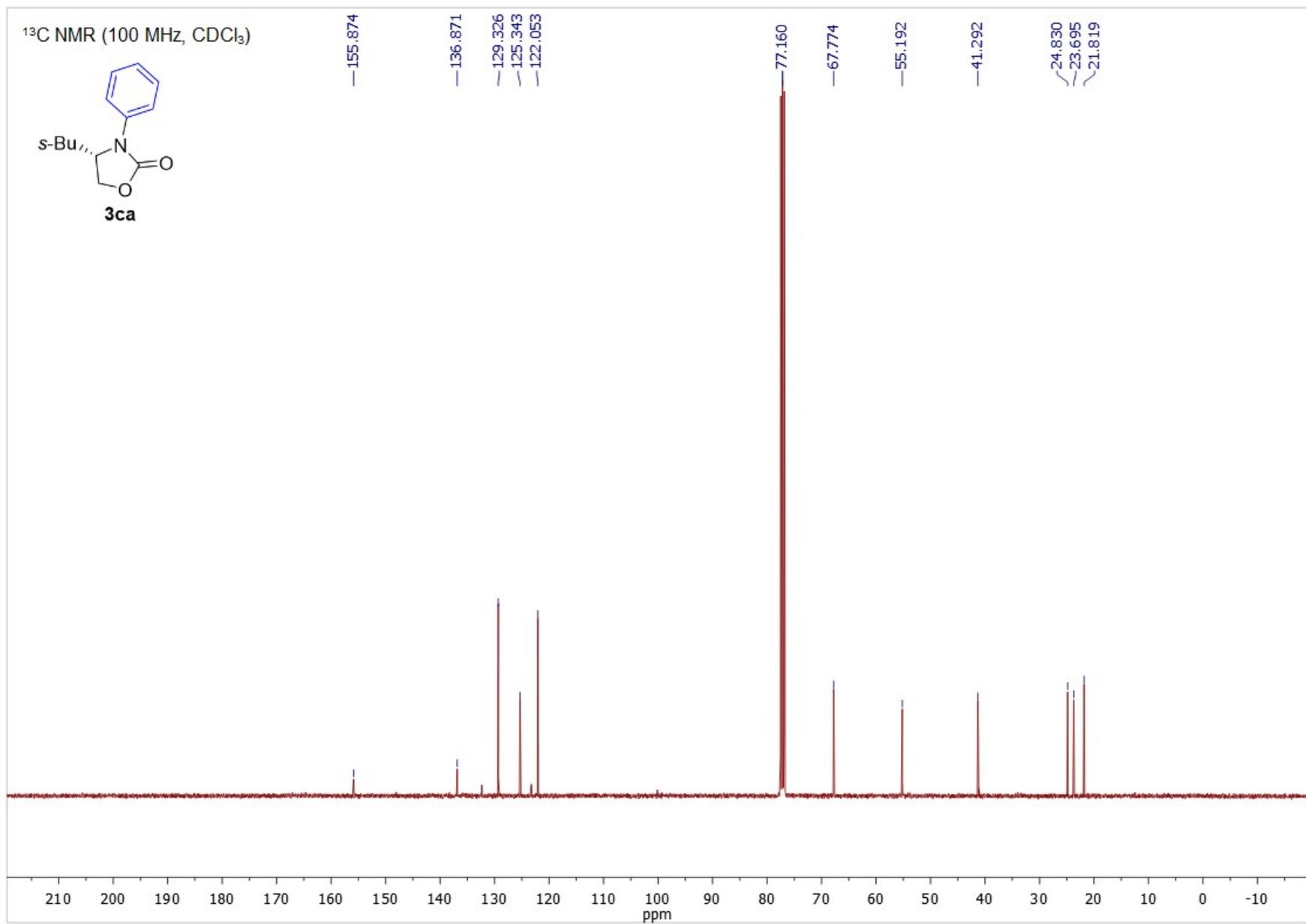


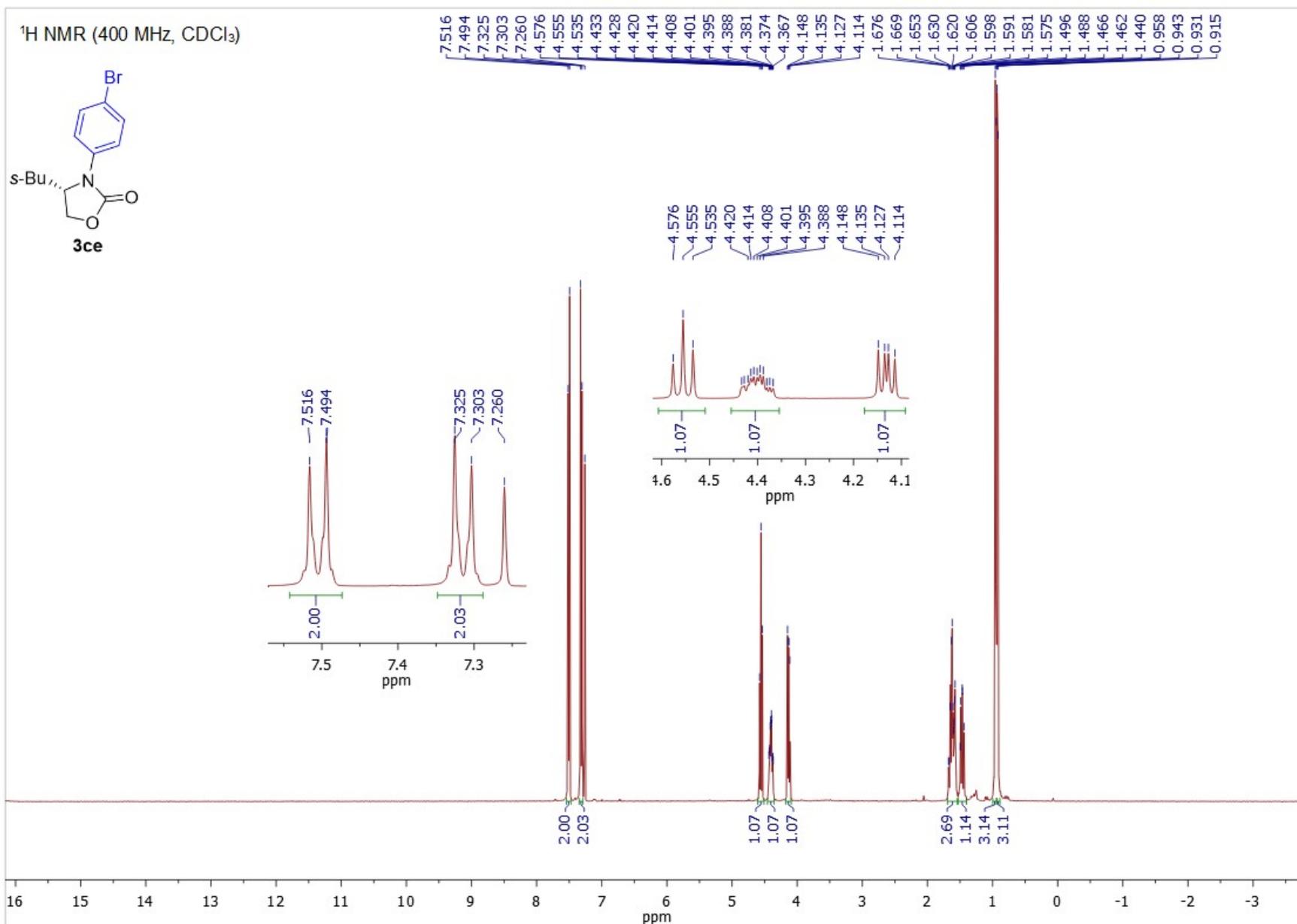


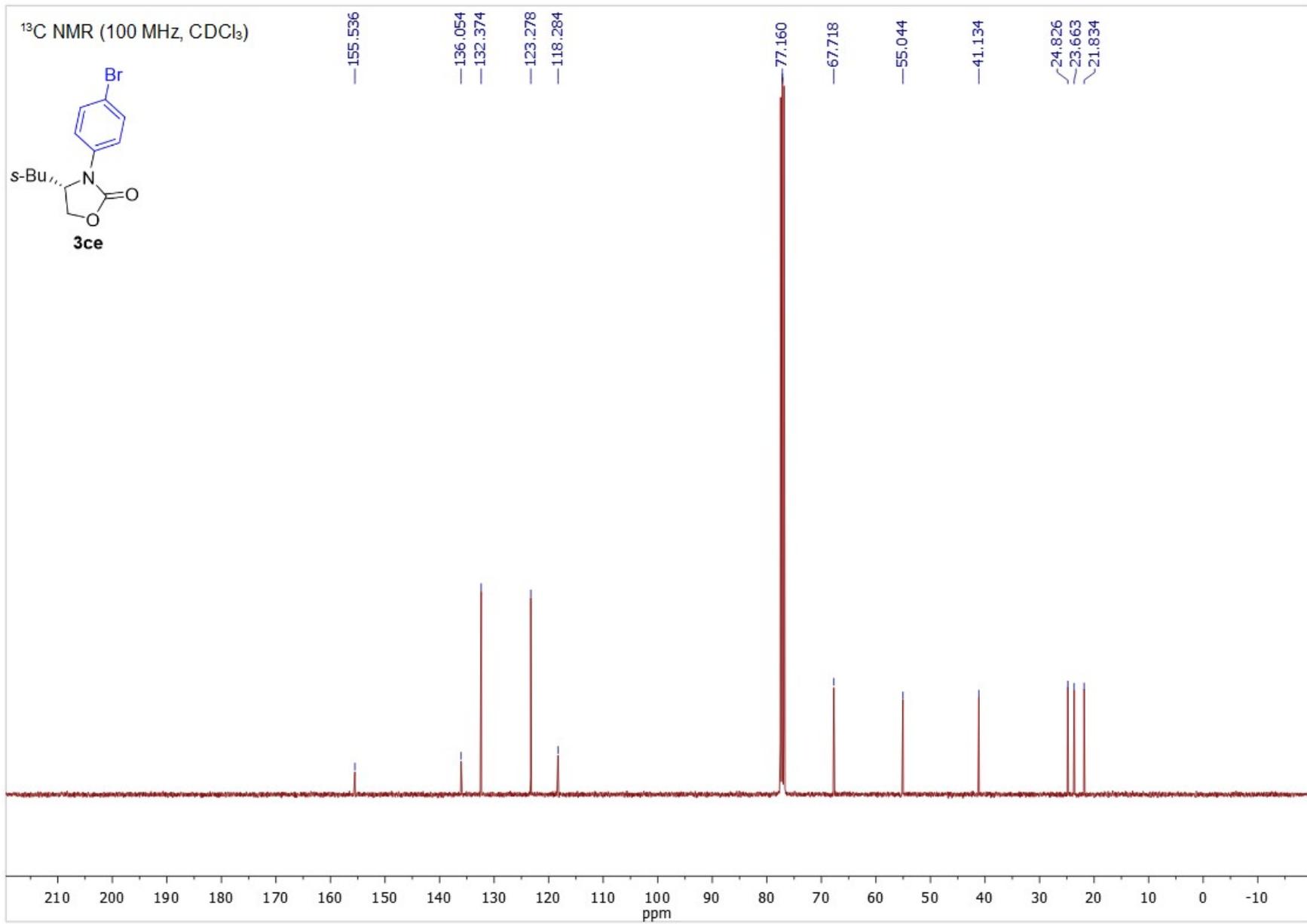
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

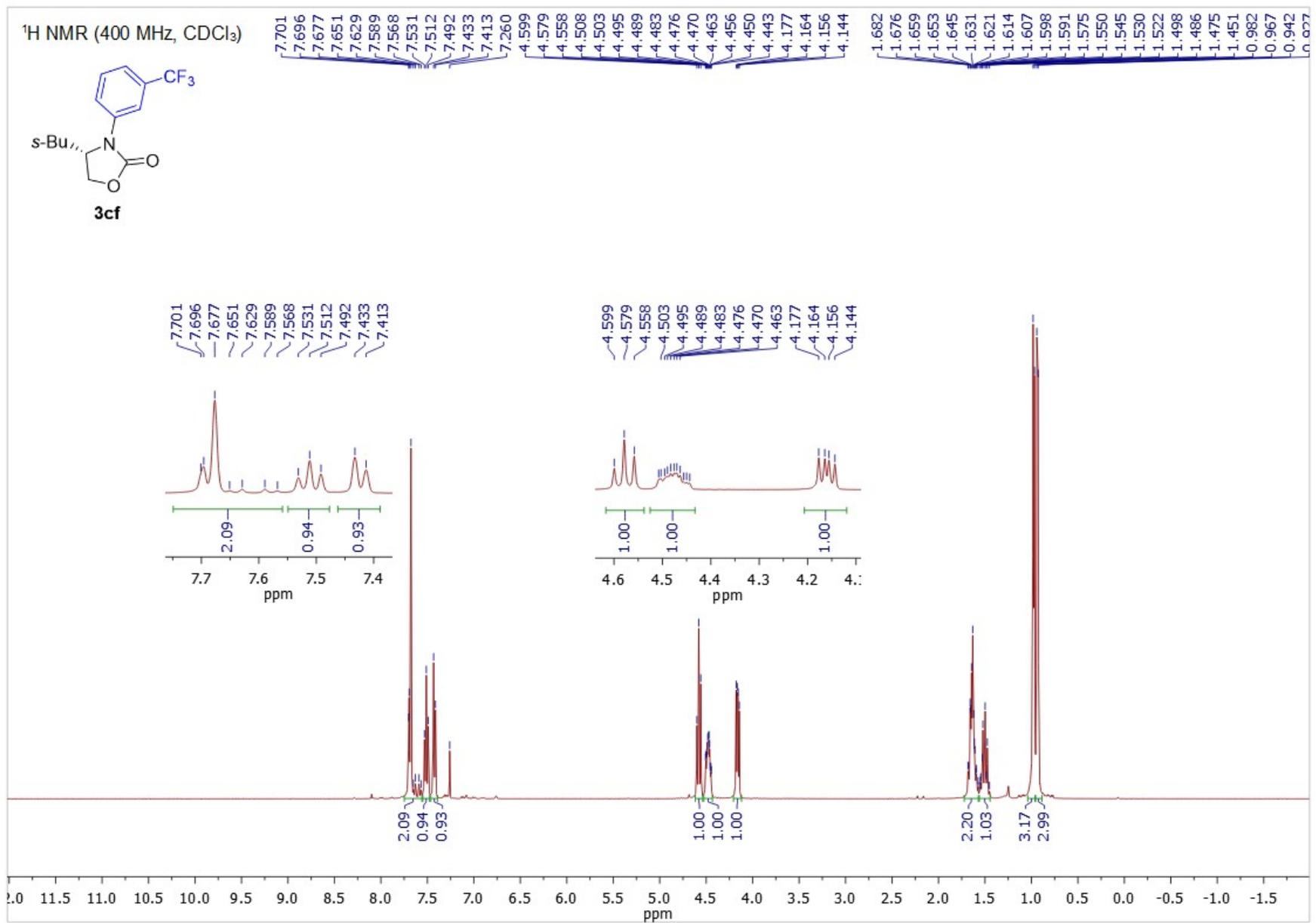




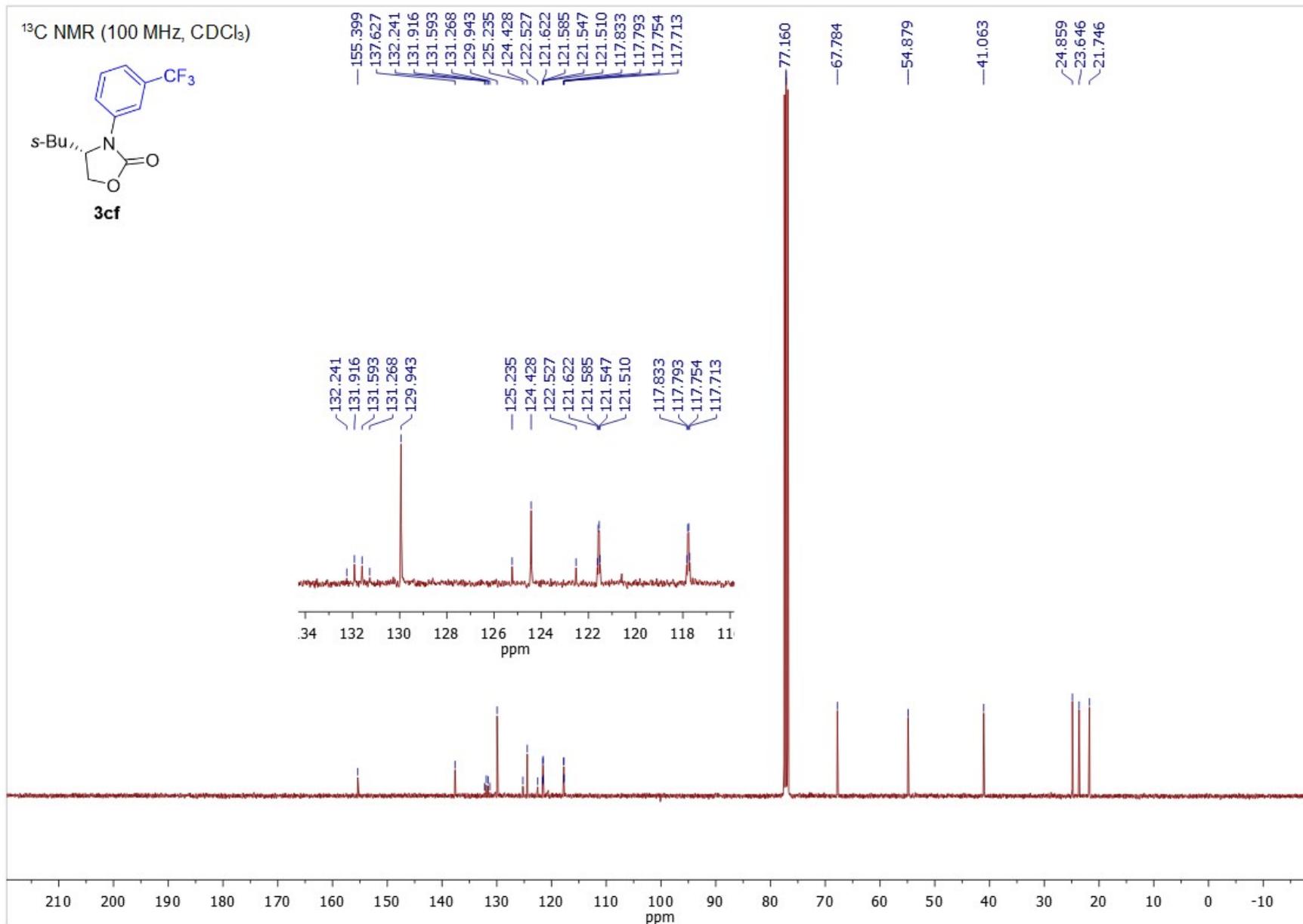
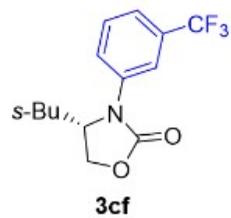




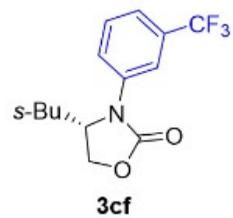




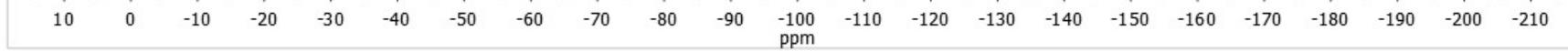
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

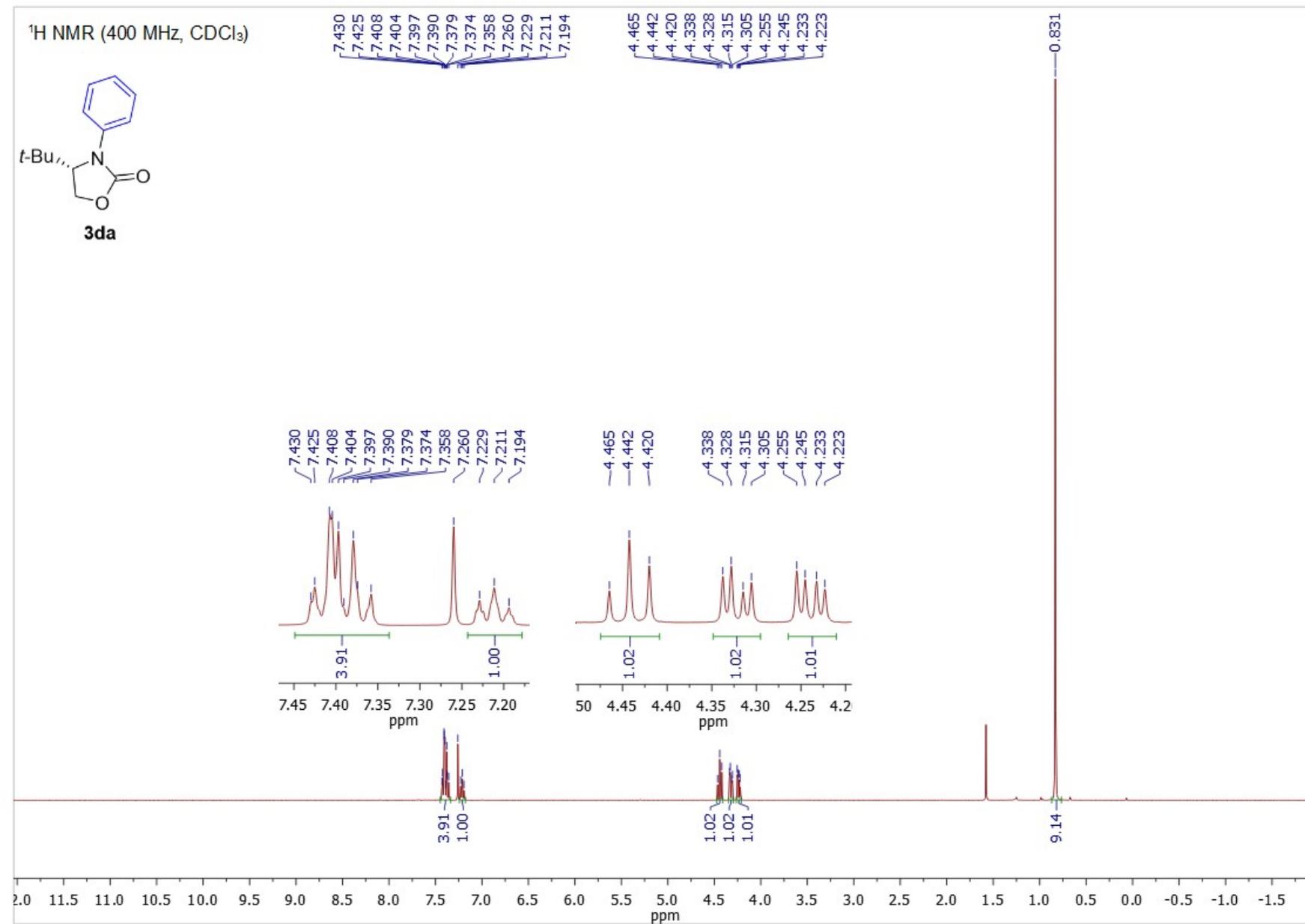


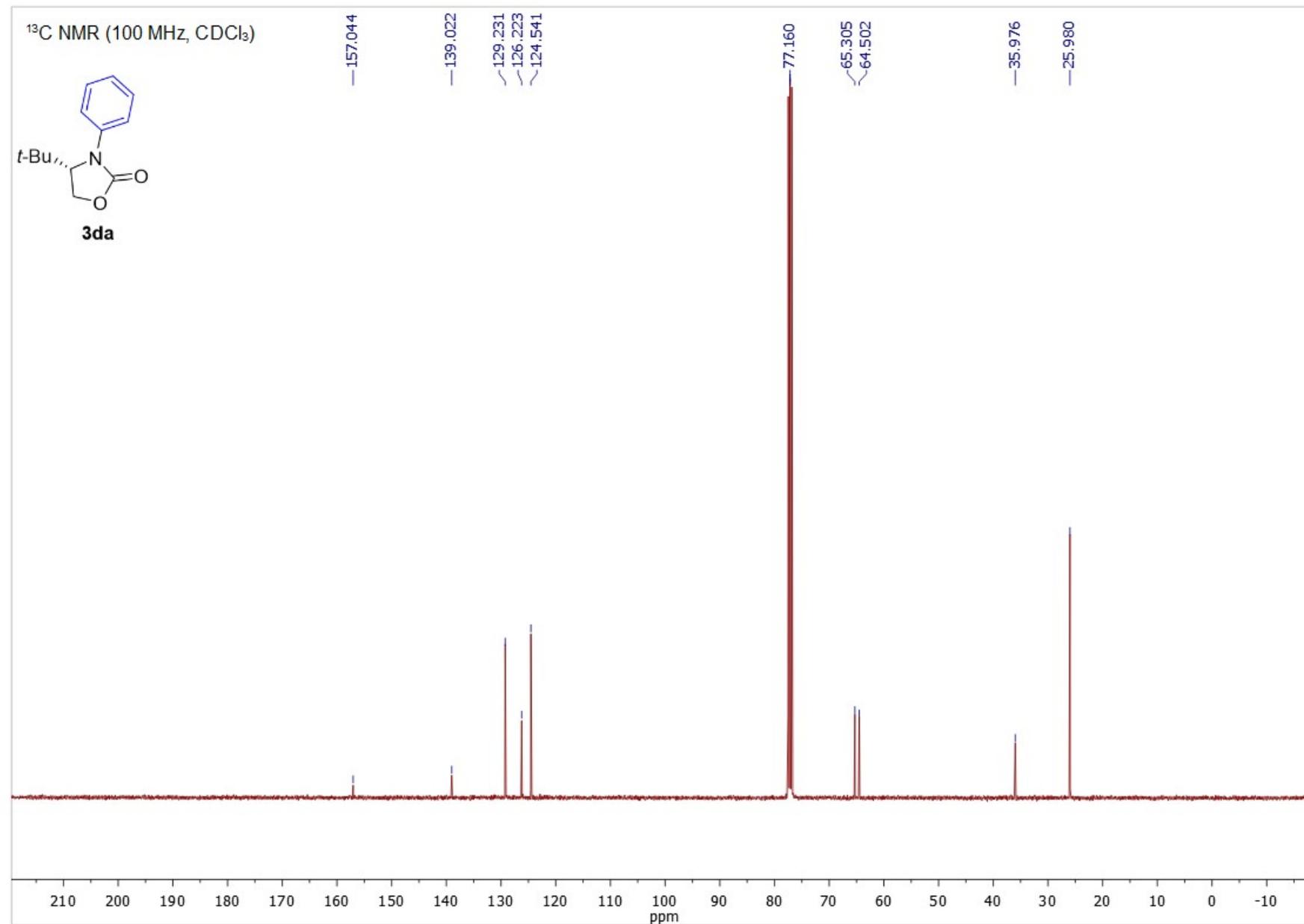
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )



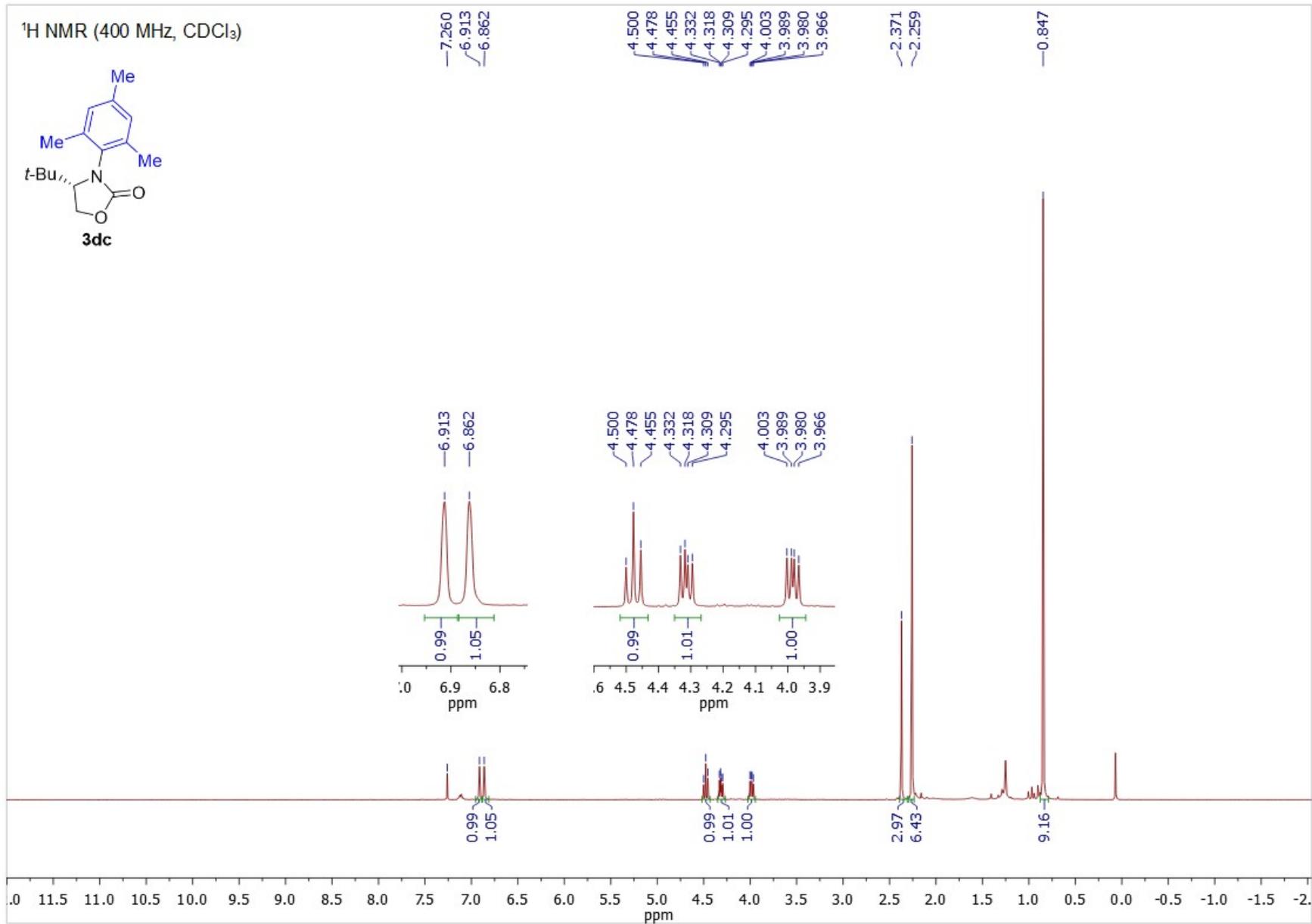
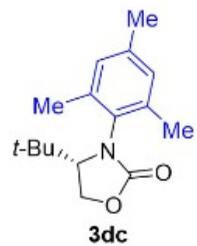
-62.784



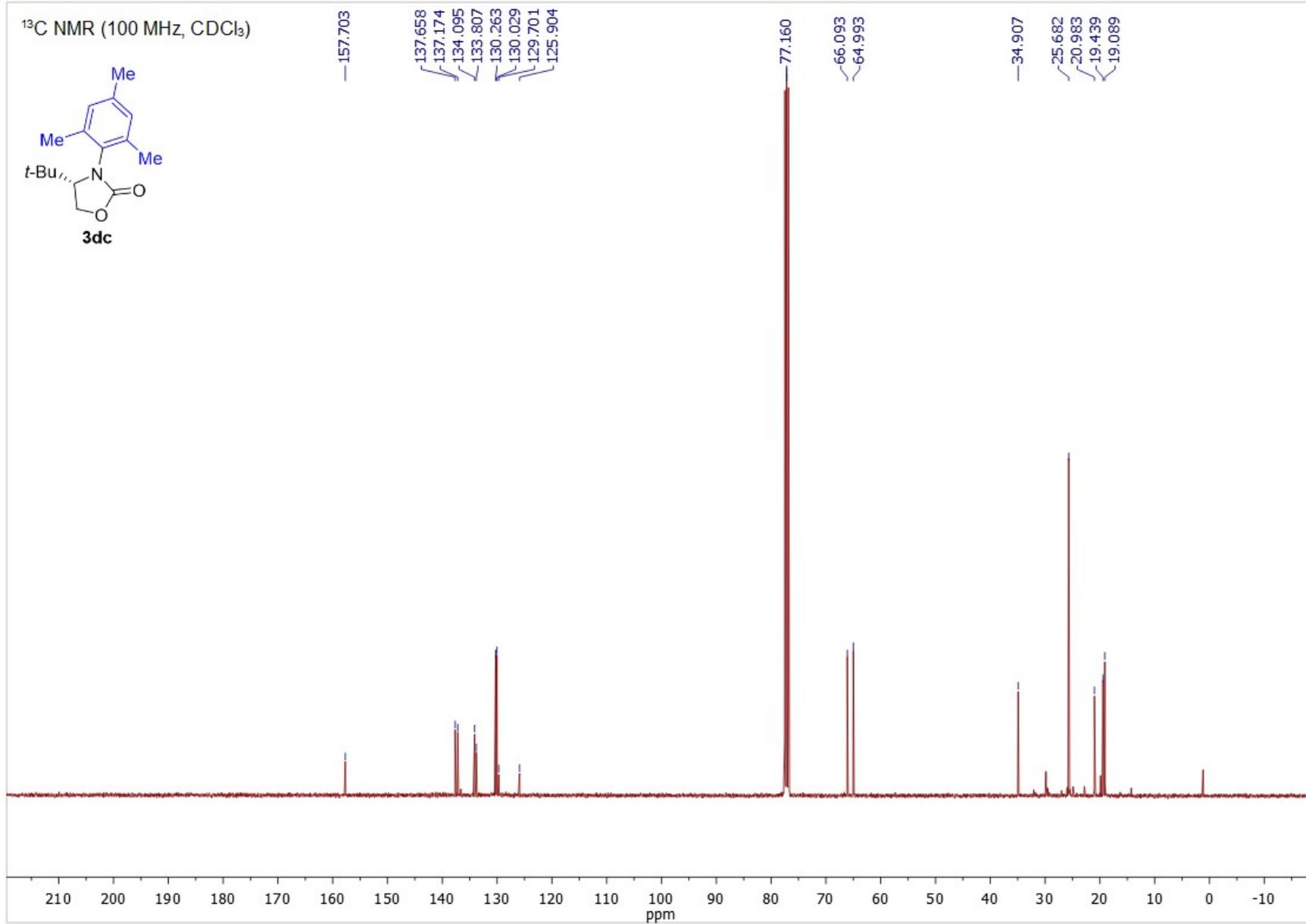
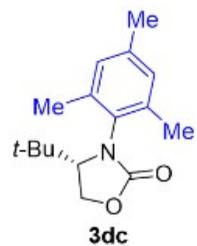


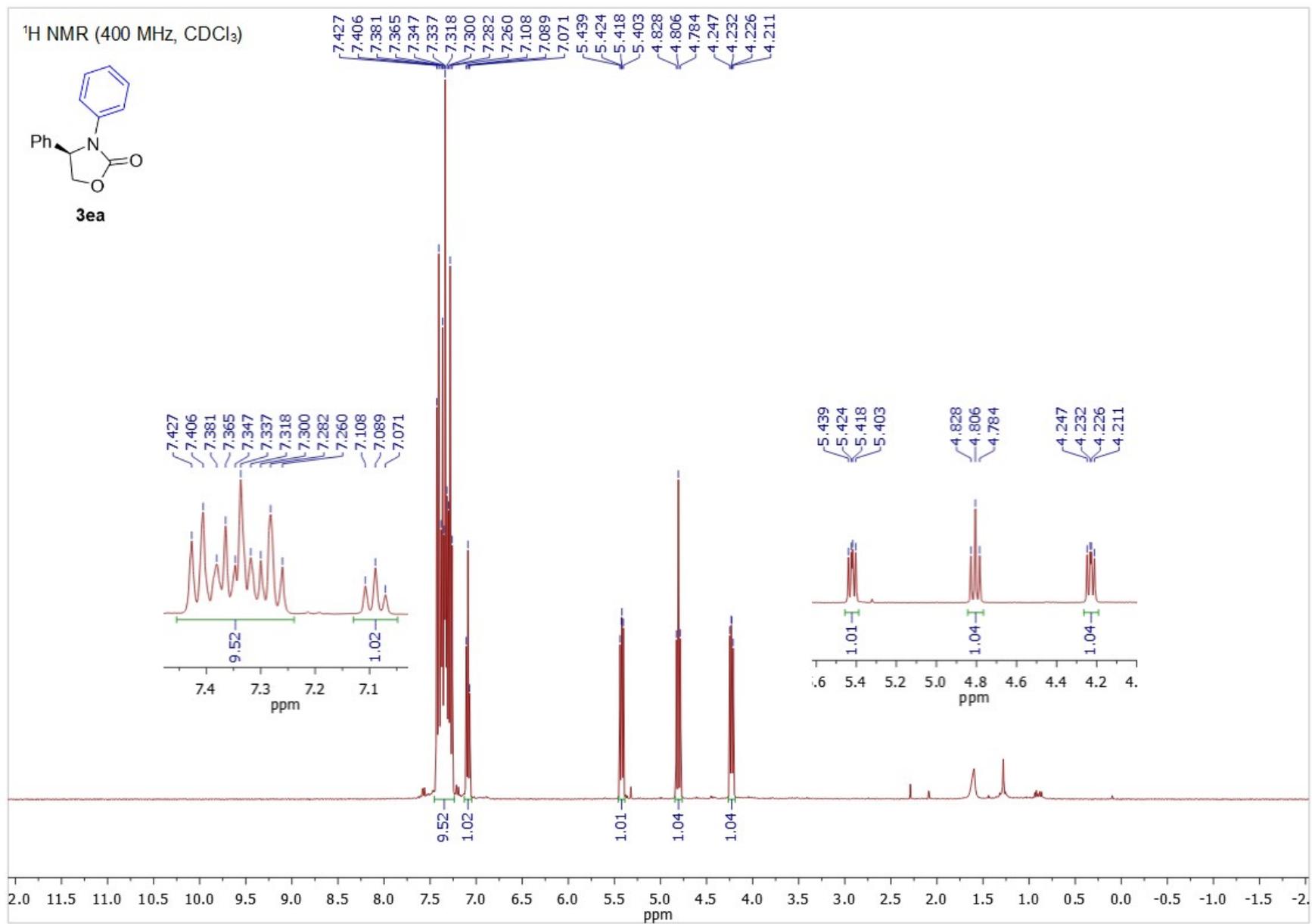


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)





<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

