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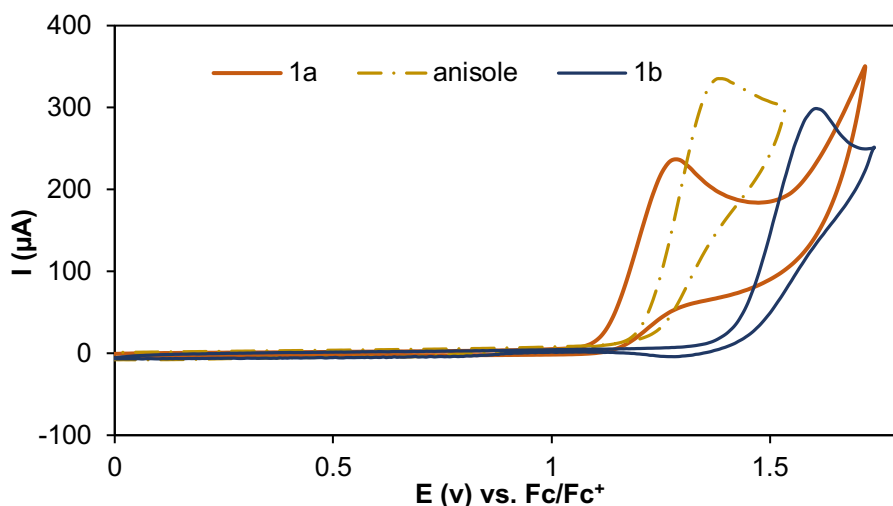
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## 1. General Considerations

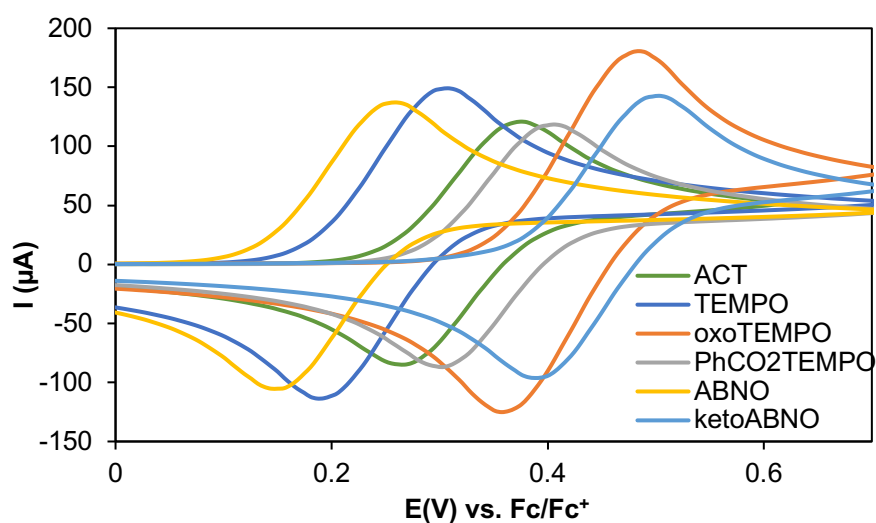
Chemicals and solvents were purchased from commercially available sources and used without any purification. Dry solvents were obtained from a solvent purification system using columns of  $\text{Al}_2\text{O}_3$  under argon.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra were obtained with Bruker Avance-400 MHz with residual solvent peaks or tetramethylsilane as the internal reference. Multiplicities are described using the following abbreviations: s = singlet, bs = broad singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet. High-resolution mass spectra were obtained using a Thermo Q Exactive<sup>TM</sup> Plus via (ASAP-MS) by the mass spectrometry facility at the University of Wisconsin-Madison (funded by NIH grant: 1S10OD020022-1). Voltammetric experiments and bulk electrolysis reactions were performed using a Nuvant Array PGStats, from Nuvant System Inc.

## 2. CV Study

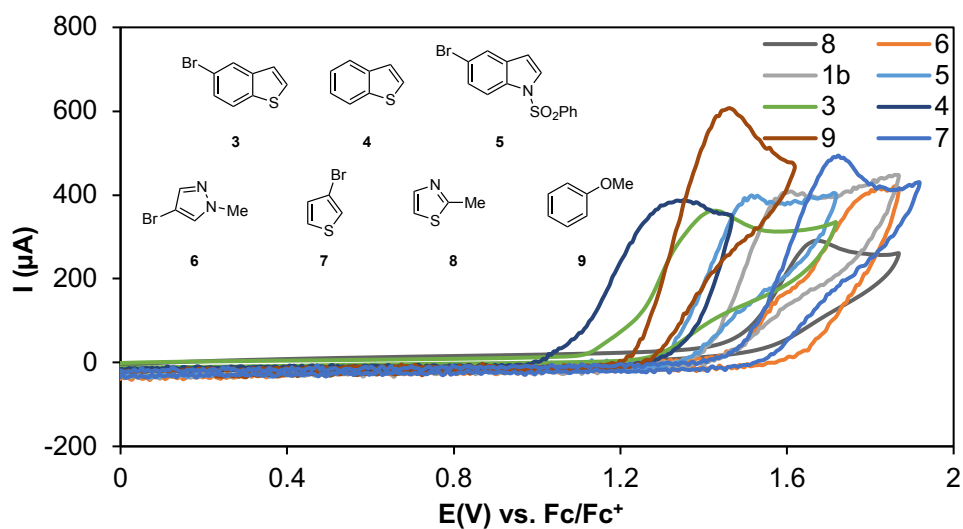
For all the voltammetric experiments, a glassy carbon disk electrode (2 mm diameter) and a platinum wire (1.0 cm, spiral wire) were used as working and counter electrodes, respectively. The working electrode potentials were measured versus  $\text{Ag}/\text{AgNO}_3$  reference electrode (internal solution, 0.1 M  $\text{Bu}_4\text{NClO}_4$  and 0.01 M  $\text{AgNO}_3$  in  $\text{CH}_3\text{CN}$ ). The redox potential of ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) was measured (same experimental conditions) and used to provide an internal reference. The potential values were then adjusted relative to  $\text{Fc}/\text{Fc}^+$ , and electrochemical studies in organic solvents were recorded accordingly.



**Figure S1.** CVs of **1a**, **1b**, and anisole (5 mM) in acetonitrile with NaClO<sub>4</sub> (0.1 M) as supporting electrolyte, glassy carbon as working electrode (~ 7.0 mm<sup>2</sup>) and a platinum wire (1.0 cm, spiral wire) as counter electrode, scan rate = 100 mV/s.



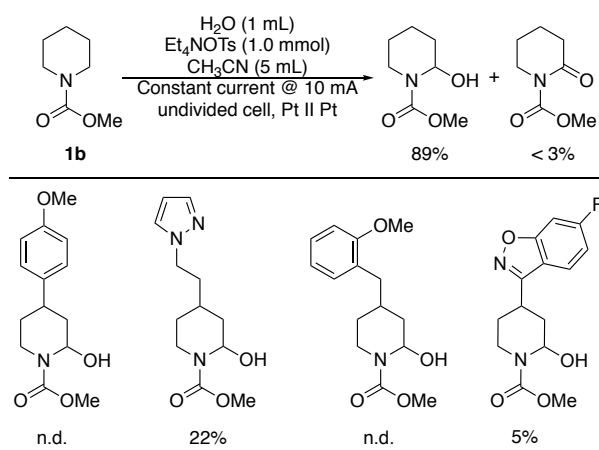
**Figure S2.** CVs of different mediators (5 mM) in acetonitrile with NaClO<sub>4</sub> (0.1 M) as supporting electrolyte, glassy carbon as working electrode (~ 7.0 mm<sup>2</sup>) and a platinum wire (1.0 cm, spiral wire) as counter electrode, scan rate = 100 mV/s.



**Figure S3.** CVs of different additives (5 mM) in acetonitrile with NaClO<sub>4</sub> (0.1 M) as supporting electrolyte, glassy carbon as working electrode (~ 7.0 mm<sup>2</sup>) and a platinum wire (1.0 cm, spiral wire) as counter electrode, scan rate = 100 mV/s.

### 3. Shono Oxidation with Water as Nucleophile

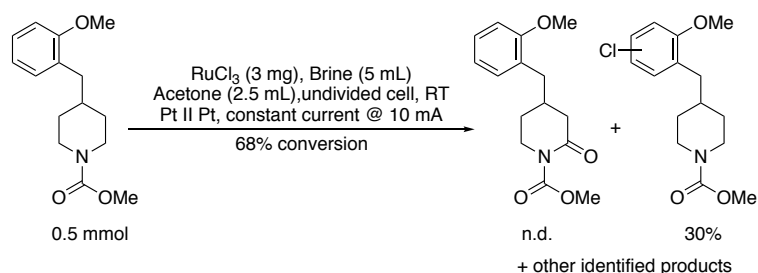
These reactions were conducted following the reported procedure.<sup>1</sup> A mixture of **1** (0.5 mmol), Et<sub>4</sub>NOTs (1.0 mmol) as supporting electrolyte, acetonitrile (5 mL), and water (1.0 mL) was electrolyzed in an undivided cell, with a Ag/Ag<sup>+</sup> reference electrode, platinum mesh as working and counter electrodes. Constant current at 10 mA was passed at room temperature with a potential of 1.3 - 2.0 V vs Ag/Ag<sup>+</sup>. After 5 F/mol had been passed, solvent was removed under reduced pressure to leave a residue. Yields were determined by crude <sup>1</sup>H NMR with mesitylene as internal standard.



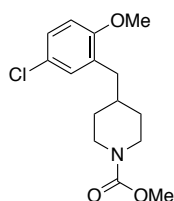
**Table S1.** Substrates evaluation under Shono oxidation conditions.

### 4. Testing of the Cl<sup>-</sup>/RuO<sub>2</sub> Dual-Mediator System

Torii and coworkers reported a Cl<sup>-</sup>/RuO<sub>2</sub> dual-mediator electrochemical system for α-oxygenation of amides and carbamates, in which the applied potential was lower than direct bulk electrolysis.<sup>2</sup> However, the involvement of Cl<sup>+</sup> species causes other side reactions. For example, when **1d** was subjected to Torii's conditions, only chlorination of aromatic ring was observed, rather than the desired oxygenation product.



A mixture of **1d** (0.5 mmol) and RuCl<sub>3</sub> (3 mg) in an aqueous NaCl (5 mL) and acetone (2.5 mL) was placed in an undivided cell. To this solution was immersed with two platinum mesh electrodes (3 cm x 2.5 cm) and the entire mixture was electrolyzed at room temperature under a constant current of 10 mA with changing the current direction every 30s. After passage of 7.0 F/mol of electricity, the mixture was filtered through a short pad of celite and the filtrate was subjected to extractive workup with DCM. The reaction was analyzed by crude <sup>1</sup>H NMR with mesitylene as internal standard.

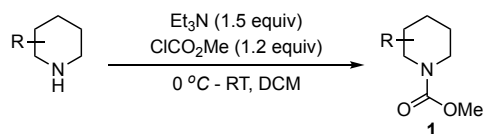


<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.13 (dd, *J* = 8.7, 2.6 Hz, 1H), 7.03 (d, *J* = 2.6 Hz, 1H), 6.75 (d, *J* = 8.7 Hz, 1H), 4.26 – 3.95 (m, 2H), 3.78 (s, 3H), 3.68 (s, 3H), 2.69 (t, *J* = 11.3 Hz, 2H), 2.50 (d, *J* = 6.6 Hz, 2H), 1.78 – 1.65 (m, 1H), 1.59 (d, *J* = 11.0 Hz, 2H), 1.26 – 1.09 (m, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 156.2, 155.9, 130.5, 130.4, 126.8, 124.9, 111.4, 55.5, 52.4, 44.1, 36.8, 36.4, 31.9.

HRMS (ESI) Calculated for [M+H<sup>+</sup>]: 298.1205, measured: 298.1205.

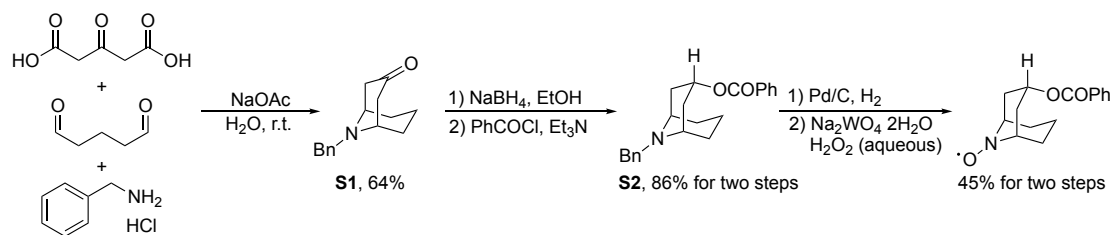
## 5. Procedures for the Synthesis of Substrates and Mediator

### 5.1 Substrate synthesis



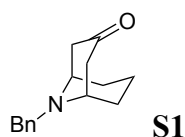
To a mixture of cyclic amine or its HCl salt (1.0 equiv, 0.1 M) and Et<sub>3</sub>N (1.5 equiv for free amine, 2.5 equiv for HCl salt) in DCM was added ClCO<sub>2</sub>Me (1.2 equiv) dropwise at 0 °C with ice-water bath. Next, the reaction was warmed to room temperature and stirred further for 1 h or full consumption of the substrate, as monitored by TLC. The mixture was then quenched with saturated aqueous NH<sub>4</sub>Cl, and extracted three times with DCM. The combined organic phase was dried, concentrated and purified by chromatography with silica thereafter to afford the desired products **1**.

## 5.2 Mediator synthesis



### Synthesis of **S1**:

The reaction was conducted following the reported procedure with the same scale.<sup>3</sup> Benzylamine hydrochloride (37.7 g, 0.263 mol) and glutaraldehyde (25% in water, 88 mL, 0.219 mol) were added in a 1.0 L beaker containing water (100 mL) under air. The mixture was cooled to 0 °C, then acetonedicarboxylic acid (32.0 g, 0.219 mol) and 10% aqueous sodium acetate (75 mL) were added. After removal of ice bath, the mixture was stirred vigorously for two hours at room temperature then stirred for 12 hours at 50 °C. The pH value was adjusted to 6-7 by careful addition of NaHCO<sub>3</sub>. The mixture was extracted with chloroform several times. The combined organic layer was washed with brine and dried over sodium sulfate. After concentration of filtered organic layer under reduced pressure, the residue was purified via flash column chromatography (hexane/ethyl acetate = 2/1) to afford **S1** as a light yellow solid in 64% yield (32.1 g). All analytical data of **S1** are consistent with reported data.<sup>iii</sup>

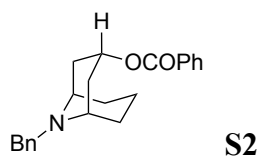


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.40 (d, *J* = 7.2 Hz, 2H), 7.37 – 7.31 (m, 2H), 7.29 – 7.24 (m, 1H), 3.90 (s, 2H), 3.31 (s, 2H), 2.73 (dd, *J* = 16.6, 6.6 Hz, 2H), 2.25 (d, *J* = 16.7 Hz, 2H), 1.98 – 1.87 (m, 2H), 1.60 – 1.40 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 211.5, 139.2, 128.3, 128.3, 127.1, 57.0, 53.5, 42.8, 29.3, 16.5.

### Synthesis of **S2**:

The reaction was conducted following the reported procedure.<sup>3,4</sup> In a round bottom flask, **S1** (10.0 g, 43.7 mmol) was dissolved in 150 mL ethanol and cooled to 0 °C. After that, sodium borohydride (2.5 g, 66.0 mmol, 1.5 equiv) was added and the reaction mixture was allowed to warm to room temperature. Upon completion, as monitored by TLC, the reaction mixture was quenched with 100 mL water. The crude

product was extracted with ethyl acetate (3 x 100 mL). The solvent was evaporated and the crude product was redissolved in DCM (200 mL) for esterification without purification. To the solution was added benzoyl chloride (7.5 mL, 66.0 mmol, 1.5 equiv), followed by cooling to 0 °C with ice bath. Et<sub>3</sub>N (12 mL, 87.4 mmol, 2.0 equiv) was added into the mixture dropwise, after which it was warmed to room temperature and stirred overnight. Then the reaction mixture was diluted with saturated aqueous sodium bicarbonate and separated using separatory funnel. The aqueous solution was further extracted with DCM, and the combined organic phases were dried over anhydrous MgSO<sub>4</sub>, filtered, concentrated. The residue was purified via flash column chromatography (hexane/ethyl acetate/Et<sub>3</sub>N = 10/1/0.2) to give **S2** (12.6 g, 86% for two steps) as a colorless viscous oil.



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.11 – 8.04 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 7.3 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.28 – 7.21 (m, 1H), 5.50 (p, *J* = 6.8 Hz, 1H), 3.84 (s, 2H), 3.07 (br, 2H), 2.60 – 2.44 (m, 2H), 2.43 – 2.24 (m, 1H), 2.08 – 1.90 (m, 2H), 1.69 – 1.52 (m, 3H), 1.24 (d, *J* = 11.7 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 166.2, 140.1, 132.7, 130.9, 129.5, 128.3, 128.2, 126.8, 68.0, 56.2, 49.3, 31.6, 25.3, 14.8.

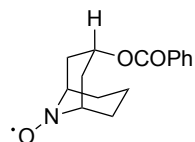
**HRMS (ESI)** Calculated for [M+H<sup>+</sup>]: 336.1958, measured: 336.1953.

Synthesis of PhCO<sub>2</sub>ABNO:

The reaction was conducted following the reported procedure.<sup>3</sup> **S2** (12.6 g, 37.6 mmol), Pd/C (10% Pd, 5 mol%, 2.0 g) and degassed methanol (200 mL) were added under inert gas to a 500 mL three-neck round-bottom flask equipped with reflux condenser. Afterwards, the flask was purged with hydrogen gas and a balloon with pure hydrogen gas (1 atm) was attached to the reflux condenser. The reaction mixture was stirred at 50 °C for 24 hours and afterwards cooled to room temperature. The black suspension was filtered over celite and washed with methanol. All volatiles were removed under reduced pressure, and the residue was subjected to the next step without purification. The above crude product was dissolved in acetonitrile (75 mL), Na<sub>2</sub>WO<sub>4</sub>·H<sub>2</sub>O (1.3 g, 4.0 mmol) and 30% hydrogen peroxide (8.5 mL, 120.0 mmol) were added and the



reaction mixture was stirred at room temperature overnight. Water was added to the reaction mixture and the aqueous solution was extracted with chloroform. The organic layer was dried over  $\text{MgSO}_4$  and concentrated. The residue was purified by flash column chromatography (hexane/ethyl acetate = 1/1).  $\text{PhCO}_2\text{ABNO}$  was obtained as a yellow solid (4.4 g, 45% for two steps).

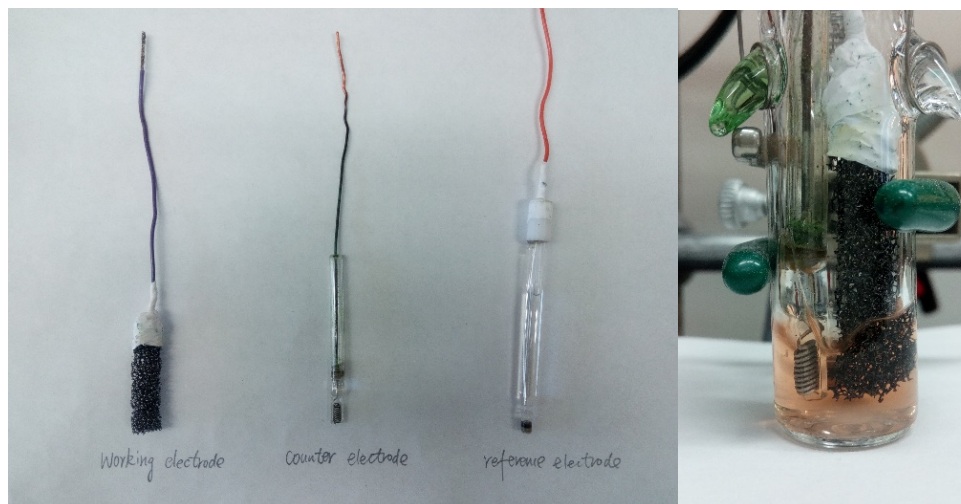


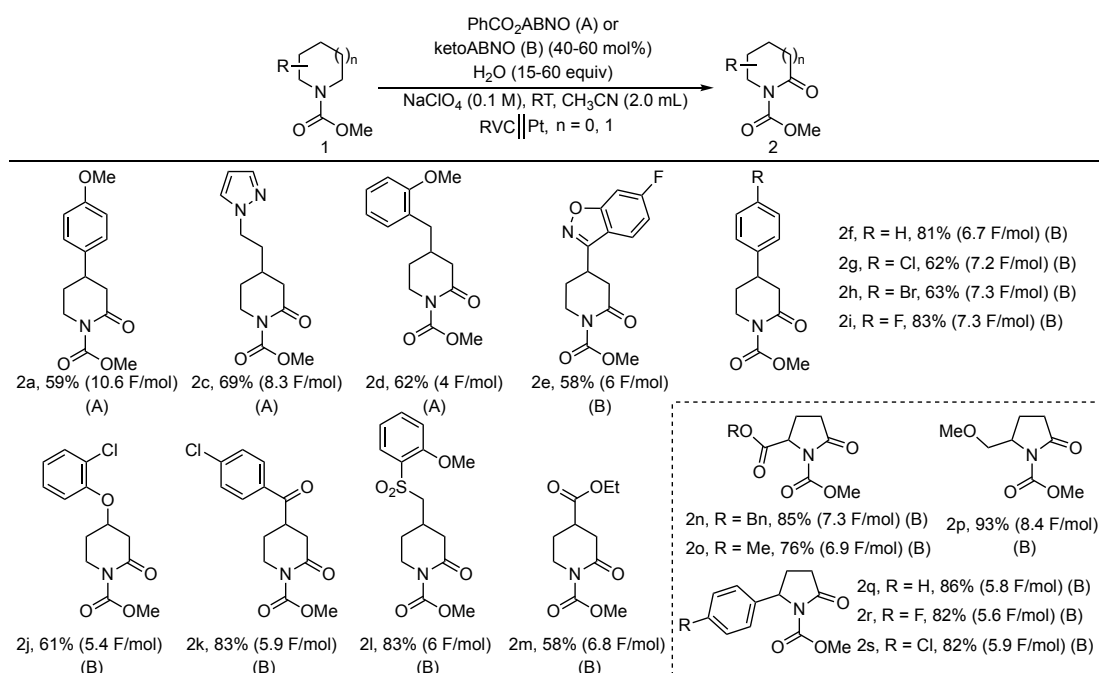
**$\text{PhCO}_2\text{ABNO}$**

**HRMS (ESI)** Calculated for  $[\text{M}+\text{Na}^+]$ : 283.1179, measured: 283.1174.

## 6. Procedures for Electrochemical Oxygenation

Reactions were carried out using an undivided cell equipped with a reticulated vitreous carbon anode (RVC, 60 PPI, 4.0 cm x 1.0 cm x 0.6 cm, ~ 0.5 cm was immersed in the solution), a platinum wire cathode (1.0 cm, spiral wire) and a  $\text{Ag}/\text{Ag}^+$  reference electrode. A mixture of **1** (0.2 mmol),  $\text{NaClO}_4$  (0.2 mmol) as supporting electrolyte, mediator (0.08-0.12 mmol), acetonitrile (2 mL), and water (45-180  $\mu\text{L}$ ) was electrolyzed at room temperature with magnetic stirring, and constant current at 3 mA or 5 mA was applied. The working electrode potential was tracked with the cutoff potential at 0.5 V above the initial potential. The reaction was stopped automatically when reached to cutoff potential or manually after full consumption of substrates detected by TLC. After that, solvent was removed under reduced pressure to leave a residue. The reaction was analyzed by crude  $^1\text{H}$  NMR spectroscopy with mesitylene as internal standard, followed by chromatography on silica to afford the pure products.



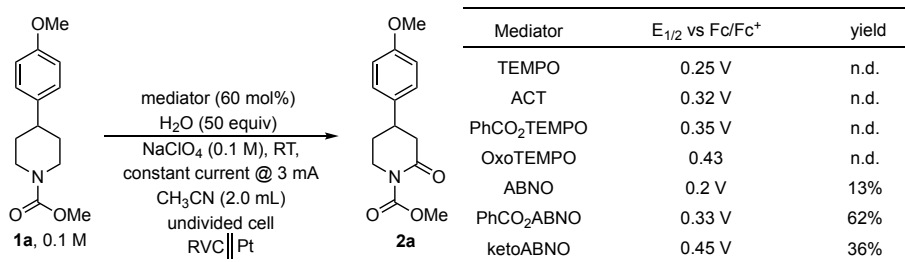


**Table S2.** Yields and consumed charge.

## 7. Optimization of Conditions

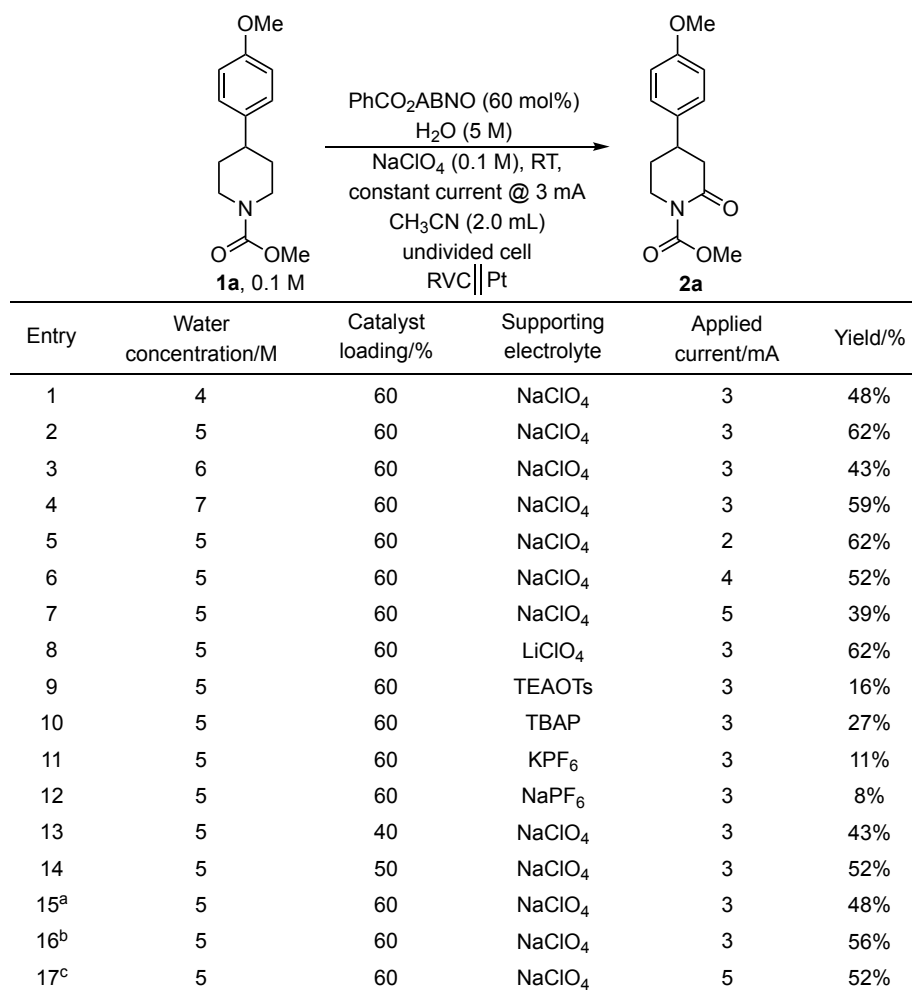
These reactions were carried out using an undivided cell equipped with a reticulated vitreous carbon anode (RVC, 60 PPI, 4.0 cm x 1.0 cm x 0.6 cm, ~ 0.5 cm immersed in the solution), a platinum wire cathode (1.0 cm, spiral wire) and a Ag/Ag<sup>+</sup> reference electrode. A mixture of **1** (0.2 mmol), NaClO<sub>4</sub> (0.2 mmol) as supporting electrolyte, acetonitrile (2 mL), and water (180 μL) was electrolyzed at room temperature with magnetic stirring, and constant current at 3 mA was applied. The working electrode potential was tracked with the cutoff potential at 0.5 V above the initial applied potential. After that, the reactions were analyzed by <sup>1</sup>H NMR spectroscopy with mesitylene as internal standard.

### 7.1 Evaluation of different mediators



**Scheme S1.** Evaluation of different mediators.

## 7.2 Evaluation of other parameters



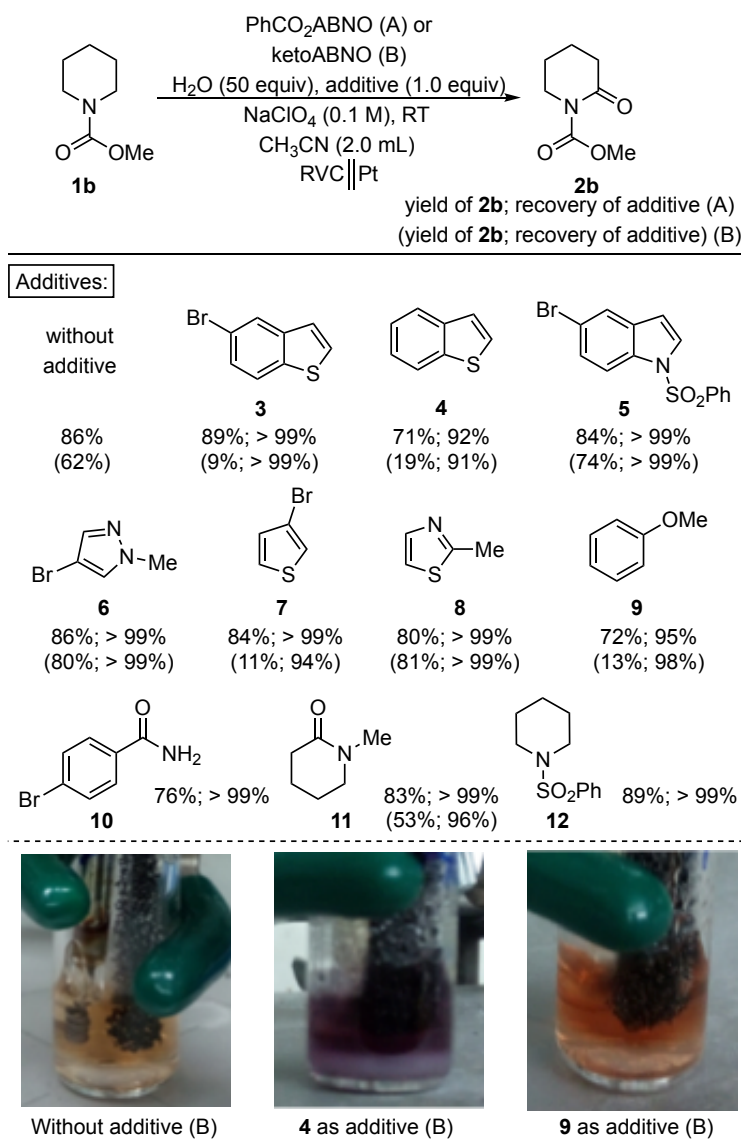
[a] 0.05 M **1a**. [b] With graphite as working electrode. [c] IKA<sup>®</sup> ElectroSyn 2.0 was used, 0.4 mmol scale, 0.1 M, constant current @ 5 mA for 24 h. The reaction was conducted with 0.2 mmol scale, and <sup>1</sup>H NMR yield with mesitylene as internal standard was shown.

**Scheme S2.** Evaluation of other parameters.

## 8. Robustness Screening of Mediated Electrolysis

These reactions were carried out by following the general procedure with  $\text{PhCO}_2\text{ABNO}$  (@ 3 mA) or ketoABNO (@ 5 mA) as mediator, **1b** as model substrate and 1 equiv of additive. After bulk electrolysis, these experiments were analyzed by crude <sup>1</sup>H NMR with mesitylene as internal standard. These data clearly showed that reactions proceeded well in the presence of these sensitive functional groups and negligible effect

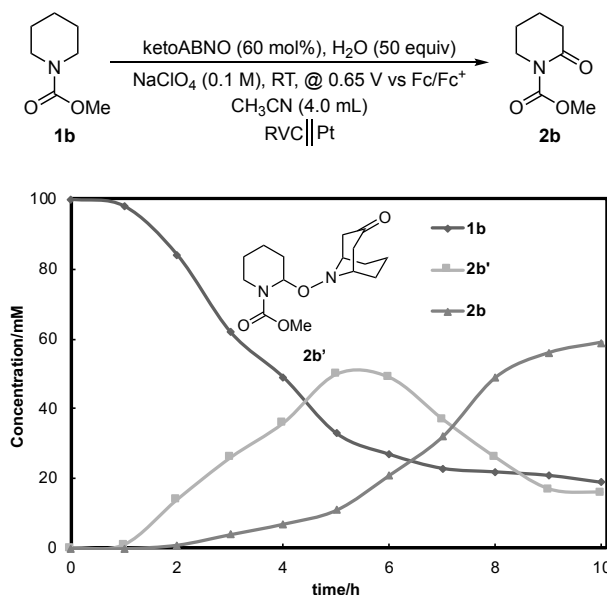
was observed in the presence of PhCO<sub>2</sub>ABNO, with almost all the additives recovered. On the other hand, although most of additives were recovered from the reaction with ketoABNO as mediator, low yields and darker color were observed for these reactions with electron rich additives (**3**, **4**, **7**, **9**). The origin of this observation is not known, but it may reflect formation of a non-productive adduct between the electrophilic ketoABNO<sup>+</sup> species and the electron-rich aromatic ring (i.e., a donor-acceptor interaction), which could hinder the desired reactivity.



**Table S3.** Robustness screening of mediated electrolysis with PhCO<sub>2</sub>ABNO (ketoABNO) as mediator.

## 9. Time Course and Control Experiment

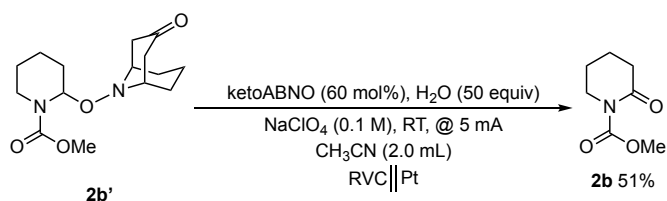
The reaction was conducted under constant potential @ 0.65 V vs Fc/Fc<sup>+</sup>, and during the bulk electrolysis, an aliquot of reaction mixture (~ 50 μL) was withdrawn and submitted for <sup>1</sup>H NMR with mesitylene as internal standard.



These data reveal formation of an intermediate **2b'** during the first five hours, which subsequently converts to product. The concentration of **2b** grows in only slowly at the beginning of the reaction, followed by more rapid growth following formation of **2b'**.

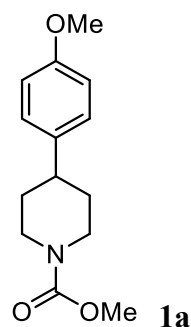
**2b'**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 5.59 (br, 1H), 3.90 – 3.74 (m, 1H), 3.73 – 3.56 (m, 5H), 3.00 – 2.83 (m, 3H), 2.08 (d, *J* = 16.1 Hz, 2H), 1.80 – 1.72 (m, 3H), 1.67 – 1.51 (m, 6H), 1.45 – 1.35 (m, 1H), 1.33 – 1.17 (m, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 210.6, 157.4, 81.4, 58.7, 57.5, 52.5, 41.0, 40.9, 31.84, 31.83, 28.5, 24.8, 18.6, 15.4. HRMS (ESI) Calculated for [M+H<sup>+</sup>]: 297.1809, measured: 297.1806.

Furthermore, when **2b'** was subjected to the standard condition, **2b** was obtained with 51% yield.



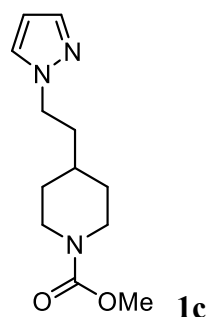
## 10. Substrate and Product Characterization Data

### 10.1 Characterization of substrates



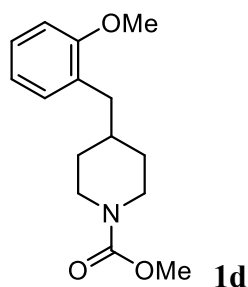
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.14 – 7.08 (m, 2H), 6.88 – 6.82 (m, 2H), 4.27 (br, 2H), 3.79 (s, 3H), 3.72 (s, 3H), 2.85 (t,  $J = 12.1$  Hz, 2H), 2.61 (tt,  $J = 12.1, 3.5$  Hz, 1H), 1.81 (d,  $J = 12.9$  Hz, 2H), 1.68 – 1.49 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.1, 155.9, 137.8, 127.6, 113.9, 55.2, 52.5, 44.6, 41.7, 33.3.

**HRMS (ESI)** Calculated for  $[\text{M}+\text{H}^+]$ : 250.1438, measured: 250.1434.



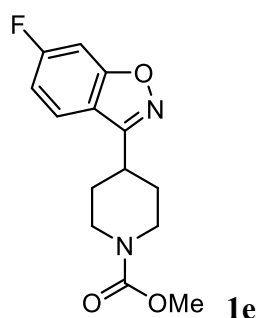
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (d,  $J = 1.6$  Hz, 1H), 7.36 (d,  $J = 2.2$  Hz, 1H), 6.24 (t,  $J = 2.0$  Hz, 1H), 4.20 – 4.01 (m, 4H), 3.67 (s, 3H), 2.71 (t,  $J = 11.8$  Hz, 2H), 1.82 (q,  $J = 7.0$  Hz, 2H), 1.68 (d,  $J = 12.6$  Hz, 2H), 1.44 – 1.34 (m, 1H), 1.15 (qd,  $J = 12.5, 4.0$  Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  155.9, 139.1, 128.7, 105.4, 52.5, 49.4, 43.9, 36.9, 33.2, 31.7.

**HRMS (ESI)** Calculated for  $[\text{M}+\text{H}^+]$ : 238.1550, measured: 238.1546.



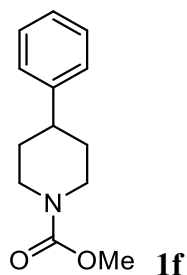
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.19 (td,  $J = 8.0, 1.7$  Hz, 1H), 7.06 (dd,  $J = 7.3, 1.6$  Hz, 1H), 6.90 – 6.82 (m, 2H), 4.10 (br, 2H), 3.81 (s, 3H), 3.68 (s, 3H), 2.70 (t,  $J = 12.0$  Hz, 2H), 2.55 (d,  $J = 7.1$  Hz, 2H), 1.79 – 1.68 (m, 1H), 1.61 (d,  $J = 12.6$  Hz, 2H), 1.29 – 1.09 (m, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  157.6, 156.0, 130.9, 128.6, 127.2, 120.1, 110.3, 55.2, 52.4, 44.2, 37.1, 36.4, 32.0.

**HRMS (ESI)** Calculated for  $[\text{M}+\text{H}^+]$ : 264.1594, measured: 264.1591.



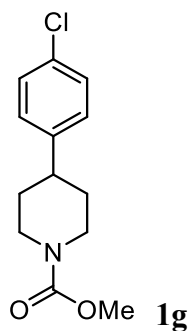
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 (dd,  $J = 8.7, 5.1$  Hz, 1H), 7.22 (dd,  $J = 8.5, 2.1$  Hz, 1H), 7.04 (td,  $J = 8.8, 2.1$  Hz, 1H), 4.24 (s, 2H), 3.70 (s, 3H), 3.23 (tt,  $J = 11.4, 3.8$  Hz, 1H), 3.01 (t,  $J = 12.0$  Hz, 2H), 2.05 (d,  $J = 11.4$  Hz, 2H), 1.99 – 1.81 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.06 (d,  $J = 250.9$  Hz), 163.79 (d,  $J = 13.6$  Hz), 160.36 (s), 155.79 (s), 122.18 (d,  $J = 11.1$  Hz), 117.02 (d,  $J = 1.2$  Hz), 112.45 (d,  $J = 25.4$  Hz), 97.44 (d,  $J = 26.8$  Hz), 52.60 (s), 43.63 (s), 34.16 (s), 30.02 (s).  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -109.26 (s).

**HRMS (ESI)** Calculated for  $[\text{M}+\text{H}^+]$ : 279.1140, measured: 279.1136.



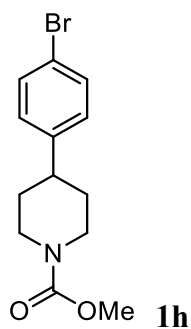
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 – 7.28 (m, 2H), 7.23 – 7.17 (m, 3H), 4.29 (br, 2H), 3.72 (s, 3H), 2.86 (t,  $J = 12.0$  Hz, 2H), 2.66 (tt,  $J = 12.2, 3.6$  Hz, 1H), 1.84 (d,  $J = 12.9$  Hz, 2H), 1.74 – 1.53 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.9, 145.6, 128.5, 126.7, 126.4, 52.5, 44.5, 42.6, 33.1.

**HRMS (ESI)** Calculated for  $[\text{M}+\text{H}^+]$ : 220.1332, measured: 220.1330.



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 – 7.26 (m, 2H), 7.15 – 7.09 (m, 2H), 4.28 (br, 2H), 3.72 (s, 3H), 2.85 (t,  $J = 12.0$  Hz, 2H), 2.64 (tt,  $J = 12.2, 3.5$  Hz, 1H), 1.81 (d,  $J = 13.3$  Hz, 2H), 1.60 (qd,  $J = 12.9, 6.4$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.9, 144.0, 132.0, 128.6, 128.1, 52.6, 44.4, 42.0, 33.0.

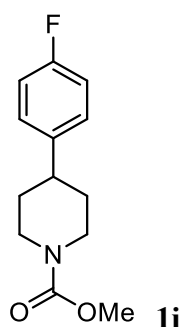
**HRMS (ESI)** Calculated for  $[\text{M}+\text{H}^+]$ : 254.0942, measured: 254.0939.





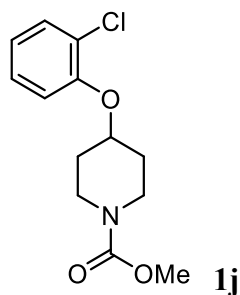
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 – 7.38 (m, 2H), 7.07 (dd,  $J = 8.7, 2.0$  Hz, 2H), 4.28 (br, 2H), 3.71 (s, 3H), 2.85 (t,  $J = 11.8$  Hz, 2H), 2.63 (tt,  $J = 12.2, 3.5$  Hz, 1H), 1.81 (d,  $J = 13.0$  Hz, 2H), 1.69 – 1.47 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.9, 144.5, 131.6, 128.5, 120.1, 52.6, 44.4, 42.1, 33.0.

**HRMS (ESI)** Calculated for  $[\text{M}+\text{H}^+]$ : 298.0437, measured: 298.0435.



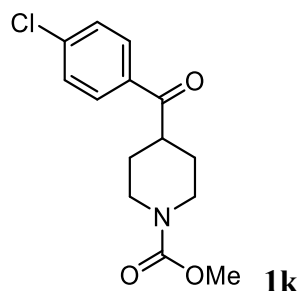
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.18 – 7.09 (m, 2H), 7.03 – 6.93 (m, 2H), 4.28 (br, 2H), 3.72 (s, 3H), 2.85 (t,  $J = 11.8$  Hz, 2H), 2.65 (tt,  $J = 12.2, 3.6$  Hz, 1H), 1.82 (d,  $J = 12.9$  Hz, 2H), 1.68 – 1.49 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.4 (d,  $J = 244.2$  Hz), 155.9, 141.2 (d,  $J = 3.2$  Hz), 128.1 (d,  $J = 7.8$  Hz), 115.2 (d,  $J = 21.1$  Hz), 52.6, 44.5, 41.9, 33.2.

**HRMS (ESI)** Calculated for  $[\text{M}+\text{H}^+]$ : 238.1238, measured: 238.1234.



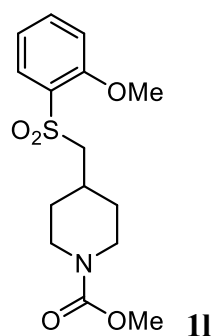
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 (dd,  $J = 7.9, 1.6$  Hz, 1H), 7.23 – 7.15 (m, 1H), 6.98 – 6.88 (m, 2H), 4.60 – 4.52 (m, 1H), 3.74 – 3.64 (m, 5H), 3.54 (s, 2H), 1.97 – 1.78 (m, 4H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  155.9, 152.8, 130.6, 127.6, 124.7, 122.1, 116.3, 73.2, 52.6, 40.4, 30.2.

**HRMS (ESI)** Calculated for  $[\text{M}+\text{H}^+]$ : 270.0892, measured: 270.0890.



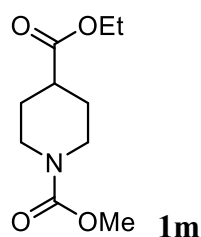
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (d,  $J = 8.6$  Hz, 2H), 7.45 (d,  $J = 8.6$  Hz, 2H), 4.19 (br, 2H), 3.70 (s, 3H), 3.37 (tt,  $J = 11.0, 3.8$  Hz, 1H), 2.96 (t,  $J = 12.1$  Hz, 2H), 1.84 (d,  $J = 11.5$  Hz, 2H), 1.77 – 1.64 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  200.6, 155.8, 139.6, 134.0, 129.7, 129.1, 52.6, 43.3, 43.2, 28.2.

**HRMS (ESI)** Calculated for  $[\text{M}+\text{H}^+]$ : 282.0892, measured: 282.0888.



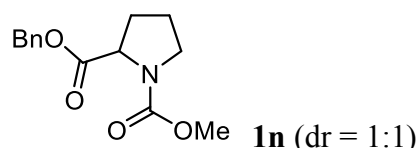
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (dd,  $J = 7.8, 1.7$  Hz, 1H), 7.64 – 7.54 (m, 1H), 7.15 – 7.07 (m, 1H), 7.04 (d,  $J = 8.3$  Hz, 1H), 4.06 (s, 2H), 3.97 (s, 3H), 3.66 (s, 3H), 3.28 (d,  $J = 5.5$  Hz, 2H), 2.76 (t,  $J = 11.7$  Hz, 2H), 2.28 – 2.09 (m, 1H), 1.84 (d,  $J = 9.7$  Hz, 2H), 1.25 (qd,  $J = 12.3, 4.4$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.2, 155.8, 135.6, 130.1, 127.8, 120.9, 112.4, 60.0, 56.3, 52.5, 43.6, 31.8, 31.0.

**HRMS (ESI)** Calculated for  $[\text{M}+\text{H}^+]$ : 328.1207, measured: 328.1213.



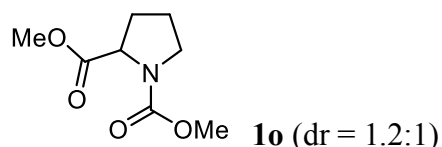
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.12 (q,  $J = 7.1$  Hz, 2H), 4.03 (br, 2H), 3.67 (s, 3H), 2.89 (t,  $J = 11.6$  Hz, 2H), 2.43 (tt,  $J = 10.9, 3.9$  Hz, 1H), 1.87 (d,  $J = 11.7$  Hz, 2H), 1.68 – 1.57 (m, 2H), 1.24 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  174.4, 155.8, 60.5, 52.5, 43.2, 40.9, 27.8, 14.1.

**HRMS (ESI)** Calculated for  $[\text{M}+\text{H}^+]$ : 216.1230, measured: 216.1229.



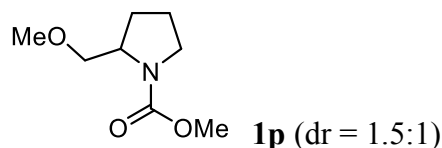
Two isomers:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 – 7.28 (m, 5H), 5.27 – 5.10 (m, 2H), 4.43 (dd,  $J = 8.6, 3.4$  Hz, 0.5H), 4.33 (dd,  $J = 8.6, 3.8$  Hz, 0.5H), 3.72 (s, 1.5H), 3.57 (s, 1.5H), 3.64 – 3.39 (m, 2H), 2.31 – 2.14 (m, 1H), 2.07 – 1.82 (m, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  (172.6, 172.5), (155.5, 155.0), 135.7, (128.6, 128.5), (128.3, 128.2), (128.1, 128.), (66.8, 66.6), (59.2, 58.9), (52.5, 52.4), (46.9, 46.3), (30.9, 29.9), (24.3, 23.5).

**HRMS (ESI)** Calculated for  $[\text{M}+\text{H}^+]$ : 264.1230, measured: 264.1227.



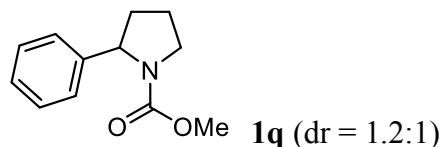
Major:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.36 (dd,  $J = 8.6, 3.4$  Hz, 1H), 3.73 (s, 3H), 3.70 (s, 3H), 3.62 – 3.38 (m, 2H), 2.27 – 2.13 (m, 1H), 2.06 – 1.81 (m, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.2, 155.5, 59.1, 52.2, 46.3, 29.9, 24.3. Minor:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.29 (dd,  $J = 8.6, 3.6$  Hz, 1H), 3.71 (s, 3H), 3.66 (s, 3H), 3.61 – 3.38 (m, 2H), 2.27 – 2.13 (m, 1H), 2.04 – 1.83 (m, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.3, 155.0, 58.7, 52.5, 46.8, 30.9, 23.4.

**HRMS (ESI)** Calculated for  $[\text{M}+\text{H}^+]$ : 188.0917, measured: 188.0915.



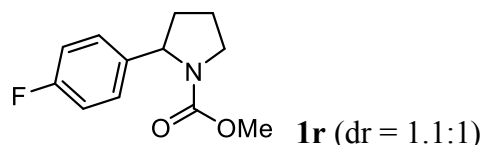
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.99 (s, 0.6H), 3.89 (s, 0.4zzH), 3.68 (s, 3H), 3.56 – 3.16 (m, 7H), 1.96 – 1.85 (s, 3H), 1.84 – 1.77 (m, 1H). Major:  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  155.7, 72.9, 59.0, 56.9, 52.2, 46.6, 27.9, 23.8. Minor:  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  155.7, 73.5, 59.0, 56.3, 52.2, 46.9, 28.7, 22.9.

**HRMS (ESI)** Calculated for  $[\text{M}+\text{H}^+]$ : 174.1125, measured: 174.1124.



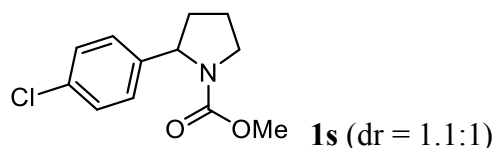
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (t,  $J = 7.5$  Hz, 2H), 7.25 – 7.12 (m, 3H), 5.08 – 4.81 (m, 1H), 3.79 – 3.49 (m, 5H), 2.37 – 2.23 (m, 1H), 1.97 – 1.78 (m, 3H). Major:  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  155.9, 144.0, 128.3, 126.6, 125.2, 60.7, 52.3, 47.5, 35.7, 22.6. Minor:  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  155.5, 143.6, 128.3, 126.6, 125.5, 61.2, 52.3, 47.1, 34.7, 23.6.

**HRMS (ESI)** Calculated for  $[\text{M}+\text{H}^+]$ : 206.1176, measured: 206.1174.



$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.19 – 7.07 (m, 2H), 7.02 – 6.93 (m, 2H), 4.94 (br, 0.48H), 4.89 (br, 0.52H), 3.76 – 3.47 (m, 5H), 2.29 (br, 1H), 2.00 – 1.75 (m, 3H). Major:  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  161.7 (d,  $J = 245.8$  Hz), 155.8, 139.5 (d,  $J = 57.5$  Hz), 126.9 (d,  $J = 24.7$  Hz), 115.1 (d,  $J = 21.4$  Hz), 60.2, 52.4, 47.5, 35.7, 22.6. Minor:  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  161.7 (d,  $J = 245.8$  Hz), 155.6, 139.5 (d,  $J = 57.5$  Hz), 126.9 (d,  $J = 24.7$  Hz), 115.1 (d,  $J = 21.4$  Hz), 60.7, 52.4, 47.1, 34.8, 23.6. Major:  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -116.58 (s). Minor:  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -116.63 (s)

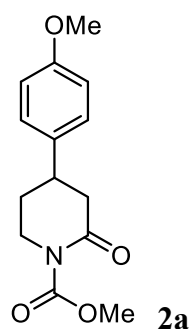
**HRMS (ESI)** Calculated for  $[\text{M}+\text{H}^+]$ : 224.1081, measured: 224.1079.



$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 – 7.24 (m, 2H), 7.17 – 7.06 (m, 2H), 4.90 (d,  $J$  = 21.9 Hz, 1H), 3.80 – 3.43 (m, 5H), 2.30 (s, 1H), 1.99 – 1.75 (m, 3H). Major:  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  155.8, 142.6, 132.4, 128.5, 126.7, 60.3, 52.4, 47.5, 35.7, 22.6. Minor:  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  155.6, 142.2, 132.4, 128.5, 126.9, 60.8, 52.4, 47.1, 34.7, 23.7.

**HRMS (ESI)** Calculated for  $[\text{M}+\text{H}^+]$ : 240.0786, measured: 240.0783.

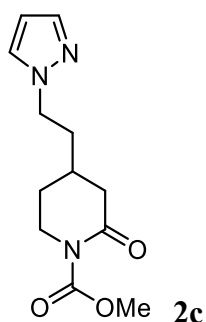
## 10.2 Characterization of products



The reaction was conducted with  $\text{PhCO}_2\text{ABNO}$ , 50 equiv of water @ 3 mA, and the product was obtained with 31 mg as colorless oil (59%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.11 (d,  $J$  = 8.6 Hz, 2H), 6.87 (d,  $J$  = 8.7 Hz, 2H), 3.95 (dt,  $J$  = 12.9, 4.7 Hz, 1H), 3.88 (s, 3H), 3.79 (s, 3H), 3.66 (ddd,  $J$  = 12.9, 10.8, 4.3 Hz, 1H), 3.10 (ddd,  $J$  = 15.5, 10.8, 4.7 Hz, 1H), 2.85 (ddd,  $J$  = 17.2, 5.4, 2.0 Hz, 1H), 2.62 (dd,  $J$  = 17.2, 11.0 Hz, 1H), 2.19 (dq,  $J$  = 12.6, 4.2, 2.1 Hz, 1H), 1.93 (dtd,  $J$  = 13.7, 10.8, 5.0 Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.5, 158.5, 155.0, 134.9, 127.4, 114.2, 55.3, 53.9, 45.9, 42.2, 37.5, 30.4.

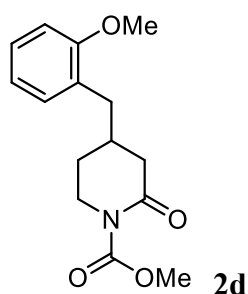
**HRMS (ESI)** Calculated for  $[\text{M}+\text{H}^+]$ : 264.1230, measured: 264.1228.



The reaction was conducted with PhCO<sub>2</sub>ABNO, 30 equiv of water @ 5 mA, and the product was obtained with 35 mg as light yellow oil (69%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.48 (d, *J* = 1.4 Hz, 1H), 7.35 (d, *J* = 2.1 Hz, 1H), 6.23 (t, *J* = 2.0 Hz, 1H), 4.24 – 4.11 (m, 2H), 3.88 (dt, *J* = 13.0, 4.7 Hz, 1H), 3.83 (s, 3H), 3.52 (ddd, *J* = 13.0, 10.9, 4.4 Hz, 1H), 2.65 (ddd, *J* = 16.9, 5.2, 1.8 Hz, 1H), 2.19 (dd, *J* = 17.0, 10.2 Hz, 1H), 2.00 – 1.79 (m, 4H), 1.54 – 1.41 (m, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 170.1, 154.7, 139.4, 128.9, 105.6, 53.9, 49.1, 45.4, 40.7, 36.1, 29.7, 28.5.

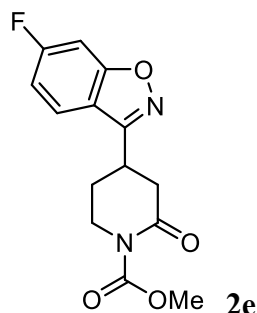
**HRMS (ESI)** Calculated for [M+H<sup>+</sup>]: 252.1343, measured: 252.1339.



The reaction was conducted with PhCO<sub>2</sub>ABNO, 30 equiv of water @ 5 mA, and the product was obtained with 34 mg as light yellow oil (62%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.21 (t, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 7.3 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 8.5 Hz, 1H), 3.89 (dt, *J* = 12.9, 4.7 Hz, 1H), 3.85 (s, 3H), 3.81 (s, 3H), 3.51 (ddd, *J* = 12.9, 11.2, 4.4 Hz, 1H), 2.74 – 2.50 (m, 3H), 2.30 – 2.15 (m, 2H), 2.01 – 1.83 (m, 1H), 1.58 – 1.41 (m, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 171.1, 157.5, 155.0, 130.8, 127.8, 127.1, 120.4, 110.4, 55.2, 53.8, 45.9, 41.1, 36.3, 32.9, 28.7.

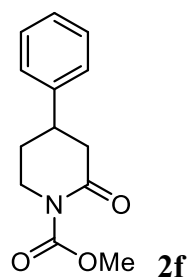
**HRMS (ESI)** Calculated for [M+H<sup>+</sup>]: 278.1387, measured: 278.1383.



The reaction was conducted with ketoABNO, 50 equiv of water @ 5 mA, and the product was obtained with 34 mg as white solid (58%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 (dd,  $J = 8.7, 5.0$  Hz, 1H), 7.25 (dd,  $J = 8.4, 2.0$  Hz, 1H), 7.09 (td,  $J = 8.8, 2.1$  Hz, 1H), 3.95 (dt,  $J = 13.2, 5.3$  Hz, 1H), 3.86 (s, 3H), 3.85 – 3.79 (m, 1H), 3.74 – 3.65 (m, 1H), 3.07 (ddd,  $J = 17.3, 6.0, 1.4$  Hz, 1H), 2.99 (dd,  $J = 17.3, 9.7$  Hz, 1H), 2.51 – 2.39 (m, 1H), 2.25 (dtd,  $J = 14.3, 9.5, 4.9$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.2, 164.3 (d,  $J = 251.8$  Hz), 164.1 (d,  $J = 13.6$  Hz), 158.7, 154.5, 121.8 (d,  $J = 11.1$  Hz), 116.6, 113.0 (d,  $J = 25.5$  Hz), 97.7 (d,  $J = 26.9$  Hz), 54.1, 45.0, 38.5, 30.4, 27.3.  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -108.40 (s).

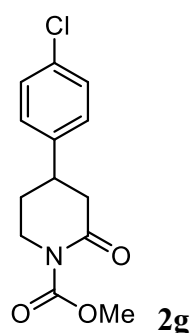
**HRMS (ESI)** Calculated for  $[\text{M}+\text{H}^+]$ : 293.0932, measured: 293.0931.



The reaction was conducted with ketoABNO, 40 equiv of water @ 5 mA, and the product was obtained with 38 mg as white solid (81%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 (t,  $J = 7.5$  Hz, 2H), 7.28 – 7.24 (m, 1H), 7.20 (d,  $J = 7.2$  Hz, 2H), 3.96 (dt,  $J = 13.0, 4.7$  Hz, 1H), 3.88 (s, 3H), 3.68 (ddd,  $J = 13.0, 10.8, 4.3$  Hz, 1H), 3.15 (ddd,  $J = 15.5, 10.8, 4.7$  Hz, 1H), 2.87 (ddd,  $J = 17.2, 5.4, 2.0$  Hz, 1H), 2.66 (dd,  $J = 17.2, 11.0$  Hz, 1H), 2.27 – 2.18 (m, 1H), 1.98 (dtd,  $J = 13.7, 10.8, 5.0$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.4, 154.9, 142.8, 128.9, 127.1, 126.4, 54.0, 45.9, 42.0, 38.2, 30.2.

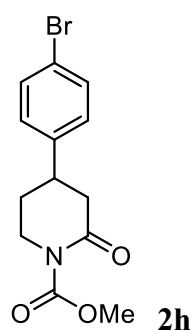
**HRMS (ESI)** Calculated for  $[\text{M}+\text{H}^+]$ : 234.1125, measured: 234.1122.



The reaction was conducted with ketoABNO, 40 equiv of water @ 5 mA, and the product was obtained with 33 mg as light yellow oil (62%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (d,  $J = 8.5$  Hz, 2H), 7.13 (d,  $J = 8.5$  Hz, 2H), 3.96 (dt,  $J = 13.0, 4.7$  Hz, 1H), 3.89 (s, 3H), 3.67 (ddd,  $J = 13.0, 10.8, 4.3$  Hz, 1H), 3.13 (ddd,  $J = 15.5, 10.7, 4.7$  Hz, 1H), 2.86 (ddd,  $J = 17.2, 5.4, 2.0$  Hz, 1H), 2.61 (dd,  $J = 17.2, 11.0$  Hz, 1H), 2.21 (dq,  $J = 12.7, 4.2, 2.1$  Hz, 1H), 1.94 (dtd,  $J = 13.7, 10.9, 5.0$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  169.0, 153.8, 140.3, 131.9, 128.0, 126.8, 53.0, 44.7, 40.9, 36.7, 29.2.

**HRMS (ESI)** Calculated for  $[\text{M}+\text{H}^+]$ : 268.0735, measured: 268.0730.

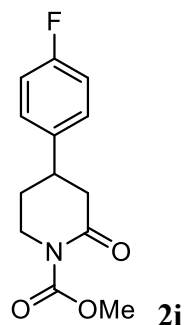


The reaction was conducted with ketoABNO, 50 equiv of water @ 5 mA, and the product was obtained with 39 mg as light yellow solid (63%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (d,  $J = 8.4$  Hz, 2H), 7.07 (d,  $J = 8.4$  Hz, 2H), 3.96 (dt,  $J = 13.0, 4.7$  Hz, 1H), 3.88 (s, 3H), 3.66 (ddd,  $J = 13.0, 10.9, 4.3$  Hz, 1H), 3.11 (ddd,  $J = 15.4, 10.7, 4.7$  Hz, 1H), 2.85 (ddd,  $J = 17.2, 5.4, 2.0$  Hz, 1H), 2.60 (dd,  $J = 17.2, 11.0$  Hz, 1H), 2.23 – 2.16 (m, 1H), 1.93 (dtd,  $J = 13.8, 10.9, 5.0$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.9, 154.8, 141.8, 131.9, 128.1, 120.8, 54.0, 45.7, 41.8, 37.7, 30.0.



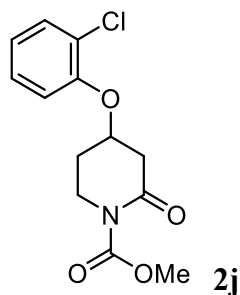
**HRMS (ESI)** Calculated for  $[M+H^+]$ : 312.0230, measured: 312.0225.



The reaction was conducted with ketoABNO, 40 equiv of water @ 5 mA, and the product was obtained with 42 mg as light yellow oil (83%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.16 (dd,  $J = 8.6, 5.3$  Hz, 2H), 7.05 – 7.00 (m, 2H), 3.96 (dt,  $J = 13.0, 4.6$  Hz, 1H), 3.88 (s, 3H), 3.67 (ddd,  $J = 13.0, 10.9, 4.3$  Hz, 1H), 3.14 (ddd,  $J = 15.5, 10.7, 4.7$  Hz, 1H), 2.86 (ddd,  $J = 17.2, 5.4, 1.9$  Hz, 1H), 2.61 (dd,  $J = 17.2, 11.0$  Hz, 1H), 2.23 – 2.16 (m, 1H), 1.94 (dtd,  $J = 13.7, 10.9, 5.0$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.0, 161.7 (d,  $J = 245.5$  Hz), 154.8, 138.5 (d,  $J = 3.2$  Hz), 127.8 (d,  $J = 8.0$  Hz), 115.6 (d,  $J = 21.3$  Hz), 53.9, 45.7, 42.1, 37.5, 30.2.  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -115.58 (s).

**HRMS (ESI)** Calculated for  $[M+H^+]$ : 252.1031, measured: 252.1027.

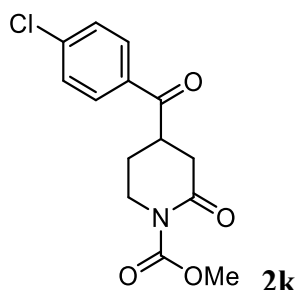


The reaction was conducted with ketoABNO, 50 equiv of water @ 5 mA, and the product was obtained with 34.5 mg as light yellow oil (61%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 (dd,  $J = 7.9, 1.6$  Hz, 1H), 7.23 – 7.18 (m, 1H), 6.97 (td,  $J = 7.7, 1.4$  Hz, 1H), 6.93 (dd,  $J = 8.2, 1.3$  Hz, 1H), 4.80 – 4.75 (m, 1H), 4.03 (ddd,  $J = 13.9, 8.9, 4.4$  Hz, 1H), 3.89 (s, 3H), 3.85 (dt,  $J = 13.1, 5.3$  Hz, 1H), 2.92 (ddd,  $J = 18.4, 5.1, 1.7$  Hz, 1H), 2.87 (dd,  $J = 17.5, 4.9$  Hz, 1H), 2.29 – 2.21 (m, 1H), 2.15 (ddd,

$J = 14.2, 9.1, 4.6$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  168.3, 154.6, 152.2, 130.8, 127.7, 125.0, 123.1, 116.8, 71.5, 54.1, 41.9, 40.2, 28.01.

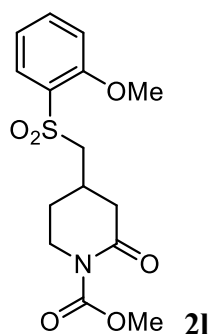
**HRMS (ESI)** Calculated for  $[\text{M}+\text{H}^+]$ : 284.0684, measured: 284.0681.



The reaction was conducted with ketoABNO, 40 equiv of water @ 5 mA, and the product was obtained with 49 mg as yellow solid (83%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (d,  $J = 8.6$  Hz, 2H), 7.47 (d,  $J = 8.6$  Hz, 2H), 3.88 (s, 3H), 3.91 – 3.80 (m, 2H), 3.78 – 3.72 (m, 1H), 2.89 (dd,  $J = 16.8, 9.3$  Hz, 1H), 2.69 (dd,  $J = 16.8, 5.7$  Hz, 1H), 2.21 (dq,  $J = 6.3, 5.4$  Hz, 1H), 2.02 (dtd,  $J = 12.6, 7.9, 4.7$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  197.2, 168.6, 153.5, 139.4, 132.2, 128.8, 128.3, 53.1, 43.1, 38.0, 35.4, 25.0.

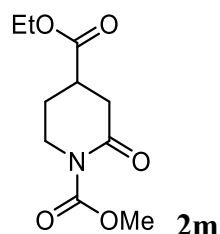
**HRMS (ESI)** Calculated for  $[\text{M}+\text{H}^+]$ : 296.0684, measured: 296.0681.



The reaction was conducted with ketoABNO, 50 equiv of water @ 5 mA, and the product was obtained with 57 mg as white solid (83%).

$^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  7.90 (dd,  $J = 7.8, 1.7$  Hz, 1H), 7.71 (ddd,  $J = 8.4, 7.4, 1.8$  Hz, 1H), 7.23 (d,  $J = 8.1$  Hz, 1H), 7.17 (td,  $J = 7.8, 0.9$  Hz, 1H), 3.99 (s, 3H), 3.80 (dt,  $J = 12.9, 4.8$  Hz, 1H), 3.76 (s, 3H), 3.51 (ddd,  $J = 12.9, 10.7, 4.3$  Hz, 1H), 3.44 (dd,  $J = 14.3, 6.5$  Hz, 1H), 3.40 (dd,  $J = 14.3, 6.7$  Hz, 1H), 2.61 (ddd,  $J = 16.8, 5.3, 1.9$  Hz,

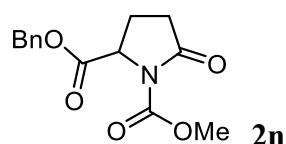
1H), 2.48 – 2.38 (m, 1H), 2.31 (dd,  $J = 16.8, 10.3$  Hz, 1H), 2.09 (dq,  $J = 10.7, 4.4, 2.0$  Hz, 1H), 1.65 (dtd,  $J = 13.8, 10.5, 5.0$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  169.6, 158.0, 155.1, 136.5, 130.1, 128.0, 121.3, 113.6, 59.0, 56.6, 53.7, 45.5, 40.4, 28.5, 28.4. **HRMS (ESI)** Calculated for  $[\text{M}+\text{H}^+]$ : 342.1006, measured: 342.1002.



The reaction was conducted with ketoABNO, 30 equiv of water @ 5 mA, and the product was obtained with 27 mg as colorless oil (58%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.18 (q,  $J = 7.2$  Hz, 2H), 3.87 (s, 3H), 3.86 – 3.81 (m, 1H), 3.71 (ddd,  $J = 13.3, 8.9, 4.5$  Hz, 1H), 2.96 – 2.81 (m, 1H), 2.77 (d,  $J = 7.5$  Hz, 2H), 2.19 (ddd,  $J = 15.8, 11.0, 4.9$  Hz, 1H), 2.07 – 1.95 (m, 1H), 1.27 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.8, 169.0, 154.5, 61.2, 53.9, 44.5, 37.4, 36.4, 25.4, 14.0.

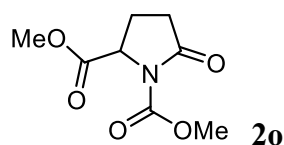
**HRMS (ESI)** Calculated for  $[\text{M}+\text{H}^+]$ : 230.1023, measured: 230.1021.



The reaction was conducted with ketoABNO, 20 equiv of water, constant applied potential @ 0.68 V vs  $\text{Fc}/\text{Fc}^+$ , and the product was obtained with 47 mg as light yellow oil (85%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 – 7.31 (m, 5H), 5.24 (d,  $J = 12.2$  Hz, 1H), 5.20 (d,  $J = 12.2$  Hz, 1H), 4.72 (dd,  $J = 9.4, 2.6$  Hz, 1H), 3.80 (s, 3H), 2.63 (dt,  $J = 17.6, 9.9$  Hz, 1H), 2.51 (ddd,  $J = 17.6, 9.3, 3.2$  Hz, 1H), 2.40 – 2.31 (m, 1H), 2.11 – 2.03 (m, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  172.5, 170.6, 151.6, 134.9, 128.5, 128.4, 128.1, 67.2, 58.6, 53.6, 30.9, 21.6.

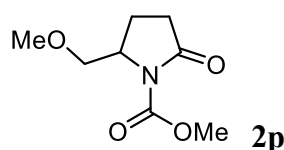
**HRMS (ESI)** Calculated for  $[\text{M}+\text{H}^+]$ : 278.1023, measured: 278.1019.



The reaction was conducted with ketoABNO, 20 equiv of water, constant applied potential @ 0.68 V vs Fc/Fc<sup>+</sup>, and the product was obtained with 31 mg as light yellow oil (76%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.69 (dd, *J* = 9.5, 2.6 Hz, 1H), 3.86 (s, 3H), 3.79 (s, 3H), 2.72 – 2.61 (m, 1H), 2.52 (ddd, *J* = 17.6, 9.3, 3.1 Hz, 1H), 2.41 – 2.31 (m, 1H), 2.13 – 2.05 (m, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 172.6, 171.5, 151.9, 58.7, 53.9, 52.8, 31.1, 21.8.

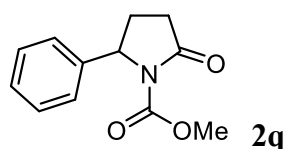
**HRMS (ESI)** Calculated for [M+H<sup>+</sup>]: 202.0710, measured: 202.0708.



The reaction was conducted with ketoABNO, 40 equiv of water @ 5 mA, and the product was obtained with 34 mg as white solid (93%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.35 – 4.28 (m, 1H), 3.87 (s, 3H), 3.63 (dd, *J* = 9.7, 4.6 Hz, 1H), 3.50 (dd, *J* = 9.7, 2.6 Hz, 1H), 3.34 (s, 3H), 2.79 – 2.69 (m, 1H), 2.40 (ddd, *J* = 17.7, 9.7, 1.8 Hz, 1H), 2.19 – 2.09 (m, 1H), 2.04 (dd, *J* = 11.9, 10.6 Hz, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 174.5, 152.3, 73.2, 59.3, 57.5, 53.5, 32.1, 21.5.

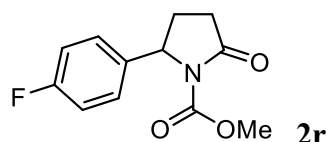
**HRMS (ESI)** Calculated for [M+H<sup>+</sup>]: 188.0917, measured: 188.0916.



The reaction was conducted with ketoABNO (40 mol%), 15 equiv of water @ 5 mA, and the product was obtained with 38 mg as white solid (86%).

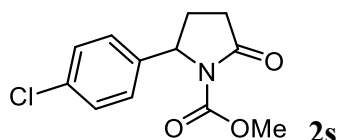
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (t,  $J = 7.4$  Hz, 2H), 7.29 (t,  $J = 7.3$  Hz, 1H), 7.21 (d,  $J = 7.3$  Hz, 2H), 5.27 (dd,  $J = 8.3, 2.8$  Hz, 1H), 3.75 (s, 3H), 2.78 – 2.65 (m, 1H), 2.57 – 2.48 (m, 2H), 2.00 – 1.91 (m, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  174.2, 151.9, 141.5, 128.9, 127.7, 125.0, 61.2, 53.5, 31.1, 27.5.

**HRMS (ESI)** Calculated for  $[\text{M}+\text{H}^+]$ : 220.0968, measured: 220.0966.



The reaction was conducted with ketoABNO (40 mol%), 30 equiv of water @ 5 mA, and the product was obtained with 39 mg as light yellow oil (82%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.19 (dd,  $J = 8.5, 5.2$  Hz, 2H), 7.04 (t,  $J = 8.6$  Hz, 2H), 5.24 (dd,  $J = 8.1, 2.7$  Hz, 1H), 3.75 (s, 3H), 2.75 – 2.63 (m, 1H), 2.59 – 2.46 (m, 2H), 1.97 – 1.88 (m, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.7, 162.0 (d,  $J = 246.3$  Hz), 151.7, 137.2 (d,  $J = 3.2$  Hz), 126.6 (d,  $J = 8.2$  Hz), 115.6 (d,  $J = 21.7$  Hz), 60.4, 53.4, 30.9, 27.3.  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -114.50 (s).

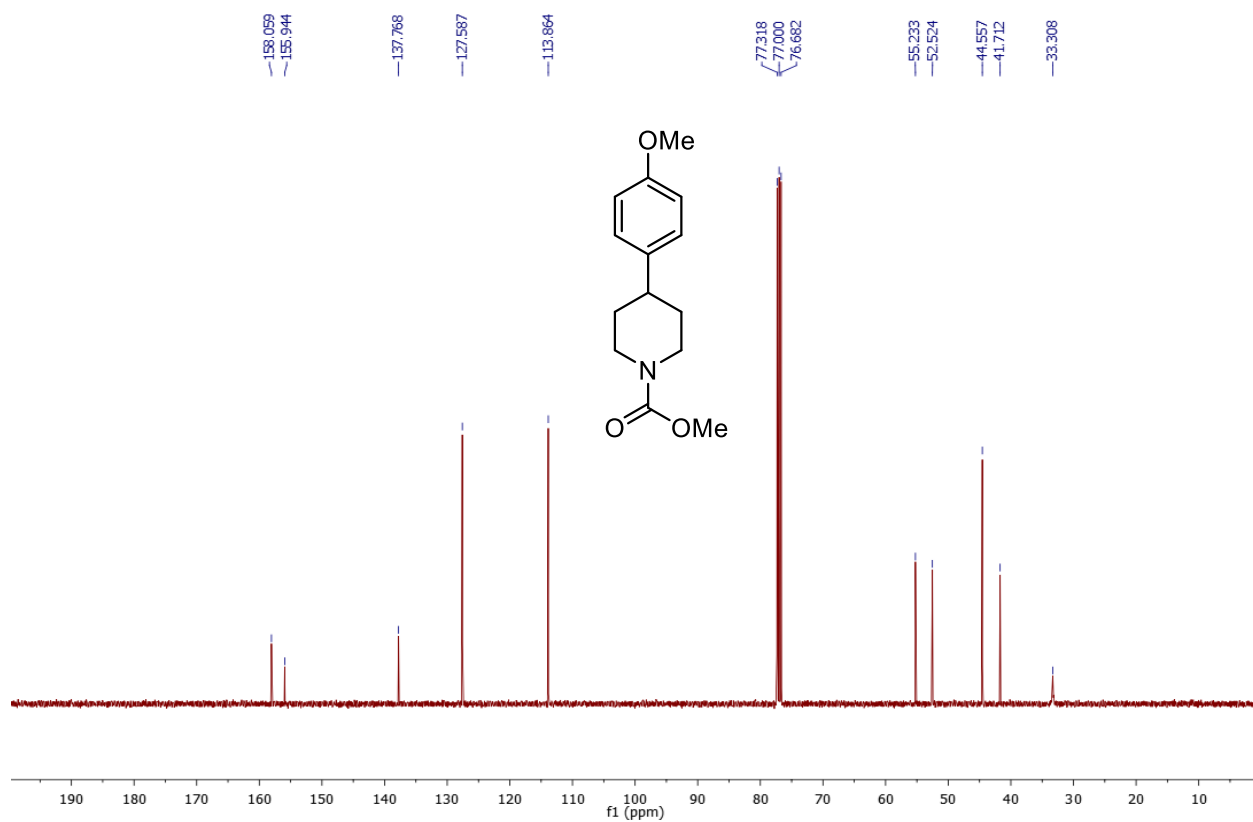
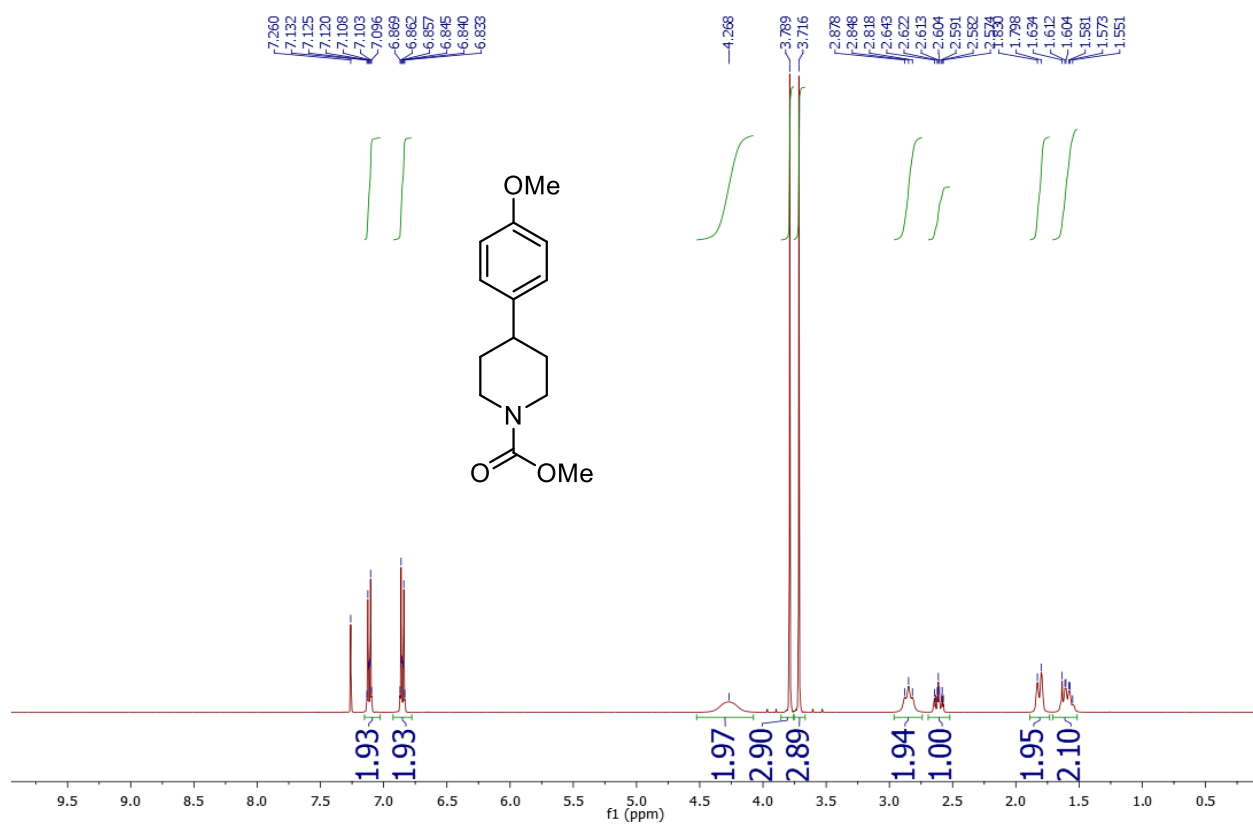


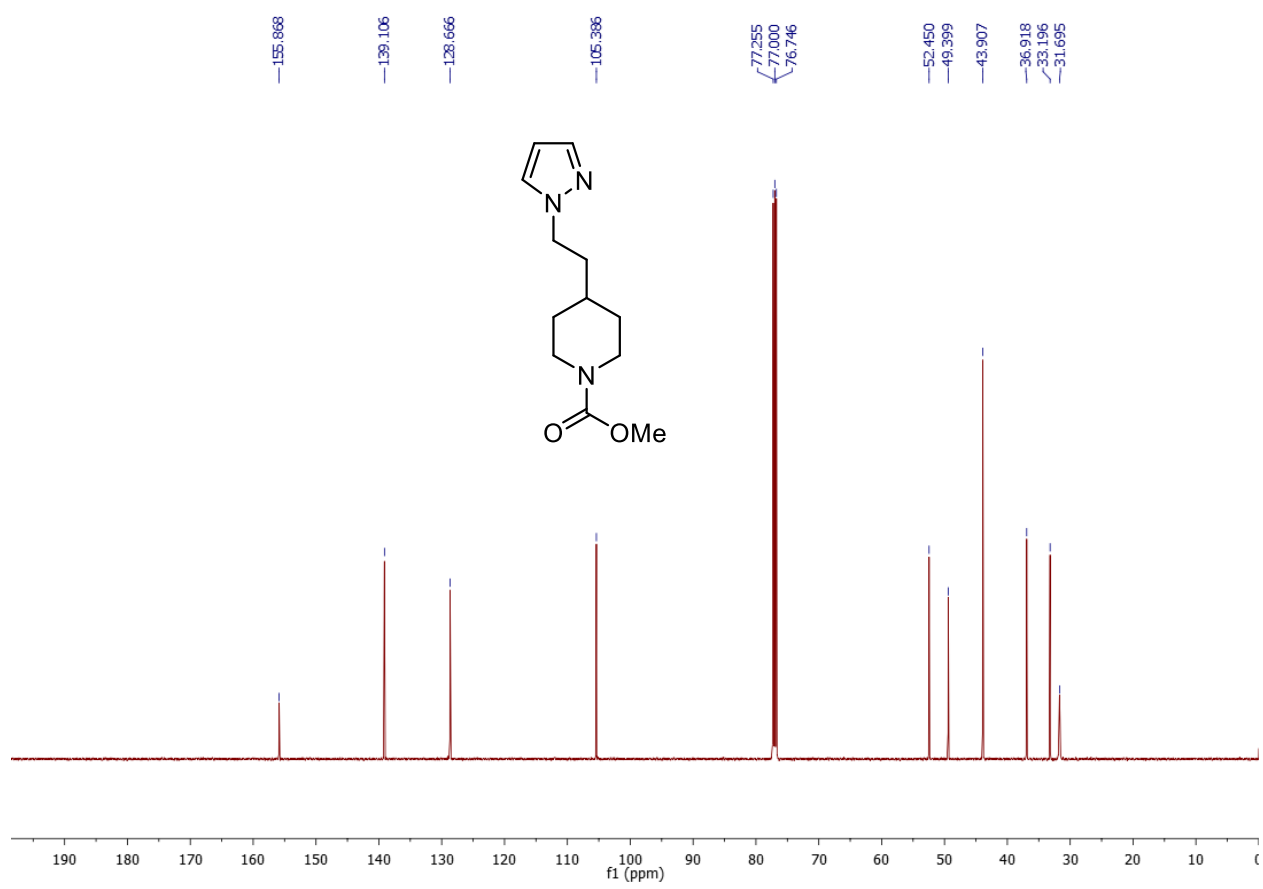
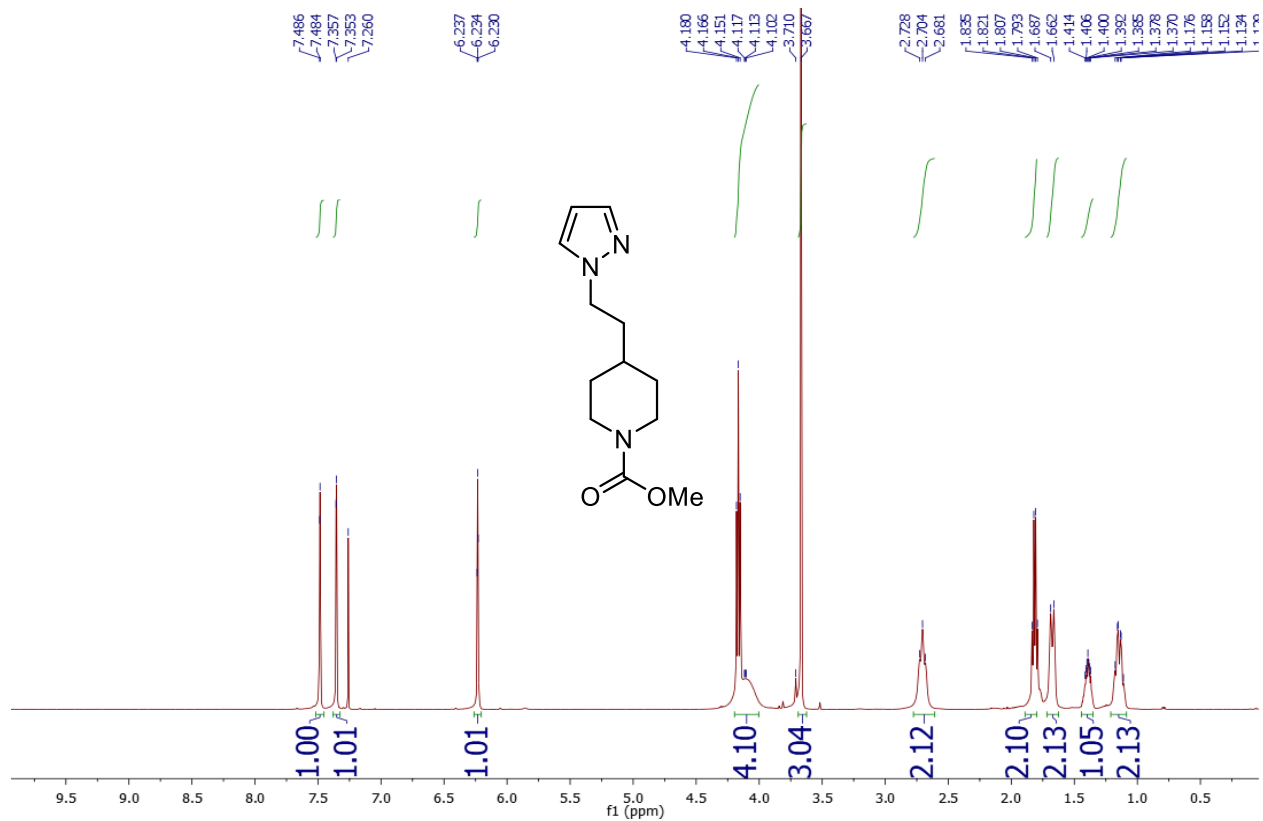
The reaction was conducted with ketoABNO (40 mol%), 30 equiv of water @ 5 mA, and the product was obtained with 41 mg as white solid (82%).

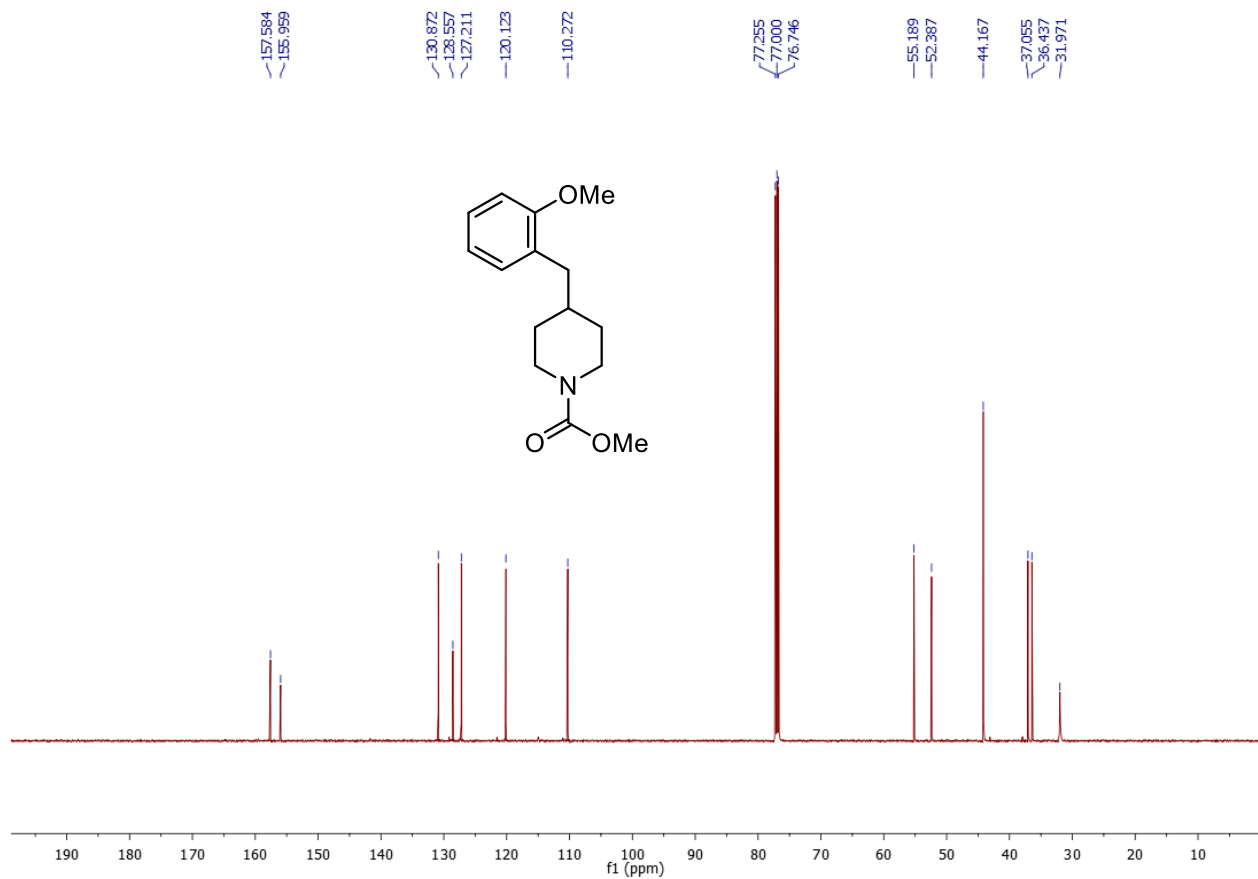
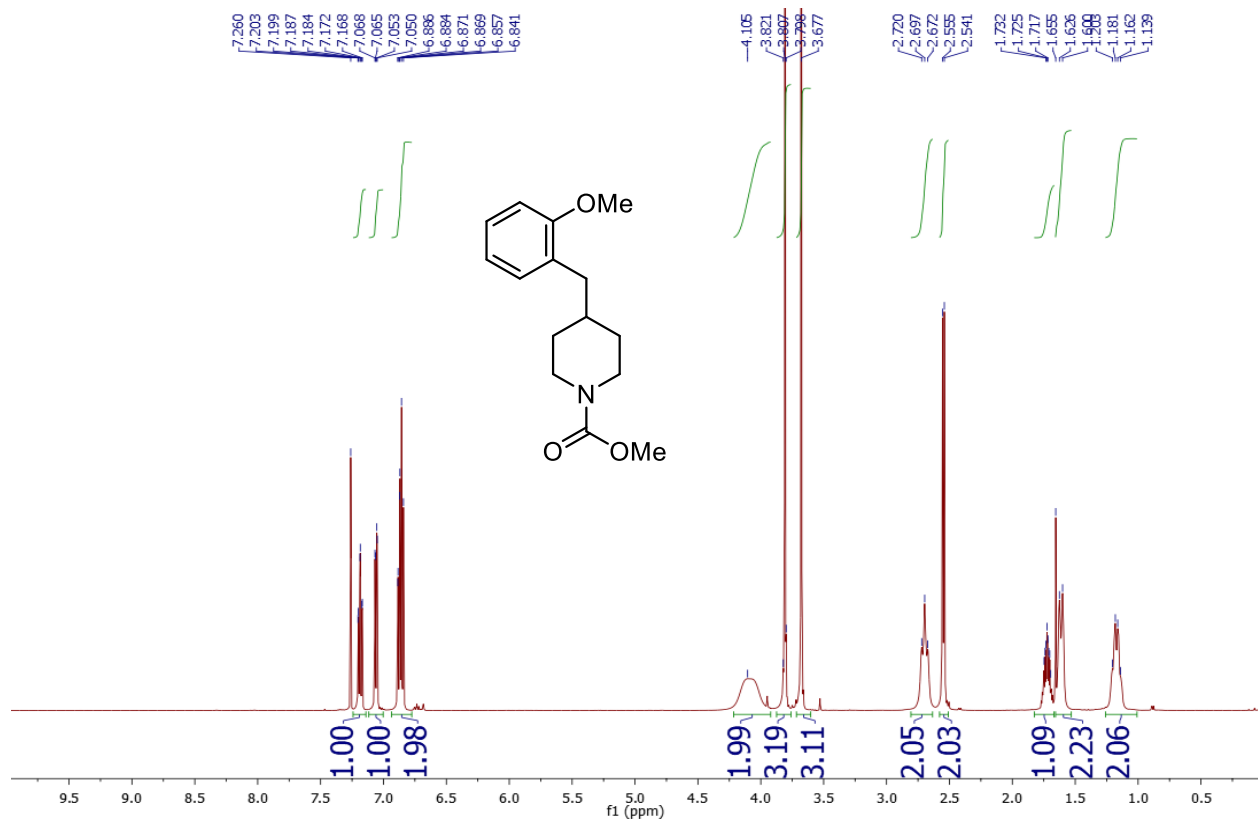
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 (d,  $J = 8.2$  Hz, 2H), 7.16 (d,  $J = 7.4$  Hz, 2H), 5.23 (d,  $J = 7.0$  Hz, 1H), 3.76 (s, 3H), 2.74 – 2.63 (m, 1H), 2.60 – 2.46 (m, 2H), 1.96 – 1.88 (m, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.7, 151.8, 140.0, 133.5, 129.0, 126.4, 60.5, 53.6, 30.9, 27.3.

**HRMS (ESI)** Calculated for  $[\text{M}+\text{H}^+]$ : 254.0579, measured: 254.0575.

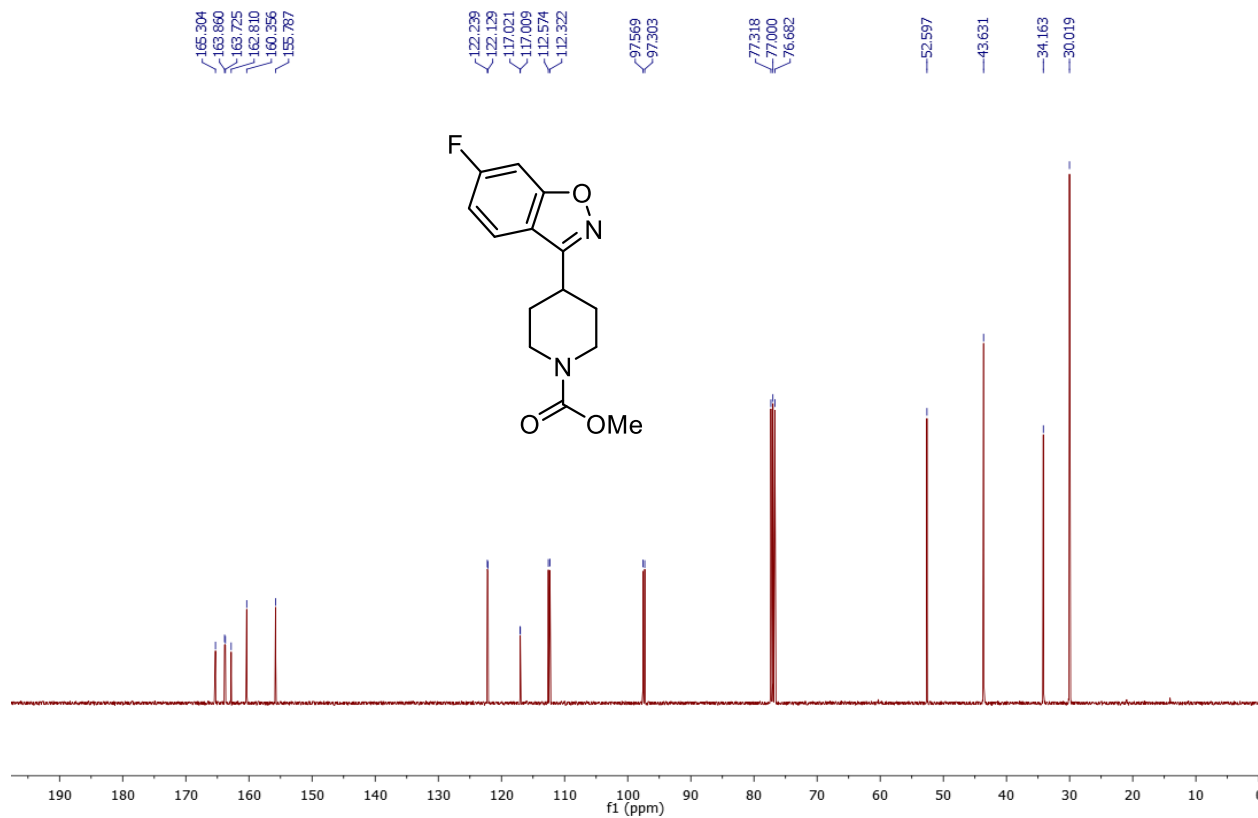
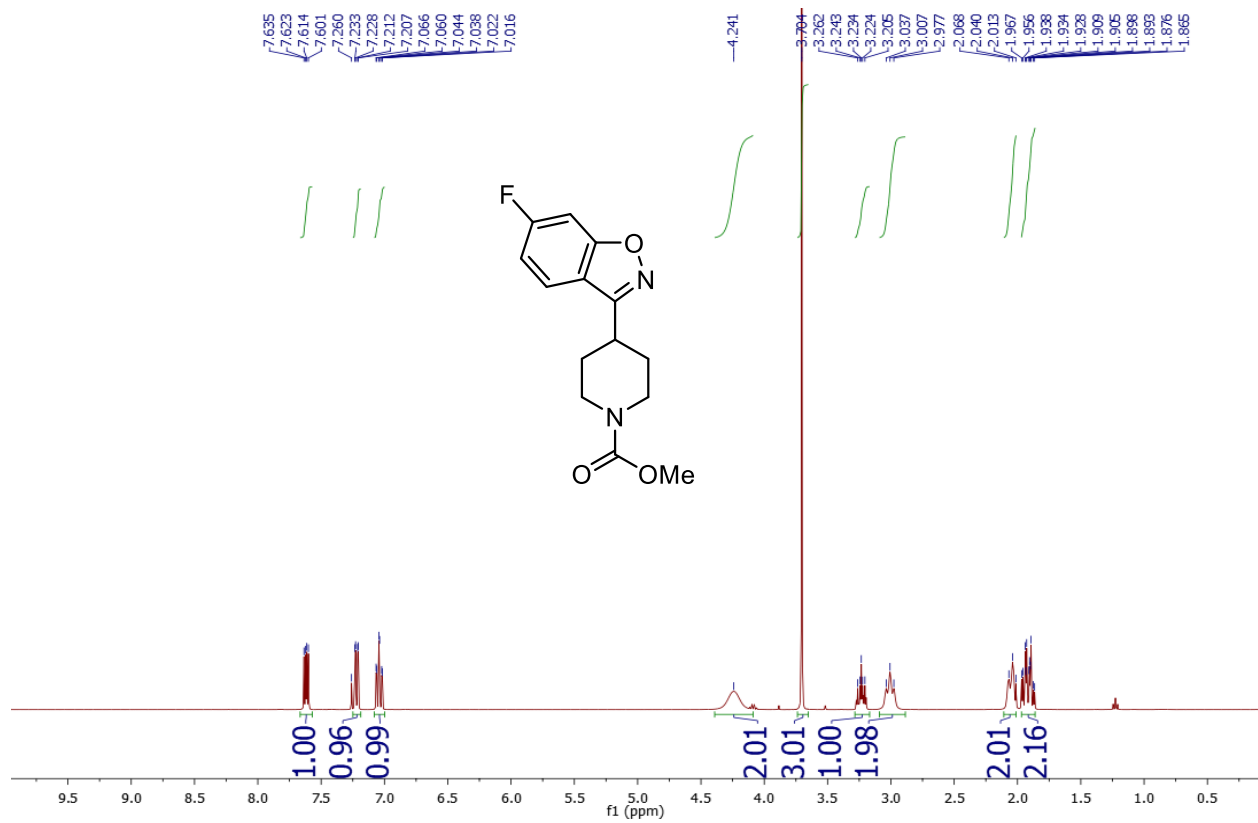
# 11.NMR Spectrum

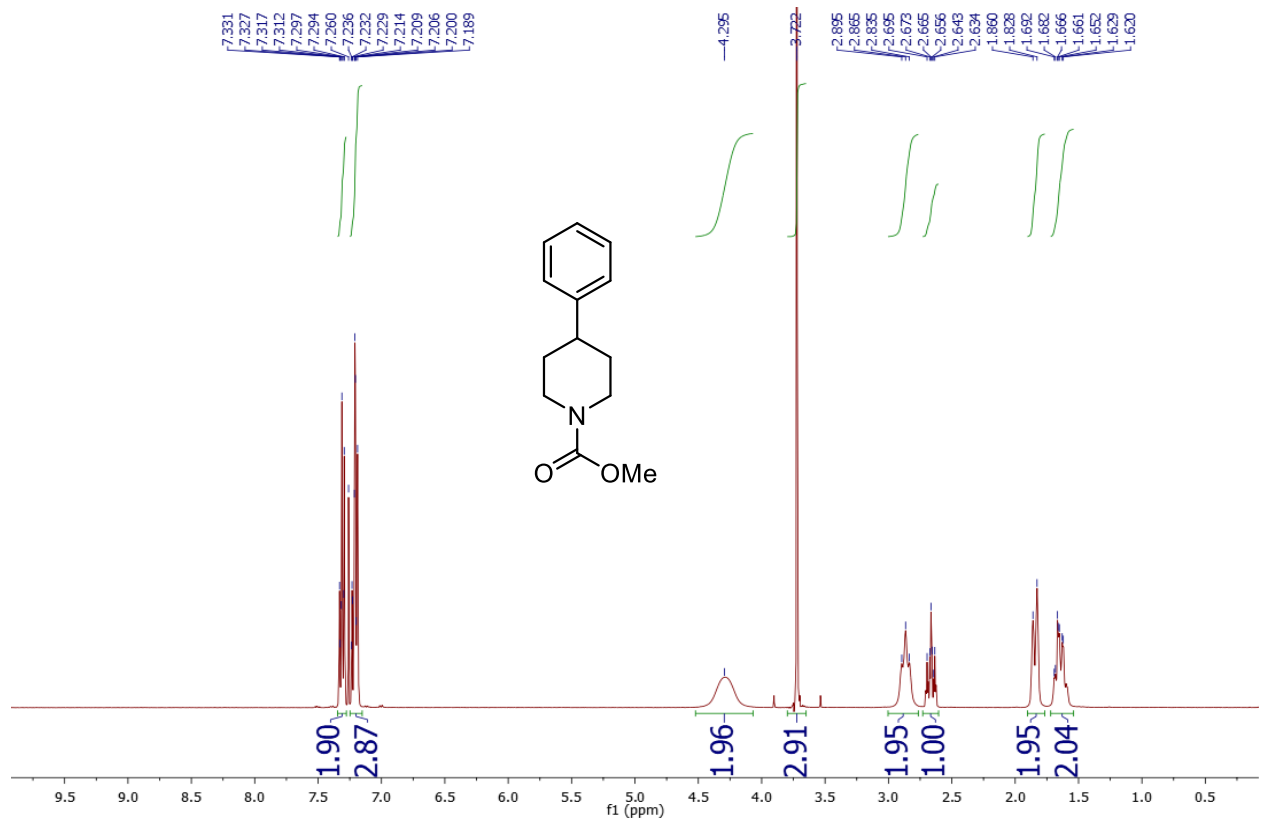
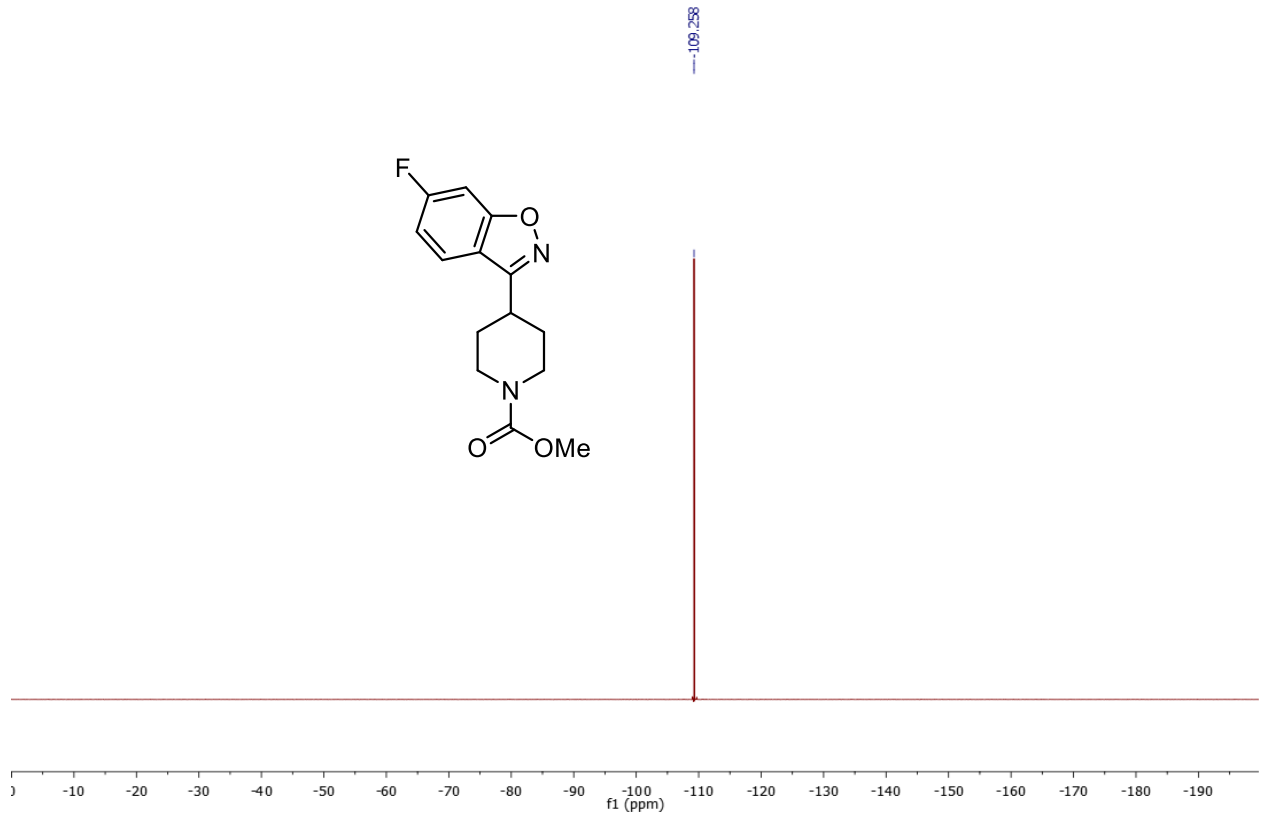


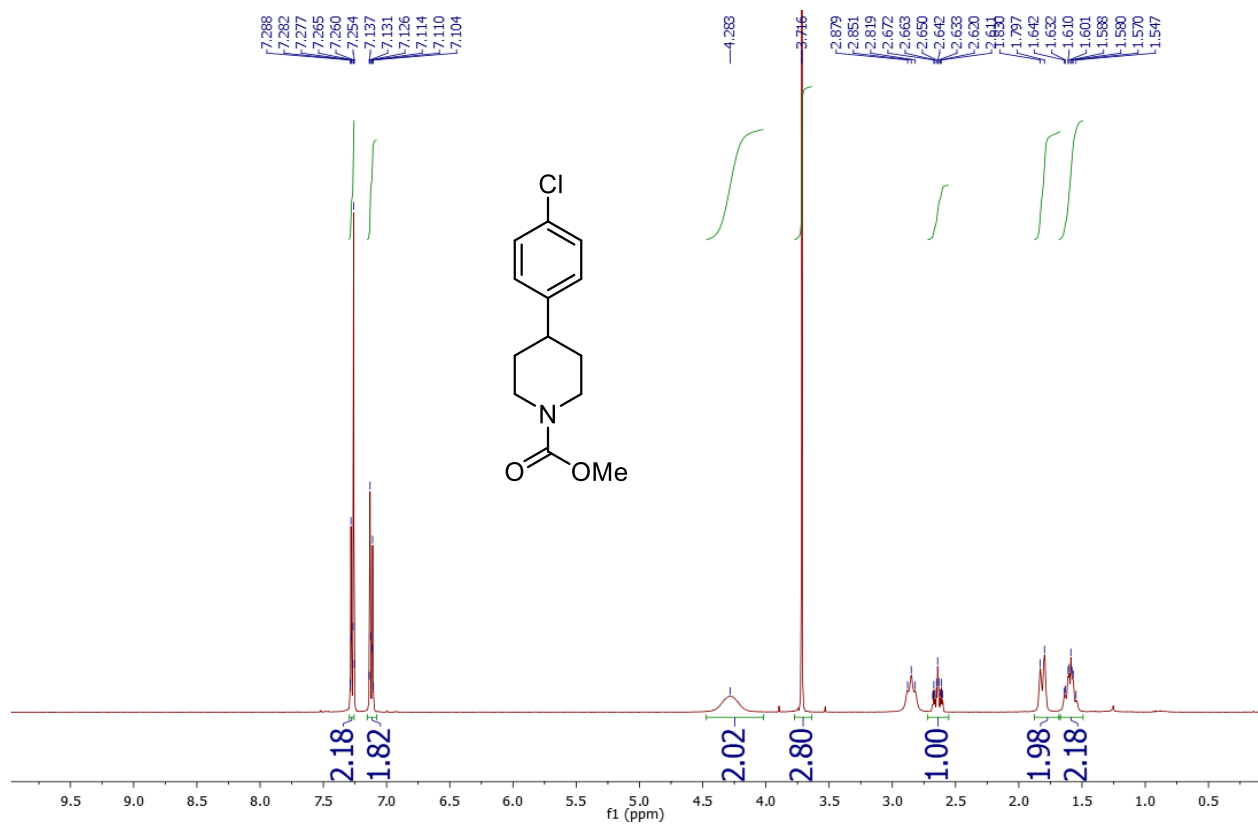
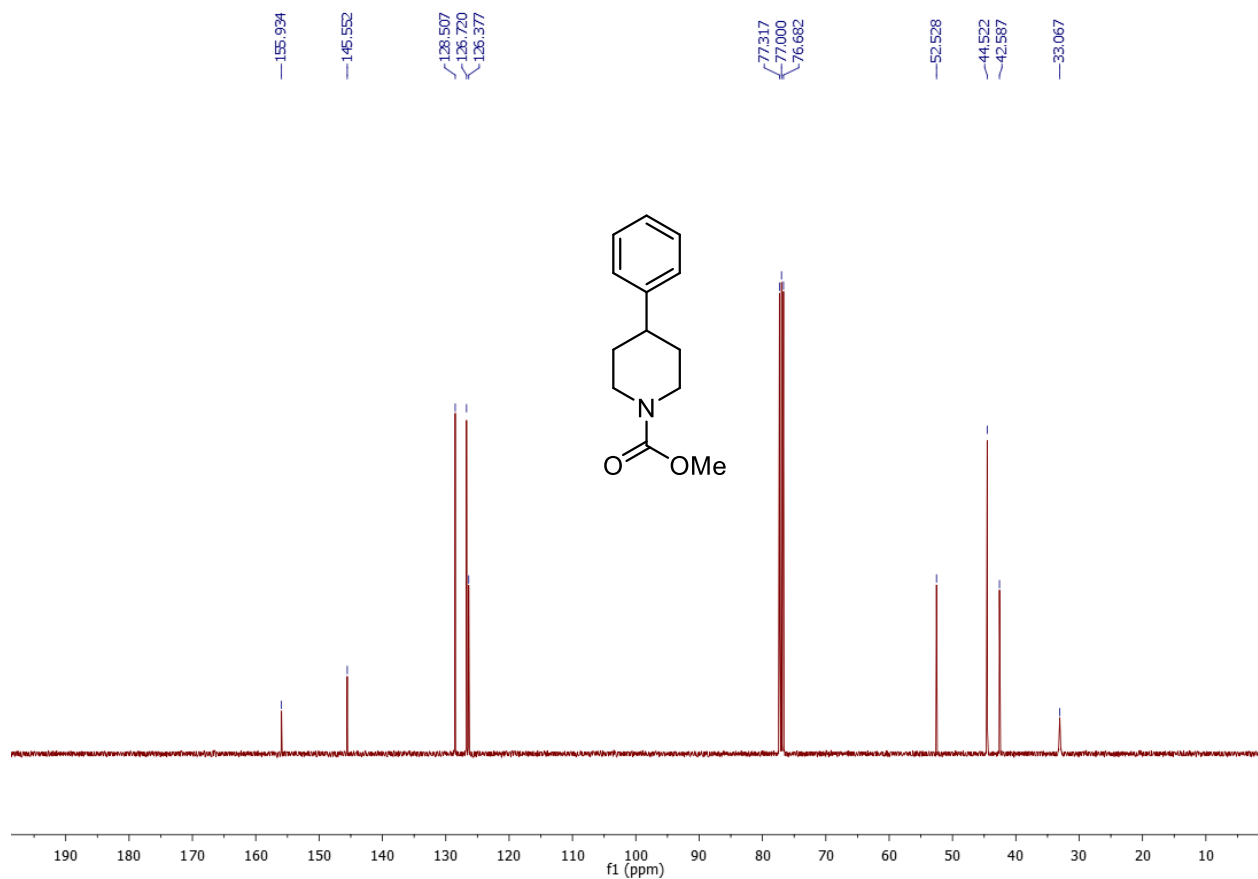


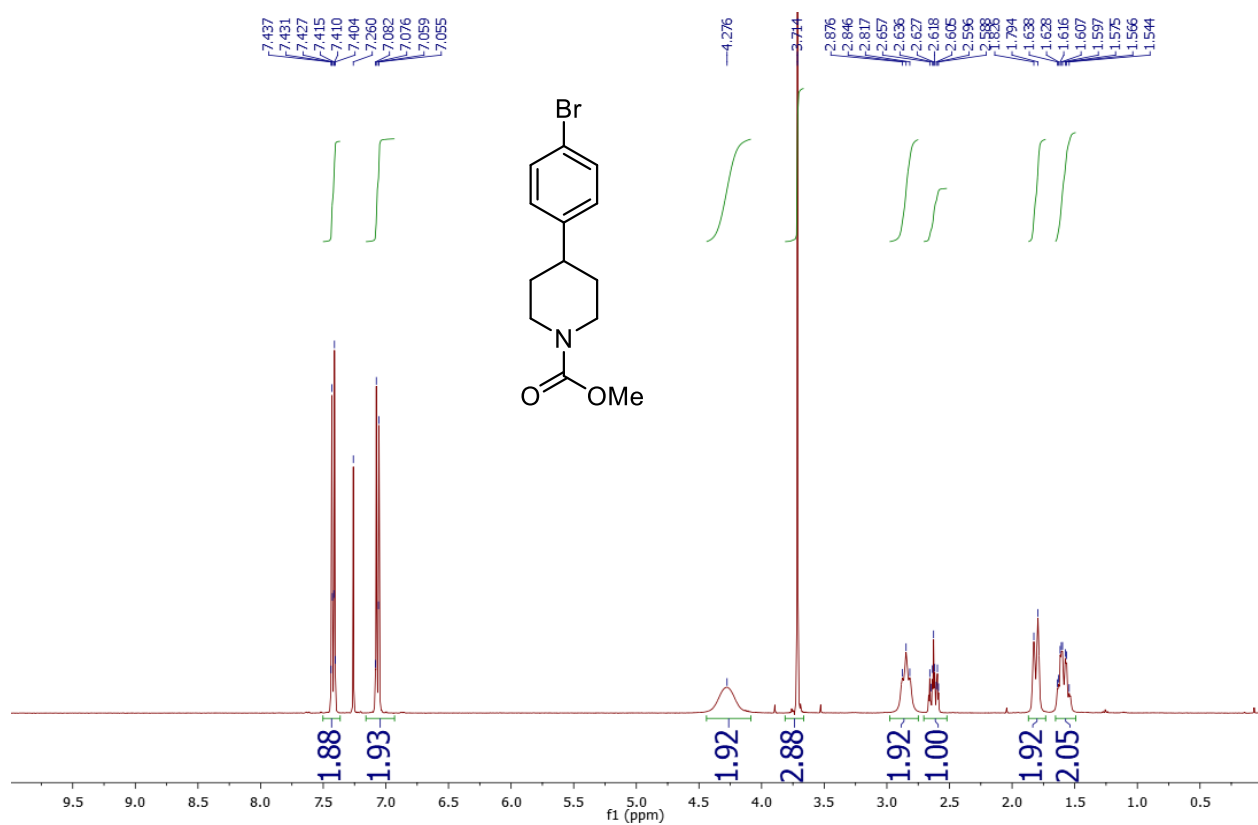
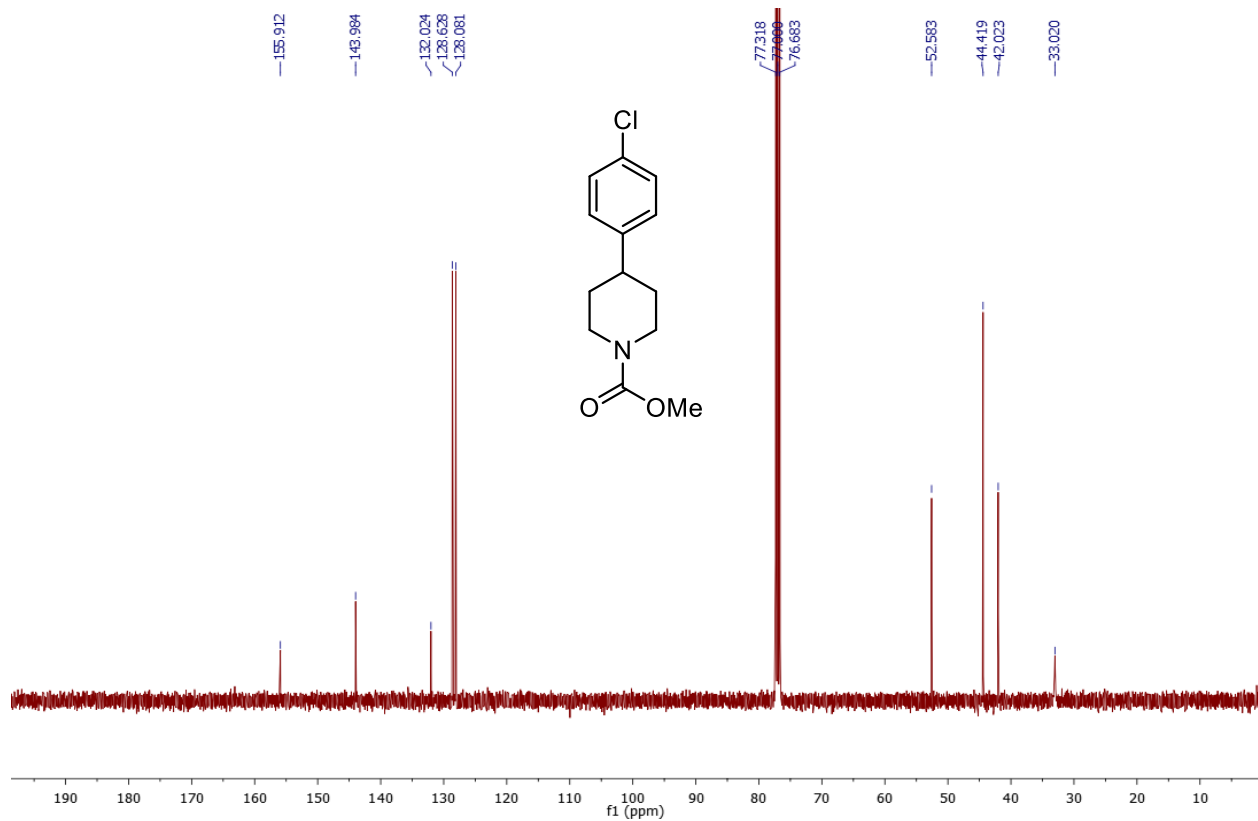


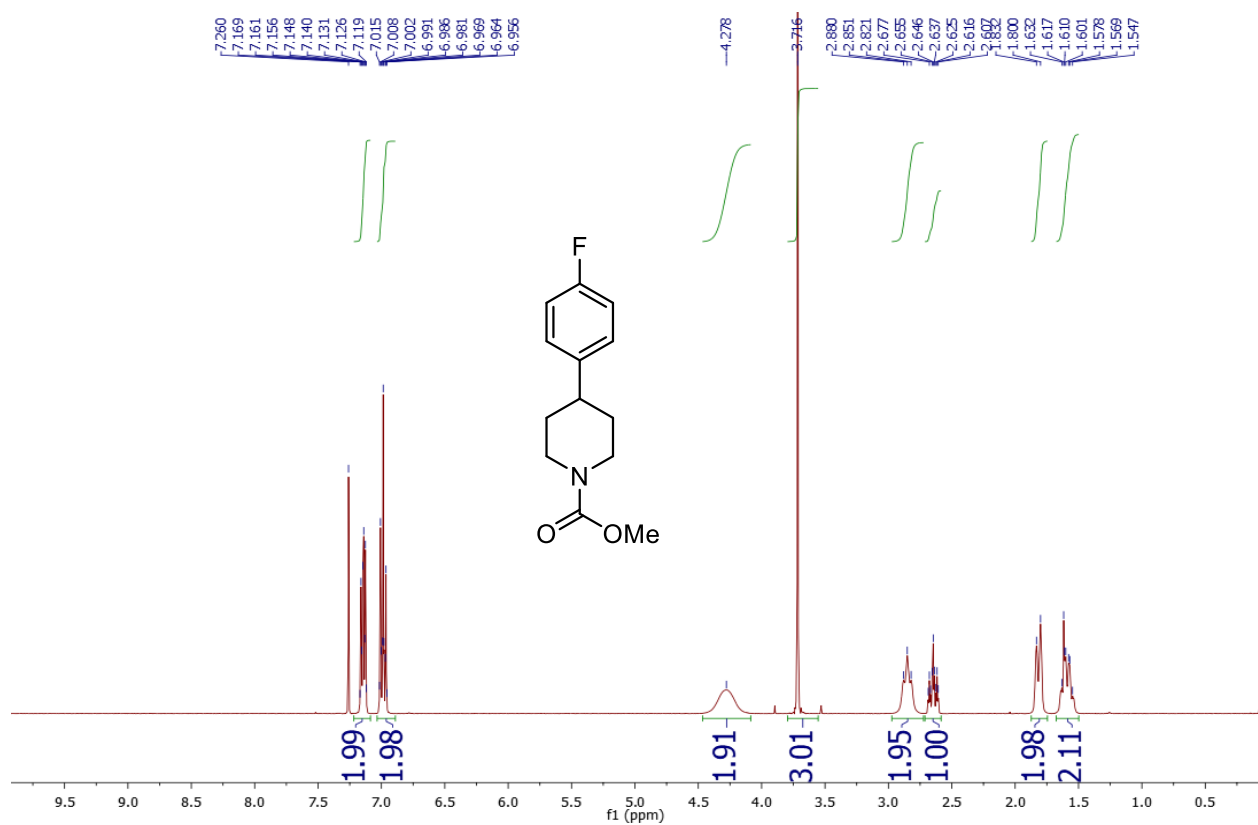
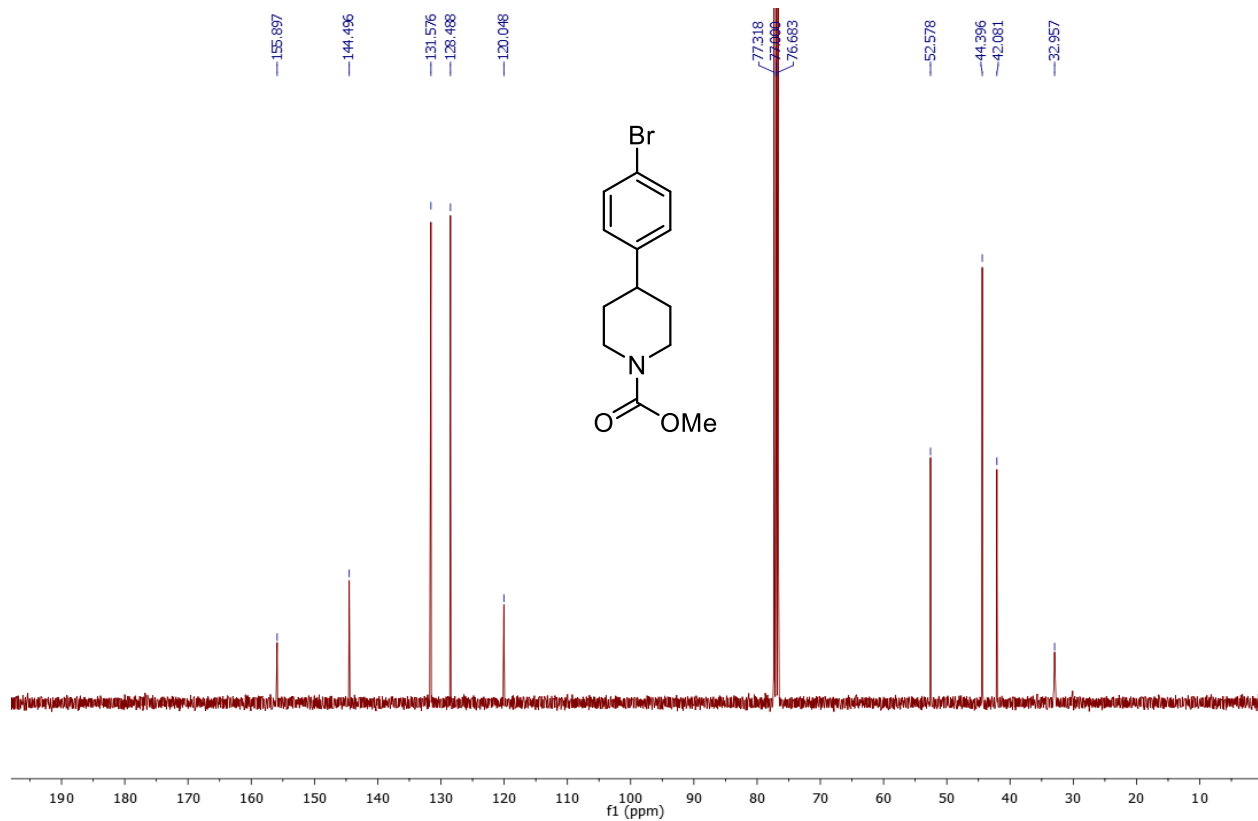


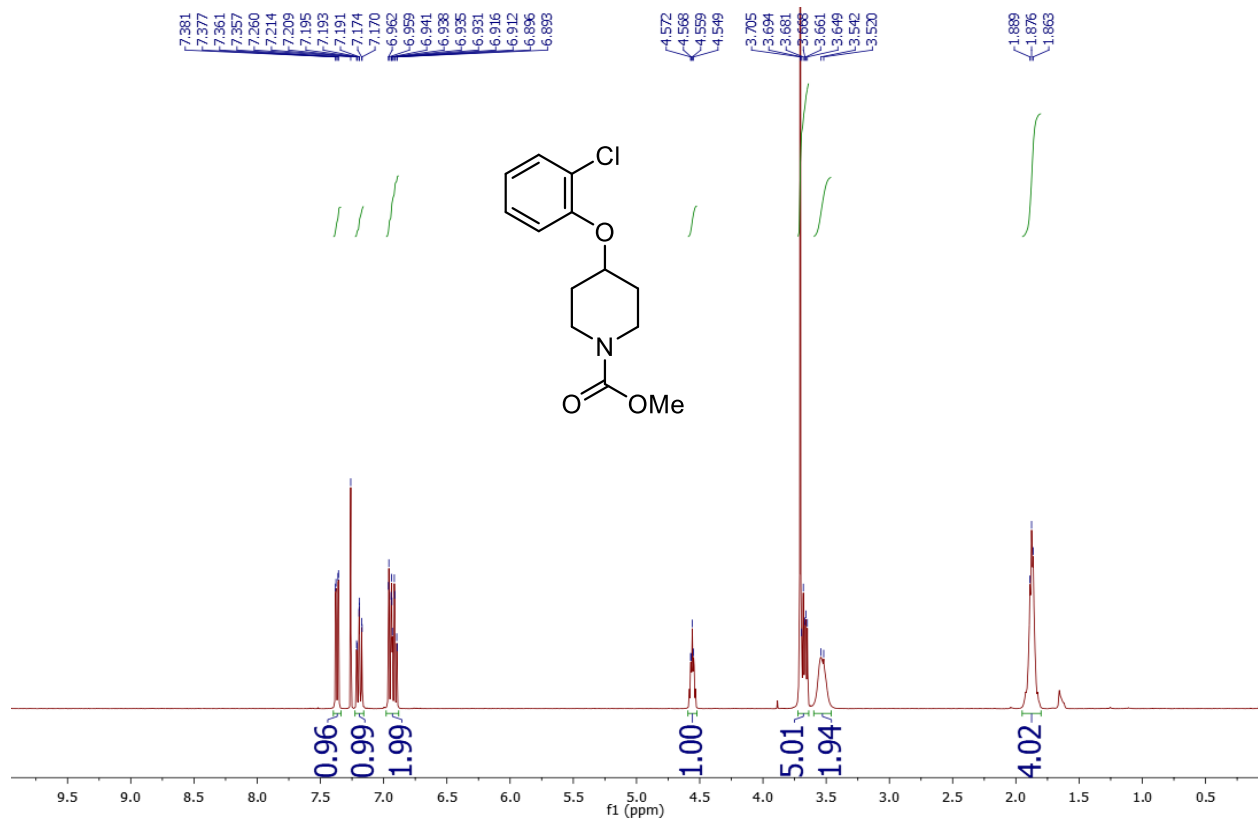
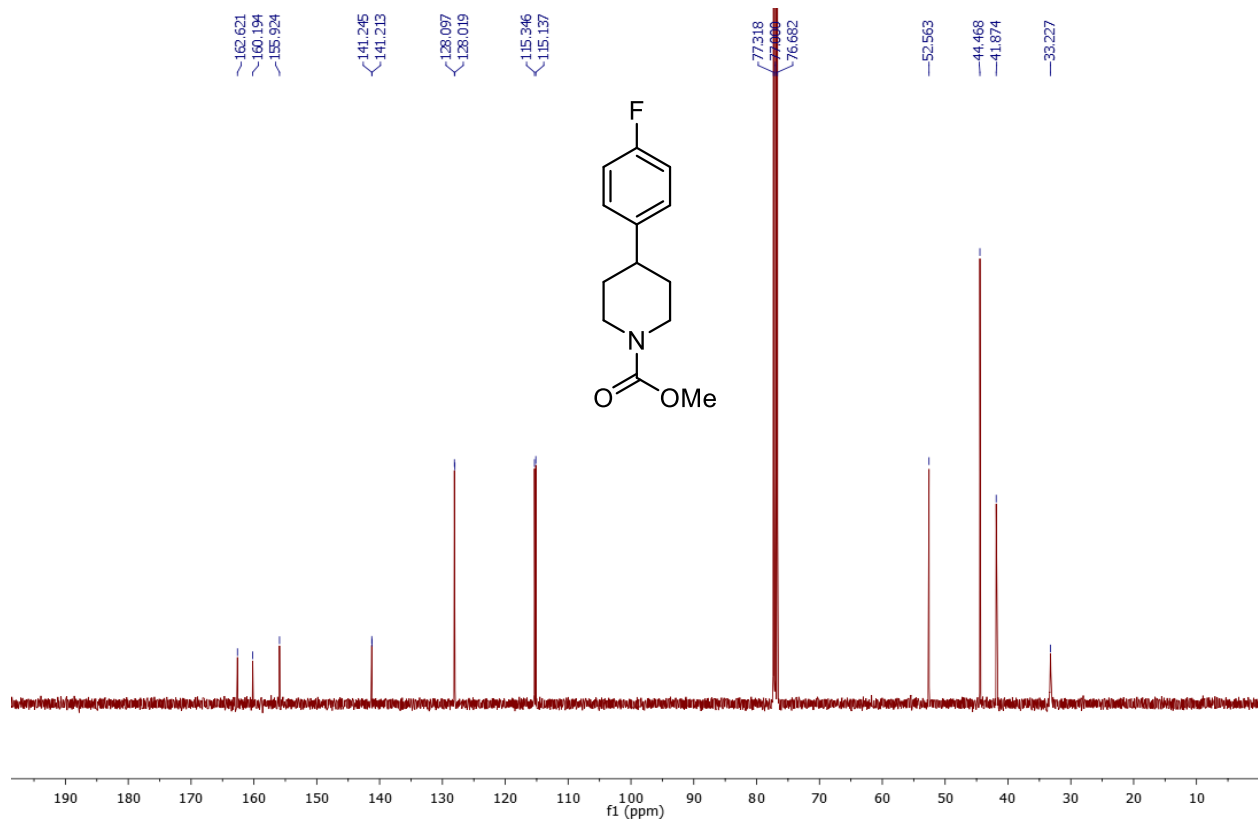


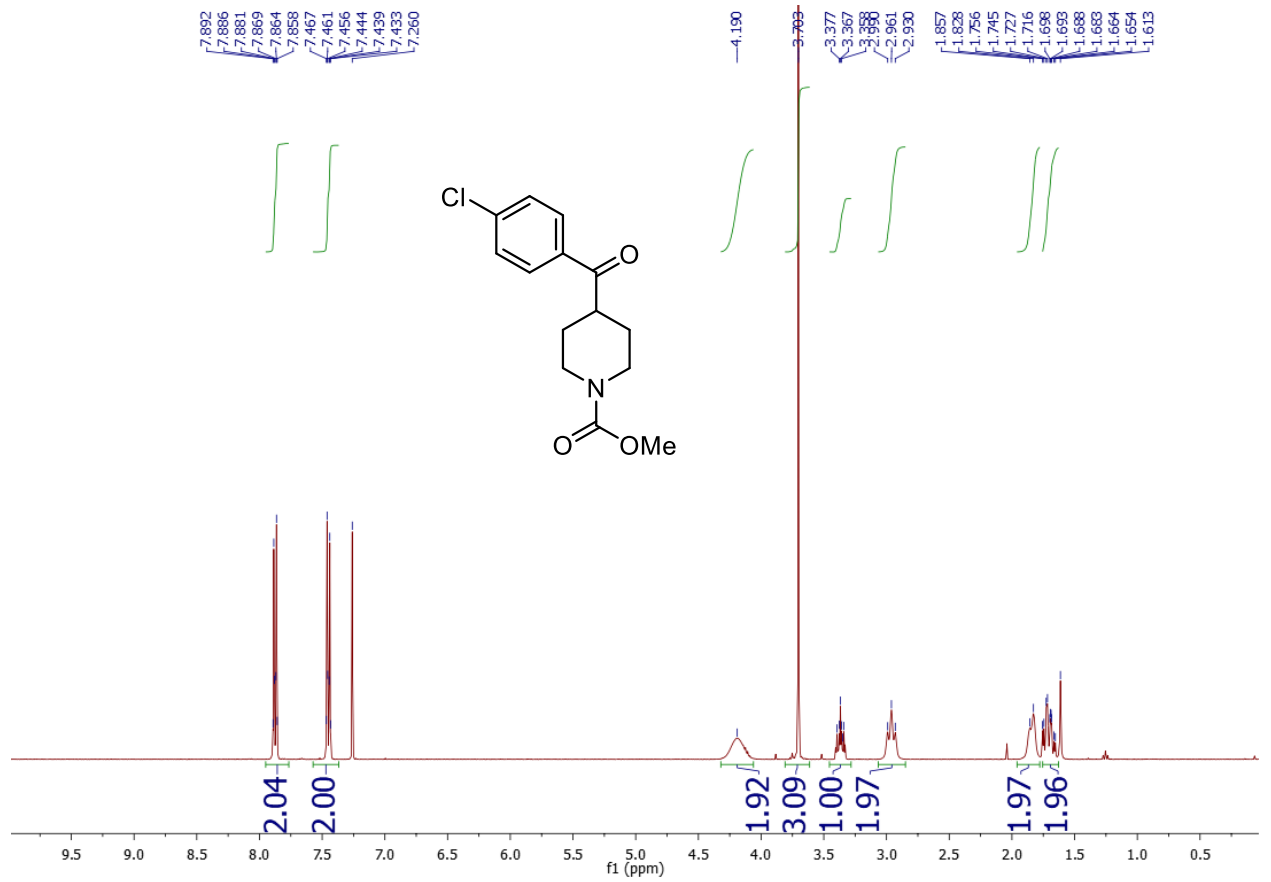
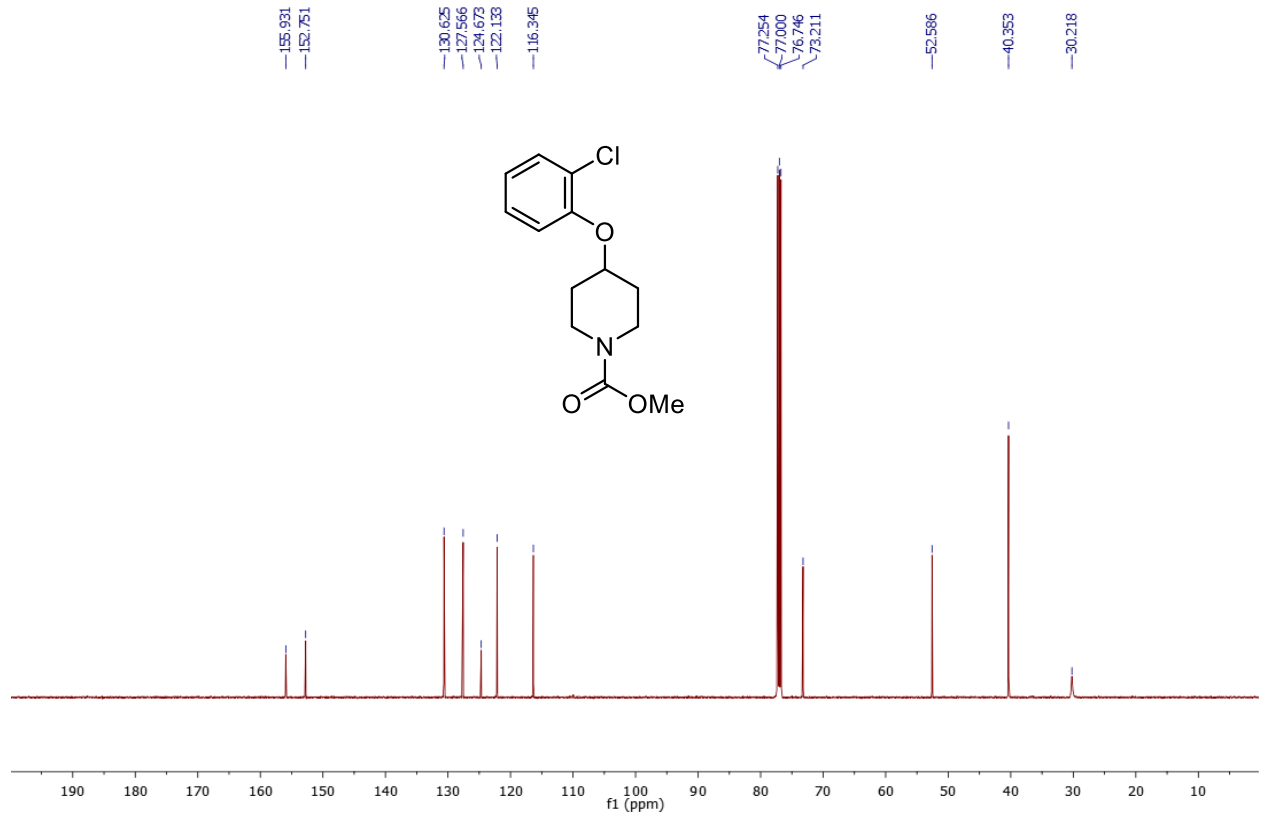


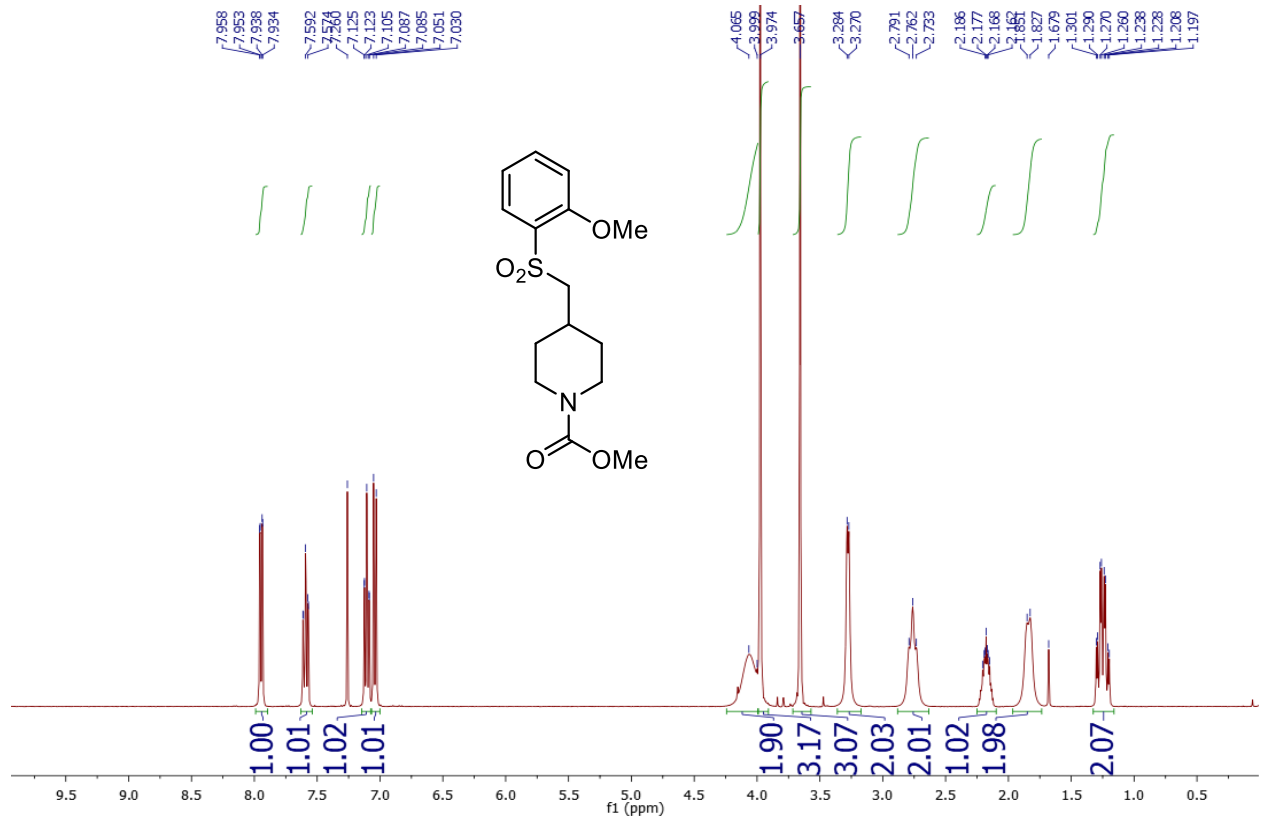
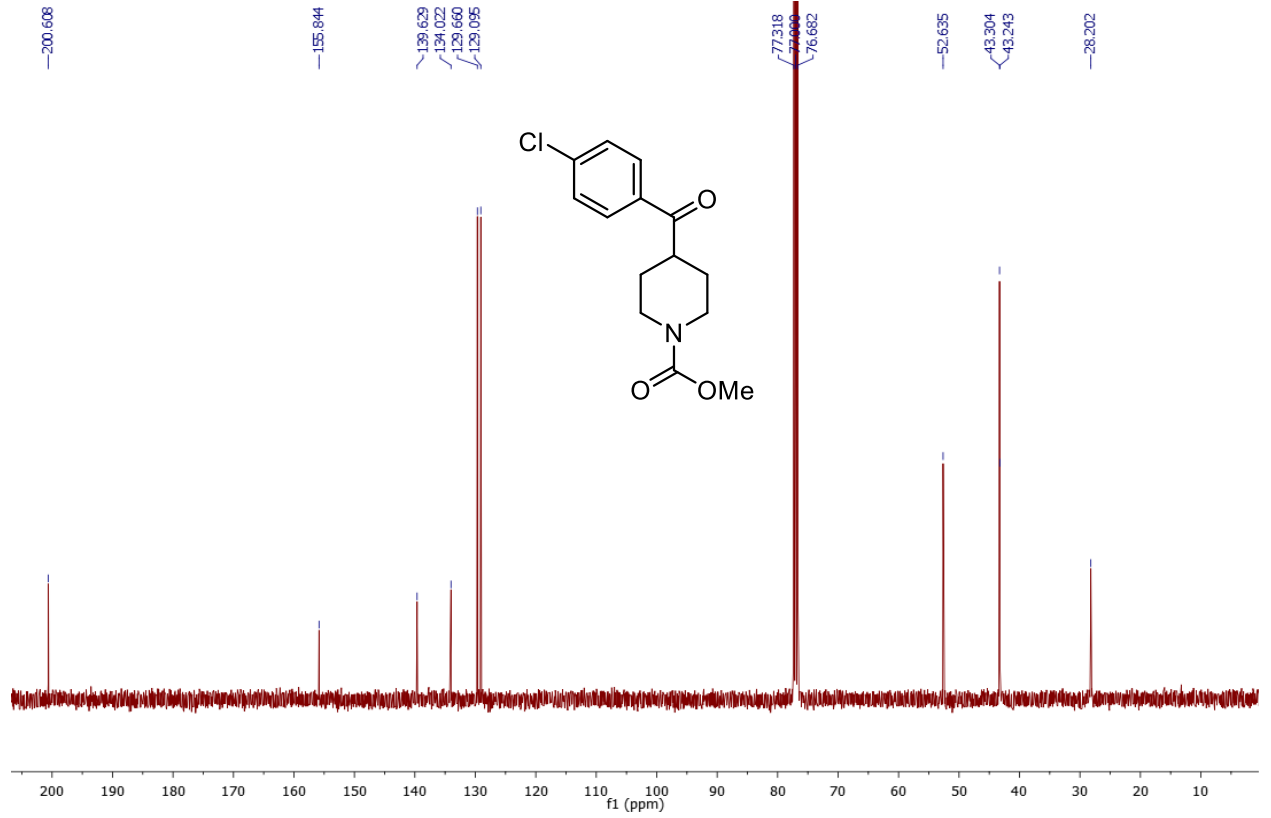




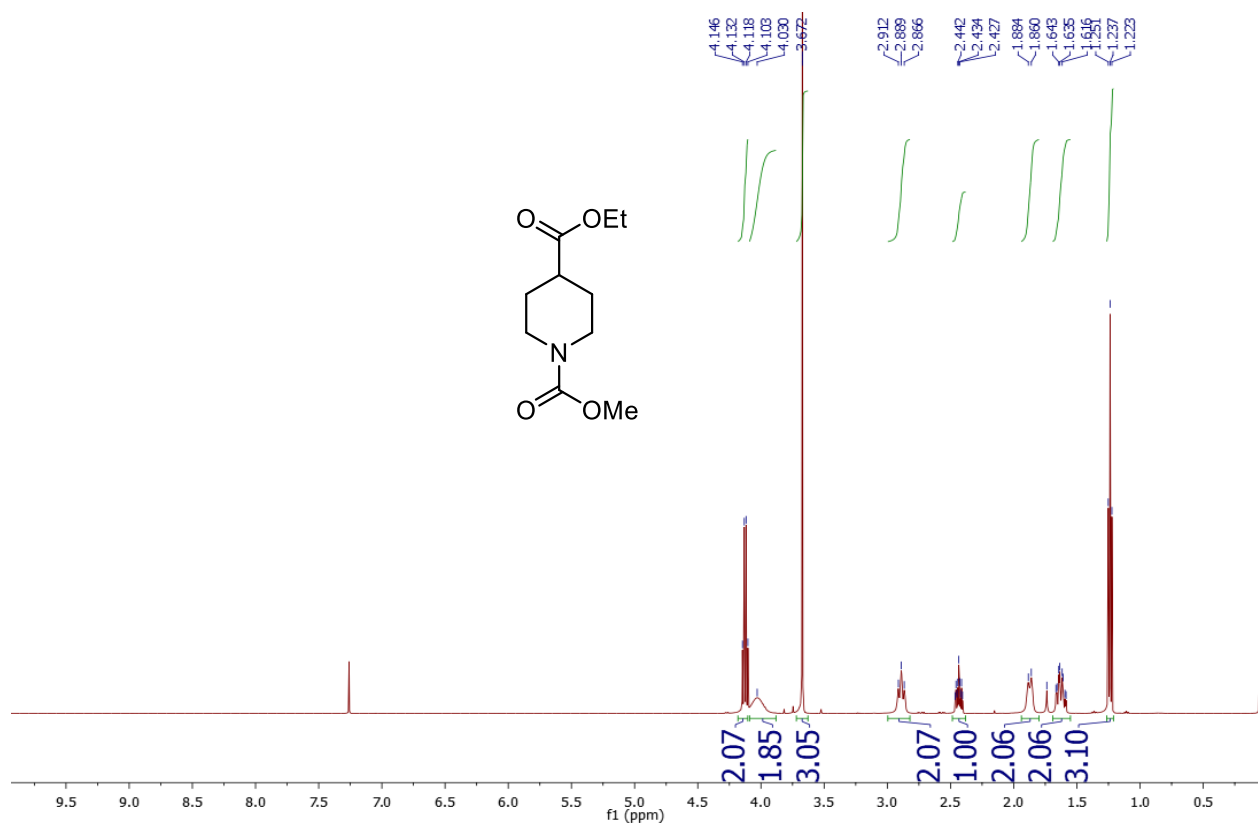
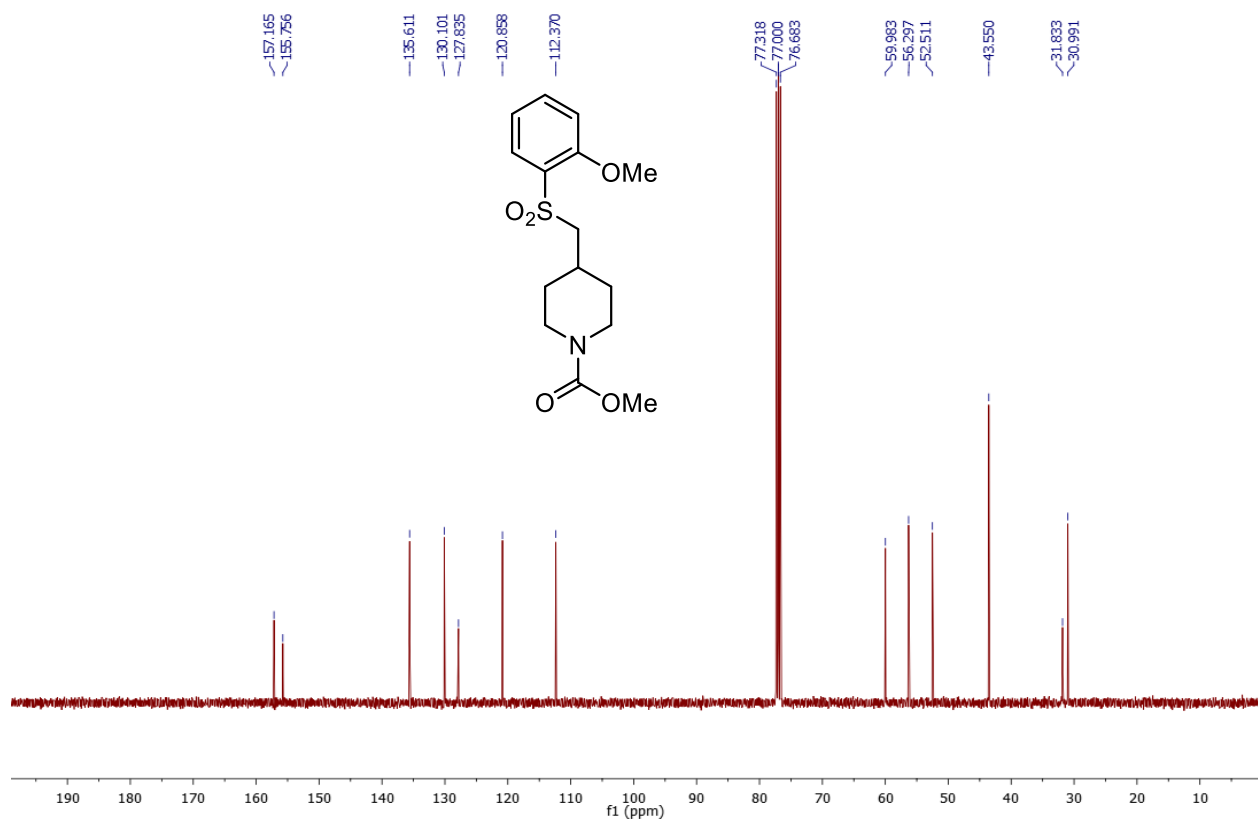


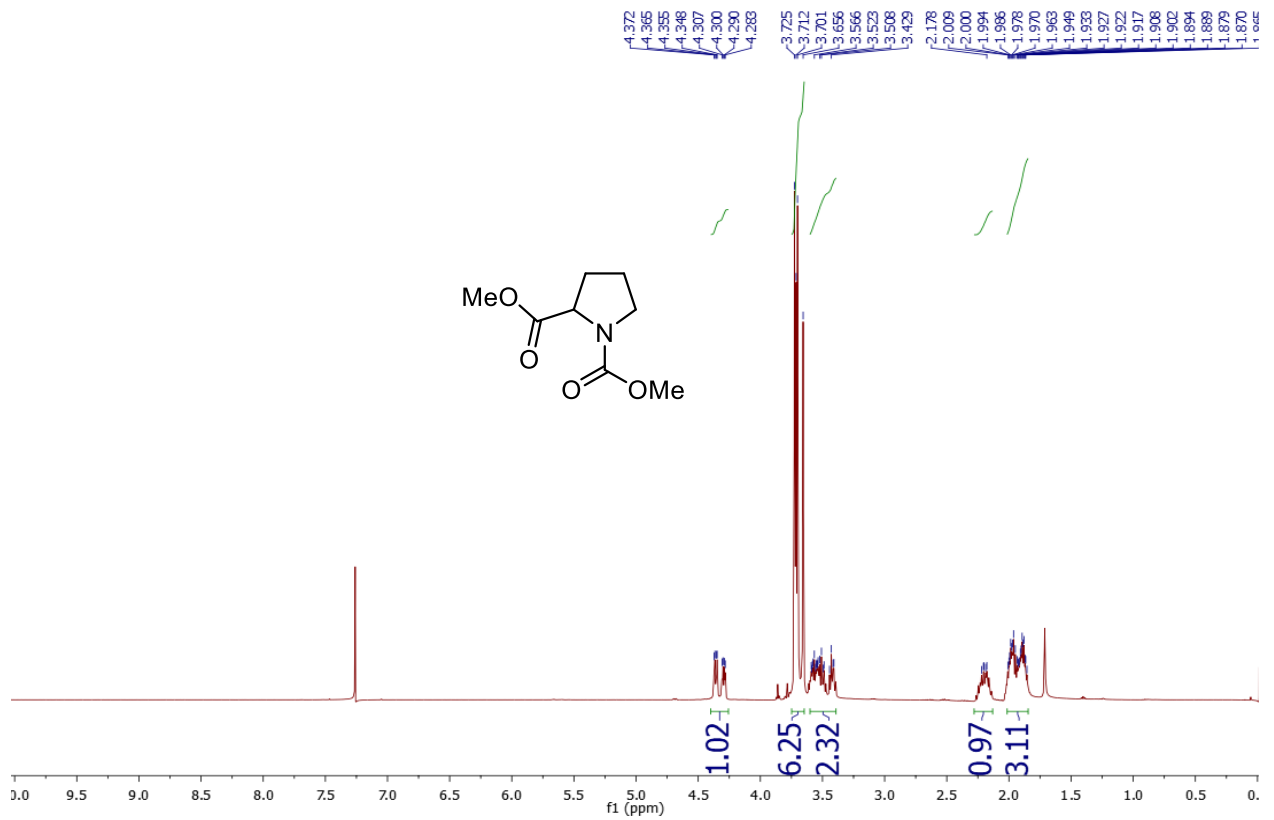
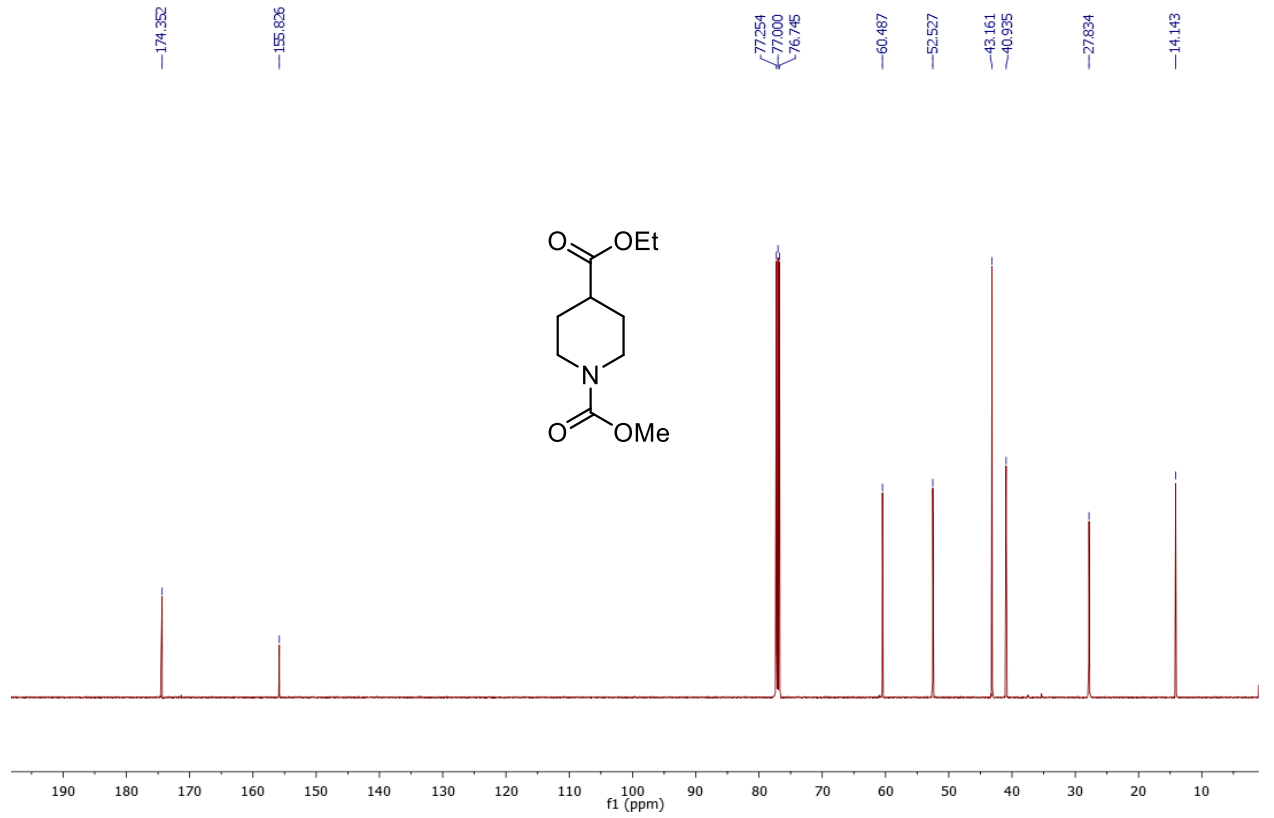


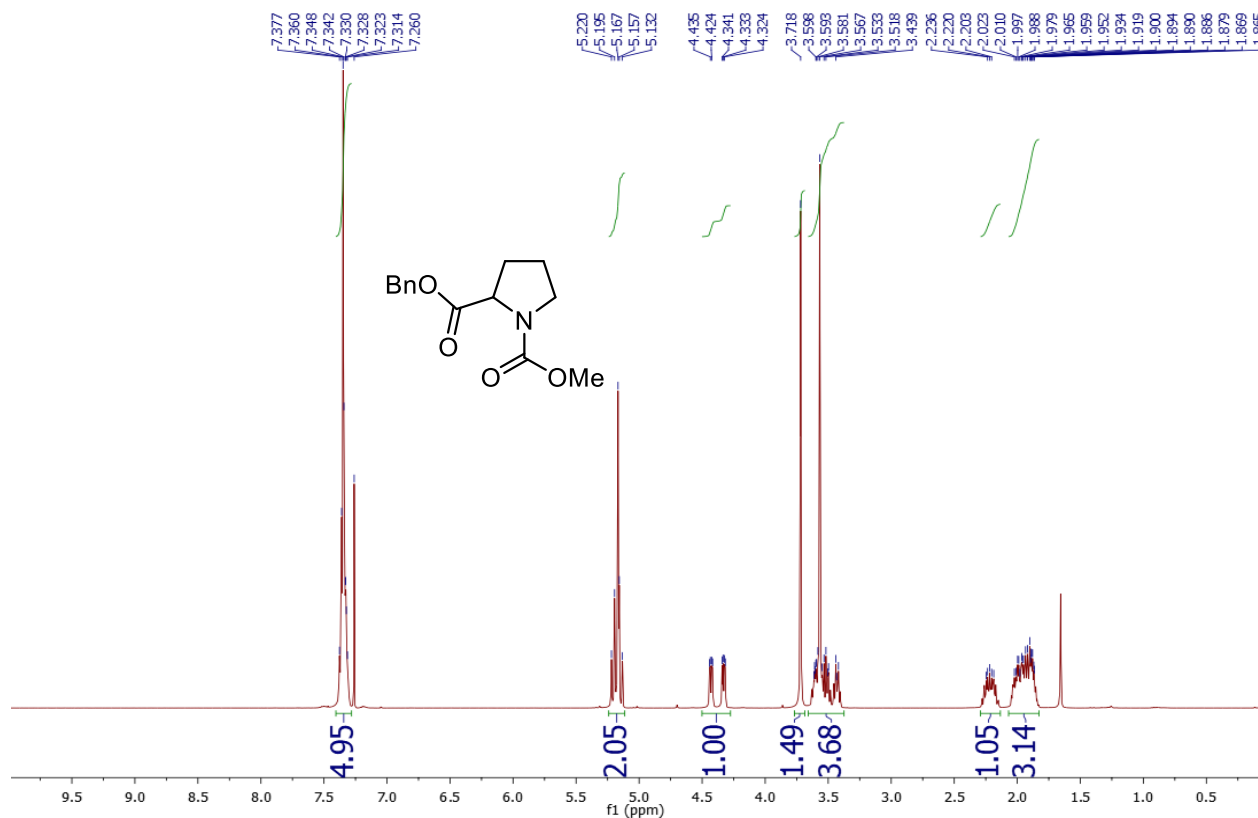
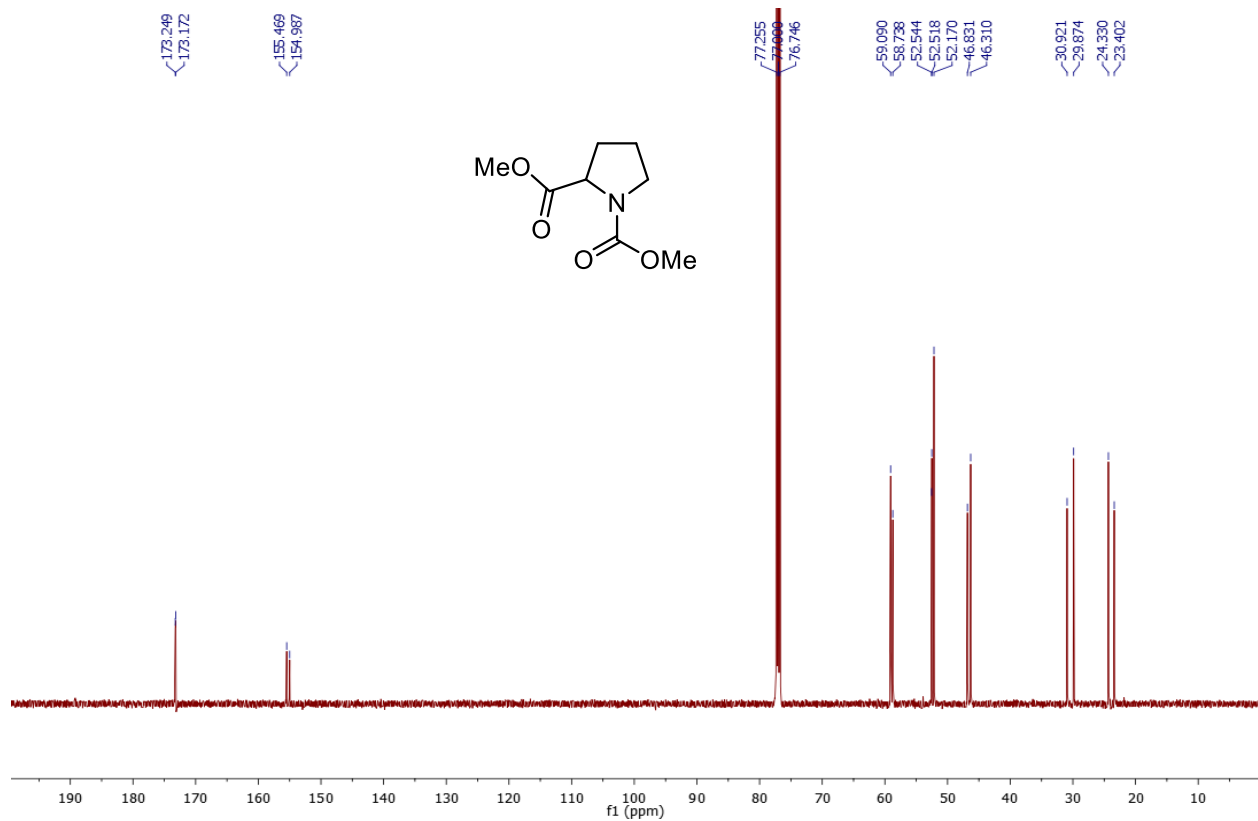


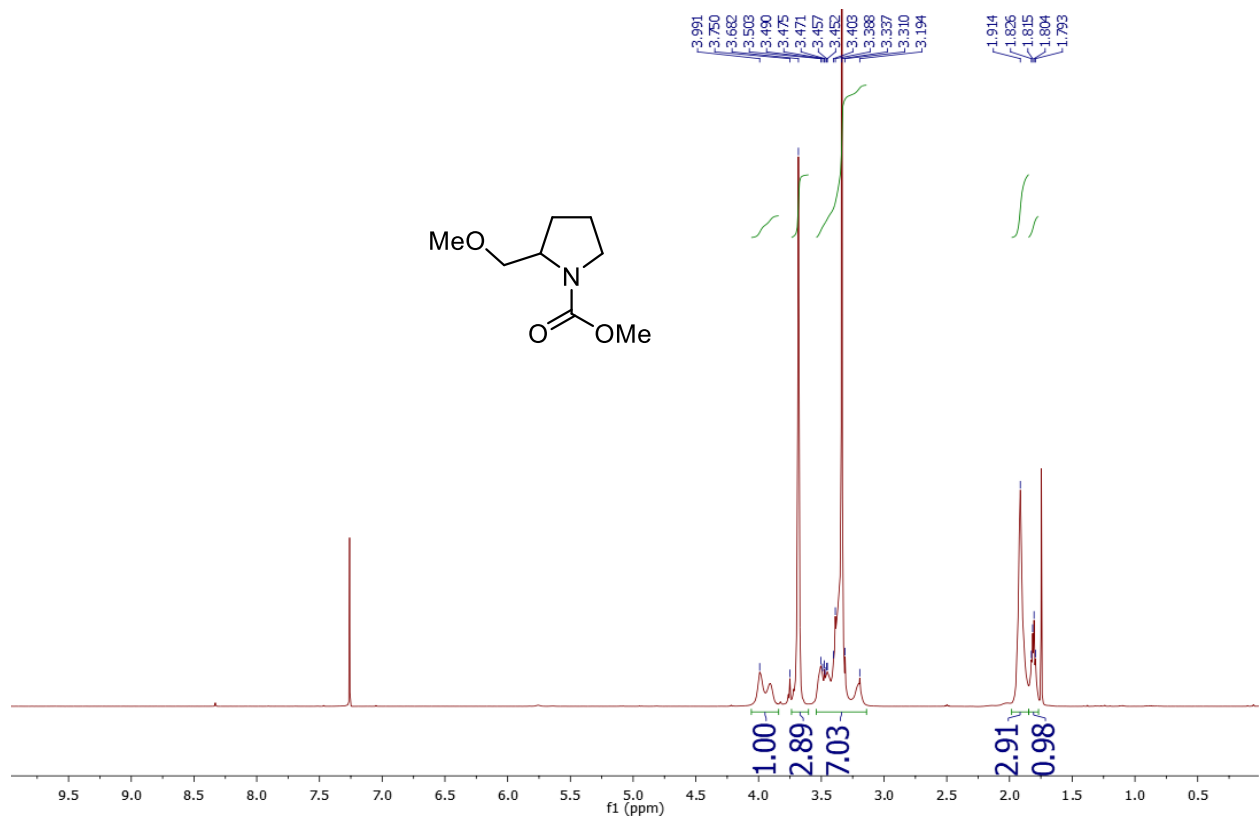
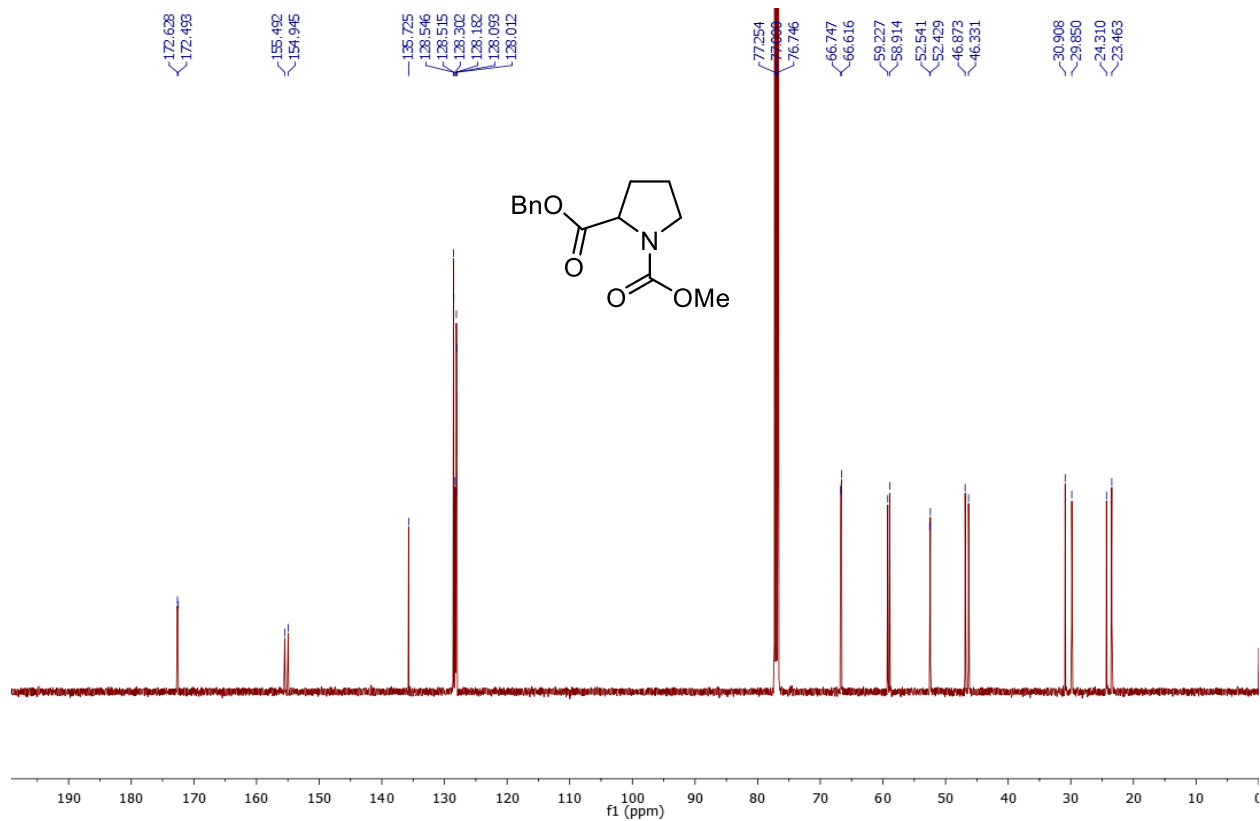


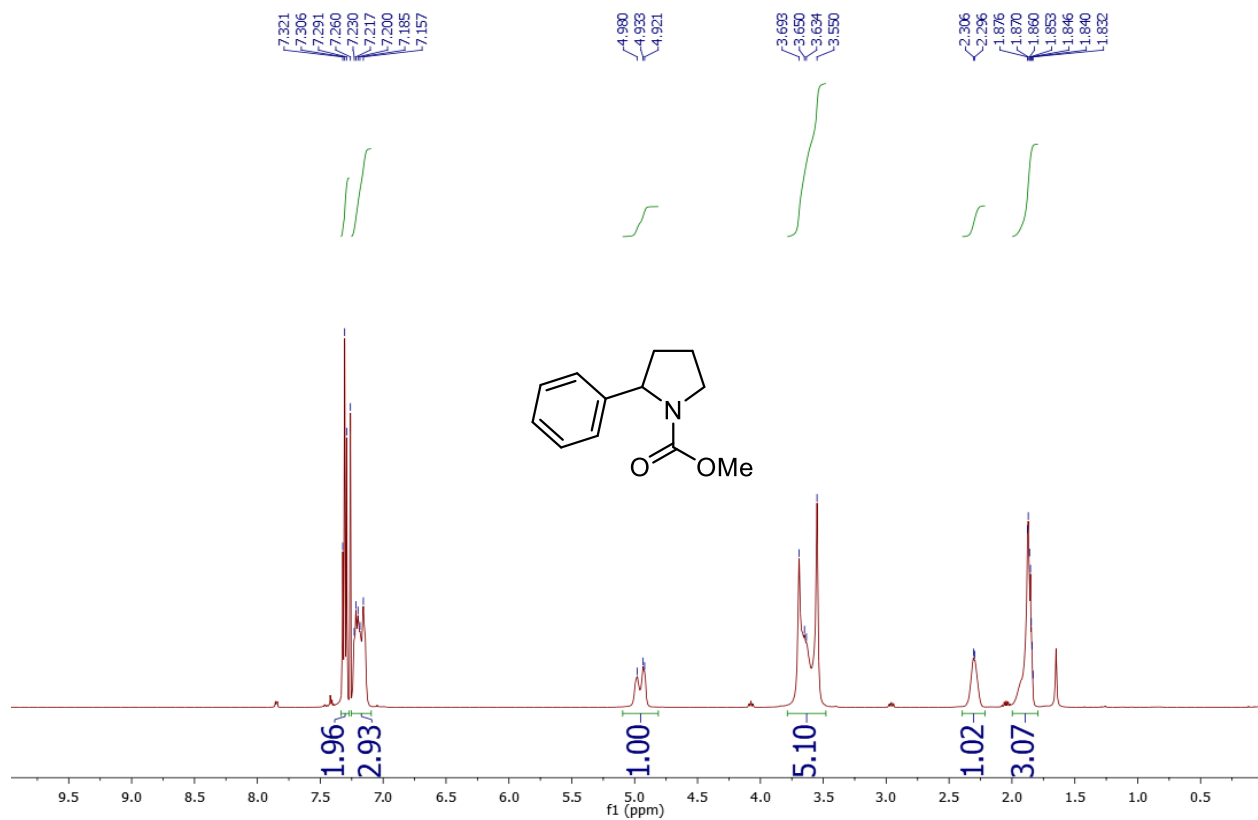
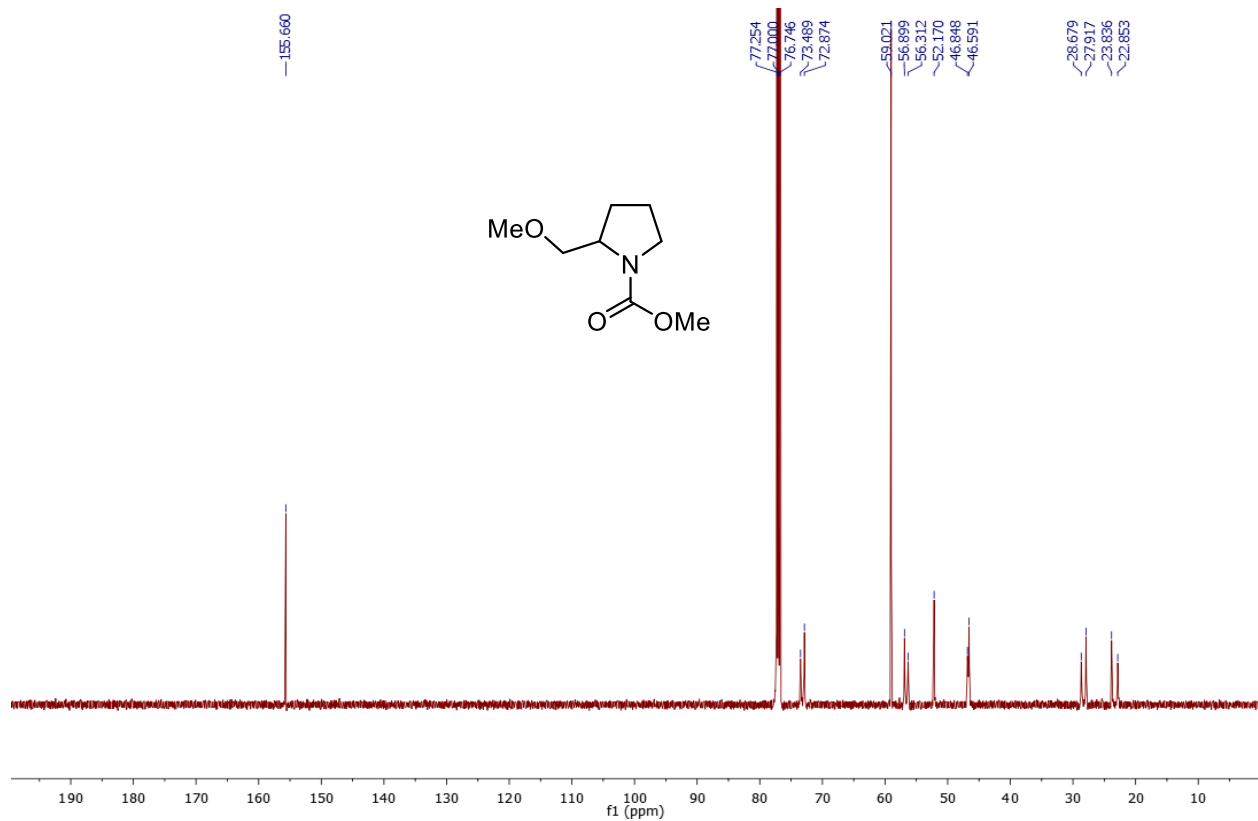


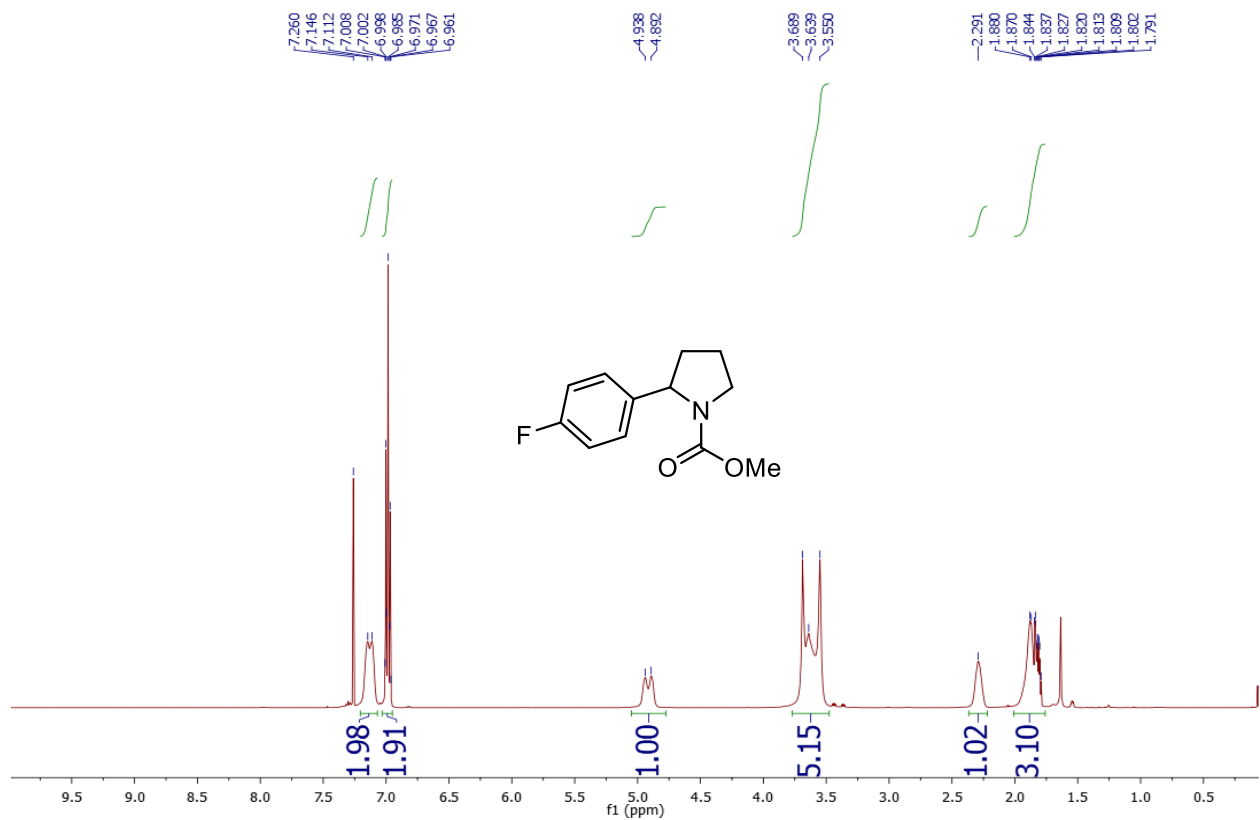
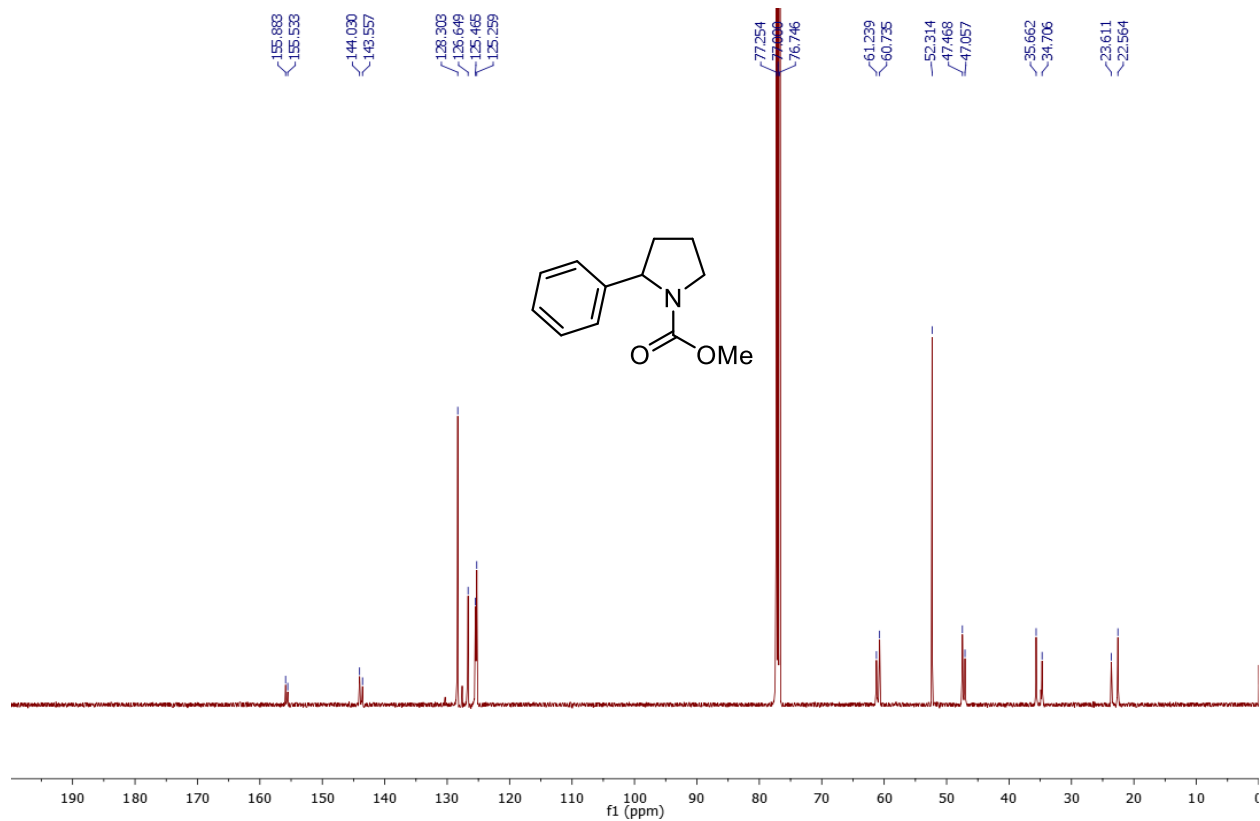


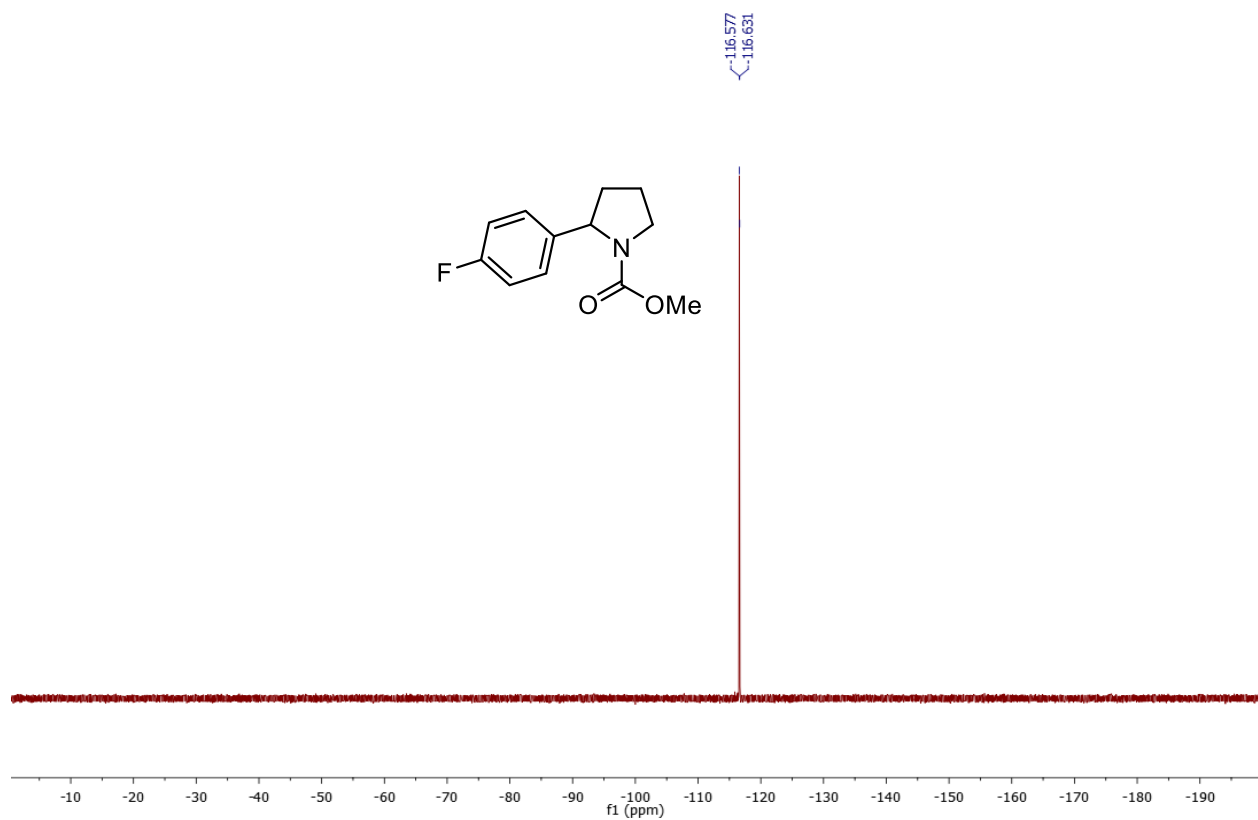
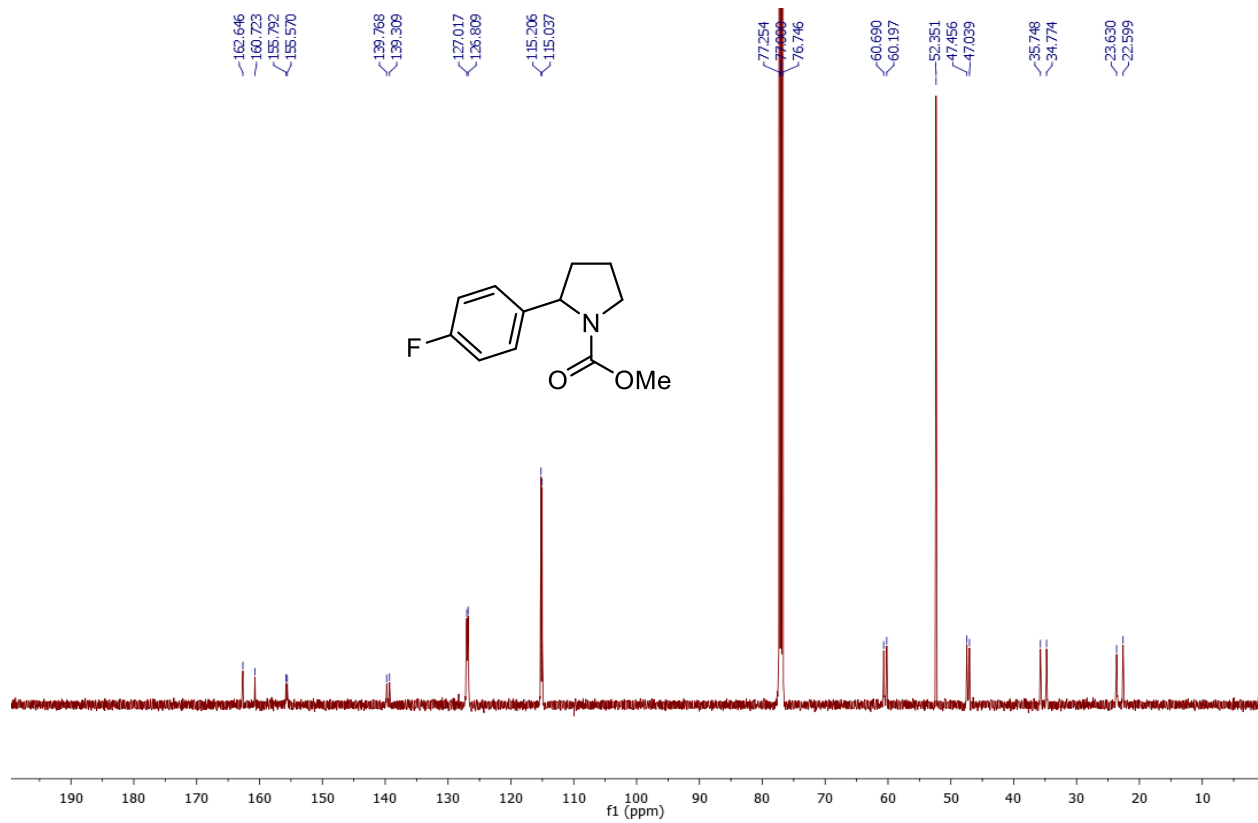


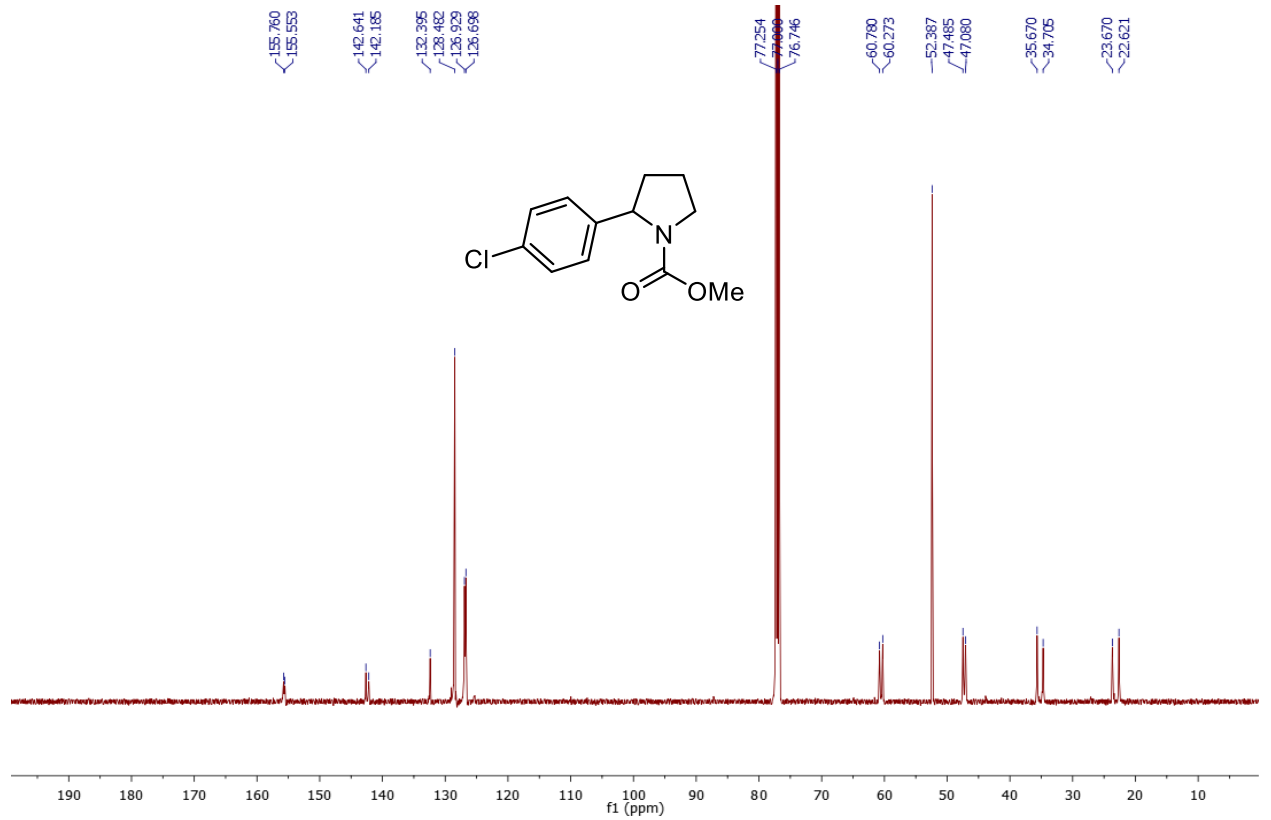
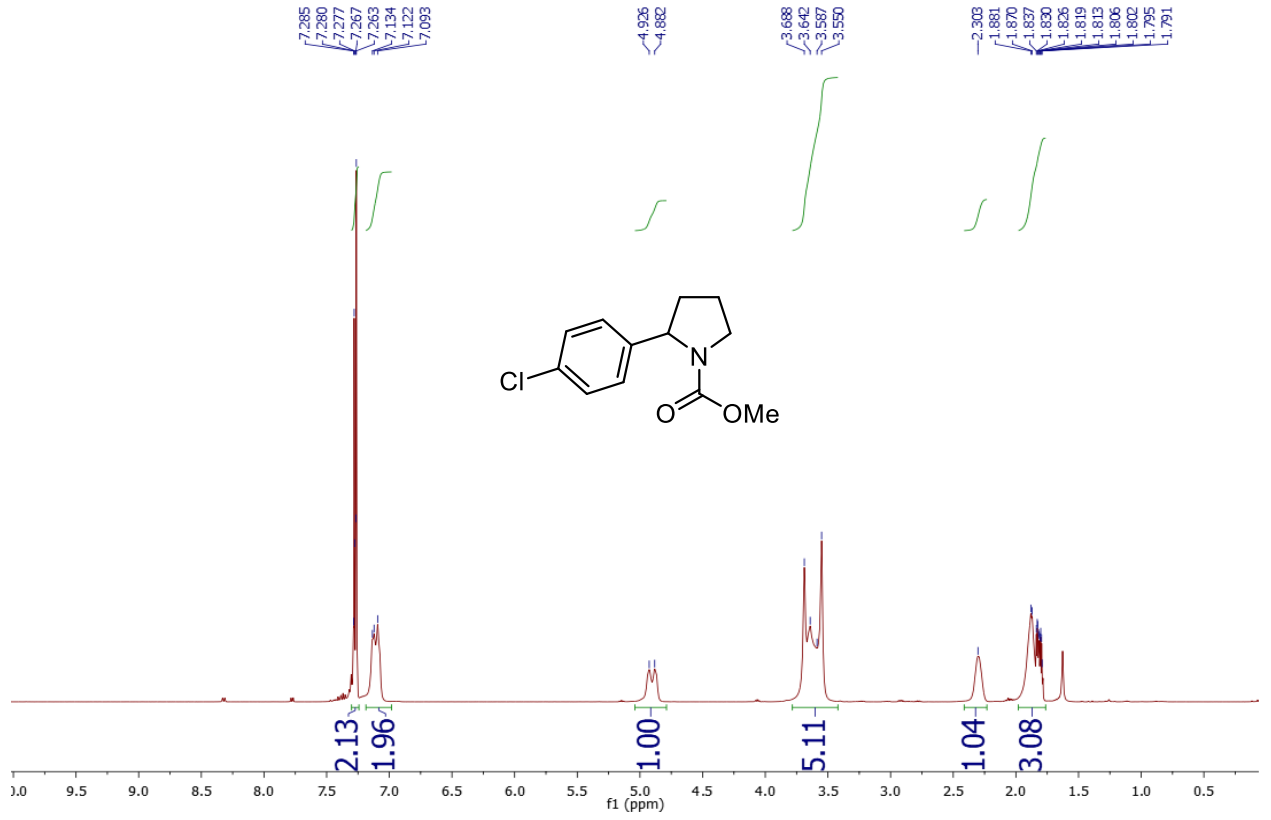




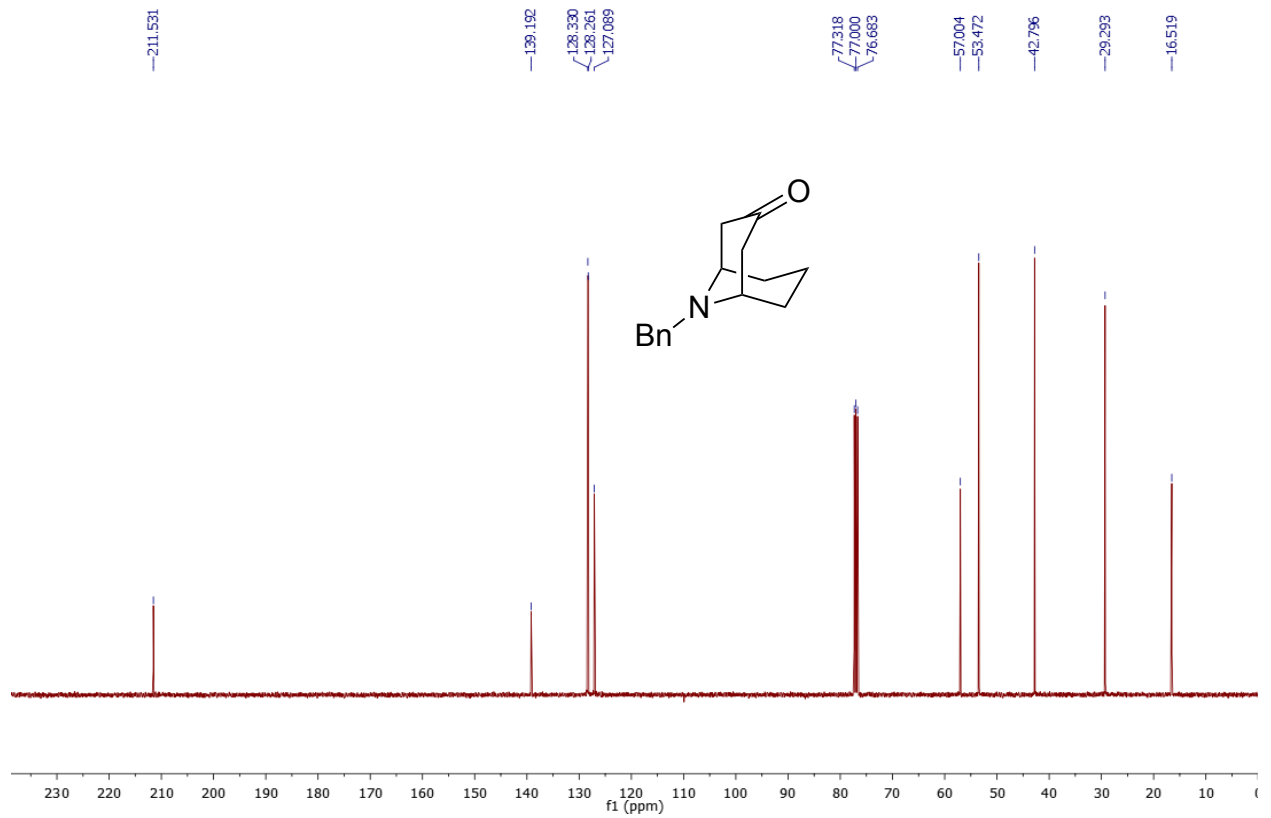
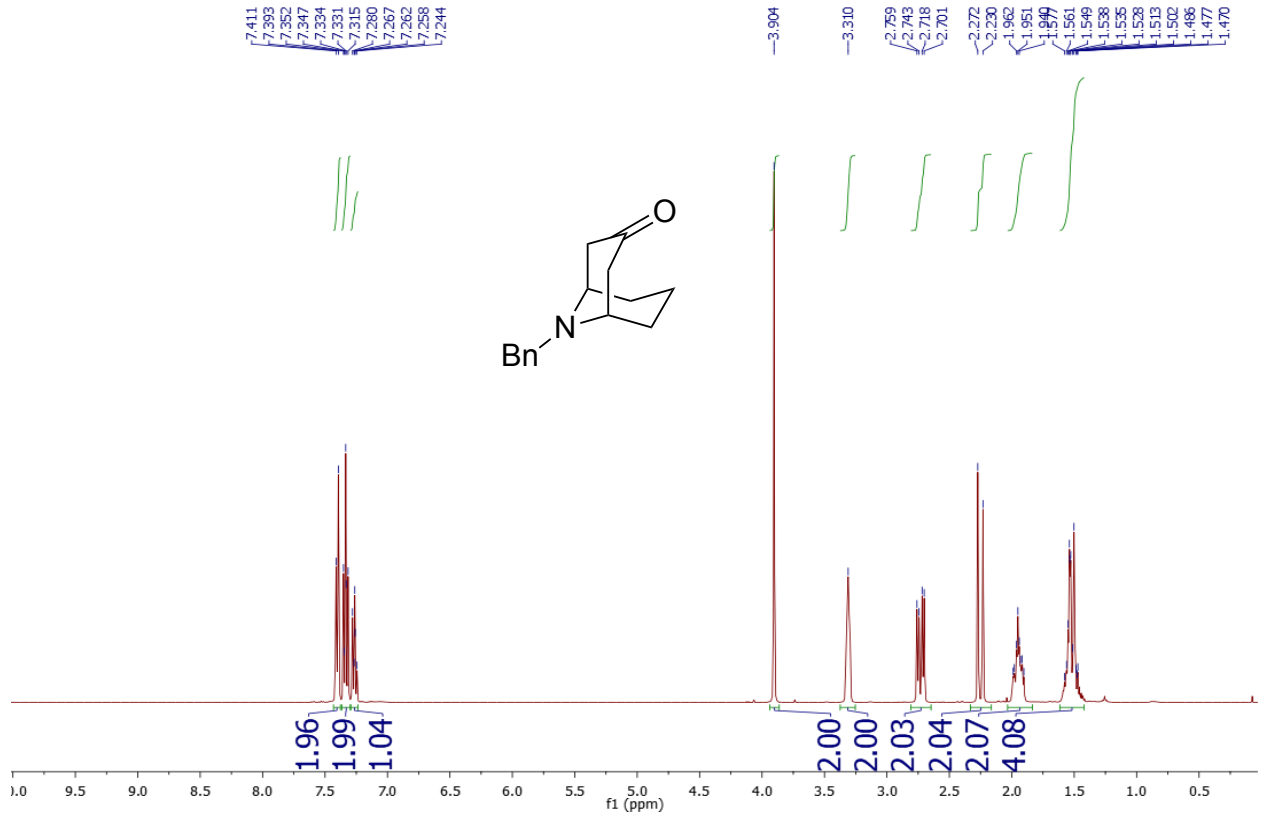


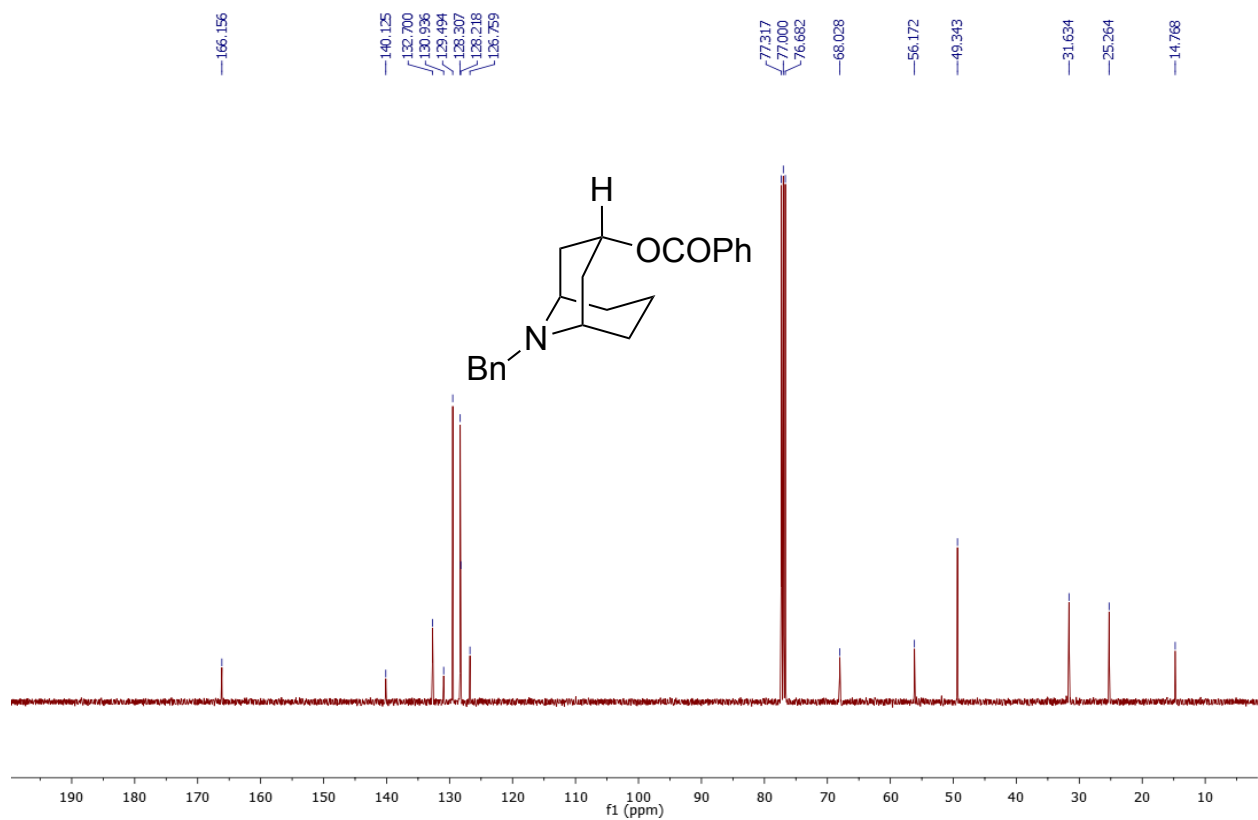
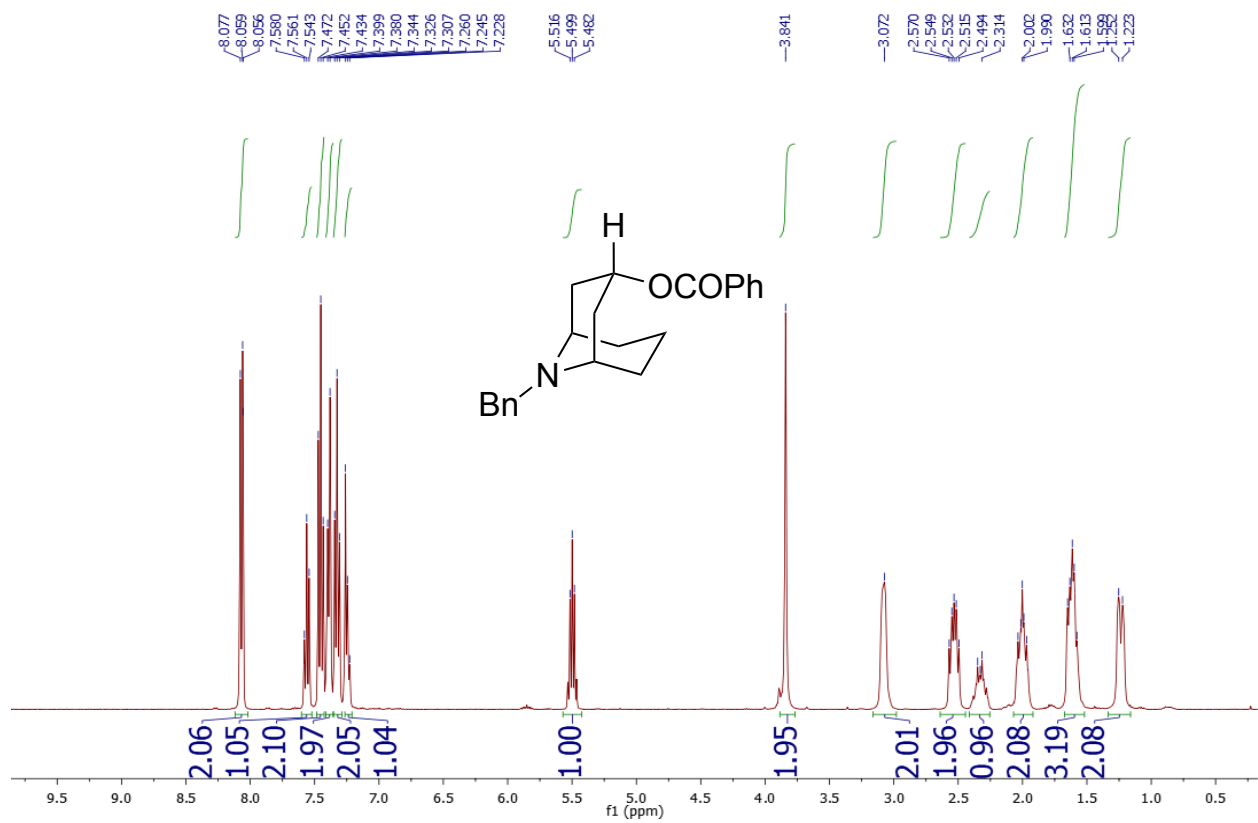


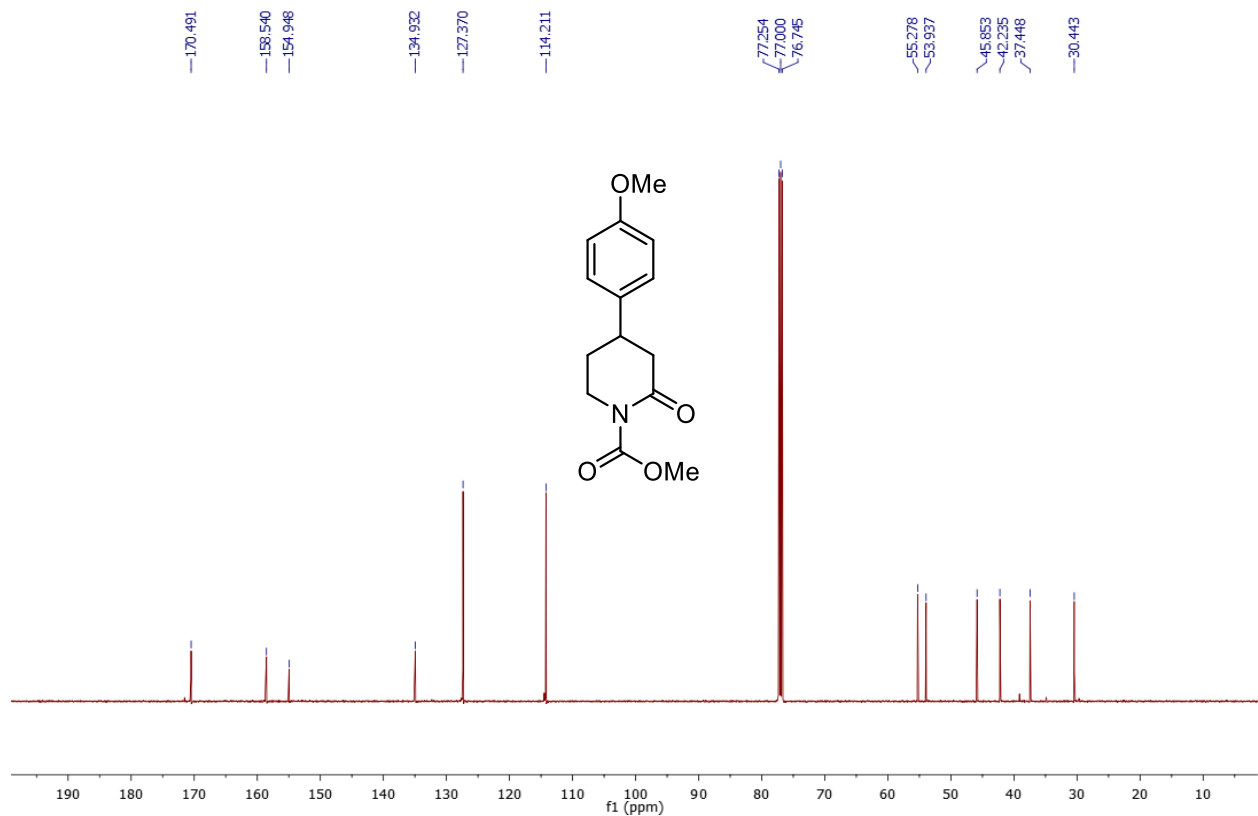
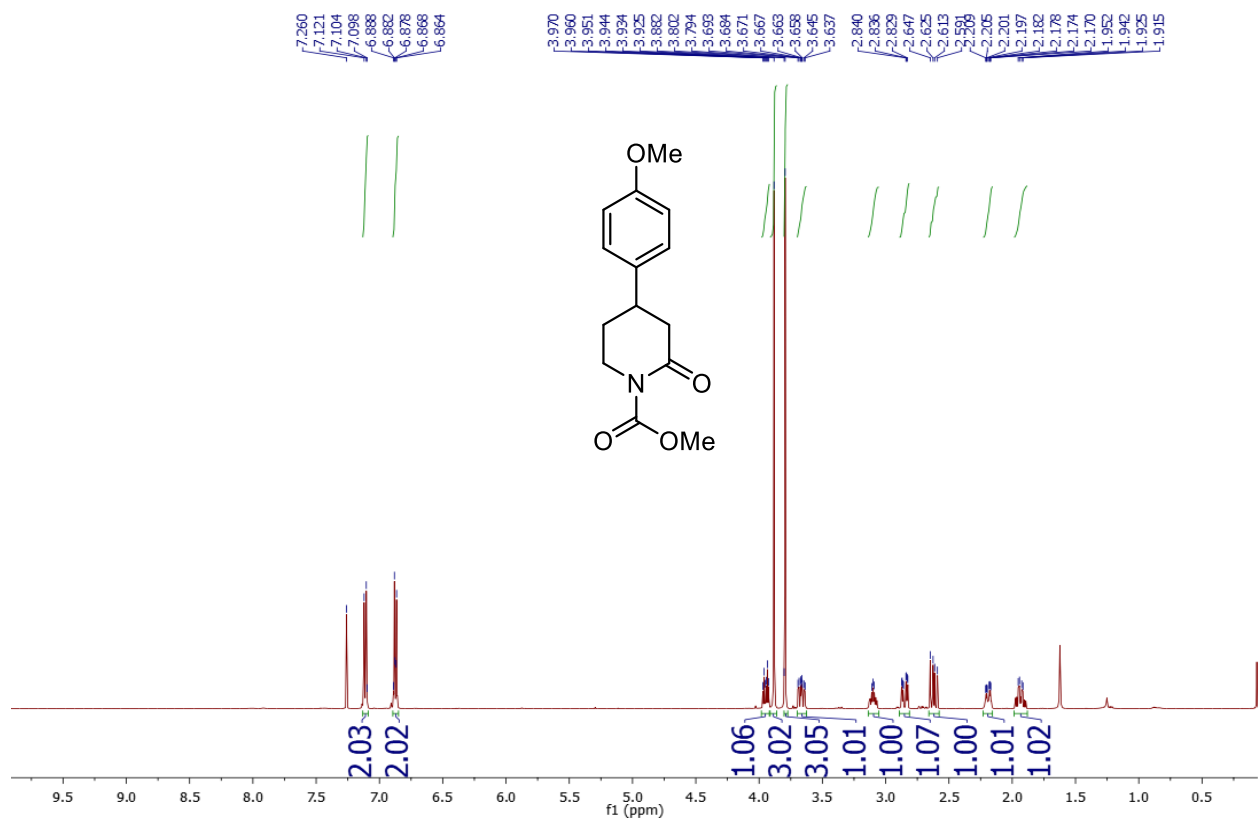


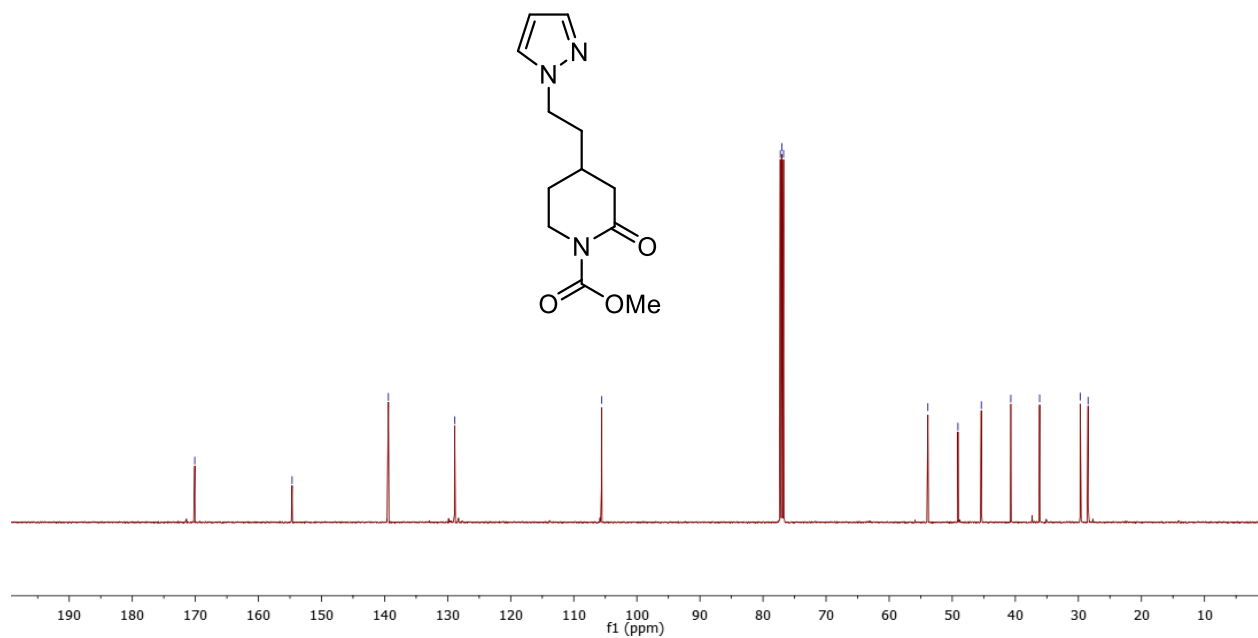
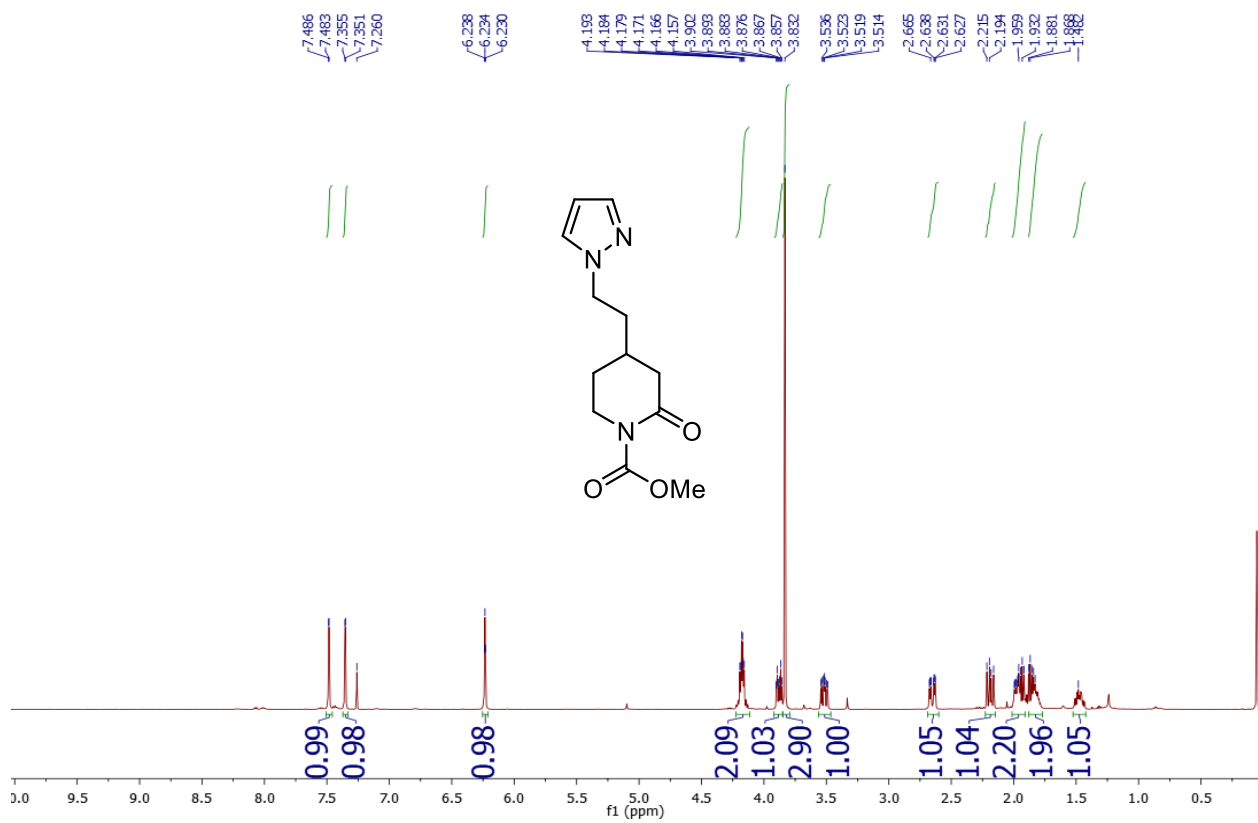


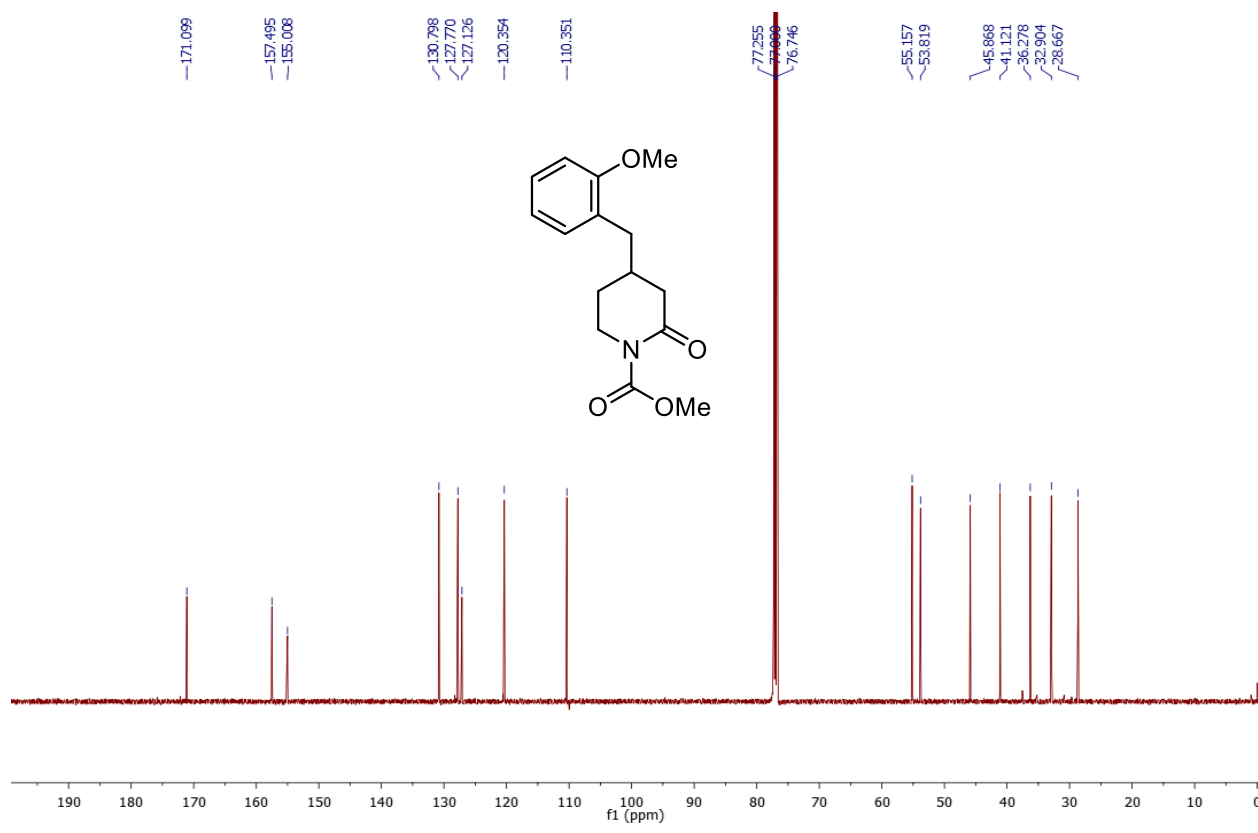
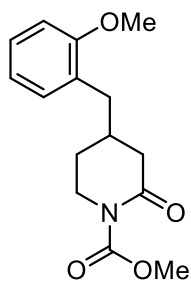
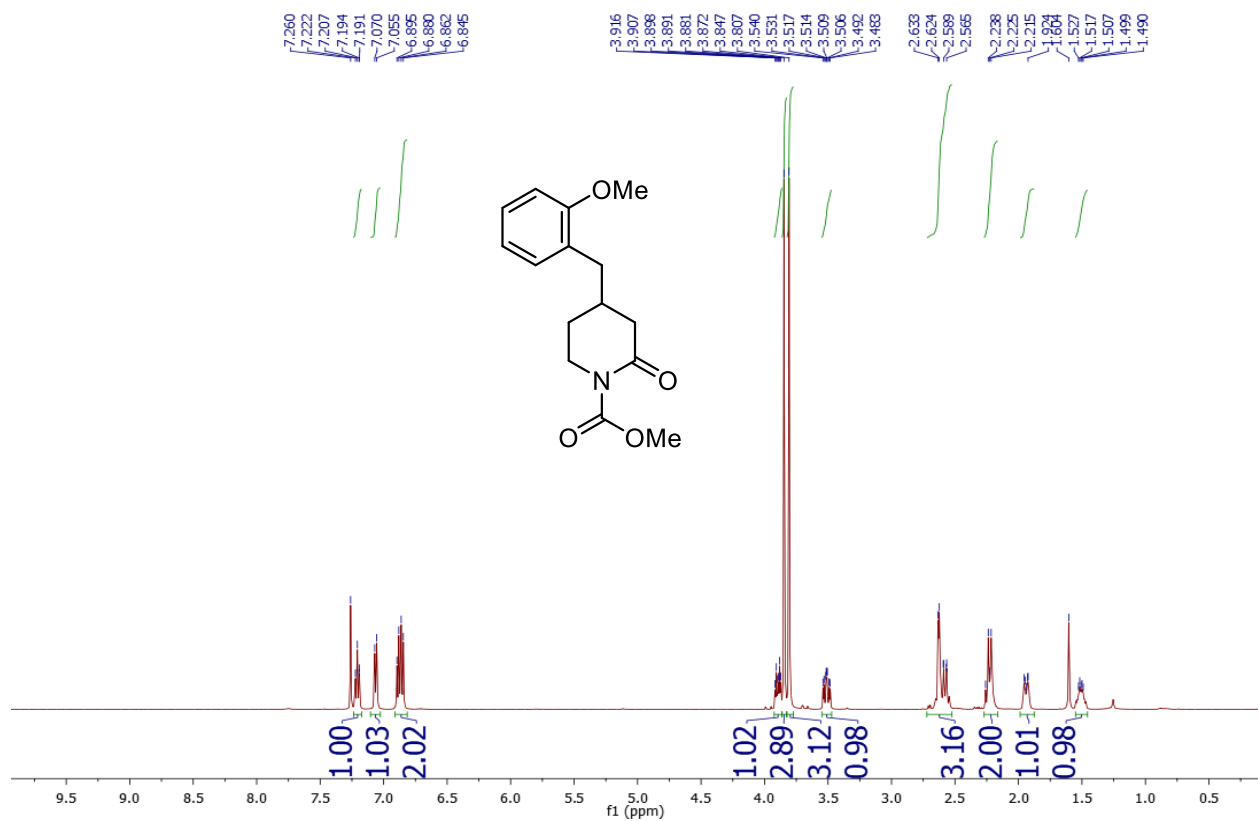


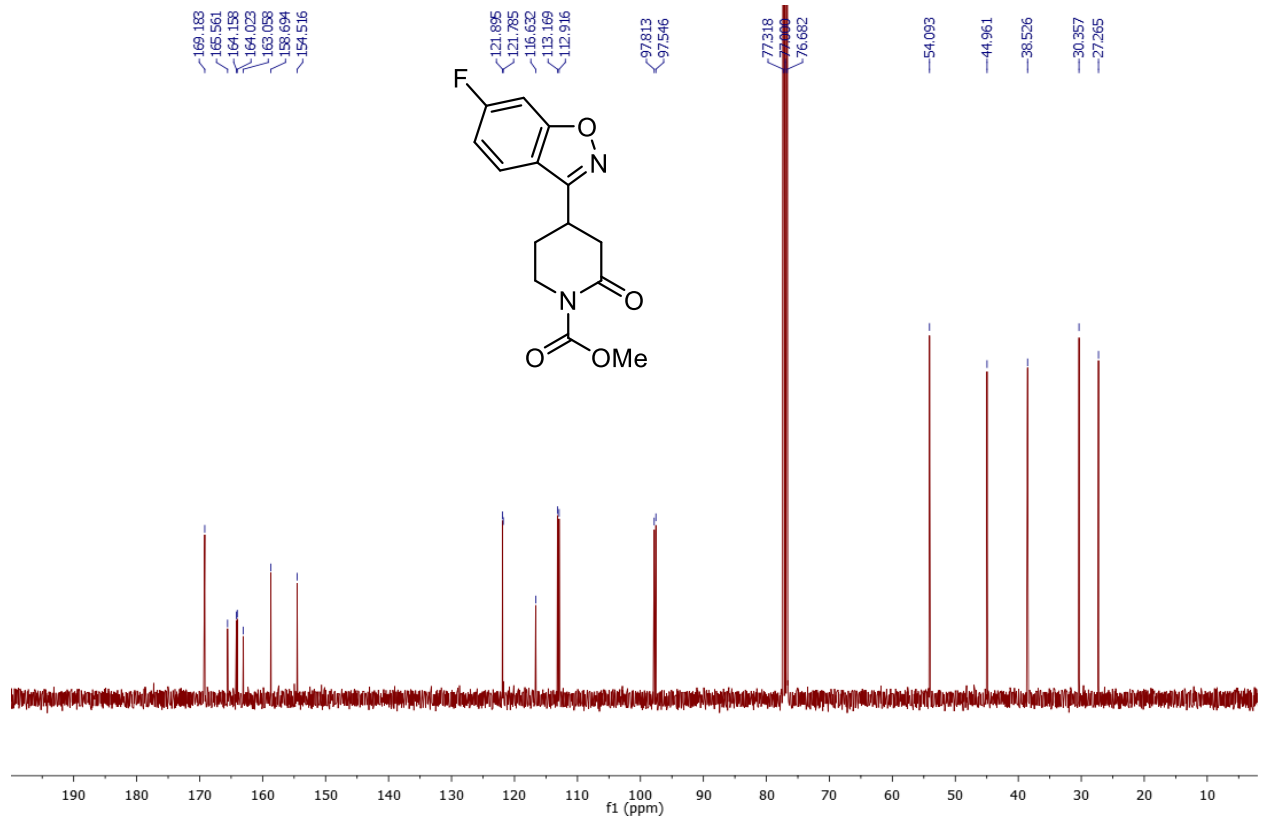
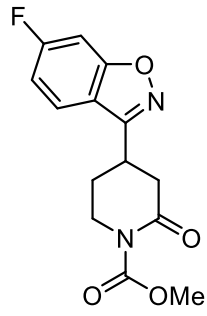
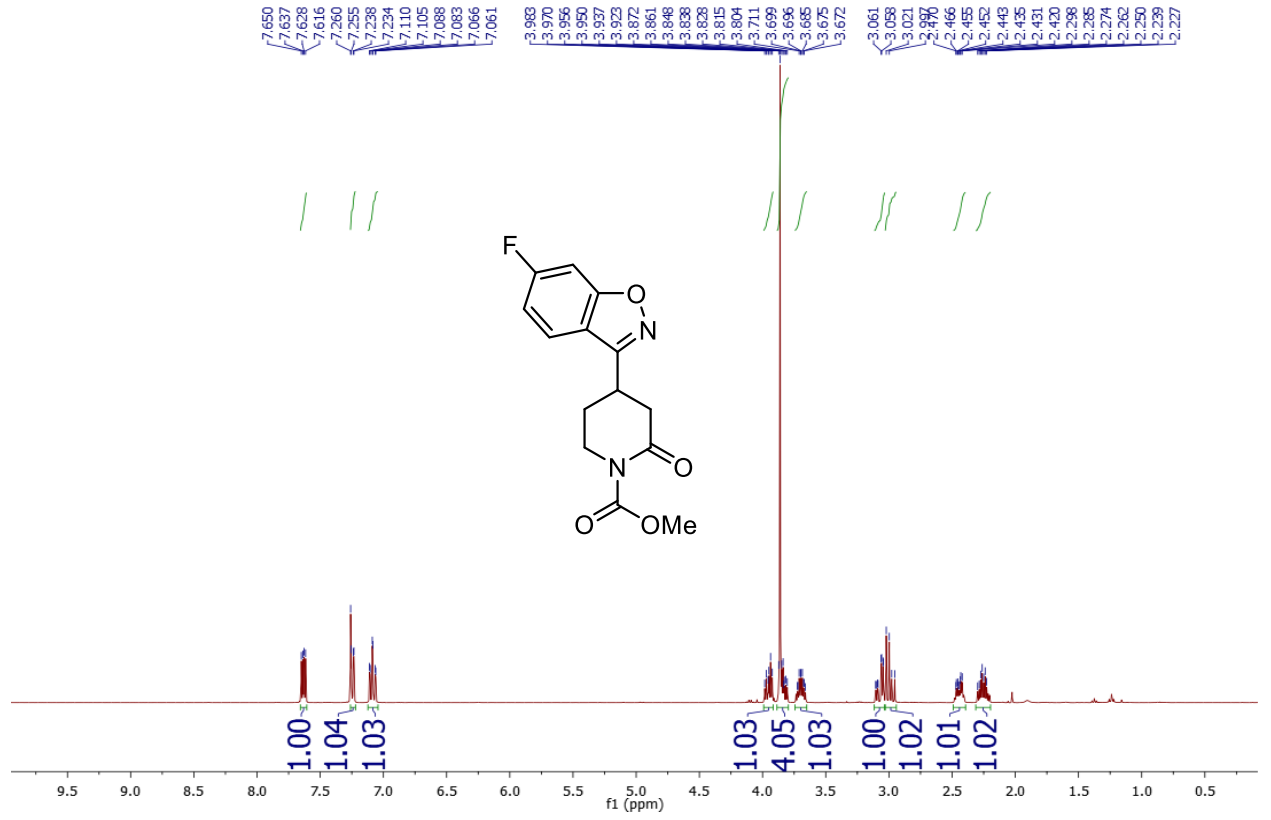


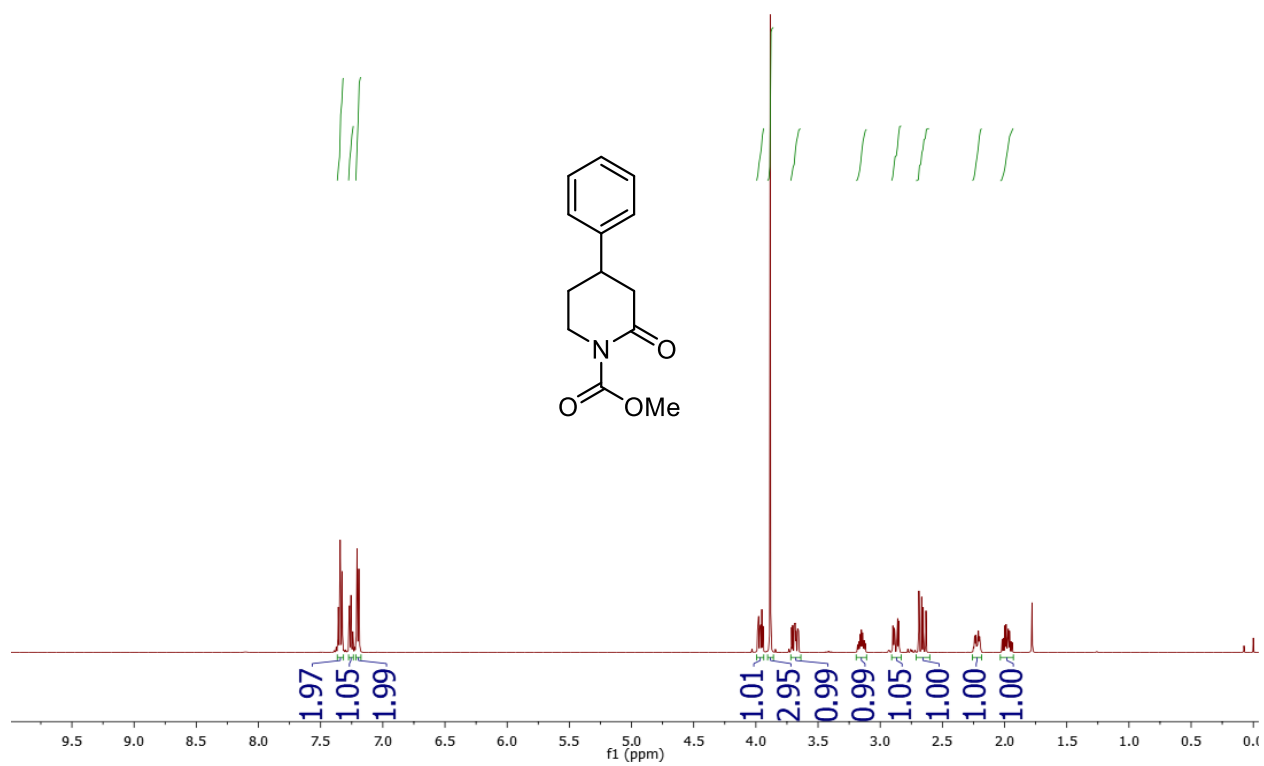
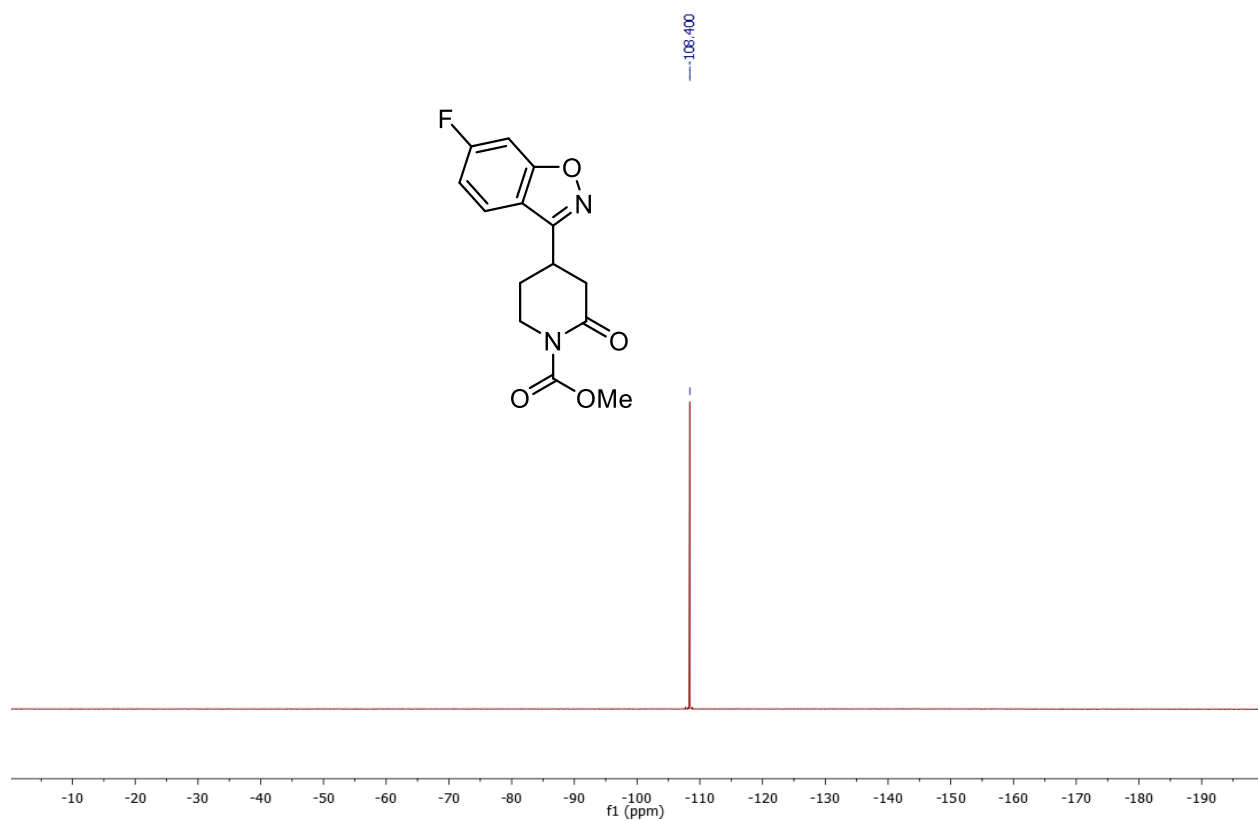


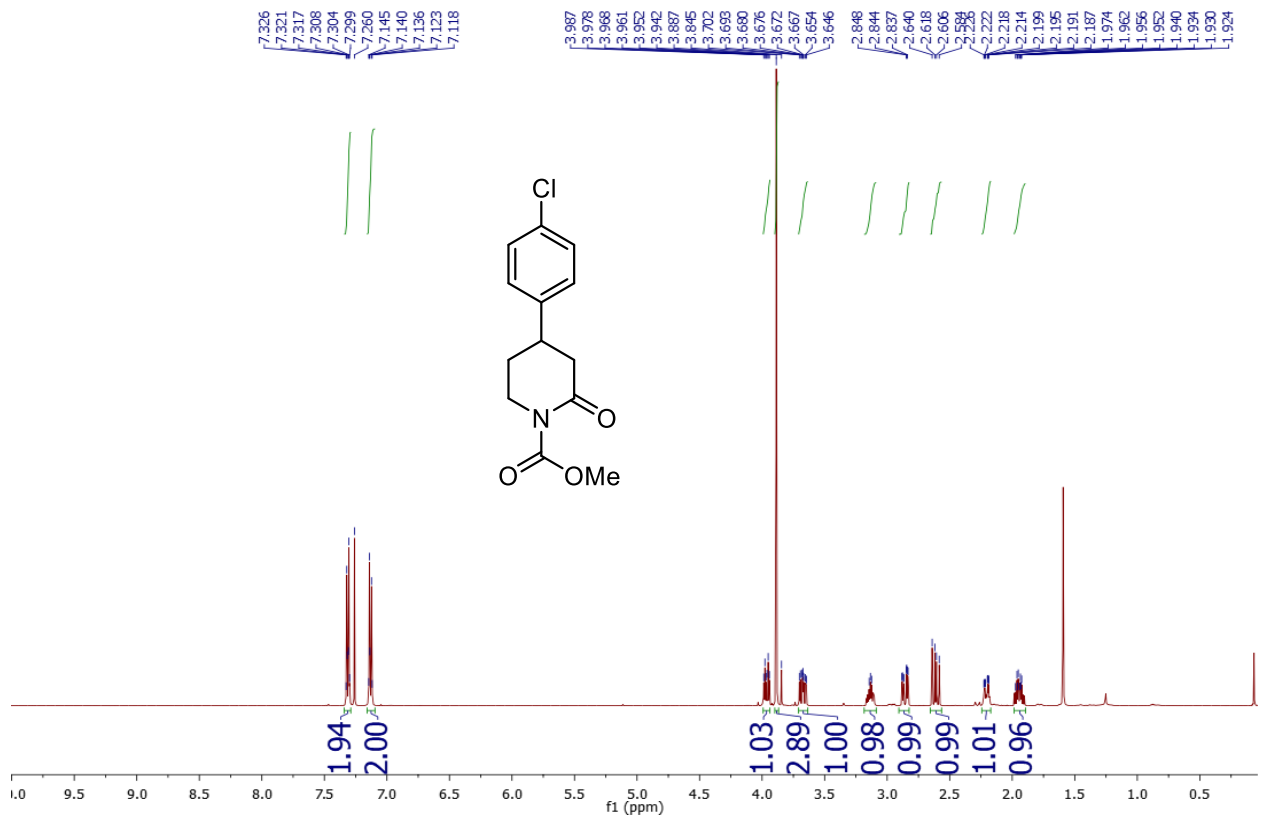
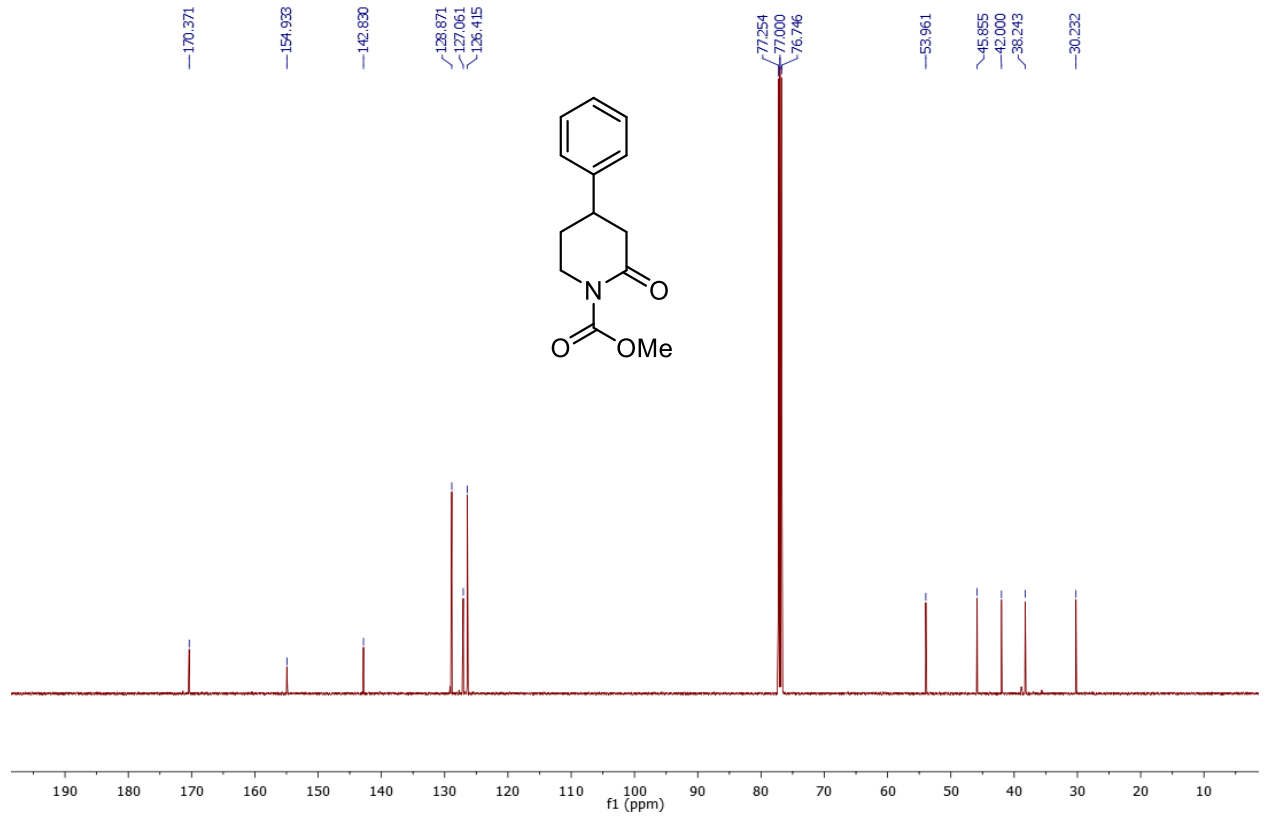




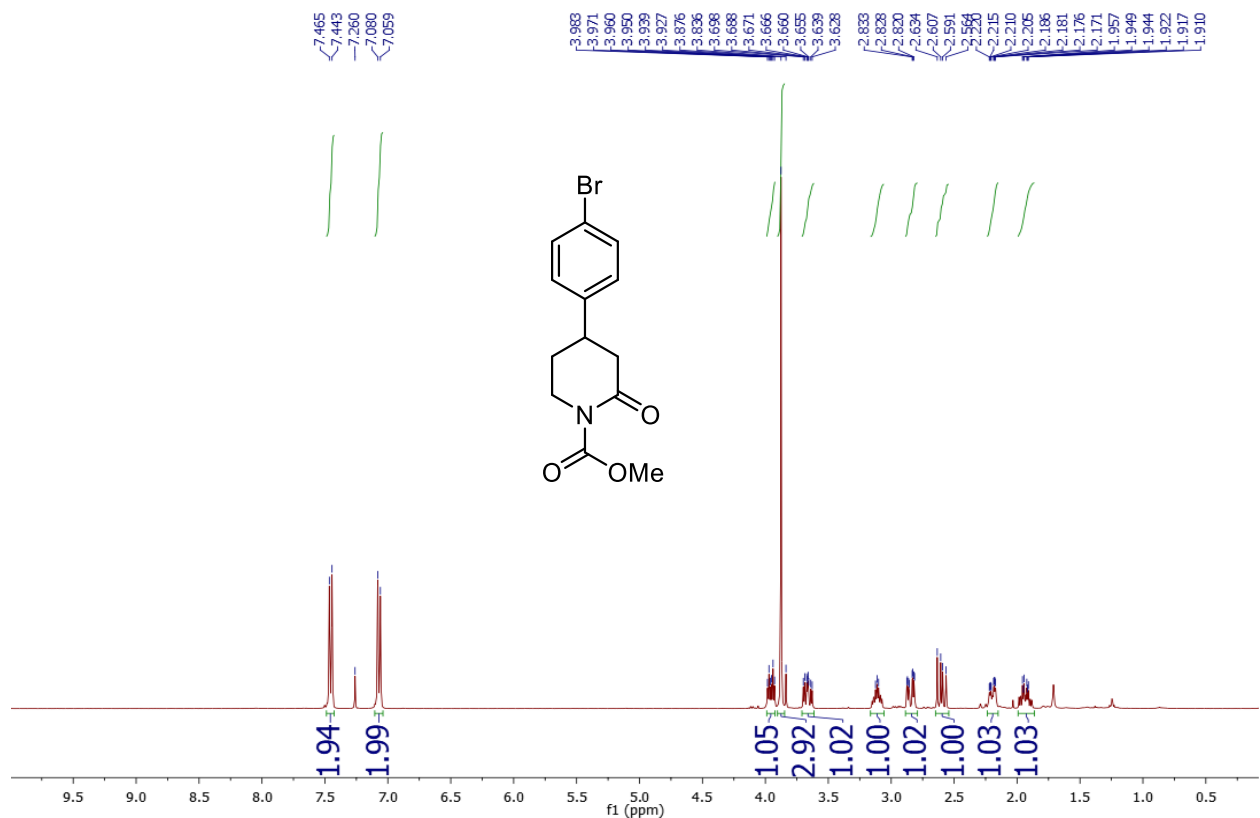
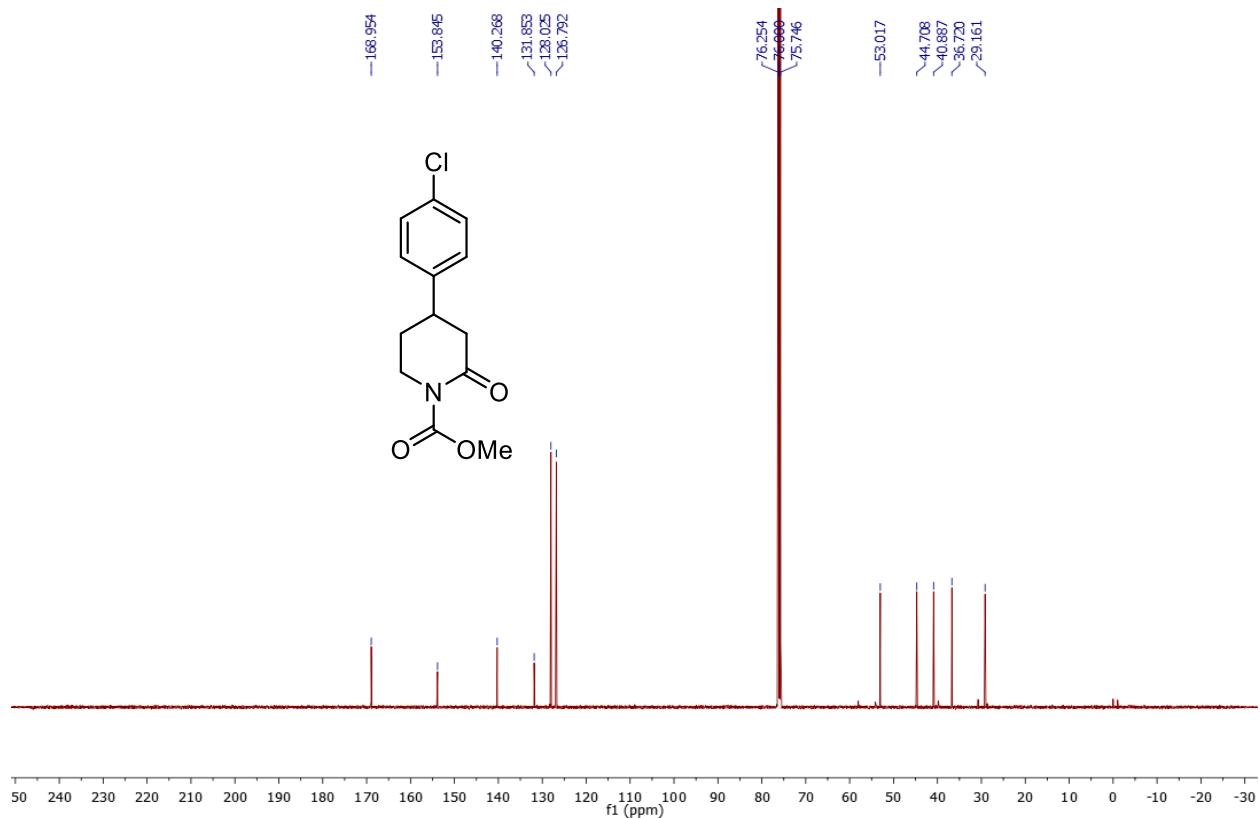


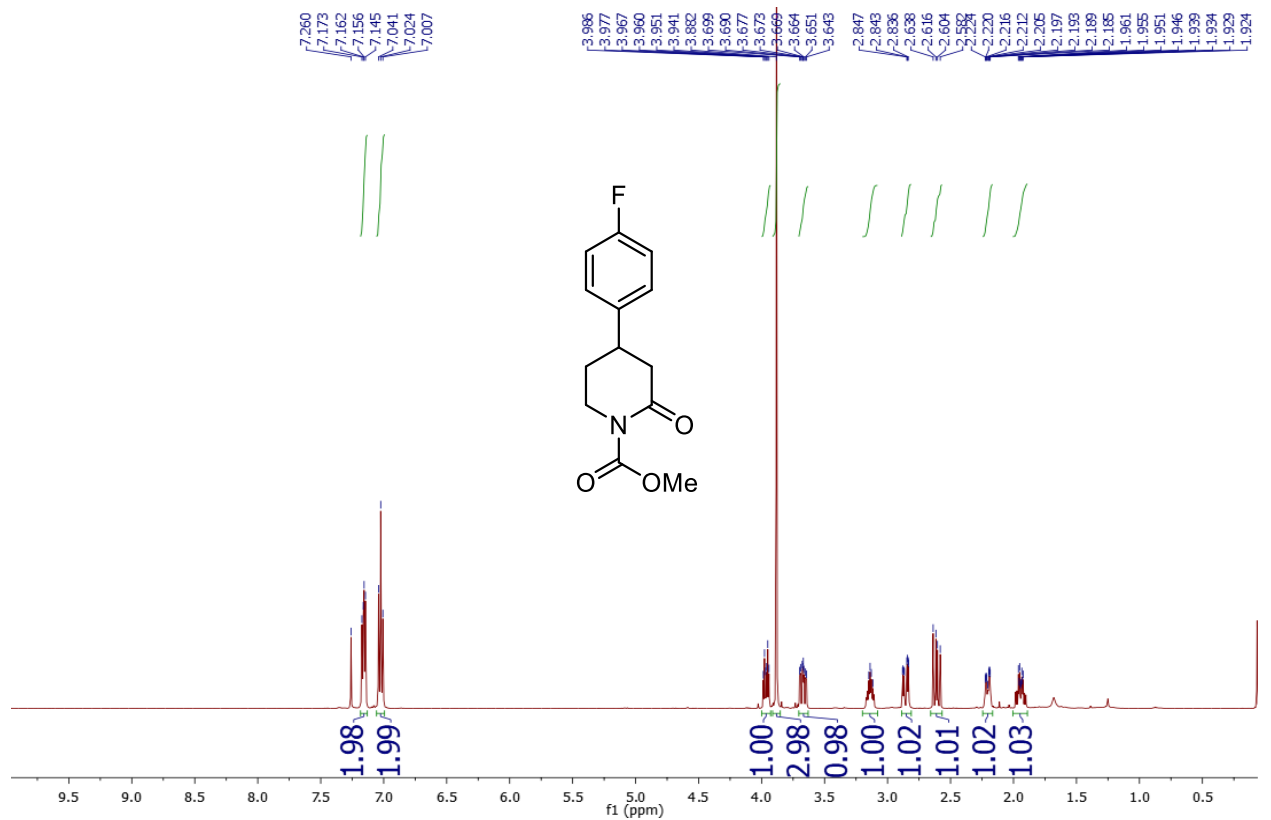
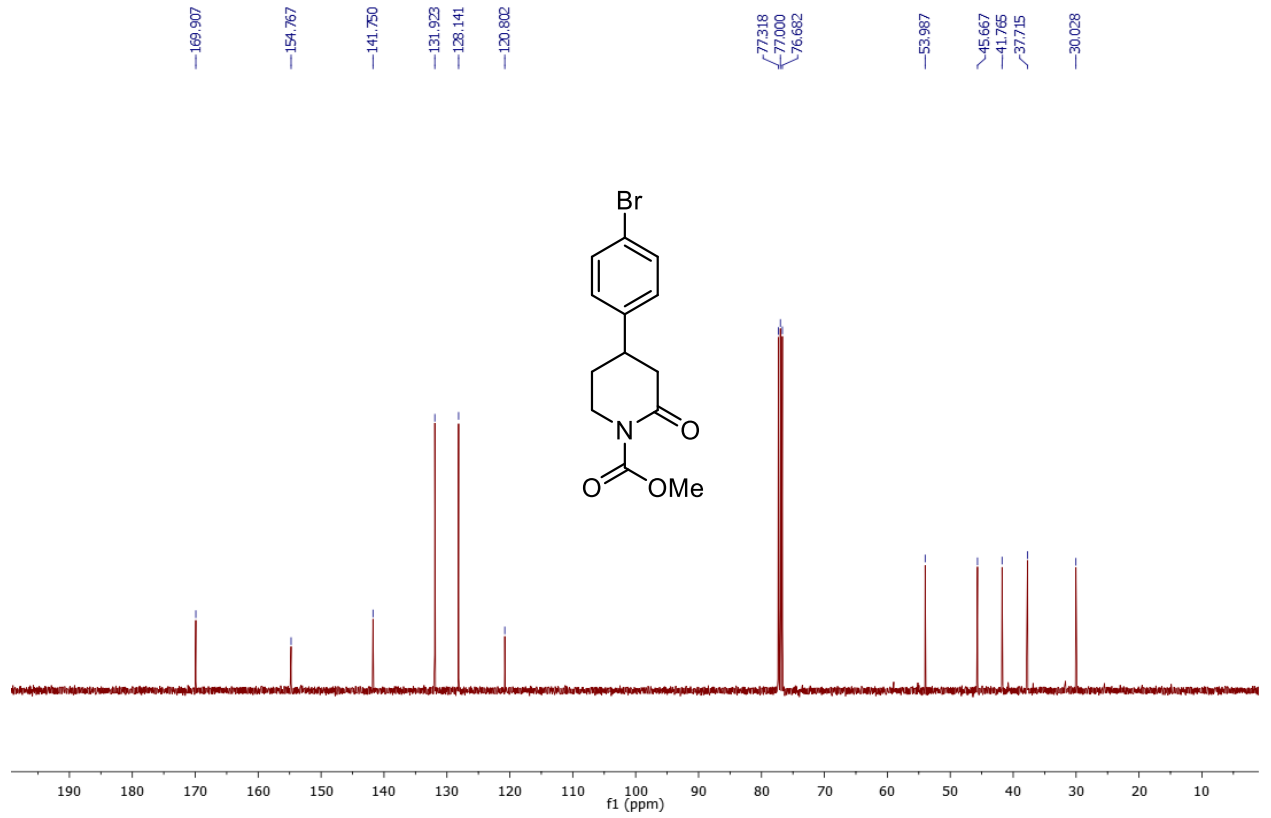


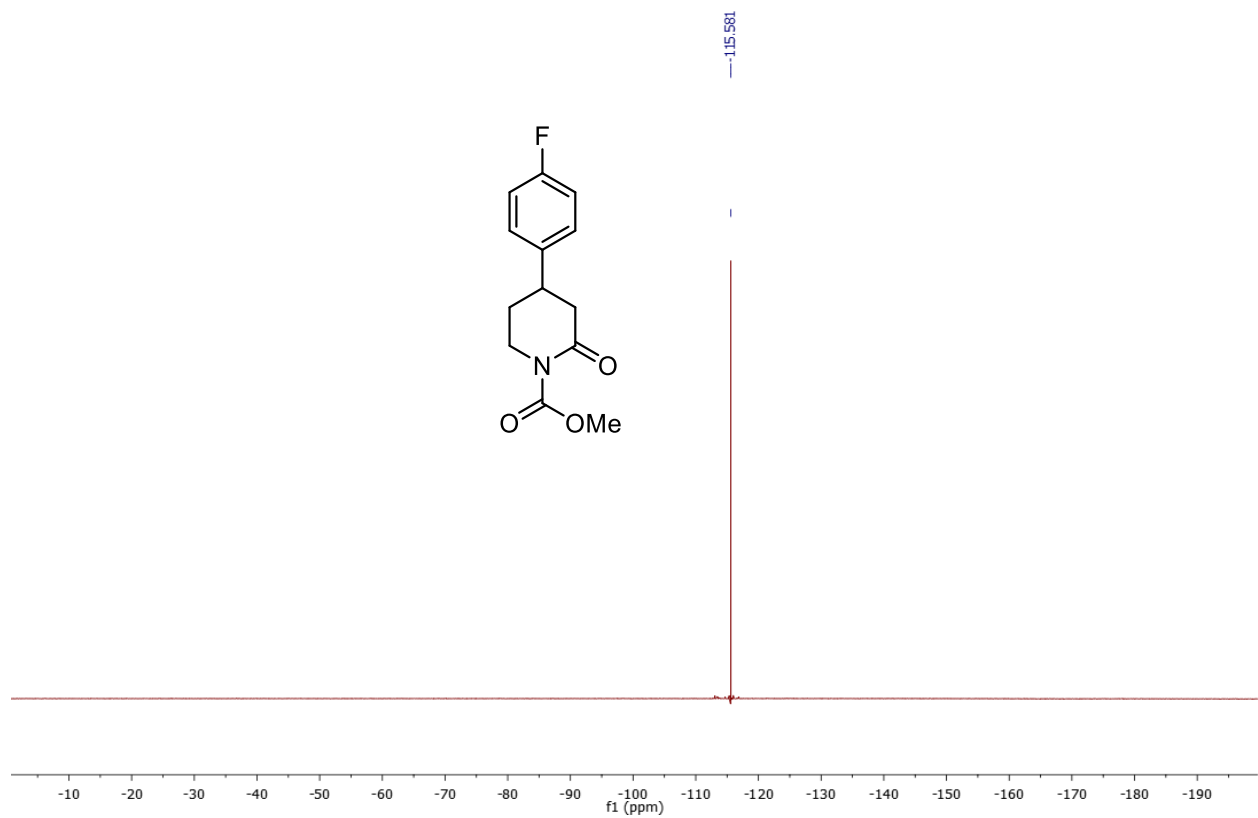
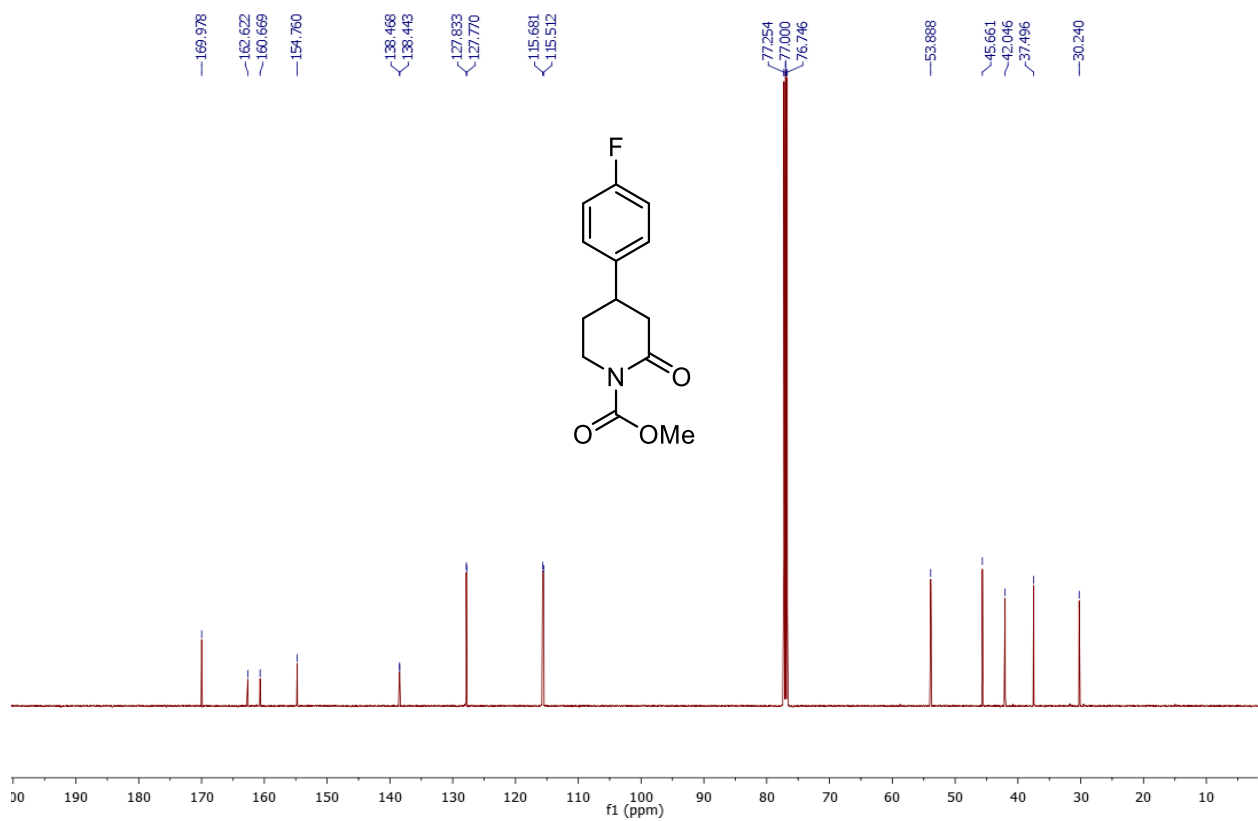


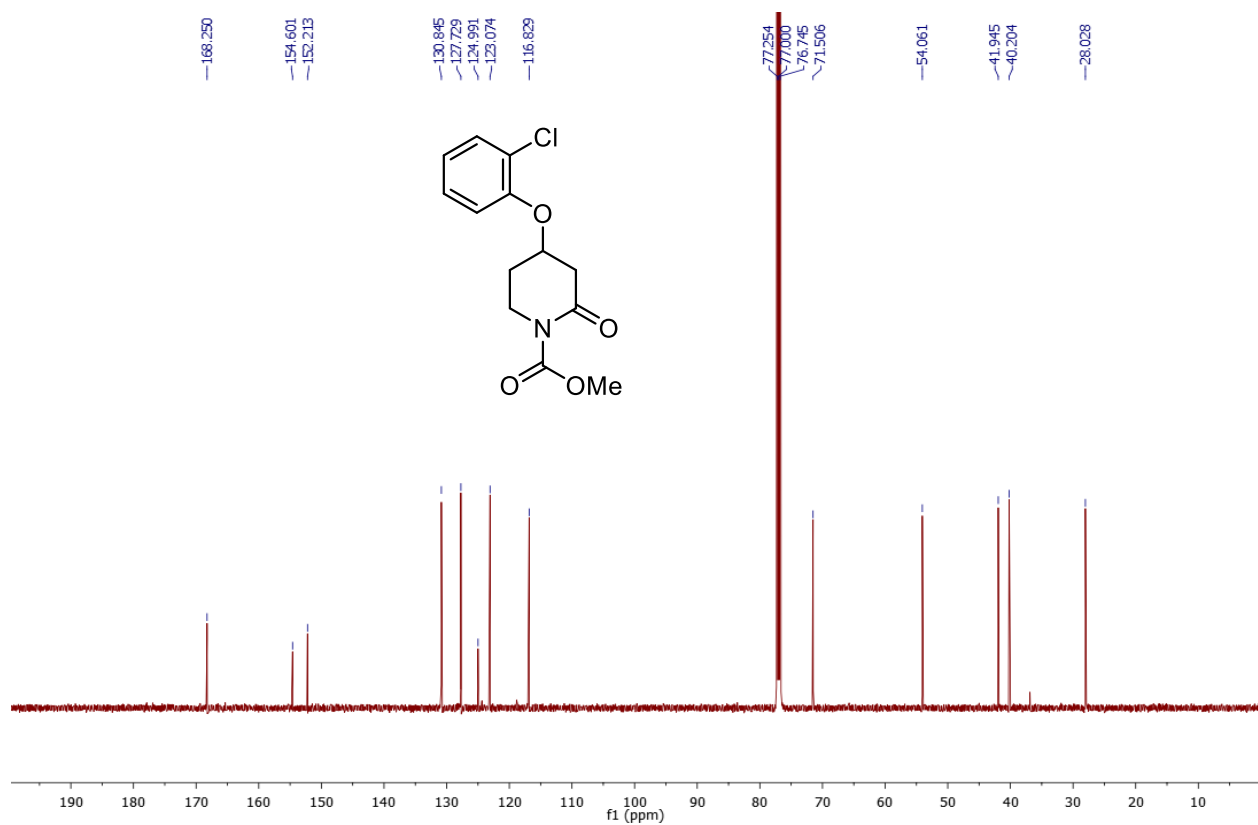
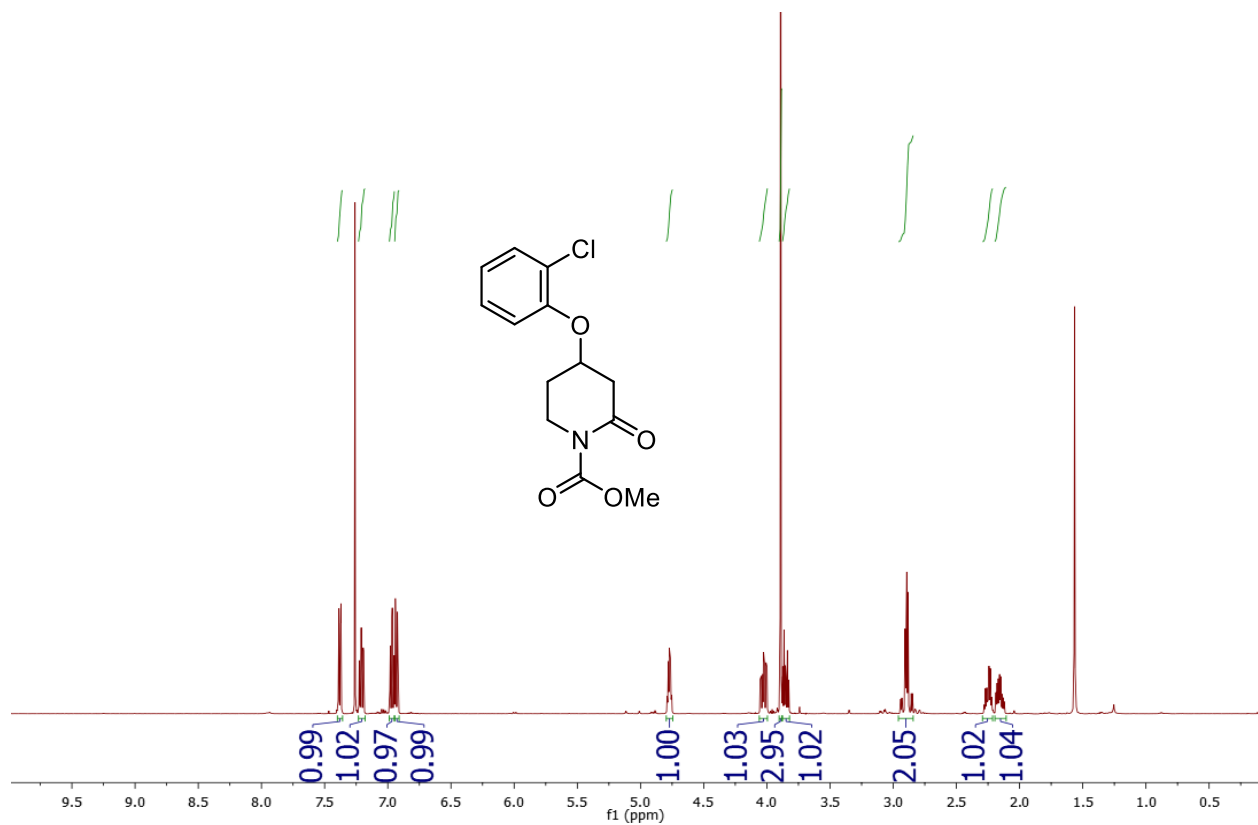


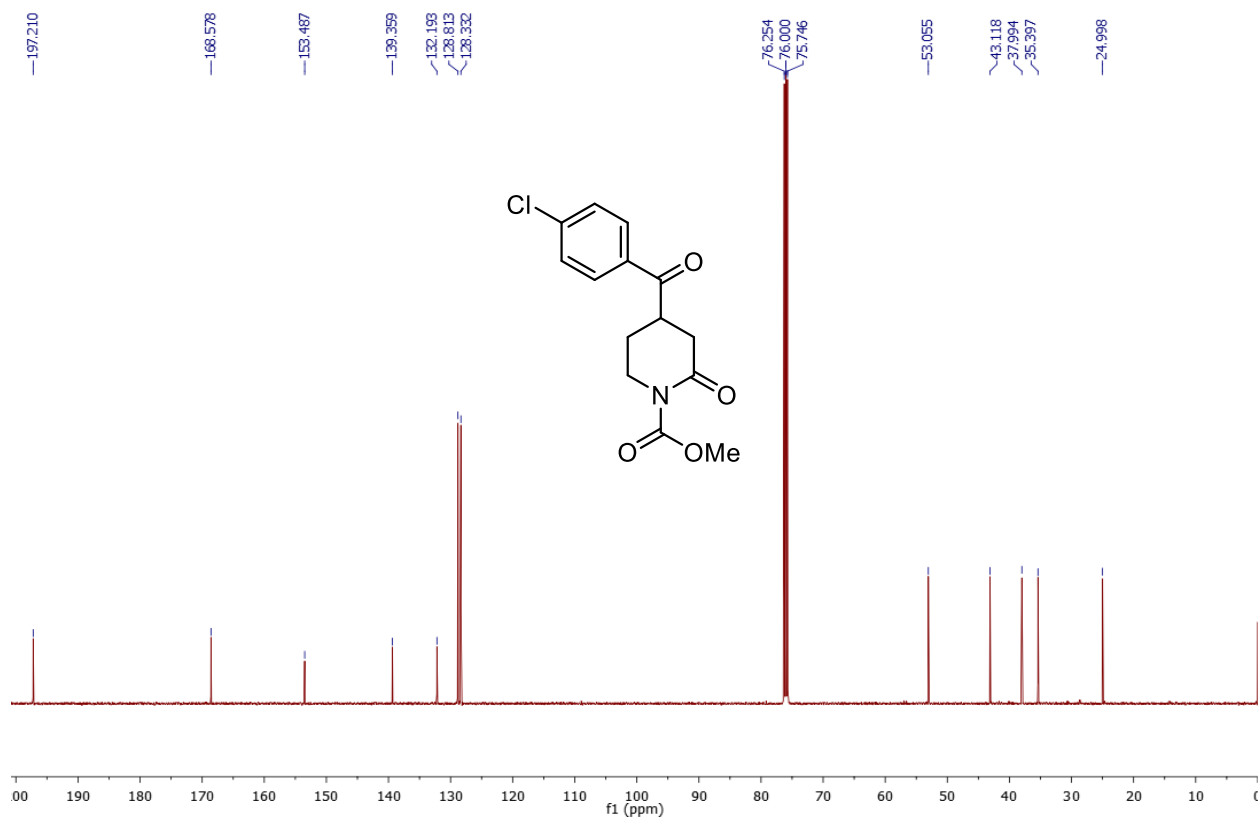
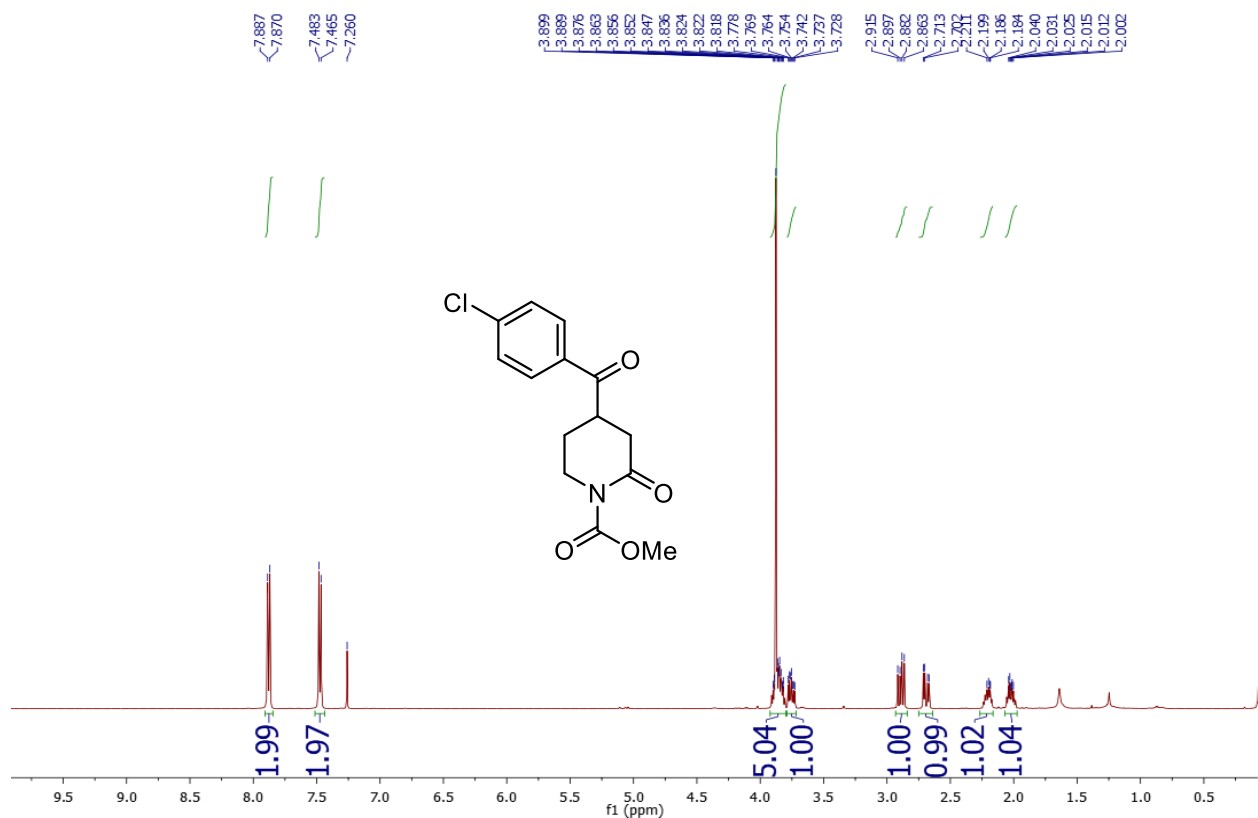


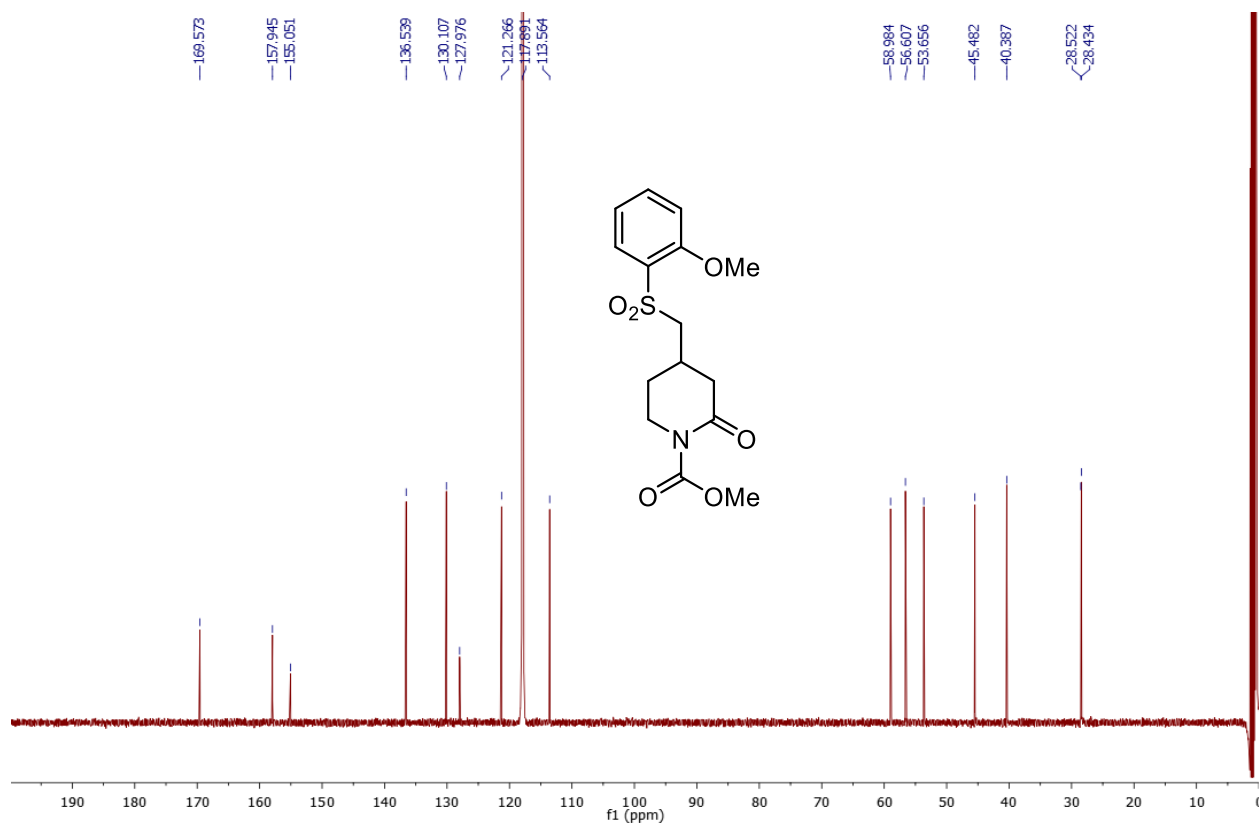
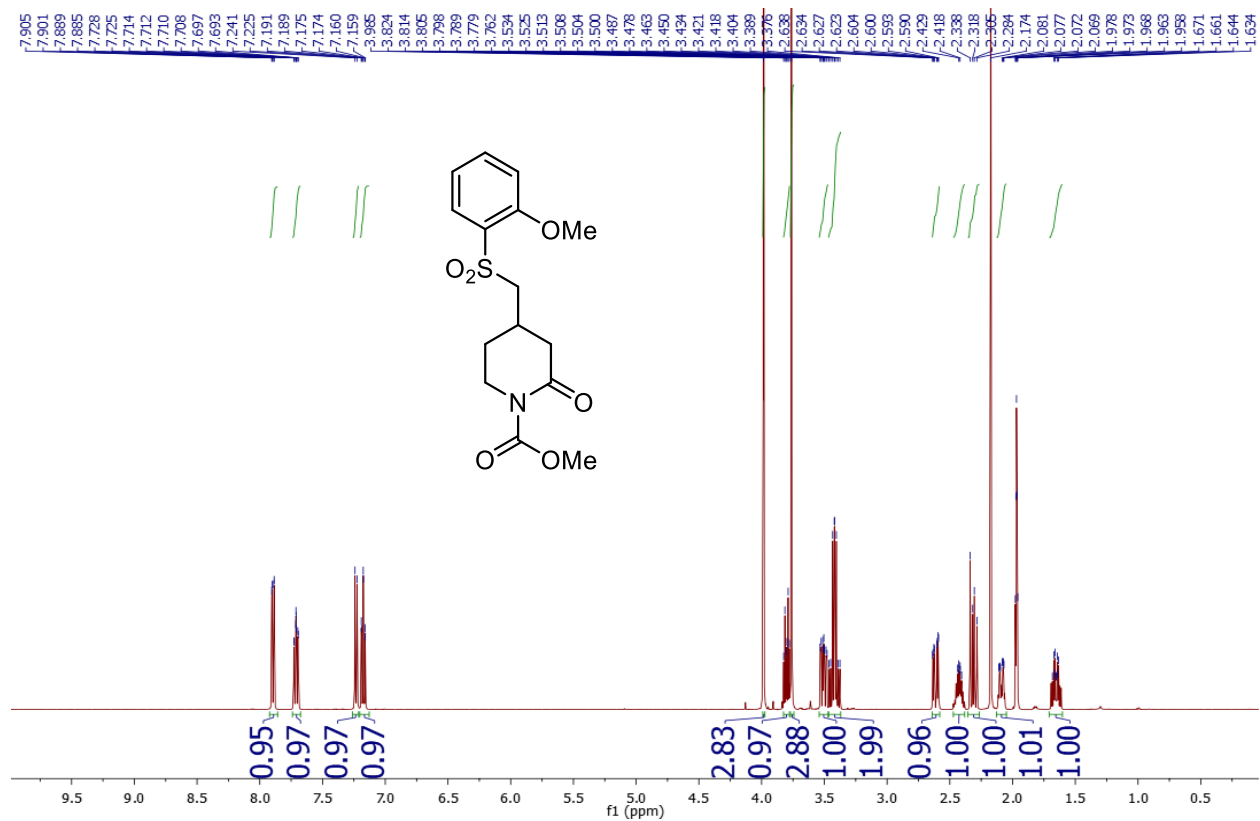


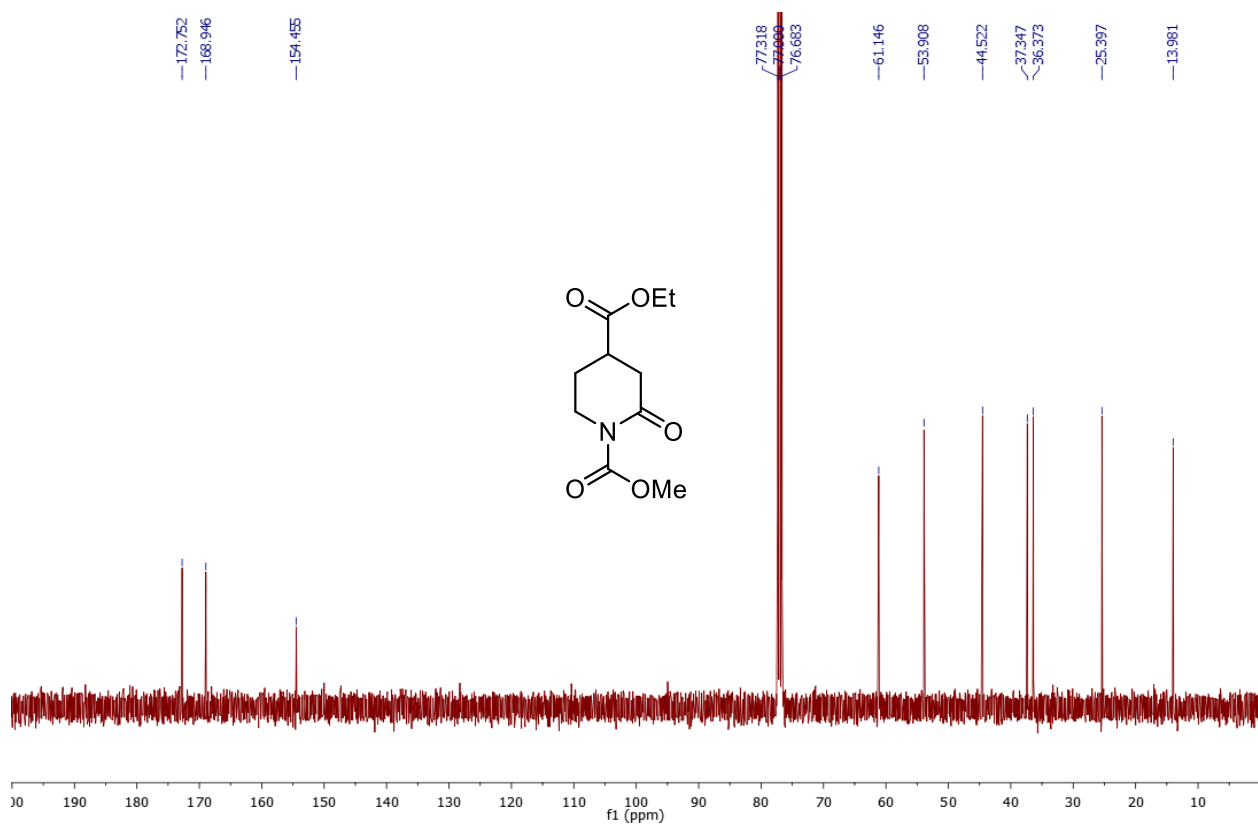
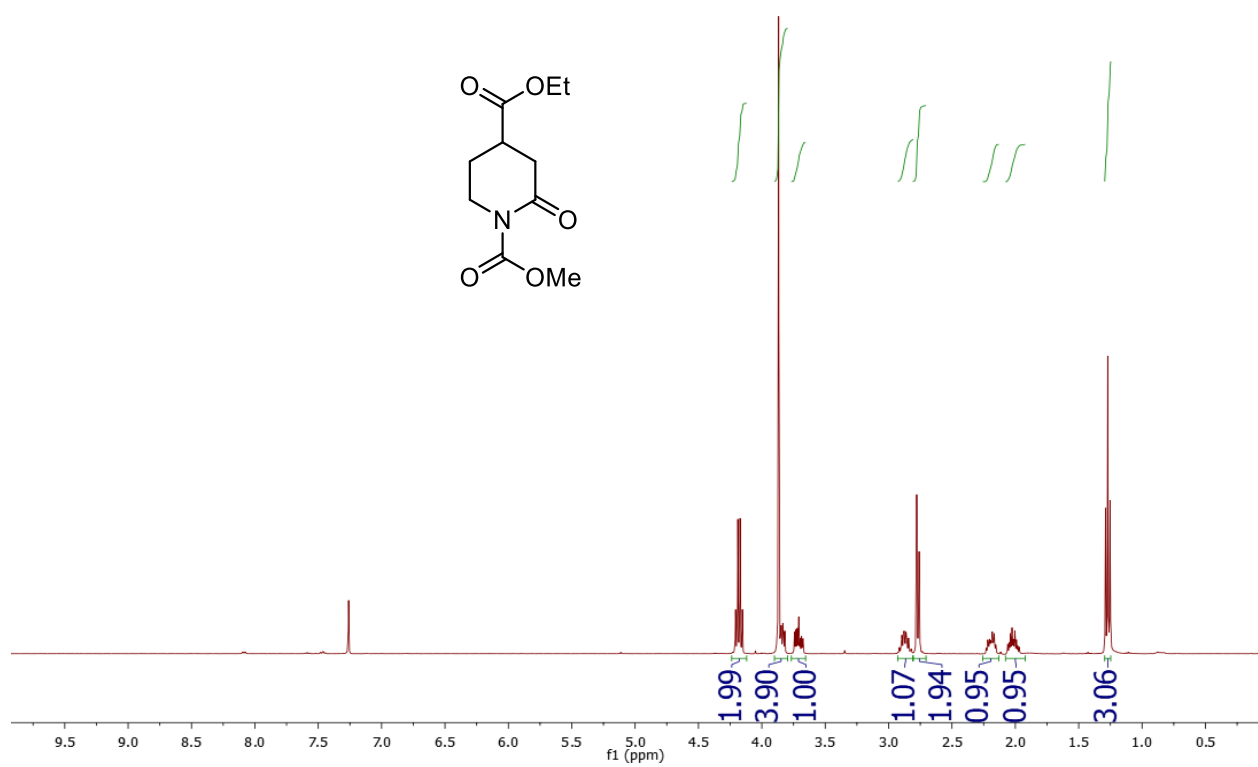


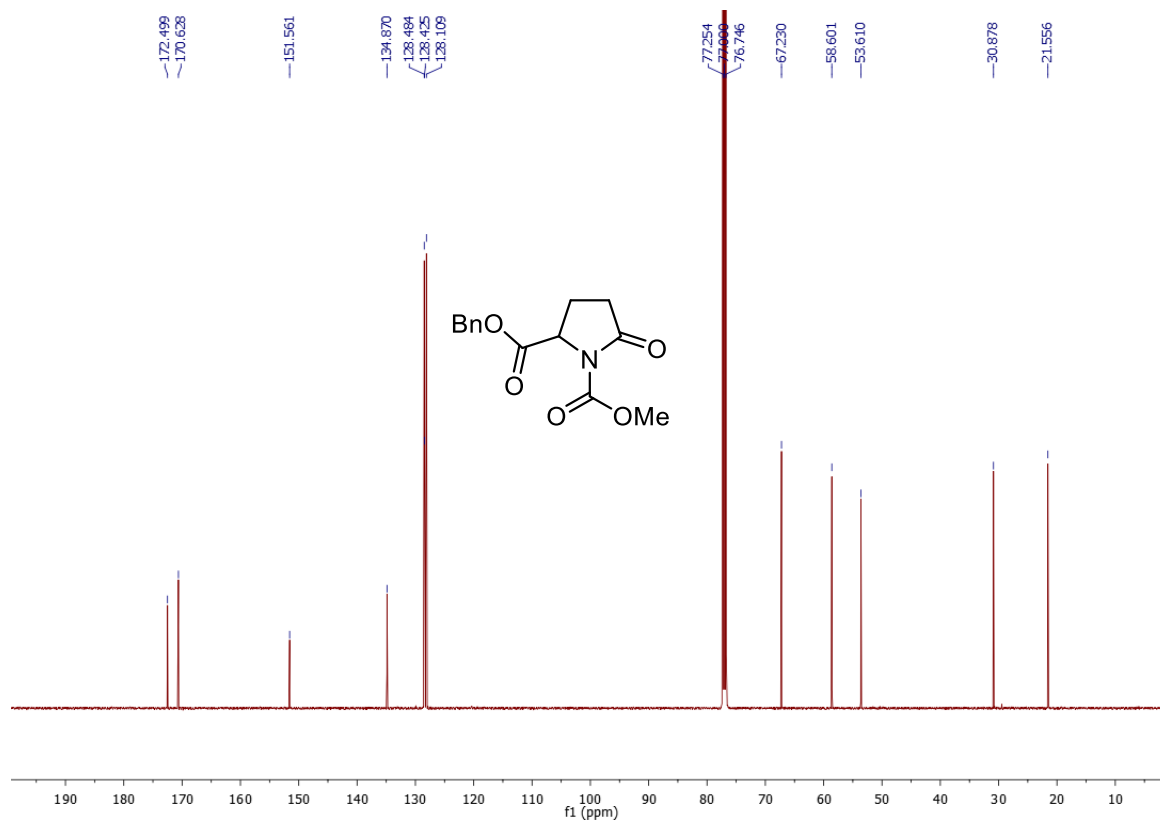
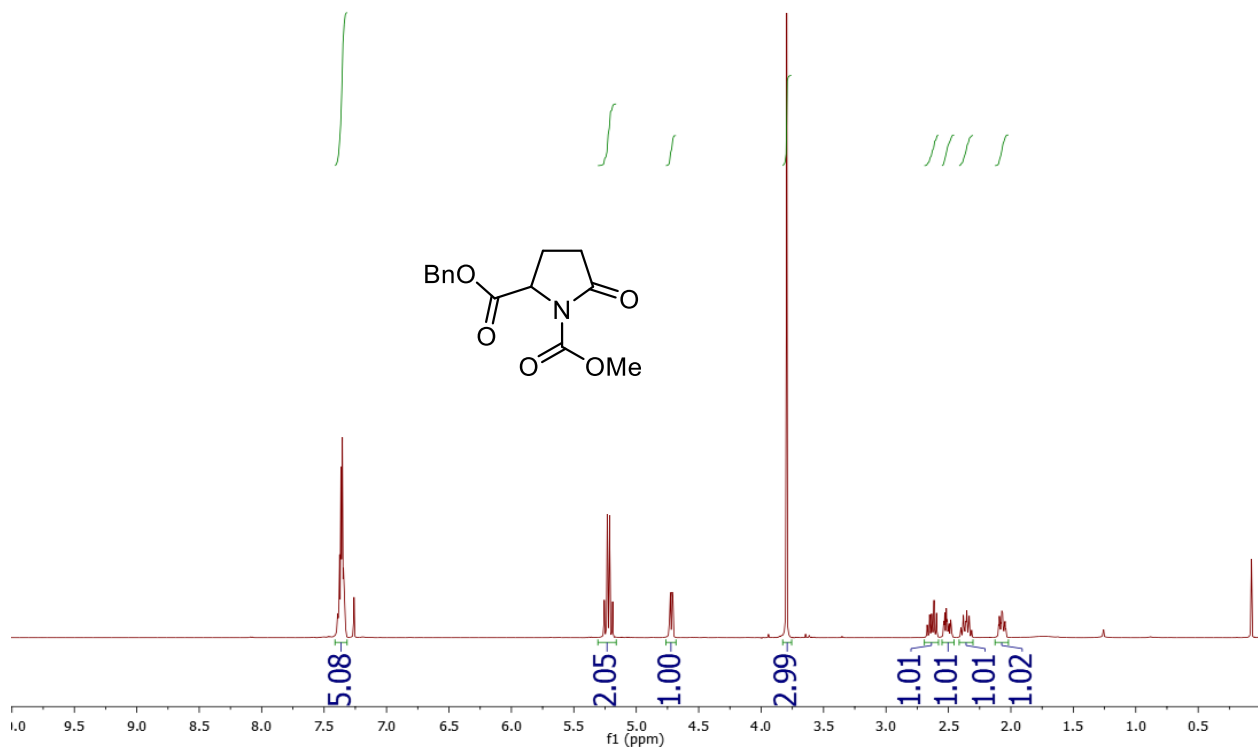




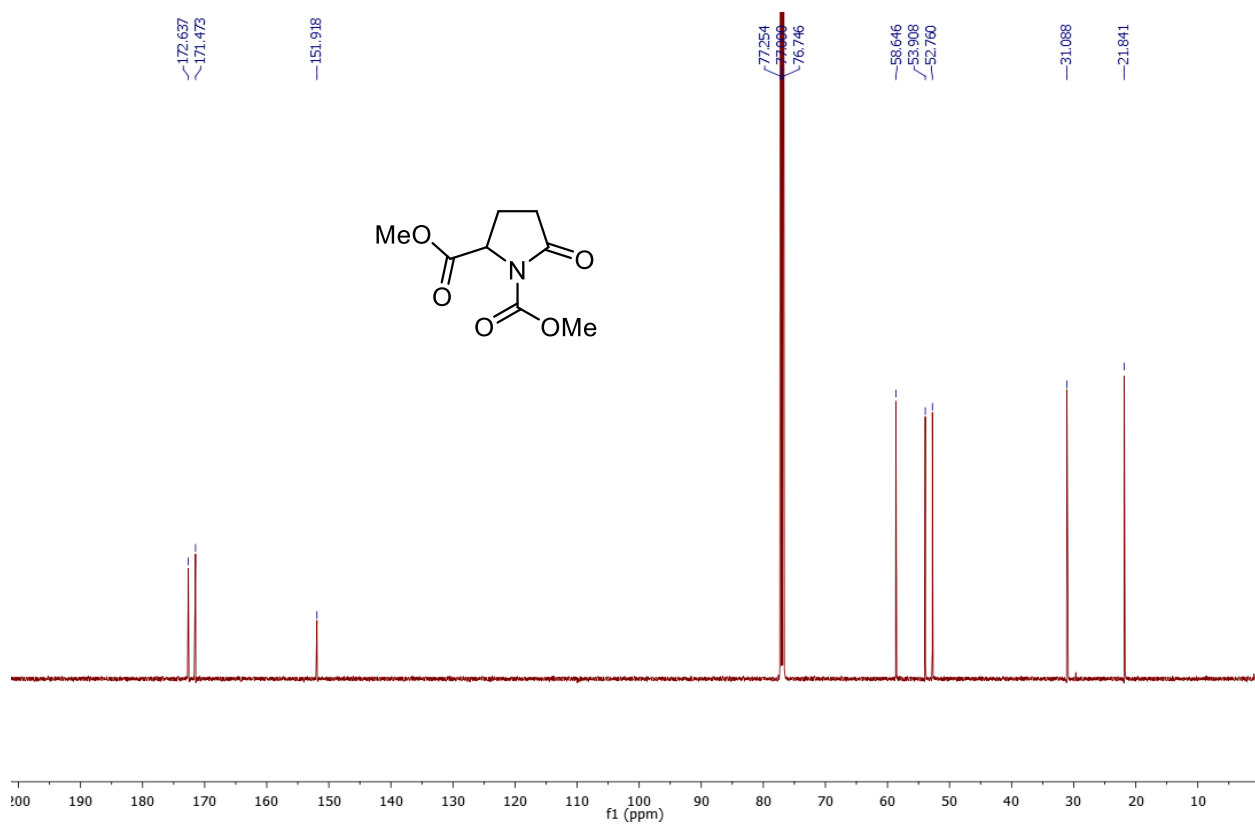
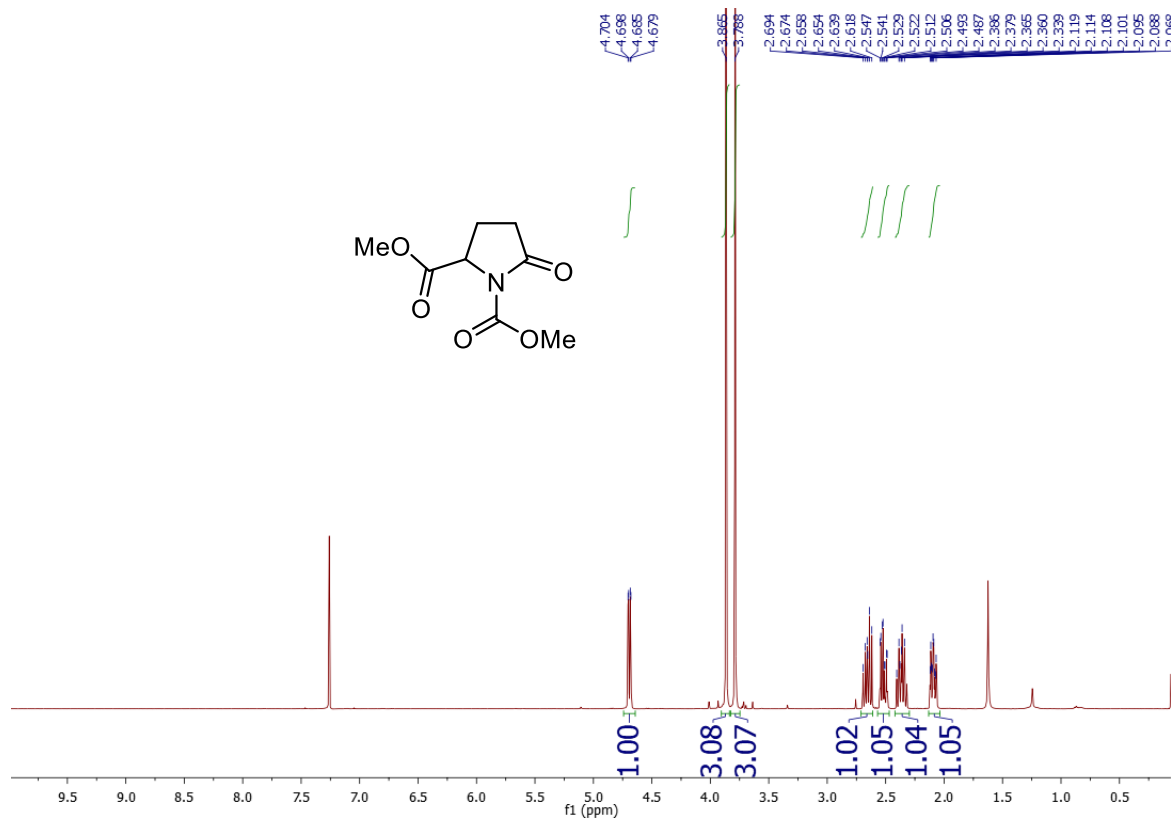


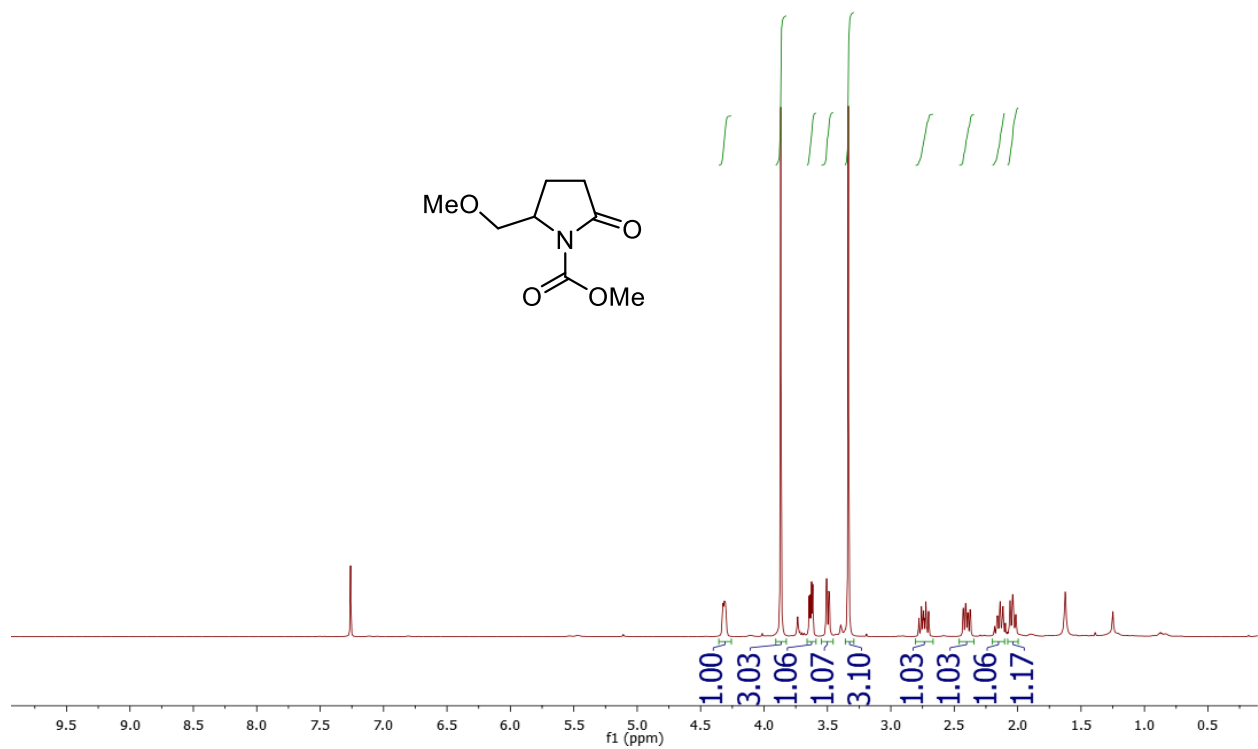




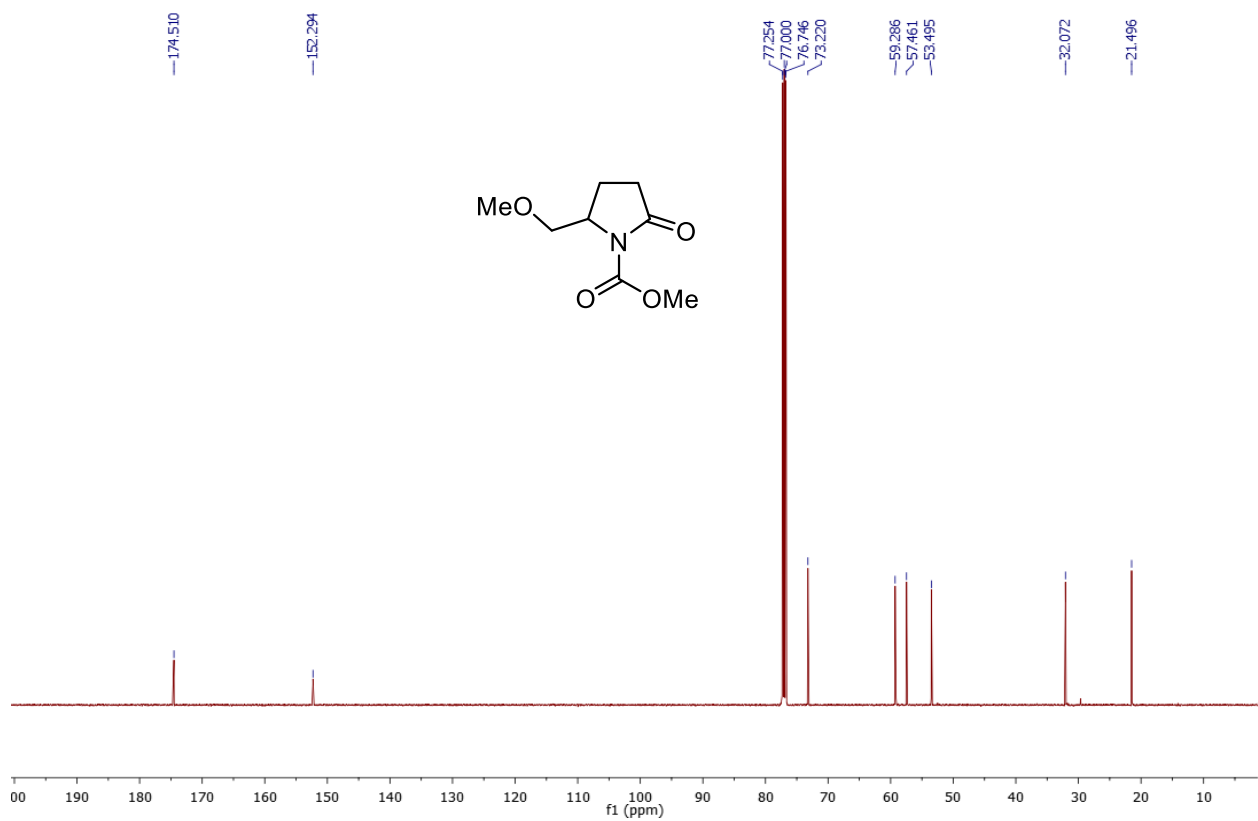


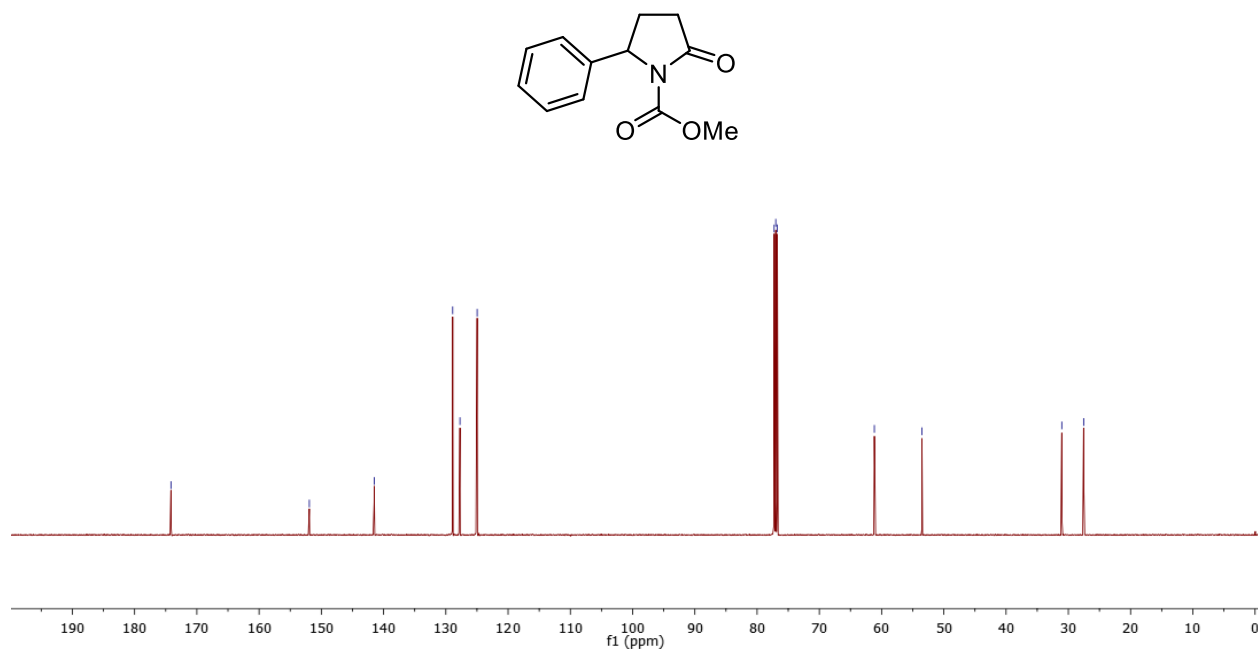
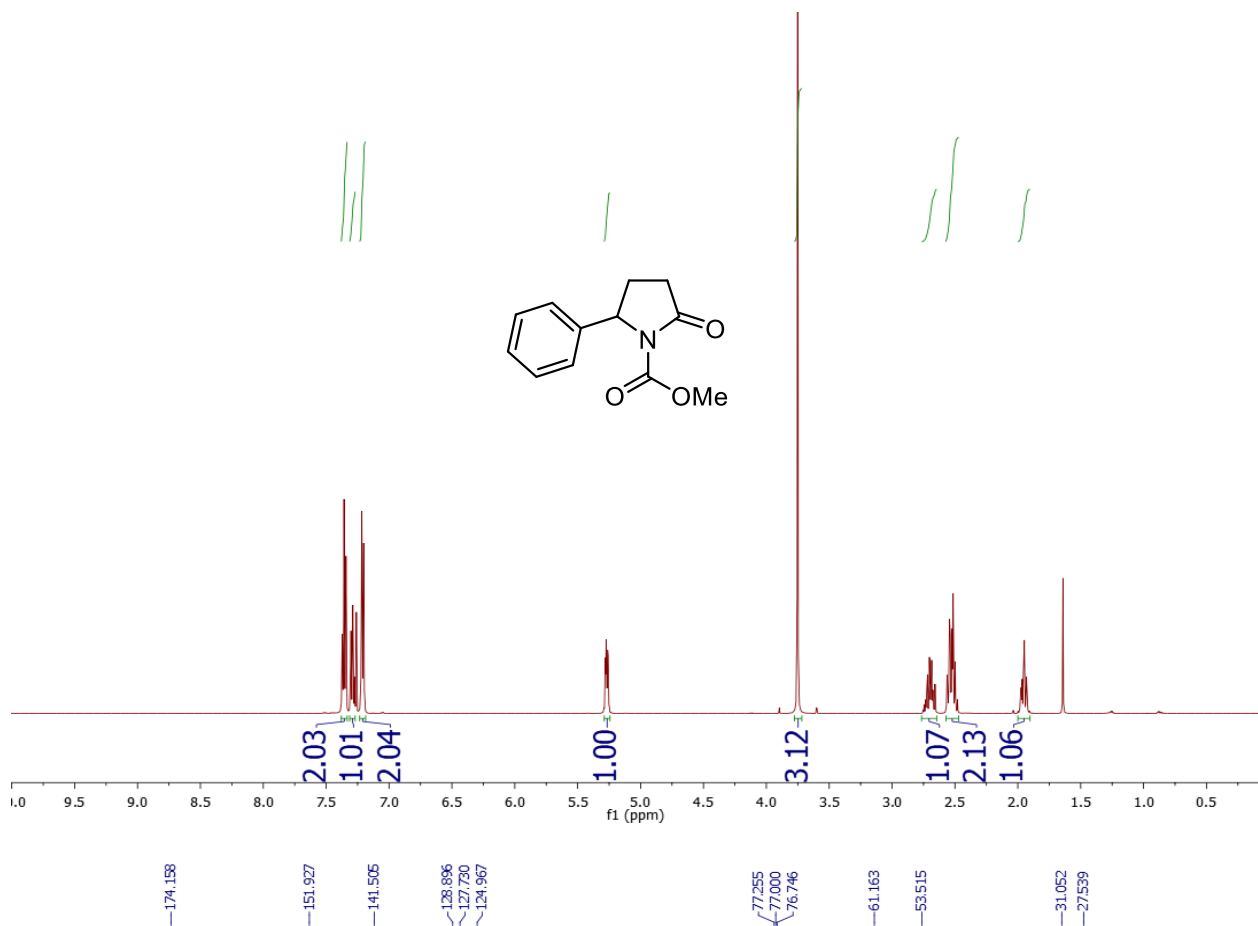


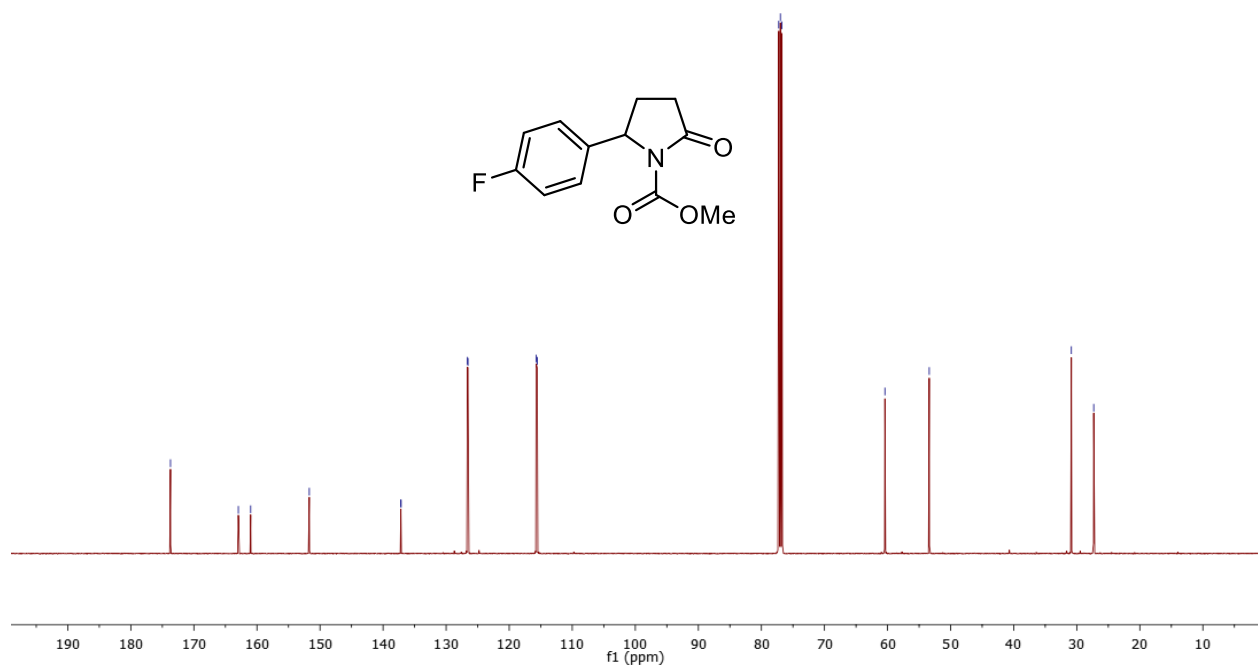
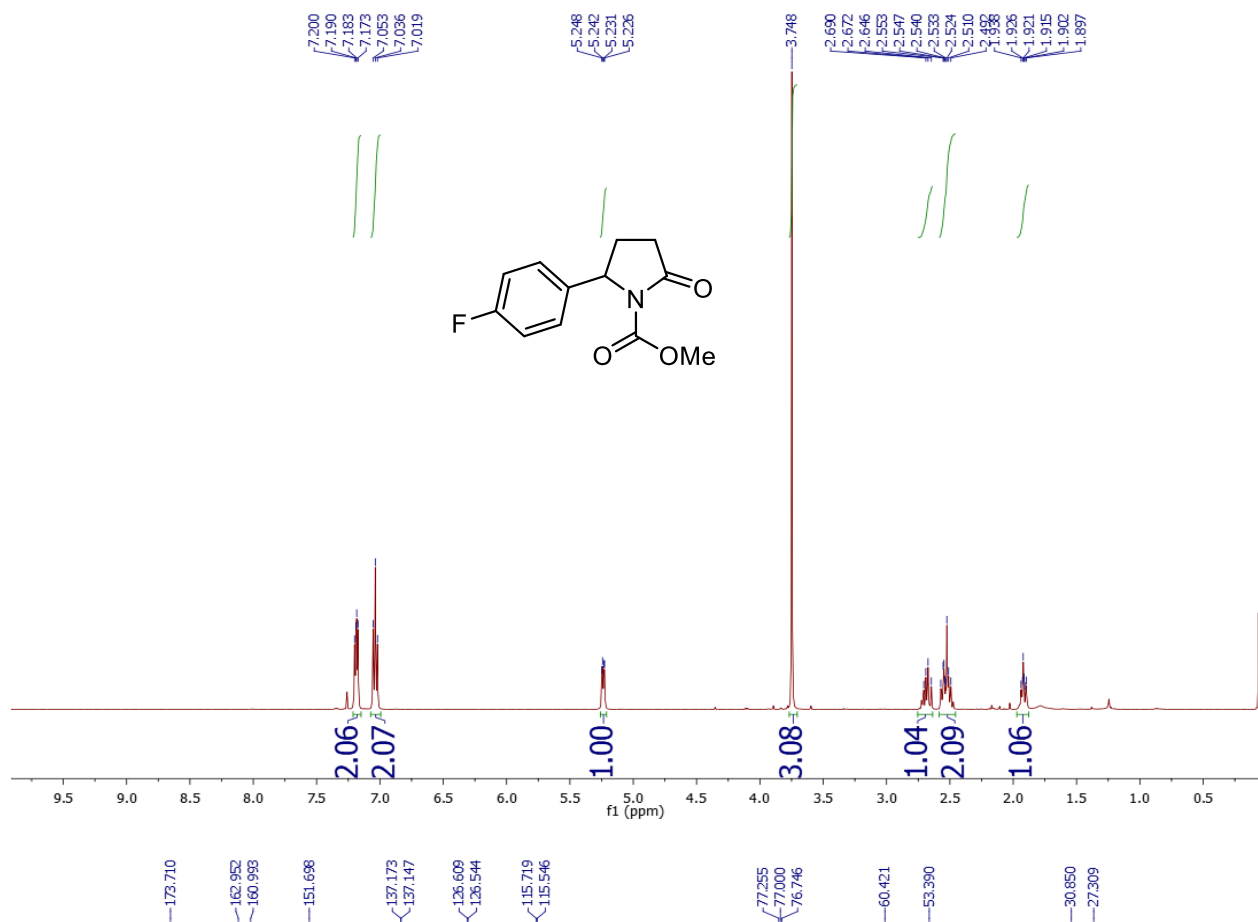


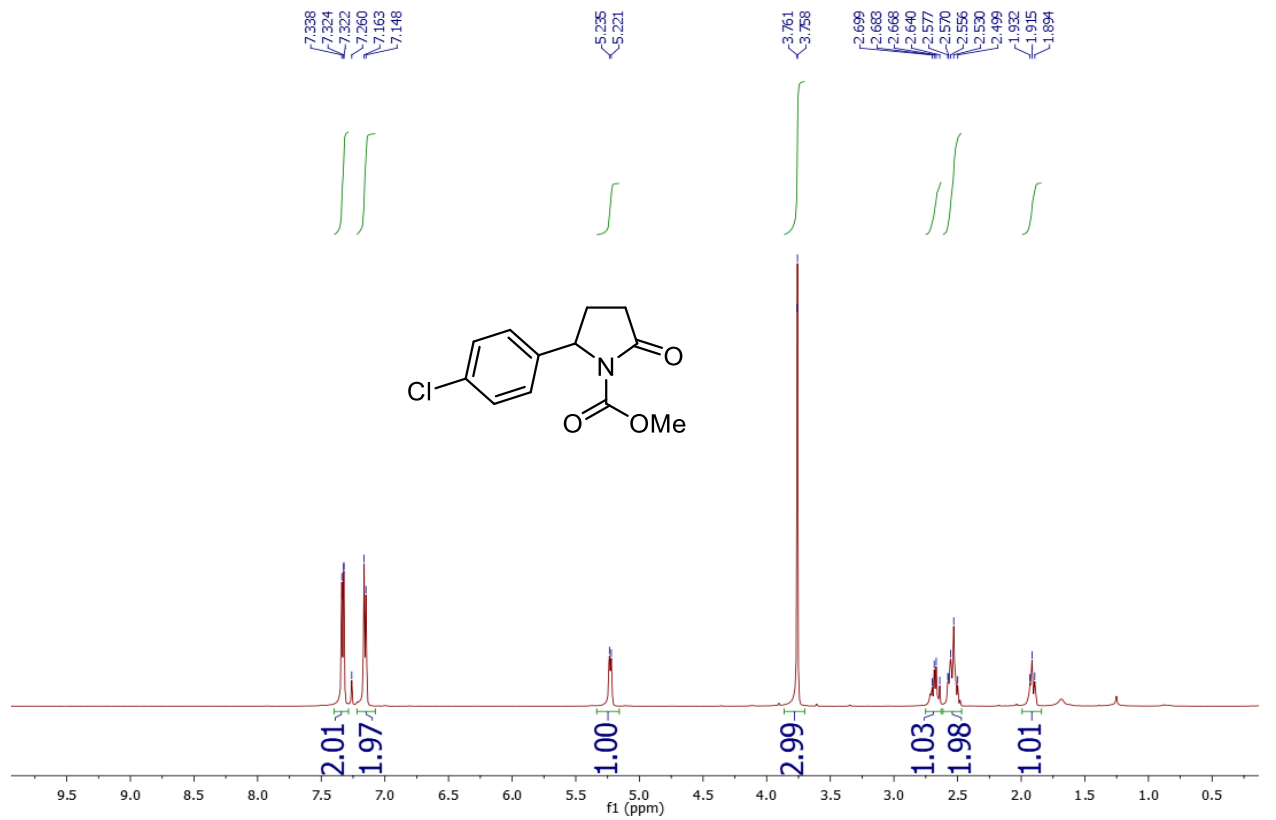
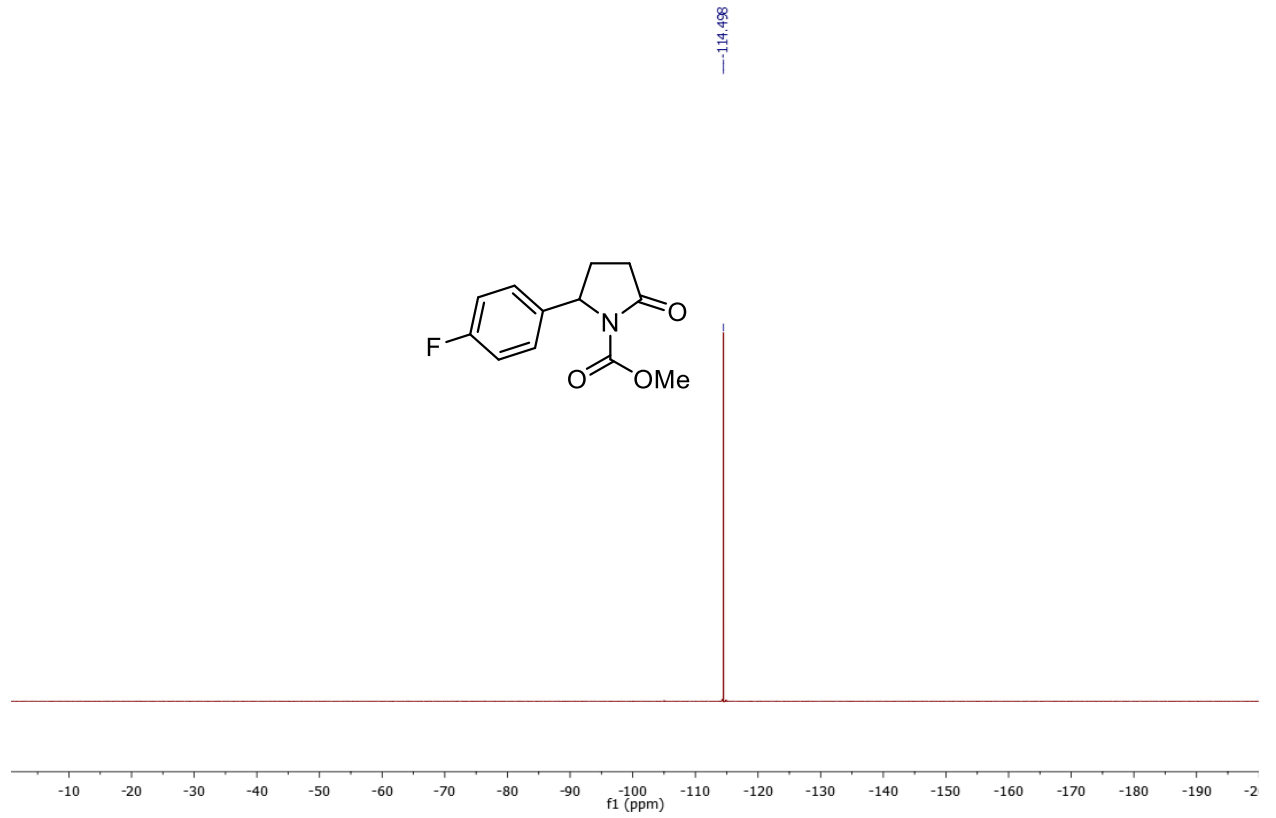


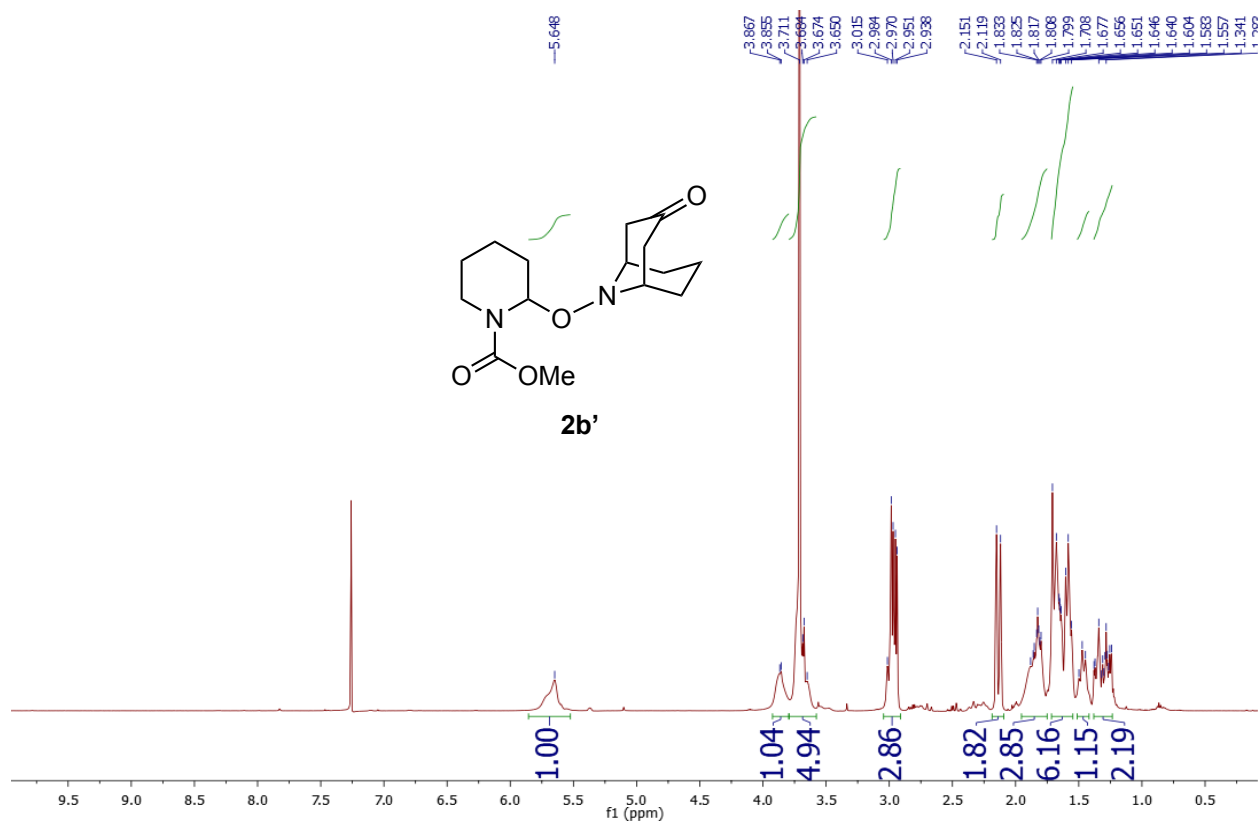
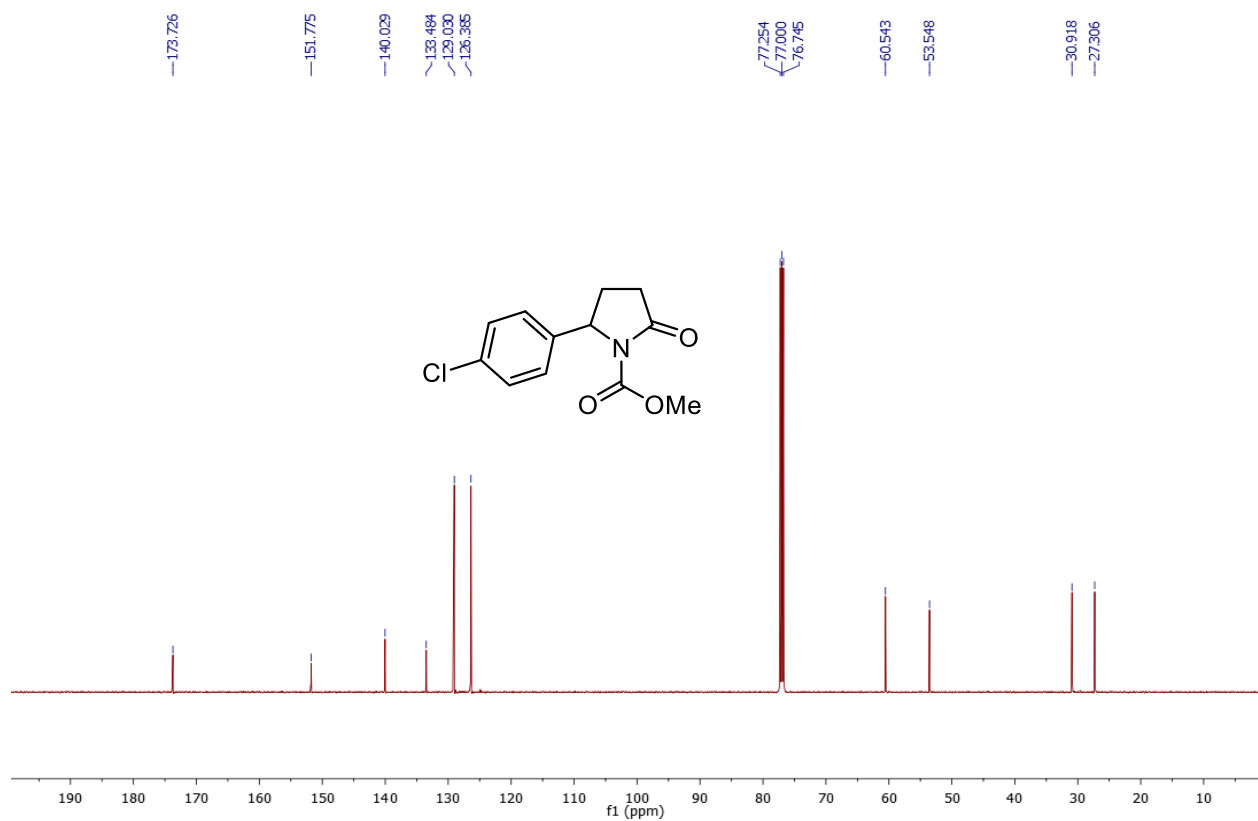
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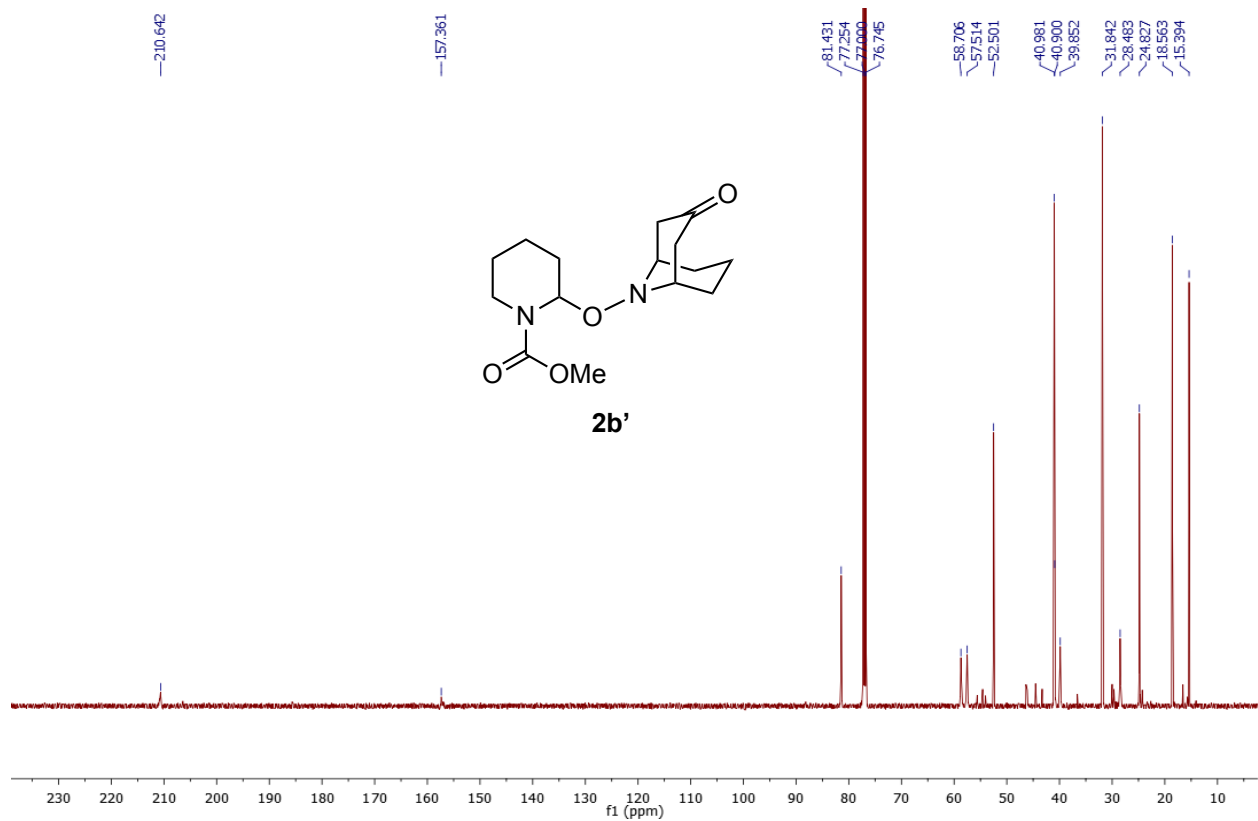












## 12. References

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