

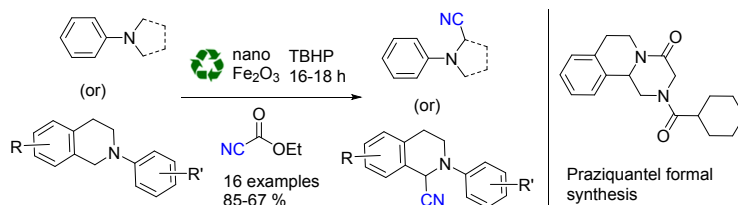
# Supporting information

## Magnetically recyclable iron oxide nanoparticles for the $\alpha$ -cyanation of amines under acid free conditions and the formal synthesis of Praziquantel†

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### *Materials and Methods:*

All reagents and starting materials were obtained commercially from Sigma-Aldrich and Alfa Aesar and Merck. The amines were purified and *N*-arylated derivatives are synthesised by reported procedures from their respective precursors. TLC chromatography was performed on silica (Silica Gel 60 F<sub>254</sub>) pre-coated aluminium plates and the products were visualized by UV lamp (PHILIPS TUV 8W lamp) and I<sub>2</sub> stain. X-ray powder diffraction (XRD) patterns were recorded using a Cu K $\alpha$  radiation source on a PAN Analytical, Holland, X'pert Pro powder diffractometer instrument. Transmission electron microscopy studies were performed using a PHILIPS CM200 Transmission Electron Microscope (TEM) at 100 kV. ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometer) were performed using ARCOS model instrument from M/s Spectro, Germany. The <sup>1</sup>H and <sup>13</sup>C NMR was recorded in CDCl<sub>3</sub> using residual solvent peak as a reference on a Avance III, Bruker spectrophotometer at 400 MHz and 100 MHz, respectively.

### *Catalytic studies*

In a typical experiment, Tertiary amine (1mmol), Ethyl Cyanoformate (248  $\mu$ L, 2.5 mmol) and methanol (2mL) were taken into 25ml single neck round bottomed flask back filled with nitrogen (a few drops of acetonitrile and hexane were in the case of tetrahydroisoquinoline derivatives to ensure the complete dissolution of starting materials]. Nano  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (16 mg, 10 mol %) and 70% aqueous *tert*-Butyl hydrogen peroxide (350  $\mu$ L, 2.5 equivalents) were added successively after 2 minutes at room temperature. The reaction mixture was heated up to 65° C for the respective time and then allowed to cool to room temperature. The catalyst was recovered by an external laboratory magnet and the solvent was removed under *vacuo*. Water (5mL) was added to the residue followed by extraction with ethyl acetate (3 X 5 mL). The aqueous phase was discarded, the combined organic layers were dried over sodium sulfate and concentrated under reduced pressure and purified on a short pad of neutral silica gel (neutral silica gel made by basifying the acidic sites of silica with

triethyl amine) as stationary phase and pet ether/ethyl acetate = 90:10 as mobile phase, to give the desired product. The product identity was further confirmed by NMR.

*Neutral silica gel preparation: Triethylamine (2-3 ml) was added to 150 gm 60-120 silica gel and made into slurry by addition of petroleum ether for the evenly distribution of the amine. The solvent was removed under reduced pressure on a rotary evaporator and dried in vacuum overnight.*

**Modified general procedure for the synthesis of N-Aryl amines :** - Copper (I) Iodide (10 mol%) and potassium phosphate (2 equiv) were taken into the round bottomed flask filled with nitrogen, 2-propanol and ethylene glycol (2 equiv) were added and allowed to stir for 5 min, secondary amine (1.3 equiv) and aryl iodides (1 equiv ) were added successively at room temperature. The reaction mixture was heated up to reflux temp (oil bath temp=105° C) for 30 hours and then allowed to cool to room temperature. The solvent was removed under *vacuo*, water *ca* 10mL was added and extracted with dichloromethane/diethyl ether. The organic layer was dried over sodium sulfate. The solvent was concentrated under reduced pressure and purified by column chromatography on neutral silica gel (hexane/ethyl acetate = 95:5) to give the desired product.

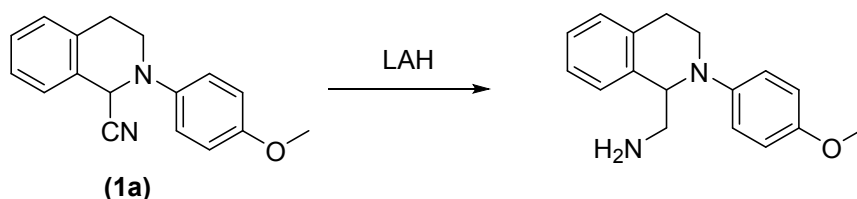
*Neutral silica gel preparation: Triethylamine (2-3 ml) was added to 150 gm 60-120 silica gel and made into slurry by addition of petroleum ether for the evenly distribution of the amine. The solvent was removed under reduced pressure on a rotary evaporator and dried in vacuum overnight.*

**Procedure for N-arylation of pyrrolidines:** - Copper (I) iodide (10 mol %) and potassium phosphate (2 equiv) were taken into the round bottomed flask backfilled with nitrogen. To this, 2-propanol and ethylene glycol (2 equiv) were added and allowed to stir for 5 min, pyrrolidine (3 equiv) and aryl iodides (1 equiv) were added successively at room temperature. The reaction mixture was heated up to 90° C (oil bath temp) for 24 hours and then allowed to cool to room temperature. Water 5 mL was added to the reaction mixture and the products were extracted with diethyl ether (3 X 5mL). The combined organic layers were dried over anhydrous sodium sulfate.

The solvent was concentrated under reduced pressure and purified by column chromatography on neutral silica gel (hexane/ethyl acetate = 95:5), to give the desired product.

*Neutral silica gel preparation: Triethylamine (2-3 ml) was added to 150 gm 60-120 silica gel and made into slurry by addition of petroleum ether for the evenly distribution of the amine. The solvent was removed under reduced pressure on a rotary evaporator and dried in vacuum overnight.*

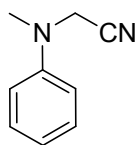
**Procedure for reduction of 2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile**



A solution of **1a** (1mmol) in dry ether (5ml) was added drop wise to a solution of LiAlH<sub>4</sub> (6mmol) in dry ether (8ml) at 0°C under N<sub>2</sub> atmosphere within 10-15 min (A few drops of dry THF was added for the complete dissolution of **1a**). After the complete addition, the resulting suspension was allowed to come to room temperature and stirred for 5-6 hrs. The reaction mass was quenched by drop wise addition of water (*ca.* 6ml) at 0-5°C. The resulting reaction mass was filtered through celite bed and the bed was washed with ether (2 X 10 mL). Filtrate was collected and then extracted with ether (3 X 20mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Purification by column chromatography on neutral silica gel\* (95:4.5:0.5, CH<sub>2</sub>Cl<sub>2</sub>: MeOH: NH<sub>3</sub>) afforded a brown color oil (63% yield).

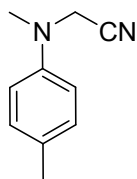
*Neutral silica gel preparation: Triethylamine (2-3 ml) was added to 150 gm 60-120 silica gel and made into slurry by addition of petroleum ether for the evenly distribution of the amine. The solvent was removed under reduced pressure on a rotary evaporator and dried in vacuum overnight.*

## 2-(Methyl(phenyl)amino)acetonitrile<sup>1</sup>



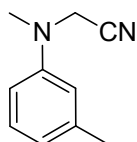
Known compound, Yellow oil, 80% yield (116.8mg, 1.0 mmol),  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.31 – 7.24 (m, 2H), 6.89 (tt,  $J = 7.5$ , 1.0 Hz, 1H), 6.84 – 6.79 (m, 2H), 4.05 (s, 2H), 2.91 (s, 3H);  $\delta_{\text{C}}$  (101 MHz,  $\text{CDCl}_3$ ) 147.8, 129.5, 120.1, 115.7, 114.8, 42.1, 39.2

## 2-(Methyl(*p*-tolyl)amino)acetonitrile<sup>1</sup>



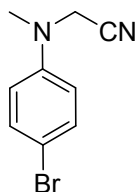
Known compound, Yellow oil, 83% yield (132.8mg, 1.0 mmol),  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.11 (d,  $J = 8.5$  Hz, 2H), 6.79 (d,  $J = 8.4$  Hz, 2H), 4.12 (s, 2H), 2.95 (s, 3H), 2.28 (s, 3H);  $\delta_{\text{C}}$  (101 MHz,  $\text{CDCl}_3$ ) 145.64, 129.96, 129.89, 115.47, 115.42, 42.84, 39.48, 20.39

## 2-(Methyl(*m*-tolyl)amino)acetonitrile<sup>1</sup>



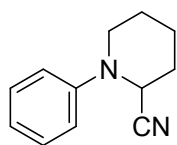
Known compound, Yellow oil, 78% yield (124.8mg, 1.0 mmol),  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ) 7.23 – 7.17 (m, 1H), 6.75 (d,  $J = 7.5$  Hz, 1H), 6.69 (d,  $J = 5.7$  Hz, 2H), 4.17 (s, 2H), 3.00 (s, 3H), 2.35 (s, 3H);  $\delta_{\text{C}}$  (126 MHz,  $\text{CDCl}_3$ ): 147.8, 139.3, 129.3, 121.2, 115.7, 115.5, 112.1, 42.4, 39.3, 21.8

## 2-((4-Bromophenyl)(methyl)amino)acetonitrile<sup>1</sup>



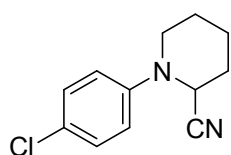
Known compound, Brown oil, 75% yield (168.75mg, 1.0 mmol),  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ) 7.44 – 7.35 (m, 2H), 6.80 – 6.66 (m, 2H), 4.14 (d,  $J = 5.5$  Hz, 2H), 2.98 (d,  $J = 5.6$  Hz, 3H);  $\delta_{\text{C}}$  (126 MHz,  $\text{CDCl}_3$ ) 146.8, 132.2, 116.4, 115.2, 112.5, 42.2, 39.3

### 1-Phenylpiperidine-2-carbonitrile<sup>1</sup>



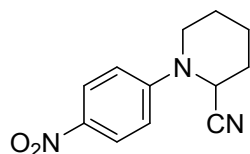
Known compound, White solid, 78% yield (145.2mg, 1.0 mmol), mp 58-61 °C,  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.35 – 7.27 (m, 2H), 7.03 – 6.95 (m, 3H), 4.62 (t,  $J = 3.5$  Hz, 1H), 3.49 – 3.40 (m, 1H), 3.03 (td,  $J = 12.0, 2.6$  Hz, 1H), 2.07 – 1.94 (m, 2H), 1.89 – 1.80 (m, 2H), 1.77 – 1.62 (m, 2H);  $\delta_{\text{C}}$  (101 MHz,  $\text{CDCl}_3$ ) 149.8, 129.3, 122.1, 118.3, 117.2, 52.0, 46.6, 29.2, 25.1, 20.2

### 1-(4-Chlorophenyl)piperidine-2-carbonitrile



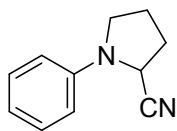
Pale yellow solid, 80% yield (176.56mg, 1.0 mmol), mp 105-107 °C;  $R_f$  0.6 (2:8, EtOAc: Hexane);  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ) 7.37 – 7.17 (m, 2H), 7.04 – 6.83 (m, 2H), 4.57 (t,  $J = 3.3$  Hz, 1H), 3.38 (d,  $J = 10.8$  Hz, 1H), 3.00 (td,  $J = 11.9, 2.4$  Hz, 1H), 2.14 – 1.95 (m, 2H), 1.86 (dd,  $J = 8.7, 2.9$  Hz, 2H), 1.77 – 1.61 (m, 2H);  $\delta_{\text{C}}$  (75 MHz,  $\text{CDCl}_3$ ) 148.4, 129.3, 127.3, 119.7, 116.89, 52.11, 46.69, 29.18, 25.04, 20.06. **HRMS**  $m/z$  (ESI-MS): Calculated for  $\text{C}_{12}\text{H}_{14}\text{ClN}_2$   $[\text{M}+\text{H}]^+$ : 221.0846, Found: 221.0972

### 1-(4-Nitrophenyl) piperidine-2-carbonitrile



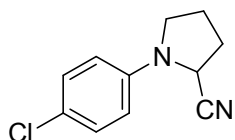
Yellow solid; Colourless oil, 82% yield (189.6mg, 1.0 mmol), mp 109-111 °C;  $R_f$  0.4 (2:8, EtOAc : Hexane),  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ) 8.25 – 8.13 (m, 2H), 7.04 – 6.94 (m, 2H), 4.85 (s, 1H), 3.77 (d,  $J = 12.6$  Hz, 1H), 3.12 (td,  $J = 12.5, 2.5$  Hz, 1H), 2.14 (d,  $J = 12.9$  Hz, 1H), 2.06 – 1.88 (m, 3H), 1.76 (m,  $J = 16.3, 12.2, 8.0, 3.8$  Hz, 2H);  $\delta_{\text{C}}$  (75 MHz,  $\text{CDCl}_3$ ) 154.0, 141.0, 125.7, 116.6, 115.5, 49.1, 45.8, 28.9, 24.7, 19.9. **HRMS**  $m/z$  (ESI-MS): Calculated  $\text{C}_{12}\text{H}_{17}\text{N}_3\text{O}_2$   $[\text{M}+4\text{H}]^+$ : 235.1321; Found: 235.2352.

### 1-Phenylpyrrolidine-2-carbonitrile<sup>1</sup>



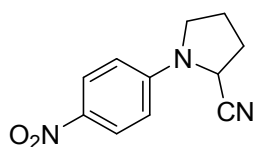
Known compound, Brownish yellow oil, 63% yield (108.5mg, 1.0 mmol),  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.29 (dd,  $J = 8.5, 7.5$  Hz, 2H), 6.82 (t,  $J = 7.3$  Hz, 1H), 6.69 (d,  $J = 8.0$  Hz, 2H), 4.48 – 4.39 (m, 1H), 3.49 – 3.41 (m, 1H), 3.36 (dd,  $J = 15.7, 8.2$  Hz, 1H), 2.47 – 2.36 (m, 1H), 2.35 – 2.13 (m, 3H);  $\delta_{\text{C}}$  (101 MHz,  $\text{CDCl}_3$ ) 145.16, 129.45, 119.28, 118.19, 112.65, 49.07, 47.45, 31.54, 23.95

### 1-(4-Chlorophenyl) pyrrolidine-2-carbonitrile<sup>2</sup>



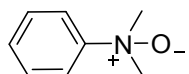
White solid, 67% yield (138.4mg, 1.0 mmol), mp 80-83 °C,  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.23 (d,  $J = 8.9$  Hz, 2H), 6.60 (d,  $J = 8.9$  Hz, 2H), 4.39 (d,  $J = 7.5$  Hz, 1H), 3.46 – 3.38 (m, 1H), 3.34 (dd,  $J = 15.7, 8.2$  Hz, 1H), 2.46 – 2.37 (m, 1H), 2.36 – 2.23 (m, 2H), 2.19 (m,  $J = 11.6, 7.5, 3.0$  Hz, 1H);  $\delta_{\text{C}}$  (101 MHz,  $\text{CDCl}_3$ ) 143.8, 129.3, 123.2, 118.9, 113.8, 49.2, 47.7, 31.5, 23.9

### 1-(4-Nitrophenyl) pyrrolidine-2-carbonitrile<sup>2</sup>



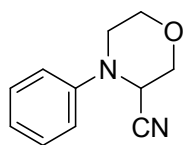
Known compound, Yellow solid, 73% yield (158.7mg, 1.0 mmol), mp 111-113 °C,  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 8.17 (d,  $J = 9.2$  Hz, 2H), 6.66 (d,  $J = 9.2$  Hz, 2H), 4.60 – 4.51 (m, 1H), 3.67 – 3.56 (m, 1H), 3.47 (dd,  $J = 16.5, 8.7$  Hz, 1H), 2.60 – 2.24 (m, 4H);  $\delta_{\text{C}}$  (101 MHz,  $\text{CDCl}_3$ ) 149.7, 139.0, 126.1, 117.9, 111.8, 48.9, 48.0, 31.6, 24.1

### *N,N*-Dimethylaniline oxide<sup>8</sup>



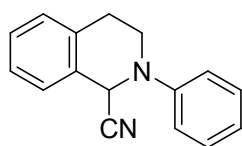
Known compound, White solid, 99% yield (135.8 mg, 1.0 mmol), mp 124-126 °C,  $\delta_{\text{H}}$  (400 MHz,  $\text{D}_2\text{O}$ ) 5.88 (d,  $J = 7.9$  Hz, 2H), 5.65 – 5.55 (m, 3H), 2.88 (s, 6H);  $\delta_{\text{C}}$  (101 MHz,  $\text{D}_2\text{O}$ ) 151.43, 129.70, 129.53, 119.14, 61.15

### 4-Phenylmorpholine-3-carbonitrile<sup>3</sup>



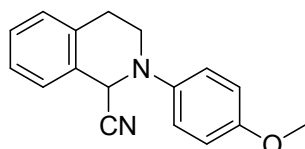
Known compound, White solid, 67% yield (126.1mg, 1.0 mmol),  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ) 7.40 – 7.30 (m, 2H), 7.09 – 7.01 (m, 1H), 7.01 – 6.95 (m, 2H), 4.45 – 4.39 (m, 1H), 4.19 – 4.13 (m, 1H), 4.12 – 4.06 (m, 1H), 3.91 (dd,  $J = 11.5, 2.8$  Hz, 1H), 3.80 – 3.69 (m, 1H), 3.28 (dd,  $J = 8.1, 2.7$  Hz, 2H);  $\delta_{\text{C}}$  (101 MHz,  $\text{CDCl}_3$ ) 148.26, 129.59, 122.66, 117.27, 115.96, 68.09, 66.90, 51.05, 45.47

### 2-Phenyl-1, 2, 3, 4-tetrahydroisoquinoline-1-carbonitrile<sup>4</sup>



Known compound, White solid, 80% yield (187.4mg, 1.0 mmol), mp 98-101°C,  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.38 – 7.31 (m, 2H), 7.30 – 7.19 (m, 4H), 7.09 – 7.04 (m, 2H), 7.03 – 6.97 (m, 1H), 5.49 (s, 1H), 3.74 (m,  $J = 12.4, 5.9, 3.0, 1.1$  Hz, 1H), 3.45 (m,  $J = 12.4, 10.7, 4.1$  Hz, 1H), 3.13 (m,  $J = 16.5, 10.7, 6.0$  Hz, 1H), 2.93 (dt,  $J = 16.3, 3.5$  Hz, 1H);  $\delta_{\text{C}}$  (101 MHz,  $\text{CDCl}_3$ ) 148.42, 134.68, 129.66, 129.63, 129.41, 128.81, 127.12, 126.90, 121.91, 117.83, 117.62, 53.22, 44.24, 28.58

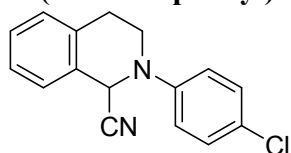
### 2-(4-Methoxyphenyl)-1, 2, 3, 4-tetrahydroisoquinoline-1-carbonitrile<sup>1</sup>



Known compound, Pale yellow solid, 85% yield (224.6mg, 1.0 mmol),  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.31 – 7.18 (m, 4H), 7.10 – 7.04 (m, 2H), 6.93 – 6.87 (m, 2H), 5.35 (s, 1H), 3.77 (s, 3H), 3.56 (dd,  $J = 12.1, 6.0$  Hz, 1H), 3.41 (td,  $J = 11.7, 3.9$  Hz, 1H), 3.14 (m,  $J = 17.1, 11.1, 6.3$  Hz, 1H), 2.90 (d,  $J = 16.4$  Hz, 1H);  $\delta_{\text{C}}$  (101 MHz,  $\text{CDCl}_3$ ) 155.65, 142.55, 134.31, 129.62, 129.45, 128.64, 127.06, 126.68, 121.02, 117.58, 114.74, 55.63, 55.52, 44.86, 28.69. **HRMS**  $m/z$  (ESI-MS): Calculated for  $\text{C}_{17}\text{H}_{17}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$ : 265.1341, Found : 265.1345

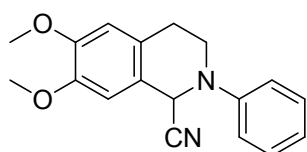


### 2-(4-Chlorophenyl)-1, 2, 3, 4-tetrahydroisoquinoline-1-carbonitrile<sup>5</sup>



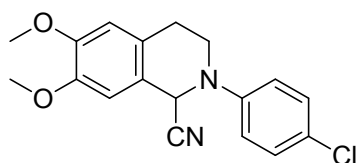
Known compound, White solid, 78% yield (209.5mg, 1.0 mmol),  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.34 – 7.27 (m, 5H), 7.26 – 7.22 (m, 1H), 7.03 – 6.98 (m, 2H), 5.45 (s, 1H), 3.76 – 3.65 (m, 1H), 3.46 (m,  $J = 12.3$ , 10.8, 4.1 Hz, 1H), 3.15 (m,  $J = 16.5$ , 10.6, 5.9 Hz, 1H), 2.97 (dt,  $J = 16.3$ , 3.5 Hz, 1H);  $\delta_{\text{C}}$  (101 MHz,  $\text{CDCl}_3$ ) 147.2, 134.5, 129.7, 129.5, 129.4, 129.1, 127.2, 127.1, 119.1, 117.6, 53.3, 44.5, 28.6.

### 6, 7-Dimethoxy-2-phenyl-1, 2, 3, 4-tetrahydroisoquinoline-1-carbonitrile<sup>6</sup>



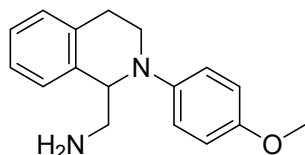
Known compound, Pale yellow solid, 72% yield (211.9mg, 1.0 mmol),  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.35 (t,  $J = 7.7$  Hz, 2H), 7.08 (d,  $J = 8.0$  Hz, 2H), 7.01 (t,  $J = 7.3$  Hz, 1H), 6.71 (d,  $J = 26.9$  Hz, 2H), 5.45 (s, 1H), 3.88 (s, 6H), 3.77 (dd,  $J = 12.0$ , 4.6 Hz, 1H), 3.44 (td,  $J = 11.9$ , 3.6 Hz, 1H), 3.15 – 3.02 (m, 1H), 2.84 (d,  $J = 16.1$  Hz, 1H);  $\delta_{\text{C}}$  (101 MHz,  $\text{CDCl}_3$ ) 149.4, 148.4, 148.1, 129.5, 126.9, 121.9, 121.1, 117.9, 117.7, 111.5, 109.3, 56.1, 56.0, 53.1, 44.2, 28.1. **HRMS**  $m/z$  (ESI): Calculated for  $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_2$  (M+H): 295.1446, found (M+H): 295.1454

### 2-(4-Chlorophenyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile



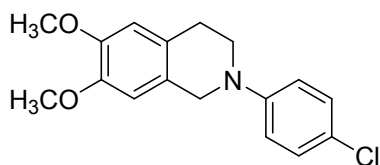
Known compound, White crystalline solid; 70% yield (230.1mg, 1.0 mmol), mp 153-155 °C;  $R_f$  0.4 (3:7, EtOAc: Hexane),  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.30 (d,  $J = 8.9$  Hz, 2H), 6.99 (d,  $J = 8.9$  Hz, 2H), 6.71 (d,  $J = 23.2$  Hz, 2H), 5.39 (s, 1H), 3.88 (d,  $J = 2.1$  Hz, 6H), 3.70 (dd,  $J = 12.3$ , 4.2 Hz, 1H), 3.48 – 3.33 (m, 1H), 3.06 (m,  $J = 16.6$ , 11.0, 5.9 Hz, 1H), 2.84 (dt,  $J = 16.1$ , 3.1 Hz, 1H);  $\delta_{\text{C}}$  (101 MHz,  $\text{CDCl}_3$ ) 149.5, 148.1, 147.0, 129.5, 127.0, 126.7, 120.7, 119.0, 117.6, 111.5, 109.3, 56.1, 56.0, 52.9, 44.3, 28.0. **HRMS**  $m/z$  (ESI-MS): Calculated for  $\text{C}_{18}\text{H}_{18}\text{ClN}_2\text{O}_2$  [M+H]<sup>+</sup>: 329.1057, Found : 329.1049

## (2-(4-Methoxyphenyl)-1, 2, 3, 4-tetrahydroisoquinolin-1-yl) methanamine<sup>7</sup>



Known compound, Brownish yellow oil, 63% yield (174.3mg, 1.0 mmol),  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22 – 7.05 (m, 4H), 6.93 (d,  $J$  = 8.9 Hz, 2H), 6.78 (d,  $J$  = 8.9 Hz, 2H), 4.46 (dd,  $J$  = 8.3, 5.0 Hz, 1H), 3.73 (s, 3H), 3.52 (dd,  $J$  = 7.7, 4.1 Hz, 2H), 3.05 (dd,  $J$  = 13.1, 8.7 Hz, 1H), 2.99 – 2.84 (m, 2H), 2.62 (dt,  $J$  = 16.3, 3.9 Hz, 1H), 2.24 (s, 2H);  $\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 153.3, 144.8, 136.2, 135.4, 128.9, 127.2, 126.5, 126.0, 118.9, 114.5, 62.4, 55.6, 46.7, 43.5, 25.8

## 2-(4-chlorophenyl)-6, 7-dimethoxy-1, 2, 3, 4-tetrahydroisoquinoline

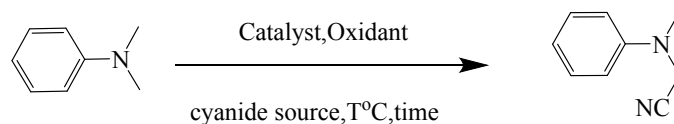


Pale yellow solid; mp 105-106 °C;  $R_f$  0.5 (2:8, EtOAc: Hexane)  
 $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.22 (d,  $J$  = 9.0 Hz, 2H), 6.88 (d,  $J$  = 9.0 Hz, 2H), 6.64 (s, 2H), 4.30 (s, 2H), 3.87 (d,  $J$  = 2.4 Hz, 6H), 3.51 (t,  $J$  = 5.8 Hz, 2H), 2.89 (t,  $J$  = 5.7 Hz, 2H);  $\delta_{\text{C}}$  (101 MHz,  $\text{CDCl}_3$ ) 149.07, 147.59, 147.47, 128.95, 126.41, 125.70, 123.38, 116.33, 111.21, 109.21, 55.94, 55.90, 50.41, 46.73, 28.32. **HRMS**  $m/z$  ESI-MS: calculated  $\text{C}_{17}\text{H}_{19}\text{ClNO}_2$   $[\text{M}+\text{H}]^+$ , 304.1104, Found: 304.1122

## References:-

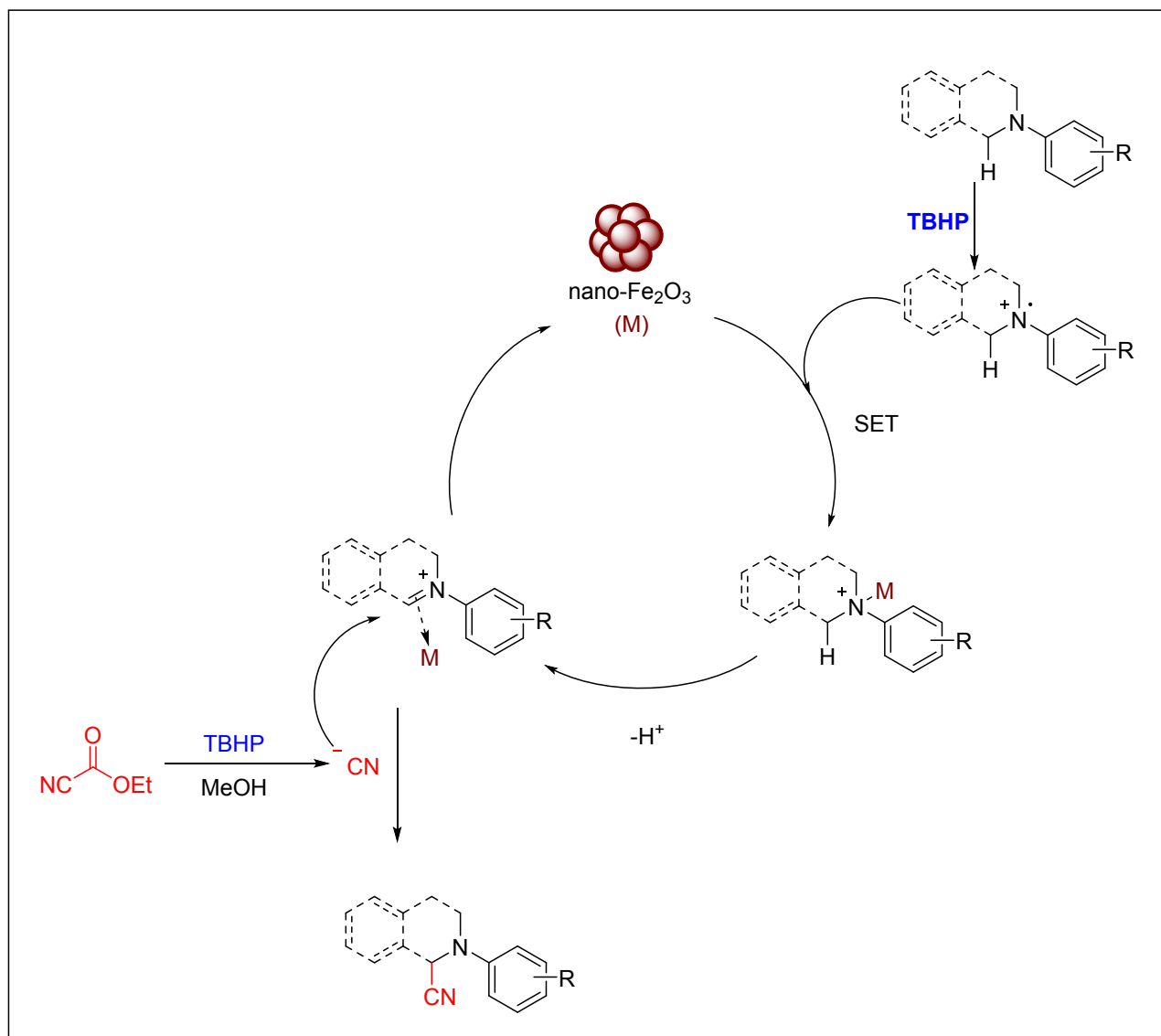
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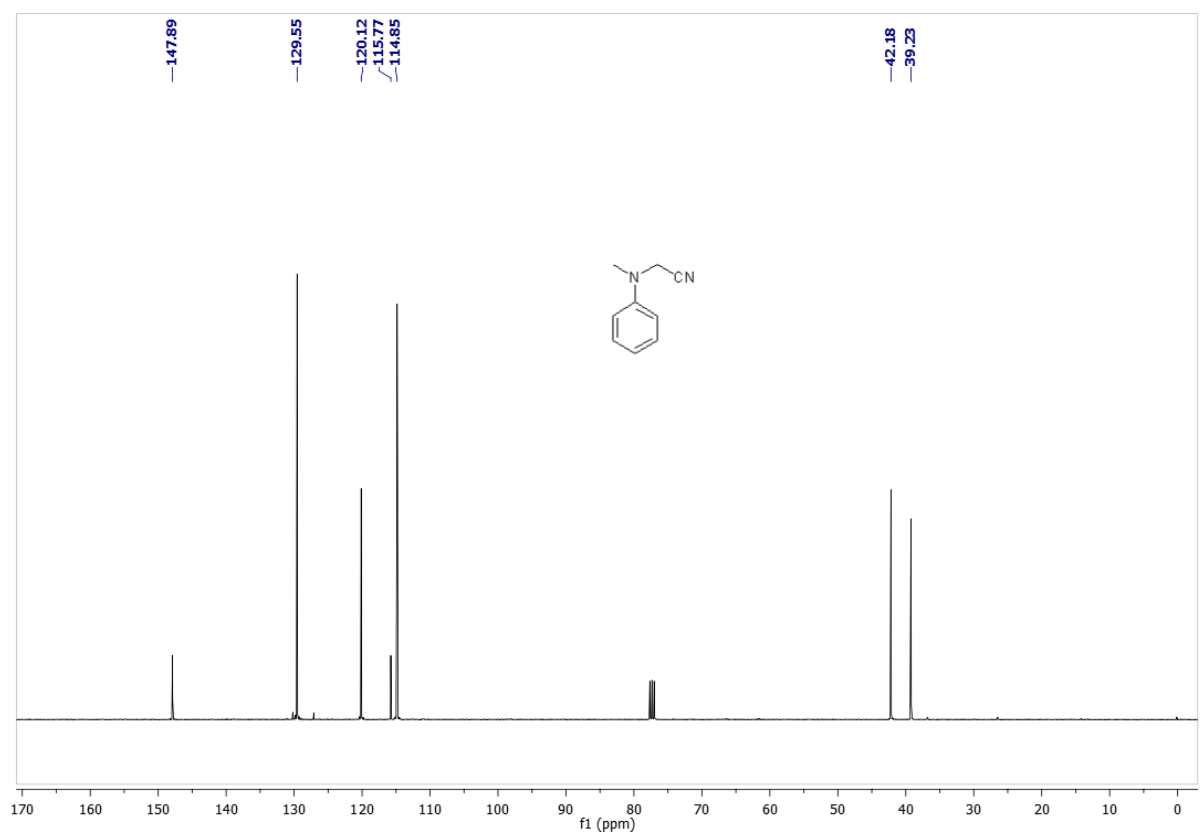
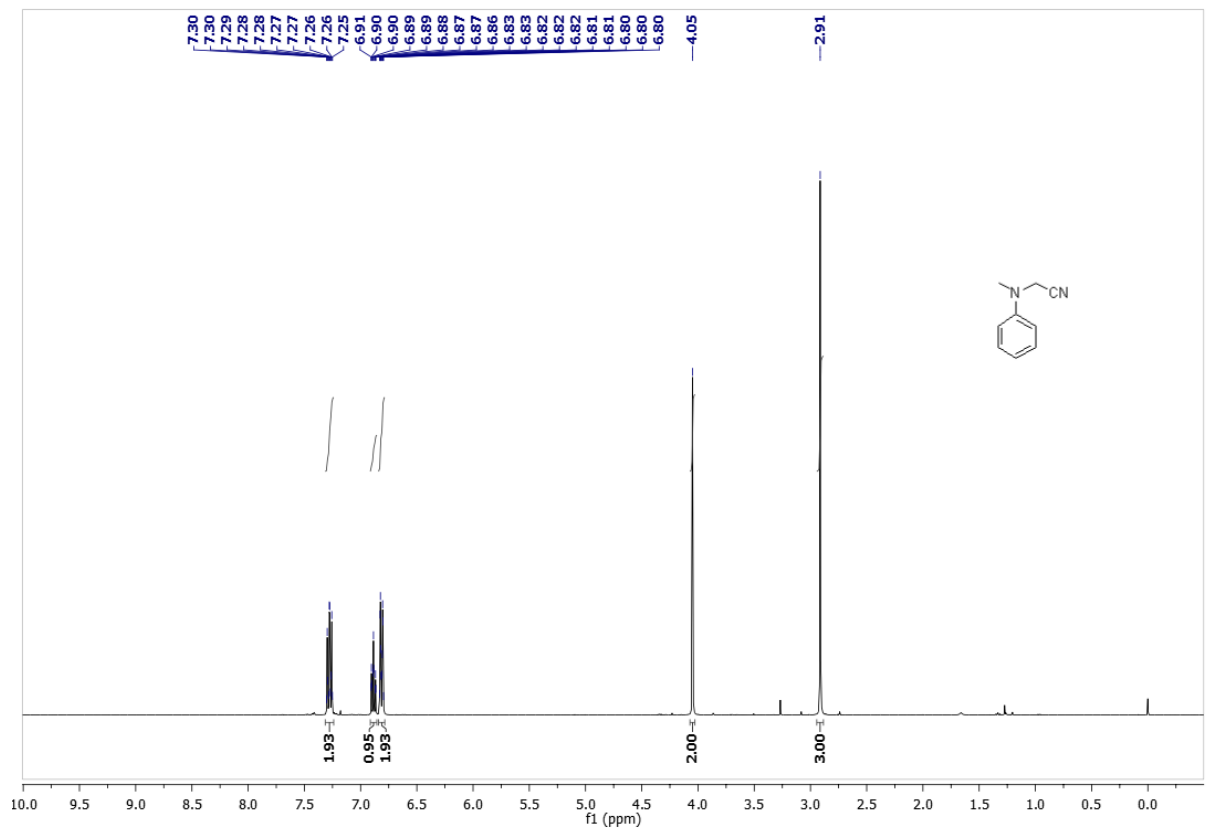
**Table** Optimization of reaction conditions of cyanation of amines

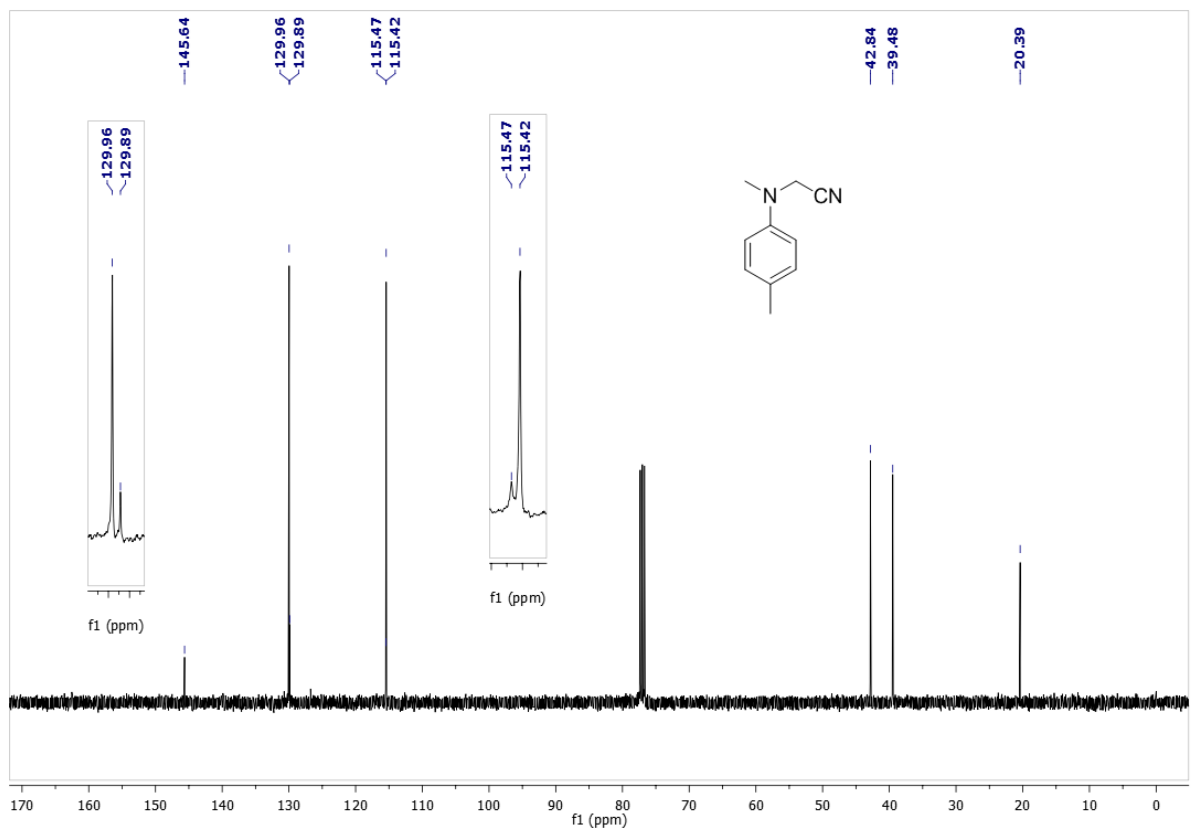
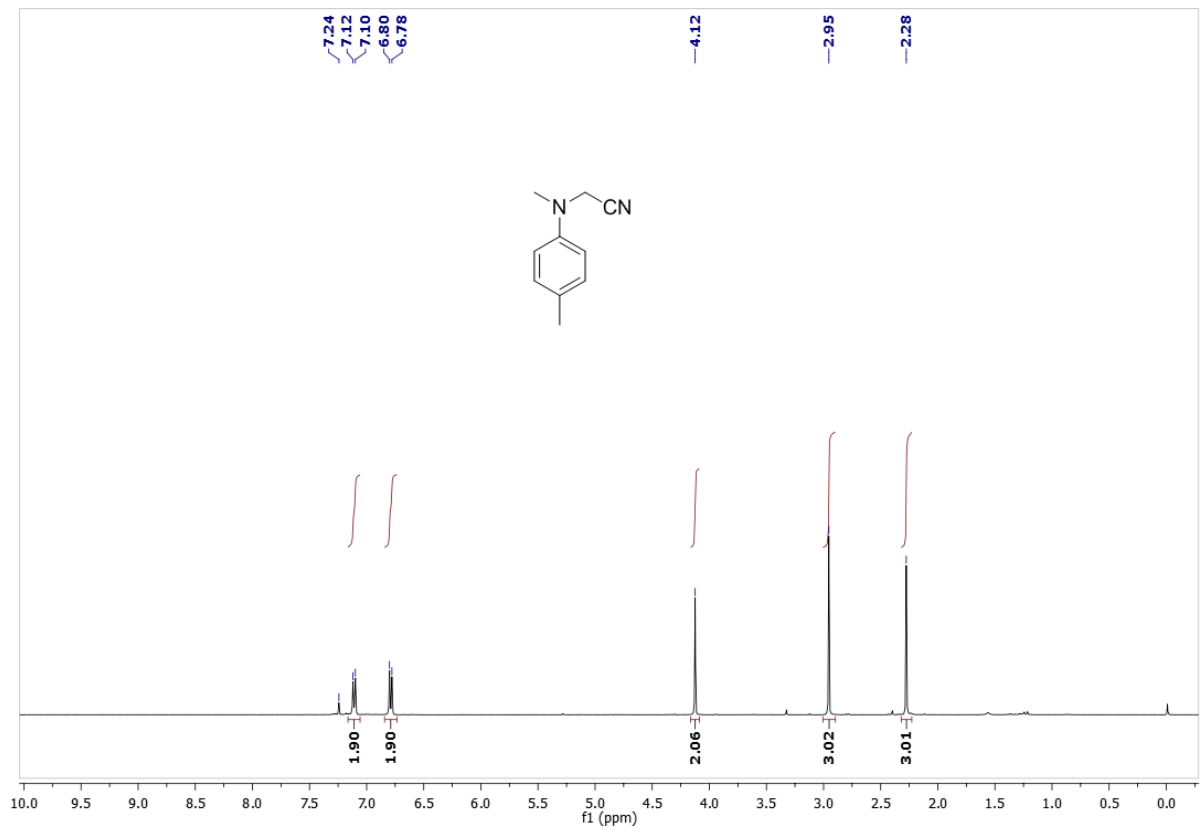
Entry	Catalyst <sup>a</sup>	Solvent	Cyanide source	Temperature <sup>o</sup> C/ Time(h)	Oxidant	%Yield <sup>b</sup>
1	bulk Fe <sub>2</sub> O <sub>3</sub>	MeOH	Ethyl cyanoformate	65°C/16	TBHP	55
2	Fe-BTC MOF (Basolite F-300)	MeOH	Ethyl cyanoformate	65°C/16	TBHP	15 <sup>c</sup>
3	Fe <sup>III</sup> (OH)(OAc) <sub>2</sub>	MeOH	Ethyl cyanoformate	65°C/16	TBHP	30
4	CuFe <sub>2</sub> O <sub>4</sub>	MeOH	Ethyl cyanoformate	65°C/16	TBHP	40
5	FeCl <sub>3</sub>	H <sub>2</sub> O	Ethyl cyanoformate	65°C/16	TBHP	45 <sup>d</sup>
6	nano-Fe <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O	Ethyl cyanoformate	65°C/16	TBHP	10
7	nano-Fe <sub>2</sub> O <sub>3</sub>	MeOH	Ethyl cyanoformate	65°C/16	TBHP	80
8	nano-Fe <sub>2</sub> O <sub>3</sub>	EtOH	Ethyl cyanoformate	65°C/16	TBHP	73
9	nano-Fe <sub>2</sub> O <sub>3</sub>	CH <sub>3</sub> CN	EtOH	65°C/16	TBHP	60
10	nano-Fe <sub>2</sub> O <sub>3</sub>	Isopropyl alcohol	Ethyl cyanoformate	65°C/16	TBHP	45
11	nano-Fe <sub>2</sub> O <sub>3</sub>	MeOH	TMSCN	65°C/16	TBHP	73
12	nano-Fe <sub>3</sub> O <sub>4</sub>	MeOH	Ethyl cyanoformate	65°C/16	TBHP	55
13	nano-Fe <sub>2</sub> O <sub>3</sub>	MeOH	PhCH <sub>2</sub> CN	65°C/16	TBHP	12
14	nano-Fe <sub>2</sub> O <sub>3</sub>	MeOH	Mandelonitrile	65°C/16	TBHP	40
15	nano-Fe <sub>2</sub> O <sub>3</sub>	MeOH	K <sub>3</sub> [Fe(CN) <sub>6</sub> ]	65°C/16	TBHP	15
16	nano-Fe <sub>2</sub> O <sub>3</sub>	MeOH	D/L-lactonitrile	60°C/16	TBHP	55 <sup>e</sup>
17	nano-Fe <sub>2</sub> O <sub>3</sub>	MeOH	Malononitrile	65°C/16	TBHP	0
18	nano-Fe <sub>2</sub> O <sub>3</sub>	MeOH	KSCN	65°C/16	TBHP	45
19	nano-Fe <sub>2</sub> O <sub>3</sub>	MeOH	Ethyl cyanoformate	65°C/16	O <sub>2</sub>	30
20	nano-Fe <sub>2</sub> O <sub>3</sub>	MeOH	Ethyl cyanoformate	65°C/16	H <sub>2</sub> O <sub>2</sub>	0 <sup>f</sup>

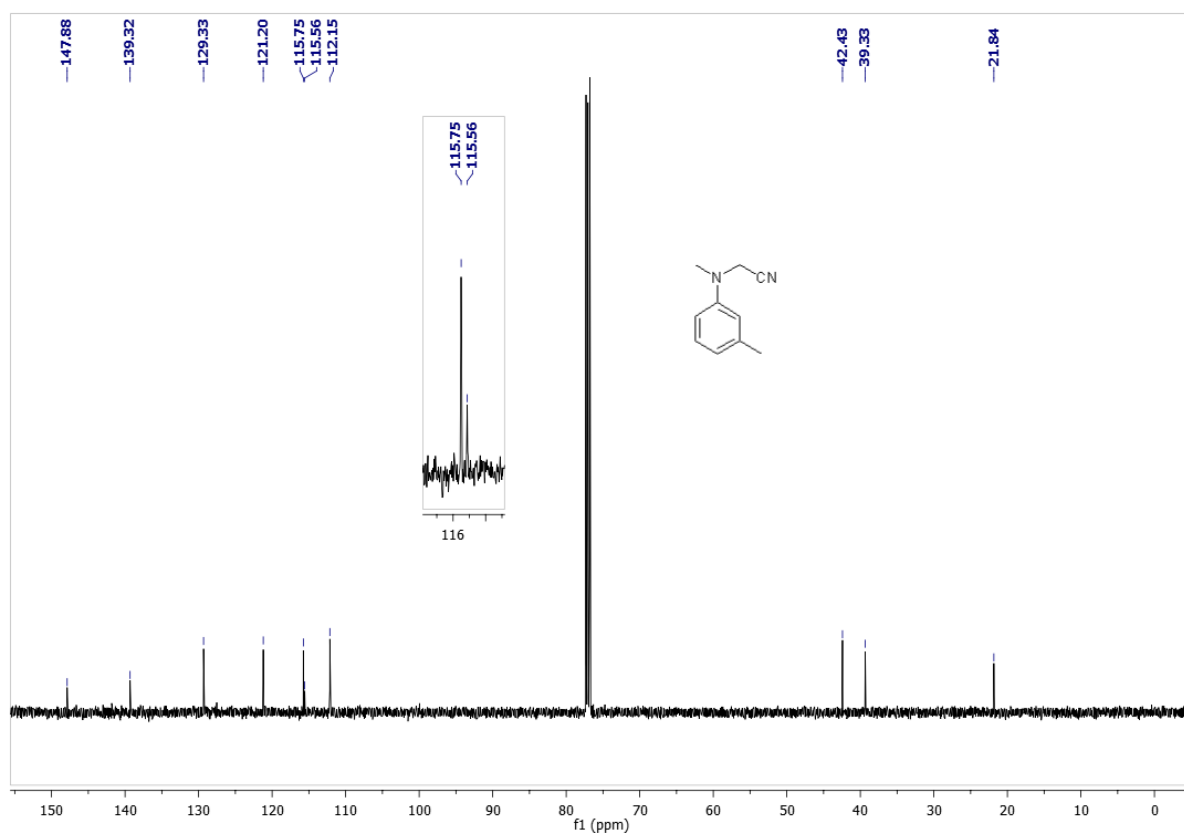
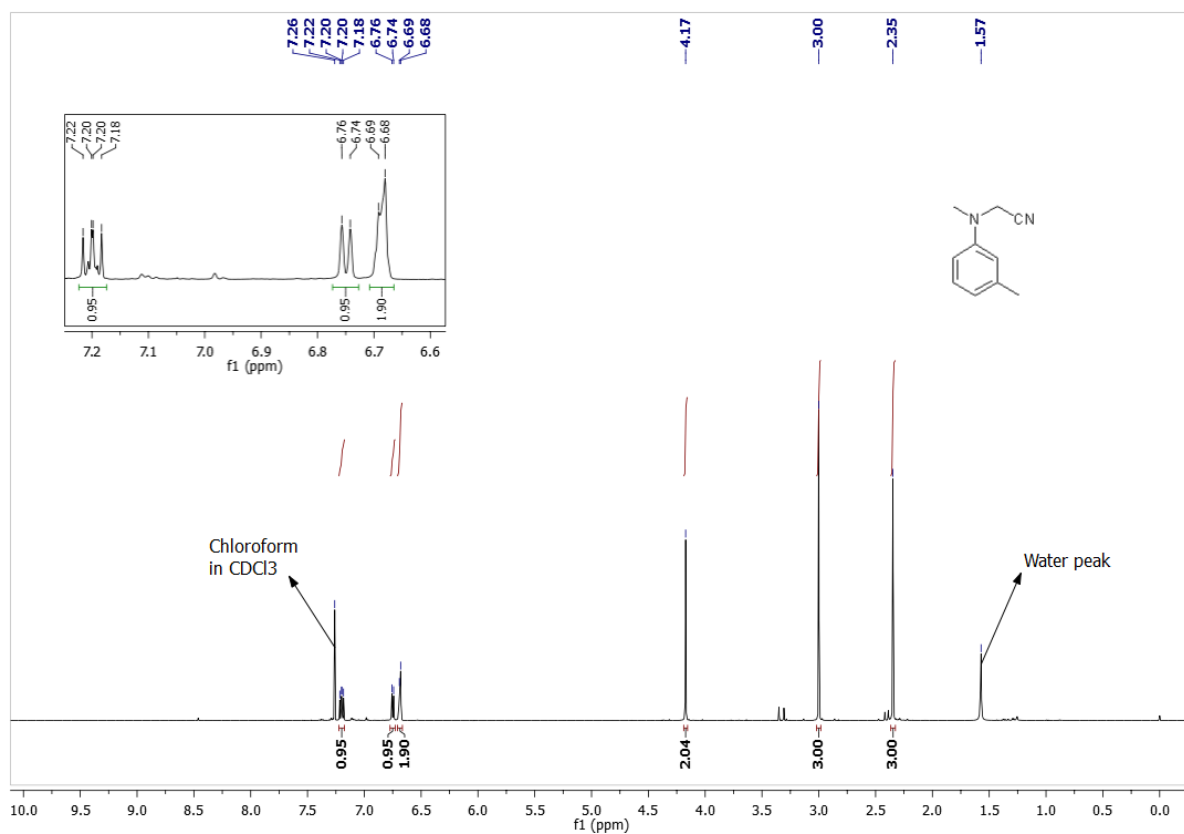
<sup>a</sup> Catalyst(10mol%), <sup>b</sup> Isolated yield ,cyanide source (2 equiv), solvent (2 mL), oil bath temperature, <sup>c</sup>catalyst decomposed, <sup>d</sup> $\beta$ -Cyclodextrin was added as additive, <sup>e</sup> no change even after prolonged heating, <sup>f</sup>N-oxide was formed in 99% yield



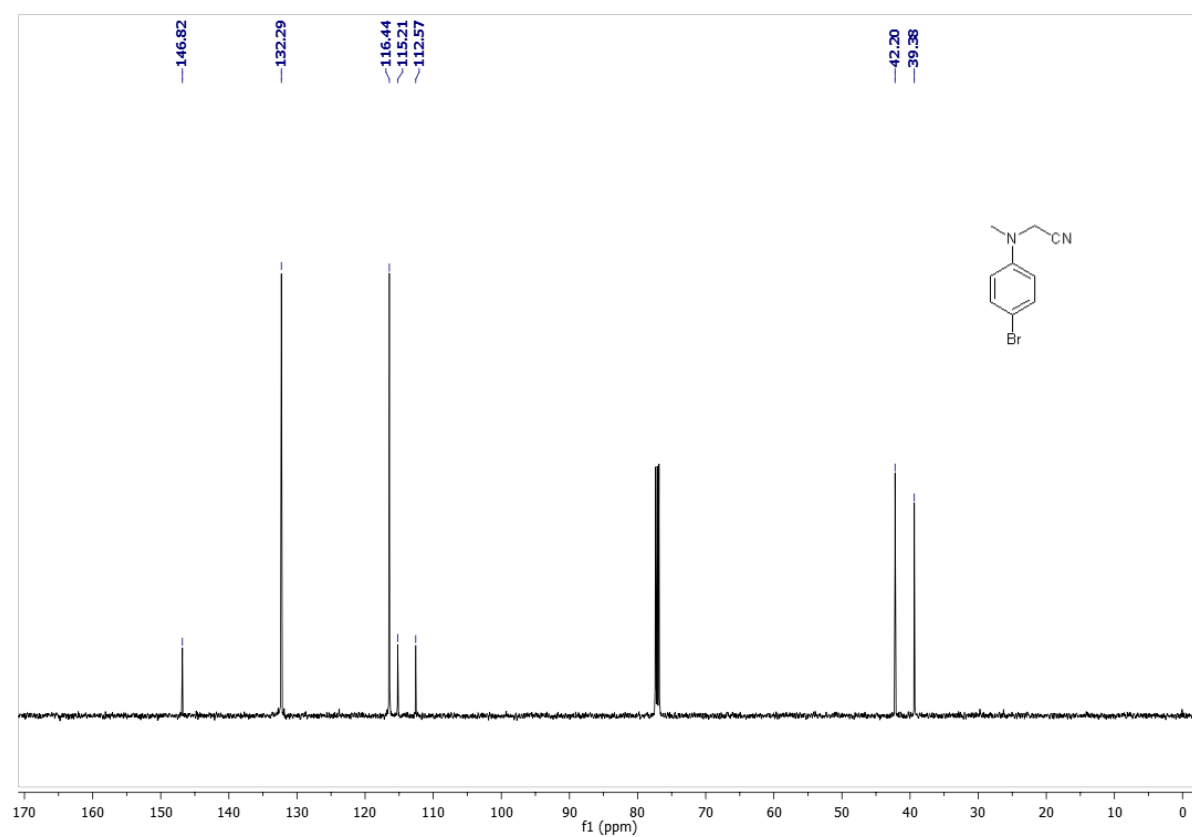
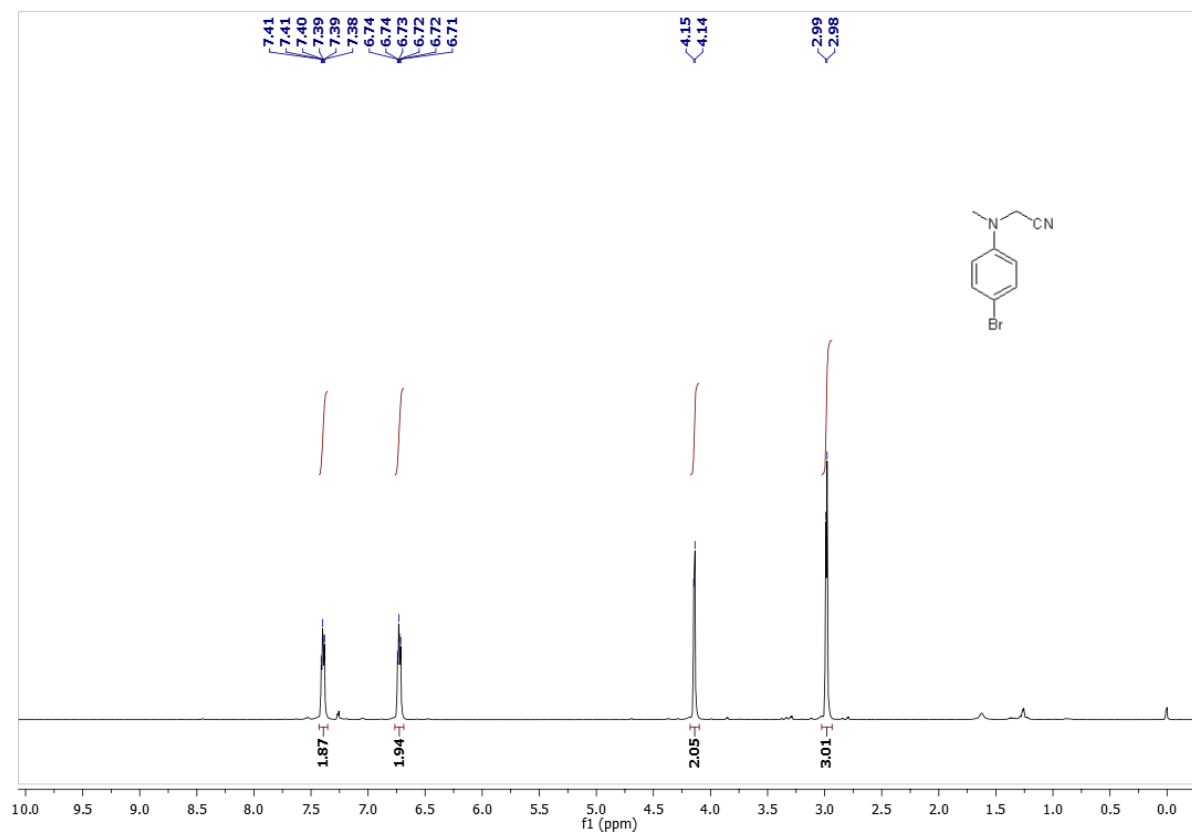
Plausible mechanism of cyanation using nano-Fe<sub>2</sub>O<sub>3</sub>

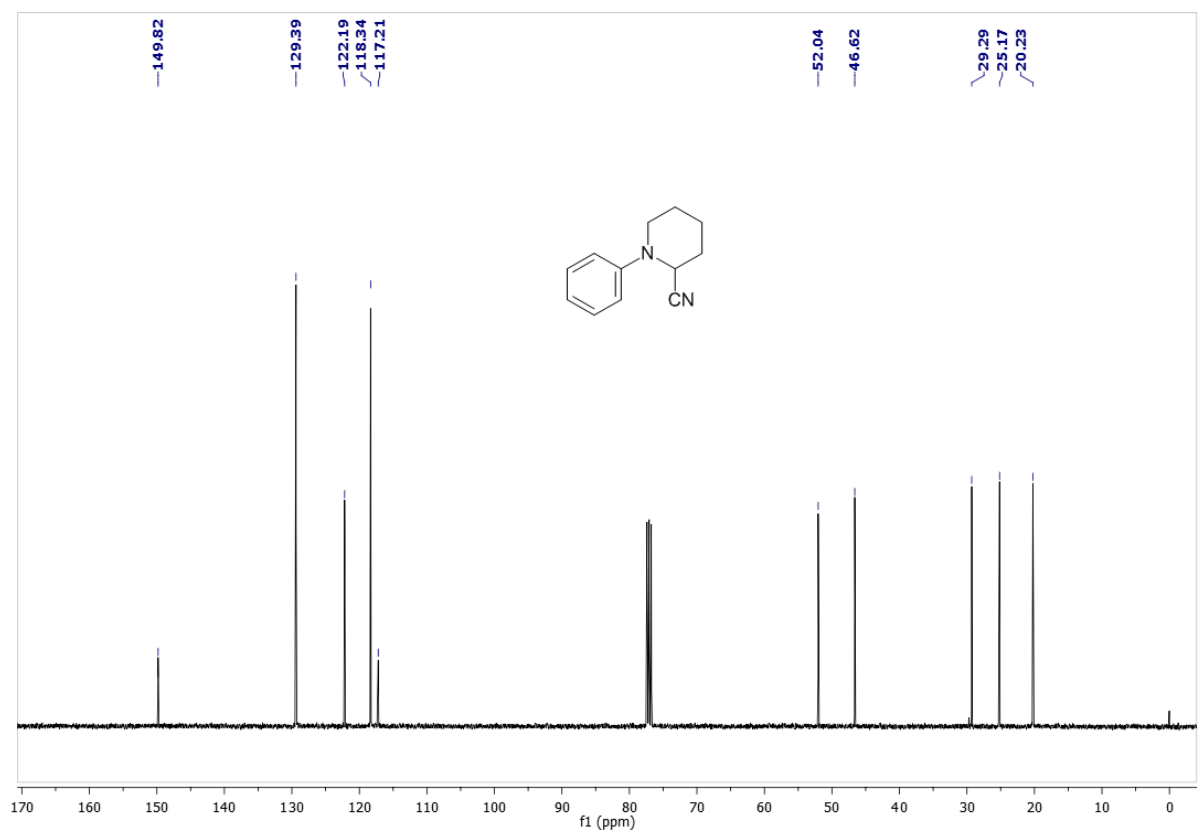
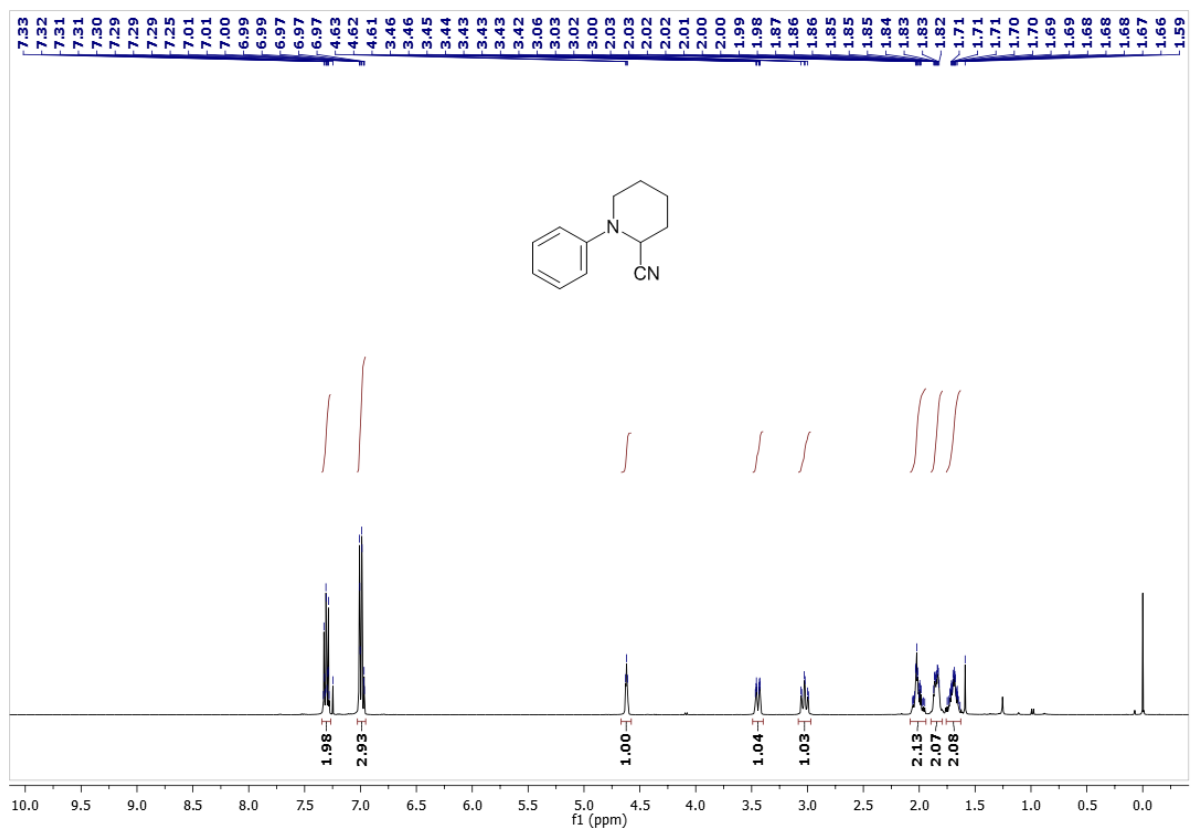


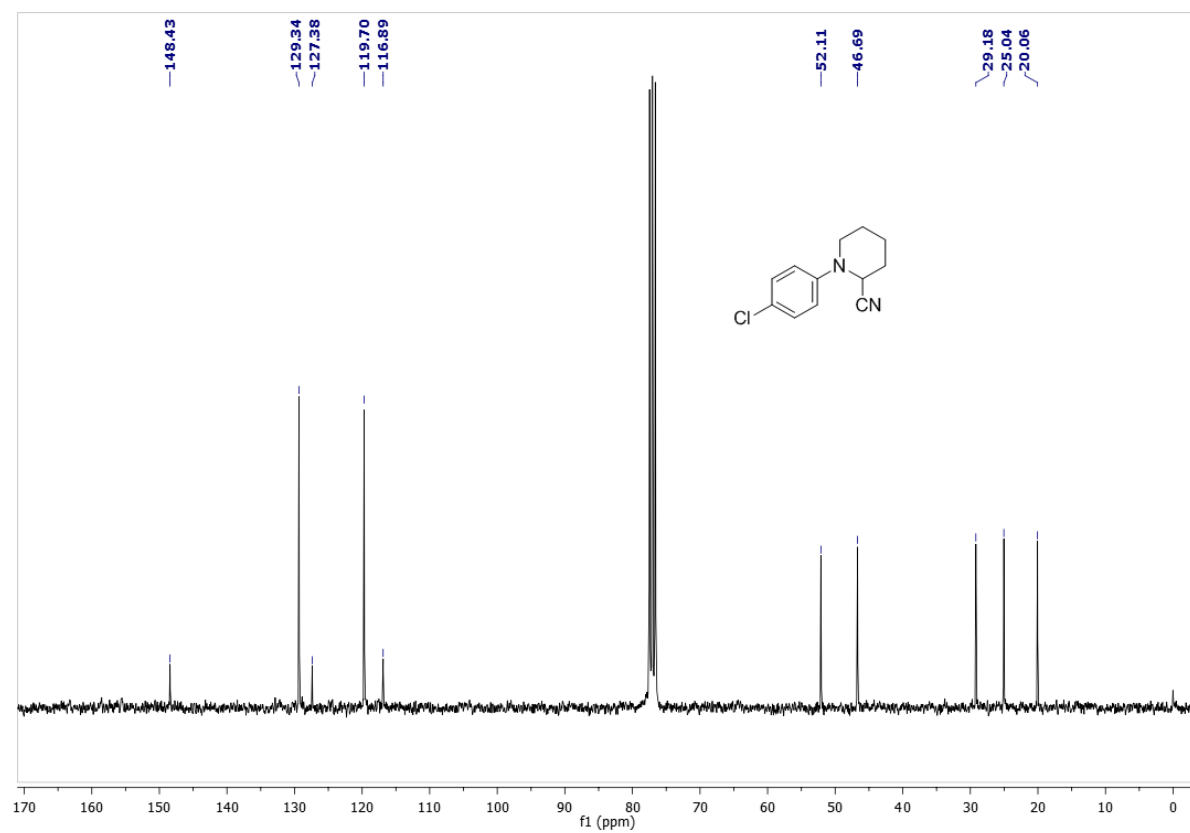
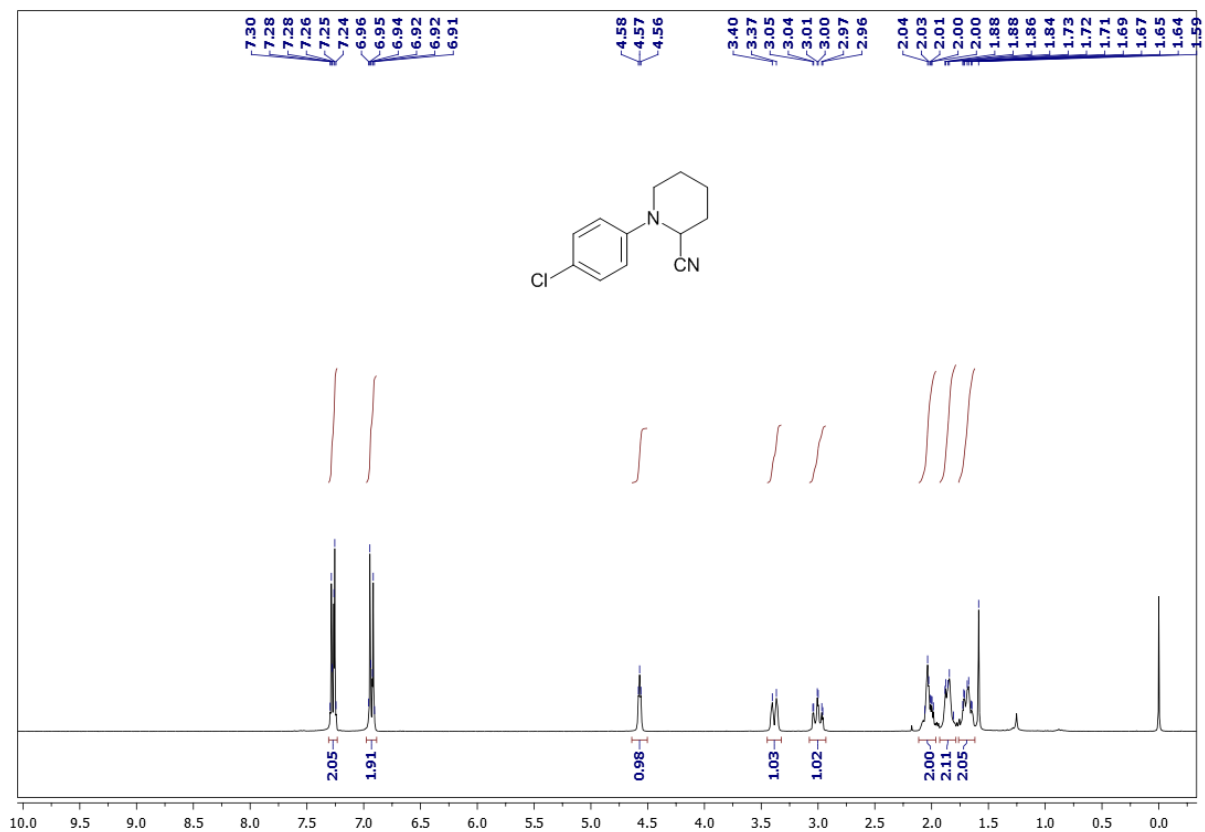


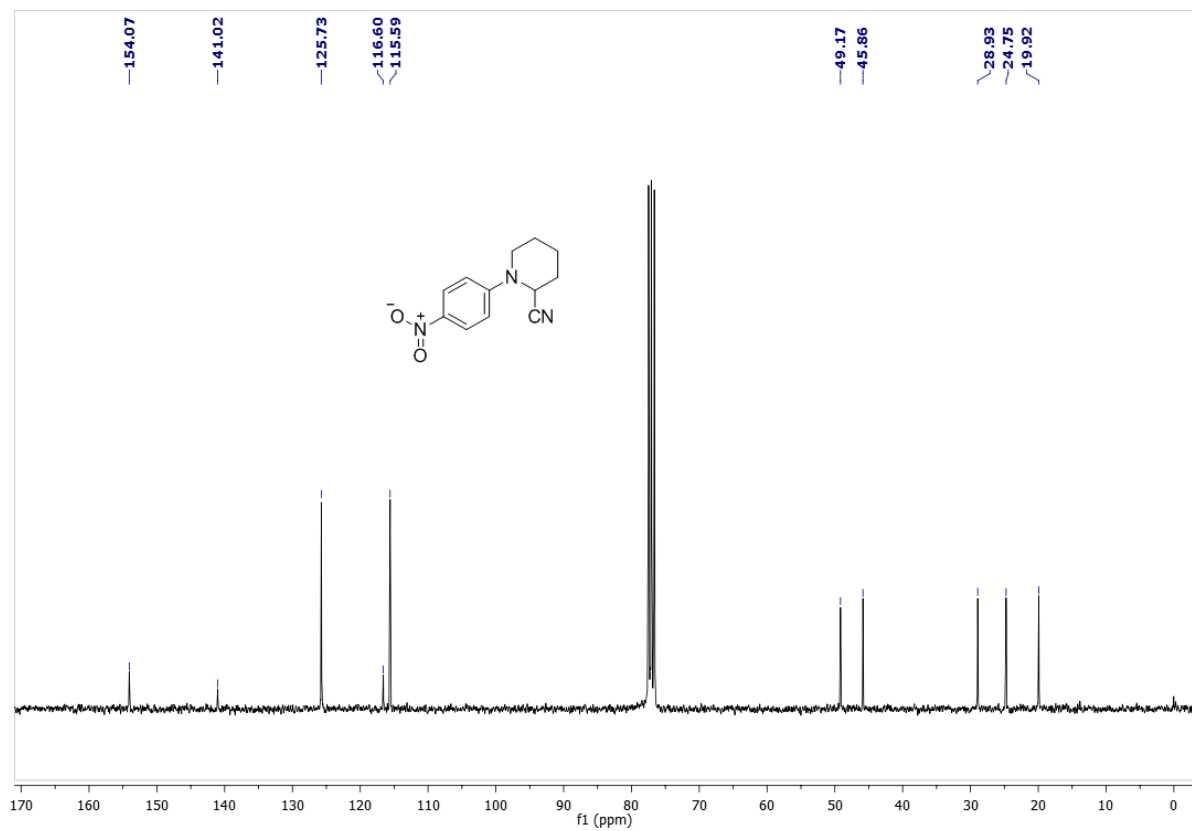
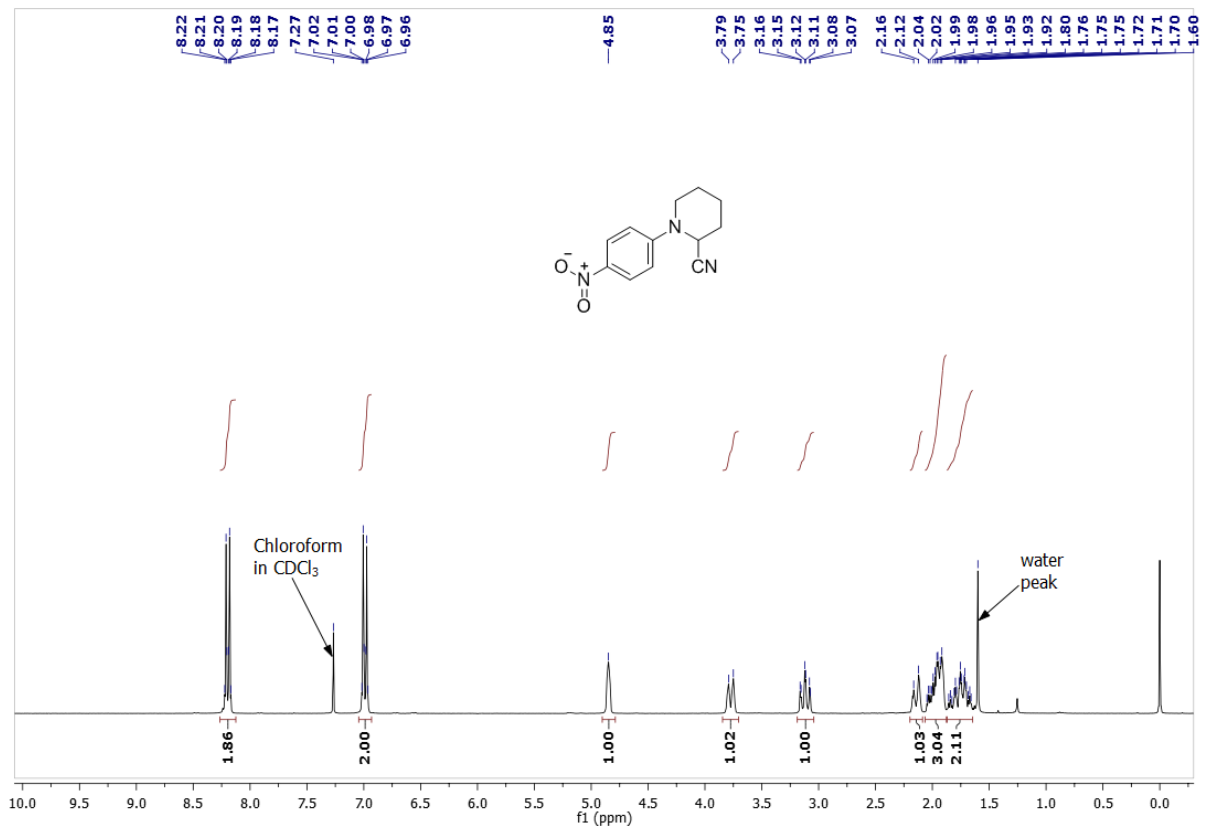


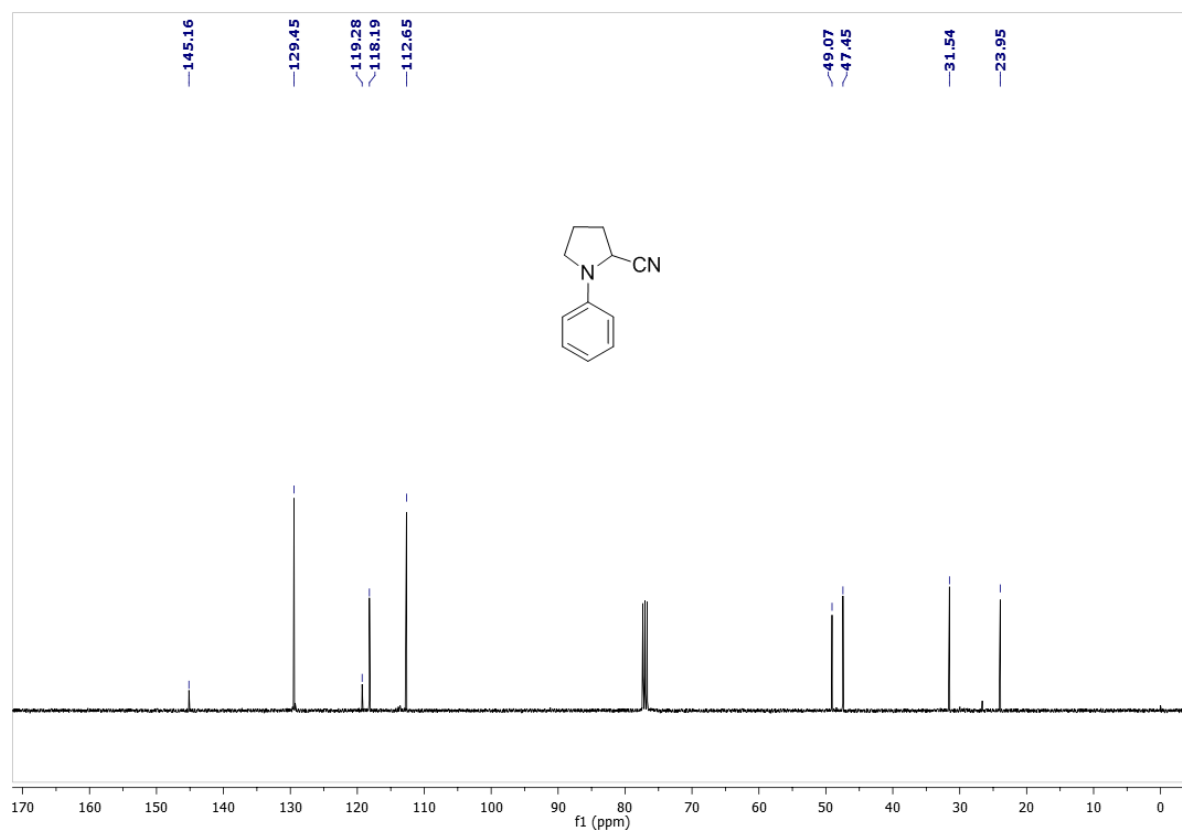
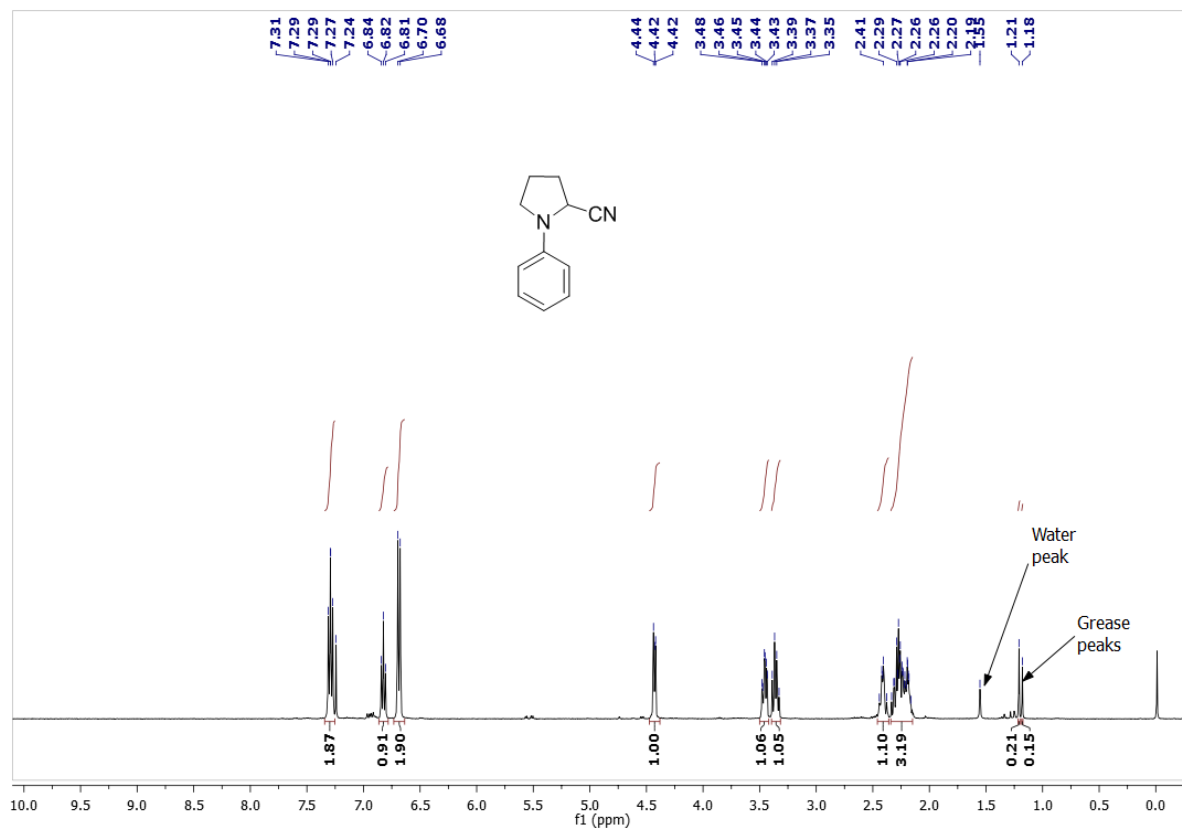


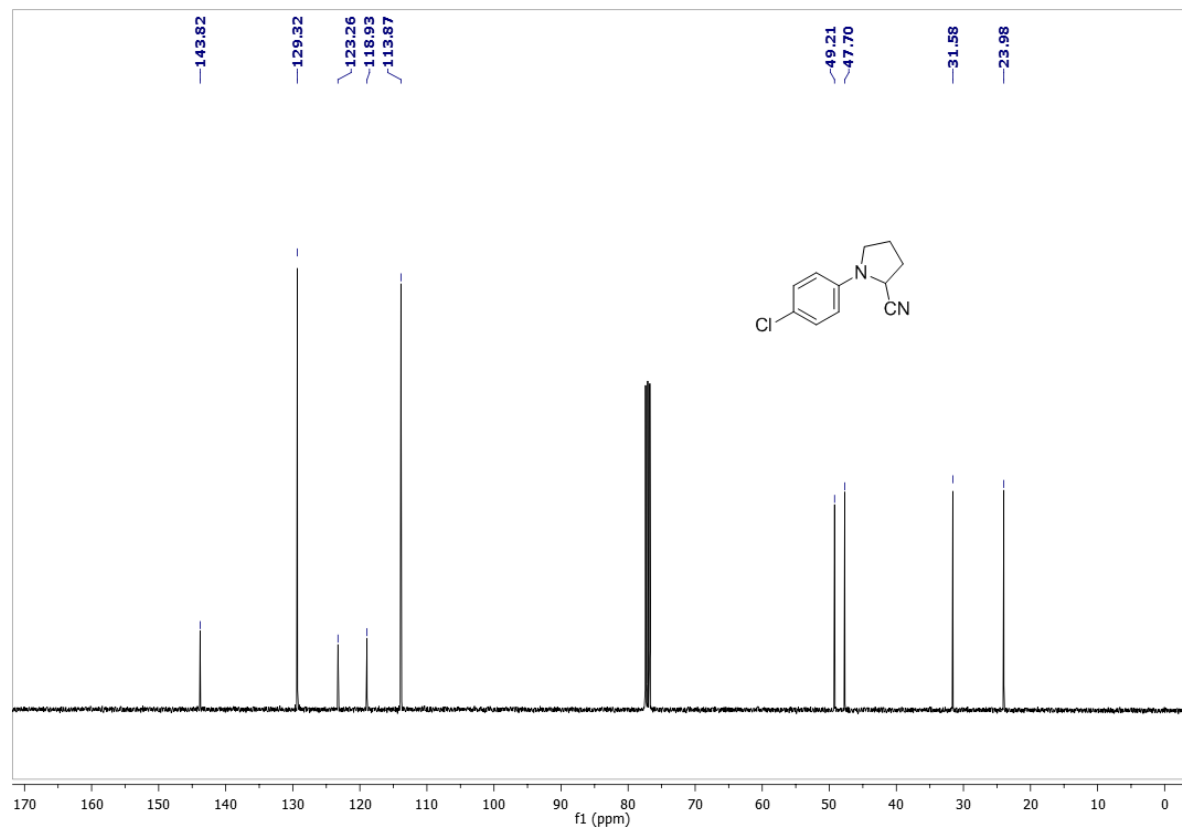
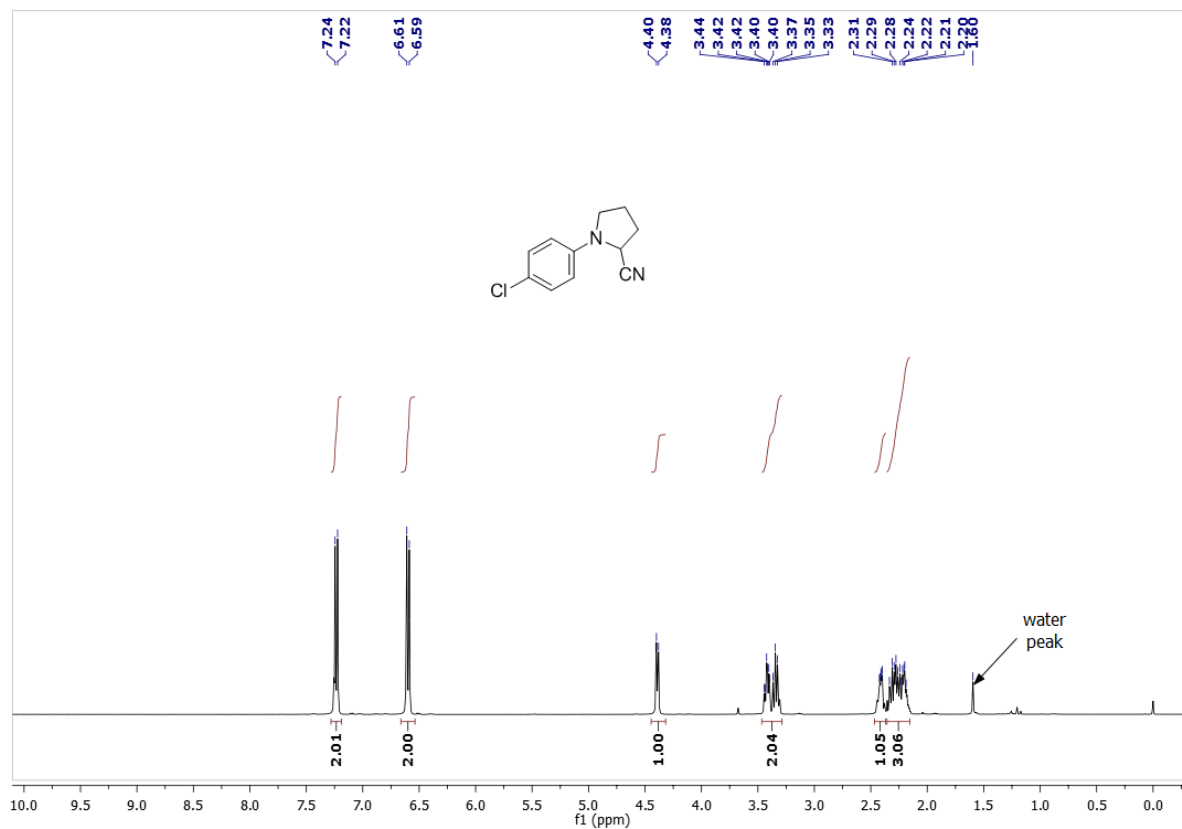


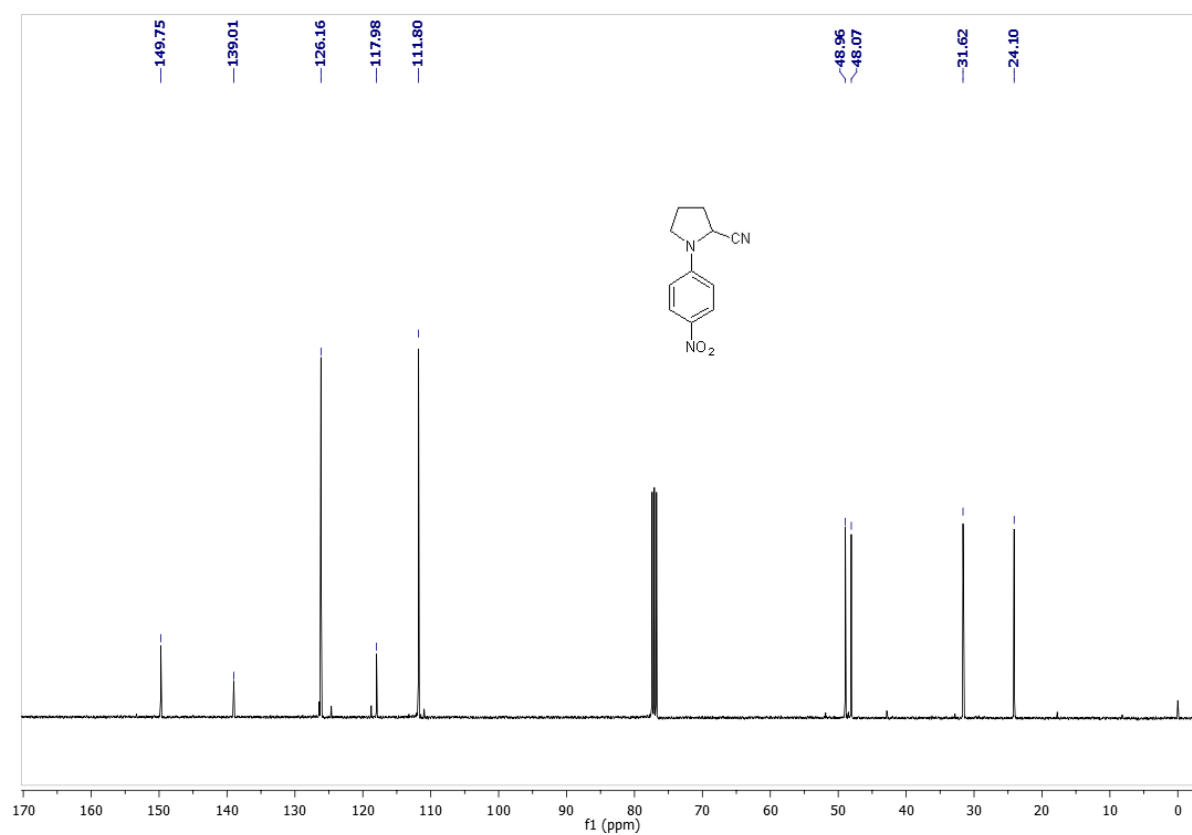
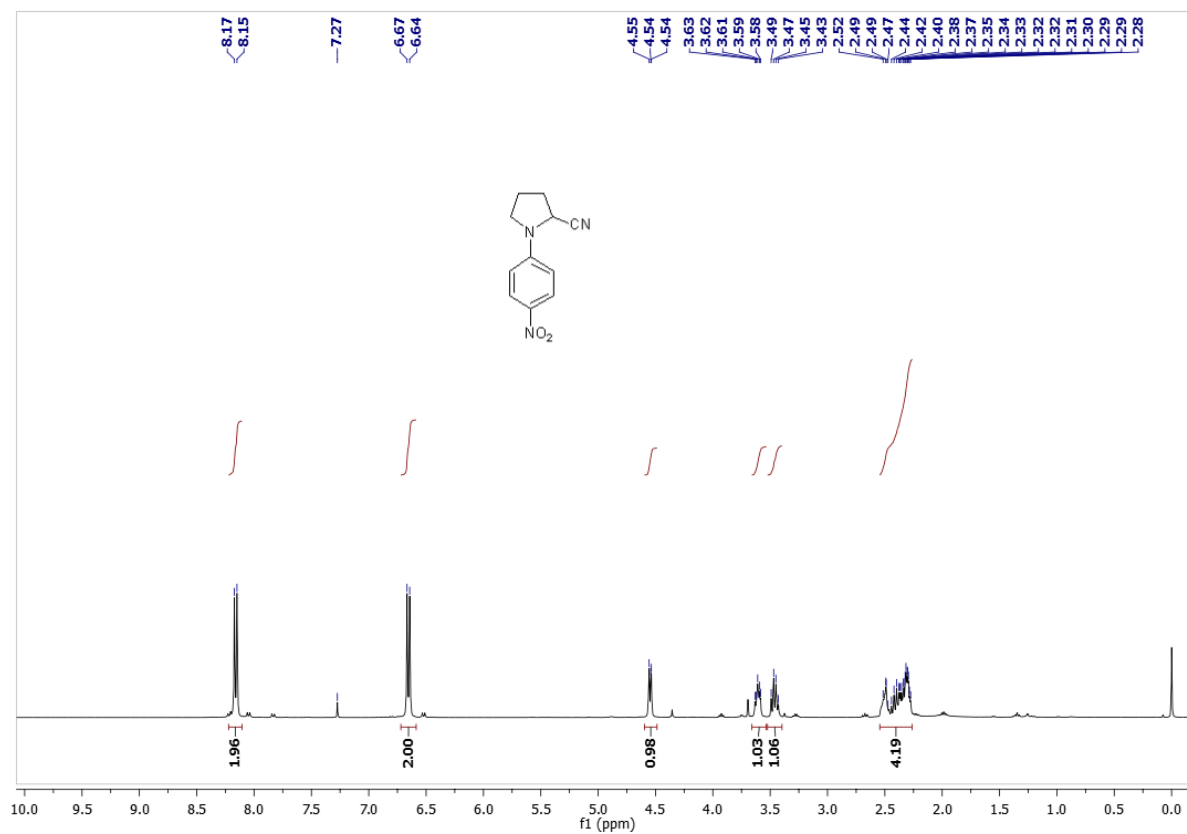


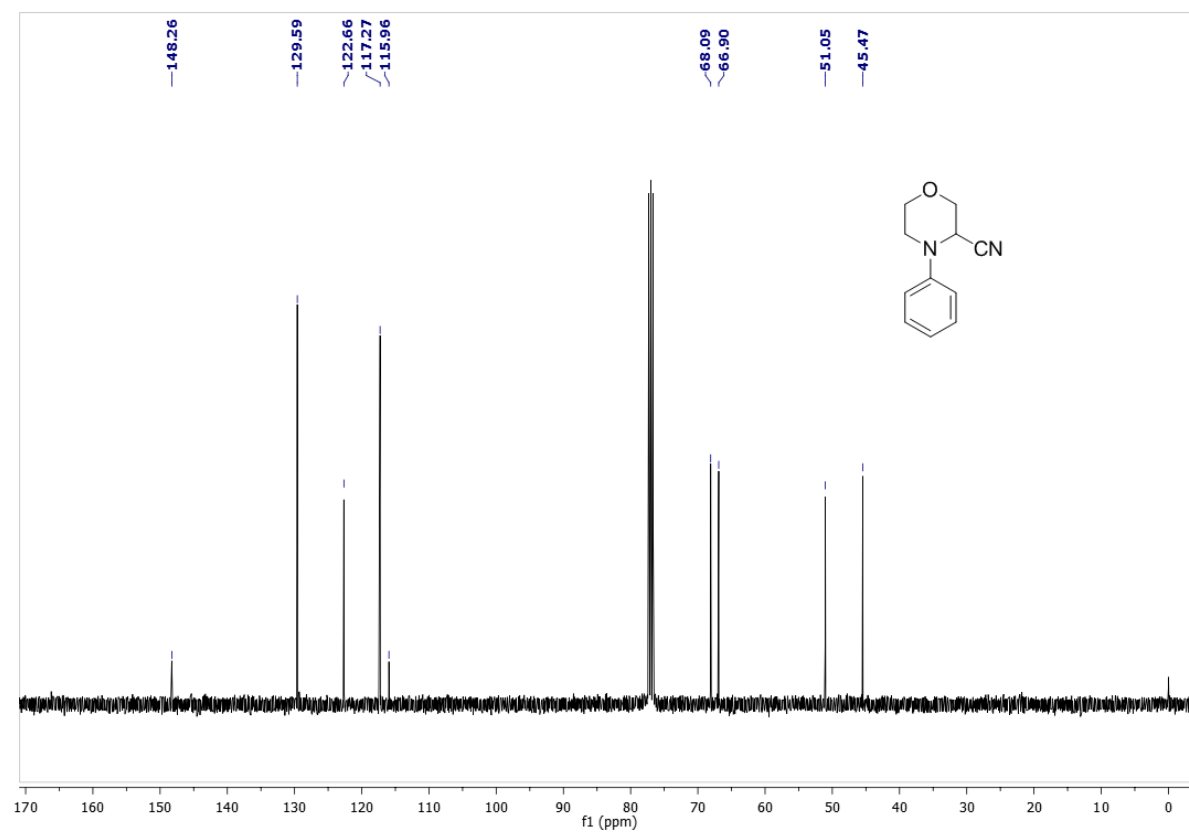
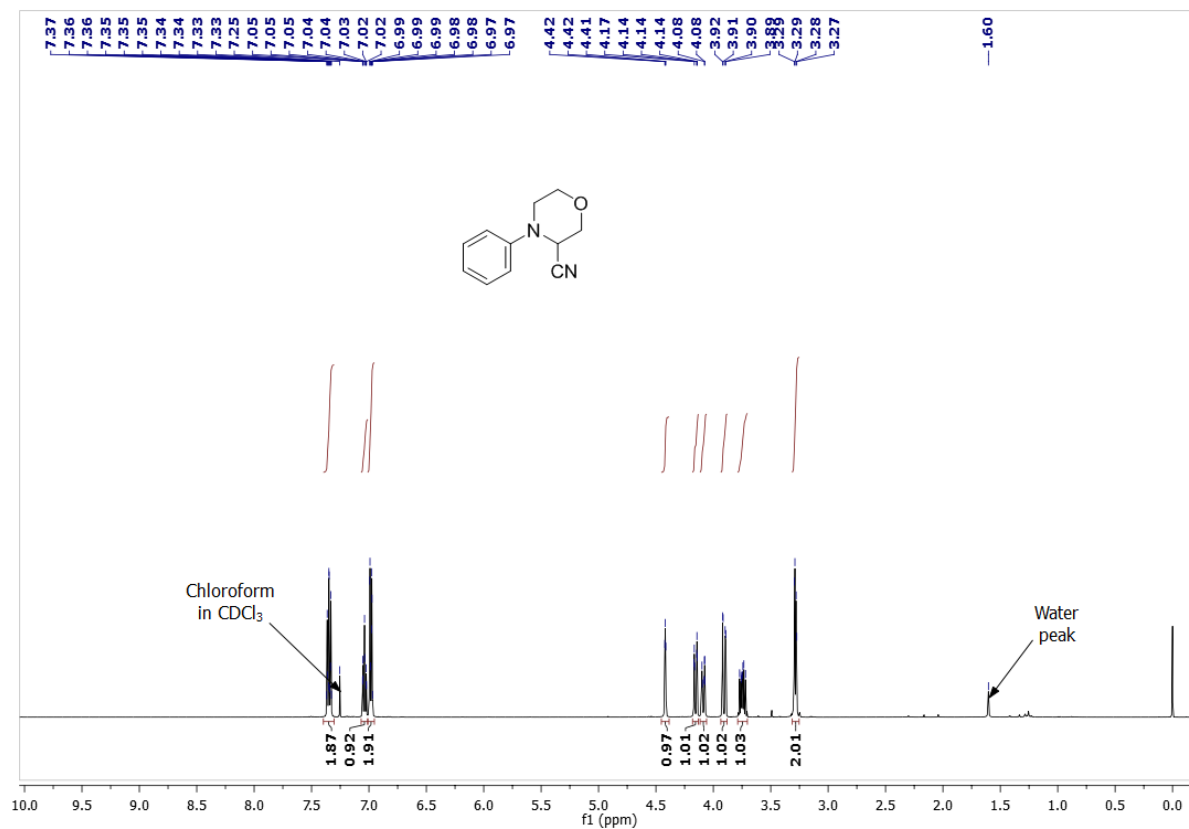




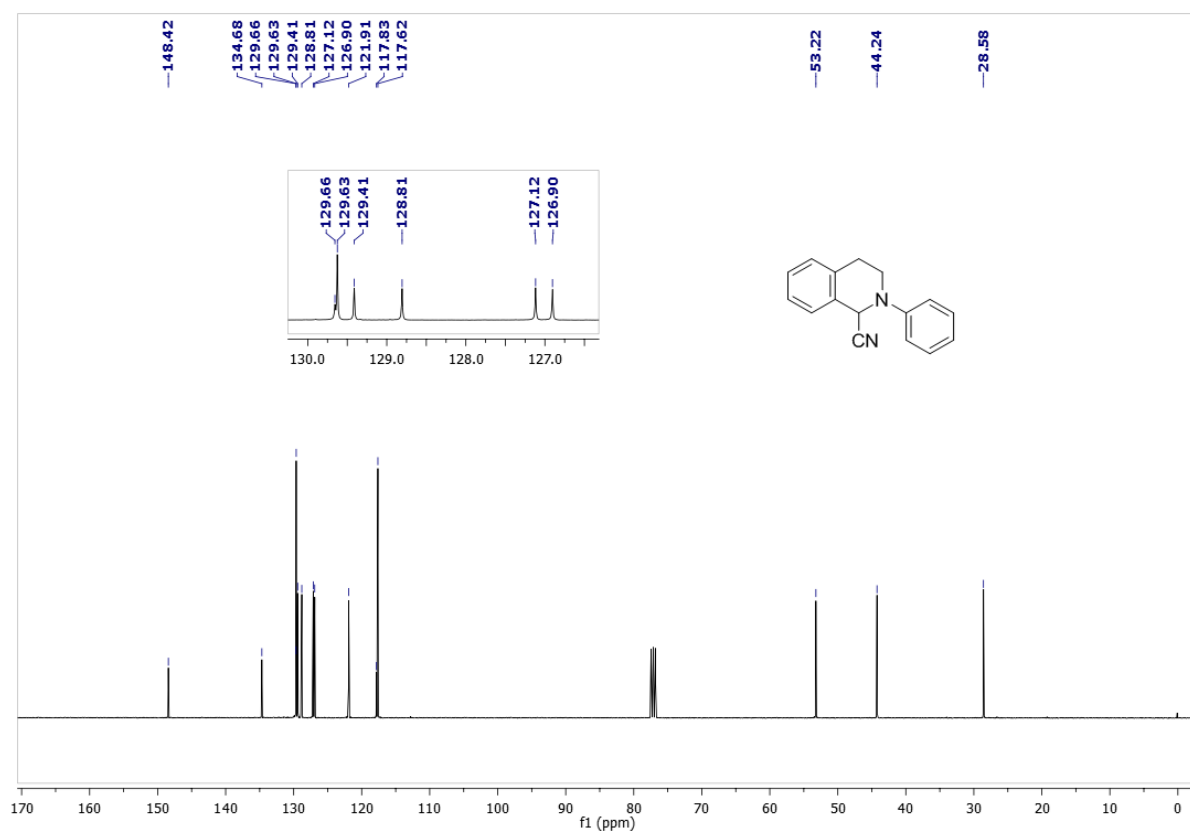
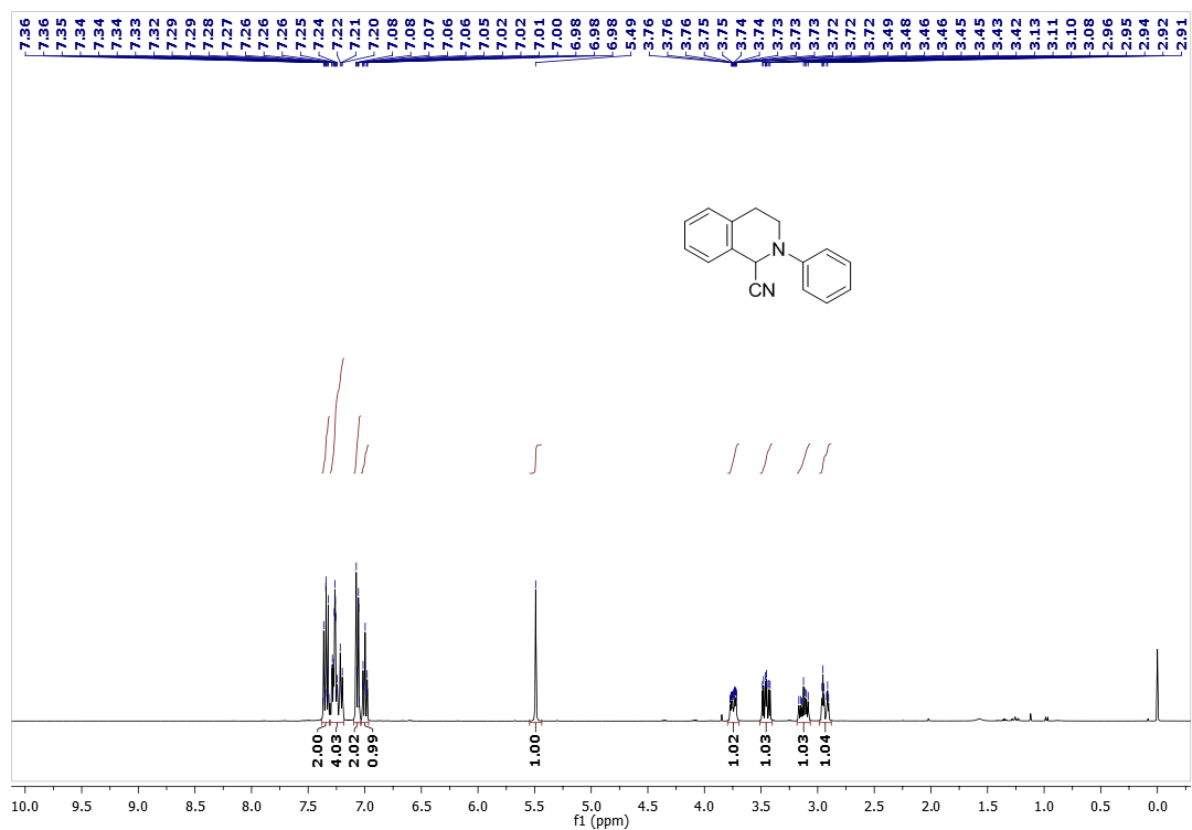


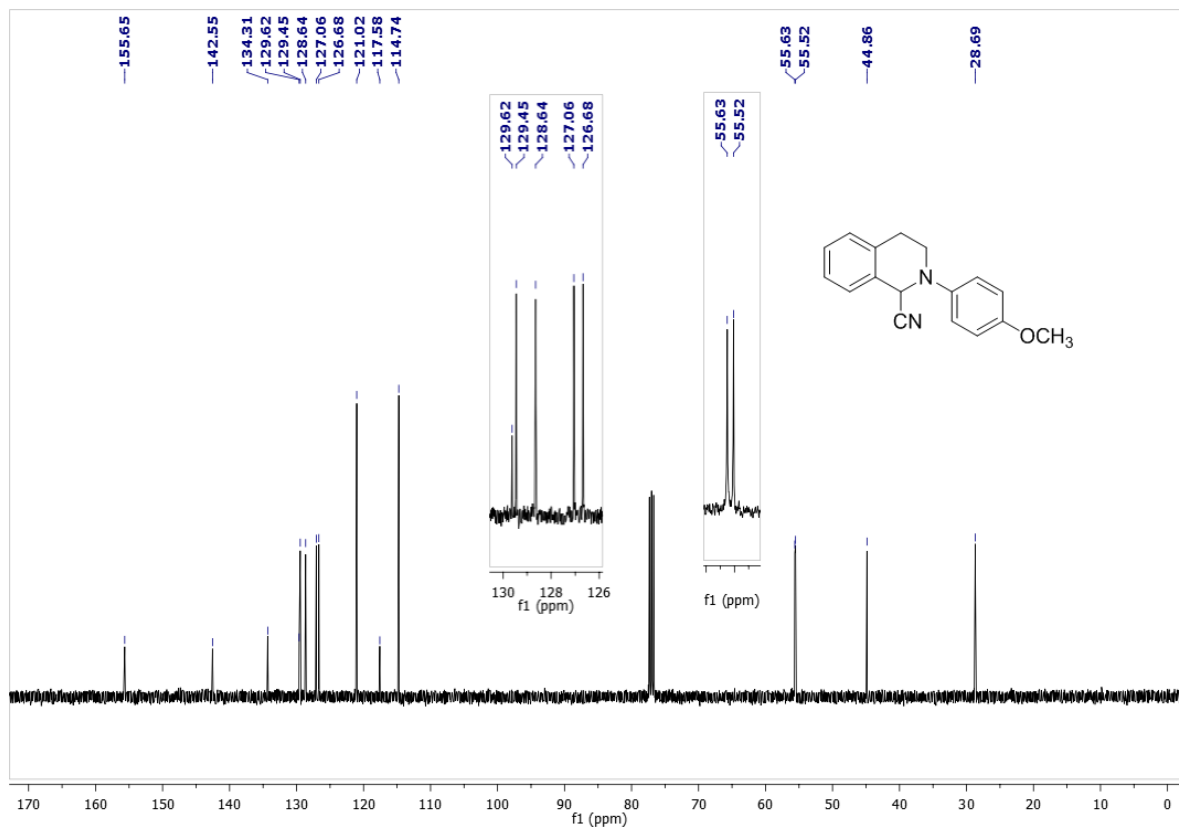
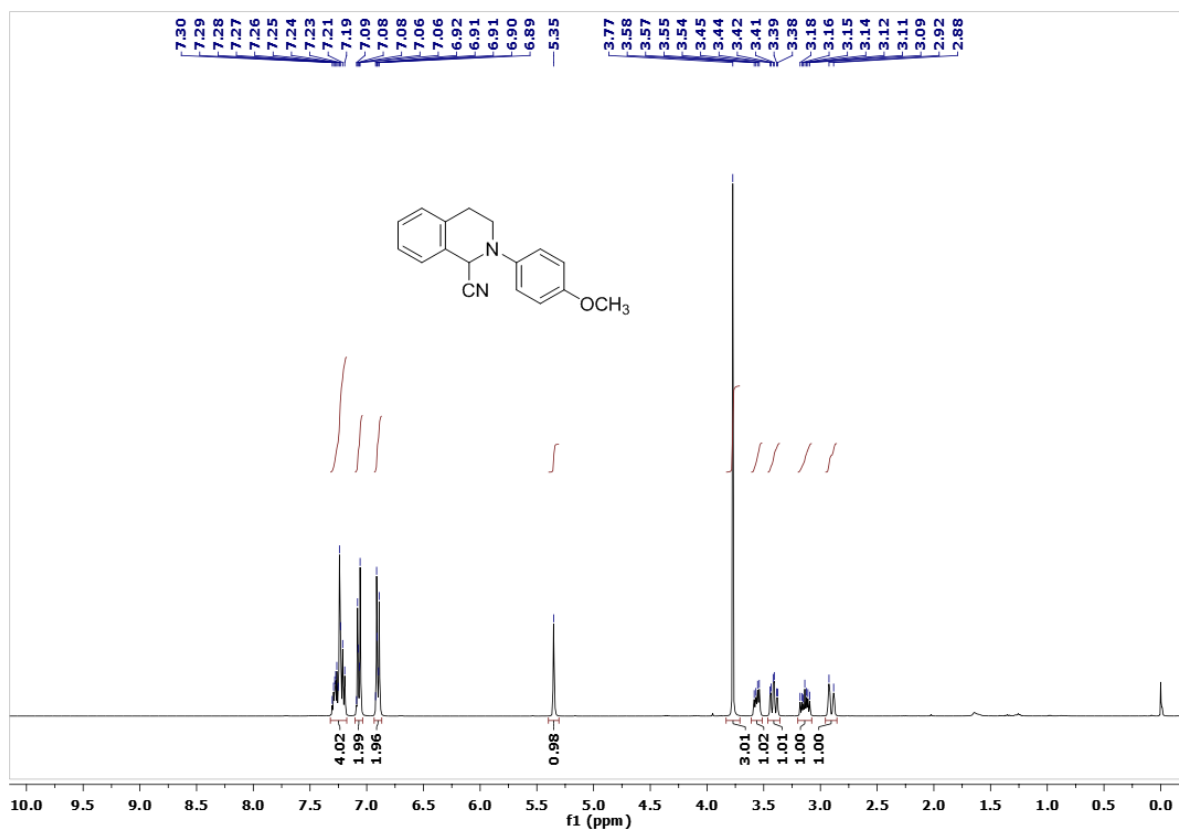


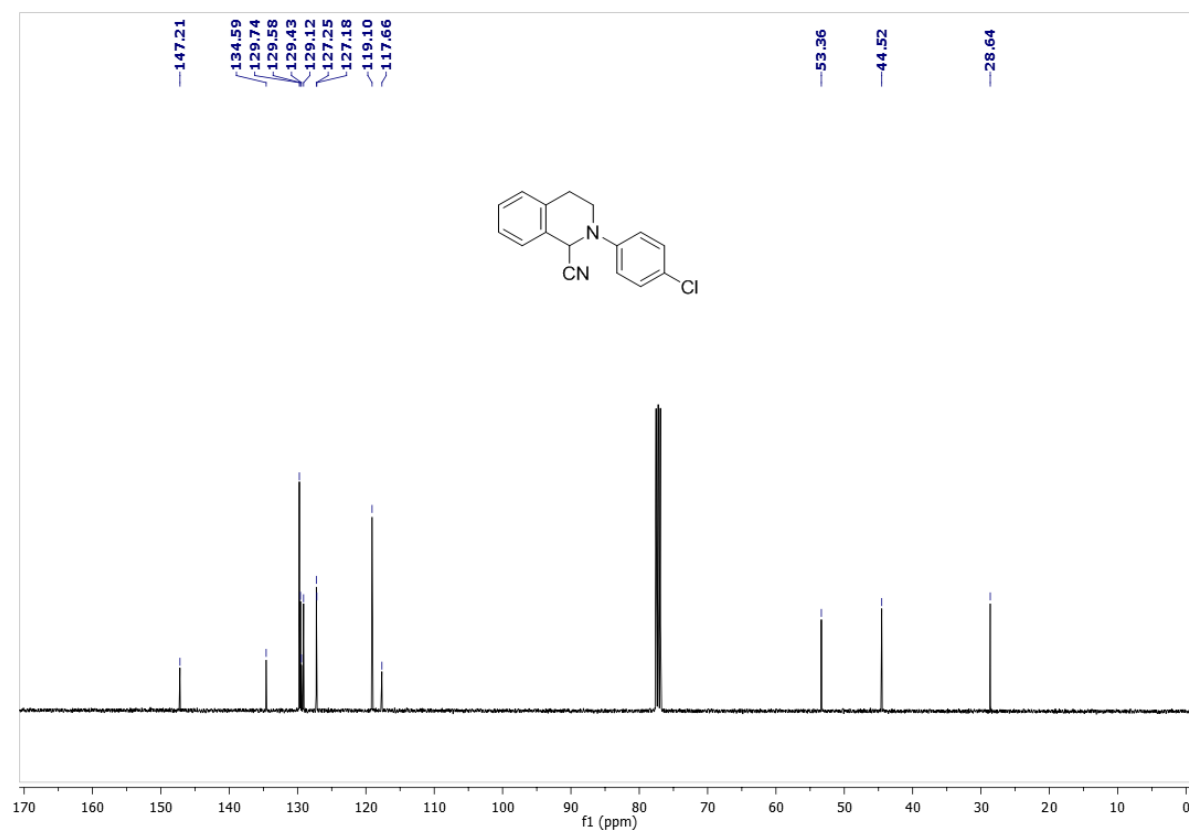
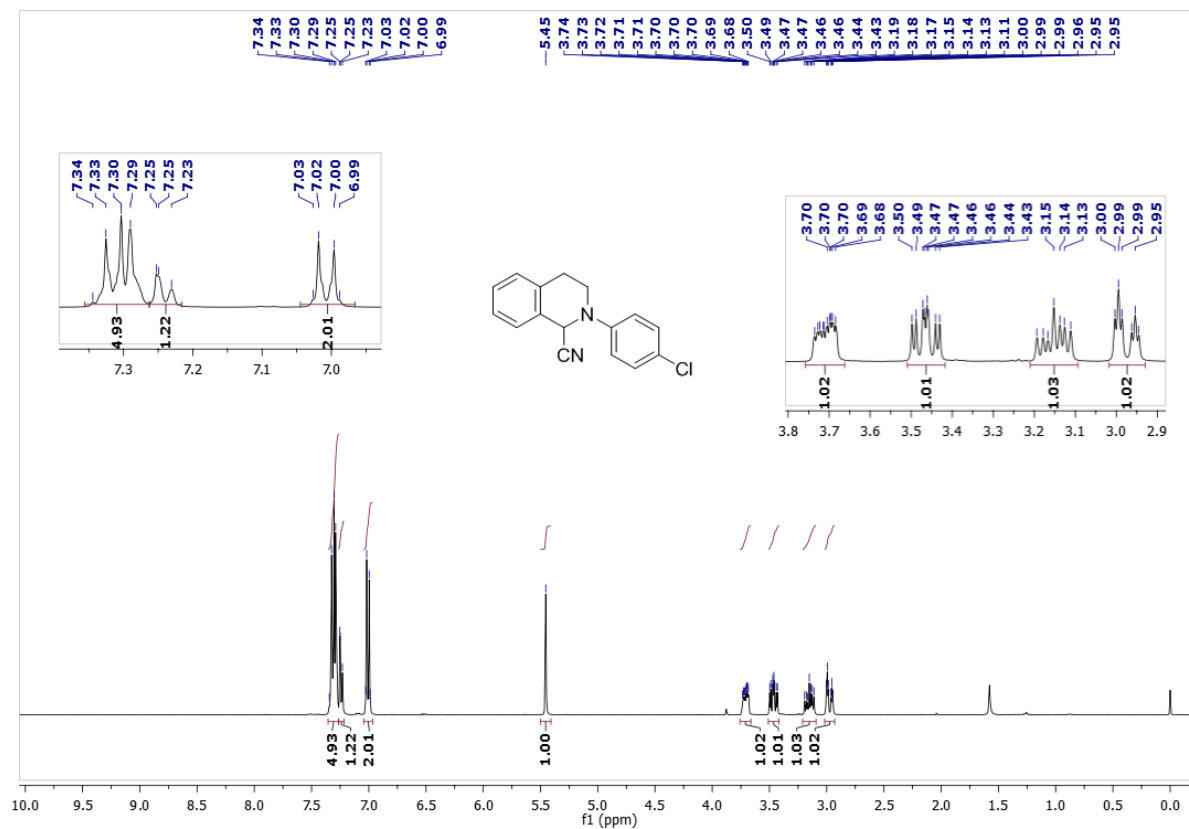


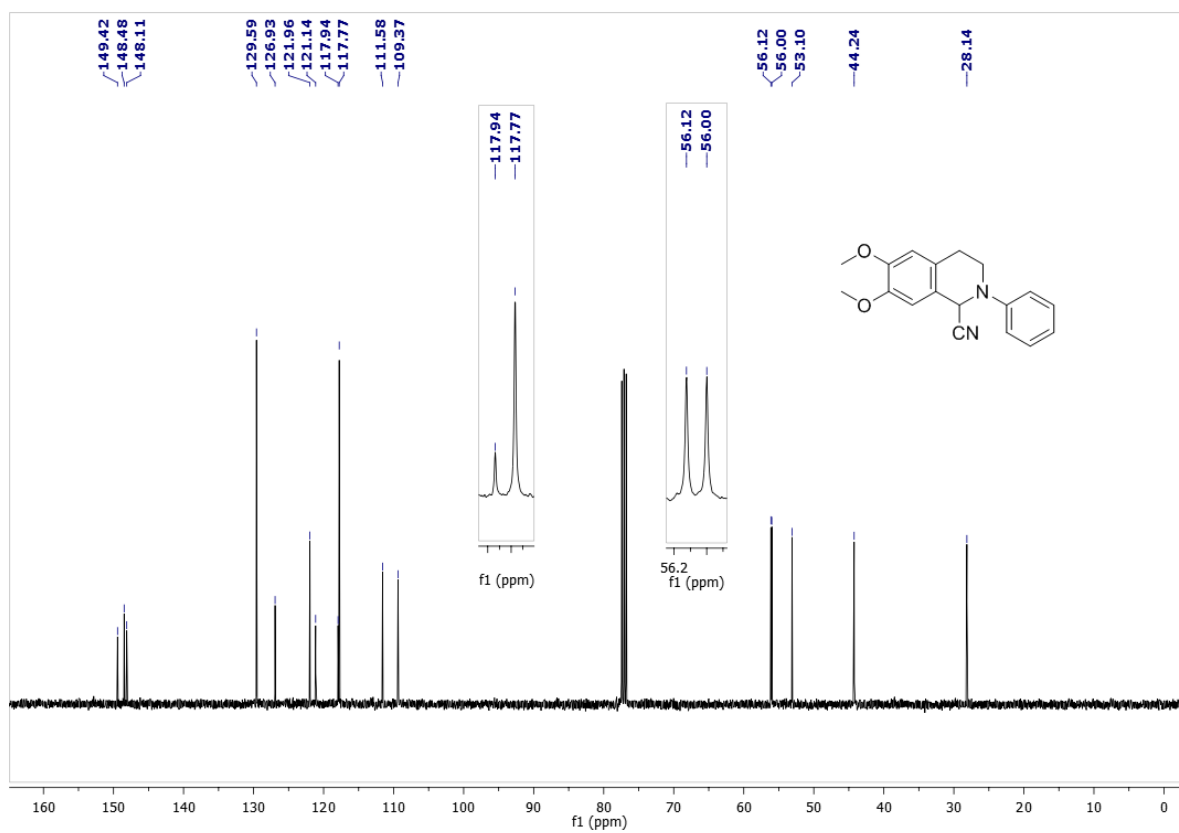
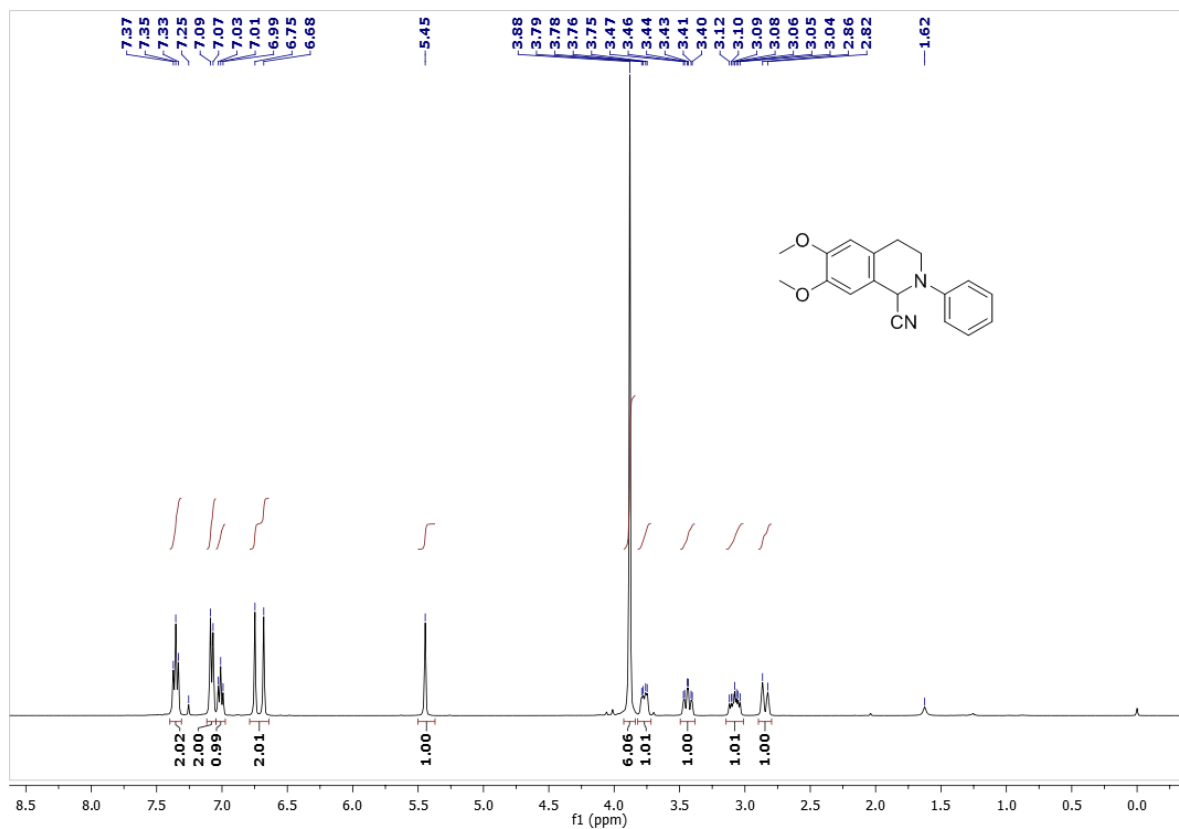


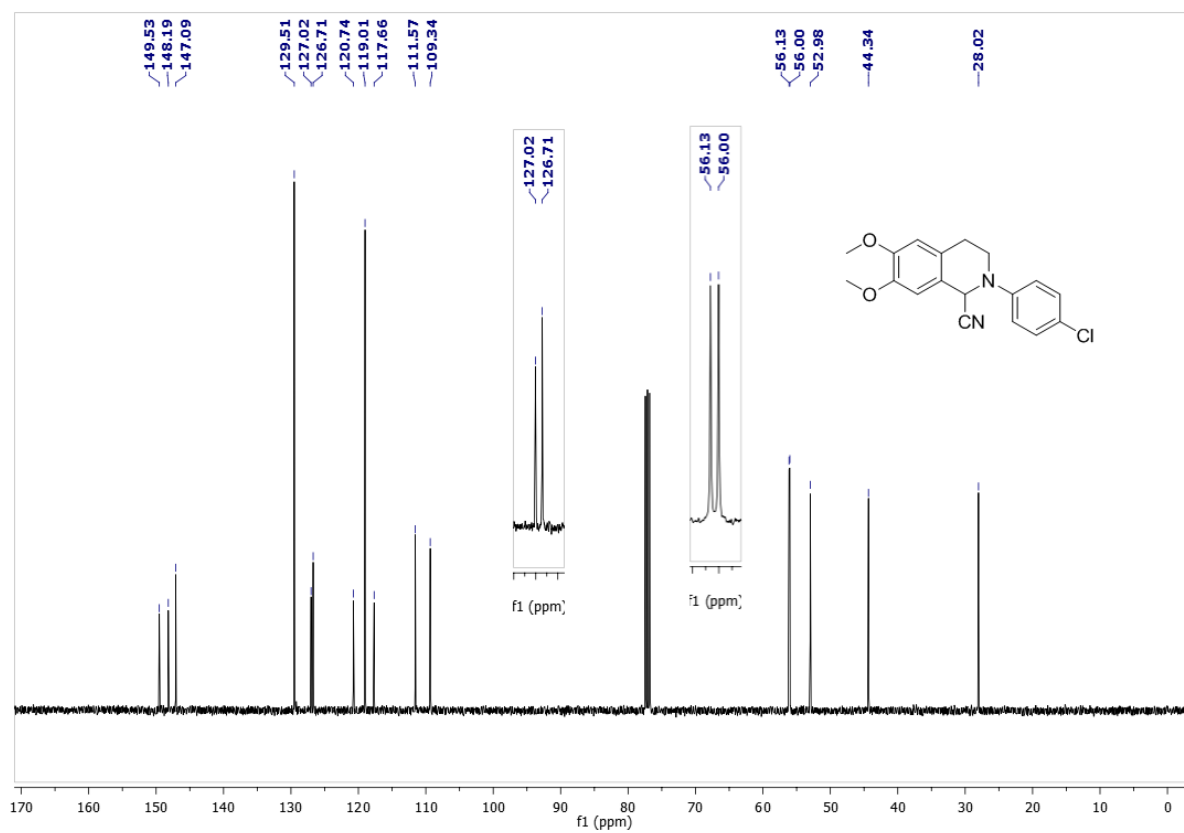
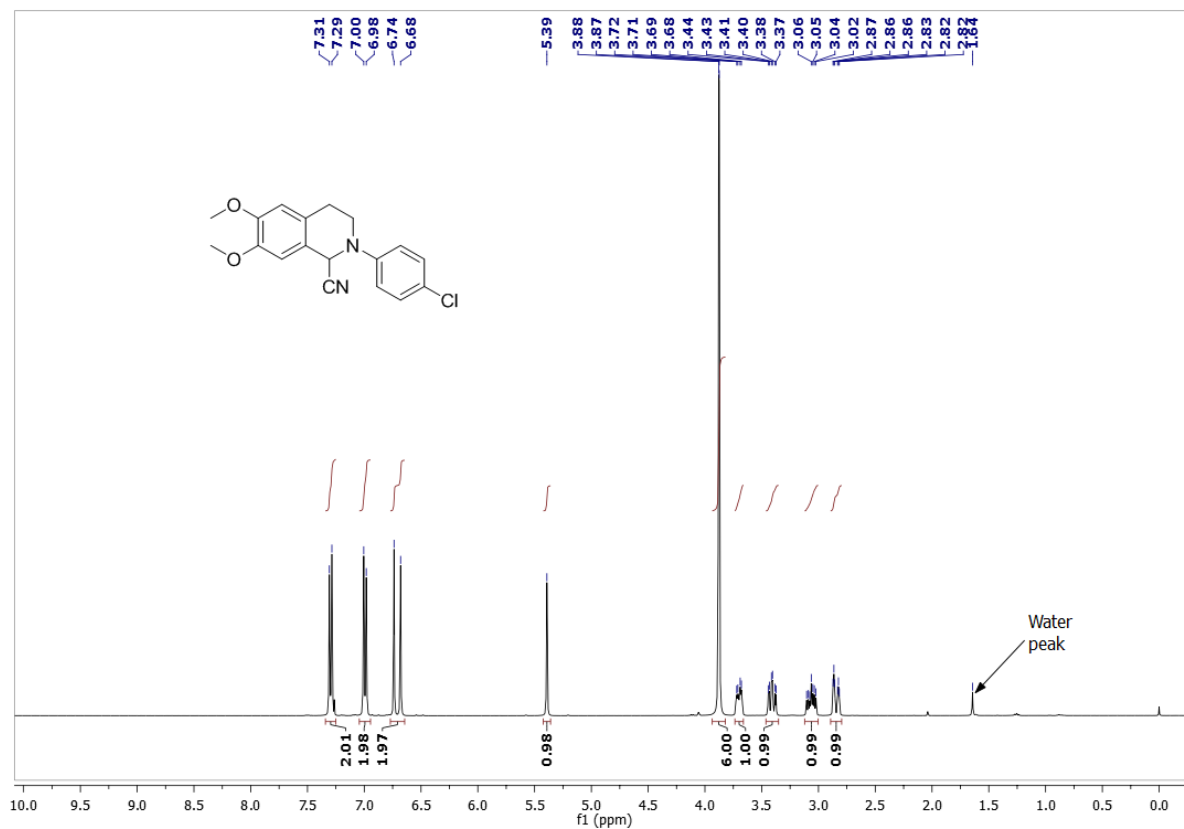


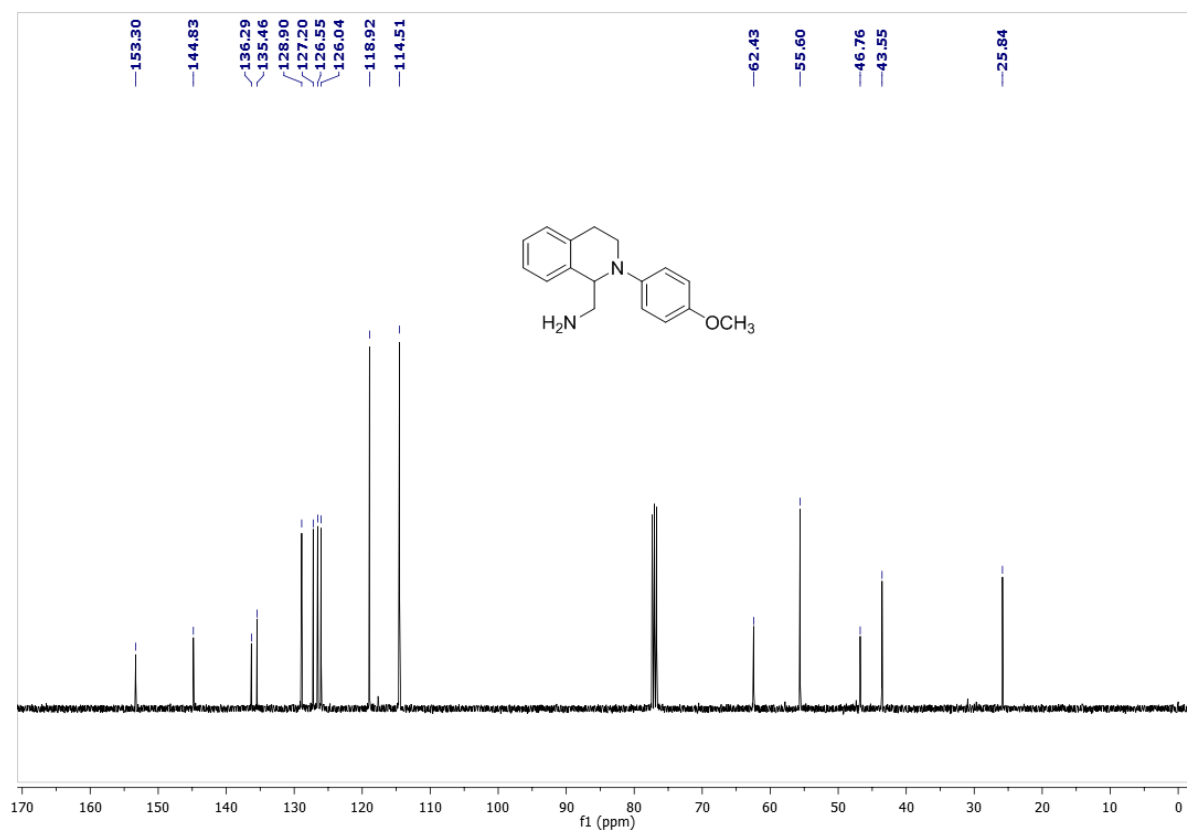
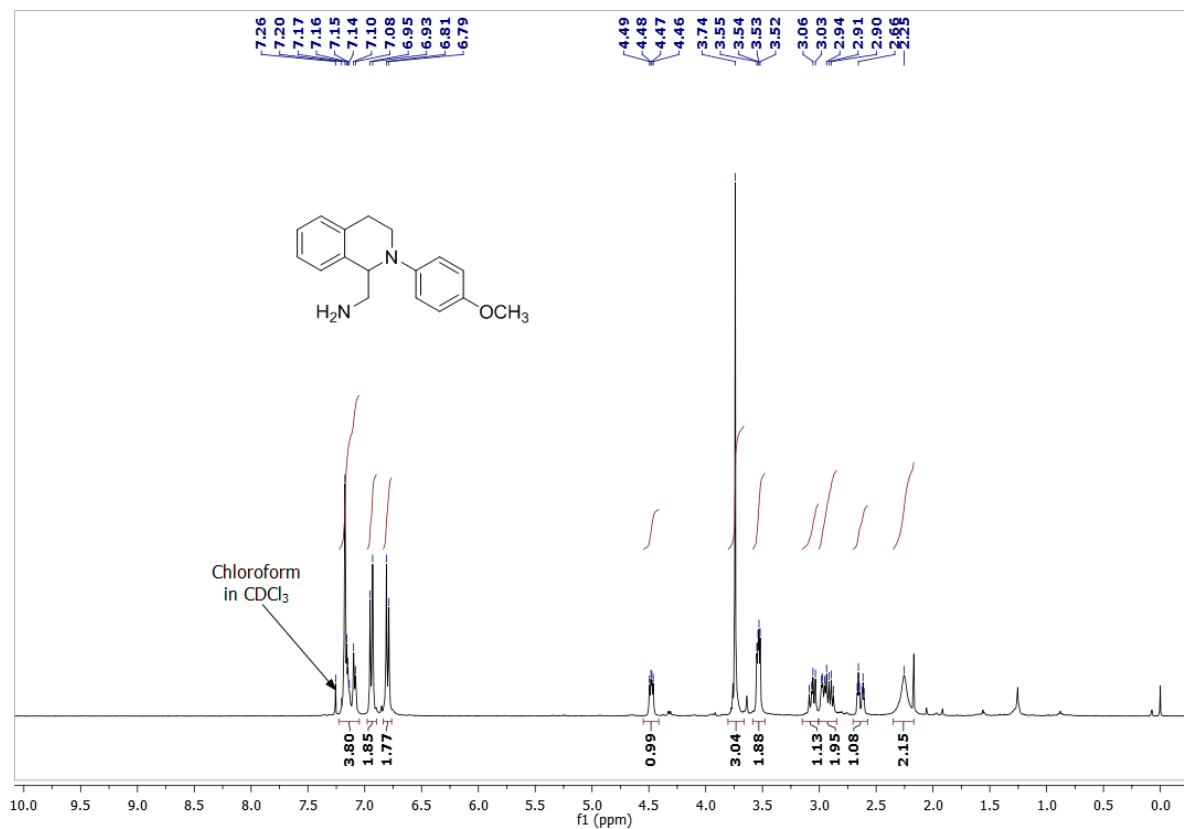


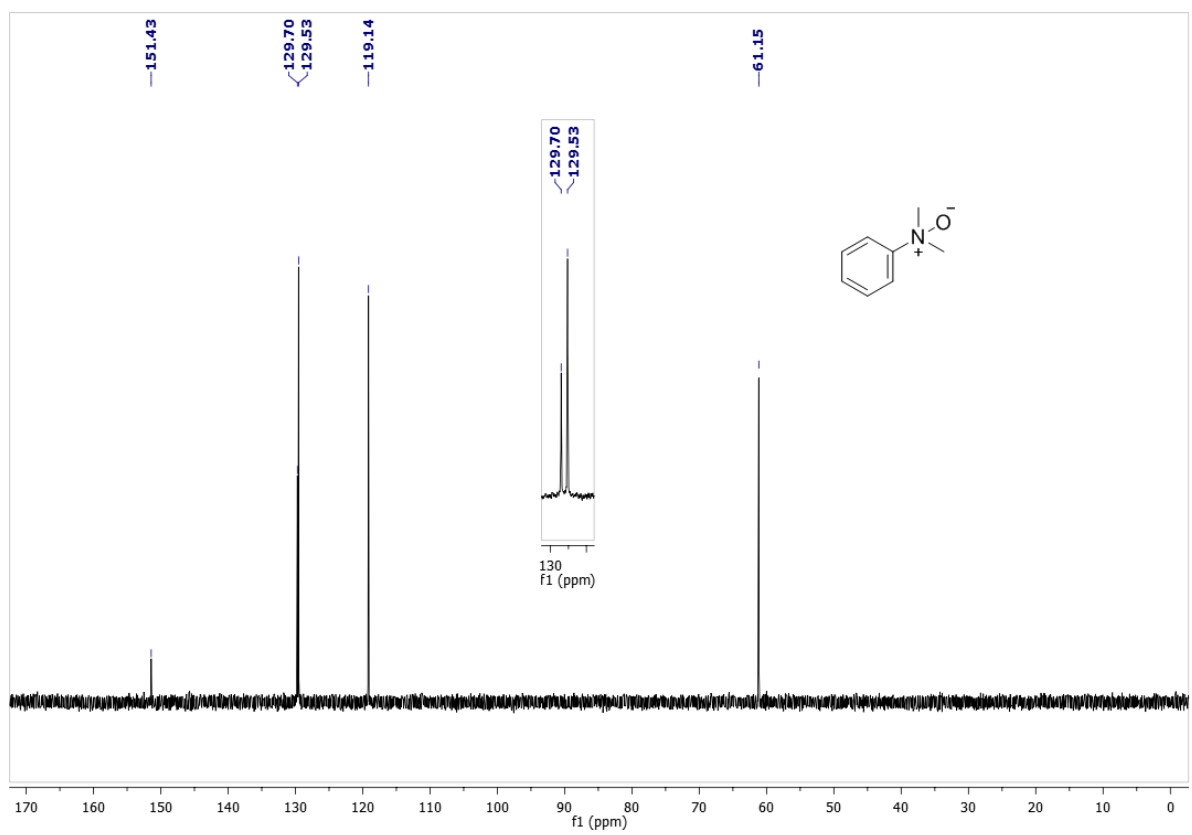
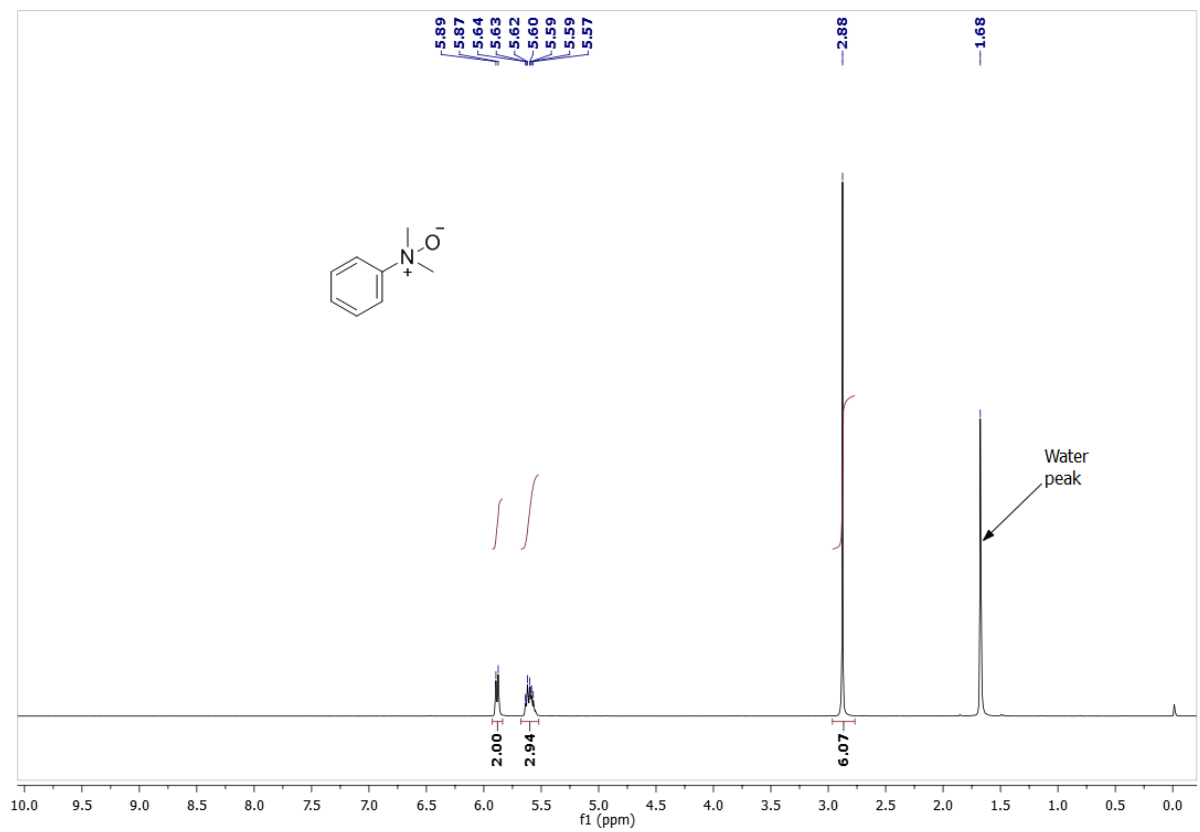


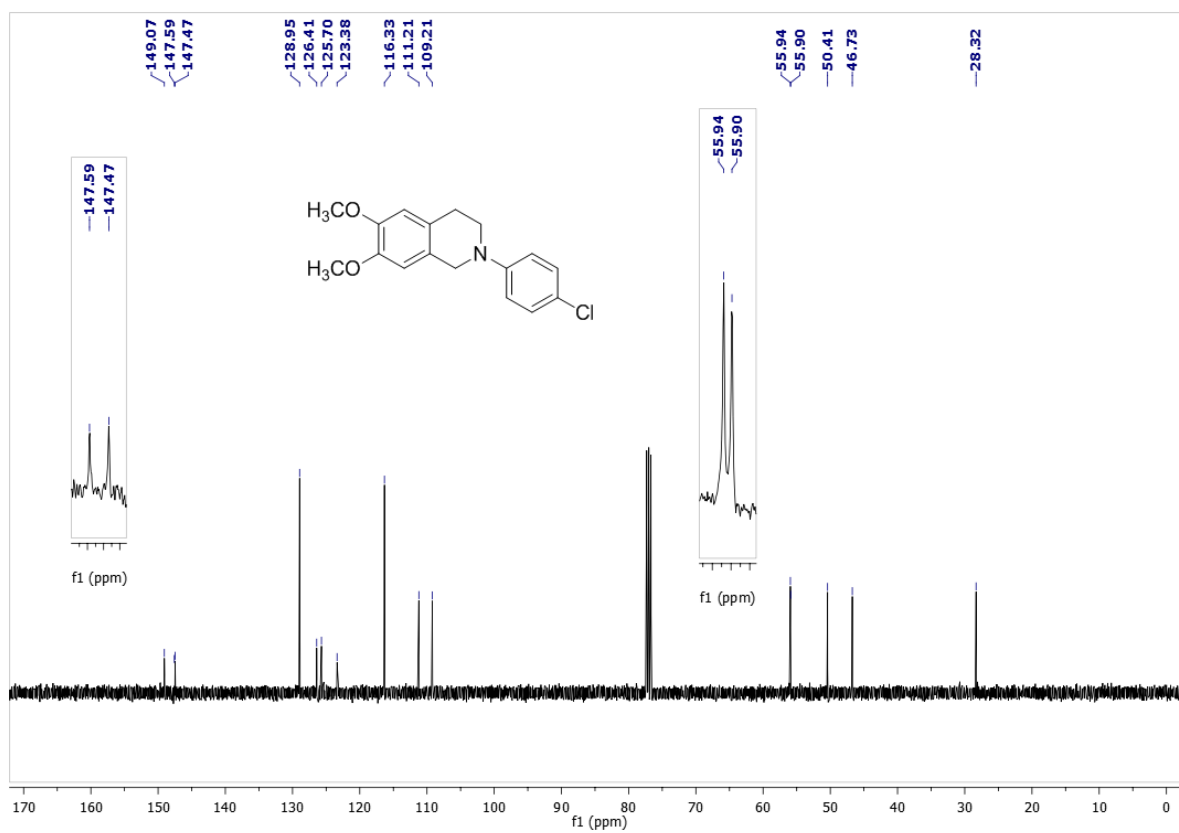
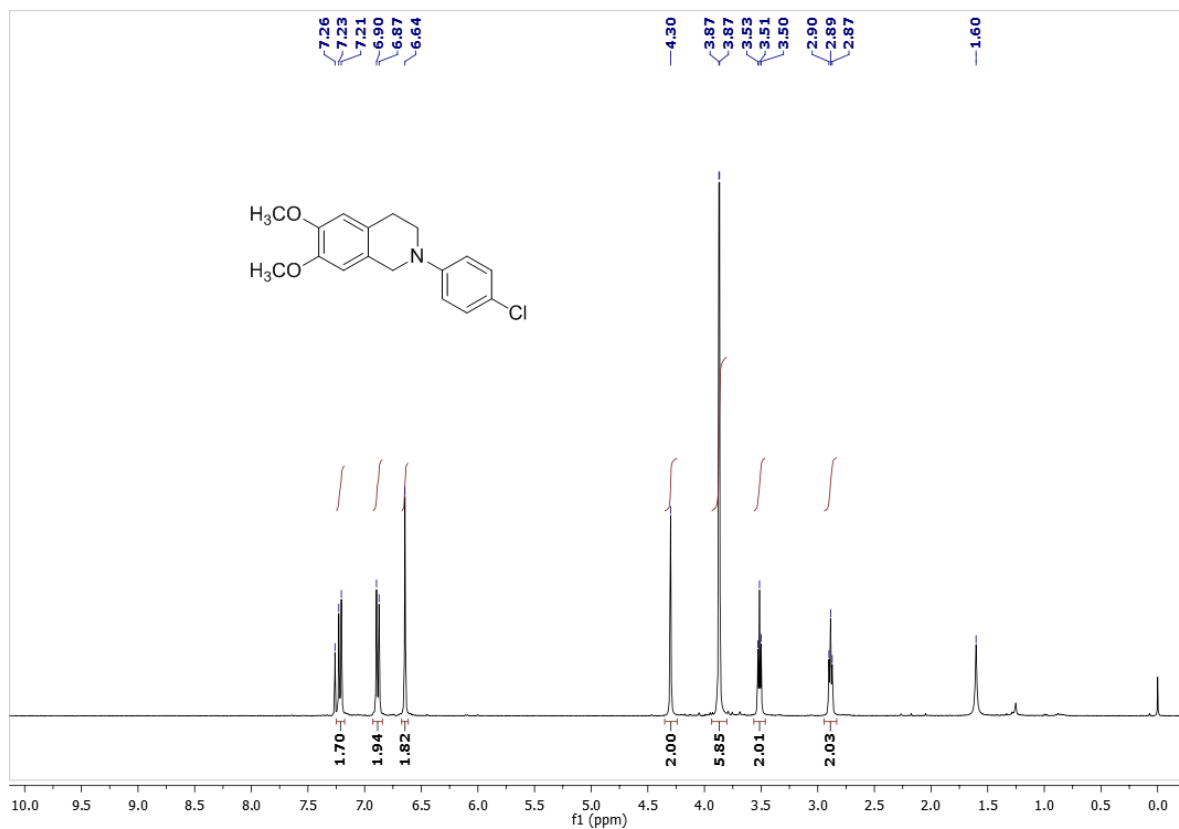






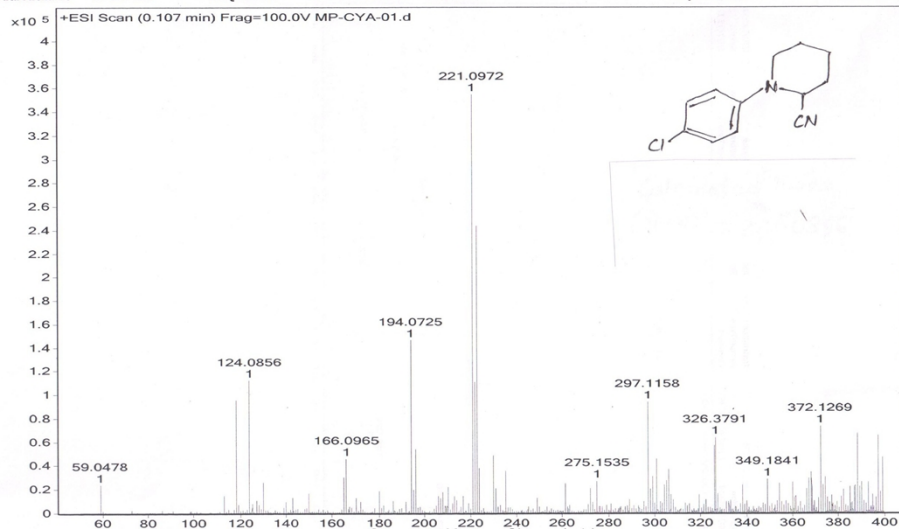




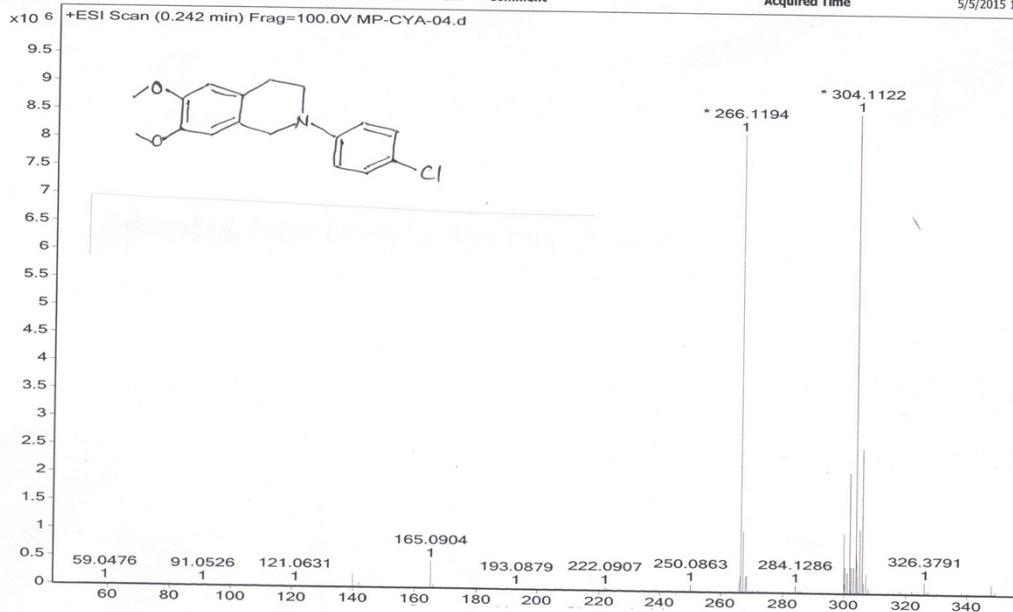




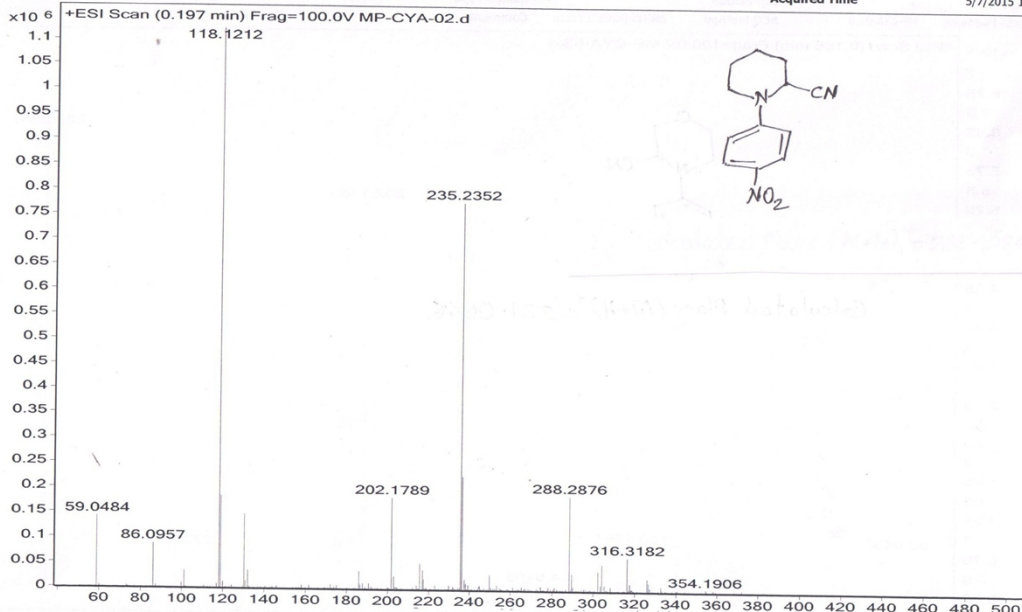
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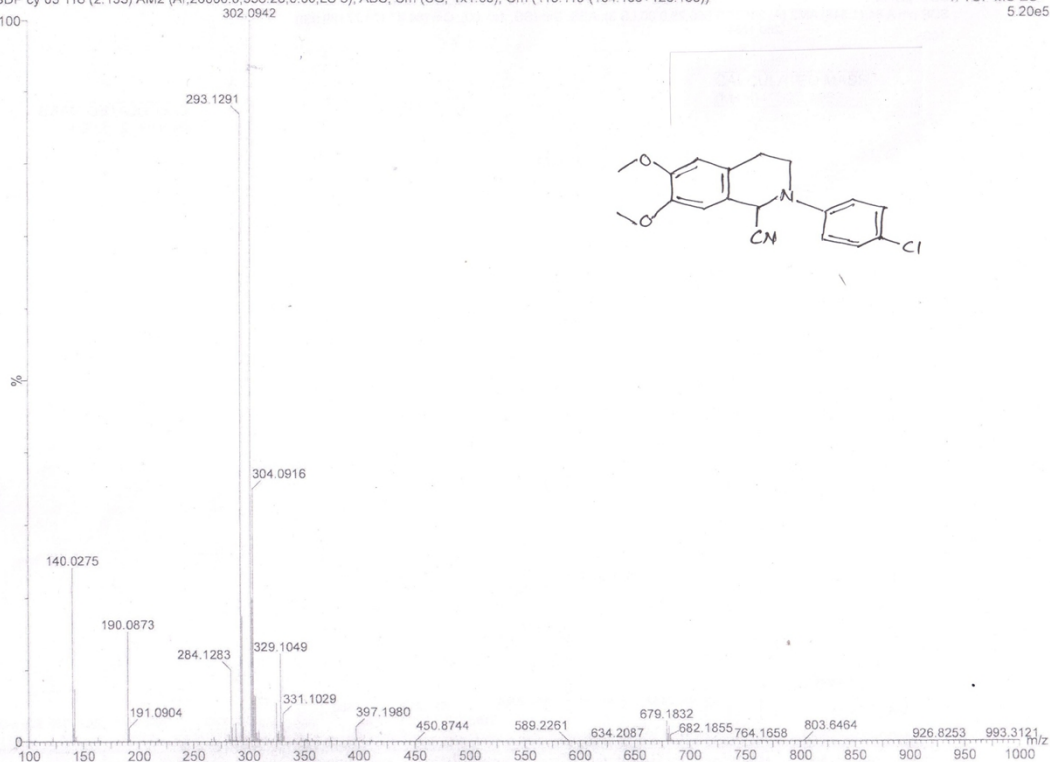


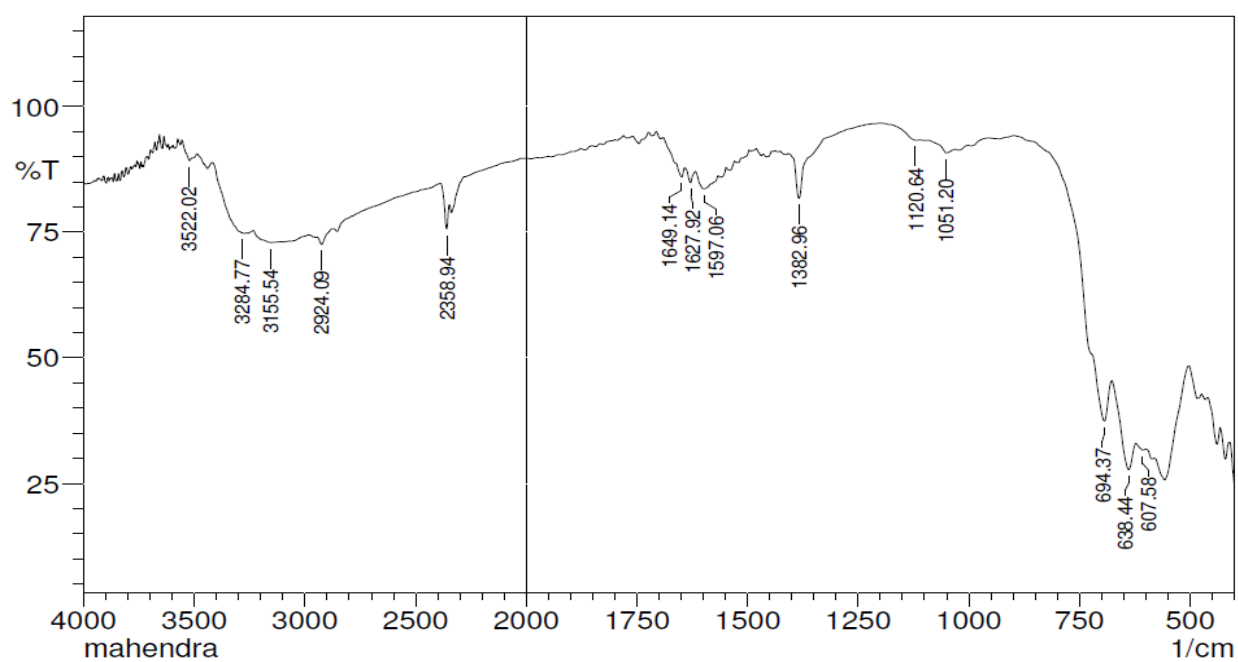
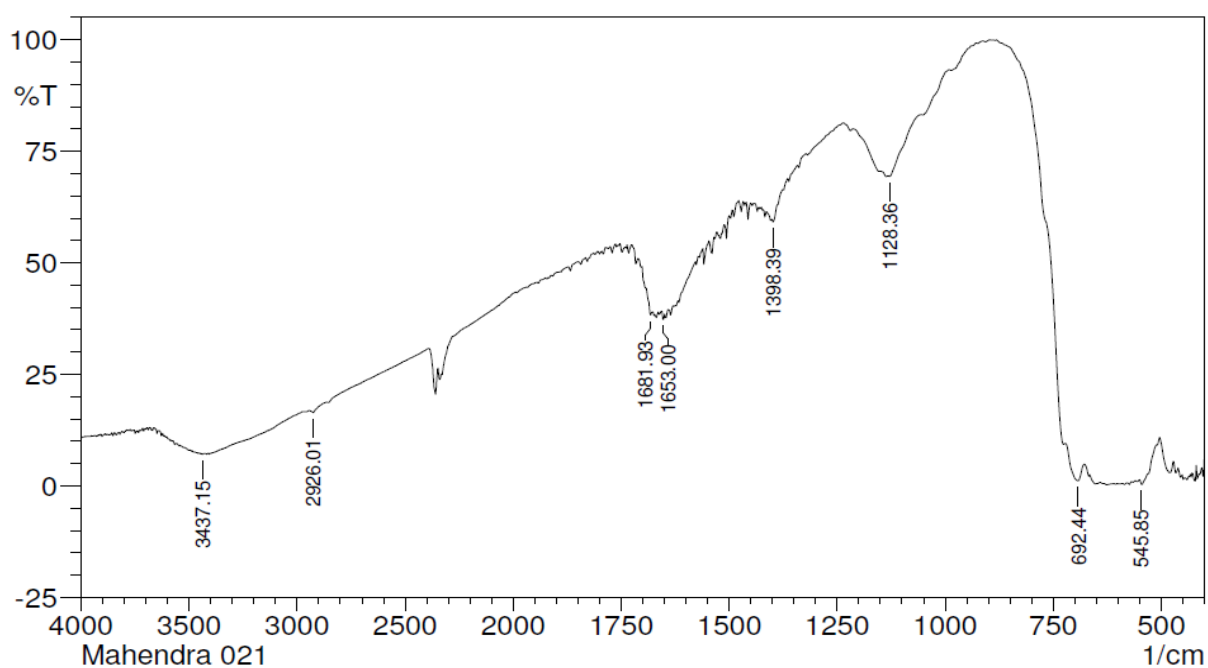
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SDP cy 05  
SDP cy 05 116 (2.133) AM2 (Ar:20000.0,556.28,0.00,LS 3); ABS; Sm (SG, 1x1.00); Cm (115-119-(104-108+128-133))

1: TOF MS ES+  
5.20e5



FTIR of native nano- $\text{Fe}_2\text{O}_3$ FTIR of used nano- $\text{Fe}_2\text{O}_3$