

# Supporting Information

## **Polydopamine: An Amine Oxidase Mimicking Sustainable Catalyst for the Synthesis of Nitrogen Heterocycles under Aqueous Conditions**

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## **EXPERIMENTAL SECTION:**

### **General Information:**

All reagents and starting materials were obtained from commercial sources and were utilized without further purification. Thin Layer Chromatography (TLC) was carried out on silica (Silica Gel 60 F254) pre-coated aluminium plates and the products were visualized by UV lamp (PHILIPS TUV 8W lamp) and iodine stain. The catalysts were characterized by techniques such as SEM, EDX, TEM, FTIR, XRD, DSC-TGA, XPS, ICP-AES and Zeta Potential Analysis. Field emission gun-scanning electron microscopy (FEG-SEM) analysis was carried on JEOL JSM-7600 F model with secondary electron (SE) detector between 10.0 kV to 20.0 kV. Transmission Electron Microscopy (TEM) was carried on PHILIPS, CM 200 model operating at voltage 20-200 kV. FTIR was carried on Bruker make instrument. X-ray powder diffraction (XRD) patterns were recorded on Shimadzu XRD-6100 (CuK $\alpha$  radiations = 1.5405 Å) powder diffractometer instrument with a scanning rate 2° per min and 2 theta ( $\theta$ ) angle ranging from 5° to 80° with current 30 mA and voltage 40 kV. Thermogravimetric analysis (TGA) was carried out using Perkin Elmer STA 6000 in nitrogen gas flow, heated from room temperature to 800 °C with a ramp rate of 20 °C/min. X-ray photoelectron spectra (XPS) was carried out by using PHI 5000 Versa Probe with a monochromatic focused (100  $\mu\text{m}\times 100\ \mu\text{m}$ ) Al K $\alpha$  X-ray radiation (15 kV, 30 mA) and dual beam neutralization using a combination of argon ion gun and electron irradiation. ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy) was performed using ARCOS model instrument from M/s Spectro, Germany. Zeta potential was recorded on Malvern make instrument. Products were purified by column chromatography on silica gel (60-120) mesh size using petroleum ether and ethyl acetate as eluents. The products were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy on an Agilent NMR spectrophotometer (400 MHz for <sup>1</sup>H NMR; 100 MHz for <sup>13</sup>C NMR). The following abbreviations were used to denote the multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad. The chemical shifts of <sup>1</sup>H NMR spectra were recorded with respect to TMS ( $\delta$  0.00) or residual protiated solvents (CDCl<sub>3</sub>:  $\delta$  7.26; DMSO:  $\delta$  2.50). The chemical shifts of <sup>13</sup>C NMR spectra were recorded with respect to solvent resonance (CDCl<sub>3</sub>:  $\delta$  77.16; DMSO:  $\delta$  39.52).

### **Experimental procedure for polydopamine preparation:**

Polydopamine was synthesized according to a method reported in literature with some modifications (Lee, H.; Dellatore, S. M.; Miller, W. M.; Messersmith, P. B. Mussel-inspired surface chemistry for multifunctional coatings. *Science* **2007**, *318*, 426–430). 300 mL

deionized water was taken in a 500 mL beaker and the pH was adjusted to 8.5 by using 10 mM TrisHCl buffer. To this 1.1 g dopamine hydrochloride was added and the solution was allowed to stir on a magnetic stirrer overnight for 24 h at room temperature. The as formed polydopamine was collected by centrifugation and washed three times with deionised water, followed by washings with ethanol and acetone once. The synthesized polydopamine was dried overnight in a desiccator at room temperature.

#### **Benzimidazole Synthesis (Experimental Procedure A):**

To a 15 mL round bottom flask equipped with a teflon coated magnetic bar, *o*-phenylenediamine (0.30 mmol, 32 mg) and polydopamine (100 wt%, 32 mg) catalyst were added. To this, water (2 mL) was added along with the substrate benzylamine (1.2 equiv., 0.36 mmol, 39  $\mu$ L). The reaction mixture was allowed to stir for the indicated time at 80 °C under oxygen atmosphere and the progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was filtered to separate the catalyst followed by washings with water and ethyl acetate. The filtered solution was extracted three to four times with ethyl acetate. The organic solvent was evaporated on rotary evaporator and the crude product was purified by column chromatography using neutral silica gel with petroleum ether/ethyl acetate as eluents.

#### **Quinoxaline Synthesis (Experimental Procedure B):**

To a 15 mL round bottom flask, equipped with a teflon coated magnetic bar, *o*-phenylenediamine (0.30 mmol, 32 mg) and polydopamine catalyst (100 wt%, 32 mg) were added. To this water (2 mL) was added along with the substrate phenylethylamine (1.5 equiv., 0.45 mmol, 56  $\mu$ L). The reaction mixture was allowed to stir for the indicated time at 80 °C under oxygen atmosphere and the progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was filtered to separate the catalyst followed by washings with water and ethyl acetate. The filtered solution was extracted three to four times with ethyl acetate. The organic solvent was evaporated on rotary evaporator and the crude product was purified by column chromatography using neutral silica gel with petroleum ether/ethyl acetate as eluents.

#### **Quinazolinone Synthesis (Experimental Procedure C):**

To a 15 mL round bottom flask, equipped with a teflon coated magnetic bar, anthranilamide (0.30 mmol, 41 mg) and polydopamine catalyst (100 wt%, 41 mg) were added. To this water (2 mL) was added along with the substrate benzylamine (2.0 equiv., 0.60 mmol, 66  $\mu$ L). The reaction mixture was allowed to stir for the indicated time at 100 °C under oxygen

atmosphere and the progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was filtered to separate the catalyst followed by washings with water and ethyl acetate. The filtered solution was extracted three to four times with ethyl acetate. The organic solvent was evaporated on rotary evaporator and the crude product was purified by column chromatography using neutral silica gel with petroleum ether/ethyl acetate as eluents.

#### **Oxidation of Secondary Amines (Experimental Procedure D):**

To a 15 mL round bottom flask, equipped with a teflon coated magnetic bar, secondary amine (0.30 mmol) and polydopamine catalyst (100 wt%) were added. To this water (2 mL) was added and the reaction mixture was allowed to stir for the indicated time at 80 °C under oxygen atmosphere and the progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was filtered to separate the catalyst followed by washings with water and ethyl acetate. The filtered solution was extracted three to four times with ethyl acetate. The organic solvent was evaporated on rotary evaporator and the crude product was purified by column chromatography using neutral silica gel with petroleum ether/ethyl acetate as eluents.

#### **PDA Catalyst Recyclability Study:**

To a 25 mL round bottom flask, equipped with teflon coated magnetic bar, *o*-phenylenediamine (1.5 mmol, 162 mg) and polydopamine (100 wt%, 162 mg) were added. To this, water (4 mL) was added along with the substrate benzylamine (1.8 mmol, 197  $\mu$ L). The reaction mixture was allowed to stir for the indicated time at 80 °C under oxygen atmosphere and the progress of the reaction was monitored by TLC. After completion of the reaction, diethyl ether was added to the reaction mixture and stirred for 5 minutes at room temperature; the product was extracted using diethyl ether several times by simple decantation. The solvent was evaporated on rotary evaporator and the crude product was purified by column chromatography using neutral silica gel with petroleum ether/ethyl acetate as eluents. The aqueous part containing the catalyst was freshly charged with substrates *i.e.* *o*-phenylenediamine and benzylamine and checked for conversion. Likewise the catalyst was recycled upto three cycles. After third cycle, the reaction mixture was filtered, the catalyst was thoroughly washed with ethyl acetate, water and methanol, followed by vacuum drying in a desiccator and characterised by spectroscopic techniques.

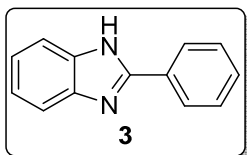
**Fe<sub>3</sub>O<sub>4</sub>@PDA Catalyst Recyclability Study:**

To a 15 mL round bottom flask, equipped with teflon coated magnetic bar, *o*-phenylenediamine (0.3 mmol, 32 mg) and Fe<sub>3</sub>O<sub>4</sub>@PDA (100 wt%, 32 mg) were added. To this, water (2 mL) was added along with the substrate benzylamine (0.36 mmol, 39  $\mu$ L). The reaction mixture was allowed to stir for the indicated time at 80 °C under oxygen atmosphere and the progress of the reaction was monitored by TLC. After completion of the reaction, diethyl ether was added to the reaction mixture and stirred for 5 minutes at room temperature; the product was extracted using diethyl ether several times by simple decantation and the catalyst was hold externally by a neodymium magnet. The solvent was evaporated on rotary evaporator and the crude product was purified by column chromatography using neutral silica gel with petroleum ether/ethyl acetate as eluents. The round bottom flask containing the aqueous part with the catalyst was sonicated for 5 minutes at room temperature. Later, freshly charged with substrates *i.e.* *o*-phenylenediamine and benzylamine and checked for conversion. Likewise the catalyst was recycled upto two cycles. After second cycle, diethyl ether was added to the reaction mixture and organic phase was extracted. Then the catalyst was thoroughly washed with water, ethanol, and acetone followed by overnight vacuum drying in a desiccator and characterised by spectroscopic techniques.

## Characterization data for products:

### Benzimidazole Products:

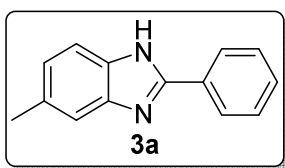
#### 2-Phenylbenzimidazole:<sup>1</sup>



<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  12.60 (s, 1H), 8.21 (d,  $J$  = 7.1 Hz, 2H), 7.60-7.45 (m, 5H), 7.20 (m, 2H).

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$  151.71, 144.45, 135.84, 130.64, 130.24, 129.36, 126.90, 122.55, 119.13, 112.05

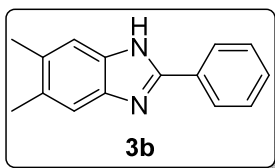
#### 5-Methyl-2-phenylbenzimidazole:<sup>2</sup>



<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  12.74 (s, 1H), 8.15 (d,  $J$  = 8.0 Hz, 2H), 7.52-7.29 (m, 5H), 6.99 (m, 1H).

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$  151.14, 132.27, 130.74, 130.05, 129.32, 126.71, 124.39, 118.88, 111.46, 21.80

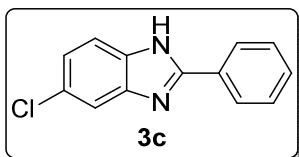
#### 5,6-Dimethyl-2-phenylbenzimidazole:<sup>1</sup>



<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  12.60 (s, 1H), 8.12 (d,  $J$  = 7.1 Hz, 2H), 7.51-7.33 (m, 5H), 2.29 (s, 6H).

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$  150.75, 130.89, 129.85, 129.67, 129.26, 128.72, 126.62, 20.44.

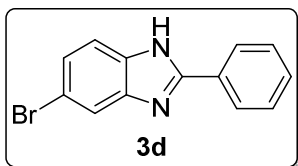
#### 5-Chloro-2-phenylbenzimidazole:<sup>1</sup>



<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  13.07 (s, 1H), 8.15 (d,  $J$  = 6.9 Hz, 2H), 7.54-7.47 (m, 5H), 7.20 (d,  $J$  = 7.0 Hz, 1H)

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$  153.07, 130.60, 130.12, 129.40, 127.0, 122.78

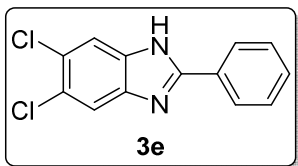
### 5-Bromo-2-phenylbenzimidazole:<sup>1</sup>



<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  13.09 (s, 1H), 8.16 (d,  $J = 6.9$  Hz, 2H), 7.77 (br, 1H), 7.53-7.46 (m, 4H), 7.31 (d,  $J = 8.2$  Hz, 1H)

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$  152.89, 130.62, 130.08, 129.41, 127.03, 125.39, 114.59

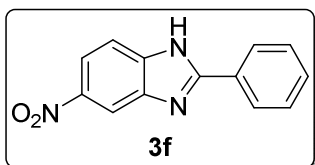
### 5,6-Dichloro-2-phenylbenzimidazole:<sup>3</sup>



<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  13.14 (br s, 1H), 8.13 (d,  $J = 5.8$  Hz, 2H), 7.79 (s, 2H), 7.52-7.50 (m, 3H)

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$  154.23, 130.90, 129.72, 129.43, 127.15, 124.90, 116.80

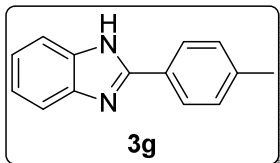
### 5-Nitro-2-phenylbenzimidazole:<sup>1</sup>



<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  8.37 (s, 1H), 8.09-8.01 (m, 3H), 7.66 (d,  $J = 7.1$  Hz, 1H), 7.50 (m, 3H)

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$  156.15, 143.04, 131.48, 129.57, 129.08, 127.29, 118.44

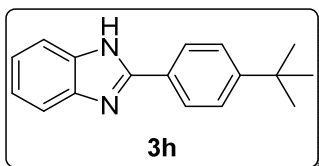
### 2-(4-Methylphenyl)benzimidazole:<sup>1</sup>



<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  12.80 (s, 1H), 8.05 (d,  $J = 7.3$  Hz, 2H), 7.61 (m, 2H), 7.33 (d,  $J = 7.1$  Hz, 2H), 7.16 (m, 2H), 2.34 (s, 3H)

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$  151.81, 144.26, 139.96, 129.91, 127.88, 126.81, 122.72, 121.97, 119.13, 111.58, 21.39

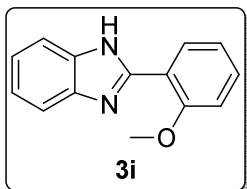
**2-(4-(*tert*-Butyl)phenyl)benzimidazole:<sup>1</sup>**



<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 12.82 (s, 1H), 8.09 (d, *J* = 8.2 Hz, 2H), 7.63-7.52 (m, 4H), 7.16 (m, 2H), 1.29 (s, 9H)

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ 152.98, 151.72, 144.26, 127.86, 126.66, 126.14, 122.75, 121.97, 119.15, 111.63, 35.0, 31.40

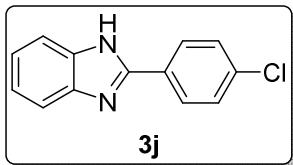
**2-(2-Methoxyphenyl)benzimidazole:<sup>2</sup>**



<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 12.10 (s, 1H), 8.32 (d, *J* = 6.3 Hz, 1H), 7.60 (m, 2H), 7.46-7.42 (m, 1H), 7.21-7.06 (m, 4H), 3.99 (s, 3H)

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ 157.19, 149.38, 131.64, 130.17, 122.12, 121.28, 118.57, 112.50, 56.18

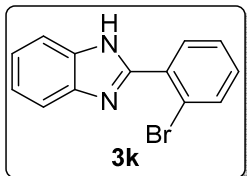
**2-(4-(Chloro)phenyl)benzimidazole:<sup>1</sup>**



<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 12.96 (s, 1H), 8.17 (d, *J* = 8.4 Hz, 2H), 7.63-7.52 (m, 4H), 7.18 (m, 2H)

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ 150.58, 144.17, 135.45, 134.91, 129.47, 128.55, 123.19, 122.25, 119.38, 111.83

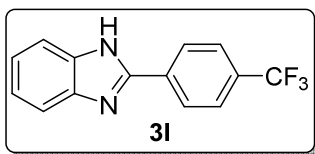
**2-(2-Bromophenyl)benzimidazole:<sup>3</sup>**



<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 12.71 (s, 1H), 7.79-7.73 (dd, *J*<sub>1</sub> = 7.9 Hz, *J*<sub>2</sub> = 6.1 Hz, 2H), 7.60 (s, 2H), 7.53-7.50 (t, *J* = 7.0 Hz, 1H), 7.44-7.41 (t, *J* = 6.8 Hz, 1H), 7.21-7.20 (m, 2H)

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ 150.84, 133.82, 132.84, 132.68, 131.77, 128.20, 122.51, 121.97

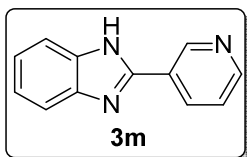
### 2-(4-(Trifluoromethyl)phenyl)benzimidazole:<sup>1</sup>



<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  13.14 (s, 1H), 8.37 (d,  $J$  = 7.9 Hz, 2H), 7.90 (d,  $J$  = 8.1 Hz, 2H), 7.69 (d,  $J$  = 6.6 Hz, 1H), 7.55 (d,  $J$  = 6.5 Hz, 1H), 7.23 (m, 2H)

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$  150.06, 144.14, 135.52, 134.37, 130.21, 127.46, 126.36, 126.32, 123.59, 122.47, 119.67, 112.06

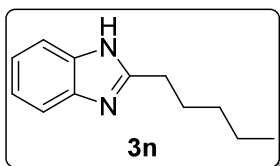
### 2-(Pyridin-3-yl)benzimidazole:<sup>2</sup>



<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  13.14 (s, 1H), 9.34 (s, 1H), 8.65 (d,  $J$  = 3.4 Hz, 1H), 8.49 (m, 1H), 7.61-7.54 (m, 3H), 7.21 (m, 2H)

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$  150.92, 149.28, 147.94, 134.17, 126.58, 124.44, 122.94, 119.69

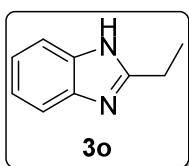
### 2-Pentylbenzimidazole:<sup>4</sup>



<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  12.13 (brs, 1H), 7.46-7.11 (m, 4H), 2.80 (m, 2H), 1.77 (m, 2H), 1.31 (m, 4H), 0.87 (m, 3H)

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$  155.57, 140.54, 121.42, 114.81, 31.30, 28.90, 27.69, 22.25, 14.24

### 2-Ethylbenzimidazole:<sup>5</sup>

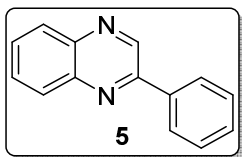


<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  7.43-7.41 (m, 2H), 7.08-7.06 (m, 2H), 2.82-2.77 (q,  $J$  = 7.4 Hz, 2H), 1.30-1.26 (t,  $J$  = 7.2 Hz, 3H)

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$  156.57, 121.47, 114.74 (br s), 22.87, 12.62

## Quinoxaline Products:

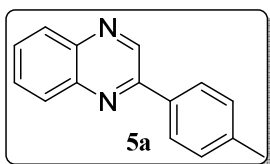
### **2-Phenylquinoxaline:<sup>1</sup>**



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.23 (s, 1H), 8.11-8.02 (m, 4H), 7.69-7.65 (m, 2H), 7.48-7.43 (m, 3H)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  151.80, 143.31, 142.27, 141.56, 136.76, 130.22, 130.13, 129.59, 129.48, 129.10, 127.51

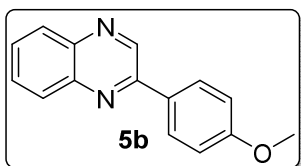
### **2-(4-Methylphenyl)quinoxaline:<sup>1</sup>**



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.31 (s, 1H), 8.15-8.10 (m, 4H), 7.77-7.73 (m, 2H), 7.36 (d,  $J$  = 7.5 Hz, 2H), 2.45 (s, 3H)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  151.80, 143.27, 142.30, 141.41, 140.45, 133.95, 130.15, 129.86, 129.50, 129.25, 129.05, 127.40, 21.39

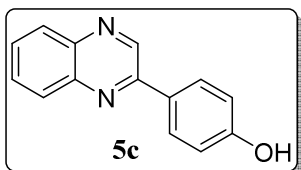
### **2-(4-Methoxyphenyl)quinoxaline:<sup>1</sup>**



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.29 (s, 1H), 8.18 (d,  $J$  = 7.5 Hz, 2H), 8.10 (t,  $J$  = 8.9 Hz, 2H), 7.78-7.69 (m, 2H), 7.09 (d,  $J$  = 7.5 Hz, 2H), 3.90 (s, 3H)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  161.43, 151.41, 143.03, 142.28, 141.15, 130.15, 129.34, 129.25, 129.02, 128.94, 114.56, 55.41

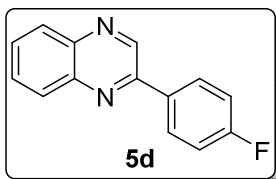
### **2-(4-Hydroxyphenyl)quinoxaline:<sup>6</sup>**



<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  10.03 (s, 1H), 9.45 (s, 1H), 8.19 (d,  $J$  = 8.4 Hz, 2H), 8.03 (d,  $J$  = 7.5 Hz, 2H), 7.79-7.73 (dd,  $J$  = 16.9, 7.0 Hz, 2H), 6.95 (d,  $J$  = 8.5 Hz, 2H)

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$  160.28, 151.38, 143.75, 141.91, 140.96, 130.79, 129.52, 129.29, 129.19, 116.41

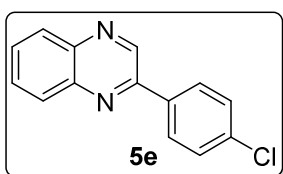
### 2-(4-Fluorophenyl)quinoxaline:<sup>1</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.26 (s, 1H), 8.19-8.11 (m, 4H), 7.77-7.73 (m, 2H), 7.25-7.21 (m, 2H)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  165.45, 162.96, 150.68, 142.87, 142.14, 141.44, 129.54, 129.49, 129.41, 129.09, 116.28, 116.07

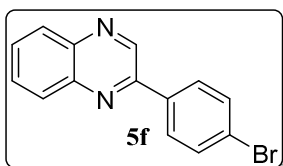
### 2-(4-Chlorophenyl)quinoxaline:<sup>1</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.28 (s, 1H), 8.15-8.11 (m, 4H), 7.79-7.75 (m, 2H), 7.54 (d,  $J$  = 8.1 Hz, 2H)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.51, 142.80, 142.16, 141.60, 136.53, 135.11, 130.41, 129.72, 129.54, 129.34, 129.11, 128.71

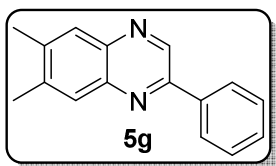
### 2-(4-Bromophenyl)quinoxaline:<sup>1</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.27 (s, 1H), 8.11-8.05 (m, 4H), 7.76-7.67 (m, 4H)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.56, 142.72, 142.16, 141.61, 135.54, 132.29, 130.43, 129.76, 129.54, 129.10, 128.94, 124.94

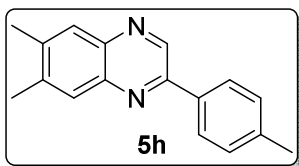
### 6,7-Dimethyl-2-phenylquinoxaline:<sup>1</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.14 (s, 1H), 8.09 (d,  $J$  = 6.9 Hz, 2H), 7.82 (d,  $J$  = 20.5 Hz, 2H), 7.49-7.42 (m, 3H), 2.43 (s, 6H)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.98, 142.35, 141.20, 140.76, 140.52, 140.08, 137.10, 129.78, 129.02, 128.61, 128.09, 127.34, 20.33, 20.29

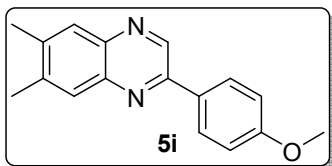
### 6,7-Dimethyl-2-(4-methylphenyl)quinoxaline:<sup>1</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.18 (s, 1H), 8.06 (d, *J* = 6.9 Hz, 2H), 7.86 (d, *J* = 20.5 Hz, 2H), 7.34 (d, *J* = 5.9 Hz, 2H), 2.47 (s, 6H), 2.42 (s, 3H)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 150.93, 142.26, 141.18, 140.60, 140.35, 139.99, 139.75, 134.26, 129.75, 128.53, 128.06, 127.19, 21.35, 20.31, 20.26

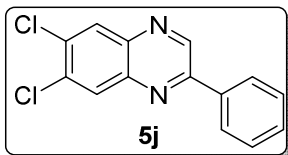
### 6,7-Dimethyl-2-(4-methoxyphenyl)quinoxaline:<sup>1</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.16 (s, 1H), 8.13 (d, *J* = 8.3 Hz, 2H), 7.85 (d, *J* = 15.4 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 3.88 (s, 3H), 2.48 (s, 6H)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 161.15, 150.59, 142.04, 140.59, 139.50, 129.62, 128.70, 128.41, 128.05, 114.46, 55.37, 20.31, 20.24

### 6,7-Dichloro-2-phenylquinoxaline:<sup>7</sup>

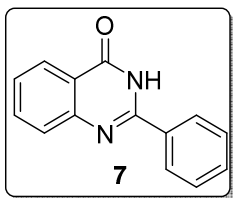


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.29 (s, 1H), 8.25-8.15 (m, 4H), 7.54 (m, 3H)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 152.59, 144.21, 141.05, 140.22, 135.94, 134.89, 133.97, 130.72, 130.14, 129.73, 129.22, 127.53

### Quinazolinone Synthesis:

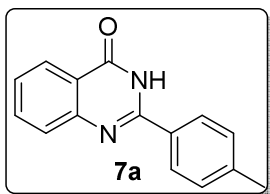
#### 2-Phenylquinazolin-4(3H)-one:<sup>2</sup>



<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 12.51 (s, 1H), 8.14-8.12 (m, 3H), 7.79-7.70 (m, 2H), 7.53-7.49 (m, 4H)

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ 162.70, 152.77, 149.09, 134.97, 133.16, 131.78, 129.00, 128.18, 127.84, 126.97, 126.27, 121.40

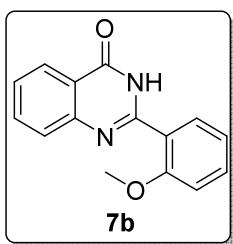
**2-(4-Methylphenyl)quinazolin-4(3H)-one:**<sup>2</sup>



<sup>1</sup>H NMR (400MHz, DMSO-d<sub>6</sub>) δ 12.38 (s, 1H), 8.12-8.05 (m, 3H), 7.81-7.68 (m, 2H), 7.49-7.45 (m, 1H), 7.33 (d, *J* = 7.9 Hz, 2H), 2.35 (s, 3H)

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ 162.73, 152.64, 149.25, 141.85, 134.95, 130.31, 129.59, 128.09, 127.78, 126.77, 126.25, 121.30, 21.40

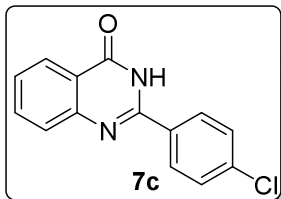
**2-(2-Methoxyphenyl)quinazolin-4(3H)-one:**<sup>8</sup>



<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 12.03 (s, 1H), 8.13 (d, *J* = 6.7 Hz, 1H), 7.79-7.66 (m, 3H), 7.49 (m, 2H), 7.17-7.05 (m, 2H), 3.83 (s, 3H)

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ 161.71, 157.55, 152.93, 149.57, 134.91, 132.72, 130.84, 127.77, 127.04, 126.20, 122.91, 120.91, 112.31, 56.21

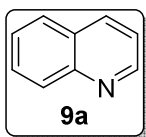
**2-(4-Chlorophenyl)quinazolin-4(3H)-one:**<sup>2</sup>



<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 12.56 (s, 1H), 8.17-8.10 (m, 2H), 7.87-7.80 (m, 1H), 7.71 (m, 1H), 7.59-7.5 (m, 3H), 7.33-7.30 (m, 1H)

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ 162.64, 151.74, 148.99, 135.08, 130.03, 129.59, 129.54, 129.10, 128.85, 128.65, 127.95, 127.21, 126.28

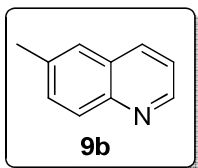
**Quinoline**<sup>9</sup>:



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.92 (d, *J* = 2.4 Hz, 1H), 8.15-8.11 (t, *J* = 8.8 Hz, 2H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.73-7.70 (t, *J* = 7.0 Hz, 1H), 7.56-7.52 (t, *J* = 7.1 Hz, 1H), 7.40-7.37 (dd, *J* = 8.1, 4.2 Hz, 1H)

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.37, 148.26, 136.01, 129.41, 128.26, 127.74, 126.50, 121.03

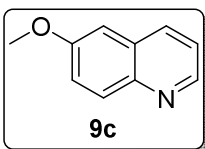
**6-Methylquinoline<sup>9</sup>:**



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.77 (m, 1H), 8.00-7.92 (dd,  $J = 23.0, 7.6$  Hz, 2H), 7.54-7.46 (m, 2H), 7.29-7.27 (m, 1H), 2.46 (s, 3H)

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.34, 146.75, 136.75, 135.33, 131.90, 129.01, 128.34, 126.74, 121.01, 21.51

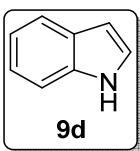
**6-Methoxyquinoline<sup>9</sup>:**



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.76 (d,  $J = 3.6$  Hz, 1H), 8.05 (dd,  $J = 14.0, 8.8$  Hz, 2H), 7.38-7.33 (m, 2H), 7.06 (d,  $J = 1.8$  Hz, 1H), 3.92 (s, 3H)

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.77, 147.55, 143.98, 135.05, 130.45, 129.32, 122.40, 121.32, 105.11, 55.49

**1H-indole<sup>10</sup>:**



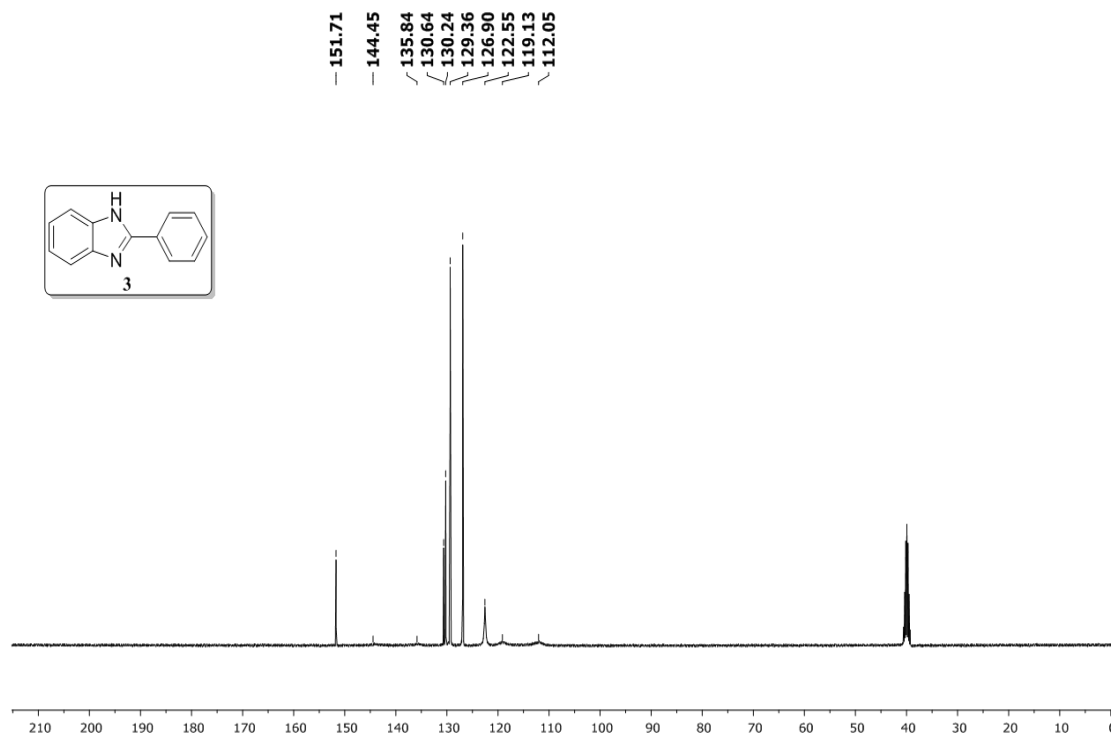
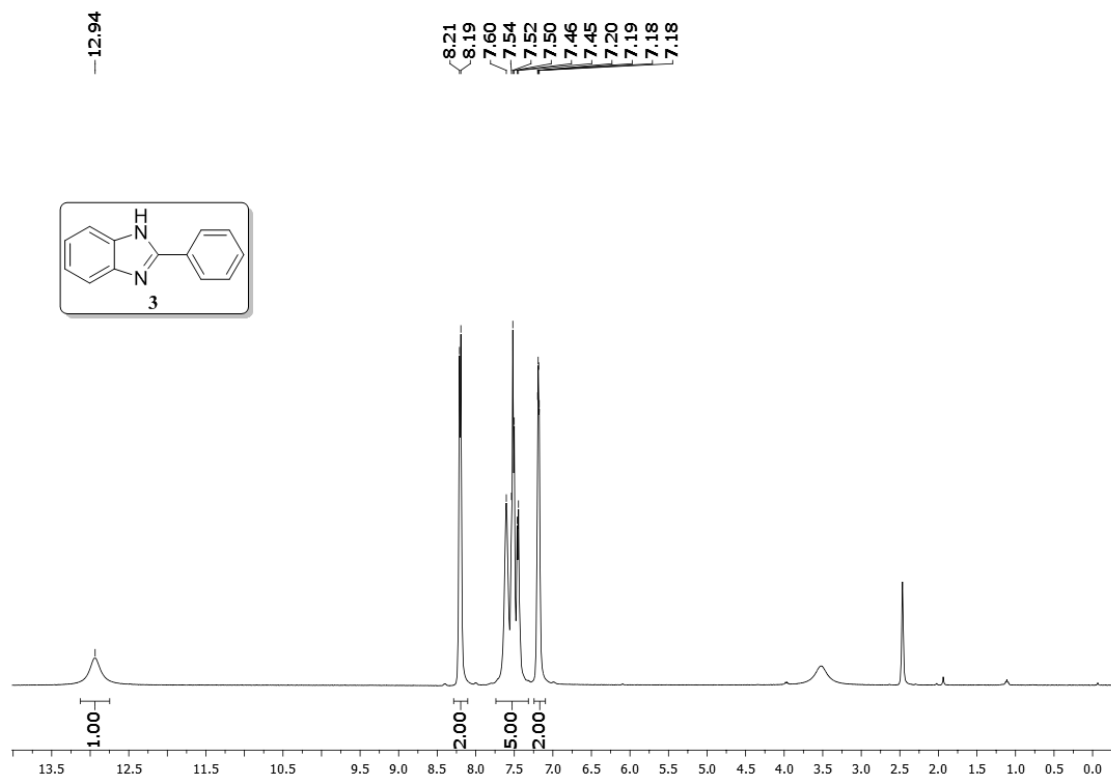
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (s, 1H), 7.66 (d,  $J = 7.0$  Hz, 1H), 7.35 (d,  $J = 7.6$  Hz, 2H), 7.19-7.17 (m, 1H), 7.13-7.10 (m, 2H), 6.54 (m, 1H)

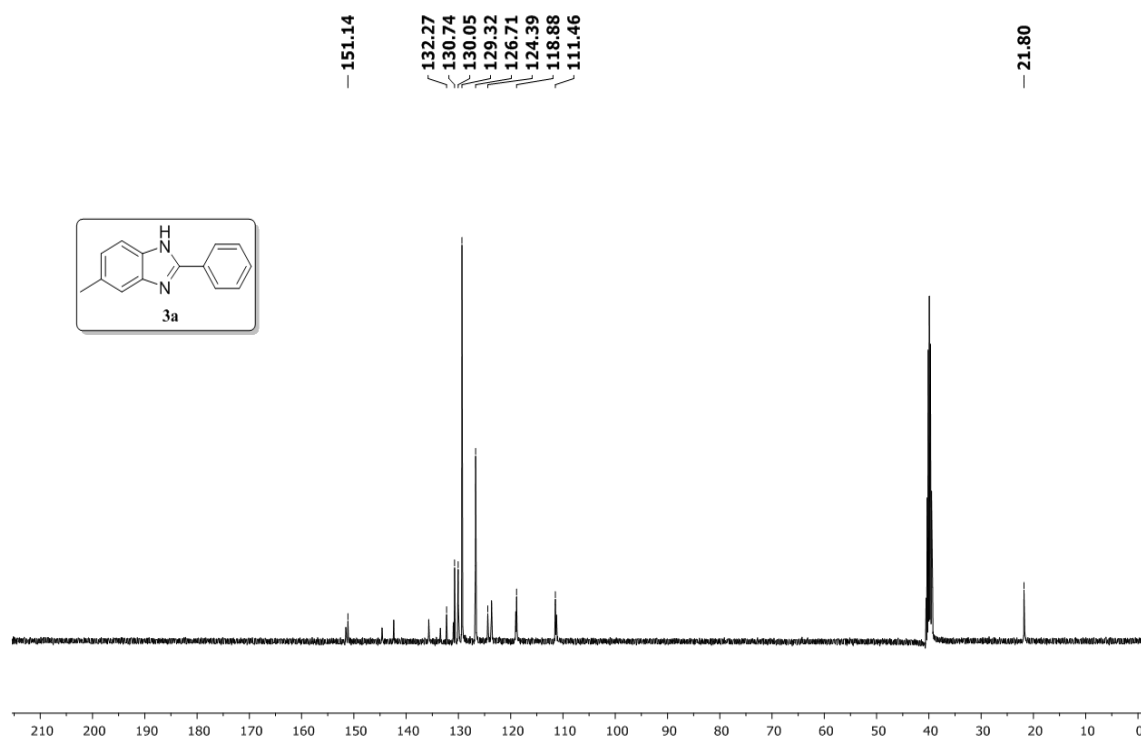
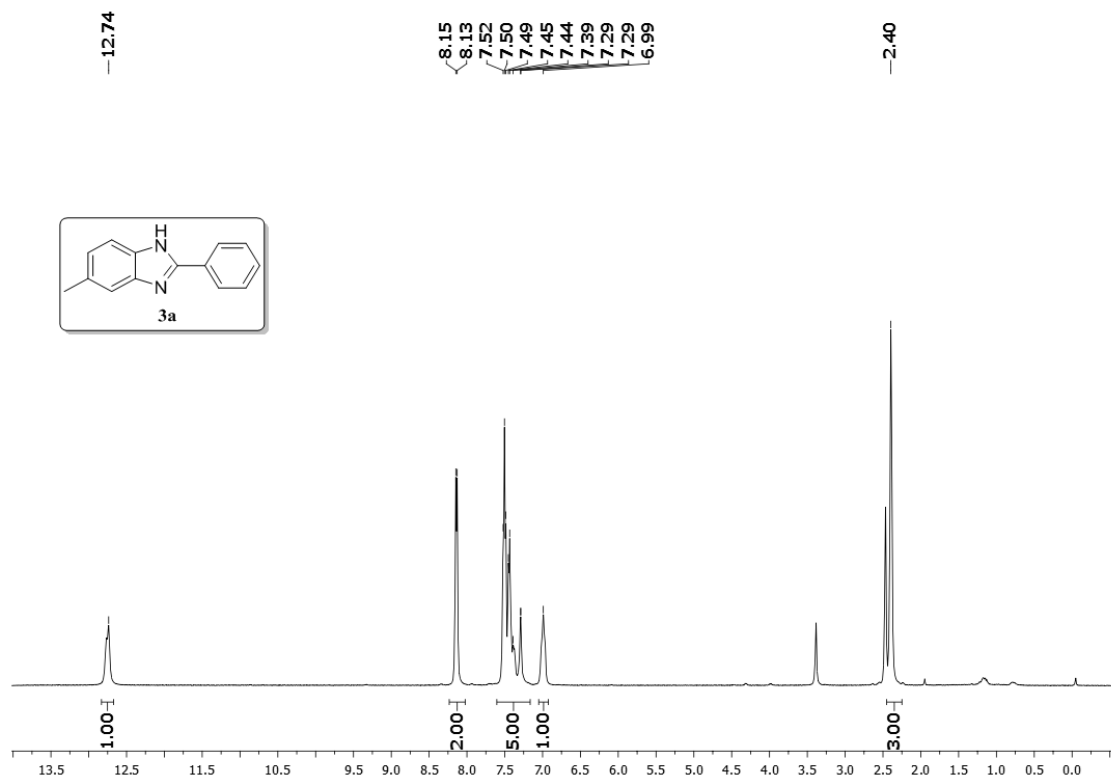
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  135.79, 127.86, 124.15, 121.98, 120.74, 119.82, 111.04, 102.59

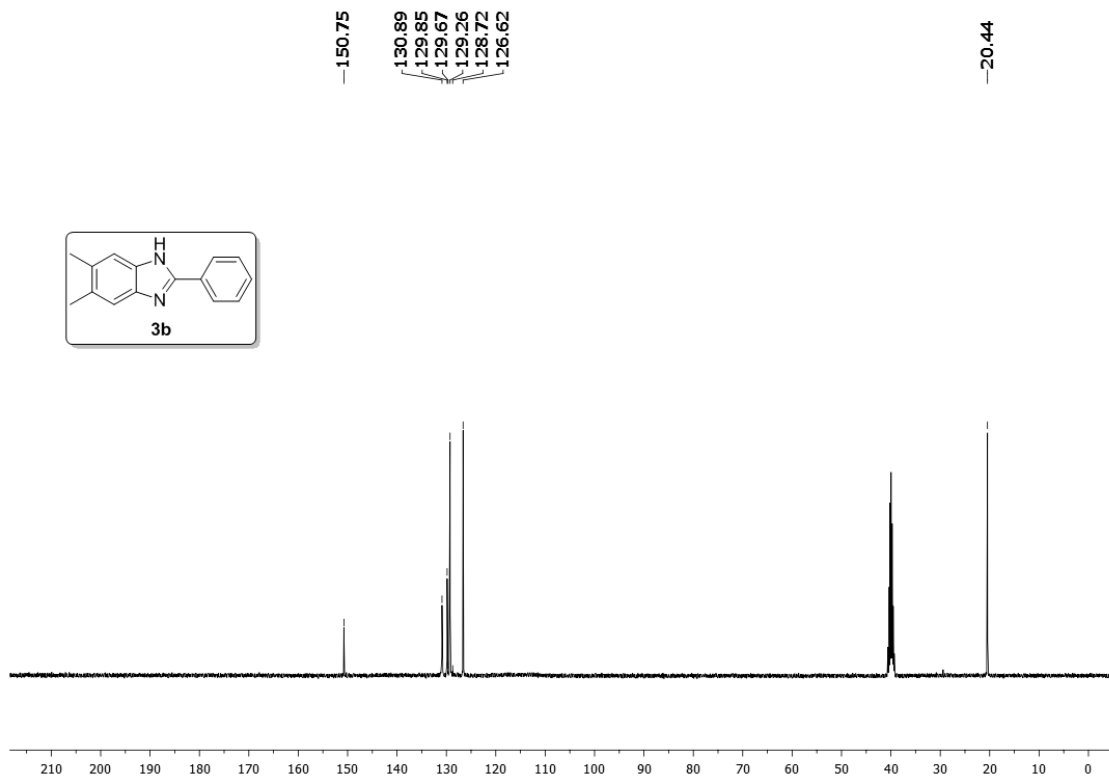
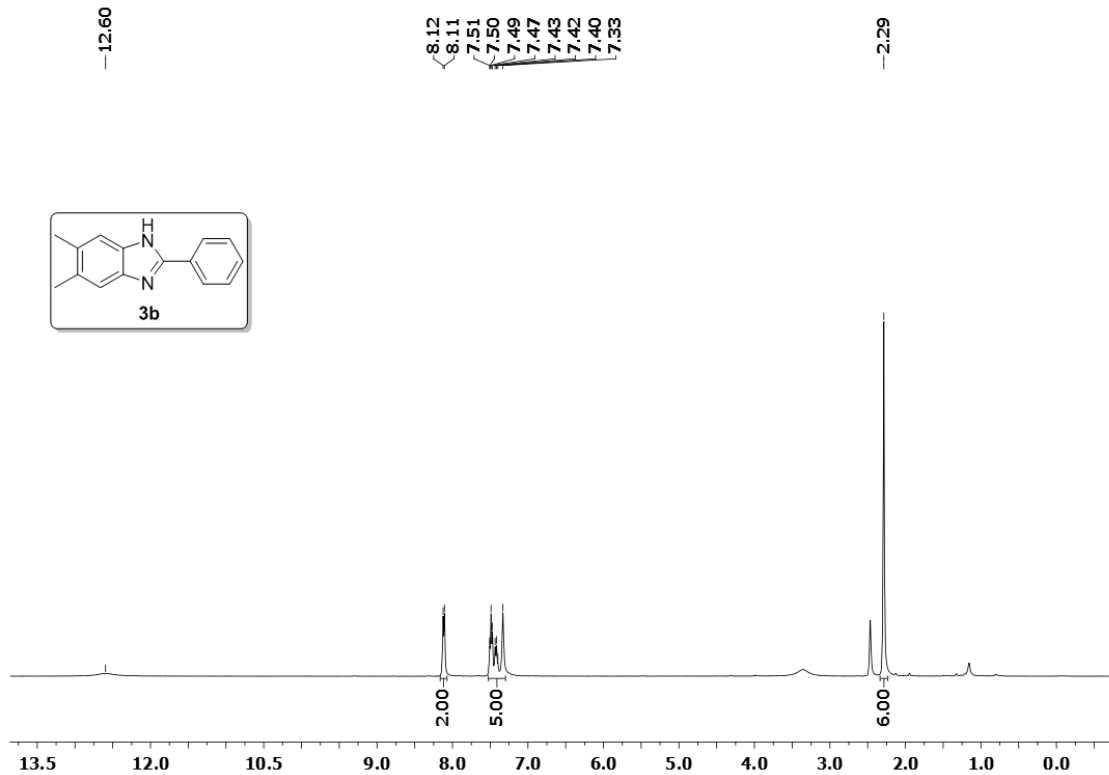
## References:

- 1) Zhang, R.; Qin, Y.; Zhang, L.; Luo, S. Oxidative synthesis of benzimidazoles, quinoxalines, and benzoxazoles from primary amines by *ortho*-quinone catalysis. *Org. Lett.* **2017**, *19*, 5629–5632.
- 2) Nguyen, T. B.; Ermolenko, L.; Al-Mourabit, A. Selective autoxidation of benzylamines: application to the synthesis of some nitrogen heterocycles. *Green Chem.* **2013**, *15*, 2713–2717.
- 3) Lai, Y. -L.; Ye, J. -S.; Huang, J. -M. Electrochemical synthesis of benzazoles from alcohols and *o*-substituted anilines with a catalytic amount of Co<sup>II</sup> salt. *Chem.- Eur. J.* **2016**, *22*, 5425–5429.
- 4) Chari, M. A.; Shobha, D.; Sasaki, T. Room temperature synthesis of benzimidazole derivatives using reusable cobalt hydroxide (II) and cobalt oxide (ii) as efficient solid catalysts. *Tetrahedron Lett.* **2011**, *52*, 5575–5580.
- 5) Nguyen, T. B., Ermolenko, L., Dean, W. A.; Al- Mourabit, A. Benzazoles from aliphatic amines and *o*-amino/mercaptan/hydroxy anilines – elemental sulfur as a highly efficient and traceless oxidizing agent. *Org. Lett.* **2012**, *14*, 5948–5951.
- 6) Lian, M.; Li, Q.; Zhu, Y.; Yin, G.; Wu, A. Logic design and synthesis of quinoxalines via the integration of iodination/oxidation/cyclization sequences from ketones and 1, 2-diamines. *Tetrahedron* **2012**, *68*, 9598–9605.
- 7) Zhang, C.; Xu, Z.; Zhang, L.; Jiao, N. Et<sub>3</sub>N-catalyzed oxidative dehydrogenative coupling of  $\alpha$ -unsubstituted aldehydes and ketones with aryl diamines leading to quinoxalines using molecular oxygen as oxidant. *Tetrahedron* **2012**, *68*, 5258–5262.
- 8) Upadhyaya, K.; Thakur, R. K.; Shukla, S. K.; Tripathi, R. P. One-pot copper (I)-catalyzed ligand/base-free tandem cyclooxidative synthesis of quinazolinones. *J. Org. Chem.* **2016**, *81*, 5046–5055.
- 9) Wendlandt, A. E.; Stahl, S. S. Modular *o*-quinone catalyst system for dehydrogenation of tetrahydroquinolines under ambient conditions. *J. Am. Chem. Soc.* **2014**, *136*, 11910–11913.
- 10) Pankhurst, J. R.; Curcio, M.; Sproules, S.; Lloyd-Jones, G. C.; Love, J. B. Earth-abundant mixed-metal catalysts for hydrocarbon oxygenation. *Inorg. Chem.* **2018**, *57*, 5915–5928.

# NMR SPECTRA

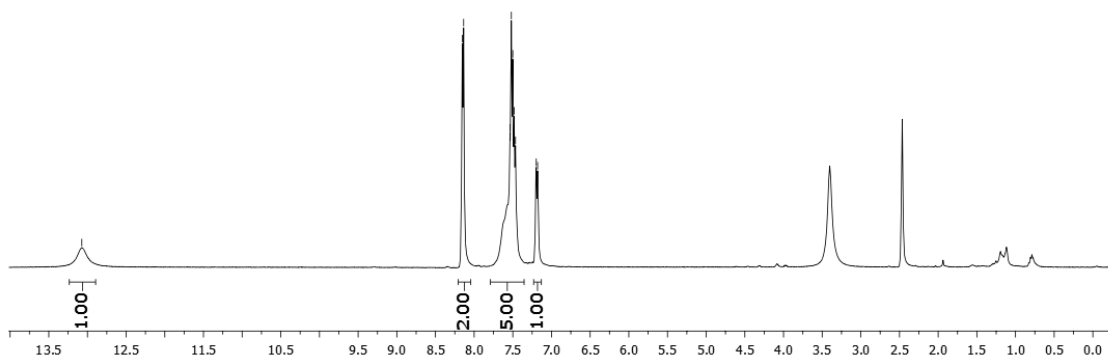
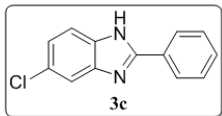






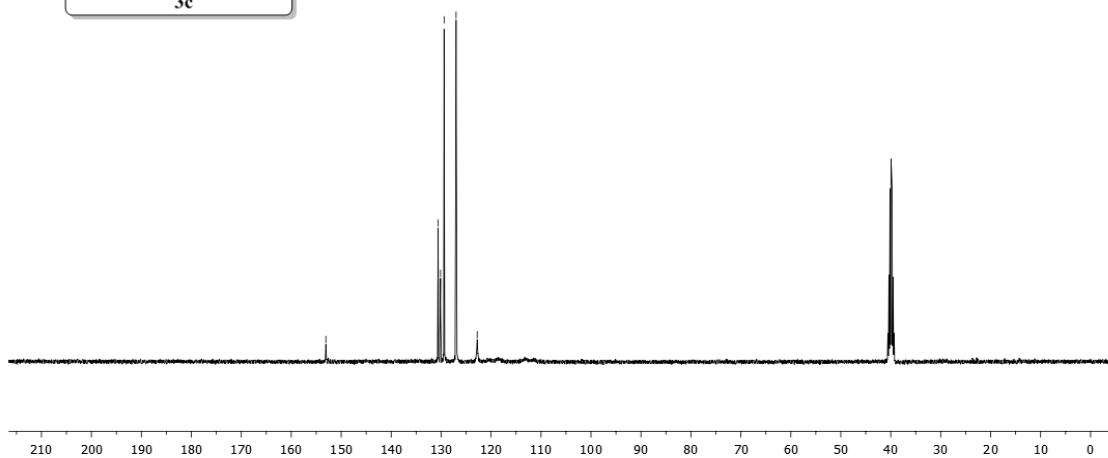
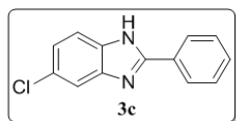
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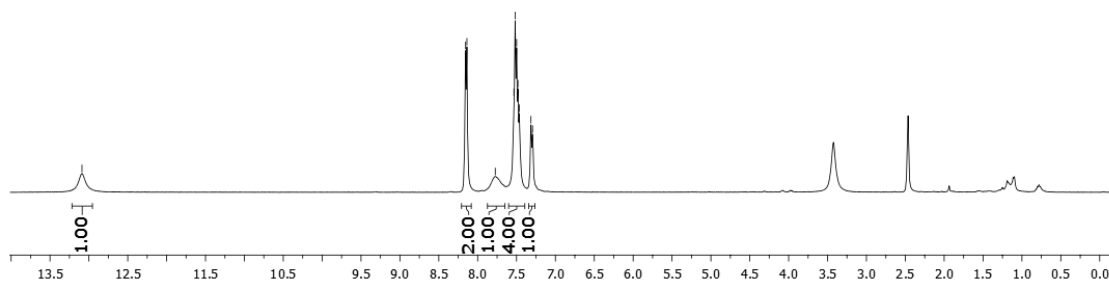
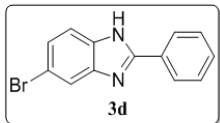
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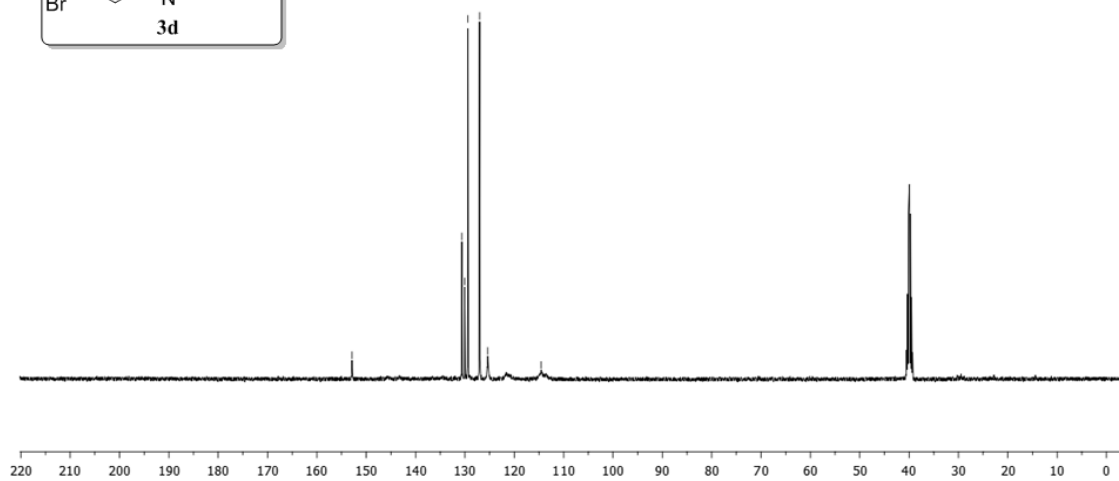
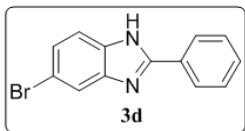
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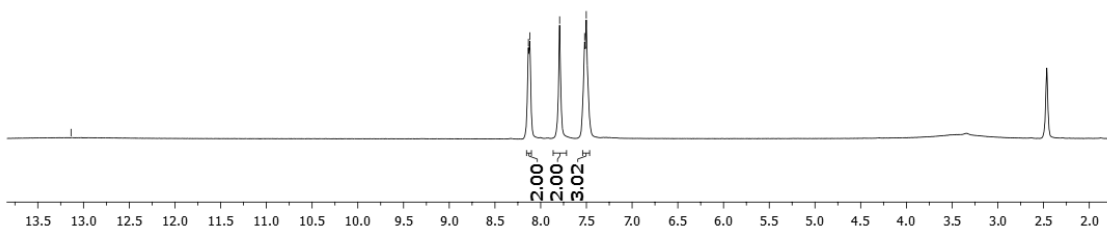
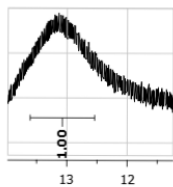
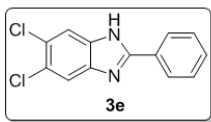
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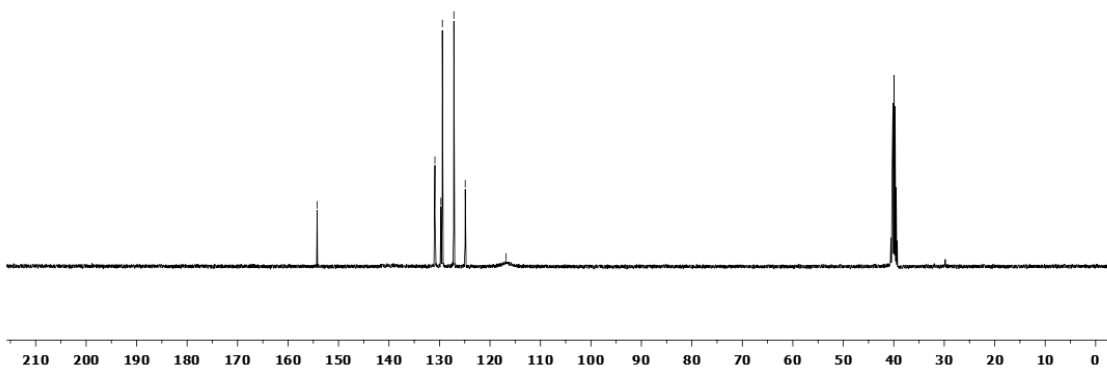
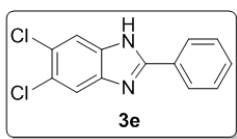
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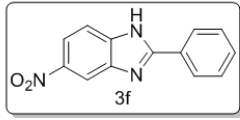
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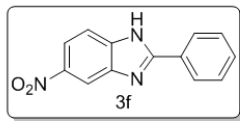
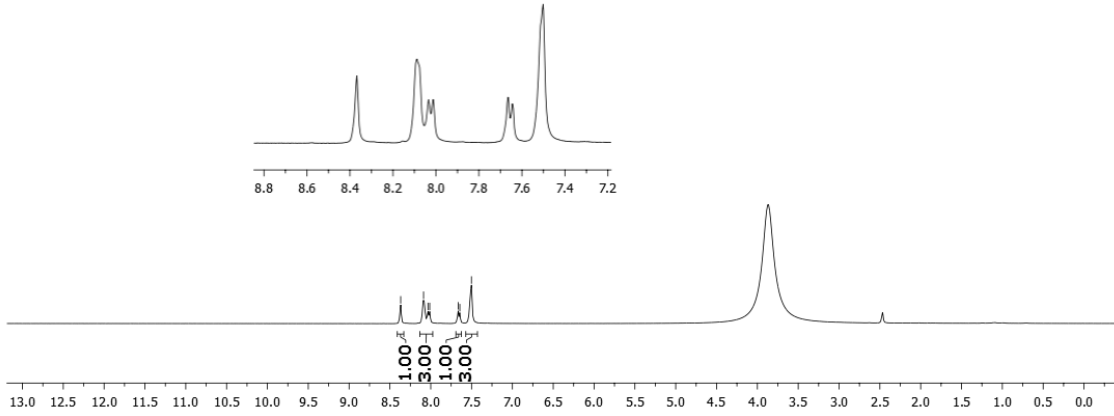
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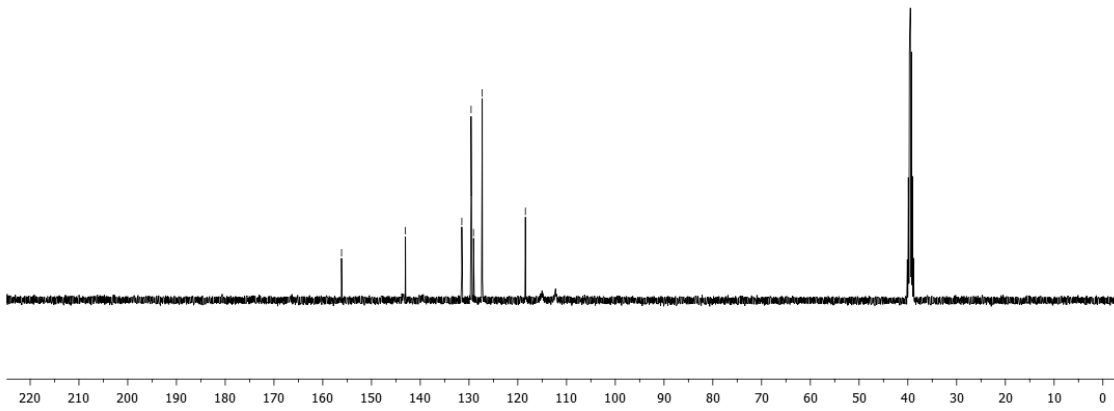


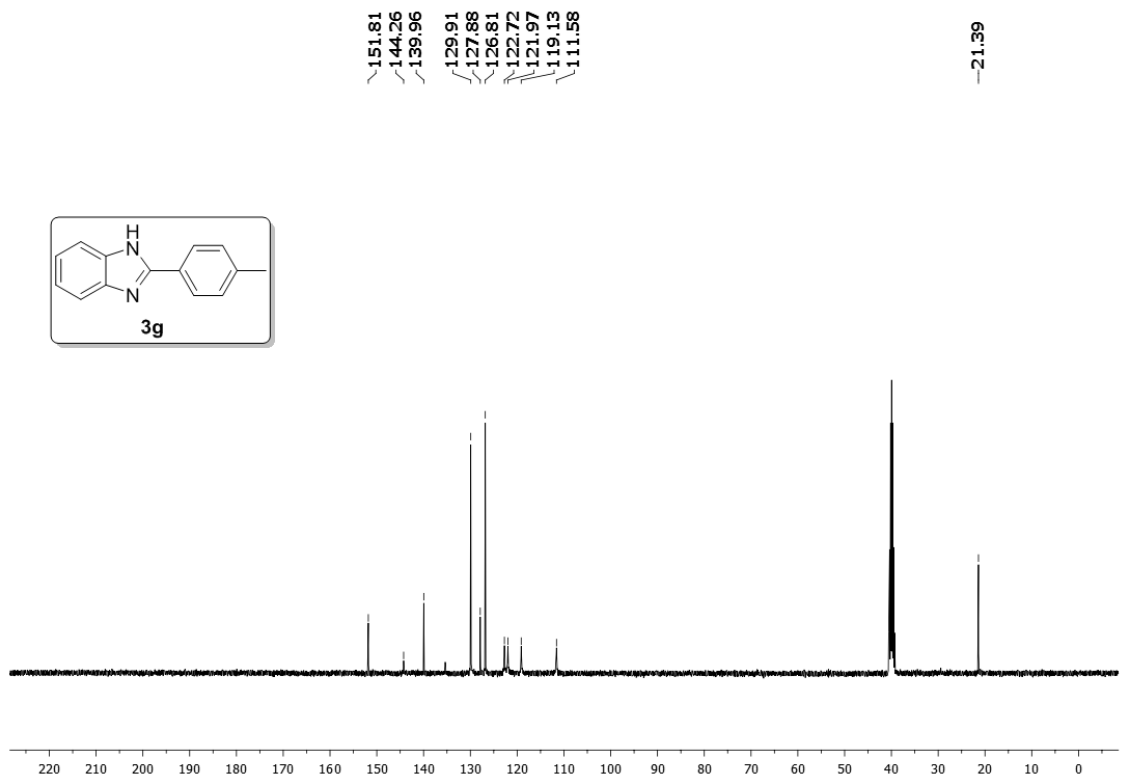
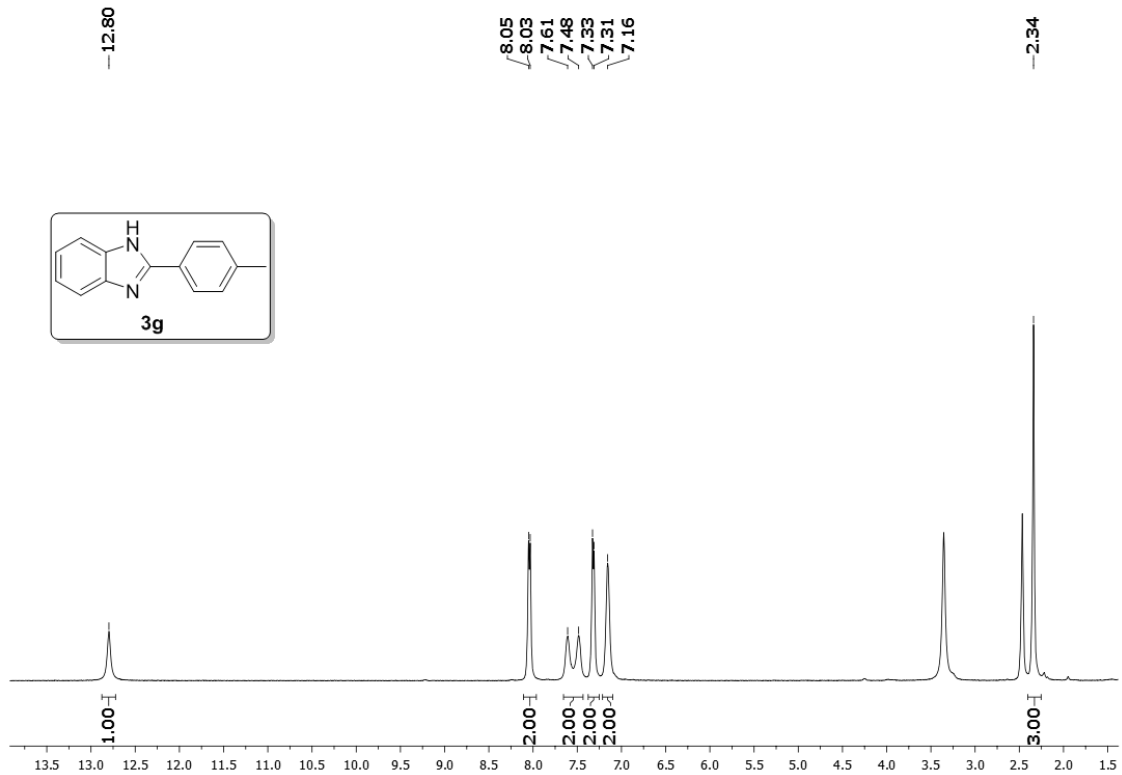


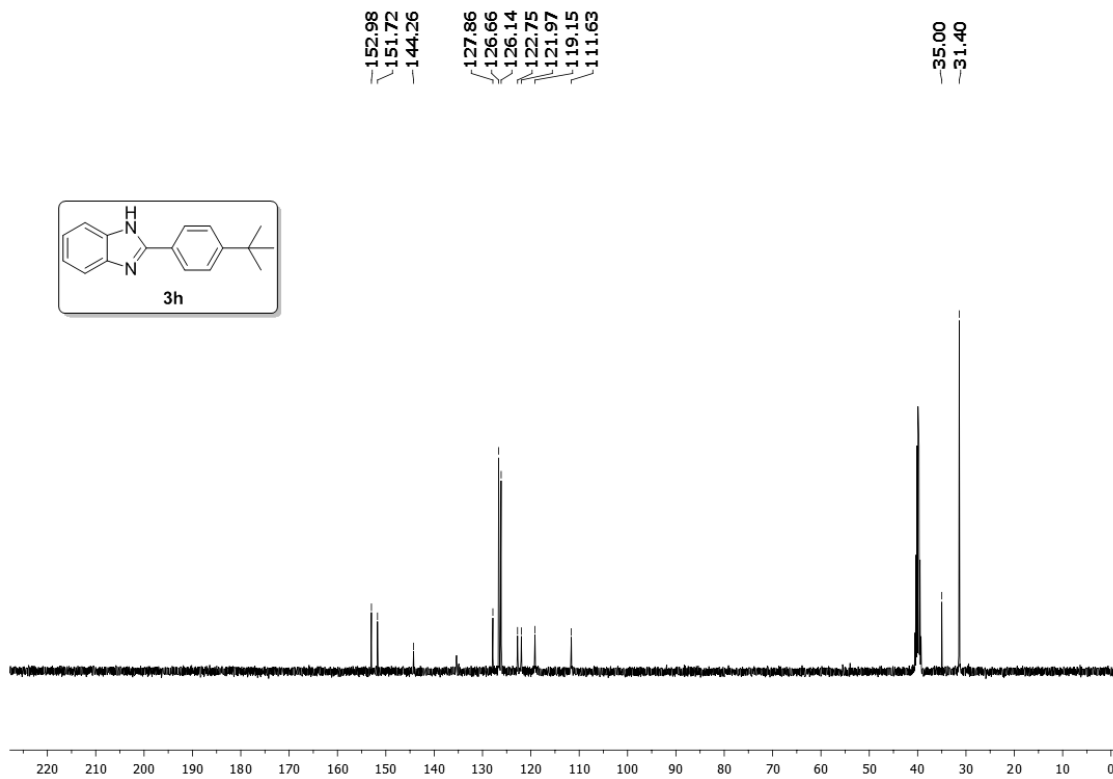
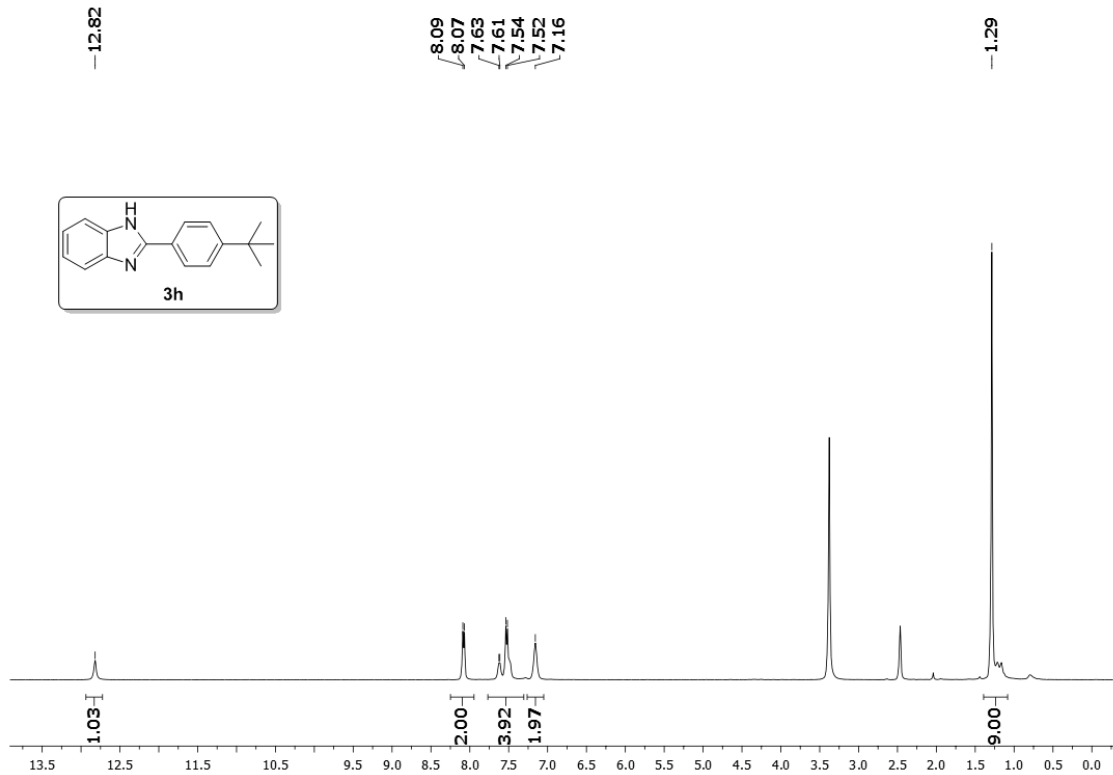
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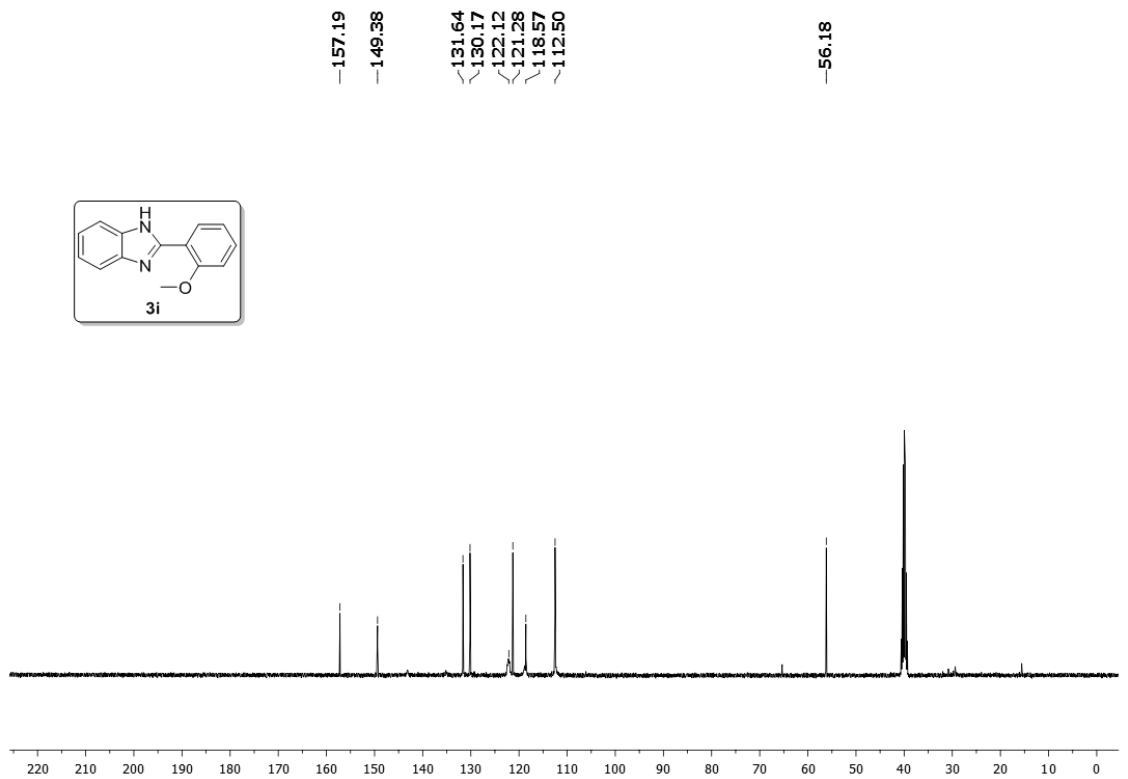
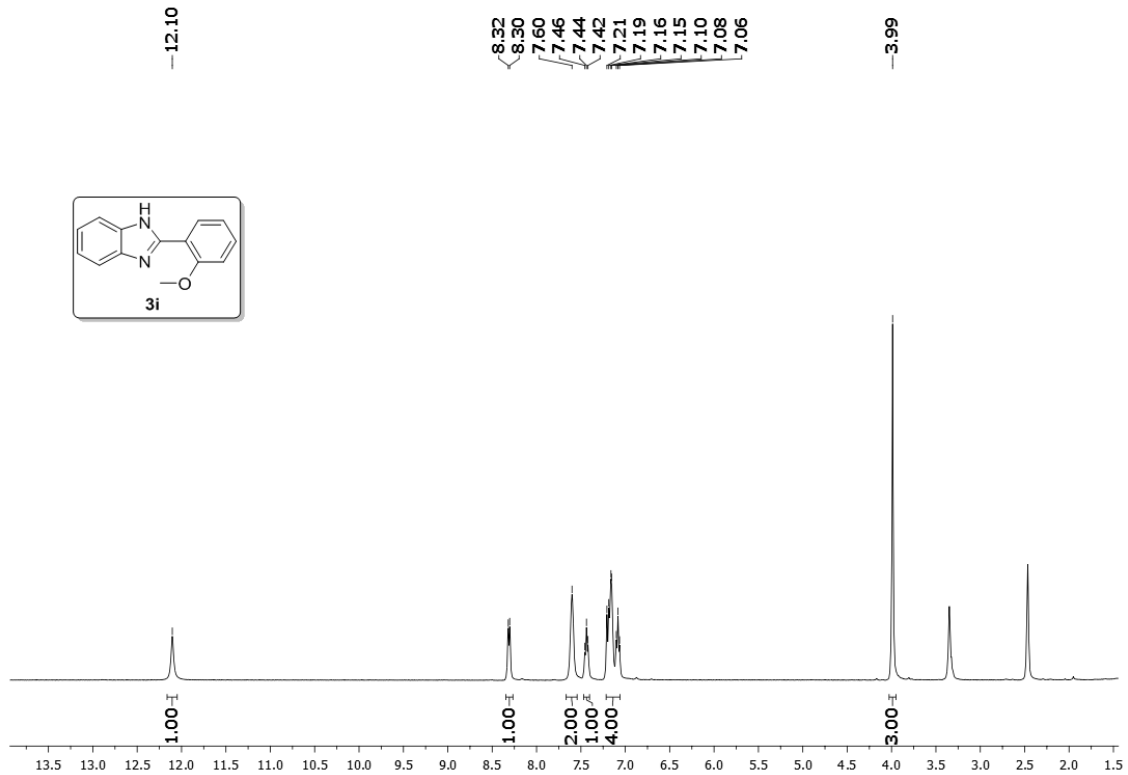


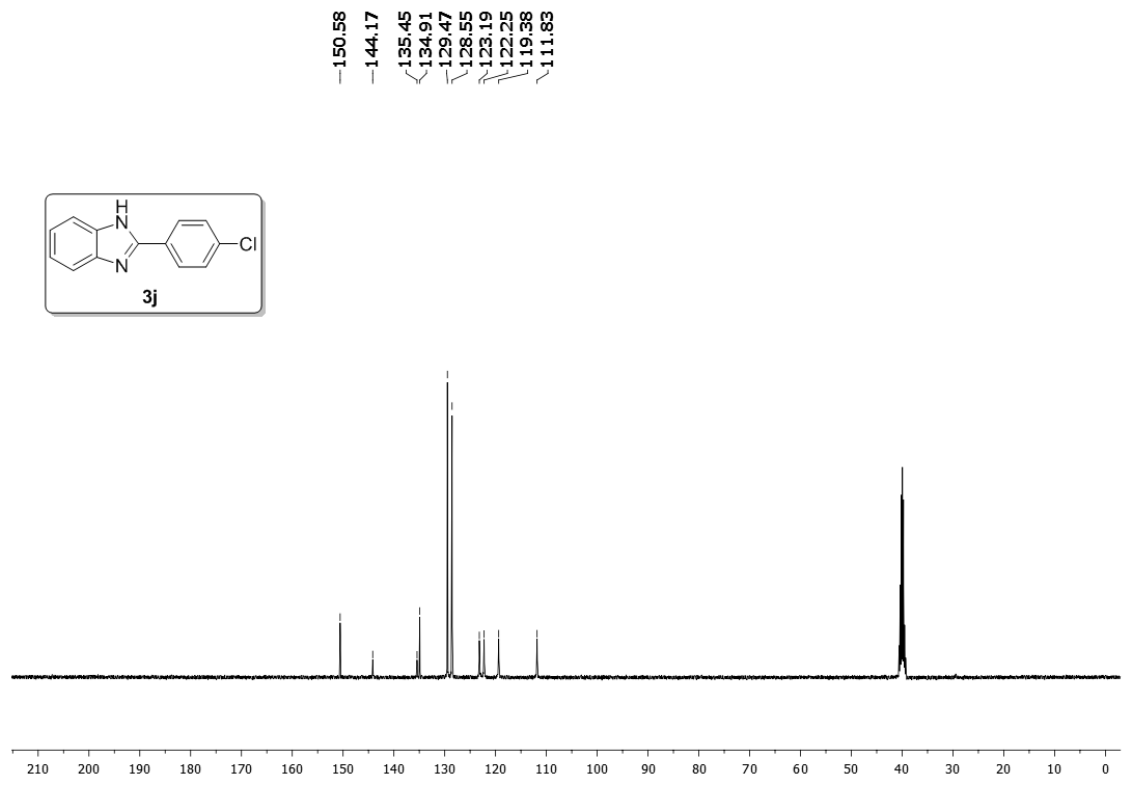
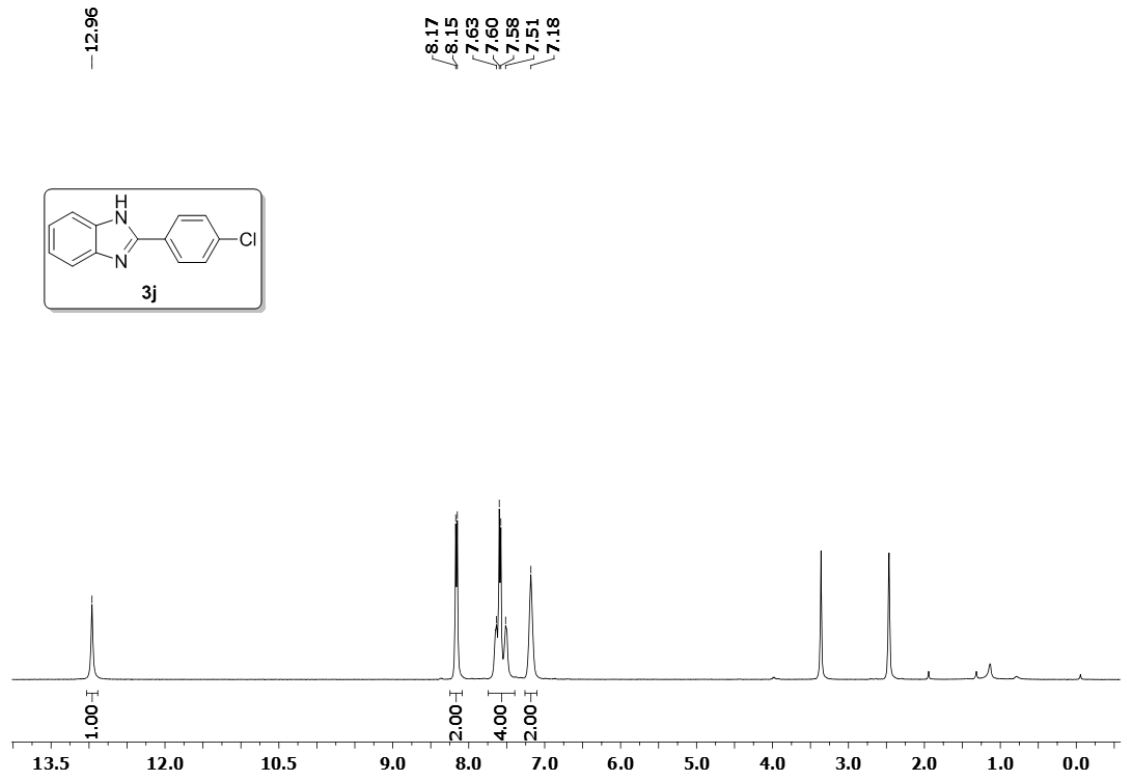
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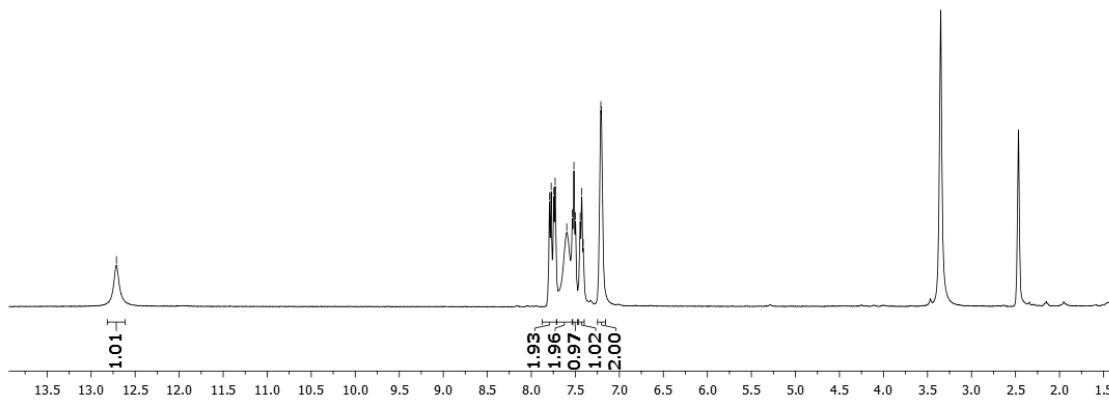
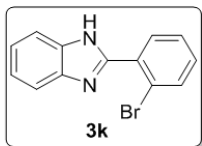






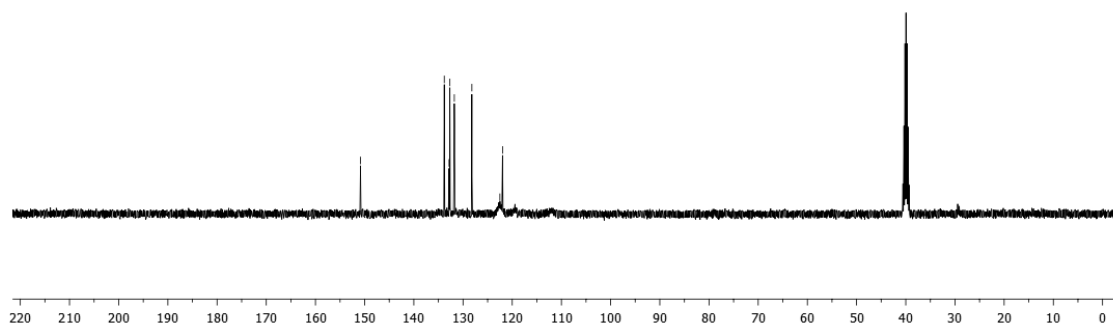
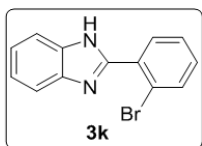
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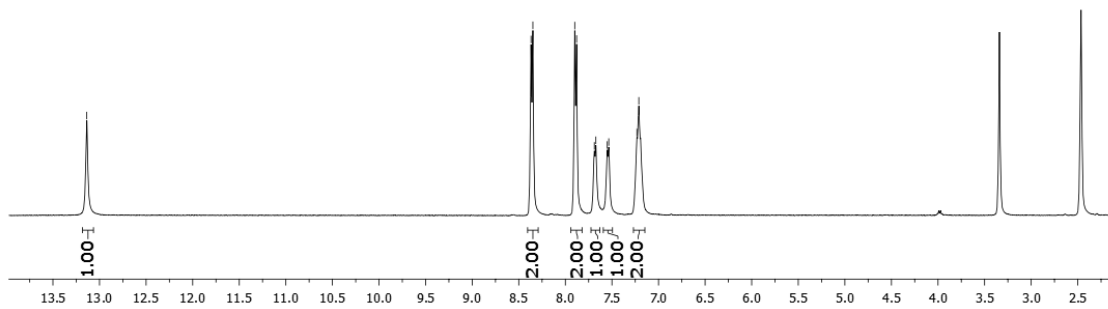
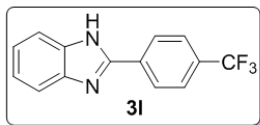
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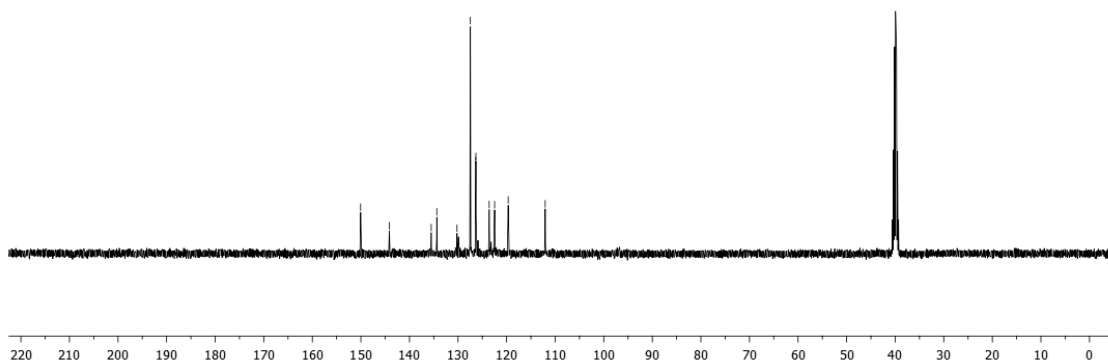
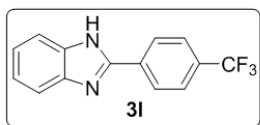


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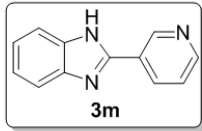
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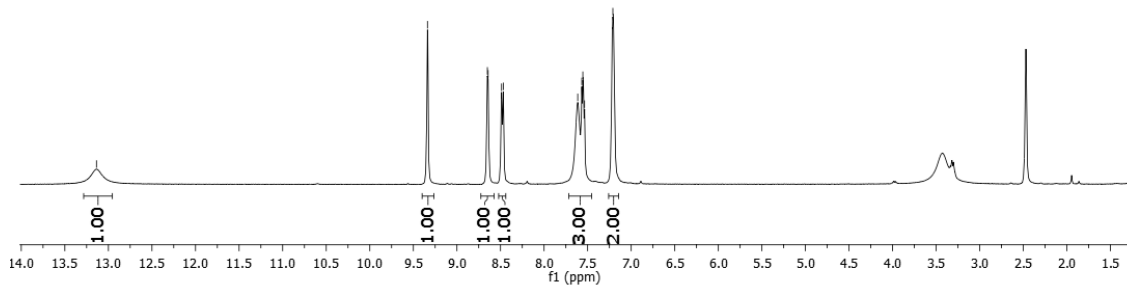
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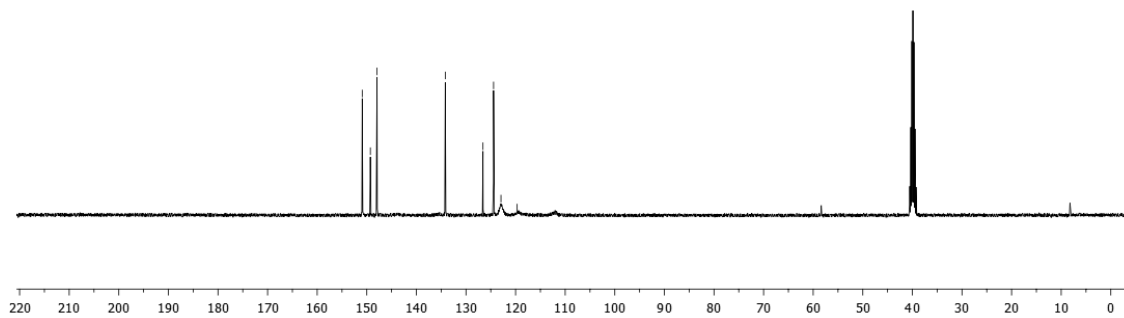
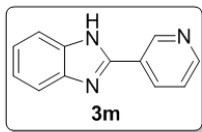
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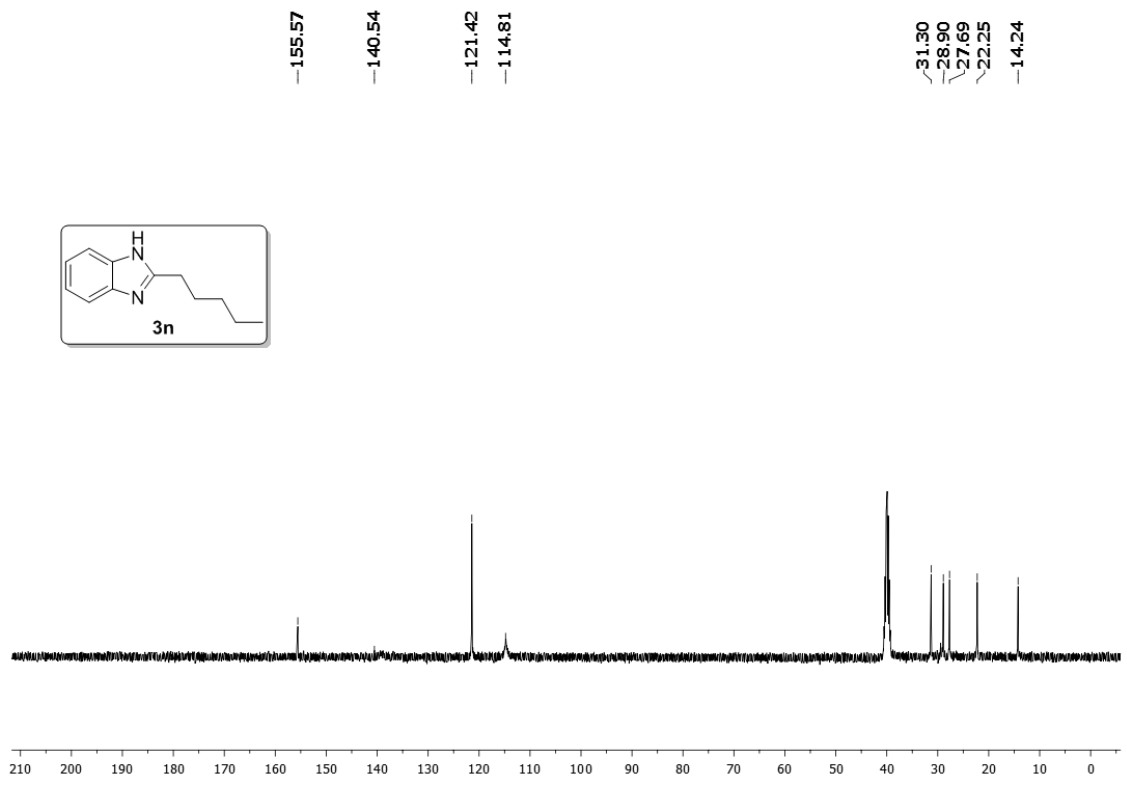
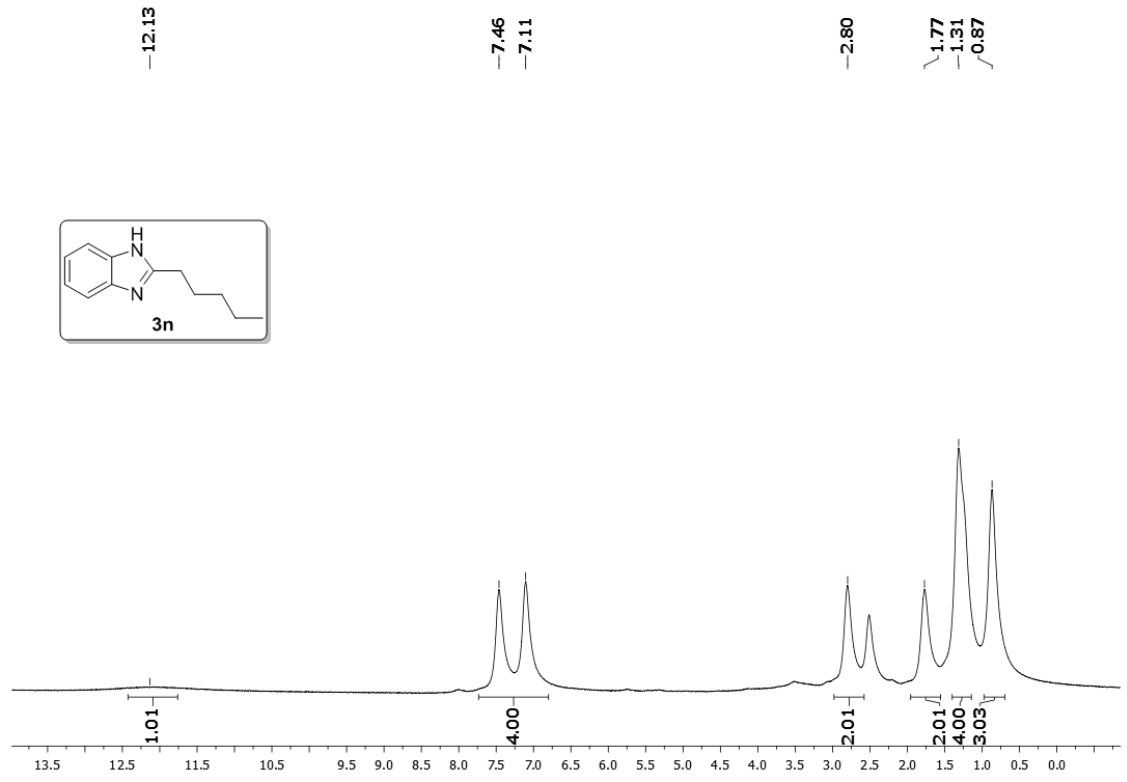


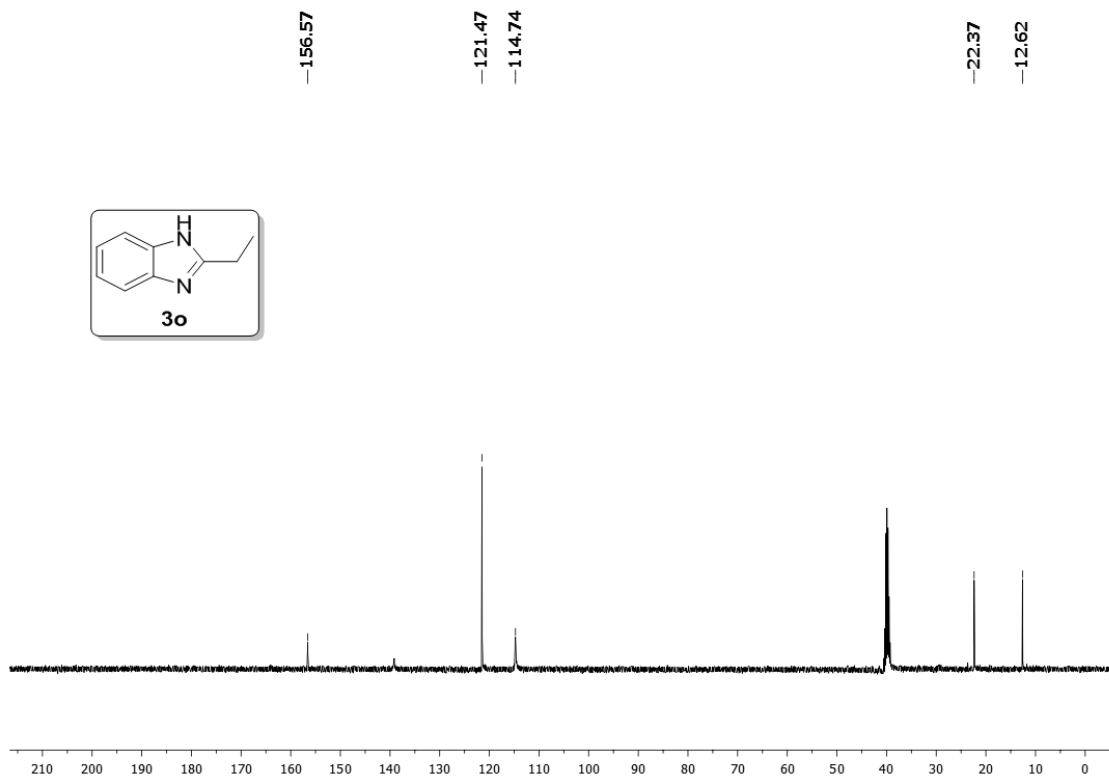
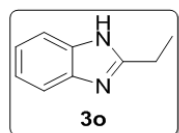
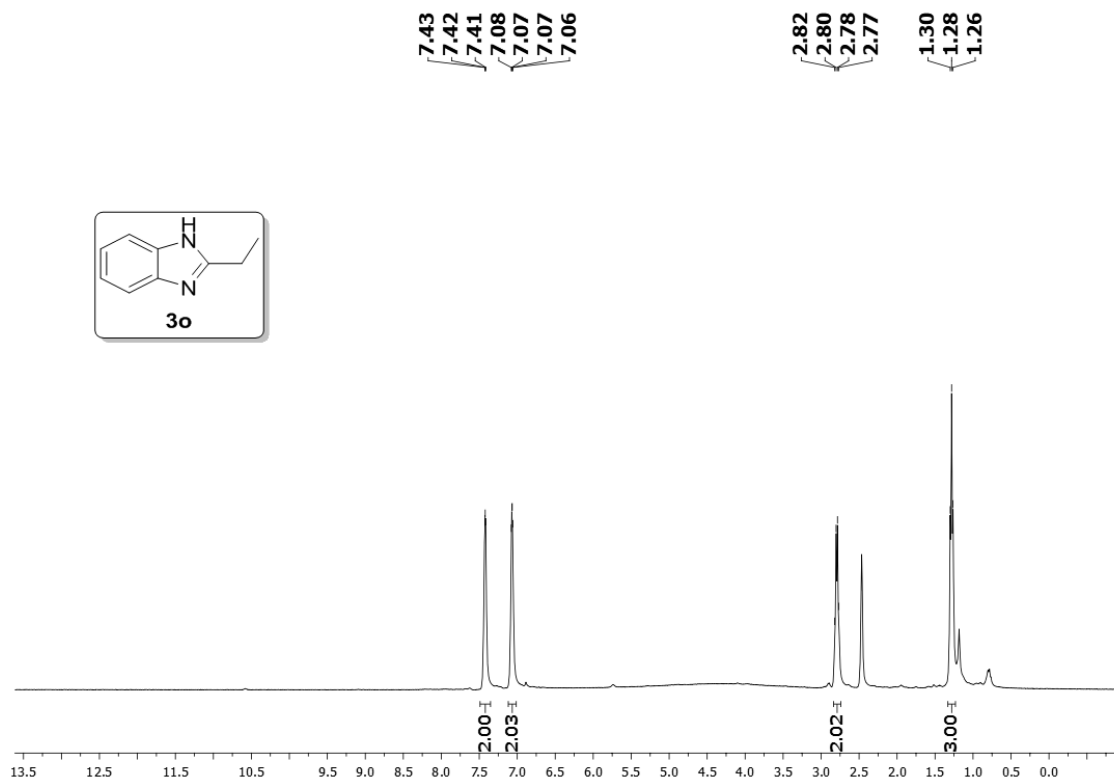
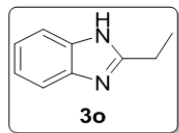
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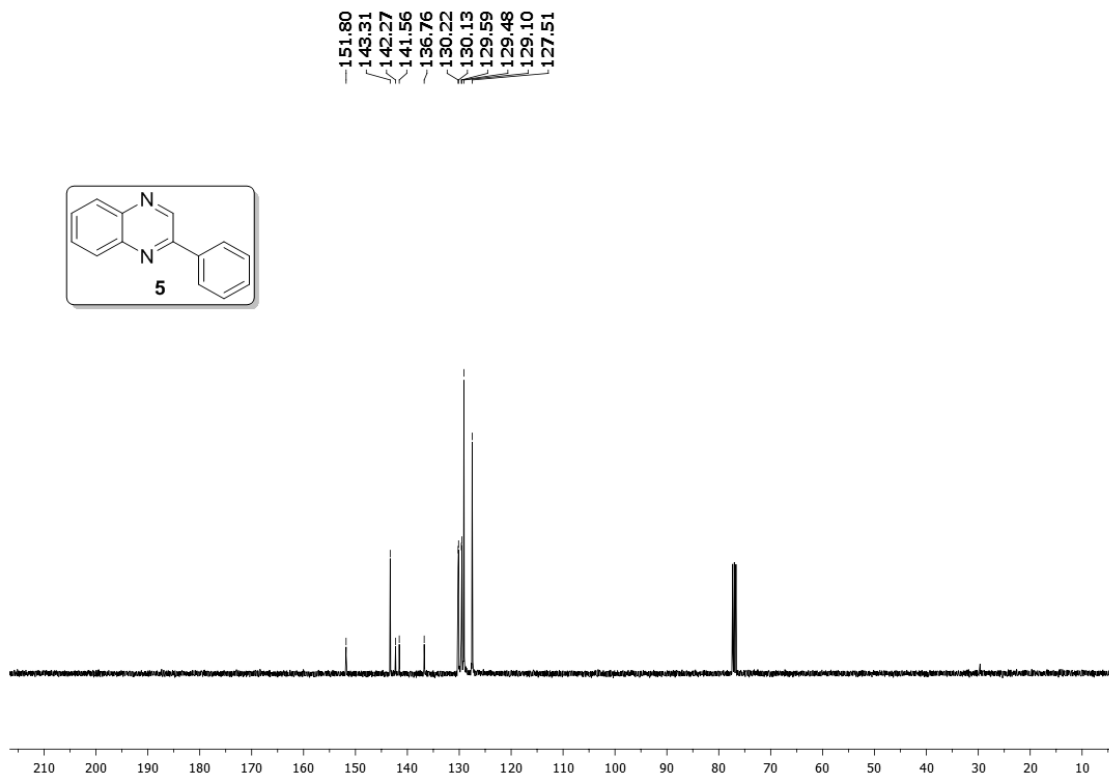
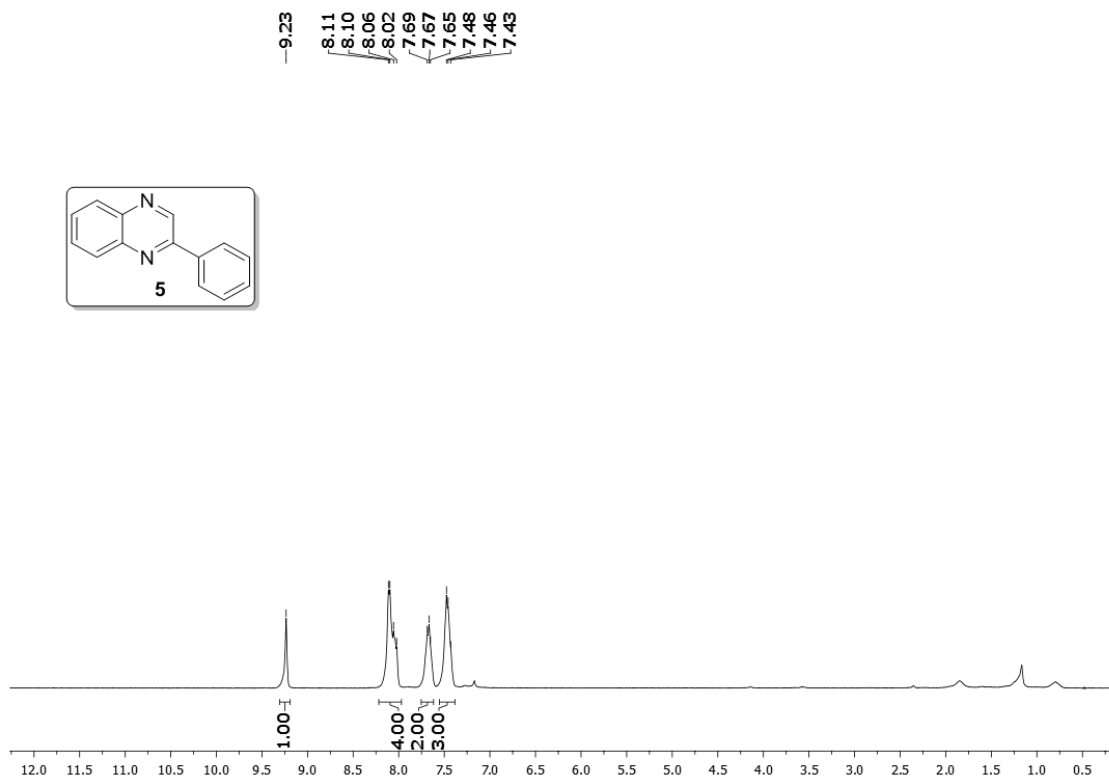


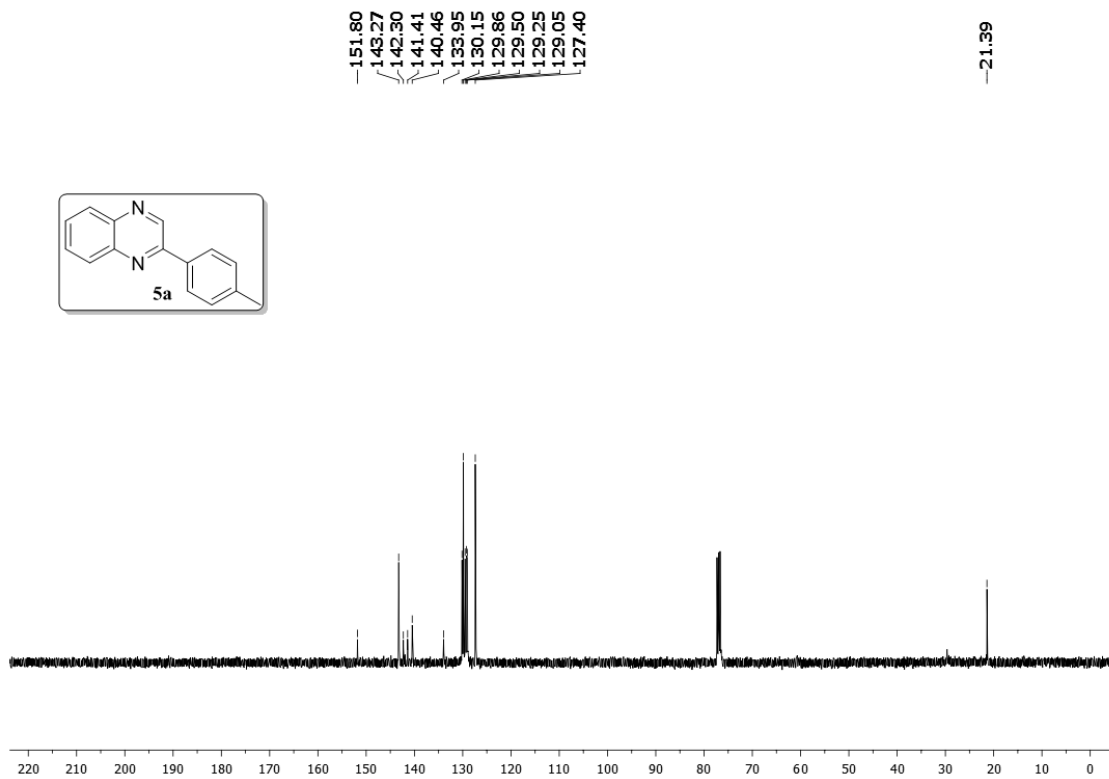
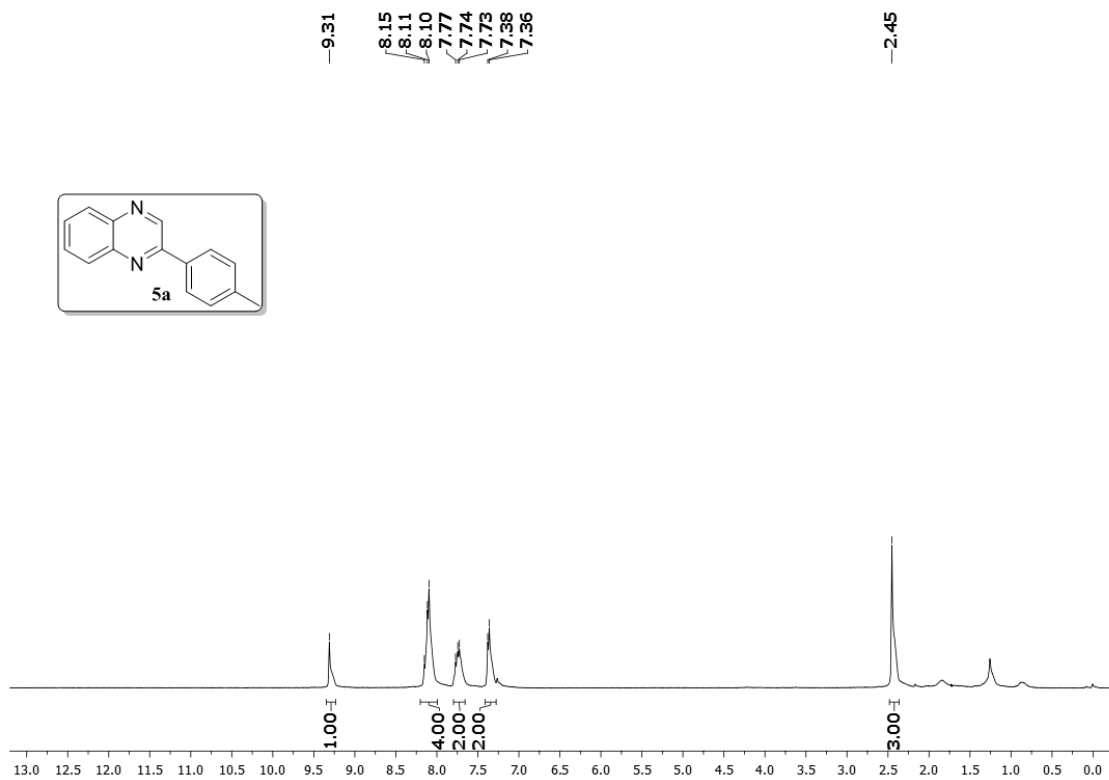
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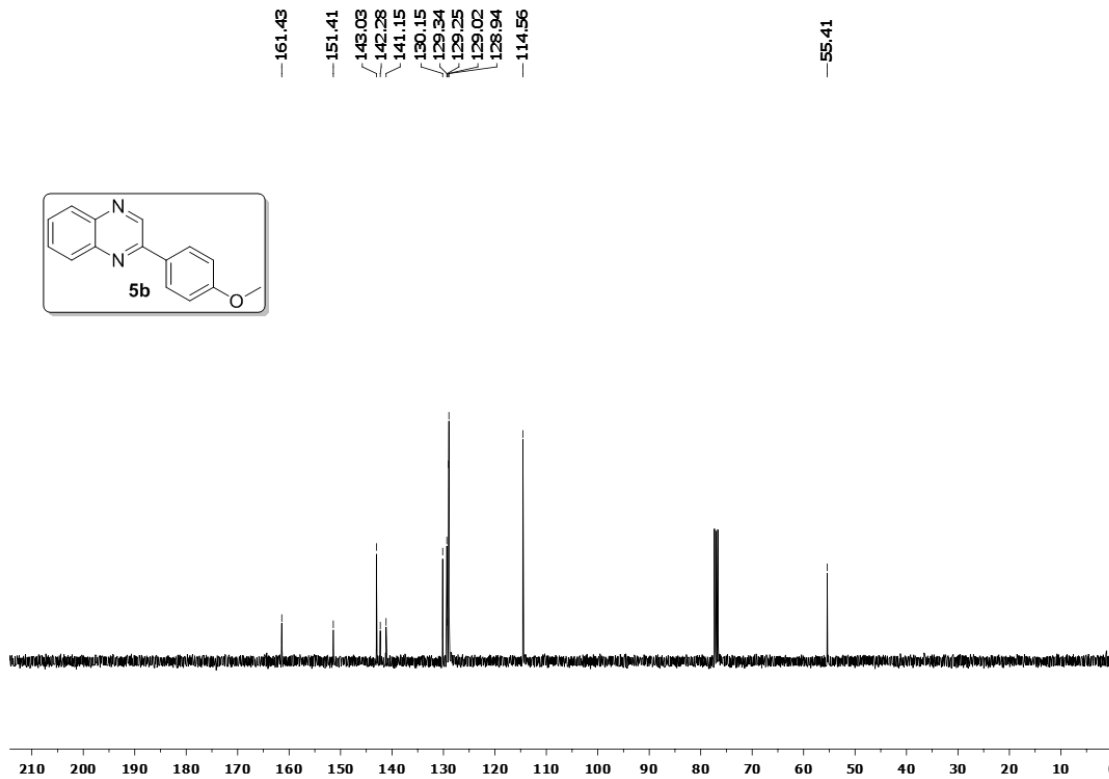
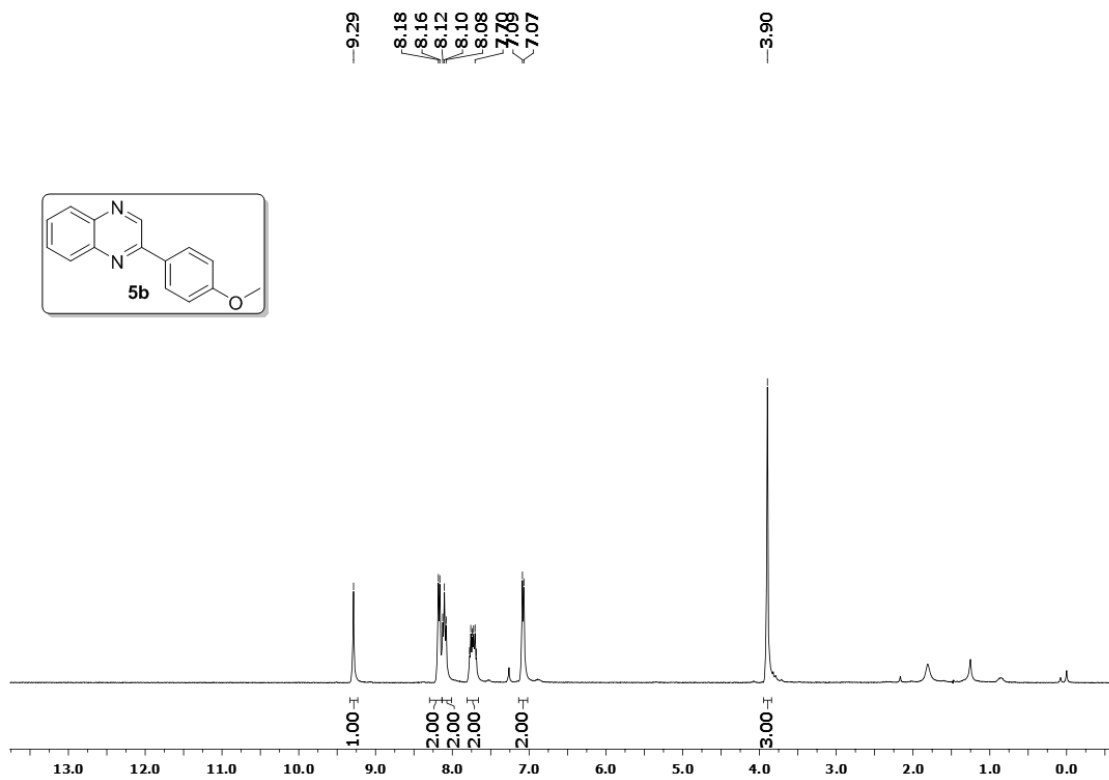


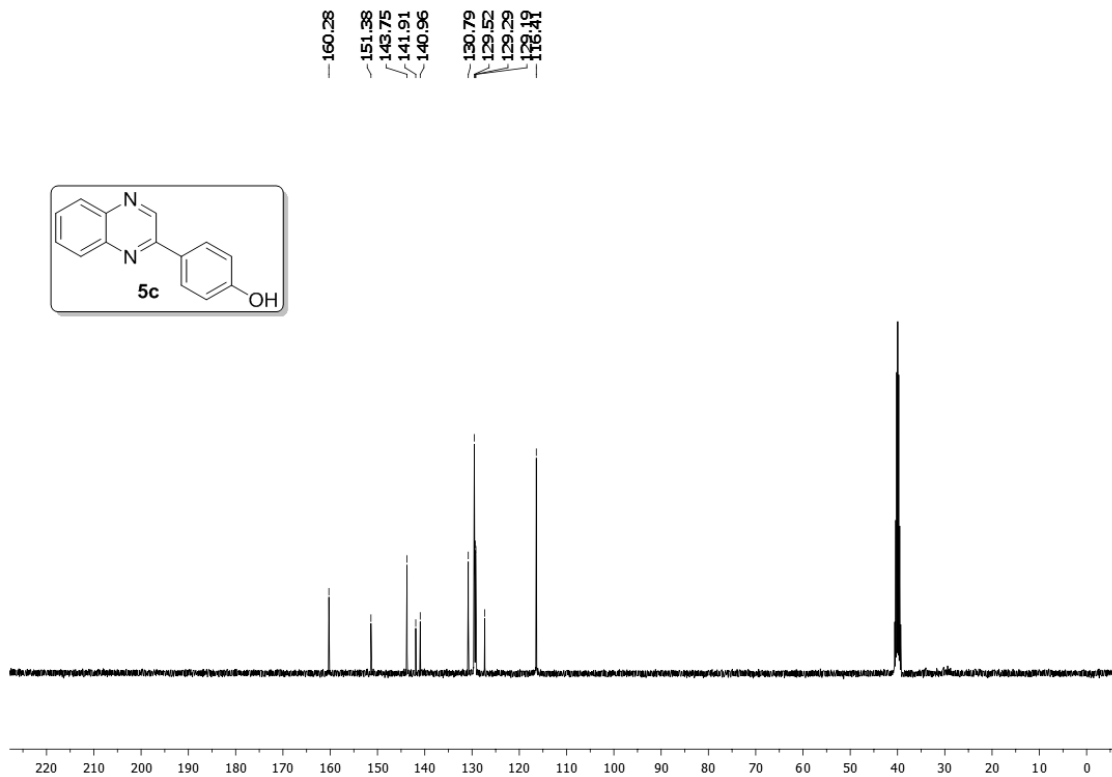
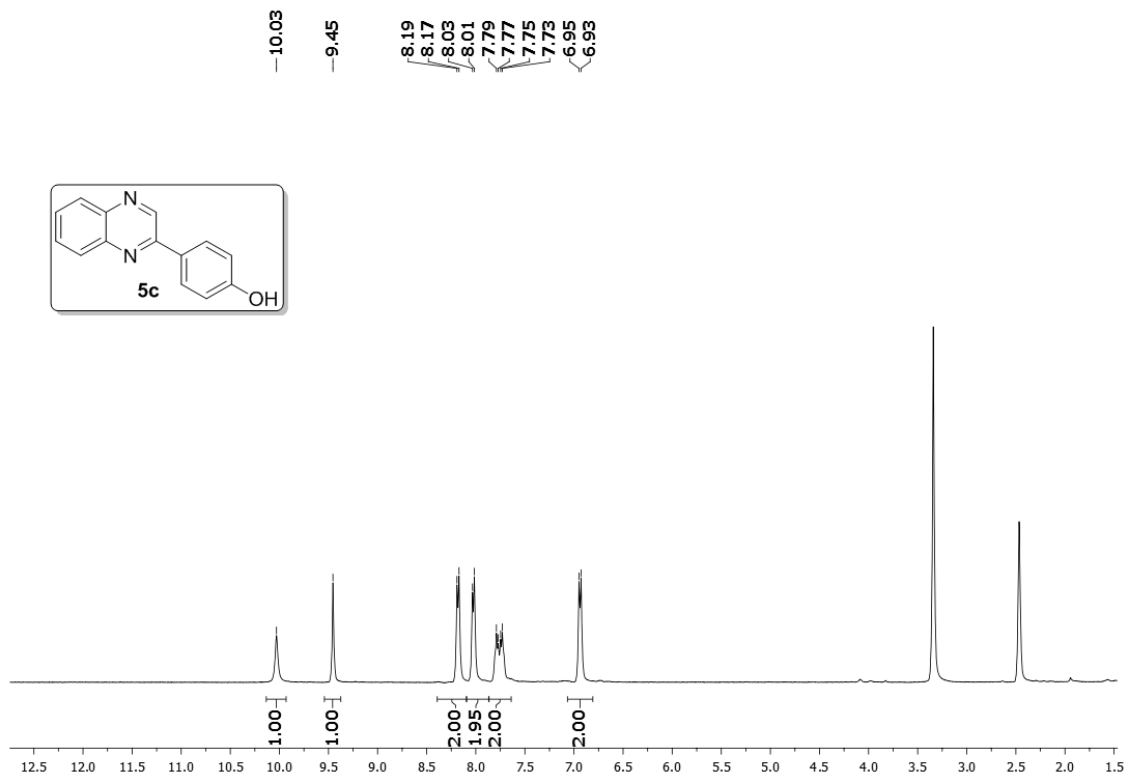


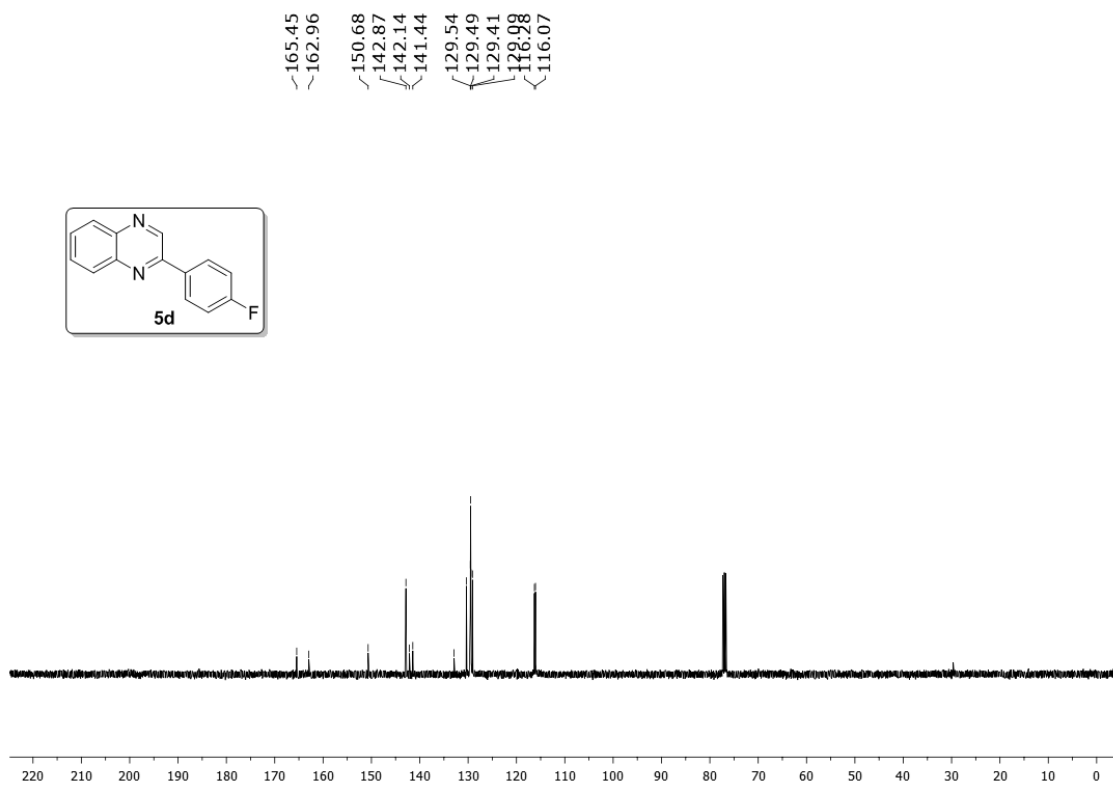
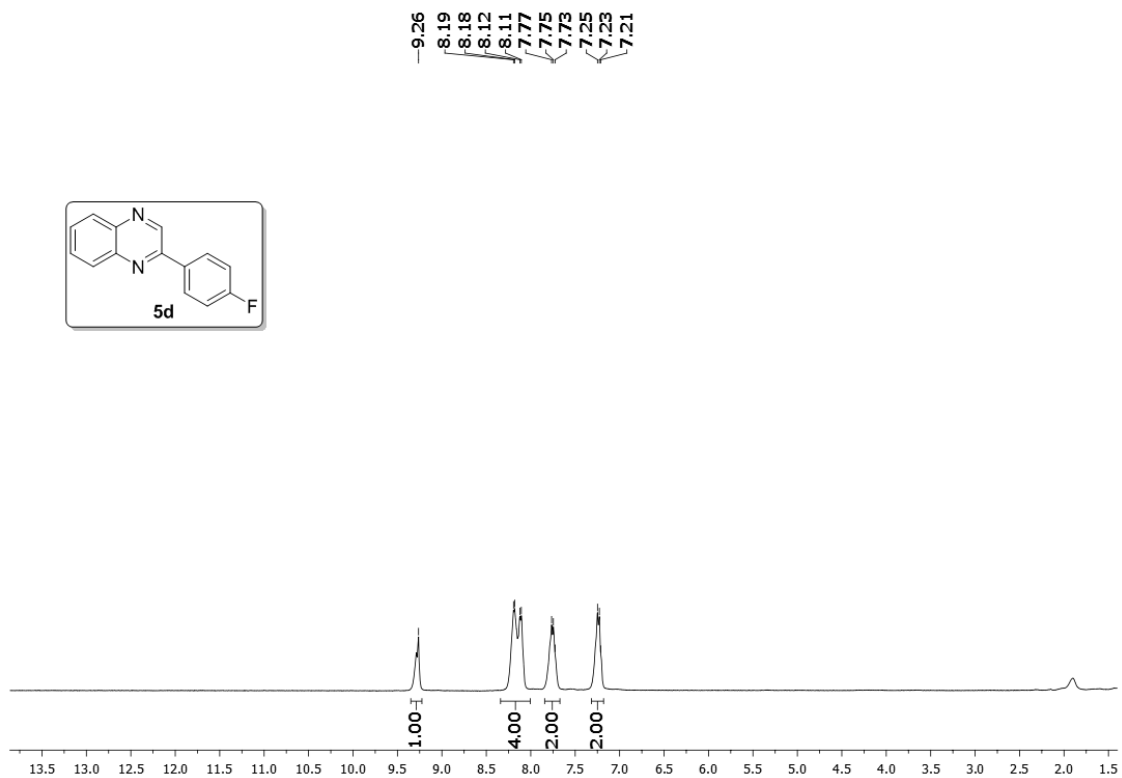


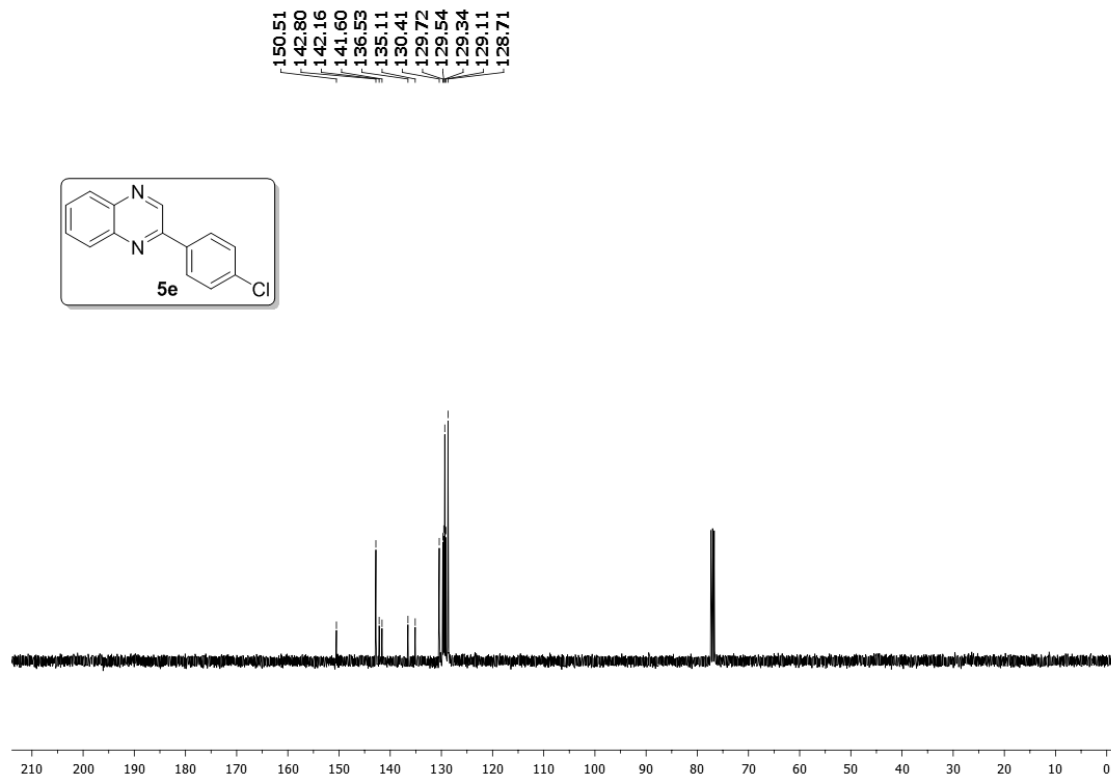
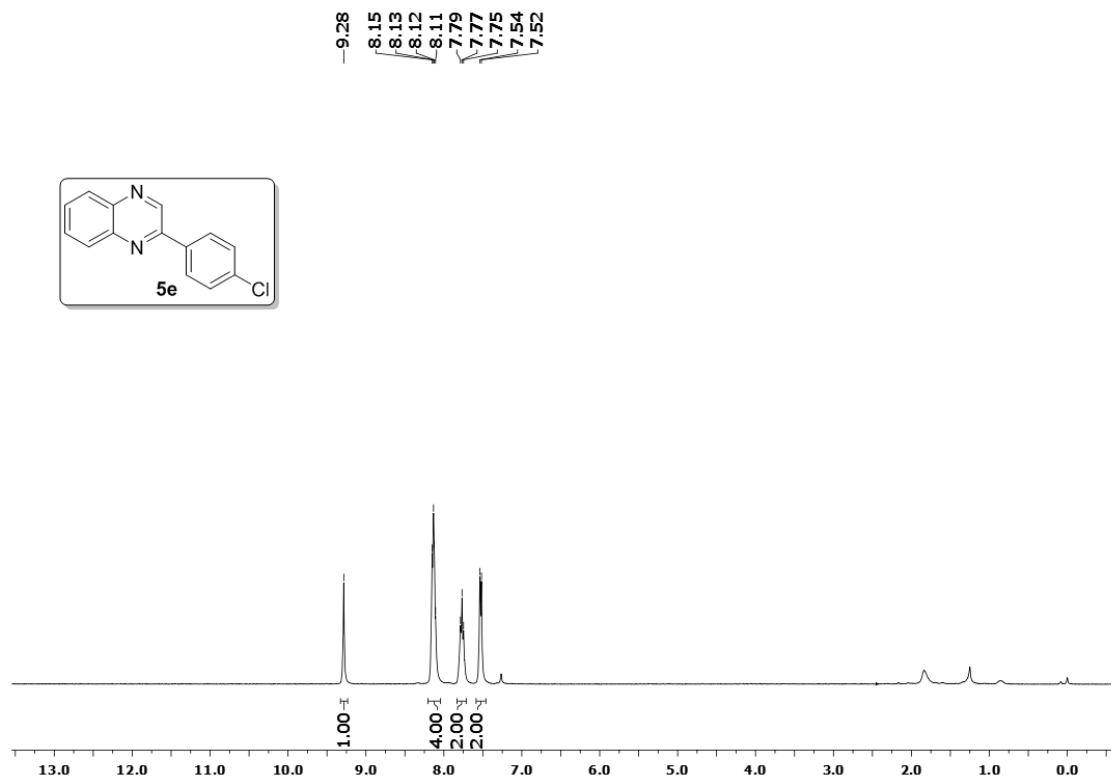


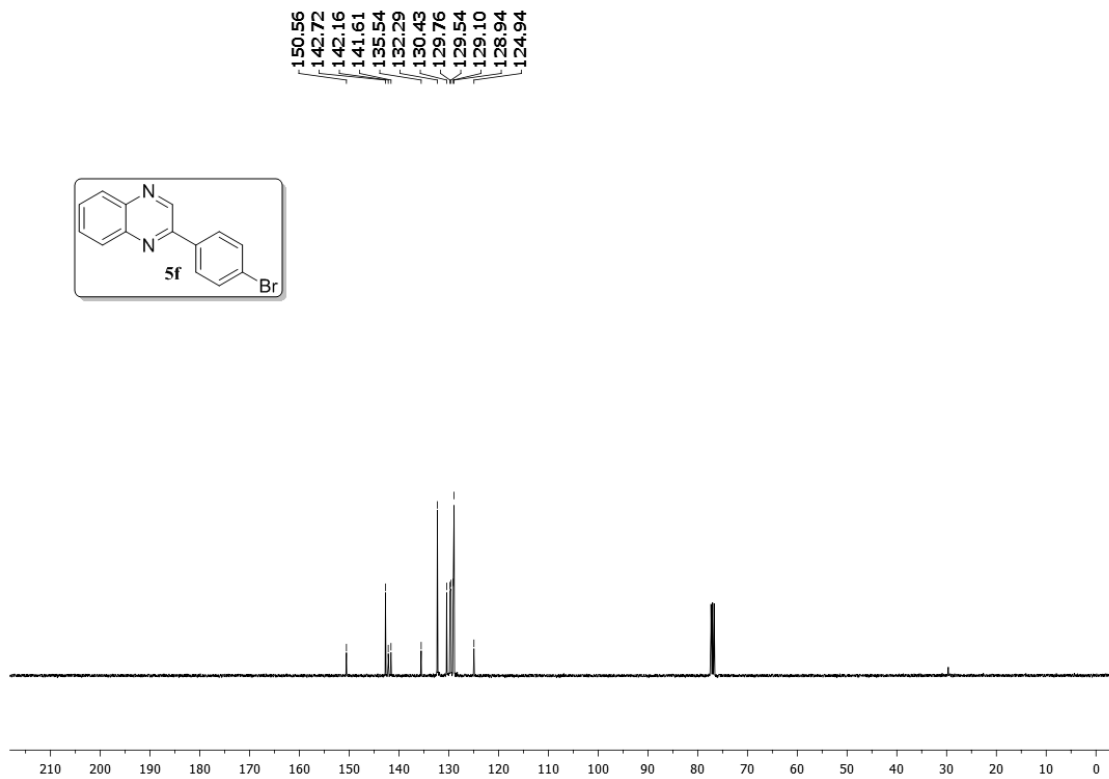
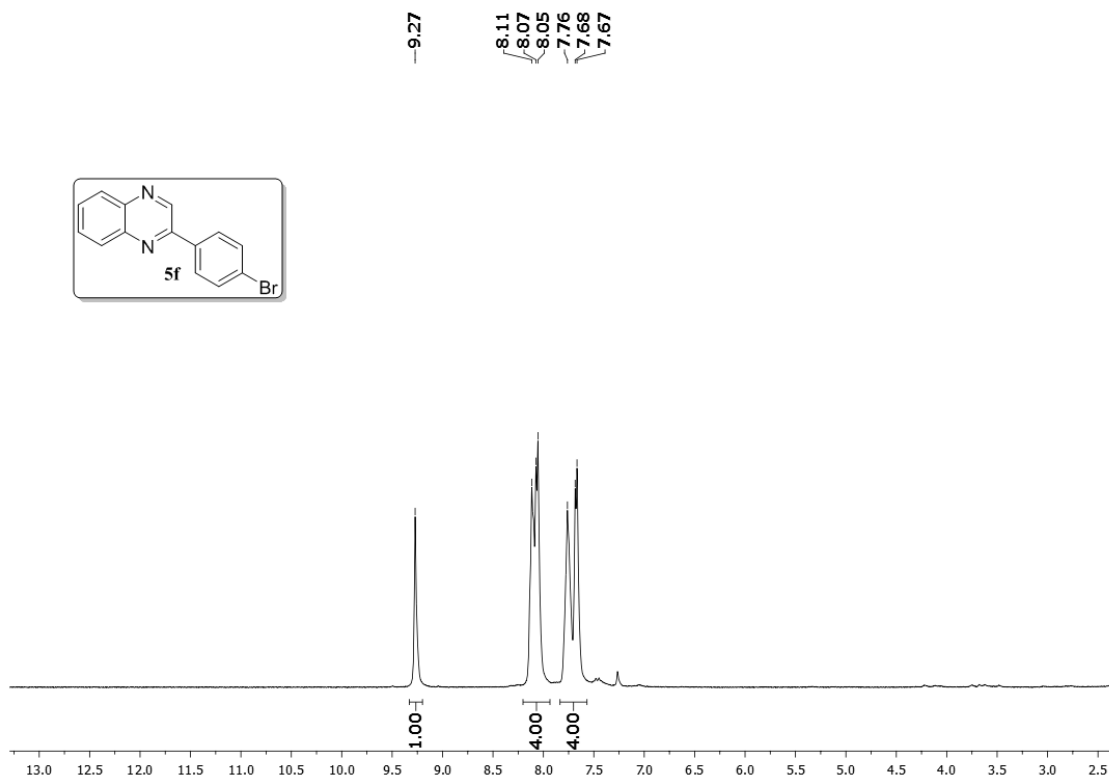


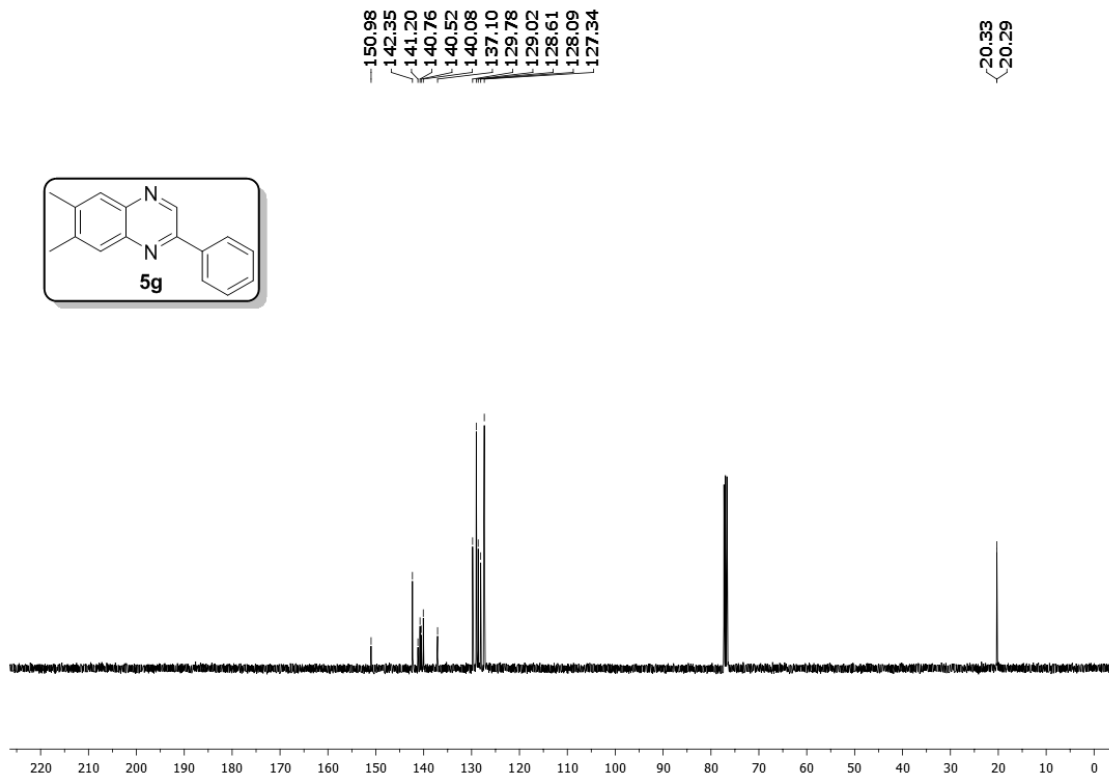
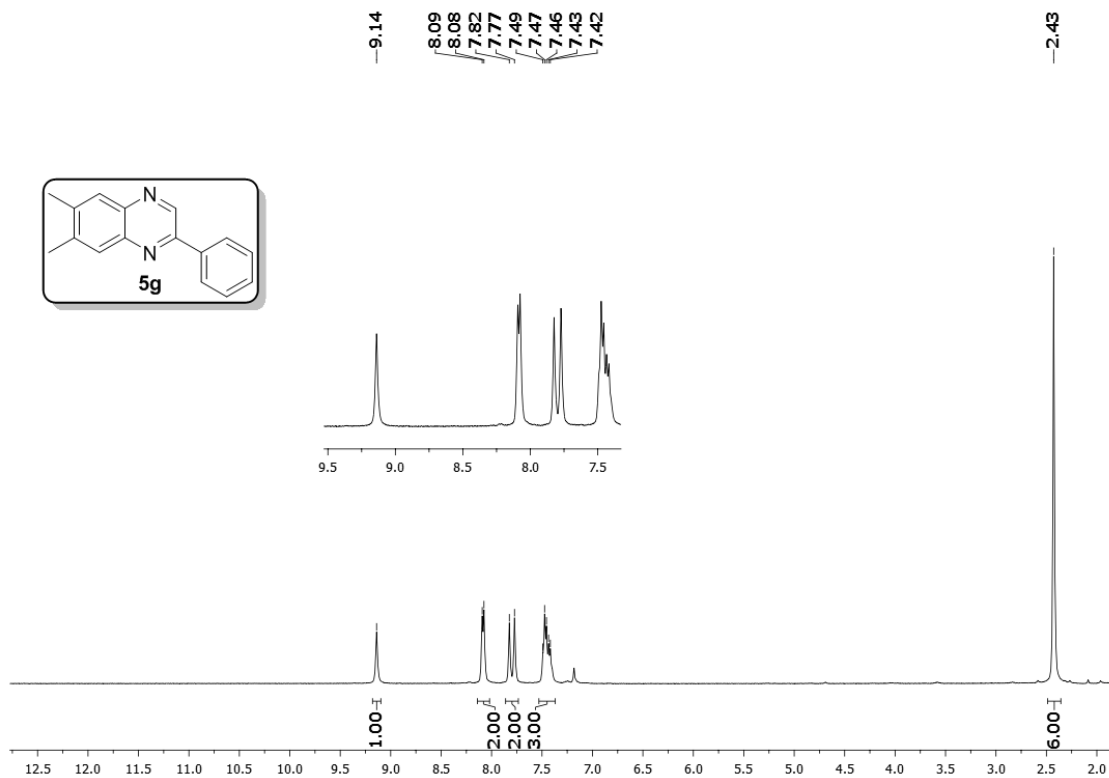


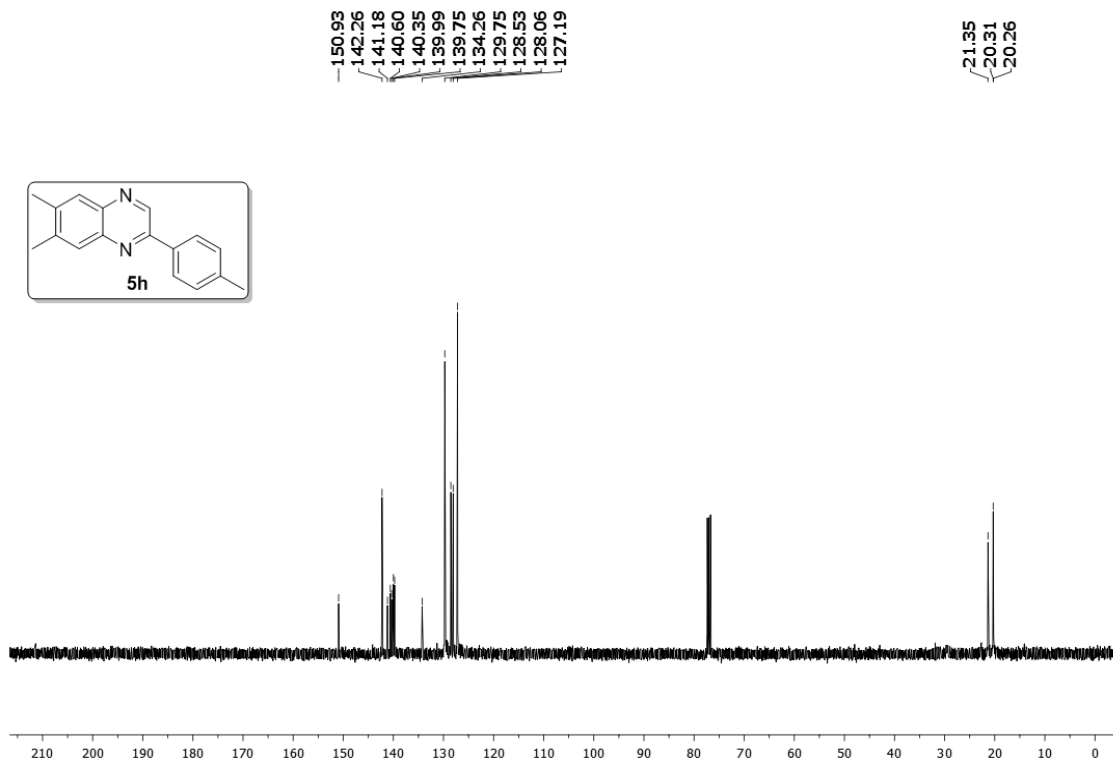
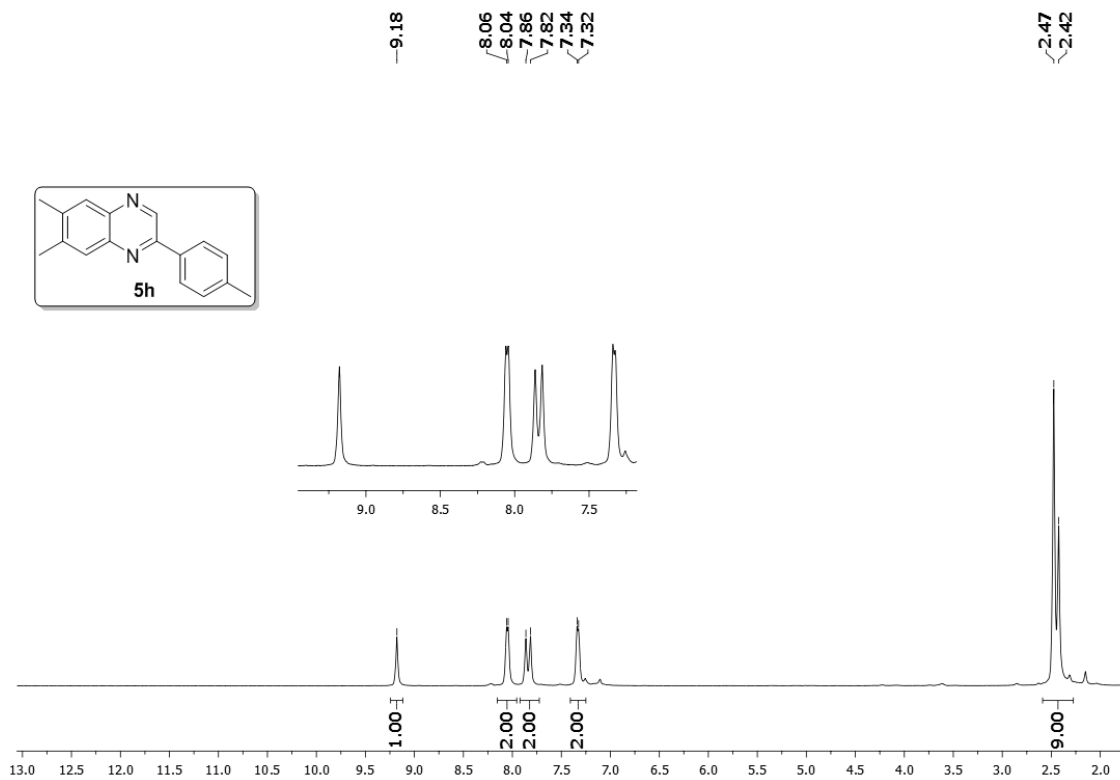


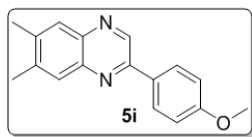






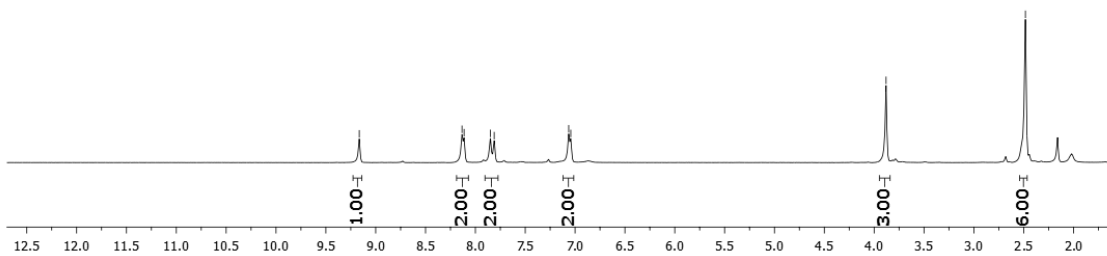
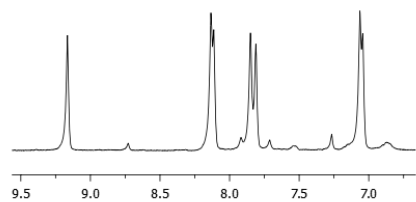






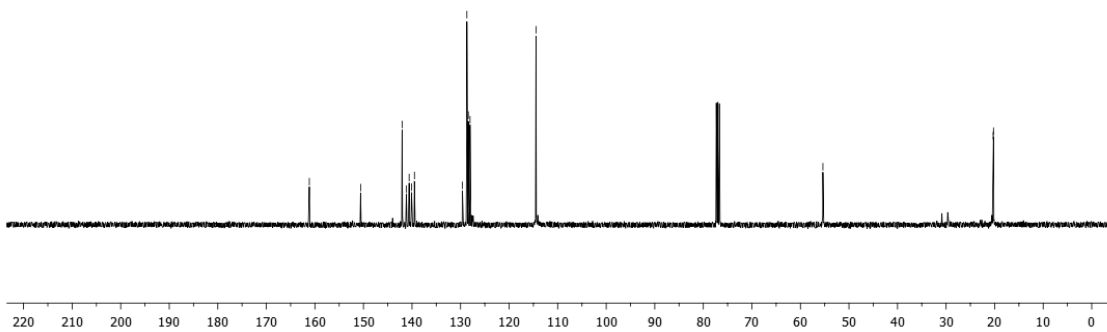
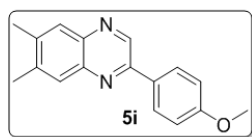
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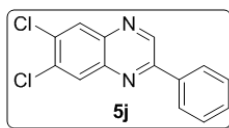
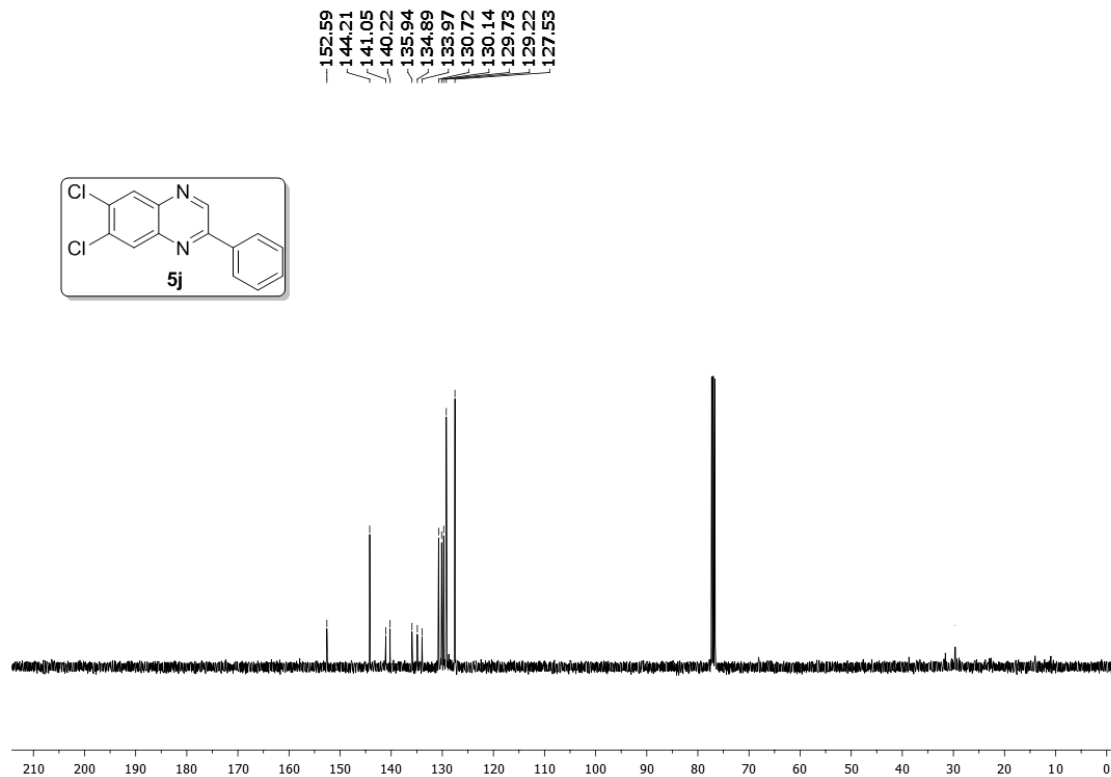
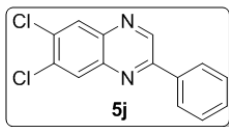
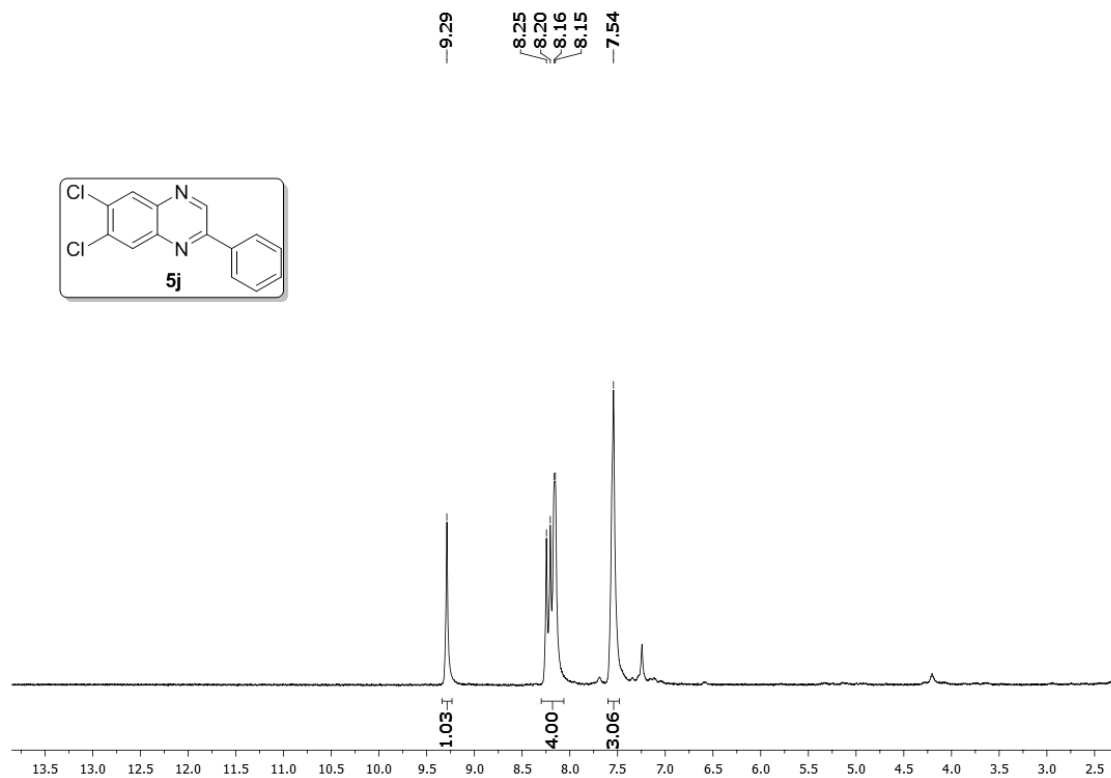
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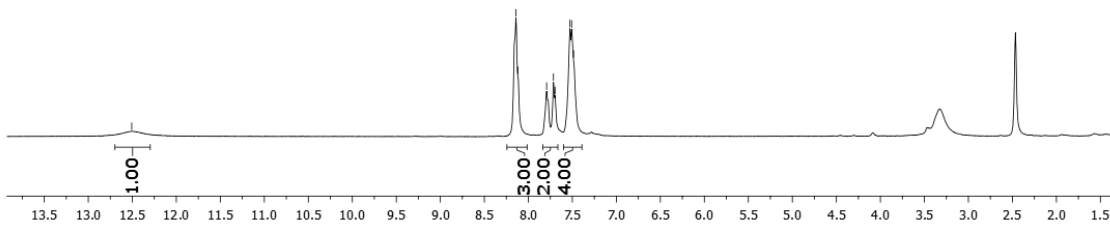
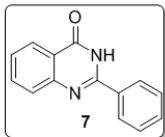
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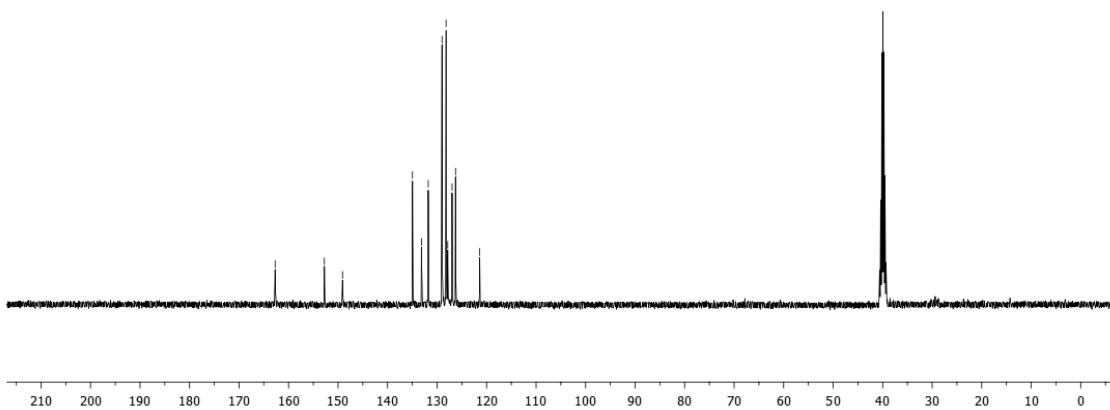
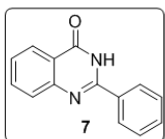


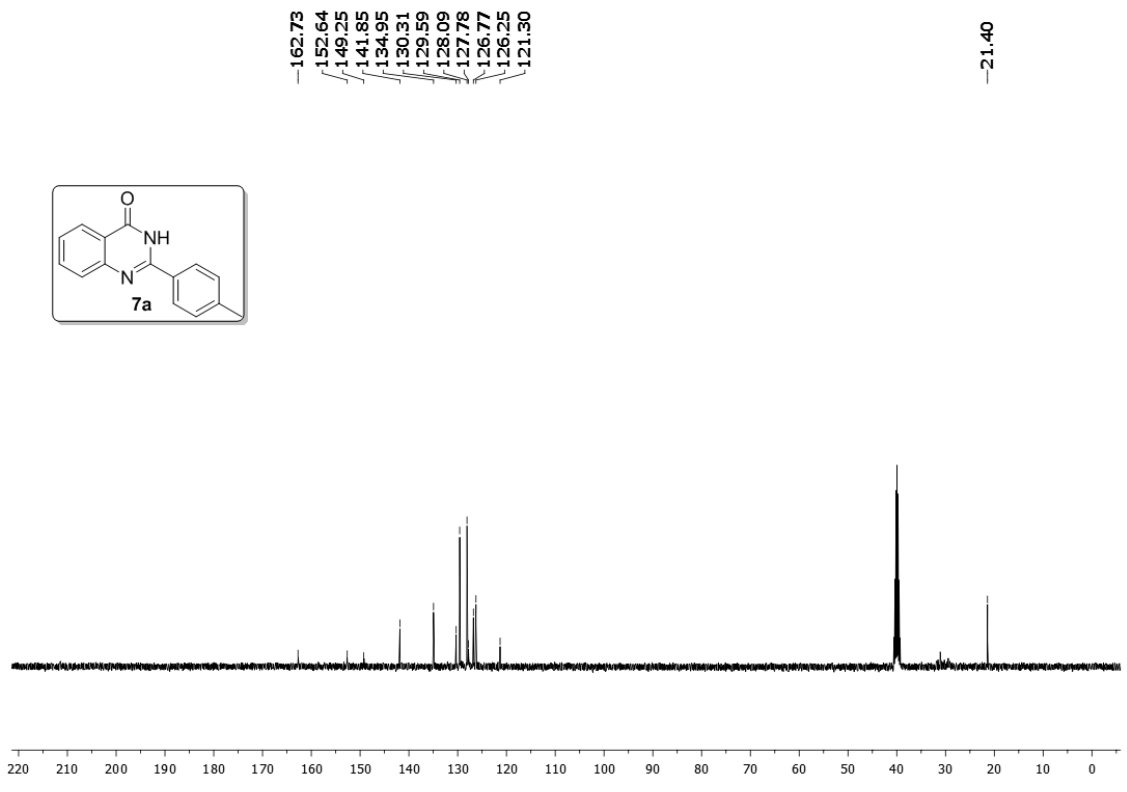
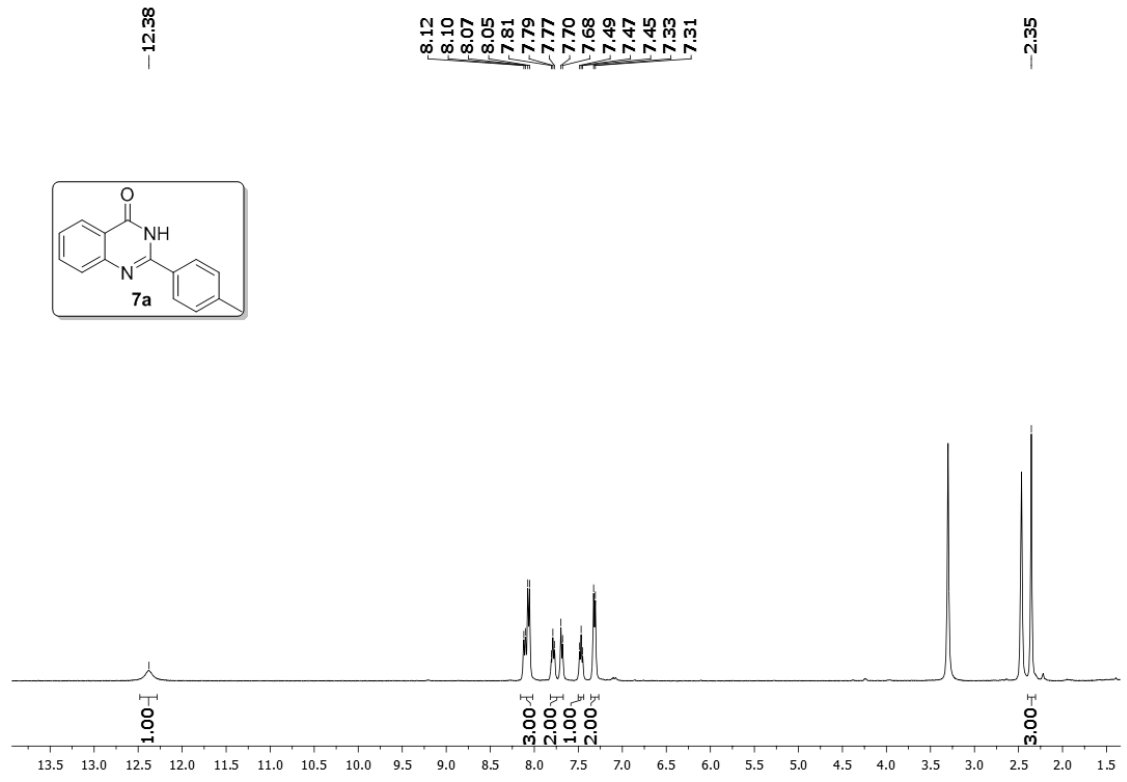
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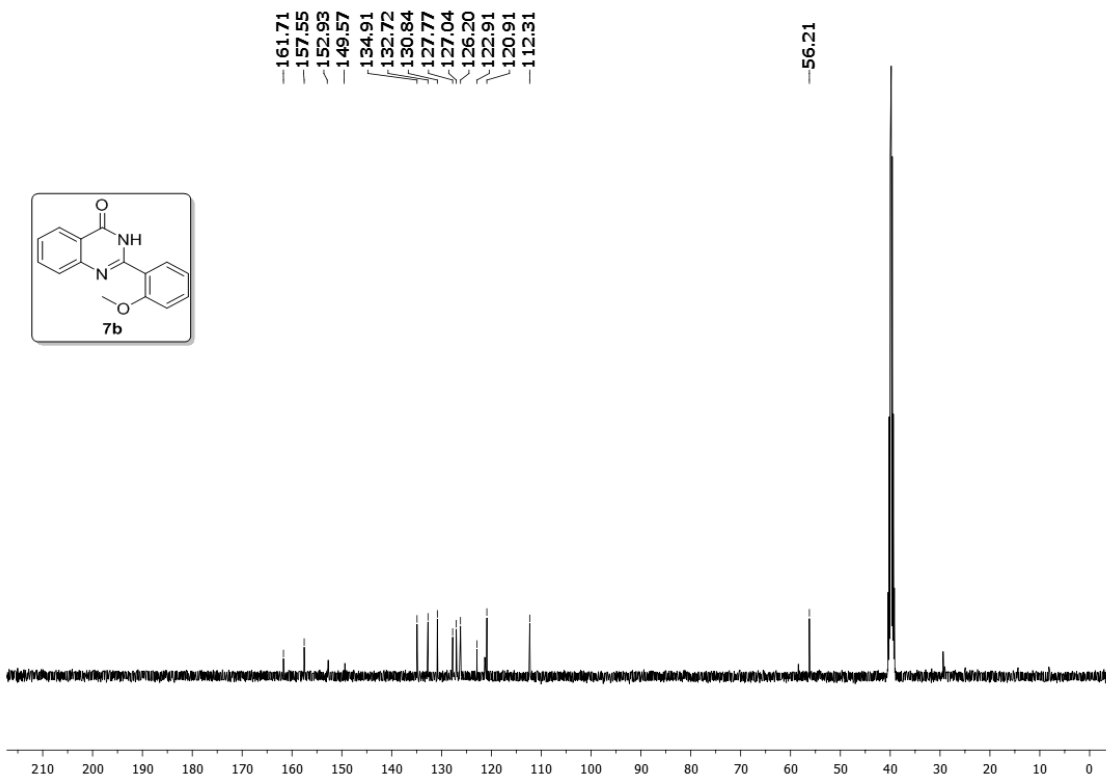
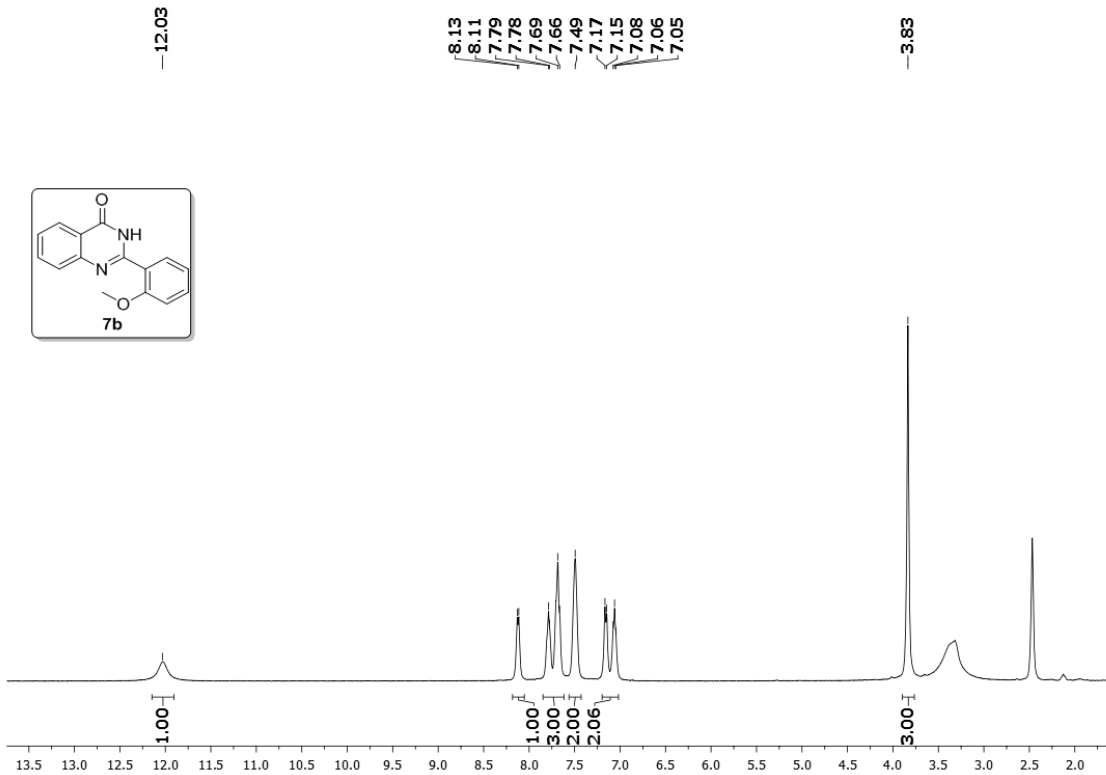
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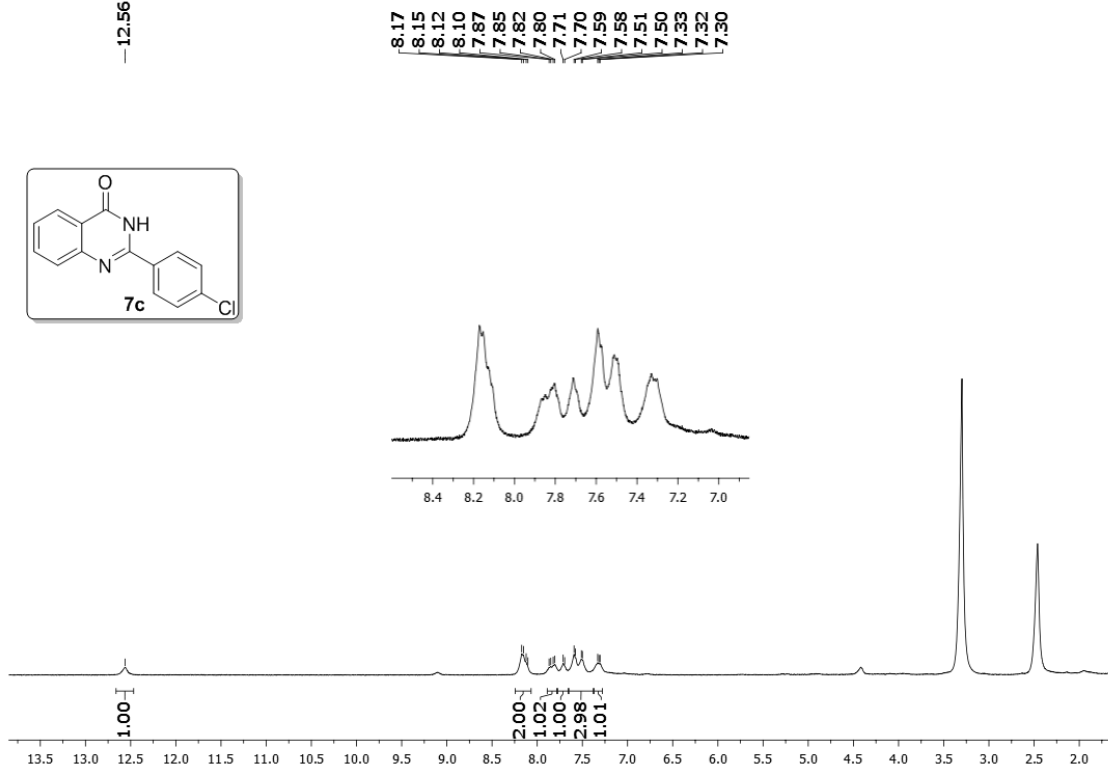
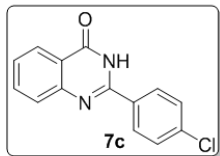
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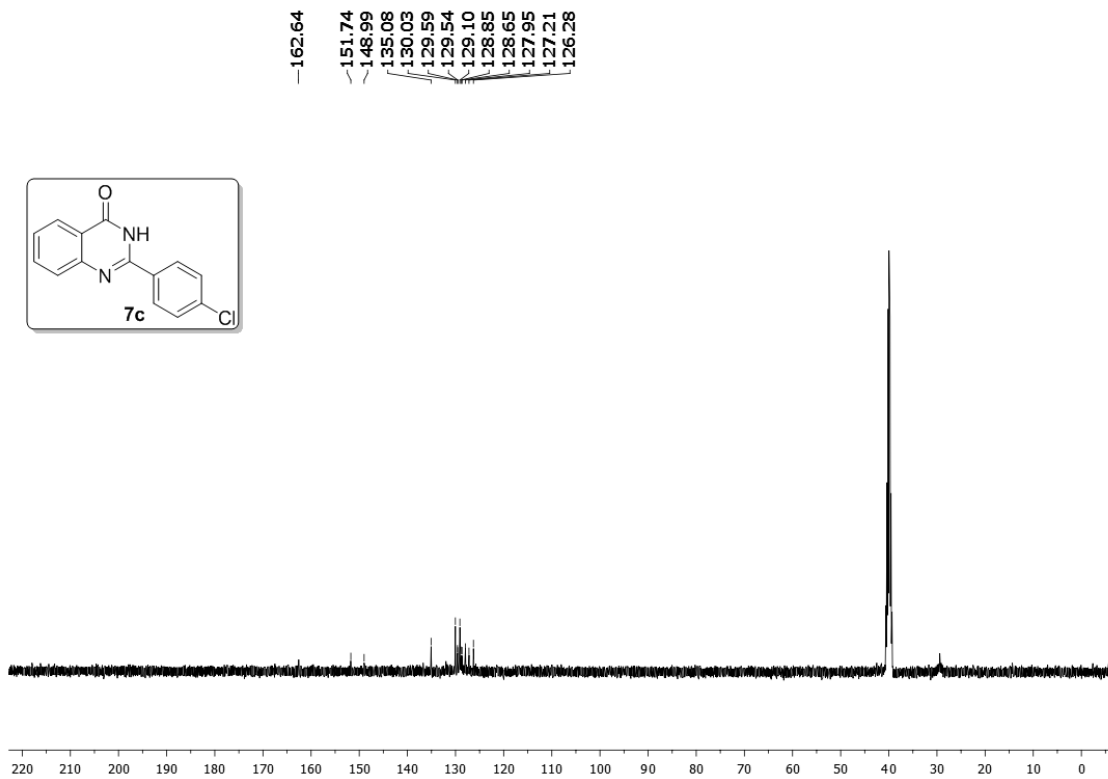
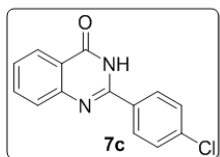


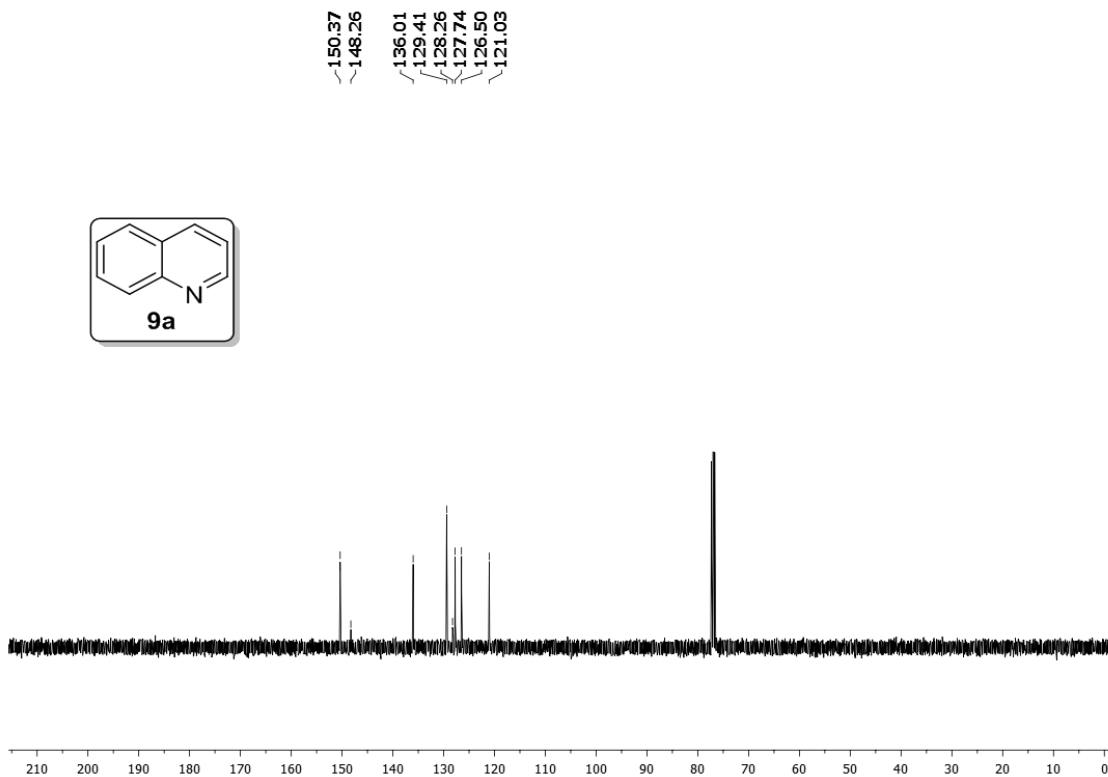
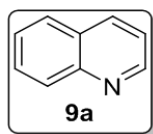
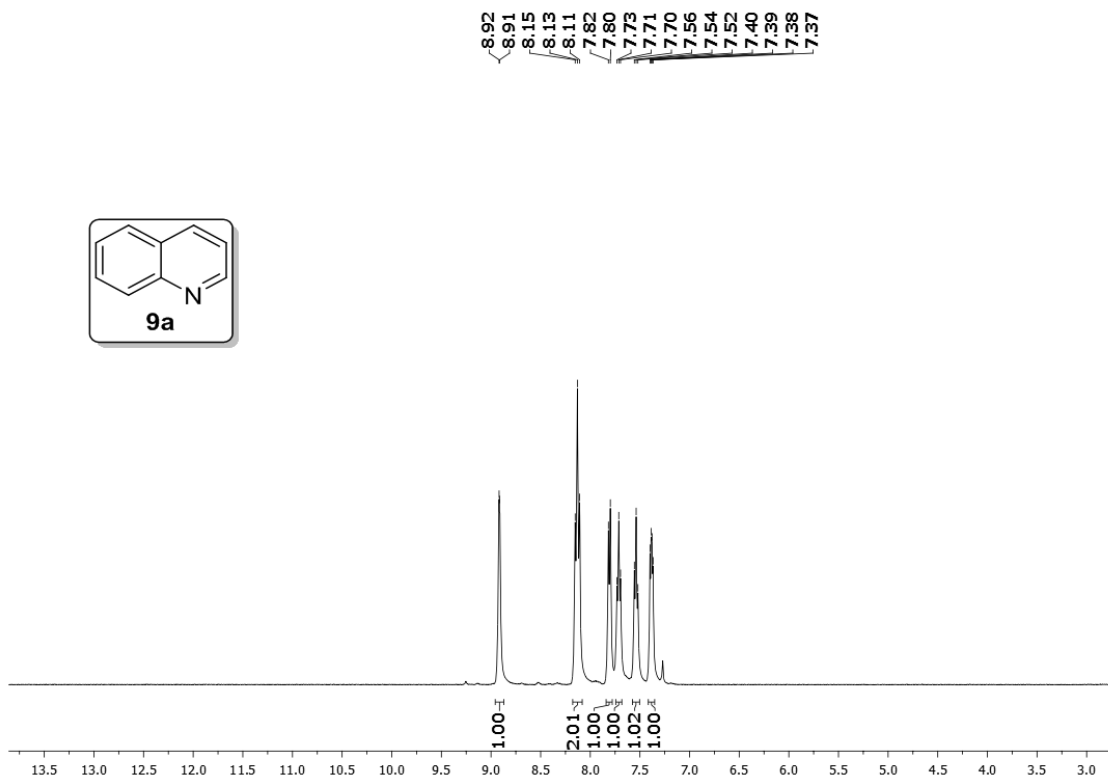
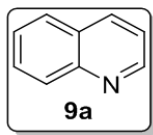


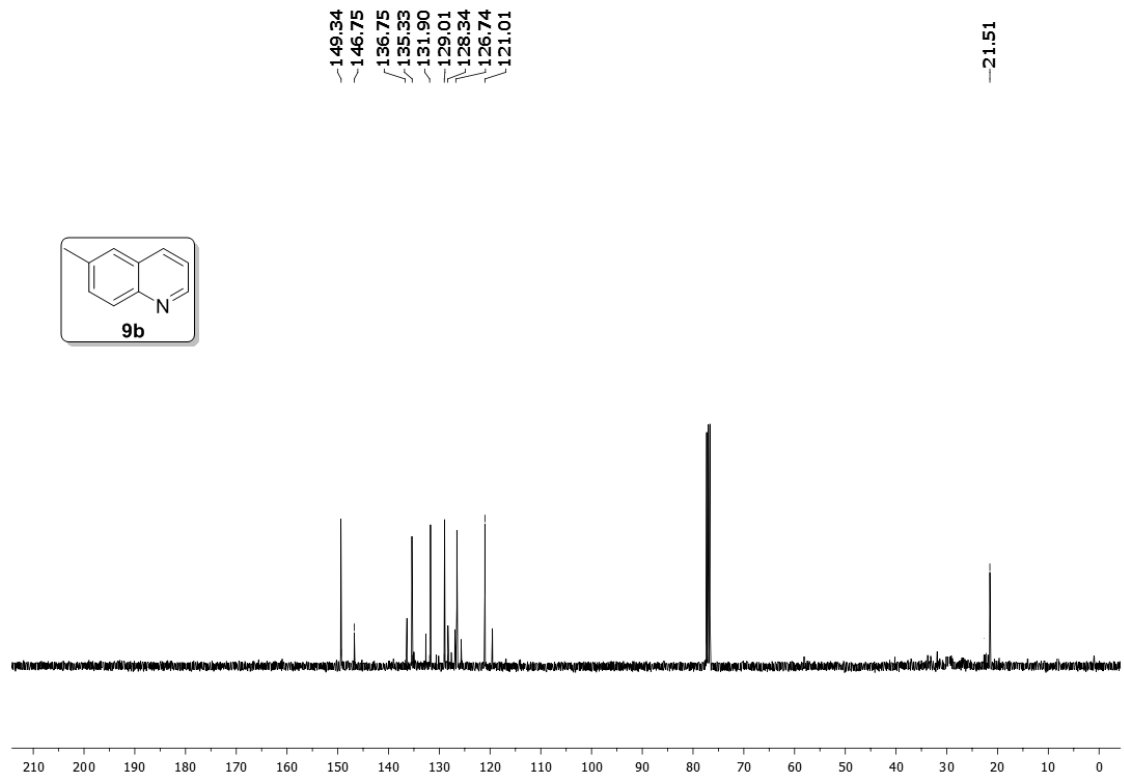
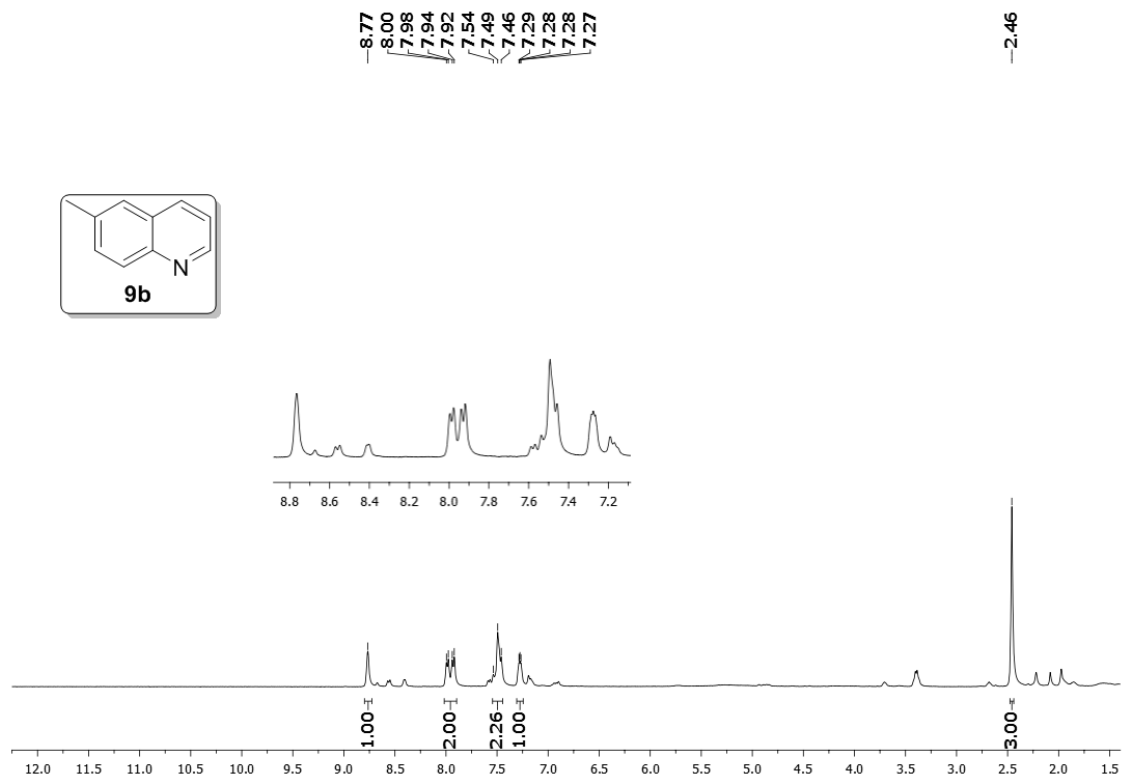
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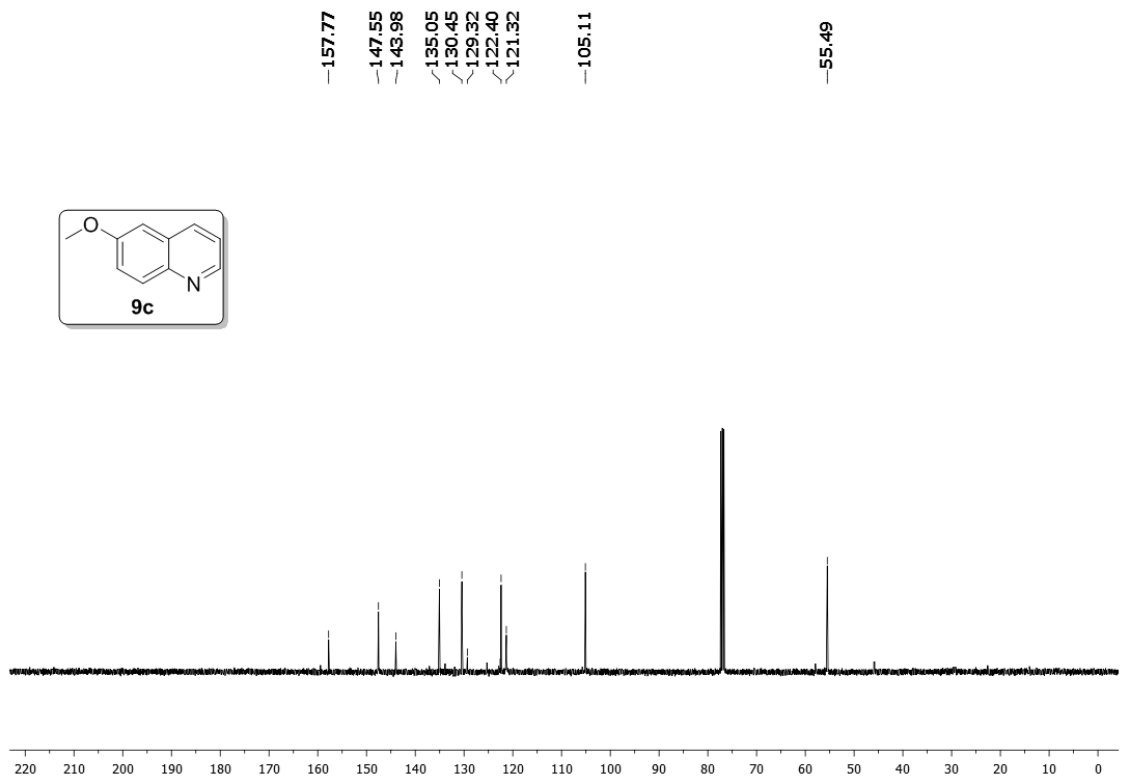
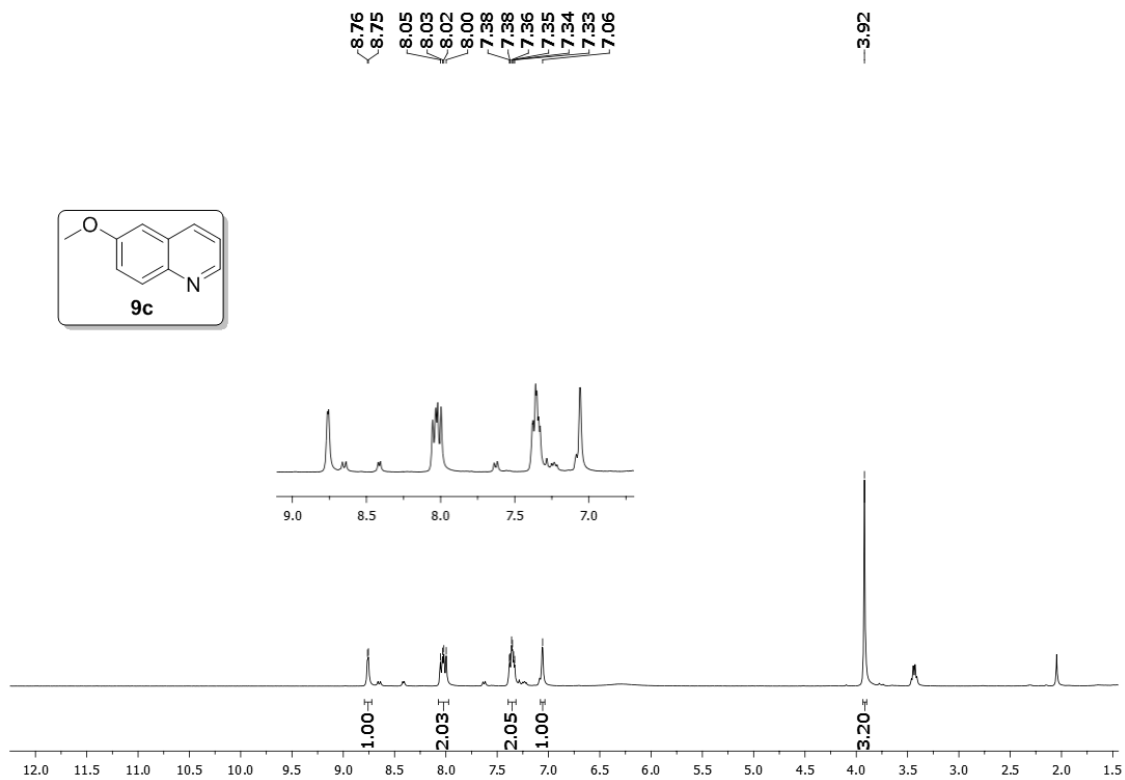


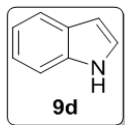
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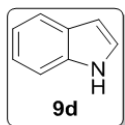
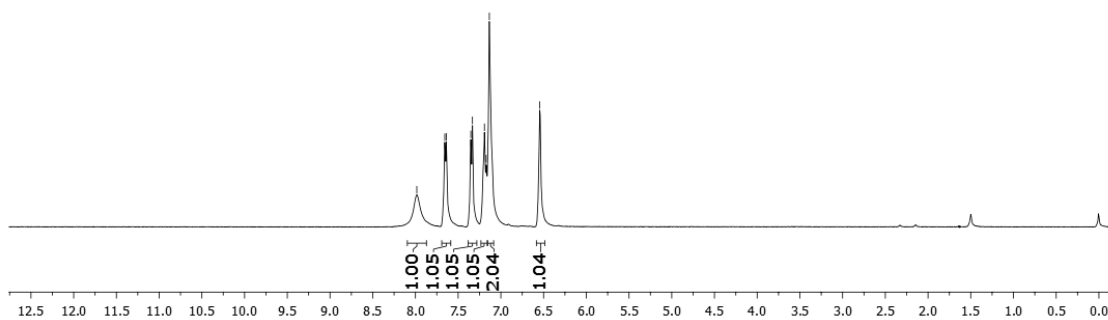








7.98  
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135.79  
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