

## Supporting Information

### Convenient Semihydrogenation of Azoarenes to Hydrazoarenes using H<sub>2</sub>

**Manoj K. Sahoo,<sup>a,†</sup> Ganesan Sivakumar,<sup>a,†</sup> Sanjay Jadhav,<sup>b</sup> Samrin Shaikh,<sup>b</sup> and Ekambaram Balaraman<sup>a\*</sup>**

<sup>a</sup>Department of Chemistry, Indian Institute of Science Education and Research (IISER) Tirupati, Tirupati - 517507, India; E-mail: [eb.raman@iisertirupati.ac.in](mailto:eb.raman@iisertirupati.ac.in)

<sup>b</sup>Organic Chemistry Division, Dr. Homi Bhabha Road, CSIR-National Chemical Laboratory (CSIR-NCL), Pune - 411008, India.

<sup>†</sup>Contributed equally to this work.

### Table of Contents

1.	Experimental Section	S2-S5
2.	Characterization Data	S7-S11
3.	References	S11
4.	Copy of <sup>1</sup> H and <sup>13</sup> C Spectra	S12-S34
5.	Copy of HRMS data	S35-S43

# 1. Experimental Section

## 1.1 General Information

All catalytic experiments were carried out using standard techniques. All solvents used were reagent grade or better and dried prior to use using standard procedures. Deuterated solvents were used as received without any further purification. All transition metal catalysts of Palladium, Ruthenium, and Rhodium were purchased from Sigma Aldrich and used as received. All other chemicals were purchased from commercial sources and used as received. Thin layer chromatography (TLC) analyses were performed on commercial aluminium plates bearing a 0.25 mm layer of Merck Silica gel 60 F<sub>254</sub>, which were visualized with UV light at 254 nm or under iodine. Column chromatography was performed with SiO<sub>2</sub> (Silicycle Siliaflash F60 (230-400 mesh). <sup>1</sup>H NMR (200, 400 or 500 MHz), <sup>13</sup>C NMR spectra were recorded on the 50, 101 or 126 MHz NMR spectrometer. Deuterated chloroform was used as the solvent, and chemical shift values ( $\delta$ ) are reported in parts per million relatives to the residual signals of this solvent [ $\delta$  7.27 for <sup>1</sup>H (chloroform-d),  $\delta$  77.0 for <sup>13</sup>C (chloroform-d)]. Abbreviations used in the NMR follow-up experiments: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. High-resolution mass spectra (HRMS) were obtained by fast atom bombardment (FAB) using a double focusing magnetic sector mass spectrometer and electron impact (EI) ionization technique (magnetic sector-electric sector double focusing mass analyser).

## 1.2 General procedure:

In an oven-dried 25 mL round-bottomed flask with a magnetic stirring bar was charged with **1** (0.5 mmol), 2.1 mg 5 wt% Pd/C (0.2% of Pd loading), MeOH (5 mL) followed by pyridine (10 mol %) under nitrogen atmosphere. The round-bottomed flask was fitted to an adapter which is connected to a hydrogen balloon (1 atm.). The N<sub>2</sub> gas from the round-bottomed flask was flushed out by releasing hydrogen gas and then the reaction flask was placed on a magnetic stirrer under hydrogen atmosphere and allowed to stir at room temperature. After 15-30 minutes the color of the reaction mixture disappears which indicates the completion of the reaction (completion of the reaction was confirmed by checking TLC). Then the catalyst was removed by a quick filtration. The solvent of the reaction mixture was removed under reduced pressure, and the residue

was washed with cold n-hexane (5 mL×3) to afford desired pure product **2** as colourless solid.

### 1.3 General procedure for gram scale azoarene hydrogenation

To an oven-dried 100 mL round-bottomed flask with a magnetic stirring bar was charged with **1** or **3** (5 mmol), 21 mg 5 wt% Pd/C (0.2% of Pd loading), MeOH (50 mL) followed by pyridine (10 mol %) under nitrogen atmosphere. The round-bottomed flask was fitted with a two-way vacuum adapter. One of the two ways is connected to a vacuum line and the other one is connected to a hydrogen balloon (1 atm.). The round bottomed flask was kept under vacuum for few seconds to remove the N<sub>2</sub> gas and then filled with H<sub>2</sub> gas. Then the reaction mixture was allowed to stir at room temperature till completion of the reaction indicated by disappearance of the color of the reaction mixture and confirmed by checking TLC. After completion of the reaction, the catalyst from the reaction mixture was removed by quick filtration followed by washing with 5 mL MeOH. The solvent of the reaction mixture was removed under reduced pressure, and the residue was washed with cold n-hexane (5 mL×4) to afford desired pure product **2** or **4**.

### 1.4 Time-dependent reaction monitoring

Time-dependent product formation and analysis was carried out to monitor the reaction progress over time. Following the general procedure for substrate **1a** the reaction was carried out. Thus, an aliquot volume of reaction mixture was withdrawn at regular time intervals. The solvent of the reaction mixture was evaporated under reduced pressure and NMR was taken using mesitylene as an internal standard to evaluate the amount of product formation. The NMR yield of the reactant and product was calculated referencing to the internal standard and a graph was plotted taking yield against time.

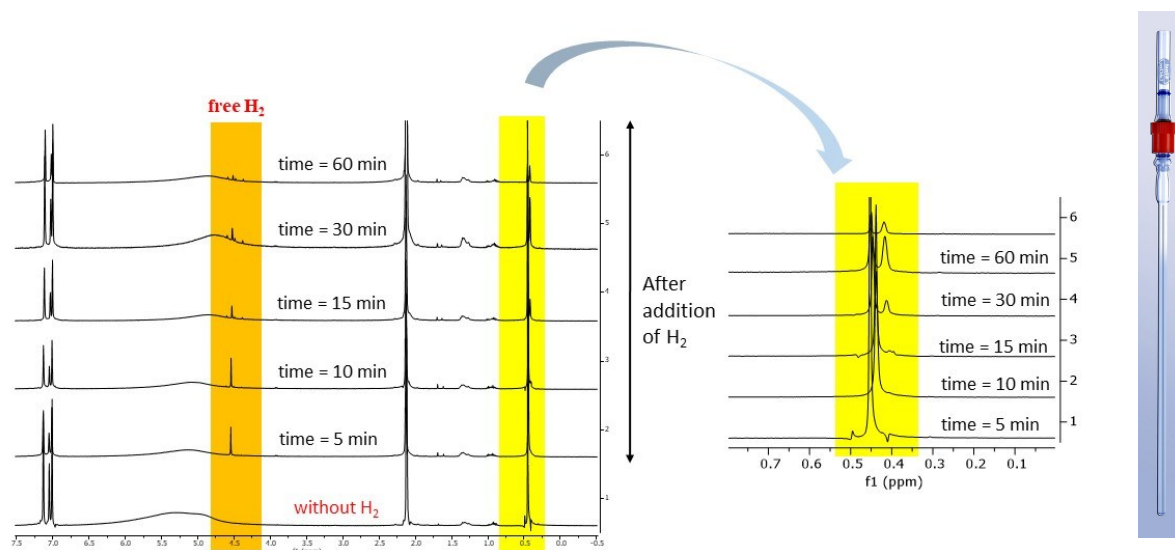
### 1.5 Catalyst recyclability test

To an oven-dried 100 mL round-bottomed flask with a magnetic stirring bar was charged with **1a** (5 mmol), 21 mg 5 wt% Pd/C (0.2% of Pd loading), MeOH (50 mL) followed by pyridine (10 mol %) under nitrogen atmosphere. The round-bottomed flask was fitted with a two-way vacuum adapter. One of the two ways is connected to a vacuum line and the other is connected to a hydrogen balloon. The round bottomed flask was kept under vacuum for few seconds to remove the N<sub>2</sub> gas and then filled with H<sub>2</sub> gas. The reaction mixture was then allowed to stir at room temperature till completion of the reaction as indicated by disappearance of the color of

the reaction mixture and confirmed by checking TLC. Then the catalyst from the reaction mixture was removed by quick filtration using sintered glass Buchner funnel and Whatman filter paper followed by washing with 5 mL MeOH. The solvent of the reaction mixture was removed under reduced pressure, and the residue was scratched and washed with cold n-hexane (5 mL×4 of n-hexane) to afford desired pure product **2a**. Then, the filter paper was dried under air to collect the Pd/C and used for next catalytic cycle.

### 1.6 Formation of Pd-hydride species

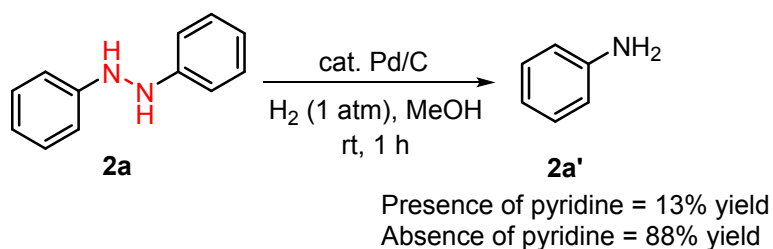
We have performed NMR studies to identify the formation of Pd-hydride species (Figure S1). Initially, at time = 0 (Pd/C and hydrogen in d<sub>6</sub>-benzene) there was a peak at 4.50 ppm that corresponds to free hydrogen.<sup>S1</sup> As time progresses, the intensity of the free hydrogen peak decreases with the formation of a new broad peak at 0.4 ppm. This result indicates the formation of Pd-non classical hydrogen (i.e. hydrogen molecules adsorbed on Pd/C surface).



**Figure S1.** NMR study to identify Pd-non classical hydride formation (Right: J-Young NMR tube used for the study).

### 1.7a Effect of pyridine in the semihydrogenation

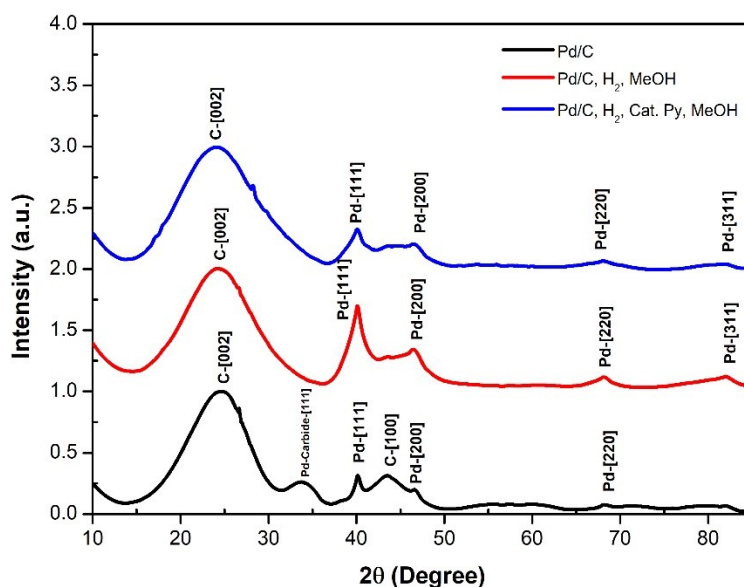
A catalytic amount of pyridine accelerates the H-atom transfer by increasing electron density on the metal center and thus increases the catalytic activity in a controlled manner. Also, pyridine is known to poison by partially preventing access to the metal center.<sup>S2</sup> We believe after semihydrogenation of azobenzene pyridine molecules prevent the over hydrogenation of hydrazobenzene to aniline by preventing the sterically hindered hydrazobenzene molecules from access to Pd-center. To support this a control experiment was performed (Scheme S1).



Thus, performing the hydrogenation reaction in the presence of a catalytic pyridine as an additive the hydrogenation of azobenzene is slower (13% yield of aniline (**2a'**) was observed). However, in the absence of pyridine (only Pd/C) hydrogenation proceeded efficiently and aniline was observed in 88% yield (after 1 h at room temperature). This experiment demonstrates the role of additive such as pyridine.

### 1.7b PXRD Analysis

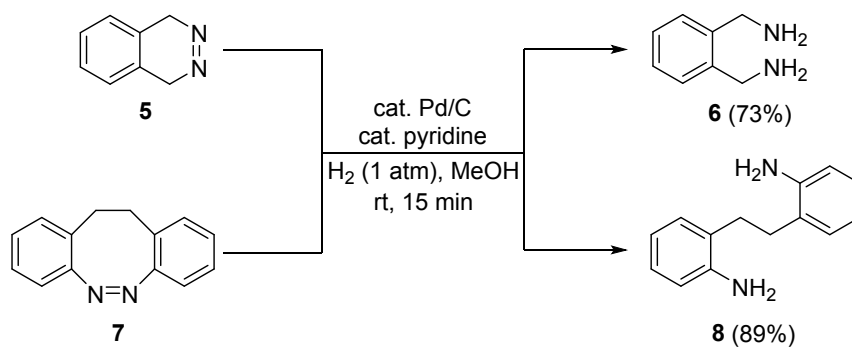
The XRD of fresh Pd/C and spent catalysts showed in Figure S2. Notably, no changes in the Pd(111) and Pd(200) peak positions were found. However, the spent catalyst (in the presence of pyridine) the intensity of the Pd(111) peak diminished. This illustrates that pyridine partially poisons the Pd/C catalyst and preventing access to the metal center for the complete hydrogenation of azoarenes to aniline.



**Figure S2.** PXRD of fresh Pd/C and spent catalysts.

### 1.8 Catalytic hydrogenation of cyclic diazocines

The Pd-catalyzed catalytic hydrogenation of cyclic diazocines under our optimized conditions has been performed using the procedure described in section 1.3. Indeed, cyclic diazocines such as 1,4-dihydrophthalazine (**5**) and (*Z*)-11,12-dihydrodibenzo[*c,g*][1,2]diazocine (**7**) yielded the complete hydrogenated products 1,2-phenylenedimethanamine (**6**) and 2,2'-ethylenedianiline (**8**), respectively (Scheme S2).



**Scheme S2.** Catalytic hydrogenation of cyclic diazocines.

## 2 Characterization Data

### (2a) 1,2-diphenylhydrazine

White solid;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.19$  (t,  $J = 7.6$  Hz, 4H), 6.83-6.80 (m, 6H), 5.51 (s, 2H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta = 148.80, 129.29, 119.81, 112.26$ . HRMS-ESI (m/z) calculated for  $\text{C}_{12}\text{H}_{13}\text{N}_2$   $[\text{M}+\text{H}]^+$  185.1073; found 185.1075.

### (2b) 1-(2-chlorophenyl)-2-phenylhydrazine<sup>S3</sup>

Pale yellow solid;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (d, 1H,  $J = 8.3$  Hz), 7.24 (d, 2H,  $J = 7.6$  Hz), 7.14 (t, 1H,  $J = 7.6$  Hz), 7.06 (d, 1H,  $J = 6.8$  Hz), 6.89 (d, 1H,  $J = 7.6$  Hz), 6.85 (d, 2H,  $J = 8.3$  Hz), 6.79 (t, 1H,  $J = 7.6$  Hz), 6.21 (s, 1H), 5.67 (s, 1H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  148.24, 144.33, 129.39, 129.29, 127.91, 120.25, 119.83, 117.66, 113.06, 112.32; HRMS-ESI (m/z) calculated for  $\text{C}_{12}\text{H}_{12}\text{ClN}_2$   $[\text{M}+\text{H}]^+$  219.0684; found 219.0683.

### (2c) 1-(2-ethylphenyl)-2-phenylhydrazine

White solid;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23-7.28 (m, 2H), 7.11-7.17 (m, 2H), 7.00 (d, 1H,  $J = 6.00$  Hz), 6.85-6.89 (m, 4H), 5.69 (s, 1H), 5.60 (s, 1H), 2.60-2.65 (q, 2H), 1.35 (t, 3H,  $J = 6.00$  Hz);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  148.91, 145.68, 129.35, 128.28, 127.12, 119.86, 119.57, 112.32, 111.32, 23.79, 13.13; HRMS-ESI (m/z) calculated for  $\text{C}_{14}\text{H}_{17}\text{N}_2$   $[\text{M}+\text{H}]^+$  213.1386; found 213.1385.

### (2d) 1-(3-fluorophenyl)-2-phenylhydrazine

Pale yellow solid;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24-7.28 (m, 2H), 7.15-7.20 (m, 1H), 6.90 (t, 1H,  $J = 7.30$  Hz), 6.84 (d, 2H,  $J = 7.60$  Hz), 6.53-6.63 (m, 3H), 5.64 (s, 1H), 5.60 (s, 1H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  163.71 (d,  $J_{\text{C-F}} = 243.2$  Hz), 150.78, 148.29, 130.53, 129.34, 120.13, 112.26, 107.71 (d,  $J_{\text{C-F}} = 1.9$  Hz), 106.21 (d,  $J_{\text{C-F}} = 22.2$  Hz), 99.38 (d,  $J_{\text{C-F}} = 26.7$  Hz); HRMS-ESI (m/z) calculated for  $\text{C}_{12}\text{H}_{12}\text{FN}_2$   $[\text{M}+\text{H}]^+$  203.0979; found 203.0973.

### (2e) 1-(3-Ethylphenyl)-2-phenylhydrazine

White solid;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  7.07-7.23 (m, 3H), 6.79-6.83 (m, 3H), 7.61-7.69 (m, 3H), 5.50-5.49 (d, 2H,  $J = 2.7$  Hz), 2.50-2.61 (q, 2H), 1.18 (t, 3H,  $J = 7.5$  Hz);  $^{13}\text{C}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  148.92, 145.57, 129.24, 129.20, 119.69, 119.47, 112.25, 111.78, 109.62, 28.88, 15.44. HRMS-ESI (m/z) calculated for  $\text{C}_{14}\text{H}_{17}\text{N}_2$   $[\text{M}+\text{H}]^+$  213.1386; found 213.1385.

**(2f) N-(4-(2-phenylhydrazinyl)phenyl)acetamide**

White solid;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  9.70 (s, 1H), 7.60 (s, 2H), 6.91-7.10 (m, 5H), 6.63-6.72 (m, 3H), 6.42 (s, 1H), 1.98 (s, 3H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  168.10, 150.53, 149.93, 140.07, 128.82, 117.62, 111.63, 108.95, 106.77, 102.36, 24.02; HRMS-ESI (m/z) calculated for  $\text{C}_{14}\text{H}_{16}\text{N}_3\text{O}$   $[\text{M}+\text{H}]^+$  242.1288; found 242.1285.

**(2g) 1-(4-fluorophenyl)-2-phenylhydrazine<sup>S4</sup>**

Pale yellow solid;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23 (t, 2H,  $J = 7.63$  Hz), 6.79-6.95 (m, 7H) 5.61 (s, 1H), 5.53 (s, 1H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  157.10 (d,  $J_{\text{C-F}} = 236.7$  Hz), 148.67, 144.97, 129.35, 119.98, 115.79 (d,  $J_{\text{C-F}} = 27$  Hz), 113.33 (d,  $J_{\text{C-F}} = 7.7$  Hz), 112.29; HRMS-ESI (m/z) calculated for  $\text{C}_{12}\text{H}_{12}\text{FN}_2$   $[\text{M}+\text{H}]^+$  203.0979; found 203.0973.

**(2h) 1-(4-chlorophenyl)-2-phenylhydrazine<sup>S4</sup>**

Pale yellow solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.20-7.29 (m, 4H), 6.82-6.92 (m, 5H) 6.64 (s, 1H), 6.66 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.06, 147.09, 129.05, 128.86, 124.00, 119.80, 113.13, 111.96; HRMS-ESI (m/z) calculated for  $\text{C}_{12}\text{H}_{12}\text{ClN}_2$   $[\text{M}+\text{H}]^+$  219.0684; found 219.0683.

**(2i) 1-(4-bromophenyl)-2-phenylhydrazine<sup>S5</sup>**

Pale yellow solid;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30-7.36 (m, 4H), 6.78-6.89 (m, 5H), 5.68 (s, 2H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  112.32, 113.95, 120.20, 122.93, 124.34, 129.40, 132.10, 147.93 148.35. HRMS-ESI (m/z) calculated for  $\text{C}_{12}\text{H}_{12}\text{BrN}_2$   $[\text{M}+\text{H}]^+$  263.0178; found 263.0178.

**(2j) 1-phenyl-2-(4-(trifluoromethyl)phenyl)hydrazine<sup>S5</sup>**

White solid;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (d, 2H,  $J = 4.0$  Hz), 7.24 (t, 2H,  $J = 7.63$  Hz), 6.90 (d, 3H,  $J = 8.3$  Hz), 6.82 (d, 3H,  $J = 8.3$  Hz), 5.83 (s, 1H), 5.67 (s, 1H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  151.48, 147.99, 129.45, 126.73 (q,  $J_{\text{C-F}} = 3.9$  Hz), 124.65 (q,  $J_{\text{C-F}} = 271.0$  Hz), 121.46 (q,  $J_{\text{C-F}} = 32.7$  Hz), 120.43, 112.33, 111.52; HRMS-ESI (m/z) calculated for  $\text{C}_{13}\text{H}_{11}\text{F}_3\text{N}_2$   $[\text{M}+\text{H}]^+$  253.0947; found 253.0947.

**(2k) 1-(4-ethoxyphenyl)-2-phenylhydrazine<sup>S5</sup>**

White solid;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24 (d, 1H,  $J = 7.9$  Hz), 7.05 (d, 1H,  $J = 8.55$  Hz), 6.83-6.90 (m, 6H), 5.61 (s, 1H), 5.46 (s, 1H), 3.97-4.02 (q, 2H), 1.41 (t, 3H,  $J = 7.30$  Hz);  $^{13}\text{C}$



NMR (50 MHz, CDCl<sub>3</sub>)  $\delta$  161.46, 152.98, 149.11, 142.66, 129.28, 124.73, 122.50, 119.68, 115.57, 115.08, 113.65, 112.30, 63.83, 14.93.

**(2l) N-(4-(2-phenylhydrazinyl)phenyl)pivalamide**

White solid; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  8.63-8.64 (d, 1H, *J* = 4.2 Hz), 7.20-7.36 (m, 5H), 6.81-6.85 (m, 4H), 5.70 (s, 1H), 5.64 (s, 1H), 1.31 (s, 9H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>)  $\delta$  176.41, 149.78, 148.80, 145.74, 135.92, 130.41, 129.57, 123.70, 122.09, 119.79, 112.60, 112.31, 39.30, 27.62; HRMS-ESI (*m/z*) calculated for C<sub>17</sub>H<sub>22</sub>N<sub>3</sub>O [M+H]<sup>+</sup> 284.1757; found 284.1755.

**(2m) 4-(2-phenylhydrazinyl)phenylpivalate**

White solid; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  7.21-7.24 (m, 2H), 6.91 (d, 2H, *J* = 8.7 Hz), 6.87-6.87 (m, 5H), 5.64 (s, 1H), 5.62 (s, 1H), 1.35 (s, 9H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>)  $\delta$  177.56, 148.69, 146.45, 144.19, 129.33, 122.13, 119.96, 112.85, 112.35, 38.95, 27.15; HRMS-ESI (*m/z*) calculated for C<sub>17</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup> 285.1598; found 285.1591.

**(2n) Methyl 4-(2-phenylhydrazinyl)benzoate**

White solid; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  7.90, (d, 2H, *J* = 8.03 Hz), 7.22 (t, 2H, *J* = 7.63 Hz), 6.80-6.86 (m, 5H), 5.94 (s, 1H), 5.71 (s, 1H), 3.85 (s, 3H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>)  $\delta$  167.05, 152.76, 147.98, 131.57, 121.13, 120.40, 112.34, 111.13, 51.68; HRMS-ESI (*m/z*) calculated for C<sub>14</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup> 243.1128; found 243.1129.

**(2o) 1-(4-(2-phenylhydrazinyl)phenyl)ethanone<sup>S6</sup>**

White solid; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  7.85, (d, 2H, *J* = 9.16 Hz), 7.20-7.25 (m, 2H), 6.79-6.87 (m, 5H), 6.01 (s, 1H), 5.73 (s, 1H), 2.50 (s, 3H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>)  $\delta$  195.59, 152.93, 147.87, 130.74, 129.45, 129.16, 120.51, 112.35, 111.08, 26.16.

**(2p) 1-(3-chloro-2-methylphenyl)-2-phenylhydrazine**

White solid; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  7.24-7.25, (d, 1H, *J* = 8.3 Hz), 7.06-7.07 (d, 2H, *J* = 8.01 Hz), 6.87-6.90 (m, 3H), 6.80-6.81 (d, 2H, *J* = 8.7 Hz), 5.62 (s, 1H), 5.56 (s, 1H), 2.30 (s, 3H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>)  $\delta$  149.01, 146.52, 129.81, 129.30, 129.18, 119.75, 112.45, 112.30, 20.47; HRMS-ESI (*m/z*) calculated for C<sub>13</sub>H<sub>14</sub>ClN<sub>2</sub> [M+H]<sup>+</sup> 233.0854; found 233.0856.

**(2q) 1-(2,5-dimethylphenyl)-2-phenylhydrazine<sup>S7</sup>**

White solid; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 7.25-7.29 (m, 2H), 7.03 (d, 1H, *J* = 7.30 Hz), 6.84-6.91 (m, 4H), 6.64-6.65 (d, 1H, *J* = 7.30 Hz), 5.59 (s, 1H), 5.53 (s, 1H), 2.27 (s, 3H), 2.24 (s, 3H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ 148.98, 146.11, 136.97, 130.26, 129.32, 120.04, 119.80, 118.04, 112.30, 111.79, 21.41, 16.68; HRMS-ESI (m/z) calculated for C<sub>14</sub>H<sub>17</sub>N<sub>2</sub> [M+H]<sup>+</sup> 213.1386; found 213.1385.

**(2r) 1,2-bis(2-chlorophenyl)hydrazine<sup>S3</sup>**

Pale yellow solid; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 7.33 (d, 2H, *J* = 4.0 Hz), 7.16 (s, 2H), 7.16 (s, 2H), 6.99 (s, 5H), 6.82 (s, 1H), 6.24 (s, 1H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ 143.85, 129.36, 127.98, 120.23, 117.95, 112.88; HRMS-ESI (m/z) calculated for C<sub>12</sub>H<sub>11</sub>Cl<sub>2</sub>N<sub>2</sub> [M+H]<sup>+</sup> 253.0296; found 253.0294.

**(2s) 1,2-bis(4-fluorophenyl)hydrazine<sup>S4</sup>**

White solid; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 7.14-7.23 (m, 3H), 6.78-6.86 (m, 5H), 5.61 (s, 2H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ 147.92 (d, *J*<sub>C-F</sub> = 97.8 Hz), 129.30 (d, *J*<sub>C-F</sub> = 18.2 Hz), 122.28 (d, *J*<sub>C-F</sub> = 424.7 Hz), 112.90 (d, *J*<sub>C-F</sub> = 117.9 Hz). HRMS-ESI (m/z) calculated for C<sub>12</sub>H<sub>11</sub>F<sub>2</sub>N<sub>2</sub> [M+H]<sup>+</sup> 221.0885; found 221.0883.

**(2t) 1,2-bis(4-chlorophenyl)hydrazine<sup>S3</sup>**

White solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.18 (d, *J* = 8.8 Hz, 4H), 6.77 (d, *J* = 8.8 Hz, 4H), 5.63 (s, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ = 146.97, 129.25, 124.64, 113.45. HRMS-ESI (m/z) calculated for C<sub>12</sub>H<sub>11</sub>Cl<sub>2</sub>N<sub>2</sub> [M+H]<sup>+</sup> 253.0294; found 253.0296.

**(2u) 1,1'-(hydrazine-1,2-diylbis(4,1-phenylene))diethanone<sup>S8</sup>**

White solid; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 6.94 (d, 6H, *J* = 8.7 Hz), 5.93 (d, 4H, *J* = 8.7 Hz), 2.94 (s, 6H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ 166.38, 152.89, 130.75, 119.17, 110.39, 50.95.

**(4a) 1,2-di(pyridin-4-yl)hydrazine<sup>S5</sup>**

Pale red solid; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 8.65 (s, 2H), 8.15 (d, 4H, *J* = 6.0 Hz), 6.61-6.64 (q, 4H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ 153.20, 148.16, 105.04; HRMS-ESI (m/z) calculated for C<sub>10</sub>H<sub>11</sub>N<sub>4</sub> [M+H]<sup>+</sup> 187.0979; found 187.0978.

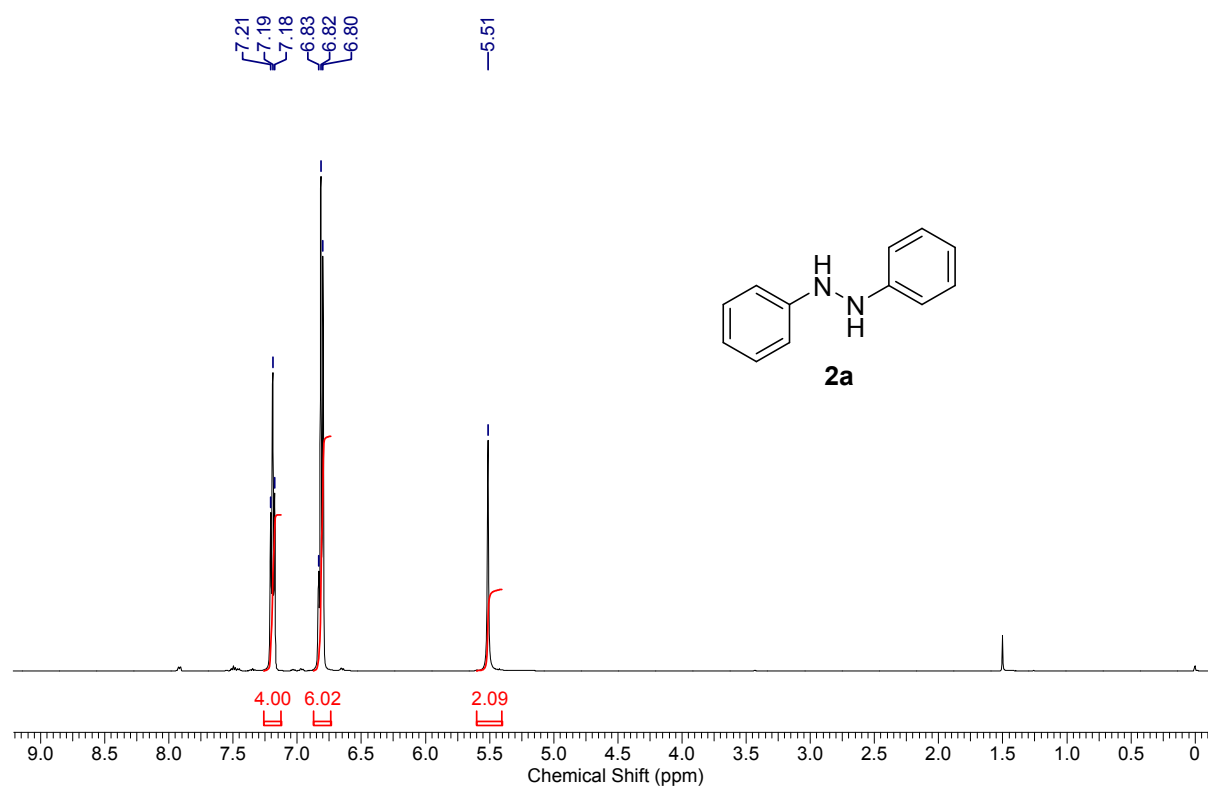
**(4b) 1,2-bis(5-methylisoxazol-3-yl)hydrazine<sup>S5</sup>**

Pale yellow solid; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 6.30 (s, 2H), 5.74 (s, 2H), 2.32 (s, 6H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ 169.87, 166.69, 92.83, 12.58; HRMS-ESI (m/z) calculated for C<sub>8</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup> 195.0877; found 195.0877.

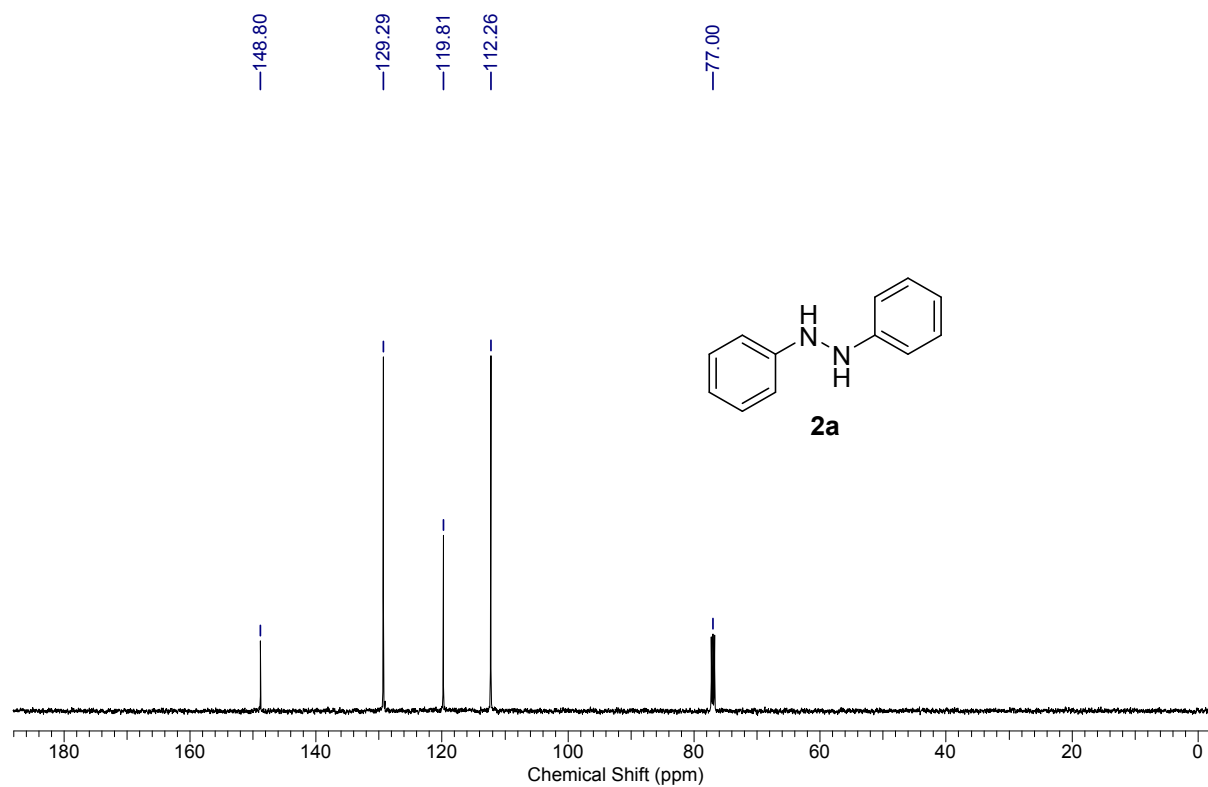
### 3. References

- S1. G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics* 2010, **29**, 2176-2179.
- S2. F. Zaera, *ACS Catal.* 2017, **7**, 4947-4967.
- S3. G. Zhang, L. Wang, K. Shen, D. Zhao and H. S. Freeman *Chem. Eng. Trans.* 2008, **141**, 368-374.
- S4. X. Wang, X. Wang, C. Xia and L. Wu, *Green Chem.* 2019, **21**, 4189-4193.
- S5. L. Wang, A. Ishida, Y. Hashidoko and M. Hashimoto, *Angew. Chem. Int. Ed.* 2017, **56**, 870-873.
- S6. K.-S. Du, J.-M. Huang, *Green Chem.* 2019, **21**, 1680-1685.
- S7. R. J. Lundgren and M. Stradiotto, *Angew. Chem. Int. Ed.* 2010, **49**, 8686-8690.
- S8. N. Sakai, K. Fujii, S. Nabeshima, R. Ikeda, T. Konakahara, *Chem. Commun.* 2010, **46**, 3173-3175.

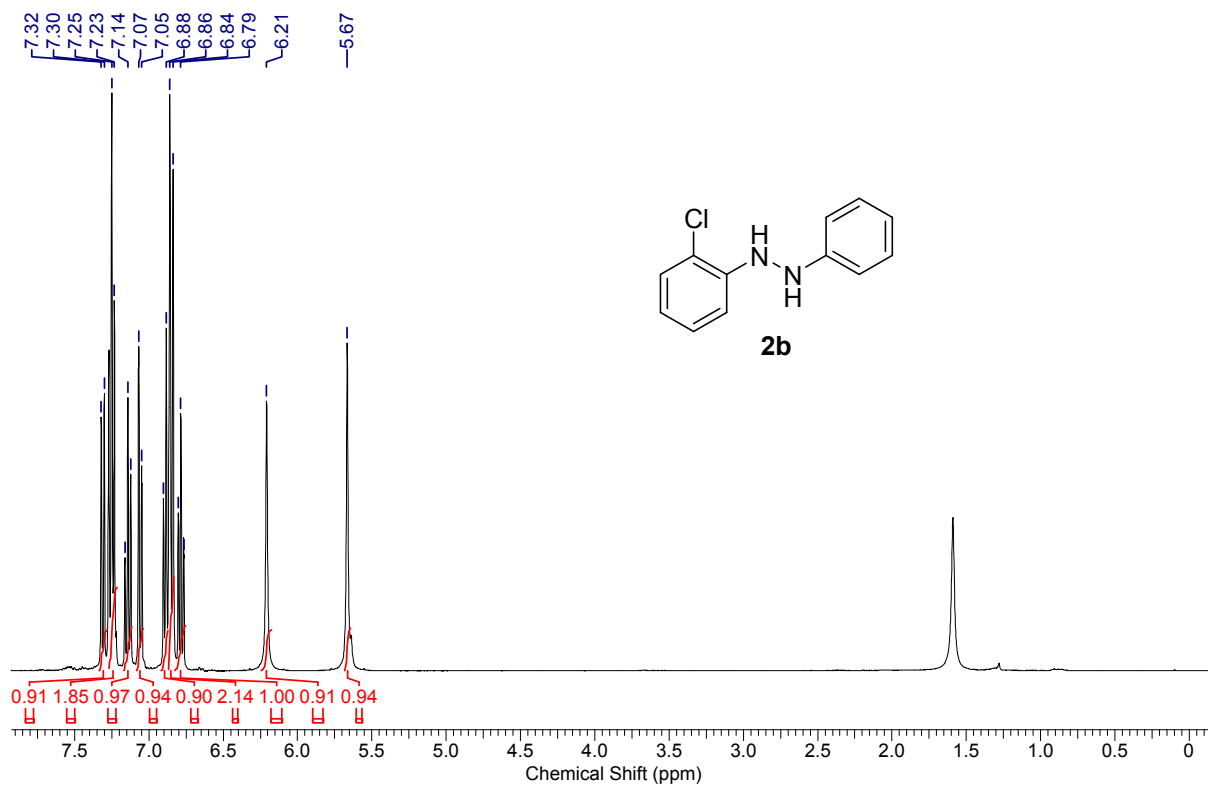
#### 4. Copy of $^1\text{H}$ and $^{13}\text{C}$ Spectra



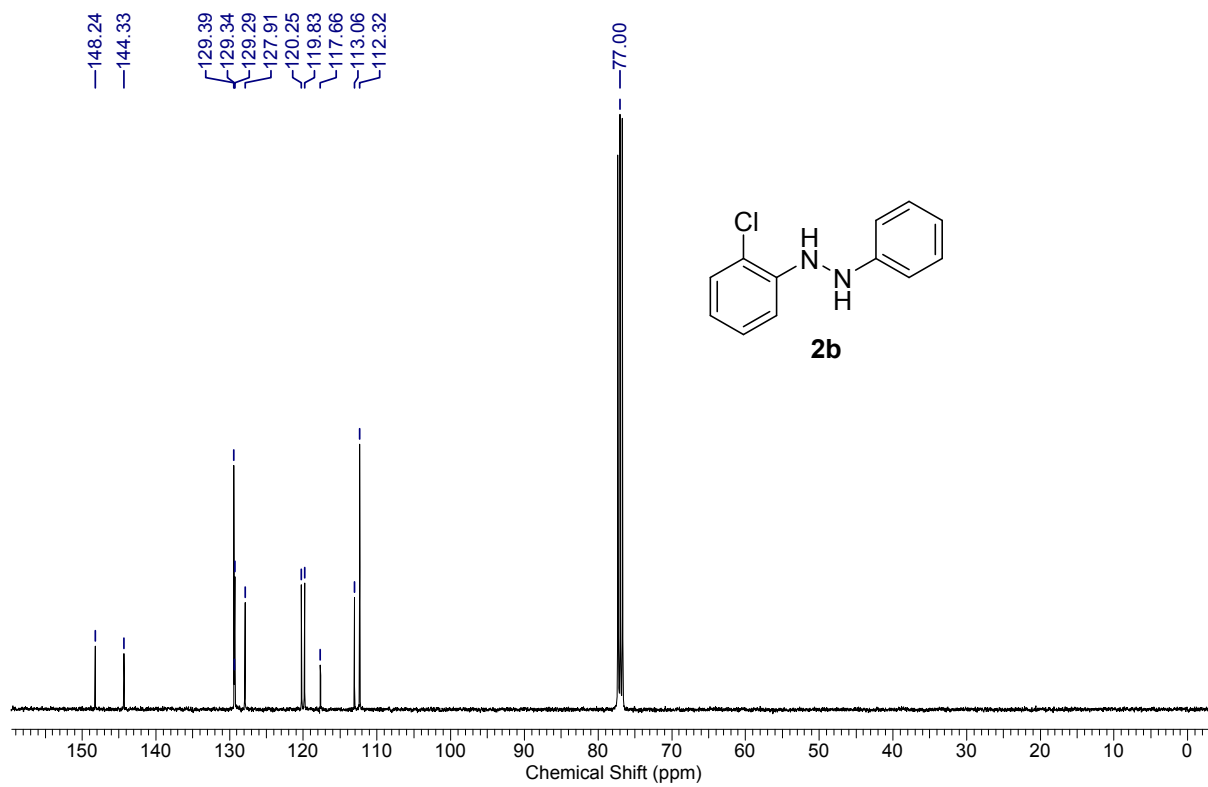
$^1\text{H}$  NMR of **2a**



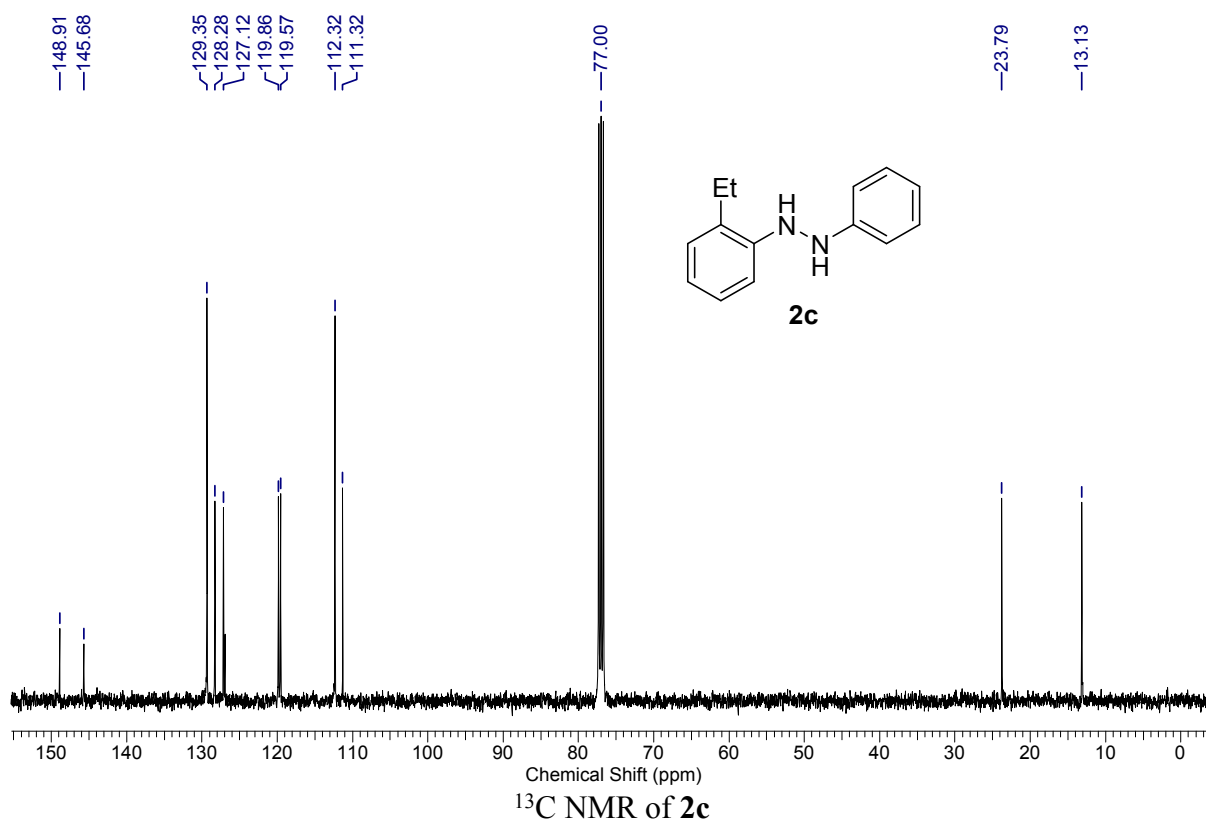
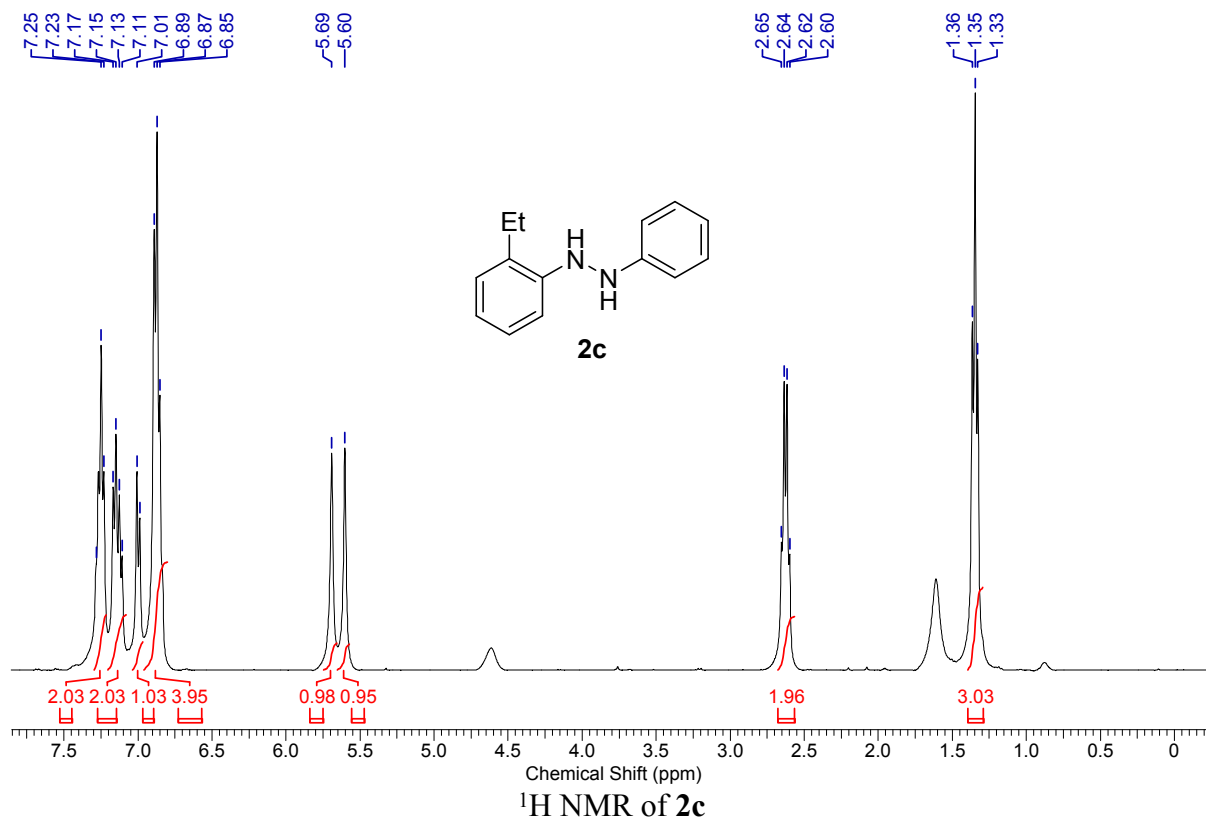
<sup>13</sup>C NMR of **2a**

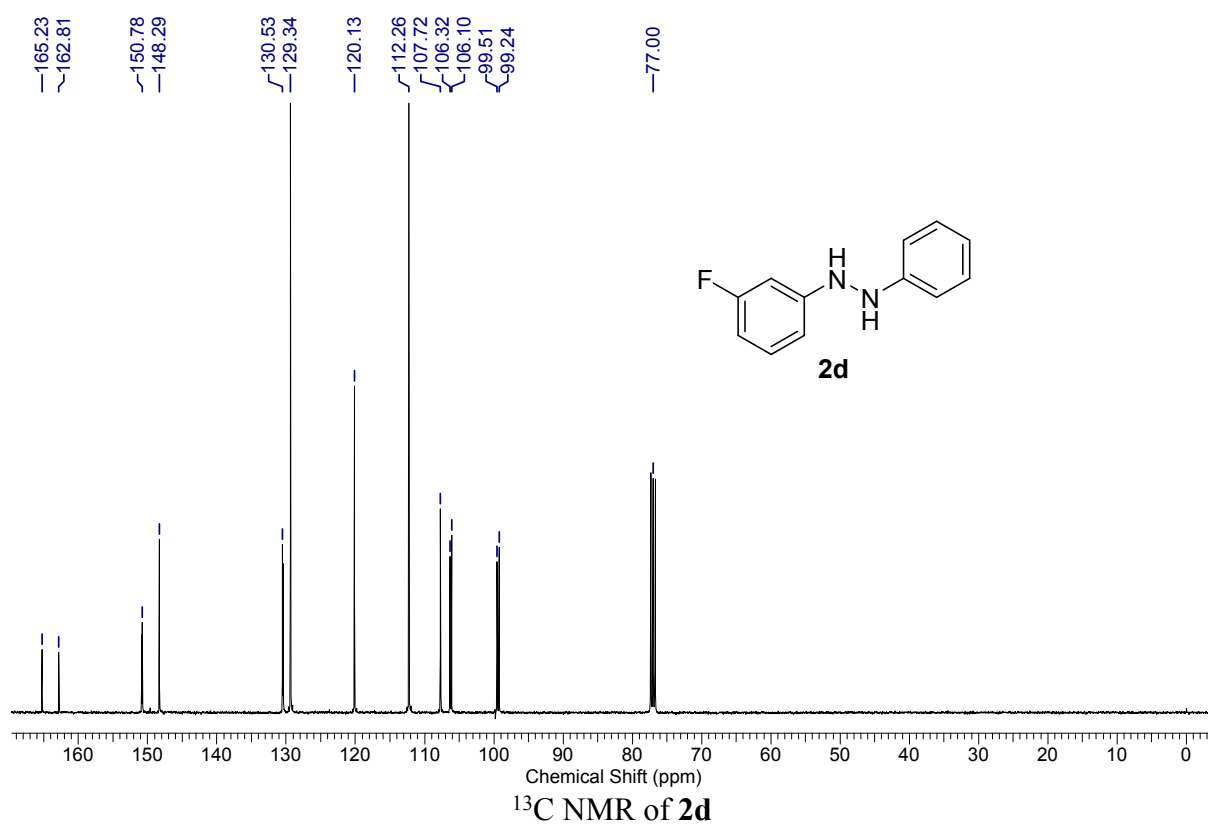
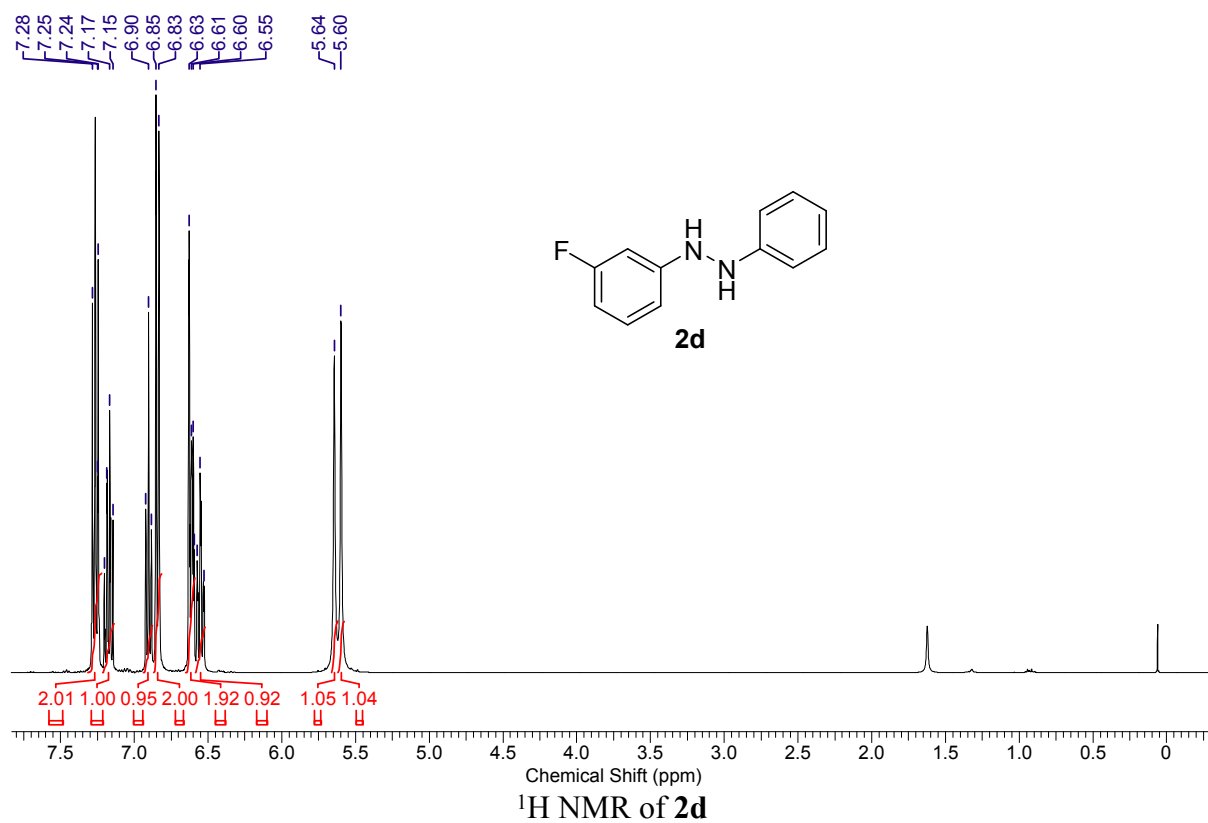


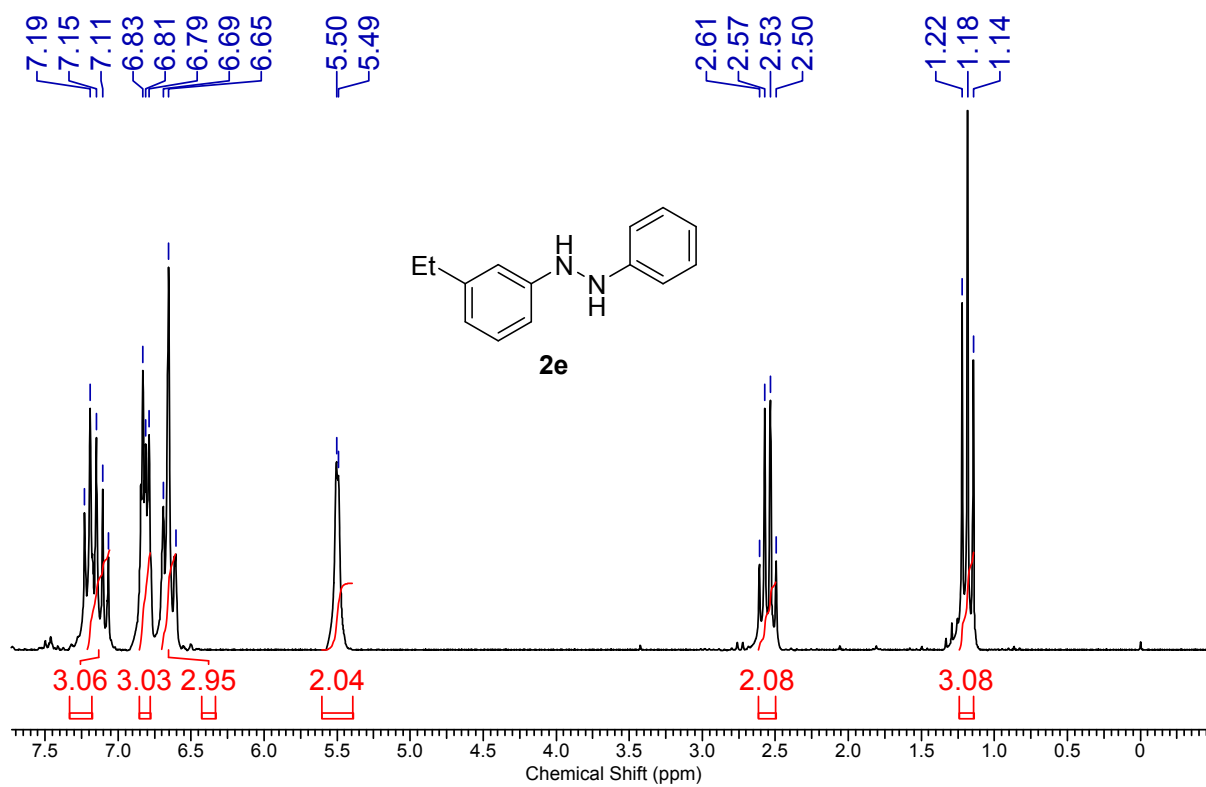
<sup>1</sup>H NMR of **2b**



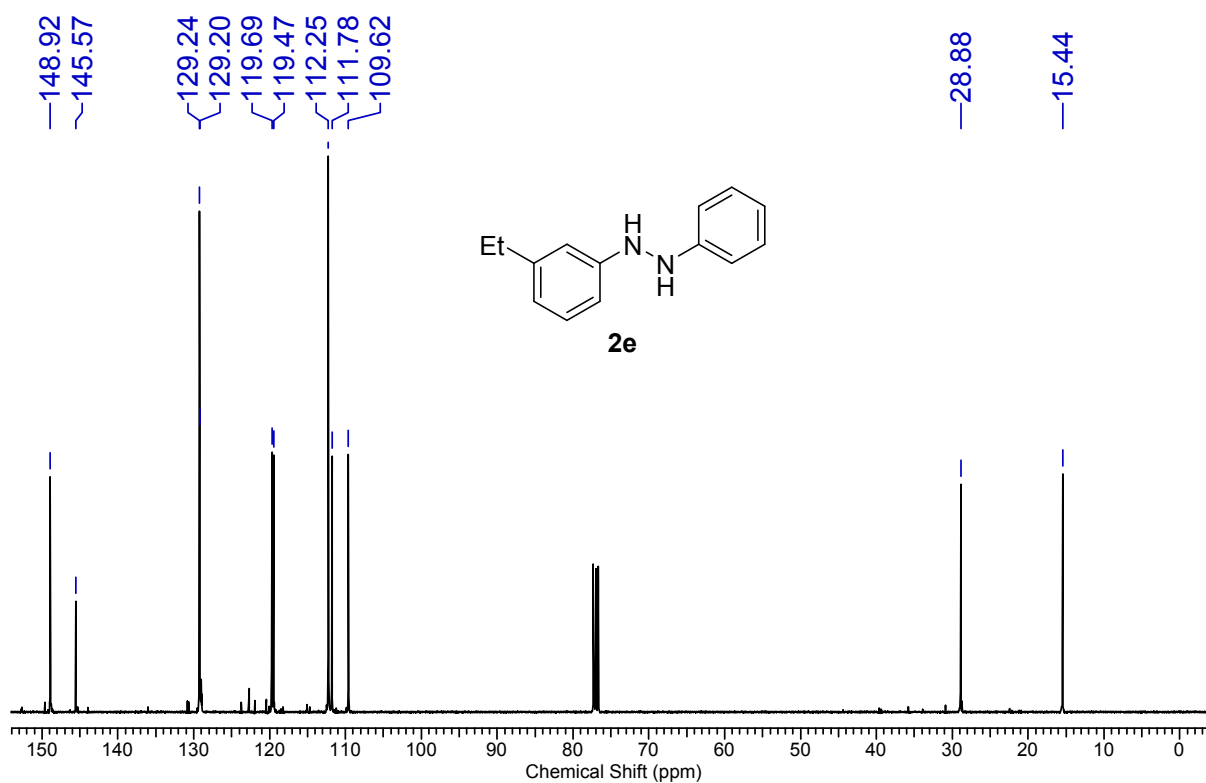
<sup>13</sup>C NMR of **2b**





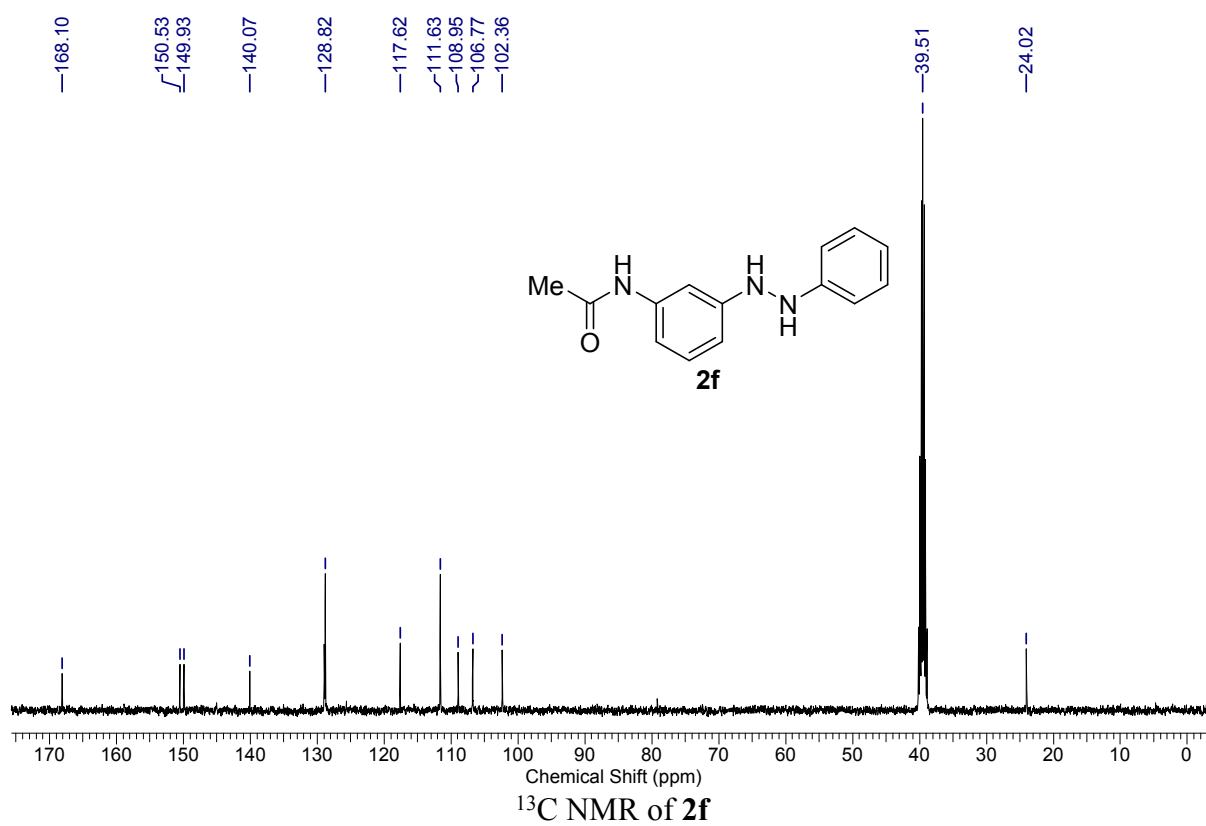
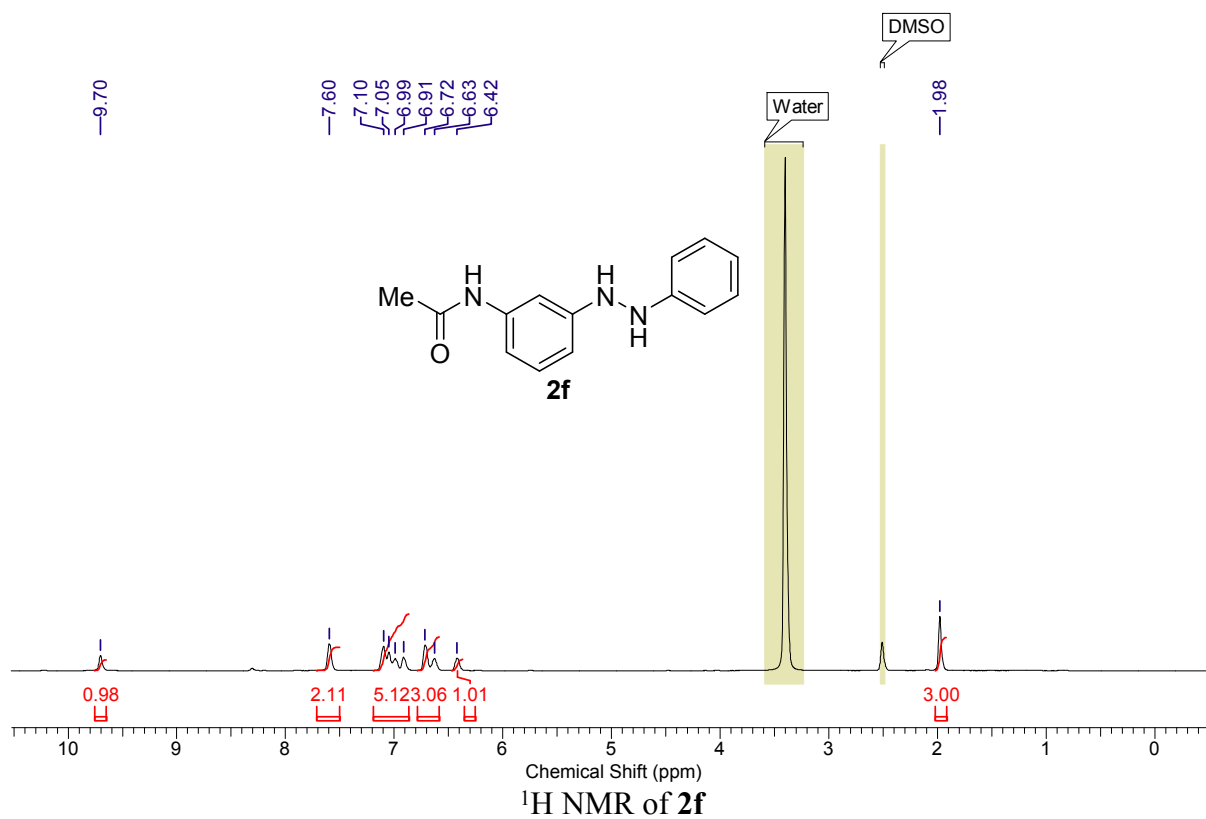


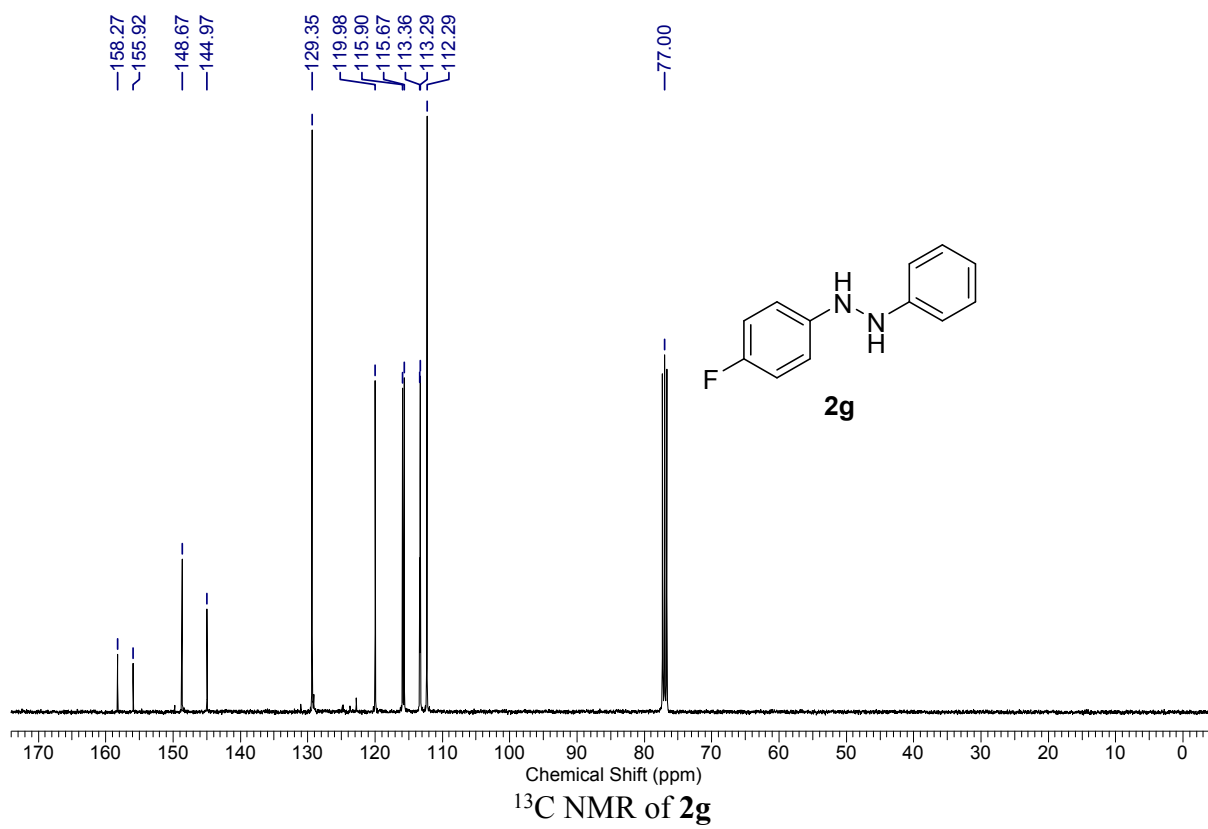
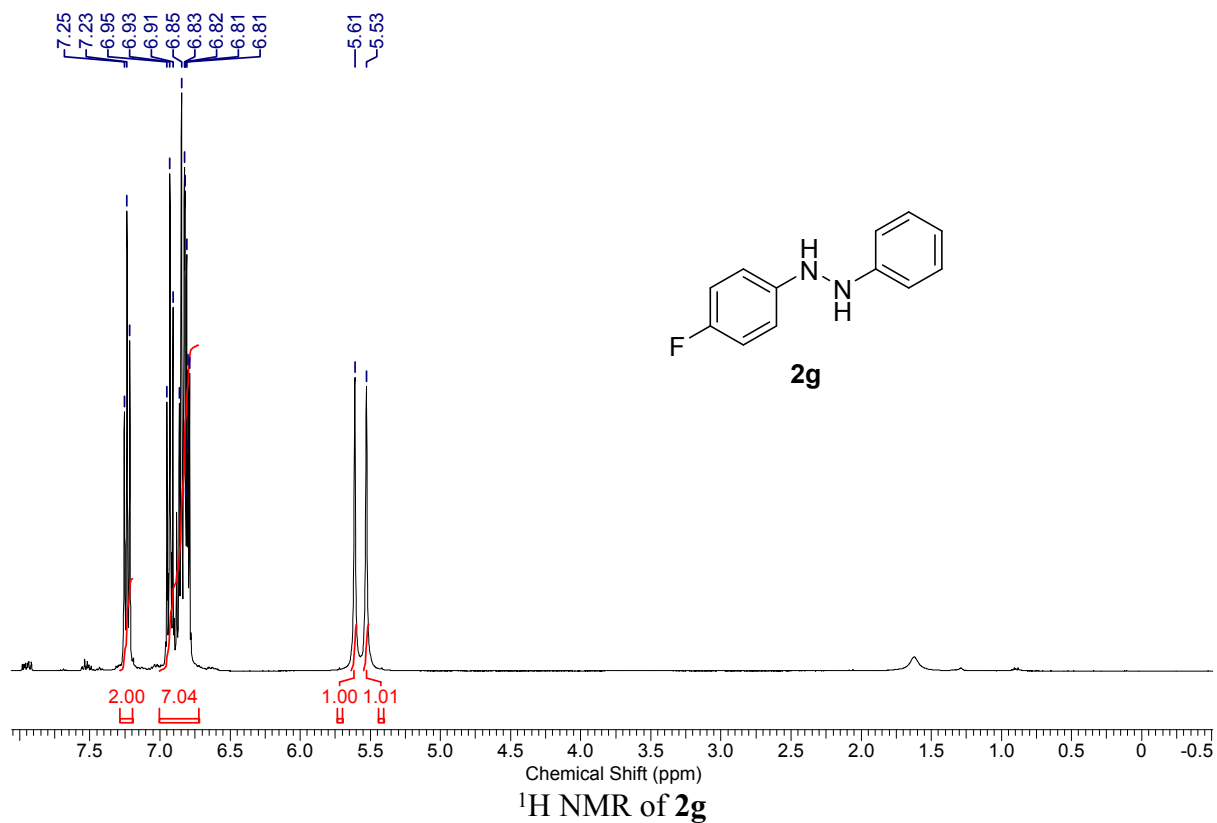
<sup>1</sup>H NMR of **2e**

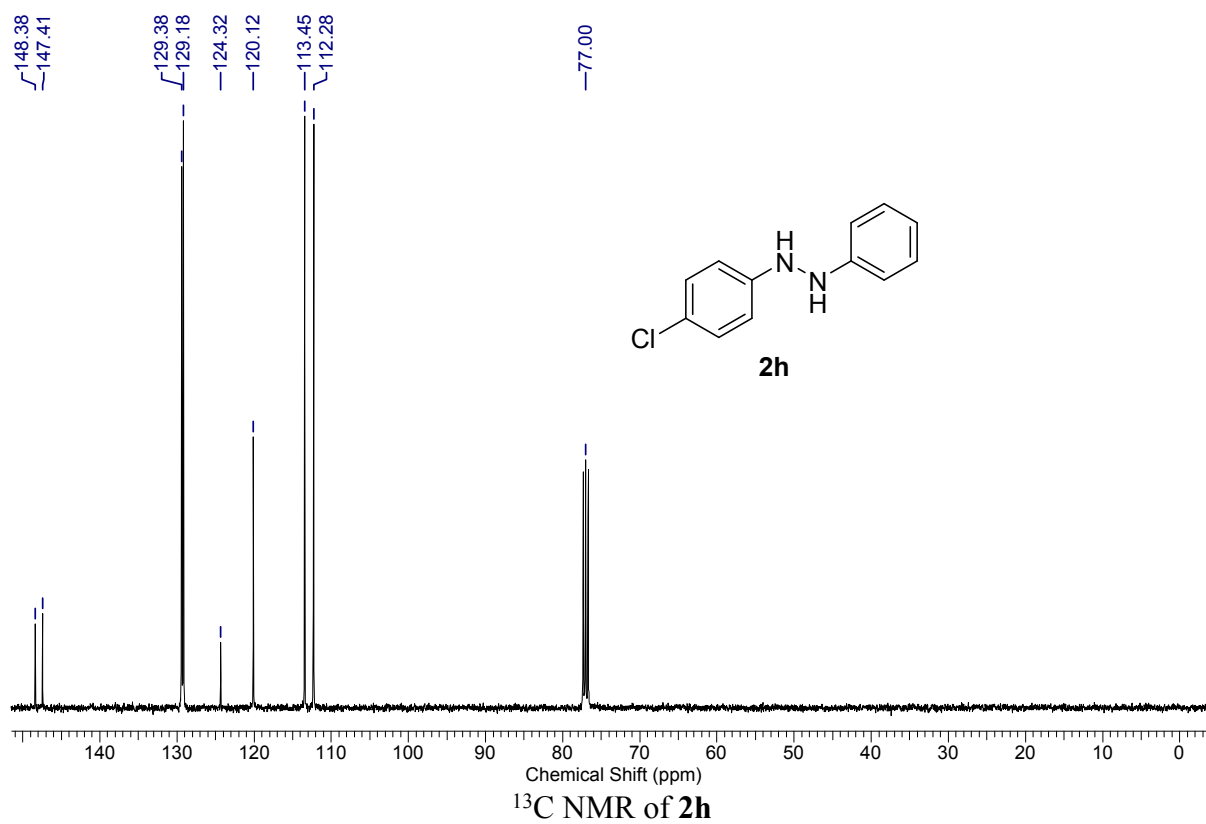
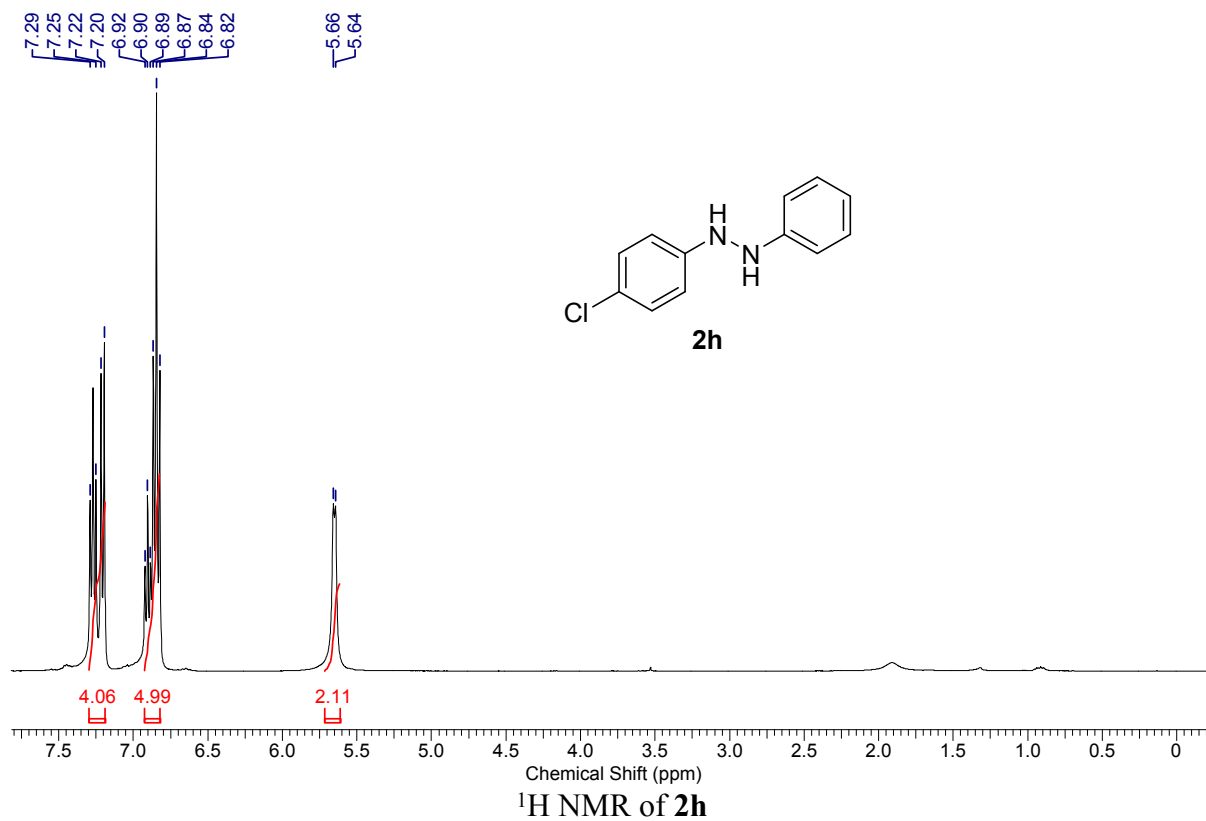


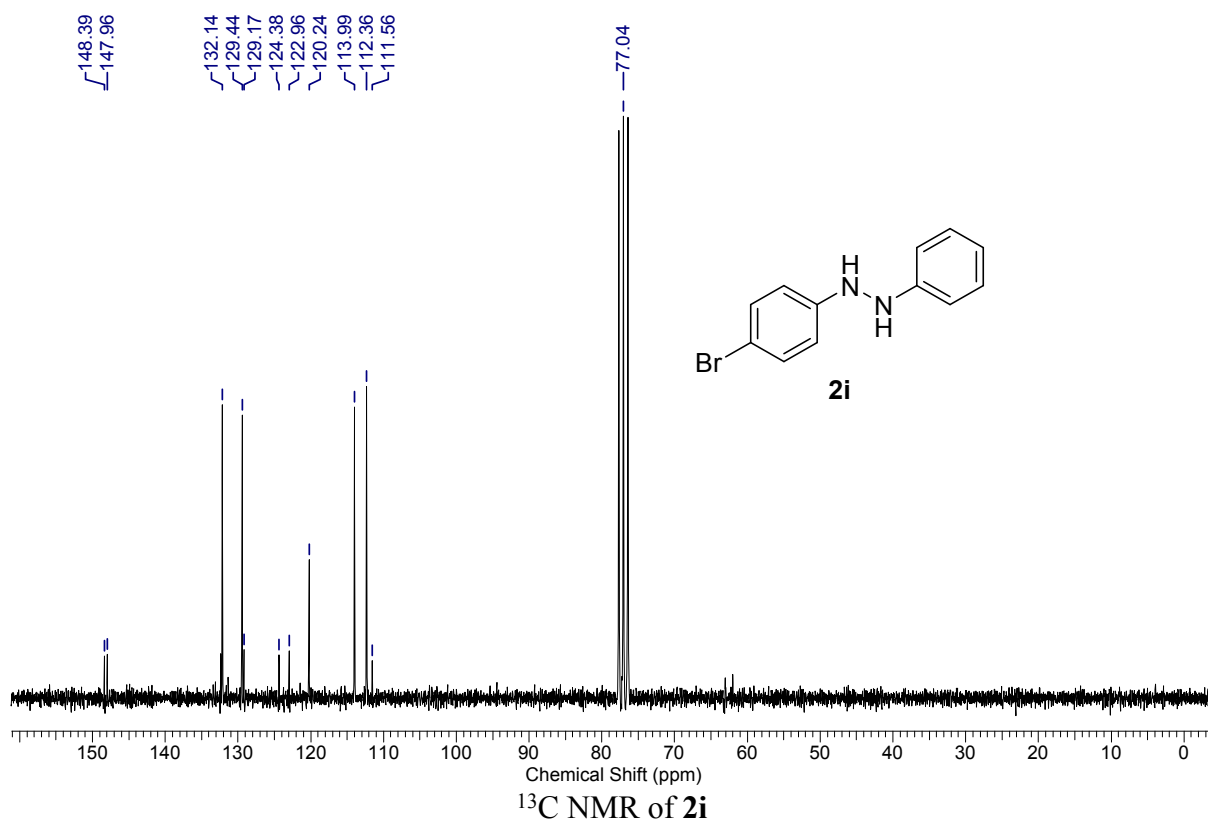
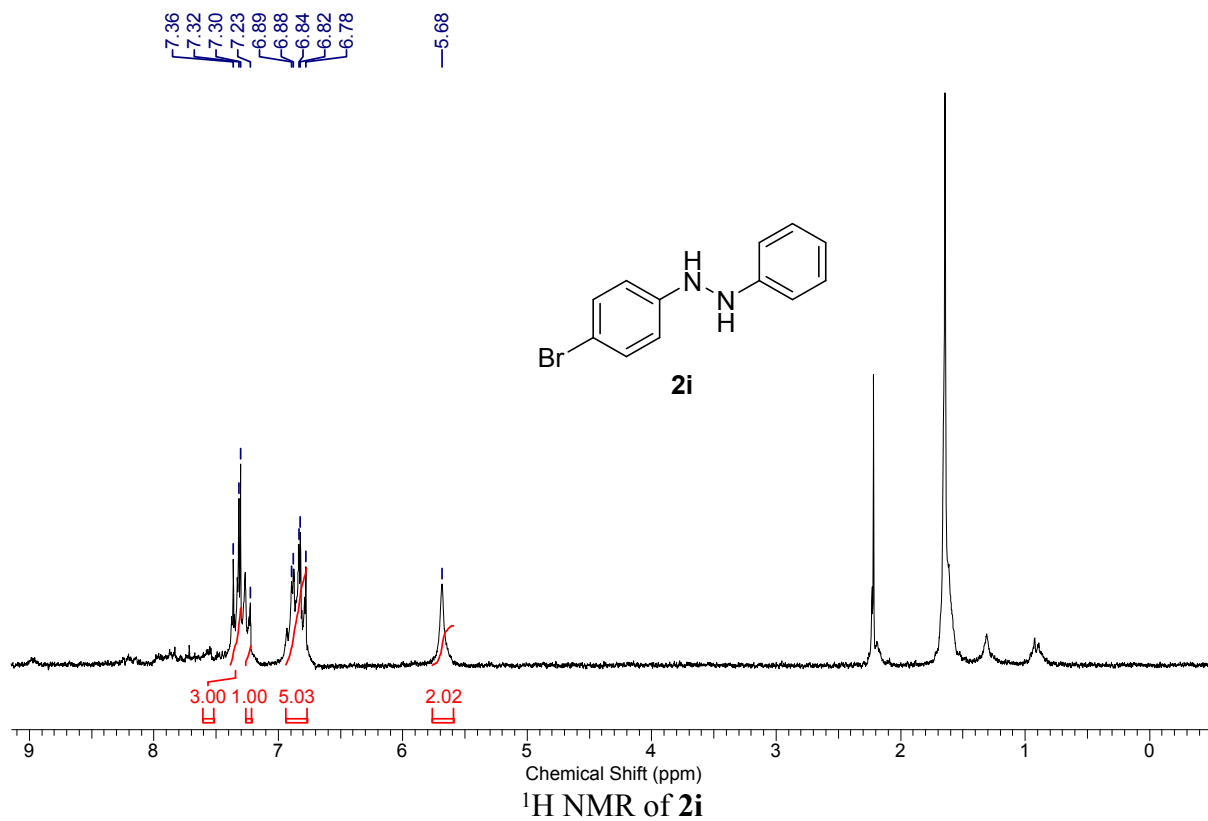
<sup>13</sup>C NMR of **2e**

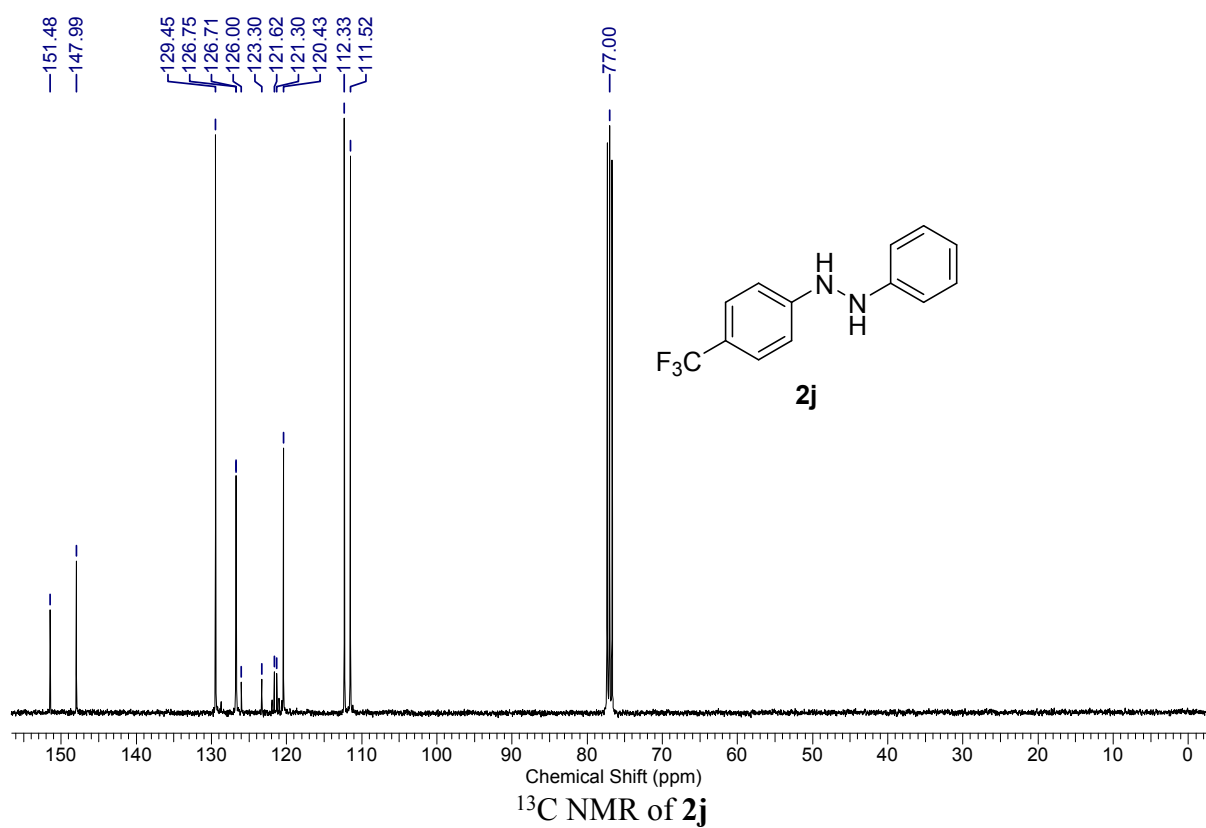
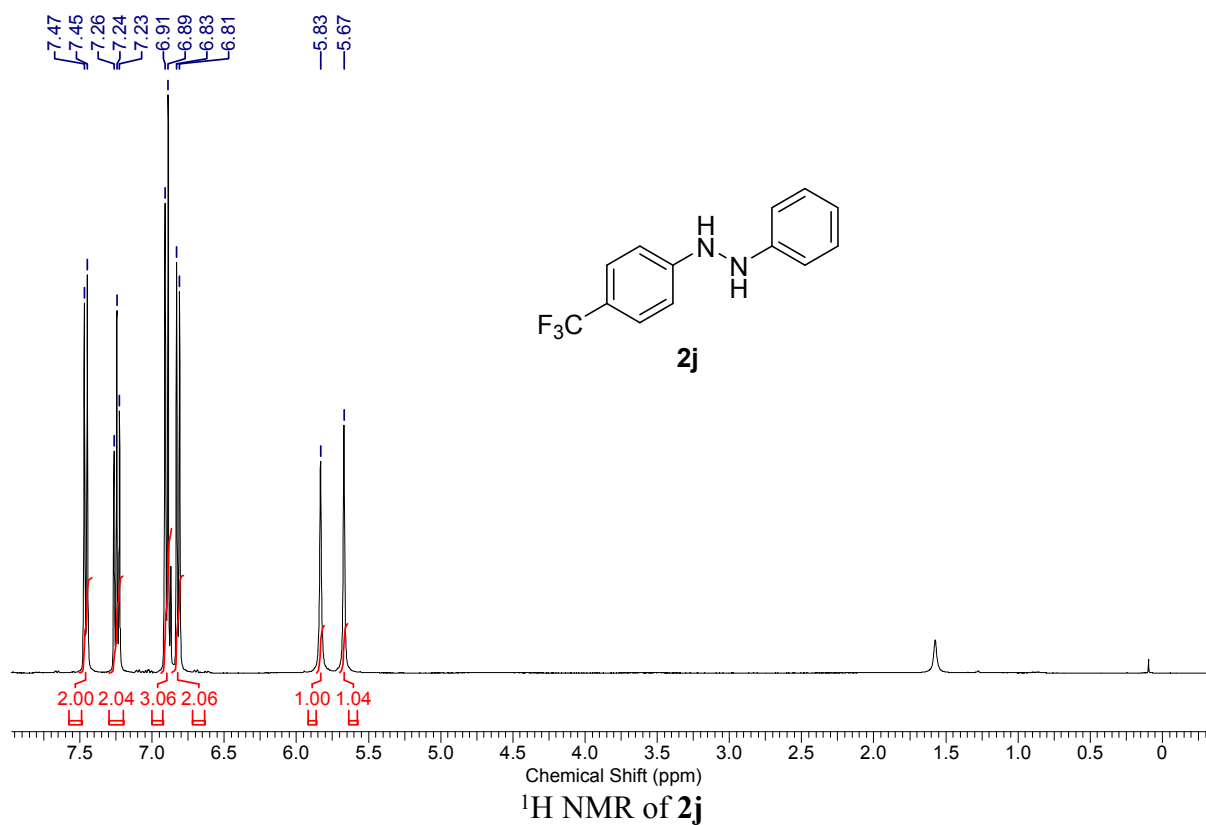


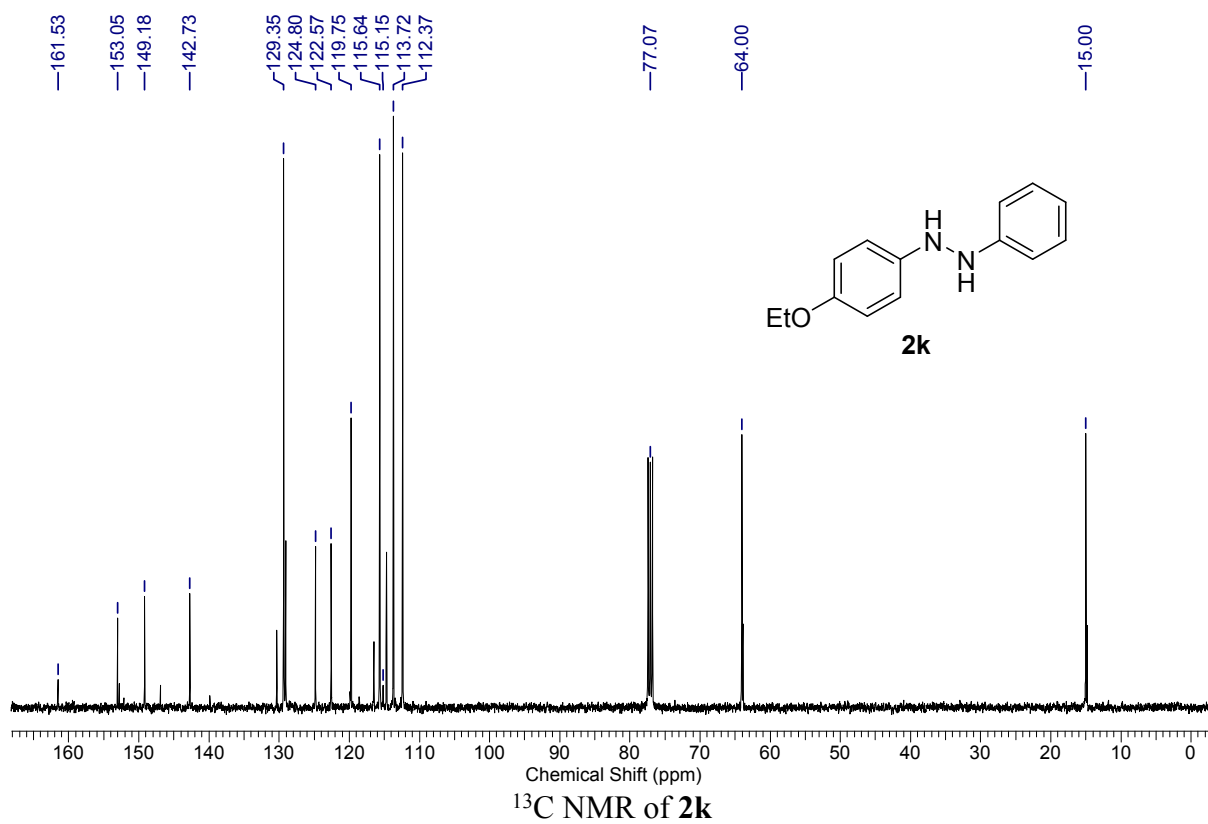
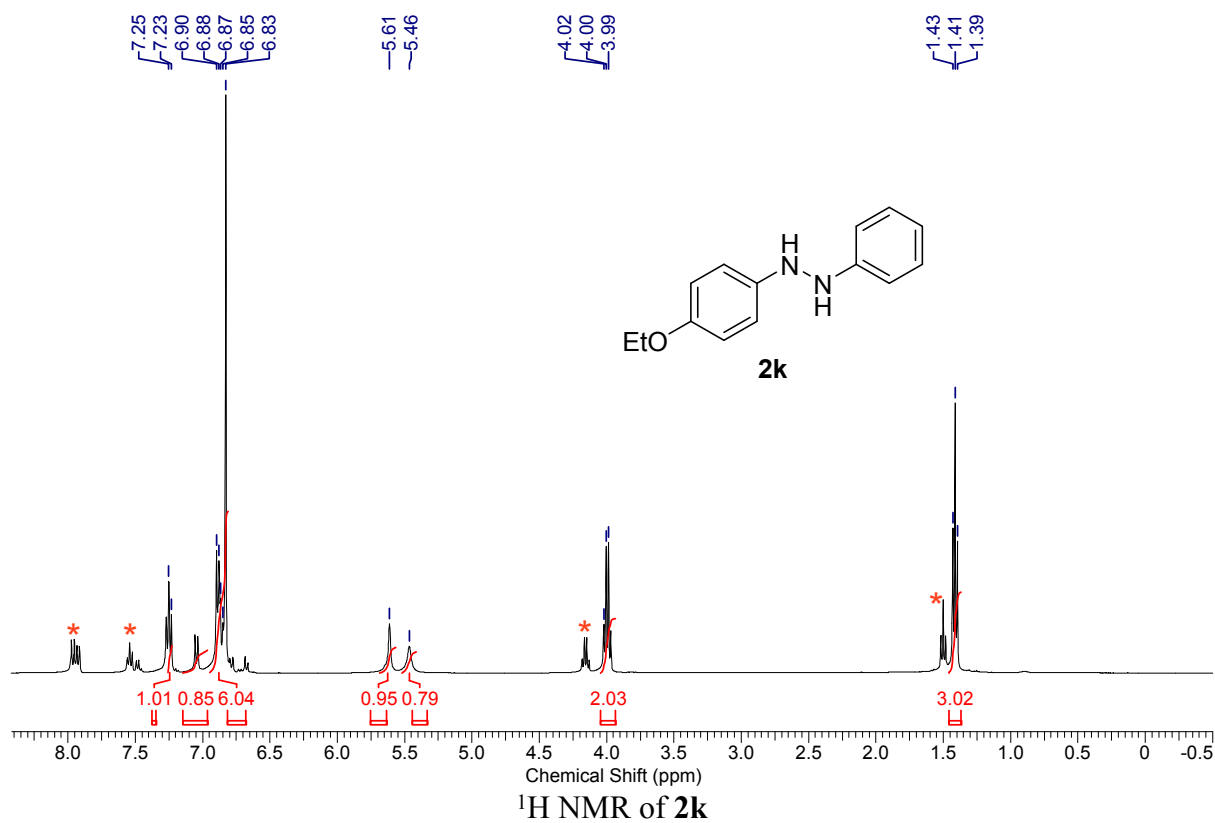


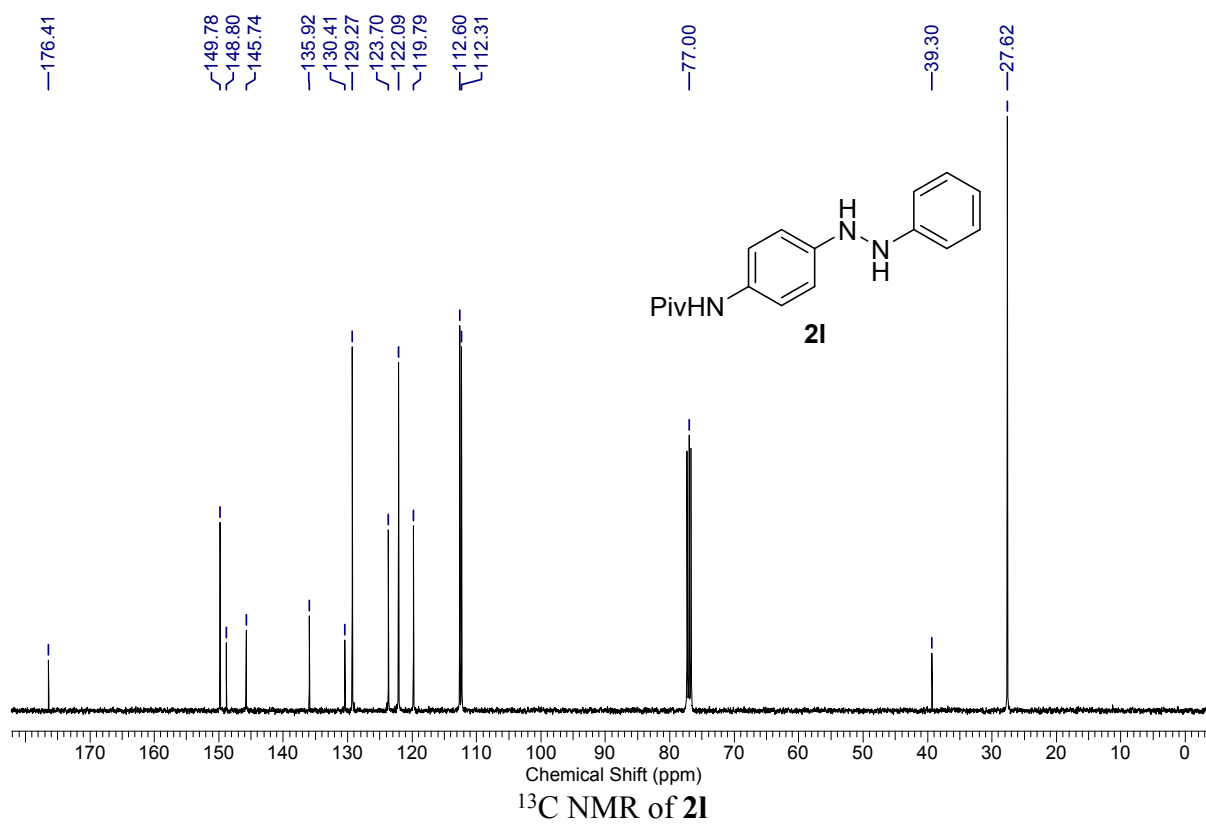
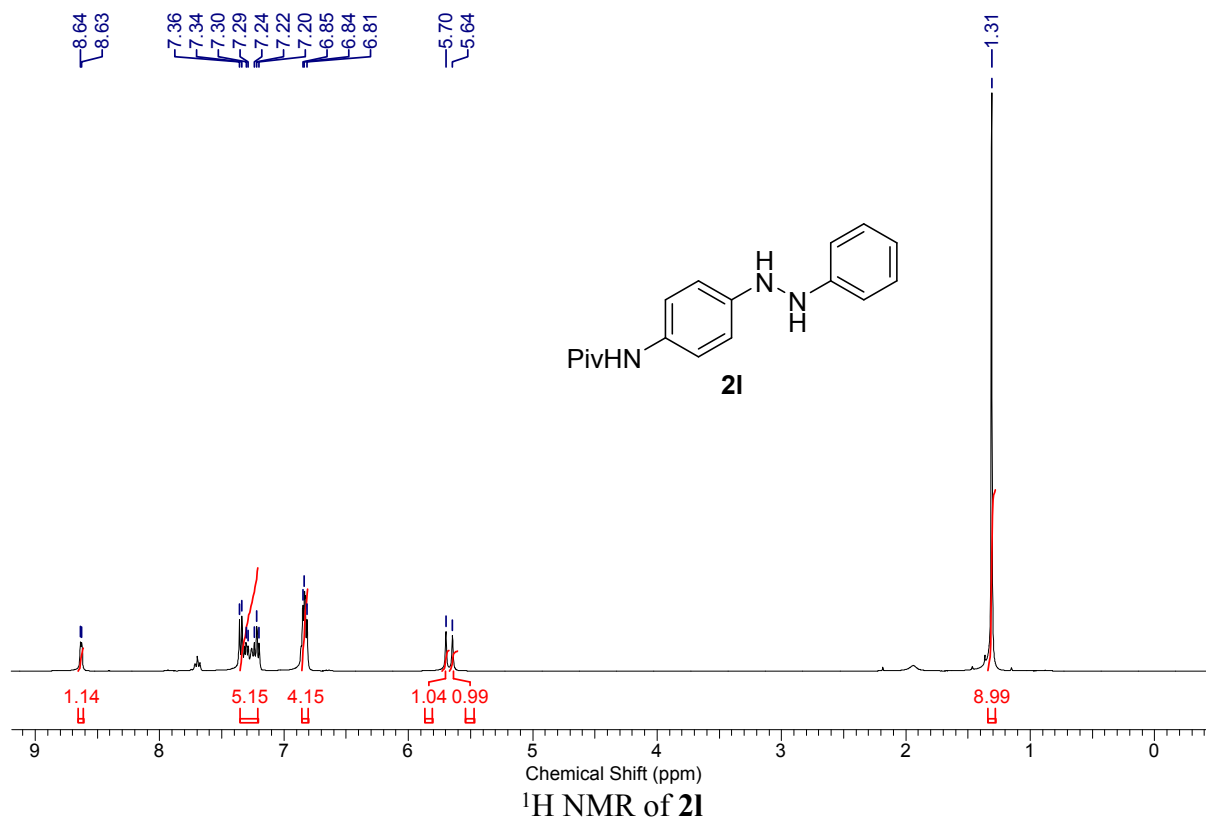


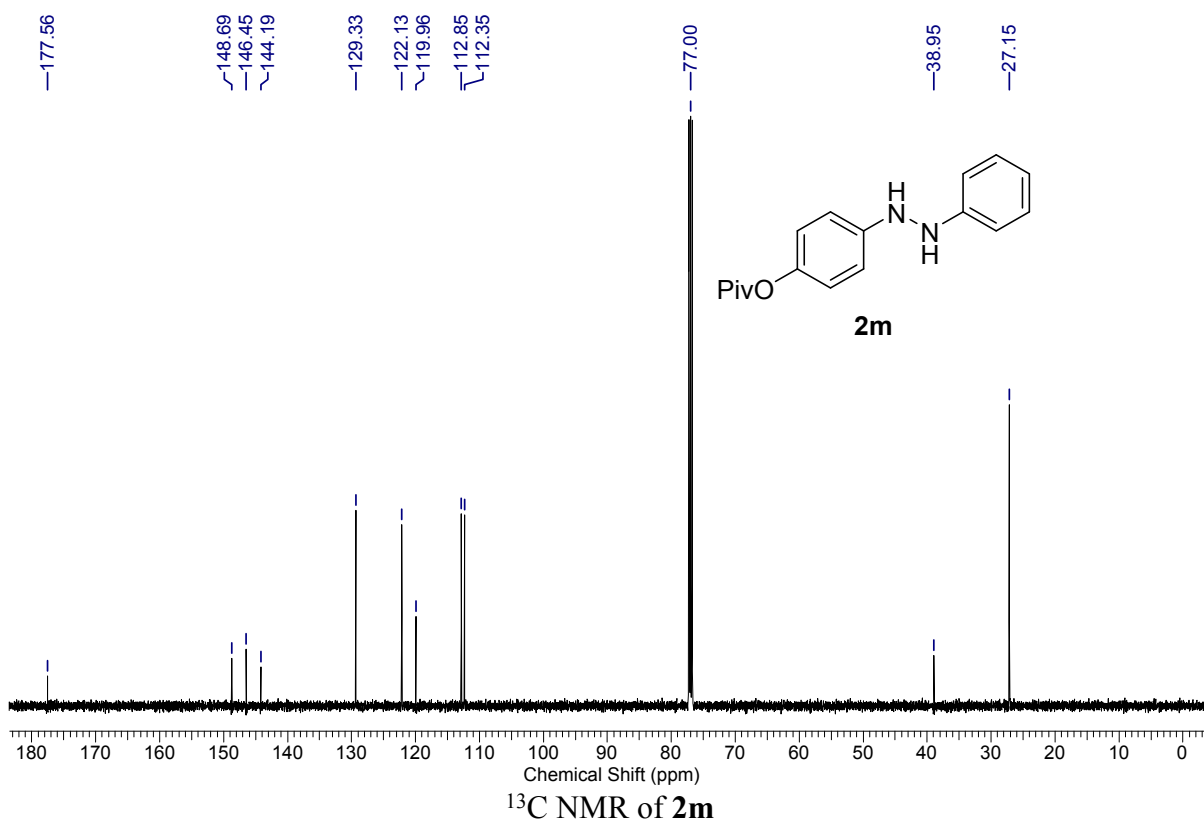
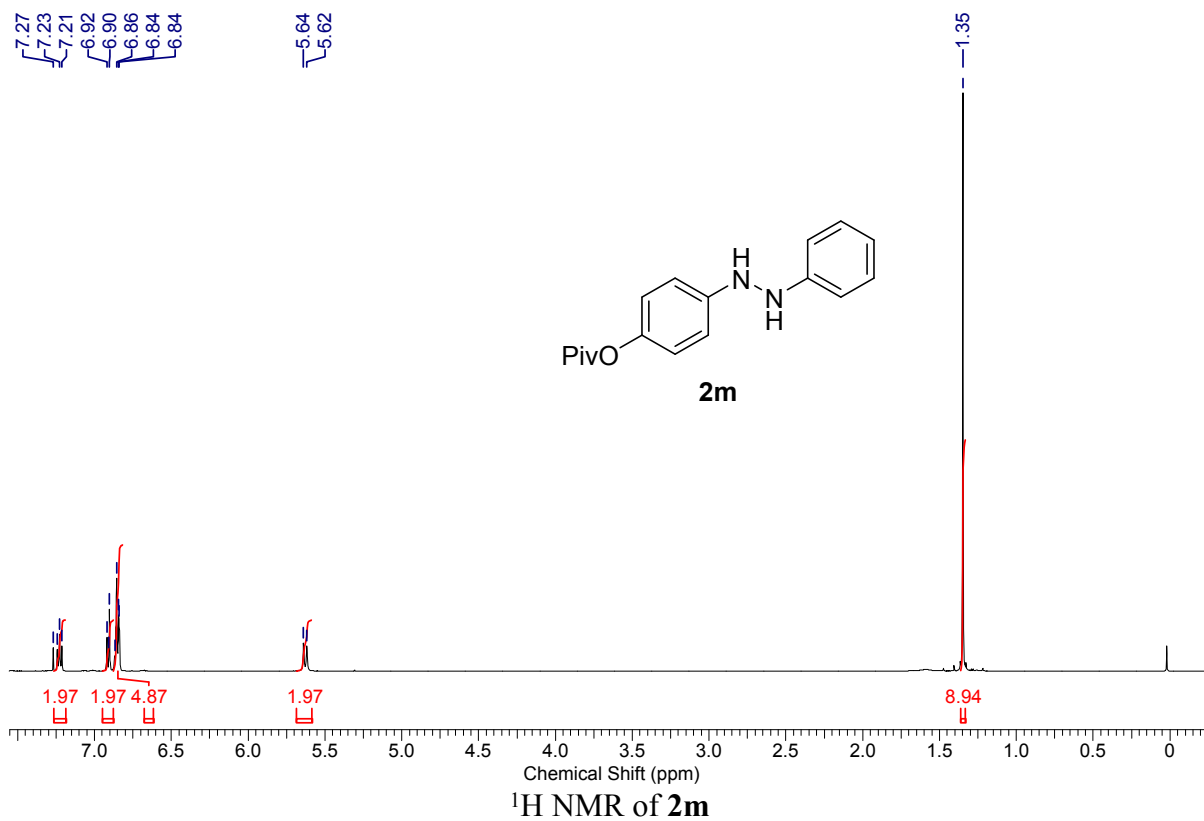




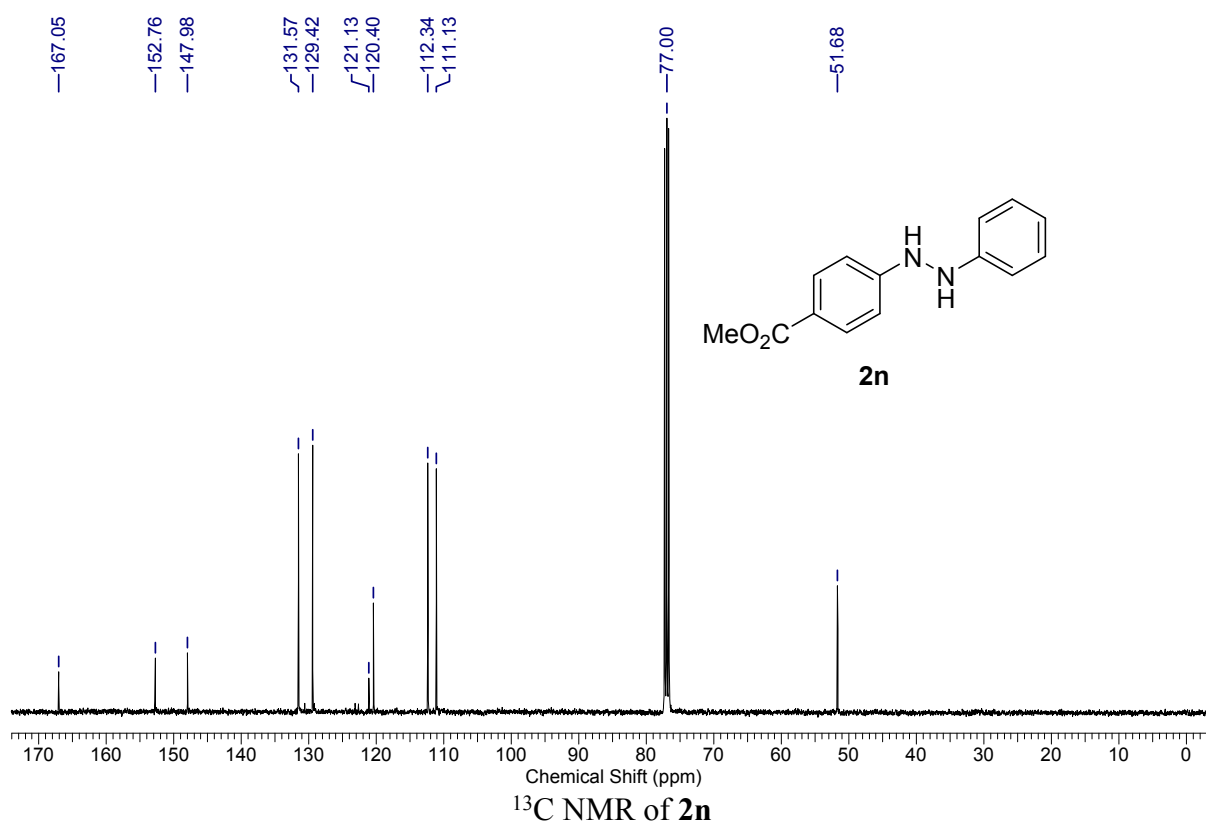
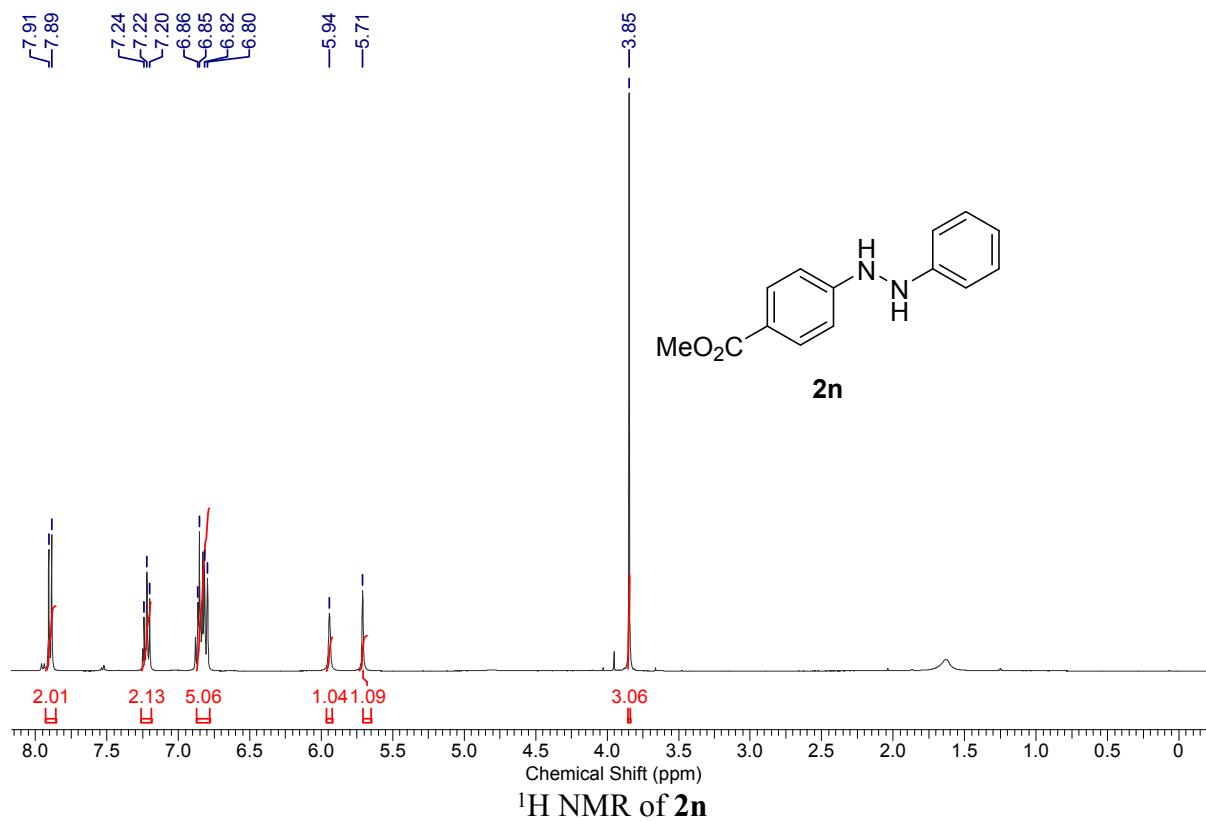


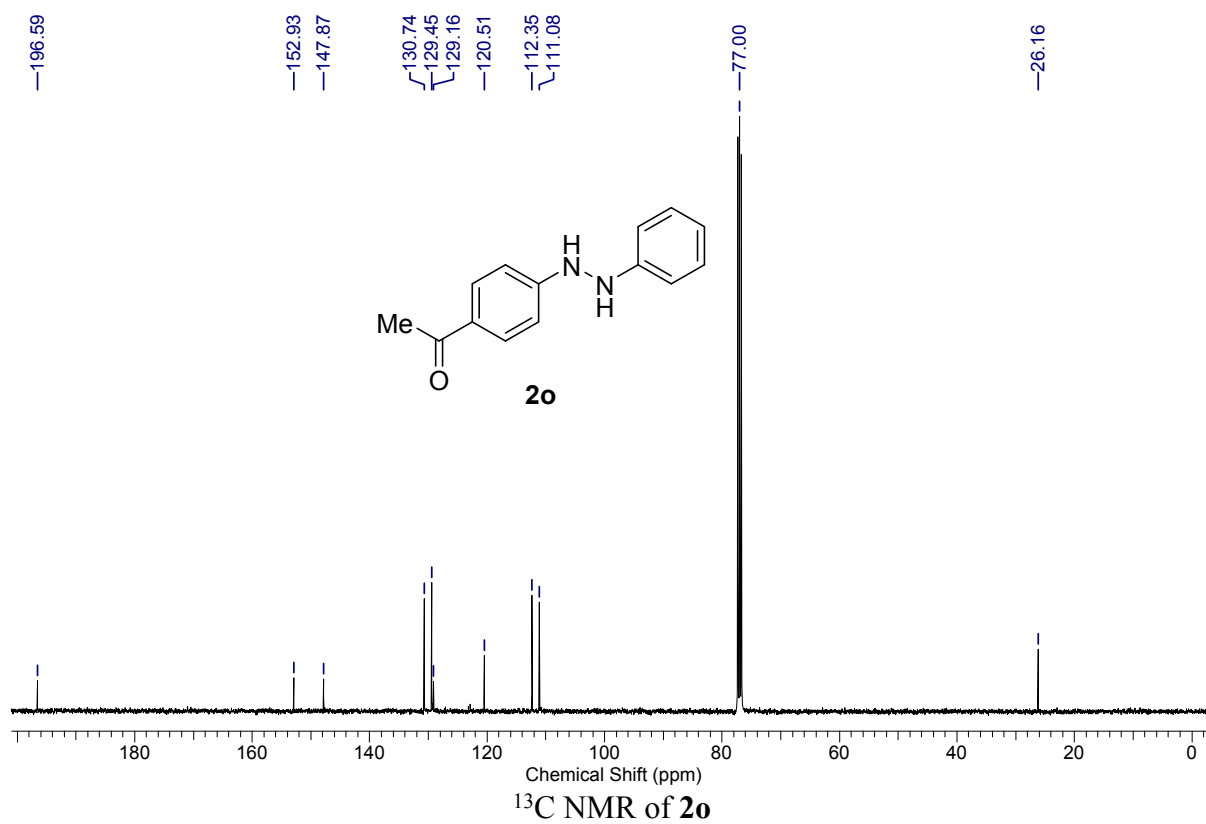
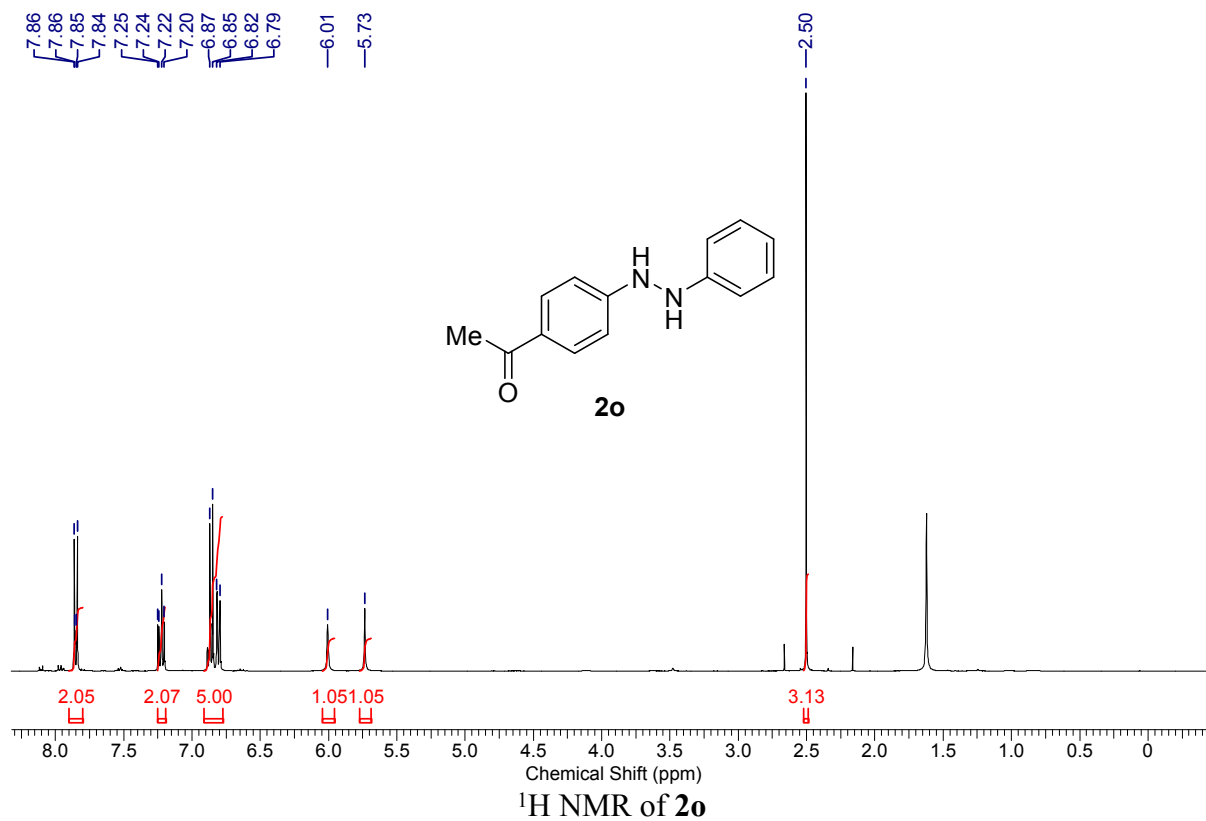


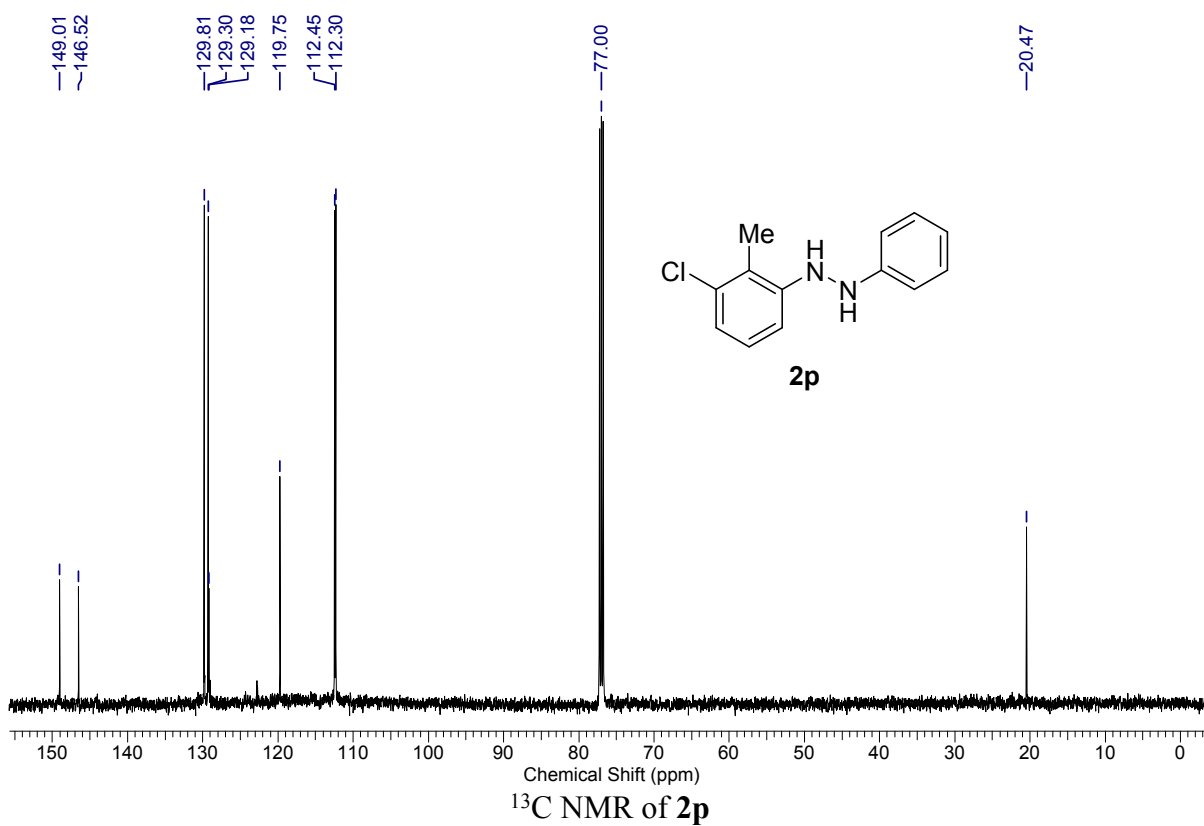
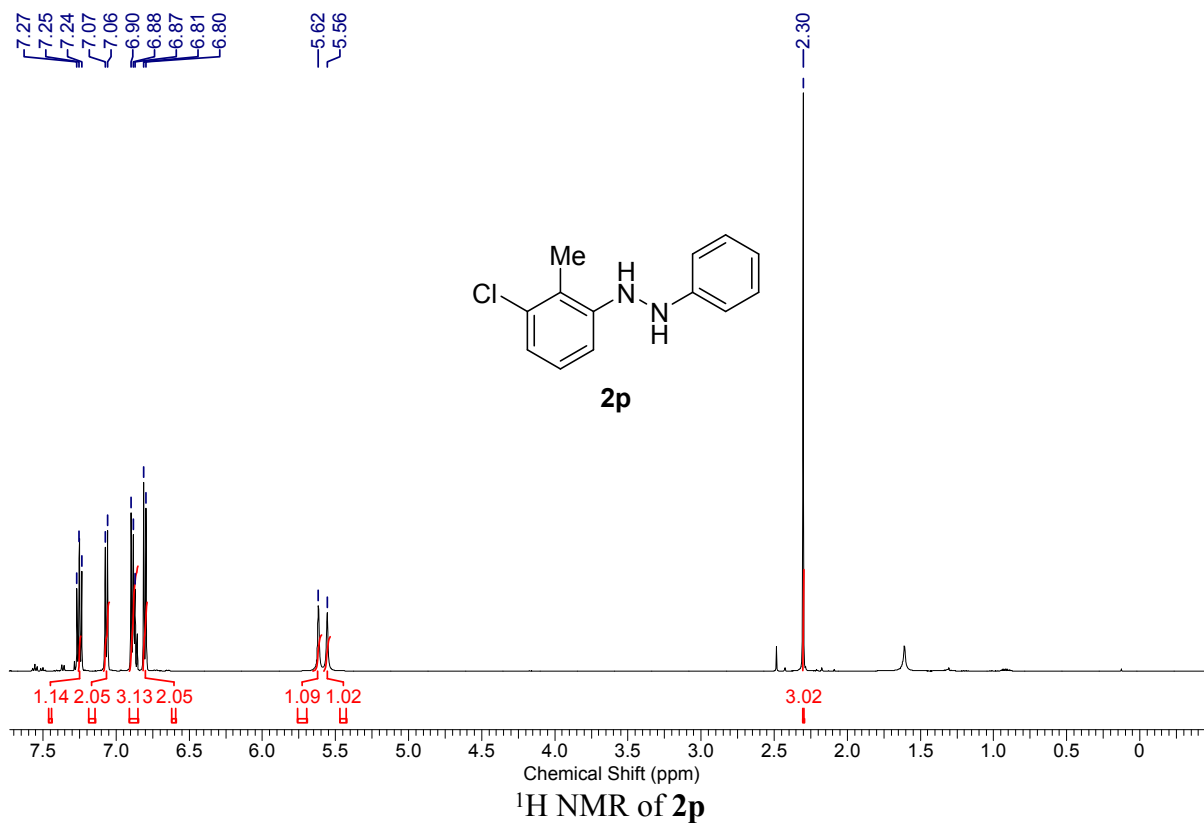


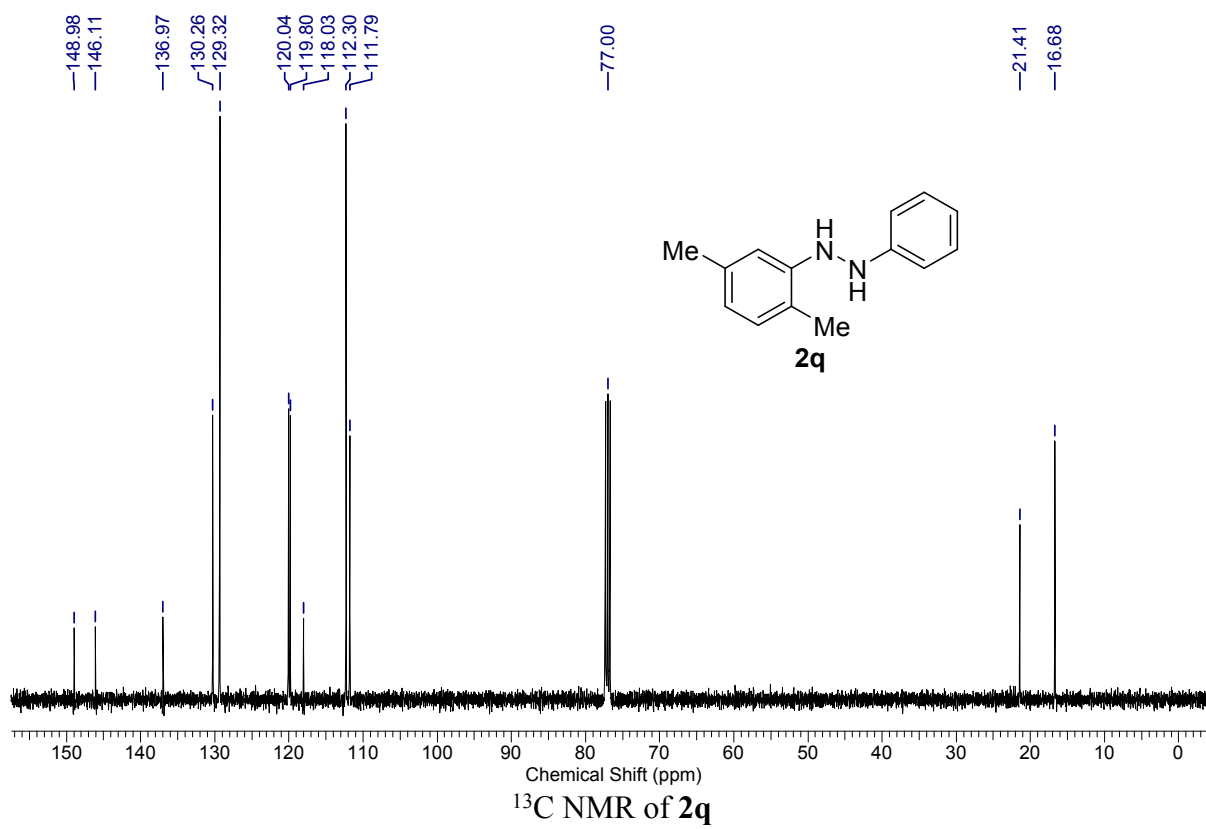
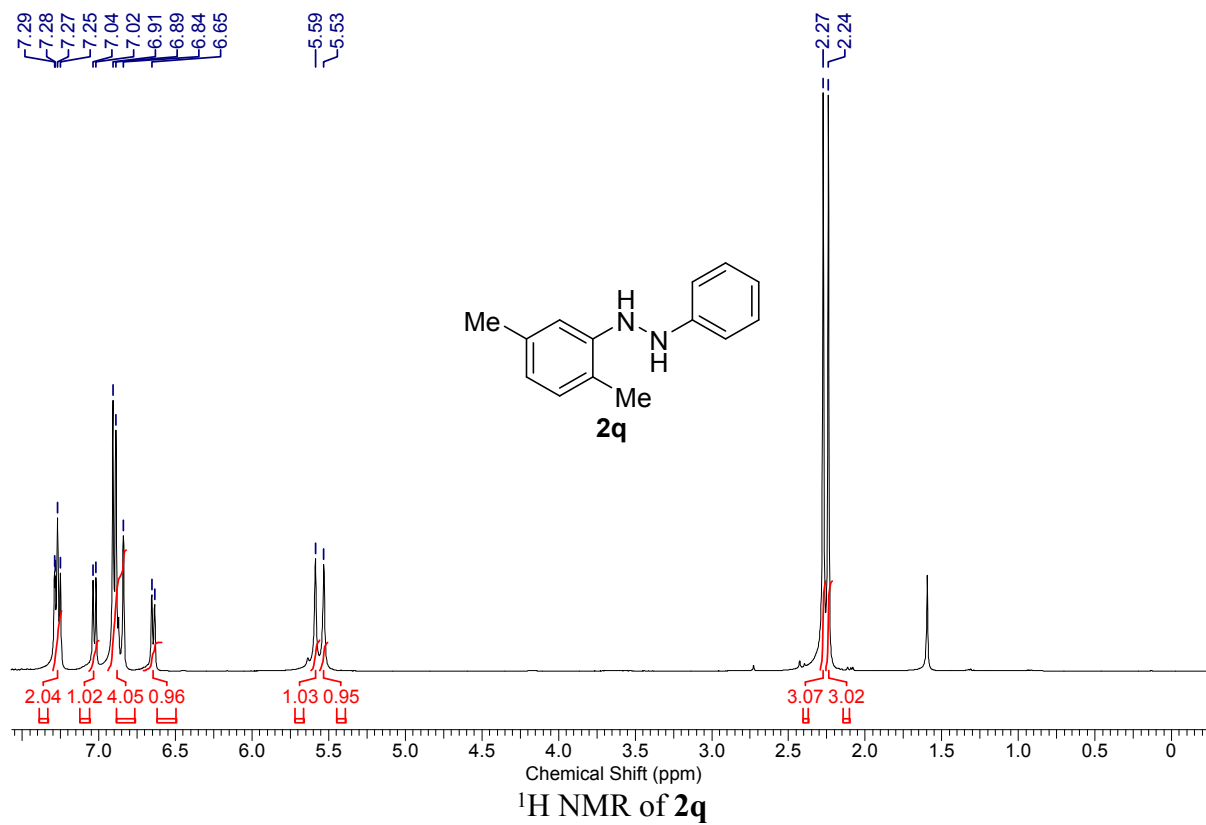


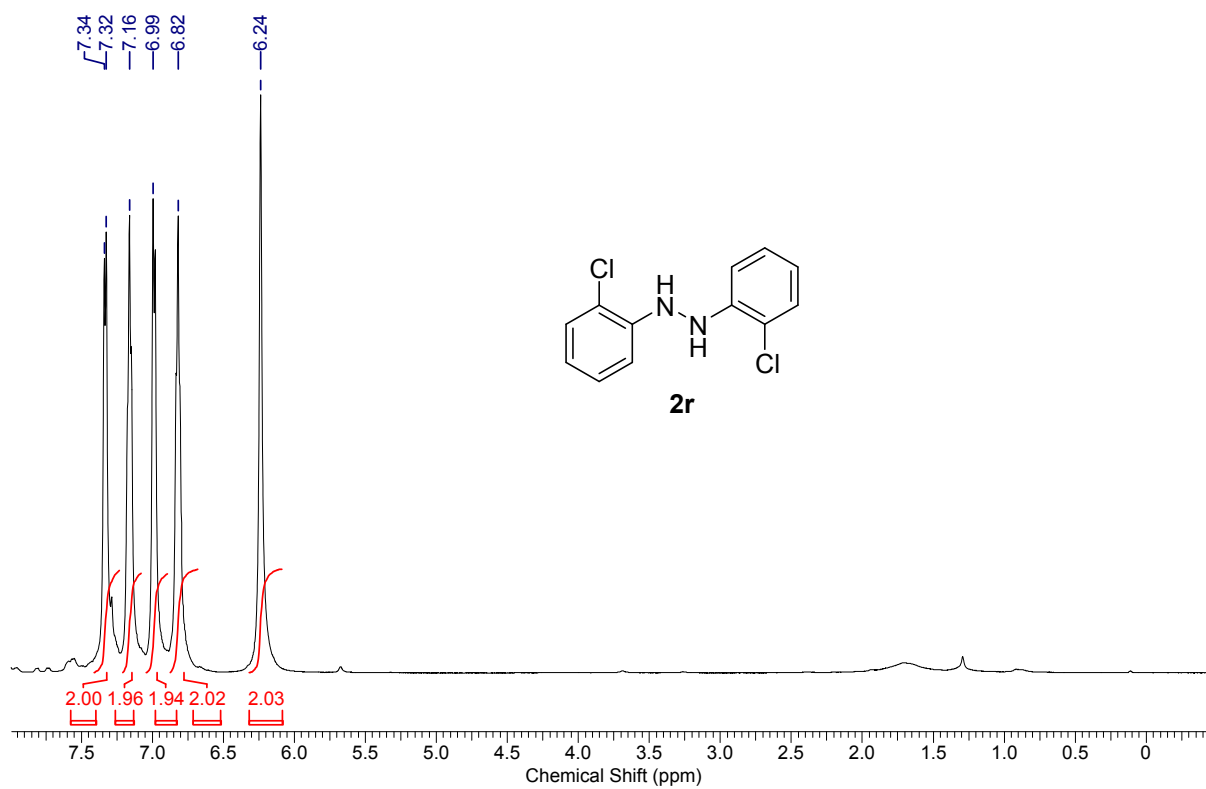




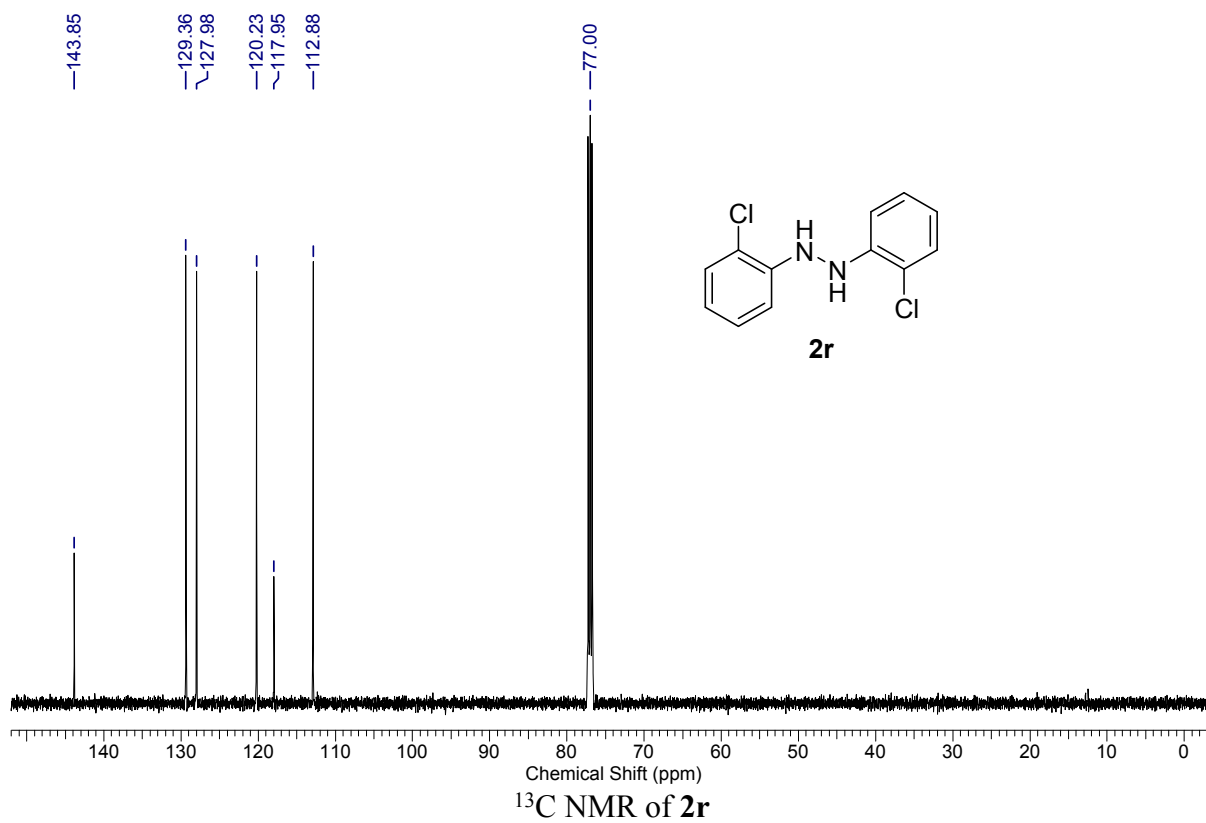


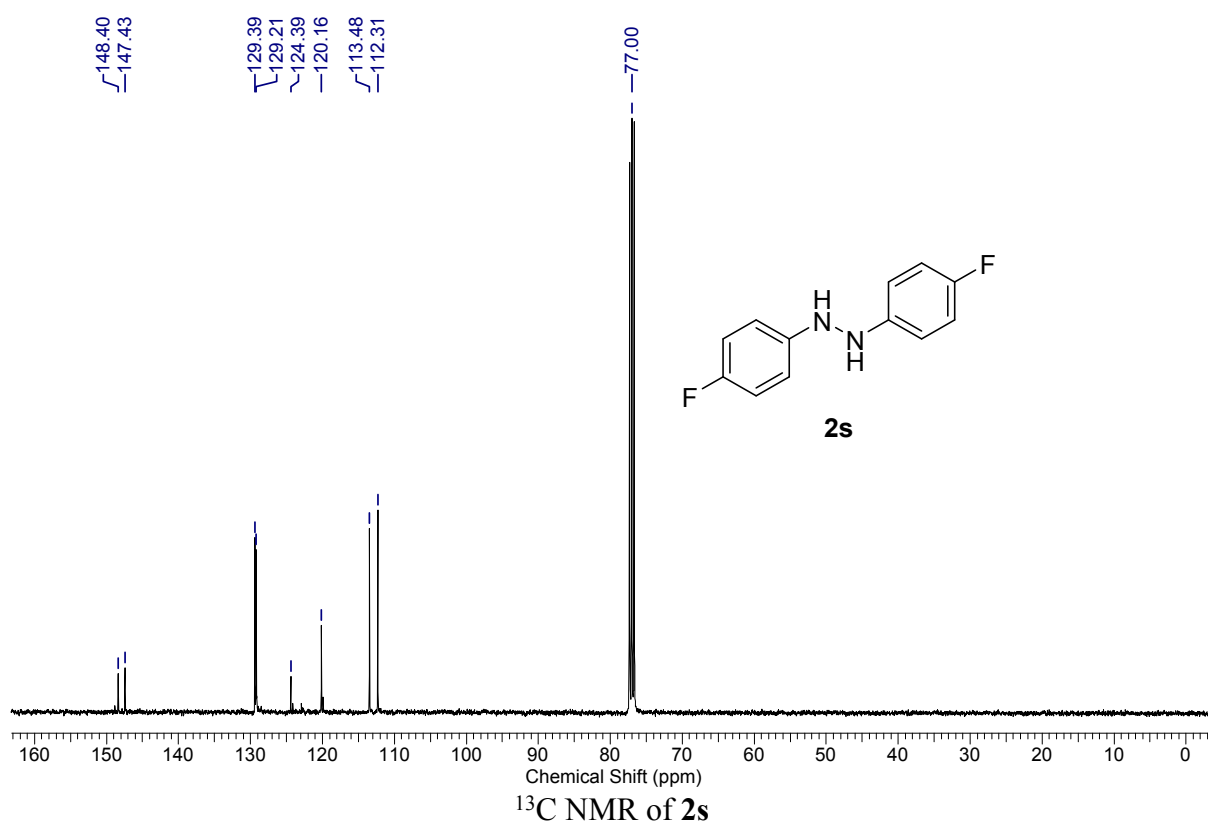
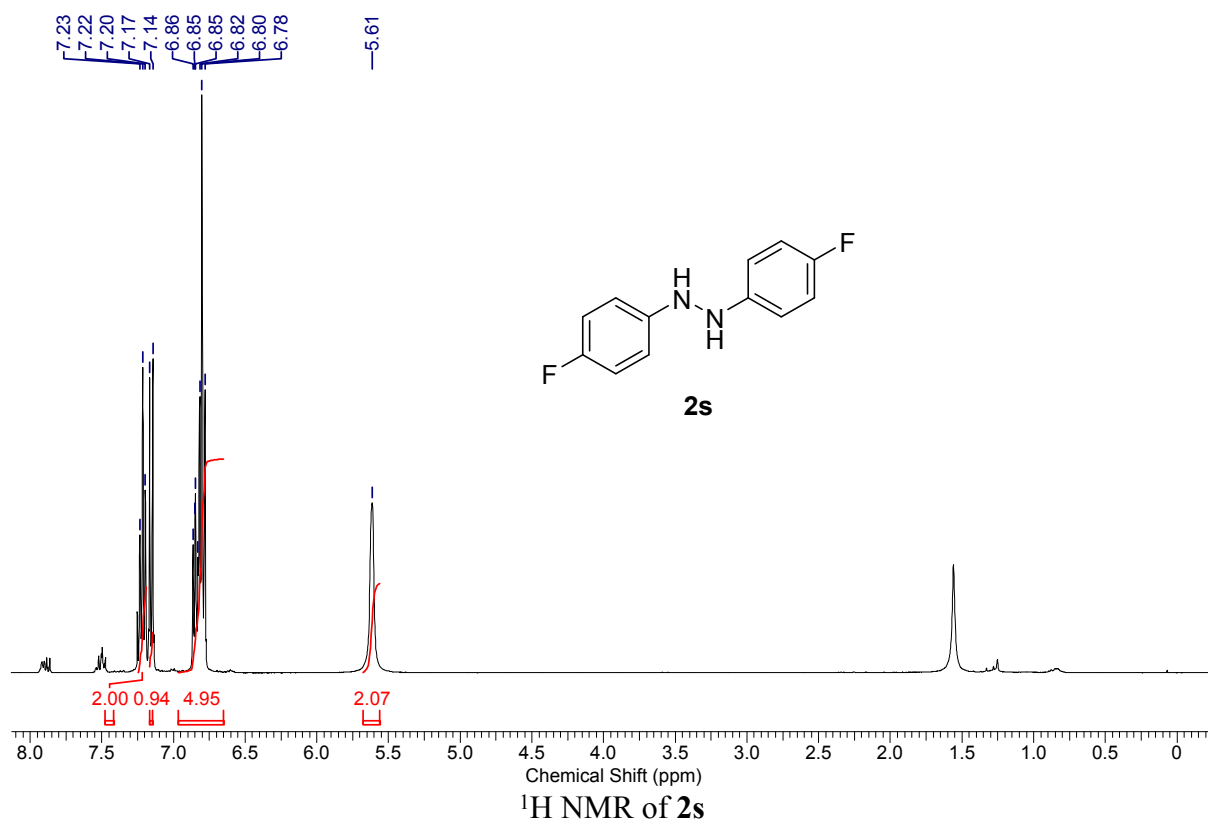


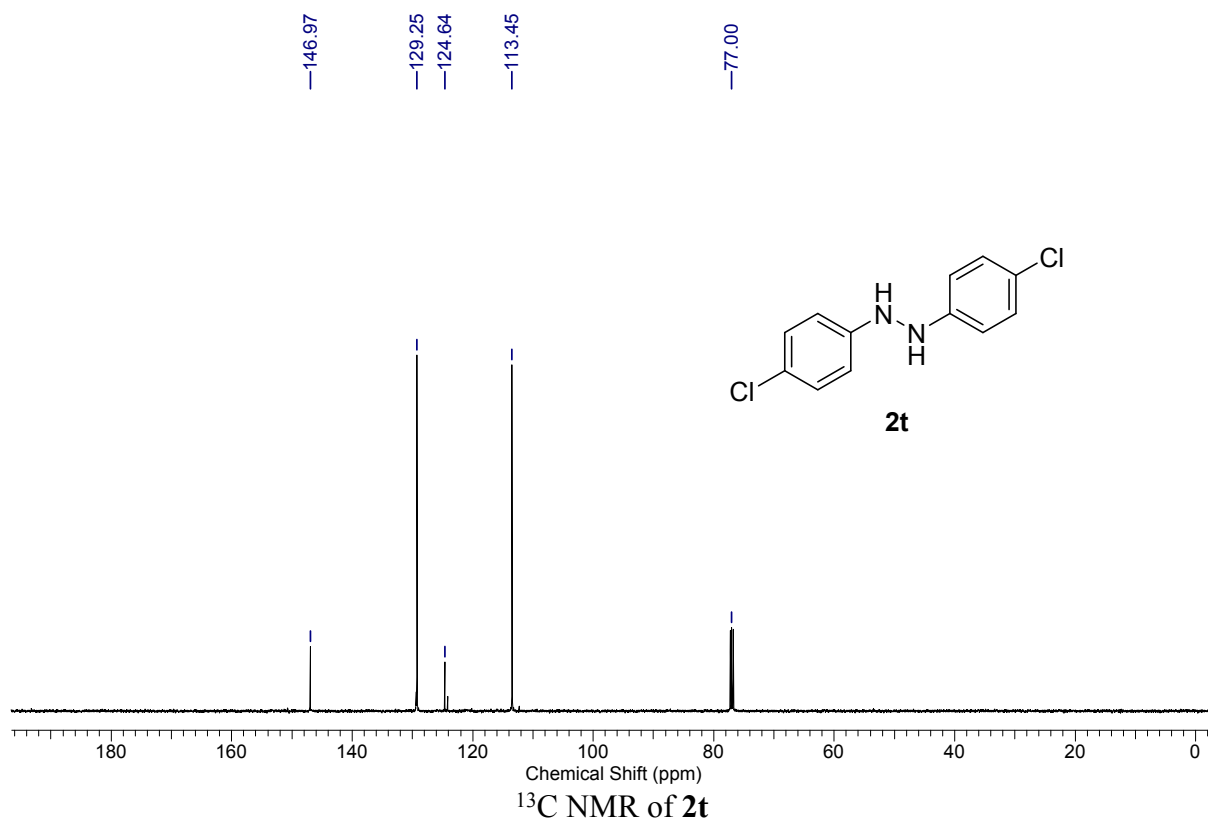
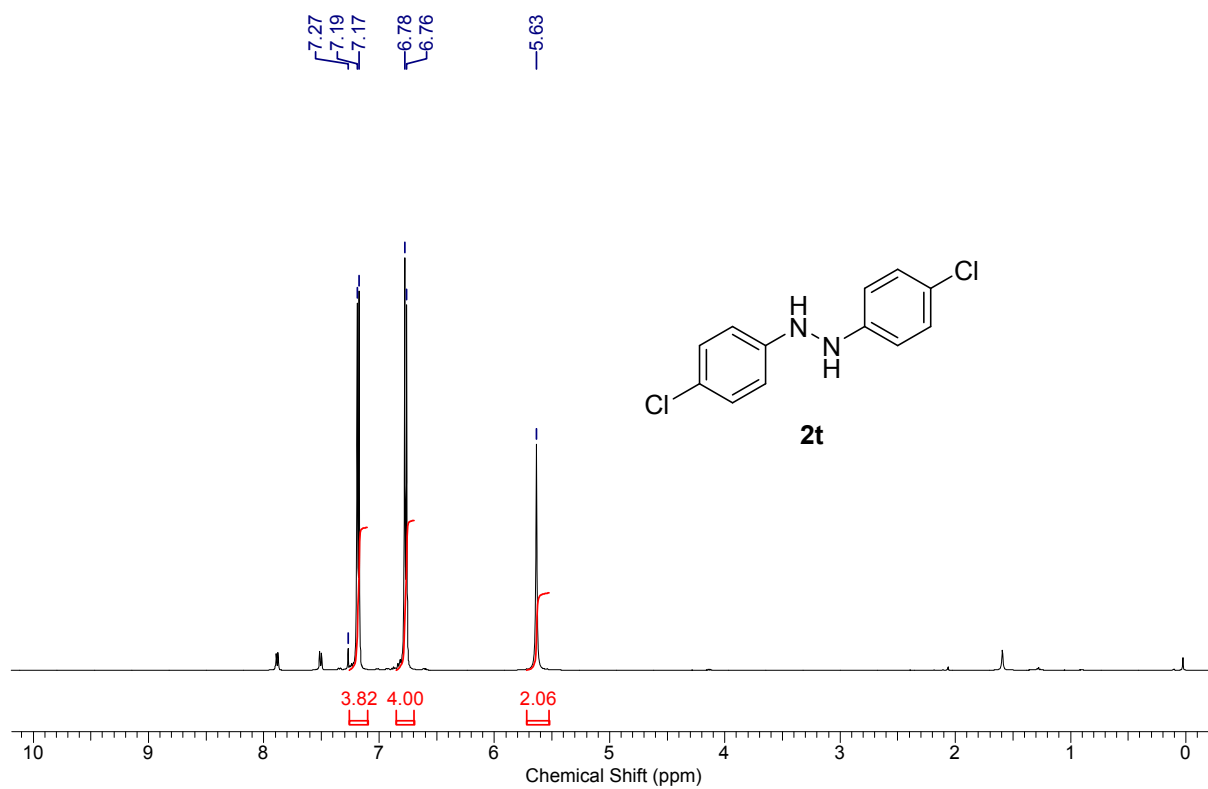


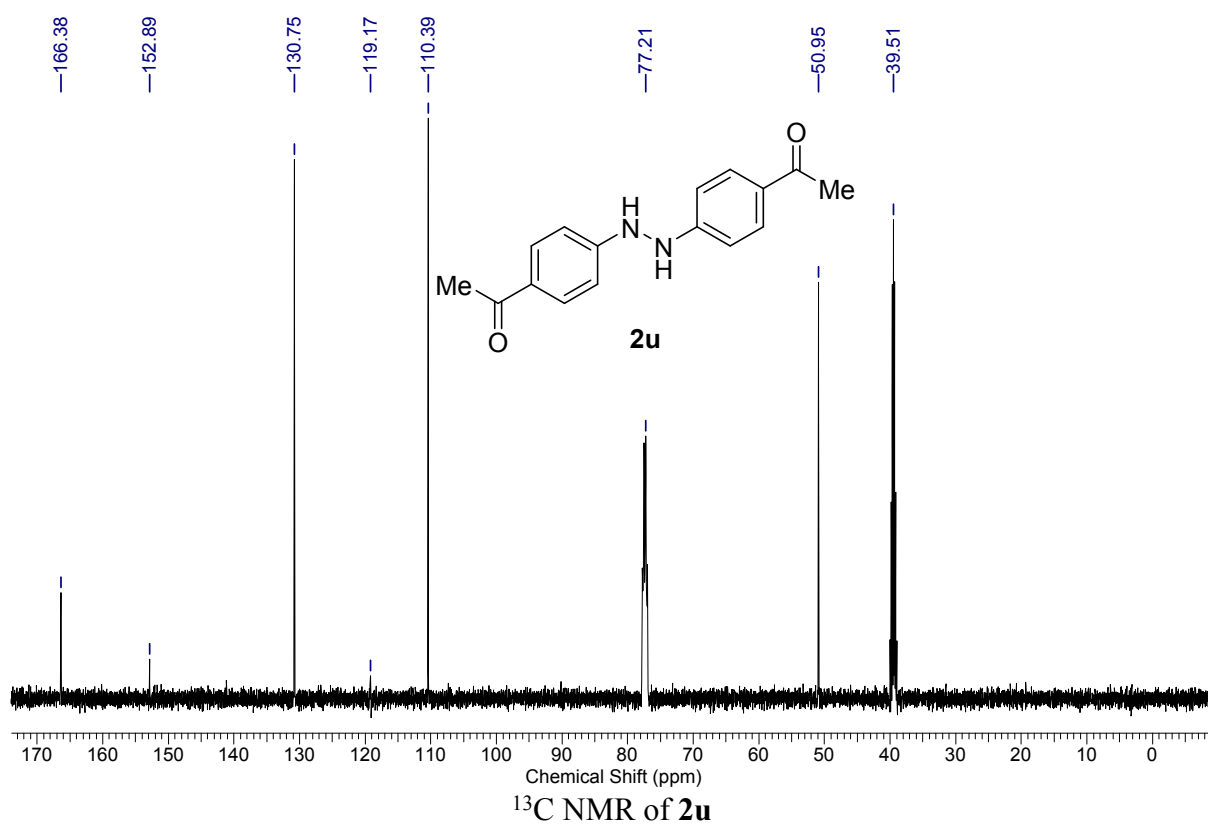
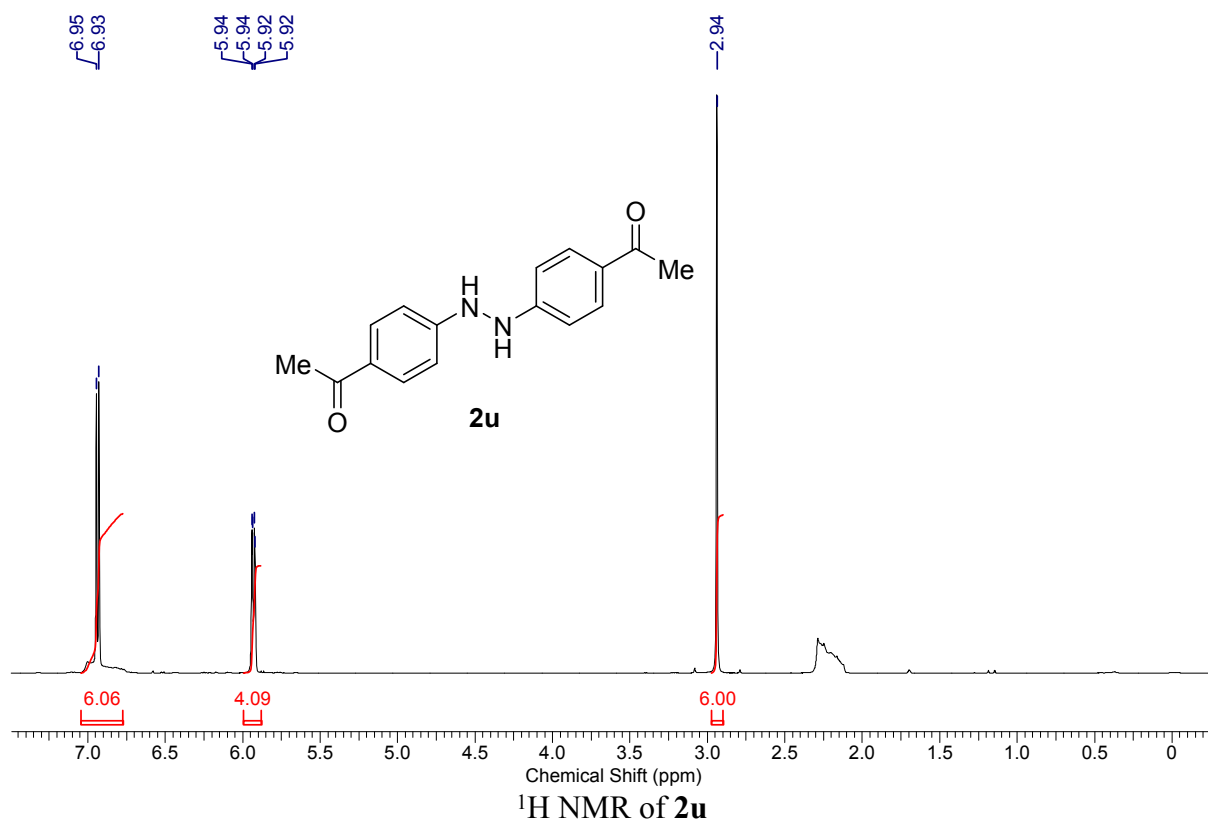


**<sup>1</sup>H NMR of 2r**

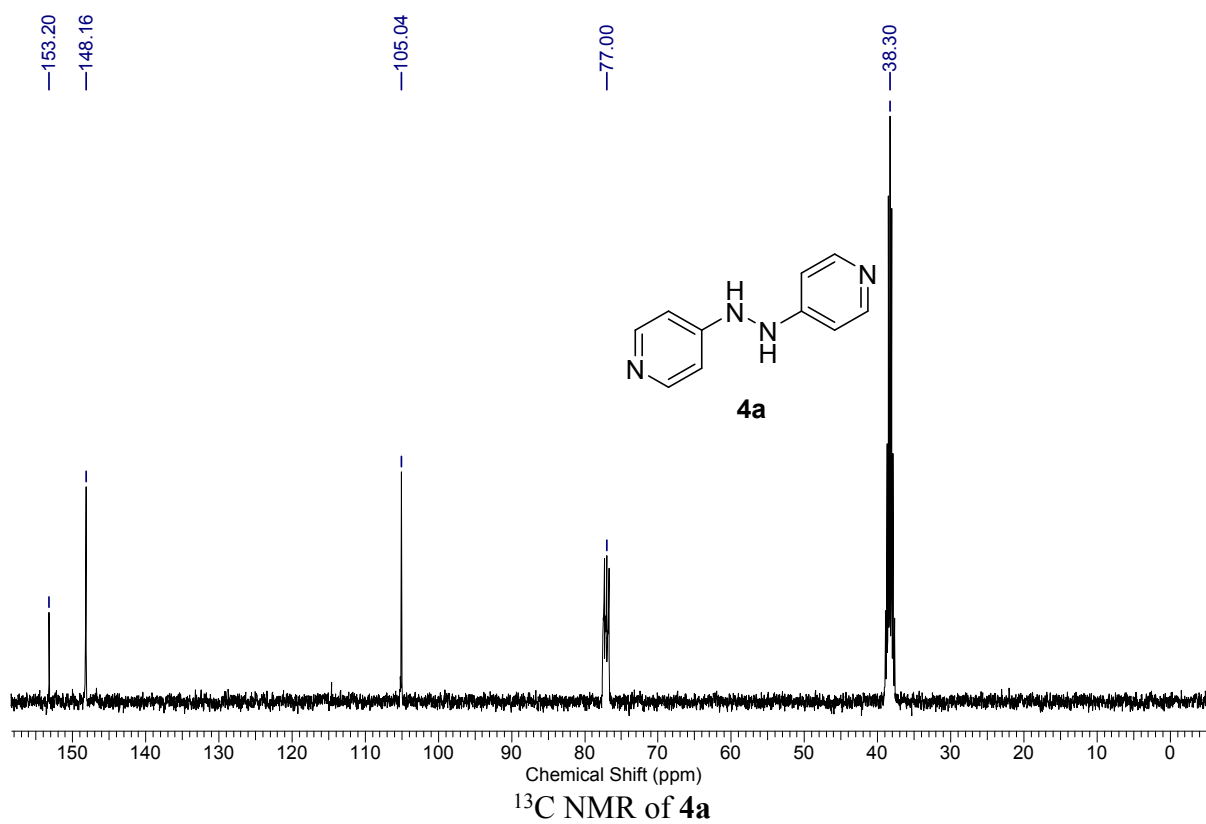
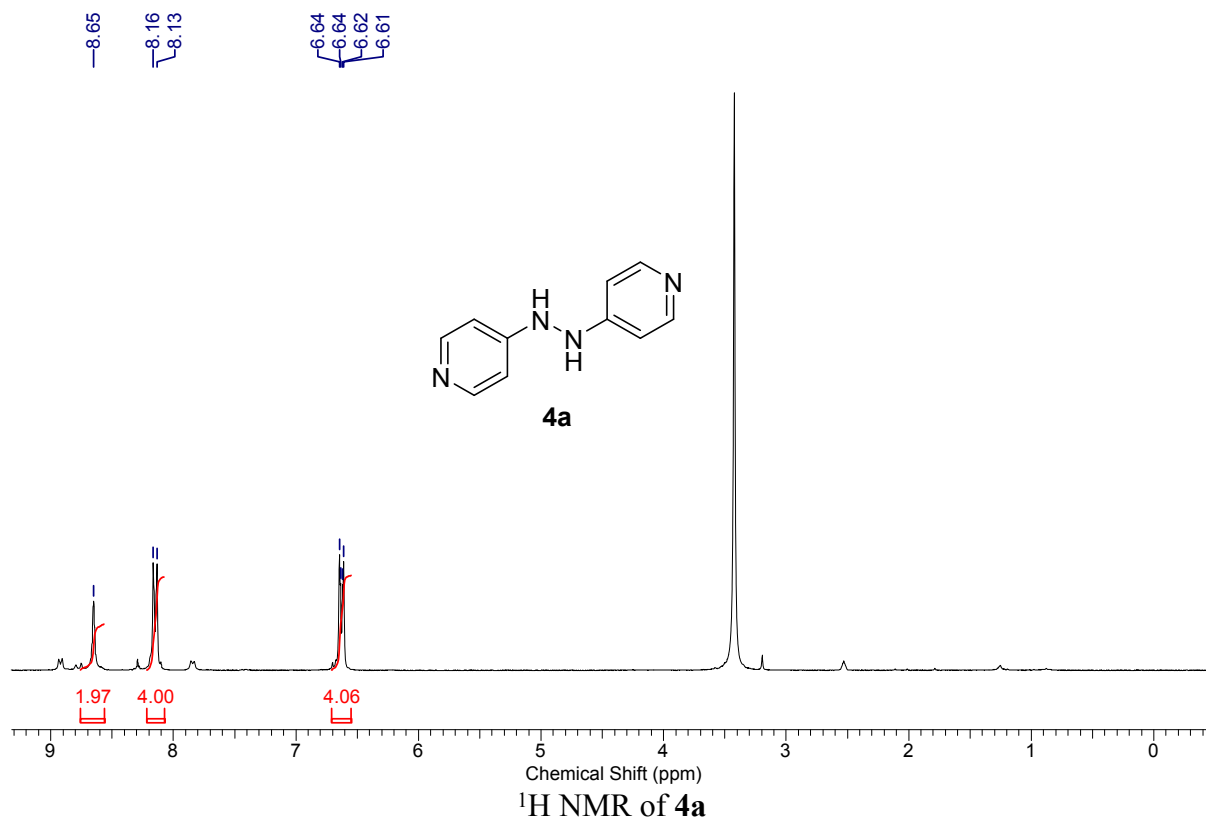


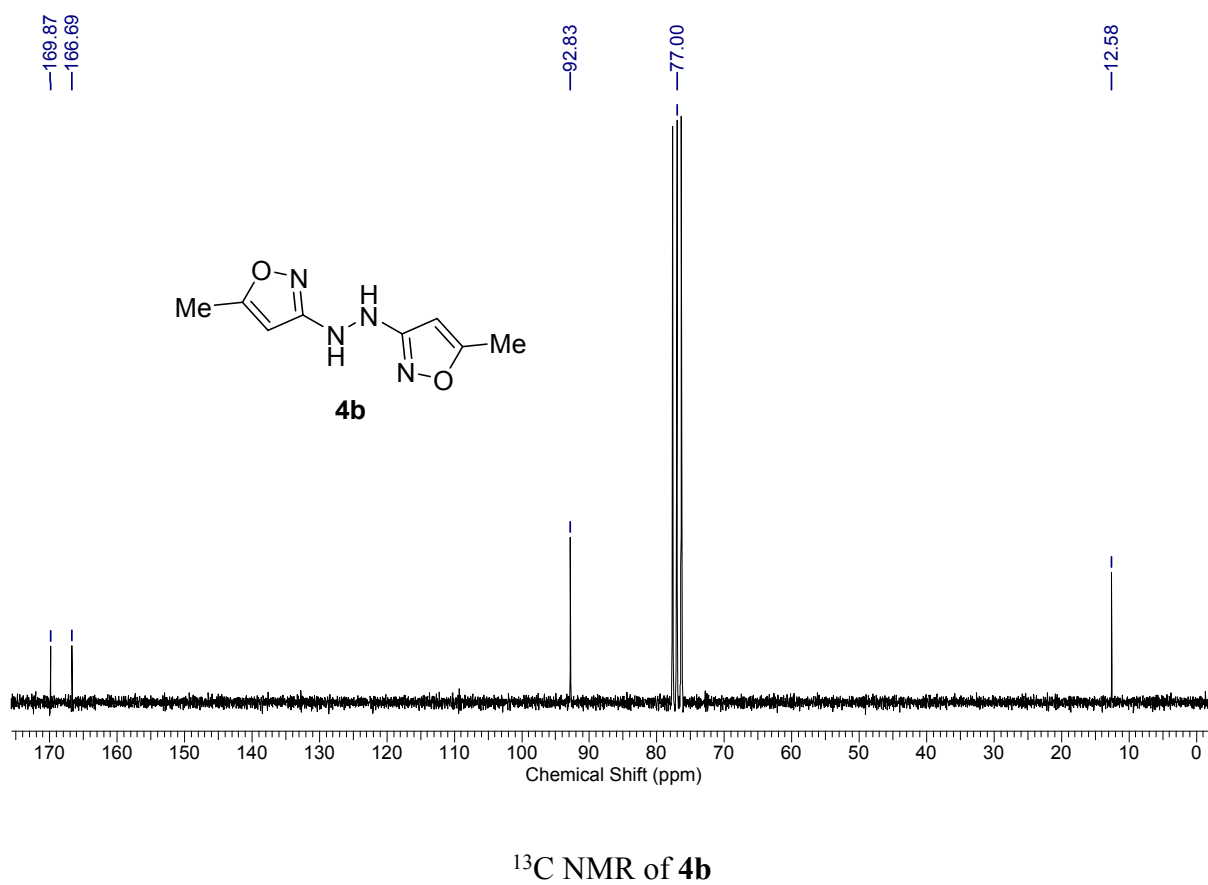
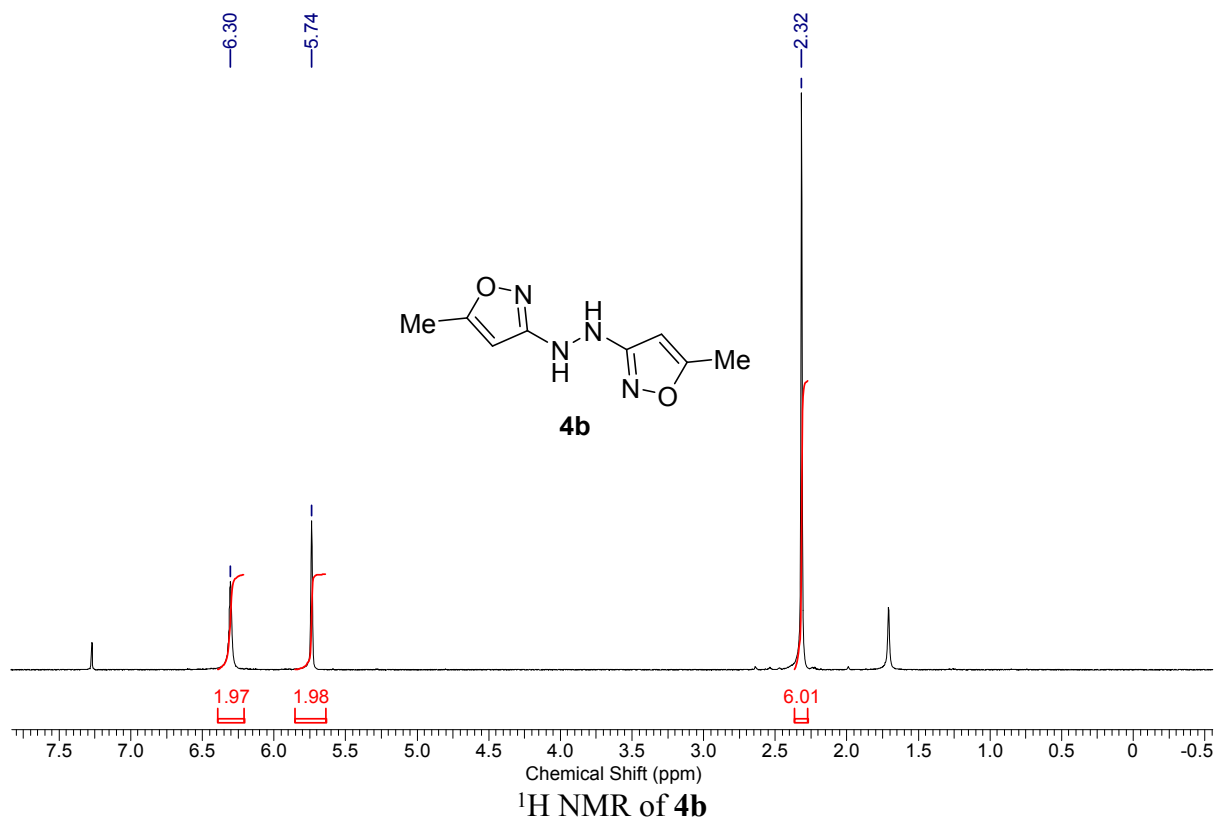






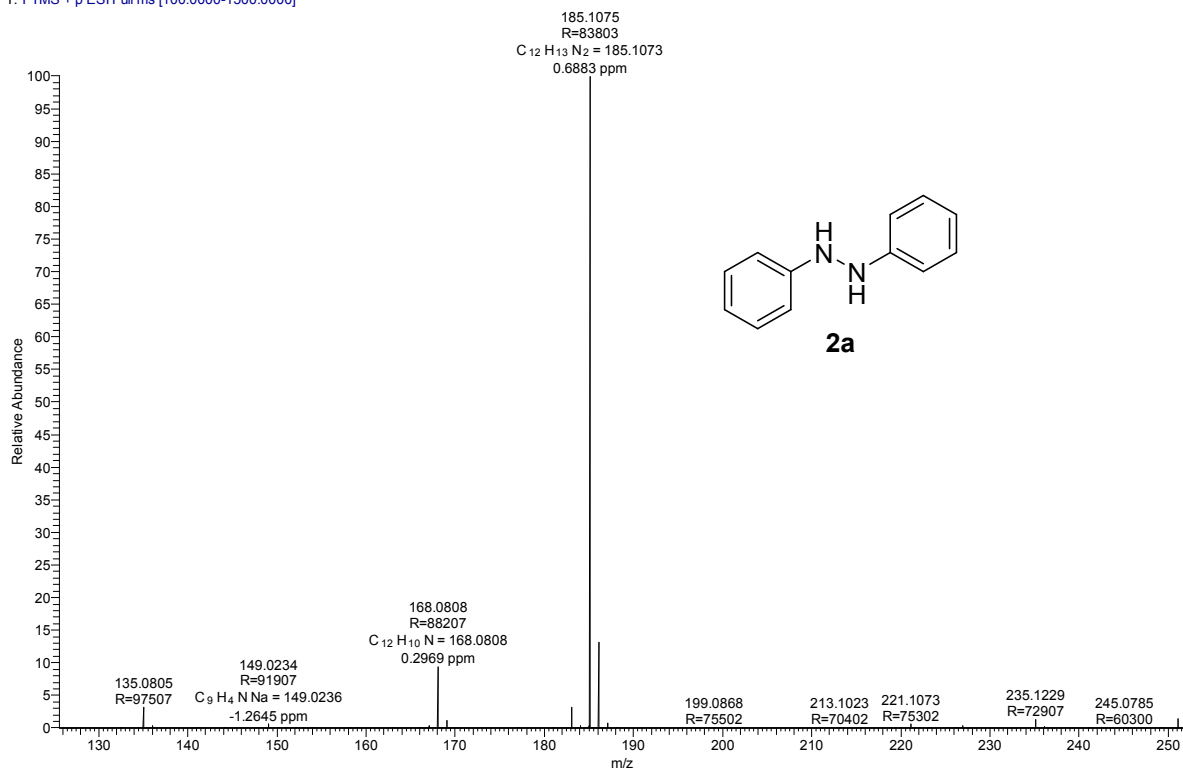






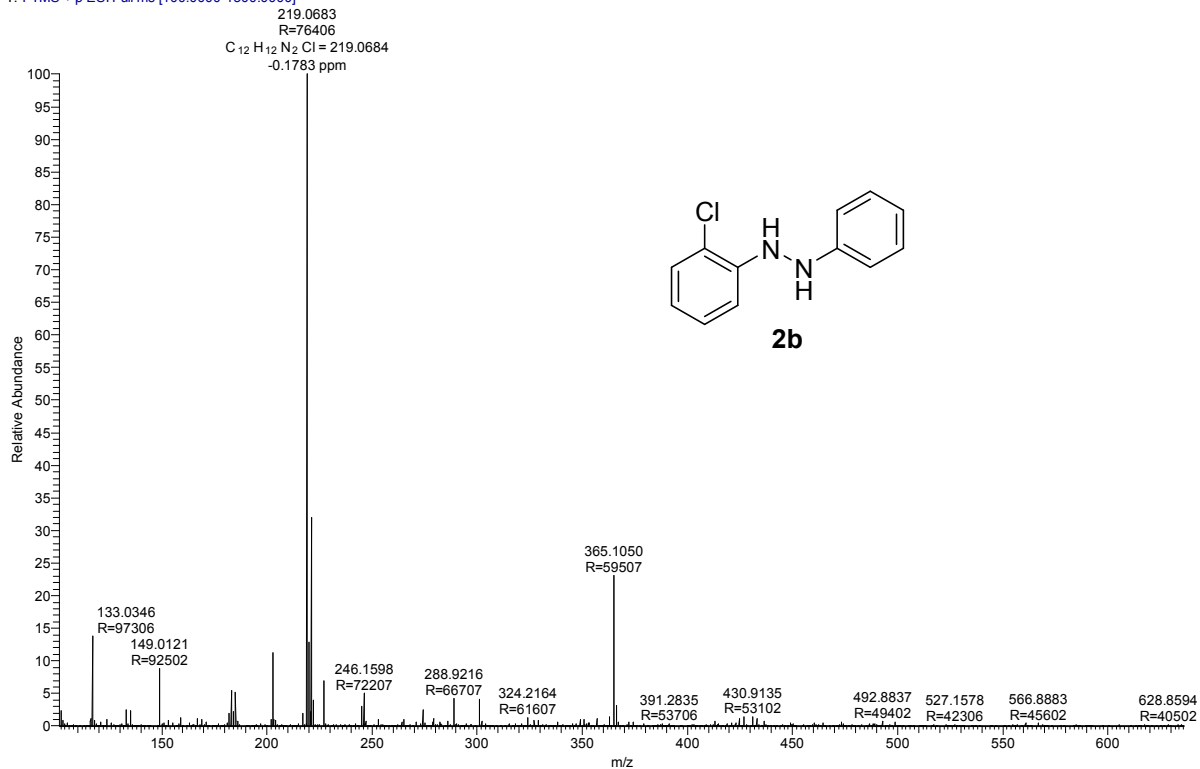
## 5. Copy of HRMS data

SAM-A\_18070516124 #268 RT: 1.19 AV: 1 NL: 6.16E9  
T: FTMS + p ESI Full ms [100.0000-1500.0000]



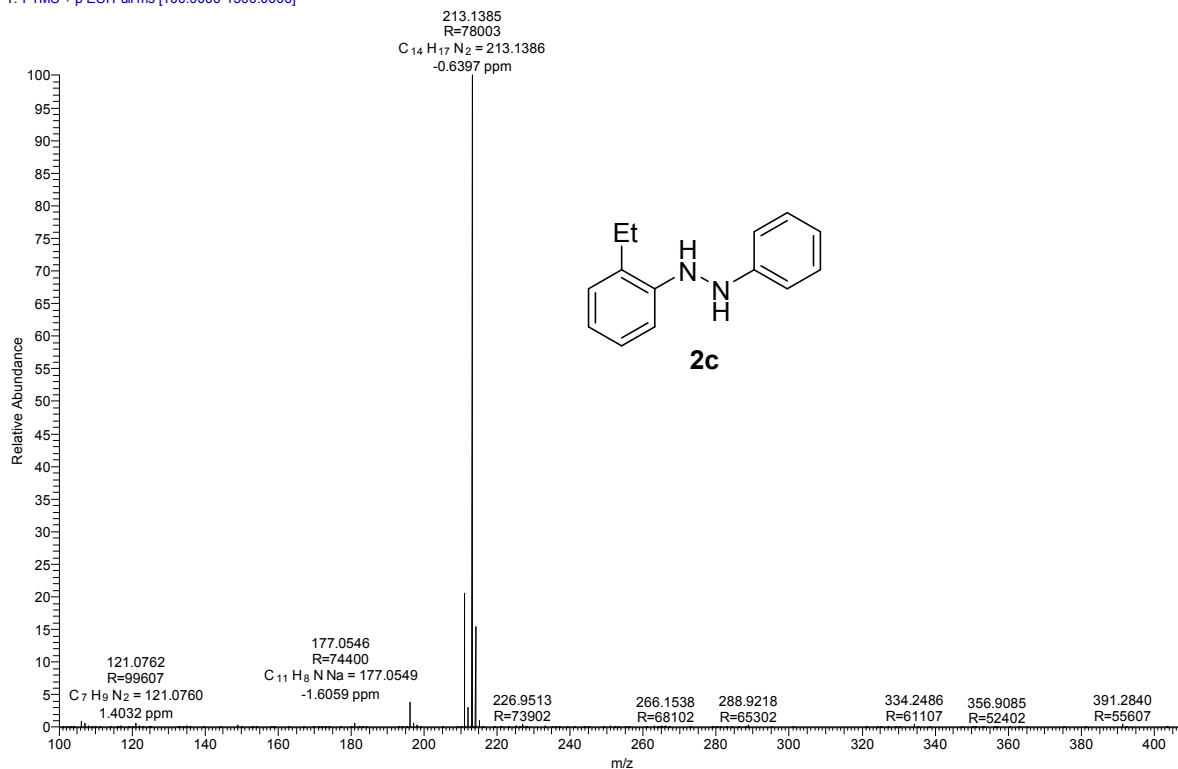
HRMS of **2a**

SS-110-J#286 RT: 1.27 AV: 1 NL: 1.62E8  
T: FTMS + p ESI Full ms [100.0000-1500.0000]



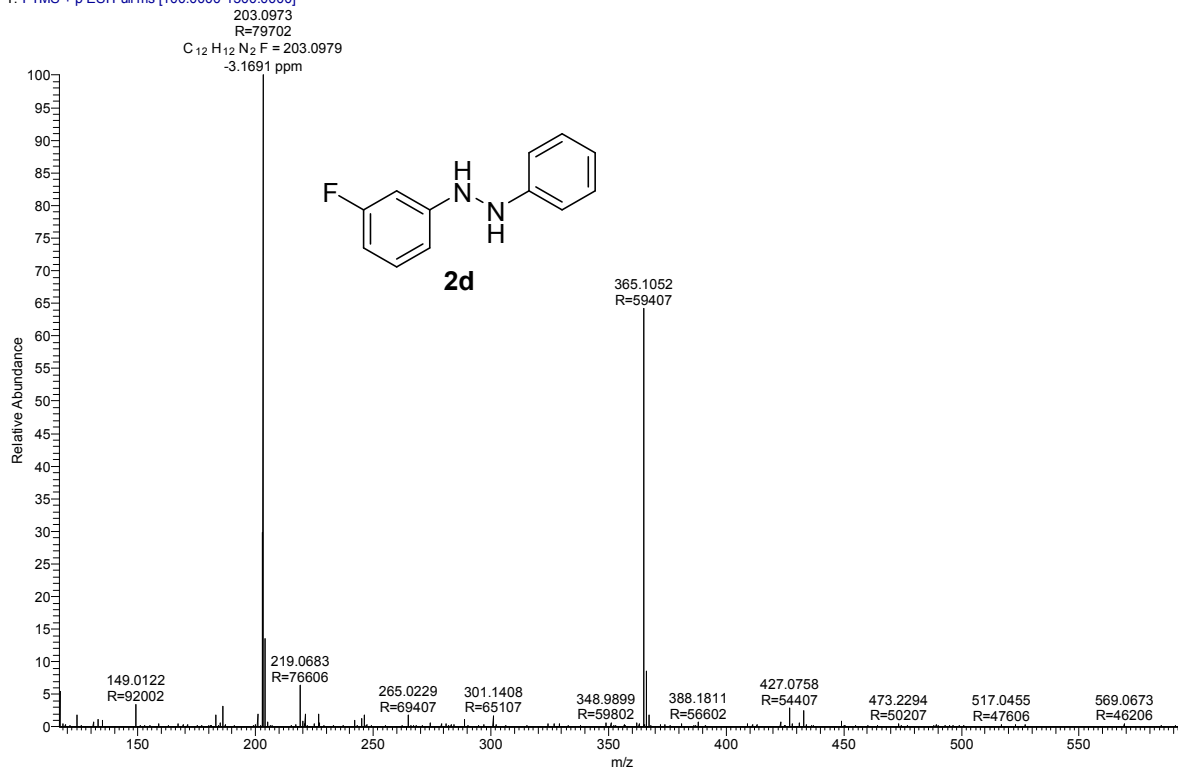
HRMS of **2b**

SAM-J #274 RT: 1.22 AV: 1 NL: 3.33E9  
T: FTMS + p ESI Full ms [100.0000-1500.0000]



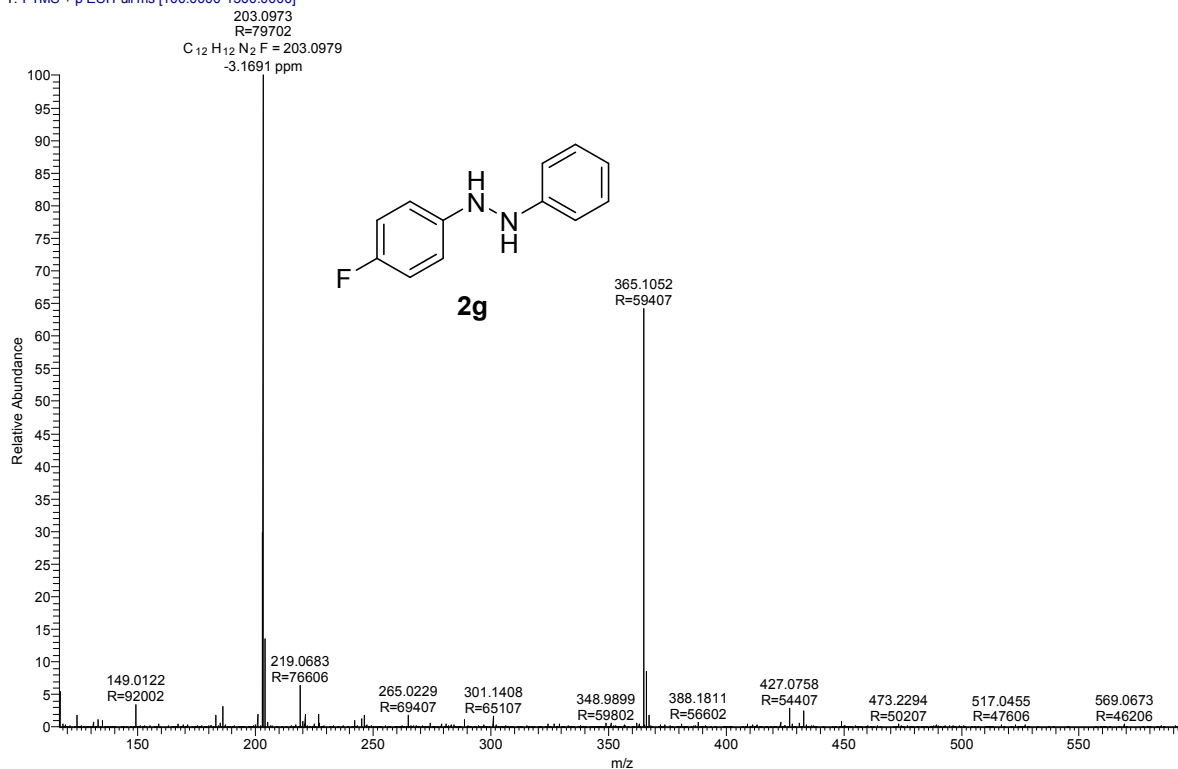
HRMS of **2c**

SS-108-H #272 RT: 1.22 AV: 1 NL: 3.88E8  
T: FTMS + p ESI Full ms [100.0000-1500.0000]



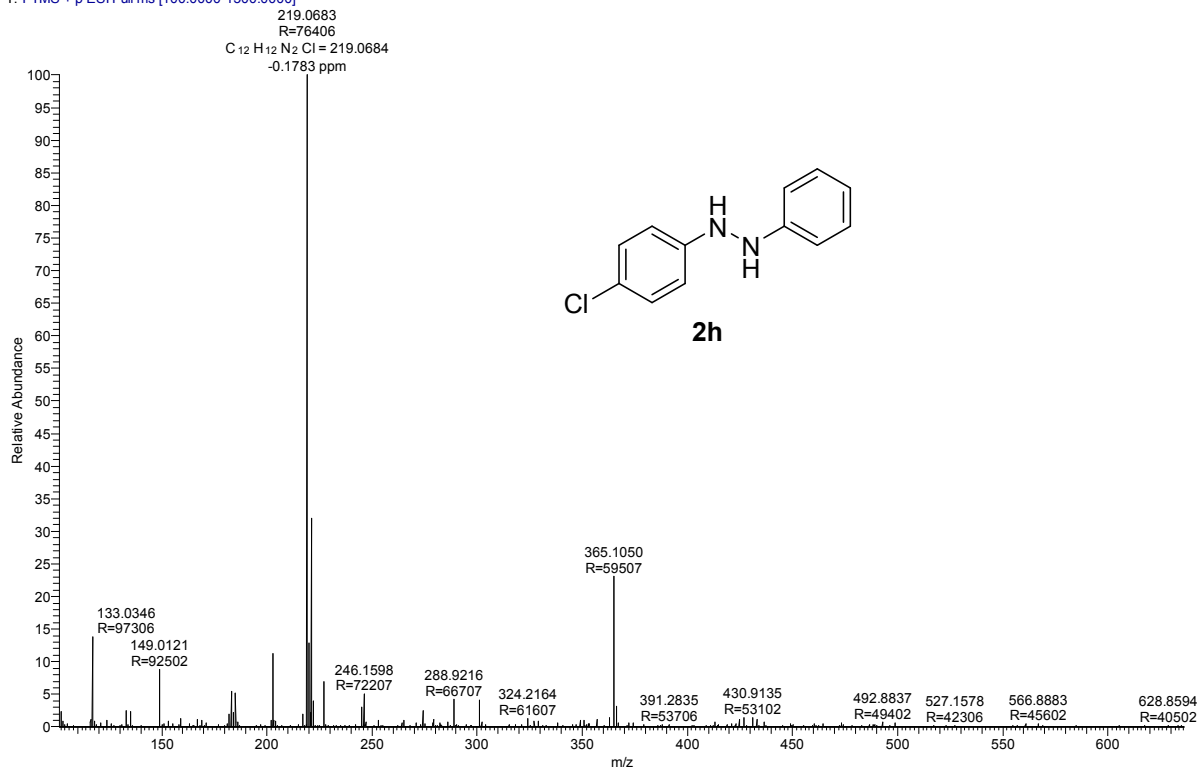
HRMS of **2d**

SS-108-H#272 RT: 1.22 AV: 1 NL: 3.88E8  
T: FTMS + p ESI Full ms [100.0000-1500.0000]



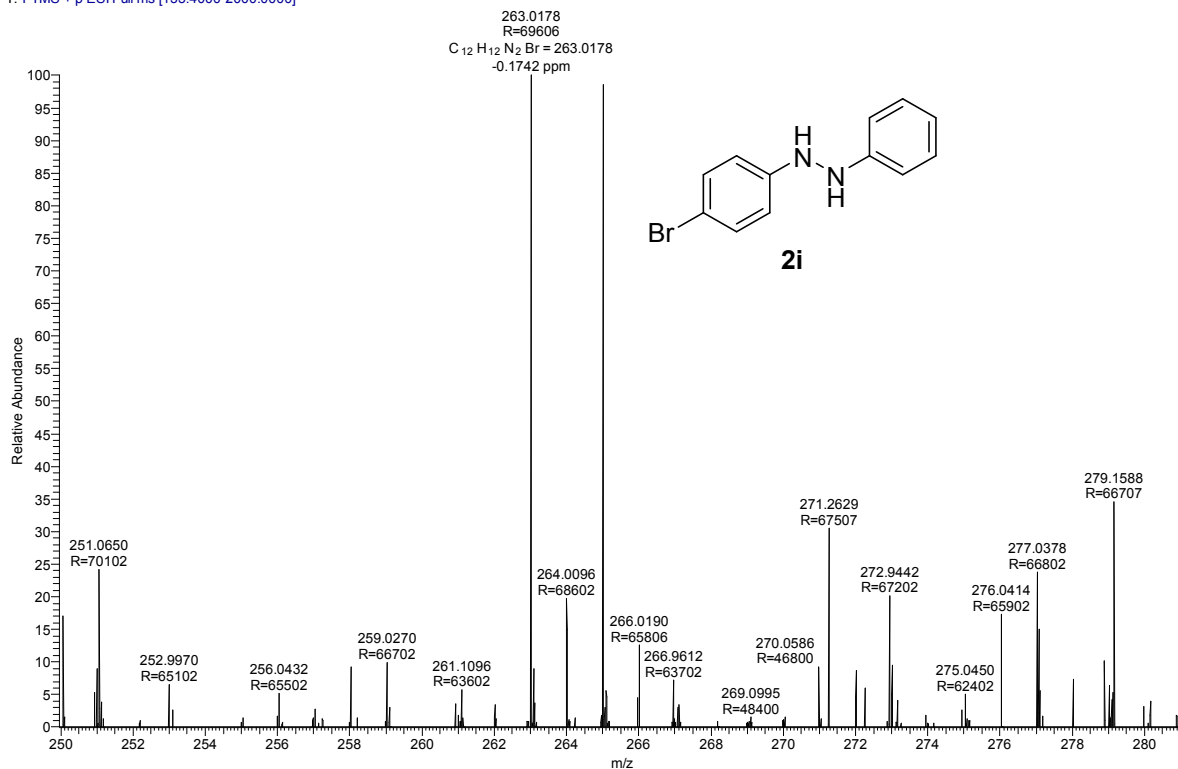
HRMS of 2g

SS-110-J#286 RT: 1.27 AV: 1 NL: 1.62E8  
T: FTMS + p ESI Full ms [100.0000-1500.0000]



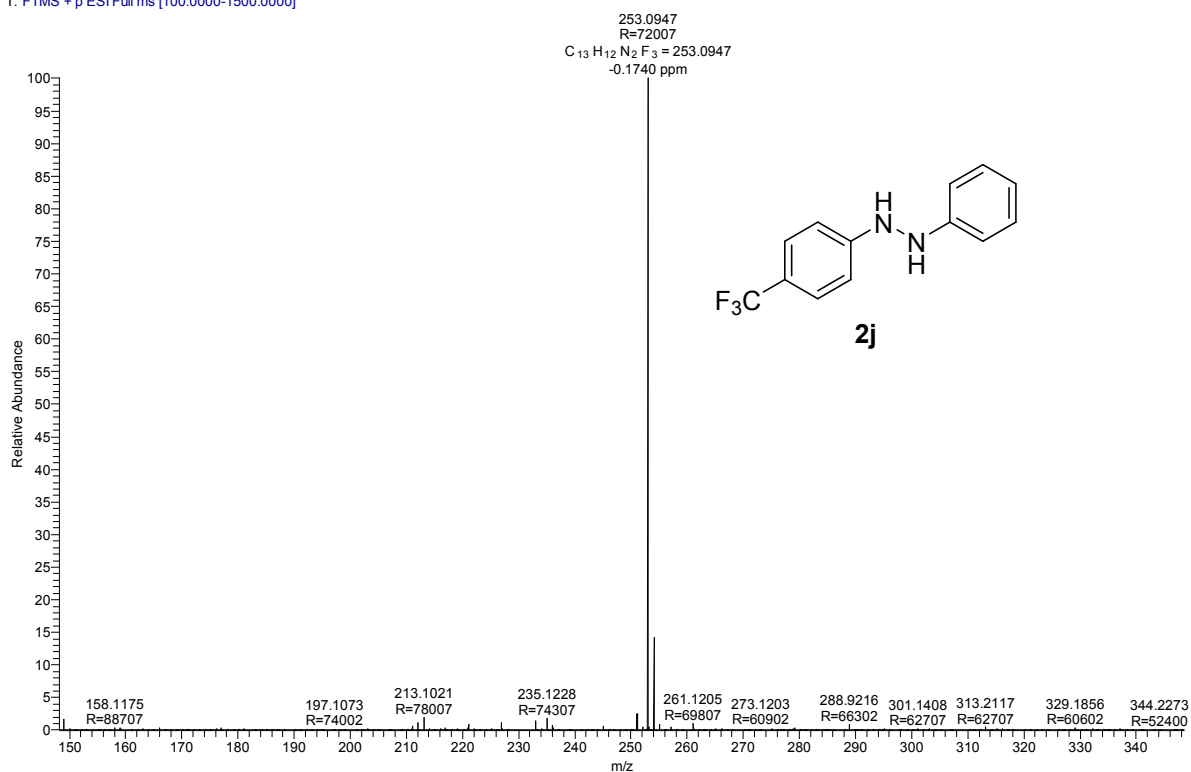
HRMS of 2h

SS-202 #268 RT: 1.20 AV: 1 NL: 6.55E5  
T: FTMS + p ESI Full ms [133.4000-2000.0000]



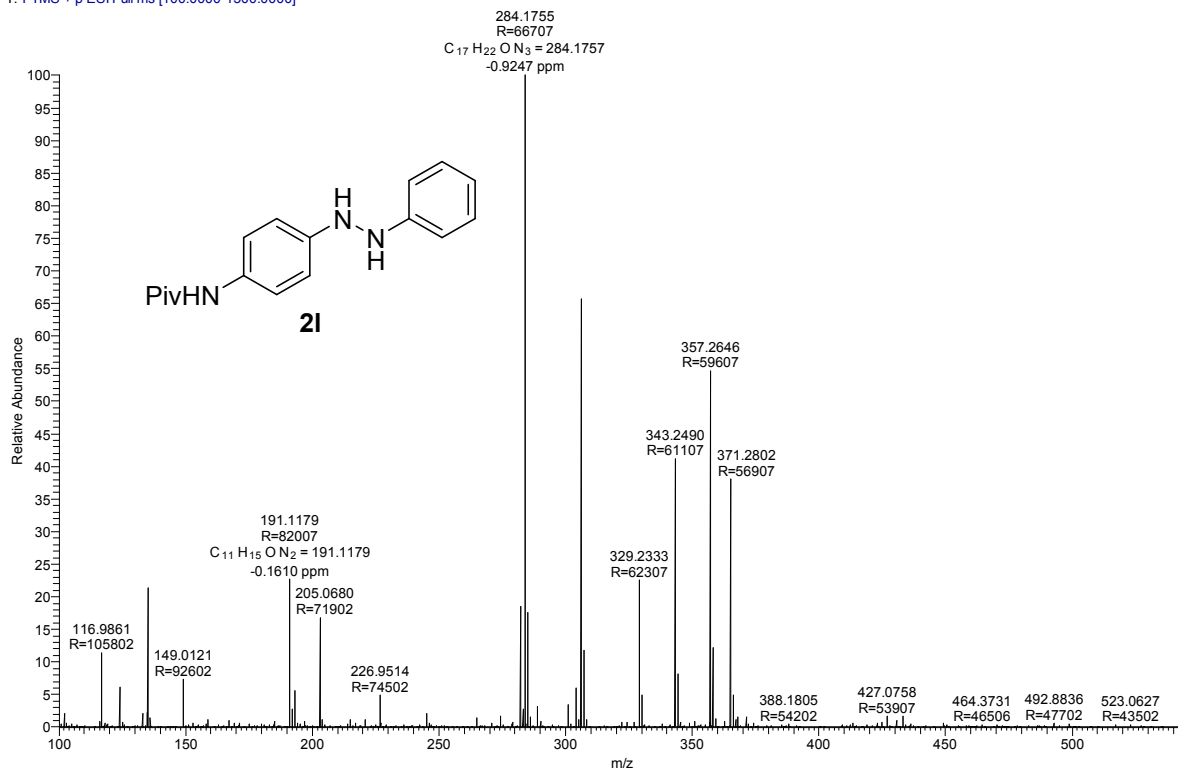
HRMS of **2i**

SAM-I #263 RT: 1.17 AV: 1 NL: 1.00E9  
T: FTMS + p ESI Full ms [100.0000-1500.0000]



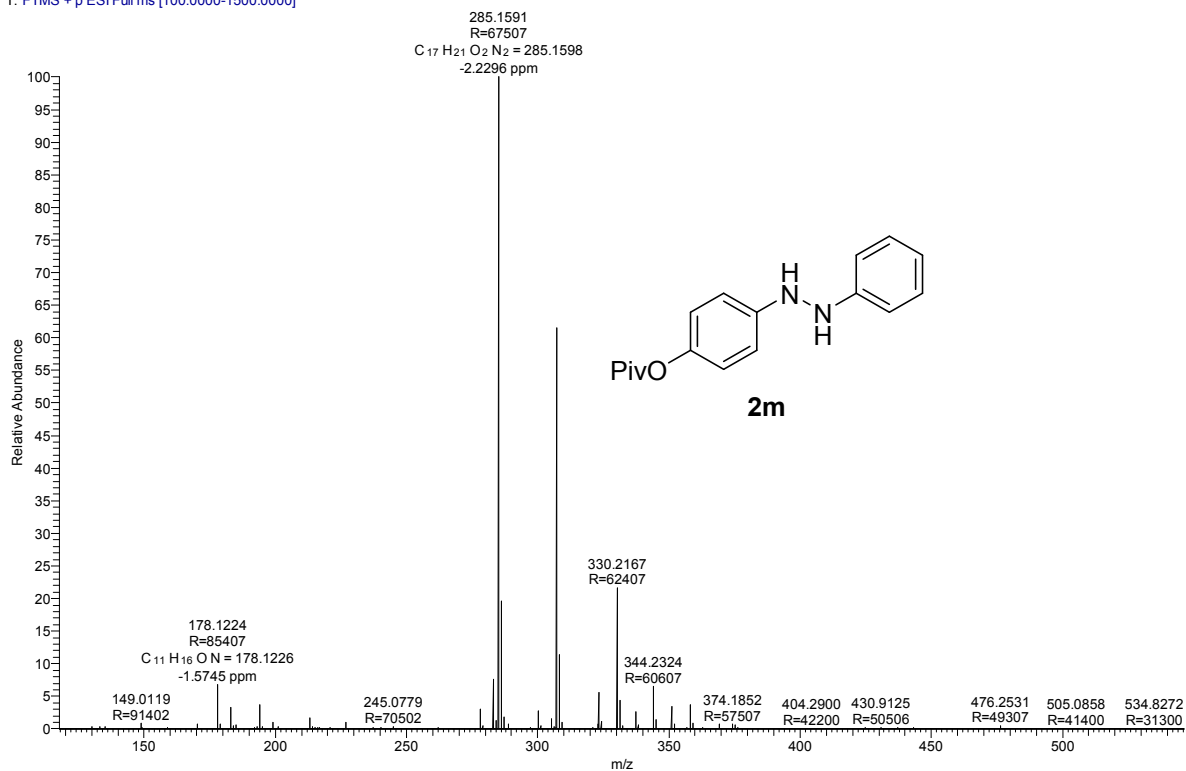
HRMS of **2j**

SS-105-E #265 RT: 1.19 AV: 1 NL: 1.97E8  
T: FTMS + p ESI Full ms [100.0000-1500.0000]



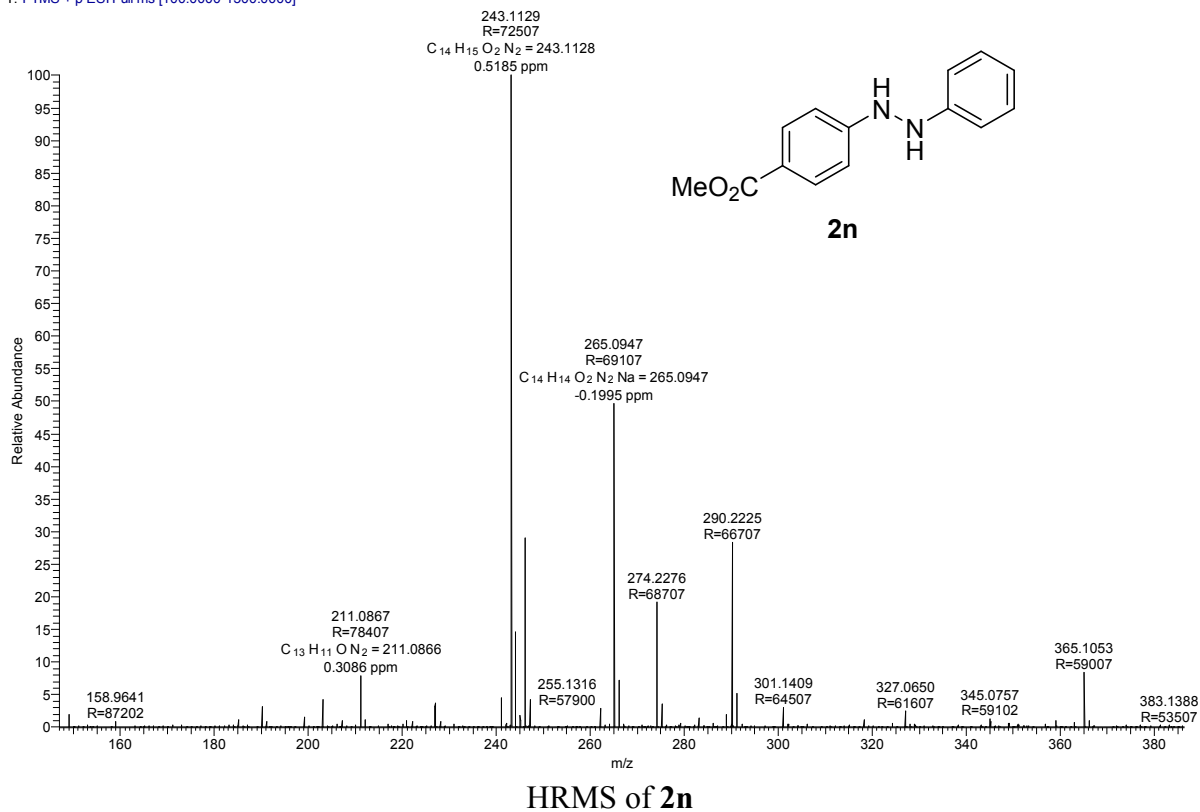
HRMS of **2i**

SS-103 #285 RT: 1.27 AV: 1 NL: 1.00E9  
T: FTMS + p ESI Full ms [100.0000-1500.0000]

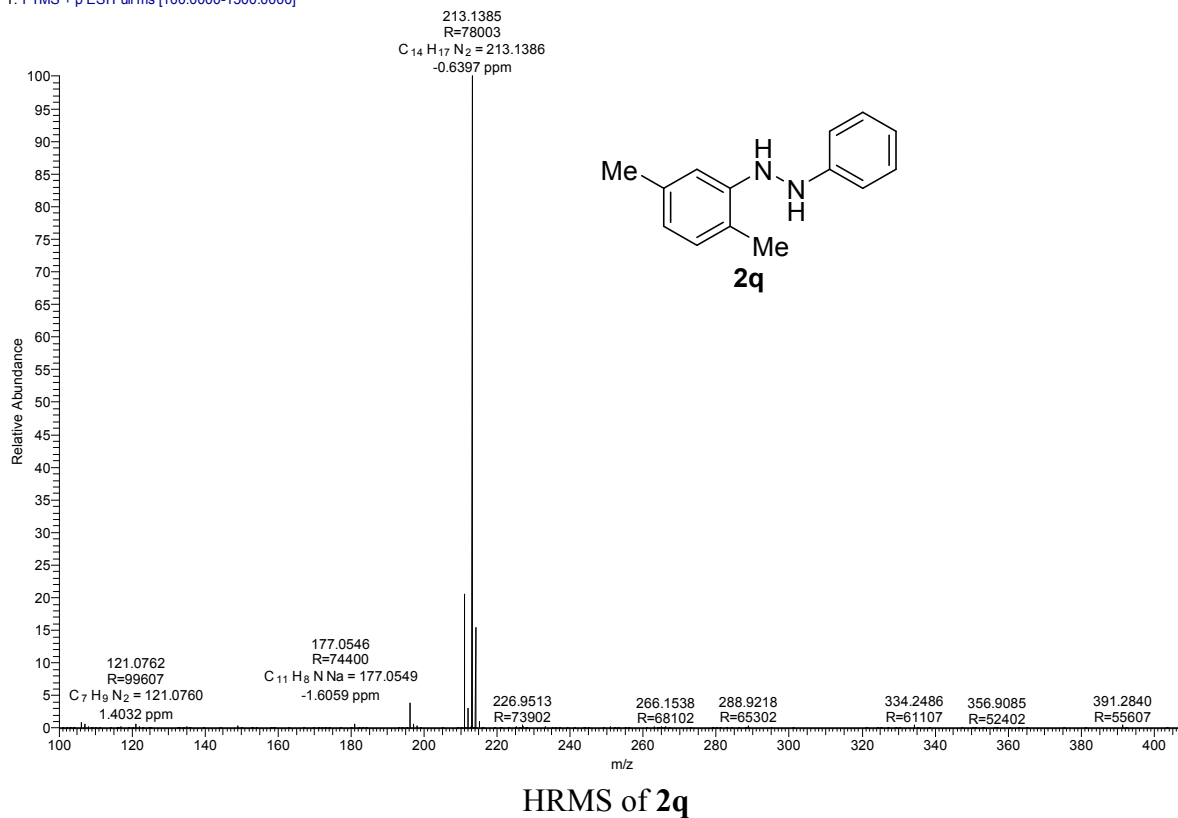


HRMS of **2m**

SAM-I 180730151225 #278 RT: 1.24 AV: 1 NL: 2.79E8  
T: FTMS + p ESI Full ms [100.0000-1500.0000]

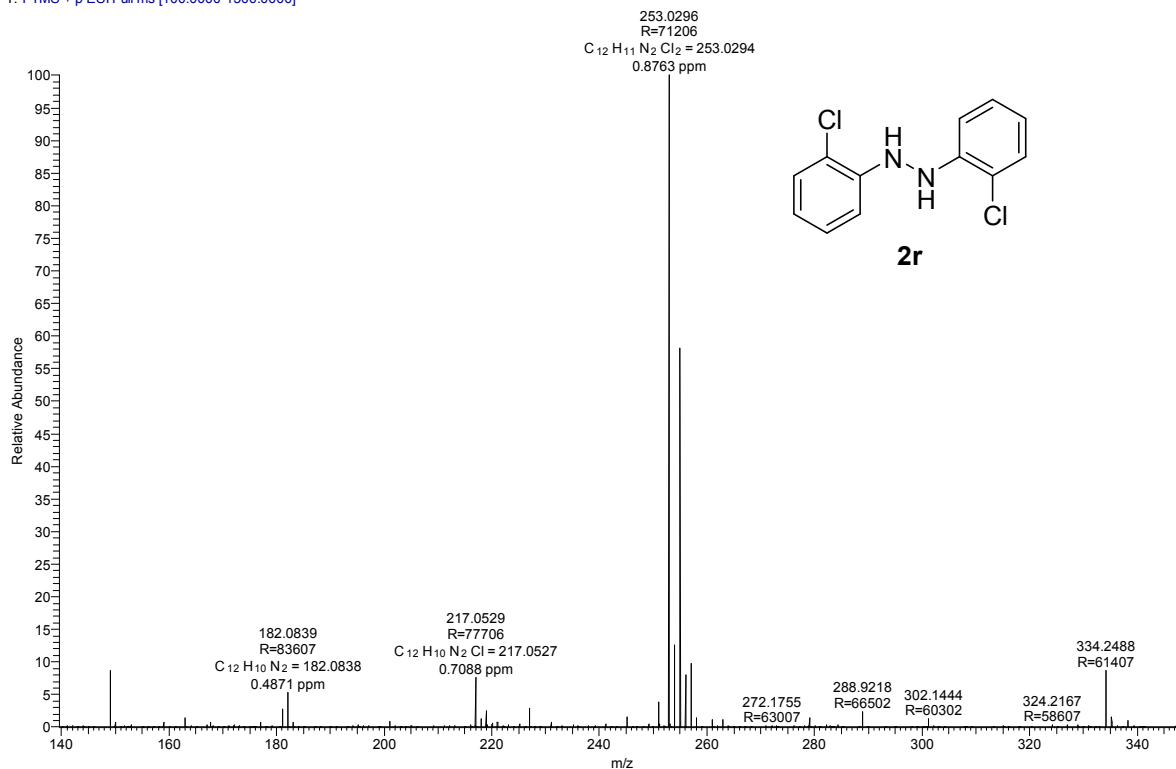


SAM-J #274 RT: 1.22 AV: 1 NL: 3.33E9  
T: FTMS + p ESI Full ms [100.0000-1500.0000]



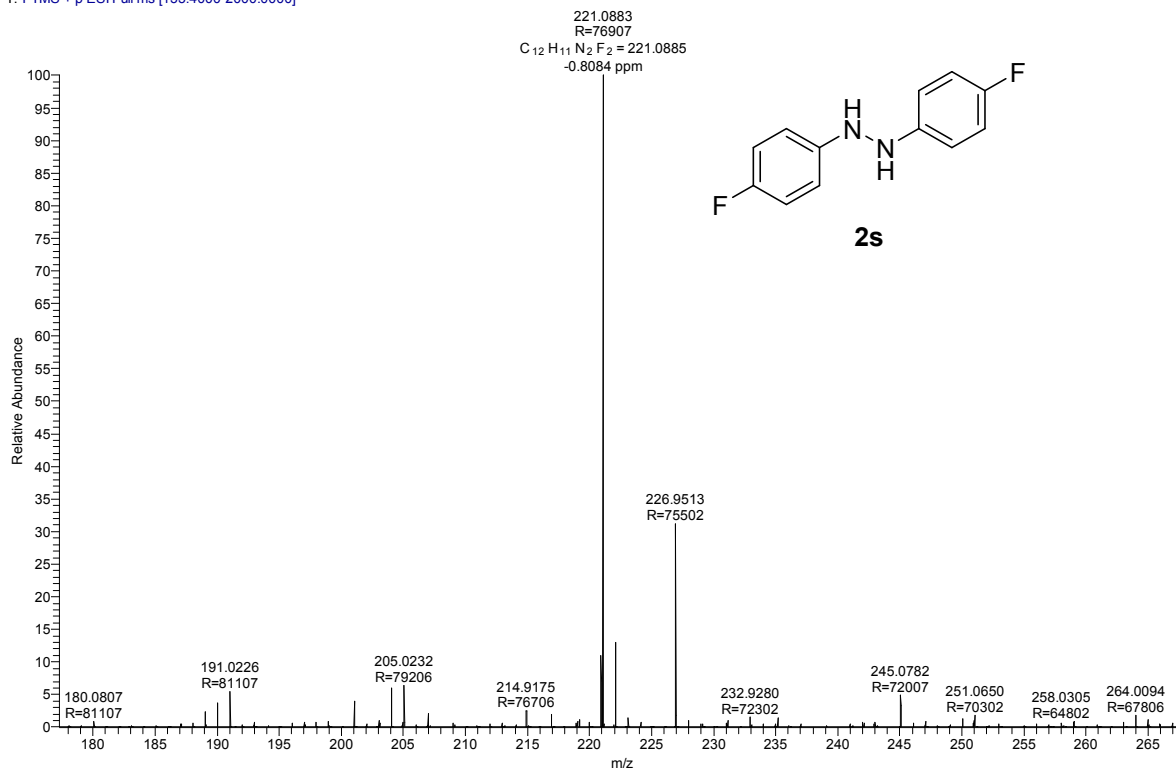


SAM-E #305 RT: 1.36 AV: 1 NL: 2.79E8  
T: FTMS + p ESI Full ms [100.0000-1500.0000]



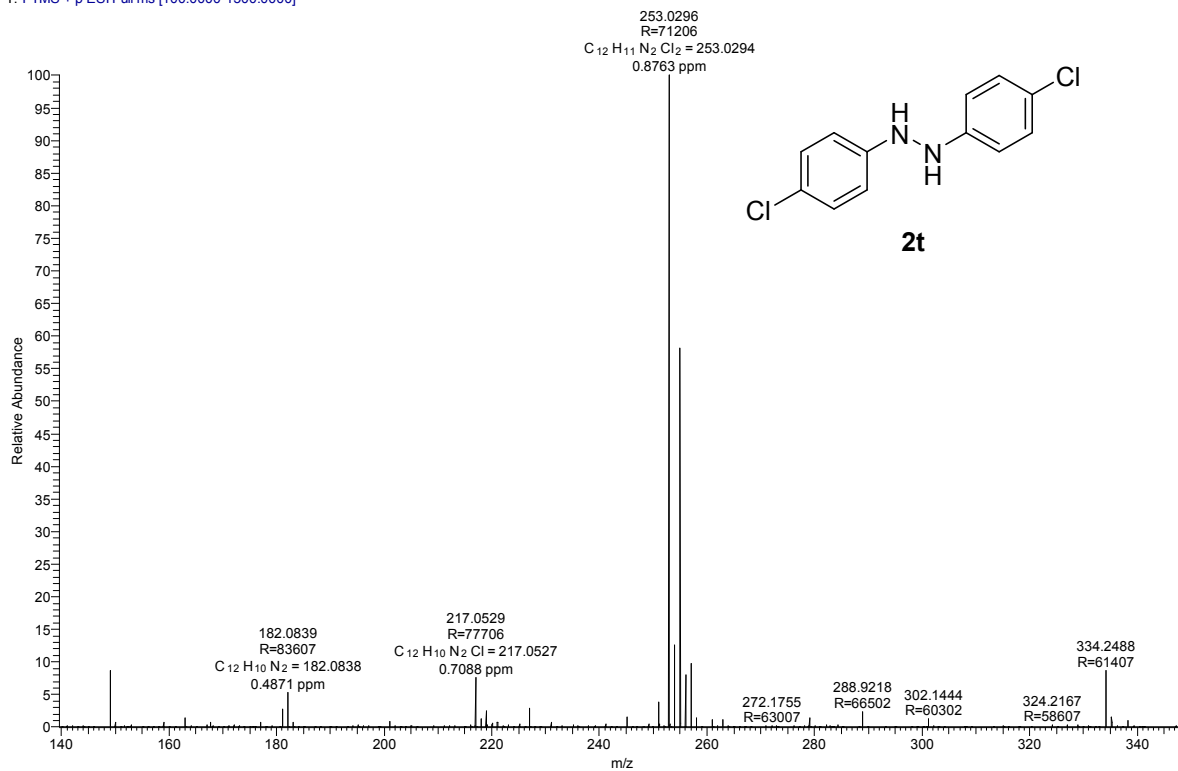
HRMS of **2r**

SS-203 #260 RT: 1.16 AV: 1 NL: 7.85E6  
T: FTMS + p ESI Full ms [133.4000-2000.0000]

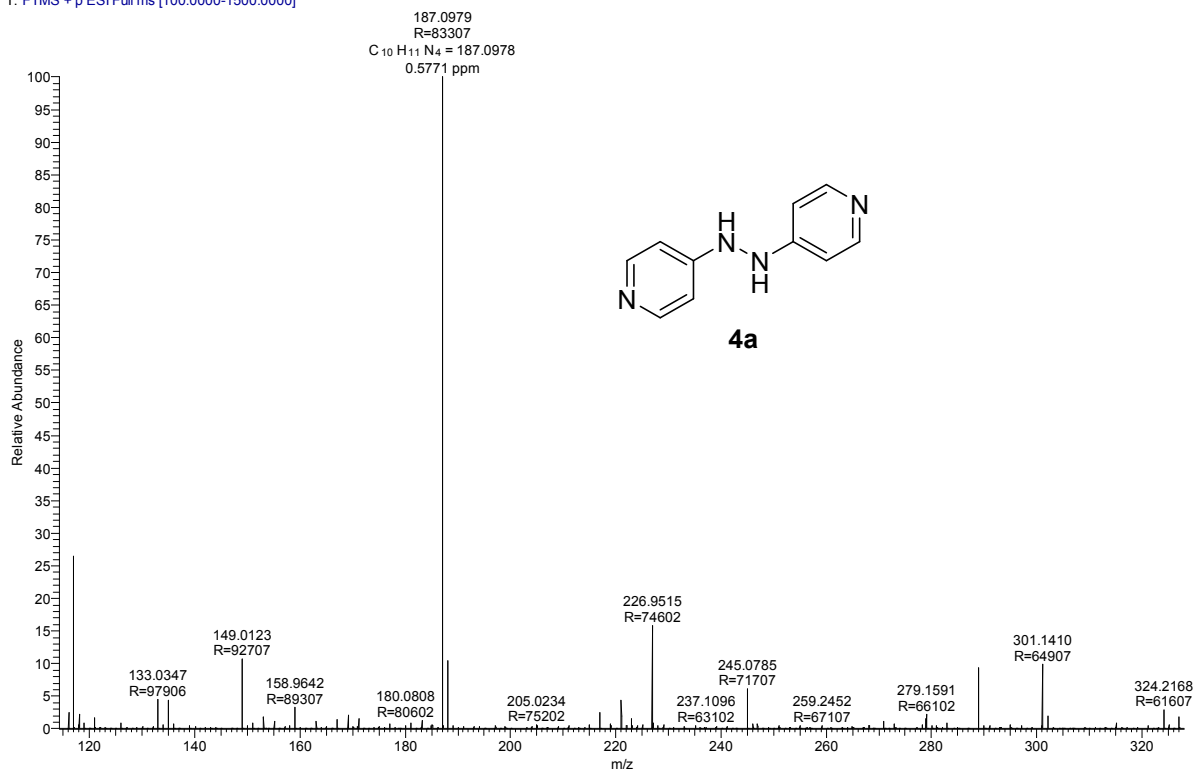


HRMS of **2s**

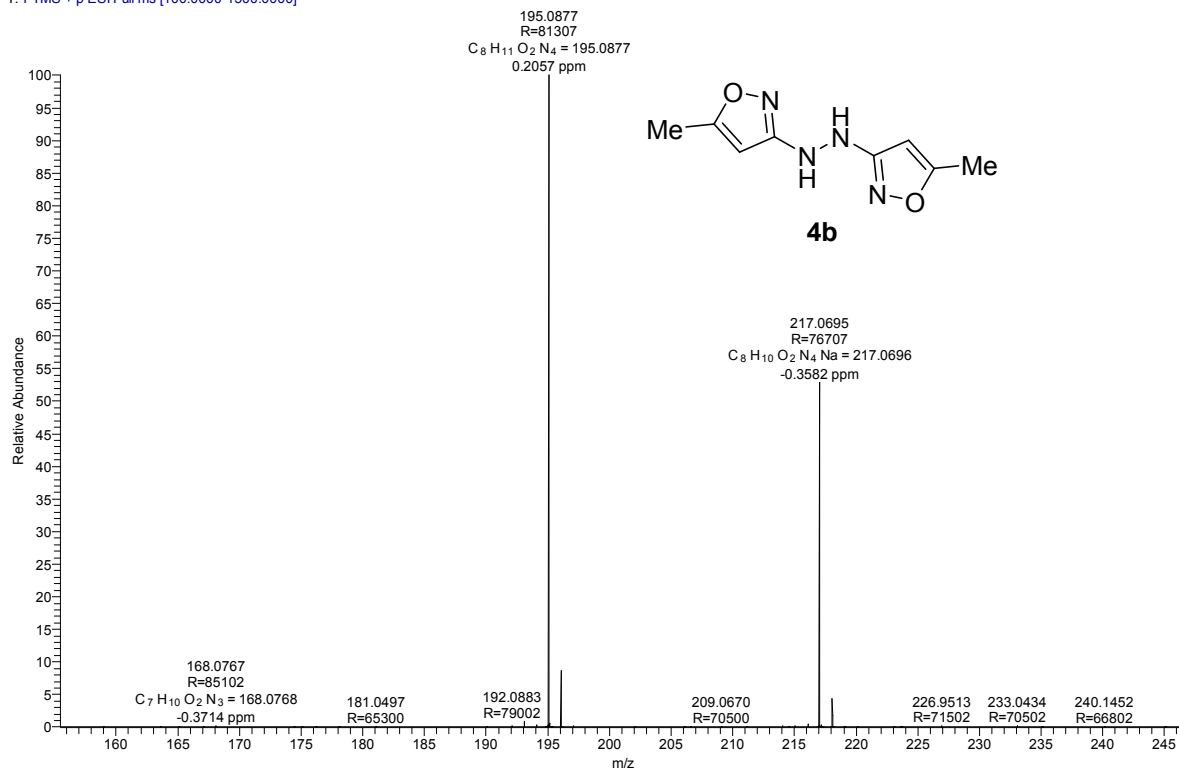
SAM-E #305 RT: 1.36 AV: 1 NL: 2.79E8  
T: FTMS + p ESI Full ms [100.0000-1500.0000]



SAM-B\_180730144323 #632 RT: 2.82 AV: 1 NL: 6.64E7  
T: FTMS + p ESI Full ms [100.0000-1500.0000]



SAM-K #255 RT: 1.13 AV: 1 NL: 4.63E9  
T: FTMS + p ESI Full ms [100.0000-1500.0000]



HRMS of **4b**