

Disulfide Catalyzed Iodination of Electron-rich Aromatic Compounds

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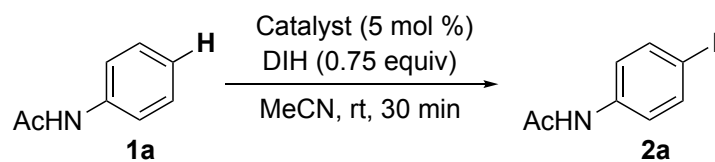
Supporting information

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Mechanistic study

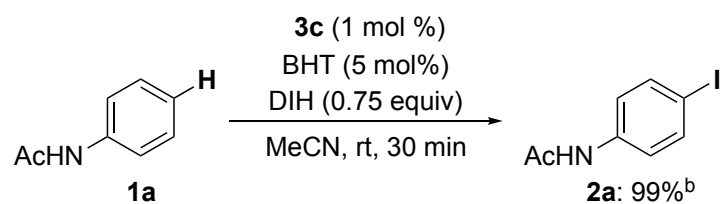
Reactivity of thiosulfonate **4** and in *N*-sulfenyl hydantoin derivatives **5-7**^a



entry	Catalyst	yield ^a (%)
1	4	8
2	5	10
3	6	8
4	7	15

^aReaction were carried out with **1a** (0.3 mmol), and catalyst (5 mol %) in solvent (1 mL) for 30 min at rt. ^bYield was determined by ¹H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.

A control experiment in the presence of radical quencher^a



^aReaction were carried out with **1a** (0.3 mmol), and catalyst (5 mol %) in solvent (1 mL) for 30 min at rt. ^bYield was determined by ¹H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.

NMR experiment for **3c** and DIH

To a solution of **3c** (0.1 mmol) in acetonitrile- d_3 (0.75 mL) was added DIH (0.1 mmol) at room temperature. After 30 min and 2 h, ^1H NMR spectra were measured at room temperature.

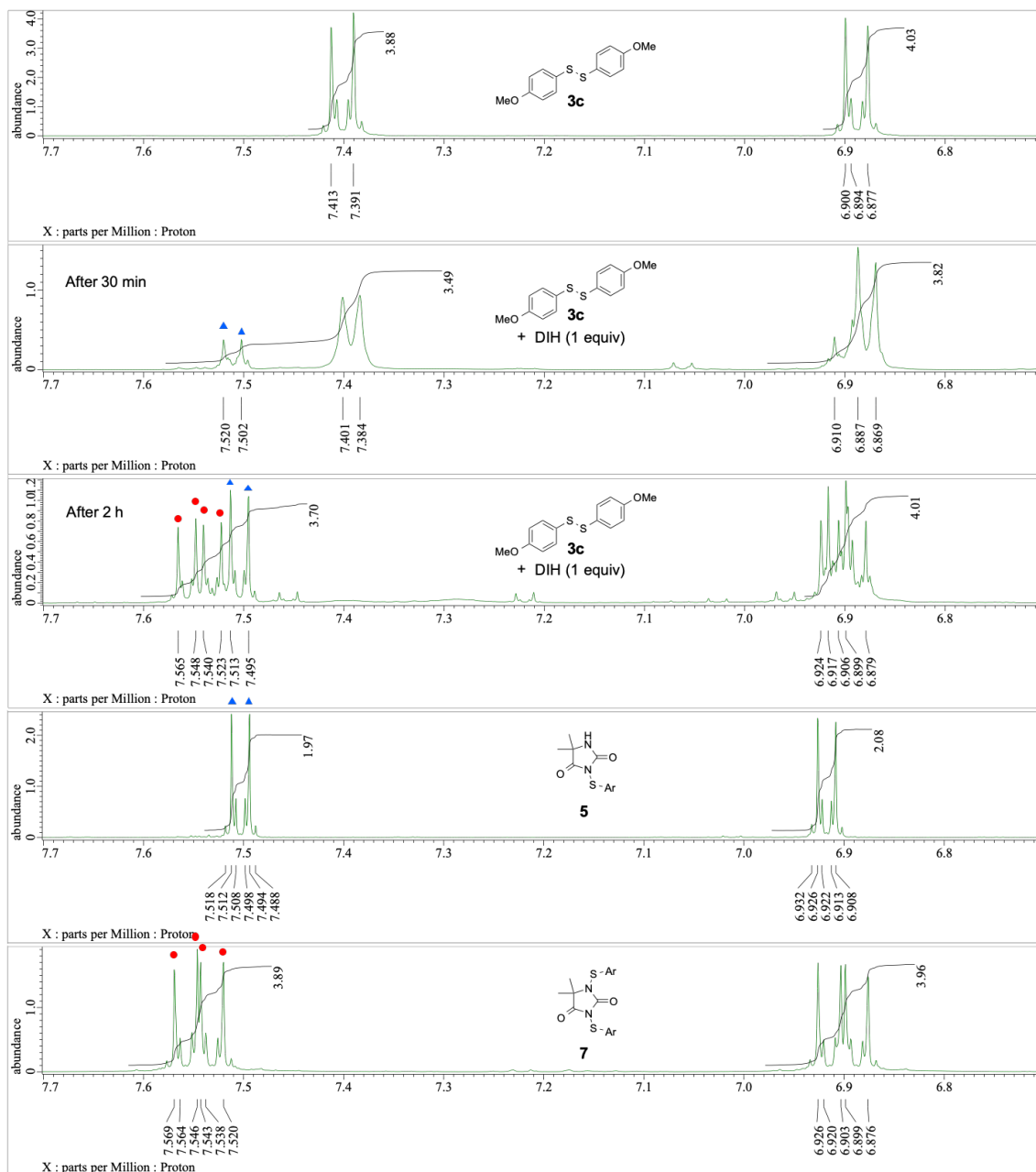


Figure S1. ^1H NMR spectra of **3c** in acetonitrile- d_3 following the addition of DIH.

After 30 min, proton peaks of **5** gradually appeared. After 2 h, proton peaks of **3c** were completely disappeared, and proton peaks of **5** and **7** were only observed.

NMR experiment for **3c** (or 4-methoxythiophenol) and DCDMH

To a solution of **3c** (0.1 mmol) or 4-methoxythiophenol (0.2 mmol) in acetonitrile- d_3 (0.75 mL) was added DCDMH (0.1 mmol) at room temperature. After 30 min, ^1H NMR spectra were measured at room temperature.

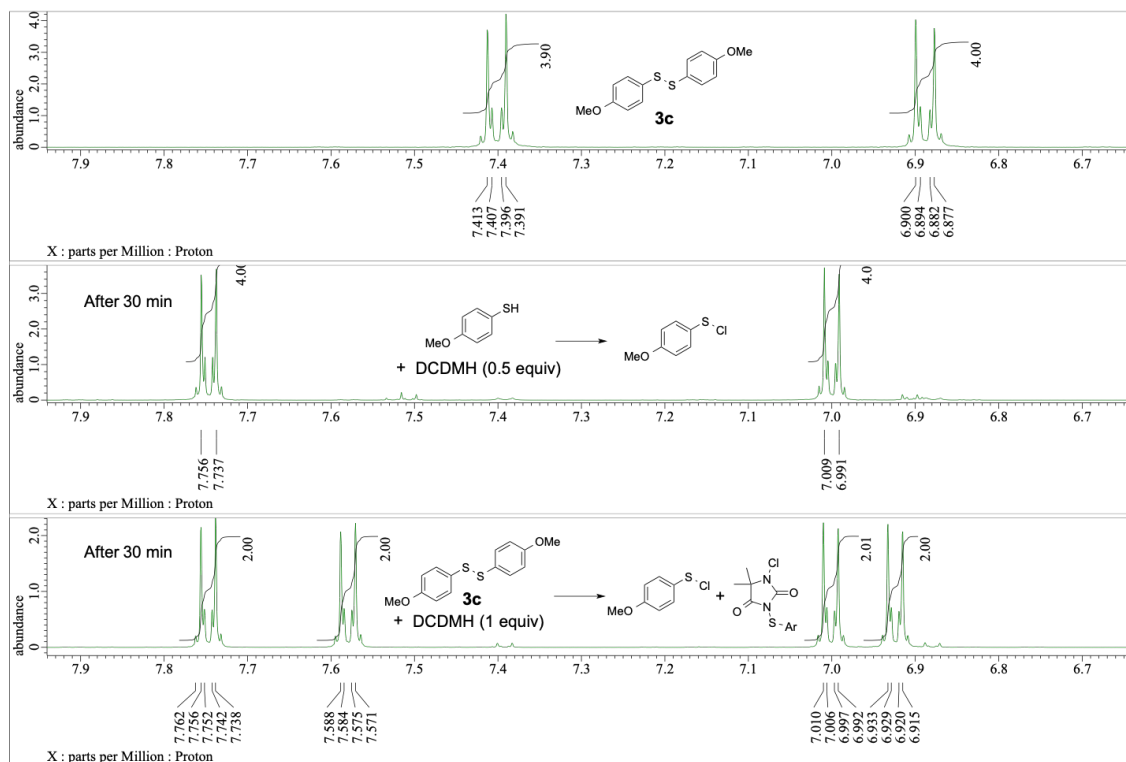


Figure S2. ^1H NMR spectra of 4-methoxythiophenol or **3c** in acetonitrile- d_3 following the addition of DCDMH.

In case of 4-methoxythiophenol, proton peaks of **3c** were completely disappeared, and proton peaks of corresponding sulfonyl chloride were only observed. Whereas, mixture of **3c** and DCDMH gave corresponding sulfonyl chloride and *N*-sulfonyl hydantoin at a ratio of 1:1.

NMR experiment for **3c** and ICl (or selectfluor)

To a solution of **3a** (0.1 mmol) in acetonitrile- d_3 (0.75 mL) was added ICl (0.1 mmol) or selectfluor (0.05 mmol) at room temperature. After 30 min, ^1H NMR spectra were measured at room temperature.

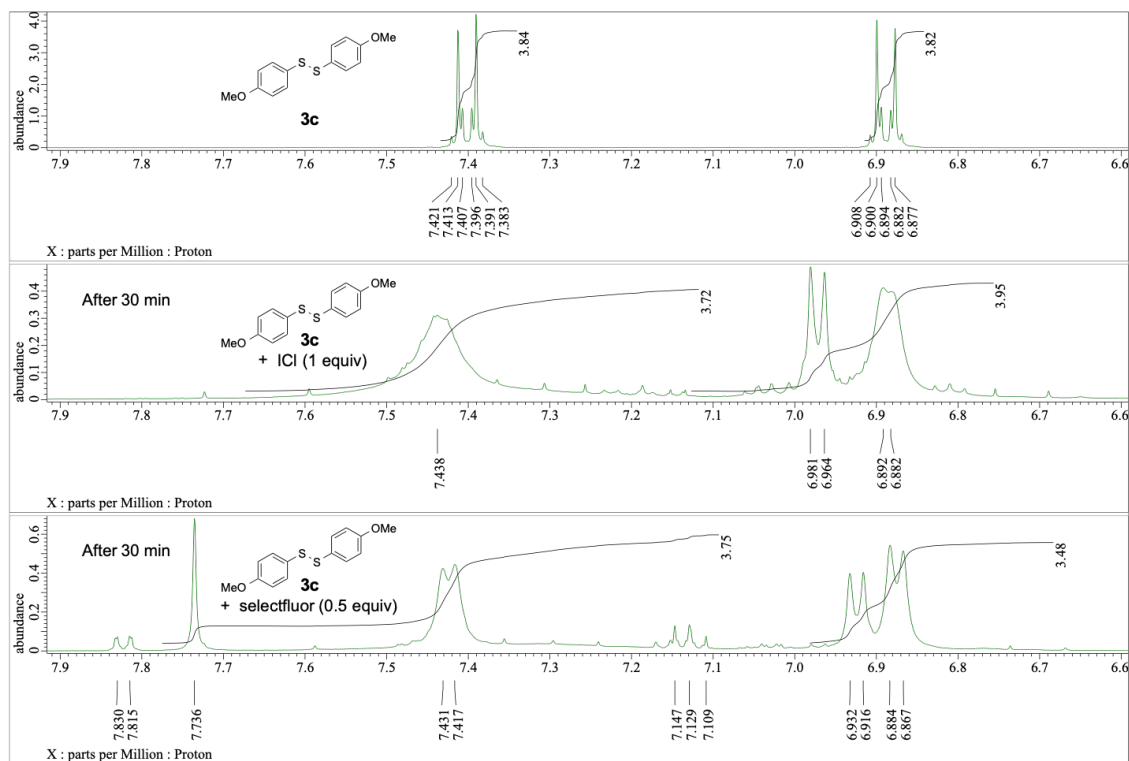
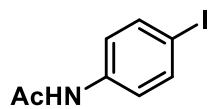


Figure S3. ^1H NMR spectra of **3c** in acetonitrile- d_3 following the addition of ICl or selectfluor.

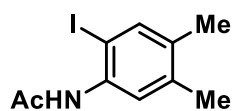
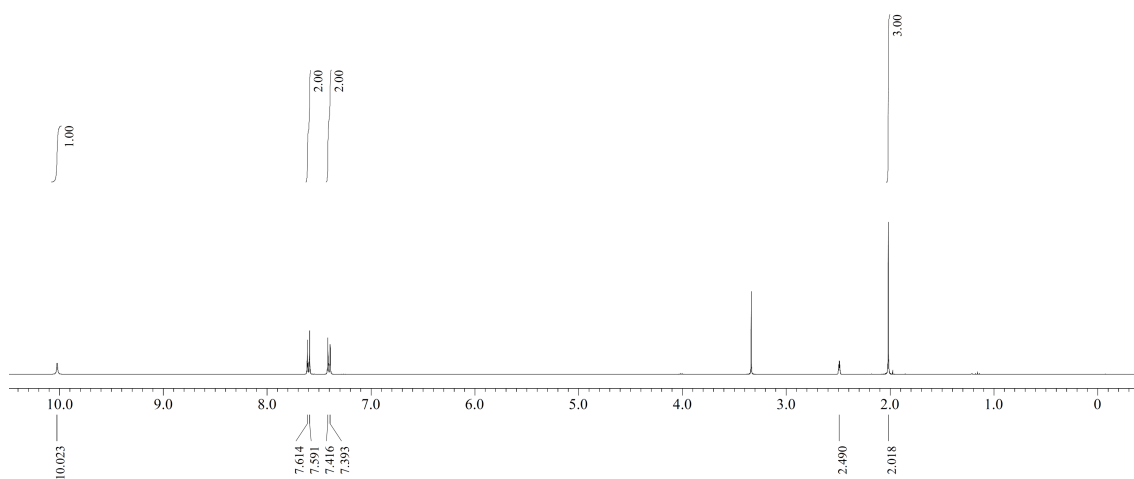
In both case, proton peaks of **3c** were broadened and slightly downfield shifted, and new peaks were observed. Considering disulfide **3c** and selectfluor previously gave halogen adduct, this indicate disulfide **3c** partially reacted with ICl, and formed transient halogen-bonding adduct.

^1H -NMR and ^{13}C -NMR spectra



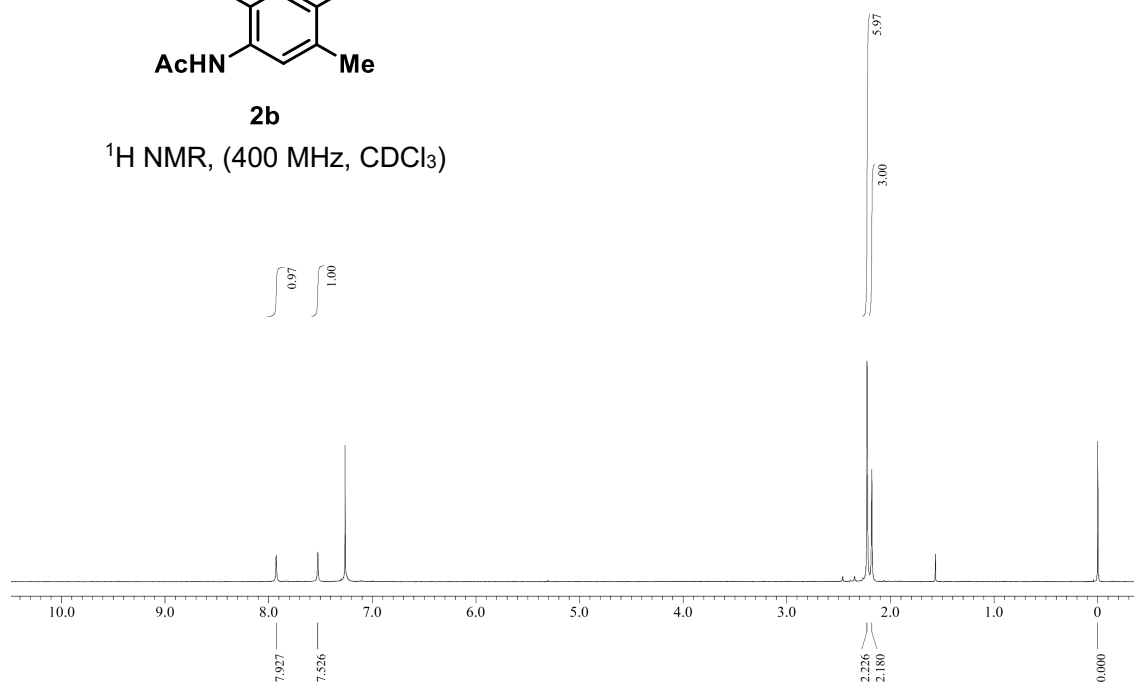
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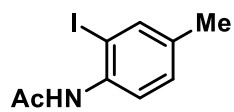
^1H NMR, (400 MHz, $\text{DMSO}-d_6$)



2b

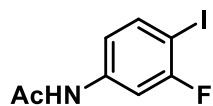
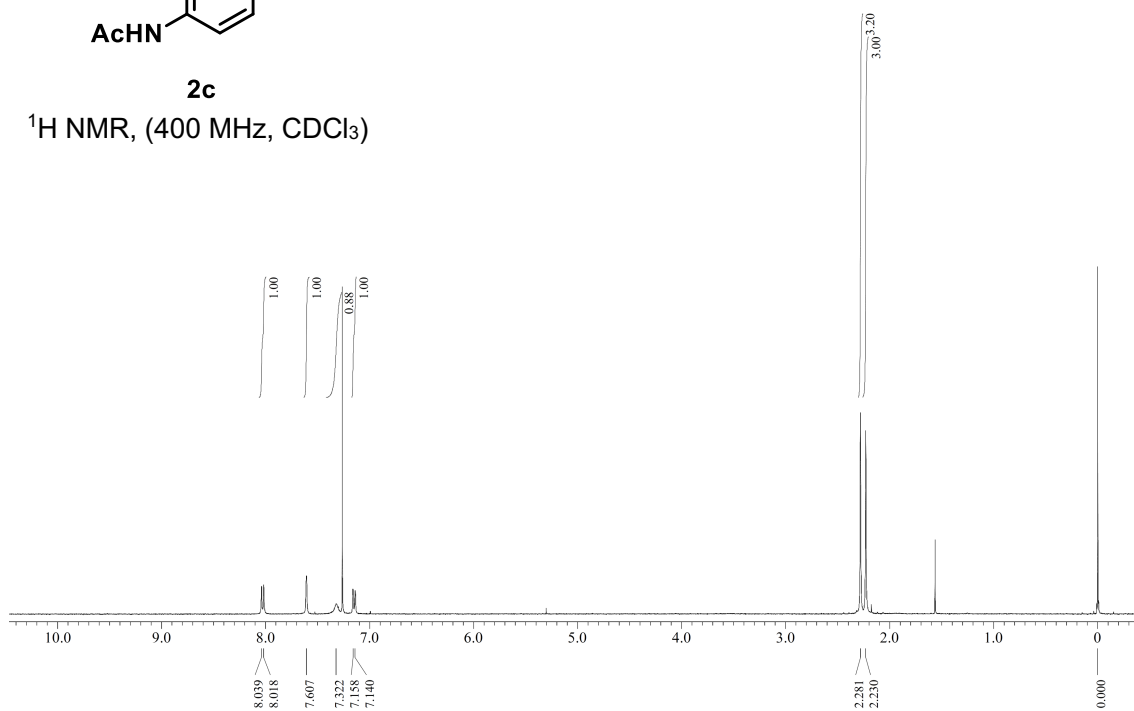
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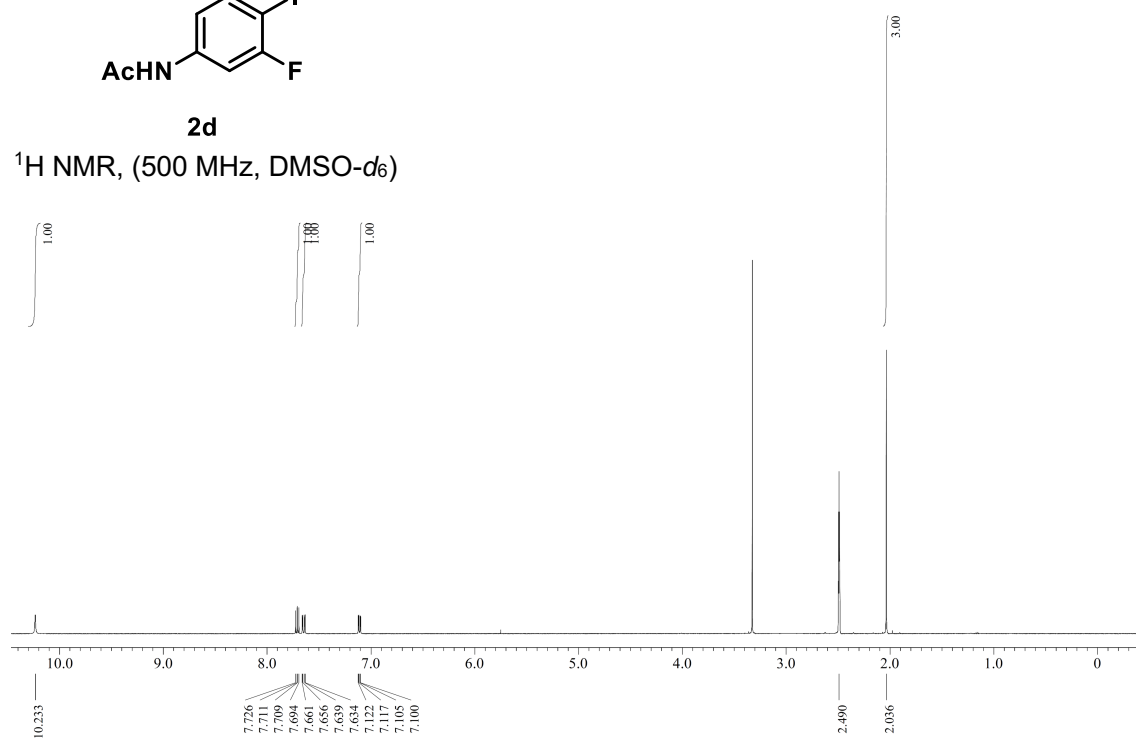
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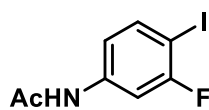
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2d

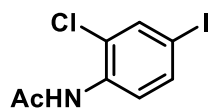
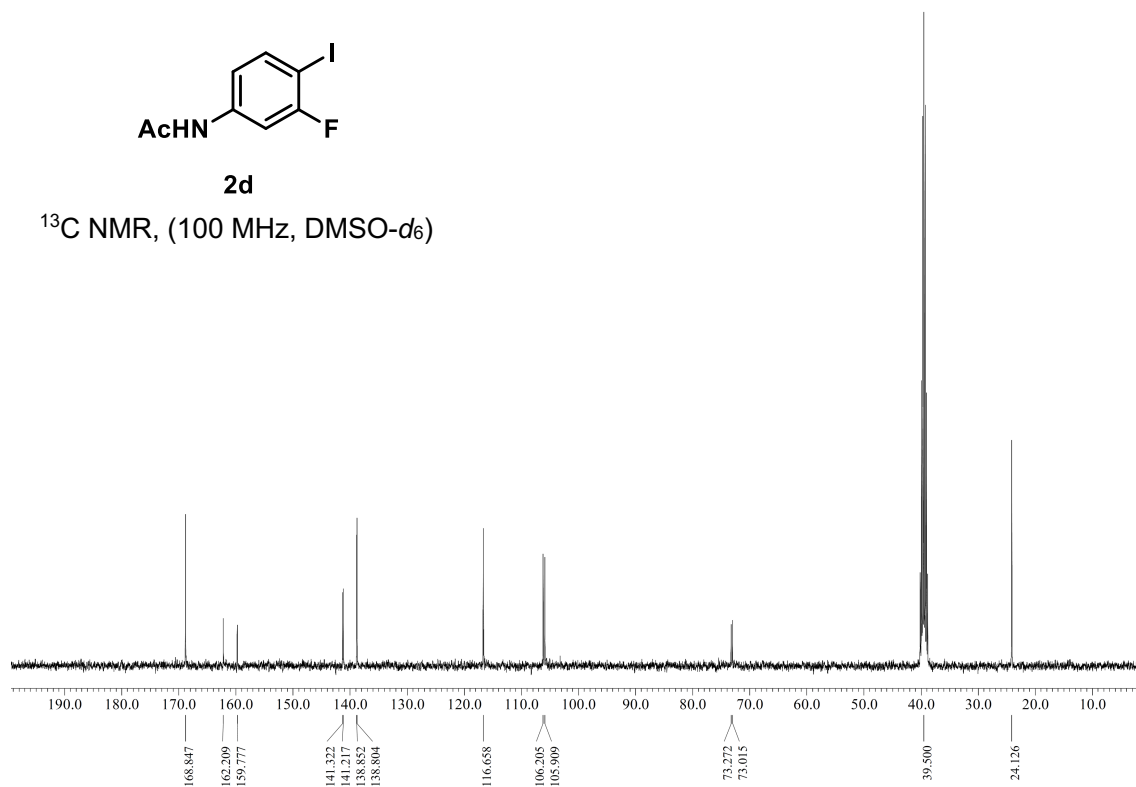
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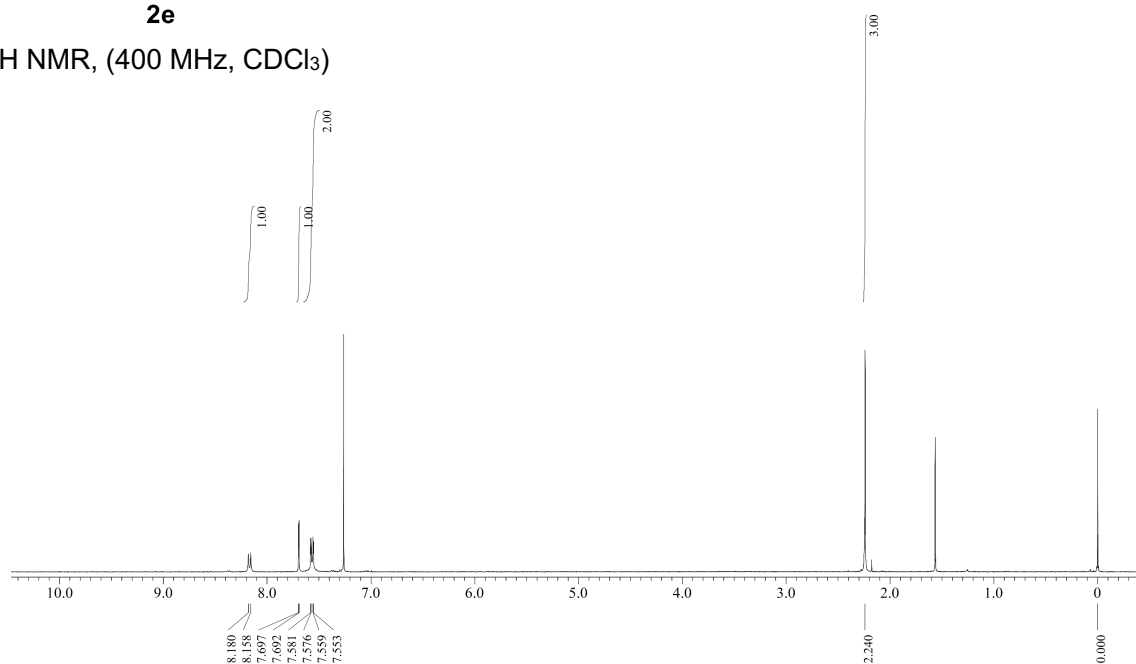
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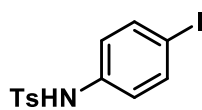
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2e

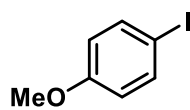
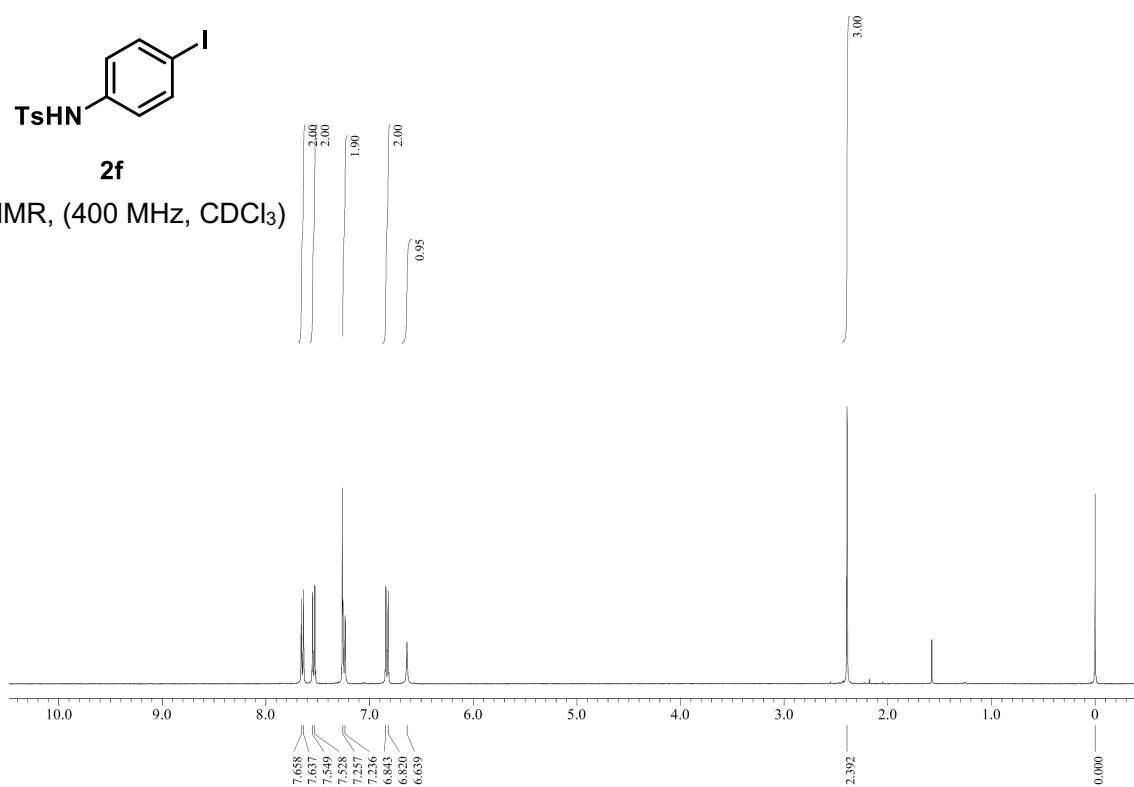
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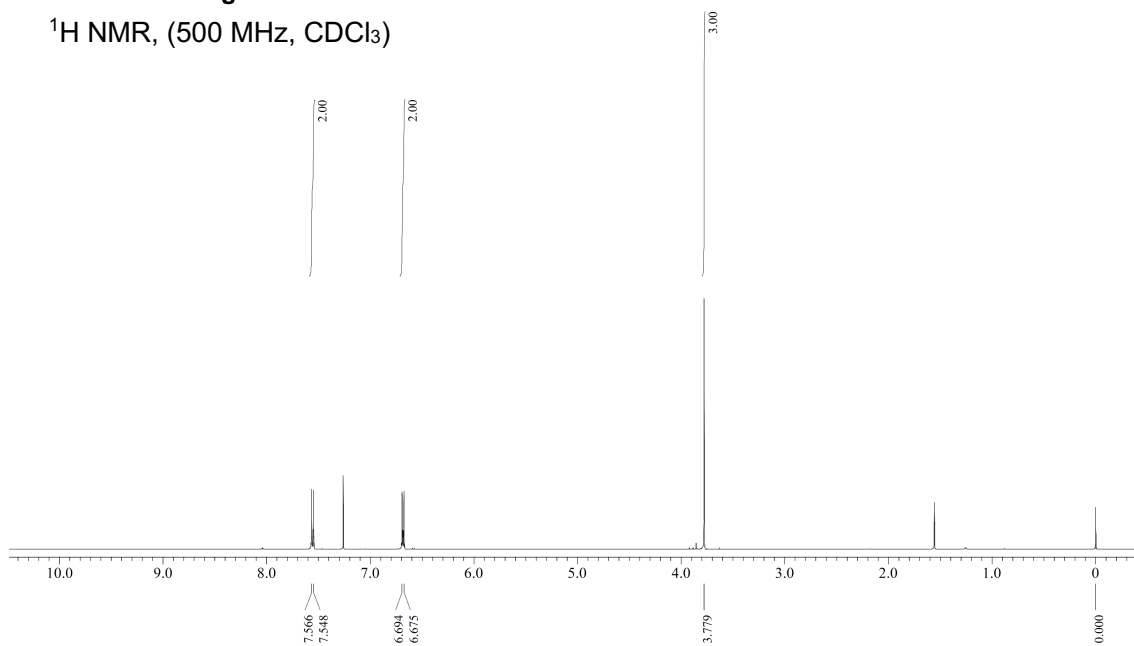
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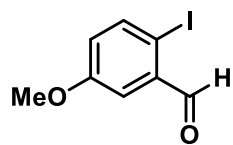
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2g

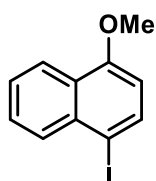
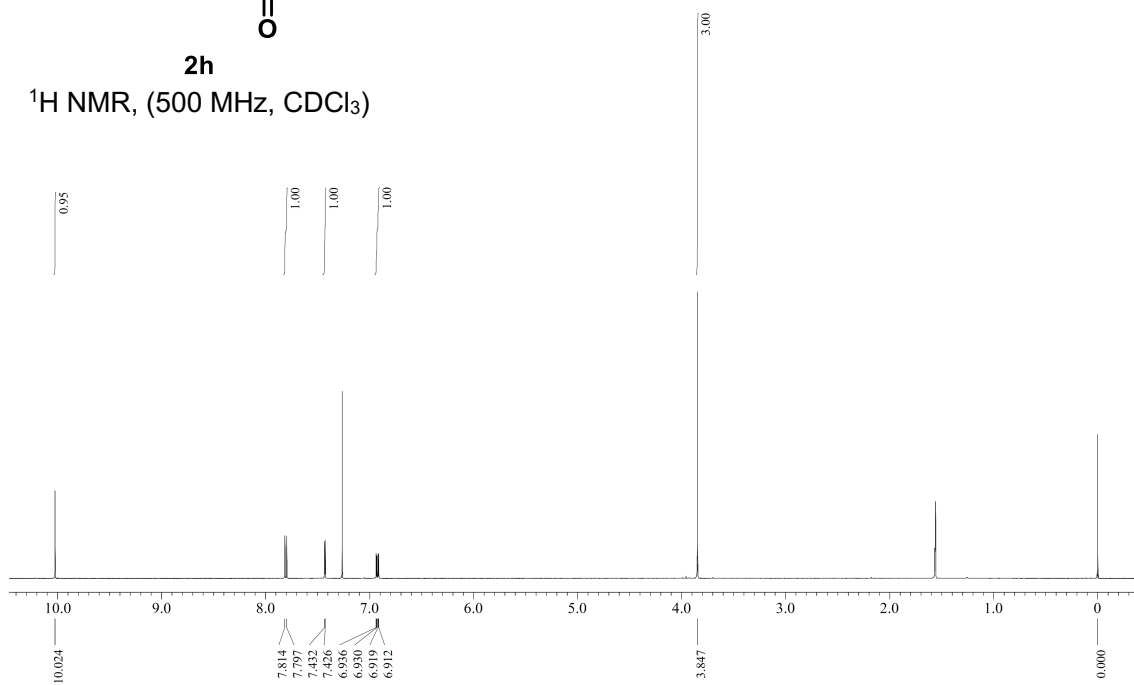
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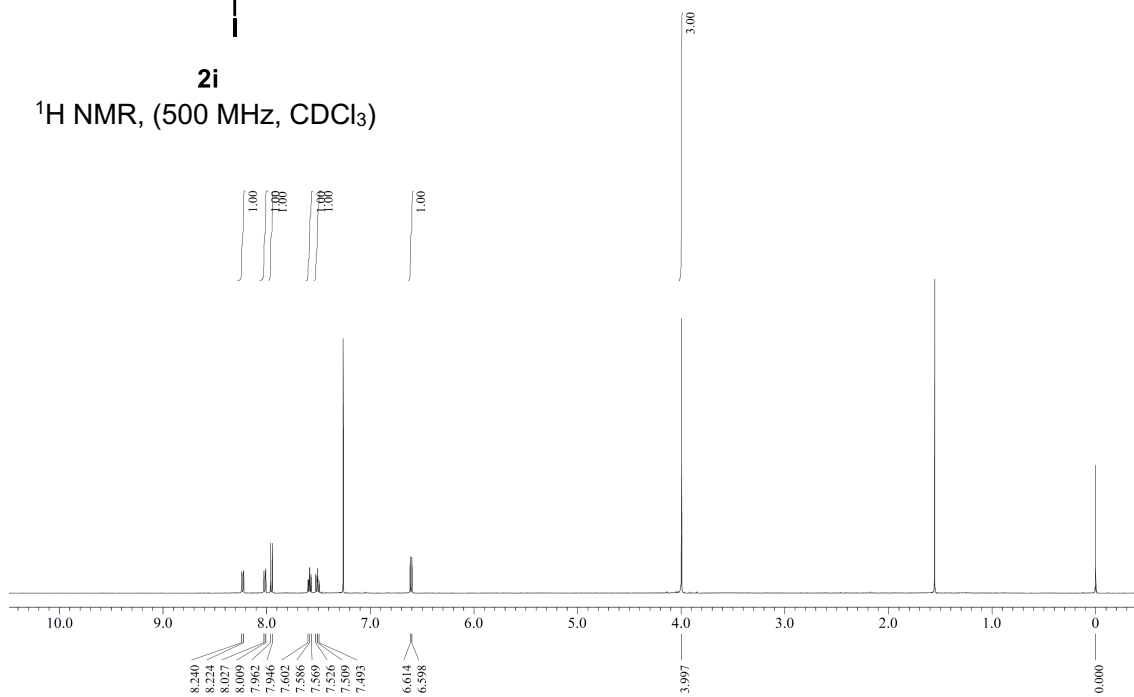
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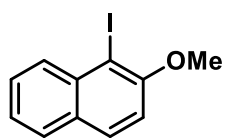
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2i

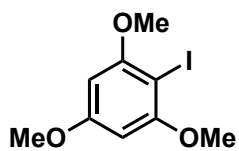
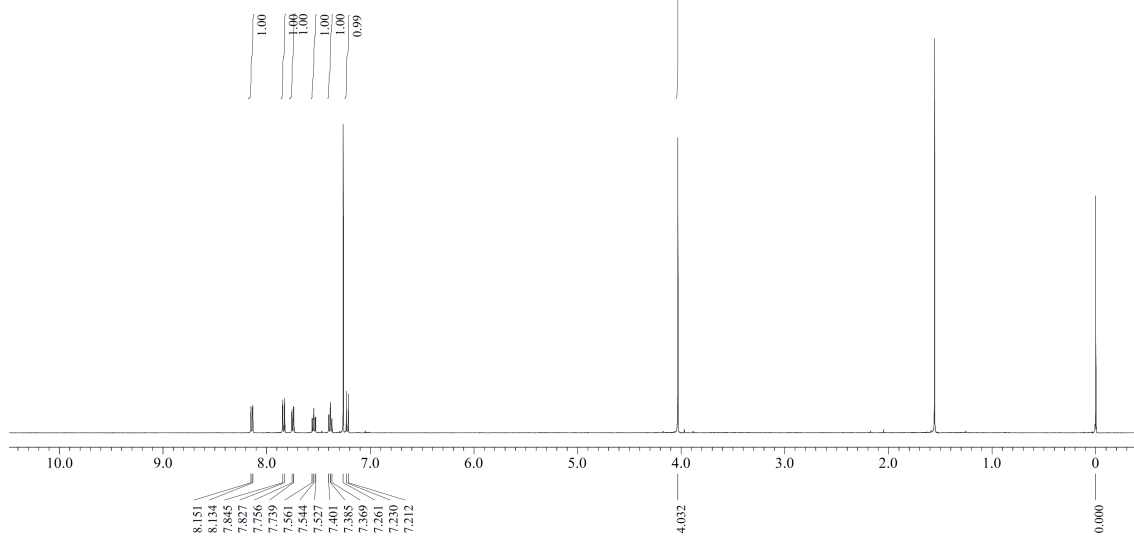
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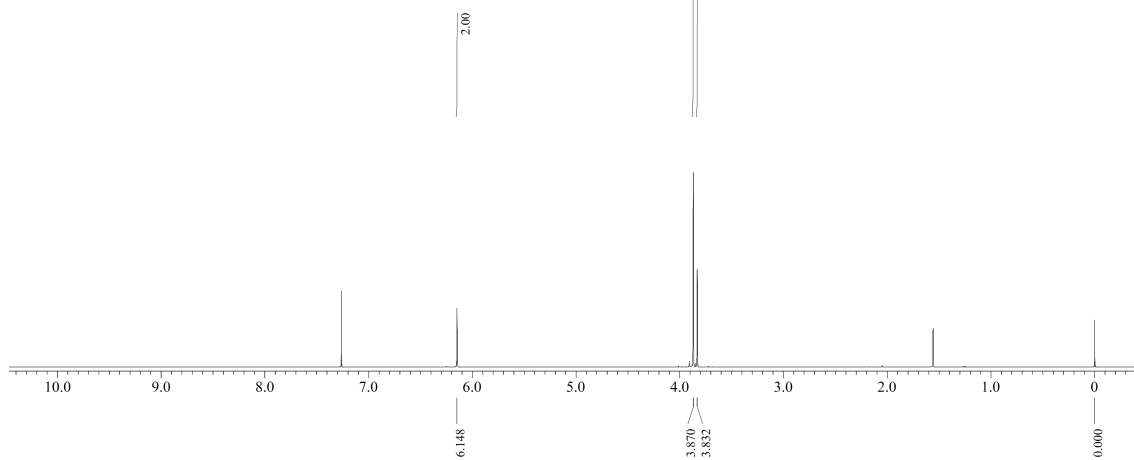
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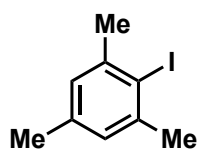
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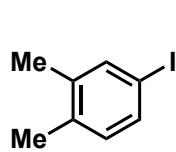
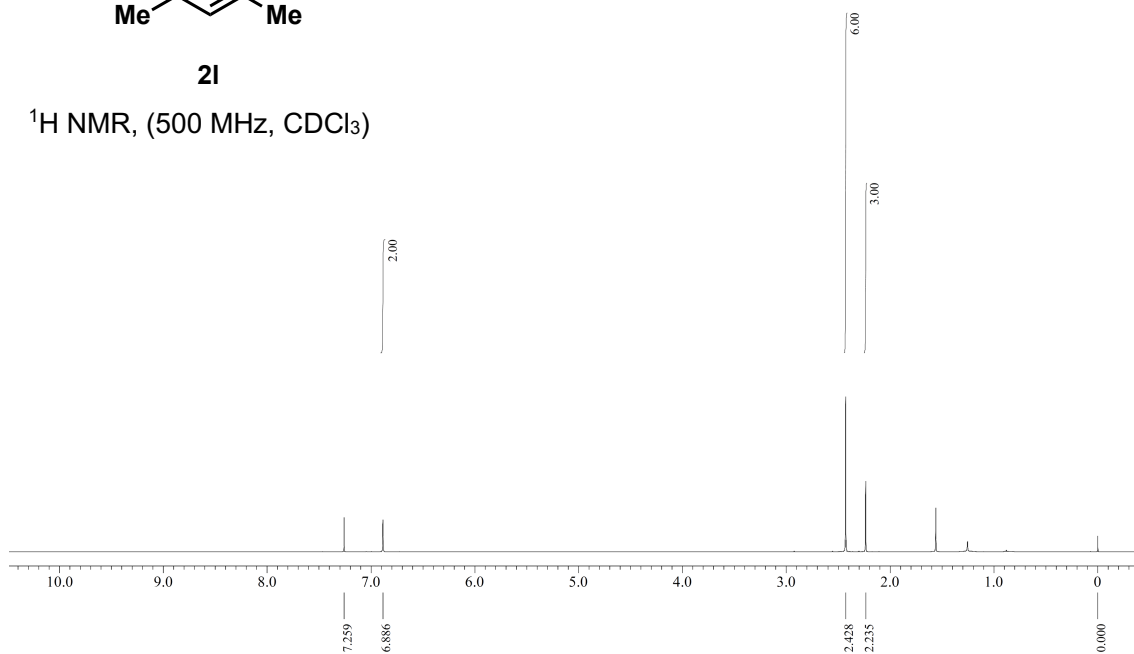
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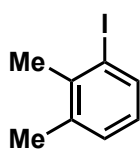


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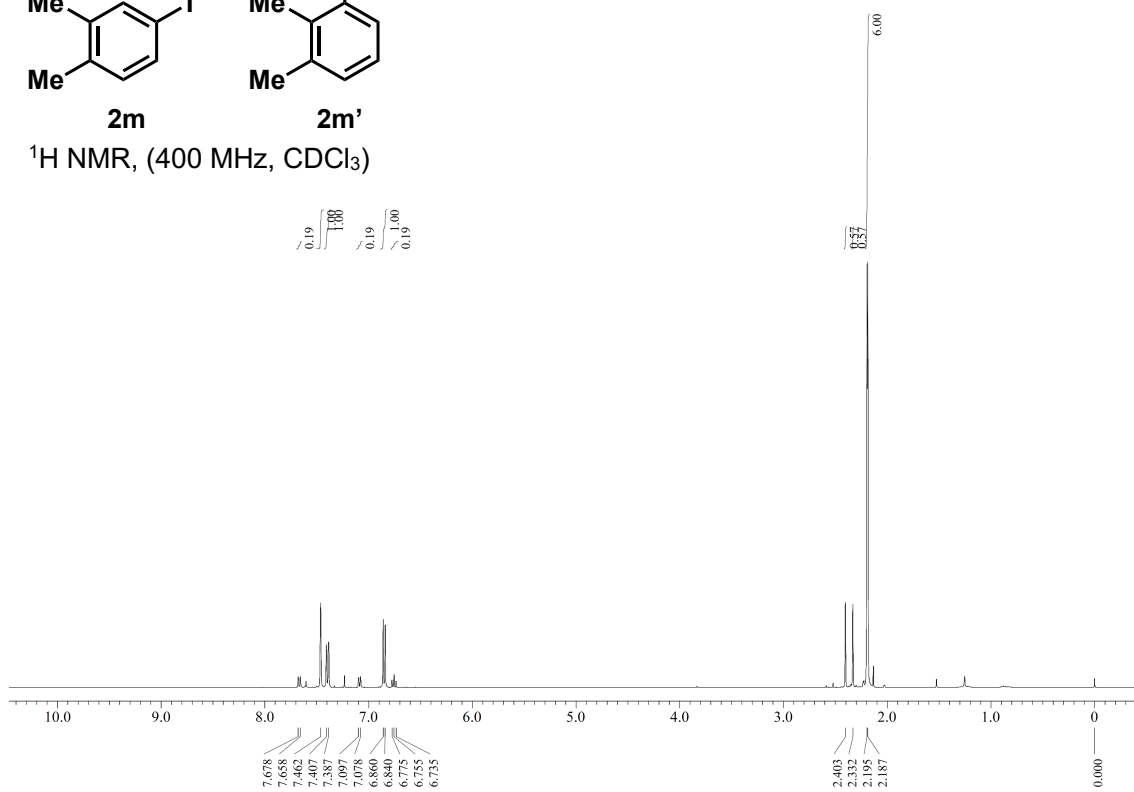


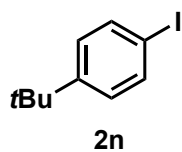
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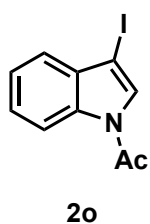
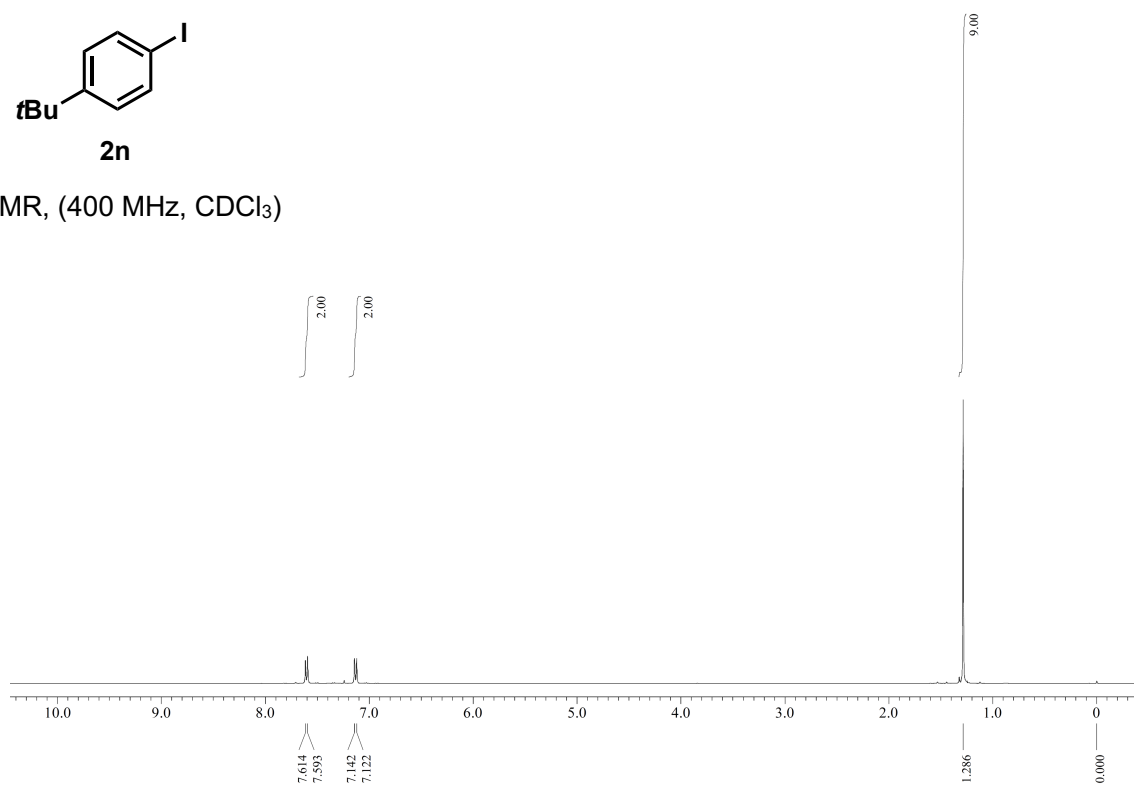
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^1H NMR, (400 MHz, CDCl_3)

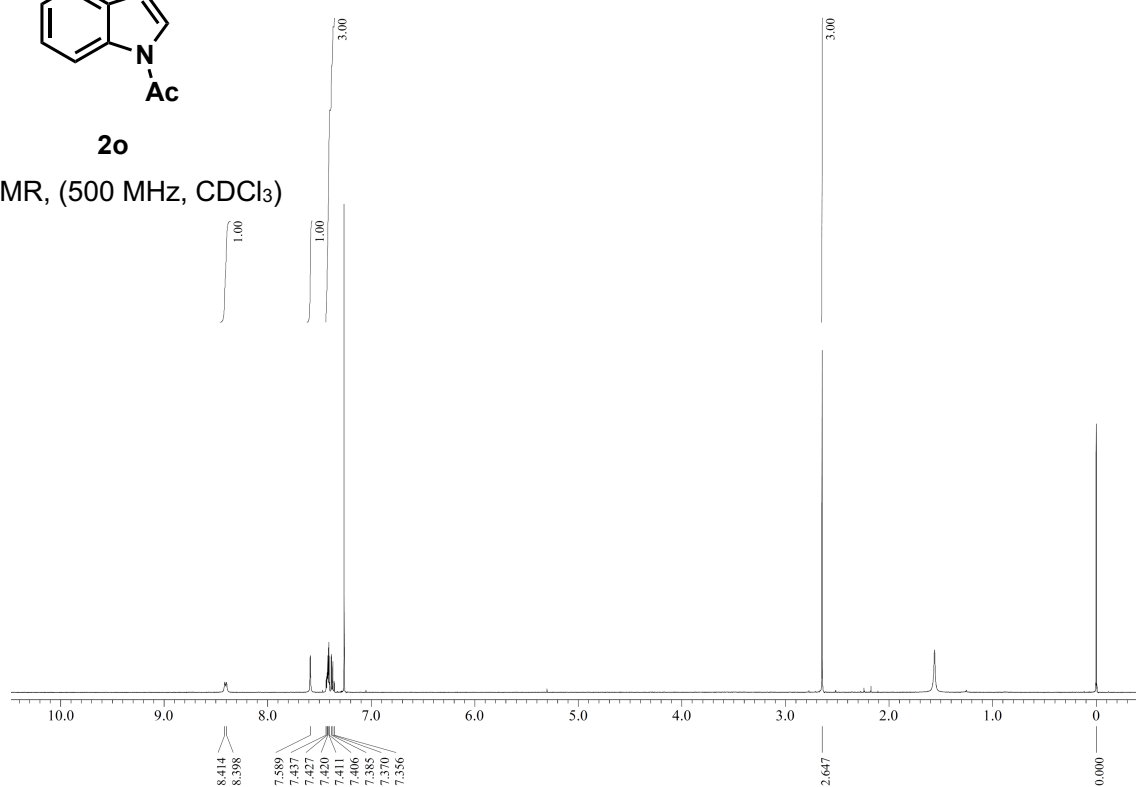


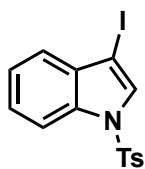


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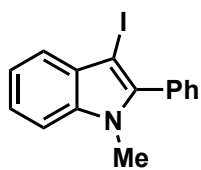
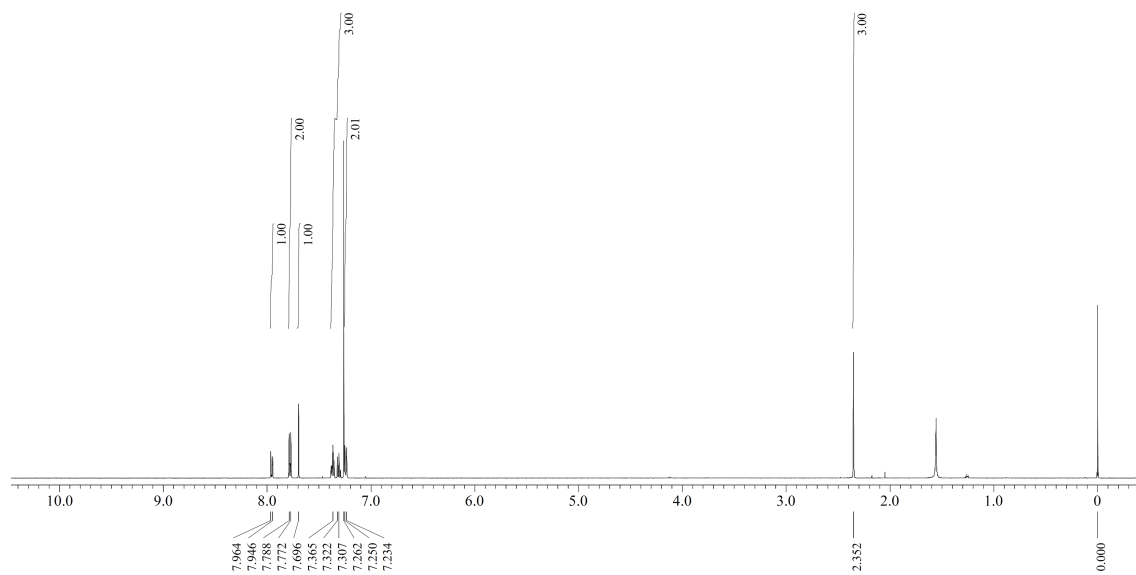
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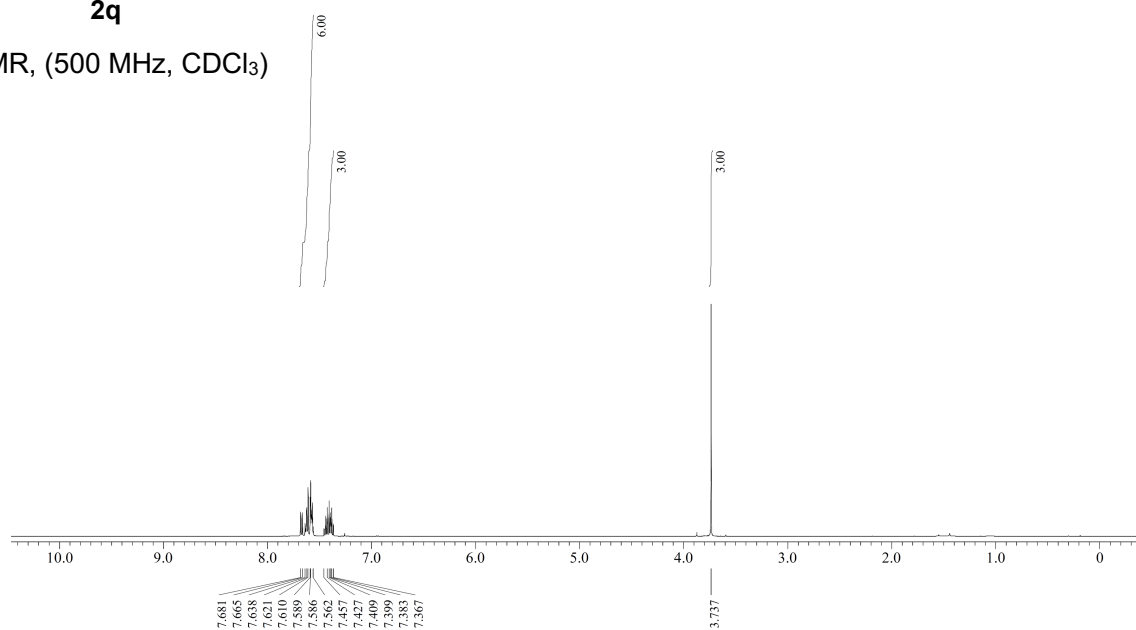
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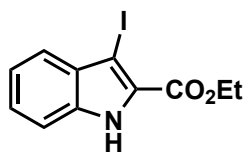
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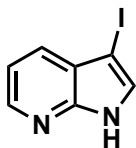
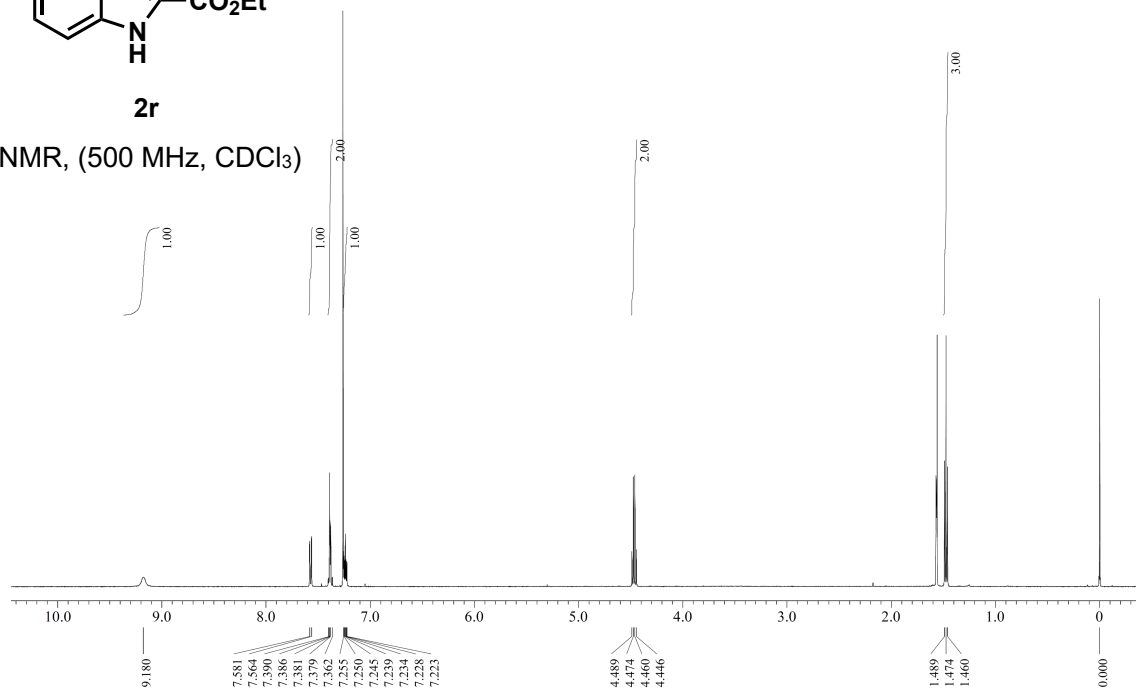
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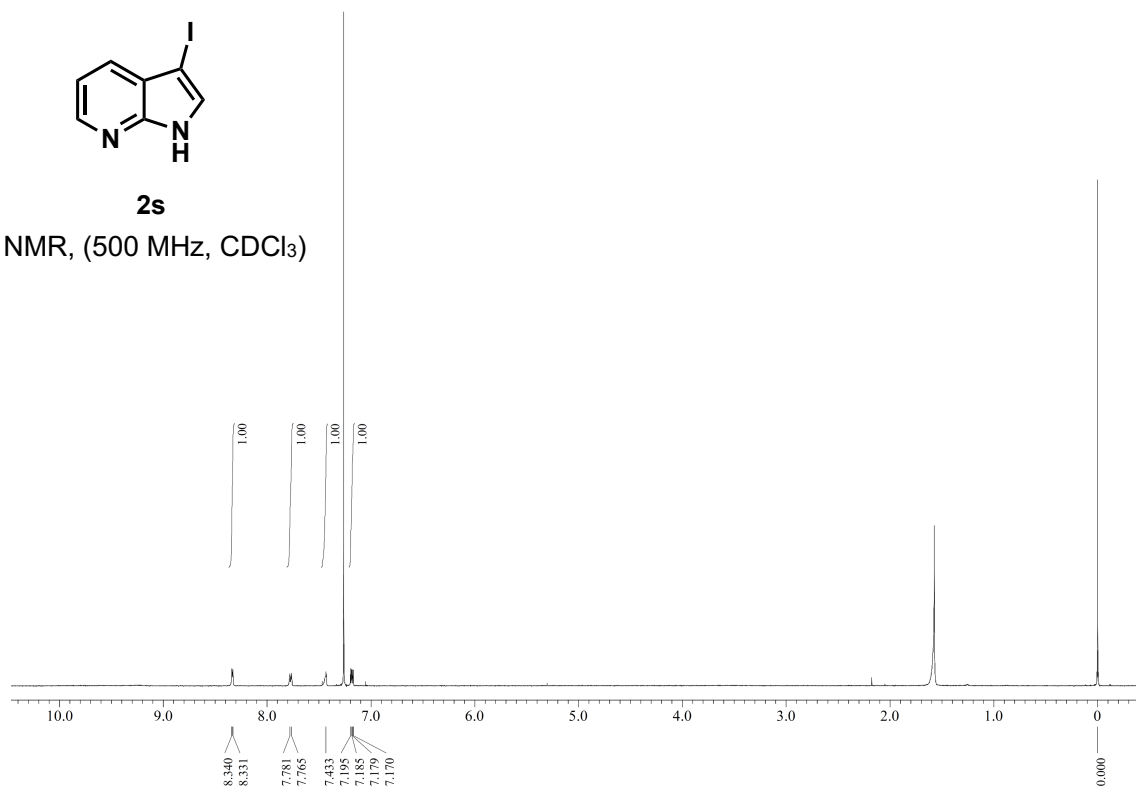
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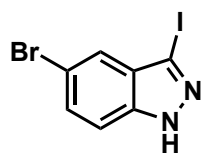
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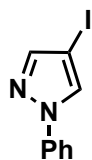
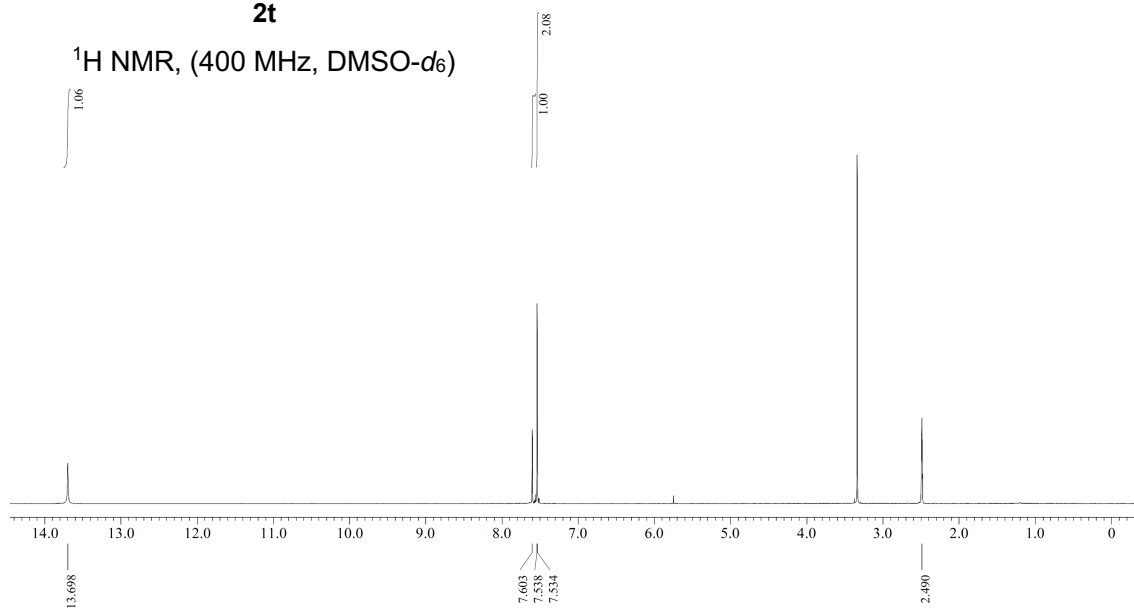
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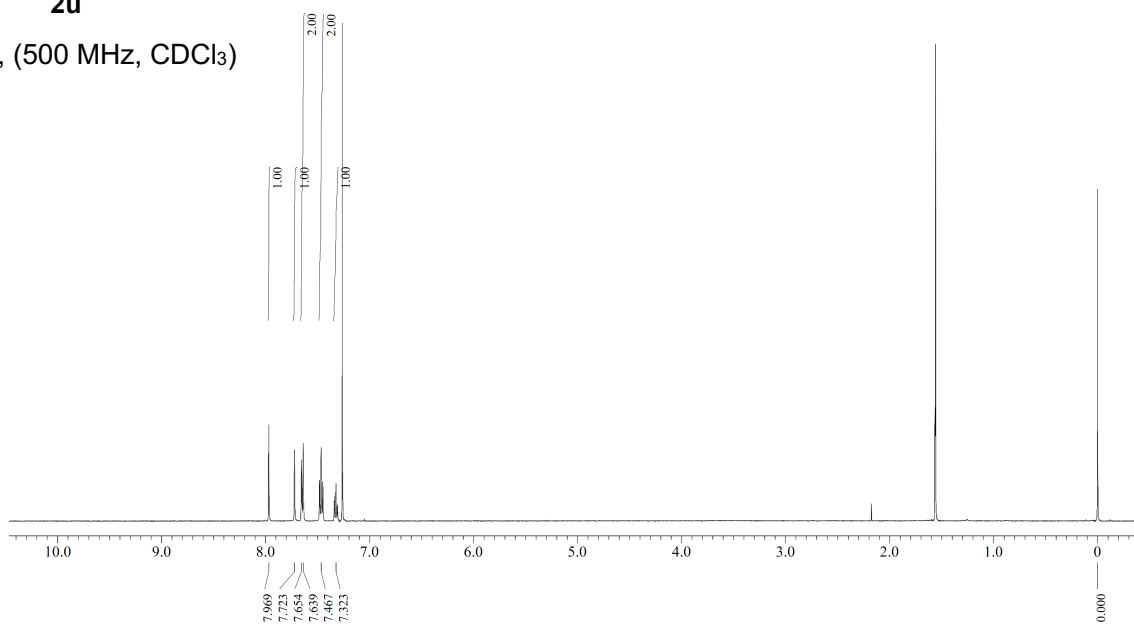
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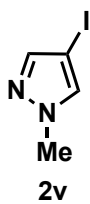
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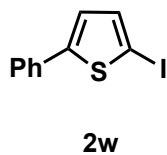
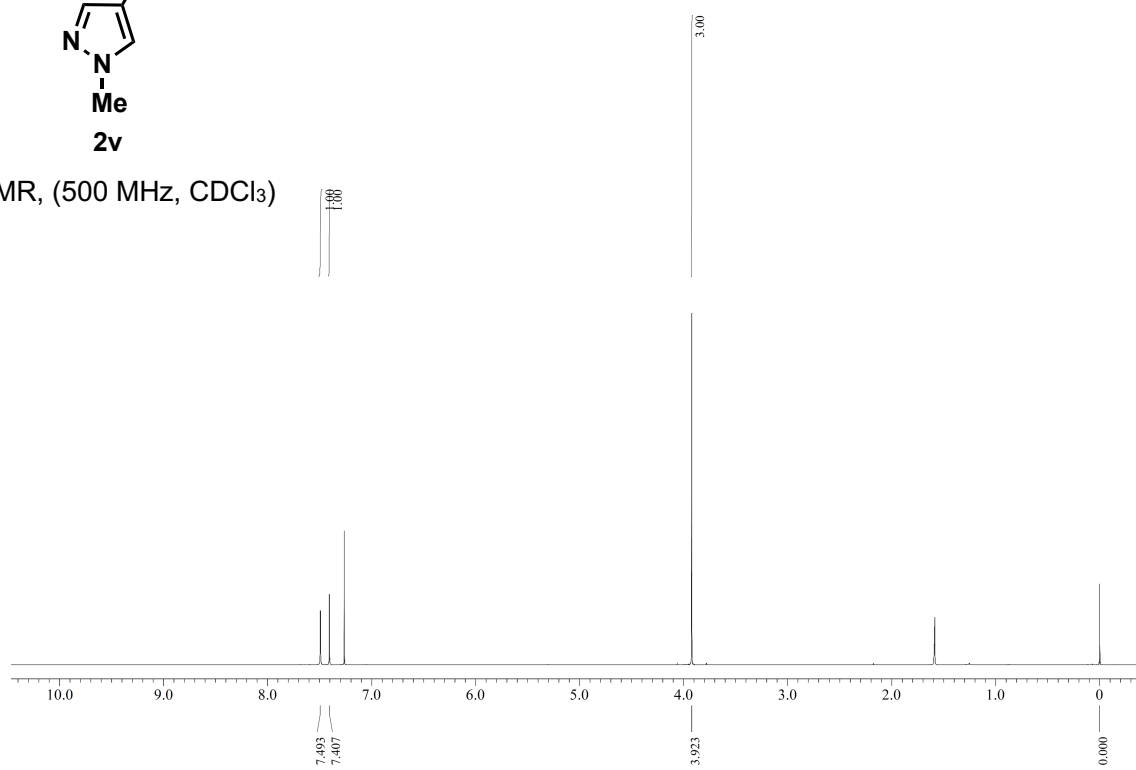
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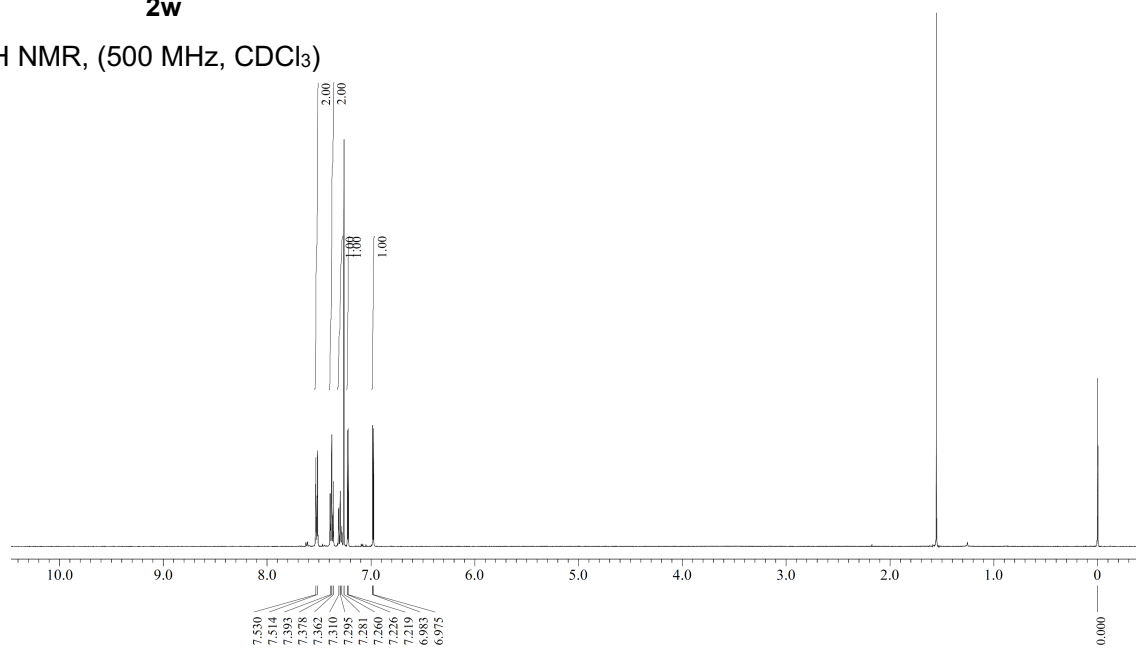


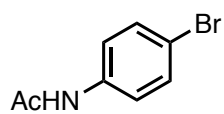


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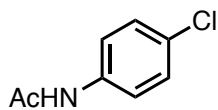
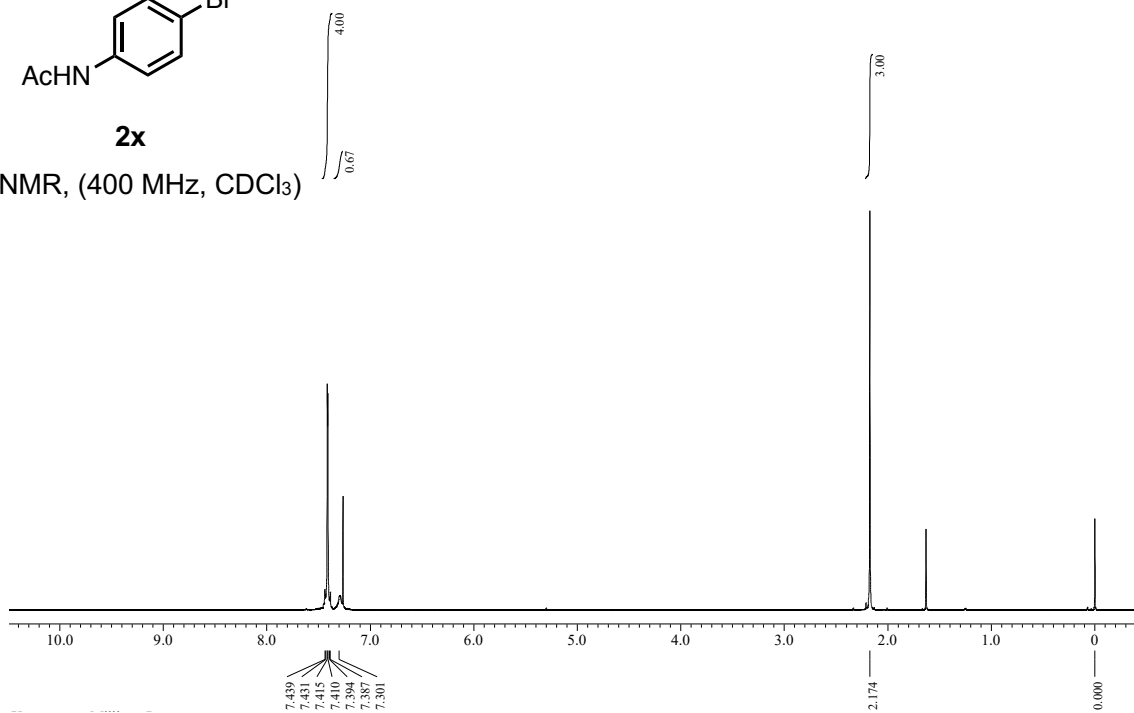
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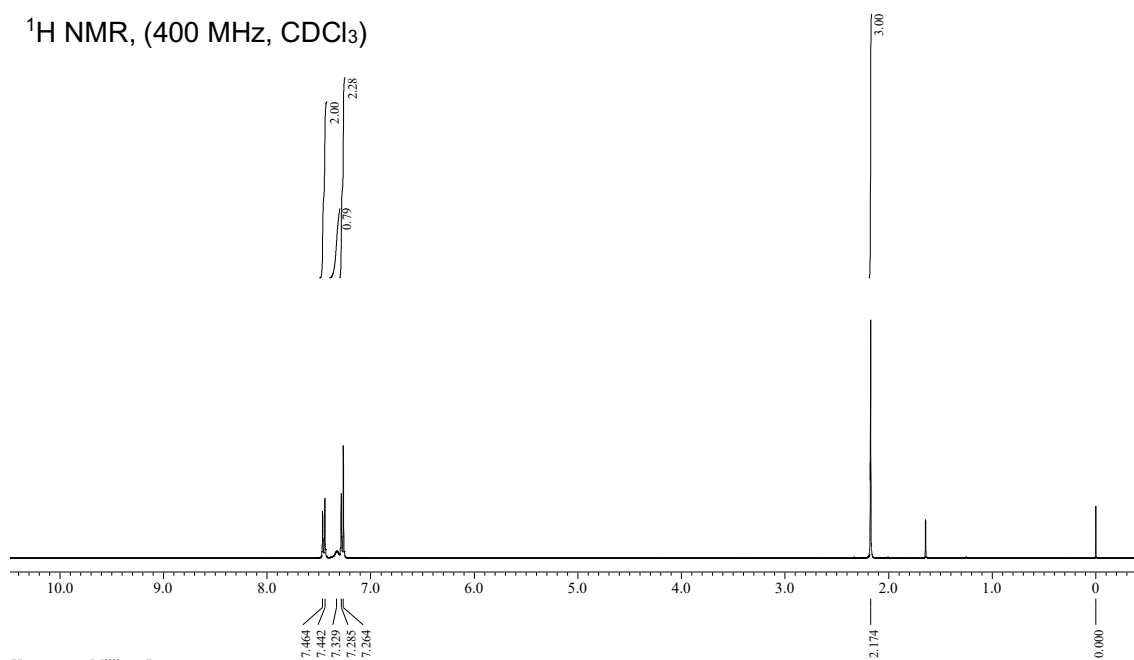
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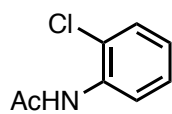
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2y

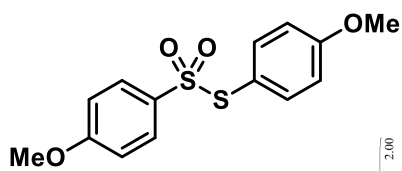
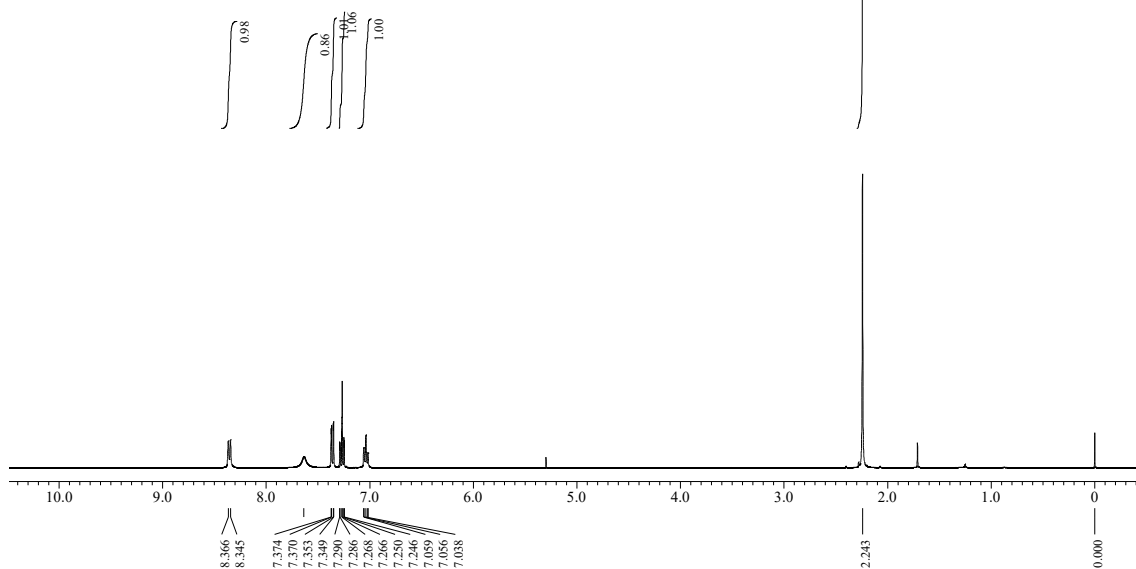
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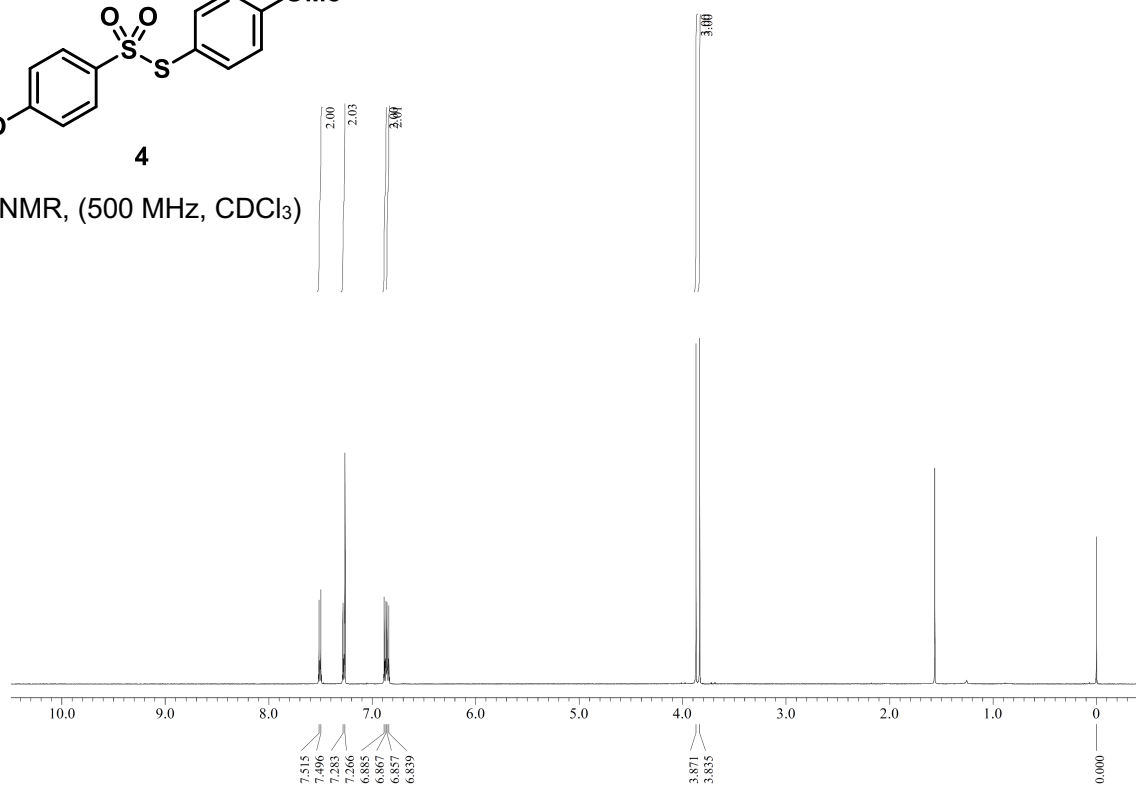
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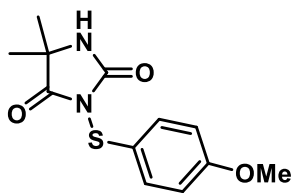
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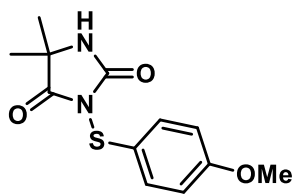
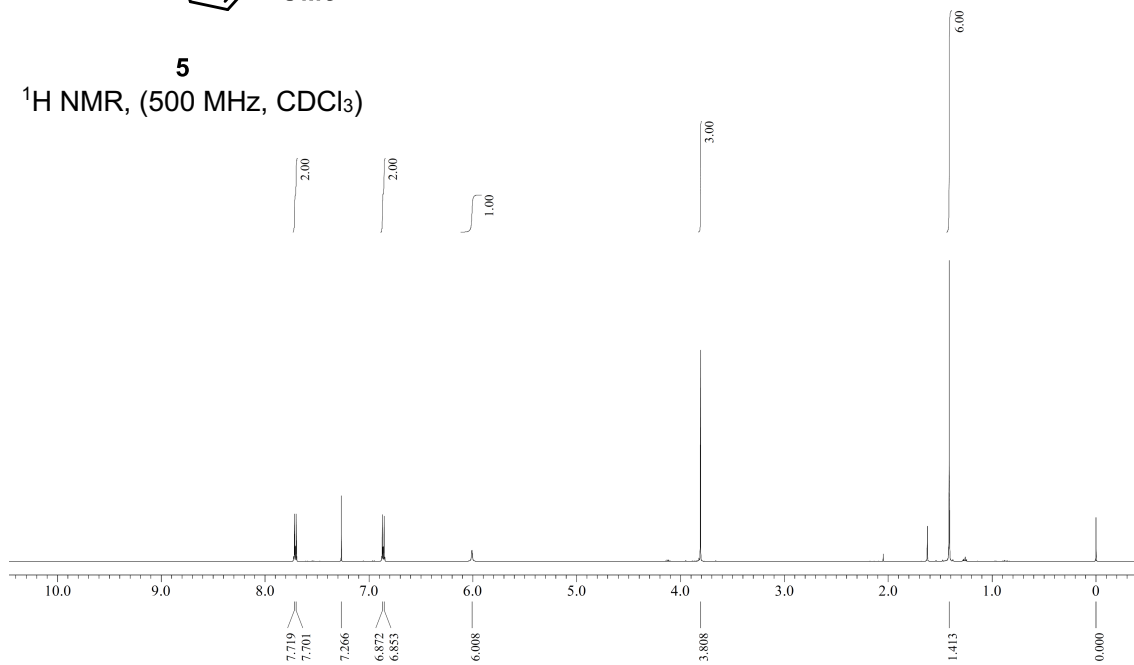
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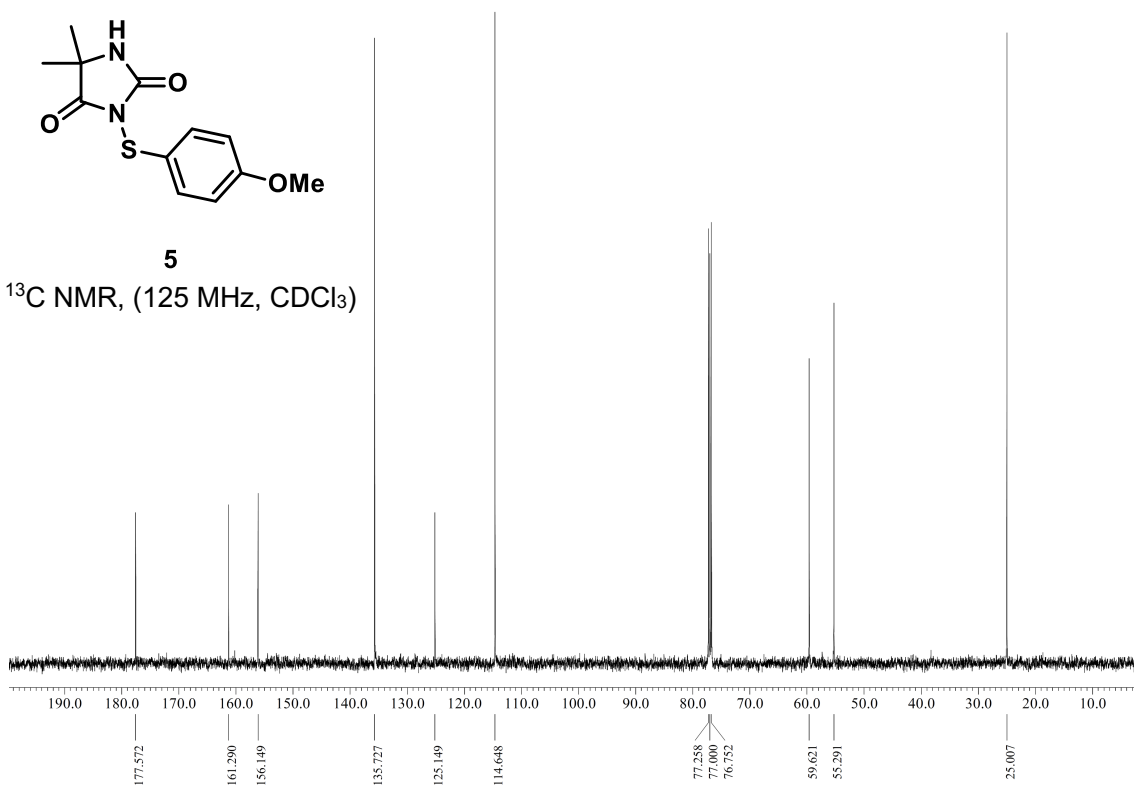
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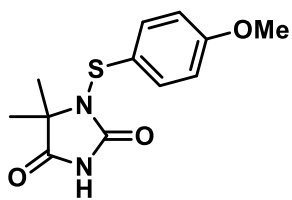
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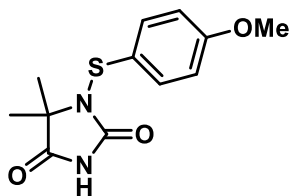
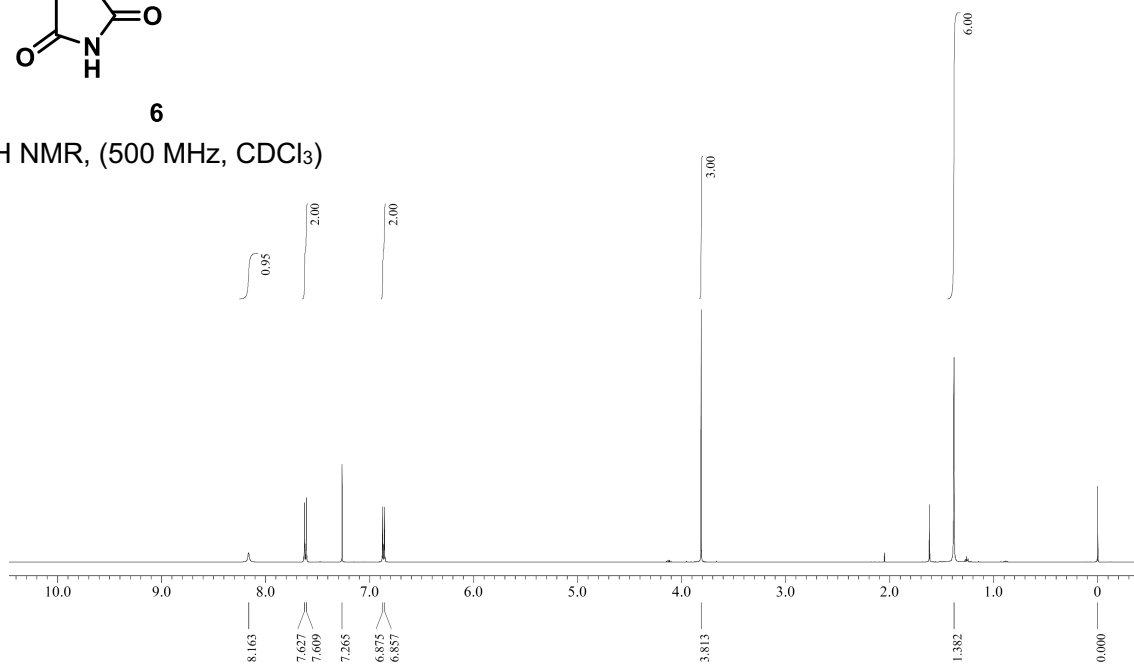
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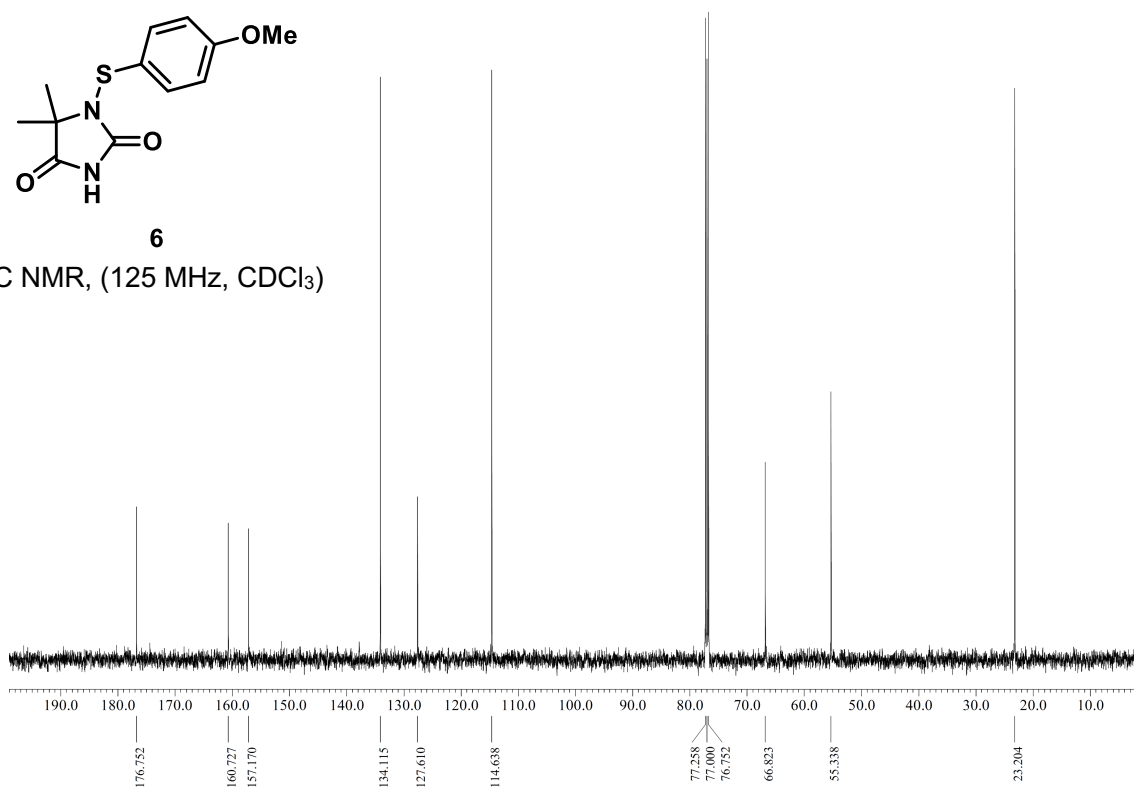
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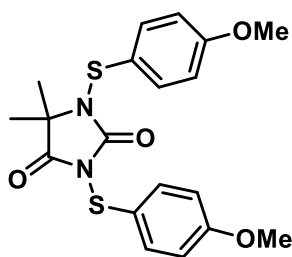
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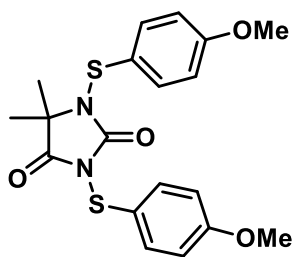
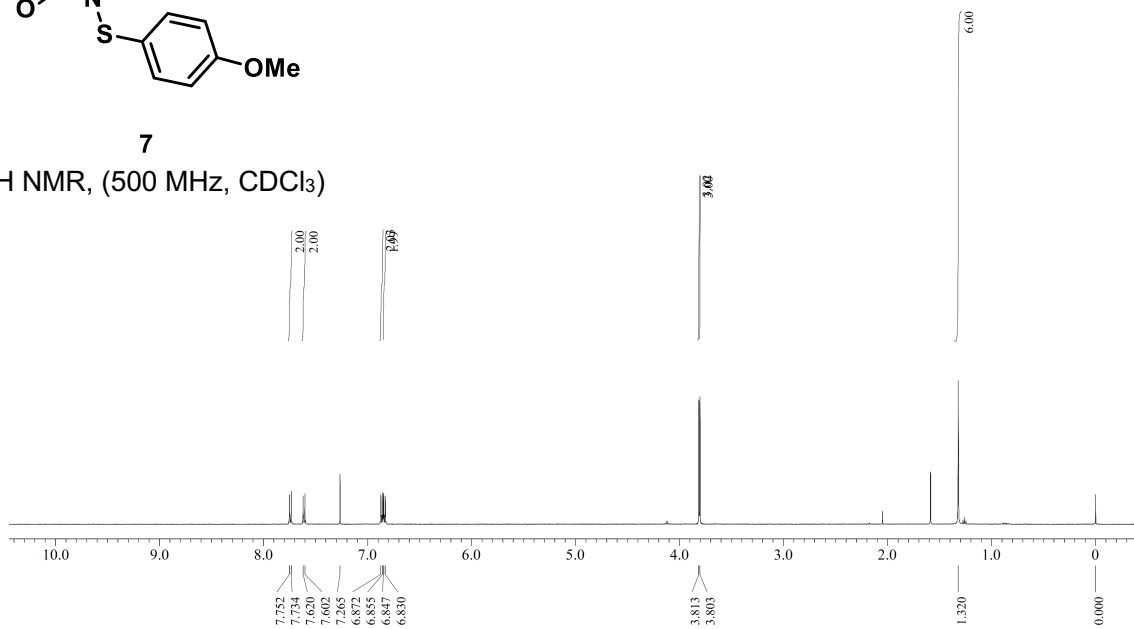
^{13}C NMR, (125 MHz, CDCl_3)





7

¹H NMR, (500 MHz, CDCl₃)



7

¹³C NMR, (125 MHz, CDCl₃)

