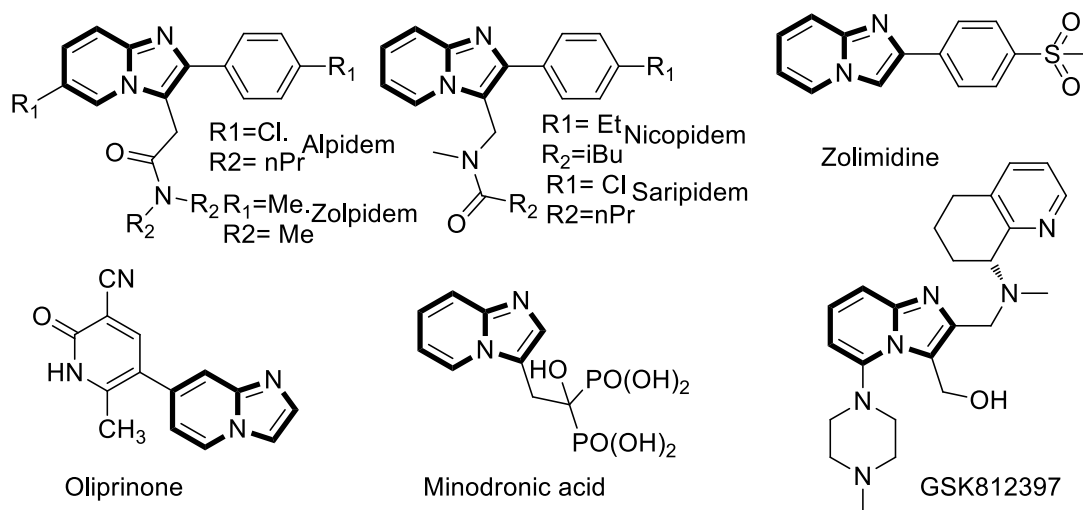


# **Dual role of p-tosylchloride; Copper Catalyzed Sulfenylation and Metal free Methylthiolation of Imidazo [1, 2-a] Pyridines**

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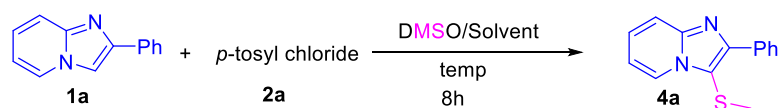


**Figure S1.** Imidazo[1,2-a]pyridine derived drugs

**Table S1.** Solvent screening for **3a**<sup>a</sup>

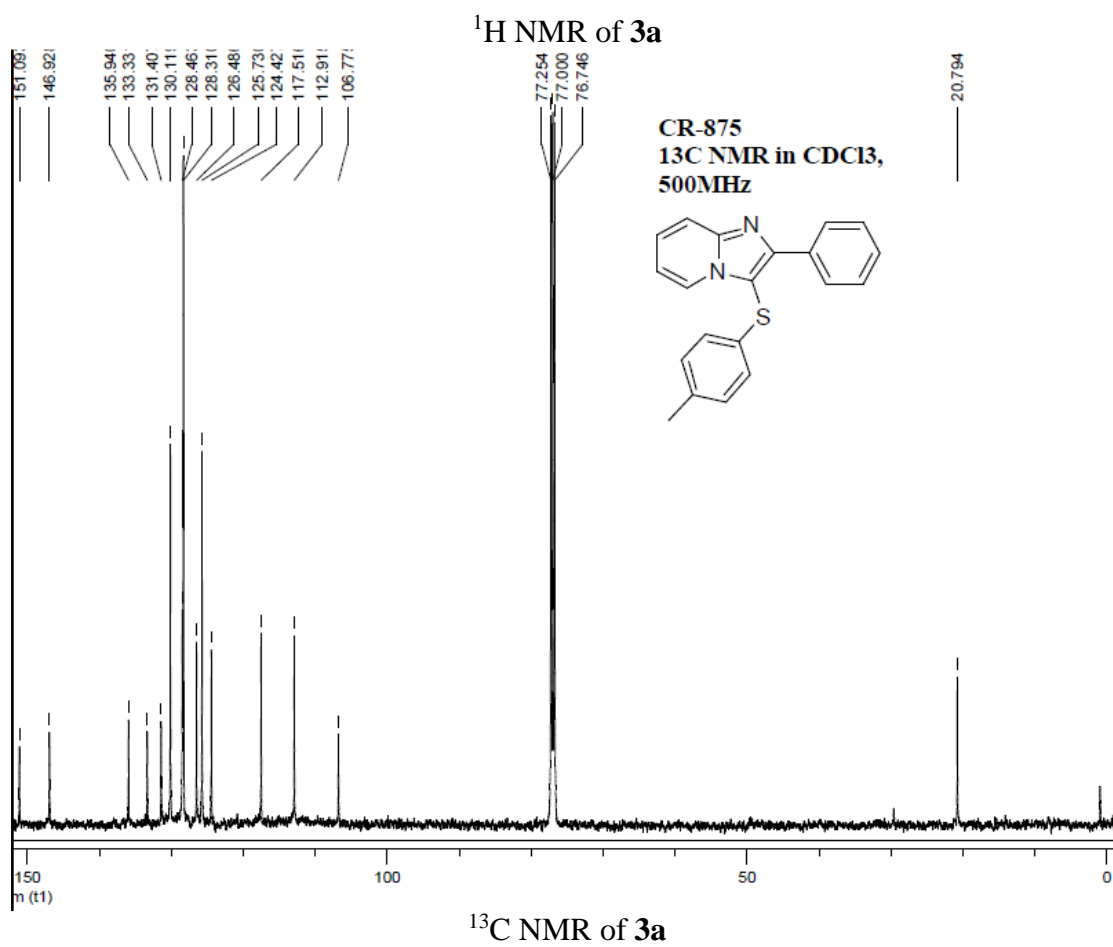
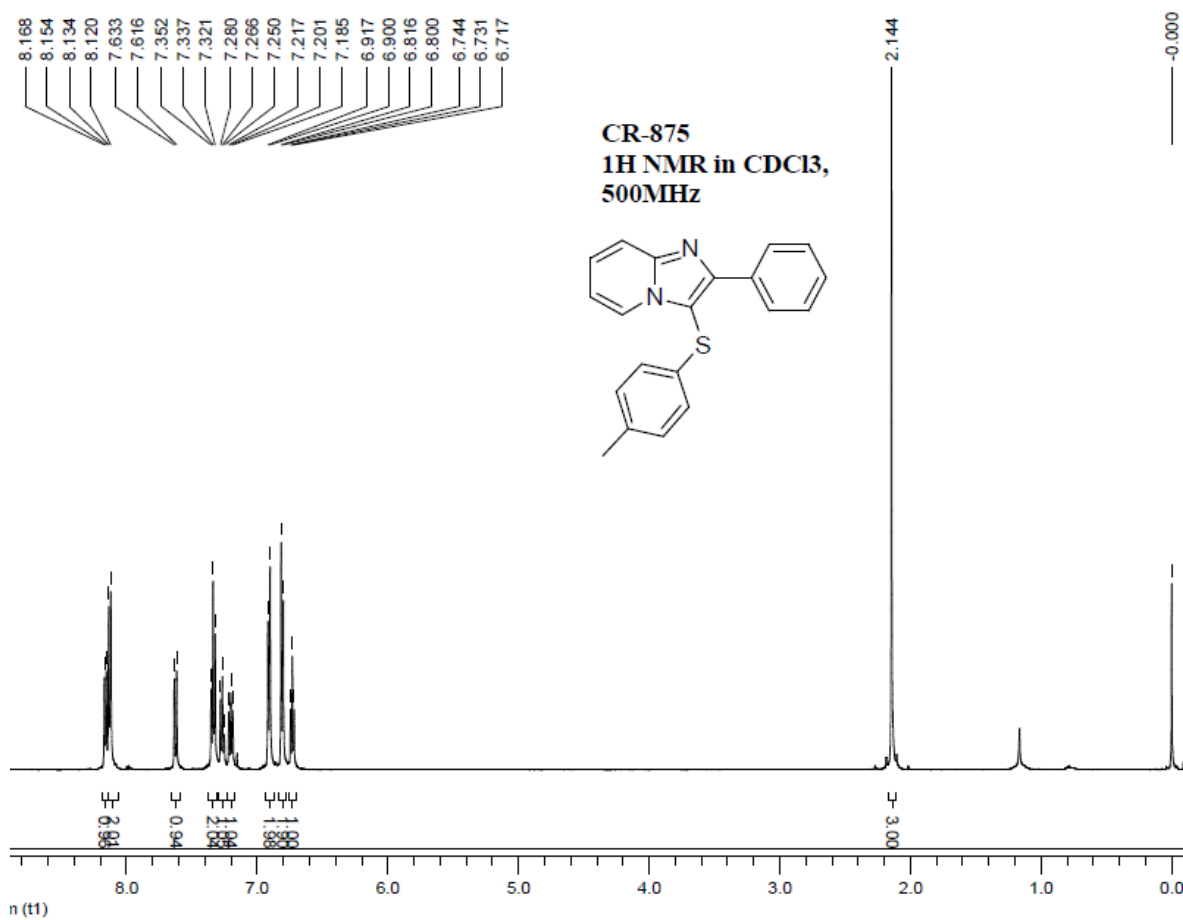
Entry	p-tosyl chloride(eq.)	catalyst(mol%)	solvent(mL)	temp(°C)	time(h)	Yield(%)
1	2	CuI(10mol%)	NMP/DCE (1:1)(1)	120	24	trace
2	2	CuI(10mol%)	DCE(1)	120	24	nr
3	2	CuI(10mol%)	DCB(1)	120	24	trace
4	2	CuI(10mol%)	toluene(1)	120	24	trace
5	2	CuI(10mol%)	1,4 Dioxane(1)	120	24	trace
6	2	CuI(10mol%)	Mesitylene(1)	120	24	nr
7	2	CuI(10mol%)	Chloro benzene(1)	120	24	nr
8	2	CuI(10mol%)	O-xylene(1)	120	24	nr
9	2	CuI(10mol%)	Diglyme(1)	120	24	trace
10	2	CuI(10mol%)	Nitrobenzene(1)	120	24	nr
11	2	CuI(10mol%)	DMSO	120	24	--(30) <sup>b</sup>
12 <sup>b</sup>	2	-	DMSO	120	24	30(39) <sup>b</sup>

<sup>a</sup>Reaction conditions: 2-phenylimidazo[1,2-a]pyridine (0.25 mmol), p-tosyl chloride(0.75 mmol), CuI(10mol%), PPh<sub>3</sub>(0.75mmol), DMSO(2 mL), 130°C, Closed tube. <sup>b</sup> Methylthiolated imidazo[1,2-a]pyridine **4a** was isolated.

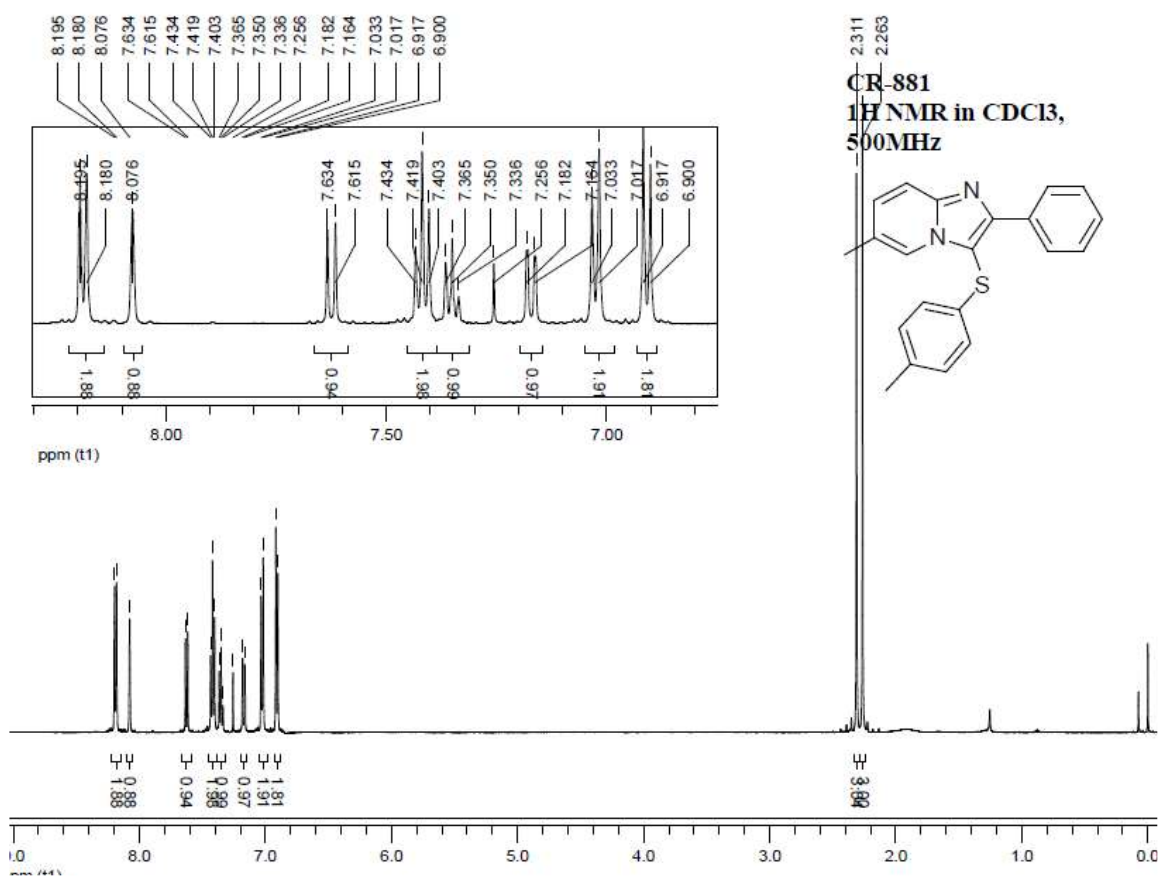
**Table S2.** Optimization of Reaction Conditions for **4a**<sup>a</sup>

Entry	<i>p</i> -tosyl chloride(eq)	DMSO/Solvent (mL)	temp(°C)	Yield(%)
1	2	1/-	120	39
2	0.2	1/-	120	33
3	0.4	1/-	120	30
4	2	1/-	100	44
5	1.5	1/-	100	66
6	1	1/-	100	60
7	1.5	0.2/-	100	66
8	1.5	0.2/toluene(0.5)	100	57
9	1.5	0.2/DCB(0.5)	100	61
<b>10</b>	<b>1.5</b>	<b>0.2/DCE(0.5)</b>	<b>100</b>	<b>91</b>
11	1.5	0.2/DCE(0.5)	rt	nr
12	1.5	0.2/DCE(0.5)	60	36
13	1.5	0.2/DCE(0.5)	80	80
14 <sup>b</sup>	1.5	0.2/DCE(0.5)	100	66
15 <sup>c</sup>	1.5	0.2/DCE(0.5)	100	47
16	--	0.2/DCE(0.5)	100	nr

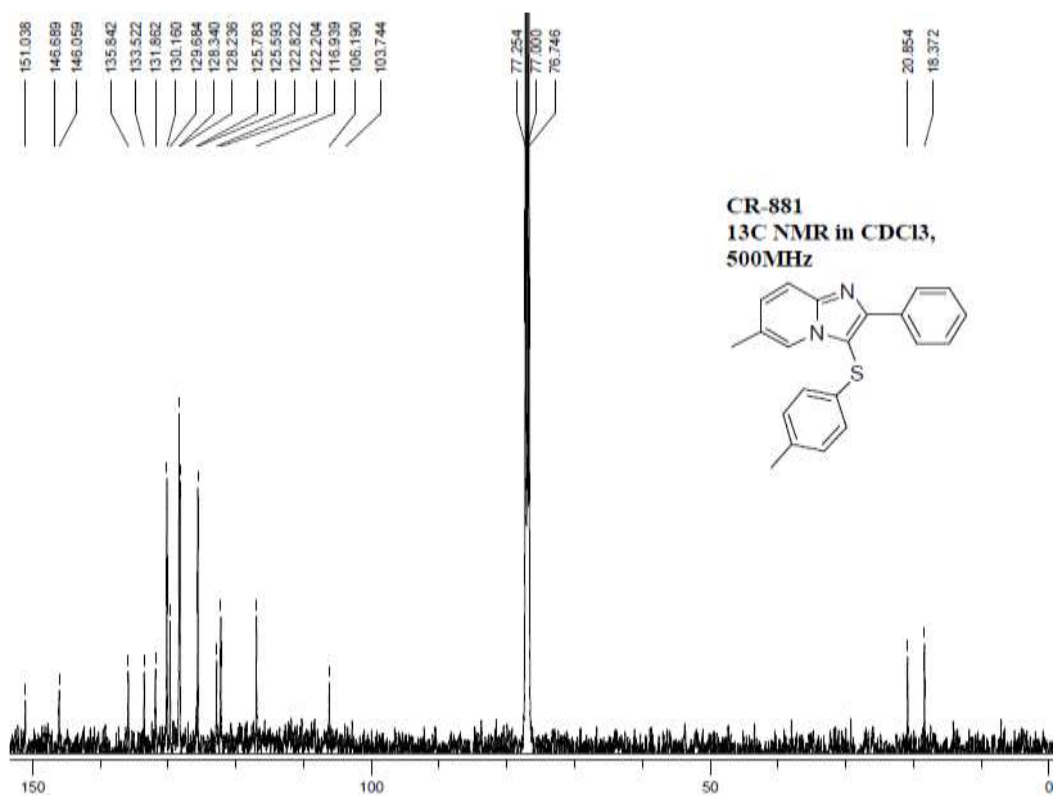
<sup>a</sup>Reaction conditions: 2-Phenylimidazo[1,2-a]pyridine **1a** (0.25 mmol), *p*-tosyl chloride, DMSO/solvent, temperature, open air, isolated yields. <sup>b</sup>Argon atmosphere. <sup>c</sup>O<sub>2</sub> balloon. nr: no reaction.



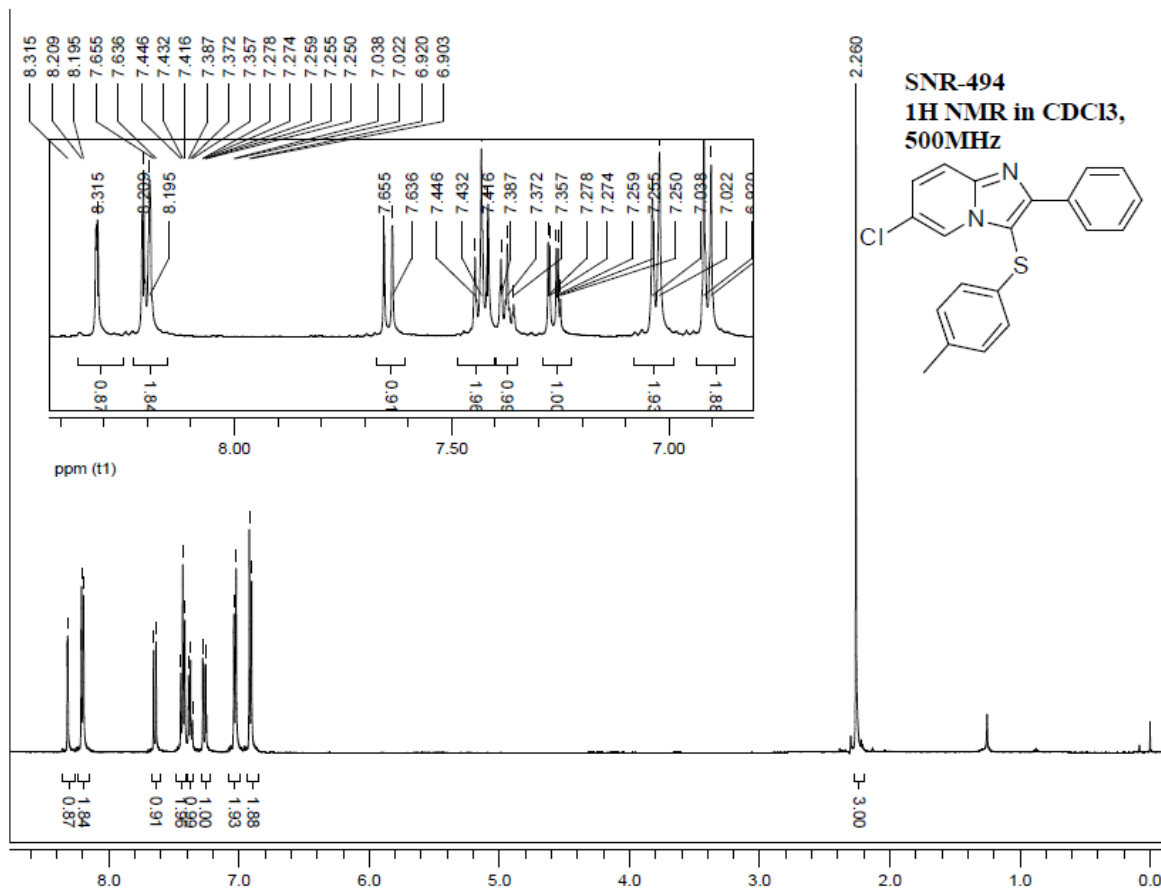




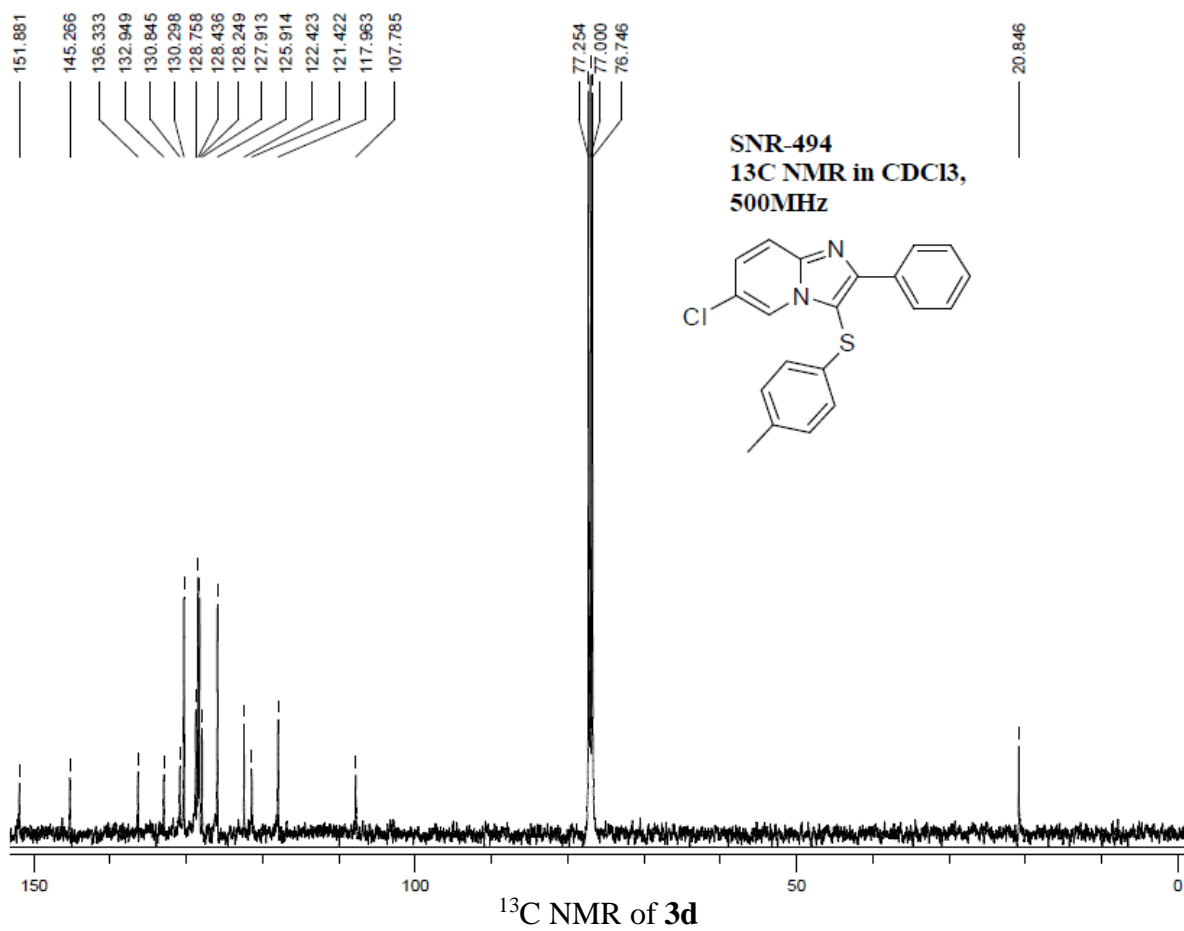
<sup>1</sup>H NMR of **3c**



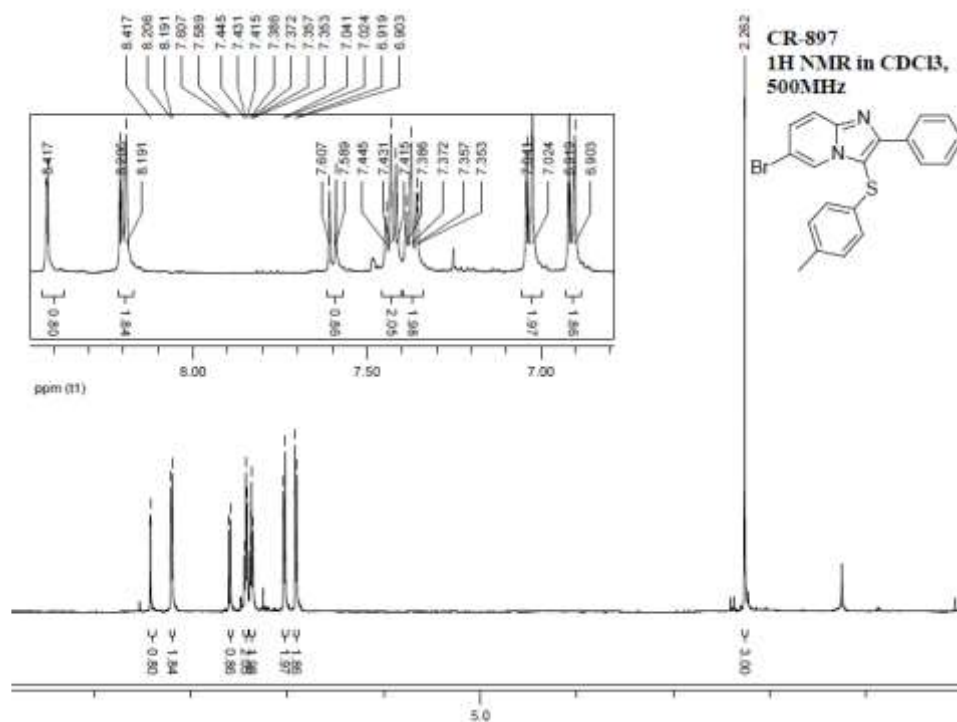
<sup>13</sup>C NMR of **3c**



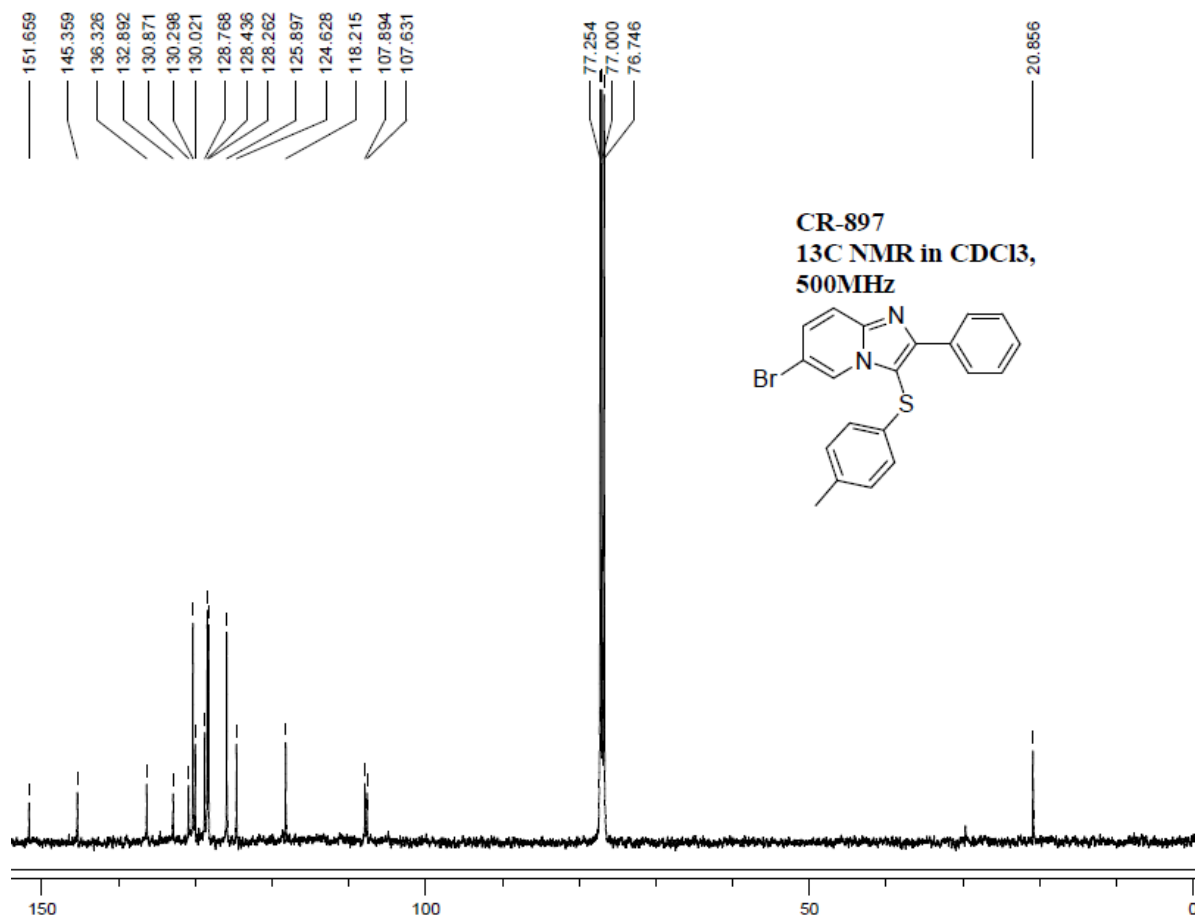
<sup>1</sup>H NMR of 3d



<sup>13</sup>C NMR of 3d

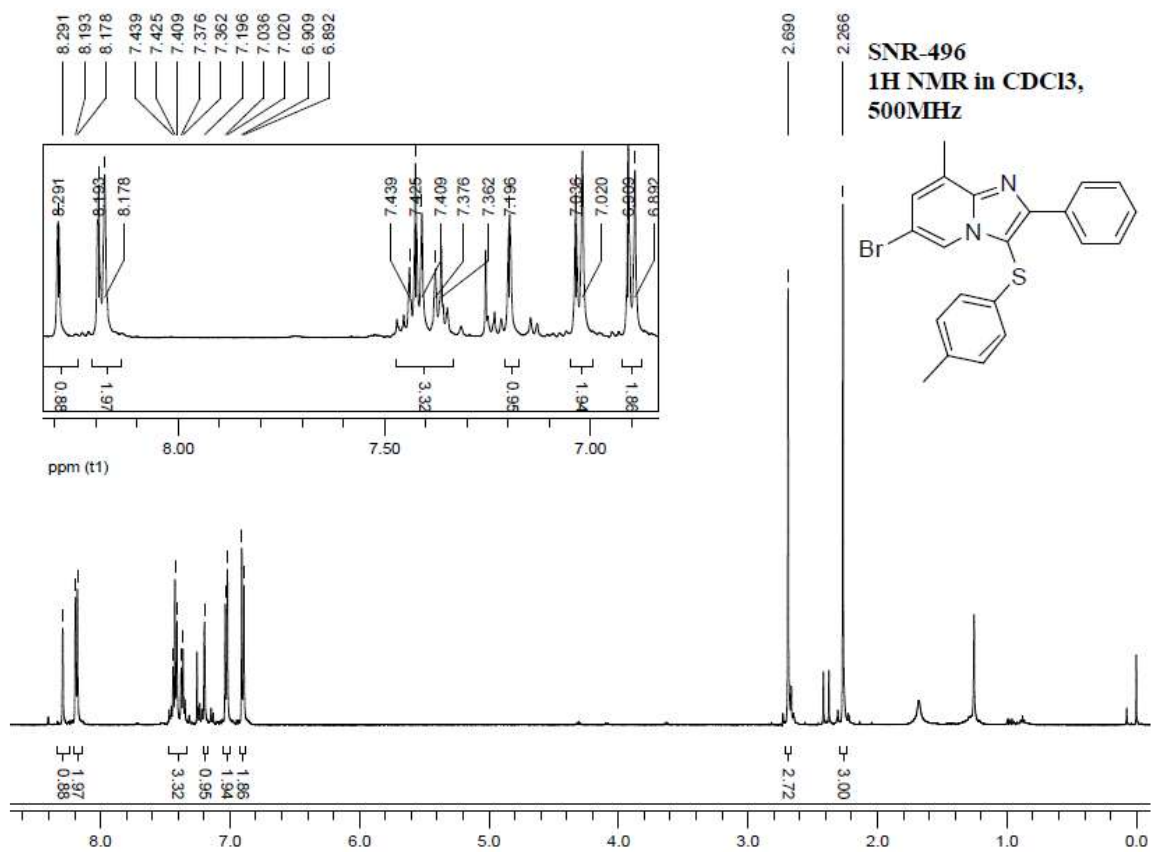


1H NMR of 3e

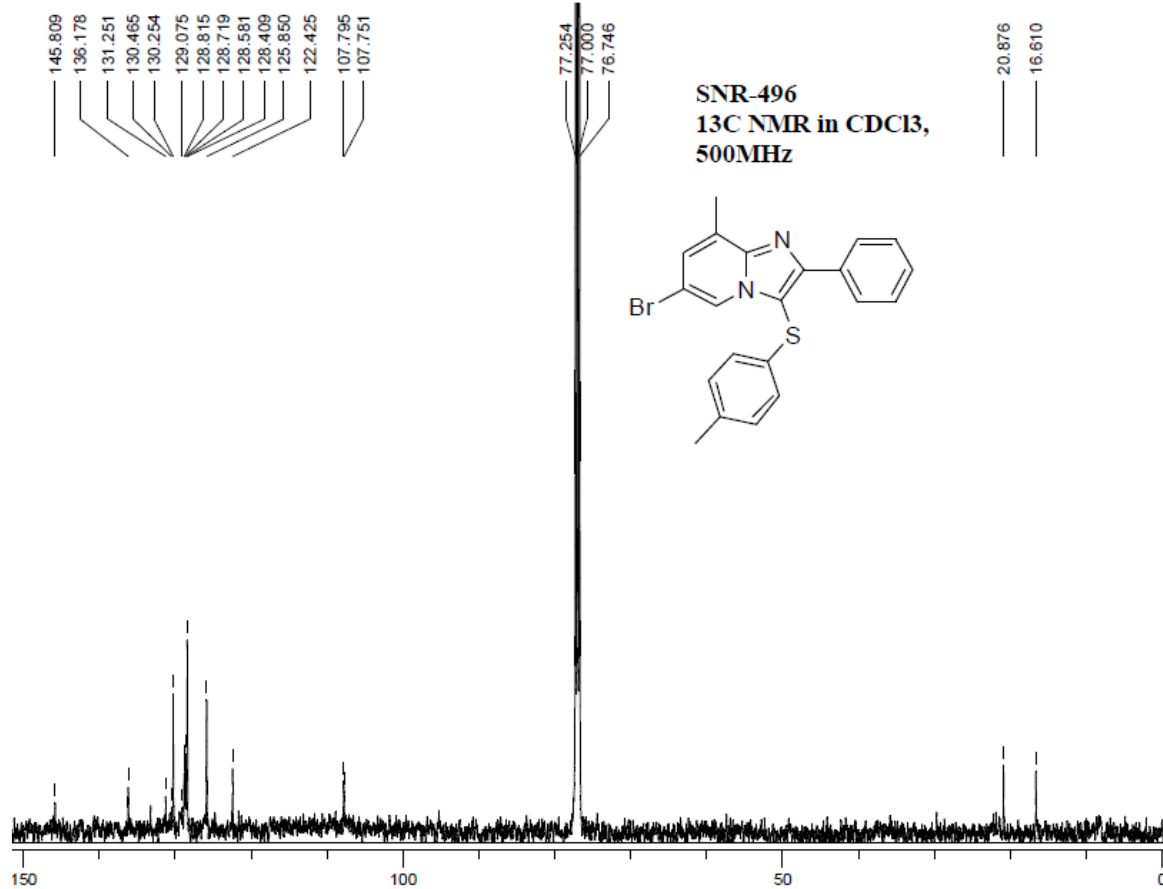


13c NMR of 3e

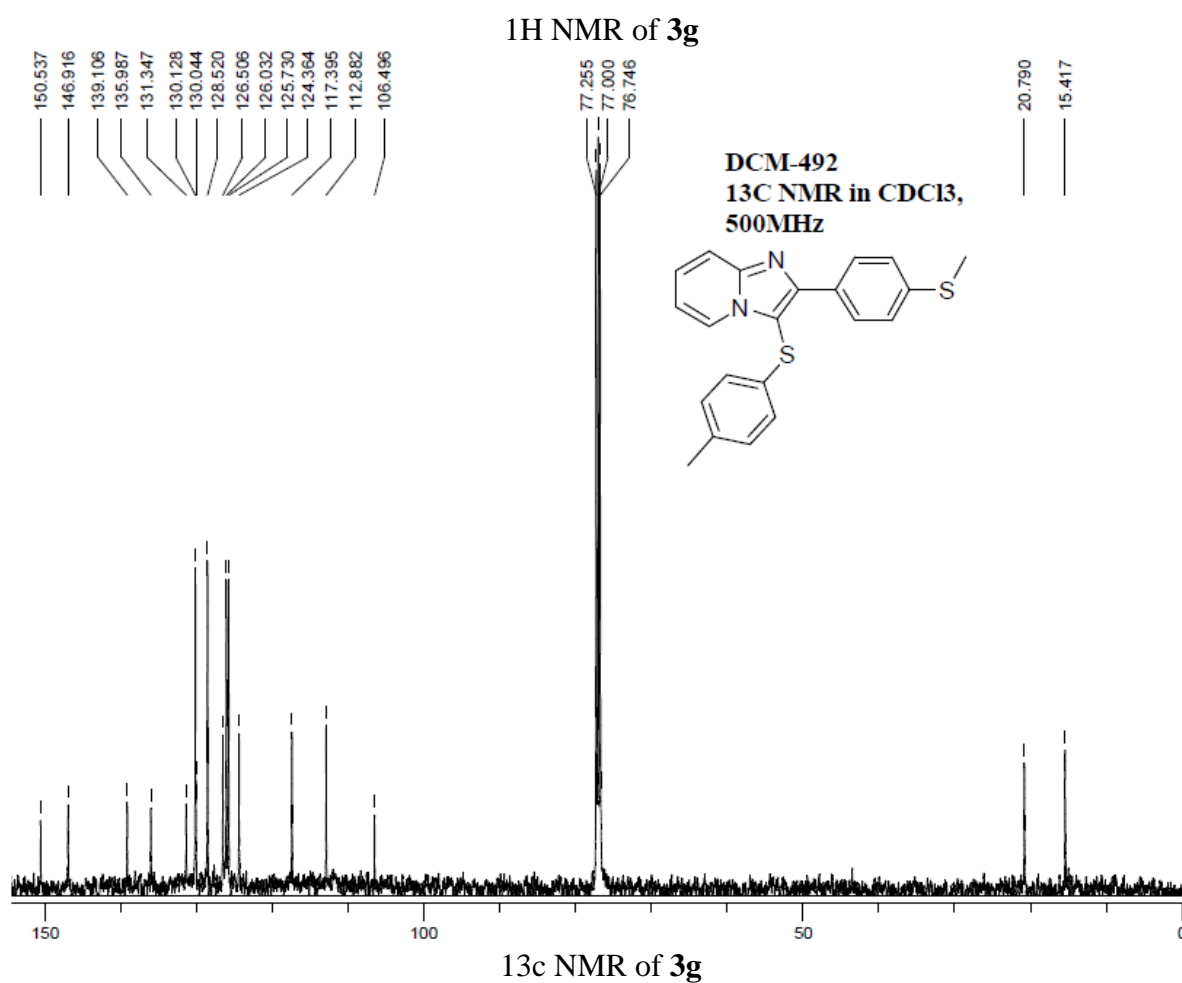
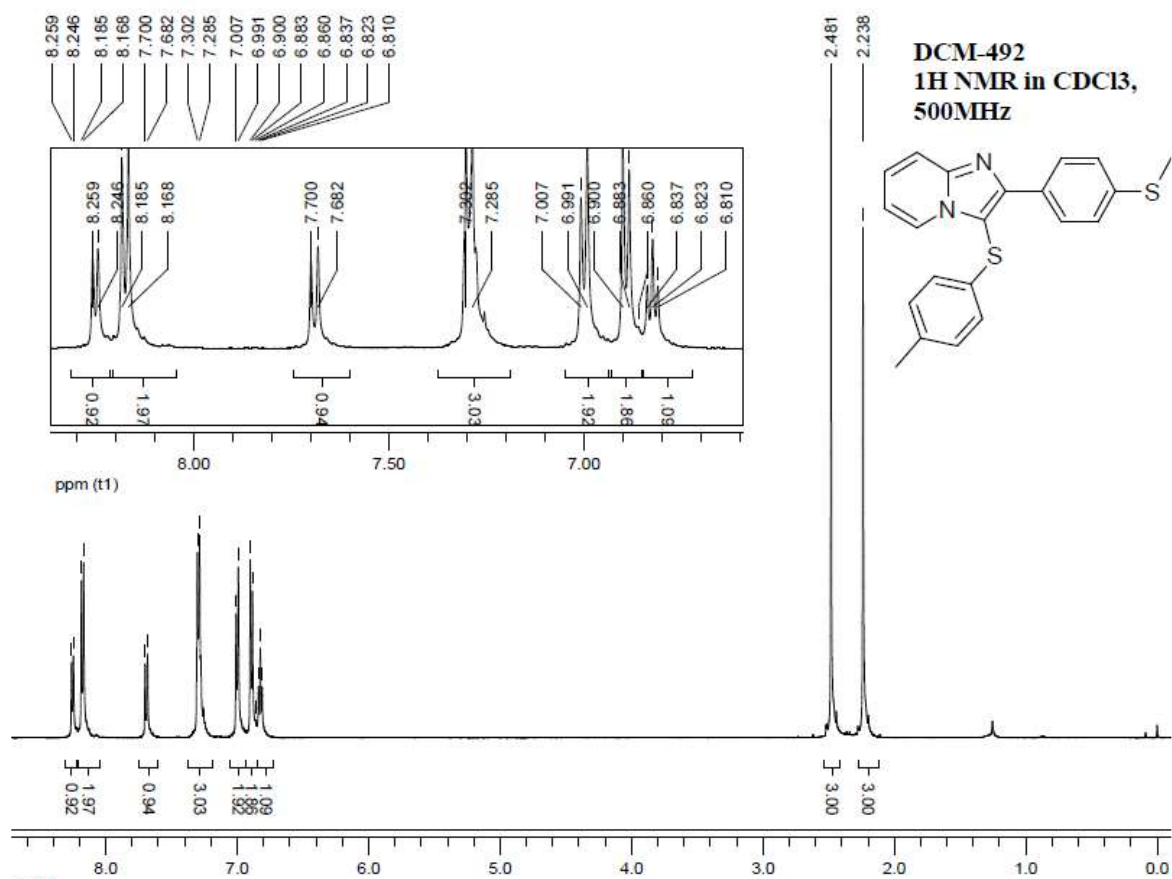


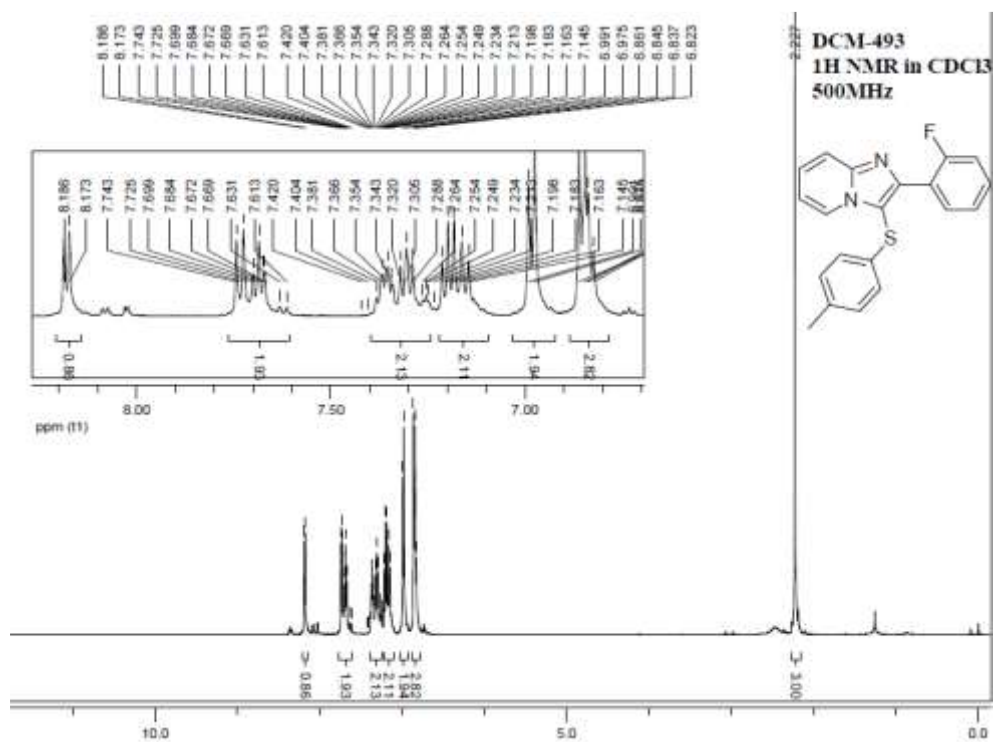


**<sup>1</sup>H NMR of 3f**

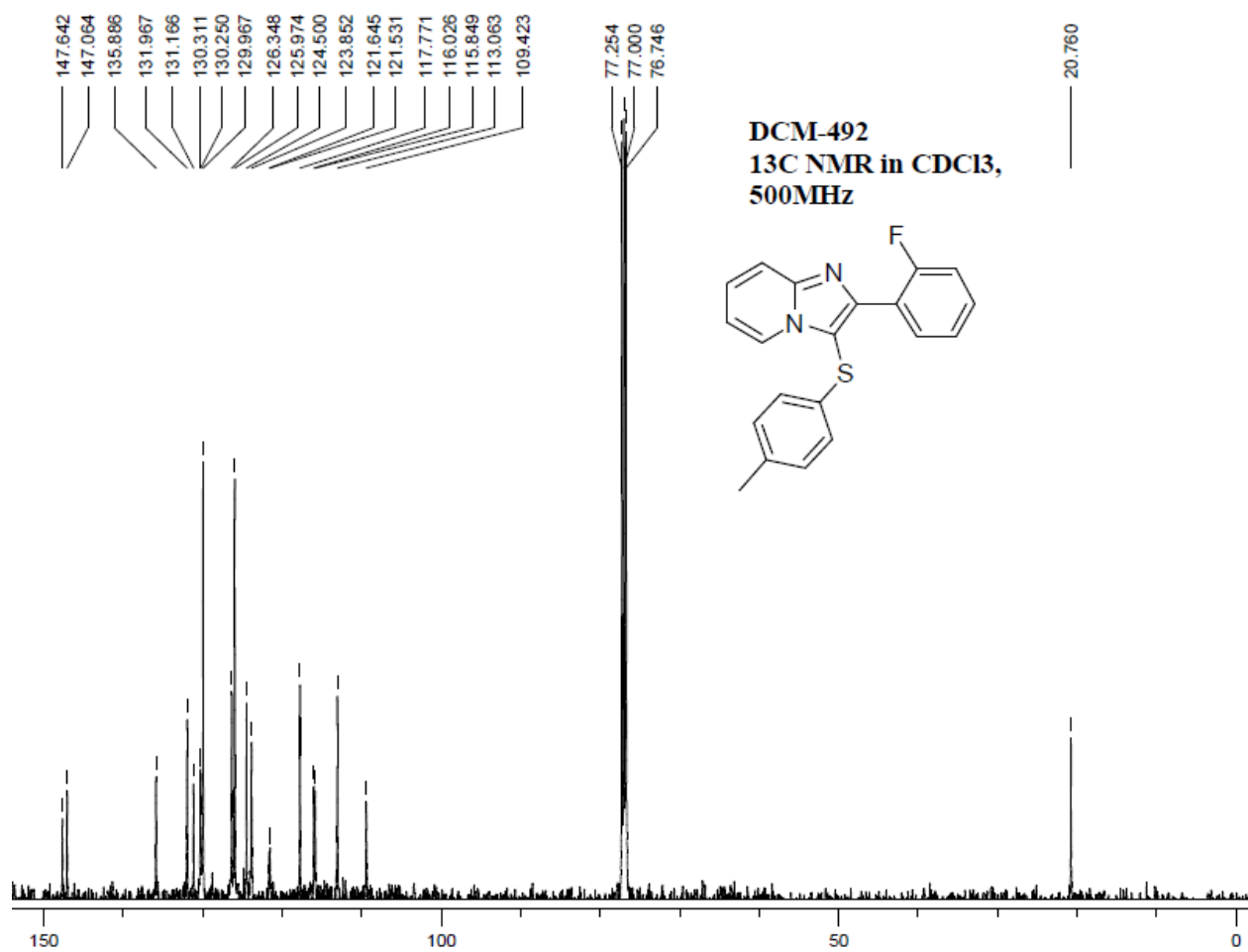


**<sup>13</sup>C NMR of 3f**

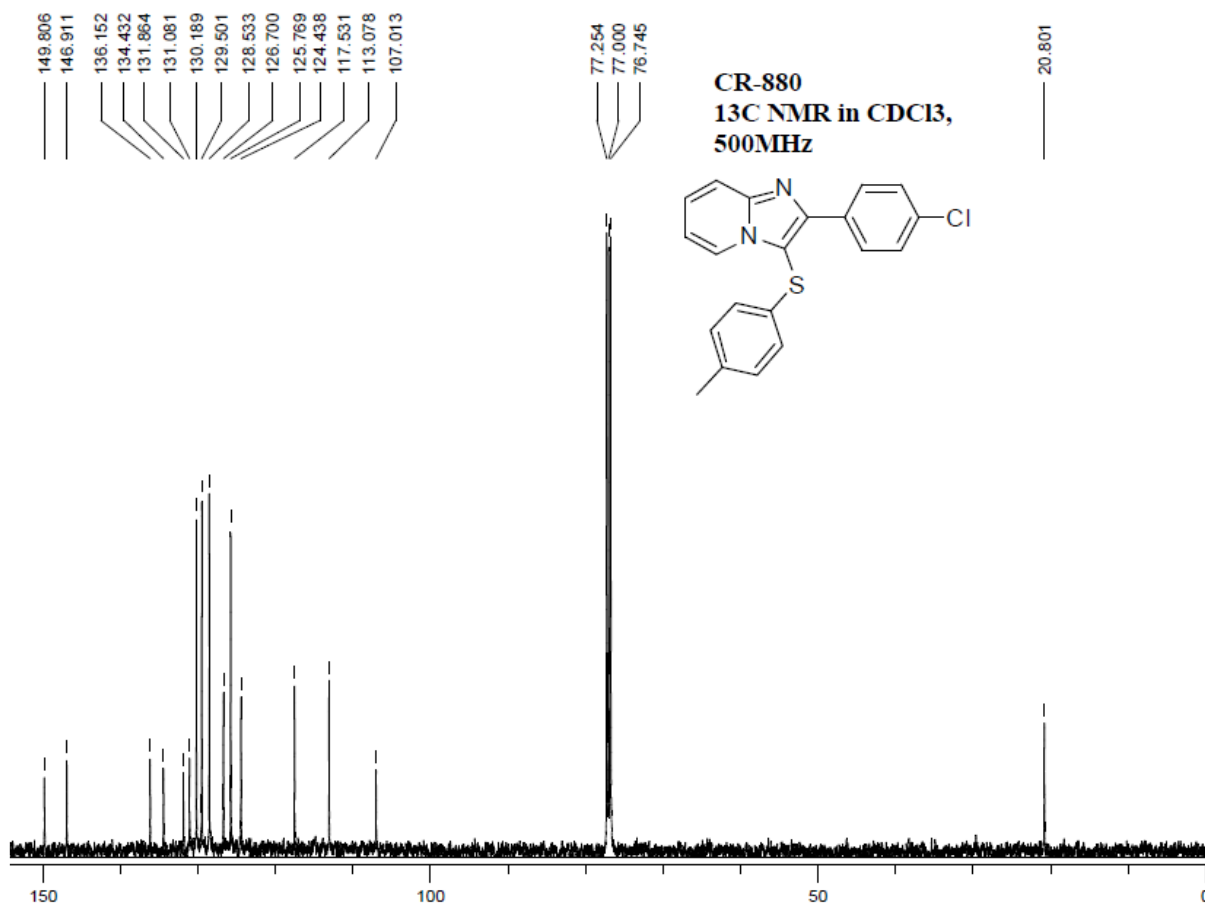
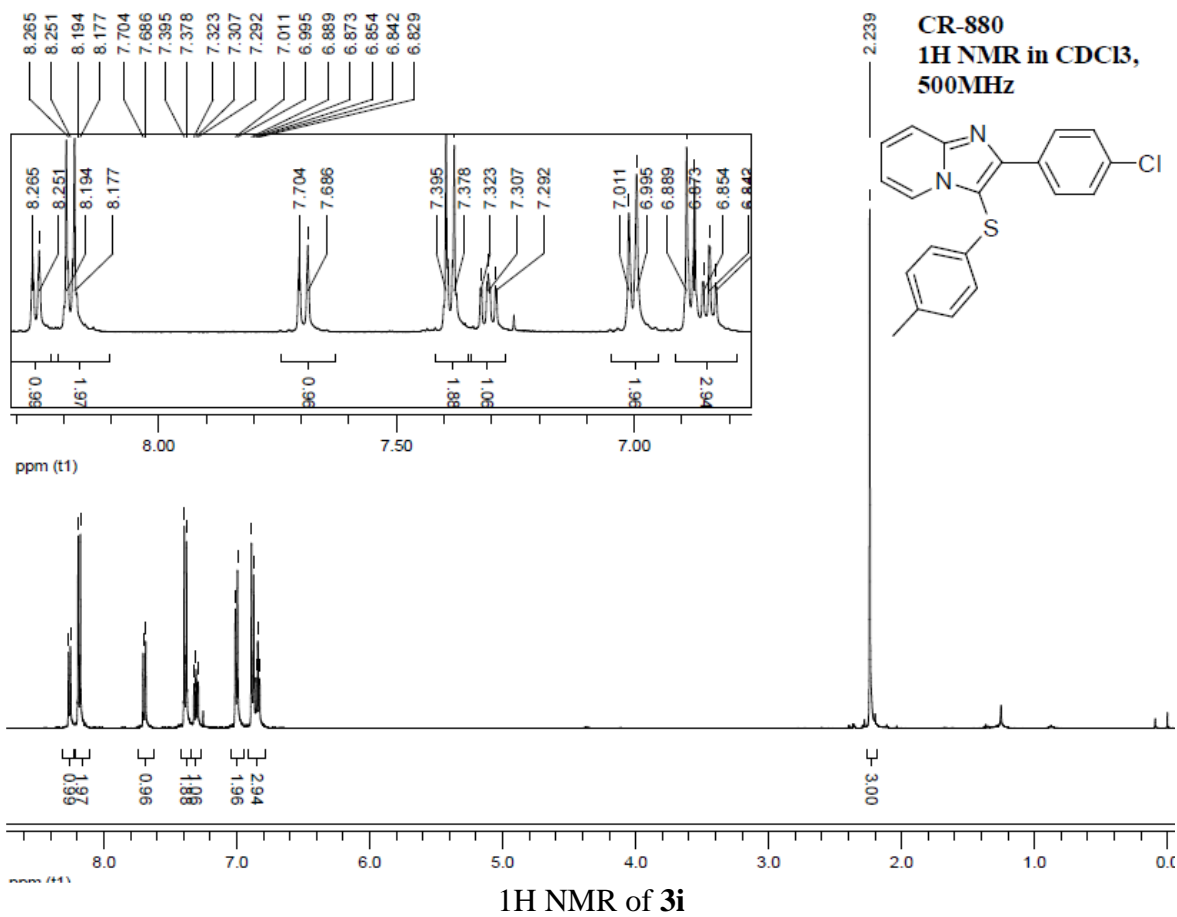




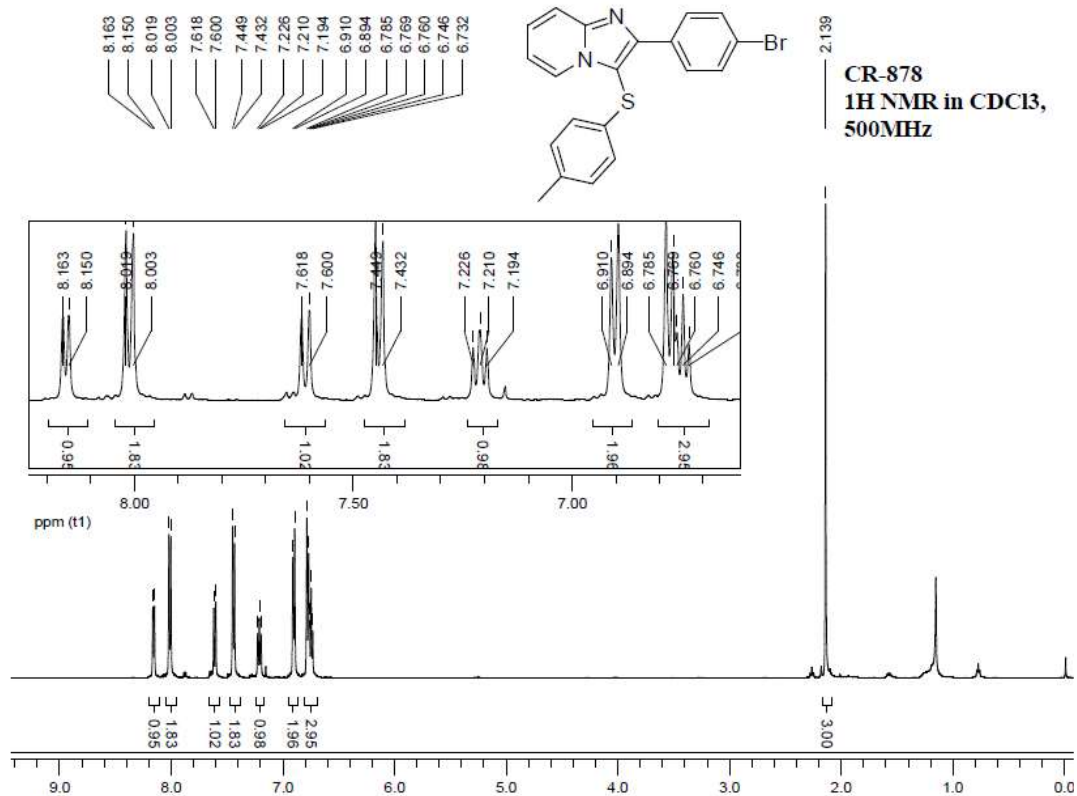
**<sup>1</sup>H NMR of 3h**



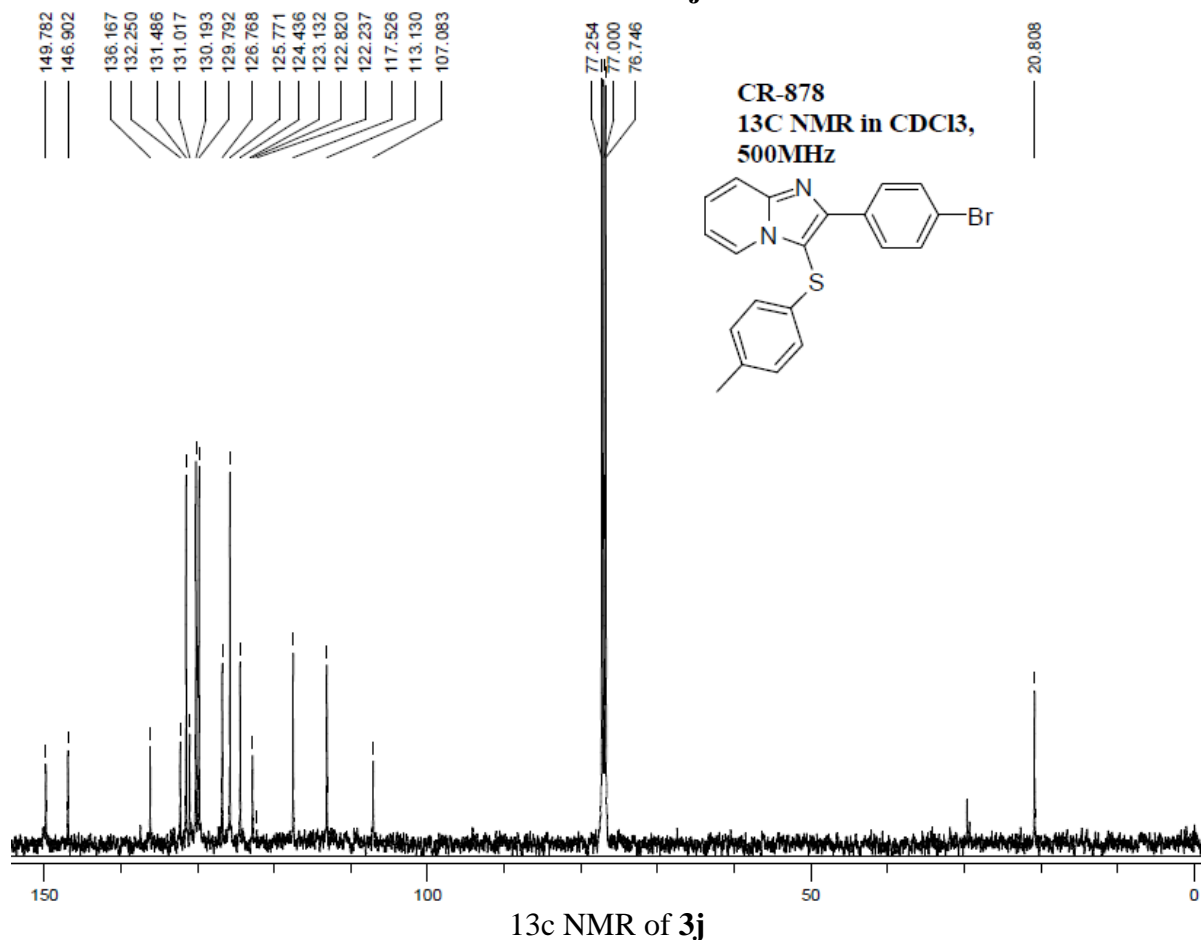
**<sup>13</sup>C NMR of 3h**



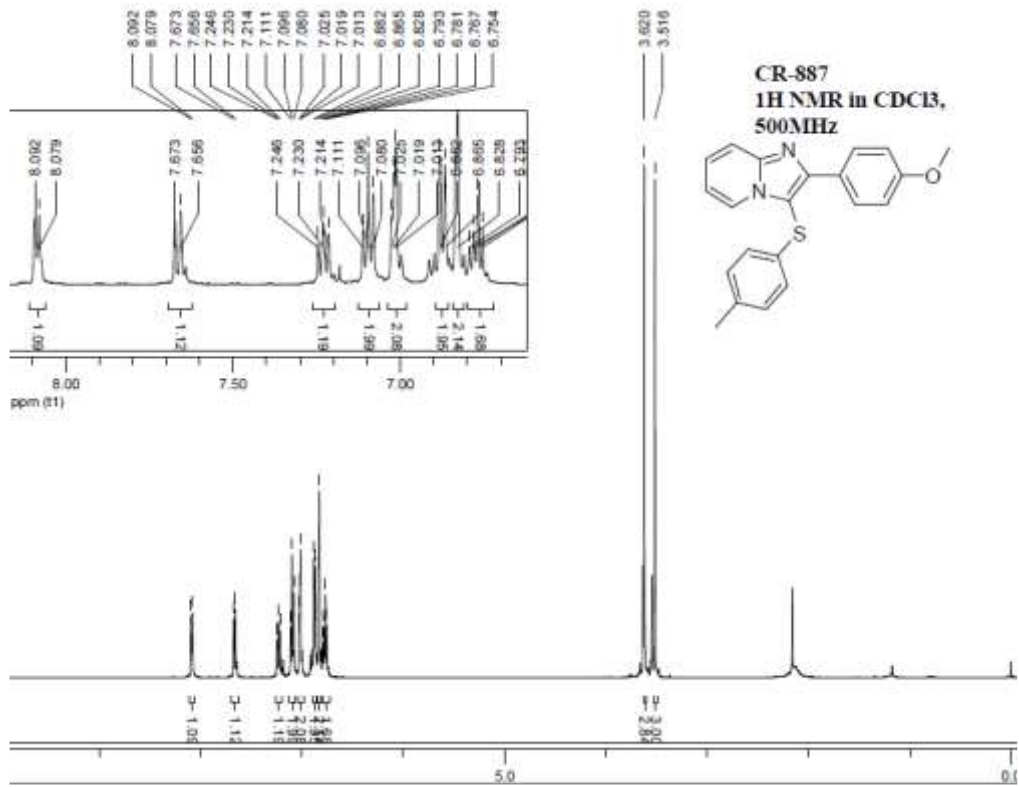
### <sup>13</sup>C NMR of **3i**



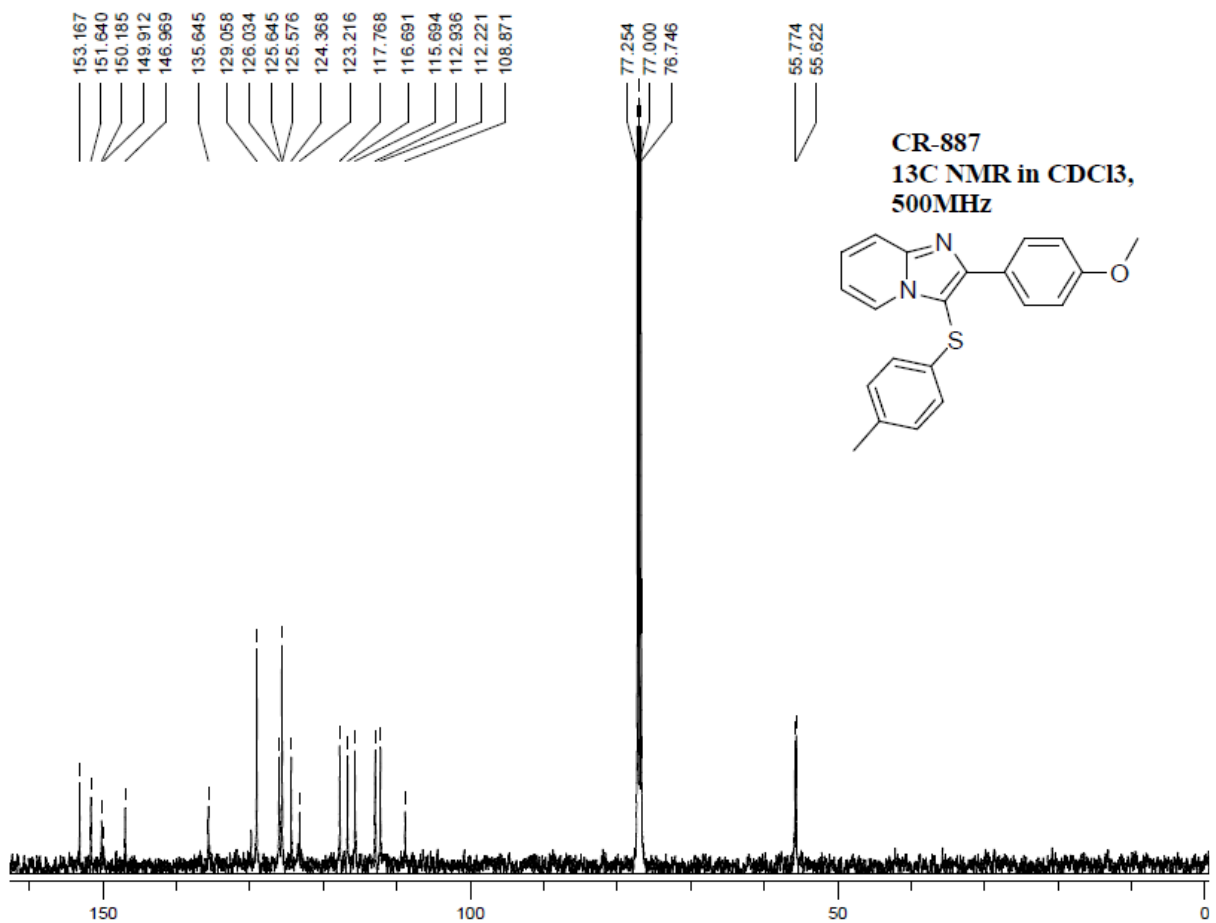
### <sup>1</sup>H NMR of **3j**



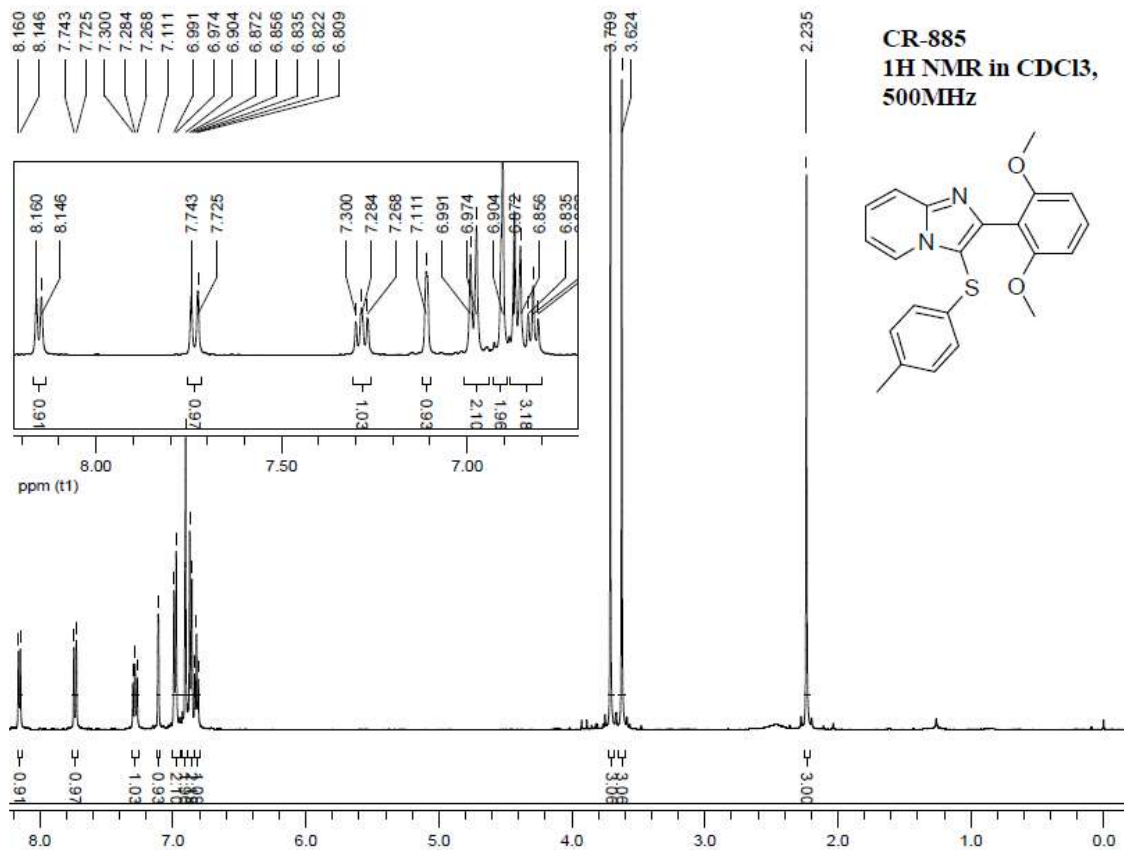
### <sup>13</sup>C NMR of **3j**



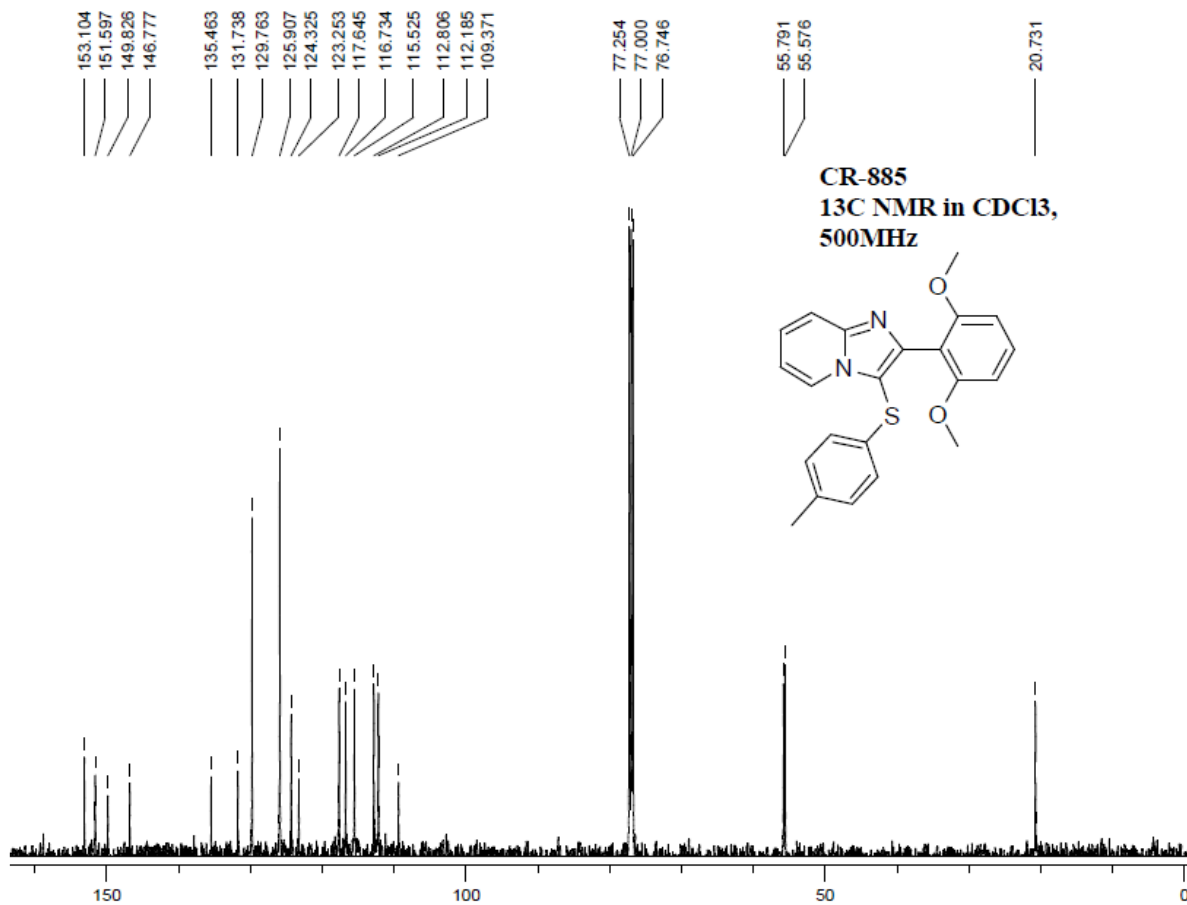
**<sup>1</sup>H NMR of 3k**



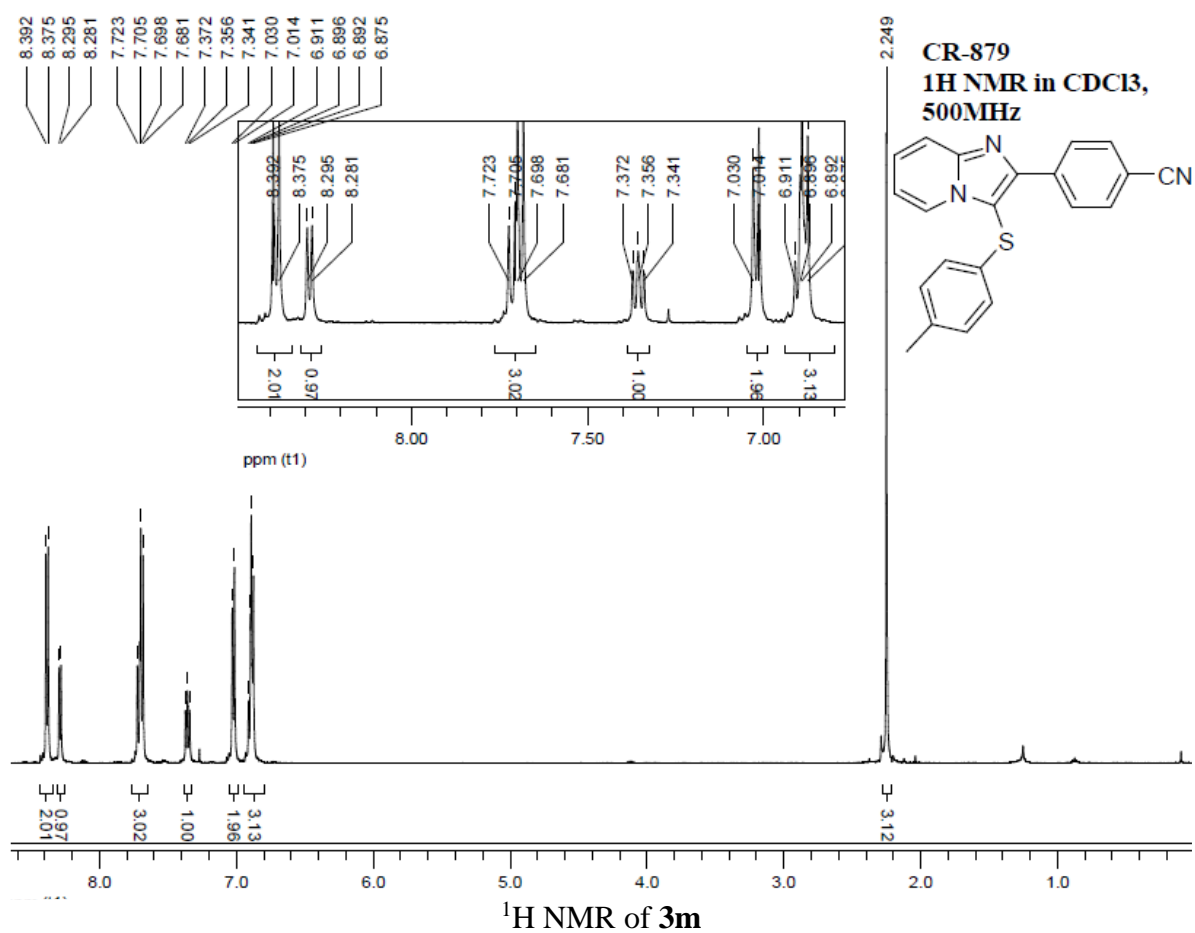
<sup>13</sup>C NMR of 3k



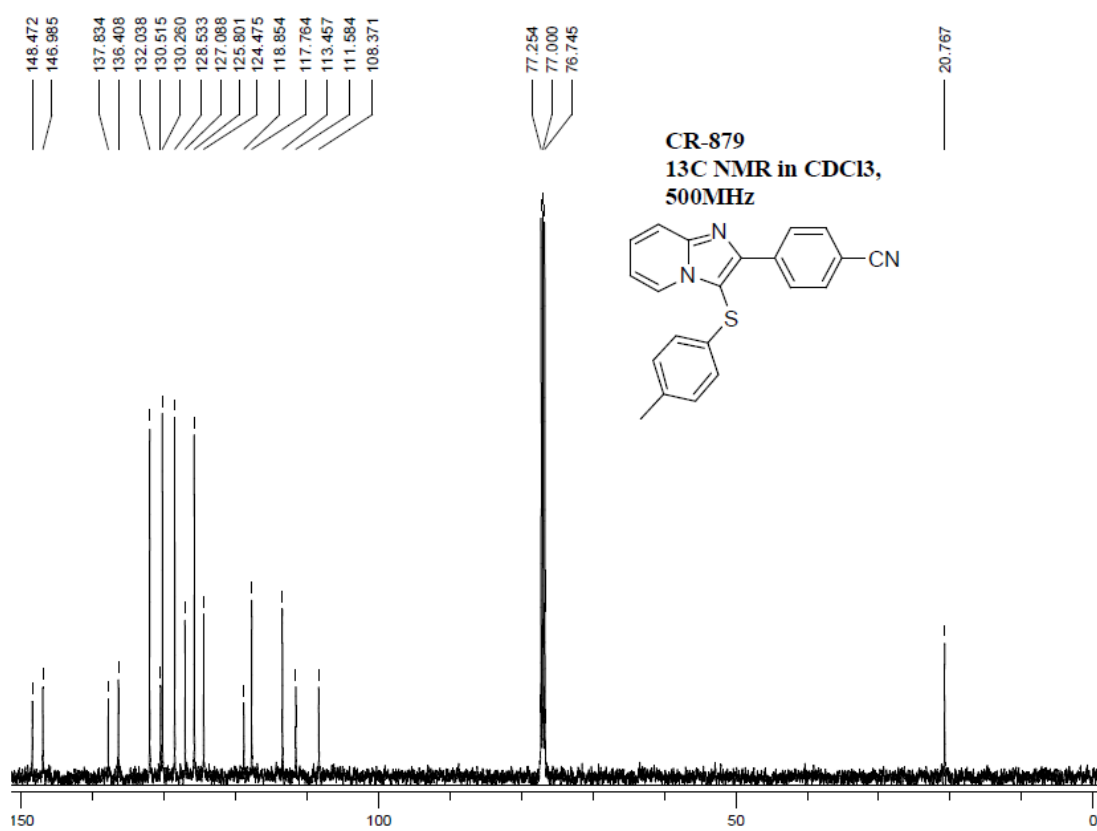
<sup>13</sup>C NMR of 3l



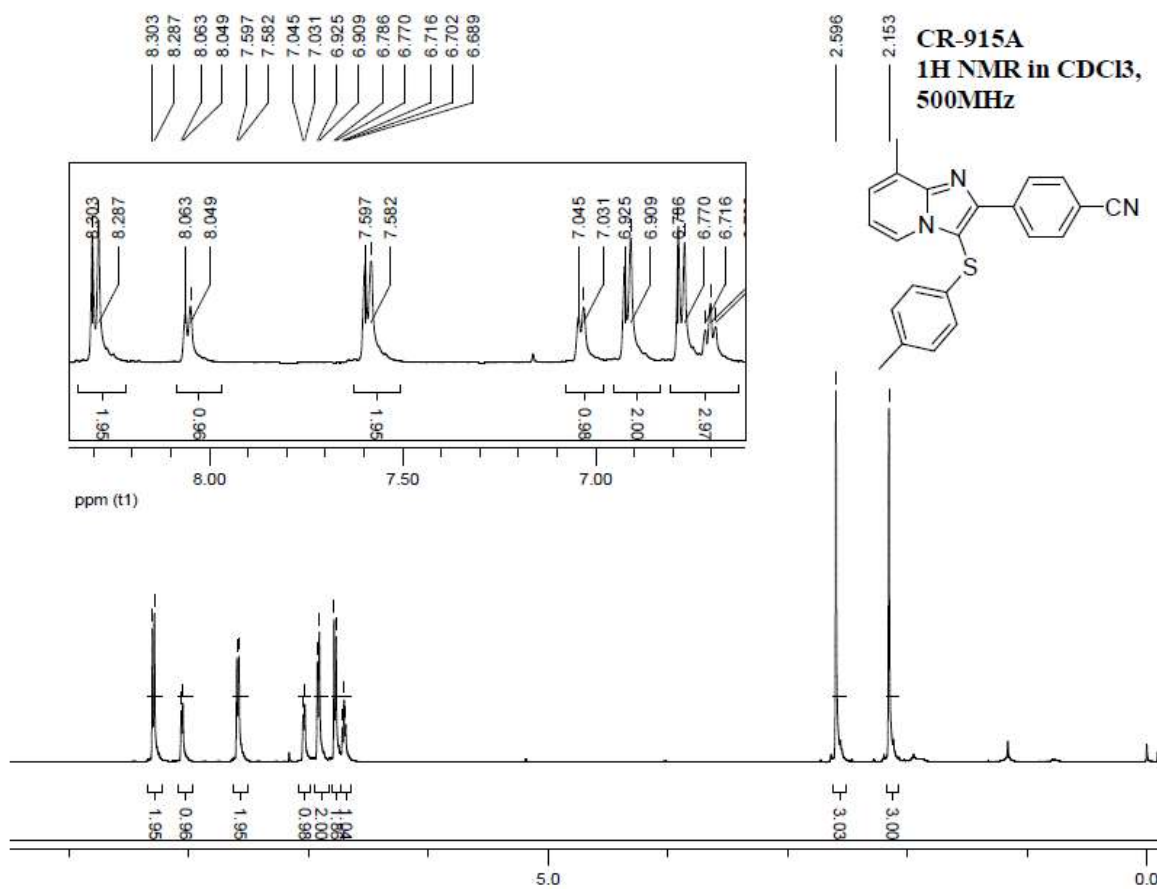
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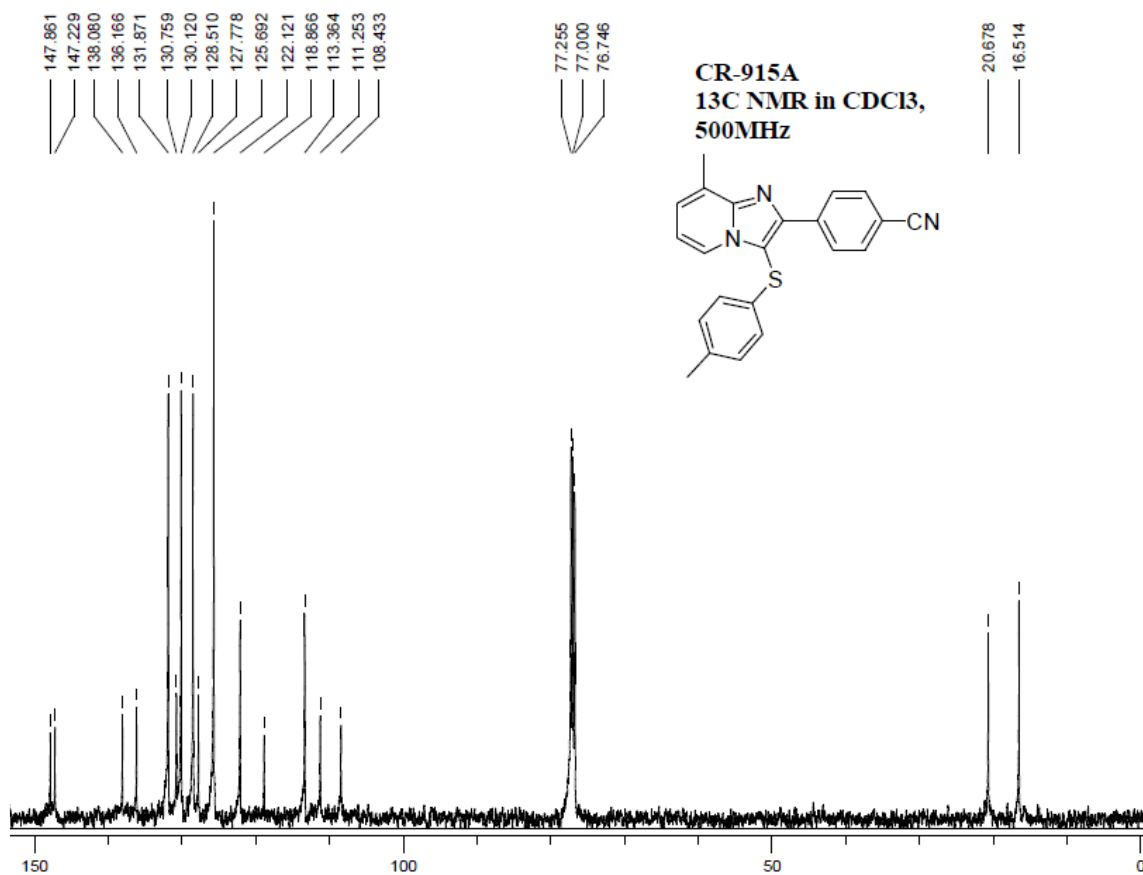




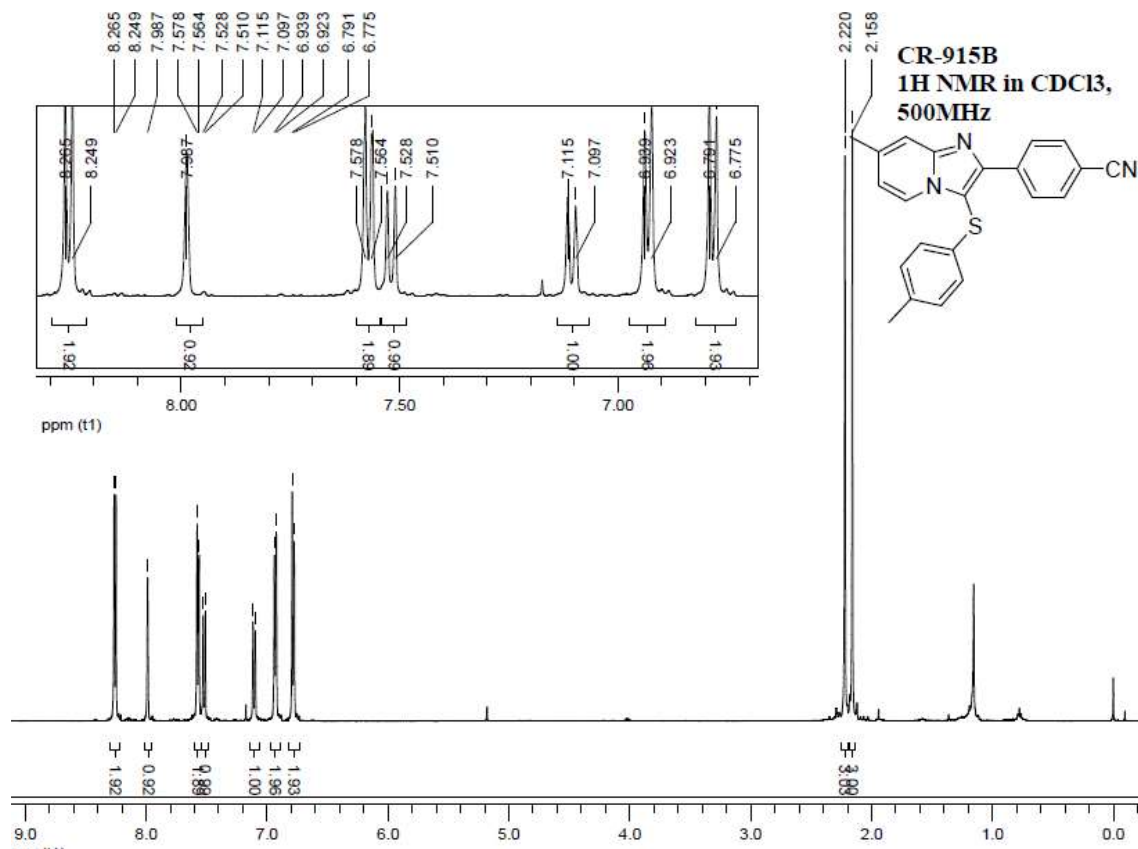
$^{13}\text{C}$  NMR of **3m**



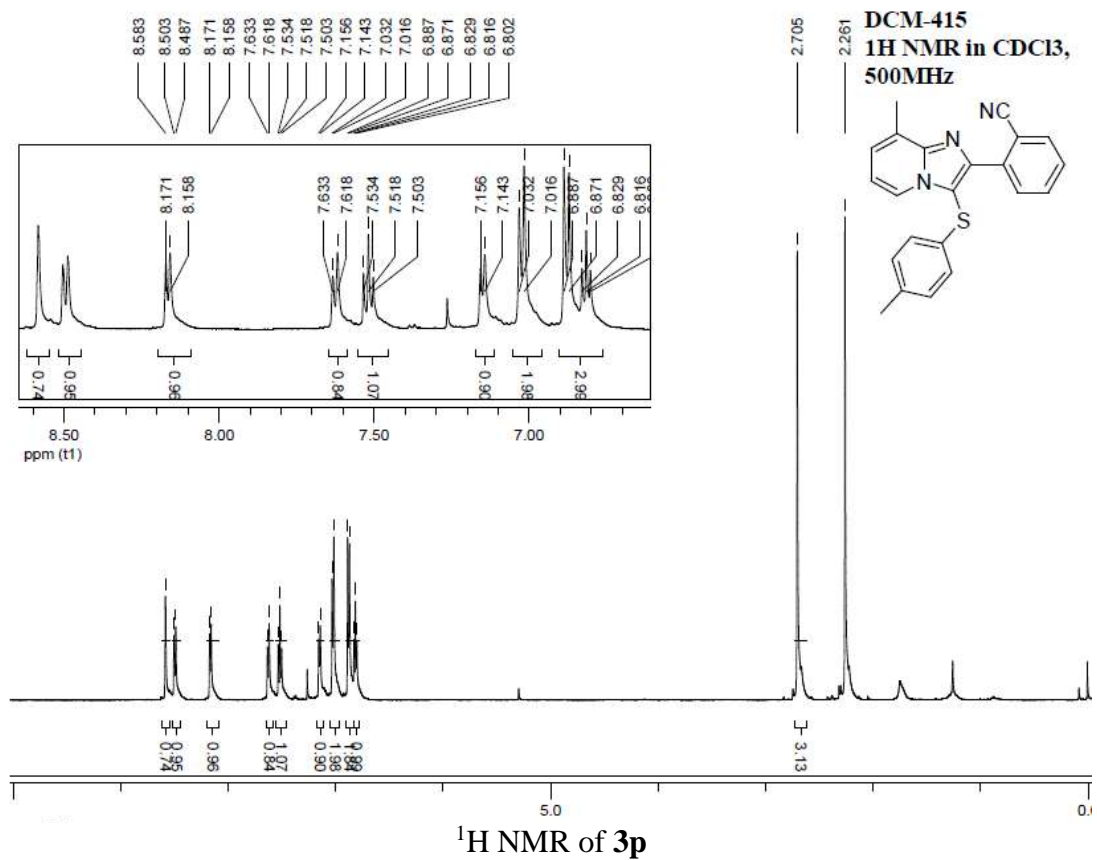
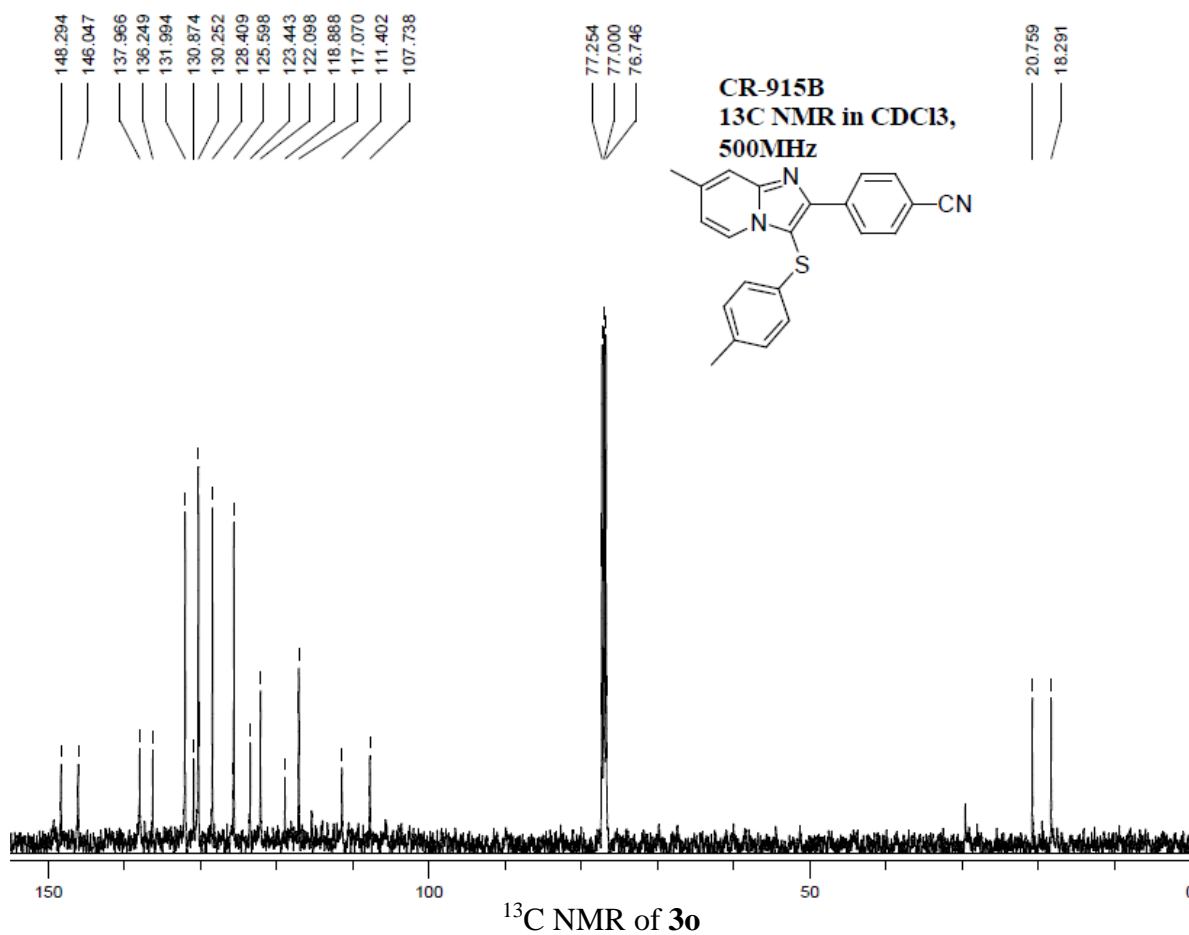
$^1\text{H}$  NMR of **3n**

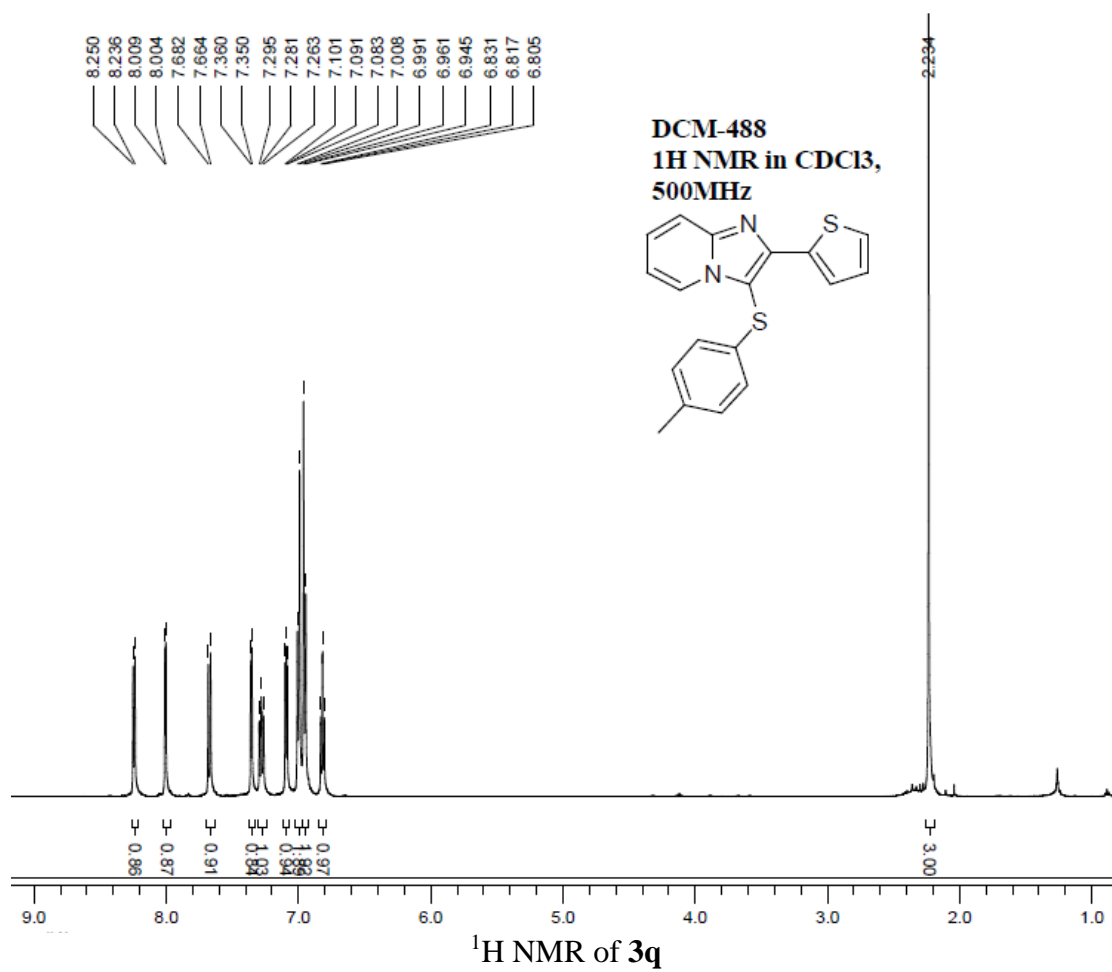
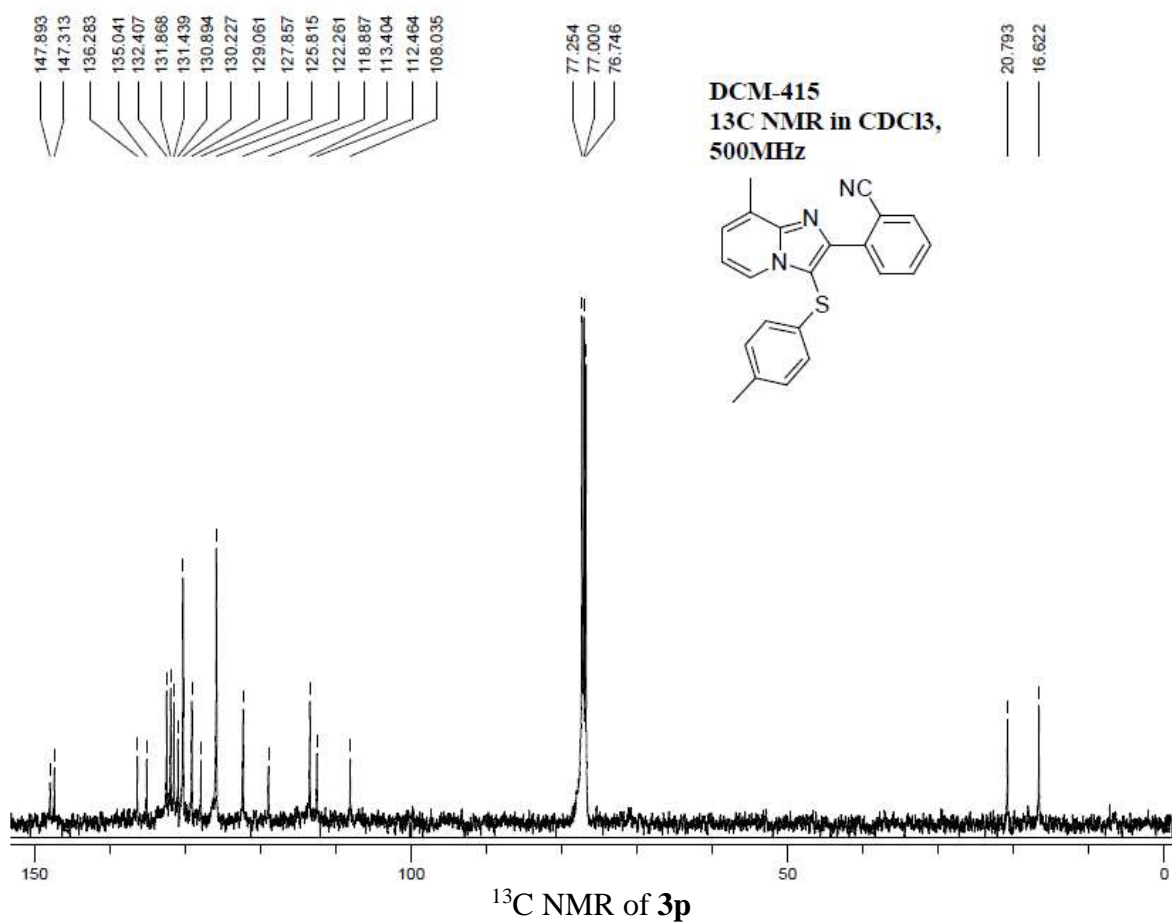


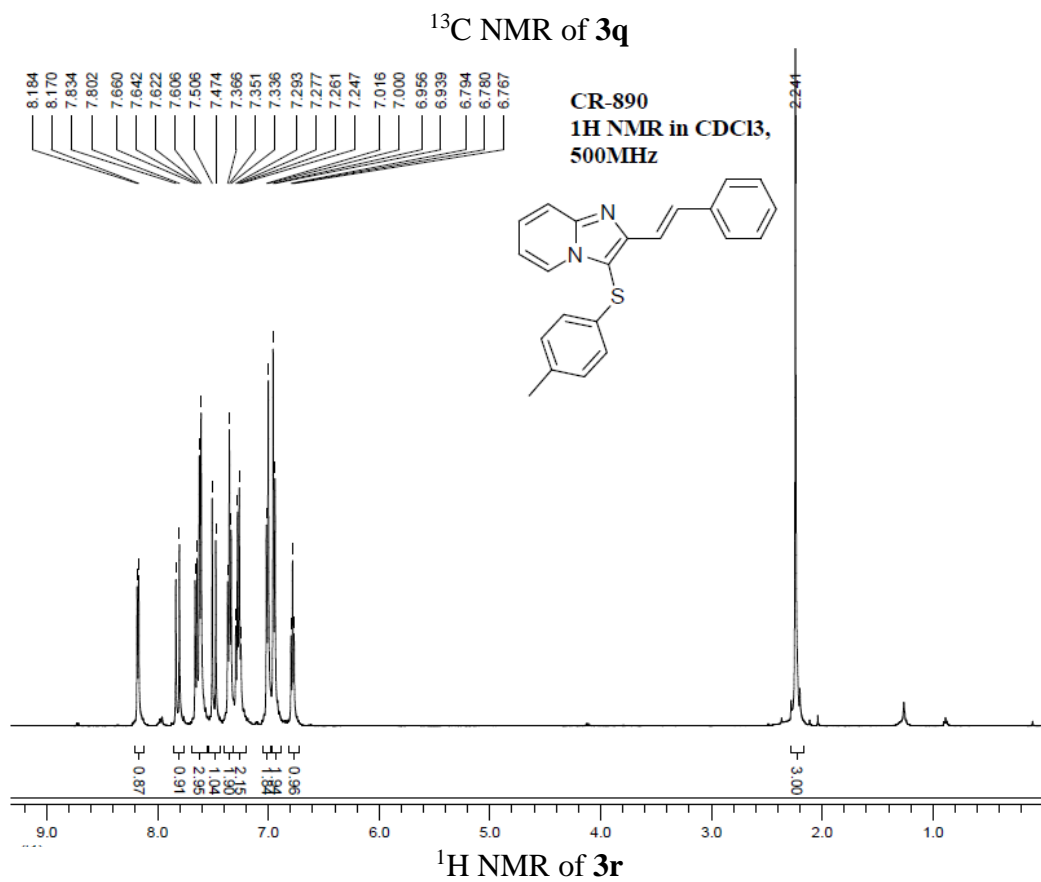
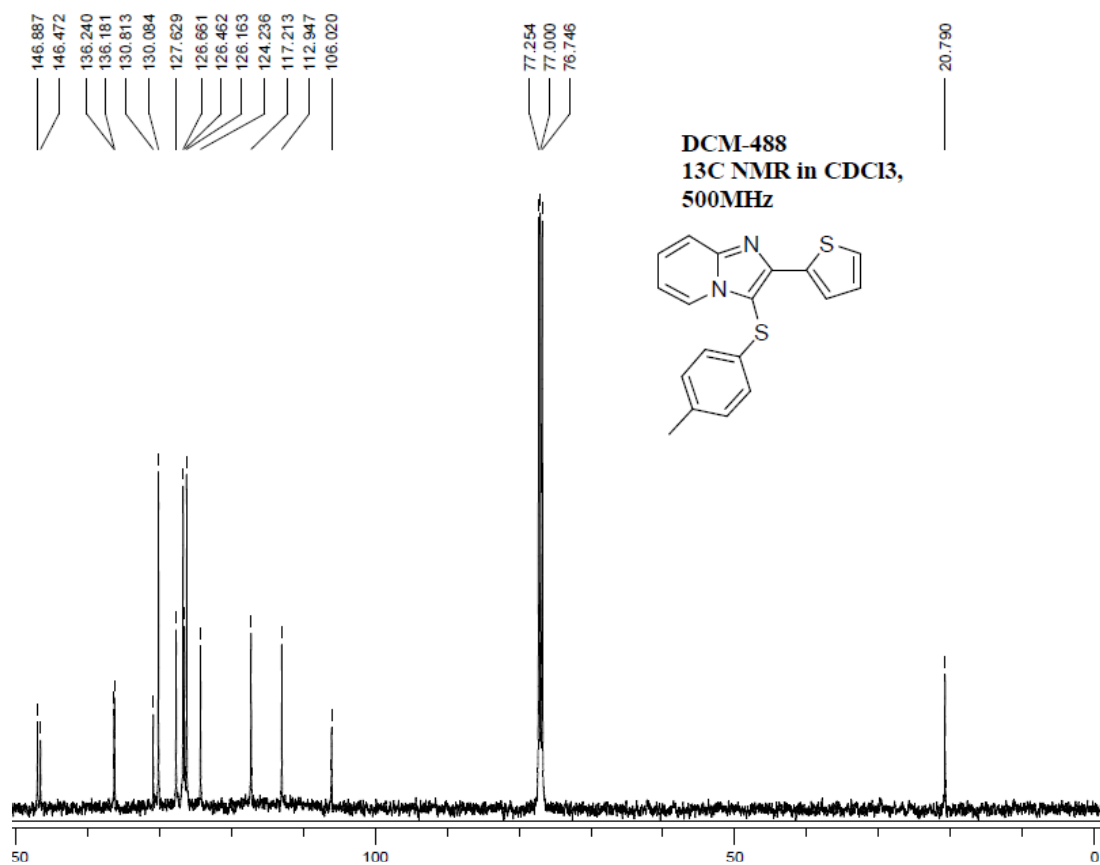
<sup>13</sup>C NMR of 3n

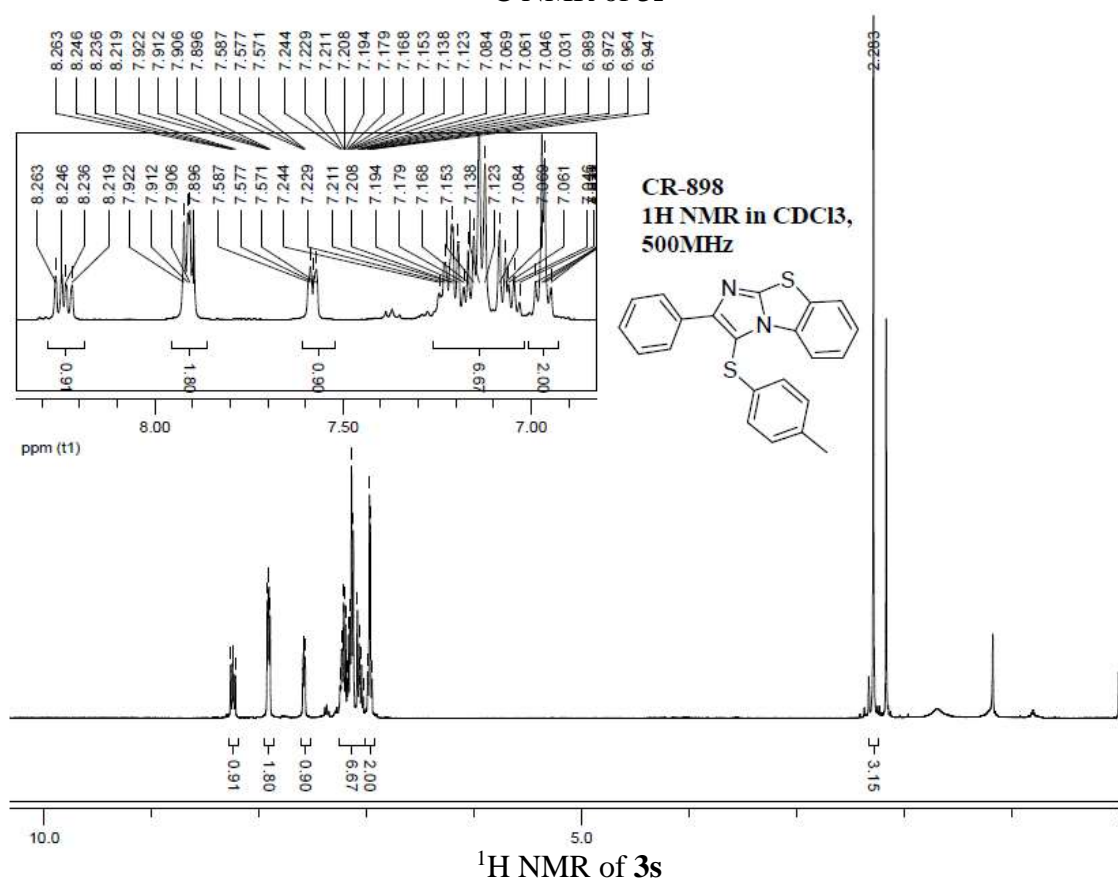
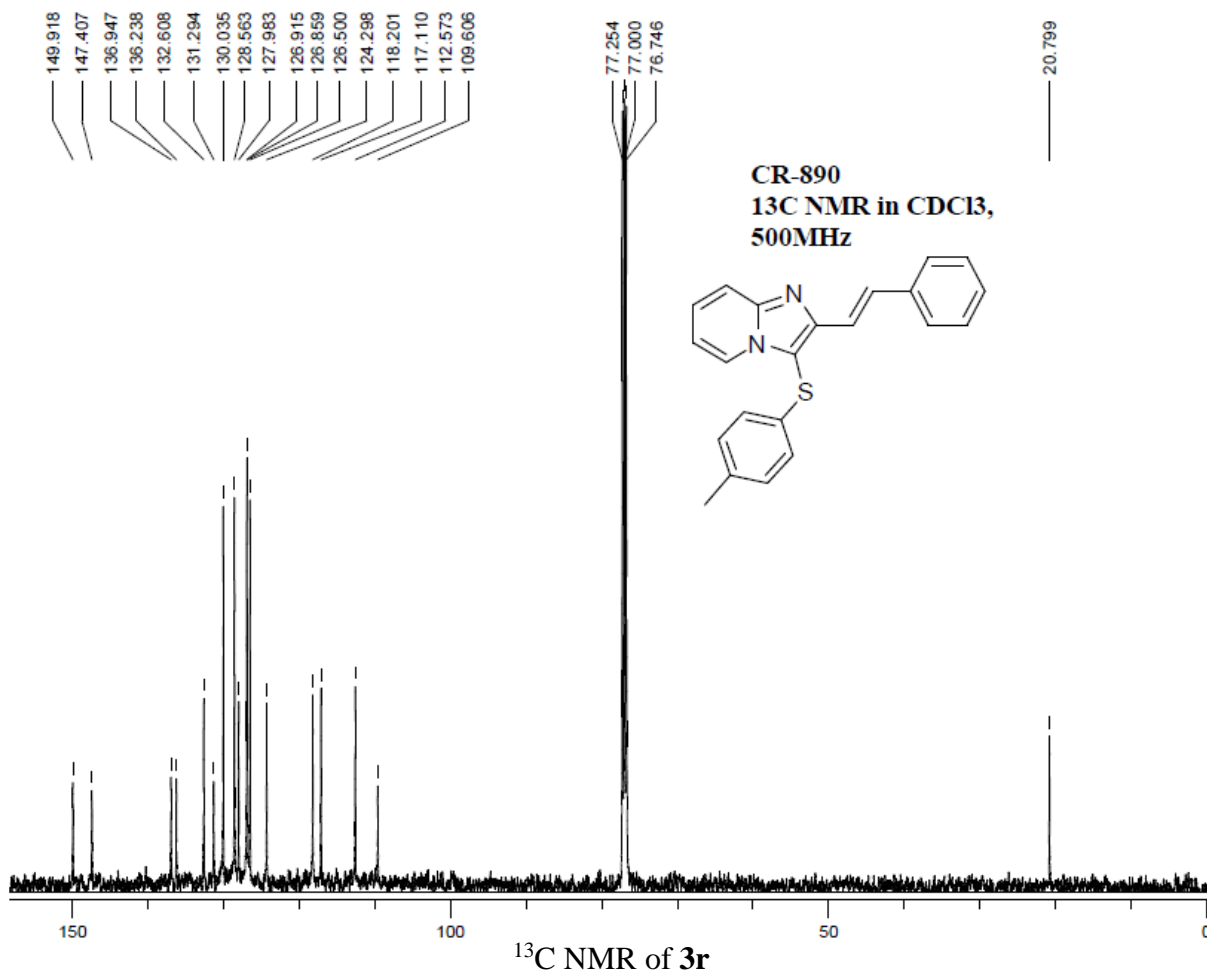


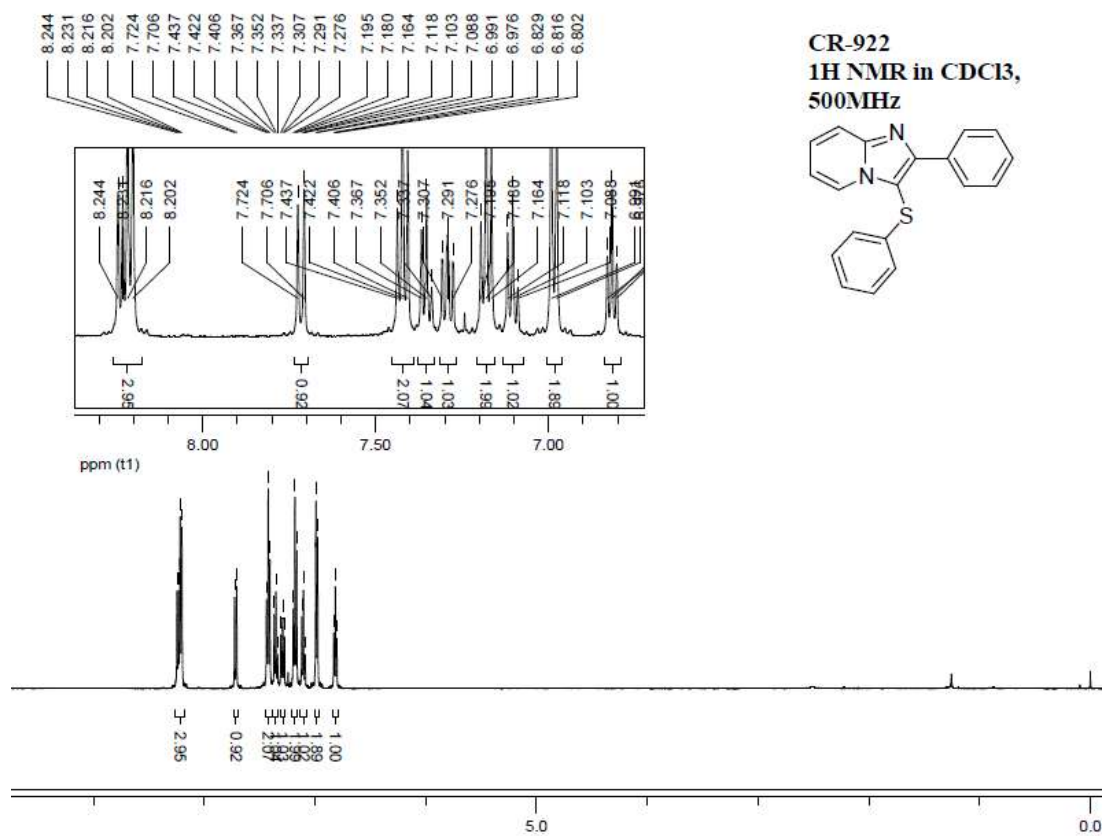
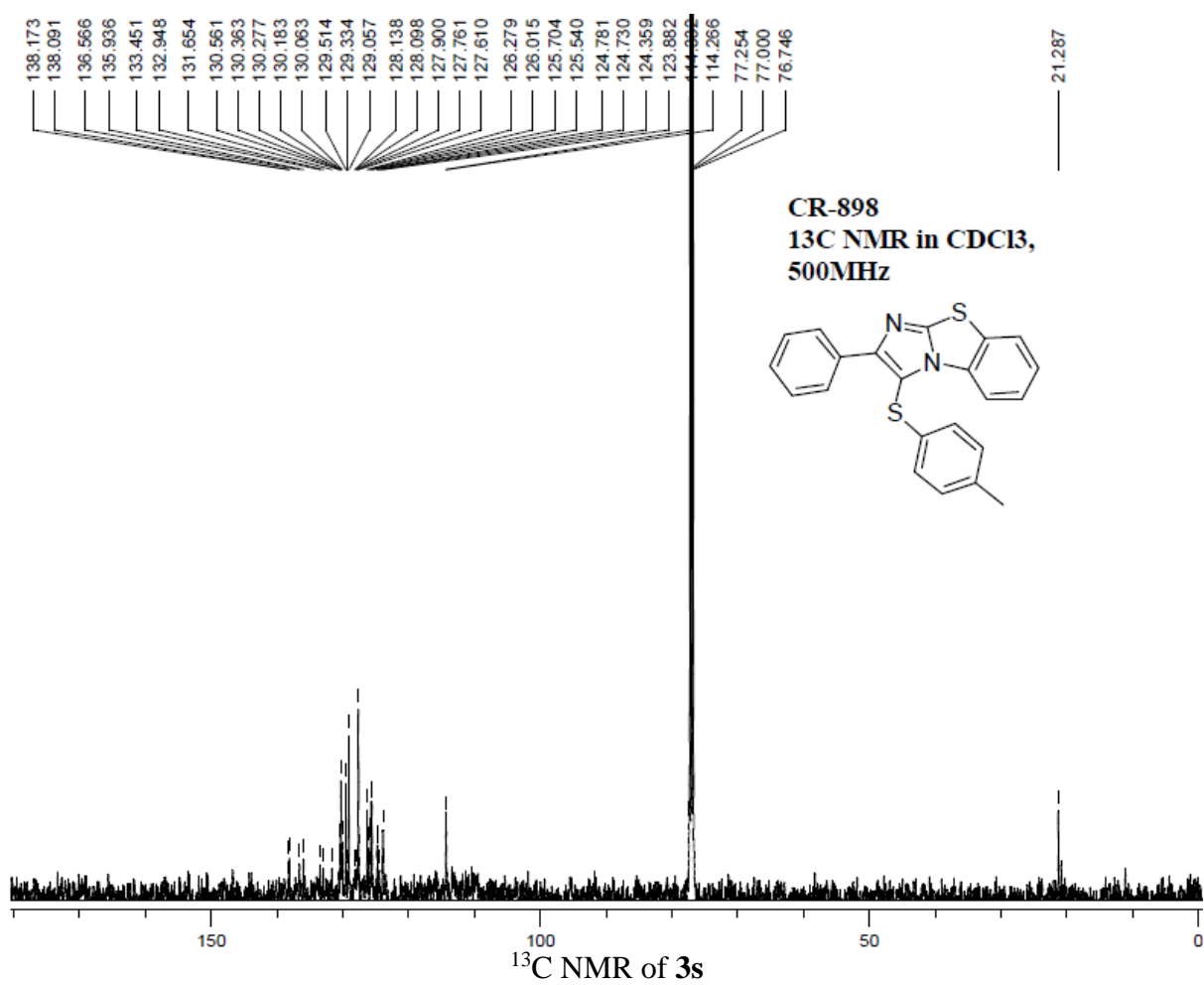
<sup>1</sup>H NMR of 3n



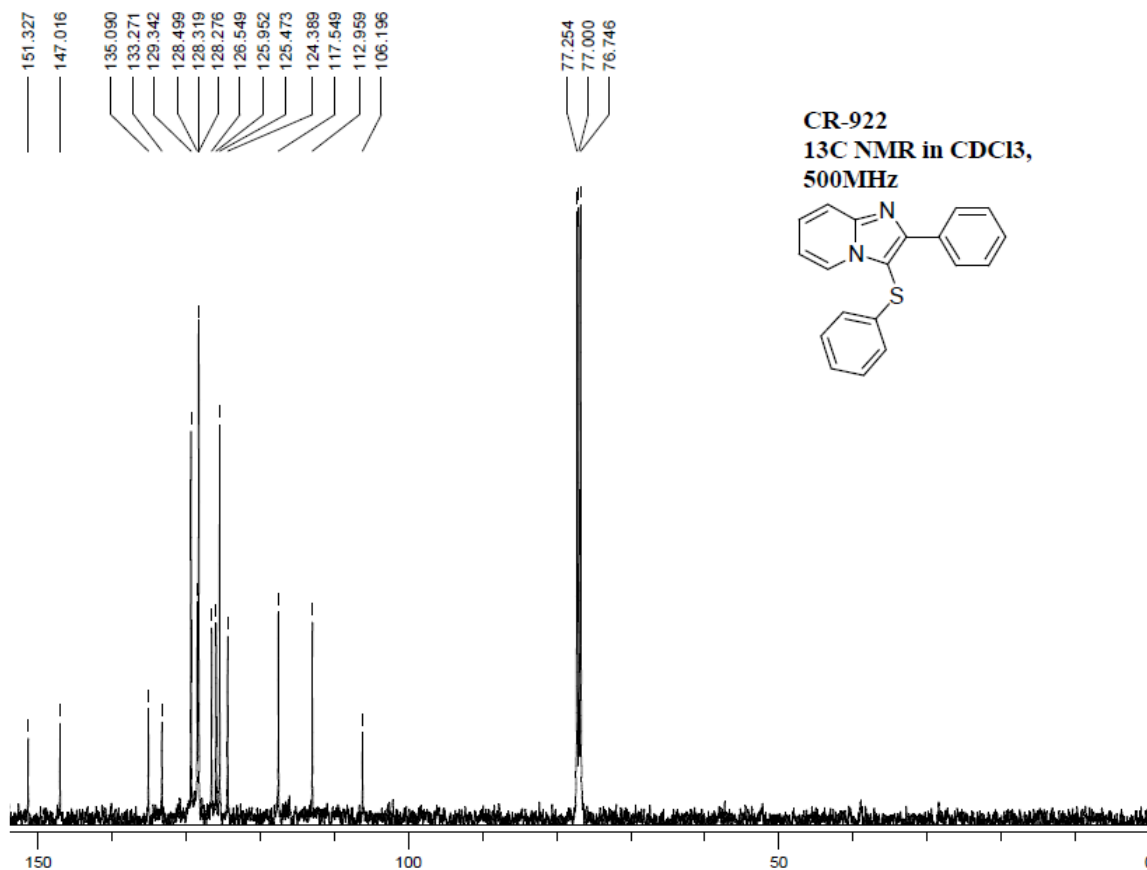




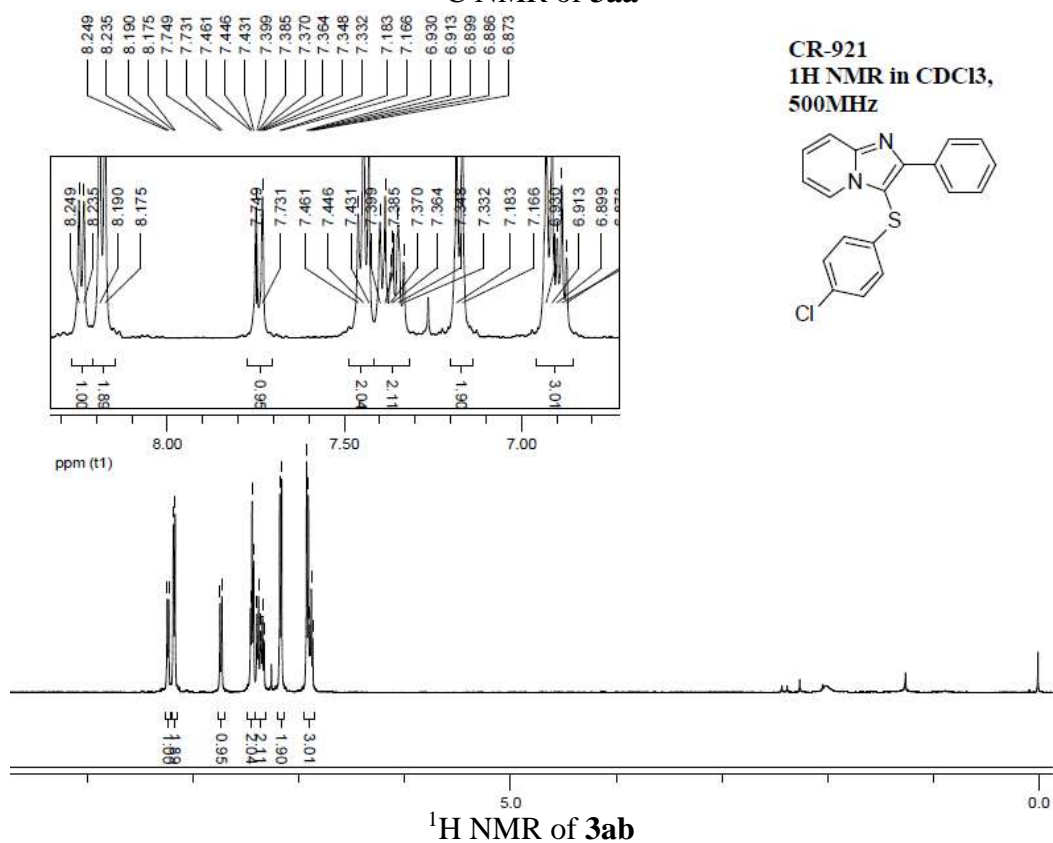




### <sup>1</sup>H NMR of 3aa

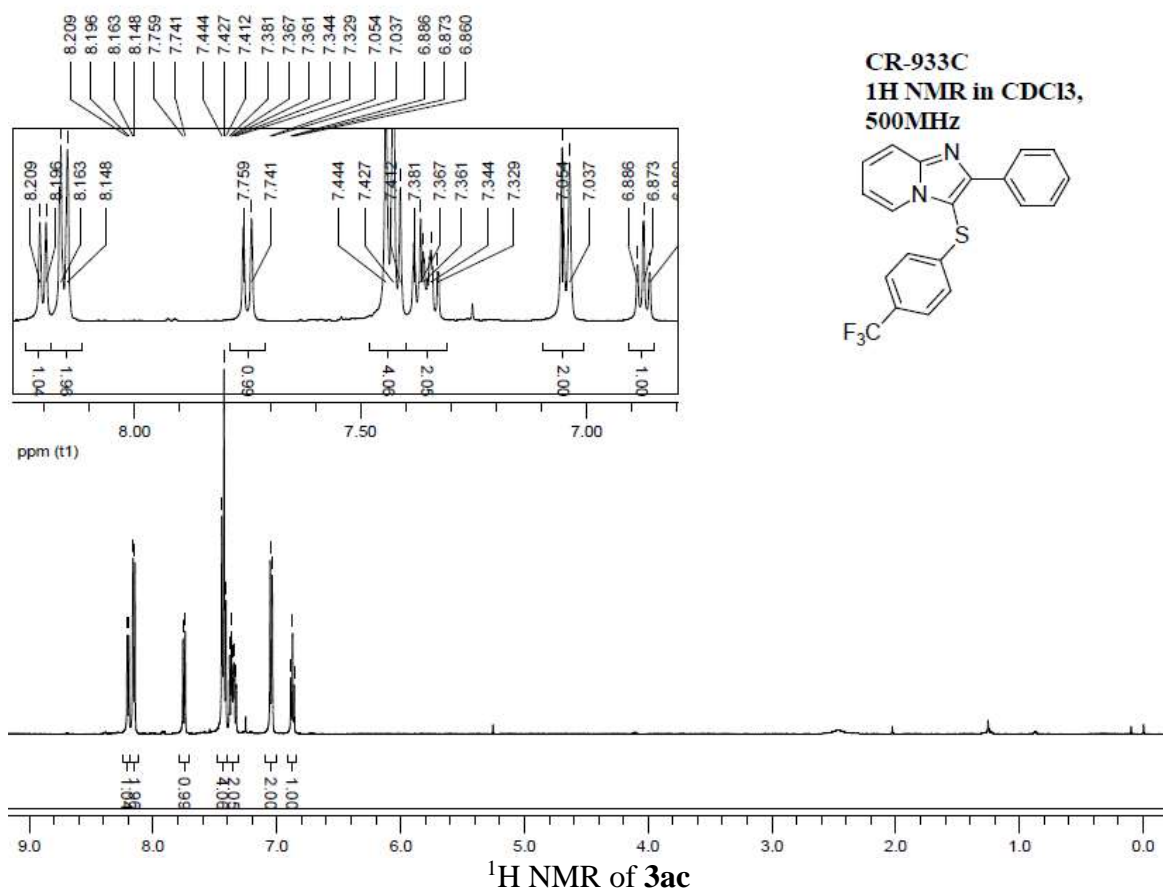
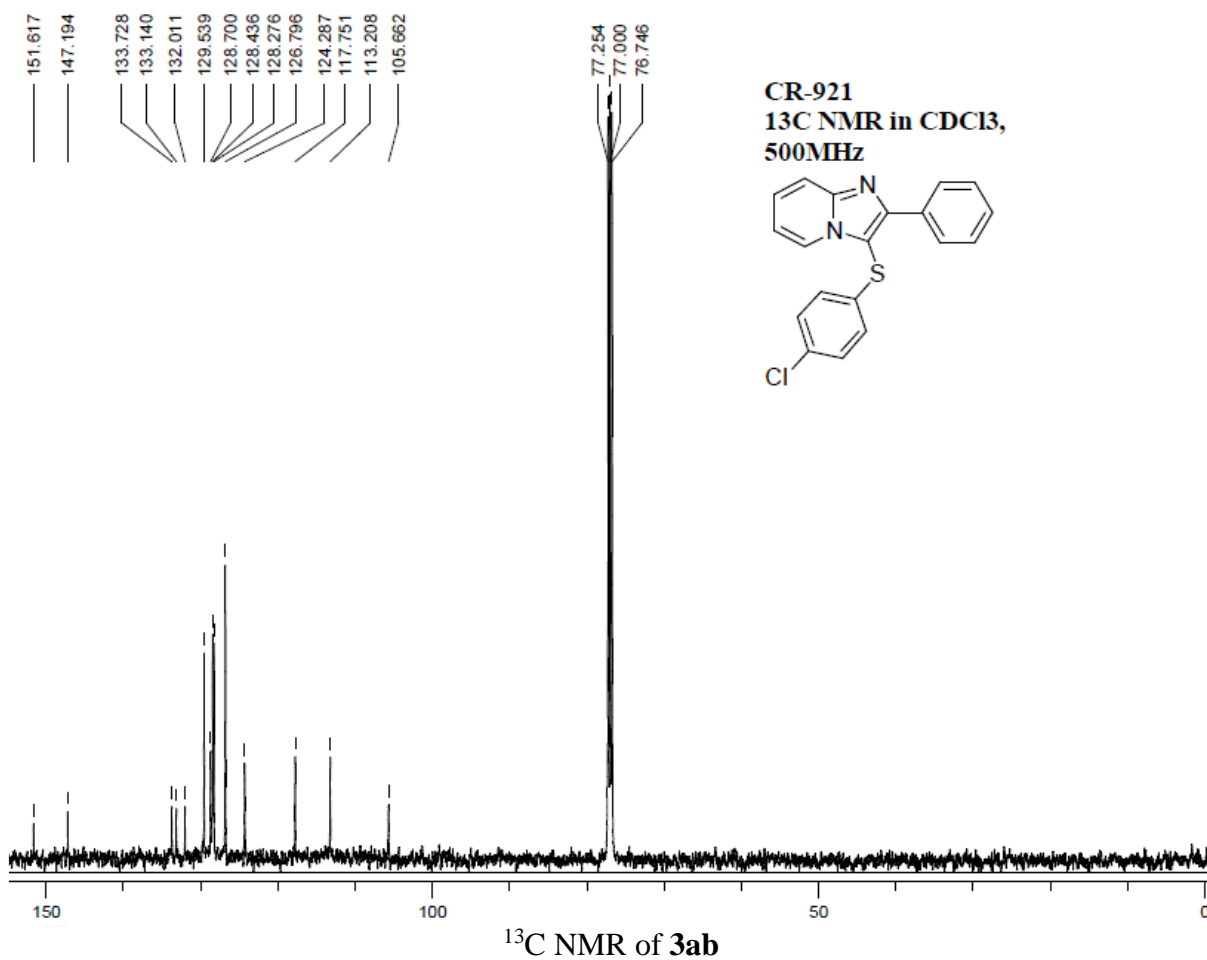


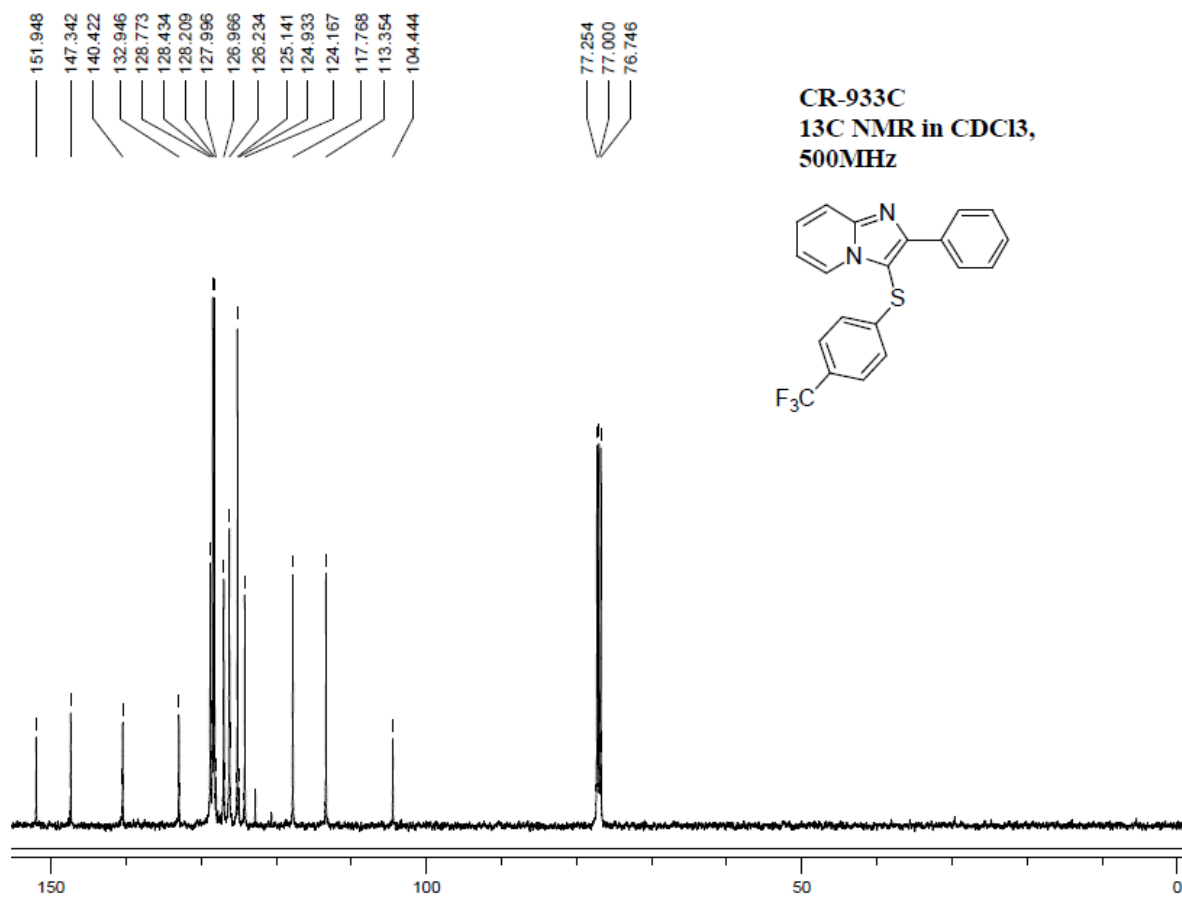
### <sup>13</sup>C NMR of 3aa



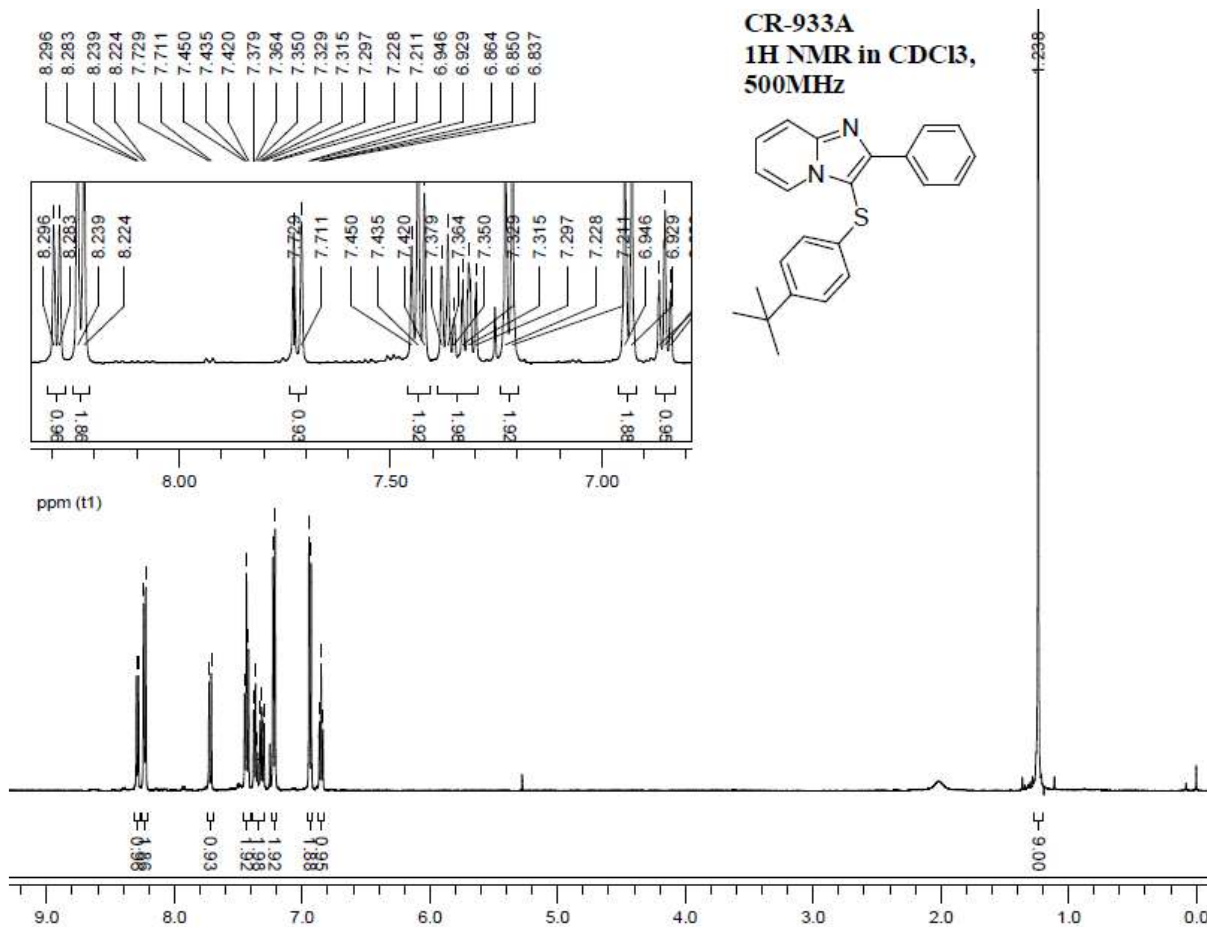
### <sup>1</sup>H NMR of 3ab



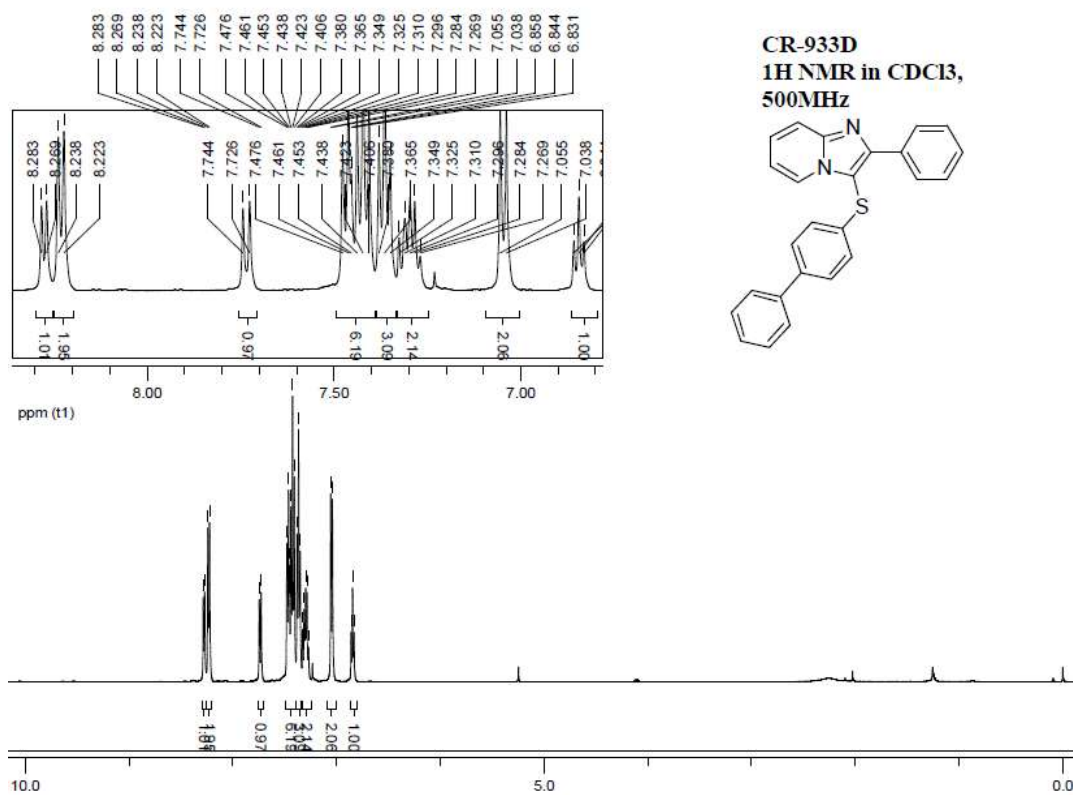
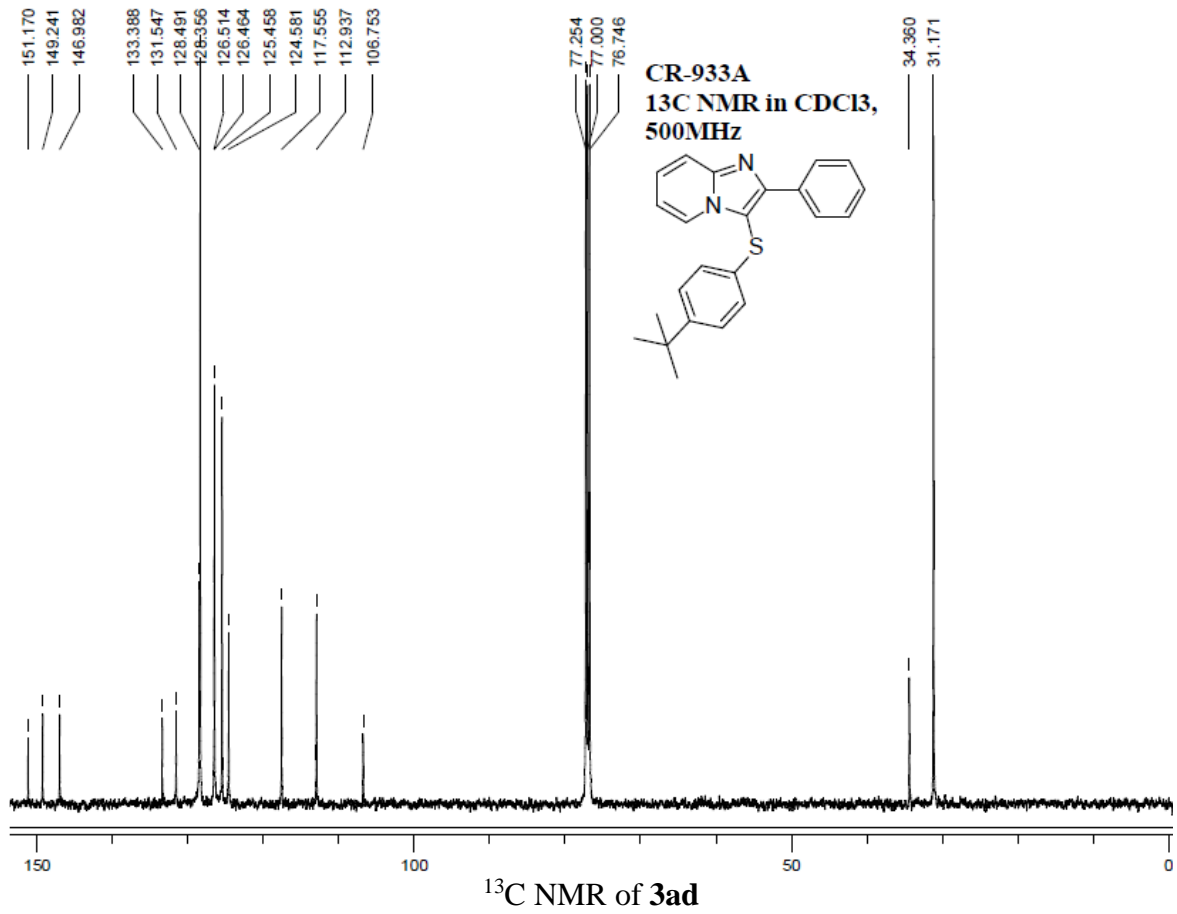




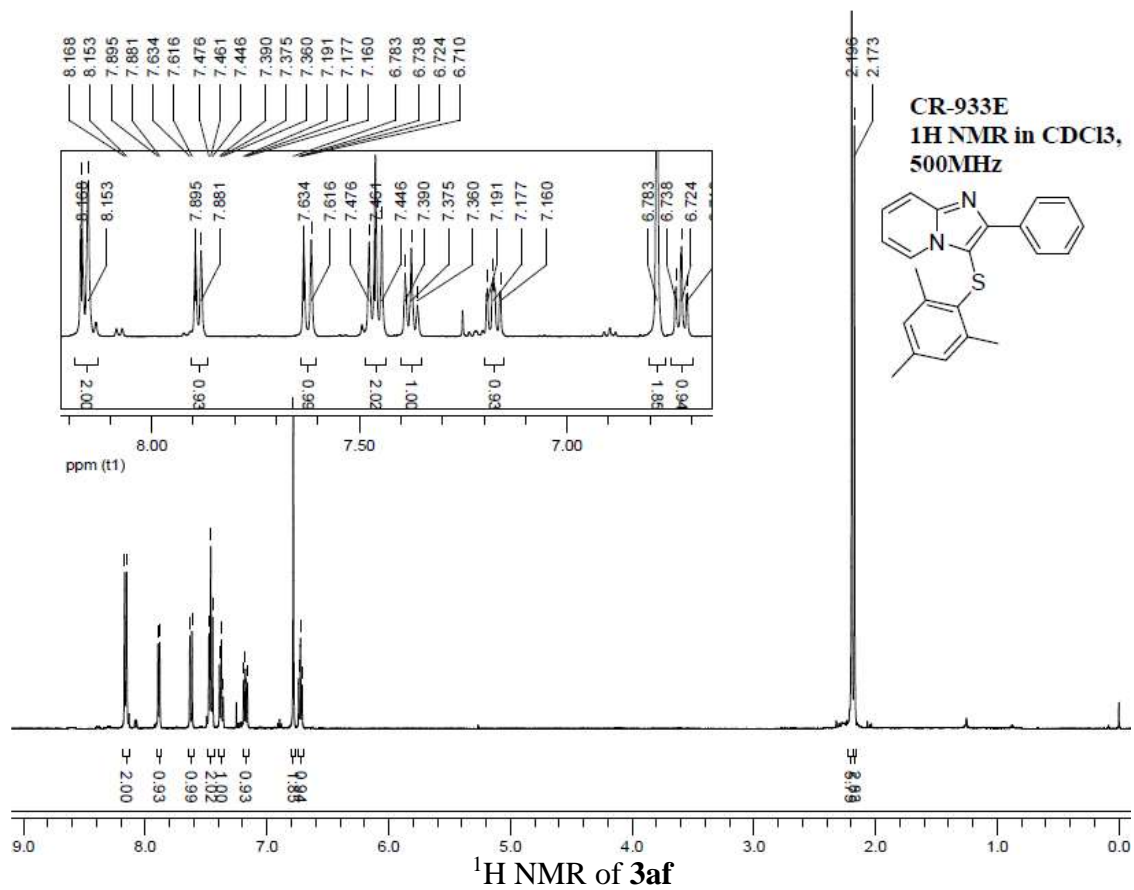
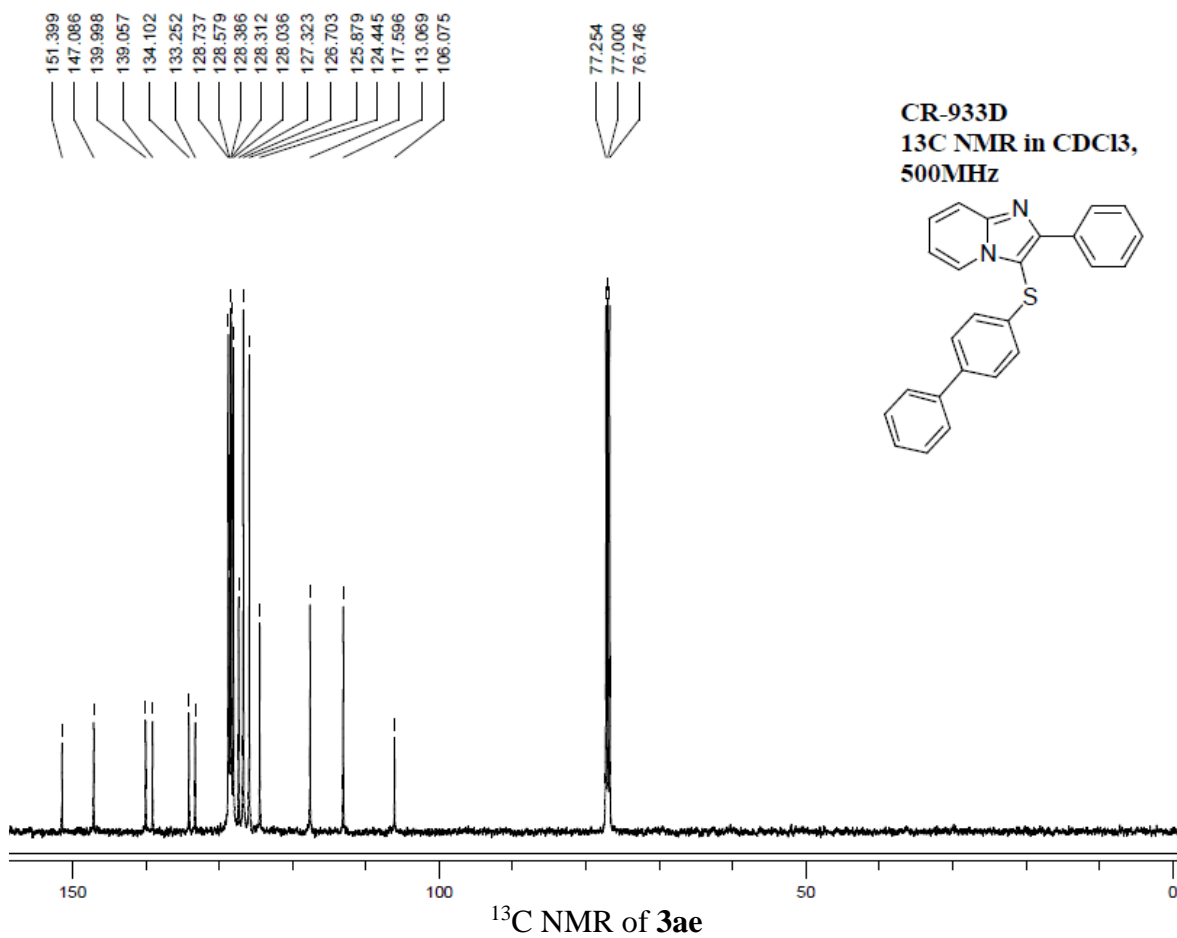
<sup>13</sup>C NMR of **3ac**

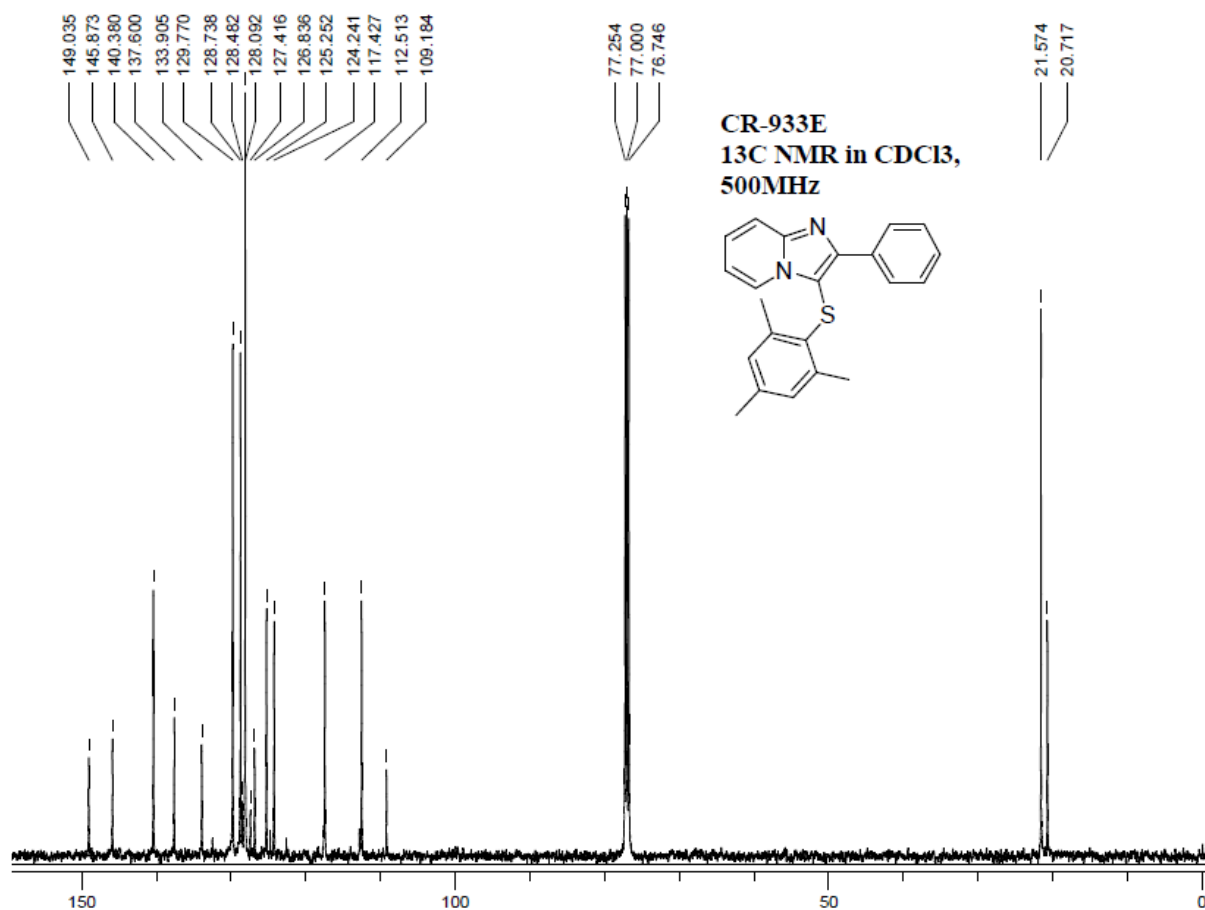


# <sup>1</sup>H NMR of 3ad

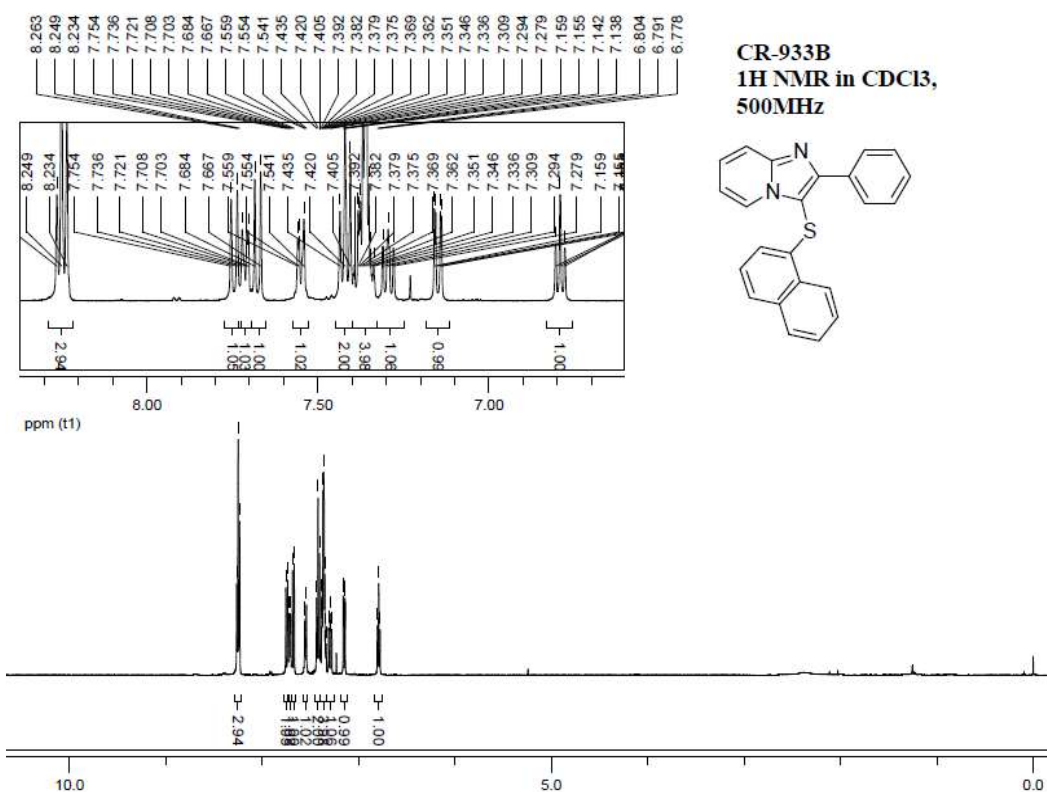


<sup>1</sup>H NMR of 3ae

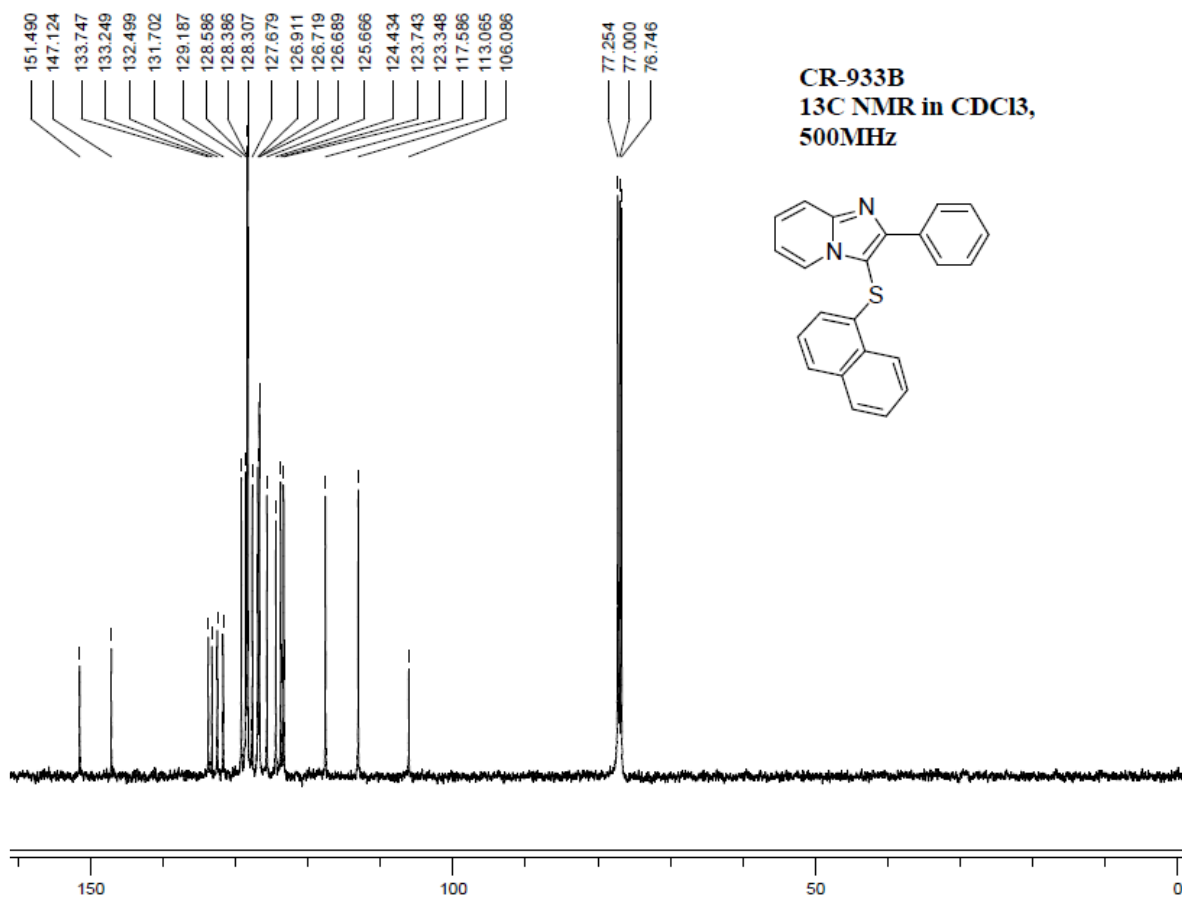




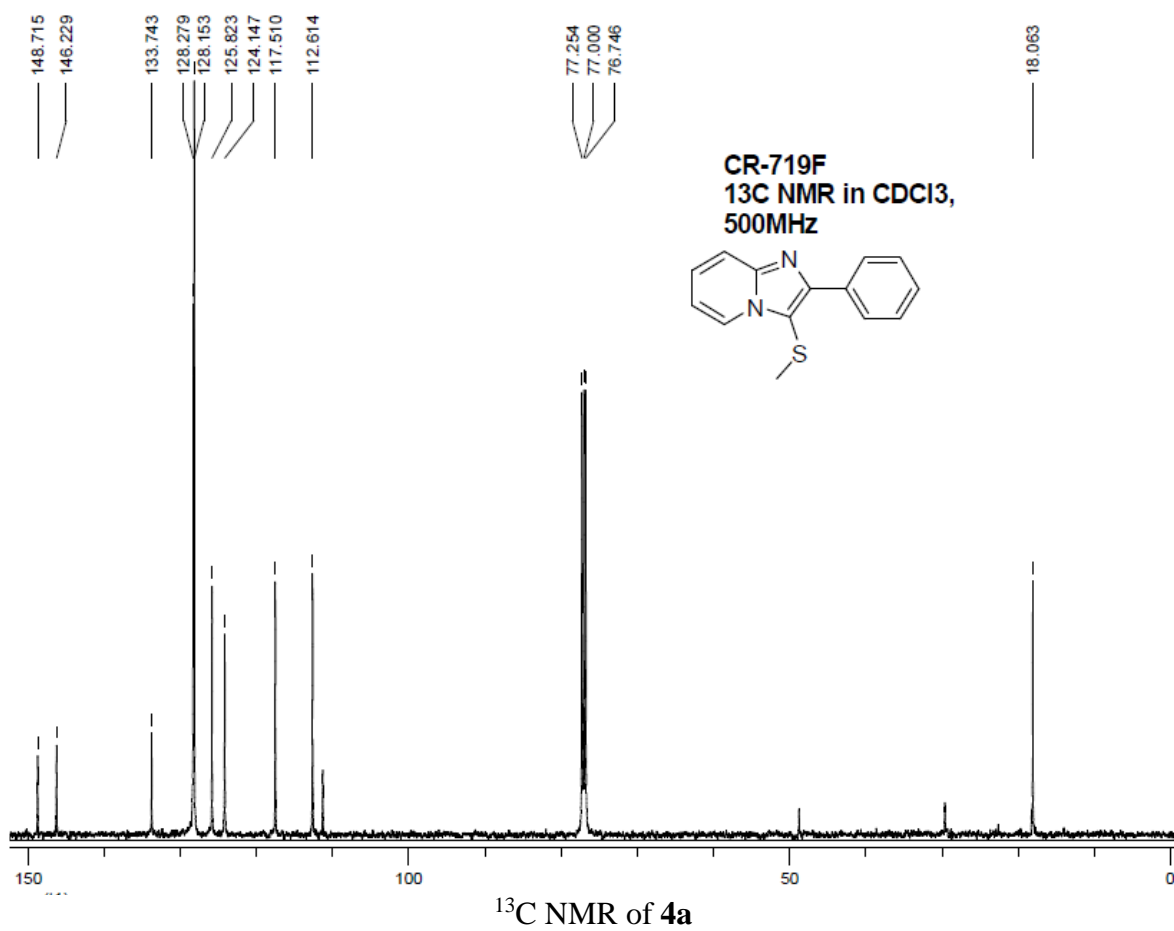
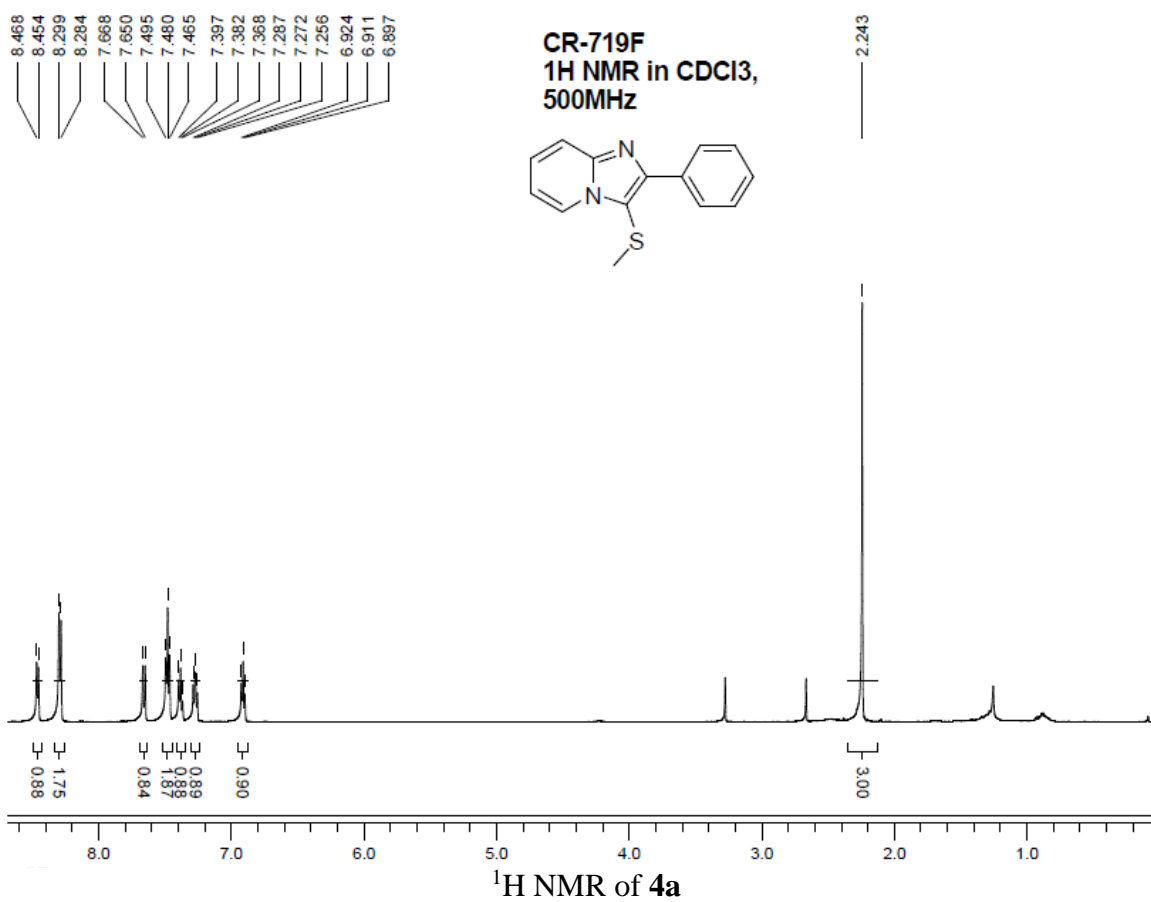
<sup>13</sup>C NMR of **3af**

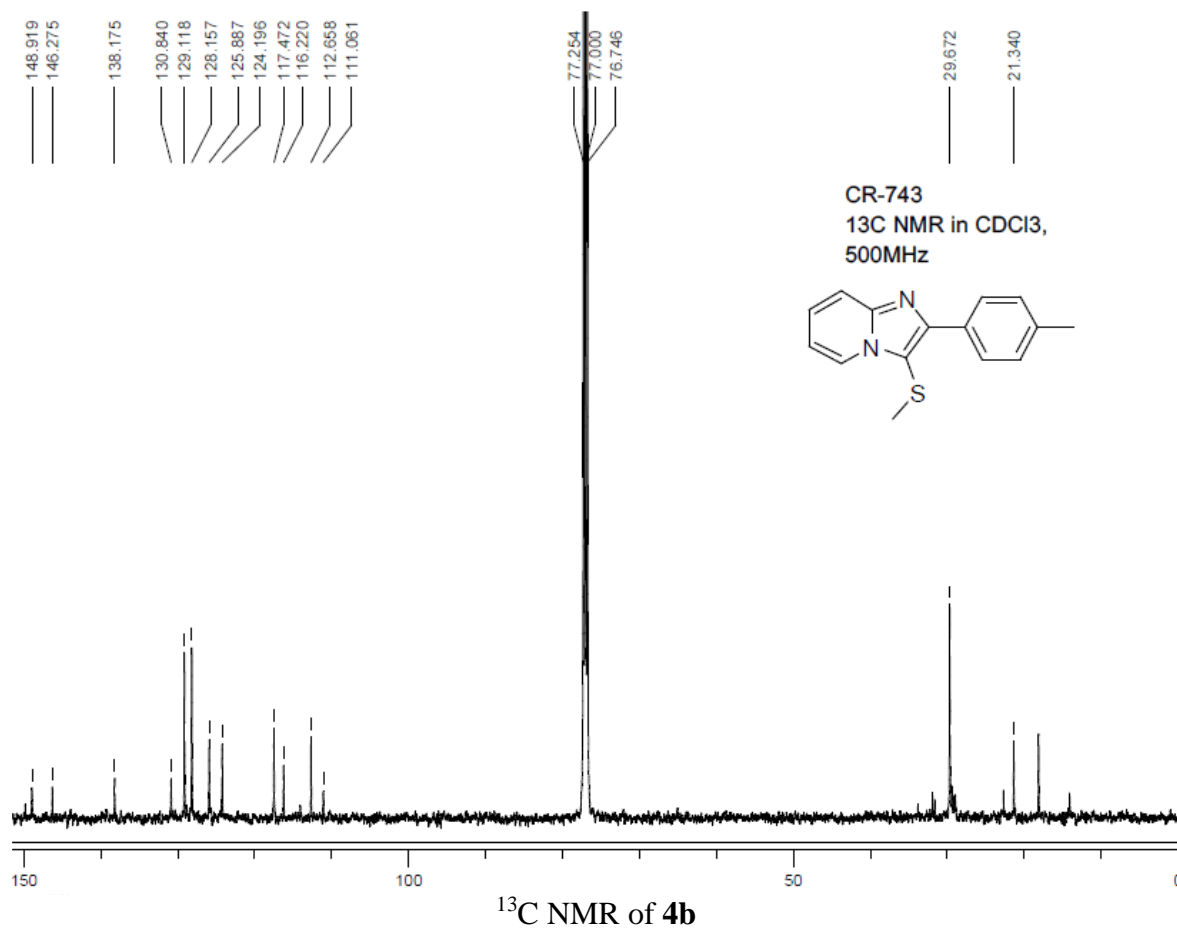
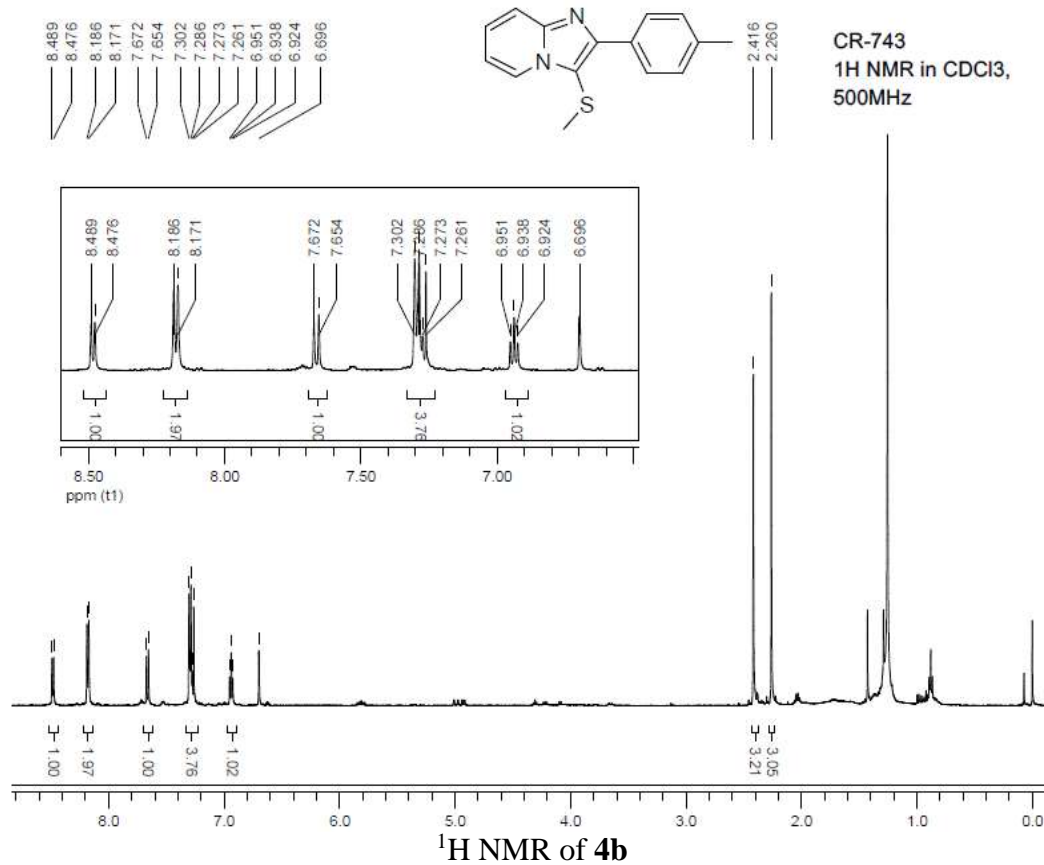


<sup>1</sup>H NMR of **3ag**

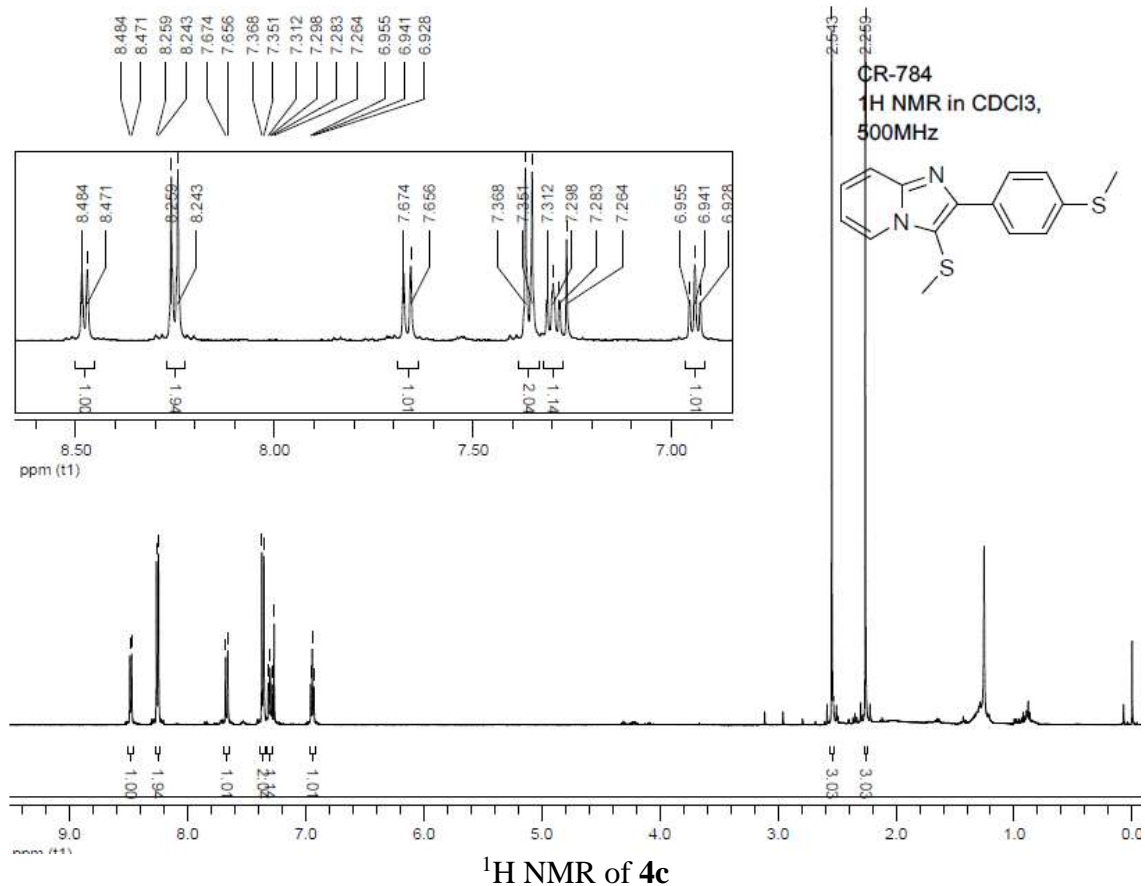


$^{13}\text{C}$  NMR of **3ag**

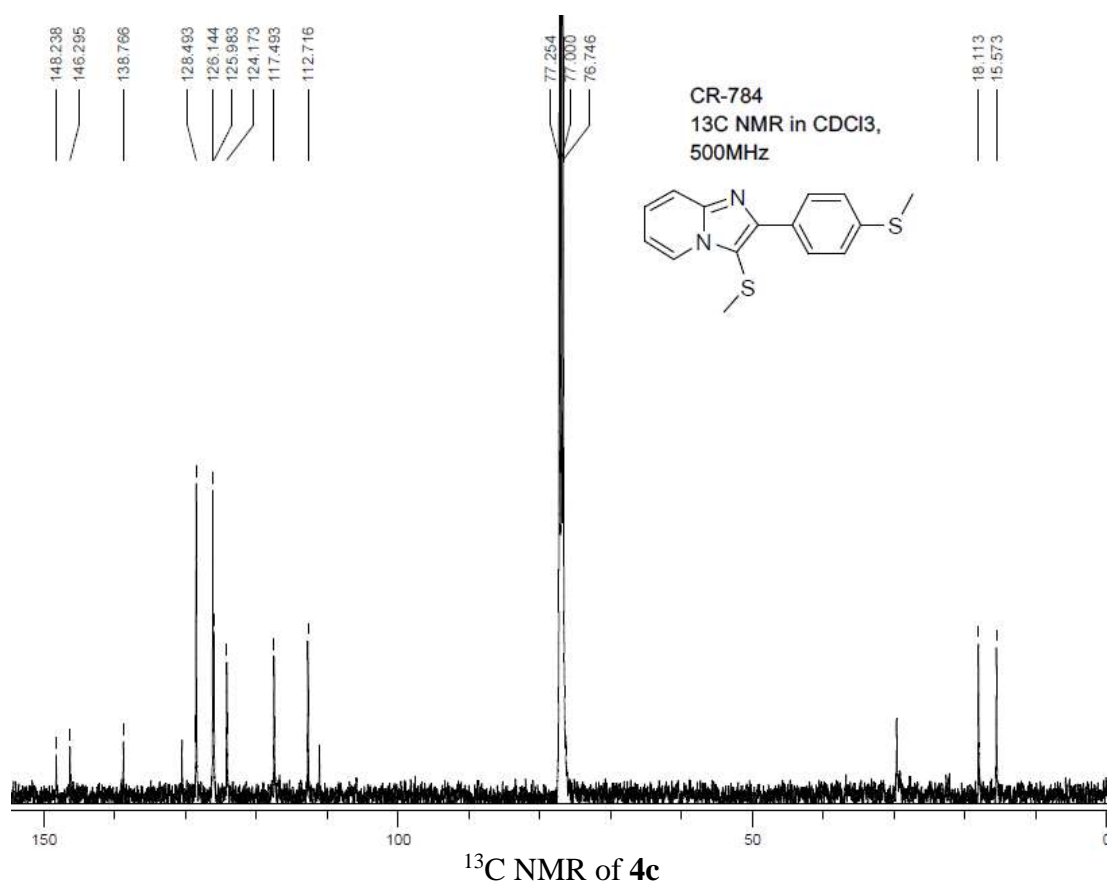




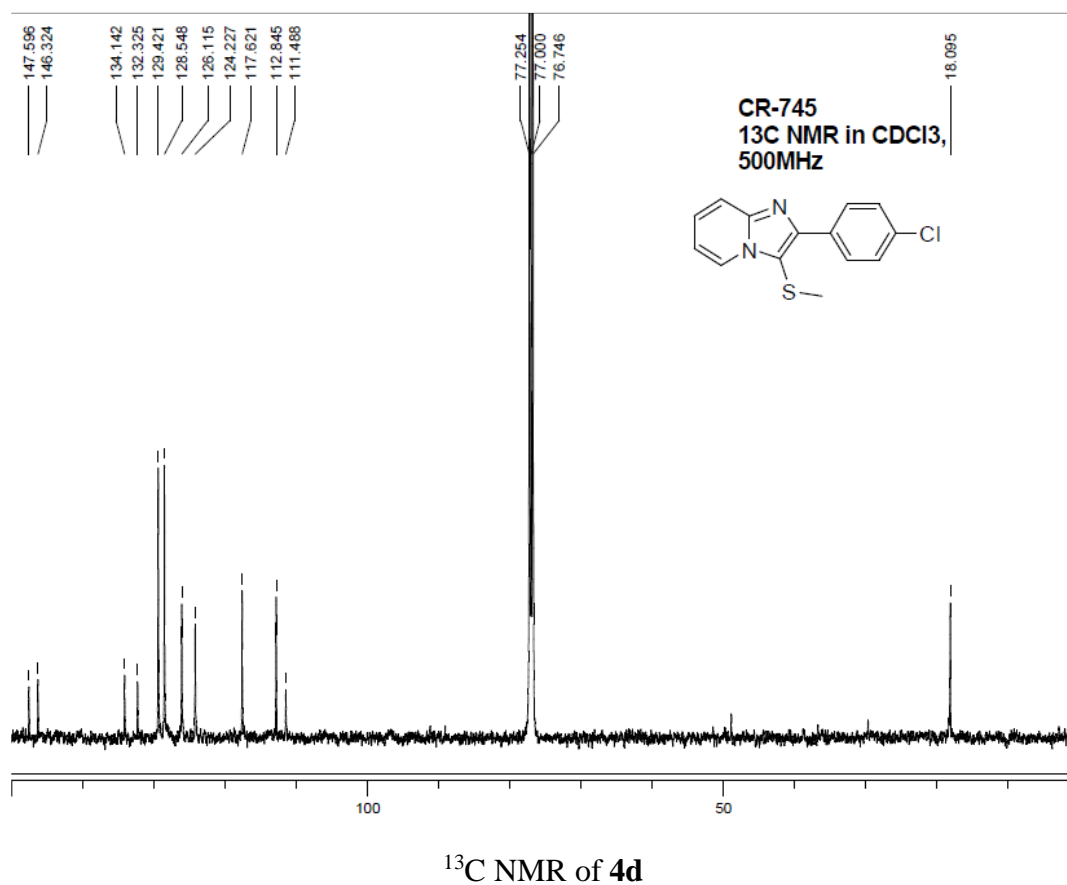
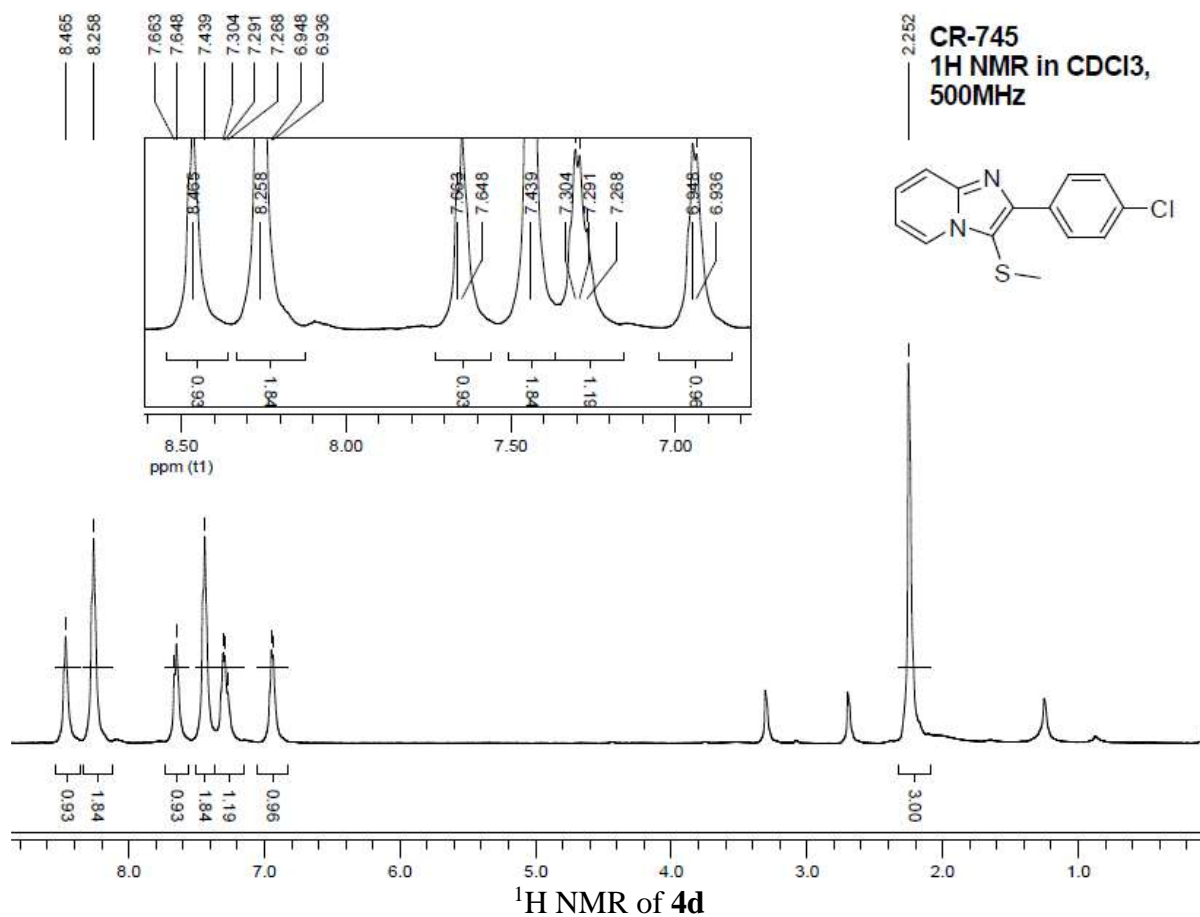




<sup>1</sup>H NMR of 4c

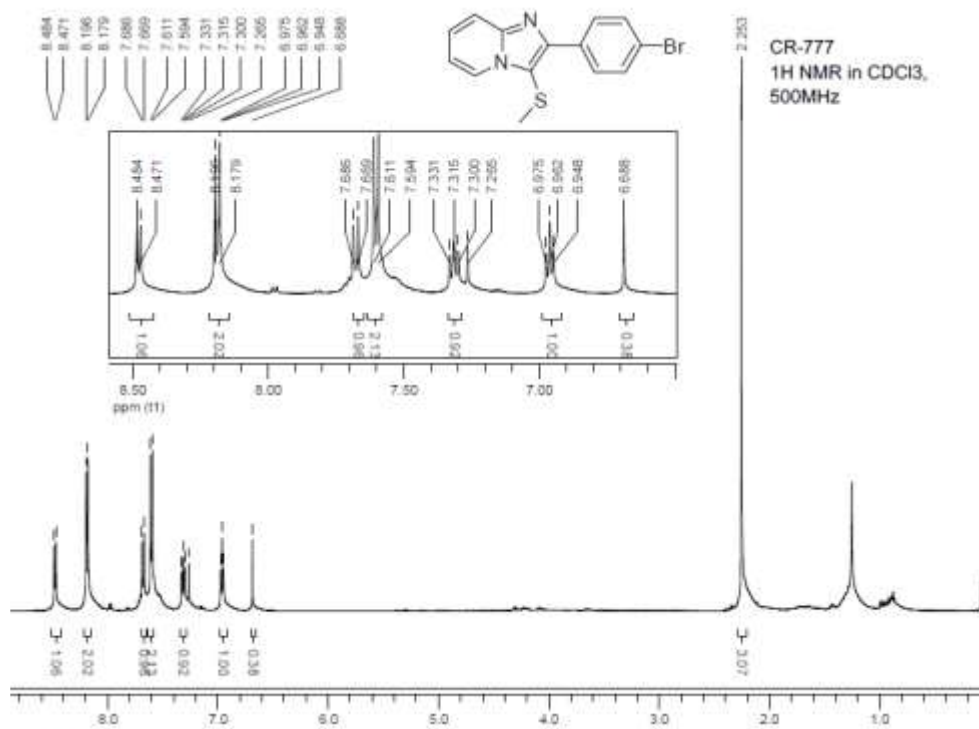


<sup>13</sup>C NMR of 4c

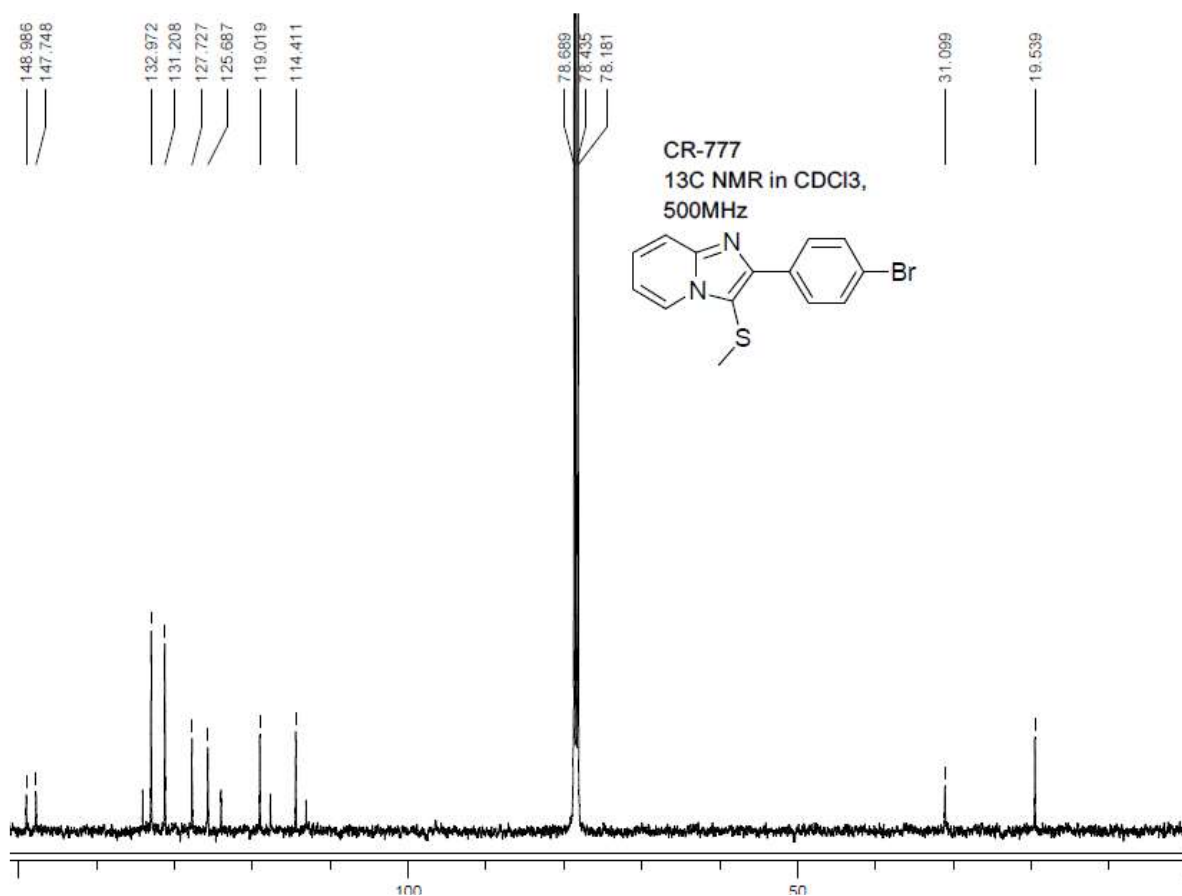




### $^{13}\text{C}$ NMR of **4e**

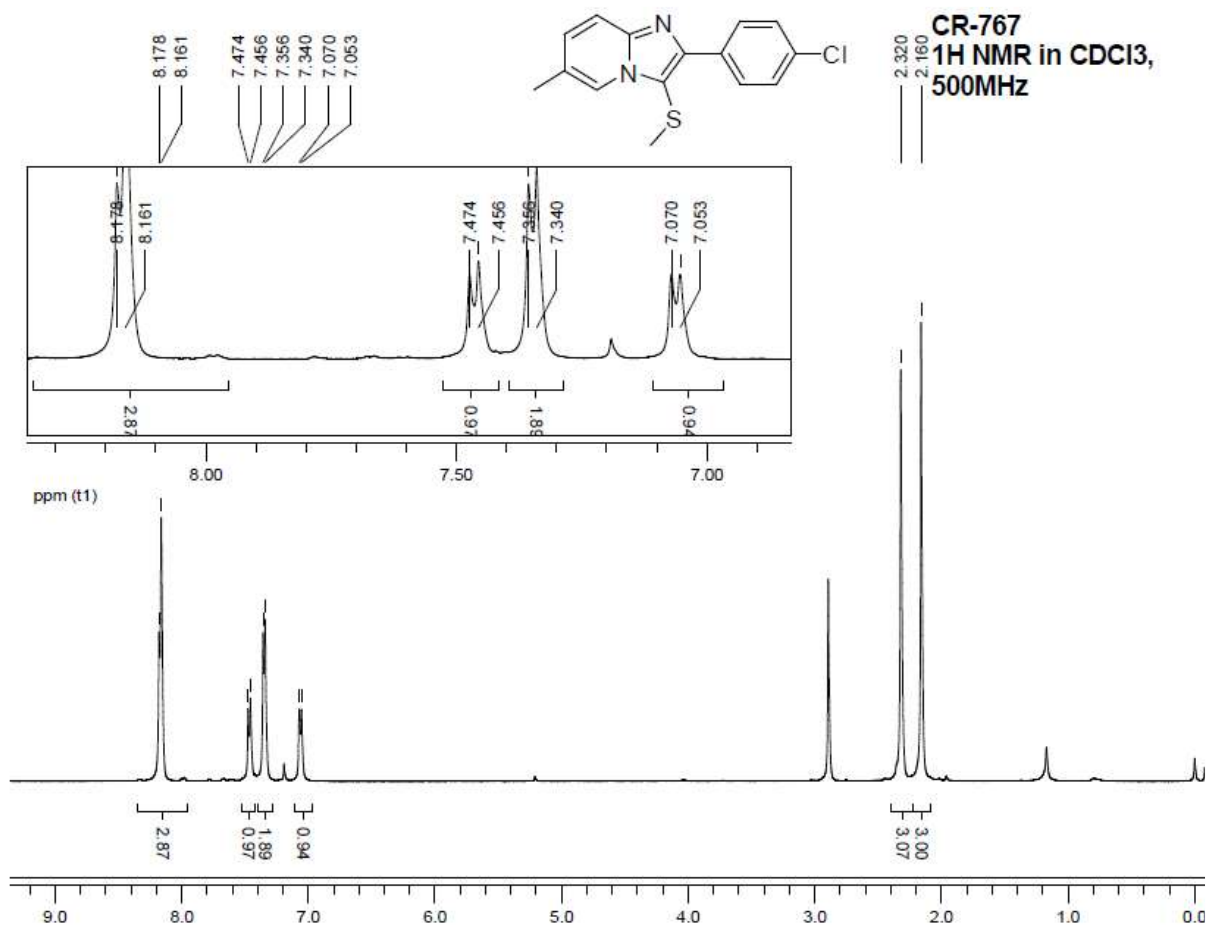


### $^1\text{H}$ NMR of **4f**

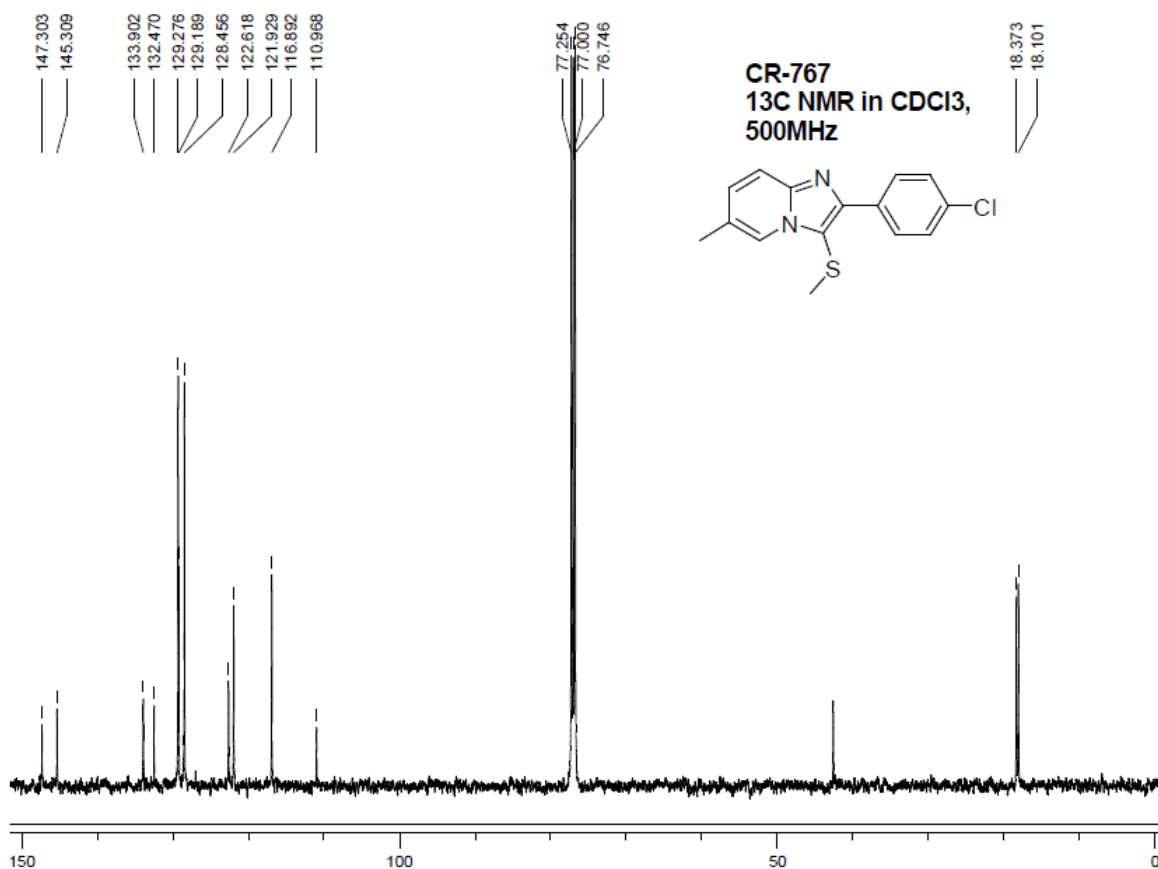


### $^{13}\text{C}$ NMR of **4f**





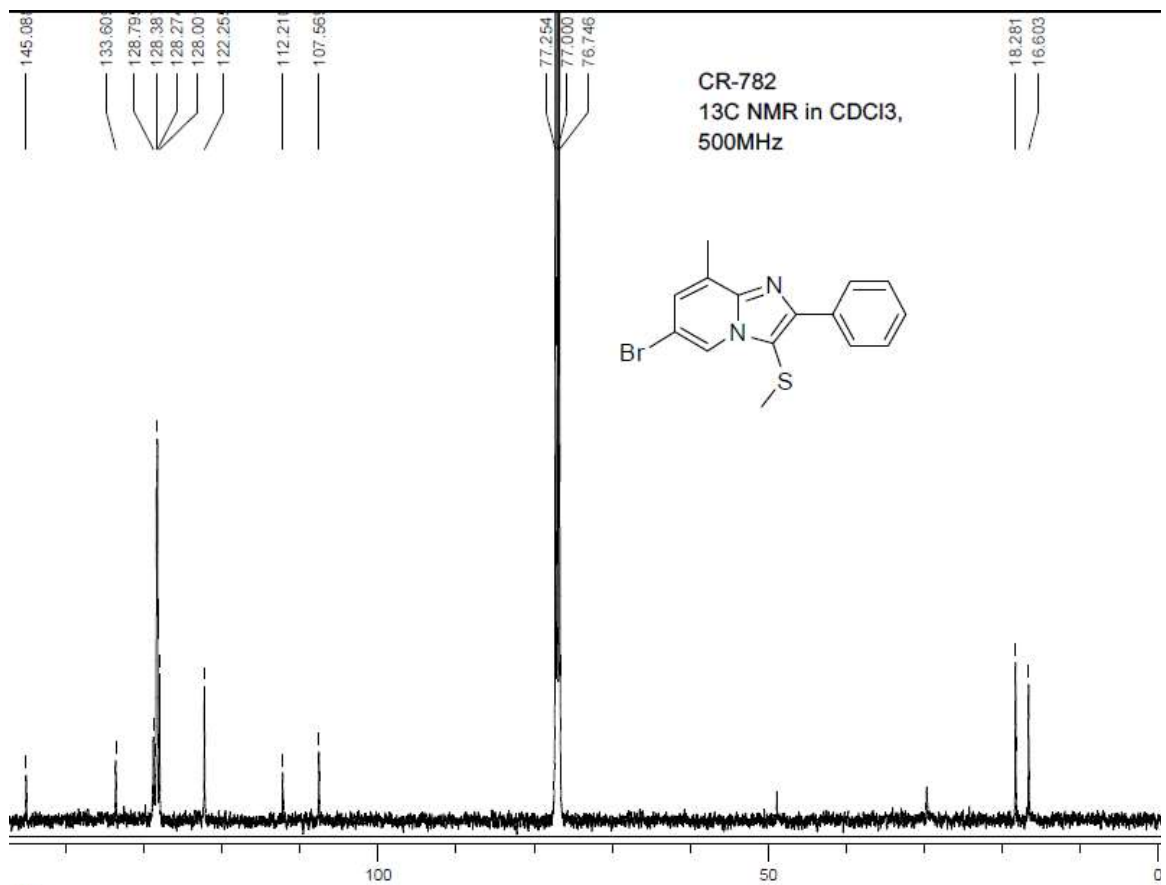
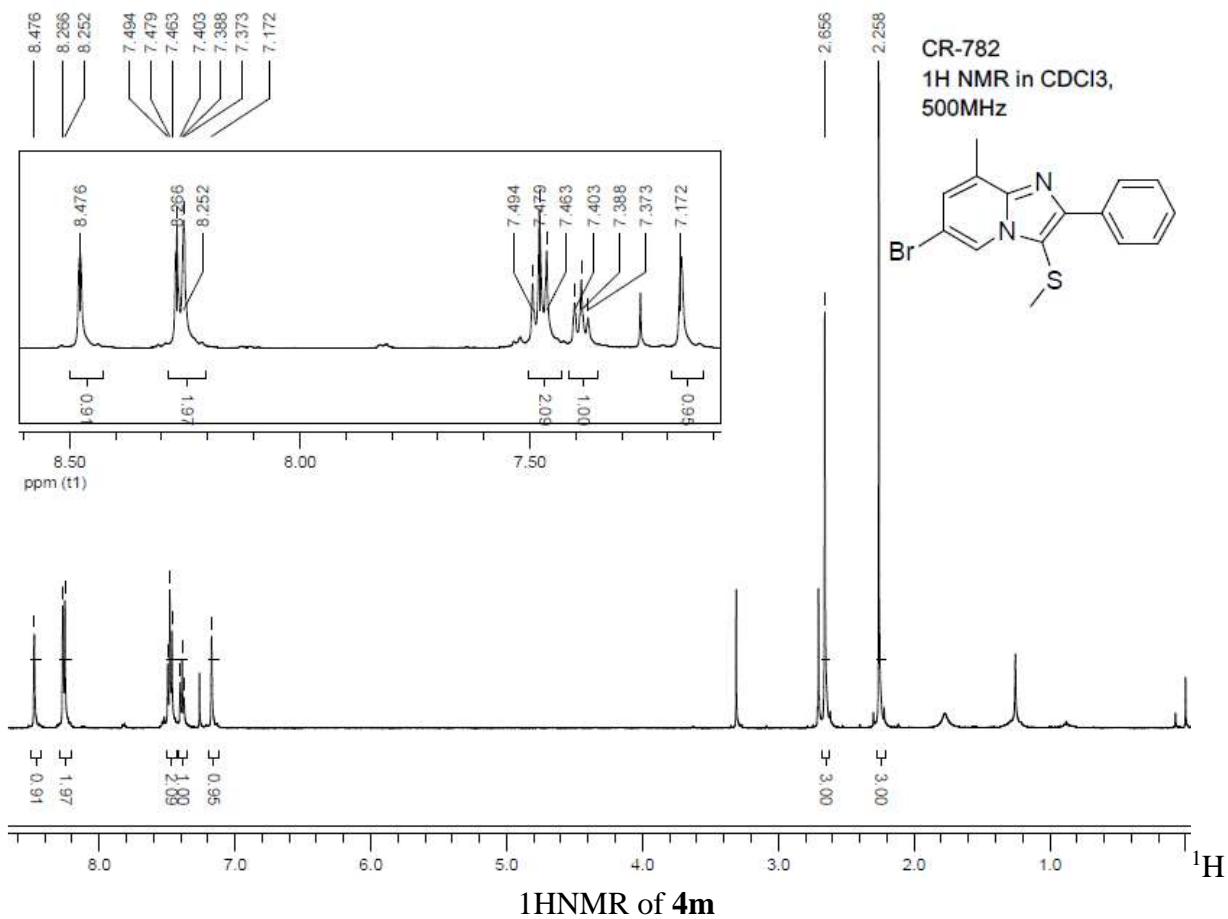
<sup>1</sup>H NMR of **4j**



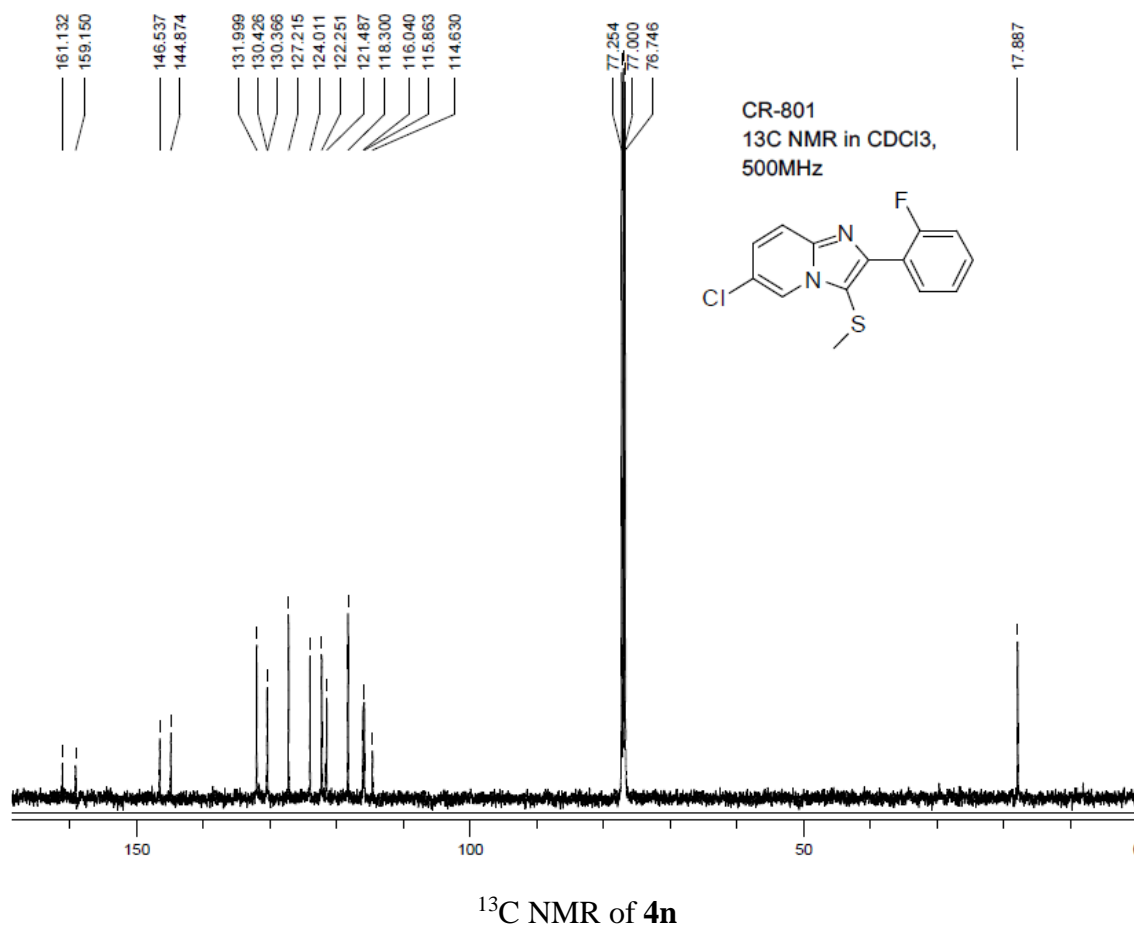
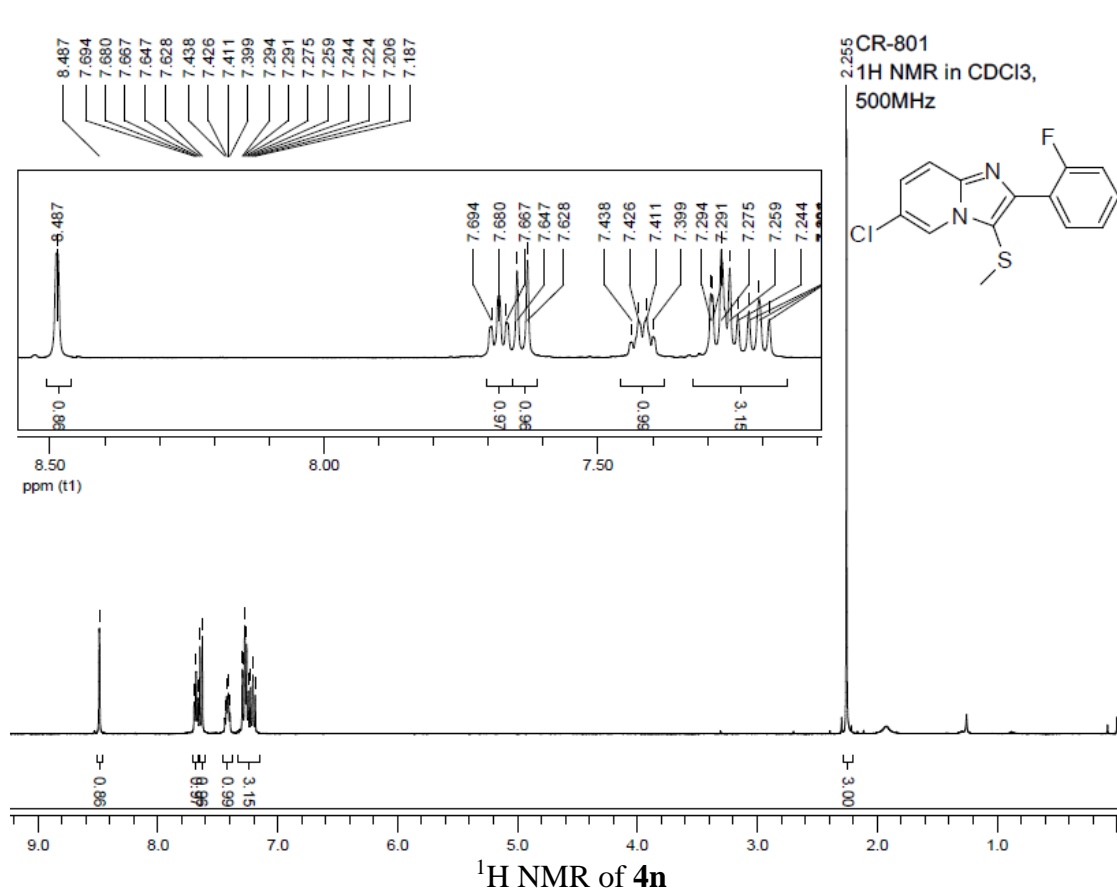


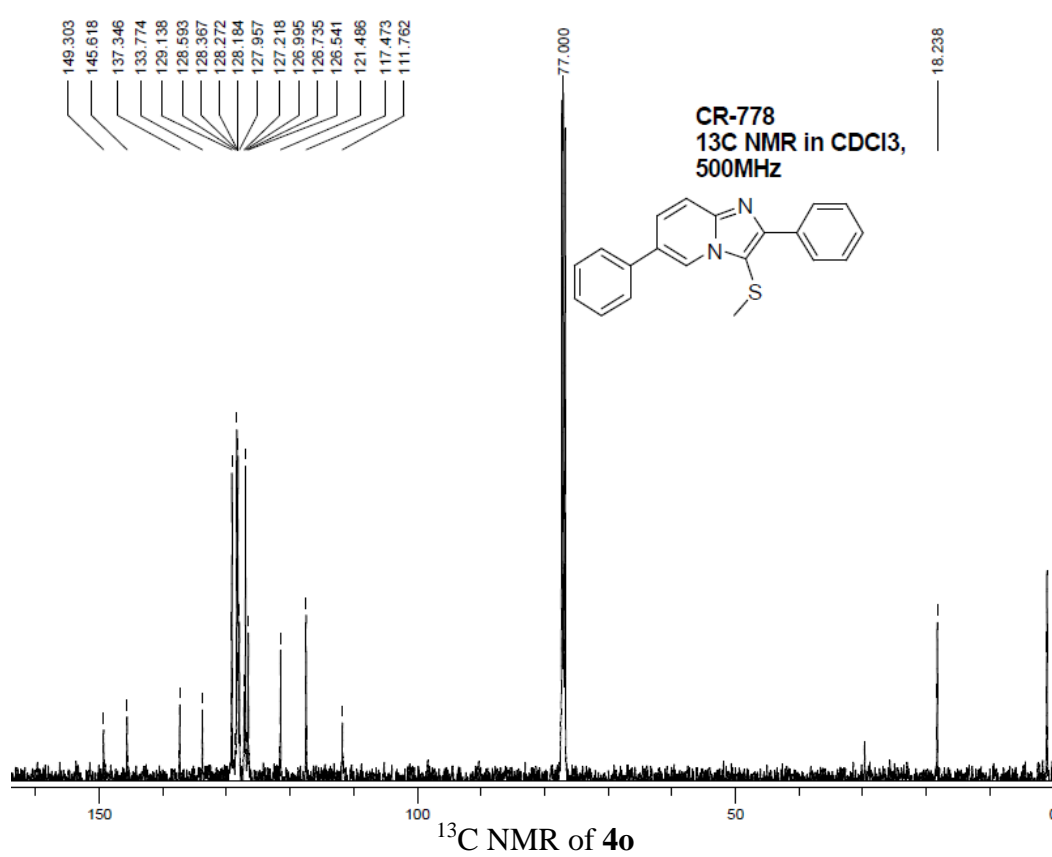
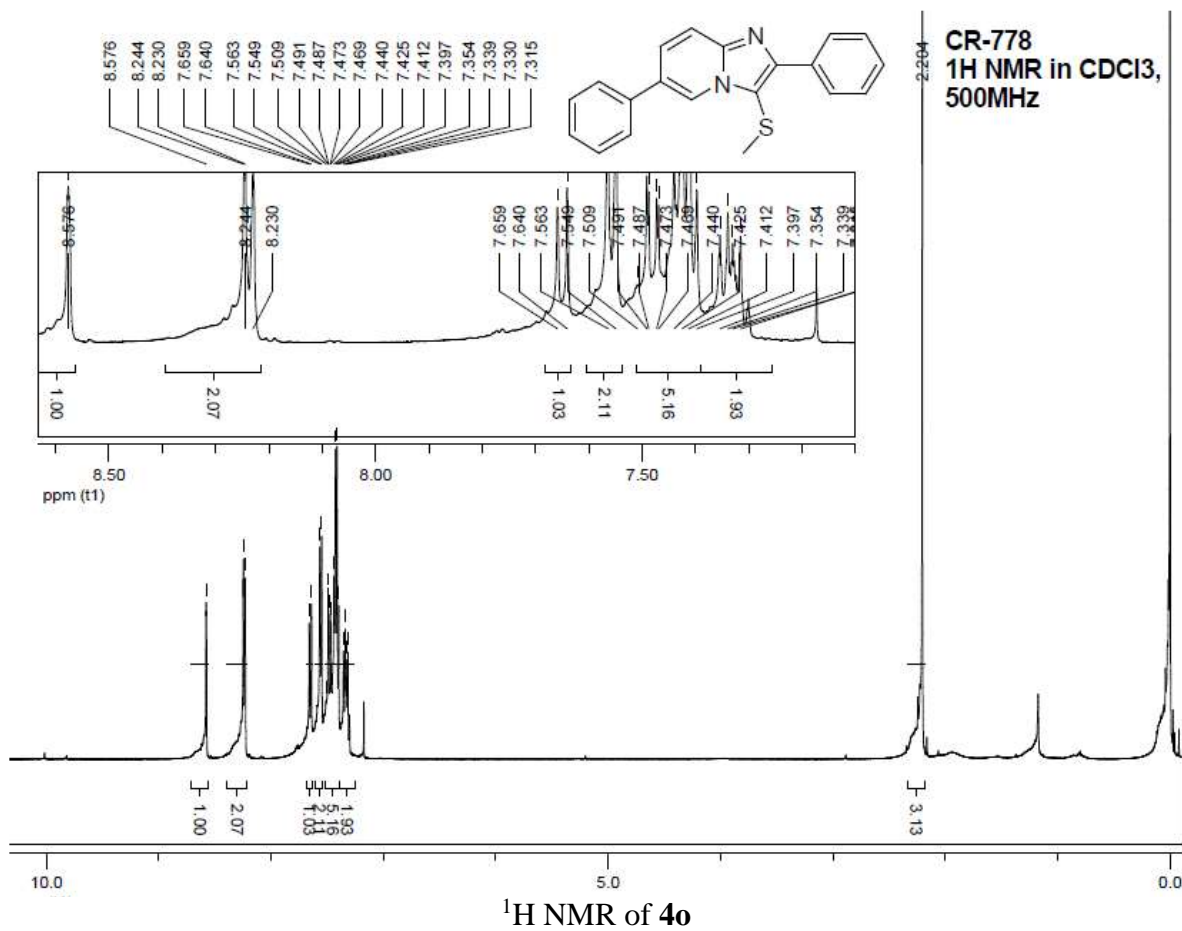


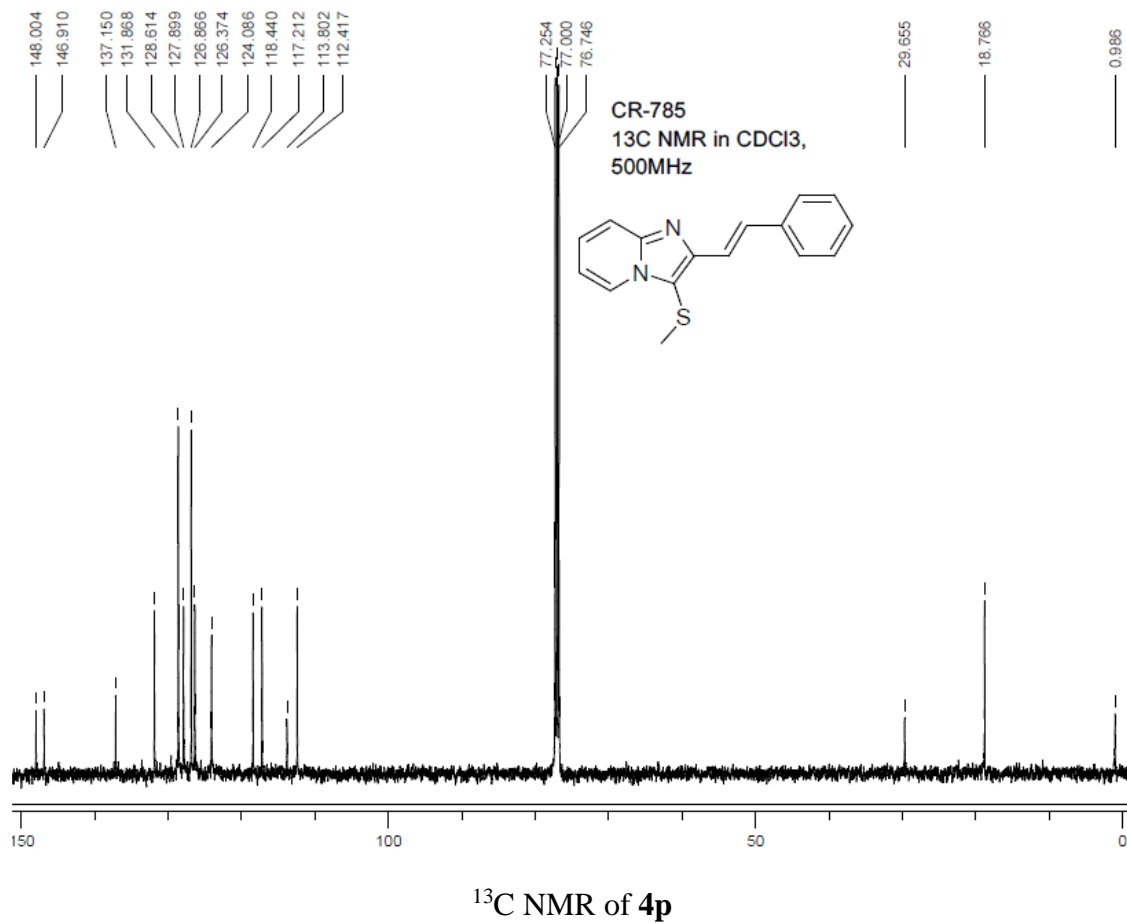
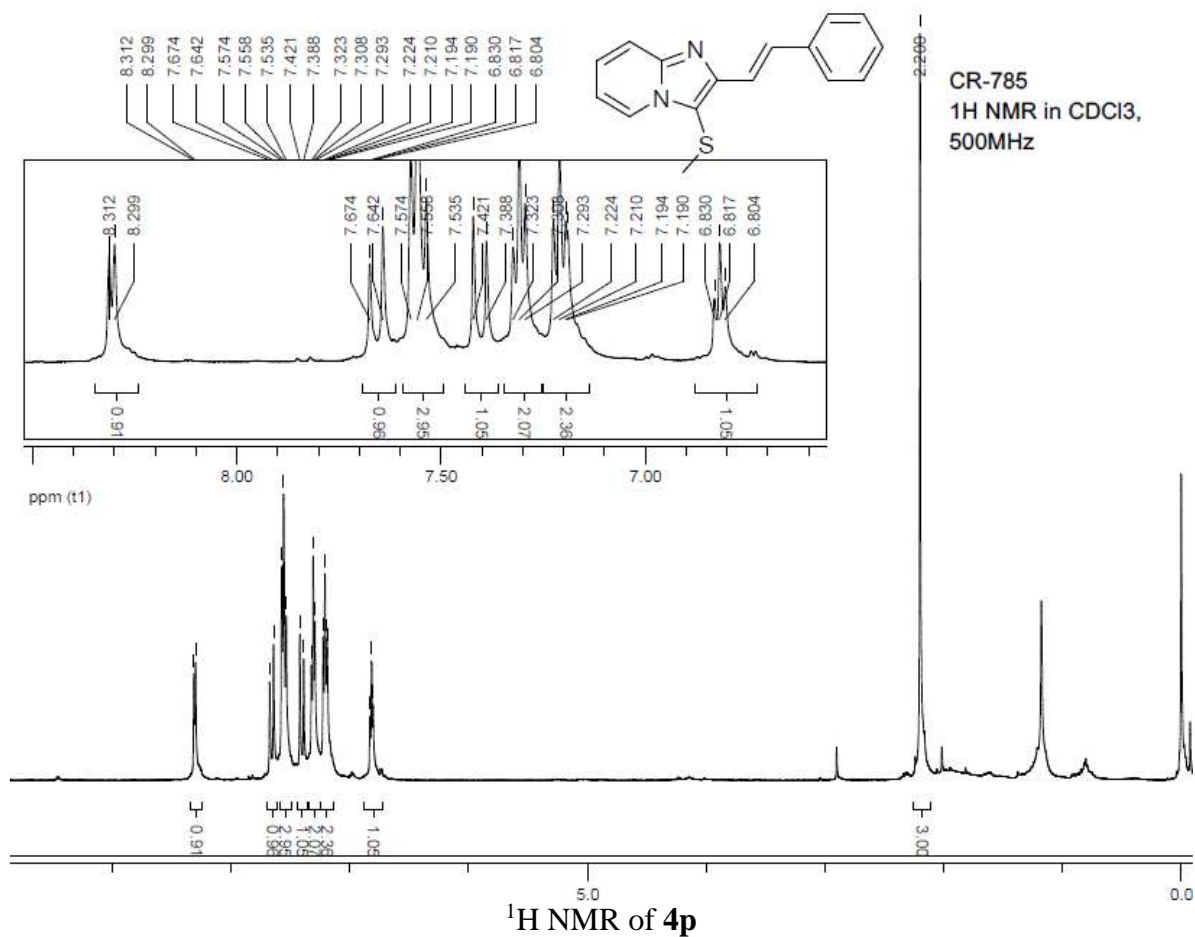


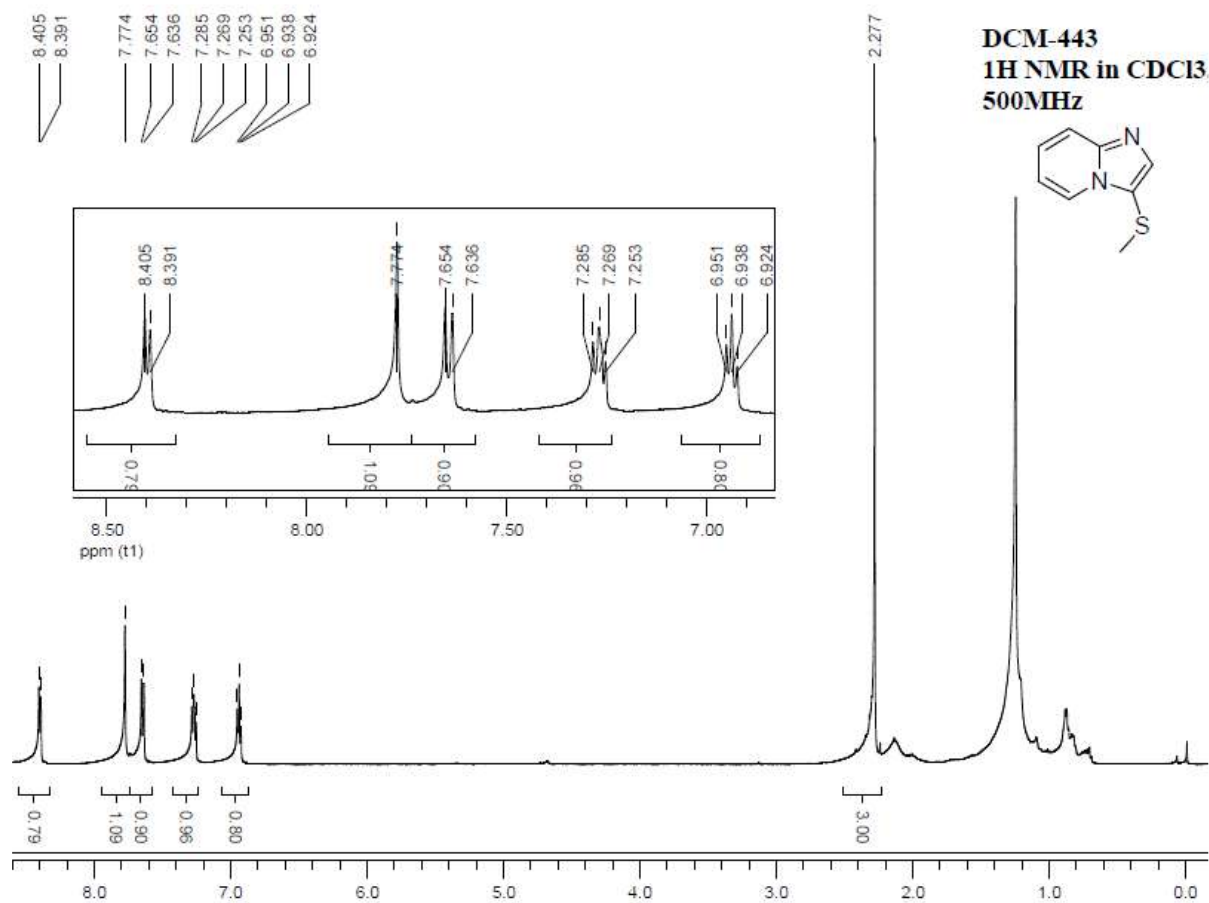


### <sup>13</sup>C NMR of 4m

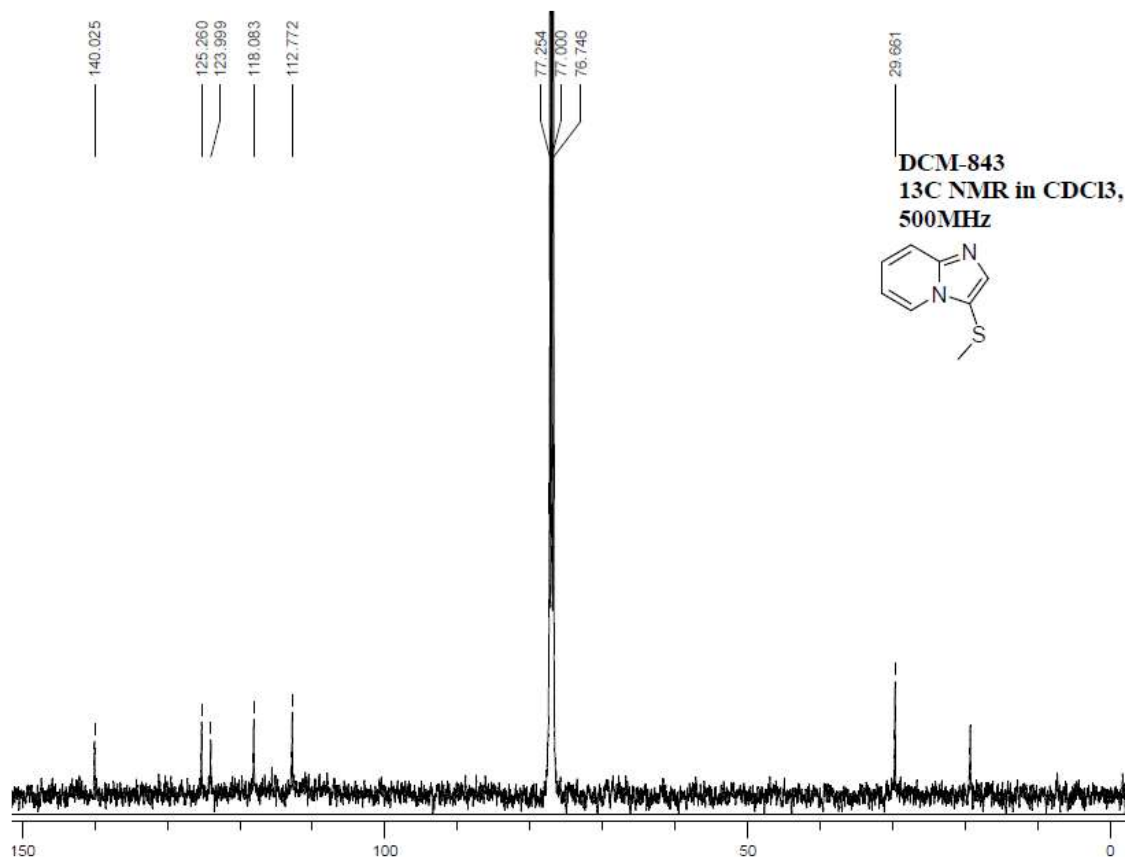








<sup>1</sup>H NMR of 7



<sup>13</sup>C NMR of 7