

# **Organic-acid catalysed Minisci-type arylation of heterocycles with aryl acyl peroxides**

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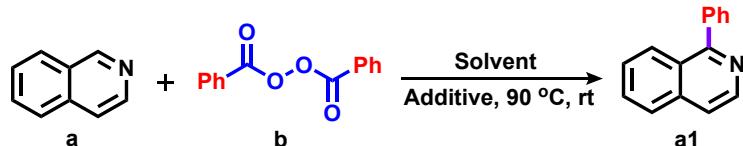
## **Supporting Information**

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## 1. Optimization of reaction conditions

### 1.1 Optimization of additives<sup>a,b</sup>

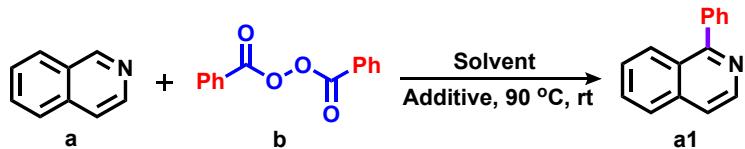


Entry	Temperature	Additive	Solvent	Time	Yield[%] <sup>b</sup>
1 <sup>a</sup>	90	TFA	EtOAc	12	80
2 <sup>c</sup>	90	-	EtOAc	12	trace
3	90	H <sub>2</sub> SO <sub>4</sub>	EtOAc	12	0
4	90	HCl	EtOAc	12	0
5	90	CH <sub>3</sub> COOH	EtOAc	12	39
6	90	methanesulfonic acid	EtOAc	12	0
7	90	trifluoromethanesulfonic acid	EtOAc	12	22
8	90	pivalic acid	EtOAc	12	trace
9	90	IRC <sup>d</sup>	EtOAc	12	trace
10	90	2-naphthalenesulfonic acid	EtOAc	12	50
11	90	<i>p</i> -aminobenzene sulfonic acid	EtOAc	12	40
12	90	methylbenzoic acid	EtOAc	12	30
13	90	phenylboronic acid	EtOAc	12	56
14	90	Taurine	EtOAc	12	55
15	90	2-naphthalene formic acid	EtOAc	12	28
16	90	malic acid	EtOAc	12	67
17	90	fluorin boric acid	EtOAc	12	43
18	90	hydroiodic acid	EtOAc	12	24

<sup>a</sup> Reaction condition: **a** (0.2 mmol), **b** (2.0 equiv), TFA (1 mol%), EtOAc (3 mL), 90 °C, rt, 12 h. <sup>b</sup>

Isolated yields. <sup>c</sup> Without additive. <sup>d</sup> IRC = Cation exchange resin.

## 1.2 Optimization of solvents<sup>a,b</sup>

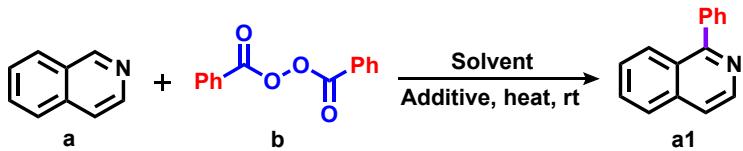


Entry	Temperature	Additive	Solvent	Time	Yield[%] <sup>b</sup>
1	90	TFA	CH <sub>3</sub> CN	12	40
2	90	TFA	C <sub>6</sub> H <sub>12</sub> <sup>c</sup>	12	45
3	90	TFA	Toluene	12	55
4	90	TFA	Acetone	12	78
5	90	TFA	DCE	12	52
6	90	TFA	EtOAc	12	80
7	90	TFA	DMF <sup>d</sup>	12	0
8	90	TFA	CCl <sub>4</sub>	12	0
9	90	TFA	THF	12	0
10	90	TFA	DMSO	12	0
11	90	TFA	H <sub>2</sub> O	12	0
12	90	TFA	1,4-Dioxane	12	0
13	90	TFA	DCM	12	20
14	90	TFA	DMAC <sup>e</sup>	12	0
15	90	TFA	<i>n</i> -Hexane	12	0
16	90	TFA	Pyridine	12	28

<sup>a</sup> Reaction condition: **a** (0.2 mmol), **b** (2.0 equiv), TFA (1 mol%), EtOAc (3 mL), 90 °C, rt, 12 h. <sup>b</sup>

Isolated yields. <sup>c</sup> C<sub>6</sub>H<sub>12</sub> = Cyclohexane. <sup>d</sup> DMF = *N*, *N*-dimethylformamide. <sup>e</sup> DMAC = *N*, *N*-dimethylacetamide.

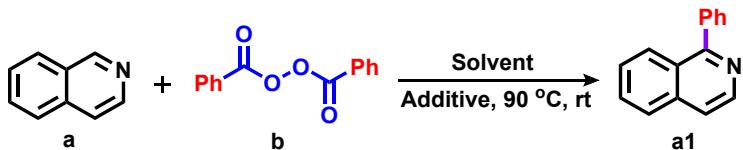
### 1.3 Optimization of temperature<sup>a,b</sup>



Entry	Temperature	Additive	Solvent	Time	Yield[%] <sup>b</sup>
1 <sup>c</sup>	-	TFA	EtOAc	12	0
2	20	TFA	EtOAc	12	0
3	40	TFA	EtOAc	12	0
4	60	TFA	EtOAc	12	20
5	70	TFA	EtOAc	12	75
6	80	TFA	EtOAc	12	72
7	90	TFA	EtOAc	12	80
8	100	TFA	EtOAc	12	68
9	120	TFA	EtOAc	12	60

<sup>a</sup> Reaction condition: **a** (0.2 mmol), **b** (2.0 equiv), TFA (1 mol%), EtOAc (3 mL), rt, 12 h. <sup>b</sup> Isolated yields. <sup>c</sup> Under room temperature.

### 1.4 Optimization of time<sup>a,b</sup>

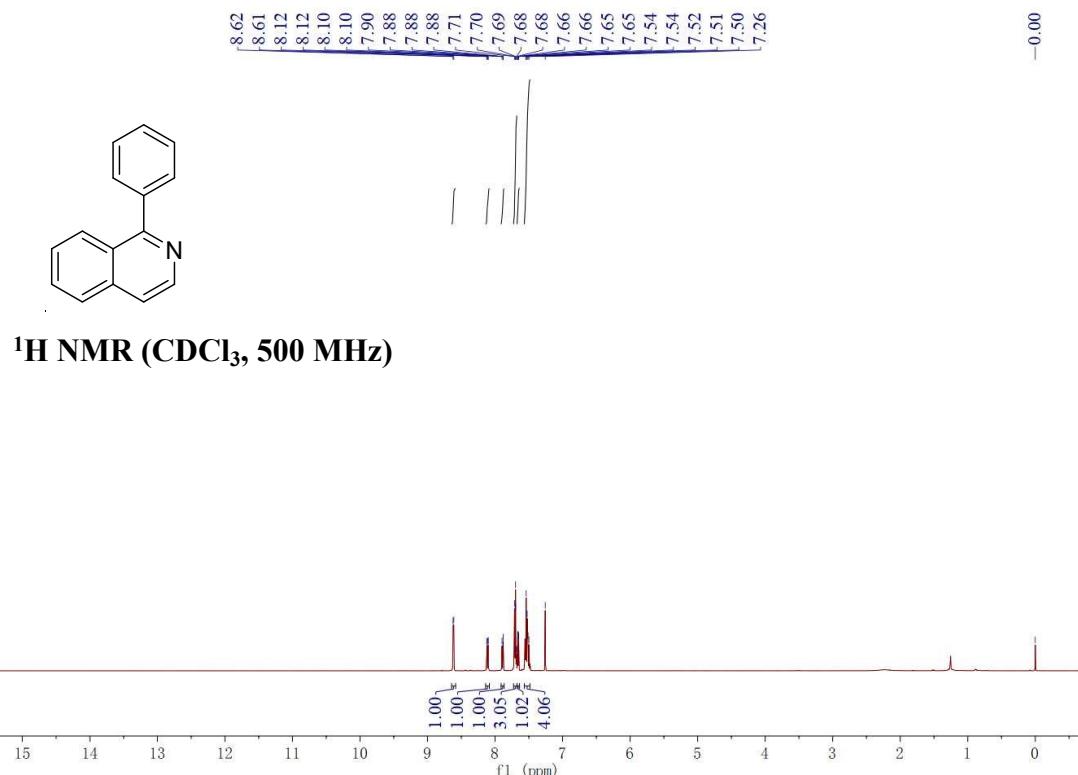


Entry	Temperature	Additive	Solvent	Time	Yield[%] <sup>b</sup>
1	90	TFA	EtOAc	2	30
2	90	TFA	EtOAc	6	50
3	90	TFA	EtOAc	10	70
4	90	TFA	EtOAc	12	80
5	90	TFA	EtOAc	24	80

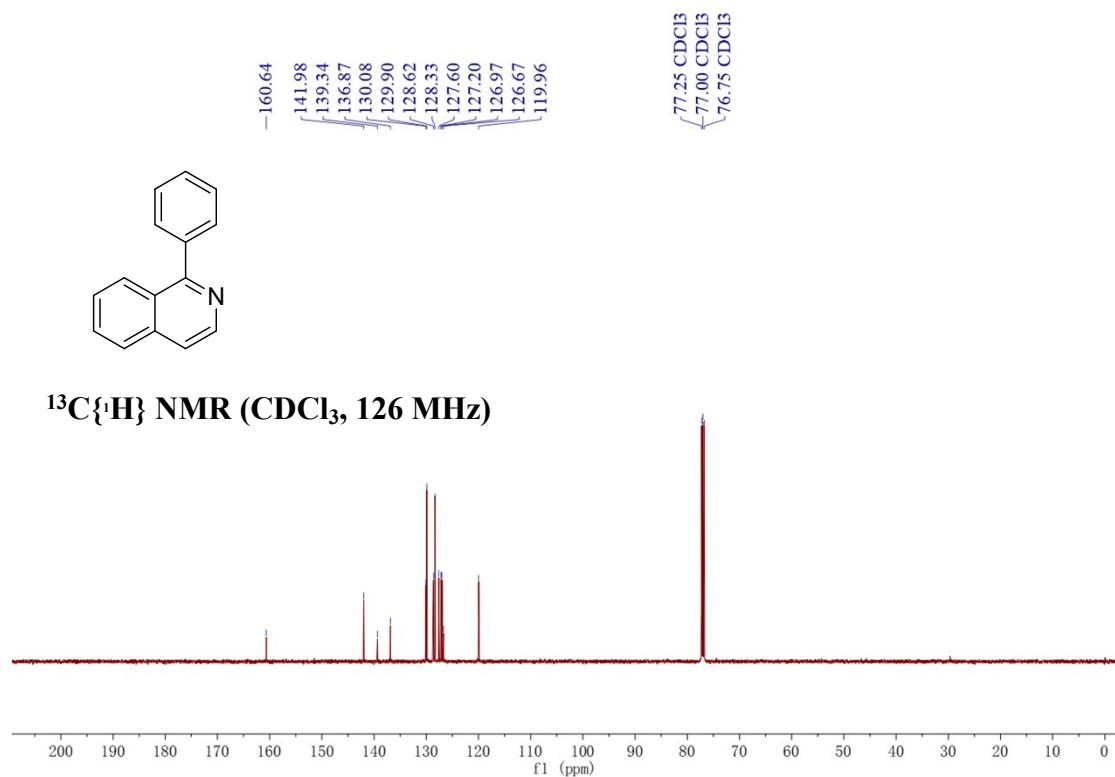
<sup>a</sup> Reaction condition: **a** (0.2 mmol), **b** (2.0 equiv), TFA (1 mol%), EtOAc (3 mL), 90 °C, rt. <sup>b</sup> Isolated yields.

## 2. Copies of NMR spectra

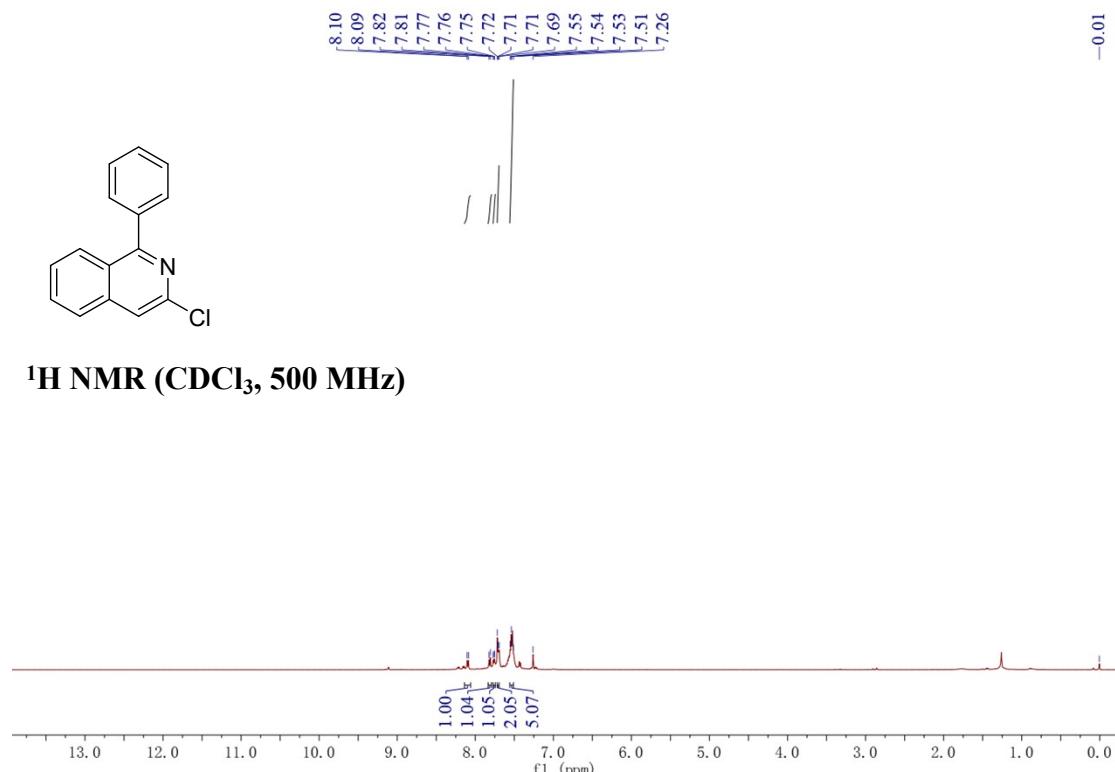
### $^1\text{H}$ NMR Spectrum of Compound a1



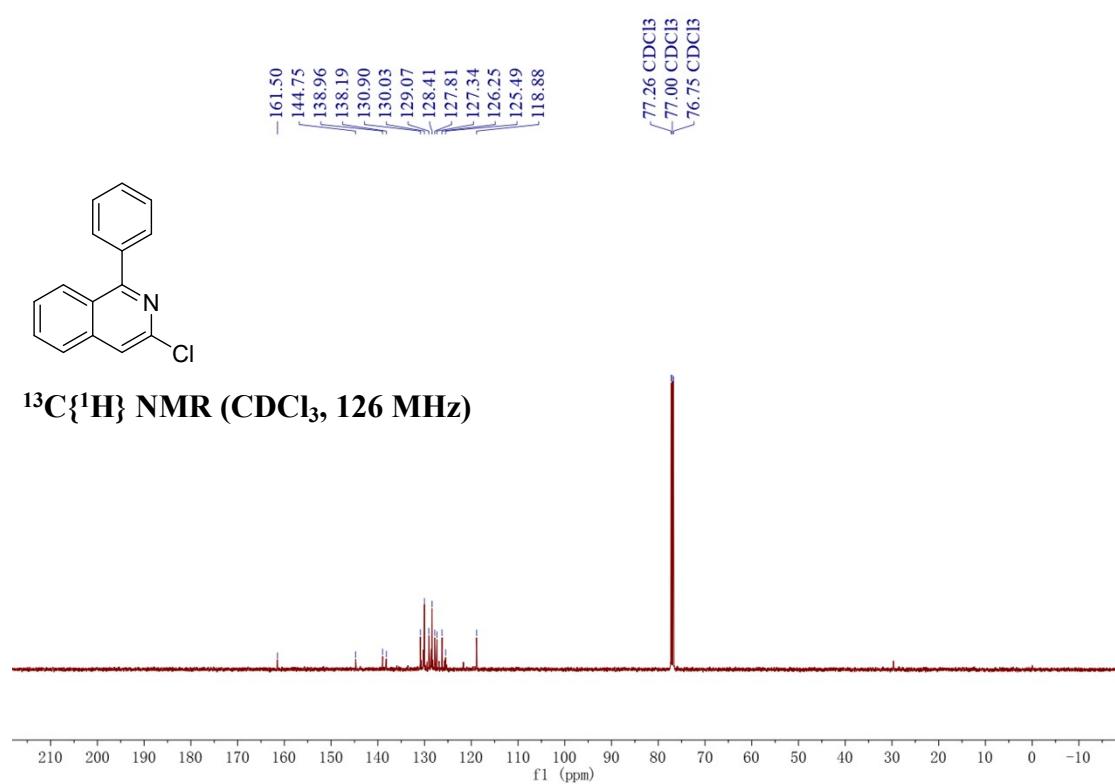
### $^{13}\text{C}\{\text{H}\}$ NMR Spectrum of Compound a1



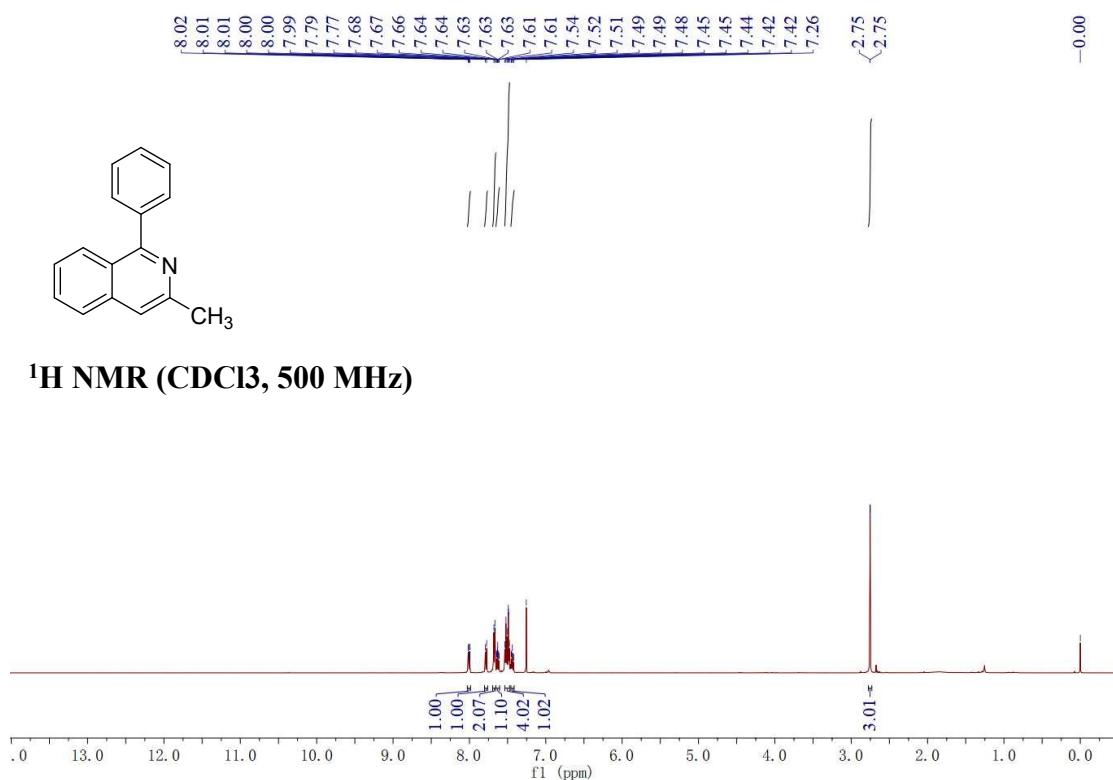
### <sup>1</sup>H NMR Spectrum of Compound a2



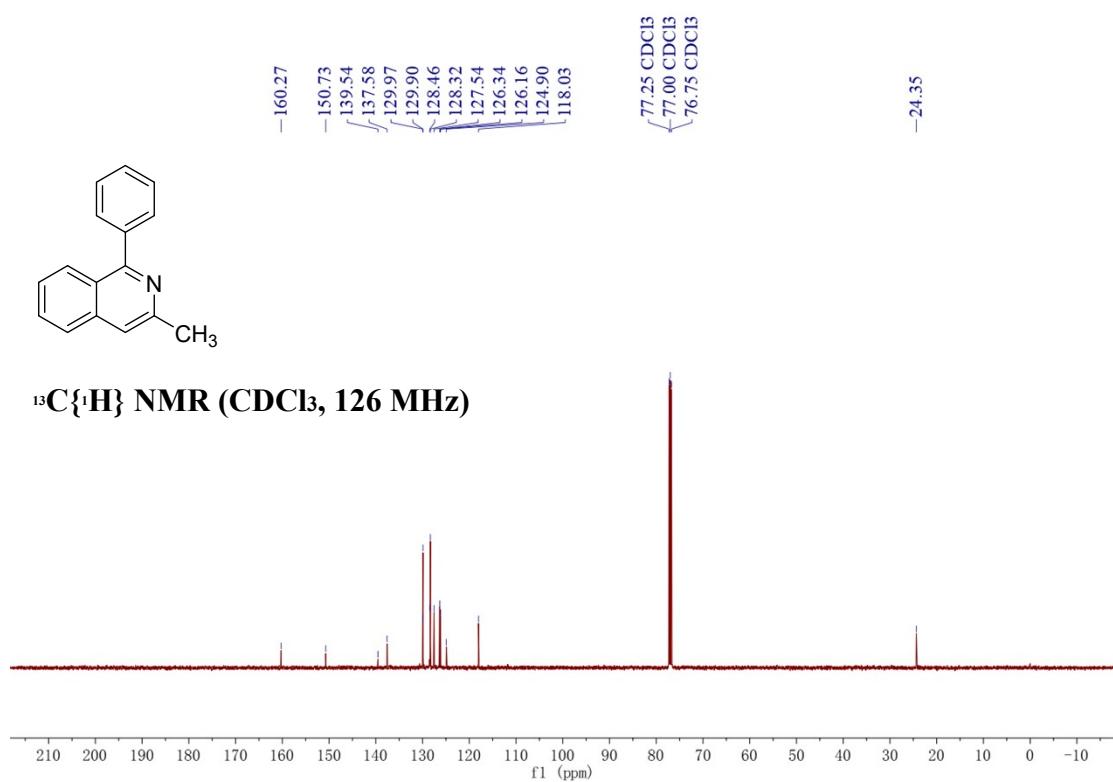
### <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of Compound a2



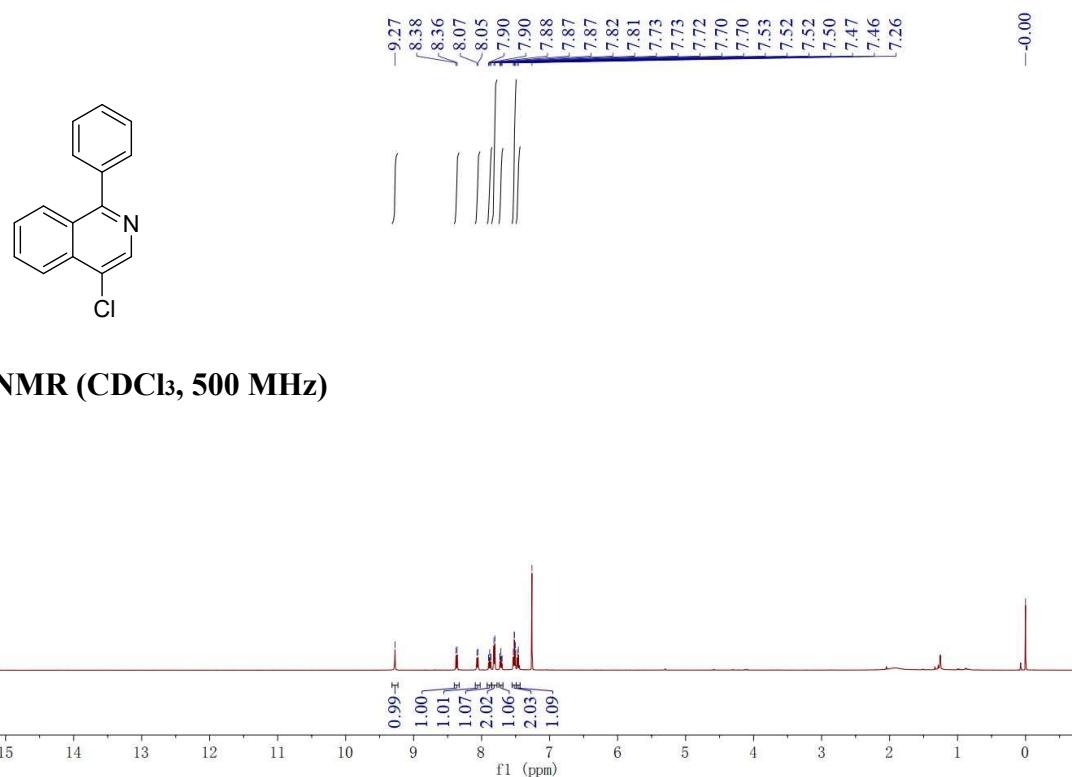
**$^1\text{H}$  NMR Spectrum of Compound a3**



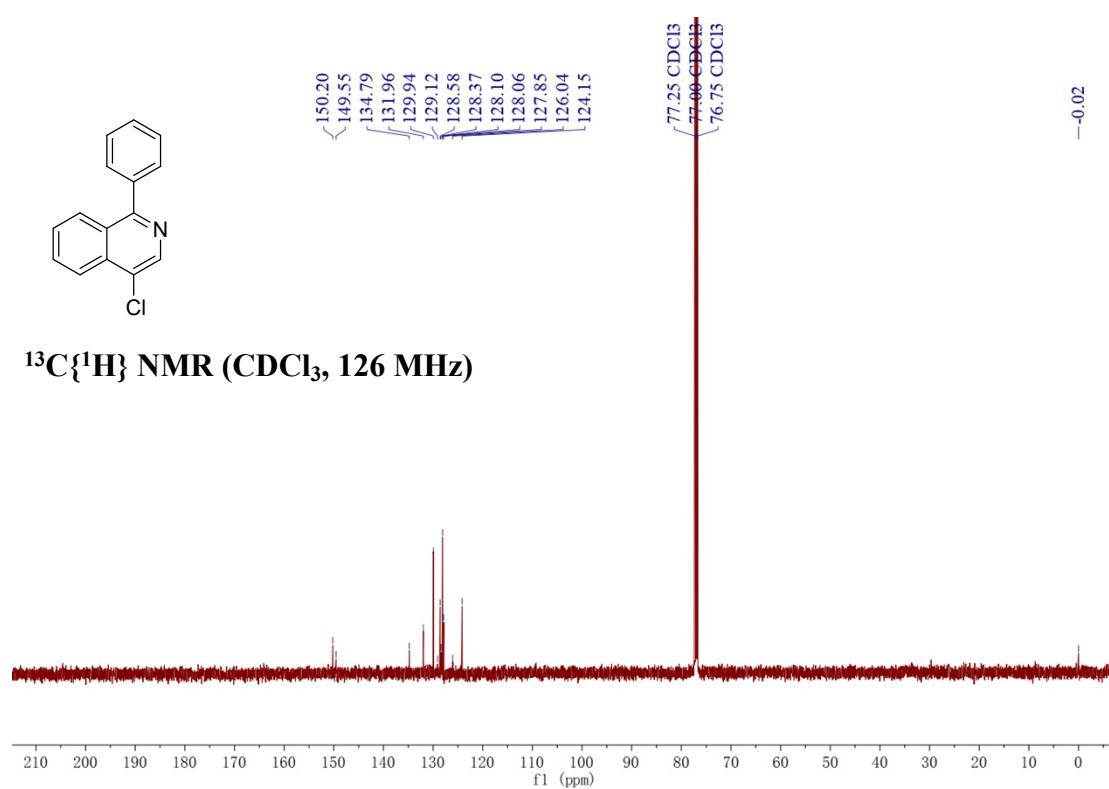
**$^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of Compound a3**



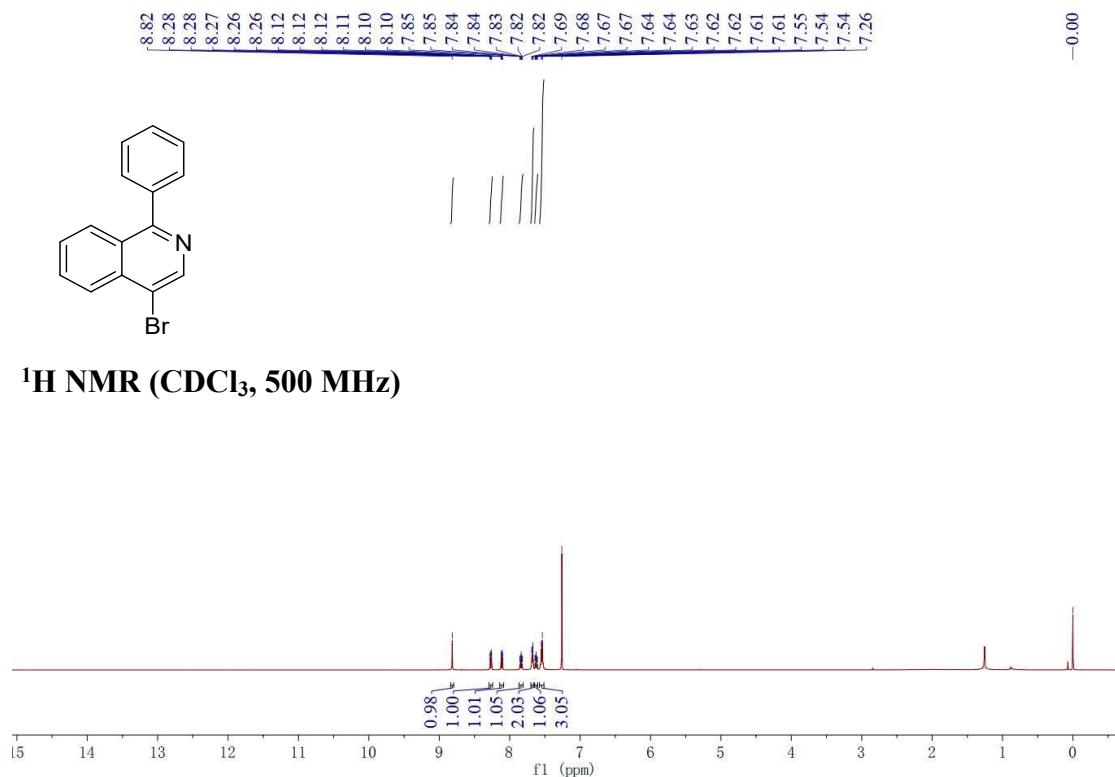
### <sup>1</sup>H NMR Spectrum of Compound a4



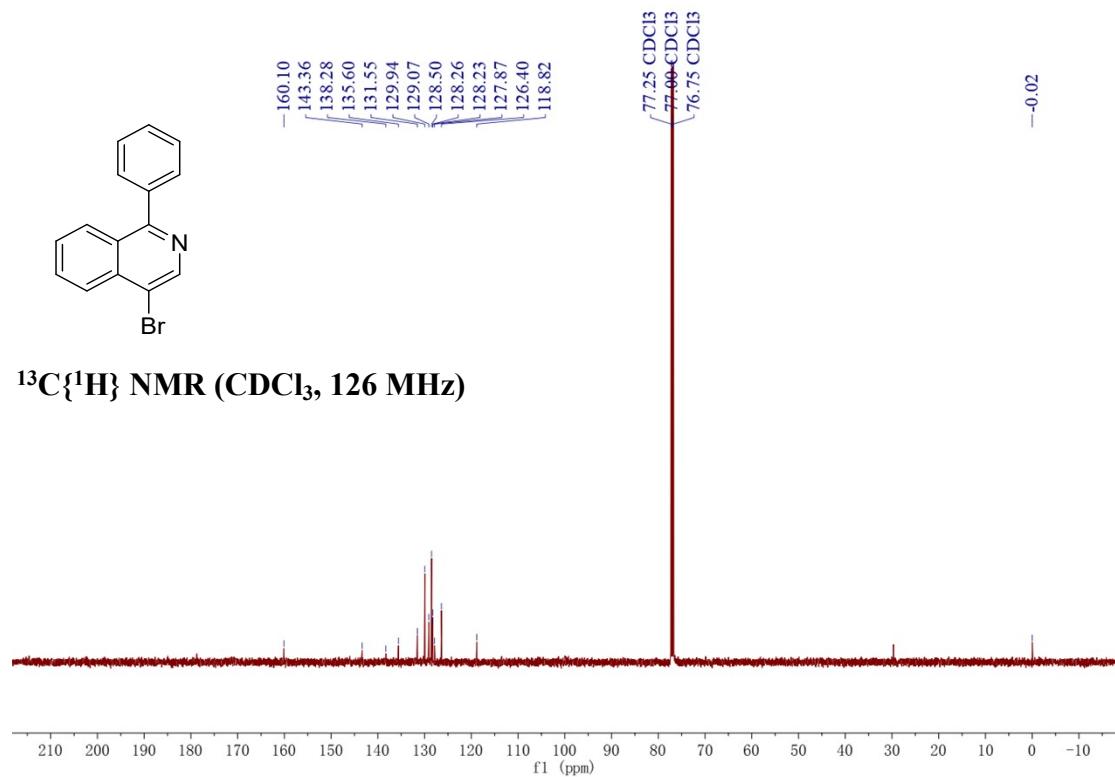
### <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of Compound a4



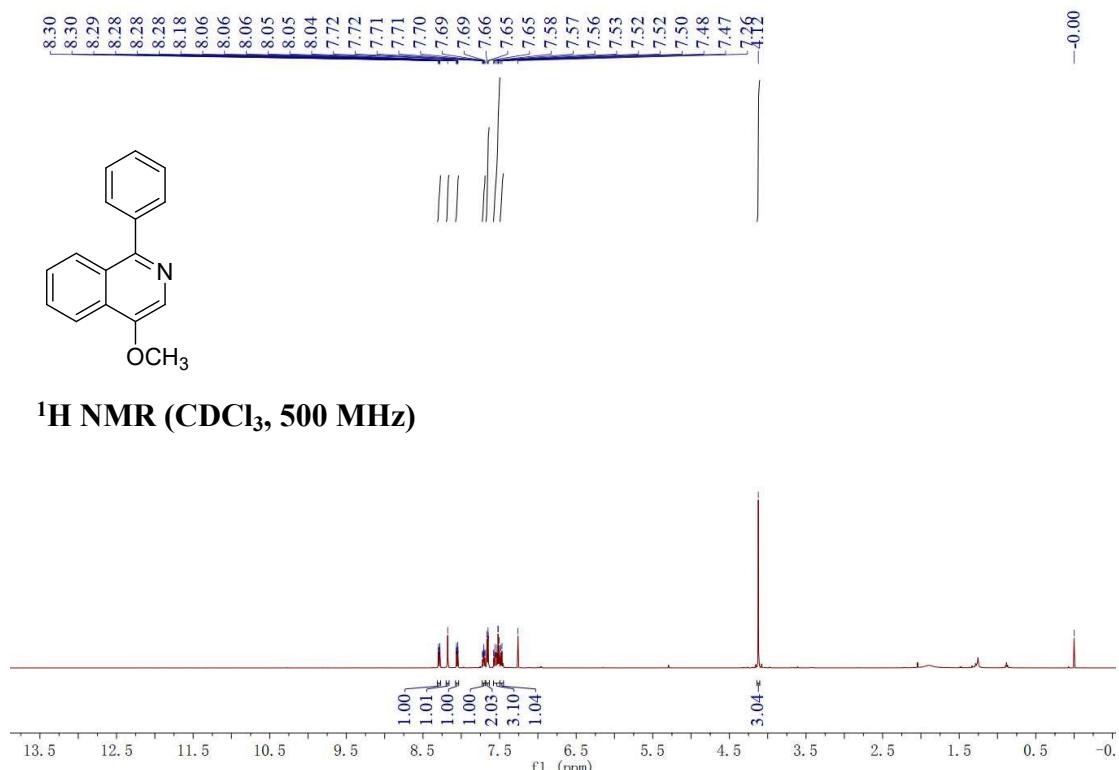
**$^1\text{H}$  NMR Spectrum of Compound a5**



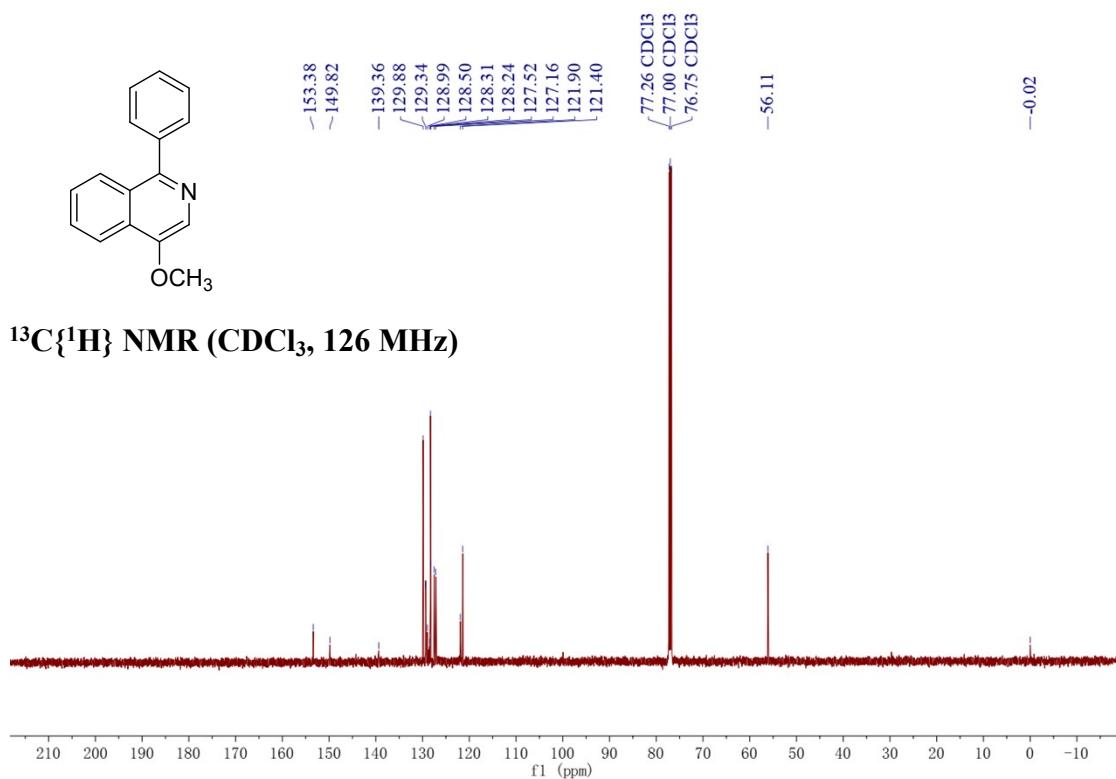
**$^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of Compound a5**



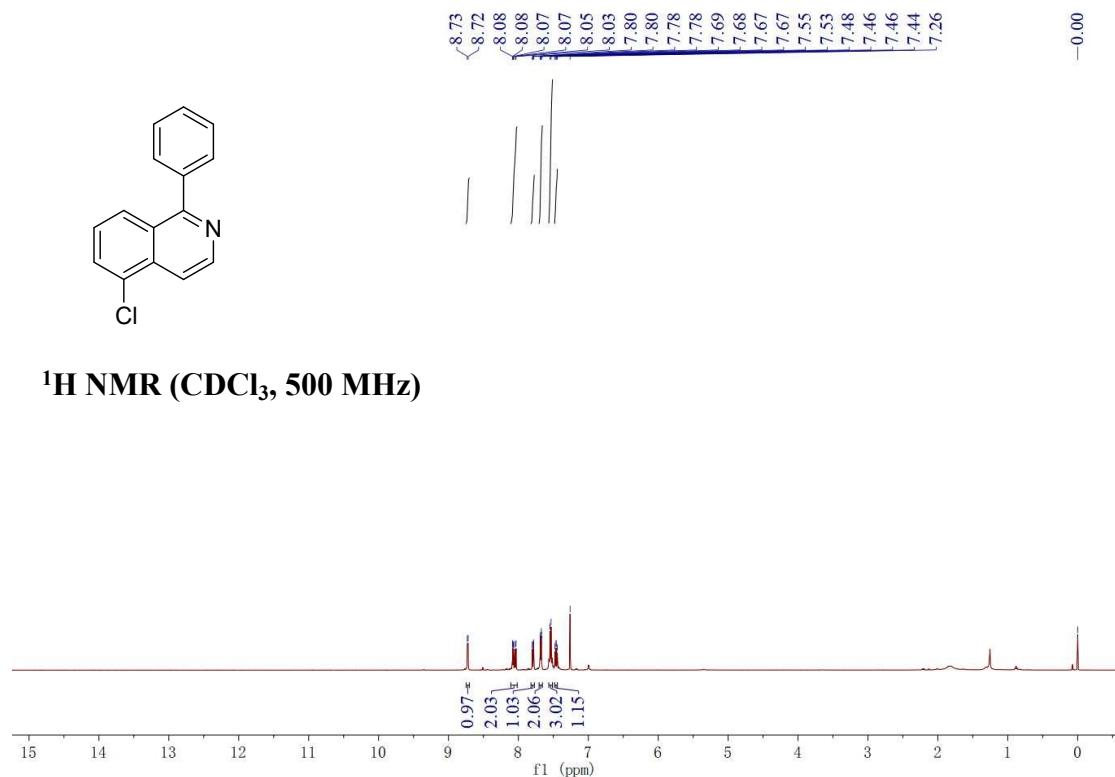
**$^1\text{H}$  NMR Spectrum of Compound a6**



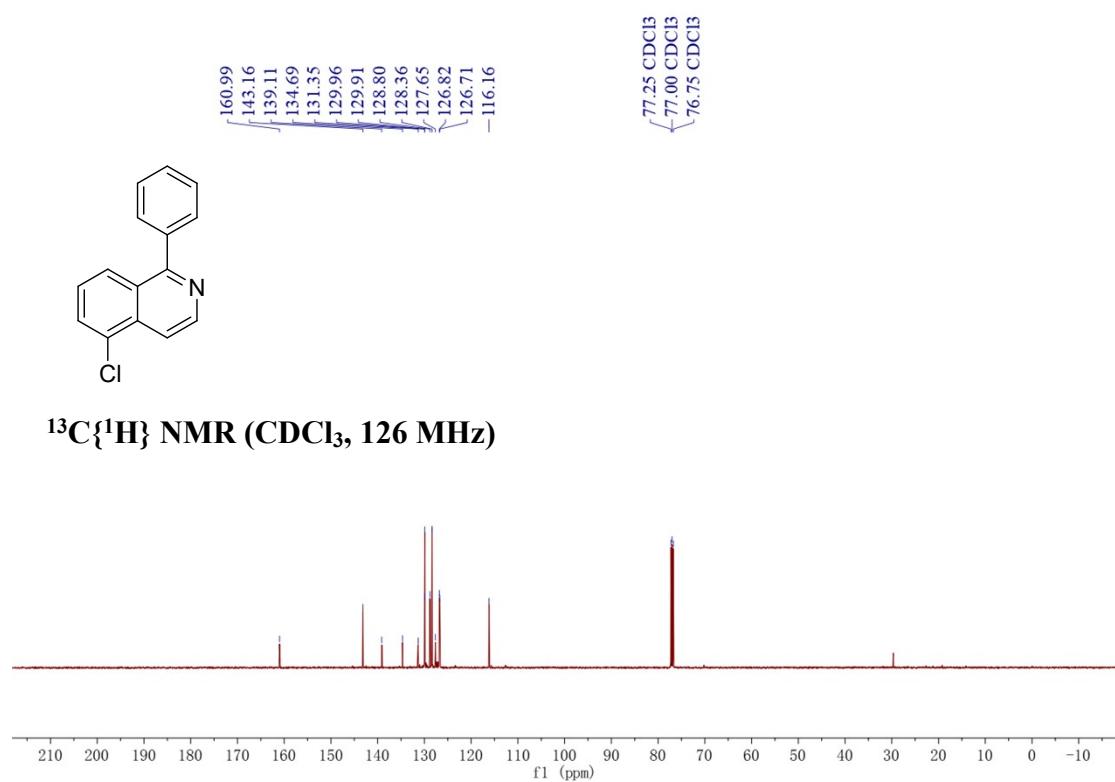
**$^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of Compound a6**



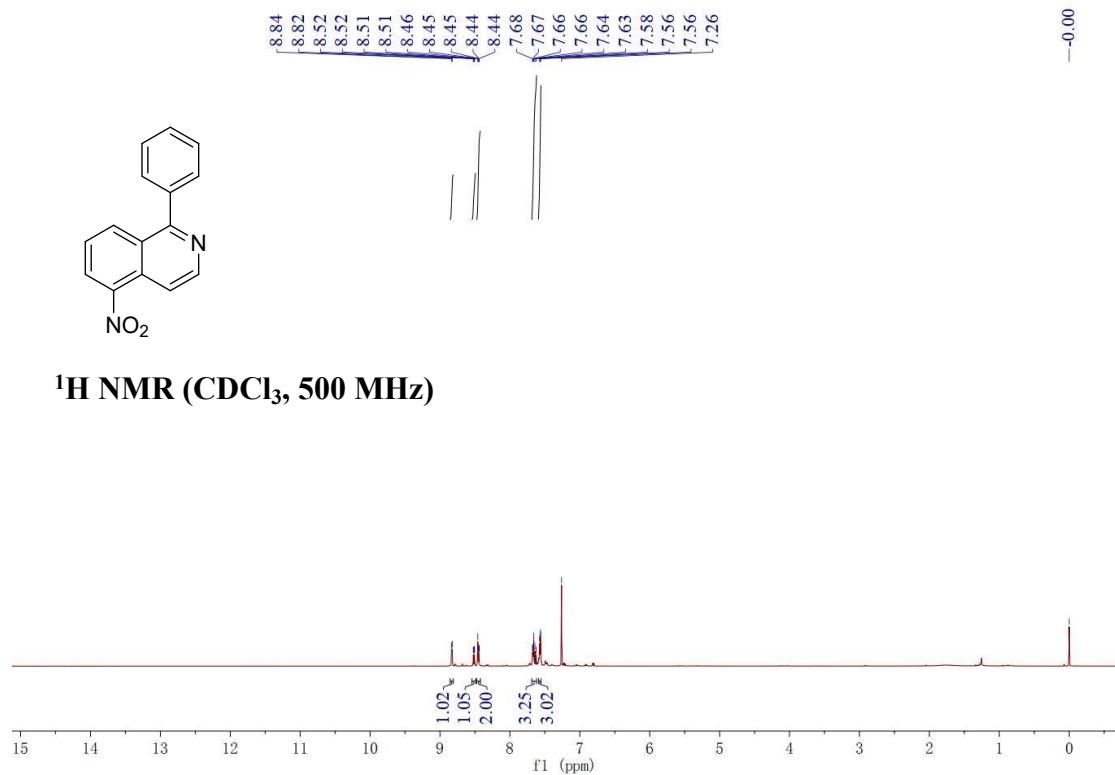
### <sup>1</sup>H NMR Spectrum of Compound a7



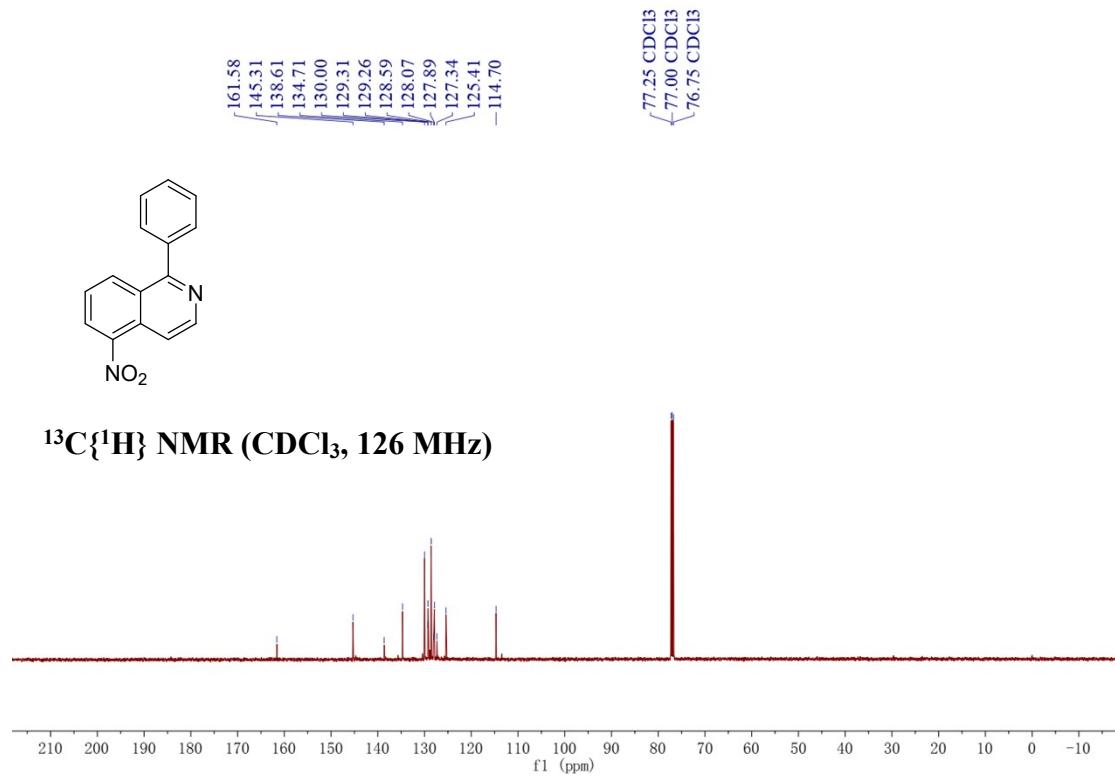
### <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of Compound a7



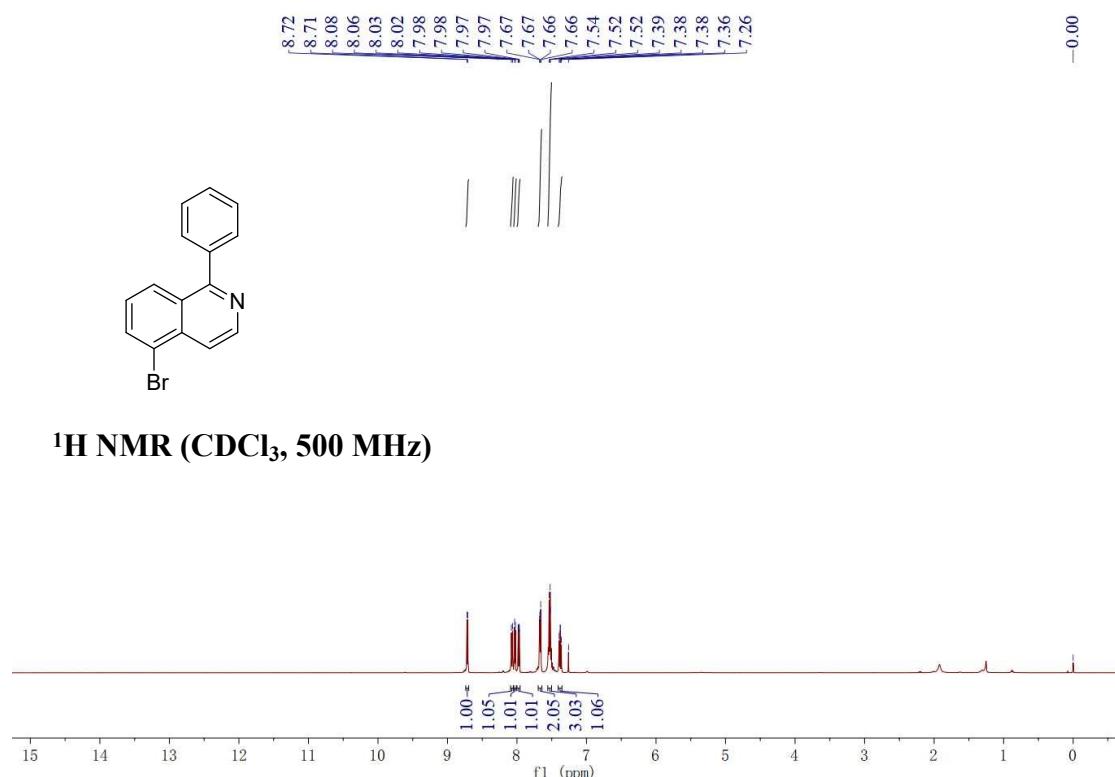
### <sup>1</sup>H NMR Spectrum of Compound a8



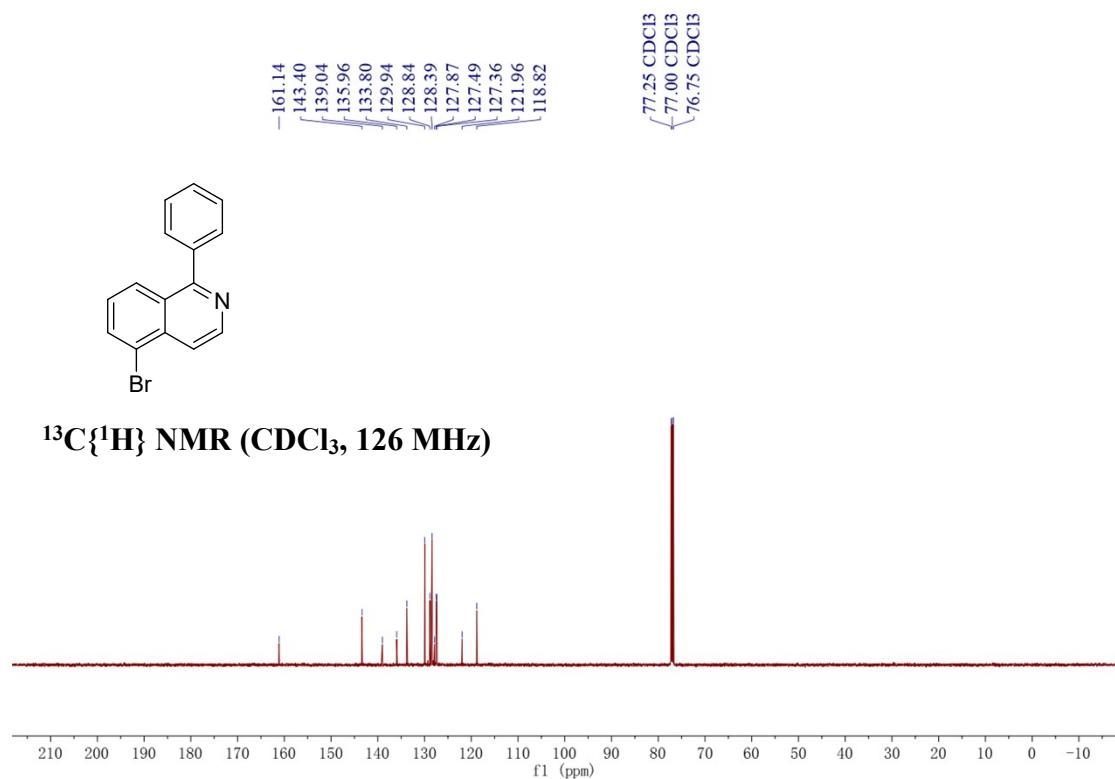
### <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of Compound a8



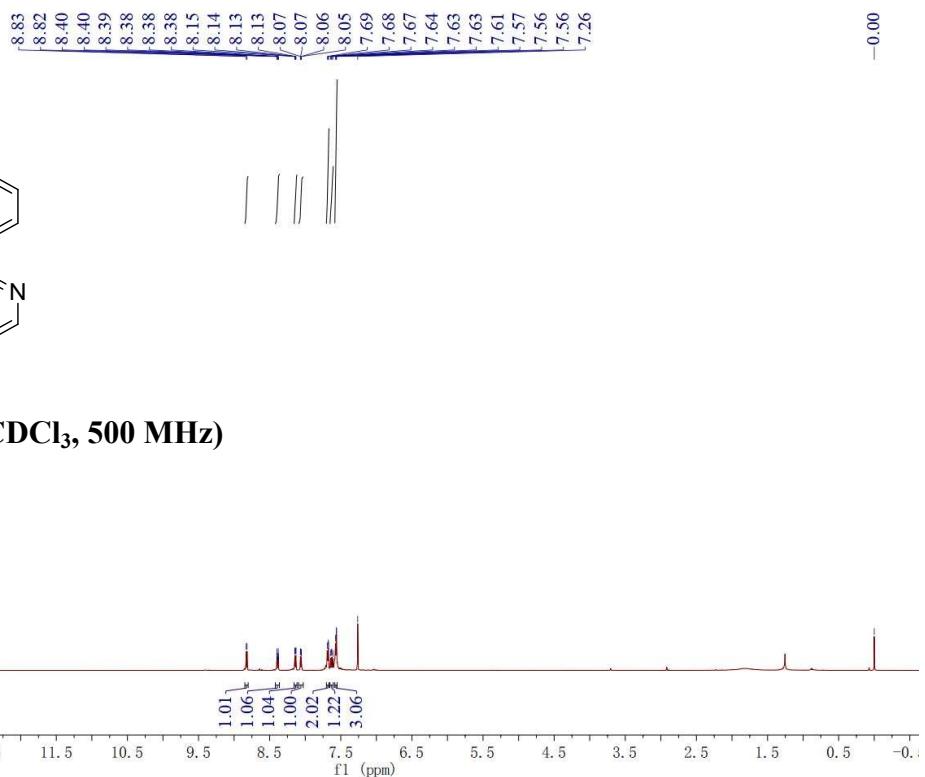
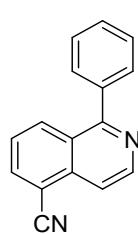
### <sup>1</sup>H NMR Spectrum of Compound a9



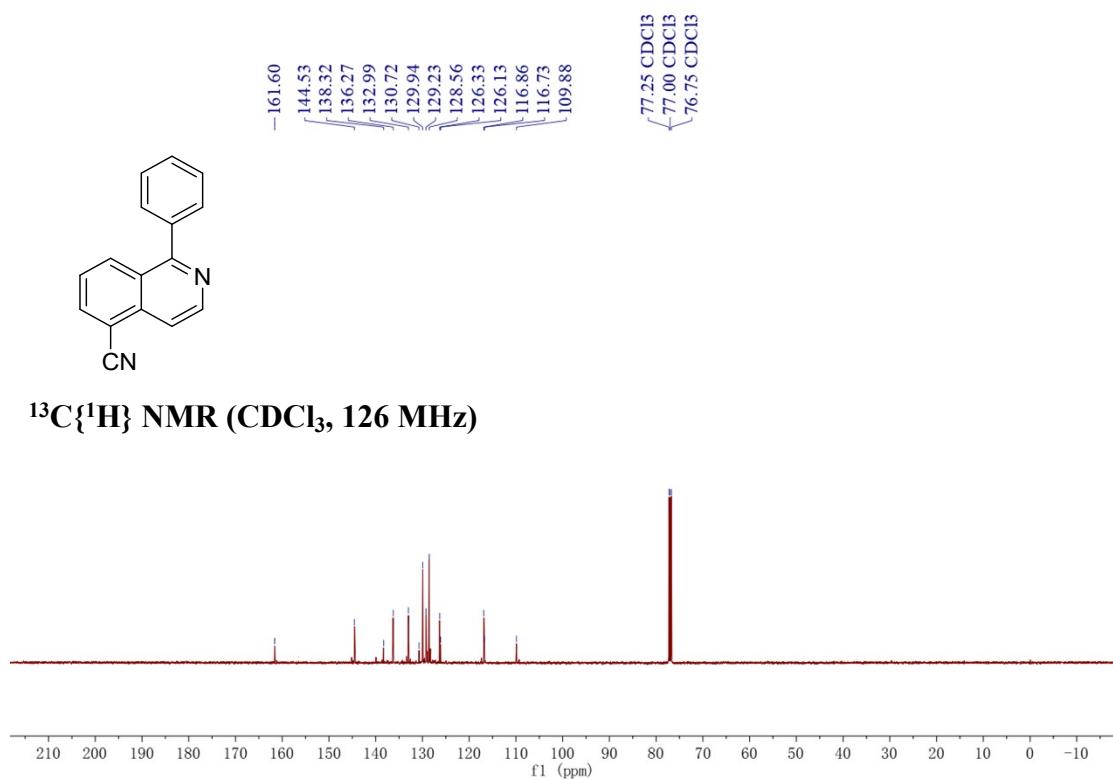
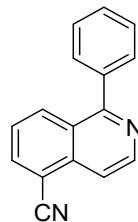
### <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of Compound a9



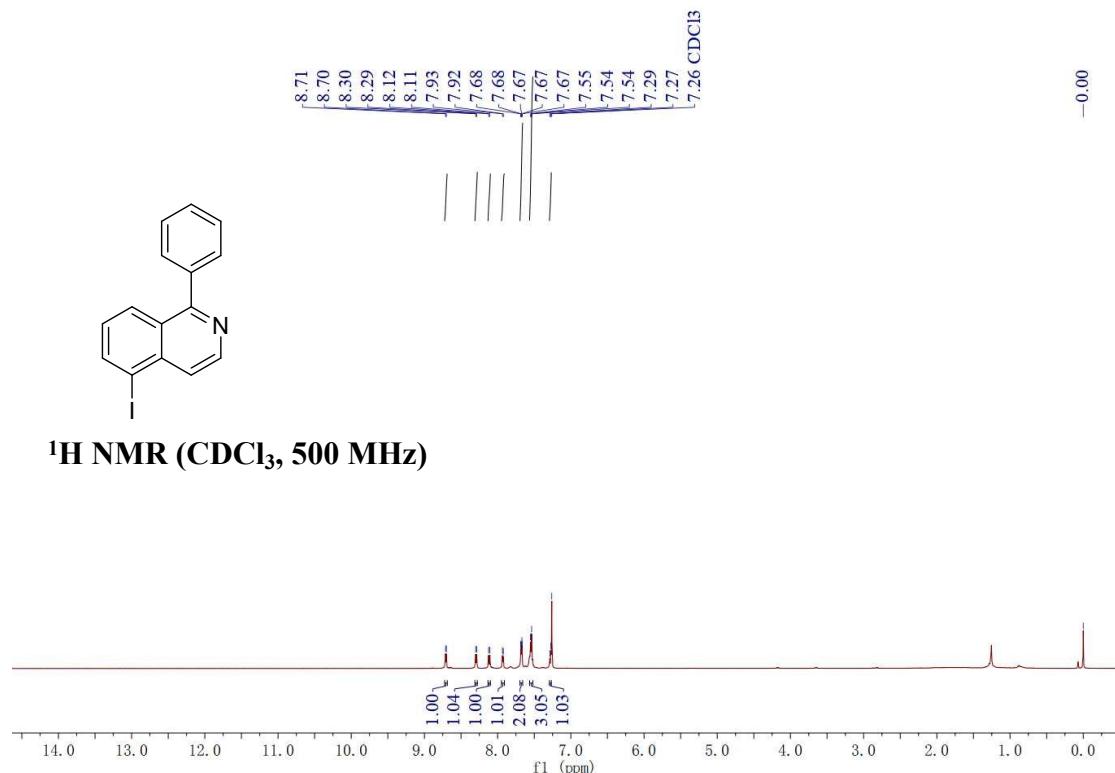
## **<sup>1</sup>H NMR Spectrum of Compound a10**



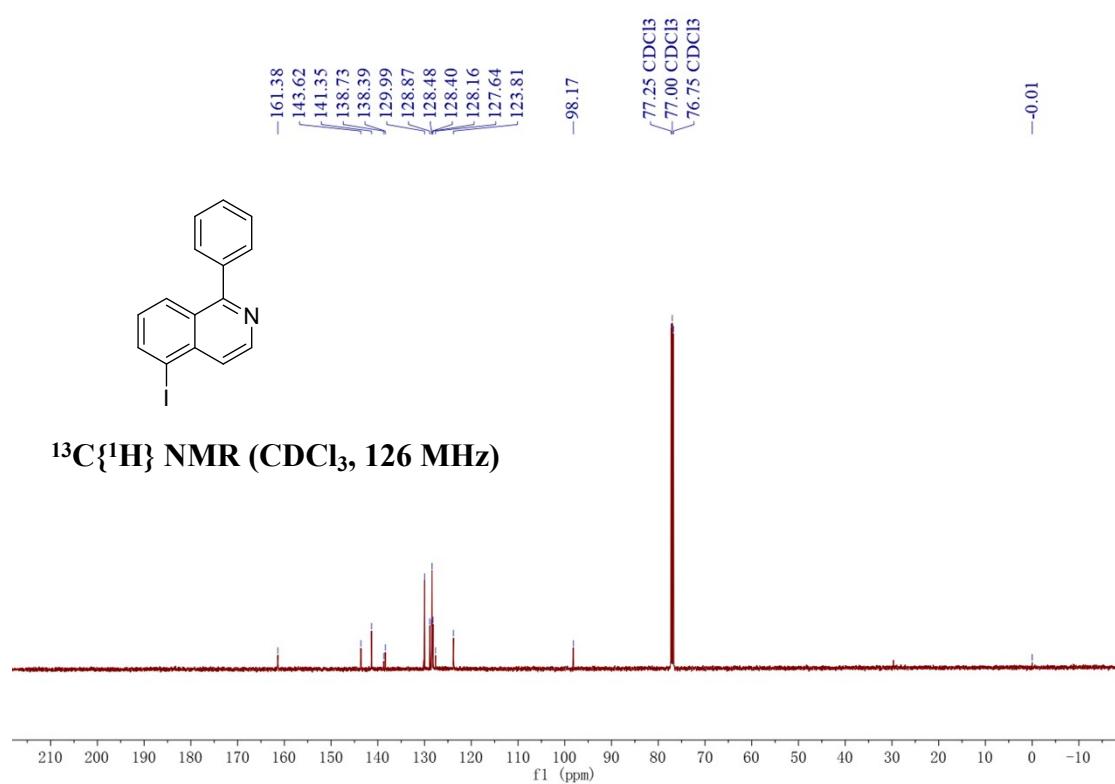
### **<sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of Compound a10**



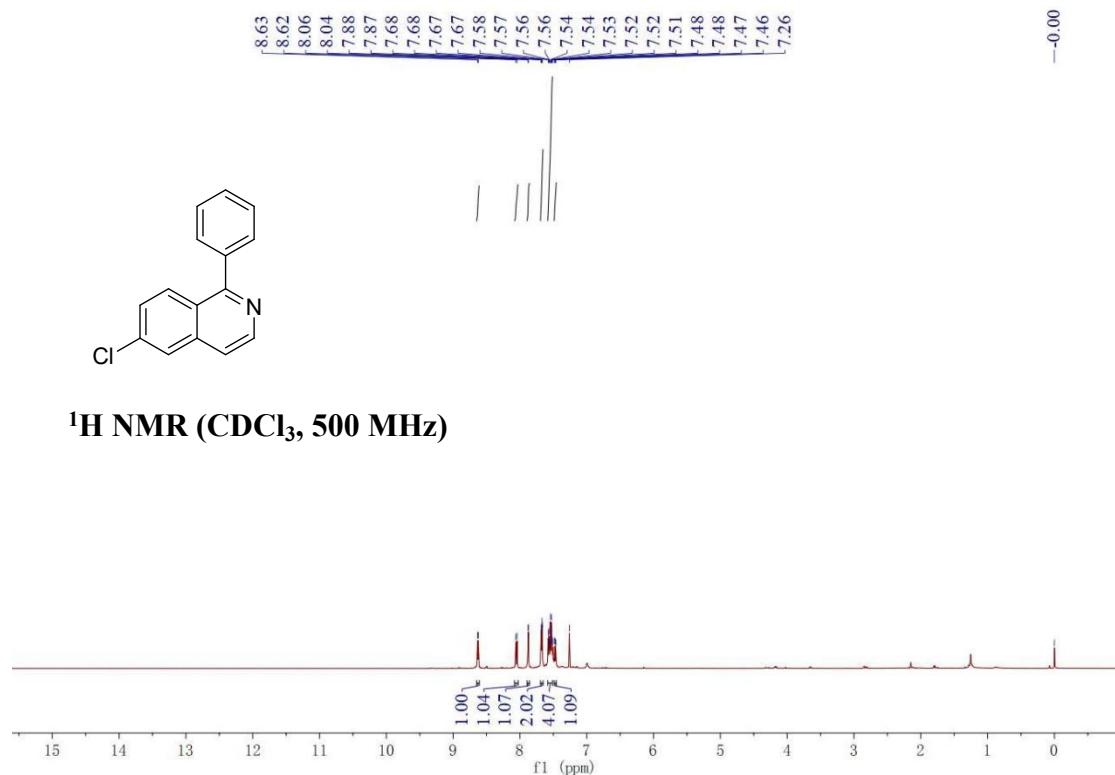
### <sup>1</sup>H NMR Spectrum of Compound a11



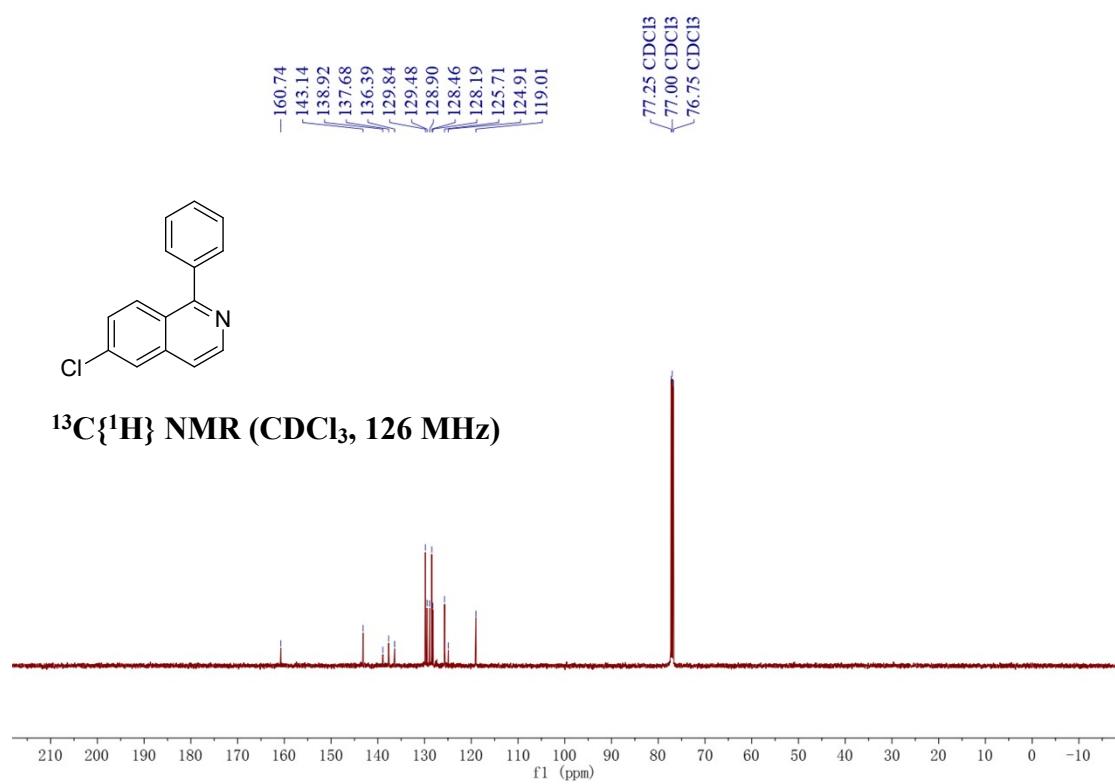
### <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of Compound a11



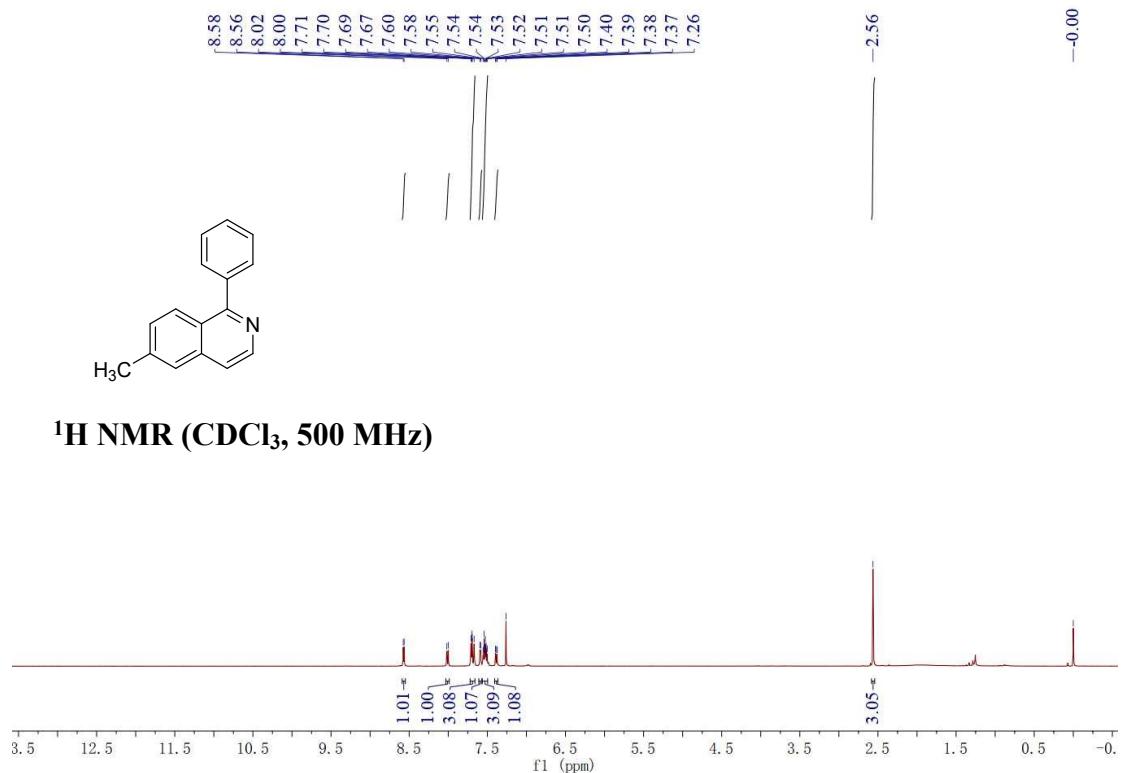
### <sup>1</sup>H NMR Spectrum of Compound a12



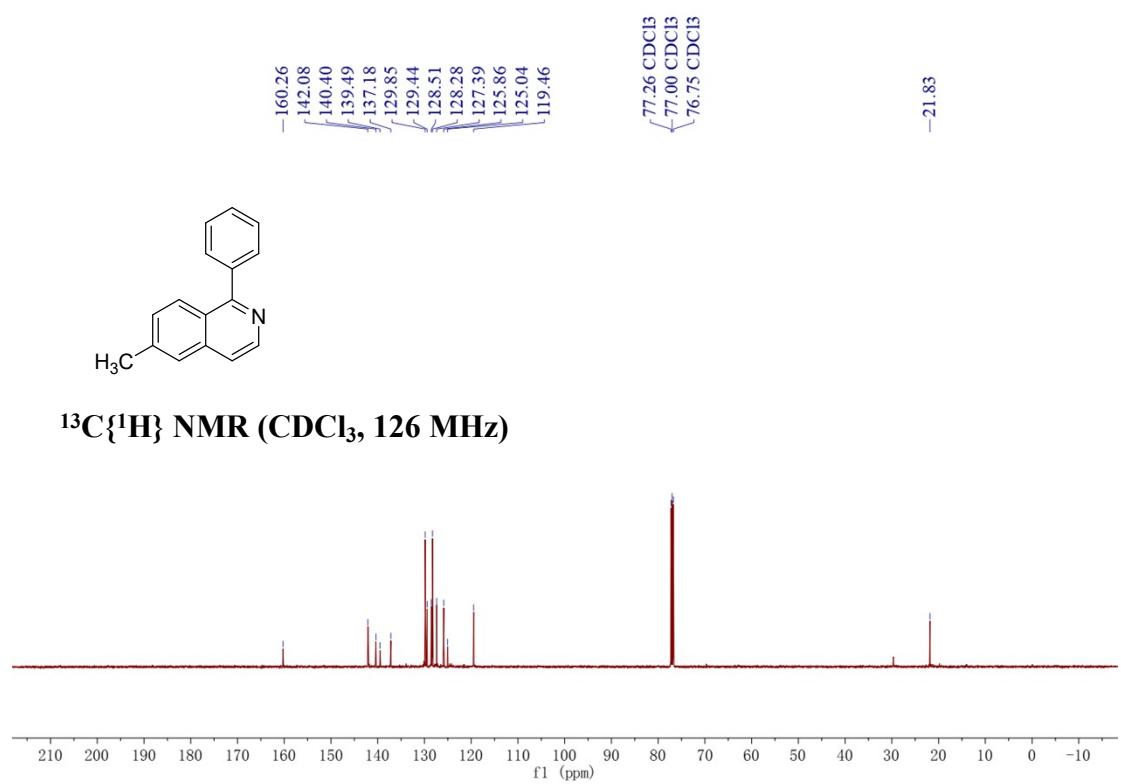
### <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of Compound a12



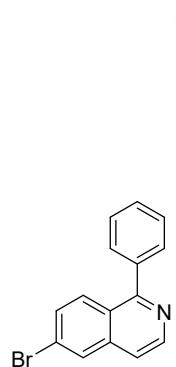
### <sup>1</sup>H NMR Spectrum of Compound a13



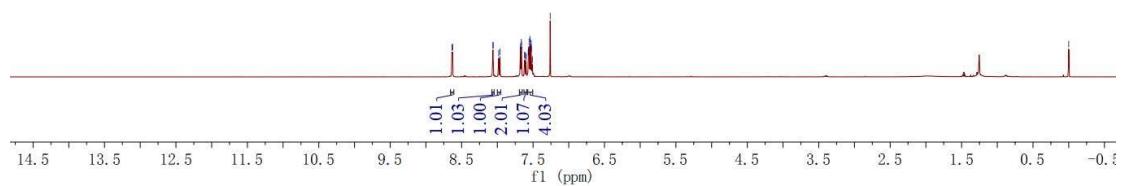
### <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of Compound a13



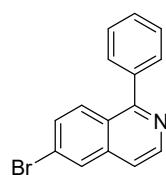
## **<sup>1</sup>H NMR Spectrum of Compound a14**



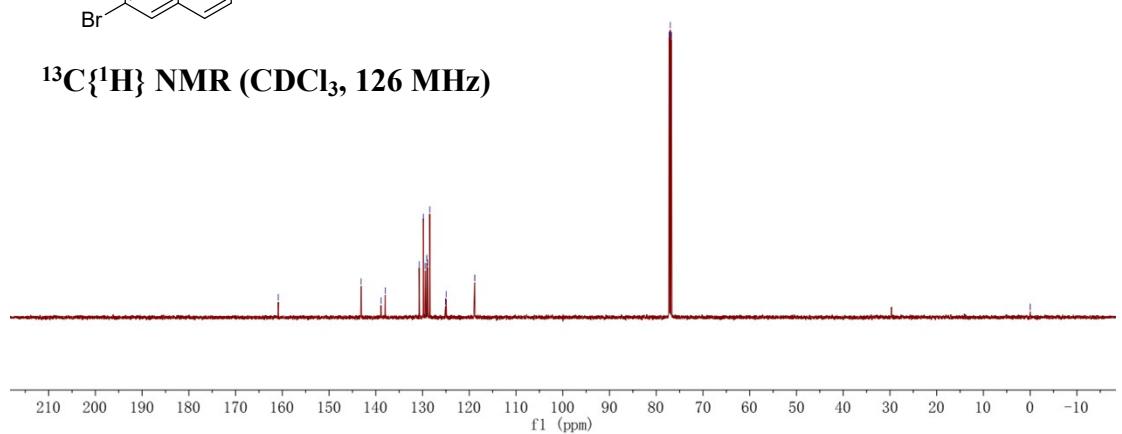
**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)**



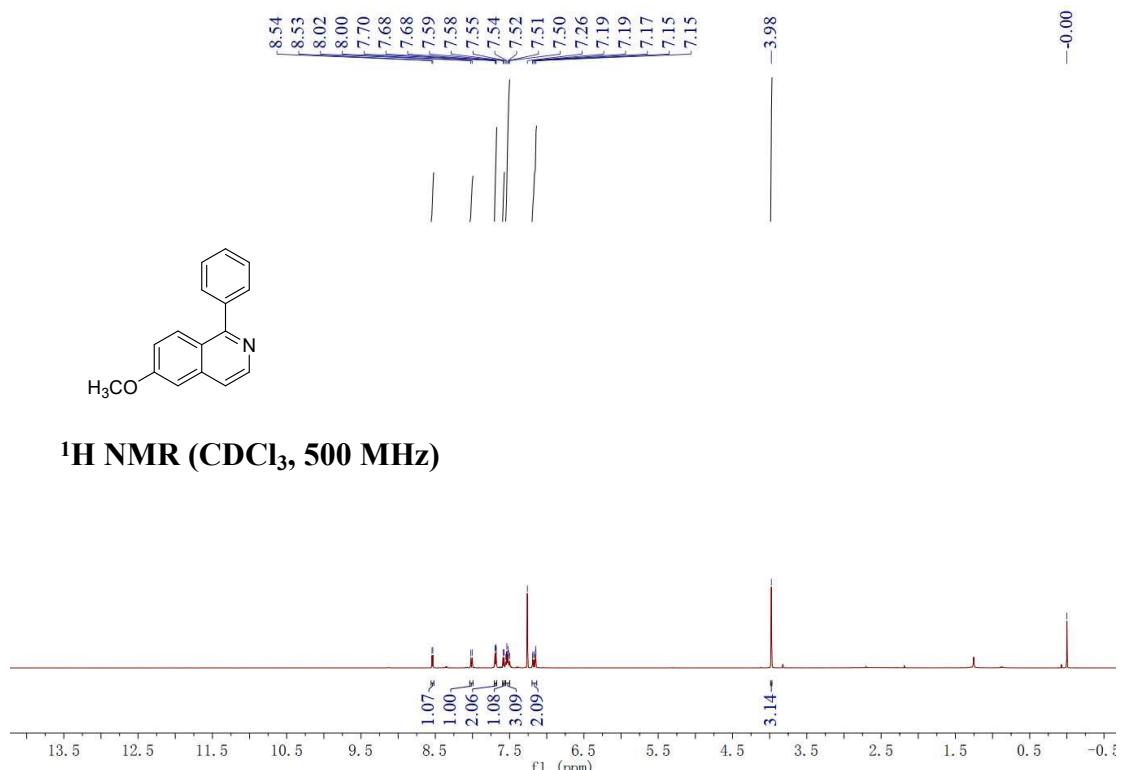
## <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of Compound a14



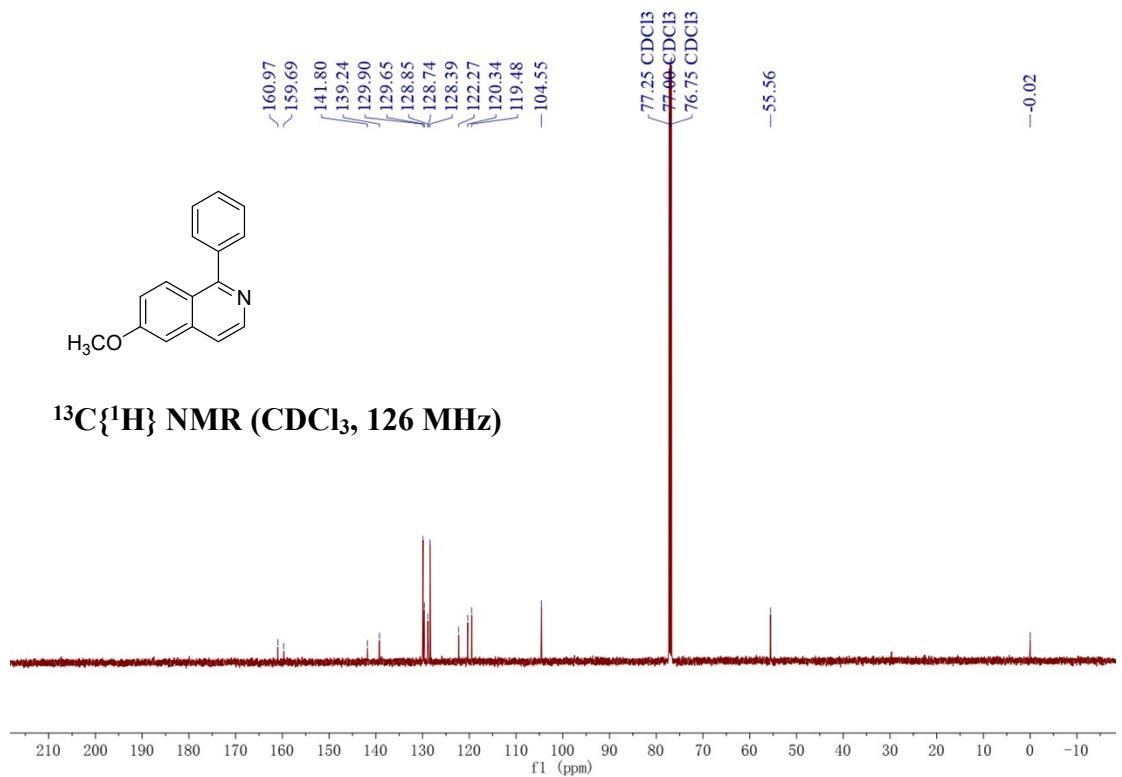
**<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 126 MHz)**



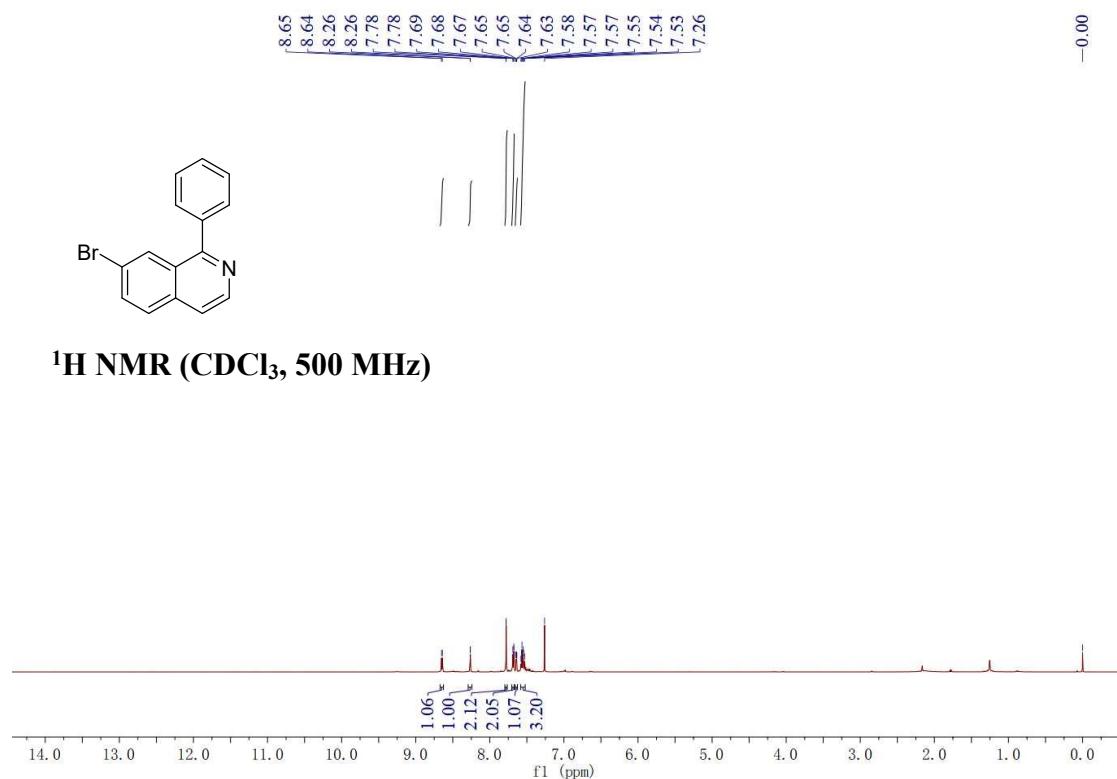
### <sup>1</sup>H NMR Spectrum of Compound a15



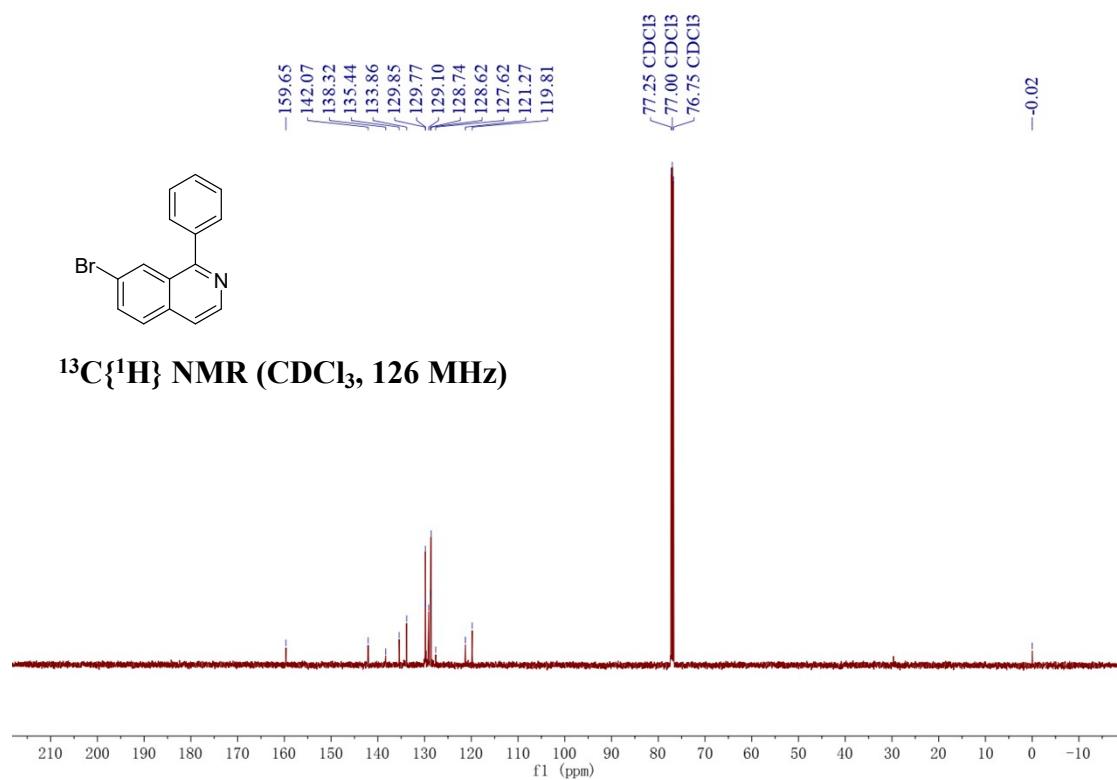
### <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of Compound a15



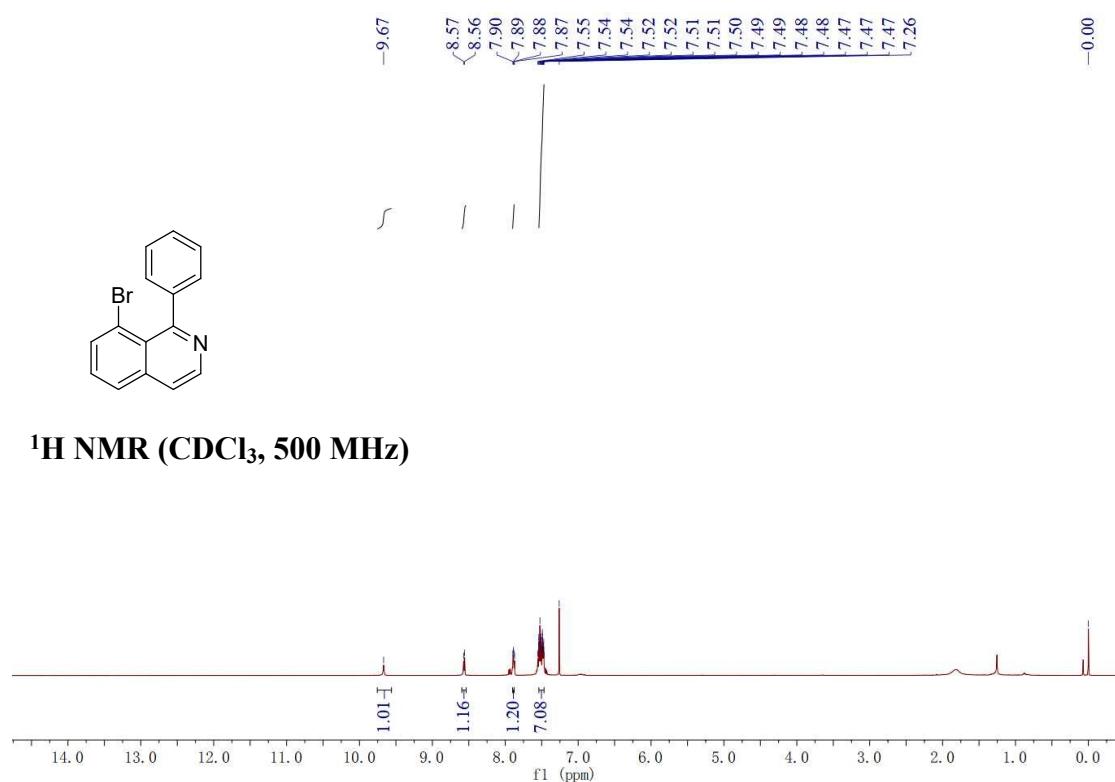
### <sup>1</sup>H NMR Spectrum of Compound a16



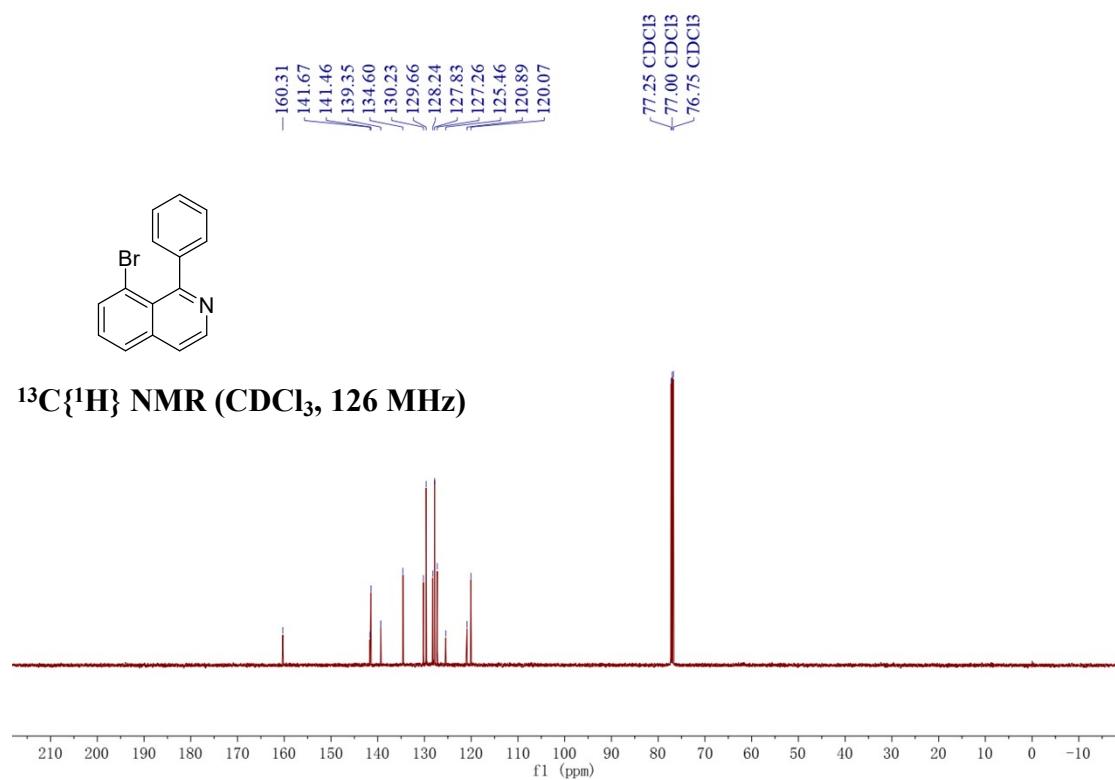
### <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of Compound a16



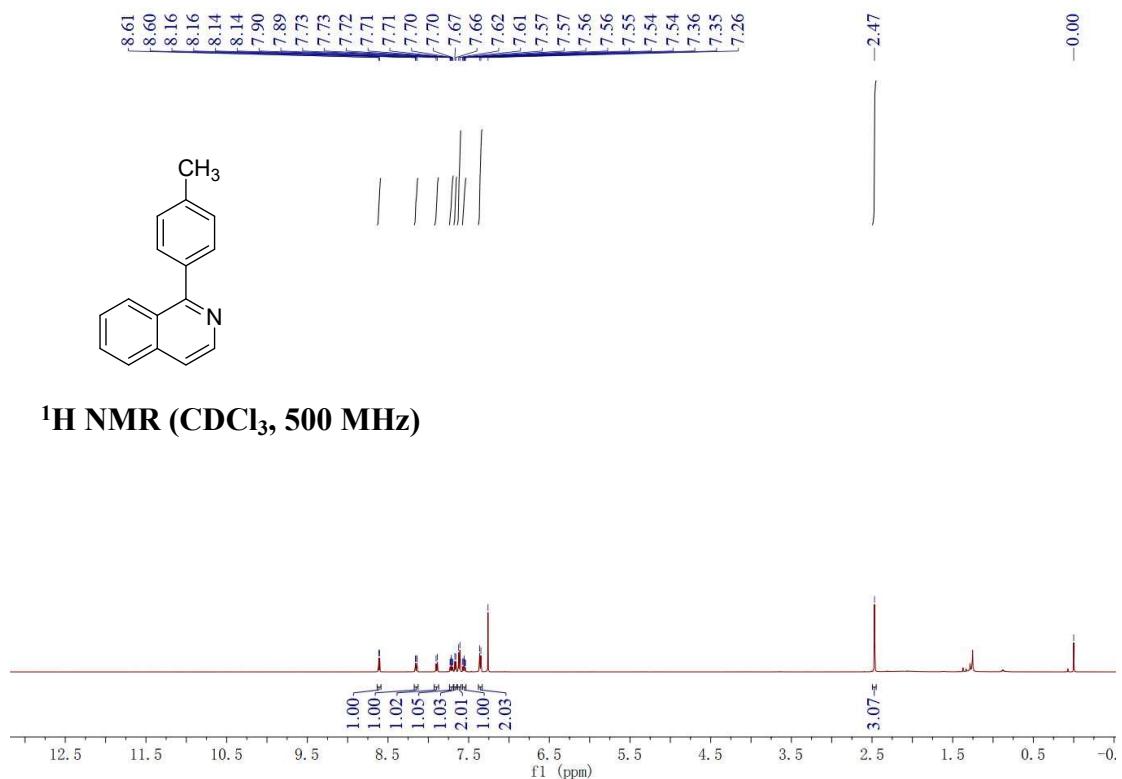
### <sup>1</sup>H NMR Spectrum of Compound a17



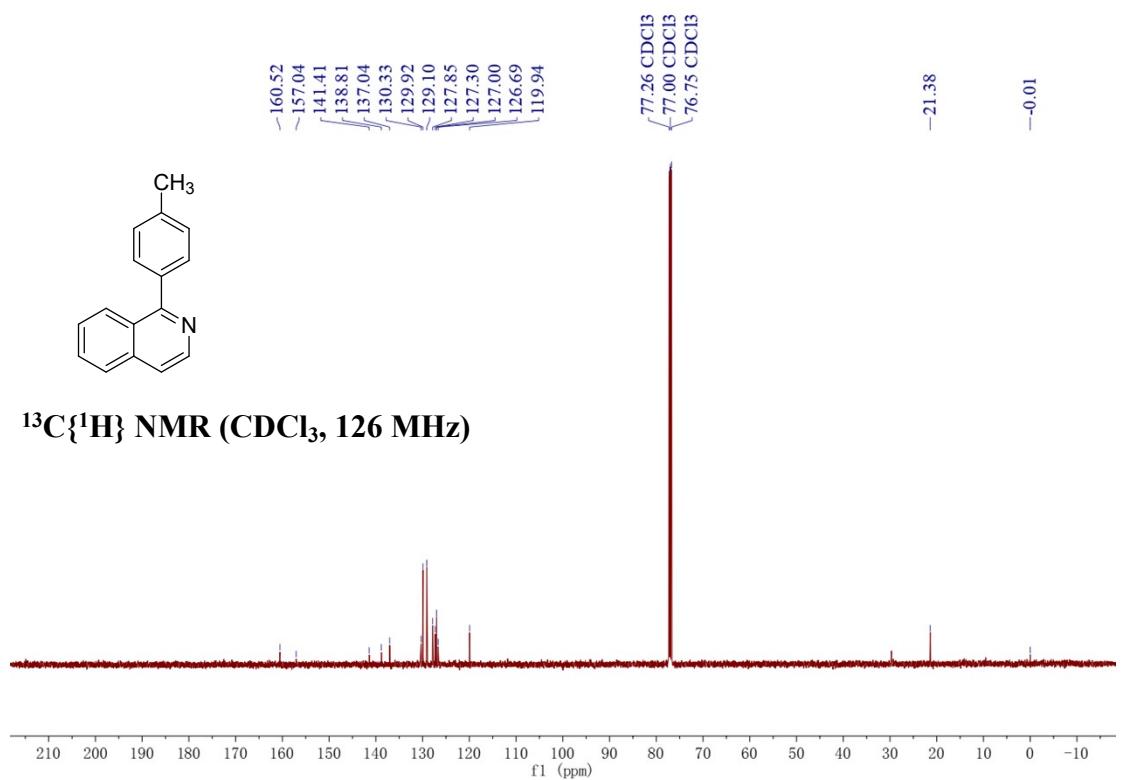
### <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of Compound a17



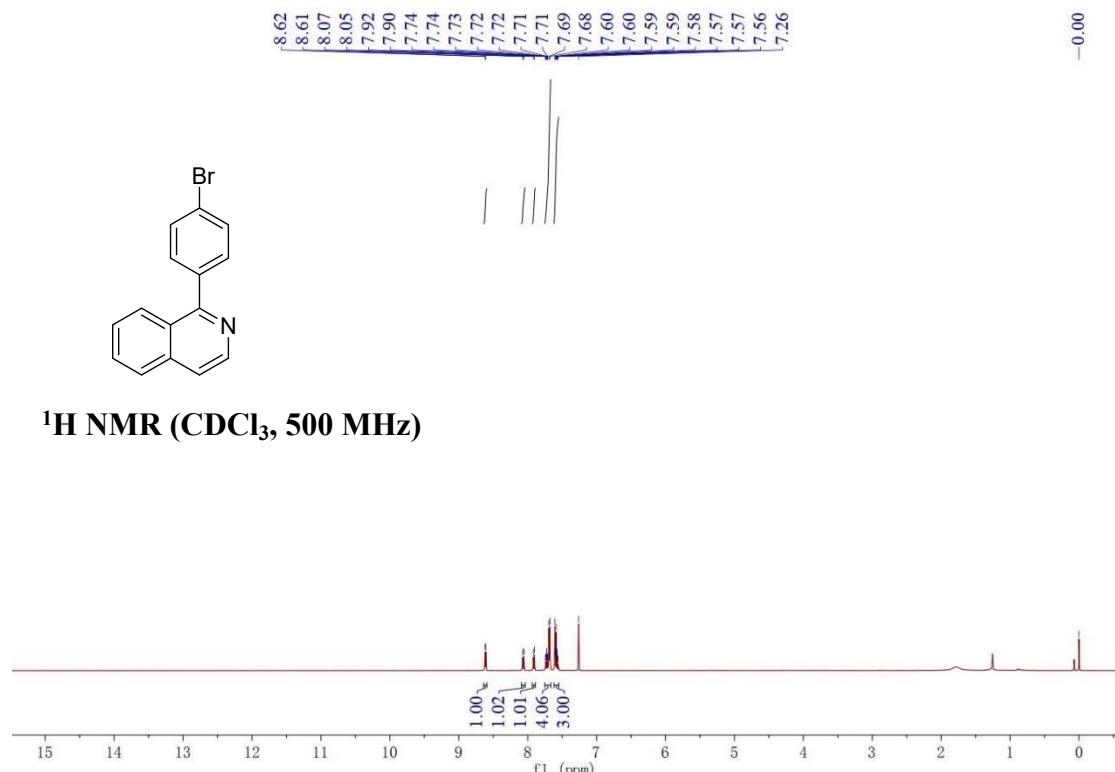
**$^1\text{H}$  NMR Spectrum of Compound b1**



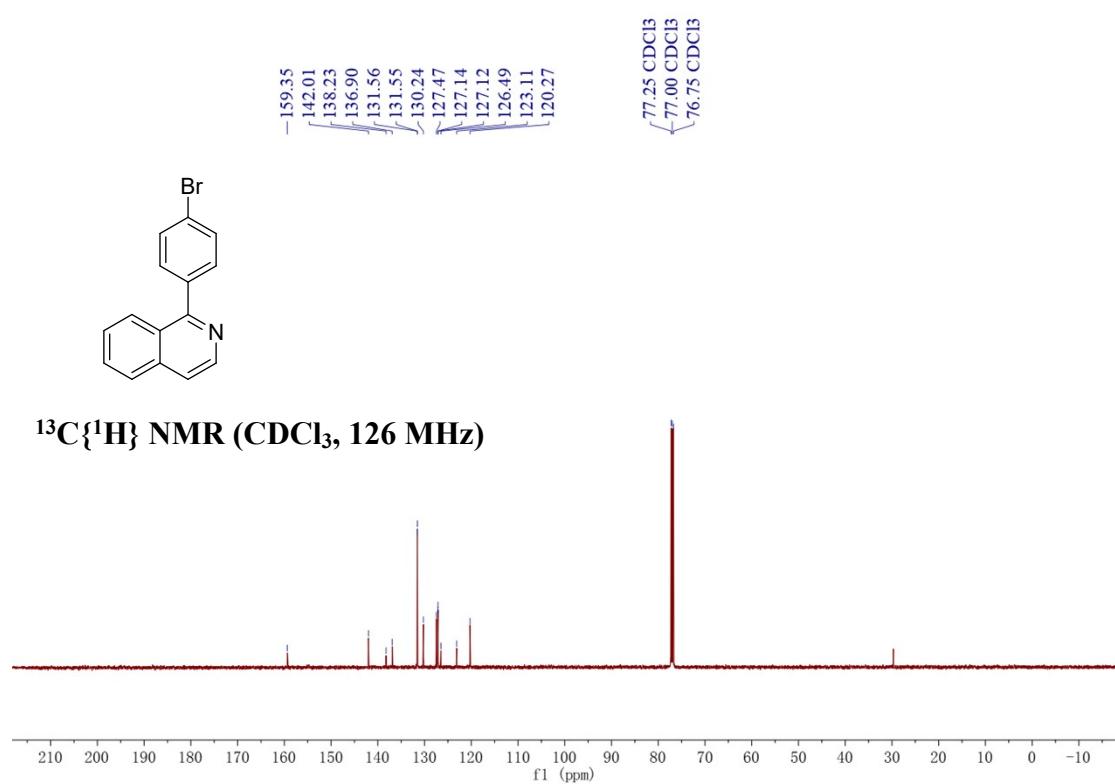
**$^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of Compound b1**



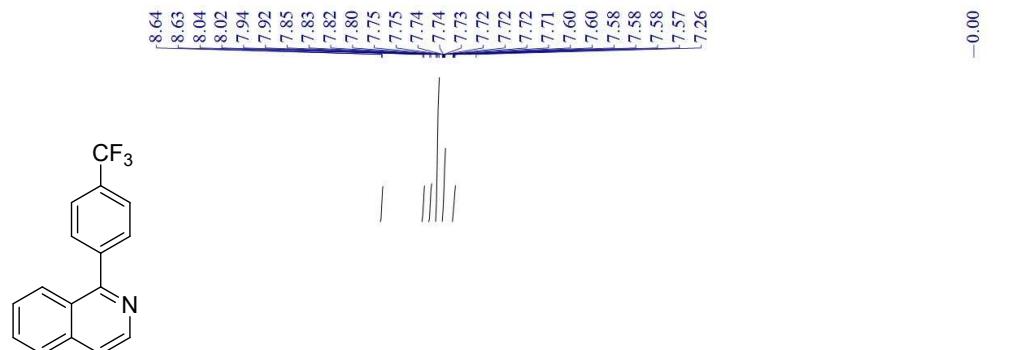
### <sup>1</sup>H NMR Spectrum of Compound b2



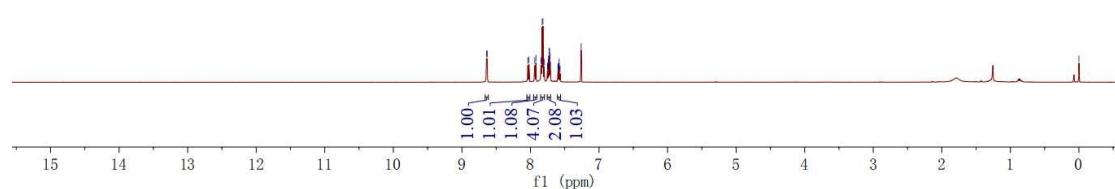
### <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of Compound b2



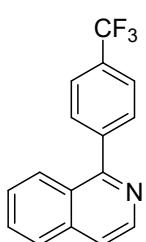
**$^1\text{H}$  NMR Spectrum of Compound b3**



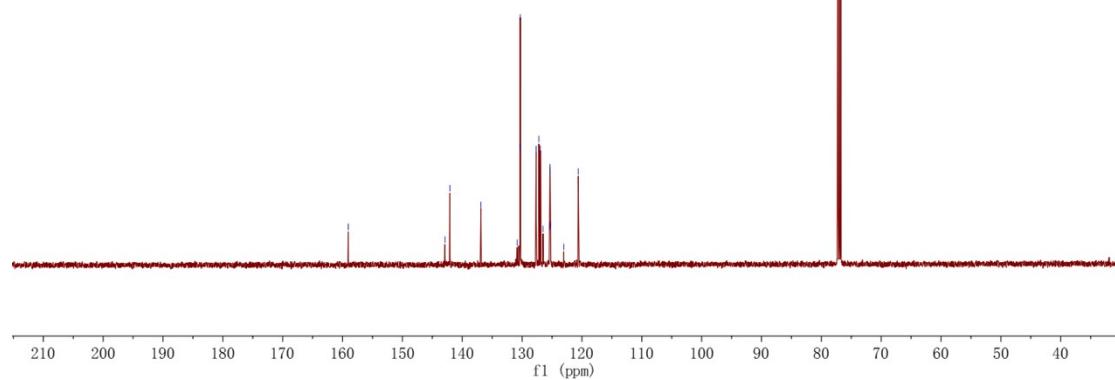
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)



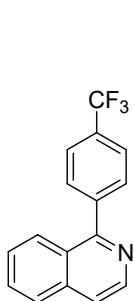
$^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of Compound b3



$^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 126 MHz)

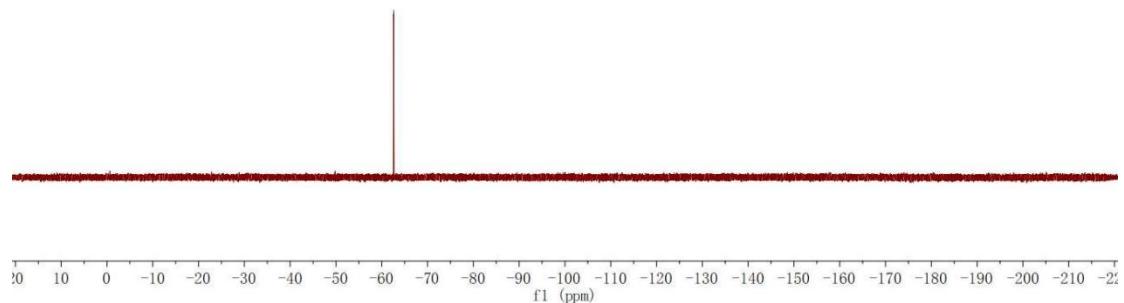


**$^{19}\text{F}\{\text{H}\}$  NMR Spectrum of Compound b3**

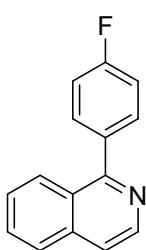


-62.59

$^{19}\text{F}\{\text{H}\}$  NMR ( $\text{CDCl}_3$ , 471 MHz)

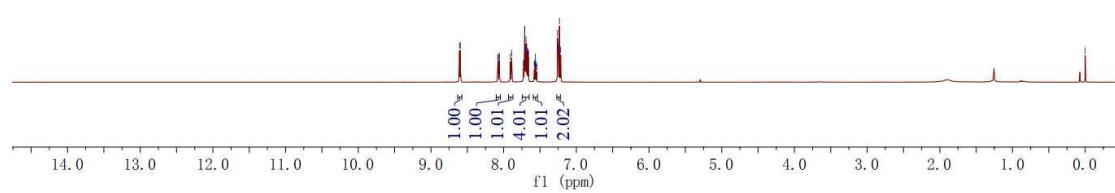


**$^1\text{H}$  NMR Spectrum of Compound b4**

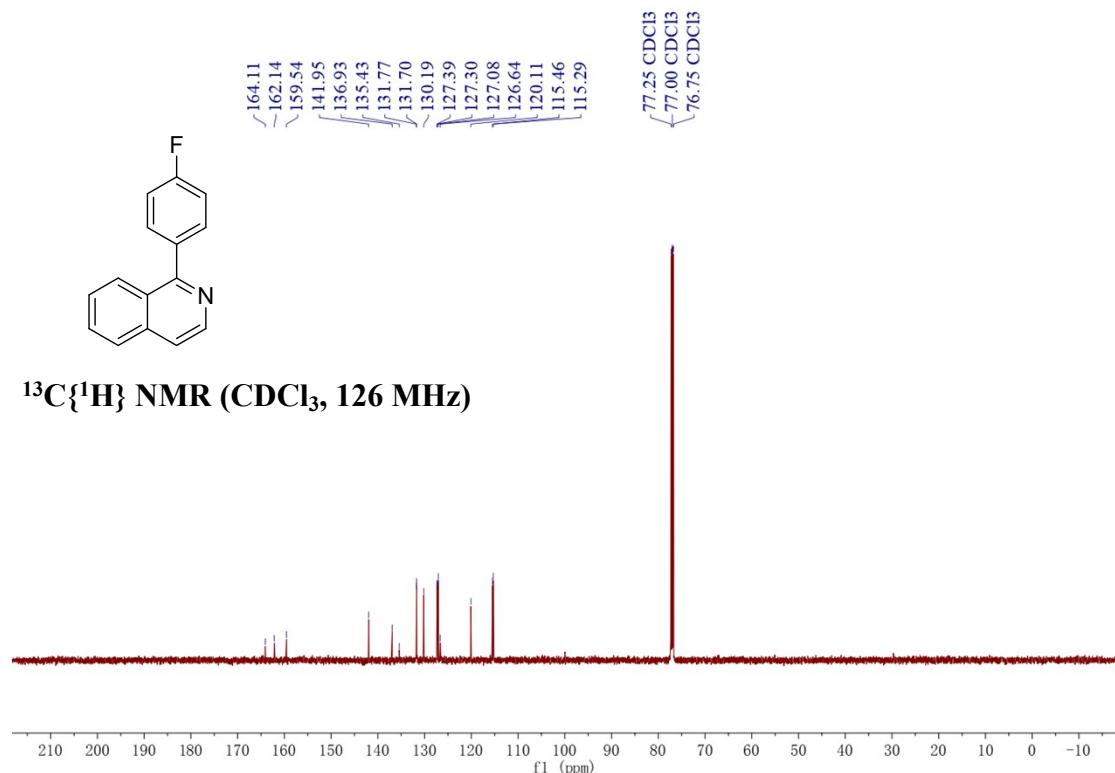


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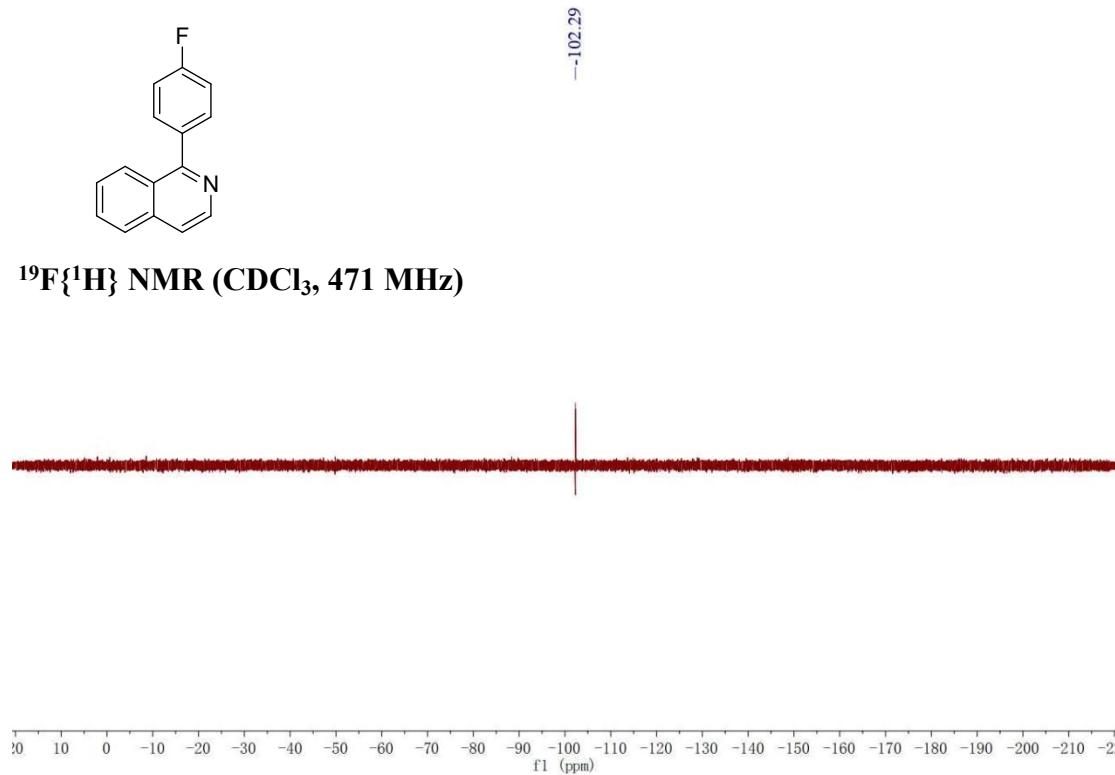
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)



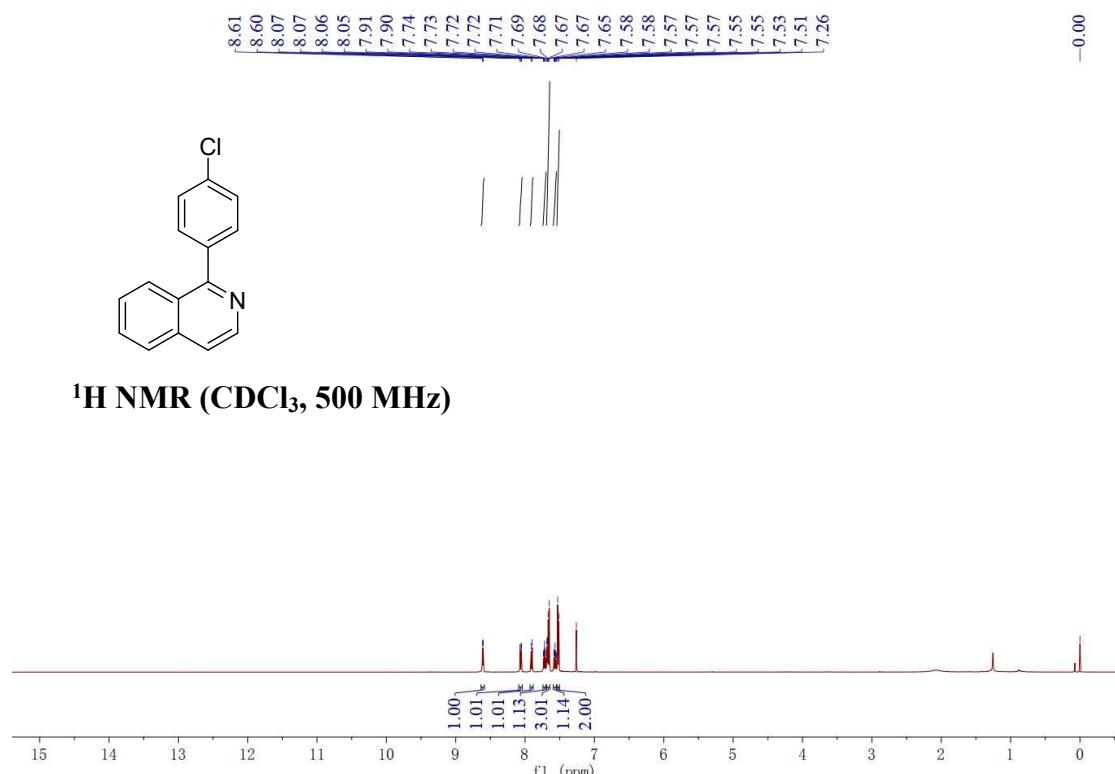
**$^{13}\text{C}\{\text{H}\}$  NMR Spectrum of Compound b4**



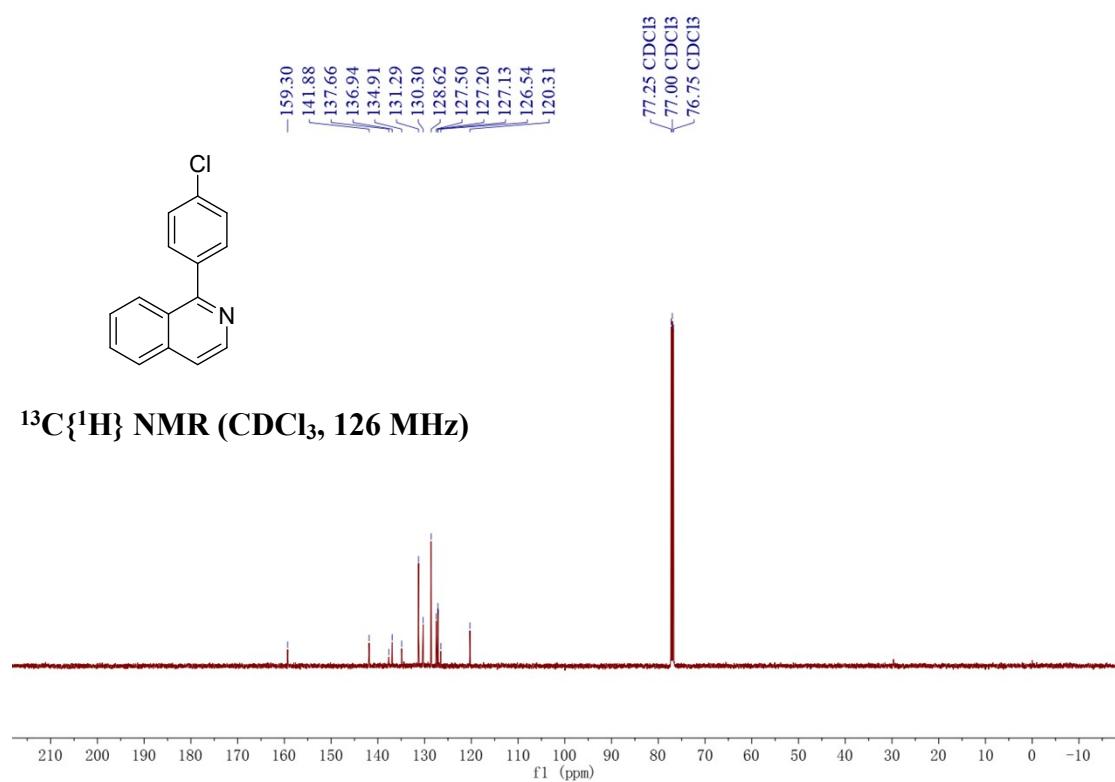
**$^{19}\text{F}\{\text{H}\}$  NMR Spectrum of Compound b4**



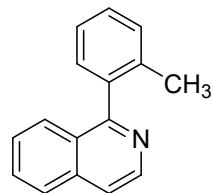
**$^1\text{H}$  NMR Spectrum of Compound b5**



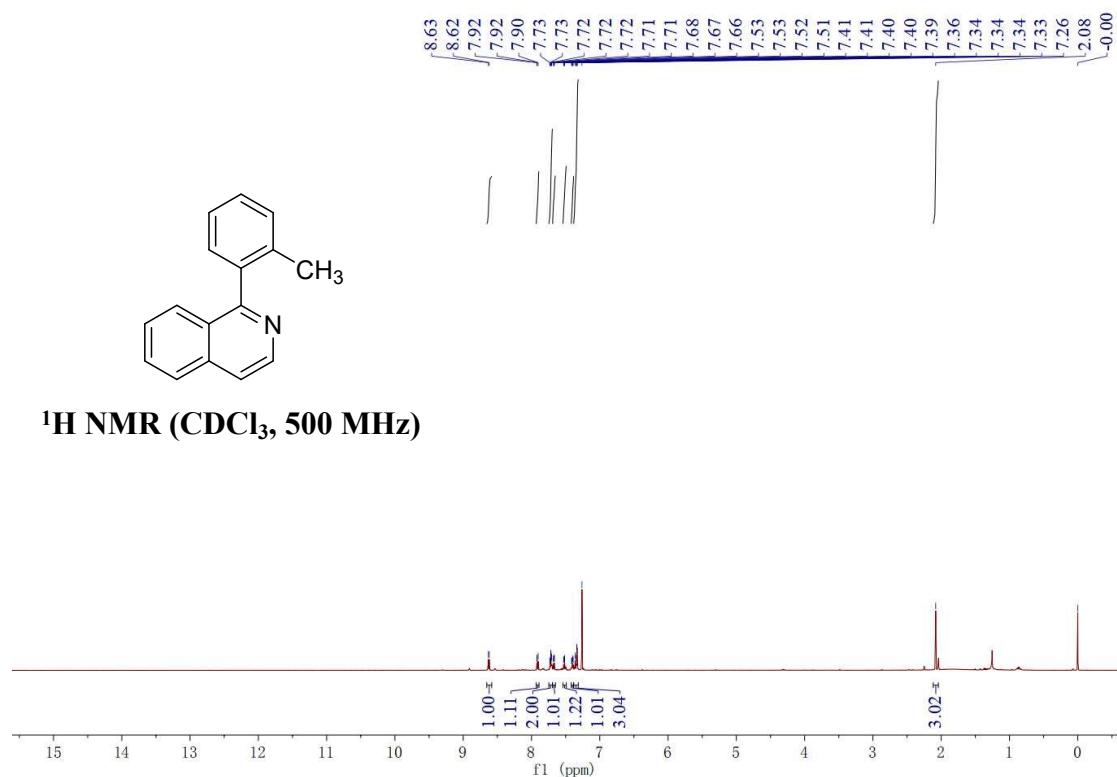
**$^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of Compound b5**



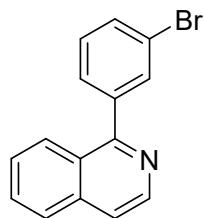
### <sup>1</sup>H NMR Spectrum of Compound b6



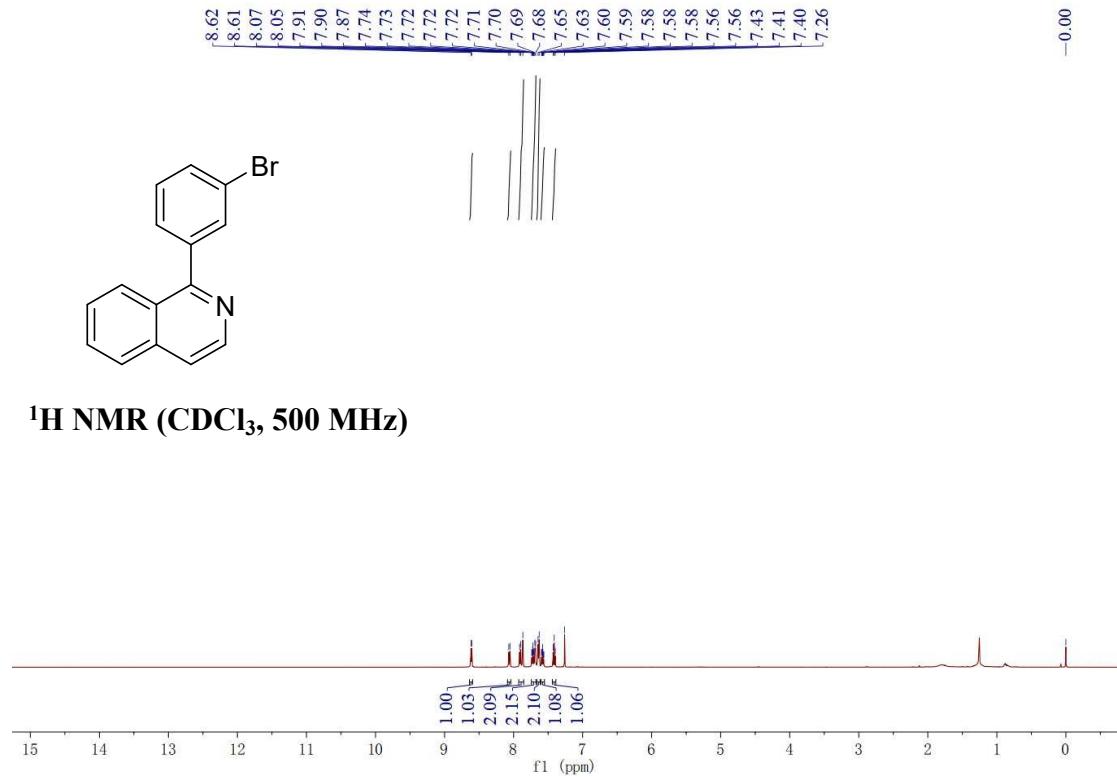
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)



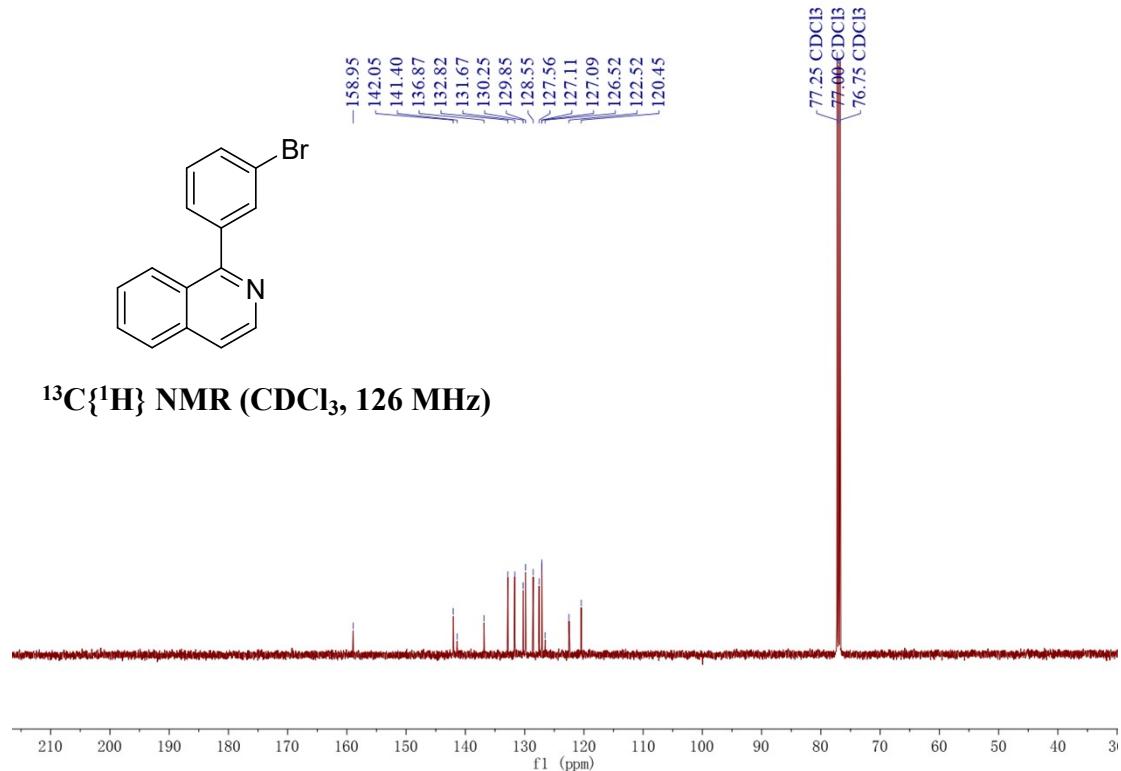
### <sup>1</sup>H NMR Spectrum of Compound b7



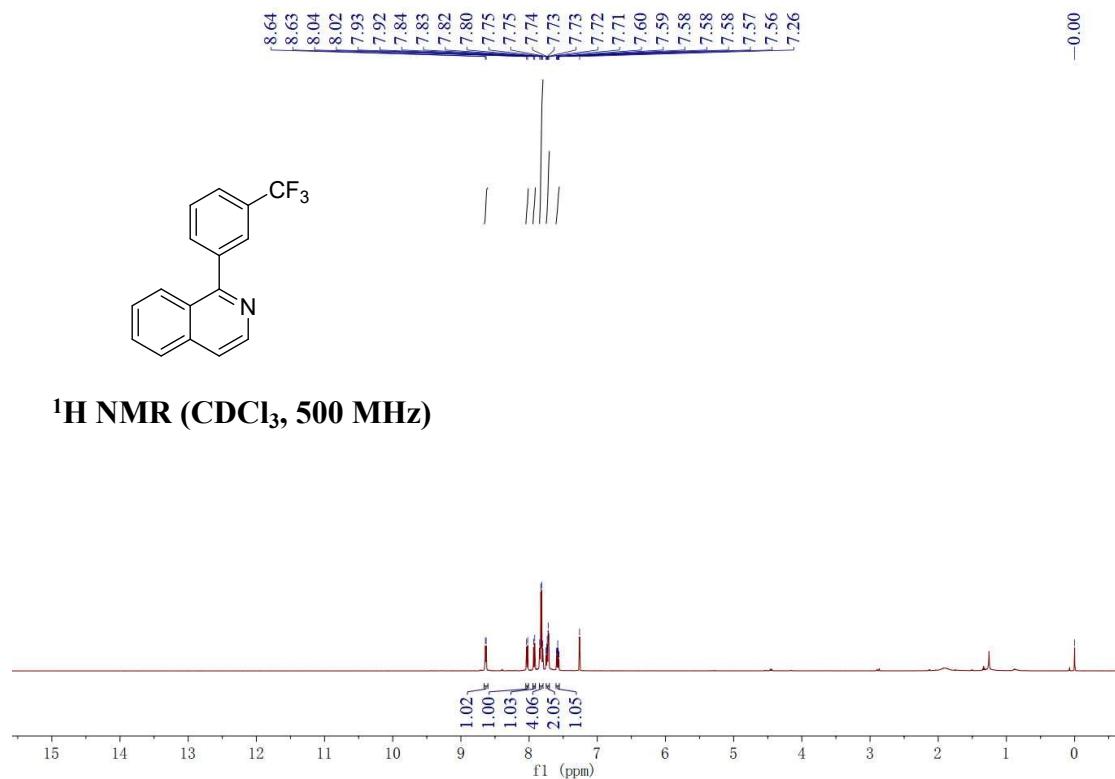
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)



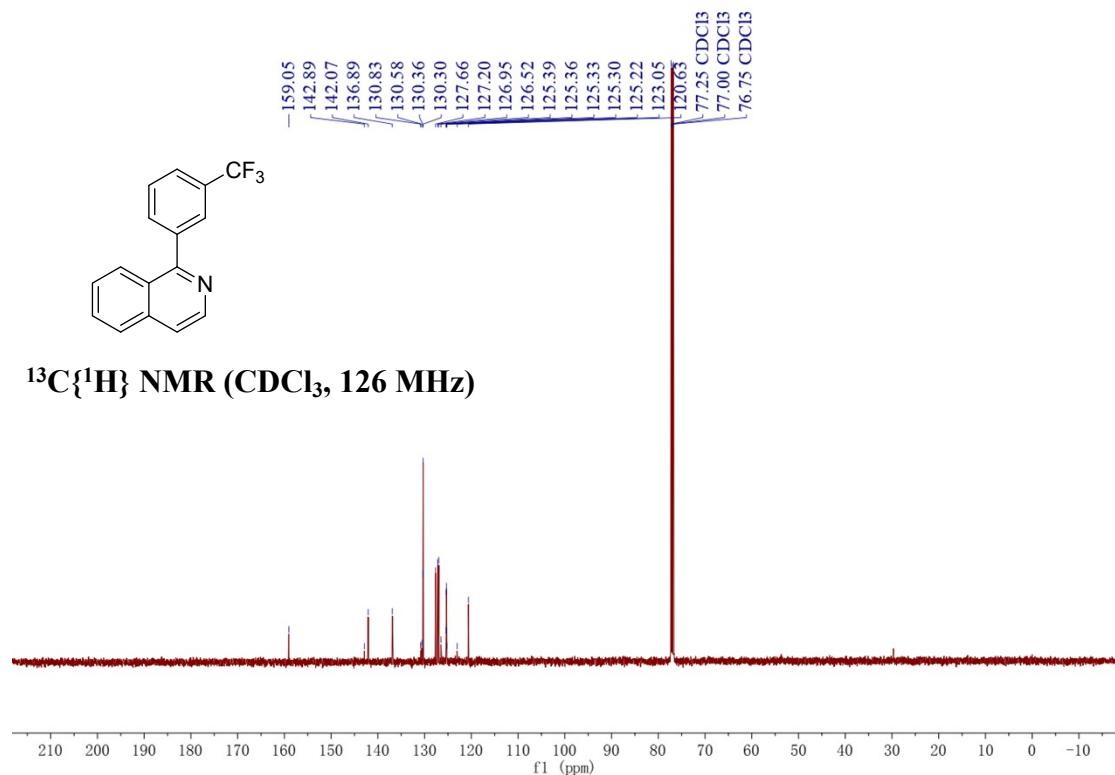
### $^{13}\text{C}\{\text{H}\}$ NMR Spectrum of Compound b7



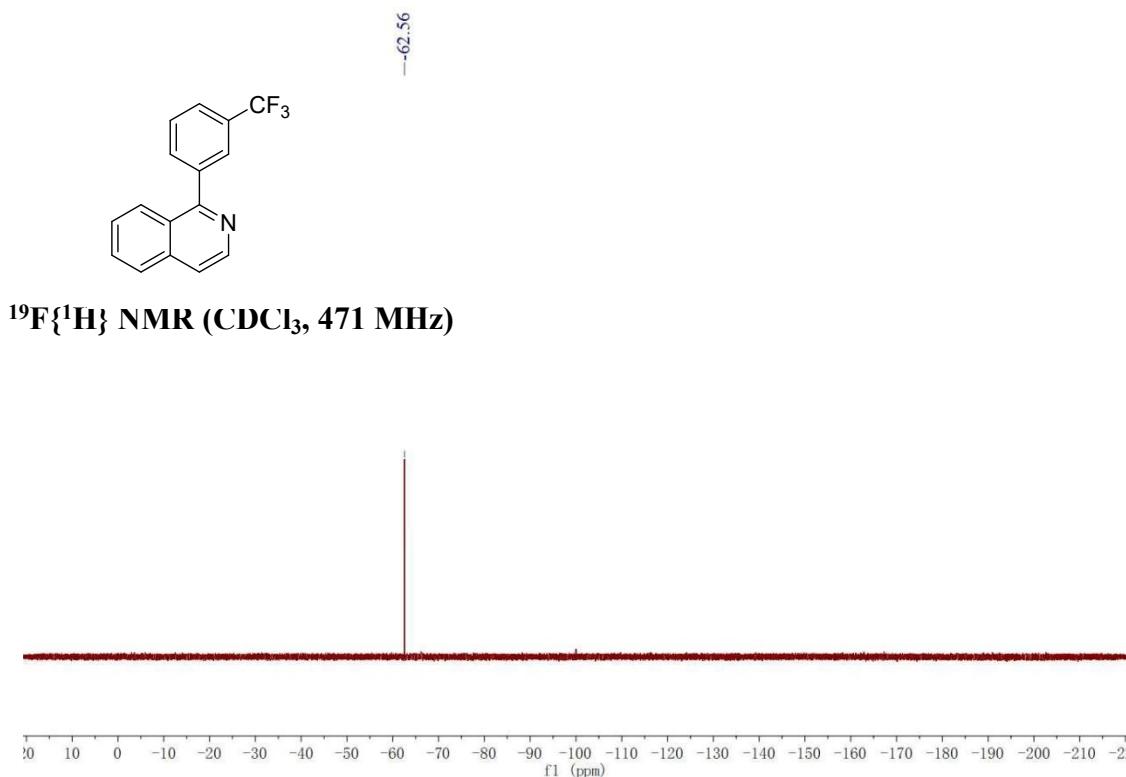
### $^1\text{H}$ NMR Spectrum of Compound b8



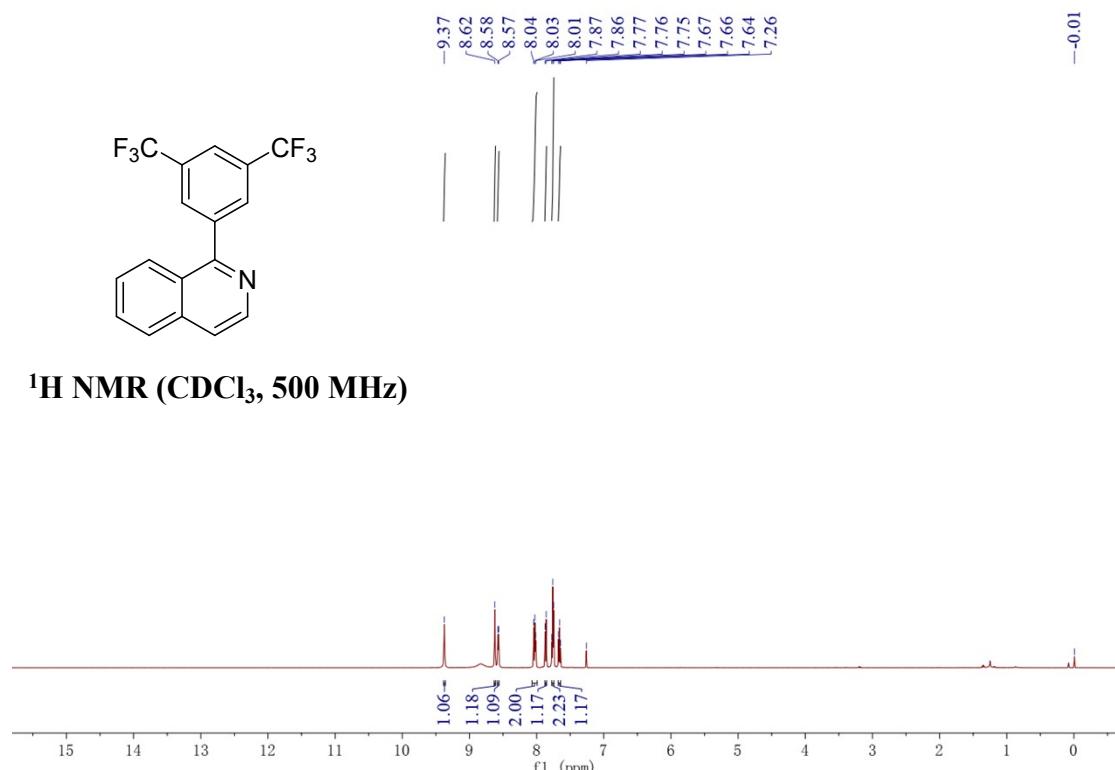
**$^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of Compound b8**



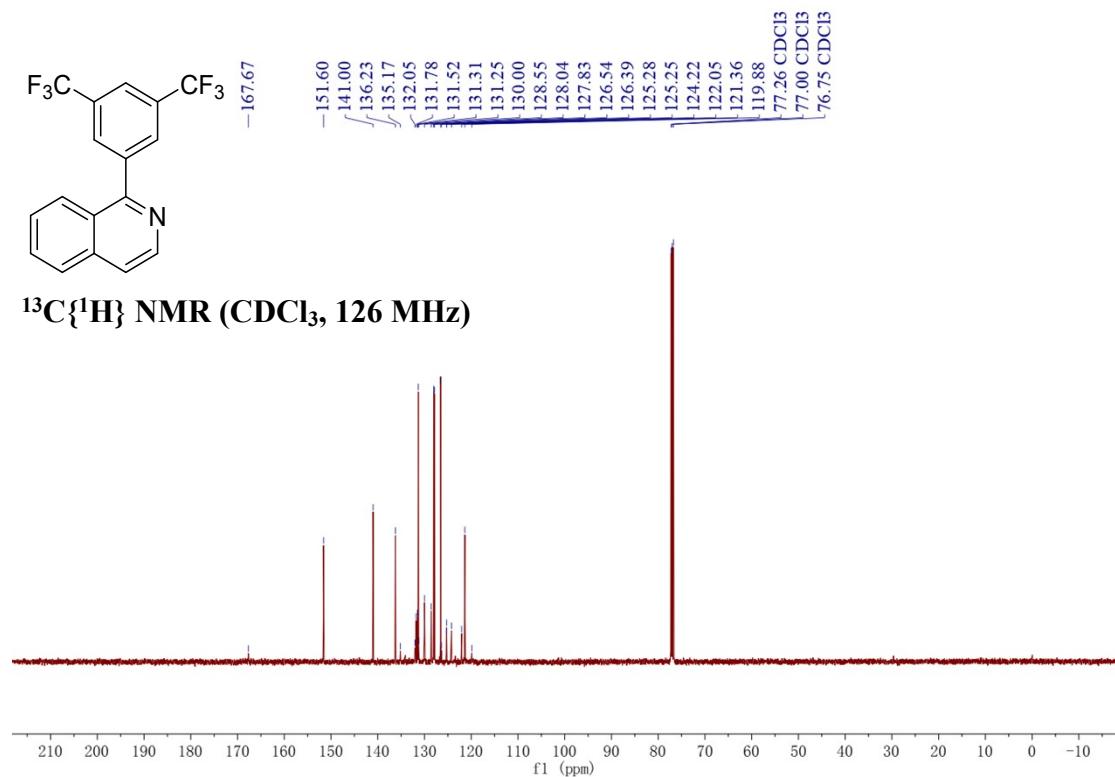
**$^{19}\text{F}\{^1\text{H}\}$  NMR Spectrum of Compound b8**



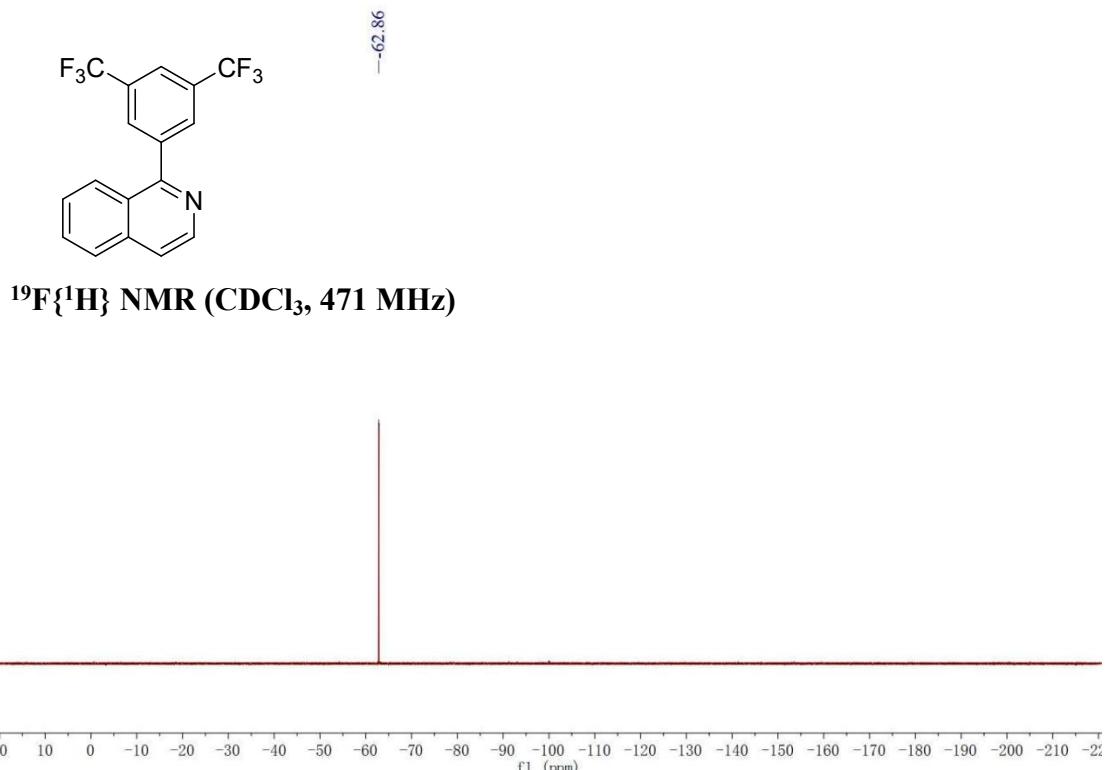
### <sup>1</sup>H NMR Spectrum of Compound b9



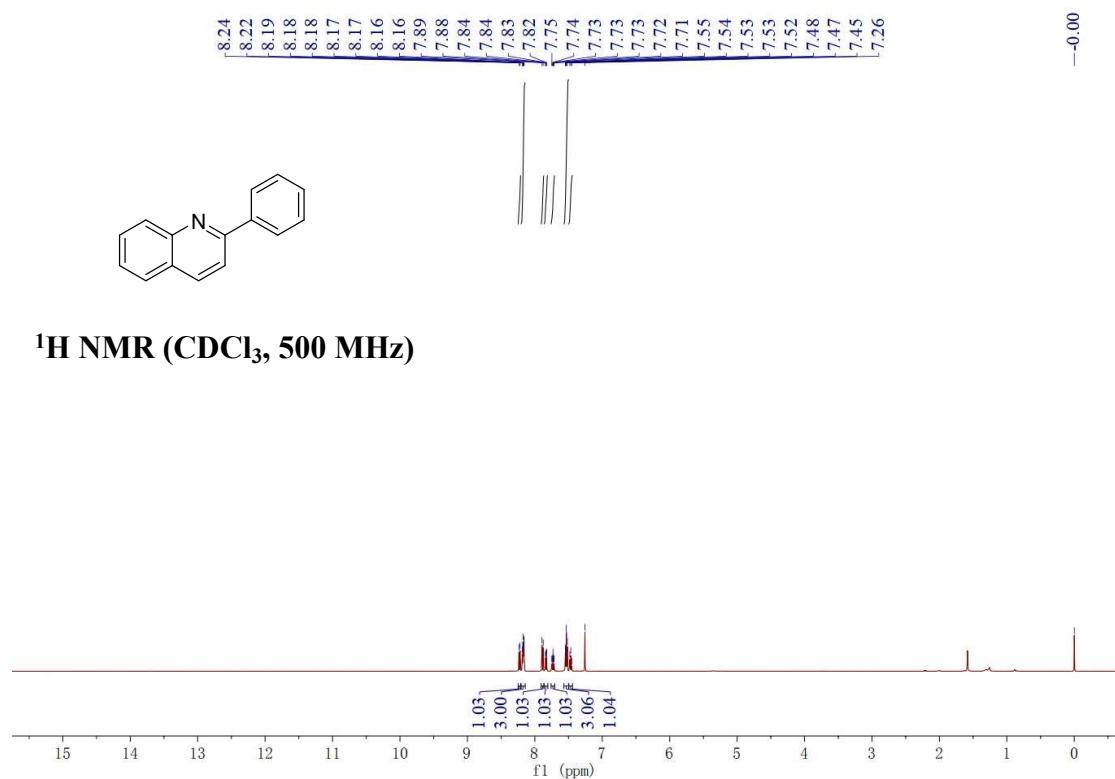
### <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of Compound b9



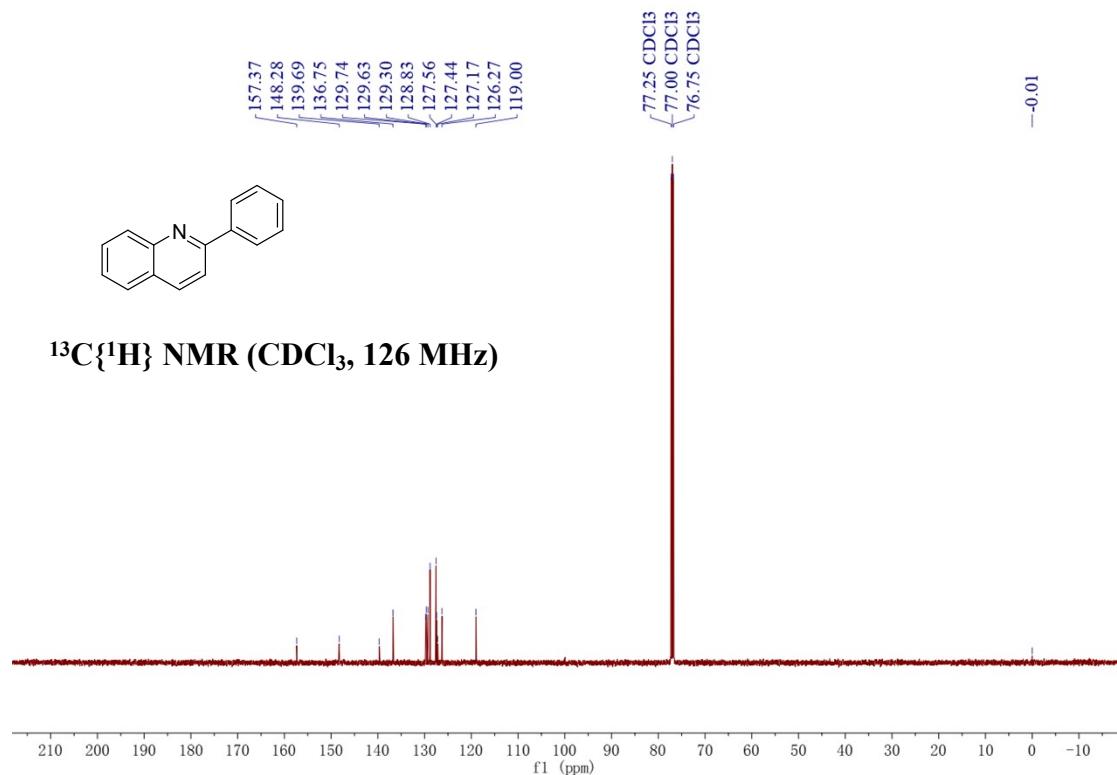
**$^{19}\text{F}\{^1\text{H}\}$  NMR Spectrum of Compound b9**



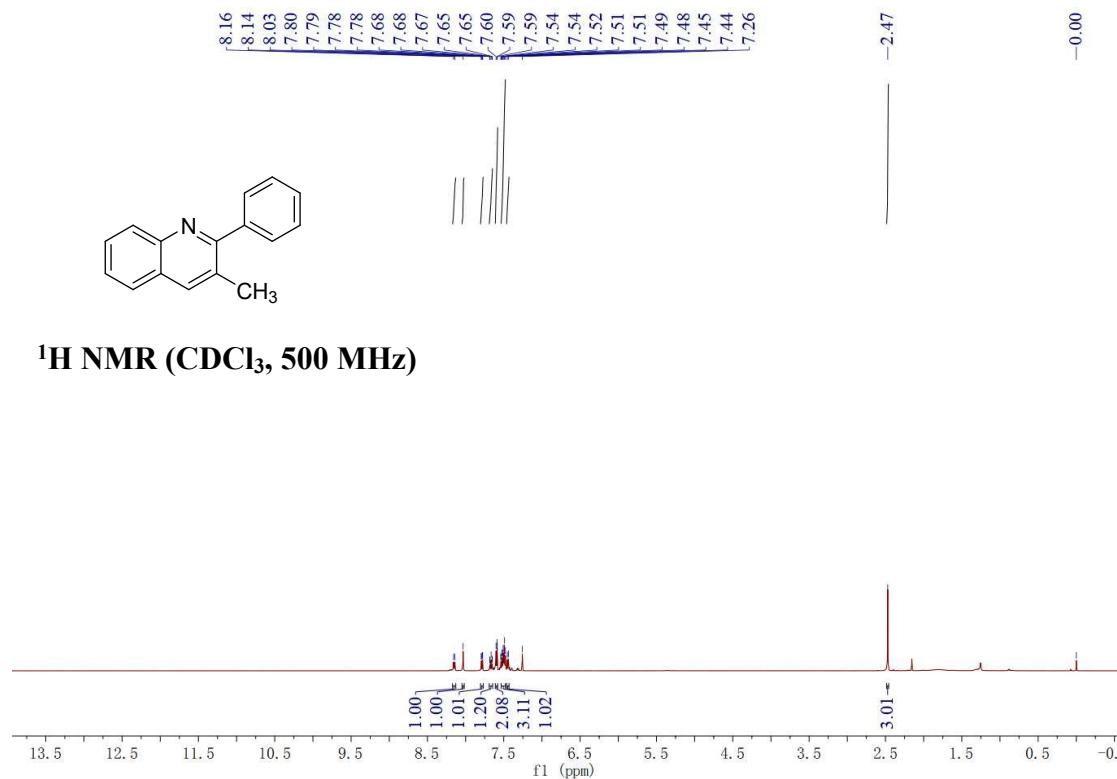
**$^1\text{H}$  NMR Spectrum of Compound c1**



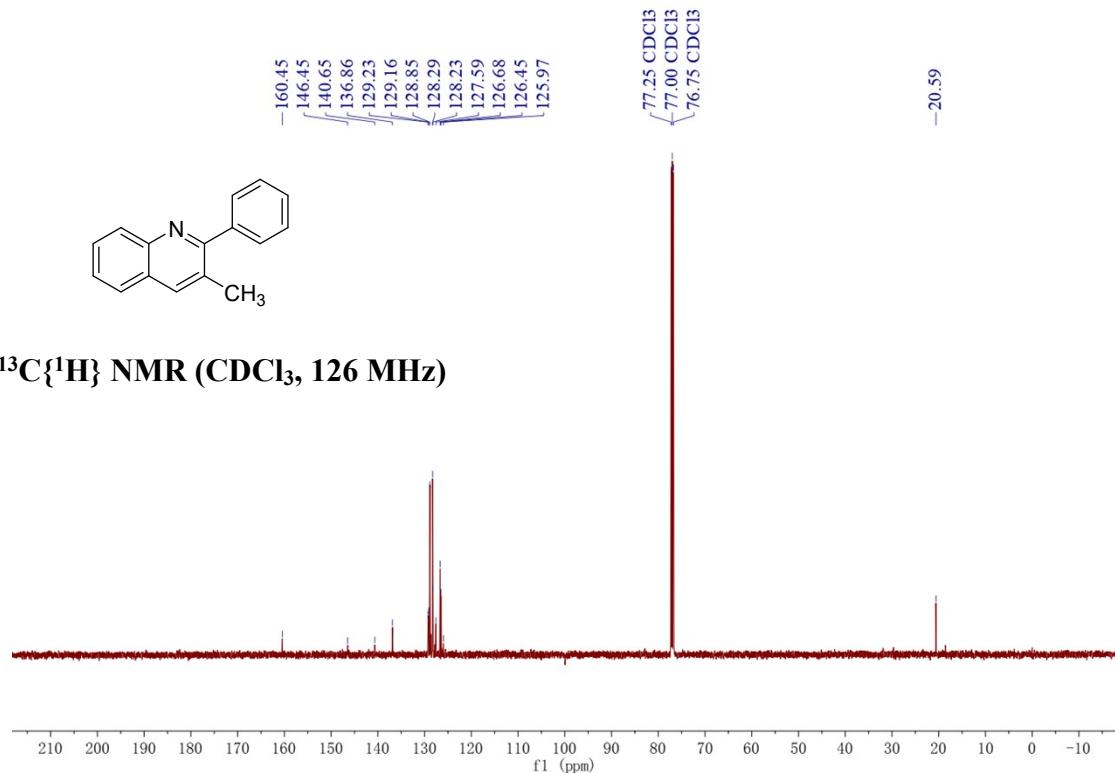
**$^{13}\text{C}\{\text{H}\}$  NMR Spectrum of Compound c1**



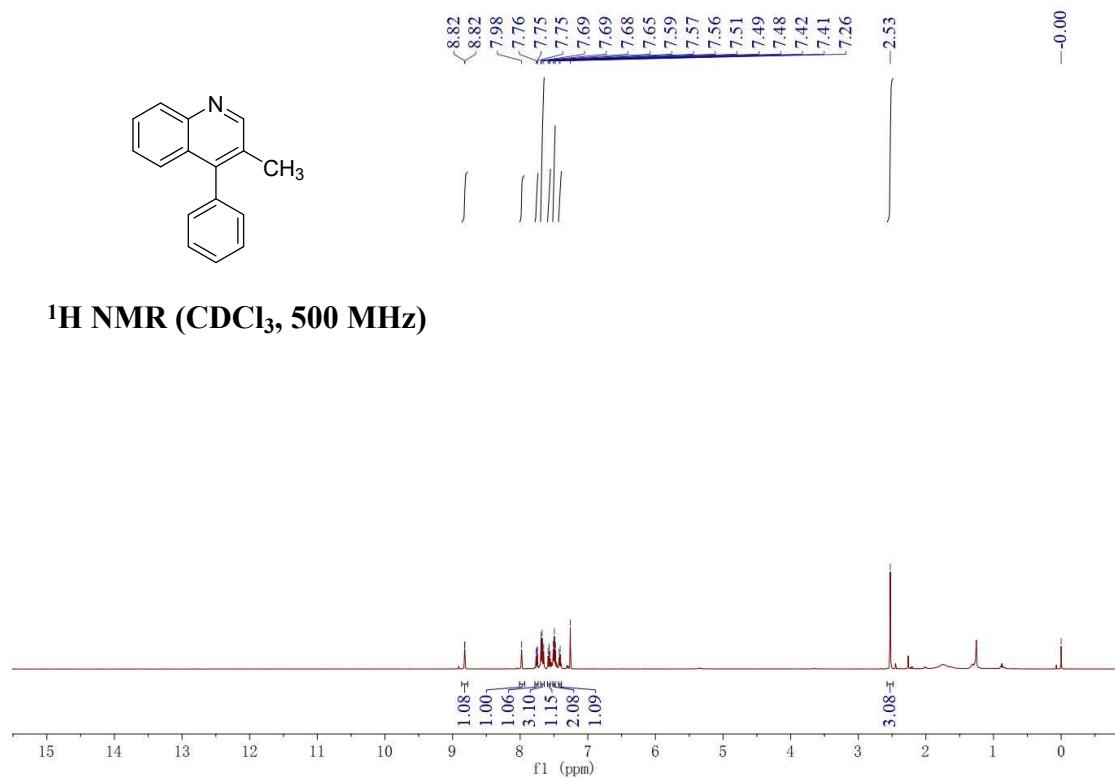
**$^1\text{H}$  NMR Spectrum of Compound c2-1**



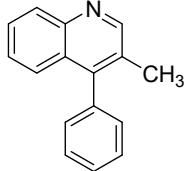
**$^{13}\text{C}\{\text{H}\}$  NMR Spectrum of Compound c2-1**



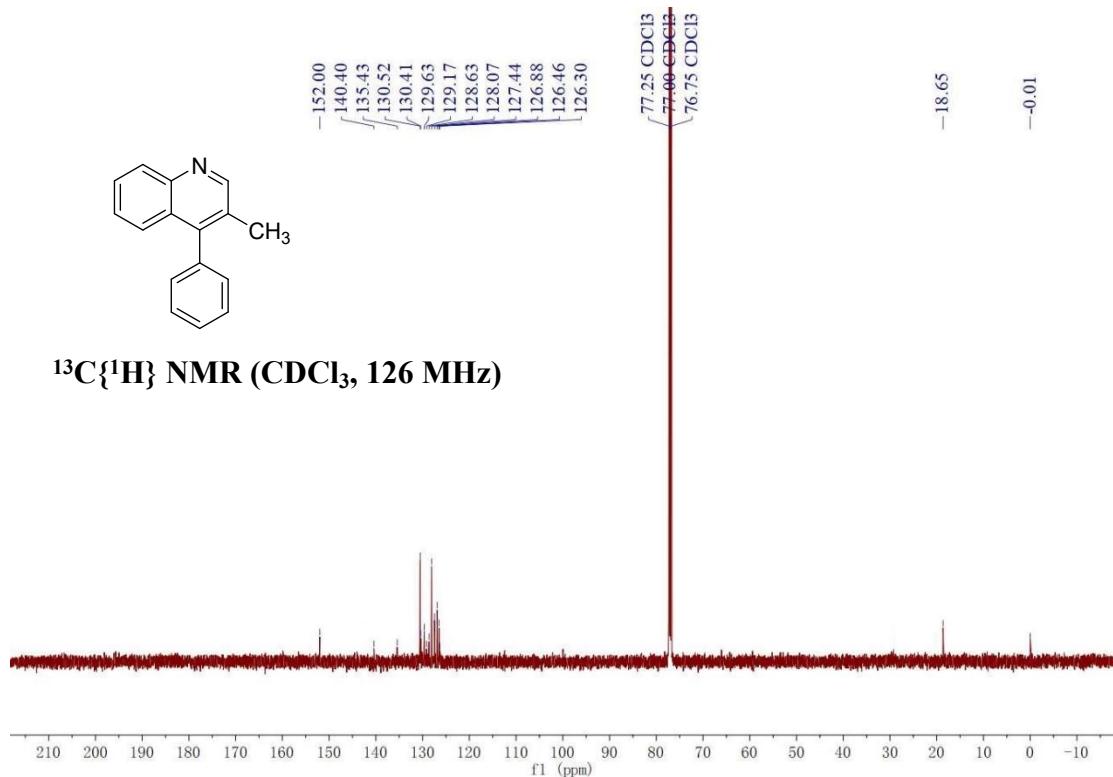
**$^1\text{H}$  NMR Spectrum of Compound c2-2**



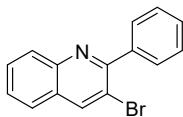
## **<sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of Compound c2-2**



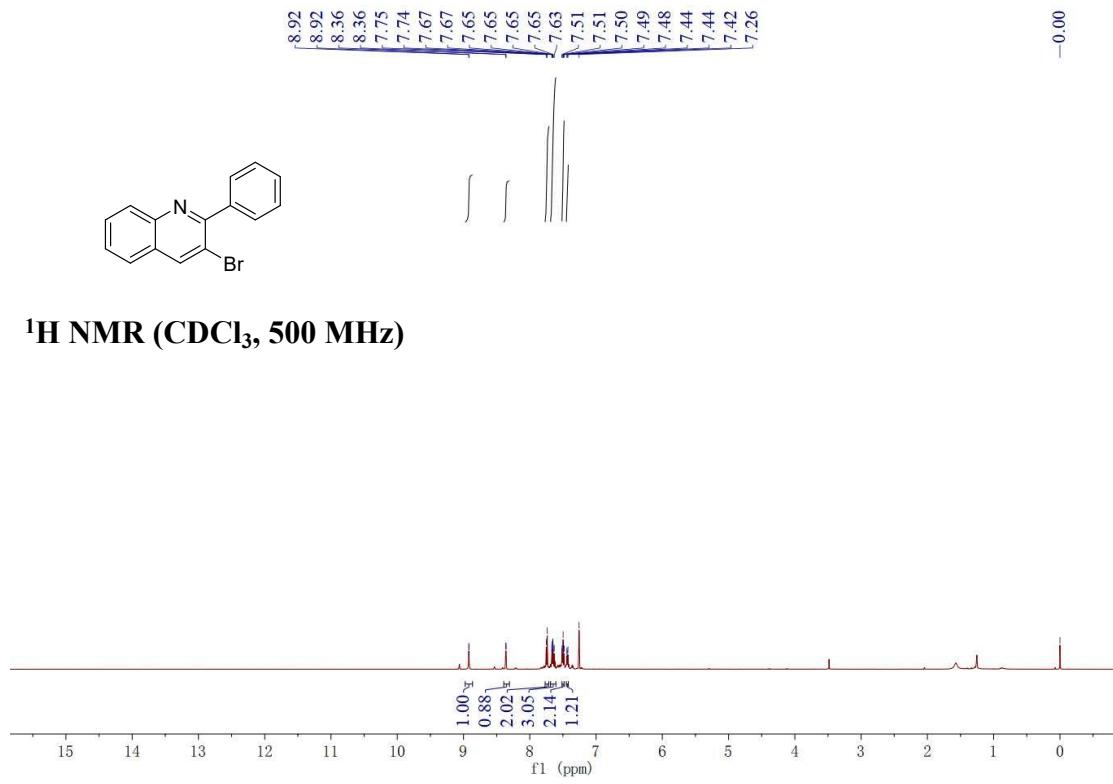
### <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 126 MHz)



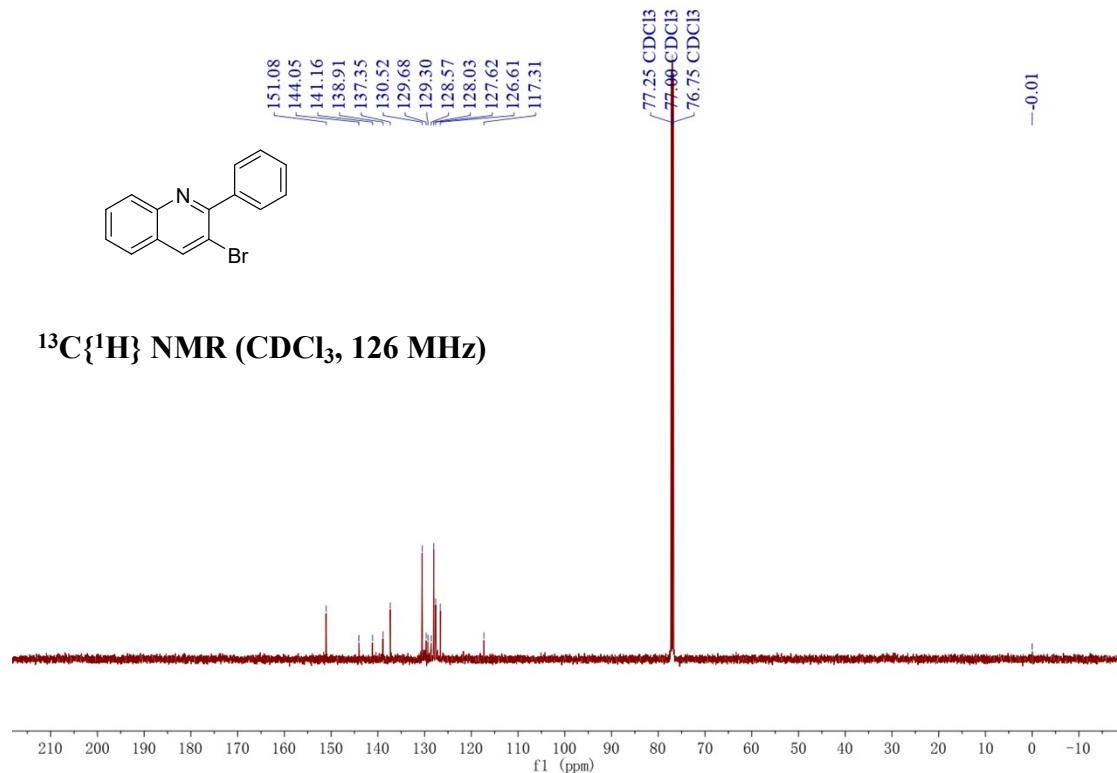
## **<sup>1</sup>H NMR Spectrum of Compound c3**



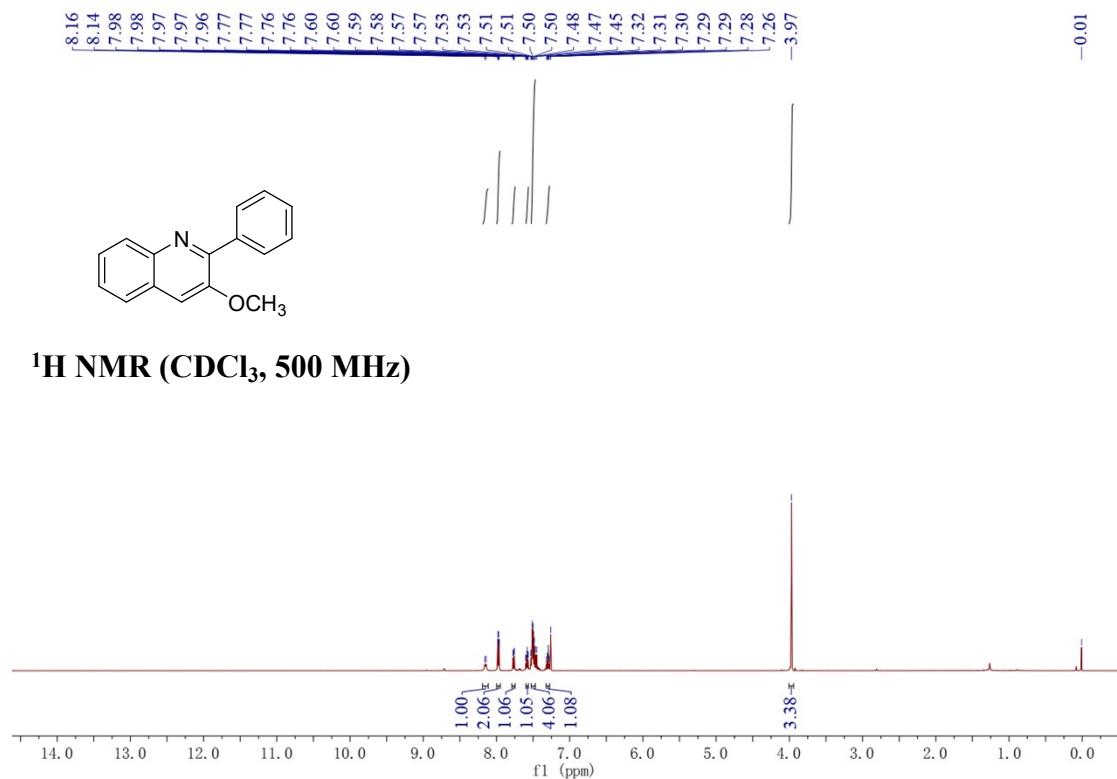
**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)**



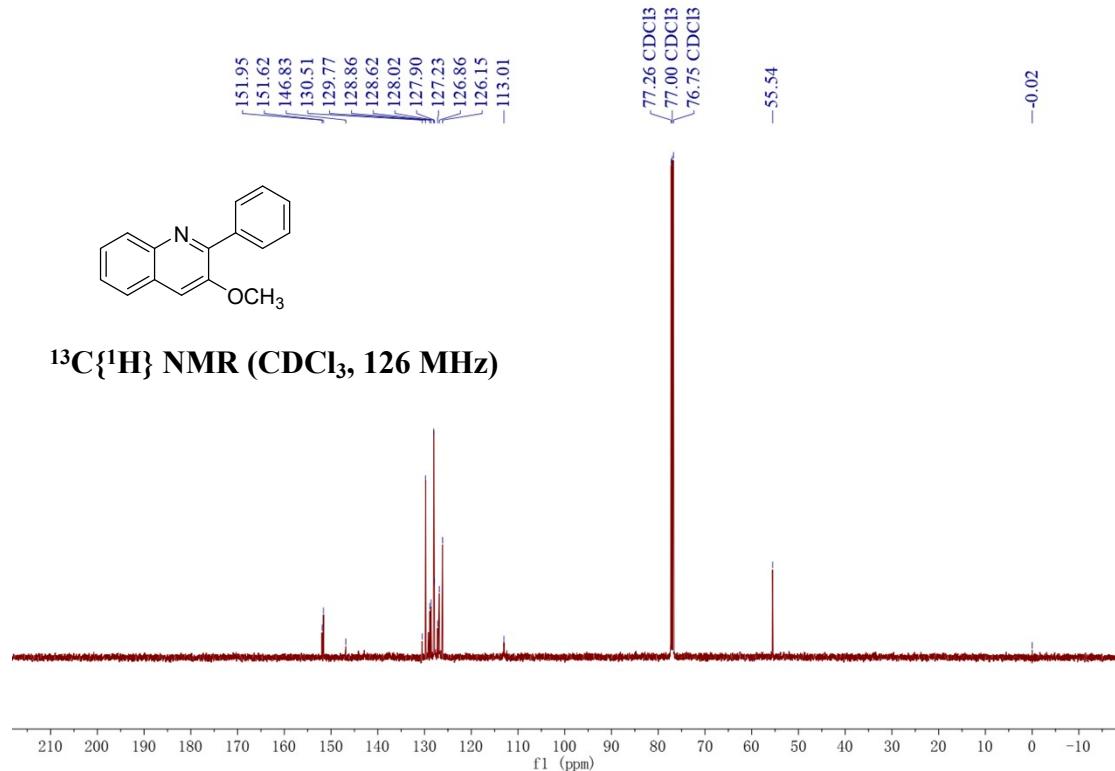
**$^{13}\text{C}\{\text{H}\}$  NMR Spectrum of Compound c3**



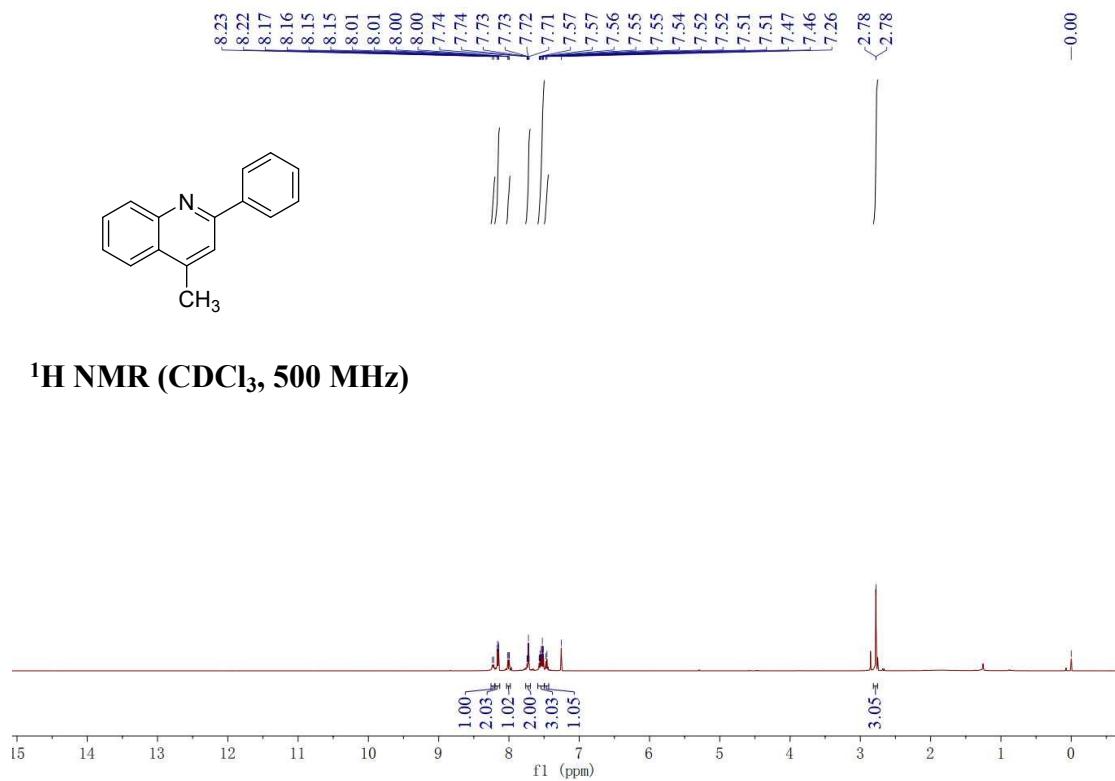
**$^1\text{H}$  NMR Spectrum of Compound c4**



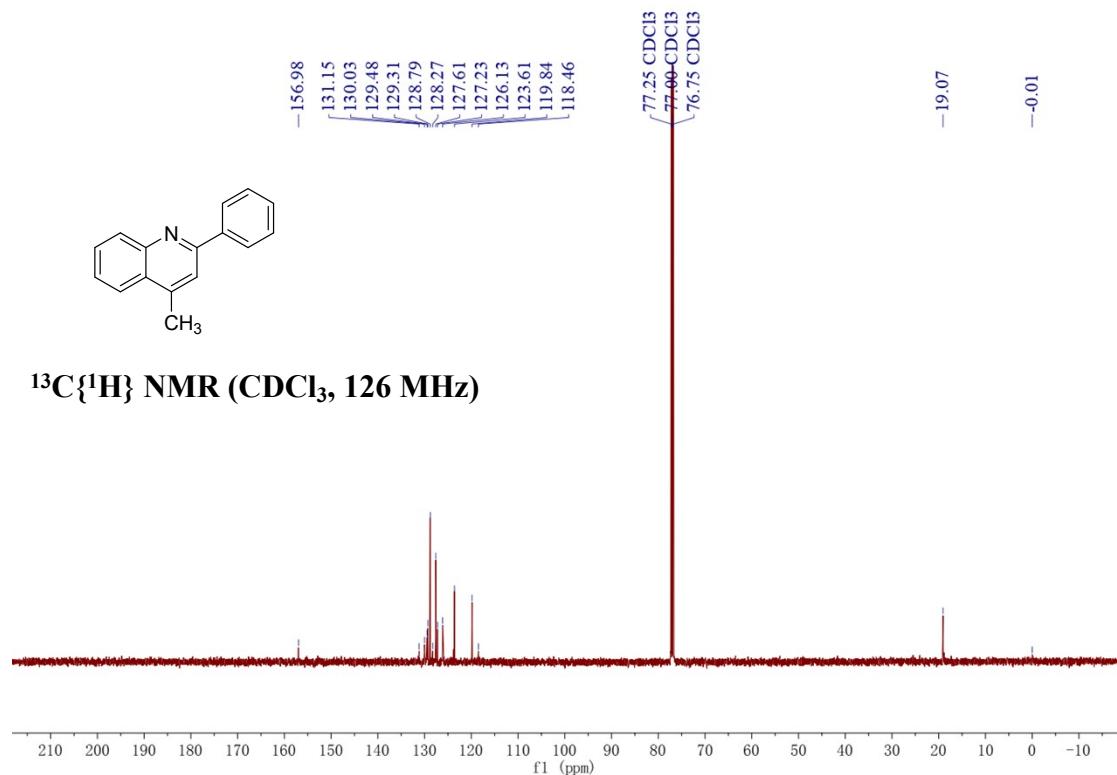
**$^{13}\text{C}\{\text{H}\}$  NMR Spectrum of Compound c4**



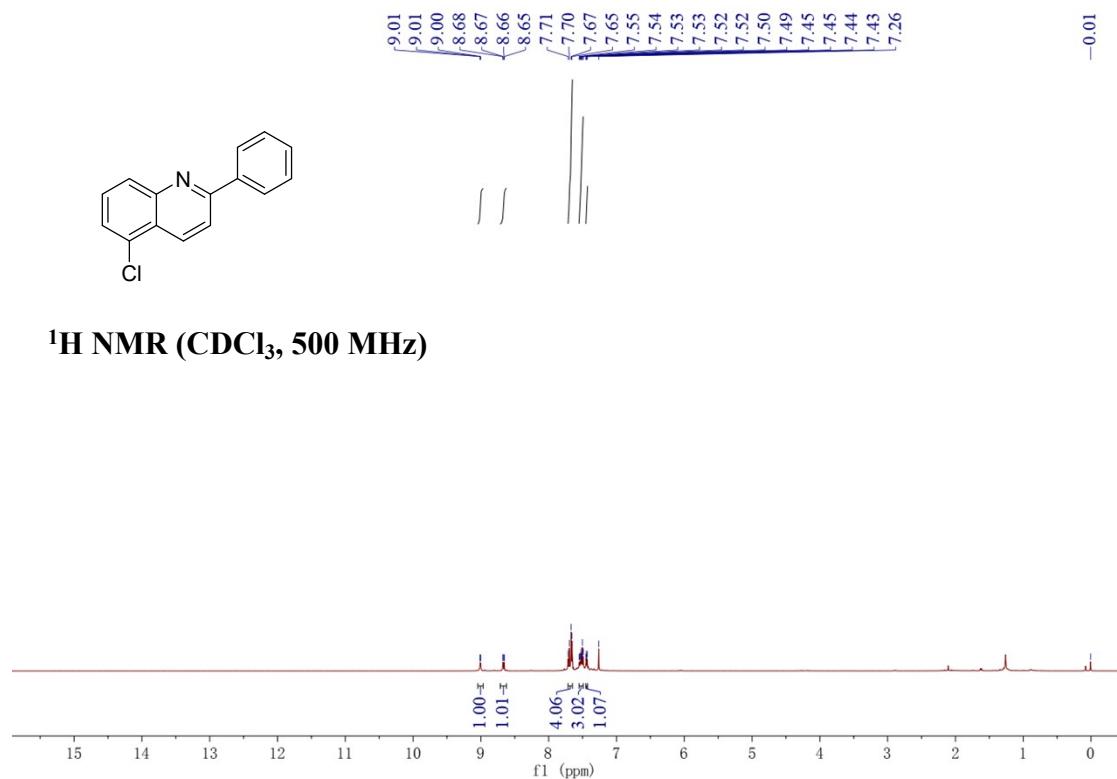
**$^1\text{H}$  NMR Spectrum of Compound c5**



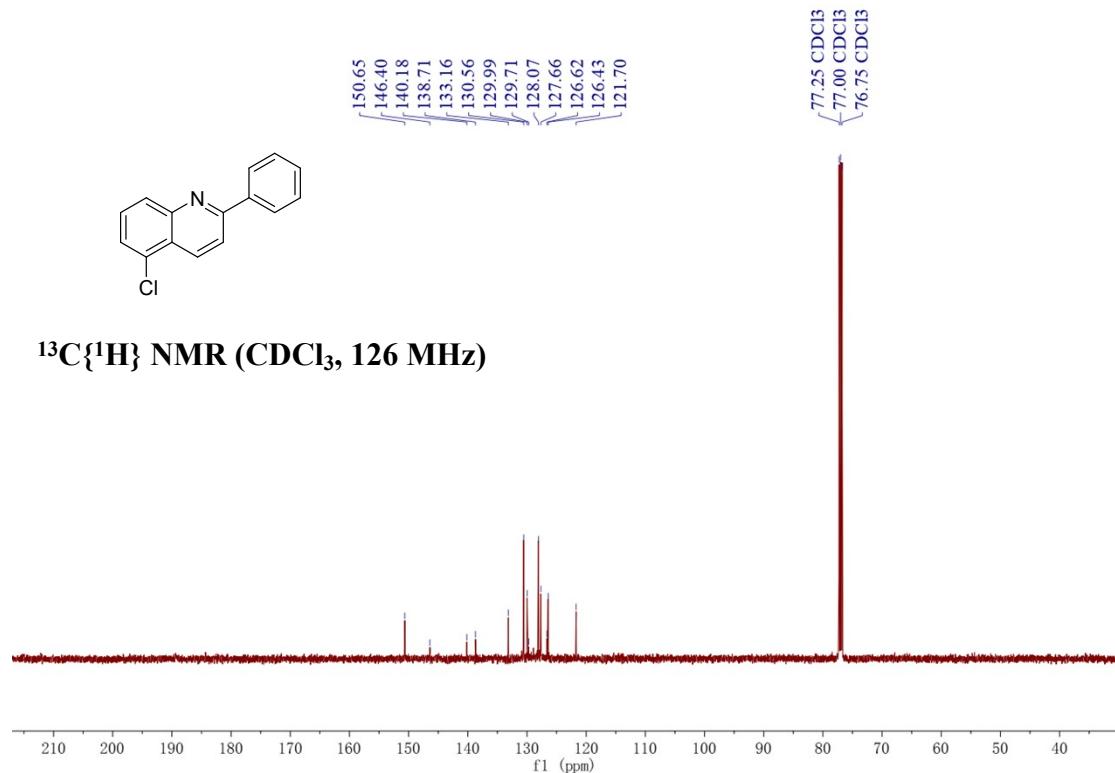
**$^{13}\text{C}\{\text{H}\}$  NMR Spectrum of Compound c5**



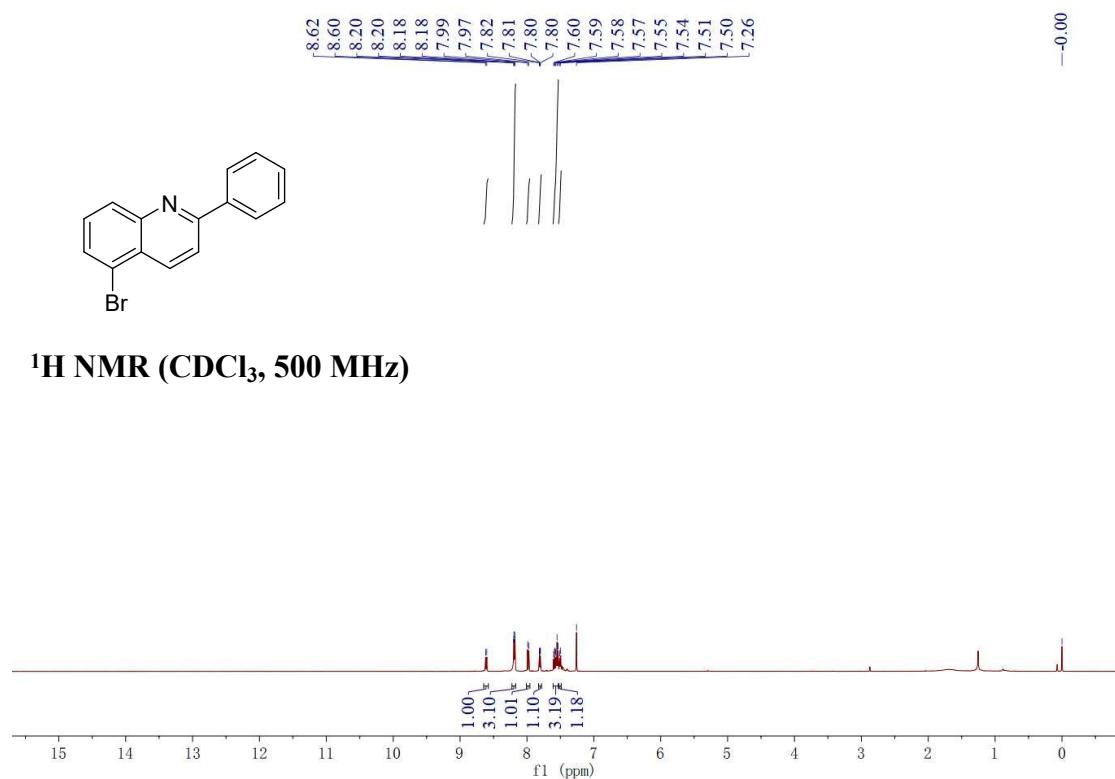
**$^1\text{H}$  NMR Spectrum of Compound c6**



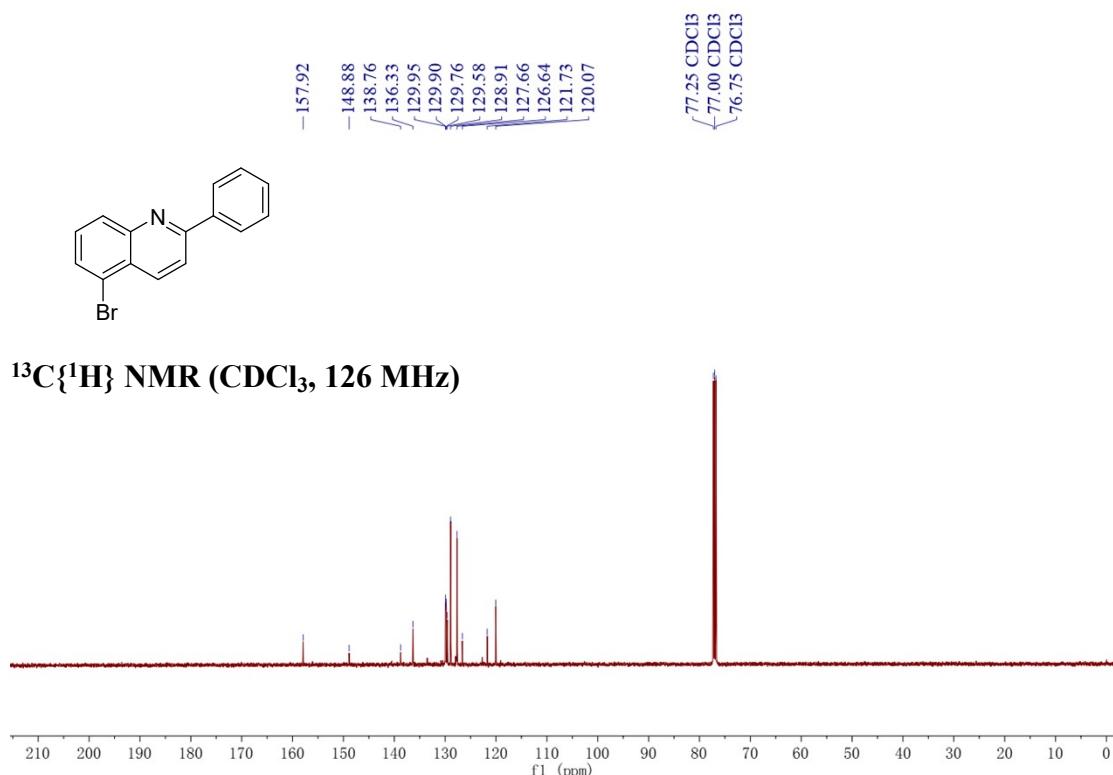
### $^{13}\text{C}\{\text{H}\}$ NMR Spectrum of Compound c6



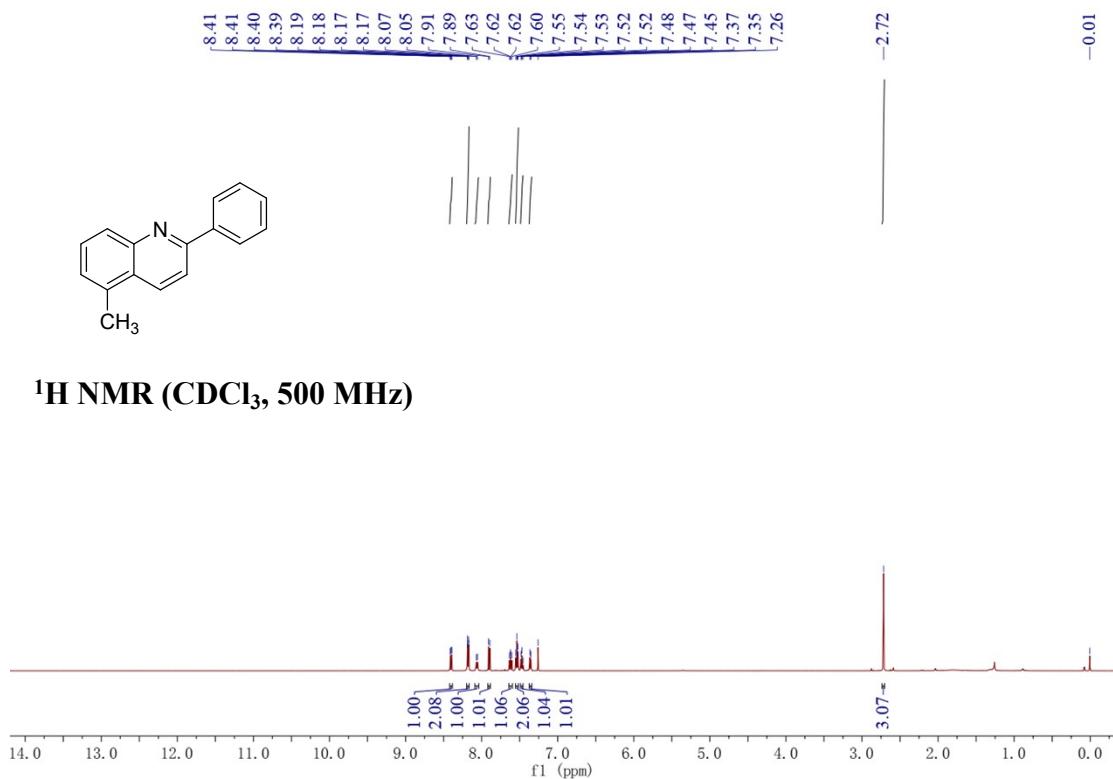
### $^1\text{H}$ NMR Spectrum of Compound c7



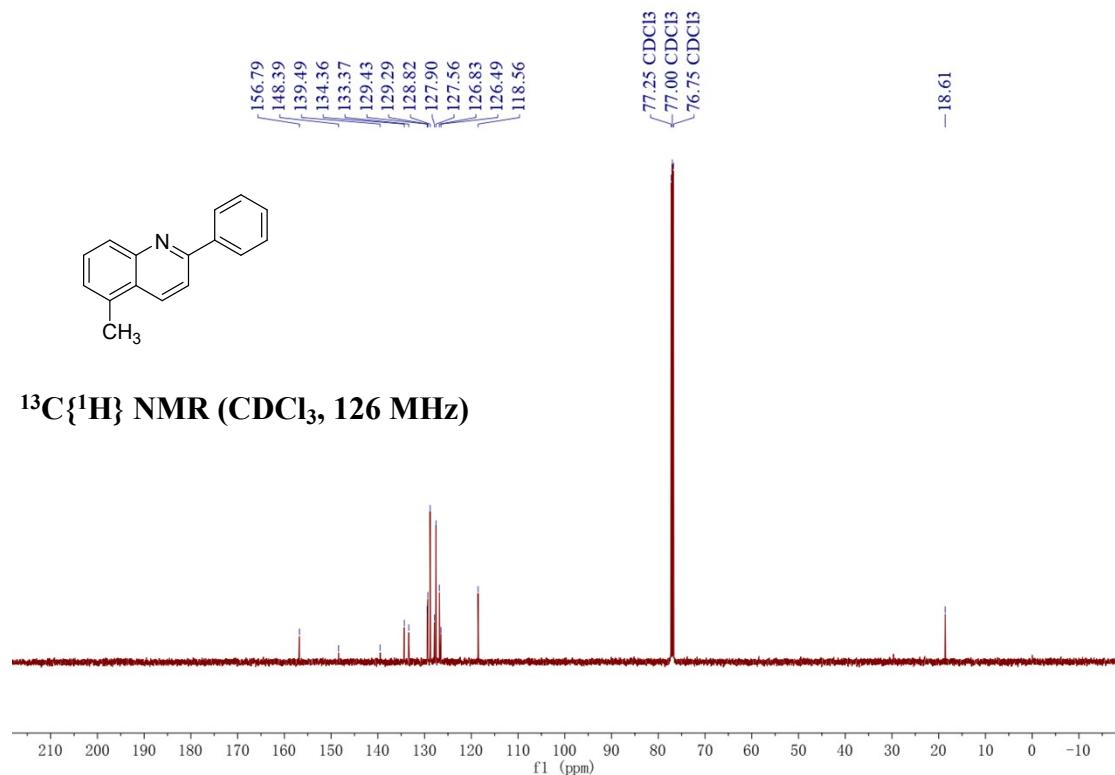
**$^{13}\text{C}\{\text{H}\}$  NMR Spectrum of Compound c7**



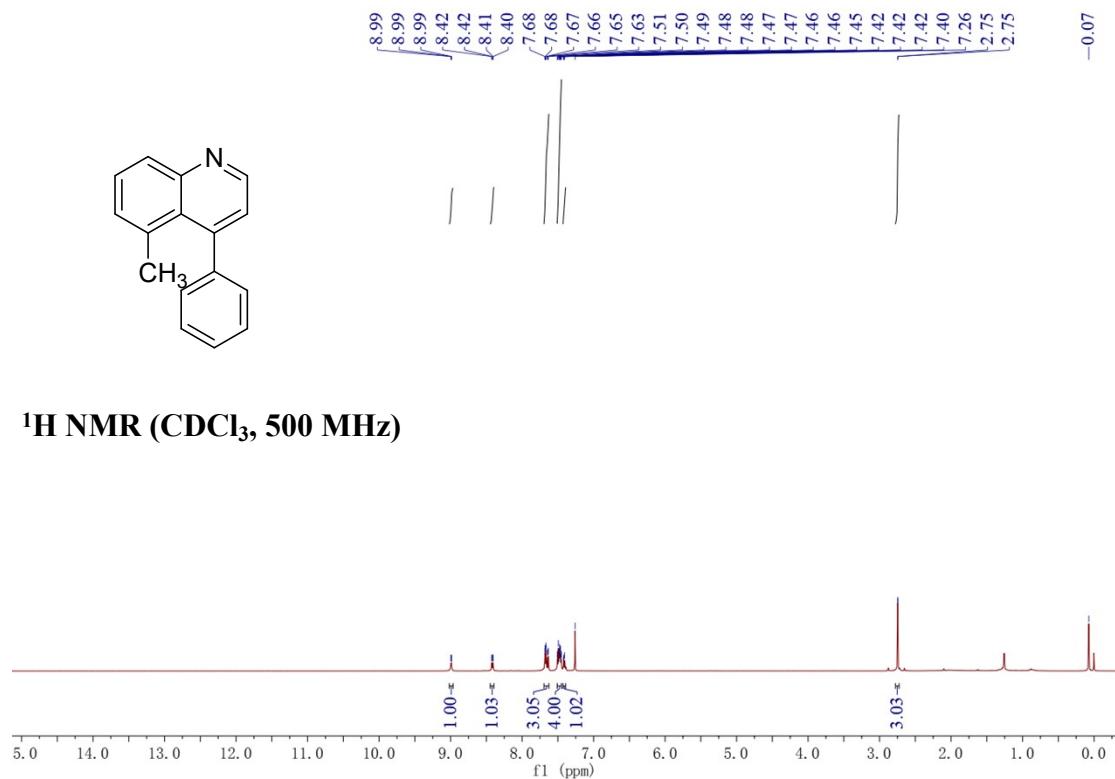
**$^1\text{H}$  NMR Spectrum of Compound c8-1**



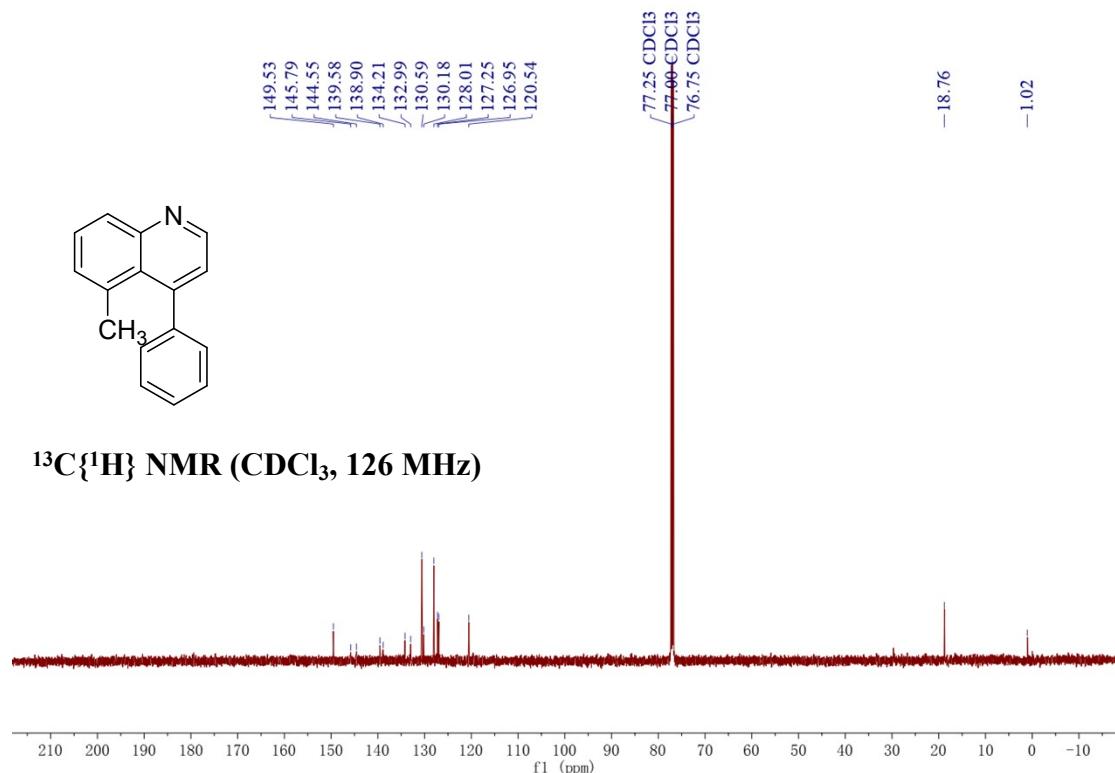
**$^{13}\text{C}\{\text{H}\}$  NMR Spectrum of Compound c8-1**



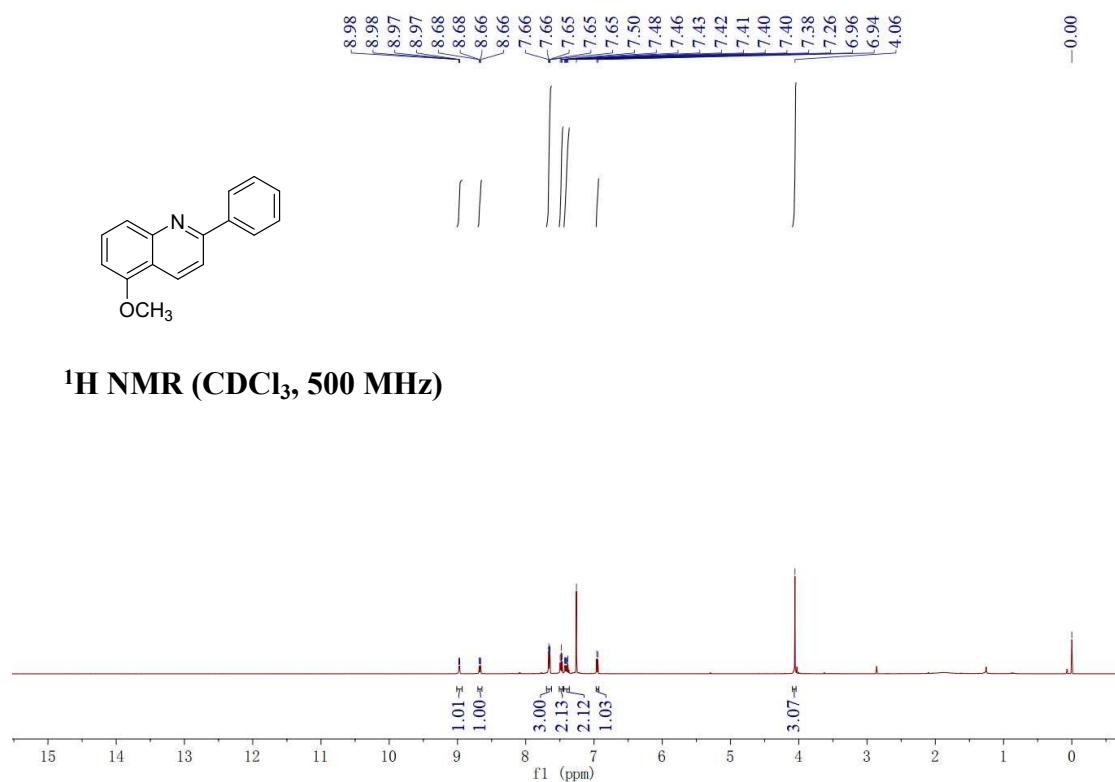
**$^1\text{H}$  NMR Spectrum of Compound c8-2**



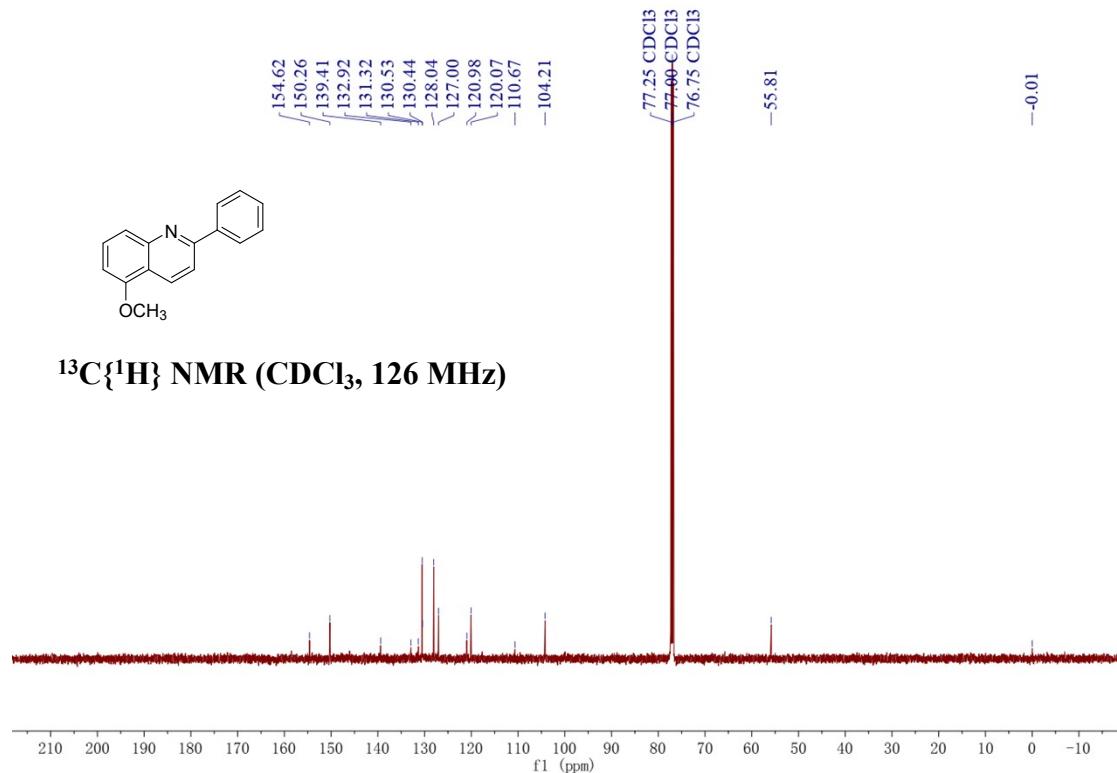
**$^{13}\text{C}\{\text{H}\}$  NMR Spectrum of Compound c8-2**



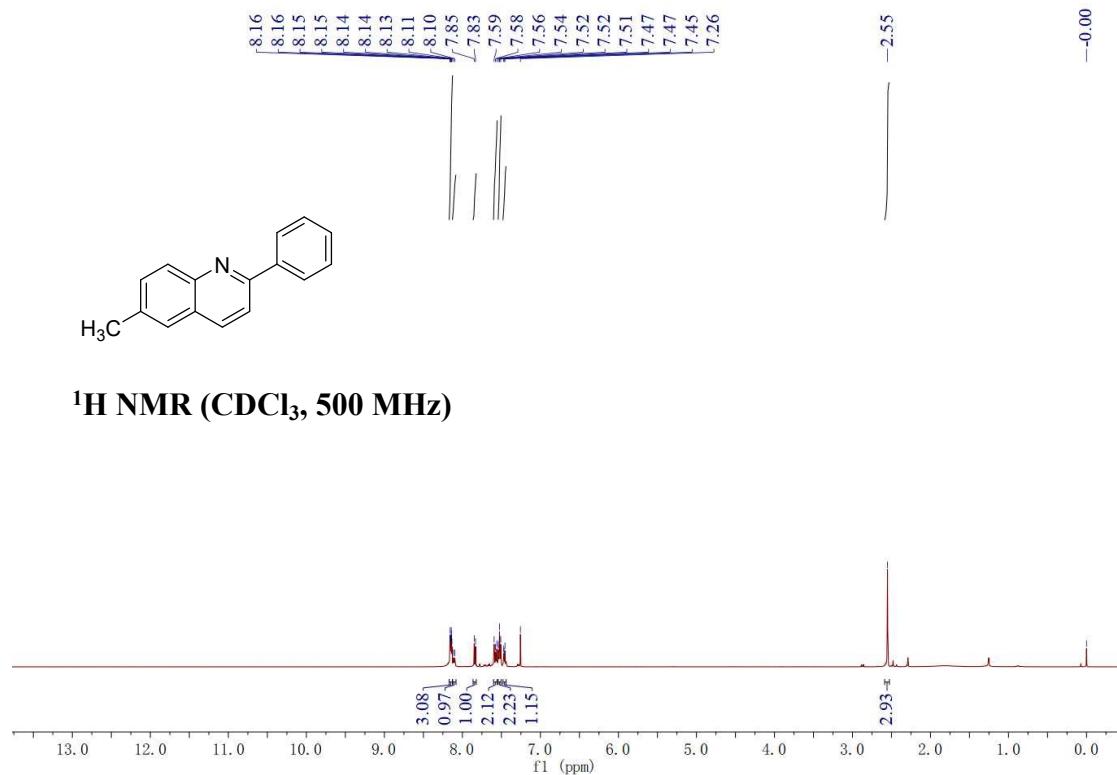
**$^1\text{H}$  NMR Spectrum of Compound c9**



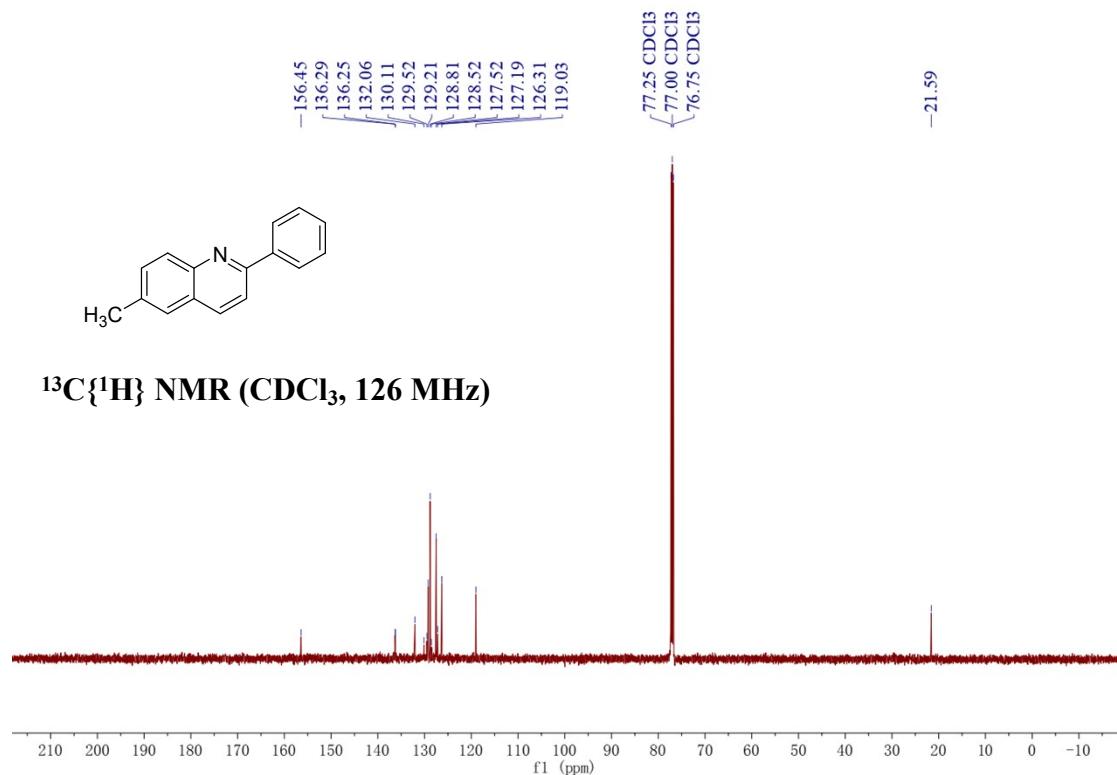
**$^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of Compound c9**



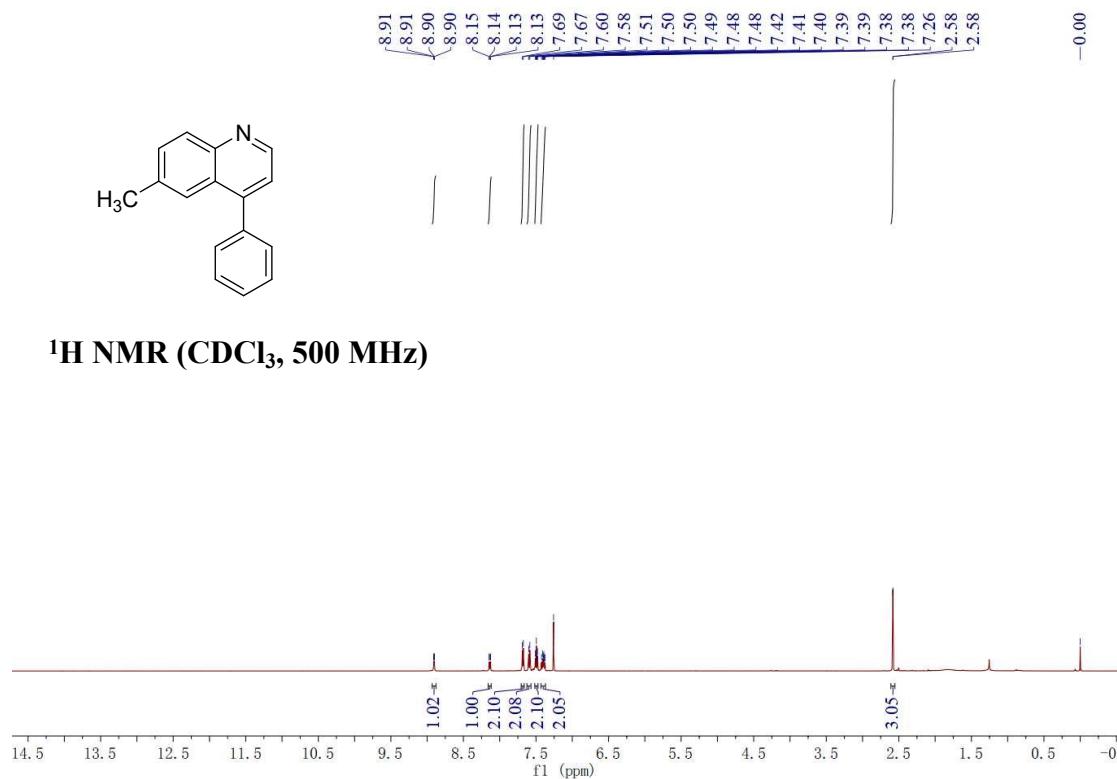
**$^1\text{H}$  NMR Spectrum of Compound c10-1**



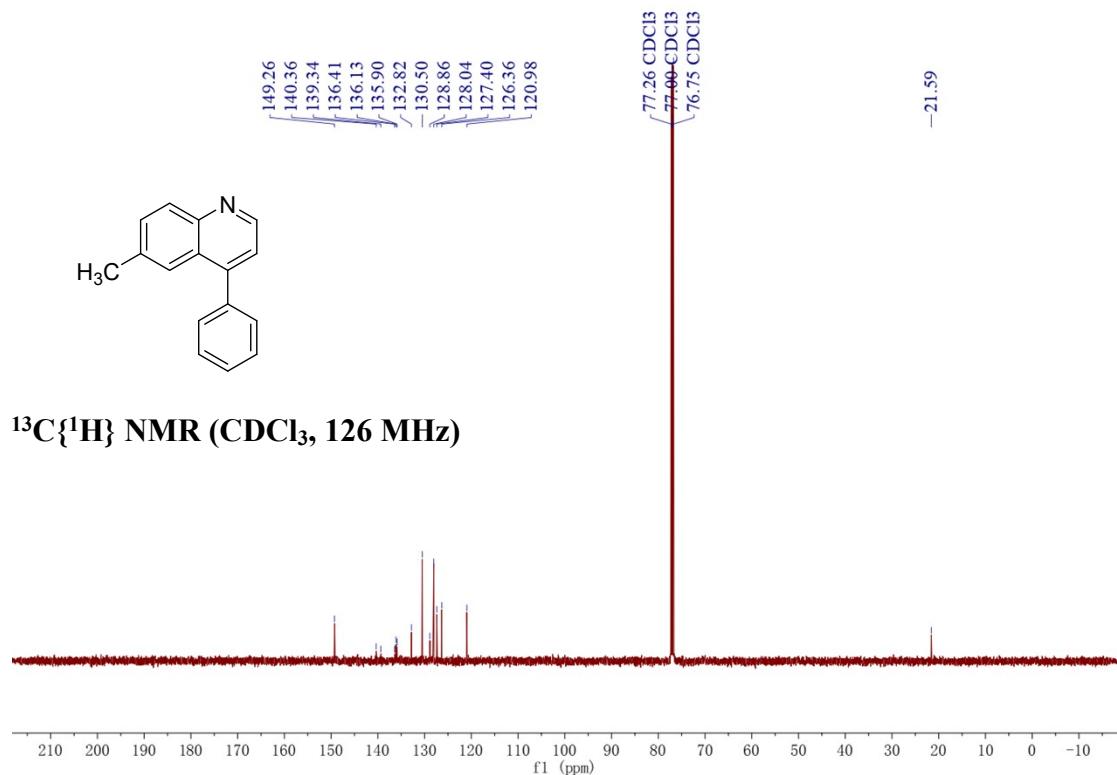
**$^{13}\text{C}\{\text{H}\}$  NMR Spectrum of Compound c10-1**



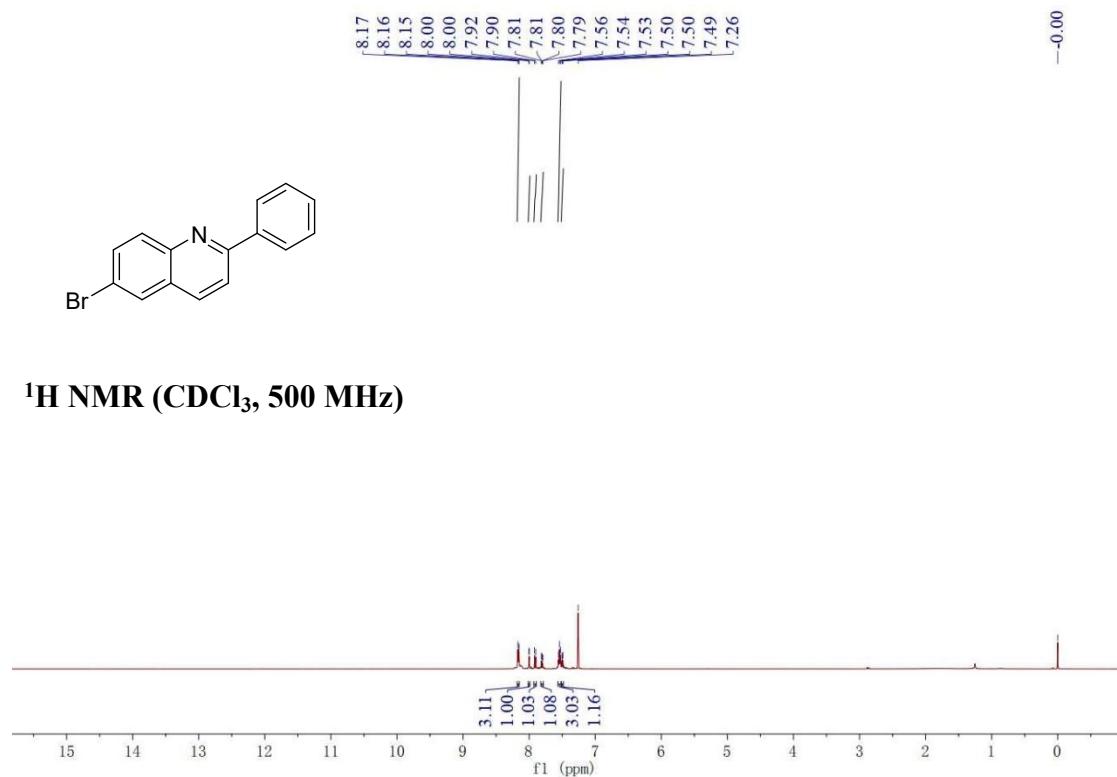
**$^1\text{H}$  NMR Spectrum of Compound c10-2**



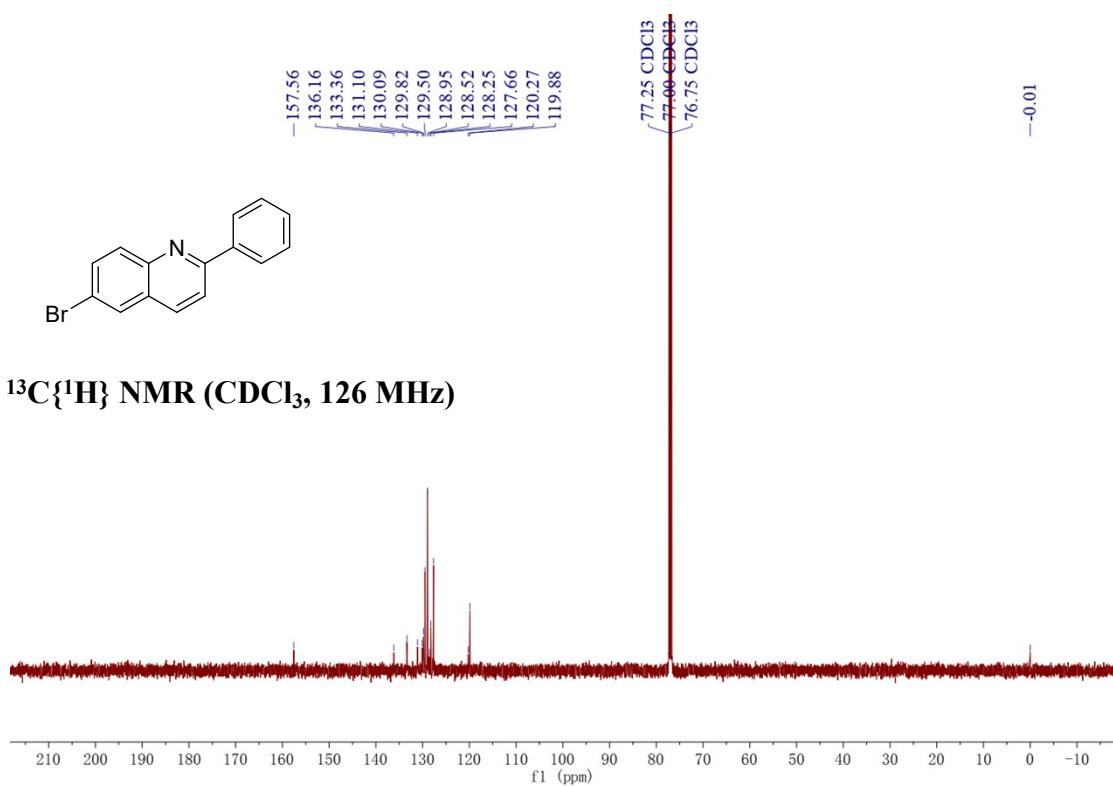
### $^{13}\text{C}\{\text{H}\}$ NMR Spectrum of Compound c10-2



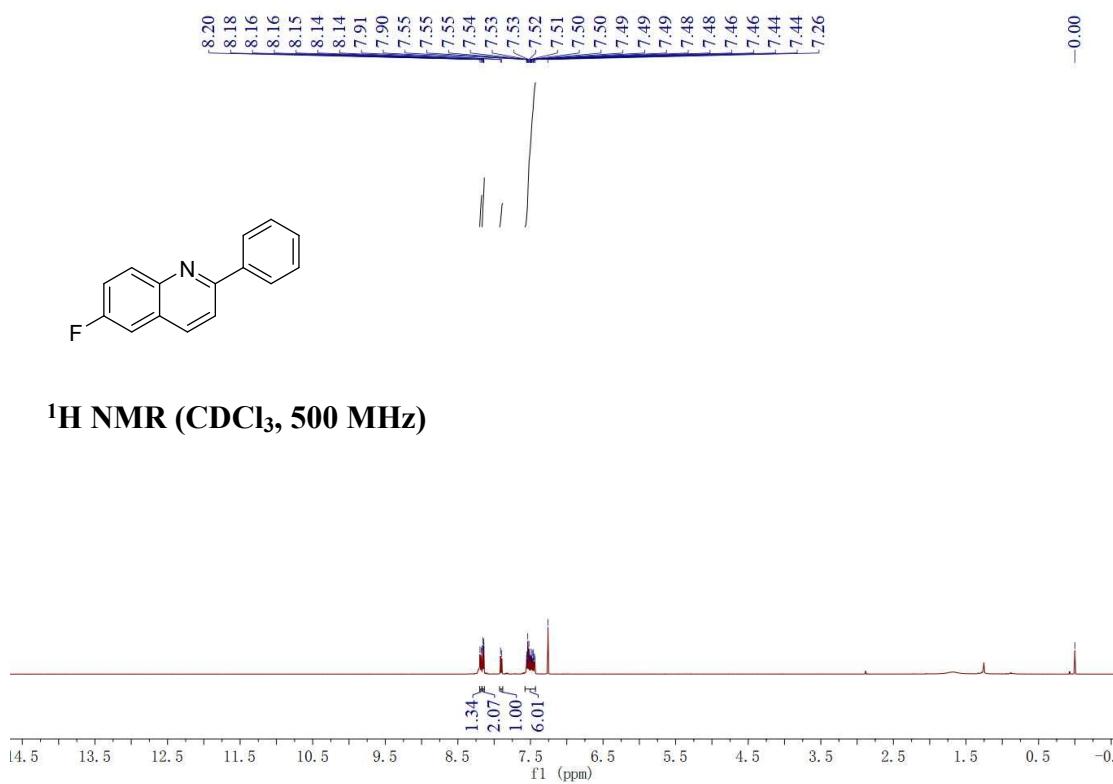
### $^1\text{H}$ NMR Spectrum of Compound c11



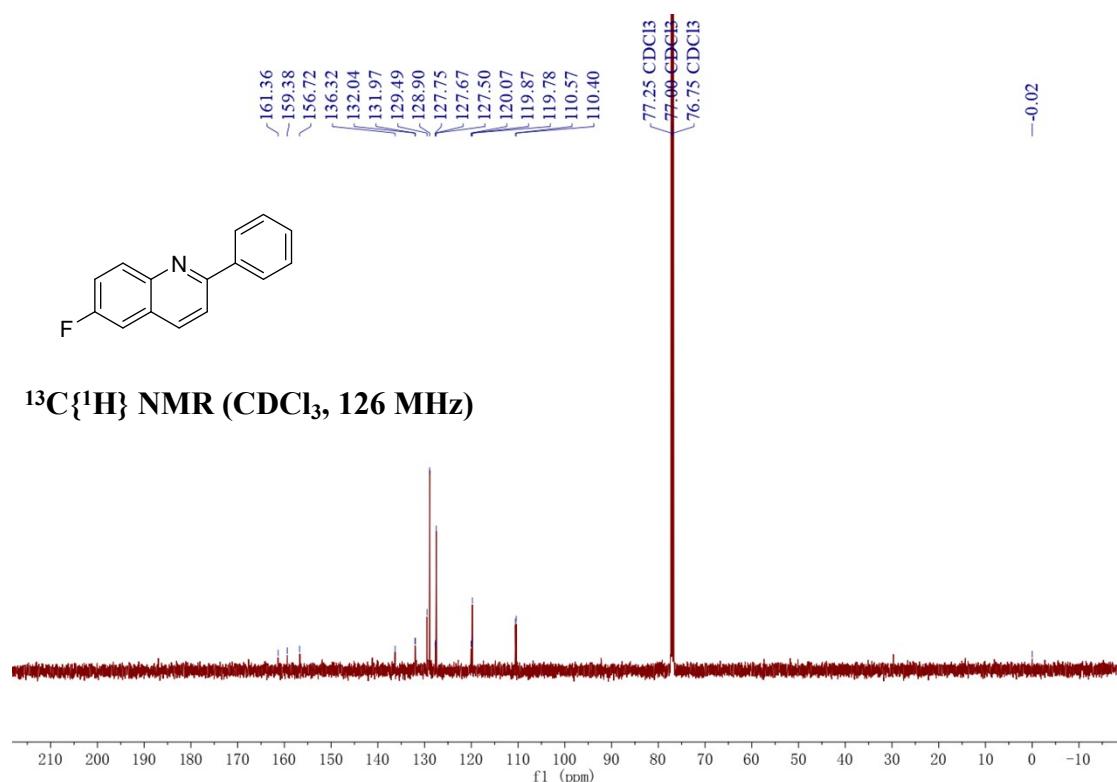
**$^{13}\text{C}\{\text{H}\}$  NMR Spectrum of Compound c11**



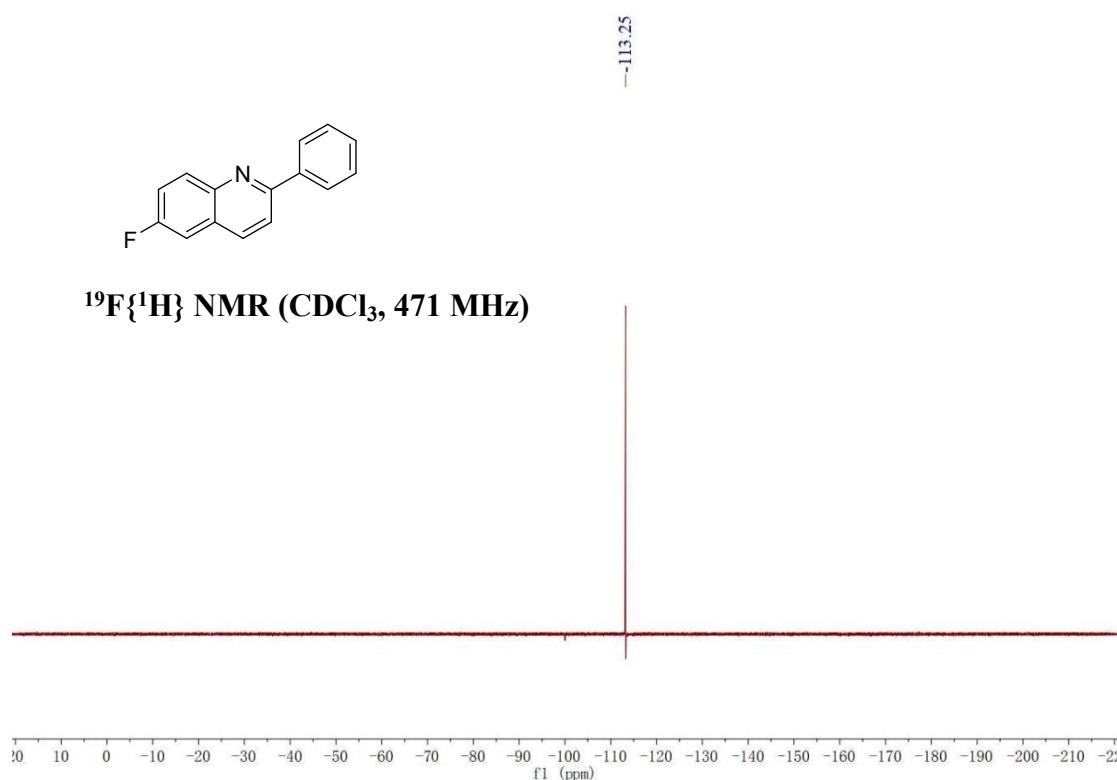
**$^1\text{H}$  NMR Spectrum of Compound c12-1**



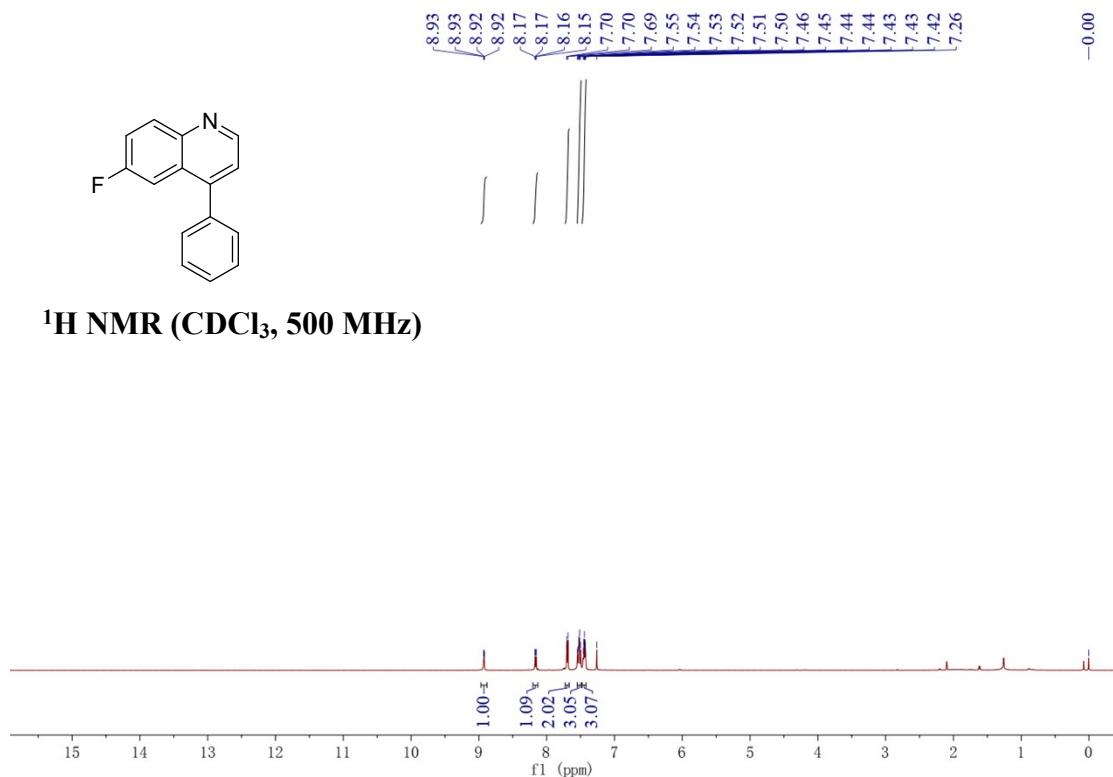
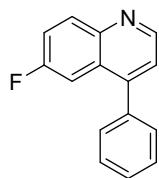
**$^{13}\text{C}\{\text{H}\}$  NMR Spectrum of Compound c12-1**



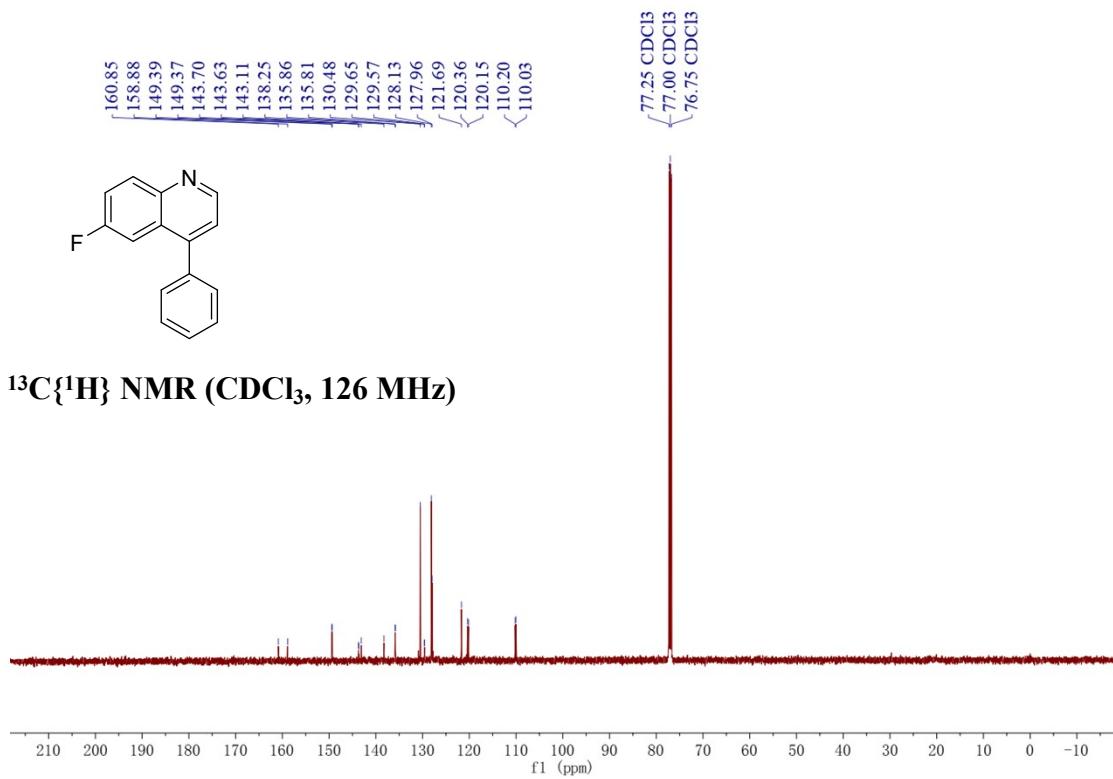
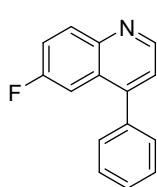
**$^{19}\text{F}$  NMR Spectrum of Compound c12-1**



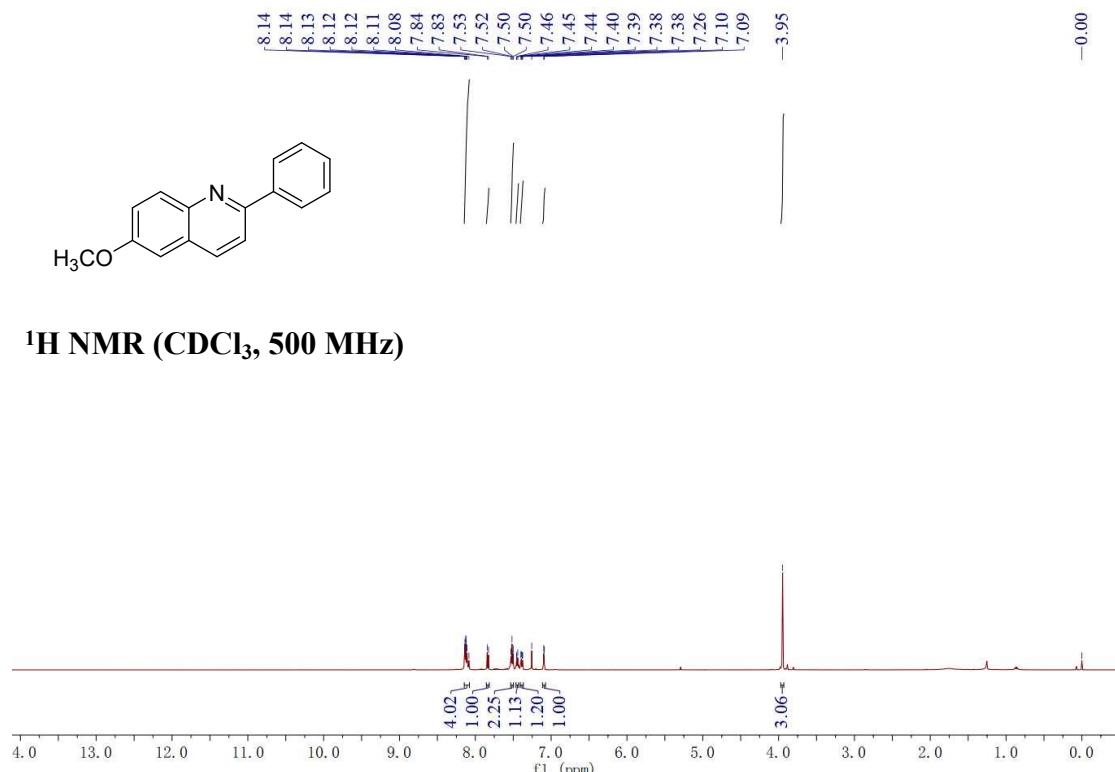
## **<sup>1</sup>H NMR Spectrum of Compound c12-2**



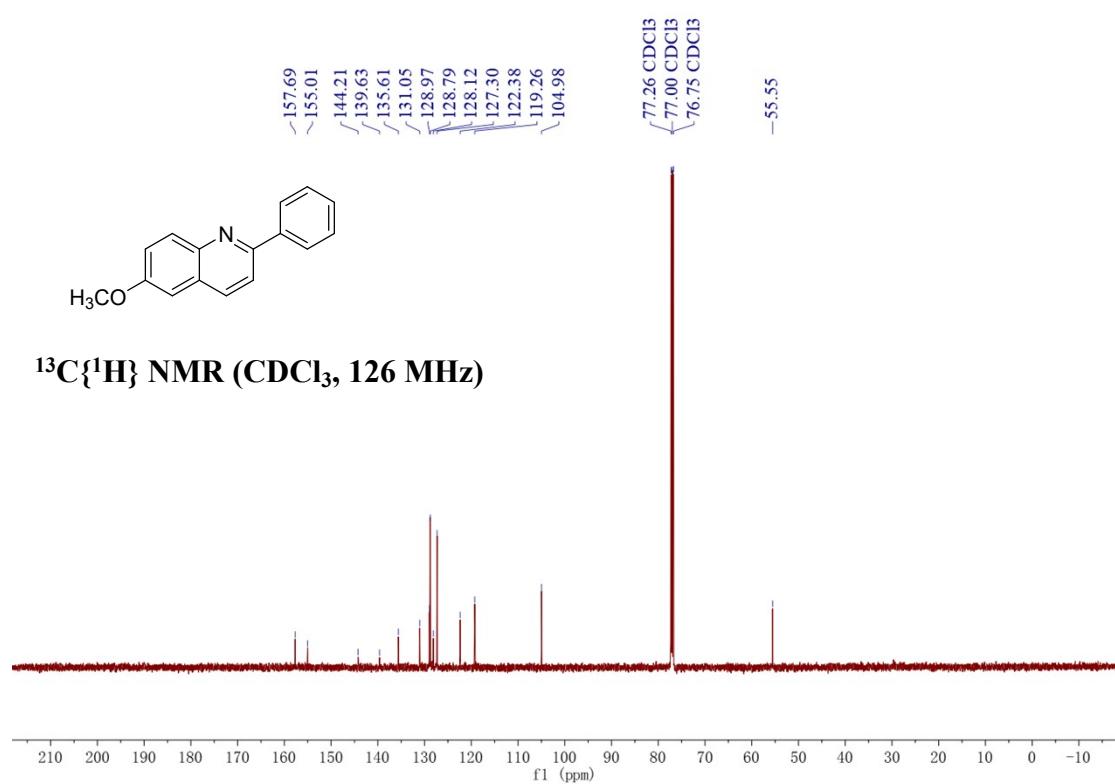
## <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of Compound c12-2



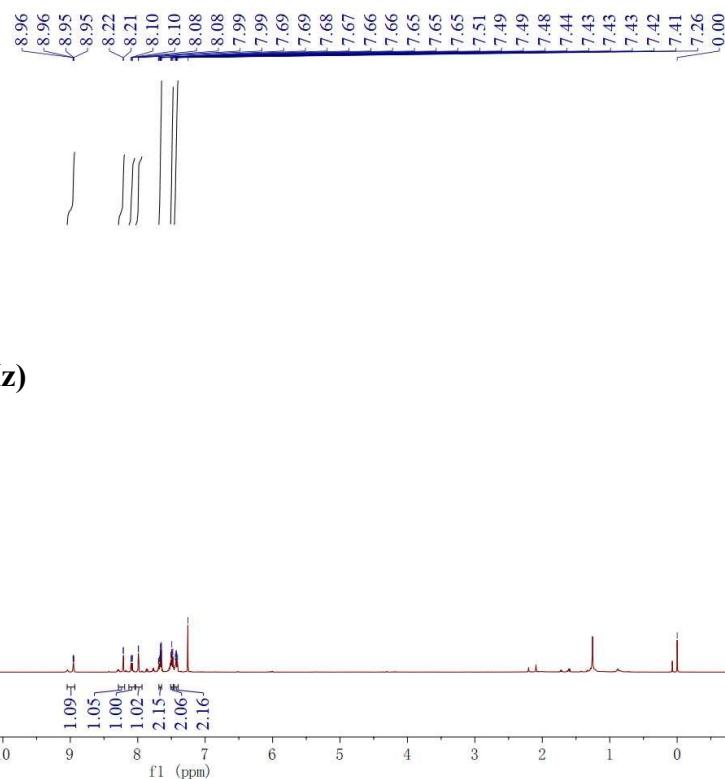
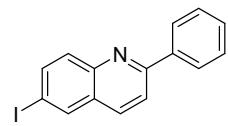
**$^1\text{H}$  NMR Spectrum of Compound c13**



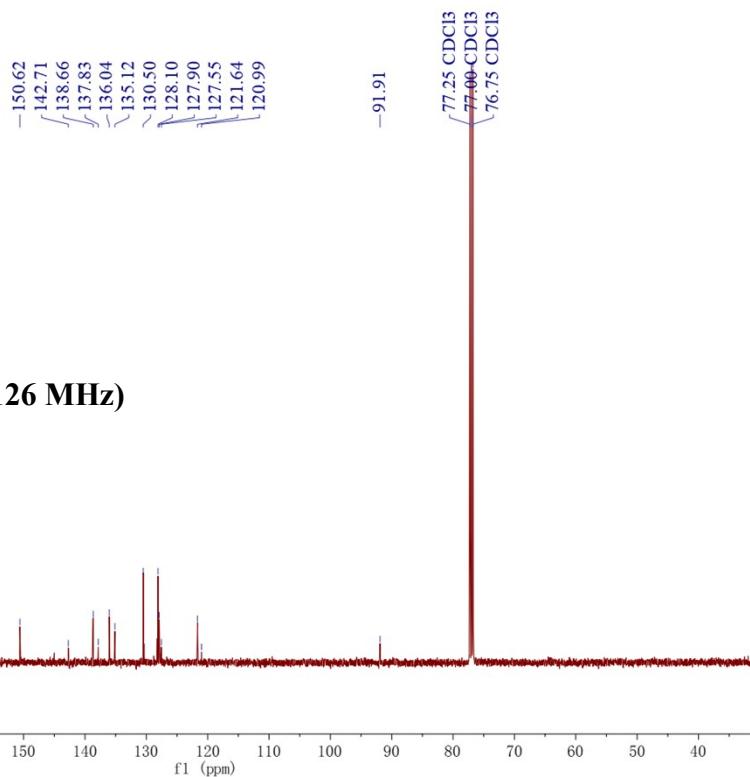
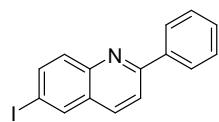
**$^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of Compound c13**



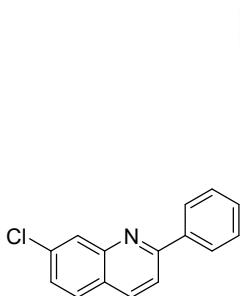
## **<sup>1</sup>H NMR Spectrum of Compound c14**



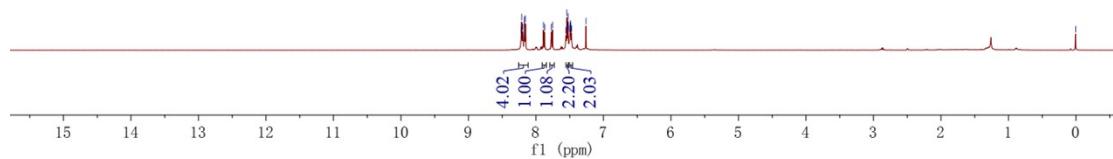
### **<sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of Compound c14**



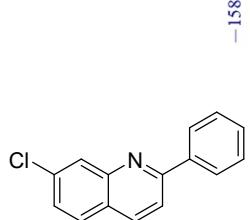
## **<sup>1</sup>H NMR Spectrum of Compound c15**



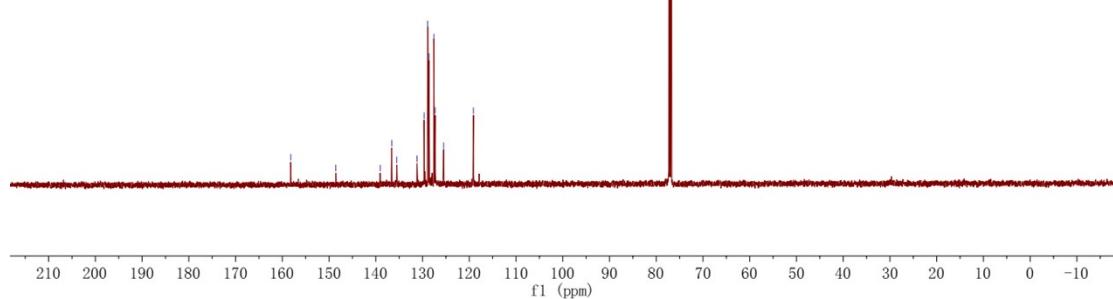
**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)**



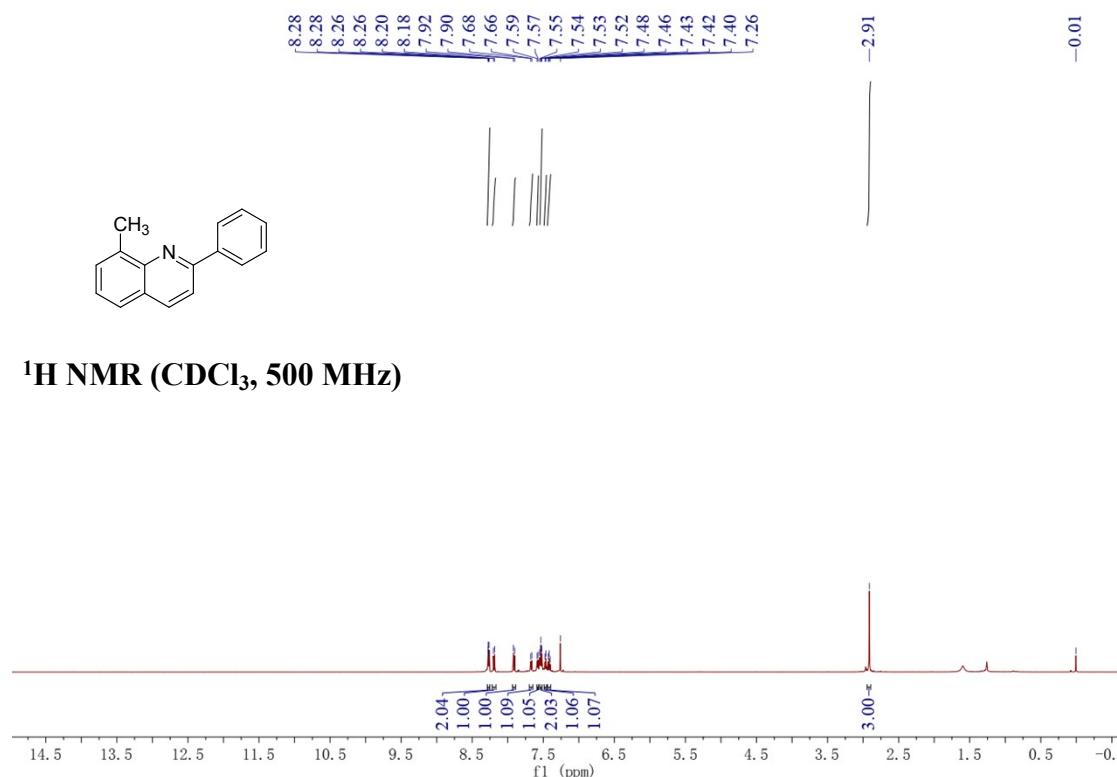
### **<sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of Compound c15**



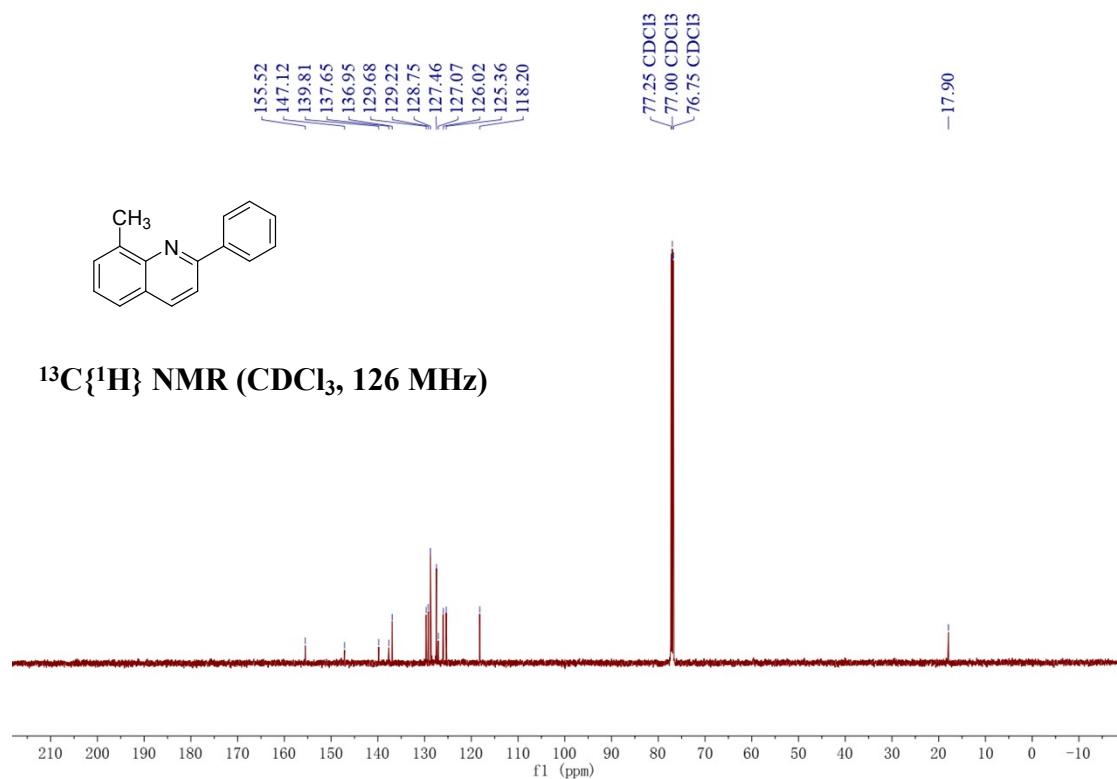
**$^{13}\text{C}\{\text{H}\}$  NMR ( $\text{CDCl}_3$ , 126 MHz)**



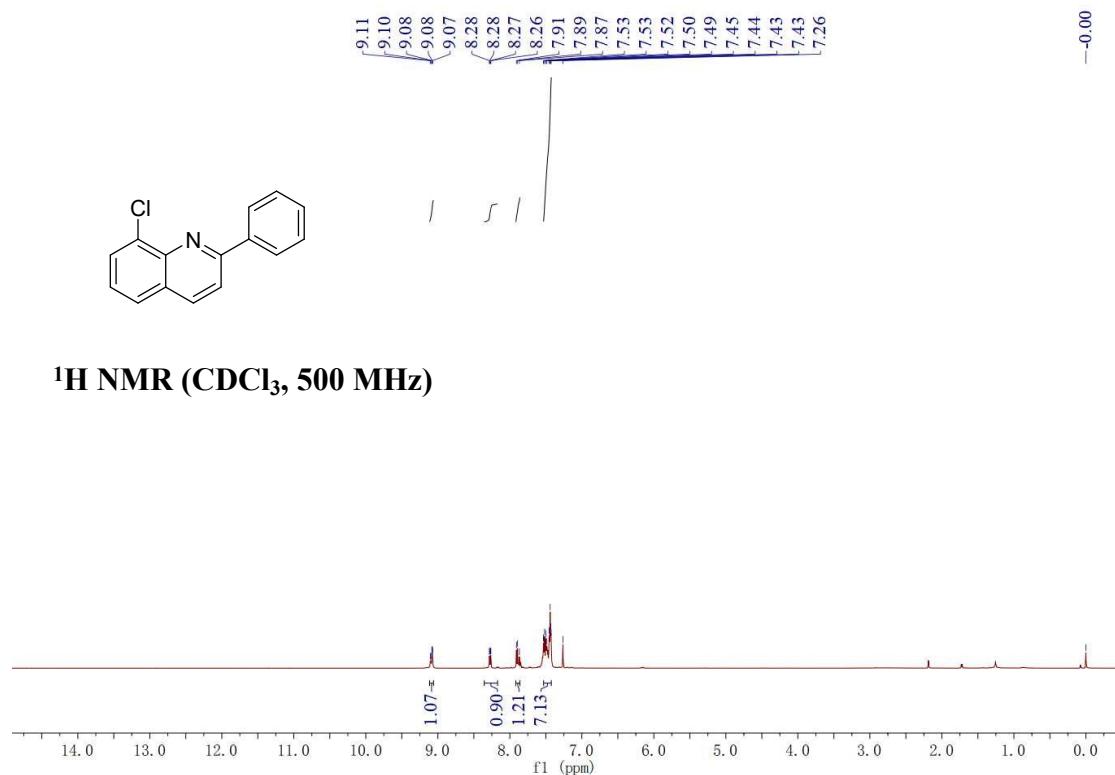
### **<sup>1</sup>H NMR Spectrum of Compound c16**



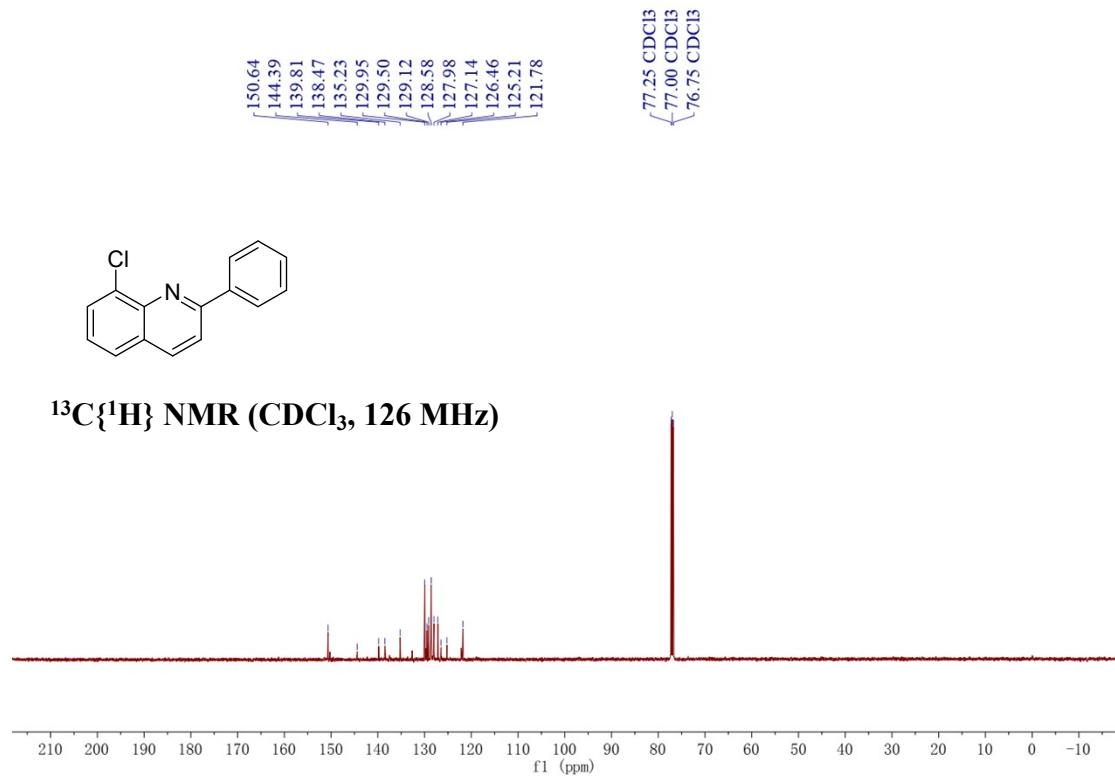
### **<sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of Compound c16**



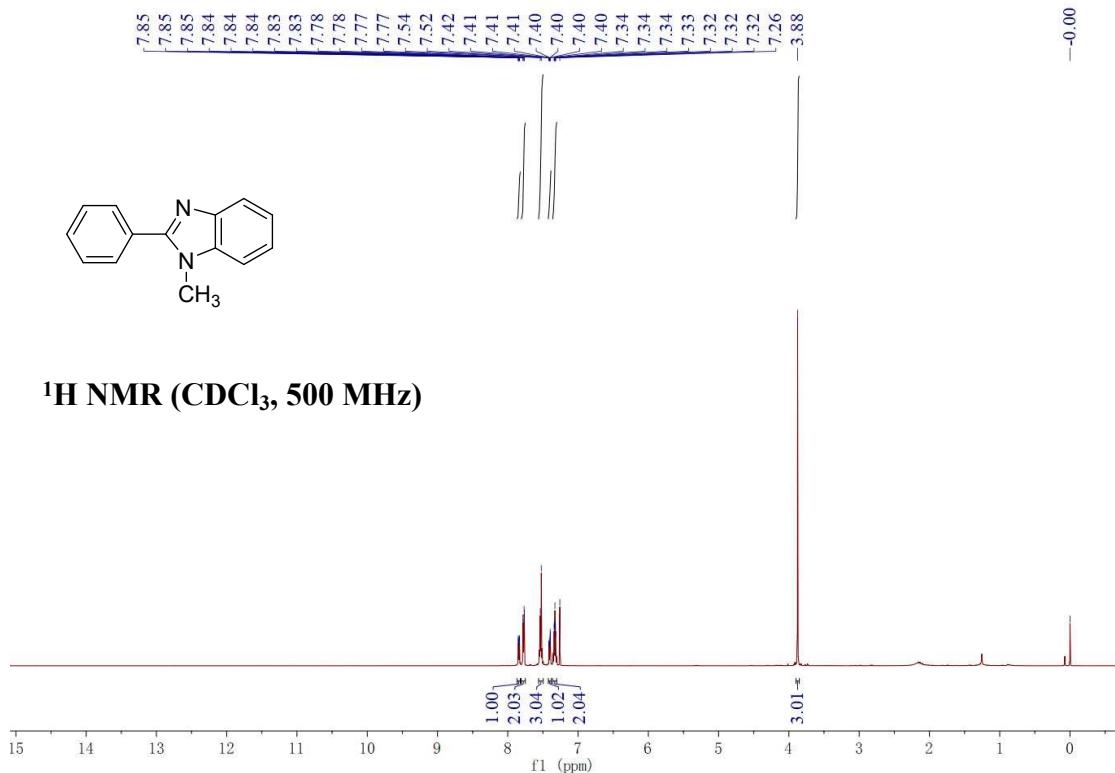
### <sup>1</sup>H NMR Spectrum of Compound c17



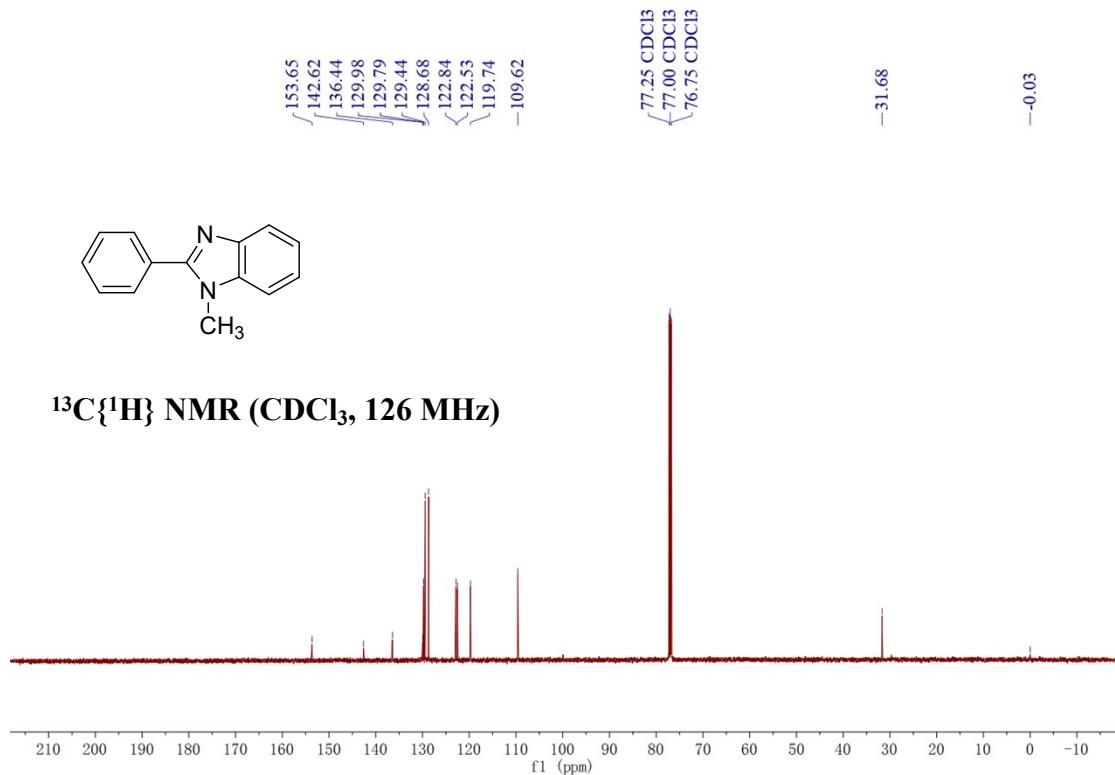
### <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of Compound c17



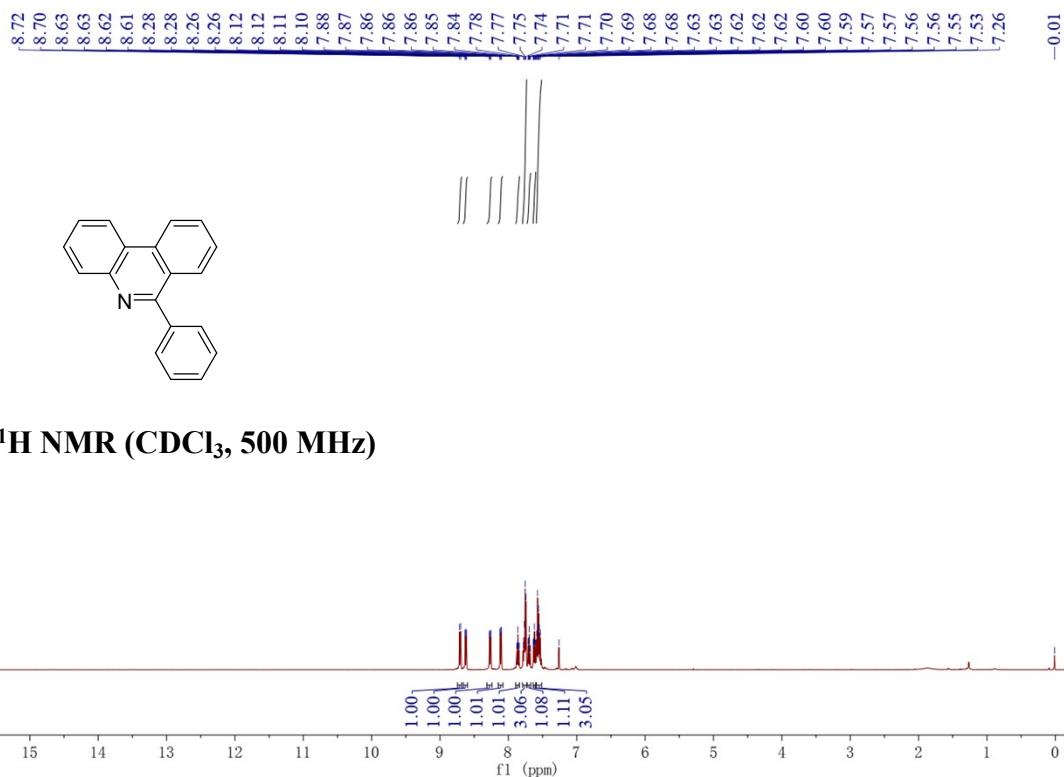
**$^1\text{H}$  NMR Spectrum of Compound c18**



**$^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of Compound c18**

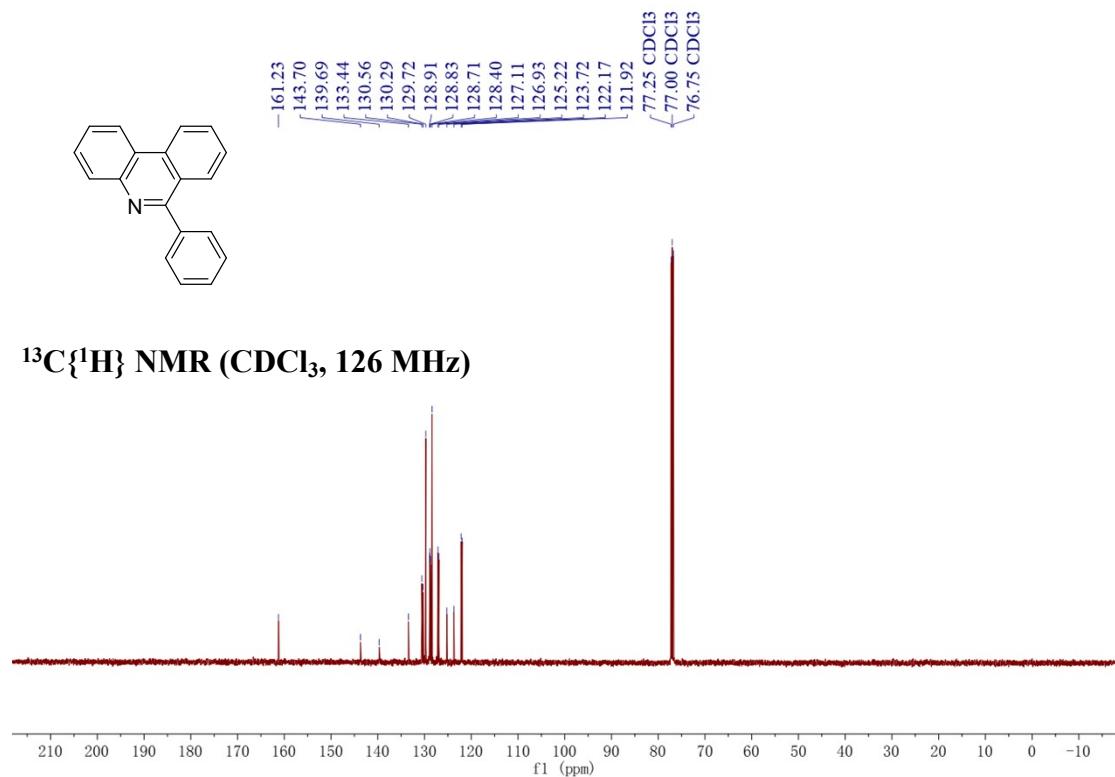


**$^1\text{H}$  NMR Spectrum of Compound c19**



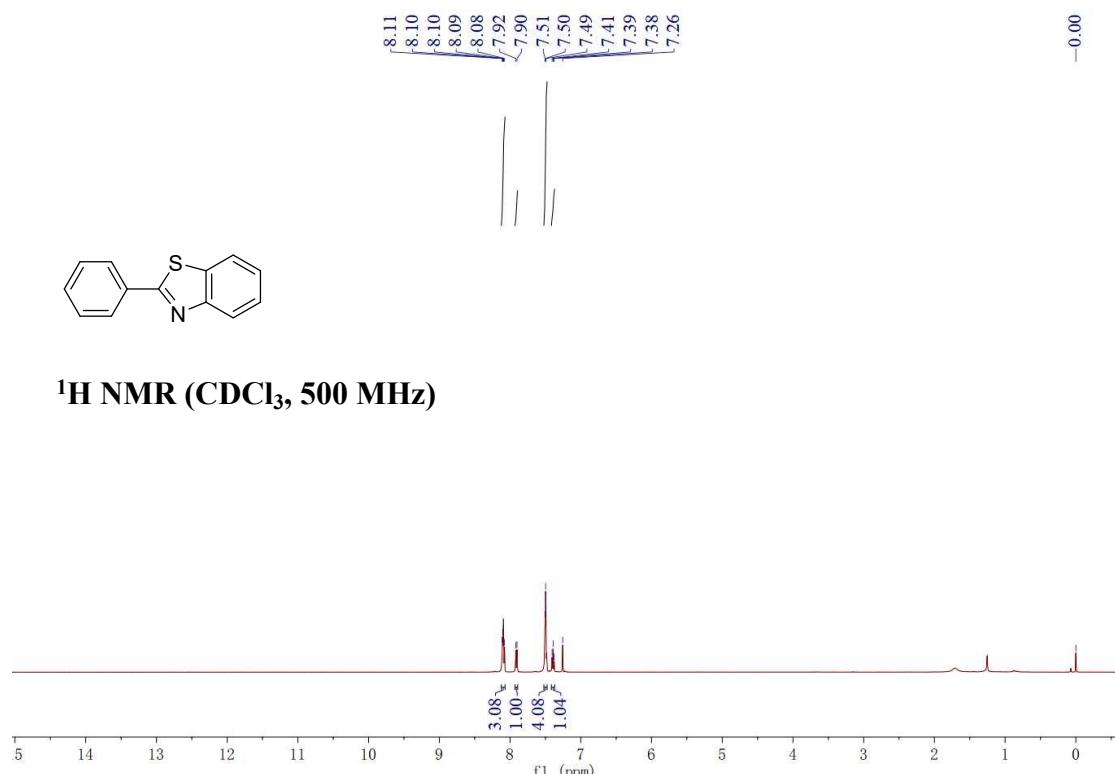
$^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz)

**$^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of Compound c19**

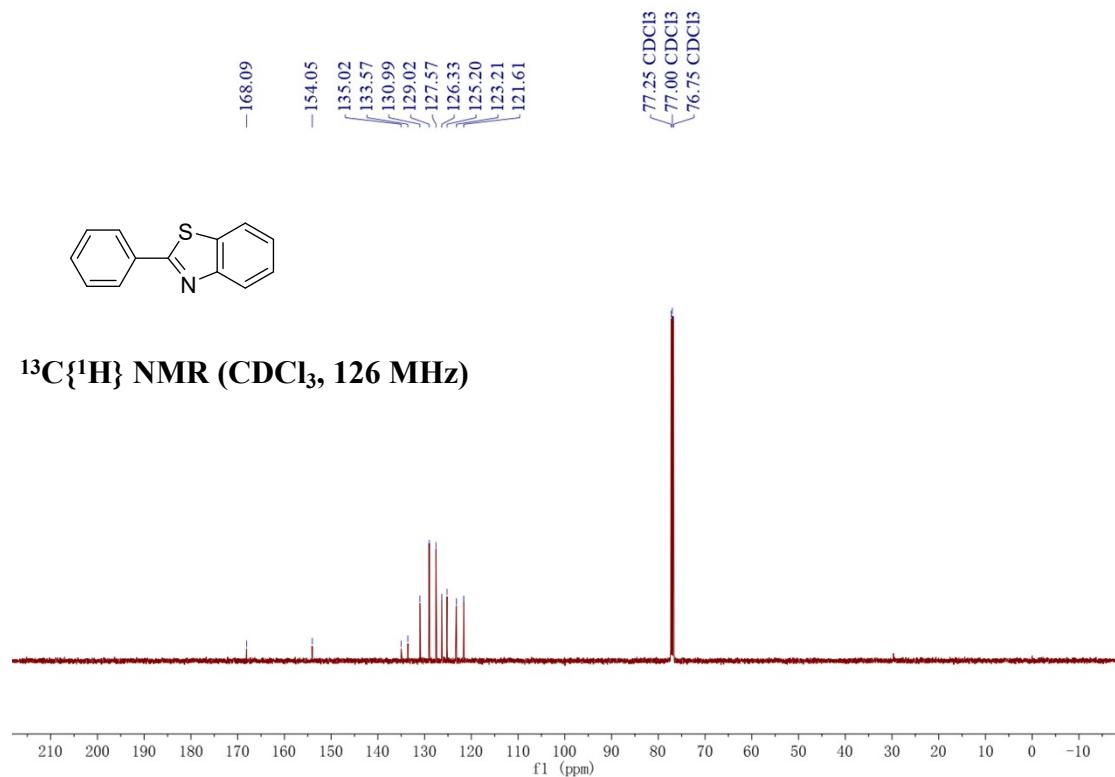


$^{13}\text{C}\{^1\text{H}\}$  NMR (CDCl<sub>3</sub>, 126 MHz)

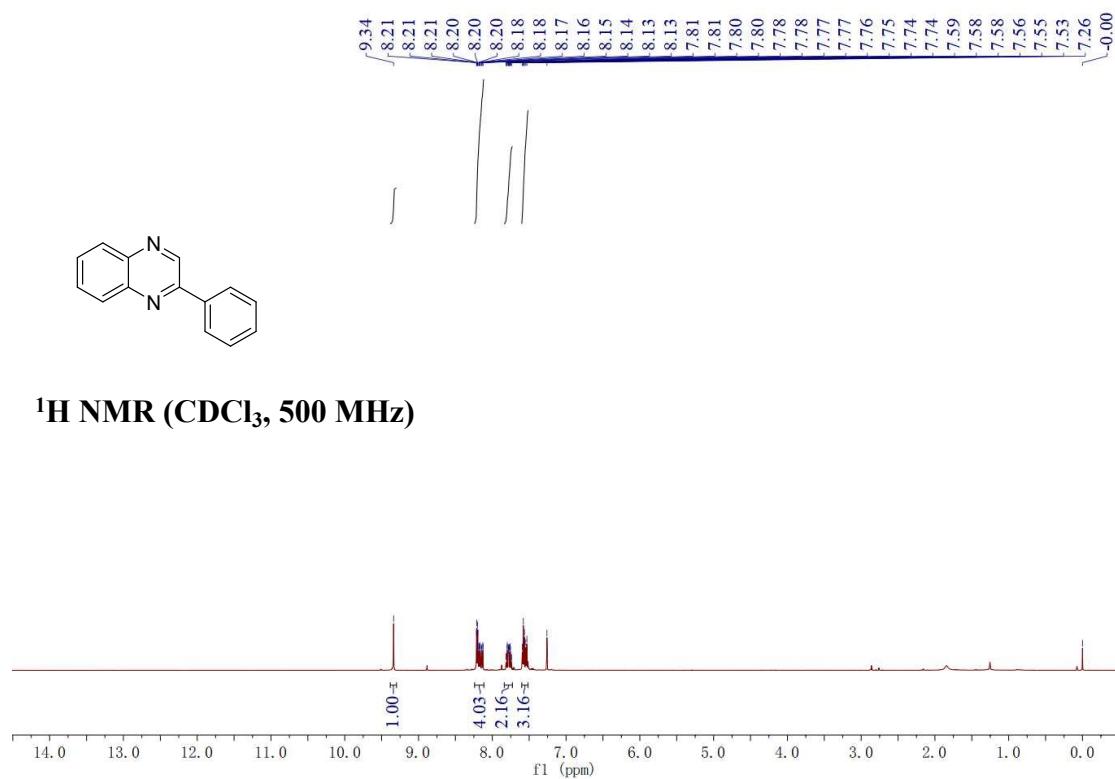
### **<sup>1</sup>H NMR Spectrum of Compound c20**



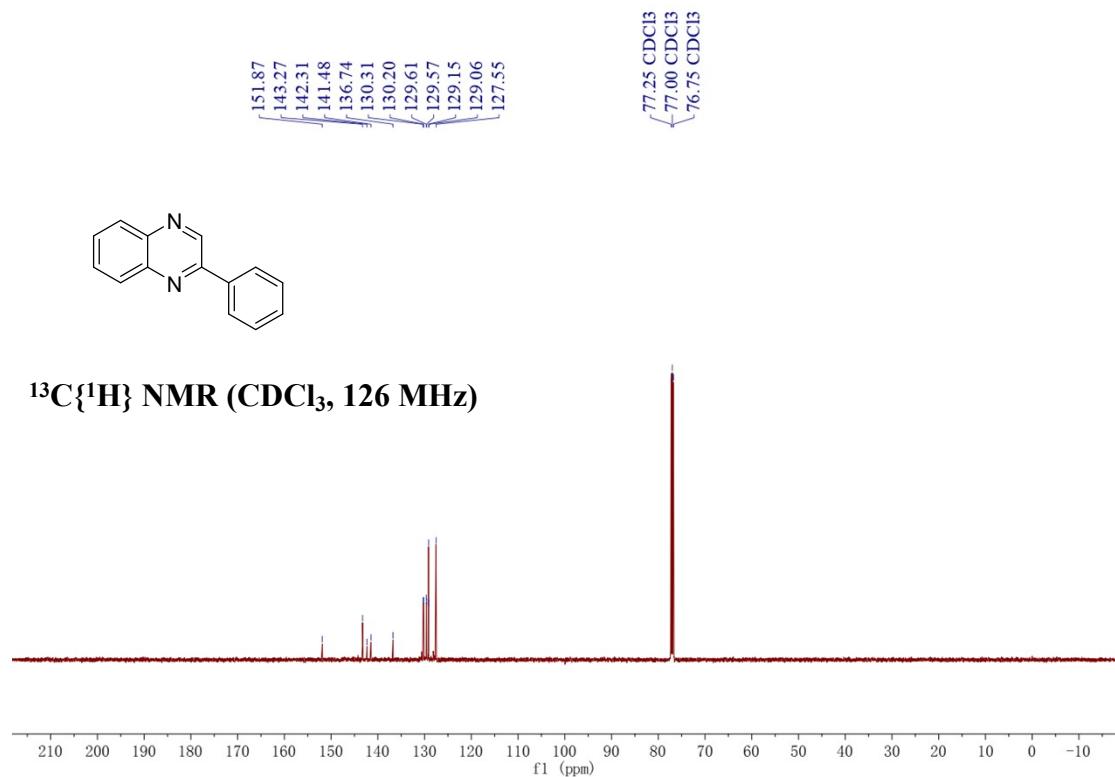
### **<sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of Compound c20**



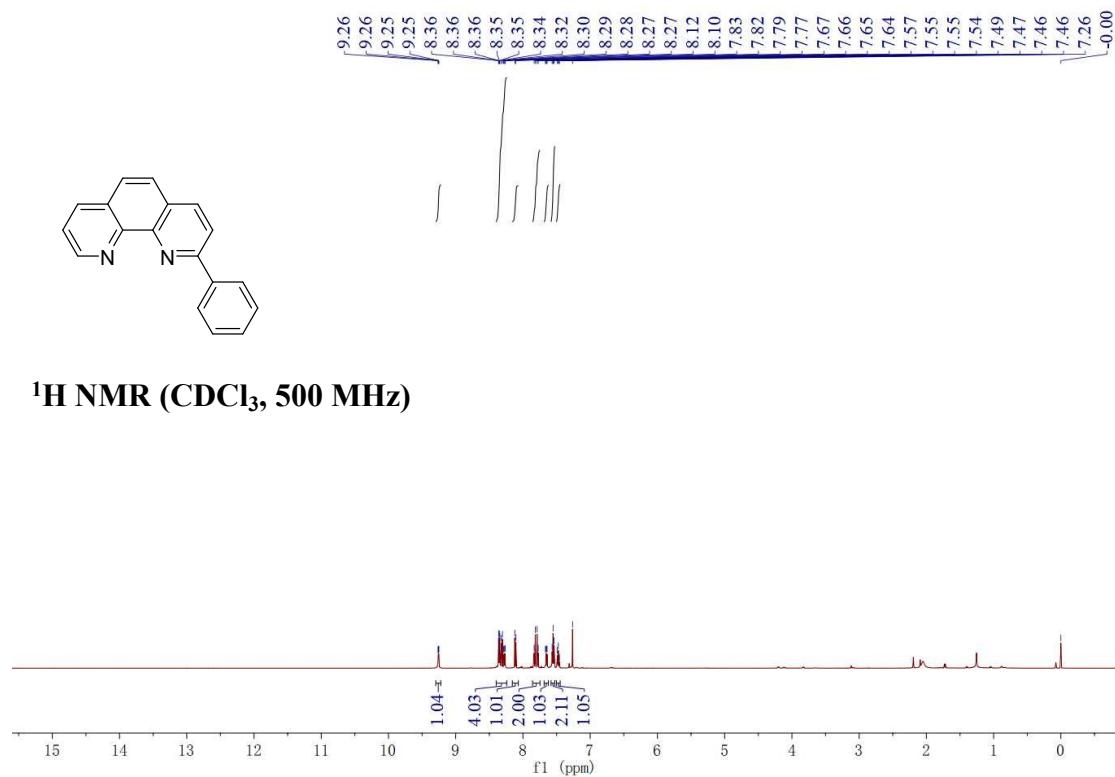
### **<sup>1</sup>H NMR Spectrum of Compound c21**



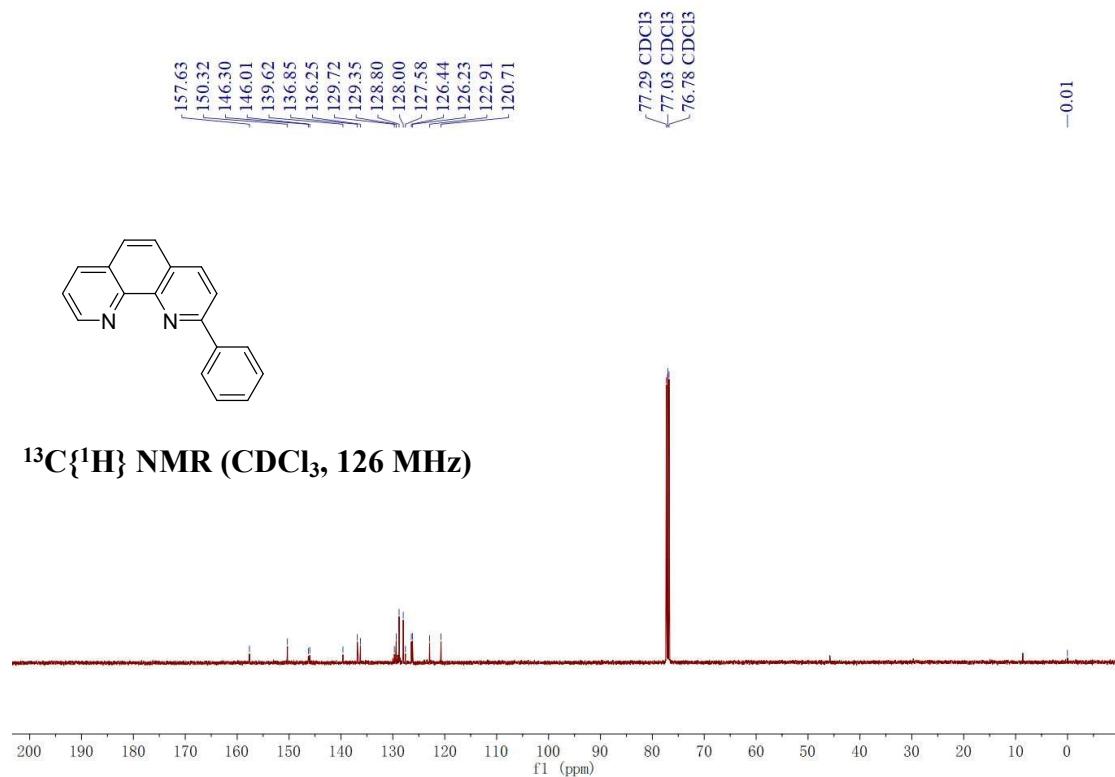
### **<sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of Compound c21**



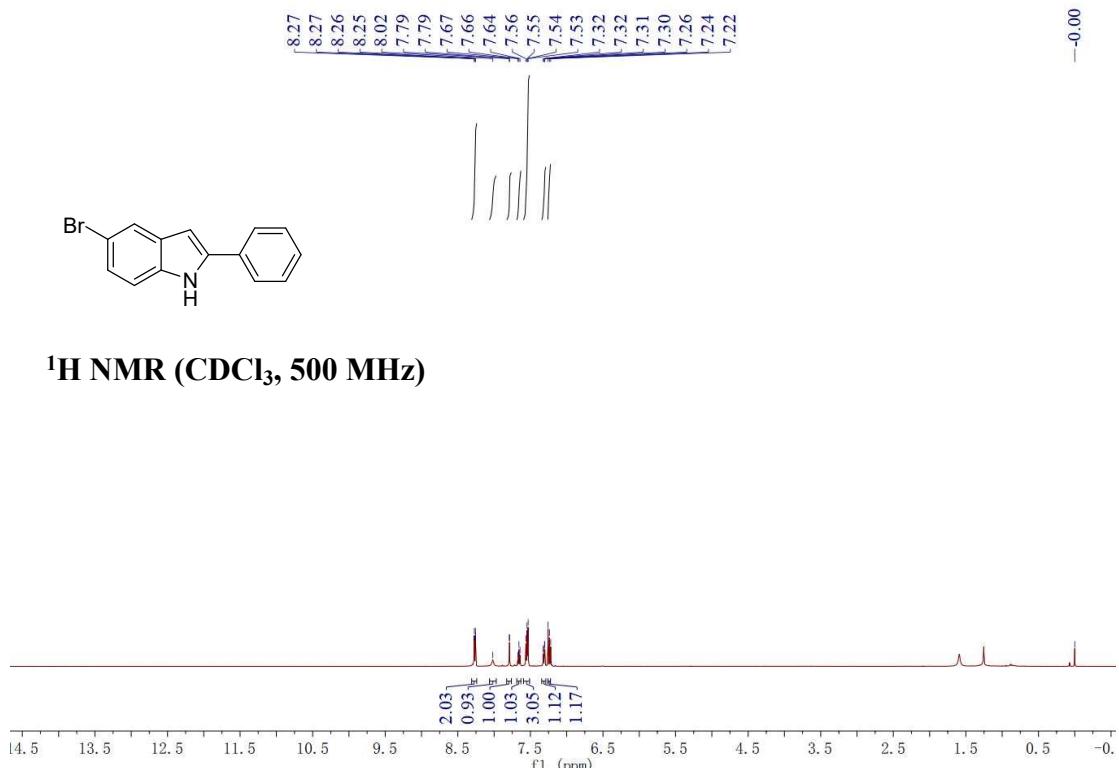
### **<sup>1</sup>H NMR Spectrum of Compound c22**



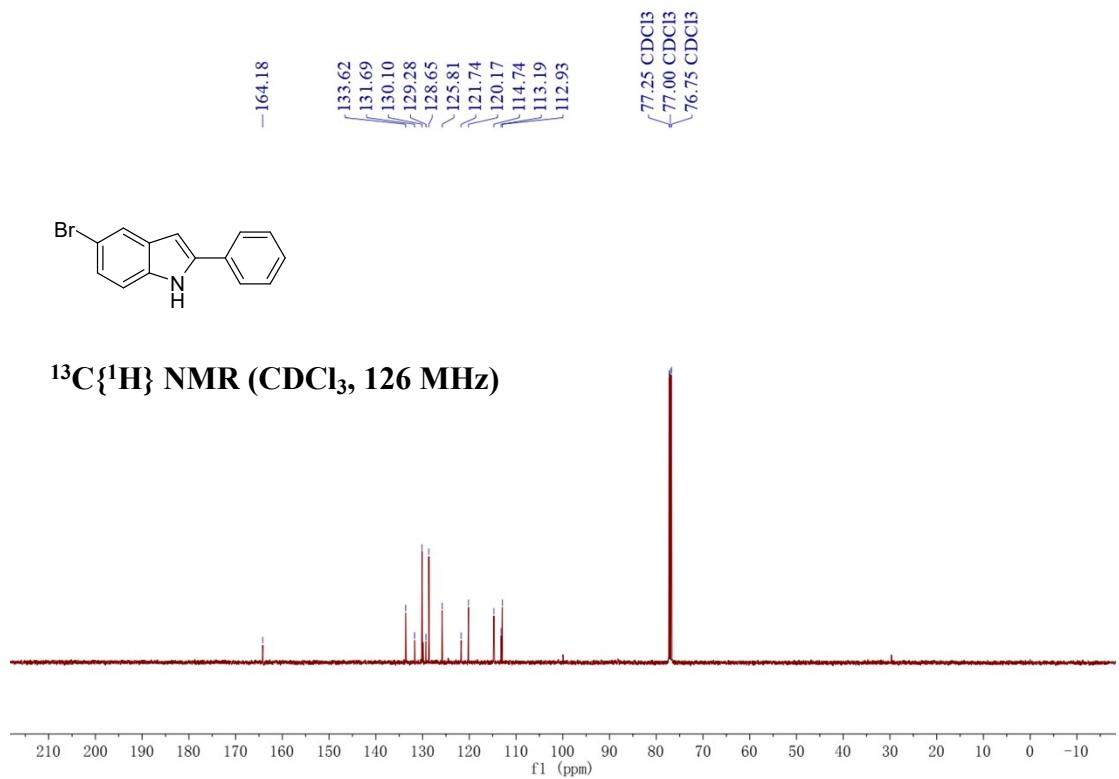
### **<sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of Compound c22**



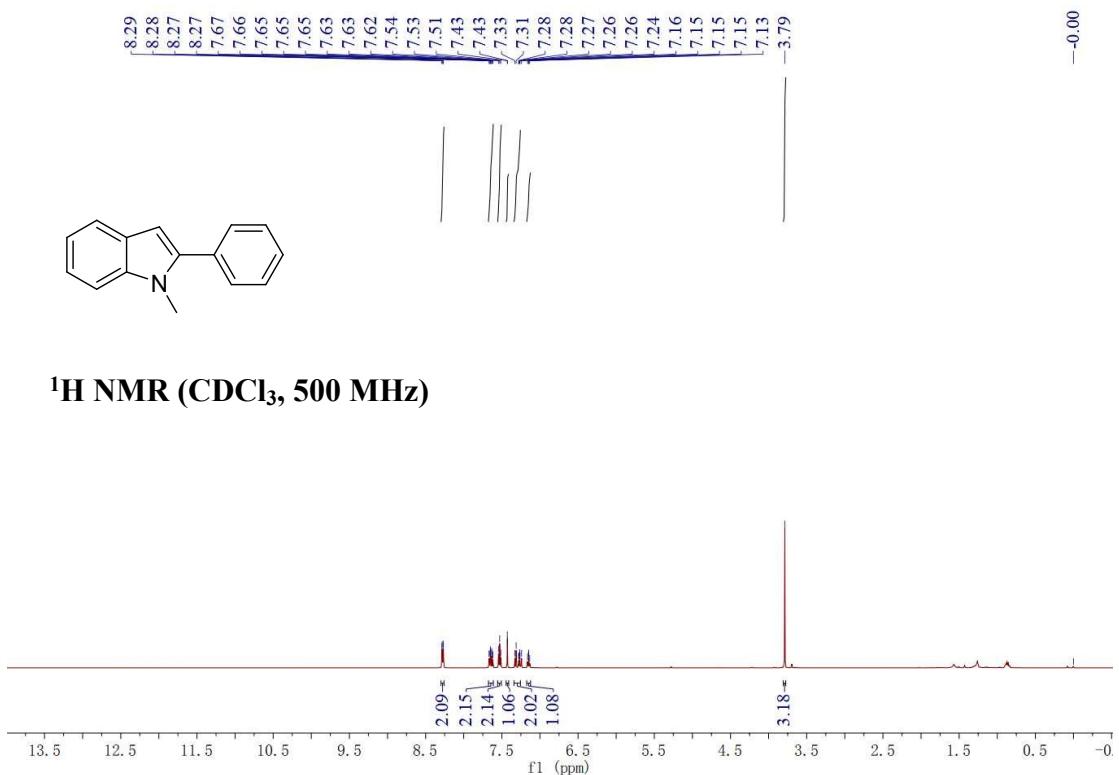
### <sup>1</sup>H NMR Spectrum of Compound c23



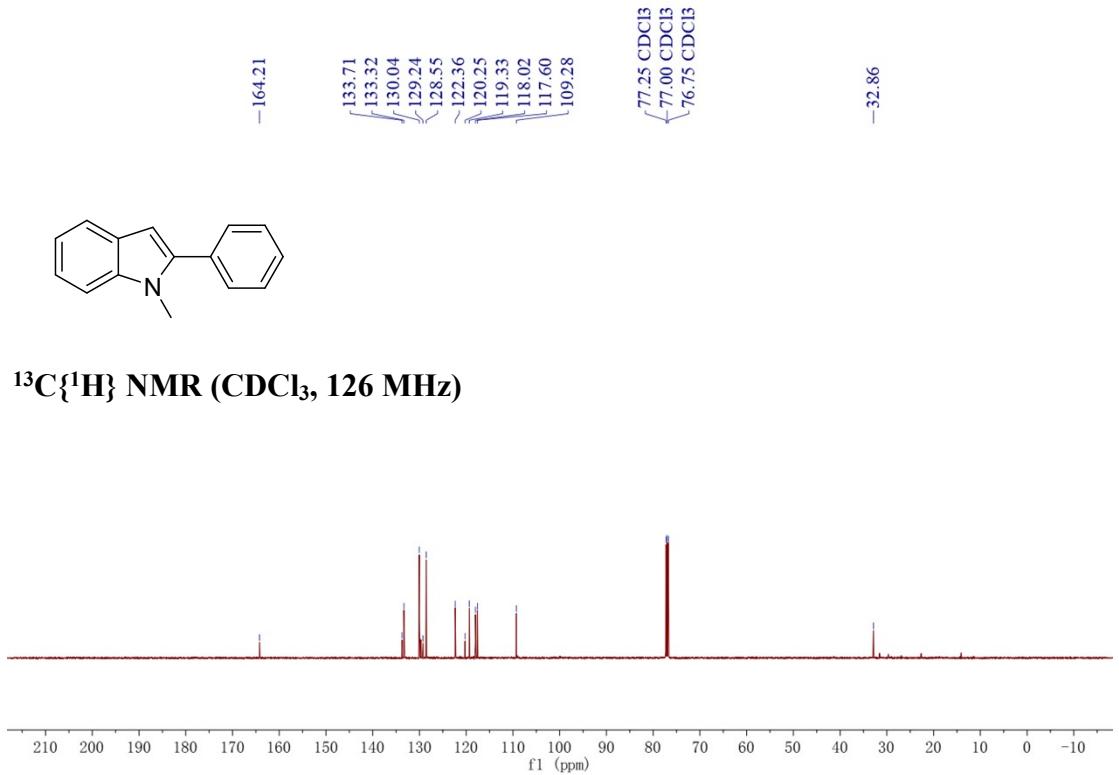
### <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of Compound c23



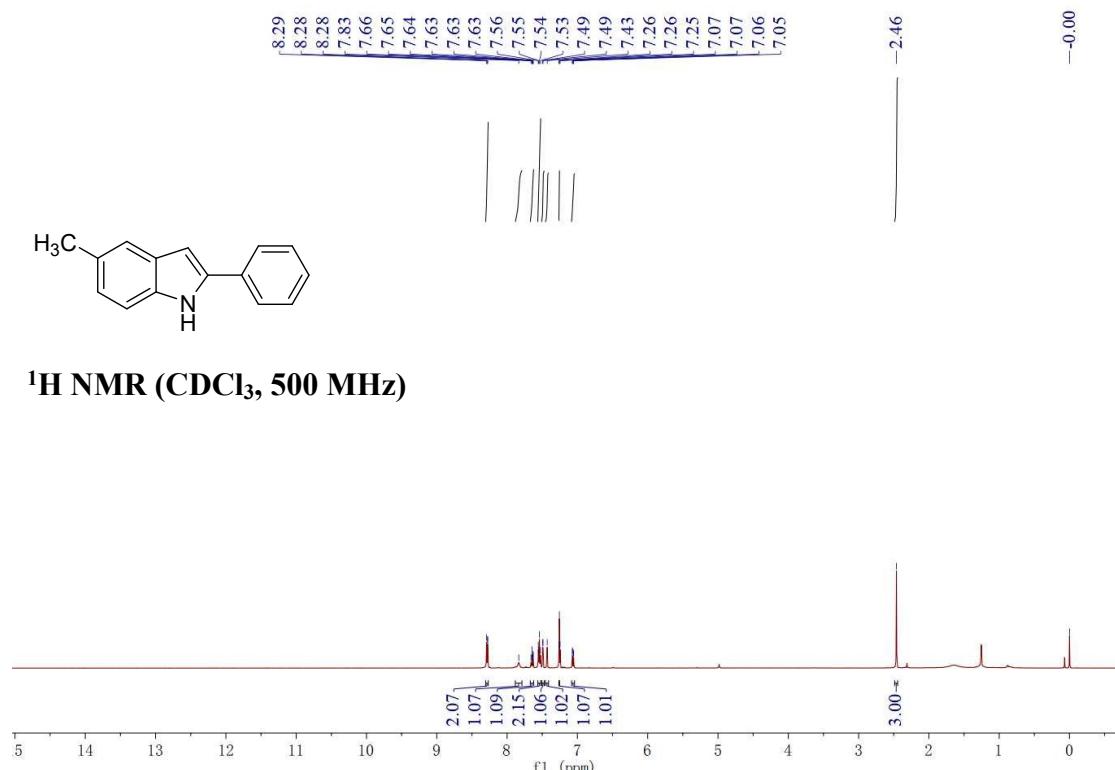
**$^1\text{H}$  NMR Spectrum of Compound c24**



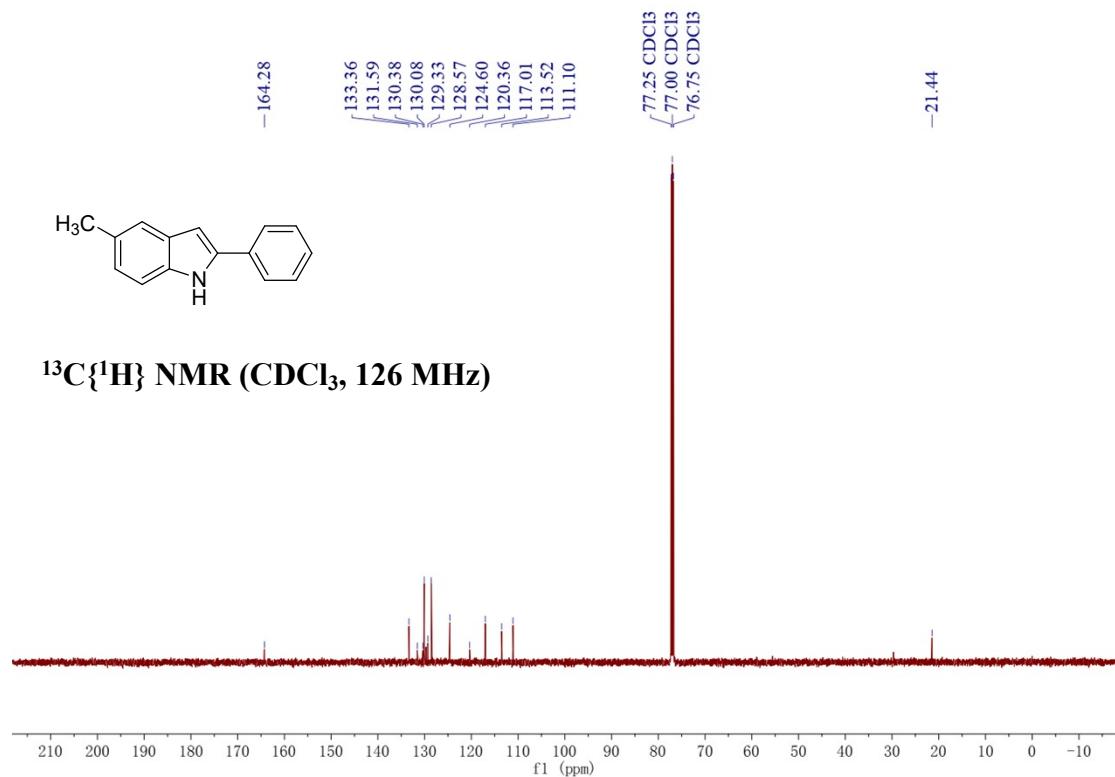
**$^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of Compound c24**



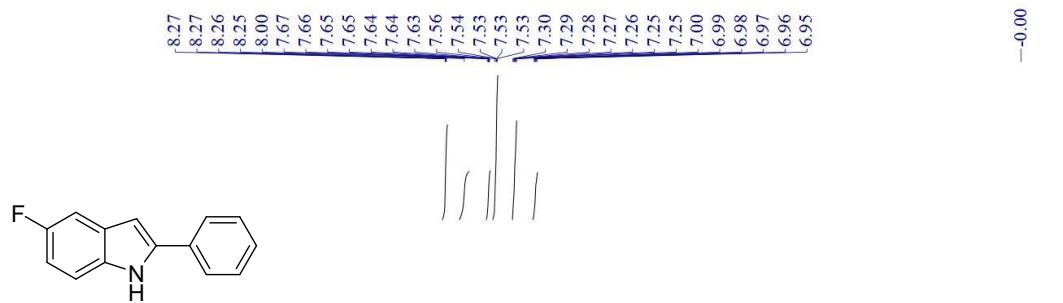
### <sup>1</sup>H NMR Spectrum of Compound c25



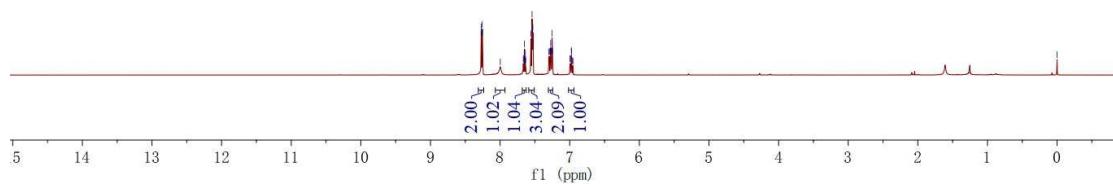
### <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of Compound c25



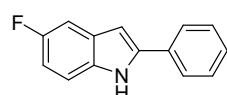
## **<sup>1</sup>H NMR Spectrum of Compound c26**



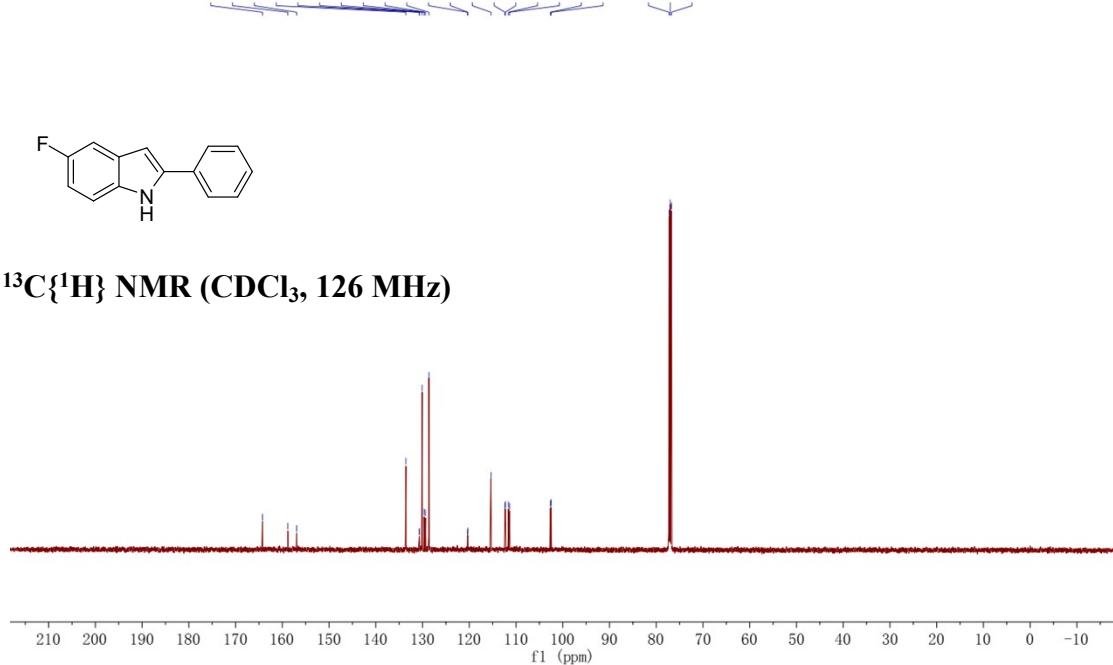
**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)**



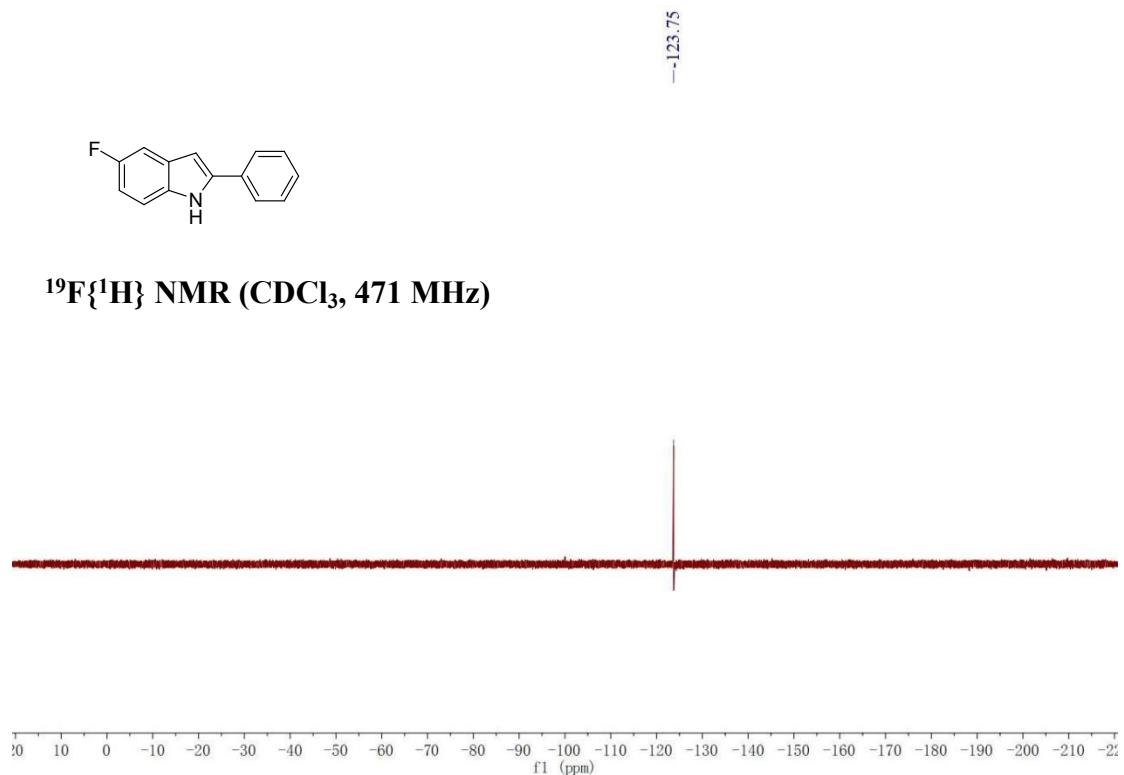
## **<sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of Compound c26**



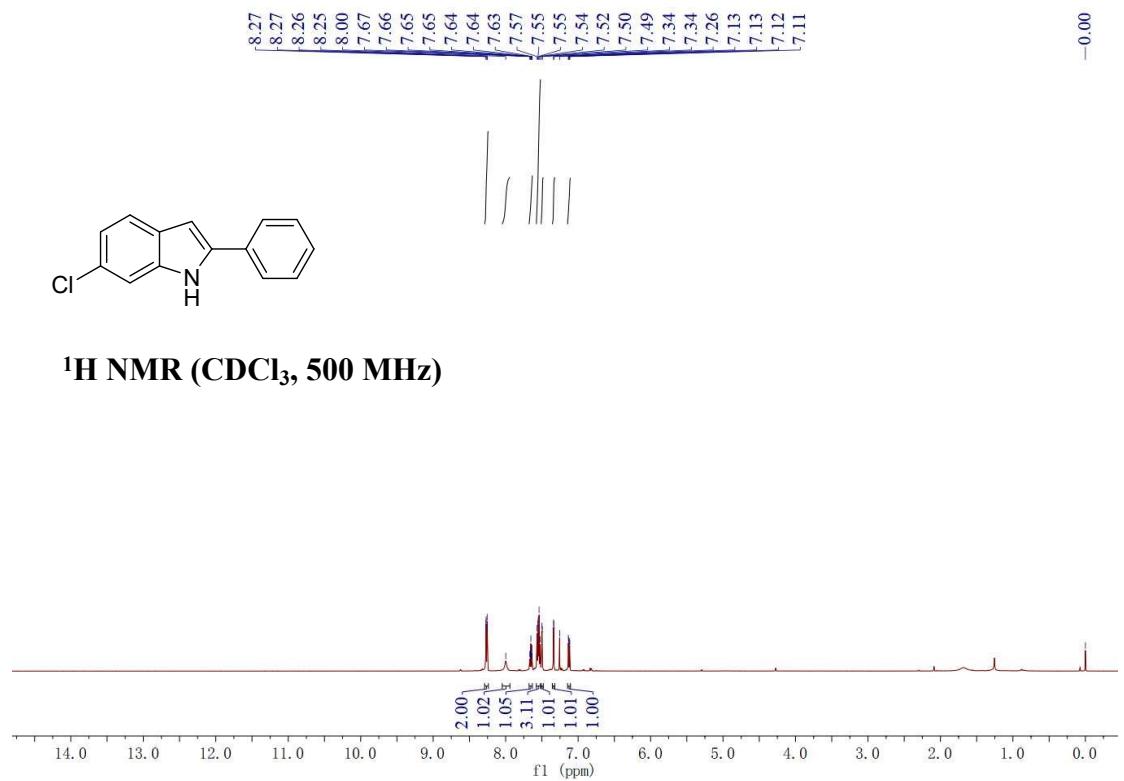
<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 126 MHz)



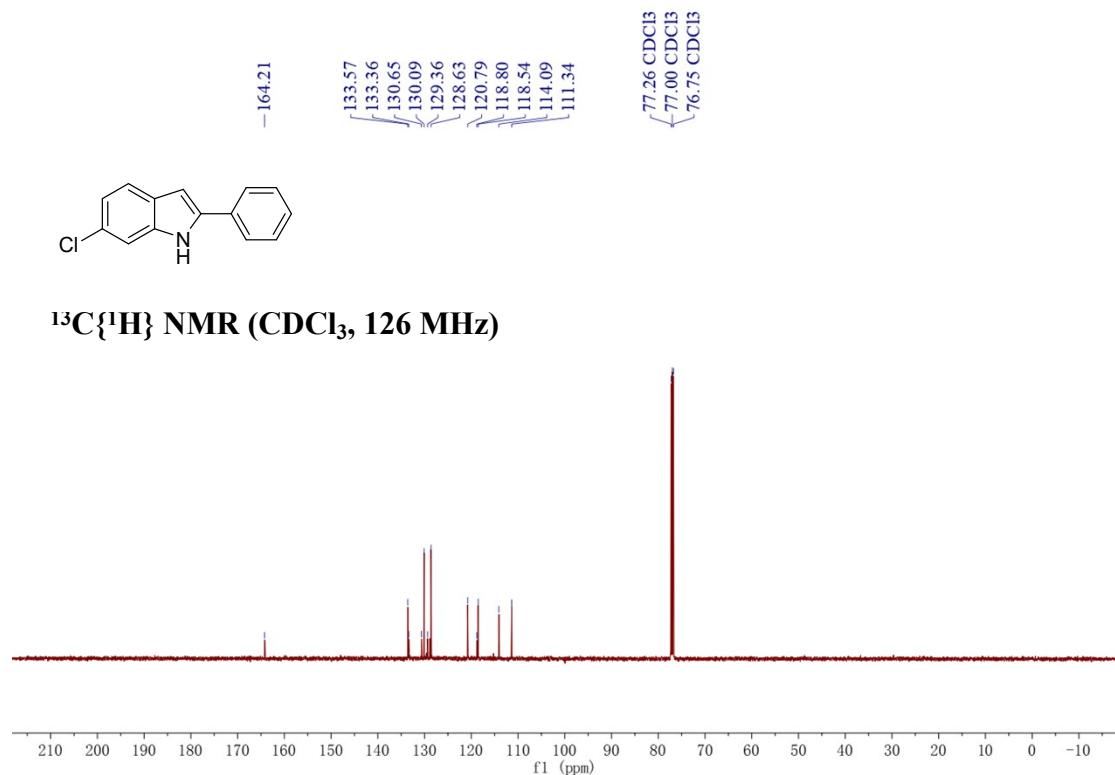
### $^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum of Compound c26



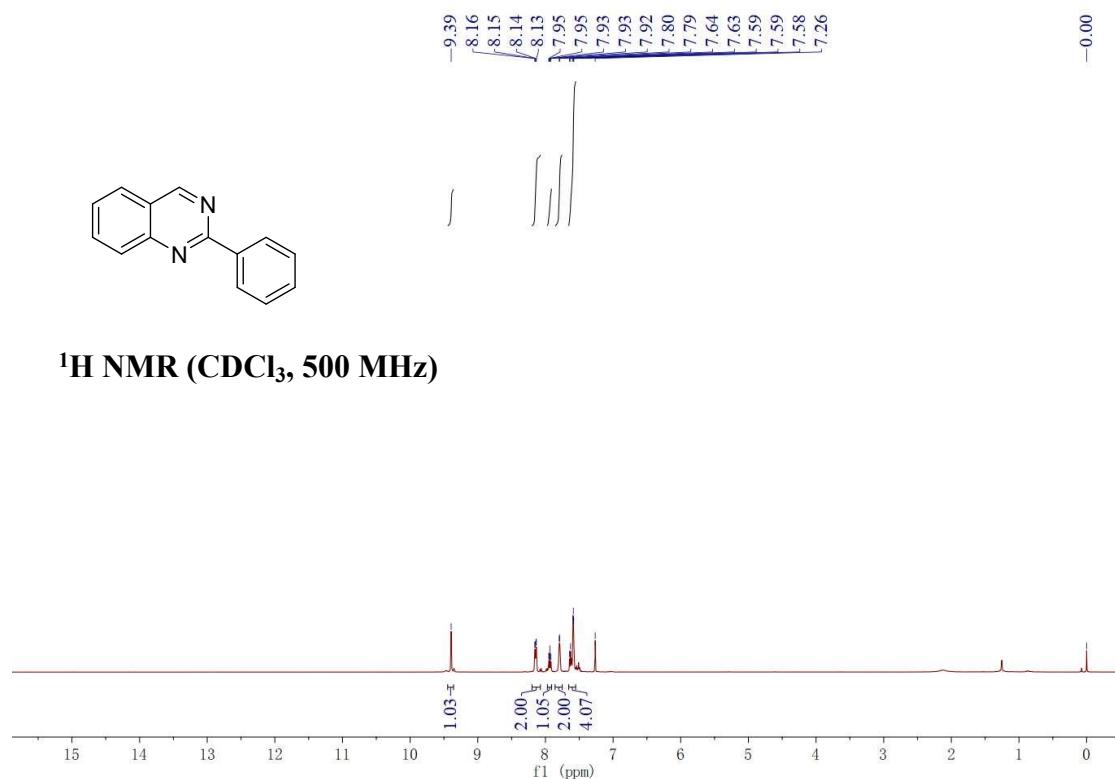
### $^1\text{H}$ NMR Spectrum of Compound c27



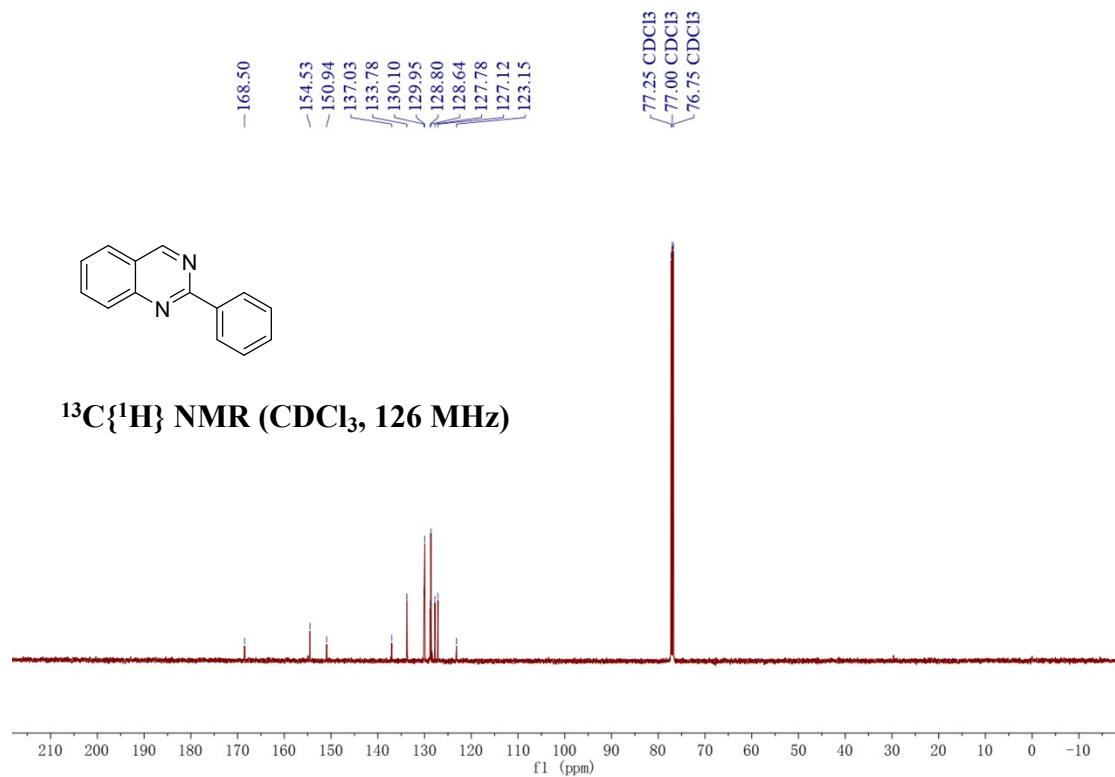
**$^{13}\text{C}\{\text{H}\}$  NMR Spectrum of Compound c27**



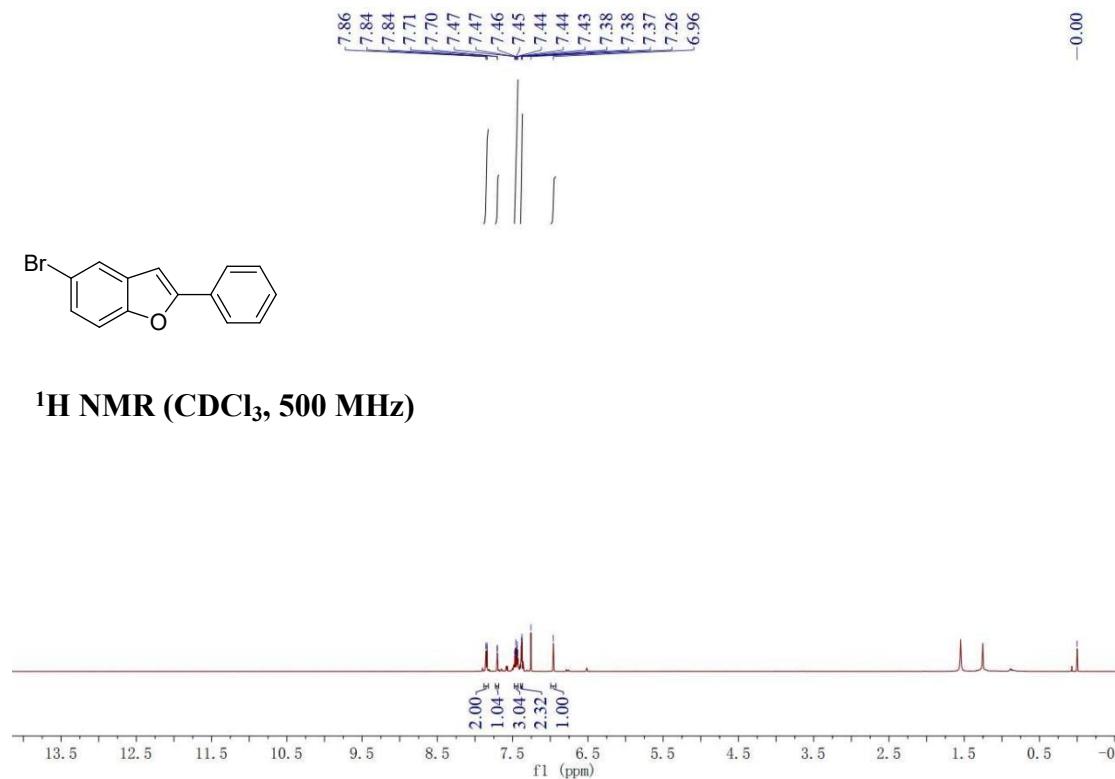
**$^1\text{H}$  NMR Spectrum of Compound c28**



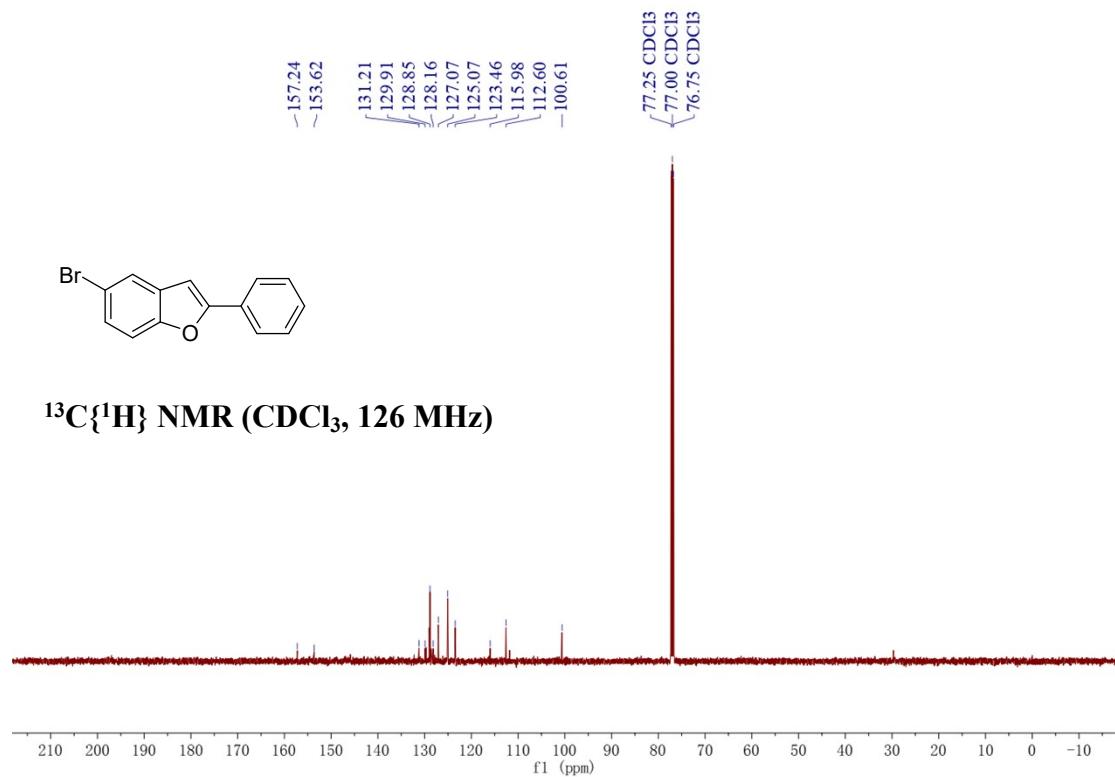
**$^{13}\text{C}\{\text{H}\}$  NMR Spectrum of Compound c28**



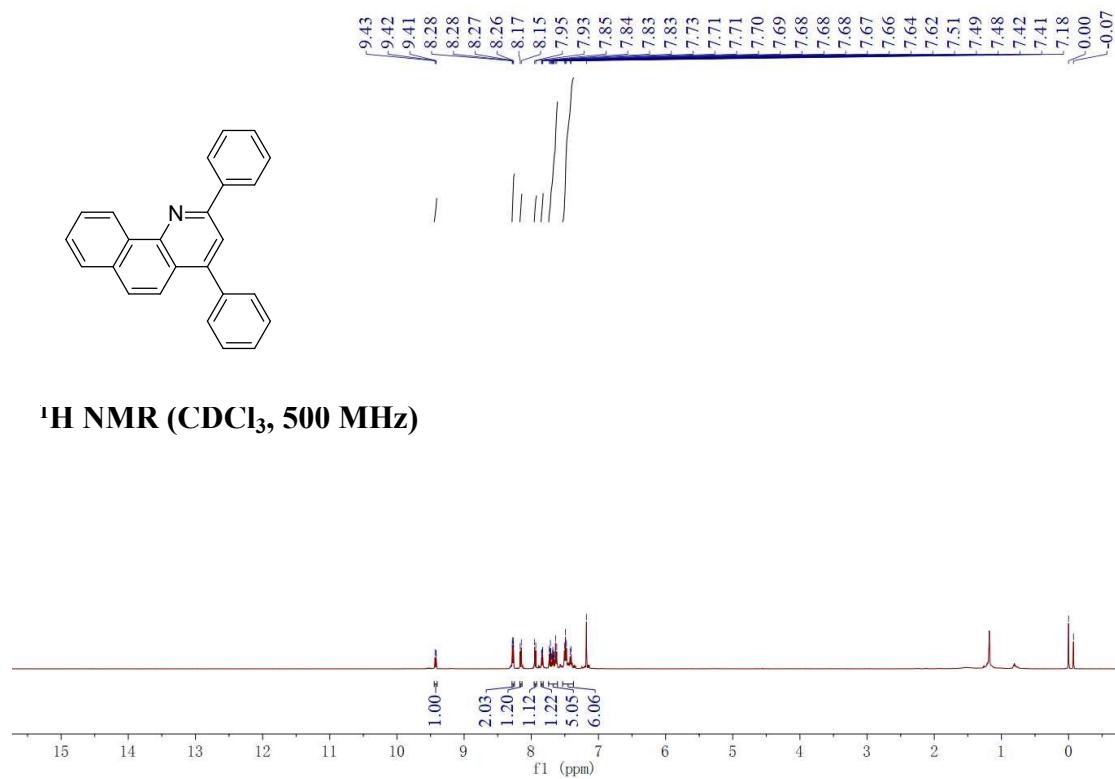
**$^1\text{H}$  NMR Spectrum of Compound c29**



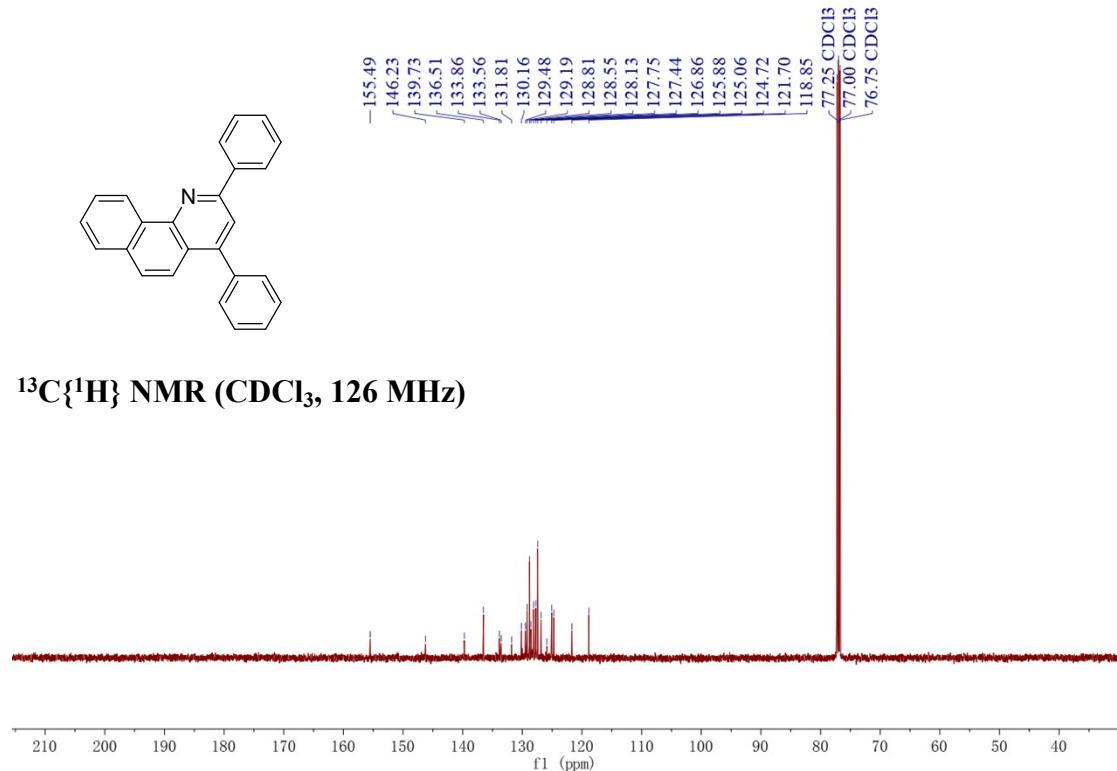
**$^{13}\text{C}\{\text{H}\}$  NMR Spectrum of Compound c29**



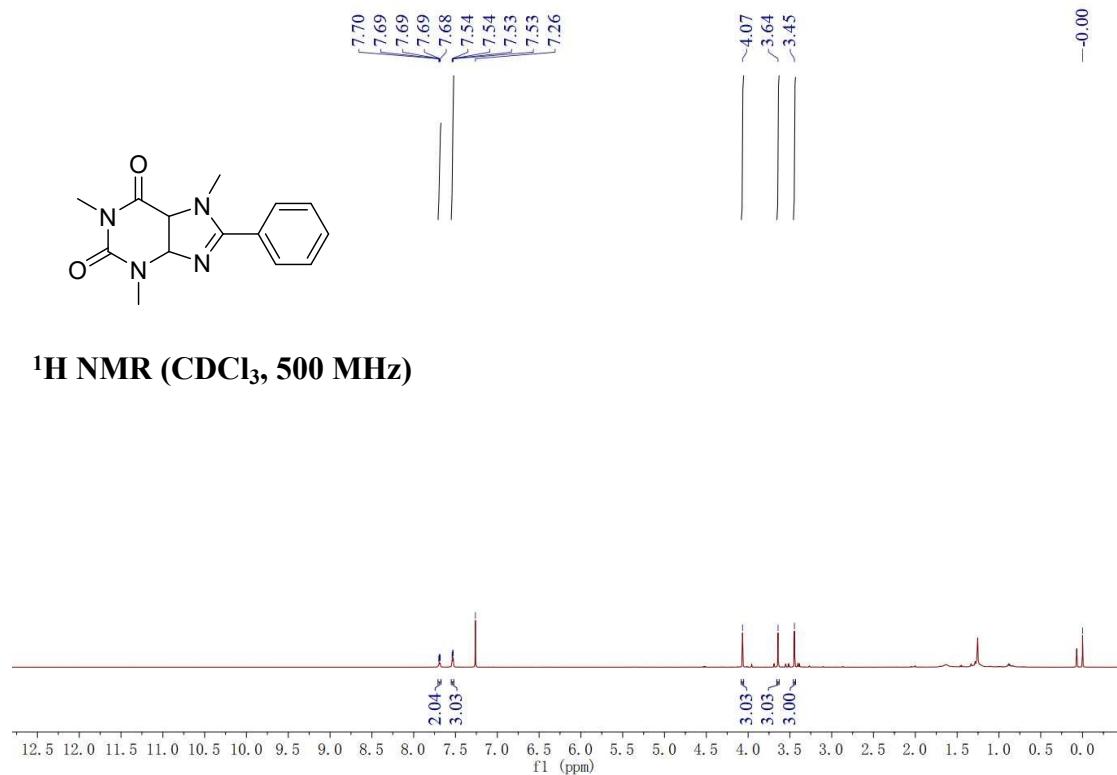
**$^1\text{H}$  NMR Spectrum of Compound c30**



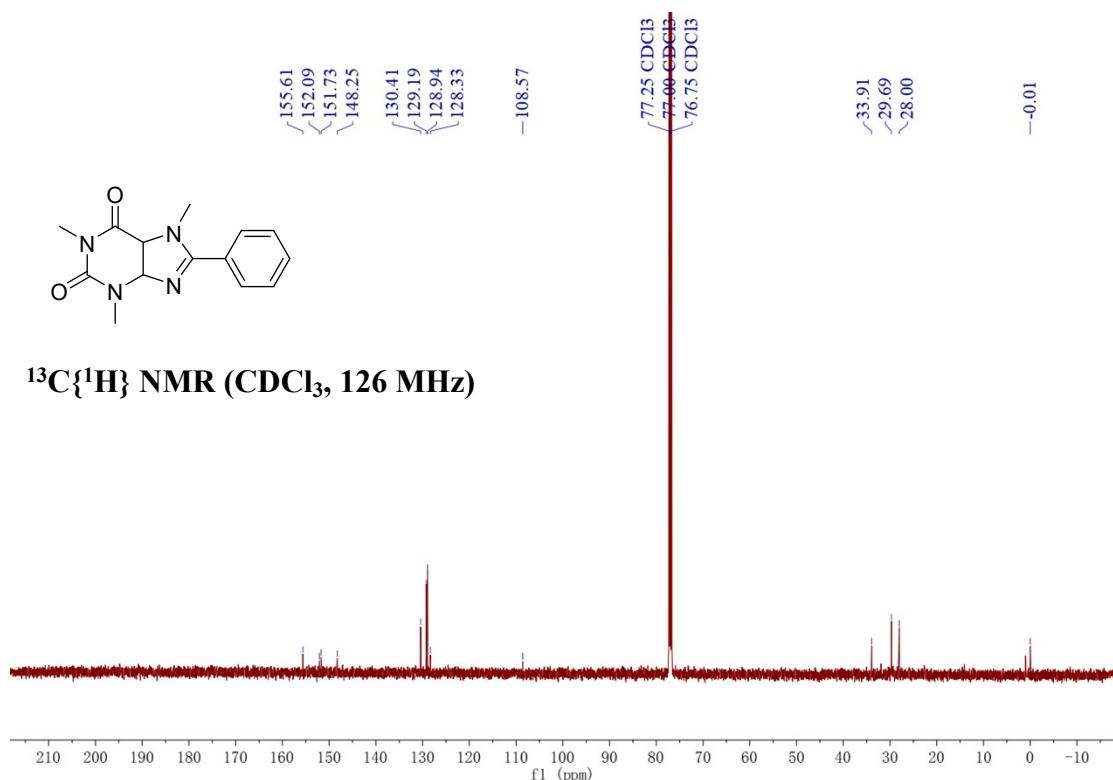
**$^{13}\text{C}\{\text{H}\}$  NMR Spectrum of Compound c30**



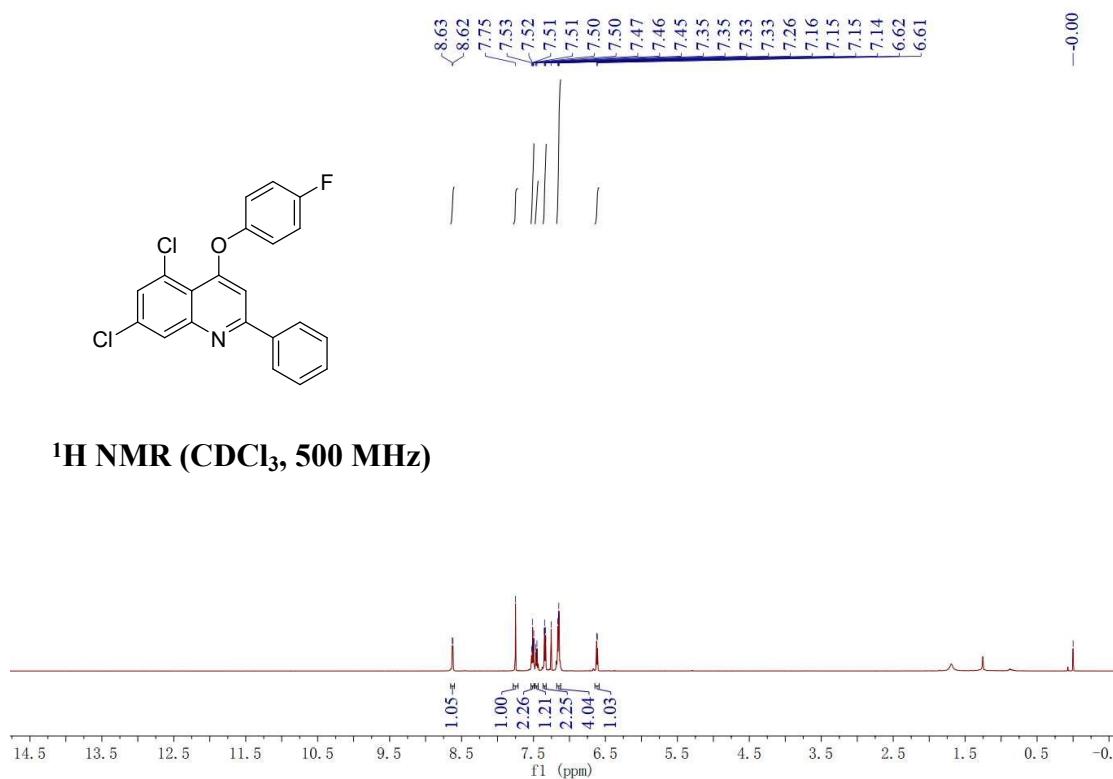
**$^1\text{H}$  NMR Spectrum of Compound d1**



**$^{13}\text{C}\{\text{H}\}$  NMR Spectrum of Compound d1**



**$^1\text{H}$  NMR Spectrum of Compound d2**



### $^{13}\text{C}\{\text{H}\}$ NMR Spectrum of Compound d2

