

## Supporting Information

### Access to 2-thio/selenoquinolines via domino reaction of isocyanides with sulfur and selenium in water

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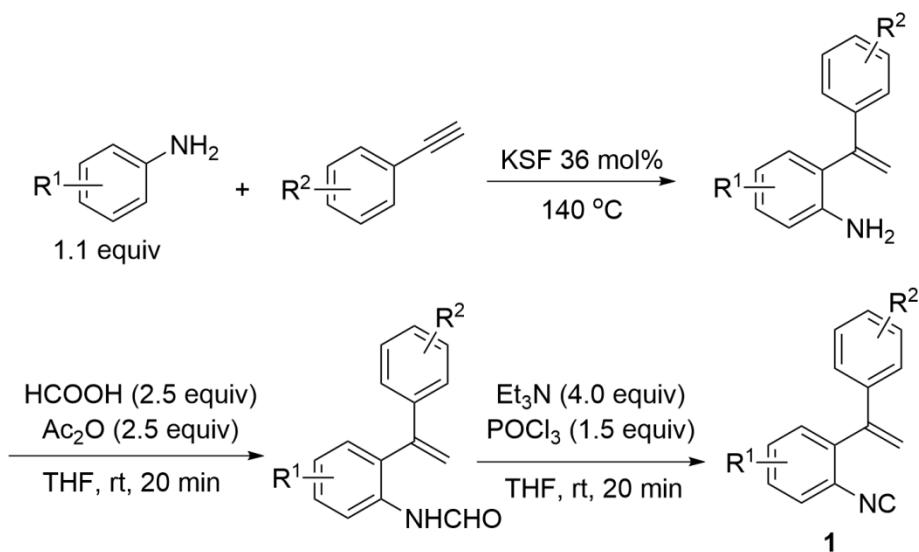
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## I. General information

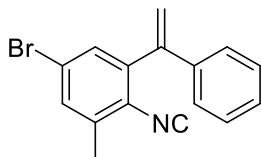
All reagents were commercially available and used without further purification, unless otherwise indicated. Chromatography was carried out on flash silica gel (300–400 mesh). All reactions were monitored by TLC, performed on glass plates with precoated silica gel 60 (F254).  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{19}\text{F}$  NMR spectra were measured on a 400 MHz Bruker instrument, with TMS as the internal standard. All chemical shifts are reported in ppm scale. High-resolution mass spectra (HRMS) were acquired using a Bruker microTOF II focusing spectrometer (ESI).

## II. Preparation and analytical data of isocyanide **1**

*o*-Vinylphenyl isocyanides **1** was prepared according to previous literature report<sup>[1-2]</sup>.



### Analytical data of **1** (**1j**, **1k**, **1n**, **1o**, **1t**)

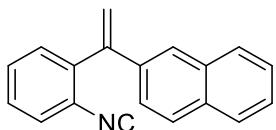


**5-bromo-2-isocyano-1-methyl-3-(1-phenylvinyl)benzene (1j).** Eluent: PE/EA (30:1), yellow oil, 504 mg, 85% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 (d,  $J = 2.0$  Hz, 1H), 7.36 - 7.31 (m, 4H), 7.27 - 7.24 (m, 2H), 5.87 (s, 1H), 5.38 (s, 1H), 2.42 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.9, 141.0, 138.8, 137.5, 132.5, 131.1, 128.5,

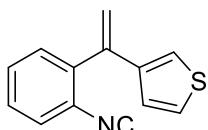
128.3, 126.7, 122.7, 118.0, 18.9. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>13</sub>BrN<sup>+</sup> 298.0226; found 298.0229.



**1-isocyano-2-(1-(m-tolyl)vinyl)benzene (1k).** Eluent: PE/EA (30:1), colorless oil, 329 mg, 76% yield. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.41 - 7.37 (m, 2H), 7.36 - 7.32 (m, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.08 (s, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 5.85 (d, *J* = 1.2 Hz, 1H), 5.37 (d, *J* = 0.8 Hz, 1H), 2.32 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 166.6, 145.5, 139.3, 139.3, 137.9, 130.8, 129.1, 128.9, 128.3, 128.2, 127.4, 127.3, 125.3, 124.0, 117.4, 21.4. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>14</sub>N<sup>+</sup> 220.1121; found 220.1126.

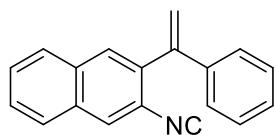


**2-(1-(2-isocyanophenyl)vinyl)naphthalene (1n).** Eluent: PE/EA (30:1), yellow oil, 382 mg, 75% yield. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.84 - 7.82 (m, 2H), 7.75 - 7.72 (m, 1H), 7.56 - 7.53 (m, 2H), 7.48 - 7.39 (m, 6H), 6.03 (s, 1H), 5.51 (s, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 145.4, 139.3, 136.7, 133.2, 133.1, 130.9, 129.3, 128.5, 128.3, 128.2, 127.6, 127.4, 126.3, 126.2, 126.1, 124.5, 118.1. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>14</sub>N<sup>+</sup> 256.1121; found 256.1127.



**3-(1-(2-isocyanophenyl)vinyl)thiophene (3o).** Eluent: PE/EA (30:1), yellow oil, 253 mg, 60% yield. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.35 - 7.25 (m, 4H), 7.21 (q, *J*<sub>1</sub> = 4.8 Hz, *J*<sub>2</sub> = 2.8 Hz, 1H), 7.12 (q, *J*<sub>1</sub> = 4.8 Hz, *J*<sub>2</sub> = 1.2 Hz, 1H), 6.78 (q, *J*<sub>1</sub> = 2.8 Hz, *J*<sub>2</sub> = 1.2 Hz, 1H), 5.77 (s, 1H), 5.20 (s, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 166.5, 141.0, 140.0, 139.1, 130.3, 129.2, 128.4, 127.2, 126.0, 125.7, 122.8, 116.0. **HRMS (ESI)** m/z:

$[M+H]^+$  calcd for  $C_{13}H_{10}NS^+$  212.0528; found 212.0523.



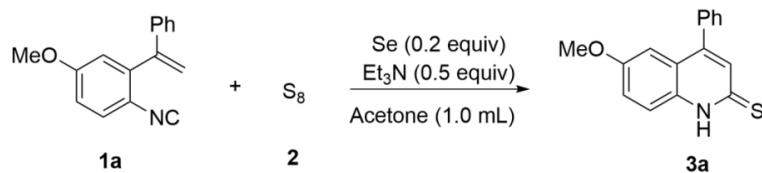
**2-isocyano-3-(1-phenylvinyl)naphthalene (3t).** Eluent: PE/EA (30:1), yellow oil, 398 mg, 78% yield.  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.92 - 7.85 (m, 3H), 7.57 - 7.45 (m, 3H), 7.30 - 7.24 (m, 5H), 6.28 (d,  $J = 2.4$  Hz, 1H), 5.42 (d,  $J = 2.4$  Hz, 1H).  **$^{13}C$  NMR** (100 MHz,  $CDCl_3$ )  $\delta$  166.4, 142.7, 138.7, 137.4, 133.0, 132.0, 129.0, 128.6, 128.2, 128.1, 127.6, 127.5, 126.9, 126.2, 123.5, 118.4. **HRMS (ESI)** m/z:  $[M+H]^+$  calcd for  $C_{19}H_{14}N^+$  256.1121; found 256.1112.

## References

- 1、Y. Liu, S.-J. Li, X.-L. Chen, L.-L. Fan, X.-Y. Li, S.-S. Zhu, L.-B. Qu and B. Yu, *Adv. Synth. Catal.*, 2020, **362**, 688 - 694.
- 2、Jyotshna Phukona, Sanjib Gogoi, *Chem. Commun.*, 2020, **56**, 1133 - 1136.

### III. Optimization of reaction conditions

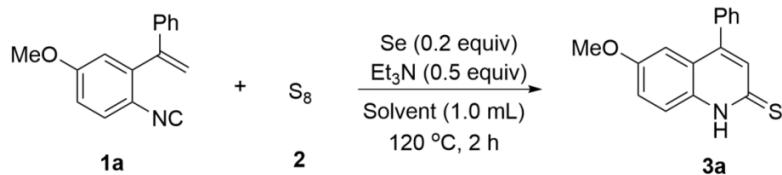
**Table 1.** Optimization of reaction temperature <sup>[a]</sup>.



Entry	1a : 2	Temp. (°C)	Time (h)	Yield (%) <sup>[b]</sup>
1	1 : 2	rt	24	Trace
2	1 : 2	40	24	Trace
3	1 : 2	60	14	40
4	1 : 2	80	9	57
5	1 : 2	100	6	76
6	1 : 2	120	2	85

a)Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), Se (0.2 equiv), Et<sub>3</sub>N (2.0 equiv) in acetone (1.0 mL), and the reaction was monitored by TLC. b) Determined by <sup>1</sup>H NMR using CH<sub>2</sub>Br<sub>2</sub> as internal standard.

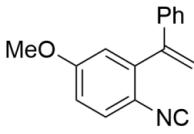
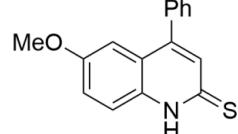
**Table 2.** Optimization of reaction solvent <sup>[a]</sup>.



Entry	1a : 2	Solvent (1.0 mL)	Yield (%) <sup>[b]</sup>
1	1 : 2	Acetone	85
2	1 : 2	MeCN	80
3	1 : 2	DMSO- <i>d</i> <sub>6</sub>	53
4	1 : 2	DMF	84
5	1 : 2	EtOH	94
6	1 : 2	THF	87
7	1 : 2	Toluene	21
8	1 : 2	DCM	73
9	1 : 2	EA	82
10	1 : 2	H <sub>2</sub> O	87

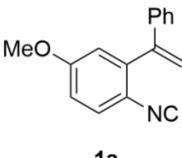
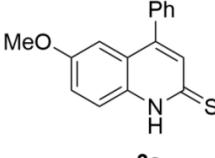
a)Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), Se (0.2 equiv), Et<sub>3</sub>N (2.0 equiv) in solvent (1.0 mL) at 120 °C for 2 hours. b) Determined by <sup>1</sup>H NMR using CH<sub>2</sub>Br<sub>2</sub> as internal standard.

**Table 3.** Optimization of base usage <sup>[a]</sup>.

	+		Se (0.2 equiv) Et <sub>3</sub> N (x equiv) H <sub>2</sub> O (1.0 mL) 120 °C, 2 h	
Entry	<b>1a : 2</b>	Base (x equiv)	Yield (%) <sup>[b]</sup>	
1	1 : 2	Et <sub>3</sub> N (2.0 equiv)	87	
2	1 : 2	Et <sub>3</sub> N (1.0 equiv)	92	
3	1 : 2	Et <sub>3</sub> N (0.5 equiv)	94	
4	1 : 2	Et <sub>3</sub> N (0.2 equiv)	79	
5	1 : 2	Et <sub>3</sub> N (0 equiv)	75	

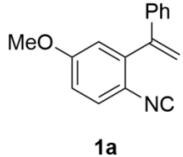
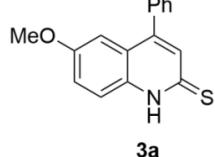
a)Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), Se (0.2 equiv), Et<sub>3</sub>N (x equiv) in water (1.0 mL) at 120 °C for 2 hours. b) Determined by <sup>1</sup>H NMR using CH<sub>2</sub>Br<sub>2</sub> as internal standard.

**Table 4.** Optimization of catalyst Se powder <sup>[a]</sup>.

	+		Se (x equiv) Et <sub>3</sub> N (0.5 equiv) H <sub>2</sub> O (1.0 mL) 120 °C, 2 h	
Entry	<b>1a : 2</b>	Se (x equiv)	Yield (%) <sup>[b]</sup>	
1	1 : 2	0.2	94	
2	1 : 2	0.1	92	
3	1 : 2	0.05	77	
4	1 : 2	0	76	
5 <sup>[c]</sup>	1 : 2	0	24	

a)Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), Se (x equiv), Et<sub>3</sub>N (0.5 equiv) in water (1.0 mL) at 120 °C for 2 hours. b) Determined by <sup>1</sup>H NMR using CH<sub>2</sub>Br<sub>2</sub> as internal standard. c) Without Et<sub>3</sub>N.

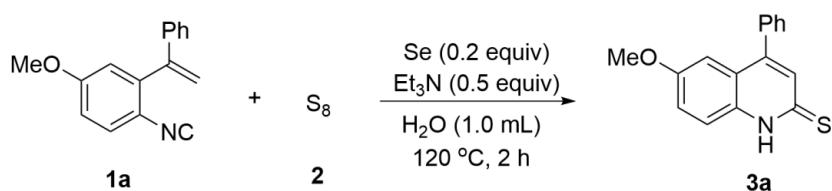
**Table 5.** Optimization of Base <sup>[a]</sup>.

	+		Se (0.2 equiv) Base (0.5 equiv) H <sub>2</sub> O (1.0 mL) 120 °C, 2 h	
Entry	<b>1a : 2</b>	Base (0.5 equiv)	Yield (%) <sup>[b]</sup>	
1	1 : 2	Et <sub>3</sub> N	94	
2	1 : 2	DIPEA	94	

3	1 : 2	$\text{K}_2\text{CO}_3$	87
4	1 : 2	DBU	92
5	1 : 2	$\text{Cs}_2\text{CO}_3$	79
6	1 : 2	NaOH	86

a)Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), Se (0.2 equiv), base (0.5 equiv) in water (1.0 mL) at 120 °C for 2 hours. b) Determined by  $^1\text{H}$  NMR using  $\text{CH}_2\text{Br}_2$  as internal standard.

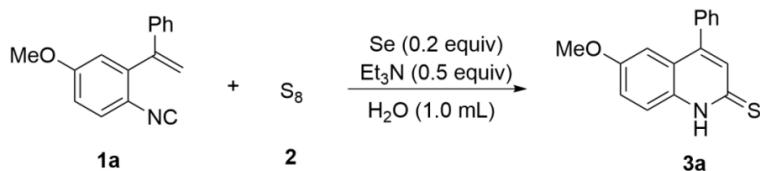
**Table 6.** Optimization of feeding ratio <sup>[a]</sup>.



Entry	<b>1a</b> : <b>2</b>	Yield <sup>[b]</sup>
1	1 : 2	94
2	1 : 1.5	94
3	1 : 1.2	86

a)Reaction conditions: **1a** (0.2 mmol), **2** (x mmol), Se (0.2 equiv),  $\text{Et}_3\text{N}$  (0.5 equiv) in water (1.0 mL) at 120 °C for 2 hours. b) Determined by  $^1\text{H}$  NMR using  $\text{CH}_2\text{Br}_2$  as internal standard.

**Table 7.** Optimization of reaction temperature <sup>[a]</sup>.

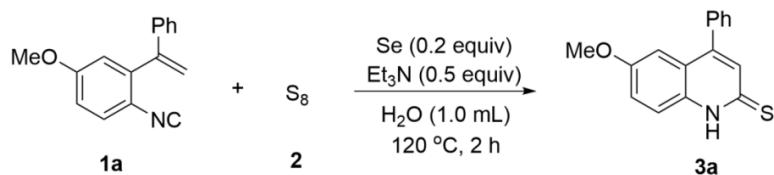


Entry	<b>1a</b> : <b>2</b>	Temp. (°C)	Yield (%) <sup>[b]</sup>
1	1 : 1.5	100	81
2	1 : 1.5	120	94(95) <sup>[c]</sup>
3	1 : 1.5	140	90

a)Reaction conditions: **1a** (0.2 mmol), **2** (0.3 mmol), Se (0.2 equiv),  $\text{Et}_3\text{N}$  (0.5 equiv) in water (1.0 mL). b) Determined by  $^1\text{H}$  NMR using  $\text{CH}_2\text{Br}_2$  as internal standard. c) Isolated yield.

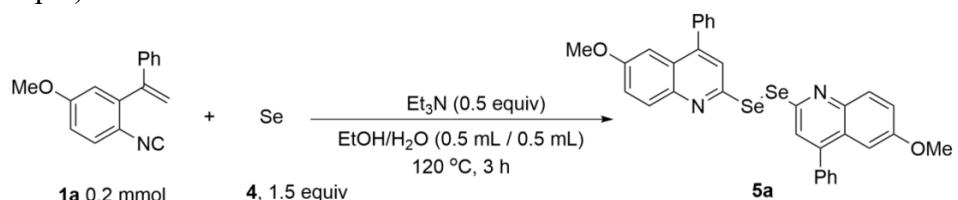
#### IV. Preparation and analytical data of quinoline 3, 5, 6, 7.

**Typical procedure for the synthesis of quinoline-2 (1H) - thione 3 (with **3a** as an example)**



A mixture of 1-isocyano-4-methoxy-2-(1-phenylvinyl)benzene **1a** (0.2 mmol, 47 mg), **2** (1.5 equiv, 0.3 mmol, 9.6 mg), Se (0.2 equiv, 3.1 mg), Et<sub>3</sub>N (0.5 equiv, 10.2 mg) and pure water (1 mL) in a sealed was heated at 120 °C. The reaction was monitored by TCL, and after 2 hours substrate **1a** was consumed. Then, the reaction mixture was cooled to room temperature and extracted with ethyl acetate (3 × 10 mL). The organic layers were combined, dried over anhydrous Mg<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether / ethyl acetate = 5 : 1) to give 6-methoxy-4-phenylquinoline-2(1H)-thione **3a** (50.7 mg, 95 %).

**Typical procedure for the synthesis of 1,2-di(quinolin-2-yl)diselane 5 (with **5a** as an example)**



A mixture of 1-isocyano-4-methoxy-2-(1-phenylvinyl)benzene **1a** (0.2 mmol, 47 mg), **4** (1.5 equiv, 0.3 mmol, 24.0 mg), Et<sub>3</sub>N (0.5 equiv, 10.2 mg), pure water (0.5 mL) and ethanol (0.5 mL) in a sealed tube was heated at 120 °C. The reaction was monitored by TCL, and the substrate was consumed after 3 hours. Then, the reaction mixture was cooled to room temperature and extracted by ethyl acetate (3 × 10 mL). The organic layers were combined, dried over anhydrous Mg<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether / ethyl acetate = 20 : 1) to give

1,2-bis(6-methoxy-4-phenylquinolin-2-yl)diselane **5a** (56.4 mg, 90 %).

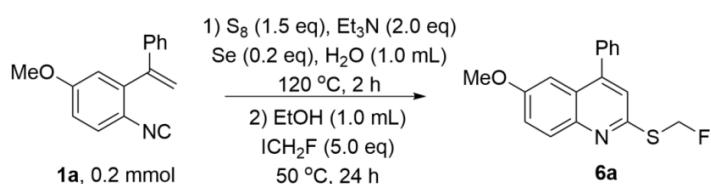
**Typical procedure for the synthesis of 2-((fluoromethyl)thio)quinolone **6**.**

**Table 8.** Optimization of reaction conditions

Entry	<b>1a</b> , 0.2 mmol			<b>6a</b>	
	Et <sub>3</sub> N	ICH <sub>2</sub> F	Sol.	Temp. (°C)	Yield (%) <sup>[d]</sup>
1 <sup>[a]</sup>	0.5 eq	2.0 eq	H <sub>2</sub> O (1.0 mL)	120 °C	9
2 <sup>[b]</sup>	0.5 eq	2.0 eq	H <sub>2</sub> O (1.0 mL)	120 °C to 50 °C	Trace
3 <sup>[b][c]</sup>	2.0 eq	5.0 eq	H <sub>2</sub> O/EtOH (1.0 mL+1.0 mL)	120 °C to 50 °C	83%

a)Reaction conditions: **1a** (0.2 mmol), **2** (0.3 mmol), Se (0.2 equiv), Et<sub>3</sub>N (0.5 equiv), ICH<sub>2</sub>F (2.0 equiv) in water (1.0 mL) at 120 °C for 2 hours. b) Two steps in one pot: **1a** (0.2 mmol), **2** (0.3 mmol), Se (0.2 equiv), Et<sub>3</sub>N (x equiv) in water at 120 °C for 2 hours, cooled to room temperature, then added ICH<sub>2</sub>F(y eq) and continued to react. c) Step 2 1.0 mL EtOH was added. d) Isolated yield.

with **6a** as an example



A mixture of 1-isocyano-4-methoxy-2-(1-phenylvinyl)benzene **1a** (0.2 mmol, 47 mg), S<sub>8</sub> (1.5 equiv, 0.3 mmol, 9.6 mg), Se (0.2 equiv, 3.1 mg), Et<sub>3</sub>N (2.0 equiv, 41 mg) and water (1.0 mL) in a sealed tube was heated at 120 °C. The reaction was monitored by TCL, and the substrate was consumed after 2 hours. Then, the reaction mixture was cooled to room temperature, ICH<sub>2</sub>F (5.0 equiv) and ethanol (1.0 mL) were added, the reaction mixture was heated at 50 °C. After the reaction is completed (24 h), the mixture was cooled to room temperature and extracted with ethyl acetate (3 × 10 mL).

The organic layers were combined, dried over anhydrous  $Mg_2SO_4$  and concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether / ethyl acetate = 20 : 1) to give 2-((fluoromethyl)thio)-6-methoxy-4-phenylquinoline **6a** (49.3 mg, 83 %).

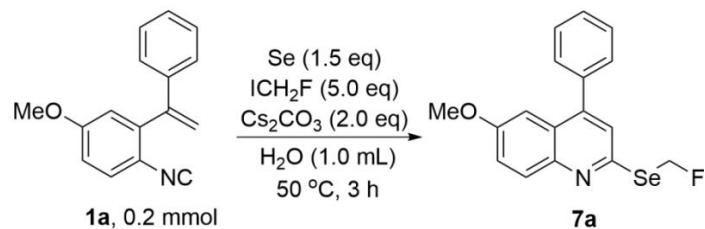
**Typical procedure for the synthesis of 2-((fluoromethyl)selanyl)quinoline **7**.**

**Table 9.** Optimization of reaction conditions<sup>[a]</sup>

Entry	Base	ICH <sub>2</sub> F	Sol.	Temp.(°C)	Yield <sup>[b]</sup>	1a, 0.2 mmol	7a
						1a, 0.2 mmol	7a
1	Et <sub>3</sub> N (1.5 eq)	1.5 eq	H <sub>2</sub> O (1.0 mL)	50	26%		
2	KOH (0.5 eq)	5.0 eq	H <sub>2</sub> O (1.0 mL)	50	52%		
3	KOH (1.0 eq)	5.0 eq	H <sub>2</sub> O (1.0 mL)	50	56%		
4	KOH (2.0 eq)	5.0 eq	H <sub>2</sub> O (1.0 mL)	50	58%		
5	KOH (2.0 eq)	5.0 eq	H <sub>2</sub> O (1.0 mL)	80	32%		
6	KOH (2.0 eq)	2.0 eq	H <sub>2</sub> O (1.0 mL)	50	50%		
7	Cs <sub>2</sub> CO <sub>3</sub> (2.0 eq)	5.0 eq	H <sub>2</sub> O (1.0 mL)	50	58%		

a)Reaction conditions: **1a** (0.2 mmol), **2** (0.3 mmol), Se (1.5 equiv), Base (x equiv), ICH<sub>2</sub>F (y equiv) reacted in solvent. b) Isolated yield.

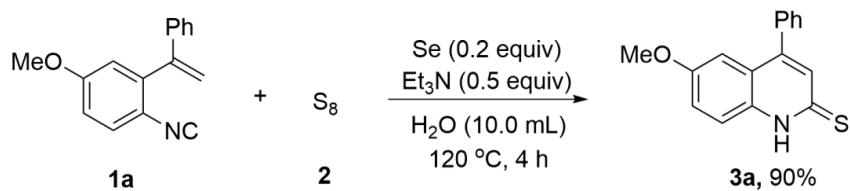
with **7a** as an example



A mixture of 1-isocyano-4-methoxy-2-(1-phenylvinyl)benzene **1a** (0.2 mmol, 47 mg), Se (1.5 equiv, 0.3 mmol, 23.7 mg), Cs<sub>2</sub>CO<sub>3</sub> (2.0 equiv, 131 mg), ICH<sub>2</sub>F (5.0 equiv, 160 mg) and pure water (1.0 mL) was heated at 120 °C. The reaction was

monitored by TLC, and the substrate was consumed after 3 hours. Then, the mixture was cooled to room temperature and extracted with ethyl acetate ( $3 \times 10$  mL). The organic layers were combined, dried over anhydrous  $\text{Mg}_2\text{SO}_4$  and concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether / ethyl acetate = 30 : 1) to give 2-((fluoromethyl)selanyl)-6-methoxy-4-phenylquinoline **7a** (40.0 mg, 58 %).

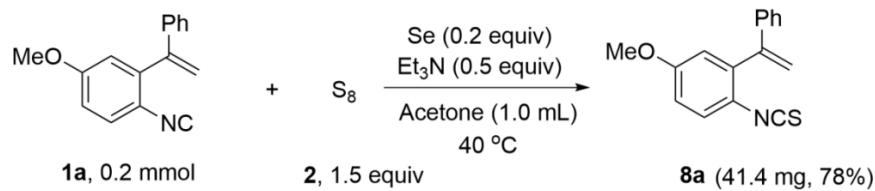
## V. Scale-up experiment



A mixture of 1-isocyano-4-methoxy-2-(1-phenylvinyl)benzene **1a** (7 mmol, 1.646 g), **2** (1.5 equiv, 10.5 mmol, 336 mg), Se (0.2 equiv, 110.6 mg),  $\text{Et}_3\text{N}$  (0.5 equiv, 357 mg) and water (10.0 mL) was heated at 120 °C. The reaction was monitored by TLC, the substrate was consumed after 4 hours. Then, the mixture was cooled to room temperature and extracted with DCM ( $3 \times 100$  mL). The organic layers were combined, dried over anhydrous  $\text{Mg}_2\text{SO}_4$  and concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether / ethyl acetate = 5 : 1) to give 6-methoxy-4-phenylquinoline-2(1H)-thione **3a** (1.6757 mg, 90 %).

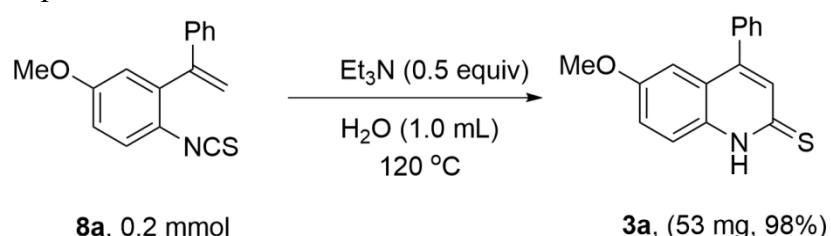
## VI. Mechanistic investigation

### Controlled experiment I



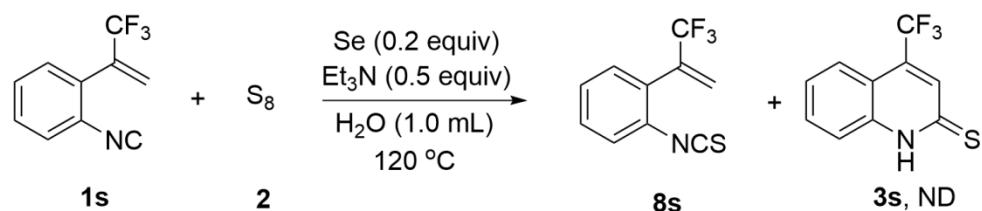
A mixture of 1-isocyano-4-methoxy-2-(1-phenylvinyl)benzene **1a** (0.2 mmol, 47 mg), **2** (1.5 equiv, 0.3 mmol, 9.6 mg), Se (0.2 equiv, 3.1 mg), Et<sub>3</sub>N (0.5 equiv, 10.2 mg) and acetone (1 mL) was heated at 40 °C. The reaction was completed for about 10 minutes (monitored by TLC). Then, the reaction mixture was concentrated by vacuum distillation, and the crude product was purified by column chromatography (petroleum ether/ethyl acetate=30/1) to obtain 1-isothiocyanato-4-methoxy-2-(1-phenylvinyl)benzene **8a** (41.4 mg, 78%).

#### Controlled experiment II



A mixture of 1-isothiocyanato-4-methoxy-2-(1-phenylvinyl)benzene **8a** (0.2 mmol, 54 mg), Et<sub>3</sub>N (0.5 equiv) and pure water (1 mL) was heated at 120 °C. The reaction was monitored by TLC, and the substrate was consumed after 2 hours. Then, the reaction mixture was cooled to room temperature and extracted with ethyl acetate (3 × 10 mL). The organic phase was combined, dried over anhydrous Mg<sub>2</sub>SO<sub>4</sub>, and concentrate under reduced pressure. Purify the crude product through column chromatography (petroleum ether/ethyl acetate=5/1) to obtain 6-methoxy-4-phenylquinoline-2(1H)-thione **3a** (53 mg, 98%)

#### Controlled experiment III



A mixture of 1-isocyano-2-(3,3,3-trifluoroprop-1-en-2-yl)benzene **1s** (0.2 mmol, 40 mg), **2** (1.5 equiv, 0.3 mmol, 9.6 mg), Se (0.2 equiv, 3.1 mg), Et<sub>3</sub>N (0.5 equiv, 10.2

mg) and water (1.0 mL) was heated at 120 °C. The reaction was monitored by TLC, and the substrate was consumed after 4 h. Afterwards, the mixture was cooled to room temperature and extracted by ethyl acetate ( $3 \times 10$  mL). The organic layers were combined, dried over anhydrous Mg<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether / ethyl acetate = 30 : 1) to give 1-isothiocyanato-2-(3,3,3-trifluoroprop-1-en-2-yl)benzene **8s** (28.5 mg, 63 %).

## VII. Analytical data of compounds

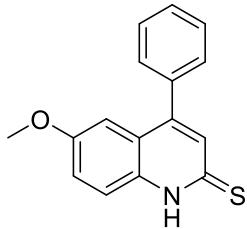
The characterization data of these compounds match the data previously reported in the literature.

6-methoxy-4-phenylquinoline-2(1H)-thione (**3a**)<sup>1</sup>,  
6-methyl-4-phenylquinoline-2(1H)-thione (**3b**)<sup>1</sup>,  
4-phenylquinoline-2(1H)-thione (**3e**)<sup>1</sup>,  
6-chloro-4-phenyl-quinoline-2(1H)-thione (**3f**)<sup>1</sup>,  
4-methylquinoline-2(1H)-thione (**3o**)<sup>1</sup>,  
8-methyl-4-phenylquinoline-2(1H)-thione (**3h**)<sup>1</sup>,  
4-(4-methoxyphenyl)quinoline-2(1H)-thione (**3m**)<sup>2</sup>,  
1-isothiocyanato-4-methoxy-2-(1-phenylvinyl)benzene (**8a**)<sup>3</sup>.

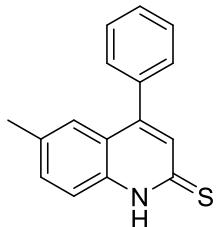
## References:

1. X. Zhang, T. Wang, et al. Base-controlled chemoselectivity reaction of vinylanilines with isothiocyanates for synthesis of quinolino-2-thione and 2-aminoquinoline derivatives. *Chem. Commun.* **2018**, *54*, 3114 - 3117.
2. T. Otani, S. Kunimatsu, et al. Synthesis of Quinoline-2-thiones via Tandem Indium(III)-Promoted Friedel-Crafts Alkenylation-Cyclization of 2-Alkynylphenyl Isothiocyanates. *Org. Lett.* **2007**, *9*, 5513 - 5516.
3. K. Kobayashi., S. Fujita, et al. One-Pot Synthesis of Quinoline-2(1H)-thiones from 2-Isocyanostyrenes via Electrocyclic Reaction of the Corresponding

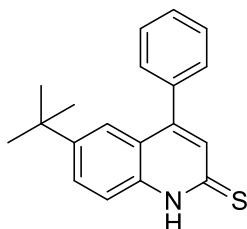
2-Isothiocyanatestyrenes. *Synthesis*, **2009**, 20, 3378 - 3382.



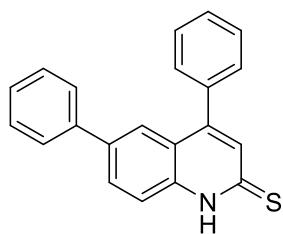
**6-methoxy-4-phenylquinoline-2(1H)-thione (3a).** Eluent: PE/EA (5:1), Yellow solid, 50.7 mg, 95% yield, m.p.: 229 - 230 °C, **1H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) δ 13.72 (s, 1H), 7.68 (d, *J* = 9.2 Hz, 1 H), 7.59 - 7.55 (m, 5 H), 7.35 (dd, *J*<sub>1</sub> = 9.2 Hz, *J*<sub>2</sub> = 2.8 Hz, 1 H), 7.13 (s, 1H), 6.91 (d, *J* = 2.4 Hz, 1 H), 3.68 (s, 3 H). **13C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) δ 178.4, 156.1, 145.9, 136.5, 135.3, 131.7, 129.6, 129.4, 129.2, 122.6, 121.2, 118.8, 107.4, 55.8. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>14</sub>NOS<sup>+</sup> 268.0791; found 268.0784.



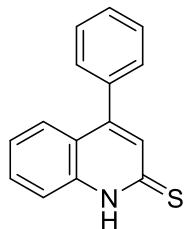
**6-methyl-4-phenylquinoline-2(1H)-thione (3b).** Eluent: PE/EA (5:1), Yellow solid, 46.7 mg, 93% yield, m.p.: 249 - 250 °C, **1H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) δ 13.71 (s, 1H), 7.61 (d, *J* = 8.4 Hz, 1 H), 7.57 - 7.52 (m, 3 H), 7.48 - 7.46(m, 3 H), 7.26 (s, 1 H), 7.09 (d, *J* = 1.6 Hz, 1 H), 2.27 (s, 3 H). **13C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) δ 179.8, 146.2, 138.5, 136.5, 134.2, 133.2, 131.4, 129.5, 129.3, 129.3, 125.7, 121.7, 117.1, 21.3. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>14</sub>NS<sup>+</sup> 252.0841; found 252.0838.



**6-(tert-butyl)-4-phenylquinoline-2(1H)-thione (3c).** Eluent: PE/EA (5:1), Yellow solid, 49.8 mg, 85% yield, m.p.: 236 - 238 °C, **1H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) δ 13.71 (s, 1H), 7.78 (dd, *J*<sub>1</sub> = 8.8 Hz, *J*<sub>2</sub> = 2.0 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 1 H), 7.59 - 7.52 (m , 5 H), 7.48 (d, *J* = 2.0 Hz, 1 H), 7.13 (s, 1 H), 1.21 (s, 9 H). **13C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) δ 180.0, 147.0, 146.6, 138.4, 136.4, 131.4, 130.1, 129.6, 129.3, 129.3, 121.6, 121.2, 117.1, 34.9, 31.2. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>20</sub>NS<sup>+</sup> 294.1311; found 294.1317.

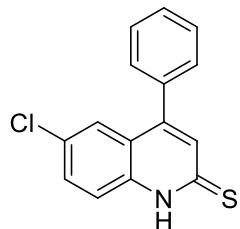


**4,6-diphenylquinoline-2(1H)-thione (3d).** Eluent: PE/EA (5:1), Yellow solid, 56.7 mg, 91% yield, m.p.: 289 - 291 °C, **1H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) δ 13.85 (s, 1H), 7.97 (dd, *J*<sub>1</sub> = 8.4 Hz, *J*<sub>2</sub> = 1.6 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1 H), 7.67 (d, *J* = 1.6 Hz, 1 H), 7.57 - 7.52 (m, 7 H), 7.42 (t, *J* = 8.0 Hz, 2 H), 7.33 (t, *J* = 7.2 Hz, 1 H), 7.17 (d, *J* = 1.2 Hz, 1 H). **13C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) δ 180.6, 146.4, 139.6, 139.6, 136.6, 136.3, 131.9, 130.7, 129.7, 129.6, 129.4, 128.2, 127.1, 124.0, 122.0, 117.9. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>16</sub>NS<sup>+</sup> 314.0998; found 314.0995.

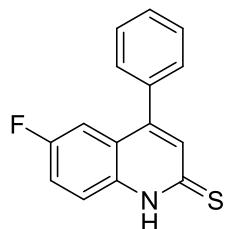


**4-phenylquinoline-2(1H)-thione (3e).** Eluent: PE/EA (5:1), Yellow solid, 39.2 mg, 83% yield, m.p.: 210 - 211 °C, **1H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) δ 13.77 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 1 H), 7.66 (t, *J* = 7.6 Hz, 1 H), 7.55 - 7.50 (m, 6 H), 7.32 (t, *J* = 7.6 Hz, 1 H), 7.14 (s, 1 H). **13C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) δ 180.7, 146.4, 140.2, 136.4,

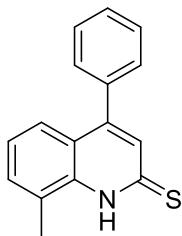
131.8, 131.4, 129.6, 129.4, 129.3, 126.5, 124.8, 121.7, 117.2. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>12</sub>NS<sup>+</sup> 238.0685; found 238.0690.



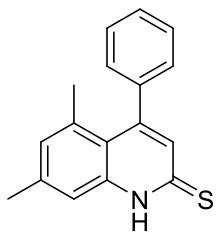
**6-chloro-4-phenylquinoline-2(1H)-thione (3f).** Eluent: PE/EA (5:1), Yellow solid, 51.6 mg, 95% yield, m.p.: 251 - 252 °C, **<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) δ 13.88 (s, 1H), 7.71 (s, 2 H), 7.60 - 7.55 (m, 3 H), 7.53 - 7.51(m, 2 H), 7.39 (s, 1 H), 7.17 (d, *J* = 1.2 Hz, 1 H). **<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) δ 181.1, 145.2, 138.9, 135.7, 132.4, 131.8, 129.8, 129.5, 129.3, 128.8, 125.3, 123.0, 119.2. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>11</sub>ClNS<sup>+</sup> 272.0295; found 272.0294.



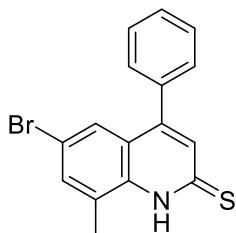
**6-fluoro-4-phenylquinoline-2(1H)-thione (3g).** Eluent: PE/EA (5:1), Yellow solid, 47 mg, 92% yield, m.p.: 246 - 248 °C, **<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) δ 13.86 (s, 1H), 7.75 (dd, *J*<sub>1</sub> = 9.2 Hz, , *J*<sub>2</sub> = 5.2 Hz, 1 H), 7.61 - 7.50 (m, 6 H), 7.18 - 7.14 (m, 2 H). **<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) δ 180.4, 158.7 (*J* = 240.5 Hz), 145.6 (*J* = 3.6 Hz), 137.2, 135.9, 132.3, 129.8, 129.5, 129.3, 122.7 ( *J* = 8.7 Hz), 120.3 (*J* = 24.7 Hz), 119.5 (*J* = 8.6 Hz), 111.1 (*J* = 23.9 Hz). **<sup>19</sup>F NMR** (376 MHz, DMSO-*d*<sub>6</sub>) δ -116.5 (s, 1F). **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>11</sub>FNS<sup>+</sup> 256.0591; found 256.0598.



**8-methyl-4-phenylquinoline-2(1H)-thione (3h).** Eluent: PE/EA (5:1), Yellow solid, 39.2 mg, 79% yield, m.p.: 170 - 172 °C, **<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) δ 12.29 (s, 1H), 7.57 - 7.54 (m, 3 H), 7.50 - 7.47 (m, 3 H), 7.33 (d, *J* = 8.0 Hz, 1 H), 7.33 (t, *J* = 7.6 Hz, 1 H), 7.16 (s, 1H), 2.63 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) δ 181.5, 146.7, 138.7, 136.7, 133.1, 131.6, 129.5, 129.3, 129.2, 125.4, 124.7, 124.5, 122.1, 18.1. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>14</sub>NS<sup>+</sup> 252.0841; found 252.0852.

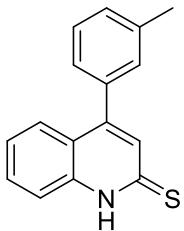


**5,7-dimethyl-4-phenylquinoline-2(1H)-thione (3i).** Eluent: PE/EA (5:1), Yellow solid, 50.9 mg, 96% yield, m.p.: 249 - 251 °C, **<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) δ 13.62 (s, 1H), 7.47 - 7.44 (m, 3H), 7.40 (s, 1H), 7.34 - 7.29 (m, 2H), 6.92 (s, 1 H), 6.88 (s, 1H), 2.34 (s, 3H), 1.73 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) δ 178.9, 147.4, 141.6, 141.5, 140.9, 136.3, 132.6, 130.3, 128.8, 128.7, 128.4, 118.9, 115.4, 23.7, 24.6. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>16</sub>NS<sup>+</sup> 266.0998; found 266.0995.

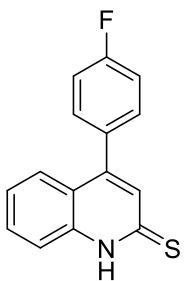


**6-bromo-8-methyl-4-phenylquinoline-2(1H)-thione (3j).** Eluent: PE/EA (5:1), Yellow solid, 61.0 mg, 93% yield, m.p.: 233 - 235 °C, **<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>)

$\delta$  12.46 (s, 1H), 7.70 (d,  $J$  = 1.2 Hz, 1H), 7.58 - 7.54 (m, 3H), 7.50 - 7.48(m, 2H), 7.35 (d,  $J$  = 1.6 Hz, 1H), 7.18 (s, 1H), 2.62 (s, 3H).  **$^{13}\text{C}$  NMR** (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  181.9, 145.3, 137.9, 136.0, 135.2, 132.7, 129.8, 129.4, 129.3, 128.3, 126.3, 123.7, 116.5, 17.9. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>13</sub>BrNS<sup>+</sup> 329.9947; found 329.9969.

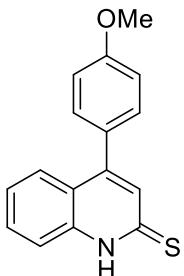


**4-(m-tolyl)quinoline-2(1H)-thione (3k).** Eluent: PE/EA (5:1), Yellow solid, 41.6 mg, 83% yield, m.p.: 195 - 197 °C,  **$^1\text{H}$  NMR** (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  13.75 (s, 1H), 7.71 (d,  $J$  = 8.4 Hz, 1 H), 7.65 (t,  $J$  = 7.2 Hz, 1H), 7.53(d,  $J$  = 8.0 Hz, 1H), 7.44 (t,  $J$  = 7.6 Hz, 1H), 7.36 - 7.28 (m, 4H), 7.12 (s, 1H), 2.40 (s, 3H).  **$^{13}\text{C}$  NMR** (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  180.7, 146.6, 140.2, 138.7, 136.3, 131.8, 131.3, 130.2, 129.8, 129.2, 126.6, 126.5, 124.8, 121.7, 117.1, 21.5. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>14</sub>NS<sup>+</sup> 252.0841; found 252.0855.

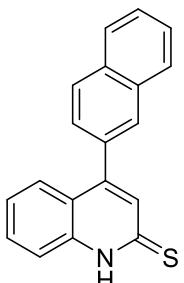


**4-(4-fluorophenyl)quinoline-2(1H)-thione (3l).** Eluent: PE/EA (5:1), Yellow solid, 45.7 mg, 90% yield, m.p.: 252 - 254 °C,  **$^1\text{H}$  NMR** (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  13.77 (s, 1H), 7.72 - 7.64 (m, 2H), 7.60 - 7.56 (m, 2H), 7.49 (d,  $J$  = 8.0 Hz, 1H), 7.39 (t,  $J$  = 8.4 Hz, 2H), 7.32(t,  $J$  = 7.2 Hz, 1H), 7.14 (s, 1H).  **$^{13}\text{C}$  NMR** (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  180.7, 163.0 ( $J$  = 244.8 Hz), 145.4, 140.2, 132.7( $J$  = 3.2 Hz), 131.8, 131.7( $J$  = 8.2 Hz),

131.6, 126.4, 124.8, 121.7, 117.2, 116.3 ( $J = 31.5$  Hz).  **$^{19}\text{F}$  NMR** (376 MHz, DMSO- $d_6$ )  $\delta$  -112.5 (s, 1F). **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>11</sub>FNS<sup>+</sup> 256.0591; found 256.0602.

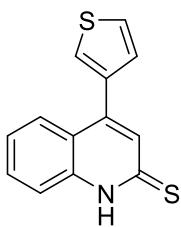


**4-(4-methoxyphenyl)quinoline-2(1H)-thione (3m).** Eluent: PE/EA (5:1), Yellow solid, 48.2 mg, 91% yield, m.p.: 236 - 278 °C,  **$^1\text{H}$  NMR** (400 MHz, DMSO- $d_6$ )  $\delta$  13.69 (s, 1H), 7.69 (t,  $J = 8.0$  Hz, 1H), 7.64 (d,  $J = 8.0$  Hz, 1H), 7.59 (d,  $J = 8.0$  Hz, 1H), 7.47 (d,  $J = 8.8$  Hz, 2H), 7.32 (t,  $J = 7.2$  Hz, 1H), 7.13 - 7.11 (m, 3H), 3.84 (s, 3H).  **$^{13}\text{C}$  NMR** (100 MHz, DMSO- $d_6$ )  $\delta$  180.6, 160.4, 146.2, 140.2, 131.7, 131.1, 130.9, 128.4, 126.6, 124.7, 121.8, 117.2, 114.8, 55.8. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>14</sub>NOS<sup>+</sup> 268.0791; found 268.0804.

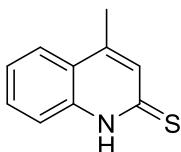


**4-(naphthalen-2-yl)quinoline-2(1H)-thione (3n).** Eluent: PE/EA (5:1), Yellow solid, 35.0 mg, 61% yield, m.p.: 259 - 261 °C.  **$^1\text{H}$  NMR** (400 MHz, DMSO- $d_6$ )  $\delta$  13.80 (s, 1H), 8.12 (s, 1H), 8.09 (d,  $J = 8.8$  Hz, 1H), 8.05 - 8.02 (m, 2H), 7.74 (d,  $J = 8.4$  Hz, 1H), 7.68 (d,  $J = 7.2$  Hz, 1H), 7.64 - 7.60 (m, 3H), 7.58 (d,  $J = 8.4$  Hz, 1H), 7.32 (t,  $J = 7.2$  Hz, 1H), 7.27 (s, 1H).  **$^{13}\text{C}$  NMR** (100 MHz, DMSO- $d_6$ )  $\delta$  180.7, 146.4, 140.2, 133.9, 133.3, 133.3, 131.8, 131.7, 128.8, 128.7, 128.2, 127.5, 127.3, 127.0, 126.7,

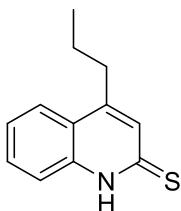
124.9, 121.8, 117.2. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>14</sub>NS<sup>+</sup> 288.0841; found 288.0858.



**4-(thiophen-3-yl)quinoline-2(1H)-thione (3o).** Eluent: PE/EA (5:1), Yellow solid, 37.0 mg, 77% yield, m.p.: 224 - 226 °C, **<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) δ 13.69 (s, 1 H), 7.97 (s, 1 H), 7.80 - (m, 2 H), 7.71 - 7.64(m, 2 H), 7.42 (d, *J* = 3.2 Hz, 1 H), 7.36 (t, *J* = 7.2 Hz, 1 H), 7.23 (s, 1 H). **<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) δ 180.6, 141.3, 140.2, 136.7, 131.8, 131.0, 128.9, 128.0, 127.3, 126.5, 124.8, 121.5, 117.1. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>18</sub>NS<sub>2</sub><sup>+</sup> 244.0249; found 244.0240.

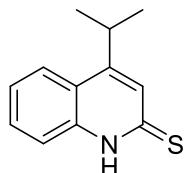


**4-methylquinoline-2(1H)-thione (3p).** Eluent: PE/EA (5:1), Yellow solid, 26.3 mg, 76% yield, m.p.: 265 - 267 °C, **<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) δ 13.48 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 1 H), 7.62 (d, *J* = 4.4 Hz, 2 H), 7.39 - 7.33(m, 1 H), 7.21 (s, 1 H), 2.45 (s, 3 H). **<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) δ 180.8, 143.8, 139.3, 131.5, 131.4, 125.2, 124.5, 123.0, 116.9, 18.4. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>10</sub>H<sub>10</sub>NS<sup>+</sup> 176.0528; found 176.0526.

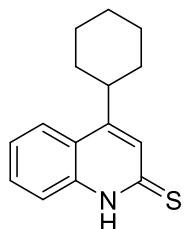


**4-propylquinoline-2(1H)-thione (3q).** Eluent: PE/EA (5:1), Yellow solid, 31 mg, 77%

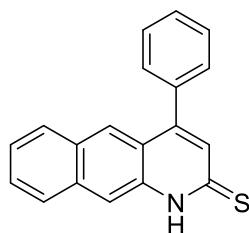
yield, m.p.: 194 - 196 °C. **<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) δ 13.51 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.65 - 7.58 (m, 2H), 7.37 - 7.33 (m, 1H), 7.16 (s, 1H), 2.81 (t, *J* = 7.6 Hz, 2H), 1.69 - 1.59 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) δ 180.7, 147.3, 139.7, 131.4, 130.6, 125.0, 124.5, 122.2, 117.2, 33.3, 22.6, 14.3. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>12</sub>H<sub>14</sub>NS<sup>+</sup> 204.0841; found 204.0853.



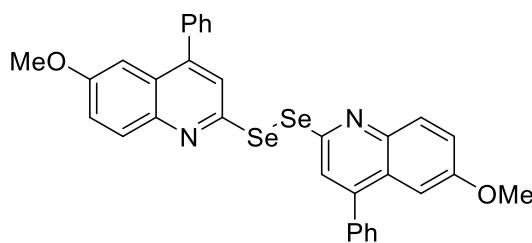
**4-isopropylquinoline-2(1H)-thione (3r).** Eluent: PE/EA (5:1), Yellow solid, 26.5 mg, 64% yield, m.p.: 177 - 179 °C, **<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) δ 13.54 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 1 H), 7.66 - 7.60 (m, 2 H), 7.40 - 7.35(m, 1 H), 7.15 (s, 1 H), 3.50 (m, 1 H), 1.27 (d, *J* = 6.8 Hz, 6 H). **<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) δ 181.0, 152.9, 139.8, 131.3, 127.3, 124.6, 124.5, 121.7, 117.3, 28.0, 22.5. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>12</sub>H<sub>14</sub>NS<sup>+</sup> 204.0841; found 204.0854.



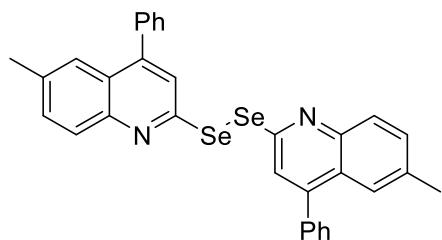
**4-cyclohexylquinoline-2(1H)-thione (3s).** Eluent: PE/EA (5:1), Yellow solid, 38.4 mg, 79 % yield, m.p.: 260 - 261 °C. **<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) δ 13.53 (s, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.65 - 7.59 (m, 2H), 7.38 - 7.34 (m, 1H), 7.11 (s, 1H), 3.11 (t, *J* = 11.6 Hz, 1H ), 1.82 (t, *J* = 12.4 Hz, 4H), 1.73 (d, *J* = 12.8 Hz, 1H), 1.55 - 1.36 (m, 4H), 1.31 - 1.15 (m, 2H) . **<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) δ 180.9, 151.8, 139.8, 131.3, 127.8, 124.6, 124.4, 121.6, 117.4, 38.1, 32.9, 26.6, 26.1. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>18</sub>NS<sup>+</sup> 244.1154; found 244.1162.



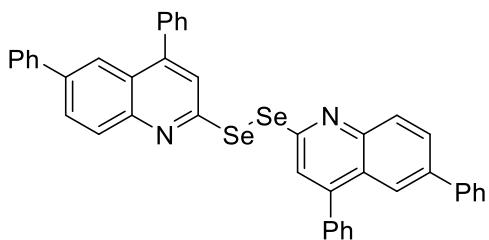
**4-phenylbenzo[g]quinoline-2(1H)-thione (3v).** Eluent: PE/EA (5:1), Yellow solid, 53.0 mg, 93% yield, m.p.: 266 - 268 °C, **<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) δ 14.04 (s, 1H), 8.15 (d, *J* = 9.2 Hz, 1 H), 7.95 (d, *J* = 8.0 Hz, 1 H), 7.84 (d, *J* = 9.2 Hz, 1 H), 7.56 - 7.52 (m, 3 H), 7.45 - 7.39 (m, 3 H), 7.24 (d, *J* = 8.4 Hz, 1 H), 7.16 (d, *J* = 7.2 Hz, 1 H), (s, 1 H). **<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) δ 178.2, 147.4, 141.1, 134.2, 134.1, 131.3, 129.8, 129.1, 128.0, 127.1, 126.2, 125.9, 117.4, 116.7. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>14</sub>NS<sup>+</sup> 288.0841; found 288.0830.



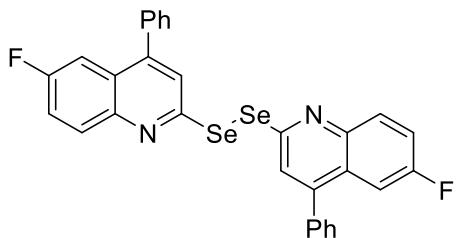
**1,2-bis(6-methoxy-4-phenylquinolin-2-yl)diselane (5a).** Eluent: PE/EA (20:1), yellow solid, 56.4 mg, 90% yield, m.p.: 169 - 171 °C, **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.94 (d, *J* = 9.2 Hz, 2H), 7.89 (s, 2H), 7.49 - 7.45 (m, 6H), 7.43 - 7.40 (m, 4H), 7.36 (dd, *J*<sub>1</sub> = 9.2 Hz, *J*<sub>2</sub> = 2.8 Hz, 2H), 7.13 (d, *J* = 2.8 Hz, 2H), 3.76 (s, 6H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 157.8, 151.6, 148.3, 144.6, 137.6, 130.3, 129.3, 128.6, 128.5, 126.1, 122.1, 121.7, 104.1, 55.4. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>32</sub>H<sub>25</sub>N<sub>2</sub>O<sub>2</sub>Se<sub>2</sub><sup>+</sup> 629.0241; found 629.0223.



**1,2-bis(6-methyl-4-phenylquinolin-2-yl)diselane (5b).** Eluent: PE/EA (20:1), yellow solid, 48.7 mg, 82% yield, m.p.: 195 - 197 °C, **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.89 (s, 2H), 7.58 (s, 2H), 7.52 (dd, *J*<sub>1</sub> = 8.4 Hz, *J*<sub>2</sub> = 1.6 Hz, 2H), 7.48 - 7.45 (m, 6H), 7.42 - 7.38 (m, 4H), 2.43 (s, 6H). **13C NMR** (100 MHz, CDCl<sub>3</sub>) δ 153.6, 148.9, 147.2, 137.5, 136.4, 132.2, 129.4, 128.5, 128.5, 128.4, 125.0, 124.7, 121.0, 21.7. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>32</sub>H<sub>25</sub>N<sub>2</sub>Se<sub>2</sub><sup>+</sup> 597.0343; found 597.0328.

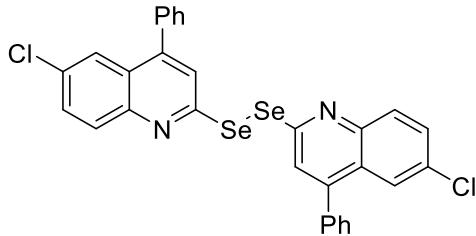


**1,2-bis(4,6-diphenylquinolin-2-yl)diselane (5c).** Eluent: PE/EA (20:1), yellow solid, 65.5 mg, 91% yield, m.p.: 238 - 240 °C, **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.12 (d, *J* = 8.8 Hz, 2H), 8.03 (d, *J* = 1.6 Hz, 2H), 7.98 - 7.95 (m, 4H), 7.57 (d, *J* = 7.2 Hz, 4H), 7.47 - 7.47 (m, 10H), 7.43 (t, *J* = 7.6 Hz, 4H), 7.35 (t, *J* = 7.2 Hz, 2H). **13C NMR** (100 MHz, CDCl<sub>3</sub>) δ 154.7, 149.7, 148.0, 140.3, 139.2, 137.3, 129.7, 129.5, 129.2, 128.9, 128.7, 127.7, 127.4, 125.3, 123.7, 121.3. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>42</sub>H<sub>29</sub>N<sub>2</sub>Se<sub>2</sub><sup>+</sup> 721.0656; found 721.0678.

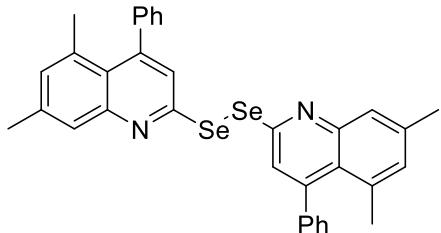


**1,2-bis(6-fluoro-4-phenylquinolin-2-yl)diselane (5d).** Eluent: PE/EA (20:1), yellow solid, 49.3 mg, 82% yield, m.p.: 205 - 207 °C, **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.05 - 8.01 (m, 2H), 7.93 (s, 2H), 7.49 - 7.44 (m, 10H), 7.40 - 7.38 (m, 4H). **13C NMR** (100 MHz, CDCl<sub>3</sub>) δ 160.5 (*J* = 246.2 Hz), 153.9 (*J* = 2.9 Hz), 149.1 (*J* = 5.4 Hz), 145.7,

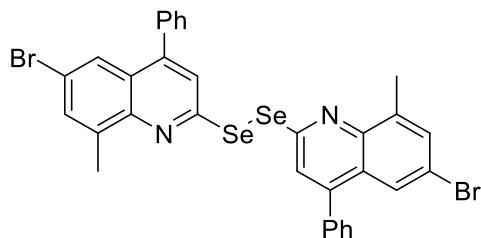
136.9, 131.2 ( $J = 9.0$  Hz), 129.3, 128.9, 128.8, 126.0 ( $J = 9.5$  Hz), 121.6, 120.1 ( $J = 25.5$  Hz), 109.5 ( $J = 23.1$  Hz).  **$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -112.4 (s, 2F). **HRMS (ESI)** m/z:  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{30}\text{H}_{19}\text{F}_2\text{N}_2\text{Se}_2^+$  604.9841; found 604.9828.



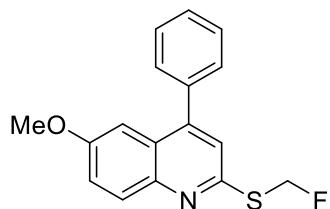
**1,2-bis(6-chloro-4-phenylquinolin-2-yl)diselane (5e).** Eluent: PE/EA (20:1), yellow solid, 49.8 mg, 79% yield, m.p.: 206 - 207 °C,  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (d,  $J = 8.8$  Hz, 2H), 7.91 (s, 2H), 7.80 (d,  $J = 2.4$  Hz, 2H), 7.63 (dd,  $J = 8.8$  Hz,  $J = 2.0$  Hz, 2H), 7.52 - 7.48 (m, 6H), 7.41 - 7.37 (m, 4H).  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.0, 148.8, 146.9, 136.4, 132.6, 130.9, 130.4, 129.3, 128.9, 128.8, 125.9, 124.8, 121.6. **HRMS (ESI)** m/z:  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{30}\text{H}_{19}\text{Cl}_2\text{N}_2\text{Se}_2^+$  636.9250; found 636.9244.



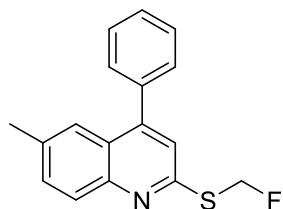
**1,2-bis(5,7-dimethyl-4-phenylquinolin-2-yl)diselane (5f).** Eluent: PE/EA (20:1), yellow solid, 46.1 mg, 74% yield, m.p.: 212 - 214 °C,  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 (s, 2H), 7.68 (s, 2H), 7.41 - 7.34 (m, 6H), 7.21 - 7.19 (m, 4H), 7.06 (s, 2H), 2.46 (s, 6H), 1.90 (s, 6H).  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  153.2, 149.9, 149.8, 141.7, 139.7, 135.3, 132.0, 128.6, 127.9, 127.8, 126.8, 122.6, 122.3, 24.2, 21.4. **HRMS (ESI)** m/z:  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{34}\text{H}_{29}\text{N}_2\text{Se}_2^+$  625.0656; found 625.0688.



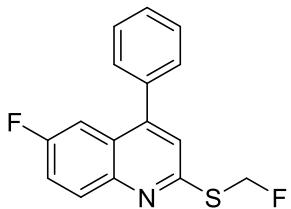
**1,2-bis(6-bromo-8-methyl-4-phenylquinolin-2-yl)diselane (5g).** PE/EA (20:1), yellow solid, 68.6 mg, 92% yield, m.p.: 226 - 228 °C,  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (s, 2H), 7.78 (d,  $J = 1.6$  Hz, 2H), 7.61 (s, 2H), 7.51 - 7.47 (m, 6H), 7.38 - 7.6 (m, 4H), 2.67 (s, 6H).  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  153.8, 148.5, 146.4, 139.2, 137.2, 133.2, 129.4, 128.7, 128.7, 126.3, 125.8, 121.5, 120.1, 17.9. **HRMS (ESI)** m/z: [M+H] $^+$  calcd for  $\text{C}_{32}\text{H}_{23}\text{Br}_2\text{N}_2\text{Se}_2^+$  752.8553; found 752.8549.



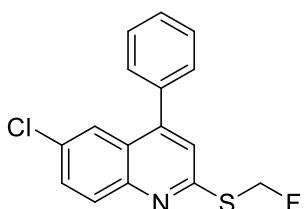
**2-((fluoromethyl)thio)-6-methoxy-4-phenylquinoline (6a).** Eluent: PE/EA (20:1), white solid, 49.3 mg, 83% yield, m.p.: 156 - 157 °C,  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (d,  $J = 9.2$  Hz, 1H), 7.53 - 7.49 (m, 5H), 7.36 (dd,  $J_1 = 9.2$  Hz,  $J_2 = 2.8$  Hz, 1H), 7.23 (s, 1H), 7.13 (d,  $J = 2.8$  Hz, 1H), 6.40 (s, 1H), 6.27 (s, 1H), 3.77 (s, 3H).  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.5, 151.7 ( $J = 3.5$  Hz), 148.0, 144.7, 137.7, 130.4, 129.2, 128.7, 128.6, 126.2, 121.8, 121.2, 104.2, 84.2 ( $J = 214.3$  Hz), 55.4.  **$^{19}\text{F NMR}$**  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -187.8 (s, 1F). **HRMS (ESI)** m/z: [M+H] $^+$  calcd for  $\text{C}_{17}\text{H}_{15}\text{FNOS}^+$  300.0853; found 300.0849.



**2-((fluoromethyl)thio)-6-methyl-4-phenylquinoline (6b).** Eluent: PE/EA (20:1), white solid, 42.0 mg, 75% yield, m.p.: 147 - 148 °C, **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.58 (s, 1H), 7.55 - 7.47 (m, 6H), 7.22 (s, 1H), 6.42 (s, 1H), 6.29 (s, 1H), 2.45 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 153.4 (*J* = 3.5 Hz), 148.6, 147.2, 137.6, 136.0, 132.0, 129.4, 128.6, 128.6, 128.5, 125.3, 124.7, 120.8, 83.0 (*J* = 214.1 Hz), 21.7. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -188.2 (s, 1F). **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>15</sub>FNS<sup>+</sup> 284.0904; found 284.0900.



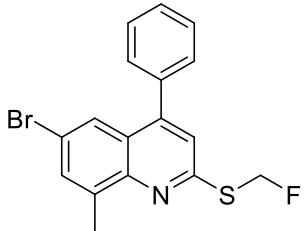
**6-fluoro-2-((fluoromethyl)thio)-4-phenylquinoline (6c).** Eluent: PE/EA (20:1), white solid, 42.0 mg, 74% yield, m.p.: 147 - 148 °C, **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.10 - 8.06 (m, 1H), 7.56 - 7.51 (m, 3H), 7.49 - 7.44 (m, 4H), 7.27 (s, 1H), 6.41 (s, 1H), 6.28 (s, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 160.3 (*J* = 245.4 Hz), 153.9, 148.7 (*J* = 5.4 Hz), 145.7, 136.9, 131.2 (*J* = 8.9 Hz), 129.2, 128.9, 128.8, 126.1 (*J* = 9.5 Hz), 121.3, 119.8 (*J* = 25.5 Hz), 109.5 (*J* = 23.1 Hz), 82.7 (*J* = 214.6 Hz). **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -113.3 (s, 1F), -188.8 (s, 1F). **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>12</sub>F<sub>2</sub>NS<sup>+</sup> 288.0653; found 288.0643.



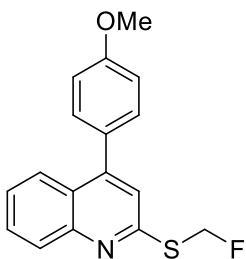
**6-chloro-2-((fluoromethyl)thio)-4-phenylquinoline (6d).** Eluent: PE/EA (20:1), white solid, 35.0 mg, 58% yield, m.p.: 150 - 152 °C, **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.02 (d, *J* = 8.8 Hz, 1H), 7.79 (d, *J* = 2.4 Hz, 1H), 7.64 (dd, *J*<sub>1</sub> = 8.8 Hz, *J*<sub>2</sub> = 2.0 Hz,

1H), 7.57 - 7.50 (m, 3H), 7.49 - 7.44 (m, 2H), 7.26 (s, 1H), 6.41 (s, 1H), 6.28 (s, 1H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 155.1 (*J* = 2.0 Hz), 148.4, 147.0, 136.7, 131.9, 130.8, 130.5, 129.3, 128.9, 128.8, 126.1, 124.8, 121.5, 82.5 (*J* = 214.7 Hz). **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -189.1 (s, 1F). **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>12</sub>ClFNS<sup>+</sup> 304.0358; found 304.0339.

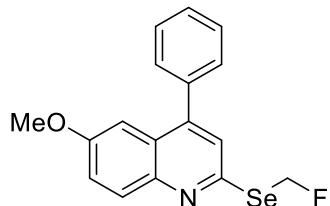


**6-bromo-2-((fluoromethyl)thio)-8-methyl-4-phenylquinoline (6e).** Eluent: PE/EA (20:1), white solid, 54.7 mg, 76% yield, m.p.: 144 - 145 °C, **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.79 (d, *J* = 2.0 Hz, 1H), 7.66 - 7.65 (m, 1H), 7.56 - 7.50 (m, 3H), 7.47 - 7.42 (m, 2H), 7.23 (s, 1H), 6.44 (s, 1H), 6.32 (s, 1H), 2.82 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 153.6 (*J* = 3.3 Hz), 148.6, 146.2, 139.0, 137.1, 133.3, 129.3, 128.8, 128.7, 126.5, 125.9, 121.2, 119.6, 82.5 (*J* = 214.9 Hz), 17.9. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -190.3 (s, 1F). **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>14</sub>BrFNS<sup>+</sup> 362.0009; found 362.0002.

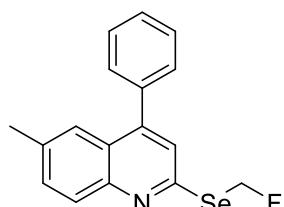


**2-((fluoromethyl)thio)-4-(4-methoxyphenyl)quinoline (6f).** Eluent: PE/EA (20:1), white solid, 49.5 mg, 83% yield, m.p.: 112 - 113 °C, **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.88 (dd, *J*<sub>1</sub> = 8.4 Hz, *J*<sub>2</sub> = 0.8 Hz, 1H), 7.71 - 7.67 (m, 1H), 7.46 - 7.38 (m, 3H), 7.23 (s, 1H), 7.07 - 7.04 (m, 2H), 6.43 (s, 1H), 6.30 (s, 1H), 3.90

(s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 160.0, 154.5 (*J* = 3.4 Hz), 148.9, 148.7, 130.7, 129.8, 129.7, 128.9, 126.0, 125.9, 125.6, 120.6, 114.1, 82.8 (*J* = 214.2 Hz), 55.4. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -188.5 (s, 1F). **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>15</sub>FNOS<sup>+</sup> 300.0853; found 300.0848.

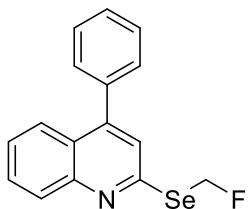


**2-((fluoromethyl)selanyl)-6-methoxy-4-phenylquinoline (7a).** Eluent: PE/EA (30:1), white solid, 40.0 mg, 58% yield, m.p.: 133 - 135 °C, **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.00 (d, *J* = 9.2 Hz, 1H), 7.53 - 7.49 (m, 5H), 7.36 (dd, *J*<sub>1</sub> = 9.2 Hz, *J*<sub>2</sub> = 2.8 Hz, 1H), 7.33 (s, 1H), 7.13 (d, *J* = 2.8 Hz, 1H), 6.66 (t, *J* = 8.8 Hz, 1H), 6.54 (t, *J* = 8.8 Hz, 1H), 3.78 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 157.6, 149.2 (*J* = 2.8 Hz), 147.6, 145.3, 137.6, 130.4, 129.2, 128.7, 128.6, 126.4, 123.6, 121.8, 104.2, 81.2 (*J* = 224.7 Hz), 55.4. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -194.4 (s, 1F). **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>15</sub>FNOSe<sup>+</sup> 348.0297; found 348.0290.

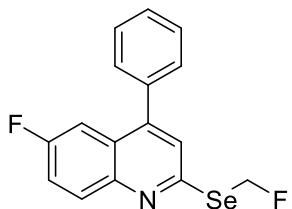


**2-((fluoromethyl)selanyl)-6-methyl-4-phenylquinoline (7b).** Eluent: PE/EA (30:1), white solid, 34.0 mg, 52% yield, m.p.: 136 - 138 °C, **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.58 - 7.48 (m, 7H), 7.32 (s, 1H), 6.69 (t, *J* = 8.0 Hz, 1H), 6.56 (t, *J* = 8.0 Hz, 1H), 2.45 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 151.2 (*J* = 2.8), 148.2, 147.7, 137.6, 136.1, 132.0, 129.4, 128.7, 128.6, 128.5, 125.5, 124.8, 123.2,

81.1 ( $J = 224.6$  Hz), 21.7.  **$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -194.8 (s, 1F). **HRMS (ESI)** m/z:  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{17}\text{H}_{15}\text{FNSe}^+$  332.0348; found 332.0335.



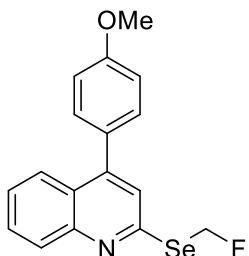
**2-((fluoromethyl)selanyl)-4-phenylquinoline (7c).** Eluent: PE/EA (30:1), white solid, 35.0 mg, 56% yield, m.p.: 115 - 117 °C,  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (d,  $J = 8.4$  Hz, 1H), 7.84 (d,  $J = 8.0$  Hz, 1H), 7.73 - 7.68 (m, 1H), 7.57 - 7.44 (m, 6H), 7.36 (s, 1H), 6.71 (t,  $J = 8.8$  Hz, 1H), 6.58 (t,  $J = 8.8$  Hz, 1H).  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.5 ( $J = 2.7$  Hz), 149.1, 148.8, 137.4, 129.8, 129.4, 129.0, 128.6, 128.6, 126.2, 126.0, 125.6, 123.1, 81.0 ( $J = 224.7$  Hz).  **$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -195.1 (s, 1F). **HRMS (ESI)** m/z:  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{16}\text{H}_{13}\text{FNSe}^+$  318.0192; found 318.0179.



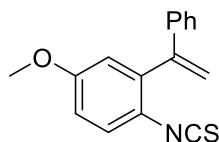
**6-fluoro-2-((fluoromethyl)selanyl)-4-phenylquinoline (7d).** Eluent: PE/EA (30:1), white solid, 32.0 mg, 48% yield, m.p.: 121 - 123 °C,  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.11 - 8.07 (m, 1H), 7.56 - 7.51 (m, 3H), 7.49 - 7.44 (m, 4H), 7.37 (s, 1H), 6.68 (t,  $J = 8.8$  Hz, 1H), 6.55 (t,  $J = 8.8$  Hz, 1H).  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.4 ( $J = 245.6$  Hz), 151.8, 148.3 ( $J = 5.2$  Hz), 146.3, 136.9, 131.3 ( $J = 9.1$  Hz), 129.2, 128.9, 128.8, 126.4 ( $J = 9.5$  Hz), 123.7, 119.8 ( $J = 25.4$  Hz), 109.6 ( $J = 23.2$  Hz), 80.9 ( $J = 225.2$  Hz).  **$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -113.0 (s, 1F), -195.2 (s, 1F). **HRMS (ESI)** m/z:  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{16}\text{H}_{12}\text{F}_2\text{NSe}^+$  336.0098; found 336.0088.



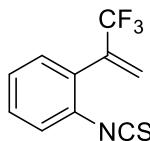
**6-chloro-2-((fluoromethyl)selanyl)-4-phenylquinoline (7e).** Eluent: PE/EA (30:1), white solid, 32.0 mg, 46% yield, m.p.: 148 - 150 °C, **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.03 (d, *J* = 9.2 Hz, 1H), 7.80 (d, *J* = 2.4 Hz, 1H), 7.65 (dd, *J*<sub>1</sub> = 8.8 Hz, *J*<sub>2</sub> = 2.4 Hz, 1H), 7.57 - 7.50 (m, 3H), 7.48 - 7.45 (m, 2H), 7.36 (s, 1H), 6.68 (t, *J* = 8.8 Hz, 1H), 6.56 (t, *J* = 8.8 Hz, 1H). **13C NMR** (100 MHz, CDCl<sub>3</sub>) δ 153.1 (*J* = 2.8 Hz), 148.0, 147.5, 136.7, 132.1, 130.7, 130.5, 129.3, 128.9, 128.8, 126.3, 124.9, 123.9, 80.8 (*J* = 225.2 Hz). **19F NMR** (376 MHz, CDCl<sub>3</sub>) δ -195.4 (s, 1F). **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>12</sub>ClFNSe<sup>+</sup> 351.9802; found 351.9814.



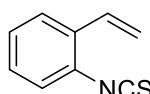
**2-((fluoromethyl)selanyl)-4-(4-methoxyphenyl)quinoline (4f).** Eluent: PE/EA (30:1), white solid, 36.5 mg, 53% yield, m.p.: 111 - 112 °C, **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.69 (t, *J* = 8.0 Hz, 1H), 7.47 - 7.39 (m, 3H), 7.34 (s, 1H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.70 (t, *J* = 8.8 Hz, 1H), 6.57 (t, *J* = 8.8 Hz, 1H), 3.90 (s, 3H). **13C NMR** (100 MHz, CDCl<sub>3</sub>) δ 160.0, 152.5 (*J* = 2.8 Hz), 149.2, 148.5, 130.7, 129.7, 129.6, 129.0, 128.0, 126.1, 125.8, 123.0, 114.1, 81.0 (*J* = 224.6 Hz), 55.4. **19F NMR** (376 MHz, CDCl<sub>3</sub>) δ -195.0 (s, 1F). **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>15</sub>FNOSe<sup>+</sup> 348.0297; found 348.0289.



**1-isothiocyanato-4-methoxy-2-(1-phenylvinyl)benzene (8a).** Eluent: PE/EA (30:1), yellow solid, 41.4 mg, 78% yield, m.p.: 124 - 126 °C, **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.36 - 7.29 (m, 5H), 7.19 - 7.17 (m, 1H), 6.87 (m, 2H), 5.84 (s, 1H), 5.37 (s, 1H), 3.82 (s, 3H). **13C NMR** (100 MHz, CDCl<sub>3</sub>) δ 158.4, 146.0, 140.5, 139.2, 128.5, 128.2, 127.5, 126.7, 122.0, 117.2, 116.1, 114.1, 55.6. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>14</sub>NOS<sup>+</sup> 268.0796; found 268.0799.



**1-isothiocyanato-2-(3,3,3-trifluoroprop-1-en-2-yl)benzene (8t).** Eluent: PE/EA (30:1), yellow oil, 28.5 mg, 63% yield. **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.41 - 7.28 (m, 4H), 6.27 (d, J = 1.2 Hz, 1H), 5.73 (d, J = 1.2 Hz, 1H). **13C NMR** (100 MHz, CDCl<sub>3</sub>) δ 134.8, 134.5, 130.4, 130.4, 130.1, 127.0, 126.9, 125.0 (q, J<sub>1</sub> = 10.3 Hz, J<sub>2</sub> = 5.2 Hz), 122.5 (q, J<sub>1</sub> = 544.1 Hz, J<sub>2</sub> = 272.0 Hz). **19F NMR** (376 MHz, CDCl<sub>3</sub>) δ -66.7 (s, 3F). **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>10</sub>H<sub>7</sub>F<sub>3</sub>NS<sup>+</sup> 230.0246; found 230.0252.

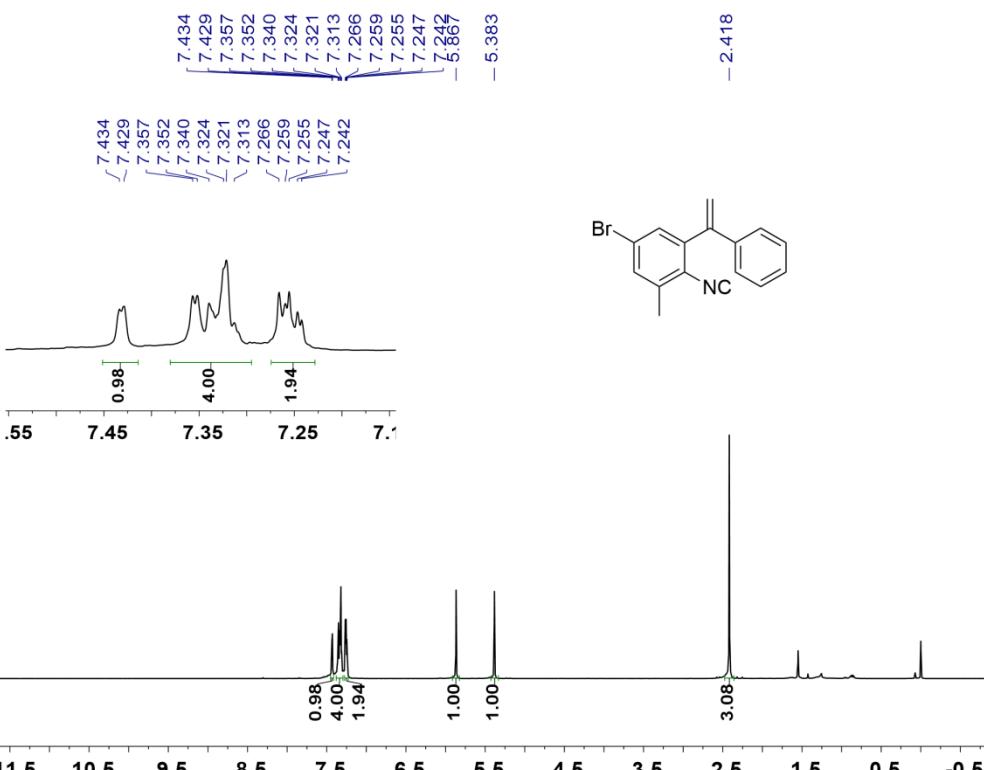


**1-isothiocyanato-2-vinylbenzene (8u).** Eluent: PE/EA (30:1), yellow oil, 18.0 mg, 56% yield. **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.56 - 7.54 (m, 1H), 7.28 - 7.24 (m, 3H), 6.98 (q, J<sub>1</sub> = 17.6 Hz, J<sub>2</sub> = 11.2 Hz, 1H), 5.82 (d, J = 17.6 Hz, 1H), 5.45 (d, J = 11.2 Hz, 1H). **13C NMR** (100 MHz, CDCl<sub>3</sub>) δ 133.8, 131.3, 128.7, 127.4, 127.0, 126.0, 117.4. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> calcd for C<sub>9</sub>H<sub>8</sub>NS<sup>+</sup> 162.0372; found 162.0381.

## IX. NMR spectra of compounds 1, 3, 5, 6, 7, 8a and 8s.

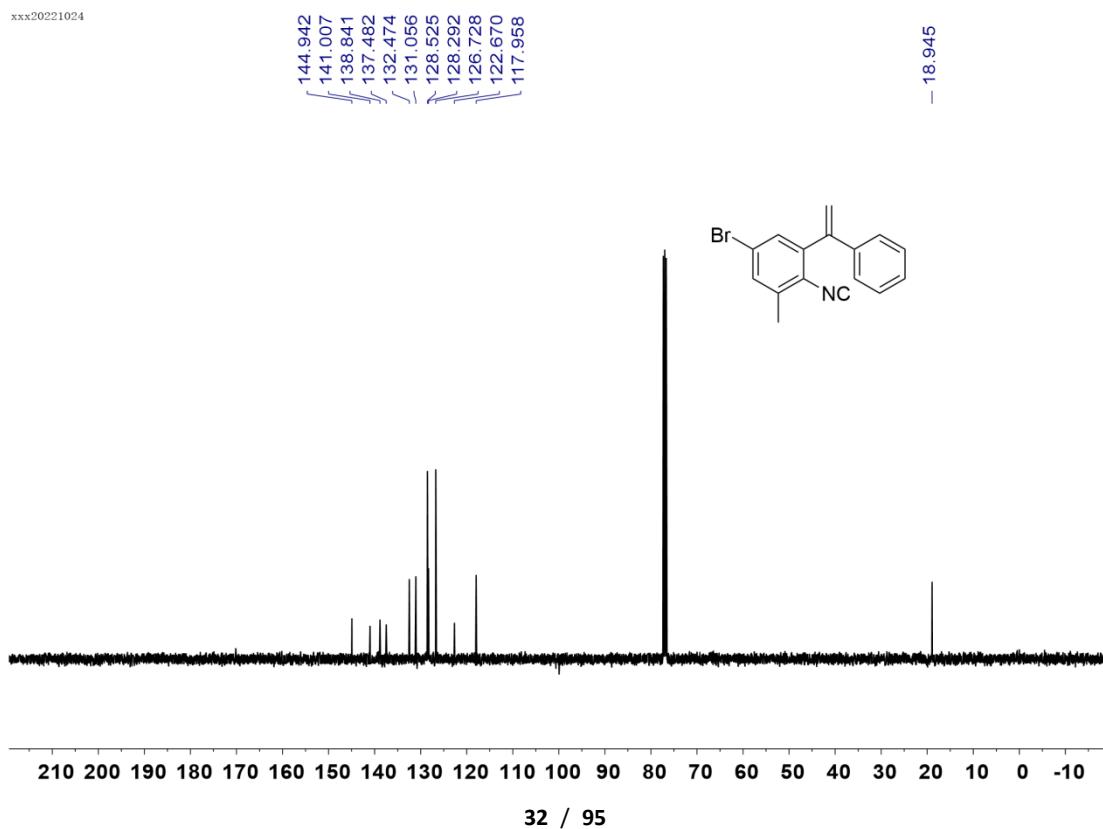
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) for 1j

xxx20221024

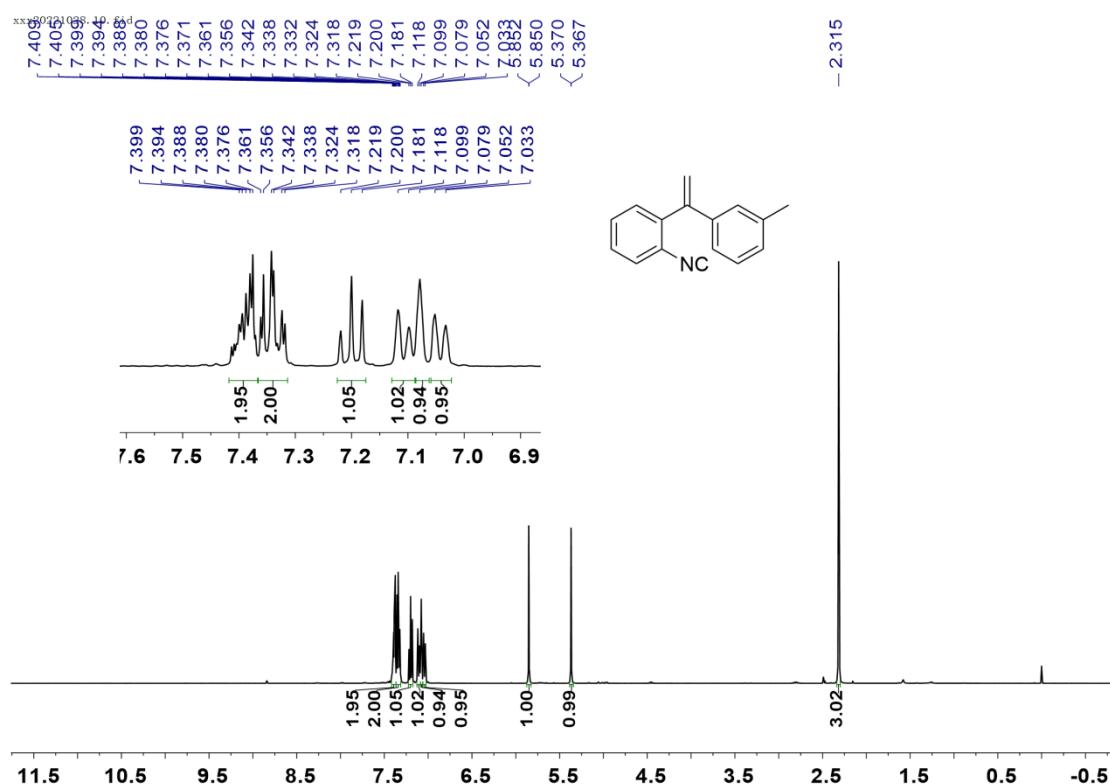


**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) for **1j**

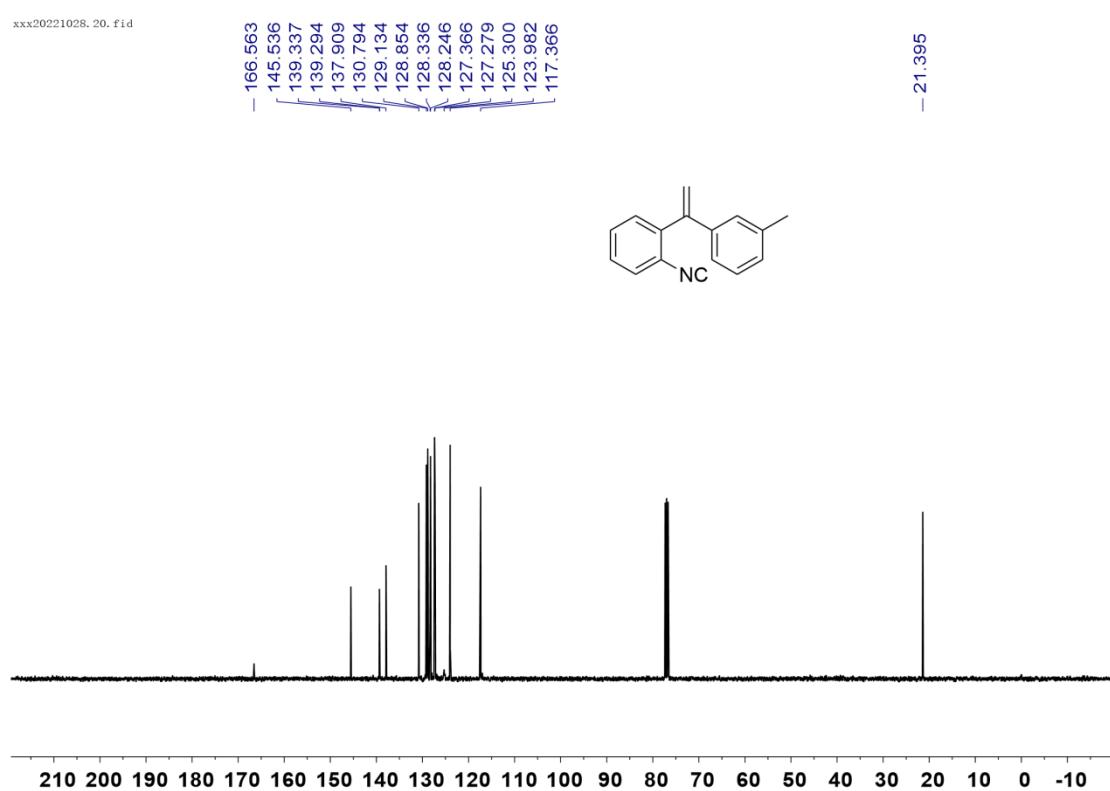
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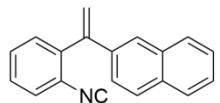
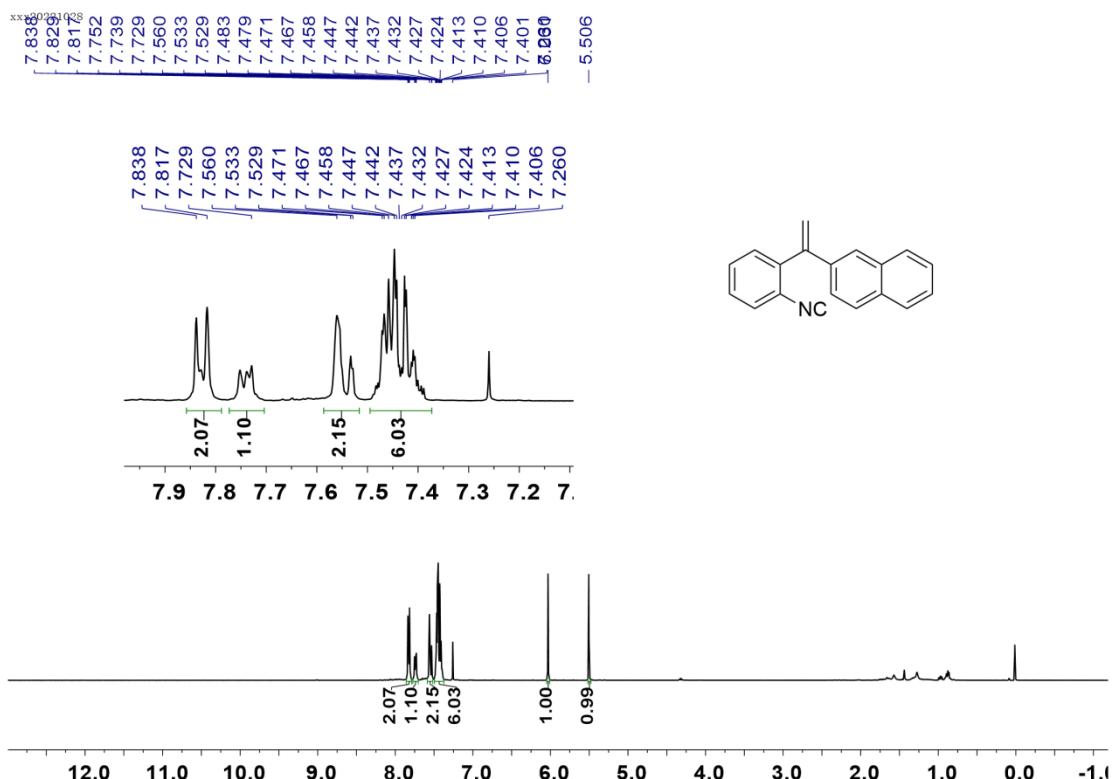
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) for **1k****



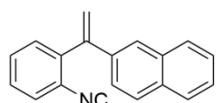
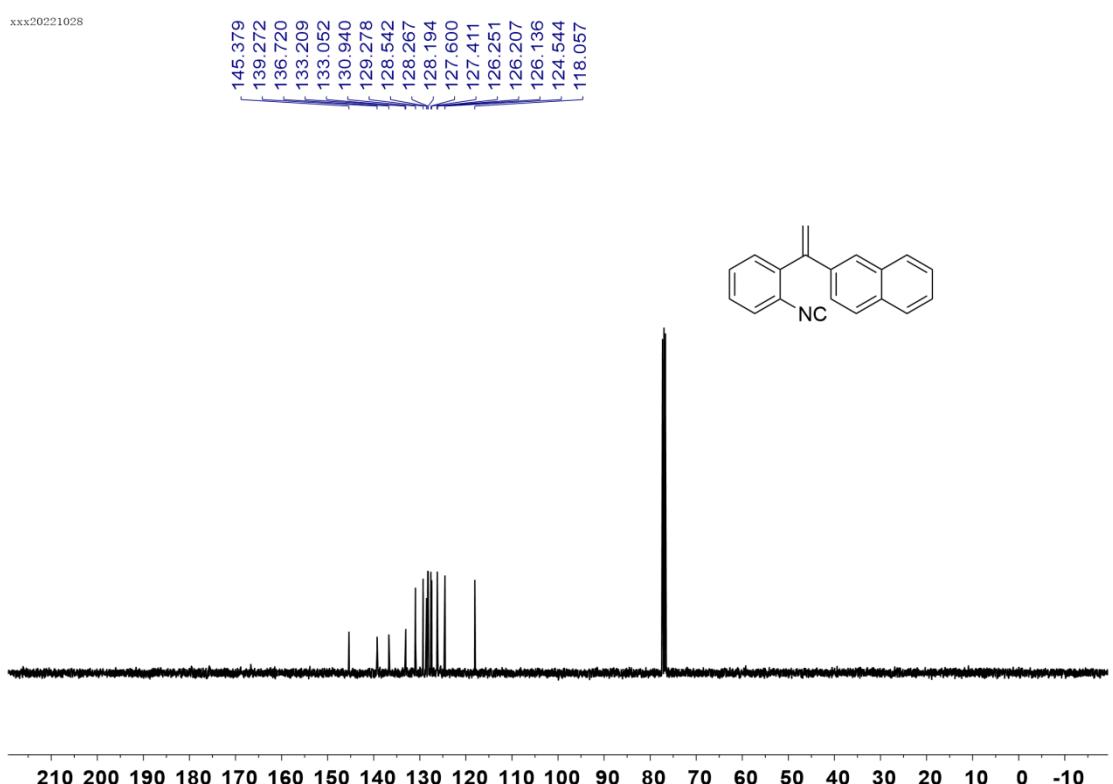
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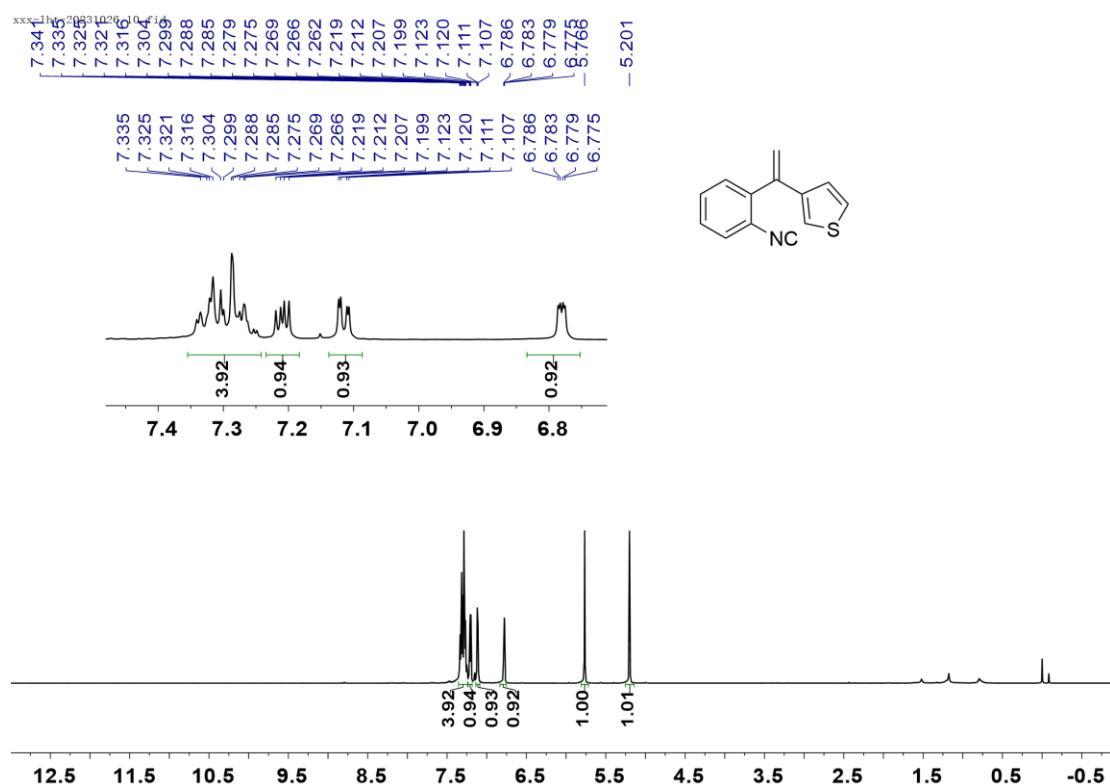
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) for **1n**



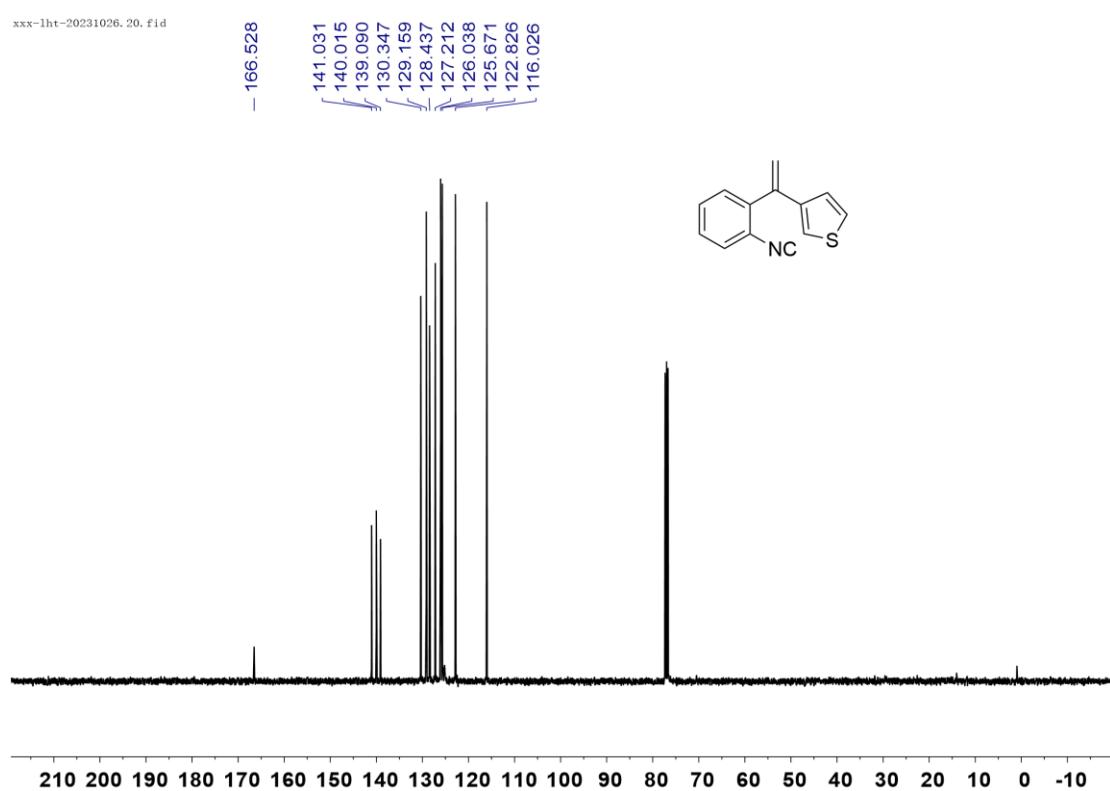
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for **1n**



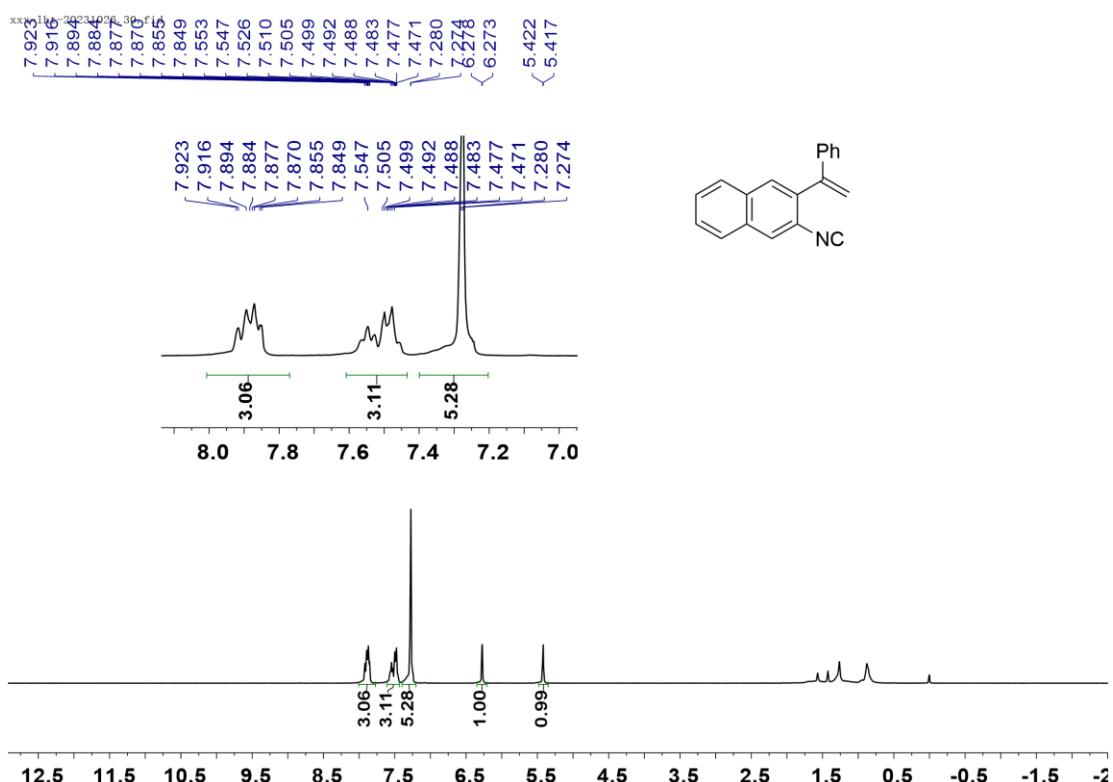
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) for **1o****



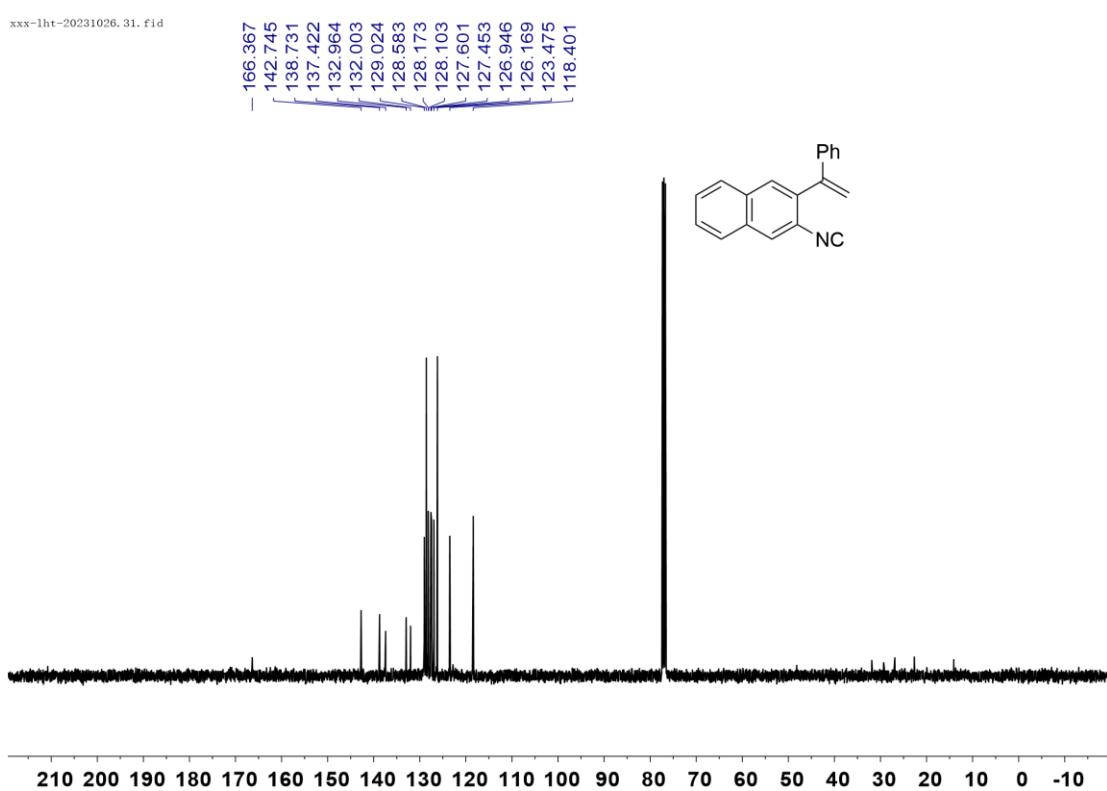
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for **1o****



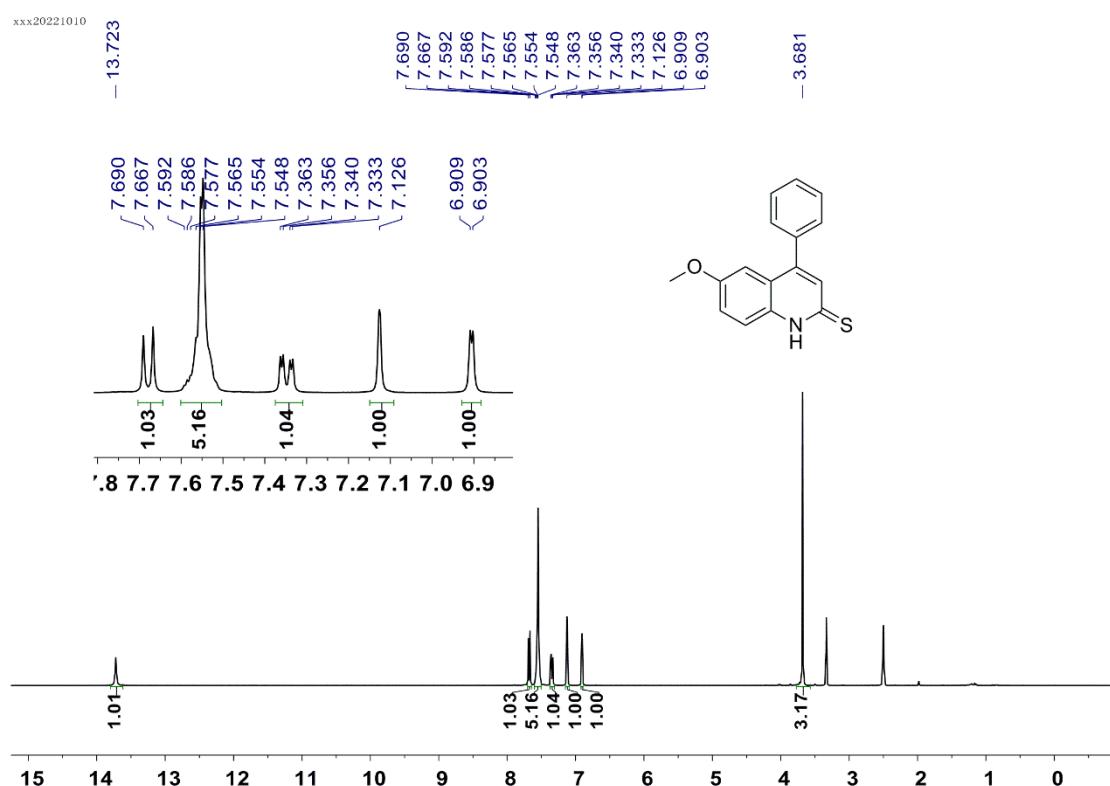
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) for 1t



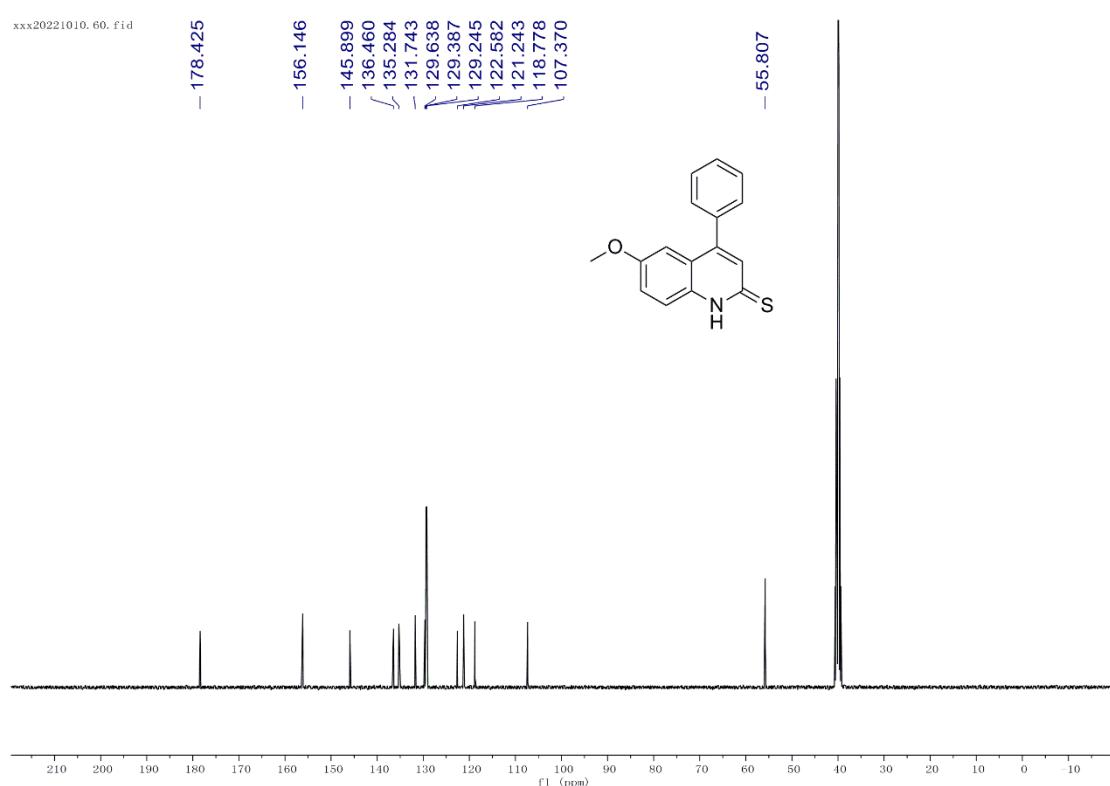
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for 1t



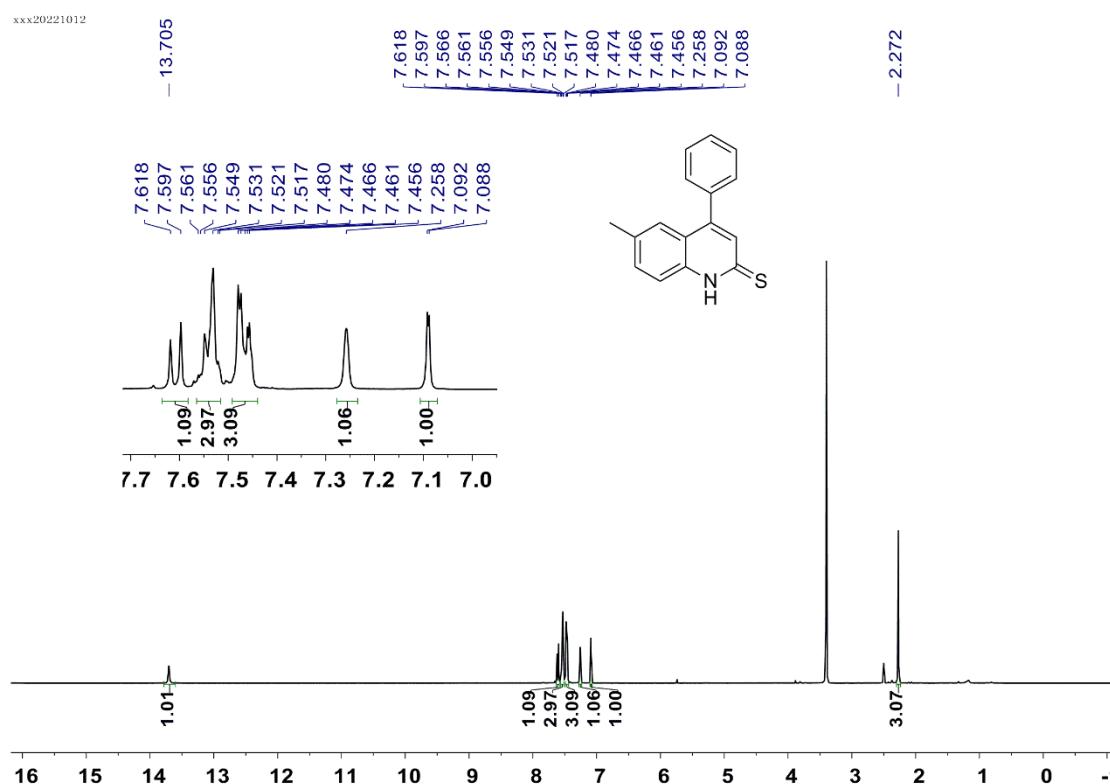
**<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) for **3a**



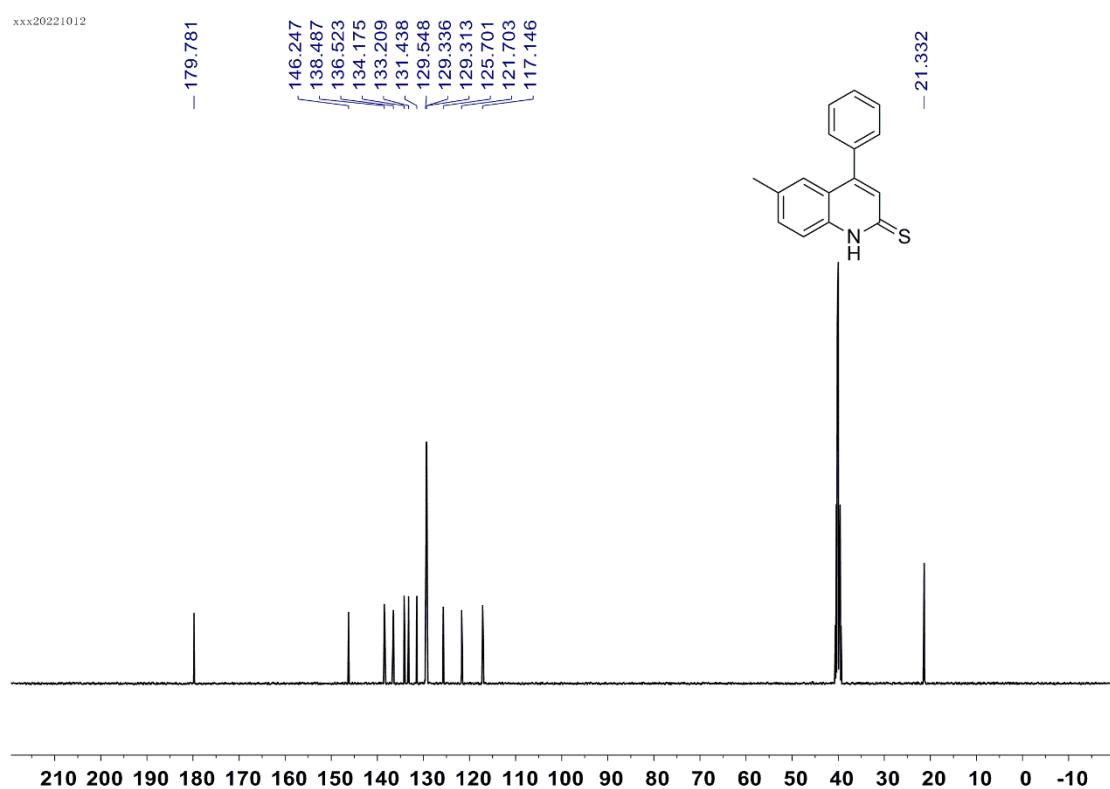
**<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) for **3a**



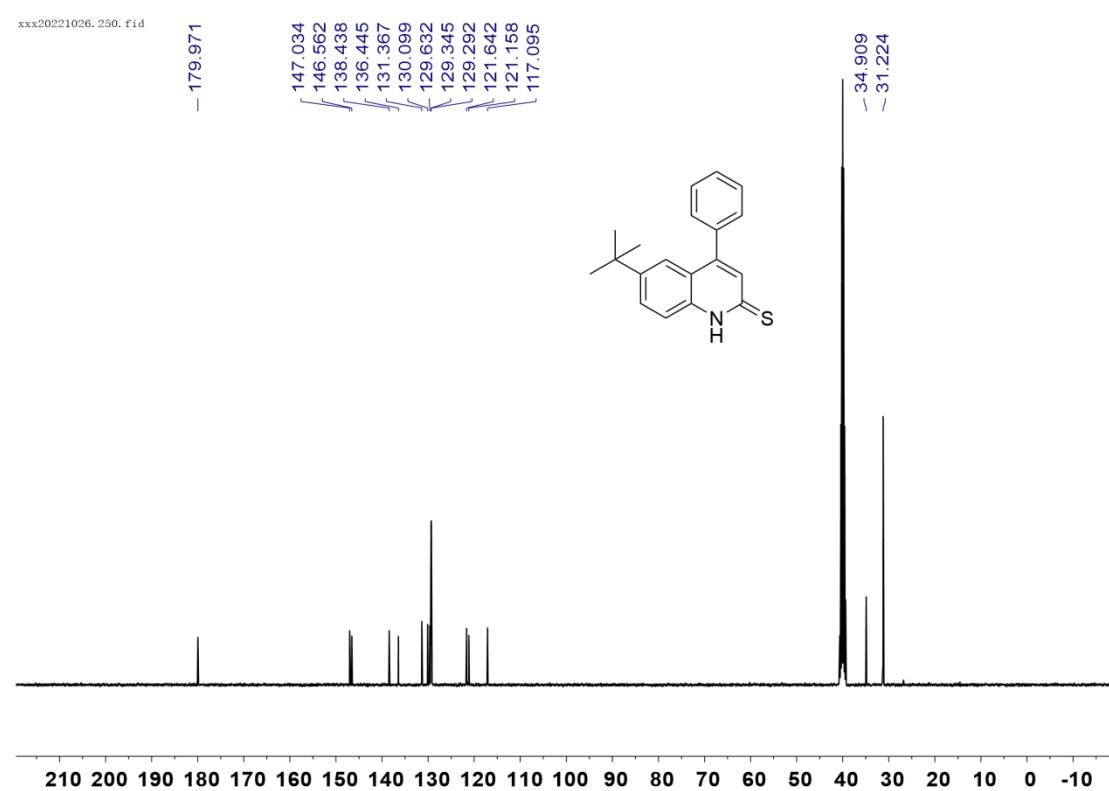
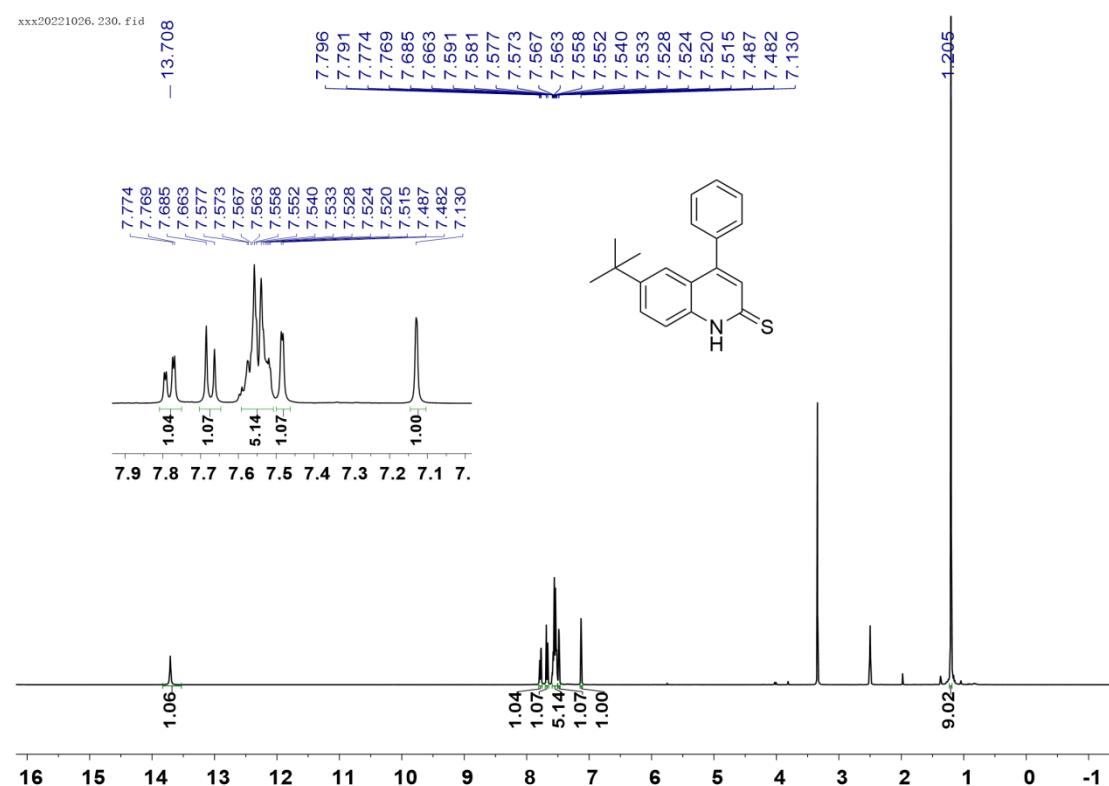
**<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) for 3b**



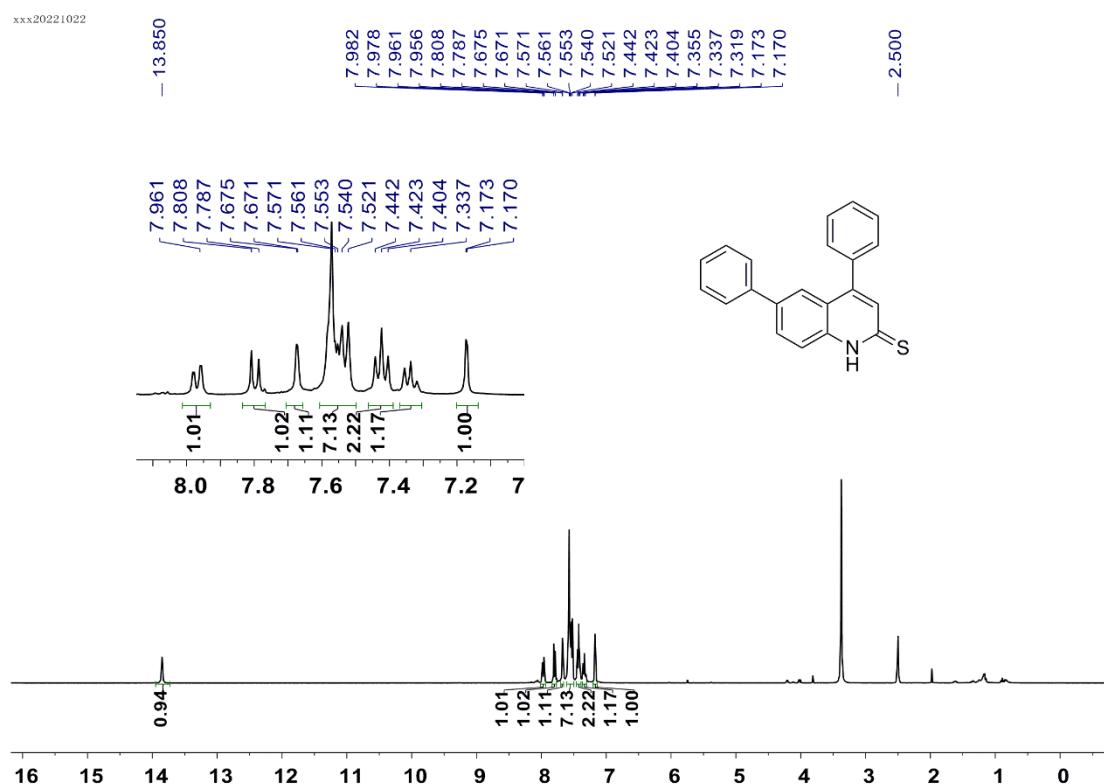
**<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) for 3b**



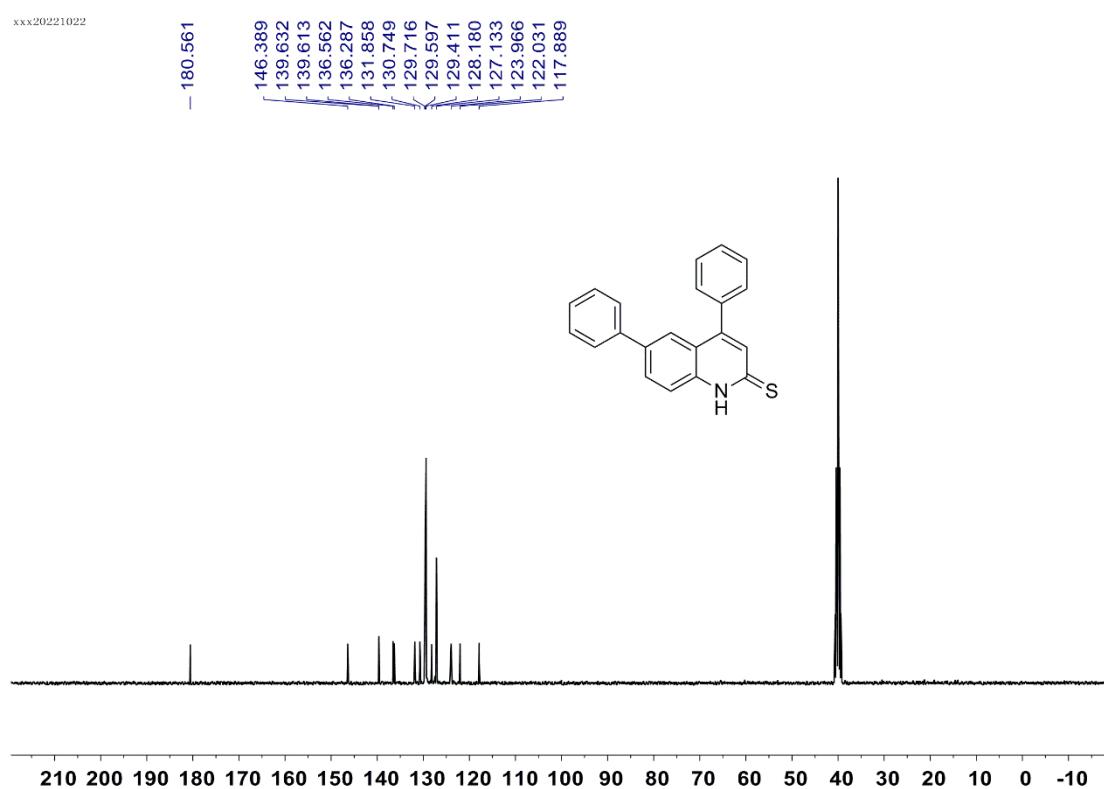
**<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) for 3c**



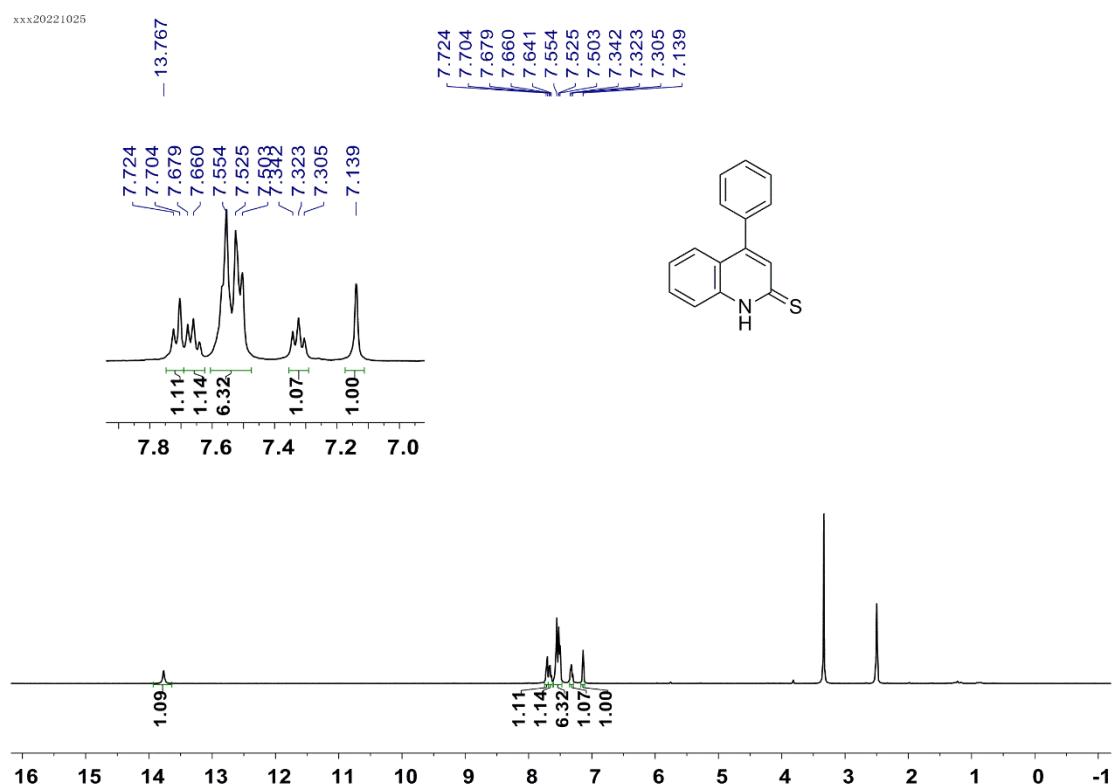
**<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) for 3d**



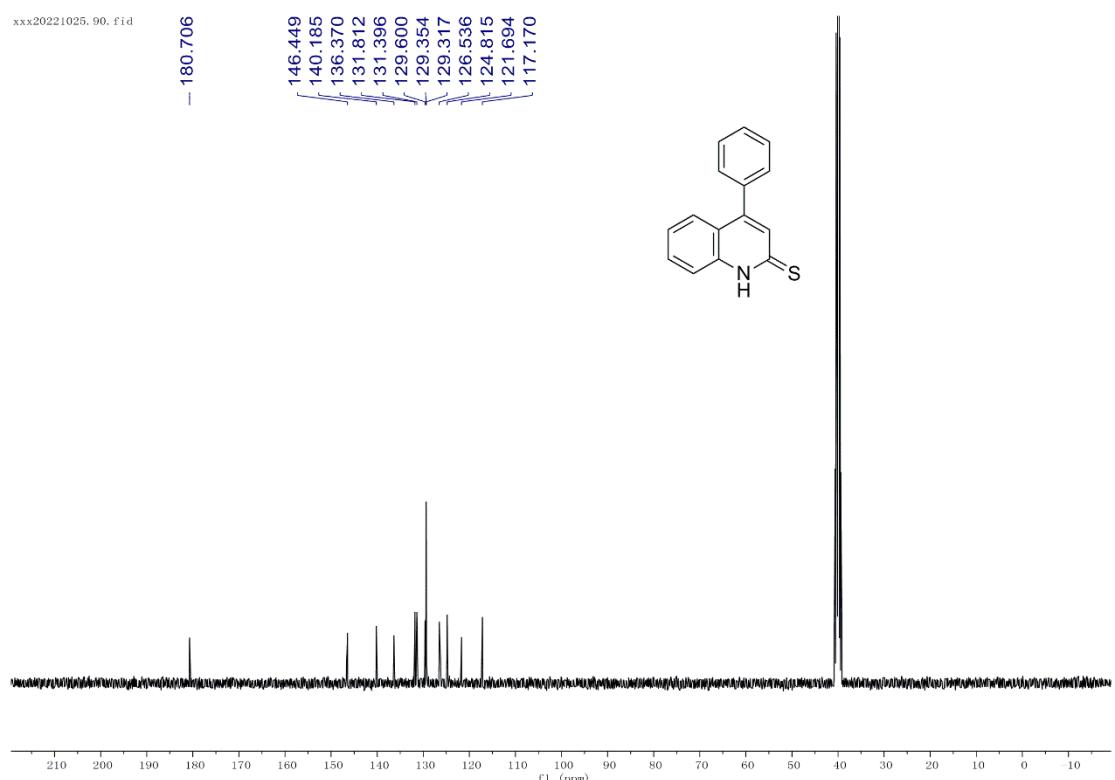
**<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) for 3d**



**<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) for **3e**

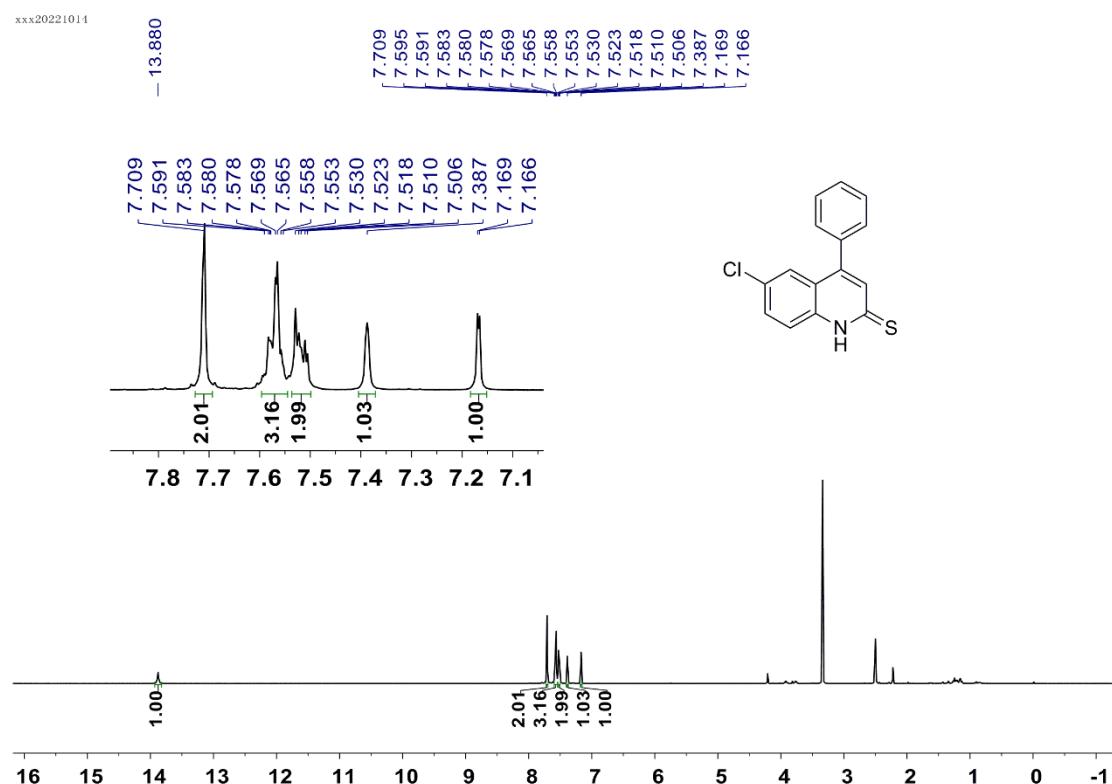


**<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) for **3e**



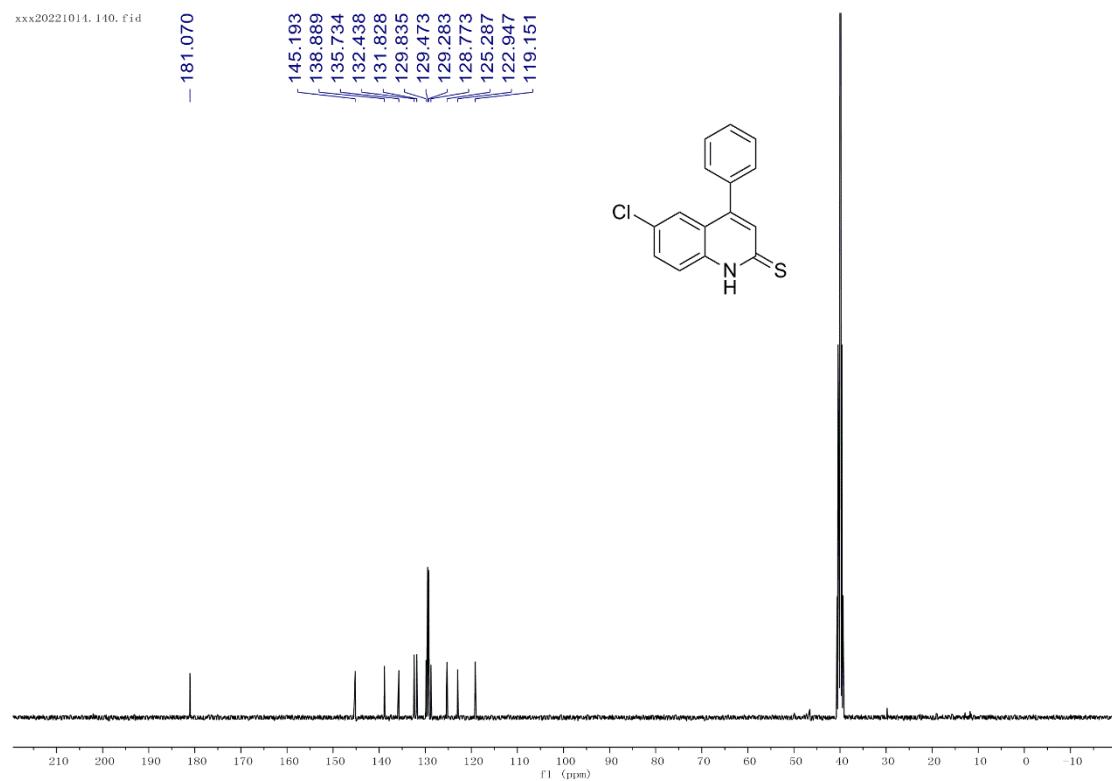
**<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) for **3f**

xxx20221014

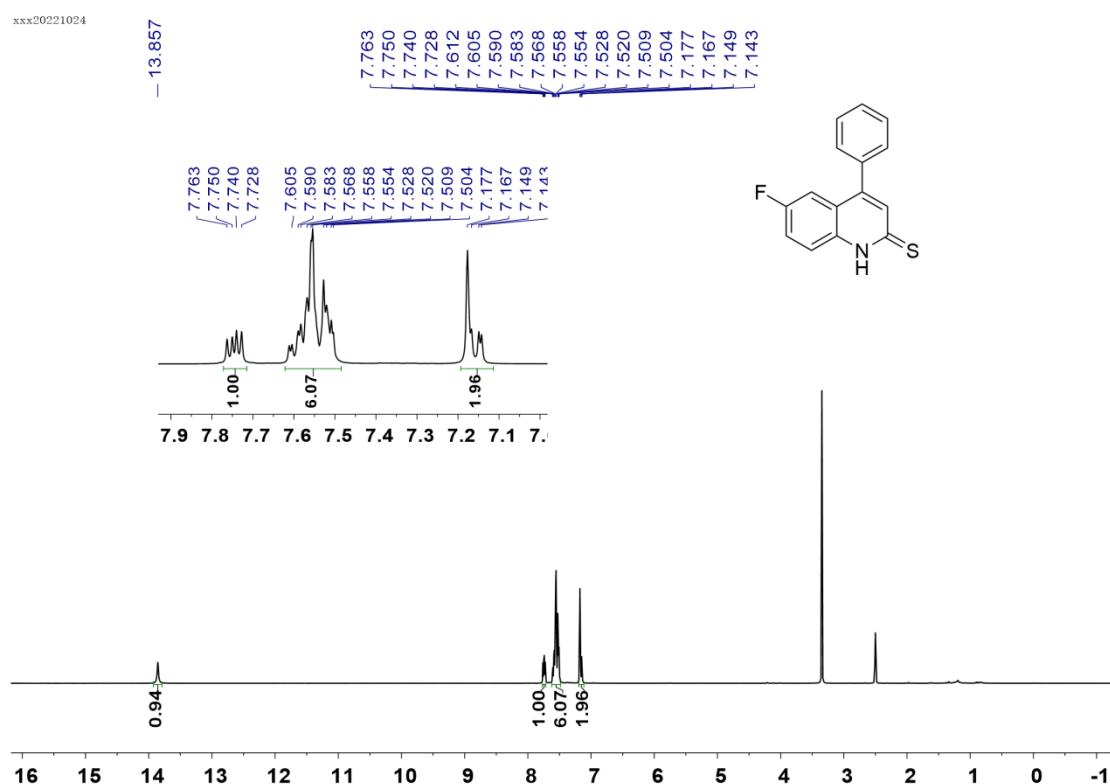


**<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) for **3f**

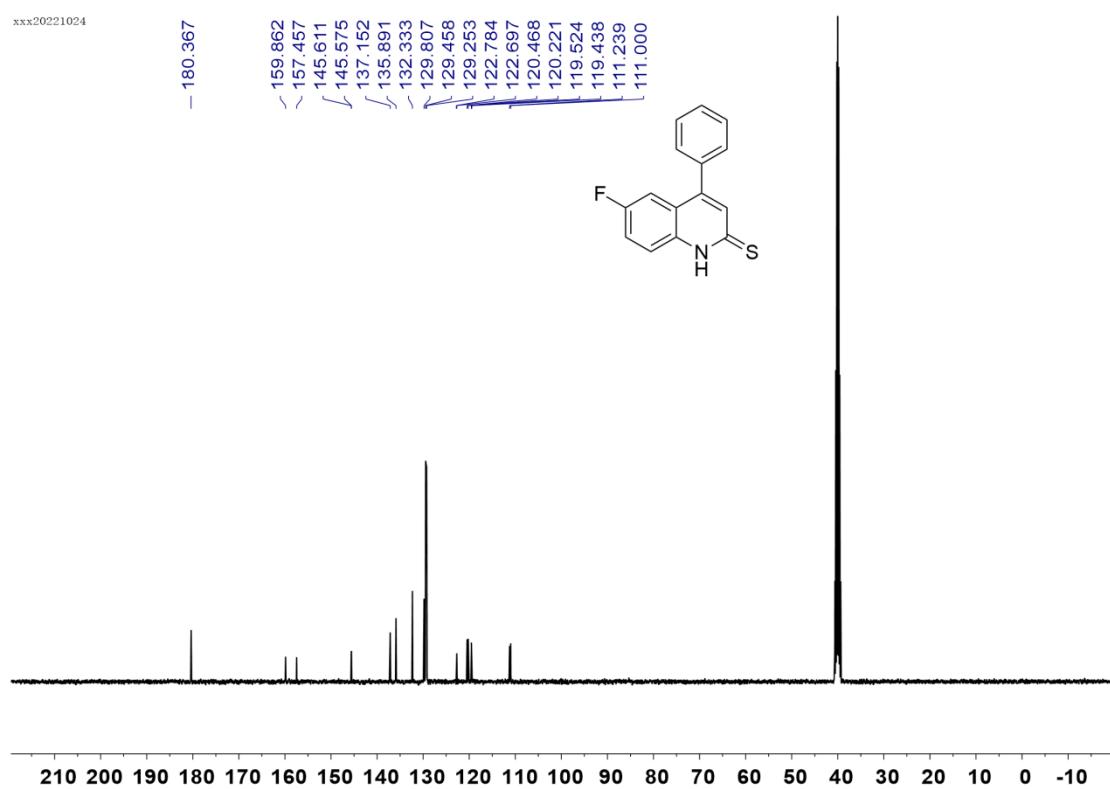
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**<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) for **3g**

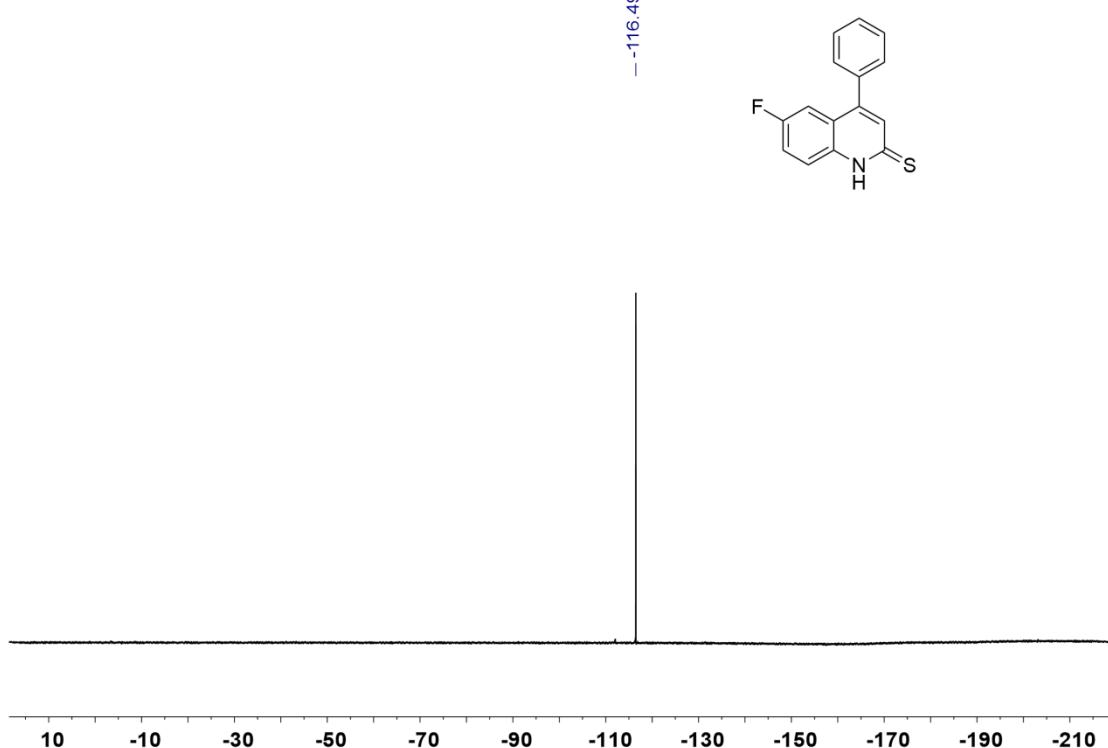


**<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) for **3g**

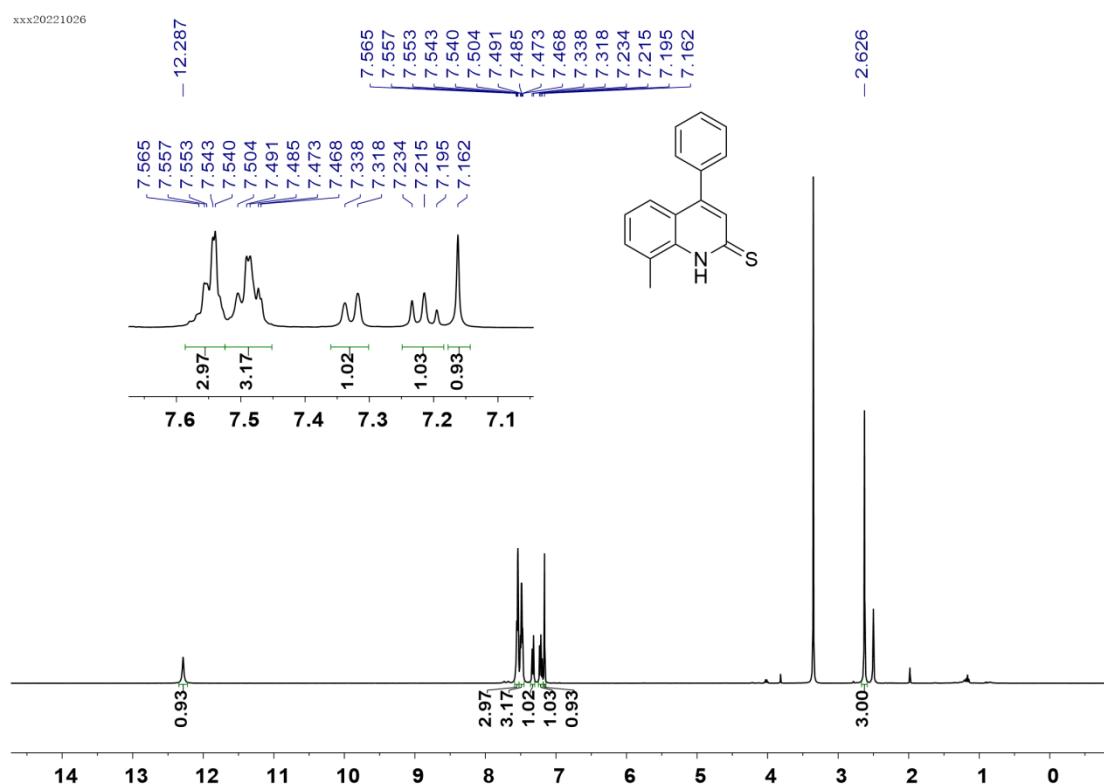


**<sup>19</sup>F NMR** (376 MHz, DMSO-*d*<sub>6</sub>) for **3g**

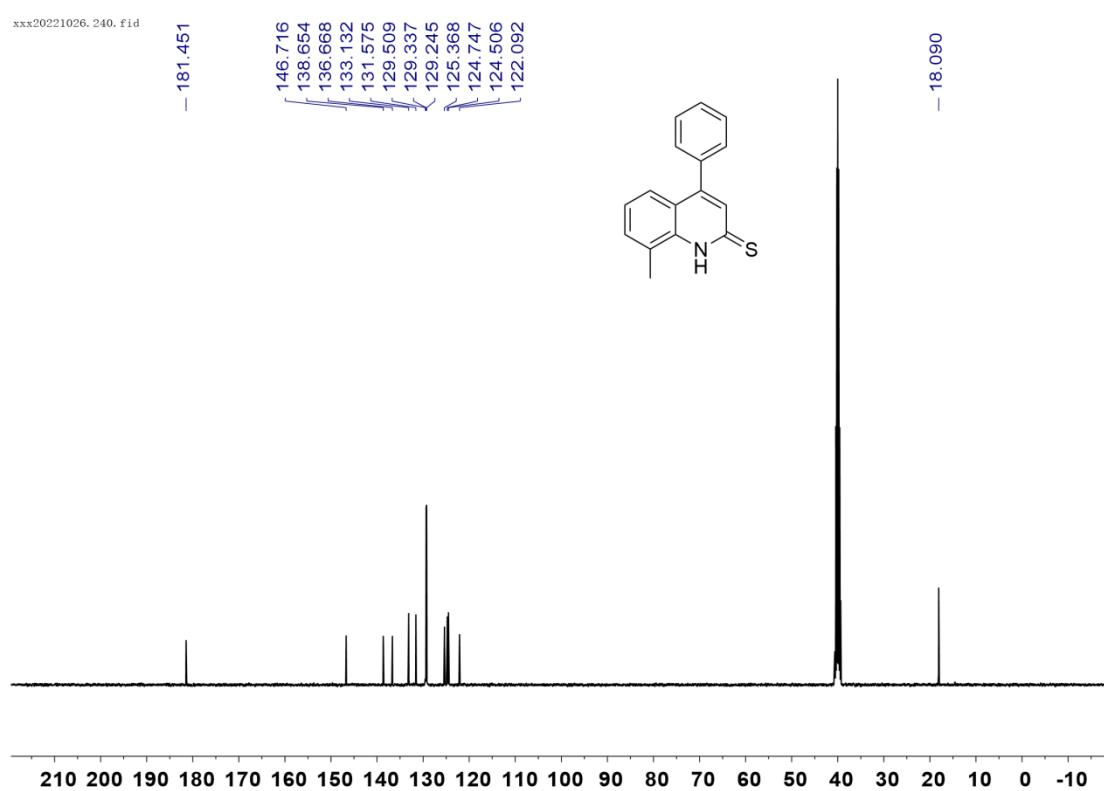
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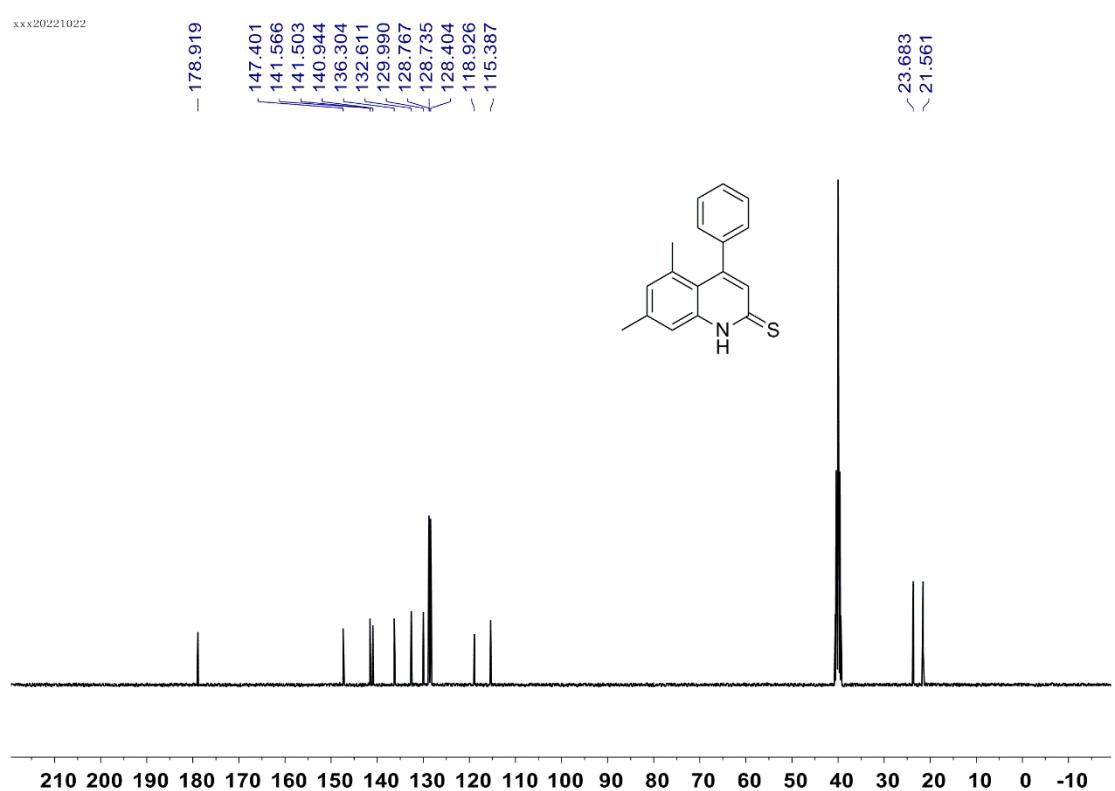
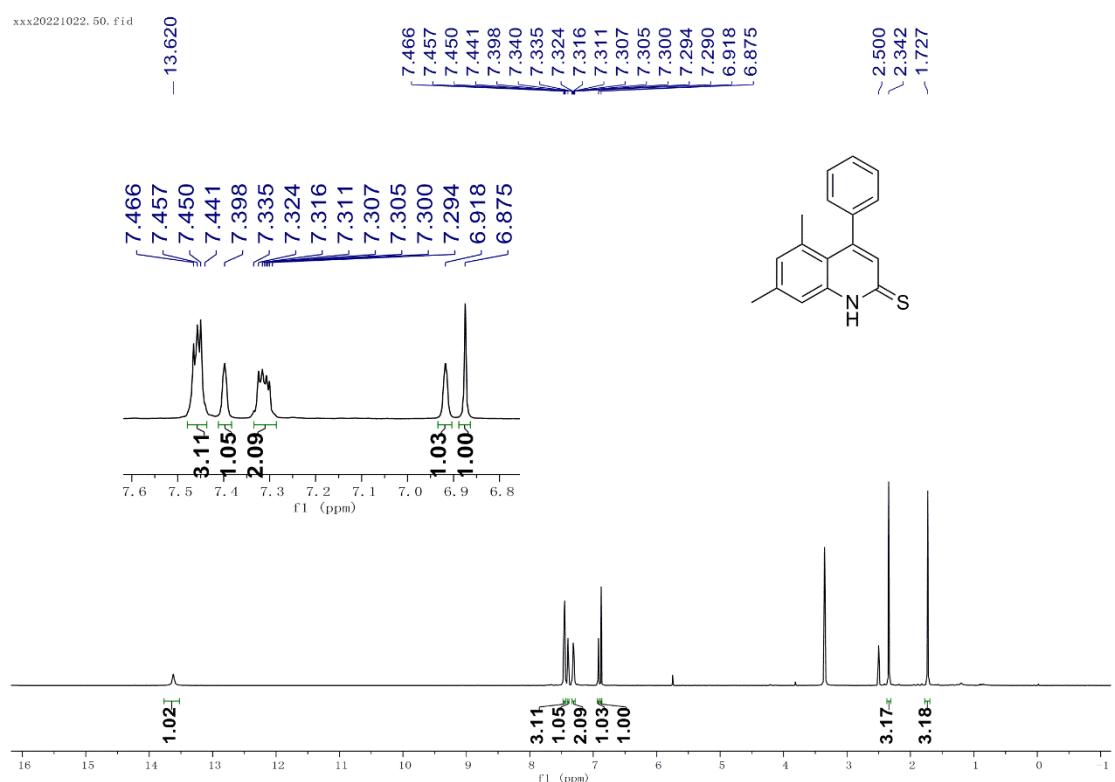
**<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) for 3h**



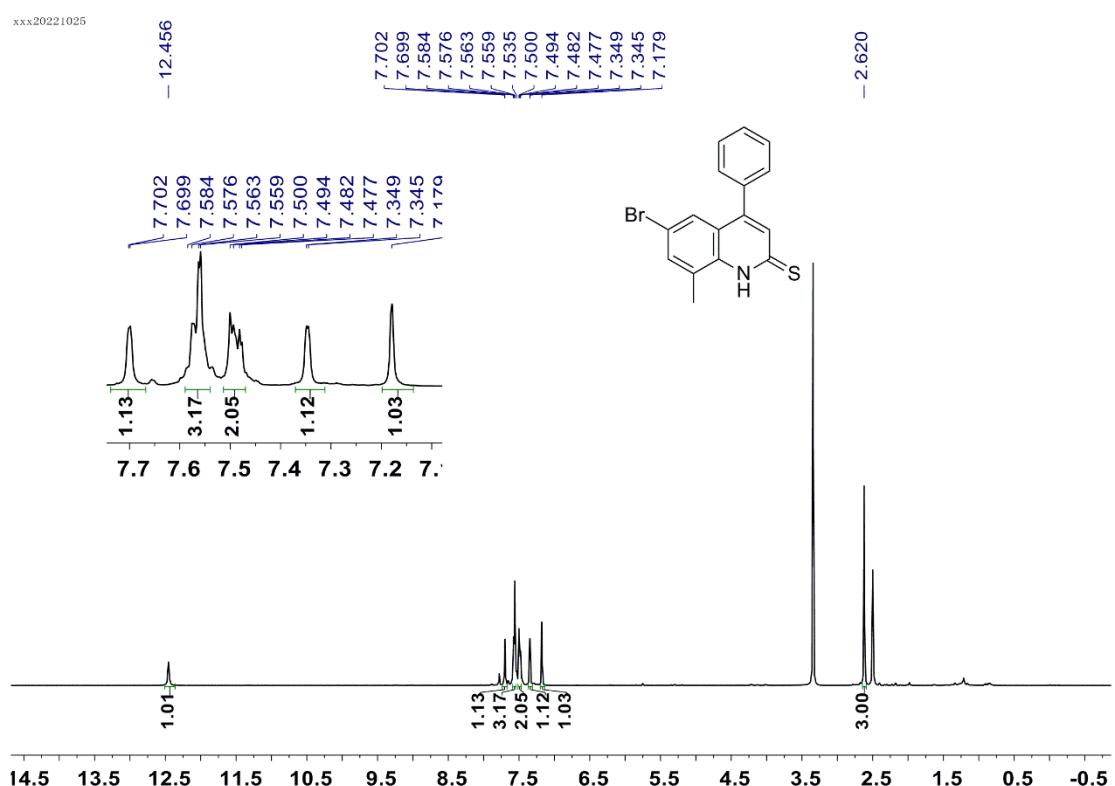
**<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) for 3h**



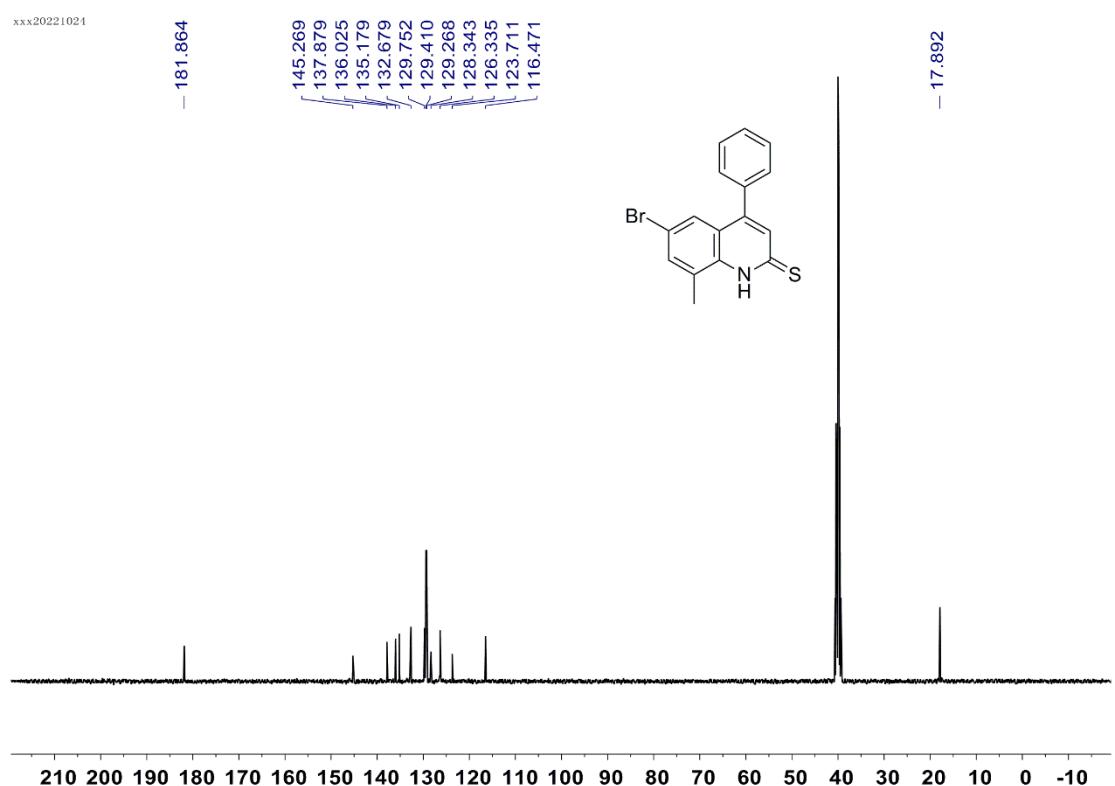
**<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) for 3i**



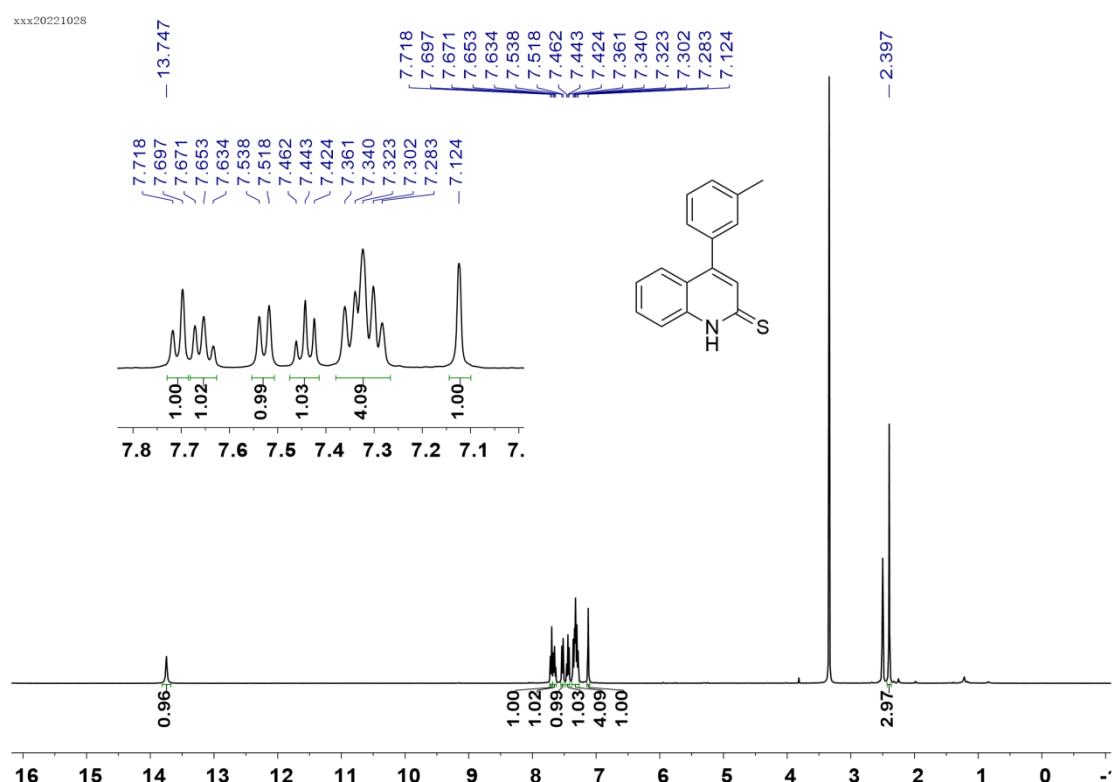
**<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) for **3j**



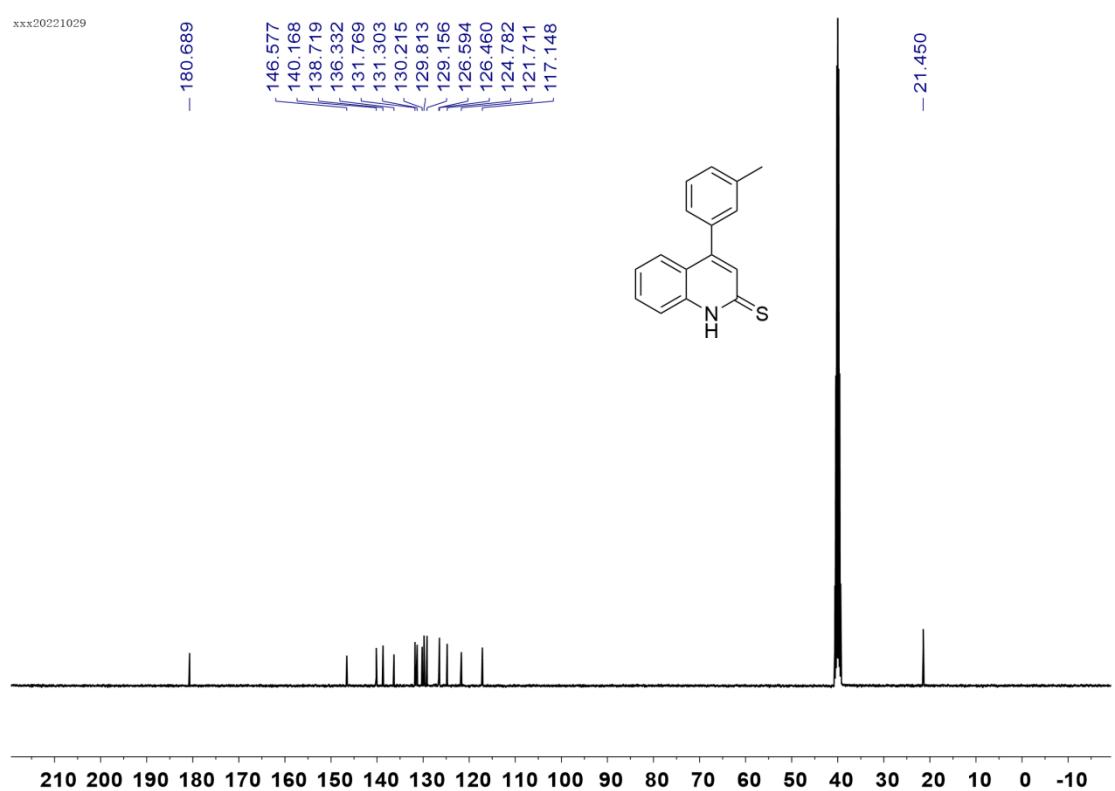
**<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) for **3j**



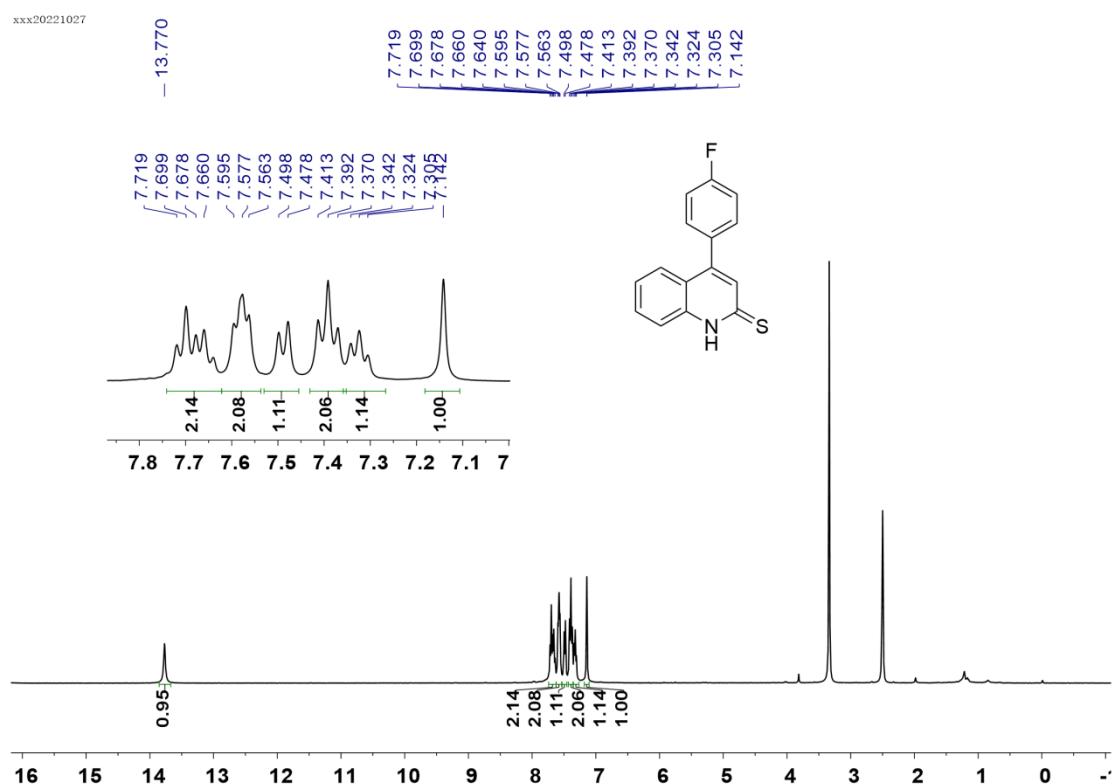
**<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) for **3k**



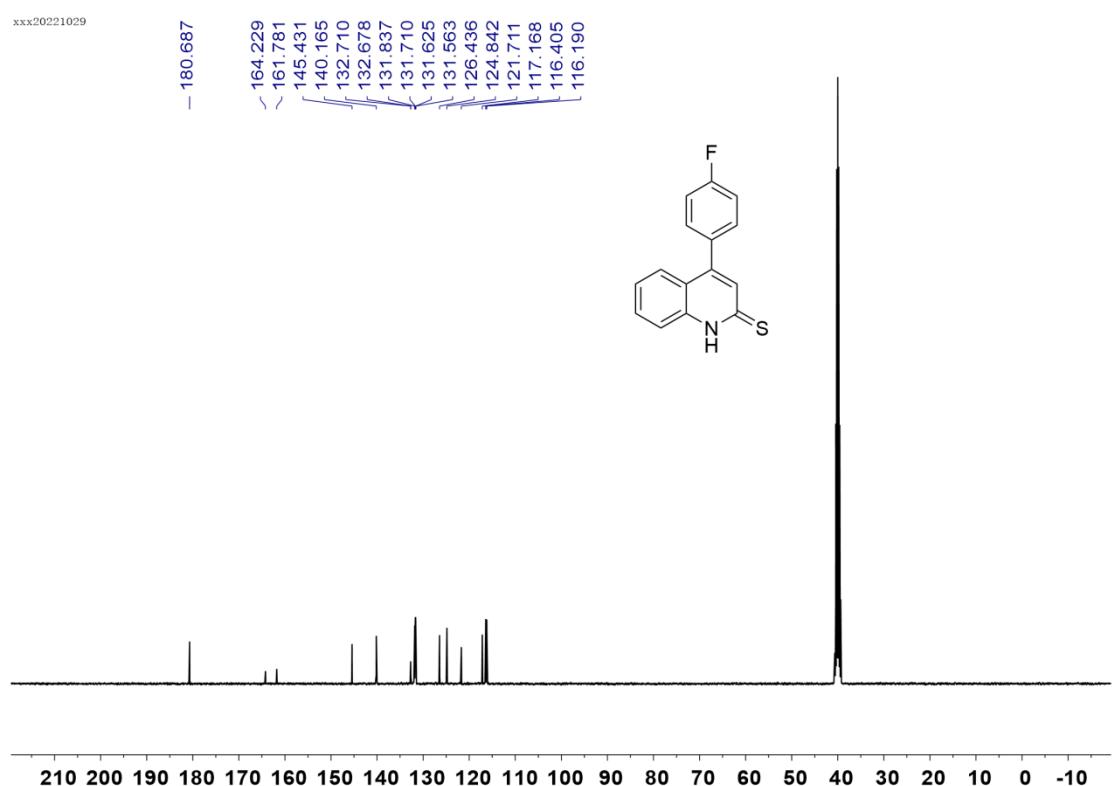
**<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) for **3k**



**<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) for **3l**

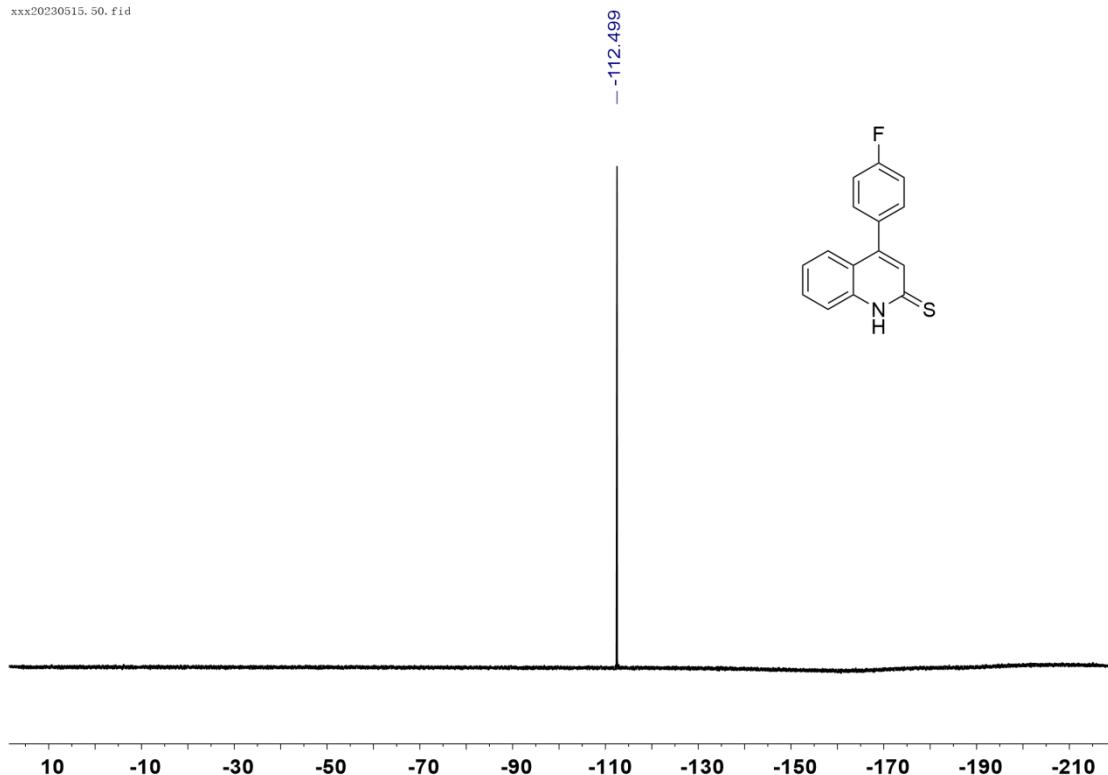


**<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) for **3l**

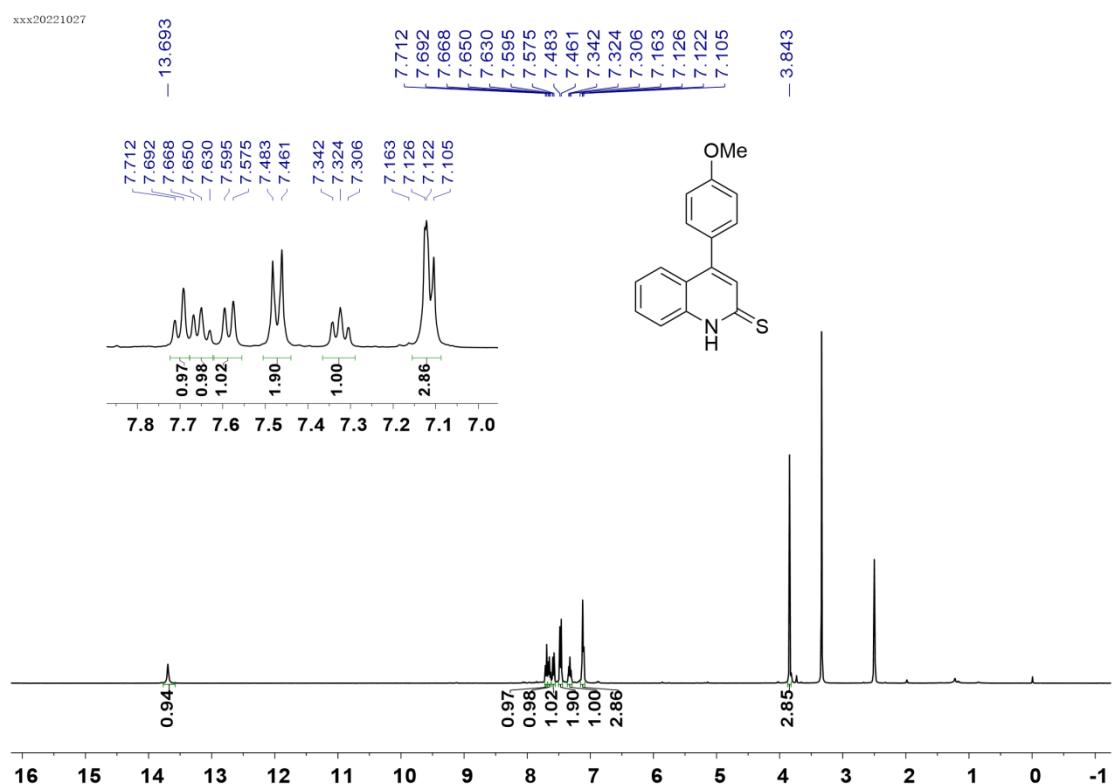


**<sup>19</sup>F NMR** (376 MHz, DMSO-*d*<sub>6</sub>) for **3l**

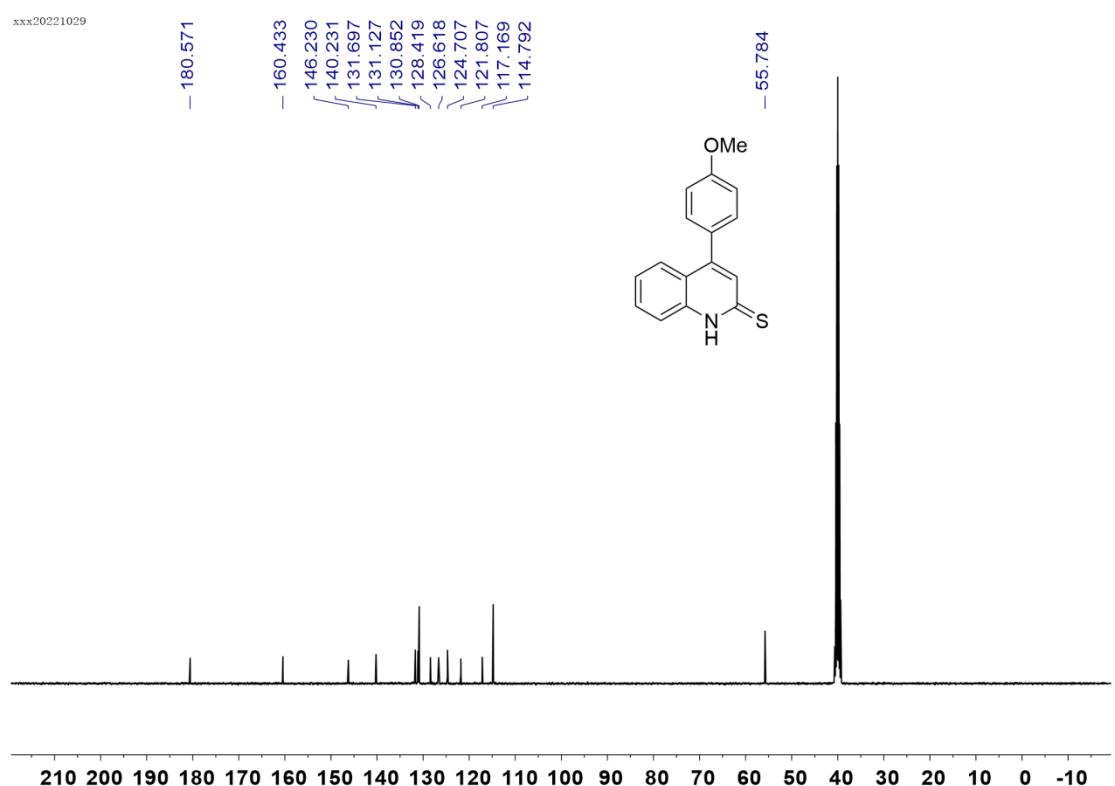
xxx20230515.50.fid



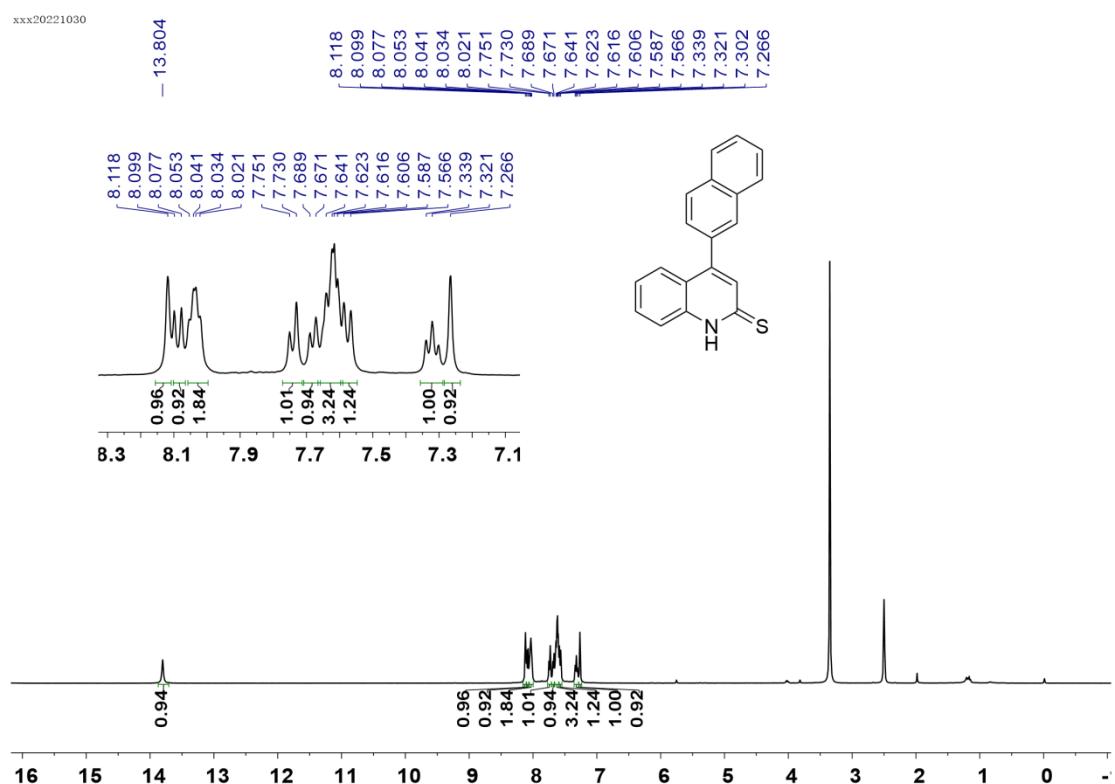
**<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) for **3m**



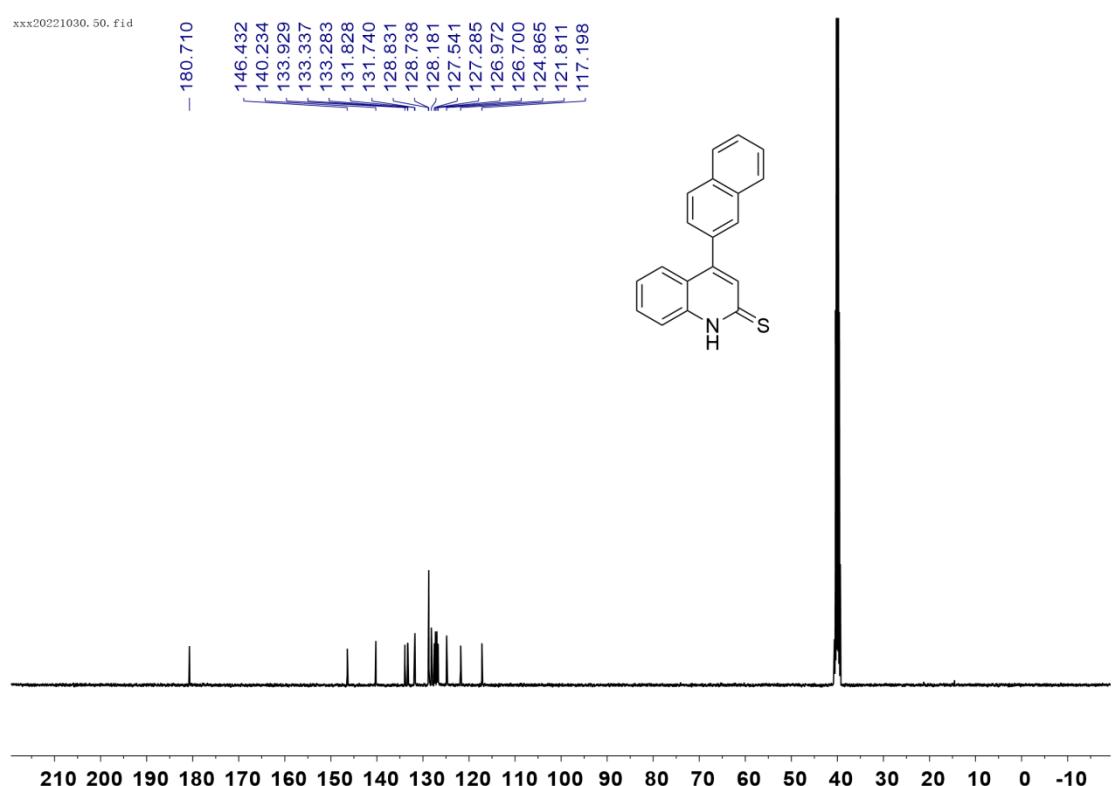
**<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) for **3m**



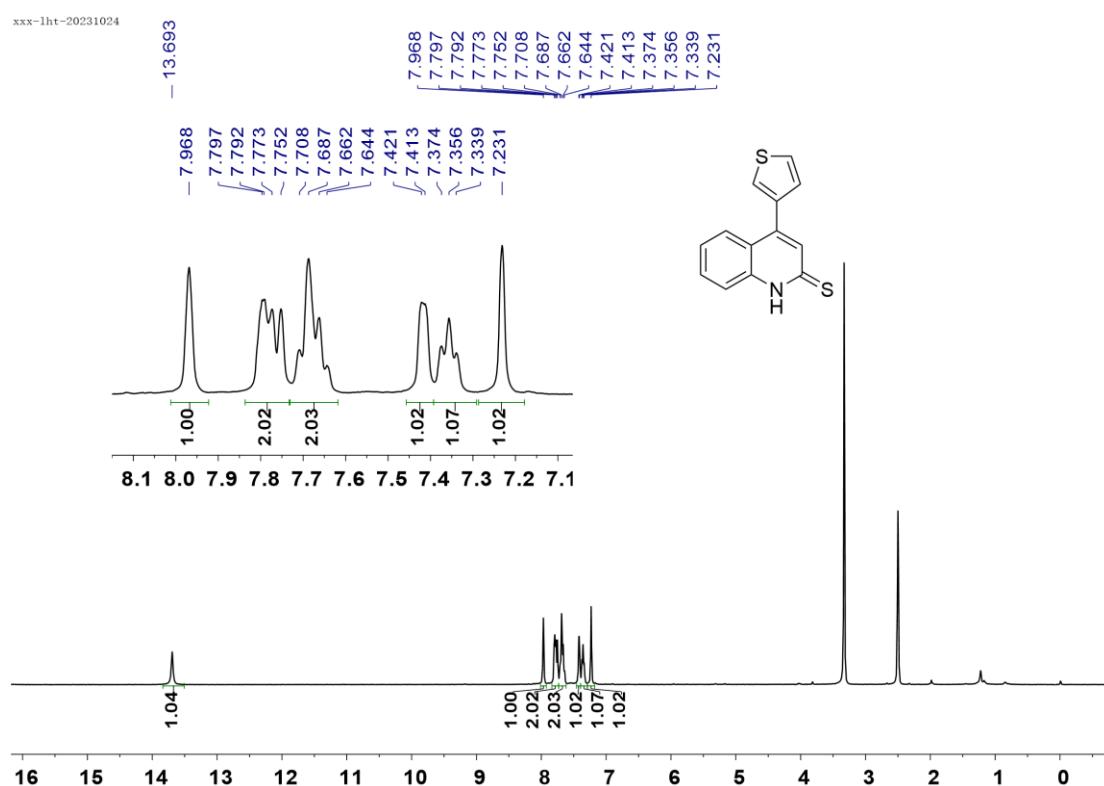
**<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) for 3n**



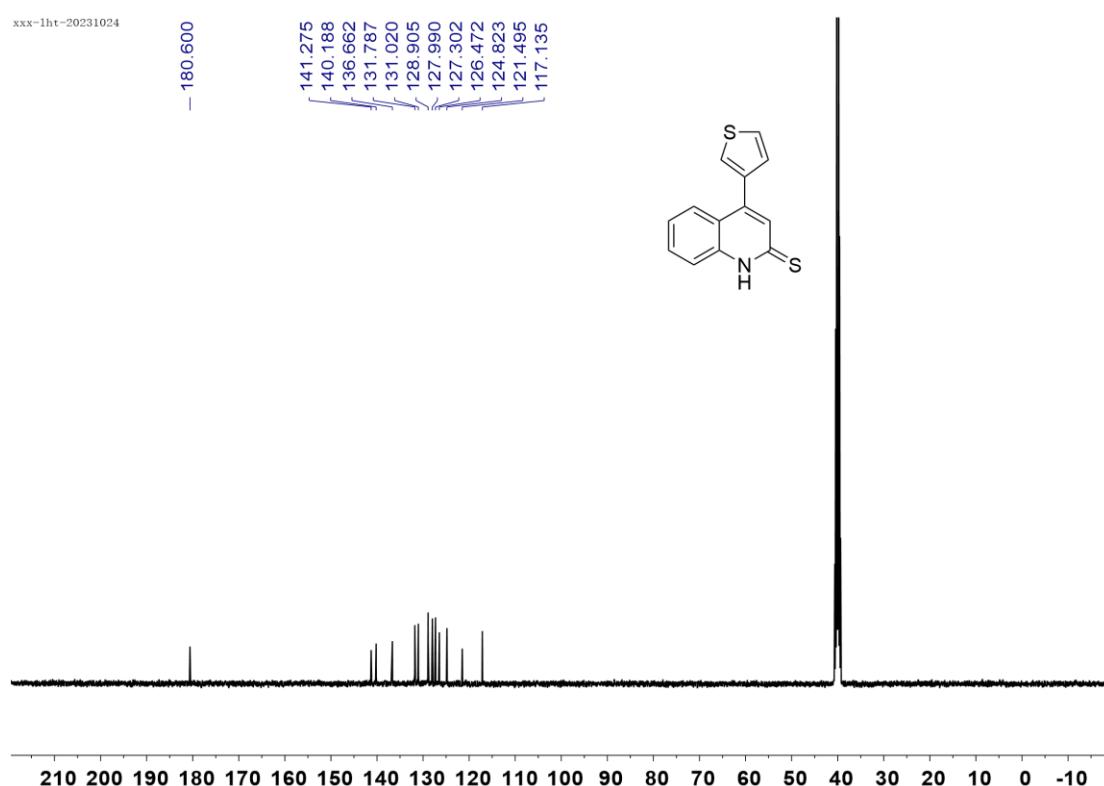
**<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) for 3n**



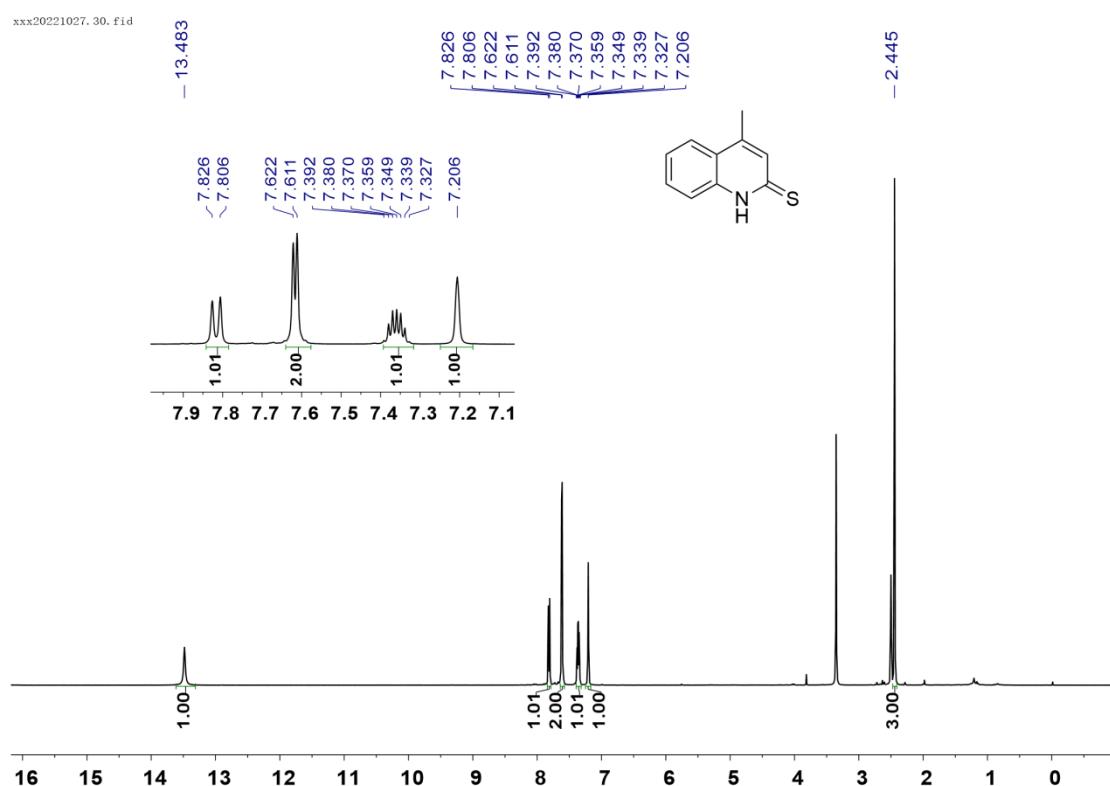
**<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) for **3o**



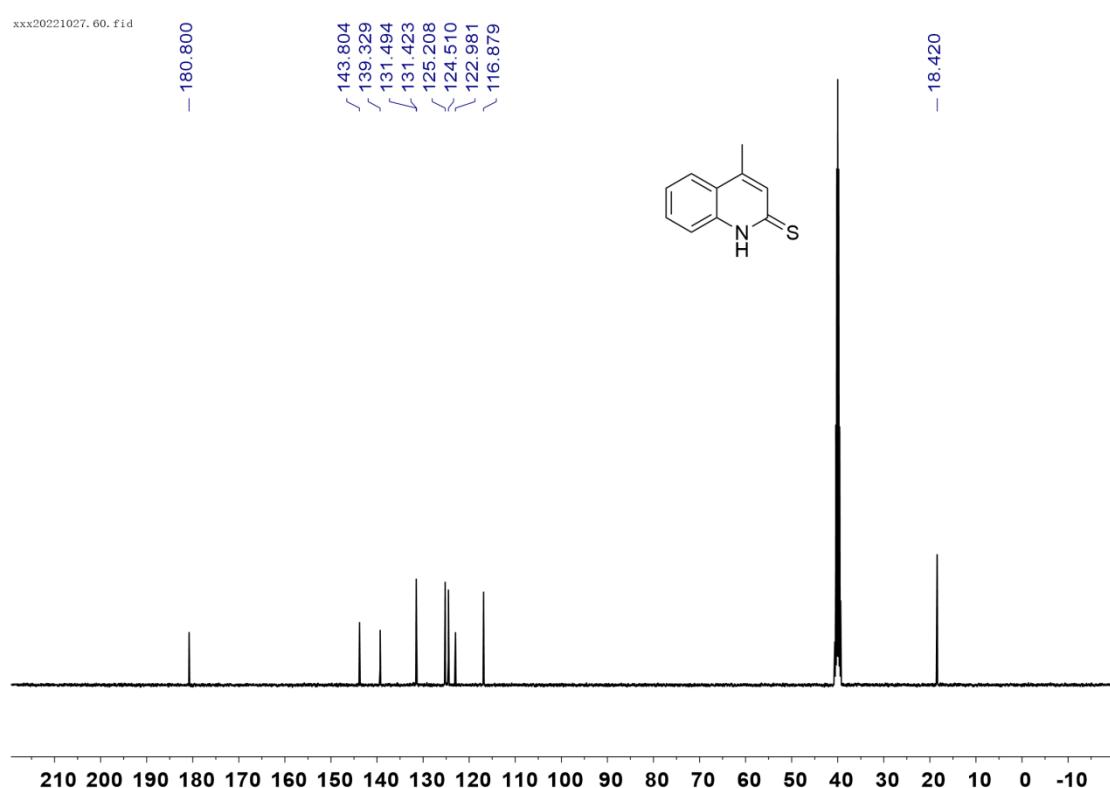
**<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) for **3o**



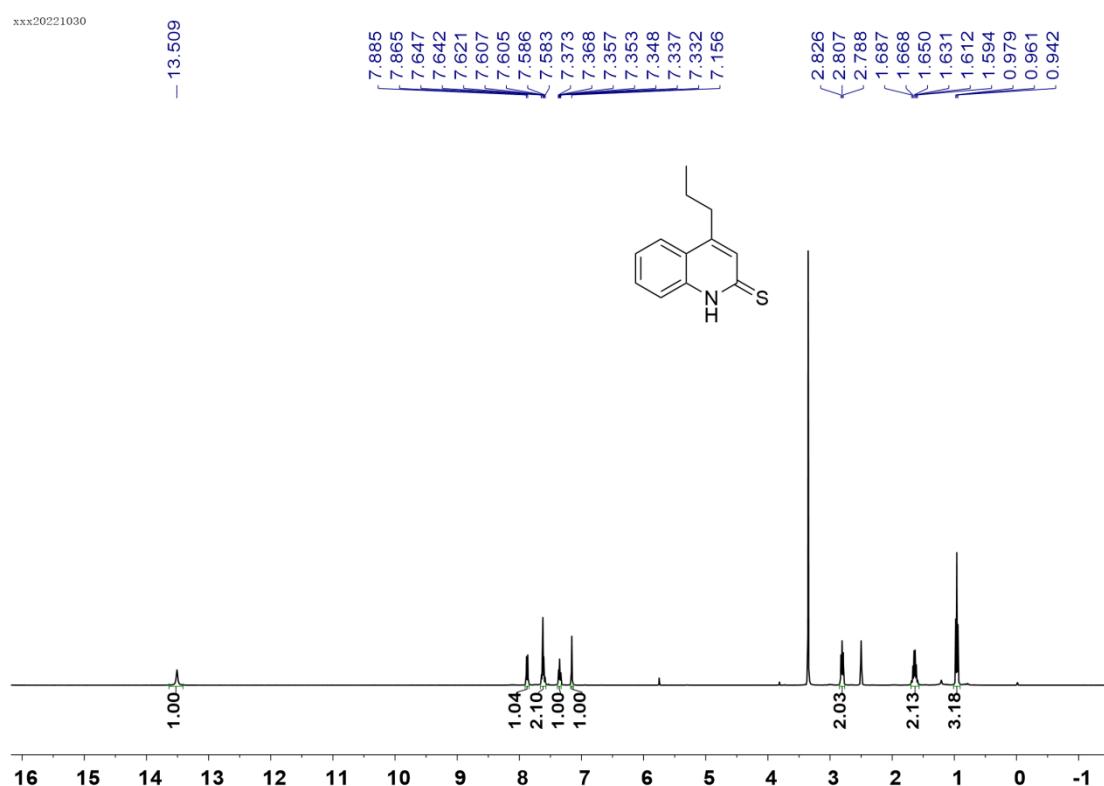
**<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) for 3p**



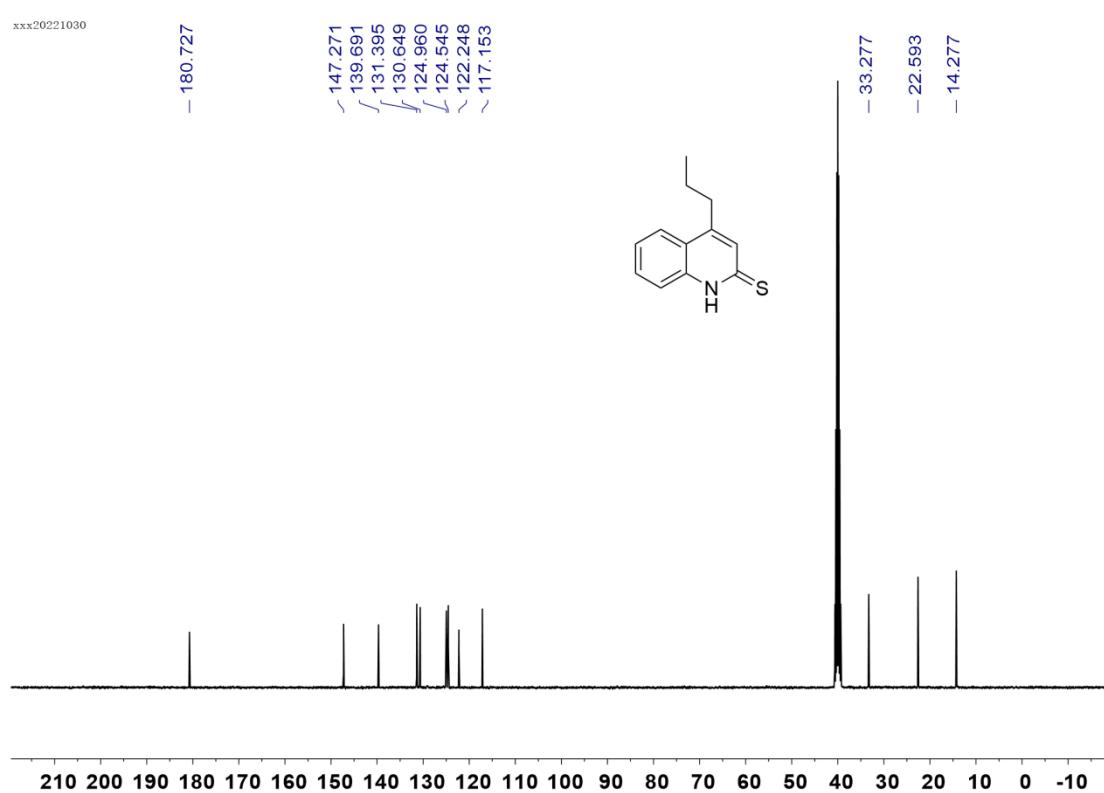
**<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) for 3p**



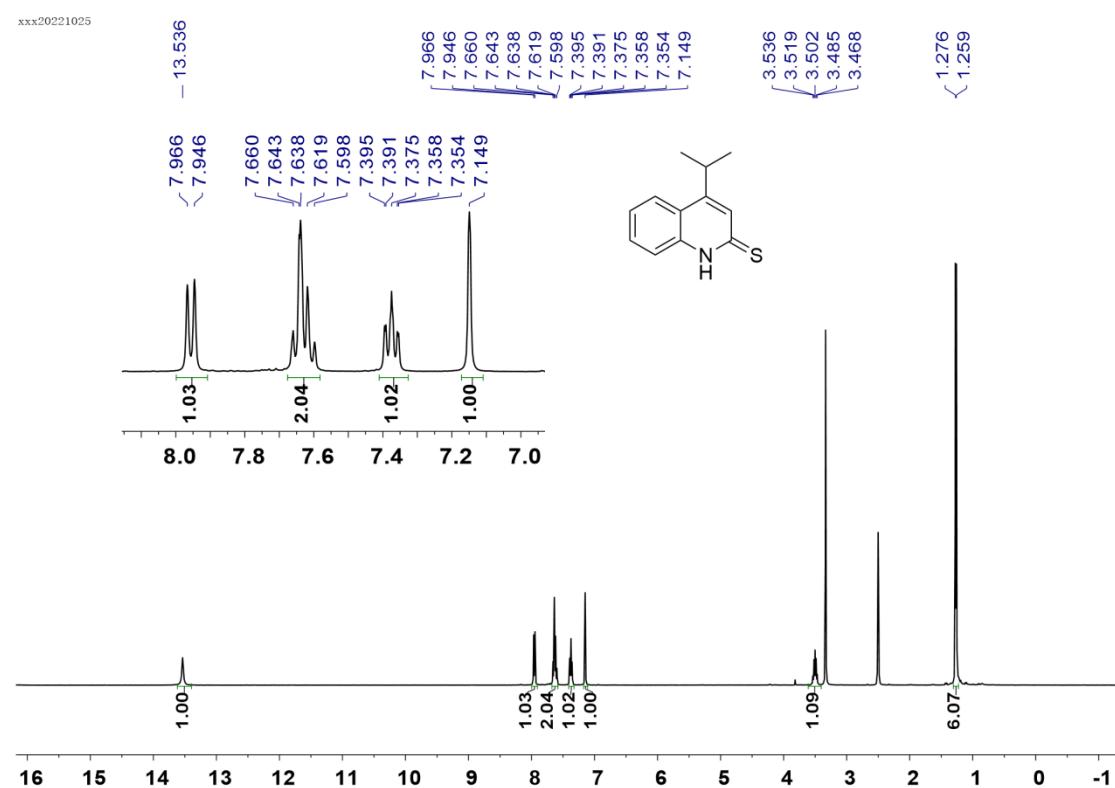
**<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) for **3q**



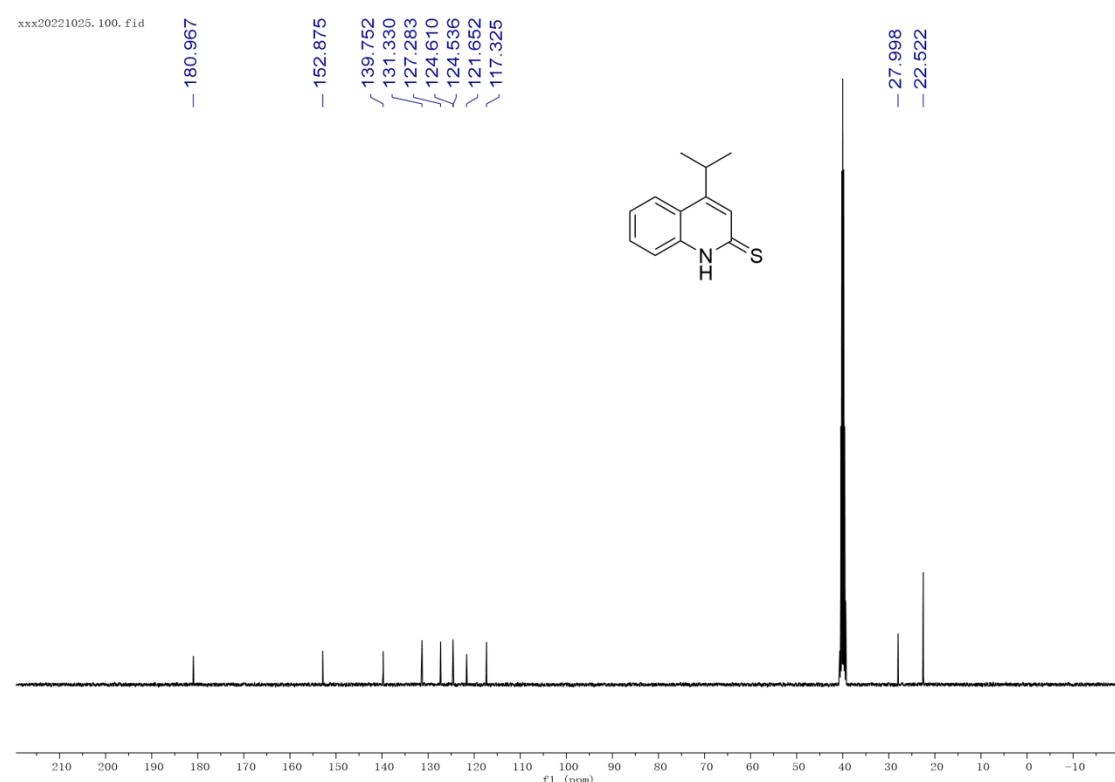
**<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) for **3q**



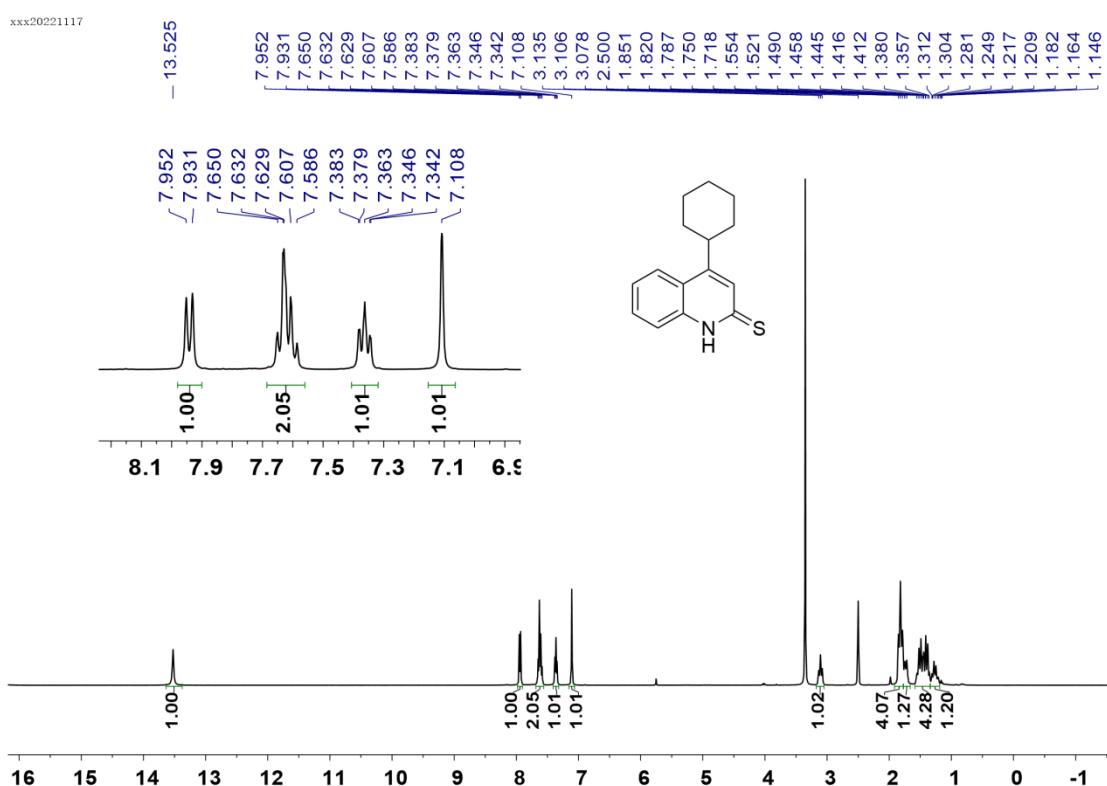
**<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) for **3r**



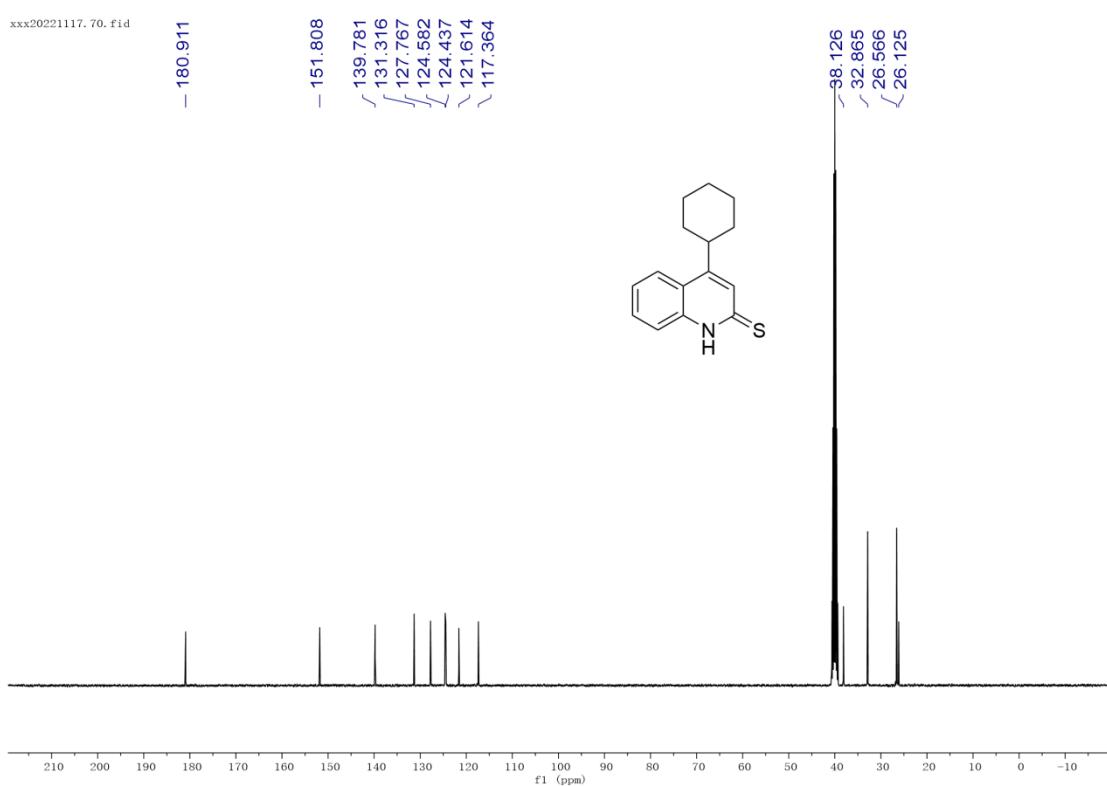
**<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) for **3r**



**<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) for **3s**

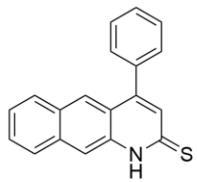
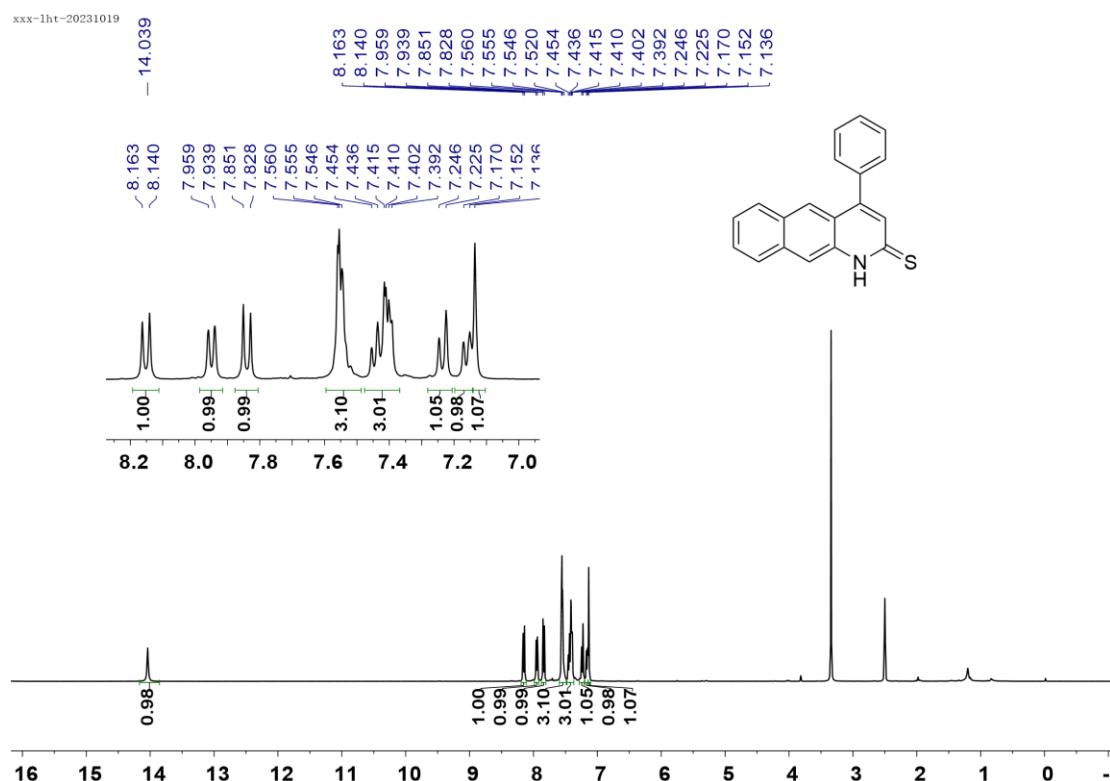


**<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) for **3s**



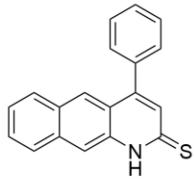
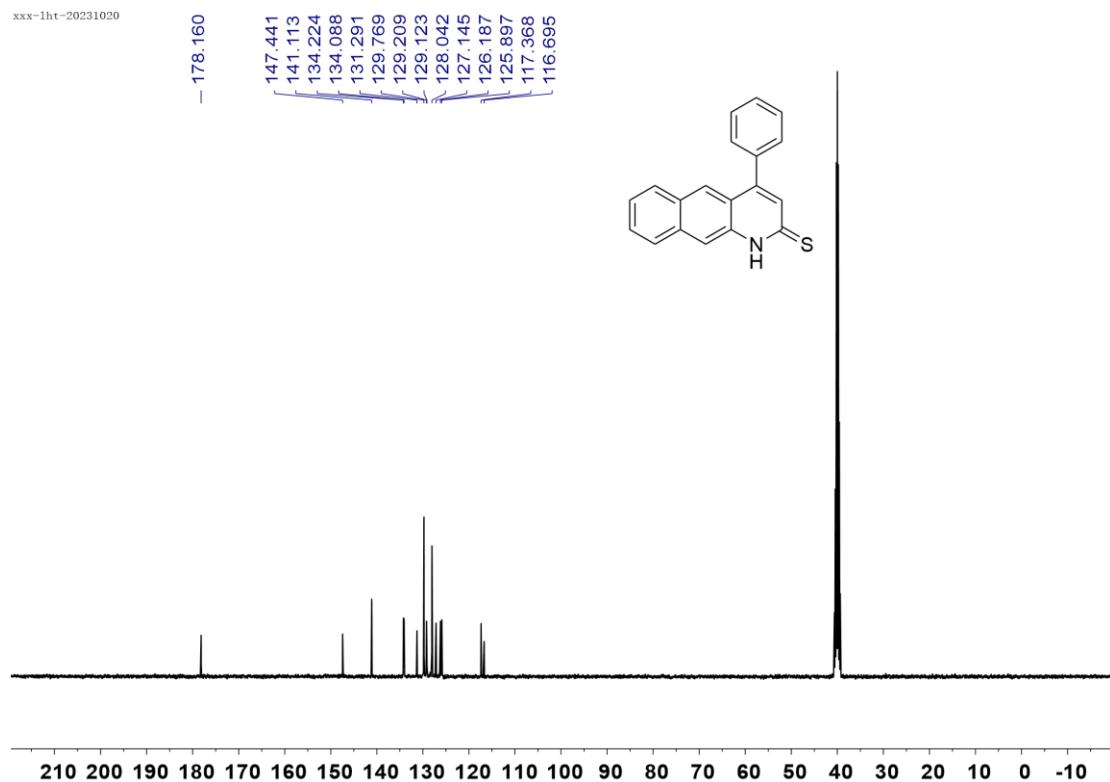
**<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) for **3v**

xxx-1ht-20231019

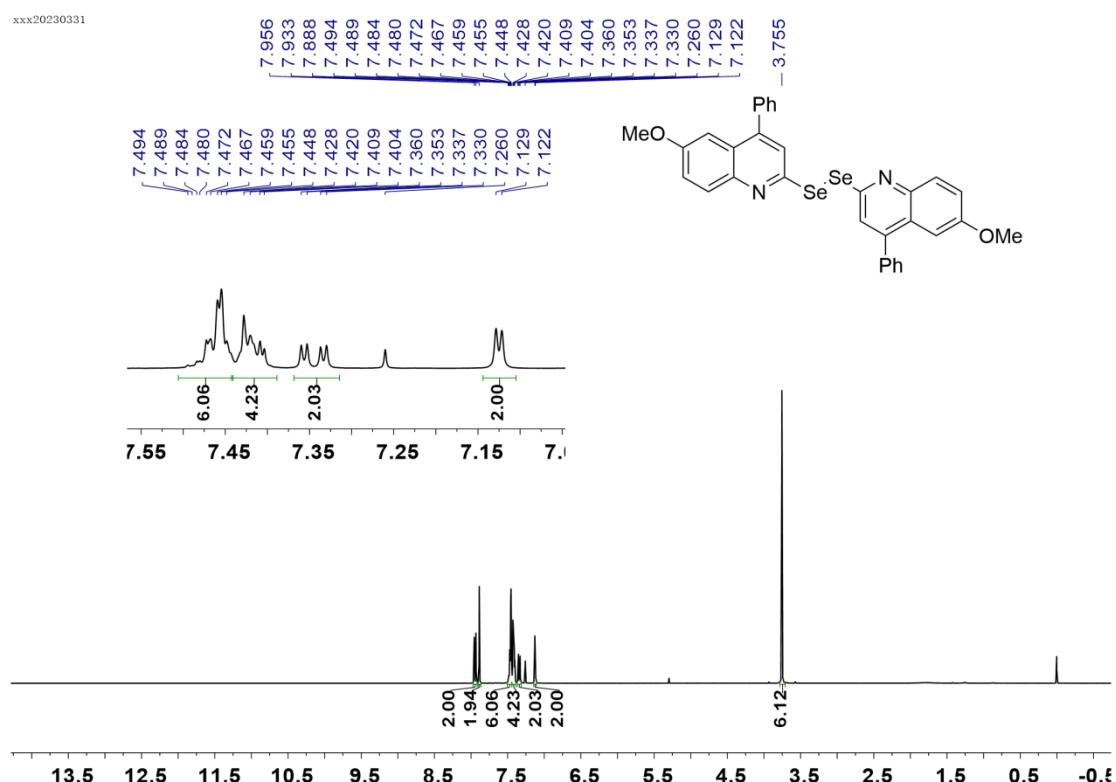


**<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) for **3v**

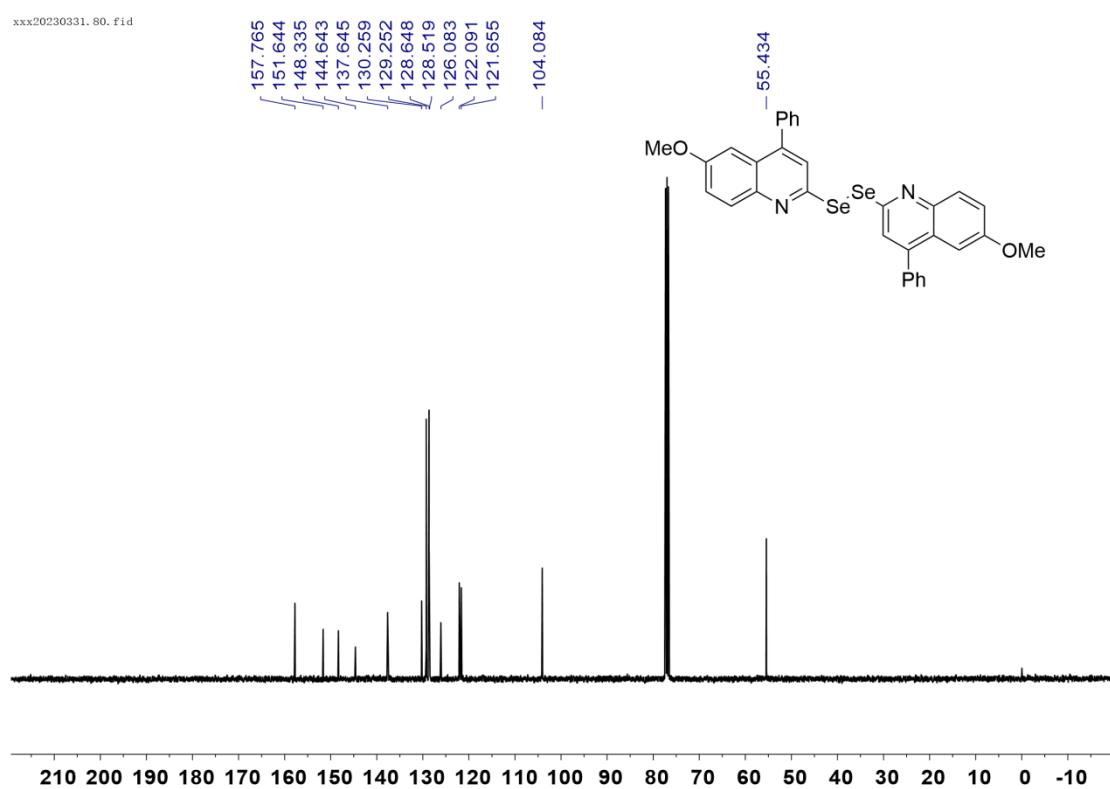
xxx-1ht-20231020



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) for 5a**

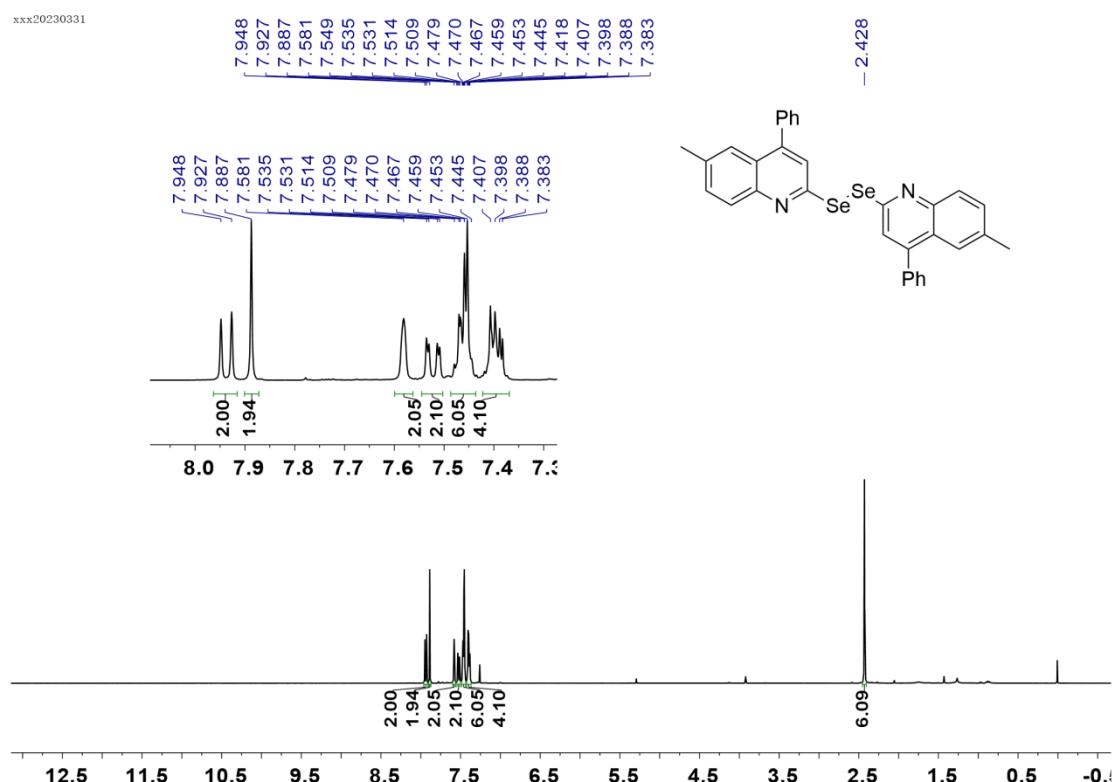


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for 5a**



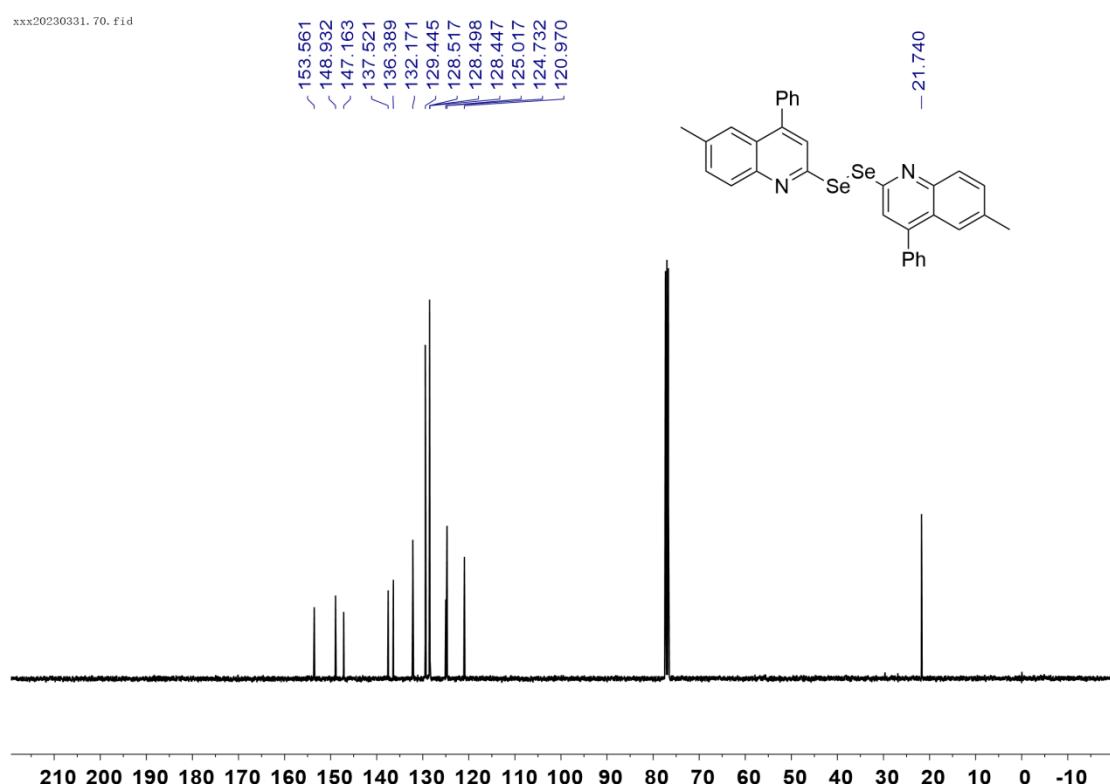
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ) for **5b**

xxx20230331



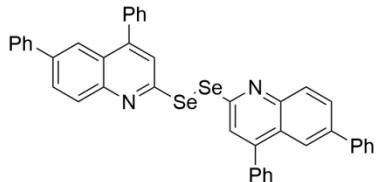
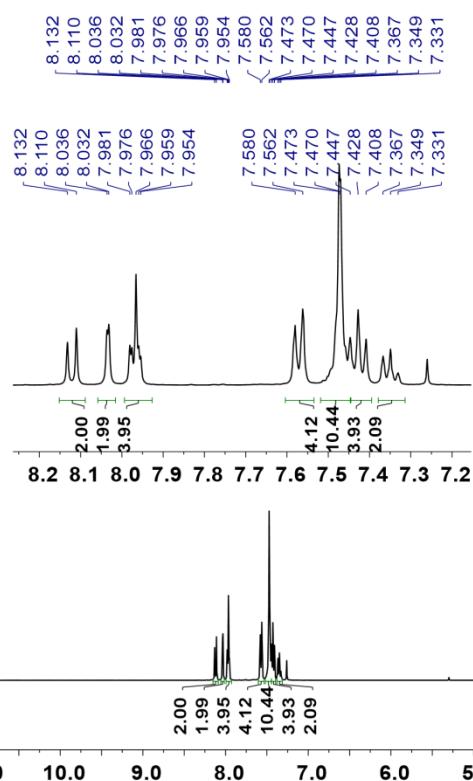
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for **5b**

xxx20230331, 70, fid



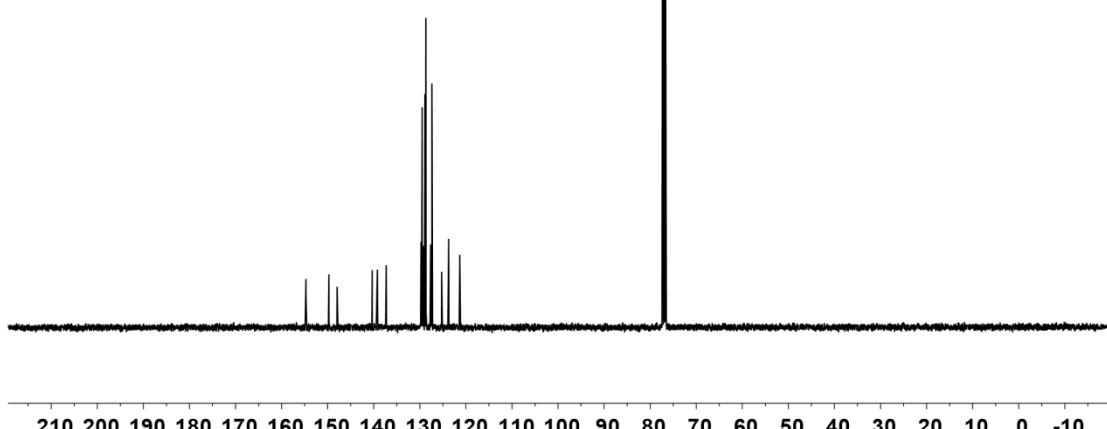
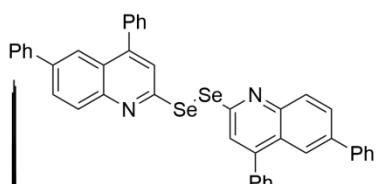
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ) for **5c**

xxx20230403



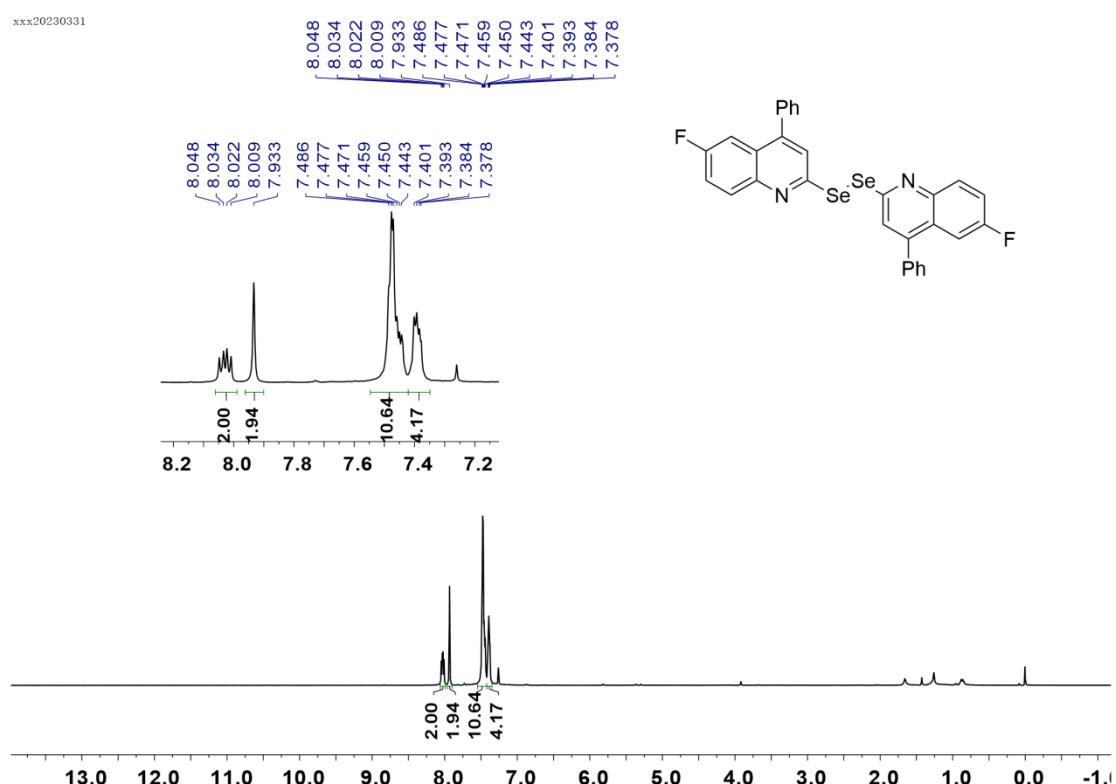
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) for **5c**

xxx20230403. 30. fid



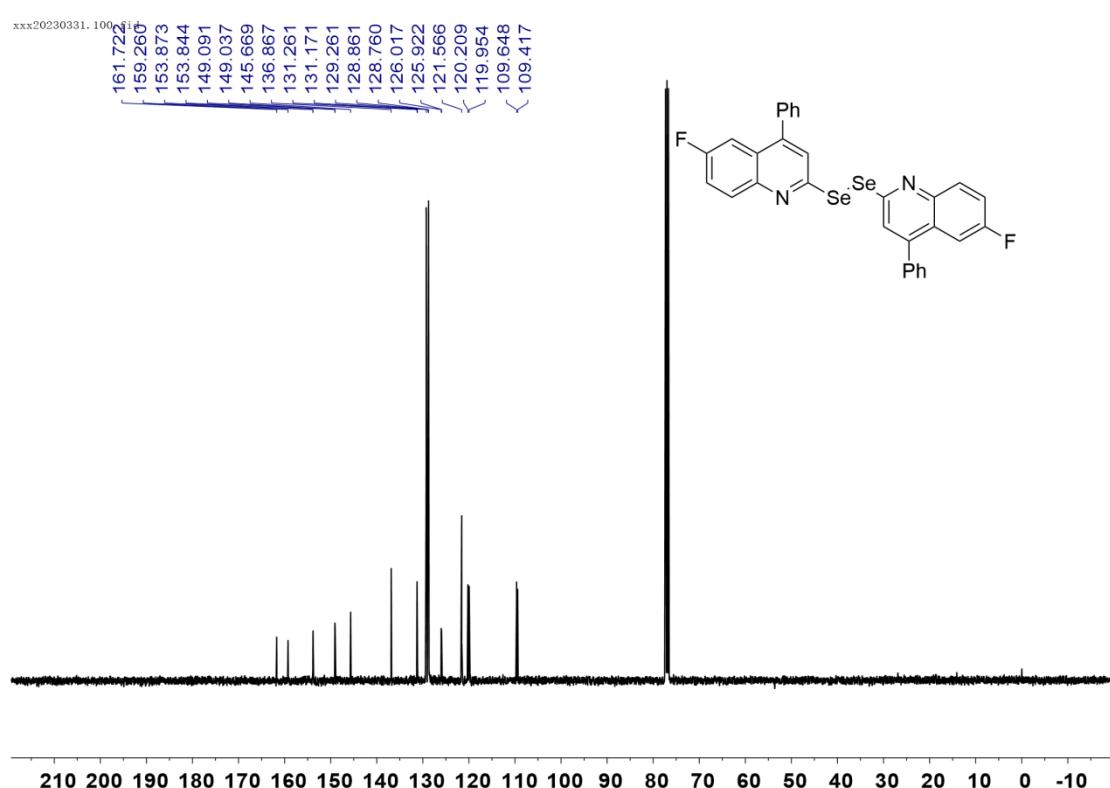
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) for 5d**

xxx20230331



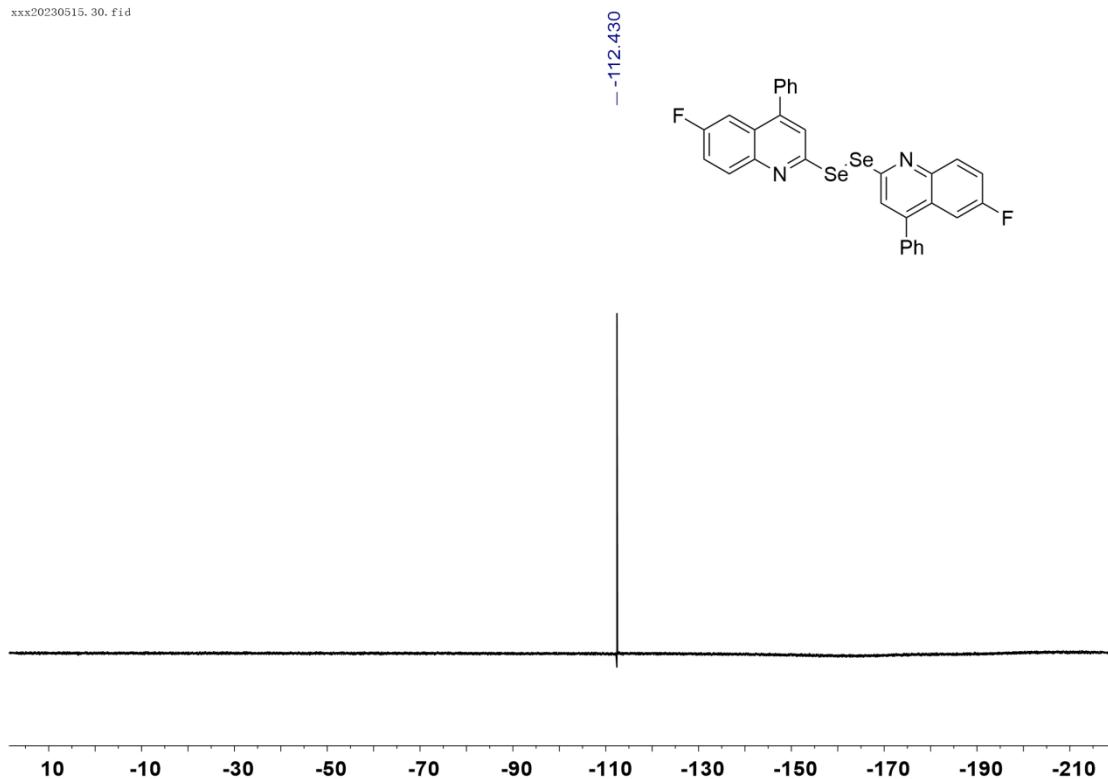
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for 5d**

xxx20230331, 100MHz



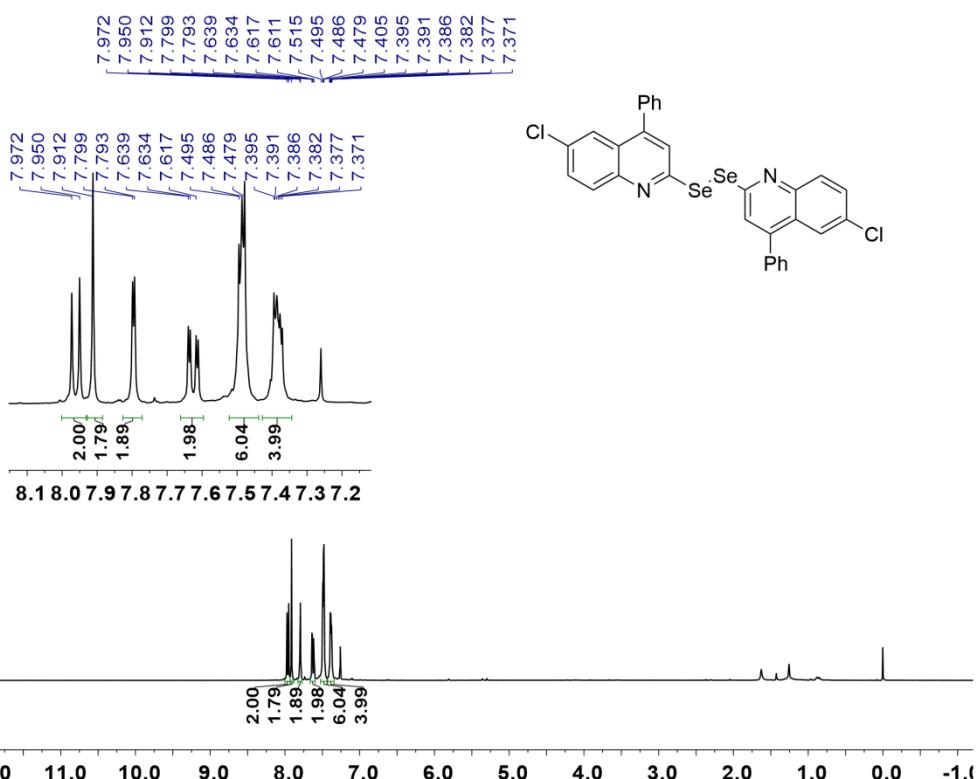
**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) for **5d**

xxx20230515.30.fid



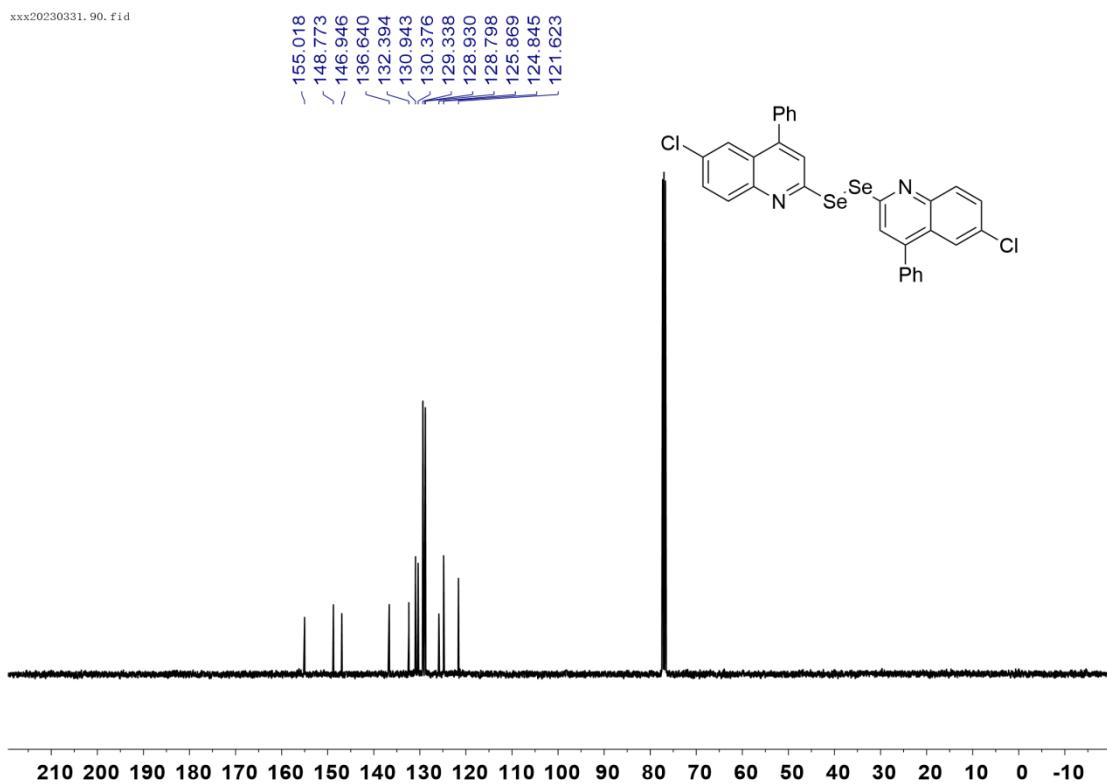
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ) for **5e**

xxx20230331



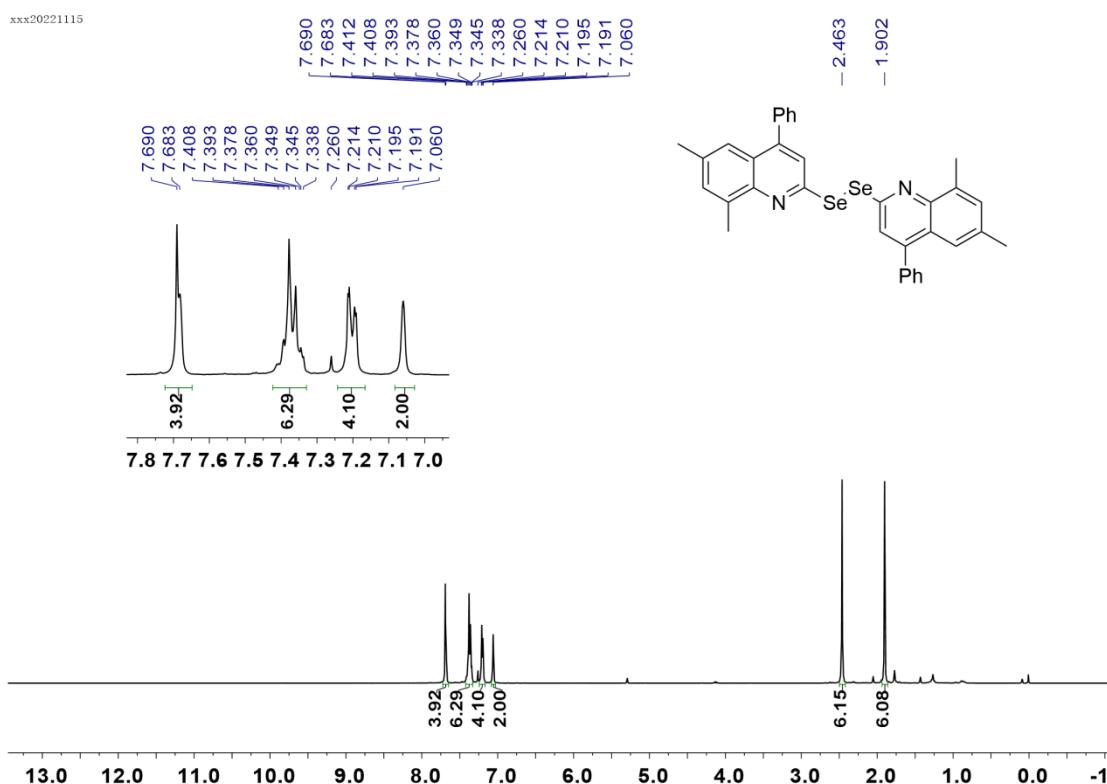
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) for **5e**

xxx20230331.90.fid



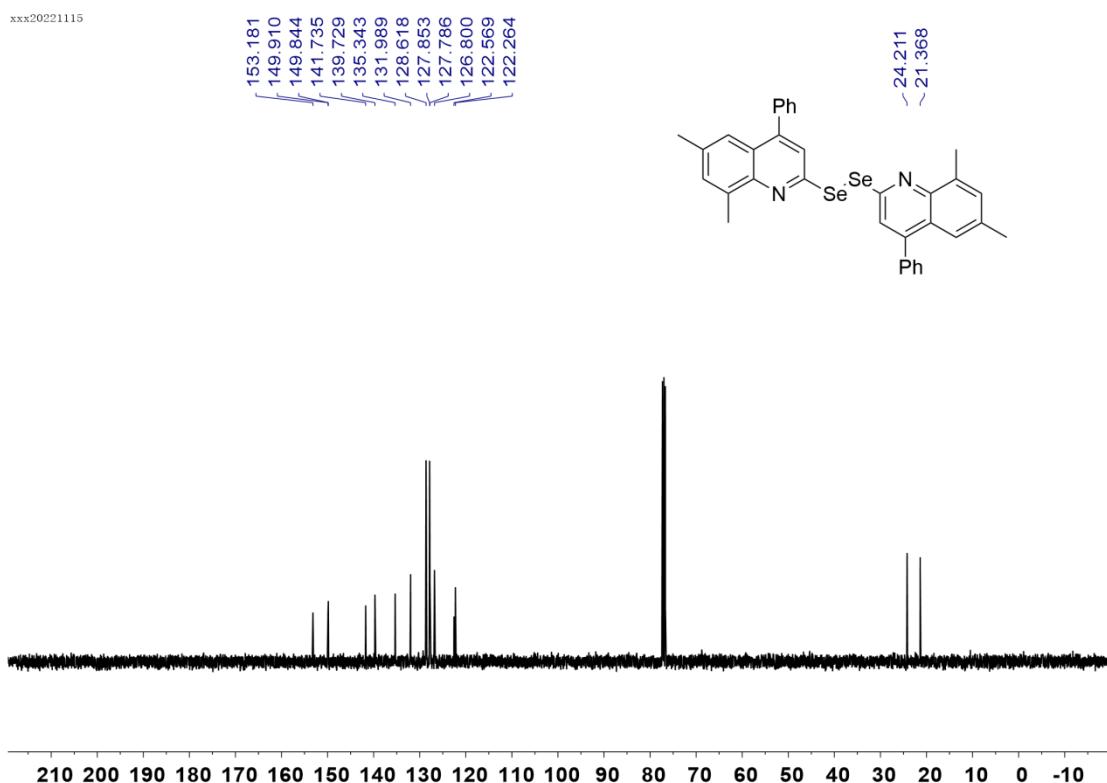
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) for **5f**

xxx20221115

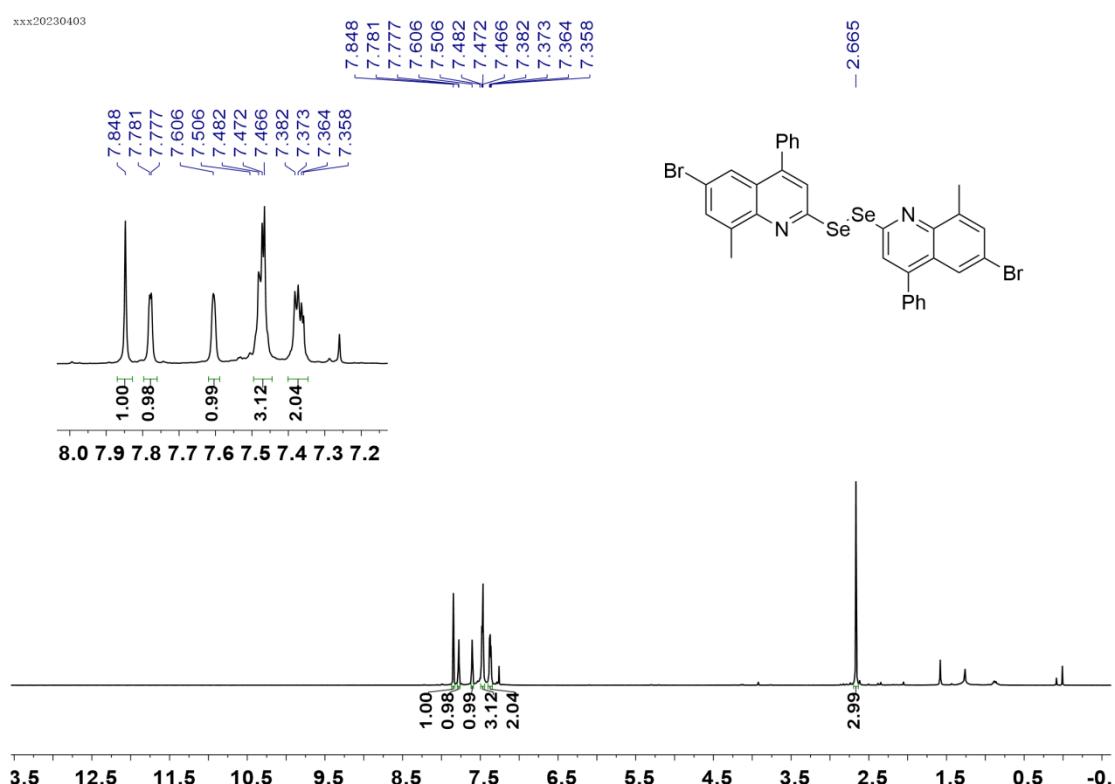


**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) for **5f**

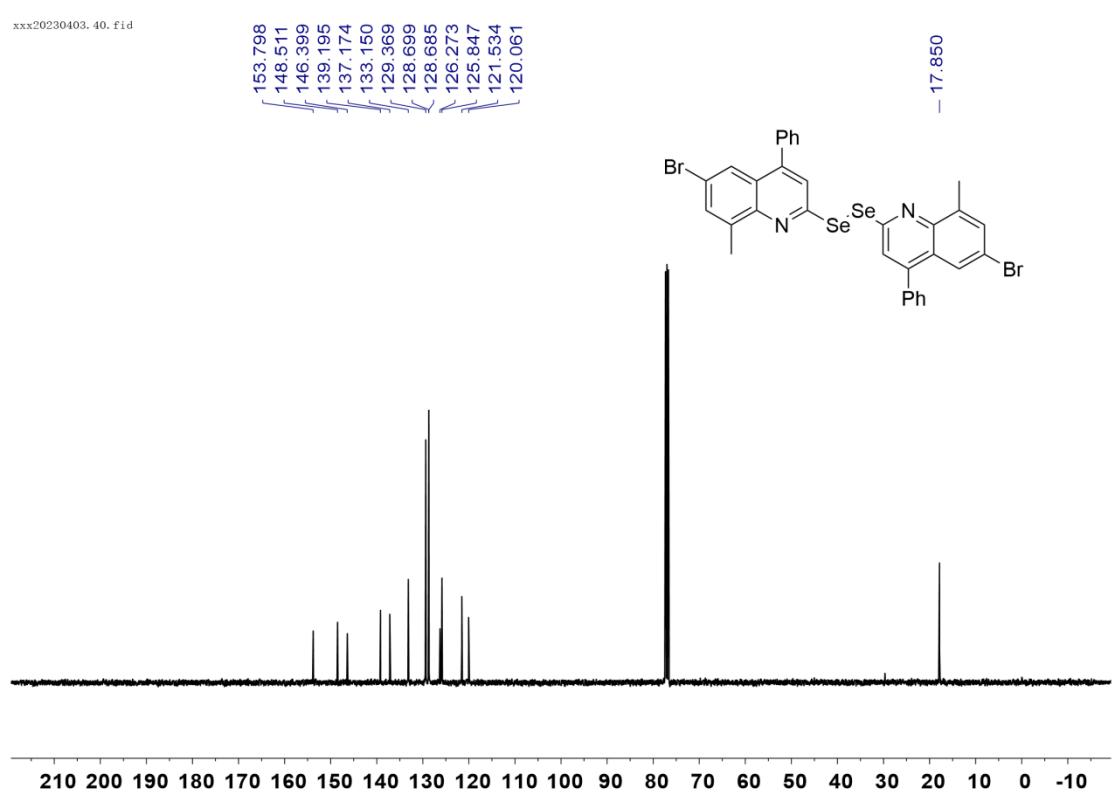
xxx20221115



**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ) for **5g**

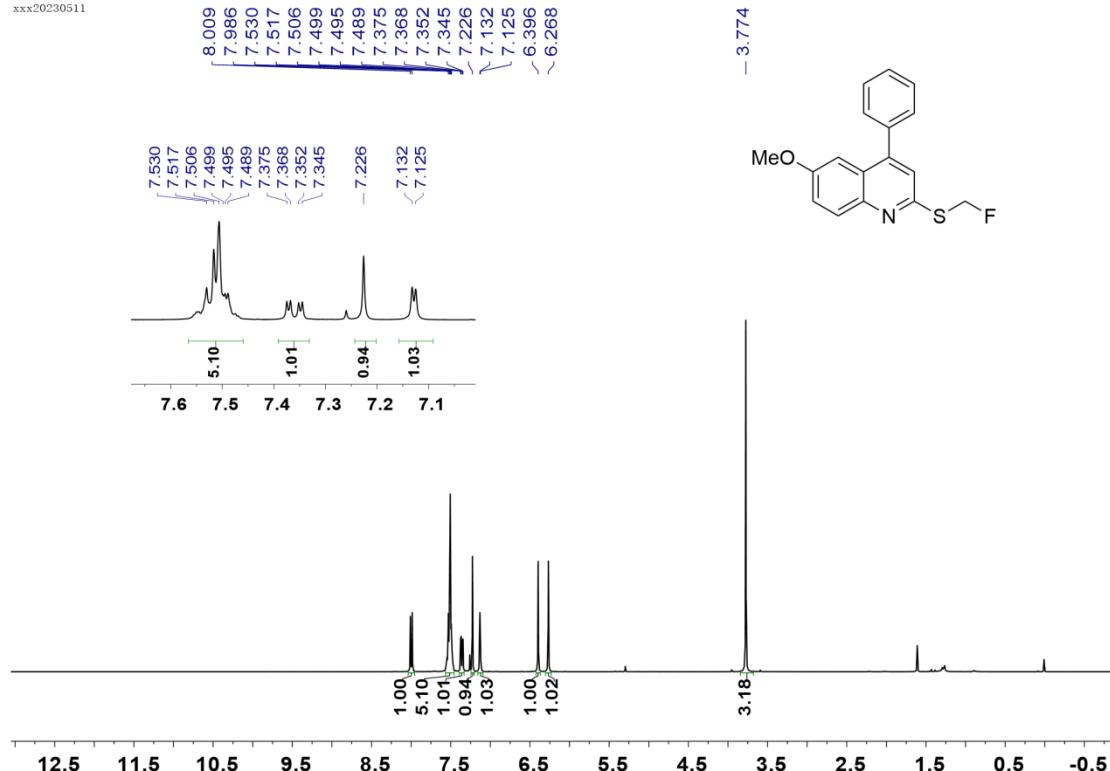


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for 5g



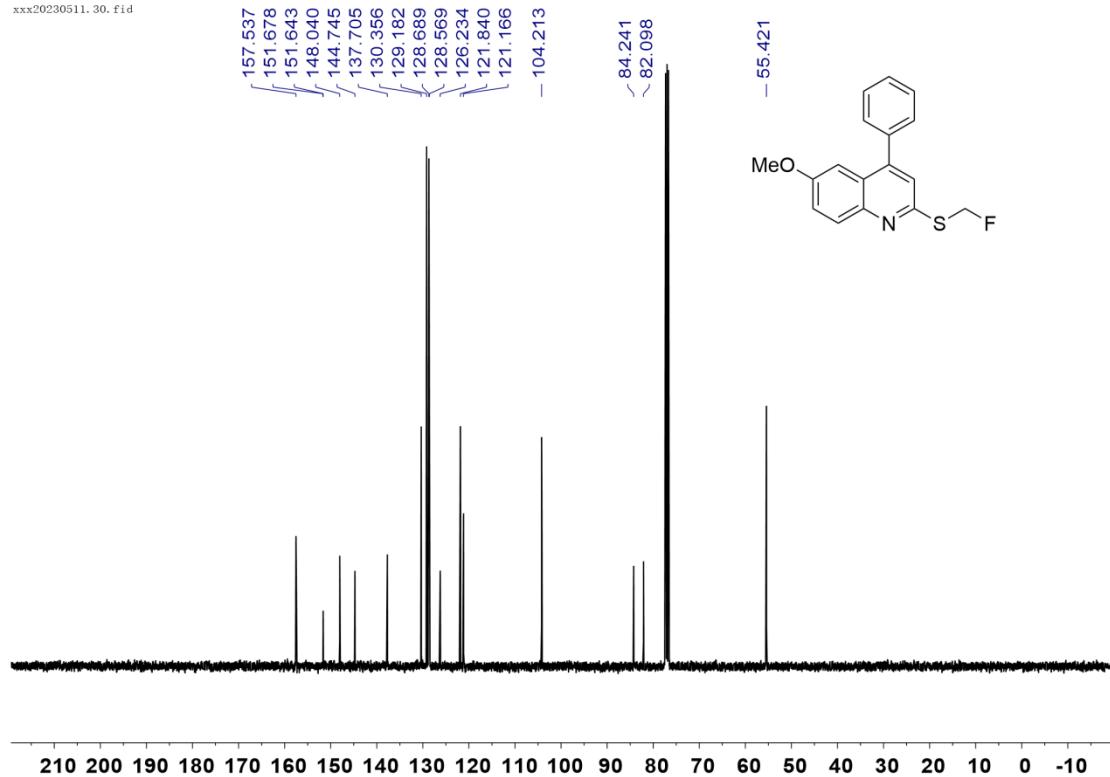
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) for **6a**

xxx20230511



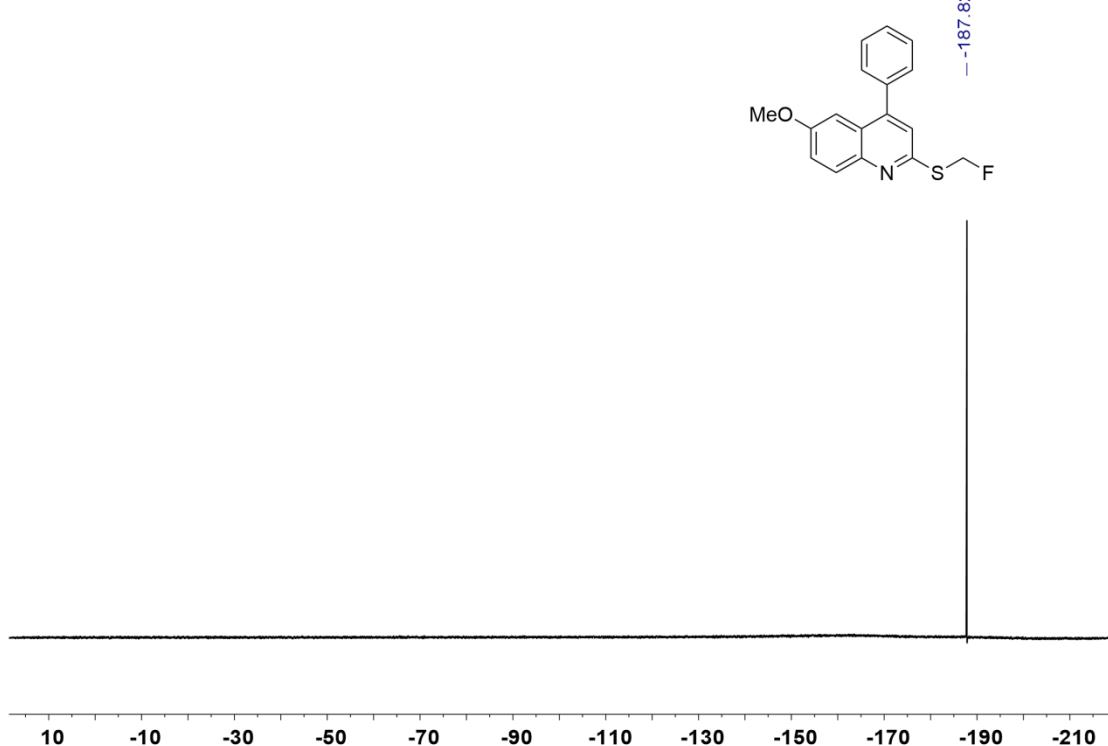
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for **6a**

xxx20230511. 30. fid



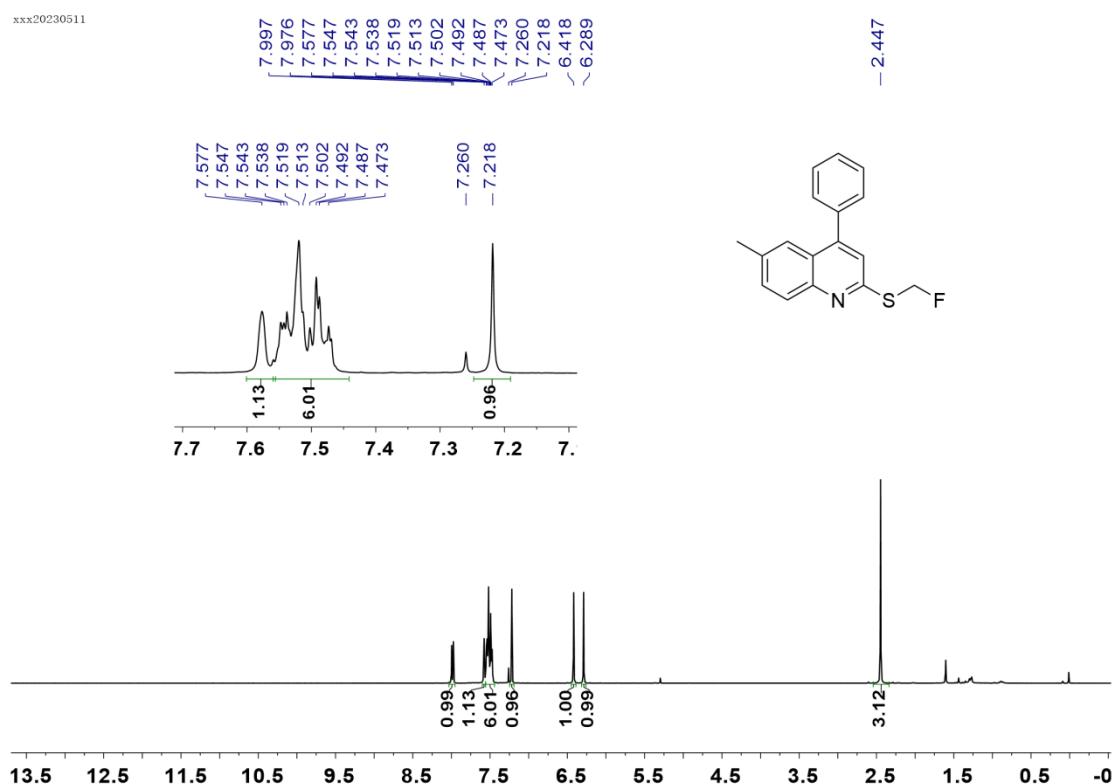
**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) for **6a**

xxx20230510.40.fid



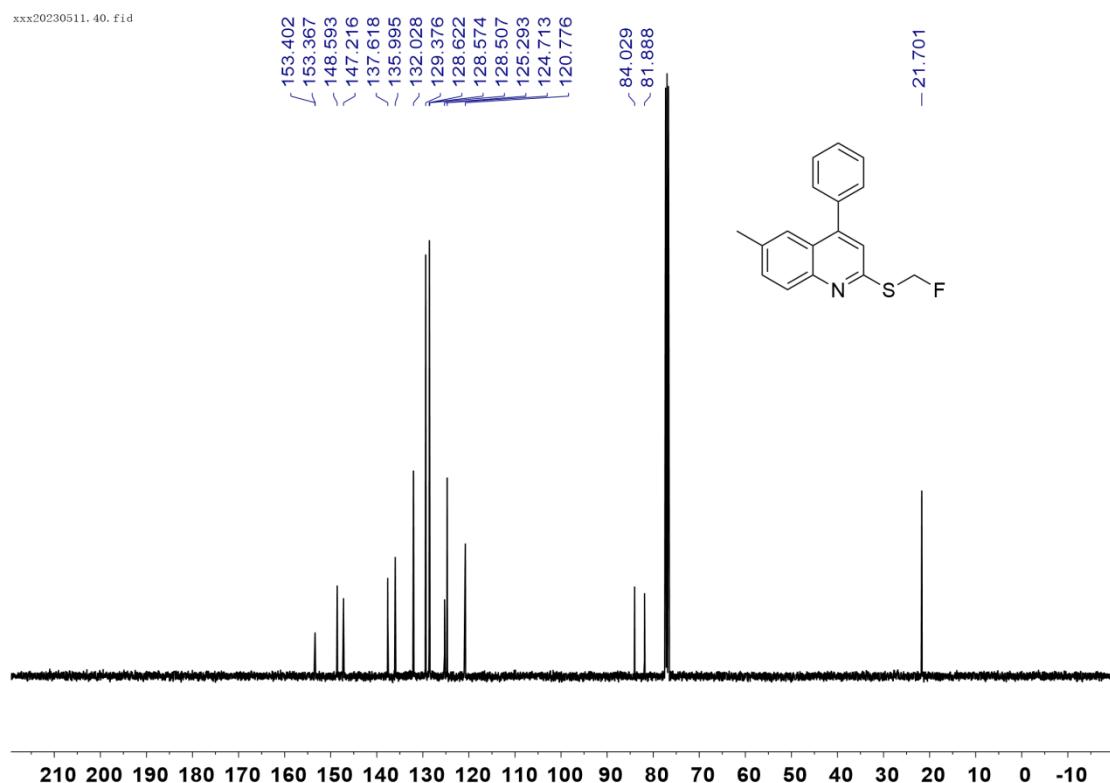
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) for **6b**

xxx20230511



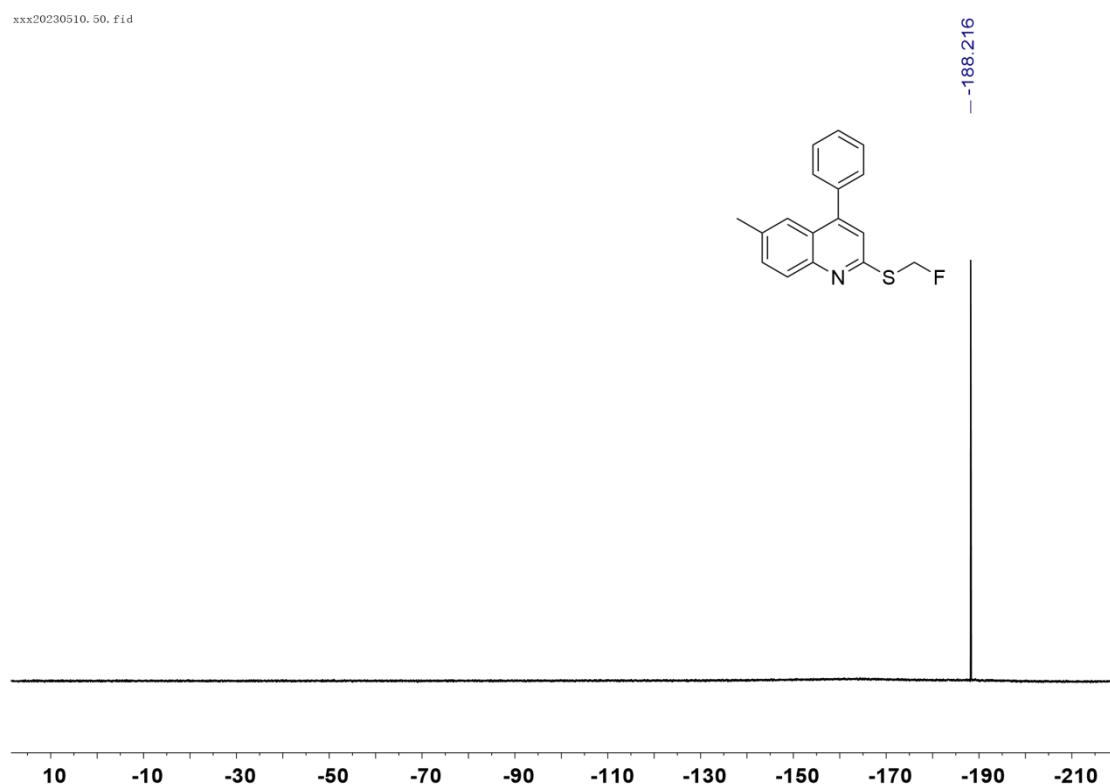
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for **6b**

xxx20230511.40.fid

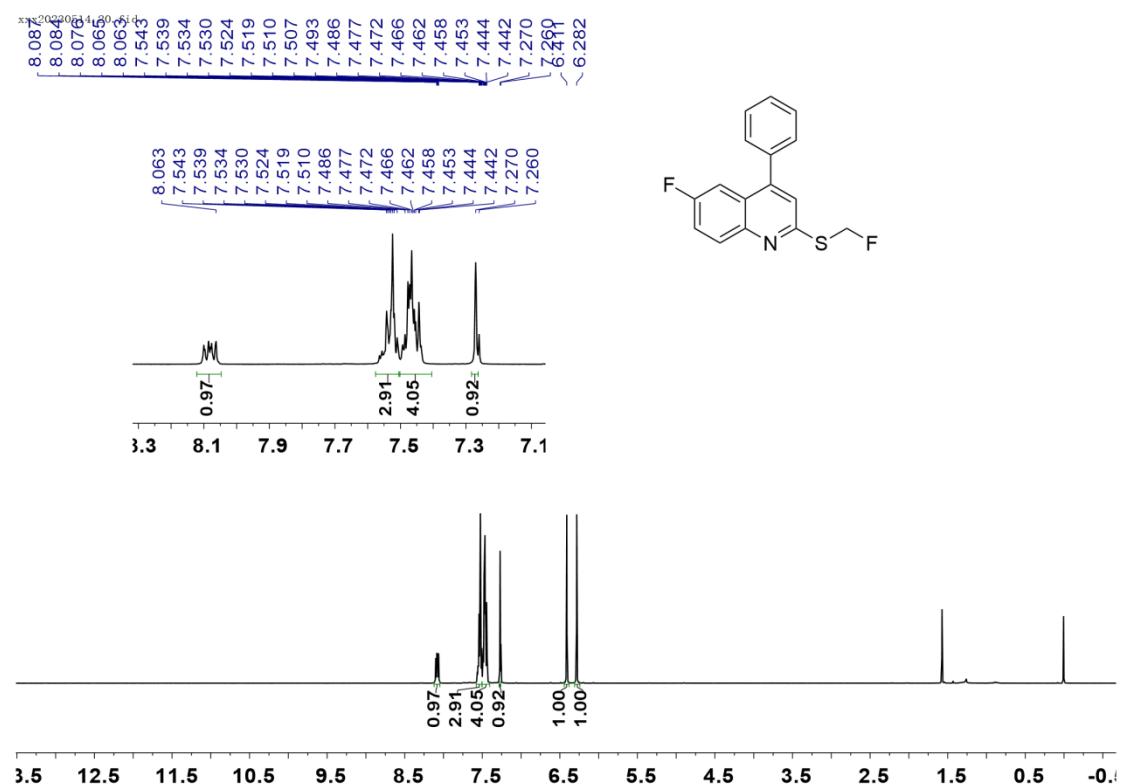


**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) for **6b**

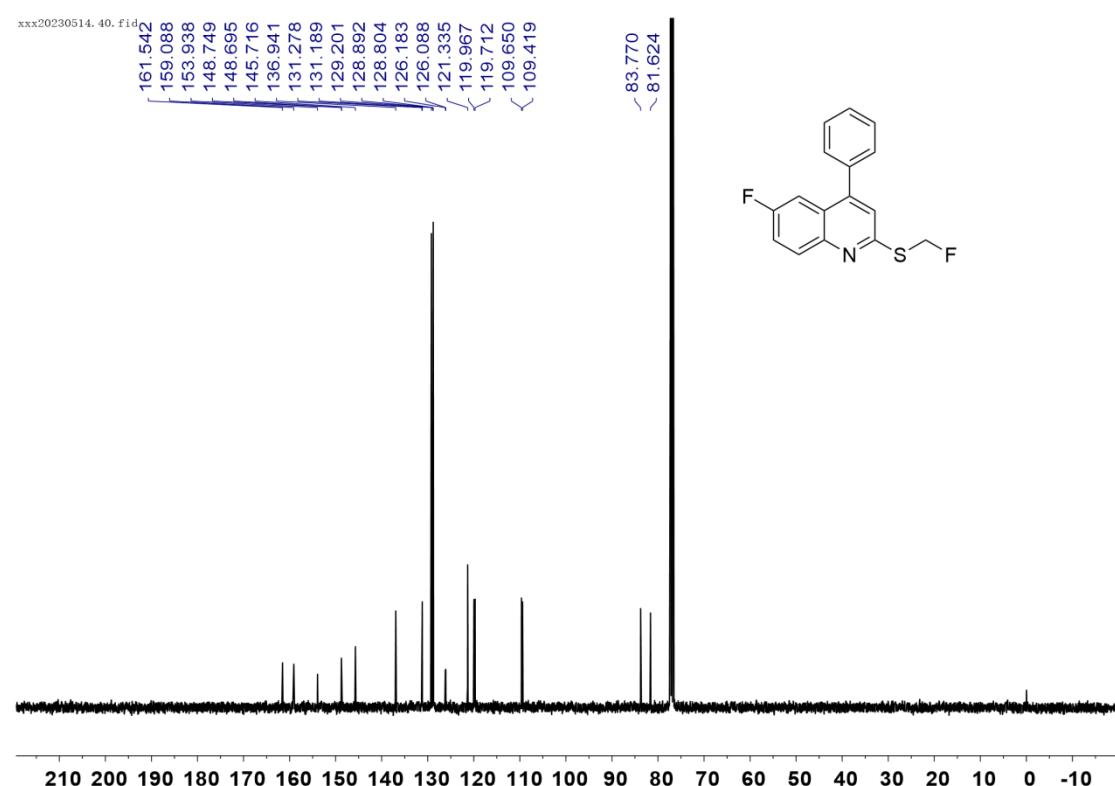
xxx20230510.50.fid



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) for 6c**

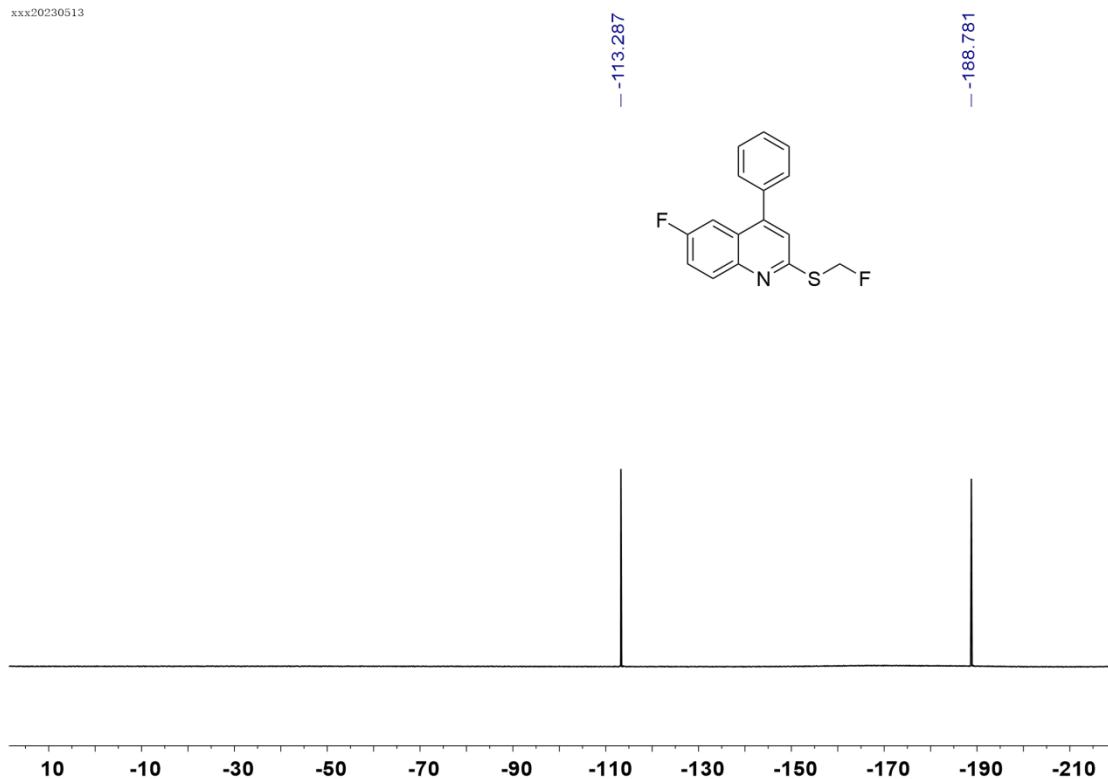


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for 6c**

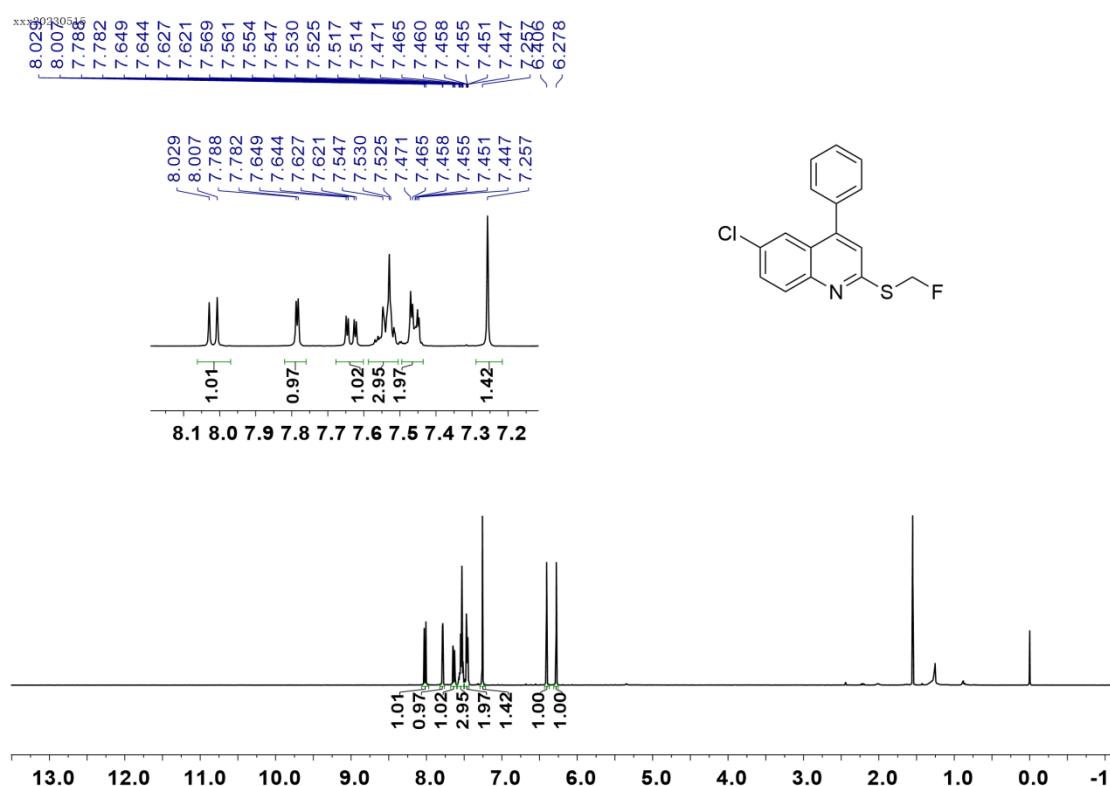


**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) for **6c**

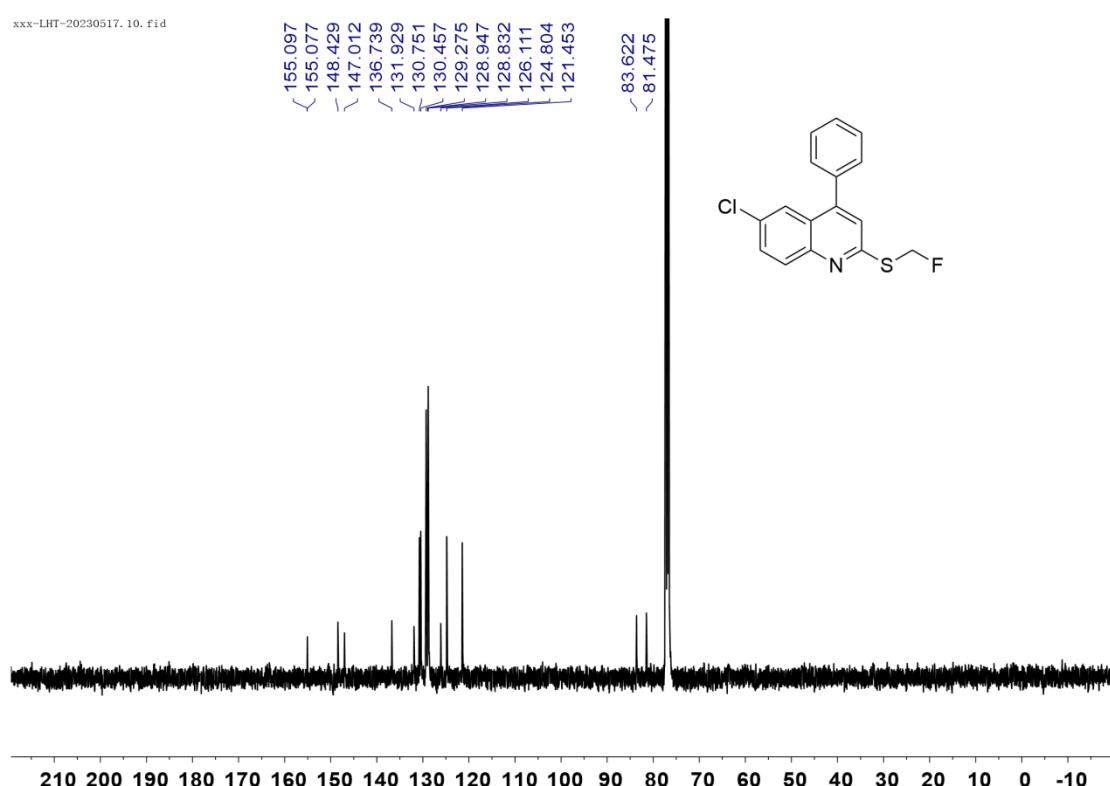
xxx20230513



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) for 6d**

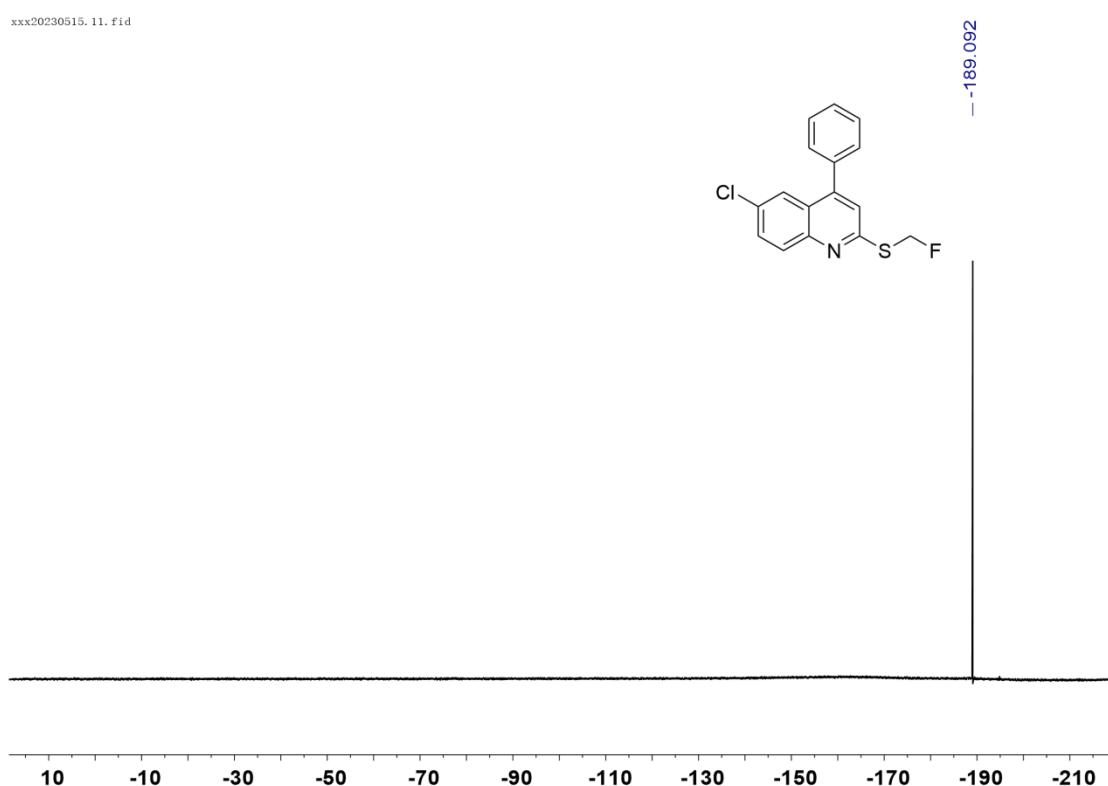


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for 6d**

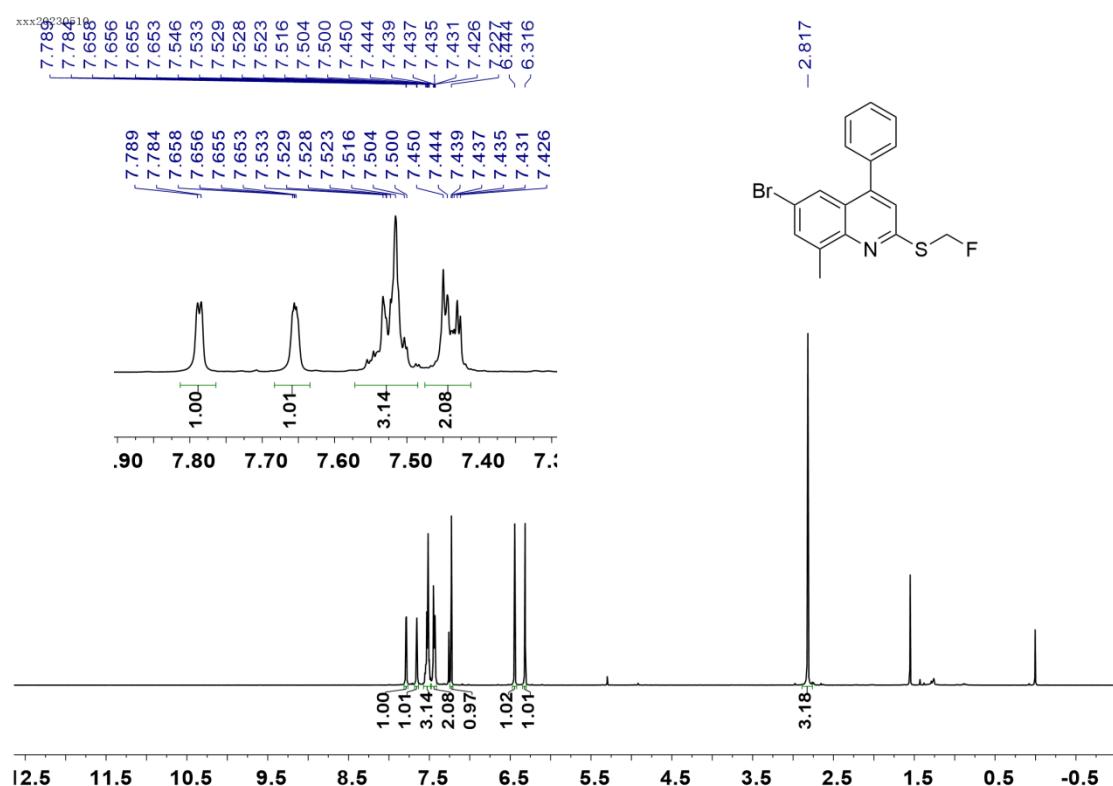


**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) for **6d**

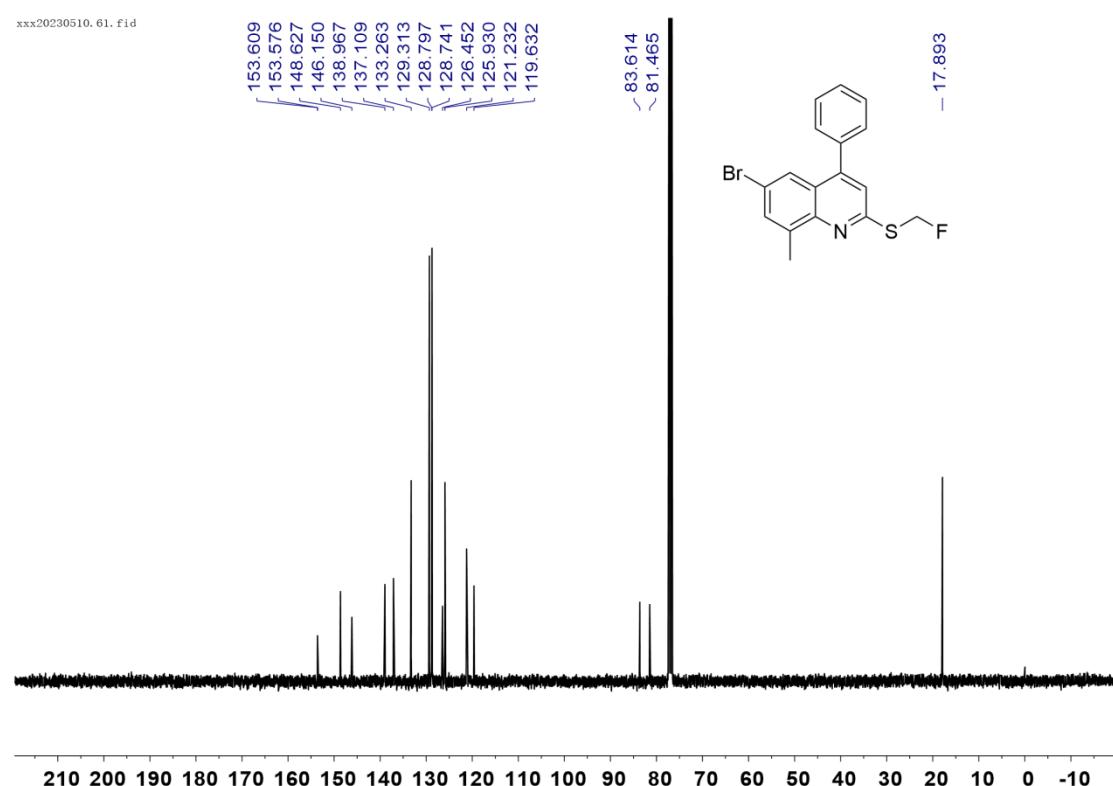
xxx20230515.11.fid



**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ) for **6e**

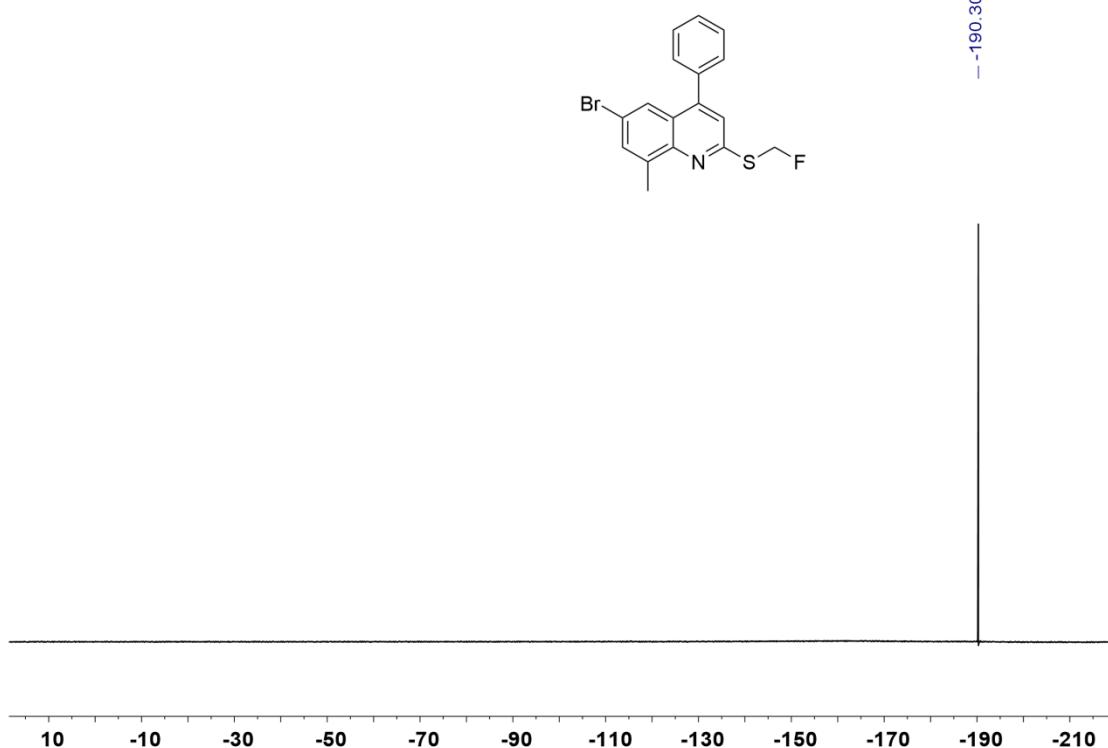


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for 6e

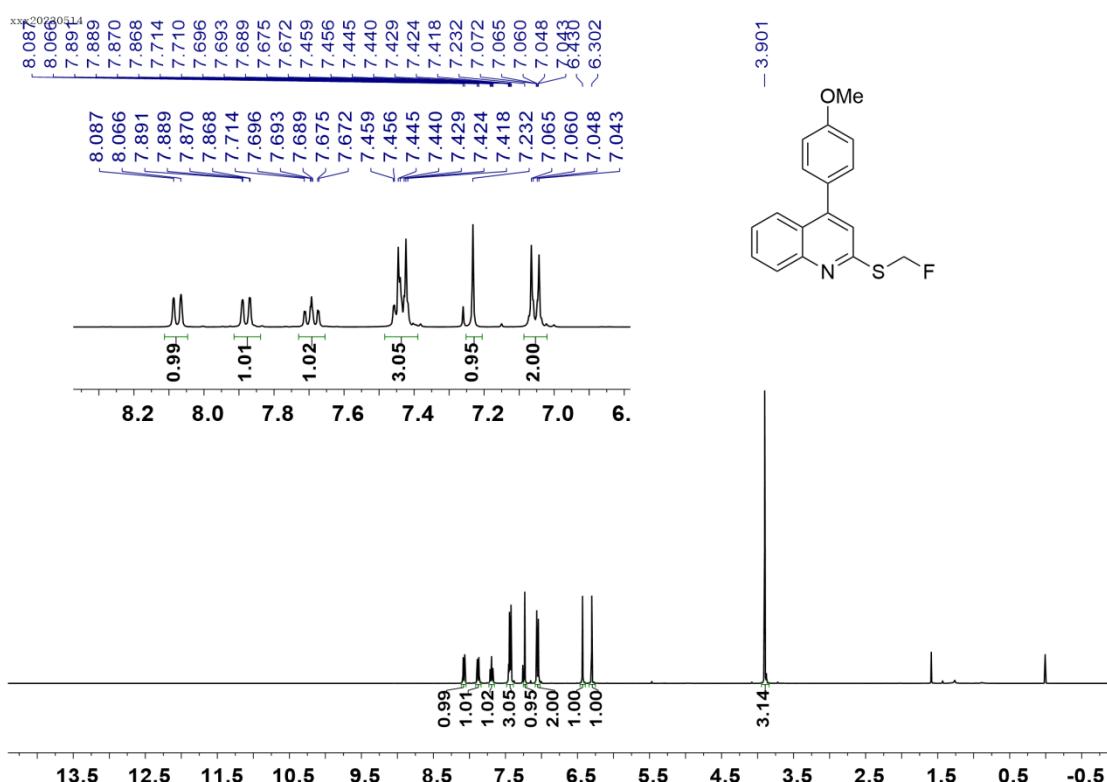


**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) for **6e**

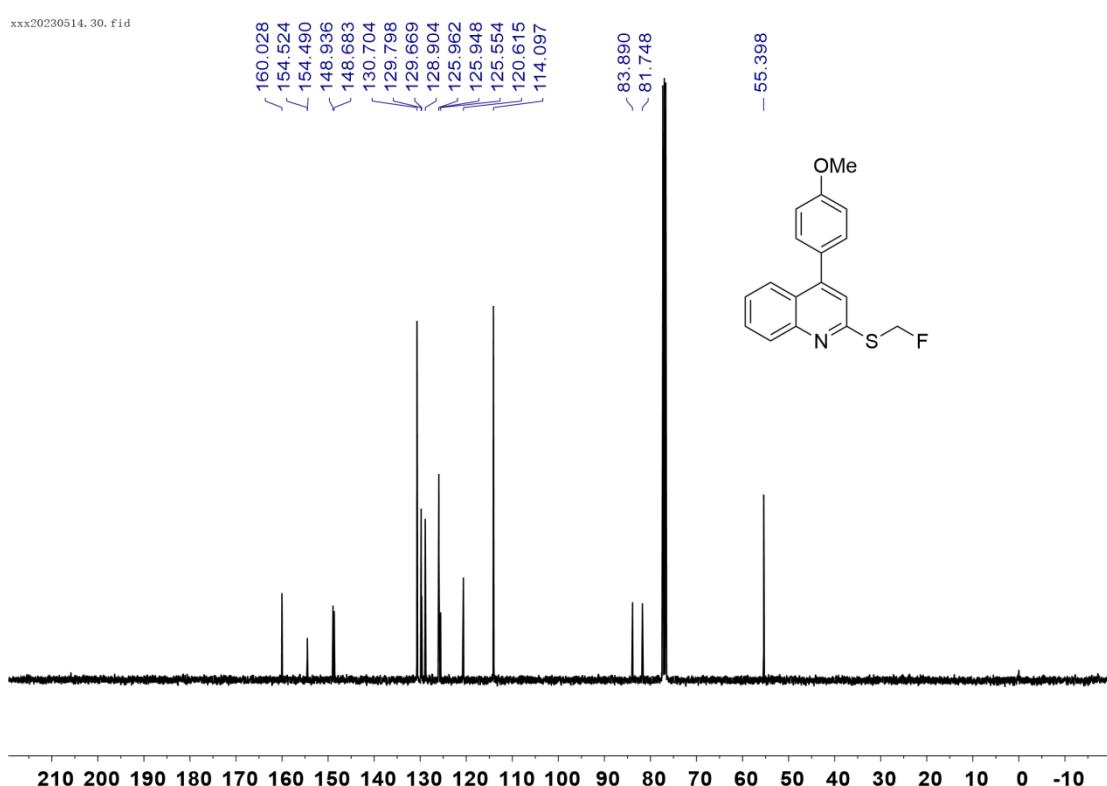
xxx20230510.60.fid



**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) for **6f**

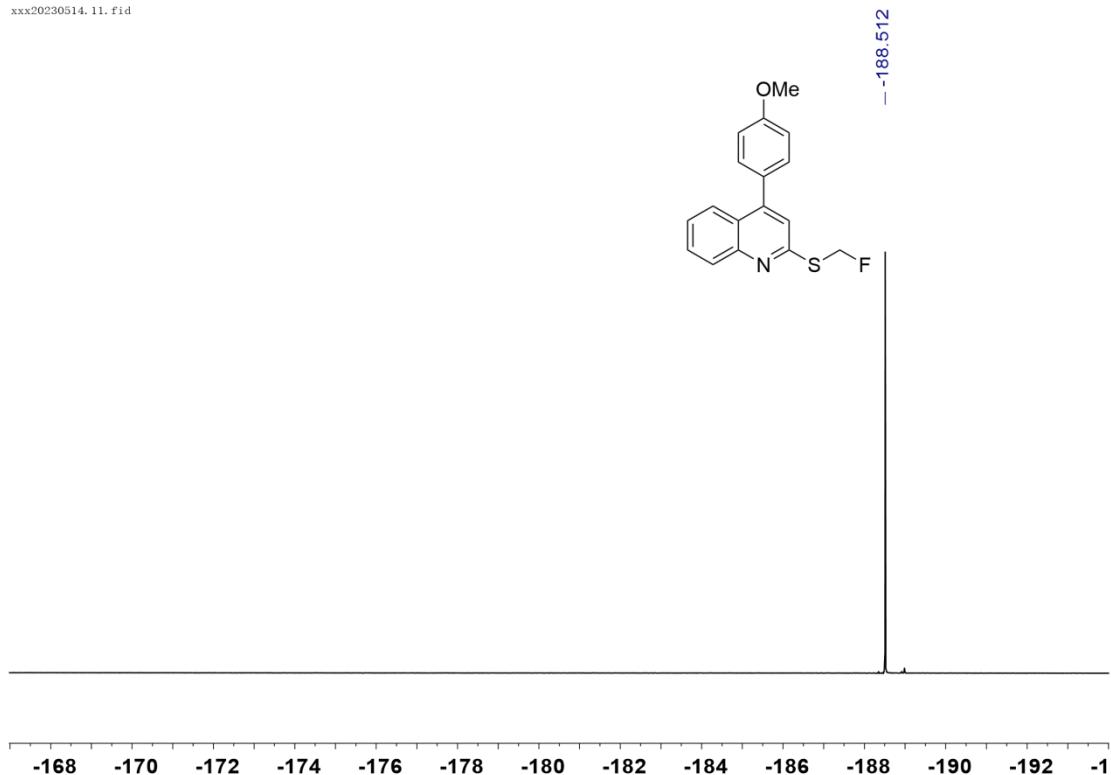


**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) for **6f**



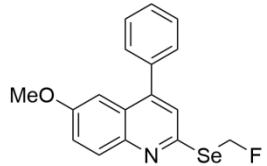
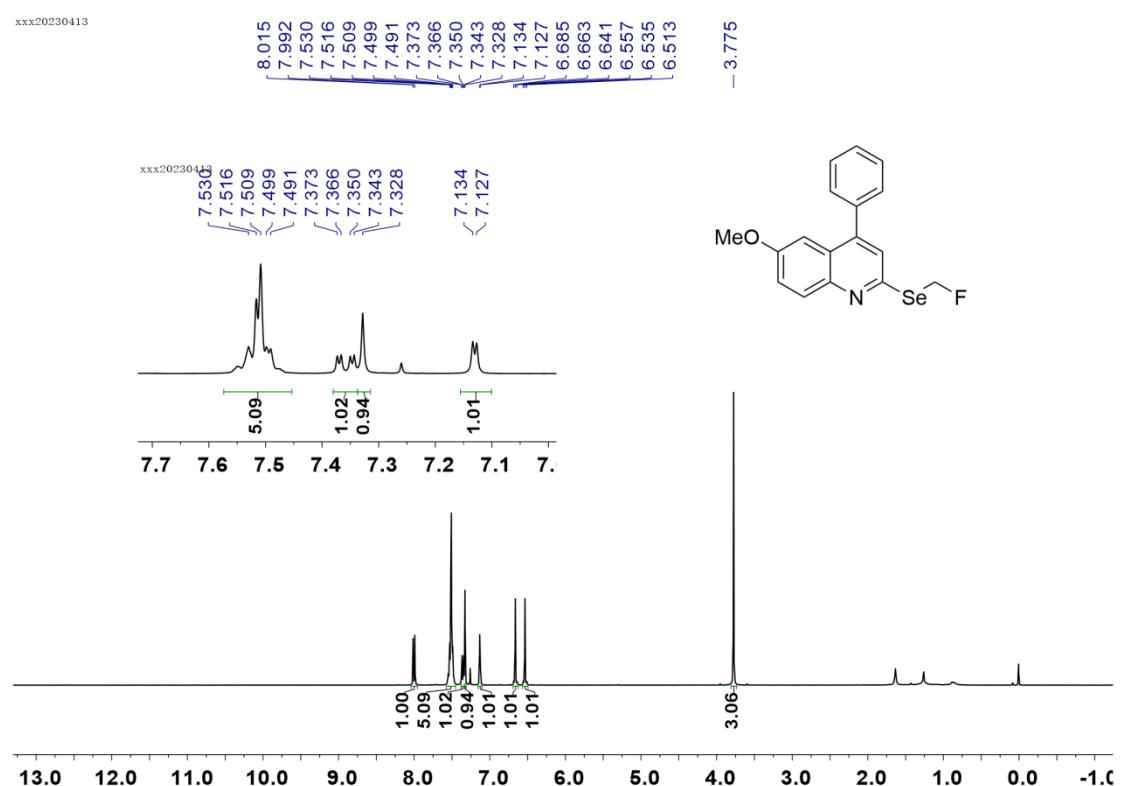
**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) for **6f**

xxx20230514.11.fid



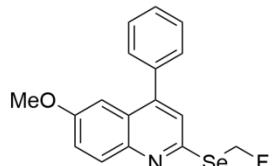
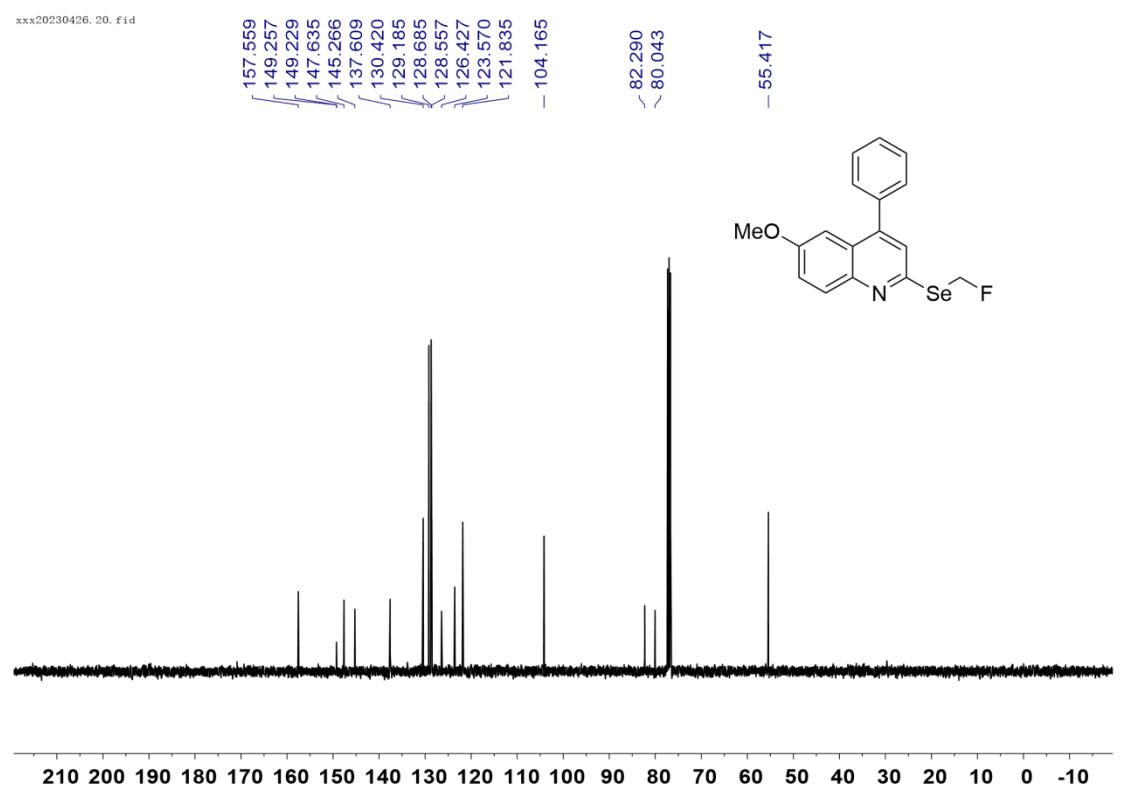
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) for **7a**

xxx20230413



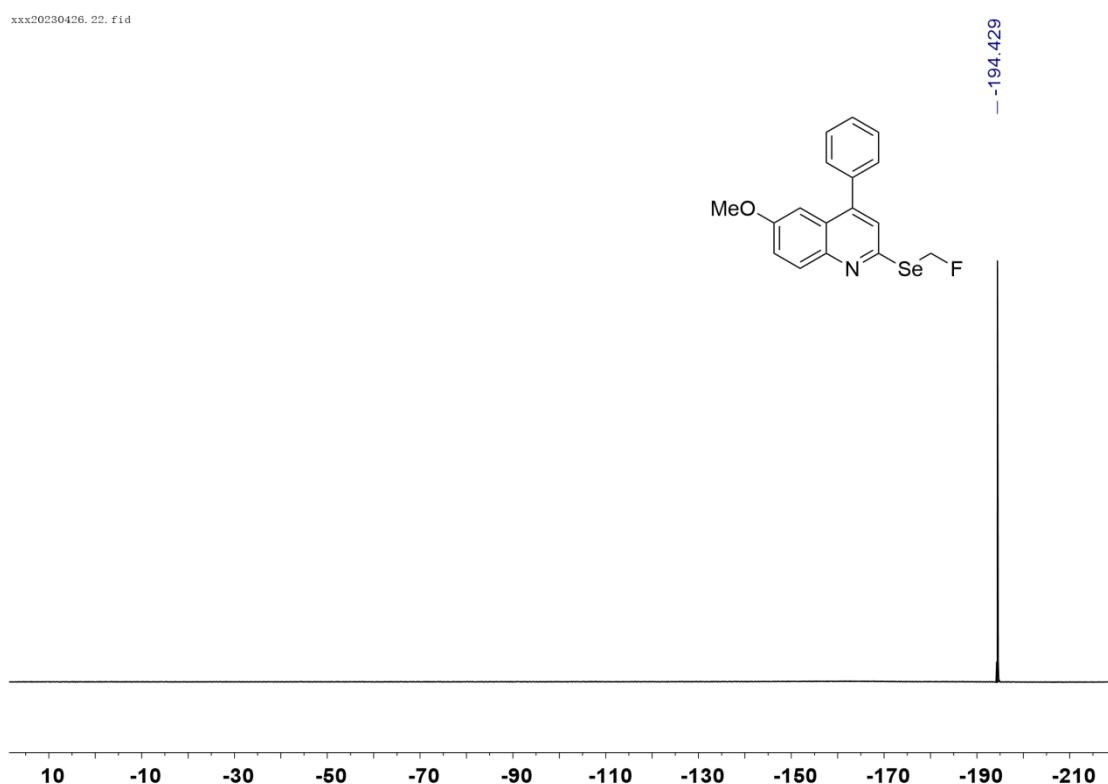
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for 7a

xxx20230426. 20. fid

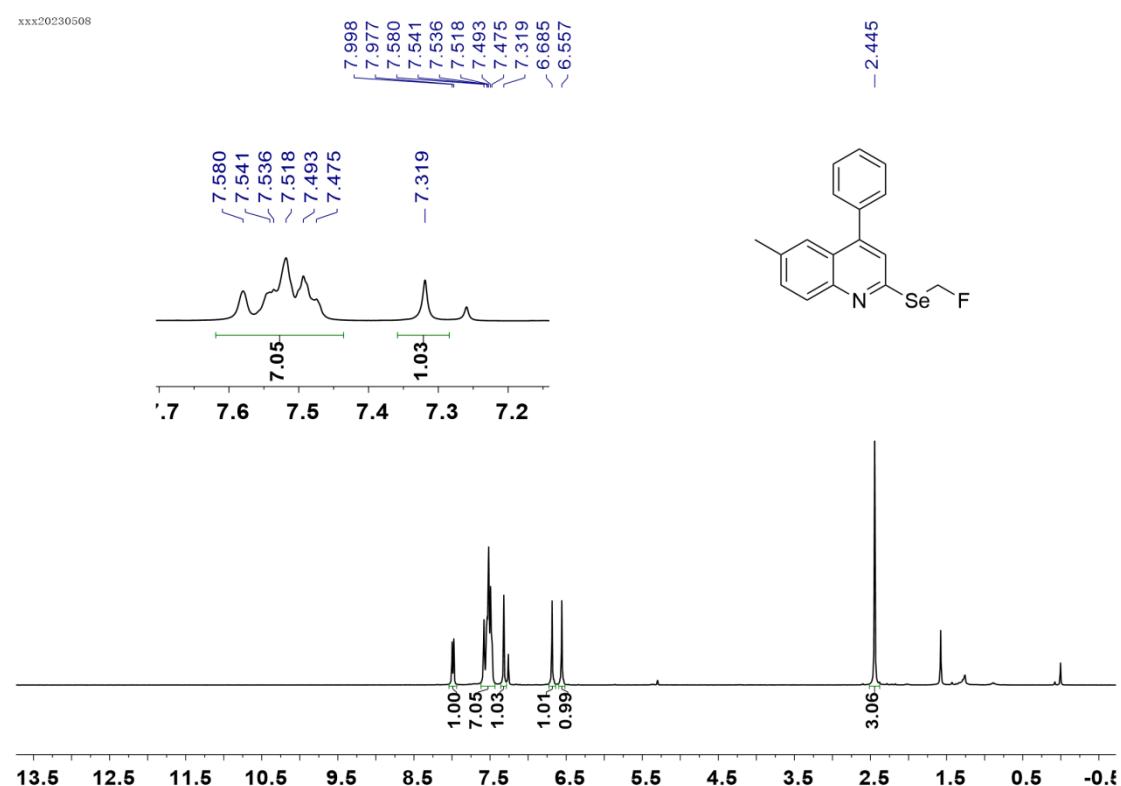


**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) for **7a**

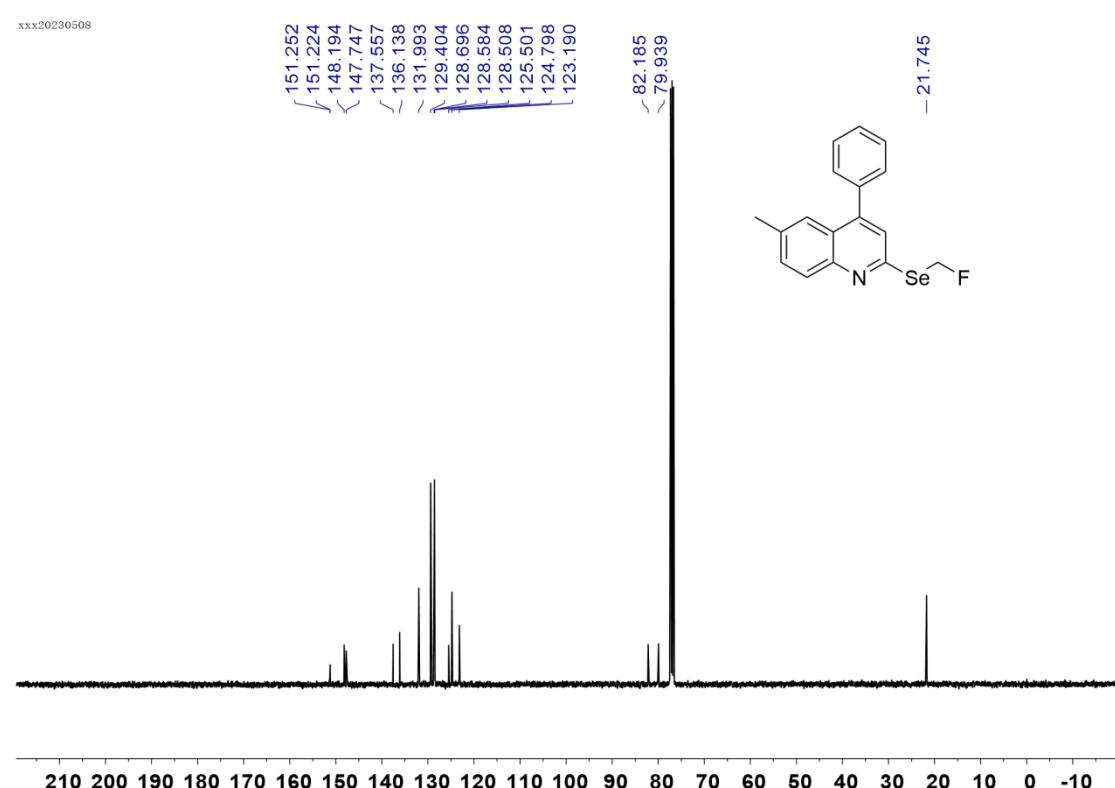
xxx20230426.22.fid



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) for 7b**

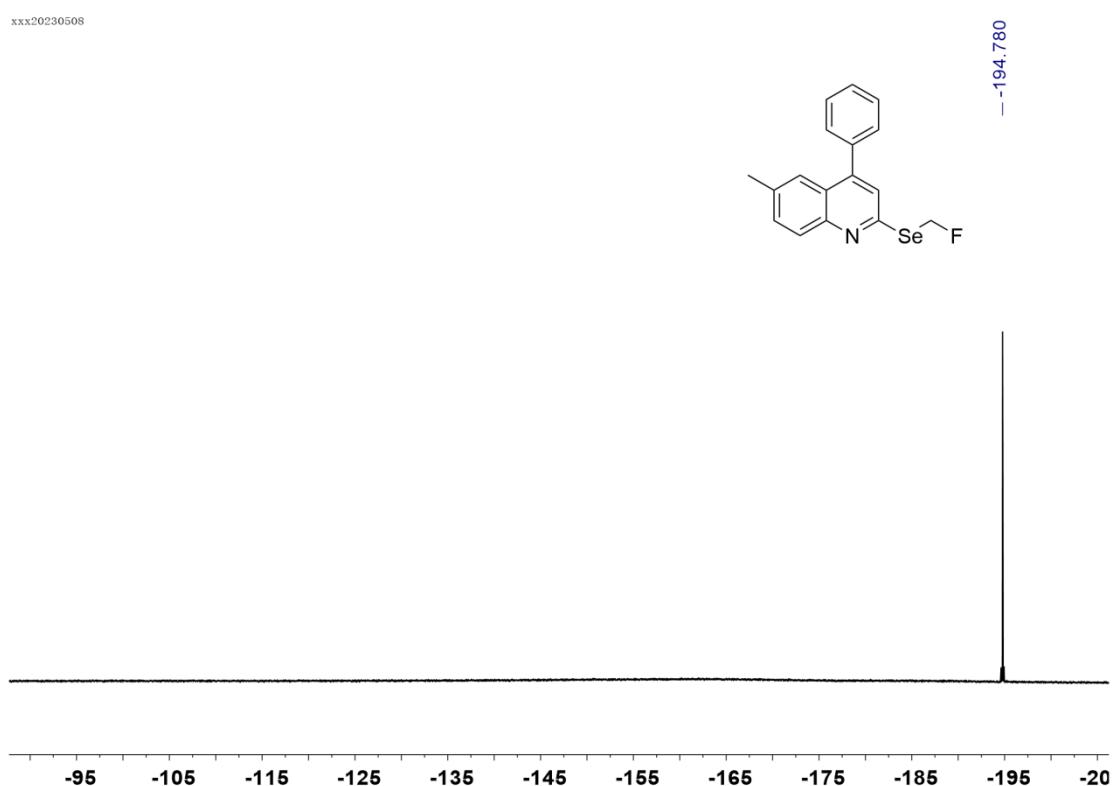


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for 7b**

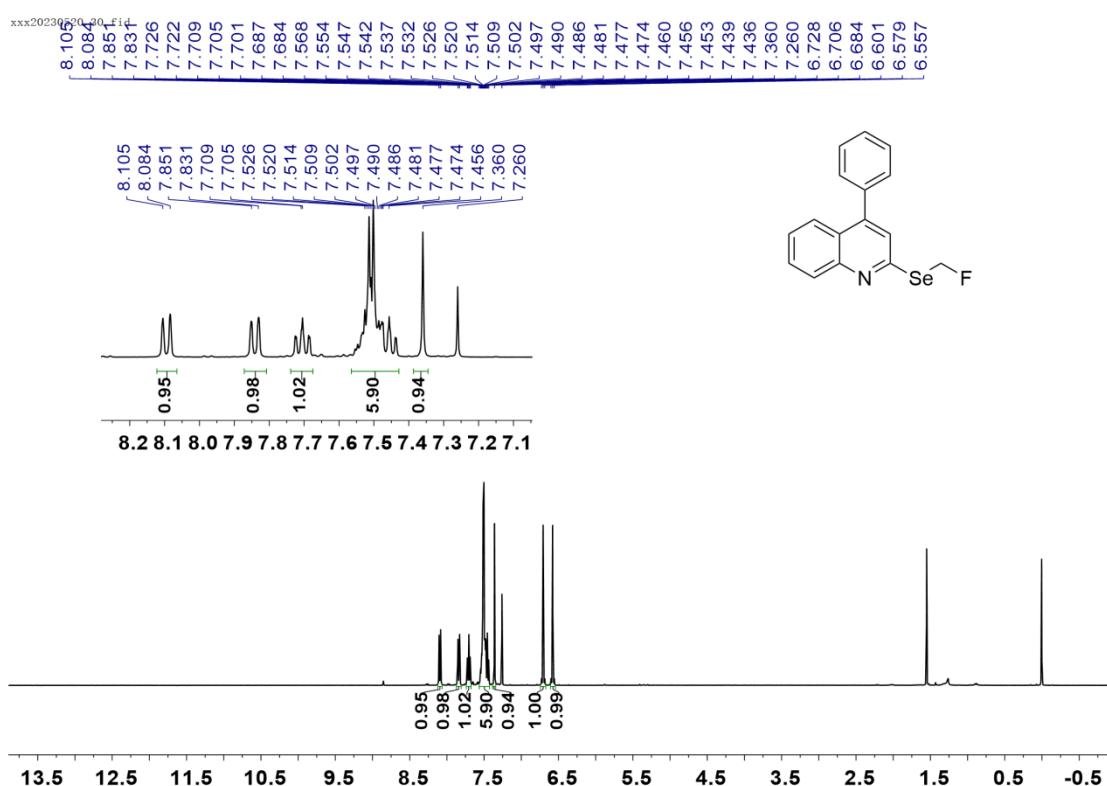


**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) for **7b**

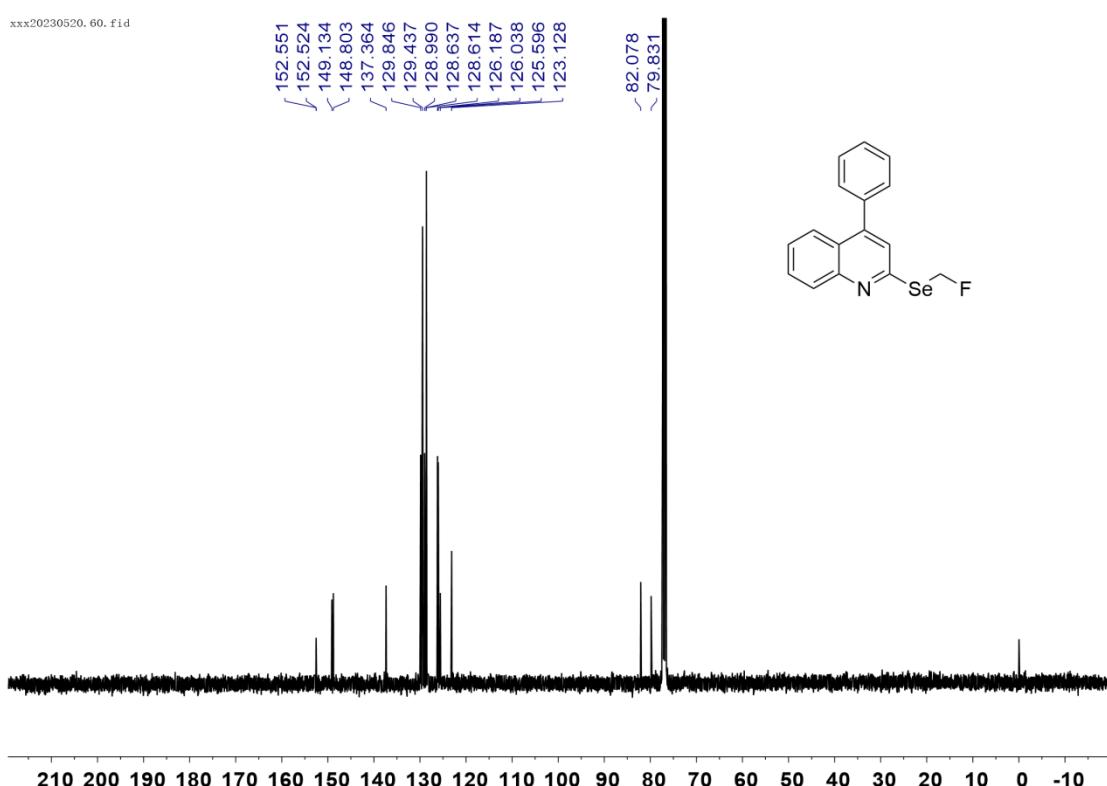
xxx20230508



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) for 7c**

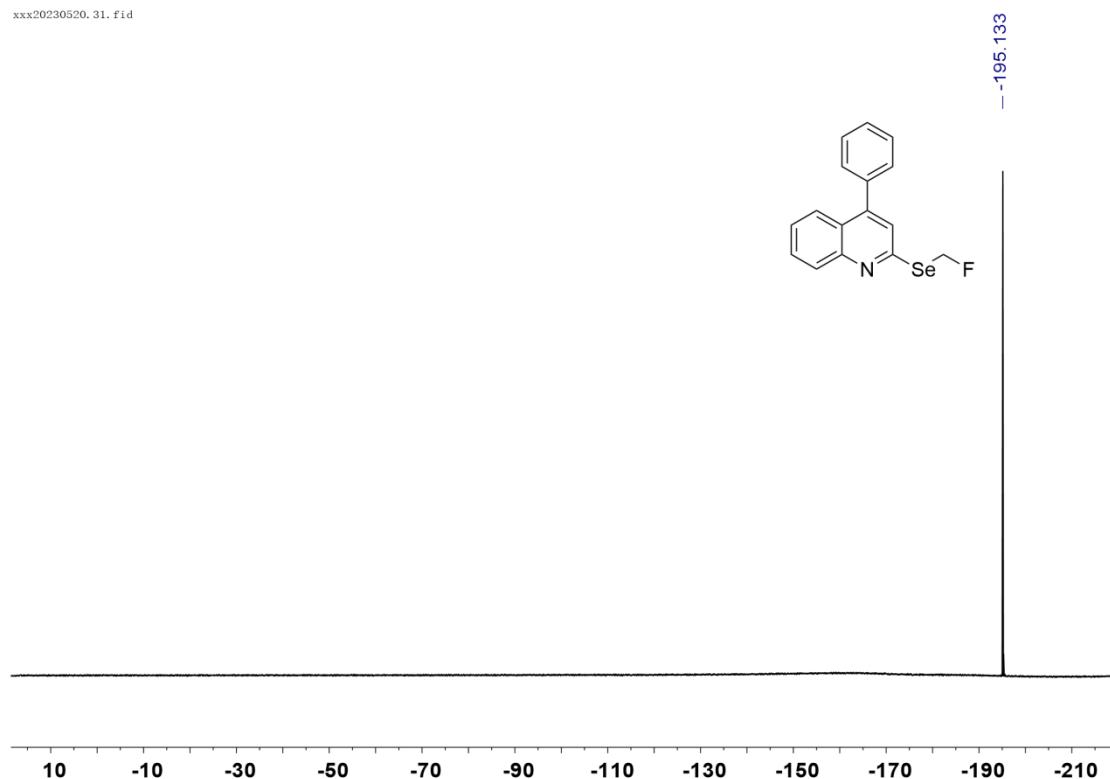


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for 7c**

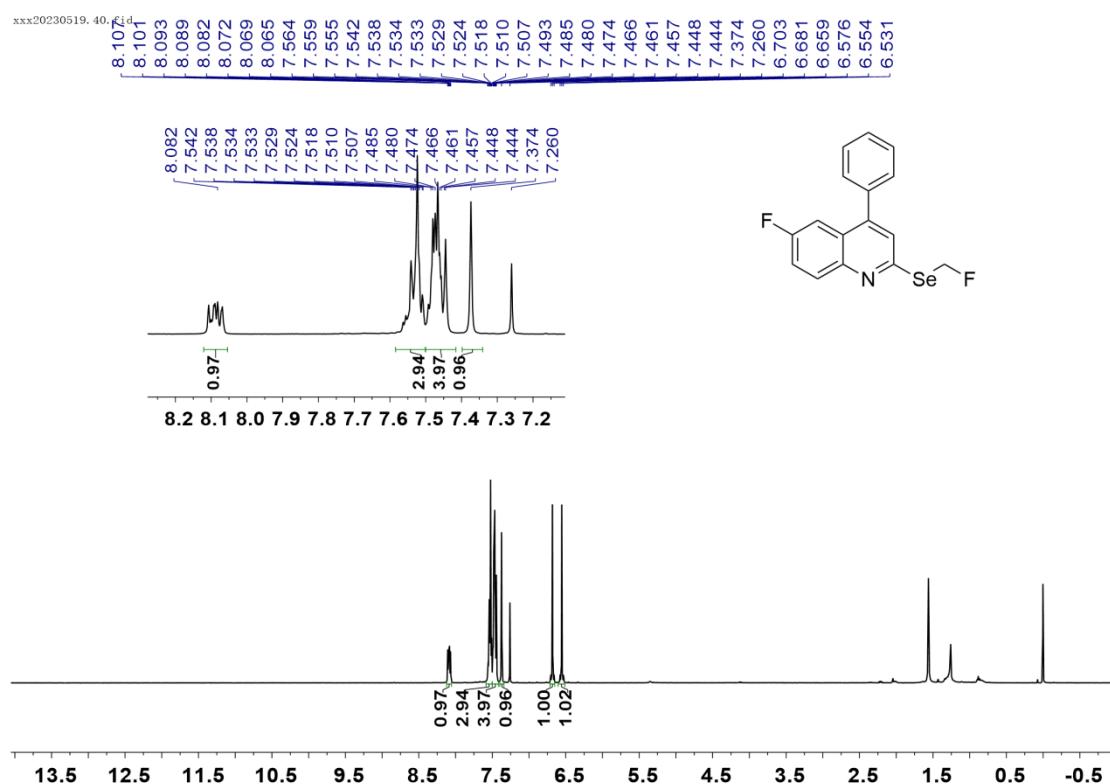


**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) for **7c**

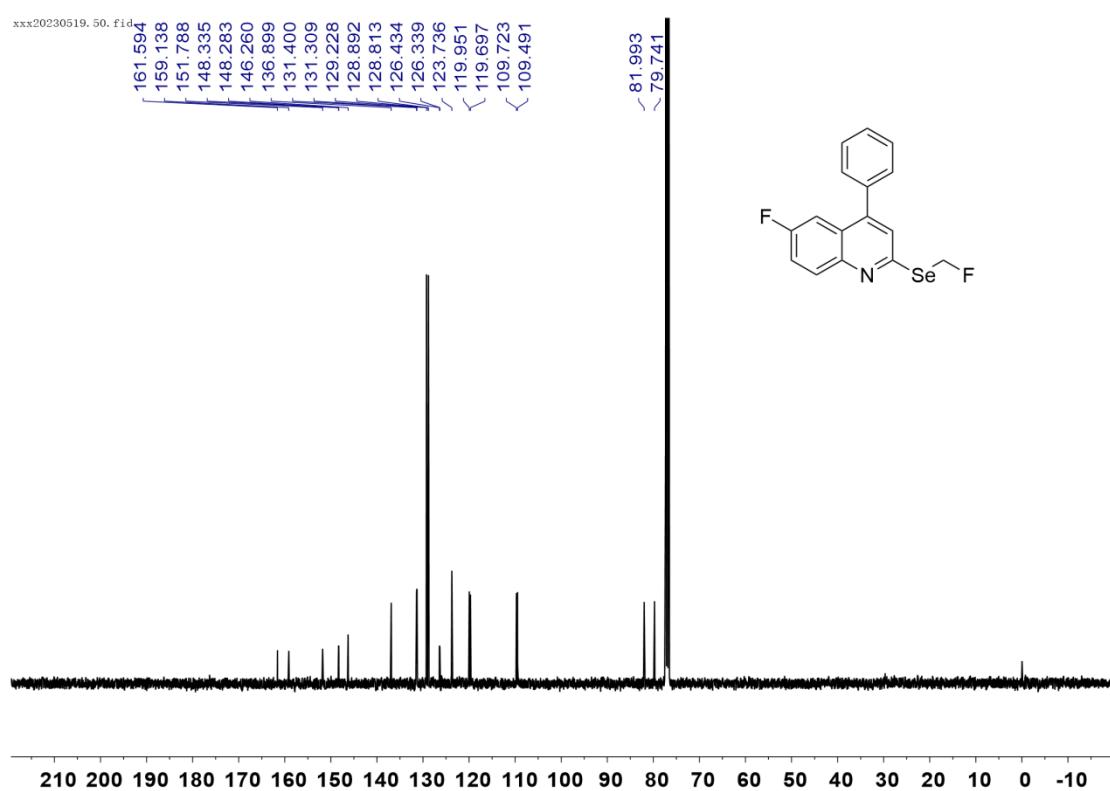
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**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) for **7d**

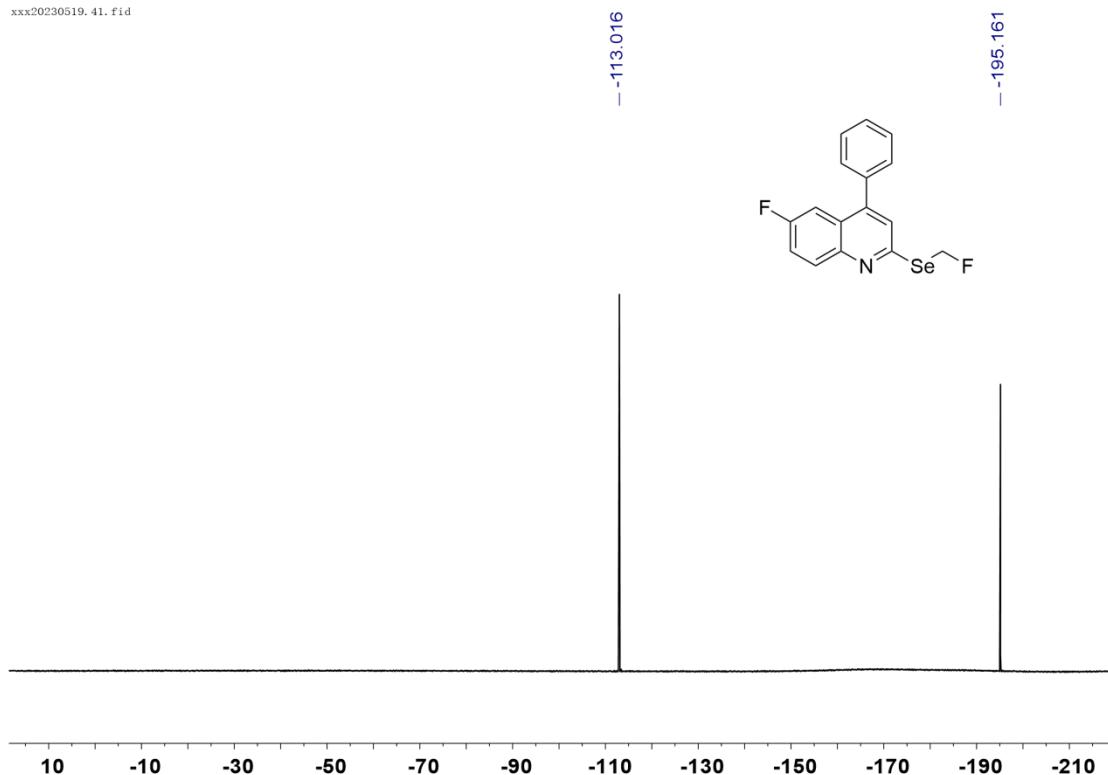


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for 7d

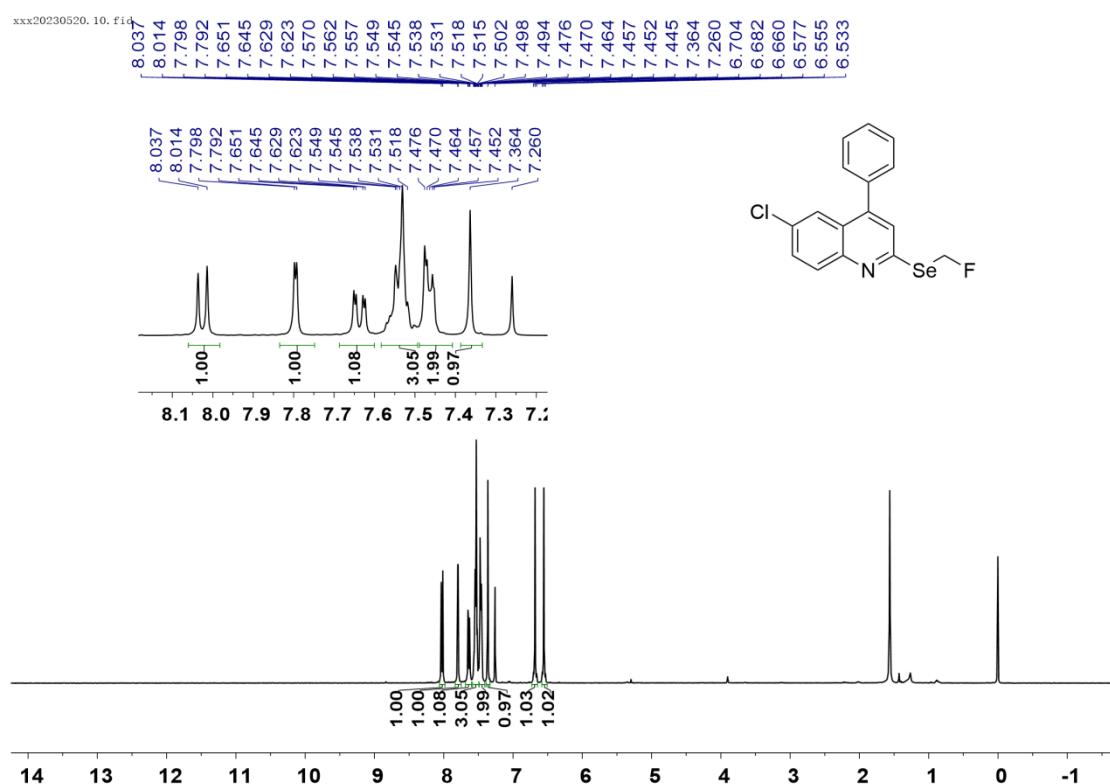


**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) for **7d**

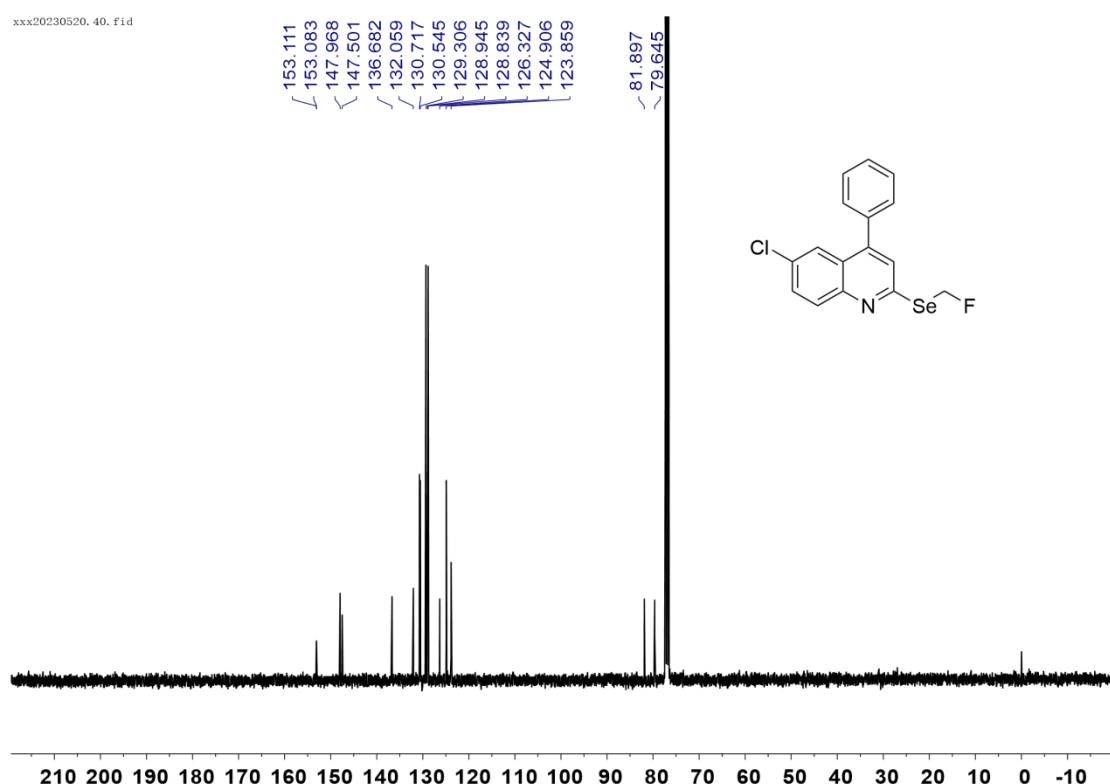
xxx20230519.41.fid



**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ) for **7e**



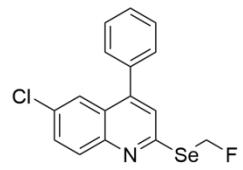
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for 7e



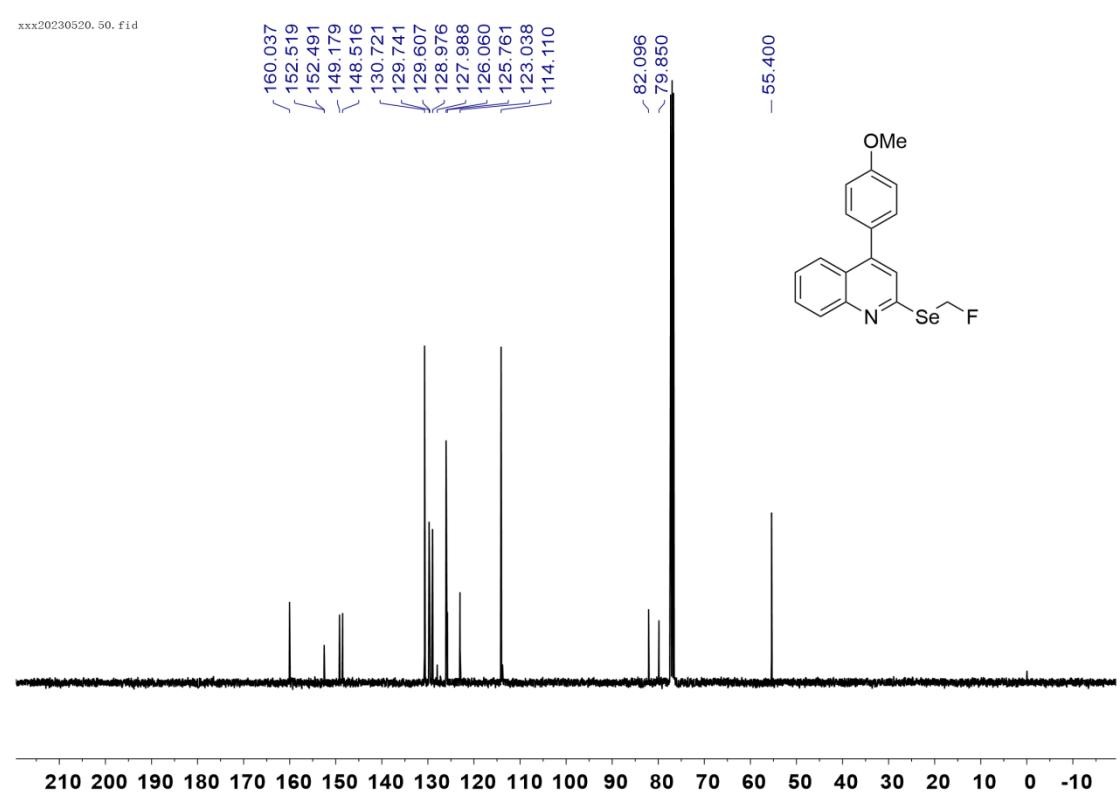
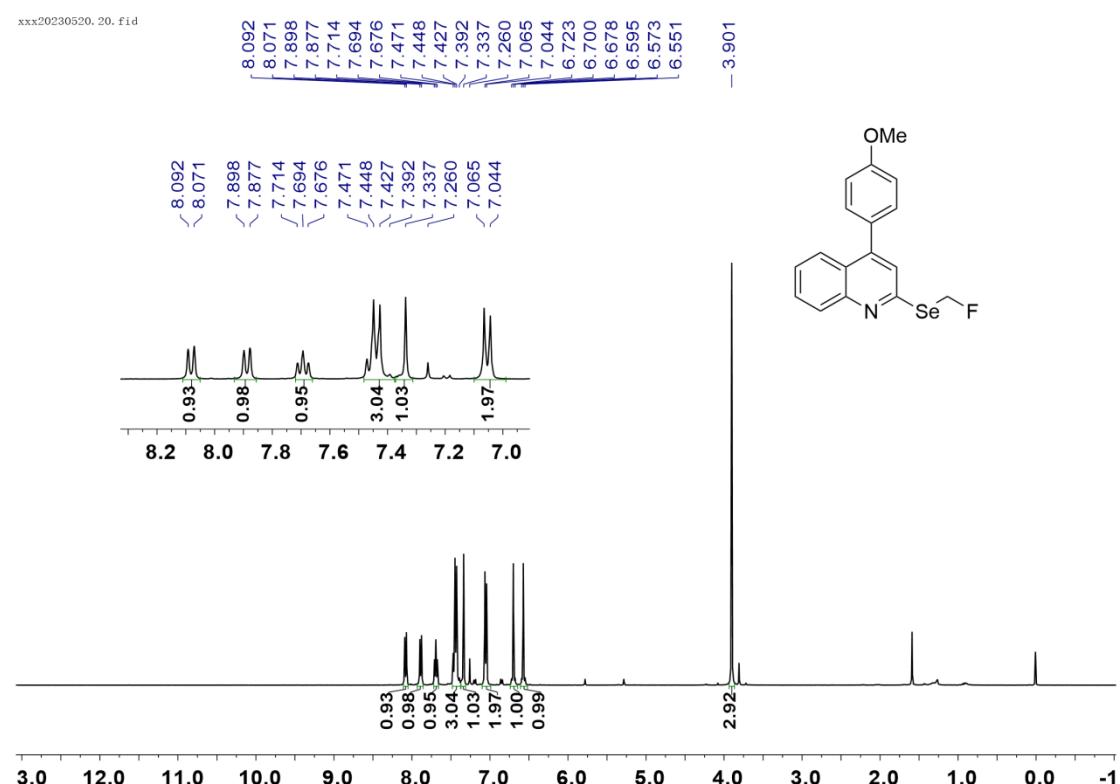
**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) for 7e

xxx20230520.11.fid

- -195.356

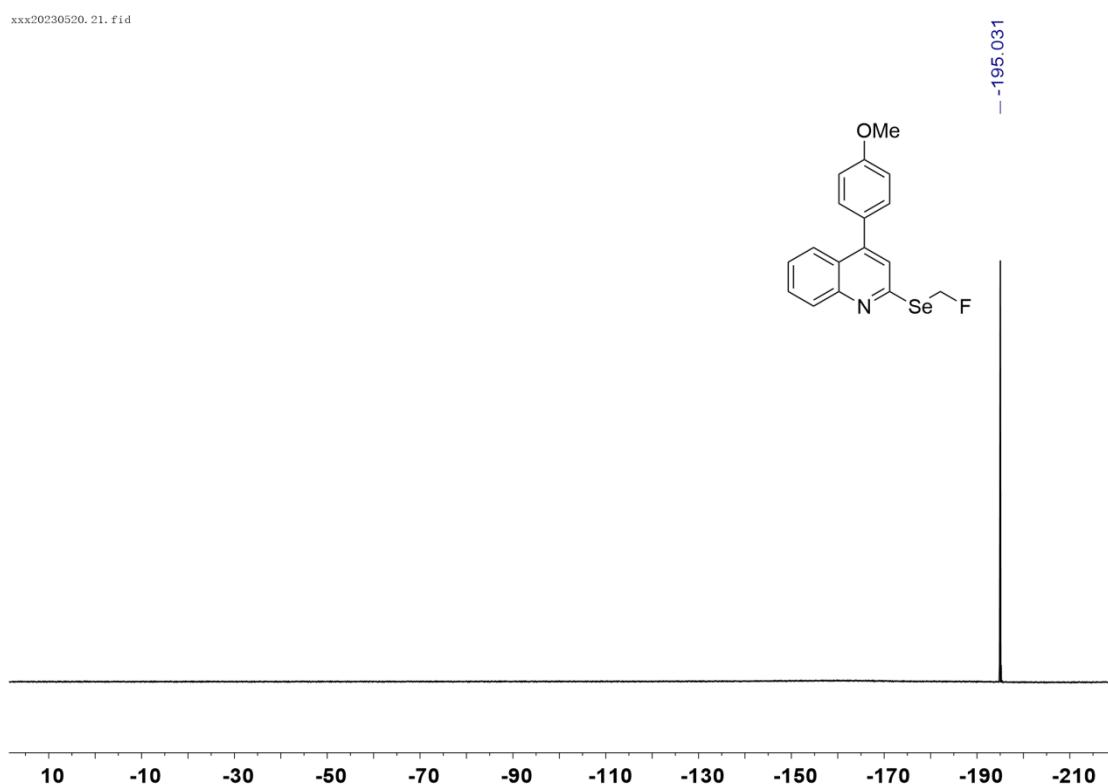


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) for 7f**

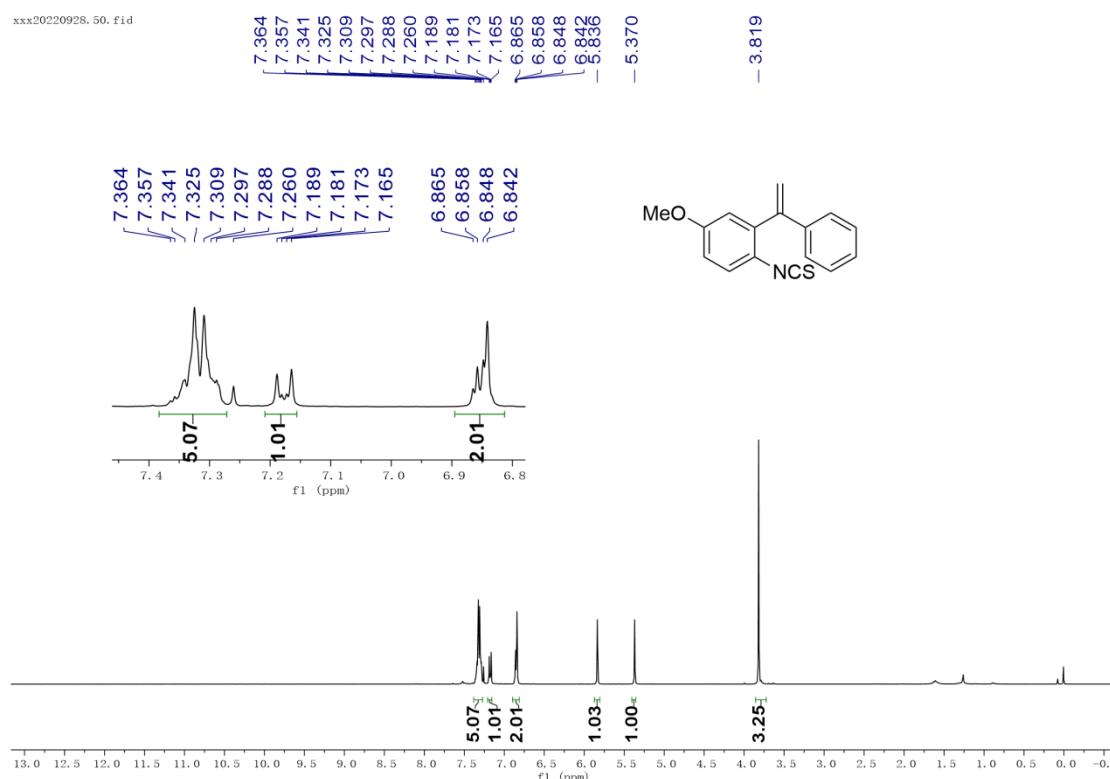


**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) for **7f**

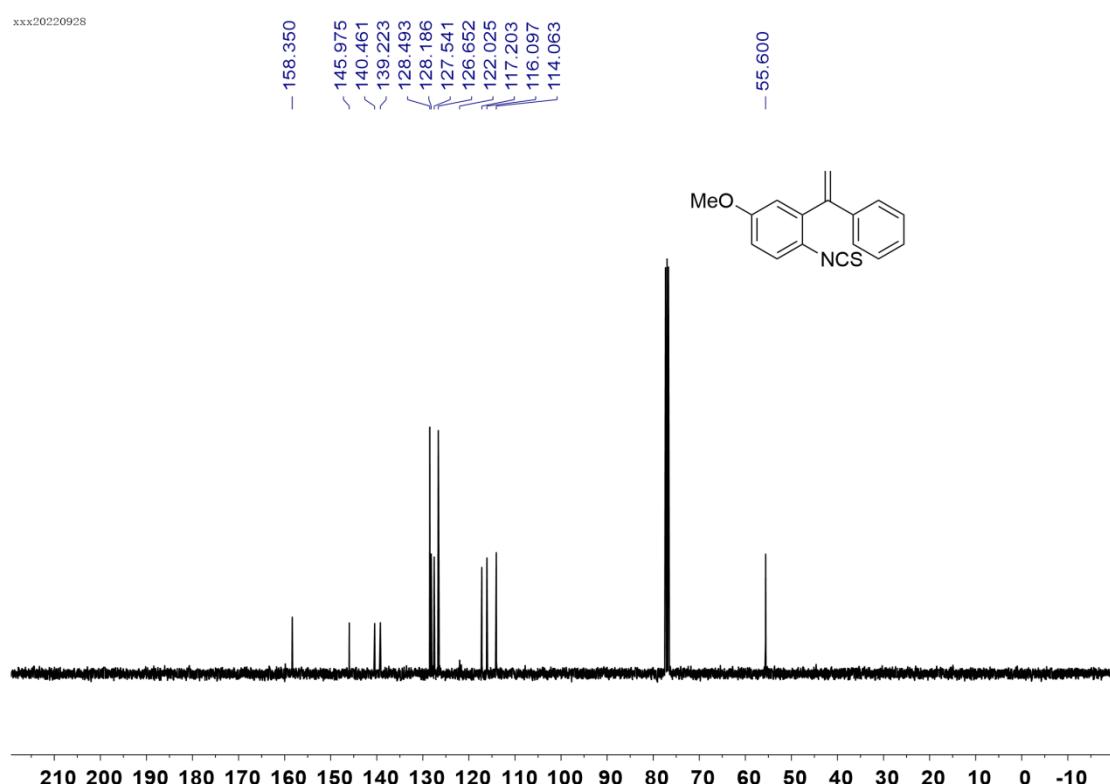
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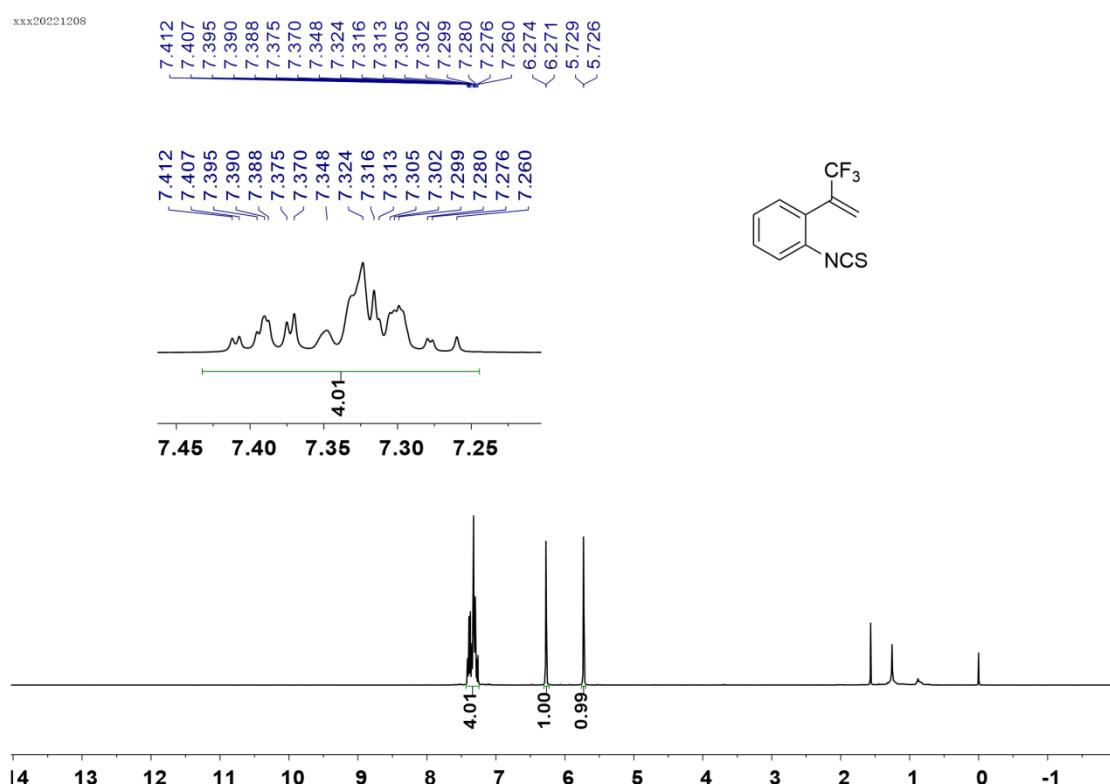
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) for 8a**



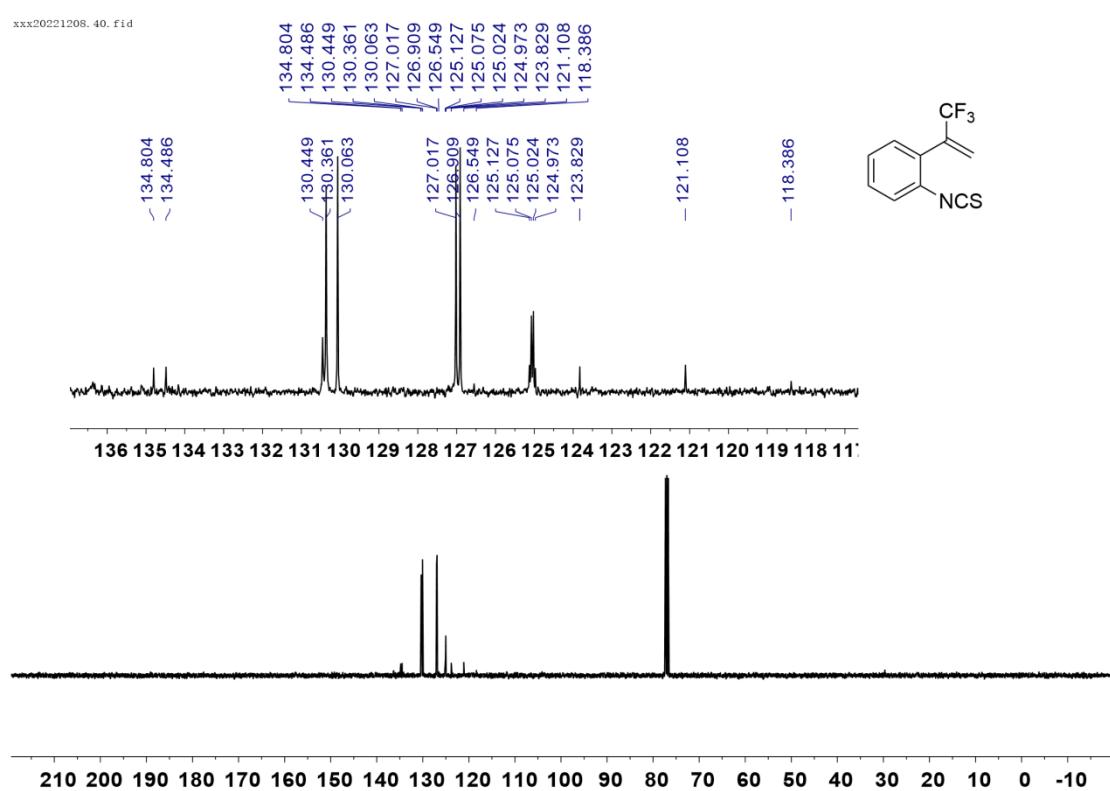
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for 8a**



**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) for **8t**



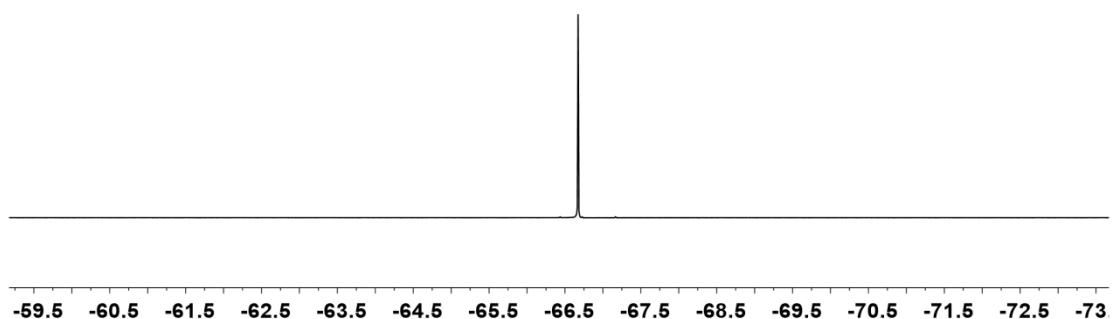
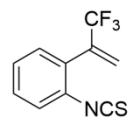
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for 8t



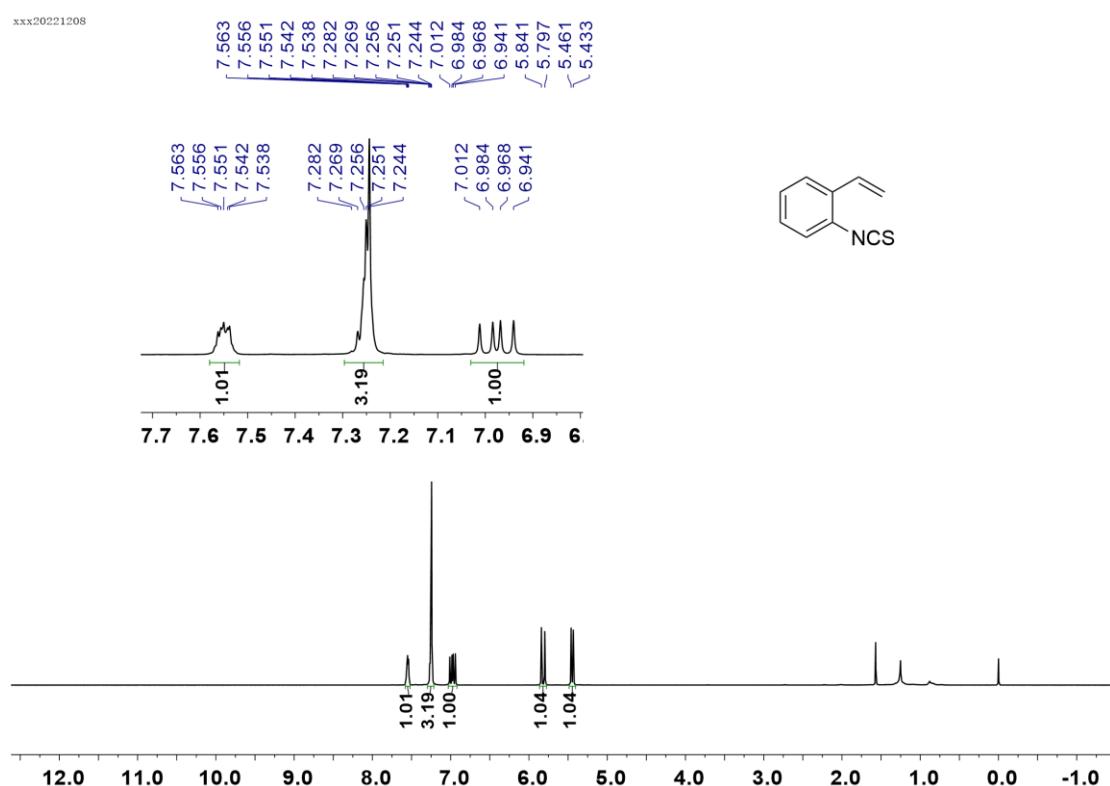
**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) for **8t**

xxx20221208

- -66.673



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) for **8u**



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for **8u**

