

## Supporting information

### **Base-Mediated [2+4] Annulation of Benzothiazolium Salts and 2-Aminobenzaldehydes: Selective Synthesis of 2-Amino and 2-Thio- Substituted Quinolines**

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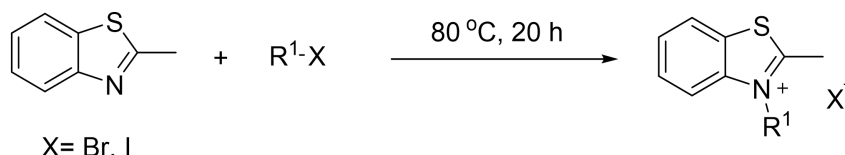
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## 1. General information

All the obtained products were characterized by melting points (m.p),  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$ . Melting points were measured on an Electrothermal SGW-X4 microscopy digital melting point apparatus and are uncorrected;  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra were obtained on Bruker-500 and referenced to 7.26 ppm and 77.16 ppm for chloroform solvent with TMS as internal standard (0 ppm). Chemical shifts were reported in parts per million (ppm,  $\delta$ ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m);  $^{19}\text{F}$  spectra correspond to proton-decoupled  $^{19}\text{F}\{^1\text{H}\}$  measurements. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm; Unless otherwise stated, all the reagents were purchased from commercial sources (Energy chemical, J&K Chemic, TCI, Fluka, Acros, SCRC), used without further purification. Mass spectroscopy data of the products were collected on an HRMS-TOF instrument.

## 2. Substrates Preparation

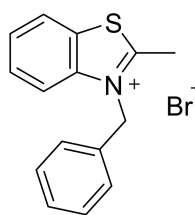
### General procedure for the synthesis of 2-methylbenzothiazole salts



The synthesis method for 2-methylbenzothiazole salt is adapted from existing an reference.<sup>1</sup> Place 2-methylbenzothiazole (10 mmol) and the corresponding halide (12 mmol) in a round-bottom flask, then add 2 mL of acetone. The reaction mixture was stirred at 80 °C for 20 hours. Upon cooling, a solid precipitate formed. The solid was collected by filtration through a Büchner funnel, washed with diethyl ether, dried under vacuum, and collected.

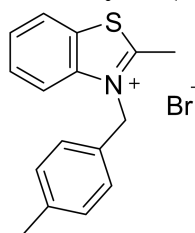
### Analytical data of 2-methylbenzothiazole salts

#### 3-Benzyl-2-methylbenzo[d]thiazol-3-ium bromide



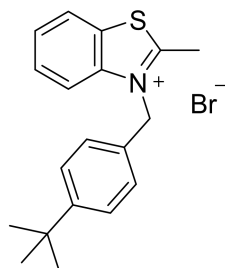
Pink solid; (2.2 g, 70% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.55 (d,  $J = 8.0$  Hz, 1H), 8.23 (d,  $J = 8.4$  Hz, 1H), 7.86 – 7.77 (m, 2H), 7.42 – 7.33 (m, 5H), 6.13 (s, 2H), 3.30 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  178.9, 141.5, 133.3, 130.0, 129.8, 129.6, 129.0, 128.7, 127.5, 125.4, 117.6, 52.4, 17.9. HRMS (ESI, Q-TOF)  $m/z$ : calcd for  $\text{C}_{15}\text{H}_{14}\text{NS}$   $[\text{M-Br}]^+$  240.0841; found 240.0839.

### 2-Methyl-3-(4-methylbenzyl)benzo[d]thiazol-3-ium bromide



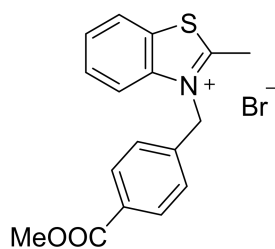
Yellow solid (2.49 g, 75% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.49 (dd,  $J = 8.0, 1.3$  Hz, 1H), 8.21 (d,  $J = 8.3$  Hz, 1H), 7.86 – 7.77 (m, 2H), 7.22 (q,  $J = 8.2$  Hz, 4H), 6.03 (s, 2H), 3.27 (s, 3H), 2.28 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  178.7, 141.4, 138.5, 130.3, 130.1, 130.0, 129.7, 128.7, 127.6, 125.3, 117.6, 52.2, 21.1, 17.8. HRMS (ESI, Q-TOF)  $m/z$ : calcd for  $\text{C}_{16}\text{H}_{16}\text{NS}$   $[\text{M-Br}]^+$  254.0998; found 254.0996.

### 3-(4-(Tert-butyl)benzyl)-2-methylbenzo[d]thiazol-3-ium bromide



White solid (2.85 g, 76% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.51 (d,  $J = 9.6$  Hz, 1H), 8.25 (d,  $J = 7.8$  Hz, 1H), 7.88 – 7.83 (m, 1H), 7.80 (t,  $J = 7.2$  Hz, 1H), 7.41 (d,  $J = 8.5$  Hz, 2H), 7.26 (d,  $J = 8.5$  Hz, 2H), 6.06 (s, 2H), 3.28 (s, 3H), 1.24 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  178.7, 151.5, 141.5, 130.3, 130.0, 129.7, 128.7, 127.3, 126.4, 125.3, 117.6, 52.1, 34.8, 31.4, 17.8. HRMS (ESI, Q-TOF)  $m/z$ : calcd for  $\text{C}_{19}\text{H}_{22}\text{NS}$   $[\text{M-Br}]^+$  296.1467; found 296.1465.

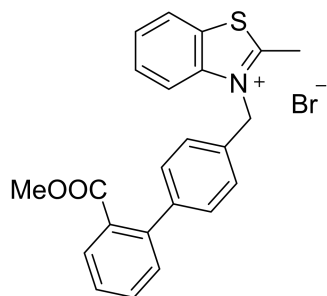
### 3-(4-(Methoxycarbonyl)benzyl)-2-methylbenzo[d]thiazol-3-ium bromide



Green solid (2.87 g, 76% yield);  $^1\text{H}$  NMR (500 MHz,

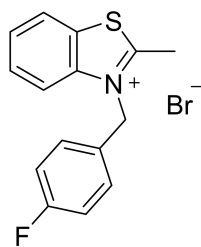
DMSO-*d*<sub>6</sub>) δ 8.57 – 8.51 (m, 1H), 8.16 (d, *J* = 8.2 Hz, 1H), 7.96 (d, *J* = 8.5 Hz, 2H), 7.86 – 7.79 (m, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 6.22 (s, 2H), 3.84 (s, 3H), 3.27 (s, 3H). <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>) δ 179.4, 166.2, 141.4, 138.6, 130.3, 130.1, 130.1, 129.8, 128.7, 127.8, 125.4, 117.4, 52.8, 52.1, 17.9. HRMS (ESI, Q-TOF) *m/z*: calcd for C<sub>17</sub>H<sub>16</sub>NO<sub>2</sub>S [M-Br]<sup>+</sup> 298.0897; found 298.0894.

**3-((2'-(Methoxycarbonyl)-[1,1'-biphenyl]-4-yl)methyl)-2-methylbenzo[d]thiazol-3-ium bromide**



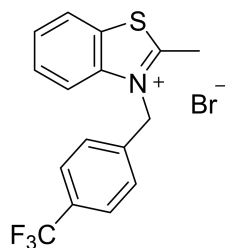
Yellow solid (3.17 g, 70% yield); <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 8.54 (d, *J* = 8.2 Hz, 1H), 8.26 (d, *J* = 8.2 Hz, 1H), 7.88 (t, *J* = 7.2 Hz, 1H), 7.81 (t, *J* = 7.7 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.64 – 7.60 (m, 1H), 7.52 – 7.48 (m, 1H), 7.41 – 7.38 (m, 3H), 7.31 (d, *J* = 8.4 Hz, 2H), 6.17 (s, 2H), 3.55 (s, 3H), 3.32 (s, 3H). <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>) δ 179.0, 168.7, 141.5, 141.2, 141.0, 132.3, 132.1, 131.1, 131.0, 130.0, 129.9, 129.8, 129.4, 128.7, 128.2, 127.5, 125.4, 117.6, 52.4, 52.2, 17.9. HRMS (ESI, Q-TOF) *m/z*: calcd for C<sub>23</sub>H<sub>20</sub>NO<sub>2</sub>S [M-Br]<sup>+</sup> 374.1209; found 374.1205.

**3-(4-Fluorobenzyl)-2-methylbenzo[d]thiazol-3-ium bromide**



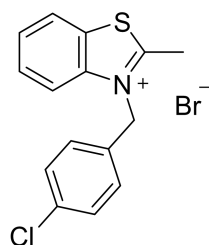
Pink solid (2.49 g, 74% yield); <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 8.56 (d, *J* = 6.6 Hz, 1H), 8.25 (d, *J* = 8.2 Hz, 1H), 7.84 (t, *J* = 7.2 Hz, 1H), 7.79 (t, *J* = 7.6 Hz, 1H), 7.45 (dd, *J* = 8.9, 5.3 Hz, 2H), 7.23 (t, *J* = 8.9 Hz, 2H), 6.12 (s, 2H), 3.31 (s, 3H). <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>) δ 179.0, 162.5 (d, *J* = 245.0 Hz), 141.4, 130.1 (d, *J* = 8.4 Hz), 130.0, 129.8, 129.6 (d, *J* = 3.1 Hz), 128.6, 125.4, 117.6, 116.5 (d, *J* = 21.8 Hz), 51.7, 18.0. <sup>19</sup>F NMR (471 MHz, DMSO-*d*<sub>6</sub>) δ -113.34. HRMS (ESI, Q-TOF) *m/z*: calcd for C<sub>15</sub>H<sub>13</sub>FNS [M-Br]<sup>+</sup> 258.0747; found 258.0747.

**2-Methyl-3-(4-(trifluoromethyl)benzyl)benzo[d]thiazol-3-ium bromide**



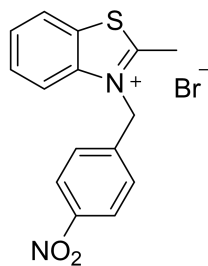
Purple solid (2.83 g, 73% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.55 (dd,  $J = 8.0, 1.5$  Hz, 1H), 8.19 (dd,  $J = 7.9, 1.3$  Hz, 1H), 7.86 – 7.83 (m, 1H), 7.81 (td,  $J = 7.6, 1.3$  Hz, 1H), 7.76 (d,  $J = 8.2$  Hz, 2H), 7.55 (d,  $J = 8.1$  Hz, 2H), 6.25 (s, 2H), 3.28 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  179.5, 141.4, 138.0, 130.1, 129.8, 129.4 (q,  $J = 31.5$  Hz), 128.7, 128.4, 126.4 (q,  $J = 3.8$  Hz), 125.5, 124.3 (q,  $J = 233.1$  Hz), 117.4, 51.9, 17.9.  $^{19}\text{F}$  NMR (471 MHz,  $\text{DMSO-}d_6$ )  $\delta$  -61.16. HRMS (ESI, Q-TOF)  $m/z$ : calcd for  $\text{C}_{16}\text{H}_{13}\text{F}_3\text{NS}$   $[\text{M-Br}]^+$  308.0715; found 308.0716.

### 3-(4-Chlorobenzyl)-2-methylbenzo[d]thiazol-3-ium bromide



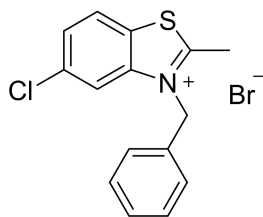
Grey solid (2.68 g, 76% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.56 (d,  $J = 8.1$  Hz, 1H), 8.22 (d,  $J = 7.8$  Hz, 1H), 7.84 (td,  $J = 7.9, 1.4$  Hz, 1H), 7.81 – 7.77 (m, 1H), 7.48 – 7.44 (m, 2H), 7.40 (d,  $J = 8.7$  Hz, 2H), 6.14 (s, 2H), 3.29 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  179.2, 141.4, 133.7, 132.3, 130.0, 129.8, 129.6, 129.5, 128.7, 125.5, 117.5, 51.7, 18.0. HRMS (ESI, Q-TOF)  $m/z$ : calcd for  $\text{C}_{15}\text{H}_{13}\text{ClNS}$   $[\text{M-Br}]^+$  274.0451; found 274.0450.

### 2-Methyl-3-(4-nitrobenzyl)benzo[d]thiazol-3-ium bromide



Purple solid (2.55 g, 70% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}$ )  $\delta$  8.57 (d,  $J = 7.8$  Hz, 1H), 8.23 (d,  $J = 8.9$  Hz, 2H), 8.17 (d,  $J = 7.8$  Hz, 1H), 7.86 – 7.79 (m, 2H), 7.61 (d,  $J = 8.9$  Hz, 2H), 6.32 (s, 2H), 3.29 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO}$ )  $\delta$  179.8, 147.9, 141.4, 140.7, 130.1, 129.8, 128.8, 128.8, 125.5, 124.5, 117.4, 51.8, 17.9. HRMS (ESI, Q-TOF)  $m/z$ : calcd for  $\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_2\text{S}$   $[\text{M-Br}]^+$  285.0692; found 285.0690.

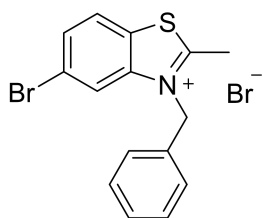
### 3-Benzyl-5-chloro-2-methylbenzo[d]thiazol-3-ium bromide



Yellow solid (2.54 g, 72% yield);  $^1\text{H}$  NMR (500 MHz, DMSO)  $\delta$

8.62 (d,  $J = 8.7$  Hz, 1H), 8.48 (d,  $J = 2.0$  Hz, 1H), 7.88 (dd,  $J = 8.9, 2.0$  Hz, 1H), 7.43 – 7.36 (m, 3H), 7.33 (d,  $J = 6.7$  Hz, 2H), 6.14 (s, 2H), 3.28 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz, DMSO)  $\delta$  180.8, 142.5, 135.0, 133.1, 129.6, 129.1, 129.0, 128.8, 127.5, 127.1, 117.4, 52.5, 18.2. HRMS (ESI, Q-TOF)  $m/z$ : calcd for  $\text{C}_{15}\text{H}_{13}\text{ClNS}$   $[\text{M}-\text{Br}]^+$  274.0451; found 274.0451.

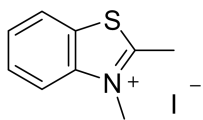
### 3-Benzyl-5-bromo-2-methylbenzo[d]thiazol-3-ium bromide



Green solid (2.98 g, 75% yield);  $^1\text{H}$  NMR (500 MHz, DMSO)  $\delta$

8.59 (d,  $J = 1.8$  Hz, 1H), 8.50 (d,  $J = 8.7$  Hz, 1H), 8.00 (dd,  $J = 8.8, 1.8$  Hz, 1H), 7.43 – 7.36 (m, 3H), 7.32 (d,  $J = 6.7$  Hz, 2H), 6.12 (s, 2H), 3.26 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz, DMSO)  $\delta$  180.6, 142.6, 133.1, 131.7, 129.6, 129.2, 129.1, 127.5, 127.2, 123.2, 120.2, 52.4, 18.0. HRMS (ESI, Q-TOF)  $m/z$ : calcd for  $\text{C}_{15}\text{H}_{13}\text{BrNS}$   $[\text{M}-\text{Br}]^+$  317.9946; found 317.9946.

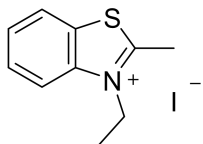
### 2,3-Dimethylbenzo[d]thiazol-3-ium iodide



Purple solid (2.18 g, 75% yield);  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$

8.47 (d,  $J = 8.2$  Hz, 1H), 8.30 (d,  $J = 8.4$  Hz, 1H), 7.90 (t,  $J = 7.9$  Hz, 1H), 7.81 (t,  $J = 8.2$  Hz, 1H), 4.22 (s, 3H), 3.19 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  177.7, 142.1, 129.7, 129.2, 128.5, 125.0, 117.3, 36.8, 17.8. HRMS (ESI, Q-TOF)  $m/z$ : calcd for  $\text{C}_9\text{H}_{10}\text{NS}$   $[\text{M}-\text{I}]^+$  164.0528; found 164.0522.

### 3-Ethyl-2-methylbenzo[d]thiazol-3-ium iodide



Green solid (2.31 mg, 76% yield);  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$

8.49 (d,  $J = 6.9$  Hz, 1H), 8.36 (d,  $J = 8.4$  Hz, 1H), 7.91 – 7.87 (m, 1H), 7.83 – 7.78 (m, 1H), 4.79 (q,  $J = 7.2$  Hz, 2H), 3.25 (s, 3H), 1.46 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  171.5, 137.0, 123.5, 47.9, 15.9, 15.0. HRMS (ESI, Q-TOF)  $m/z$ : calcd for  $\text{C}_{10}\text{H}_{12}\text{NS}$   $[\text{M}-\text{I}]^+$  178.0685; found 178.0680.

### 3. Typical procedure for the synthesis of products

#### (a-1) Synthetic procedure for 3aa-3as

Under air atmosphere, 2-methylthiazole salts **1** (0.2 mmol) and 2-aminobenzaldehyde compounds **2** (0.2 mmol), *t*-BuOLi (0.2 mmol) and CH<sub>3</sub>CN (2 mL) were introduced in a Schlenk tube, successively. Then the Schlenk tube was closed and the resulting mixture was stirred at 80 °C by heating the mantle for 12 h. After the reaction was completed and cooling to room temperature, the reaction mixture was concentrated in vacuo. The crude mixture was purified by a flash column chromatography (EtOAc/petroleumether) on silica gel to afford the products **3aa-3as**.

#### (a-2) Process parameters for gram-scale synthesis of 3aa

Under air atmosphere, 2-methylthiazole salts **1a** (10 mmol) and 2-aminobenzaldehyde **2a** (10 mmol), *t*-BuOLi (10 mmol) and CH<sub>3</sub>CN (50 mL) were introduced in a round-bottomed flask, successively. The round-bottomed flask was then closed and the resulting mixture was stirred at 80°C under a heating mantle at 600 rpm for 12 hours. After the reaction was completed and cooling to room temperature, the reaction mixture was concentrated in vacuo. The crude mixture was purified by a flash column chromatography (EtOAc/petroleumether) on silica gel to afford 1.75g of products **3aa** with a yield of 51%.

#### (b-1) Synthetic procedure for 4aa-4ao

Under air atmosphere, 2-methylthiazole salts **1** (0.2 mmol) and 2-aminobenzaldehyde compounds **2** (0.2 mmol), *t*-BuOK (0.2 mmol) and 1,2-dichloroethane (2 mL) were introduced in a Schlenk tube, successively. Then the Schlenk tube was closed and the resulting mixture was stirred at 100 °C by heating the mantle for 12 h. After the reaction was completed and cooling to room temperature, the reaction mixture was concentrated in vacuo. The crude mixture was purified by a flash column chromatography (EtOAc/petroleumether) on silica gel to afford the products **4aa-4ao**.

#### (b-2) Process parameters for gram-scale synthesis of 4aa

Under air atmosphere, 2-methylthiazole salts **1a** (10 mmol) and 2-aminobenzaldehyde **2a** (10 mmol), *t*-BuOK (10 mmol) and 1,2-dichloroethane (50 mL) were introduced in

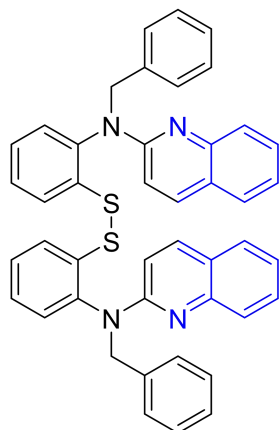
a round-bottomed flask, successively. The Schlenk tube was then closed and the resulting mixture was stirred at 100°C under a heating mantle at 600 rpm for 12 hours. After the reaction was completed and cooling to room temperature, the reaction mixture was concentrated in vacuo. The crude mixture was purified by a flash column chromatography (EtOAc/petroleum ether) on silica gel to afford 2.22g of products **4aa** with a yield of 65%.

## Reference

[1] Biesen, L.; Nirmalanathan-Budau, N.; Hoffmann, K.; Resch-Genger, U.; Muller, T. J. J. *Angew. Chem. Int. Ed.* **2020**, *59*, 10037-10041.

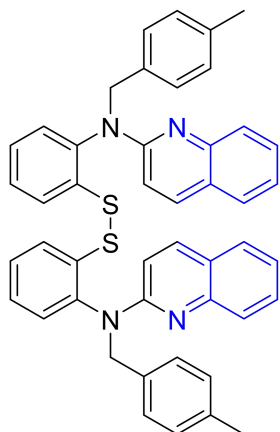
## 4. Analytical data of the obtained compounds

(1)



***N,N'*-(Disulfanediy)bis(2,1-phenylene)bis(*N*-benzylquinolin-2-amine) (3aa):** yellow oil (50.6 mg, 74% yield);  $R_f = 0.6$  (petroleum ether/ethyl acetate = 10/1, v/v);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (d,  $J = 8.6$  Hz, 2H), 7.73 (d,  $J = 9.1$  Hz, 2H), 7.65 – 7.61 (m, 4H), 7.50 – 7.45 (m, 6H), 7.31 – 7.26 (m, 10H), 7.19 (t,  $J = 7.6$  Hz, 2H), 6.97 (d,  $J = 7.6$  Hz, 2H), 6.34 (d,  $J = 9.0$  Hz, 2H), 5.91 (br s, 2H), 4.89 (br s, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.1, 147.8, 140.9, 138.6, 137.2, 130.7, 129.6, 129.5, 128.5, 128.2, 127.6, 127.3, 127.2, 127.0, 126.9, 123.7, 122.6, 111.0, 52.4. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{44}\text{H}_{34}\text{N}_4\text{S}_2$   $[\text{M}+\text{H}]^+$ : 683.2297; found 683.2290.

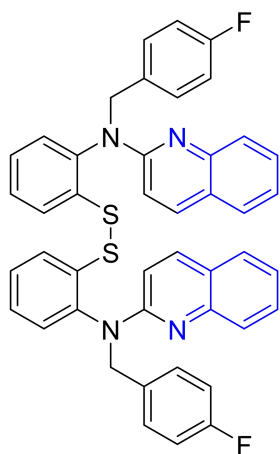
(2)



***N,N'*-(Disulfanediyldis(2,1-phenylene))bis(*N*-(4-methylbenzyl)quinolin-2-amine)**

**(3ab):** yellow oil (51.9 mg, 73% yield);  $R_f = 0.6$  (petroleum ether/ethyl acetate = 10/1, v/v);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 (d,  $J = 8.7$  Hz, 2H), 7.74 (d,  $J = 9.1$  Hz, 2H), 7.66 – 7.62 (m, 4H), 7.52 (d,  $J = 7.9$  Hz, 2H), 7.36 (d,  $J = 7.8$  Hz, 4H), 7.30 – 7.25 (m, 4H), 7.21 (td,  $J = 7.5, 1.4$  Hz, 2H), 7.11 (d,  $J = 7.8$  Hz, 4H), 6.99 (dd,  $J = 7.7, 1.3$  Hz, 2H), 6.35 (d,  $J = 9.1$  Hz, 2H), 5.89 (br s, 2H), 4.85 (br s, 2H), 2.36 (s, 6H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.1, 147.8, 141.0, 137.2, 137.1, 136.7, 135.6, 130.8, 129.5, 129.5, 128.9, 128.5, 127.6, 127.3, 127.1, 126.9, 123.7, 122.6, 111.1, 52.1, 21.3. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{46}\text{H}_{38}\text{N}_4\text{S}_2$   $[\text{M}+\text{H}]^+$ : 711.2610; found 711.2608.

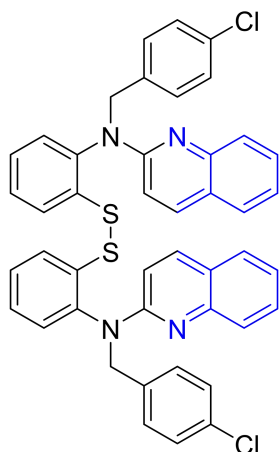
(3)



***N,N'*-(Disulfanediyldis(2,1-phenylene))bis(*N*-(4-fluorobenzyl)quinolin-2-amine)**

**(3ac):** yellow oil (35.3 mg, 49% yield);  $R_f = 0.55$  (petroleum ether/ethyl acetate = 10/1, v/v);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 (d,  $J = 8.5$  Hz, 2H), 7.73 (d,  $J = 9.2$  Hz, 2H), 7.63 (d,  $J = 7.8$  Hz, 4H), 7.46 – 7.39 (m, 6H), 7.32 – 7.28 (m, 4H), 7.21 (t,  $J = 7.5$  Hz, 2H), 6.95 (q,  $J = 7.2$  Hz, 6H), 6.31 (d,  $J = 9.0$  Hz, 2H), 5.77 (br s, 2H), 4.92 (br s, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  162.1(d,  $J = 245.7$  Hz), 155.9, 147.7, 140.7, 137.2, 137.1, 134.4, 131.3(d,  $J = 7.6$  Hz), 130.7, 129.6, 128.6, 127.8, 127.3, 127.0, 126.8, 123.7, 122.7, 114.9(d,  $J = 21.4$  Hz), 111.0, 51.7.  $^{19}\text{F NMR}$  (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -115.36. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{44}\text{H}_{32}\text{F}_2\text{N}_4\text{S}_2$   $[\text{M}+\text{H}]^+$ : 719.2109; found 719.2099.

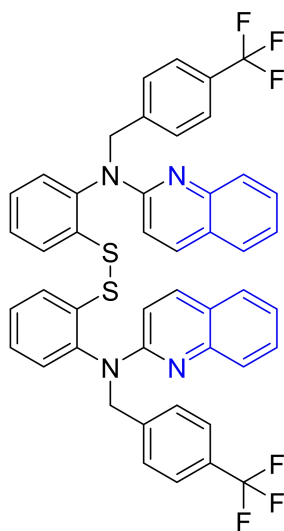
(4)



***N,N'*-(Disulfanediyldis(2,1-phenylene))bis(*N*-(4-chlorobenzyl)quinolin-2-amine)**

**(3ad)**: yellow oil (41.4 mg, 55% yield);  $R_f = 0.55$  (petroleum ether/ethyl acetate = 10/1, v/v);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 (d,  $J = 8.6$  Hz, 2H), 7.74 (d,  $J = 9.0$  Hz, 2H), 7.66 – 7.62 (m, 4H), 7.46 (d,  $J = 6.7$  Hz, 2H), 7.40 (d,  $J = 8.5$  Hz, 4H), 7.33 – 7.29 (m, 4H), 7.26 – 7.21 (m, 6H), 6.97 (dd,  $J = 7.8, 1.4$  Hz, 2H), 6.33 (d,  $J = 9.0$  Hz, 2H), 5.77 (br s, 2H), 4.92 (br s, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  155.9, 147.7, 140.8, 137.3, 137.1, 137.1, 133.0, 131.0, 130.6, 129.7, 128.7, 128.3, 127.9, 127.4, 127.0, 127.0, 123.7, 122.8, 111.0, 51.9. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{44}\text{H}_{32}\text{Cl}_2\text{N}_4\text{S}_2$   $[\text{M}+\text{K}]^+$ : 789.1077; found 789.1075.

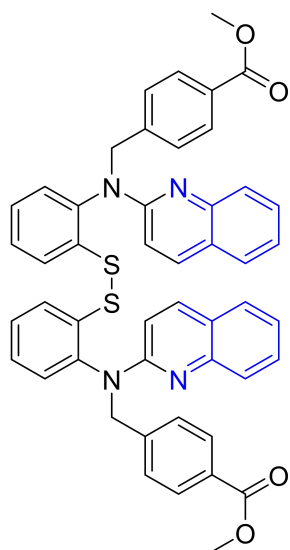
(5)



***N,N'*-(Disulfanediyldis(2,1-phenylene))bis(*N*-(4-(trifluoromethyl)benzyl)quinolin-2-amine)**

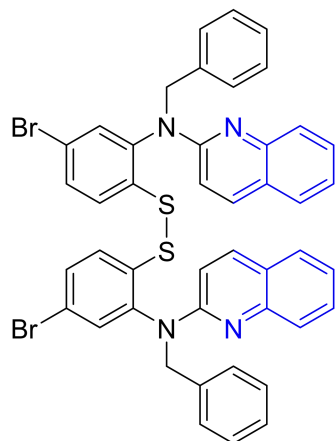
**(3ae)**: yellow oil (36.9 mg, 45% yield);  $R_f = 0.55$  (petroleum ether/ethyl acetate = 10/1, v/v);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (d,  $J = 8.9$  Hz, 2H), 7.74 (d,  $J = 9.8$  Hz, 2H), 7.65 – 7.51 (m, 16H), 7.31 – 7.29 (m, 2H), 7.26 – 7.22 (m, 2H), 6.98 (d,  $J = 7.6$  Hz, 2H), 6.34 (d,  $J = 9.0$  Hz, 2H), 5.90 (br s, 2H), 4.90 (br s, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  155.9, 147.6, 142.8, 140.9, 137.3, 137.0, 130.6, 129.7, 129.6, 129.6, 128.8, 128.4(q,  $J=249.5$  Hz), 128.0, 127.4, 127.3, 127.0, 125.1 (q,  $J=3.8$  Hz), 123.7, 123.2, 122.9, 110.9, 52.3.  $^{19}\text{F NMR}$  (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.28. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{46}\text{H}_{32}\text{F}_6\text{N}_4\text{S}_2$   $[\text{M}+\text{H}]^+$ : 819.2045; found 819.2037.

(6)



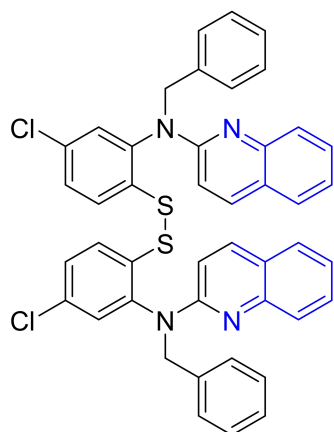
**Dimethyl 4,4'-(((disulfanediybis(2,1-phenylene))bis(quinolin-2-ylazanediyl))bis(methylene)dibenzoate (3af):** yellow oil (47.2 mg, 59% yield);  $R_f = 0.3$  (petroleum ether/ethyl acetate = 10/1, v/v);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (d,  $J = 7.9$  Hz, 4H), 7.87 (d,  $J = 8.4$  Hz, 2H), 7.78 (d,  $J = 9.0$  Hz, 2H), 7.65 – 7.61 (m, 4H), 7.54 (d,  $J = 8.2$  Hz, 4H), 7.46 (d,  $J = 7.9$  Hz, 2H), 7.31 (d,  $J = 7.5$  Hz, 2H), 7.24 (t,  $J = 7.5$  Hz, 2H), 7.11 (t,  $J = 7.7$  Hz, 2H), 6.92 (d,  $J = 7.9$  Hz, 2H), 6.37 (d,  $J = 9.0$  Hz, 2H), 5.97 (br s, 2H), 4.82 (br s, 2H), 3.91 (s, 6H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  167.1, 155.9, 147.7, 144.1, 140.3, 137.5, 133.9, 131.1, 130.1, 129.6, 129.6, 129.4, 129.0, 128.4, 127.4, 126.9, 126.8, 123.7, 122.8, 110.8, 52.1, 51.4. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{48}\text{H}_{38}\text{N}_4\text{O}_4\text{S}_2$   $[\text{M}+\text{H}]^+$ : 799.2407; found 799.2408.

(7)



***N,N'*-(Disulfanediybis(5-bromo-2,1-phenylene))bis(*N*-benzylquinolin-2-amine) (3ag):** yellow oil (42.8 mg, 51% yield);  $R_f = 0.7$  (petroleum ether/ethyl acetate = 10/1, v/v);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (d,  $J = 8.4$  Hz, 2H), 7.75 (d,  $J = 9.0$  Hz, 2H), 7.66 – 7.62 (m, 4H), 7.43 – 7.40 (m, 4H), 7.34 – 7.28 (m, 10H), 7.20 – 7.16 (m, 4H), 6.30 (d,  $J = 9.0$  Hz, 2H), 5.34 (br s, 4H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  155.5, 147.6, 142.3, 138.0, 137.4, 136.4, 133.4, 131.6, 129.7, 129.4, 128.4, 128.3, 127.4, 127.4, 127.1, 123.8, 123.0, 120.7, 110.8, 52.9. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{44}\text{H}_{32}\text{Br}_2\text{N}_4\text{S}_2$   $[\text{M}+\text{K}]^+$ : 877.0066; found 877.0065.

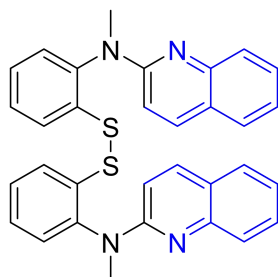
(8)



***N,N'*-(Disulfanediyldis(5-chloro-2,1-phenylene))bis(*N*-benzylquinolin-2-amine)**

**(3ah)**: yellow oil (33.8 mg, 45% yield);  $R_f = 0.7$  (petroleum ether/ethyl acetate = 10/1, v/v);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 (d,  $J = 8.6$  Hz, 2H), 7.77 (d,  $J = 8.9$  Hz, 2H), 7.69 – 7.64 (m, 4H), 7.45 (d,  $J = 3.4$  Hz, 4H), 7.36 – 7.29 (m, 10H), 7.21 (dd,  $J = 8.6, 2.2$  Hz, 2H), 7.07 (d,  $J = 2.3$  Hz, 2H), 6.34 (d,  $J = 9.2$  Hz, 2H), 5.40 (br s, 4H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  155.6, 147.6, 142.1, 138.0, 137.4, 135.7, 133.2, 130.6, 129.7, 129.4, 128.7, 128.3, 128.3, 127.4, 127.4, 127.1, 123.8, 123.0, 110.8, 52.8. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{44}\text{H}_{32}\text{Cl}_2\text{N}_4\text{S}_2$   $[\text{M}+\text{H}]^+$ : 751.1518; found 751.1513.

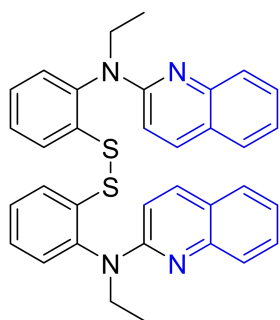
(9)



***N,N'*-(Disulfanediyldis(2,1-phenylene))bis(*N*-methylquinolin-2-amine)** **(3ai)**:

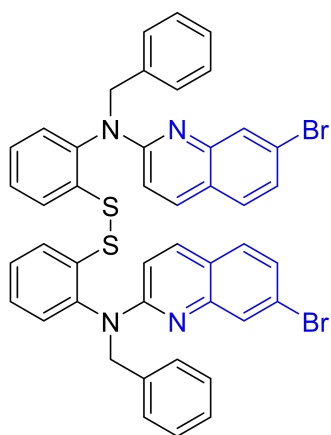
yellow oil (39.4mg, 74% yield);  $R_f = 0.6$  (petroleum ether/ethyl acetate = 5/1, v/v);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (d,  $J = 8.2$  Hz, 2H), 7.72 (d,  $J = 9.0$  Hz, 2H), 7.69 – 7.66 (m, 2H), 7.62 (d,  $J = 7.5$  Hz, 4H), 7.33 – 7.31 (m, 4H), 7.28 (d,  $J = 8.4$  Hz, 2H), 7.25 – 7.23 (m, 2H), 6.39 (d,  $J = 9.0$  Hz, 2H), 3.60 (s, 6H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.7, 147.8, 143.3, 136.9, 136.8, 129.6, 129.1, 128.5, 128.2, 127.4, 127.1, 126.8, 123.4, 122.6, 111.3, 37.7. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{32}\text{H}_{26}\text{N}_4\text{S}_2$   $[\text{M}+\text{H}]^+$  : 531.1671; found 531.1662.

(10)



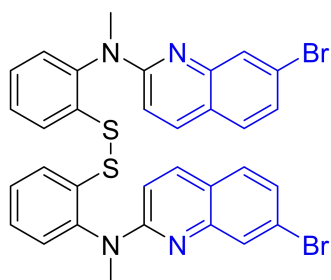
***N,N'*-(Disulfanediyldis(2,1-phenylene))bis(*N*-ethylquinolin-2-amine) (3aj):** green oil (39.2mg, 70% yield);  $R_f = 0.7$  (petroleum ether/ethyl acetate = 5/1, v/v);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (d,  $J = 8.5$  Hz, 2H), 7.73 (d,  $J = 9.2$  Hz, 2H), 7.60 (t,  $J = 7.7$  Hz, 4H), 7.49 (dd,  $J = 7.6, 1.7$  Hz, 2H), 7.29 – 7.22 (m, 8H), 6.33 (d,  $J = 9.0$  Hz, 2H), 4.37 (br s, 2H), 3.95 (br s, 2H), 1.34 (t,  $J = 7.1$  Hz, 6H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.1, 147.9, 141.3, 137.5, 136.8, 130.4, 129.4, 128.4, 127.8, 127.3, 127.0, 126.7, 123.4, 122.4, 111.4, 44.2, 13.1. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{34}\text{H}_{30}\text{N}_4\text{S}_2$   $[\text{M}+\text{H}]^+$ : 559.1984; found 559.1974.

(11)



***N,N'*-(Disulfanediyldis(2,1-phenylene))bis(*N*-benzyl-7-bromoquinolin-2-amine) (3ak):** yellow solid (36.1 mg, 43% yield); m.p: 274.2-276.2 °C;  $R_f = 0.55$  (petroleum ether/ethyl acetate = 10/1, v/v);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (s, 2H), 7.64 (s, 2H), 7.48 – 7.44 (m, 4H), 7.42 – 7.39 (m, 4H), 7.36 (dd,  $J = 8.5, 2.0$  Hz, 2H), 7.28 – 7.24 (m, 8H), 7.19 (td,  $J = 7.5, 1.5$  Hz, 2H), 6.95 (d,  $J = 6.3$  Hz, 2H), 6.31 (s, 2H), 5.84 (br s, 2H), 4.80 (br s, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.5, 148.6, 140.6, 138.2, 136.9, 136.9, 130.7, 129.4, 129.3, 128.7, 128.5, 128.2, 127.8, 127.3, 125.9, 123.6, 122.2, 111.2, 52.6. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{44}\text{H}_{32}\text{Br}_2\text{N}_4\text{S}_2$   $[\text{M}+\text{K}]^+$  : 877.0066; found 877.0070.

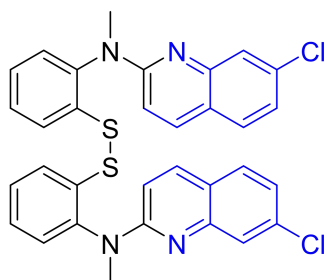
(12)



***N,N'*-(Disulfanediylobis(2,1-phenylene))bis(7-bromo-*N*-methylquinolin-2-amine)**

**(3a1):** yellow solid (35.1mg, 51% yield); m.p: 260.9-262.9 °C;  $R_f = 0.6$  (petroleum ether/ethyl acetate = 5/1, v/v);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 (s, 2H), 7.70 – 7.67 (m, 2H), 7.65 (d,  $J = 9.2$  Hz, 2H), 7.43 (d,  $J = 8.5$  Hz, 2H), 7.36 – 7.32 (m, 6H), 7.25 – 7.22 (m, 2H), 6.39 (d,  $J = 9.0$  Hz, 2H), 3.59 (s, 6H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  157.1, 148.7, 142.9, 136.7, 136.6, 129.2, 129.1, 128.7, 128.6, 128.4, 127.3, 125.9, 123.6, 122.0, 111.4, 37.7. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{32}\text{H}_{24}\text{Br}_2\text{N}_4\text{S}_2$   $[\text{M}+\text{H}]^+$  : 686.9881; found 686.9873.

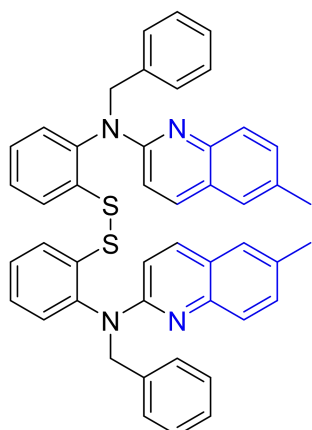
(13)



***N,N'*-(disulfanediylobis(2,1-phenylene))bis(7-chloro-*N*-methylquinolin-2-amine)**

**(3am):** yellow oil (31.8mg, 53% yield);  $R_f = 0.6$  (petroleum ether/ethyl acetate = 5/1, v/v);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (s, 2H), 7.69 – 7.65 (m, 4H), 7.52 (d,  $J = 8.5$  Hz, 2H), 7.34 – 7.32 (m, 4H), 7.24 – 7.21 (m, 4H), 6.36 (d,  $J = 9.0$  Hz, 2H), 3.58 (s, 6H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  157.2, 148.4, 142.9, 136.7, 136.6, 135.3, 129.1, 128.7, 128.5, 128.4, 127.3, 126.0, 123.3, 121.7, 111.2, 37.7. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{32}\text{H}_{24}\text{Cl}_2\text{N}_4\text{S}_2$   $[\text{M}+\text{K}]^+$ : 637.0451; found 637.0448.

(14)

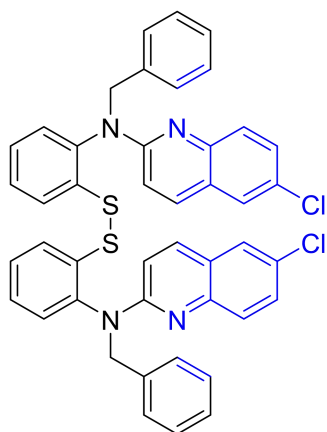


***N,N'*-(Disulfanediylobis(2,1-phenylene))bis(*N*-benzyl-6-methylquinolin-2-amine)**

**(3an):** yellow solid (44.9 mg, 63% yield); m.p: 276.2-278.2 °C;  $R_f = 0.6$  (petroleum

ether/ethyl acetate = 10/1, v/v);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (d,  $J = 8.5$  Hz, 2H), 7.67 (d,  $J = 9.0$  Hz, 2H), 7.49 – 7.44 (m, 8H), 7.41 (s, 2H), 7.29 – 7.23 (m, 8H), 7.18 (td,  $J = 7.6, 1.5$  Hz, 2H), 6.97 (dd,  $J = 7.8, 1.5$  Hz, 2H), 6.33 (d,  $J = 9.0$  Hz, 2H), 5.85 (br s, 2H), 4.92 (br s, 2H), 2.51 (s, 6H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  155.7, 146.1, 141.1, 138.8, 137.2, 136.6, 132.1, 131.5, 130.7, 129.5, 128.4, 128.1, 127.5, 127.1, 126.9, 126.8, 126.5, 123.6, 111.0, 52.4, 21.3. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{46}\text{H}_{38}\text{N}_4\text{S}_2$   $[\text{M}+\text{H}]^+$ : 711.2610; found 711.2606.

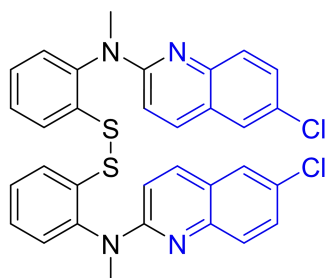
(15)



***N,N'*-(Disulfanediyldis(2,1-phenylene))bis(*N*-benzyl-6-chloroquinolin-2-amine)**

**(3a0):** yellow oil (35.3 mg, 47% yield);  $R_f = 0.6$  (petroleum ether/ethyl acetate = 10/1, v/v);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 (d,  $J = 9.5$  Hz, 2H), 7.62 (d,  $J = 8.4$  Hz, 2H), 7.58 (d,  $J = 2.4$  Hz, 2H), 7.54 (dd,  $J = 8.9, 2.4$  Hz, 2H), 7.45 (d,  $J = 7.5$  Hz, 2H), 7.43 – 7.39 (m, 4H), 7.28 – 7.24 (m, 8H), 7.19 (td,  $J = 7.6, 1.5$  Hz, 2H), 6.95 (dd,  $J = 7.6, 1.5$  Hz, 2H), 6.32 (d,  $J = 9.2$  Hz, 2H), 5.84 (br s, 2H), 4.84 (br s, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.2, 146.2, 140.6, 138.3, 137.0, 136.2, 130.7, 130.1, 129.5, 128.7, 128.5, 128.2, 127.8, 127.7, 127.3, 127.1, 126.0, 124.2, 111.8, 52.5. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{44}\text{H}_{32}\text{Cl}_2\text{N}_4\text{S}_2$   $[\text{M}+\text{H}]^+$ : 751.1518; found 751.1508.

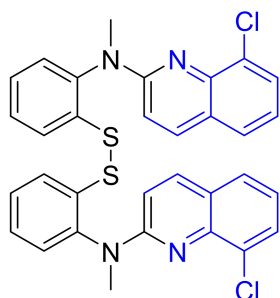
(16)



***N,N'*-(Disulfanediyldis(2,1-phenylene))bis(6-chloro-*N*-methylquinolin-2-amine)**

**(3aQ):** yellow oil (38.4mg, 64% yield);  $R_f = 0.6$  (petroleum ether/ethyl acetate = 5/1, v/v);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (d,  $J = 8.7$  Hz, 2H), 7.72 (d,  $J = 9.2$  Hz, 2H), 7.69 – 7.67 (m, 2H), 7.61 (t,  $J = 7.6$  Hz, 4H), 7.33 – 7.30 (m, 4H), 7.25 – 7.23 (m, 2H), 6.40 (d,  $J = 9.0$  Hz, 2H), 3.61 (s, 6H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.7, 147.8, 143.3, 136.9, 136.8, 129.6, 129.1, 128.5, 128.2, 127.4, 127.1, 126.8, 123.4, 122.7, 111.3, 37.7. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{32}\text{H}_{24}\text{Cl}_2\text{N}_4\text{S}_2$   $[\text{M}+\text{H}]^+$ : 599.0892; found 599.0886.

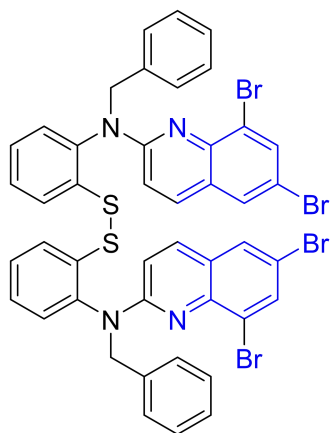
(17)



*N,N'*-(disulfanediyldis(2,1-phenylene))bis(8-chloro-*N*-methylquinolin-2-amine)

**(3ar)**: yellow oil (12.6mg, 21% yield);  $R_f$  = 0.6 (petroleum ether/ethyl acetate = 5/1, v/v);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 – 7.68 (m, 6H), 7.53 (d,  $J$  = 7.9 Hz, 2H), 7.36 – 7.32 (m, 4H), 7.26 – 7.23 (m, 2H), 7.18 (t,  $J$  = 7.8 Hz, 2H), 6.40 (s, 2H), 3.67 (s, 6H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.8, 144.0, 142.8, 137.2, 136.7, 130.7, 129.7, 129.1, 128.7, 128.4, 127.4, 126.3, 124.5, 122.3, 111.7, 37.7. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{32}\text{H}_{24}\text{Cl}_2\text{N}_4\text{S}_2[\text{M}+\text{H}]^+$  : 599.0892; found 599.0891.

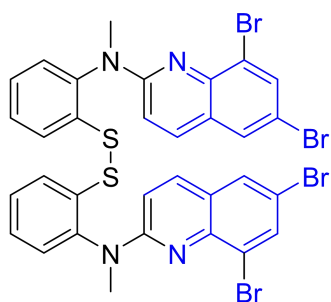
(18)



*N,N'*-(Disulfanediyldis(2,1-phenylene))bis(*N*-benzyl-6,8-dibromoquinolin-2-amine)

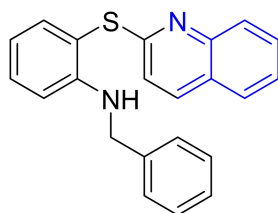
**(3as)**: yellow solid (37.8 mg, 38% yield); m.p: 272.2-274.2 °C;  $R_f$  = 0.55 (petroleum ether/ethyl acetate = 10/1, v/v);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (d,  $J$  = 2.1 Hz, 2H), 7.69 (d,  $J$  = 2.3 Hz, 2H), 7.60 – 7.44 (m, 8H), 7.30 – 7.21 (m, 10H), 6.94 (s, 2H), 6.34 – 6.18 (m, 2H), 5.91 – 5.80 (m, 2H), 5.00 – 4.87 (m, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.4, 143.7, 138.0, 137.0, 136.6, 135.5, 130.8, 129.9, 129.0, 128.9, 128.2, 127.9, 127.7, 127.5, 127.2, 125.2, 123.0, 114.5, 112.5, 52.9. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{44}\text{H}_{30}\text{Br}_4\text{N}_4\text{S}_2[\text{M}+\text{K}]^+$  : 1032.8276; found 1032.8273.

(19)



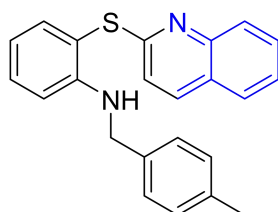
***N,N'*-(Disulfanediylbis(2,1-phenylene))bis(6,8-dibromo-*N*-methylquinolin-2-amine) (3at):** yellow solid (64.1mg, 76% yield); m.p: 187.1-189.1 °C;  $R_f = 0.65$  (petroleum ether/ethyl acetate = 5/1, v/v);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J = 2.1$  Hz, 2H), 7.68 (d,  $J = 2.3$  Hz, 4H), 7.57 (s, 2H), 7.37 – 7.33 (m, 4H), 7.24 (s, 2H), 6.36 (br s, 2H), 3.65 (s, 6H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  157.0, 143.8, 142.5, 136.6, 136.4, 135.4, 129.2, 129.1, 128.9, 128.7, 127.7, 125.0, 123.0, 114.5, 112.5, 37.9. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{32}\text{H}_{22}\text{Br}_4\text{N}_4\text{S}_2$   $[\text{M}+\text{K}]^+$  : 880.7650; found 880.7655.

(20)



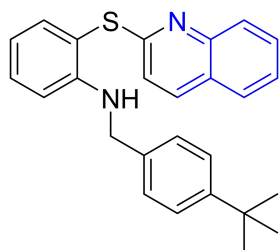
***N*-Benzyl-2-(quinolin-2-ylthio)aniline (4aa):** Brown oil (56.1 mg, 82% yield);  $R_f = 0.5$  (petroleum ether/ethyl acetate = 10/1, v/v);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (d,  $J = 8.5$  Hz, 1H), 7.91 (d,  $J = 8.7$  Hz, 1H), 7.77 – 7.68 (m, 2H), 7.64 (d,  $J = 7.6$  Hz, 1H), 7.49 (t,  $J = 7.6$  Hz, 1H), 7.36 (t,  $J = 7.9$  Hz, 1H), 7.29 – 7.18 (m, 5H), 6.95 (d,  $J = 8.7$  Hz, 1H), 6.80 (t,  $J = 7.5$  Hz, 1H), 6.72 (d,  $J = 8.3$  Hz, 1H), 5.58 (s, 1H), 4.38 (d,  $J = 5.5$  Hz, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  161.1, 149.7, 148.2, 138.8, 138.1, 136.7, 132.2, 130.1, 128.6, 128.2, 127.7, 127.2, 127.0, 126.0, 125.8, 118.3, 117.4, 112.5, 111.3, 47.5. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{22}\text{H}_{18}\text{N}_2\text{S}$   $[\text{M}+\text{H}]^+$  : 343.1263; found 343.1265.

(21)



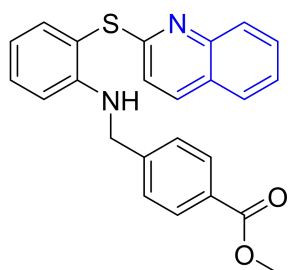
***N*-(4-Methylbenzyl)-2-(quinolin-2-ylthio)aniline (4ab):** brown oil 57.0 mg, 80% yield);  $R_f = 0.55$  (petroleum ether/ethyl acetate = 10/1, v/v);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 (d,  $J = 8.4$  Hz, 1H), 7.90 (d,  $J = 8.7$  Hz, 1H), 7.77 – 7.70 (m, 2H), 7.66 (d,  $J = 7.3$  Hz, 1H), 7.49 (t,  $J = 7.6$  Hz, 1H), 7.38 (t,  $J = 7.9$  Hz, 1H), 7.13 – 7.04 (m, 4H), 6.97 (d,  $J = 8.7$  Hz, 1H), 6.81 (t,  $J = 7.5$  Hz, 1H), 6.75 (d,  $J = 8.2$  Hz, 1H), 5.58 (s, 1H), 4.35 (d,  $J = 5.3$  Hz, 2H), 2.33 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  161.2, 149.8, 148.3, 138.1, 136.8, 136.7, 135.8, 132.2, 130.1, 129.3, 128.2, 127.7, 127.0, 126.0, 125.8, 118.3, 117.4, 112.4, 111.3, 47.3, 21.2. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{20}\text{N}_2\text{S}$   $[\text{M}+\text{H}]^+$  : 357.1419; found 357.1420.

(22)



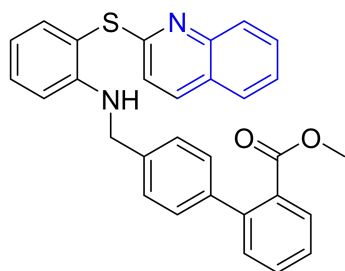
**N-(4-(tert-Butyl)benzyl)-2-(quinolin-2-ylthio)aniline (4ac):** brown oil (64.5mg, 81% yield);  $R_f = 0.6$  (petroleum ether/ethyl acetate = 10/1, v/v);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (d,  $J = 8.4$  Hz, 1H), 7.92 (d,  $J = 9.6$  Hz, 1H), 7.76 (d,  $J = 8.1$  Hz, 1H), 7.74 – 7.70 (m, 1H), 7.65 (dd,  $J = 7.6, 1.6$  Hz, 1H), 7.52 – 7.48 (m, 1H), 7.40 – 7.36 (m, 1H), 7.26 (d,  $J = 8.4$  Hz, 2H), 7.12 (d,  $J = 8.5$  Hz, 2H), 6.96 (d,  $J = 8.7$  Hz, 1H), 6.80 (td,  $J = 7.5, 1.4$  Hz, 1H), 6.77 (d,  $J = 8.2$  Hz, 1H), 5.51 (s, 1H), 4.35 (d,  $J = 5.2$  Hz, 2H), 1.32 (s, 9H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  161.2, 150.1, 149.8, 148.3, 138.1, 136.7, 135.7, 132.2, 130.1, 128.2, 127.7, 126.8, 126.0, 125.8, 125.5, 118.3, 117.3, 112.4, 111.2, 47.3, 34.5, 31.4. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{26}\text{H}_{26}\text{N}_2\text{S}$   $[\text{M}+\text{H}]^+$  : 399.1889; found 399.1881.

(23)



**Methyl 4-(((2-(quinolin-2-ylthio)phenyl)amino)methyl)benzoate (4ad):** brown oil (53.6mg, 67% yield);  $R_f = 0.3$  (petroleum ether/ethyl acetate = 10/1, v/v);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J = 8.4$  Hz, 1H), 7.89 (d,  $J = 8.4$  Hz, 3H), 7.72 (d,  $J = 8.1$  Hz, 1H), 7.68 (t,  $J = 8.5$  Hz, 1H), 7.62 (d,  $J = 7.6$  Hz, 1H), 7.46 (t,  $J = 7.1$  Hz, 1H), 7.30 (t,  $J = 7.8$  Hz, 1H), 7.23 (d,  $J = 8.2$  Hz, 2H), 6.93 (d,  $J = 8.7$  Hz, 1H), 6.77 (t,  $J = 7.5$  Hz, 1H), 6.59 (d,  $J = 8.4$  Hz, 1H), 5.65 (s, 1H), 4.40 (d,  $J = 6.0$  Hz, 2H), 3.89 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  166.9, 160.8, 149.3, 148.2, 144.4, 138.1, 136.7, 132.2, 130.2, 129.9, 129.0, 128.1, 127.7, 126.7, 126.0, 125.9, 118.3, 117.7, 112.7, 111.2, 52.1, 47.2. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_2\text{S}$   $[\text{M}+\text{H}]^+$  : 401.1318; found 401.1312.

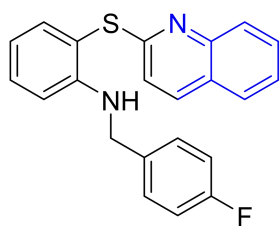
(24)



**Methyl 4'-(((2-(quinolin-2-ylthio)phenyl)amino)methyl)-[1,1'-biphenyl]-2-**

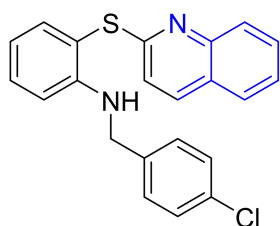
**carboxylate (4ae):** yellow oil (60.0mg, 63% yield);  $R_f = 0.2$  (petroleum ether/ethyl acetate = 10/1, v/v);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (d,  $J = 8.4$  Hz, 1H), 7.93 (d,  $J = 8.7$  Hz, 1H), 7.83 (d,  $J = 6.3$  Hz, 1H), 7.74 (d,  $J = 9.8$  Hz, 1H), 7.70 (t,  $J = 7.7$  Hz, 1H), 7.64 (dd,  $J = 7.5, 1.7$  Hz, 1H), 7.53 (t,  $J = 7.6$  Hz, 1H), 7.47 (t,  $J = 7.5$  Hz, 1H), 7.41 (t,  $J = 7.6$  Hz, 1H), 7.37 – 7.33 (m, 2H), 7.23 – 7.17 (m, 4H), 6.96 (d,  $J = 8.7$  Hz, 1H), 6.80 (t,  $J = 7.5$  Hz, 1H), 6.75 (d,  $J = 8.2$  Hz, 1H), 5.60 (s, 1H), 4.43 (d,  $J = 5.3$  Hz, 2H), 3.57 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  169.2, 161.1, 149.7, 148.2, 142.1, 140.2, 138.1, 137.8, 136.7, 132.2, 131.3, 130.8, 130.7, 130.1, 129.8, 128.5, 128.1, 127.7, 127.2, 126.7, 126.0, 125.8, 118.3, 117.5, 112.5, 111.3, 51.9, 47.3. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{30}\text{H}_{24}\text{N}_2\text{O}_2\text{S}$   $[\text{M}+\text{H}]^+$ : 477.1631; found 477.1623.

(25)



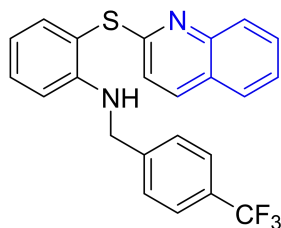
***N*-(4-Fluorobenzyl)-2-(quinolin-2-ylthio)aniline (4af):** yellow oil (40.3mg, 56% yield);  $R_f = 0.55$  (petroleum ether/ethyl acetate = 10/1, v/v);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (d,  $J = 8.5$  Hz, 1H), 7.91 (d,  $J = 8.7$  Hz, 1H), 7.75 (d,  $J = 8.1$  Hz, 1H), 7.71 (t,  $J = 6.9$  Hz, 1H), 7.63 (dd,  $J = 7.5, 1.7$  Hz, 1H), 7.49 (t,  $J = 6.9$  Hz, 1H), 7.37 – 7.33 (m, 1H), 7.11-7.13 (m, 2H), 6.93 – 6.87 (m, 3H), 6.79 (t,  $J = 7.5$  Hz, 1H), 6.68 (d,  $J = 8.2$  Hz, 1H), 5.52 (s, 1H), 4.33 (s, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  161.9(d,  $J=245.7$  Hz), 149.5, 148.2, 138.1, 136.6, 134.4(d,  $J=2.5$  Hz), 132.1, 130.1, 128.5(d,  $J=7.6$  Hz), 128.1, 127.7, 126.0, 125.8, 118.3, 117.6, 115.5, 115.3, 112.6, 111.2, 46.8.  $^{19}\text{F NMR}$  (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -115.64, -115.66, -115.66, -115.68, -115.68, -115.69, -115.70. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{22}\text{H}_{17}\text{FN}_2\text{S}$   $[\text{M}+\text{H}]^+$ : 361.1169; found 361.1170.

(26)



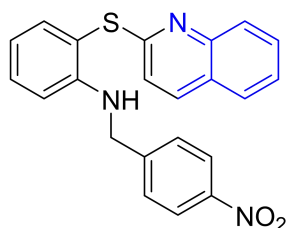
***N*-(4-Chlorobenzyl)-2-(quinolin-2-ylthio)aniline (4ag):** brown oil (55.6mg, 74% yield);  $R_f = 0.55$  (petroleum ether/ethyl acetate = 10/1, v/v);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (d,  $J = 8.5$  Hz, 1H), 7.91 (d,  $J = 8.7$  Hz, 1H), 7.77 – 7.69 (m, 2H), 7.63 (d,  $J = 7.6$  Hz, 1H), 7.49 (t,  $J = 7.5$  Hz, 1H), 7.34 (t,  $J = 6.9$  Hz, 1H), 7.20 – 7.06 (m, 4H), 6.92 (d,  $J = 8.7$  Hz, 1H), 6.80 (t,  $J = 6.9$  Hz, 1H), 6.64 (d,  $J = 8.2$  Hz, 1H), 5.56 (s, 1H), 4.33 (s, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  160.9, 149.4, 148.2, 138.1, 137.4, 136.7, 132.8, 132.2, 130.2, 128.7, 128.2, 128.1, 127.7, 126.0, 125.9, 118.3, 117.7, 112.7, 111.2, 46.8. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{22}\text{H}_{17}\text{ClN}_2\text{S}$   $[\text{M}+\text{H}]^+$ : 377.0873; found 377.0868.

(27)



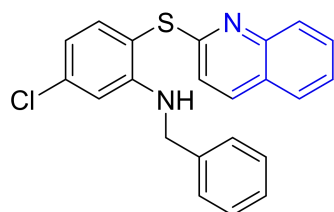
**2-(Quinolin-2-ylthio)-N-(4-(trifluoromethyl)benzyl)aniline (4ah):** brown oil (42.6mg, 52% yield);  $R_f = 0.5$  (petroleum ether/ethyl acetate = 10/1, v/v);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (d,  $J = 8.7$  Hz, 1H), 7.92 (d,  $J = 8.7$  Hz, 1H), 7.75 (d,  $J = 8.1$  Hz, 1H), 7.71 (t,  $J = 7.7$  Hz, 1H), 7.65 (dd,  $J = 7.6, 1.7$  Hz, 1H), 7.52 – 7.46 (m, 3H), 7.34 (t,  $J = 7.8$  Hz, 1H), 7.28 (d,  $J = 8.1$  Hz, 2H), 6.95 (d,  $J = 8.7$  Hz, 1H), 6.81 (t,  $J = 7.5$  Hz, 1H), 6.62 (d,  $J = 8.4$  Hz, 1H), 5.65 (s, 1H), 4.43 (d,  $J = 5.3$  Hz, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  160.8, 149.2, 148.2, 143.1, 138.2, 136.7, 132.2, 130.2, 129.4(q,  $J = 32.8$  Hz), 128.1, 127.7, 127.0, 126.3(q,  $J = 272.2$  Hz), 126.0, 125.9, 125.5(q,  $J = 3.8$  Hz), 118.3, 117.8, 112.8, 111.2, 47.0.  $^{19}\text{F NMR}$  (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.40. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{17}\text{F}_3\text{N}_2\text{S}$   $[\text{M}+\text{H}]^+$ : 411.1137; found 411.1130.

(28)



**N-(4-Nitrobenzyl)-2-(quinolin-2-ylthio)aniline (4ai):** brown oil (45.7mg, 59% yield);  $R_f = 0.3$  (petroleum ether/ethyl acetate = 10/1, v/v);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (d,  $J = 8.7$  Hz, 2H), 7.91 – 7.97 (m, 2H), 7.75 (d,  $J = 8.2$  Hz, 1H), 7.70 (t,  $J = 7.7$  Hz, 1H), 7.64 (d,  $J = 7.6$  Hz, 1H), 7.48 (t,  $J = 7.6$  Hz, 1H), 7.31 (d,  $J = 8.7$  Hz, 3H), 6.95 (d,  $J = 8.7$  Hz, 1H), 6.81 (t,  $J = 7.6$  Hz, 1H), 6.54 (d,  $J = 8.2$  Hz, 1H), 5.70 (t,  $J = 6.1$  Hz, 1H), 4.47 (d,  $J = 6.1$  Hz, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  160.5, 148.9, 148.2, 147.1, 146.9, 138.2, 136.7, 132.2, 130.3, 128.1, 127.8, 127.4, 126.0, 123.8, 118.4, 118.1, 113.0, 111.1, 46.9. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{22}\text{H}_{17}\text{N}_3\text{O}_2\text{S}$   $[\text{M}+\text{H}]^+$ : 388.1114; found 388.1109.

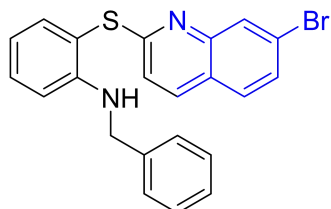
(29)



**N-Benzyl-5-chloro-2-(quinolin-2-ylthio)aniline (4aj):** brown solid (33.8mg, 45% yield); m.p: 270.2-272.2 °C;  $R_f = 0.7$  (petroleum ether/ethyl acetate = 10/1, v/v);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J = 8.5$  Hz, 1H), 7.94 (d,  $J = 8.7$  Hz, 1H), 7.76 (d,  $J = 8.1$  Hz, 1H), 7.71 (t,  $J = 7.8$  Hz, 1H), 7.54 – 7.48 (m, 2H), 7.22 (s, 3H), 7.15 (s, 2H), 6.94 (d,  $J = 8.7$  Hz, 1H), 6.76 (d,  $J = 8.2$  Hz, 1H), 6.70 (s, 1H), 5.58 (s, 1H), 4.34

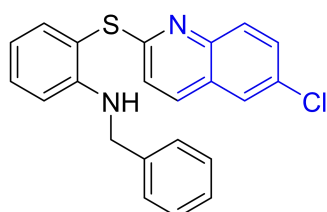
(d,  $J = 4.4$  Hz, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  160.2, 150.4, 148.2, 138.9, 138.2, 138.0, 136.8, 130.2, 128.7, 128.2, 127.7, 127.4, 127.0, 126.0, 126.0, 118.2, 117.4, 111.1, 111.0, 47.4. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{22}\text{H}_{17}\text{ClN}_2\text{S}$   $[\text{M}+\text{H}]^+$ : 377.0873; found 377.0870.

(30)



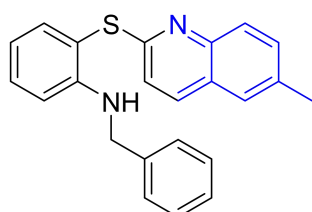
***N*-Benzyl-2-((7-bromoquinolin-2-yl)thio)aniline (4a)**: yellow oil (50.4mg, 60% yield);  $R_f = 0.5$  (petroleum ether/ethyl acetate = 10/1, v/v);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.16 (s, 1H), 7.87 (d,  $J = 8.7$  Hz, 1H), 7.62 – 7.58 (m, 2H), 7.56 (dd,  $J = 8.6$ , 1.9 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.24 (d,  $J = 7.5$  Hz, 3H), 7.20 – 7.18 (m, 2H), 6.96 (d,  $J = 8.7$  Hz, 1H), 6.78 (t,  $J = 7.5$  Hz, 1H), 6.71 (d,  $J = 6.9$  Hz, 1H), 5.51 (s, 1H), 4.38 (s, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  162.4, 149.7, 148.6, 138.7, 138.0, 136.4, 132.3, 130.5, 129.3, 128.8, 128.6, 127.2, 126.9, 124.5, 124.2, 118.7, 117.5, 111.9, 111.3, 47.5. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{22}\text{H}_{17}\text{BrN}_2\text{S}$   $[\text{M}+\text{H}]^+$ : 421.0368; found 421.0359.

(31)



***N*-Benzyl-2-((6-chloroquinolin-2-yl)thio)aniline (4am)**: brown oil (28.6mg, 38% yield);  $R_f = 0.6$  (petroleum ether/ethyl acetate = 10/1, v/v);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (d,  $J = 9.0$  Hz, 1H), 7.80 (d,  $J = 8.7$  Hz, 1H), 7.71 (d,  $J = 2.3$  Hz, 1H), 7.65 – 7.60 (m, 2H), 7.36 (t,  $J = 7.8$  Hz, 1H), 7.24 (d,  $J = 7.3$  Hz, 3H), 7.21 – 7.18 (m, 2H), 6.95 (d,  $J = 8.7$  Hz, 1H), 6.79 (t,  $J = 7.5$  Hz, 1H), 6.72 (d,  $J = 8.2$  Hz, 1H), 5.54 (s, 1H), 4.38 (s, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  161.6, 149.7, 146.6, 138.7, 138.1, 135.6, 132.3, 131.3, 130.9, 129.7, 128.6, 127.2, 127.0, 126.5, 126.4, 119.2, 117.5, 112.1, 111.3, 47.5. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{22}\text{H}_{17}\text{ClN}_2\text{S}$   $[\text{M}+\text{H}]^+$ : 377.0873; found 377.0869.

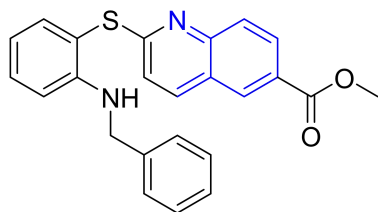
(32)



***N*-Benzyl-2-((6-methylquinolin-2-yl)thio)aniline (4an)**: brown oil (54.8mg, 77%

yield);  $R_f = 0.55$  (petroleum ether/ethyl acetate = 10/1, v/v);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (d,  $J = 8.5$  Hz, 1H), 7.83 (d,  $J = 8.7$  Hz, 1H), 7.62 (dd,  $J = 7.5, 1.7$  Hz, 1H), 7.55 – 7.50 (m, 2H), 7.35 – 7.31 (m, 1H), 7.22 (d,  $J = 7.5$  Hz, 3H), 7.19 – 7.16 (m, 2H), 6.89 (d,  $J = 8.7$  Hz, 1H), 6.77 (t,  $J = 7.5$  Hz, 1H), 6.69 (d,  $J = 8.2$  Hz, 1H), 5.57 (s, 1H), 4.37 (s, 2H), 2.53 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.9, 149.7, 146.8, 138.8, 138.1, 136.1, 135.6, 132.3, 132.1, 128.5, 127.8, 127.1, 126.9, 126.6, 126.0, 118.3, 117.3, 112.6, 111.2, 47.5, 21.5. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{20}\text{N}_2\text{S}$   $[\text{M}+\text{H}]^+$ : 357.1419; found 357.1416.

(33)

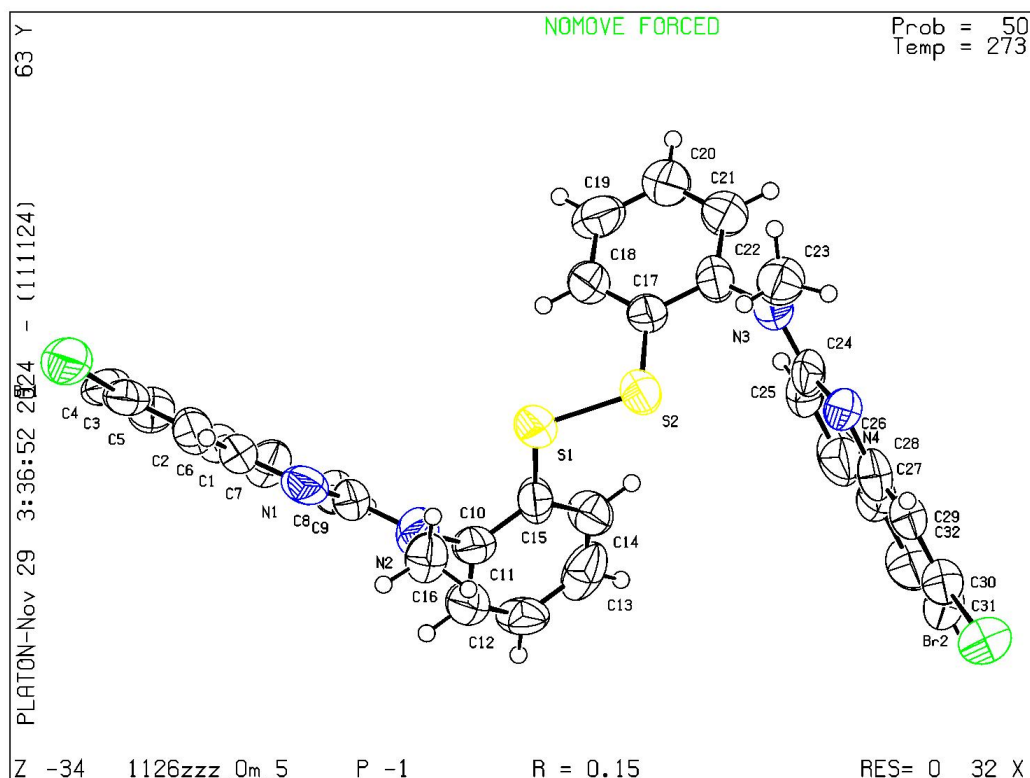


**Methyl 2-((2-(benzylamino)phenyl)thio)quinoline-6-carboxylate (4a0):** yellow solid (39.2mg, 49% yield); m.p: 197.3-199.3 °C;  $R_f = 0.3$  (petroleum ether/ethyl acetate = 5/1, v/v);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.46 (d,  $J = 2.0$  Hz, 1H), 8.25 (d,  $J = 6.9$  Hz, 1H), 7.95 (t,  $J = 8.1$  Hz, 2H), 7.60 (d,  $J = 7.6$  Hz, 1H), 7.35 (t,  $J = 7.8$  Hz, 1H), 7.21 (q,  $J = 7.7$  Hz, 5H), 6.98 (d,  $J = 8.7$  Hz, 1H), 6.78 (t,  $J = 7.5$  Hz, 1H), 6.72 (d,  $J = 7.2$  Hz, 1H), 5.56 (t,  $J = 5.9$  Hz, 1H), 4.38 (d,  $J = 5.8$  Hz, 2H), 3.98 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  166.6, 164.3, 150.0, 149.7, 138.8, 138.0, 137.5, 132.4, 130.8, 129.7, 128.6, 128.3, 127.2, 127.1, 127.0, 125.0, 119.0, 117.5, 111.8, 111.4, 52.4, 47.5. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_2\text{S}$   $[\text{M}+\text{H}]^+$ : 401.1318; found 401.1319.

## 5. Single crystal X-ray diffraction

### (1) Single crystal X-ray diffraction of **3al**

Yellow and transparent block-like single crystals of **3al** were grown by layering a dichloromethane solution with n-hexane at ambient temperature. X-Ray diffraction data of one these crystals were collected on a R-AXIS SPIDER diffractometer. The measurements were performed with Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Data were collected at 296 K, using the  $\omega$  - and  $\phi$  - scans to a maximum  $\theta$  value of 25.025 o. The data were refined by full-matrix least-squares techniques on F2 with SHELXTL-2014. And the structures were solved by direct methods SHELXS-2014. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included at geometrically idealized positions. An ORTEP representation of the structure is shown below.



**Figure 1.** ORTEP drawing of **3al** with the numbering scheme.

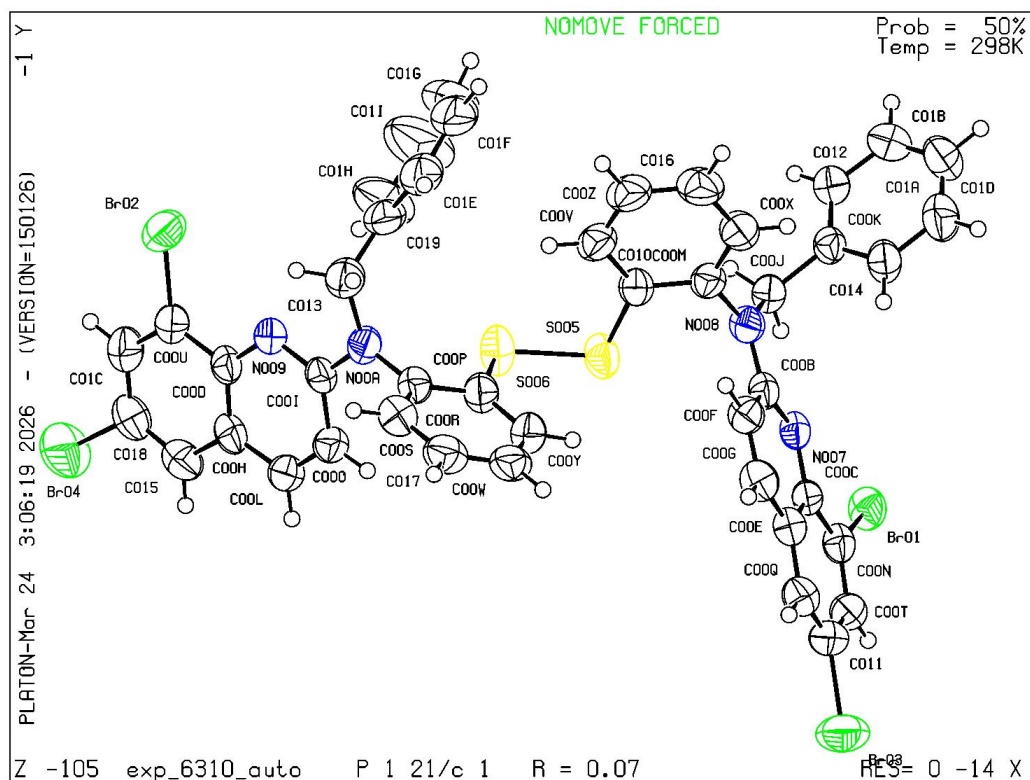
**Table 1.** Crystal data and structure refinement for **3al** (CCDC:2470502).

Identification code	<b>3al</b>
Empirical formula	$C_{32}H_{24}Br_2N_4S_2$
Formula weight	688.49
Temperature/K	273.15
Crystal system	triclinic
Space group	P-1
$a/\text{\AA}$	6.438
$b/\text{\AA}$	8.896
$c/\text{\AA}$	25.577
$\alpha/^\circ$	94.46
$\beta/^\circ$	94.35
$\gamma/^\circ$	90.41
Volume/ $\text{\AA}^3$	1456.1
Z	2
$\rho_{\text{calc}}/\text{g/cm}^3$	1.570
$\mu/\text{mm}^{-1}$	5.099
F(000)	692.0
Crystal size/ $\text{mm}^3$	$0.12 \times 0.1 \times 0.08$
Radiation	$\text{CuK}\alpha$ ( $\lambda = 1.54178$ )

2 $\theta$  range for data collection/ $^{\circ}$  3.474 to 133.622  
Index ranges  $-7 \leq h \leq 7, -10 \leq k \leq 10, 0 \leq l \leq 30$   
Reflections collected 5119  
Independent reflections 5119 [ $R_{\text{int}} = 0, R_{\text{sigma}} = 0.0317$ ]  
Data/restraints/parameters 5119/0/315  
Goodness-of-fit on  $F^2$  1.102  
Final R indexes [ $I \geq 2\sigma(I)$ ]  $R_1 = 0.1501, wR_2 = 0.3015$   
Final R indexes [all data]  $R_1 = 0.1694, wR_2 = 0.3074$   
Largest diff. peak/hole /  $e \text{ \AA}^{-3}$  0.92/-0.92

## (2) Single crystal X-ray diffraction of **3as**

Yellow and transparent block-like single crystals of **3as** were grown by layering a dichloromethane solution with n-hexane at ambient temperature. X-Ray diffraction data of one these crystals were collected on a R-AXIS SPIDER diffractometer. The measurements were performed with Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Data were collected at 296 K, using the  $\omega$  - and  $\varphi$  - scans to a maximum  $\theta$  value of 25.025  $^{\circ}$ . The data were refined by full-matrix least-squares techniques on F2 with SHELXTL-2014. And the structures were solved by direct methods SHELXS-2014. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included at geometrically idealized positions. An ORTEP representation of the structure is shown below.



**Figure 2.** ORTEP drawing of **3as** with the numbering scheme.

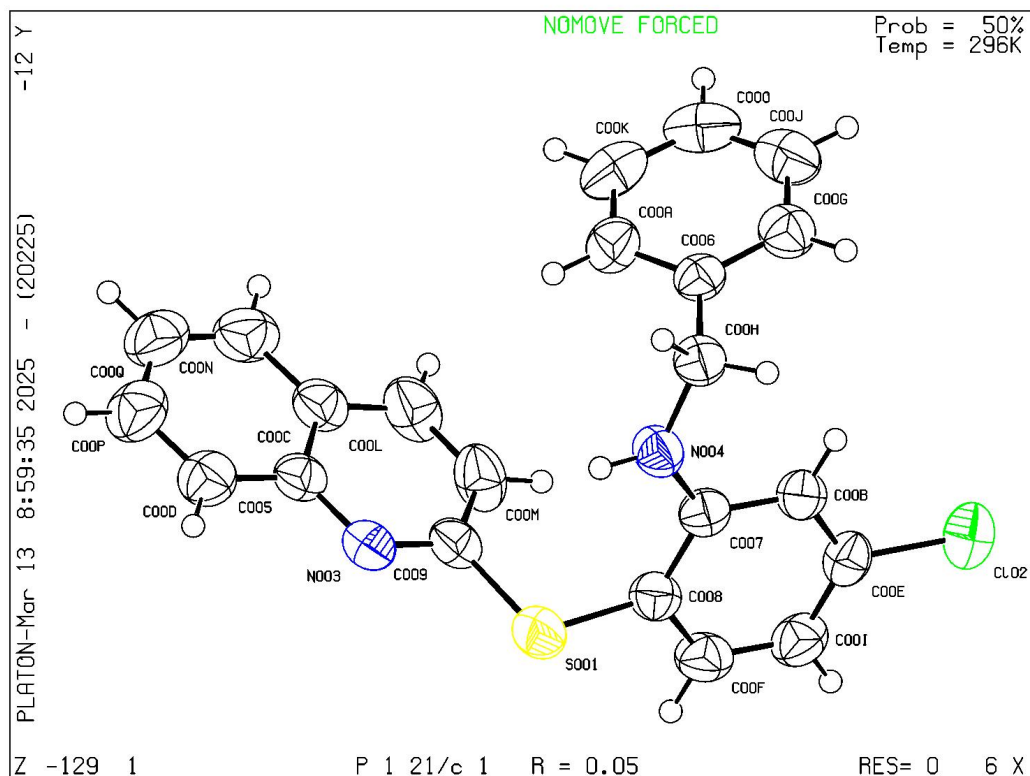
**Table 2.** Crystal data and structure refinement for **3as** (CCDC:2286834).

Identification code	<b>3as</b>
Empirical formula	$C_{44}H_{30}Br_4N_4S_2$
Formula weight	998.49
Temperature/K	298.0(7)
Crystal system	monoclinic
Space group	$P2_1/c$
$a/\text{\AA}$	13.9664(3)
$b/\text{\AA}$	26.9373(5)
$c/\text{\AA}$	10.8779(3)
$\alpha/^\circ$	90
$\beta/^\circ$	99.805(2)
$\gamma/^\circ$	90
Volume/ $\text{\AA}^3$	4032.67(16)
Z	4
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.648
$\mu/\text{mm}^{-1}$	6.131
F(000)	1984.0
Crystal size/ $\text{mm}^3$	? × ? × ?
Radiation	Cu $K\alpha$ ( $\lambda = 1.54184$ )

$2\theta$  range for data collection/ $^{\circ}$  7.214 to 154.822  
 Index ranges  $-17 \leq h \leq 17, -18 \leq k \leq 33, -13 \leq l \leq 13$   
 Reflections collected 30644  
 Independent reflections 7745 [ $R_{\text{int}} = 0.0655, R_{\text{sigma}} = 0.0484$ ]  
 Data/restraints/parameters 7745/0/492  
 Goodness-of-fit on  $F^2$  1.036  
 Final R indexes [ $I \geq 2\sigma(I)$ ]  $R_1 = 0.0733, wR_2 = 0.1979$   
 Final R indexes [all data]  $R_1 = 0.0893, wR_2 = 0.2111$   
 Largest diff. peak/hole /  $e \text{ \AA}^{-3}$  1.27/-0.94

### (3) Single crystal X-ray diffraction of **4aj**

Brown and transparent block-like single crystals of **4aj** were grown by layering a dichloromethane solution with n-hexane at ambient temperature. X-Ray diffraction data of one these crystals were collected on a R-Axis SPIDER diffractometer. The measurements were performed with Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Data were collected at 296 K, using the  $\omega$  - and  $\varphi$  - scans to a maximum  $\theta$  value of 25.025  $^{\circ}$ . The data were refined by full-matrix least-squares techniques on  $F^2$  with SHELXTL-2014. And the structures were solved by direct methods SHELXS-2014. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included at geometrically idealized positions. An ORTEP representation of the structure is shown below.



**Figure 3.** ORTEP drawing of **4aj** with the numbering scheme.

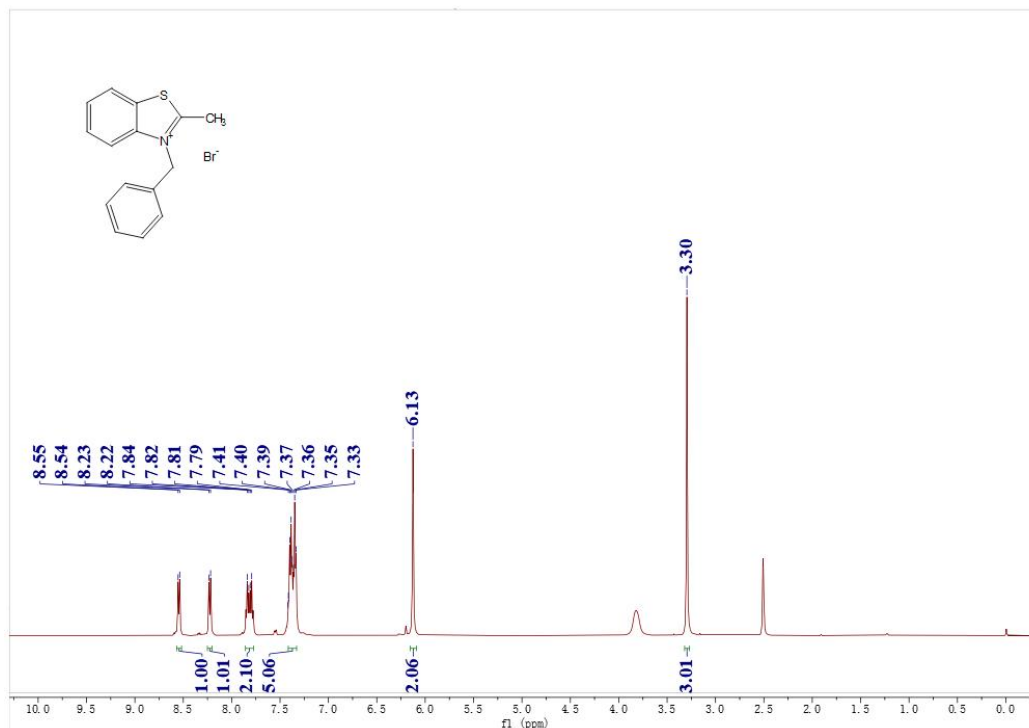
**Table 3.** Crystal data and structure refinement for **4aj** (CCDC: 2470501).

Identification code	<b>4aj</b>
Empirical formula	C <sub>22</sub> H <sub>17</sub> ClN <sub>2</sub> S
Formula weight	376.88
Temperature/K	296.15
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a/Å	9.997
b/Å	20.391
c/Å	9.256
α/°	90
β/°	99.38
γ/°	90
Volume/Å <sup>3</sup>	1861.6
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.345
μ/mm <sup>-1</sup>	0.325
F(000)	784.0
Crystal size/mm <sup>3</sup>	0.22 × 0.2 × 0.18
Radiation	MoKα (λ = 0.71073)

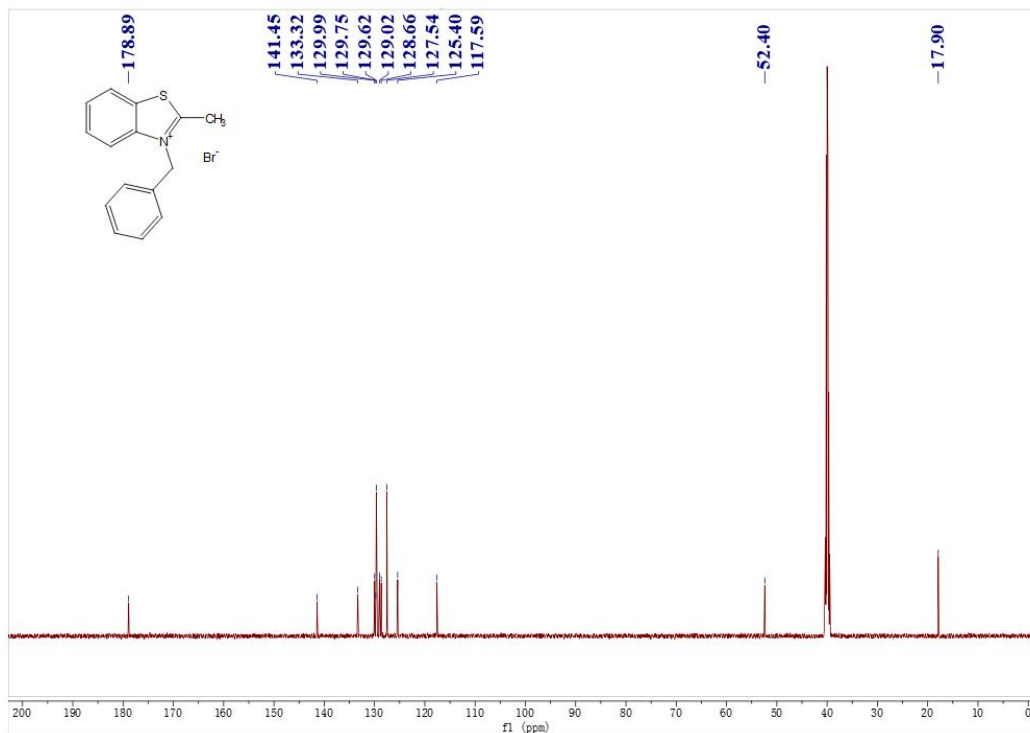
2 $\Theta$  range for data collection/° 4.888 to 50.082  
Index ranges ?  $\leq h \leq$  ?, ?  $\leq k \leq$  ?, ?  $\leq l \leq$  ?  
Reflections collected 3262  
Independent reflections 3262 [R<sub>int</sub> = 0, R<sub>sigma</sub> = 0.0507]  
Data/restraints/parameters 3262/0/235  
Goodness-of-fit on F<sup>2</sup> 1.077  
Final R indexes [I  $\geq$  2 $\sigma$  (I)] R<sub>1</sub> = 0.0540, wR<sub>2</sub> = 0.1242  
Final R indexes [all data] R<sub>1</sub> = 0.0953, wR<sub>2</sub> = 0.1443  
Largest diff. peak/hole / e  $\text{\AA}^{-3}$  0.17/-0.26

## 6. NMR spectra of 2-methylbenzothiazole salts

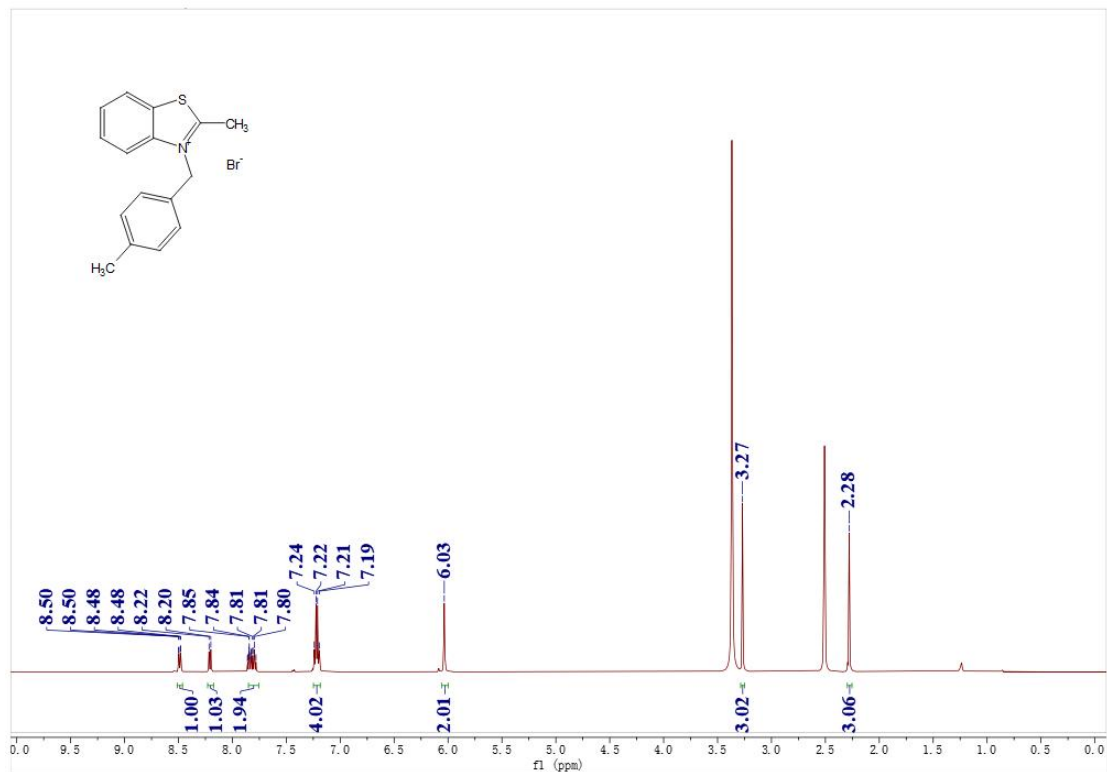
### <sup>1</sup>H NMR spectra of 3-Benzyl-2-methylbenzo[d]thiazol-3-ium bromide (500 MHz, DMSO-*d*<sub>6</sub>)



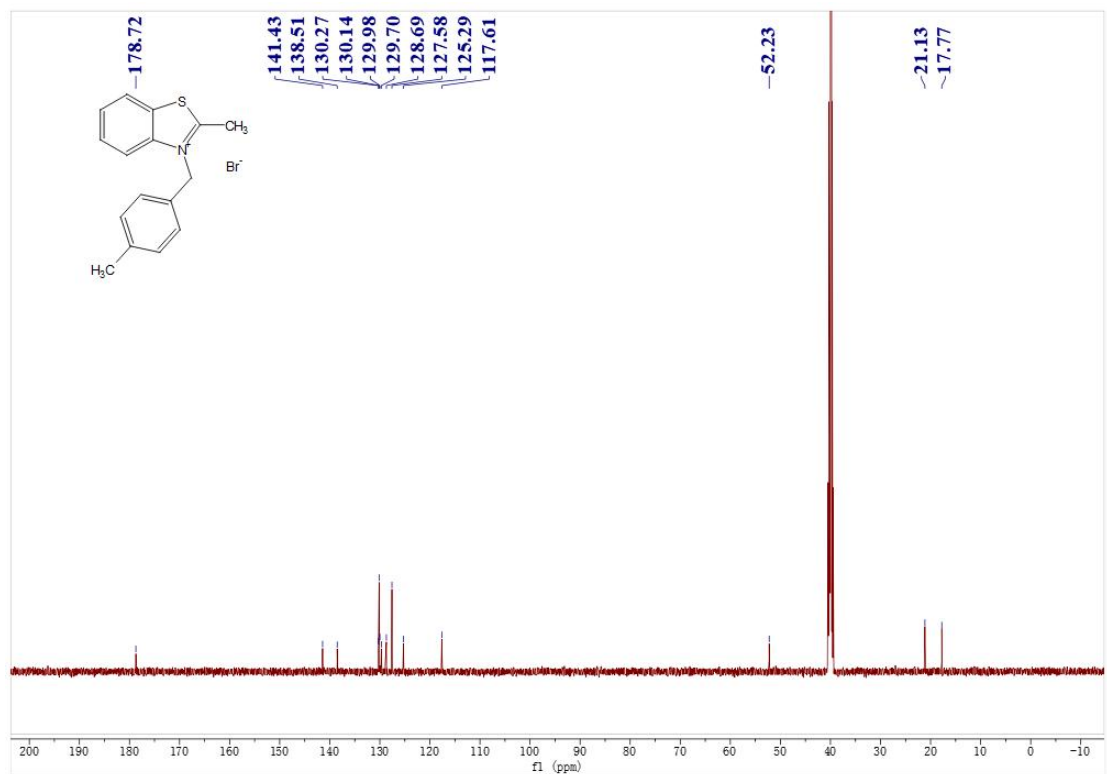
### <sup>13</sup>C NMR spectra of 3-Benzyl-2-methylbenzo[d]thiazol-3-ium bromide (126 MHz, DMSO-*d*<sub>6</sub>)



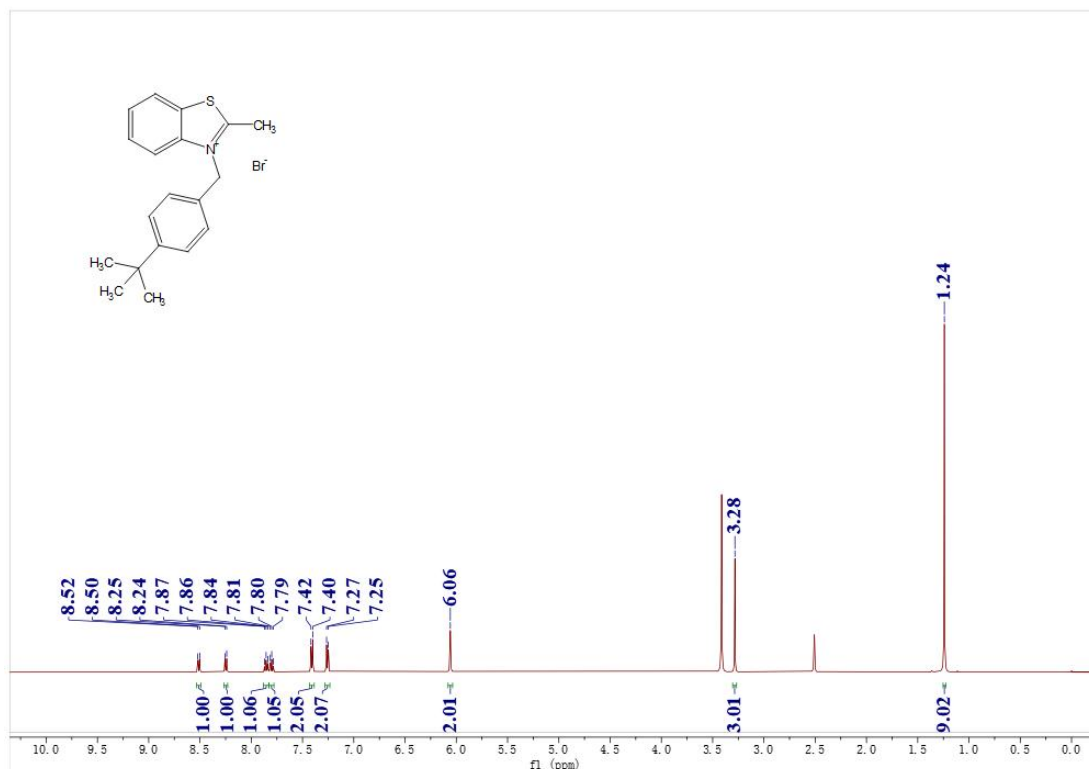
**<sup>1</sup>H NMR spectra of 2-Methyl-3-(4-methylbenzyl)benzo[d]thiazol-3-ium bromide  
(500 MHz, DMSO-*d*<sub>6</sub>)**



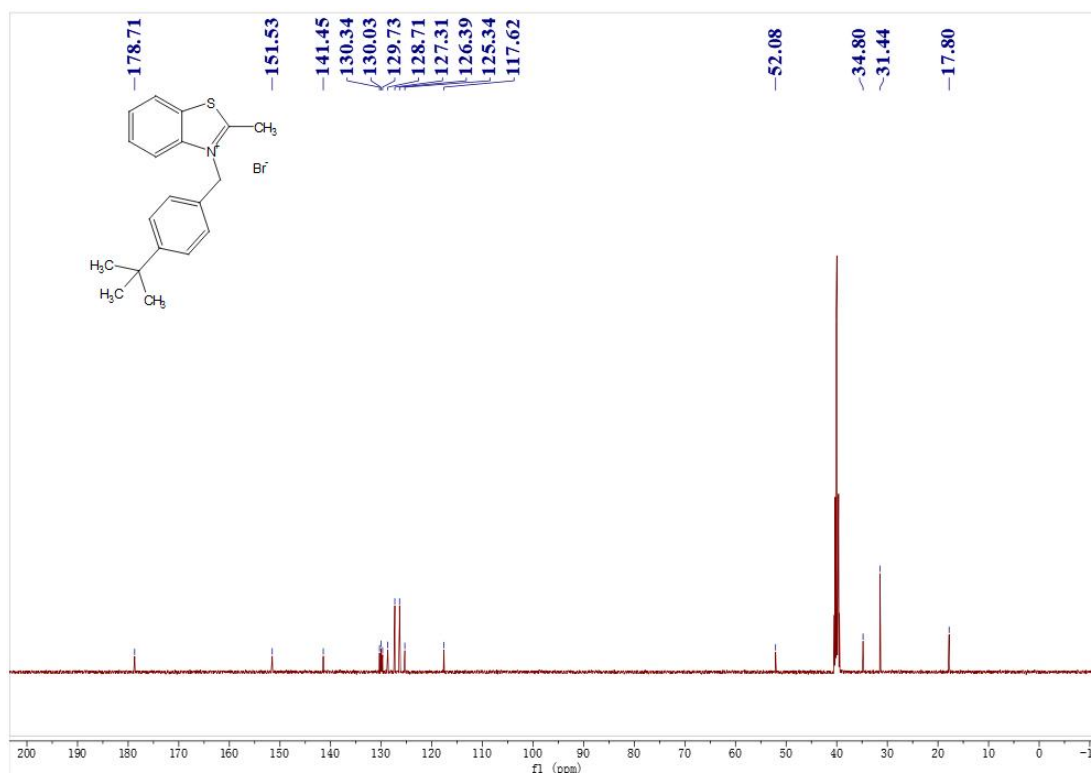
**<sup>13</sup>C NMR spectra of 2-Methyl-3-(4-methylbenzyl)benzo[d]thiazol-3-ium bromide  
(126 MHz, DMSO-*d*<sub>6</sub>)**



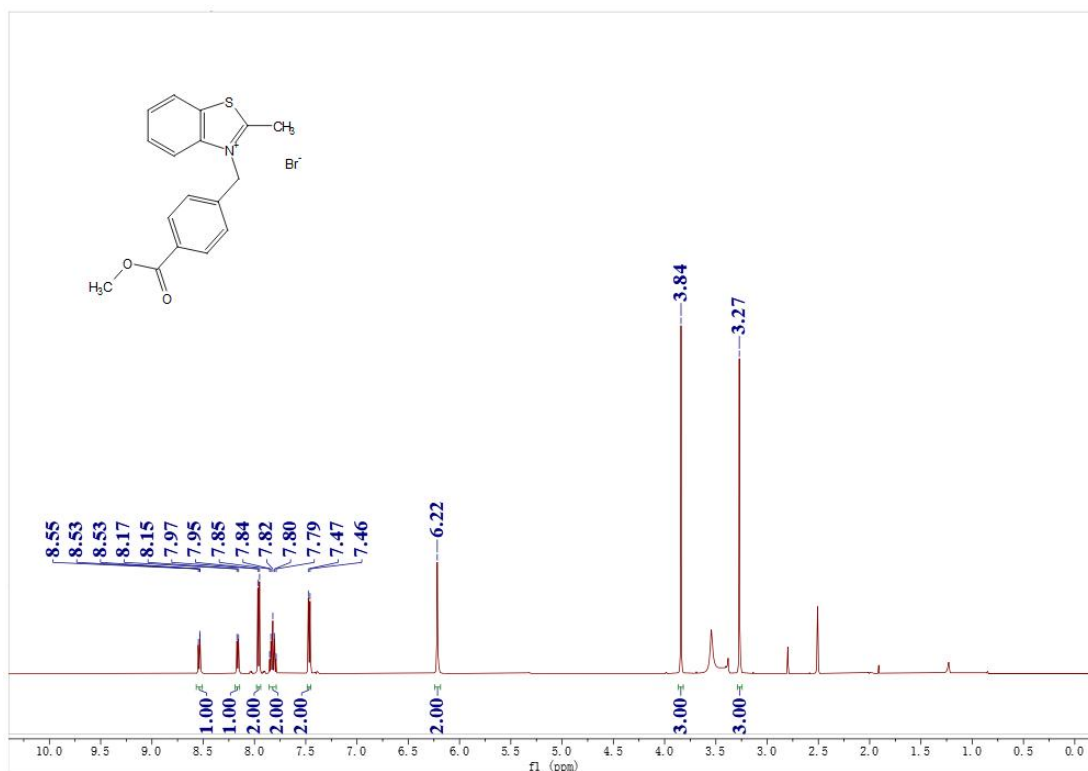
**<sup>1</sup>H NMR spectra of 3-(4-(tert-butyl)benzyl)-2-methylbenzo[d]thiazol-3-ium bromide (500 MHz, DMSO-*d*<sub>6</sub>)**



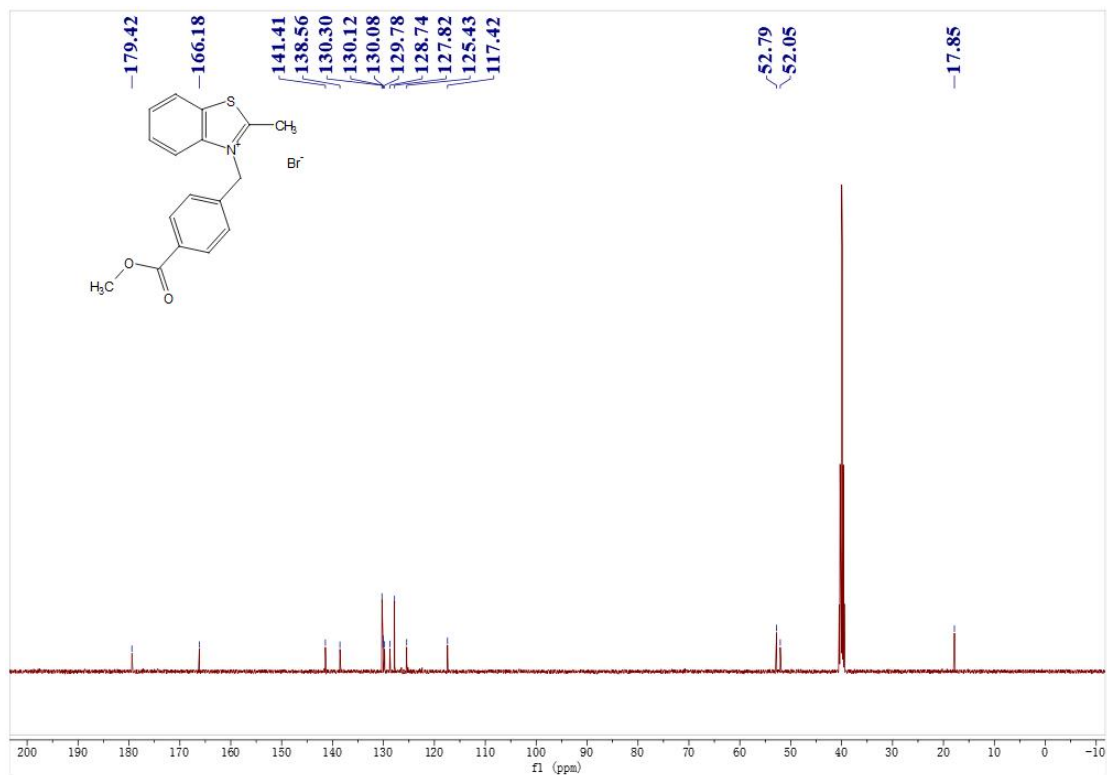
**<sup>13</sup>C NMR spectra of 3-(4-(tert-butyl)benzyl)-2-methylbenzo[d]thiazol-3-ium bromide (126 MHz, DMSO-*d*<sub>6</sub>)**



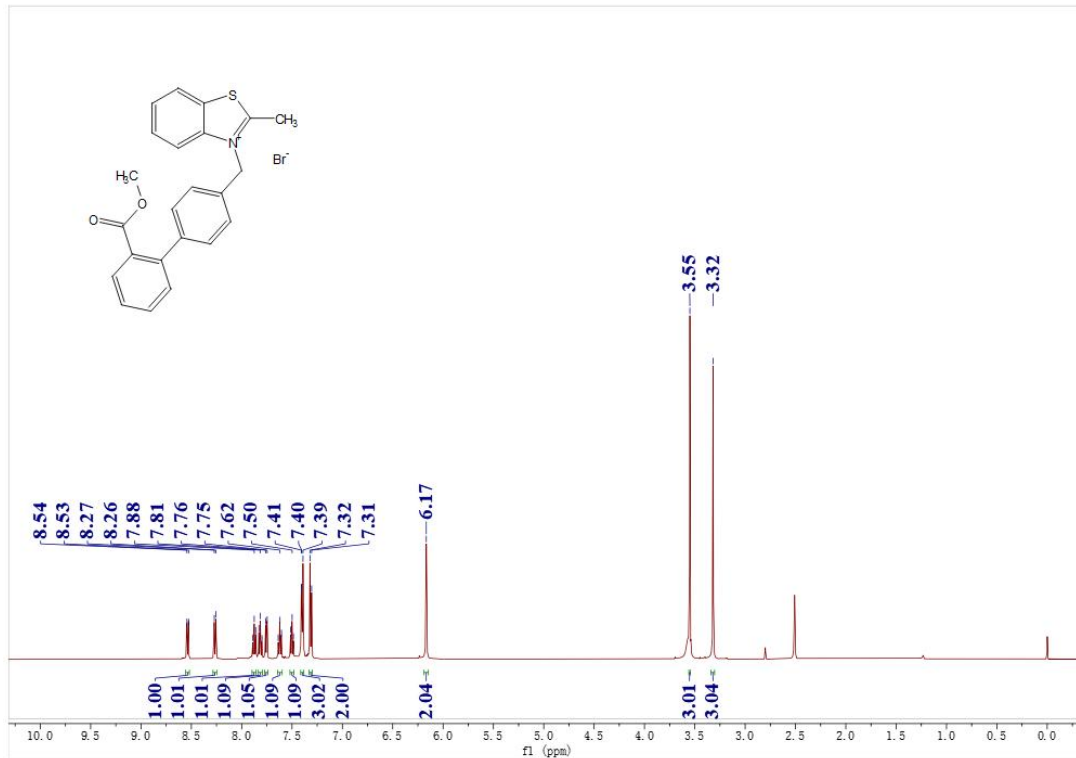
**<sup>1</sup>H NMR spectra of 3-(4-(methoxycarbonyl)benzyl)-2-methylbenzo[d]thiazol-3-ium bromide (500 MHz, DMSO-*d*<sub>6</sub>)**



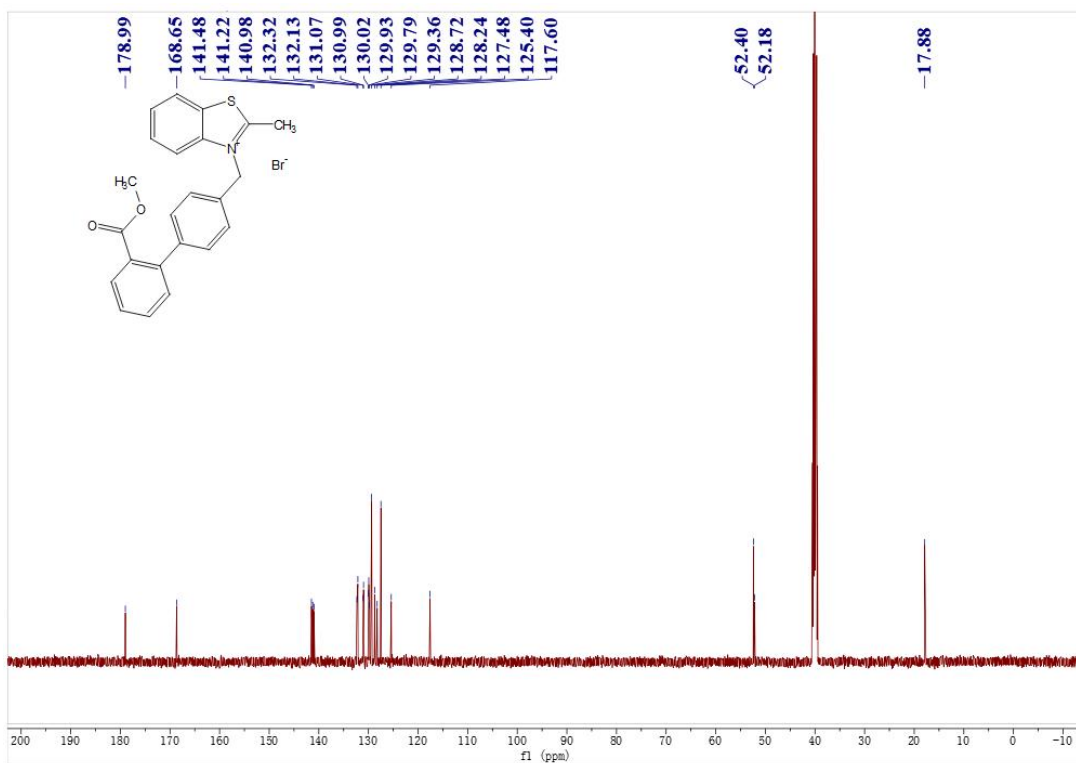
**<sup>13</sup>C NMR spectra of 3-(4-(methoxycarbonyl)benzyl)-2-methylbenzo[d]thiazol-3-ium bromide (126 MHz, DMSO-*d*<sub>6</sub>)**



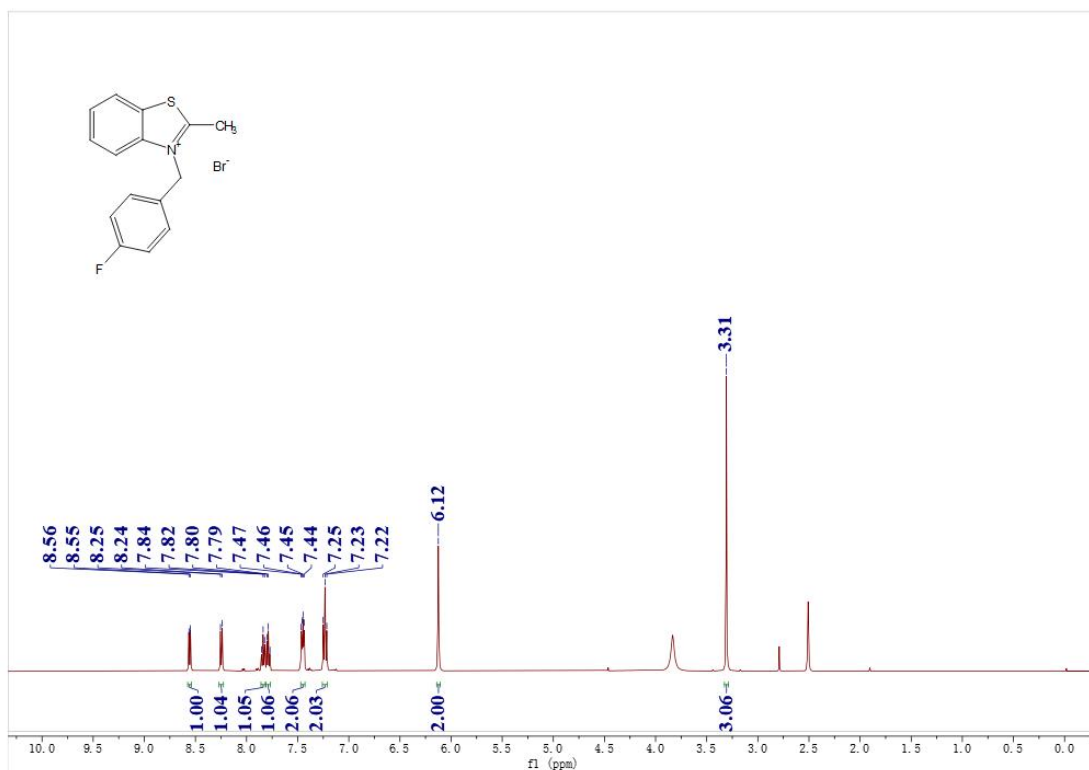
**<sup>1</sup>H NMR spectra of 3-((2'-(methoxycarbonyl)-[1,1'-biphenyl]-4-yl)methyl)-2-methylbenzo[d]thiazol-3-ium bromide (500 MHz, DMSO-*d*<sub>6</sub>)**



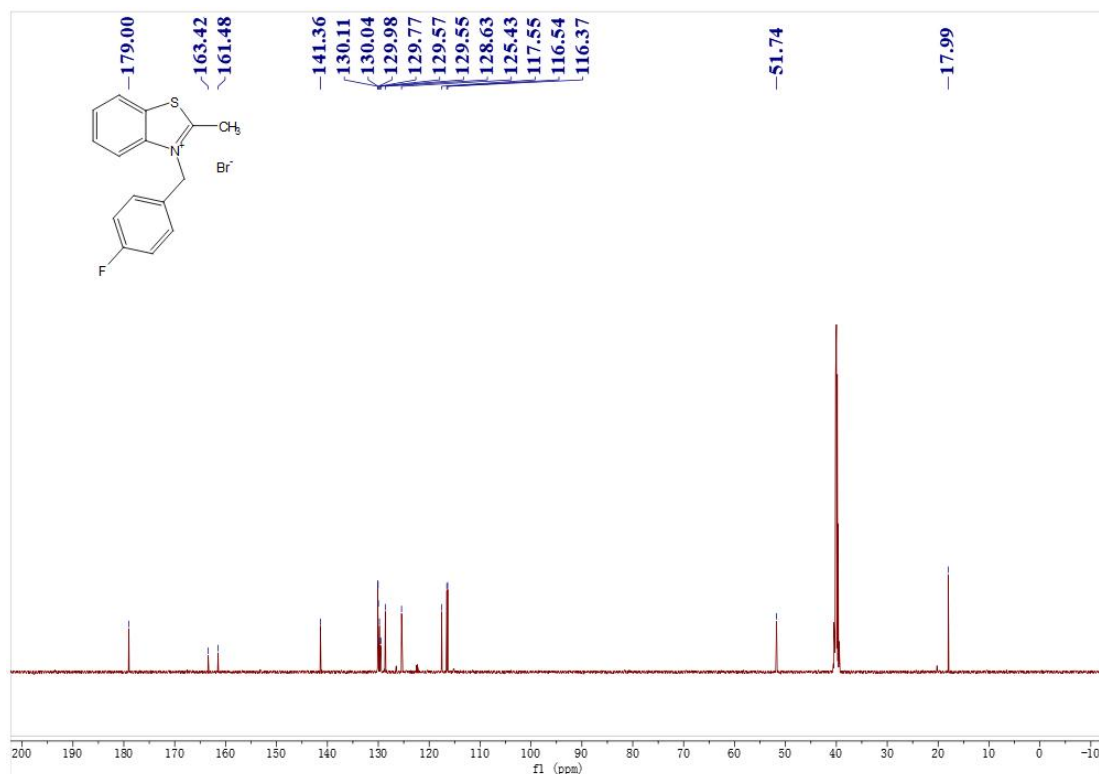
**<sup>13</sup>C NMR spectra of 3-((2'-(Methoxycarbonyl)-[1,1'-biphenyl]-4-yl)methyl)-2-methylbenzo[d]thiazol-3-ium bromide (126 MHz, DMSO-*d*<sub>6</sub>)**



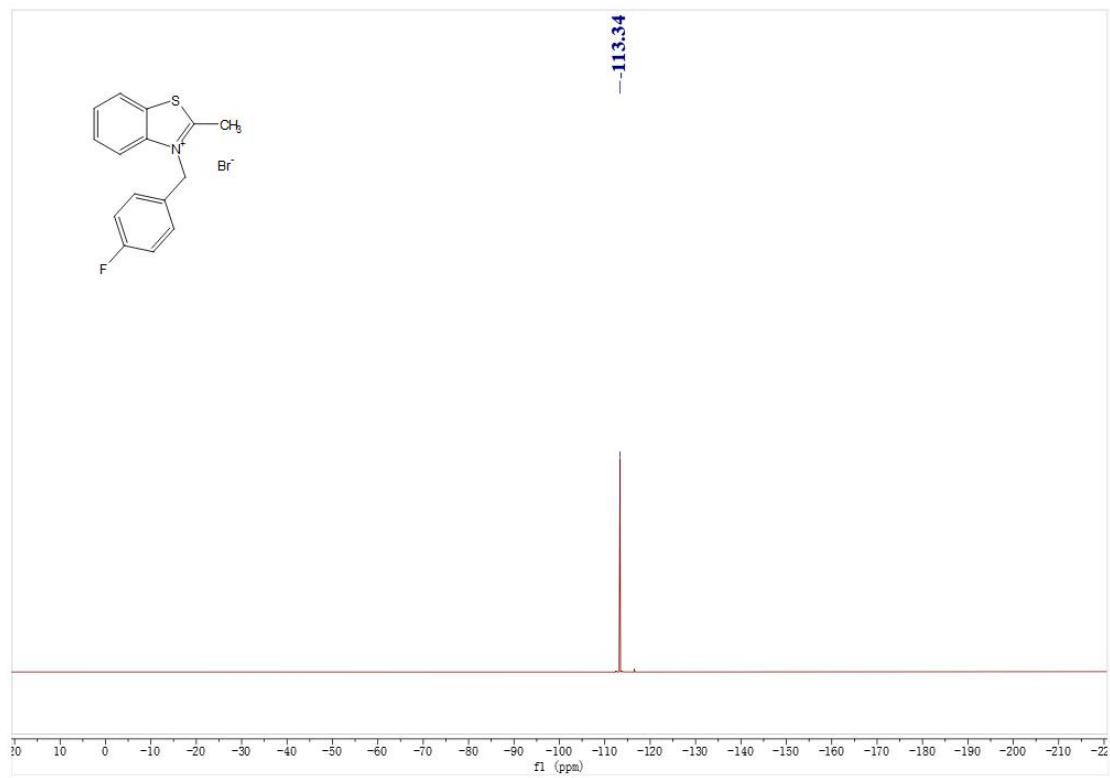
**<sup>1</sup>H NMR spectra of 3-(4-fluorobenzyl)-2-methylbenzo[d]thiazol-3-ium bromide  
(500 MHz, DMSO-*d*<sub>6</sub>)**



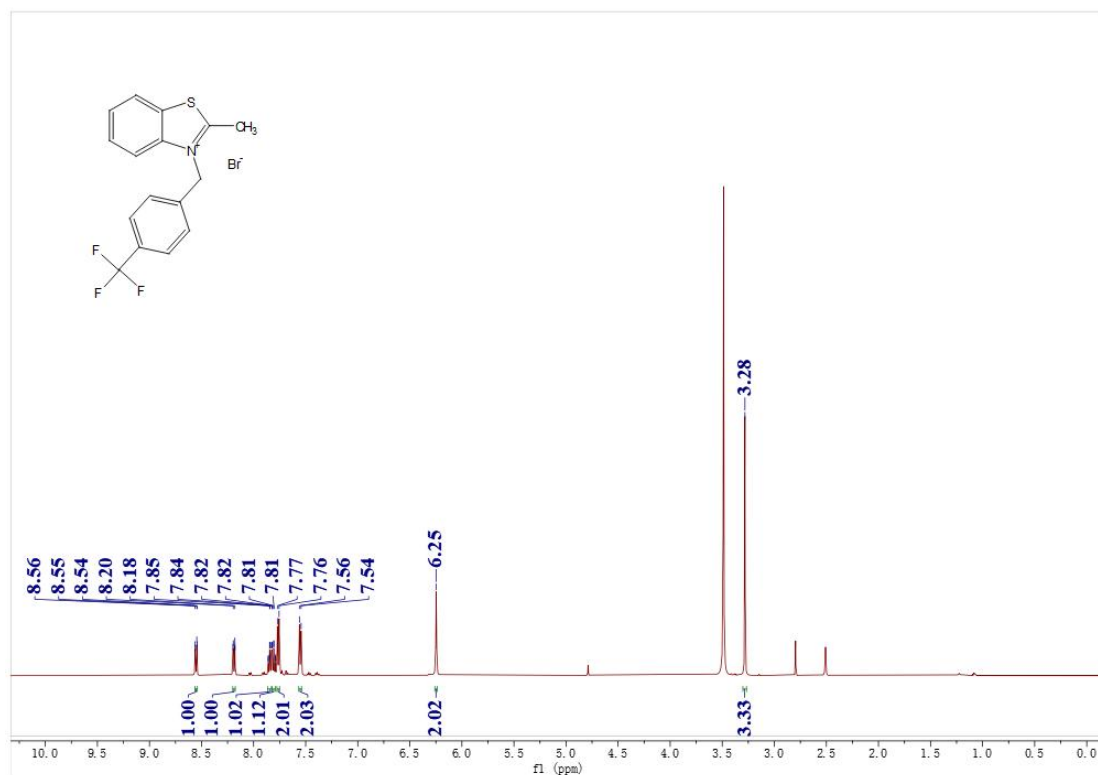
**<sup>13</sup>C NMR spectra of 3-(4-fluorobenzyl)-2-methylbenzo[d]thiazol-3-ium bromide  
(126 MHz, DMSO-*d*<sub>6</sub>)**



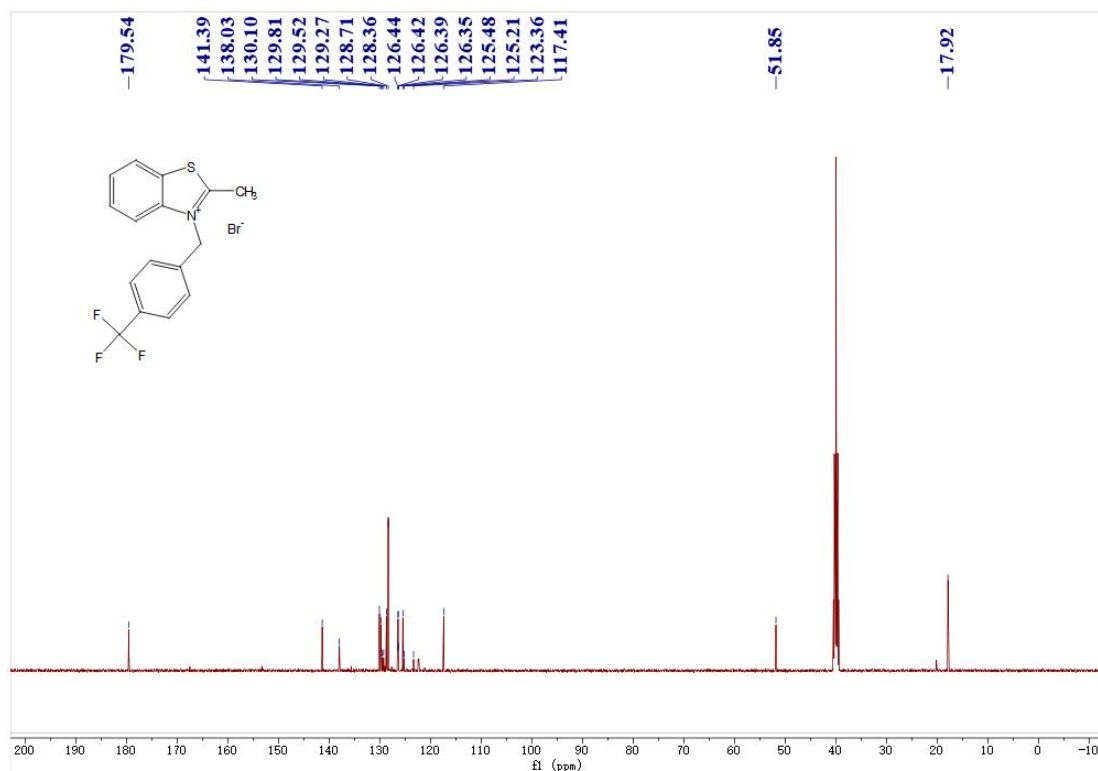
**<sup>19</sup>F NMR spectra of 3-(4-fluorobenzyl)-2-methylbenzo[d]thiazol-3-ium bromide  
(471 MHz, DMSO-*d*<sub>6</sub>)**



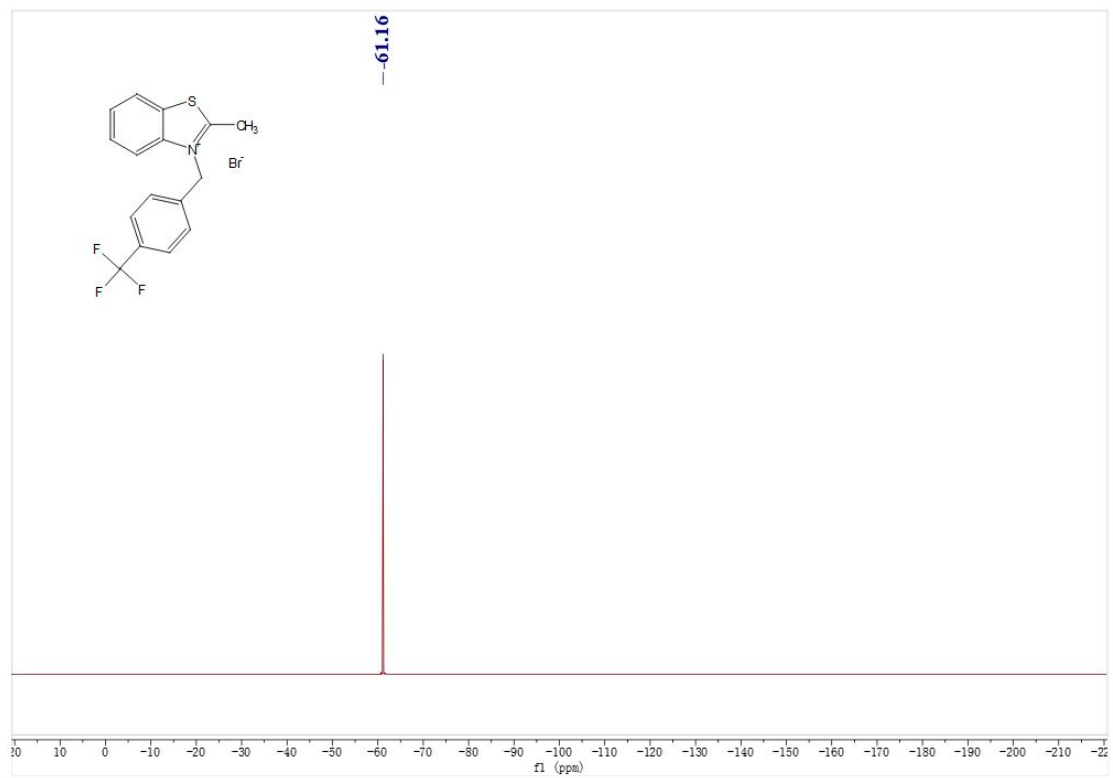
**<sup>1</sup>H NMR spectra of 2-methyl-3-(4-(trifluoromethyl)benzyl)benzo[d]thiazol-3-ium bromide (500 MHz, DMSO-*d*<sub>6</sub>)**



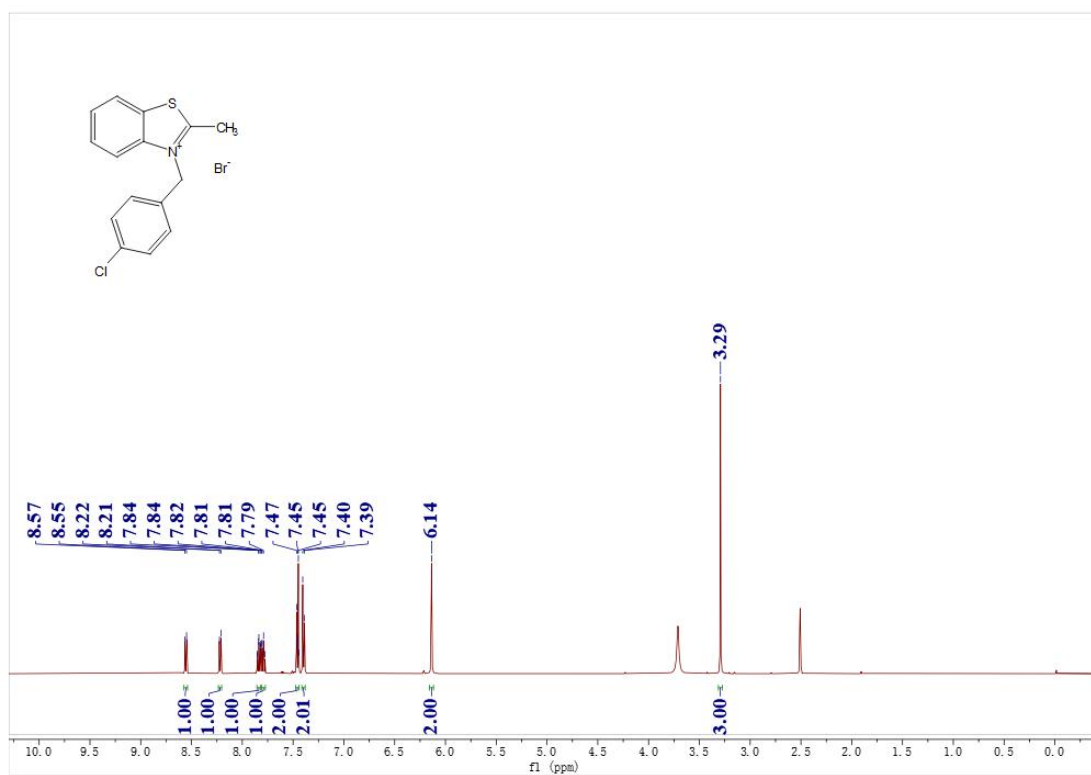
**<sup>13</sup>C NMR spectra of 2-methyl-3-(4-(trifluoromethyl)benzyl)benzo[d]thiazol-3-ium bromide (126 MHz, DMSO-*d*<sub>6</sub>)**



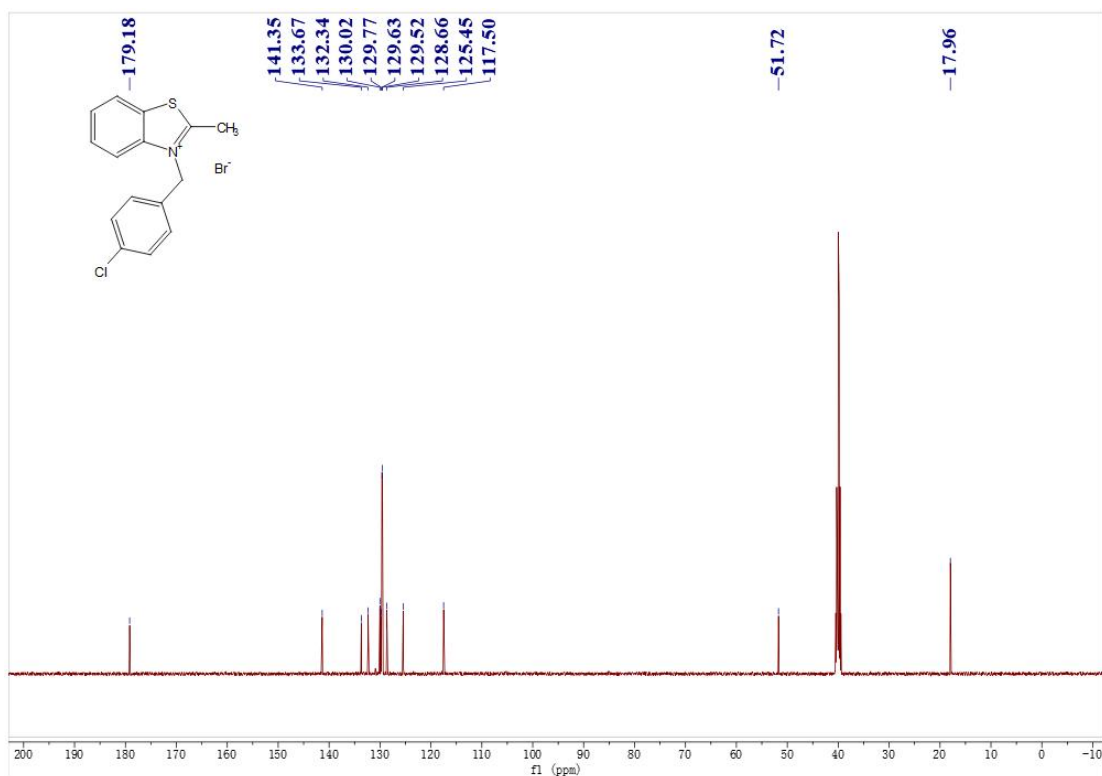
**<sup>19</sup>F NMR spectra of 2-methyl-3-(4-(trifluoromethyl)benzyl)benzo[d]thiazol-3-ium bromide (471 MHz, DMSO-*d*<sub>6</sub>)**



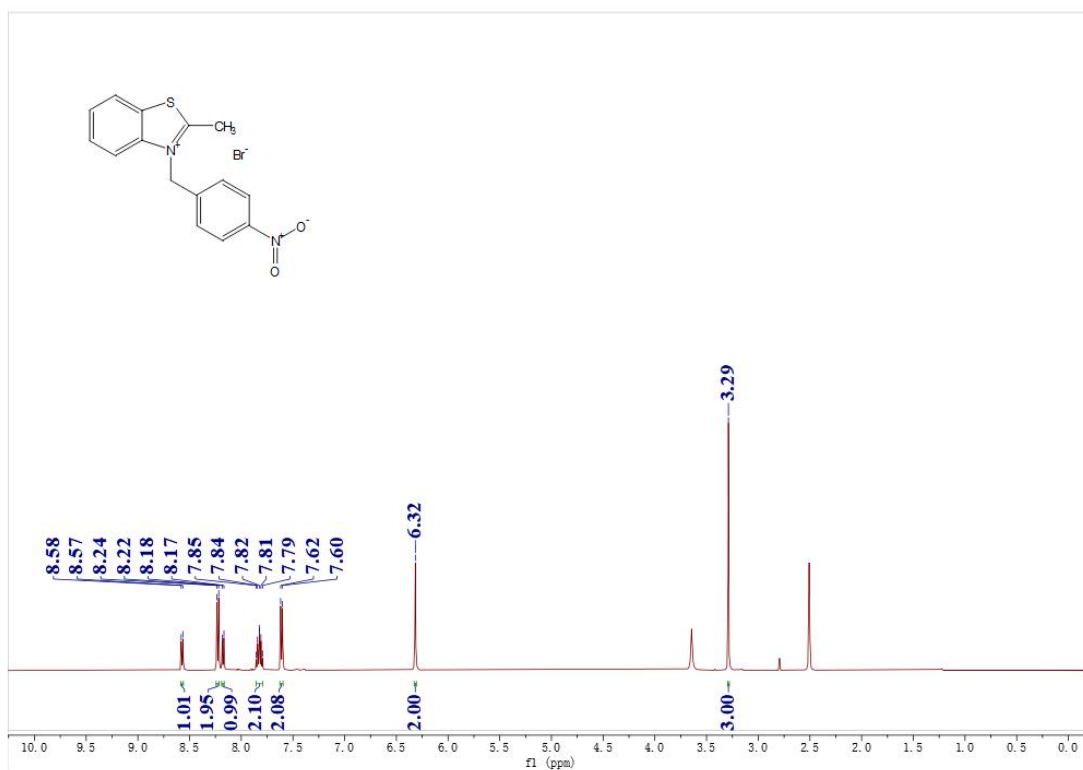
**<sup>1</sup>H NMR spectra of 3-(4-chlorobenzyl)-2-methylbenzo[*d*]thiazol-3-ium bromide  
(500 MHz, DMSO-*d*<sub>6</sub>)**



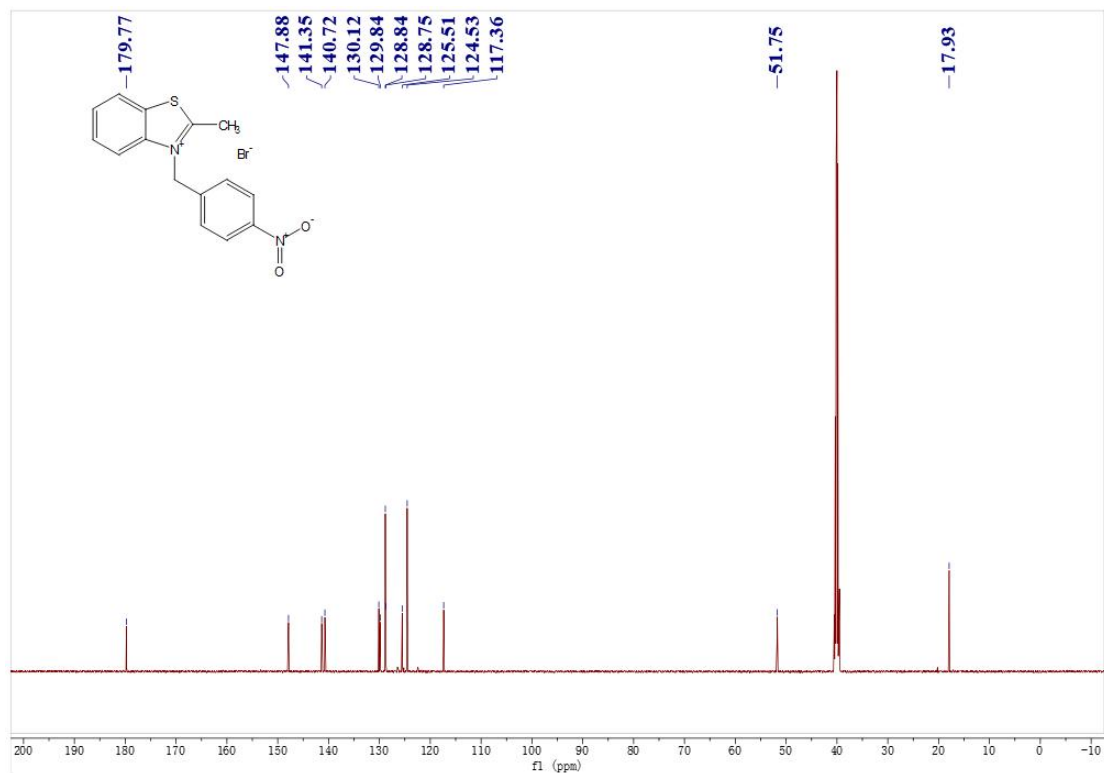
**<sup>13</sup>C NMR spectra of 3-(4-chlorobenzyl)-2-methylbenzo[*d*]thiazol-3-ium bromide  
(126 MHz, DMSO-*d*<sub>6</sub>)**



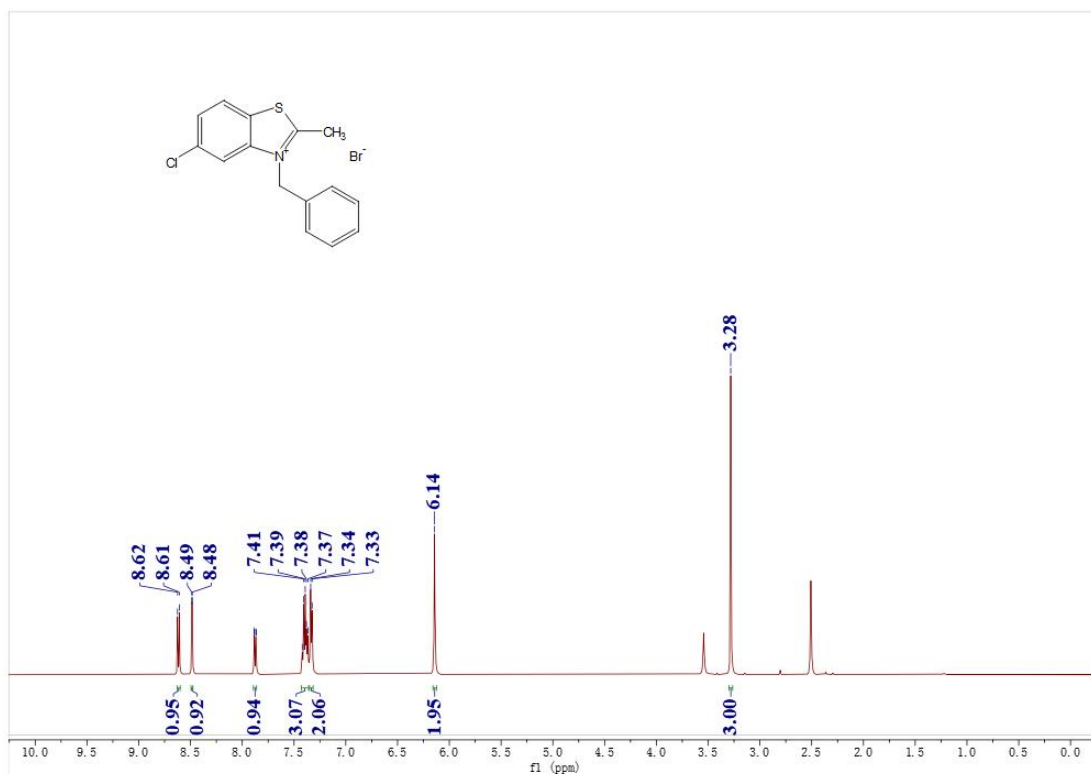
**<sup>1</sup>H NMR spectra of 2-methyl-3-(4-nitrobenzyl)benzo[d]thiazol-3-ium bromide  
(500 MHz, DMSO-*d*<sub>6</sub>)**



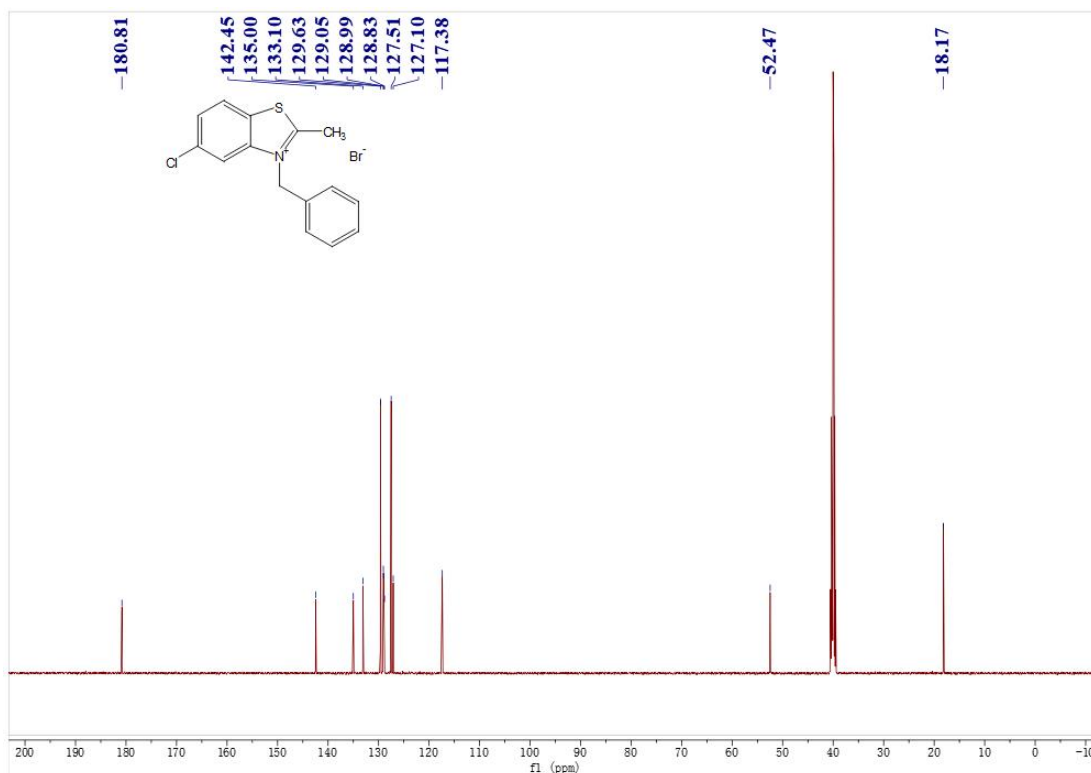
**<sup>13</sup>C NMR spectra of 2-methyl-3-(4-nitrobenzyl)benzo[d]thiazol-3-ium  
bromide(126 MHz, DMSO-*d*<sub>6</sub>)**



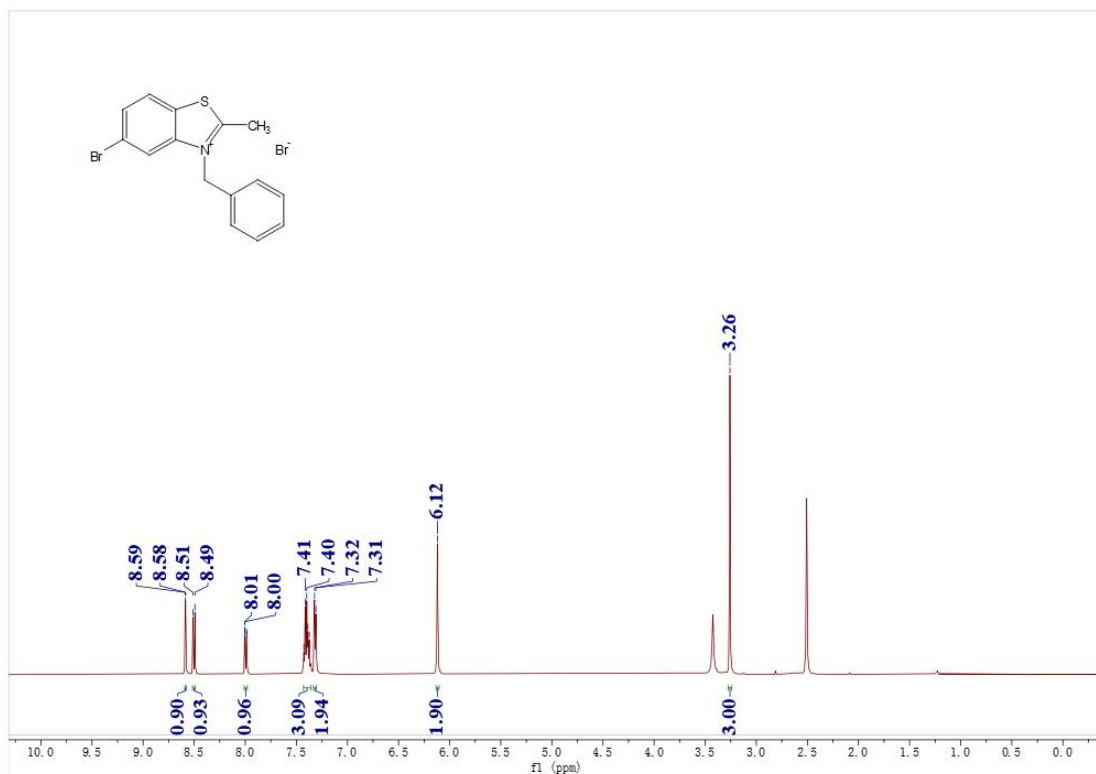
**<sup>1</sup>H NMR spectra of 3-benzyl-5-chloro-2-methylbenzo[d]thiazol-3-ium bromide  
(500 MHz, DMSO-*d*<sub>6</sub>)**



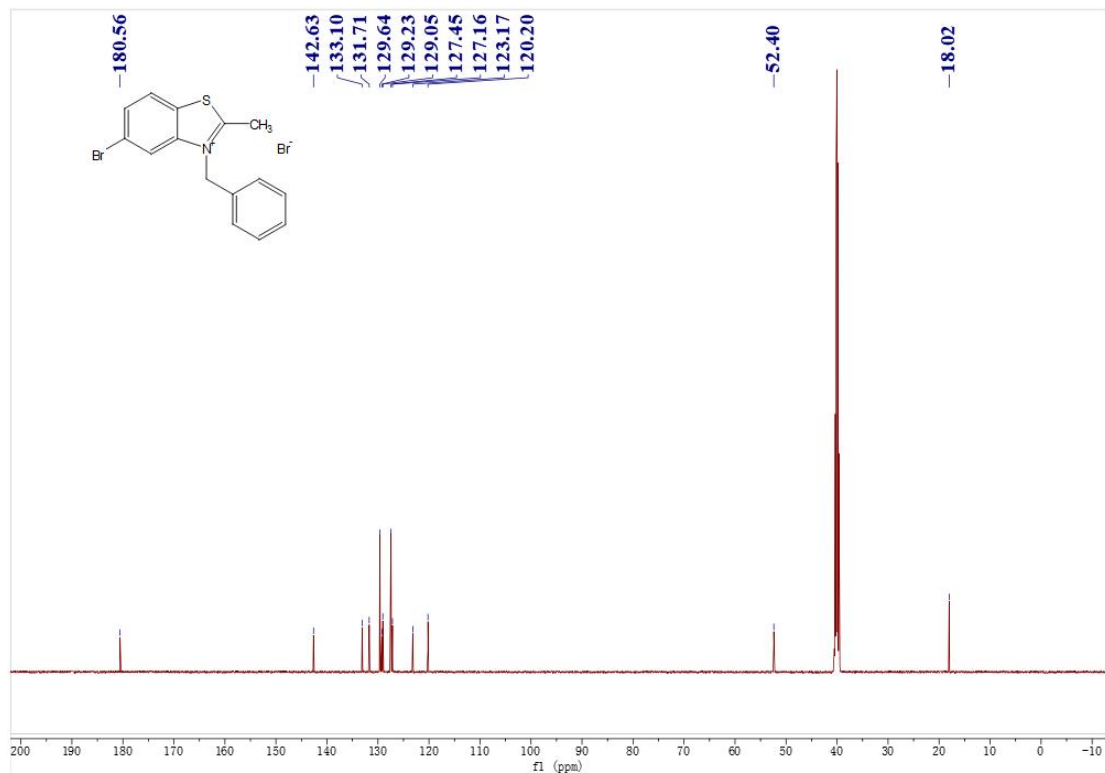
**<sup>13</sup>C NMR spectra of 3-benzyl-5-chloro-2-methylbenzo[d]thiazol-3-ium bromide  
(126 MHz, DMSO-*d*<sub>6</sub>)**



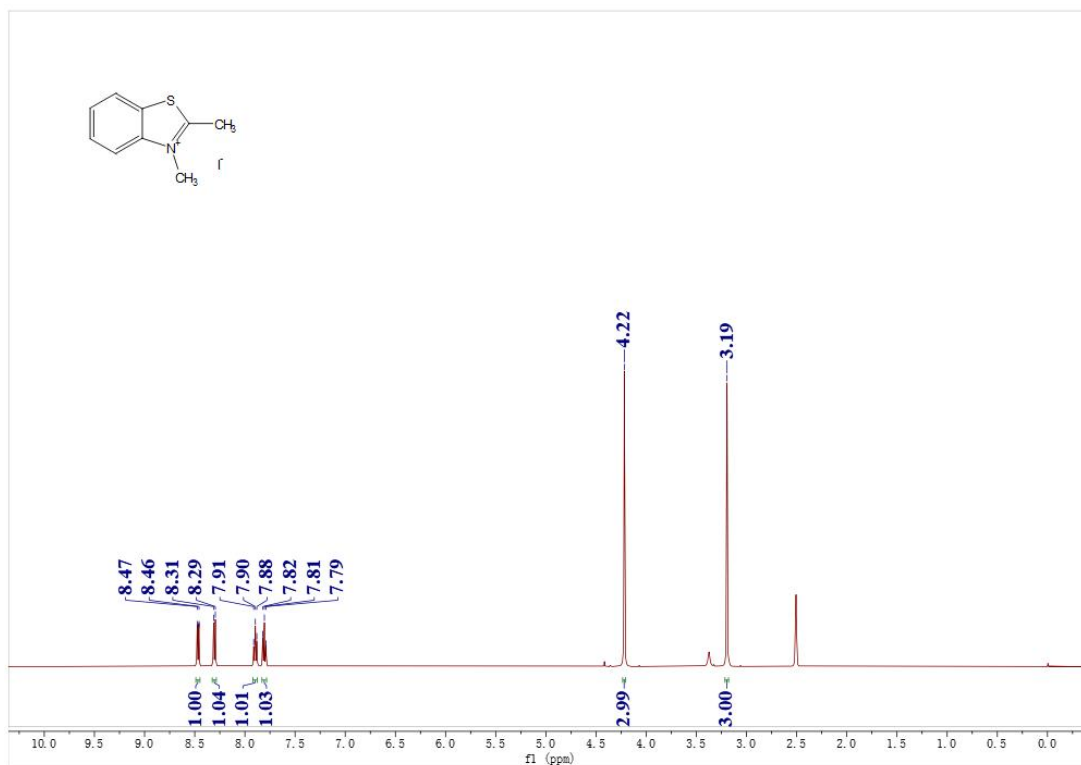
**<sup>1</sup>H NMR spectra of 3-benzyl-5-bromo-2-methylbenzo[d]thiazol-3-ium bromide  
(500 MHz, DMSO-*d*<sub>6</sub>)**



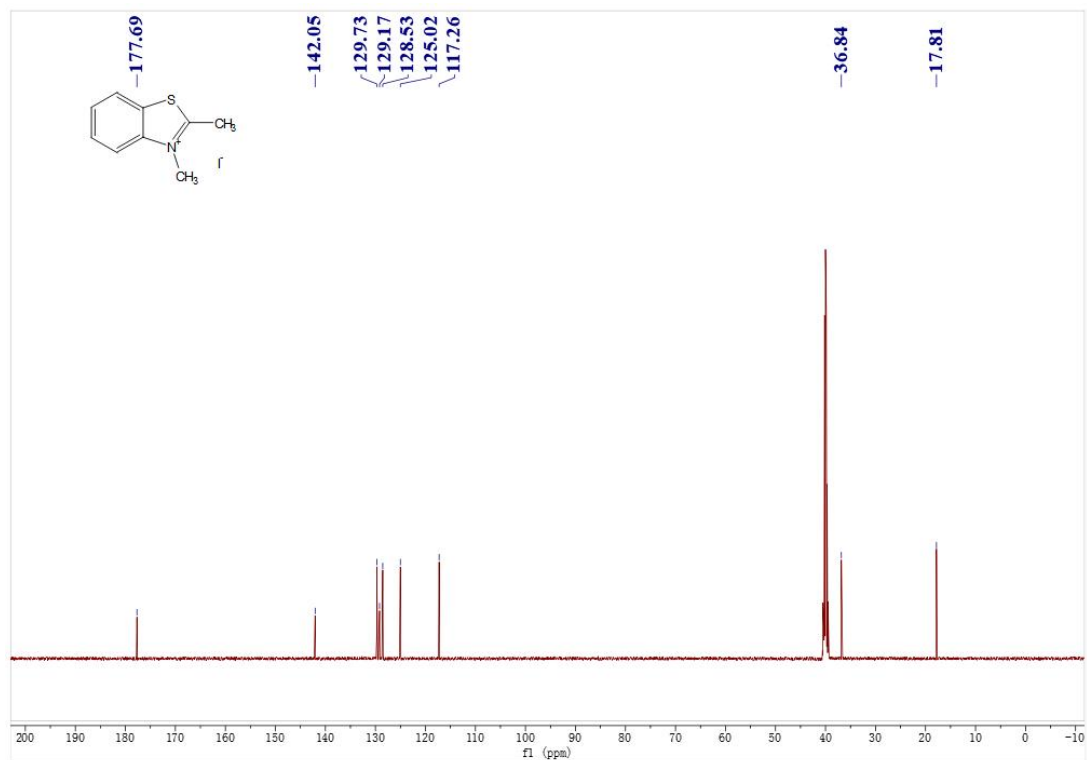
**<sup>13</sup>C NMR spectra of 3-benzyl-5-bromo-2-methylbenzo[d]thiazol-3-ium bromide  
(126 MHz, DMSO-*d*<sub>6</sub>)**



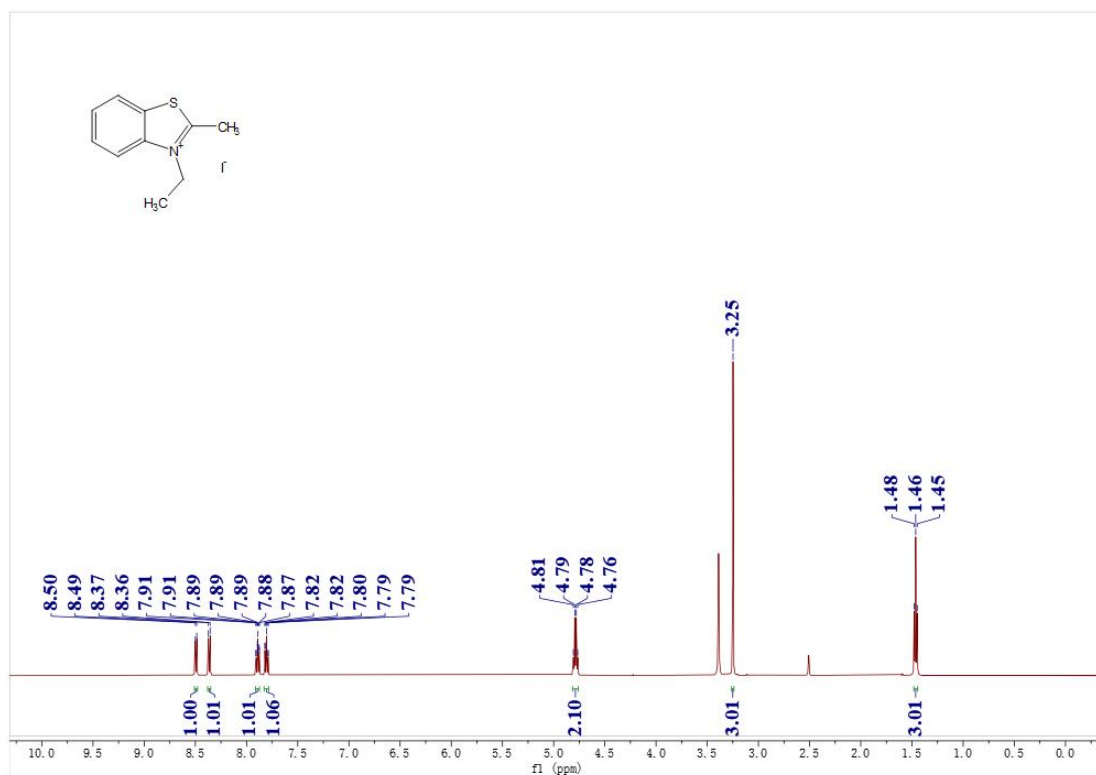
**$^1\text{H}$  NMR spectra of 2,3-dimethylbenzo[d]thiazol-3-ium iodide (500 MHz,  $\text{DMSO-}d_6$ )**



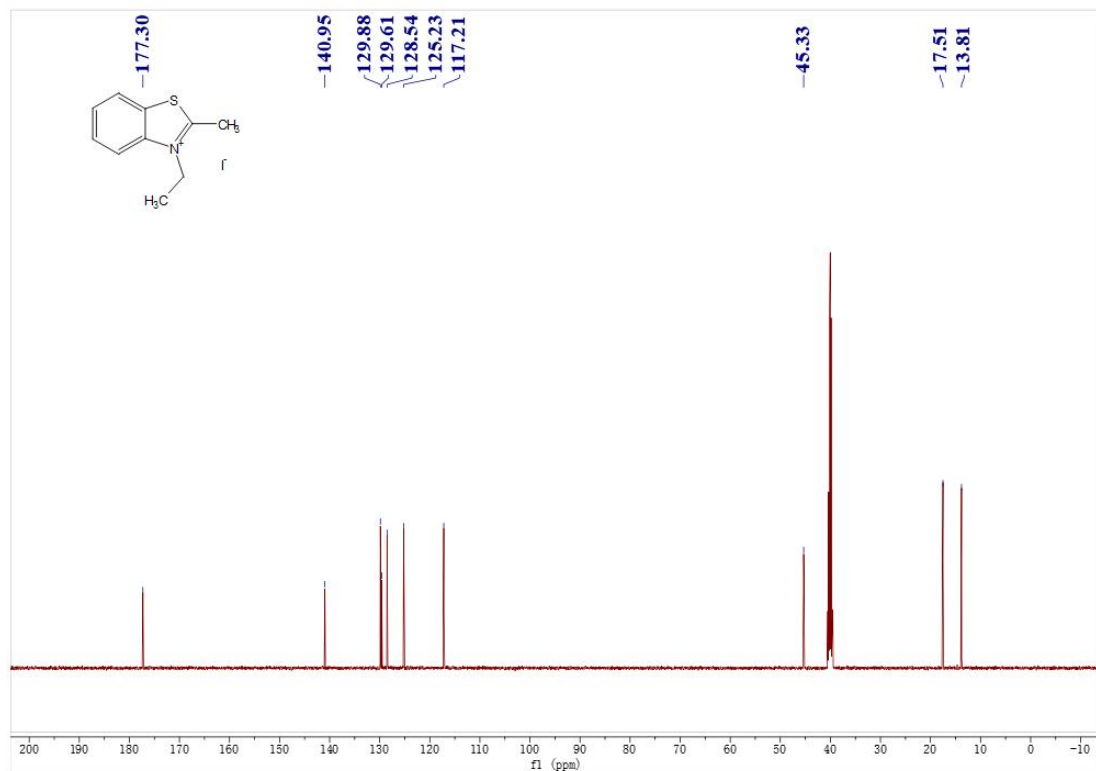
**$^{13}\text{C}$  NMR spectra of 2,3-dimethylbenzo[d]thiazol-3-ium iodide (126 MHz,  $\text{DMSO-}d_6$ )**



**$^1\text{H}$  NMR spectra of 3-ethyl-2-methylbenzo[d]thiazol-3-ium iodide(500 MHz, DMSO- $d_6$ )**

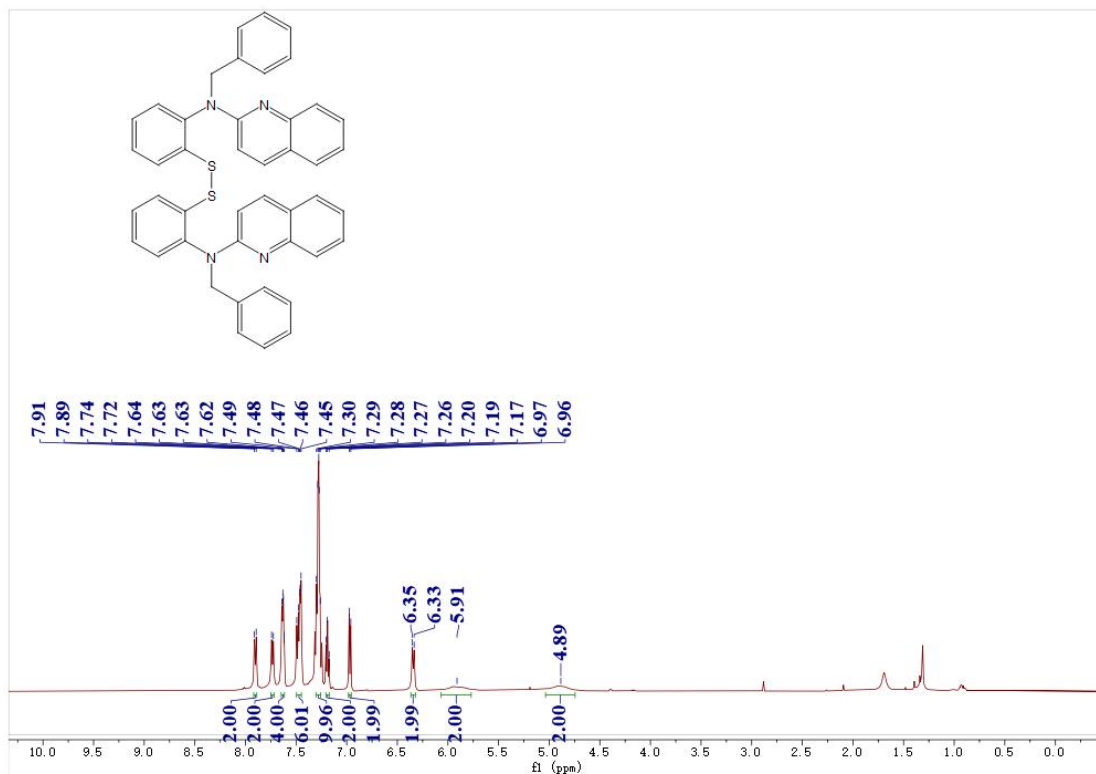


**$^{13}\text{C}$  NMR spectra of 3-ethyl-2-methylbenzo[d]thiazol-3-ium iodide(126 MHz, DMSO- $d_6$ )**

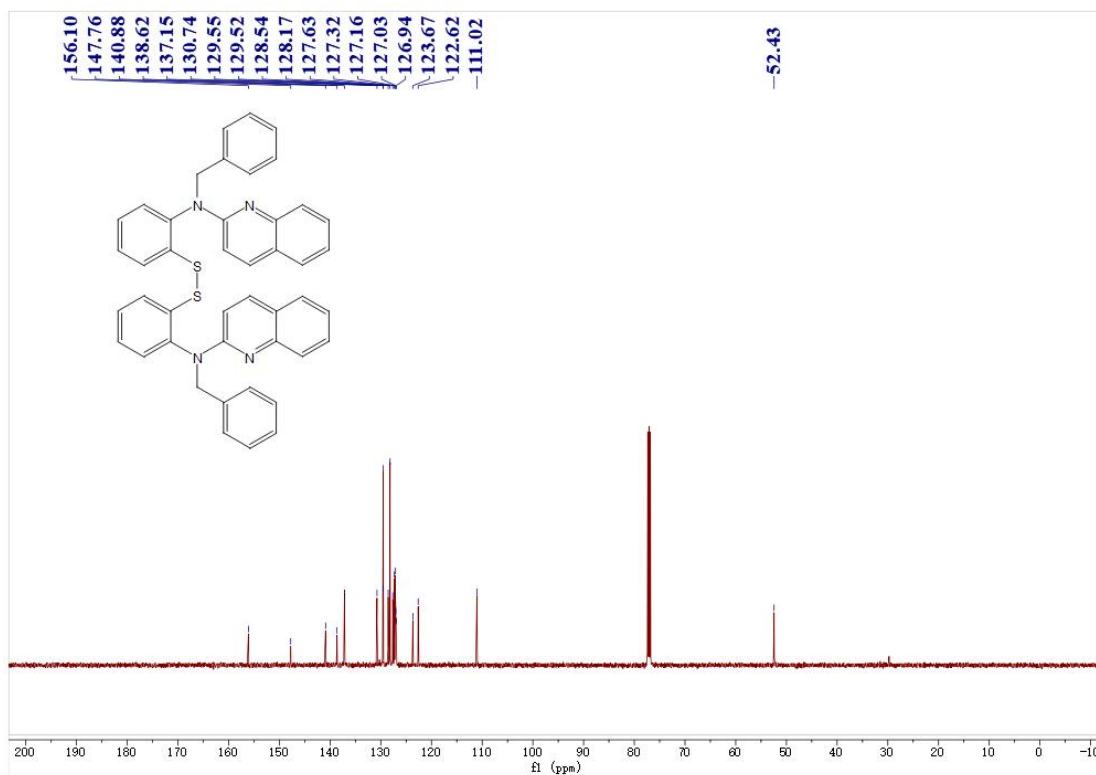


## 7. NMR spectra of the obtained compounds

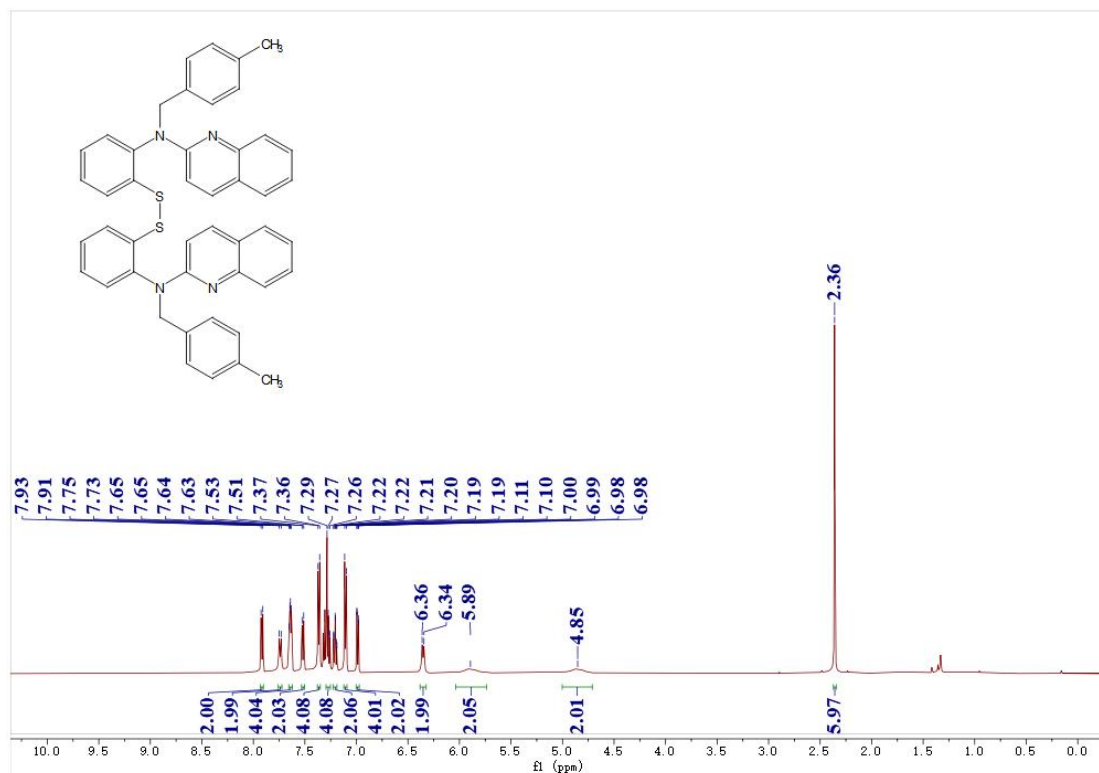
### <sup>1</sup>H NMR spectra of 3aa (500 MHz, CDCl<sub>3</sub>)



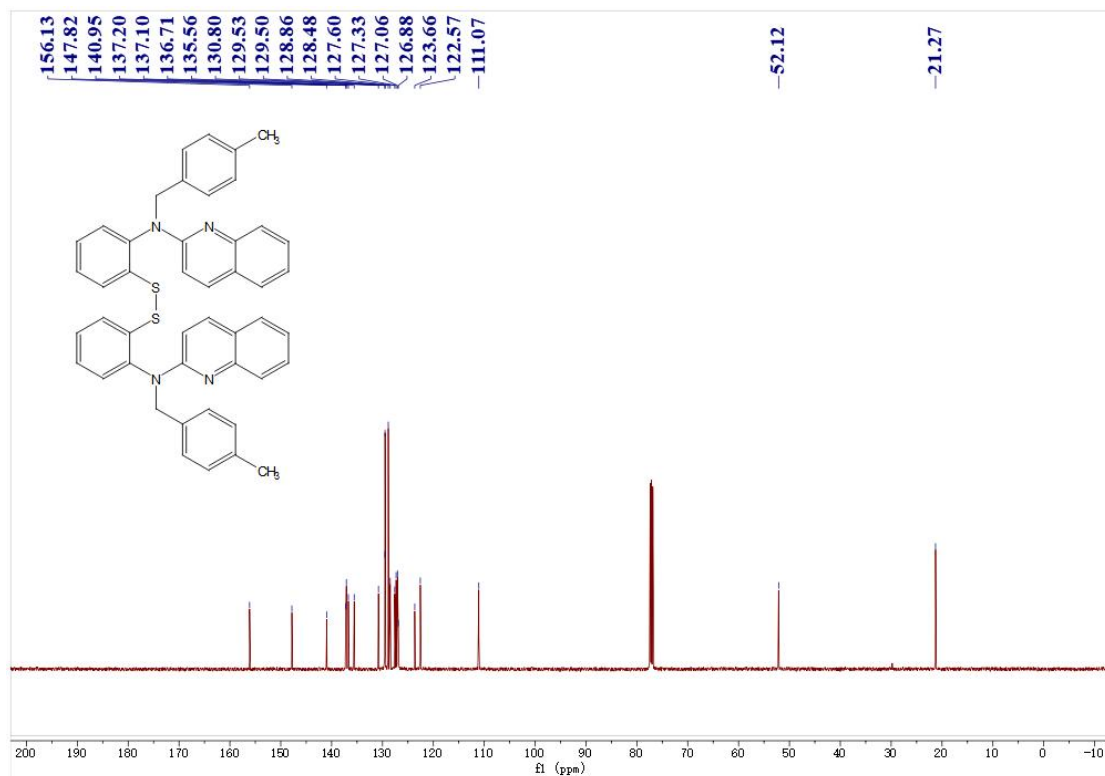
### <sup>13</sup>C NMR spectra of 3aa (126 MHz, CDCl<sub>3</sub>)



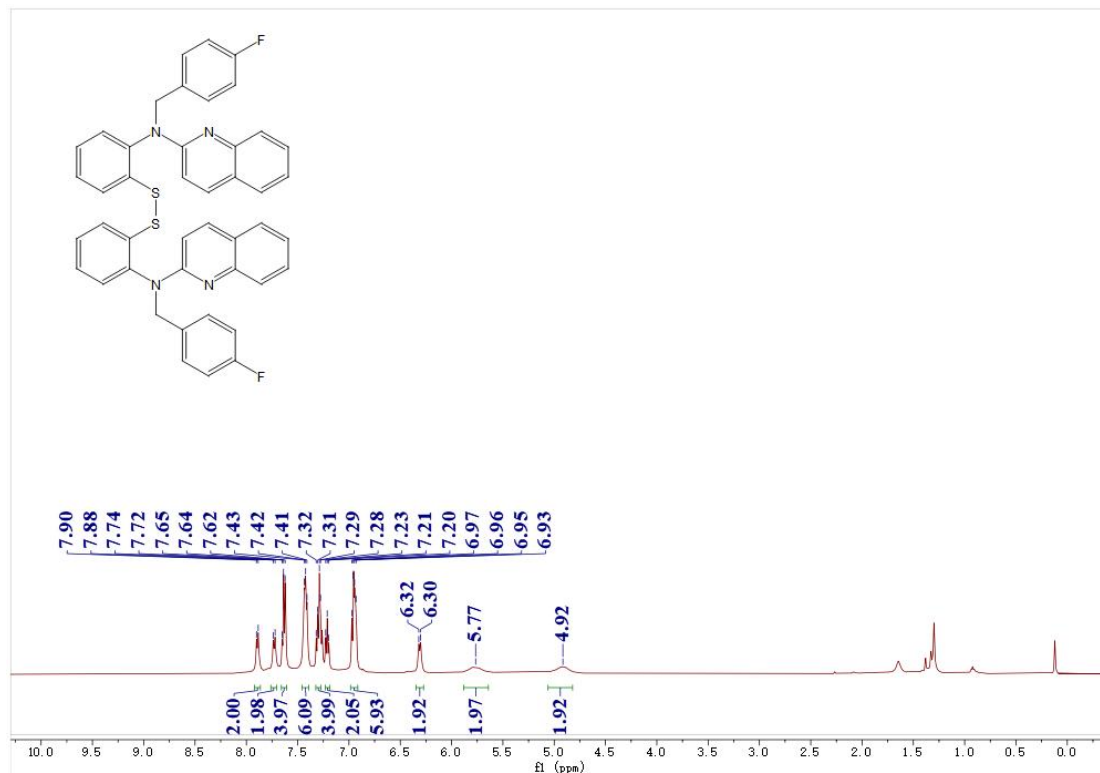
### <sup>1</sup>H NMR spectra of 3ab (500 MHz, CDCl<sub>3</sub>)



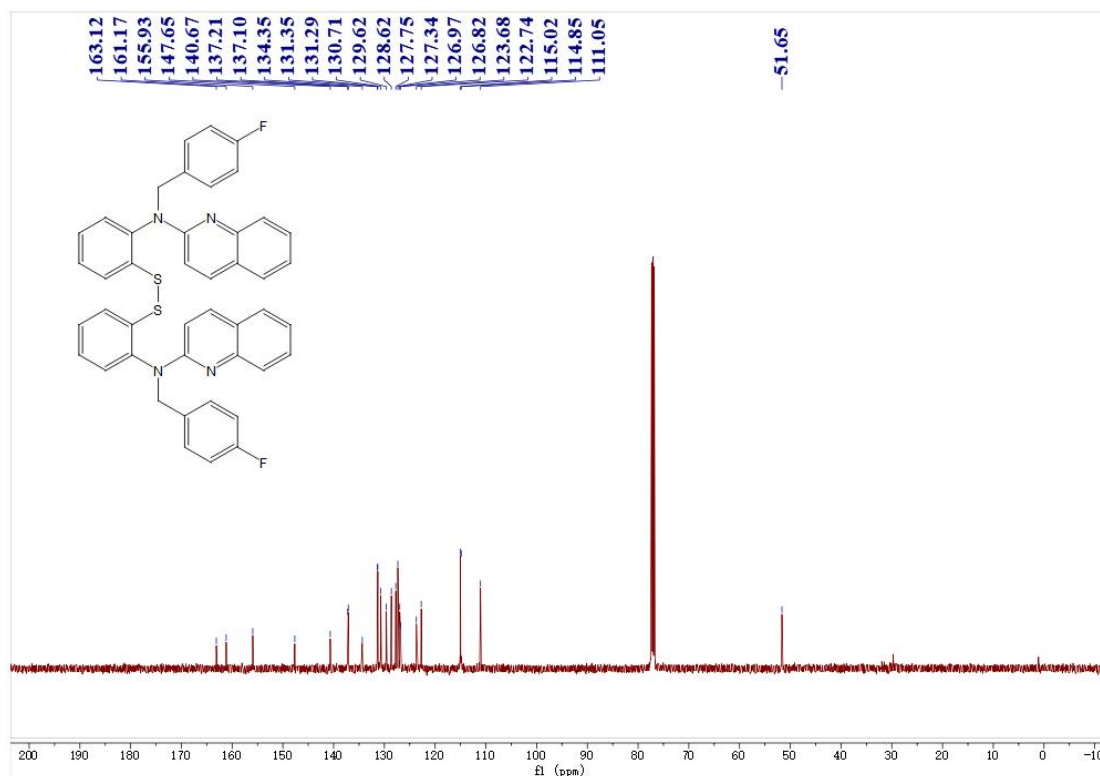
### <sup>13</sup>C NMR spectra of 3ab (126 MHz, CDCl<sub>3</sub>)



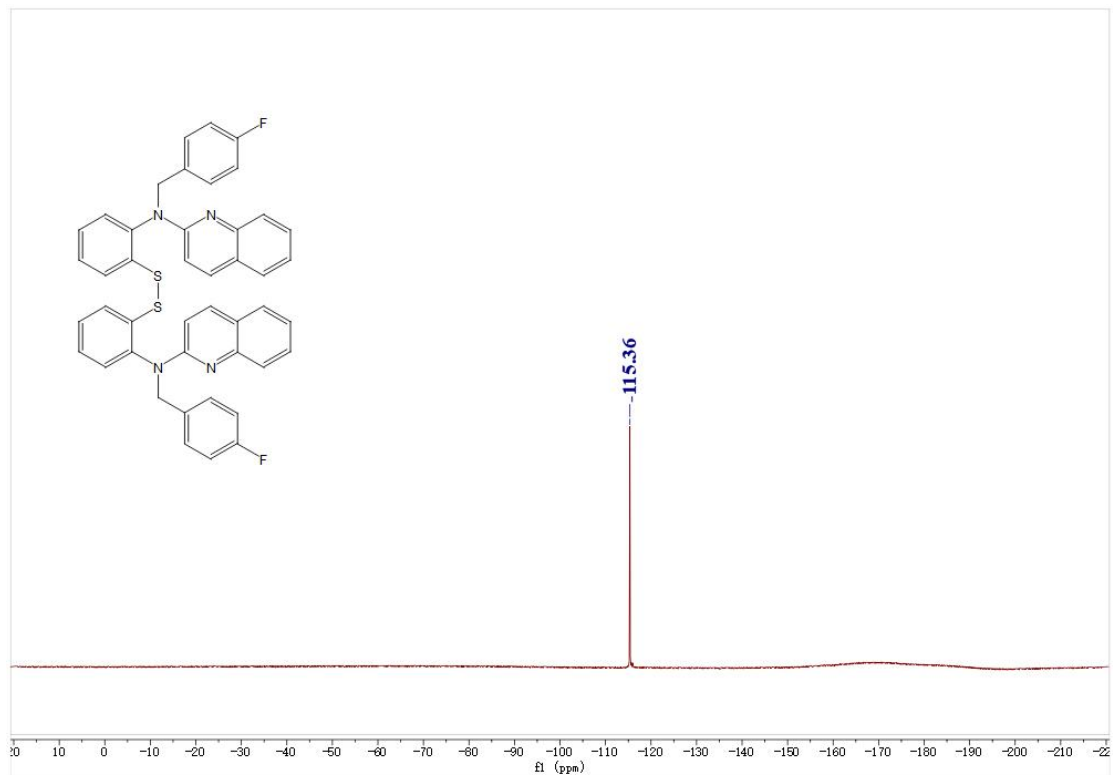
### <sup>1</sup>H NMR spectra of 3ac (500 MHz, CDCl<sub>3</sub>)



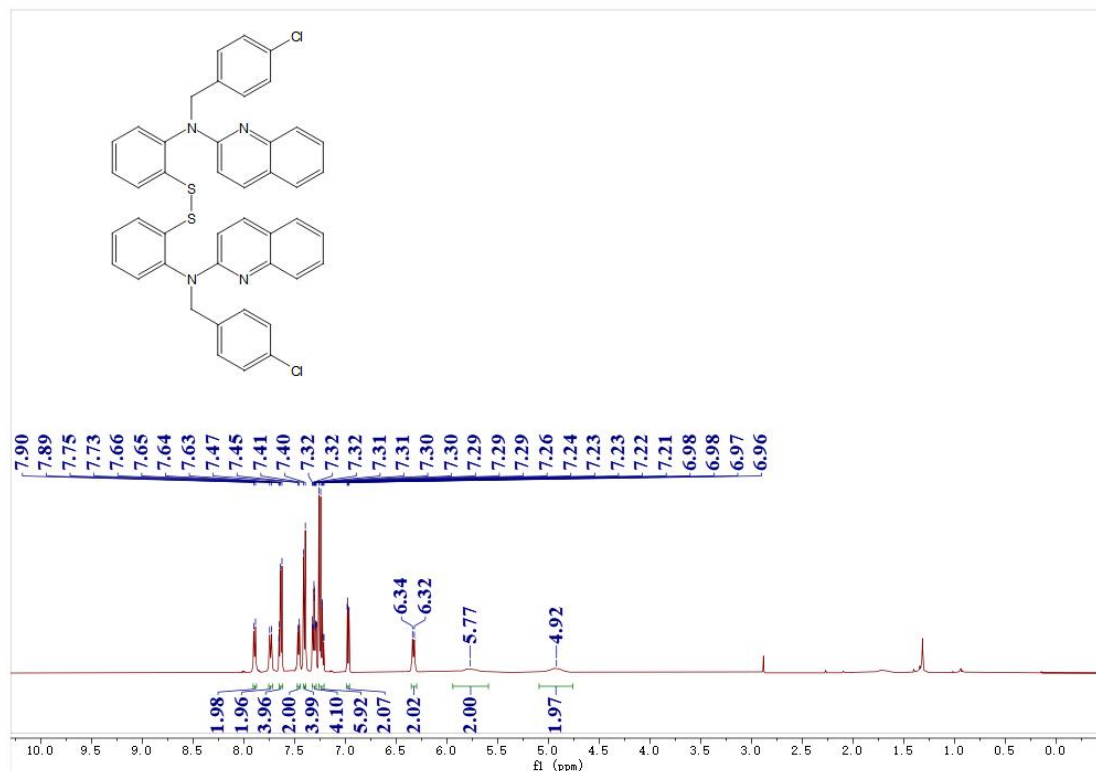
### <sup>13</sup>C NMR spectra of 3ac (126 MHz, CDCl<sub>3</sub>)



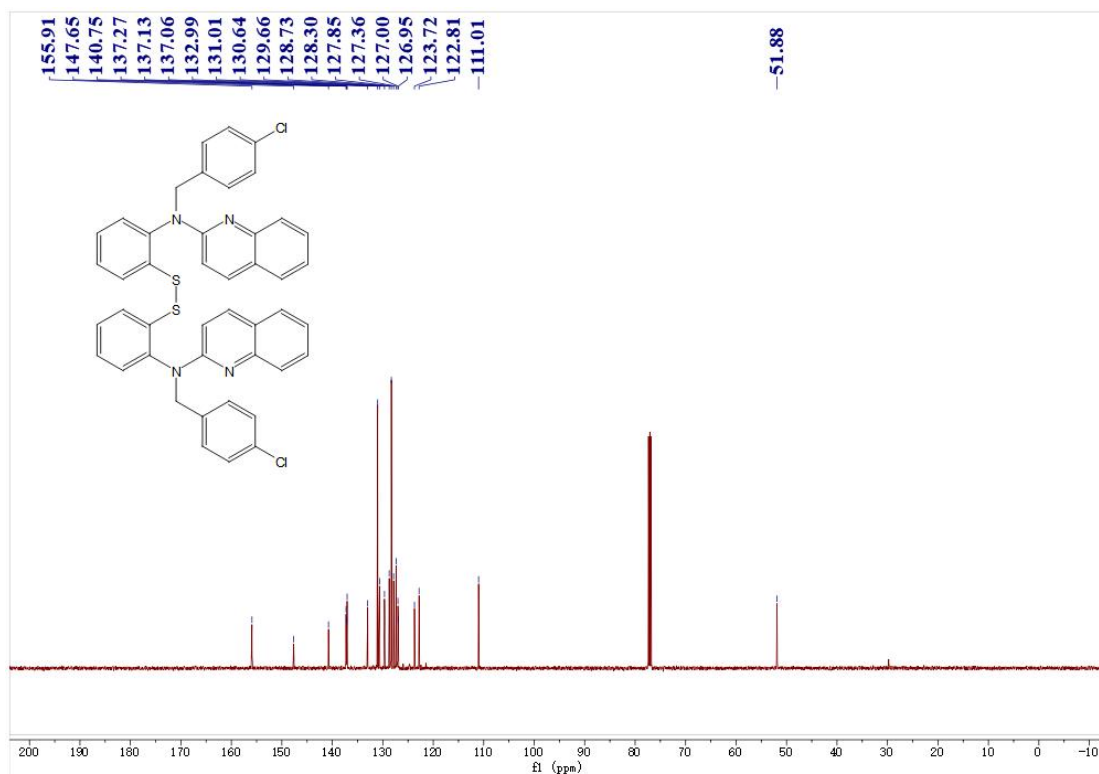
**$^{19}\text{F}$  NMR spectra of 3ac (471 MHz,  $\text{CDCl}_3$ )**



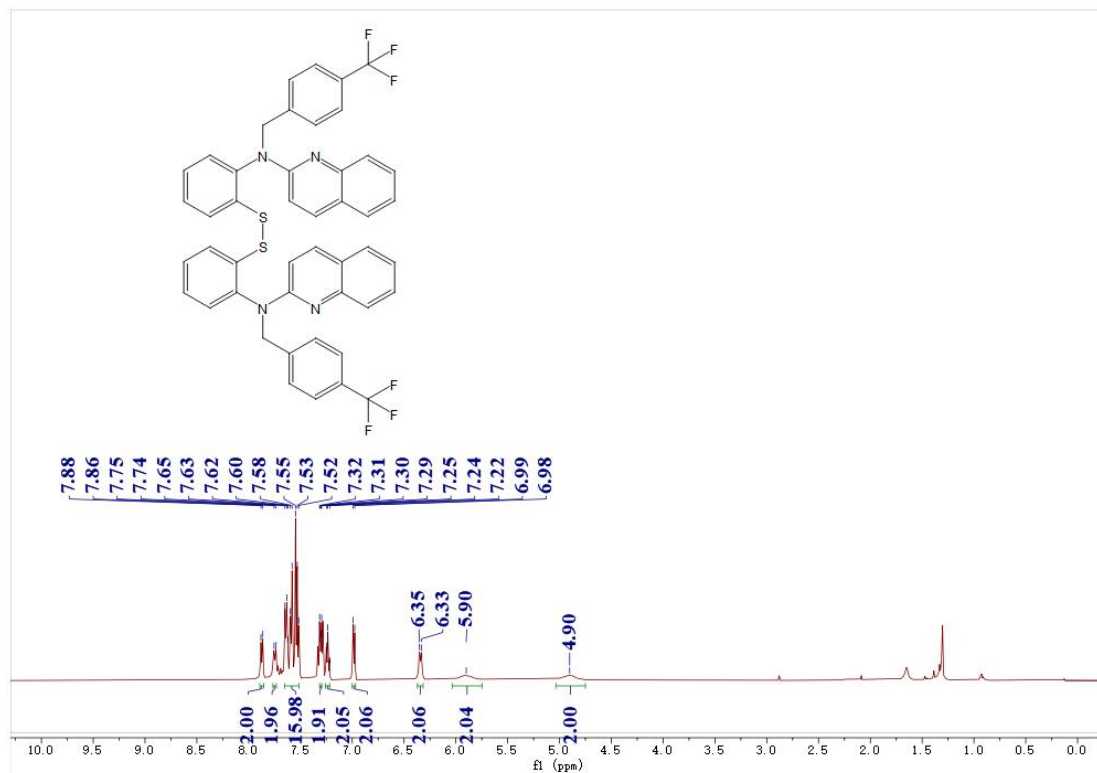
### <sup>1</sup>H NMR spectra of 3ad (500 MHz, CDCl<sub>3</sub>)



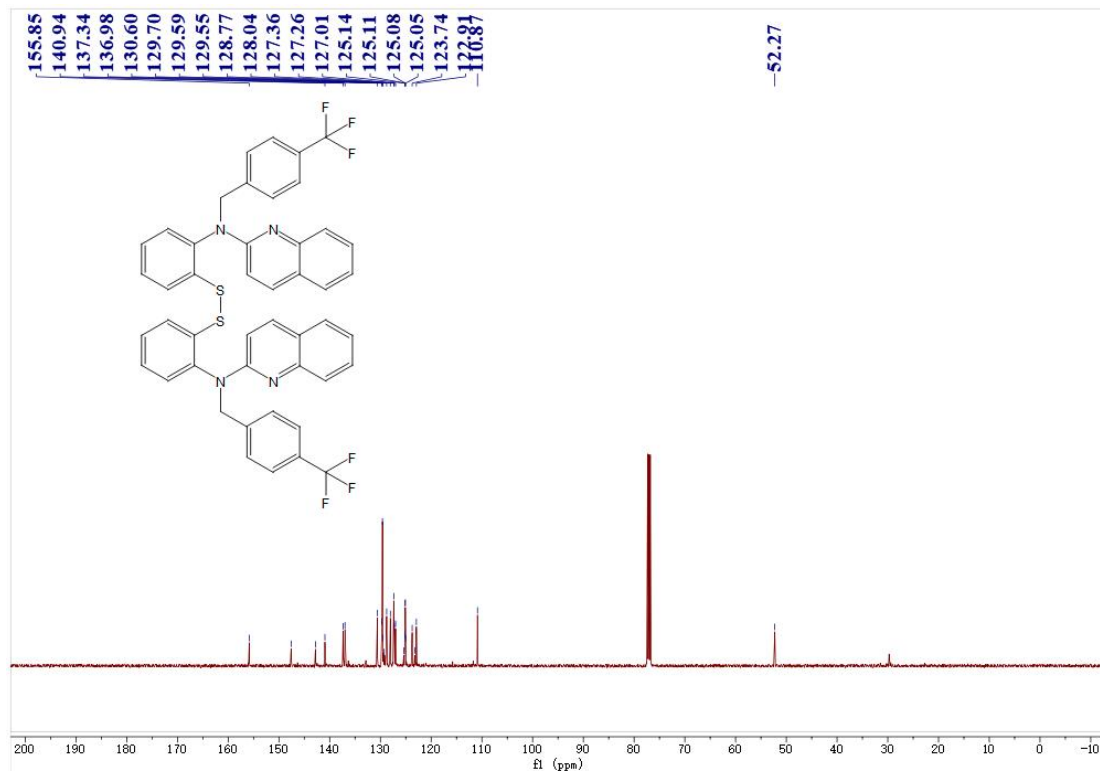
### <sup>13</sup>C NMR spectra of 3ad (126 MHz, CDCl<sub>3</sub>)



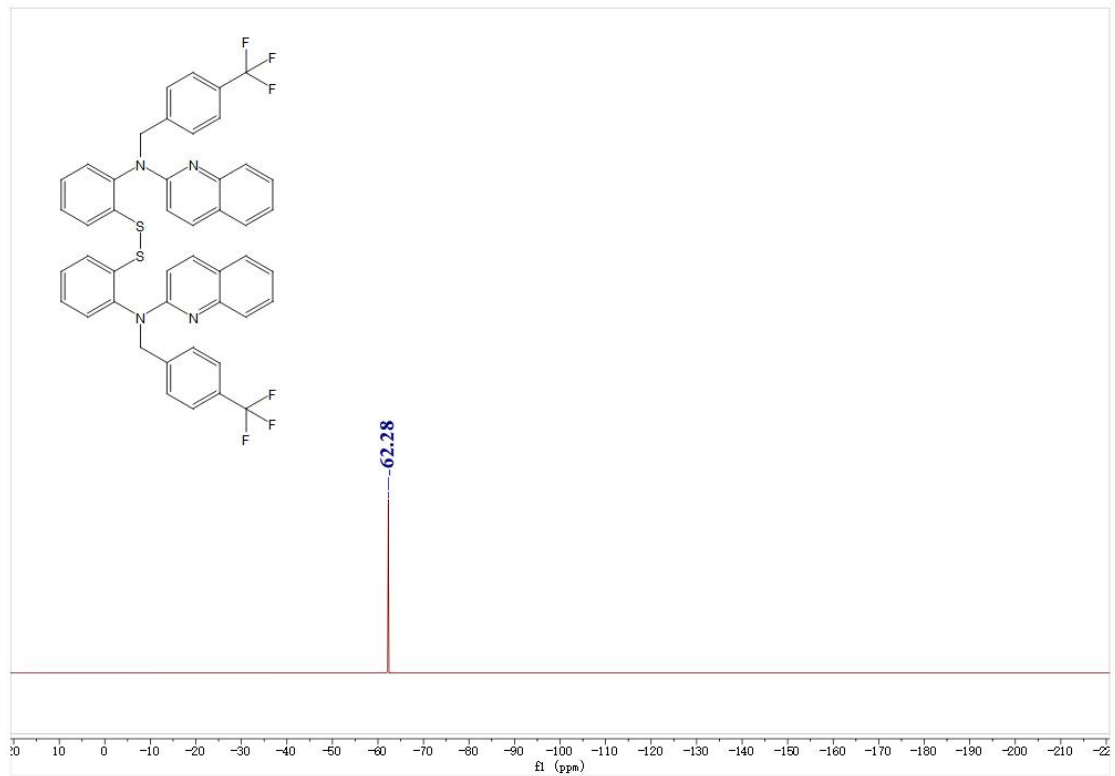
### <sup>1</sup>H NMR spectra of 3ae (500 MHz, CDCl<sub>3</sub>)



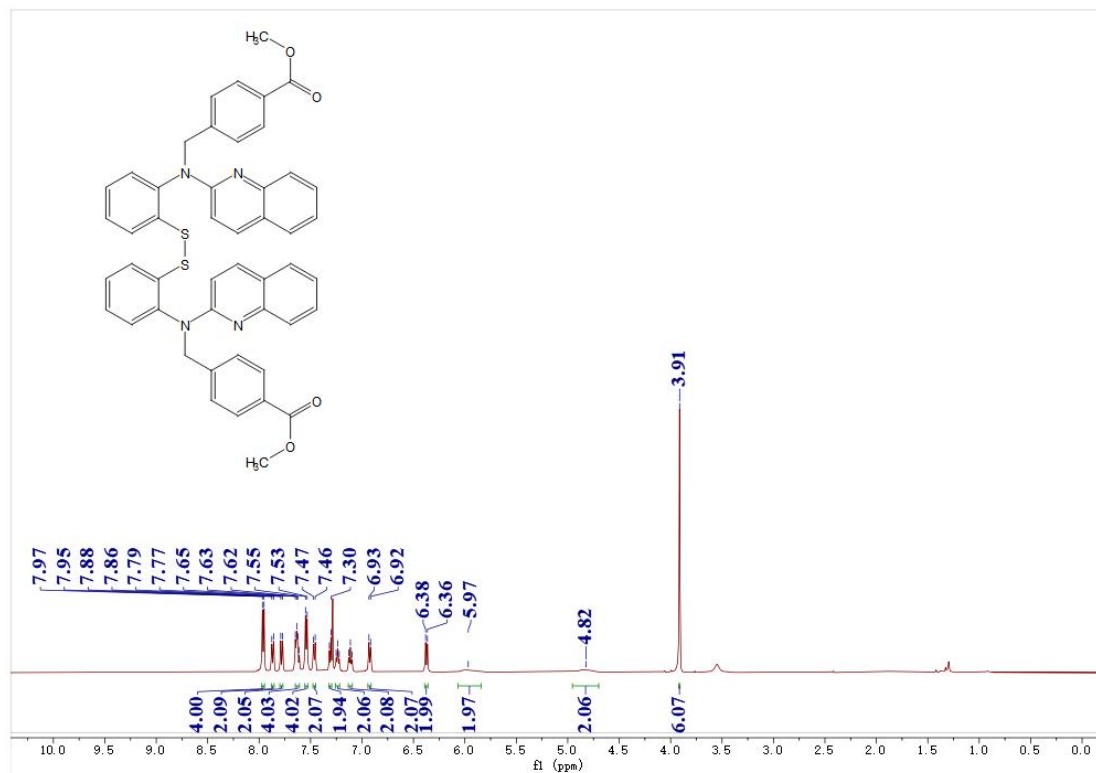
### <sup>13</sup>C NMR spectra of 3ae (126 MHz, CDCl<sub>3</sub>)



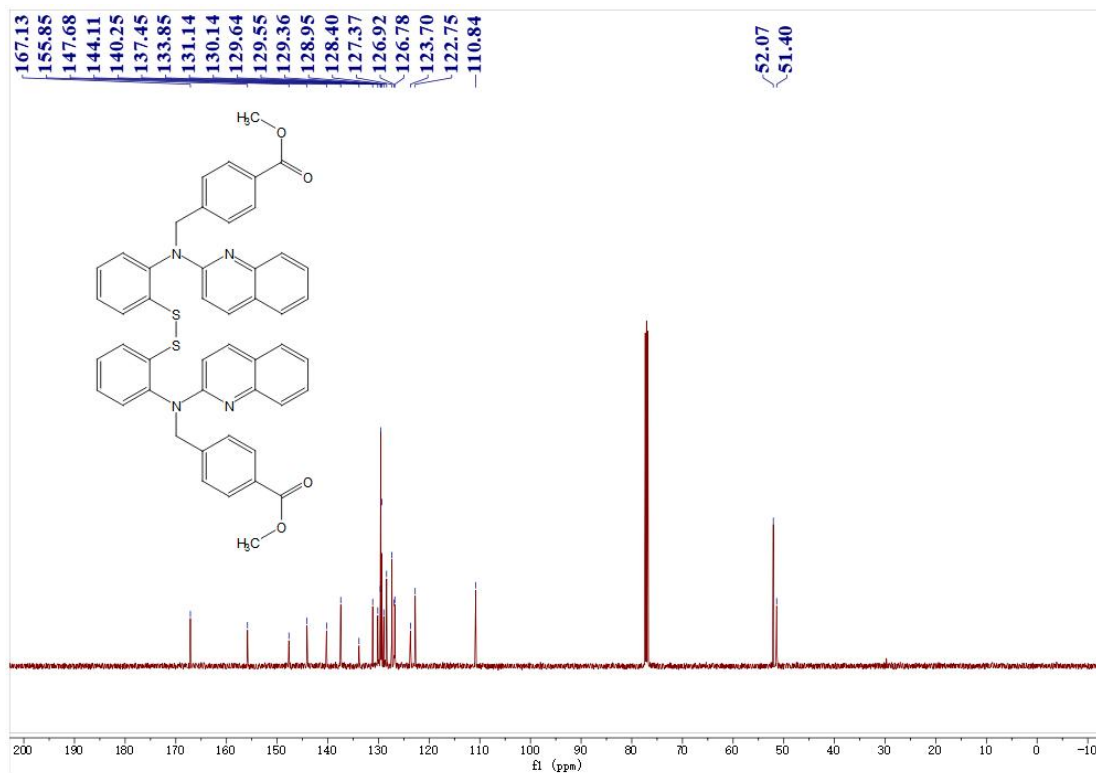
**<sup>19</sup>F NMR spectra of 3ae (471 MHz, CDCl<sub>3</sub>)**



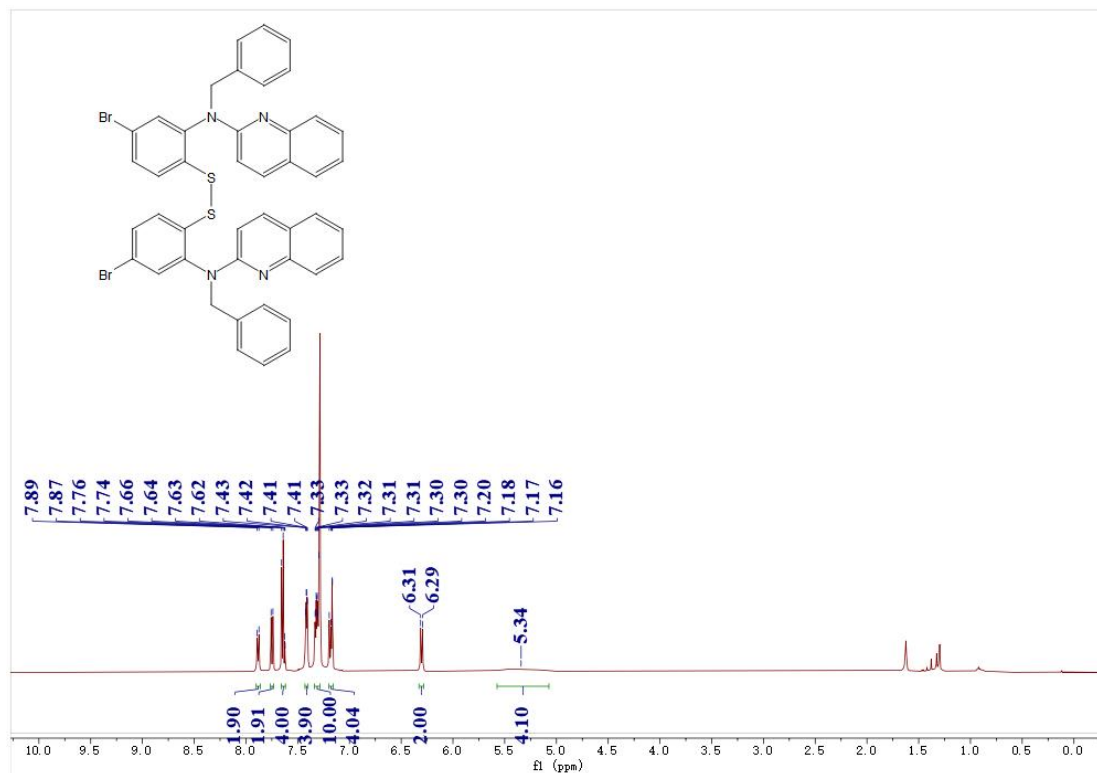
### <sup>1</sup>H NMR spectra of 3af (500 MHz, CDCl<sub>3</sub>)



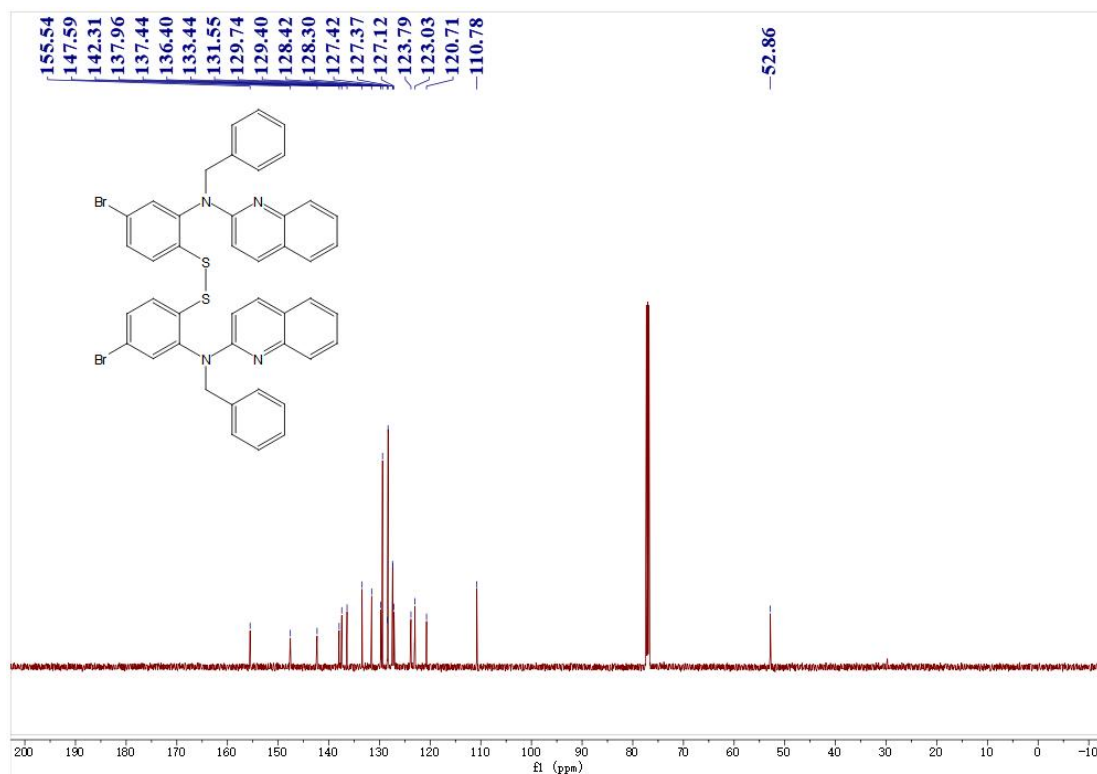
### <sup>13</sup>C NMR spectra of 3af (126 MHz, CDCl<sub>3</sub>)



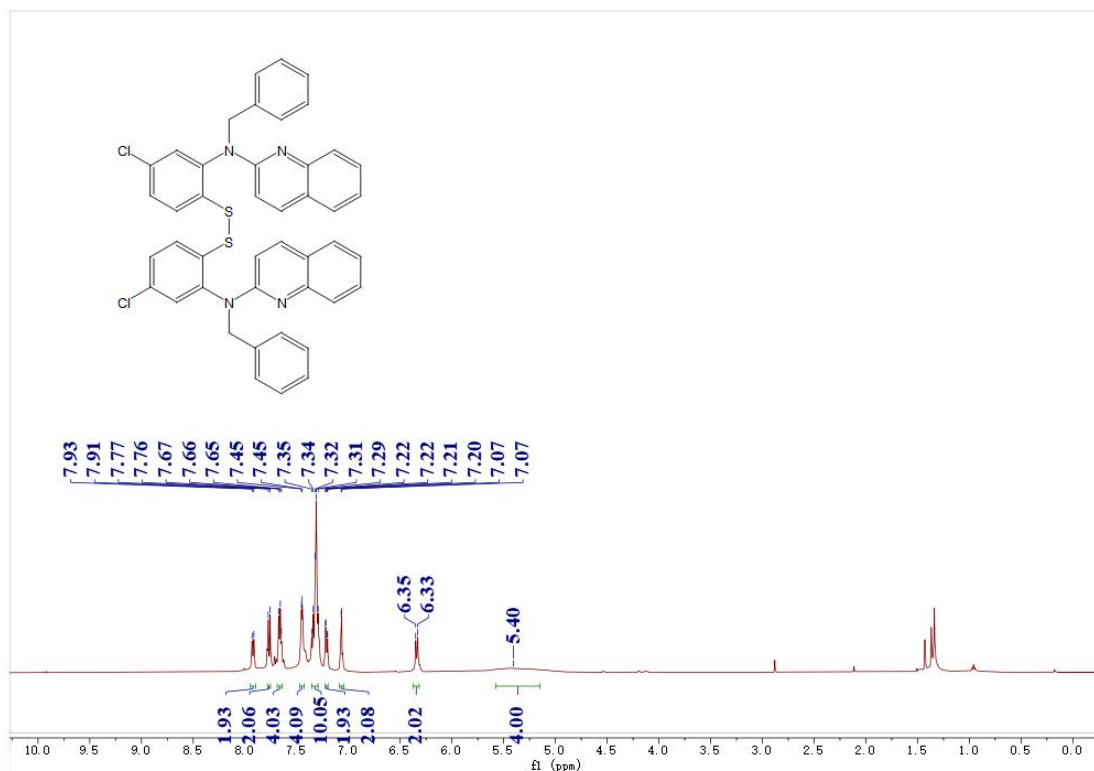
<sup>1</sup>H NMR spectra of 3ag (500 MHz, CDCl<sub>3</sub>)



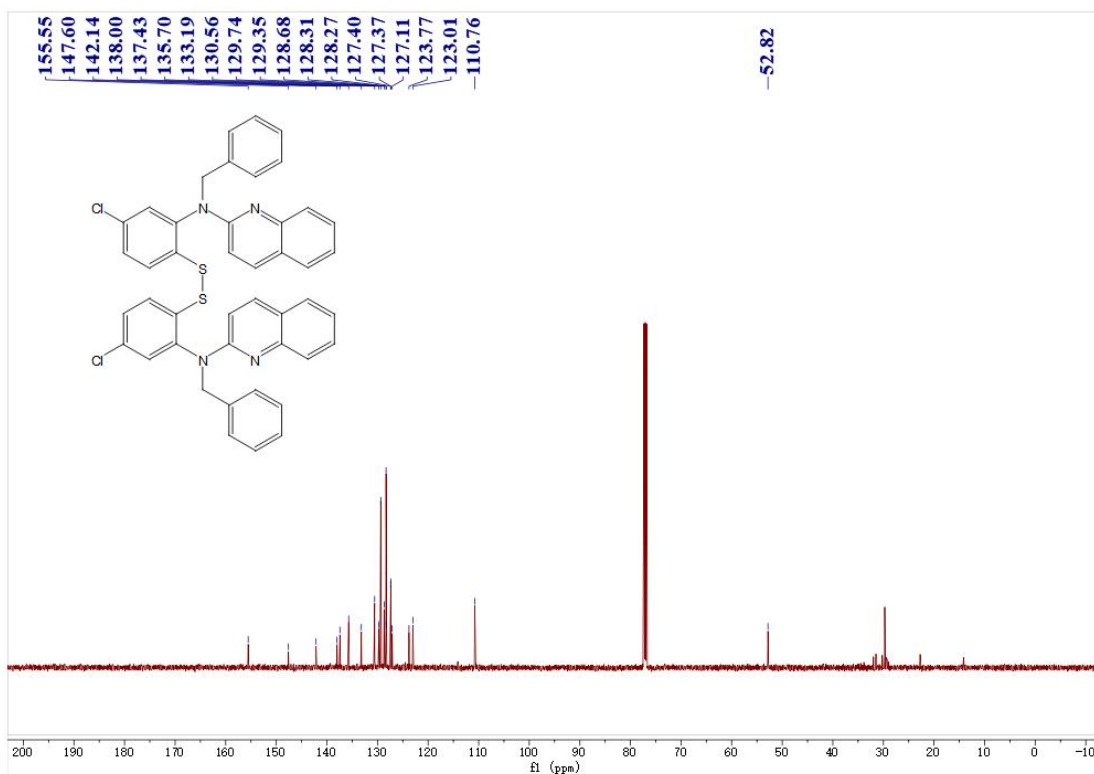
<sup>13</sup>C NMR spectra of 3ag (126 MHz, CDCl<sub>3</sub>)



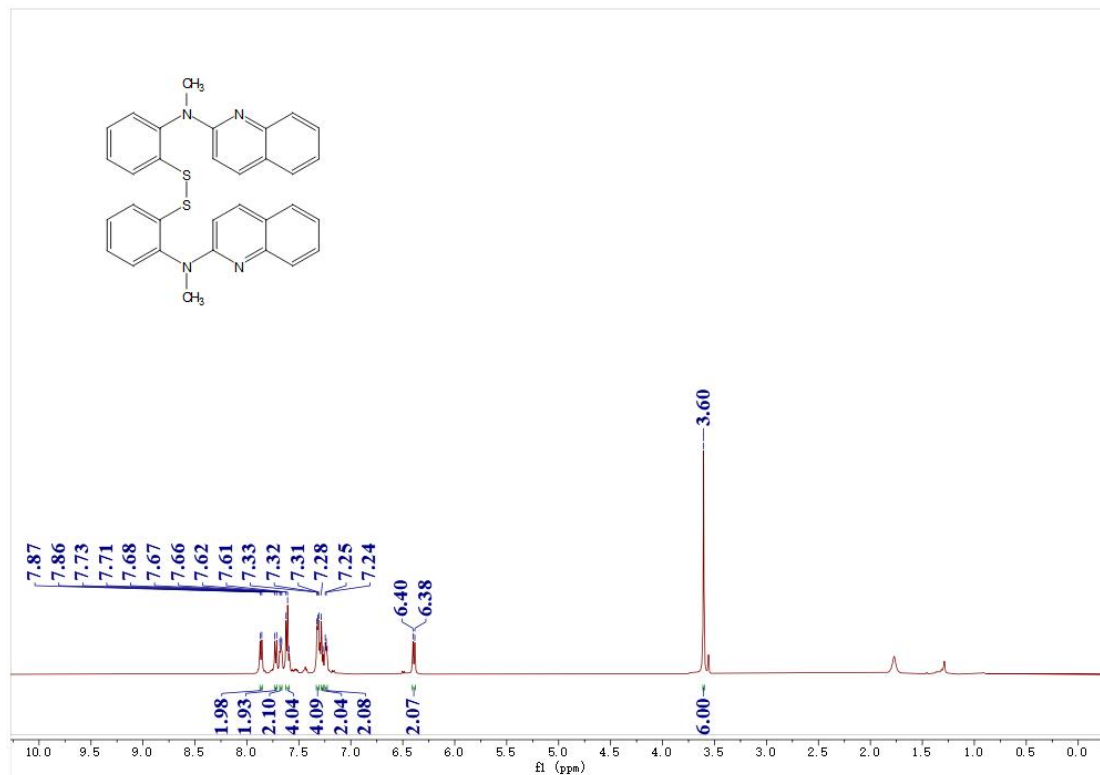
### <sup>1</sup>H NMR spectra of 3ah (500 MHz, CDCl<sub>3</sub>)



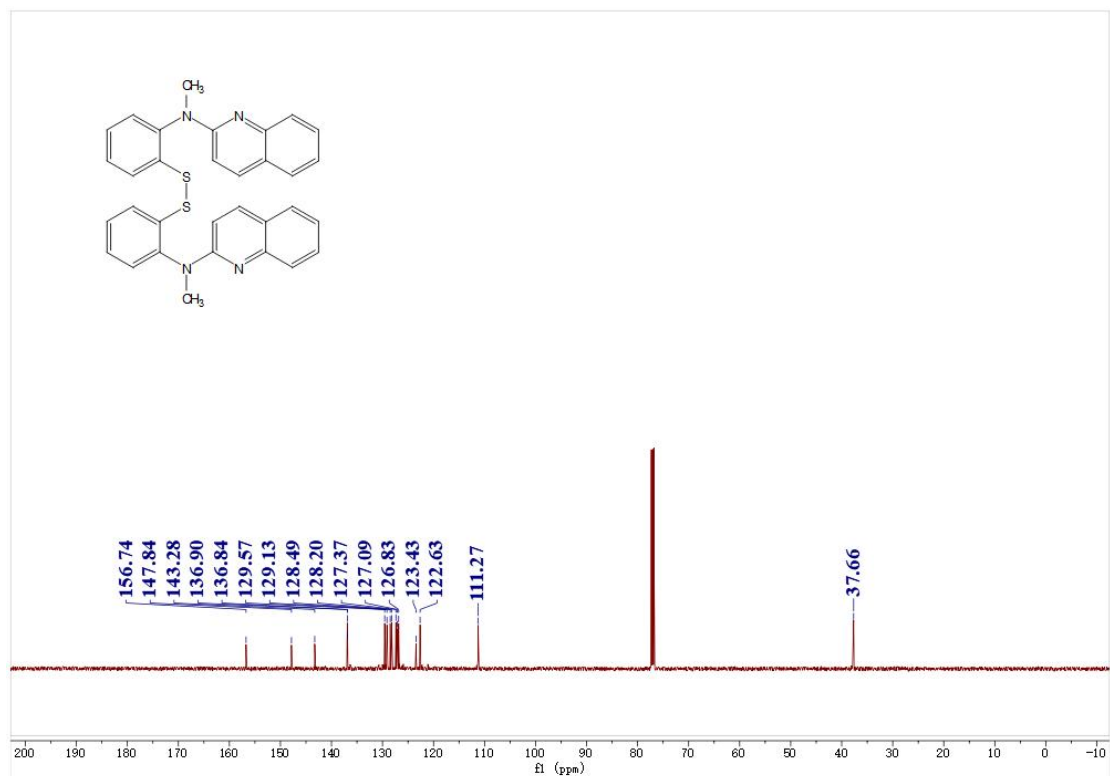
### <sup>13</sup>C NMR spectra of 3ah (126 MHz, CDCl<sub>3</sub>)



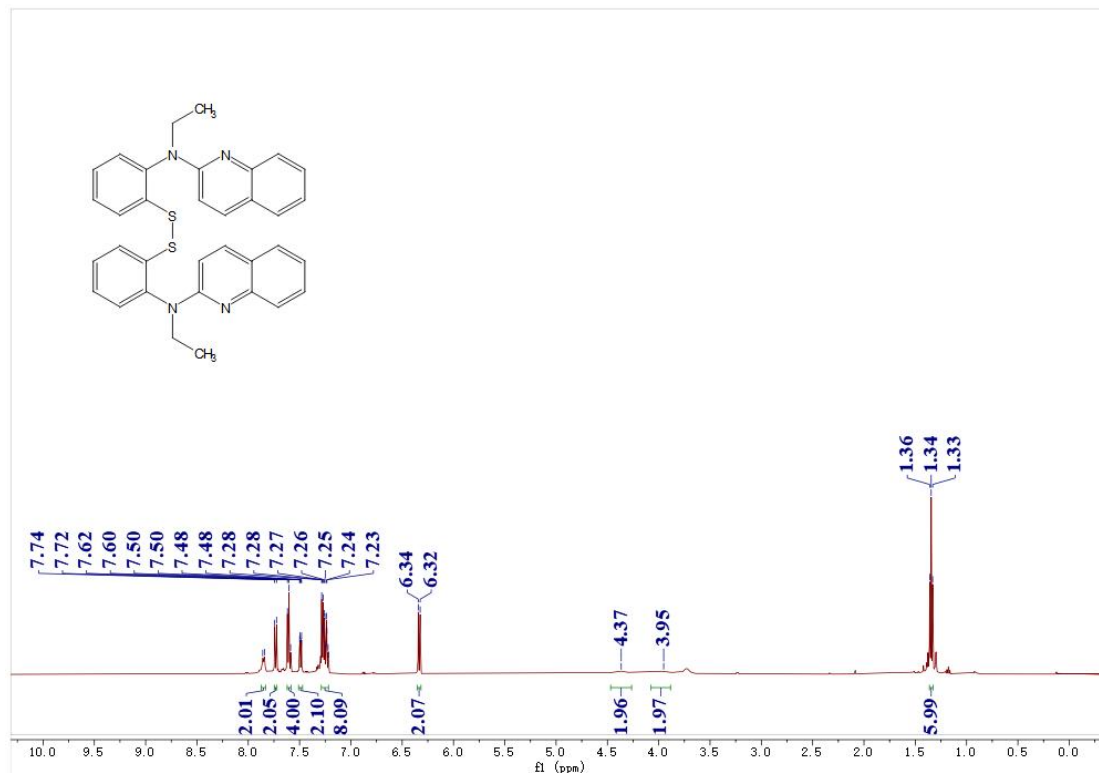
**<sup>1</sup>H NMR spectra of 3ai (500 MHz, CDCl<sub>3</sub>)**



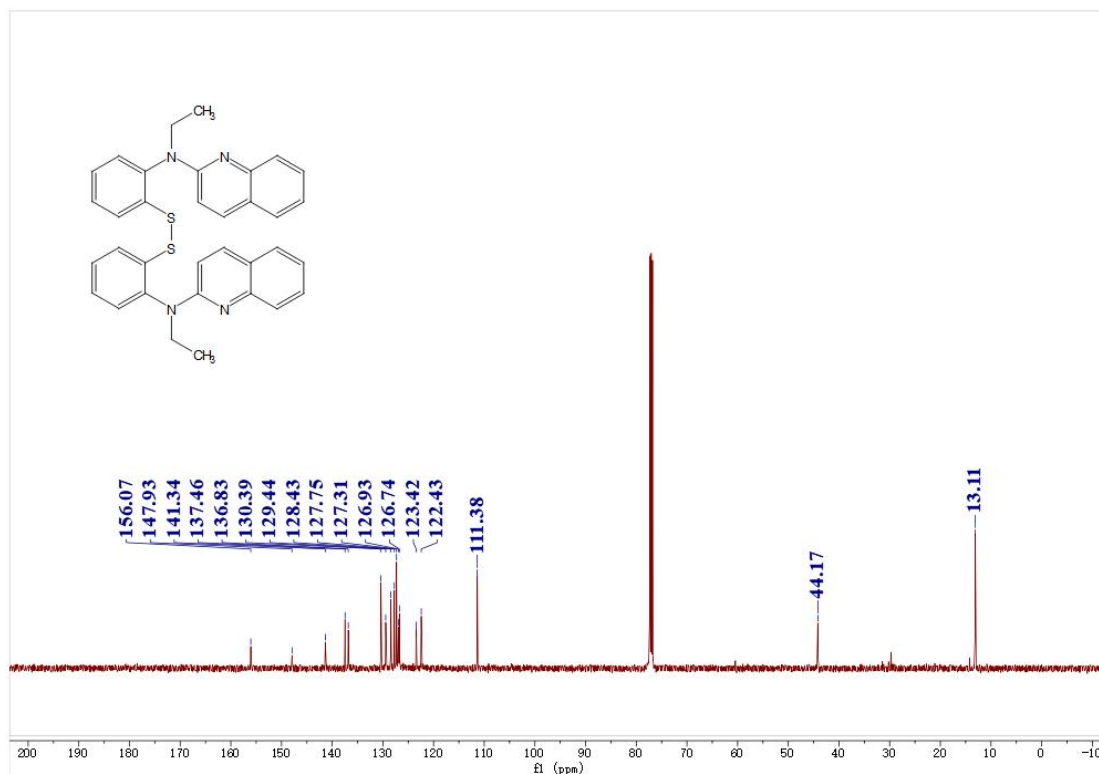
**<sup>13</sup>C NMR spectra of 3ai (126 MHz, CDCl<sub>3</sub>)**



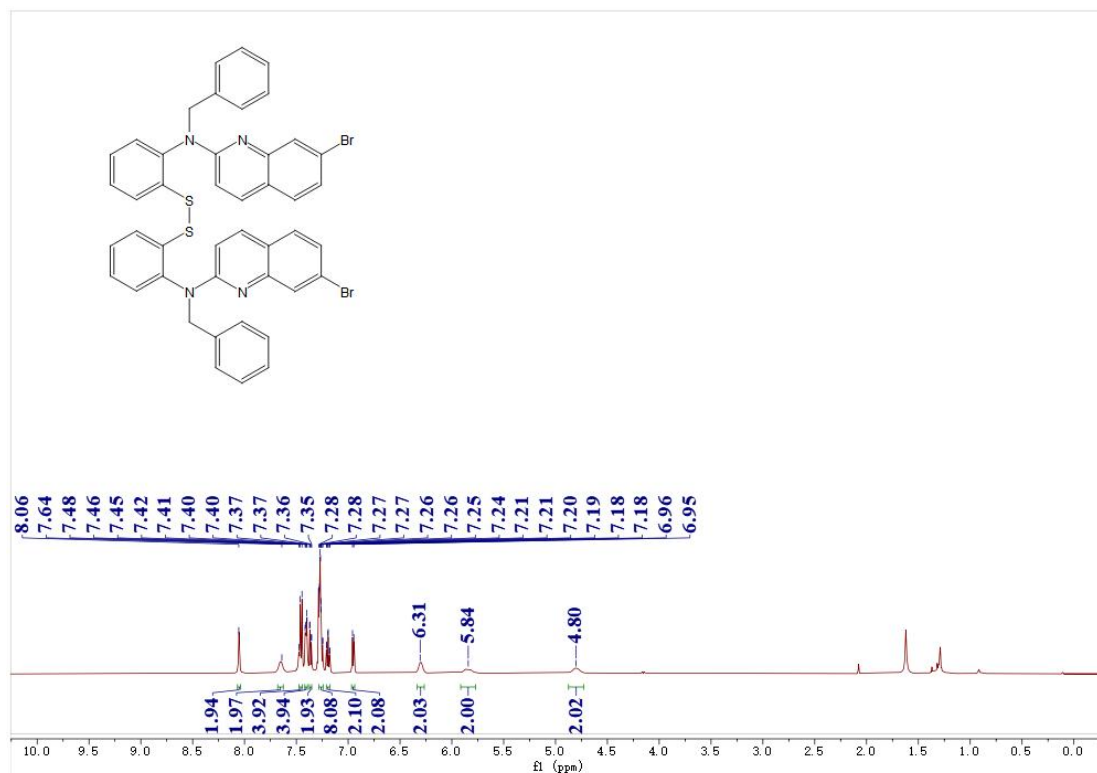
**<sup>1</sup>H NMR spectra of 3aj (500 MHz, CDCl<sub>3</sub>)**



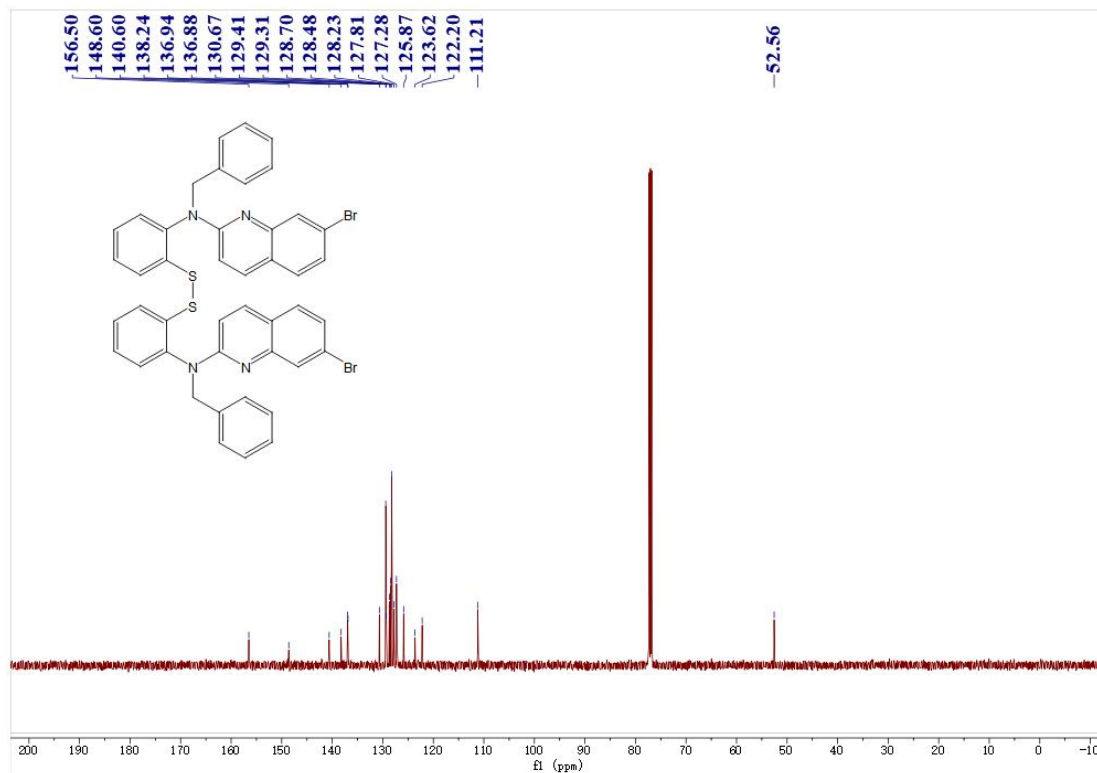
**<sup>13</sup>C NMR spectra of 3aj (126 MHz, CDCl<sub>3</sub>)**



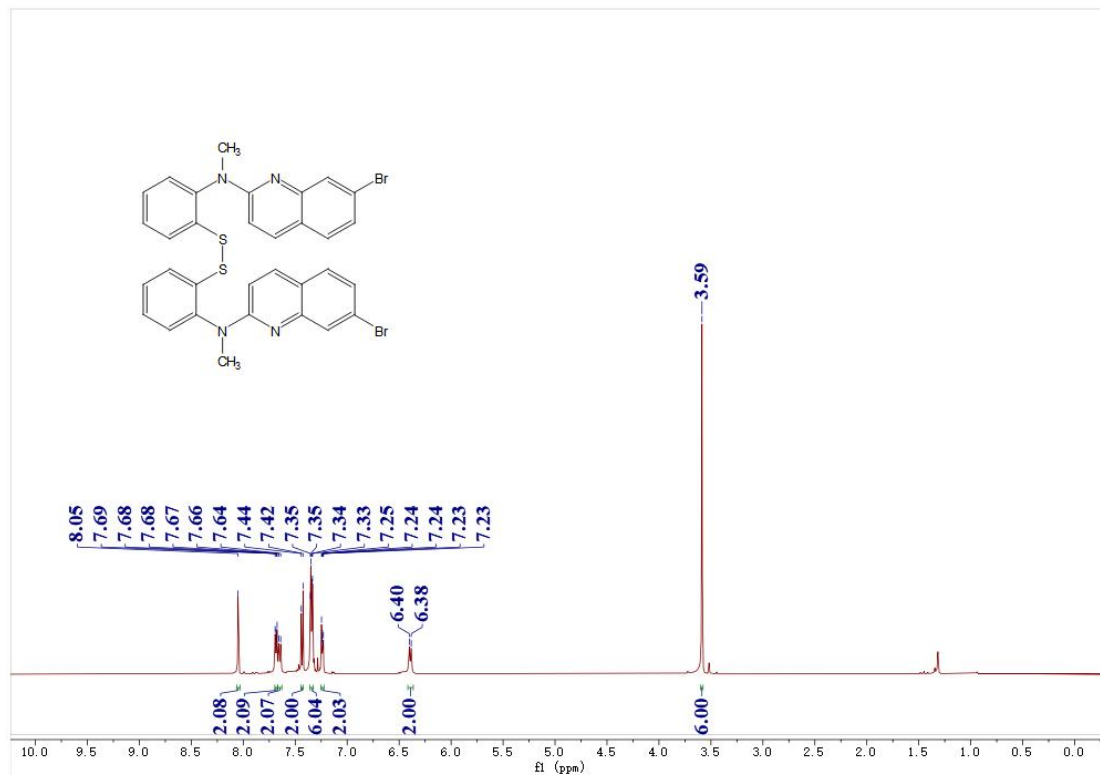
### <sup>1</sup>H NMR spectra of 3ak (500 MHz, CDCl<sub>3</sub>)



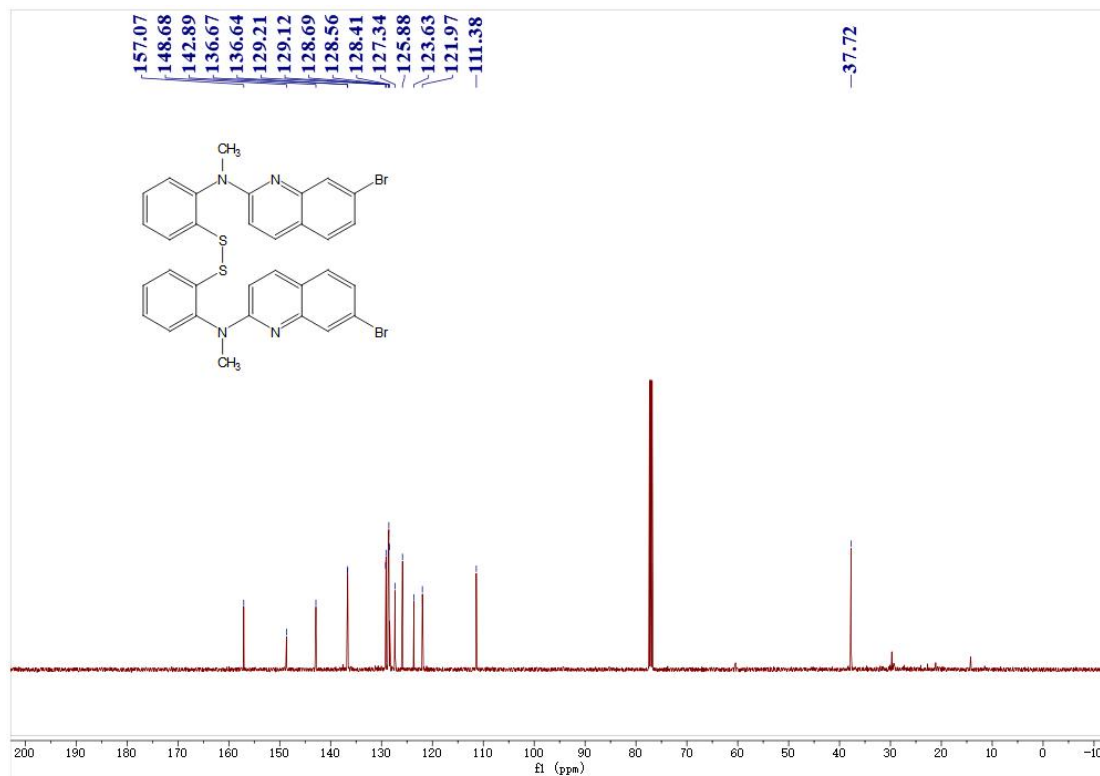
### <sup>13</sup>C NMR spectra of 3ak (126 MHz, CDCl<sub>3</sub>)



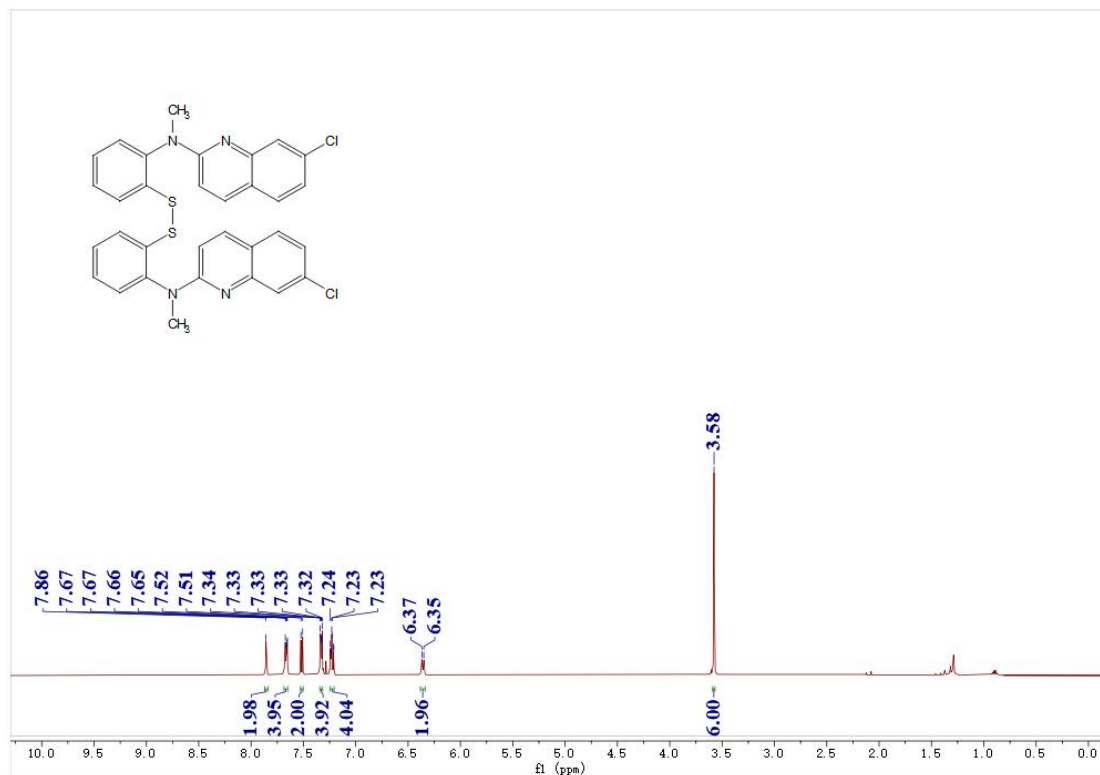
### <sup>1</sup>H NMR spectra of 3al (500 MHz, CDCl<sub>3</sub>)



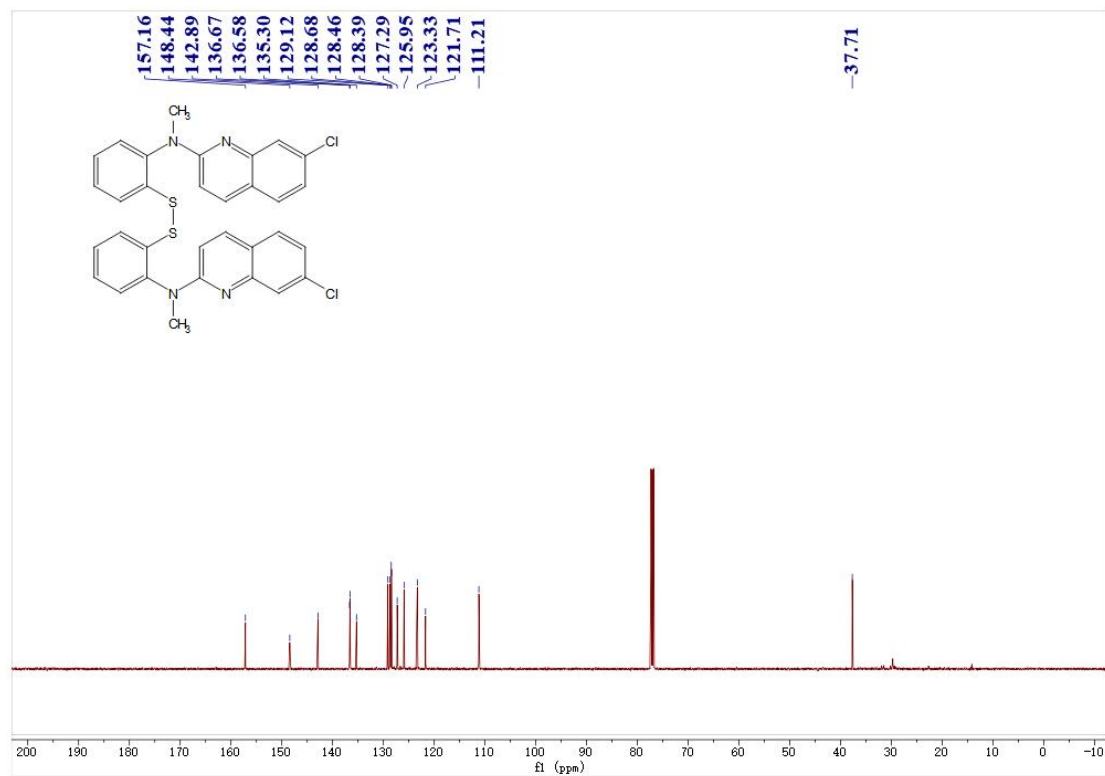
### <sup>13</sup>C NMR spectra of 3al (126 MHz, CDCl<sub>3</sub>)



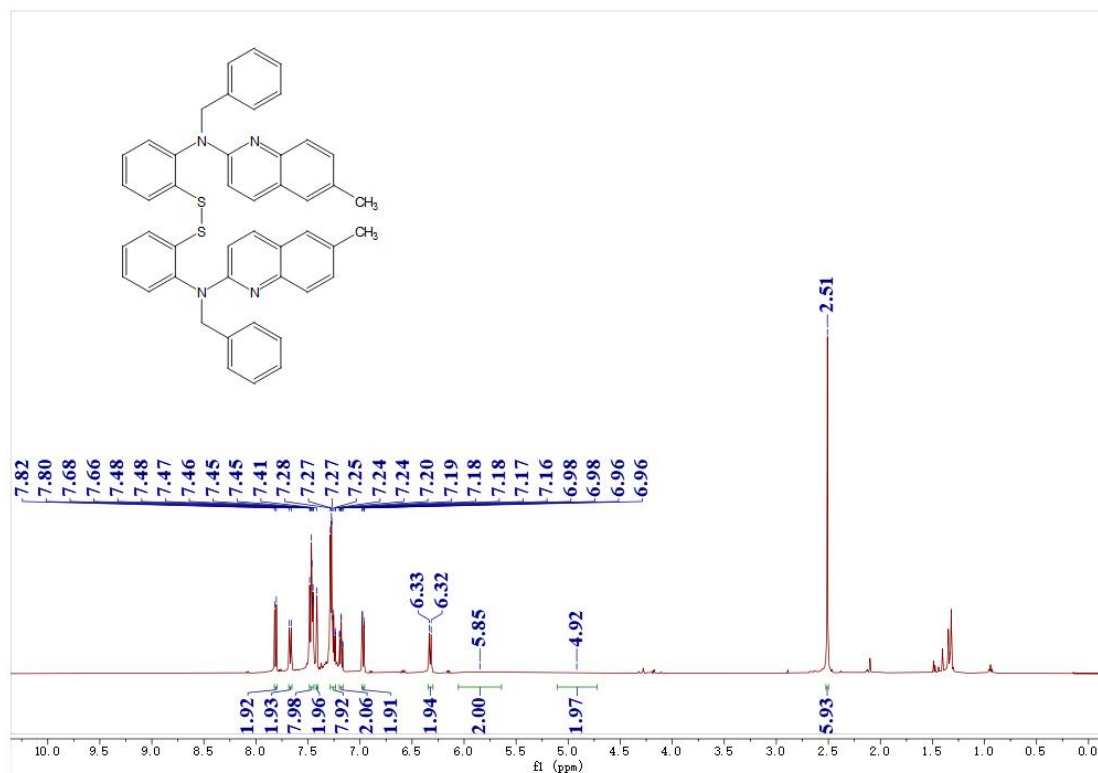
### <sup>1</sup>H NMR spectra of 3am (500 MHz, CDCl<sub>3</sub>)



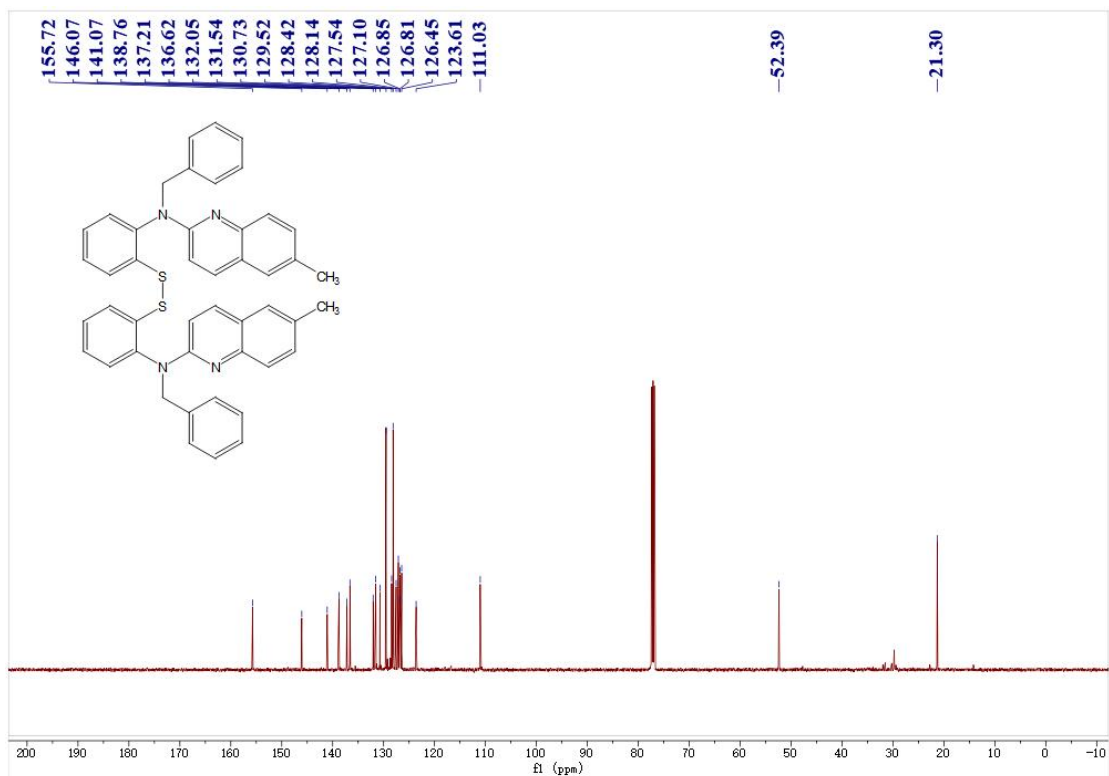
### <sup>13</sup>C NMR spectra of 3am (126 MHz, CDCl<sub>3</sub>)



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

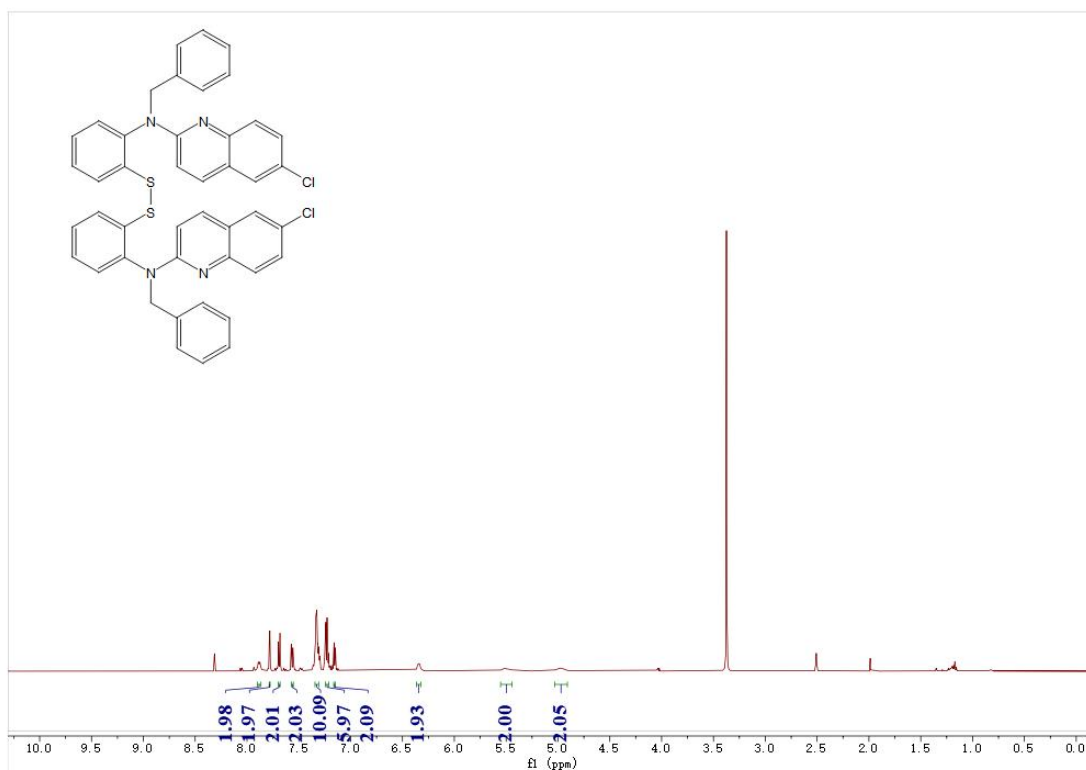


**<sup>13</sup>C NMR spectra of 3an (126 MHz, CDCl<sub>3</sub>)**

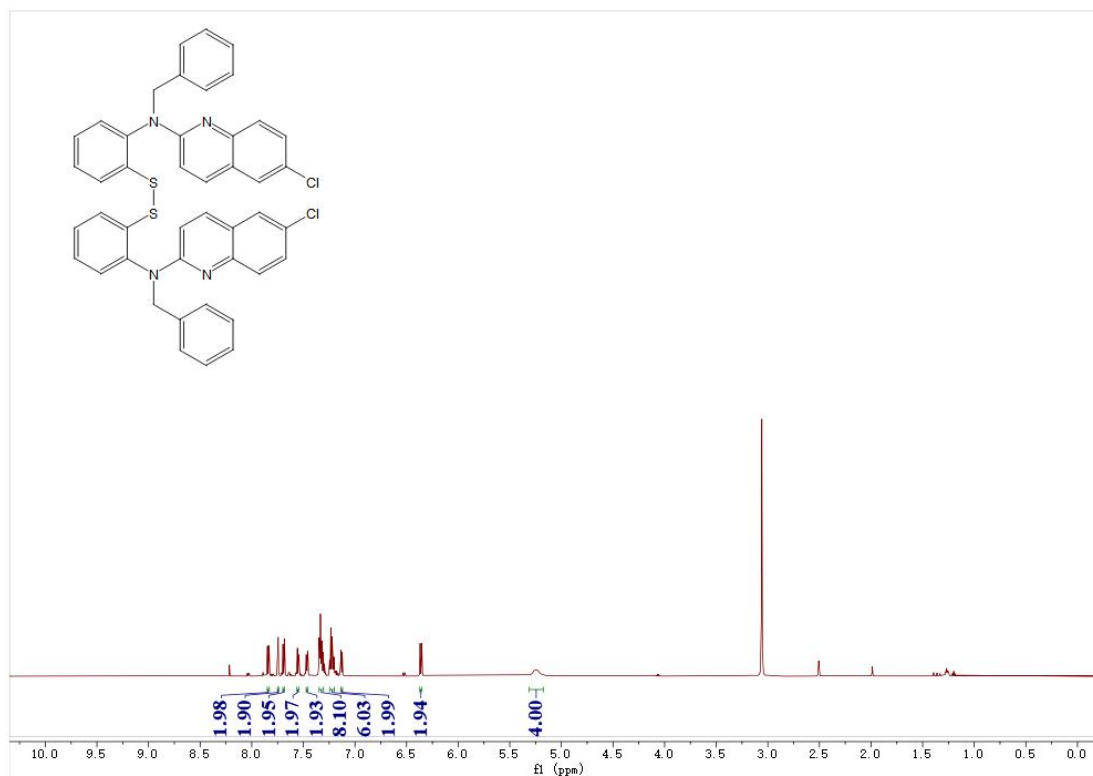




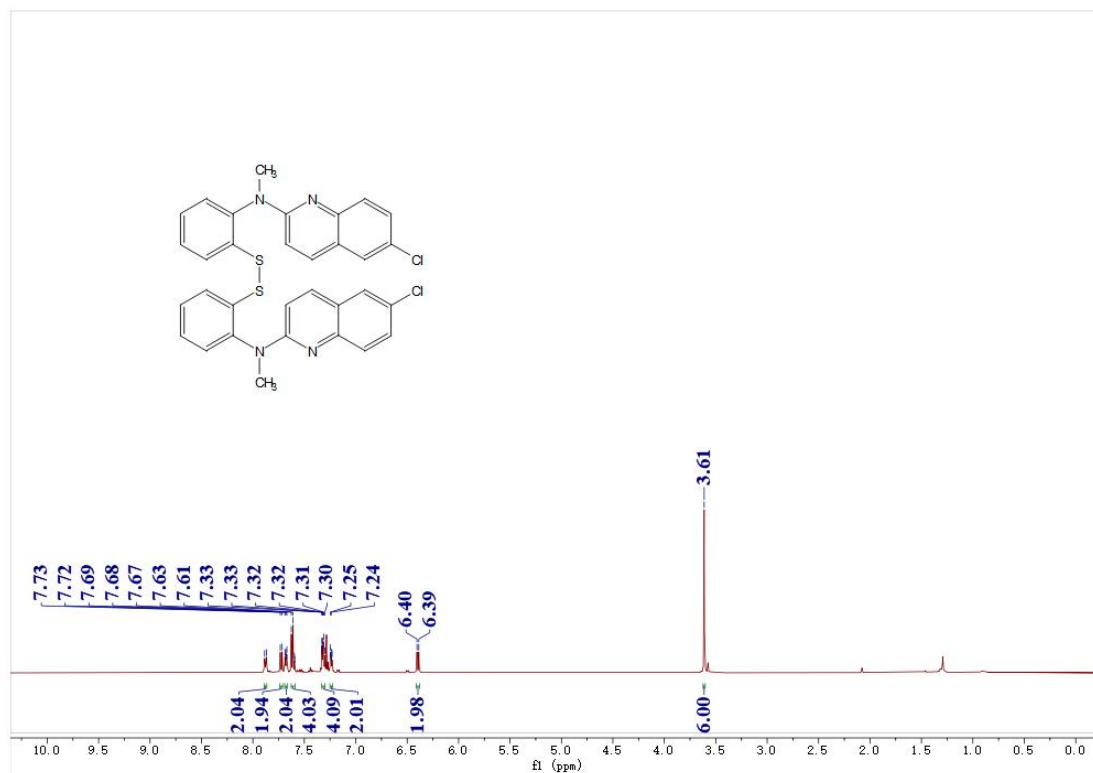
**<sup>1</sup>H NMR spectra of 3ao (600 MHz, DMSO) RT**



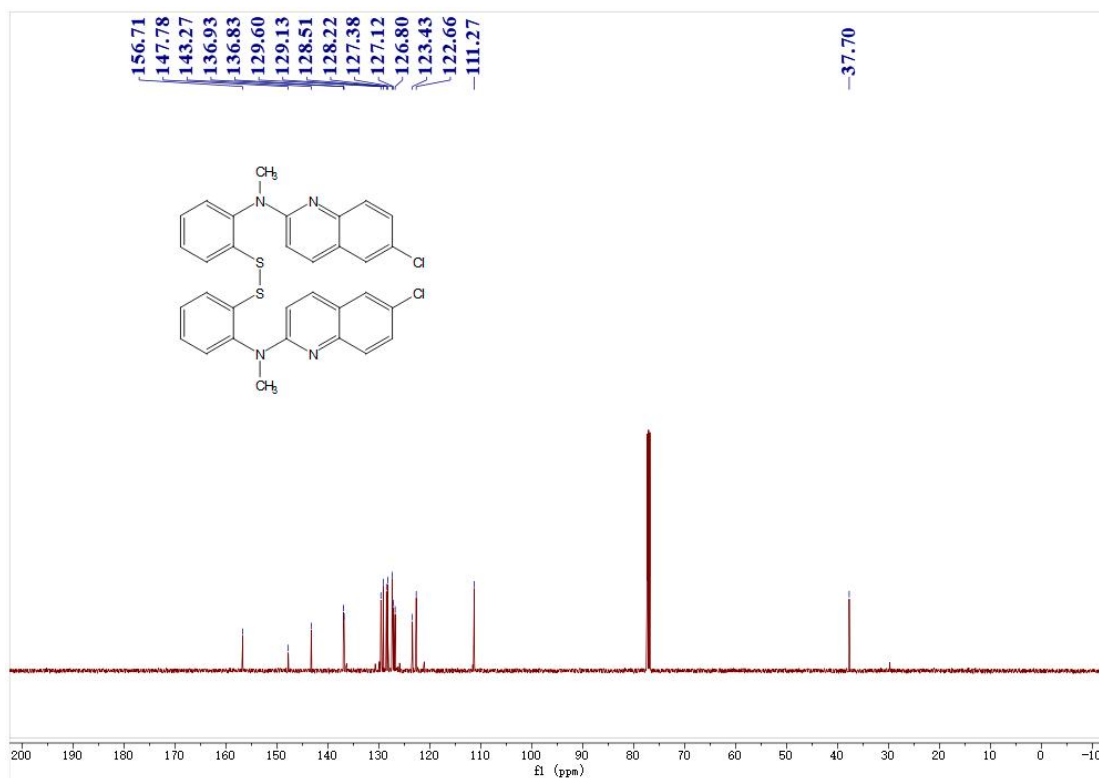
**<sup>1</sup>H NMR spectra of 3ao (600 MHz, DMSO) 80 °C**



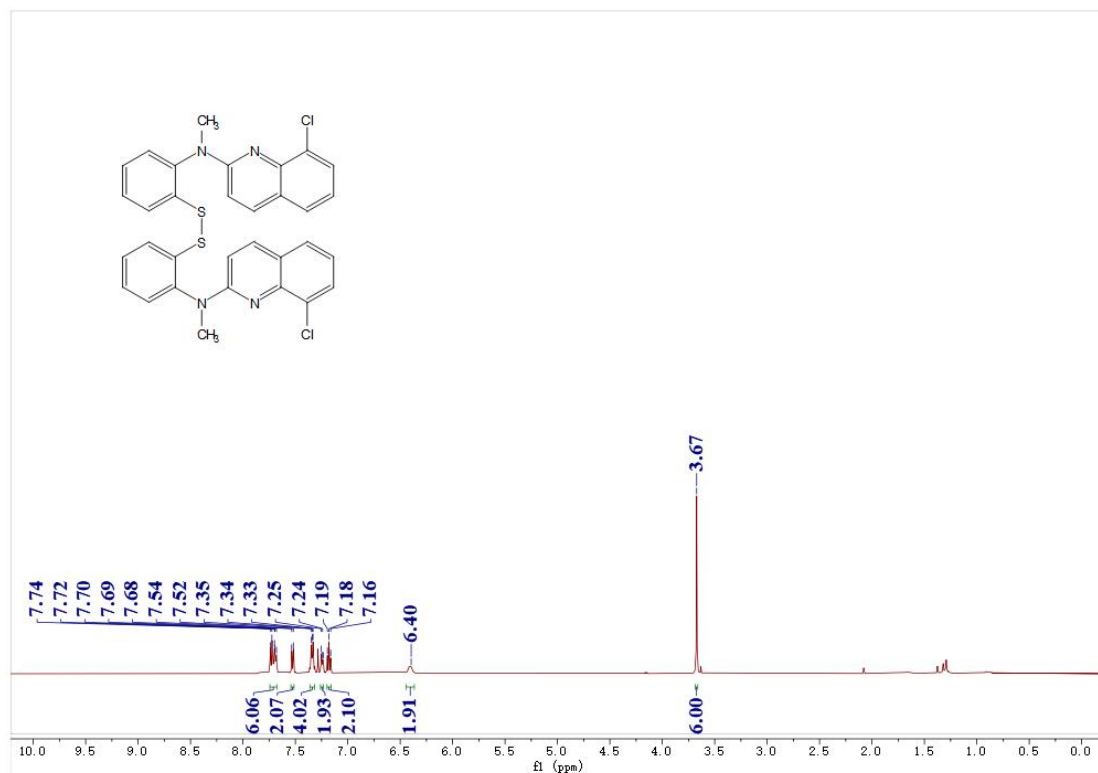
### $^1\text{H}$ NMR spectra of 3aq (500 MHz, $\text{CDCl}_3$ )



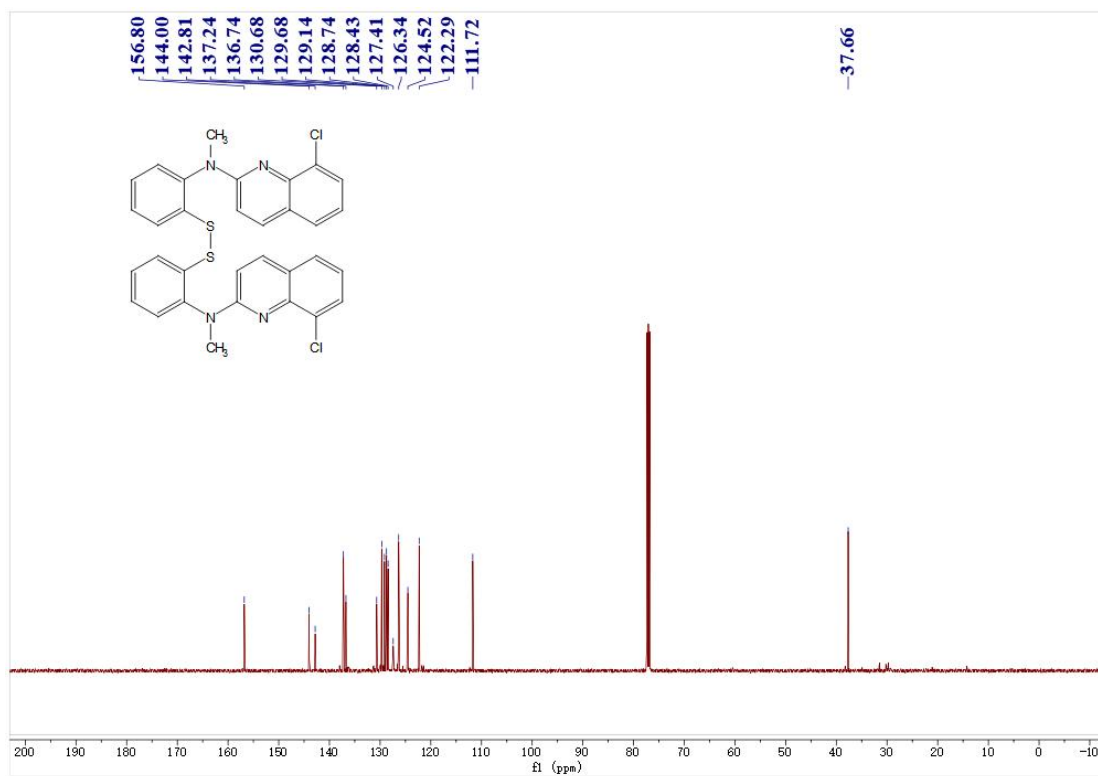
### $^{13}\text{C}$ NMR spectra of 3aq (126 MHz, $\text{CDCl}_3$ )



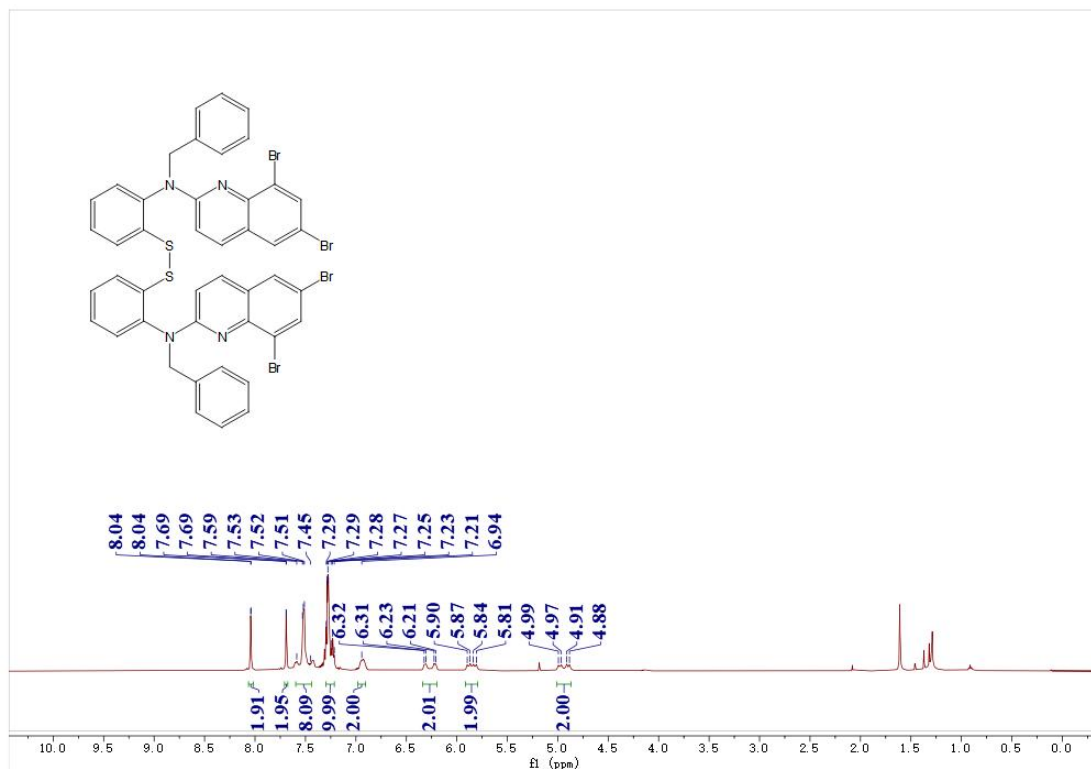
**<sup>1</sup>H NMR spectra of 3ar (500 MHz, CDCl<sub>3</sub>)**



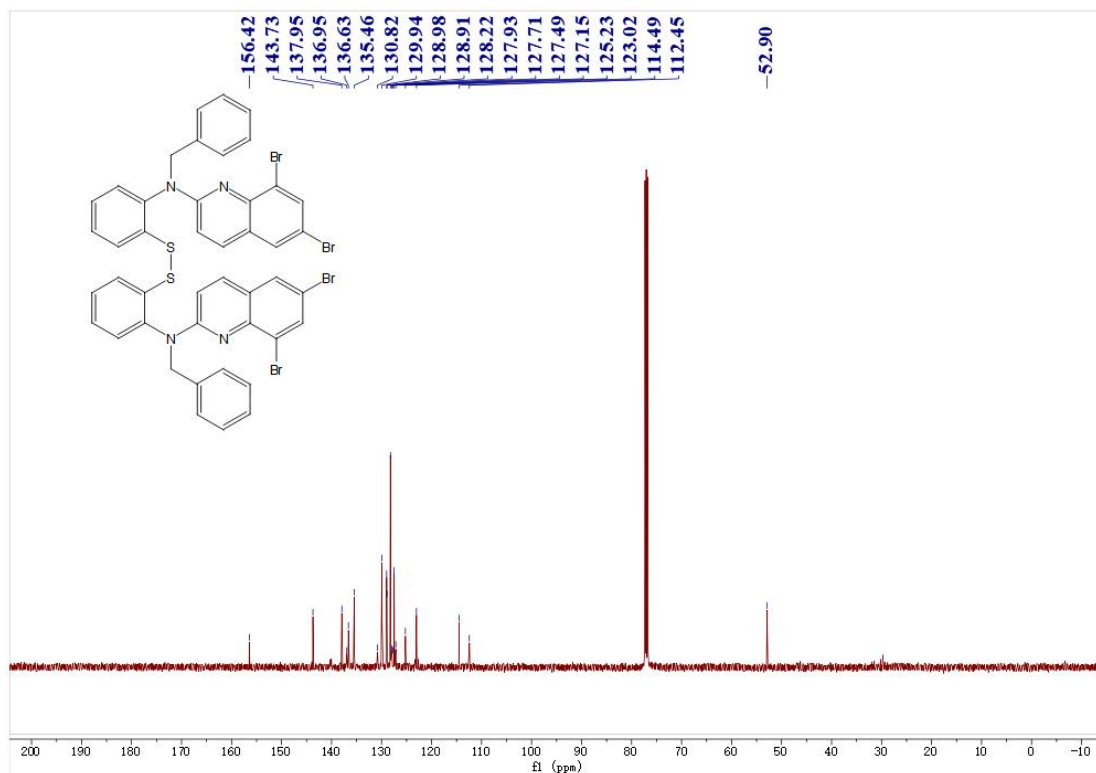
**<sup>13</sup>C NMR spectra of 3ar (126 MHz, CDCl<sub>3</sub>)**



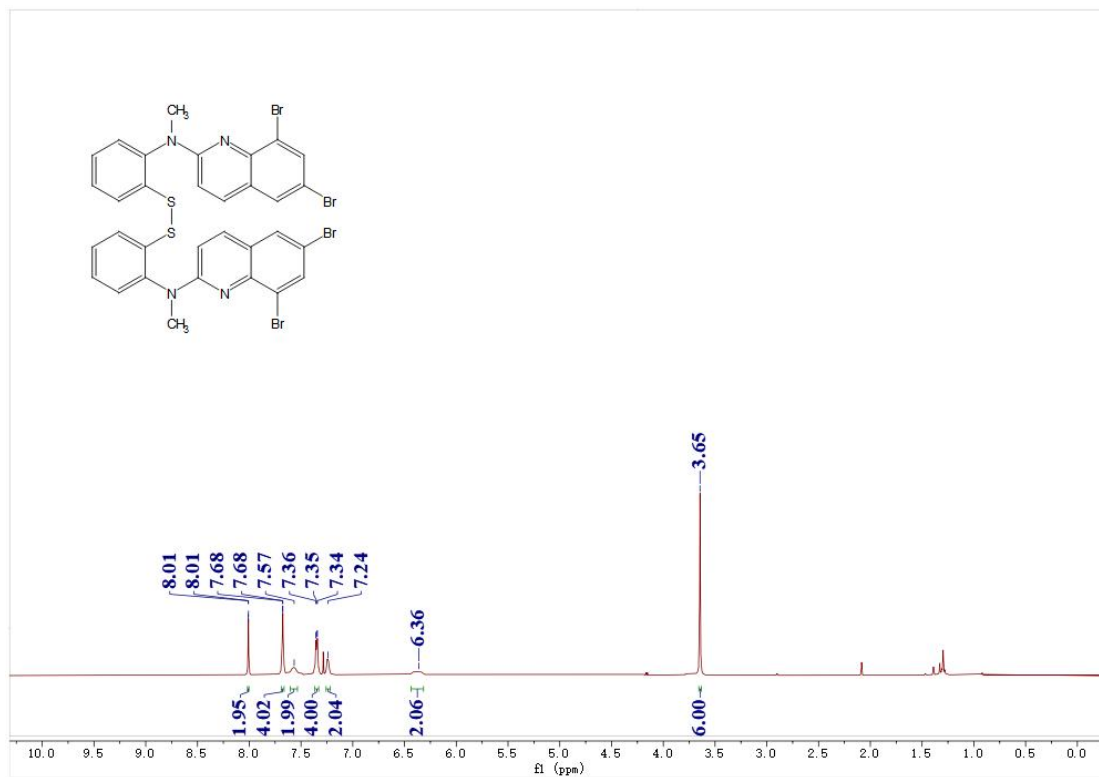
### <sup>1</sup>H NMR spectra of 3as (500 MHz, CDCl<sub>3</sub>)



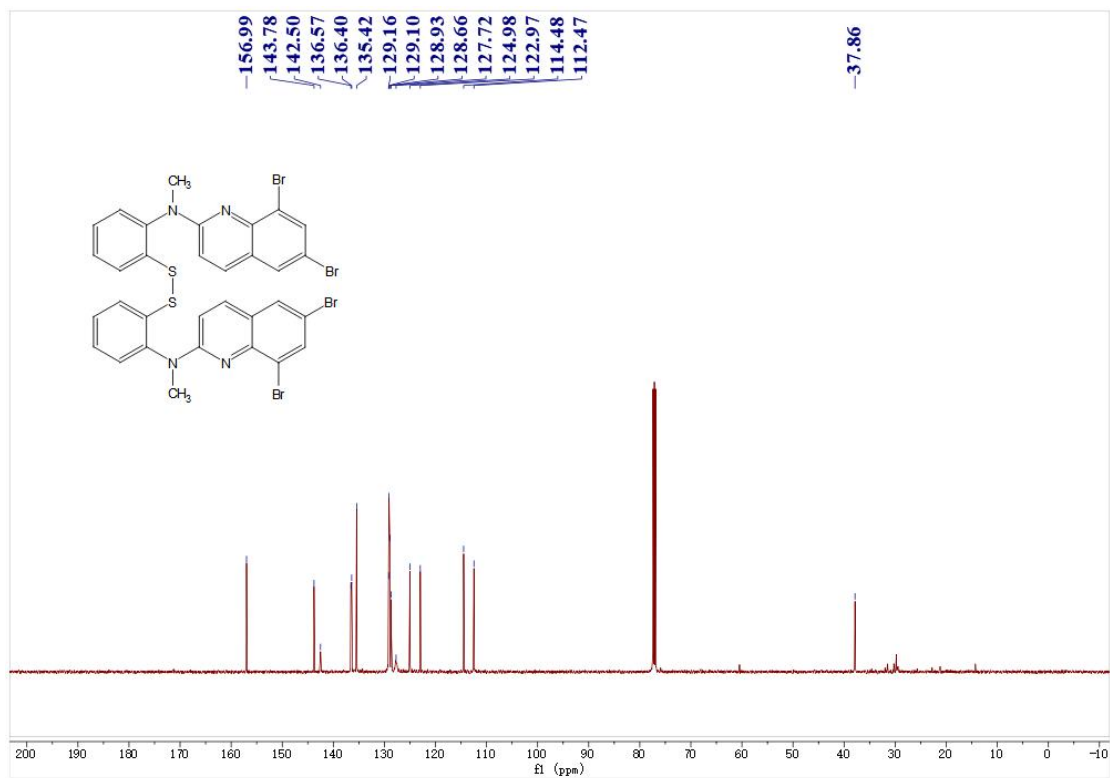
### <sup>13</sup>C NMR spectra of 3as (126 MHz, CDCl<sub>3</sub>)



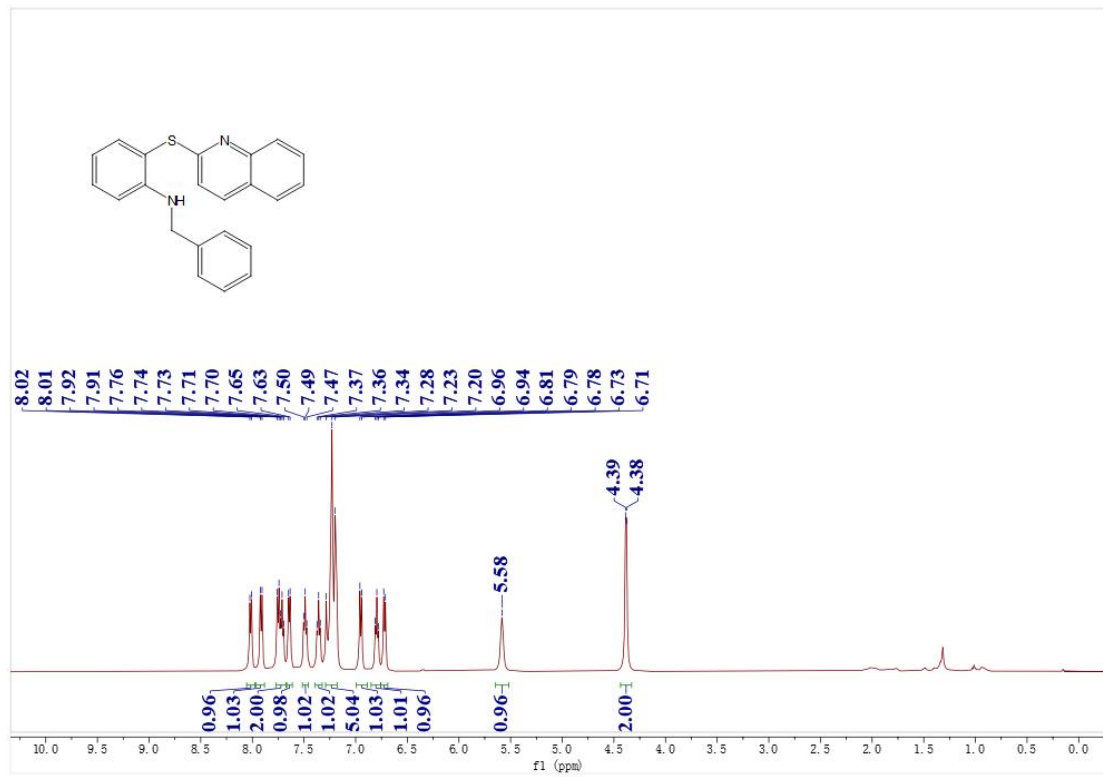
### <sup>1</sup>H NMR spectra of 3at (500 MHz, CDCl<sub>3</sub>)



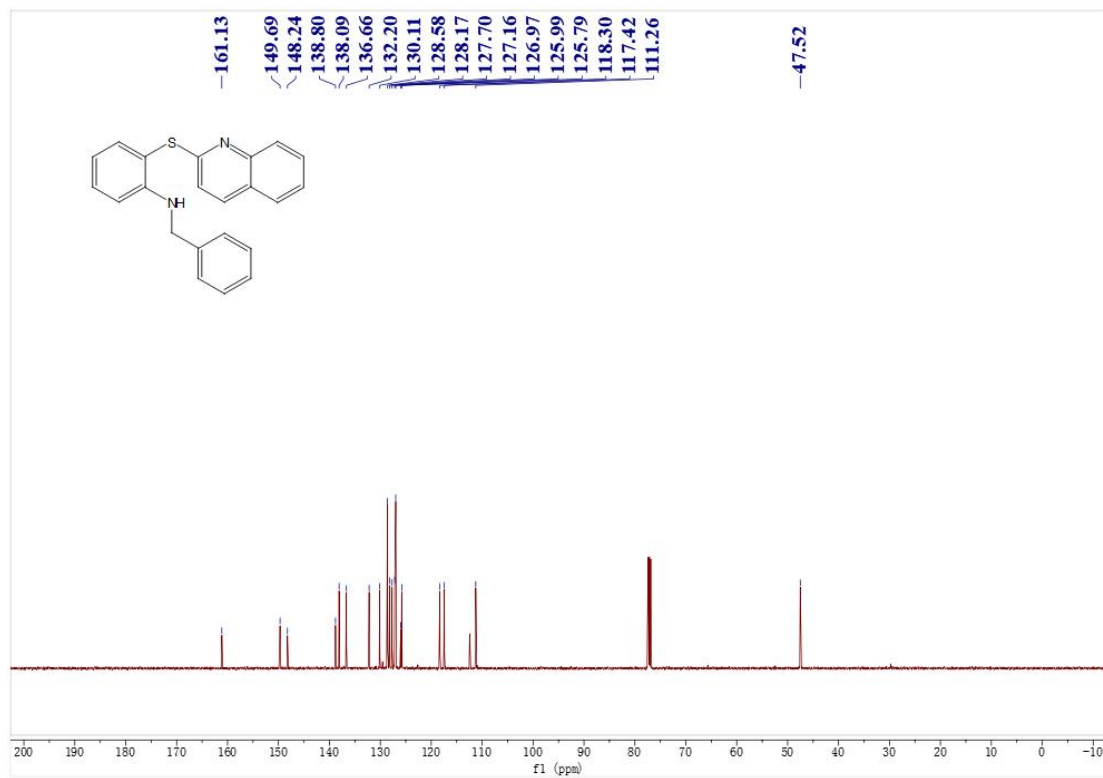
### <sup>13</sup>C NMR spectra of 3at (126 MHz, CDCl<sub>3</sub>)



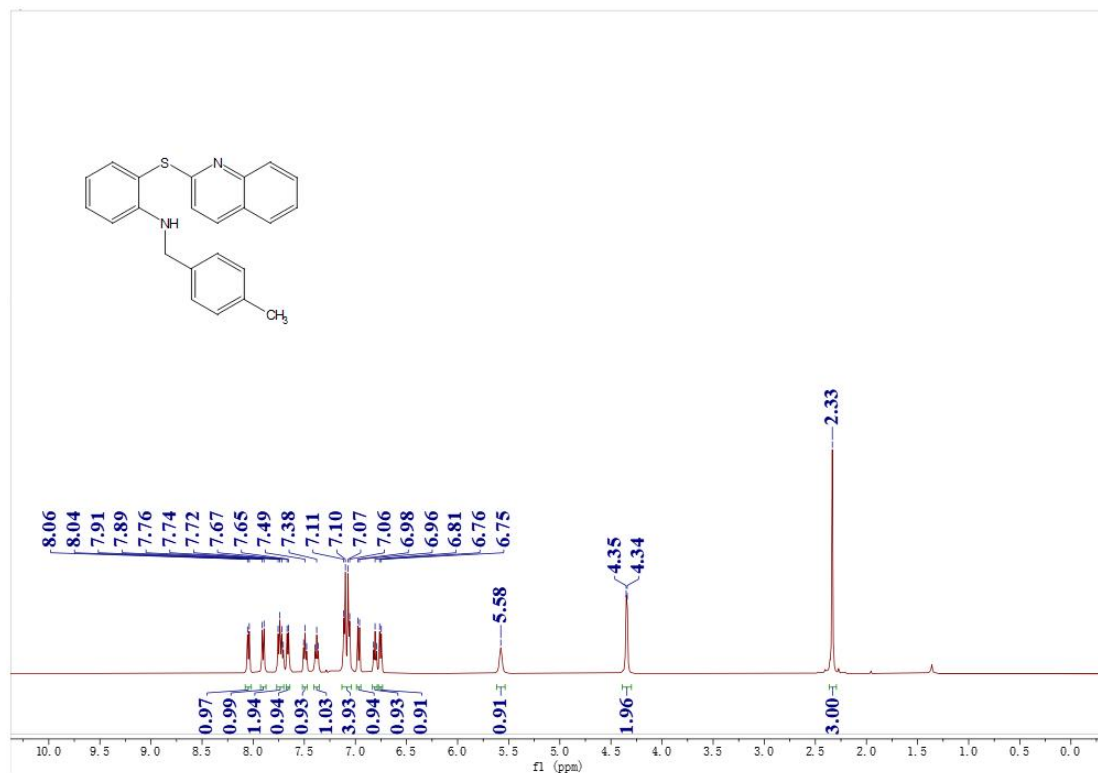
**<sup>1</sup>H NMR spectra of 4aa (500 MHz, CDCl<sub>3</sub>)**



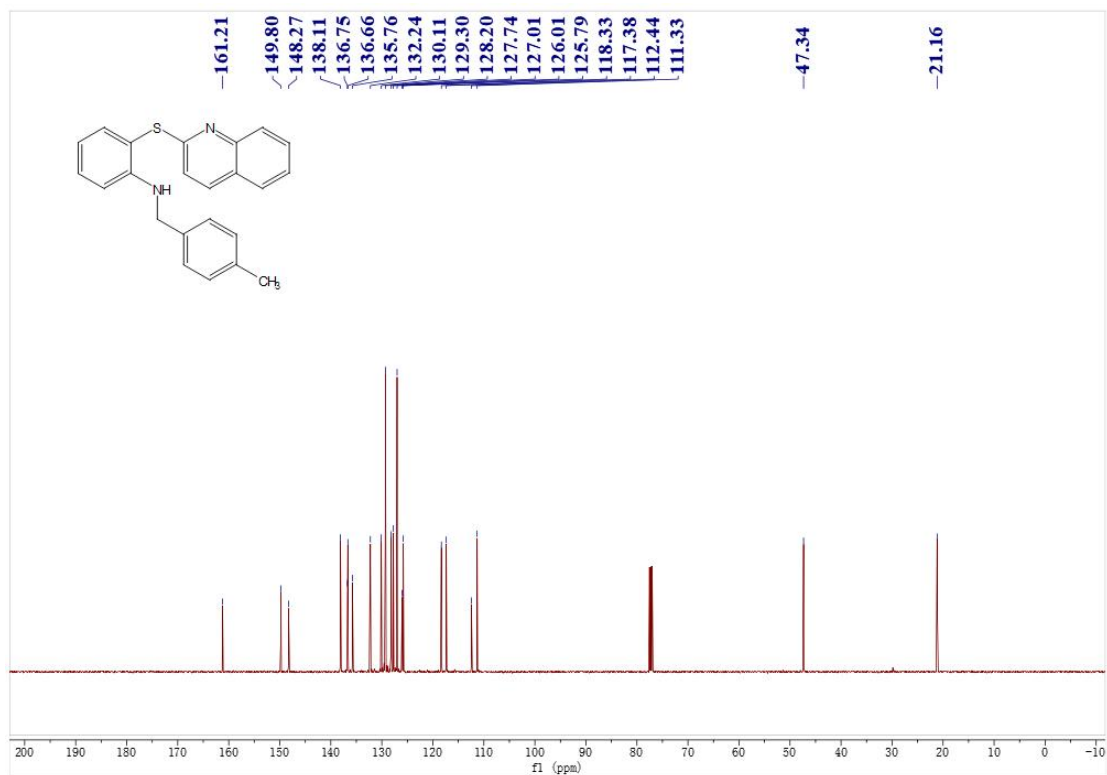
**<sup>13</sup>C NMR spectra of 4aa (126 MHz, CDCl<sub>3</sub>)**



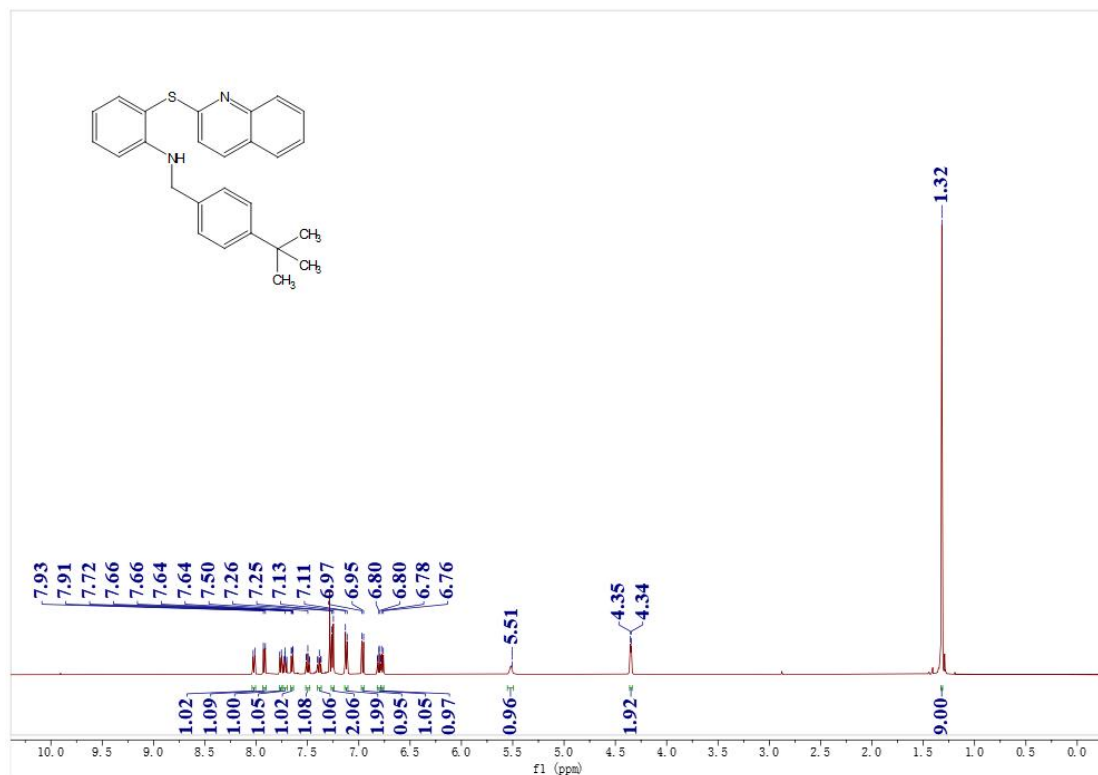
### <sup>1</sup>H NMR spectra of 4ab (500 MHz, CDCl<sub>3</sub>)



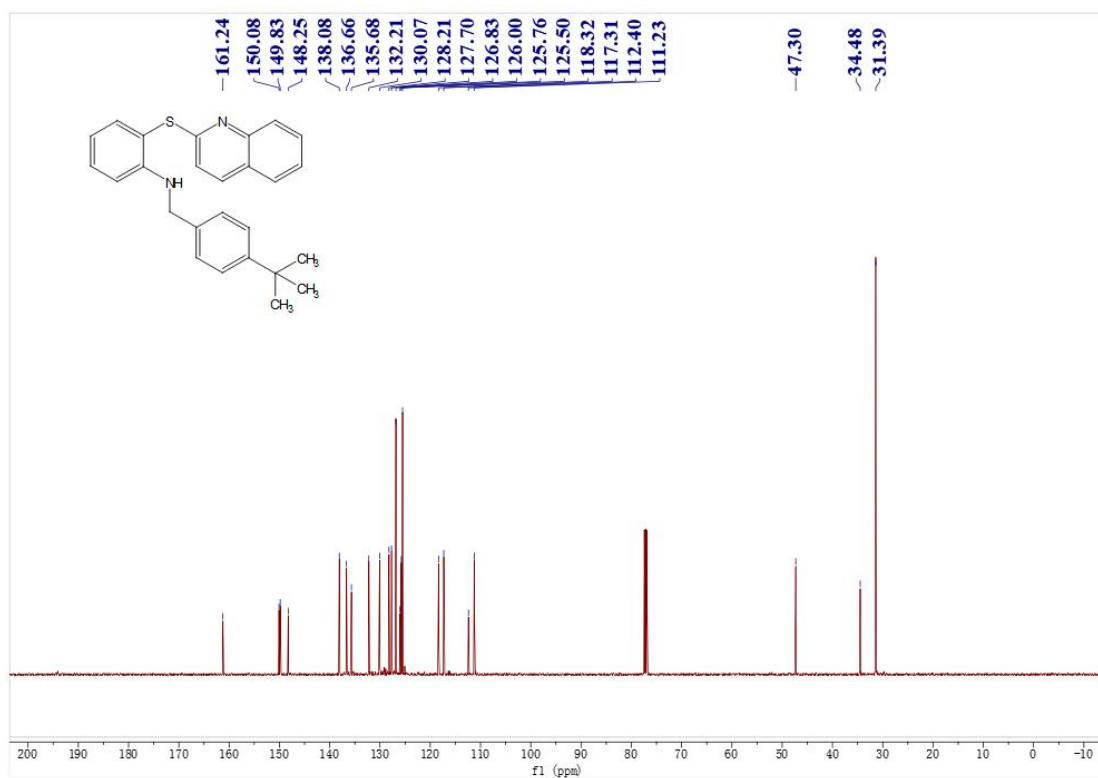
### <sup>13</sup>C NMR spectra of 4ab (126 MHz, CDCl<sub>3</sub>)



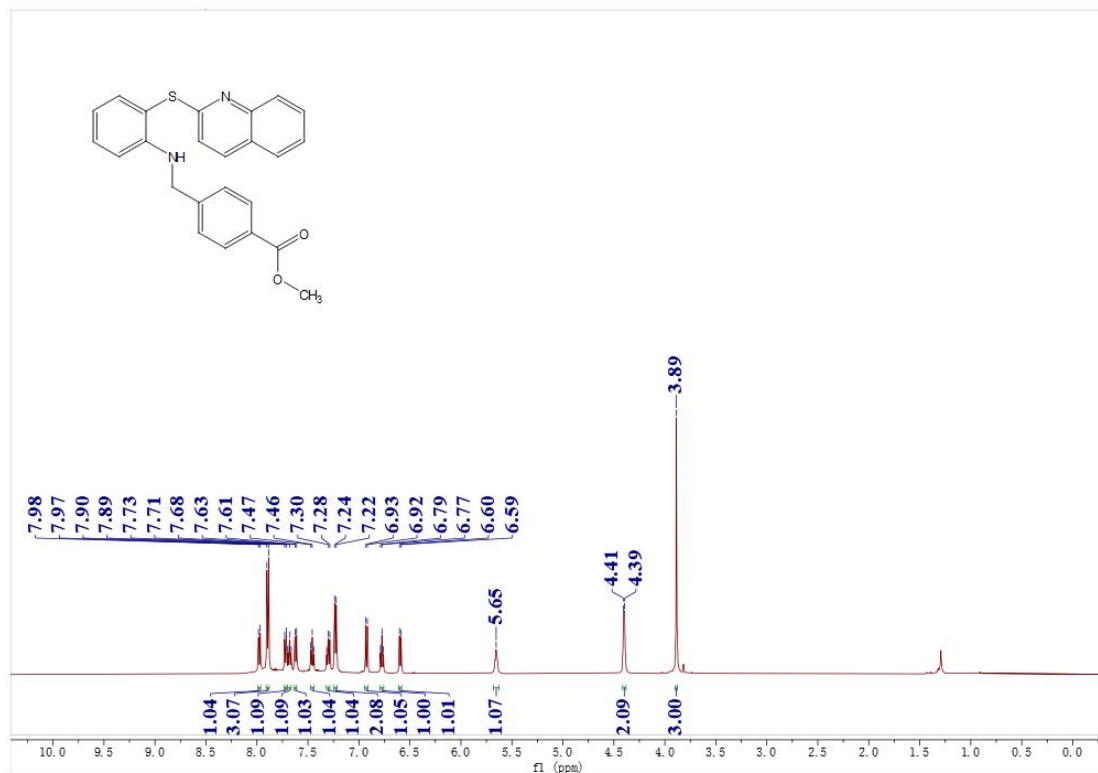
### <sup>1</sup>H NMR spectra of 4ac (500 MHz, CDCl<sub>3</sub>)



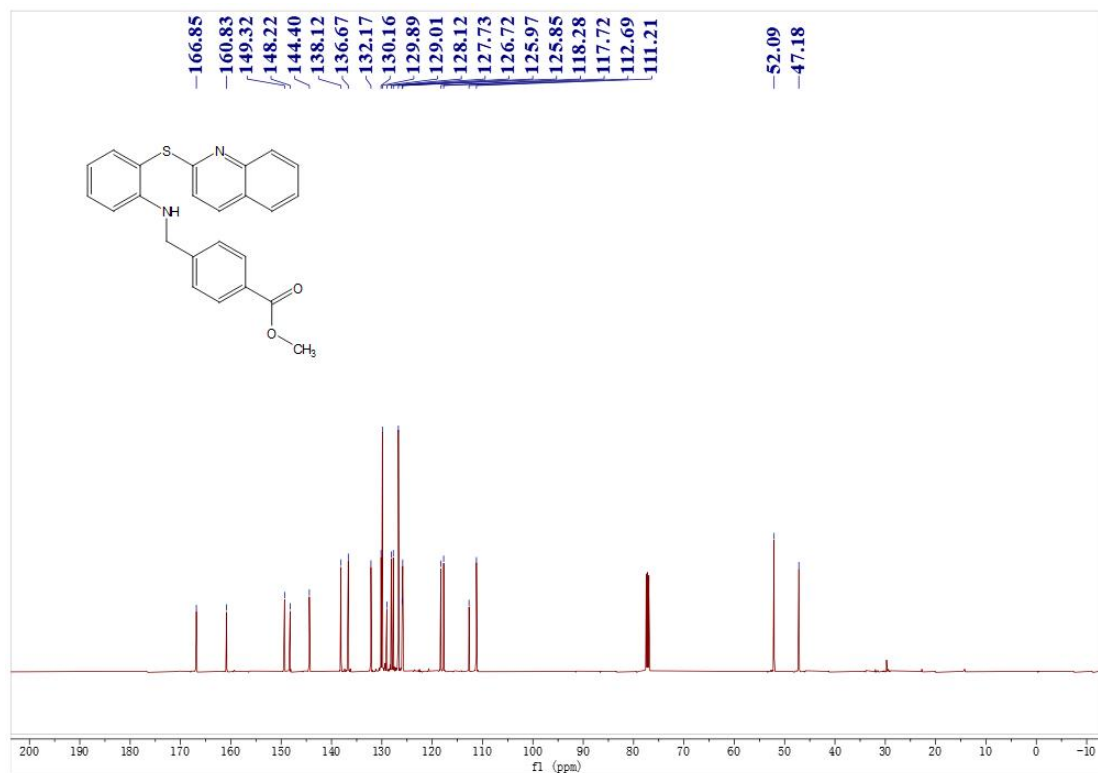
### <sup>13</sup>C NMR spectra of 4ac (126 MHz, CDCl<sub>3</sub>)



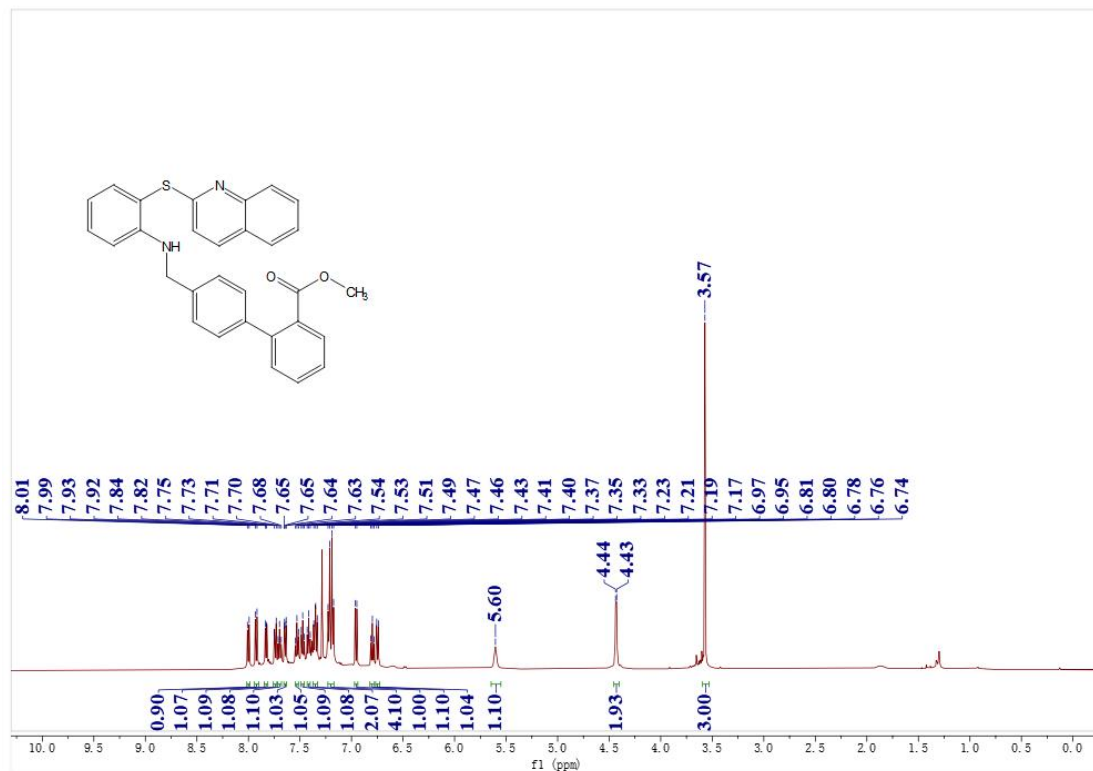
### <sup>1</sup>H NMR spectra of 4ad (500 MHz, CDCl<sub>3</sub>)



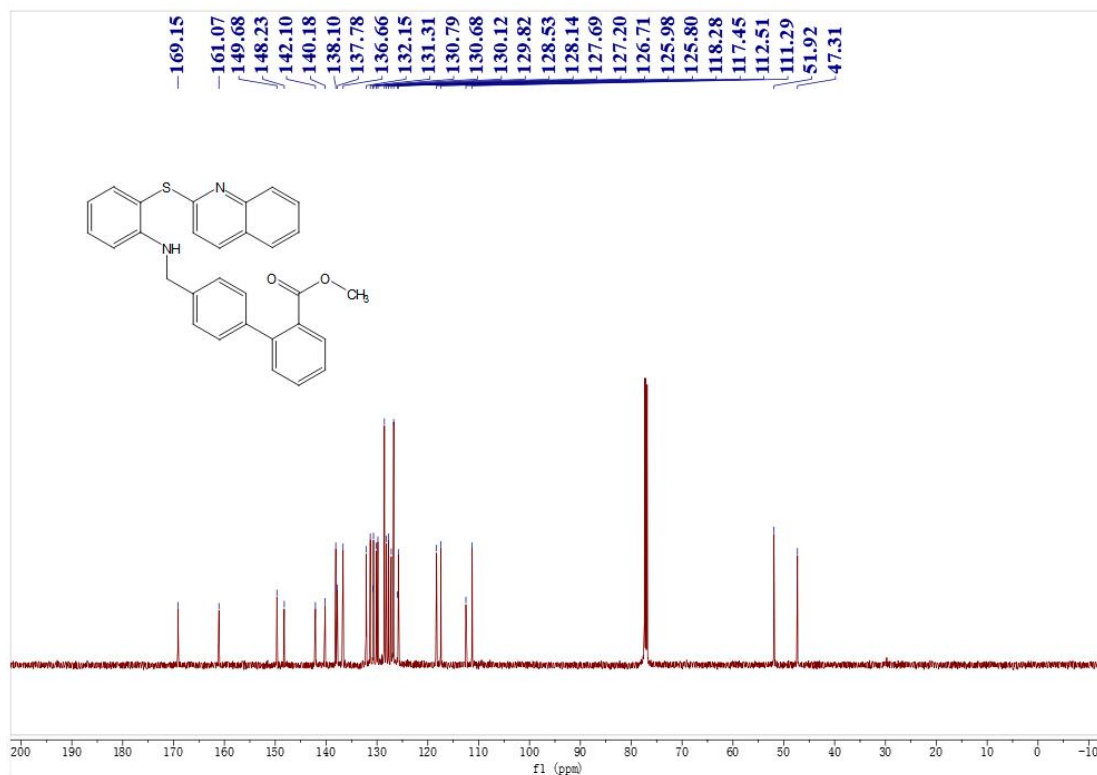
### <sup>13</sup>C NMR spectra of 4ad (126 MHz, CDCl<sub>3</sub>)



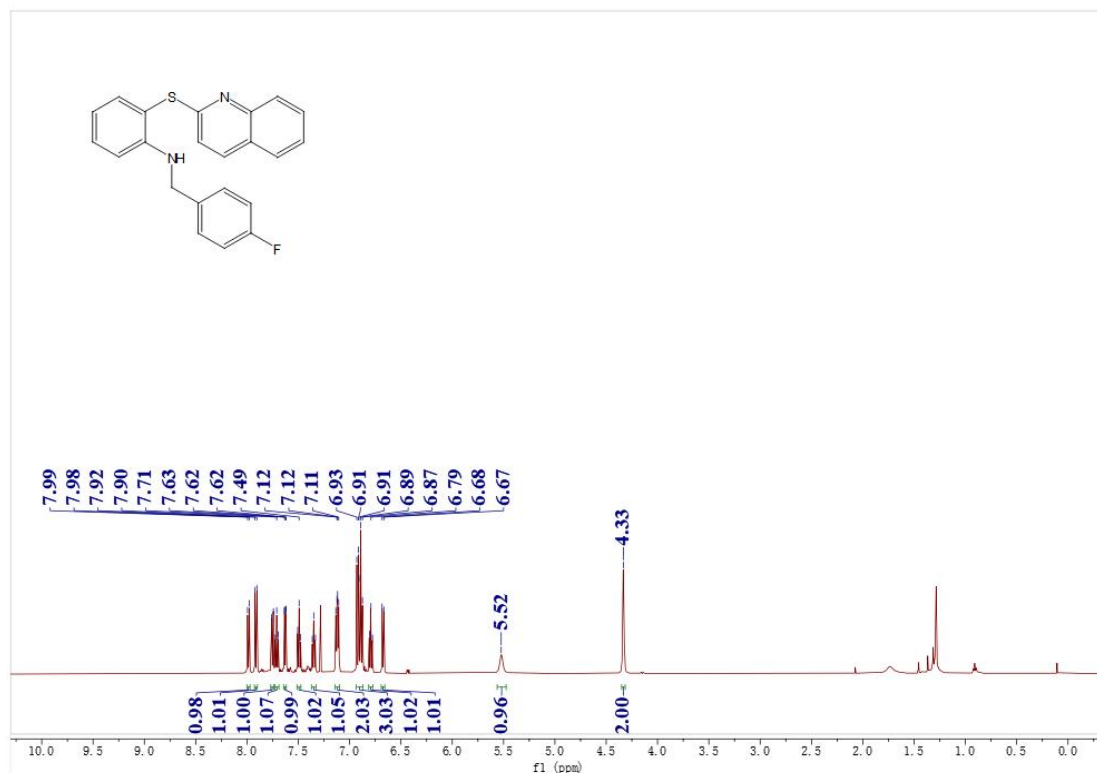
### <sup>1</sup>H NMR spectra of 4ae (500 MHz, CDCl<sub>3</sub>)



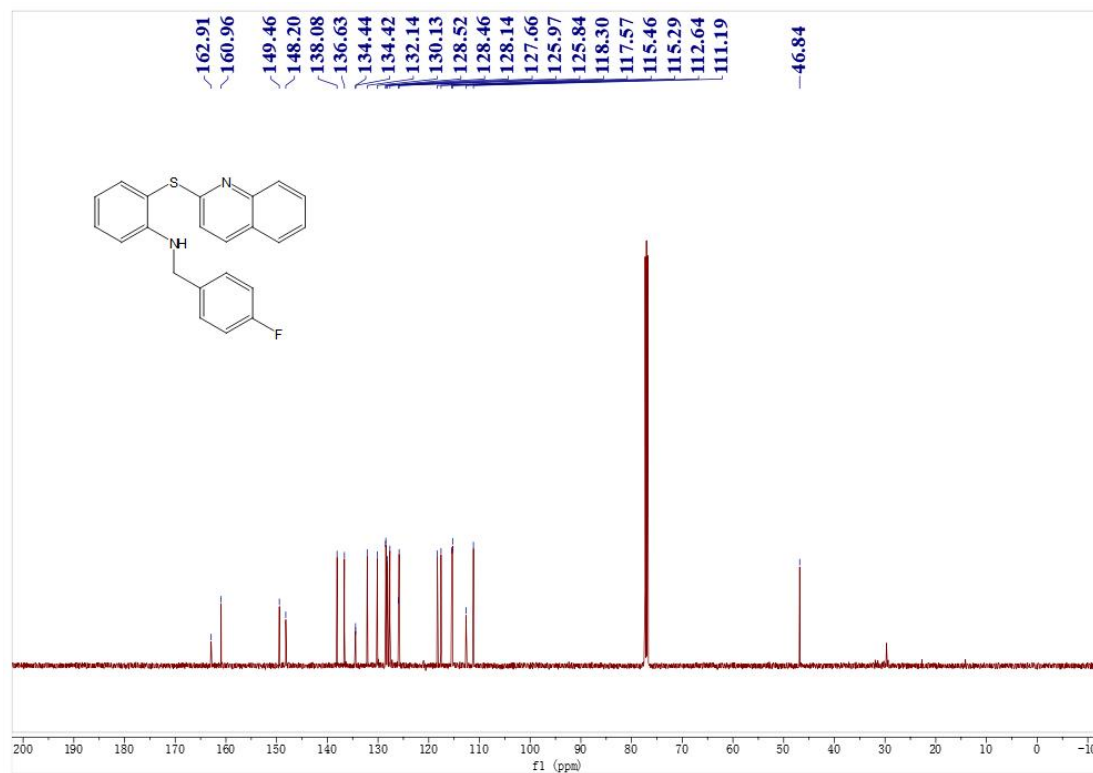
### <sup>13</sup>C NMR spectra of 4ae (126 MHz, CDCl<sub>3</sub>)



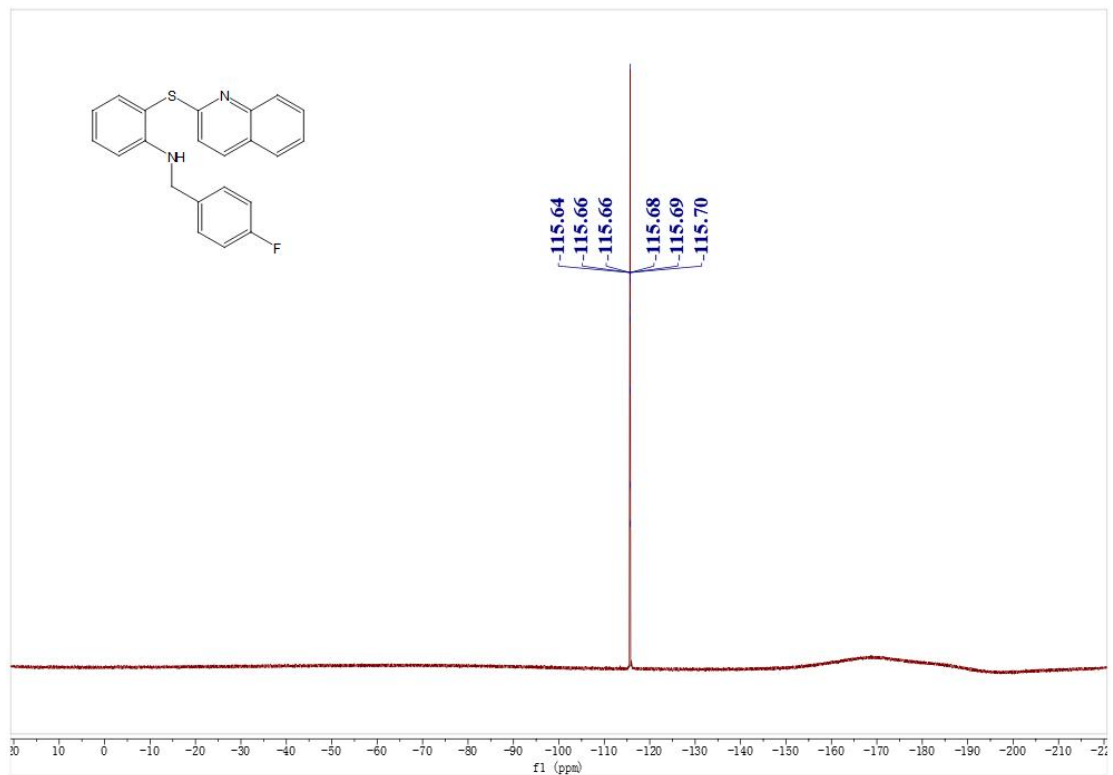
### <sup>1</sup>H NMR spectra of 4af (500 MHz, CDCl<sub>3</sub>)



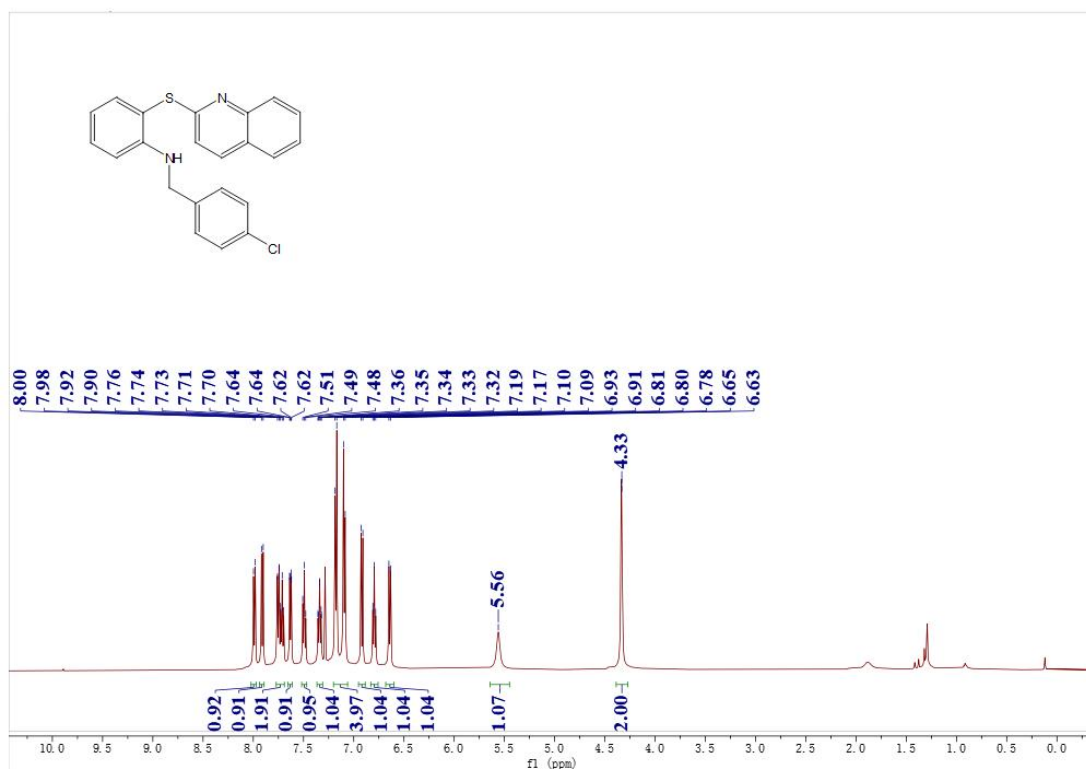
### <sup>13</sup>C NMR spectra of 4af (126 MHz, CDCl<sub>3</sub>)



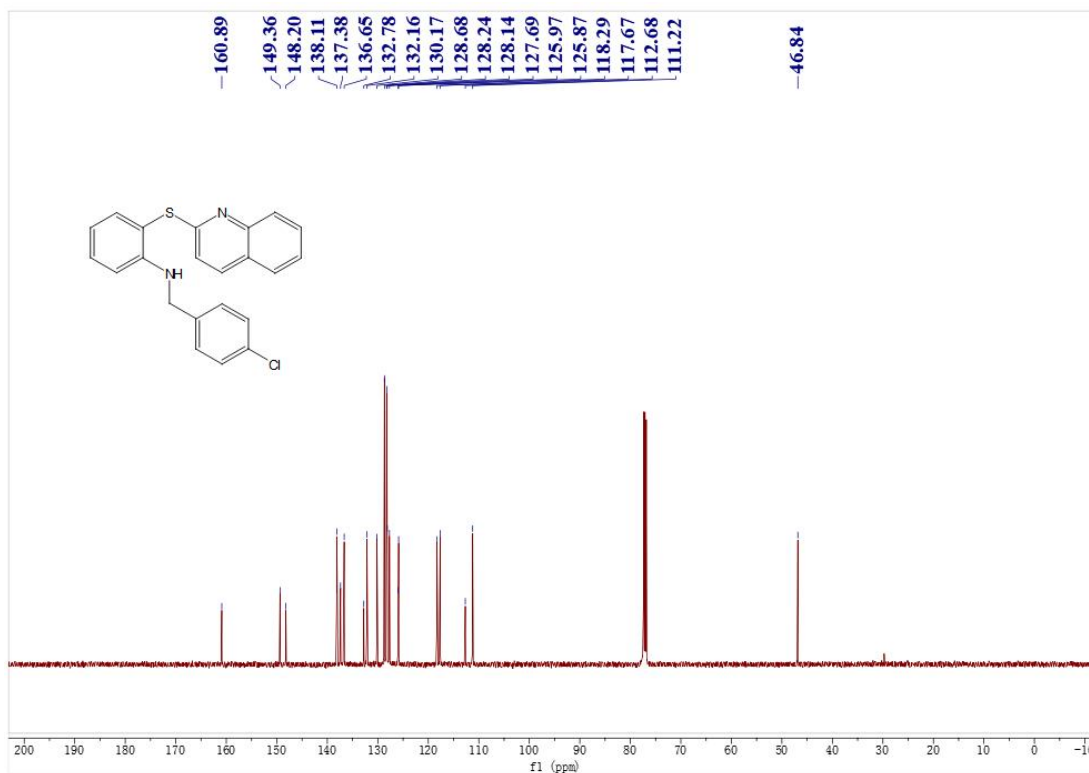
**<sup>19</sup>F NMR spectra of 4af (471 MHz, CDCl<sub>3</sub>)**



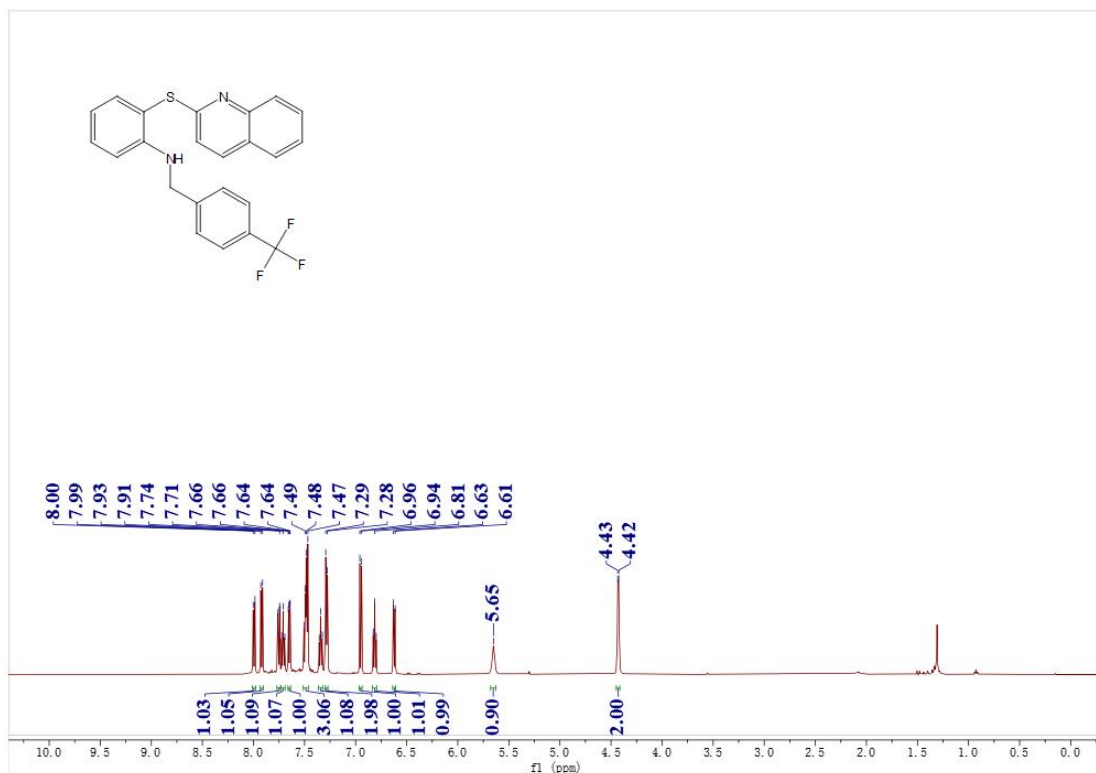
**<sup>1</sup>H NMR spectra of 4ag (500 MHz, CDCl<sub>3</sub>)**



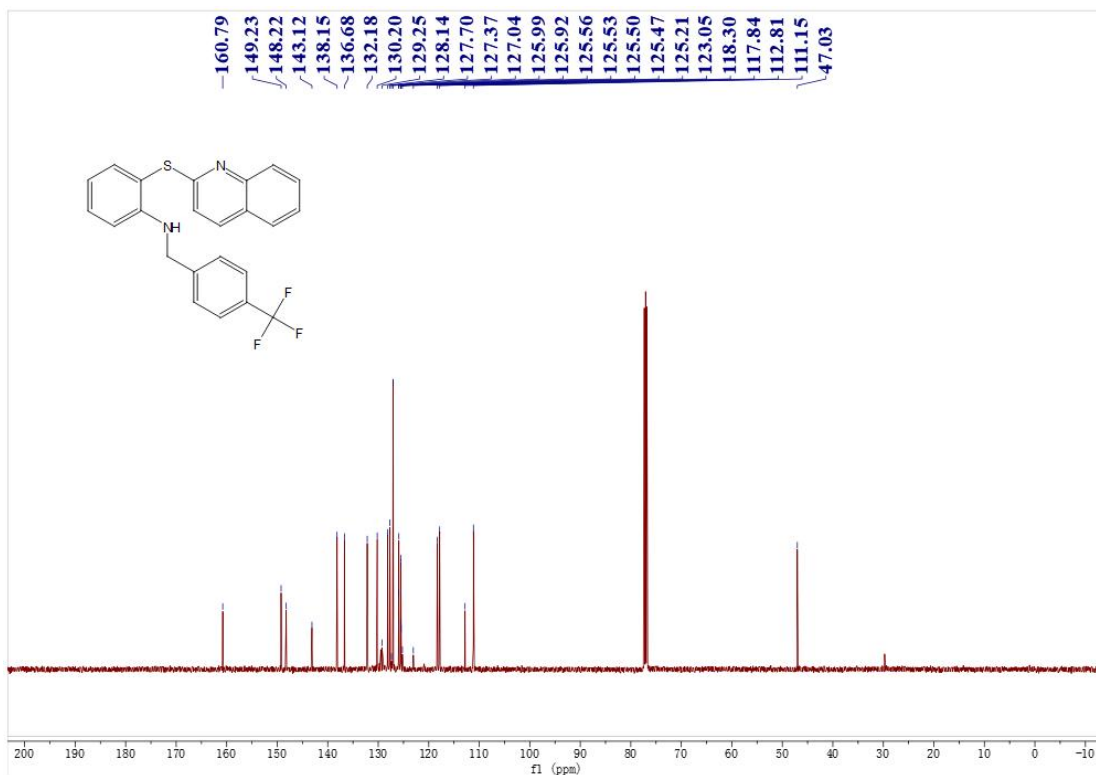
**<sup>13</sup>C NMR spectra of 4ag (126 MHz, CDCl<sub>3</sub>)**



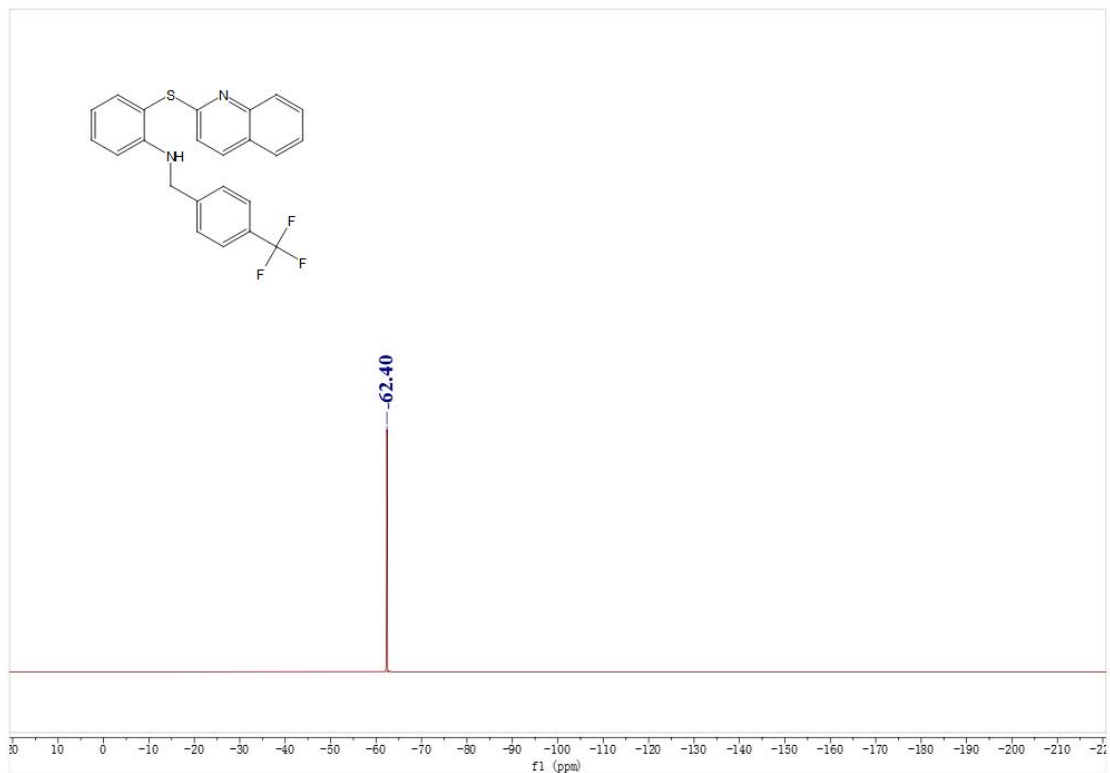
### <sup>1</sup>H NMR spectra of 4ah (500 MHz, CDCl<sub>3</sub>)



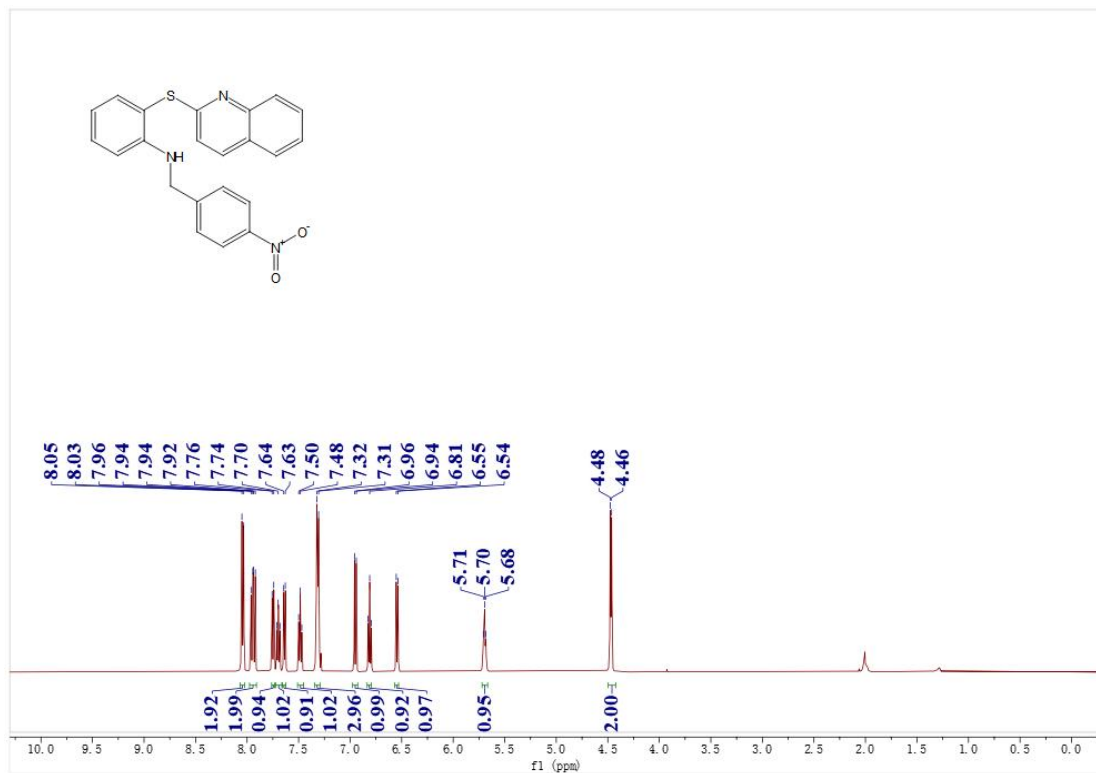
### <sup>13</sup>C NMR spectra of 4ah (126 MHz, CDCl<sub>3</sub>)



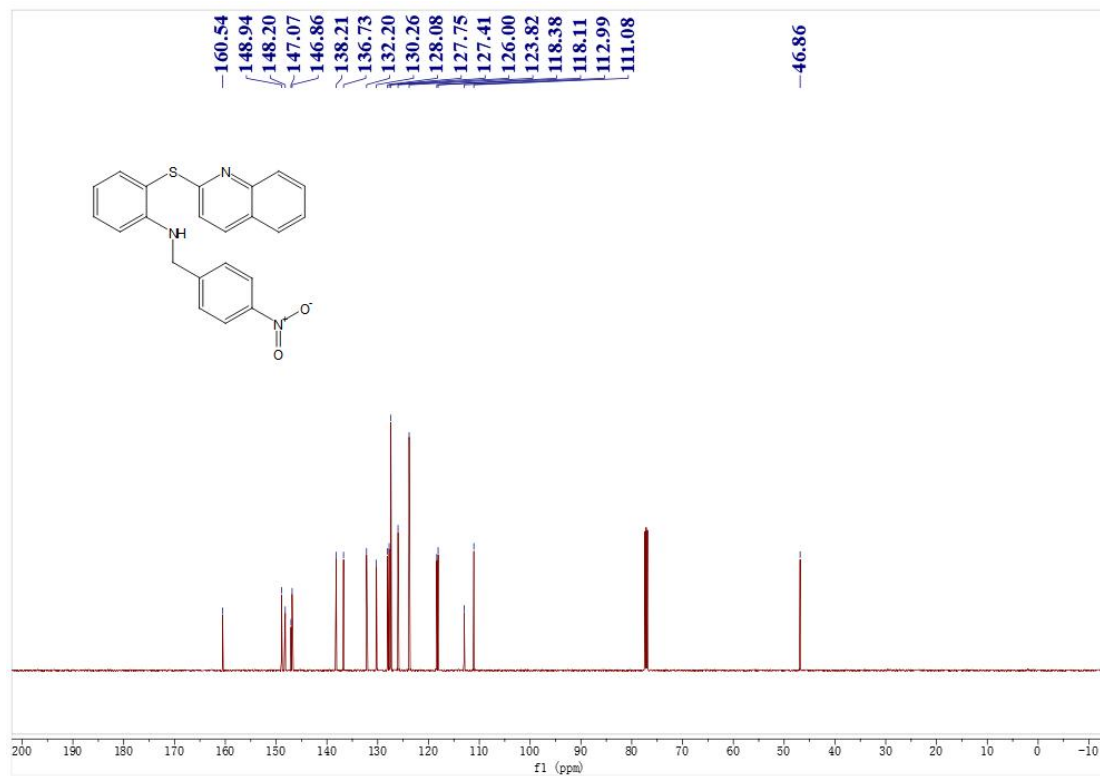
**<sup>19</sup>F NMR spectra of 4ah (471 MHz, CDCl<sub>3</sub>)**



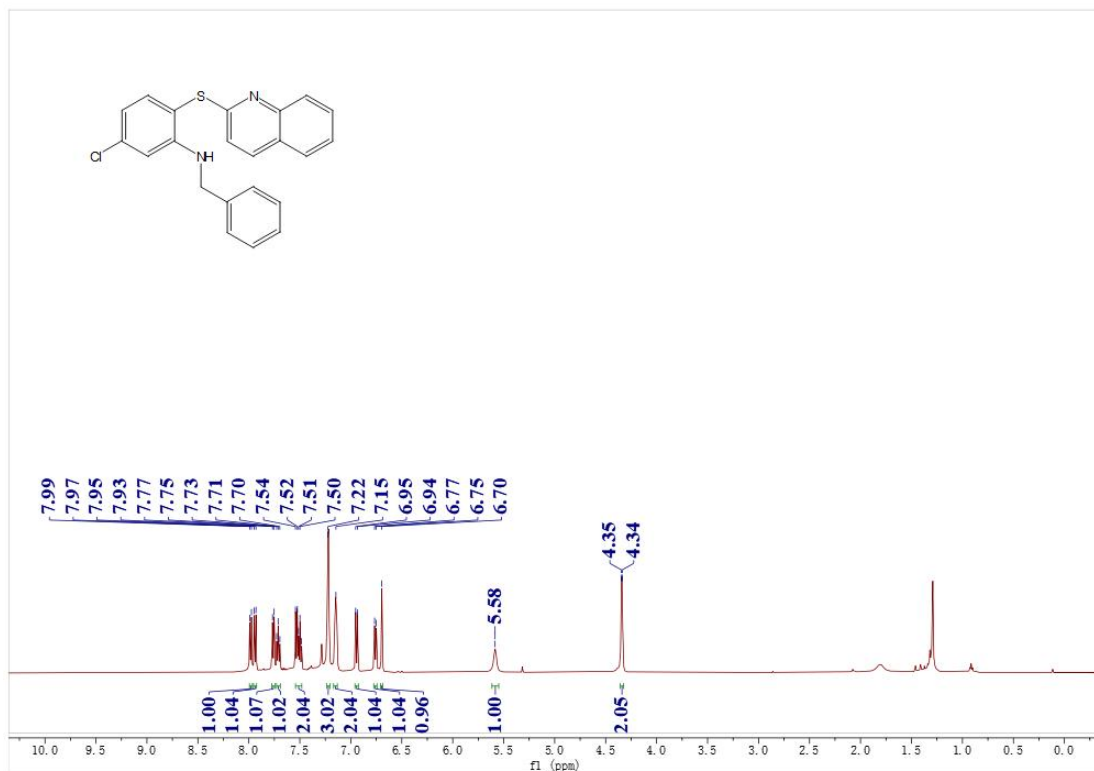
### <sup>1</sup>H NMR spectra of 4ai (500 MHz, CDCl<sub>3</sub>)



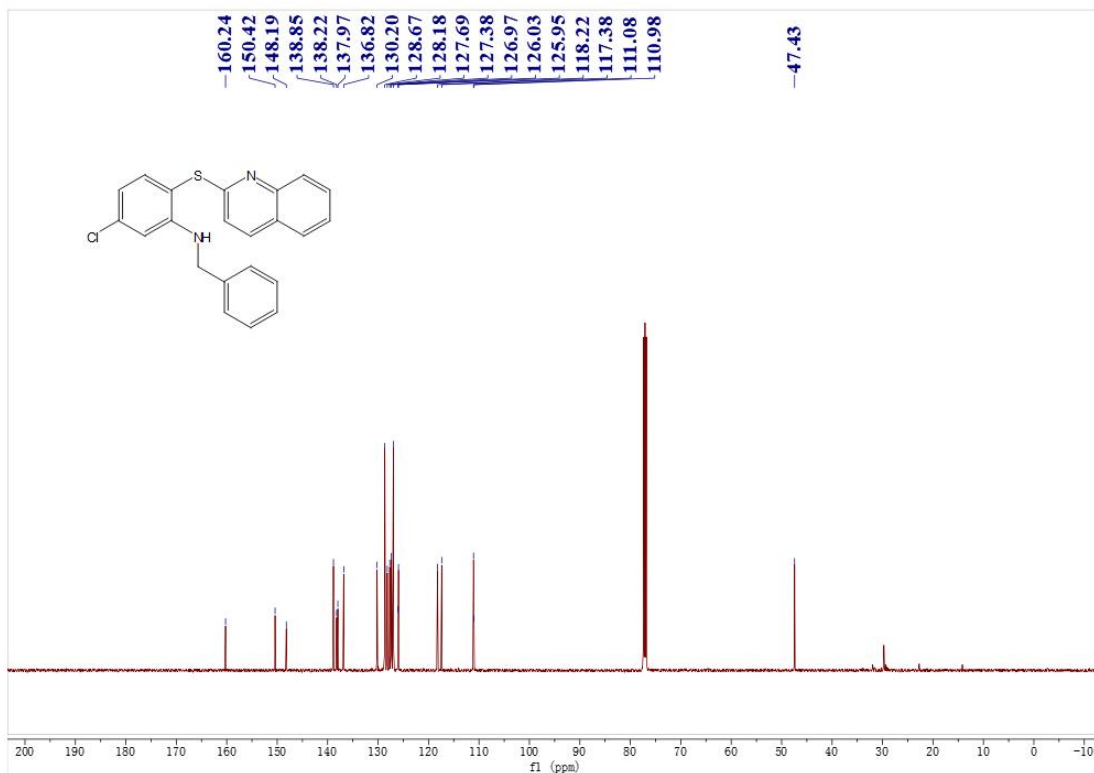
### <sup>13</sup>C NMR spectra of 4ai (126 MHz, CDCl<sub>3</sub>)



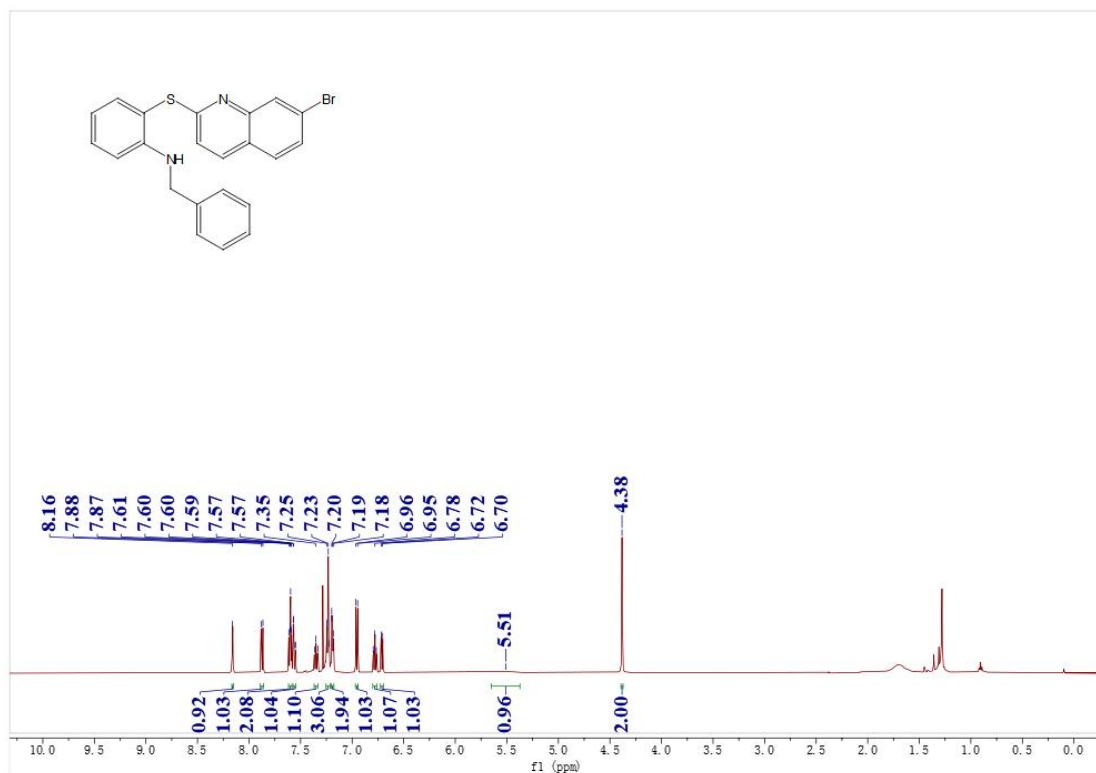
### <sup>1</sup>H NMR spectra of 4aj (500 MHz, CDCl<sub>3</sub>)



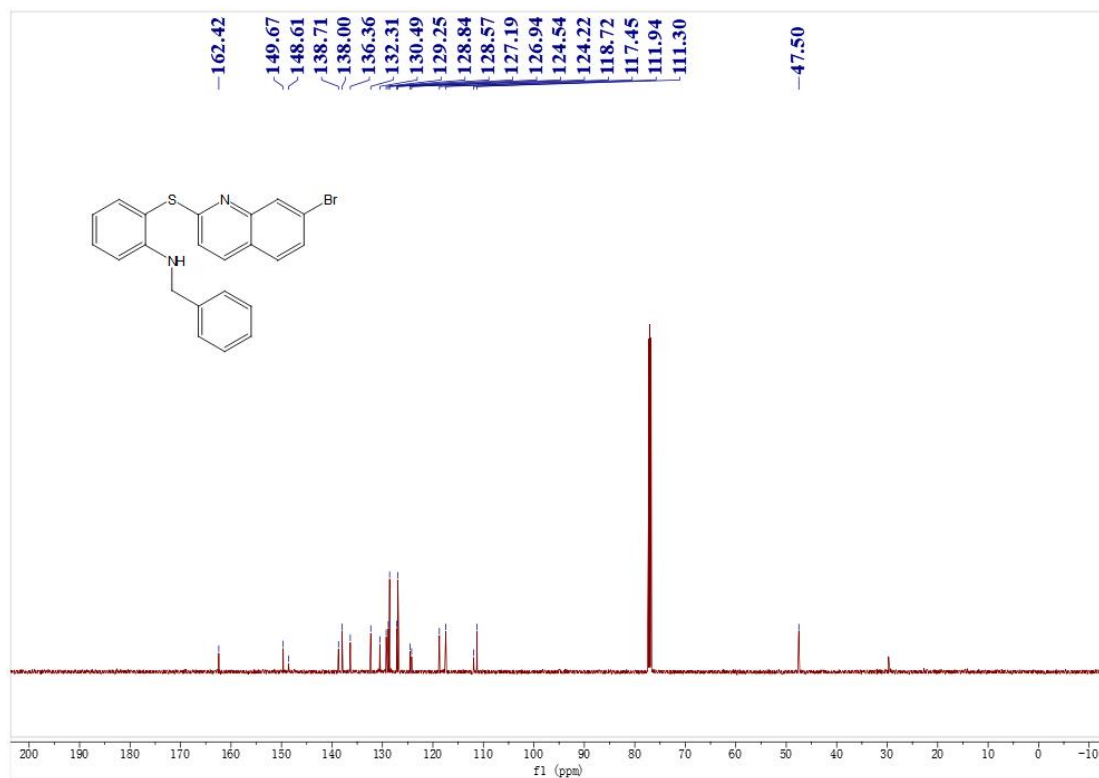
### <sup>13</sup>C NMR spectra of 4aj (126 MHz, CDCl<sub>3</sub>)



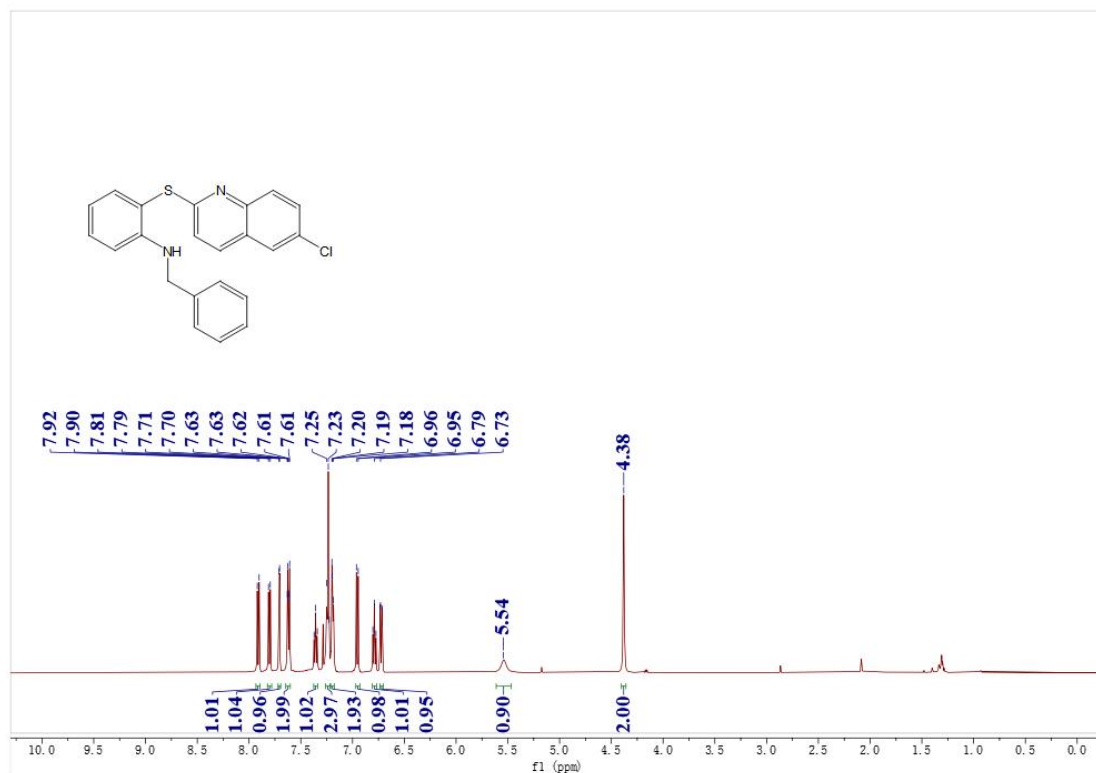
### <sup>1</sup>H NMR spectra of 4al (500 MHz, CDCl<sub>3</sub>)



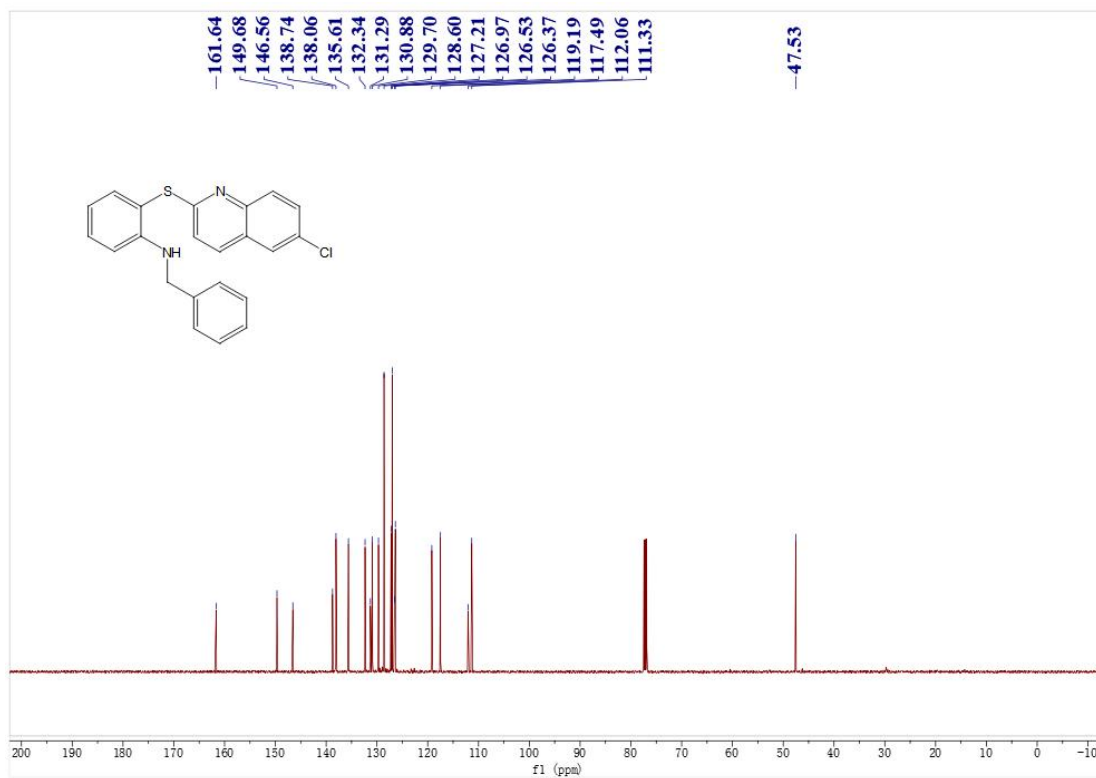
### <sup>13</sup>C NMR spectra of 4al (126 MHz, CDCl<sub>3</sub>)



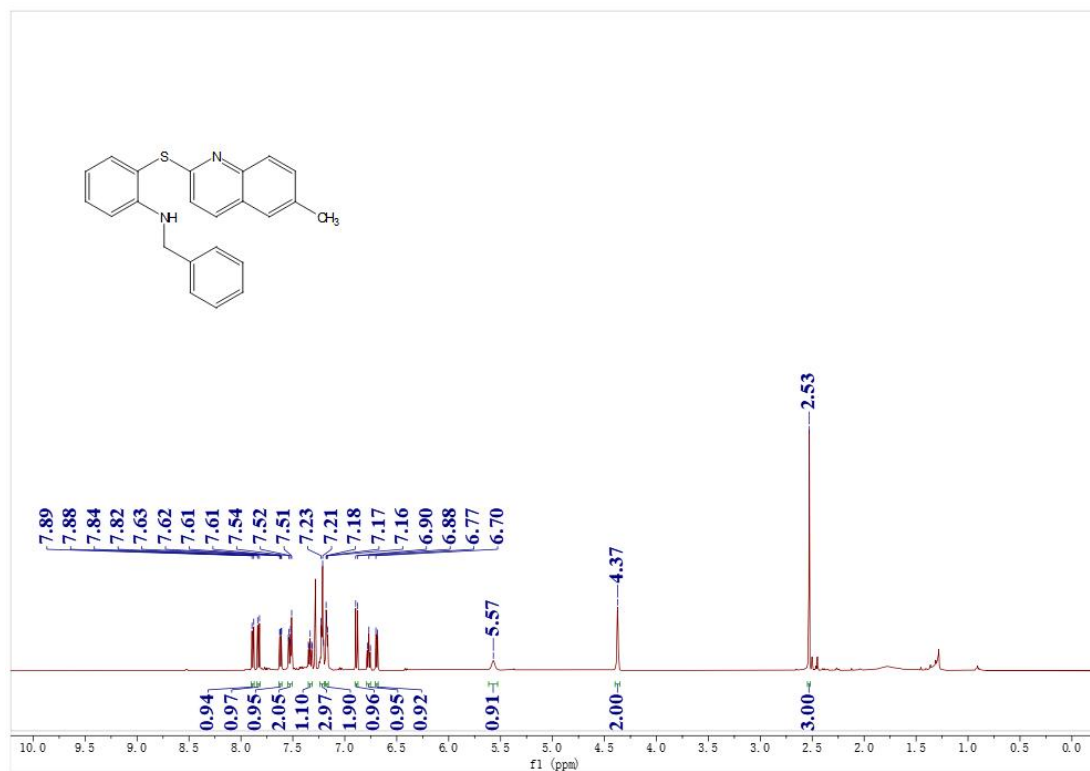
### <sup>1</sup>H NMR spectra of 4am (500 MHz, CDCl<sub>3</sub>)



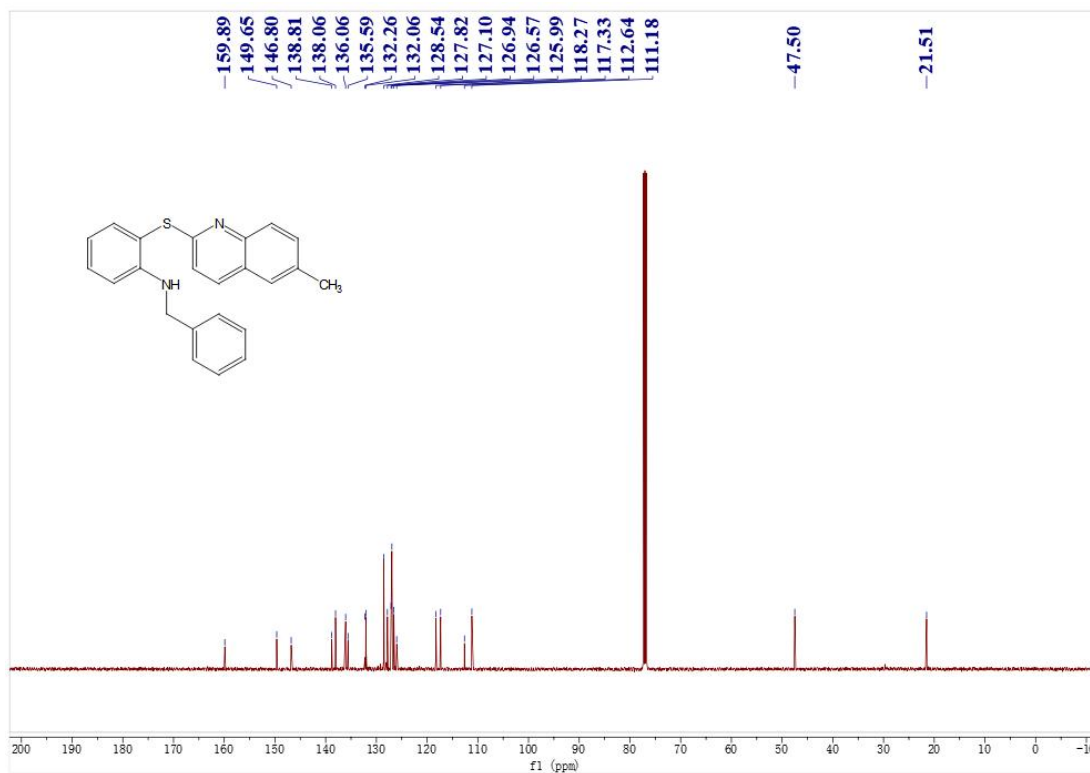
### <sup>13</sup>C NMR spectra of 4am (126 MHz, CDCl<sub>3</sub>)



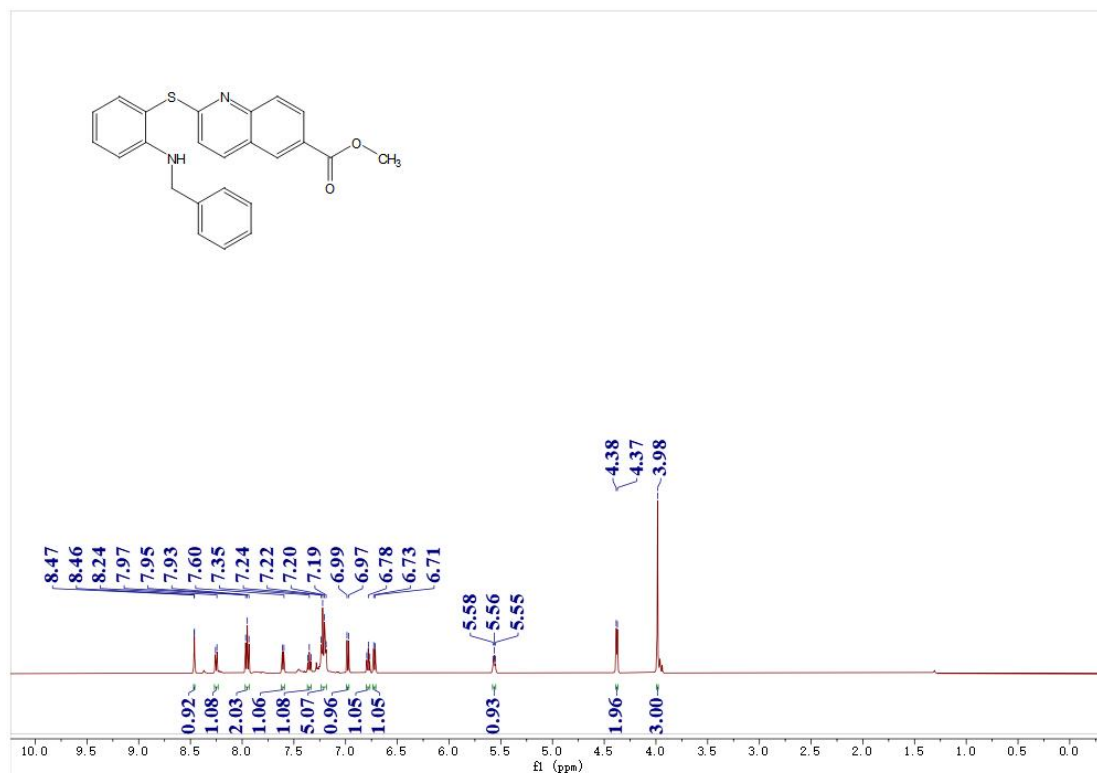
**<sup>1</sup>H NMR spectra of 4an (500 MHz, CDCl<sub>3</sub>)**



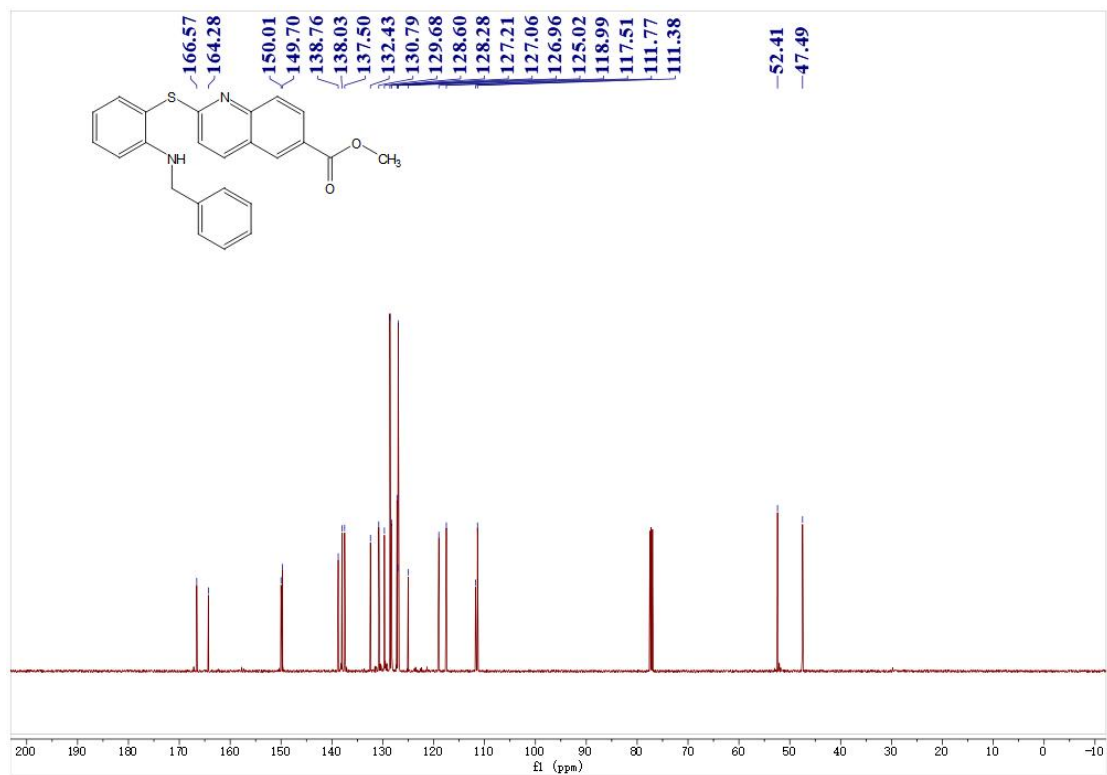
**<sup>13</sup>C NMR spectra of 4an (126 MHz, CDCl<sub>3</sub>)**



### <sup>1</sup>H NMR spectra of 4ao (500 MHz, CDCl<sub>3</sub>)

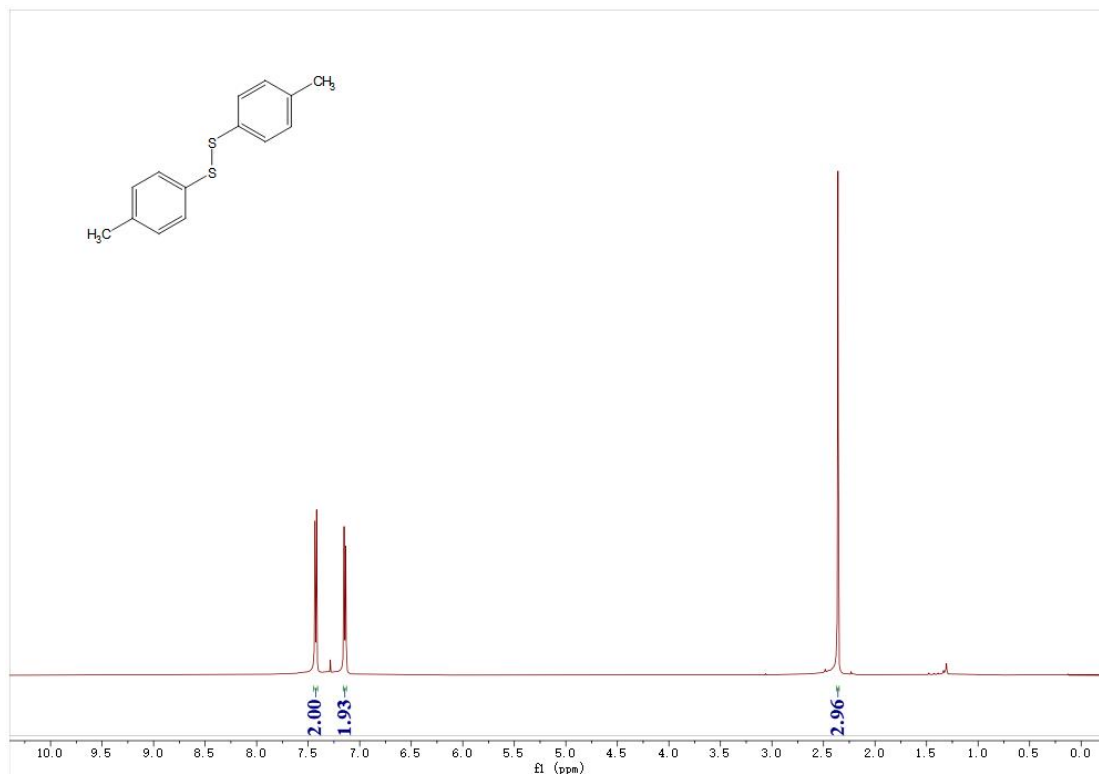


### <sup>13</sup>C NMR spectra of 4ao (126 MHz, CDCl<sub>3</sub>)



## 8. NMR spectra of 1,2-di-p-tolyldisulfane

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



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

