

# Sodium Iodide-mediated synthesis of vinyl sulfide and vinyl sulfones with Solvent-Controlled Chemical Selectivity

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### General Information

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AC-300 FT spectrometer at 400 MHz and 100 MHz, respectively, with tetramethylsilane as an internal reference. Chemical shifts ( $\delta$ ) and coupling constants ( $J$ ) were expressed in ppm and Hz, respectively. IR spectra were recorded on a Perkin-Elmer 2000 FTIR spectrometer. High resolution mass spectra (HRMS) were recorded on a LC-TOF spectrometer (Micromass). ESI-MS data were acquired using a Thermo LTQ Orbitrap XL Instrument equipped with an ESI source and controlled by Xcalibur software. Melting points were uncorrected.

Sulfinic acids were prepared according to literature procedures.<sup>1</sup> The rest of chemicals were purchased from the Sinopharm Chemical Reagent Co., Meryer, Acros, and Alfa Aesar, and used as received. Solvents were dried over MgSO<sub>4</sub> before use.

Abbreviations: Bn = benzyl, Ph = Phenyl, Tol = *p*-methylphenyl, Ts = *p*-toluenesulfonyl.

### General Procedure for The Synthesis of Vinyl Sulfides (Table 2)

To a solution of alcohol **1** (0.20 mmol) in DCE (1.0 mL) under an air atmosphere at room temperature were added sulfinic acid **2** (0.30 mmol), NaI (45.0 mg, 0.30 mmol) and TsOH·H<sub>2</sub>O (7.6 mg, 0.040 mmol). The mixture was stirred at 80 °C for 24 h, cooled to room temperature, and directly purified by preparative thin layer chromatography on silica gel, developing with petroleum ether/ethyl acetate (100:0 to 20:1), to give compound **3**.

### General Procedure for The Synthesis of Vinyl Sulfones (Table 3)

To a solution of alcohol **1** (0.20 mmol) in MeNO<sub>2</sub> (1.0 mL) under an air atmosphere at room temperature were added sulfinic acid **2** (0.30 mmol), NaI (45.0 mg, 0.30 mmol) and TsOH·H<sub>2</sub>O (7.6 mg, 0.040 mmol). The mixture was stirred at 80 °C for 24 h, cooled to room temperature, and directly purified by preparative thin layer chromatography on silica gel, developing with petroleum ether/ethyl acetate (20:1 to 5:1), to give compound **4**.

### Procedure for The Control Reaction

#### Scheme 1a

To a solution of 4-methylbenzenesulfinic acid **2a** (64.4 mg, 0.40 mmol) in DCE (2.0 mL) under an air atmosphere at room temperature were added NaI (67.2 mg, 0.48 mmol) and TsOH·H<sub>2</sub>O (15.2 mg, 0.080 mmol). The mixture was stirred at 80 °C for 24 h, cooled to room temperature, and directly purified by preparative thin layer chromatography on silica gel, developing with pure petroleum ether, to give compound **2a'** (92.1 mg) in 94% yield. Disulfane **2a'**,<sup>[2]</sup> white solid, m.p. 45-46 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.40–7.35 (m, 4H), 7.12–7.07 (m, 4H), 2.31 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  137.5, 133.9, 129.8, 128.6, 21.1.

#### Scheme 1b

To a solution of alcohol **1a** (39.6 mg, 0.20 mmol) in DCE (1.0 mL) under an air atmosphere at room temperature were added disulfane **2a'** (78.8 mg, 0.30 mmol) and I<sub>2</sub> (50.8 mg, 0.20 mmol). The mixture was stirred at 80 °C for 24 h, cooled to room

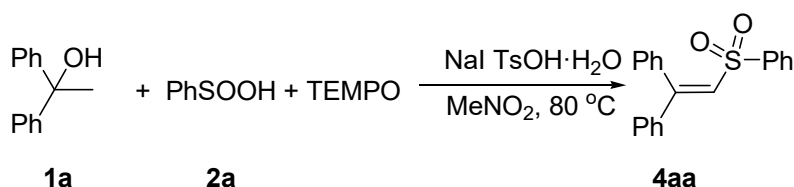
temperature, and directly purified by preparative thin layer chromatography on silica gel, developing with pure petroleum ether to give compound **3a** (54.8 mg) in 91% yield.

#### Scheme 1c

To a solution of alcohol **1a** (39.6 mg, 0.20 mmol) in DCE (1.0 mL) under an air atmosphere at room temperature were added disulfane **2a'** (78.8 mg, 0.30 mmol), NaI (45.0 mg, 0.30 mmol) and TsOH·H<sub>2</sub>O (7.6 mg, 0.040 mmol). The mixture was stirred at 80 °C for 24 h, cooled to room temperature, detected by TLC and no product **3a** was found.

#### Scheme 1d

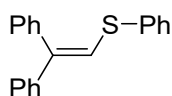
To a solution of alkene **6a** (36.0 mg, 0.20 mmol) in DCE (1.0 mL) under an air atmosphere at room temperature were added sulfinic acid **2a** (46.8 mg, 0.30 mmol), NaI (45.0 mg, 0.30 mmol) and TsOH·H<sub>2</sub>O (7.6 mg, 0.040 mmol). The mixture was stirred at 80 °C for 24 h, cooled to room temperature, and directly purified by preparative thin layer chromatography on silica gel, developing with pure petroleum ether, to give compound **3a** (56.0 mg) in 93% yield.



#### Scheme 3

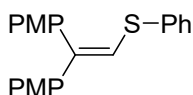
To a solution of alcohol **1a** (39.6 mg, 0.20 mmol) in DCE (1.0 mL) under an air atmosphere at room temperature were added sulfinic acid **2a** (46.8 mg, 0.30 mmol) NaI (45.0 mg, 0.30 mmol) and TsOH·H<sub>2</sub>O (7.6 mg, 0.040 mmol). The mixture was stirred at 80 °C for 24 h, cooled to room temperature, detected by TLC and no product **4a** was found.

#### Analytical Data for The Products Shown in Tables 2 and 3



**3aa**

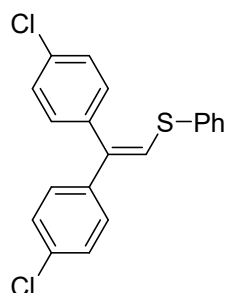
**3aa**,<sup>[3]</sup> white solid, m.p. 59-61 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.44-7.18 (m, 15H), 6.86 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 141.4, 141.1, 139.2, 136.5, 129.7, 129.5, 129.1, 128.4, 128.3, 127.8, 127.3, 127.2, 126.8, 124.1.



**3ba**

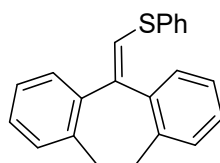
**3ba**,<sup>[3]</sup> white solid, m.p. 66-68 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.43-7.40 (m, 2H), 7.33-7.26 (m, 4H), 7.24-7.18 (m, 3H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.0 Hz, 2H), 6.87 (s, 1H), 3.83(s, 1H), 3.79 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 159.1, 141.2, 137.0, 134.6, 131.7, 131.0, 129.1, 129.0, 128.5, 126.5, 120.8, 113.6, 55.3,

55.2.



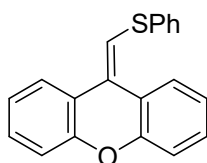
**3ca**

**3ca**,<sup>[3]</sup> white solid, m.p. 64-65 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.42-7.20 (m, 11H), 7.12 (d, *J* = 8.8 Hz, 2H), 6.83 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 139.5, 138.2, 137.1, 135.7, 133.8, 133.3, 131.1, 129.8, 129.2, 128.8, 128.5, 127.2, 125.7.



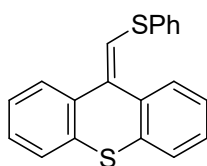
**3da**

**3da**,<sup>[3]</sup> white solid, m.p. 60-62 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.40-7.06 (m, 13H), 6.67 (s, 1H), 3.22-3.13 (m, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 142.7, 140.0, 139.1, 138.8, 137.5, 136.4, 130.1, 129.3, 130.0, 128.6, 128.4, 128.2, 127.5, 126.6, 126.2, 125.7, 125.3, 33.7, 32.2; IR (film): ν 3061, 3020, 1603, 1507, 1449 cm<sup>-1</sup>; HRMS (EI): Calcd for C<sub>22</sub>H<sub>18</sub>S (M) : 314.1129. Found: 314.1140.



**3ea**

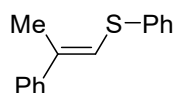
**3ea**,<sup>[3]</sup> white solid, m.p. 184-185 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.45-7.40 (m, 3H), 7.36-7.11 (m, 8H), 6.97 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 137.8, 137.6, 133.7, 133.4, 131.8, 129.8, 129.5, 129.0, 128.9, 127.6, 127.1, 127.0, 126.9, 126.7, 126.0, 125.9, 125.3; IR (film): ν 3060, 3022, 1600, 1509, 1445 cm<sup>-1</sup>; HRMS (EI): Calcd for C<sub>20</sub>H<sub>14</sub>OS (M) : 302.0765. Found: 302.0749.



**3fa**

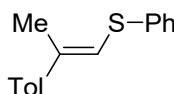
**3fa**,<sup>[3]</sup> white solid, m.p. 57-59 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.65 (d, *J* = 8.8 Hz,

2H), 7.46-7.22 (m, 11H), 6.71 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 137.2, 136.0, 134.3, 132.9, 131.2, 130.0, 129.2, 128.7, 127.7, 127.3, 127.1, 126.9, 126.1, 125.8, 125.6; IR (film):  $\nu$  3055, 3020, 1558, 1501, 1440  $\text{cm}^{-1}$ ; HRMS (EI): Calcd for  $\text{C}_{20}\text{H}_{14}\text{S}_2$  (M): 318.0537. Found: 318.0551.



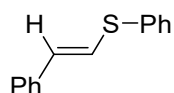
**3ga**

**3ga**,  $^{[3]}$  white solid, m.p. 42-44  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36-7.33 (m, 4H), 7.28-7.22 (m, 4H), 7.20-7.13 (m, 2H), 6.50 (s, 1H), 2.18 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 141.4, 137.1, 136.1, 128.7, 128.0, 126.8, 126.1, 125.2, 125.0, 121.0, 17.4.



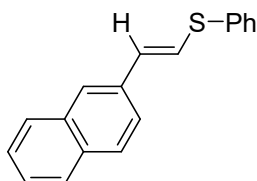
**3ha**

**3ha**,  $^{[3]}$  white solid, m.p. 46-48  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40-7.20 (m, 7H), 7.13 (d,  $J = 8.0$  Hz, 2H), 6.53 (s, 1H), 2.34 (s, 3H), 2.23 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 138.9, 137.6, 137.0, 136.6, 129.1, 129.0, 128.9, 126.3, 125.3, 120.1, 21.1, 17.8.



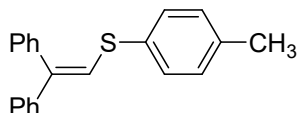
**3ja**

**3ka**,  $^{[3]}$  white solid, m.p. 40-41  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40-7.13 (m, 10H), 6.81 (d,  $J = 15.5$  Hz, 1H), 6.66 (d,  $J = 15.5$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 134.0, 132.7, 129.2, 127.3, 126.6, 126.1, 125.0, 124.4, 123.5, 120.8.



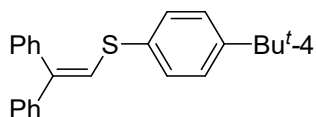
**3la**

**3la**,  $^{[3]}$  white solid, m.p. 65-67  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (s, 1H), 7.79-7.750 (m, 3H), 7.51-7.30 (m, 7H), 7.22-7.17 (m, 1H), 6.90 (d,  $J = 15$  Hz, 1H), 6.72 (d,  $J = 15.6$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 136.7, 133.9, 133.8, 132.5, 129.0, 128.7, 128.5, 127.9, 127.6, 127.4, 127.0, 126.4, 126.3, 126.0, 123.4.



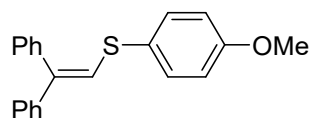
**3ab**

**3ab**,  $^{[3]}$  white solid, m.p. 64-65  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44-7.32 (m, 7H), 7.27-7.22 (m, 5H), 7.13 (d,  $J = 7.6$  Hz, 2H), 6.82 (s, 1H), 2.33 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 141.5, 140.1, 139.2, 137.0, 132.8, 130.1, 129.9, 129.8, 128.4, 128.3, 127.7, 127.1, 125.2, 21.1.



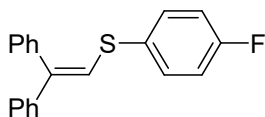
**3ac**

**3ac**,<sup>[4]</sup> white solid, m.p. 67-69 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.43-7.26 (m, 9H), 7.25-7.21 (m, 5H), 6.85 (s, 1H), 1.31 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 150.2, 141.5, 140.2, 139.2, 132.9, 129.8, 129.7, 128.4, 128.3, 128.0, 127.7, 127.1, 126.2, 125.1, 34.5, 31.3.



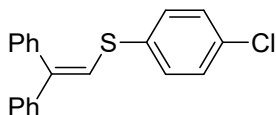
**3ad**

**3ad**,<sup>[4]</sup> white solid, m.p. 71-73 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.44-7.35 (m, 7H), 7.25-7.21 (m, 5H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.76 (s, 1H), 3.78 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 159.3, 141.6, 139.3, 132.6, 129.8, 128.5, 128.3, 127.8, 127.2, 127.1, 126.9, 126.6, 114.9, 55.4.



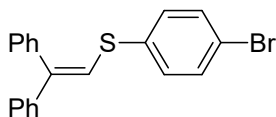
**3ae**

**3ae**,<sup>[4]</sup> white solid, m.p. 68-70 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.44-7.22 (m, 12H), 7.05-7.00 (m, 2H), 6.75 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 162.1 (d, *J* = 246 Hz), 141.4, 140.8, 139.0, 129.7, 128.4, 128.3, 127.2, 116.3 (d, *J* = 22 Hz).



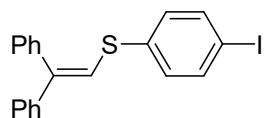
**3af**

**3af**,<sup>[3]</sup> white solid, m.p. 72-73 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.44-7.21 (m, 14H), 6.77 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 141.9, 141.2, 139.0, 135.0, 132.8, 130.7, 129.7, 129.2, 128.4, 128.3, 127.9, 127.5, 127.2, 123.2.



**3ag**

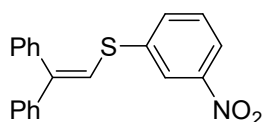
**3ag**,<sup>[3]</sup> white solid, m.p. 86-88 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45-7.23 (m, 14H), 6.77 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 142.1, 141.2, 139.0, 135.7, 132.1, 130.9, 129.7, 128.4, 128.0, 127.7, 127.5, 127.2, 122.9, 120.7.



**3ah**

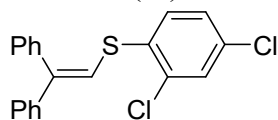
**3ah**,<sup>[3]</sup> white solid, m.p. 99-101 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.60 (d, *J* = 8.8 Hz, 2H), 7.43-7.21(m, 10H), 7.14 (d, *J* = 8.8 Hz, 2H), 6.67 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 142.3, 141.2, 138.9, 138.0, 136.6, 130.9, 129.7, 128.4, 128.3, 127.9, 127.5,

127.2, 122.6, 91.6.



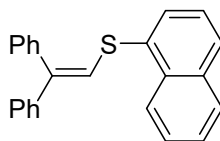
**3ai**

**3ai**, white solid, m.p. 107-109 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.25 (s, 1H), 8.05 (d,  $J = 8.8$  Hz, 1H), 7.69 (d,  $J = 8.0$  Hz, 1H), 7.50-7.24 (m, 11H), 6.81 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 148.6, 144.8, 140.9, 139.6, 138.7, 134.2, 129.8, 129.6, 128.5, 128.2, 128.0, 127.4, 123.0, 121.2, 120.2; IR (film):  $\nu$  3056, 3030, 1599, 1511, 1446  $\text{cm}^{-1}$ ; HRMS (EI): Calcd for  $\text{C}_{20}\text{H}_{15}\text{NO}_2\text{S}$  (M) :333.0823. Found: 333.0833.



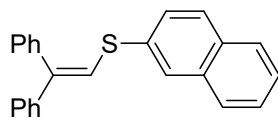
**3aj**

**3aj**, white solid, m.p. 84-85 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43-7.23 (m, 12H), 7.12-7.09 (m, 1H), 6.71 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 145.9, 141.1, 138.7, 138.1, 133.2, 131.3, 130.6, 129.7, 128.5, 128.4, 128.2, 128.0, 127.5, 127.1, 119.5; IR (film):  $\nu$  3060, 3022, 1603, 1509, 1449  $\text{cm}^{-1}$ ; HRMS (EI): Calcd for  $\text{C}_{20}\text{H}_{14}\text{Cl}_2\text{S}$  (M) :356.0193. Found: 356.0171.



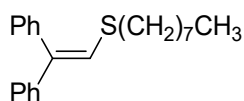
**3ak**

**3ak**, white solid, m.p. 76-78 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.33 (d,  $J = 8.8$  Hz, 1H), 7.76-7.71 (m, 3H), 7.50-7.40 (m, 8H), 7.25-7.20 (m, 5H), 6.79 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 141.5, 140.9, 139.3, 134.2, 133.5, 133.0, 129.9, 129.7, 128.7, 128.6, 128.4, 127.9, 127.4, 127.3, 126.8, 126.5, 125.8, 125.4, 125.2; IR (film):  $\nu$  3060, 3025, 1602, 1507, 1458  $\text{cm}^{-1}$ ; HRMS (EI): Calcd for  $\text{C}_{24}\text{H}_{18}\text{S}$  (M) :338.1129. Found: 338.1108.



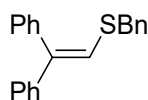
**3al**

**3al**, white solid, m.p. 74-75 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (s, 1H), 7.79-7.74 (m, 3H), 7.50-7.23 (m, 13H), 6.96 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 141.7, 141.5, 139.3, 134.0, 133.8, 132.2, 129.9, 128.8, 128.5, 128.4, 128.0, 127.8, 127.7, 127.5, 127.4, 127.3, 126.8, 126.1, 123.9; IR (film):  $\nu$  3063, 3021, 1607, 1500, 1445  $\text{cm}^{-1}$ ; HRMS (EI): Calcd for  $\text{C}_{24}\text{H}_{18}\text{S}$  (M) :338.1129. Found: 338.1147.



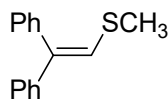
**3am**

**3am**, white solid, m.p. 67-69 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.38-7.19 (m, 10H), 6.58 (s, 1H), 2.75 (t, *J* = 7.4 Hz, 2H), 1.71-1.63 (m, 2H), 1.45-1.14 (m, 10H), 0.88 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 142.0, 139.6, 138.3, 129.7, 128.3, 128.2, 127.7, 127.4, 127.0, 126.8, 126.4, 34.9, 31.8, 31.8, 30.4, 29.2, 28.7, 22.6, 14.1; IR (film): ν 3055, 3030, 1597, 1549, 1453 cm<sup>-1</sup>; HRMS (EI): Calcd for C<sub>22</sub>H<sub>28</sub>S (M) :324.1912. Found: 324.1934.



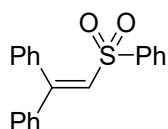
**3an**

**3an**<sup>[4]</sup>, white solid, m.p. 63-65 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.38-7.23 (m, 13H), 7.13 (d, *J* = 8.8 Hz, 2H), 6.57(s, 1H), 3.95 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 141.8, 139.5, 139.2, 137.7, 129.7, 128.9, 128.7, 128.3, 128.2, 127.5, 127.3, 127.1, 126.9, 124.7, 38.8.



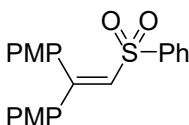
**3ao**

**3ao**,<sup>[3]</sup> white solid, m.p. 49-51 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.41-7.19 (m, 10H), 6.55 (s, 1H), 2.37 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 141.7, 139.5, 138.4, 129.7, 128.3, 128.2, 127.6, 127.5, 127.0, 126.9, 18.0.



**4aa**

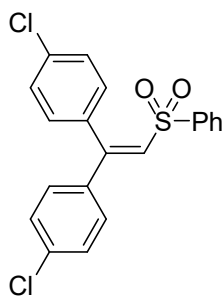
**4aa**,<sup>[3]</sup> white solid, m.p. 114-115 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.58 (d, *J* = 7.2Hz, 2H), 7.50-7.44 (m, 1H), 7.38-7.18 (m, 10H), 7.19-7.05 (m, 2H), 7.07 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 155.2, 141.5, 139.1, 135.5, 132.8, 130.3, 129.8, 128.9, 128.8, 128.7, 128.6, 128.2, 127.9, 127.6.



**4ba**

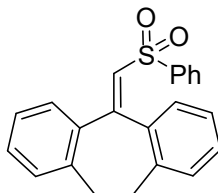
**4ba**, white solid, m.p. 121-123 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.78 (d, *J* = 7.8Hz, 2H), 7.52-7.42 (m, 2H), 7.33-7.26 (m, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.05-7.00 (m, 3H), 6.99-6.74 (m, 4H), 3.83(s, 3H), 3.77 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 161.5, 160.2, 154.2, 143.5, 138.9, 132.2, 131.5, 130.0, 129.2, 127.6, 126.3, 123.2, 115.0, 113.9; IR (film): ν 3062, 3029, 1599, 1501, 1454 cm<sup>-1</sup>; HRMS (EI): Calcd for C<sub>22</sub>H<sub>20</sub>O<sub>4</sub>S (M) :380.1082. Found: 380.1077.





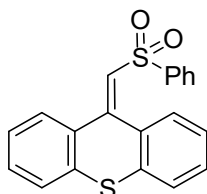
**4ca**

**4ba**, white solid, m.p. 124-126 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (d,  $J = 7.8\text{Hz}$ , 2H), 7.50 (d,  $J = 8.4\text{Hz}$ , 2H), 7.36-7.24 (m, 9H), 6.95 (s, 1H), 3.77 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 152.4, 140.8, 136.1, 134.9, 133.6, 132.6, 131.8, 129.6, 128.6, 127.5, 127.1, 125.4, 124.8, 120.5, 120.1; IR (film):  $\nu$  3060, 3029, 1598, 1499, 1445  $\text{cm}^{-1}$ ; HRMS (EI): Calcd for  $\text{C}_{20}\text{H}_{14}\text{Cl}_2\text{O}_2\text{S}$  (M) :388.0092. Found: 388.0081.



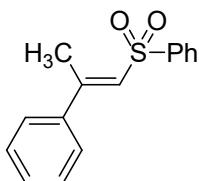
**4da**

**4da**, white solid, m.p. 113-115 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84-7.81 (m, 2H), 7.58-7.55 (m, 1H), 7.43-7.20 (m, 9H), 7.04 (s, 1H), 3.20-2.70 (m, 4H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 155.3, 144.0, 139.9, 138.2, 135.5, 130.5, 129.6, 129.3, 129.1, 129.0, 127.9, 127.0, 126.2, 126.0, 33.8, 31.6; IR (film):  $\nu$  3058, 3021, 1602, 1495, 1441  $\text{cm}^{-1}$ ; HRMS (EI): Calcd for  $\text{C}_{22}\text{H}_{18}\text{O}_2\text{S}$  (M) :346.1028. Found: 346.1050.



**4fa**

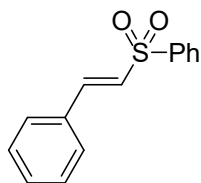
**4fa**, white solid, m.p. 118-120 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 (d,  $J = 7.2\text{Hz}$ , 2H), 7.60-7.17 (m, 11H), 7.08 (s, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 153.3, 144.7, 140.4, 136.1, 132.6, 131.0, 129.6, 129.2, 129.0, 128.5, 128.4, 128.0, 127.7, 127.1, 125.7, 124.4, 123.5, 122.1; IR (film):  $\nu$  3063, 3031, 1607, 1500, 1452  $\text{cm}^{-1}$ ; HRMS (EI): Calcd for  $\text{C}_{20}\text{H}_{14}\text{O}_2\text{S}_2$  (M) :318.0537. Found: 318.0551.



**4ga**

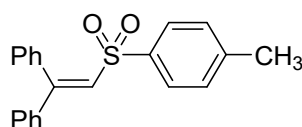
**4ga**, <sup>[5]</sup> white solid, m.p. 105-106 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10-7.98 (m, 2H), 7.59-7.57 (m, 1H), 7.44-7.25 (m, 5H), 6.72 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,

CDCl<sub>3</sub>): 145.1, 136.4, 133.8, 130.1, 129.7, 129.4, 129.3, 128.9, 128.5, 128.4, 128.2, 127.2.



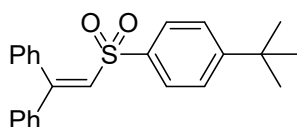
**4ja**

**4ja**, <sup>[3]</sup> white solid, m.p. 101-103 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 16 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.60-7.55 (m, 2H), 7.51-7.49 (m, 2H), 7.42-7.40 (m, 3H), 6.87 (d, *J* = 15.5 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 142.6, 140.8, 133.4, 132.5, 131.3, 129.5, 129.1, 128.6, 127.8, 127.3.



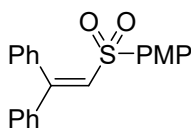
**4ab**

**4ab**, <sup>[3]</sup> white solid, m.p. 117-119 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.40-7.31 (m, 4H), 7.30-7.10 (m, 8H), 7.01 (s, 1H), 2.40 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 154.7, 143.9, 139.4, 135.7, 130.2, 129.8, 129.4, 129.1, 128.8, 128.6, 128.2, 127.8, 21.5.



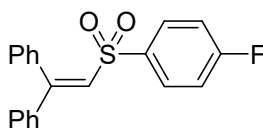
**4ac**

**4ac**, white solid, m.p. 121-123 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.40-7.19 (m, 10H), 7.08 (d, *J* = 8.1 Hz, 2H), 7.02 (s, 1H), 1.30 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 154.5, 143.4, 139.2, 138.3, 135.6, 130.2, 129.8, 129.2, 128.7, 128.5, 128.2, 127.8, 127.5, 125.6, 35.1, 31.0; IR (film): ν 3060, 3030, 1593, 1496, 1452 cm<sup>-1</sup>; HRMS (EI): Calcd for C<sub>24</sub>H<sub>24</sub>O<sub>2</sub>S (M) :376.1497. Found: 374.1506.



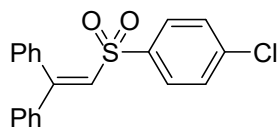
**4ad**

**4ad**, <sup>[3]</sup> white solid, m.p. 124-126 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.40-7.19 (m, 10H), 7.08 (d, *J* = 8.1 Hz, 2H), 7.02 (s, 1H), 1.30 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 161.1, 154.2, 141.7, 139.2, 135.6, 130.1, 129.8, 129.4, 128.8, 128.5, 128.1, 113.9, 55.7.

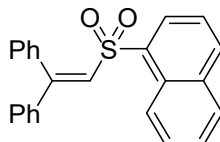


**4ae**

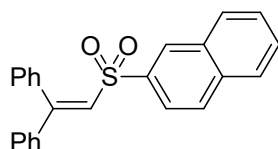
**4ae**, white solid, m.p. 119-121 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.57-7.52 (m, 2H), 7.40-7.21 (m, 9H), 7.19-6.98 (m, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 165.2 (d, *J* = 248Hz), 155.0, 138.8, 137.5, 135.3, 130.2, 130.1, 129.6, 128.7, 128.4, 128.0, 127.7, 115.6 (d, *J* = 30Hz) ; IR (film): ν 3058, 3025, 1600, 1503, 1444 cm<sup>-1</sup>; HRMS (EI): Calcd for C<sub>20</sub>H<sub>15</sub>FO<sub>2</sub>S (M) :338.0777. Found: 338.0795.

**4af**

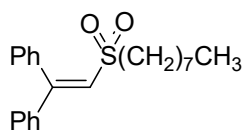
**4af**, white solid, m.p. 118-119 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.39-7.26 (m, 8H), 7.21 (d, *J* = 7.5 Hz, 2H), 7.06 (d, *J* = 7.5 Hz, 2H), 7.02 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 155.7, 139.9, 139.5, 138.9, 135.4, 130.4, 129.7, 129.1, 129.0, 128.9, 128.6, 128.2, 127.9; IR (film): ν 3055, 3025, 1602, 1501, 1454 cm<sup>-1</sup>; HRMS (EI): Calcd for C<sub>20</sub>H<sub>15</sub>ClO<sub>2</sub>S (M) :354.0481. Found: 354.0472.

**4ak**

**4ak**, white solid, m.p. 118-130 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.93-7.86 (m, 2H), 7.73 (d, *J* = 7.5 Hz, 1H), 7.69-7.63 (m, 1H), 7.60-7.55 (m, 1H), 7.37-7.15 (m, 12H), 7.13 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 155.0, 139.1, 135.2, 134.1, 133.9, 130.2, 129.9, 129.5, 129.3, 128.9, 128.8, 128.5, 127.6, 126.6, 124.7, 124.2; IR (film): ν 3060, 3029, 1599, 1500, 1459 cm<sup>-1</sup>; HRMS (EI): Calcd for C<sub>24</sub>H<sub>18</sub>O<sub>2</sub>S (M) :370.1028. Found: 370.1044.

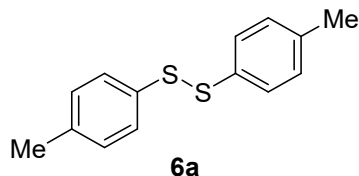
**4al**

**4al**, white solid, m.p. 129-131 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.89 (s, 1H), 7.82-7.77 (m, 3H), 7.51-7.36 (m, 8H), 7.30-7.24 (m, 5H), 6.96 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 153.3, 141.7, 139.0, 138.7, 133.4, 129.8, 128.7, 128.4, 128.3, 127.8, 127.7, 127.4, 127.3, 127.2, 126.7, 126.0, 123.8; IR (film): ν 3062, 3028, 1607, 1503, 1455 cm<sup>-1</sup>; HRMS (EI): Calcd for C<sub>24</sub>H<sub>18</sub>O<sub>2</sub>S (M) :370.1028. Found: 370.1038.

**4am**

**4am**, white solid, m.p. 101-103 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.46-7.38 (m, 7H), 7.37-7.08 (m, 3H), 6.75 (s, 1H), 2.71-2.64 (m, 2H), 1.76-1.66 (m, 2H), 1.34-1.22 (m,

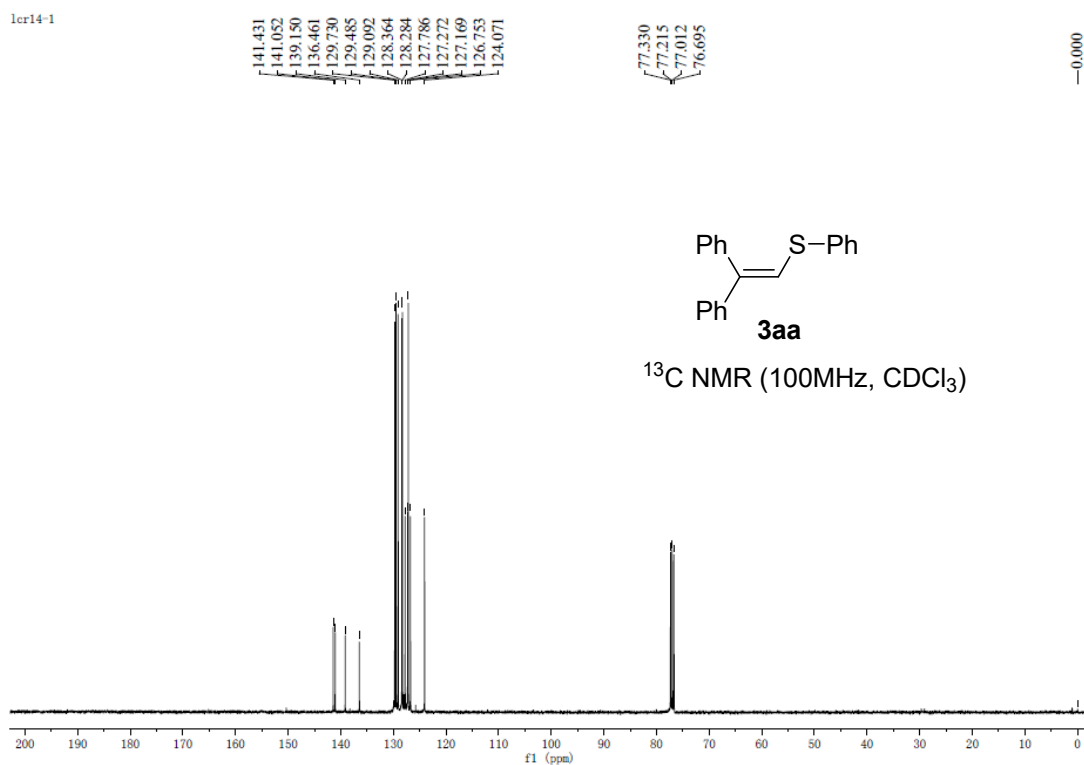
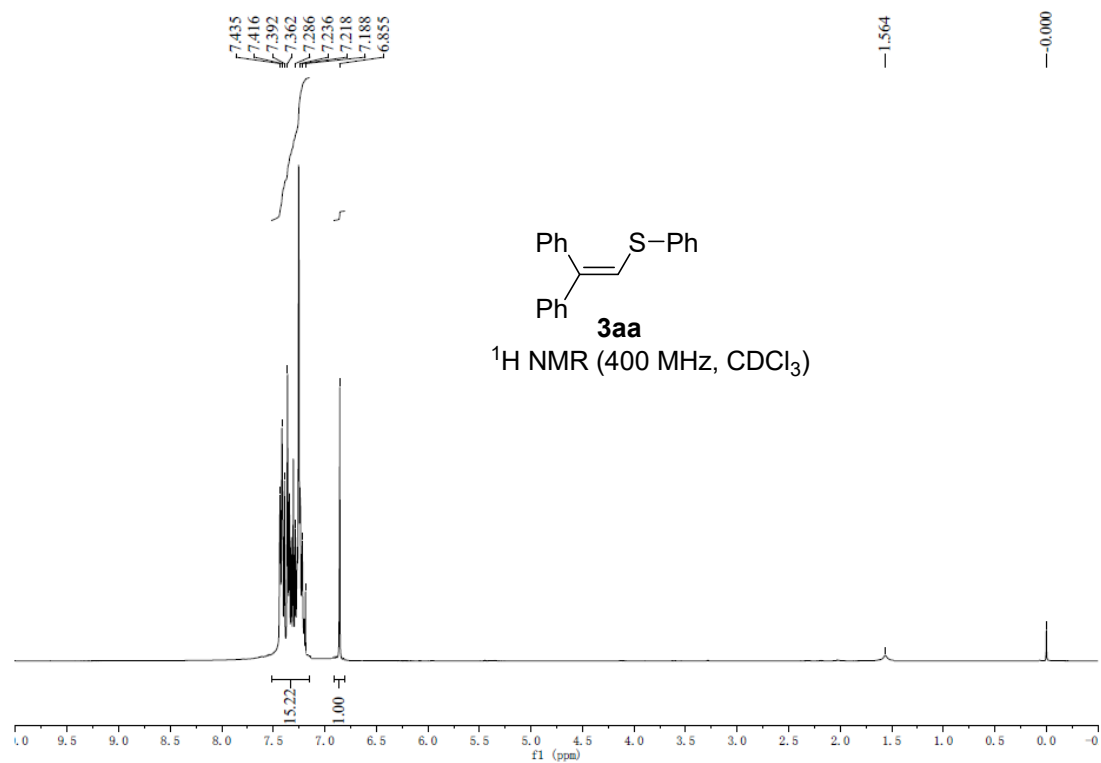
10H), 0.87 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 153.9, 142.9, 141.6, 132.5, 131.7, 129.6, 128.4, 127.6, 126.9, 129.9, 55.1, 33.5, 31.8, 30.1, 29.8, 29.5, 23.9, 22.7, 14.2; IR (film):  $\nu$  3058, 3020, 1597, 1500, 1443  $\text{cm}^{-1}$ ; HRMS (EI): Calcd for  $\text{C}_{22}\text{H}_{28}\text{O}_2\text{S}$  (M) :356.1810. Found: 356.1802.



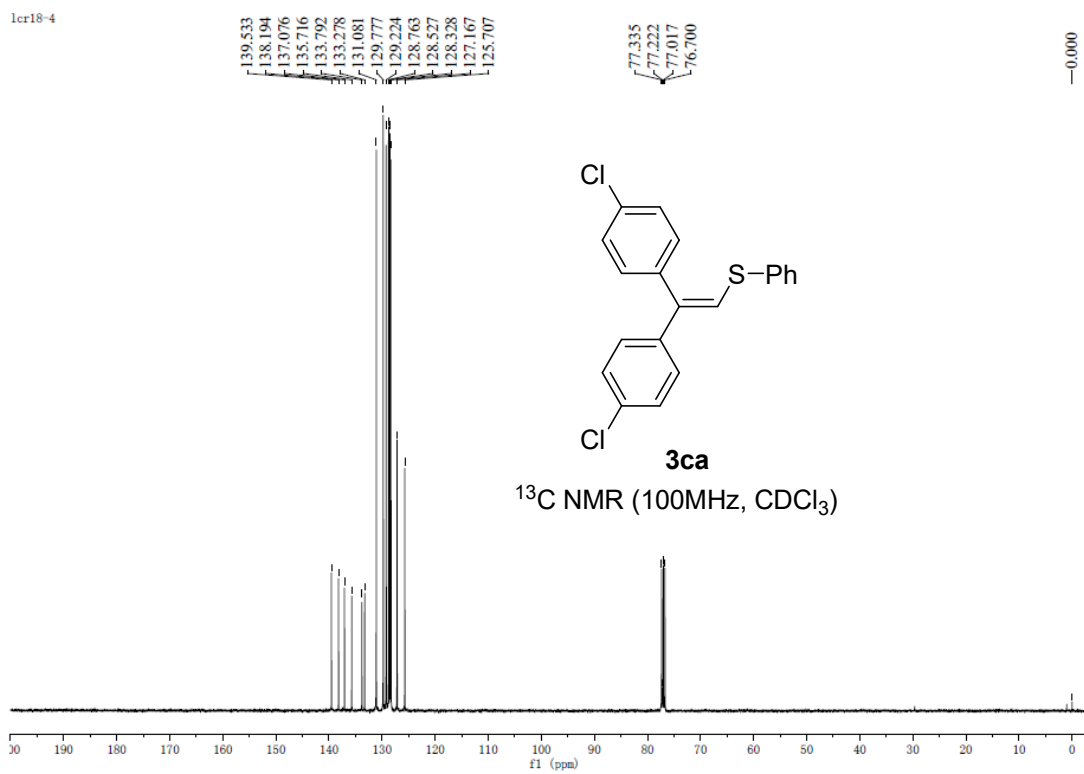
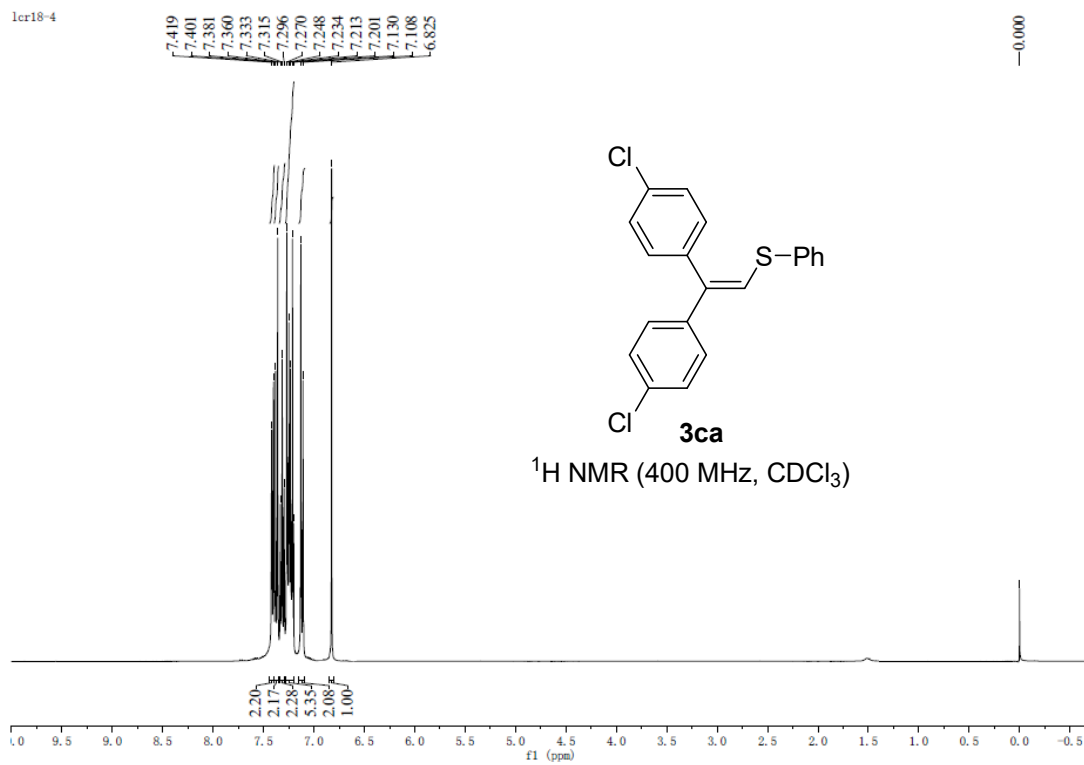
**2a'**, white solid, m.p. 45-46 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40-7.35 (m, 4H), 7.12-7.07 (m, 4H), 2.31 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.5, 133.9, 129.8, 128.6, 21.1; HRMS (EI) calcd for  $\text{C}_{14}\text{H}_{14}\text{S}_2$  (M) 246.0537, found 246.0543.

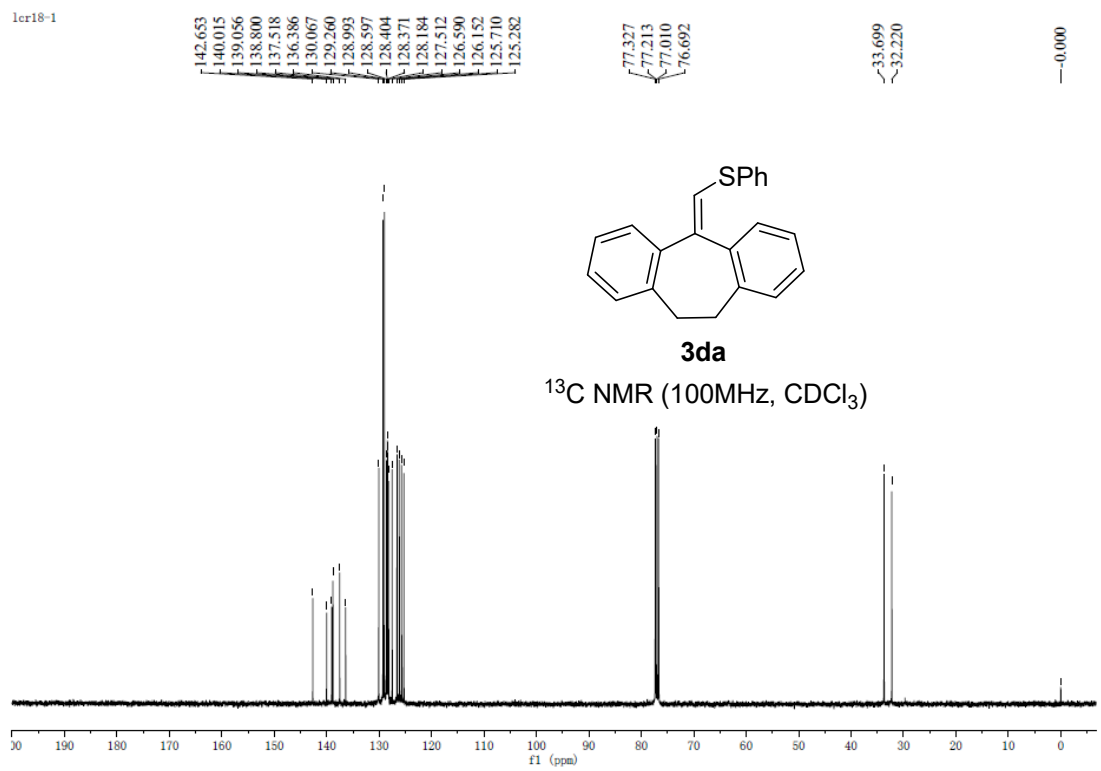
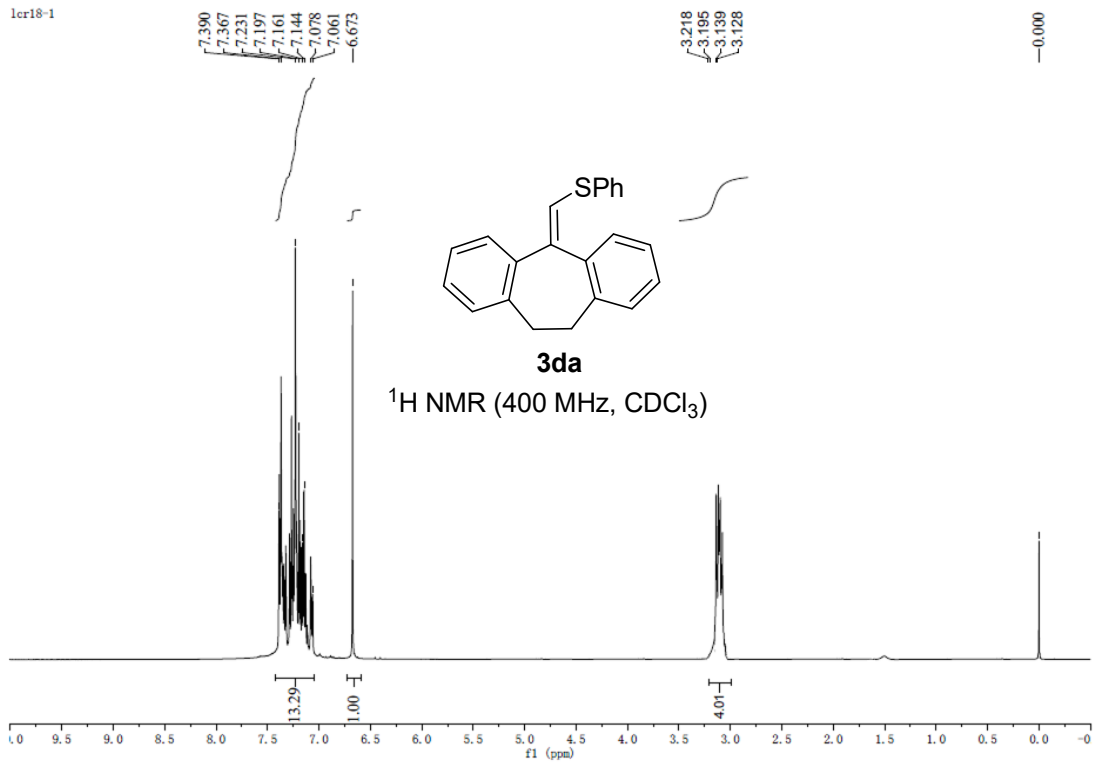
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2. M. Oba, K. Tanaka, K. Nishiyama, W. Ando, *J. Org. Chem.* **2011**, 76, 4173.
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6. C. R. Liu, L. H. Ding, *Org. Biomol. Chem.*, 2015, **13**, 2251.

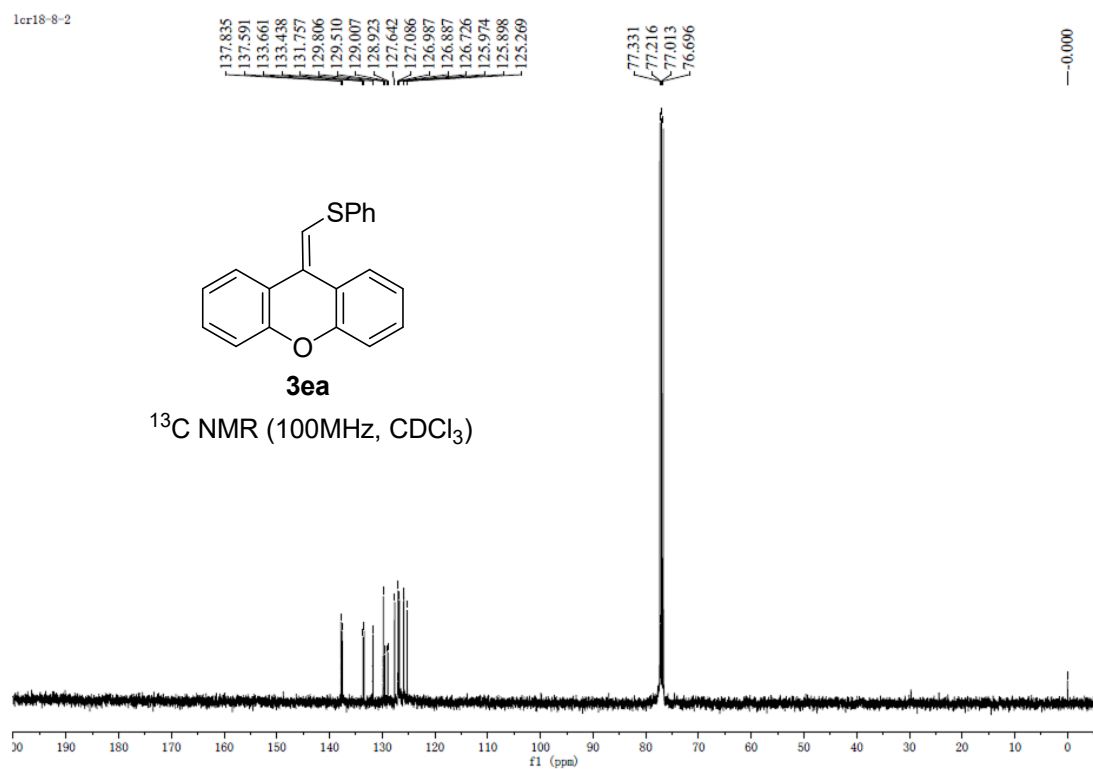
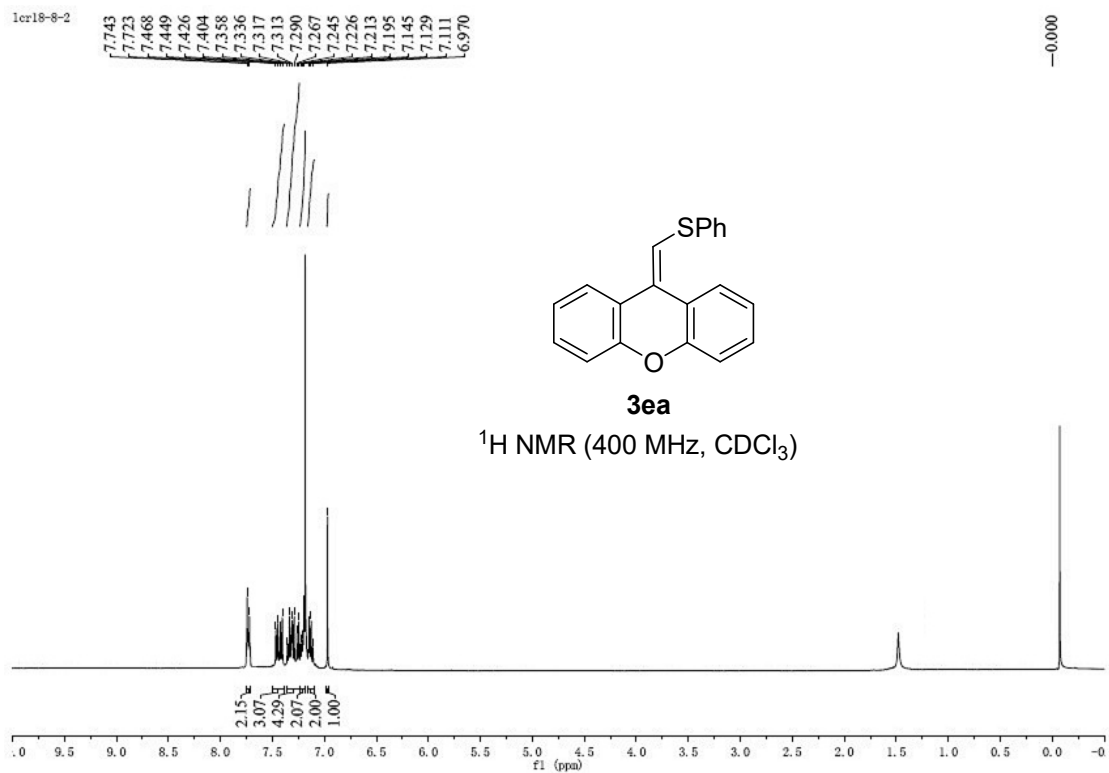


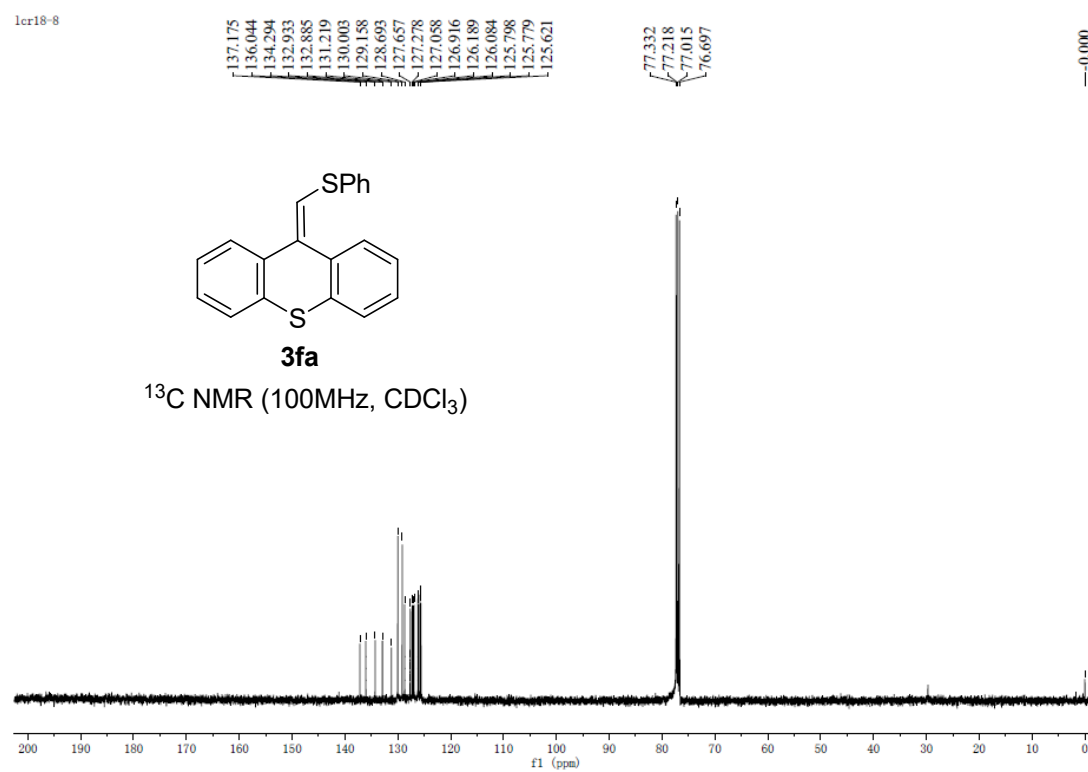
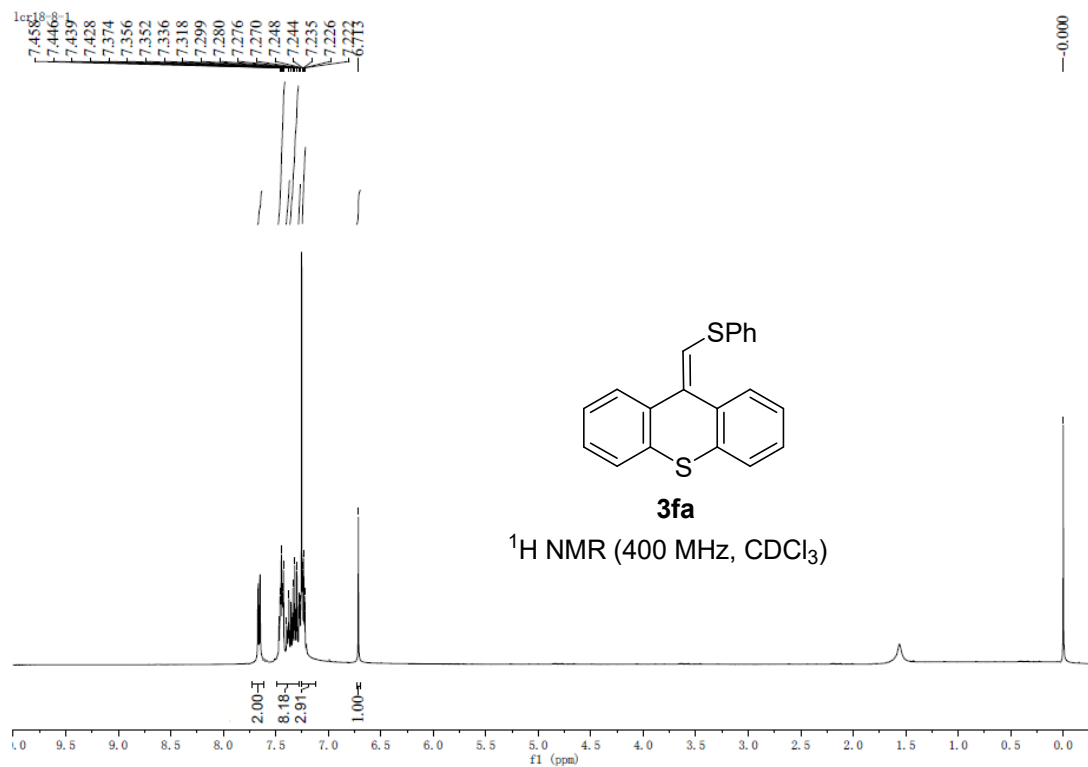


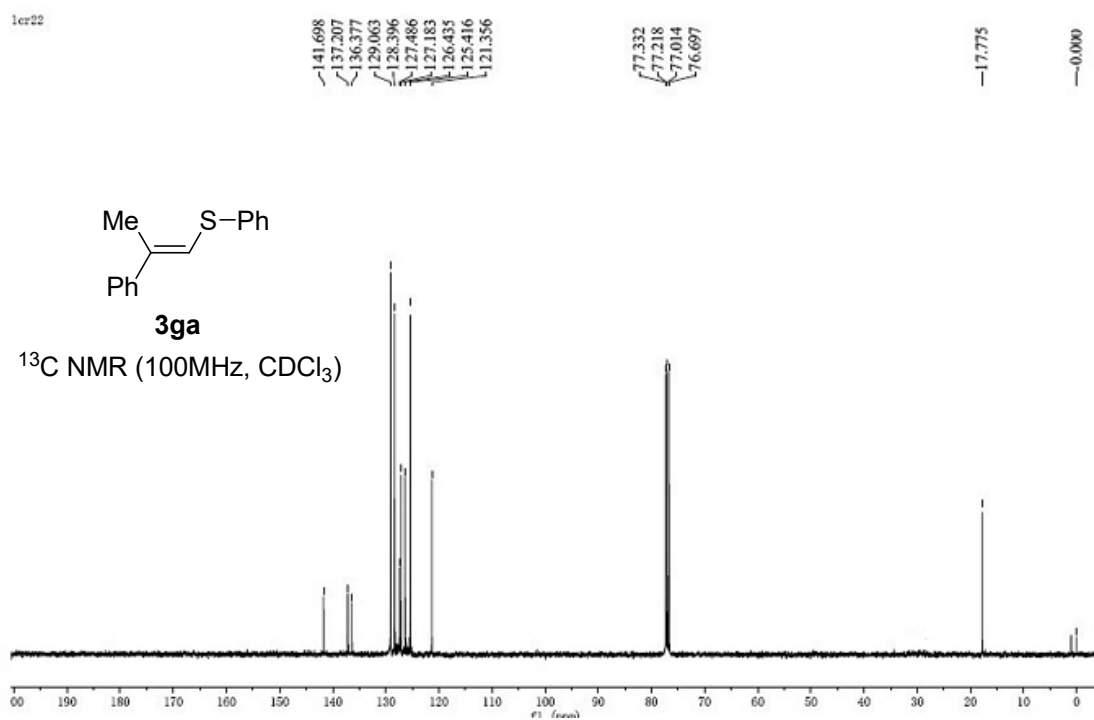
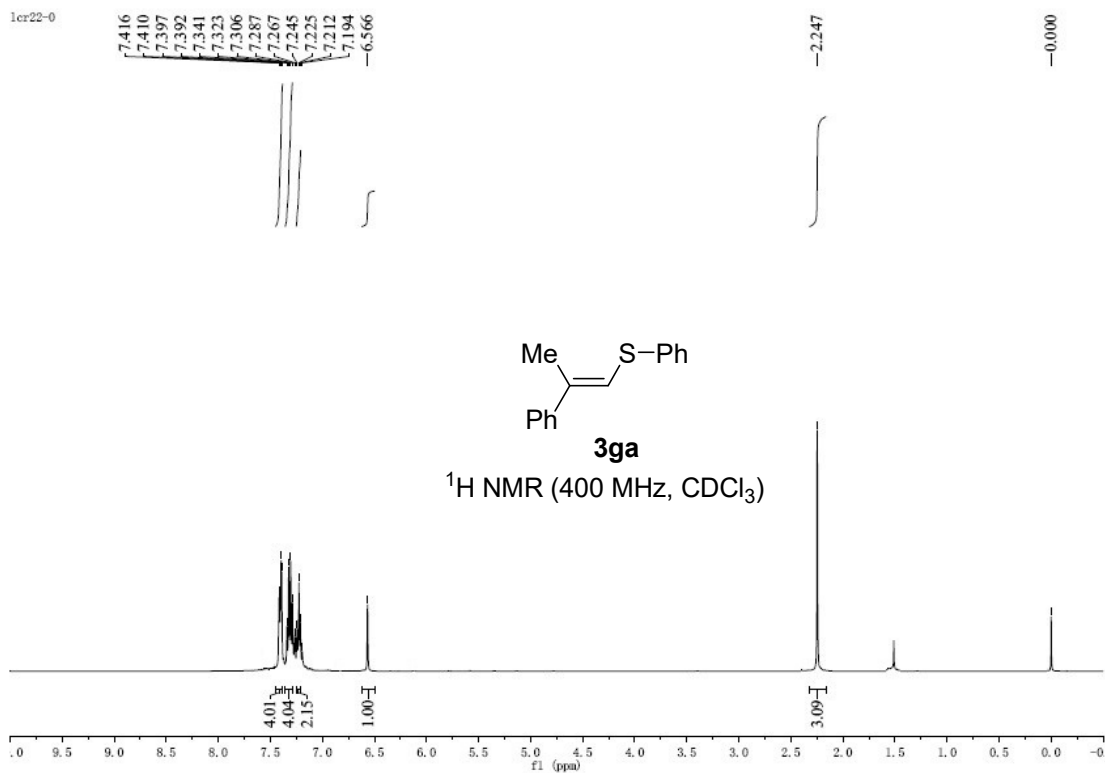


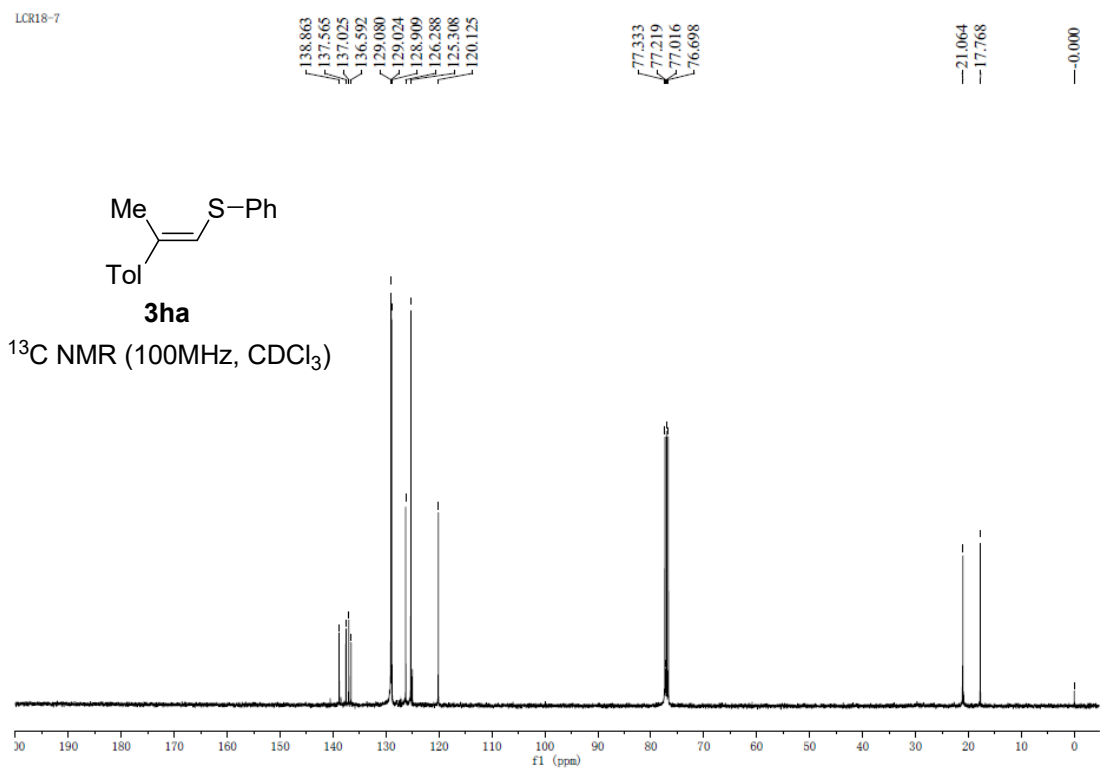
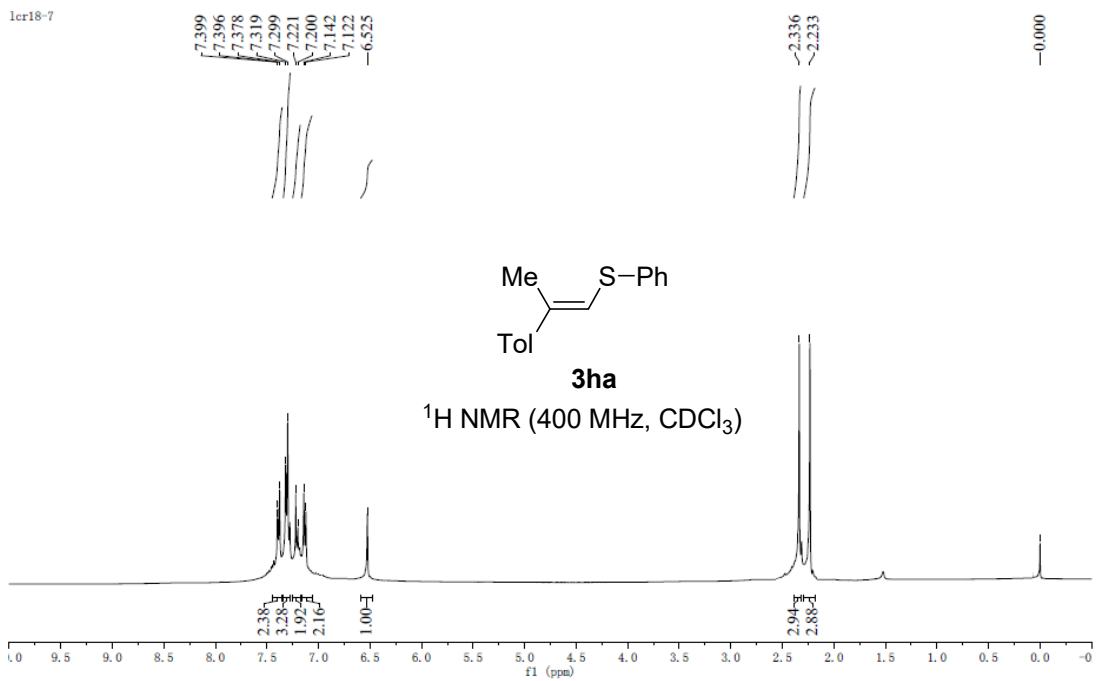


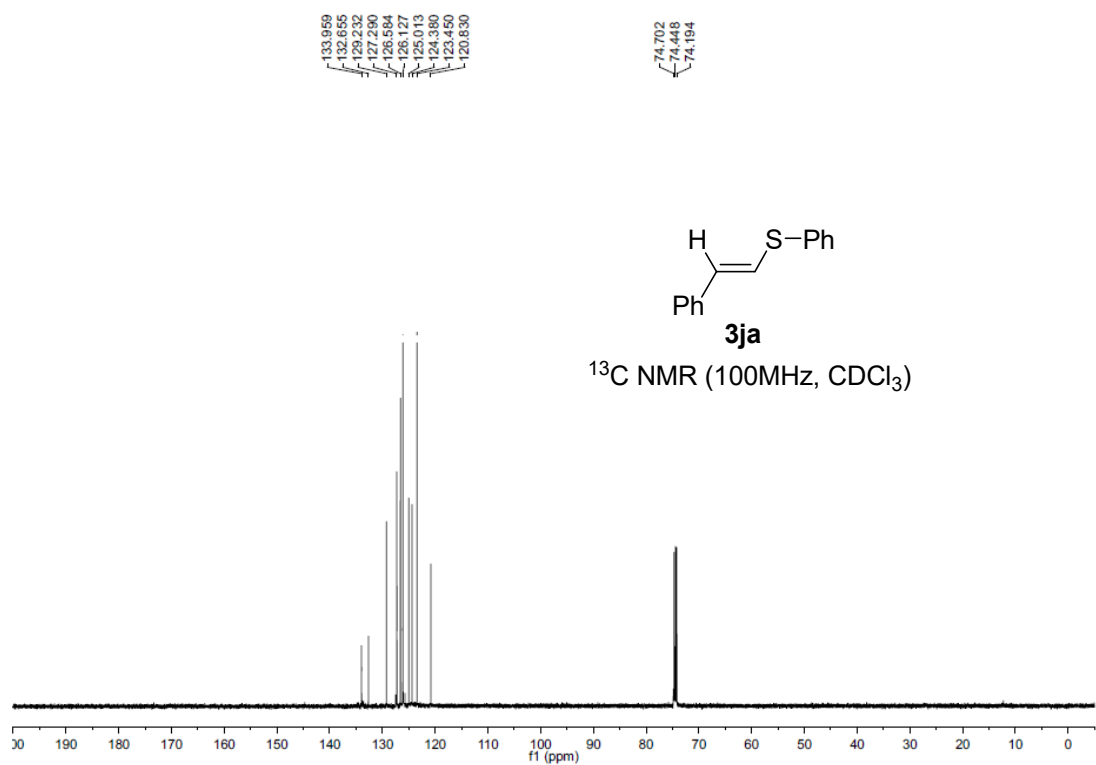
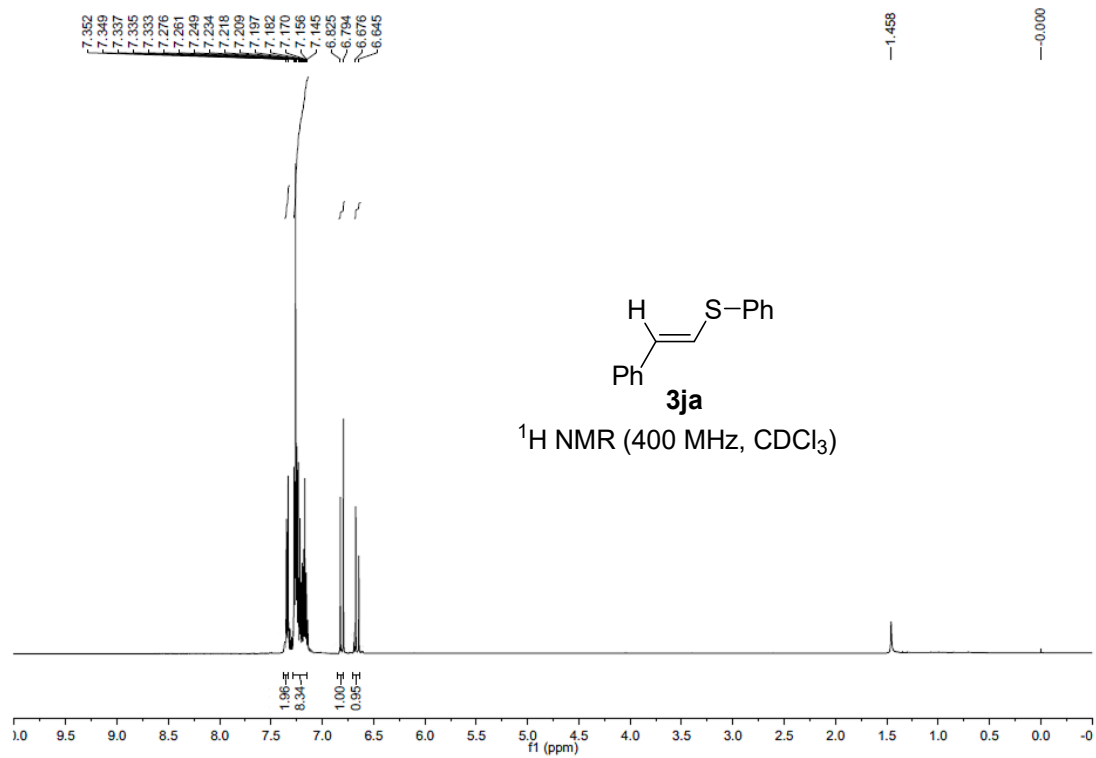


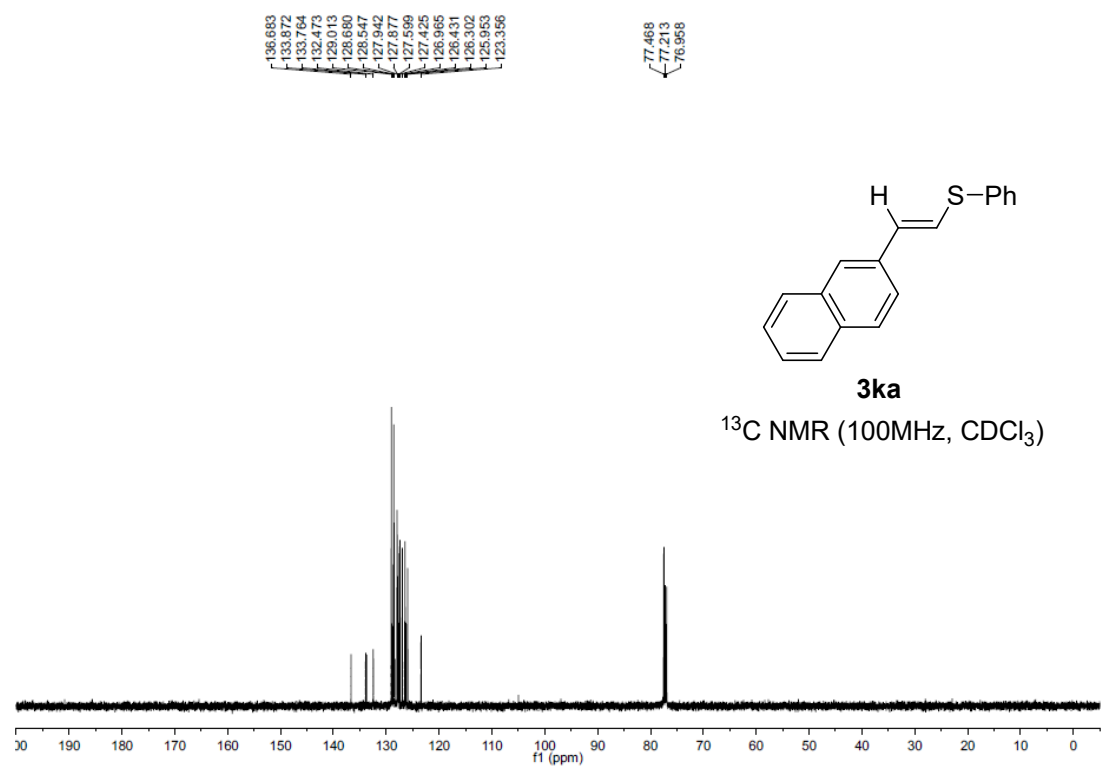
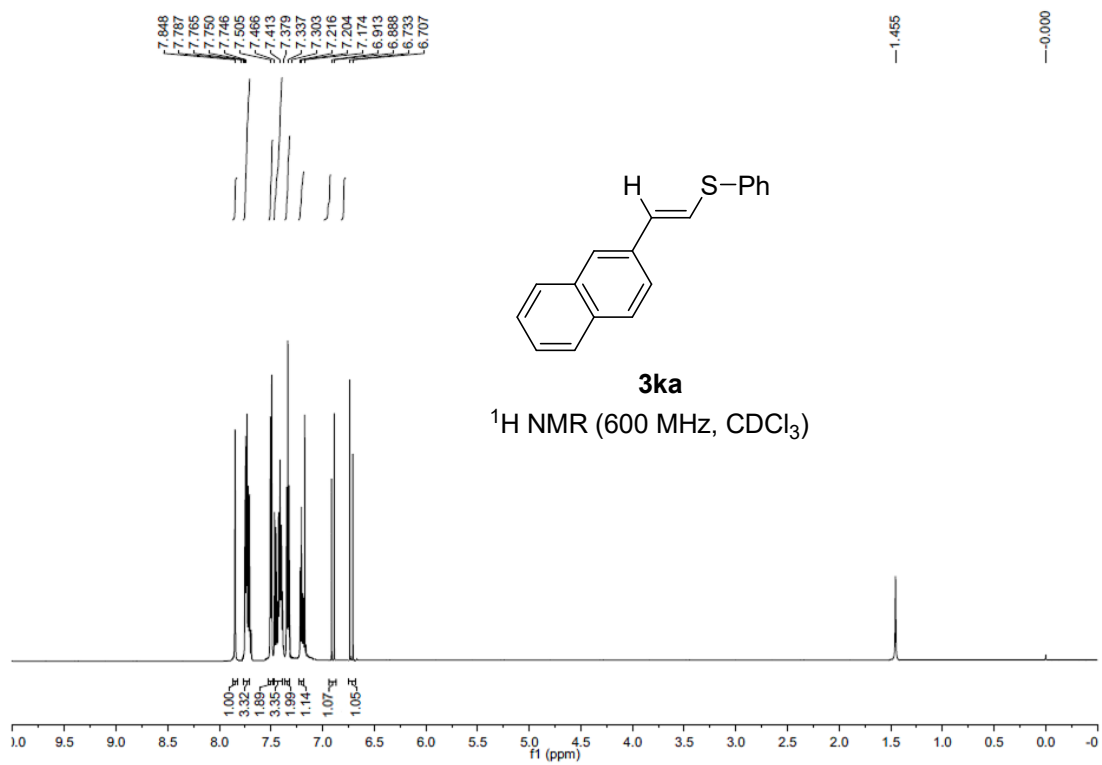


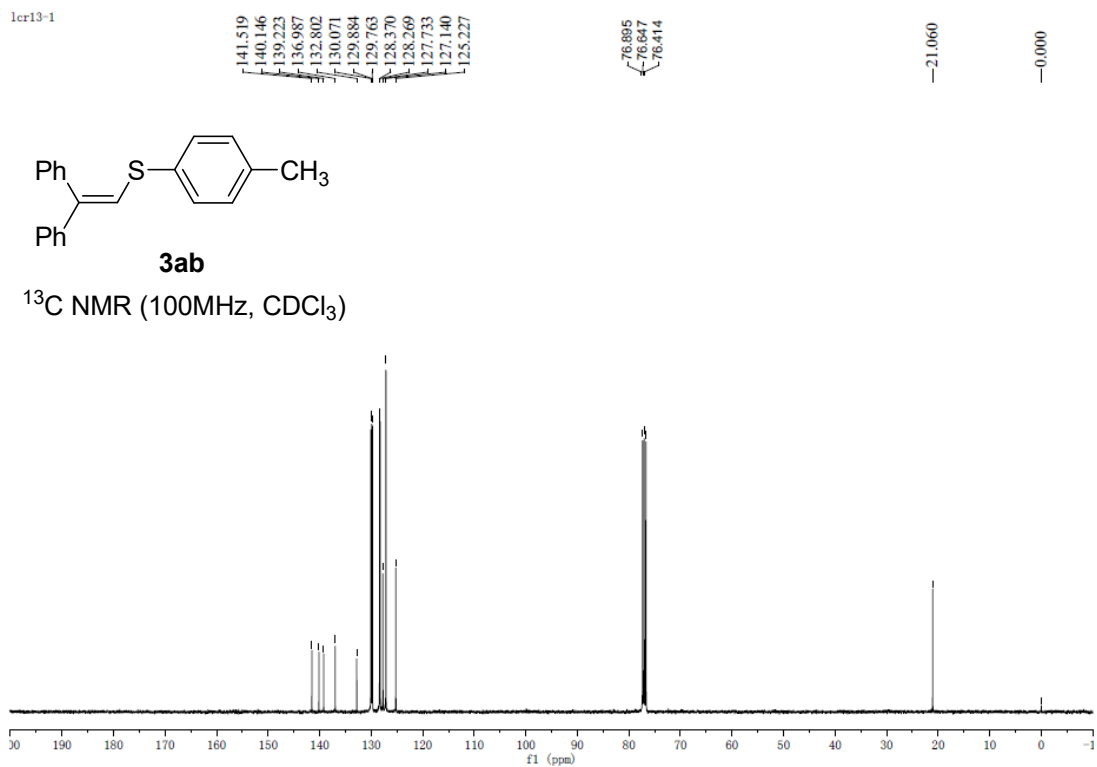
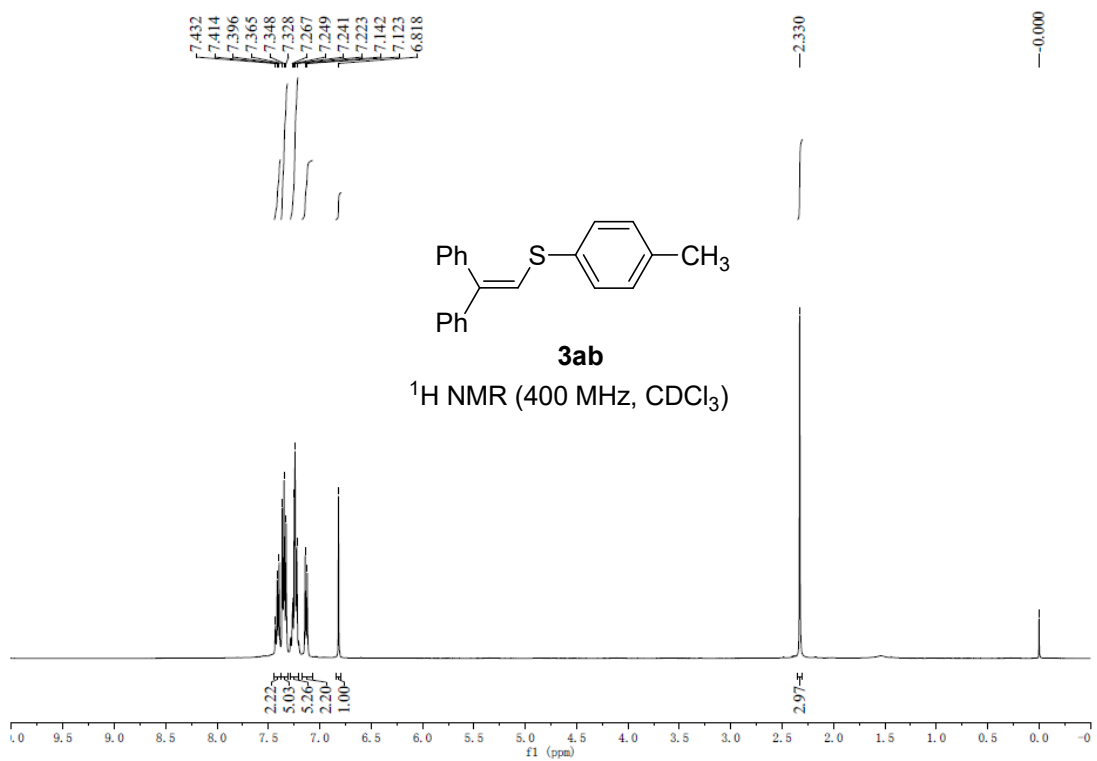


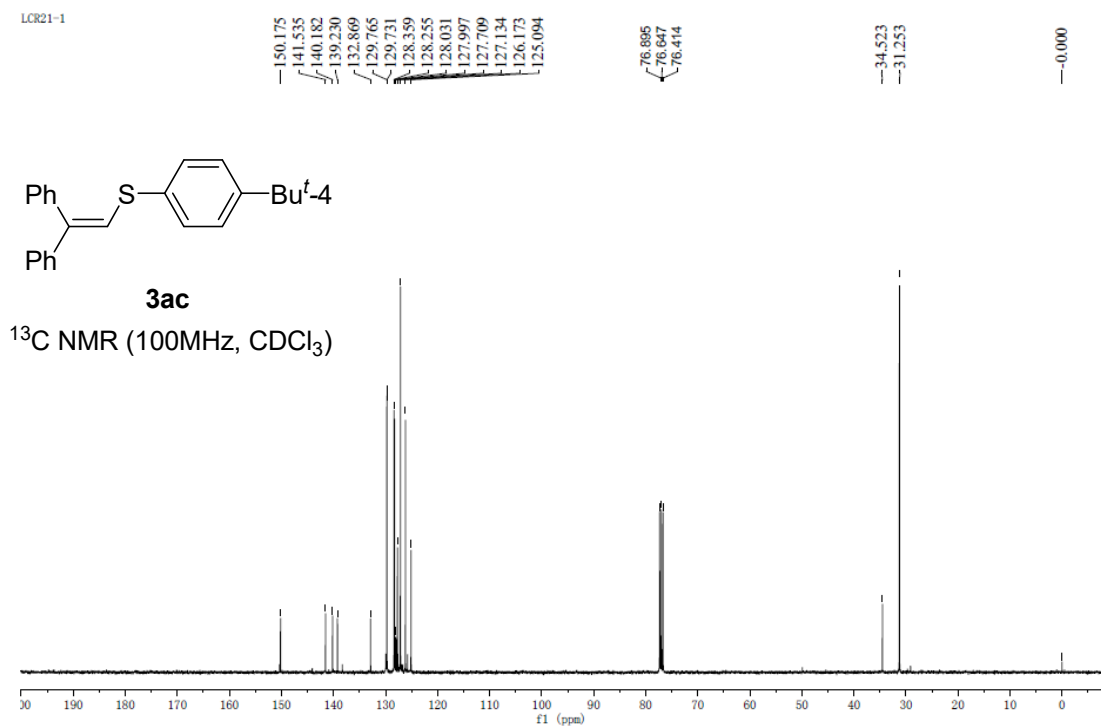
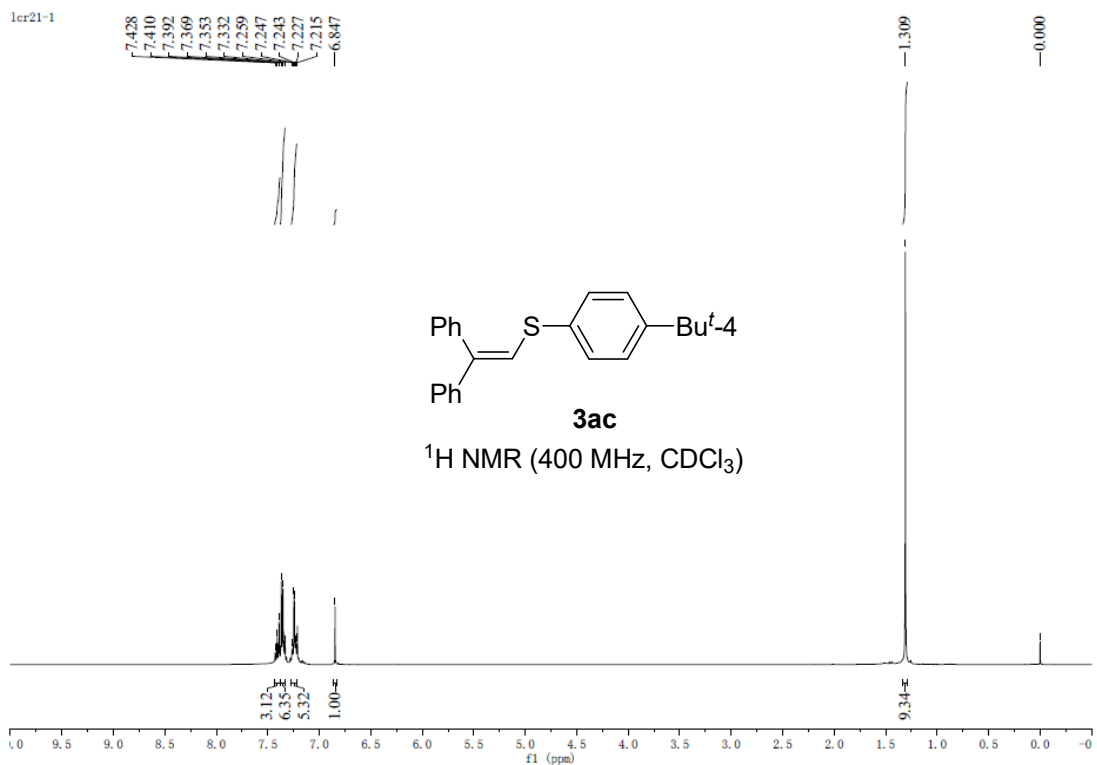




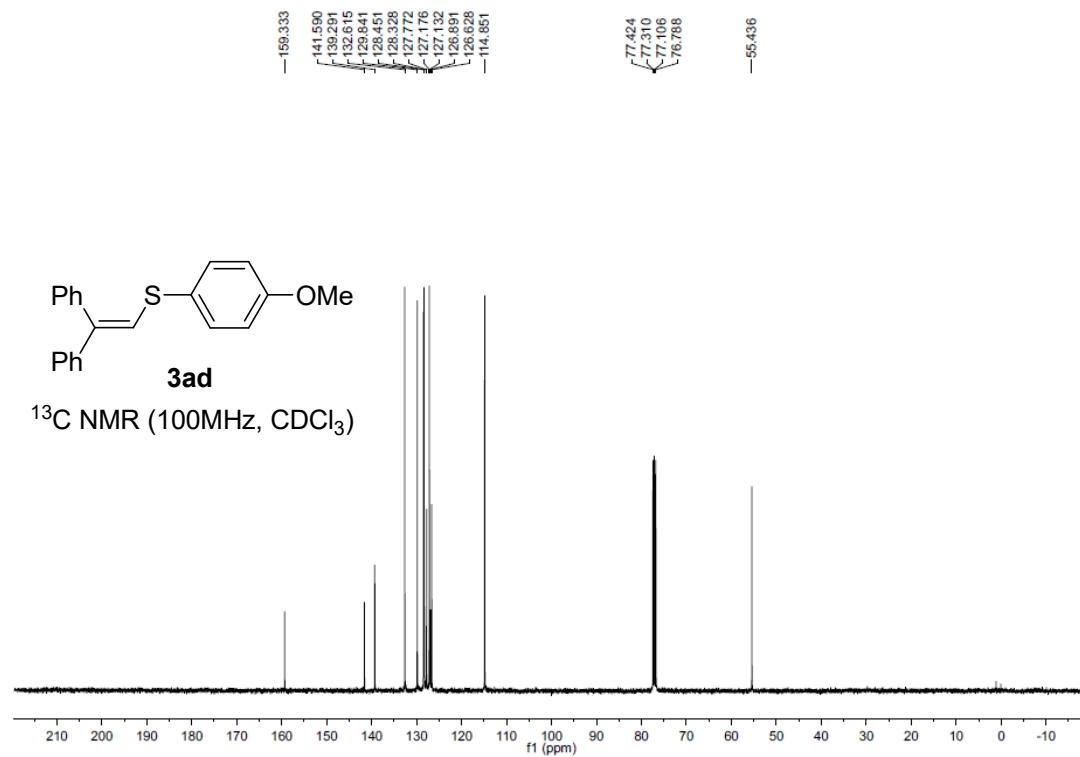
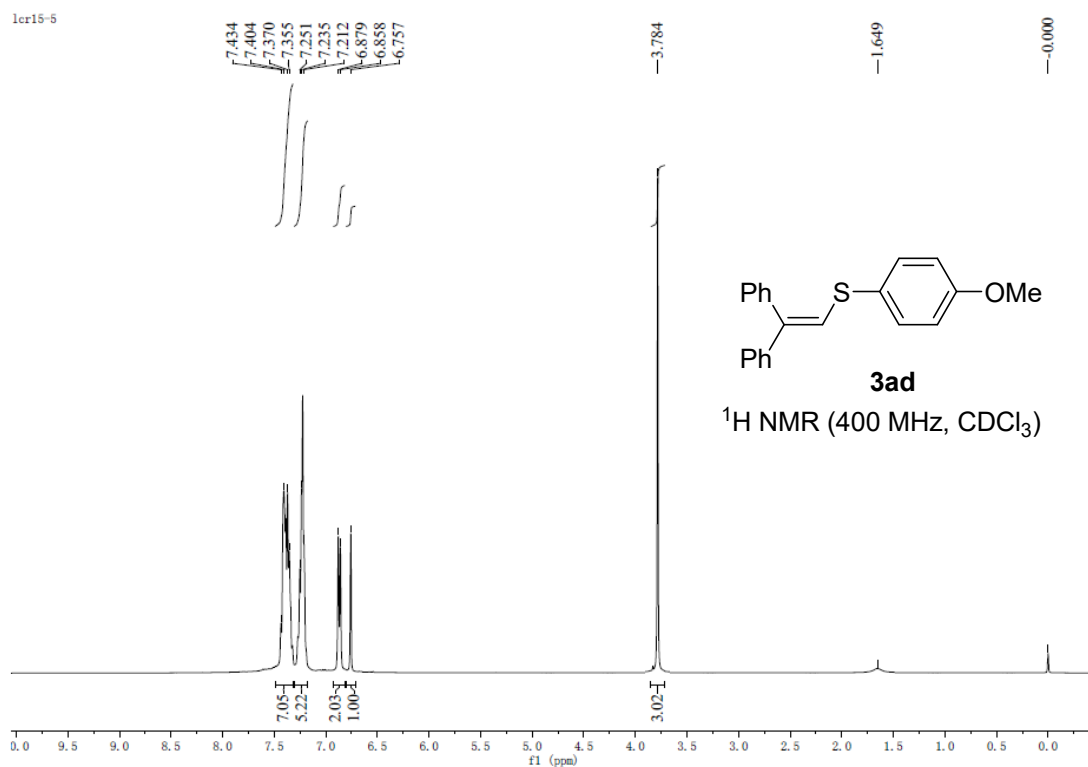


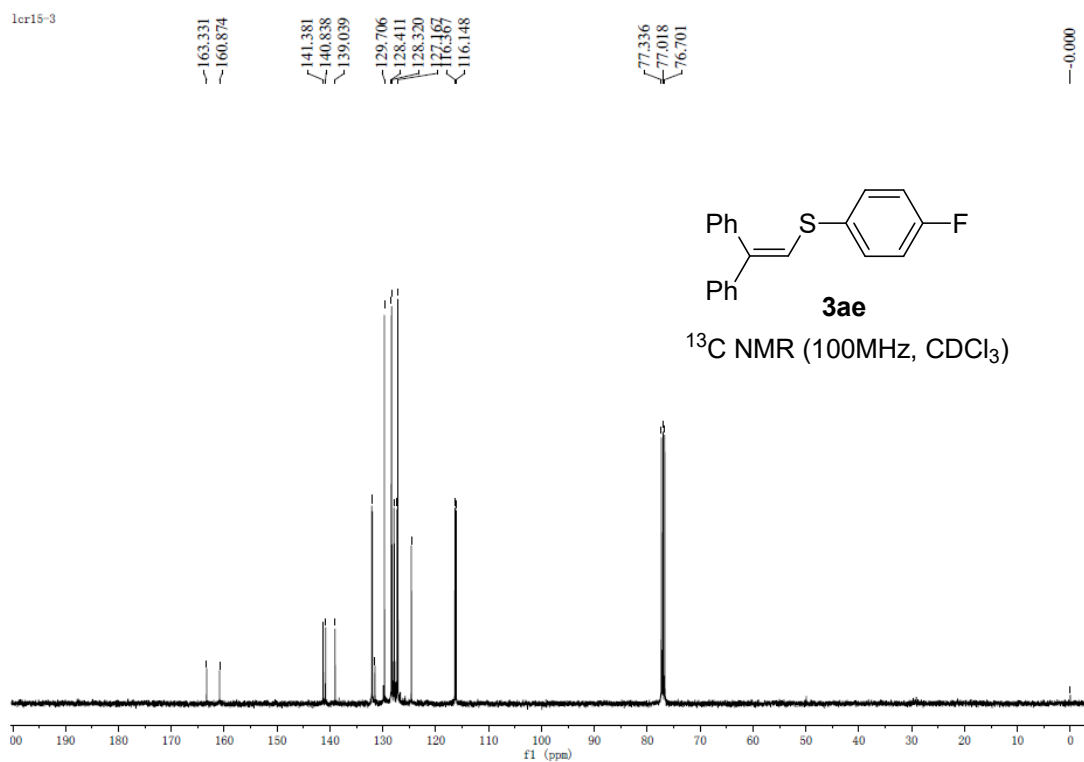
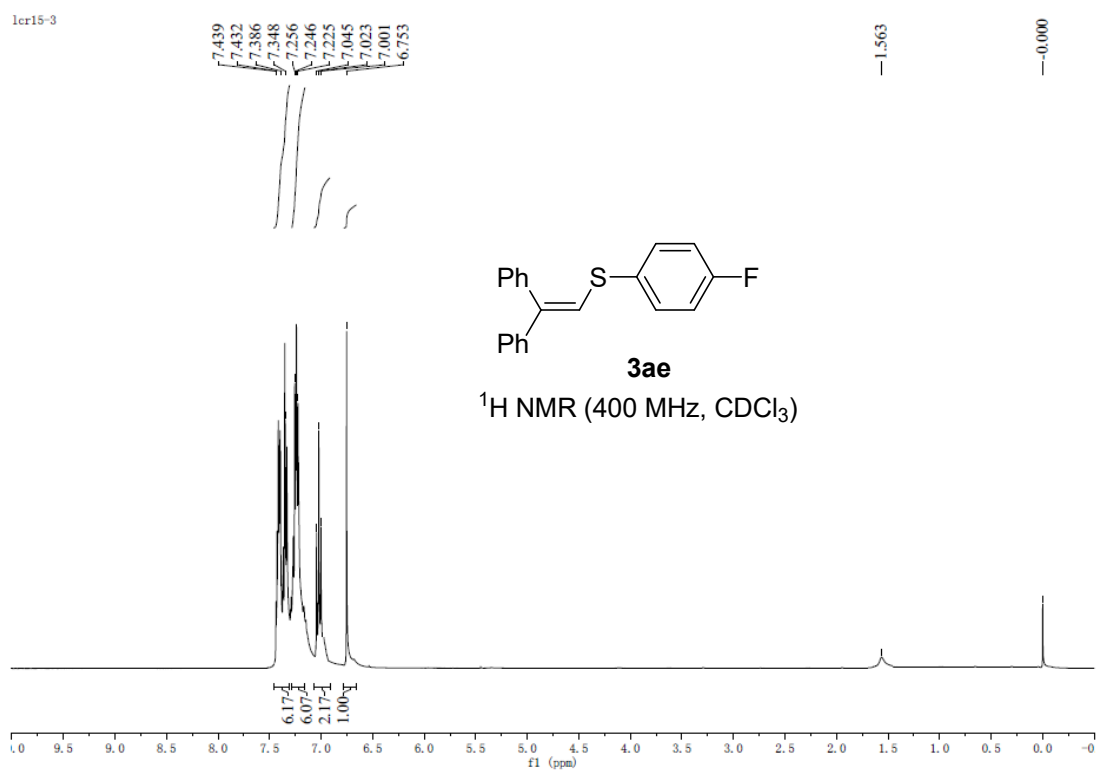


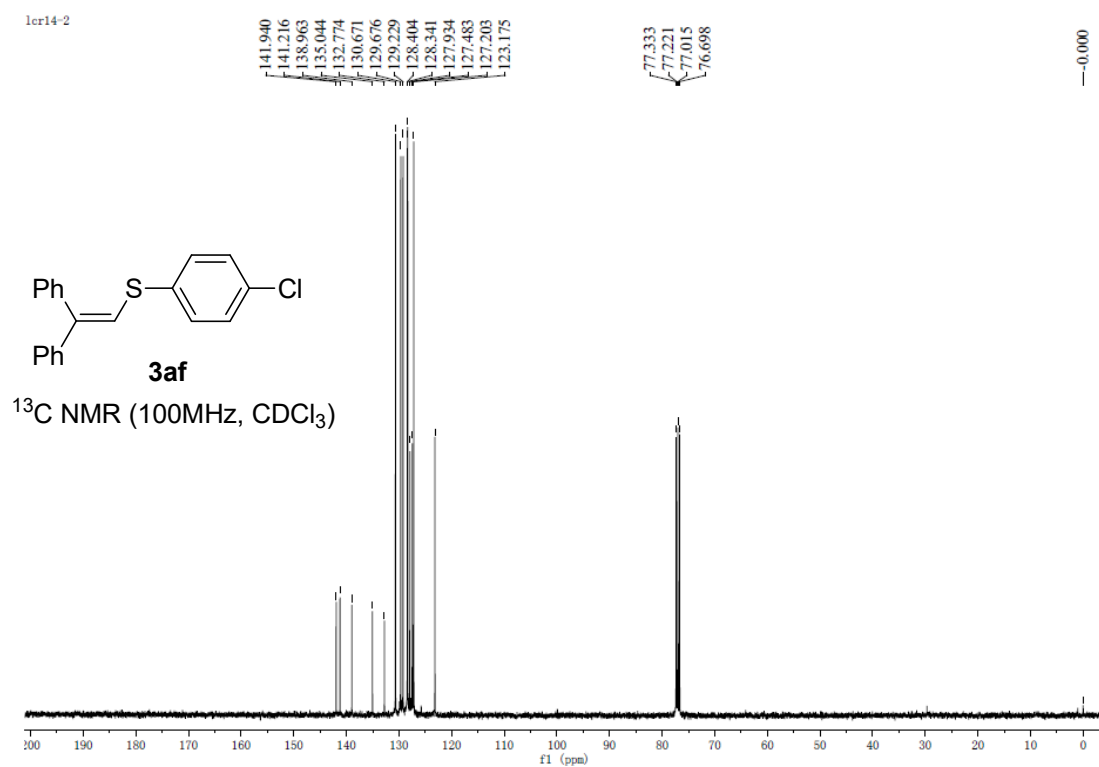
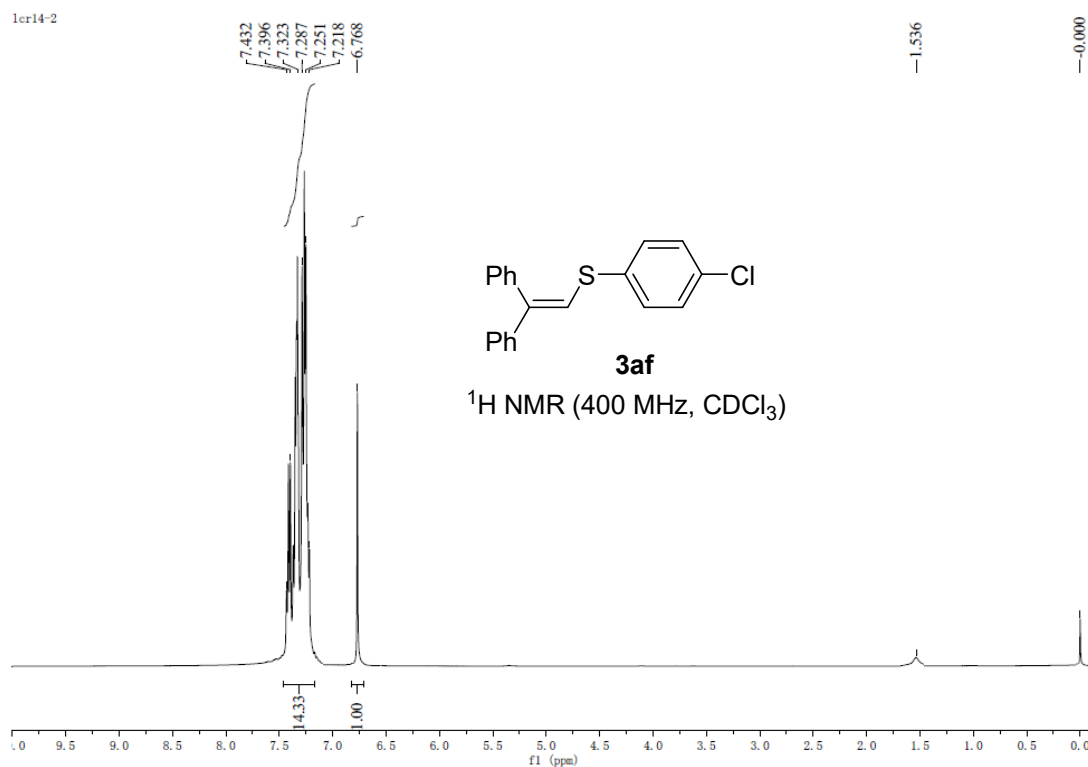


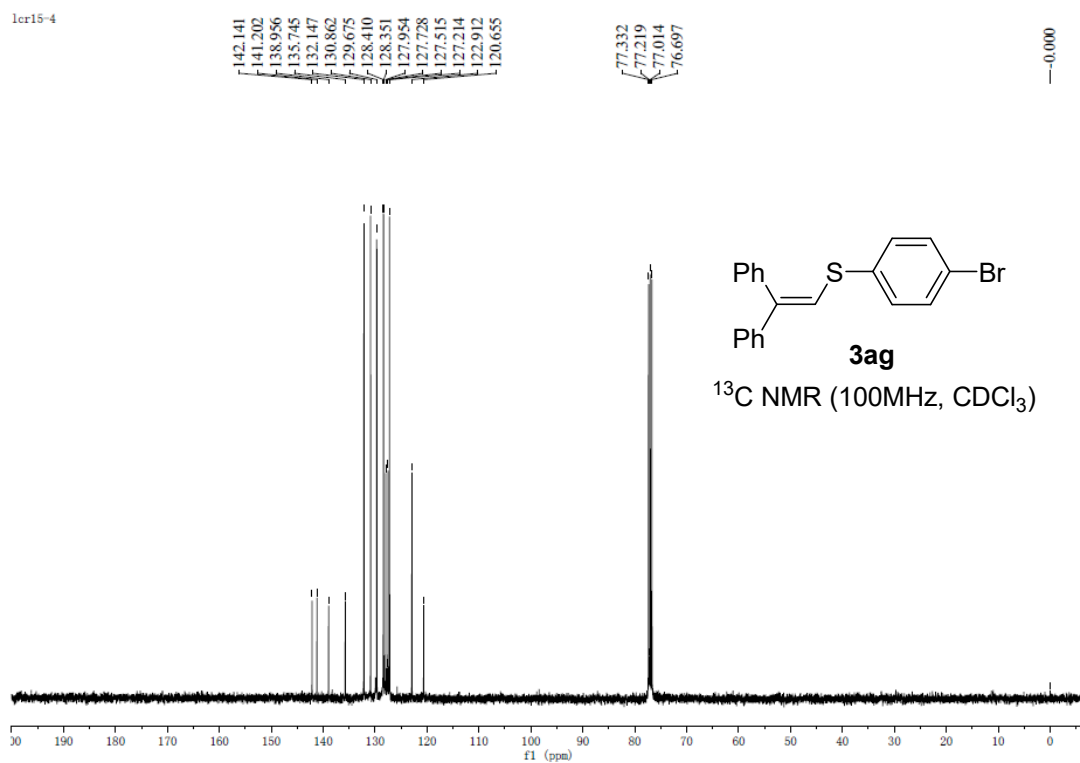
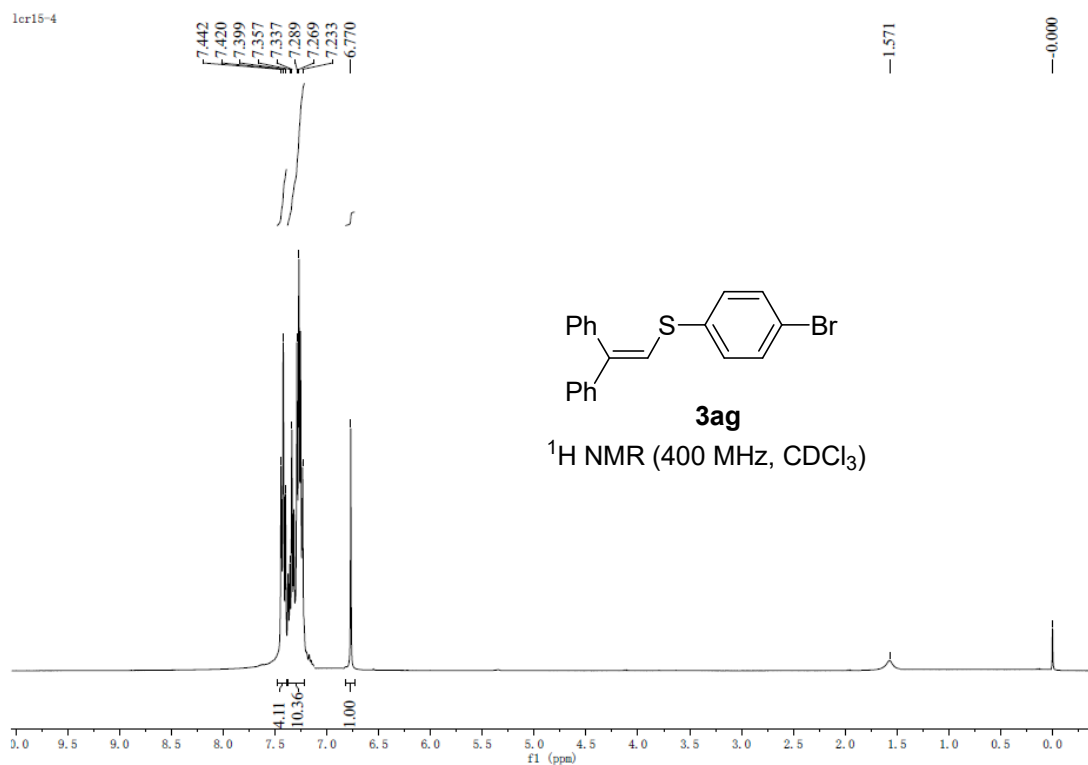


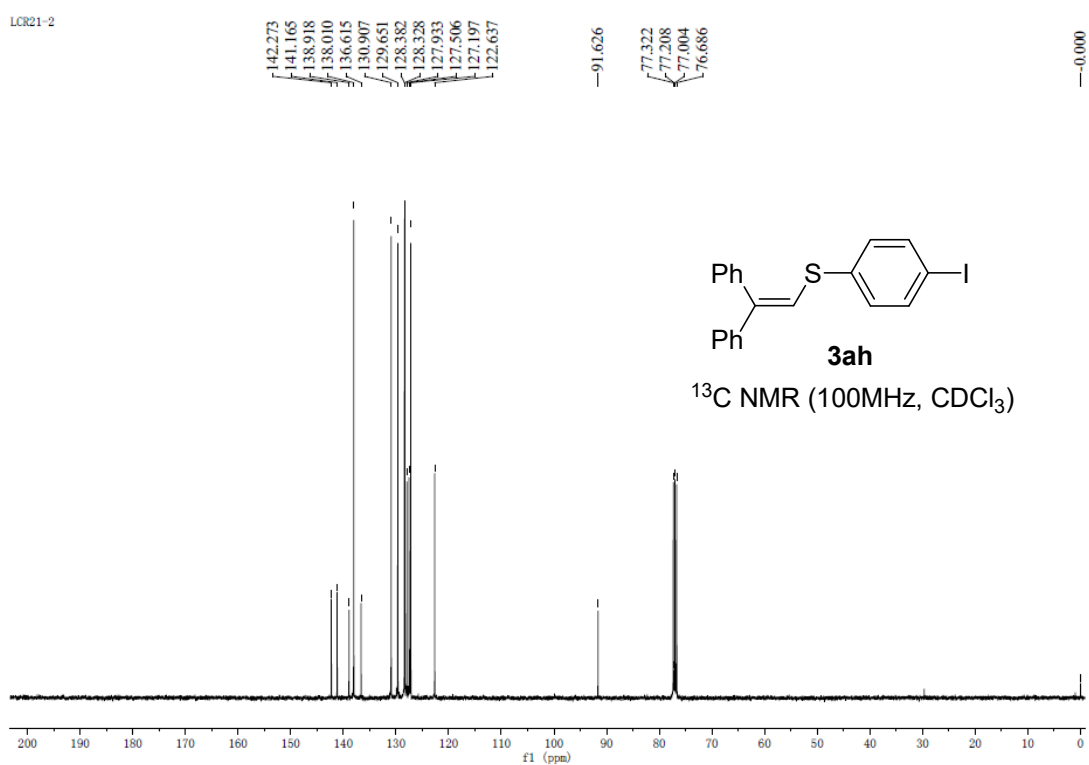
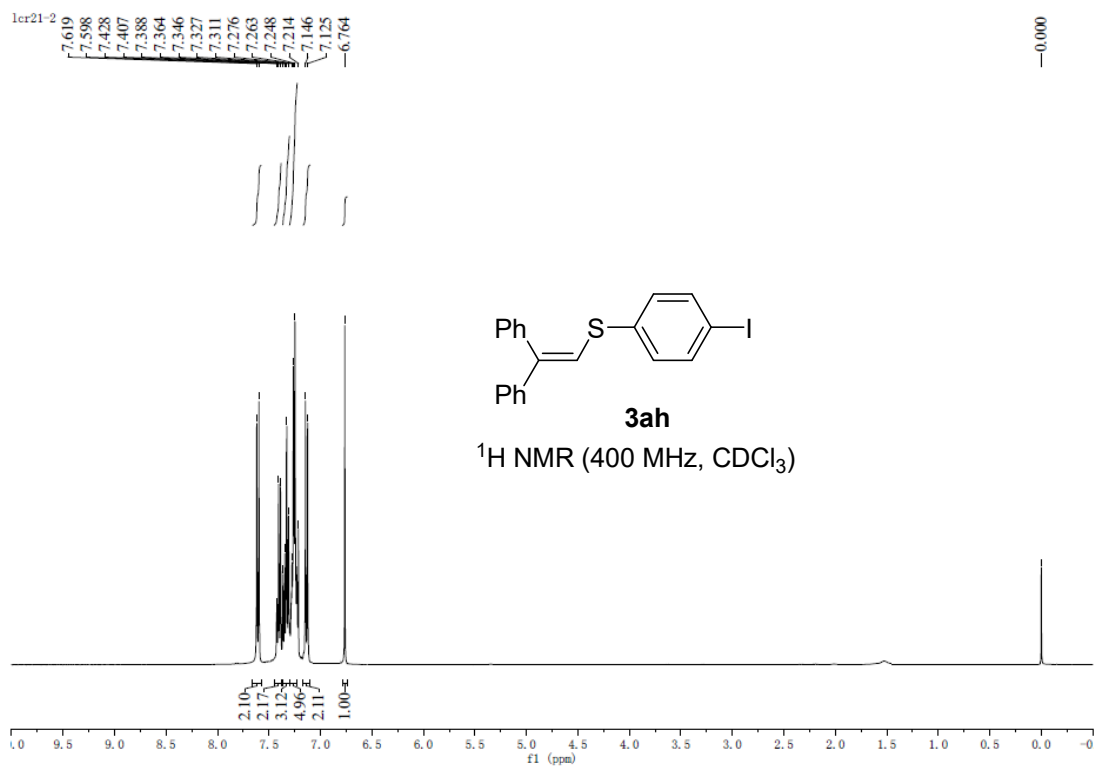


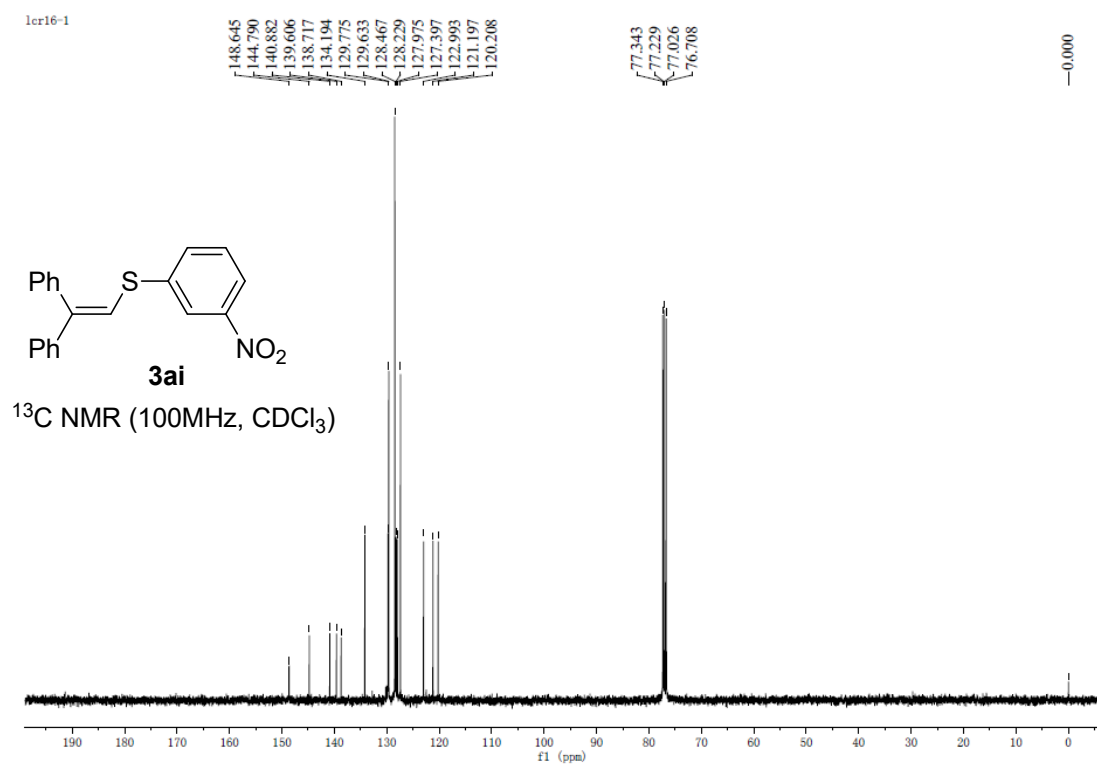
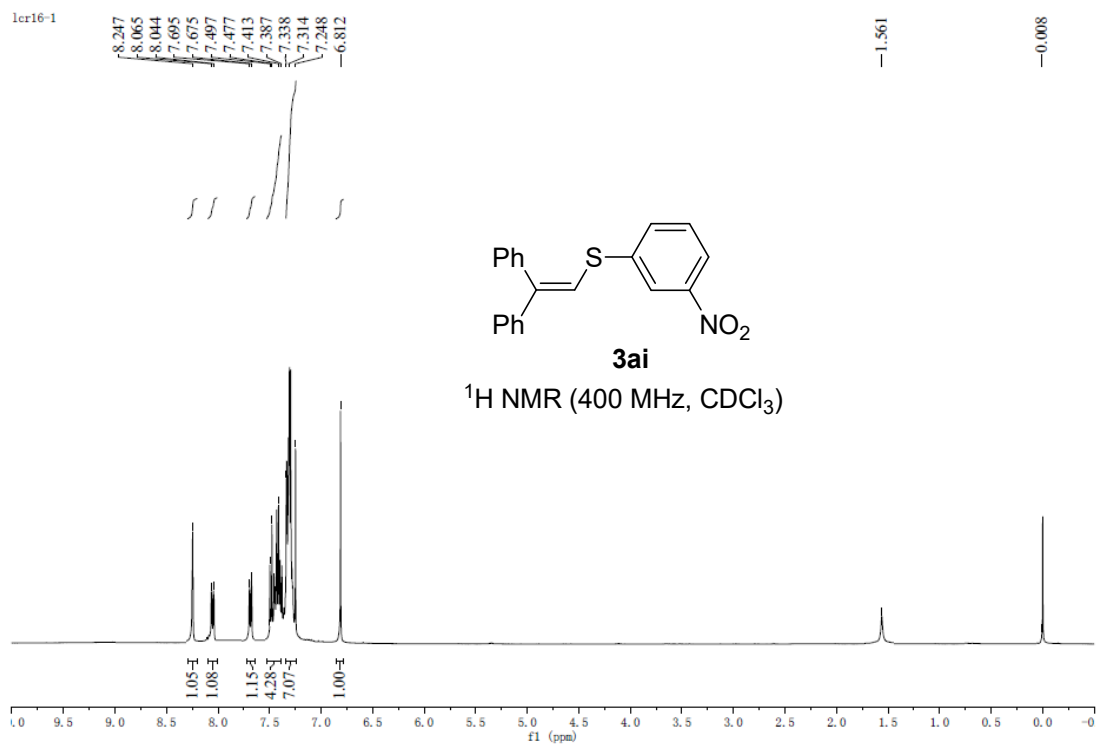


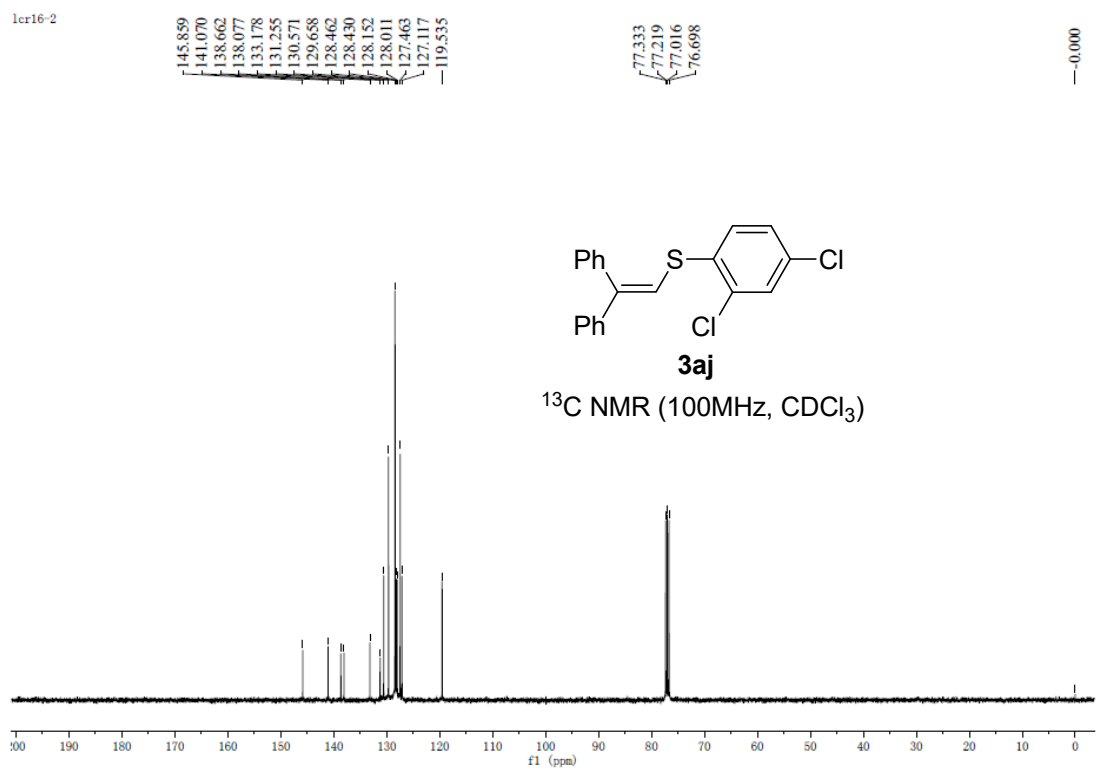
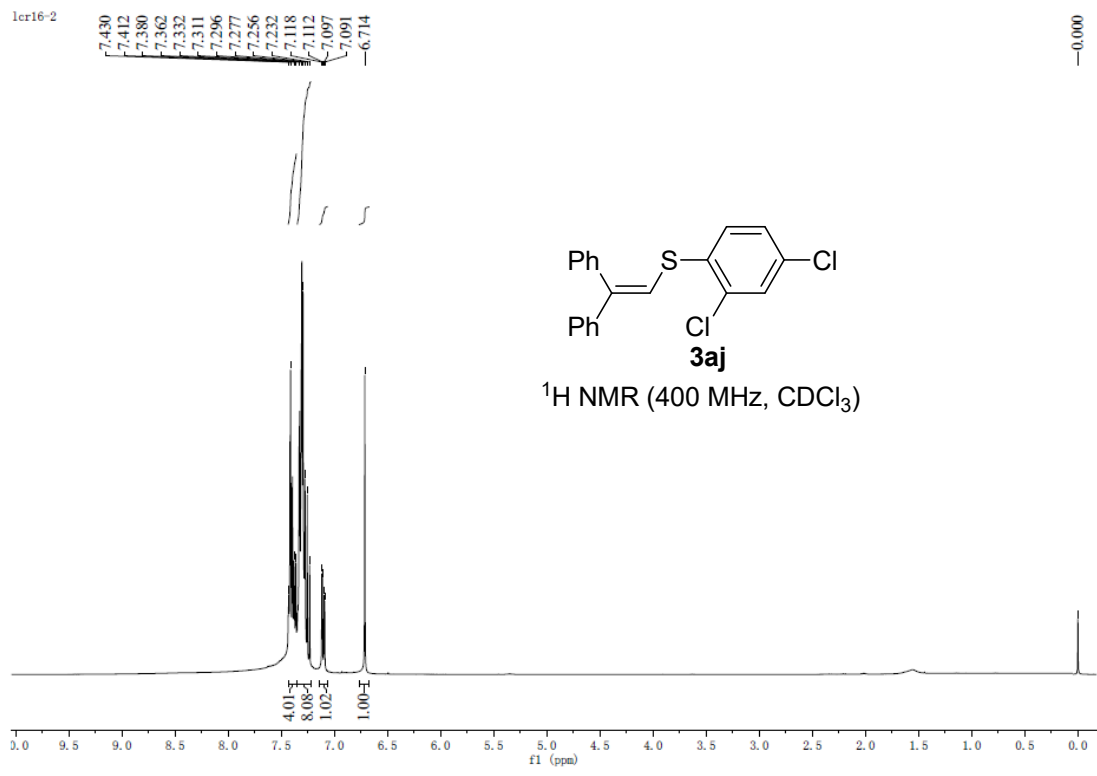


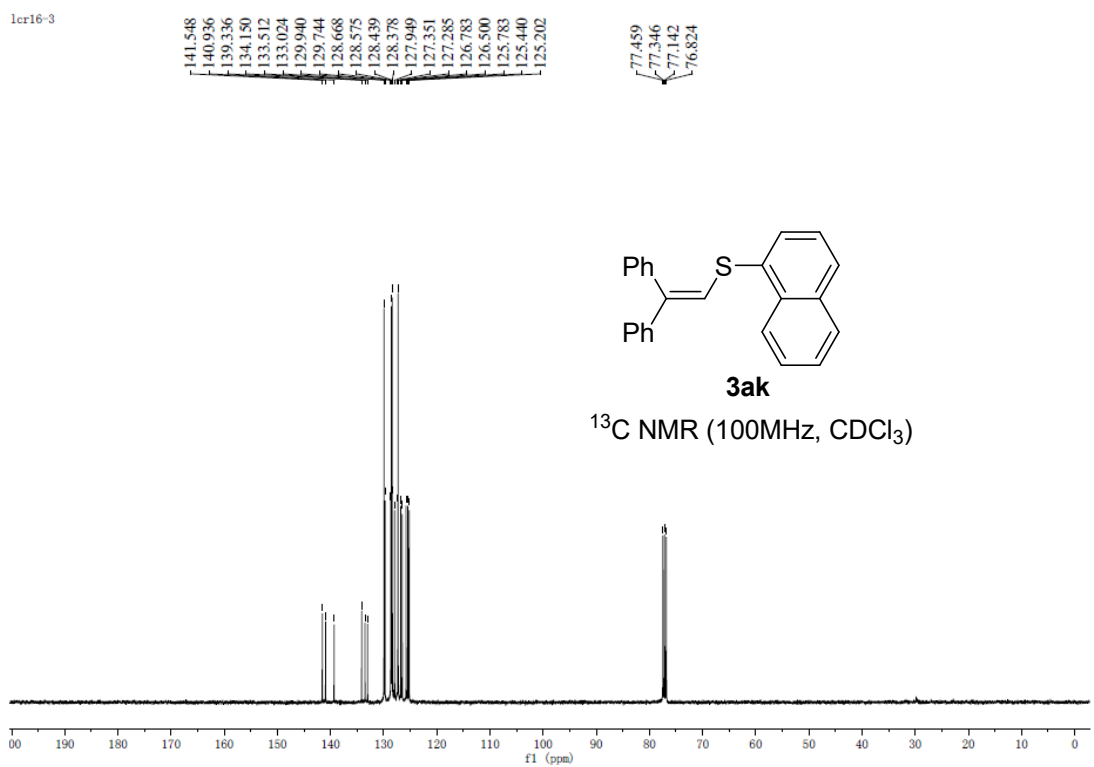
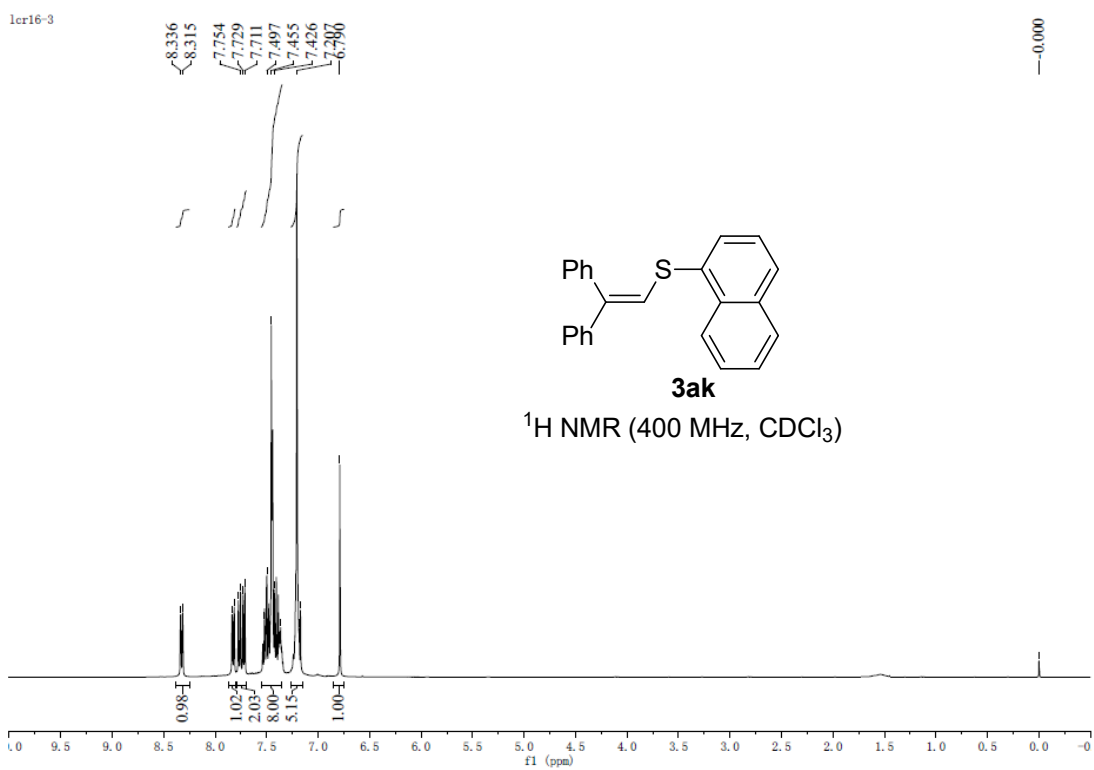




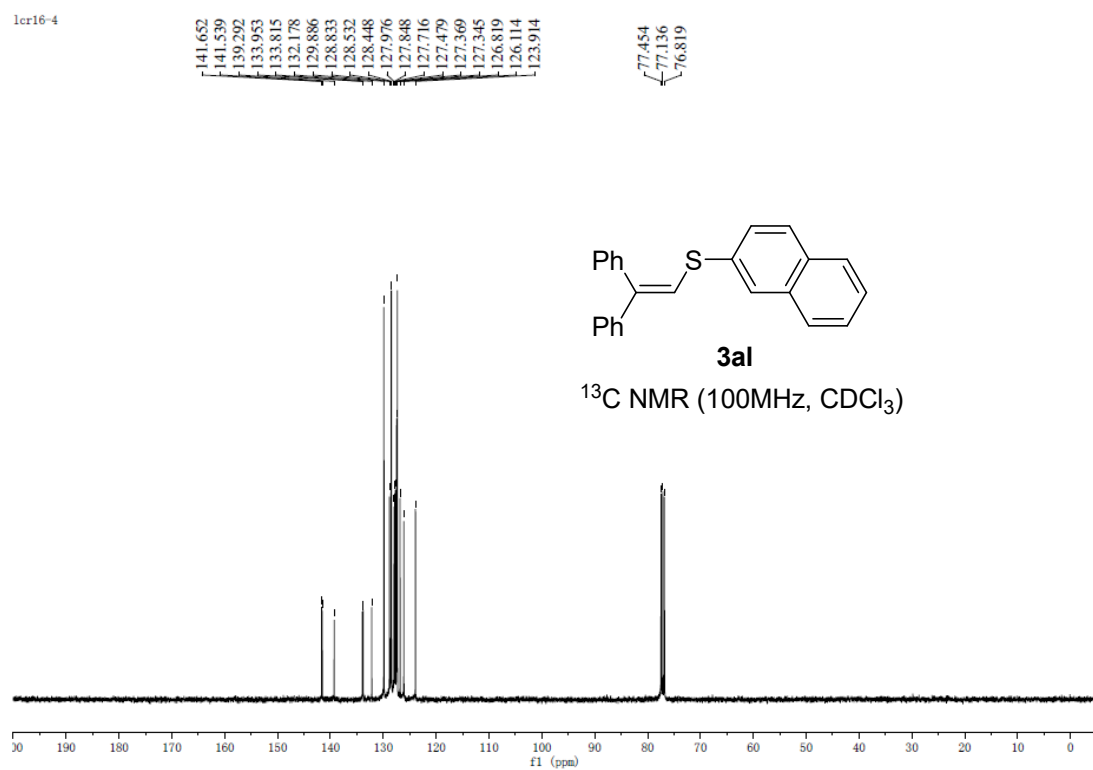
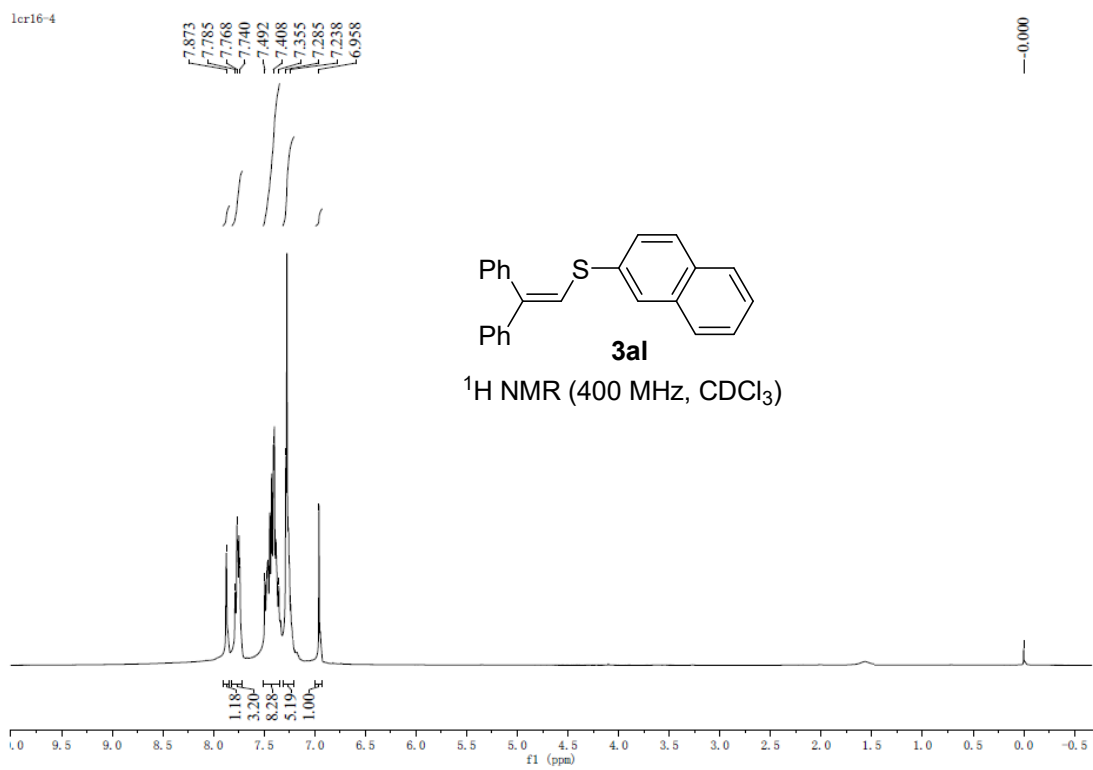


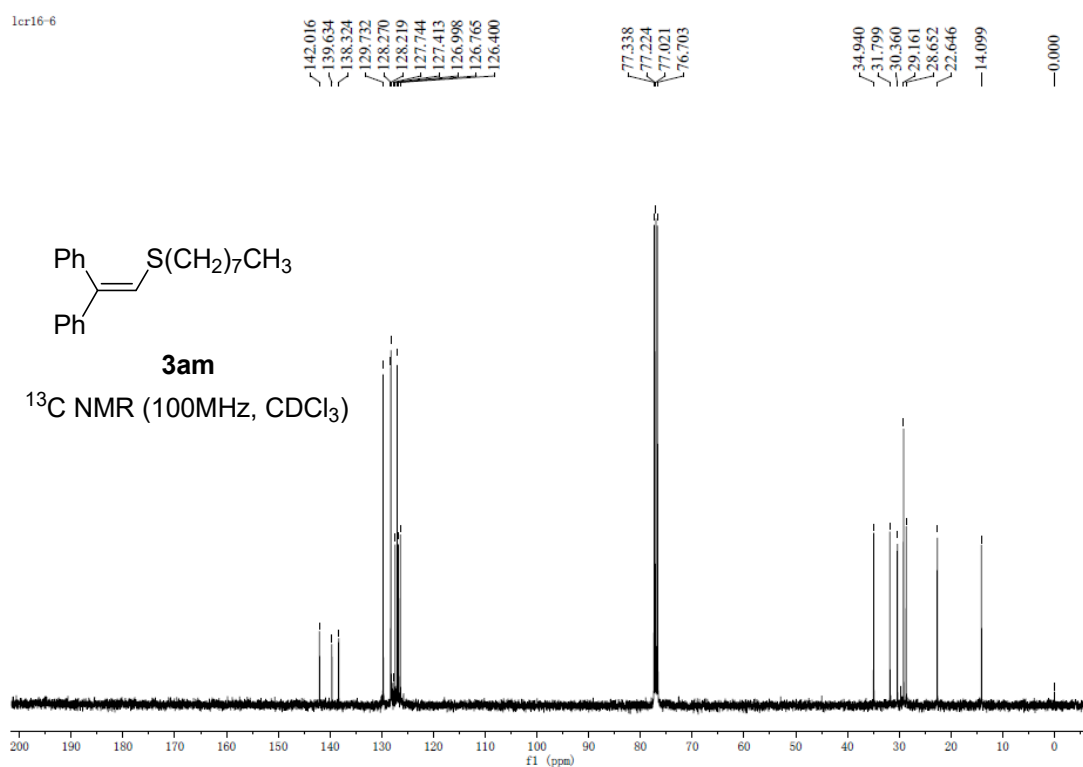
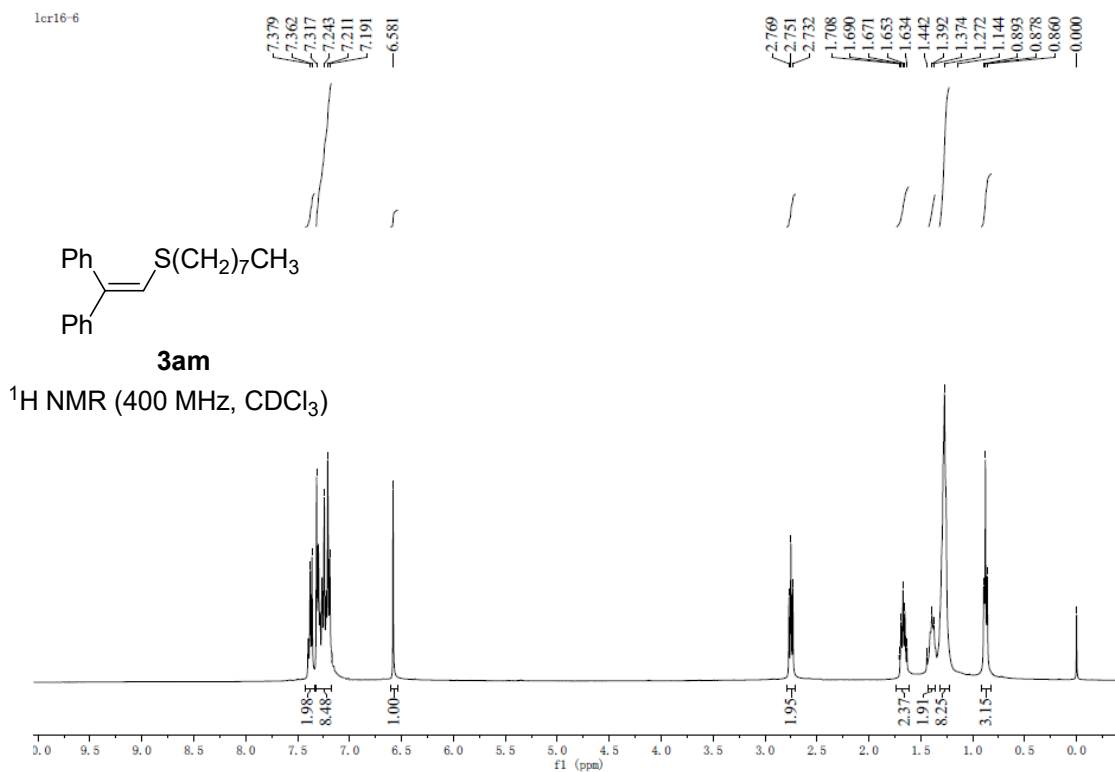




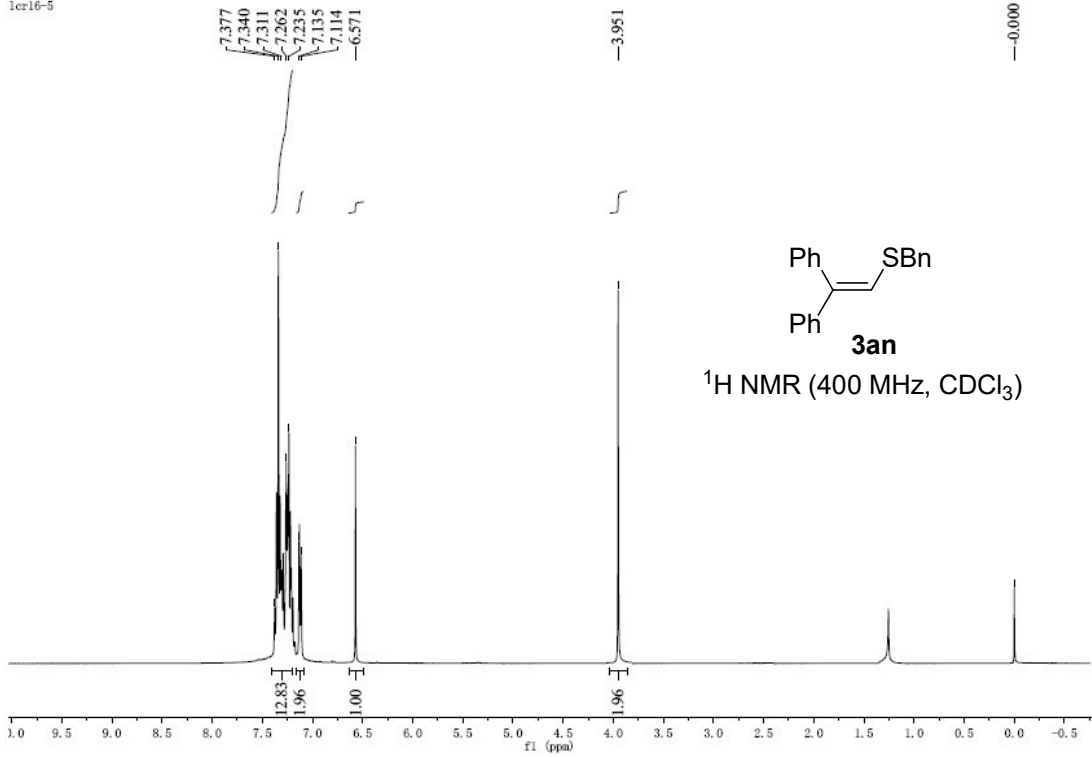








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