

# **C-SuFEx Linkage of Sulfonimidoyl Fluorides and Organotrifluoroborates**

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## **Supporting Information**

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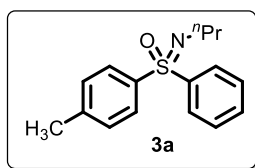
## I. General Information.

$^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra were recorded on 400 MHz NMR spectrometers (Bruker AVANCE) using  $\text{CDCl}_3$ ,  $\text{CD}_3\text{CN}$ . Chemical shifts are reported in parts per million (ppm). Chemical shifts for protons are reported in parts per million relative to chloroform ( $\delta$  7.26). Chemical shifts for carbon are reported in parts per million relative to chloroform ( $\delta$  77.0). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration. Mass spectra were recorded on a Shimadzu GCMS-QP2010 Ultra. IR spectra were recorded on TENSOR (27) Series FT-IR 241.Spectrometers. Column chromatography was performed with silica gel (300-400 mesh ASTM). Sulfonimiodyl fluoride **1**<sup>1-2</sup> and potassium aryltrifluoroborate salt **2**<sup>3</sup> were respectively obtained by reported procedures.

## II. General procedure for the synthesis of sulfoximines

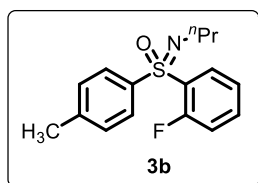
Under nitrogen atmosphere, dry CH<sub>3</sub>CN (2 mL, 0.2 M) was added to a dry 10 mL oven-dried Schlenk tube, which was equipped with sulfonimidoyl fluoride **1** (0.60 mmol, 1.5 equiv.), potassium organotrifluoroborate salt **2** (0.40 mmol, 1.0 equiv.) and a stirring bar. TMSOTf (0.08 mmol, 0.2 equiv.) was dropwise added via the microsyringe at room temperature. Then the reaction mixture was stirred at 40 °C for 30 min and quenched with saturated aqueous solution of sodium carbonate. After the extraction of DCM for three times, the organic phase was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated under reduced pressure, and the residue was purified by column chromatography to yield the corresponding sulfoximine **3**.

### III. Characterization of the products



#### Phenyl(propylimino)(*p*-tolyl)-λ<sup>6</sup>-sulfanone (**3a**).

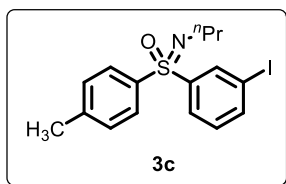
Prepared following general procedure using 4-methyl-*N*-propylbenzenesulfonimidoyl fluoride **1a** (0.6 mmol, 129.2 mg), potassium trifluoro(phenyl)borate **2a** (0.4 mmol, 73.6 mg), TMSOTf (0.08 mmol, 14.4 μL) and CH<sub>3</sub>CN (2.0 mL), the reaction was stirred at 40 °C for 30 min giving **3a** in 95% yield (102.7 mg) as a white solid by column chromatography (PE/EA = 5:1, *R*<sub>f</sub> = 0.49). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.96 (m, 2H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.50 – 7.39 (m, 3H), 7.25 (d, *J* = 8.2 Hz, 2H), 3.00 (t, *J* = 7.1 Hz, 2H), 2.36 (s, 3H), 1.74 – 1.58 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 142.9, 141.1, 137.7, 132.0, 129.7, 128.9, 128.5, 128.3, 45.6, 26.0, 21.3, 11.8. IR (film) ν 2960, 2870, 1712, 1593, 1249, 1078, 814, 711, 634, 615, 588 cm<sup>-1</sup>. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>20</sub>NOS 274.1266, found 274.1252.



#### (2-fluorophenyl)(propylimino)(*p*-tolyl)-λ<sup>6</sup>-sulfanone (**3b**).

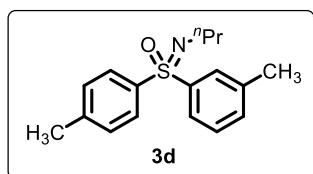
Prepared following general procedure using 4-methyl-*N*-propylbenzenesulfonimidoyl fluoride **1a** (0.6 mmol, 129.2 mg), potassium trifluoro(2-fluorophenyl) borate **2b** (0.4 mmol, 80.8 mg), TMSOTf (0.08 mmol, 14.4 μL) and CH<sub>3</sub>CN (2.0 mL), the reaction was stirred at 40 °C for 30 min giving **3b** in 83% yield (96.4 mg) as a colorless oil by column chromatography (PE/EA = 5:1, *R*<sub>f</sub> = 0.41). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.15 – 8.09 (m, 1H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.53 – 7.46 (m, 1H), 7.31 – 7.26 (m, 3H), 7.08 – 7.01 (m, 1H), 3.12 – 3.04 (m, 1H), 3.02 – 2.93 (m, 1H), 2.39 (s, 3H), 1.71 – 1.61 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.9 (d, *J* = 255.7 Hz), 143.4, 137.3, 134.6 (d, *J* = 8.4 Hz), 131.7, 129.4, 128.9 (d, *J* = 2.1 Hz), 128.5 (d, *J* = 13.7 Hz), 124.4 (d, *J* = 4.0 Hz), 117.0 (d, *J* = 22.1 Hz), 45.9, 25.9, 21.4, 11.7. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -108.0. IR (film) ν 2958, 2926, 1595, 1446, 1259, 1143, 1093, 1064,

761, 715  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ :  $[M+H]^+$  Calcd for  $\text{C}_{16}\text{H}_{19}\text{FNOS}$  292.1171, found 292.1156.



**(3-iodophenyl)(propylimino)(p-tolyl)- $\lambda^6$ -sulfanone (3c)**

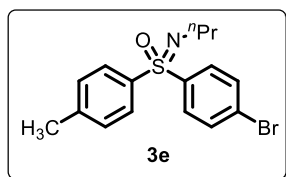
**c**). Prepared following general procedure using 4-methyl-*N*-propylbenzenesulfonimidoyl fluoride **1a** (0.6 mmol, 129.2 mg), potassium trifluoro(3-iodophenyl) borate **2c** (0.4 mmol, 124.0 mg), TMSOTf (0.2 mmol, 36  $\mu\text{L}$ ) and  $\text{CH}_3\text{CN}$  (2.0 mL), the reaction was stirred at rt for 30 min giving **3c** in 71% yield (113.0 mg) as a colorless oil by column chromatography (PE/EA = 5:1,  $R_f$  = 0.39).  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.38 (s, 1H), 7.97 (d,  $J$  = 7.9 Hz, 1H), 7.92 (d,  $J$  = 8.1 Hz, 2H), 7.88 (d,  $J$  = 7.9 Hz, 1H), 7.36 (d,  $J$  = 8.1 Hz, 2H), 7.29 – 7.23 (m, 1H), 3.14 – 3.01 (m, 2H), 2.46 (s, 3H), 1.80 – 1.69 (m, 2H), 1.05 (t,  $J$  = 7.4 Hz, 3H).  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  143.3, 143.2, 140.9, 137.2, 136.8, 130.5, 129.8, 128.5, 127.4, 94.2, 45.6, 26.0, 21.4, 11.8. **IR** (film)  $\nu$  2957, 2922, 1448, 1396, 1224, 1139, 1057, 1041, 682, 590  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ :  $[M+H]^+$  Calcd for  $\text{C}_{16}\text{H}_{19}\text{INOS}$  400.0232, found 400.0218.



**(Propylimino)(m-tolyl)(p-tolyl)- $\lambda^6$ -sulfanone (3d)**

Prepared following general procedure using 4-methyl-*N*-propylbenzenesulfonimidoyl fluoride **1a** (0.6 mmol, 129.2 mg), potassium trifluoro(*m*-tolyl)borate **2d** (0.4 mmol, 78.4 mg), TMSOTf (0.2 mmol, 36  $\mu\text{L}$ ) and  $\text{CH}_3\text{CN}$  (2.0 mL), the reaction was stirred at rt for 30 min giving **3d** in 92% yield (106.1 mg) as a colorless oil by column chromatography (PE/EA = 5:1,  $R_f$  = 0.38).  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (d,  $J$  = 7.8 Hz, 2H), 7.81 – 7.74 (m, 2H), 7.39 – 7.31 (m, 1H), 7.31 – 7.24 (m, 3H), 3.02 (t,  $J$  = 7.2 Hz, 2H), 2.38 (s, 3H), 2.39 (s, 3H), 1.75 – 1.63 (m, 2H), 0.98 (t,  $J$  = 7.4 Hz, 3H).  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.8, 141.0, 139.0, 137.9, 132.8, 129.6, 128.7, 128.5(9), 128.5(1), 125.4, 45.7, 26.1, 21.3, 21.2, 11.8. **IR** (film)  $\nu$  2957, 2926, 1595, 1475, 1452, 1228, 1141, 788, 696  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ :  $[M+H]^+$  Calcd for

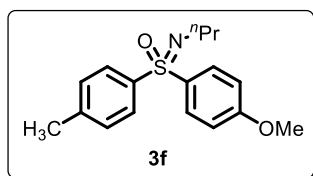
C<sub>17</sub>H<sub>22</sub>NOS 288.1422, found 288.1408.



**(4-bromophenyl)(propylimino)(*p*-tolyl)-λ<sup>6</sup>-sulfanone**

**(3e).** Prepared following general procedure using 4-methyl-*N*-propylbenzenesulfonimidoyl fluoride **1a** (0.6 mmol, 129.2 mg), potassium (4-bromophenyl)trifluorob-

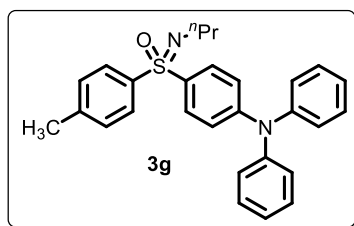
orate **2e** (0.4 mmol, 104.8 mg), TMSOTf (0.08 mmol, 14.4 μL) and CH<sub>3</sub>CN (2.0 mL), the reaction was stirred at 40 °C for 30 min giving **3e** in 79% yield (110.8 mg) as a colorless oil by column chromatography (PE/EA = 5:1, R<sub>f</sub> = 0.49). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.81 (m, 4H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 3.02 – 2.94 (m, 2H), 2.37 (s, 3H), 1.71 – 1.59 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 143.3, 140.4, 137.3, 132.2, 130.0, 129.8, 128.5, 127.1, 45.6, 26.0, 21.4, 11.8. **IR** (film) ν 2957, 2870, 1737, 1570, 1467, 1228, 1064, 1008, 742, 665 cm<sup>-1</sup>. **HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>19</sub>BrNOS 352.0371; 354.0350, found 352.0356; 354.0334.



**(4-methoxyphenyl)(propylimino)(*p*-tolyl)-λ<sup>6</sup>-sulfanone**

**one (3f).** Prepared following general procedure using 4-methyl-*N*-propylbenzenesulfonimidoyl fluoride **1a** (0.6 mmol, 129.2 mg), potassium

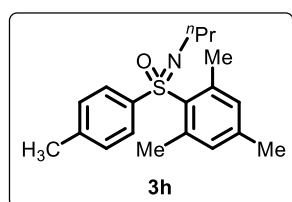
trifluoro(4-methoxyphenyl)borate **2f** (0.4 mmol, 85.6 mg), TMSOTf (0.08 mmol, 14.4 μL) and CH<sub>3</sub>CN (2.0 mL), the reaction was stirred at 40 °C for 30 min giving **3f** in 62% yield (71.5 mg) as a colorless oil by column chromatography (PE/EA = 5:1, R<sub>f</sub> = 0.21). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.88 (d, *J* = 8.9 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 2.97 (t, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 1.73 – 1.59 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 162.5, 142.6, 138.4, 132.5, 130.4, 129.6, 128.2, 114.2, 55.4, 45.7, 26.1, 21.3, 11.8. **IR** (film) ν 2958, 2926, 1591, 1492, 1307, 1253, 1222, 1095, 1026, 754 cm<sup>-1</sup>. **HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>22</sub>NO<sub>2</sub>S 304.1371, found 304.1358.



**(4-(diphenylamino)phenyl)(propylimino)(*p*-tolyl)-λ<sup>6</sup>-sulfanone (3g).**

Prepared following general procedure using 4-methyl-*N*-propylbenzenesulfonimidoyl fluoride **1a** (0.6 mmol, 129.2 mg), potassium (4-(diphenylamino)phenyl)trifluoroborate **2g** (0.4

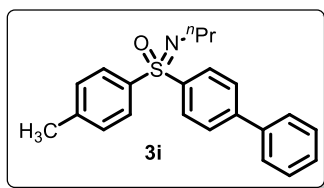
mmol, 140.0 mg), TMSOTf (0.2 mmol, 36 μL) and CH<sub>3</sub>CN (2.0 mL), the reaction was stirred at rt for 30 min giving **3g** in 66% yield (117.0 mg) as a colorless oil by column chromatography (PE/EA = 5:1, *R<sub>f</sub>* = 0.32). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.86 – 7.81 (m, 2H), 7.41 – 7.33 (m, 6H), 7.23 – 7.17 (m, 6H), 7.09 – 7.05 (m, 2H), 3.21 – 2.99 (m, 2H), 2.47 (s, 3H), 1.84 – 1.67 (m, 2H), 1.06 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 151.2, 146.3, 142.4, 138.5, 131.7, 129.6, 129.5, 128.3, 125.8, 124.5, 120.0, 45.7, 26.1, 21.3, 11.8. IR (film) ν 3061, 2957, 2870, 1579, 1487, 1267, 1224, 1095, 1087 754, 675 cm<sup>-1</sup>. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>28</sub>H<sub>29</sub>N<sub>2</sub>OS 441.2001, found 441.1984.



**Mesityl(propylimino)(*p*-tolyl)-λ<sup>6</sup>-sulfanone (3h).**

Prepared following general procedure using 4-methyl-*N*-propylbenzenesulfonimidoyl fluoride **1a** (0.6 mmol, 129.2 mg), potassium trifluoro(mesityl)borate **2h**

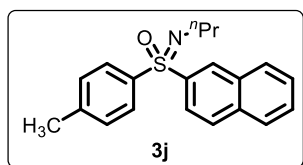
(0.4 mmol, 90.4 mg), TMSOTf (0.08 mmol, 14.4 μL) and CH<sub>3</sub>CN (2.0 mL), the reaction was stirred at 40 °C for 30 min giving **3h** in 78% yield (94.0 mg) as a colorless oil by column chromatography (PE/EA = 5:1, *R<sub>f</sub>* = 0.63). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.90 (s, 2H), 3.14 – 3.00 (m, 1H), 2.88 – 2.77 (m, 1H), 2.50 (s, 6H), 2.36 (s, 3H), 2.27 (s, 3H), 1.71 – 1.56 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 142.2, 141.6, 140.4, 140.3, 133.6, 132.2, 129.0, 127.2, 45.6, 25.9, 22.9, 21.3, 20.7, 11.9. IR (film) ν 2957, 2870, 1599, 1450, 1224, 1141, 1093, 1016, 717, 705, 615 cm<sup>-1</sup>. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>26</sub>NOS 316.1735, found 316.1732.



**[1,1'-biphenyl]-4-yl(propylimino)(*p*-tolyl)-λ<sup>6</sup>-sulfanone**

**none (3i).** Prepared following general procedure using 4-methyl-*N*-propylbenzenesulfonimidoyl fluoride **1a** (0.6 mmol, 129.2 mg), potassium

[1,1'-biphenyl]-4-yltrifluoroborate **2i** (0.4 mmol, 104.0 mg), TMSOTf (0.08 mmol, 14.4 μL) and CH<sub>3</sub>CN (2.0 mL), the reaction was stirred at 40 °C for 30 min giving **3i** in 98% yield (137.8 mg) as a colorless oil by column chromatography (PE/EA = 5:1, R<sub>f</sub> = 0.31). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.03 (d, *J* = 8.5 Hz, 2H), 7.90 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.57 – 7.52 (m, 2H), 7.47 – 7.41 (m, 2H), 7.40 – 7.35 (m, 1H), 7.28 (d, *J* = 8.1 Hz, 2H), 3.05 (t, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 1.78 – 1.64 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 144.9, 142.9, 139.8, 139.3, 137.9, 129.7, 128.8, 128.5, 128.1, 127.6, 127.1, 45.7, 26.1, 21.3, 11.8. IR (film) ν 3061, 2957, 2870, 1593, 1479, 1396, 1224, 1141, 1095, 841, 675 cm<sup>-1</sup>. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>24</sub>NOS 350.1579, found 350.1563.

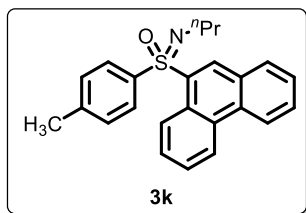


**Naphthalen-2-yl(propylimino)(*p*-tolyl)-λ<sup>6</sup>-sulfanone**

**(3j).** Prepared following general procedure using 4-methyl-*N*-propylbenzenesulfonimidoyl fluoride **1a** (0.6 mmol, 129.2 mg), potassium

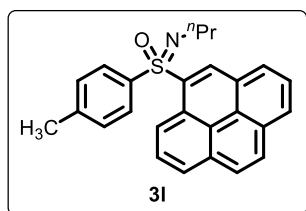
trifluoro(naphthalen-2-yl)borate **2j** (0.4 mmol, 93.6 mg), TMSOTf (0.12 mmol, 21.6 μL) and CH<sub>3</sub>CN (2.0 mL), the reaction was stirred at 40 °C for 30 min giving **3j** in 95% yield (123.1 mg) as a colorless oil by column chromatography (PE/EA = 5:1, R<sub>f</sub> = 0.35). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.58 (s, 1H), 7.97 – 7.81 (m, 6H), 7.60 – 7.51 (m, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 3.11 – 3.00 (m, 2H), 2.34 (s, 3H), 1.77 – 1.64 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 143.0, 138.1, 137.8, 134.5, 132.4, 129.7(3), 129.7(1), 129.1, 128.5, 128.4, 127.7, 127.1, 123.6, 45.8, 26.1, 21.3, 11.8. IR (film) ν 3055, 2957, 2870, 1593, 1491, 1253, 1124, 1082, 812, 673 cm<sup>-1</sup>. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>22</sub>NOS 324.1422, found 324.1408.





**Phenanthren-9-yl(propylimino)(*p*-tolyl)- $\lambda^6$ -sulfanone (**3k**).** Prepared following general procedure using 4-methyl-*N*-propylbenzenesulfonimidoyl fluoride **1a** (0.6 mmol, 129.2 mg), potassium trifluoro(phenanthrene-9-yl)borate **2k** (0.4 mmol, 113.6 mg), TMSOTf (0.2

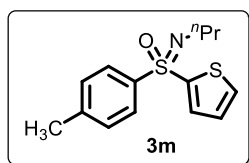
mmol, 36.0  $\mu$ L) and CH<sub>3</sub>CN (2.0 mL), the reaction was stirred at rt for 30 min giving **3k** in 63% yield (97.4 mg) as a colorless oil by column chromatography (PE/EA = 5:1, *R*<sub>f</sub> = 0.31). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.97 (s, 1H), 8.88 (dd, *J* = 8.3, 1.3 Hz, 1H), 8.72 – 8.60 (m, 2H), 8.09 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.81 – 7.74 (m, 1H), 7.72 – 7.66 (m, 1H), 7.65 – 7.60 (m, 1H), 7.59 – 7.53 (m, 1H), 7.21 (d, *J* = 8.2 Hz, 2H), 3.22 – 3.11 (m, 1H), 3.04 – 2.94 (m, 1H), 2.32 (s, 3H), 1.78 – 1.60 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  142.9, 138.0, 134.3, 133.8, 132.4, 131.1, 130.4, 129.8, 129.4(6), 129.4(1), 128.0, 127.3, 127.2, 127.0, 126.8, 125.6, 123.0, 122.6, 45.9, 26.0, 21.3, 11.8. **IR** (film)  $\nu$  2958, 2868, 1491, 1450, 1226, 1130, 1089, 860, 756, 675 cm<sup>-1</sup>. **HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>24</sub>NOS 374.1579, found 374.1563.



**Pyren-9-yl(propylimino)(*p*-tolyl)- $\lambda^6$ -sulfanone (**3l**).** Prepared following general procedure using 4-methyl-*N*-propylbenzenesulfonimidoyl fluoride **1a** (0.6 mmol, 129.2 mg), potassium trifluoro(pyren-2-yl)borate **2l** (0.4 mmol, 123.3 mg),

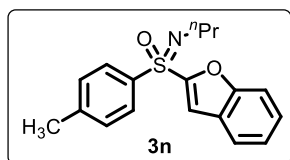
TMSOTf (0.08 mmol, 14.4  $\mu$ L) and CH<sub>3</sub>CN (2.0 mL), the reaction was stirred at 40 °C for 30 min giving **3l** in 68% yield (106.9 mg) as a yellow oil by column chromatography (PE/EA = 5:1, *R*<sub>f</sub> = 0.21). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.21 (d, *J* = 8.0 Hz, 1H), 9.02 (d, *J* = 8.2 Hz, 1H), 8.27 (d, *J* = 8.3 Hz, 1H), 8.21 (d, *J* = 7.6 Hz, 2H), 8.18 – 8.12 (m, 2H), 8.09 – 7.98 (m, 4H), 7.21 (d, *J* = 8.1 Hz, 2H), 3.22 – 3.14 (m, 1H), 3.08 – 3.00 (m, 1H), 2.30 (s, 3H), 1.80 – 1.69 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  142.7, 138.8, 134.6, 131.9, 130.8, 129.9(9), 129.9(2), 129.4(6), 129.4(0), 128.9, 128.0, 127.0,

126.5, 126.4, 125.1, 124.2, 123.9, 123.3, 45.9, 26.1, 21.3, 11.9. **IR** (film)  $\nu$  2957, 2870, 1712, 1591, 1253, 1190, 1163, 850, 756, 626  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ :  $[M+H]^+$  Calcd for  $\text{C}_{26}\text{H}_{24}\text{NOS}$  398.1579, found 398.1567.



**(Propylimino)(thiophen-2-yl)(*p*-tolyl)- $\lambda^6$ -sulfanone (3m).**

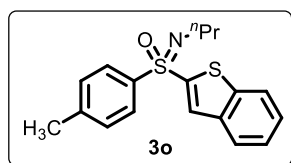
Prepared following general procedure using 4-methyl-*N*-propylbenzenesulfonimidoyl fluoride **1a** (0.6 mmol, 129.2 mg), potassium trifluoro(thiophen-2-yl)borate **2m** (0.4 mmol, 76.0 mg), TMSOTf (0.08 mmol, 14.4  $\mu\text{L}$ ) and  $\text{CH}_3\text{CN}$  (2.0 mL), the reaction was stirred at 40  $^\circ\text{C}$  for 30 min giving **3m** in 79% yield (87.8 mg) as a white solid by column chromatography (PE/EA = 5:1,  $R_f$  = 0.58).  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (d,  $J$  = 8.1 Hz, 2H), 7.54 (d,  $J$  = 5.0 Hz, 1H), 7.50 (d,  $J$  = 3.5 Hz, 1H), 7.25 (d,  $J$  = 8.1 Hz, 2H), 7.01 (dd,  $J$  = 4.8, 3.9 Hz, 1H), 3.14 – 2.99 (m, 2H), 2.36 (s, 3H), 1.73 – 1.59 (m, 2H), 0.95 (t,  $J$  = 7.3 Hz, 3H).  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  143.1(2), 143.1(0), 138.4, 133.2, 132.8, 129.6, 127.9, 127.7, 45.8, 25.9, 21.3, 11.7. **IR** (film)  $\nu$  2957, 2928, 2872, 1597, 1400, 1255, 1222, 1126, 1001, 746, 678  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ :  $[M+H]^+$  Calcd for  $\text{C}_{14}\text{H}_{18}\text{NOS}_2$  280.0830, found 280.0816.



**Benzofuran-2-yl(propylimino)(*p*-tolyl)- $\lambda^6$ -sulfanone (3n).**

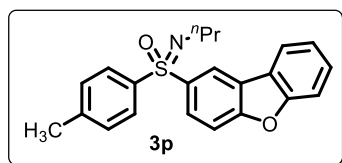
Prepared following general procedure using 4-methyl-*N*-propylbenzenesulfonimidoyl fluoride **1a** (0.6 mmol, 129.2 mg), potassium benzofuran-2-yltrifluoroborate **2n** (0.4 mmol, 89.6 mg), TMSOTf (0.08 mmol, 14.4  $\mu\text{L}$ ) and  $\text{CH}_3\text{CN}$  (2.0 mL), the reaction was stirred at 40  $^\circ\text{C}$  for 30 min giving **3n** in 99% yield (125.0 mg) as a yellow oil by column chromatography (PE/EA = 5:1,  $R_f$  = 0.41).  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (d,  $J$  = 8.4 Hz, 2H), 7.61 (d,  $J$  = 7.8 Hz, 1H), 7.48 – 7.44 (m, 2H), 7.38 – 7.32 (m, 1H), 7.29 – 7.22 (m, 3H), 3.21 – 3.13 (m, 1H), 3.06 – 2.98 (m, 1H), 2.35 (s, 3H), 1.72 – 1.60 (m, 2H), 0.95 (t,  $J$  = 7.4 Hz, 3H).  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.2, 151.2, 143.9, 135.9, 129.6, 128.6, 127.0, 126.5, 123.7, 122.5, 114.1, 112.2, 46.0, 25.8, 21.4, 11.7. **IR** (film)  $\nu$  2958, 2872, 1595, 1533, 1442, 1284, 1251, 1143, 927, 812

cm<sup>-1</sup>. **HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>20</sub>NO<sub>2</sub>S 314.1215, found 314.1201.



**Benzo[*b*]thiophen-2-yl(propylimino)(*p*-tolyl)-λ<sup>6</sup>-sulfone (3o).** Prepared following general procedure using 4-methyl-*N*-propylbenzenesulfonimidoyl fluoride

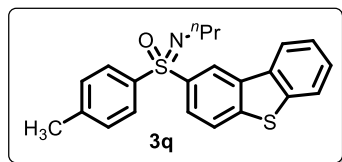
**1a** (0.6 mmol, 129.2 mg), potassium benzo[*b*]thiophen-2-yltrifluoroborate **2o** (0.4 mmol, 96.0 mg), TMSOTf (0.08 mmol, 14.4 μL) and CH<sub>3</sub>CN (2.0 mL), the reaction was stirred at 40 °C for 30 min giving **3o** in 93% yield (122.2 mg) as a colorless oil by column chromatography (PE/EA = 5:1, *R<sub>f</sub>* = 0.43). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.84 – 7.76 (m, 3H), 7.43 – 7.35 (m, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 3.22 – 3.07 (m, 2H), 2.38 (s, 3H), 1.78 – 1.65 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 143.8, 143.5, 143.0, 138.3, 137.9, 130.0, 129.7, 128.3, 126.6, 125.4, 125.0, 122.5, 46.0, 26.0, 21.4, 11.8. **IR** (film) ν 3061, 2957, 2870, 1593, 1498, 1255, 1141, 910, 852, 746 cm<sup>-1</sup>. **HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>20</sub>NOS<sub>2</sub> 330.0986, found 330.0972.



**Dibenzob[*b,d*]furan-2-yl(propylimino)(*p*-tolyl)-λ<sup>6</sup>-sulfanone (3p).** Prepared following general procedure using 4-methyl-*N*-propylbenzenesulfonimidoyl fluoride **1a** (0.6 mmol, 129.2 mg), potassium

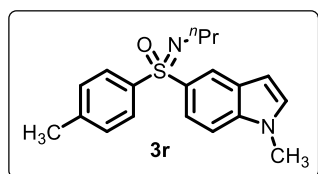
dibenzob[*b,d*]furan-2-yltrifluoroborate **2p** (0.4 mmol, 109.6 mg), TMSOTf (0.2 mmol, 36.0 μL) and CH<sub>3</sub>CN (2.0 mL), the reaction was stirred at rt for 30 min giving **3p** in 60% yield (87.6 mg) as a yellow oil by column chromatography (PE/EA = 5:1, *R<sub>f</sub>* = 0.29). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.61 (d, *J* = 1.9 Hz, 1H), 8.04 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.96 (dd, *J* = 7.3, 1.0 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.50 – 7.44 (m, 1H), 7.38 – 7.33 (m, 1H), 7.27 – 7.23 (m, 2H), 3.05 (t, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 1.77 – 1.65 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 157.9, 156.8, 142.9, 138.2, 135.7, 129.7, 128.4, 128.1, 127.5, 124.9, 123.4, 123.2, 121.9, 121.1, 112.1, 111.8, 45.8, 26.2, 21.3, 11.8. **IR** (film) ν 2957, 2870, 1593,

1446, 1442, 1248, 1226, 1082, 1020, 841, 748  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ :  $[M+H]^+$   
Calcd for  $\text{C}_{22}\text{H}_{22}\text{NO}_2\text{S}$  364.1371, found 364.1366.



**Dibenzo[*b,d*]thiophen-2-yl(propylimino)(*p*-tolyl)- $\lambda^6$ -sulfanone (3q).** Prepared following general procedure using 4-methyl-*N*-propylbenzenesulfonimidoyl fluoride **1a** (0.6 mmol, 129.2 mg), potassium

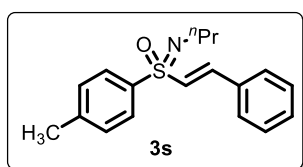
dibenzo[*b,d*]thiophen-2-yltrifluoroborate **2q** (0.4 mmol, 116.1 mg), TMSOTf (0.2 mmol, 36.0  $\mu\text{L}$ ) and  $\text{CH}_3\text{CN}$  (2.0 mL), the reaction was stirred at rt for 30 min giving **3q** in 54% yield (81.6 mg) as a yellow oil by column chromatography (PE/EA = 5:1,  $R_f$  = 0.33).  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.77 (d,  $J$  = 1.7 Hz, 1H), 8.23 – 8.18 (m, 1H), 7.96 (dd,  $J$  = 8.5, 1.8 Hz, 1H), 7.92 (d,  $J$  = 8.3 Hz, 2H), 7.87 (d,  $J$  = 8.5 Hz, 1H), 7.84 – 7.76 (m, 1H), 7.49 – 7.44 (m, 2H), 7.25 (d,  $J$  = 6.4 Hz, 2H), 3.09 – 3.04 (m, 2H), 2.34 (s, 3H), 1.77 – 1.66 (m, 2H), 0.99 (t,  $J$  = 7.3 Hz, 3H).  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  143.5, 142.9, 139.7, 138.1, 137.4, 135.8, 134.6, 129.7, 128.4, 127.5, 125.8, 124.8, 123.2, 122.7, 122.0, 45.8, 26.1, 21.3, 11.8. **IR** (film)  $\nu$  3059, 2957, 2870, 1595, 1456, 1226, 1141, 1091, 812, 732, 677  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ :  $[M+H]^+$  Calcd for  $\text{C}_{22}\text{H}_{22}\text{NOS}_2$  380.1143, found 380.1128.



**(1-methyl-1*H*-indol-5-yl)(propylimino)(*p*-tolyl)- $\lambda^6$ -sulfanone (3r).** Prepared following general procedure using 4-methyl-*N*-propylbenzenesulfonimidoyl fluoride **1a** (0.6 mmol, 129.2 mg), potassium

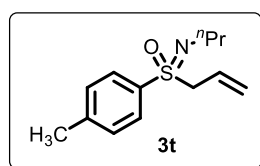
trifluoro(1-methyl-1*H*-indol-5-yl)borate **2r** (0.4 mmol, 94.8 mg), TMSOTf (0.2 mmol, 36.0  $\mu\text{L}$ ) and  $\text{CH}_3\text{CN}$  (2.0 mL), the reaction was stirred at rt for 30 min giving **3r** in 66% yield (87.5 mg) as a yellow solid by column chromatography (PE/EA = 5:1,  $R_f$  = 0.08).  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.31 (d,  $J$  = 1.8 Hz, 1H), 7.87 (d,  $J$  = 8.3 Hz, 2H), 7.77 (dd,  $J$  = 8.7, 1.8 Hz, 1H), 7.33 (d,  $J$  = 8.7 Hz, 1H), 7.21 (d,  $J$  = 8.1 Hz, 2H), 7.12 (d,  $J$  = 3.2 Hz, 1H), 6.57 (d,  $J$  = 3.1 Hz, 1H), 3.77 (s, 3H), 3.03 (t,  $J$  = 7.0 Hz, 2H), 2.33 (s, 3H), 1.75 – 1.63 (m, 2H), 0.97 (t,  $J$  =

7.4 Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 142.2, 139.1, 138.1, 131.3, 130.7, 129.5, 128.2, 128.1, 122.8, 121.3, 109.5, 102.5, 45.9, 33.0, 26.2, 21.3, 11.9. **IR** (film) ν 2957, 2924, 2870, 1604, 1512, 1220, 1136. 1080, 1055, 814, 678 cm<sup>-1</sup>. **HRMS** (ESI) m/z: [M+H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>23</sub>N<sub>2</sub>OS 327.1531, found 327.1517.



**(E)-(propylimino)(styryl)(p-tolyl)-λ<sup>6</sup>-sulfanone (3s).**

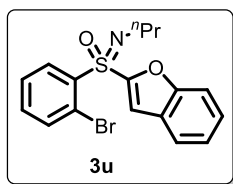
Prepared following general procedure using 4-methyl-N-propylbenzenesulfonimidoyl fluoride **1a** (0.6 mmol, 129.2 mg), potassium (E)-trifluoro(styryl)borate **2s** (0.4 mmol, 84.0 mg), TMSOTf (0.12 mmol, 21.6 μL) and CH<sub>3</sub>CN (2.0 mL), the reaction was stirred at 40 °C for 30 min giving **3s** in 72% yield (86.6 mg) as a colorless oil by column chromatography (PE/EA = 5:1, R<sub>f</sub> = 0.35). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.83 (d, J = 8.3 Hz, 2H), 7.52 (d, J = 15.4 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.37 – 7.29 (m, 5H), 6.88 (d, J = 15.4 Hz, 1H), 3.08 – 2.99 (m, 1H), 2.98 – 2.90 (m, 1H), 2.41 (s, 3H), 1.70 – 1.58 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 143.3, 141.8, 137.0, 132.9, 130.5, 129.9, 128.8, 128.6, 128.3, 128.0, 45.6, 26.1, 21.4, 11.8. **IR** (film) ν 2957, 2872, 1710, 1448, 1361, 1253, 1219, 1080, 1039, 785 cm<sup>-1</sup>. **HRMS** (ESI) m/z: [M+H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>22</sub>NOS 300.1422, found 300.1407.



**Allyl(propylimino)(p-tolyl)-λ<sup>6</sup>-sulfanone (3t).**

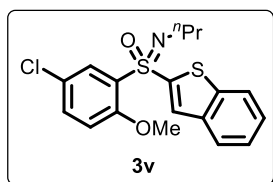
Prepared following general procedure using 4-methyl-N-propylbenzenesulfonimidoyl fluoride **1a** (0.6 mmol, 129.2 mg), potassium allyltrifluoroborate **2t** (0.4 mmol, 94.8 mg), TMSOTf (0.12 mmol, 21.6 μL) and CH<sub>3</sub>CN (2.0 mL), the reaction was stirred at 40 °C for 30 min giving **3t** in 54% yield (51.5 mg) as a yellow oil by column chromatography (PE/EA = 5:1, R<sub>f</sub> = 0.29). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.67 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 5.81 – 5.68 (m, 1H), 5.21 (dd, J = 10.2, 1.2 Hz, 1H), 5.01 (dd, J = 17.1, 1.3 Hz, 1H), 3.81 (d, J = 7.3 Hz, 2H), 2.98 – 2.89 (m, 1H), 2.87 – 2.75 (m, 1H), 2.40 (s, 3H), 1.60 – 1.49 (m, 2H), 0.87 (t, J = 7.4 Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 143.4, 134.4, 129.6, 129.5, 125.6, 123.5, 60.9, 45.7, 26.0, 21.4, 11.6. **IR** (film) ν 2957, 2872,

1595, 1421, 1253, 1222, 1136, 1082, 885, 773, 640  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ :  $[M+H]^+$  Calcd for  $\text{C}_{13}\text{H}_{20}\text{NOS}$  238.1266, found 238.1254.



**Benzofuran-2-yl(2-bromophenyl)(propylimino)- $\lambda^6$ -sulfanone (3u).**

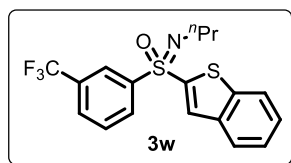
Prepared following general procedure using 2-bromo-*N*-propylbenzenesulfonimidoyl fluoride **1b** (0.6 mmol, 168.1 mg), potassium benzofuran-2-yltrifluoroborate **2n** (0.4 mmol, 89.6 mg), TMSOTf (0.08 mmol, 14.4  $\mu\text{L}$ ) and  $\text{CH}_3\text{CN}$  (2.0 mL), the reaction was stirred at 40  $^\circ\text{C}$  for 30 min giving **3u** in 72% yield (109.5 mg) as a yellow oil by column chromatography (PE/EA = 5:1,  $R_f$  = 0.60).  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.53 (dd,  $J$  = 8.0, 1.7 Hz, 1H), 7.69 – 7.62 (m, 3H), 7.52 – 7.44 (m, 2H), 7.41 – 7.32 (m, 2H), 7.31 – 7.24 (m, 1H), 3.22 – 3.13 (m, 1H), 3.11 – 3.03 (m, 1H), 1.74 – 1.62 (m, 2H), 0.96 (t,  $J$  = 7.4 Hz, 3H).  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.1, 149.4, 137.4, 135.8, 133.9, 133.0, 127.8, 127.3, 126.3, 123.9, 122.7, 121.5, 115.9, 112.3, 45.8, 25.7, 11.7. **IR** (film)  $\nu$  2958, 2872, 2848, 1533, 1442, 1249, 1149, 1070, 790, 723, 601  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ :  $[M+H]^+$  Calcd for  $\text{C}_{17}\text{H}_{17}\text{BrNO}_2\text{S}$  378.0163; 380.0143, found 378.0148; 380.0125.



**Benzo[*b*]thiophen-2-yl(5-chloro-2-methoxyphenyl)(propylimino)- $\lambda^6$ -sulfanone (3v).**

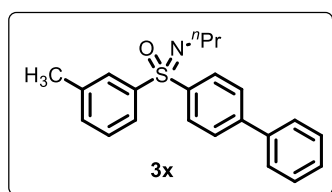
Prepared following general procedure using 5-chloro-2-methoxy-*N*-propyl benzenesulfonimidoyl fluoride **1c** (0.6 mmol, 159.0 mg), potassium benzo[*b*]thiophen-2-yltrifluoroborate **2o** (0.4 mmol, 96.0 mg), TMSOTf (0.12 mmol, 21.6  $\mu\text{L}$ ) and  $\text{CH}_3\text{CN}$  (2.0 mL), the reaction was stirred at 40  $^\circ\text{C}$  for 30 min giving **3v** in 60% yield (90.6 mg) as a white solid by column chromatography (PE/EA = 5:1,  $R_f$  = 0.31).  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.24 (d,  $J$  = 2.7 Hz, 1H), 7.91 (s, 1H), 7.86 – 7.79 (m, 2H), 7.47 – 7.36 (m, 3H), 6.86 (d,  $J$  = 8.8 Hz, 1H), 3.83 (s, 3H), 3.07 (t,  $J$  = 7.0 Hz, 2H), 1.72 – 1.59 (m, 2H), 0.96 (t,  $J$  = 7.4 Hz, 3H).  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.8, 143.1, 142.9, 138.0, 134.3, 131.1, 131.0, 129.4, 126.7, 125.7, 125.4, 124.9, 122.4, 113.7, 56.0, 46.1, 25.8, 11.7. **IR** (film)  $\nu$  2953, 2872, 1589, 1475, 1275, 1151, 756, 725, 646,

601 cm<sup>-1</sup>. **HRMS** (ESI) m/z: [M+H]<sup>+</sup> Calcd for : C<sub>18</sub>H<sub>19</sub>ClNO<sub>2</sub>S<sub>2</sub> 380.0546, found 380.0530.



**Benzo[*b*]thiophen-2-yl(propylimino)(3-(trifluoromethyl)phenyl)-λ<sup>6</sup>-sulfanone (3w).** Prepared following general procedure using *N*-propyl-3-(trifluoromethyl)benzenesulfonimidoyl fluoride **1d** (0.6 mmol, 161.6 mg),

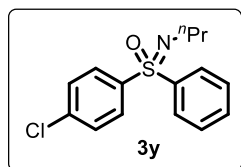
potassium benzo[*b*]thiophen-2-yltrifluoroborate **2o** (0.4 mmol, 96.0 mg), TMSOTf (0.08 mmol, 14.4 μL) and CH<sub>3</sub>CN (2.0 mL), the reaction was stirred at 40 °C for 30 min giving **3w** in 99% yield (152.8 mg) as a yellow oil by column chromatography (PE/EA = 5:1, R<sub>f</sub> = 0.63). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.40 (s, 1H), 8.30 (d, *J* = 8.0 Hz, 1H), 7.89 (s, 1H), 7.87 – 7.76 (m, 3H), 7.66 – 7.61 (m, 1H), 7.48 – 7.37 (m, 2H), 3.22 – 3.12 (m, 2H), 1.79 – 1.67 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 143.2, 142.4(8), 142.4(1), 138.2, 131.7 (q, *J* = 33.5 Hz), 131.5, 131.0, 129.8, 129.2 (q, *J* = 3.5 Hz), 127.1, 125.6, 125.3(6) (q, *J* = 4.04 Hz), 125.3(0), 123.1 (q, *J* = 273.0 Hz), 122.6, 45.9, 25.9, 11.7. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -62.6. **IR** (film) ν 2960, 2874, 1498, 1423, 1323, 1124, 1068, 746 cm<sup>-1</sup>. **HRMS** (ESI) m/z: [M+H]<sup>+</sup> Calcd for : C<sub>18</sub>H<sub>17</sub>F<sub>3</sub>NOS<sub>2</sub> 384.0704, found 384.0689.



**[1,1'-biphenyl]-4-yl(propylimino)(*m*-tolyl)-λ<sup>6</sup>-sulfanone (3x).** Prepared following general procedure using 3-methyl-*N*-propylbenzenesulfonimidoyl fluoride **1e** (0.6 mmol, 129.0 mg), potassium

[1,1'-biphenyl]-4-yltrifluoroborate **2i** (0.4 mmol, 104.0 mg), TMSOTf (0.08 mmol, 14.4 μL) and CH<sub>3</sub>CN (2.0 mL), the reaction was stirred at 40 °C for 30 min giving **3x** in 98% yield (137.0 mg) as a colorless oil by column chromatography (PE/EA = 5:1, R<sub>f</sub> = 0.40). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.06 – 8.01 (m, 2H), 7.86 – 7.80 (m, 2H), 7.68 – 7.63 (m, 2H), 7.57 – 7.52 (m, 2H), 7.46 – 7.40 (m, 2H), 7.39 – 7.33 (m, 2H), 7.30 (d, *J* = 7.9 Hz, 1H), 3.07 (t, *J* = 7.1 Hz, 2H), 2.39

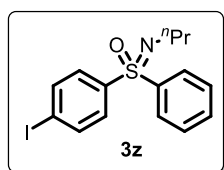
(s, 3H), 1.77 – 1.66 (m, 2H), 1.00 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.0, 140.7, 139.5, 139.3, 139.1, 133.0, 128.9, 128.8, 128.7, 128.1, 127.6, 127.1, 125.5, 45.6, 26.0, 21.2, 11.7. IR (film)  $\nu$  2926, 2870, 1593, 1477, 1226, 1124, 1006, 761, 694  $\text{cm}^{-1}$ . HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for :  $\text{C}_{22}\text{H}_{24}\text{NOS}$  350.1579, found 350.1562.



**(4-chlorophenyl)(phenyl)(propylimino)- $\lambda^6$ -sulfanone**

**(3y).** Prepared following general procedure using 4-chloro-*N*-propylbenzenesulfonimidoyl fluoride **1f** (0.6 mmol, 141.0 mg), potassium trifluoro(phenyl)borate **2a** (0.4

mmol, 73.6 mg), TMSOTf (0.12 mmol, 21.6  $\mu\text{L}$ ) and  $\text{CH}_3\text{CN}$  (2.0 mL), the reaction was stirred at 40  $^\circ\text{C}$  for 30 min giving **3y** in 93% yield (109.0 mg) as a yellow oil by column chromatography (PE/EA = 5:1,  $R_f$  = 0.57).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 – 7.92 (m, 2H), 7.91 – 7.86 (m, 2H), 7.52 – 7.43 (m, 3H), 7.43 – 7.39 (m, 2H), 3.01 – 2.97 (m, 2H), 1.71 – 1.59 (m, 2H), 0.95 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.6, 139.6, 138.7, 132.3, 129.9, 129.2, 129.1, 128.4, 45.6, 26.0, 11.7. IR (film)  $\nu$  2957, 2841, 1577, 1473, 1253, 1143, 1078, 763, 744  $\text{cm}^{-1}$ . HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for :  $\text{C}_{15}\text{H}_{17}\text{ClNOS}$  294.0719, found 294.0703.



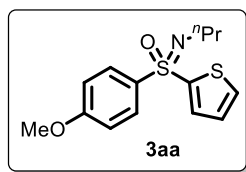
**(4-iodophenyl)(phenyl)(propylimino)- $\lambda^6$ -sulfanone (3z).**

Prepared following general procedure using 4-iodo-*N*-propylbenzenesulfonimidoyl fluoride **1g** (0.6 mmol, 196.0 mg), potassium trifluoro(phenyl)borate **2a** (0.4 mmol,

73.6 mg), TMSOTf (0.08 mmol, 14.4  $\mu\text{L}$ ) and  $\text{CH}_3\text{CN}$  (2.0 mL), the reaction was stirred at 40  $^\circ\text{C}$  for 30 min giving **3z** in 77% yield (118.8 mg) as a white solid by column chromatography (PE/EA = 5:1,  $R_f$  = 0.60).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 – 7.91 (m, 2H), 7.81 – 7.75 (m, 2H), 7.68 – 7.63 (m, 2H), 7.51 – 7.41 (m, 3H), 3.01 – 2.96 (m, 2H), 1.70 – 1.59 (m, 2H), 0.94 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.8, 140.5, 138.2, 132.3, 129.9, 129.0, 128.3, 99.8, 45.5, 26.0, 11.7. IR (film)  $\nu$  3063, 2957, 2870, 1564, 1381, 1228, 1143,

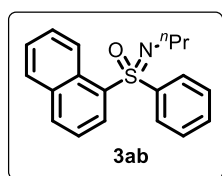


1004, 815, 732  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ :  $[M+H]^+$  Calcd for :  $\text{C}_{15}\text{H}_{17}\text{INOS}$  386.0076, found 386.0061.



**(4-methoxyphenyl)(propylimino)(thiophen-2-yl)- $\lambda^6$ -sulfanone (3aa).** Prepared following general procedure

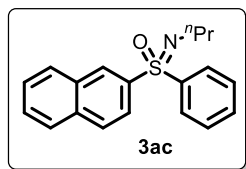
using 4-methoxy-*N*-propylbenzenesulfonimidoyl fluoride **1h** (0.6 mmol, 133.9 mg), potassium trifluoro(thiophen-2-yl)borate **2m** (0.4 mmol, 76.0 mg), TMSOTf (0.08 mmol, 14.4  $\mu\text{L}$ ) and  $\text{CH}_3\text{CN}$  (2.0 mL), the reaction was stirred at rt for 30 min giving **3aa** in 95% yield (112.8 mg) as a colorless oil by column chromatography (PE/EA = 5:1,  $R_f$  = 0.23).  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 – 7.92 (m, 2H), 7.52 (dd,  $J$  = 5.0, 1.3 Hz, 1H), 7.48 (dd,  $J$  = 3.8, 1.4 Hz, 1H), 7.00 (dd,  $J$  = 5.0, 3.8 Hz, 1H), 6.95 – 6.88 (m, 2H), 3.79 (s, 3H), 3.18 – 2.92 (m, 2H), 1.75 – 1.56 (m, 2H), 0.94 (t,  $J$  = 7.4 Hz, 3H).  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.7, 143.5, 132.9(5), 132.9(1), 132.6, 130.1, 127.6, 114.1, 55.4, 45.8, 25.9, 11.7. **IR** (film)  $\nu$  3101, 2957, 2872, 1710, 1591, 1492, 1402, 1307, 829, 746, 680  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ :  $[M+H]^+$  Calcd for :  $\text{C}_{14}\text{H}_{18}\text{NO}_2\text{S}_2$  296.0779, found 296.0766.



**Naphthalen-1-yl(phenyl)(propylimino)- $\lambda^6$ -sulfanone (3ab).**

Prepared following general procedure using *N*-propylnaphthalene-1-sulfonimidoyl fluoride **1i** (0.6 mmol, 151.0 mg), potassium trifluoro(phenyl)borate **2a** (0.4 mmol, 73.6 mg), TMSOTf (0.12 mmol, 21.6  $\mu\text{L}$ ) and  $\text{CH}_3\text{CN}$  (2.0 mL), the reaction was stirred at 40  $^\circ\text{C}$  for 30 min giving **3ab** in 60% yield (74.6 mg) as a white solid by column chromatography (PE/EA = 5:1,  $R_f$  = 0.40).  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.87 – 8.82 (m, 1H), 8.56 (dd,  $J$  = 7.4, 1.3 Hz, 1H), 8.08 – 8.01 (m, 3H), 7.87 (dd,  $J$  = 8.0, 1.6 Hz, 1H), 7.60 (dd,  $J$  = 8.2, 7.4 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.46 – 7.39 (m, 3H), 3.14 – 3.06 (m, 1H), 3.00 – 2.93 (m, 1H), 1.75 – 1.61 (m, 2H), 0.95 (t,  $J$  = 7.4 Hz, 3H).  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.3, 135.4, 134.3, 134.2, 132.1, 131.5, 129.2, 128.8, 128.0, 127.7, 126.4, 124.7, 124.6, 45.8, 26.1, 11.8. **IR** (film)  $\nu$  3059, 2957, 2870, 1712, 1504, 1226, 1122,

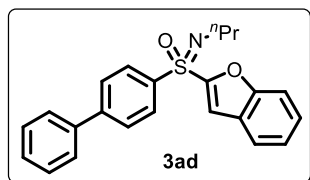
1024, 769, 686, 592  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ :  $[M+H]^+$  Calcd for :  $\text{C}_{19}\text{H}_{20}\text{NOS}$  310.1266, found 310.1253.



**Naphthalen-2-yl(phenyl)(propylimino)- $\lambda^6$ -sulfanone**

**(3ac).** Prepared following general procedure using *N*-propylnaphthalene-2-sulfonimidoyl fluoride **1j** (0.6 mmol, 151.0 mg), potassium trifluoro(phenyl)borate **2a** (0.4 mmol, 73.6 mg), TMSOTf (0.12 mmol, 21.6  $\mu\text{L}$ ) and  $\text{CH}_3\text{CN}$  (2.0 mL), the reaction

was stirred at 40  $^\circ\text{C}$  for 30 min giving **3ac** in 97% yield (124.0 mg) as a colorless oil by column chromatography (PE/EA = 5:1,  $R_f$  = 0.45).  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.60 (s, 1H), 8.08 – 8.03 (m, 2H), 7.98 – 7.81 (m, 4H), 7.57 (m, 2H), 7.51 – 7.42 (m, 3H), 3.13 – 3.01 (m, 2H), 1.77 – 1.66 (m, 2H), 0.99 (t,  $J$  = 7.3 Hz, 3H).  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.8, 137.7, 134.5, 132.4, 132.2, 129.9, 129.2, 129.1, 129.0, 128.5(6), 128.5(0), 127.7, 127.1, 123.7, 45.7, 26.1, 11.8. **IR** (film)  $\nu$  2972, 2922, 1448, 1222, 1116, 1080, 848, 742, 630  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ :  $[M+H]^+$  Calcd for :  $\text{C}_{19}\text{H}_{20}\text{NOS}$  310.1266, found 310.1250.

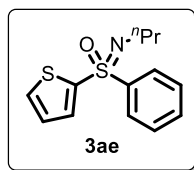


**[1,1'-biphenyl]-4-yl(benzofuran-2-yl)(propylimino)- $\lambda^6$ -sulfanone (3ad).**

Prepared following general procedure using *N*-propyl-[1,1'-biphenyl]-4-sulfonimidoyl fluoride **1k** (0.6 mmol, 166.4 mg), potassium benzofuran-2-yltrifluoroborate **2n** (0.4 mmol, 89.6 mg), TMSOTf (0.08 mmol, 14.4  $\mu\text{L}$ ) and  $\text{CH}_3\text{CN}$  (2.0 mL), the reaction was stirred at 40  $^\circ\text{C}$  for

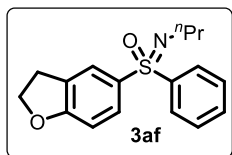
30 min giving **3ad** in 92% yield (138.2 mg) as a yellow oil by column chromatography (PE/EA = 5:1,  $R_f$  = 0.38).  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.19 (d,  $J$  = 8.5 Hz, 2H), 7.68 – 7.64 (m, 2H), 7.61 (d,  $J$  = 7.8 Hz, 1H), 7.53 – 7.45 (m, 4H), 7.42 – 7.30 (m, 4H), 7.27 – 7.19 (m, 1H), 3.24 – 3.16 (m, 1H), 3.10 – 3.02 (m, 1H), 1.73 – 1.63 (m, 2H), 0.96 (t,  $J$  = 7.4 Hz, 3H).  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.3, 151.0, 145.9, 139.2, 137.5, 129.1, 128.8, 128.3, 127.6, 127.2(6), 127.2(0), 126.5, 123.8, 122.6, 114.4, 112.2, 46.1, 25.8, 11.7. **IR** (film)  $\nu$  2955, 2870, 1593, 1533, 1259, 1136, 931, 790, 696, 680  $\text{cm}^{-1}$ . **HRMS** (ESI)

m/z:  $[M+H]^+$  Calcd for :  $C_{23}H_{22}NO_2S$  376.1371, found 376.1356.



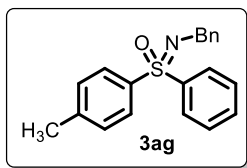
**Phenyl(propylimino)(thiophen-2-yl)- $\lambda^6$ -sulfanone (3ae).**

Prepared following general procedure using *N*-propylthiophene-2-sulfonimidoyl fluoride **1i** (0.6 mmol, 124.4 mg), potassium trifluoro(phenyl)borate **2a** (0.4 mmol, 73.6 mg), TMSOTf (0.08 mmol, 14.4  $\mu$ L) and  $CH_3CN$  (2.0 mL), the reaction was stirred at 40 °C for 30 min giving **3ae** in 63% yield (66.8 mg) as a white solid by column chromatography (PE/EA = 5:1,  $R_f$  = 0.29).  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  8.06 – 8.01 (m, 2H), 7.56 (dd,  $J$  = 5.0, 1.4 Hz, 1H), 7.53 (dd,  $J$  = 3.7, 1.4 Hz, 1H), 7.50 – 7.43 (m, 3H), 7.03 (dd,  $J$  = 5.0, 3.8 Hz, 1H), 3.15 – 3.01 (m, 2H), 1.73 – 1.60 (m, 2H), 0.96 (t,  $J$  = 7.4 Hz, 3H).  **$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  143.0, 141.7, 133.5, 133.2, 132.3, 129.0, 128.0, 127.8, 45.9, 26.0, 11.8. **IR** (film)  $\nu$  2957, 2928, 1446, 1253, 1126, 1010, 850, 752, 684, 599  $cm^{-1}$ . **HRMS** (ESI) m/z:  $[M+H]^+$  Calcd for :  $C_{13}H_{16}NOS_2$  266.0673, found 266.0660.



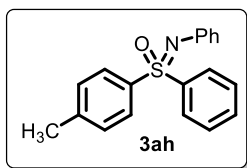
**(2,3-dihydrobenzofuran-5-yl)(phenyl)(propylimino)- $\lambda^6$ -sulfanone (3af).**

Prepared following general procedure using *N*-propyl-2,3-dihydrobenzofuran-5-sulfonimidoyl fluoride **1m** (0.6 mmol, 146.0 mg), potassium trifluoro(phenyl)borate **2a** (0.4 mmol, 73.6 mg), TMSOTf (0.12 mmol, 21.6  $\mu$ L) and  $CH_3CN$  (2.0 mL), the reaction was stirred at 40 °C for 30 min giving **3af** in 90% yield (108.4 mg) as a colorless oil by column chromatography (PE/EA = 5:1,  $R_f$  = 0.21).  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.93 – 7.89 (m, 2H), 7.78 – 7.71 (m, 2H), 7.46 – 7.38 (m, 3H), 6.77 (d,  $J$  = 8.4 Hz, 1H), 4.58 (t,  $J$  = 8.8 Hz, 2H), 3.17 (t,  $J$  = 8.8 Hz, 2H), 3.04 – 2.90 (m, 2H), 1.70 – 1.57 (m, 2H), 0.94 (t,  $J$  = 7.4 Hz, 3H).  **$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  163.5, 141.7, 132.1, 131.7, 129.9, 128.8, 128.2, 128.1, 125.6, 109.4, 72.1, 45.6, 28.9, 26.0, 11.7. **IR** (film)  $\nu$  3068, 2953, 2901, 1602, 1483, 1288, 1224, 1103, 1062, 759, 601  $cm^{-1}$ . **HRMS** (ESI) m/z:  $[M+H]^+$  Calcd for :  $C_{17}H_{20}NO_2S$  302.1215, found 302.1201.



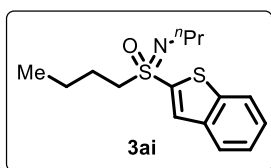
**(Benzylimino)(phenyl)(*p*-tolyl)-λ<sup>6</sup>-sulfanone (3ag).**

Prepared following general procedure using *N*-benzyl-4-methylbenzenesulfonimidoyl fluoride **1n** (0.6 mmol, 158.0 mg), potassium trifluoro(phenyl)borate **2a** (0.4 mmol, 73.6 mg), TMSOTf (0.08 mmol, 14.4 μL) and CH<sub>3</sub>CN (2.0 mL), the reaction was stirred at 40 °C for 30 min giving **3ag** in 85% yield (109.5 mg) as a colorless oil by column chromatography (PE/EA = 5:1, R<sub>f</sub> = 0.33). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 (dd, *J* = 7.9, 1.8 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.43 – 7.35 (m, 5H), 7.29 – 7.23 (m, 2H), 7.21 – 7.13 (m, 3H), 4.24 (s, 2H), 2.29 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 143.1, 141.5, 140.9, 137.5, 132.1, 129.6, 128.9, 128.5, 128.2, 128.0, 127.2, 126.2, 47.0, 21.2. IR (film) ν 3061, 3026, 2918, 2833, 1595, 1444, 1257, 1136, 1093, 844, 696 cm<sup>-1</sup>. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> Calcd for : C<sub>20</sub>H<sub>20</sub>NOS 322.1266, found 322.1251.



**Phenyl(phenylimino)(*p*-tolyl)-λ<sup>6</sup>-sulfanone (3ah).**

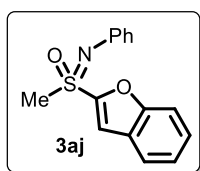
Prepared following general procedure using 4-methyl-*N*-phenylbenzenesulfonimidoyl fluoride **1o** (0.6 mmol, 150.0 mg), potassium trifluoro(phenyl)borate **2a** (0.4 mmol, 73.6 mg), TMSOTf (0.08 mmol, 14.4 μL) and CH<sub>3</sub>CN (2.0 mL), the reaction was stirred at 40 °C for 30 min giving **3ah** in 64% yield (78.4 mg) as a white solid by column chromatography (PE/EA = 5:1, R<sub>f</sub> = 0.45). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.04 – 8.00 (m, 2H), 7.93 – 7.89 (m, 2H), 7.46 – 7.37 (m, 3H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.17 – 7.07 (m, 4H), 6.87 – 6.81 (m, 1H), 2.31 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 144.7, 143.4, 141.2, 137.7, 132.3, 129.8, 129.1, 128.8, 128.5, 128.2, 123.6, 121.4, 21.3. IR (film) ν 3059, 2922, 1593, 1444, 1265, 1199, 1072, 775, 754, 686 cm<sup>-1</sup>. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> Calcd for : C<sub>19</sub>H<sub>18</sub>NOS 308.1109, found 308.1096.



**Benzo[*b*]thiophen-2-yl(butyl)(propylimino)-λ<sup>6</sup>-sulfanone (3ai).**

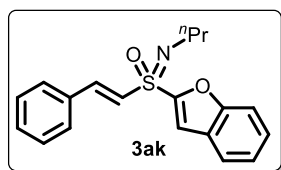
Prepared following general procedure using *N*-propylbutane-1-sulfonimidoyl fluoride **1p** (0.6 mmol,

109.0 mg), potassium benzo[*b*]thiophen-2-yltrifluoroborate **2o** (0.4 mmol, 96.0 mg), TMSOTf (0.12 mmol, 21.6  $\mu$ L) and CH<sub>3</sub>CN (2.0 mL), the reaction was stirred at 40 °C for 30 min giving **3ai** in 90% yield (105.7 mg) as a colorless oil by column chromatography (PE/EA = 5:1, *R*<sub>f</sub> = 0.34). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.90 – 7.84 (m, 2H), 7.79 (s, 1H), 7.48 – 7.40 (m, 2H), 3.34 – 3.24 (m, 2H), 3.12 – 3.03 (m, 1H), 2.97 – 2.88 (m, 1H), 1.91 – 1.80 (m, 1H), 1.78 – 1.67 (m, 1H), 1.66 – 1.54 (m, 2H), 1.43 – 1.30 (m, 2H), 0.89 (m, 6H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  143.0, 141.0, 138.3, 131.1, 126.7, 125.4, 125.1, 122.6, 57.6, 45.8, 25.8, 24.8, 21.3, 13.4, 11.6. **IR** (film)  $\nu$  2957, 2872, 1500, 1456, 1224, 1122, 976, 748, 725, 605 cm<sup>-1</sup>. **HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> Calcd for : C<sub>15</sub>H<sub>22</sub>NOS<sub>2</sub> 296.1143, found 296.1130.



**Benzofuran-2-yl(methyl)(phenylimino)- λ<sup>6</sup>-sulfanone (3aj).**

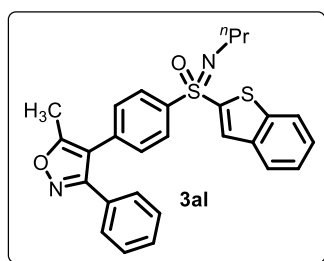
Prepared following general procedure using *N*-phenylmethanesulfonimidoyl fluoride **1q** (0.6 mmol, 104.0 mg), potassium benzofuran-2-yltrifluoroborate **2n** (0.4 mmol, 89.6 mg), TMSOTf (0.12 mmol, 21.6  $\mu$ L) and CH<sub>3</sub>CN (2.0 mL), the reaction was stirred at 40 °C for 30 min giving **3aj** in 73% yield (79.3 mg) as a red solid by column chromatography (PE/EA = 5:1, *R*<sub>f</sub> = 0.19). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.64 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 1H), 7.49 – 7.41 (m, 2H), 7.36 – 7.28 (m, 1H), 7.18 – 7.12 (m, 2H), 7.13 – 7.06 (m, 2H), 6.98 – 6.88 (m, 1H), 3.43 (s, 3H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  156.1, 149.4, 143.7, 128.9, 127.7, 126.1, 124.1, 123.4, 122.8, 122.5, 115.0, 112.3, 44.7. **IR** (film)  $\nu$  2926, 1593, 1487, 1294, 1211, 1078, 1045, 960, 792, 694 cm<sup>-1</sup>. **HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> Calcd for : C<sub>15</sub>H<sub>14</sub>NO<sub>2</sub>S 272.0745, found 272.0736.



**(*E*)-benzofuran-2-yl(propylimino)(styryl)-λ<sup>6</sup>-sulfanone (3ak).**

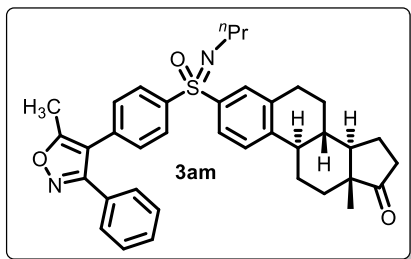
Prepared following general procedure using (*E*)-2-phenyl-*N*-propylethene-1-sulfonimidoyl fluoride **1r** (0.6 mmol, 136.0 mg), potassium benzofuran-2-yltrifluoroborate **2n** (0.4 mmol, 89.6 mg), TMSOTf (0.12 mmol,

21.6  $\mu\text{L}$ ) and  $\text{CH}_3\text{CN}$  (2.0 mL), the reaction was stirred at 40  $^\circ\text{C}$  for 30 min giving **3ak** in 96% yield (124.4 mg) as a yellow oil by column chromatography (PE/EA = 5:1,  $R_f$  = 0.41).  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 – 7.62 (m, 2H), 7.52 (d,  $J$  = 8.4 Hz, 1H), 7.48 – 7.43 (m, 3H), 7.43 – 7.36 (m, 1H), 7.36 – 7.22 (m, 4H), 7.05 (d,  $J$  = 15.3 Hz, 1H), 3.20 – 3.10 (m, 1H), 3.03 – 2.90 (m, 1H), 1.71 – 1.55 (m, 2H), 0.93 (t,  $J$  = 7.3 Hz, 3H).  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.2, 150.6, 144.1, 132.4, 130.9, 128.8, 128.4, 127.2, 126.5, 125.6, 123.8, 122.5, 114.0, 112.2, 45.9, 25.7, 11.6. **IR** (film)  $\nu$  2958, 2928, 1710, 1533, 1444, 1261, 1068, 927, 815, 738, 611  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for :  $\text{C}_{19}\text{H}_{20}\text{NO}_2\text{S}$  326.1215, found 326.1204.



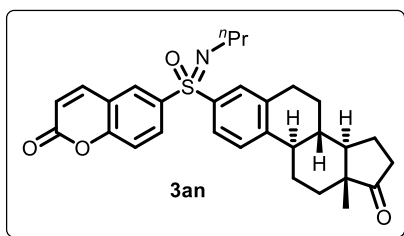
**Benzo[*b*]thiophen-2-yl(4-(5-methyl-3-phenylisoxazol-4-yl)phenyl)(propylimino)- $\lambda^6$ -sulfanone (**3al**).**

Prepared following general procedure using 4-(5-methyl-3-phenylisoxazol-4-yl)-*N*-propylbenzene sulfonimidoyl fluoride **1s** (0.3 mmol, 108.0 mg), potassium benzo[*b*]thiophen-2-yltrifluoroborate **2o** (0.2 mmol, 48.0 mg), TMSOTf (0.06 mmol, 10.8  $\mu\text{L}$ ) and  $\text{CH}_3\text{CN}$  (1.0 mL), the reaction was stirred at 40  $^\circ\text{C}$  for 30 min giving **3al** in 97% yield (102.0 mg) as a red oil by column chromatography (PE/EA = 2:1,  $R_f$  = 0.57).  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (d,  $J$  = 8.5 Hz, 2H), 7.88 – 7.76 (m, 3H), 7.45 – 7.32 (m, 5H), 7.31 – 7.21 (m, 4H), 3.27 – 3.05 (m, 2H), 2.41 (s, 3H), 1.78 – 1.64 (m, 2H), 0.99 (t,  $J$  = 7.4 Hz, 3H).  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.2, 160.9, 143.1, 142.9, 140.1, 138.3, 135.1, 130.7, 130.1, 129.5, 128.5(9), 128.5(2), 128.3, 126.8, 125.5, 125.1, 122.6, 114.3, 46.0, 25.9, 11.7, 11.6. **IR** (film)  $\nu$  2958, 2872, 1710, 1618, 1464, 1257, 1141, 977, 773, 725, 623  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for :  $\text{C}_{27}\text{H}_{25}\text{N}_2\text{O}_2\text{S}_2$  473.1357, found 473.1341.



**((8*S*,9*R*,13*R*,14*R*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl)(4-(5-methyl-3-phenylisoxazol-4-yl)phenyl)(propylimino)-λ<sup>6</sup>-sulfanone (**3am**).** Prepared following general

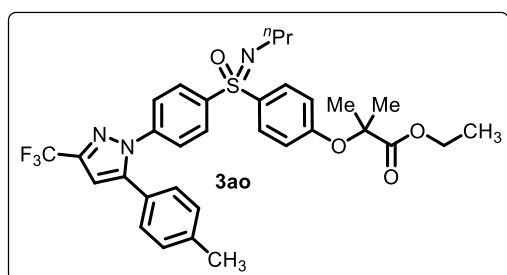
procedure using 4-(5-methyl-3-phenylisoxazol-4-yl)-*N*-propylbenzene-sulfonimidoyl fluoride **1s** (0.3 mmol, 108.0 mg), potassium trifluoro((8*S*,9*R*,13*R*,14*R*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl)borate **2u** (0.2 mmol, 90.8 mg), TMSOTf (0.06 mmol, 10.8 μL) and CH<sub>3</sub>CN (1.0 mL), the reaction was stirred at 40 °C for 30 min giving **3am** in 55% yield (65.3 mg) as a red oil by column chromatography (PE/EA = 2:1, R<sub>f</sub> = 0.29). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.71 – 7.66 (m, 2H), 7.43 – 7.33 (m, 4H), 7.33 – 7.22 (m, 4H), 3.06 – 2.92 (m, 4H), 2.55 – 2.37 (m, 5H), 2.36 – 2.25 (m, 1H), 2.19 – 1.91 (m, 4H), 1.72 – 1.39 (m, 8H), 0.99 – 0.92 (m, 3H), 0.89 (d, *J* = 2.2 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.0, 160.9, 144.8, 140.5, 140.4, 137.9, 137.4(5), 137.4(3), 134.5, 130.1, 129.5, 129.1, 128.6(5), 128.6(4), 128.5, 128.4, 128.3, 126.2, 125.9, 114.4, 50.3, 47.7, 45.7(2), 45.7(1), 44.4, 37.5, 35.6, 31.4, 29.3(2), 29.3(0), 26.0(9), 26.0(6), 26.0(4), 25.4, 21.4, 13.7, 11.8, 11.6. IR (film) ν 2924, 2870, 1734, 1452, 1224, 1138, 1080, 773, 727, 632 cm<sup>-1</sup>. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> Calcd for : C<sub>37</sub>H<sub>41</sub>N<sub>2</sub>O<sub>3</sub>S 593.2838, found 593.2812.



**6-((8*S*,9*R*,13*R*,14*R*)-13-methyl-17-oxo-*N*-propyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthrene-3-sulfonimidoyl)-2*H*-chromen-2-one (**3an**).** Prepared

following general procedure using 2-oxo-*N*-propyl-2*H*-chromene-6-sulfonimidoyl fluoride **1t** (0.3 mmol, 80.8 mg), potassium trifluoro((8*S*,9*R*,13*R*,14*R*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl)borate **2u** (0.2 mmol, 90.8 mg), TMSOTf (0.06 mmol, 10.8 μL) and CH<sub>3</sub>CN (1.0 mL), the reaction was

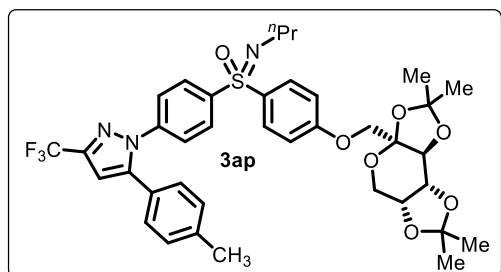
stirred at 40 °C for 30 min giving **3an** in 92% yield (92.7 mg) as a white solid by column chromatography (PE/EA = 2:1,  $R_f$  = 0.51).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13 (d,  $J$  = 2.2 Hz, 1H), 7.99 (dd,  $J$  = 8.7, 2.2 Hz, 1H), 7.72 (d,  $J$  = 9.7 Hz, 1H), 7.66 – 7.60 (m, 2H), 7.33 (d,  $J$  = 7.8 Hz, 1H), 7.30 (d,  $J$  = 8.8 Hz, 1H), 6.41 (d,  $J$  = 9.7 Hz, 1H), 2.97 – 2.85 (m, 4H), 2.47 – 2.37 (m, 1H), 2.36 – 2.28 (m, 1H), 2.26 – 2.18 (m, 1H), 2.11 – 1.93 (m, 3H), 1.90 – 1.84 (m, 1H), 1.64 – 1.32 (m, 8H), 0.91 – 0.86 (m, 3H), 0.80 (d,  $J$  = 2.3 Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.2, 155.8, 144.9, 142.6, 137.9, 137.5(6), 137.5(4), 137.2(4), 137.2(2), 131.2, 128.5, 126.1, 125.4, 118.7, 117.5(7), 117.5(3), 50.1, 47.4, 44.5, 44.1, 37.3, 35.4, 31.2, 29.0, 25.8, 25.7, 25.2, 21.2, 13.5, 11.6. IR (film)  $\nu$  2930, 2870, 1736, 1622, 1599, 1427, 1136, 1105, 702, 659  $\text{cm}^{-1}$ . HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for :  $\text{C}_{30}\text{H}_{34}\text{NO}_4\text{S}$  504.2209, found 504.2194.



**Ethyl 2-methyl-2-(4-(*N*-propyl-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)phenylsulfonyl)phenoxy)propanoate (**3ao**).** Prepared following general procedure using *N*-propyl-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfonyl fluoride **1u** (0.3 mmol, 128.0 mg), potassium (4-((1-ethoxy-2-methyl-1-oxopropan-2-yl)oxy)phenyl)trifluoroborate **2v** (0.2 mmol, 62.8 mg), TMSOTf (0.10 mmol, 18.0  $\mu\text{L}$ ) and  $\text{CH}_3\text{CN}$  (1.0 mL), the reaction was stirred at rt for 30 min giving **3ao** in 54% yield (66.7 mg) as a white solid by column chromatography (PE/EA = 5:1,  $R_f$  = 0.26).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 (dd,  $J$  = 8.8, 2.1 Hz, 2H), 7.79 (dd,  $J$  = 8.9, 2.1 Hz, 2H), 7.40 (dd,  $J$  = 8.7, 2.1 Hz, 2H), 7.17 – 7.04 (m, 4H), 6.83 (dd,  $J$  = 9.0, 2.2 Hz, 2H), 6.70 (s, 1H), 4.25 – 4.16 (m, 2H), 2.98 (t,  $J$  = 7.1 Hz, 2H), 2.36 (s, 3H), 1.73 – 1.52 (m, 8H), 1.24 – 1.14 (m, 3H), 1.00 – 0.90 (m, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.4, 159.2, 145.1, 143.8 (q,  $J$  = 38.8 Hz), 142.0, 141.0, 139.6, 132.3, 130.3, 129.6, 129.3, 128.6, 125.6, 125.4, 121.0 (q,  $J$  = 280.78 Hz), 118.0, 106.0, 79.5, 61.6, 45.6, 26.0, 25.2(9), 25.2(4), 21.2, 13.9, 11.8.  $^{19}\text{F NMR}$

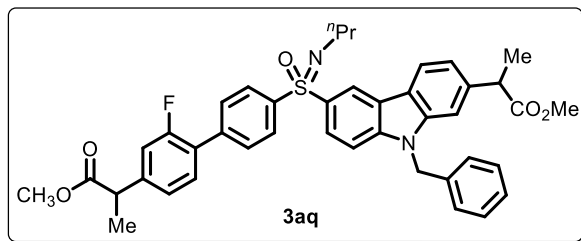


(376 MHz, CDCl<sub>3</sub>)  $\delta$  -62.4. **IR** (film)  $\nu$  2960, 2874, 1734, 1591, 1471, 1234, 1130, 1095, 974, 970, 742 cm<sup>-1</sup>. **HRMS** (ESI)  $m/z$ : [M+H]<sup>+</sup> Calcd for : C<sub>32</sub>H<sub>35</sub>F<sub>3</sub>N<sub>3</sub>O<sub>4</sub>S 614.2300, found 614.2283.



**(Propylimino)(4-(((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methoxy)phenyl)(4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)phenyl)- $\lambda^6$ -sulfanone (3ap).** Prepared following

general procedure using *N*-propyl-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfonamidoyl fluoride **1u** (0.3 mmol, 128.0 mg), potassium trifluoro(4-(((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methoxy)phenyl)borate **2w** (0.2 mmol, 88.5 mg), TMSOTf (0.10 mmol, 18.0  $\mu$ L) and CH<sub>3</sub>CN (1.0 mL), the reaction was stirred at rt for 30 min giving **3ap** in 56% yield (83.2 mg) as a white solid by column chromatography (PE/EA = 5:1,  $R_f$  = 0.14). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.92 (d,  $J$  = 7.9 Hz, 2H), 7.84 (dd,  $J$  = 9.0, 1.1 Hz, 2H), 7.39 (d,  $J$  = 8.7 Hz, 2H), 7.13 (d,  $J$  = 7.9 Hz, 2H), 7.07 (d,  $J$  = 8.2 Hz, 2H), 6.98 (d,  $J$  = 8.8 Hz, 2H), 6.70 (s, 1H), 4.62 (dd,  $J$  = 7.9, 2.6 Hz, 1H), 4.48 (d,  $J$  = 2.6 Hz, 1H), 4.25 (dd,  $J$  = 7.9, 1.6 Hz, 1H), 4.18 (dd,  $J$  = 10.3, 0.9 Hz, 1H), 4.06 (dd,  $J$  = 10.3, 1.1 Hz, 1H), 3.95 (dd,  $J$  = 13.0, 1.9 Hz, 1H), 3.77 (d,  $J$  = 13.0 Hz, 1H), 2.98 (t,  $J$  = 7.1 Hz, 2H), 2.36 (s, 3H), 1.71 – 1.57 (m, 2H), 1.54 (s, 3H), 1.46 (s, 3H), 1.41 (s, 3H), 1.33 (s, 3H), 0.94 (t,  $J$  = 7.4 Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  161.8(3), 161.8(1), 145.0, 143.8 (q,  $J$  = 38.5 Hz), 142.0, 141.1, 139.5, 132.0, 130.7, 129.6, 129.2, 128.6, 125.6, 125.3, 121.0 (q,  $J$  = 269.0 Hz), 115.1, 109.0, 108.9, 106.0, 101.7, 70.8, 70.0, 69.9, 69.0(5), 69.0(2), 61.2, 45.6, 26.4, 26.0, 25.8, 25.2, 23.9, 21.2, 11.7. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -62.4. **IR** (film)  $\nu$  2989, 2933, 2874, 1712, 1591, 1371, 1234, 1134, 1068, 731 cm<sup>-1</sup>. **HRMS** (ESI)  $m/z$ : [M+H]<sup>+</sup> Calcd for : C<sub>38</sub>H<sub>43</sub>F<sub>3</sub>N<sub>3</sub>O<sub>7</sub>S 742.2774, found 742.2753.

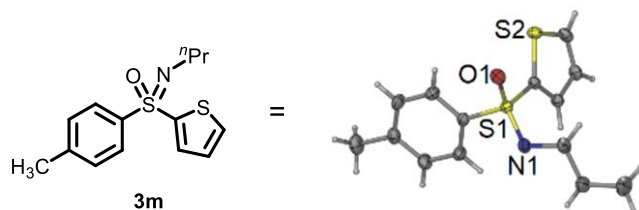


**Methyl 2-(9-benzyl-6-(2'-fluoro-4'-(1-methoxy-1-oxopropan-2-yl)-N-propyl-[1,1'-biphenyl]-4-sulfonimidoyl)-9H-carbazol-2-yl)propanoate (3aq).** Prepared

following general procedure using methyl 2-(2-fluoro-4'-(S-fluoro-N-propylsulfonimidoyl)

-[1,1'-biphenyl]-4-yl)propanoate **1v** (0.3 mmol, 114.4 mg), potassium (9-benzyl-7-(1-methoxy-1-oxopropan-2-yl)-9H-carbazol-3-yl)trifluoroborate **2x** (0.2 mmol, 89.9 mg), TMSOTf (0.10 mmol, 18.0  $\mu$ L) and CH<sub>3</sub>CN (1.0 mL), the reaction was stirred at rt for 30 min giving **3aq** in 51% yield (71.6 mg) as a red oil by column chromatography (PE/EA = 2:1, R<sub>f</sub> = 0.34). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.77 (d, *J* = 1.8 Hz, 1H), 8.10 (d, *J* = 8.1 Hz, 1H), 8.08 – 8.03 (m, 2H), 8.00 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.58 (dd, *J* = 8.5, 1.6 Hz, 2H), 7.39 – 7.29 (m, 3H), 7.27 – 7.20 (m, 4H), 7.14 – 7.06 (m, 4H), 5.48 (s, 2H), 3.86 (q, *J* = 7.1 Hz, 1H), 3.73 (q, *J* = 7.2 Hz, 1H), 3.66 (s, 3H), 3.60 (s, 3H), 3.12 – 3.05 (m, 2H), 1.77 – 1.67 (m, 2H), 1.53 (d, *J* = 7.1 Hz, 3H), 1.50 (d, *J* = 7.2 Hz, 3H), 0.99 (t, *J* = 7.3 Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  174.8, 174.1, 159.5 (d, *J* = 249.5 Hz), 142.8, 142.7, 141.6, 141.0, 139.8, 139.0, 136.0, 130.7, 130.6 (d, *J* = 3.7 Hz), 129.4 (d, *J* = 3.2 Hz), 128.8, 128.4, 127.7, 126.3, 126.0, 123.7 (d, *J* = 3.3 Hz), 123.0, 121.9, 121.7, 121.0, 120.1, 115.4, 115.2, 109.3, 108.2, 52.1, 52.0, 46.7, 45.9, 45.8, 44.8, 26.2, 18.9, 18.3, 11.8. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -117.0. **IR** (film)  $\nu$  2953, 2872, 1732, 1595, 1496, 1286, 1124, 848, 823, 727 cm<sup>-1</sup>. **HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> Calcd for : C<sub>42</sub>H<sub>42</sub>FN<sub>2</sub>O<sub>5</sub>S 705.2798, found 705.2773.

## IV. X-Ray Crystal Structure

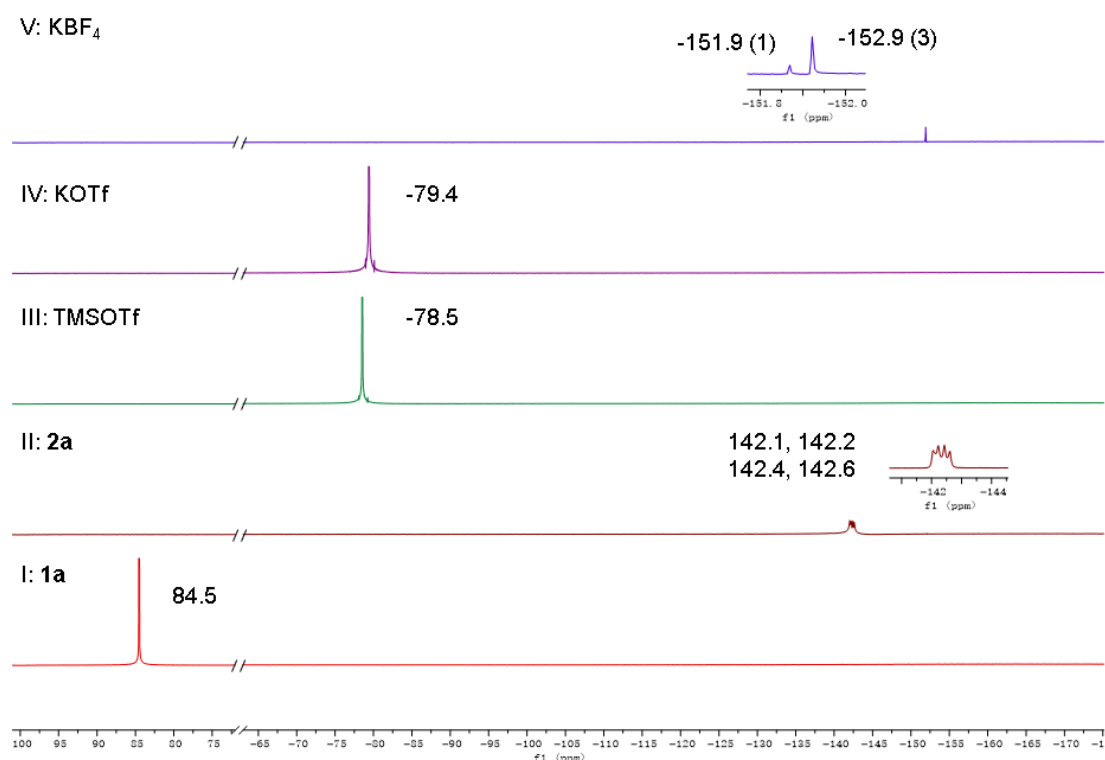


**Supplementary Table 1.** Sample and crystal data for **3m** (CCDC2240513).

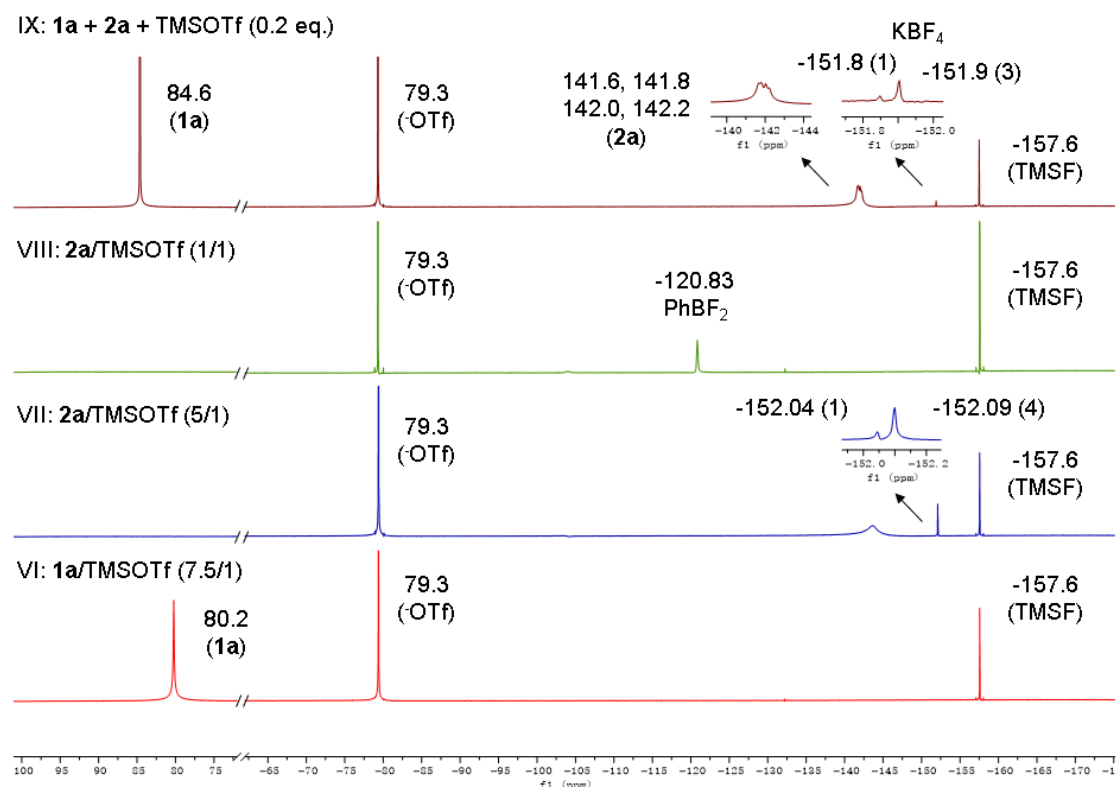
|                                     |                                                    |
|-------------------------------------|----------------------------------------------------|
| Bond precision                      | C-C = 0.0027 Å                                     |
|                                     | Wavelength = 1.54184                               |
| Cell                                | a = 5.9748(2)      α = 89.999(4)                   |
|                                     | b = 7.8641(4)      β = 80.991(3)                   |
|                                     | c = 16.8240(7)      γ = 68.477(4)                  |
| Temperature                         | 173 K                                              |
| Volume                              | 724.89(6)                                          |
| Space group                         | P -1                                               |
| Sum formula                         | C <sub>14</sub> H <sub>17</sub> N O S <sub>2</sub> |
| Mr                                  | 279.40                                             |
| D <sub>x</sub> , g cm <sup>-3</sup> | 1.280                                              |
| Z                                   | 2                                                  |
| Mu (mm <sup>-1</sup> )              | 3.224                                              |
| F <sub>000</sub>                    | 296.0                                              |
| h,k,l <sub>max</sub>                | 7,9,20                                             |
| N <sub>ref</sub>                    | 2532                                               |
| T <sub>min</sub> , T <sub>max</sub> | 0.520, 1.000                                       |
| Correction method= # Reported       | T <sub>min</sub> =0.520 T <sub>max</sub> =1.000    |
| T Limits                            |                                                    |
| AbsCorr = MULTI-SCAN                |                                                    |
| Data completeness                   | 0.977                                              |
| Theta(max)                          | 67.080                                             |
| R(reflections)                      | 0.0317(2384)                                       |
| wR <sub>2</sub> (reflections)       | 0.0889(2532)                                       |
| S                                   | 1.062                                              |
| N <sub>par</sub>                    | 165                                                |

## V. Fluorine spectra

Under nitrogen atmosphere, dry CD<sub>3</sub>CN (1 mL, 0.2 M) was added to a dry 10 mL oven-dried Schlenk tube, which was equipped with sulfonimidoyl fluoride **1a** or potassium aryltrifluoroborate salt **2a**. TMSOTf was dropwise added via the microsyringe at room temperature. Then the reaction mixture was stirred at 40 °C for 5 min, and the fluorine spectra tracking experiments were conducted.



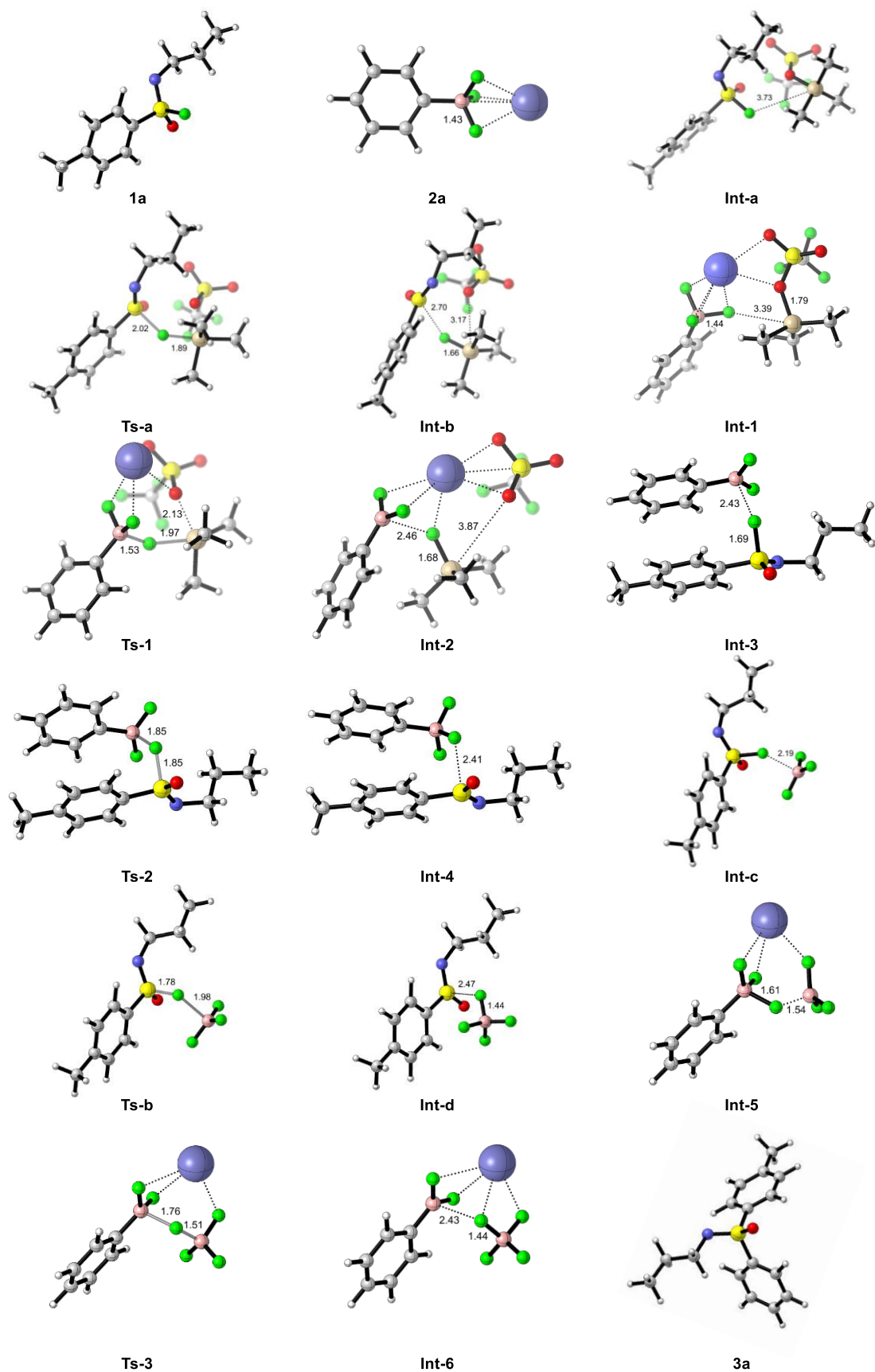
**Supplementary Figure 1.** Fluorine spectra involving I-V experiments.



**Supplementary Figure 2.** Fluorine spectra involving VI-IX experiments.

## VI. Computational details of DFT calculations

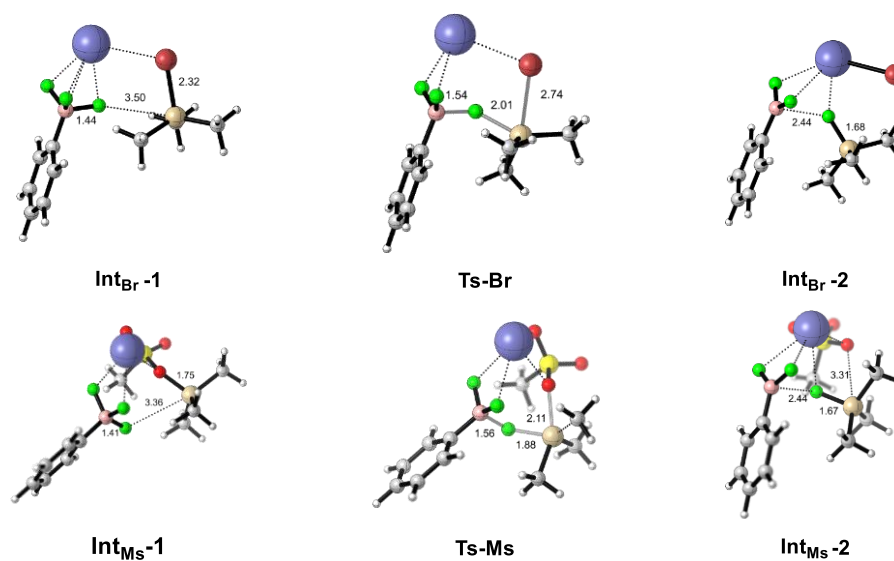
All calculations were performed with the Gaussian 16<sup>4</sup> package. Geometry optimizations and frequency calculations were performed with M06-2X<sup>5</sup> and the 6-311+G(d,p) basis set with the SMD solvation model.<sup>6</sup> Meanwhile, transition states structures were verified by frequency calculations and only one imaginary frequency was found in the transition states. Intrinsic Reaction Coordinate (IRC) was utilized to confirm the reaction pathway. All optimized structures were visualized using CYLView program.<sup>7</sup>



**Supplementary Table 2.** Calculated energy data for all structures at the level of M06-2X/6-311+G(d,p)/SMD(CH<sub>3</sub>CN).

|                      | <b>H (T)</b><br><b>(Hartree)</b> | <b>ΔH</b><br><b>(kcal/mol)</b> | <b>G (T)</b><br><b>(Hartree)</b> | <b>ΔG</b><br><b>(kcal/mol)</b> |
|----------------------|----------------------------------|--------------------------------|----------------------------------|--------------------------------|
| <b>R<sup>1</sup></b> | -3543.66236                      | 0.0                            | -3543.83189                      | 0.0                            |
| <b>Int-a</b>         | -3543.66871                      | -4.0                           | -3543.81563                      | 10.2                           |
| <b>Ts-a</b>          | -3543.63252                      | 18.7                           | -3543.77557                      | 35.3                           |
| <b>Int-b</b>         | -3543.66791                      | -3.5                           | -3543.81862                      | 8.3                            |
| <b>Int-1</b>         | -3543.67890                      | -10.4                          | -3543.83216                      | -0.2                           |
| <b>Ts-1</b>          | -3543.64606                      | 10.2                           | -3543.79149                      | 25.3                           |
| <b>Int-2</b>         | -3543.67878                      | -10.3                          | -3543.83093                      | 0.6                            |
| <b>Int-3</b>         | -3543.66225                      | 0.07                           | -3543.82936                      | 1.6                            |
| <b>Ts-2</b>          | -3543.65783                      | 2.8                            | -3543.82565                      | 3.9                            |
| <b>Int-4</b>         | -3543.66635                      | -2.5                           | -3543.83486                      | -1.9                           |
| <b>3a</b>            | -3543.69521                      | -20.6                          | -3543.88149                      | -31.0                          |
| <b>R<sup>2</sup></b> | -2497.68722                      | 0.0                            | -2497.82601                      | 0.0                            |
| <b>Int-c</b>         | -2497.69649                      | -5.8                           | -2497.81945                      | 4.1                            |
| <b>Ts-b</b>          | -2497.69747                      | -6.4                           | -2497.81961                      | 4.0                            |
| <b>Int-d</b>         | -2497.71391                      | -16.7                          | -2497.83762                      | -7.3                           |
| <b>Int-5</b>         | -2497.71542                      | -17.7                          | -2497.83465                      | -6.8                           |
| <b>Ts-3</b>          | -2497.71487                      | -17.3                          | -2497.83963                      | -5.4                           |
| <b>Int-6</b>         | -2497.71729                      | -18.9                          | -2497.83963                      | -8.5                           |

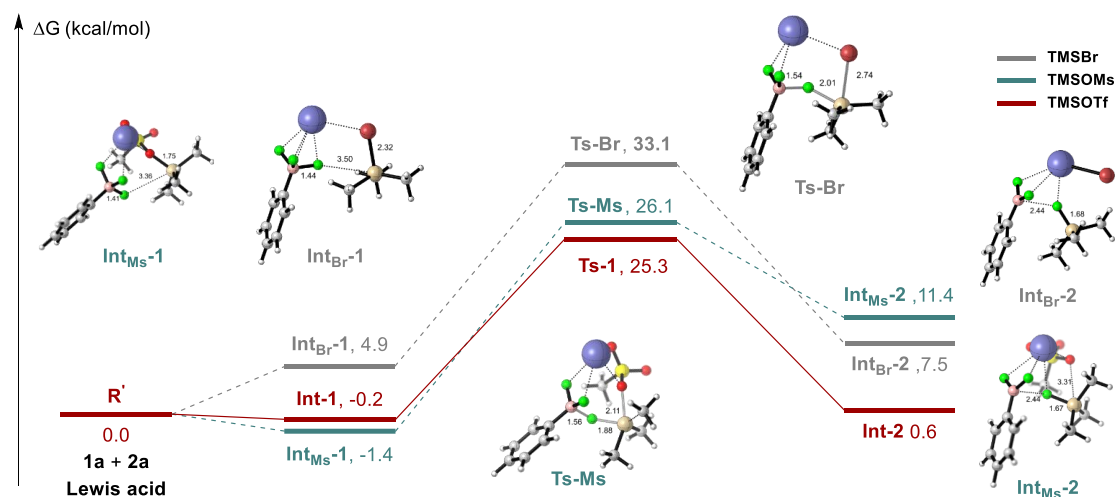




**Supplementary Figure 4.** Calculated Structures including intermediates and transition states of TMSBr or TMSOTf as Lewis acid.

**Supplementary Table 3.** Calculated energy data for structures at the level of M06-2X/6-311+G(d,p)/SMD(CH<sub>3</sub>CN).

|                           | H (T)<br>(Hartree) | ΔH<br>(kcal/mol) | G (T)<br>(Hartree) | ΔG<br>(kcal/mol) |
|---------------------------|--------------------|------------------|--------------------|------------------|
| <b>1a+2a+TMSBr</b>        | -5156.47693        | 0.0              | -5156.63015        | 0.0              |
| <b>Int<sub>Br</sub>-1</b> | -5156.48526        | -5.2             | -5156.62234        | 4.9              |
| <b>Ts-Br</b>              | -5156.44550        | 19.7             | -5156.57745        | 33.1             |
| <b>Int<sub>Br</sub>-2</b> | -5156.48109        | -22.3            | -5156.61814        | 7.5              |
| <b>1a+2a+TMSOMs</b>       | -3245.93940        | 0.0              | -3246.10224        | 0.0              |
| <b>Int<sub>Ms</sub>-1</b> | -3245.96098        | -13.5            | -3246.10456        | -1.4             |
| <b>Ts-Ms</b>              | -3245.92154        | 11.2             | -3246.06058        | 26.1             |
| <b>Int<sub>Ms</sub>-2</b> | -3245.93845        | 0.60             | -3246.08403        | 11.4             |



**Supplementary Figure 5.** Density functional theory (DFT) calculation of the activation of **2a** with TMSOTf, TMSBr and TMSOMs.

## Cartesian coordinates for all optimized structures

### 1a

Imaginary frequency: none

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | 3.23831800  | 0.92271100  | -0.23463000 |
| C | 1.87936100  | 1.21804400  | -0.22336400 |
| C | 0.98217100  | 0.17758000  | -0.02957100 |
| C | 1.39592100  | -1.13925200 | 0.15881500  |
| C | 2.75398700  | -1.40605200 | 0.14459500  |
| C | 3.69213600  | -0.38355700 | -0.05215600 |
| H | 3.95394900  | 1.72236700  | -0.38801800 |
| H | 1.52745700  | 2.23255600  | -0.36578600 |
| H | 0.67040800  | -1.92975100 | 0.30513500  |
| H | 3.09793800  | -2.42442700 | 0.28891000  |
| C | 5.15961600  | -0.70613400 | -0.07506400 |
| H | 5.44026200  | -1.28244000 | 0.80934100  |
| H | 5.39981200  | -1.31414100 | -0.95149300 |
| H | 5.76308000  | 0.20085200  | -0.10940300 |
| S | -0.73079000 | 0.56684600  | -0.01433200 |
| O | -0.97786200 | 1.96896200  | -0.29171700 |
| N | -1.47163700 | -0.56487600 | -0.65328100 |
| C | -2.91754000 | -0.45667800 | -0.92623200 |
| H | -3.14267400 | -1.24679100 | -1.64390800 |
| H | -3.14898800 | 0.50188600  | -1.40253200 |
| C | -3.77323400 | -0.63733900 | 0.32419400  |
| H | -3.47187700 | -1.56155700 | 0.82556000  |
| H | -3.57856800 | 0.18557600  | 1.01907700  |
| C | -5.25663800 | -0.68103800 | -0.02743900 |
| H | -5.47346000 | -1.51737500 | -0.69729700 |
| H | -5.86857200 | -0.79981000 | 0.86873000  |

|   |             |            |             |
|---|-------------|------------|-------------|
| H | -5.56712500 | 0.24036900 | -0.52750200 |
| F | -0.96769200 | 0.51954200 | 1.63892300  |

## 2a

Imaginary frequency: none

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | 3.09516400  | -1.20526600 | 0.00262900  |
| C | 1.70253200  | -1.19736400 | -0.00998100 |
| C | 0.98120500  | 0.00219100  | -0.01367400 |
| C | 1.70561700  | 1.19938000  | -0.01023900 |
| C | 3.09860700  | 1.20325400  | 0.00199600  |
| C | 3.79665600  | -0.00183800 | 0.00952200  |
| H | 3.63430600  | -2.14642800 | 0.00347300  |
| H | 1.16581300  | -2.14147800 | -0.02445700 |
| H | 1.17130000  | 2.14465500  | -0.02467000 |
| H | 3.64030400  | 2.14295100  | 0.00218800  |
| H | 4.88105200  | -0.00338700 | 0.01679100  |
| B | -0.61209200 | 0.00128900  | -0.00071500 |
| F | -1.18433100 | -0.06117700 | 1.31449100  |
| F | -1.18752900 | 1.17001900  | -0.59374300 |
| F | -1.18619100 | -1.10876300 | -0.70009800 |
| K | -3.45729100 | -0.00029600 | -0.00195400 |

## TMSOTf

Imaginary frequency: none

|    |            |             |             |
|----|------------|-------------|-------------|
| Si | 1.95498000 | 0.15403200  | -0.00302600 |
| C  | 3.26959400 | -0.86918600 | -0.80595200 |
| H  | 3.20201300 | -1.91299000 | -0.48955600 |
| H  | 3.18688300 | -0.82760000 | -1.89488900 |
| H  | 4.25645700 | -0.49002800 | -0.52458700 |
| C  | 1.91086600 | 0.00454200  | 1.84341400  |

|   |             |             |             |
|---|-------------|-------------|-------------|
| H | 1.07638700  | 0.55402900  | 2.28444300  |
| H | 1.85089600  | -1.03828600 | 2.16230100  |
| H | 2.83929300  | 0.42873900  | 2.23947100  |
| C | 1.89111000  | 1.90070600  | -0.61796200 |
| H | 1.73826000  | 1.92338300  | -1.70020600 |
| H | 1.09234800  | 2.47212900  | -0.13992300 |
| H | 2.84003700  | 2.40024800  | -0.40031500 |
| O | 0.46872400  | -0.56292900 | -0.64138300 |
| S | -0.91133600 | -0.97238500 | -0.08964500 |
| O | -1.62303600 | -1.70901700 | -1.09832600 |
| O | -0.82954600 | -1.46221700 | 1.26224500  |
| C | -1.70844000 | 0.69130800  | 0.01270400  |
| F | -2.96468100 | 0.55014300  | 0.39394200  |
| F | -1.66479000 | 1.28687900  | -1.16561300 |
| F | -1.05706700 | 1.42977500  | 0.90127400  |

### Int-a

Imaginary frequency: none

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | -4.91735000 | -1.45170000 | 0.11231400  |
| C | -3.58632500 | -1.17018500 | -0.17692100 |
| C | -3.15777600 | 0.14635200  | -0.08856500 |
| C | -4.00975800 | 1.18399200  | 0.28299500  |
| C | -5.32919300 | 0.87693700  | 0.56775500  |
| C | -5.80160100 | -0.44012500 | 0.48643300  |
| H | -5.27048700 | -2.47426400 | 0.04396900  |
| H | -2.89966800 | -1.95571000 | -0.46784800 |
| H | -3.64666600 | 2.20267700  | 0.33973800  |
| H | -6.00908000 | 1.67006800  | 0.85919200  |
| C | -7.24195200 | -0.74107400 | 0.79193100  |
| H | -7.43370200 | -1.81395100 | 0.77434600  |

|    |             |             |             |
|----|-------------|-------------|-------------|
| H  | -7.51510000 | -0.35153500 | 1.77534500  |
| H  | -7.89401200 | -0.26070400 | 0.05759500  |
| S  | -1.47181500 | 0.48178600  | -0.45735400 |
| O  | -0.77036500 | -0.70467000 | -0.90848000 |
| N  | -1.39974200 | 1.81460500  | -1.13350100 |
| C  | -0.13602800 | 2.27446600  | -1.74241500 |
| H  | -0.41983700 | 2.87226200  | -2.61078300 |
| H  | 0.45934100  | 1.42778100  | -2.09595300 |
| C  | 0.68757500  | 3.12684600  | -0.78387700 |
| H  | 0.09828000  | 3.99718100  | -0.48129700 |
| H  | 0.89682400  | 2.54506600  | 0.11815000  |
| C  | 1.99351600  | 3.56326600  | -1.43982300 |
| H  | 1.79998900  | 4.09380800  | -2.37653200 |
| H  | 2.56224600  | 4.23077800  | -0.78952800 |
| H  | 2.62168000  | 2.69659300  | -1.66778000 |
| F  | -0.91853300 | 0.61565200  | 1.10951700  |
| Si | 2.77124000  | 0.59360100  | 1.66022300  |
| C  | 4.00590000  | 1.89770900  | 1.20379700  |
| H  | 4.66539800  | 1.55766400  | 0.40123600  |
| H  | 3.50771100  | 2.81651900  | 0.88463200  |
| H  | 4.62513800  | 2.13465300  | 2.07459200  |
| C  | 3.54661400  | -0.96920400 | 2.29932700  |
| H  | 2.80960900  | -1.76485700 | 2.43730300  |
| H  | 4.34884700  | -1.33416000 | 1.65601300  |
| H  | 3.97597200  | -0.75044000 | 3.28276500  |
| C  | 1.43425600  | 1.20014500  | 2.78567400  |
| H  | 0.91248500  | 2.07274100  | 2.38934200  |
| H  | 0.70176300  | 0.41712300  | 2.98976500  |
| H  | 1.90477400  | 1.48570300  | 3.73285000  |
| O  | 1.94393400  | 0.19207500  | 0.14170000  |

|   |            |             |             |
|---|------------|-------------|-------------|
| S | 2.43124700 | -0.77179800 | -0.97013200 |
| O | 1.86441400 | -0.40051000 | -2.23713300 |
| O | 3.85713500 | -0.98440700 | -0.86517600 |
| C | 1.62369900 | -2.38480200 | -0.42603900 |
| F | 2.58854900 | -3.25907500 | -0.17645000 |
| F | 0.86238600 | -2.85102200 | -1.39305600 |
| F | 0.91404500 | -2.21479100 | 0.67346000  |

### **Ts-a**

Imaginary frequency: -202.12

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | -4.36709000 | -1.39641500 | -0.62320100 |
| C | -3.05045400 | -1.00575600 | -0.80155300 |
| C | -2.71638900 | 0.30881300  | -0.48847200 |
| C | -3.63340100 | 1.23078300  | 0.00490300  |
| C | -4.94244800 | 0.80742900  | 0.17268000  |
| C | -5.32730600 | -0.50119800 | -0.13854800 |
| H | -4.65426700 | -2.41440100 | -0.85975200 |
| H | -2.30597700 | -1.69992400 | -1.17251200 |
| H | -3.33264400 | 2.24247800  | 0.24367400  |
| H | -5.67907900 | 1.50590800  | 0.55260200  |
| C | -6.75629100 | -0.93324400 | 0.01751800  |
| H | -7.29507100 | -0.77297400 | -0.92138100 |
| H | -6.82014200 | -1.99466100 | 0.26026900  |
| H | -7.25902300 | -0.35608600 | 0.79418200  |
| S | -1.04976300 | 0.77342300  | -0.73283400 |
| O | -0.34474200 | -0.05242200 | -1.68055300 |
| N | -0.82866000 | 2.19559000  | -0.39481600 |
| C | 0.37150400  | 2.97566700  | -0.75569800 |
| H | -0.00757000 | 3.82939600  | -1.32321800 |
| H | 1.04416500  | 2.39473900  | -1.38908100 |

|    |             |             |             |
|----|-------------|-------------|-------------|
| C  | 1.08731000  | 3.45723400  | 0.49800600  |
| H  | 0.38035600  | 4.00774600  | 1.12487700  |
| H  | 1.42661700  | 2.58658400  | 1.06130800  |
| C  | 2.27345200  | 4.34053500  | 0.12438600  |
| H  | 1.94768500  | 5.21953600  | -0.43805300 |
| H  | 2.79550800  | 4.68619400  | 1.01844400  |
| H  | 2.98903200  | 3.79028800  | -0.49250800 |
| F  | -0.54338200 | -0.31735000 | 0.89049300  |
| Si | 0.92469000  | -0.71460900 | 2.01267900  |
| C  | 0.80299500  | 0.78766300  | 3.10568800  |
| H  | 1.71181200  | 1.39128800  | 3.05175100  |
| H  | -0.05312700 | 1.41715900  | 2.85176000  |
| H  | 0.68170100  | 0.45662400  | 4.14244600  |
| C  | 2.59658100  | -1.54469300 | 2.30818400  |
| H  | 2.78087900  | -2.39155100 | 1.63869400  |
| H  | 3.44150100  | -0.86057900 | 2.22849000  |
| H  | 2.56611700  | -1.94824400 | 3.32589400  |
| C  | -0.19751800 | -2.13421200 | 2.57216000  |
| H  | -1.22174000 | -1.80715100 | 2.76249600  |
| H  | -0.23336700 | -2.91662100 | 1.80670400  |
| H  | 0.20773800  | -2.58478300 | 3.48288900  |
| O  | 1.68463800  | 0.19989100  | 0.41258000  |
| S  | 2.72763300  | -0.11507600 | -0.63773200 |
| O  | 2.62690700  | 0.80293900  | -1.75235900 |
| O  | 4.04649600  | -0.36224200 | -0.09474000 |
| C  | 2.13786000  | -1.78034400 | -1.28157800 |
| F  | 3.13044000  | -2.65740000 | -1.21517900 |
| F  | 1.74128500  | -1.68445300 | -2.53618300 |
| F  | 1.12929300  | -2.23613400 | -0.53924100 |



**Int-b**

Imaginary frequency: none

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | -4.27959000 | -0.47220200 | -1.44037200 |
| C | -2.94314500 | -0.15499400 | -1.60035000 |
| C | -2.41257100 | 0.83569500  | -0.77441500 |
| C | -3.15694500 | 1.51134300  | 0.19221900  |
| C | -4.48887900 | 1.16192300  | 0.32829000  |
| C | -5.06551500 | 0.16977700  | -0.47501300 |
| H | -4.72109900 | -1.23588400 | -2.06982000 |
| H | -2.33029800 | -0.66140000 | -2.33491100 |
| H | -2.70893400 | 2.28000000  | 0.80846300  |
| H | -5.09474900 | 1.67078600  | 1.06873800  |
| C | -6.49863100 | -0.22480100 | -0.28252500 |
| H | -6.55307900 | -1.06654400 | 0.41539400  |
| H | -7.08036800 | 0.59648500  | 0.13646400  |
| H | -6.94691100 | -0.54456700 | -1.22385000 |
| S | -0.72809600 | 1.21851900  | -0.99109600 |
| O | -0.10609800 | 0.63248400  | -2.14711500 |
| N | -0.27134900 | 2.27031500  | -0.05936300 |
| C | 1.04315500  | 2.93071100  | -0.05255800 |
| H | 0.86883200  | 3.90514800  | -0.52194900 |
| H | 1.77087700  | 2.37042400  | -0.64047400 |
| C | 1.51276900  | 3.11120700  | 1.38282800  |
| H | 0.74079500  | 3.64268100  | 1.94574500  |
| H | 1.63928200  | 2.12509300  | 1.83295500  |
| C | 2.82813000  | 3.88254000  | 1.40872600  |
| H | 2.71051200  | 4.87377900  | 0.96271200  |
| H | 3.17607400  | 4.01337600  | 2.43501600  |
| H | 3.59669800  | 3.34018300  | 0.85345500  |
| F | -0.75806900 | -1.35849700 | -0.18636900 |

|    |             |             |             |
|----|-------------|-------------|-------------|
| Si | -0.87240500 | -1.74612800 | 1.41977500  |
| C  | -0.80940100 | -0.18530600 | 2.42888200  |
| H  | 0.11143200  | 0.36963900  | 2.24480800  |
| H  | -1.66897300 | 0.46472400  | 2.24510500  |
| H  | -0.83740500 | -0.46295500 | 3.48842400  |
| C  | 0.51957200  | -2.91165800 | 1.79936900  |
| H  | 0.51148900  | -3.76744700 | 1.11849900  |
| H  | 1.48503600  | -2.40634900 | 1.71820600  |
| H  | 0.41599100  | -3.29473300 | 2.81942400  |
| C  | -2.55224800 | -2.53639600 | 1.56587700  |
| H  | -3.33139700 | -1.82585900 | 1.26875700  |
| H  | -2.63920700 | -3.42447600 | 0.93382600  |
| H  | -2.74935600 | -2.83554900 | 2.59970400  |
| O  | 1.52609300  | 0.03462900  | 0.35278100  |
| S  | 2.97028000  | -0.20498300 | 0.25205400  |
| O  | 3.75393700  | 0.96339000  | -0.14685800 |
| O  | 3.53386700  | -1.00660000 | 1.33657700  |
| C  | 3.08998500  | -1.31875000 | -1.21222400 |
| F  | 4.35521600  | -1.68176500 | -1.42600300 |
| F  | 2.64398000  | -0.71019300 | -2.30797800 |
| F  | 2.36891900  | -2.42457800 | -1.02596300 |

### Int-1

Imaginary frequency: none

|    |             |            |             |
|----|-------------|------------|-------------|
| Si | 1.35863200  | 1.99849600 | -0.64157300 |
| C  | 0.22051900  | 2.03606700 | -2.09824300 |
| H  | 0.72963800  | 1.70166500 | -3.00628000 |
| H  | -0.66004600 | 1.41268200 | -1.92378000 |
| H  | -0.12442100 | 3.06091800 | -2.26618100 |
| C  | 2.97006000  | 2.87651700 | -0.88901700 |

|   |             |             |             |
|---|-------------|-------------|-------------|
| H | 3.64031600  | 2.73870000  | -0.03662600 |
| H | 3.47988600  | 2.54273100  | -1.79562900 |
| H | 2.76798300  | 3.94810600  | -0.98571200 |
| C | 0.54811800  | 2.38349300  | 0.97602500  |
| H | -0.27602200 | 1.69454800  | 1.16892600  |
| H | 1.25147700  | 2.35066000  | 1.81044300  |
| H | 0.13976500  | 3.39822000  | 0.92428100  |
| O | 1.75504200  | 0.25473000  | -0.58732300 |
| S | 2.95119200  | -0.63088300 | -0.17416800 |
| O | 2.61867000  | -1.97896400 | -0.58146500 |
| O | 4.22279100  | -0.05243800 | -0.50447400 |
| C | 2.78488200  | -0.58064000 | 1.66849500  |
| F | 3.61577000  | -1.45625700 | 2.19644800  |
| F | 1.54320500  | -0.87465000 | 2.00365700  |
| F | 3.08572200  | 0.63599400  | 2.08991300  |
| C | -4.90565900 | 0.42273400  | 2.13252400  |
| C | -3.73698800 | -0.03661100 | 1.53110000  |
| C | -3.65188500 | -0.21253000 | 0.14428900  |
| C | -4.78046500 | 0.09469800  | -0.62282600 |
| C | -5.95503200 | 0.55554900  | -0.03127800 |
| C | -6.01959200 | 0.71945400  | 1.34983500  |
| H | -4.94955400 | 0.55259000  | 3.20845400  |
| H | -2.87343200 | -0.25975100 | 2.15148600  |
| H | -4.73926700 | -0.02458200 | -1.70121500 |
| H | -6.81809600 | 0.78870400  | -0.64545300 |
| H | -6.93120000 | 1.07897800  | 1.81406000  |
| B | -2.31318300 | -0.76246700 | -0.52385300 |
| F | -2.14601500 | -2.18072000 | -0.40370400 |
| F | -2.22060000 | -0.49082700 | -1.92564200 |
| F | -1.12292100 | -0.20500300 | 0.05312800  |

|   |            |             |             |
|---|------------|-------------|-------------|
| K | 0.11982800 | -1.75013000 | -1.68591100 |
|---|------------|-------------|-------------|

# **Ts-1**

Imaginary frequency: -161.26

|    |             |             |             |
|----|-------------|-------------|-------------|
| Si | -0.67063700 | 2.16188400  | 0.03026000  |
| C  | -0.27239400 | 2.67555500  | 1.76405800  |
| H  | -0.88044500 | 2.15280400  | 2.50413700  |
| H  | 0.78243400  | 2.53365300  | 2.00051200  |
| H  | -0.49746300 | 3.74540900  | 1.83717200  |
| C  | -2.39548200 | 2.66293200  | -0.49934200 |
| H  | -2.68931700 | 2.23167100  | -1.45969100 |
| H  | -3.15780100 | 2.41405400  | 0.23845100  |
| H  | -2.36623000 | 3.75007100  | -0.63114700 |
| C  | 0.39977300  | 3.04555200  | -1.23266900 |
| H  | 1.45919100  | 3.02284600  | -0.96988900 |
| H  | 0.28549400  | 2.59505500  | -2.22358600 |
| H  | 0.07292500  | 4.08733000  | -1.30493000 |
| O  | -1.54139100 | 0.32281000  | 0.65525000  |
| S  | -2.57114600 | -0.61456100 | 0.08067600  |
| O  | -2.51860200 | -1.88301700 | 0.79988000  |
| O  | -3.87136500 | -0.02432700 | -0.14030200 |
| C  | -1.91529800 | -0.97394600 | -1.62519700 |
| F  | -2.92270100 | -1.29773400 | -2.42016600 |
| F  | -1.04670200 | -1.96570300 | -1.60505600 |
| F  | -1.32079000 | 0.11493500  | -2.11117200 |
| C  | 4.67341700  | -1.45980900 | -1.22015200 |
| C  | 3.36618500  | -1.43026600 | -0.73863500 |
| C  | 2.90424100  | -0.35826800 | 0.03031600  |
| C  | 3.79225100  | 0.68889900  | 0.30544900  |
| C  | 5.09897700  | 0.66853700  | -0.17272200 |

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | 5.54145500  | -0.40884200 | -0.93805800 |
| H | 5.01499800  | -2.30061100 | -1.81371200 |
| H | 2.69606200  | -2.25474700 | -0.96124900 |
| H | 3.45851900  | 1.53132600  | 0.90517900  |
| H | 5.77312400  | 1.48809200  | 0.05031800  |
| H | 6.55935400  | -0.42888500 | -1.31100100 |
| B | 1.41643000  | -0.31482100 | 0.57432000  |
| F | 0.69182100  | -1.50358000 | 0.42627300  |
| F | 1.27833200  | 0.11464300  | 1.90713800  |
| F | 0.64666900  | 0.72331800  | -0.23698800 |
| K | -0.66912100 | -1.42558200 | 2.65032700  |

## Int-2

Imaginary frequency: none

|    |             |             |             |
|----|-------------|-------------|-------------|
| Si | 0.90808400  | 1.68616000  | 0.45305700  |
| C  | 1.18702100  | 1.34636000  | 2.25523800  |
| H  | 0.33086000  | 0.82443200  | 2.69198200  |
| H  | 2.08415100  | 0.74314300  | 2.41640900  |
| H  | 1.31451900  | 2.28924800  | 2.79601000  |
| C  | -0.65468000 | 2.62633900  | 0.12639100  |
| H  | -0.87920000 | 2.67454900  | -0.94229100 |
| H  | -1.49602900 | 2.16233900  | 0.64525500  |
| H  | -0.54713100 | 3.65174700  | 0.49393800  |
| C  | 2.37981500  | 2.42436100  | -0.40302600 |
| H  | 3.31411200  | 1.94195700  | -0.10582600 |
| H  | 2.27958400  | 2.35540300  | -1.48990600 |
| H  | 2.44923600  | 3.48536500  | -0.14222100 |
| O  | -2.46553200 | -0.01336700 | 1.28427600  |
| S  | -3.69171200 | -0.43358100 | 0.58641300  |
| O  | -3.57176900 | -1.79468500 | 0.04153800  |

|   |             |             |             |
|---|-------------|-------------|-------------|
| O | -4.94956200 | -0.09856300 | 1.22719200  |
| C | -3.64154900 | 0.59467300  | -0.94286600 |
| F | -4.62088000 | 0.26194500  | -1.77500500 |
| F | -2.47350600 | 0.38990500  | -1.56481400 |
| F | -3.74607400 | 1.88803100  | -0.66211800 |
| C | 5.22765300  | 0.16340700  | -1.58002200 |
| C | 4.06015000  | -0.57838000 | -1.44871600 |
| C | 3.58469600  | -0.93243700 | -0.17949300 |
| C | 4.30401200  | -0.53875800 | 0.95645600  |
| C | 5.47470600  | 0.19900700  | 0.82619200  |
| C | 5.93233900  | 0.55174300  | -0.44205200 |
| H | 5.58935100  | 0.44021800  | -2.56327300 |
| H | 3.50825900  | -0.87814400 | -2.33341800 |
| H | 3.94501400  | -0.81222700 | 1.94305000  |
| H | 6.02942900  | 0.50004800  | 1.70704800  |
| H | 6.84348300  | 1.13040400  | -0.54404100 |
| B | 2.26690200  | -1.70209700 | -0.03747300 |
| F | 1.59631800  | -2.20917700 | -1.07939400 |
| F | 1.69273200  | -1.95595200 | 1.14583600  |
| F | 0.67474600  | 0.16947800  | -0.22938100 |
| K | -0.89926400 | -1.86578800 | 0.10213000  |

### Int-3

Imaginary frequency: none

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | -2.50684800 | -1.43052000 | 1.02352000  |
| C | -1.17746100 | -1.13649900 | 1.27002100  |
| C | -0.24021500 | -1.44538200 | 0.28523900  |
| C | -0.59221300 | -2.04660200 | -0.91452300 |
| C | -1.93487800 | -2.33221700 | -1.13627400 |
| C | -2.90409000 | -2.02645300 | -0.18071400 |

|   |             |             |             |
|---|-------------|-------------|-------------|
| H | -3.25386300 | -1.18741800 | 1.77129500  |
| H | -0.87648300 | -0.66794600 | 2.19995900  |
| H | 0.16203600  | -2.27648000 | -1.65583400 |
| H | -2.23067300 | -2.79735800 | -2.06982700 |
| C | -4.35985000 | -2.28296300 | -0.44308600 |
| H | -4.49975500 | -2.92956700 | -1.30956200 |
| H | -4.83721900 | -2.74305200 | 0.42446600  |
| H | -4.87302700 | -1.33503800 | -0.63536300 |
| S | 1.44830600  | -1.11683900 | 0.64179100  |
| O | 1.87590000  | -1.65576400 | 1.91925100  |
| N | 2.23771100  | -1.20981100 | -0.62144100 |
| C | 3.71266000  | -1.20100900 | -0.58376500 |
| H | 4.03798000  | -1.65387000 | -1.52127600 |
| H | 4.08417100  | -1.82366500 | 0.23686900  |
| C | 4.27714600  | 0.21150200  | -0.46679700 |
| H | 3.86019000  | 0.82377900  | -1.27078600 |
| H | 3.94976800  | 0.65505100  | 0.47914400  |
| C | 5.80040000  | 0.20167000  | -0.54043300 |
| H | 6.14126800  | -0.21729100 | -1.49095900 |
| H | 6.20267800  | 1.21285400  | -0.45493600 |
| H | 6.22766400  | -0.40031900 | 0.26601500  |
| C | -1.69016700 | 1.38511500  | -1.28662000 |
| C | -3.05918800 | 1.14598800  | -1.24853000 |
| C | -3.80690100 | 1.57359000  | -0.15307600 |
| C | -3.18723700 | 2.23653100  | 0.90429600  |
| C | -1.81911200 | 2.48153000  | 0.85947500  |
| C | -1.05587700 | 2.06050900  | -0.23632000 |
| H | -1.10767700 | 1.05032500  | -2.13902600 |
| H | -3.54371300 | 0.62338100  | -2.06587000 |
| H | -4.87495900 | 1.38742500  | -0.12242700 |

|   |             |            |             |
|---|-------------|------------|-------------|
| H | -3.77148400 | 2.56453100 | 1.75626100  |
| H | -1.33758300 | 3.00409900 | 1.67951800  |
| B | 0.45864700  | 2.35460300 | -0.29752700 |
| F | 1.24147200  | 0.50888200 | 1.07179500  |
| F | 1.21554600  | 1.92295200 | -1.30487900 |
| F | 1.06146600  | 3.14072500 | 0.59118600  |

## Ts-2

Imaginary frequency: -320.49

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | -2.49422800 | -1.57743500 | 0.93750700  |
| C | -1.18375200 | -1.30261400 | 1.28792900  |
| C | -0.20189000 | -1.45144100 | 0.31070200  |
| C | -0.48392600 | -1.85611900 | -0.98818200 |
| C | -1.80608200 | -2.13190500 | -1.30698200 |
| C | -2.82318600 | -1.98980600 | -0.35954500 |
| H | -3.27879700 | -1.45775700 | 1.67646300  |
| H | -0.93049500 | -0.97531700 | 2.28933500  |
| H | 0.30584200  | -1.94905100 | -1.72228100 |
| H | -2.05321400 | -2.44621500 | -2.31459000 |
| C | -4.25443700 | -2.26757700 | -0.71754500 |
| H | -4.39732300 | -2.27095400 | -1.79847000 |
| H | -4.55663900 | -3.24534400 | -0.33067900 |
| H | -4.91420300 | -1.51991000 | -0.27214300 |
| S | 1.43303300  | -1.04255600 | 0.76926300  |
| O | 1.68907900  | -1.17976500 | 2.18441500  |
| N | 2.37280500  | -1.33417800 | -0.33945700 |
| C | 3.83209800  | -1.16137900 | -0.21125600 |
| H | 4.27598900  | -1.85497500 | -0.92606700 |
| H | 4.17234500  | -1.43630000 | 0.79136500  |
| C | 4.24315800  | 0.27044900  | -0.54295600 |



|   |             |             |             |
|---|-------------|-------------|-------------|
| H | 3.85270700  | 0.52741700  | -1.53111200 |
| H | 3.78147400  | 0.95375500  | 0.17607400  |
| C | 5.76044900  | 0.41940300  | -0.51319500 |
| H | 6.23160800  | -0.24500300 | -1.24218400 |
| H | 6.05416600  | 1.44336600  | -0.75096300 |
| H | 6.15885400  | 0.17467100  | 0.47488700  |
| C | -1.97733900 | 1.35357400  | -1.16889400 |
| C | -3.34655700 | 1.34070200  | -0.91043500 |
| C | -3.82578600 | 1.80499400  | 0.31074600  |
| C | -2.93527400 | 2.29029900  | 1.26842100  |
| C | -1.57122000 | 2.31132900  | 0.99939100  |
| C | -1.07173100 | 1.83632900  | -0.22016800 |
| H | -1.60896600 | 0.98096700  | -2.11940200 |
| H | -4.03660700 | 0.96190400  | -1.65682100 |
| H | -4.89018600 | 1.79057000  | 0.51775000  |
| H | -3.30760200 | 2.65355300  | 2.21971700  |
| H | -0.88342600 | 2.69257700  | 1.74825100  |
| B | 0.46565700  | 1.85926800  | -0.53042500 |
| F | 1.15120600  | 0.78063800  | 0.80391000  |
| F | 0.92237100  | 1.16824800  | -1.60283400 |
| F | 1.20238000  | 2.94568800  | -0.20525000 |

#### Int-4

Imaginary frequency: none

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | -2.37615900 | -1.65189600 | 0.87766200  |
| C | -1.05731700 | -1.47070400 | 1.25607700  |
| C | -0.08429400 | -1.55855200 | 0.26103800  |
| C | -0.37318400 | -1.80735800 | -1.08243600 |
| C | -1.69935400 | -1.98933500 | -1.42041200 |
| C | -2.71462100 | -1.90615000 | -0.45546200 |

|   |             |             |             |
|---|-------------|-------------|-------------|
| H | -3.15715500 | -1.57598200 | 1.62524800  |
| H | -0.79316500 | -1.25676200 | 2.28439200  |
| H | 0.41356800  | -1.84972200 | -1.82378800 |
| H | -1.96050700 | -2.18056400 | -2.45480600 |
| C | -4.14769500 | -2.09546300 | -0.85110200 |
| H | -4.32405500 | -1.73007300 | -1.86376000 |
| H | -4.39601700 | -3.16158600 | -0.83415500 |
| H | -4.81648600 | -1.58289300 | -0.15867500 |
| S | 1.54589400  | -1.26137100 | 0.74536300  |
| O | 1.77310300  | -1.20853300 | 2.16586800  |
| N | 2.50691300  | -1.28618900 | -0.37385300 |
| C | 3.94957100  | -1.00985800 | -0.26898700 |
| H | 4.42278200  | -1.64459600 | -1.01831500 |
| H | 4.33018600  | -1.27114200 | 0.72063700  |
| C | 4.20064300  | 0.46607400  | -0.58000300 |
| H | 3.77016500  | 0.69846500  | -1.55646400 |
| H | 3.68296200  | 1.07837800  | 0.16294400  |
| C | 5.69687100  | 0.75834400  | -0.56739200 |
| H | 6.21807000  | 0.16054100  | -1.31907700 |
| H | 5.88018200  | 1.81169800  | -0.78582800 |
| H | 6.13234100  | 0.53401700  | 0.40943200  |
| C | -2.03305100 | 1.45069400  | -1.12115400 |
| C | -3.41711400 | 1.42166200  | -0.95134700 |
| C | -3.96786900 | 1.65280300  | 0.30637700  |
| C | -3.12770400 | 1.91749700  | 1.38751600  |
| C | -1.74784000 | 1.94435000  | 1.20412300  |
| C | -1.17000000 | 1.70823800  | -0.05109100 |
| H | -1.61433500 | 1.25456100  | -2.10401800 |
| H | -4.06524900 | 1.21416000  | -1.79660400 |
| H | -5.04338900 | 1.62831500  | 0.44439200  |

|   |             |            |             |
|---|-------------|------------|-------------|
| H | -3.55070600 | 2.09850400 | 2.36998700  |
| H | -1.10396000 | 2.13914600 | 2.05765400  |
| B | 0.42341400  | 1.74780300 | -0.24874200 |
| F | 1.08273900  | 1.10105300 | 0.88261900  |
| F | 0.83860900  | 1.04159700 | -1.40064300 |
| F | 0.94586100  | 3.05379100 | -0.30550000 |

### 3a

Imaginary frequency: none

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | -3.66290600 | 0.12044500  | 0.73057100  |
| C | -2.33828700 | 0.17052900  | 1.15228000  |
| C | -1.36441900 | -0.43485300 | 0.36988700  |
| C | -1.68107900 | -1.08036300 | -0.82222000 |
| C | -3.00804100 | -1.12094500 | -1.22298800 |
| C | -4.01516200 | -0.52135100 | -0.45729700 |
| H | -4.43325400 | 0.58417100  | 1.33666200  |
| H | -2.06844000 | 0.66202400  | 2.07967200  |
| H | -0.90306700 | -1.55124600 | -1.40961000 |
| H | -3.27112900 | -1.62750600 | -2.14566500 |
| C | -5.44542400 | -0.57474700 | -0.91851700 |
| H | -5.55783900 | -0.06012000 | -1.87632200 |
| H | -5.76365300 | -1.60977200 | -1.06504100 |
| H | -6.11153400 | -0.10550800 | -0.19419400 |
| S | 0.32466800  | -0.31753100 | 0.92090300  |
| O | 0.32322900  | -0.04866900 | 2.37275100  |
| N | 1.01082200  | -1.54280300 | 0.30269500  |
| C | 2.47696500  | -1.61181300 | 0.42037400  |
| H | 2.76697100  | -1.96354700 | 1.41803800  |
| H | 2.94900100  | -0.62878600 | 0.27679200  |
| C | 3.01366100  | -2.57603300 | -0.62827100 |

|   |            |             |             |
|---|------------|-------------|-------------|
| H | 2.52288500 | -3.54518400 | -0.49639000 |
| H | 2.73289500 | -2.20633100 | -1.61956500 |
| C | 4.52754200 | -2.73342300 | -0.53170000 |
| H | 4.81866600 | -3.11812500 | 0.44965100  |
| H | 4.90173100 | -3.42700600 | -1.28755300 |
| H | 5.03135200 | -1.77387300 | -0.67818500 |
| C | 0.91803400 | 1.20708500  | 0.15784600  |
| C | 1.03075700 | 2.36148300  | 0.92178900  |
| C | 1.24067500 | 1.18479900  | -1.19588200 |
| C | 1.47698300 | 3.52851400  | 0.30750100  |
| H | 0.77986900 | 2.34036600  | 1.97509600  |
| C | 1.68511400 | 2.35632700  | -1.79658900 |
| H | 1.15147500 | 0.26585000  | -1.76536300 |
| C | 1.80113900 | 3.52488600  | -1.04578600 |
| H | 1.57206400 | 4.43819300  | 0.88821200  |
| H | 1.94368100 | 2.35684500  | -2.84861300 |
| H | 2.14873900 | 4.43577400  | -1.51893800 |

### **BF<sub>3</sub>**

Imaginary frequency: none

|   |             |             |            |
|---|-------------|-------------|------------|
| B | 0.00000000  | 0.00000000  | 0.00000000 |
| F | 0.00000000  | 1.31394800  | 0.00000000 |
| F | 1.13791300  | -0.65697400 | 0.00000000 |
| F | -1.13791300 | -0.65697400 | 0.00000000 |

### **Int-c**

Imaginary frequency: none

|   |            |             |             |
|---|------------|-------------|-------------|
| C | 3.44070400 | 0.24135400  | -0.83307600 |
| C | 2.06707100 | 0.21786300  | -1.04391700 |
| C | 1.29130200 | -0.57862300 | -0.21250500 |

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | 1.83461000  | -1.33882100 | 0.82074500  |
| C | 3.20509000  | -1.29565700 | 1.00794200  |
| C | 4.02538700  | -0.50927700 | 0.18735500  |
| H | 4.06549100  | 0.85220700  | -1.47440400 |
| H | 1.61341400  | 0.79983200  | -1.83667900 |
| H | 1.19981300  | -1.94932500 | 1.45033500  |
| H | 3.65162700  | -1.88109100 | 1.80410900  |
| C | 5.51072800  | -0.48922400 | 0.41133600  |
| H | 5.73849900  | -0.18935000 | 1.43702800  |
| H | 5.93020700  | -1.48755200 | 0.26236900  |
| H | 6.00406000  | 0.20057700  | -0.27321300 |
| S | -0.43883300 | -0.58852800 | -0.49254300 |
| O | -0.81422800 | 0.12795800  | -1.69335900 |
| N | -1.00372400 | -1.89590200 | -0.05311000 |
| C | -2.41775500 | -2.23487300 | -0.31206000 |
| H | -2.51698800 | -3.29089200 | -0.05953900 |
| H | -2.64235600 | -2.12005200 | -1.37715400 |
| C | -3.39224300 | -1.40578200 | 0.51969500  |
| H | -3.09755200 | -1.46417500 | 1.57122900  |
| H | -3.32213100 | -0.35481900 | 0.22085100  |
| C | -4.82265700 | -1.90196400 | 0.33754500  |
| H | -4.91846800 | -2.94154400 | 0.66156400  |
| H | -5.52137400 | -1.30054900 | 0.92197500  |
| H | -5.12501600 | -1.84565400 | -0.71156100 |
| F | -0.85131000 | 0.59884700  | 0.69755200  |
| B | -1.15793700 | 2.72259600  | 0.24875400  |
| F | -0.02913100 | 2.81828800  | -0.43007500 |
| F | -2.29394200 | 2.51932000  | -0.38997900 |
| F | -1.17692100 | 3.04060400  | 1.52920100  |

**Ts-b**

Imaginary frequency: -207.88

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | -3.42824800 | 0.16089400  | 0.86379600  |
| C | -2.05743400 | 0.14842200  | 1.09034100  |
| C | -1.26193600 | -0.59888200 | 0.23197100  |
| C | -1.77990400 | -1.31890300 | -0.84245000 |
| C | -3.14834000 | -1.28623800 | -1.04381300 |
| C | -3.98921400 | -0.54928000 | -0.19843700 |
| H | -4.06973200 | 0.73113800  | 1.52556600  |
| H | -1.62171900 | 0.70097300  | 1.91350100  |
| H | -1.12879300 | -1.89033000 | -1.49170200 |
| H | -3.57700600 | -1.84099300 | -1.87103300 |
| C | -5.46980600 | -0.52573100 | -0.44975600 |
| H | -5.86137100 | -1.54236000 | -0.52900600 |
| H | -5.99794100 | -0.00585800 | 0.34933400  |
| H | -5.68381900 | -0.01839600 | -1.39435300 |
| S | 0.46223700  | -0.59794200 | 0.53010600  |
| O | 0.83131300  | 0.10371000  | 1.73909500  |
| N | 1.06511500  | -1.86109800 | 0.02789500  |
| C | 2.48822600  | -2.18014700 | 0.26362500  |
| H | 2.60971400  | -3.21813800 | -0.04624900 |
| H | 2.71353300  | -2.11522900 | 1.33237800  |
| C | 3.43398500  | -1.28152600 | -0.52825400 |
| H | 3.13612000  | -1.29469700 | -1.58025900 |
| H | 3.33561500  | -0.24985200 | -0.17543400 |
| C | 4.87800800  | -1.74731300 | -0.37588500 |
| H | 5.00067500  | -2.76591800 | -0.75288900 |
| H | 5.55660800  | -1.09763900 | -0.93153800 |
| H | 5.18350800  | -1.73575900 | 0.67366500  |
| F | 0.86058100  | 0.67149700  | -0.65924200 |

|   |             |            |             |
|---|-------------|------------|-------------|
| B | 1.02781900  | 2.60673500 | -0.26322200 |
| F | -0.09047300 | 2.70803100 | 0.44813000  |
| F | 2.19090600  | 2.53871300 | 0.37212800  |
| F | 1.01358600  | 2.98694700 | -1.53461800 |

### Int-d

Imaginary frequency: none

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | -3.10543500 | -0.51816900 | 0.94682100  |
| C | -1.76453100 | -0.51947600 | 1.29195600  |
| C | -0.85430000 | -0.93149100 | 0.32101300  |
| C | -1.22084900 | -1.32145300 | -0.96969600 |
| C | -2.56520800 | -1.30568200 | -1.27636200 |
| C | -3.52201000 | -0.90346100 | -0.33071500 |
| H | -3.84017300 | -0.20850700 | 1.68011800  |
| H | -1.43723700 | -0.20838100 | 2.27535300  |
| H | -0.47614100 | -1.61718500 | -1.69694500 |
| H | -2.88644100 | -1.60112300 | -2.26845500 |
| C | -4.97179800 | -0.87074700 | -0.70859700 |
| H | -5.14864400 | -0.05636200 | -1.41729300 |
| H | -5.26083600 | -1.80094500 | -1.20216400 |
| H | -5.60590200 | -0.71384500 | 0.16326500  |
| S | 0.81747400  | -0.87642700 | 0.74296200  |
| O | 1.12081400  | -0.31860700 | 2.03370600  |
| N | 1.69557600  | -1.55119100 | -0.23399800 |
| C | 3.16733500  | -1.60249100 | -0.16156400 |
| H | 3.45755200  | -2.43301900 | -0.80345500 |
| H | 3.48667800  | -1.80768700 | 0.86272200  |
| C | 3.77319500  | -0.29197700 | -0.66466700 |
| H | 3.37077200  | -0.07394300 | -1.65655100 |
| H | 3.47137500  | 0.52138700  | 0.00047000  |

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | 5.29306100  | -0.40260400 | -0.71171300 |
| H | 5.60580600  | -1.20029000 | -1.38972400 |
| H | 5.73131200  | 0.53279300  | -1.06341100 |
| H | 5.70071500  | -0.61691300 | 0.27924000  |
| F | 0.92223400  | 1.31073100  | -0.40162700 |
| B | -0.15358000 | 2.23399400  | -0.16230800 |
| F | -0.48029500 | 2.16318400  | 1.19358000  |
| F | 0.27900100  | 3.51078100  | -0.50116200 |
| F | -1.24236600 | 1.85412500  | -0.94518600 |

### Int-5

Imaginary frequency: none

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | 3.87897200  | 0.40205000  | -1.05790500 |
| C | 2.49799800  | 0.57630700  | -1.09515800 |
| C | 1.69760100  | 0.20244700  | -0.01143300 |
| C | 2.31593100  | -0.35039200 | 1.11572100  |
| C | 3.69529000  | -0.52779200 | 1.15947500  |
| C | 4.47837200  | -0.15160000 | 0.07033600  |
| H | 4.48709900  | 0.69722100  | -1.90559600 |
| H | 2.03760600  | 1.01173100  | -1.97641800 |
| H | 1.71161900  | -0.64304100 | 1.96897600  |
| H | 4.16072600  | -0.95719500 | 2.03953200  |
| H | 5.55347700  | -0.28848000 | 0.10205900  |
| B | 0.13620700  | 0.38701500  | -0.05301700 |
| F | -0.48066200 | -1.02686000 | -0.49692500 |
| F | -0.50812000 | 0.61744600  | 1.15948600  |
| F | -0.38023900 | 1.24826500  | -1.01317000 |
| K | -2.48706200 | 2.10781600  | 0.30570500  |
| B | -1.91458000 | -1.49649700 | -0.17284000 |
| F | -1.87156800 | -1.98314700 | 1.09723600  |



|   |             |             |             |
|---|-------------|-------------|-------------|
| F | -2.19759700 | -2.42021400 | -1.13021500 |
| F | -2.69397800 | -0.34964900 | -0.28239900 |

### **Ts-3**

Imaginary frequency: -61.61

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | -3.72145700 | -0.63043100 | -0.99068200 |
| C | -2.37894600 | -0.98725800 | -0.91152200 |
| C | -1.56391700 | -0.48566000 | 0.10898300  |
| C | -2.12506300 | 0.37982900  | 1.05423800  |
| C | -3.46735500 | 0.73775700  | 0.98066700  |
| C | -4.26578500 | 0.23306400  | -0.04331000 |
| H | -4.34302000 | -1.02486100 | -1.78643300 |
| H | -1.96019000 | -1.66540700 | -1.64827300 |
| H | -1.50505300 | 0.77872800  | 1.84986900  |
| H | -3.89199000 | 1.40851400  | 1.71886700  |
| H | -5.31199000 | 0.51160700  | -0.10189400 |
| B | -0.06219000 | -0.89611400 | 0.19017700  |
| F | 0.81795800  | 0.25679000  | -0.80829500 |
| F | 0.64075200  | -0.70923300 | 1.35378800  |
| F | 0.37706800  | -2.01331100 | -0.47349800 |
| K | 2.94591500  | -1.39296900 | 0.15549900  |
| B | 1.41392900  | 1.54656800  | -0.29375600 |
| F | 1.59331100  | 2.34397600  | -1.38715800 |
| F | 0.54535900  | 2.05210700  | 0.63194600  |
| F | 2.62736400  | 1.14986700  | 0.27666600  |

### **Int-6**

Imaginary frequency: none

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | -3.79760300 | -0.47118400 | -1.03014000 |
| C | -2.52364200 | -1.00124500 | -0.86479100 |

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | -1.69857200 | -0.55374300 | 0.17477400  |
| C | -2.17241700 | 0.43374400  | 1.04800800  |
| C | -3.44597000 | 0.96391500  | 0.88421700  |
| C | -4.25675900 | 0.51038200  | -0.15472400 |
| H | -4.43219200 | -0.82008000 | -1.83627500 |
| H | -2.16567300 | -1.76738300 | -1.54436800 |
| H | -1.53618900 | 0.79045300  | 1.85013200  |
| H | -3.80846200 | 1.72853500  | 1.56122600  |
| H | -5.25075700 | 0.92416600  | -0.28240200 |
| B | -0.29999400 | -1.15188000 | 0.36459900  |
| F | 1.14547400  | 0.29326700  | -0.94376900 |
| F | 0.50393100  | -0.83712800 | 1.39007600  |
| F | 0.19499400  | -2.12209200 | -0.41843700 |
| K | 2.84072100  | -1.42421900 | 0.05365000  |
| B | 1.59681400  | 1.48675100  | -0.28127200 |
| F | 1.97344000  | 2.41766700  | -1.23049400 |
| F | 0.58823100  | 1.95977300  | 0.53846500  |
| F | 2.71673700  | 1.09283300  | 0.49434100  |

# **TMSBr**

Imaginary frequency: none

|    |             |             |             |
|----|-------------|-------------|-------------|
| Si | -0.85311800 | 0.00000600  | -0.00012700 |
| C  | -1.37897700 | -0.81429400 | -1.58899300 |
| H  | -1.01320300 | -0.26054000 | -2.45693900 |
| H  | -1.00825300 | -1.84042700 | -1.64893400 |
| H  | -2.47238800 | -0.84247300 | -1.63742000 |
| C  | -1.38058500 | 1.78284200  | 0.08931900  |
| H  | -1.01140300 | 2.26006600  | 1.00031900  |
| H  | -1.01593800 | 2.34726200  | -0.77211500 |
| H  | -2.47431200 | 1.83677300  | 0.09452500  |

|    |             |             |            |
|----|-------------|-------------|------------|
| C  | -1.38004200 | -0.96929700 | 1.49918200 |
| H  | -1.01439100 | -1.99797500 | 1.45357200 |
| H  | -1.01031200 | -0.50860100 | 2.41847000 |
| H  | -2.47359600 | -0.99709500 | 1.54665500 |
| Br | 1.43643000  | 0.00021200  | 0.00018900 |

### Int<sub>Br</sub>-1

Imaginary frequency: none

|    |             |             |             |
|----|-------------|-------------|-------------|
| Si | -2.10897200 | -1.59626700 | 0.22345900  |
| C  | -0.73382100 | -1.76495700 | -1.01390900 |
| H  | -0.09391000 | -0.88248200 | -1.01069500 |
| H  | -0.12352200 | -2.63737300 | -0.75738500 |
| H  | -1.13464900 | -1.90974800 | -2.02045600 |
| C  | -3.47204000 | -2.83312500 | -0.04504500 |
| H  | -4.30205700 | -2.66620000 | 0.64555100  |
| H  | -3.85220800 | -2.79002700 | -1.06842000 |
| H  | -3.07908500 | -3.84011200 | 0.13060500  |
| C  | -1.55632200 | -1.53291900 | 1.99548800  |
| H  | -0.81090400 | -0.75221700 | 2.15092200  |
| H  | -2.40427100 | -1.36085200 | 2.66290700  |
| H  | -1.10647200 | -2.49640300 | 2.25822500  |
| C  | 4.95336700  | -0.64677400 | 0.92886000  |
| C  | 3.85587700  | 0.21041600  | 0.91678200  |
| C  | 2.86633400  | 0.11252800  | -0.06862800 |
| C  | 3.01683900  | -0.87461100 | -1.04930500 |
| C  | 4.11067400  | -1.73776900 | -1.04621900 |
| C  | 5.08190500  | -1.62513500 | -0.05456800 |
| H  | 5.70938100  | -0.55194500 | 1.70078600  |
| H  | 3.77037700  | 0.97429400  | 1.68426200  |
| H  | 2.26936600  | -0.96614700 | -1.83192100 |

|    |             |             |             |
|----|-------------|-------------|-------------|
| H  | 4.20848200  | -2.49467100 | -1.81690200 |
| H  | 5.93571700  | -2.29357600 | -0.04958400 |
| B  | 1.59732000  | 1.07541200  | -0.05130600 |
| F  | 1.87450200  | 2.39928200  | 0.40294200  |
| F  | 0.97940400  | 1.22416700  | -1.33497200 |
| F  | 0.54083100  | 0.60858800  | 0.81070800  |
| K  | -0.74146200 | 2.72425100  | -0.02183500 |
| Br | -3.10425600 | 0.45551800  | -0.21210700 |

### TS-Br

Imaginary frequency: -164.03

|    |             |             |             |
|----|-------------|-------------|-------------|
| Si | 0.69889400  | -1.73584000 | -0.16190100 |
| C  | 0.32217700  | -1.71616900 | 1.65766800  |
| H  | 0.12841300  | -0.70131500 | 2.00816600  |
| H  | -0.55991800 | -2.33187700 | 1.85996700  |
| H  | 1.17045400  | -2.11419000 | 2.21854600  |
| C  | 1.96067500  | -3.00947500 | -0.72010900 |
| H  | 2.33122000  | -2.77476700 | -1.72157600 |
| H  | 2.81407900  | -3.07697800 | -0.04662500 |
| H  | 1.44994700  | -3.97780700 | -0.77146000 |
| C  | -0.78145000 | -2.19260000 | -1.22234600 |
| H  | -1.71375300 | -1.76216400 | -0.85465500 |
| H  | -0.64211600 | -1.86889300 | -2.25853300 |
| H  | -0.87654800 | -3.28286800 | -1.22850100 |
| C  | -4.40319900 | 0.07557000  | -0.99993400 |
| C  | -3.12784000 | 0.62954000  | -1.05641300 |
| C  | -2.28722700 | 0.62379100  | 0.06270000  |
| C  | -2.76905100 | 0.06293900  | 1.24955100  |
| C  | -4.04394800 | -0.49508600 | 1.31444200  |
| C  | -4.86088800 | -0.49365300 | 0.18678400  |

|    |             |             |             |
|----|-------------|-------------|-------------|
| H  | -5.04052700 | 0.08574400  | -1.87720200 |
| H  | -2.77680700 | 1.06793200  | -1.98586600 |
| H  | -2.13983400 | 0.05926400  | 2.13404700  |
| H  | -4.40125100 | -0.92824400 | 2.24210900  |
| H  | -5.85321700 | -0.92806900 | 0.23368800  |
| B  | -0.81843200 | 1.19813400  | -0.03968600 |
| F  | -0.64445200 | 2.25271500  | -0.95153800 |
| F  | -0.22114300 | 1.56411600  | 1.17586100  |
| F  | 0.15351600  | 0.14971700  | -0.60660000 |
| K  | 1.80007200  | 2.66627100  | -0.11537800 |
| Br | 2.93055200  | -0.18348300 | 0.15175800  |

### Int<sub>Br</sub>-2

Imaginary frequency: none

|    |             |             |             |
|----|-------------|-------------|-------------|
| Si | -0.04096300 | 1.73457900  | -0.40460200 |
| C  | -0.33490900 | 1.72320400  | 1.42518600  |
| H  | -1.30765500 | 1.27157800  | 1.64157300  |
| H  | 0.44467400  | 1.17281600  | 1.95816600  |
| H  | -0.34150600 | 2.74964400  | 1.80565400  |
| C  | -1.38596600 | 2.57506500  | -1.36376700 |
| H  | -1.22967400 | 2.47015000  | -2.44103900 |
| H  | -2.35933700 | 2.15182400  | -1.09988400 |
| H  | -1.40034500 | 3.64394000  | -1.12895000 |
| C  | 1.65385900  | 2.32512400  | -0.88324400 |
| H  | 2.43291200  | 1.89467700  | -0.24880500 |
| H  | 1.87735600  | 2.08268700  | -1.92603900 |
| H  | 1.69744200  | 3.41403800  | -0.77818100 |
| C  | 4.60185600  | -0.13777500 | -0.73817400 |
| C  | 3.40814300  | -0.83944600 | -0.85488100 |
| C  | 2.54651200  | -0.95926800 | 0.24298300  |

|    |             |             |             |
|----|-------------|-------------|-------------|
| C  | 2.90529100  | -0.37157900 | 1.46278600  |
| C  | 4.10103100  | 0.32706200  | 1.58219100  |
| C  | 4.94560500  | 0.44544100  | 0.48007400  |
| H  | 5.26387000  | -0.04342000 | -1.59090000 |
| H  | 3.13757100  | -1.29118600 | -1.80352900 |
| H  | 2.24529800  | -0.46278800 | 2.31903200  |
| H  | 4.37534300  | 0.77937700  | 2.52794000  |
| H  | 5.87675400  | 0.99319200  | 0.57156700  |
| B  | 1.20394000  | -1.68538900 | 0.09453400  |
| F  | 0.85739500  | -2.36606900 | -1.00523600 |
| F  | 0.28527700  | -1.72885100 | 1.06705300  |
| F  | -0.11512000 | 0.12292600  | -0.87475000 |
| K  | -1.86498800 | -1.78918600 | -0.76074800 |
| Br | -3.84630400 | 0.07233800  | 0.54391000  |

### TMSOMs

Imaginary frequency: none

|    |             |             |             |
|----|-------------|-------------|-------------|
| Si | -1.46587500 | 0.02104400  | 0.01996100  |
| C  | -2.57111600 | 0.38334900  | 1.46424400  |
| H  | -2.50408300 | -0.40703500 | 2.21628400  |
| H  | -2.30558400 | 1.33340200  | 1.93475100  |
| H  | -3.61128400 | 0.44769700  | 1.13143300  |
| C  | -1.79291300 | -1.63739600 | -0.74730700 |
| H  | -1.11147100 | -1.82366400 | -1.58006600 |
| H  | -1.67168700 | -2.43851000 | -0.01295900 |
| H  | -2.81919800 | -1.67823600 | -1.12470800 |
| C  | -1.43017100 | 1.39577700  | -1.23104900 |
| H  | -1.18173700 | 2.35326700  | -0.76508700 |
| H  | -0.70943800 | 1.19377900  | -2.02767600 |
| H  | -2.41822400 | 1.49466400  | -1.69133300 |

|   |            |             |             |
|---|------------|-------------|-------------|
| O | 0.10653300 | -0.04072800 | 0.76415900  |
| S | 1.51615300 | -0.17900800 | 0.06990400  |
| O | 2.36446100 | -0.94069800 | 0.96228600  |
| O | 1.32523600 | -0.66779300 | -1.28608400 |
| C | 2.07258100 | 1.49869600  | 0.01390600  |
| H | 3.06754900 | 1.49073400  | -0.43116500 |
| H | 1.38095000 | 2.07278300  | -0.60152400 |
| H | 2.10789000 | 1.88183300  | 1.03248800  |

### Int<sub>MS</sub>-1

Imaginary frequency: none

|    |             |             |             |
|----|-------------|-------------|-------------|
| Si | 2.41773900  | 1.57053700  | -0.36278100 |
| C  | 4.23415600  | 1.55668600  | -0.75092400 |
| H  | 4.82230300  | 1.22111500  | 0.10573100  |
| H  | 4.44984600  | 0.90042500  | -1.59859000 |
| H  | 4.55885600  | 2.56768500  | -1.01619400 |
| C  | 2.04415900  | 2.46321000  | 1.22098300  |
| H  | 0.99520300  | 2.34583700  | 1.50030400  |
| H  | 2.67802100  | 2.12063500  | 2.04368100  |
| H  | 2.24303300  | 3.53018300  | 1.07721000  |
| C  | 1.38261500  | 2.11103400  | -1.80002800 |
| H  | 1.63427300  | 1.54777800  | -2.70347000 |
| H  | 0.32127700  | 1.98201900  | -1.58413800 |
| H  | 1.57315500  | 3.16861800  | -2.00705900 |
| O  | 1.93475300  | -0.10437100 | -0.16985500 |
| S  | 2.34471900  | -1.16388100 | 0.92862500  |
| O  | 2.00824100  | -2.44905200 | 0.32749300  |
| O  | 3.71597600  | -0.93384200 | 1.33622100  |
| C  | 1.25060900  | -0.83901800 | 2.27537600  |
| C  | -5.42433800 | 0.04627800  | -0.71680600 |

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | -4.05602300 | -0.05366500 | -0.96177900 |
| C | -3.11565300 | 0.16098100  | 0.05173200  |
| C | -3.59689900 | 0.48681700  | 1.32584900  |
| C | -4.96173600 | 0.58805700  | 1.58326100  |
| C | -5.88030900 | 0.36654100  | 0.55922600  |
| H | -6.13449800 | -0.12260500 | -1.51916700 |
| H | -3.71240400 | -0.29782300 | -1.96255300 |
| H | -2.89070800 | 0.66996400  | 2.13096200  |
| H | -5.31087800 | 0.84213600  | 2.57833300  |
| H | -6.94399400 | 0.44626700  | 0.75443400  |
| B | -1.54303400 | 0.01697500  | -0.21323100 |
| F | -1.05454800 | -1.29146000 | 0.16519200  |
| F | -1.21203100 | 0.13370800  | -1.60428200 |
| F | -0.77554500 | 0.95902000  | 0.50320600  |
| K | 0.51364700  | -1.77085300 | -1.80826300 |
| H | 1.47498300  | 0.14904000  | 2.67358000  |
| H | 1.44924800  | -1.60777300 | 3.02282700  |
| H | 0.23219500  | -0.90242900 | 1.89892400  |

### TS-Ms

Imaginary frequency: -114.28

|    |             |            |             |
|----|-------------|------------|-------------|
| Si | -0.72564000 | 1.92189000 | 0.16395000  |
| C  | -1.45678600 | 2.12926000 | 1.87443400  |
| H  | -2.52929000 | 1.93621000 | 1.89315000  |
| H  | -0.96804200 | 1.45572900 | 2.58409200  |
| H  | -1.26130500 | 3.15067800 | 2.21472400  |
| C  | -1.64001800 | 2.60902600 | -1.30069800 |
| H  | -1.09510400 | 2.39672900 | -2.22528800 |
| H  | -2.66254400 | 2.24164000 | -1.39597400 |
| H  | -1.66799500 | 3.69813500 | -1.19095300 |



|   |             |             |             |
|---|-------------|-------------|-------------|
| C | 0.87082300  | 2.92211600  | 0.30258500  |
| H | 1.51351500  | 2.53355500  | 1.09960000  |
| H | 1.44715100  | 2.92135700  | -0.62667800 |
| H | 0.62735700  | 3.95982500  | 0.55393000  |
| O | -1.89018600 | 0.15811200  | 0.21098600  |
| S | -2.74759500 | -0.62966500 | -0.77260000 |
| O | -2.94559400 | -1.96898300 | -0.18763700 |
| O | -3.96655100 | 0.08986700  | -1.12644500 |
| C | -1.78022200 | -0.82990300 | -2.24570900 |
| C | 4.89742400  | 0.20207400  | 0.53070300  |
| C | 3.54263300  | 0.12175800  | 0.84477100  |
| C | 2.63186000  | -0.46589000 | -0.03875100 |
| C | 3.11567500  | -0.97415100 | -1.25010000 |
| C | 4.46716800  | -0.89558900 | -1.57190200 |
| C | 5.36054400  | -0.30587800 | -0.67980500 |
| H | 5.59073000  | 0.65868900  | 1.22819500  |
| H | 3.18940900  | 0.51685800  | 1.79213400  |
| H | 2.42745500  | -1.43902900 | -1.95011800 |
| H | 4.82596200  | -1.29349900 | -2.51456600 |
| H | 6.41438800  | -0.24474200 | -0.92734700 |
| B | 1.09287100  | -0.54338300 | 0.30607300  |
| F | 0.43460600  | -1.72242800 | -0.04862100 |
| F | 0.73666300  | -0.20486600 | 1.61905600  |
| F | 0.35415500  | 0.54374500  | -0.53215000 |
| K | -1.35526500 | -1.83397200 | 1.90974100  |
| H | -1.57332900 | 0.15140500  | -2.66984400 |
| H | -2.37739300 | -1.42154900 | -2.93940600 |
| H | -0.85960100 | -1.34839800 | -1.98775000 |

**Int<sub>MS</sub>-1**

Imaginary frequency: none

|    |             |             |             |
|----|-------------|-------------|-------------|
| Si | 0.01871600  | 2.02945700  | -0.08579000 |
| C  | 0.82185300  | 2.42629400  | -1.71495300 |
| H  | 1.87314900  | 2.12770400  | -1.71980700 |
| H  | 0.29430900  | 1.95985000  | -2.55367200 |
| H  | 0.78469700  | 3.50734500  | -1.88296000 |
| C  | 0.95867600  | 2.65154500  | 1.38327400  |
| H  | 0.55441000  | 2.25083500  | 2.31675900  |
| H  | 2.01258400  | 2.38100700  | 1.30240500  |
| H  | 0.87929400  | 3.74256800  | 1.42547000  |
| C  | -1.76953500 | 2.53074000  | -0.05225500 |
| H  | -2.29674300 | 2.19246400  | -0.94782000 |
| H  | -2.28266600 | 2.12731500  | 0.82581100  |
| H  | -1.84181600 | 3.62225100  | -0.01170600 |
| O  | 2.98508400  | 0.55966000  | -0.17972500 |
| S  | 3.40171400  | -0.56523000 | 0.70462500  |
| O  | 2.91837500  | -1.85361100 | 0.13845400  |
| O  | 4.83284200  | -0.56038200 | 1.02695900  |
| C  | 2.52059100  | -0.34732400 | 2.23667800  |
| C  | -5.01705000 | 0.10636400  | 0.03563700  |
| C  | -3.88054000 | -0.21267200 | -0.69744100 |
| C  | -2.84236800 | -0.94888700 | -0.11287700 |
| C  | -2.96299800 | -1.36141400 | 1.22028300  |
| C  | -4.09412500 | -1.03370100 | 1.95832800  |
| C  | -5.11956700 | -0.30057000 | 1.36440500  |
| H  | -5.81920000 | 0.67305800  | -0.42225700 |
| H  | -3.79570400 | 0.11165500  | -1.72929200 |
| H  | -2.16434900 | -1.93292500 | 1.68151900  |
| H  | -4.17975900 | -1.34819100 | 2.99176600  |

|   |             |             |             |
|---|-------------|-------------|-------------|
| H | -6.00317400 | -0.04674500 | 1.93913400  |
| B | -1.57190200 | -1.27218600 | -0.91091500 |
| F | -0.65637100 | -2.15895800 | -0.50811900 |
| F | -1.30979900 | -0.72887600 | -2.10888900 |
| F | -0.00444000 | 0.35702300  | -0.00559500 |
| K | 1.48715800  | -0.88960300 | -1.80766900 |
| H | 2.84608600  | 0.58395700  | 2.69828900  |
| H | 2.75508100  | -1.19144300 | 2.88453600  |
| H | 1.45331600  | -0.31631700 | 2.02061400  |

## VII. Bond heterolysis energy and binding energy

Bond heterolysis energy of Si-X (X = O, Br) is calculated according to the following formula (1). Binding energy of PhBF<sub>2</sub> with sylvite is calculated according to the following formula (2).

$$E_{\text{Si-X heterolysis}} = E(\text{cation}) + E(\text{anion}) - E(\text{Lewis acid}) \quad (1)$$

$$E_b = E(\text{PhBF}_2) + E(\text{KX}) - E(\text{PhBF}_2\text{-KX}) \quad (2)$$

**Supplementary Table 4.** Bond heterolysis energies of Si-X (X = O, Br). Calculated energy data at the level of M06-2X/6-311+G(d,p)/SMD(CH<sub>3</sub>CN).

|               | <b>E(Lewis acid)<br/>(kcal/mol)</b> | <b>E(cation)<br/>(kcal/mol)</b> | <b>E(anion)<br/>(kcal/mol)</b> | <b>E<sub>Si-X heterolysis</sub><br/>(kcal/mol)</b> |
|---------------|-------------------------------------|---------------------------------|--------------------------------|----------------------------------------------------|
| <b>TMSOTf</b> | -1370.57358                         | -408.93896                      | -961.57120                     | 39.8                                               |
| <b>TMSOMs</b> | -1072.84394                         | -408.93896                      | -663.81884                     | 54.0                                               |
| <b>TMSOAc</b> | -637.60376                          | -408.93896                      | -228.55245                     | 70.5                                               |
| <b>TMSBr</b>  | -2983.37184                         | -408.93896                      | -2574.35247                    | 50.4                                               |

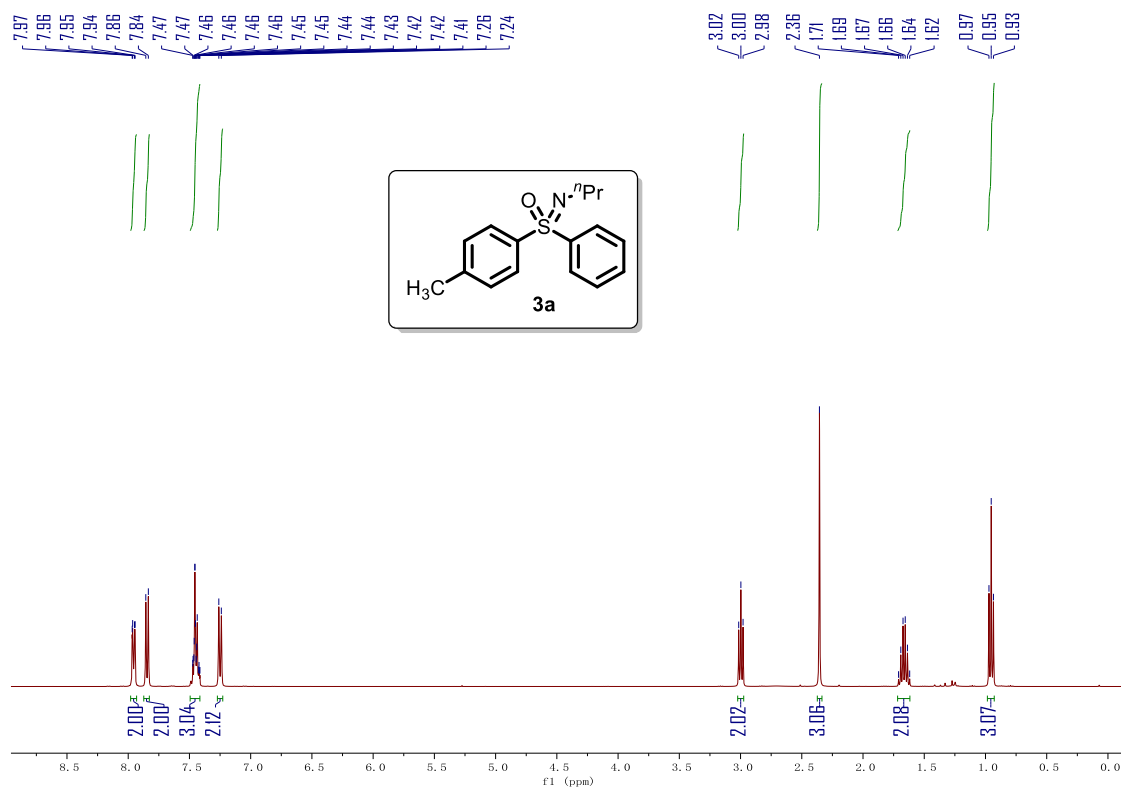
**Supplementary Table 5.** Binding energies of PhBF<sub>2</sub> with sylvite. Calculated energy data at the level of M06-2X/6-311+G(d,p)/SMD(CH<sub>3</sub>CN).

|             | <b>E(PhBF<sub>2</sub>)<br/>(kcal/mol)</b> | <b>E(KX)<br/>(kcal/mol)</b> | <b>E(PhBF<sub>2</sub>-KX)<br/>(kcal/mol)</b> | <b>E<sub>b</sub><br/>(kcal/mol)</b> |
|-------------|-------------------------------------------|-----------------------------|----------------------------------------------|-------------------------------------|
| <b>KOTf</b> | -456.21061                                | -1561.44240                 | -2017.66147                                  | 5.3                                 |
| <b>KOMs</b> | -456.21061                                | -1263.69712                 | -1719.92994                                  | 13.9                                |
| <b>KOAc</b> | -456.21061                                | -828.44440                  | -1284.69561                                  | 25.4                                |
| <b>KBr</b>  | -456.21061                                | -3174.22783                 | -3630.44114                                  | 1.7                                 |

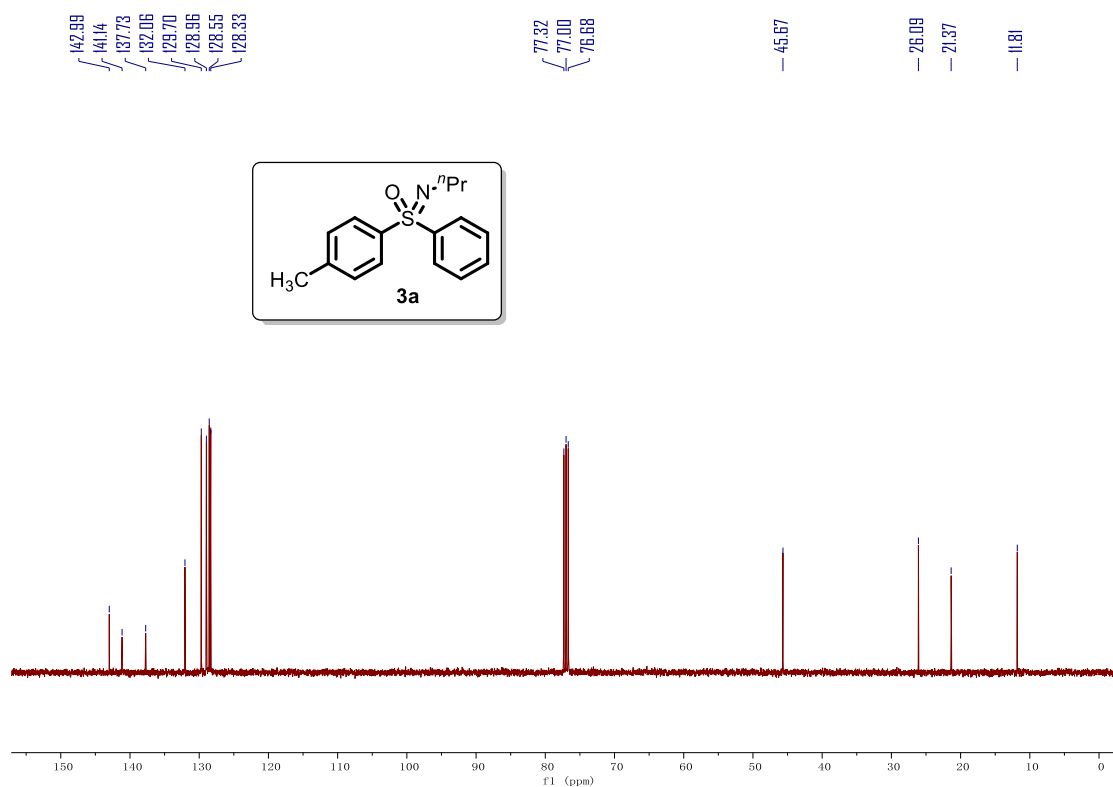
## VIII. References

- (1) D. Zeng, Y. Ma, W.-P. Deng, M. Wang, X. Jiang, *Angew. Chem. Int. Ed.* **2022**, *61*, e202207100.
- (2) D. Zeng, Y. Ma, W.-P. Deng, M. Wang, X. Jiang, *Nat. Synth.* **2022**, *1*, 455-463.
- (3) Q. Gao, C. Wu, S. Deng, Q. Zhou, *J. Am. Chem. Soc.* **2021**, *143*, 7253-7260.
- (4) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria; M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
- (5) Z. Yan, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *119*, 525-525.
- (6) A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B.* **2009**, *113*, 6378-6396.
- (7) Legault, C. Y. CYLView, 1.0b, Université de Sherbrooke, <http://www.cylview.org>. 2009.

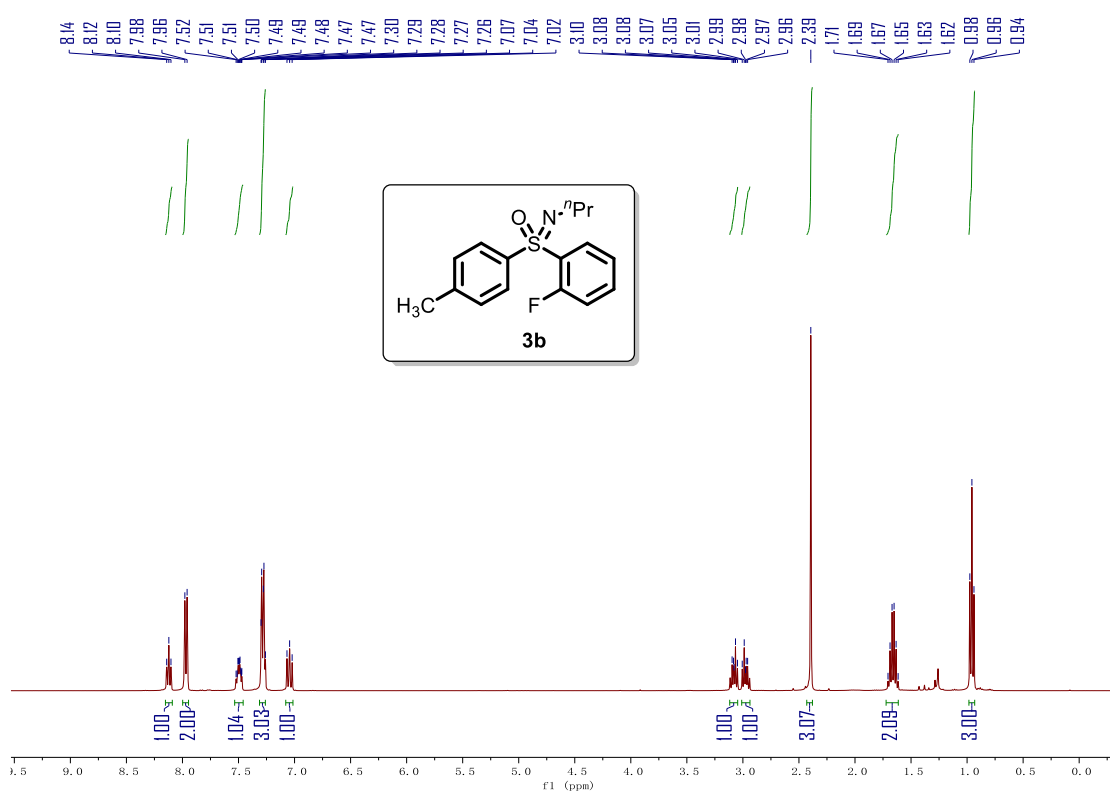
## IX. NMR Spectra



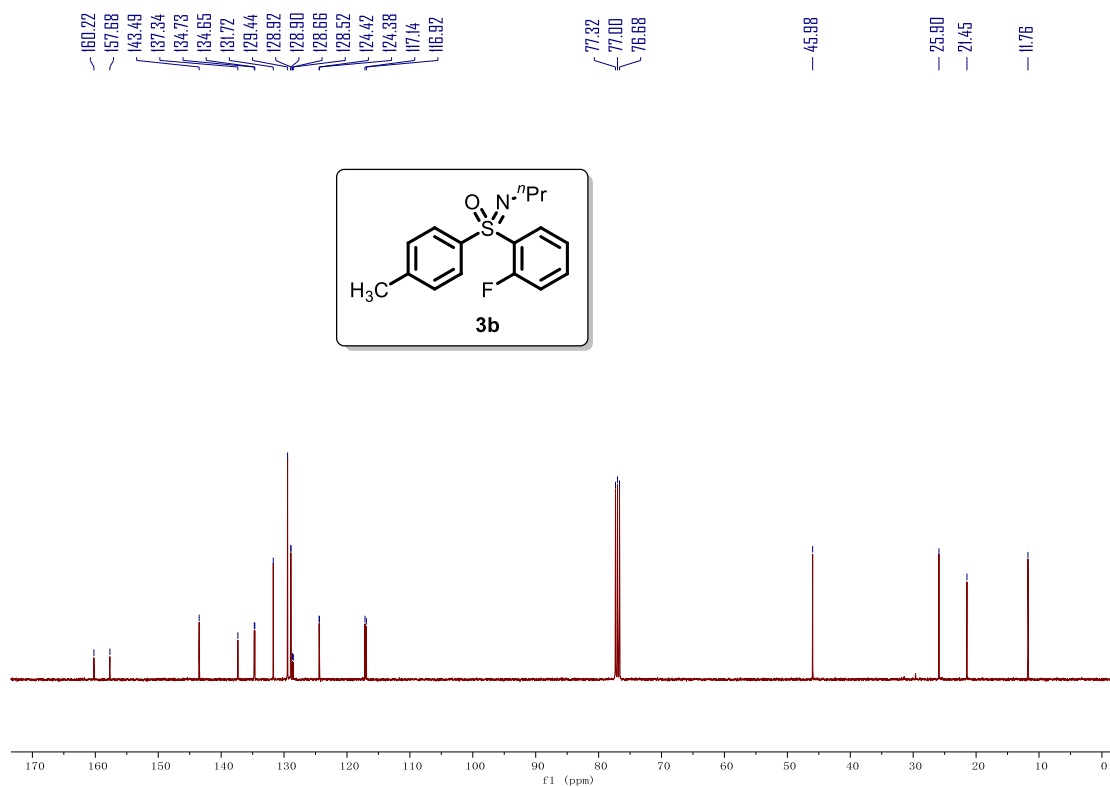
Supplementary Figure 6. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3a**.



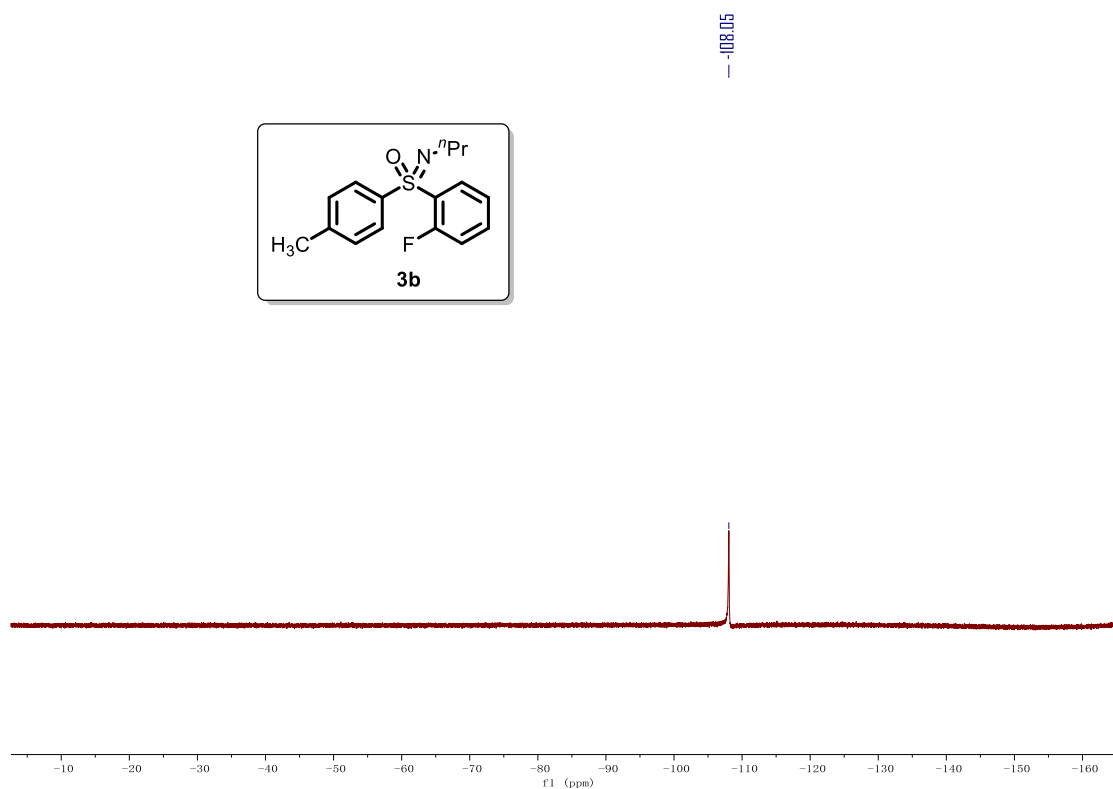
Supplementary Figure 7. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3a**.



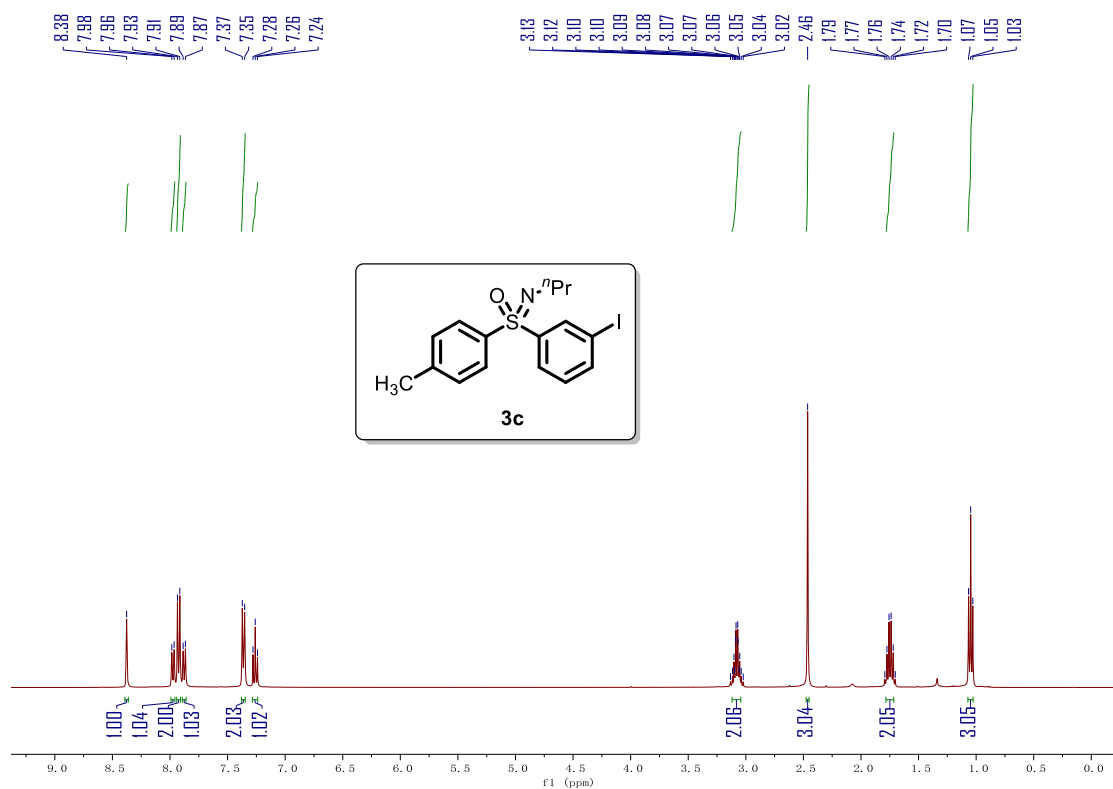
**Supplementary Figure 8.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3b**.



**Supplementary Figure 9.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3b**.

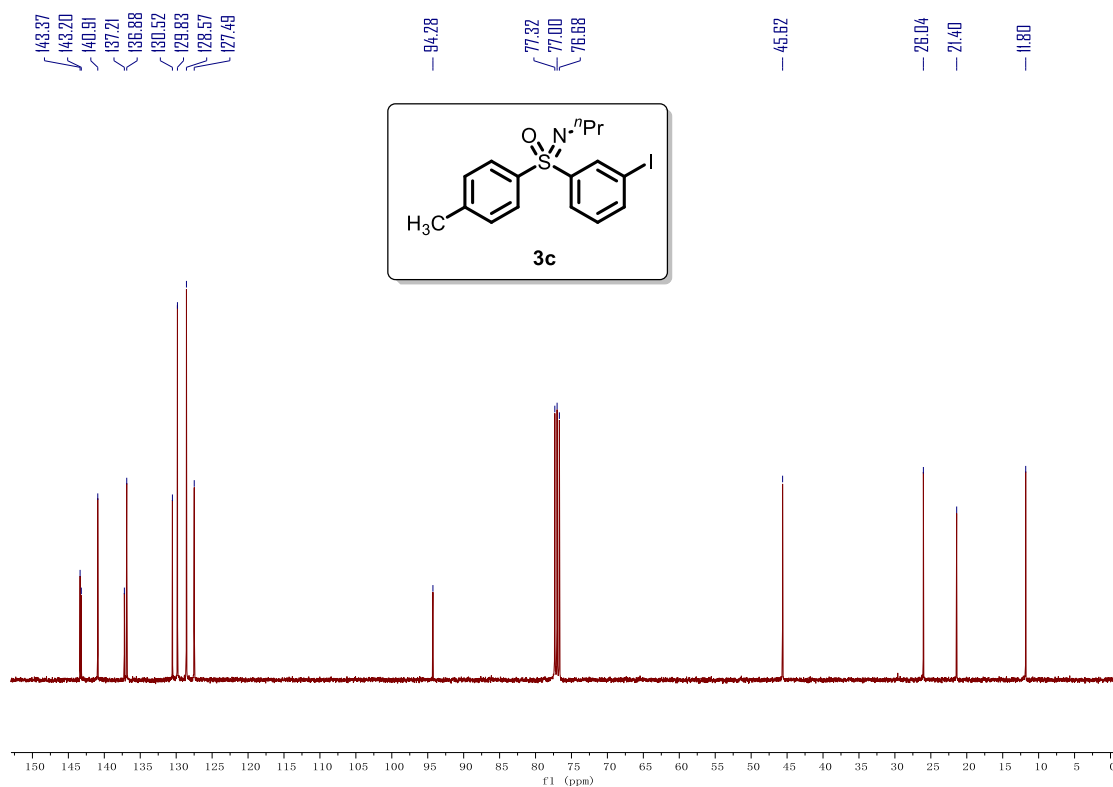


**Supplementary Figure 10.** <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) spectra of compound **3b**.

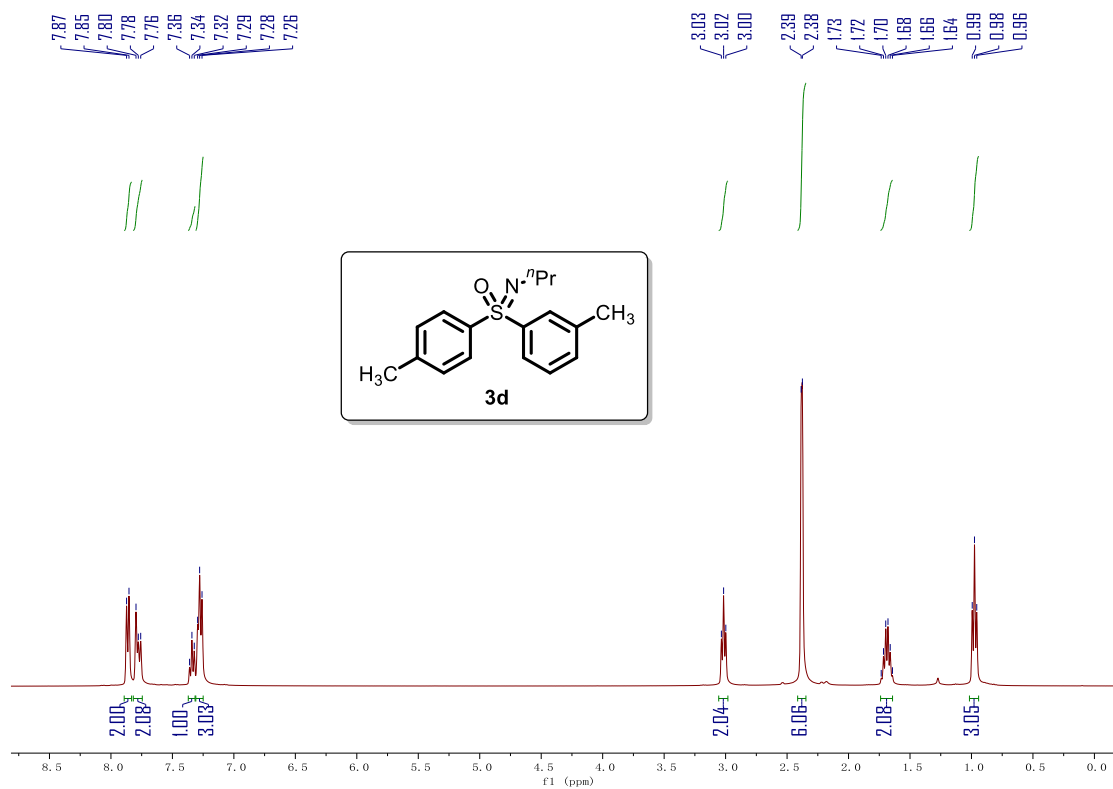


**Supplementary Figure 11.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3c**.

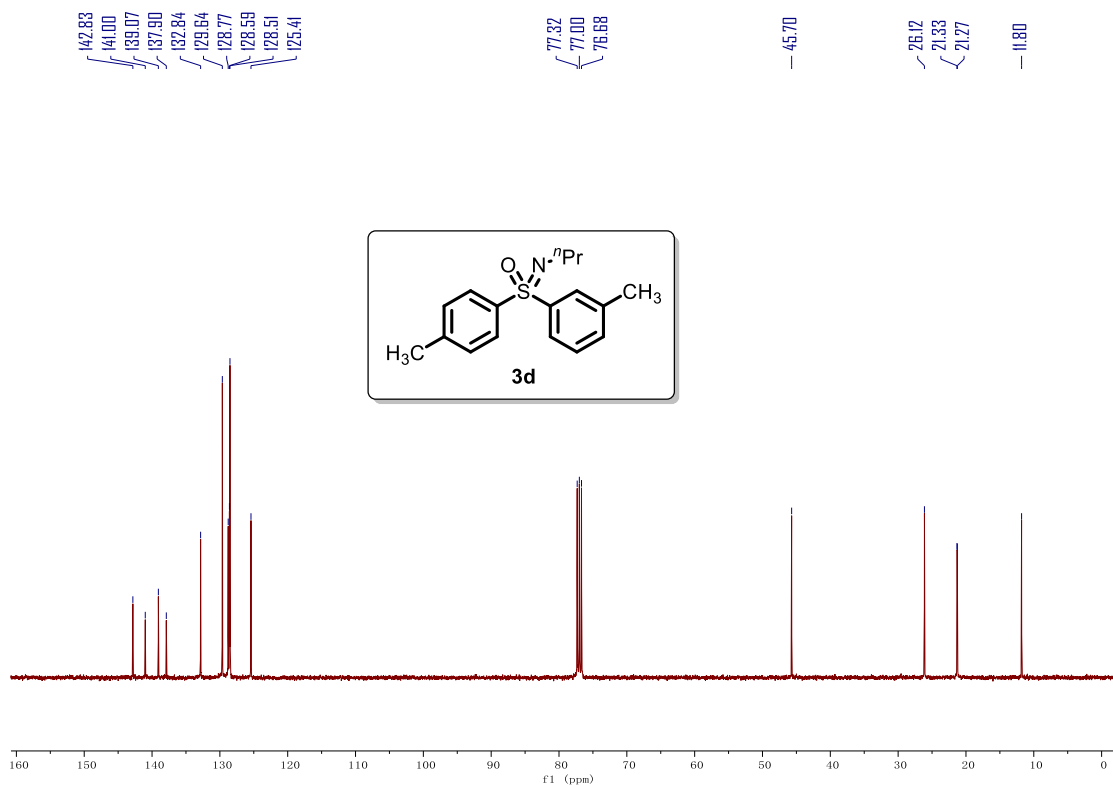




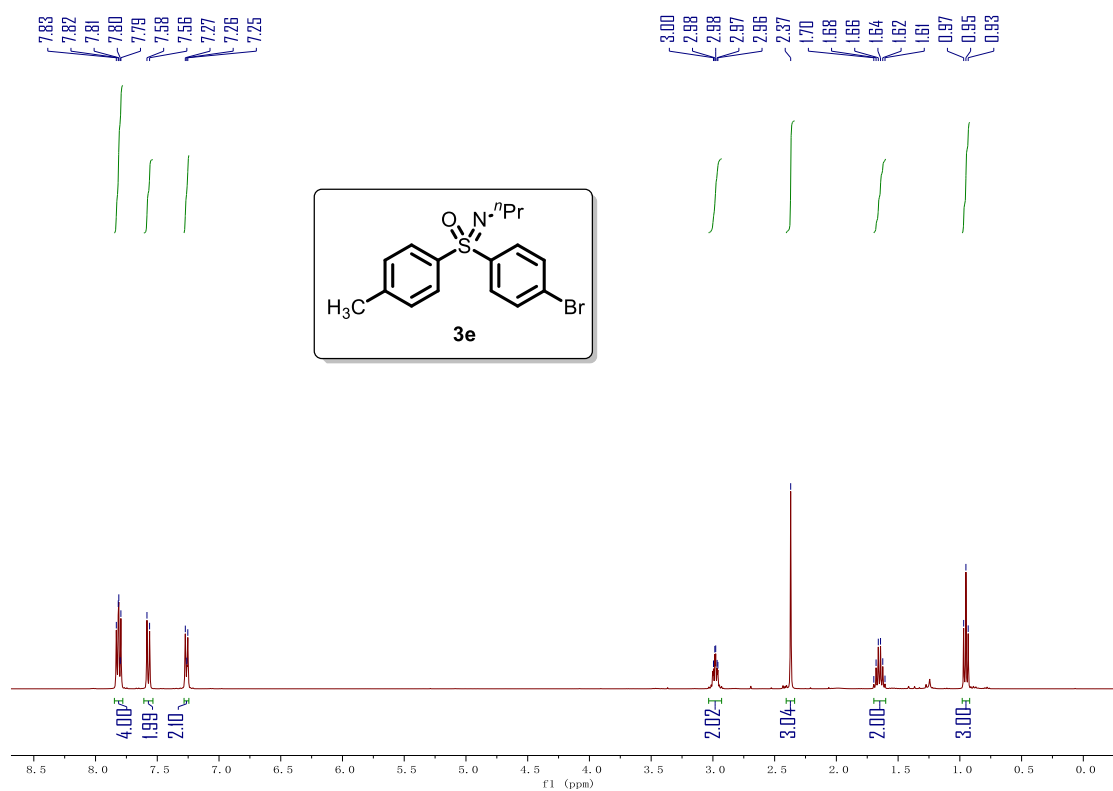
**Supplementary Figure 12.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3c**.



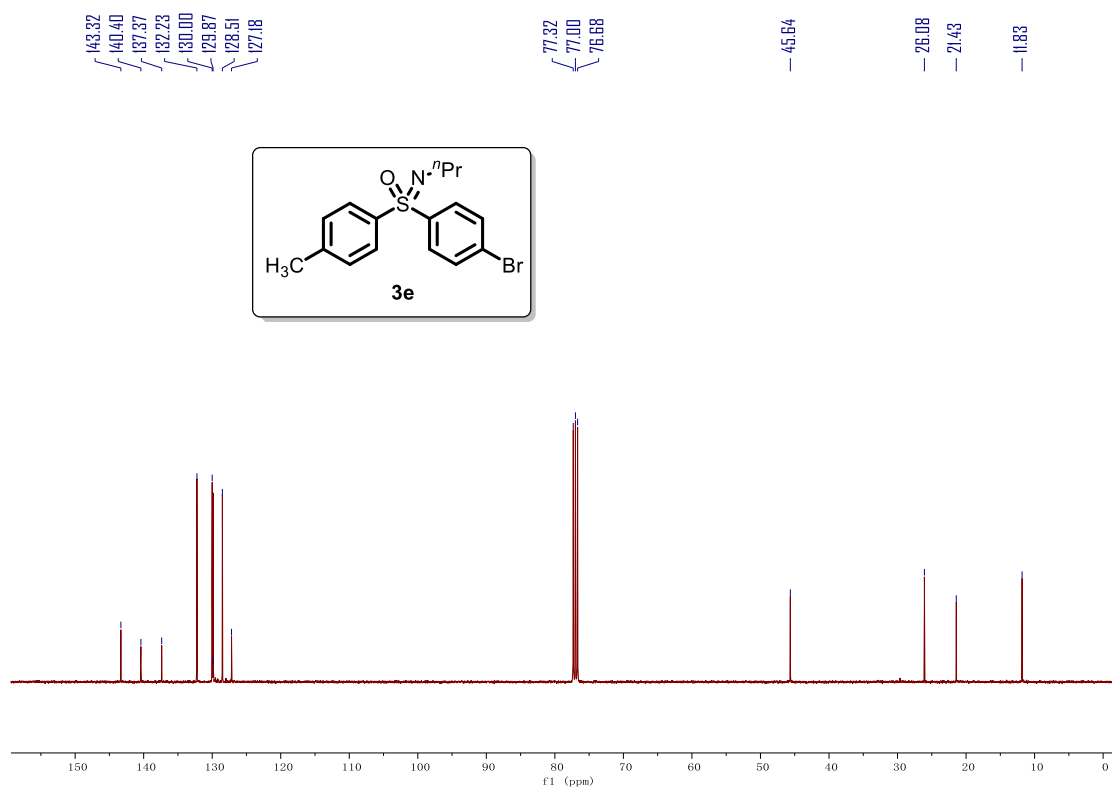
**Supplementary Figure 13.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3d**.



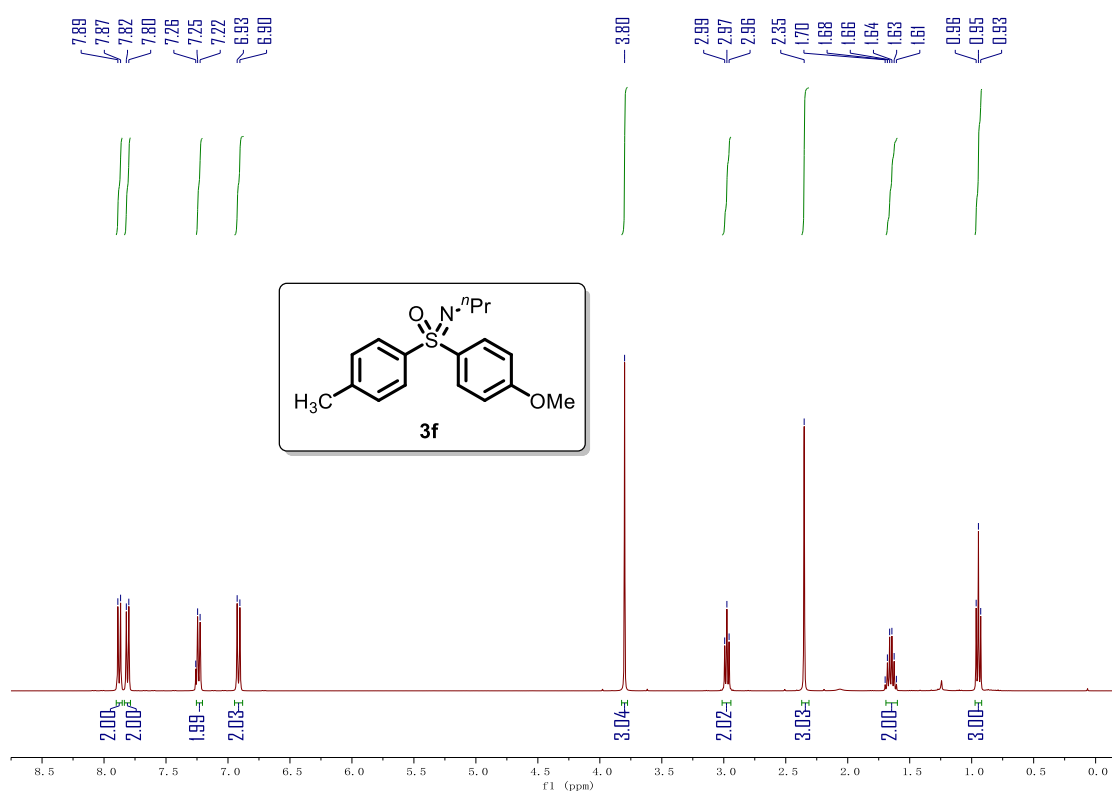
**Supplementary Figure 14.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3d**.



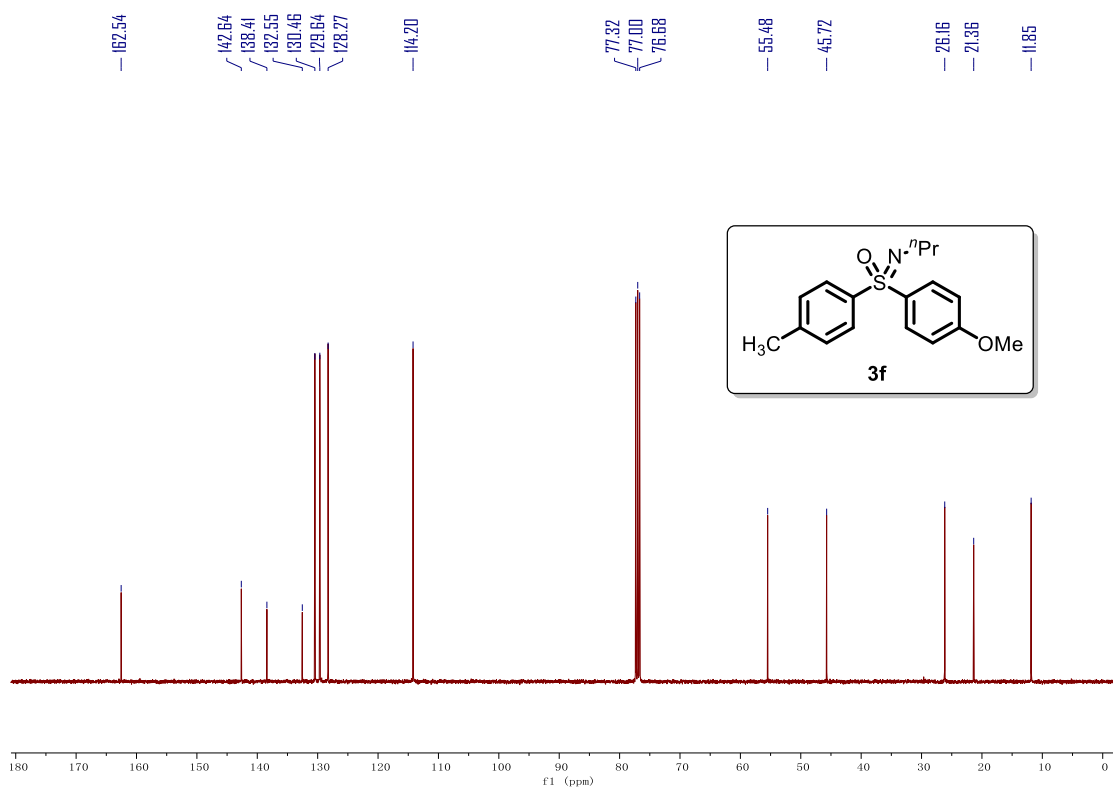
**Supplementary Figure 15.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3e**.



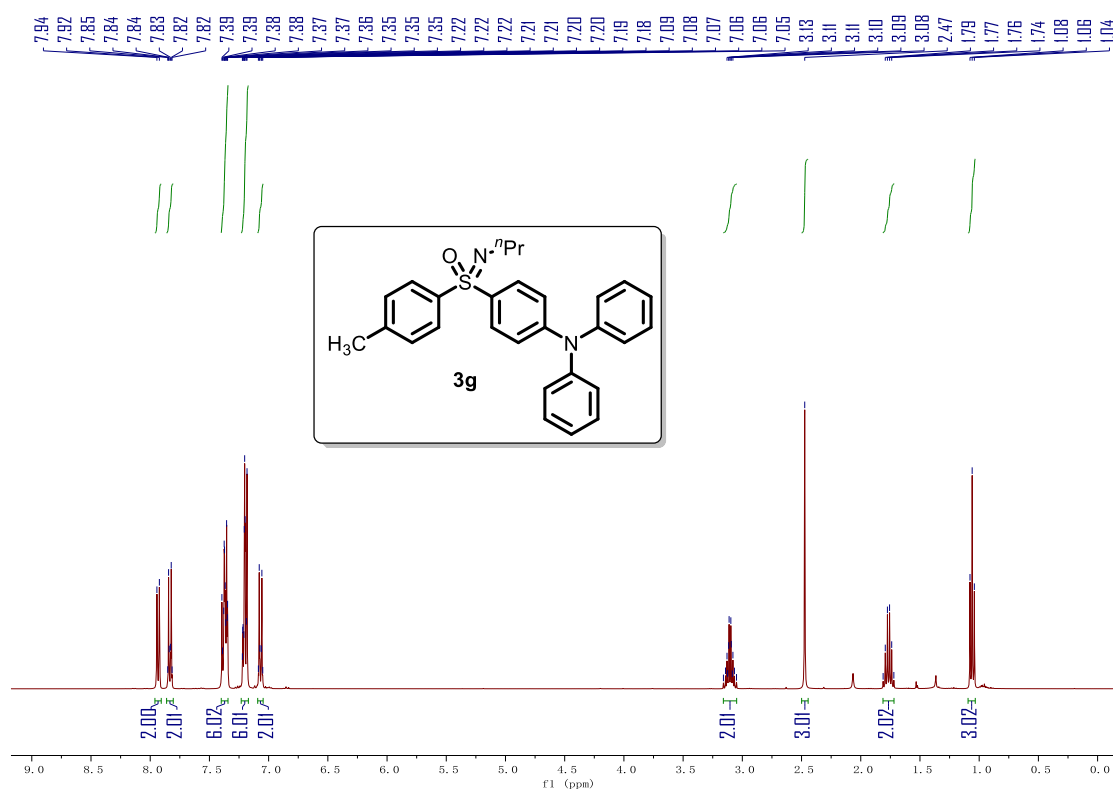
Supplementary Figure 16. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3e**.



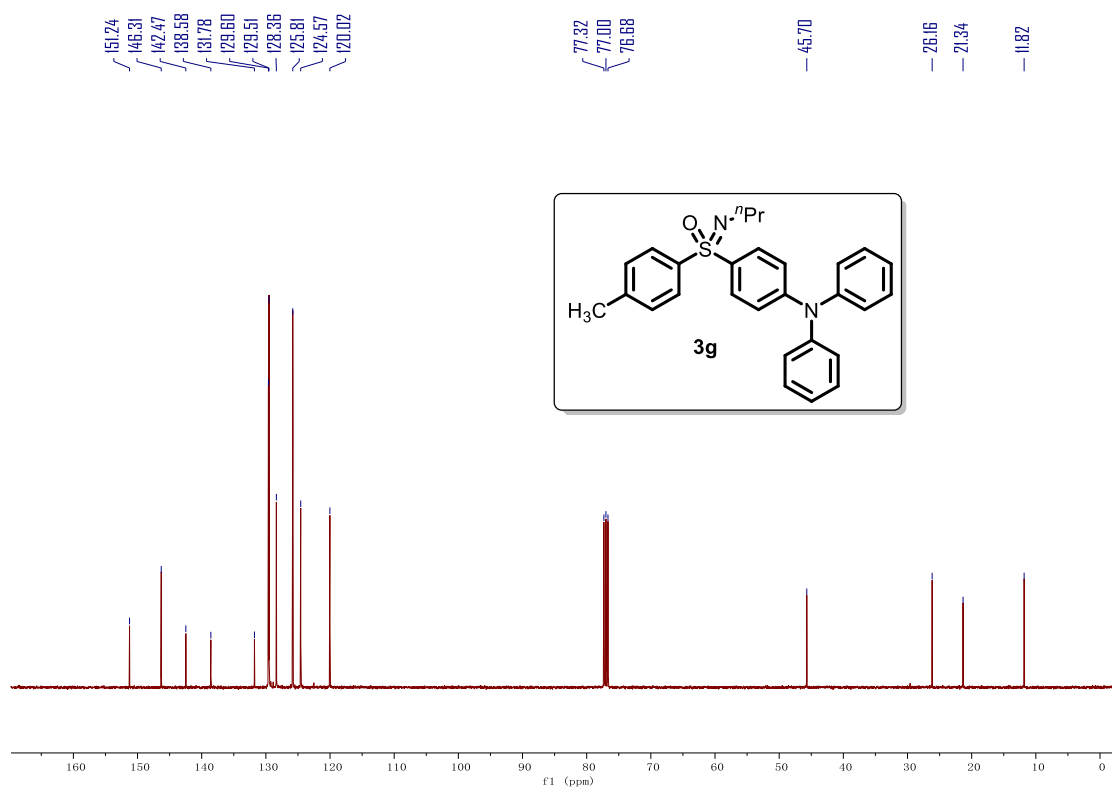
Supplementary Figure 17. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3f**.



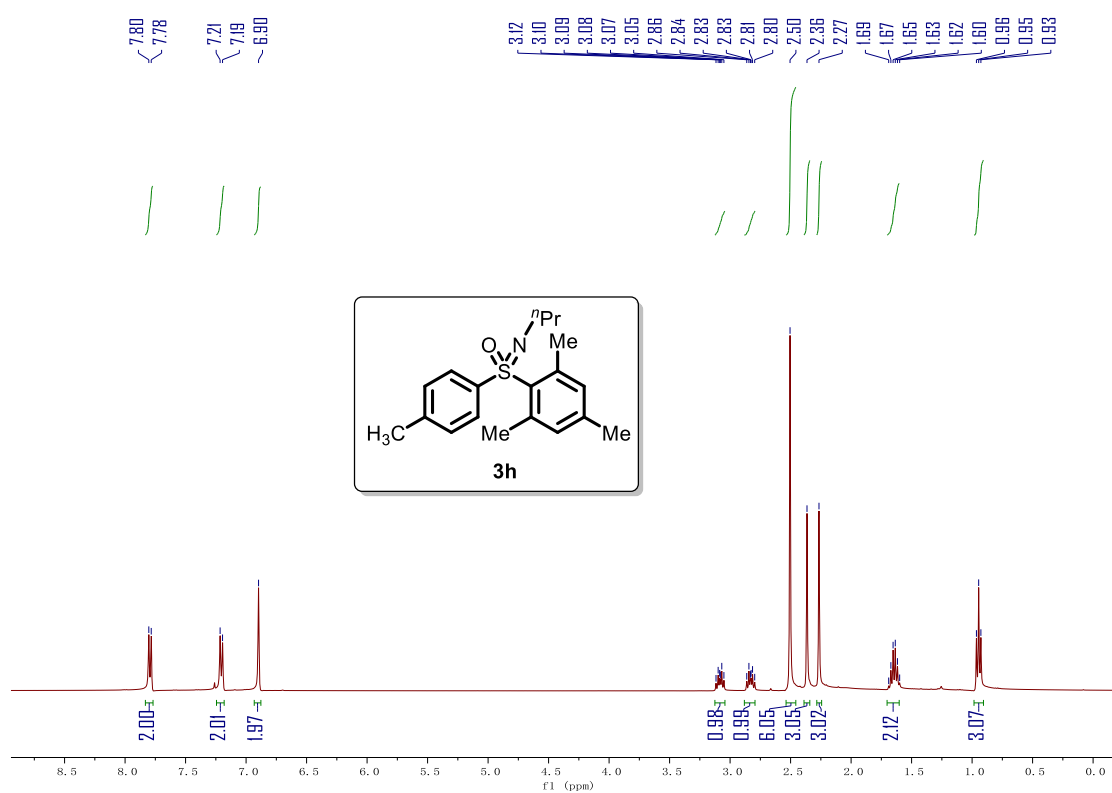
Supplementary Figure 18.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) spectra of compound **3f**.



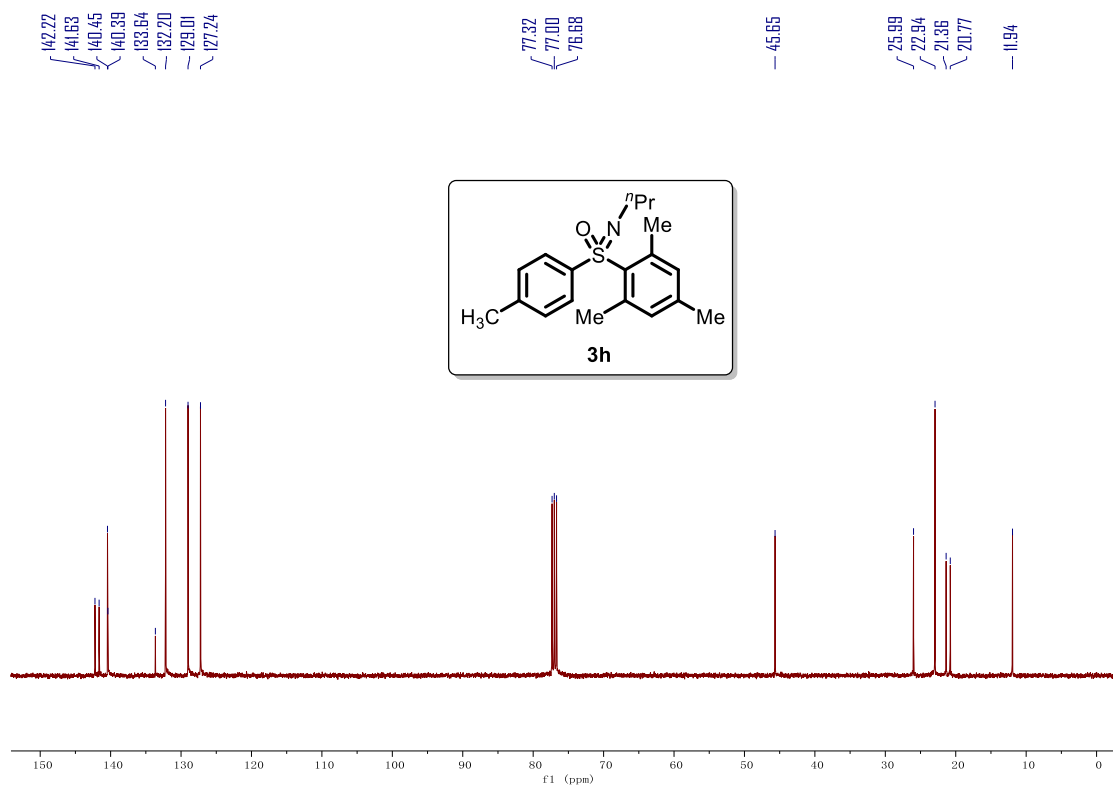
Supplementary Figure 19.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectra of compound **3g**.



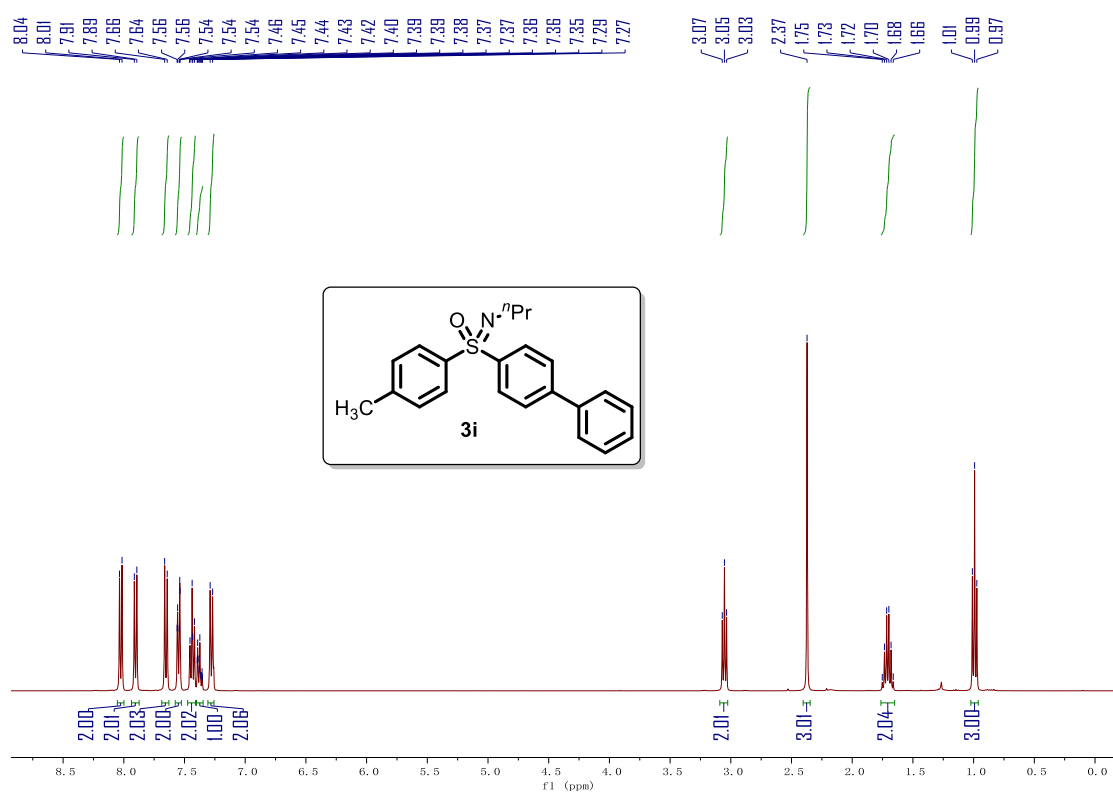
Supplementary Figure 20. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3g**.



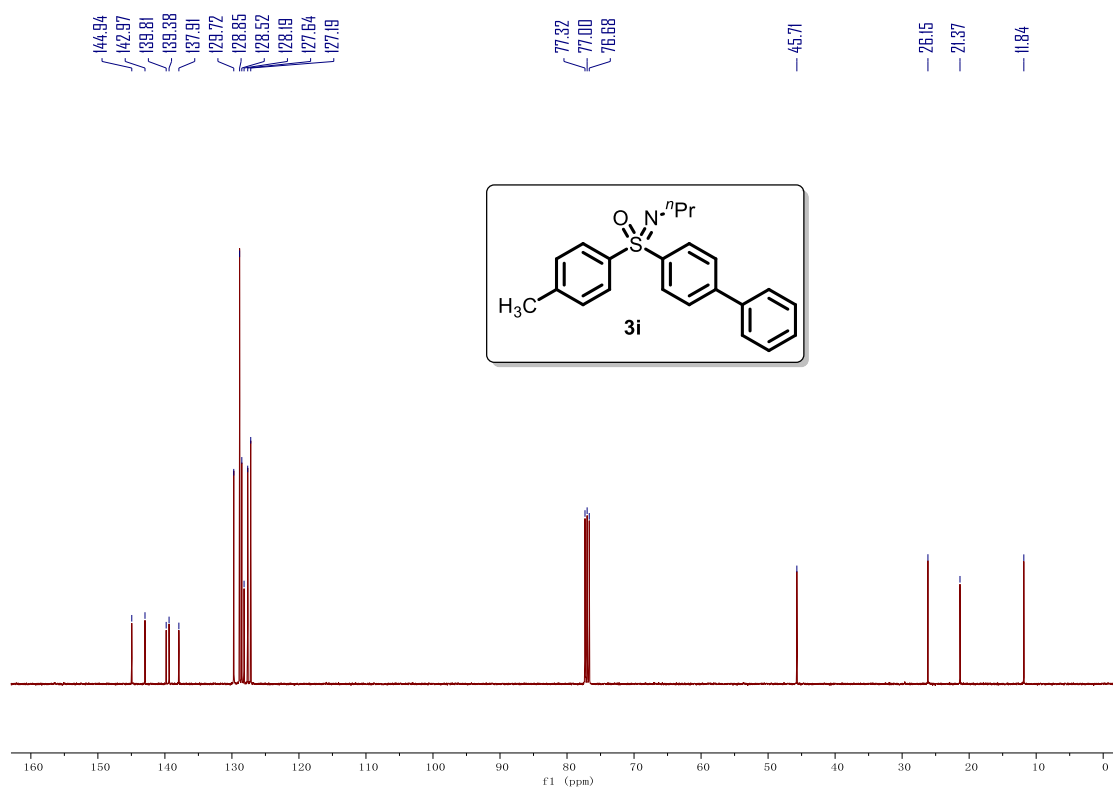
Supplementary Figure 21. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3h**.



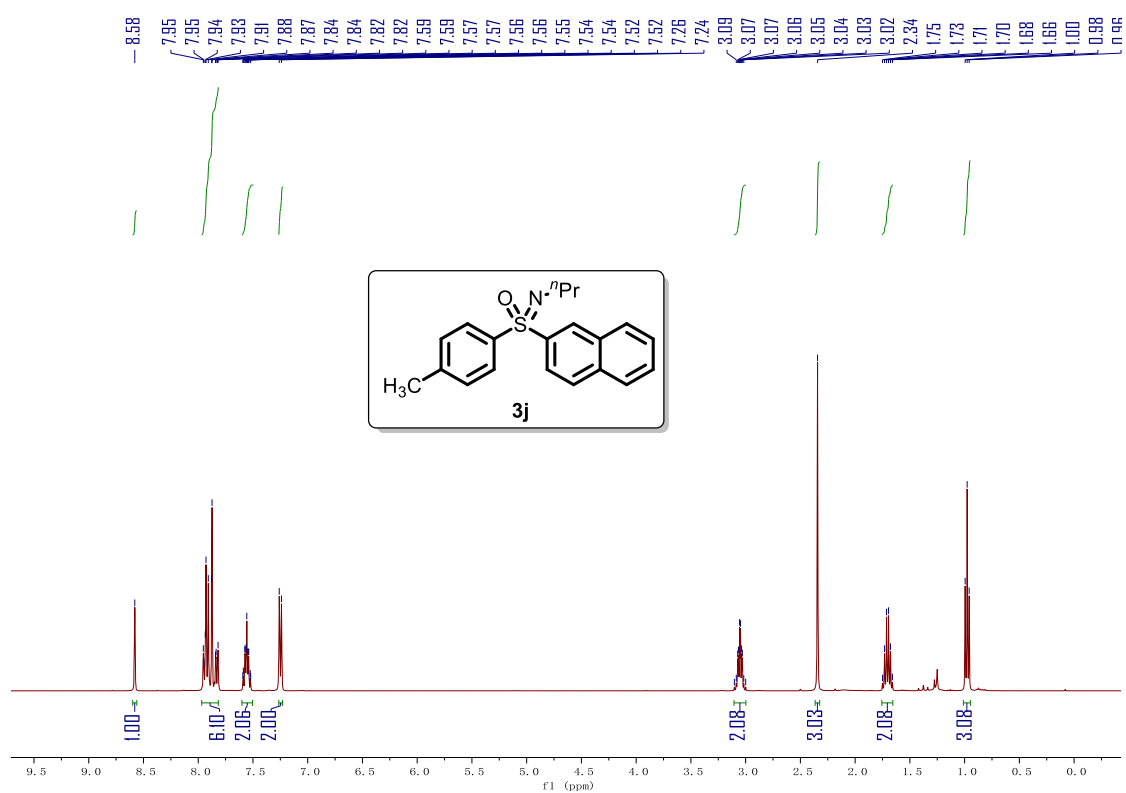
**Supplementary Figure 22.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3h**.



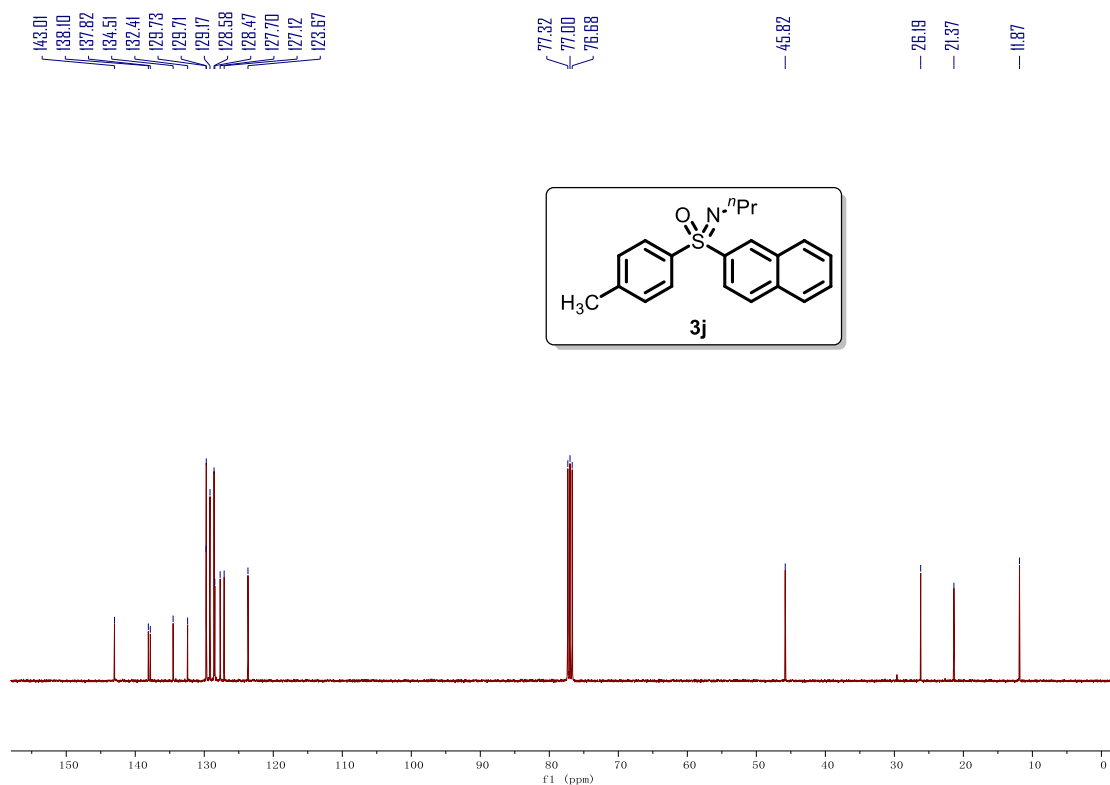
**Supplementary Figure 23.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3i**.



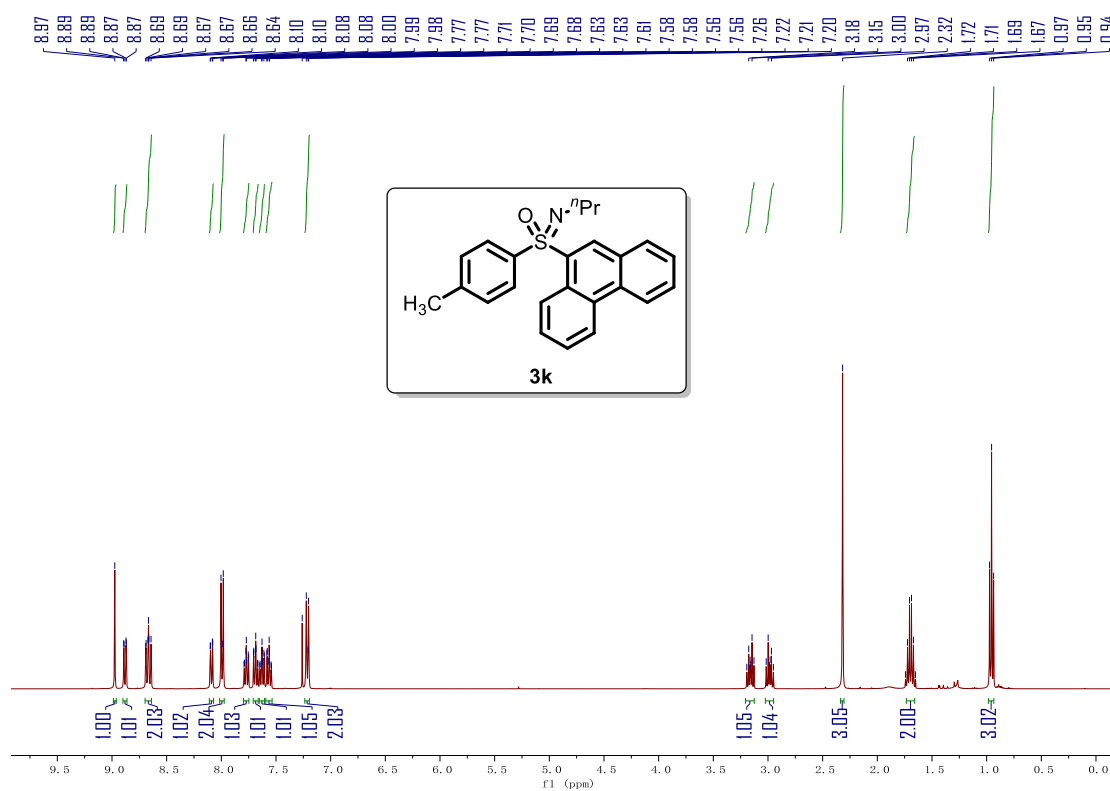
**Supplementary Figure 24.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3i**.



**Supplementary Figure 25.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3j**.

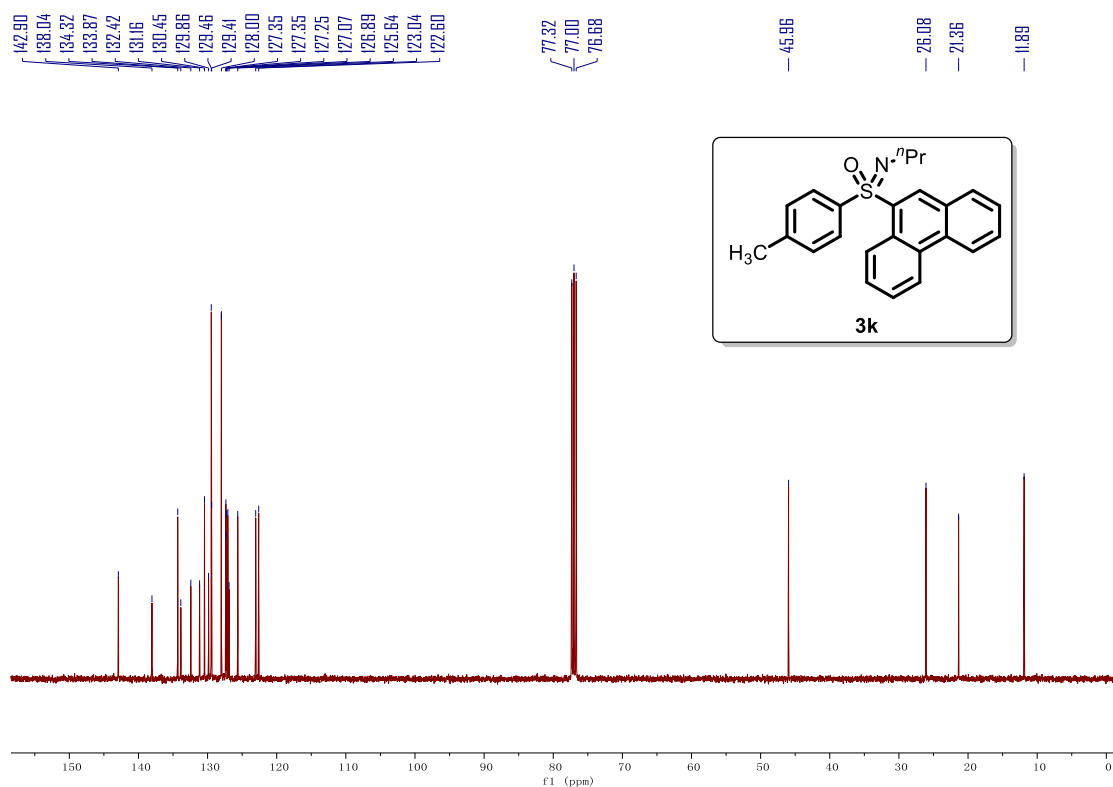


Supplementary Figure 26. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3j**.

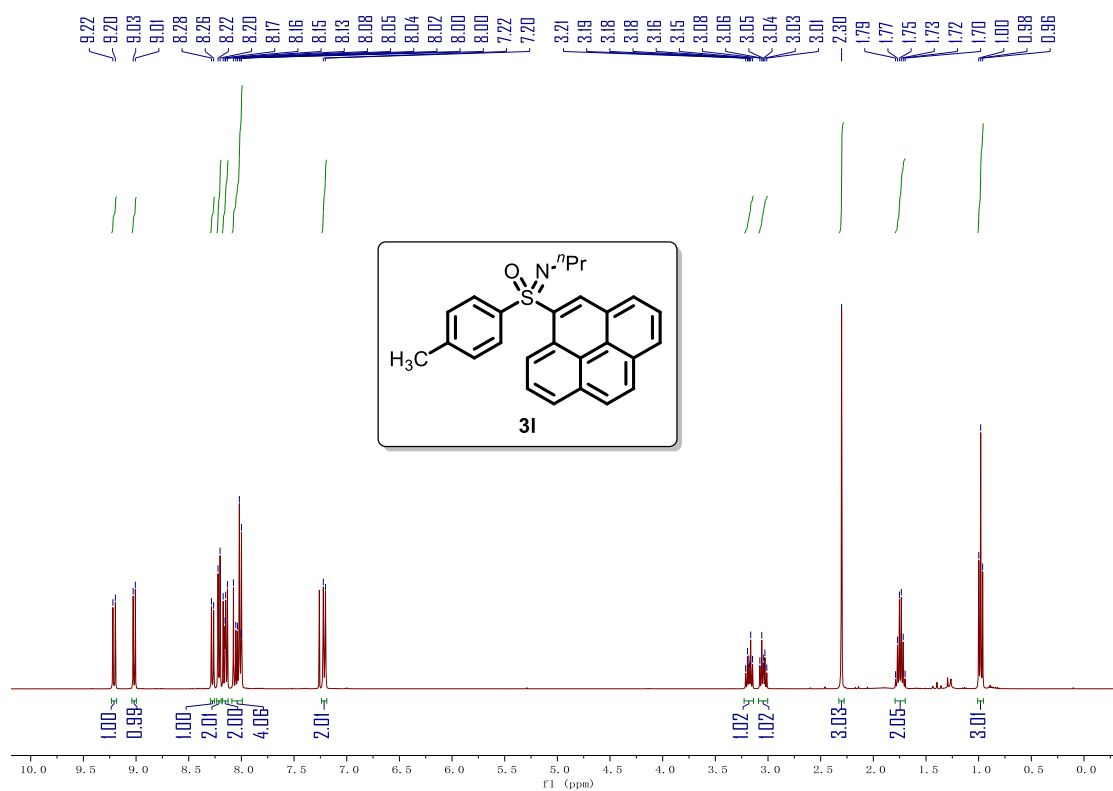


Supplementary Figure 27. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3k**.

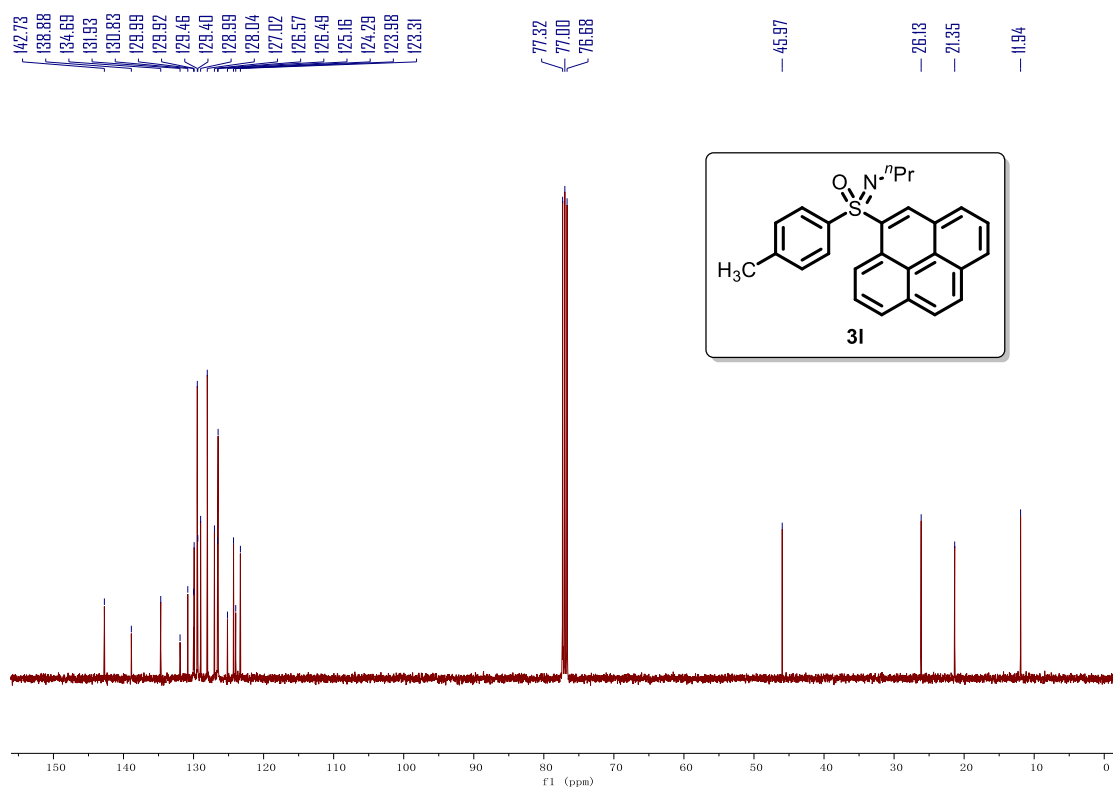




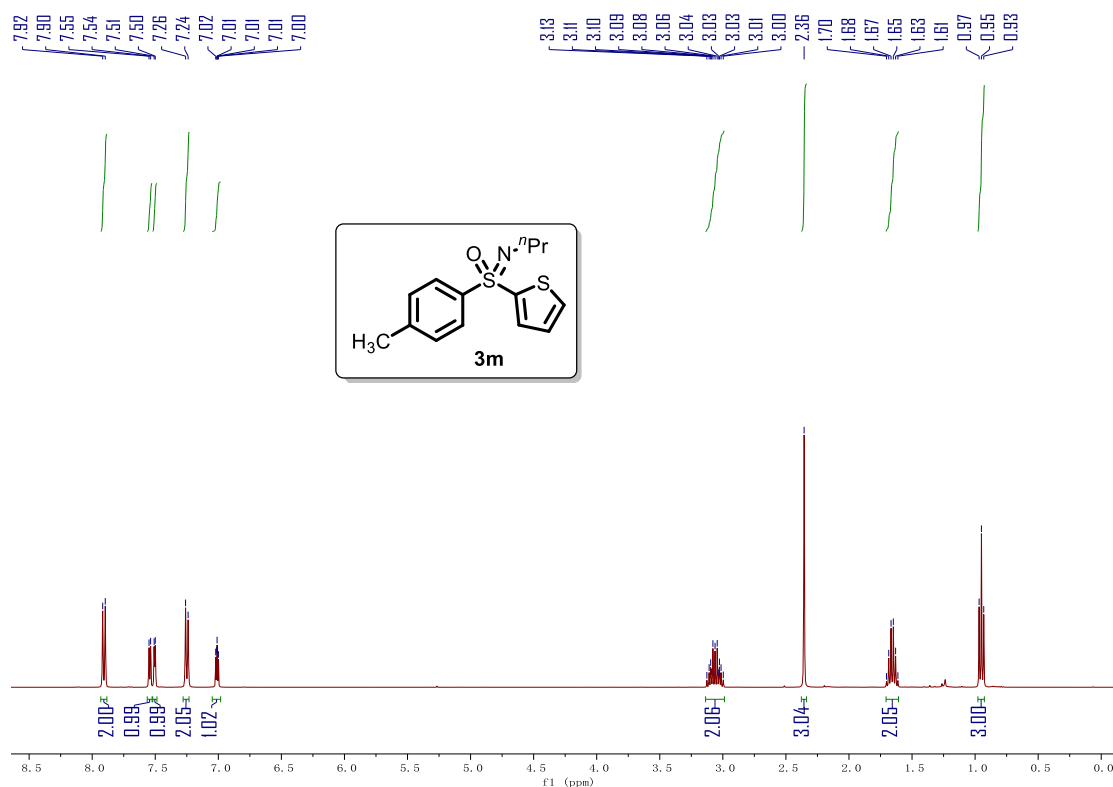
Supplementary Figure 28. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3k**.



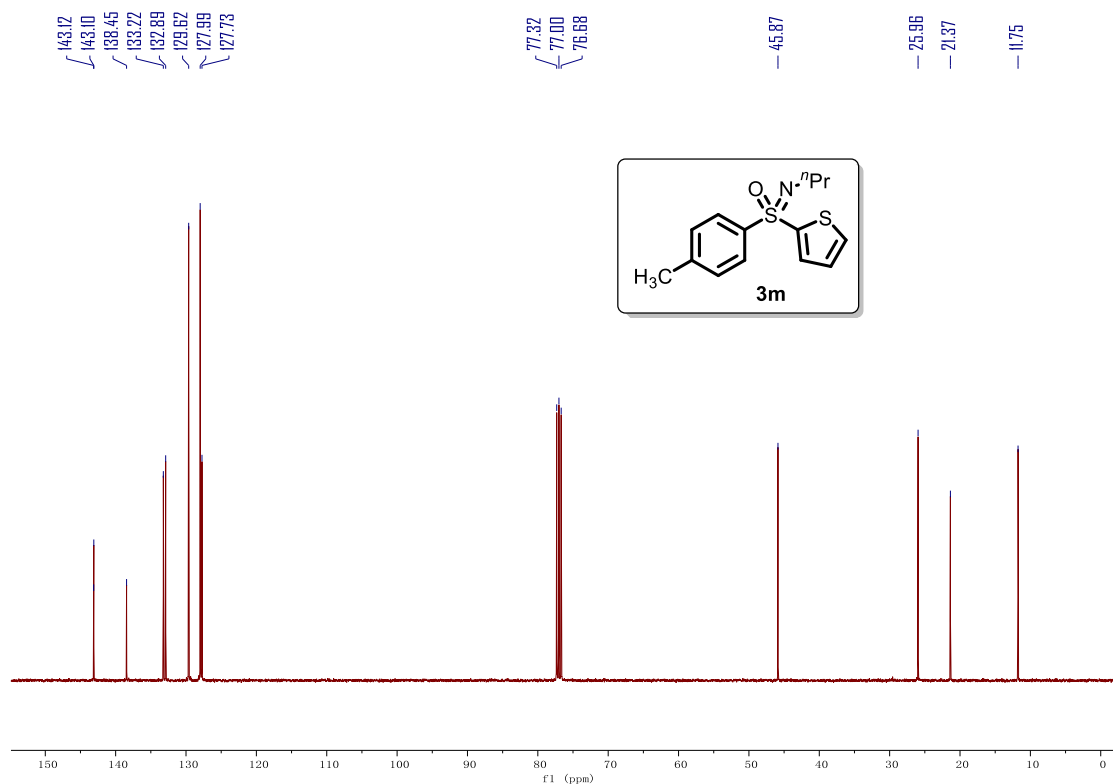
Supplementary Figure 29. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3l**.



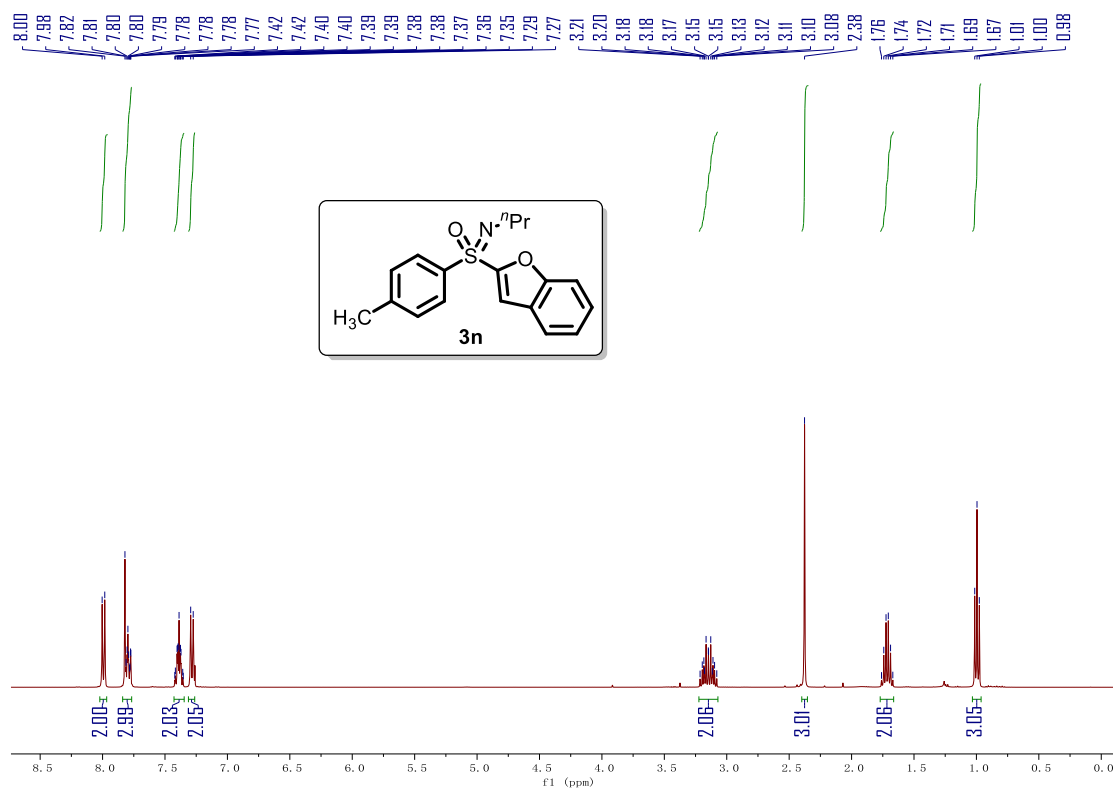
Supplementary Figure 30. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3l**.



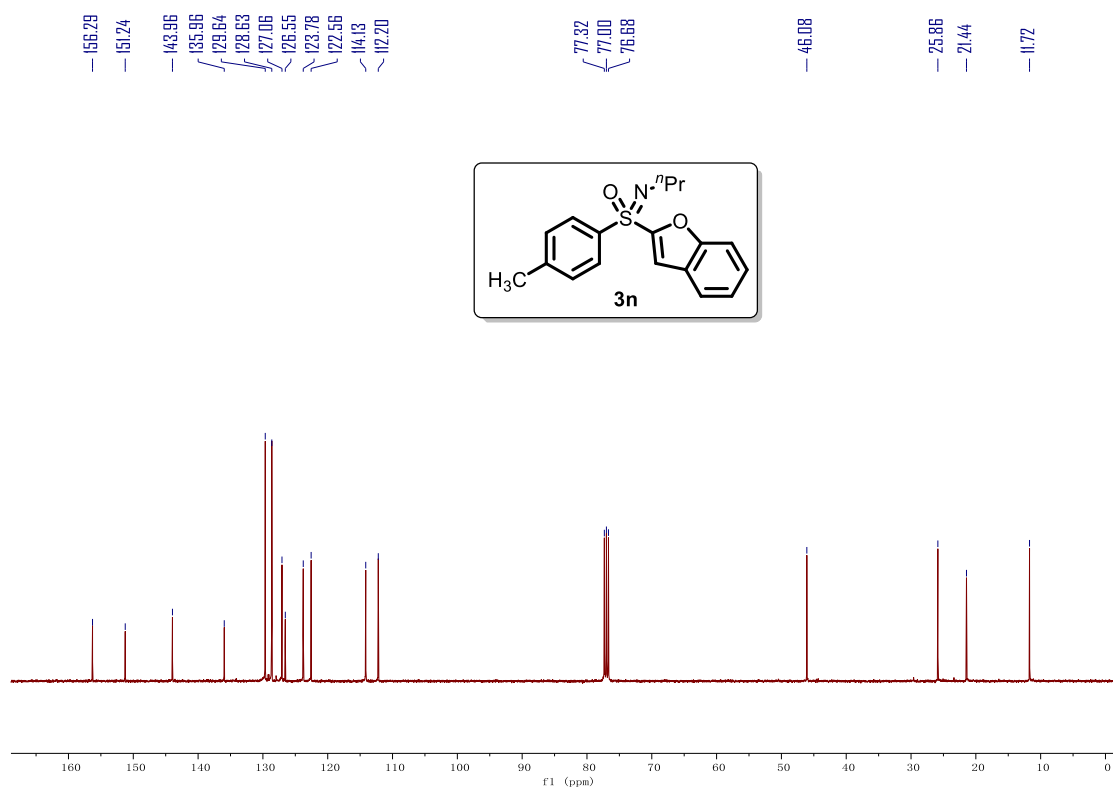
Supplementary Figure 31. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3m**.



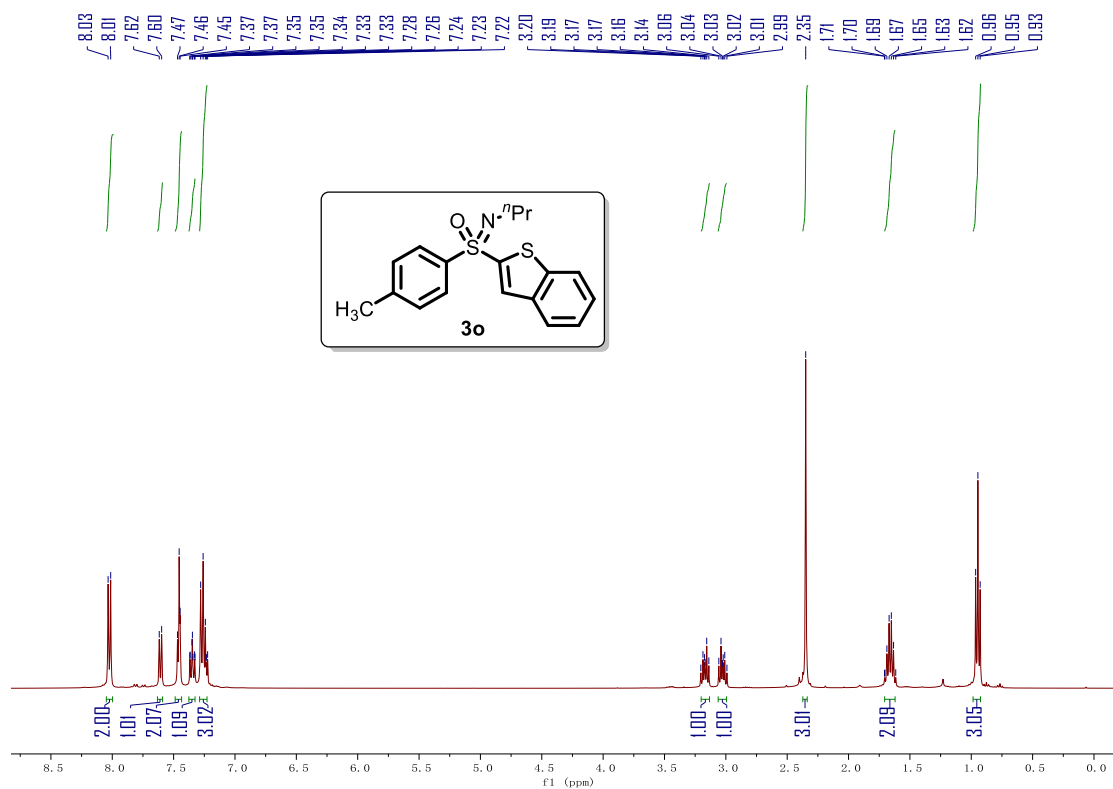
Supplementary Figure 32.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) spectra of compound **3m**.



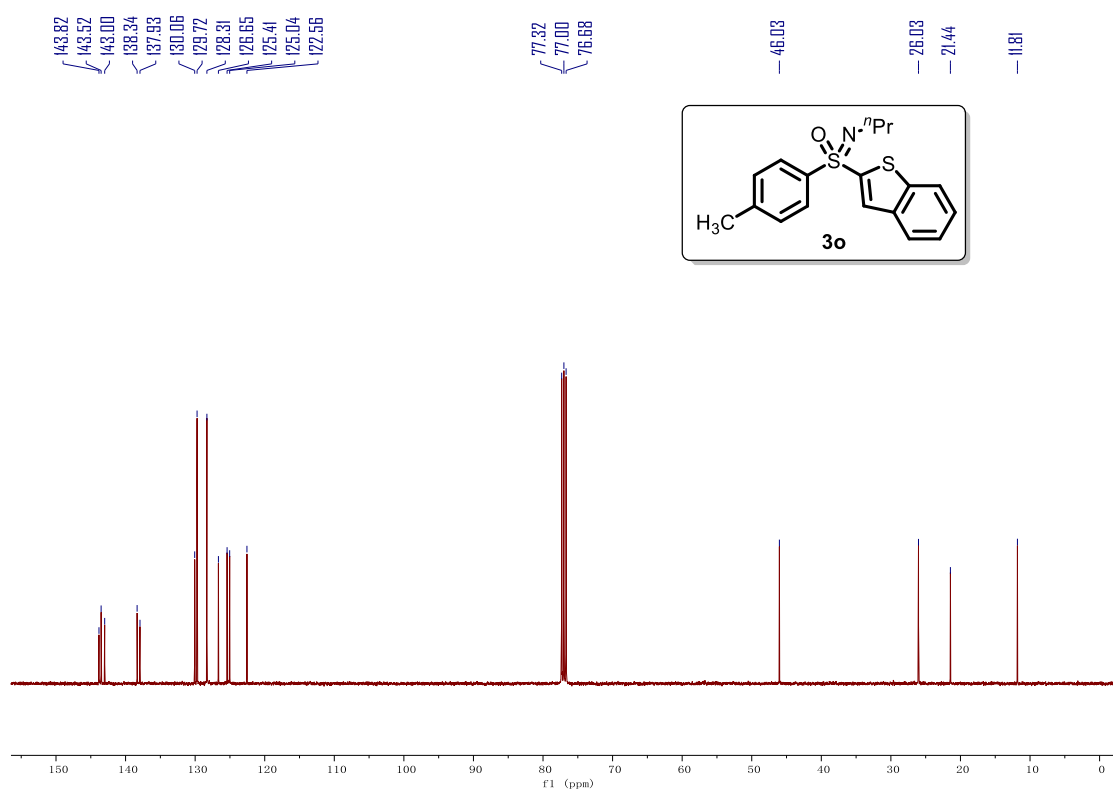
Supplementary Figure 33.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectra of compound **3n**.



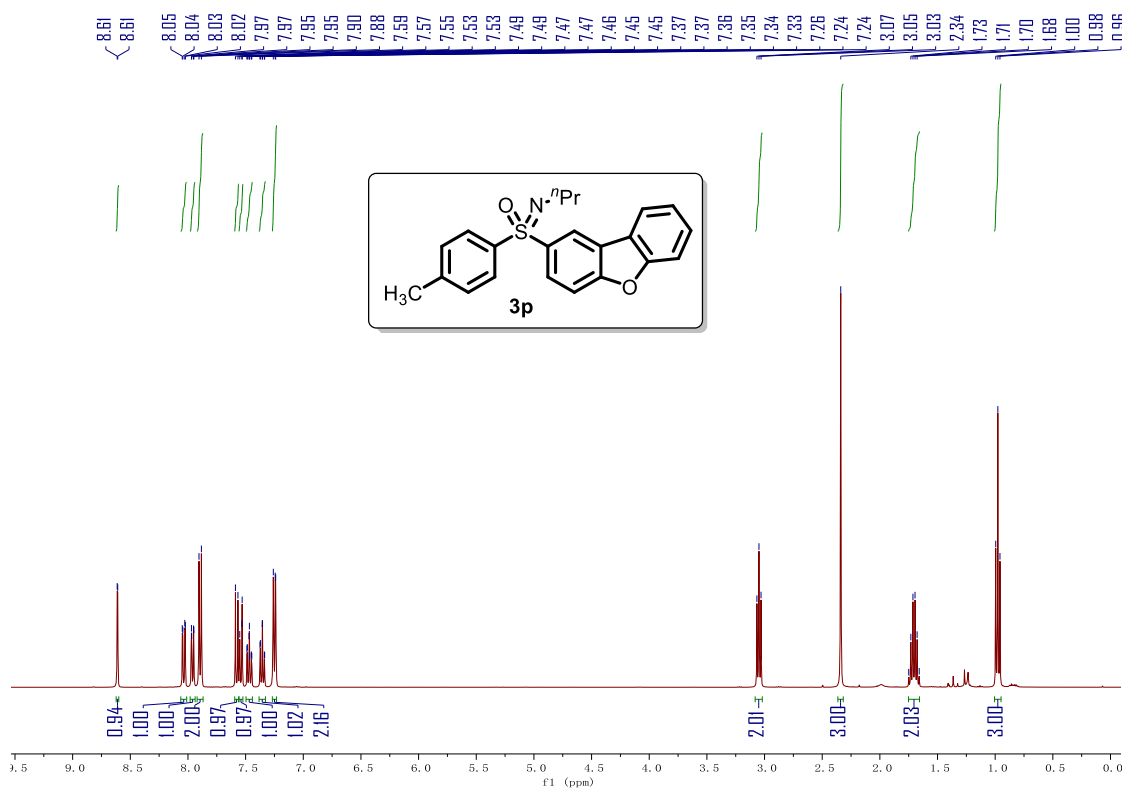
**Supplementary Figure 34.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3n**.



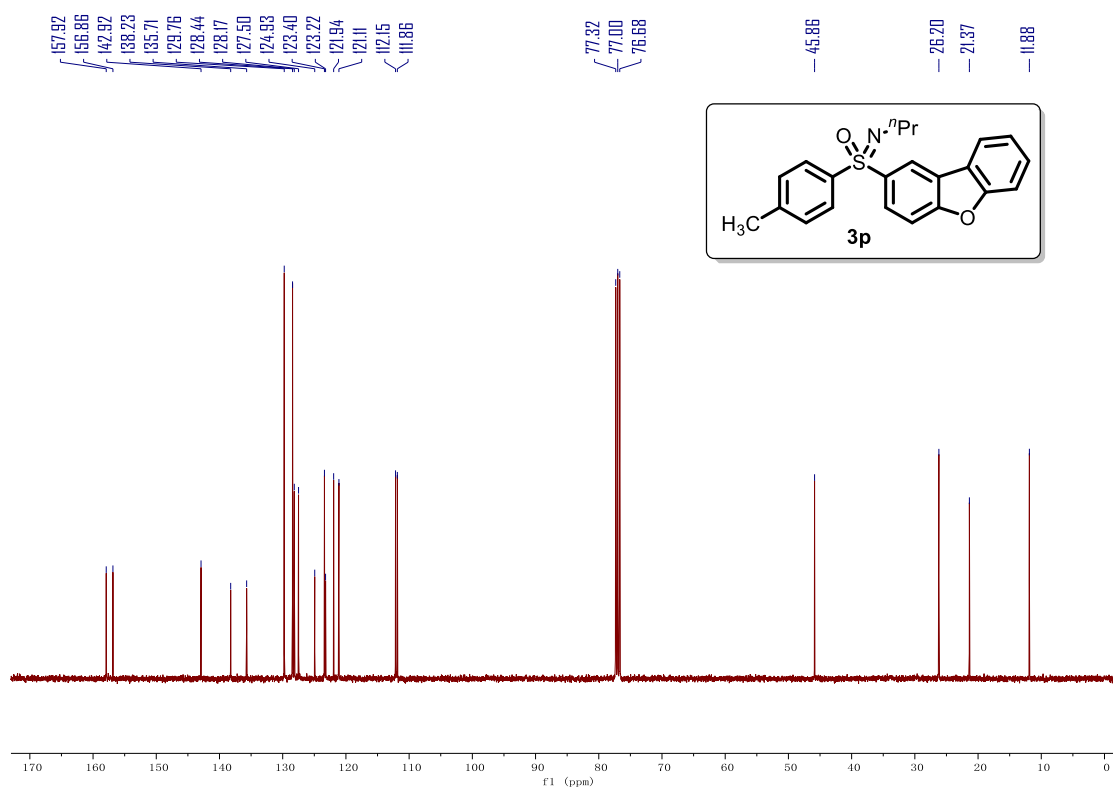
**Supplementary Figure 35.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3o**.



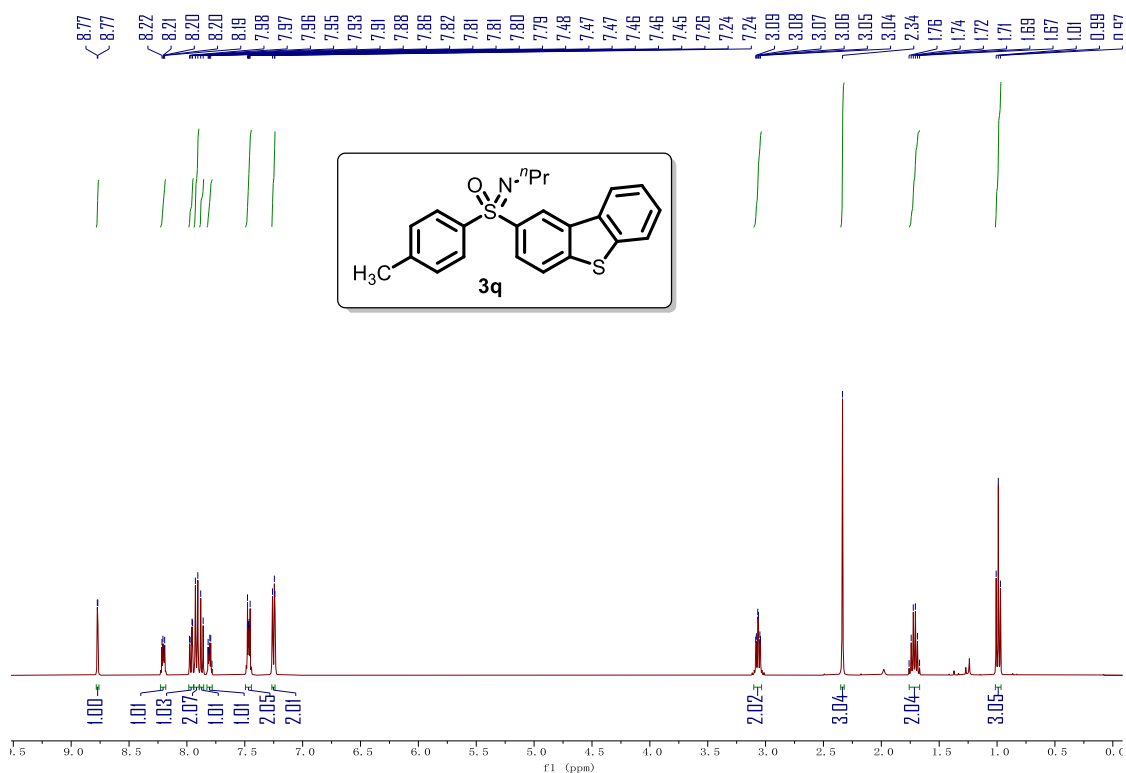
Supplementary Figure 36. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3o**.



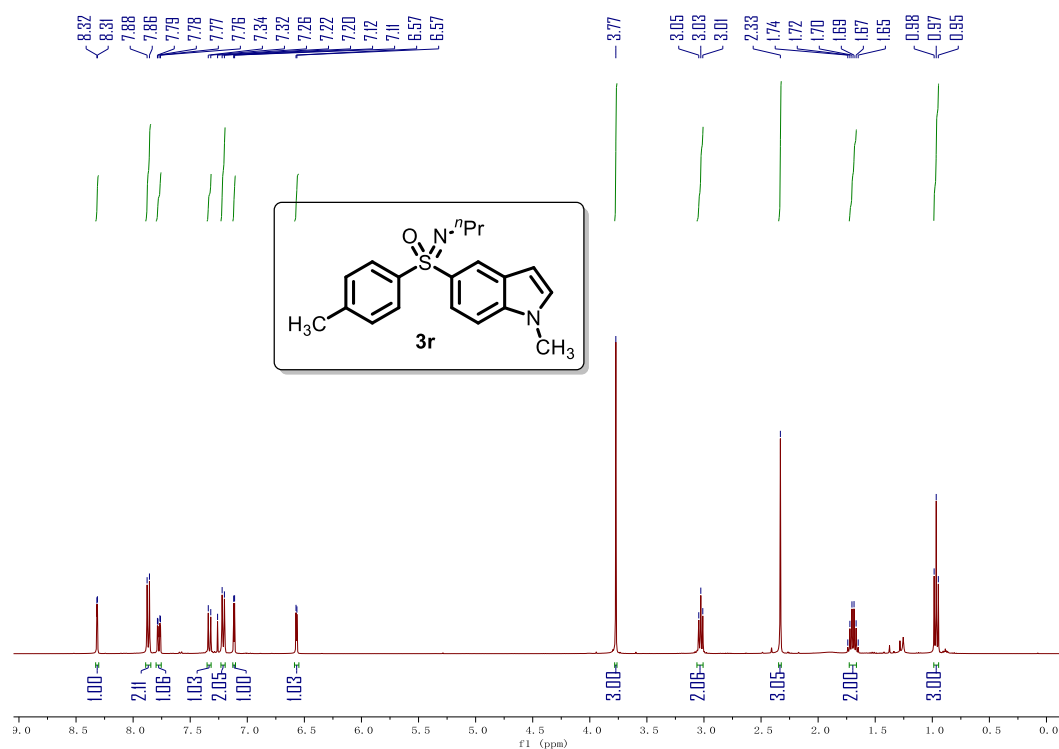
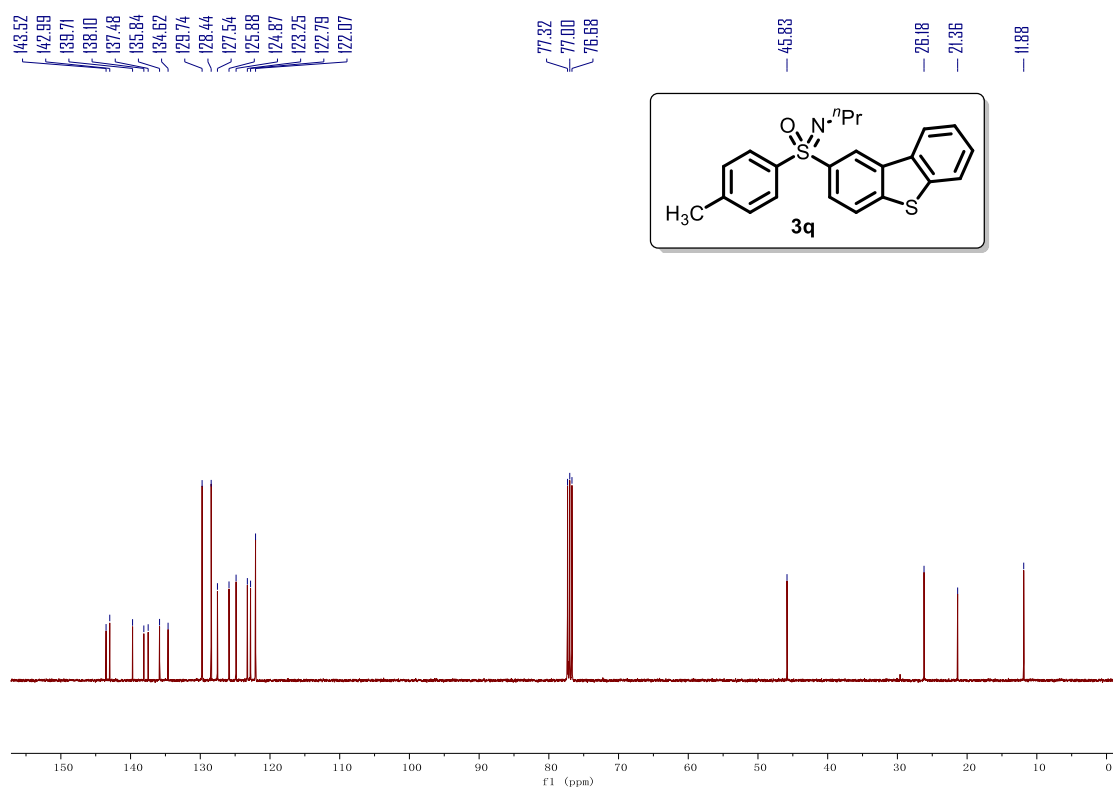
Supplementary Figure 37. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3p**.

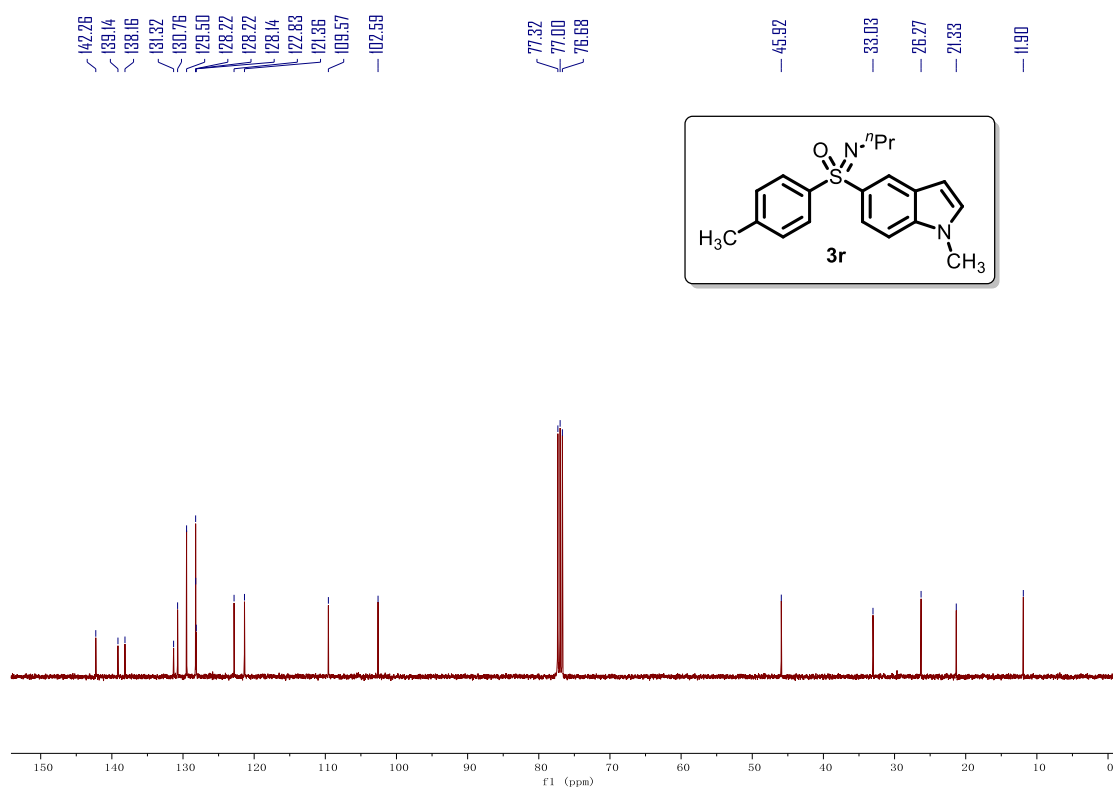


**Supplementary Figure 38.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3p**.

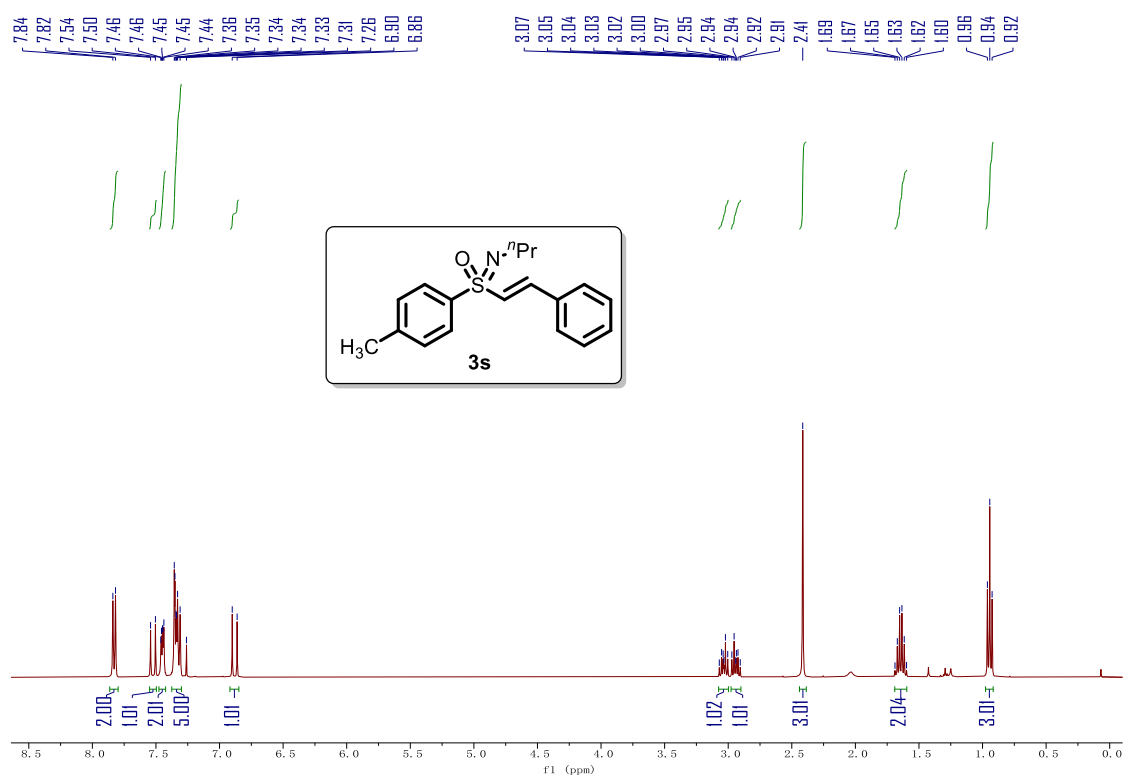


**Supplementary Figure 39.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3q**.



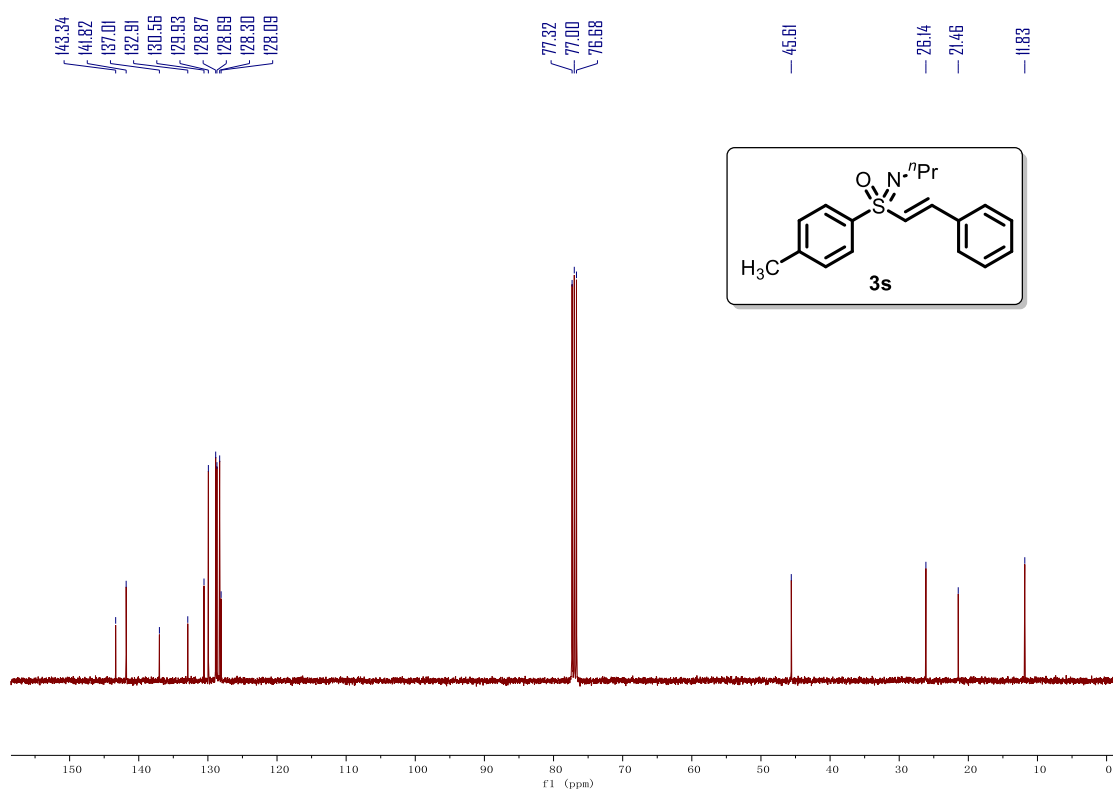


**Supplementary Figure 42.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3r**.

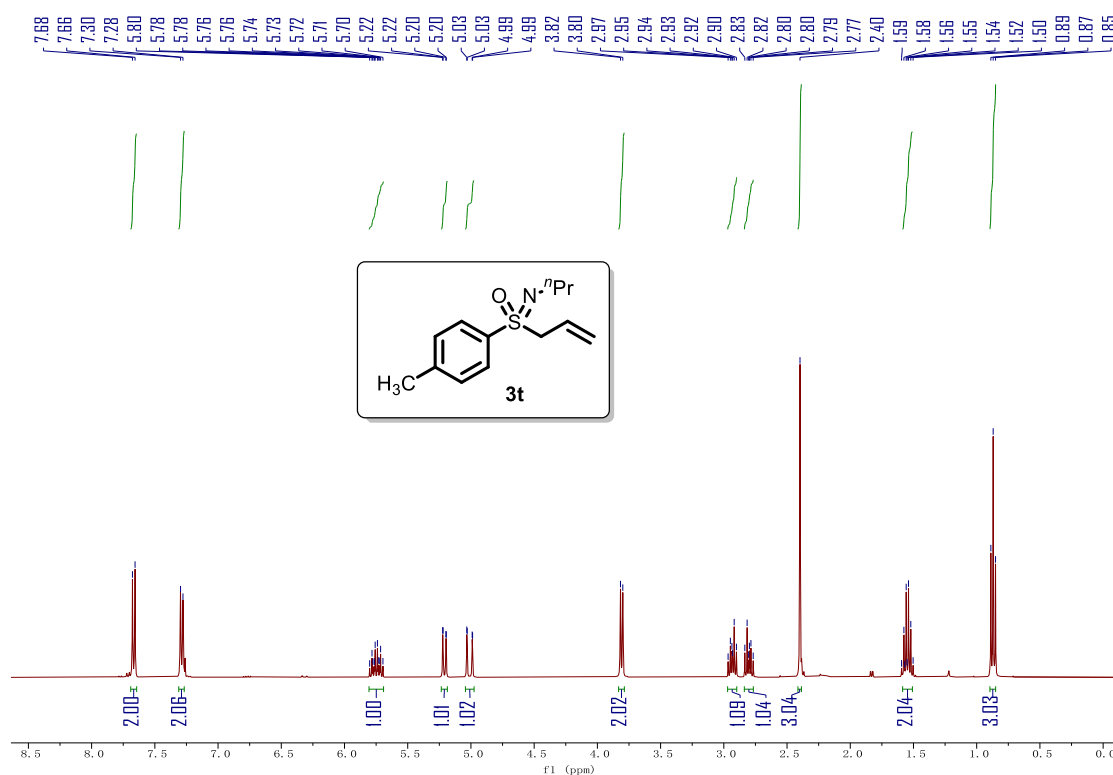


**Supplementary Figure 43.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3s**.

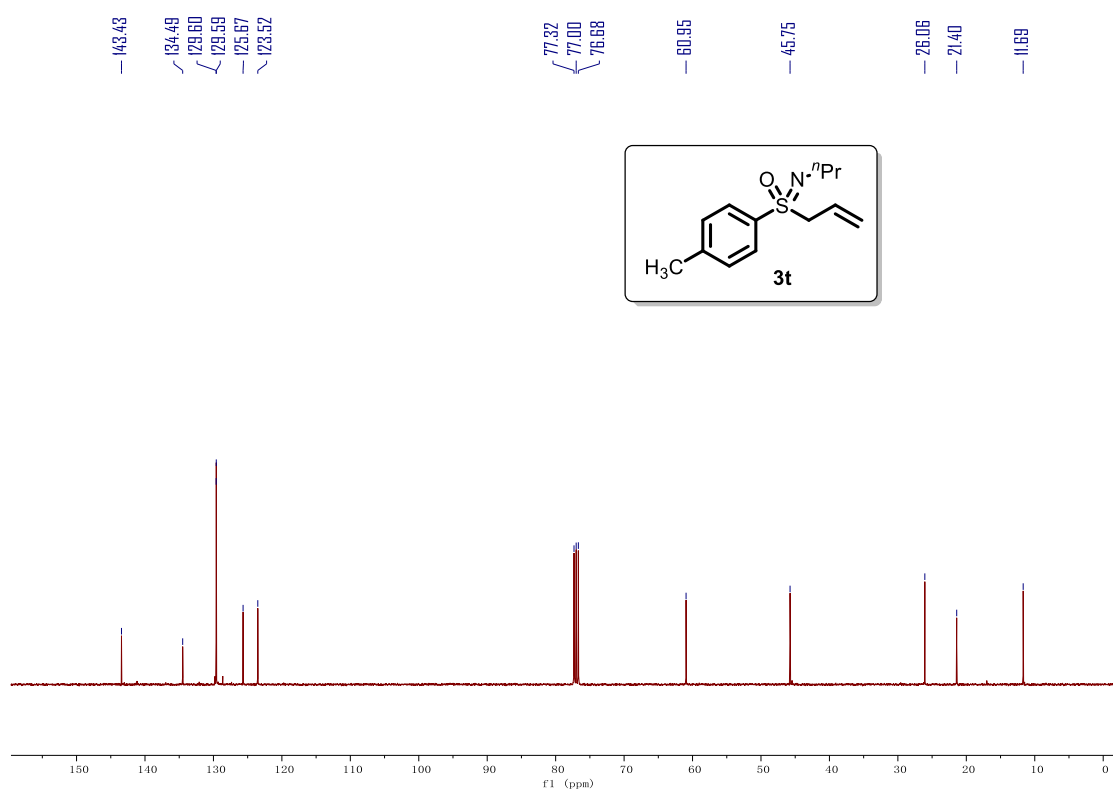




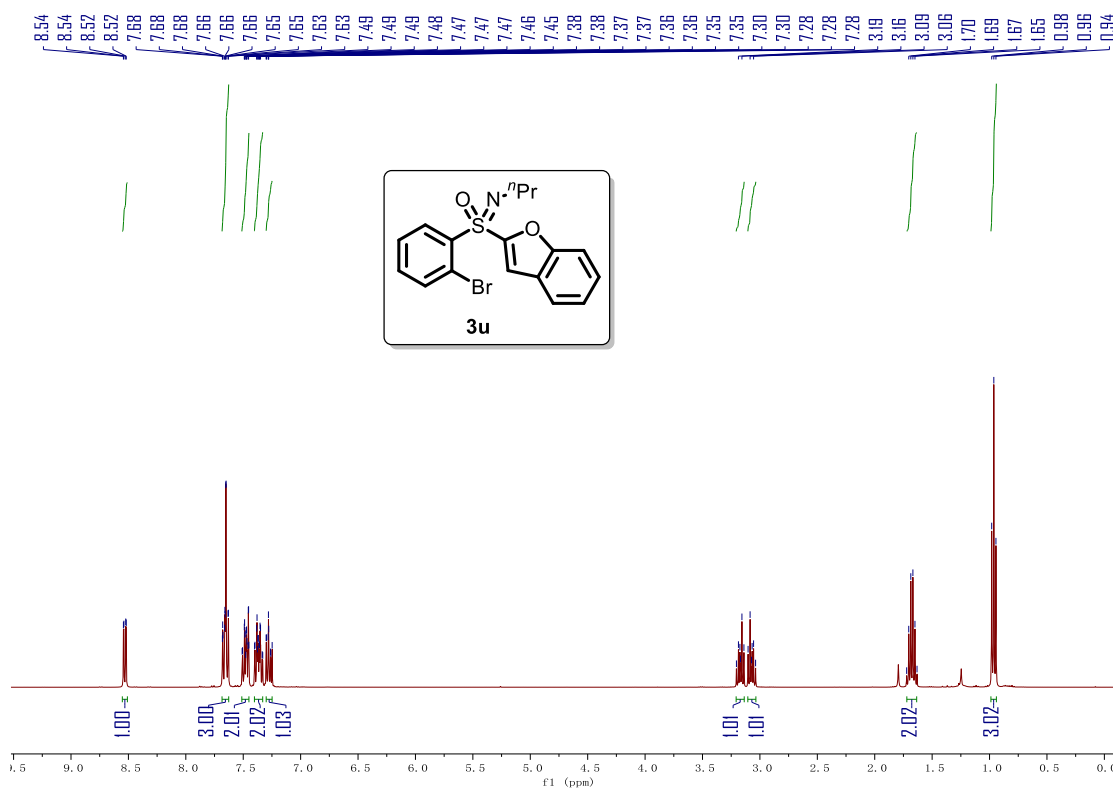
**Supplementary Figure 44.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3s**.



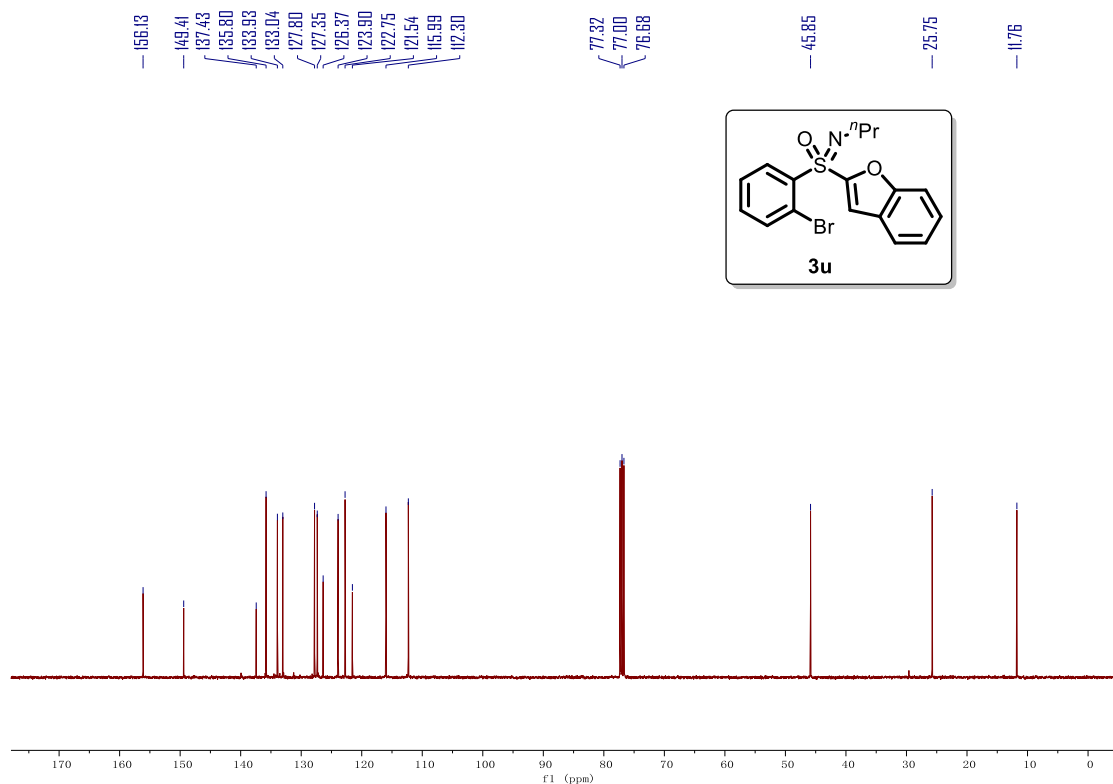
**Supplementary Figure 45.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3t**.



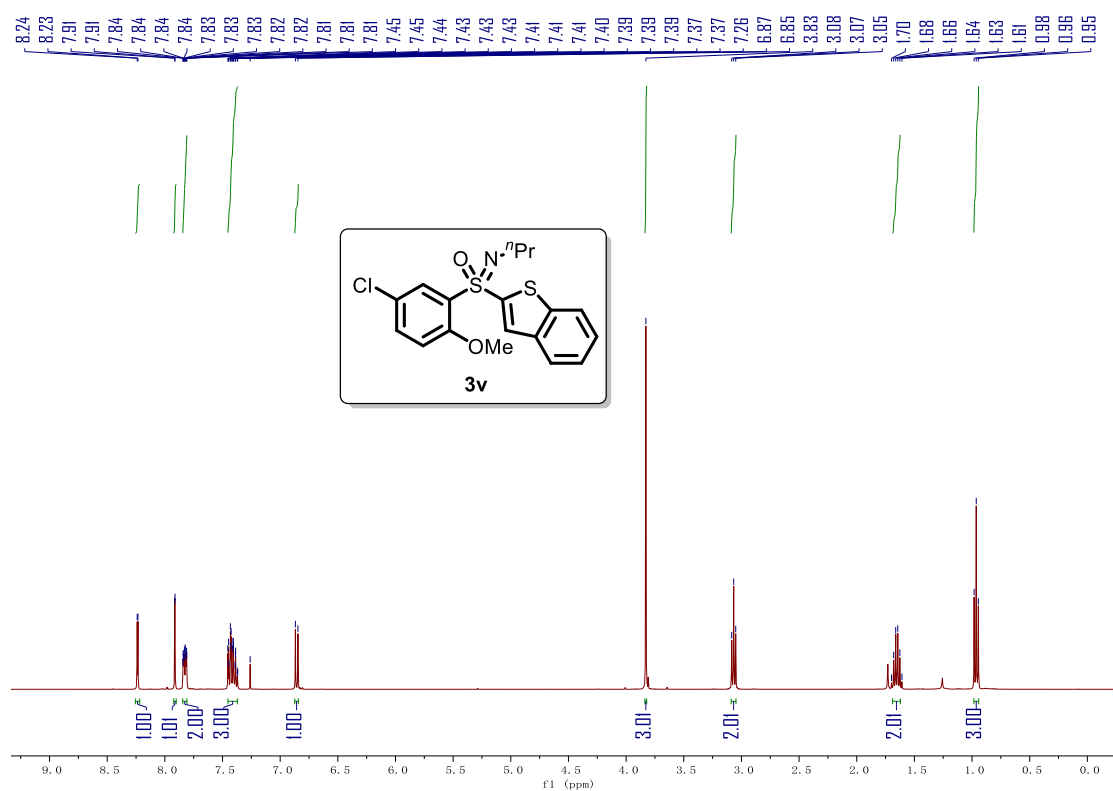
Supplementary Figure 46. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3t**.



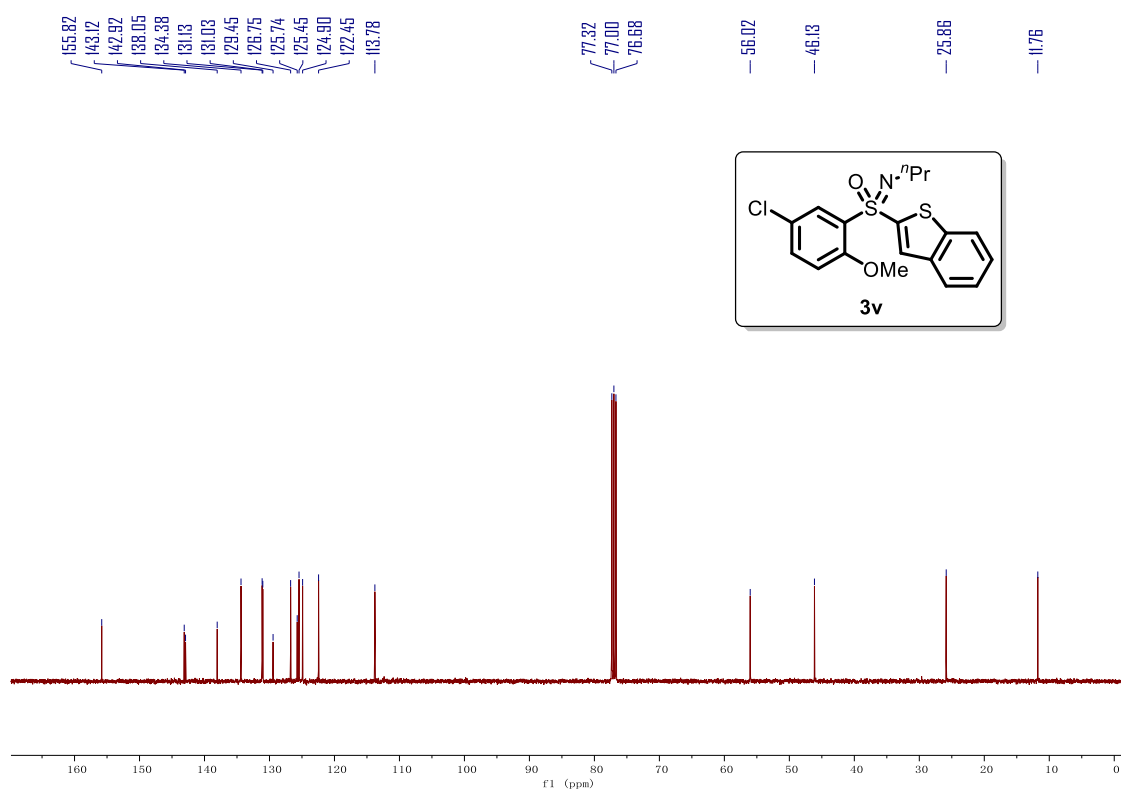
Supplementary Figure 47. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3u**.



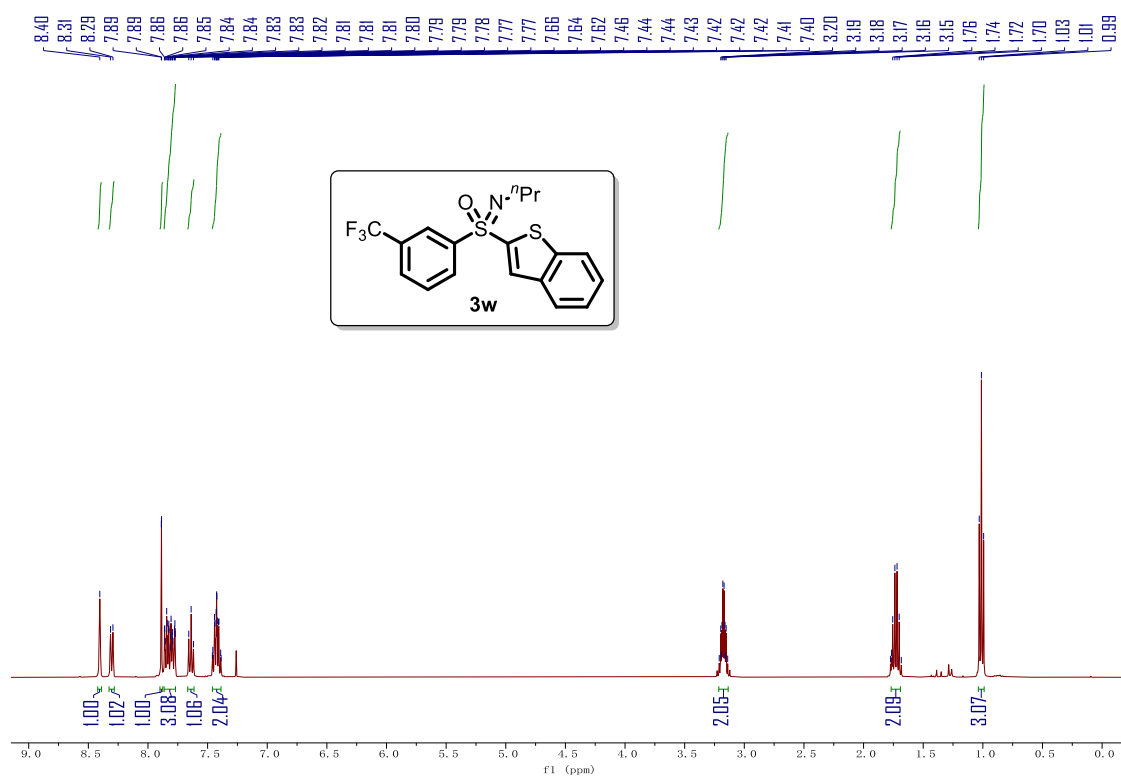
Supplementary Figure 48. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3u**.



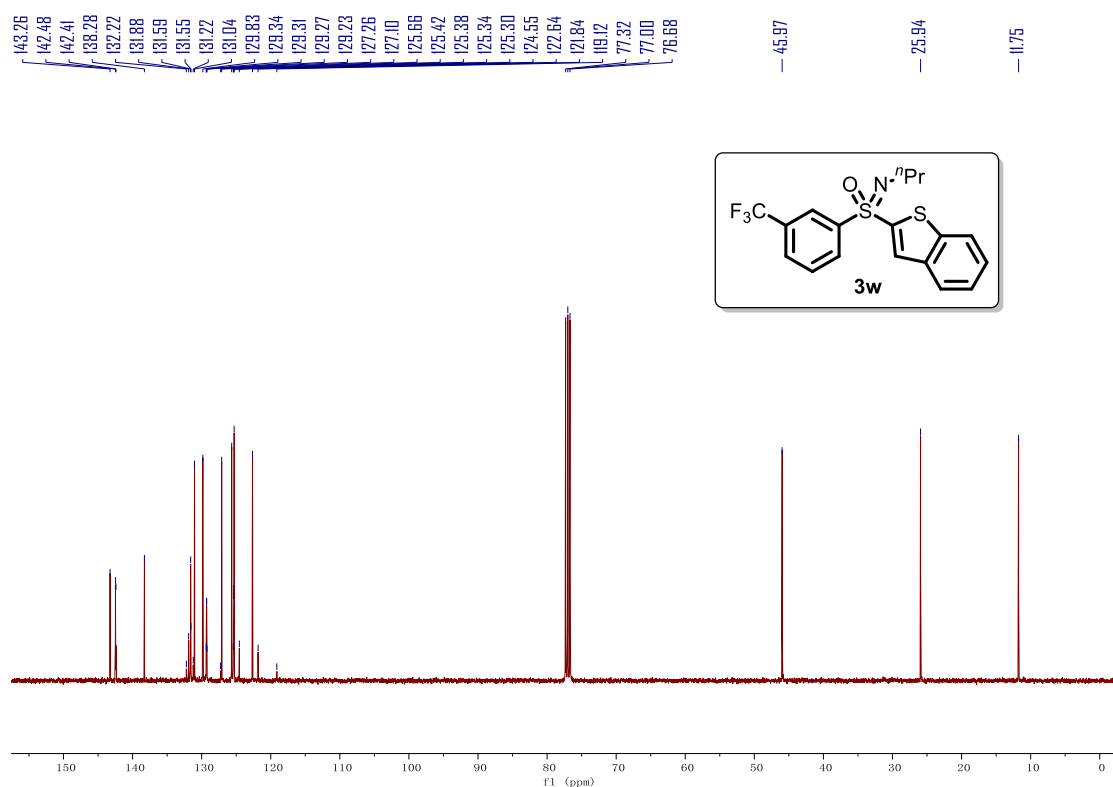
Supplementary Figure 49. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3v**.



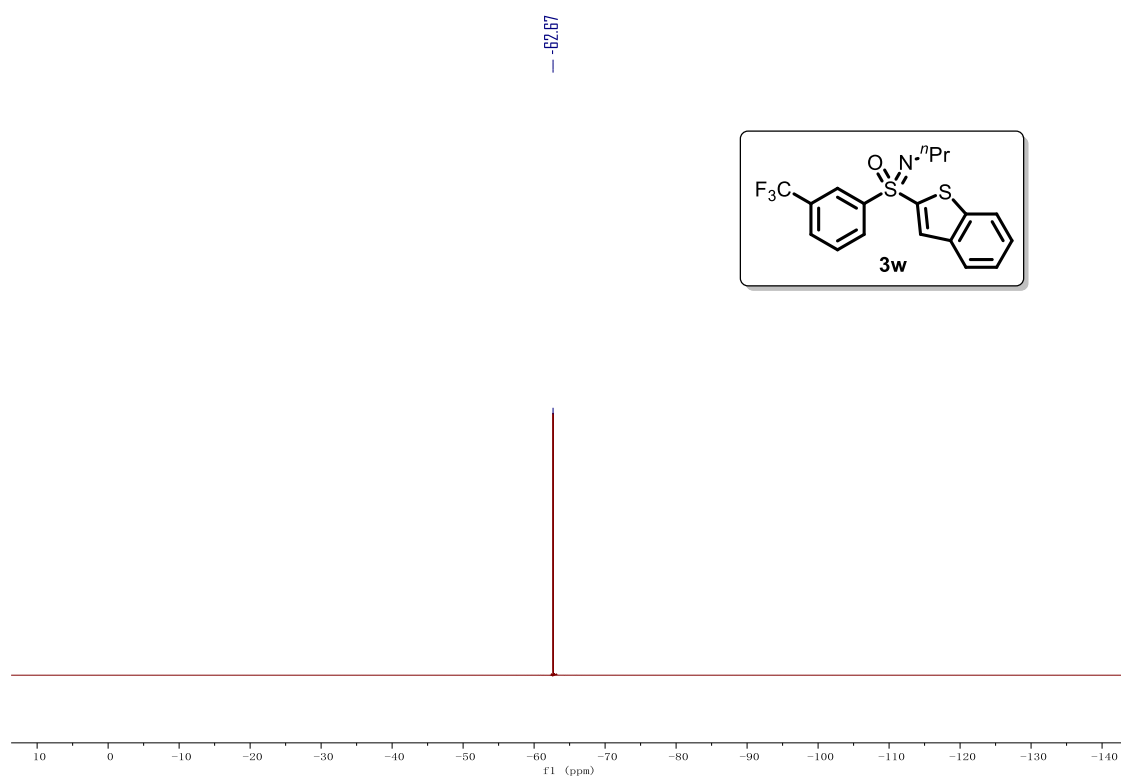
**Supplementary Figure 50.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3v**.



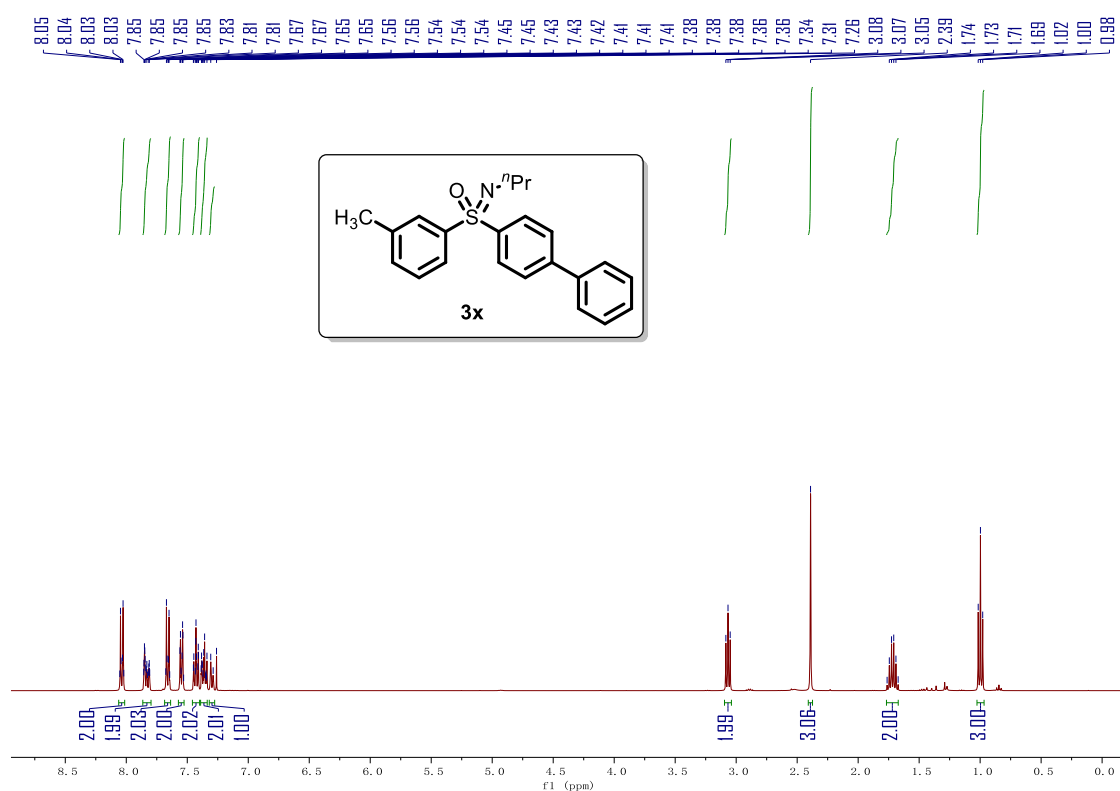
**Supplementary Figure 51.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3w**.



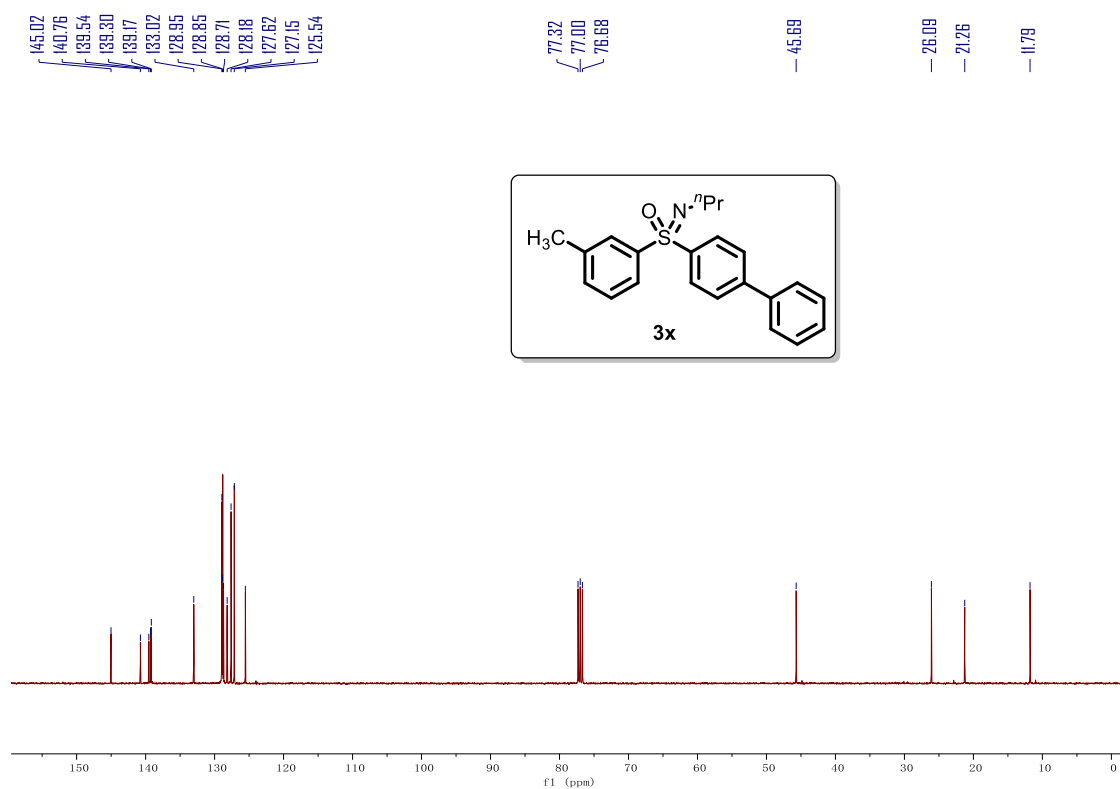
**Supplementary Figure 52.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3w**.



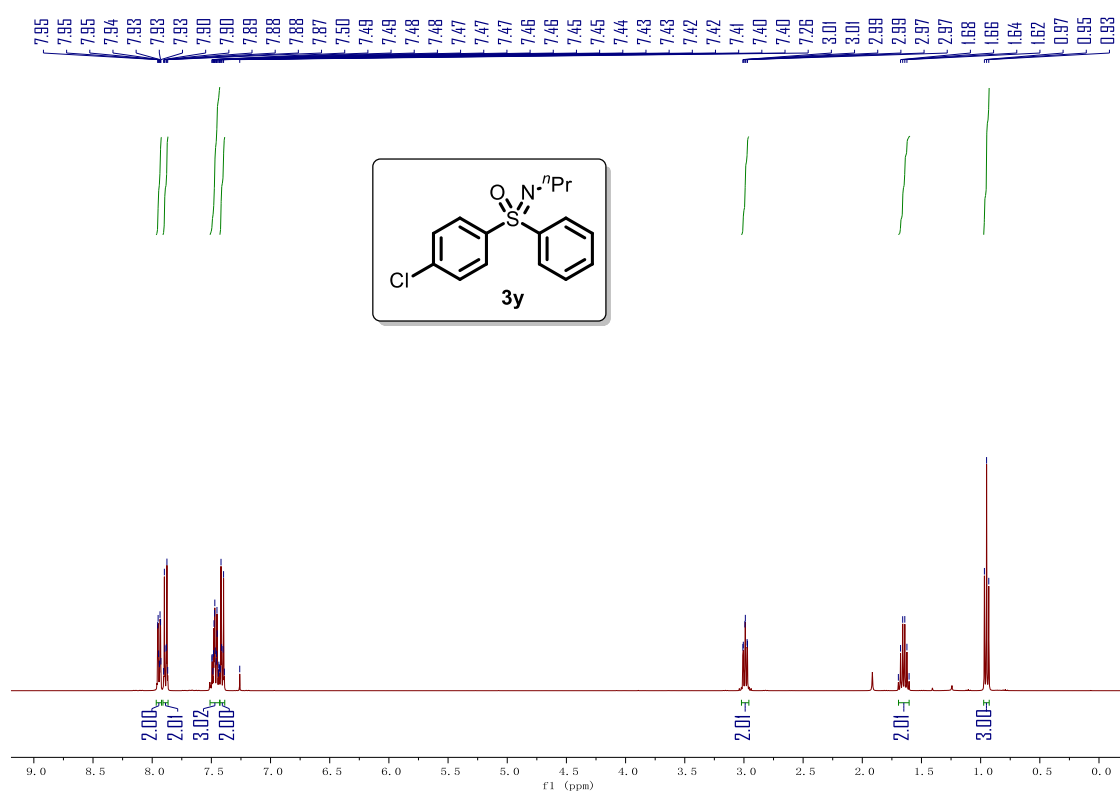
**Supplementary Figure 53.** <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) spectra of compound **3w**.



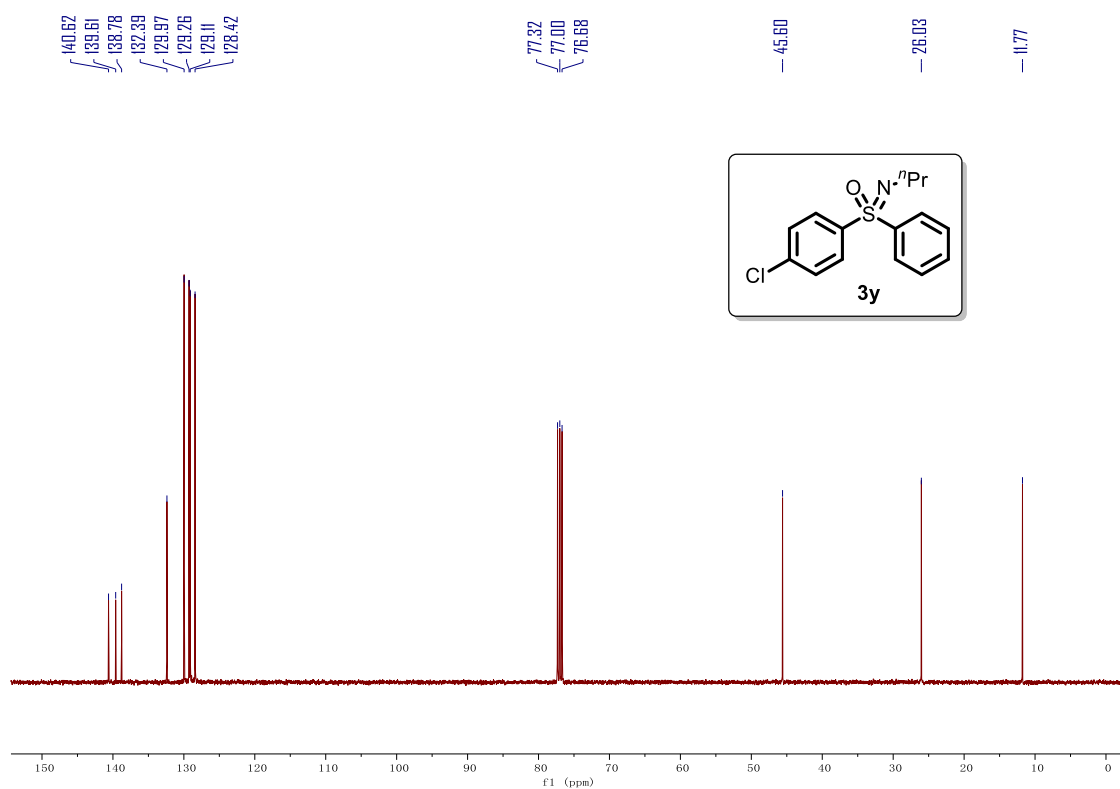
**Supplementary Figure 54.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3x**.



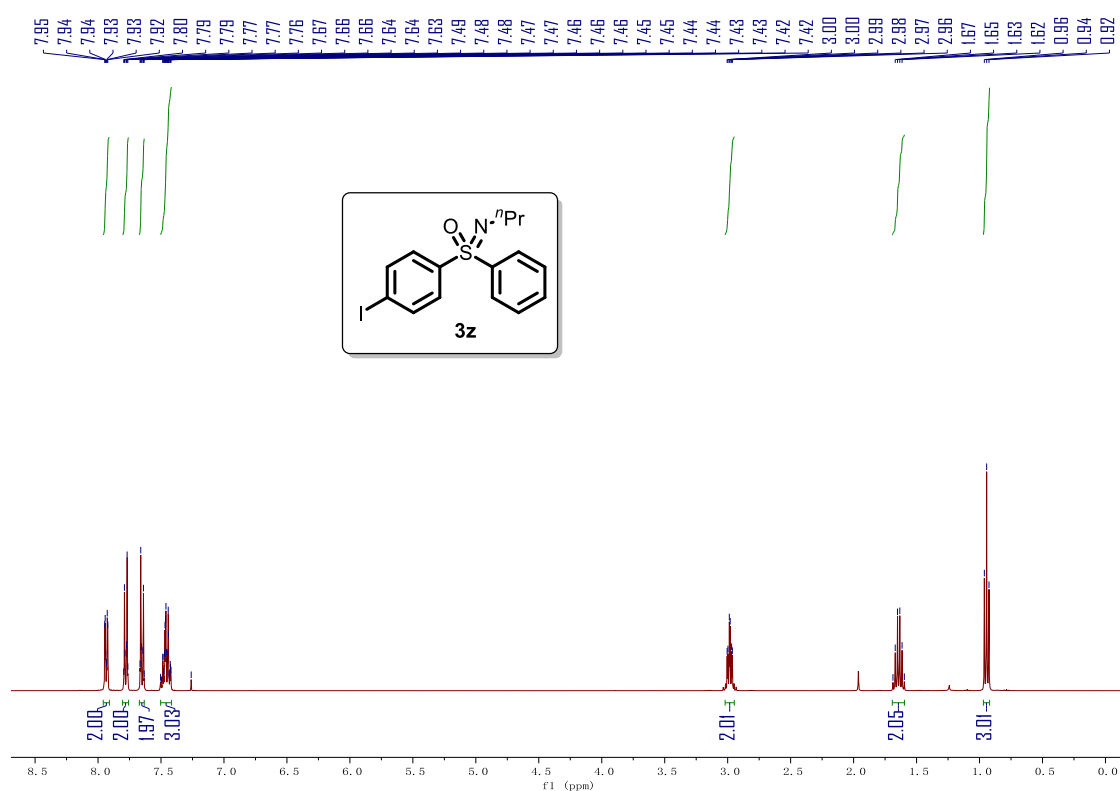
**Supplementary Figure 55.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3x**.



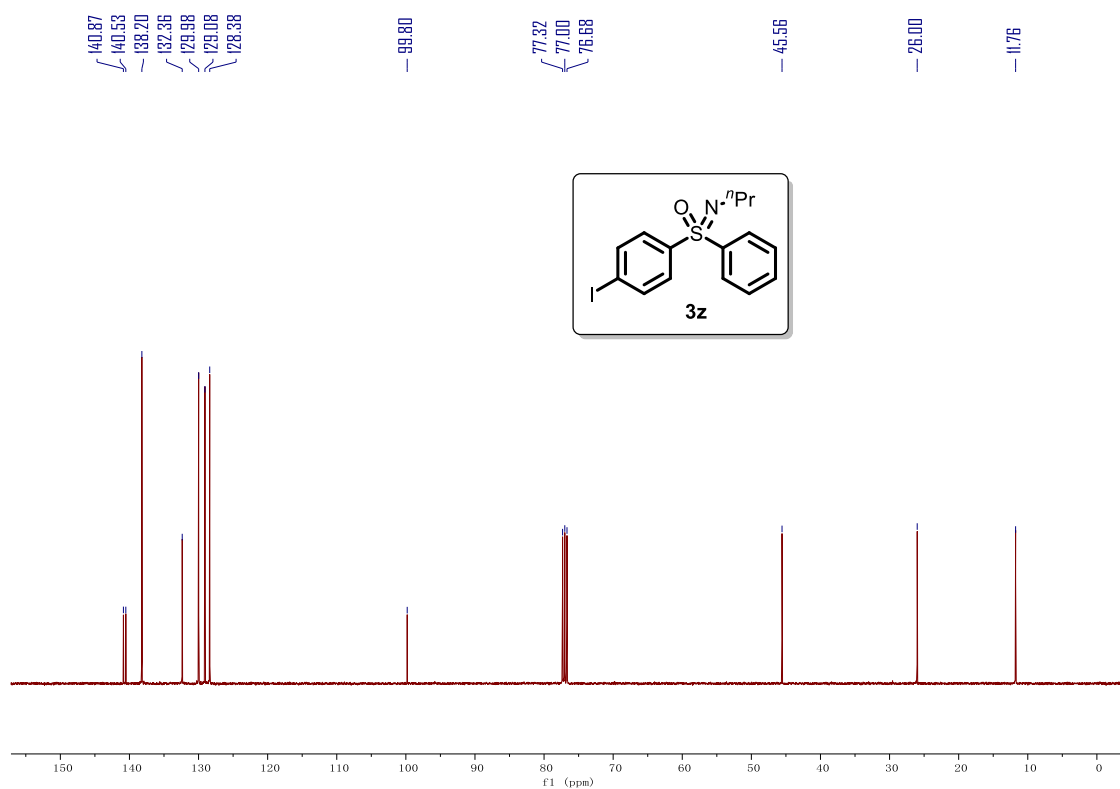
**Supplementary Figure 56.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3y**.



**Supplementary Figure 57.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3y**.

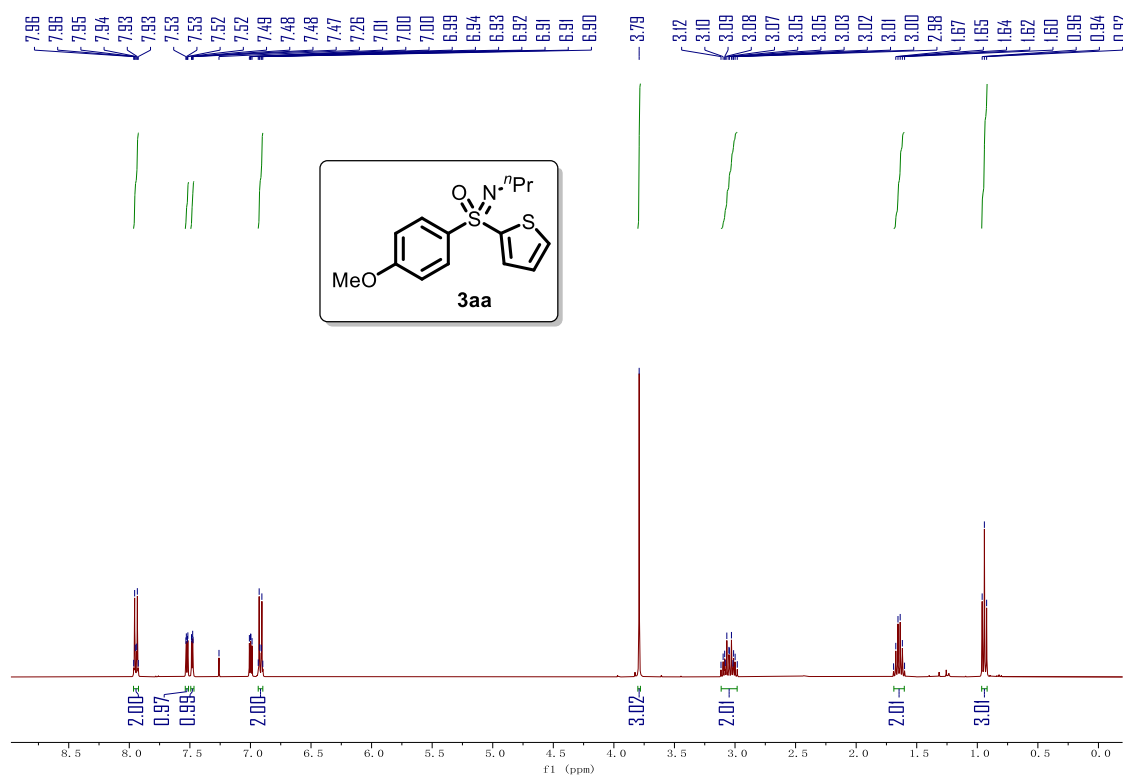


**Supplementary Figure 58.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3z**.

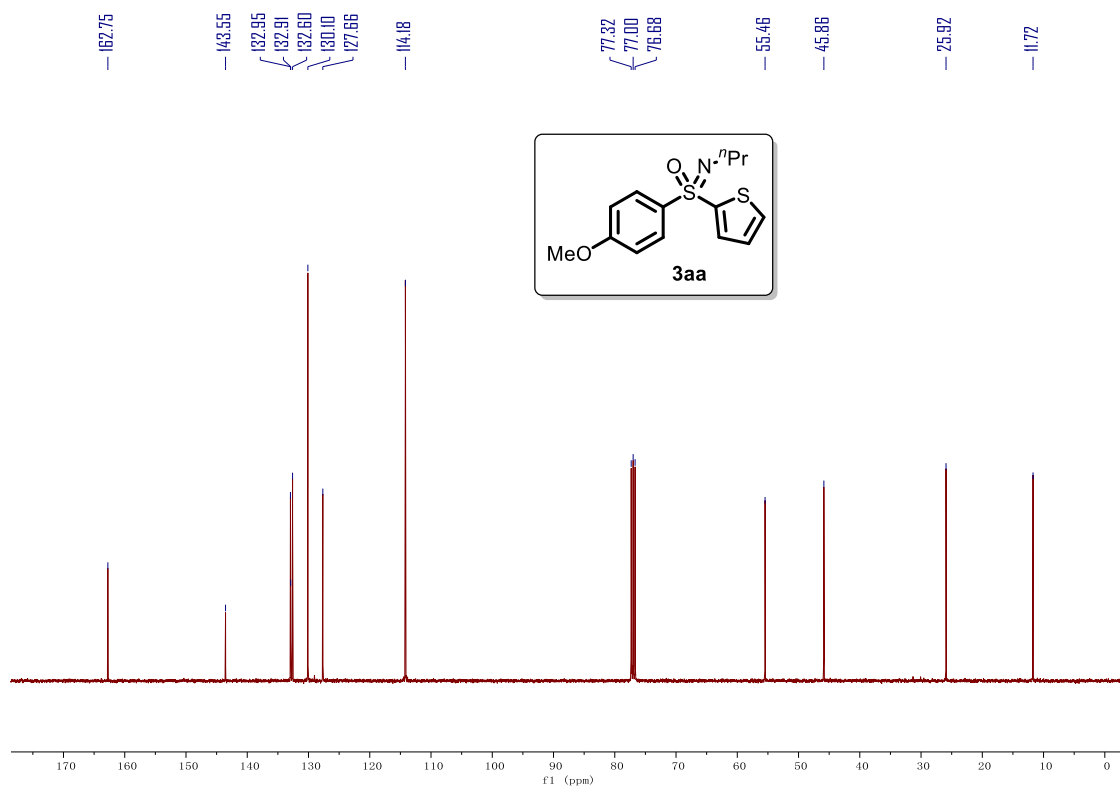


**Supplementary Figure 59.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3z**.

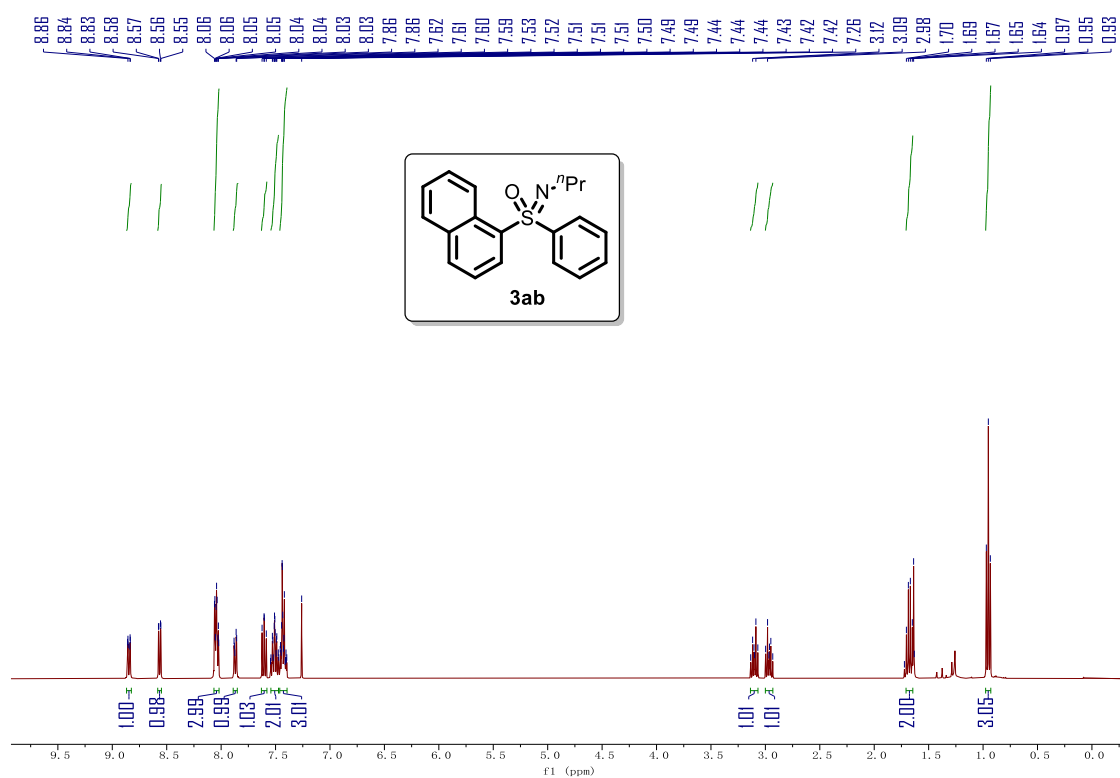




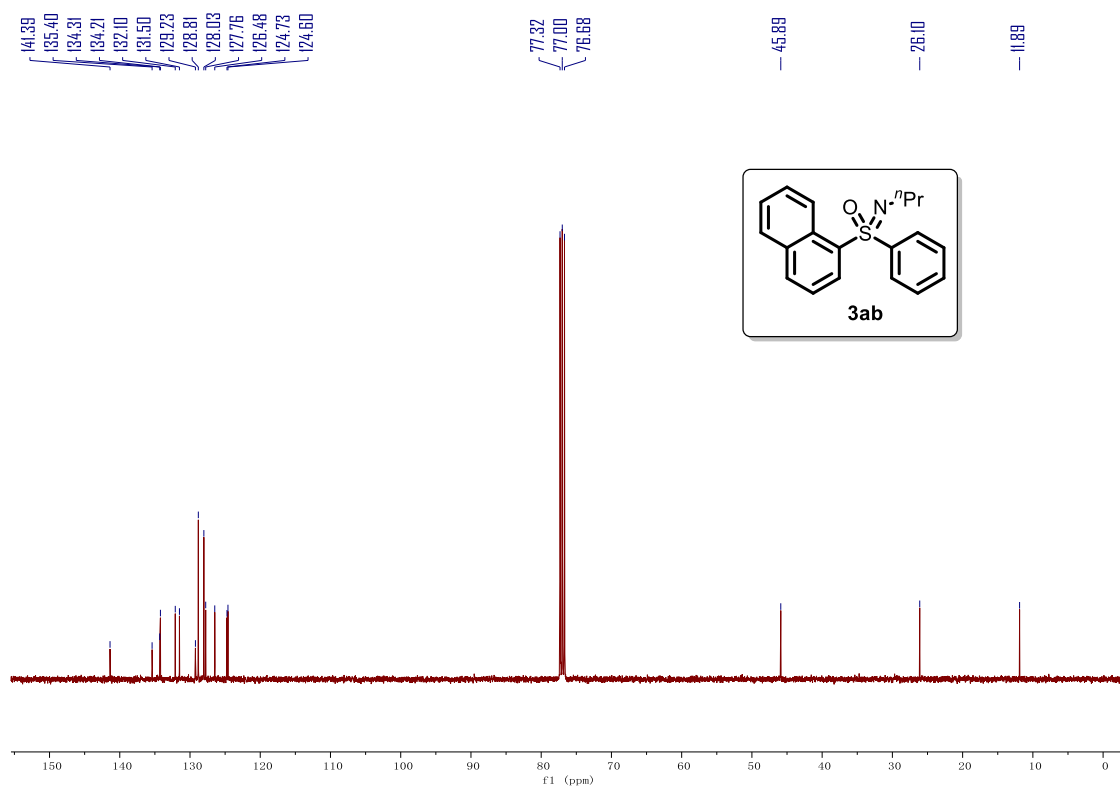
**Supplementary Figure 60.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3aa**.



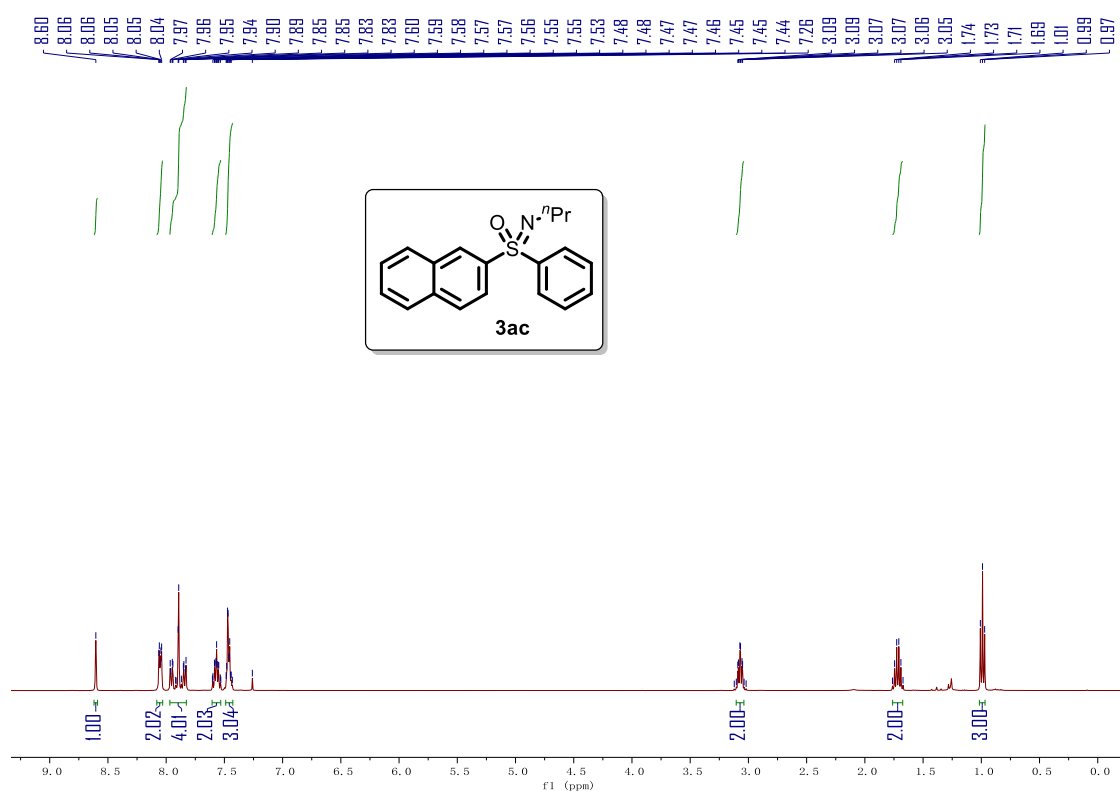
**Supplementary Figure 61.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3aa**.



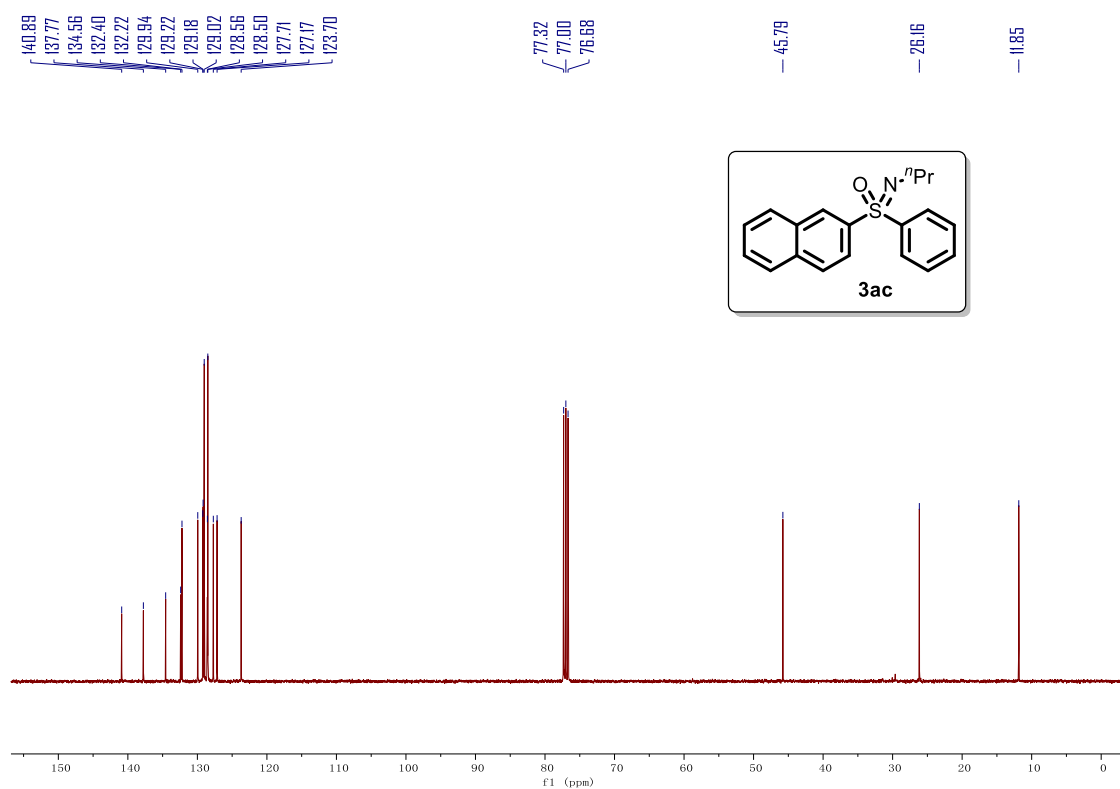
**Supplementary Figure 62.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3ab**.



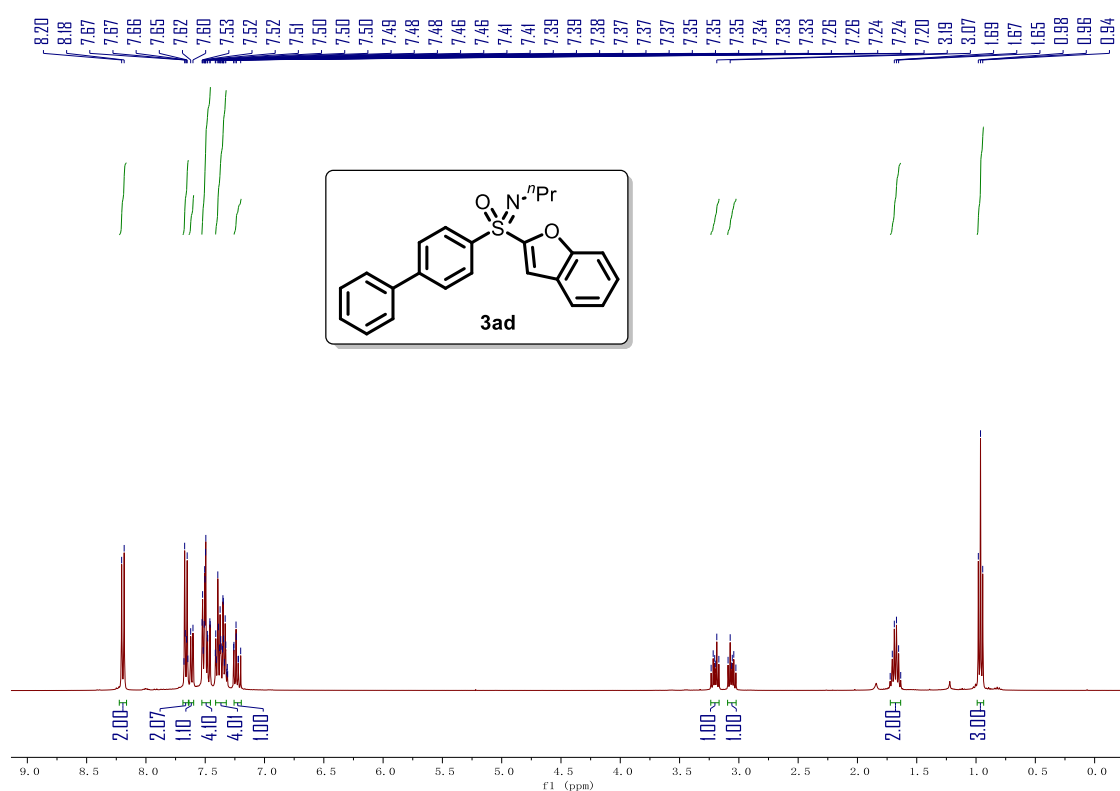
**Supplementary Figure 63.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3ab**.



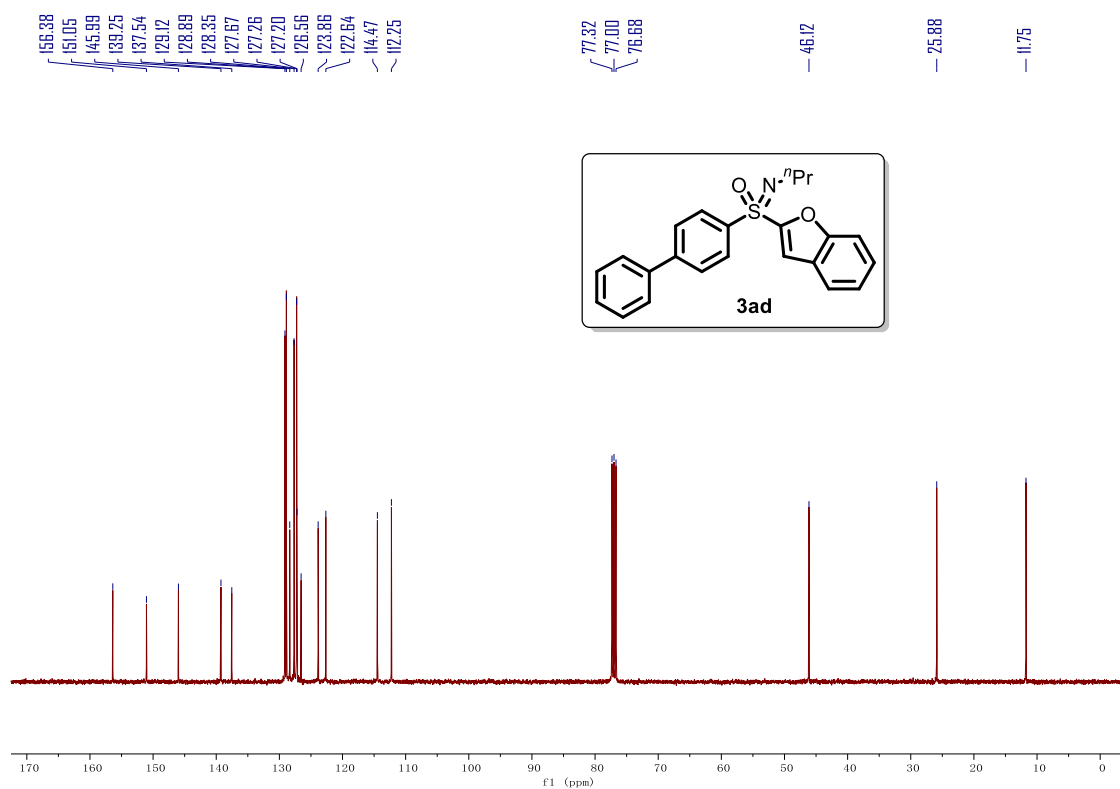
**Supplementary Figure 64.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3ac**.



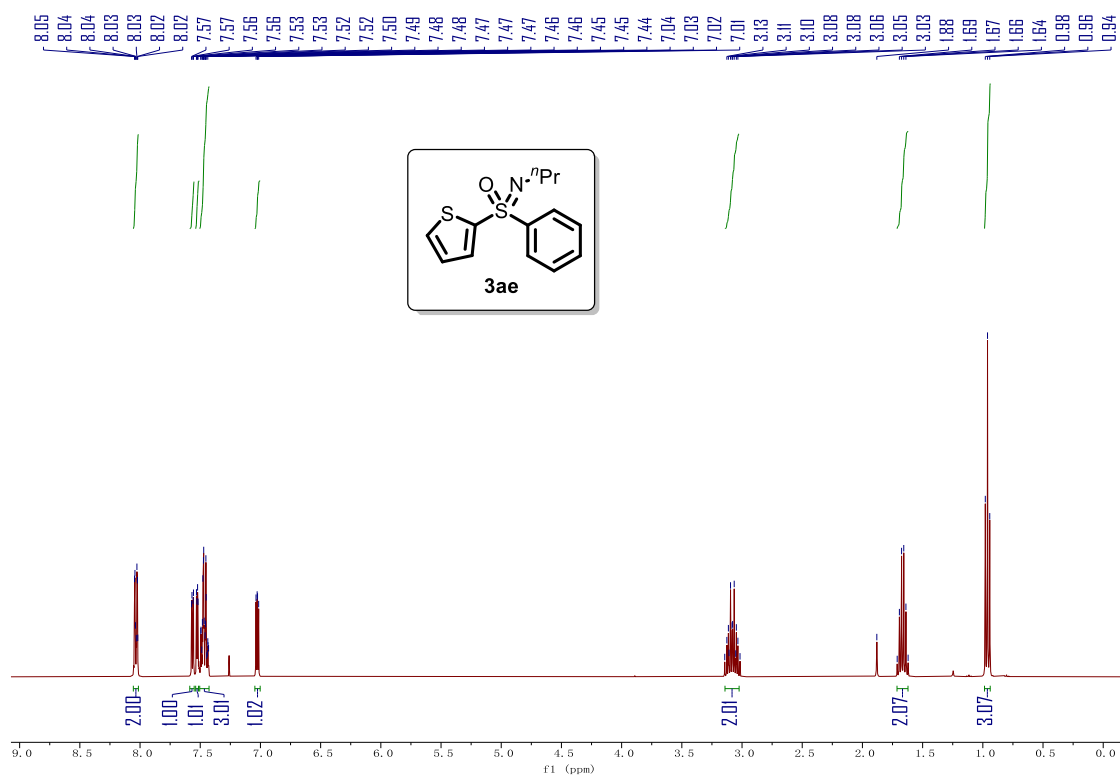
**Supplementary Figure 65.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3ac**.



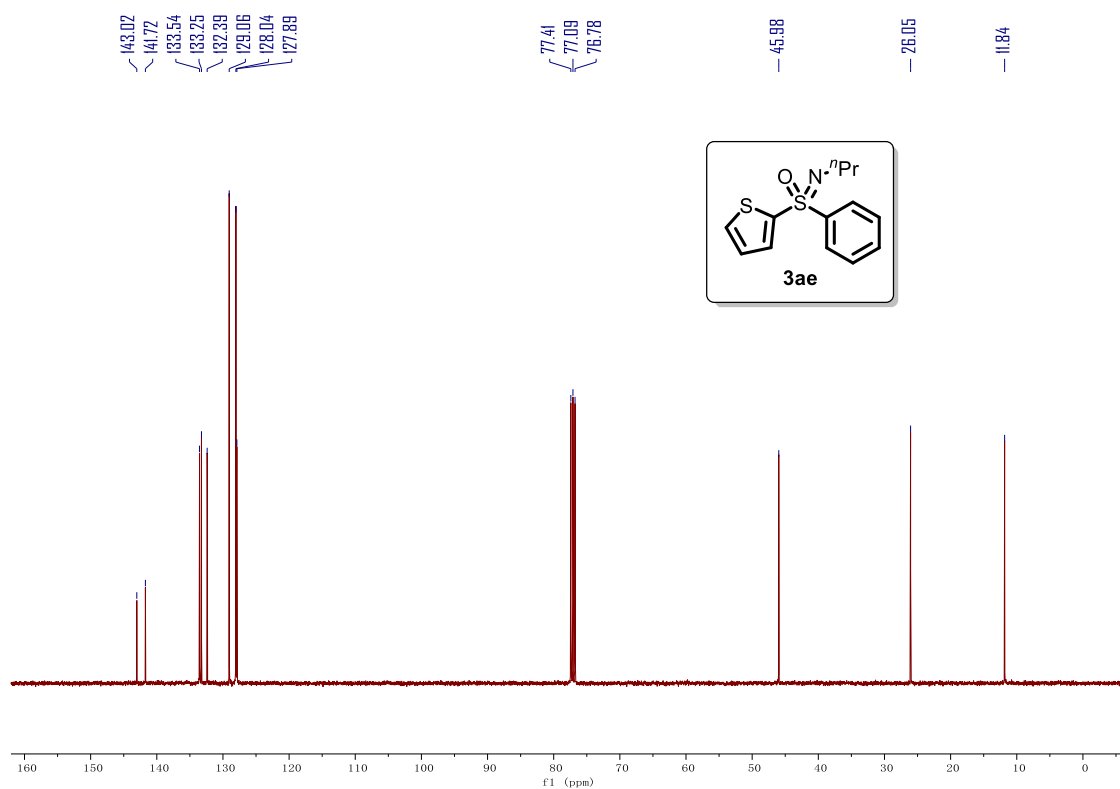
**Supplementary Figure 66.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3ad**.



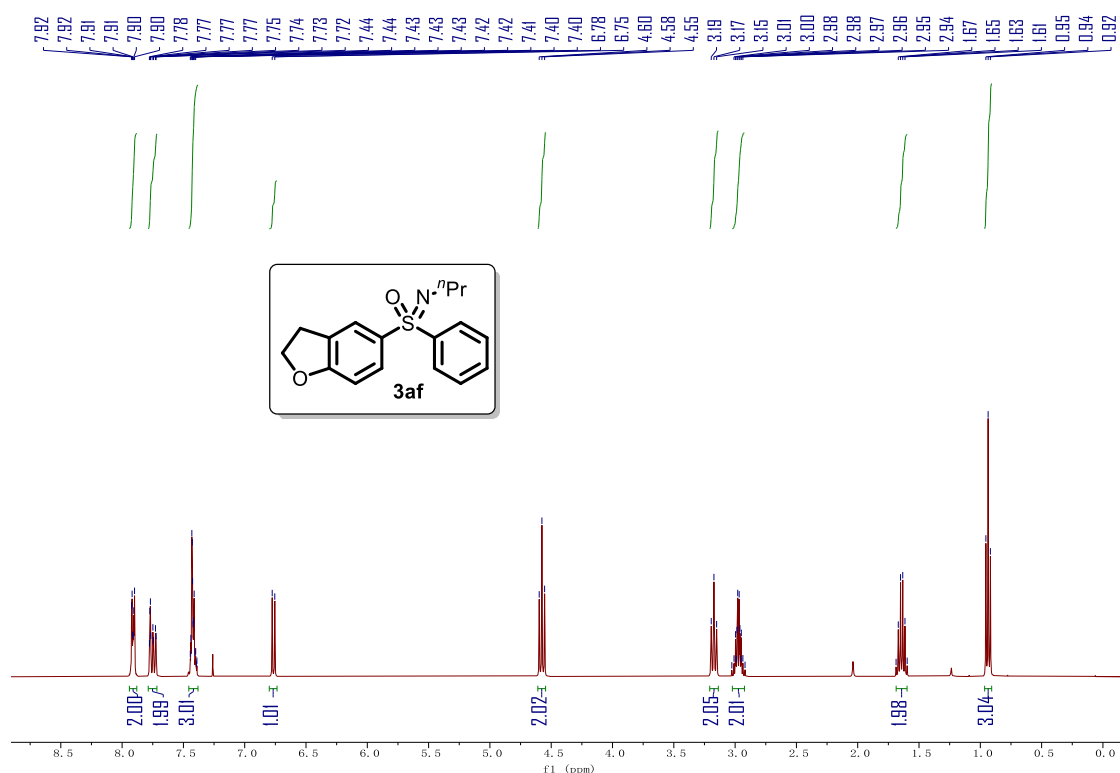
**Supplementary Figure 67.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3ad**.



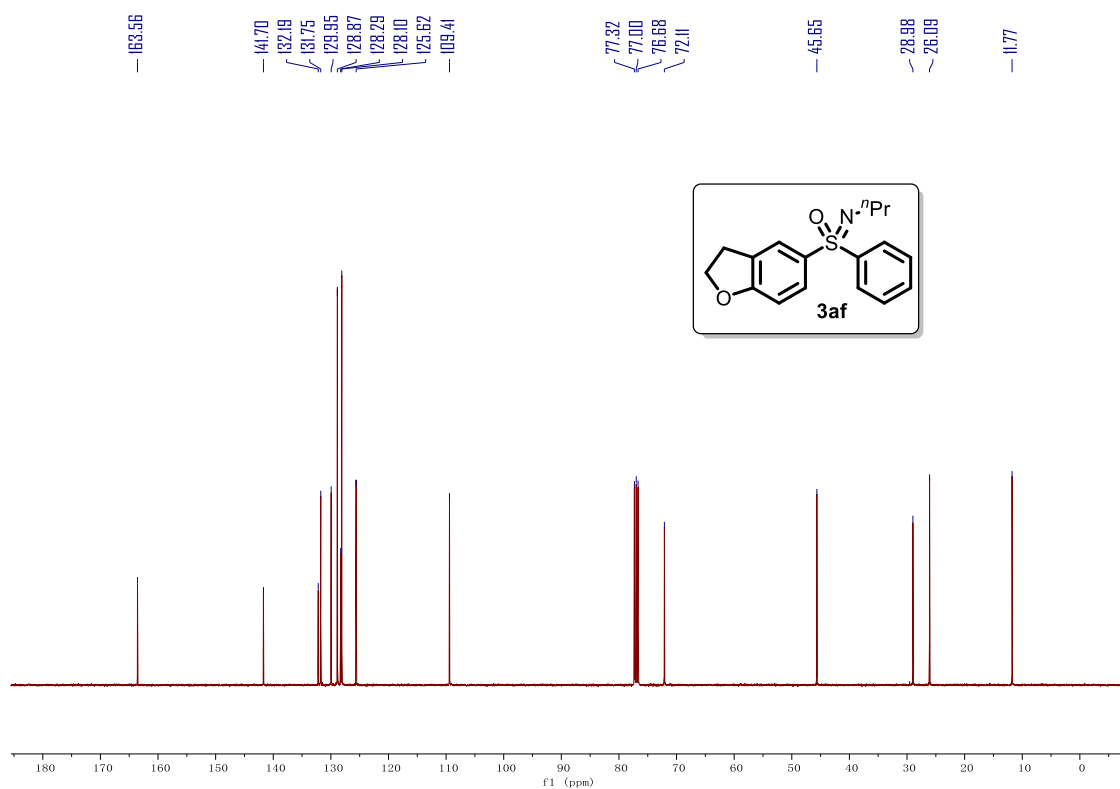
**Supplementary Figure 68.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3ae**.



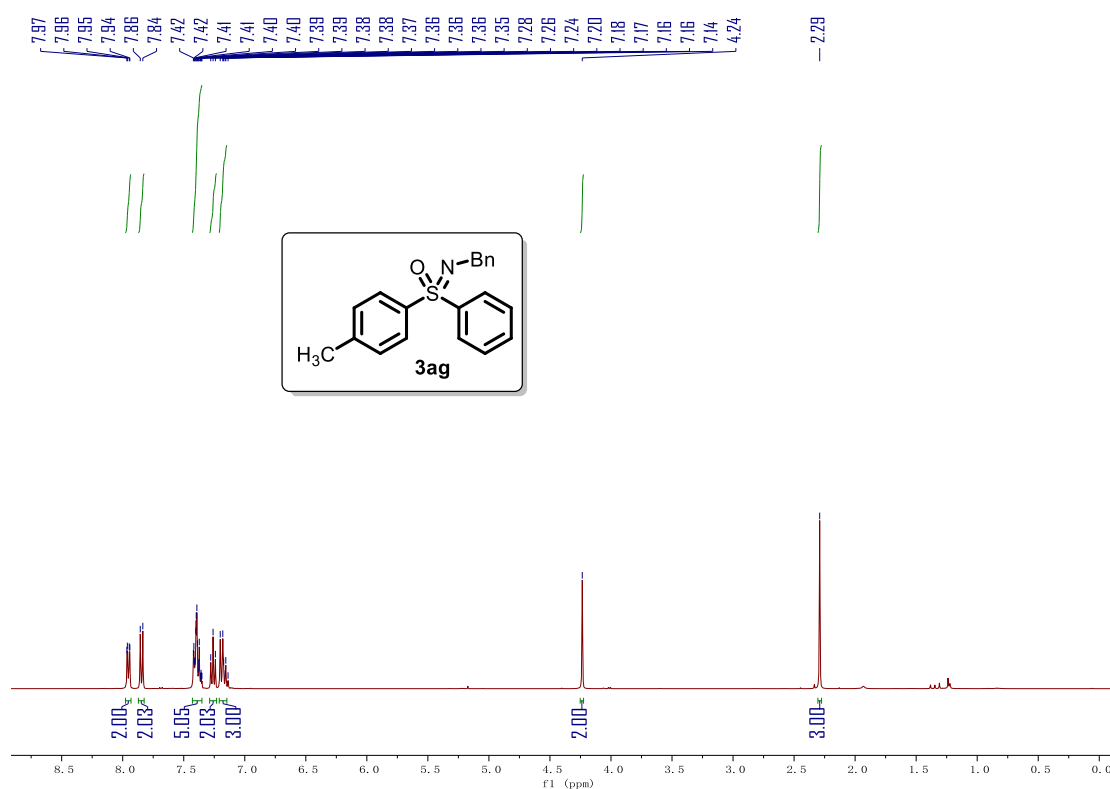
**Supplementary Figure 69.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3ae**.



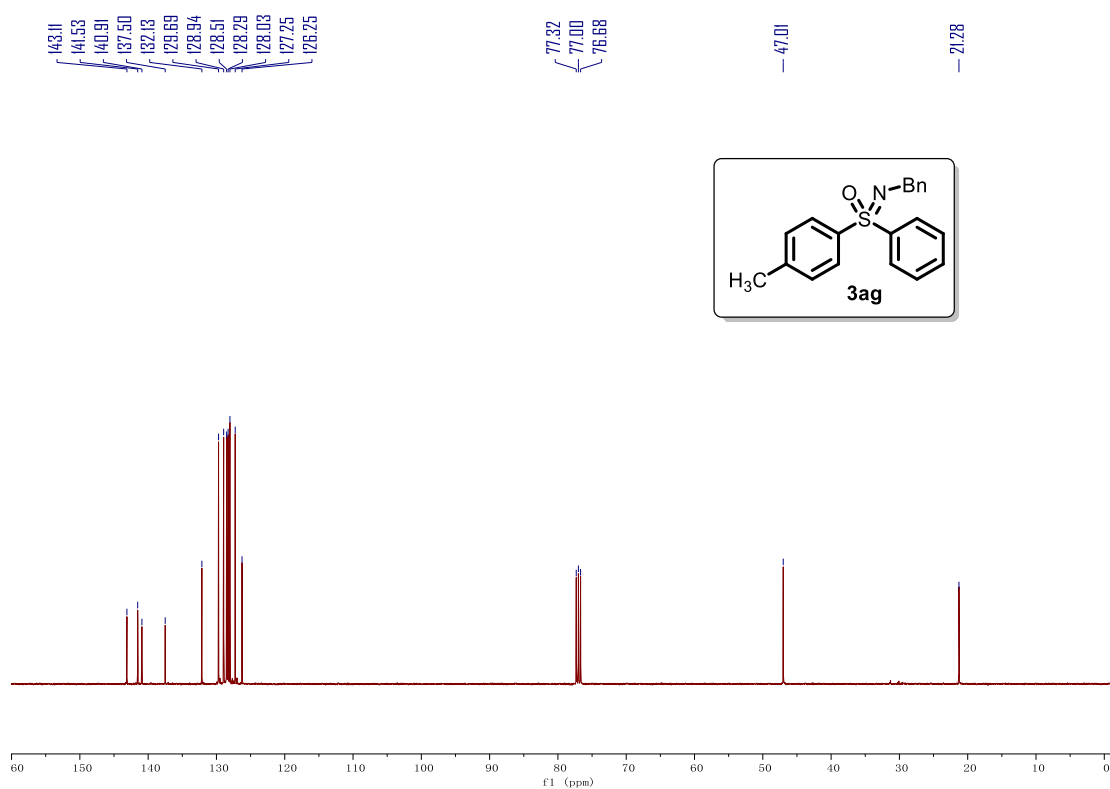
**Supplementary Figure 70.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3af**.



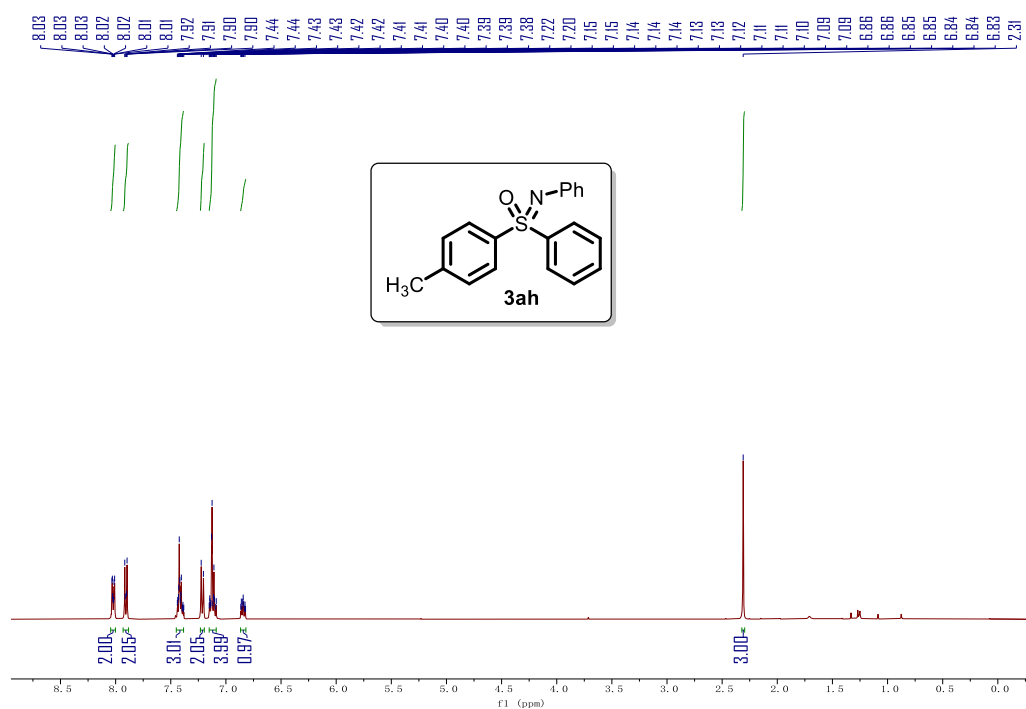
**Supplementary Figure 71.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3af**.



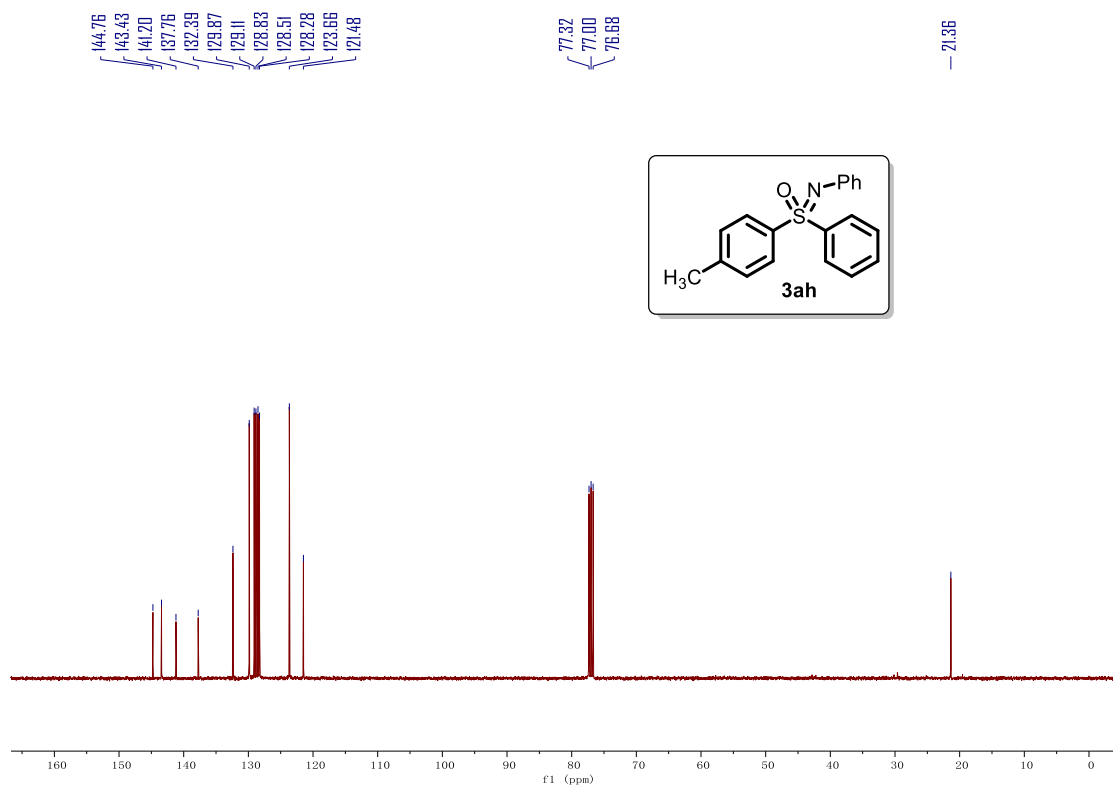
**Supplementary Figure 72.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3ag**.



**Supplementary Figure 73.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3ag**.

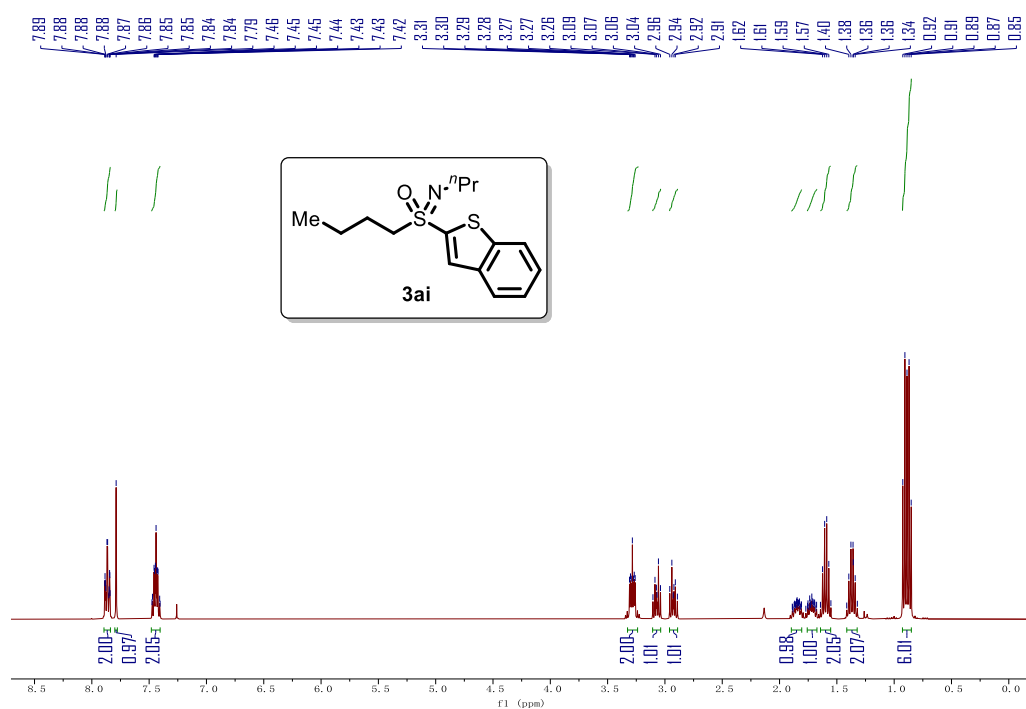


Supplementary Figure 74. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3ah**.

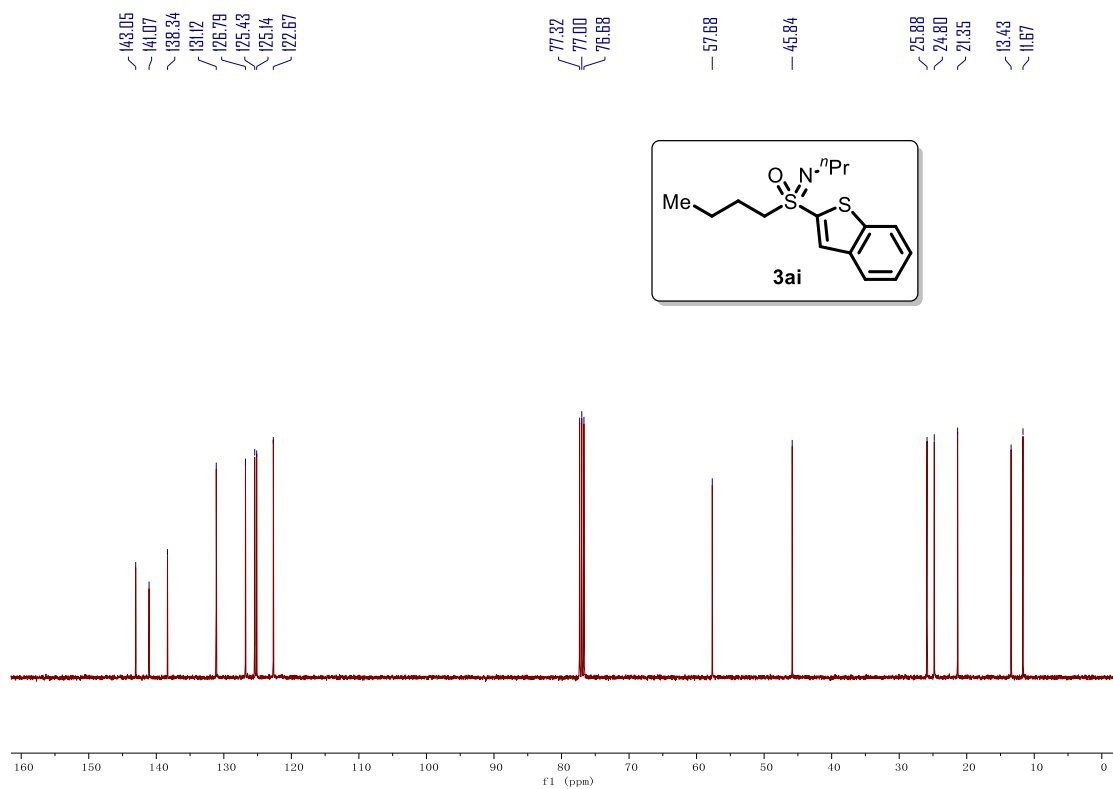


Supplementary Figure 75. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3ah**.

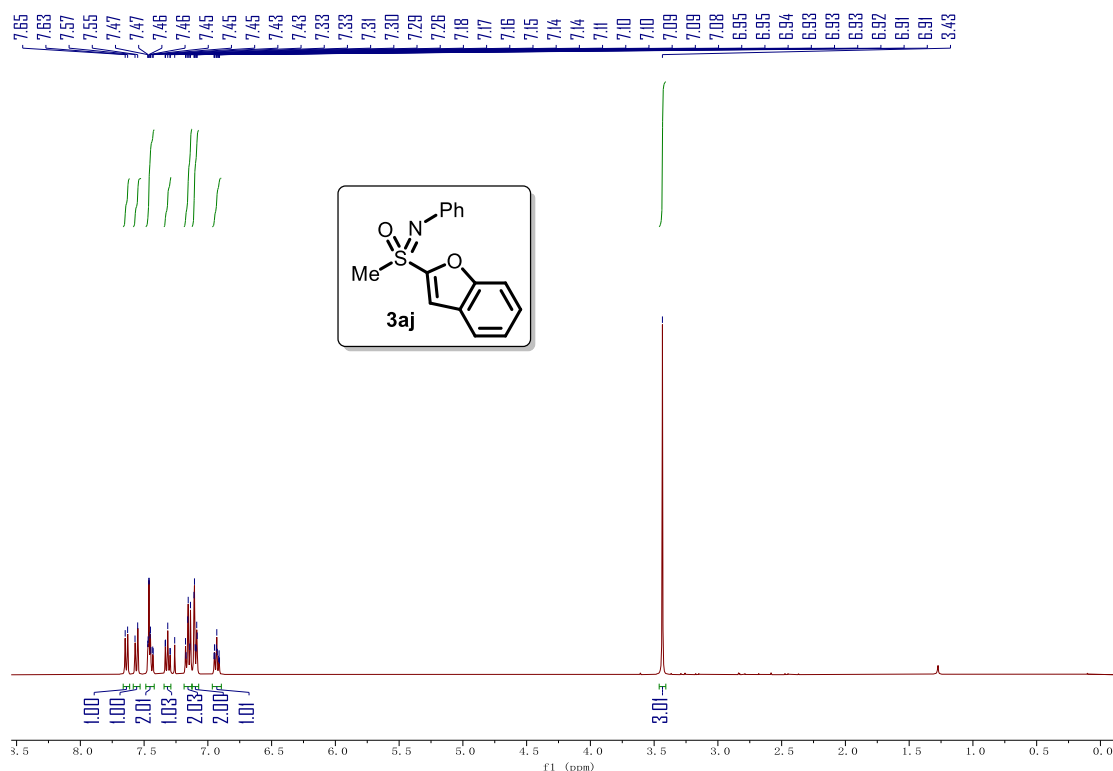




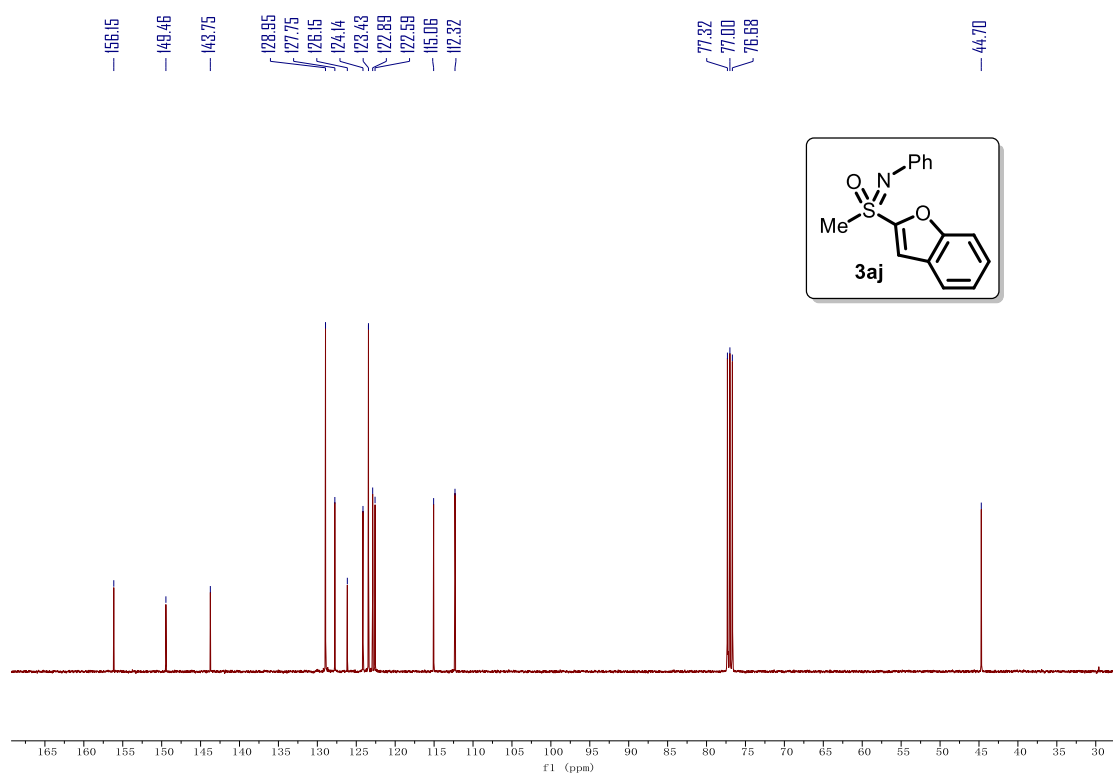
Supplementary Figure 76. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3ai**.



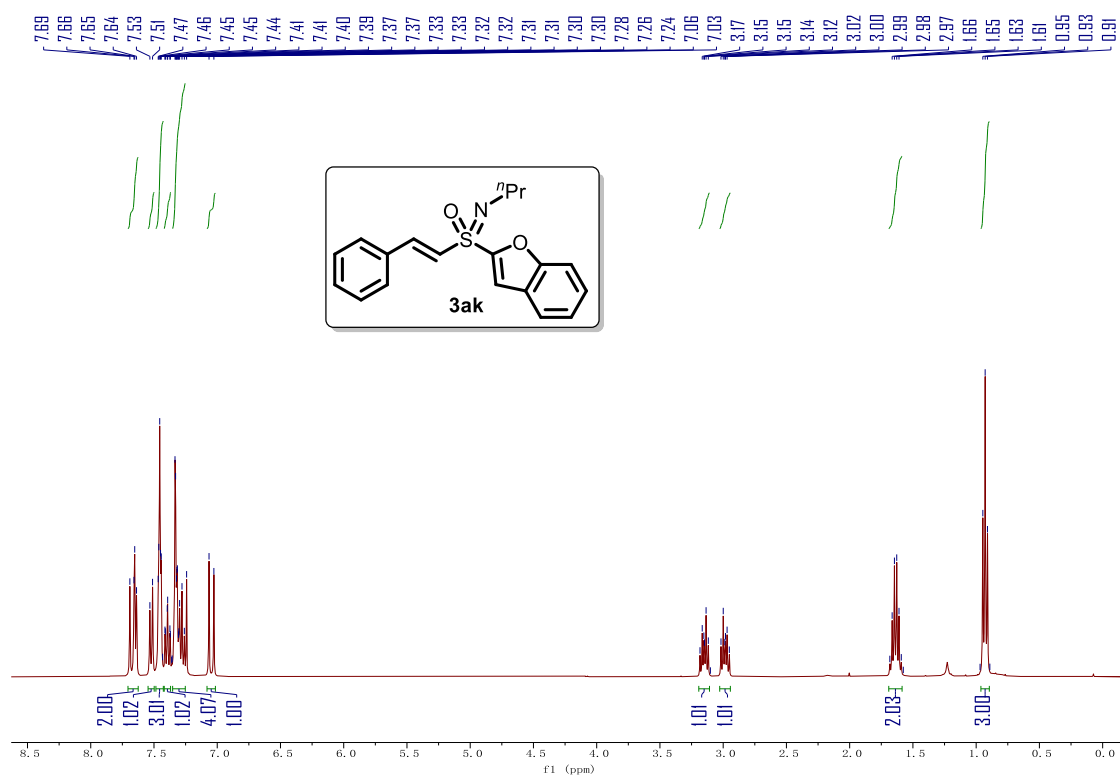
Supplementary Figure 77. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3ai**.



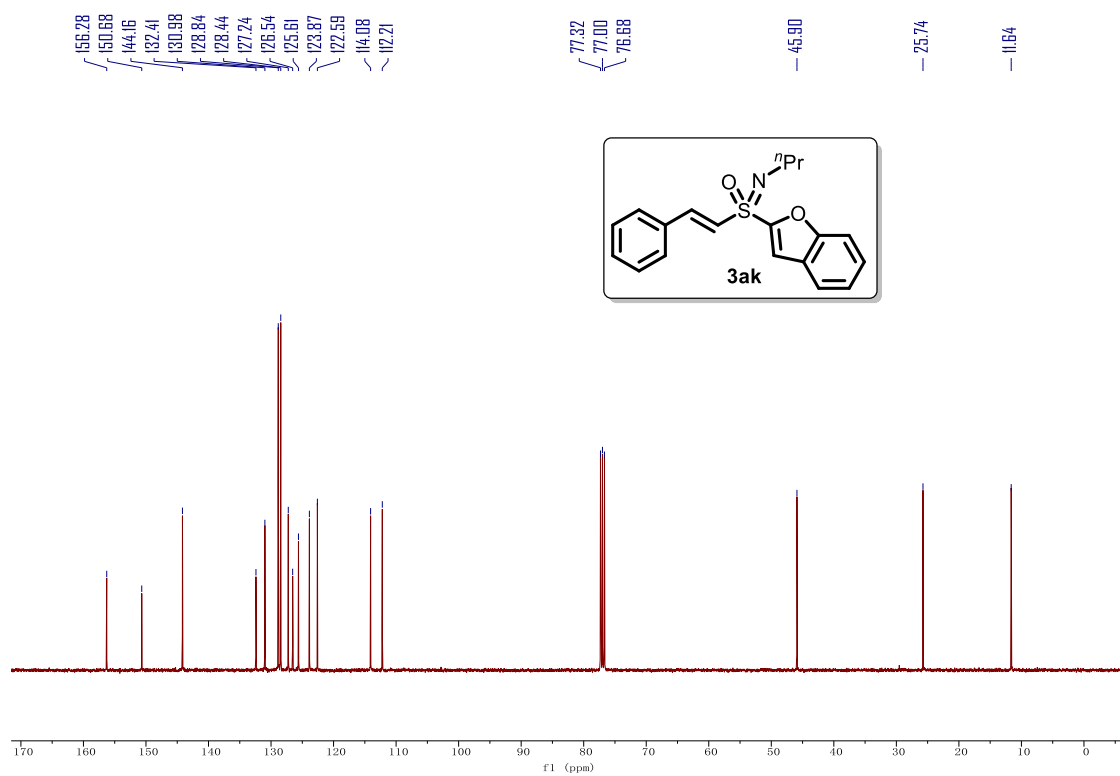
**Supplementary Figure 78.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3aj**.



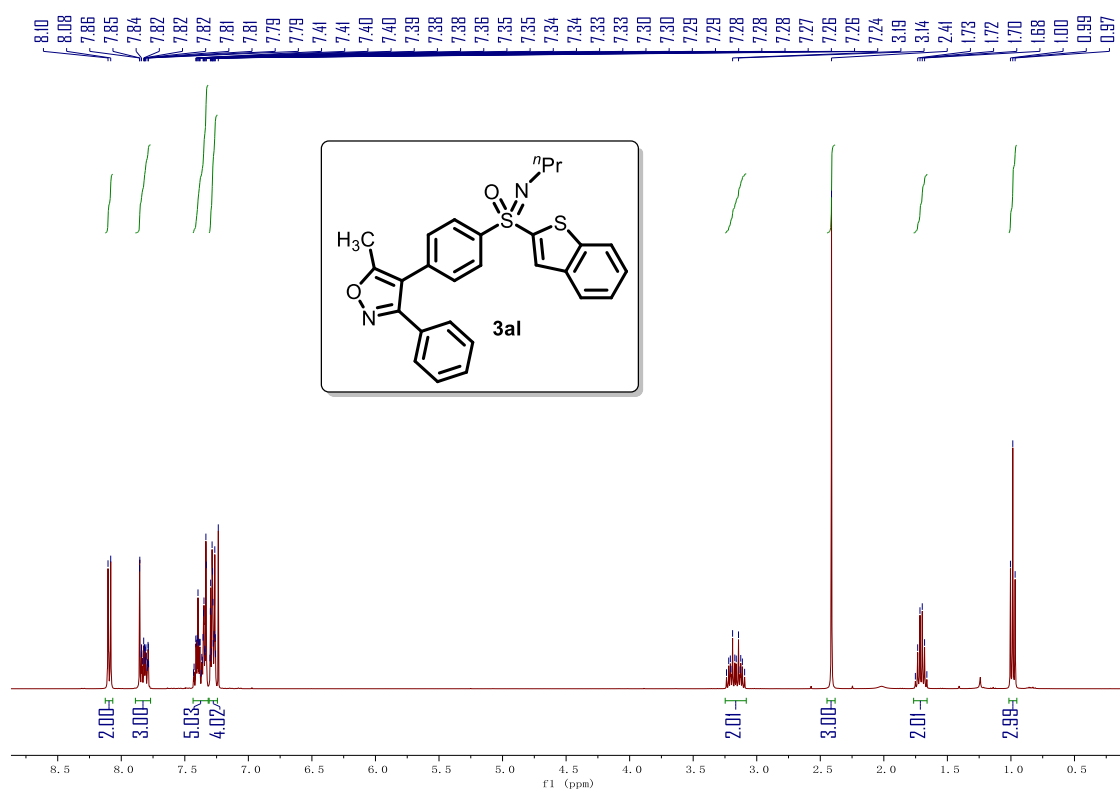
**Supplementary Figure 79.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3aj**.



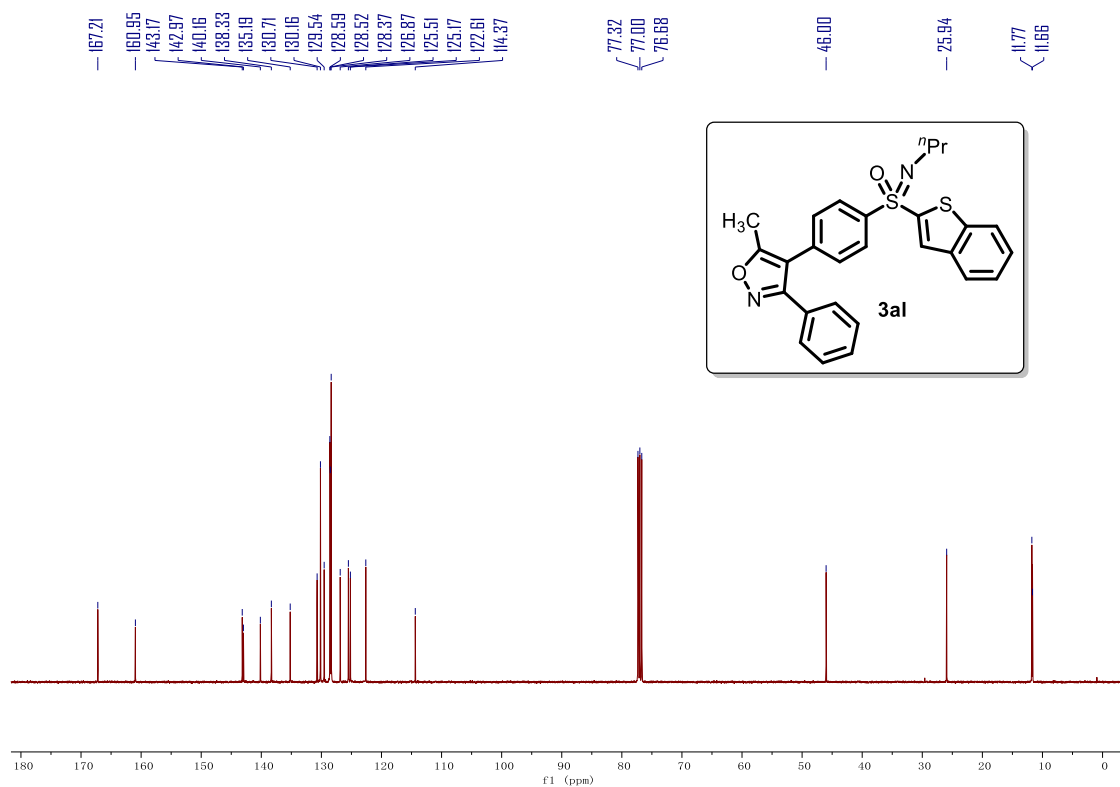
**Supplementary Figure 80.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3ak**.



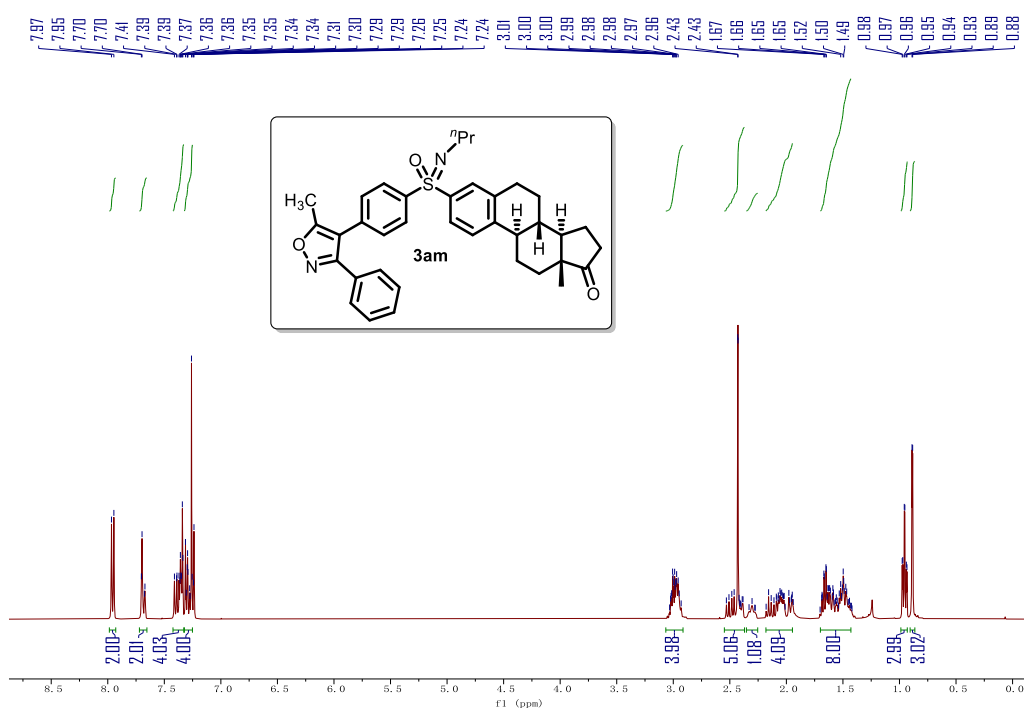
**Supplementary Figure 81.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3ak**.



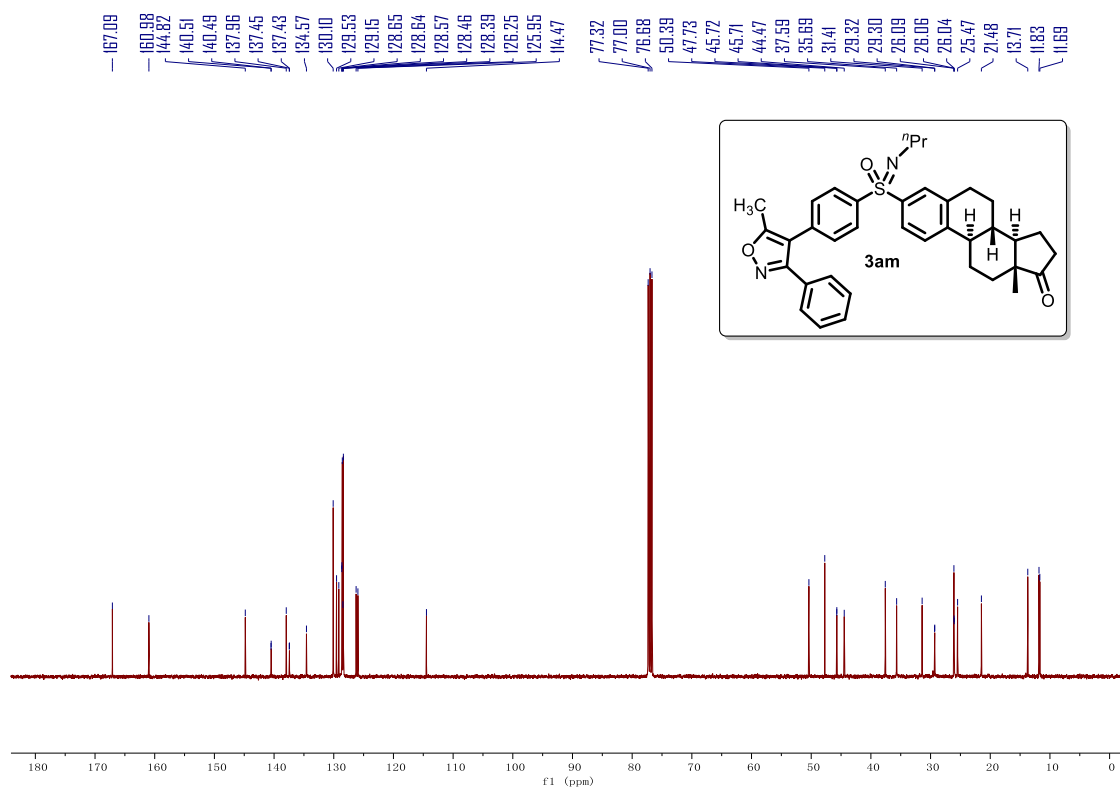
**Supplementary Figure 82.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3al**.



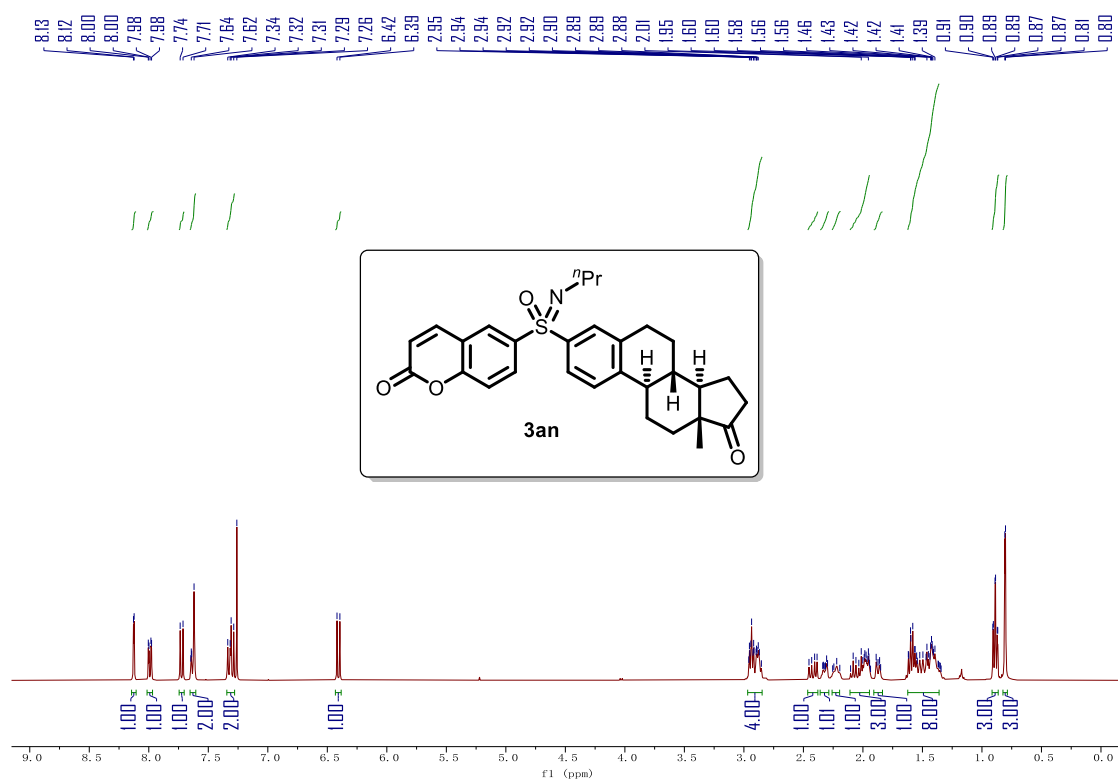
**Supplementary Figure 83.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3al**.



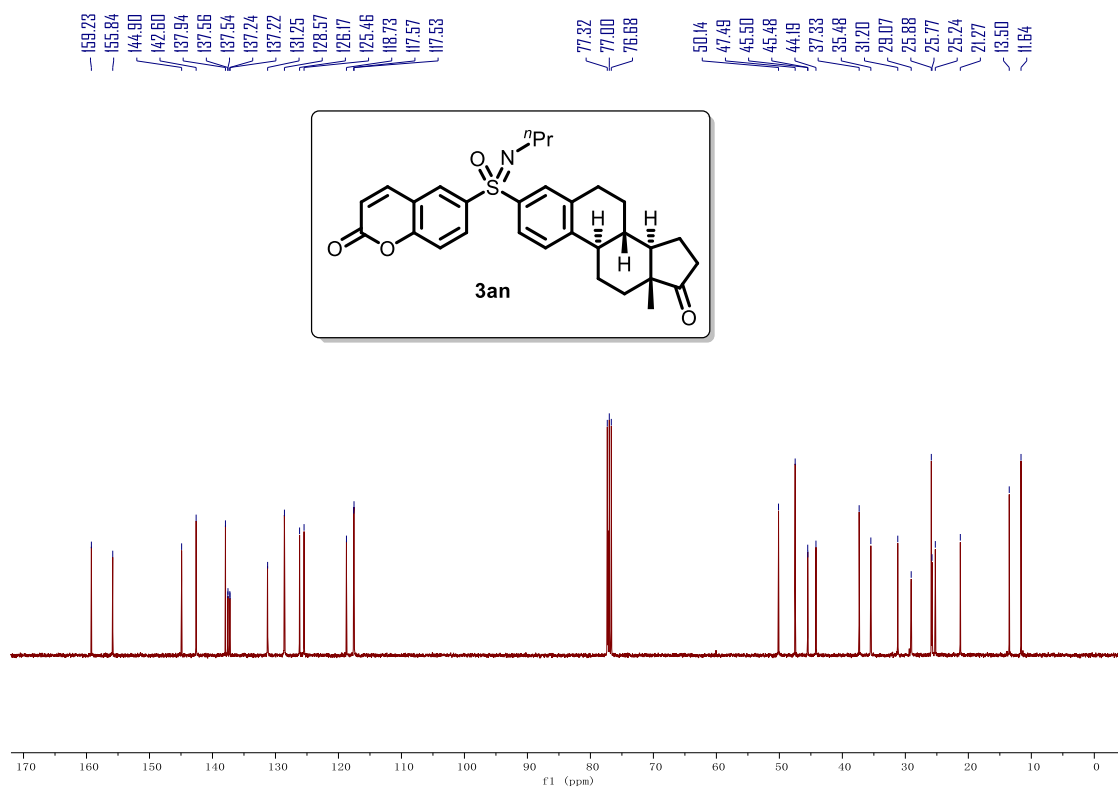
**Supplementary Figure 84.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3am**.



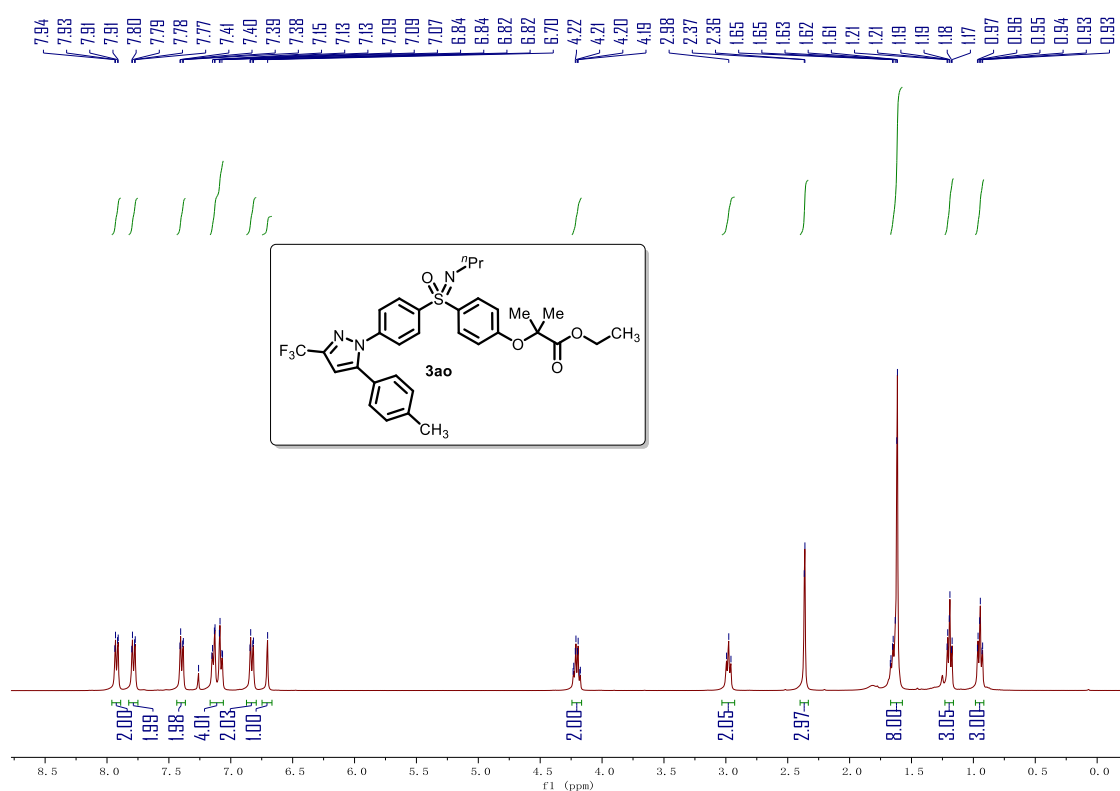
**Supplementary Figure 85.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3am**.



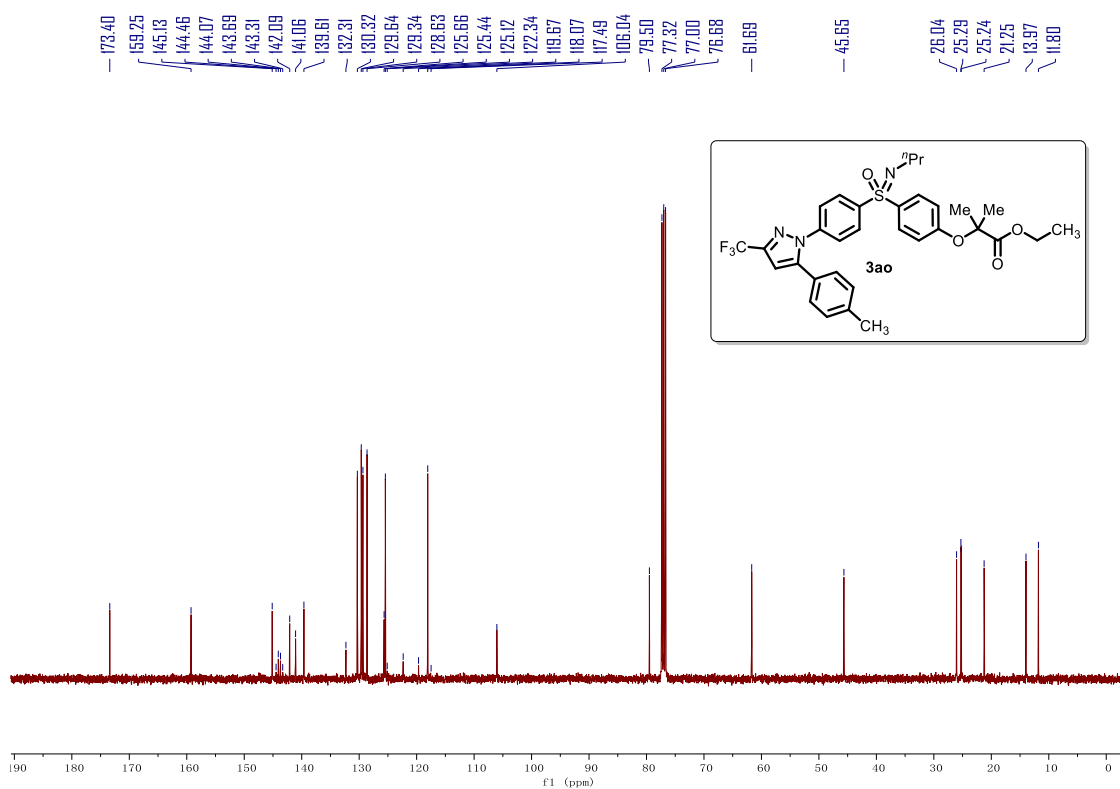
**Supplementary Figure 86.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3an**.



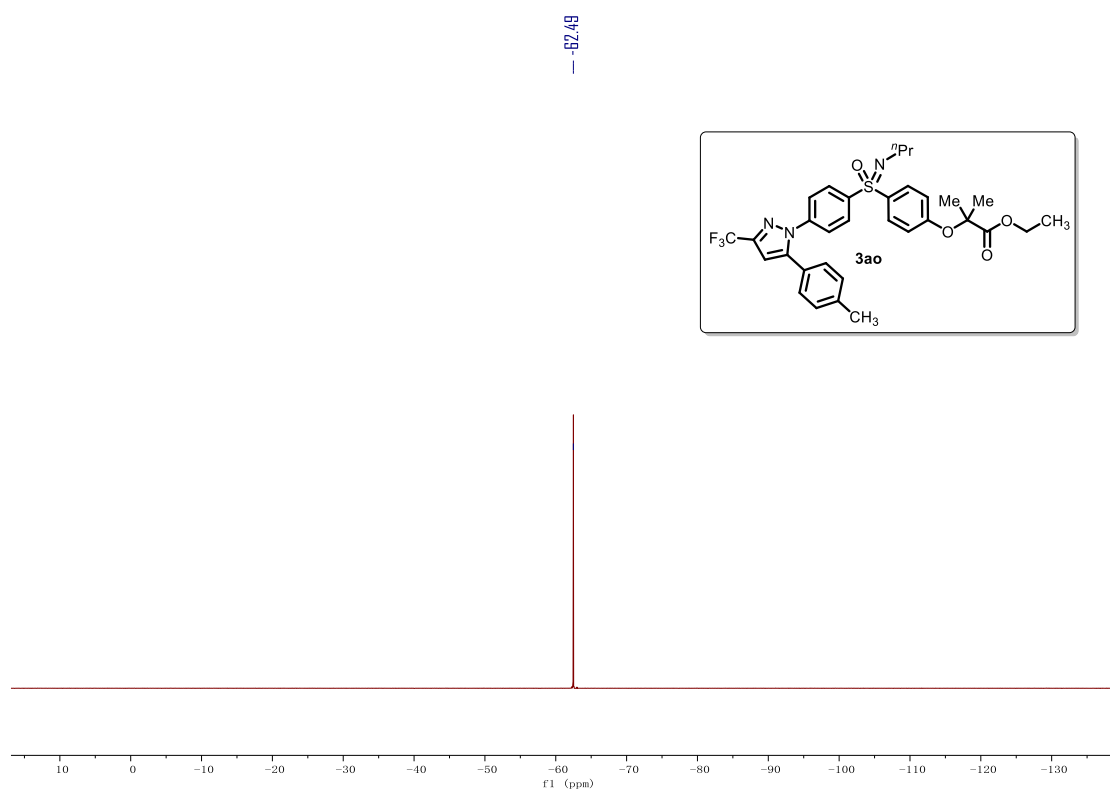
**Supplementary Figure 87.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3an**.



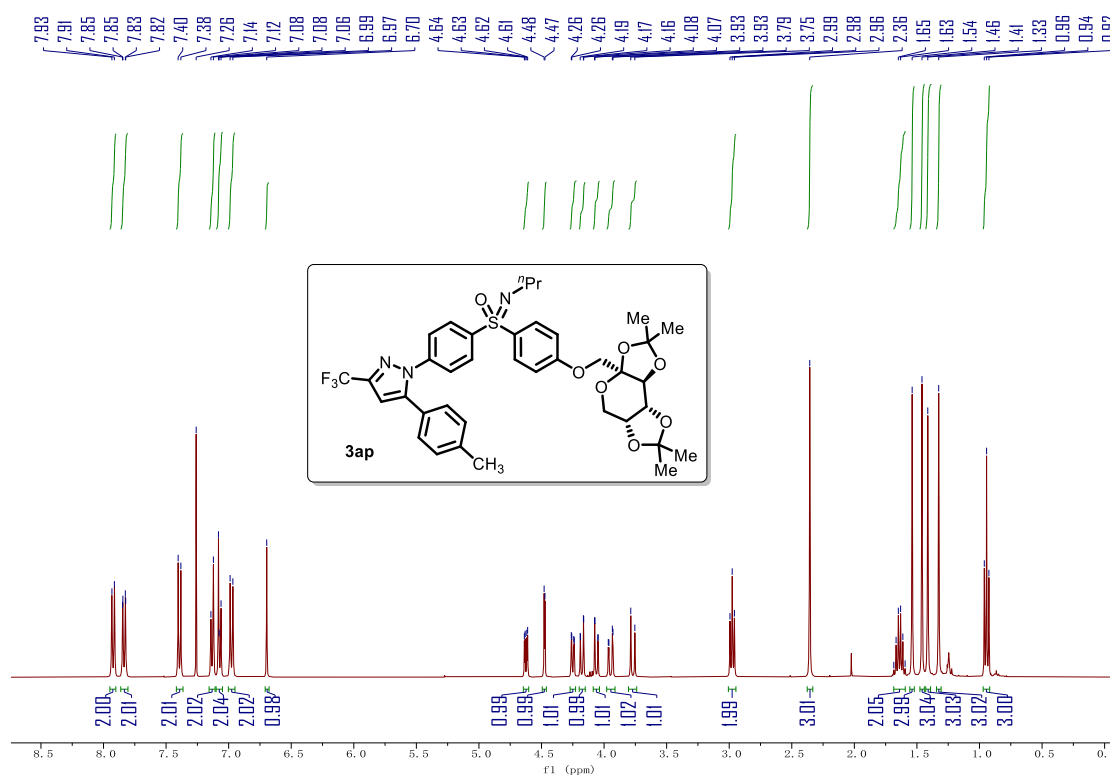
**Supplementary Figure 88.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3ao**.



**Supplementary Figure 89.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3ao**.

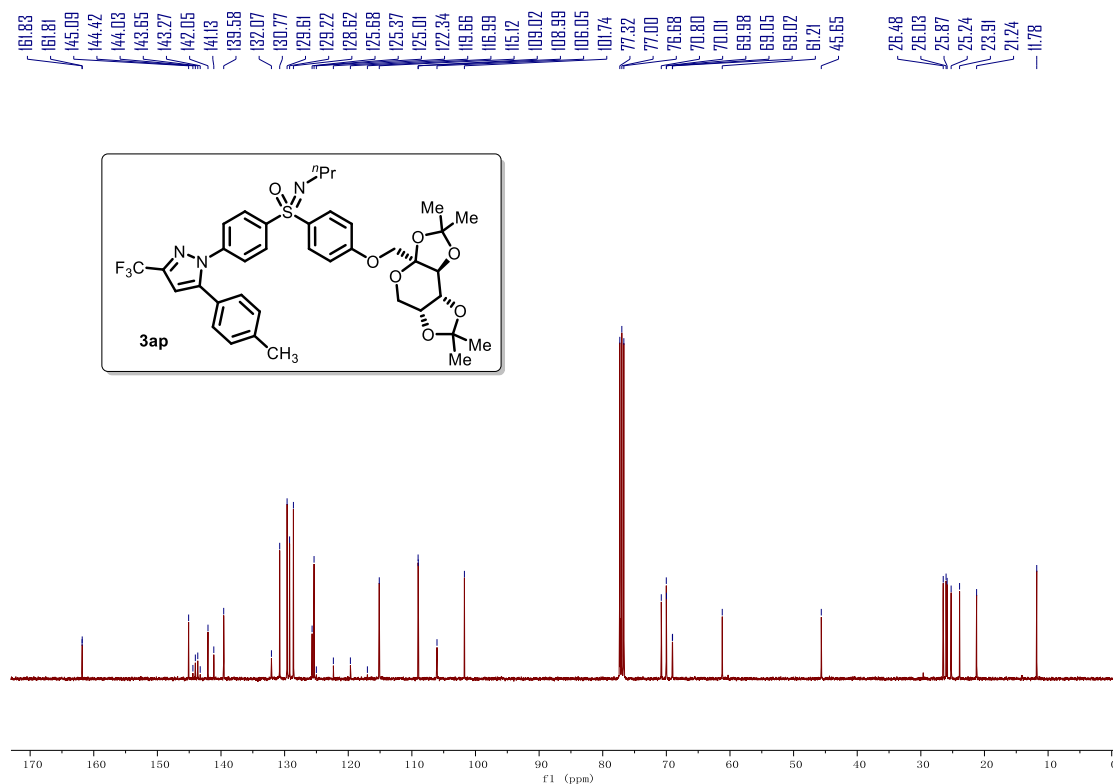


**Supplementary Figure 90.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) spectra of compound **3ao**.

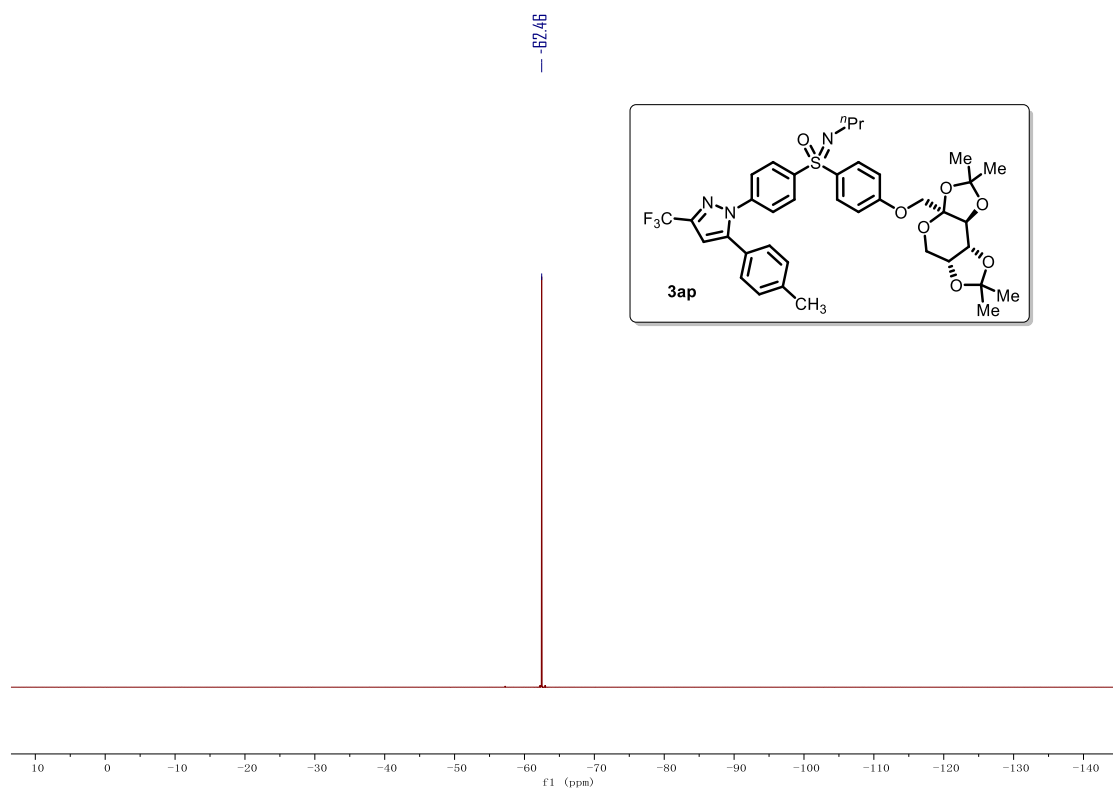


**Supplementary Figure 91.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectra of compound **3ap**.

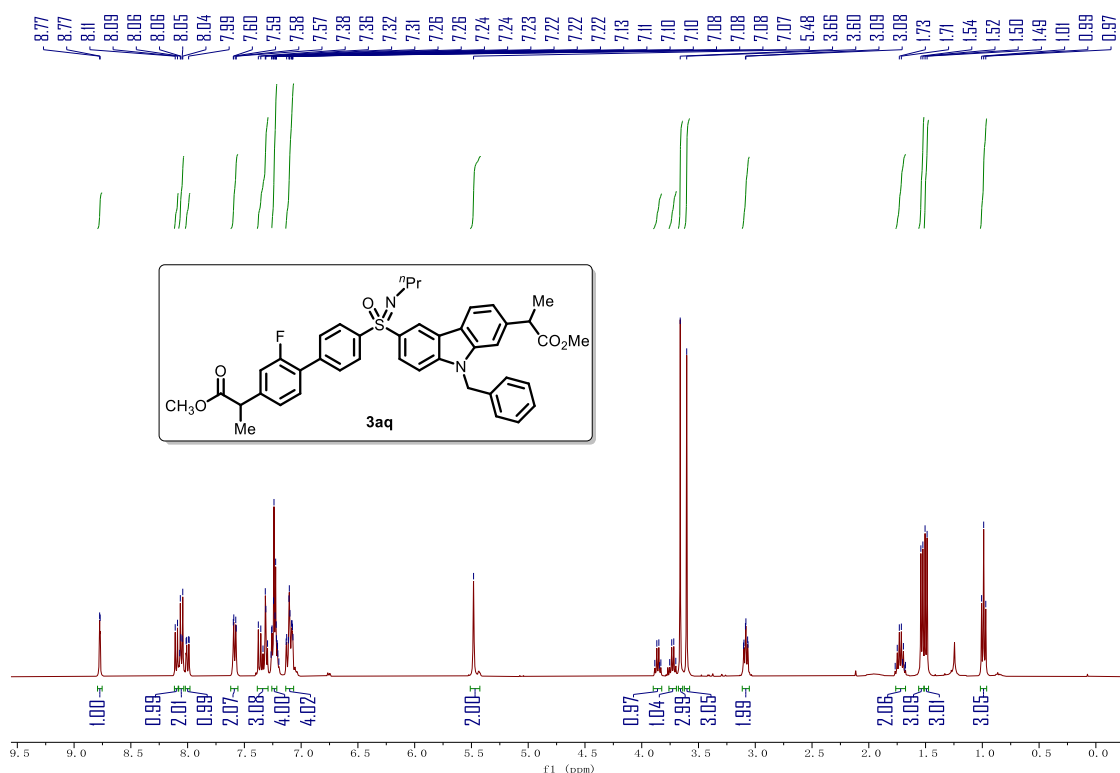




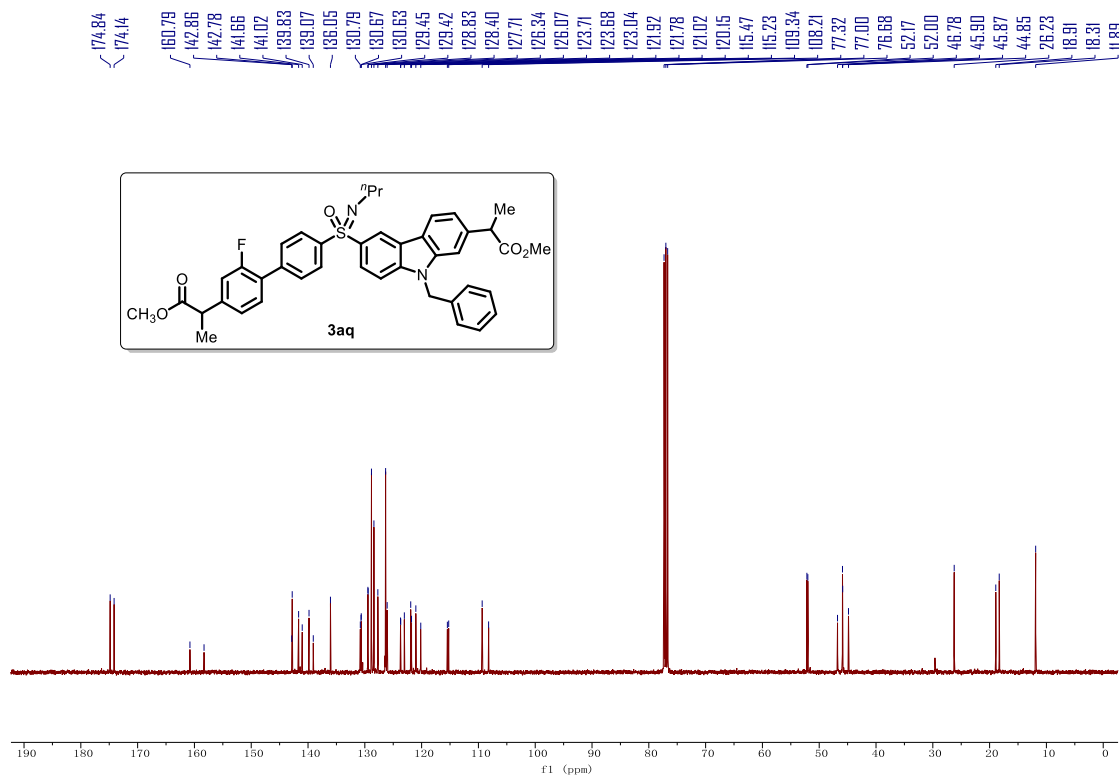
**Supplementary Figure 92.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3ap**.



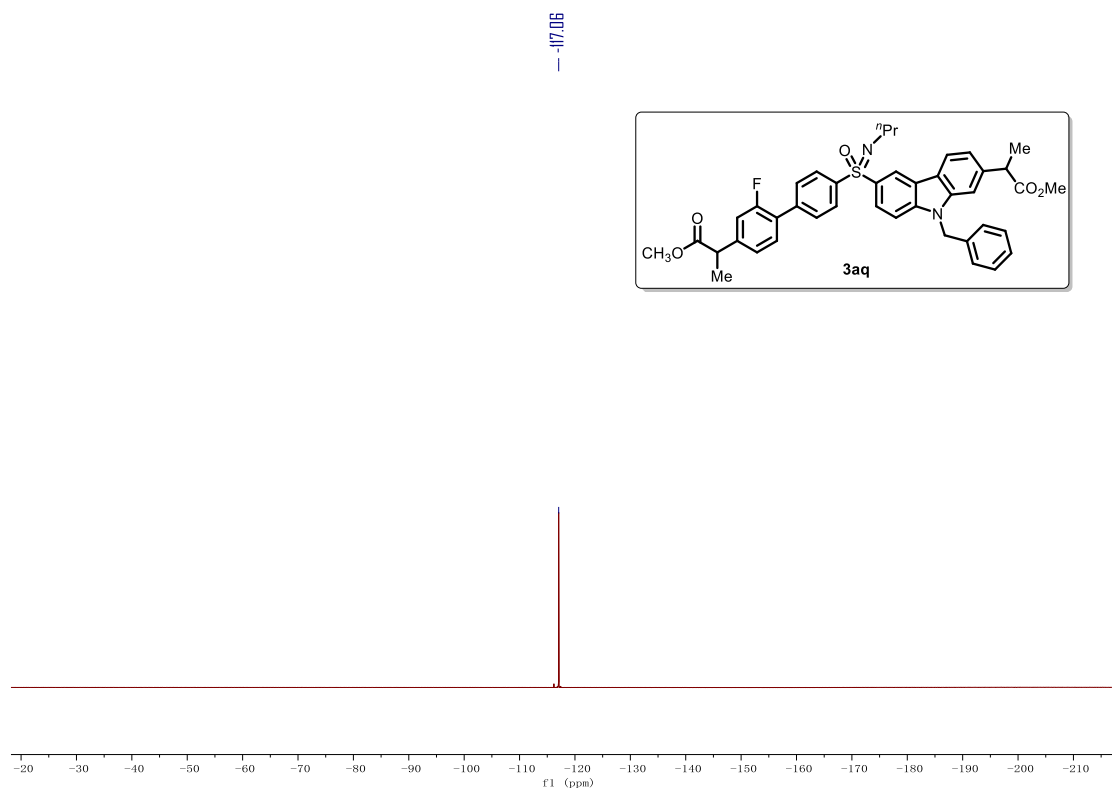
**Supplementary Figure 93.** <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) spectra of compound **3ap**.



**Supplementary Figure 94.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3aq**.



**Supplementary Figure 95.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectra of compound **3aq**.



**Supplementary Figure 96.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) spectra of compound **3aq**.