

## Supporting Information

### Iminyl radical-triggered relay annulation for the construction of bridged aza-tetracycles bearing four contiguous stereogenic centers

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## Materials and Methods

### 1. Materials and Methods

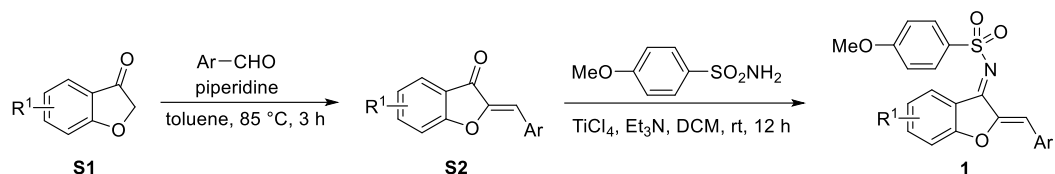
**General.** All reactions dealing with air- and moisture-sensitive compounds were carried out in dry reaction vessels under N<sub>2</sub> atmosphere. <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were recorded on Bruker 600 MHz NMR spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra are reported in parts per million (ppm) downfield from an internal standard, tetramethylsilane (0 ppm) and CHCl<sub>3</sub> (77.0 ppm), respectively. HRMS (m/z) was recorded using ESI (Q-TOF) mode. Single crystal X-ray data were recorded in a diffractometer with Mo K $\alpha$  radiation. Melting points were determined using a capillary melting point apparatus and are uncorrected.

**Materials.** Unless otherwise noted, materials were purchased from commercial suppliers and were used as received. Anhydrous acetonitrile was distilled over CaH<sub>2</sub> and stored under N<sub>2</sub>.

## 2. Preparation of Substrates

Azadienes<sup>1</sup> and peresters<sup>2</sup> were synthesized according to the literature procedures. The characterization data of newly synthesized azadienes (**1b-m**) and peresters (**4a-4f**, **4h-4o**) were summarized below. <sup>1</sup>H and <sup>13</sup>C NMR spectra data for the rest of known ones showed good agreement with the literature data.<sup>1,2</sup>

### General Procedure for the Synthesis of Azadienes

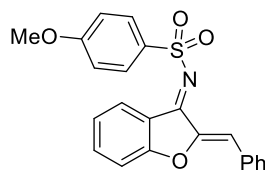


#### Step 1:

To a solution of benzofuran-3(2H)-one **S1** (10 mmol, 1 equiv) and aldehyde (12 mmol, 1.2 equiv) in toluene was added piperidine (6-8 drops) at 85 °C. The reaction mixture was stirred at 85 °C for 3 hours. Then toluene was removed by concentration, and the reaction was quenched with an aqueous solution of saturated NH<sub>4</sub>Cl. The aqueous layer was extracted with ethyl acetate. The combined organic layer was washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. The crude product was purified by flash chromatography to give the compounds **S2**.

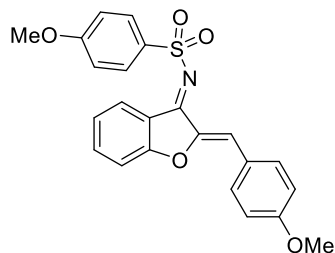
#### Step 2:

To a solution of compounds **S2** (10 mmol, 1 equiv), 4-methoxybenzenesulfonamide (12 mmol, 1.2 equiv), and Et<sub>3</sub>N (20 mmol, 2 equiv) in DCM (40 mL) was slowly added TiCl<sub>4</sub> (10 mmol, 1 equiv) at 0 °C. Then, the mixture was stirred at room temperature for 12 h. The reaction was quenched with water and extracted with DCM. The combined organic layers were washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. The crude product was purified by flash chromatography to give the azadienes **1**.

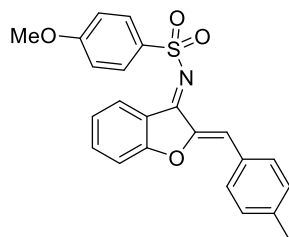


#### *N*-((*E*)-2-((*Z*)-benzylidene)benzofuran-3(2H)-ylidene)-4-methoxybenzenesulfonamide (**1b**):

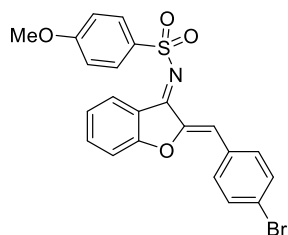
This compound was prepared according to the general procedure. Yellow solid (2.5 g, 60% yield, eluent = petroleum ether/EtOAc (10:1)); Mp = 140-142 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.78 (d, *J* = 7.8 Hz, 1H), 8.04 (d, *J* = 9.0 Hz, 2H), 7.87 (d, *J* = 7.2 Hz, 2H), 7.67 (t, *J* = 7.8 Hz, 1H), 7.44-7.37 (m, 3H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.29-7.25 (m, 1H), 7.10 (s, 1H), 7.04 (d, *J* = 9.0 Hz, 2H), 3.90 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 164.9, 164.8, 163.0, 149.7, 137.5, 133.8, 132.5, 131.7, 131.1, 130.2, 129.2, 128.9, 123.8, 118.4, 115.5, 114.0, 112.3, 55.6; HRMS (ESI): Calcd for C<sub>22</sub>H<sub>17</sub>NO<sub>4</sub>S [M+H]<sup>+</sup> 392.0951, found 392.0951.



**4-methoxy-N-((E)-2-((Z)-4-methoxybenzylidene)benzofuran-3(2H)-ylidene)benzenesulfonamide (1c):** This compound was prepared according to the general procedure. Yellow solid (2.2 g, 52% yield, eluent = petroleum ether/EtOAc (5:1)); Mp = 149-151 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.77 (d, *J* = 7.8 Hz, 1H), 8.04 (d, *J* = 8.8 Hz, 2H), 7.86 (d, *J* = 8.7 Hz, 2H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 8.3 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.11 (s, 1H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 3.89 (s, 3H), 3.85 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 164.7, 164.5, 162.8, 161.5, 148.4, 137.1, 134.1, 133.8, 130.9, 129.1, 125.3, 123.6, 118.7, 116.4, 114.6, 114.0, 112.2, 55.6, 55.4; HRMS (ESI): Calcd for C<sub>23</sub>H<sub>19</sub>NO<sub>5</sub>S [M+H]<sup>+</sup> 422.1056, found 422.1057.

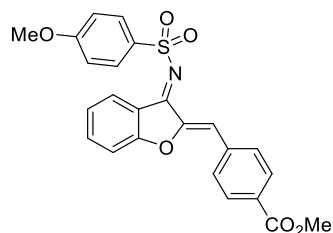


**4-methoxy-N-((E)-2-((Z)-4-methylbenzylidene)benzofuran-3(2H)-ylidene)benzenesulfonamide (1d):** This compound was prepared according to the general procedure. Yellow solid (2.92 g, 72% yield, eluent = petroleum ether/EtOAc (10:1)); Mp = 130-132 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.77 (d, *J* = 7.7 Hz, 1H), 8.06 – 8.02 (m, 2H), 7.78 (d, *J* = 7.9 Hz, 2H), 7.68-7.63 (m, 1H), 7.31 (d, *J* = 8.3 Hz, 1H), 7.28 – 7.21 (m, 3H), 7.10 (s, 1H), 7.05-7.02 (m, 2H), 3.89 (s, 3H), 2.38 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 164.6, 164.7, 162.9, 149.2, 141.0, 137.3, 134.0, 131.7, 131.0, 129.8, 129.1, 123.7, 118.5, 116.0, 114.0, 112.3, 55.6, 21.6; HRMS (ESI): Calcd for C<sub>23</sub>H<sub>19</sub>NO<sub>4</sub>S [M+H]<sup>+</sup> 406.1107, found 406.1108.



**N-((E)-2-((Z)-4-bromobenzylidene)benzofuran-3(2H)-ylidene)-4-methoxybenzenesulfonamide (1e):** This compound was prepared according to the general procedure. Yellow solid (3.15 g, 62% yield, eluent = petroleum ether/EtOAc (10:1)); Mp = 151-152 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.77 (d, *J* = 7.1 Hz, 1H), 8.03 (d, *J* = 8.7 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.68 (t, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.32-7.27 (m, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 7.00 (s, 1H), 3.90 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 164.6, 163.0, 150.0, 137.6, 133.6, 132.8,

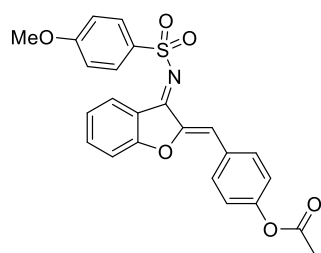
132.2, 131.3, 131.2, 129.2, 124.7, 123.9, 118.2, 114.1, 112.3, 55.6; **HRMS** (ESI): Calcd for  $C_{22}H_{16}BrNO_4S$   $[M+H]^+$  470.0054, found 470.0056.



#### methyl

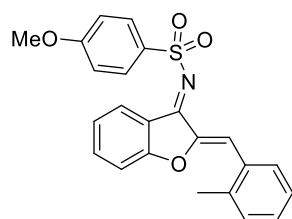
#### -(((2Z,3E)-3-(((4-methoxyphenyl)sulfonyl)imino)benzofuran-2(3H)-ylidene)methyl)benzoate

**(1f)**: This compound was prepared according to the general procedure. Yellow solid (3.29 g, 73% yield); eluent = petroleum ether/EtOAc (10:1); Mp = 165-166 °C; **<sup>1</sup>H NMR** (600 MHz,  $CDCl_3$ ):  $\delta$  8.78 (d,  $J$  = 7.1 Hz, 1H), 8.07 (d,  $J$  = 8.4 Hz, 2H), 8.04 (d,  $J$  = 8.9 Hz, 2H), 7.92 (d,  $J$  = 8.3 Hz, 2H), 7.69 (m, 1H), 7.33 (d,  $J$  = 8.4 Hz, 1H), 7.30 (t,  $J$  = 7.8 Hz, 1H), 7.05 (d,  $J$  = 8.9 Hz, 3H), 3.93 (s, 3H), 3.91 (s, 3H); **<sup>13</sup>C NMR** (151 MHz,  $CDCl_3$ ):  $\delta$  166.4, 164.8, 164.7, 163.1, 150.9, 137.8, 136.6, 136.5, 133.5, 131.2, 130.8, 130.0, 129.2, 124.1, 114.1, 112.3, 55.6, 52.3; **HRMS** (ESI): Calcd for  $C_{24}H_{20}NO_6S$   $[M+H]^+$  450.1007, found 450.1006.



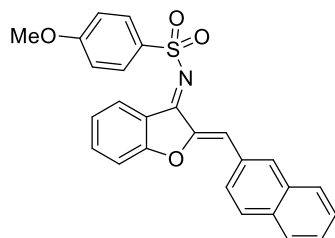
#### 4-(((2Z,3E)-3-(((4-methoxyphenyl)sulfonyl)imino)benzofuran-2(3H)-ylidene)methyl)phenyl

**acetate (1g)**: This compound was prepared according to the general procedure. Yellow solid (2.3 g, 52% yield); eluent = petroleum ether/EtOAc (10:1); Mp = 145-146 °C; **<sup>1</sup>H NMR** (600 MHz,  $CDCl_3$ ):  $\delta$  8.78 (d,  $J$  = 7.7 Hz, 1H), 8.04 (d,  $J$  = 8.8 Hz, 2H), 7.90 (d,  $J$  = 8.6 Hz, 2H), 7.67 (t,  $J$  = 7.4 Hz, 1H), 7.33 – 7.26 (m, 2H), 7.18 (d,  $J$  = 8.6 Hz, 2H), 7.10 – 7.02 (m, 3H), 3.90 (s, 3H), 2.31 (s, 3H); **<sup>13</sup>C NMR** (151 MHz,  $CDCl_3$ ):  $\delta$  168.9, 164.8, 164.7, 163.0, 151.9, 137.5, 133.7, 132.8, 131.2, 130.1, 129.2, 123.8, 122.1, 114.1, 112.3, 55.6, 21.1; **HRMS** (ESI): Calcd for  $C_{24}H_{19}NO_6S$   $[M + Na]^+$  472.0825, found 472.0827.

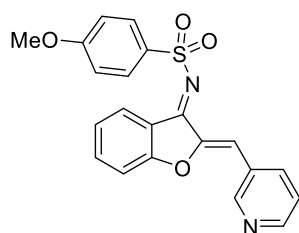


**4-methoxy-N-((E)-2-((Z)-2-methylbenzylidene)benzofuran-3(2H)-ylidene)benzenesulfonamide (1h)**: This compound was prepared according to the general procedure. Yellow solid (3.04 g, 75% yield); eluent = petroleum ether/EtOAc (10:1); Mp = 152-153 °C; **<sup>1</sup>H NMR** (600 MHz,  $CDCl_3$ )  $\delta$

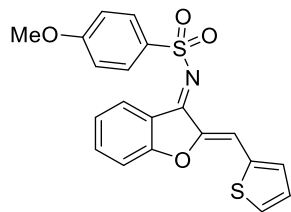
8.76 (s, 1H), 8.21 (d,  $J = 7.4$  Hz, 1H), 8.04 (d,  $J = 8.8$  Hz, 2H), 7.66 (t,  $J = 7.7$  Hz, 1H), 7.40 (s, 1H), 7.33 – 7.19 (m, 5H), 7.03 (d,  $J = 8.8$  Hz, 2H), 3.89 (s, 3H), 2.42 (s, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.9, 164.8, 162.9, 149.6, 139.2, 137.5, 133.9, 131.3 131.0, 130.7, 130.1, 129.1 126.5, 123.7, 114.0, 112.3, 55.6 20.2; **HRMS (ESI)**: Calcd for  $\text{C}_{23}\text{H}_{19}\text{NO}_4\text{S}$   $[\text{M}+\text{H}]^+$  406.1107, found 406.1109.



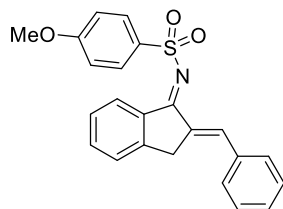
**4-methoxy-*N*-((2*Z*,3*E*)-2-(naphthalen-2-ylmethylene)benzofuran-3(2*H*)-ylidene)benzenesulfonamide (1i)**: This compound was prepared according to the general procedure. Yellow solid (3.44 g, 78 % yield; eluent = petroleum ether/EtOAc (10:1)); Mp = 158-160 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.79 (d,  $J = 7.8$  Hz, 1H), 8.25 (s, 1H), 8.06 (d,  $J = 8.4$  Hz, 2H), 8.04 (m, 1H) 7.85 (t,  $J = 7.7$  Hz, 2H), 7.81 (d,  $J = 7.7$  Hz, 1H), 7.67 (t,  $J = 7.8$  Hz, 1H), 7.54 – 7.47 (m, 2H), 7.35 (d,  $J = 8.3$  Hz, 1H), 7.28 (t,  $J = 7.6$  Hz, 1H), 7.24 (d,  $J = 7.2$  Hz 1H), 7.05 (d,  $J = 8.8$  Hz, 2H), 3.90 (s, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.8, 164.7, 162.6, 149.9, 137.4, 133.9, 133.8, 133.3, 132.7 131.1 130.1 129.2, 128.8, 128.6, 127.7, 126.7, 123.8, 118.5, 115.8, 114., 112.3, 55.6; **HRMS (ESI)**: Calcd for  $\text{C}_{26}\text{H}_{20}\text{NO}_4\text{S}$   $[\text{M}+\text{H}]^+$  442.1106, found 442.1108.



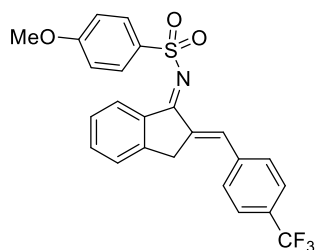
**4-methoxy-*N*-((2*Z*,3*E*)-2-(pyridin-3-ylmethylene)benzofuran-3(2*H*)-ylidene)benzenesulfonamide (1j)**: This compound was prepared according to the general procedure. Yellow solid (2.95 g, 75% yield; eluent = petroleum ether/EtOAc (3:1)); Mp = 178-180 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.98 (s, 1H), 8.79 (s, 1H), 8.59 (d,  $J = 3.5$  Hz, 1H), 8.30 (d,  $J = 7.9$  Hz, 1H), 8.04 (d,  $J = 8.7$  Hz, 2H), 7.71 (t,  $J = 7.7$  Hz, 1H), 7.39 (dd,  $J = 7.7, 4.9$  Hz, 1H), 7.33 - 7.3. (m, 2H), 7.05 (m, 3H), 3.91 (s, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.3, 163.1, 152.0, 149.9, 137.9, 137.8, 133.4, 131.3, 129.3, 128.8, 124.1, 123.9, 114.1, 112.3, 55.65; **HRMS (ESI)**: Calcd for  $\text{C}_{21}\text{H}_{17}\text{N}_2\text{O}_4\text{S}$   $[\text{M}+\text{H}]^+$  393.0903, found 393.0904.



**4-methoxy-N-((2Z,3E)-2-(thiophen-2-ylmethylene)benzofuran-3(2H)-ylidene)benzenesulfonamide (1k):** This compound was prepared according to the general procedure. Yellow solid (2.8 g, 67 % yield; eluent = petroleum ether/EtOAc (10:1)); Mp = 153-154 °C;  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.74 (s, 1H), 8.04 (d,  $J = 8.6$  Hz, 2H), 7.67 (t,  $J = 7.7$  Hz, 1H), 7.62 (d,  $J = 4.8$  Hz, 1H), 7.52 (d,  $J = 3.6$  Hz, 1H), 7.41 (s, 1H), 7.33 (d,  $J = 8.3$  Hz, 1H), 7.29-7.26 (m, 1H), 7.14 (t,  $J = 4.2$  Hz, 1H), 7.04 (d,  $J = 8.6$  Hz, 2H), 3.90 (s, 3H);  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.3, 163.9, 162.9, 149.2, 145.8, 137.2, 133.9, 130.8, 129.1, 123.8, 118.2, 114.0, 113.5, 112.2, 55.6; **HRMS (ESI):** Calcd for  $\text{C}_{24}\text{H}_{20}\text{NO}_6\text{S}$   $[\text{M}+\text{Na}]^+$  420.0337, found 420.0335.

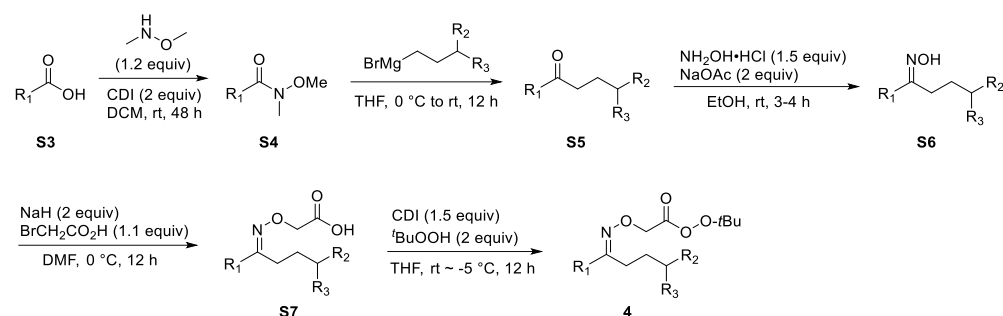


**N-((E)-2-((E)-benzylidene)-2,3-dihydro-1H-inden-1-ylidene)-4-methoxybenzenesulfonamide (1l):** This compound was prepared according to the general procedure. White solid; (65% yield, eluent = pentane/ethyl acetate = 15:1); Mp = 149 – 150 °C;  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.89 (s, 1H), 8.07 (d,  $J = 8.6$  Hz, 2H), 7.84 (s, 1H), 7.65 – 7.58 (m, 3H), 7.55 – 7.36 (m, 5H), 7.04 (d,  $J = 8.6$  Hz, 2H), 4.05 (s, 2H), 3.90 (s, 3H);  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  175.4, 162.6, 150.4, 136.4, 135.4, 135.0, 134.9, 130.8, 129.8, 128.9, 128.9, 127.9, 125.6, 113.9, 55.6, 34.3; **HRMS (ESI):** Calcd for  $\text{C}_{23}\text{H}_{19}\text{NO}_3\text{S}$   $[\text{M} + \text{Na}]^+$  412.0978, found 412.0978.



**4-methoxy-N-((E)-2-((E)-4-(trifluoromethyl)benzylidene)-2,3-dihydro-1H-inden-1-ylidene)benzenesulfonamide (1m):** This compound was prepared according to the general procedure. White solid; (60% yield, eluent = pentane/ethyl acetate = 15:1); Mp = 154-155 °C;  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.93 (s, 1H), 8.09 (d,  $J = 8.7$  Hz, 2H), 7.84 (s, 1H), 7.73 – 7.69 (m, 4H), 7.67 (t,  $J = 7.4$  Hz, 1H), 7.59 – 7.51 (m, 2H), 7.08 (d,  $J = 8.7$  Hz, 2H), 4.08 (s, 2H), 3.94 (s, 3H);  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  174.8, 162.8, 150.0, 138.8, 135.3, 134.6, 129.8 (q,  $^1J_{\text{C-F}} = 245.9$  Hz), 128.7, 128.2, 125.7 (q,  $^3J_{\text{C-F}} = 3.7$  Hz), 125.6, 114.3, 114.0, 55.6, 34.1;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -62.81; **HRMS (ESI):** Calcd for  $\text{C}_{24}\text{H}_{18}\text{F}_3\text{NO}_3\text{S}$   $[\text{M} + \text{Na}]^+$  480.0852, found 480.0849.

## General Procedure for the Synthesis of Oxime-derived Peresters



### Step 1:

To a solution of benzoic acids **S3** (10 mmol, 1 equiv) in DCM was slowly added CDI (15 mmol, 1.5 equiv). The reaction mixture was stirred at rt for 1 h. Then, *N,O*-dimethylhydroxylamine hydrochloride (12 mmol, 1.2 equiv) was slowly added and the mixture was stirred at rt for 48 h. The reaction was quenched with an aqueous solution of saturated NaHCO<sub>3</sub>. The aqueous layers were extracted with ethyl acetate. The combined organic layers were washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. Then the mixture was filtered, concentrated to give the crude Weinreb amides **S4**, which were used in the next step without further purification.

### Step 2:

To a 100 mL three-necked flask was charged with the crude Weinreb amide (10 mmol), the flask was evacuated and backfilled with N<sub>2</sub> (3 times). Dry THF (20 mL, 0.5 M) was added, then the solution was cooled to 0 °C. Subsequently, Grignard reagent (12 mmol, 1.2 equiv) was added dropwise. The reaction was warmed to rt and stirred for 12 h. The reaction was quenched with an aqueous solution of saturated NH<sub>4</sub>Cl. The aqueous layers were extracted with ethyl acetate. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>. Then the solution was filtered, concentrated to give the crude ketones, which were purified by flash chromatography to give the pure ketones **S5**.

### Step 3:

A mixture of ketones (5 mmol), hydroxylamine hydrochloride (10 mmol, 1.5 equiv), and NaOAc (20 mmol, 2 equiv) was dissolved in EtOH/H<sub>2</sub>O (50 mL/50 mL). The mixture was stirred at rt for 3-4 h. Then EtOH was removed by concentration, and the residue was diluted with 1N HCl and ethyl acetate. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with saturated NaHCO<sub>3</sub> solution and brine, and then dried over Na<sub>2</sub>SO<sub>4</sub>. The combined organic solution was concentrated by rotary evaporation to give the crude compounds **S6**, which were used in the next step without further purification.

### Step 4:

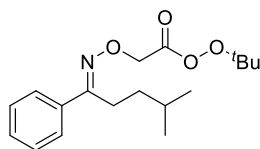
**S6** (10 mmol, 1.0 equiv) was dissolved in dry DMF (50 mL, 0.2 M), then the solution was cooled to 0 °C, and NaH (20 mmol, 2 equiv) was added slowly. The mixture was stirred at 0 °C for 1 h. Subsequently,  $\alpha$ -bromo acid (11 mmol, 1.1 equiv) was added and the mixture was stirred at 0 °C for 10 h. The mixture was diluted with H<sub>2</sub>O and ethyl acetate, the layers were separated and the aqueous layer was treated with 1N HCl. Then the aqueous layer was washed with ethyl acetate, the combined organic extractions were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated. The crude product was purified by flash chromatography to give the imino-oxyacetic acids **S7**.

### Step 5:

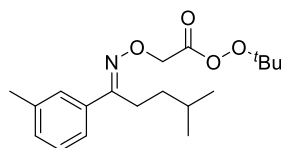
The iminoxyacetic acids **S7** (10 mmol, 1.0 equiv) was added to a stirred solution of CDI (12 mmol, 1.2 equiv) in THF at rt. After 1 h, a solution of *tert*-butyl hydroperoxide (22 mmol, 2.2 equiv) was



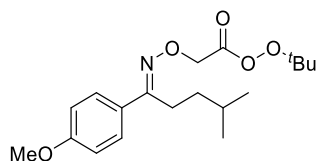
added dropwise at -5 °C, and the mixture was stirred at -5 °C for 12 h. The mixture was poured into ice-water and extracted with cold diethyl ether. The organic phase was washed twice with cold water and the combined organic extractions were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was removed under reduced pressure ensuring the bath temperature does not exceed 30 °C. The crude product was purified by flash chromatography to give the peresters **4**.



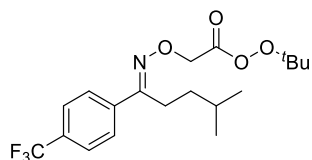
**(E)-tert-butyl-2-(((4-methyl-1-phenylpentylidene)amino)oxy)ethaneperoxoate (4a):** This compound was prepared according to the general procedure. Colorless oil (65% yield; eluent = petroleum ether/EtOAc (50:1)); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.62-7.59 (m, 2H), 7.36-7.33 (m, 3H), 4.80 (s, 2H), 2.81-2.76 (m, 2H), 1.67-1.59 (m, 1H), 1.49-1.44 (m, 2H), 1.31 (s, 9H), 0.93 (d, *J* = 6.7 Hz, 6H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 167.8, 161.1, 135.1, 129.4, 128.4, 126.4, 84.0, 69.8, 35.3, 28.4, 26.1, 25.1, 22.3; **HRMS (ESI):** Calcd for C<sub>18</sub>H<sub>28</sub>NO<sub>4</sub> [M+H]<sup>+</sup> 322.2014, found 322.2013.



**tert-butyl (E)-2-(((4-methyl-1-(m-tolyl)pentylidene)amino)oxy)ethaneperoxoate (4b):** This compound was prepared according to the general procedure. Colorless oil (53% yield; eluent = petroleum ether/EtOAc (50:1)); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.43 (s, 1H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.26-7.23 (m, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 4.79 (s, 2H), 2.83 – 2.72 (m, 2H), 2.36 (s, 3H), 1.65 - 1.61 (m, 1H), 1.50 - 1.35 (m, 2H), 1.32 (s, 9H), 0.93 (d, *J* = 6.6 Hz, 6H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 167.8, 161.3, 138.1, 135.1, 130.2, 128.3, 127.1, 123.6, 84.0, 69.7, 35.3, 28.4, 26.1, 25.2, 22.3, 21.4; **HRMS (ESI):** Calcd for C<sub>19</sub>H<sub>30</sub>NO<sub>4</sub> [M+H]<sup>+</sup> 336.2169, found 336.2169.



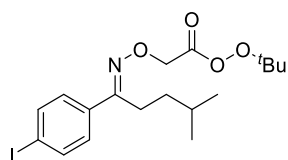
**tert-butyl(E)-2-(((1-(4-methoxyphenyl)-4-methylpentylidene)amino)oxy)ethaneperoxoate (4c):** This compound was prepared according to the general procedure. Colorless oil (45% yield; eluent = petroleum ether/EtOAc (50:5)); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.55 (d, *J* = 1.5 Hz, 2H), 6.87 (d, *J* = 3.9 Hz, 2H), 4.75 (s, 2H), 3.79 (s, 3H), 2.75 (q, *J* = 9.8 Hz, 2H), 1.42 (dd, *J* = 13.7, 7.1 Hz, 3H), 1.32 (s, 9H), 0.92 (d, *J* = 4.1 Hz, 6H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 167.9, 160.7, 160.5, 127.8, 127.5, 113.8, 83.9, 69.7, 55.2, 35.4, 28.4, 26.0, 24.9, 22.3; **HRMS (ESI):** Calcd for C<sub>19</sub>H<sub>30</sub>NO<sub>5</sub> [M+H]<sup>+</sup> 352.2118 found 352.2118.



**tert-butyl**

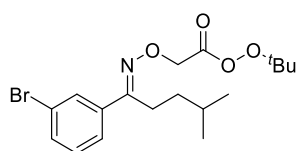
**(E)-2-(((4-methyl-1-(4-(trifluoromethyl)phenyl)pentylidene)amino)oxy)ethaneperoxoate (4d):**

This compound was prepared according to the general procedure. Colorless oil (50% yield; eluent = petroleum ether/EtOAc (50:1));  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.72 (d,  $J = 8.1$  Hz, 2H), 7.61 (d,  $J = 8.1$  Hz, 2H), 4.82 (s, 2H), 2.87 – 2.71 (m, 2H), 1.67-1.60 (m, 1H), 1.46 – 1.42 (m, 2H), 1.31 (s, 9H), 0.94 (d,  $J = 6.6$  Hz, 6H);  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.6, 159.9, 154.1, 138.5, 131.2 (q,  $^2J_{\text{C-F}} = 32.6$  Hz), 126.7, 125.4 (q,  $^3J_{\text{C-F}} = 3.7$  Hz), 124.0 (q,  $^1J_{\text{C-F}} = 272.3$  Hz), 85.2, 84.1, 69.8, 35.1, 28.4, 26.1, 24.9, 22.3; **HRMS (ESI)**: Calcd for  $\text{C}_{19}\text{H}_{27}\text{F}_3\text{NO}_4$   $[\text{M}+\text{H}]^+$  390.1887, found 390.1887.



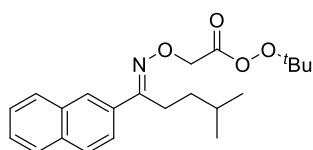
**tert-butyl (E)-2-(((1-(4-iodophenyl)-4-methylpentylidene)amino)oxy)ethaneperoxoate (4e):**

This compound was prepared according to the general procedure. Colorless oil (53% yield; eluent = petroleum ether/EtOAc (50:1));  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.69 (d,  $J = 7.9$  Hz, 2H), 7.34 (d,  $J = 7.9$  Hz, 2H), 4.79 (s, 2H), 2.74 (t,  $J = 7.8$  Hz, 2H), 1.65-1.60 (m, 1H), 1.44-1.42 (m, 2H), 1.31 (s, 9H), 0.93 (d,  $J = 6.6$  Hz, 6H);  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.7, 160.2, 137.6, 134.6, 128.1, 95.6, 84.0, 69.8, 35.2, 28.4, 26.1, 24.7, 22.3; **HRMS (ESI)**: Calcd for  $\text{C}_{18}\text{H}_{26}\text{INO}_4$   $[\text{M}+\text{H}]^+$  448.0979, found 448.0979.



**tert-butyl (E)-2-(((1-(3-bromophenyl)-4-methylpentylidene)amino)oxy)ethaneperoxoate (4f):**

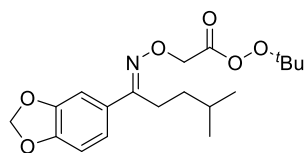
This compound was prepared according to the general procedure. Colorless oil (50% yield; eluent = petroleum ether/EtOAc (50:3));  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.78 (s, 1H), 7.55-7.46 (m, 2H), 7.23 (t,  $J = 7.9$  Hz, 1H), 4.80 (s, 2H), 2.81 – 2.70 (m, 2H), 1.66-1.58 (m, 1H), 1.45 – 1.42 (m, 2H), 1.32 (s, 9H), 0.94 (d,  $J = 6.6$  Hz, 6H);  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.6, 159.75, 137.1, 132.3, 130.0, 129.5, 125.0, 122.7, 84.1, 69.8, 35.2, 28.4, 26.1, 24.9, 22.3; **HRMS (ESI)**: Calcd for  $\text{C}_{18}\text{H}_{27}\text{BrNO}_4$   $[\text{M}+\text{H}]^+$  400.1118, found 400.1118.



**tert-butyl (E)-2-(((4-methyl-1-(naphthalen-2-yl)pentylidene)amino)oxy)ethaneperoxoate (4h):**

This compound was prepared according to the general procedure. Colorless oil (46% yield; eluent

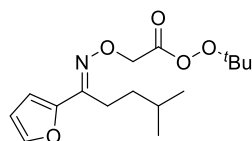
= petroleum ether/EtOAc (50:1));  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.0 (s, 1H), 7.83-7.78 (m, 4H), 7.48-7.47 (m, 2H), 4.85 (s, 2H), 2.92-2.90 (m, 2H), 1.71-1.66 (m, 1H), 1.55-1.51 (m, 2H), 1.32 (s, 9H), 0.96 (d,  $J = 6.6$  Hz, 6H);  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.8, 160.9, 133.8, 133.1, 132.4, 128.5, 128.1, 127.6, 126.7, 126.4, 126.2, 123.8, 84.0, 69.9, 35.5, 28.5, 26.1, 24.8, 22.4; **HRMS (ESI)**: Calcd for  $\text{C}_{22}\text{H}_{30}\text{NO}_4$   $[\text{M}+\text{H}]^+$  372.2169, found 372.2168.



**tert-butyl**

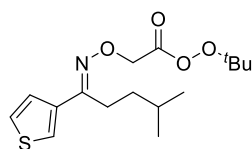
**(*E*)-2-(((1-(benzo[d][1,3]dioxol-5-yl)-4-methylpentylidene)amino)oxy)ethaneperoxoate (4i):**

This compound was prepared according to the general procedure. Colorless oil (48% yield; eluent = petroleum ether/EtOAc (50:1));  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.13 (d,  $J = 1.4$  Hz, 1H), 7.05 (dd,  $J = 8.1, 1.6$  Hz, 1H), 6.75 (d,  $J = 8.2$  Hz, 1H), 5.93 (s, 2H), 4.74 (s, 2H), 2.70 (dd,  $J = 9.3, 7.1$  Hz, 2H), 1.62 – 1.58 (m, 1H), 1.44 – 1.40 (m, 2H), 1.29 (s, 9H), 0.91 (d,  $J = 6.7$  Hz, 6H);  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.8, 160.4, 148.8, 147.9, 129.2, 120.7, 108.0, 106.6, 101.3, 83.9, 69.7, 35.4, 28.4, 26.1, 25.0, 22.3; **HRMS (ESI)**: Calcd for  $\text{C}_{19}\text{H}_{27}\text{NO}_6$   $[\text{M}+\text{H}]^+$  366.1911, found 366.1911.



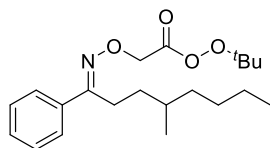
**tert-butyl (*E*)-2-(((1-(furan-2-yl)-4-methylpentylidene)amino)oxy)ethaneperoxoate (4j):**

This compound was prepared according to the general procedure. Colorless oil (49% yield; eluent = petroleum ether/EtOAc (50:1));  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.36 (s, 1H), 7.28 (d,  $J = 3$  Hz, 1H), 6.41-6.40 (m, 1H), 4.69 (s, 2H), 2.54-2.51 (m, 2H), 1.56-1.50 (m, 1H), 1.43-1.39 (m, 2H), 1.21 (s, 9H), 0.83 (d,  $J = 6.6$  Hz);  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.4, 149.0, 145.2, 142.6, 118.8, 120.0, 83.9, 70.0, 36.6, 29.5, 27.8, 26.0, 22.3; **HRMS (ESI)**: Calcd for  $\text{C}_{16}\text{H}_{25}\text{NO}_5$   $[\text{M}+\text{Na}]^+$  334.1625, found 334.1626.

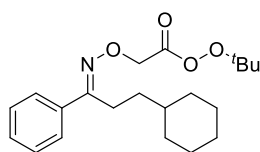


**tert-butyl (*E*)-2-(((4-methyl-1-(thiophen-3-yl)pentylidene)amino)oxy)ethaneperoxoate (4k):**

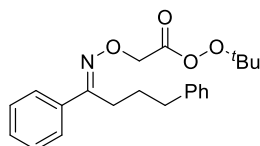
This compound was prepared according to the general procedure. Colorless oil (56% yield; eluent = petroleum ether/EtOAc (50:1));  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.46 (dd,  $J = 2.8, 1.1$  Hz, 1H), 7.38 (dd,  $J = 5.0, 1.1$  Hz, 1H), 7.28-7.26 (m, 1H), 4.76 (s, 2H), 2.75 – 2.69 (m, 2H), 1.64-1.66 (m, 1H), 1.49-1.51 (m, 2H), 1.31 (s, 9H), 0.95 (d,  $J = 6.6$  Hz, 6H);  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.9, 157.3, 137.3, 126.0, 125.5, 124.1, 84.0, 69.8, 35.6, 28.5, 26.1, 25.7, 22.3; **HRMS (ESI)**: Calcd for  $\text{C}_{16}\text{H}_{26}\text{NO}_4\text{S}$   $[\text{M}+\text{Na}]^+$  328.1577, found 328.1578.



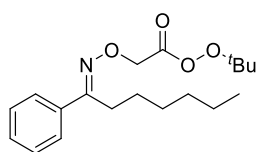
**tert-butyl (E)-2-(((4-methyl-1-phenyloctylidene)amino)oxy)ethaneperoxoate (4l):** This compound was prepared according to the general procedure. Colorless oil (45% yield; eluent = petroleum ether/EtOAc (50:1)); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ 7.55 – 7.50 (m, 2H), 7.27 (d, *J* = 4.6 Hz, 3H), 4.72 (s, 2H), 2.79-2.63 (m, 2H), 1.53 – 1.46 (m, 1H), 1.43-1.37 (m, 1H), 1.35 – 1.30 (m, 1H), 1.26 (s, 1H), 1.23 (s, 9H), 1.21 – 1.17 (m, 3H), 1.15 – 1.10 (m, 1H), 1.10 – 1.03 (m, 1H), 0.85 (d, *J* = 6.5 Hz, 3H), 0.80 (t, *J* = 6.2 Hz, 3H); **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>): δ 167.8, 161.2, 135.1, 129.4, 128.4, 126.4, 84.0, 69.8, 36.3, 33.4, 33.2, 29.2, 26.1, 24.8, 23.0, 19.4, 14.1; **HRMS (ESI):** Calcd for C<sub>21</sub>H<sub>34</sub>NO<sub>4</sub> [M+H]<sup>+</sup> 364.2482, found 364.2482.



**tert-butyl (E)-2-(((3-cyclohexyl-1-phenylpropylidene)amino)oxy)ethaneperoxoate (4m):** This compound was prepared according to the general procedure. Colorless oil (46% yield; eluent = petroleum ether/EtOAc (50:1)); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ 7.61 – 7.60 (m, 2H), 7.36 – 7.35 (m, 3H), 4.80 (s, 2H), 2.80 – 2.78 (m, 2H), 1.78 – 1.64 (m, 5H), 1.48 – 1.44 (m, 2H), 1.32 (s, 9H), 1.27 – 1.10 (m, 4H), 0.96-0.87 (m, 2H); **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>): δ 167.8, 161.2, 135.1, 129.4, 128.4, 126.4, 84.0, 69.8, 38.1, 33.8, 33.0, 26.6, 26.3, 26.1, 24.7; **HRMS (ESI):** Calcd for C<sub>21</sub>H<sub>32</sub>NO<sub>4</sub> [M+H]<sup>+</sup> 362.2325, found 362.2326.



**tert-butyl (E)-2-(((1,4-diphenylbutylidene)amino)oxy)ethaneperoxoate (4n):** This compound was prepared according to the general procedure. Colorless oil (50% yield; eluent = petroleum ether/EtOAc (50:2)); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ 7.58 – 7.52 (m, 2H), 7.38 – 7.30 (m, 3H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.20 – 7.13 (m, 3H), 4.79 (s, 2H), 2.82 (t, *J* = 7.8 Hz, 2H), 2.69 (t, *J* = 7.7 Hz, 2H), 1.93 – 1.91 (m, 2H), 1.30 (s, 9H); **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>): δ 167.8, 160.6, 141.7, 135.0, 129.5, 128.6, 128.5, 128.3, 126.5, 125.9, 84.0, 69.7, 35.9, 28.0, 26.6, 26.1; **HRMS (ESI):** Calcd for C<sub>22</sub>H<sub>28</sub>NO<sub>4</sub> [M+H]<sup>+</sup> 370.2013, found 370.2012.

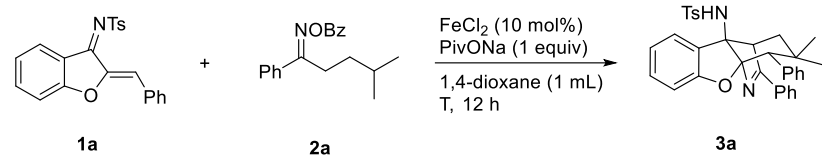


**tert-butyl (E)-2-(((1-phenyloctylidene)amino)oxy)ethaneperoxoate (4o):** This compound was prepared according to the general procedure. Colorless oil (46% yield; eluent = petroleum

ether/EtOAc (50:1)); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ 7.62-7.61 (m, 2H), 7.36-7.35 (m, 3H), 4.80 (s, 2H), 2.78 (t, *J* = 2.1 Hz 2H), 1.61 – 1.54 (m, 2H), 1.41-1.36 (m, 2H), 1.32 (s, 9H), 1.31-1.24 (m, 4H), 0.87 (t, *J* = 6.0 Hz, 3H); **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>): δ 167.8, 160.9, 135.2, 129.4, 128.4, 126.5, 84.0, 69.8, 31.5, 29.5, 27.0, 26.5, 26.0, 22.5, 14.0; **HRMS (ESI)**: Calcd for C<sub>20</sub>H<sub>32</sub>NO<sub>4</sub> [M+H]<sup>+</sup> 350.2326, found 350.2327.

### 3. Screening the Reaction Parameters using Oxime Ester as the Substrate

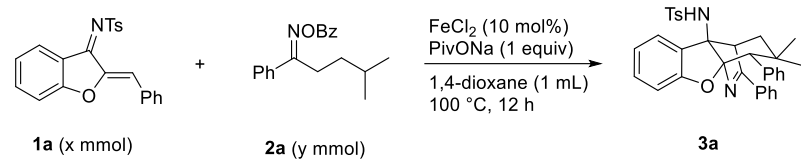
**Table S1.** Screening the temperature.<sup>[a]</sup>



Entry	T (°C)	Yield (%) <sup>[b]</sup>
1	120	10
2	100	18
3	90	8

[a] Reaction conditions: **1a** (0.15 mmol), **2a** (0.1 mmol), FeCl<sub>2</sub> (10 mol%), PivONa (1 equiv), 1,4-dioxane (1 mL), T °C, 12 h, in a sealed tube, under Ar. [b] Isolated yields.

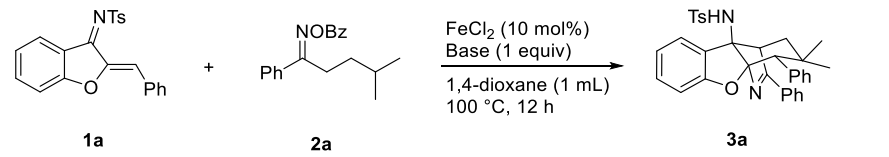
**Table S2.** Screening the ratio of two substrates.<sup>[a]</sup>



Entry	x/y	Yield (%) <sup>[b]</sup>
1	0.1 : 0.15	11
2	0.15 : 0.1	18
3	0.2 : 0.1	16

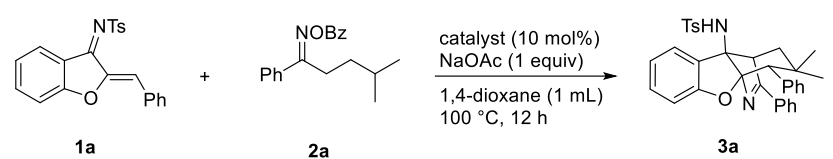
[a] Reaction conditions: **1a** (x mmol), **2a** (y mmol), FeCl<sub>2</sub> (10 mol%), PivONa (1 equiv), 1,4-dioxane (1 mL), 100 °C, 12 h, in a sealed tube, under Ar. [b] Isolated yields.

**Table S3.** Screening the bases.<sup>[a]</sup>



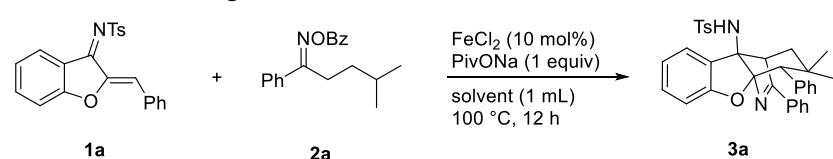
Entry	Base	Yield (%) <sup>[b]</sup>
1	PivONa	18
2	K <sub>3</sub> PO <sub>4</sub>	5
3	PhCO <sub>2</sub> Na	17
4	NaHCO <sub>3</sub>	10
5	Na <sub>2</sub> CO <sub>3</sub>	6
6	CH <sub>3</sub> CO <sub>2</sub> Na	16
7	<i>t</i> BuONa	trace
8	Et <sub>3</sub> N	3
9	Pyridine	6
10	Na <sub>2</sub> SO <sub>3</sub>	12

[a] Reaction conditions: **1a** (0.15 mmol), **2a** (0.1 mmol), FeCl<sub>2</sub> (10 mol%), base (1 equiv), 1,4-dioxane (1 mL), 100 °C, 12 h, in a sealed tube, under Ar. [b] Isolated yields.

**Table S4.** Screening the catalysts.<sup>[a]</sup>

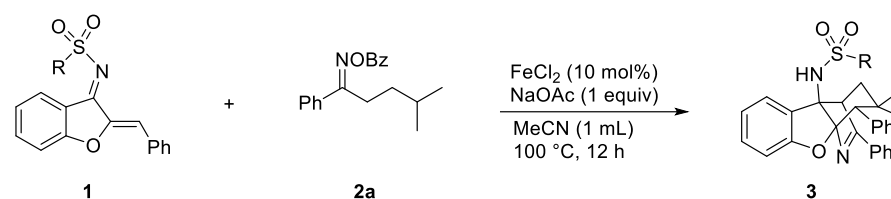
Entry	Catalyst	Yield(%) <sup>[b]</sup>
1	FeCl <sub>2</sub>	17
2	Fe(OAc) <sub>2</sub>	17
3	FeCl <sub>3</sub>	20
4	FeBr <sub>2</sub>	19
5	FeBr <sub>3</sub>	16
6	Fe(OTf) <sub>3</sub>	15
7	Fe(OTf) <sub>2</sub>	14
8	Fe(acac) <sub>3</sub>	15
9	Fe(acac) <sub>2</sub>	9
10	FeF <sub>2</sub>	10
11	FeI <sub>2</sub>	10
12	CuCl	0

[a] Reaction conditions: **1a** (0.15 mmol), **2a** (0.1 mmol), catalyst (10 mol%), NaOAc (1 equiv), 1,4-dioxane (1 mL), 100 °C, 12 h, in a sealed tube, under Ar. [b] Isolated yields.

**Table S5.** Screening the solvents.<sup>[a]</sup>

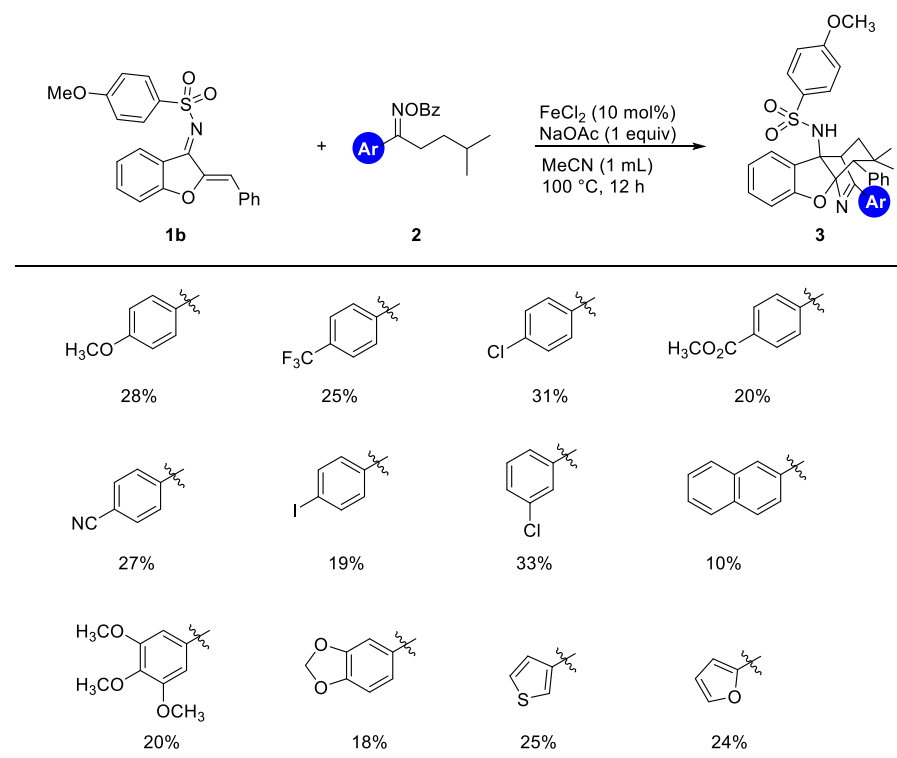
Entry	Solvent	Yield (%) <sup>[b]</sup>
1	1,4-dioxane	18
2	THF	13
3	MeCN	14
4	Toluene	7
5	DCE	12
6	DCM	15
7	DMSO	trace
8	DMF	trace
9	<i>t</i> -BuOMe	14
10	CHCl <sub>3</sub>	10

[a] Reaction conditions: **1a** (0.15 mmol), **2a** (0.1 mmol), FeCl<sub>2</sub> (10 mol %), PivONa (1 equiv), solvent (1 mL), 100 °C, 12 h, in a sealed tube, under Ar. [b] Isolated yields.

**Table S6.** Screening the R group on **1**.<sup>[a]</sup>

Entry	R	Yield (%) <sup>[b]</sup>
1	4-MeO-C <sub>6</sub> H <sub>4</sub>	49
2	4-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	26
3	Ph	22
4	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	<10
5	4-CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	0
6	CH <sub>3</sub>	15
7	2,4-MeO-C <sub>6</sub> H <sub>4</sub>	20

[a] Reaction conditions: **1** (0.15 mmol), **2a** (0.15 mmol), FeCl<sub>2</sub> (10 mol%), NaOAc (1 equiv), MeCN (1 mL), 100 °C, 12 h, in a sealed tube, under Ar. [b] Isolated yields.

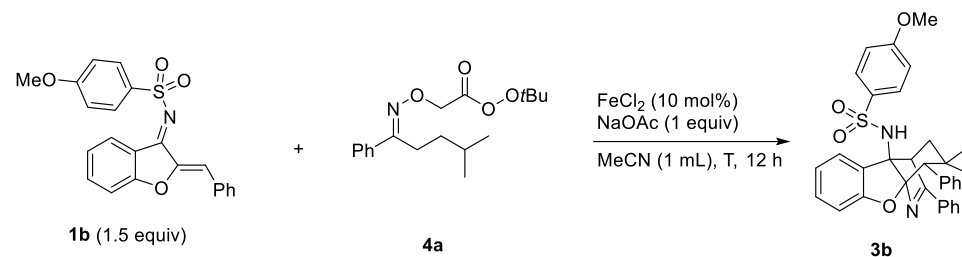
**Table S7.** Some substrates of oxime esters.<sup>[a]</sup>

[a] Reaction conditions: **1b** (0.15 mmol), **2** (0.1 mmol), FeCl<sub>2</sub> (10 mol%), NaOAc (1 equiv), MeCN (1 mL), 100 °C, 12 h, in a sealed tube, under Ar. Isolated yields.



#### 4. Screening the Reaction Parameters using Peresters as the Substrate

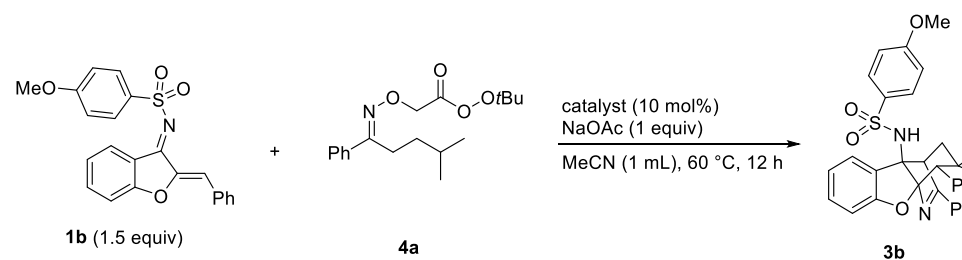
**Table S8.** Screening the temperature.<sup>[a]</sup>



Entry	T (°C)	Yield(%) <sup>[b]</sup>
1	100	35
2	60	32
3	40	trace

[a] Reaction conditions: **1b** (0.15 mmol), **4a** (0.1 mmol), FeCl<sub>2</sub> (10 mol%), NaOAc (1 equiv), MeCN (1 mL), 12 h, in a sealed tube, under Ar. [b] Isolated yields.

**Table S9.** Screening the catalysts.<sup>[a]</sup>



Entry	Catalyst	Yield(%) <sup>[b]</sup>
1	none	15
2	FeCl <sub>2</sub>	41
3	CuBr	11
4	CuBr <sub>2</sub>	trace
5	NiCl <sub>2</sub>	15
6	FeI <sub>2</sub>	trace
7	FeCl <sub>3</sub>	30
8	Fe(acac) <sub>3</sub>	32
9	AgOAc	trace
10	PdCl <sub>2</sub>	36

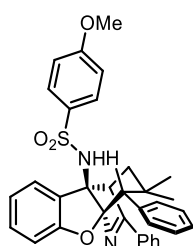
Continued

11	Pd(PPh <sub>3</sub> )Cl <sub>2</sub>	60
12	Pd <sub>2</sub> (dba) <sub>3</sub>	40
13	[Pd(allyl)Cl] <sub>2</sub>	43
14	Pd(OAc) <sub>2</sub>	35
15	Pd(PCy <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	43
16	ZnCl <sub>2</sub>	trace
17	Sc(OTf) <sub>3</sub>	trace
18	Pd(PPh <sub>3</sub> )Cl <sub>2</sub>	trace <sup>[c]</sup>
19	Pd(PPh <sub>3</sub> )Cl <sub>2</sub>	67 <sup>[d]</sup>
20	Pd(PPh <sub>3</sub> )Cl <sub>2</sub>	trace <sup>[e]</sup>
21	Pd(PPh <sub>3</sub> )Cl <sub>2</sub>	trace <sup>[f]</sup>
22	Pd(PPh <sub>3</sub> )Cl <sub>2</sub>	trace <sup>[g]</sup>

[a] Reaction conditions: **1b** (0.15 mmol), **4a** (0.1 mmol), catalyst (10 mol%), NaOAc (1 equiv), MeCN (1 mL), 12 h, in a sealed tube, under Ar. [b] Isolated yields. [c] Reaction was run at 40 °C. [d] NaOAc (0.5 equiv) was used. [e] Et<sub>3</sub>N (1 equiv) was used instead of NaOAc. [f] DBU (1,8-diazabicyclo[5.4.0]undec-7-ene, 1 equiv) was used instead of NaOAc. [g] DABCO (1,4-diazabicyclo[2.2.2]octane, 1 equiv) was used instead of NaOAc.

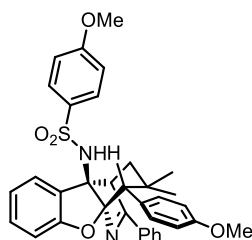
## 5. General Procedures for the Synthesis Bridged Aza-Tetracycles

An oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with the azadiene **1** (0.3 mmol, 1.5 equiv). The Schlenk tube was then introduced into a glove box, where it was charged with Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (10 mol%, 14 mg) and NaOAc (8.2 mg, 0.1 mmol). The tube was fitted with a rubber septum and removed out of the glove box. Then perster **4** (0.2 mmol) and MeCN (2 mL) were added in turn to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced by a Teflon screwcap under N<sub>2</sub> flow. The reaction mixture was stirred at 60 °C for 12 h. Upon cooling to room temperature, the reaction mixture was diluted with 5 mL of ethyl acetate and filtered through a pad of silica gel with additional ethyl acetate (30 mL) as the eluent. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product.



### N-(3,3-dimethyl-4,11-diphenyl-1,2,3,4-tetrahydro-9bH-4a,1-(azenometheno)dibenzo[b,d]furan-9b-yl)-4-methoxybenzenesulfonamide (**3b**):

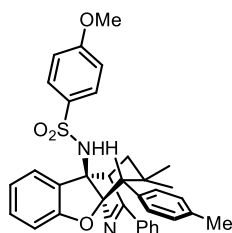
According to the general procedure, a mixture consisting of oxime **4a** (0.2 mmol, 64.2 mg), azadiene **1b** (0.3 mmol, 117.4 mg), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.02 mmol, 14.2 mg), NaOAc (0.1 mmol, 8.2 mg) and MeCN (2 mL) under a N<sub>2</sub> atmosphere was stirred at 60 °C for 12 h to afford **3b** (75.6 mg). Yellow solid (67% yield; eluent = pentane/ethyl acetate = 10:1); Mp = 213-215 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.93 (d, *J* = 7.6 Hz, 2H), 7.72 (s, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.50 – 7.46 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.12 (d, *J* = 7.4 Hz, 1H), 6.99 (t, *J* = 7.7 Hz, 1H), 6.79 (t, *J* = 9.5 Hz, 3H), 6.52 (t, *J* = 7.5 Hz, 1H), 4.86 (s, 1H), 4.52 (s, 1H), 3.82 (s, 3H), 3.38 (s, 1H), 2.46 (d, *J* = 14.3 Hz, 1H), 1.64 (d, *J* = 13.9 Hz, 1H), 1.09 (s, 3H), 0.52 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 176.7, 162.8, 157.78, 136.28, 133.4, 132.3, 131.9, 131.7, 129.8, 129.1, 128.8, 128.6, 127.9, 127.8, 126.8, 125.0, 121.0, 114.0, 113.8, 111.8, 72.8, 55.6, 50.2, 49.2, 35.8, 35.0, 33.1, 28.4; HRMS (ESI): Calcd for C<sub>34</sub>H<sub>32</sub>N<sub>2</sub>NaO<sub>4</sub>S [M+Na]<sup>+</sup> 582.1975, found 582.1976.



### N-(3,3-dimethyl-4,11-diphenyl-1,2,3,4-tetrahydro-9bH-4a,1-(azenometheno)dibenzo[b,d]furan-9b-yl)-4-methoxybenzenesulfonamide (**3f**):

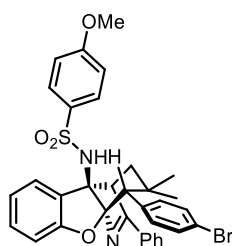
According to the general procedure, a mixture consisting of oxime **4a** (0.2 mmol, 64.2 mg), azadiene **1c** (0.3 mmol, 126.3 mg), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.02 mmol, 14.2 mg), NaOAc (0.1 mmol, 8.2 mg) and MeCN (2 mL) under a N<sub>2</sub> atmosphere was stirred at 60 °C for 12 h to afford **3f** (66.2

mg). Yellow solid (55% yield; eluent = pentane/ethyl acetate = 8:1); Mp = 224.2-224.6 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.92 (d, *J* = 7.8 Hz, 2H), 7.68-7.54 (m, 4H), 7.49-7.42 (m, 3H), 7.10 (d, *J* = 7.5 Hz, 1H), 6.98 (t, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 2H), 6.80-6.79 (m, 3H), 6.51 (t, *J* = 7.5 Hz, 1H), 4.85 (s, 1H), 4.51 (s, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 3.32 (s, 1H), 2.44 (dd, *J* = 13.2, 1.8 Hz, 1H), 1.63 (dd, *J* = 12.2, 1.8 Hz, 1H), 1.07 (s, 3H), 0.52 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 176.7, 162.8, 158.6, 157.7, 133.3, 132.6, 132.4, 131.8, 129.8, 129.2, 128.8, 128.6, 128.3, 127.8, 125.1, 121.0, 113.9, 113.4, 111.8, 72.7, 55.6, 55.12, 49.4, 49.2, 35.8, 35.0, 33.1, 28.5; HRMS (ESI): Calcd for C<sub>35</sub>H<sub>34</sub>N<sub>2</sub>NaO<sub>5</sub>S [M+Na]<sup>+</sup> 617.2082, found 617.2081.



**N-(3,3-dimethyl-11-phenyl-4-(p-tolyl)-1,2,3,4-tetrahydro-9bH-4a,1-(azeno)thienopyridin-4-yl)-4-methoxybenzenesulfonamide (3g):**

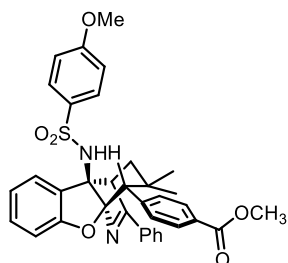
According to the general procedure, a mixture consisting of oxime **4a** (0.2 mmol, 64.2 mg), azadiene **1g** (0.3 mmol, 121.5 mg), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.02 mmol, 14.2 mg), NaOAc (0.1 mmol, 8.2 mg) and MeCN (2 mL) under a N<sub>2</sub> atmosphere was stirred at 60 °C for 12 h to afford **3g** (55.3 mg). Yellow solid (47% yield; eluent = pentane/ethyl acetate = 8:1); Mp = 216-217 °C; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>): δ 8.35 (s, 1H), 7.89 (d, *J* = 7.2 Hz, 2H), 7.55-7.47 (m, 7H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.00-6.96 (m, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 6.74 (d, *J* = 7.9 Hz, 1H), 6.41 (t, *J* = 7.4 Hz, 1H), 4.44 (s, 1H), 3.78 (s, 3H), 3.72 (s, 1H), 2.37 (d, *J* = 12.8 Hz, 1H), 2.32 (s, 3H), 1.48 (d, *J* = 12.0 Hz, 1H), 0.97 (s, 3H), 0.39 (s, 3H); <sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>): δ 176.3, 162.2, 158.0, 135.7, 135.1, 134.5, 132.4, 132.1, 130.2, 129.7, 129.5, 128.6, 128.4, 127.9, 125.0, 120.8, 114.2, 114.1, 111.3, 72.7, 56.1, 49.8, 48.3, 35.6, 35.1, 32.9, 28.8, 21.2; HRMS (ESI): Calcd for C<sub>35</sub>H<sub>34</sub>N<sub>2</sub>NaO<sub>5</sub>S [M+Na]<sup>+</sup> 601.2131, found 601.2129.



**N-(4-(4-bromophenyl)-3,3-dimethyl-11-phenyl-1,2,3,4-tetrahydro-9bH-4a,1-(azeno)thienopyridin-4-yl)-4-methoxybenzenesulfonamide (3h):**

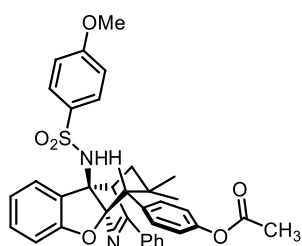
According to the general procedure, a mixture consisting of oxime **4a** (0.2 mmol, 64.2 mg), azadiene **1e** (0.3 mmol, 140.7 mg), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.02 mmol, 14.2 mg), NaOAc (0.1 mmol, 8.2 mg) and MeCN (2 mL) under a N<sub>2</sub> atmosphere was stirred at 60 °C for 12 h to afford **3h** (84.7 mg). Yellow solid (66% yield; eluent = pentane/ethyl acetate = 10:1); Mp = 210-212 °C; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>): δ 8.38 (s, 1H), 7.90 (d, *J* = 7.4 Hz, 2H), 7.68-7.45 (m, 9H), 7.00-6.95 (m, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.76 (d, *J* = 7.9 Hz, 1H), 6.42 (t, *J* = 7.4 Hz, 1H), 4.45 (s, 1H), 3.78 (s, 3H), 3.77 (s, 1H), 2.37 (d, *J* = 13.4 Hz, 1H), 1.50 (d, *J* = 12.5 Hz, 1H), 0.98 (s, 3H), 0.39 (s, 3H).

$^{13}\text{C}$  NMR (151 MHz, DMSO- $d_6$ ):  $\delta$  176.7, 162.3, 157.9, 137.1, 135.0, 134.3, 132.5, 132.3, 131.0, 129.9, 129.8, 129.6, 128.4, 127.9, 125.0, 120.9, 120.4, 114.2, 113.8, 111.4, 72.7, 56.1, 49.9, 48.2, 35.5, 35.1, 32.8, 28.7; **HRMS (ESI)**: Calcd for  $\text{C}_{34}\text{H}_{32}\text{BrN}_2\text{O}_4\text{S}$   $[\text{M}+\text{H}]^+$  643.1261, found 643.1260.



**Methyl 4-(9b-((4-methoxyphenyl)sulfonamido)-3,3-dimethyl-11-phenyl-1,3,4,9b-tetrahydro-2H-4a,1-(azenometheno)dibenzo[b,d]furan-4-yl)benzoate (3i):**

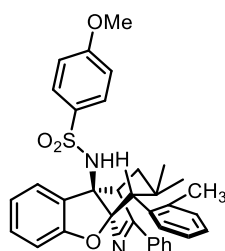
According to the general procedure, a mixture consisting of oxime **4a** (0.2 mmol, 64.2 mg), azadiene **1f** (0.3 mmol, 134.7 mg),  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (0.02 mmol, 14.2 mg), NaOAc (0.1 mmol, 8.2 mg) and MeCN (2 mL) under a  $\text{N}_2$  atmosphere was stirred at 60 °C for 12 h to afford **3i** (95.79 mg). Yellow solid (77% yield; eluent = pentane/ethyl acetate = 10:1); Mp = 202-204 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.04 (d,  $J$  = 8.4 Hz, 2H), 7.93 (d,  $J$  = 7.3 Hz, 2H), 7.79 (s, 2H), 7.56 (d,  $J$  = 8.9 Hz, 2H), 7.50-7.42 (m, 3H), 7.09 (d,  $J$  = 7.4 Hz, 1H), 7.00 (t,  $J$  = 7.7 Hz, 1H), 6.80-6.76 (m, 3H), 6.52 (t,  $J$  = 7.5 Hz, 1H), 5.07 (s, 1H), 4.53 (s, 1H), 3.92 (s, 3H), 3.82 (s, 3H), 3.49 (s, 1H), 2.47 (dd,  $J$  = 14.3, 2.1 Hz, 1H), 1.62 (dd,  $J$  = 14.6, 3.1 Hz, 1H), 1.08 (s, 3H), 0.49 (s, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  176.9, 167.3, 162.9, 157.6, 141.9, 133.3, 132.2, 132.0, 131.7, 129.9, 129.1, 129.0, 128.9, 128.6, 127.8, 125.0, 121.2, 114.0, 113.5, 111.8, 72.8, 55.6, 52.0, 50.1, 49.2, 35.9, 35.0, 33.0, 28.4; **HRMS (ESI)**: Calcd for  $\text{C}_{36}\text{H}_{34}\text{N}_2\text{O}_6\text{S}$   $[\text{M}+\text{H}]^+$  623.2210, found 623.2212.



**4-(9b-((4-methoxyphenyl)sulfonamido)-3,3-dimethyl-11-phenyl-1,3,4,9b-tetrahydro-2H-4a,1-(azenometheno)dibenzo[b,d]furan-4-yl)phenyl acetate (3j):**

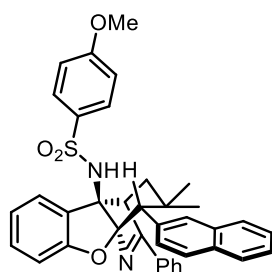
According to the general procedure, a mixture consisting of oxime **4a** (0.2 mmol, 64.2 mg), azadiene **1g** (0.3 mmol, 134.7 mg),  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (0.02 mmol, 14.2 mg), NaOAc (0.1 mmol, 8.2 mg) and MeCN (2 mL) under a  $\text{N}_2$  atmosphere was stirred at 60 °C for 12 h to afford **3j** (82.3 mg). Yellow solid (66% yield; eluent = pentane/ethyl acetate = 10:1); Mp = 238-241 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (d,  $J$  = 7.3 Hz, 2H), 7.71 (s, 2H), 7.55 (d,  $J$  = 8.9 Hz, 2H), 7.47 (t,  $J$  = 7.3 Hz, 1H), 7.42 (t,  $J$  = 7.4 Hz, 2H), 7.10 (d,  $J$  = 8.1 Hz, 3H), 6.99 (t,  $J$  = 7.8 Hz, 1H), 6.79 (t,  $J$  = 9.2 Hz, 3H), 6.52 (t,  $J$  = 7.5 Hz, 1H), 4.93 (s, 1H), 4.51 (s, 1H), 3.82 (s, 3H), 3.40 (s, 1H), 2.44 (dd,  $J$  = 14.4, 2.4 Hz, 1H), 2.30 (s, 3H), 1.62 (dd,  $J$  = 14.4, 3.0 Hz, 1H), 1.07 (s, 3H), 0.52 (s, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  176.9, 169.4, 162.8, 157.6, 149.7, 133.8, 133.3, 132.6, 131.9, 129.9, 128.8, 128.7, 127.8, 125.0, 121.1, 120.8, 114.0, 113.7, 111.8, 72.7, 55.6, 49.6, 49.2, 35.8, 35.0,

33.0, 28.4, 21.2; **HRMS (ESI)**: Calcd for C<sub>36</sub>H<sub>34</sub>N<sub>2</sub>O<sub>6</sub>S [M + H]<sup>+</sup> 623.2210, found 623.2219.



**N-(3,3-dimethyl-11-phenyl-4-(o-tolyl)-1,2,3,4-tetrahydro-9bH-4a,1-(azenometheno)dibenzo[b,d]furan-9b-yl)-4-methoxybenzenesulfonamide (3k):**

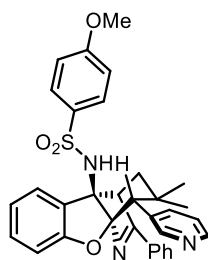
According to the general procedure, a mixture consisting of oxime **4a** (0.2 mmol, 64.2 mg), azadiene **1h** (0.3 mmol, 121.5 mg), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.02 mmol, 14.2 mg), NaOAc (0.1 mmol, 8.2 mg) and MeCN (2 mL) under a N<sub>2</sub> atmosphere was stirred at 60 °C for 12 h to afford **3k** (53.2 mg). Yellow solid (46% yield; eluent = pentane/ethyl acetate = 10:1); Mp = 210-212 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.04 (d, *J* = 7.7 Hz, 1H), 7.93 (d, *J* = 7.2 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.49-7.40 (m, 3H), 7.27-7.18 (m, 3H), 7.08 (d, *J* = 7.3 Hz, 1H), 6.99 (t, *J* = 7.7 Hz, 1H), 6.81 (d, *J* = 9 Hz, 2H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.53 (t, *J* = 7.4 Hz, 1H), 4.98 (s, 1H), 4.47 (s, 1H), 3.93 (s, 1H), 3.83 (s, 3H), 2.49 (s, 3H), 2.34 (d, *J* = 14.4 Hz, 1H), 1.59 (d, *J* = 14.5 Hz, 1H), 0.99 (s, 3H), 0.65 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 176.1, 162.8, 158.0, 137.6, 134.6, 133.5, 133.3, 132.3, 131.8, 130.6, 129.8, 129.2, 128.8, 128.7f, 127.8, 126.6, 125.5, 125.0, 121.1, 114.0, 113.8, 112.0, 73.3, 55.6, 49.1, 43.5, 37.3, 34.9, 34.0, 28.8, 21.2; **HRMS (ESI)**: Calcd for C<sub>35</sub>H<sub>35</sub>N<sub>2</sub>O<sub>4</sub>S [M+H]<sup>+</sup> 579.2312, found 579.2310.



**N-(3,3-dimethyl-4-(naphthalen-2-yl)-11-phenyl-1,2,3,4-tetrahydro-9bH-4a,1-(azeno)thienopyridine)-4-methoxybenzenesulfonamide (3l):**

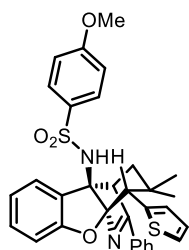
According to the general procedure, a mixture consisting of oxime **4a** (0.2 mmol, 64.2 mg), azadiene **1i** (0.3 mmol, 132.3 mg), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.02 mmol, 14.2 mg), NaOAc (0.1 mmol, 8.2 mg) and MeCN (2 mL) under a N<sub>2</sub> atmosphere was stirred at 60 °C for 12 h to afford **3l** (65.2 mg). Yellow solid (53% yield; eluent = pentane/ethyl acetate = 10:1); Mp = 214.7-216.9 °C, <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.11-7.98 (m, 4H), 7.89-7.86 (m, 3H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.50-7.45 (m, 5H), 7.14 (d, *J* = 7.4 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 8.6 Hz, 2H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.53 (t, *J* = 7.4 Hz, 1H), 4.95 (s, 1H), 4.56 (s, 1H), 3.82 (s, 3H), 3.58 (s, 1H), 2.50 (d, *J* = 14.0 Hz, 1H), 1.66 (d, *J* = 14.7 Hz, 1H), 1.15 (s, 3H), 0.56 (s, 3H); <sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>): δ 176.5, 162.3, 158.0, 135.5, 135.0, 133.1, 132.5, 132.4, 130.8, 130.6, 130.1, 129.7, 129.6, , 128.5, 128.2, 128.0, 127.8, 127.1, 126.3, 126.1, 125.0, 120.9, 114.2, 111.3, 72.8, 56.1,

49.9, 48.9, 35.9, 35.1, 33.0, 28.8. **HRMS (ESI)**: Calcd for C<sub>38</sub>H<sub>35</sub>N<sub>2</sub>O<sub>4</sub>S [M+H]<sup>+</sup> 615.2312, found 615.2313.



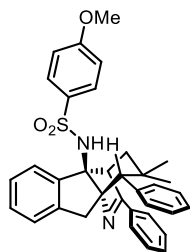
**N-(3,3-dimethyl-11-phenyl-4-(pyridin-3-yl)-1,2,3,4-tetrahydro-9bH-4a,1-(azeno)thieno[2,3-b]furan-9b-yl)-4-methoxybenzenesulfonamide (3m):**

According to the general procedure, a mixture consisting of oxime **4a** (0.2 mmol, 64.2 mg), azadiene **1j** (0.3 mmol, 117.6 mg), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.02 mmol, 14.2 mg), NaOAc (0.1 mmol, 8.2 mg) and MeCN (2 mL) under a N<sub>2</sub> atmosphere was stirred at 60 °C for 12 h to afford **3m** (63.4 mg). Yellow solid (56% yield; eluent = pentane/ethyl acetate = 3:1); Mp = 219-221 °C; **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ 8.67 (s, 1H), 8.55 (d, *J* = 3.3 Hz, 1H), 8.34 (s, 1H), 7.92 (d, *J* = 7.2 Hz, 2H), 7.61 (d, *J* = 8.9 Hz, 2H), 7.49 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.33 (dd, *J* = 7.7, 4.8 Hz, 1H), 7.10 (d, *J* = 6.9 Hz, 1H), 7.00 (t, *J* = 7.2 Hz, 1H), 6.81 (d, *J* = 8.9 Hz, 2H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.52 (t, *J* = 7.3 Hz, 1H), 6.04 (s, 1H), 4.58 (s, 1H), 3.82 (s, 3H), 3.48 (s, 1H), 2.54 (dd, *J* = 14.3, 1.6 Hz, 1H), 1.65 (dd, *J* = 14.2, 3.0 Hz, 1H), 1.06 (s, 3H), 0.51 (s, 3H); **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>): δ 177.1, 165.9, 162.8, 157.5, 151.8, 148.2, 139.8, 133.6, 132.1, 132.0, 129.8, 128.9, 128.6, 127.8, 125.0, 123.2, 121.2, 114.0, 113.4, 111.6, 72.7, 55.6, 49.4, 47.5, 35.7, 35.0, 32.9, 28.5; **HRMS (ESI)**: Calcd for C<sub>33</sub>H<sub>31</sub>N<sub>3</sub>O<sub>4</sub>S [M+H]<sup>+</sup> 566.2108, found 566.2115.



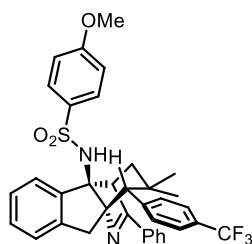
**N-(3,3-dimethyl-11-phenyl-4-(thiophen-2-yl)-1,2,3,4-tetrahydro-9bH-4a,1-(azeno)thieno[2,3-b]furan-9b-yl)-4-methoxybenzenesulfonamide (3n):**

According to the general procedure, a mixture consisting of oxime **4a** (0.2 mmol, 64.2 mg), azadiene **1k** (0.3 mmol, 119.1 mg), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.04 mmol, 28.1 mg), NaOAc (0.1 mmol, 8.2 mg) and MeCN (2 mL) under a N<sub>2</sub> atmosphere was stirred at 80 °C for 12 h to afford **3n** (43.5 mg). Yellow solid (38% yield; eluent = pentane/ethyl acetate = 10:1); Yellow solid; Mp = 210-212 °C; **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ 7.93 (d, *J* = 7.4 Hz, 2H), 7.56 (d, *J* = 8.7 Hz, 2H), 7.49-7.41 (m, 4H), 7.28 (d, *J* = 4.2 Hz, 1H), 7.14 (d, *J* = 7.3 Hz, 1H), 7.07-6.98 (m, 2H), 6.86-6.78 (m, 3H), 6.55 (t, *J* = 7.4 Hz, 1H), 4.82 (s, 1H), 4.53 (s, 1H), 3.83 (s, 3H), 3.69 (s, 1H), 2.47 (d, *J* = 13.8 Hz, 1H), 1.68 (d, *J* = 12.7 Hz, 1H), 1.14 (s, 3H), 0.56 (s, 3H); **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>): δ 177.5, 162.9, 157.5, 138.4, 133.2, 132.2, 132.0, 130.0, 128.9, 128.8, 128.7, 128.6, 127.8, 126.4, 125.3, 125.0, 121.2, 114.0, 113.5, 111.9, 72.3, 55.6, 49.2, 45.9, 35.8, 33.2, 29.3; **HRMS (ESI)**: Calcd for C<sub>32</sub>H<sub>31</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub> [M+H]<sup>+</sup> 571.1720, found 571.1722.



**N-(7,7-dimethyl-8,11-diphenyl-5,6,7,8-tetrahydro-8a,5-(azenometheno)fluoren-4b(9H)-yl)-4-methoxybenzenesulfonamide (3o):**

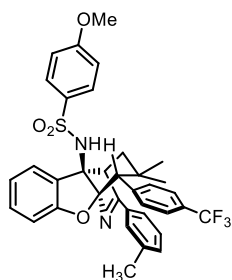
According to the general procedure, a mixture consisting of oxime **4a** (0.2 mmol, 64.2 mg), azadiene **11** (0.3 mmol, 116.4 mg), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.02 mmol, 14.2 mg), NaOAc (0.1 mmol, 8.2 mg) and MeCN (2 mL) under a N<sub>2</sub> atmosphere was stirred at 60 °C for 12 h to afford **3ad** (38.2 mg). Yellow solid (34% yield; eluent = pentane/ethyl acetate = 10:1); Mp = 250-252 °C <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.07 (s, 1H), 7.85 (d, *J* = 6.2 Hz, 2H), 7.43 - 7.38 (m, 6H), 7.28 (d, *J* = 6.6 Hz, 2H), 7.18 (s, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 6.93 (dt, *J* = 14.4, 7.1 Hz, 2H), 6.69 – 6.66 (m, 3H), 4.93 (s, 1H), 4.30 (s, 1H), 3.78 (s, 3H), 3.15 (d, *J* = 16.1 Hz, 1H), 3.07 (s, 1H), 2.80 (d, *J* = 16.2 Hz, 1H), 2.39 (d, *J* = 13.5 Hz, 1H), 1.68 (d, *J* = 11.8 Hz, 1H), 1.09 (s, 3H), 0.54 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 176.3, 162.3, 141.8, 141.7, 138.9, 133.6, 133.5, 131.8, 130.9, 128.6, 128.5, 128.1, 127.4, 126.4, 125.6, 125.2, 124.7, 113.7, 86.0, 74.5, 55.6, 51.6, 49.1, 38.9, 34.4, 33.9, 33.8, 28.8.



**N-(7,7-dimethyl-11-phenyl-8-(4-(trifluoromethyl)phenyl)-5,6,7,8-tetrahydro-8a,5-(azenometheno)fluoren-4b(9H)-yl)-4-methoxybenzenesulfonamide (3p):**

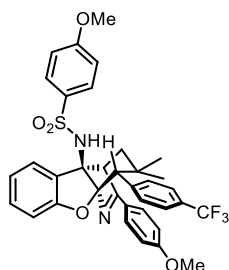
According to the general procedure, a mixture consisting of oxime **4a** (0.2 mmol, 64.2 mg), azadiene **1m** (0.3 mmol, 136.8 mg), Pd(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub> (0.02 mmol, 14.2 mg), NaOAc (0.1 mmol, 8.2 mg) and MeCN (2 mL) under a N<sub>2</sub> atmosphere was stirred at 60 °C for 12 h to afford **3ae** (47.8 mg). Yellow solid (37% yield; eluent = pentane/ethyl acetate = 10:1); Mp = 315-317 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.21 (s, 1H), 7.83 (d, *J* = 7.0 Hz, 2H), 7.61-7.52 (m, 2H), 7.41-7.38 (m, 5H), 7.18 (s, 1H), 6.97 (t, *J* = 7.8 Hz, 2H), 6.92 (t, *J* = 7.1 Hz, 1H), 6.69 (d, *J* = 8.6 Hz, 2H), 6.64 - 6.62 (m, 1H), 5.18 (s, 1H), 4.28 (s, 1H), 3.79 (s, 3H), 3.19 (s, 1H), 3.10 (d, *J* = 16.0 Hz, 1H), 2.84 (d, *J* = 16.0 Hz, 1H), 2.40 (d, *J* = 13.2 Hz, 1H), 1.66 (d, *J* = 12.3 Hz, 2H), 1.05 (s, 3H), 0.50 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 176.5, 162.4, 143.2, 141.5, 141.4, 133.4, 131.1, 128.7, 128.6 (<sup>2</sup>*J*<sub>C-F</sub> = 32.6 Hz), 128.5, 128.3, 127.4, 125.7, 125.2, 124.5, 124.4 (<sup>1</sup>*J*<sub>C-F</sub> = 267.6 Hz), 113.8, 85.5, 74.5, 55.6, 51.2, 49.1, 38.8, 34.5, 33.8, 33.8, 28.7; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -62.4;





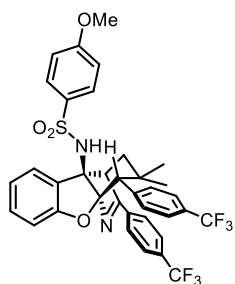
**N-(3,3-dimethyl-11-(m-tolyl)-4-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydro-9bH-4a,1-(azetometheno)dibenzo[b,d]furan-9b-yl)-4-methoxybenzenesulfonamide (3q):**

According to the general procedure, a mixture consisting of oxime **4b** (0.2 mmol, 67.2 mg), azadiene **1n** (0.3 mmol, 137.7 mg), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.02 mmol, 14.2 mg), NaOAc (0.1 mmol, 8.2 mg) and MeCN (2 mL) under a N<sub>2</sub> atmosphere was stirred at 60 °C for 12 h to afford **3o** (80.7 mg). Yellow solid (61% yield; eluent = pentane/ethyl acetate = 10:1); Mp = 279-281 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.84 (s, 2H), 7.74 (s, 1H), 7.69 (d, *J* = 7.2 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.9 Hz, 2H), 7.33 – 7.29 (m, 2H), 7.07 (d, *J* = 6.7 Hz, 1H), 7.00 (t, *J* = 7.8 Hz, 1H), 6.78 (t, *J* = 9.1 Hz, 3H), 6.51 (t, *J* = 7.2 Hz, 1H), 5.00 (s, 1H), 4.51 (s, 1H), 3.82 (s, 3H), 3.49 (s, 1H), 2.46 (dd, *J* = 14.3, 2.1 Hz, 1H), 2.38 (s, 3H), 1.63 (dd, *J* = 14.4, 2.9 Hz, 1H), 1.08 (s, 3H), 0.50 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 177.1, 162.9, 157.6, 140.6, 138.7, 133.2, 132.9, 132.0, 132.0, 129.9, 128.9, 128.8, 128.7, 128.2, 125.0, 125.0, 124.8 (q, <sup>3</sup>*J*<sub>C-F</sub> = 3.5 Hz), 124.4 (q, <sup>1</sup>*J*<sub>C-F</sub> = 272.3 Hz), 121.2, 114.0, 113.4, 111.8, 72.7, 55.7, 49.9, 49.3, 35.9, 35.0, 33.0, 28.4, 21.3. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -62.4.



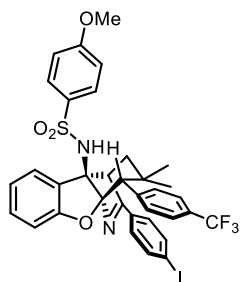
**4-methoxy-N-(11-(4-methoxyphenyl)-3,3-dimethyl-4-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydro-9bH-4a,1-(azetometheno)dibenzo[b,d]furan-9b-yl)benzenesulfonamide (3r):**

According to the general procedure, a mixture consisting of oxime **4c** (0.2 mmol, 70.2 mg), azadiene **1n** (0.3 mmol, 137.7 mg), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.02 mmol, 14.2 mg), NaOAc (0.1 mmol, 8.2 mg) and MeCN (2 mL) under a N<sub>2</sub> atmosphere was stirred at 60 °C for 12 h to afford **3p** (34.1 mg). Yellow solid (25% yield; eluent = pentane/ethyl acetate = 8:1); Mp = 288-289 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.87 (d, *J* = 8.8 Hz, 4H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.9 Hz, 2H), 7.07 (d, *J* = 6.7 Hz, 1H), 7.00 (dd, *J* = 11.1, 4.3 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.78 (dd, *J* = 11.8, 8.6 Hz, 3H), 6.51 (t, *J* = 7.2 Hz, 1H), 4.94 (s, 1H), 4.47 (s, 1H), 3.83 (d, *J* = 9.0 Hz, 6H), 3.46 (s, 1H), 2.44 (dd, *J* = 14.3, 2.1 Hz, 1H), 1.60 (dd, *J* = 14.2, 2.9 Hz, 1H), 1.08 (s, 3H), 0.50 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 176.10, 162.84, 162.79, 157.58, 147.11, 140.72, 133.21, 131.96, 129.88, 129.66, 129.09, 129.0 (q, <sup>2</sup>*J*<sub>C-F</sub> = 31.9 Hz), 128.67, 125.4 (q, <sup>1</sup>*J*<sub>C-F</sub> = 272.0 Hz), 124.97, 124.84, 124.7 (q, <sup>3</sup>*J*<sub>C-F</sub> = 3.5 Hz), 121.18, 114.27, 113.99, 113.34, 111.77, 72.64, 55.64, 55.44, 49.97, 49.08, 35.92, 35.05, 32.97, 28.34; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -62.4.



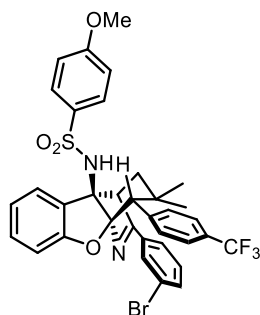
**N-(3,3-dimethyl-4,11-bis(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydro-9bH-4a,1-(azenometheno)dibenzo[b,d]furan-9b-yl)-4-methoxybenzenesulfonamide (3s):**

According to the general procedure, a mixture consisting of oxime **4d** (0.2 mmol, 77.8 mg), azadiene **1n** (0.3 mmol, 137.7 mg), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.02 mmol, 14.2 mg), NaOAc (0.1 mmol, 8.2 mg) and MeCN (2 mL) under a N<sub>2</sub> atmosphere was stirred at 60 °C for 12 h to afford **3q** (67.5 mg). Yellow solid (47% yield; eluent = pentane/ethyl acetate = 10:1); Mp = 285-286 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.03 (d, *J* = 6.4 Hz, 2H), 7.83 (s, 2H), 7.70 (d, *J* = 6.6 Hz, 2H), 7.64 (d, *J* = 6.6 Hz, 2H), 7.58 (d, *J* = 7.2 Hz, 2H), 7.11 (d, *J* = 6.0 Hz, 1H), 7.04 (t, *J* = 7.2 Hz, 1H), 6.86 - 6.76 (m, 3H), 6.56 (t, *J* = 7.2 Hz, 1H), 4.92 (s, 1H), 4.54 (s, 1H), 3.83 (s, 3H), 3.50 (s, 1H), 2.51 (d, *J* = 14.4 Hz, 1H), 1.63 (d, *J* = 14.2 Hz, 1H), 1.10 (s, 3H), 0.48 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 176.1, 163.0, 157.5, 140.2, 135.2, 133.0, 131.9, 130.2, 128.7, 128.1, 125.9 (q, <sup>3</sup>*J*<sub>C-F</sub> = 3.6 Hz), 125.0, 124.8 (q, <sup>3</sup>*J*<sub>C-F</sub> = 3.6 Hz), 121.5, 114.1, 113.5, 111.8, 72.9, 55.7, 49.9, 49.4, 35.8, 34.9, 33.0, 28.4; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -62.4, -63.1.



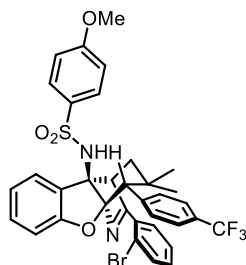
**N-(11-(4-iodophenyl)-3,3-dimethyl-4-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydro-9bH-4a,1-(azenometheno)dibenzo[b,d]furan-9b-yl)-4-methoxybenzenesulfonamide (3t):**

According to the general procedure, a mixture consisting of oxime **4e** (0.2 mmol, 77.8 mg), azadiene **1n** (0.3 mmol, 137.7 mg), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.02 mmol, 14.2 mg), NaOAc (0.1 mmol, 8.2 mg) and MeCN (2 mL) under a N<sub>2</sub> atmosphere was stirred at 60 °C for 12 h to afford **3r** (40.3 mg). Yellow solid (26% yield; eluent = pentane/ethyl acetate = 10:1); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.05 (s, 1H), 7.82 (d, *J* = 7.1 Hz, 3H), 7.66–7.53 (m, 5H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 1H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.83–6.75 (m, 3H), 6.55 (t, *J* = 7.2 Hz, 1H), 4.99 (s, 1H), 4.47 (s, 1H), 3.83 (s, 3H), 3.49 (s, 1H), 2.48 (d, *J* = 13.9 Hz, 1H), 1.62 (d, *J* = 14.7 Hz, 1H), 1.09 (s, 3H), 0.49 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 175.9, 163.0, 157.6, 140.4, 135.0, 134.1, 133.1, 131.9, 130.5, 130.1, 128.9 (q, <sup>2</sup>*J*<sub>C-F</sub> = 31.7 Hz), 128.7, 126.3, 125.0, 124.8 (q, <sup>3</sup>*J*<sub>C-F</sub> = 3.02 Hz), 124.4 (q, <sup>1</sup>*J*<sub>C-F</sub> = 273.3 Hz), 123.3, 121.4, 114.1, 113.4, 111.8, 72.8, 55.6, 49.9, 49.3, 35.9, 34.9, 33.0, 28.4; <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>): δ -62.4; HRMS (ESI): Calcd for C<sub>36</sub>H<sub>35</sub>F<sub>3</sub>IN<sub>2</sub>O<sub>4</sub>S [M+H]<sup>+</sup> 775.1309, found 775.1311.



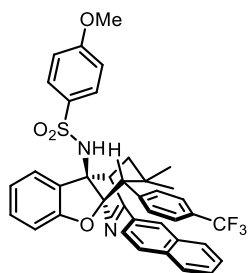
**N-(11-(3-bromophenyl)-3,3-dimethyl-4-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydro-9bH-4a,1-azeno)thienopyridine-9b-yl)-4-methoxybenzenesulfonamide (3u):**

According to the general procedure, a mixture consisting of oxime **4f** (0.2 mmol, 79.8 mg), azadiene **1n** (0.3 mmol, 137.7 mg), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.02 mmol, 14.2 mg), NaOAc (0.1 mmol, 8.2 mg) and MeCN (2 mL) under a N<sub>2</sub> atmosphere was stirred at 60 °C for 12 h to afford **3s** (68.2 mg). Yellow solid (47% yield; eluent = pentane/ethyl acetate = 10:1); Mp = 263-265 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.92 (d, *J* = 7.8 Hz), 7.86 (s, 1H), 7.62 (d, *J* = 7.8 Hz), 7.56 (d, *J* = 8.4 Hz), 7.50-7.43 (m, 3H), 7.10 (d, *J* = 7.2 Hz, 1H), 7.02 (t, *J* = 7.2 Hz, 1H), 6.82-6.78 (m, 3H), 6.54 (t, *J* = 7.2 Hz, 1H), 4.99 (s, 1H), 4.47 (s, 1H), 3.83 (s, 3H), 3.49 (s, 1H), 2.47 (d, *J* = 12.6 Hz, 1H), 1.63 (dd, *J* = 14.4, 3 Hz, 1H), 1.09 (s, 3H), 0.50 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 175.9, 162.9, 157.5, 140.3, 135.0, 134.0, 133.1, 131.9, 130.5, 130.5, 130.1, 129.1 (<sup>2</sup>J<sub>C-F</sub> = 32.2 Hz); 128.7, 128.7, 126.3, 125.0, 124.8 (<sup>3</sup>J<sub>C-F</sub> = 3.5 Hz), 124.4 (<sup>1</sup>J<sub>C-F</sub> = 272.0 Hz), 123.3, 121.4, 114.0, 113.4, 111.8, 72.8, 55.7, 49.9, 49.3, 35.9, 34.9, 33.0, 28.4; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -62.4.



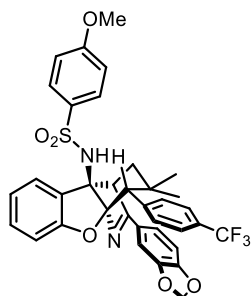
**N-(11-(2-bromophenyl)-3,3-dimethyl-4-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydro-9bH-4a,1-azeno)thienopyridine-9b-yl)-4-methoxybenzenesulfonamide (3v):**

According to the general procedure, a mixture consisting of oxime **4g** (0.2 mmol, 79.8 mg), azadiene **1n** (0.3 mmol, 137.7 mg), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.02 mmol, 14.2 mg), NaOAc (0.1 mmol, 8.2 mg) and MeCN (2 mL) under a N<sub>2</sub> atmosphere was stirred at 60 °C for 12 h to afford **3t** (85.8 mg). Yellow solid (59% yield; eluent = pentane/ethyl acetate = 10:1); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.92 (d, *J* = 7.8 Hz, 2H), 7.86 (s, 1H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.52-7.42 (m, 3H), 7.10 (d, *J* = 7.3 Hz, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.84-6.76 (m, 3H), 6.54 (t, *J* = 7.4 Hz, 1H), 4.86 (s, 1H), 4.53 (s, 1H), 3.83 (s, 3H), 3.48 (s, 1H), 2.46 (d, *J* = 12.7 Hz, 1H), 1.63 (dd, *J* = 11.4 Hz, 3 Hz, 1H), 1.09 (s, 3H), 0.50 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 177.0, 162.9, 157.6, 140.6, 133.2, 132.1, 131.9, 130.0, 128.9, 128.7, 127.8, 124.9, 124.75 (q, <sup>3</sup>J<sub>C-F</sub> = 3.0 Hz), 123.5 (q, <sup>1</sup>J<sub>C-F</sub> = 277.5 Hz), 121.3, 114., 113.4, 111.8, 72.8, 55.6, 50.1, 49.2, 35.8, 35.0, 33.0, 28.4; <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>): δ -62.38; HRMS (ESI): Calcd for C<sub>36</sub>H<sub>35</sub>BrF<sub>3</sub>N<sub>2</sub>O<sub>4</sub>S [M+H]<sup>+</sup> 727.1448, found 727.1451.



**N-(3,3-dimethyl-11-(naphthalen-2-yl)-4-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydro-9bH-4a,1-(azenometheno)dibenzo[b,d]furan-9b-yl)-4-methoxybenzenesulfonamide (3w):**

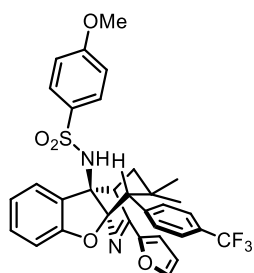
According to the general procedure, a mixture consisting of oxime **4h** (0.2 mmol, 74.2 mg), azadiene **1n** (0.3 mmol, 137.7 mg), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.02 mmol, 14.2 mg), NaOAc (0.1 mmol, 8.2 mg) and MeCN (2 mL) under a N<sub>2</sub> atmosphere was stirred at 60 °C for 12 h to afford **3u** (70.1 mg). Yellow solid (51% yield; eluent = pentane/ethyl acetate = 10:1); Mp = 285-287 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.31 (s, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 7.5 Hz, 1H), 7.90 (s, 1H), 7.87-7.84 (m, 2H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.57 – 7.55 (m, 2H), 7.14 (d, *J* = 7.4 Hz, 1H), 7.02 (t, *J* = 7.7 Hz, 1H), 6.88 – 6.78 (m, 3H), 6.53 (t, *J* = 7.4 Hz, 1H), 4.85 (s, 1H), 4.70 (s, 1H), 3.84 (s, 3H), 3.50 (s, 1H), 2.54 (d, *J* = 14.0 Hz, 1H), 1.72 (d, *J* = 14.3 Hz, 1H), 1.11 (s, 3H), 0.51 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 177.0, 170.2, 162.9, 157.6, 137.9, 135.2, 133.2, 132.9, 132.0, 130.0, 129.5, 129.1, 129.0, 128.8, 128.7, 128.1, 127.8, 126.8, 126.1, 125.0, 124.8 (<sup>3</sup>*J*<sub>C-F</sub> = 3.6 Hz), 123.8, 121.3, 114.0, 113.5, 111.8, 72.8, 55.7, 50.0, 49.2, 35.9, 35.2, 33.0, 28.4; <sup>19</sup>F NMR (376 MHz, DMSO): δ -60.72; HRMS (ESI): Calcd for C<sub>39</sub>H<sub>34</sub>F<sub>3</sub>N<sub>2</sub>O<sub>4</sub>S [M+H]<sup>+</sup> 683.2186, found 683.2186.



**N-(11-(benzo[d][1,3]dioxol-5-yl)-3,3-dimethyl-4-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydro-9bH-4a,1-(azenometheno)dibenzo[b,d]furan-9b-yl)-4-methoxybenzenesulfonamide (3x):**

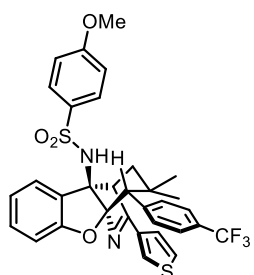
According to the general procedure, a mixture consisting of oxime **4i** (0.2 mmol, 73.0 mg), azadiene **1n** (0.3 mmol, 137.7 mg), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.02 mmol, 14.2 mg), NaOAc (0.1 mmol, 8.2 mg) and MeCN (2 mL) under an argon atmosphere was stirred at 60 °C for 12 h to afford **3v** (63.5 mg). Yellow solid (51% yield; eluent = pentane/ethyl acetate = 10:1); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.84 (s, 2H), 7.62 (d, *J* = 7.9 Hz, 2H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 1.2 Hz, 1H), 7.38 (dd, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.08 (d, *J* = 7.2 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.86-6.76 (m, 4H), 6.53 (t, *J* = 7.4 Hz, 1H), 6.00 (d, *J* = 3.8 Hz, 2H), 4.92 (s, 1H), 4.43 (s, 1H), 3.82 (s, 3H), 3.46 (s, 1H), 2.43 (dd, *J* = 13.8 Hz, 1.2 Hz, 1H), 1.61 (d, *J* = 3.0 Hz, 1H), 1.08 (s, 3H), 0.50 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 175.9, 162.9, 157.6, 151.1, 148.5, 140.6, 133.2, 131.9, 129.9, 129.2 (q, <sup>2</sup>*J*<sub>C-F</sub> = 22 Hz), 128.7, 126.7, 125.0, 124.7 (q, <sup>3</sup>*J*<sub>C-F</sub> = 3.6 Hz), 123.5, 121.1, 124.4 (q, <sup>1</sup>*J*<sub>C-F</sub> = 272

Hz), 114.0, 113.2, 111.8, 108.3, 107.2, 101.7, 72.7, 55.6, 49.9, 49.2, 35.9, 35.11, 32.0, 28.3; <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>): δ -62.4; HRMS (ESI): Calcd for C<sub>36</sub>H<sub>31</sub>F<sub>3</sub>N<sub>2</sub>O<sub>6</sub>S [M+H]<sup>+</sup> 677.1920, found 677.1918.



**N-(11-(furan-2-yl)-3,3-dimethyl-4-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydro-9bH-4a,1-(azenometheno)dibenzo[b,d]furan-9b-yl)-4-methoxybenzenesulfonamide (3y):**

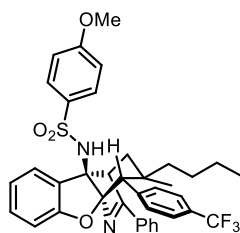
According to the general procedure, a mixture consisting of oxime **4j** (0.2 mmol, 62.2 mg), azadiene **1n** (0.3 mmol, 137.7 mg), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.04 mmol, 28.1 mg), NaOAc (0.1 mmol, 8.2 mg) and MeCN (2 mL) under a N<sub>2</sub> atmosphere was stirred at 60 °C for 12 h to afford **3w** (65.1 mg). White solid (51% yield; eluent = pentane/ethyl acetate = 10:1); Mp = 262 - 264 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.82 (s, 2H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.57 – 7.43 (m, 3H), 7.10 (d, *J* = 7.8 Hz, 1H), 7.05 (d, *J* = 3.2 Hz, 1H), 7.04 – 7.00 (m, 1H), 6.81 (d, *J* = 8.9 Hz, 2H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.56 (t, *J* = 7.2 Hz, 1H), 6.53 – 6.52 (m, 1H), 4.88 (s, 1H), 4.35 (s, 1H), 3.83 (s, 3H), 3.46 (s, 1H), 2.44 (dd, *J* = 14.4, 1.8, 1H), 1.62 (dd, *J* = 14.4, 3 Hz, 1H), 1.08 (s, 3H), 0.55 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 167.7, 162.9, 157.6, 148.1, 146.6, 140.3, 133.1, 132.0, 130.0, 129.1 (q, <sup>2</sup>*J*<sub>C-F</sub> = 32.2 Hz), 128.7, 125.0, 124.7 (q, <sup>3</sup>*J*<sub>C-F</sub> = 3.6 Hz), 124.4 (q, <sup>1</sup>*J*<sub>C-F</sub> = 272.4 Hz), 121.3, 116.0, 114.0, 113.4, 112.3, 112.0, 72.6, 55.7, 50.1, 35.8, 35.3, 32.9, 28.3; <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>): δ -62.4.



**N-(3,3-dimethyl-11-(thiophen-3-yl)-4-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydro-9bH-4a,1-(azenometheno)dibenzo[b,d]furan-9b-yl)-4-methoxybenzenesulfonamide (3z):**

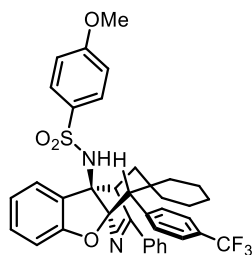
According to the general procedure, a mixture consisting of oxime **4k** (0.2 mmol, 65.4 mg), azadiene **1n** (0.3 mmol, 137.7 mg), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.04 mmol, 28.1 mg), NaOAc (0.1 mmol, 8.2 mg) and MeCN (2 mL) under a N<sub>2</sub> atmosphere was stirred at 80 °C for 12 h to afford **3x** (48.4 mg). White solid (37% yield; eluent = pentane/ethyl acetate = 10:1); Mp = 282 - 285 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.82 (s, 2H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.58 (d, *J* = 0.6 Hz, 1H), 7.56 (d, *J* = 9 Hz, 2H), 7.10 (d, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 3.2 Hz, 1H), 7.01 – 7.04 (m, 1H), 6.81 (d, *J* = 8.9 Hz, 2H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.56 (t, *J* = 7.2 Hz, 1H), 6.52 (dd, *J* = 3.3, 1.6 Hz, 1H), 4.88 (s, 1H), 4.35 (s, 1H), 3.83 (s, 3H), 3.46 (s, 1H), 2.44 (dd, *J* = 14.2, 1.9 Hz, 1H), 1.62 (dd, *J* = 14.4, 2.9 Hz, 1H), 1.08 (s, 3H), 0.55 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 172.5, 162.9, 157.5, 140.6, 136.0,

133.1, 132.0, 123.0, 129.5, 129.1 (q,  $^2J_{C-F} = 32.4$  Hz), 128.7, 127.1, 126.3, 125.0, 124.7 (q,  $^3J_{C-F} = 3.8$  Hz), 124.4 (q,  $^1J_{C-F} = 272.0$  Hz), 121.3, 114.0, 113.3, 111.8, 72.7, 55.7, 50.7, 49.9, 35.9, 35.2, 32.9, 28.4; 23;  $^{19}F$  NMR (565 MHz,  $CDCl_3$ ):  $\delta$  -62.4.



**N-(3-butyl-3-methyl-11-phenyl-4-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydro-9bH-4a,1-(azenometheno)dibenzo[b,d]furan-9b-yl)-4-methoxybenzenesulfonamide (3aa):**

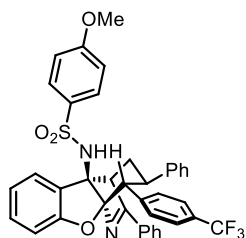
According to the general procedure, a mixture consisting of oxime **4l** (0.2 mmol, 72.6 mg), azadiene **1n** (0.3 mmol, 137.7 mg),  $Pd(PPh_3)_2Cl_2$  (0.02 mmol, 14.2 mg), NaOAc (0.1 mmol, 8.2 mg) and MeCN (2 mL) under a  $N_2$  atmosphere was stirred at 60 °C for 12 h to afford **3y** (51.2 mg). Yellow solid (38% yield; eluent = pentane/ethyl acetate = 10:1); Mp = 215-217 °C;  $^1H$  NMR (600 MHz,  $CDCl_3$ ):  $\delta$  7.85 (d,  $J = 7.4$  Hz, 2H), 7.76 (s, 2H), 7.55 (t,  $J = 6.8$  Hz, 4H), 7.41 (d,  $J = 6.9$  Hz, 1H), 7.36 (t,  $J = 7.2$  Hz, 2H), 7.14 (d,  $J = 7.3$  Hz, 1H), 6.96 (t,  $J = 7.6$  Hz, 1H), 6.77 (d,  $J = 8.5$  Hz, 2H), 6.72 (d,  $J = 7.9$  Hz, 1H), 6.53 (t,  $J = 7.4$  Hz, 1H), 4.80 (s, 1H), 4.50 (s, 1H), 3.76 (s, 3H), 3.36 (s, 1H), 2.30 (d,  $J = 14.1$  Hz, 1H), 1.46 (d,  $J = 13.4$  Hz, 1H), 1.37 – 1.28 (m, 1H), 1.20 – 1.15 (m, 1H), 1.13 – 0.96 (m, 4H), 0.77 (t,  $J = 6.5$  Hz, 3H), 0.43 (s, 3H);  $^{13}C$  NMR (151 MHz,  $CDCl_3$ ):  $\delta$  177.0, 162.9, 157.5, 140.7, 133.4, 132.2, 132.1, 130.0, 129.5, 128.9, 128.7, 127.8, 125.2, 124.7 ( $^3J_{C-F} = 3.8$  Hz), 124.4 ( $^1J_{C-F} = 272.6$  Hz), 121.5, 114.0, 113.3, 111.8, 72.9, 55.6, 49.5, 49.0, 45.1, 38.6, 32.5, 25.9, 23.5, 14.1;  $^{19}F$  NMR (565 MHz,  $CDCl_3$ ):  $\delta$  62.4; HRMS (ESI): Calcd for  $C_{38}H_{37}F_3N_2O_4S$   $[M + Na]^+$  697.2318, found 673.2308.



**4-methoxy-N-(11'-phenyl-4'-(4-(trifluoromethyl)phenyl)-1',2'-dihydro-4'H,9b'H-spiro[cyclohexane-1,3'-[4a,1](azenometheno)dibenzo[b,d]furan]-9b'-yl)benzenesulfonamide (3ab):**

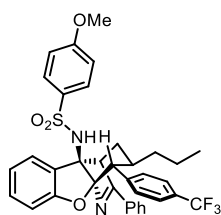
According to the general procedure, a mixture consisting of oxime **4m** (0.2 mmol, 72.2 mg), azadiene **1n** (0.3 mmol, 137.7 mg),  $Pd(PPh_3)_2Cl_2$  (0.02 mmol, 14.2 mg), NaOAc (0.1 mmol, 8.2 mg) and MeCN (2 mL) under an argon atmosphere was stirred at 60 °C for 12 h to afford **3aa** (60.1 mg). Yellow solid (44% yield; eluent = pentane/ethyl acetate = 10:1); Mp = 252 - 255 °C;  $^1H$  NMR (600 MHz,  $CDCl_3$ ):  $\delta$  7.89 (d,  $J = 7.3$  Hz, 2H), 7.67 – 7.53 (m, 4H), 7.50 – 7.37 (m, 3H), 7.11 (d,  $J = 7.2$  Hz, 1H), 7.00 (t,  $J = 7.5$  Hz, 1H), 6.81 (d,  $J = 8.4$  Hz, 2H), 6.76 (d,  $J = 7.9$  Hz, 1H), 6.54 (t,  $J = 7.2$  Hz, 1H), 4.98 (s, 1H), 4.54 (s, 1H), 3.82 (s, 3H), 3.36 (s, 1H), 2.07 (dd,  $J = 32.1, 13.8$  Hz, 2H), 1.40-1.50 (m, 2H), 1.40 – 1.19 (m, 4H), 1.10-1.01 (m, 1H), 1.00-0.90 (m, 1H),

0.70-0.60(m, 1H), 0.39 (t,  $J = 12.0$  Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  176.5, 162.9, 157.5, 140.3, 133.3, 132.5, 132.0, 131.9, 129.9, 129.0, 128.9, 128.7, 127.6, 125.1, 124.6, 124.5 ( $^1J_{\text{C-F}} = 273.3$  Hz), 121.3, 114.0, 113.2, 111.8, 77.0, 72.8, 55.7, 52.1, 49.1, 41.0, 38.9, 33.0, 26.5, 24.9, 22.0, 21.5;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -62.3; HRMS (ESI): Calcd for  $\text{C}_{38}\text{H}_{36}\text{F}_3\text{N}_2\text{O}_4\text{S}$  [ $\text{M} + \text{H}$ ] $^+$  673.2342, found 673.2343.



**N-(3,11-diphenyl-4-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydro-9bH-4a,1-(azenometheno)dibenzo[b,d]furan-9b-yl)-4-methoxybenzenesulfonamide (3ac):**

According to the general procedure, a mixture consisting of oxime **4n** (0.2 mmol, 73.8 mg), azadiene **1n** (0.3 mmol, 137.7 mg),  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (0.02 mmol, 14.2 mg), NaOAc (0.1 mmol, 8.2 mg) and MeCN (2 mL) under a  $\text{N}_2$  atmosphere was stirred at 60 °C for 12 h to afford **3ab** (41 mg). Yellow solid (30% yield; eluent = pentane/ethyl acetate = 10:1); Mp = 254-256 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.98 (d,  $J = 7.4$  Hz, 2H), 7.72 (d,  $J = 8.8$  Hz, 2H), 7.54 (t,  $J = 7.2$  Hz, 1H), 7.51–7.41 (m, 6H), 7.23 (d,  $J = 7.3$  Hz, 1H), 7.12–7.01 (m, 4H), 6.90 (d,  $J = 8.8$  Hz, 2H), 6.84 (d,  $J = 8.4$  Hz, 2H), 6.81 (d,  $J = 7.2$  Hz, 2H), 6.66 (t,  $J = 7.5$  Hz, 1H), 5.02 (s, 1H), 4.79 (s, 1H), 3.86 (s, 3H), 3.65 (d,  $J = 9.7$  Hz, 1H), 2.70–2.60 (m, 2H), 1.96 (dd,  $J = 7.6, 3.6$  Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  175.6, 163.2, 157.5, 141.7, 141.3, 133.2, 132.2, 131.6, 130.4, 130.1, 129.4, 129.1 (q,  $^2J_{\text{C-F}} = 32.3$  Hz), 128.9, 128.8, 128.4, 128.3, 128.0, 126.8, 125.0 (q,  $^3J_{\text{C-F}} = 3.2$  Hz), 124.3 (q,  $^1J_{\text{C-F}} = 273.3$  Hz), 121.7, 114.3, 113.0, 112.0, 72.5, 55.7, 50.0, 47.7, 46.9, 28.9;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -62.5; HRMS (ESI): Calcd for  $\text{C}_{39}\text{H}_{32}\text{F}_3\text{N}_2\text{O}_4\text{S}$  [ $\text{M} + \text{H}$ ] $^+$  681.2029, found 681.2030.



**4-methoxy-N-(11-phenyl-3-propyl-4-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydro-9bH-4a,1-(azenometheno)dibenzo[b,d]furan-9b-yl)benzenesulfonamide (3ad):**

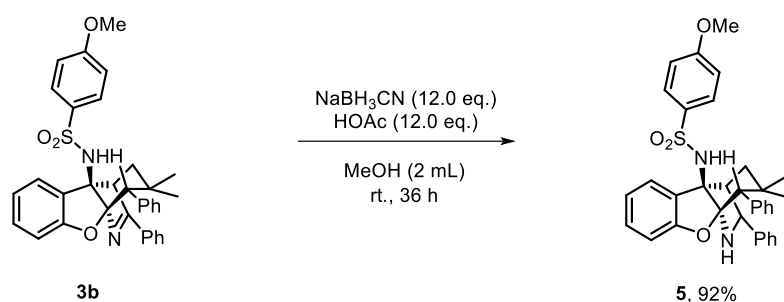
According to the general procedure, a mixture consisting of oxime **4o** (0.2 mmol, 69.8 mg), azadiene **1n** (0.3 mmol, 137.7 mg),  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (0.02 mmol, 14.2 mg), NaOAc (0.1 mmol, 8.2 mg) and MeCN (2 mL) under a  $\text{N}_2$  atmosphere was stirred at 60 °C for 12 h to afford **3ac** (42.3 mg). Yellow solid (32% yield; eluent = pentane/ethyl acetate = 10:1); Mp = 247 - 250 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.90 (d,  $J = 7.3$  Hz, 2H), 7.69 – 7.53 (m, 6H), 7.53 – 7.39 (m, 3H), 7.03 (d,  $J = 7.2$  Hz, 1H), 6.97 (t,  $J = 7.4$  Hz, 1H), 6.80 (d,  $J = 8.5$  Hz, 2H), 6.74 (d,  $J = 7.9$  Hz, 1H), 6.49 (t,  $J = 7.3$  Hz, 1H), 5.06 (s, 1H), 4.57 (s, 1H), 3.82 (s, 3H), 3.19 (d,  $J = 9.9$  Hz, 1H), 2.10 (t,  $J = 11.9$  Hz, 1H), 1.89 – 1.80 (m, 1H), 1.67 – 1.62 (m, 1H), 1.26 – 1.08 (m, 3H), 0.97 – 0.86 (m, 1H), 0.67

(t,  $J = 6.5$  Hz, 3H);  **$^{13}\text{C}$  NMR** (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  175.8, 162.8, 157.6, 142.7, 133.3, 132.1, 131.7, 130.5, 129.8, 128.9, 128.7, 128.6, 127.8, 125.2 ( $^3J_{\text{C-F}} = 3.9$  Hz), 124.9, 121.3, 114.01, 112.8, 111.8, 71.8, 55.6, 49.5, 46.3, 38.4, 35.5, 25.9, 19.9, 14.1;  **$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -62.4; **HRMS (ESI)**: Calcd for  $\text{C}_{36}\text{H}_{34}\text{F}_3\text{N}_2\text{O}_4\text{S}$   $[\text{M} + \text{H}]^+$  647.2186, found 647.2189.



## 6. Reduction of Product 3b

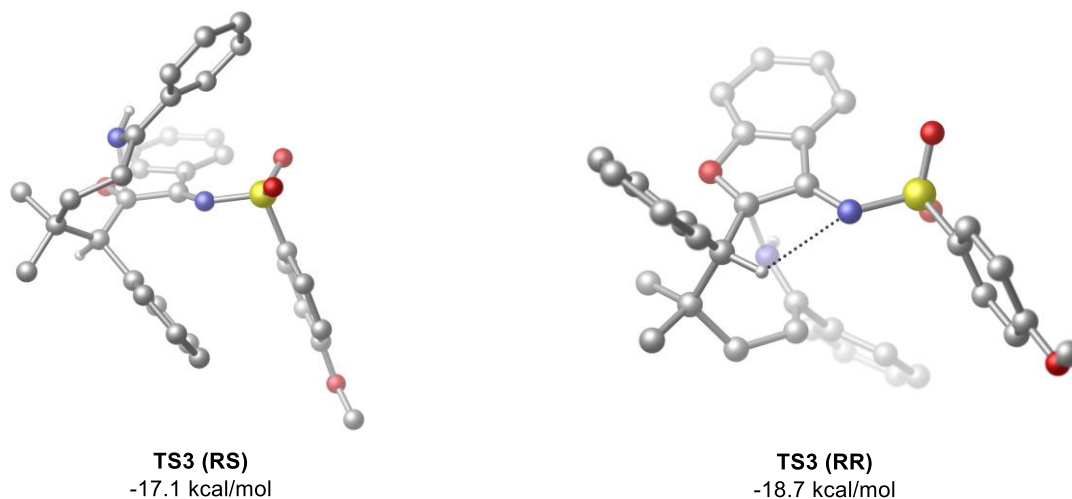
A 10 mL of Schlenk tube equipped with a stirrer bar was charged with **3b** (0.2 mmol, 112.8 mg), NaBH<sub>3</sub>CN (2.4 mmol, 150.8 mg), followed by addition of AcOH (2.4 mmol, 144.1 mg) and MeOH (2 mL). The Schlenk tube was sealed with a Teflon screwcap and the reaction mixture was stirred at room temperature for 36 h. The reaction was neutralized with 1M NaOH, and extracted with EA. The organic phases were combined, dried and subjected to column chromatography on silica gel to afford the product **5** (104.1 mg).



**5**: White solid; (92% yield, eluent = petroleum ether/EtOAc (8:1)); Mp = 237-238 °C; **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ 7.71 (s, 2H), 7.59 (d, *J* = 8.7 Hz, 2H), 7.37–7.28 (m, 8H), 7.18 (t, *J* = 6.0 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.86–6.80 (m, 3H), 6.71 (t, *J* = 7.4 Hz, 1H), 4.79 (s, 1H), 4.50 (d, *J* = 5.0 Hz, 1H), 3.86 (s, 1H), 3.84 (s, 3H), 3.37 (s, 1H), 2.13 (dd, *J* = 15.0, 4.1 Hz, 1H), 1.88 (d, *J* = 8.2 Hz, 1H), 1.71 (d, *J* = 14.9 Hz, 1H), 0.95 (s, 3H), 0.55 (s, 3H); **<sup>13</sup>C NMR** (151 MHz, DMSO-*d*<sub>6</sub>): δ 162.1, 159.3, 142.4, 139.6, 135.4, 131.3, 129.7, 129.4, 128.5, 128.2, 127.7, 126.8, 126.6, 126.1, 125.3, 120.9, 114.1, 112.5, 106.4, 72.6, 62.0, 56.1, 52.9, 45.2, 38.1, 35.6, 34.0, 30.0; **HRMS (ESI)**: Calcd for C<sub>34</sub>H<sub>34</sub>N<sub>2</sub>O<sub>4</sub>S [M+H]<sup>+</sup> 567.2312, found 567.2311.

## 7. Computational Studies

All the calculations in this study were performed using the Gaussian 16 program package.<sup>[3]</sup> All the geometries were optimized at the M06-2X<sup>[4]</sup>/Def2-SVP level, and the solvent effect was utilized the polarizable continuum model using integral equation formalism model (IEFPCM) in acetonitrile solvent.<sup>[5]</sup> All the optimized stationary points had been identified as minima (zero imaginary frequencies) and transition states (one imaginary frequency), via the vibrational analysis. The solution-translational entropy correction has been calculated with THERMO program.<sup>[6]</sup>



**Scheme S1** DFT studies regarding the diastereoselectivity.

In order to understand the origin of diastereoselectivity, the corresponding transition state **TS3 (RS)** have been located at the same level (Scheme S1). The calculated results show the free energy barrier for the **TS3 (RS)** would be higher than that of **TS3 (RR)**. Furthermore, the possible hydrogen bond C-H $\cdots$ N would play an important role in the diastereoselectivity.

**Table S10.** The calculated free energies for the species in the calculation.

Species	G(a,u)	Species	G(a,u)
<b>4a</b>	-1056.07445	CO <sub>2</sub>	-188.37136
CH <sub>2</sub> O	-114.34964	<i>t</i> BuO $\cdot$	-232.60698
<b>M1</b>	-520.76952	<b>TS1</b>	-520.74816
<b>M2</b>	-520.76747	<b>1b</b>	-1600.51672
<b>TS2</b>	-2121.28258	<b>M3</b>	-2121.3228
<b>TS3 (RR)</b>	-2121.29294	<b>M4</b>	-2121.32515
<b>TS4</b>	-2121.29057	<b>M5</b>	-2121.32143
<b>TS5</b>	-2121.2904	<b>Pre-P</b>	-2121.33034
<b>TS6</b>	-2121.28552	<b>M6</b>	-2121.32800
<b>TS7</b>	-2121.28814	<b>M7</b>	-2121.31055
<b>TS8</b>	-2121.2887	<b>TS3 (RS)</b>	-2121.29046

**Table S11.** The coordinates for the calculated species

<b>4a</b>				<b>1b</b>			
C	-2.79382	0.01356	0.22618	C	-4.84230	2.33347	-0.12061
C	-1.37663	-0.35383	0.57431	C	-6.03637	2.42727	-0.85454
C	-0.37049	0.63066	-0.03816	C	-6.67329	3.63243	-1.12080
H	-1.28350	-0.35077	1.66823	C	-6.06811	4.78263	-0.62339
H	-1.16511	-1.37432	0.22506	C	-4.86710	4.72596	0.10316
C	1.08871	0.18201	0.08232	C	-4.24286	3.51162	0.35621
H	-0.60910	0.77997	-1.10470	C	-4.53910	0.89910	-0.04798
H	-0.50005	1.61267	0.44931	C	-5.63427	0.26127	-0.81953
H	1.18231	-0.78208	-0.44973	H	-7.59943	3.66057	-1.69335
C	2.00760	1.19402	-0.59882	H	-6.53595	5.75051	-0.80978
H	1.94220	2.17127	-0.09341	H	-4.41284	5.64844	0.46433
H	3.05657	0.86572	-0.56154	H	-3.29460	3.47396	0.88437
H	1.73206	1.34082	-1.65363	O	-6.50002	1.22288	-1.27243
C	1.50841	-0.03348	1.53511	C	-5.76599	-1.05836	-1.04772
H	1.37983	0.89686	2.11114	H	-4.97015	-1.65563	-0.59551
H	0.91892	-0.82049	2.02703	C	-6.79417	-1.77569	-1.79380
H	2.56760	-0.32317	1.59663	C	-7.88030	-1.14595	-2.43293
N	-3.47066	0.88523	0.87579	C	-6.68176	-3.17580	-1.87480
C	-3.47121	-0.60065	-0.94994	C	-8.81764	-1.90385	-3.12766
C	-4.86403	-0.50550	-1.10142	H	-7.98640	-0.06382	-2.38373
C	-2.72991	-1.27144	-1.93177	C	-7.62219	-3.92889	-2.57069
C	-5.49575	-1.06939	-2.20460	H	-5.84215	-3.67082	-1.38269
H	-5.44344	0.01237	-0.33709	C	-8.69390	-3.29354	-3.19968
C	-3.36527	-1.83091	-3.04132	H	-9.65455	-1.40574	-3.61935
H	-1.64547	-1.35433	-1.84424	H	-7.51875	-5.01349	-2.62277
C	-4.74815	-1.73434	-3.18038	H	-9.43400	-3.87982	-3.74643
H	-6.57976	-0.99394	-2.30365	N	-3.64645	0.15399	0.51242
H	-2.77272	-2.34561	-3.79903	S	-2.37251	0.72643	1.41602
H	-5.24469	-2.17763	-4.04482	O	-1.54614	-0.44325	1.66954
O	-2.77247	1.43183	1.92508	O	-1.74384	1.89114	0.79355
C	-3.62934	2.24235	2.69054	C	-3.12312	1.22880	2.93881
H	-4.34333	1.64519	3.27547	C	-2.88358	2.50236	3.44107
H	-4.18414	2.93941	2.04175	C	-3.89143	0.30252	3.65700
C	-2.79013	3.03906	3.66965	C	-3.43357	2.88160	4.66517
O	-3.01633	3.15534	4.83508	H	-2.25657	3.19976	2.88376
O	-1.76776	3.62741	3.01225	C	-4.44184	0.67696	4.86868
O	-0.94362	4.36251	3.88226	H	-4.05717	-0.70152	3.26259
C	0.34302	3.70303	3.97600	C	-4.21986	1.96979	5.38210
C	0.16091	2.26517	4.44647	H	-3.23806	3.88181	5.04694
C	1.04366	3.77950	2.62576	H	-5.05006	-0.01486	5.45150
C	1.05069	4.54858	5.02535	O	-4.79475	2.24014	6.56182
H	-0.41382	2.24037	5.38265	C	-4.61083	3.52002	7.13157

H	-0.36483	1.66647	3.68763	H	-5.01012	4.30731	6.47407
H	1.14373	1.80550	4.62045	H	-5.16320	3.52151	8.07642
H	1.15276	4.82725	2.31247	H	-3.54637	3.71627	7.33155
H	2.04245	3.32494	2.69138	<b>CO<sub>2</sub></b>			
H	0.46591	3.24064	1.86178	C	0.48651	0.34022	0.79760
H	2.07283	4.17377	5.16862	O	1.03221	0.21480	1.80915
H	1.10295	5.59696	4.70090	O	-0.05920	0.46564	-0.21394
H	0.51575	4.49730	5.98339	<b>CH<sub>2</sub>O</b>			
<b>tBuO·</b>				C	1.81295	-0.13252	-0.09292
C	-4.87513	0.11519	-0.01991	O	3.01266	-0.13246	-0.09296
C	-3.32769	0.10196	0.00450	H	1.22159	0.80995	-0.09293
H	-5.24962	1.14718	-0.01574	H	1.22153	-1.07495	-0.09289
H	-5.24816	-0.40494	-0.91181	<b>M1</b>			
H	-5.23510	-0.40415	0.87891	C	-2.33314	-0.41932	0.25229
C	-2.81228	-1.33986	-0.03434	C	-1.07799	0.42465	0.08957
C	-2.81214	0.85837	1.23169	C	0.00422	-0.31100	-0.70480
H	-1.71351	-1.34533	-0.07254	H	-1.35751	1.37140	-0.39602
H	-3.13077	-1.89188	0.86113	H	-0.70360	0.67345	1.09278
H	-3.19705	-1.85215	-0.92693	C	1.31400	0.47229	-0.84063
H	-3.12933	0.35841	2.15765	H	0.20794	-1.27236	-0.20562
H	-1.71338	0.89514	1.21662	H	-0.36960	-0.55699	-1.71395
H	-3.19781	1.88728	1.22972	H	1.67346	0.70521	0.17741
O	-2.98851	0.76685	-1.15475	C	2.36797	-0.38968	-1.53328
<b>TS1</b>				H	2.04482	-0.64009	-2.55641
C	0.70506	1.08727	0.37761	H	3.32915	0.14001	-1.60299
C	-0.71931	0.65272	0.72036	H	2.53432	-1.33206	-0.99113
C	-1.59703	0.56946	-0.52503	C	1.11783	1.78845	-1.59229
H	-0.65812	-0.32000	1.23765	H	0.70140	1.59725	-2.59522
H	-1.14780	1.35785	1.44565	H	0.43672	2.47224	-1.06585
C	-0.89474	-0.13738	-1.66817	H	2.07705	2.31088	-1.72095
H	-2.54680	0.06201	-0.27647	N	-2.63982	-0.85304	1.38933
H	-1.85599	1.59161	-0.84431	C	-3.17446	-0.74506	-0.94680
H	0.27075	0.44078	-1.49802	C	-3.08384	0.00941	-2.12240
C	-0.63364	-1.61027	-1.44210	C	-4.08267	-1.81199	-0.88505
H	-1.58354	-2.17437	-1.44679	C	-3.89423	-0.29495	-3.21639
H	0.00385	-2.02680	-2.23567	H	-2.38269	0.84238	-2.19284
H	-0.13965	-1.79751	-0.47702	C	-4.88780	-2.11505	-1.97878
C	-1.41550	0.19951	-3.04543	H	-4.14670	-2.40531	0.02848
H	-2.44087	-0.19291	-3.17395	C	-4.79618	-1.35584	-3.14774
H	-1.45416	1.28670	-3.20722	H	-3.81761	0.30130	-4.12664
H	-0.79020	-0.24898	-3.83102	H	-5.58737	-2.95026	-1.92177
N	1.20816	0.97830	-0.77961	H	-5.42585	-1.59378	-4.00633
C	1.55297	1.64016	1.48999	<b>M2</b>			
C	1.18089	1.49778	2.83230	C	-0.03281	-0.31669	-0.43979

C	2.75445	2.29616	1.18386	C	-0.87387	0.93375	-0.60720
C	1.99610	1.99876	3.84858	C	-2.33725	0.69568	-0.96753
H	0.25664	0.98445	3.09957	H	-0.79840	1.52686	0.31914
C	3.56196	2.80273	2.19713	H	-0.40380	1.55247	-1.38798
H	3.03965	2.40273	0.13660	C	-3.16335	-0.02802	0.05831
C	3.18494	2.65442	3.53443	H	-2.79411	1.68747	-1.16363
H	1.69741	1.87492	4.89060	H	-2.39925	0.16087	-1.93211
H	4.49080	3.31713	1.94541	H	-1.48064	-1.50488	-0.72205
H	3.81843	3.05080	4.32941	C	-2.87491	0.17210	1.51135
<b>TS2</b>				H	-3.07995	1.21427	1.82943
C	-5.55180	-0.27421	0.03628	H	-3.50019	-0.48475	2.13255
C	-4.18612	-0.92070	0.18439	H	-1.82060	-0.03091	1.75871
C	-3.05095	0.09291	0.36432	C	-4.53880	-0.44223	-0.35283
H	-4.22110	-1.60950	1.04406	H	-5.24128	0.41569	-0.33395
H	-4.00622	-1.54898	-0.70251	H	-4.55273	-0.83832	-1.37986
C	-1.70819	-0.55270	0.51569	H	-4.95189	-1.20655	0.32209
H	-3.03625	0.76659	-0.50808	N	-0.47292	-1.50753	-0.53706
H	-3.27105	0.70686	1.25167	C	1.42569	-0.11972	-0.14064
H	-4.90928	1.51004	0.22150	C	1.99151	1.15432	-0.00102
C	-1.10618	-1.14556	-0.71486	C	2.25238	-1.24336	0.00746
H	-0.08572	-1.51322	-0.54553	C	3.35106	1.30024	0.28041
H	-1.71057	-2.01709	-1.02970	H	1.37873	2.04980	-0.10735
H	-1.11007	-0.43306	-1.55429	C	3.60713	-1.09859	0.28675
C	-1.37465	-1.19080	1.82459	H	1.80348	-2.23061	-0.10223
H	-0.29857	-1.40545	1.89882	C	4.16212	0.17663	0.42432
H	-1.68898	-0.56656	2.67464	H	3.77548	2.29963	0.38783
H	-1.91121	-2.15555	1.91287	H	4.23660	-1.98313	0.39735
N	-5.77203	0.97859	0.07662	H	5.22481	0.29224	0.64346
C	-6.71758	-1.19562	-0.17636	<b>M3</b>			
C	-6.57385	-2.58896	-0.18124	C	-1.66209	3.06906	0.84255
C	-7.99383	-0.64847	-0.37743	C	-2.59056	2.12097	0.10891
C	-7.68125	-3.41539	-0.37930	C	-3.25934	1.05620	0.97458
H	-5.59691	-3.04893	-0.02959	H	-3.35808	2.72545	-0.40124
C	-9.09685	-1.47160	-0.57656	H	-1.99018	1.66470	-0.69194
H	-8.09687	0.43651	-0.37372	C	-3.73449	-0.20543	0.22192
C	-8.94397	-2.86063	-0.57763	H	-2.57581	0.72966	1.77741
H	-7.55262	-4.49871	-0.37889	H	-4.13183	1.49280	1.48731
H	-10.08268	-1.02993	-0.73165	H	-2.08005	2.41112	2.57347
H	-9.80826	-3.50821	-0.73368	C	-4.66133	0.17771	-0.93484
C	2.13346	0.50388	-1.62208	H	-5.08349	-0.71735	-1.41404
C	1.36259	1.50656	-2.23468	H	-5.49630	0.78585	-0.55496
C	1.56807	1.93785	-3.53935	H	-4.13604	0.75974	-1.70691
C	2.59651	1.32012	-4.24488	C	-4.50671	-1.08394	1.20986
C	3.38287	0.30970	-3.66318	H	-4.89449	-1.98928	0.72339

C	3.16135	-0.10976	-2.35835	H	-3.88374	-1.38429	2.06460
C	1.60905	0.38887	-0.26307	H	-5.36629	-0.51844	1.59922
C	0.52899	1.34789	-0.20952	N	-1.49724	3.10790	2.10465
H	0.94696	2.71929	-3.97562	C	-0.88670	4.03438	-0.00487
H	2.79307	1.62468	-5.27391	C	-1.14550	4.20066	-1.37079
H	4.17474	-0.15662	-4.24953	C	0.12762	4.80063	0.58671
H	3.75586	-0.90902	-1.92318	C	-0.41627	5.12113	-2.12497
O	0.40563	1.99865	-1.40652	H	-1.92338	3.61813	-1.86516
C	-0.33343	1.49771	0.85043	C	0.85896	5.71379	-0.16487
H	0.01480	0.98294	1.74768	H	0.32933	4.65800	1.64801
C	-1.38857	2.49255	1.02426	C	0.58709	5.87911	-1.52588
C	-1.97585	3.19345	-0.04545	H	-0.63371	5.24213	-3.18732
C	-1.89016	2.69893	2.32235	H	1.64784	6.29980	0.30988
C	-3.04215	4.05921	0.18391	H	1.16015	6.59556	-2.11691
H	-1.60750	3.04262	-1.05937	C	0.50973	-0.78776	1.89534
C	-2.95236	3.56967	2.54764	C	-0.37856	-1.70984	2.46204
H	-1.44007	2.16052	3.15947	C	-0.15687	-2.38604	3.64929
C	-3.53628	4.24866	1.47678	C	1.04004	-2.09968	4.30420
H	-3.49584	4.58873	-0.65526	C	1.94988	-1.16995	3.77882
H	-3.32963	3.71542	3.56078	C	1.69981	-0.50393	2.58186
H	-4.37333	4.92678	1.64889	C	-0.13749	-0.35552	0.64532
N	1.86872	-0.34323	0.79750	C	-1.37848	-1.06821	0.61783
S	2.79067	-1.69009	0.76155	H	-0.88480	-3.09607	4.03993
O	2.52400	-2.37694	2.02203	H	1.26667	-2.60357	5.24454
O	2.59006	-2.45384	-0.47672	H	2.87064	-0.95755	4.32259
C	4.47712	-1.13474	0.78802	H	2.39789	0.23727	2.20251
C	5.41608	-1.76110	-0.02362	O	-1.50459	-1.85388	1.68685
C	4.85981	-0.13082	1.68528	C	-2.47729	-0.95227	-0.37551
C	6.75527	-1.37662	0.03446	H	-2.06024	-0.28872	-1.14481
H	5.09982	-2.55095	-0.70738	C	-2.79828	-2.26776	-1.07140
C	6.18680	0.25712	1.74315	C	-3.00124	-3.46668	-0.37503
H	4.11638	0.34722	2.32575	C	-2.91236	-2.27619	-2.46722
C	7.14494	-0.36123	0.91816	C	-3.31762	-4.63973	-1.06064
H	7.47892	-1.87201	-0.61036	H	-2.91003	-3.48779	0.71103
H	6.51881	1.04213	2.42283	C	-3.23465	-3.44674	-3.15315
O	8.40454	0.08373	1.04168	H	-2.74670	-1.35058	-3.02342
C	9.41261	-0.49589	0.23979	C	-3.43880	-4.63361	-2.45029
H	9.20230	-0.34779	-0.83056	H	-3.47127	-5.56477	-0.50273
H	10.34625	0.01323	0.49873	H	-3.32083	-3.43065	-4.24067
H	9.51447	-1.57242	0.44583	H	-3.68723	-5.55218	-2.98403
<b>TS3 (RR)</b>				N	0.16168	0.44685	-0.35943
C	-3.52409	-0.33679	-0.29551	S	1.59879	1.26961	-0.45176
C	-3.73512	1.08301	-0.74387	O	1.50801	2.06015	-1.66916
C	-3.56114	2.13688	0.36370	O	1.91537	1.95645	0.80200

H	-2.99697	1.25800	-1.53887	C	2.80397	-0.00832	-0.70337
H	-4.72488	1.19809	-1.20043	C	4.00063	0.03365	0.00274
C	-2.36748	2.04659	1.34578	C	2.57418	-0.99330	-1.67261
H	-3.52498	3.11208	-0.14488	C	4.98525	-0.92360	-0.23808
H	-4.47282	2.16107	0.98206	H	4.16746	0.81779	0.74315
H	-2.18686	-1.60334	0.42314	C	3.54533	-1.94955	-1.90860
C	-2.62393	1.05545	2.50050	H	1.63604	-1.01110	-2.23053
H	-1.93160	1.27677	3.32670	C	4.75932	-1.92173	-1.19579
H	-3.64943	1.17668	2.88129	H	5.91688	-0.88067	0.32314
H	-2.47740	0.00497	2.23445	H	3.39765	-2.73489	-2.65006
C	-2.27239	3.43039	2.01427	O	5.64170	-2.88466	-1.49776
H	-1.41765	3.47226	2.70643	C	6.89463	-2.88785	-0.84487
H	-2.15846	4.23789	1.27838	H	6.77642	-3.01971	0.24155
H	-3.18879	3.61842	2.59361	H	7.45533	-3.73427	-1.25373
N	-2.34419	-0.65655	0.06914	H	7.44555	-1.95544	-1.04211
C	-4.65196	-1.30078	-0.24685	<b>M4</b>			
C	-5.94736	-0.84627	0.03477	C	-2.07397	2.11693	-0.06466
C	-4.42607	-2.67081	-0.44353	C	-3.52396	0.03611	-1.97015
C	-6.99742	-1.75524	0.14512	C	-2.06614	0.23909	-2.41371
H	-6.13529	0.21745	0.19066	H	-3.77735	-1.02954	-1.89087
C	-5.48151	-3.57295	-0.35290	H	-4.18843	0.48350	-2.72486
H	-3.42627	-3.03014	-0.69606	H	-2.02829	0.89151	1.57180
C	-6.76658	-3.11692	-0.05184	C	-1.75249	1.75125	-2.55249
H	-8.00013	-1.39781	0.38193	H	-0.97402	1.88362	-3.32138
H	-5.30220	-4.63531	-0.52179	H	-2.65722	2.25475	-2.93023
H	-7.59189	-3.82622	0.02412	C	-1.91242	-0.36183	-3.81869
C	0.64846	-1.09488	-1.07089	H	-0.85931	-0.35663	-4.13882
C	-0.05489	-0.37397	-2.05350	H	-2.27913	-1.39534	-3.86734
C	0.02303	-0.62696	-3.41109	H	-2.49175	0.24207	-4.53352
C	0.85794	-1.67497	-3.80587	N	-1.73504	0.95244	0.60178
C	1.56542	-2.42731	-2.85611	C	-3.16114	2.90667	0.42507
C	1.47109	-2.15588	-1.49374	C	-3.40894	4.22249	-0.05856
C	0.28524	-0.47894	0.19527	C	-4.06061	2.40833	1.41130
C	-0.75161	0.48382	-0.14416	C	-4.46025	4.98387	0.42836
H	-0.54308	-0.02999	-4.12564	H	-2.76044	4.65356	-0.82071
H	0.95293	-1.91379	-4.86580	C	-5.10916	3.18306	1.88998
H	2.19866	-3.24997	-3.19065	H	-3.95852	1.38521	1.77718
H	2.00014	-2.76785	-0.76699	C	-5.32049	4.47963	1.41195
O	-0.80947	0.62133	-1.49327	H	-4.61357	5.99078	0.03528
C	-0.96821	1.72703	0.70974	H	-5.78224	2.76317	2.64009
H	-0.33833	1.51387	1.58593	H	-6.14595	5.08382	1.78960
C	-0.32144	2.91222	0.00467	C	-0.51658	-2.07230	1.51011
C	-0.85223	3.47448	-1.16492	C	-1.87133	-2.24064	1.17872
C	0.82837	3.48697	0.55608	C	-2.61206	-3.33360	1.62596

C	-0.25531	4.58687	-1.75453	C	-1.95482	-4.25768	2.42972
H	-1.73674	3.03728	-1.62999	C	-0.60134	-4.10507	2.78214
C	1.43260	4.59865	-0.03432	C	0.12759	-3.01534	2.33022
H	1.24988	3.06507	1.47203	C	-0.10091	-0.84735	0.84747
C	0.88963	5.15391	-1.19106	C	-1.33829	-0.31446	0.07728
H	-0.68575	5.01209	-2.66260	H	-3.65969	-3.44364	1.34854
H	2.32758	5.03163	0.41529	H	-2.50547	-5.12559	2.79665
H	1.35652	6.02383	-1.65544	H	-0.12254	-4.85215	3.41474
N	0.61825	-0.63232	1.47989	H	1.17472	-2.89738	2.60099
S	1.75150	-1.68871	1.94956	O	-2.37758	-1.27167	0.39877
O	1.90521	-1.52038	3.39291	C	-1.01625	-0.40008	-1.44271
O	1.48562	-3.05669	1.47940	H	-0.09292	0.18552	-1.55312
C	3.26802	-1.16031	1.16848	C	-0.60331	-1.83348	-1.76086
C	4.20711	-2.11863	0.80429	C	-1.51533	-2.89665	-1.83307
C	3.53289	0.20082	0.98760	C	0.75501	-2.11521	-1.94977
C	5.42617	-1.73006	0.25004	C	-1.07843	-4.19638	-2.08160
H	3.98102	-3.17728	0.94394	H	-2.57952	-2.71344	-1.68204
C	4.73923	0.59342	0.43042	C	1.19752	-3.41544	-2.19480
H	2.78659	0.94553	1.27001	H	1.48237	-1.30337	-1.87445
C	5.69642	-0.36768	0.06079	C	0.28050	-4.46205	-2.26053
H	6.14936	-2.49305	-0.03259	H	-1.80566	-5.00833	-2.13306
H	4.97045	1.64633	0.26629	H	2.26351	-3.60736	-2.32699
O	6.83723	0.10536	-0.46901	H	0.62066	-5.48144	-2.44957
C	7.83696	-0.81406	-0.85383	N	0.98111	-0.17254	0.73726
H	7.47216	-1.49333	-1.63986	S	2.39139	-0.73821	1.45285
H	8.67029	-0.22197	-1.24532	O	2.26119	-0.62632	2.90294
H	8.18394	-1.40728	0.00637	O	2.73833	-2.03399	0.87413
<b>TS4</b>				C	3.55896	0.45406	0.88991
C	2.83511	0.20716	-0.58300	C	4.32230	0.17202	-0.23731
C	1.38905	2.78353	-1.64111	C	3.69910	1.66190	1.58097
C	0.39646	1.61193	-1.73570	C	5.24166	1.11074	-0.70089
H	0.87008	3.70986	-1.35960	H	4.20447	-0.78515	-0.74711
H	1.83480	2.94374	-2.63497	C	4.61124	2.59568	1.12207
H	2.56081	0.93064	1.29028	H	3.10116	1.85729	2.47232
C	1.04327	0.41064	-2.44489	C	5.38668	2.32948	-0.02259
H	0.26218	-0.34997	-2.61605	H	5.83790	0.88050	-1.58183
H	1.36134	0.75950	-3.43931	H	4.75341	3.54816	1.63286
C	-0.74470	2.07817	-2.65508	O	6.24204	3.29308	-0.39022
H	-1.49889	1.28772	-2.78508	C	7.04552	3.09177	-1.53489
H	-1.24297	2.96983	-2.25102	H	6.42631	2.94722	-2.43339
H	-0.34042	2.33377	-3.64566	H	7.64964	3.99685	-1.65212
N	2.09969	0.58727	0.45020	H	7.71053	2.22420	-1.40550
C	4.30216	0.20701	-0.38057	H	-3.74784	0.50396	-1.00262
C	5.14371	0.57449	-1.43952	C	-1.26864	2.45344	-1.27641



C	4.85635	-0.14623	0.85858	H	-0.22389	2.17673	-1.06901
C	6.52338	0.60207	-1.25542	H	-1.26303	3.53629	-1.45052
H	4.71130	0.86202	-2.39929	<b>M5</b>			
C	6.23727	-0.13153	1.03277	C	2.74983	0.84583	-0.78839
H	4.21054	-0.46747	1.67841	C	0.67076	3.23039	-1.62163
C	7.07034	0.24638	-0.02168	C	-0.02393	1.86683	-1.75434
H	7.17355	0.90255	-2.07761	H	-0.03428	3.99661	-1.27157
H	6.66502	-0.42383	1.99234	H	1.03030	3.53808	-2.61576
H	8.15210	0.26011	0.11845	H	2.44921	1.21192	1.18901
C	0.00258	-1.54585	1.91709	C	0.88410	0.90901	-2.54542
C	0.02900	-0.36663	2.69682	H	0.35561	-0.05858	-2.66728
C	-0.26709	-0.33590	4.04179	H	0.95603	1.30466	-3.57148
C	-0.60541	-1.55710	4.65126	C	-1.28056	2.07676	-2.61276
C	-0.62887	-2.74618	3.91158	H	-1.79586	1.12389	-2.80478
C	-0.32826	-2.76367	2.54990	H	-1.98980	2.76095	-2.12717
C	0.35761	-1.16287	0.59747	H	-0.99833	2.51438	-3.58182
C	0.63904	0.34360	0.61710	N	1.94981	1.16821	0.30672
H	-0.23183	0.59990	4.59946	C	4.19334	0.64143	-0.47600
H	-0.84670	-1.57456	5.71471	C	5.19273	1.12361	-1.33177
H	-0.88569	-3.68076	4.41265	C	4.57144	-0.05880	0.67900
H	-0.34743	-3.68494	1.96940	C	6.53810	0.90083	-1.04464
O	0.39334	0.72145	1.95848	H	4.90866	1.69323	-2.21837
C	-0.25297	1.17886	-0.37042	C	5.91721	-0.28298	0.96415
H	-1.06021	0.48354	-0.65375	H	3.80647	-0.45778	1.35001
C	-0.92601	2.35253	0.31911	C	6.90474	0.19696	0.10364
C	-0.19624	3.31787	1.02622	H	7.30491	1.28880	-1.71693
C	-2.31150	2.51433	0.21542	H	6.19381	-0.84129	1.85977
C	-0.83181	4.41274	1.60637	H	7.95853	0.02559	0.32832
H	0.88405	3.20492	1.13599	C	0.52572	-1.48577	1.73962
C	-2.95379	3.61305	0.79128	C	0.30503	-0.36426	2.57048
H	-2.89650	1.77607	-0.33973	C	0.09456	-0.46393	3.93189
C	-2.21522	4.56609	1.48903	C	0.11601	-1.75088	4.48921
H	-0.24467	5.15017	2.15609	C	0.35277	-2.88199	3.69386
H	-4.03520	3.72205	0.69153	C	0.56145	-2.77124	2.32199
H	-2.71287	5.42409	1.94369	C	0.67724	-0.97621	0.42871
N	0.55366	-1.86544	-0.55781	C	0.62798	0.56377	0.49541
S	-0.49644	-2.96516	-1.14104	H	-0.07474	0.42725	4.53564
O	-0.05406	-3.25502	-2.50460	H	-0.04725	-1.87019	5.56097
O	-0.68711	-4.10027	-0.23388	H	0.37714	-3.86766	4.16020
C	-2.03810	-2.08437	-1.20914	H	0.74141	-3.64657	1.70018
C	-2.77379	-1.92738	-0.03743	O	0.33652	0.79633	1.87594
C	-2.41062	-1.42390	-2.38330	C	-0.48719	1.23606	-0.38842
C	-3.87056	-1.06740	-0.01327	H	-1.17792	0.42063	-0.66070
H	-2.48587	-2.47098	0.86461	C	-1.30902	2.23749	0.40916

C	-3.50748	-0.57578	-2.36686	C	-0.70681	3.26675	1.14837
H	-1.83324	-1.57491	-3.29714	C	-2.70558	2.18130	0.37440
C	-4.22673	-0.37099	-1.17671	C	-1.47786	4.20554	1.82782
H	-4.42896	-0.94276	0.91282	H	0.38198	3.31926	1.19962
H	-3.82364	-0.03906	-3.26203	C	-3.48471	3.12515	1.04904
O	-5.22759	0.52446	-1.23616	H	-3.19617	1.39455	-0.20376
C	-5.99052	0.76408	-0.07160	C	-2.87291	4.14036	1.77995
H	-5.35852	1.14972	0.74409	H	-0.98684	4.99498	2.39957
H	-6.73716	1.51860	-0.33873	H	-4.57341	3.06477	0.99905
H	-6.50090	-0.15151	0.26451	H	-3.47644	4.87790	2.31126
H	2.20975	2.63379	-0.92926	N	0.87331	-1.71222	-0.72706
C	2.25460	-0.26397	-1.79120	S	-0.17688	-2.90762	-1.29207
H	1.58469	-1.26887	-1.28627	O	0.20688	-3.07399	-2.68632
H	3.00290	-0.61677	-2.50368	O	-0.12682	-4.03294	-0.37434
<b>TS5</b>				C	-1.78389	-2.19570	-1.18632
C	2.70470	1.06053	-0.58664	C	-2.42857	-2.16978	0.04877
C	0.46881	3.37835	-1.60228	C	-2.34567	-1.59421	-2.31627
C	-0.01090	1.96251	-1.96255	C	-3.64047	-1.49764	0.17673
H	-0.37031	3.99413	-1.24965	H	-1.98388	-2.66976	0.91143
H	0.87672	3.85625	-2.50607	C	-3.55744	-0.93585	-2.19236
H	1.84105	1.58696	1.22205	H	-1.82920	-1.64439	-3.27663
C	1.15026	1.17900	-2.63796	C	-4.20087	-0.86461	-0.94349
H	0.73426	0.40001	-3.29744	H	-4.13405	-1.46989	1.14634
H	1.60731	1.88163	-3.35724	H	-4.02977	-0.45027	-3.04660
C	-1.11093	2.11546	-3.02275	O	-5.33452	-0.15196	-0.90606
H	-1.51647	1.13677	-3.32526	C	-6.03201	-0.03901	0.31967
H	-1.93946	2.72860	-2.64025	H	-5.40508	0.44082	1.08732
H	-0.70890	2.61193	-3.91868	H	-6.90670	0.58758	0.12022
N	1.66627	1.29501	0.26741	H	-6.36172	-1.02531	0.67958
C	4.07938	0.97880	-0.08015	H	1.52637	3.20433	-0.93682
C	5.16882	1.18402	-0.94500	C	2.29049	0.70729	-2.05160
C	4.33791	0.68292	1.27143	H	1.38601	-1.27639	-1.49213
C	6.47561	1.08648	-0.47545	H	3.02080	0.38331	-2.79579
H	4.98040	1.43971	-1.98943	<b>Pre-P</b>			
C	5.64647	0.59552	1.73842	C	-2.91676	-0.06882	-0.18794
H	3.51030	0.47843	1.95497	C	-1.73096	-2.76241	-1.58764
C	6.72032	0.79596	0.86860	C	-0.79165	-1.56524	-1.80842
H	7.30898	1.24977	-1.16057	H	-1.15695	-3.65934	-1.31565
H	5.82990	0.35656	2.78718	H	-2.25940	-2.97622	-2.52878
H	7.74477	0.72606	1.23712	H	-2.25020	-0.89924	1.62639
C	1.50458	-1.55422	0.49942	C	-1.62310	-0.33000	-2.30469
C	0.91427	-0.99682	1.64708	H	-1.05756	0.21422	-3.07791
C	1.15086	-1.48566	2.92161	H	-2.51116	-0.71041	-2.83136
C	2.03034	-2.57004	3.03597	C	0.16931	-1.95671	-2.93940

C	2.63115	-3.13994	1.90726	H	0.89520	-1.15439	-3.14559
C	2.36291	-2.64562	0.62964	H	0.72881	-2.86776	-2.67968
C	0.98813	-0.81457	-0.65722	H	-0.39317	-2.15686	-3.86369
C	0.46554	0.47193	0.04346	N	-2.01745	-0.66356	0.66688
H	0.67177	-1.03515	3.79099	C	-4.31353	-0.28588	-0.16253
H	2.24982	-2.97469	4.02521	C	-5.17991	0.34295	-1.10198
H	3.31492	-3.98079	2.02958	C	-4.90919	-1.15102	0.80001
H	2.80988	-3.10025	-0.25572	C	-6.54851	0.12856	-1.06265
O	0.07892	0.05017	1.35161	H	-4.76305	1.00514	-1.86253
C	-0.63040	1.19541	-0.73335	C	-6.28200	-1.35194	0.82509
H	-1.26859	0.40483	-1.15482	H	-4.28228	-1.67755	1.52170
C	-1.54302	2.04993	0.12585	C	-7.11841	-0.71571	-0.09911
C	-1.07520	2.83765	1.18626	H	-7.18752	0.62542	-1.79519
C	-2.91578	2.06148	-0.14763	H	-6.70905	-2.02263	1.57336
C	-1.95669	3.59454	1.95674	H	-8.19615	-0.87944	-0.07514
H	-0.01020	2.86134	1.41806	C	-1.09138	1.97112	0.83919
C	-3.80317	2.81909	0.61756	C	-0.49567	1.32009	1.92153
H	-3.29706	1.45281	-0.96972	C	-0.41923	1.89163	3.18117
C	-3.32487	3.58663	1.67859	C	-0.98204	3.16359	3.33424
H	-1.57135	4.19560	2.78209	C	-1.60266	3.81978	2.26736
H	-4.87032	2.79435	0.38906	C	-1.65430	3.22672	1.00233
H	-4.01199	4.17752	2.28651	C	-0.88659	1.10126	-0.38129
N	0.32665	-1.53830	-1.66544	C	-0.64858	-0.25787	0.37041
S	-0.80747	-2.75905	-1.44771	H	0.05236	1.36407	4.00997
O	-1.14684	-3.15588	-2.80816	H	-0.94352	3.64585	4.31229
O	-0.26150	-3.72622	-0.51100	H	-2.04410	4.80480	2.42304
C	-2.24014	-2.04279	-0.70193	H	-2.11281	3.74425	0.15755
C	-2.27063	-1.84688	0.67549	O	-0.01298	0.06708	1.59737
C	-3.29993	-1.62899	-1.51690	C	0.09218	-1.23678	-0.53235
C	-3.35926	-1.20035	1.25650	H	0.95579	-0.67921	-0.91862
H	-1.44463	-2.19891	1.29676	C	0.66197	-2.44611	0.17696
C	-4.39204	-1.00668	-0.93804	C	-0.05262	-3.16815	1.14301
H	-3.25985	-1.80719	-2.59223	C	1.95963	-2.86647	-0.14035
C	-4.41744	-0.76317	0.44786	C	0.51797	-4.27299	1.77341
H	-3.36658	-1.03607	2.33242	H	-1.06984	-2.87016	1.39927
H	-5.23816	-0.67280	-1.53931	C	2.53081	-3.97763	0.48133
O	-5.48513	-0.09637	0.90865	H	2.53333	-2.30638	-0.88337
C	-5.55203	0.21029	2.28690	C	1.81081	-4.68368	1.44401
H	-4.70032	0.83885	2.59150	H	-0.05321	-4.81901	2.52605
H	-6.48430	0.76435	2.43596	H	3.54250	-4.28813	0.21404
H	-5.57130	-0.70622	2.89633	H	2.25497	-5.54988	1.93683
H	1.24687	3.38077	-0.83025	N	0.17516	1.59534	-1.24820
C	2.29458	0.59588	-1.82956	S	1.47573	2.59752	-1.00673
H	0.18263	-1.10499	-2.57332	O	1.67462	3.26521	-2.28543

H	3.05236	0.09427	-2.43842	O	1.26051	3.38084	0.19748
<b>TS6</b>				C	2.90245	1.57923	-0.72534
C	-1.00319	-3.32853	0.86009	C	2.84409	0.62091	0.28041
C	0.18059	-2.80265	0.13569	C	4.08537	1.82177	-1.42631
C	1.46746	-2.66983	0.91071	C	3.97184	-0.12358	0.60765
H	0.28019	-3.14331	-0.90083	H	1.86954	0.43265	0.72978
H	-0.21844	-1.53902	-0.13935	C	5.21479	1.08439	-1.10299
C	2.72822	-2.16758	0.16746	H	4.11262	2.57616	-2.21306
H	1.30205	-2.02082	1.79085	C	5.16957	0.11422	-0.08563
H	1.71067	-3.66302	1.33447	H	3.90177	-0.88753	1.38022
H	-0.22254	-3.10732	2.58447	H	6.15855	1.23812	-1.62682
C	3.08223	-3.10979	-0.98551	O	6.31187	-0.54884	0.15116
H	4.03191	-2.81057	-1.45140	C	6.32047	-1.54545	1.15179
H	3.19577	-4.13749	-0.60912	H	5.60608	-2.34981	0.91710
H	2.31144	-3.11359	-1.77073	H	7.33484	-1.95598	1.17352
C	3.87551	-2.16652	1.18217	H	6.07850	-1.11989	2.13781
H	4.82886	-1.90307	0.70463	H	-2.48178	-2.58465	-0.80837
H	3.68837	-1.45808	2.00290	C	-2.10843	0.66441	-1.22004
H	3.98348	-3.17099	1.61814	H	0.12004	1.34912	-2.23161
N	-1.08798	-3.41786	2.13543	H	-2.63551	1.51220	-1.67661
C	-2.20913	-3.69926	0.05234	<b>M6</b>			
C	-2.11353	-4.19542	-1.25261	C	3.27775	0.05204	-1.30992
C	-3.47703	-3.54497	0.62868	C	2.26694	0.05316	-2.32426
C	-3.26318	-4.53125	-1.96756	C	1.50543	1.24376	-2.78979
H	-1.13930	-4.34236	-1.72098	H	2.04032	-0.89566	-2.81101
C	-4.62493	-3.86992	-0.08769	H	2.17308	-0.43293	0.90830
H	-3.54237	-3.15394	1.64407	C	-0.02917	1.04327	-2.89937
C	-4.52104	-4.36401	-1.39010	H	1.70754	2.12508	-2.16196
H	-3.17334	-4.92579	-2.98085	H	1.86343	1.50722	-3.80304
H	-5.60707	-3.73488	0.36865	H	3.08046	1.90677	-0.85933
H	-5.42014	-4.61943	-1.95340	C	-0.34104	-0.04855	-3.92937
C	0.28214	1.10744	1.97659	H	-1.42145	-0.10470	-4.12098
C	1.59511	1.34260	2.41777	H	0.15827	0.18416	-4.88195
C	1.91585	2.08130	3.54937	H	-0.00862	-1.04405	-3.59954
C	0.84698	2.59593	4.27602	C	-0.64118	2.35810	-3.39345
C	-0.48030	2.36618	3.87388	H	-1.73004	2.26420	-3.51081
C	-0.78019	1.62831	2.73383	H	-0.43526	3.18910	-2.70623
C	0.44953	0.33582	0.74980	H	-0.21679	2.61034	-4.37695
C	1.81260	0.15518	0.59372	N	3.62110	1.08085	-0.58948
H	2.95355	2.23754	3.84268	C	3.95295	-1.25248	-0.98620
H	1.04434	3.18056	5.17536	C	4.04212	-2.30327	-1.90782
H	-1.29558	2.77177	4.47404	C	4.52397	-1.42220	0.28370
H	-1.81220	1.43544	2.44922	C	4.67563	-3.49741	-1.56361
O	2.50015	0.74144	1.59310	H	3.63851	-2.19171	-2.91513

C	2.47756	-0.72329	-0.41329	C	5.14566	-2.61851	0.63231
H	1.71202	-0.84711	-1.19444	H	4.47976	-0.59304	0.99224
C	3.68506	-0.09753	-1.09191	C	5.22267	-3.66192	-0.29138
C	4.72820	0.51224	-0.38104	H	4.74486	-4.30200	-2.29716
C	3.76761	-0.14155	-2.48963	H	5.57464	-2.73609	1.62871
C	5.82166	1.05759	-1.05389	H	5.71289	-4.59869	-0.02212
H	4.68631	0.56824	0.70635	C	1.10287	2.26085	1.38757
C	4.86239	0.39874	-3.16355	C	0.46999	3.29007	0.68171
H	2.95970	-0.60809	-3.05870	C	0.55906	4.63233	1.03692
C	5.89463	1.00153	-2.44569	C	1.33707	4.92154	2.15407
H	6.62232	1.53194	-0.48394	C	1.99062	3.90511	2.87881
H	4.90456	0.35233	-4.25283	C	1.88208	2.56947	2.51093
H	6.75103	1.43063	-2.96816	C	0.75518	1.05422	0.66747
N	-0.39103	-0.26734	-0.15866	C	-0.03576	1.43066	-0.38060
S	-2.03526	0.01599	-0.24055	H	0.04850	5.40701	0.46522
O	-2.48380	-0.80762	-1.35321	H	1.44280	5.95857	2.47524
O	-2.69671	-0.14348	1.05215	H	2.58956	4.17637	3.74925
C	-2.07933	1.72135	-0.69525	H	2.36881	1.77677	3.07982
C	-2.86169	2.60698	0.03706	O	-0.21767	2.77898	-0.37821
C	-1.37979	2.14091	-1.83488	C	-0.59202	0.60753	-1.49682
C	-2.94480	3.94225	-0.35394	H	-0.18189	-0.39739	-1.30352
H	-3.41510	2.25468	0.90852	C	-2.10764	0.48326	-1.46936
C	-1.45528	3.46569	-2.21999	C	-2.94224	1.55700	-1.13111
H	-0.77822	1.43123	-2.40547	C	-2.69939	-0.73283	-1.83108
C	-2.23703	4.37765	-1.48304	C	-4.32970	1.41974	-1.17251
H	-3.56095	4.62720	0.22530	H	-2.50419	2.51304	-0.84153
H	-0.92031	3.83231	-3.09618	C	-4.08611	-0.87037	-1.88372
O	-2.24718	5.63834	-1.93281	H	-2.06353	-1.58611	-2.07811
C	-3.02158	6.60152	-1.24654	C	-4.90662	0.20933	-1.55886
H	-2.68171	6.71371	-0.20580	H	-4.96307	2.26855	-0.90885
H	-2.88096	7.54791	-1.77773	H	-4.52538	-1.82909	-2.16414
H	-4.08862	6.33172	-1.25656	H	-5.99242	0.10871	-1.60611
<b>TS7</b>				N	1.16186	-0.27134	0.92442
C	0.07847	3.29803	-0.12987	S	0.51686	-1.04541	2.26575
C	-0.55165	2.42520	-1.12160	O	1.31271	-2.25830	2.39901
C	-2.04959	2.48653	-1.36418	O	0.41926	-0.12364	3.39228
H	0.02137	2.36005	-2.04911	C	-1.12262	-1.44640	1.76100
H	0.56465	0.34992	-2.61841	C	-2.17279	-0.61221	2.13080
C	-3.09138	1.79164	-0.43411	C	-1.34662	-2.62449	1.04000
H	-2.33253	3.55365	-1.40577	C	-3.47790	-0.94911	1.77921
H	-2.22065	2.07570	-2.37152	H	-1.97003	0.29258	2.70534
H	-0.04514	4.51704	1.32019	C	-2.64228	-2.96289	0.69531
C	-4.43536	1.85714	-1.16947	H	-0.50879	-3.27105	0.77447
H	-5.23579	1.40356	-0.56722	C	-3.71615	-2.12939	1.06218

H	-4.70630	2.90625	-1.36381	H	-4.29433	-0.29195	2.07264
H	-4.39053	1.33056	-2.13551	H	-2.86208	-3.87497	0.13986
C	-3.26229	2.47395	0.92361	O	-4.93464	-2.54288	0.68737
H	-4.13687	2.05517	1.44242	C	-6.06114	-1.80119	1.10858
H	-2.37577	2.36741	1.55899	H	-6.03025	-0.77573	0.71027
H	-3.42495	3.55102	0.77975	H	-6.94016	-2.31892	0.71149
N	-0.64322	3.93935	0.72250	H	-6.12053	-1.76684	2.20737
C	1.57661	3.40634	-0.13788	<b>M7</b>			
C	2.32392	3.39799	-1.32295	C	-0.00298	3.20587	0.11594
C	2.25410	3.52608	1.08307	C	0.55017	2.17315	1.09037
C	3.71414	3.50505	-1.28483	C	2.05198	2.33062	1.40828
H	1.82412	3.32376	-2.29005	H	0.01702	2.37935	2.03306
C	3.64206	3.62582	1.12282	H	-0.54733	0.39558	2.69209
H	1.68846	3.49880	2.01738	C	3.12654	1.69313	0.48746
C	4.37777	3.61322	-0.06272	H	2.26636	3.40505	1.50504
H	4.28159	3.50641	-2.21693	H	2.20098	1.88365	2.40430
H	4.15270	3.69816	2.08461	H	0.26125	4.61510	-1.11171
H	5.46598	3.68827	-0.03489	C	4.45680	1.76121	1.24567
C	0.99149	0.36179	0.25056	H	5.27132	1.32221	0.65100
C	0.44141	0.32062	1.53209	H	4.71703	2.80931	1.45995
C	1.20874	0.26241	2.68870	H	4.40014	1.22014	2.20315
C	2.59111	0.21547	2.51068	C	3.30931	2.39633	-0.85842
C	3.16693	0.22272	1.22947	H	4.19303	1.98688	-1.36951
C	2.37537	0.30440	0.08653	H	2.43504	2.27794	-1.51054
C	-0.16114	0.42682	-0.66473	H	3.45776	3.47348	-0.70627
C	-1.27751	0.19133	0.16118	N	0.79160	3.93076	-0.56276
H	0.74727	0.23032	3.67538	C	-1.48899	3.40402	0.05532
H	3.23787	0.16248	3.38777	C	-2.28201	3.45210	1.20832
H	4.25242	0.17322	1.13039	C	-2.09638	3.58086	-1.19501
H	2.82608	0.31950	-0.90765	C	-3.65692	3.66501	1.10916
O	-0.92448	0.26115	1.47181	H	-1.83328	3.33114	2.19594
C	-2.68975	0.28129	-0.28271	C	-3.47059	3.77829	-1.29414
H	-2.66968	-0.11665	-1.30701	H	-1.48872	3.52491	-2.10142
C	-3.65927	-0.58104	0.50171	C	-4.25597	3.81865	-0.14089
C	-3.75844	-0.53510	1.89977	H	-4.26296	3.70776	2.01551
C	-4.49672	-1.46128	-0.19562	H	-3.93267	3.89142	-2.27624
C	-4.67744	-1.33893	2.57471	H	-5.33363	3.97164	-0.21619
H	-3.10694	0.12856	2.46720	C	-0.97110	0.47030	-0.20555
C	-5.41865	-2.26307	0.47675	C	-0.44254	0.24670	-1.47347
H	-4.41383	-1.52160	-1.28316	C	-1.23073	0.08910	-2.60420
C	-5.51349	-2.20268	1.86691	C	-2.61457	0.11424	-2.41211
H	-4.73865	-1.28948	3.66327	C	-3.16855	0.27239	-1.13632
H	-6.06106	-2.94025	-0.08871	C	-2.34736	0.45349	-0.02045
H	-6.23225	-2.82908	2.39762	C	0.20477	0.65933	0.74110

N	-0.14034	-0.06245	-2.00802	C	1.30309	0.09278	-0.12364
S	-0.23657	-1.71915	-2.28976	H	-0.78281	-0.07829	-3.58367
O	-1.56230	-2.15366	-1.87488	H	-3.27395	-0.01433	-3.27198
O	0.18925	-1.86755	-3.67369	H	-4.25242	0.26106	-1.01252
C	0.93957	-2.48237	-1.22070	H	-2.78105	0.58532	0.97308
C	2.25249	-2.63679	-1.65378	O	0.92428	0.13320	-1.44605
C	0.56240	-2.80500	0.08809	C	2.72498	0.19299	0.29338
C	3.22043	-3.10162	-0.76762	H	2.72066	-0.23579	1.30786
H	2.51916	-2.38746	-2.68222	C	3.68832	-0.64778	-0.51980
C	1.52467	-3.25530	0.97376	C	3.76074	-0.58865	-1.91936
H	-0.47803	-2.69072	0.39945	C	4.55598	-1.51906	0.15165
C	2.86215	-3.39116	0.55835	C	4.67797	-1.37325	-2.61921
H	4.24538	-3.22120	-1.11394	H	3.08814	0.07038	-2.46711
H	1.27424	-3.50422	2.00532	C	5.47611	-2.30226	-0.54497
O	3.72882	-3.80426	1.49244	H	4.50095	-1.58582	1.24073
C	5.09374	-3.92707	1.14850	C	5.54082	-2.23067	-1.93617
H	5.50511	-2.96161	0.81524	H	4.71676	-1.31385	-3.70838
H	5.61455	-4.25021	2.05524	H	6.14091	-2.97289	0.00215
H	5.23844	-4.67909	0.35796	H	6.25728	-2.84237	-2.48687
<b>TS8</b>				N	0.11951	-0.01763	2.04104
C	-1.10861	2.41623	-0.55925	S	0.16168	-1.66781	2.27382
C	-0.81150	1.37983	-1.59710	O	1.47326	-2.15870	1.87543
C	-2.01514	0.82509	-2.39043	O	-0.28270	-1.82671	3.65310
H	-0.03048	1.70309	-2.29958	C	-1.03253	-2.40466	1.20418
H	0.47184	-0.59748	-2.52248	C	-2.33964	-2.55776	1.65347
C	-3.12206	-0.02299	-1.66884	C	-0.66901	-2.74342	-0.10347
H	-2.50994	1.67352	-2.88676	C	-3.31637	-3.04023	0.78587
H	-1.59781	0.20991	-3.19957	H	-2.59412	-2.29845	2.68225
H	-2.02617	2.49418	1.16810	C	-1.63909	-3.21376	-0.97002
C	-3.57108	-1.10328	-2.66419	H	0.36540	-2.62061	-0.43096
H	-4.37601	-1.71885	-2.23382	C	-2.97074	-3.35143	-0.53788
H	-3.95399	-0.64288	-3.58798	H	-4.33675	-3.15859	1.14581
H	-2.72976	-1.76306	-2.92784	H	-1.39948	-3.47404	-2.00138
C	-4.34574	0.85817	-1.37768	O	-3.84486	-3.78631	-1.45661
H	-5.18363	0.25399	-1.00153	C	-5.20337	-3.91824	-1.09304
H	-4.11941	1.64020	-0.64459	H	-5.62137	-2.95242	-0.76893
H	-4.67213	1.33614	-2.31422	H	-5.73284	-4.26102	-1.98756
N	-1.97920	1.96014	0.29437	H	-5.32985	-4.65919	-0.28889
C	-0.22514	3.57663	-0.36006				
C	0.38404	4.21222	-1.45686				
C	0.04105	4.07276	0.93032				
C	1.22989	5.30315	-1.26951				
H	0.18052	3.85822	-2.46918				
C	0.89319	5.15598	1.11462				

H	-0.39524	3.58320	1.80417
C	1.49212	5.77889	0.01582
H	1.68821	5.78507	-2.13471
H	1.09975	5.51339	2.12487
H	2.16066	6.62831	0.16250
C	0.78551	0.50395	0.34017
C	0.27526	0.11856	1.58021
C	1.00783	0.22947	2.75503
C	2.30164	0.74454	2.64558
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C	2.07454	1.01471	0.24307
C	-0.27171	0.19755	-0.69701
C	-1.43089	-0.10394	0.21653
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H	2.48363	1.31489	-0.72450
O	-1.00695	-0.35352	1.49594
C	-2.60811	-0.79007	-0.37296
H	-2.21157	-1.75108	-0.74179
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C	-4.13325	-0.23302	1.59451
C	-4.29556	-2.40198	0.56517
C	-5.16042	-0.57488	2.47195
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C	-5.76604	-1.83115	2.39465
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H	-5.78600	-3.73503	1.37434
H	-6.57198	-2.09605	3.08099
N	0.08221	-0.88321	-1.62475
S	0.66207	-2.36365	-1.16023
O	-0.17082	-2.81971	-0.05432
O	0.73989	-3.12209	-2.40087
C	2.30759	-2.17469	-0.53835
C	3.33212	-1.84952	-1.42251
C	2.55198	-2.32667	0.82843
C	4.62098	-1.64062	-0.93948
H	3.13163	-1.75591	-2.49160
C	3.83479	-2.13051	1.30990
H	1.73214	-2.58695	1.49860
C	4.87464	-1.77391	0.43479
H	5.41573	-1.38051	-1.63629



H	4.06114	-2.23178	2.37163
O	6.07846	-1.58053	0.99526
C	7.16119	-1.20700	0.16882
H	6.96226	-0.24954	-0.33710
H	8.02947	-1.09644	0.82601
H	7.37112	-1.98117	-0.58510
<b>TS3 (RS)</b>			
C	-2.85453	0.20552	-0.99579
C	-2.29583	1.21835	-1.94631
C	-2.54119	2.69171	-1.61025
H	-1.21740	0.98280	-1.98122
H	-2.67422	1.02461	-2.95915
C	-2.01671	3.31267	-0.27935
H	-2.11838	3.26471	-2.44985
H	-3.62605	2.87693	-1.65690
H	-3.23911	-0.24303	0.85939
C	-3.17947	3.50912	0.71281
H	-2.81890	3.98739	1.63662
H	-3.93215	4.17266	0.26142
H	-3.66640	2.56485	0.97839
C	-1.49067	4.72633	-0.58673
H	-1.17143	5.23303	0.33698
H	-0.64340	4.71955	-1.28400
H	-2.29651	5.32412	-1.03824
N	-2.90566	0.51202	0.25315
C	-3.20732	-1.15016	-1.48372
C	-3.85678	-1.33924	-2.71258
C	-2.87391	-2.27244	-0.70756
C	-4.17943	-2.62266	-3.14765
H	-4.13143	-0.47932	-3.32519
C	-3.17631	-3.55413	-1.15696
H	-2.32494	-2.15053	0.22943
C	-3.83643	-3.73251	-2.37390
H	-4.69627	-2.75708	-4.09882
H	-2.88528	-4.41789	-0.55752
H	-4.07752	-4.73761	-2.72314
C	-0.73405	-0.70878	2.30951
C	-1.43441	0.22762	3.09018
C	-1.80037	0.02471	4.41083
C	-1.42910	-1.19085	4.98390
C	-0.72600	-2.15074	4.24064
C	-0.37632	-1.92993	2.91168
C	-0.56269	-0.06859	1.00102
C	-1.25946	1.21076	1.11833

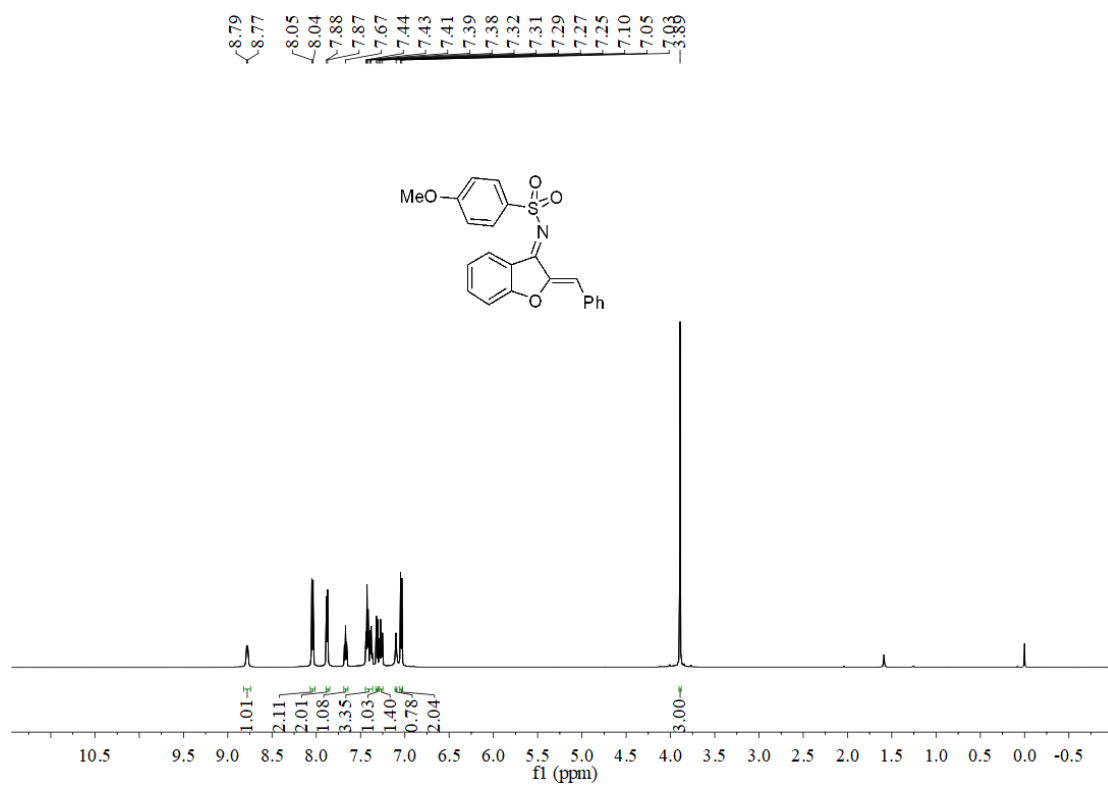
H	-2.34502	0.79100	4.96165
H	-1.68994	-1.39598	6.02299
H	-0.45170	-3.09503	4.71220
H	0.14861	-2.69016	2.33860
O	-1.69136	1.37407	2.39599
C	-0.88115	2.53183	0.45186
H	-0.70660	3.15358	1.34562
C	0.50079	2.45985	-0.19937
C	0.75607	2.57369	-1.56901
C	1.59558	2.27999	0.65813
C	2.05922	2.49215	-2.06521
H	-0.05854	2.73974	-2.27251
C	2.89686	2.19320	0.17023
H	1.42050	2.19802	1.73512
C	3.13410	2.29615	-1.20089
H	2.22950	2.58456	-3.13915
H	3.72764	2.04506	0.86257
H	4.151073	2.22515	-1.59063
N	-0.12343	-0.40146	-0.19620
S	0.59916	-1.78794	-0.63200
O	0.24826	-2.92263	0.23229
O	0.36254	-1.94831	-2.06460
C	2.32387	-1.44105	-0.40520
C	3.11843	-1.18448	-1.51458
C	2.85805	-1.39949	0.88813
C	4.46974	-0.87991	-1.34786
H	2.67682	-1.22370	-2.51097
C	4.19527	-1.08917	1.05886
H	2.22800	-1.60927	1.75543
C	5.01003	-0.82245	-0.05759
H	5.08242	-0.67932	-2.22520
H	4.64514	-1.04392	2.05097
O	6.29224	-0.52164	0.20926
C	7.15888	-0.23538	-0.86756
H	6.81500	0.64580	-1.43181
H	8.14024	-0.02543	-0.43014
H	7.24130	-1.09433	-1.55136

## 8. References

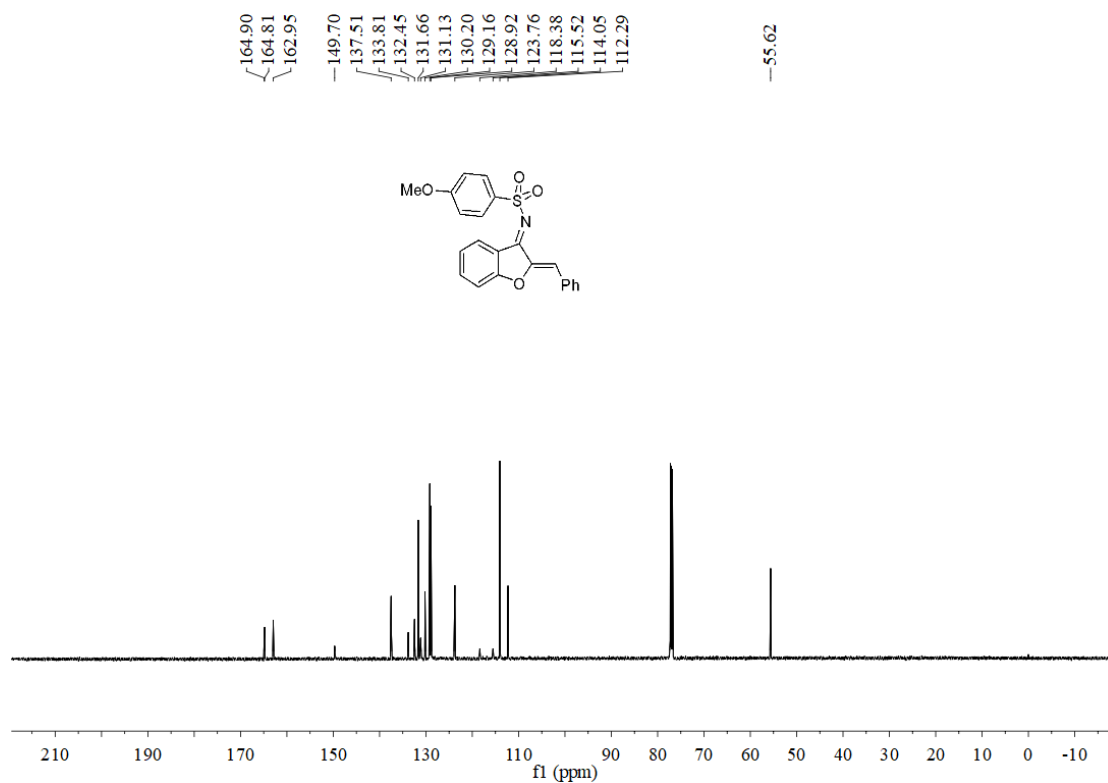
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## 9. $^1\text{H}$ , $^{13}\text{C}$ , and $^{19}\text{F}$ NMR Spectra

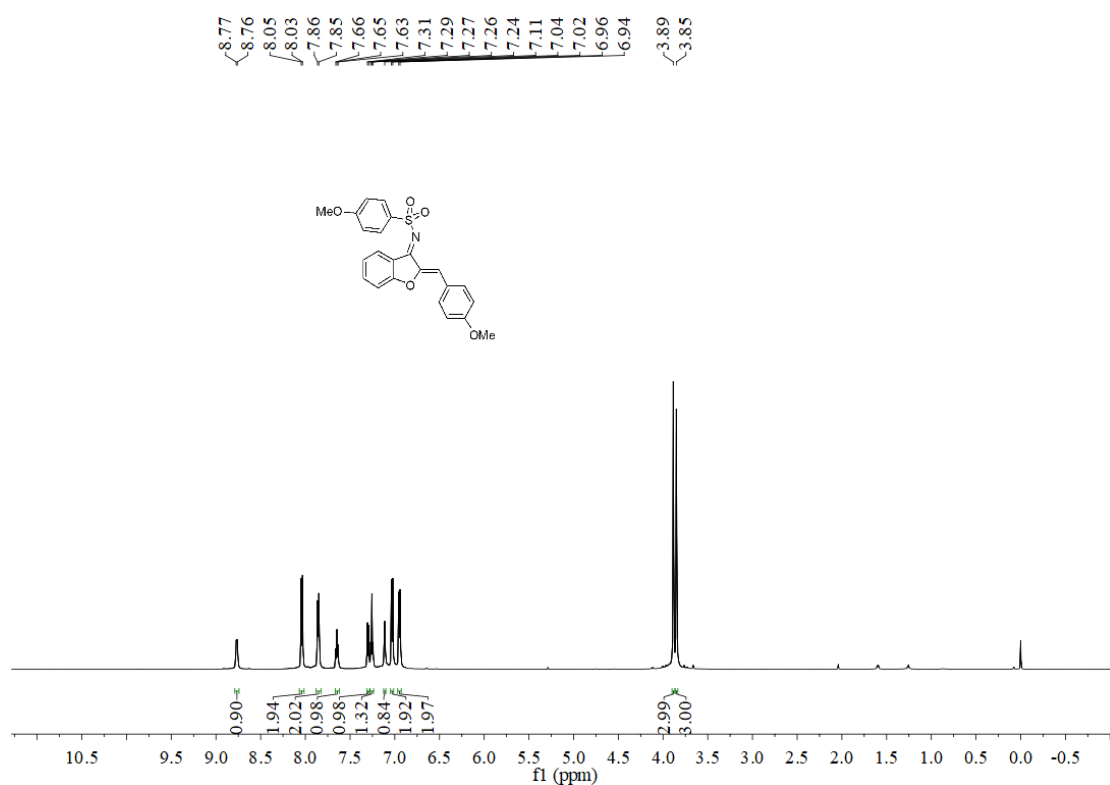
### $^1\text{H}$ NMR Spectrum of 1b



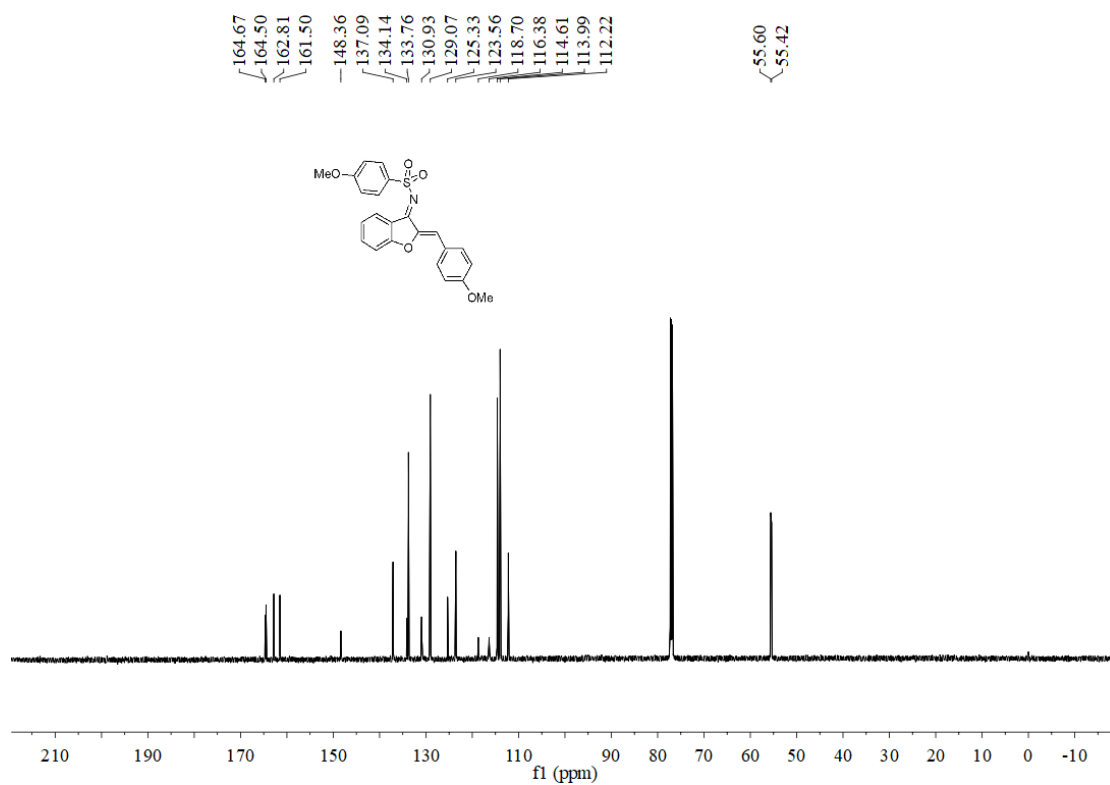
### $^{13}\text{C}$ NMR Spectrum of 1b



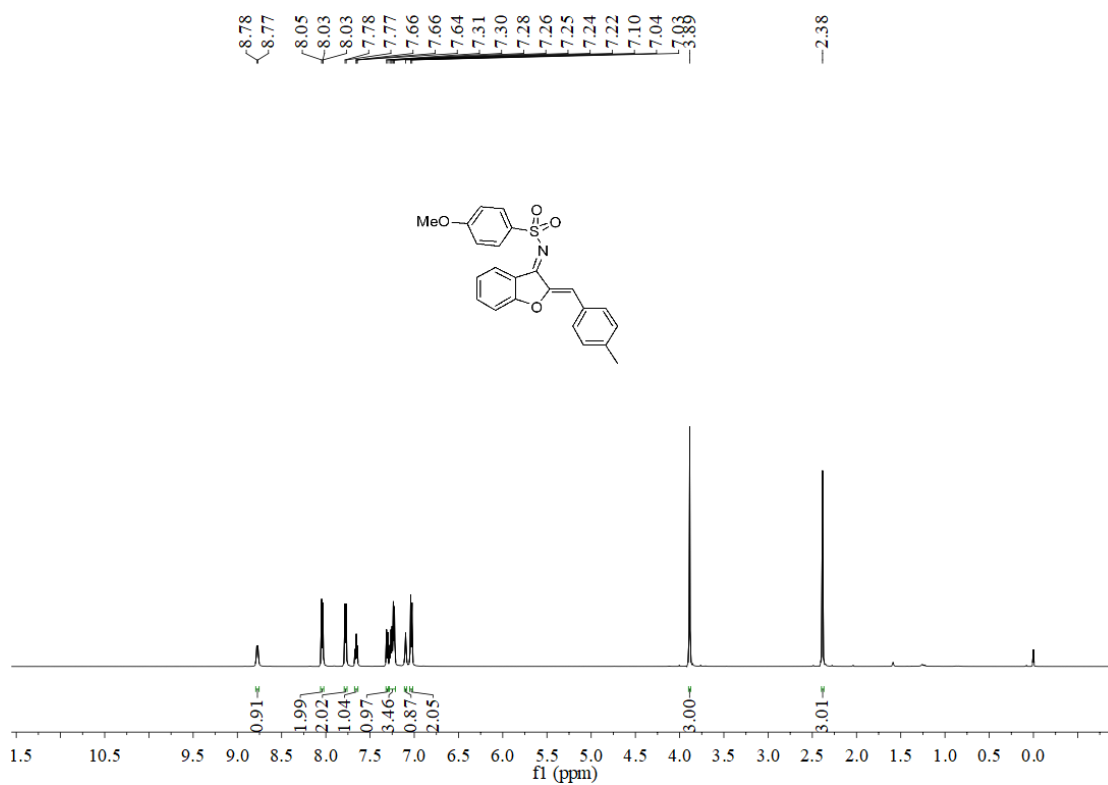
### <sup>1</sup>H NMR Spectrum of 1c



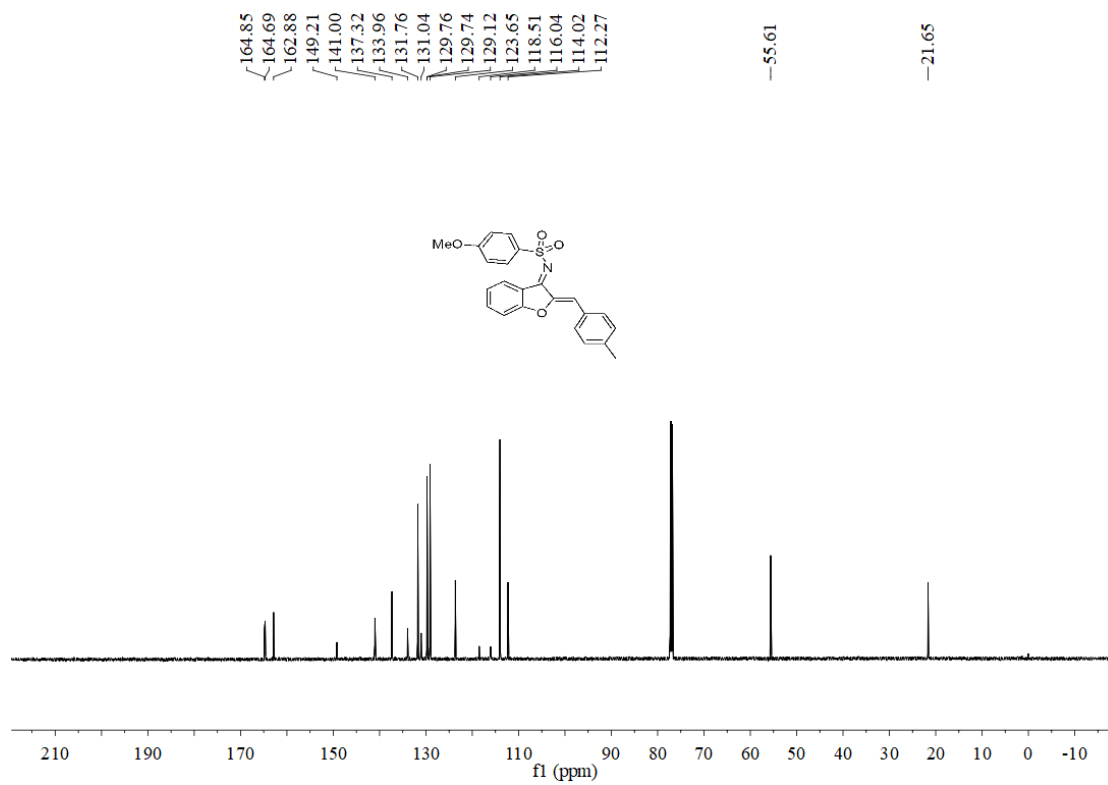
### <sup>13</sup>C NMR Spectrum of 1c



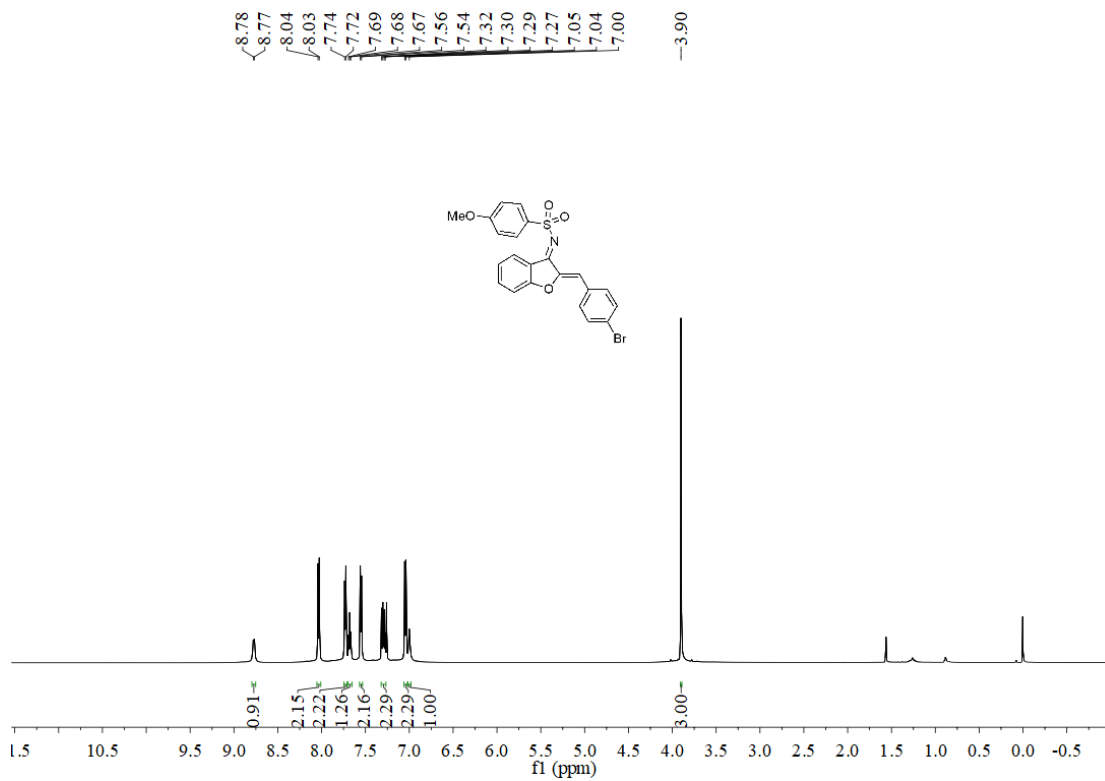
### <sup>1</sup>H NMR Spectrum of 1d



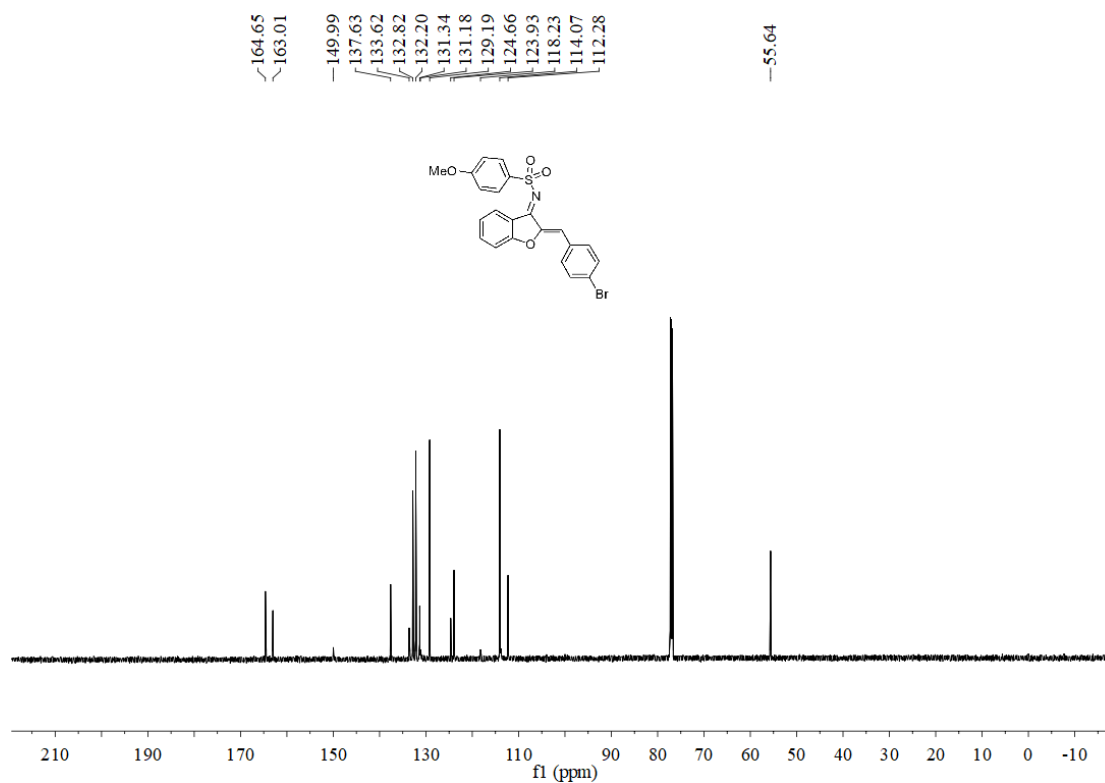
### <sup>13</sup>C NMR Spectrum of 1d



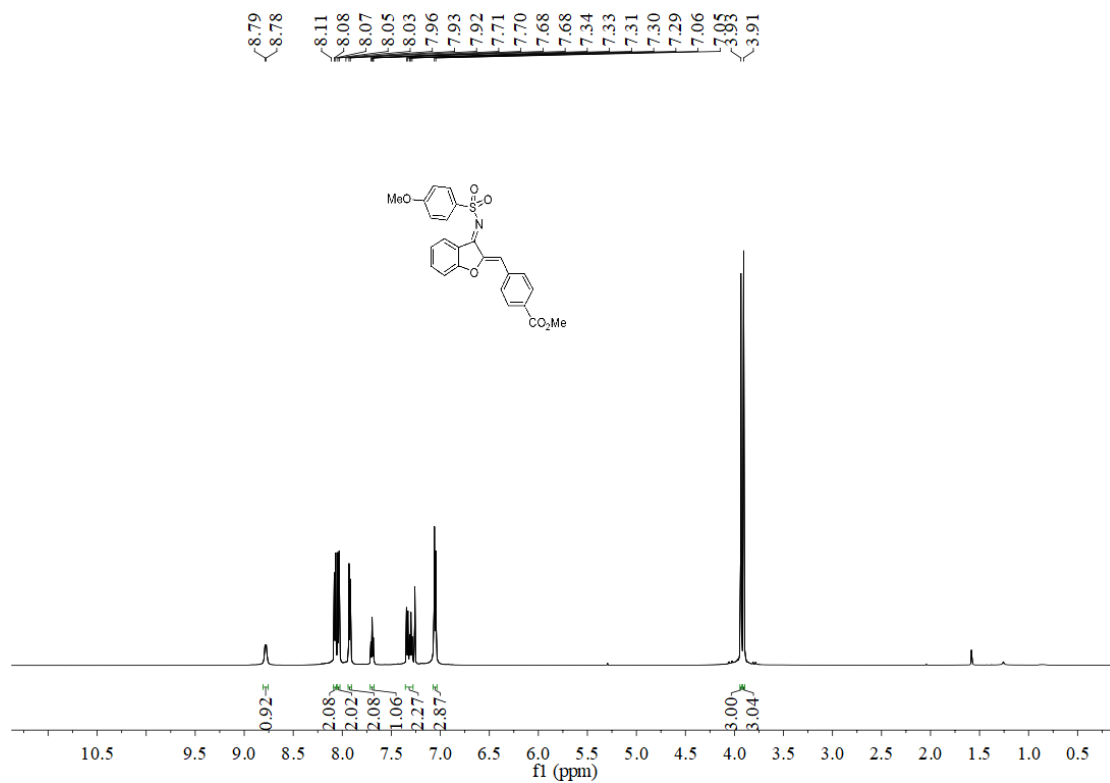
### <sup>1</sup>H NMR Spectrum of 1e



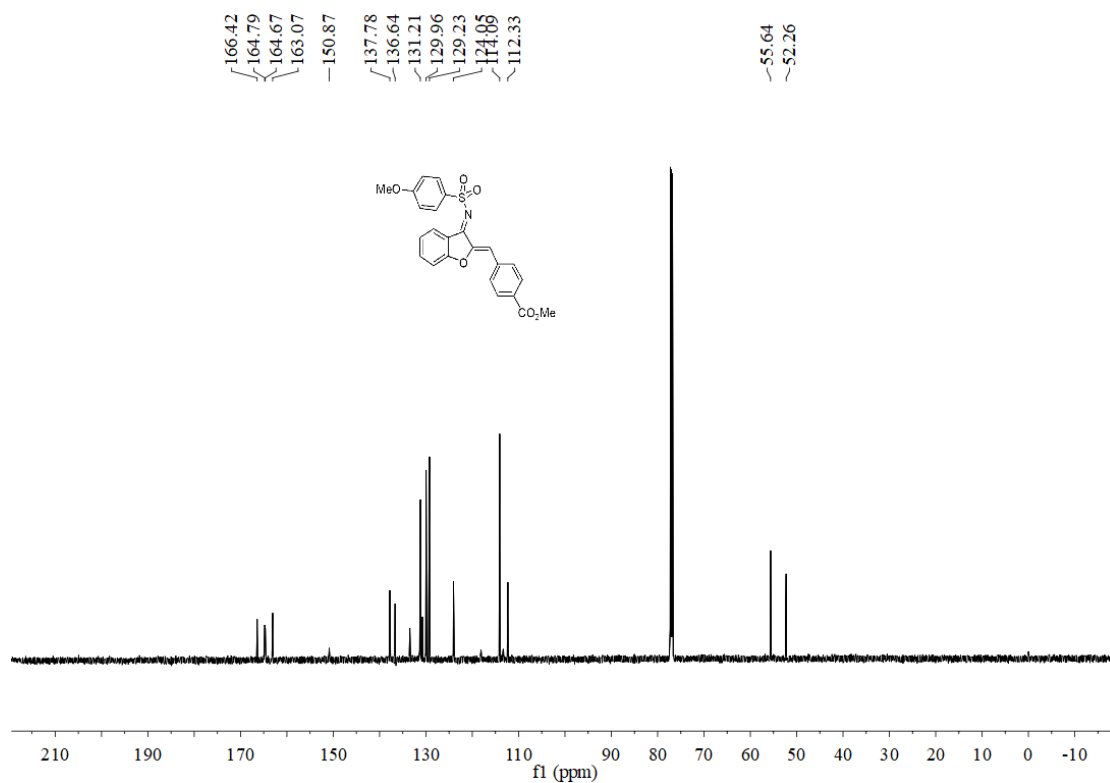
### <sup>13</sup>C NMR Spectrum of 1e



### <sup>1</sup>H NMR Spectrum of 1f

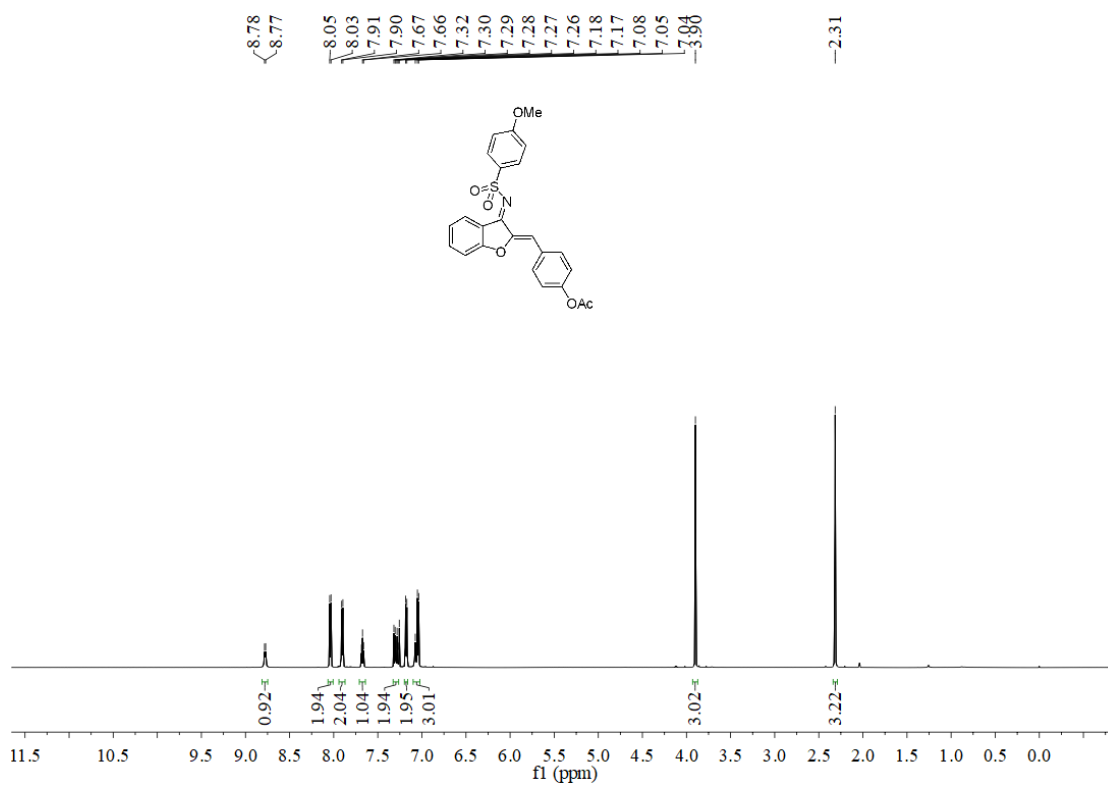


### <sup>13</sup>C NMR Spectrum of 1f

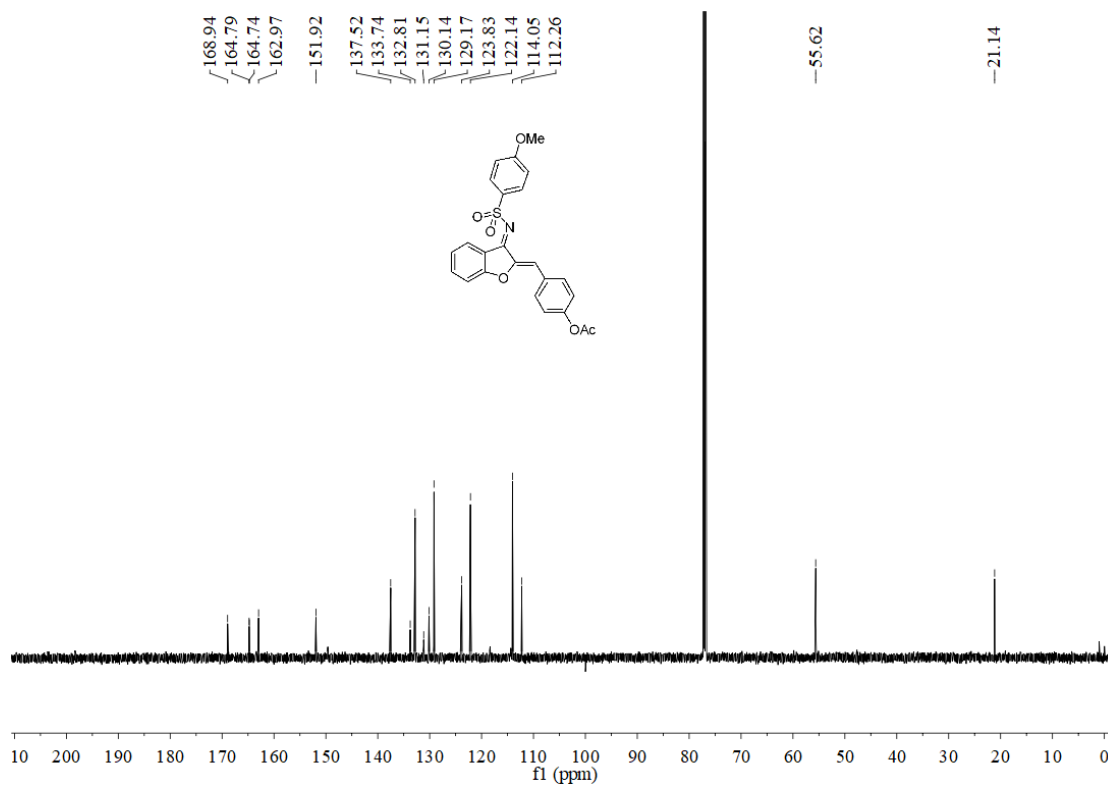




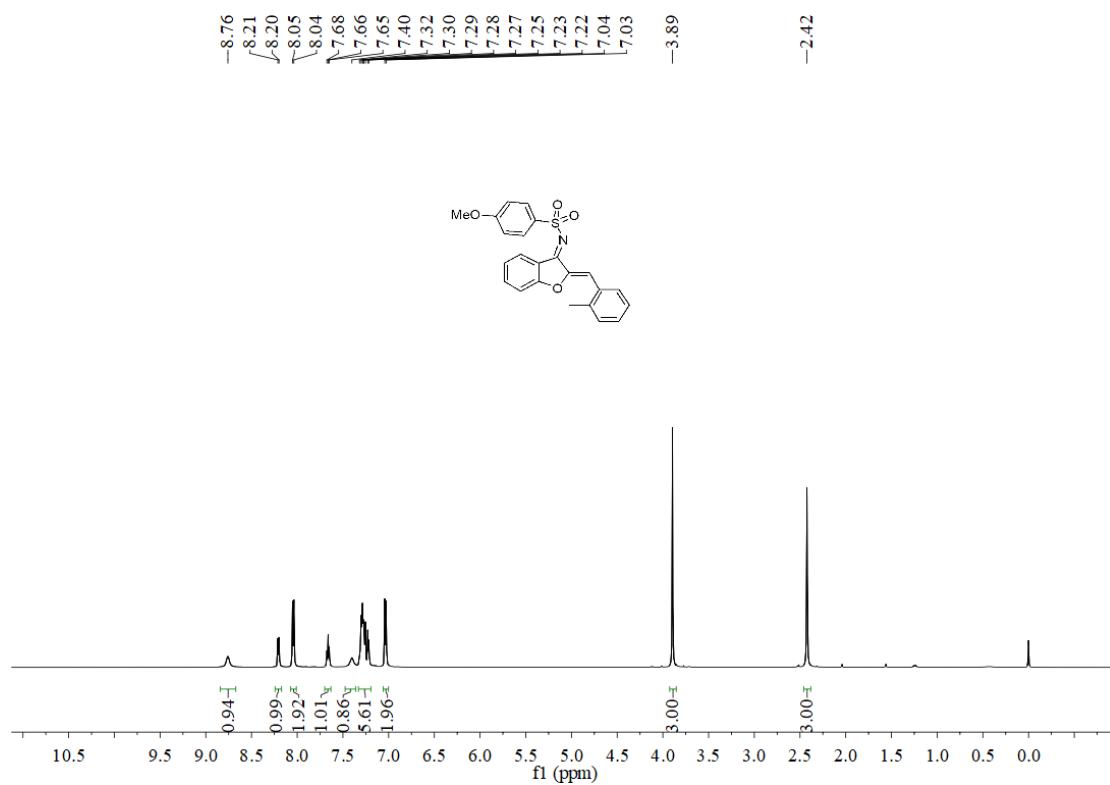
### <sup>1</sup>H NMR Spectrum of 1g



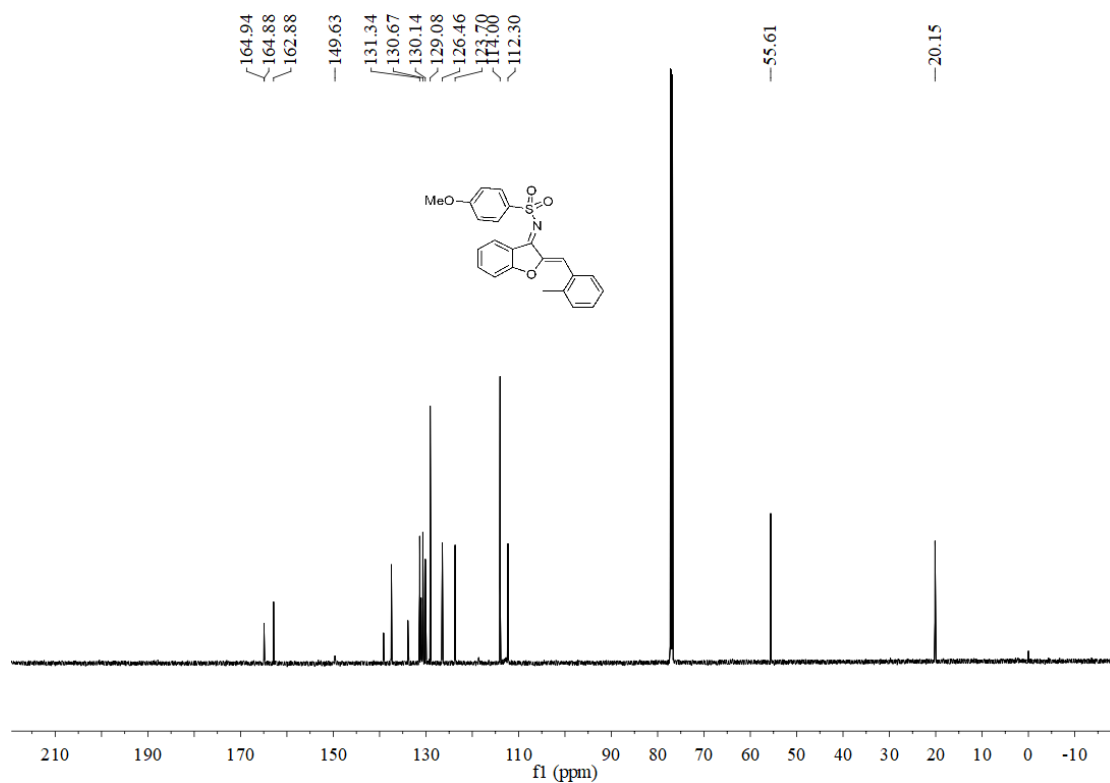
### <sup>13</sup>C NMR Spectrum of 1g



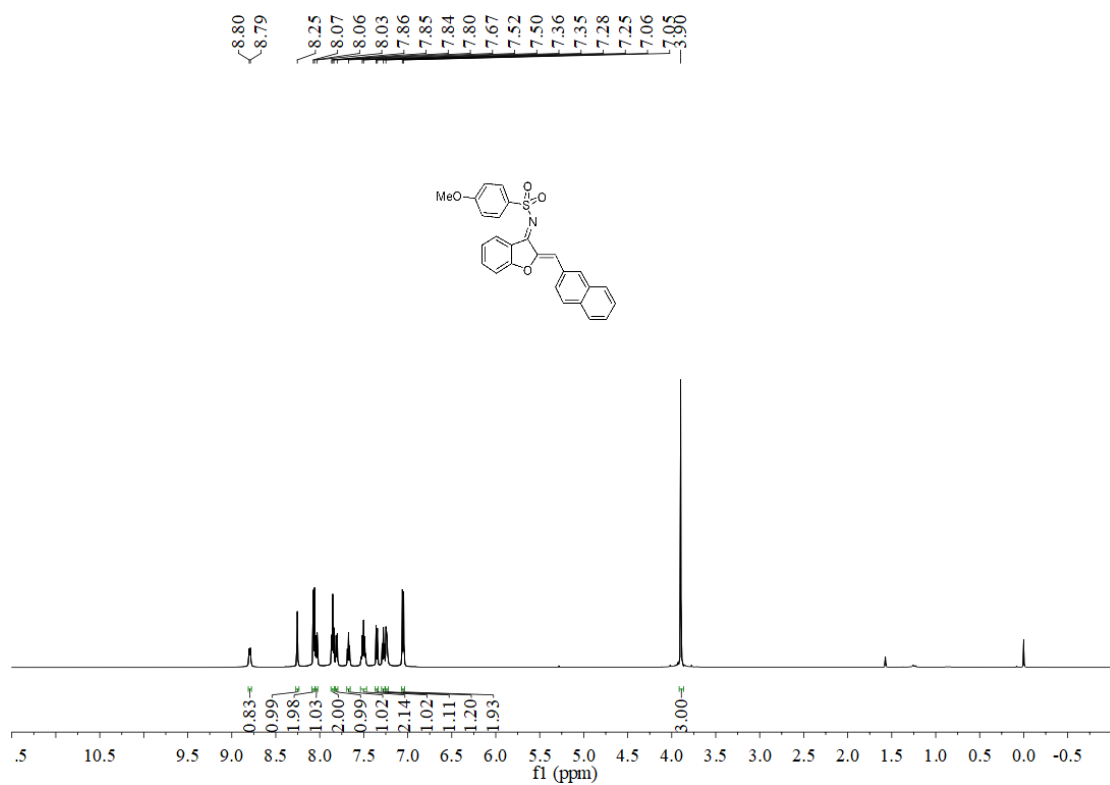
### <sup>1</sup>H NMR Spectrum of 1h



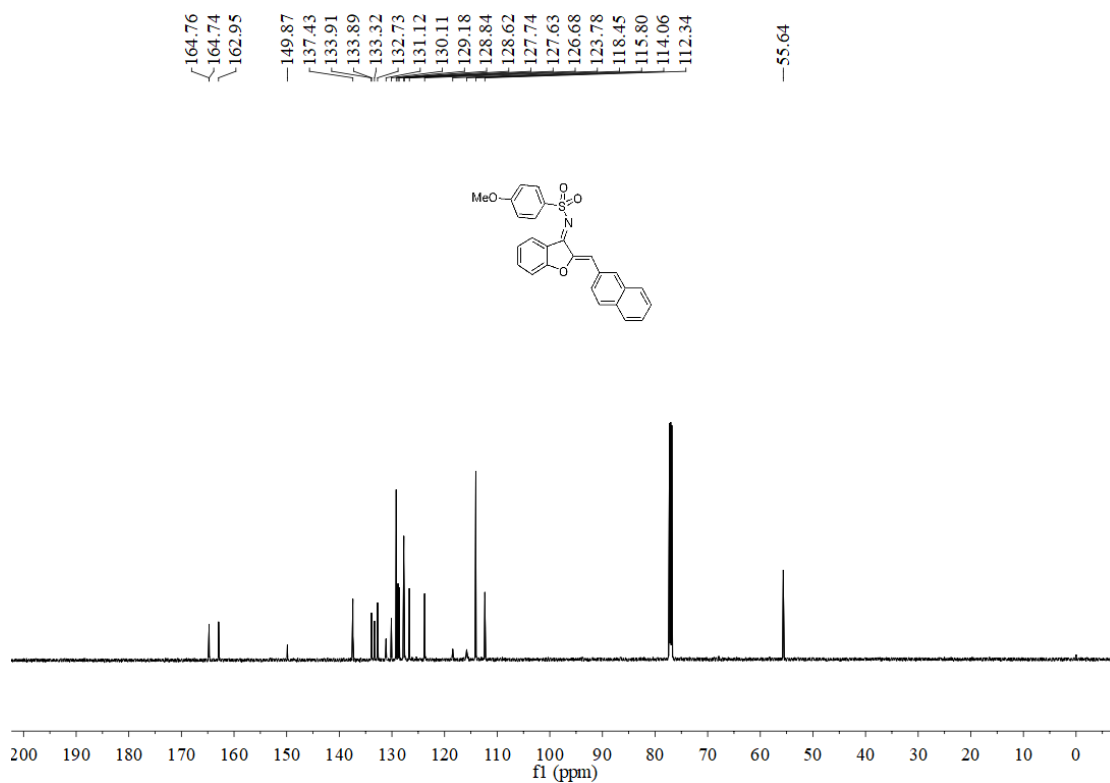
### <sup>13</sup>C NMR Spectrum of 1h



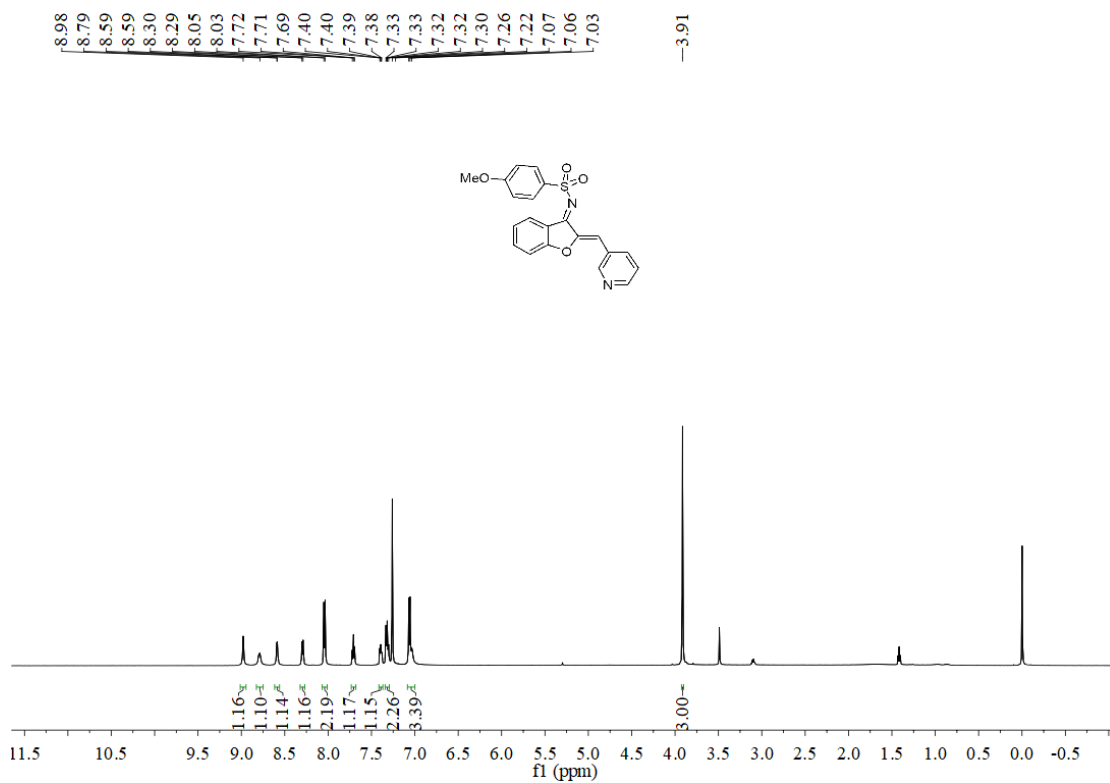
### <sup>1</sup>H NMR Spectrum of 1i



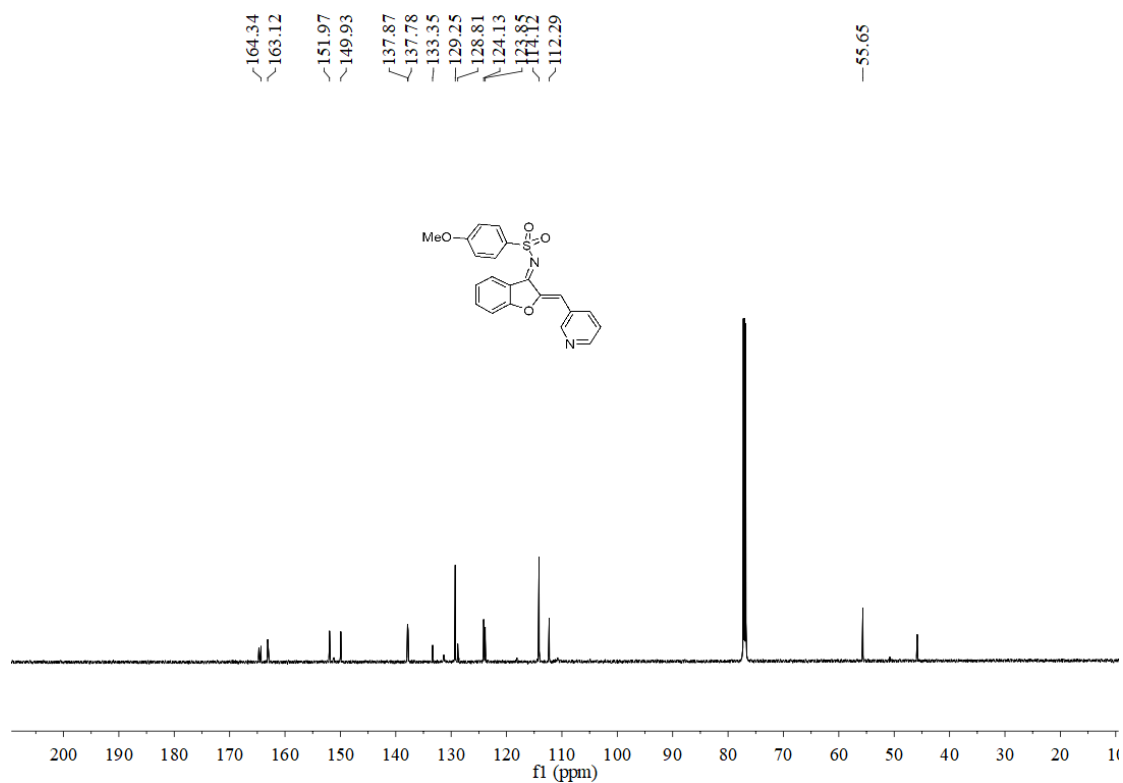
### <sup>13</sup>C NMR Spectrum of 1i



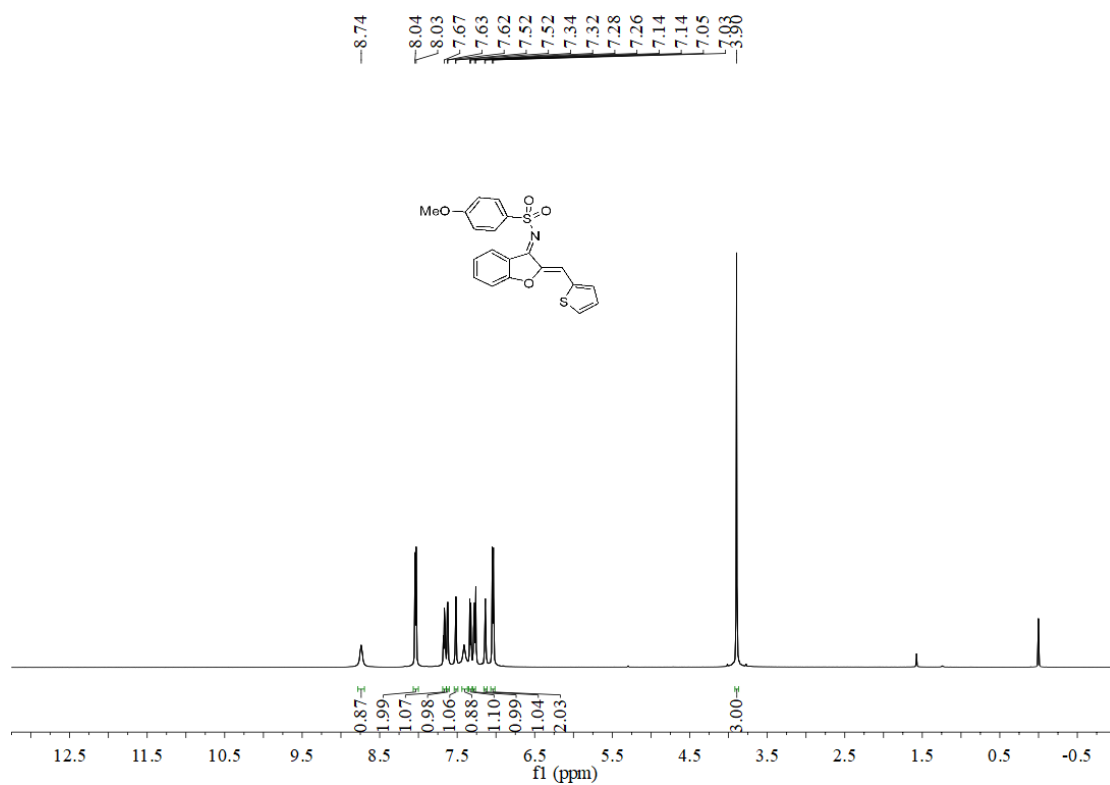
### <sup>1</sup>H NMR Spectrum of 1j



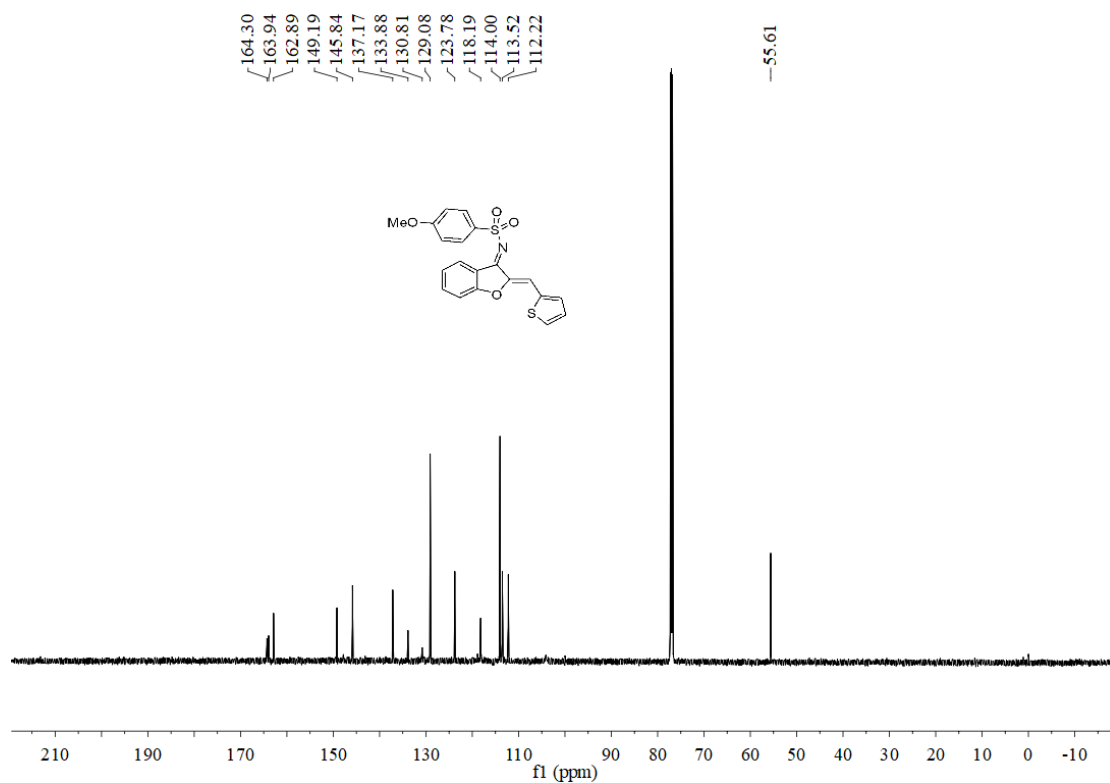
### <sup>13</sup>C NMR Spectrum of 1j



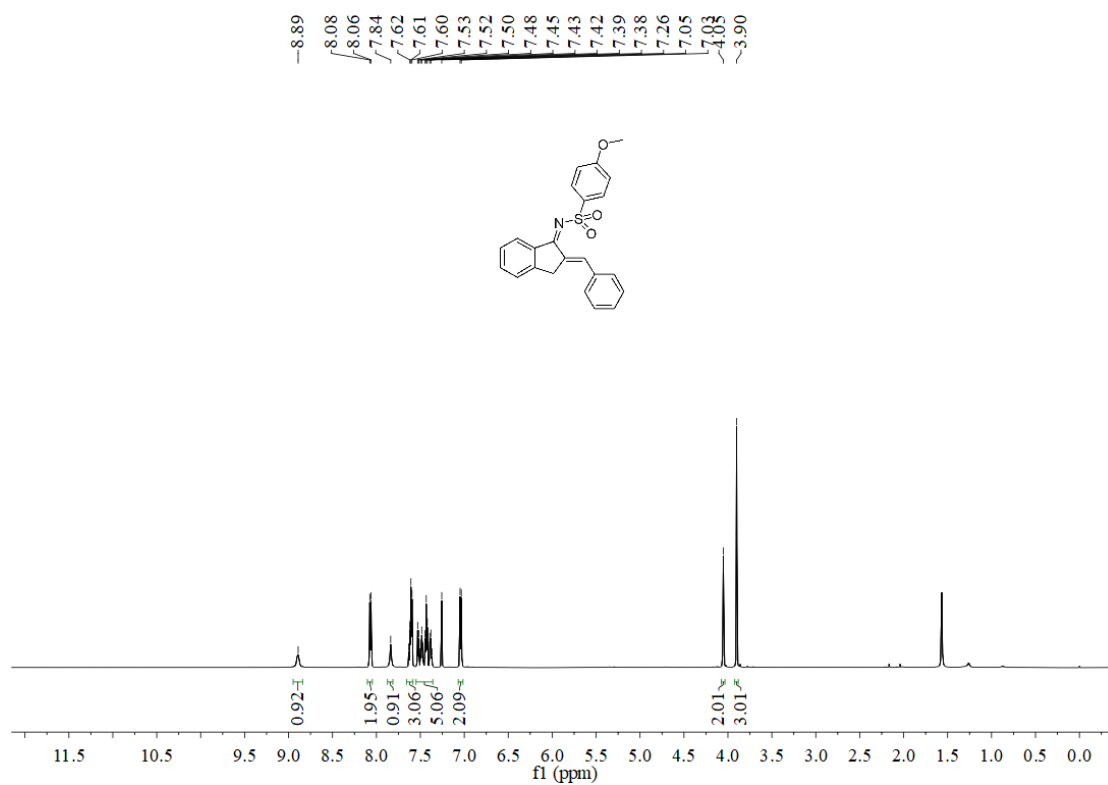
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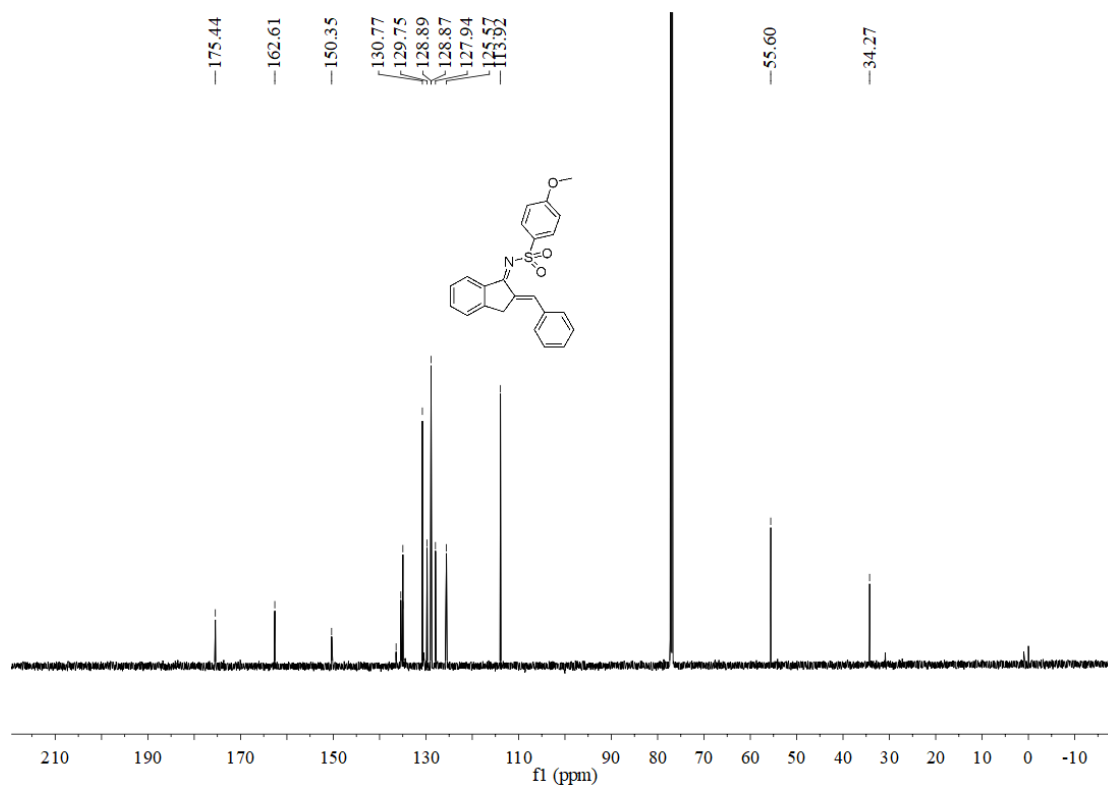
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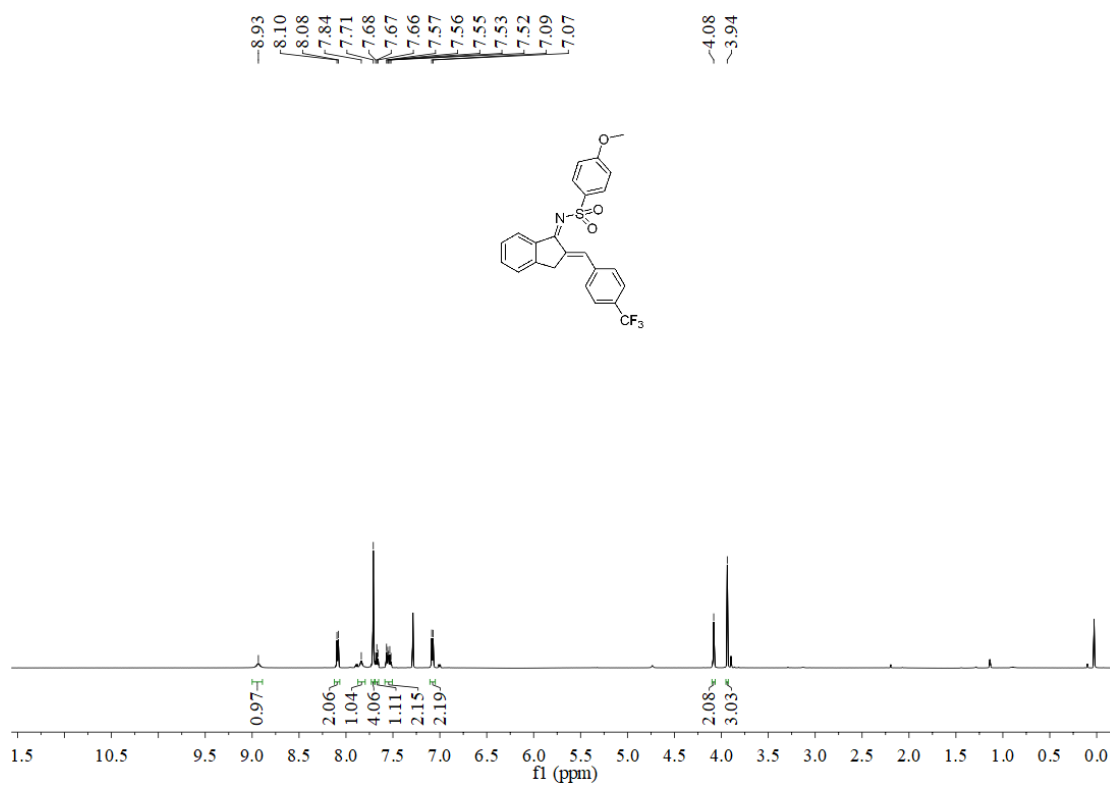
### <sup>1</sup>H NMR Spectrum of 11



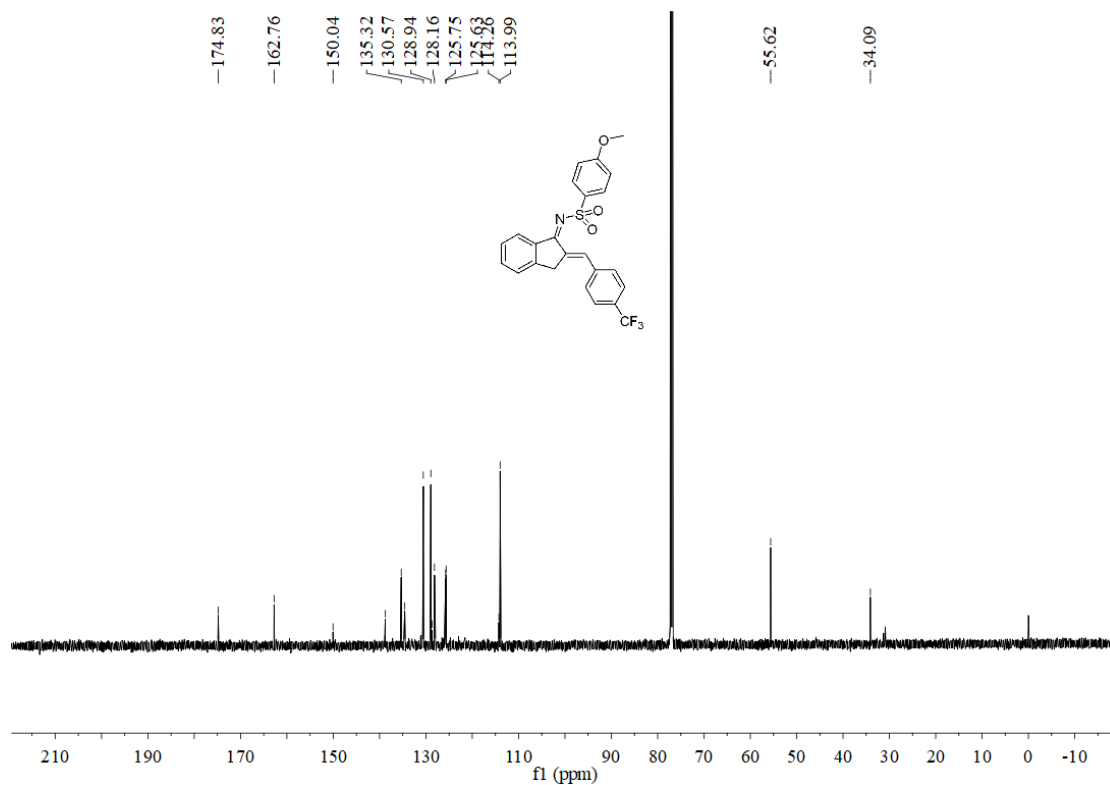
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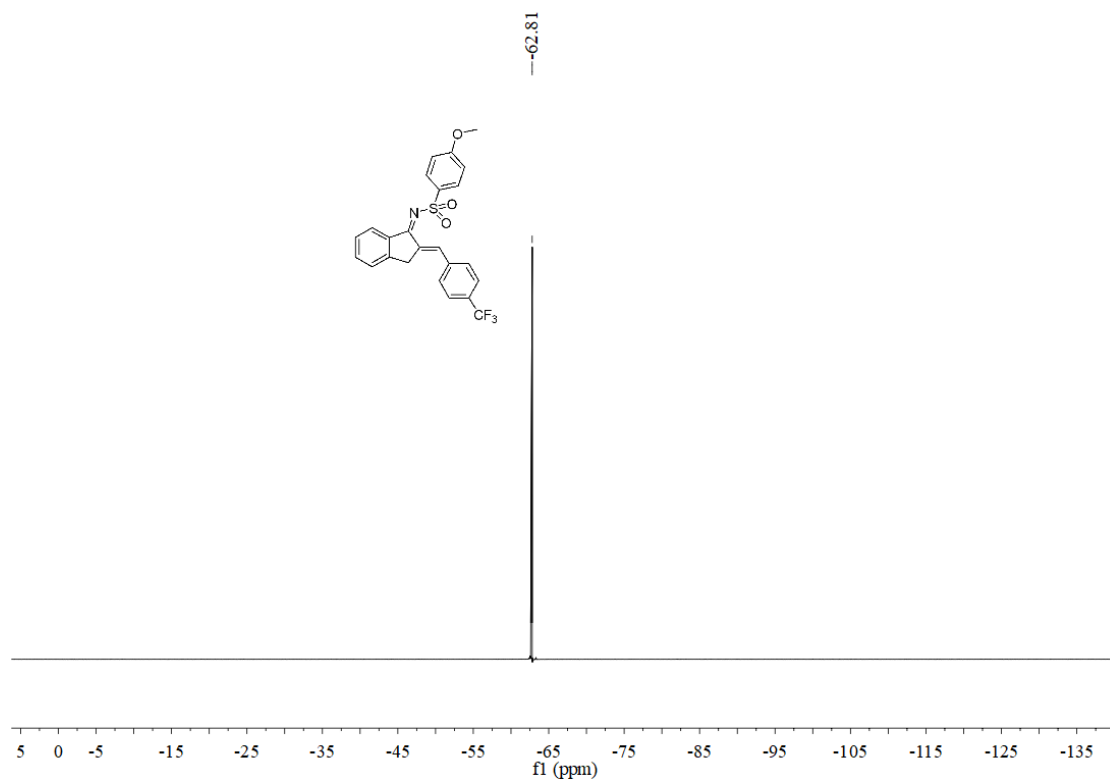
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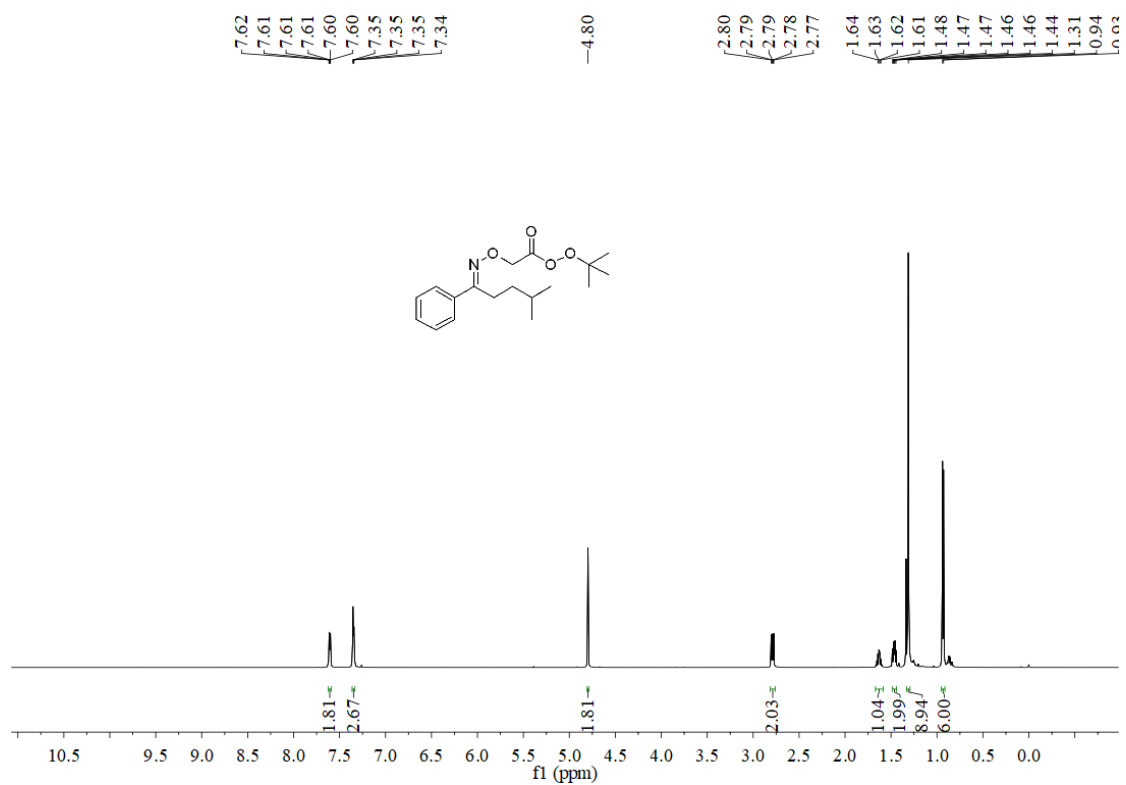
### <sup>13</sup>C NMR Spectrum of 1m



### <sup>19</sup>F NMR Spectrum of 1m

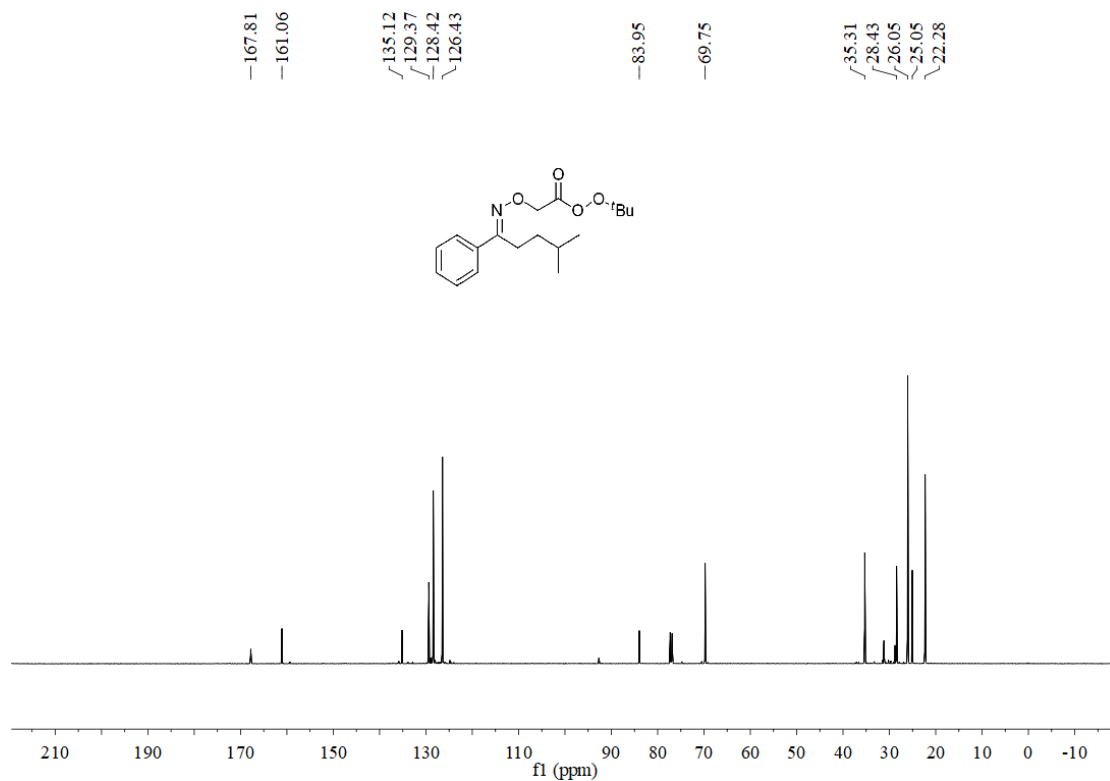


### <sup>1</sup>H NMR Spectrum of 4a

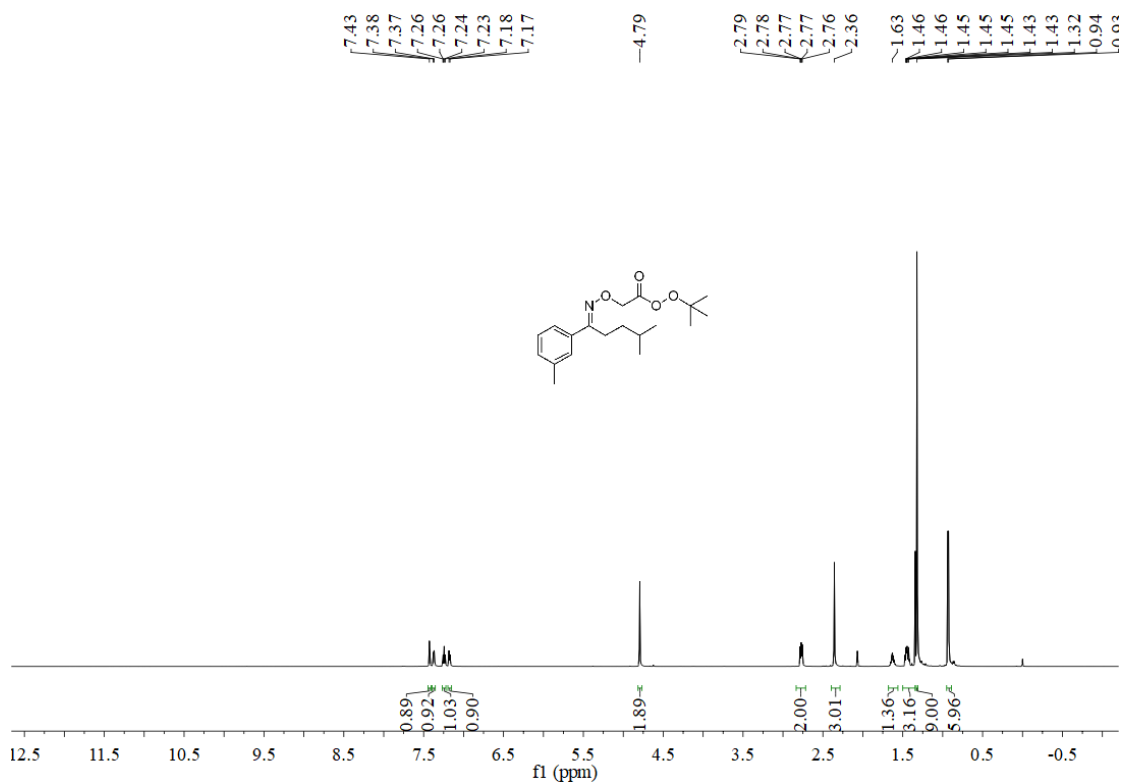




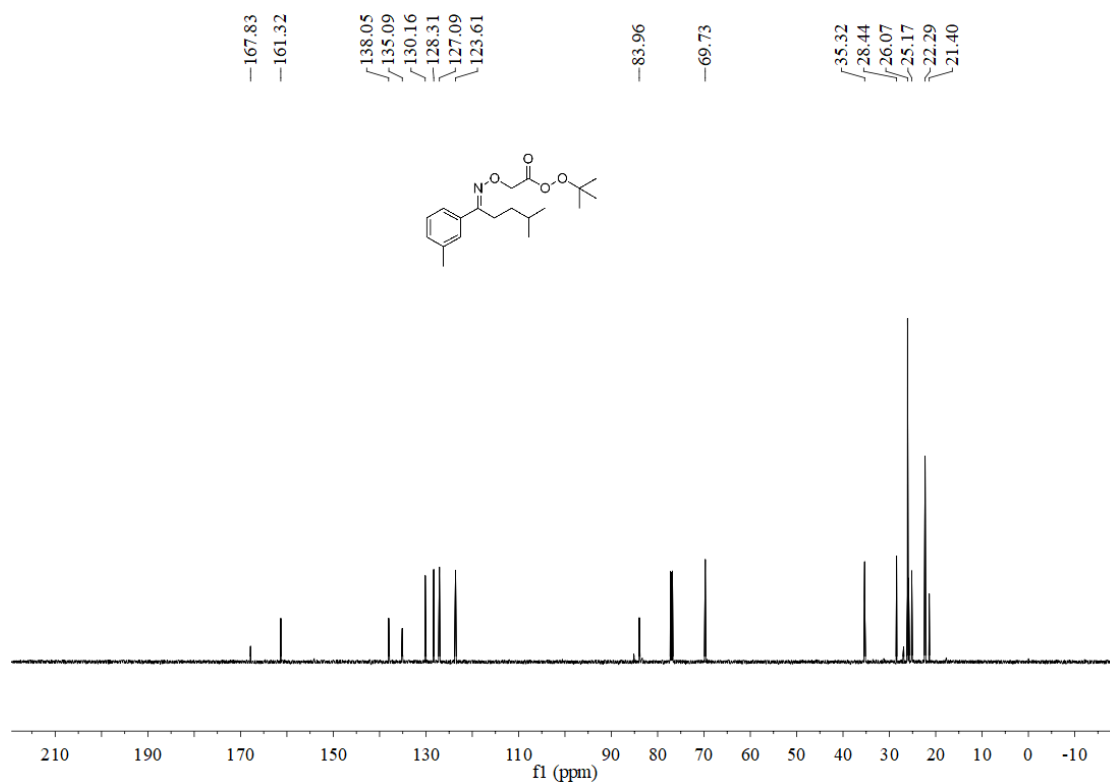
### <sup>13</sup>C NMR Spectrum of 4a



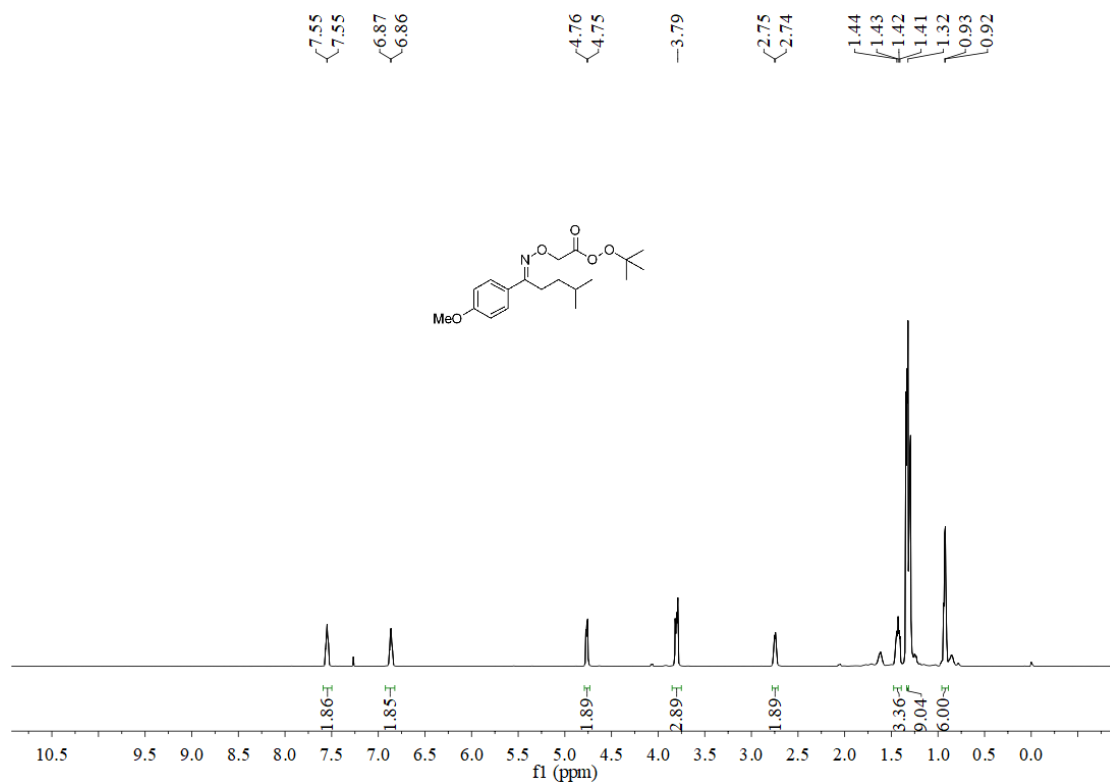
### <sup>1</sup>H NMR Spectrum of 4b



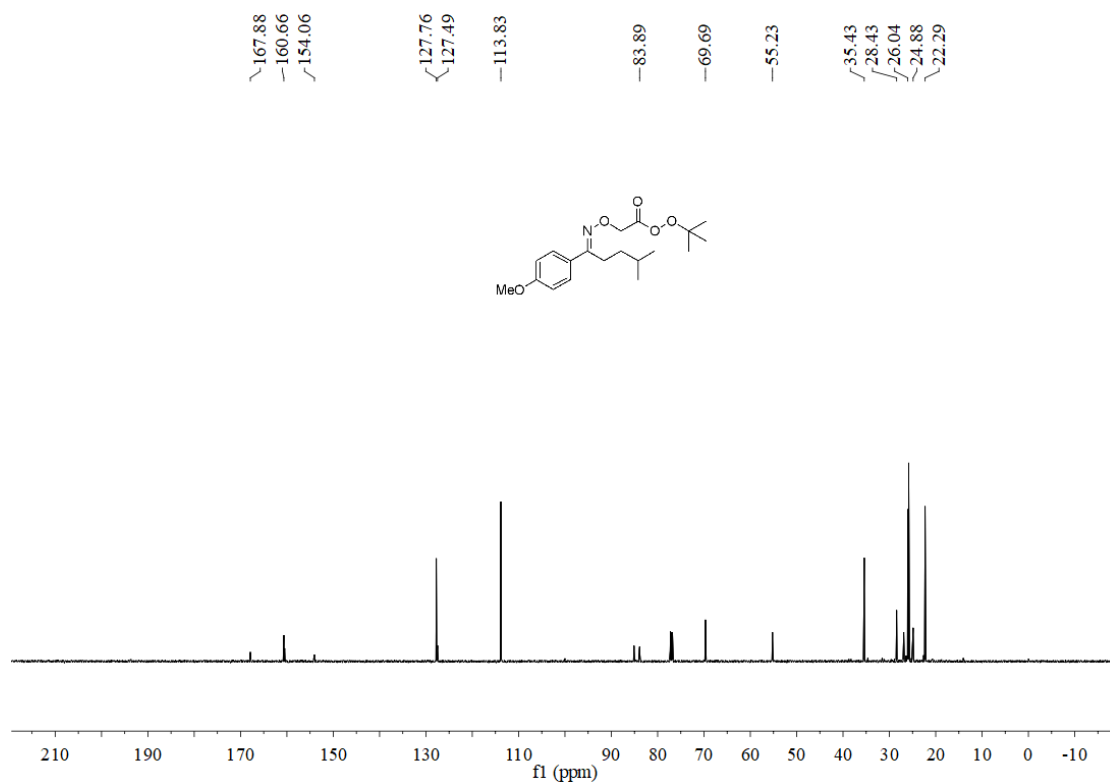
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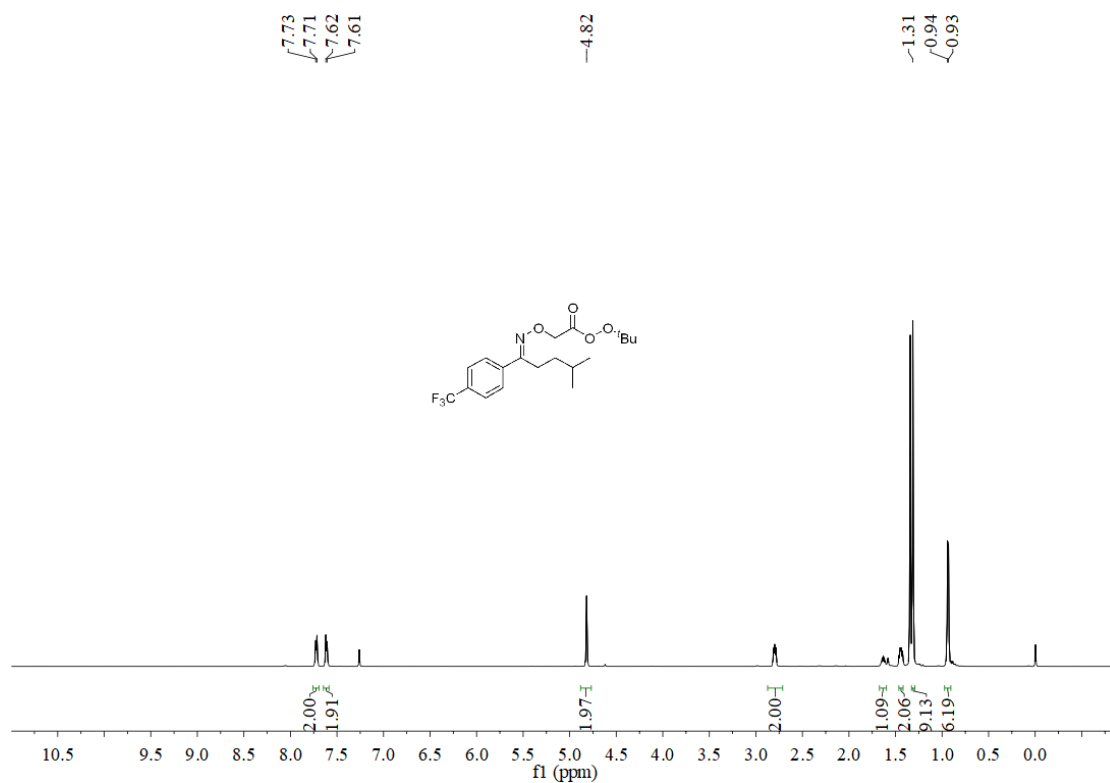
### <sup>1</sup>H NMR Spectrum of 4c



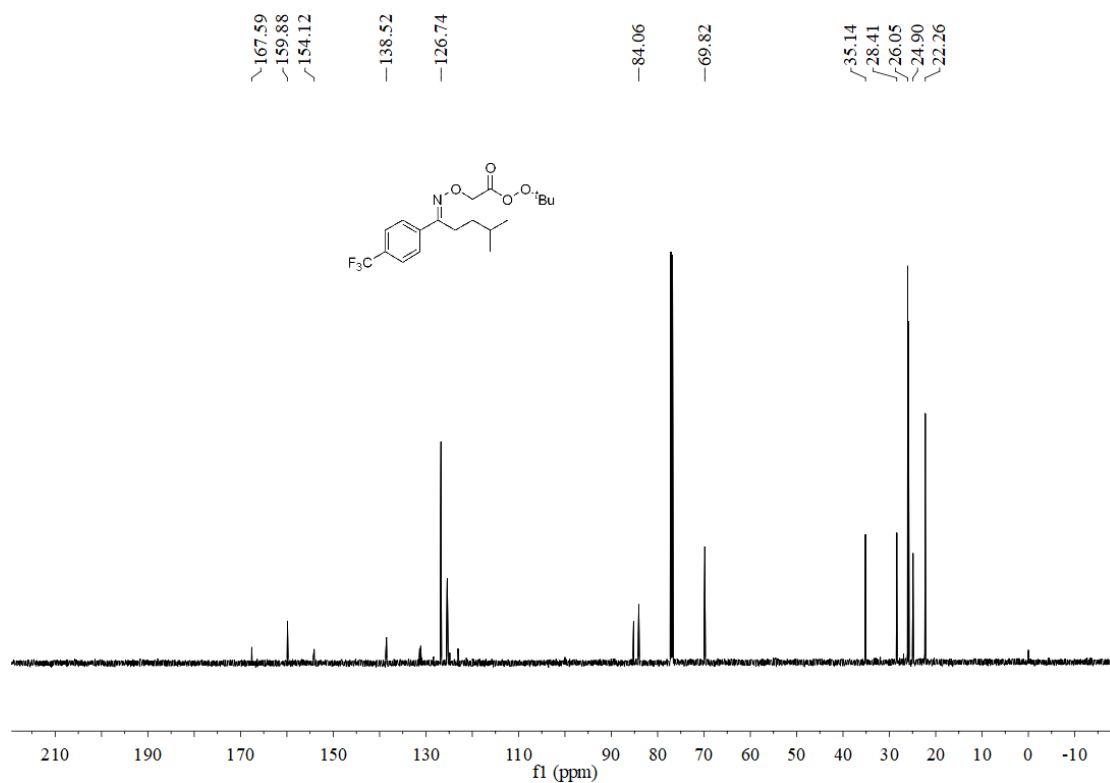
### <sup>13</sup>C NMR Spectrum of 4c



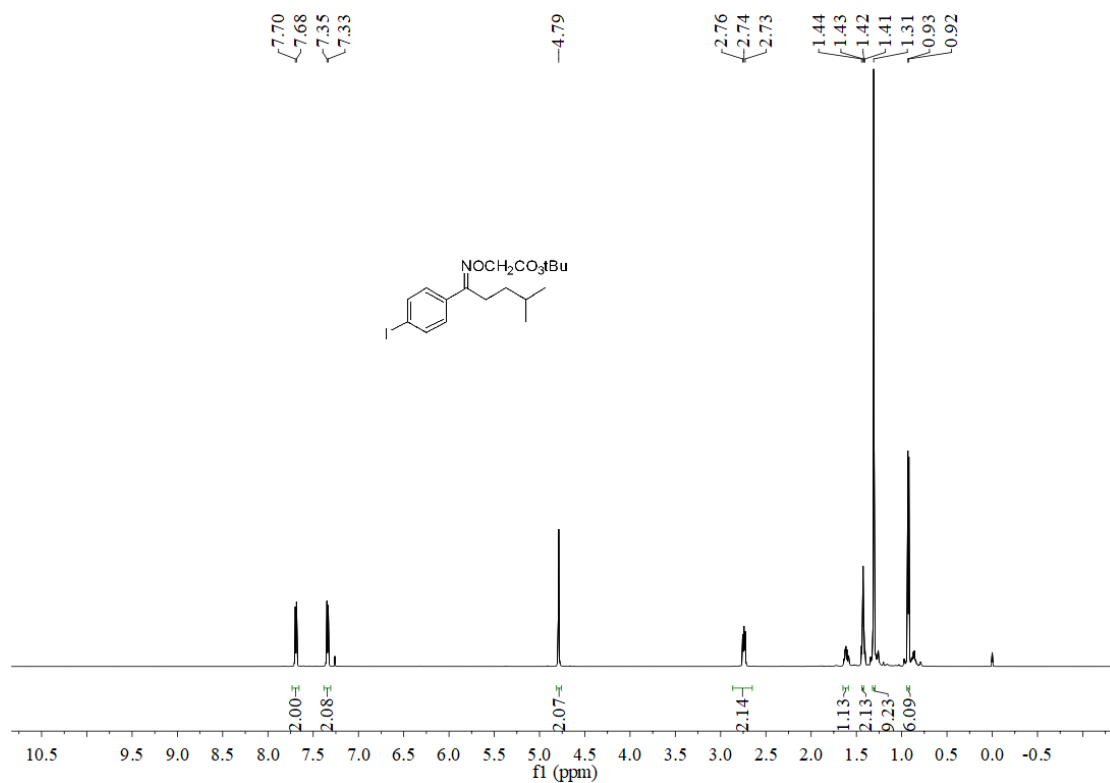
### <sup>1</sup>H NMR Spectrum of 4d



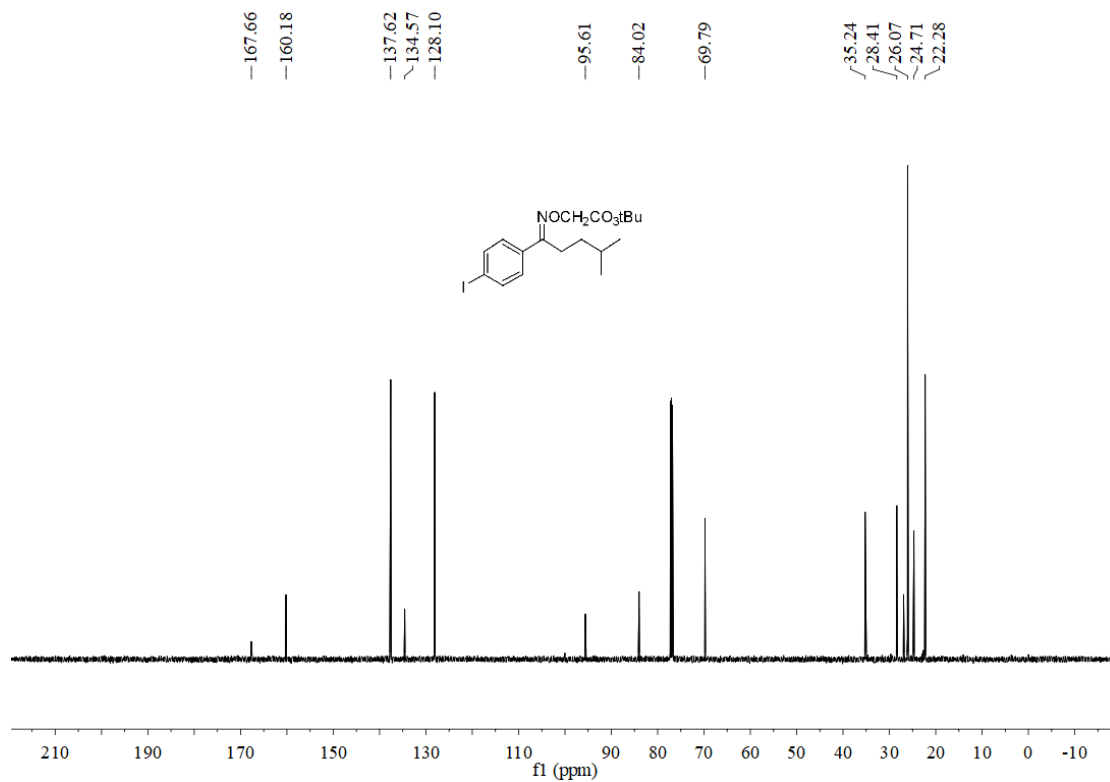
### <sup>13</sup>C NMR Spectrum of 4d



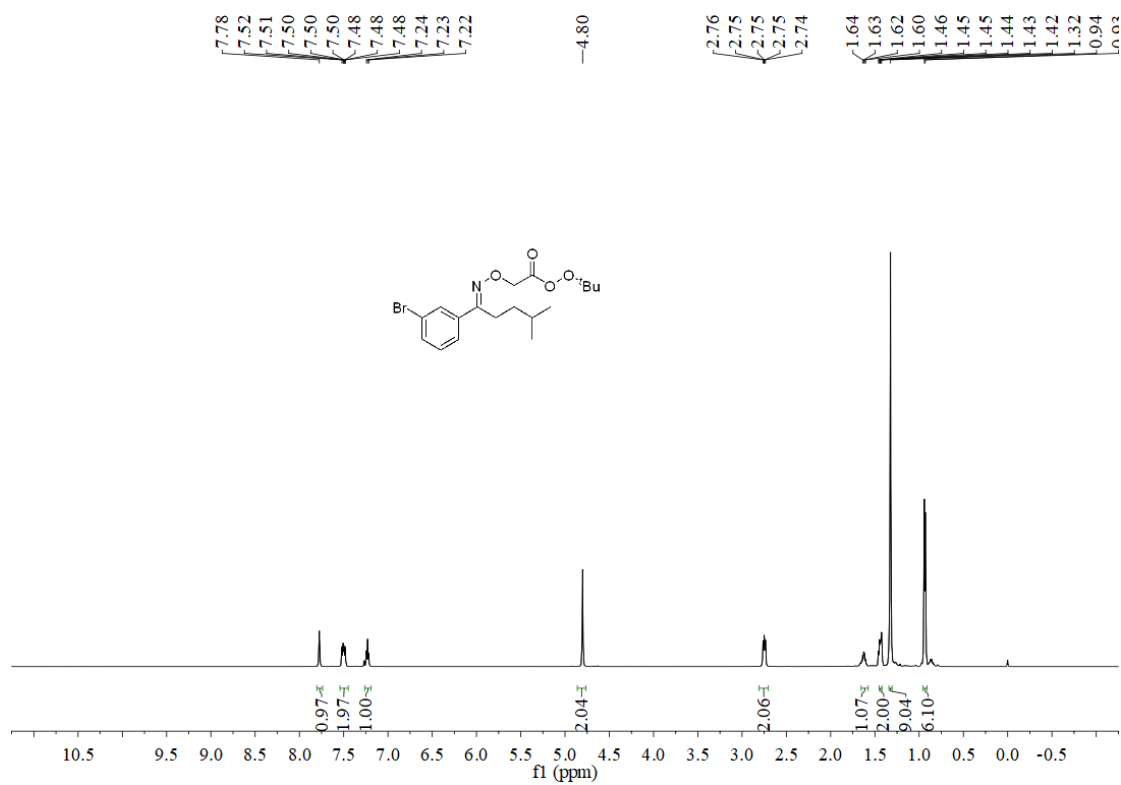
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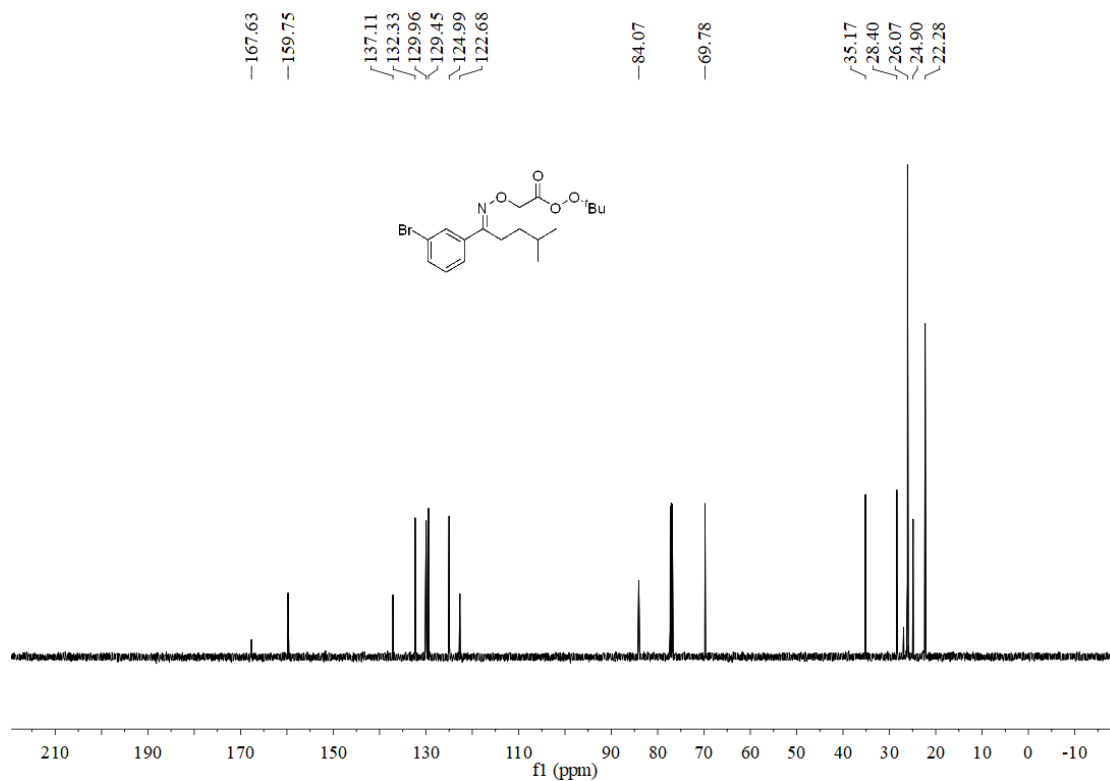
### <sup>13</sup>C NMR Spectrum of 4e



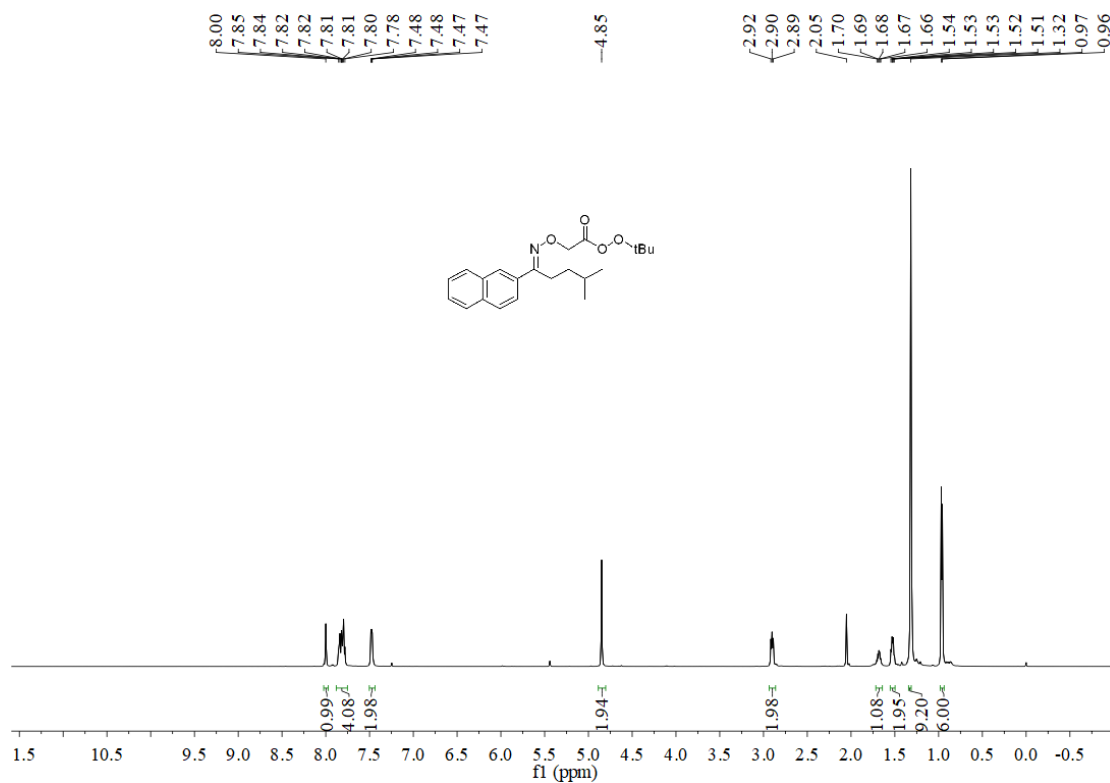
### <sup>1</sup>H NMR Spectrum of 4f



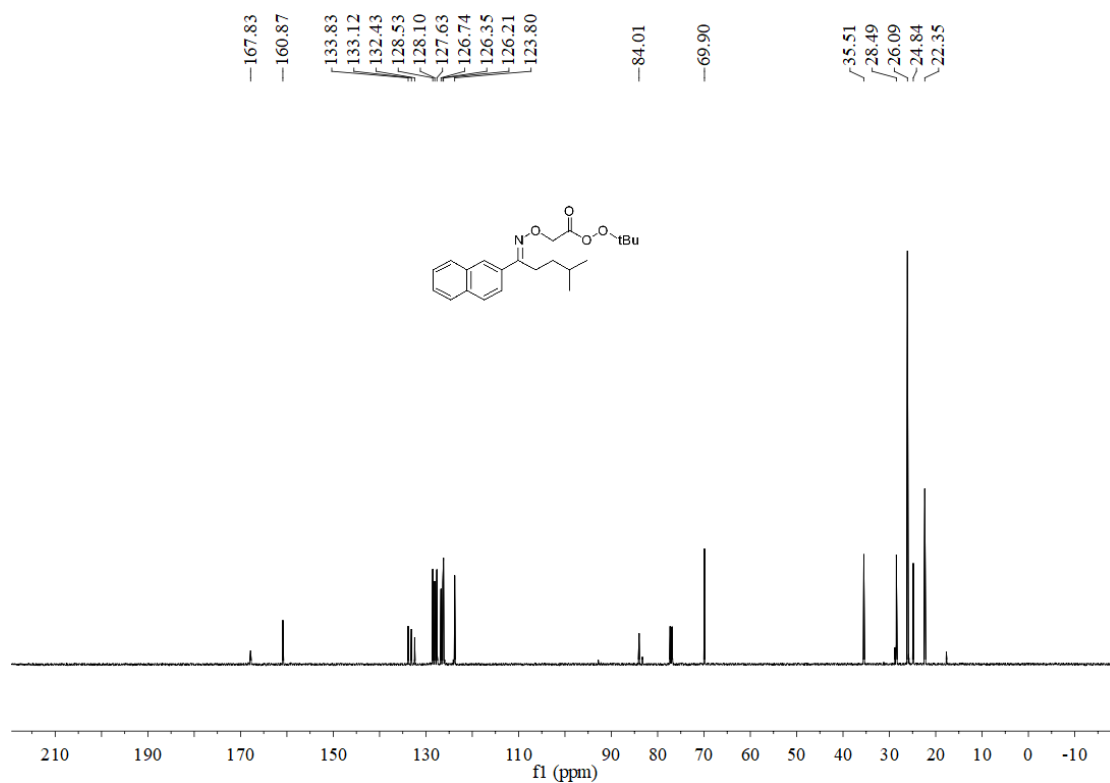
### <sup>13</sup>C NMR Spectrum of 4f



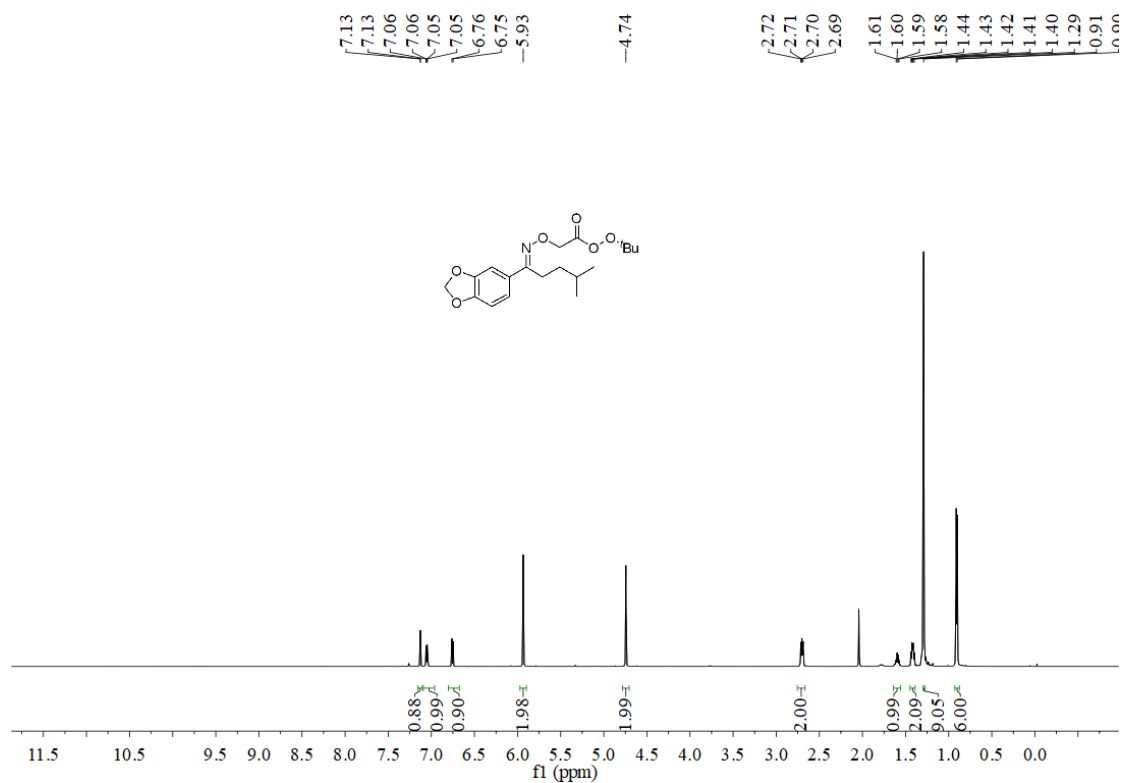
### <sup>1</sup>H NMR Spectrum of 4h



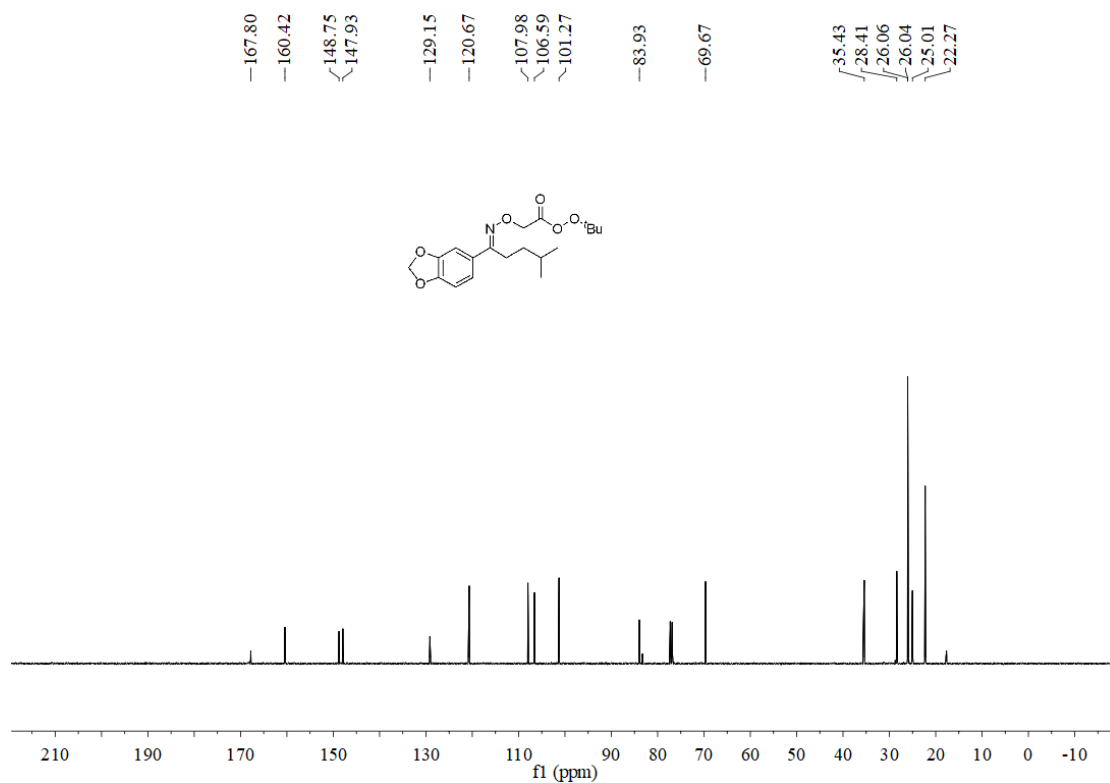
### <sup>13</sup>C NMR Spectrum of 4h



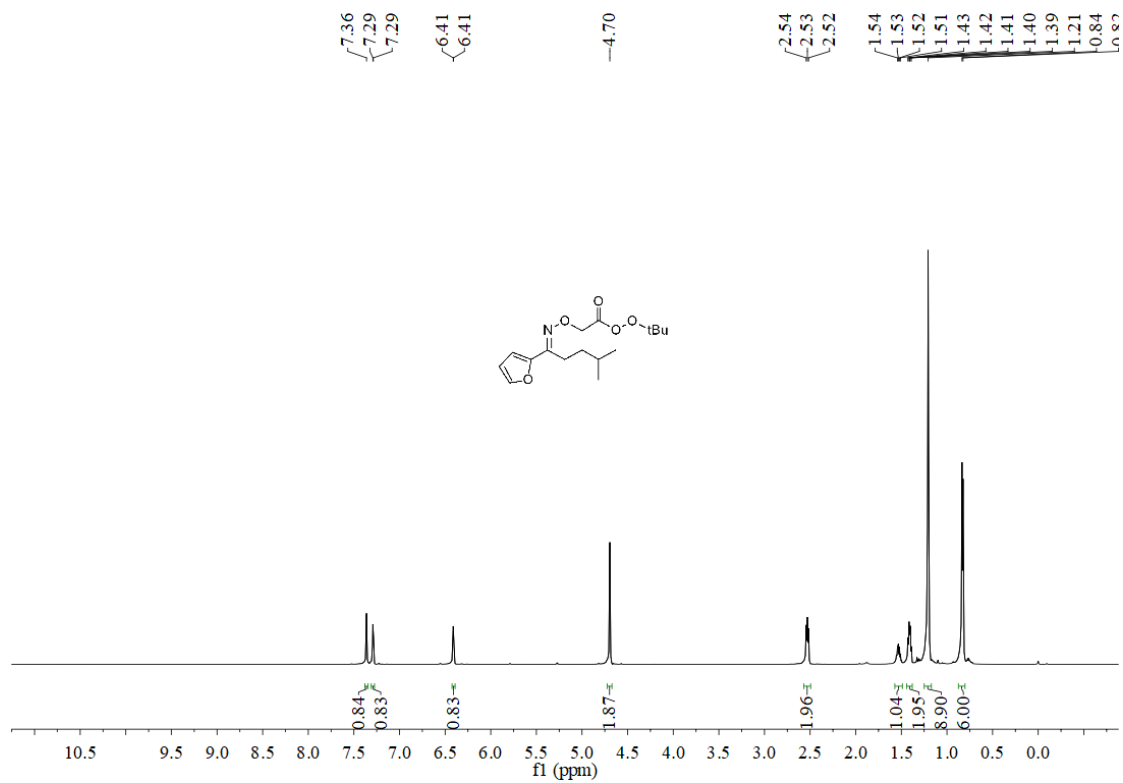
### <sup>1</sup>H NMR Spectrum of 4i



### <sup>13</sup>C NMR Spectrum of 4i

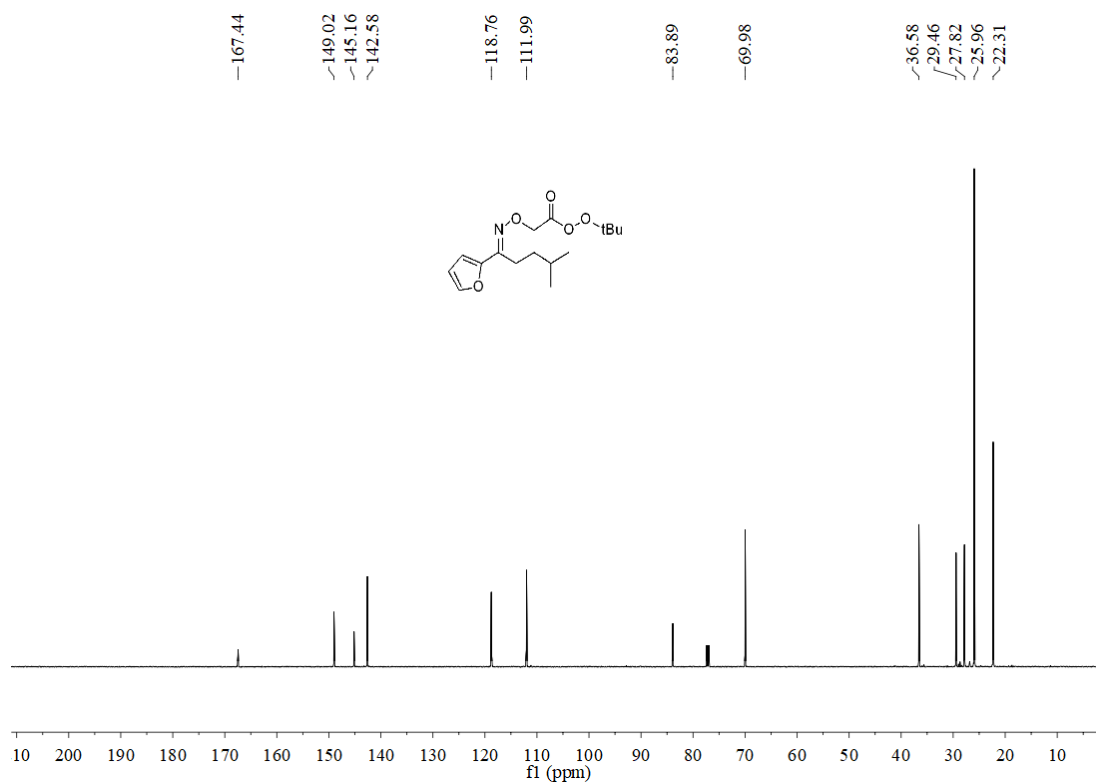


### <sup>1</sup>H NMR Spectrum of 4j

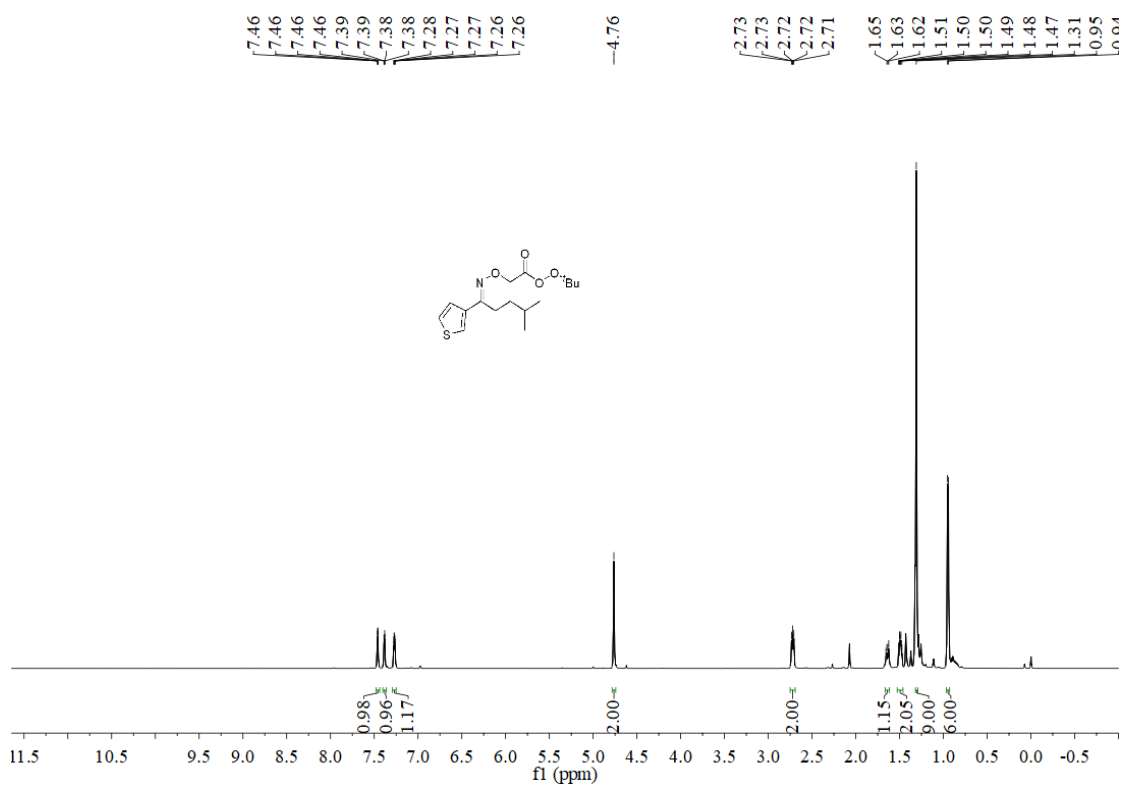




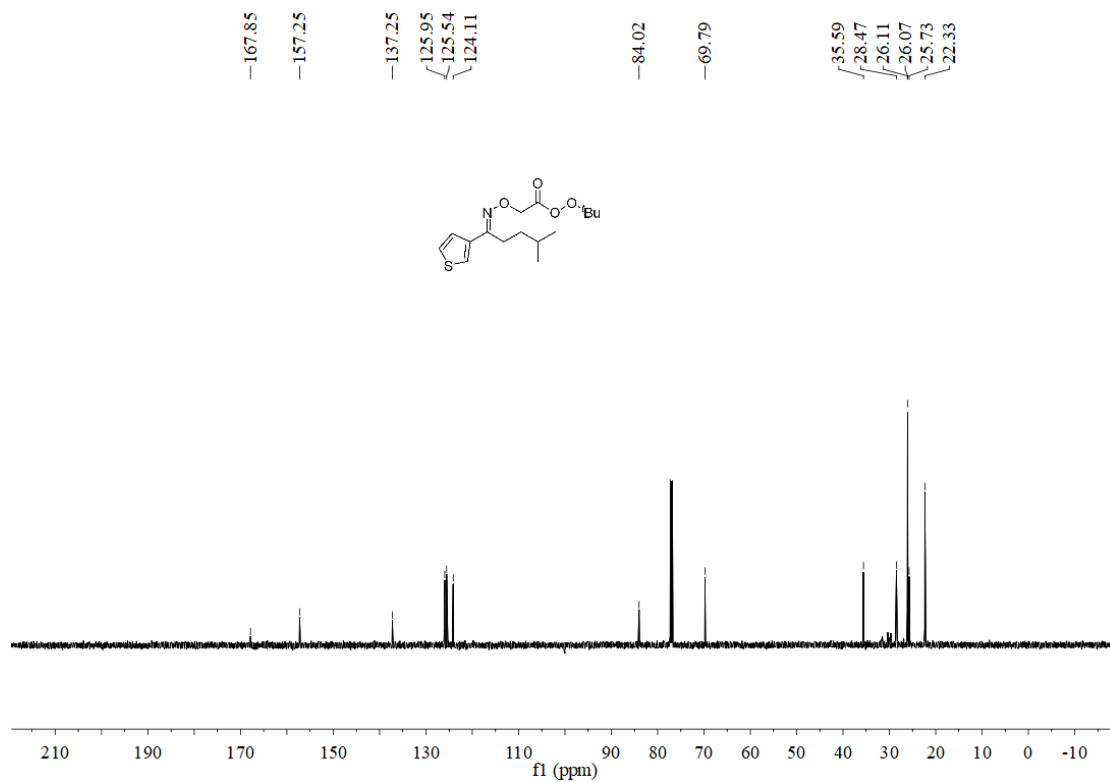
### <sup>13</sup>C NMR Spectrum of 4j



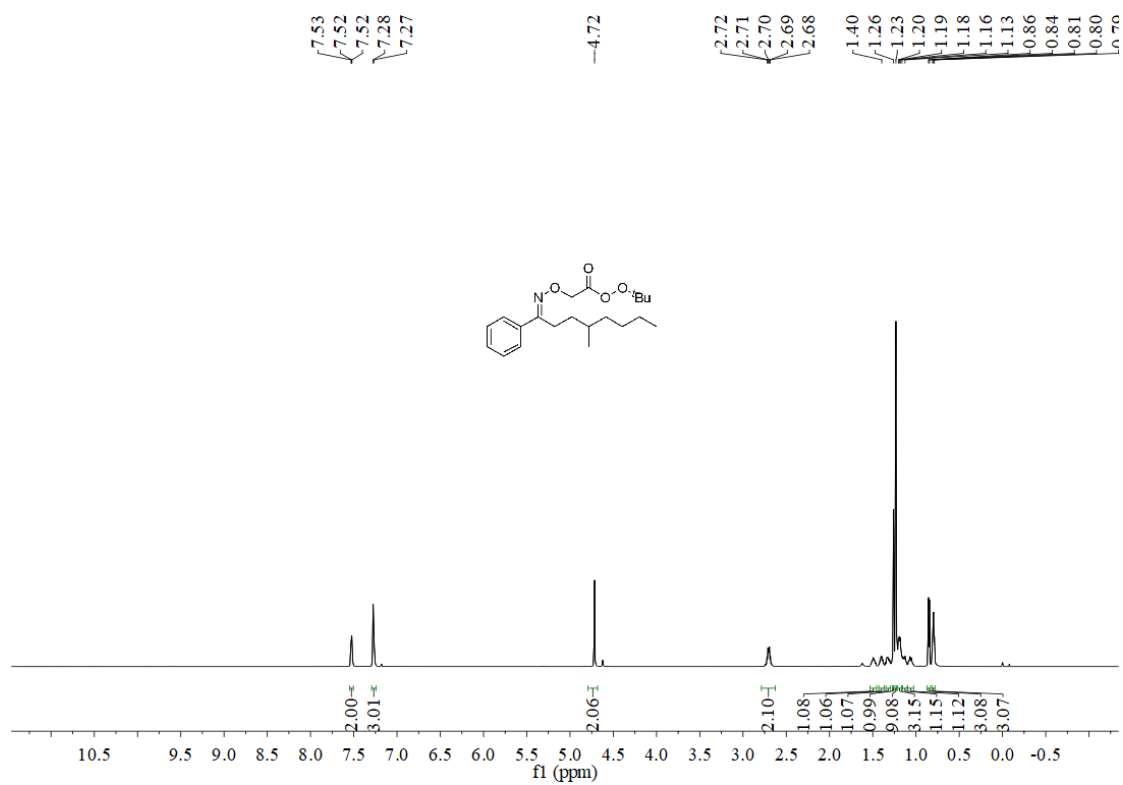
### <sup>1</sup>H NMR Spectrum of 4k



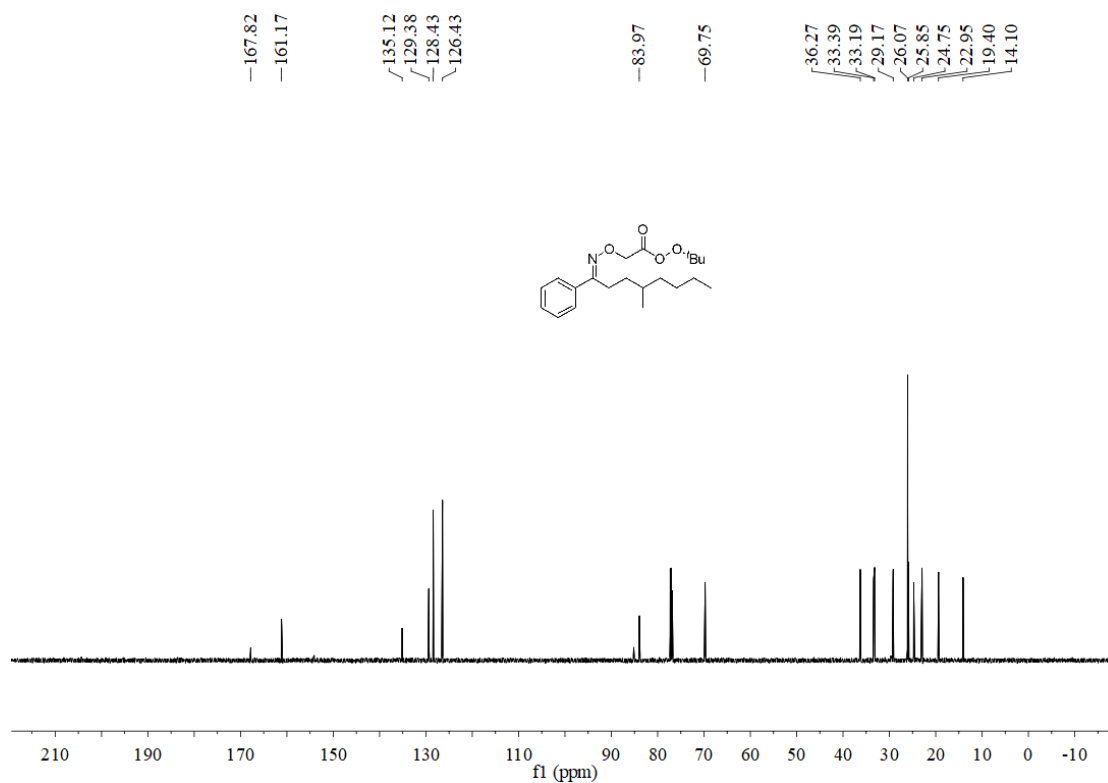
### <sup>13</sup>C NMR Spectrum of 4k



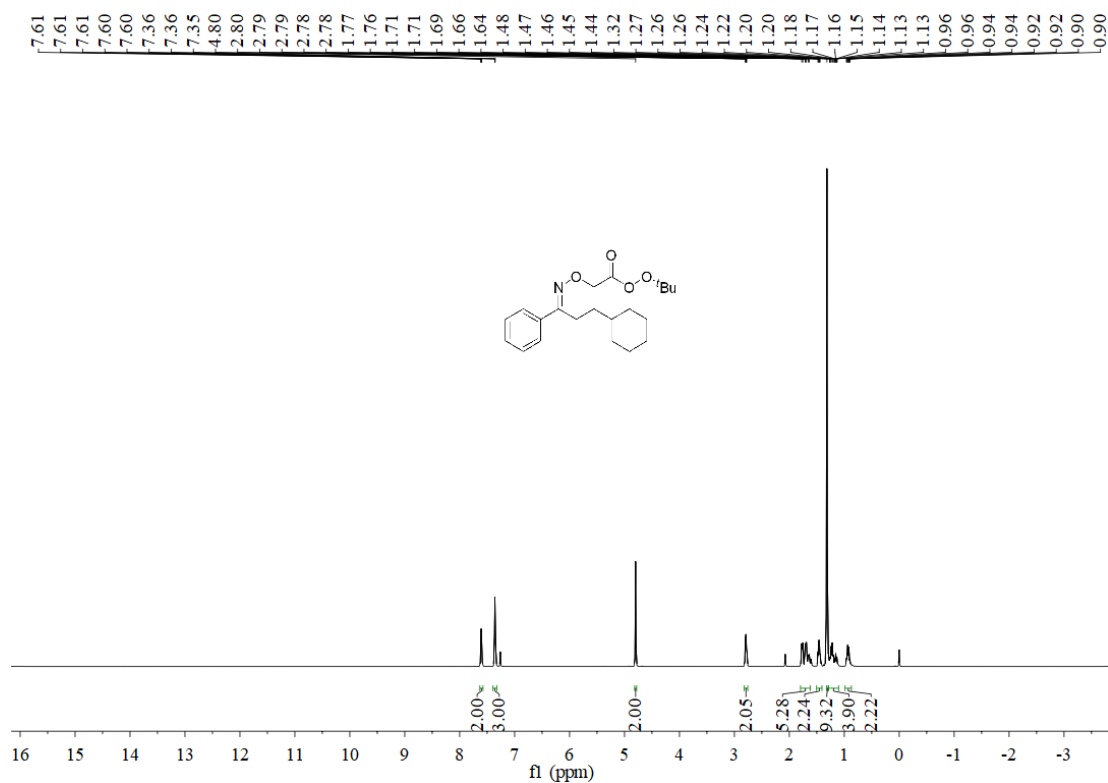
### <sup>1</sup>H NMR Spectrum of 4l



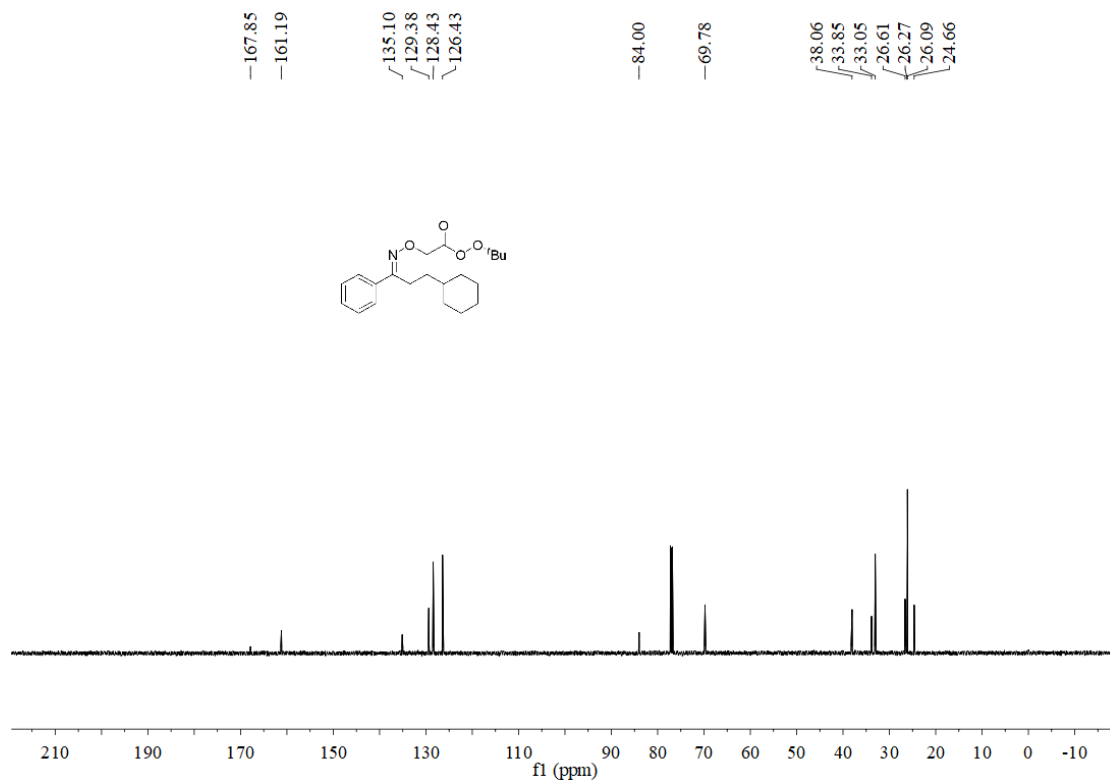
### <sup>13</sup>C NMR Spectrum of 4l



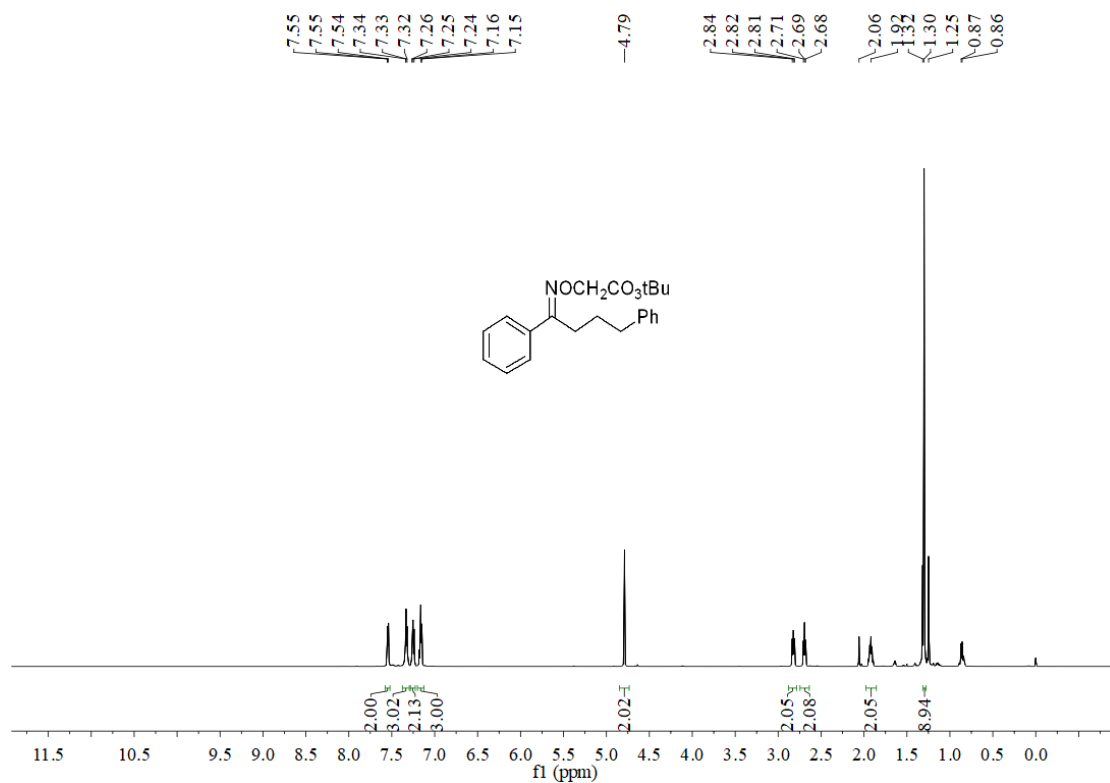
### <sup>1</sup>H NMR Spectrum of 4m



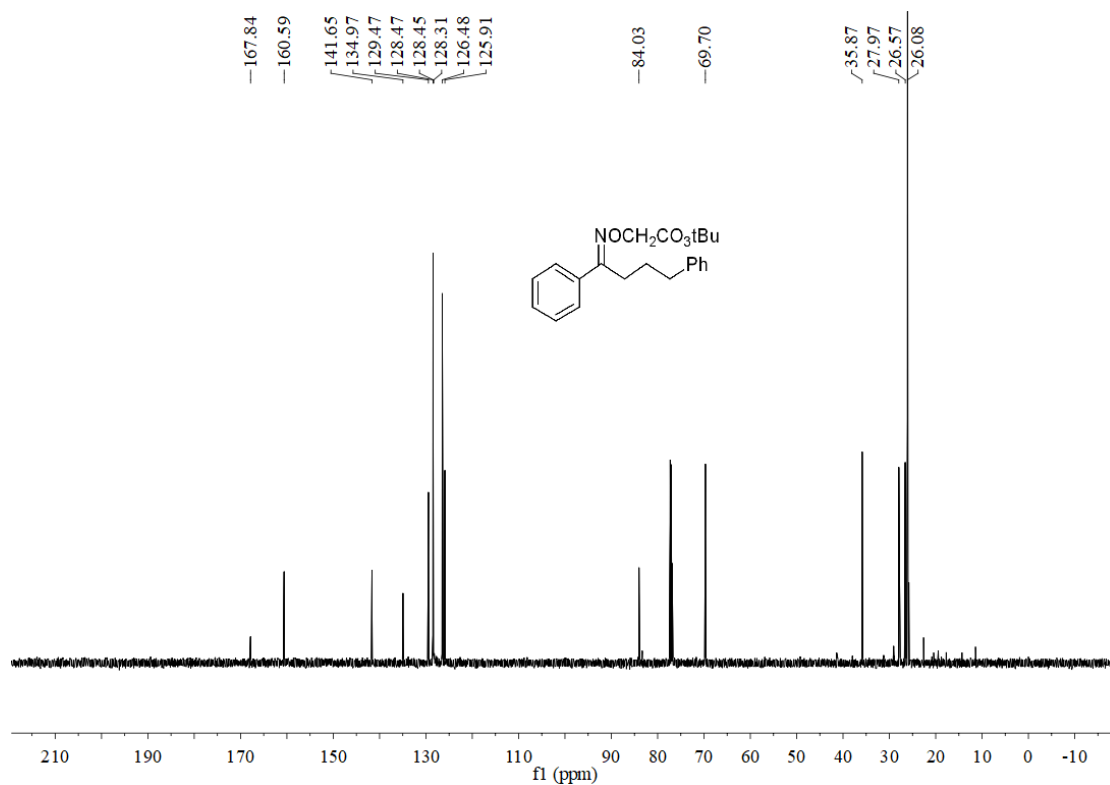
### <sup>13</sup>C NMR Spectrum of 4m



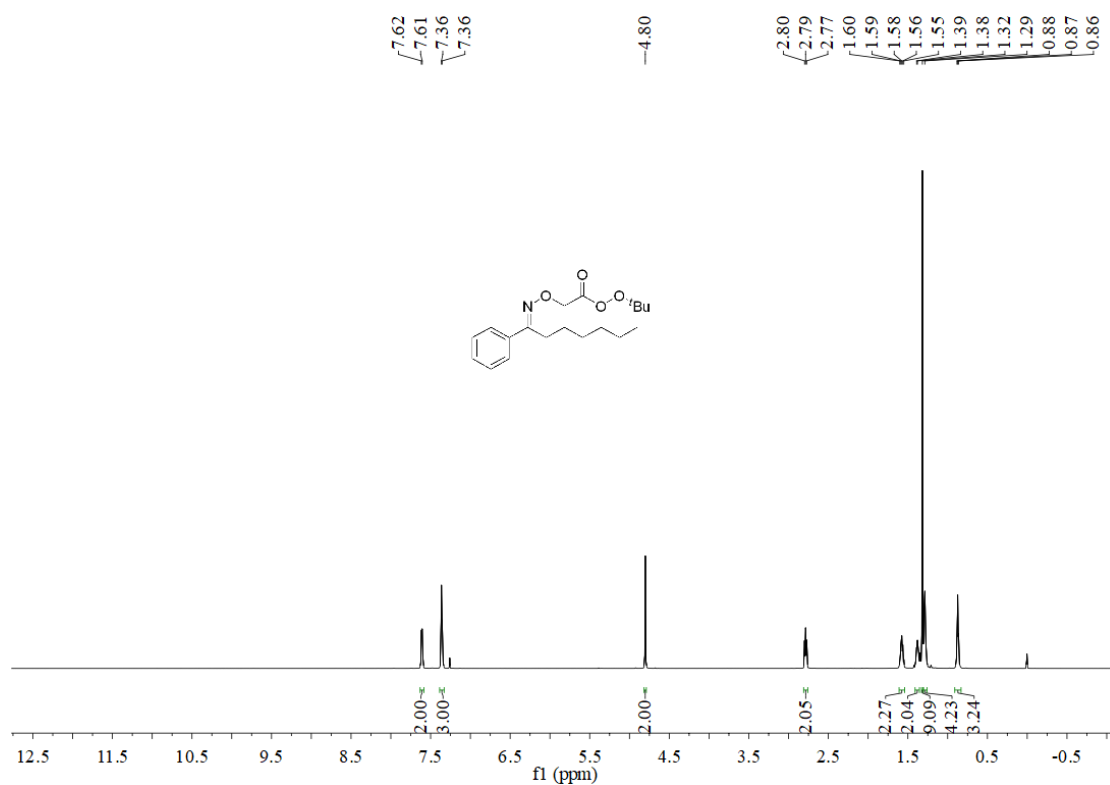
### <sup>1</sup>H NMR Spectrum of 4n



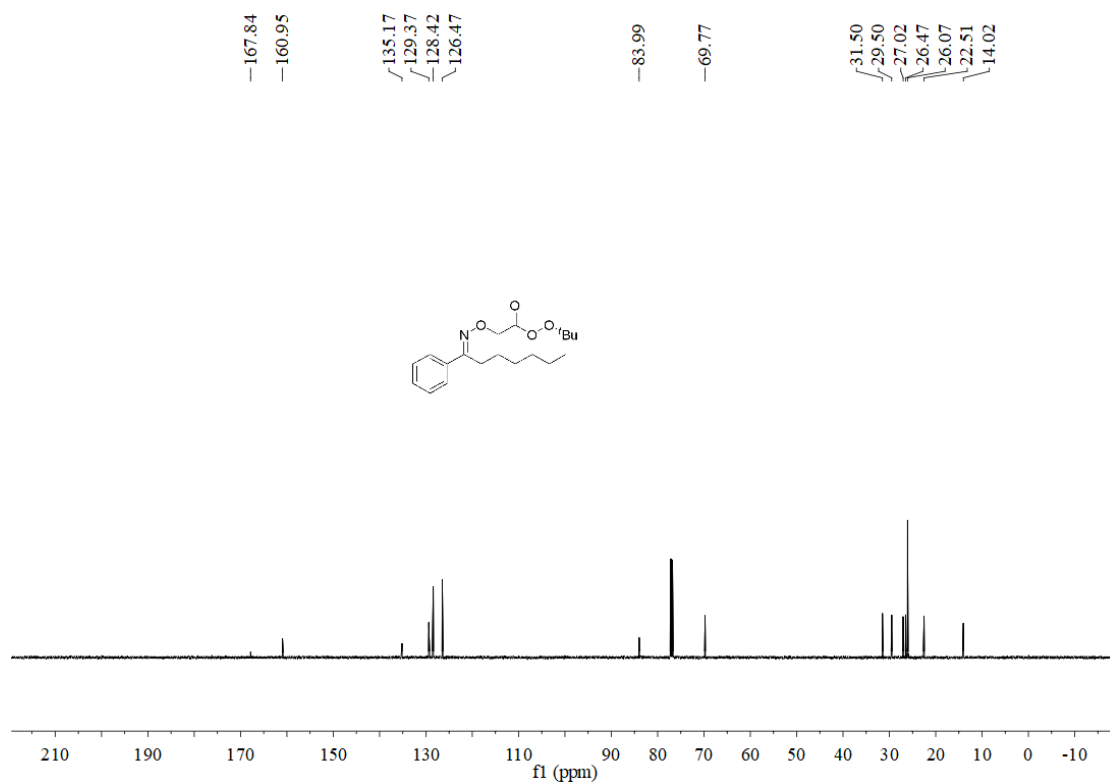
### <sup>13</sup>C NMR Spectrum of 4n



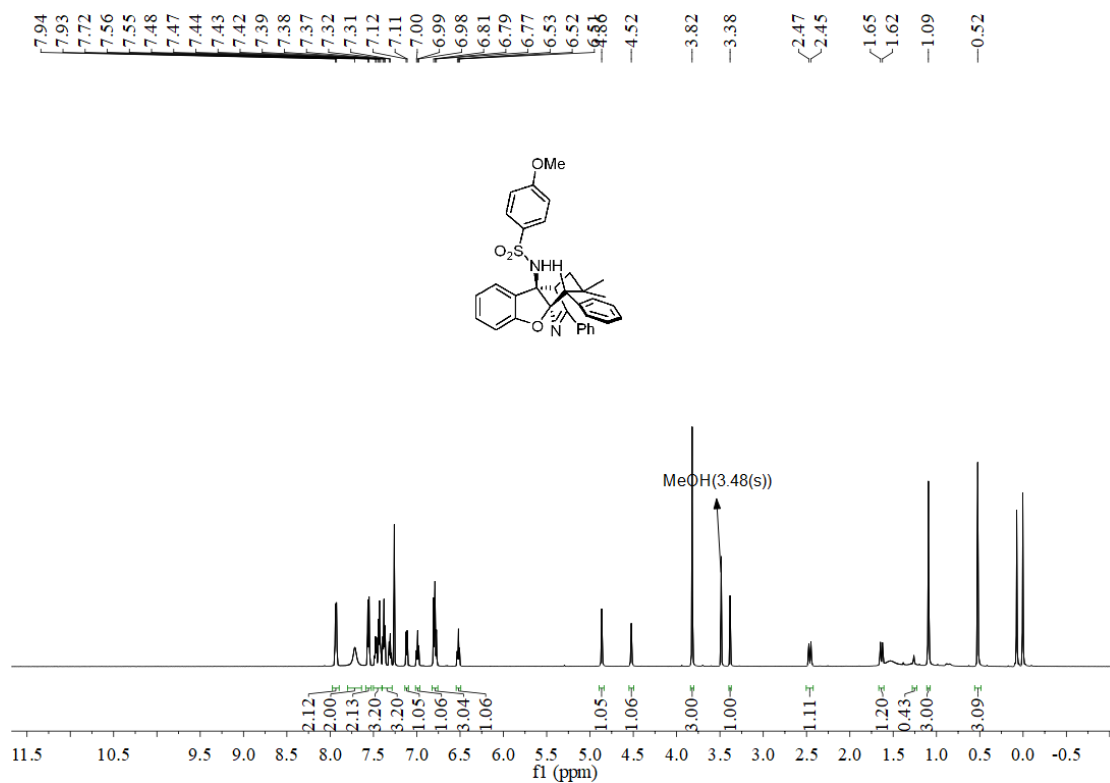
### <sup>1</sup>H NMR Spectrum of 4o



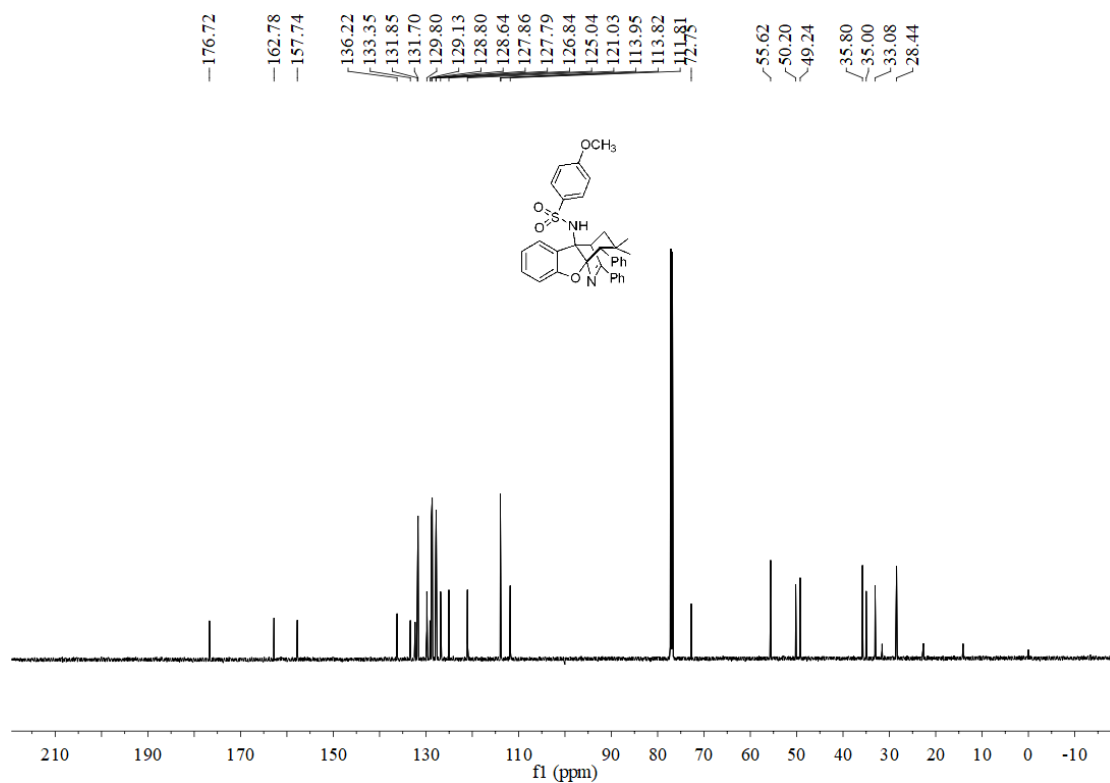
### <sup>13</sup>C NMR Spectrum of 4o



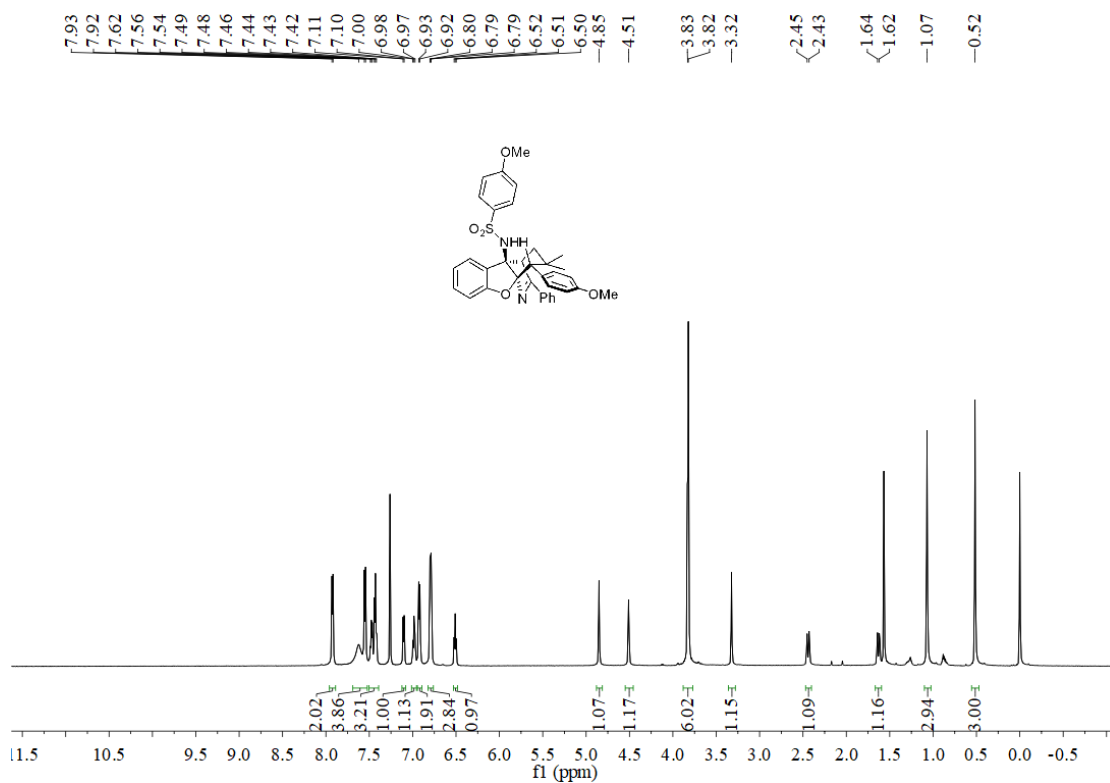
### <sup>1</sup>H NMR Spectrum of 3b



### <sup>13</sup>C NMR Spectrum of 3b



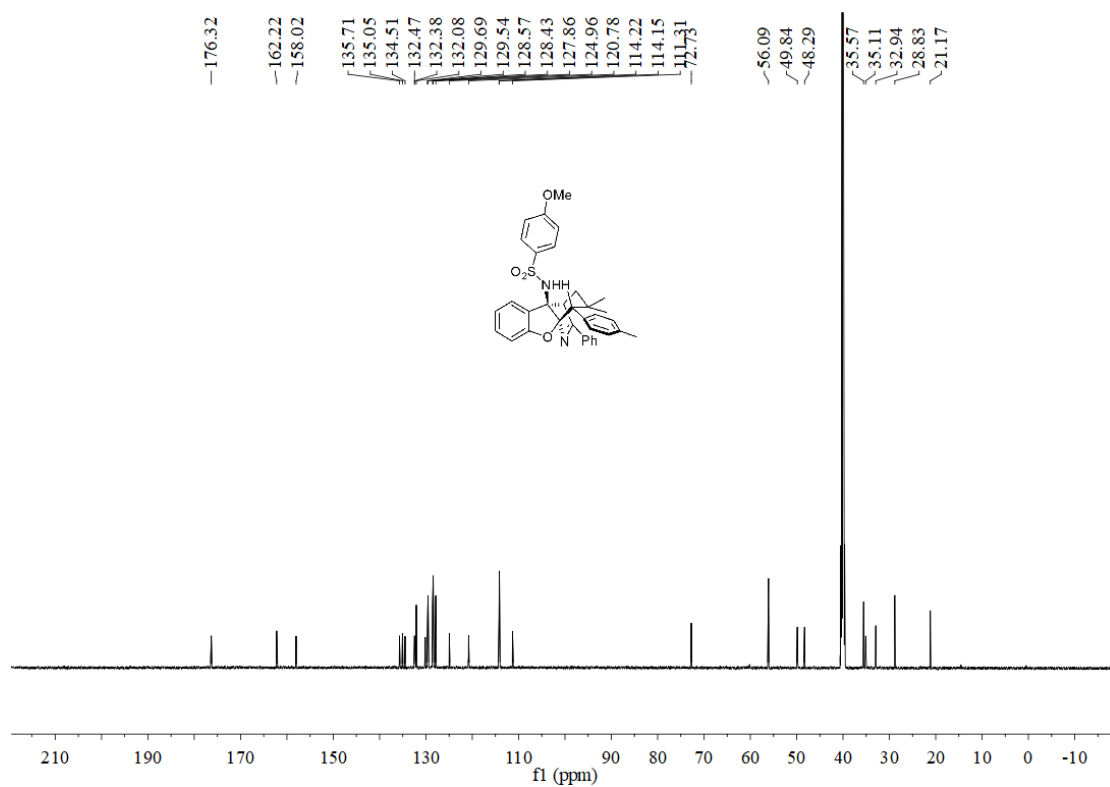
### <sup>1</sup>H NMR Spectrum of 3f



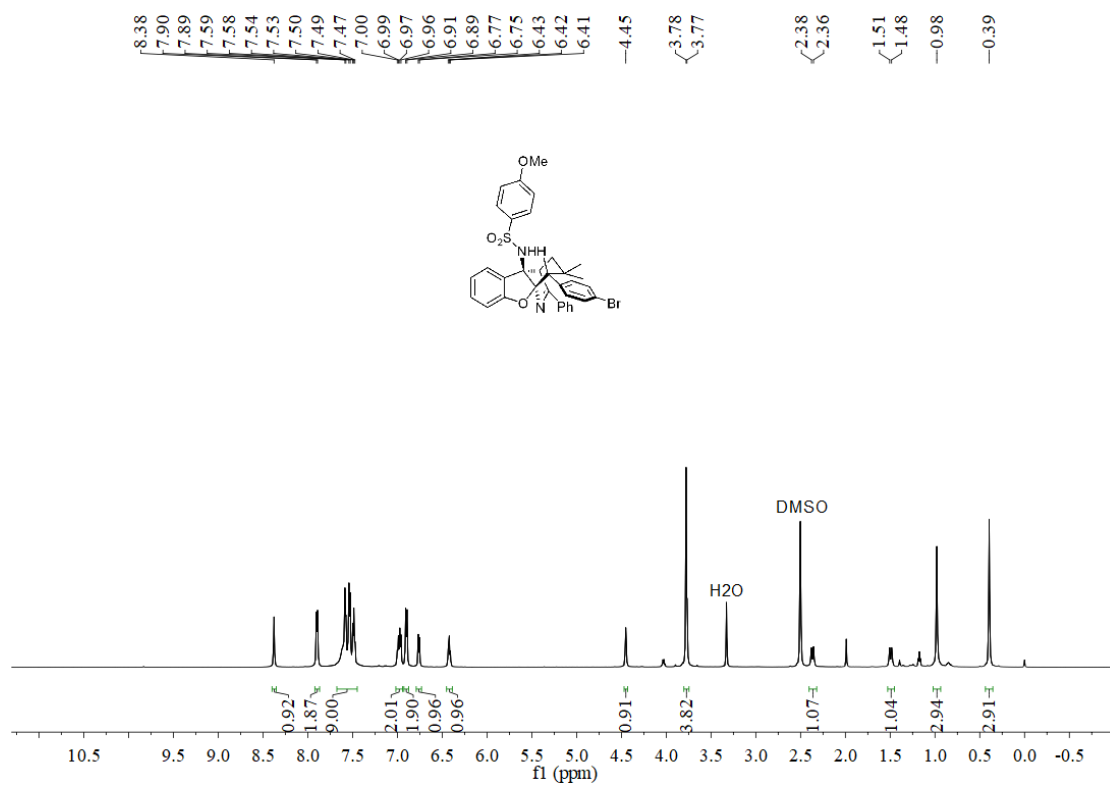




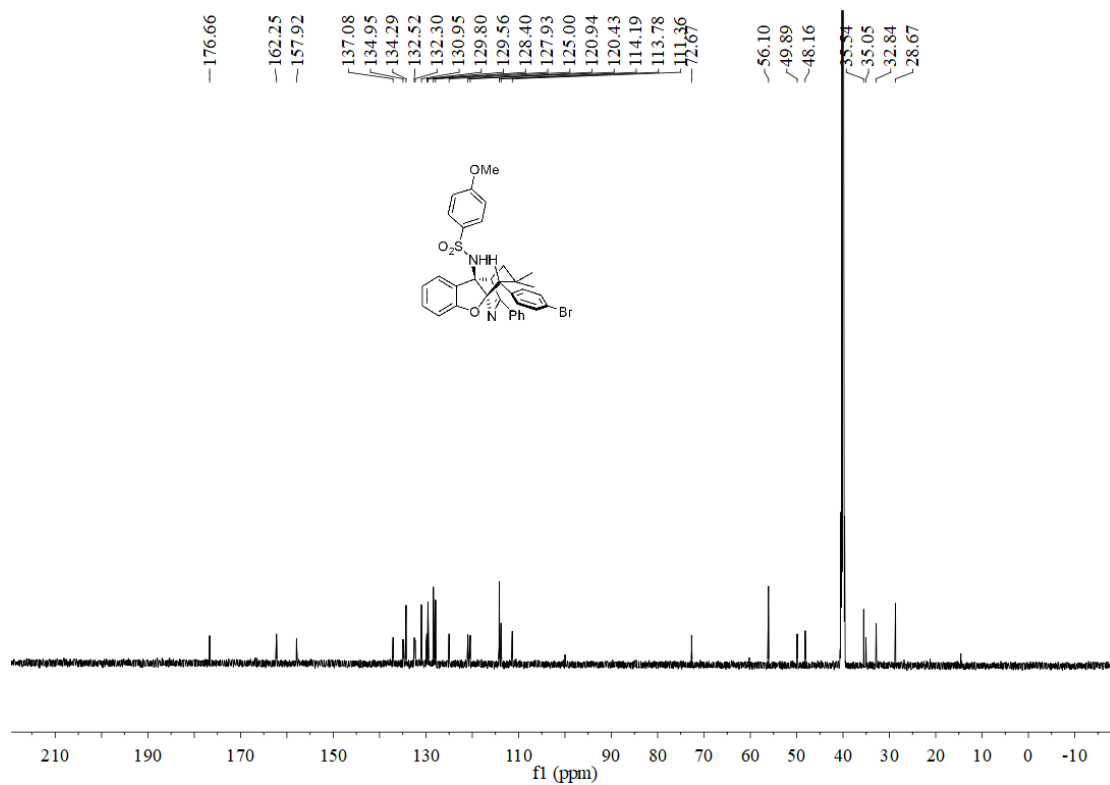
### <sup>13</sup>C NMR Spectrum of 3g



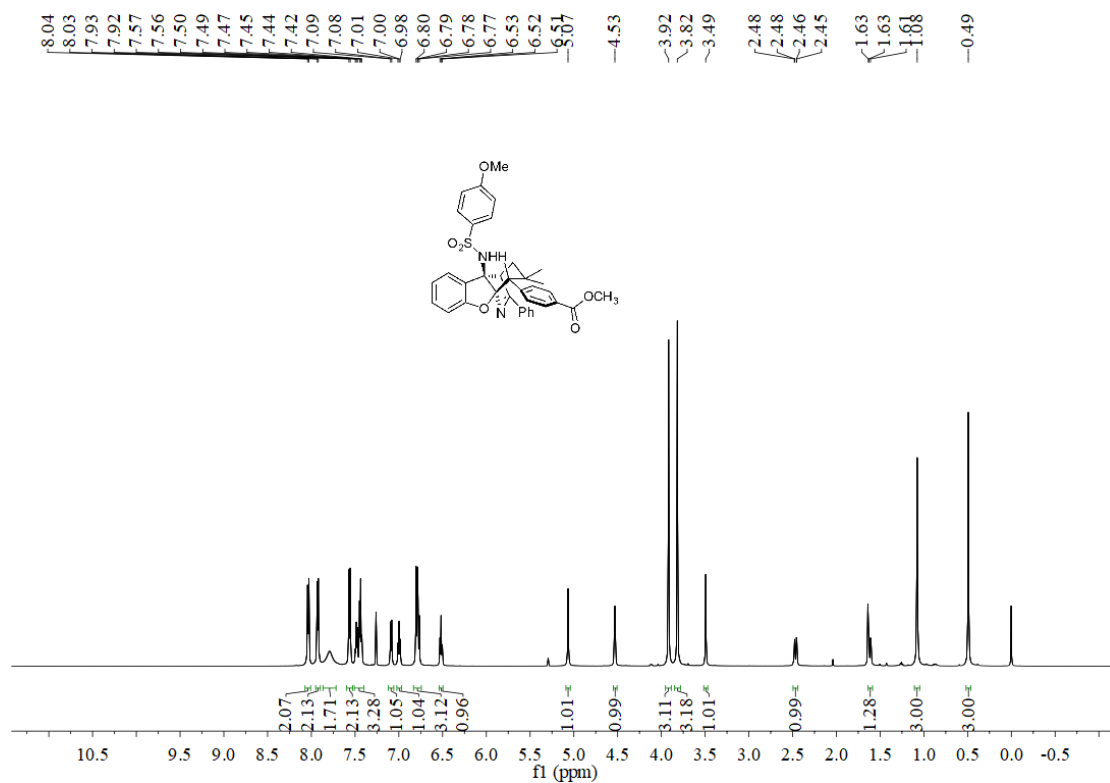
### <sup>1</sup>H NMR Spectrum of 3h



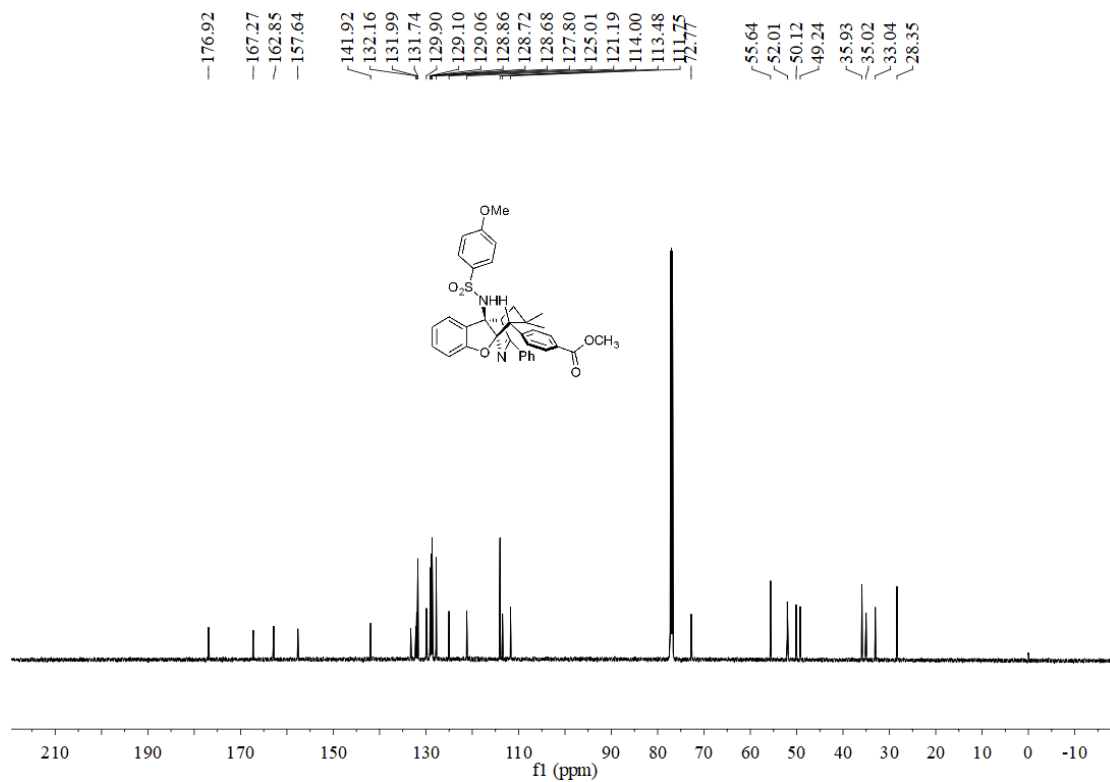
### <sup>13</sup>C NMR Spectrum of 3h



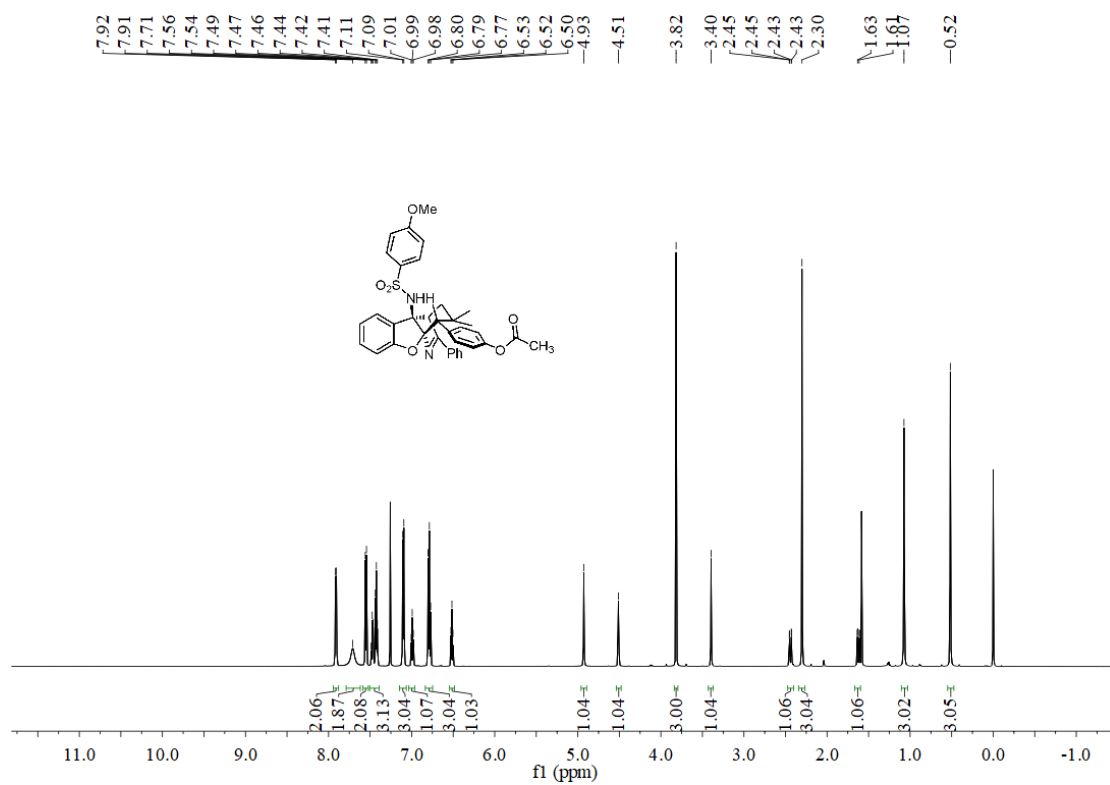
### <sup>1</sup>H NMR Spectrum of 3i



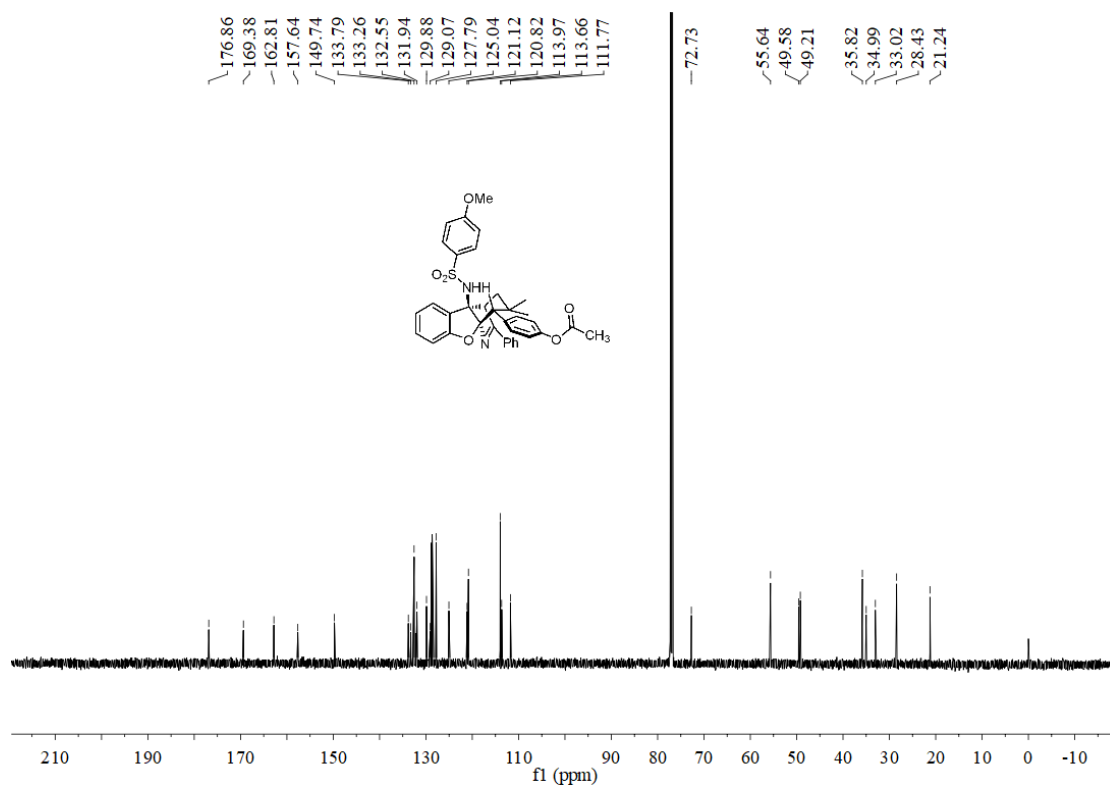
### <sup>13</sup>C NMR Spectrum of 3i



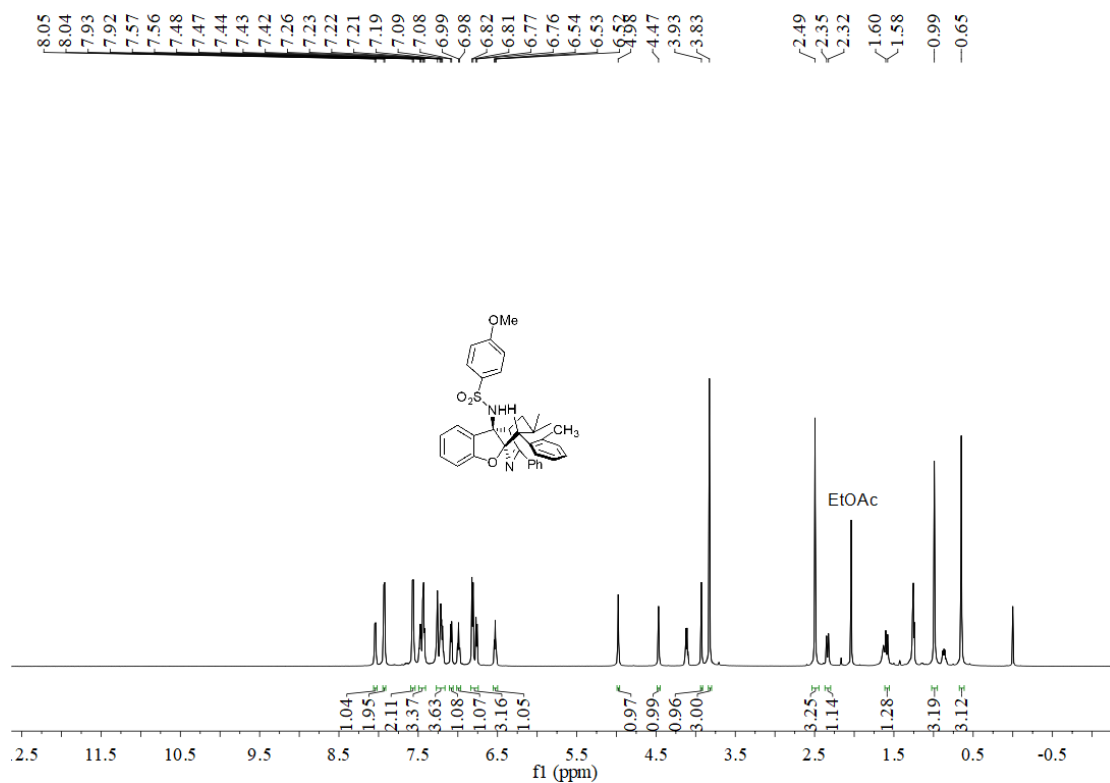
### <sup>1</sup>H NMR Spectrum of 3j



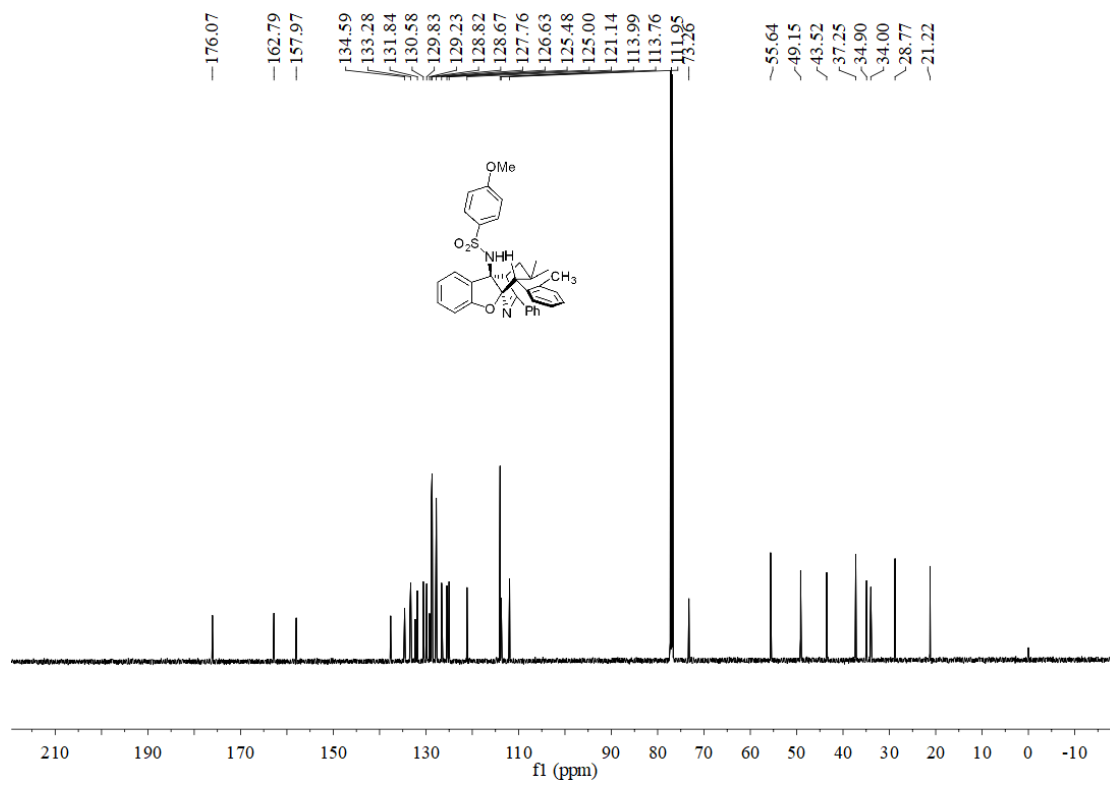
### <sup>13</sup>C NMR Spectrum of 3j



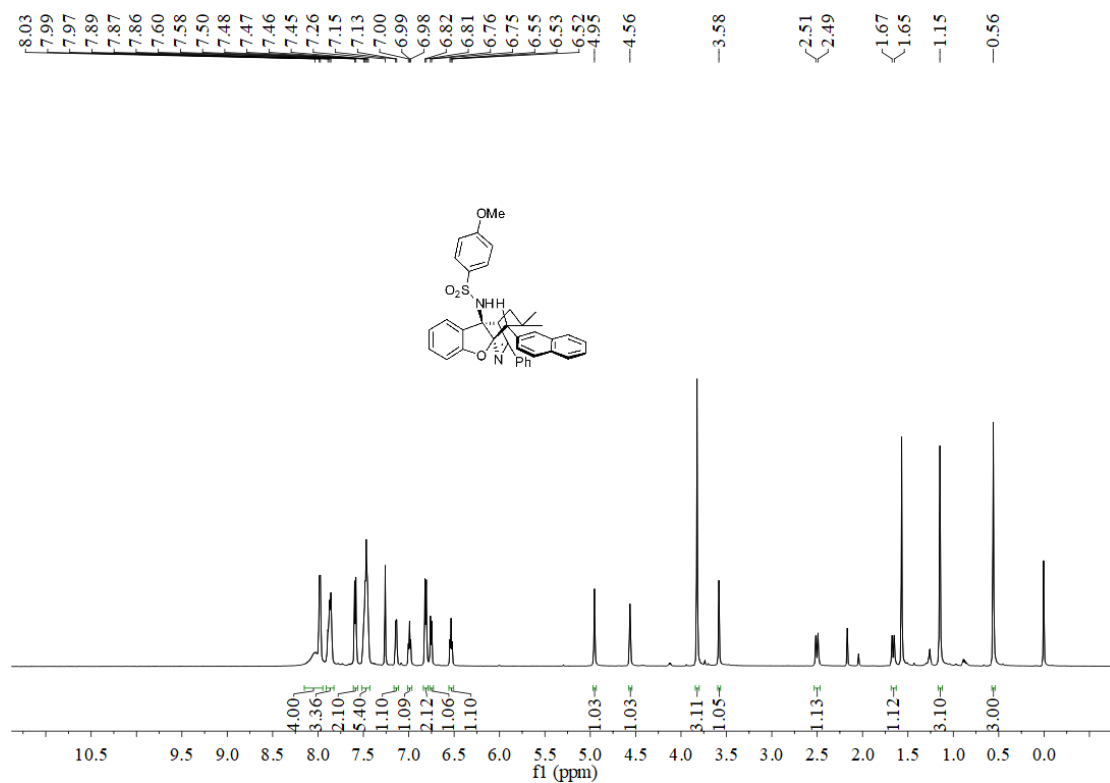
### <sup>1</sup>H NMR Spectrum of 3k



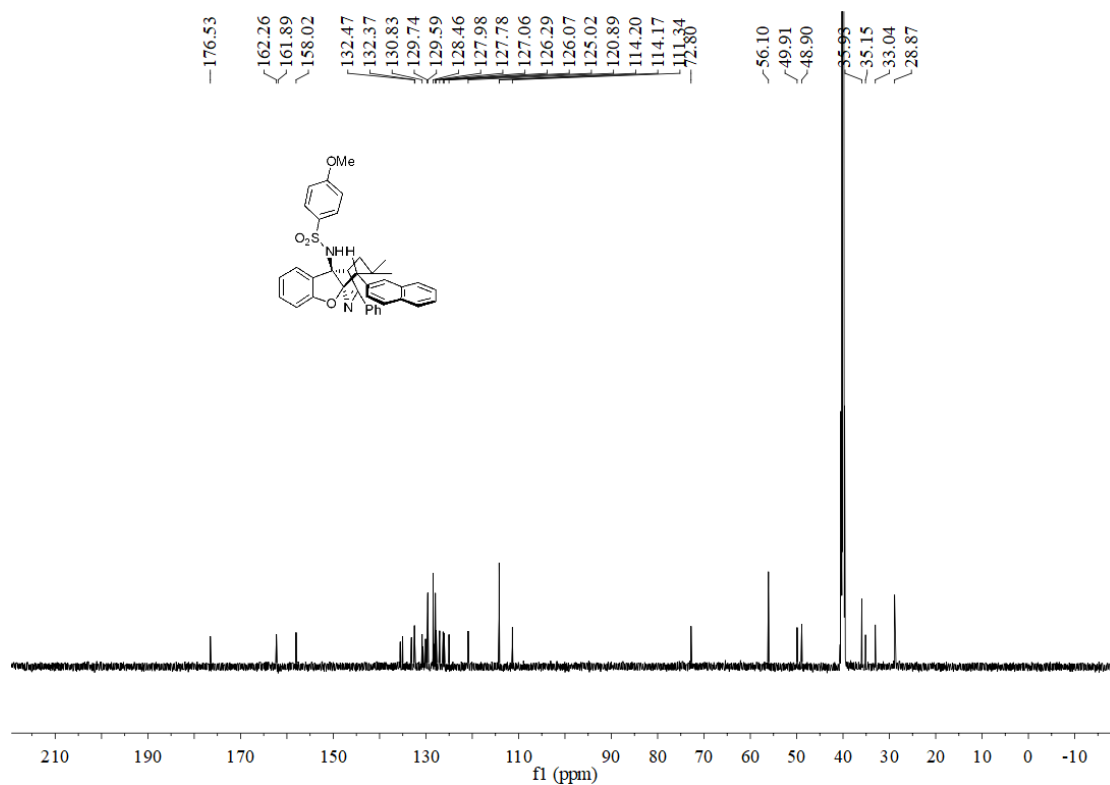
### <sup>13</sup>C NMR Spectrum of 3k



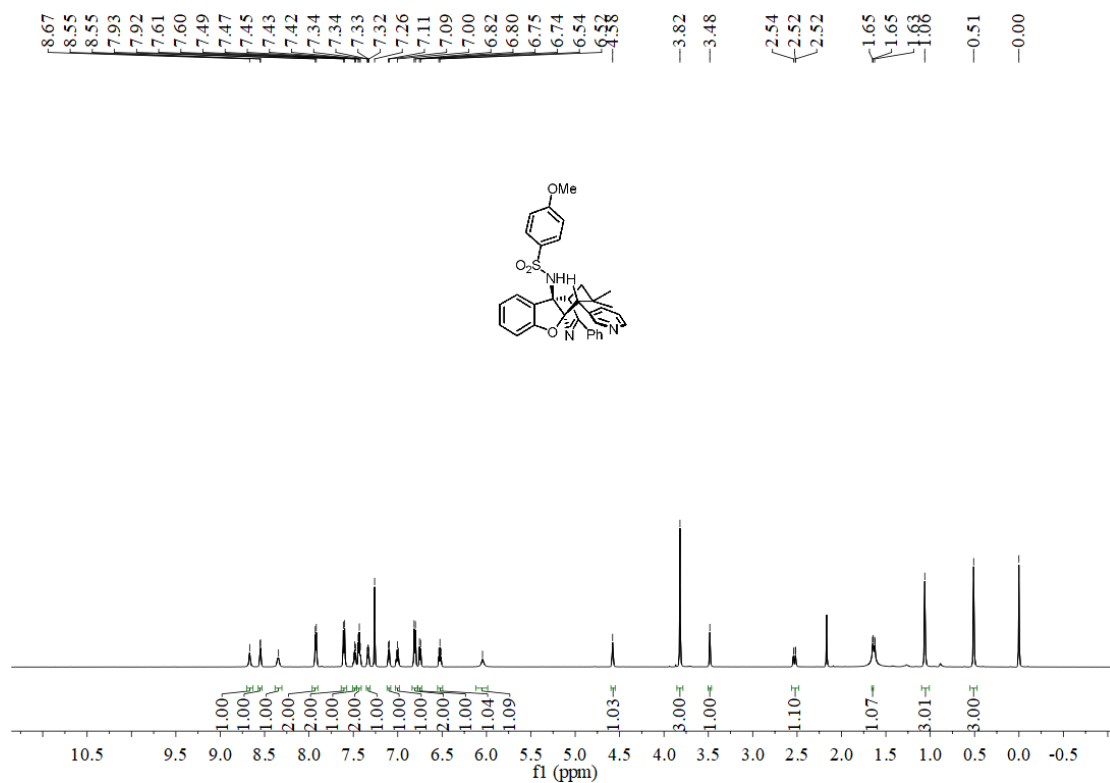
### <sup>1</sup>H NMR Spectrum of 3l



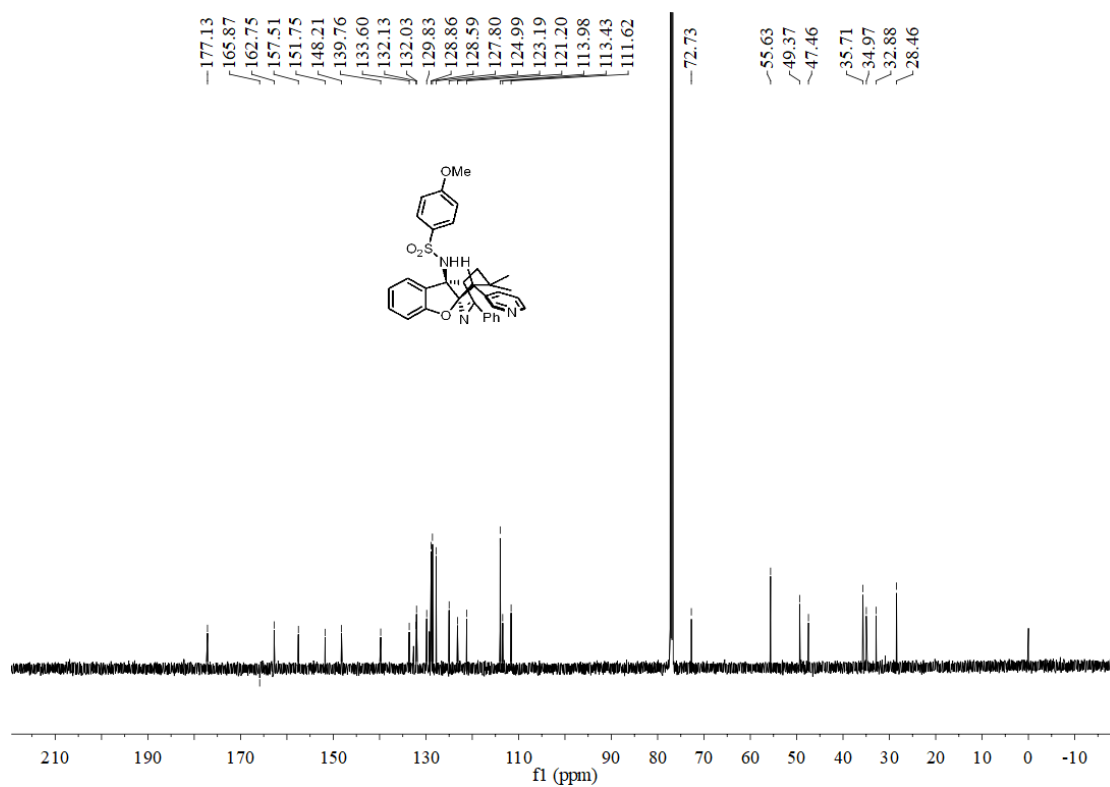
### <sup>13</sup>C NMR Spectrum of 3l



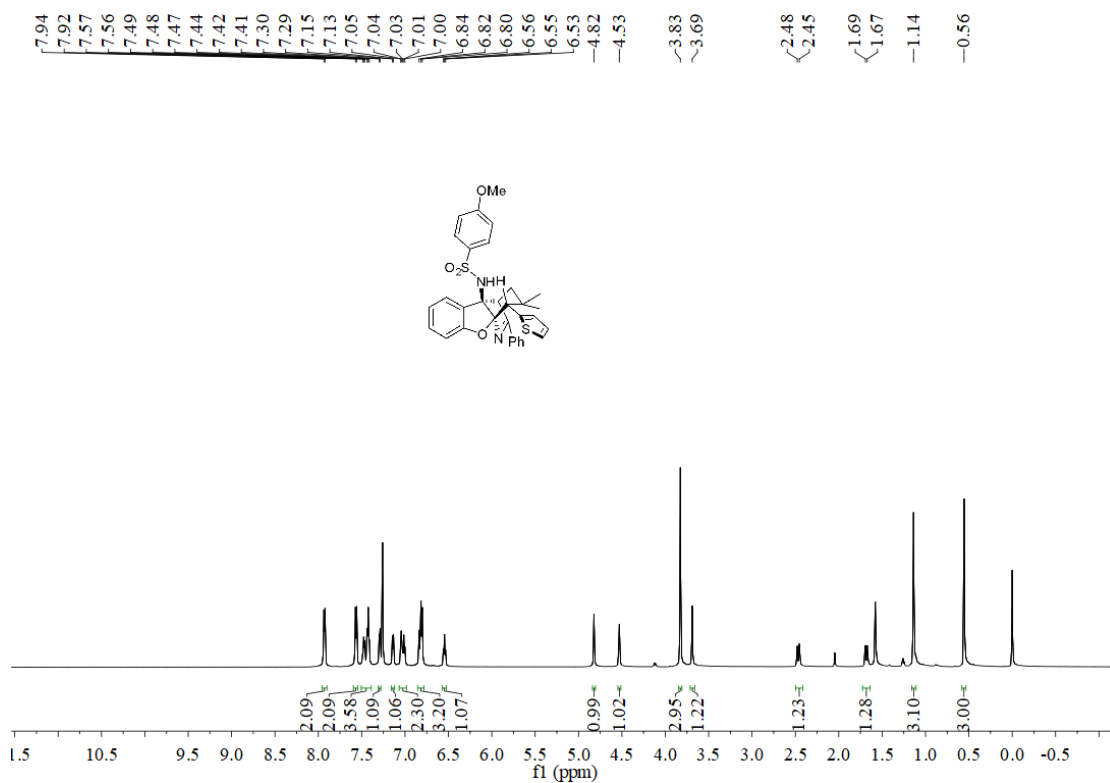
### <sup>1</sup>H NMR Spectrum of 3m



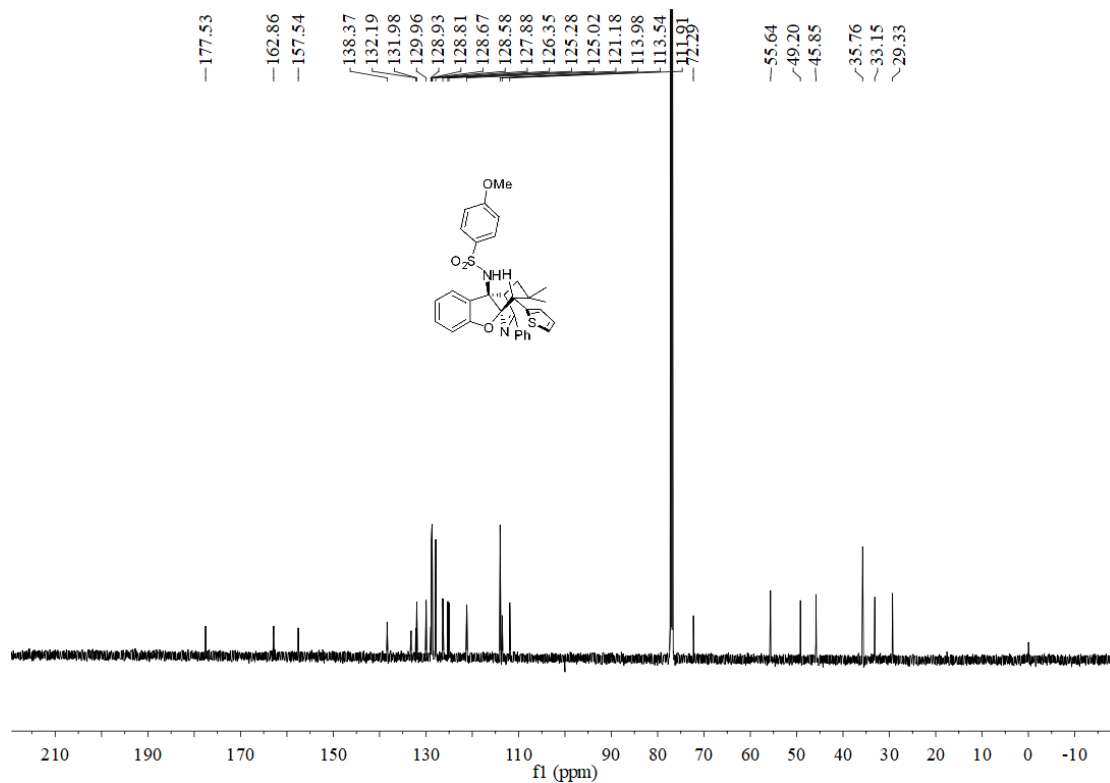
### <sup>13</sup>C NMR Spectrum of 3m



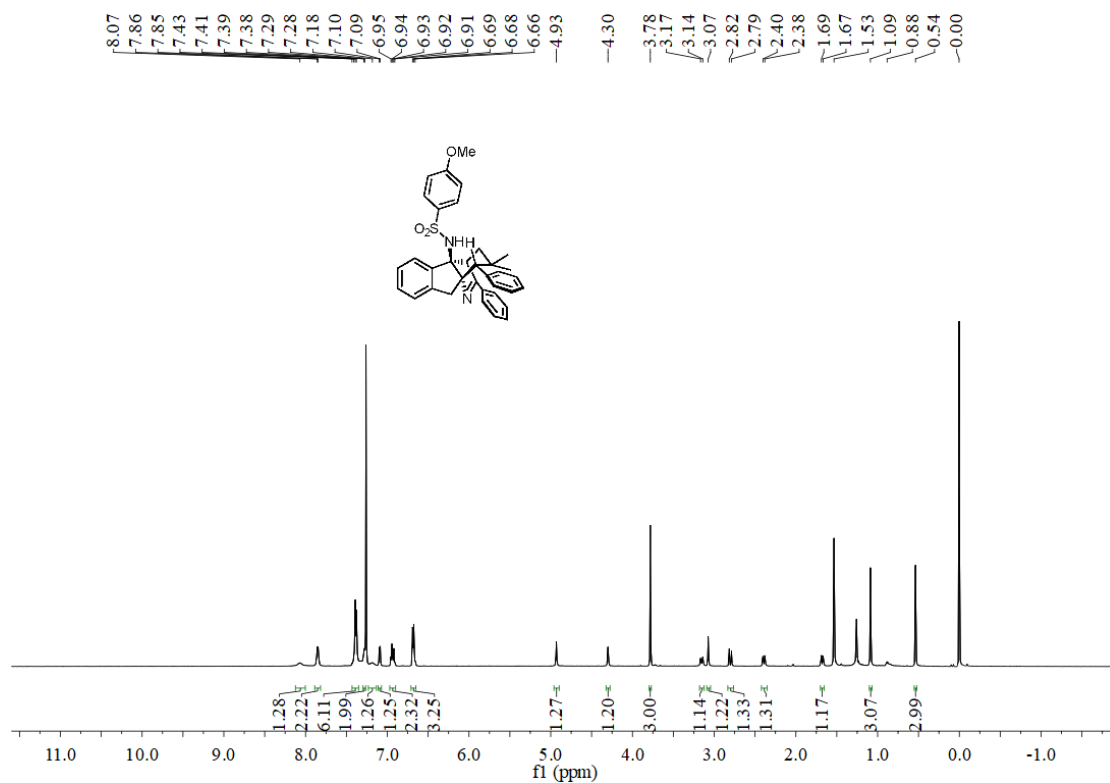
### <sup>1</sup>H NMR Spectrum of 3n



### <sup>13</sup>C NMR Spectrum of 3n

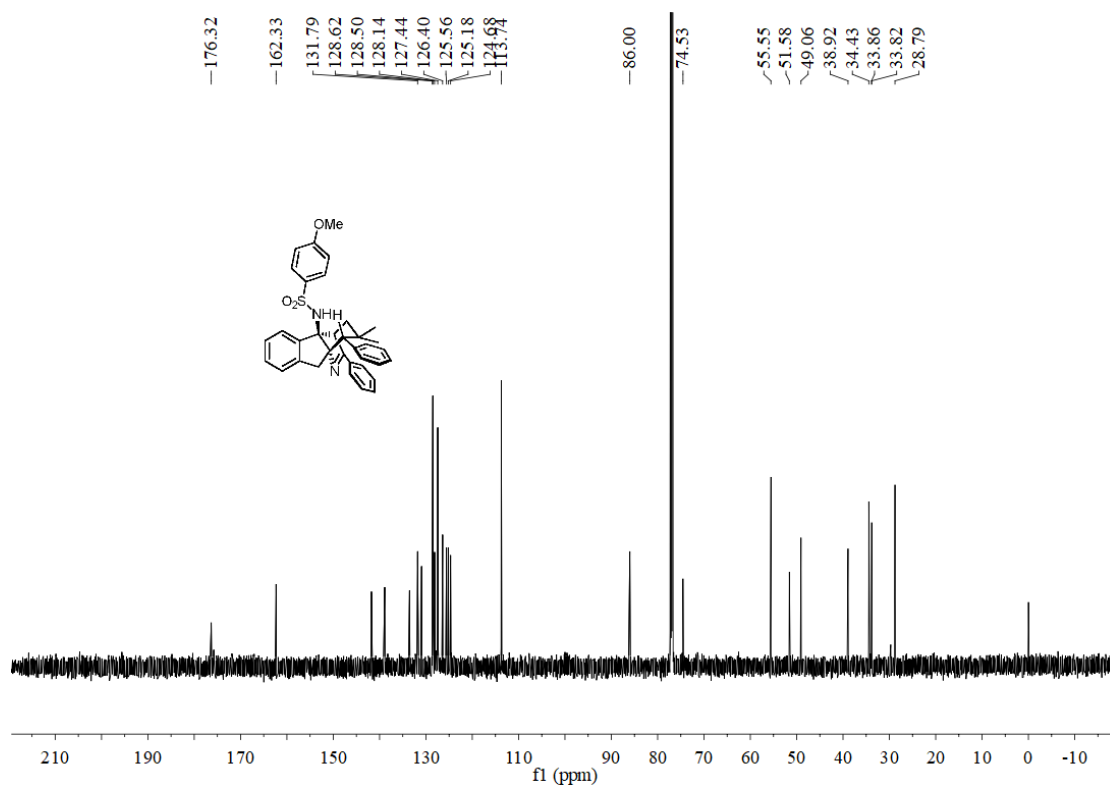


### <sup>1</sup>H NMR Spectrum of 3o

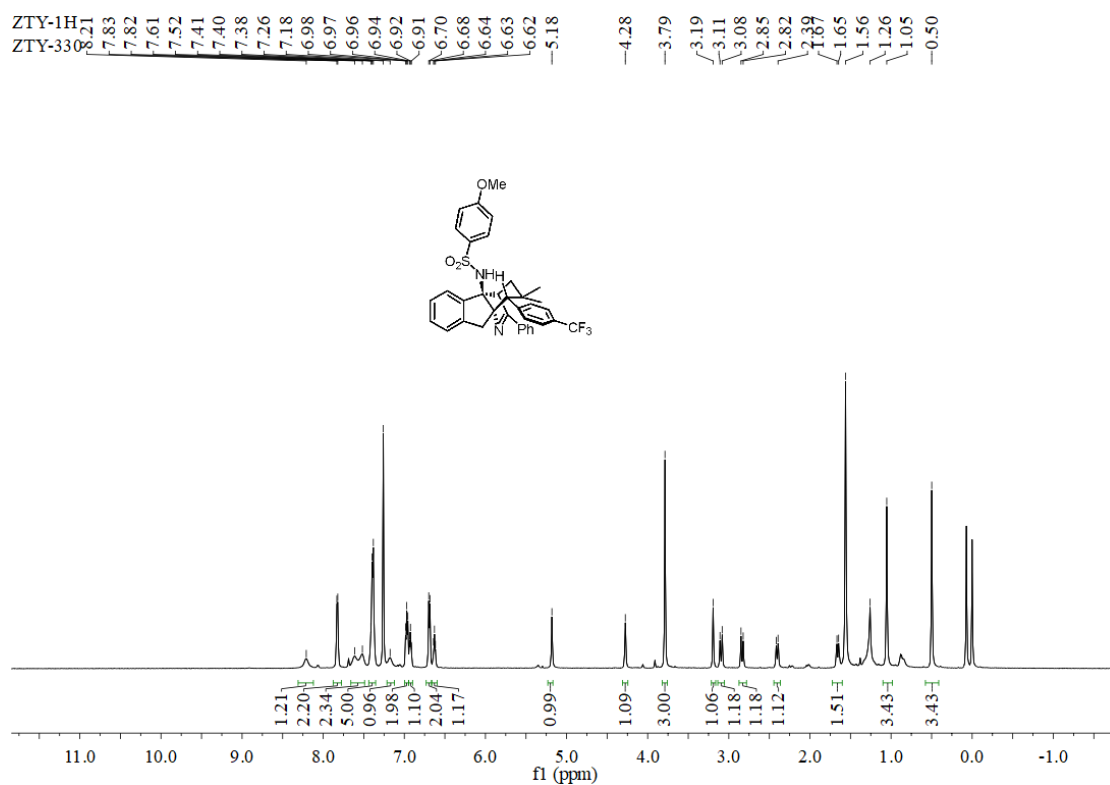




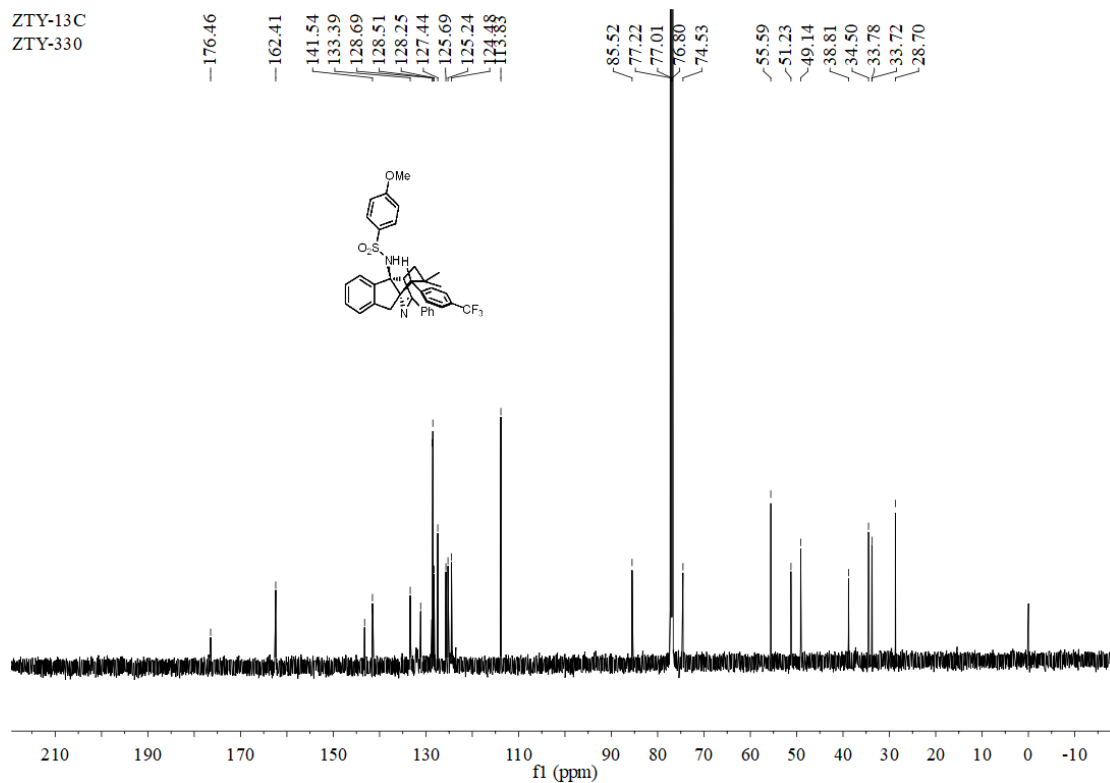
### <sup>13</sup>C NMR Spectrum of 3o



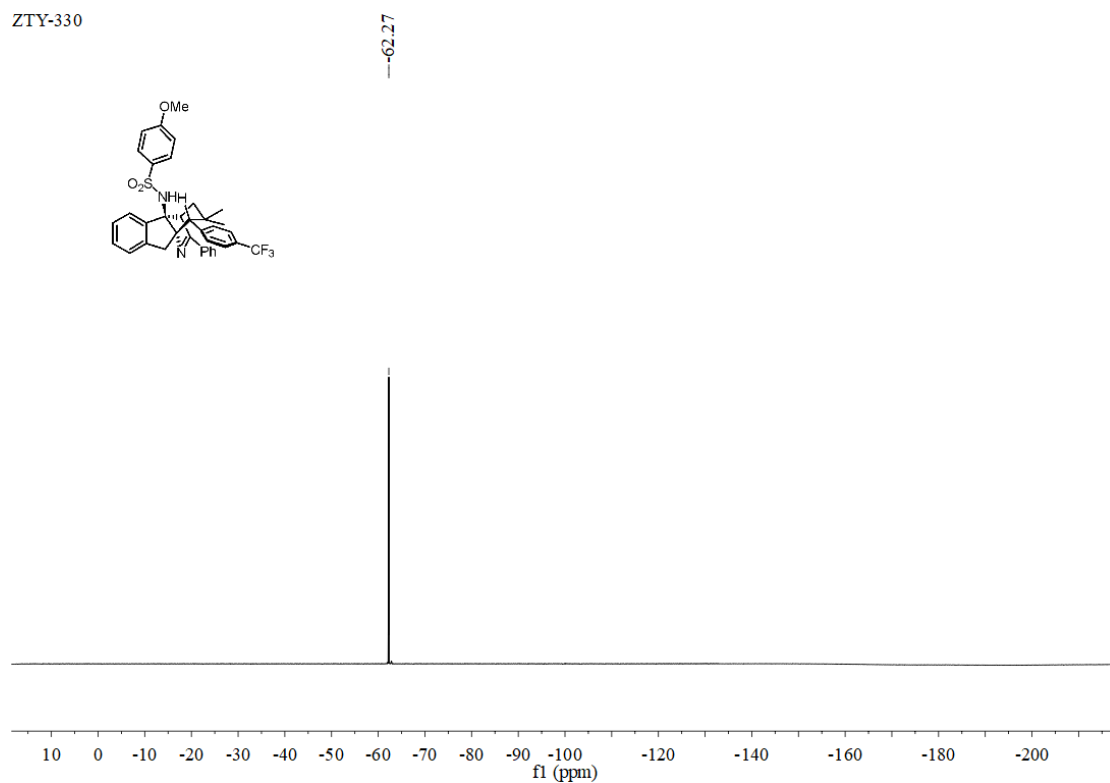
### <sup>1</sup>H NMR Spectrum of 3p



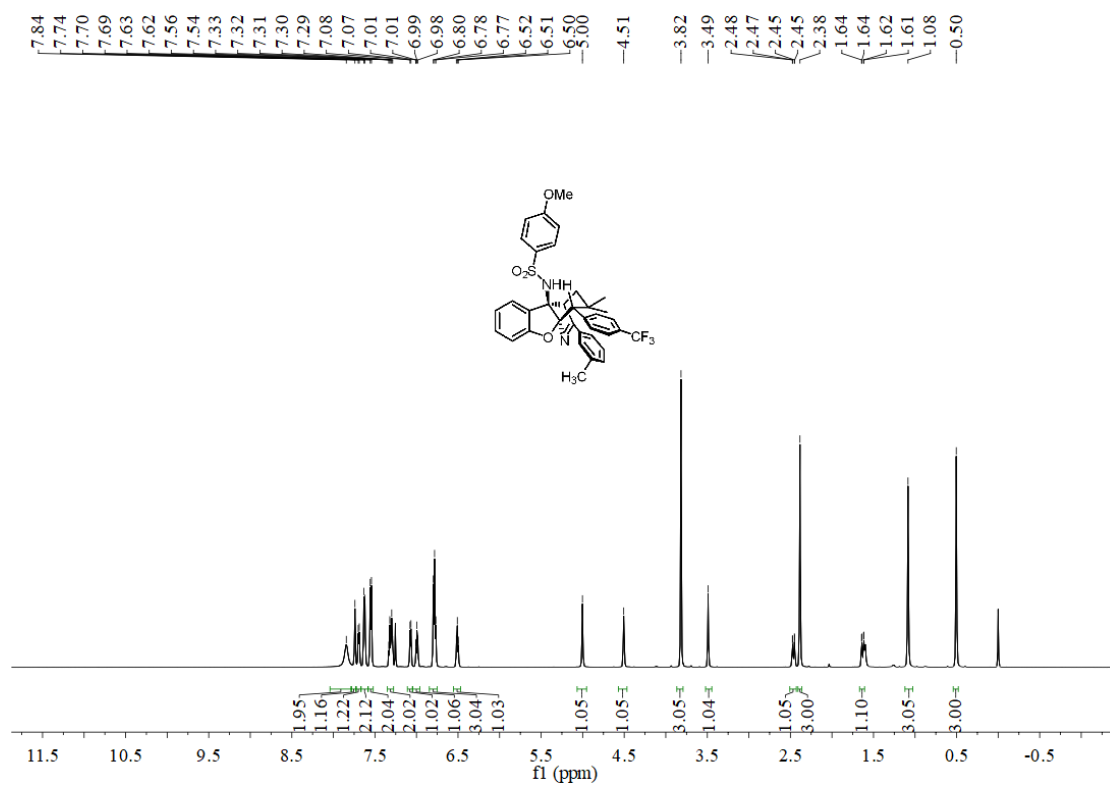
### <sup>13</sup>C NMR Spectrum of 3p



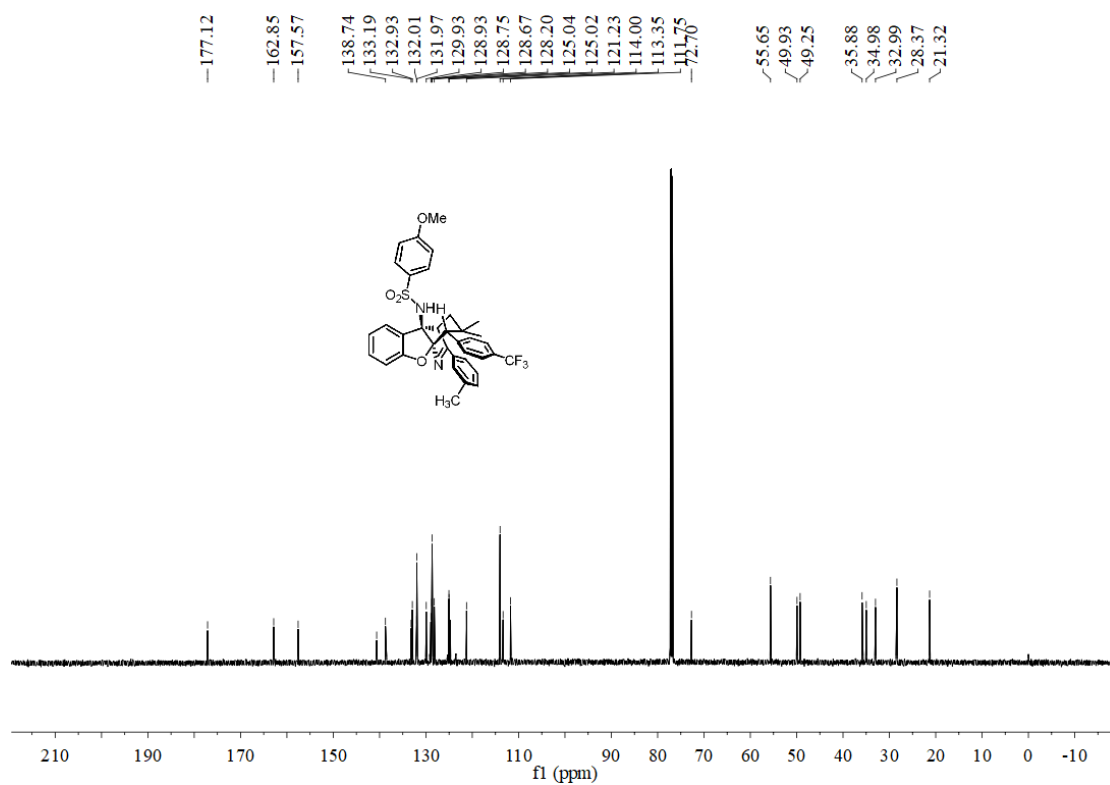
### <sup>19</sup>F NMR Spectrum of 3p



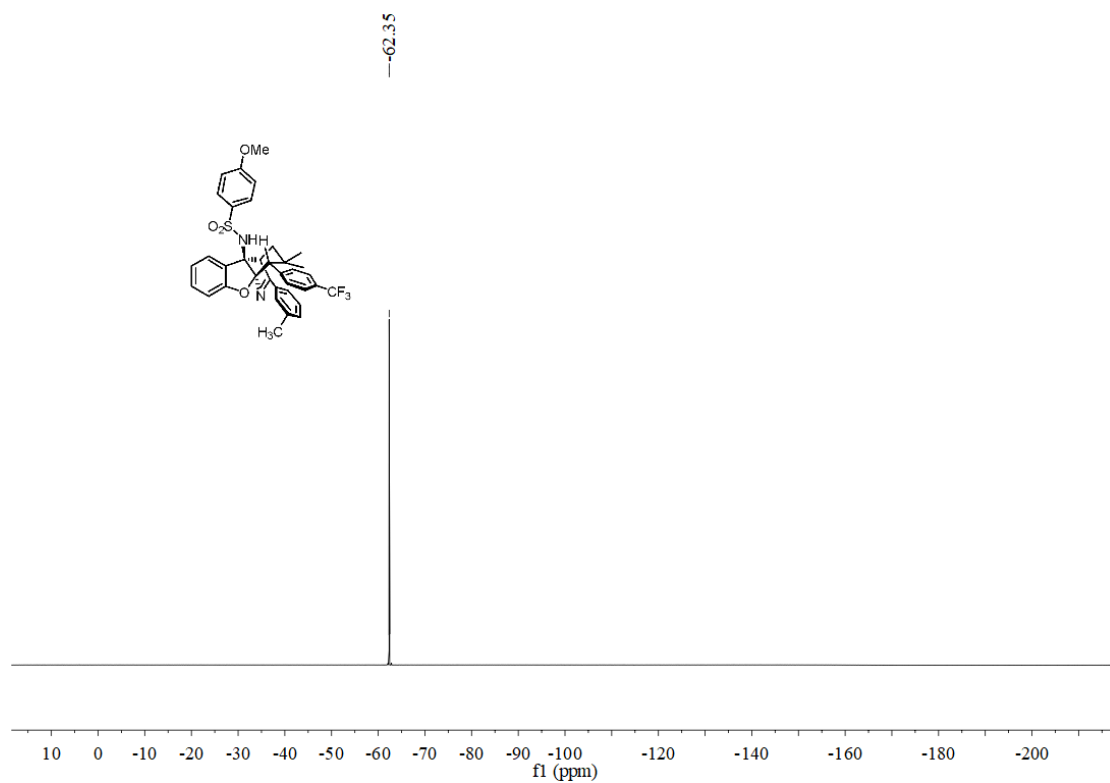
### <sup>1</sup>H NMR Spectrum of 3q



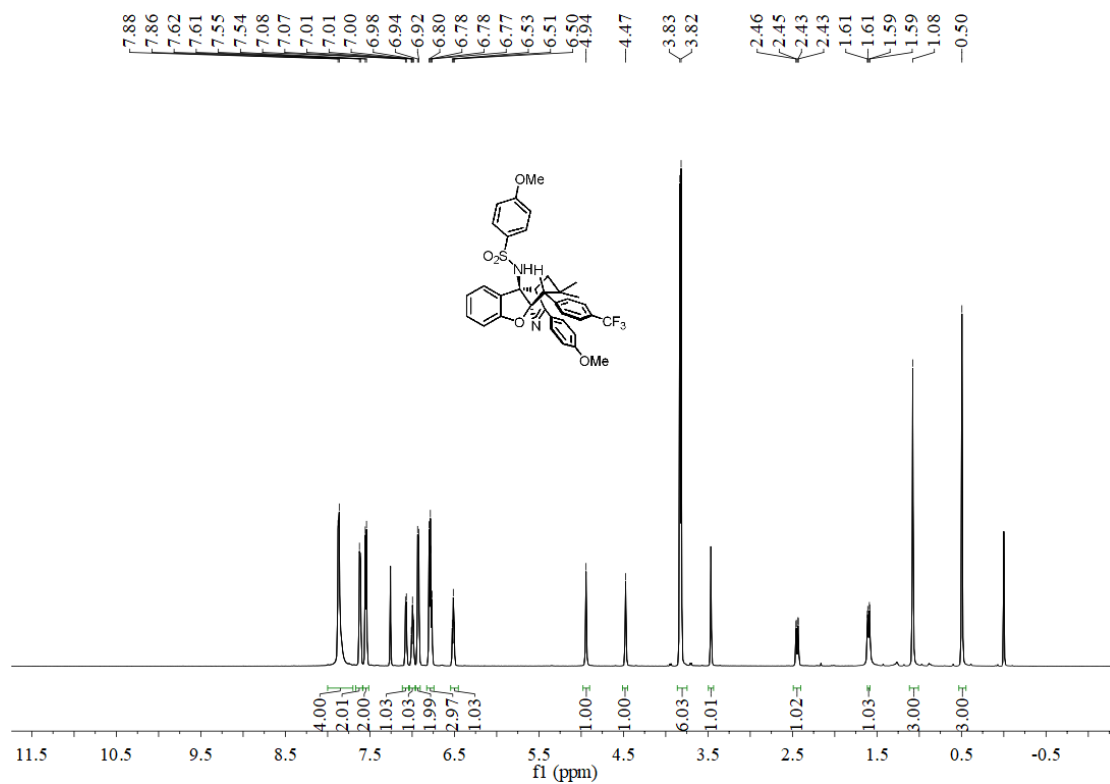
### <sup>13</sup>C NMR Spectrum of 3q



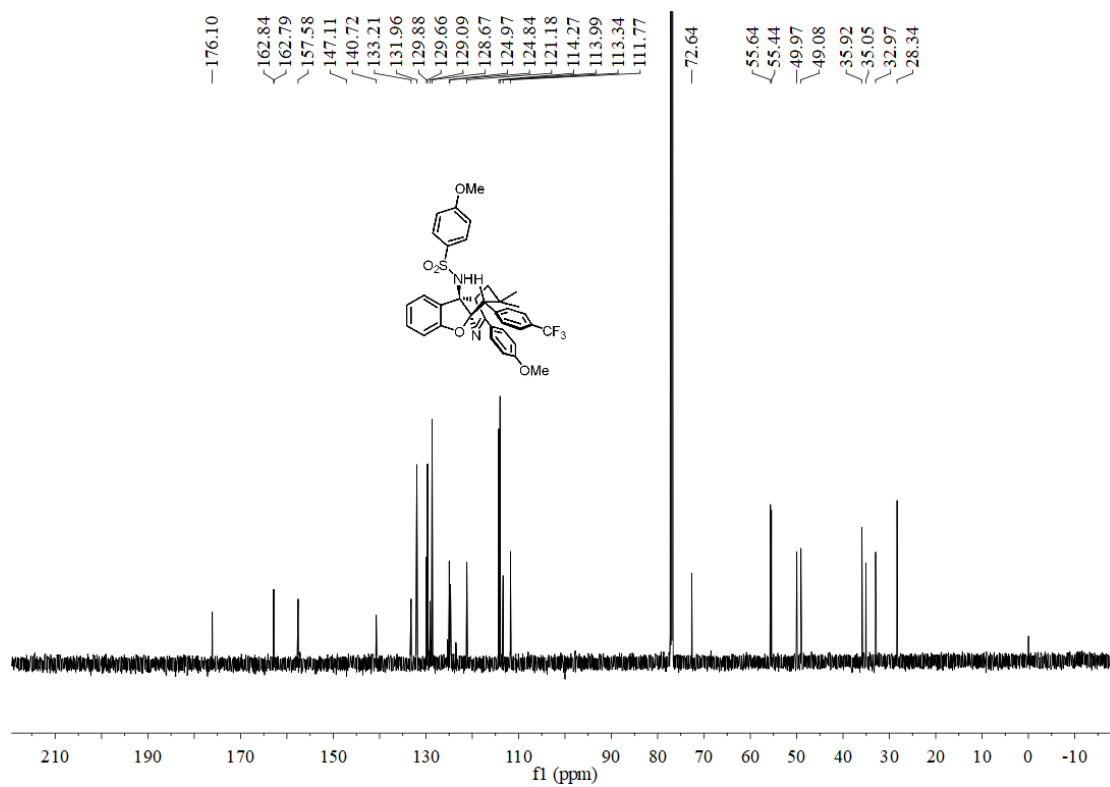
### <sup>19</sup>F NMR Spectrum of 3q



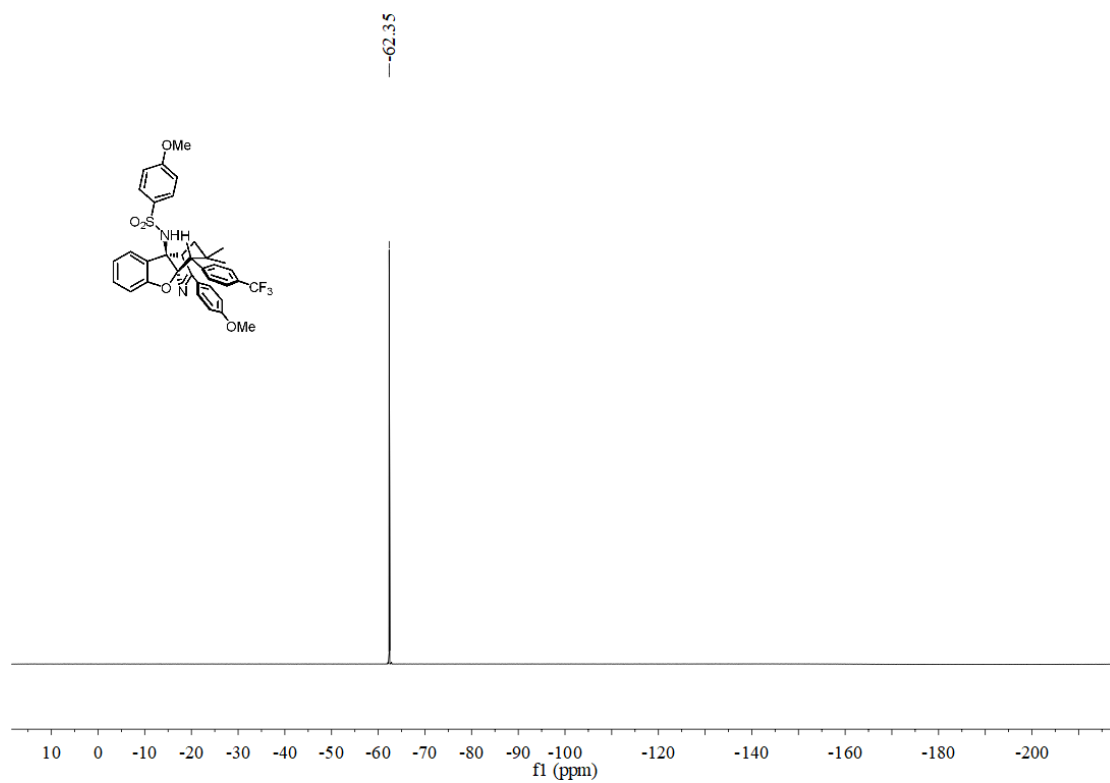
### <sup>1</sup>H NMR Spectrum of 3r



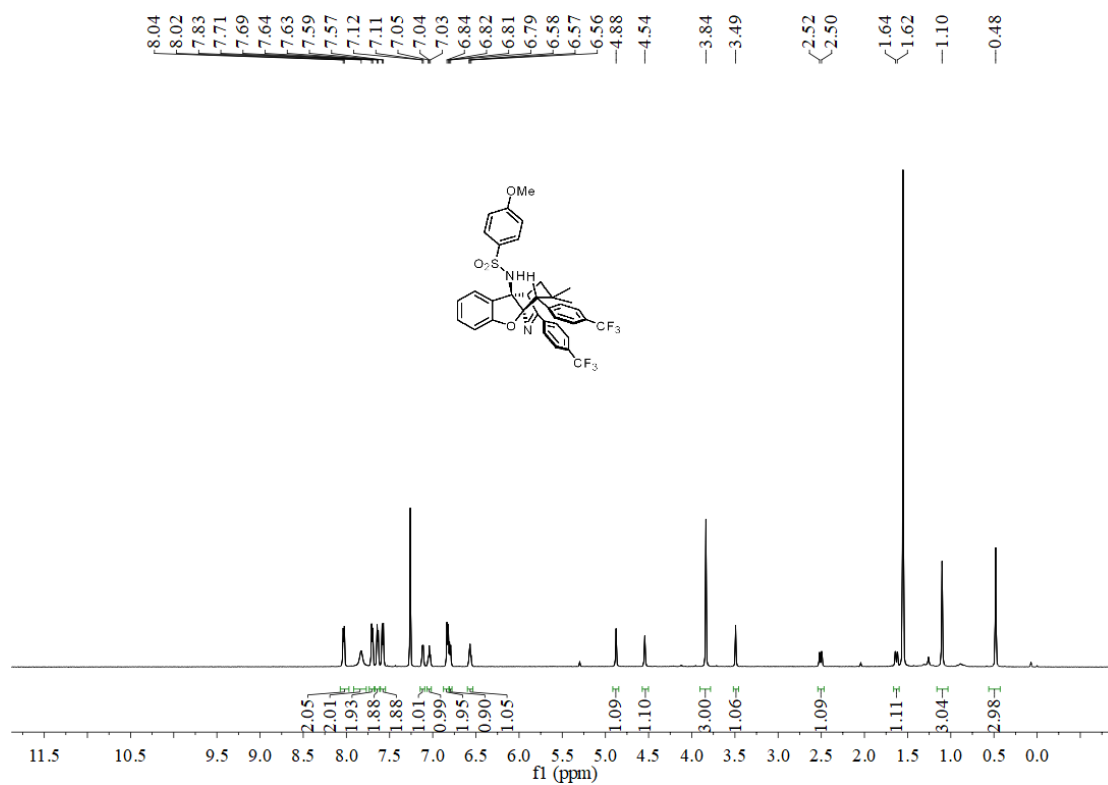
### <sup>13</sup>C NMR Spectrum of 3r



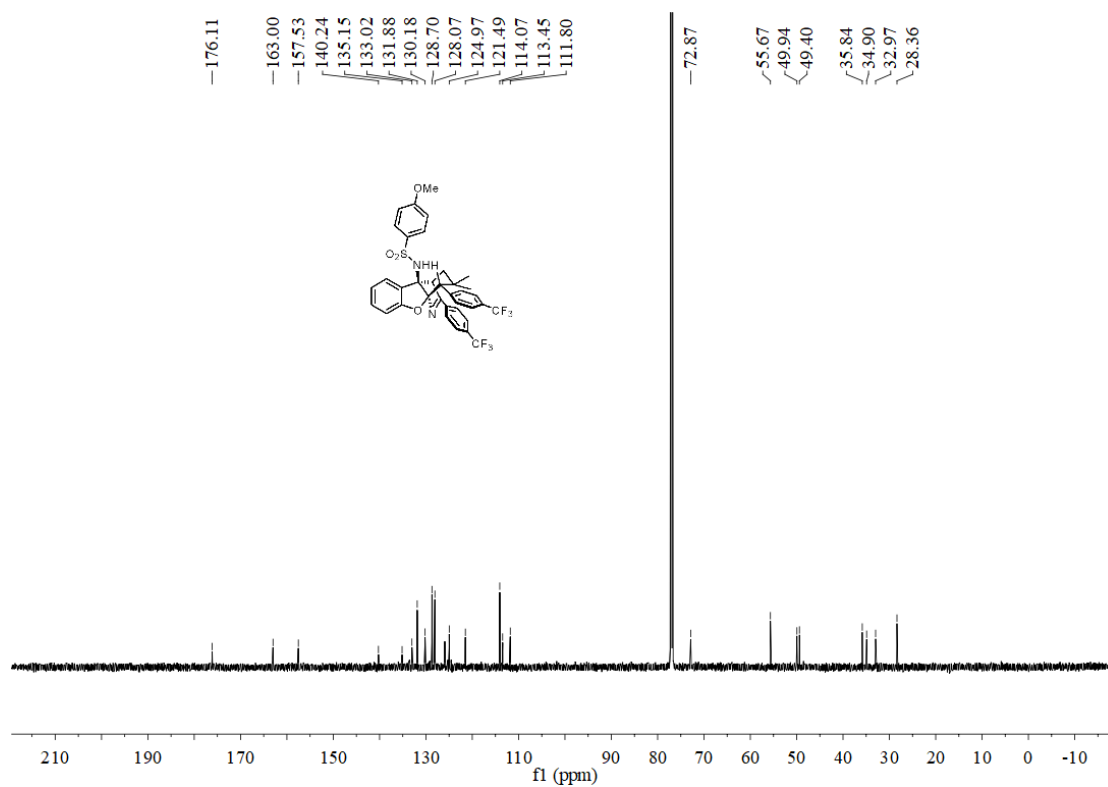
### <sup>19</sup>F NMR Spectrum of 3r



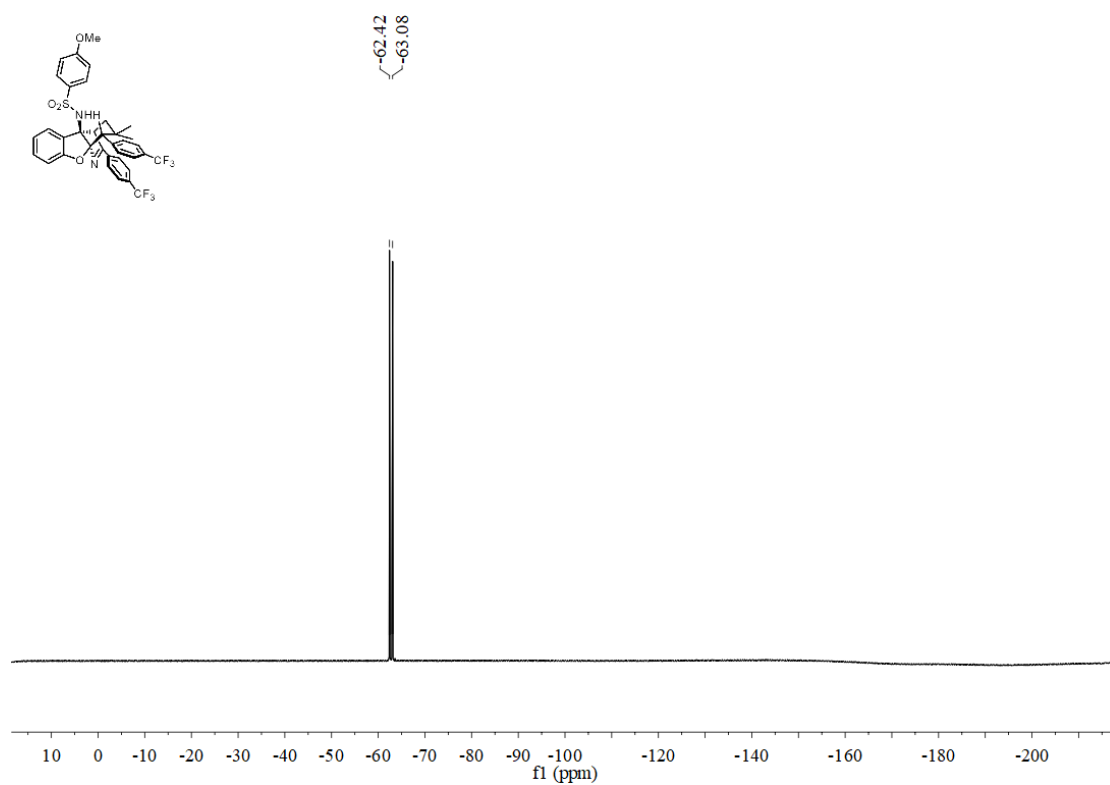
### <sup>1</sup>H NMR Spectrum of 3s



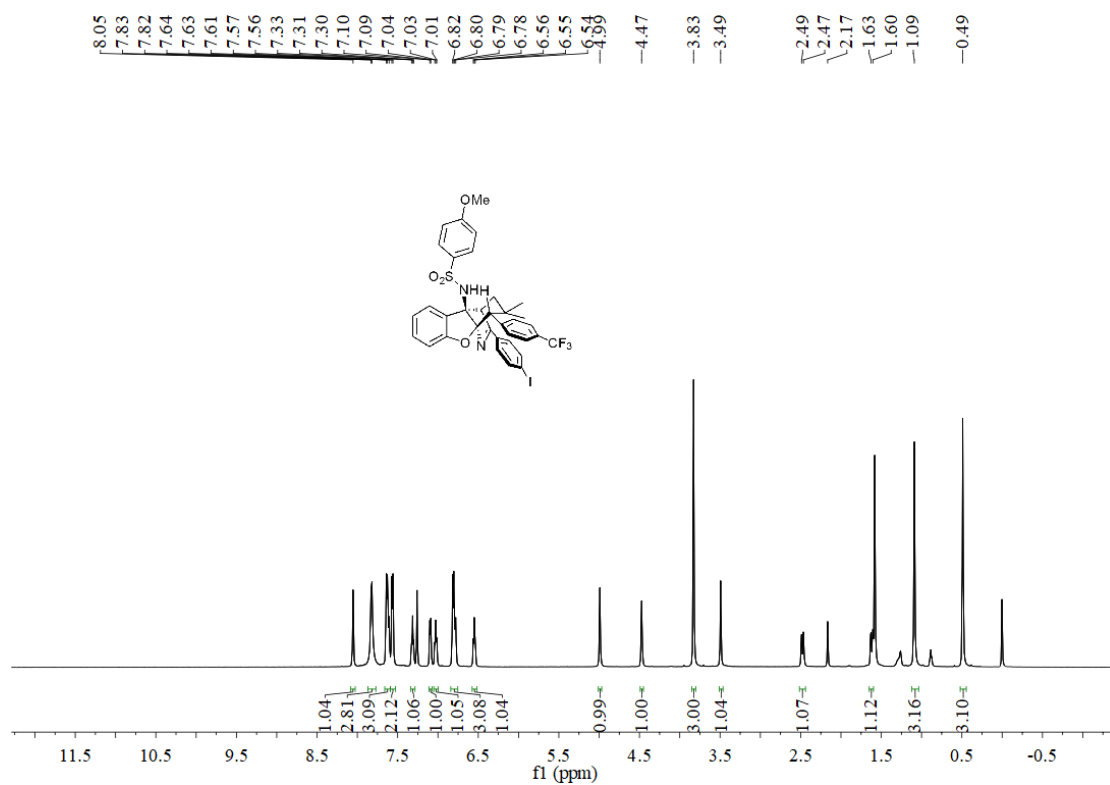
### <sup>13</sup>C NMR Spectrum of 3s



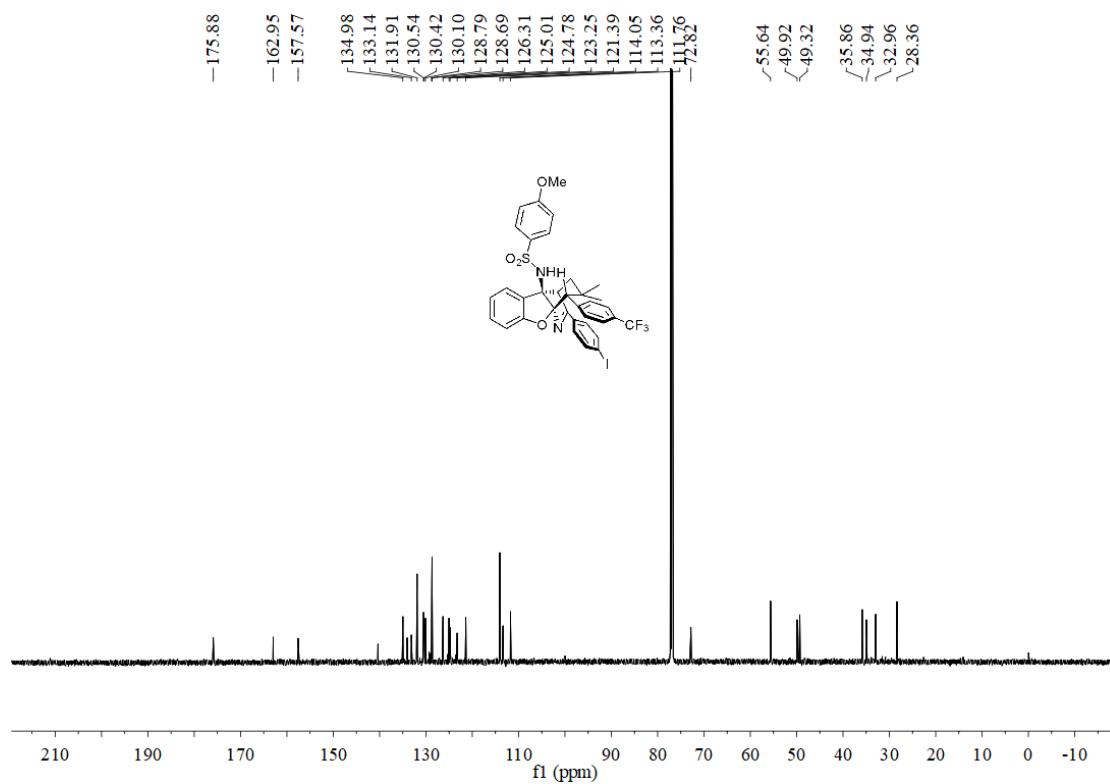
### <sup>19</sup>F NMR Spectrum of 3s



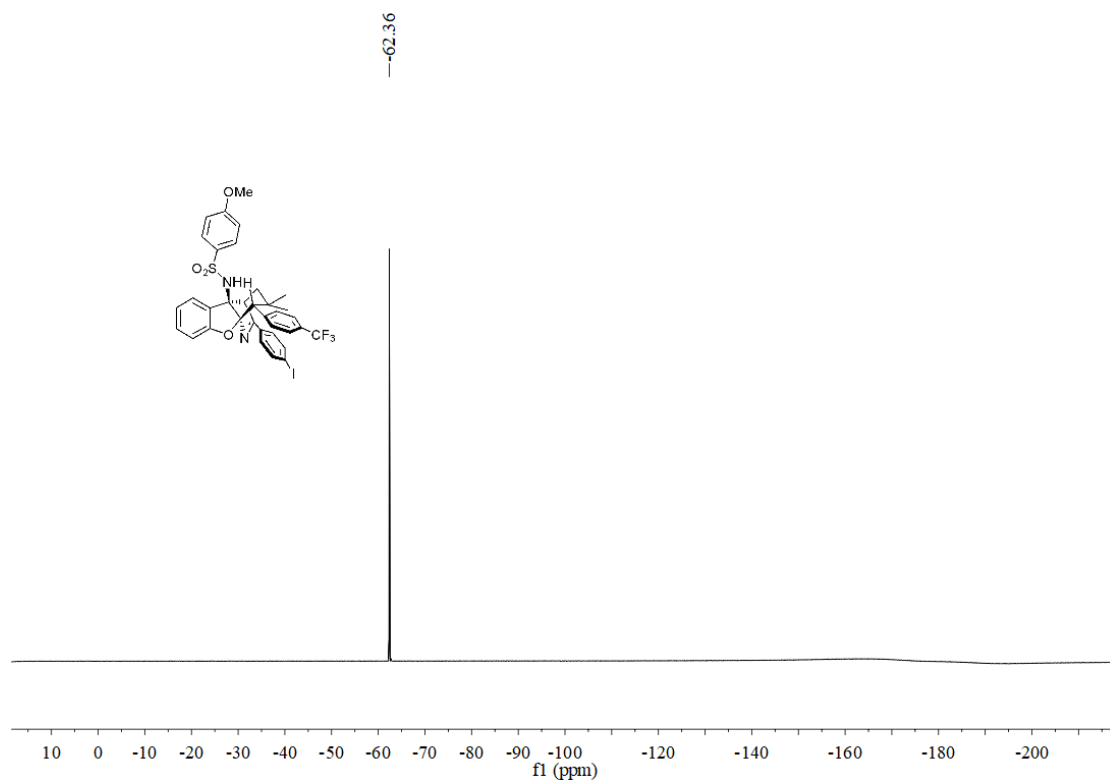
### <sup>1</sup>H NMR Spectrum of 3t



### <sup>13</sup>C NMR Spectrum of 3t

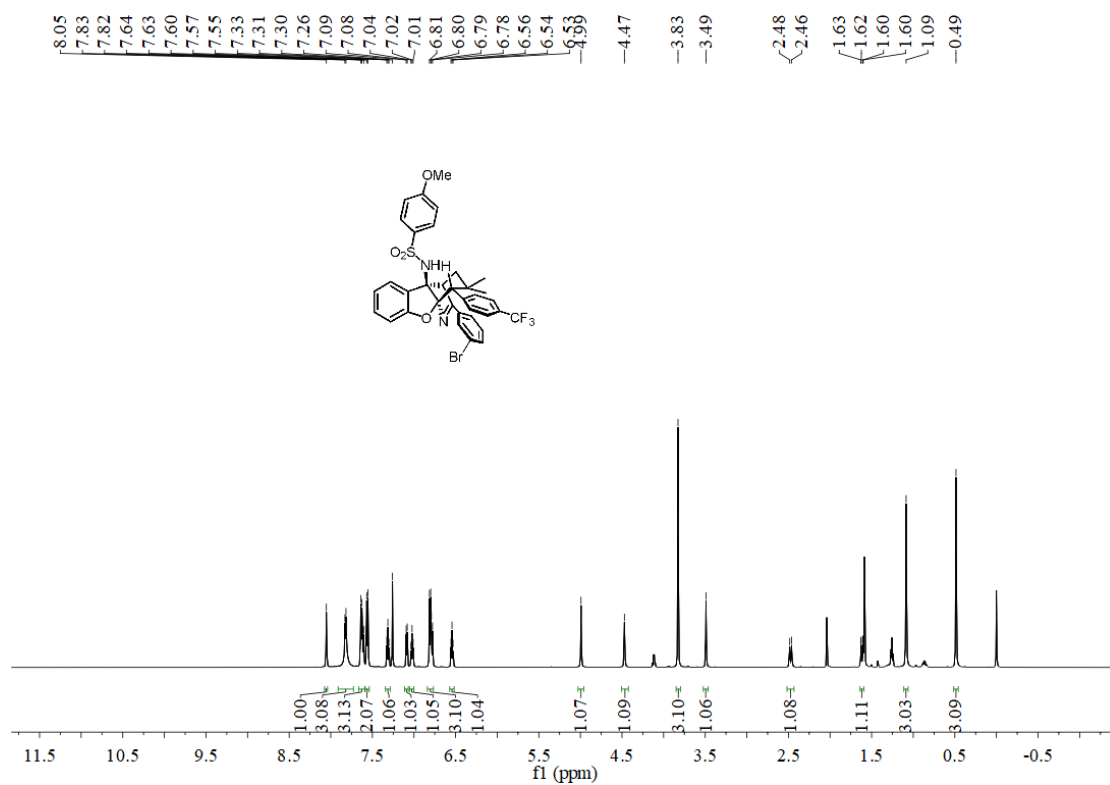


### <sup>19</sup>F NMR Spectrum of 3t

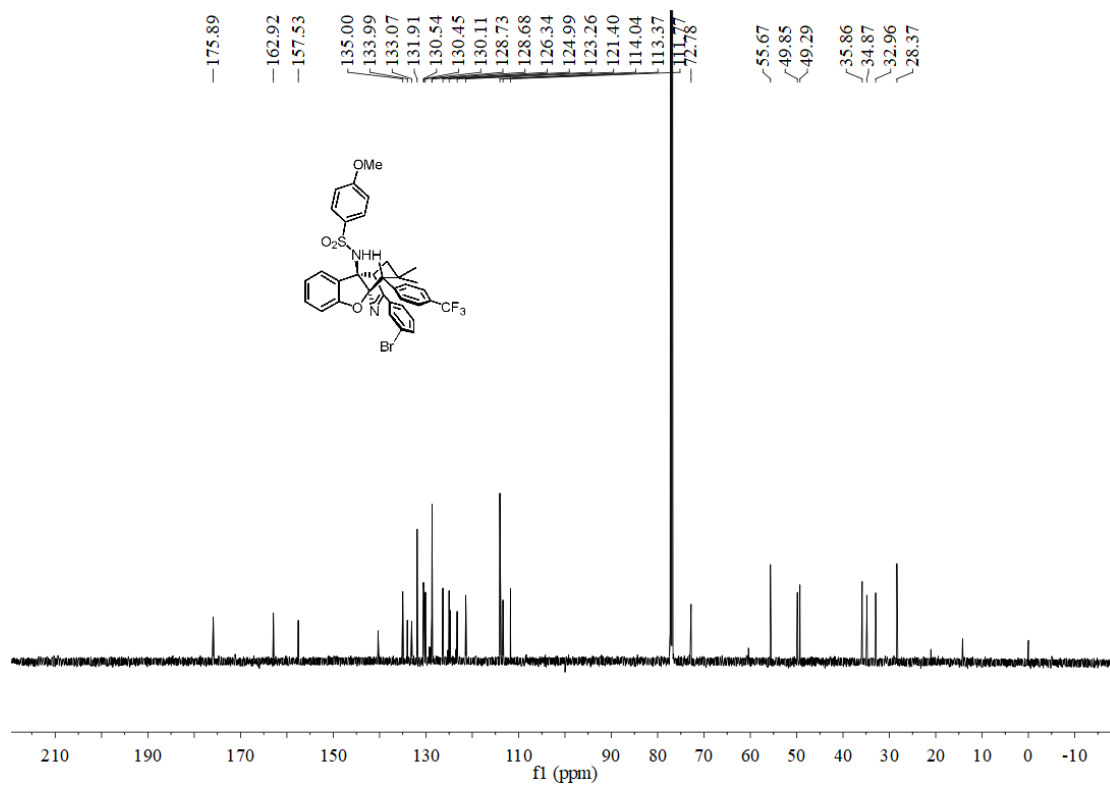




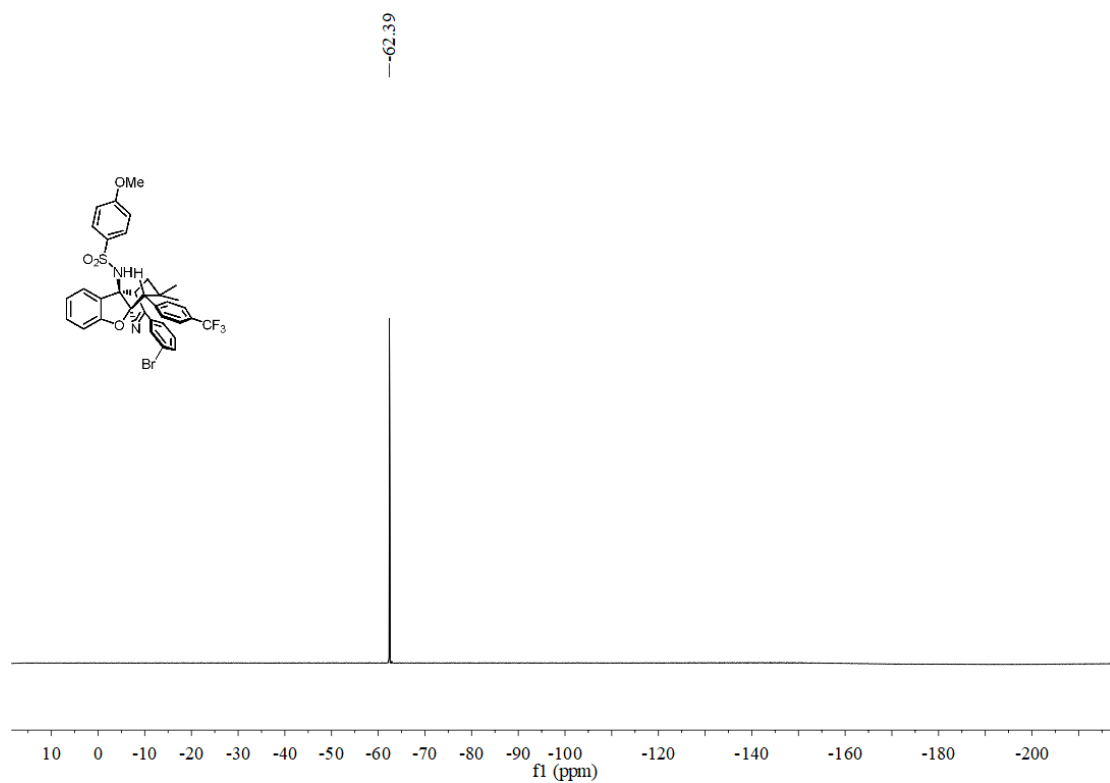
### <sup>1</sup>H NMR Spectrum of 3u



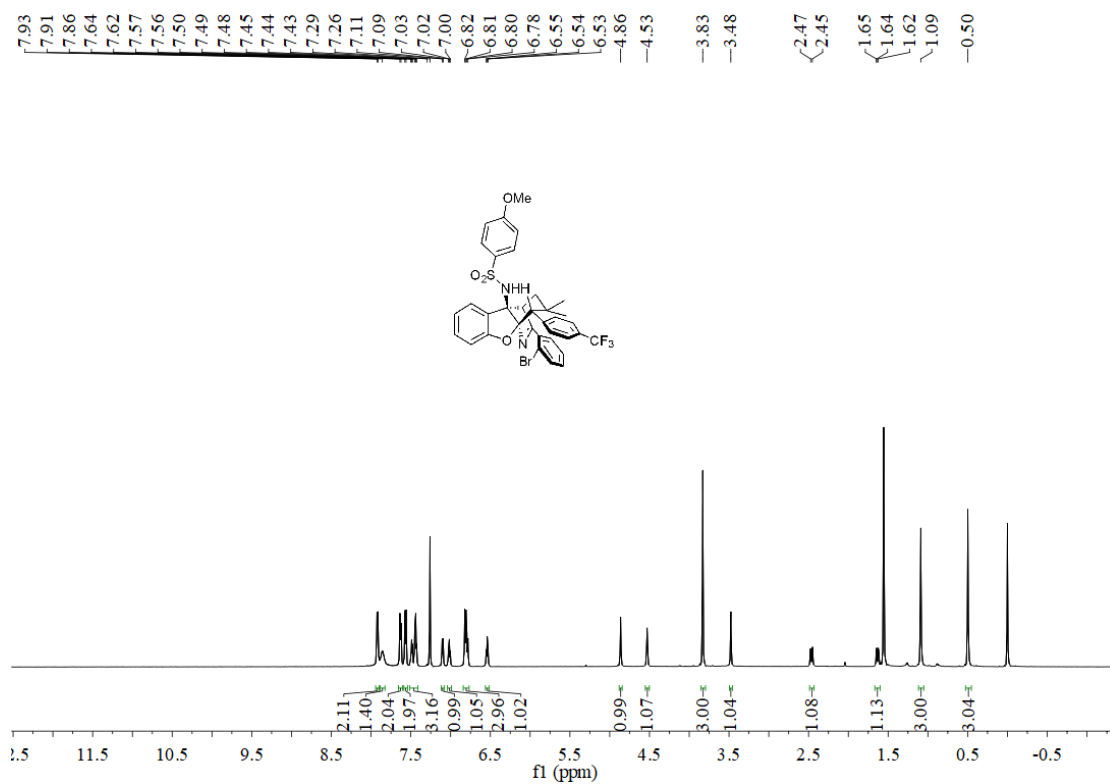
### <sup>13</sup>C NMR Spectrum of 3u



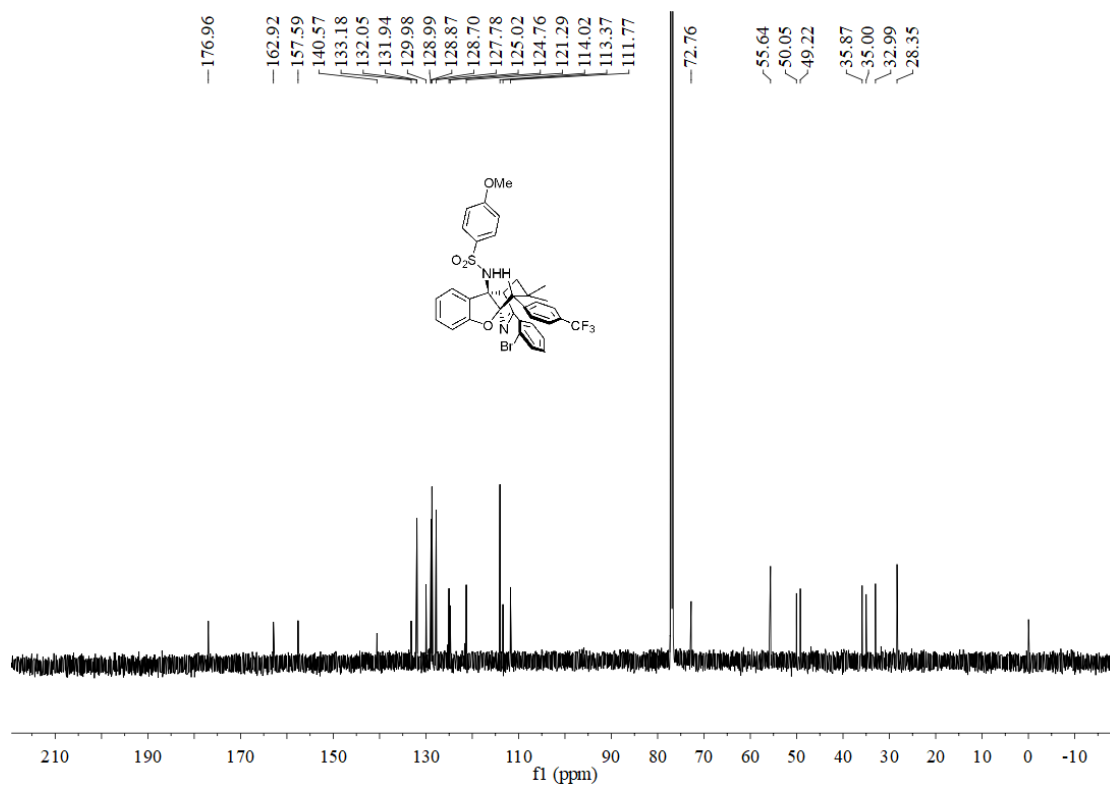
### <sup>19</sup>F NMR Spectrum of 3u



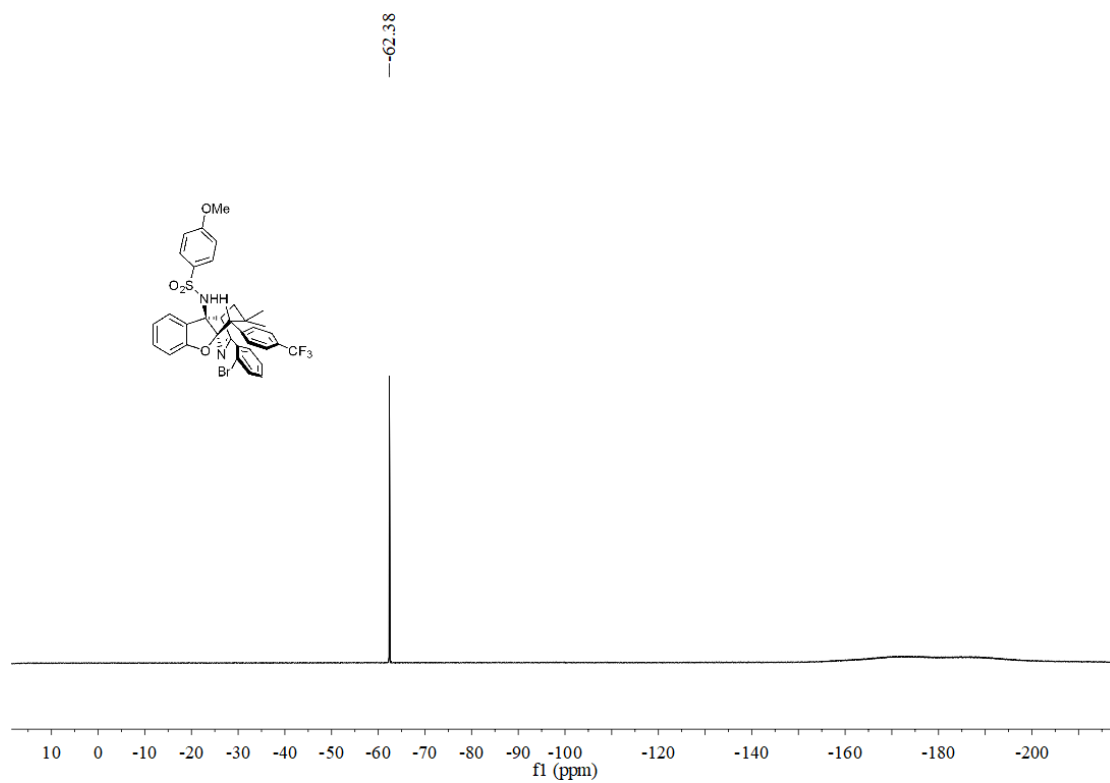
### <sup>1</sup>H NMR Spectrum of 3v



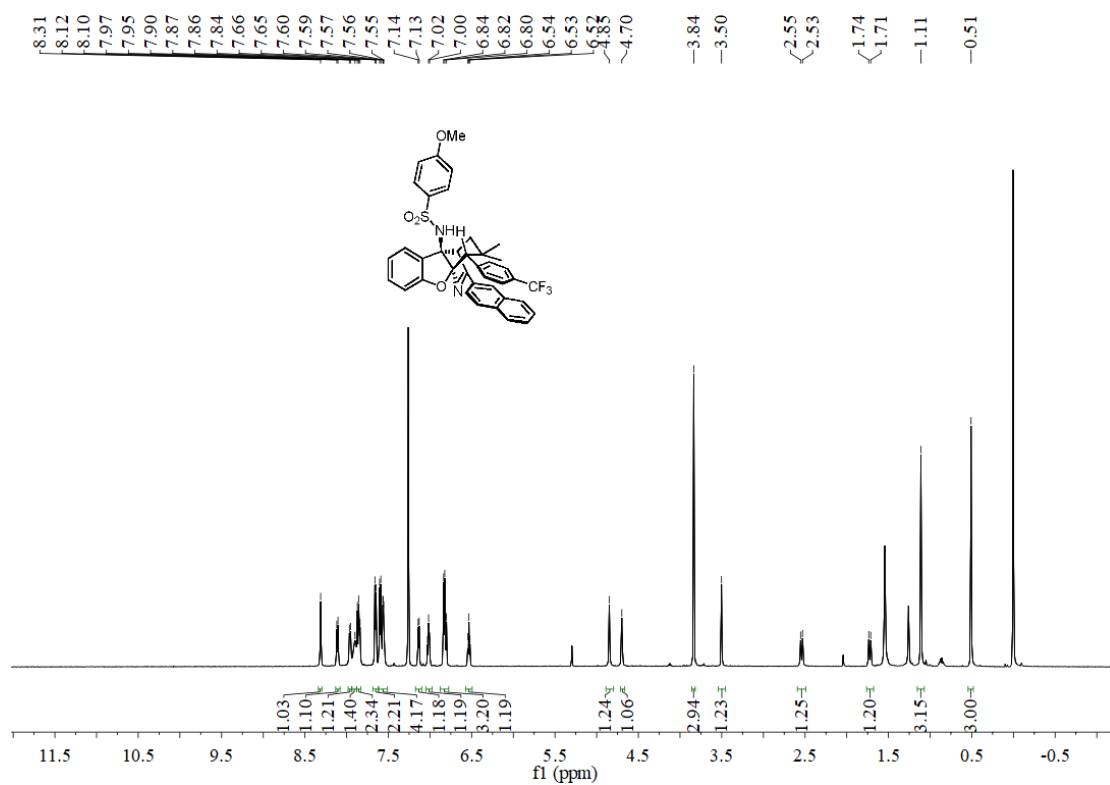
### <sup>13</sup>C NMR Spectrum of 3v



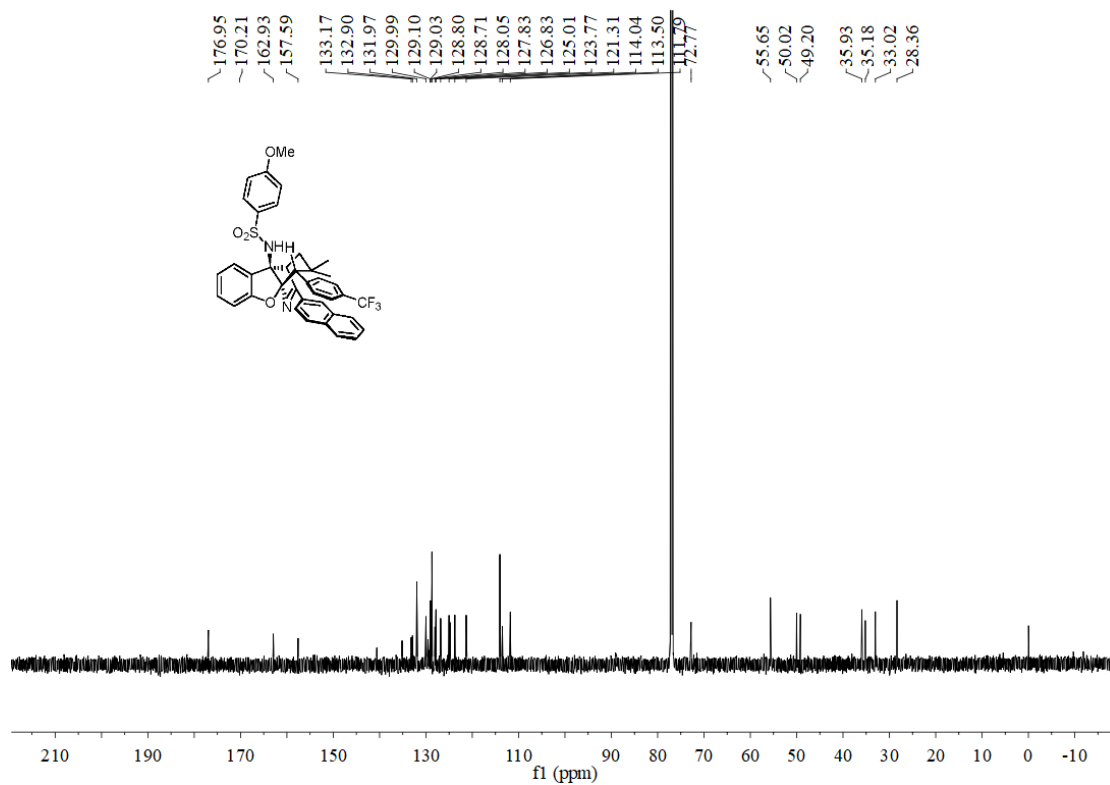
### <sup>19</sup>F NMR Spectrum of 3v



### <sup>1</sup>H NMR Spectrum of 3w

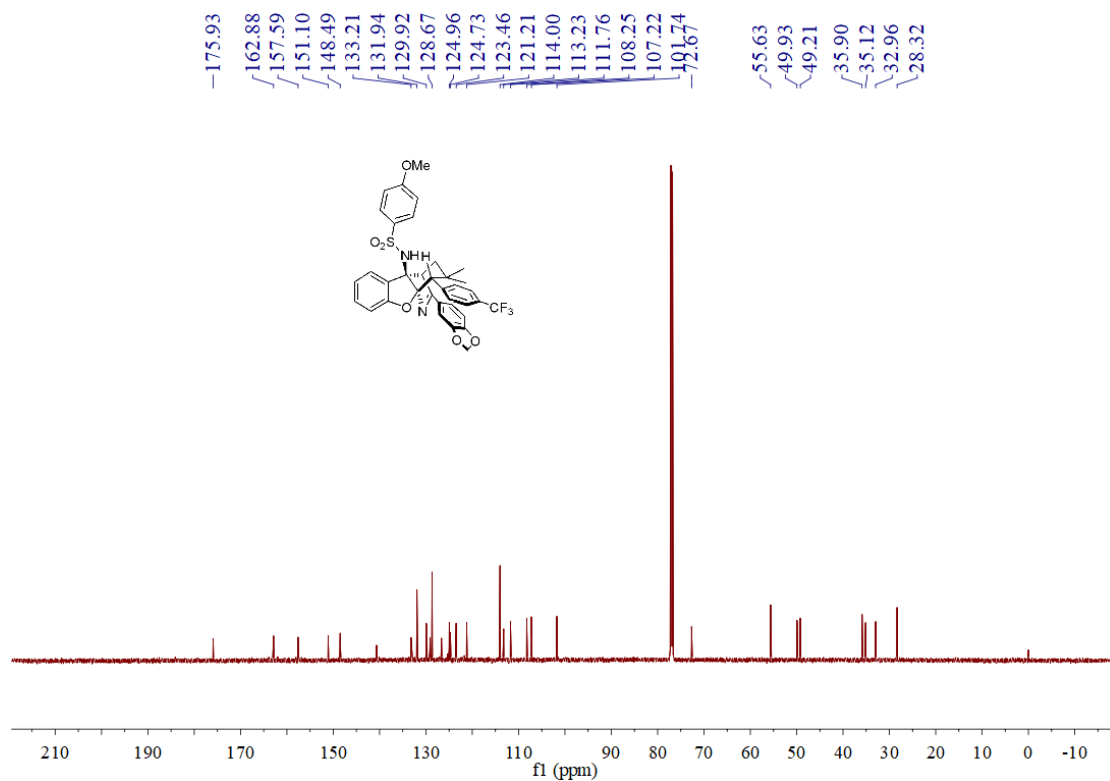


### <sup>13</sup>C NMR Spectrum of 3w

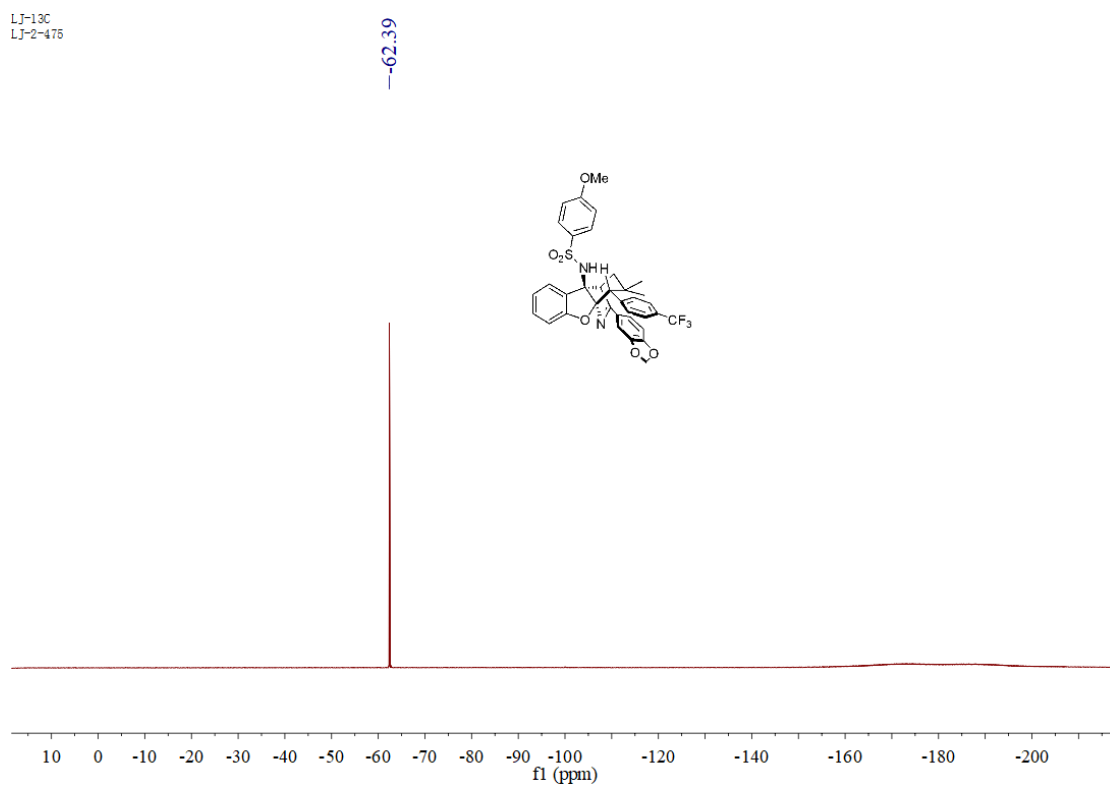




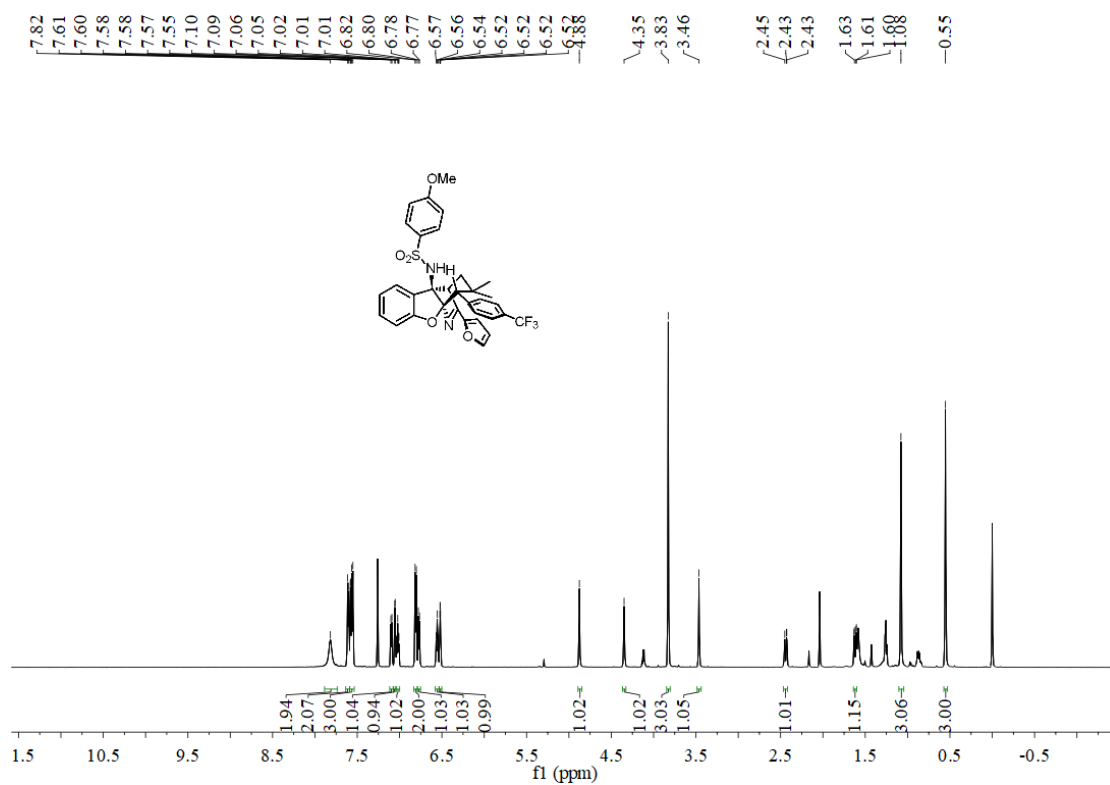
### <sup>13</sup>C NMR Spectrum of 3x



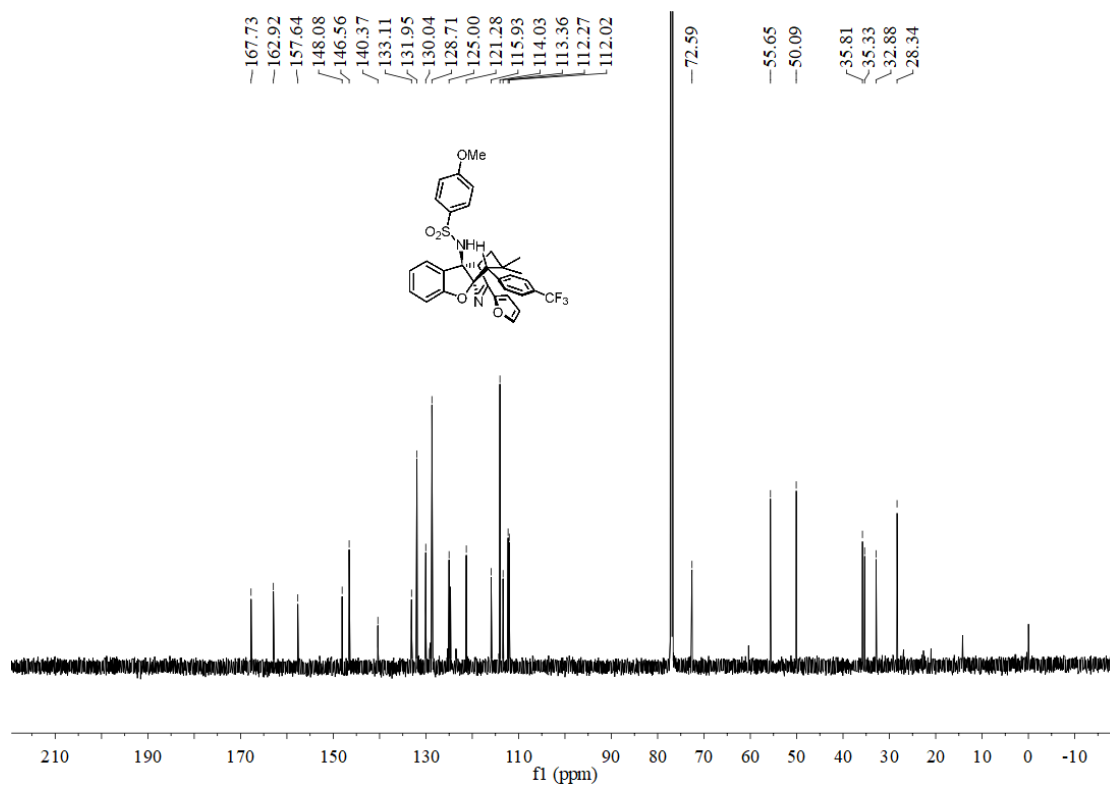
### <sup>19</sup>F NMR Spectrum of 3x



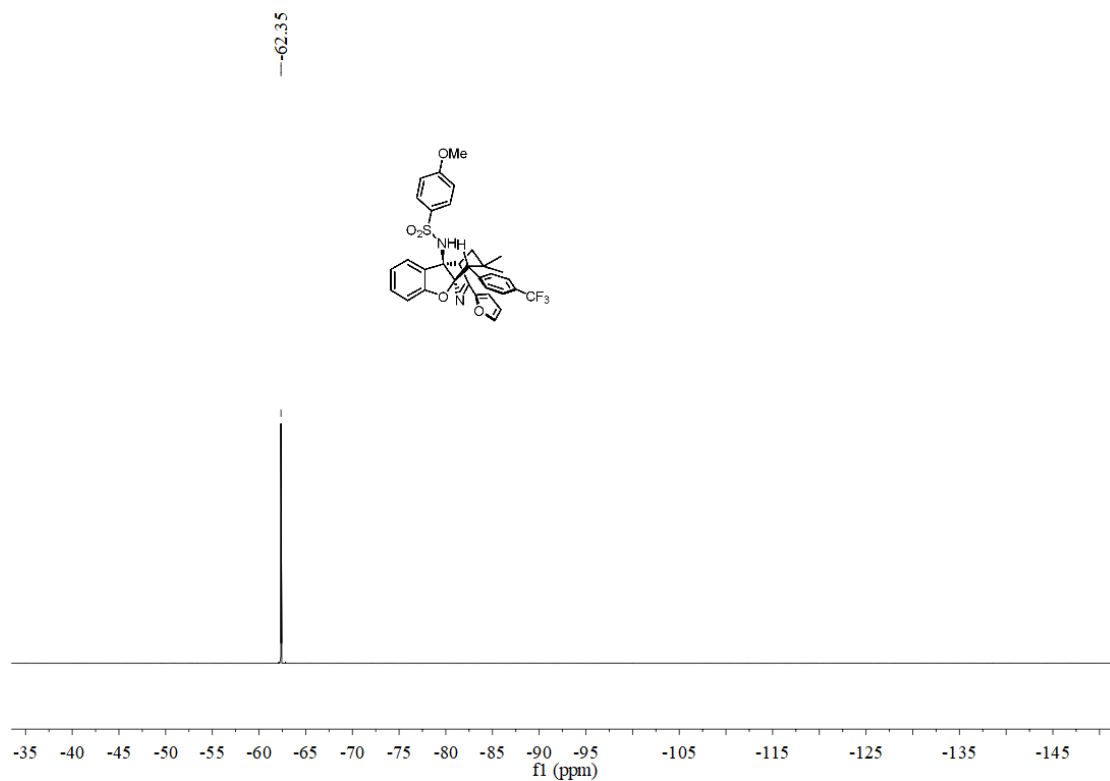
### <sup>1</sup>H NMR Spectrum of 3y



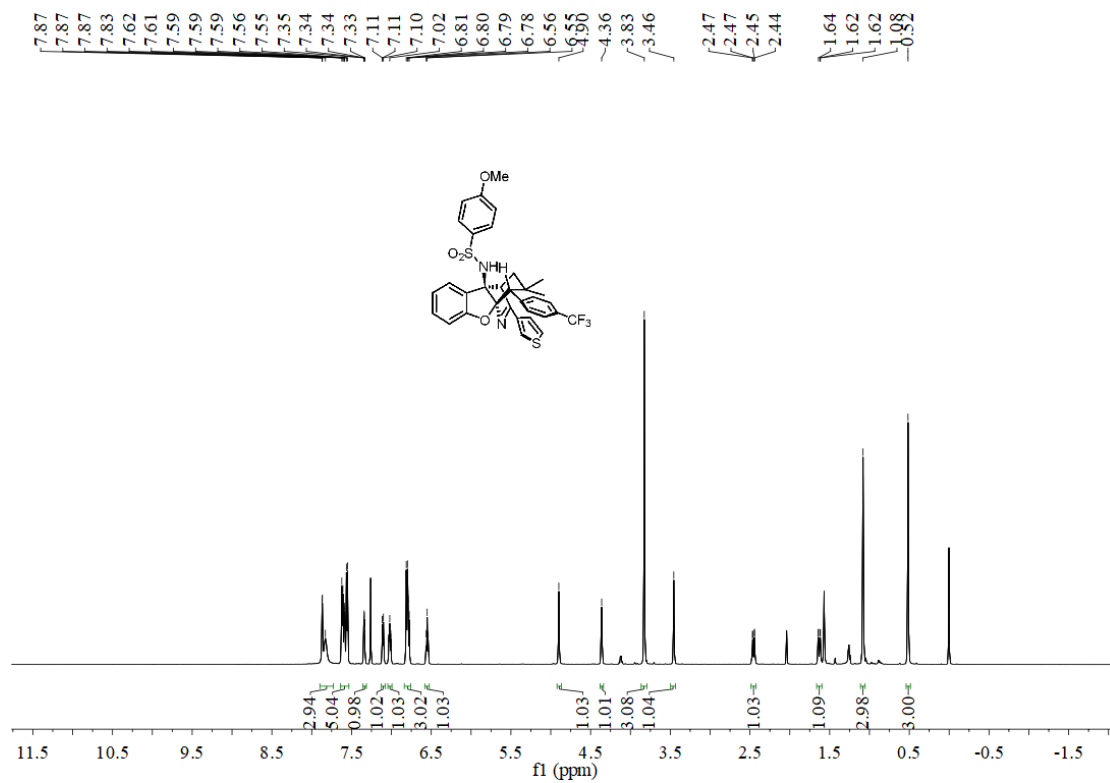
### <sup>13</sup>C NMR Spectrum of 3y



**<sup>19</sup>F NMR Spectrum of 3y**

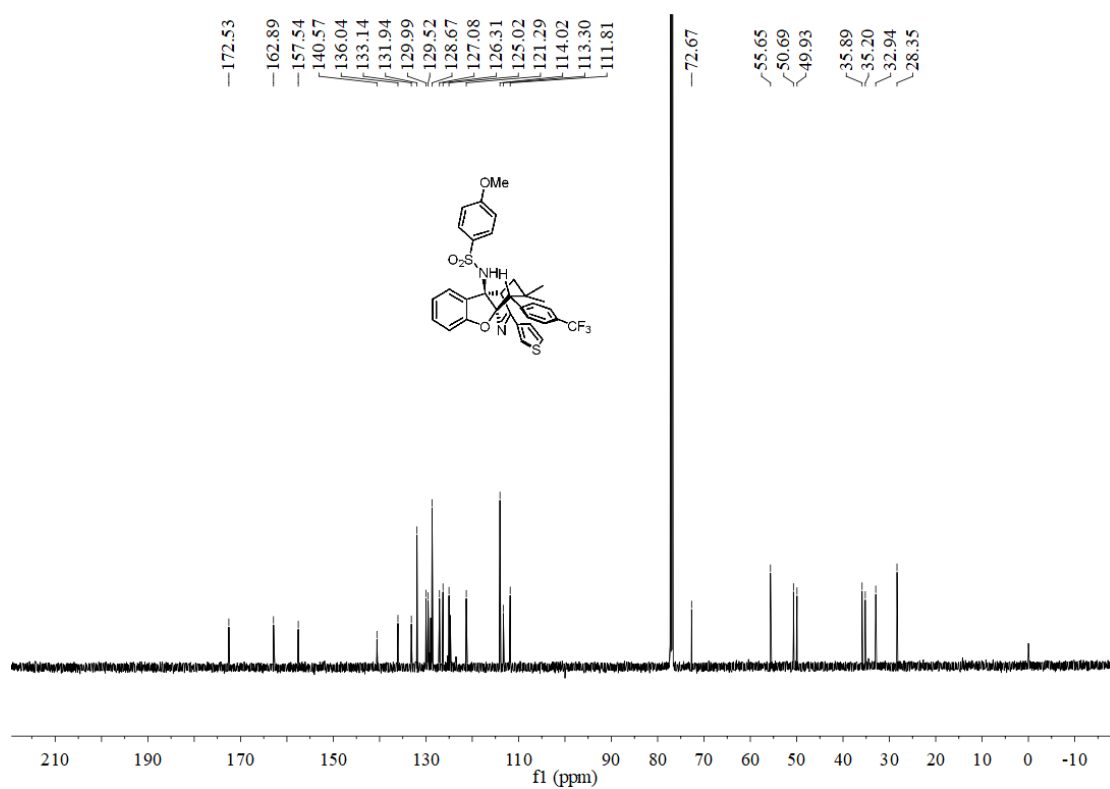


**<sup>1</sup>H NMR Spectrum of 3z**

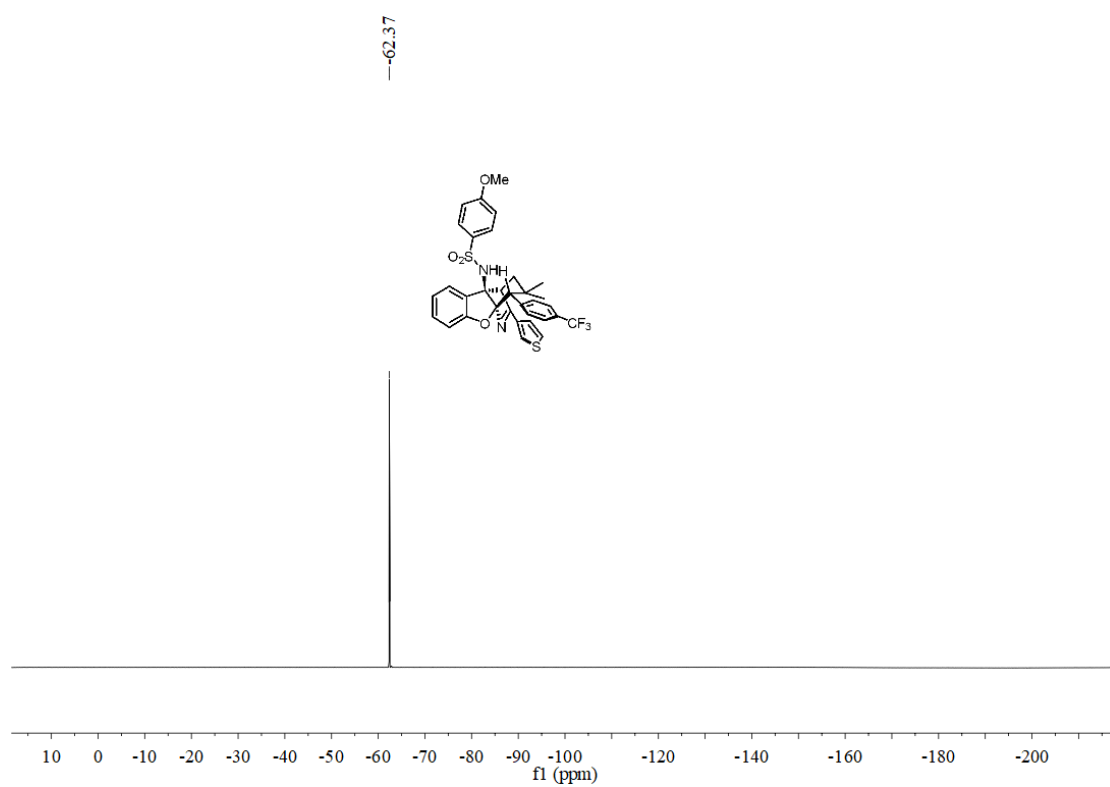




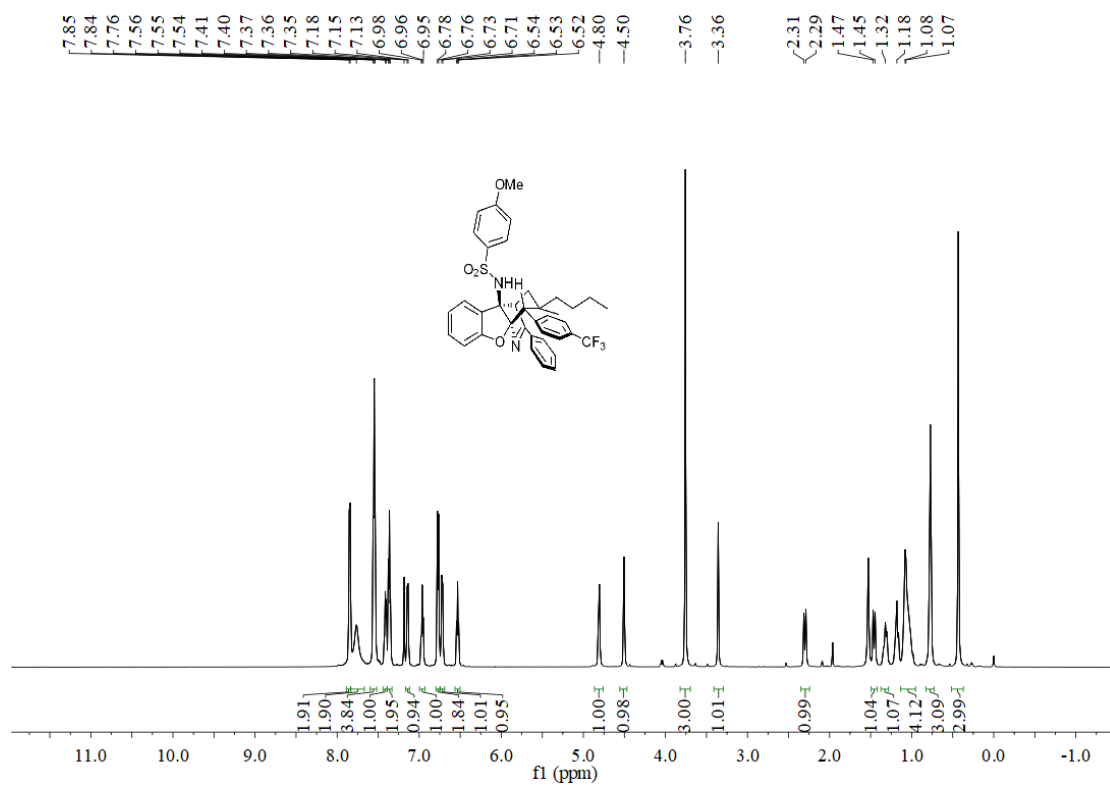
### <sup>13</sup>C NMR Spectrum of 3z



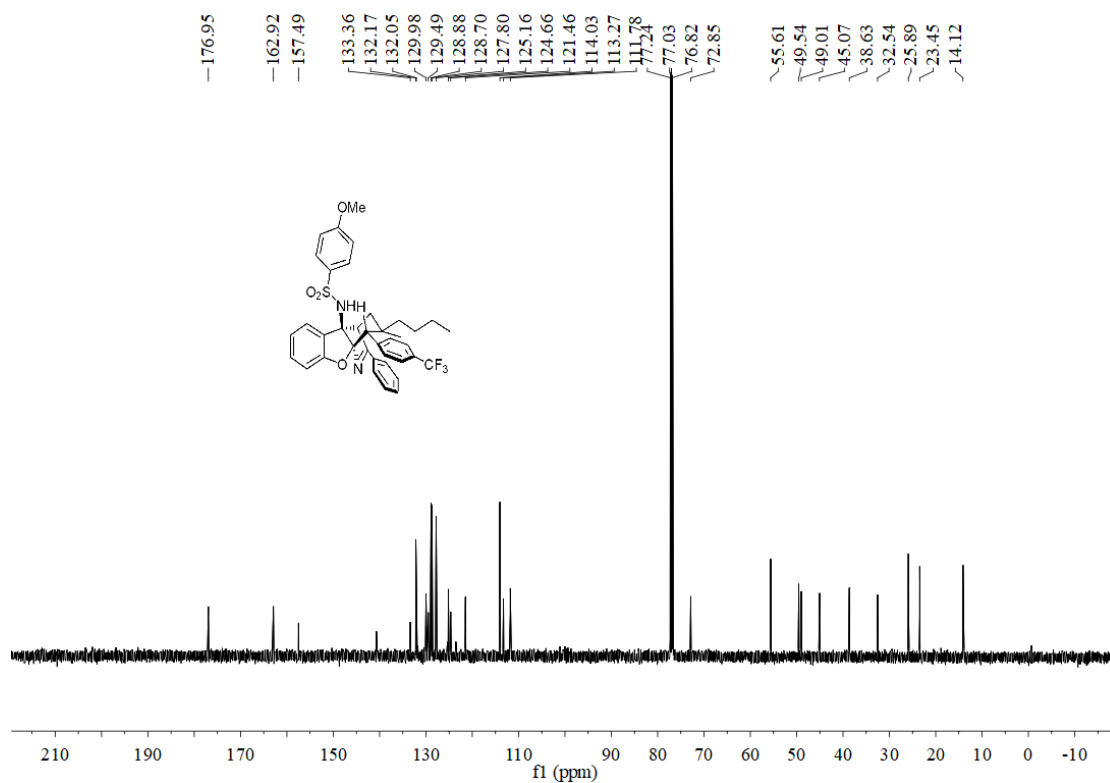
### <sup>19</sup>F NMR Spectrum of 3z



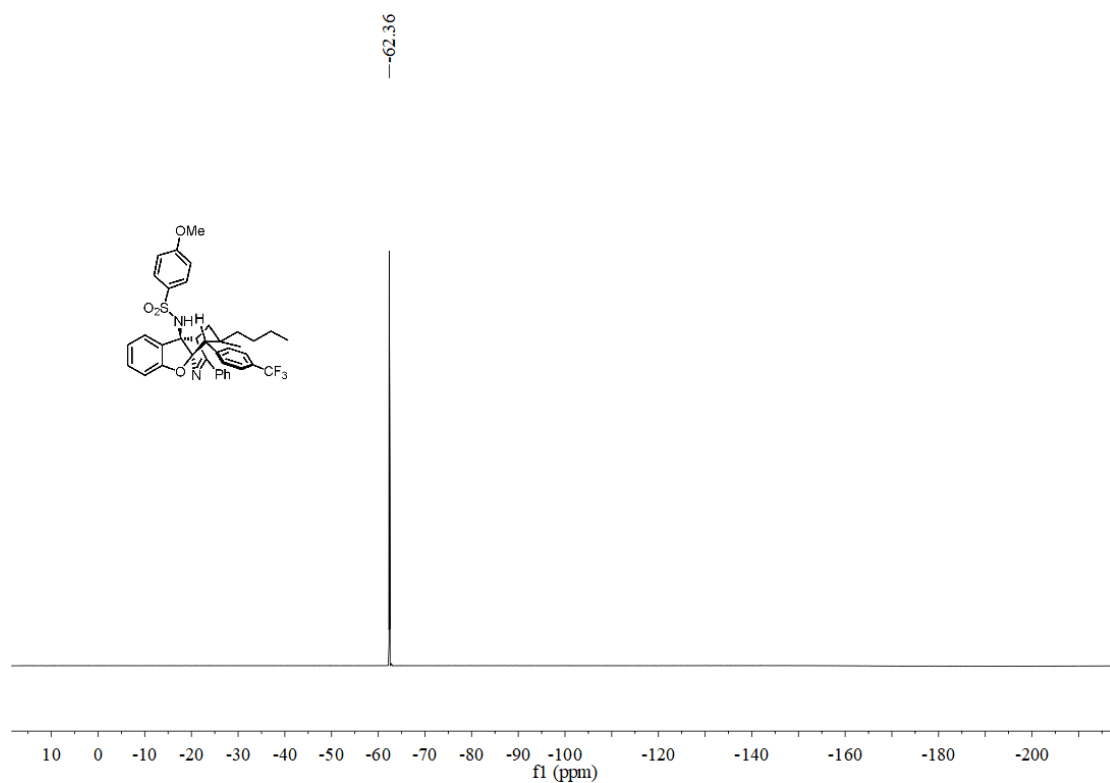
### <sup>1</sup>H NMR Spectrum of 3aa



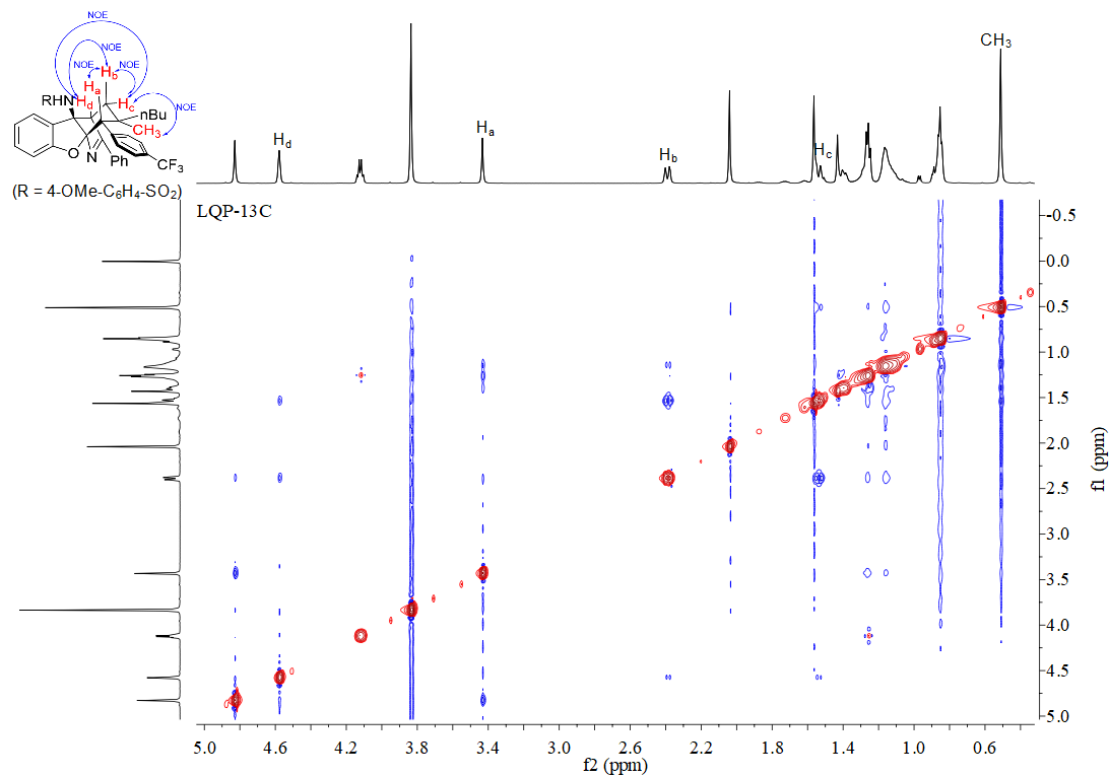
### <sup>13</sup>C NMR Spectrum of 3aa



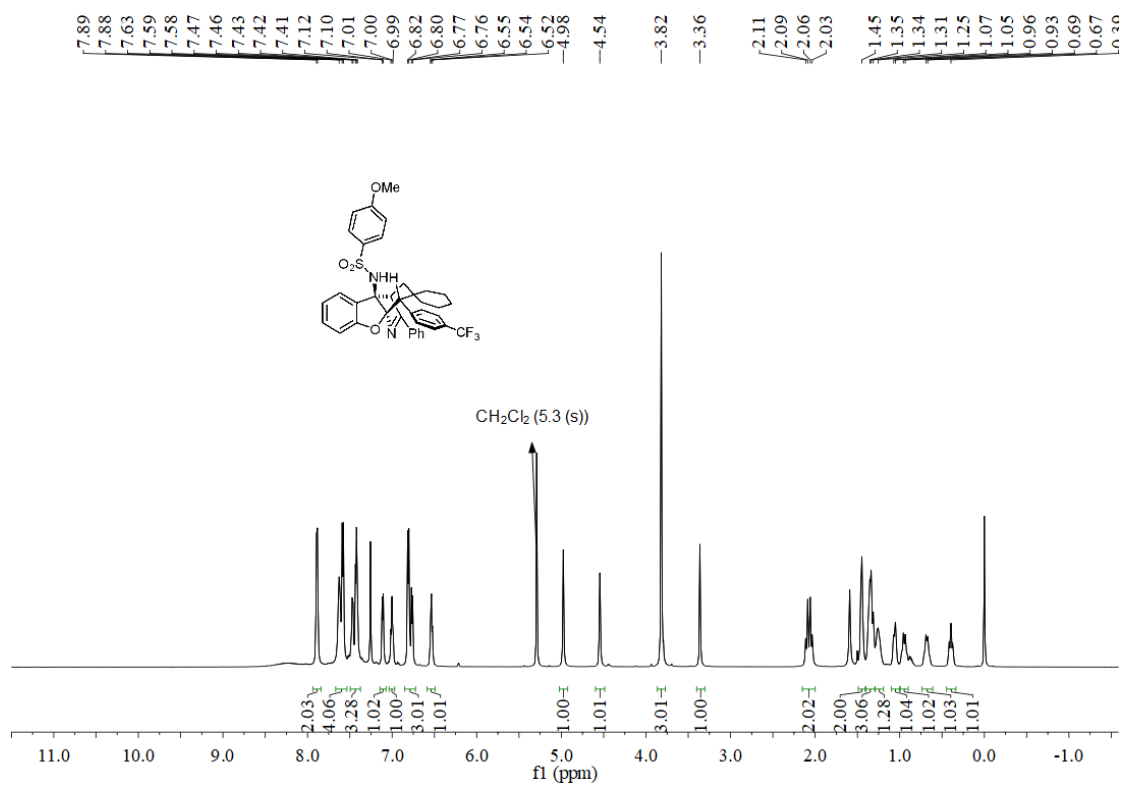
# <sup>19</sup>F NMR Spectrum of 3aa



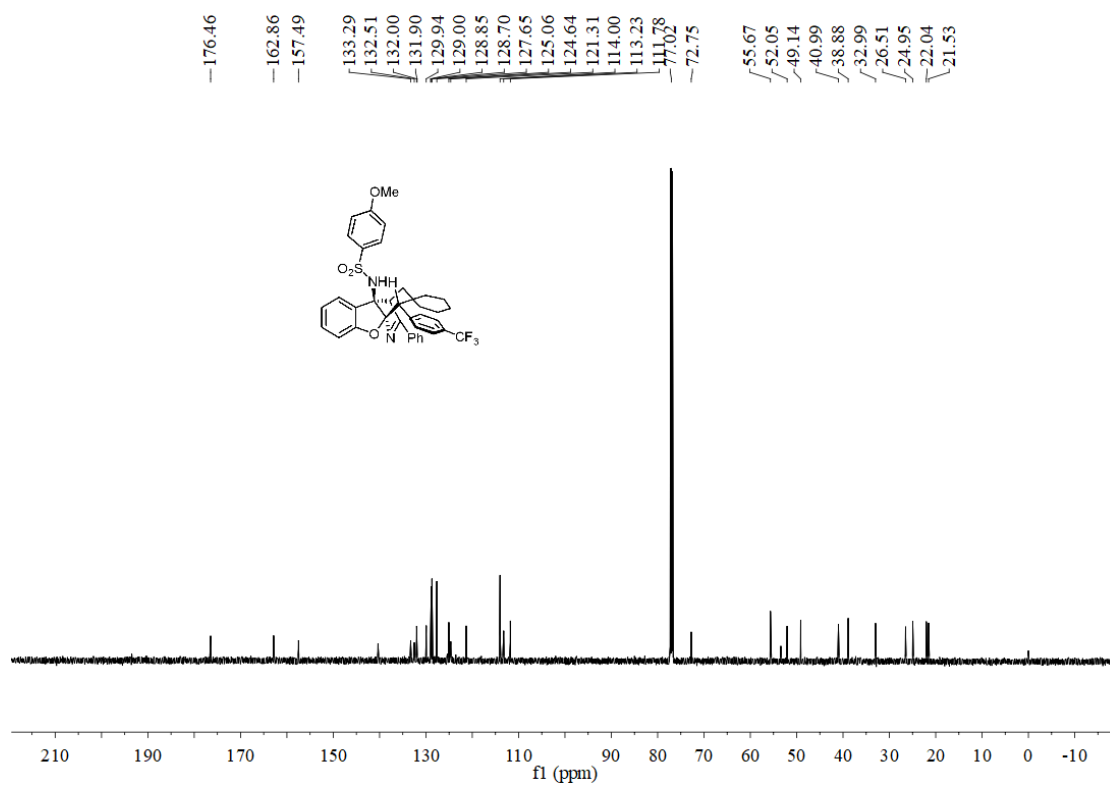
# Noesy Spectrum of 3aa



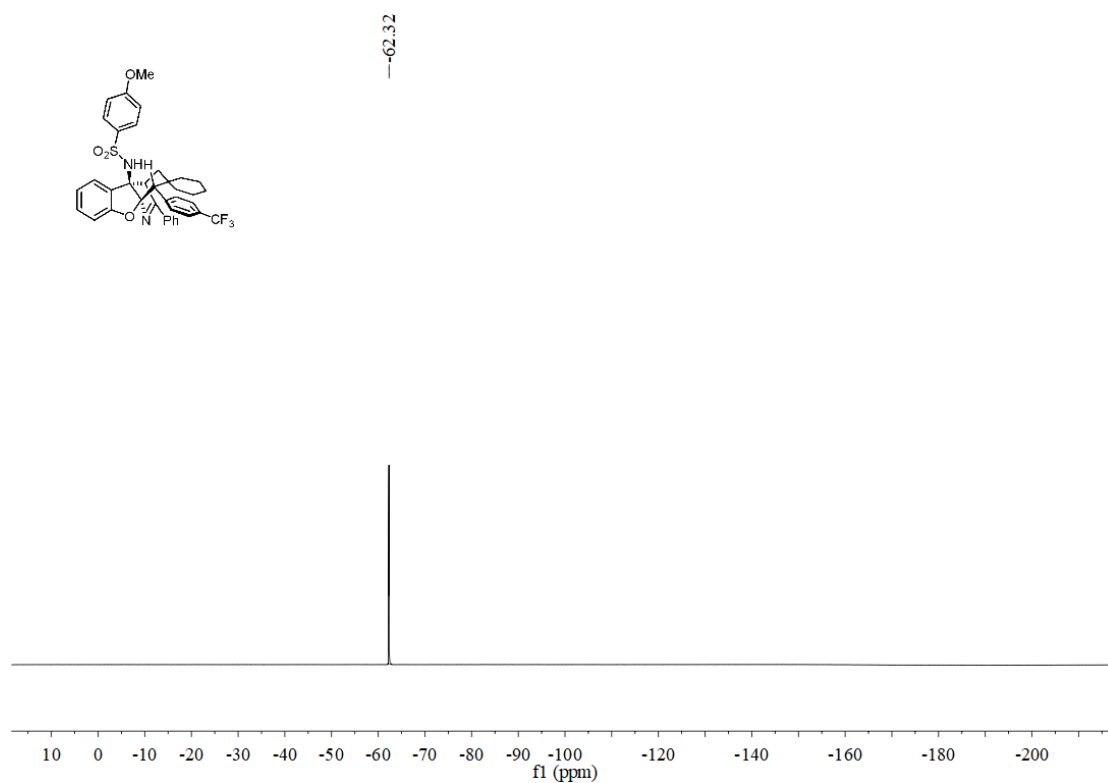
### <sup>1</sup>H NMR Spectrum of 3ab



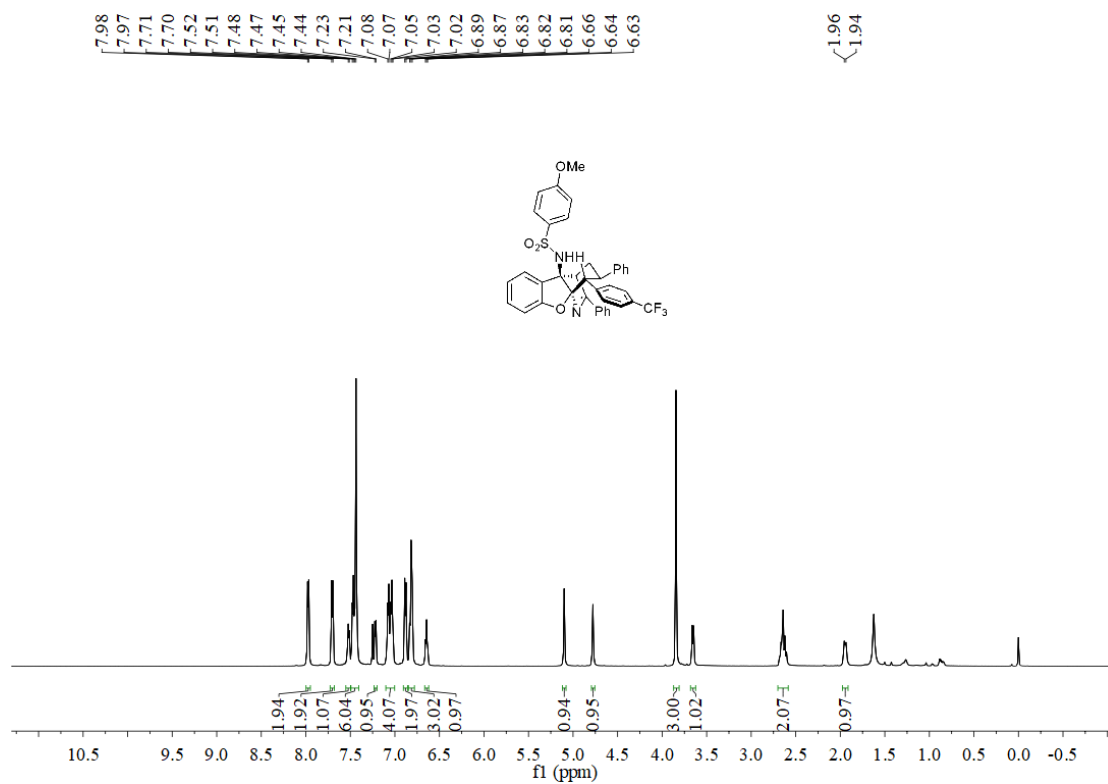
### <sup>13</sup>C NMR Spectrum of 3ab



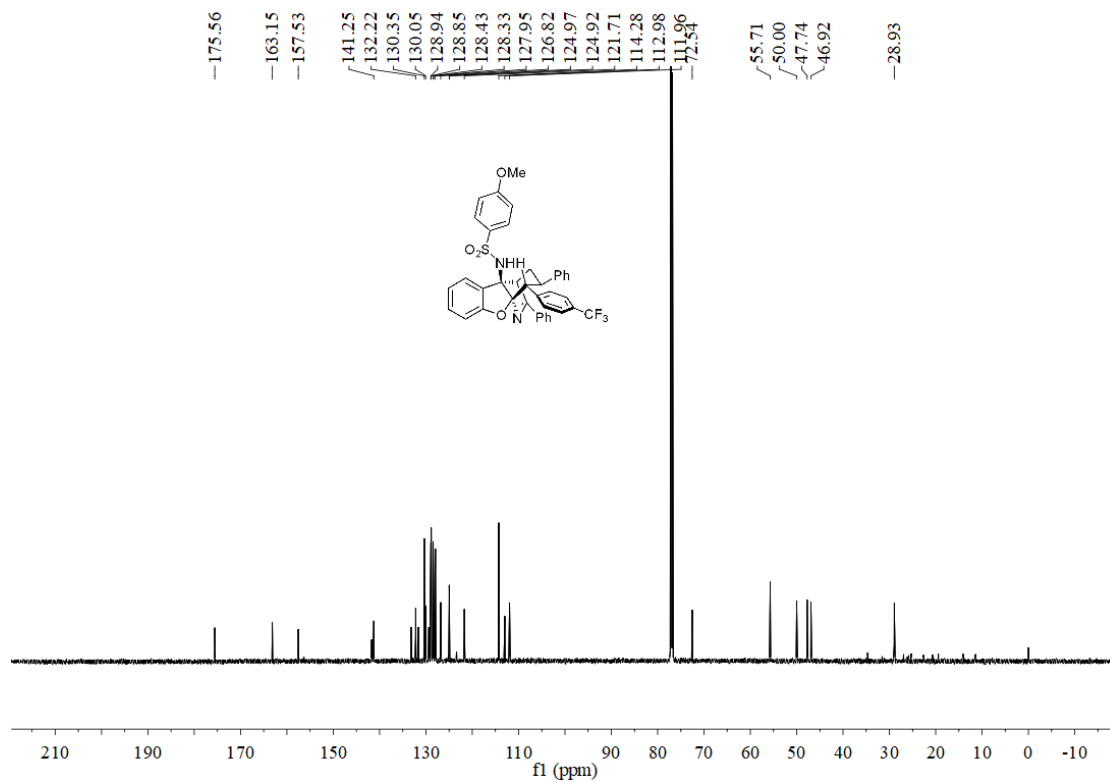
### <sup>19</sup>F NMR Spectrum of 3ab



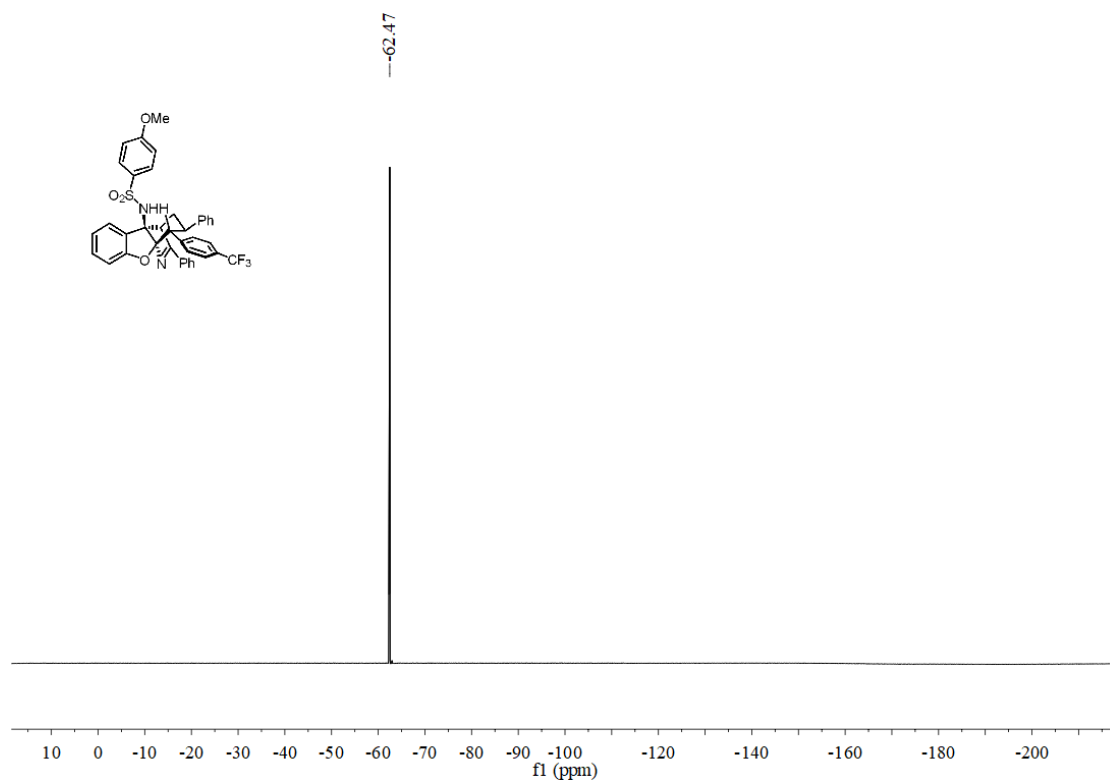
### <sup>1</sup>H NMR Spectrum of 3ac



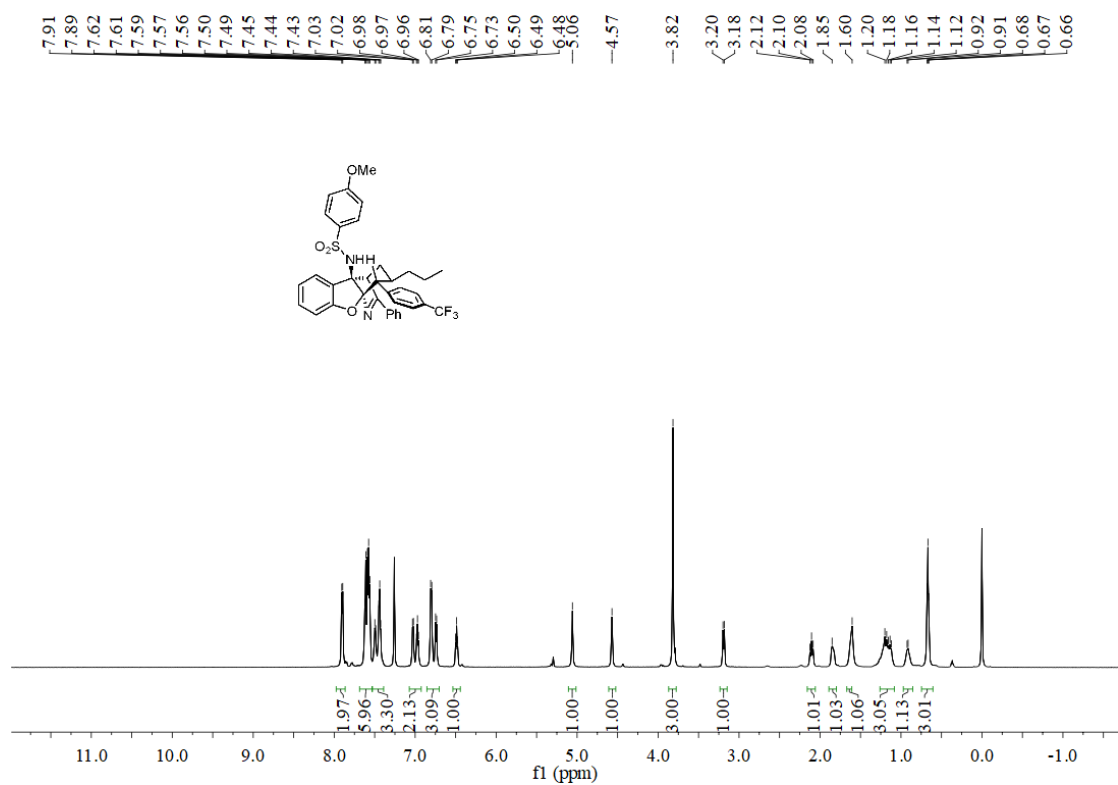
### <sup>13</sup>C NMR Spectrum of 3ac



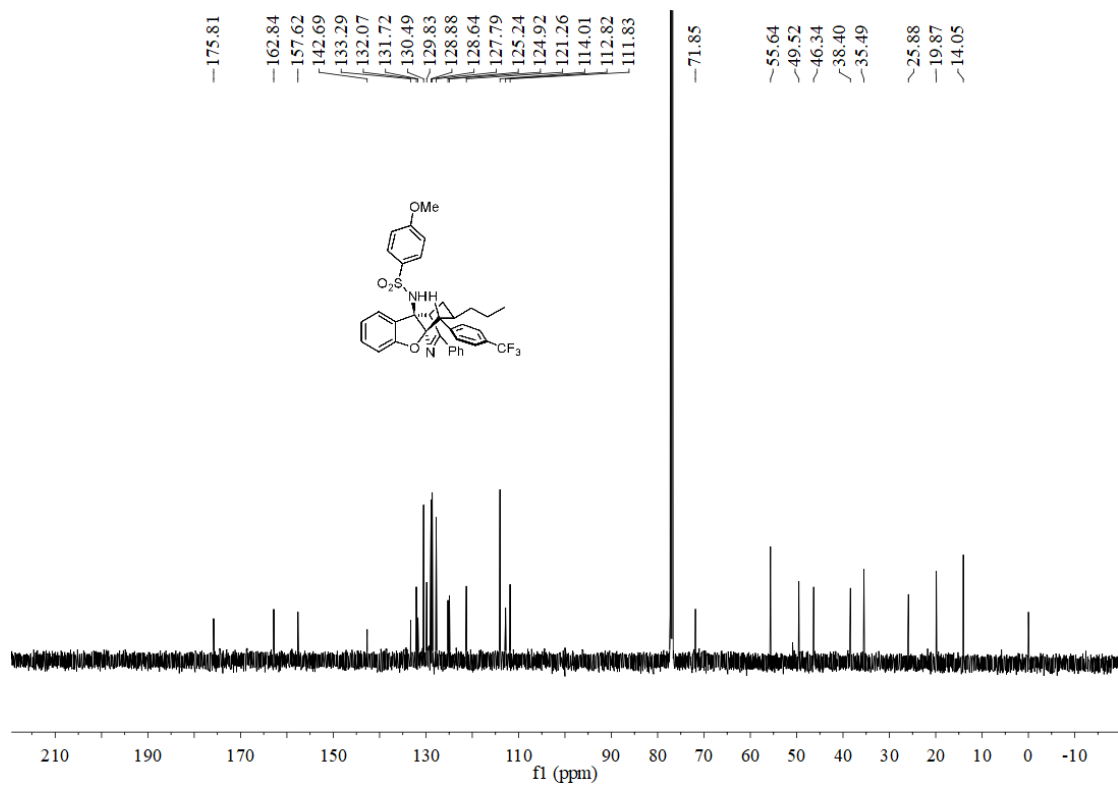
### <sup>19</sup>F NMR Spectrum of 3ac



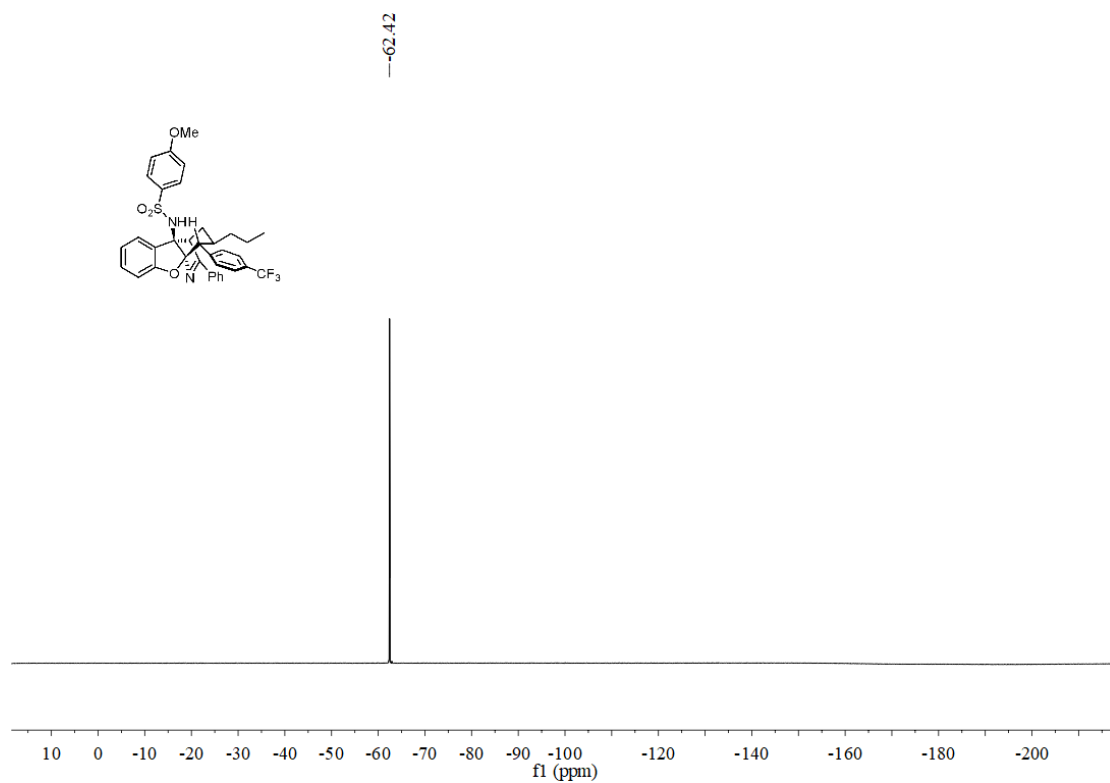
### <sup>1</sup>H NMR Spectrum of 3ad



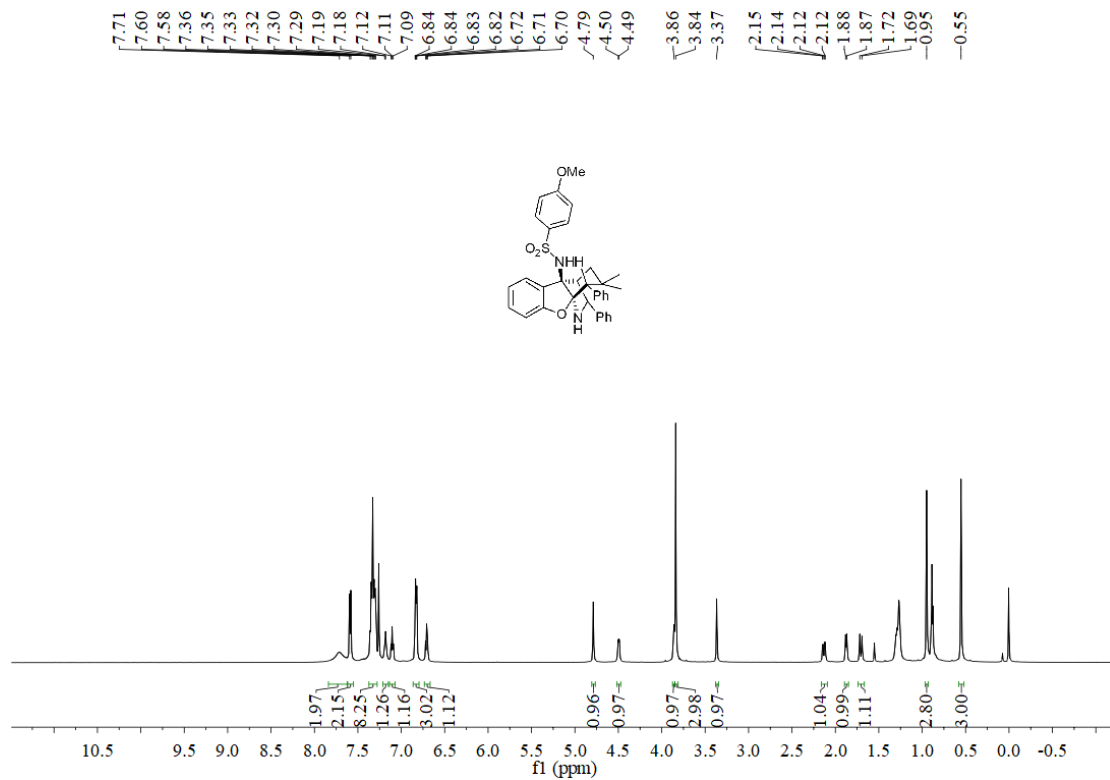
### <sup>13</sup>C NMR Spectrum of 3ad



### <sup>19</sup>F NMR Spectrum of 3ad



### <sup>1</sup>H NMR Spectrum of 5





# <sup>13</sup>C NMR Spectrum of 5

