

## Supporting Information

# Photoinduced Decatungstate-Catalyzed C(sp<sup>3</sup>)-H Thioetherification by Sodium Sulfite

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## 1. General information

$^1\text{H}$  NMR (400 MHz),  $^{13}\text{C}$  NMR (100 MHz) and  $^{19}\text{F}$  NMR (376 MHz) spectra were recorded on a Quantum-I Plus 400 NMR spectrometer with  $\text{CDCl}_3$  as solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts were reported in parts per million (ppm,  $\delta$  scale) downfield from TMS at 0.00 ppm and referenced to  $\text{CDCl}_3$  at 7.26 ppm (for  $^1\text{H}$  NMR) and 77.16 ppm (for  $^{13}\text{C}$  NMR). HR-MS spectra were recorded on a Waters Xevo G2QTOF/UPLC mass spectrometer using electrospray ionization. All commercially available reagents and solvents were purchased from Energy Chemical and Adamas-beta® and used as received unless otherwise specified.

## 2. Photochemical reaction setup



**Figure S1:** Reaction setup

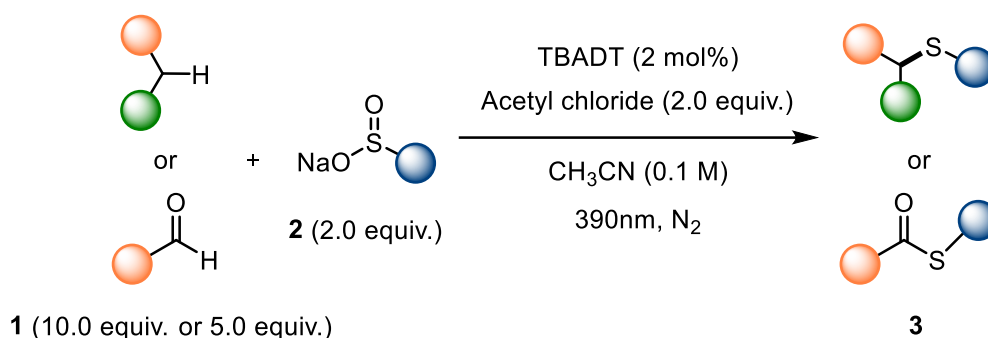
**Light source:** Purple LEDs was purchased from Shanghai 3S Technology Co., Ltd (390-395 nm), China (Figure S1).

### 3. General procedures for synthesis of substrates

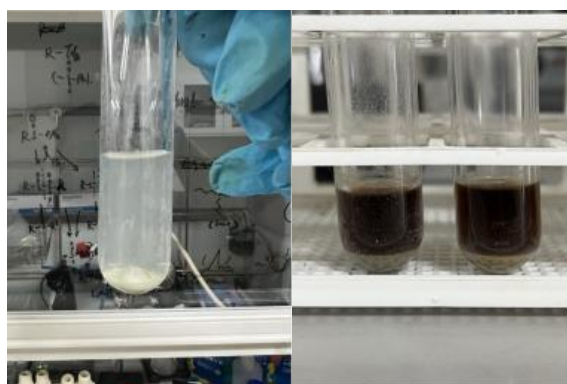
#### 3.1 Synthesis of substrates

All required substrates were synthesized according to the literature (*J. Am. Chem. Soc.* 2023, **145**, 13, 7600–7611).

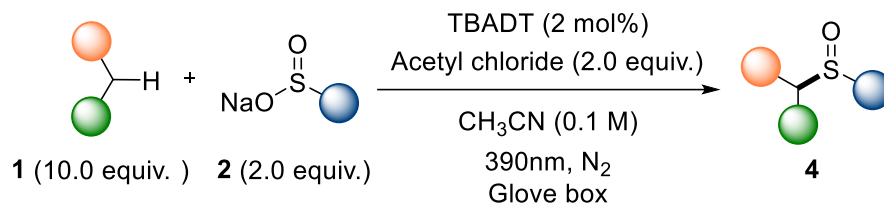
#### 4. General procedures reaction



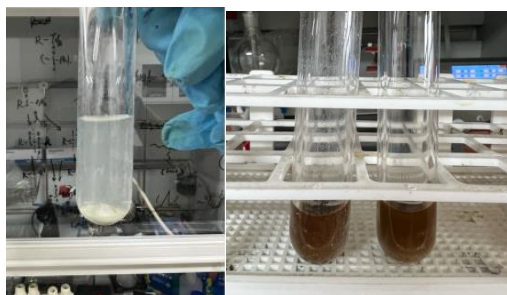
**General procedure 1:** To a 25 mL quartz tube equipped with a magnetic stir bar, **1** ( 5.0 equiv. or 10.0 equiv. ), sodium benzenesulfonate (0.4 mmol, 2.0 equiv.), TBADT (2 mol%), acetyl chloride ( 2.0 equiv.) and MeCN (0.1 M) were added. The resulting mixture was stirred in nitrogen atmosphere under a purple LEDs and irradiated for 6 hours. After the reaction was finished (monitored by TLC), the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel.



**Figure S2.** Before and after the photochemical reaction

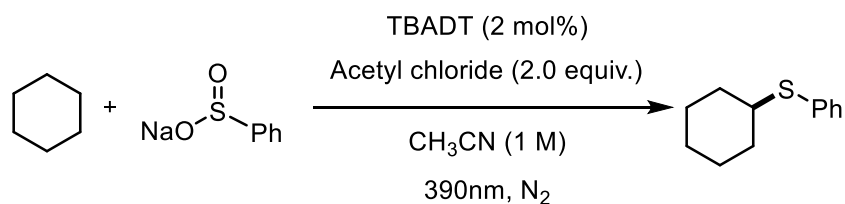


**General procedure 2:** To a 25 mL quartz tube equipped with a magnetic stir bar in the glove box, **1** ( 5.0 equiv. or 10.0 equiv. ), sodium benzenesulfinate (0.4 mmol, 2.0 equiv.), TBADT (2 mol%), acetyl chloride ( 2.0 equiv.) and MeCN (0.1 M) were added. The resulting mixture was stirred in nitrogen atmosphere under a purple LEDs and irradiated for 6 hours. After the reaction was finished (monitored by TLC), the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel.



**Figure S3.** Before and after the photochemical reaction in glove box

### Scale-up synthesis of compound 3a



To a 100 mL two necked flasks with a magnetic stir bar, sodium benzenesulfinate (8.20 g, 5 mmol, 2.0 equiv.), cyclohexane (27.0 ml, 25 mmol, 10 equiv.), TBADT (250 mg, 2 mol%), acetyl chloride (5 mmol, 2.0 equiv.) and MeCN (50 mL) were added. The resulting mixture was stirred in N<sub>2</sub> under a 390 nm LEDs and irradiated for 12 hours. After the reaction was finished (monitored by TLC), the solvent was removed under

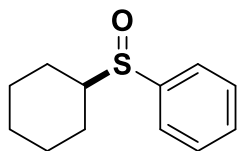
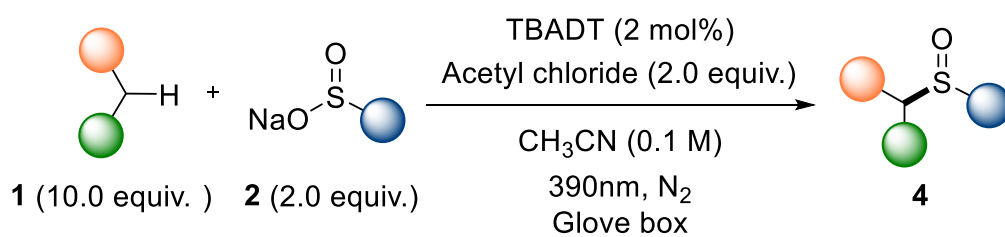
reduced pressure and the residue was purified by silica column to give **3a** (6.30 g, 65% yield) as a colorless oil.



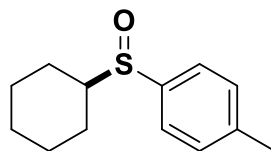
**Figure S4.** Enlarged experiment of **3a**

## 5. Mechanistic studies

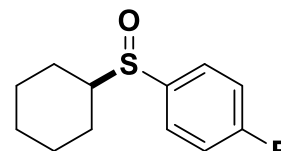
### 5.1 C(sp<sup>3</sup>)-H sulfonylation experiment



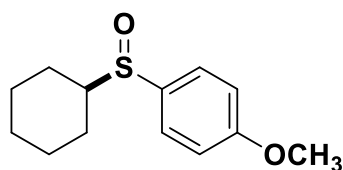
**4a**, 45%



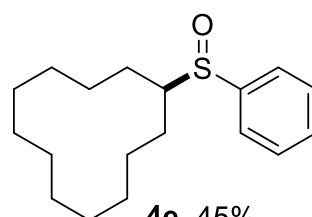
**4b**, 40%



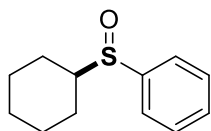
**4c**, 39%



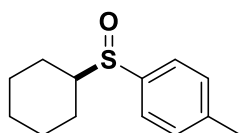
**4d**, 38%



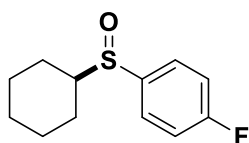
**4e**, 45%



**(cyclohexylsulfinyl)benzene (4a):** Followed the general procedure 2 with sodium benzenesulfinate (16.4 mg, 0.1 mmol), cyclohexane (54.0  $\mu$ l, 0.5 mmol) and acetyl chloride (15.7 mg, 0.2 mmol) purified using flash chromatography (petroleum ether:ethyl acetate=50:1) to give 8.7 mg of the title compound (Colorless oil); 45% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 – 7.57 (m, 2H), 7.55 – 7.47 (m, 3H), 2.61 – 2.53 (m, 1H), 1.89 – 1.81 (m, 4H), 1.68 – 1.62 (m, 1H), 1.50 – 1.33 (m, 2H), 1.30 – 1.16 (m, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.8, 131.0, 129.0, 125.1, 63.2, 26.3, 25.7, 25.5, 25.4, 24.1. **HRMS (ESI)** calcd  $\text{C}_{12}\text{H}_{17}\text{OS}$   $[\text{M} + \text{H}]^+$ : 208.0922, found: 208.0923.

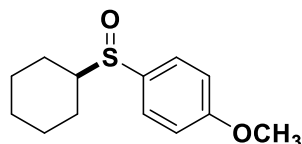


**1-(cyclohexylsulfinyl)-4-methylbenzene (4b):** Followed the general procedure 2 with sodium p-methylbenzene sulfinate (17.8 mg, 0.1 mmol), cyclohexane (54.0  $\mu$ l, 0.5 mmol) and acetyl chloride (15.7 mg, 0.2 mmol) purified using flash chromatography (petroleum ether:ethyl acetate=50:1) to give 8.9 mg of the title compound (Colorless oil); 40% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 (d,  $J=4.9$  Hz, 2H), 7.36 – 7.28 (m, 2H), 2.60 – 2.52 (m, 1H), 2.42 (s, 3H), 1.92 – 1.76 (m, 4H), 1.66 (s, 1H), 1.49 – 1.32 (m, 2H), 1.30 – 1.15 (m, 4H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.5, 138.5, 129.7, 125.1, 63.2, 35.6, 26.2, 25.6, 25.5, 25.4, 24.3, 21.5. **HRMS (ESI)** calcd  $\text{C}_{13}\text{H}_{19}\text{OS}$   $[\text{M} + \text{H}]^+$ : 222.1078, found: 222.1085.

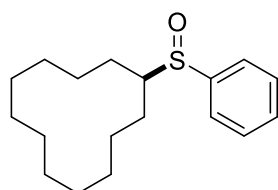


**1-(cyclohexylsulfinyl)-4-fluorobenzene (4c):** Followed the general procedure 2 with sodium p-fluorobenzenesulfonate (19.8 mg, 0.1 mmol), cyclohexane (54.0  $\mu$ l, 0.5 mmol) and acetyl chloride (15.7 mg, 0.2 mmol) purified using flash chromatography (petroleum ether:ethyl acetate=50:1) to give 8.8 mg of the title compound (Colorless

oil); 39% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 – 7.56 (m, 2H), 7.25 – 7.17 (m, 2H), 2.59 – 2.51 (m, 1H), 1.92 – 1.77 (m, 5H), 1.68 (s, 1H), 1.41 – 1.12 (m, 5H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.24 (d,  $J = 251.1$  Hz), 127.1 (d,  $J = 8.8$  Hz), 116.2 (d,  $J = 22.5$  Hz), 127.1, 116.3, 116.1, 63.2, 26.0, 25.4, 25.3, 25.2, 24.0.  $^{19}\text{F NMR}$  (376 MHz,  $\text{Chloroform-}d$ )  $\delta$  -108.9 (t,  $J=7.3$  Hz). **HRMS (ESI)** calcd  $\text{C}_{12}\text{H}_{16}\text{FOS}$   $[\text{M} + \text{H}]^+$ : 226.0828, found: 226.0833.



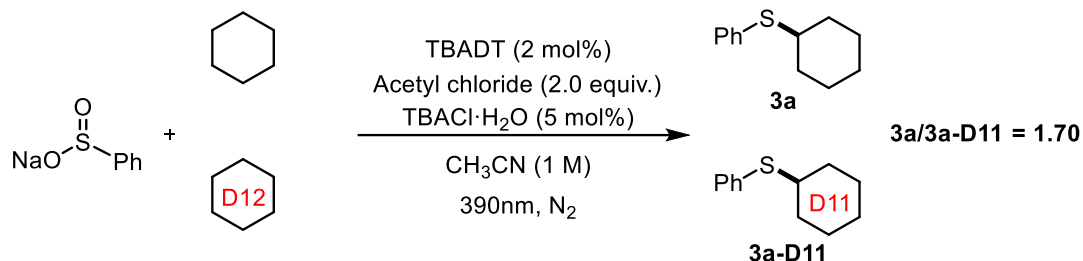
**1-(cyclohexylsulfinyl)-4-methoxybenzene (4d)**: Followed the general procedure 2 with 4-methoxybenzenesulfinic acid (19.4 mg, 0.1 mmol), cyclohexane (54.0  $\mu\text{l}$ , 0.5 mmol) and acetyl chloride (15.7 mg, 0.2 mmol) purified using flash chromatography (petroleum ether:ethyl acetate=50:1) to give 9.0 mg of the title compound (Colorless oil); 38% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 (d,  $J=8.6$  Hz, 2H), 7.02 (d,  $J=8.6$  Hz, 2H), 3.86 (s, 3H), 2.55 (t,  $J=11.3$  Hz, 1H), 1.94 (d,  $J=12.7$  Hz, 1H), 1.87 (d,  $J=12.1$  Hz, 1H), 1.81 (d,  $J=9.0$  Hz, 1H), 1.74 (d,  $J=11.5$  Hz, 1H), 1.65 (d,  $J=8.7$  Hz, 1H), 1.42 (q,  $J=11.9$  Hz, 1H), 1.30 – 1.19 (m, 5H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.0, 132.9, 127.0, 114.5, 63.5, 55.5, 26.1, 25.6, 25.4, 24.7. **HRMS (ESI)** calcd  $\text{C}_{13}\text{H}_{19}\text{O}_2\text{S}$   $[\text{M} + \text{H}]^+$ : 238.1028, found: 238.1025.



**(phenylsulfinyl)cyclododecane (4e)**: Followed the general procedure 2 with sodium benzenesulfinate (16.4 mg, 0.1 mmol), cyclododecane (84.0 mg, 0.5 mmol) and acetyl chloride (15.7 mg, 0.2 mmol) purified using flash chromatography (petroleum ether:ethyl acetate=50:1) to give 13.1 mg of the title compound (Colorless oil); 45% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 (d,  $J=7.1$  Hz, 2H), 7.29 (d,  $J=7.3$  Hz, 2H), 7.23 – 7.16 (m, 1H), 3.31 – 3.24 (m, 1H), 1.76 – 1.65 (m, 2H), 1.62 – 1.51 (m, 4H), 1.35 (s, 17H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.1, 131.2, 128.8, 126.4, 44.7, 29.9, 24.2, 23.9, 23.4, 22.2. **HRMS (ESI)** calcd  $\text{C}_{18}\text{H}_{29}\text{OS}$   $[\text{M} + \text{H}]^+$ : 292.1861, found:

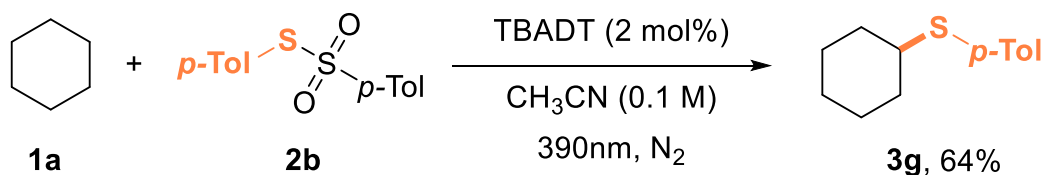
292.1855.

## 5.2 Kinetic isotopic effect (KIE) experiment



To a 10 mL quartz tube equipped with a magnetic stir bar, sodium benzenesulfinate (0.4 mmol, 2.0 equiv.), TBADT (10 mg, 2 mol %) and acetyl chloride (0.4 mmol, 2.0 equiv.) were added. MeCN (0.1 M) and cyclohexane (1.0 mmol, 5 equiv.), and cyclohexane-*d*<sub>12</sub> (1.0 mmol, 5 equiv.) were then added under nitrogen atmosphere. After that, the resulting mixture was stirred in N<sub>2</sub> under LEDs and irradiated for 3 hours. The temperature was maintained at 35 °C when the 390 nm LED light was on. After the reaction was finished (monitored by TLC), the mixture were removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the mixture of products **3a** and **3a-d<sub>7</sub>** in combined 50% yield. Comparing the <sup>1</sup>H NMR spectra, we found the ratio of **3a**:**3a-d<sub>7</sub>** was 63:37, so the intermolecular KIE value was 1.70.

## 5.3 Key intermediates in C(sp<sup>3</sup>)-H thiolation experiment



**cyclohexyl(*p*-tolyl)sulfane (**3g**):** To a 25 mL quartz tube equipped with a magnetic stir bar *p*-Toluenethiosulfonic acid *S*-*p*-tolyl ester (27.8 mg, 0.1 mmol), cyclohexane (54.0  $\mu$ l, 0.5 mmol) TBADT (2 mol%), acetyl chloride (2.0 equiv.) and MeCN (0.1 M) purified using flash chromatography (petroleum ether:ethyl acetate=50:1) to give 14.5 mg of the title compound (Colorless oil); 64% yield.



#### 5.4 Light On/Off Experiment

General procedure was set up parallel on a 0.2 mmol scale. After being irradiated for 0.5 h, 1h, 2h, 3h, 4h and 5h an aliquot (300  $\mu$ L) from the reaction mixture was transferred into a nuclear magnetic tube charged with 300  $\mu$ L of CD Cl<sub>3</sub>-d<sub>1</sub> of 1,3,5-Trimethoxybenzene (0.0083 M). The yield of product was determined by <sup>1</sup>H NMR. Then the reaction mixture was stirred for 1 h with light-off. All of the following yields were analyzed in the identical way after a 6-hour light on or off. The results was showed in Fig. S5. The experimental results indicate a low probability of short-lived radical chain reaction.

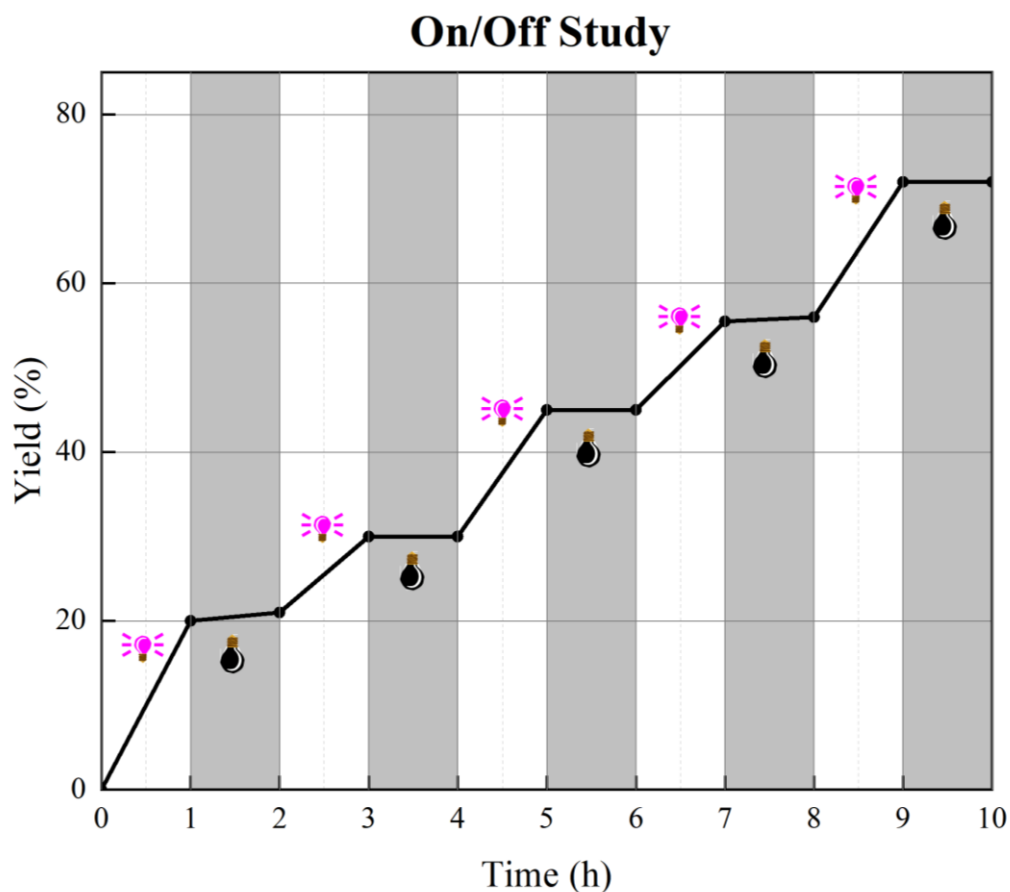
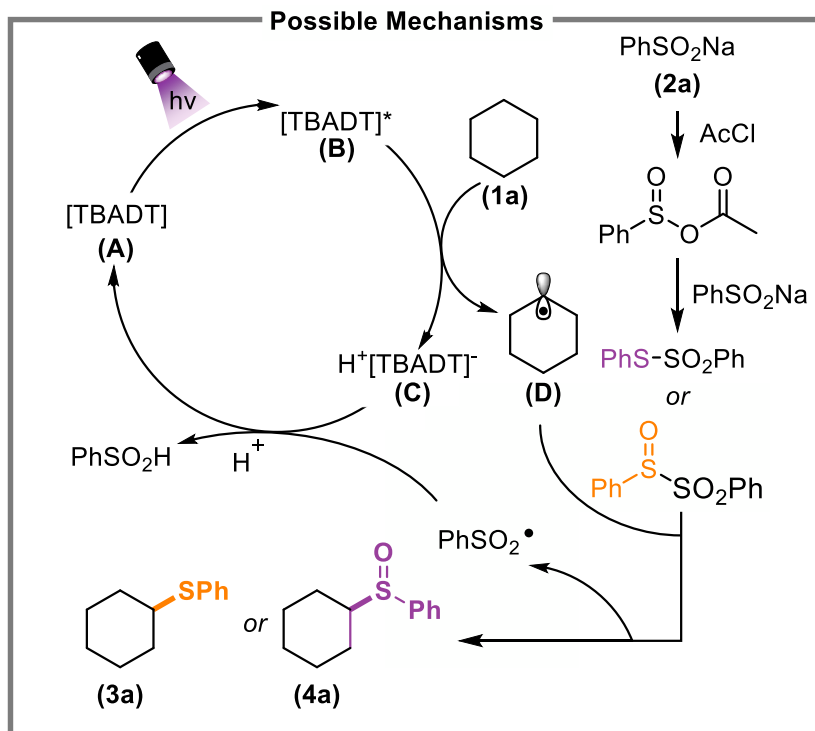
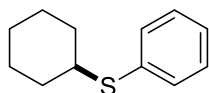


Figure. S5 light on/off experiment

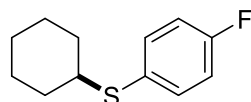
## 5.5 Proposed mechanism



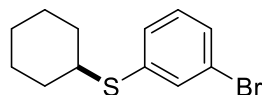
## 6. Characterization of the products



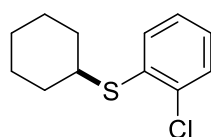
**cyclohexyl(phenyl)sulfane (3a):** Followed the general procedure 1 with sodium benzenesulfinate (16.4 mg, 0.1 mmol), cyclohexane (54.0  $\mu$ l, 0.5 mmol) and acetyl chloride (15.7 mg, 0.2 mmol) purified using flash chromatography (petroleum ether:ethyl acetate=50:1) to give 13.8 mg of the title compound (Colorless oil); 72% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.42-7.34 (m, 2H), 7.32-7.27 (m, 1H), 7.24-7.17 (m, 1H), 3.15-3.05 (m, 1H), 2.04-1.93 (m, 2H), 1.81-1.73 (m, 2H), 1.65-1.57 (m, 1H), 1.43-1.26 (m, 5H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  131.9, 128.8, 126.7, 46.6, 33.4, 26.1, 25.8. HRMS (ESI) calcd C<sub>12</sub>H<sub>17</sub>S [M + H]<sup>+</sup>: 192.0973, found: 192.0970.



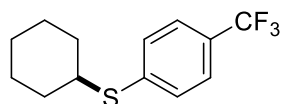
**cyclohexyl(4-fluorophenyl)sulfane (3b)**: Followed the general procedure 1 with sodium 4-fluorobenzenesulfinate (18.2 mg, 0.1 mmol), cyclohexane (54.0  $\mu$ l, 0.5 mmol) and acetyl chloride (15.7 mg, 0.2 mmol) purified using flash chromatography (petroleum ether:ethyl acetate=50:1) to give 10.9 mg of the title compound (Colorless oil); 52% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43-7.37 (m, 2H), 7.02-6.96 (m, 2H), 3.02-2.94 (m, 1H), 1.99-1.88 (m, 2H), 1.82-1.72 (m, 2H), 1.65-1.57 (m, 1H), 1.39-1.25 (m, 5H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.3 (d,  $J = 247.0$  Hz), 135.1 (d,  $J = 8.1$  Hz), 129.8 (d,  $J = 3.6$  Hz), 115.9 (d,  $J = 21.8$  Hz), 47.6, 33.3, 26.1, 25.8.  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -114.84 (t,  $J=7.8$  Hz). **HRMS (ESI)** calcd  $\text{C}_{12}\text{H}_{16}\text{FS}$  [ $\text{M} + \text{H}$ ] $^+$ : 210.0878, found: 210.0883.



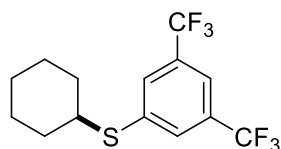
**(3-bromophenyl)(cyclohexyl)sulfane (3c)**: Followed the general procedure 1 with sodium 3-bromobenzenesulfinate (24.2 mg, 0.1 mmol), cyclohexane (54.0  $\mu$ l, 0.5 mmol) and acetyl chloride (15.7 mg, 0.2 mmol) purified using flash chromatography (petroleum ether:ethyl acetate=50:1) to give 13.0 mg of the title compound (Colorless oil); 48% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (s, 1H), 7.35-7.27 (m, 2H), 7.16-7.11 (m, 1H), 3.17-3.08 (m, 1H), 2.02-1.93 (m, 2H), 1.83-1.73 (m, 2H), 1.66-1.57 (m, 2H), 1.43-1.28 (m, 5H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  137.9, 133.8, 130.1, 129.9, 129.5, 122.6, 46.6, 33.3, 26.0, 25.8. **HRMS (ESI)** calcd  $\text{C}_{12}\text{H}_{16}^{79}\text{BrS}$  [ $\text{M} + \text{H}$ ] $^+$ : 270.0078, found: 270.0079.



**(2-chlorophenyl)(cyclohexyl)sulfane (3d)**: Followed the general procedure 1 with sodium 2-chlorobenzenesulfinate (19.9 mg, 0.1 mmol), cyclohexane (54.0  $\mu$ l, 0.5 mmol) and acetyl chloride (15.7 mg, 0.2 mmol) purified using flash chromatography (petroleum ether:ethyl acetate=50:1) to give 14.3 mg of the title compound (Colorless oil); 63% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41-7.35 (m, 2H), 7.22-7.17 (m, 1H), 7.15-7.10 (m, 1H), 3.28-3.20 (m, 1H), 2.04-1.96 (m, 2H), 1.84-1.76 (m, 2H), 1.67-1.59 (m, 1H), 1.50-1.30 (m, 5H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  131.4, 129.9, 127.2, 127.0, 45.3, 33.1, 26.1, 25.8. **HRMS (ESI)** calcd  $\text{C}_{12}\text{H}_{16}^{35}\text{ClS}$   $[\text{M} + \text{H}]^+$ : 226.0583, found: 226.0591.

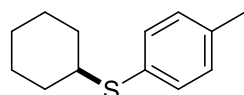


**cyclohexyl(4-(trifluoromethyl)phenyl)sulfane (3e)**: Followed the general procedure 1 with sodium 4-(trifluoromethyl)benzenesulfinate (23.2 mg, 0.1 mmol), cyclohexane (54.0  $\mu$ l, 0.5 mmol) and acetyl chloride (15.7 mg, 0.2 mmol) purified using flash chromatography (petroleum ether:ethyl acetate=50:1) to give 16.9 mg of the title compound (Colorless oil); 65% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53-7.49 (m, 2H), 7.43-7.39 (m, 2H), 3.28-3.21 (m, 1H), 2.05-1.98 (m, 2H), 1.82-1.76 (m, 2H), 1.68-1.60 (m, 1H), 1.48-1.29 (m, 5H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.2, 127.9 (q,  $J = 32.5$  Hz), 125.6 (q,  $J = 3.5$  Hz), 45.6, 33.2, 26.0, 25.7;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.41. **HRMS (ESI)** calcd  $\text{C}_{13}\text{H}_{16}\text{F}_3\text{S}$   $[\text{M} + \text{H}]^+$ : 260.0847, found: 260.0840.

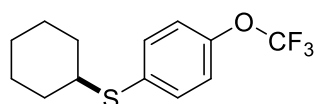


**(3,5-bis(trifluoromethyl)phenyl)(cyclohexyl)sulfane (3f)**: Followed the general procedure 1 with sodium 3,5-bis(trifluoromethyl)benzenesulfinate (30.0 mg, 0.1 mmol), cyclohexane (54.0  $\mu$ l, 0.5 mmol) and acetyl chloride (15.7 mg, 0.2 mmol) purified using flash chromatography (petroleum ether:ethyl acetate=50:1) to give 19.7 mg of the title compound (Colorless oil); 60% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (s, 2H),

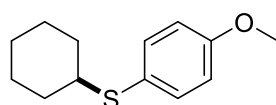
7.66 (s, 1H), 3.32-3.22 (m, 1H), 2.05-1.97 (m, 2H), 1.85-1.76 (m, 2H), 1.67-1.57 (m, 1H), 1.49-1.31 (m, 5H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.3 (d,  $J = 247.0$  Hz), 135.1 (d,  $J = 8.1$  Hz), 129.8 (d,  $J = 3.6$  Hz), 115.7 (d,  $J = 21.8$  Hz), 123.0, 124.5, 121.8, 119.8, 119.8, 119.7, 46.3, 33.0, 25.8, 25.6.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.02. HRMS (ESI) calcd  $\text{C}_{14}\text{H}_{15}\text{F}_6\text{S}$   $[\text{M} + \text{H}]^+$ : 328.0720, found: 328.0722.



**cyclohexyl(*p*-tolyl)sulfane (3g)**: Followed the general procedure 1 with sodium 4-methylbenzenesulfinate (17.8 mg, 0.1 mmol), cyclohexane (54.0  $\mu\text{l}$ , 0.5 mmol) and acetyl chloride (15.7 mg, 0.2 mmol) purified using flash chromatography (petroleum ether:ethyl acetate=50:1) to give 14.5 mg of the title compound (Colorless oil); 70% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33-7.29 (m, 2H), 7.12-7.08 (m, 2H), 3.05-2.97 (m, 1H), 2.33 (s, 3H), 1.99-1.92 (m, 2H), 1.79-1.72 (m, 2H), 1.37-1.25 (m, 5H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.9, 132.9, 131.3, 129.6, 47.2, 33.4, 26.2, 25.8, 21.1. HRMS (ESI) calcd  $\text{C}_{13}\text{H}_{19}\text{S}$   $[\text{M} + \text{H}]^+$ : 206.1129, found: 206.1131.

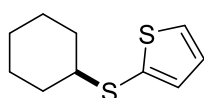


**cyclohexyl(4-(trifluoromethoxy)phenyl)sulfane (3h)**: Followed the general procedure 1 with sodium 4-(trifluoromethoxy)benzenesulfinate (24.8 mg, 0.1 mmol), cyclohexane (54.0  $\mu\text{l}$ , 0.5 mmol) and acetyl chloride (15.7 mg, 0.2 mmol) purified using flash chromatography (petroleum ether:ethyl acetate=50:1) to give 18.5 mg of the title compound (Colorless oil); 67% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43-7.38 (m, 2H), 7.16-7.10 (m, 2H), 3.12-3.04 (m, 1H), 2.03-1.91 (m, 2H), 1.83-1.73 (m, 2H), 1.66-1.55 (m, 2H), 1.42-1.27 (m, 5H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  148.1, 134.0, 133.2, 121.4, 47.0, 33.3, 26.1, 25.8.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -57.89. HRMS (ESI) calcd  $\text{C}_{13}\text{H}_{16}\text{F}_3\text{OS}$   $[\text{M} + \text{H}]^+$ : 276.0796, found: 276.0797.

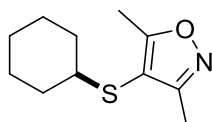


**cyclohexyl(4-methoxyphenyl)sulfane (3i)**: Followed the general procedure 1 with

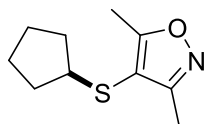
sodium 4-methoxybenzenesulfinate (19.4 mg, 0.1 mmol), cyclohexane (54.0  $\mu$ l, 0.5 mmol) and acetyl chloride (15.7 mg, 0.2 mmol) purified using flash chromatography (petroleum ether:ethyl acetate=50:1) to give 16.5 mg of the title compound (Colorless oil); 74% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41-7.36 (m, 2H), 6.86-6.81 (m, 2H), 3.81-3.78 (m, 3H), 2.93-2.85 (m, 1H), 1.97-1.89 (m, 2H), 1.78-1.71 (m, 2H), 1.68-1.54 (m, 2H), 1.36-1.22 (m, 5H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.4, 135.7, 125.0, 114.4, 55.4, 48.0, 33.4, 26.2, 25.8. **HRMS (ESI)** calcd  $\text{C}_{13}\text{H}_{19}\text{OS}$   $[\text{M} + \text{H}]^+$ : 222.1078, found: 222.1080.



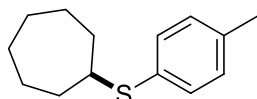
**2-(cyclohexylthio)thiophene (3j)**: Followed the general procedure 1 with sodium thiophene-2-sulfinate (17.0 mg, 0.1 mmol), cyclohexane (54.0  $\mu$ l, 0.5 mmol) and acetyl chloride (15.7 mg, 0.2 mmol) purified using flash chromatography (petroleum ether:ethyl acetate=50:1) to give 12.1 mg of the title compound (Colorless oil); 61% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37-7.34 (m, 1H), 7.12-7.10 (m, 1H), 7.01-6.97 (m, 1H), 2.89-2.82 (m, 1H), 2.01-1.93 (m, 2H), 1.81-1.73 (m, 2H), 1.63-1.55 (m, 2H), 1.39-1.27 (m, 5H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  135.0, 132.9, 129.8, 127.5, 49.9, 33.2, 26.1, 25.7. **HRMS (ESI)** calcd  $\text{C}_{10}\text{H}_{15}\text{S}_2$   $[\text{M} + \text{H}]^+$ : 198.0537, found: 198.0535.



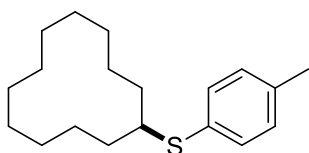
**3-(cyclohexylthio)-3,5-dimethylisoxazole (3k)**: Followed the general procedure 1 with sodium 3,5-dimethylisoxazole-4-sulfinate (18.3 mg, 0.1 mmol), cyclohexane (54.0  $\mu$ l, 0.5 mmol) and acetyl chloride (15.7 mg, 0.2 mmol) purified using flash chromatography (petroleum ether:ethyl acetate=50:1) to give 12.2 mg of the title compound (Colorless oil); 58% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.70-2.61 (m, 1H), 2.44 (s, 3H), 2.28 (s, 3H), 1.85 (s, 2H), 1.76 (s, 2H), 1.64-1.57 (m, 1H), 1.33-1.20 (m, 5H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.0, 162.9, 105.4, 47.6, 33.5, 26.1, 25.7, 11.8, 10.6. **HRMS (ESI)** calcd  $\text{C}_{11}\text{H}_{18}\text{NOS}$   $[\text{M} + \text{H}]^+$ : 211.1031, found: 211.1032.



**4-(cyclopentylthio)-3,5-dimethylisoxazole (3l):** Followed the general procedure 1 with sodium 3,5-dimethylisoxazole-4-sulfinate (18.3 mg, 0.1 mmol), cyclopentane (47.0  $\mu$ l, 0.5 mmol) and acetyl chloride (15.7 mg, 0.2 mmol) purified using flash chromatography (petroleum ether:ethyl acetate=50:1) to give 10.3 mg of the title compound (Colorless oil); 52% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 (d,  $J=8.1$  Hz, 2H), 7.09 (d,  $J=7.9$  Hz, 2H), 3.57 – 3.49 (m, 1H), 2.32 (s, 3H), 2.06 – 1.95 (m, 2H), 1.82 – 1.70 (m, 2H), 1.63 – 1.57 (m, 4H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.2, 133.3, 131.0, 129.6, 46.7, 33.6, 24.8, 21.1. **HRMS (ESI)** calcd  $\text{C}_{10}\text{H}_{16}\text{NOS}$   $[\text{M} + \text{H}]^+$ : 197.0874, found: 197.0880.

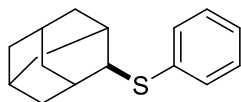


**cycloheptyl(p-tolyl)sulfane (3m):** Followed the general procedure 1 with sodium 4-methylbenzenesulfinate (17.8 mg, 0.1 mmol), cycloheptane (60.0  $\mu$ l, 0.5 mmol) and acetyl chloride (15.7 mg, 0.2 mmol) purified using flash chromatography (petroleum ether:ethyl acetate=50:1) to give 15.0 mg of the title compound (Colorless oil); 68% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32-7.26 (m, 2H), 7.12-7.06 (m, 2H), 3.30-3.20 (m, 1H), 2.32 (s, 3H), 2.04-1.93 (m, 2H), 1.70 (s, 2H), 1.59-1.50 (m, 6H), 1.47-1.39 (m, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.6, 132.3, 132.1, 129.6, 48.6, 34.7, 28.3, 26.0, 21.1. **HRMS (ESI)** calcd  $\text{C}_{14}\text{H}_{21}\text{S}$   $[\text{M} + \text{H}]^+$ : 220.1286, found: 220.1291.

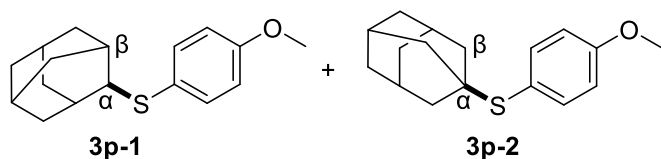


**cyclododecyl(p-tolyl)sulfane (3n):** Followed the general procedure 1 with sodium 4-methylbenzenesulfinate (17.8 mg, 0.1 mmol), cyclododecane (84.0 mg, 0.5 mmol) and acetyl chloride (15.7 mg, 0.2 mmol) purified using flash chromatography (petroleum ether:ethyl acetate=50:1) to give 15.1 mg of the title compound (Colorless oil); 52% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 (d,  $J=7.8$  Hz, 2H), 7.09 (d,  $J=7.7$  Hz, 2H),

3.18 (s, 1H), 2.32 (s, 3H), 1.72 – 1.62 (m, 2H), 1.60 – 1.50 (m, 4H), 1.33 (s, 17H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.6, 132.2, 132.0, 129.6, 45.3, 29.9, 24.2, 23.9, 23.4, 23.4, 22.2, 21.2. HRMS (ESI) calcd C<sub>19</sub>H<sub>31</sub>S [M + H]<sup>+</sup>: 290.2068, found: 290.2065.

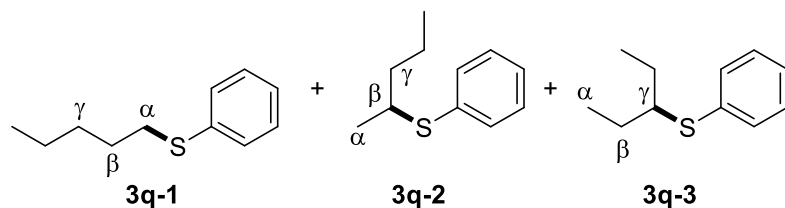


**adamantan-1-yl(phenyl)sulfane (3o)**: Followed the general procedure 1 with sodium benzenesulfinate (16.4 mg, 0.1 mmol), adamantane (68.1 mg, 0.5 mmol) and acetyl chloride (15.7 mg, 0.2 mmol) purified using flash chromatography (petroleum ether:ethyl acetate=50:1) to give 12.0 mg of the title compound (Colorless oil); 49% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.40-7.35 (m, 2H), 7.29-7.27 (m, 1H), 7.21-7.15 (m, 1H), 3.58-3.55 (m, 1H), 2.28-2.20 (m, 2H), 2.07-2.01 (m, 2H), 1.95-1.85 (m, 4H), 1.78-1.71 (m, 3H), 1.60-1.54 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.7, 130.8, 128.8, 126.1, 55.5, 38.7, 37.7, 32.9, 32.0, 27.7, 27.4. HRMS (ESI) calcd C<sub>16</sub>H<sub>21</sub>S [M + H]<sup>+</sup>: 244.1286, found: 244.1286.

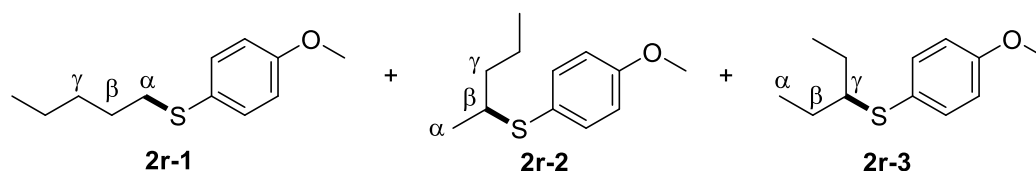


**adamantan-2-yl(4-methoxyphenyl)sulfane (3p-1), adamantan-1-yl(4-methoxyphenyl)sulfane (3p-2)**: Followed the general procedure 1 with sodium 4-methoxybenzenesulfinate (19.4 mg, 0.1 mmol), adamantane (68.4 mg, 0.5 mmol) and acetyl chloride (15.7 mg, 0.2 mmol) purified using flash chromatography (petroleum ether:ethyl acetate=50:1) to give 12.9 mg of the title compound (Colorless oil); 47% yield (α:β=63:37); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.43 – 7.35 (m, 2H), 6.87 – 6.80 (m, 2H), 3.81 (s, 1.10H, **3p-2**), 3.79 (s, 1.91H, **3p-1**), 3.39 – 3.34 (m, 0.62H, **3p-1**), 2.26 (d, J=10.4 Hz, 1.28H, **3p-1**), 1.99 (d, J=11.6 Hz, 2.50H), 1.88 (d, J=12.6 Hz, 2.67H), 1.76 (d, J=19.2 Hz, 5H), 1.67 – 1.51 (m, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 160.2, 159.1, 139.1, 134.6, 127.3, 126.7, 121.4, 114.8, 114.5, 113.9, 57.5, 55.4, 55.3, 47.5, 43.5, 38.8, 37.8, 36.3, 32.7, 31.8, 30.0, 29.8, 27.8, 27.5. HRMS (ESI) calcd C<sub>17</sub>H<sub>23</sub>OS [M + H]<sup>+</sup>: 274.1391, found: 274.1400.



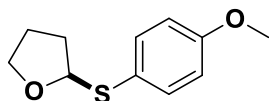


**pentyl(phenyl)sulfane (3q-1), (S)-pentan-2-yl(phenyl)sulfane (3q-2), pentan-3-yl(phenyl)sulfane (3q-3):** Followed the general procedure 1 with sodium benzenesulfinate (16.4 mg, 0.1 mmol), pentane (58.0  $\mu$ l, 0.5 mmol) and acetyl chloride (15.7 mg, 0.2 mmol) purified using flash chromatography (petroleum ether:ethyl acetate=50:1) to give 11.8 mg of the title compound (Colorless oil); 56% yield ( $\alpha$ : $\beta$ : $\gamma$ =19:55:26);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 (d,  $J$ =7.0 Hz, 1.62H), 7.34 – 7.26 (m, 2.36H), 7.24 – 7.14 (m, 1.05H), 3.27 – 3.18 (m, 0.57H, **3q-1**), 3.05 – 2.96 (m, 0.31H, **3q-2**), 2.95 – 2.87 (m, 0.48H, **3q-3**), 1.70 – 1.50 (m, 3.99H), 1.50 – 1.44 (m, 1.34H), 1.27 (d,  $J$ =6.8 Hz, 2.01H), 1.03 – 0.99 (m, 1.40H), 0.93 – 0.89 (m, 2.27H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  131.9, 131.8, 128.9, 128.8, 126.6, 126.5, 125.7, 52.3, 43.1, 38.9, 33.6, 31.1, 29.8, 28.9, 26.7, 22.3, 21.2, 20.3, 14.0, 14.0, 11.3. **HRMS (ESI)** calcd  $\text{C}_{11}\text{H}_{17}\text{S}$   $[\text{M} + \text{H}]^+$ : 180.0973, found: 180.0975.

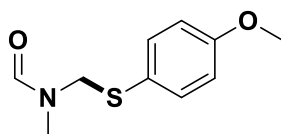


**(3-methoxyphenyl)(pentyl)sulfane (2r-1), (4-methoxyphenyl)(pentan-2-yl)sulfane (2r-2), (4-methoxyphenyl)(pentan-3-yl)sulfane (2r-3):** Followed the general procedure 1 with sodium 4-methoxybenzenesulfinate (19.4 mg, 0.1 mmol), pentane (58.0  $\mu$ l, 0.5 mmol) and acetyl chloride (15.7 mg, 0.2 mmol) purified using flash chromatography (petroleum ether:ethyl acetate=50:1) to give 11.6 mg of the title compound (Colorless oil); 55% yield ( $\alpha$ : $\beta$ : $\gamma$ =29:44:27);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40-7.32 (m, 1.95H), 6.86-6.80 (m, 2H), 3.80 (s, 3H), 3.07-2.97 (m, 0.60H), 2.84-2.73 (m, 0.71H), 1.63-1.25 (m, 5.10H), 1.23-1.18 (m,

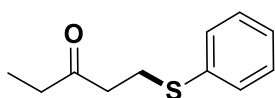
1.90H, **2o-1**), 1.03-0.97 (m, 1.16H, **2o-2**), 0.92-0.84 (m, 2.45H, **2o-3**). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.4, 135.7, 135.6, 133.0, 125.3, 55.4, 53.8, 44.4, 38.8, 35.9, 31.0, 29.1, 26.6, 22.3, 21.2, 20.3, 14.1, 14.0, 11.3. HRMS (ESI) calcd C<sub>12</sub>H<sub>19</sub>OS [M + H]<sup>+</sup>: 210.1078, found: 210.1077.



**adamantan-1-yl(phenyl)sulfane (3s)**: Followed the general procedure 1 with sodium 4-methoxybenzenesulfinate (19.4 mg, 0.1 mmol), THF (40.6 μl, 0.5 mmol) and acetyl chloride (15.7 mg, 0.2 mmol) purified using flash chromatography (petroleum ether:ethyl acetate=50:1) to give 14.1 mg of the title compound (Colorless oil); 67% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.46 (d, J=8.7 Hz, 2H), 6.85 (d, J=8.7 Hz, 2H), 5.49 – 5.45 (m, 1H), 4.05 – 3.98 (m, 1H), 3.96 – 3.90 (m, 1H), 3.79 (s, 3H), 2.36 – 2.27 (m, 1H), 2.05 – 1.80 (m, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.5, 134.7, 125.6, 114.5, 88.3, 67.2, 55.4, 32.5, 24.9. HRMS (ESI) calcd C<sub>11</sub>H<sub>15</sub>O<sub>2</sub>S [M + H]<sup>+</sup>: 210.0715, found: 210.0713.

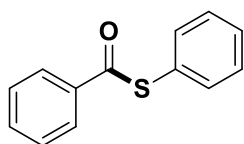


**N-(((4-methoxyphenyl)thio)methyl)-N-methylformamide (3t)**: Followed the general procedure 1 with sodium 4-methoxybenzenesulfinate (19.4 mg, 0.1 mmol), DMA (64.0 μl, 0.5 mmol) and acetyl chloride (15.7 mg, 0.2 mmol) purified using flash chromatography (petroleum ether:ethyl acetate=50:1) to give 15.4 mg of the title compound (Colorless oil); 73% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.44 – 7.36 (m, 1H), 7.31 (d, J=7.1 Hz, 2H), 6.85 – 6.79 (m, 2H), 4.42 (s, 2H), 3.76 (d, J=2.9 Hz, 3H), 2.94 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 162.4, 161.9, 160.6, 136.9, 134.9, 122.0, 115.1, 114.8, 57.8, 55.4, 49.9, 33.6, 29.0. HRMS (ESI) calcd C<sub>10</sub>H<sub>14</sub>NO<sub>2</sub>S [M + H]<sup>+</sup>: 211.0667, found: 211.0659.

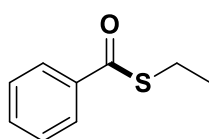


**1-(phenylthio)pentan-3-one (3u)**: Followed the general procedure 1 with sodium

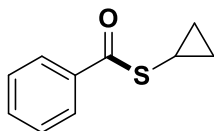
benzenesulfinate (16.40 mg, 0.1 mmol), 3-pentanone (52.0  $\mu$ l, 0.5 mmol) and acetyl chloride (15.7 mg, 0.2 mmol) purified using flash chromatography (petroleum ether:ethyl acetate=50:1) to give 10.1 mg of the title compound (Colorless oil); 52% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 – 7.27 (m, 4H), 7.22 – 7.17 (m, 1H), 3.18 – 3.13 (m, 2H), 2.76 – 2.71 (m, 2H), 2.45 – 2.38 (m, 2H), 1.08 – 1.02 (m, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  209.5, 135.8, 129.5, 129.1, 126.3, 41.8, 36.3, 27.6, 7.7. **HRMS (ESI)** calcd  $\text{C}_{11}\text{H}_{15}\text{OS}$  [ $\text{M} + \text{H}$ ] $^+$ : 194.0765, found: 194.0770.



**phenyl benzothioate (3v)**: Followed the general procedure 1 with sodium benzenesulfinate (16.4 mg, 0.1 mmol), benzaldehyde (50.8  $\mu$ l, 0.5 mmol) and acetyl chloride (15.7 mg, 0.2 mmol) purified using flash chromatography (petroleum ether:ethyl acetate=50:1) to give 9.0 mg of the title compound (Colorless oil); 42% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 (d,  $J=8.1$  Hz, 2H), 7.66 – 7.60 (m, 1H), 7.57 – 7.42 (m, 7H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  190.3, 136.7, 135.2, 133.8, 129.6, 129.3, 128.8, 127.6, 127.4. **HRMS (ESI)** calcd  $\text{C}_{13}\text{H}_{11}\text{OS}$  [ $\text{M} + \text{H}$ ] $^+$ : 214.0452, found: 214.0447.



**ethyl benzothioate (3w)**: Followed the general procedure 1 with ethanesulfinate (11.6 mg, 0.1 mmol), benzaldehyde (51.0  $\mu$ l, 0.5 mmol) and acetyl chloride (15.7 mg, 0.2 mmol) purified using flash chromatography (petroleum ether:ethyl acetate=50:1) to give 6.2 mg of the title compound (Colorless oil); 37% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (d,  $J=7.8$  Hz, 2H), 7.60 – 7.54 (m, 1H), 7.48 – 7.42 (m, 2H), 3.12 – 3.04 (m, 2H), 1.43 – 1.32 (m, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  192.2, 137.3, 133.3, 128.6, 127.2, 23.5, 14.8. **HRMS (ESI)** calcd  $\text{C}_9\text{H}_{11}\text{OS}$  [ $\text{M} + \text{H}$ ] $^+$ : 166.0452, found: 166.0455.

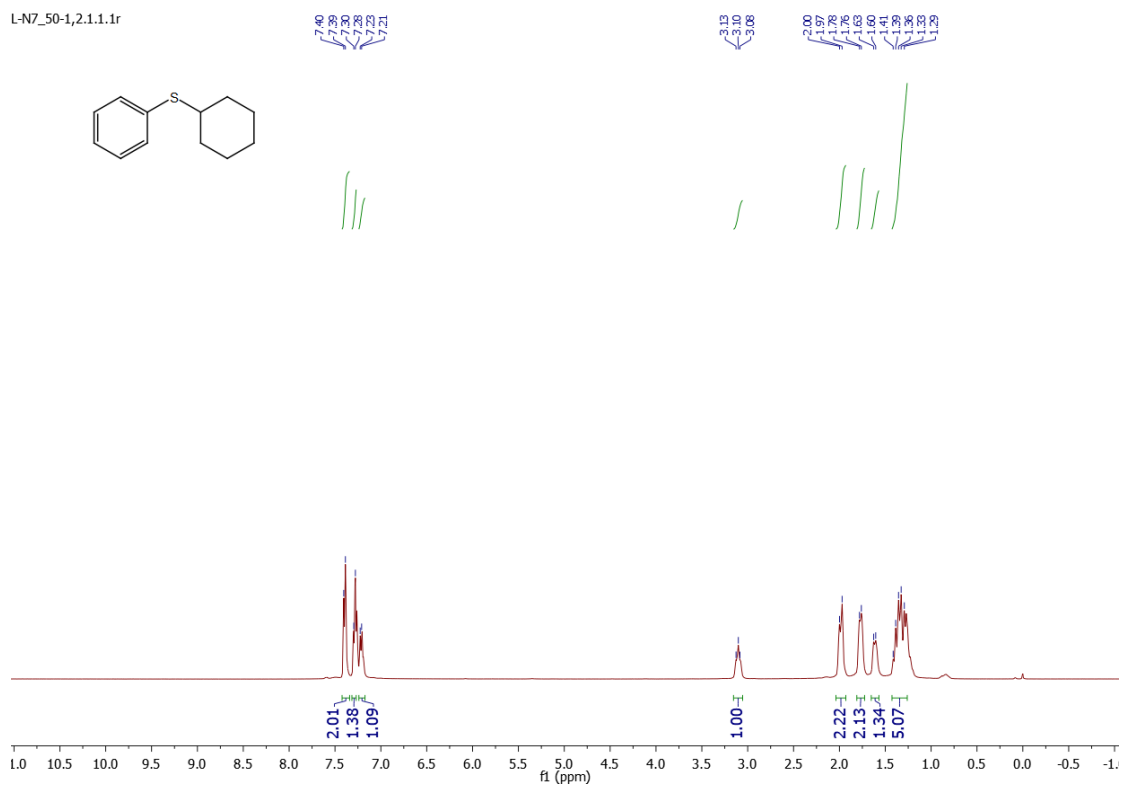


**cyclopropyl benzothioate (3x):** Followed the general procedure 1 with cyclopropanesulfinic acid (13.0 mg, 0.1 mmol), benzaldehyde (50.8  $\mu$ l, 0.5 mmol) and acetyl chloride (15.7 mg, 0.2 mmol) purified using flash chromatography (petroleum ether:ethyl acetate=50:1) to give 8.0 mg of the title compound (Colorless oil); 45% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 – 7.89 (m, 2H), 7.59 – 7.53 (m, 1H), 7.47 – 7.41 (m, 2H), 2.32 – 2.25 (m, 1H), 1.18 – 1.12 (m, 2H), 0.70 – 0.65 (m, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  193.9, 137.1, 133.3, 128.7, 127.1, 10.2, 7.4. **HRMS (ESI)** calcd  $\text{C}_{10}\text{H}_{11}\text{OS}$   $[\text{M} + \text{H}]^+$ : 178.0452, found: 178.0446.

## 7. NMR Spectra for the substrates and products

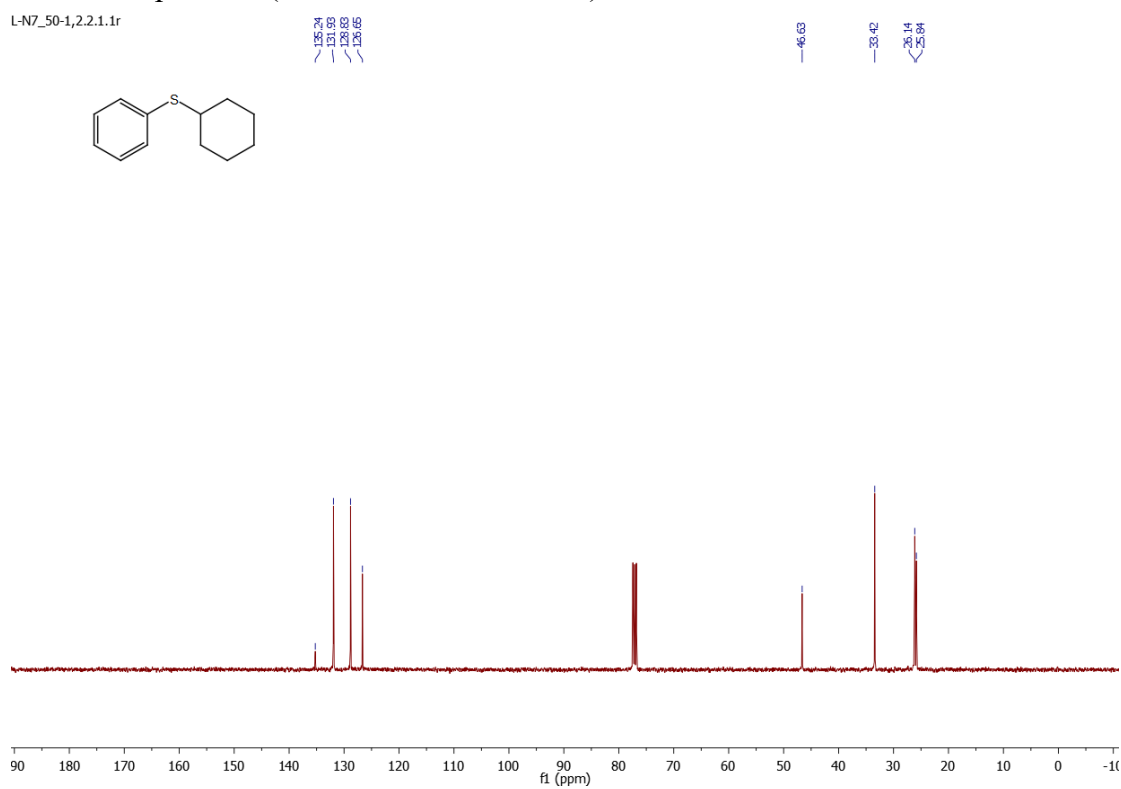
$^1\text{H NMR}$  spectrum (400 MHz,  $\text{CDCl}_3$ , 23  $^\circ\text{C}$ ) of **3a**

L-N7\_50-1,2.1.1.1r



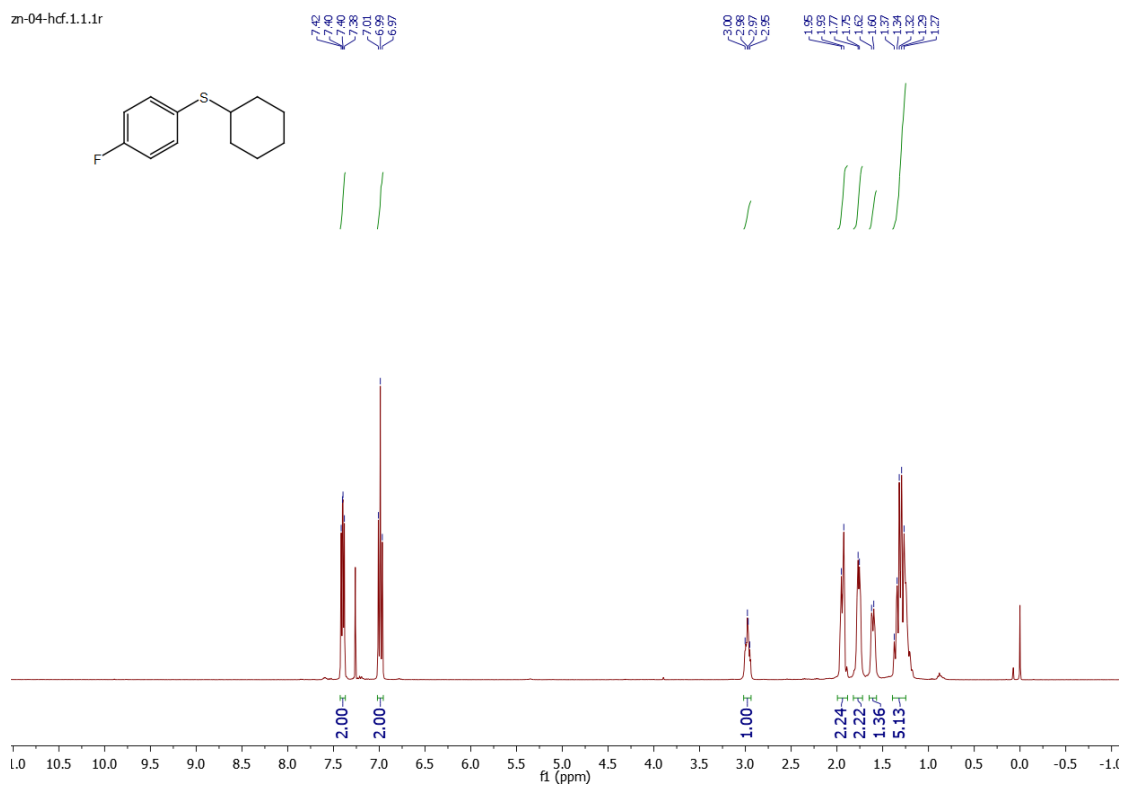
<sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>, 23 °C) of **3a**

L-N7\_50-1,2.2.1.1r



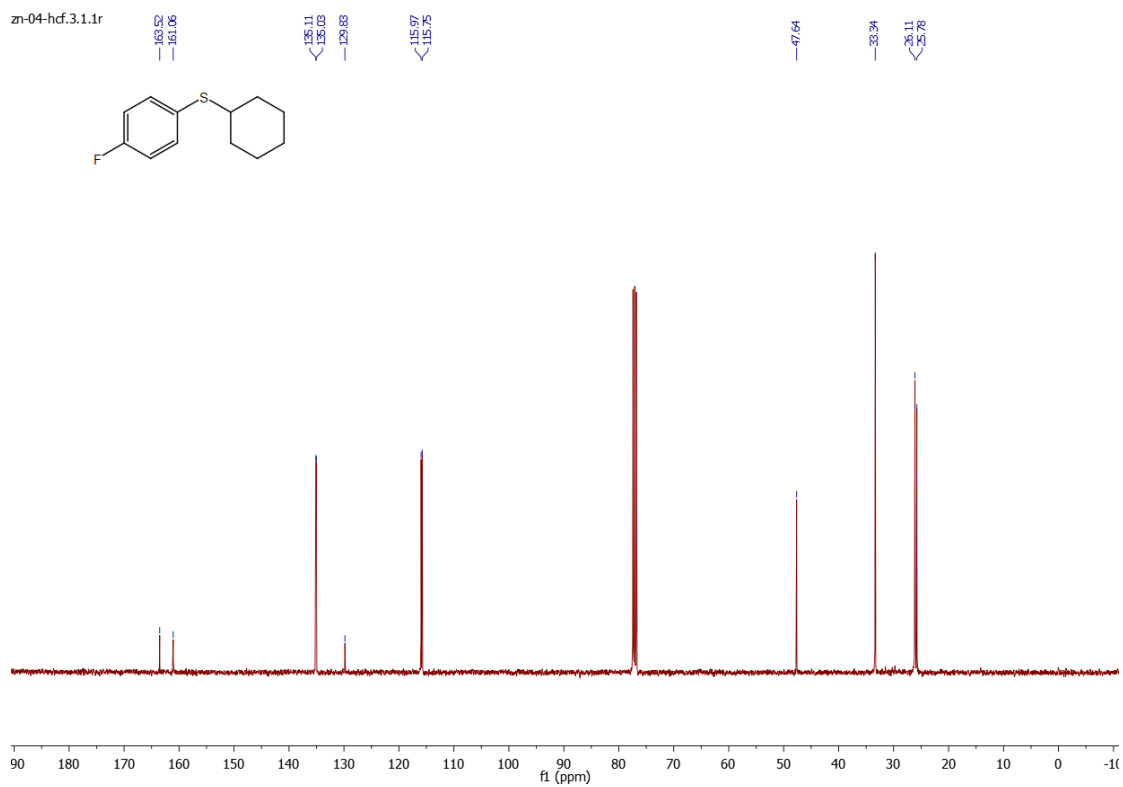
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 23 °C) of **3b**

zn-04-hcf.1.1.1r



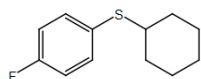
<sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>, 23 °C) of **3b**

zn-04-hcf.3.1.1r

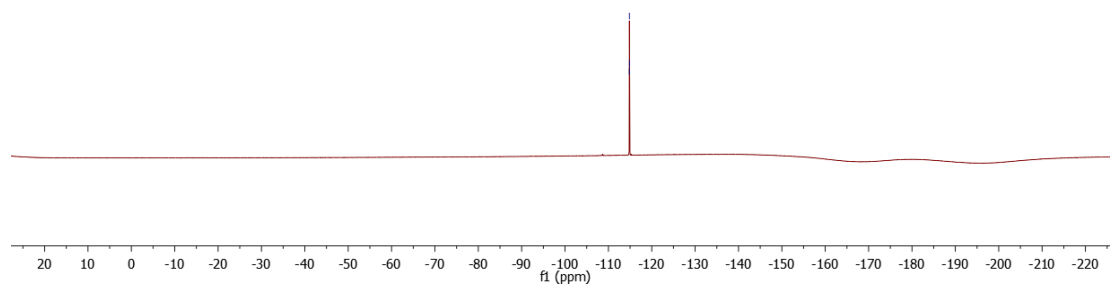


<sup>19</sup>F NMR spectrum (376 MHz, CDCl<sub>3</sub>, 23 °C) of **3b**

zn-04-hcf.2.1.1r

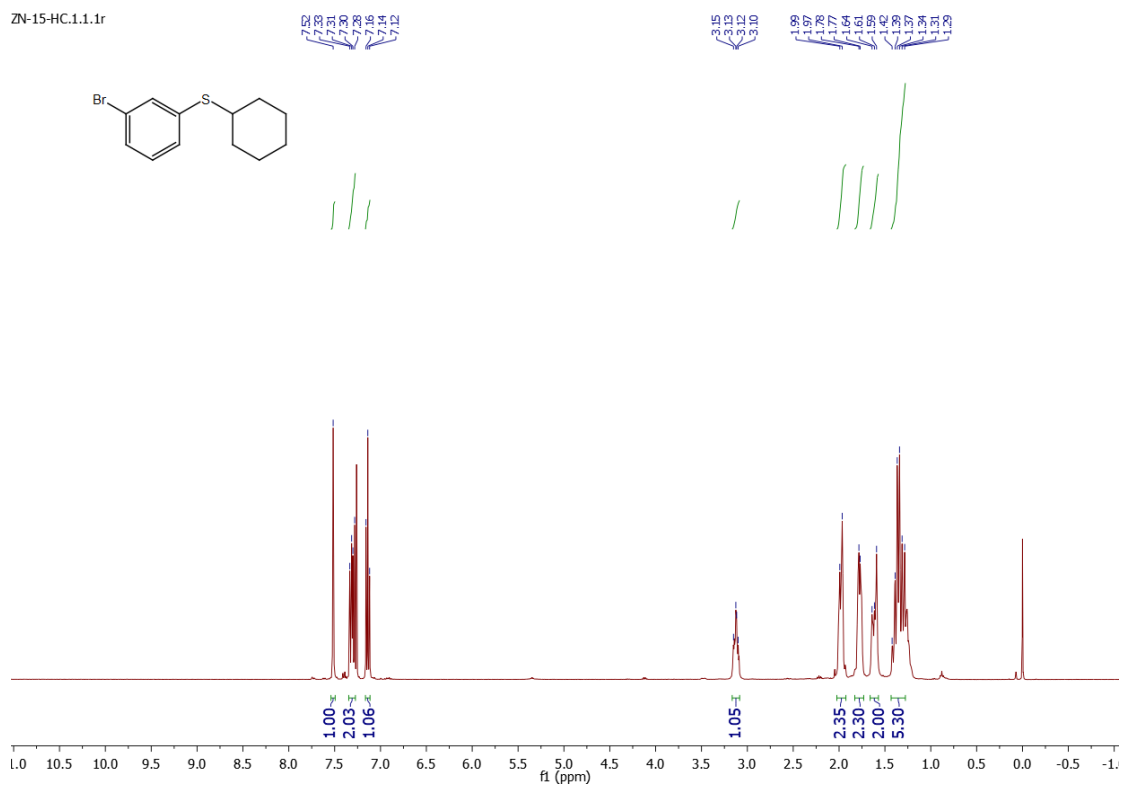


111.82  
111.81  
111.80



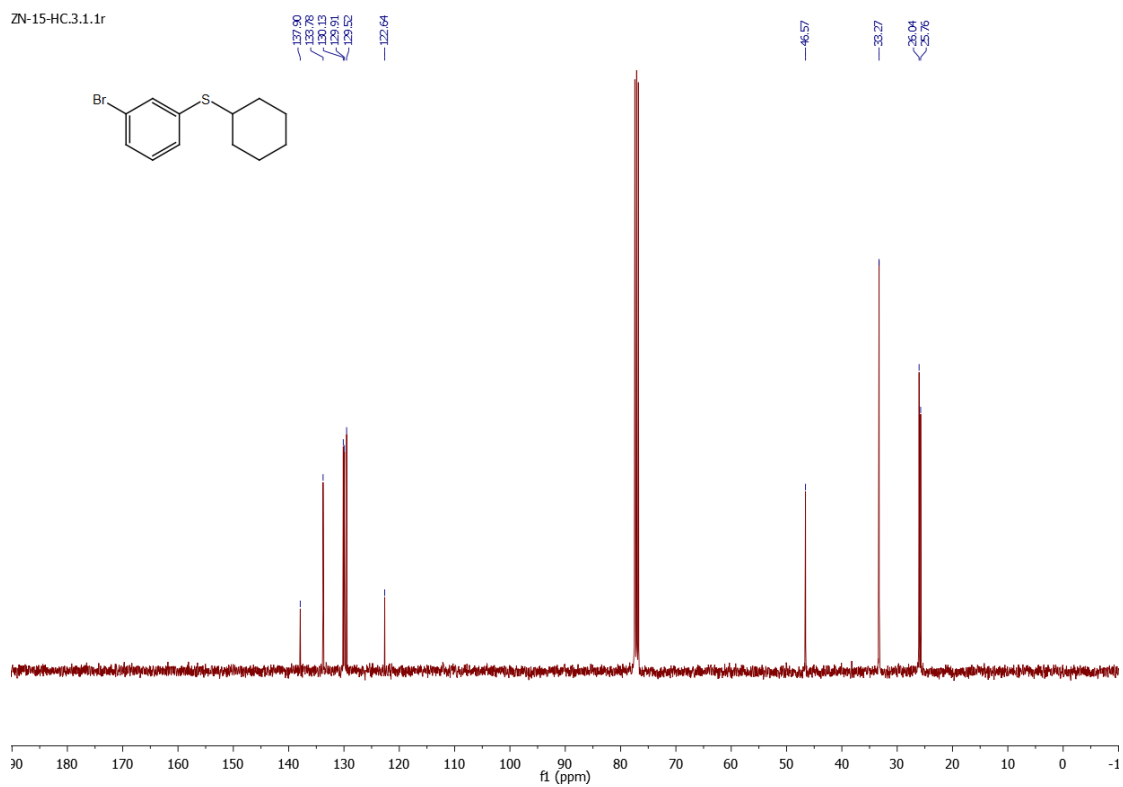
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 23 °C) of **3c**

ZN-15-HC.1.1.1r



$^{13}\text{C}$  NMR spectrum (100 MHz,  $\text{CDCl}_3$ , 23 °C) of **3c**

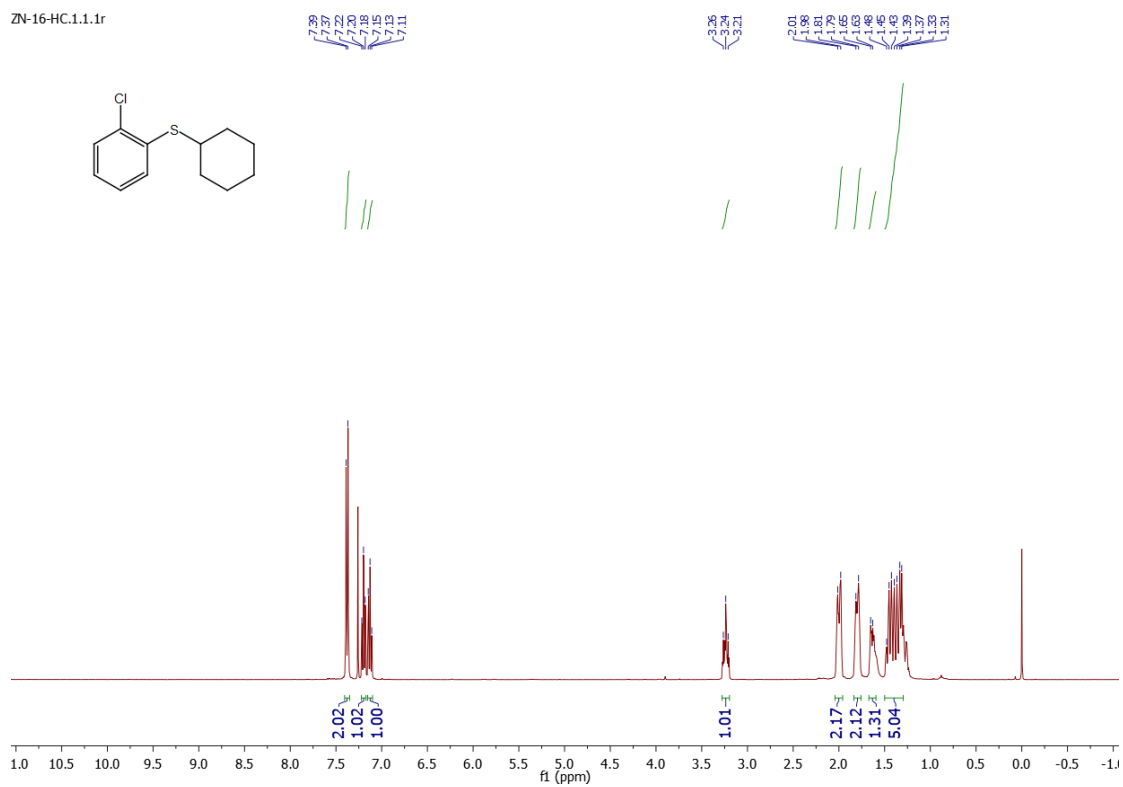
ZN-15-HC.3.1.1r



$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , 23 °C) of **3d**

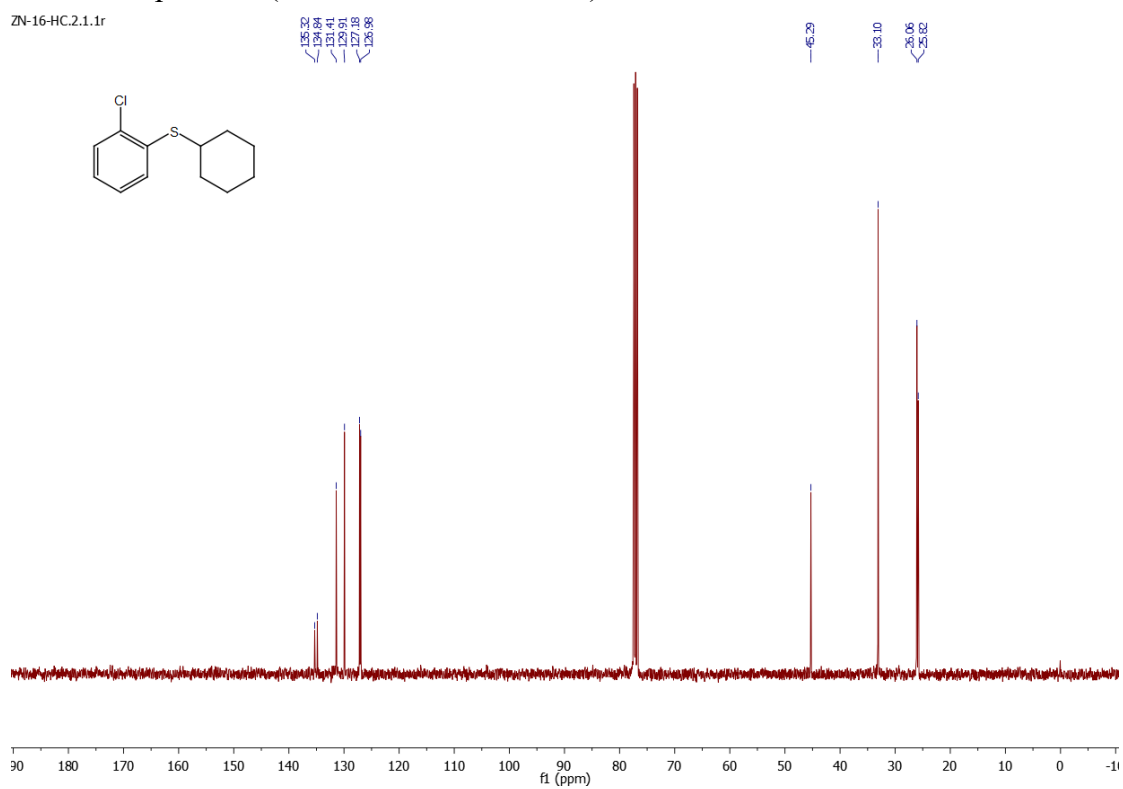


ZN-16-HC.1.1.1r



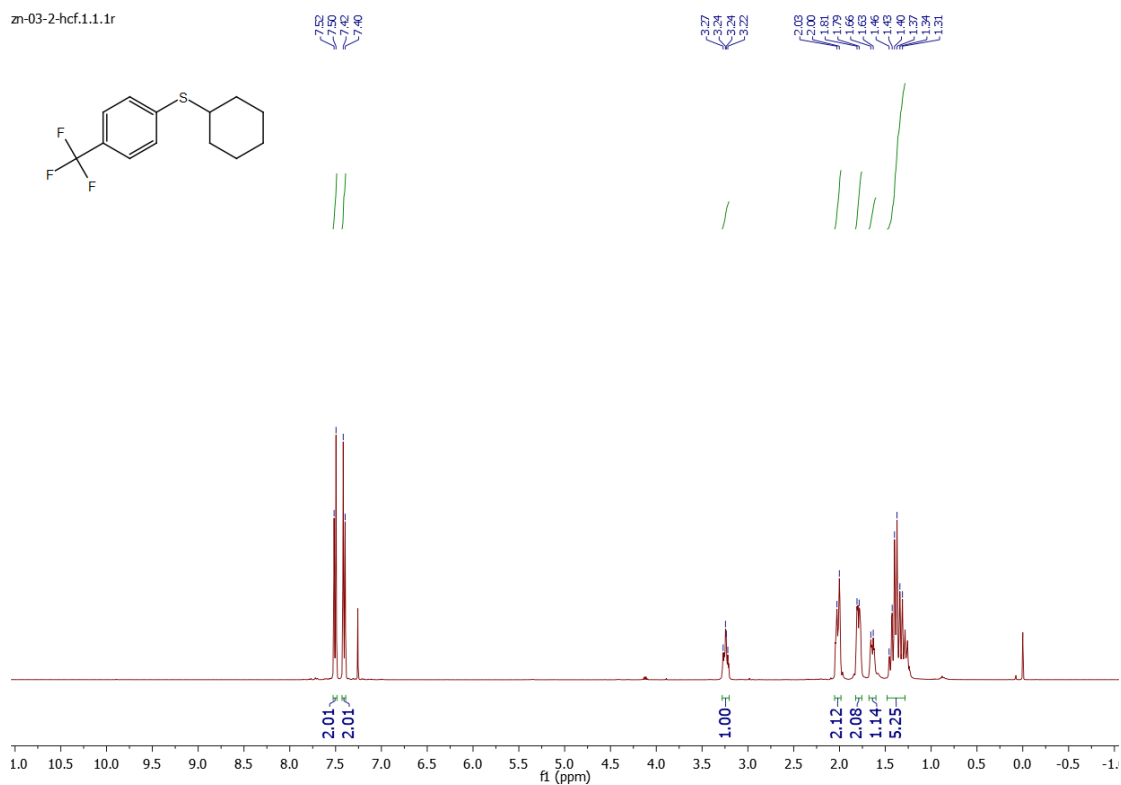
<sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>, 23 °C) of **3d**

ZN-16-HC.2.1.1r



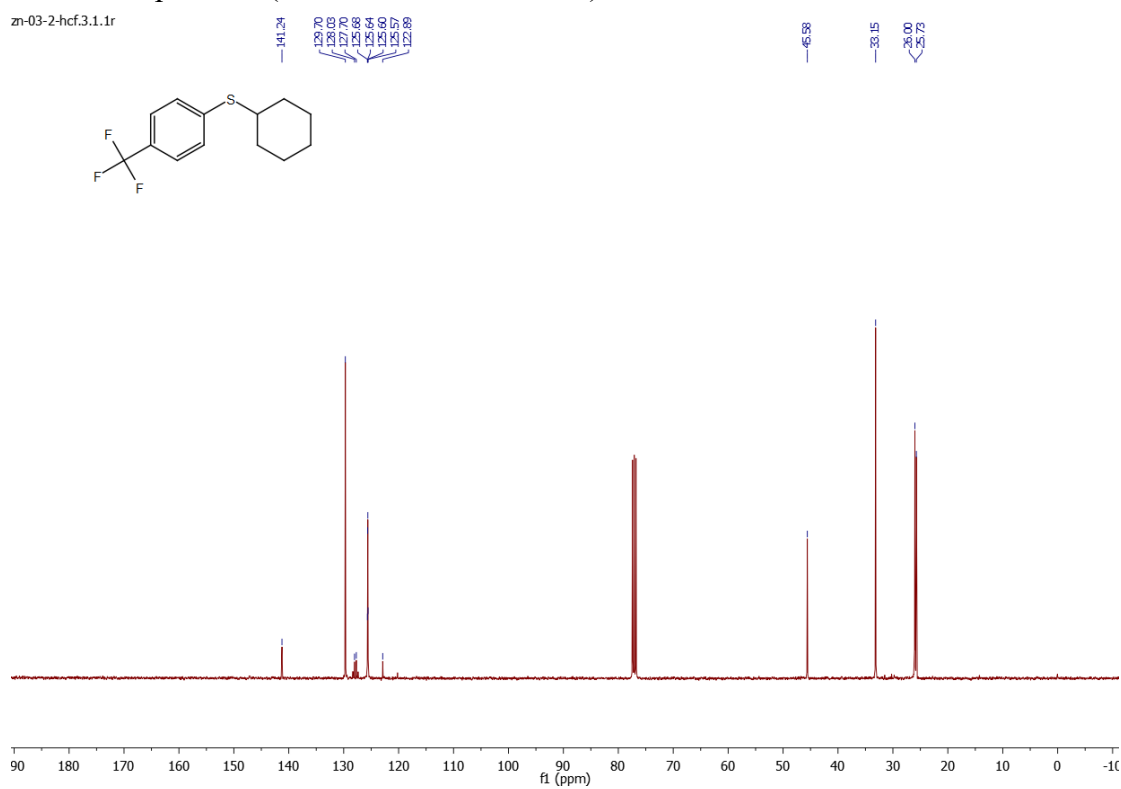
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 23 °C) of **3e**

zn-03-2-hcf.1.1.1r



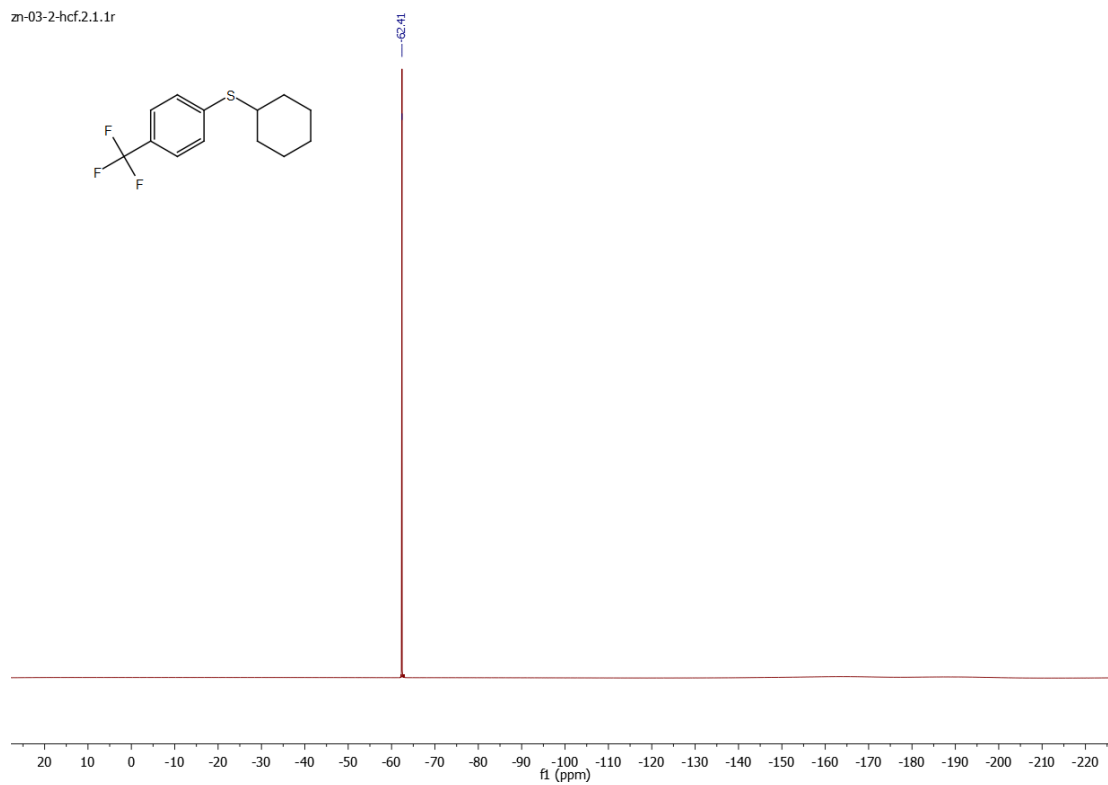
<sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>, 23 °C) of **3e**

zn-03-2-hcf.3.1.1r



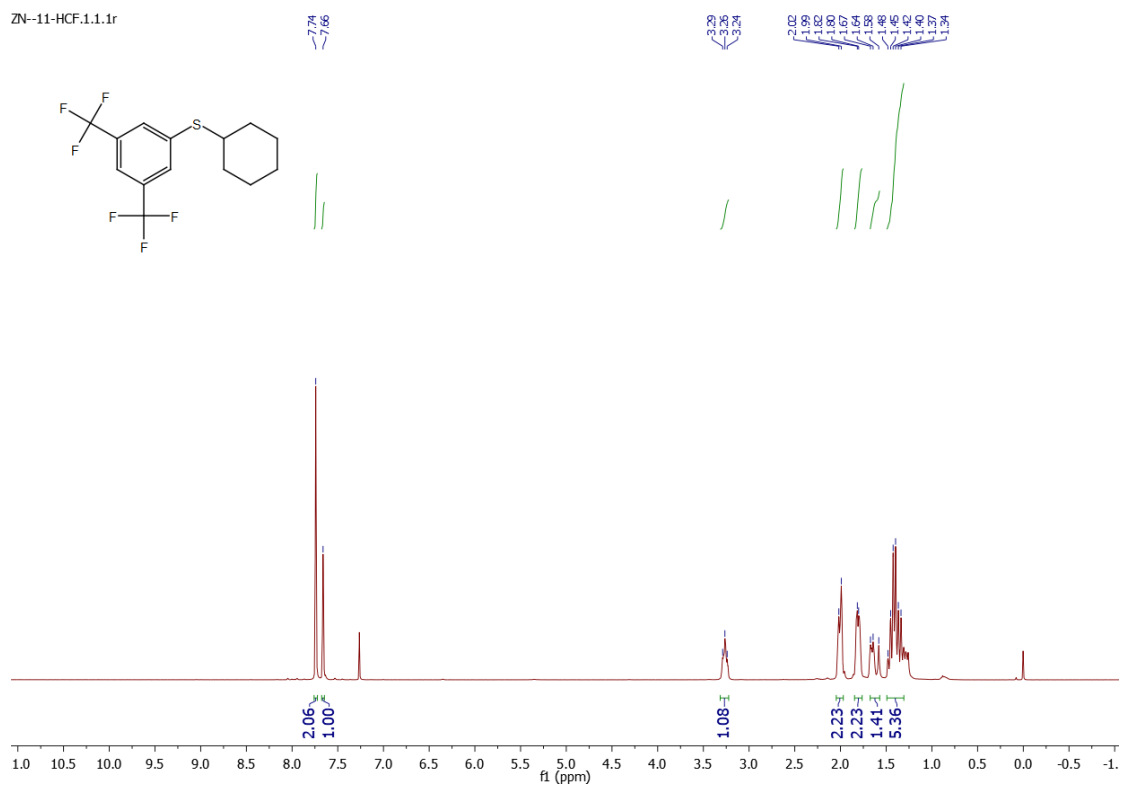
<sup>19</sup>F NMR spectrum (376 MHz, CDCl<sub>3</sub>, 23 °C) of **3e**

zn-03-2-hcf.2.1.1r



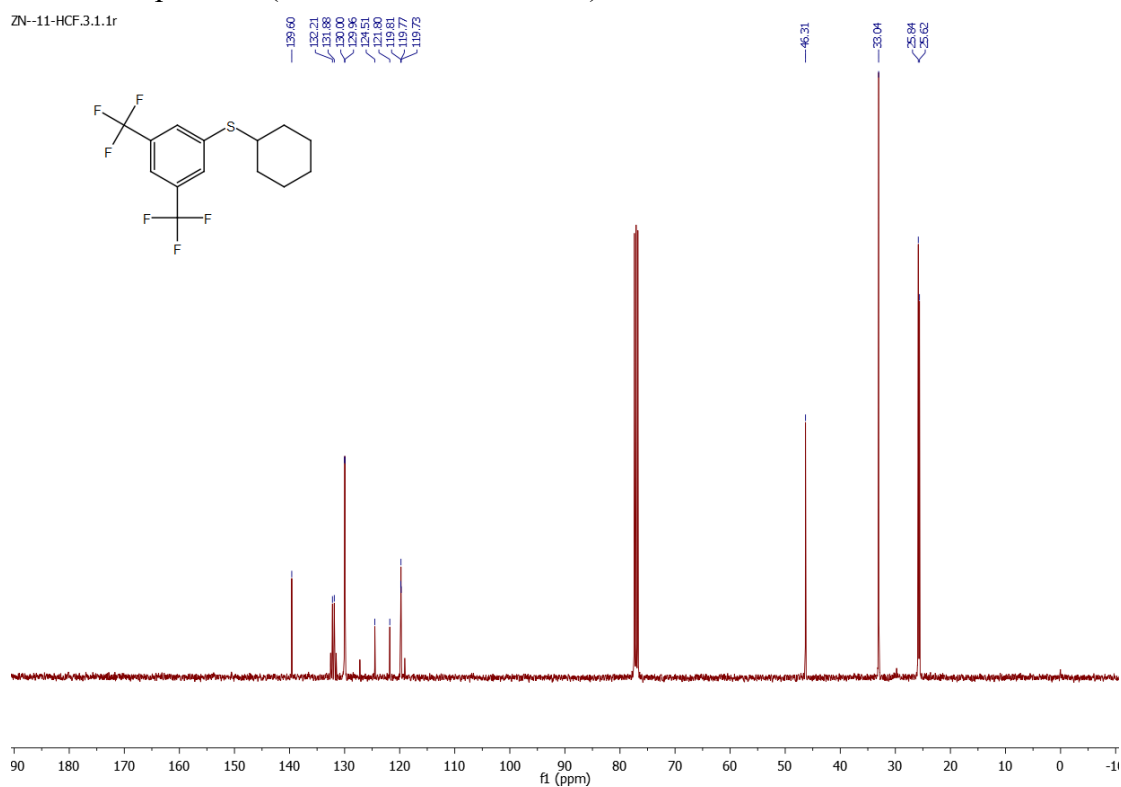
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , 23 °C) of **3f**

ZN-11-HCF.1.1.1r



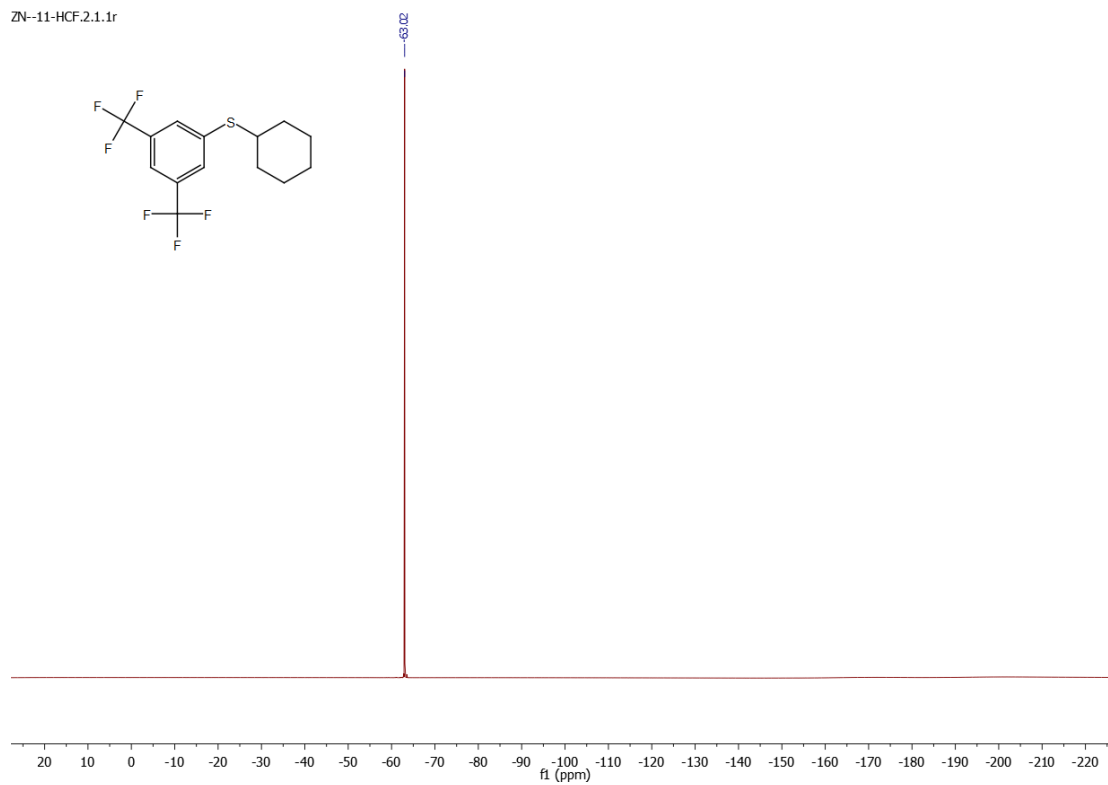
<sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>, 23 °C) of **3f**

ZN-11-HCF.3.1.1r



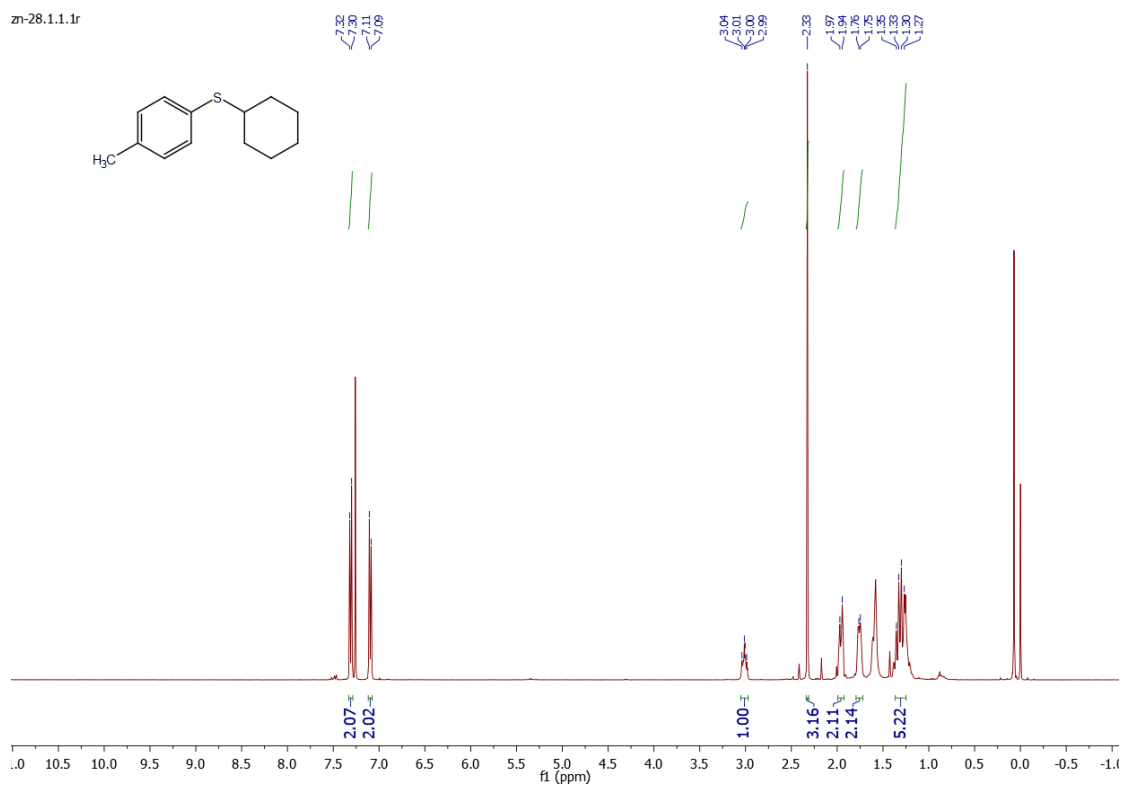
<sup>19</sup>F NMR spectrum (376 MHz, CDCl<sub>3</sub>, 23 °C) of **3f**

ZN-11-HCF.2.1.1r



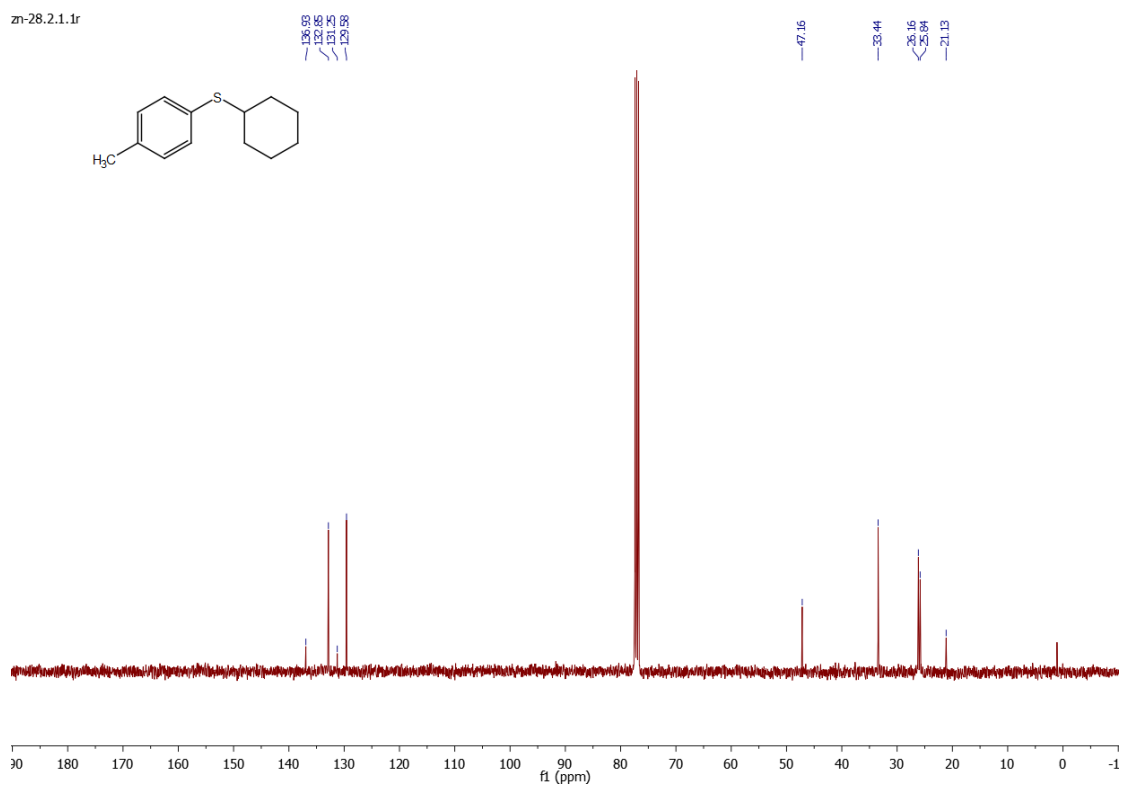
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 23 °C) of **3g**

zn-28.1.1.1r



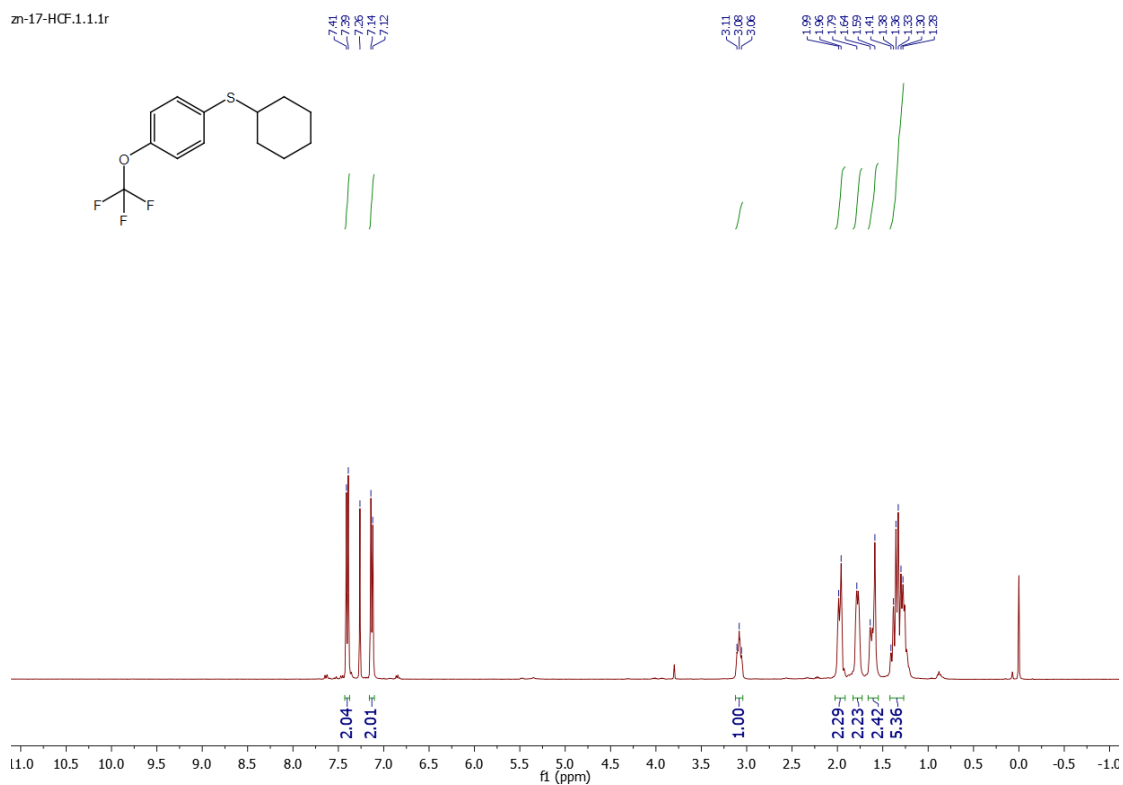
<sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>, 23 °C) of **3g**

zn-28.2.1.1r



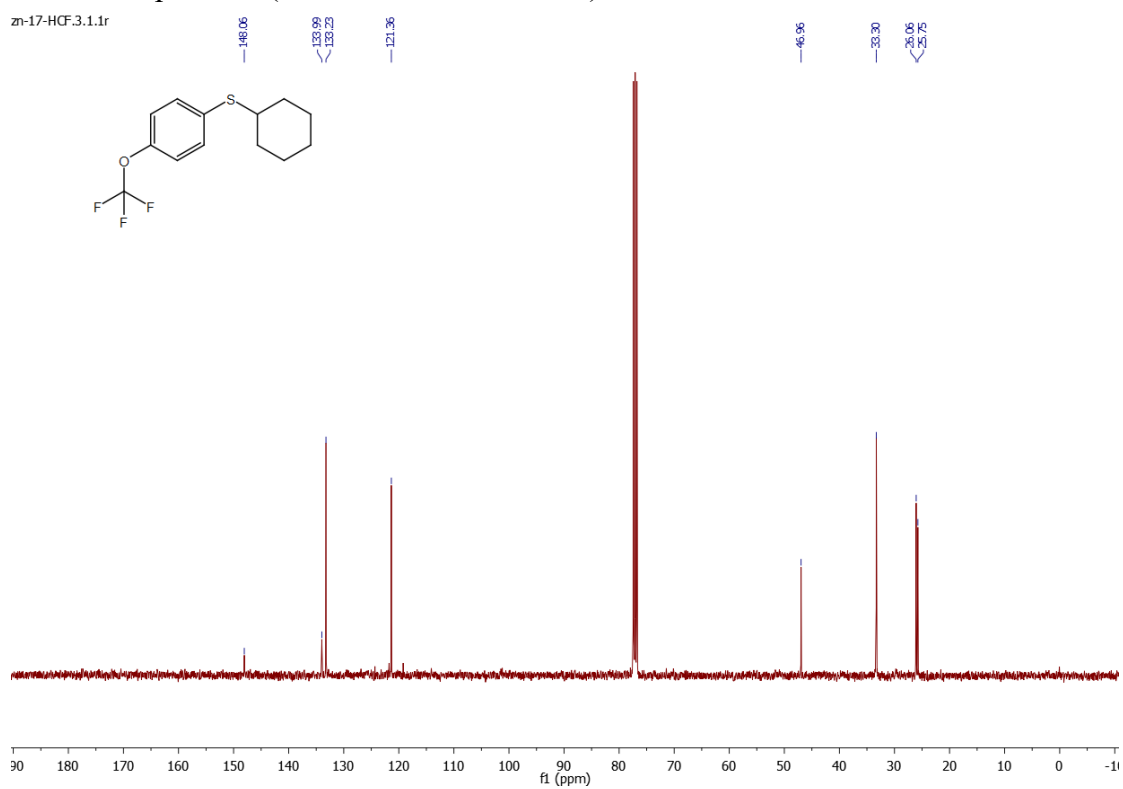
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 23 °C) of **3h**

zn-17-HCF.1.1.1r



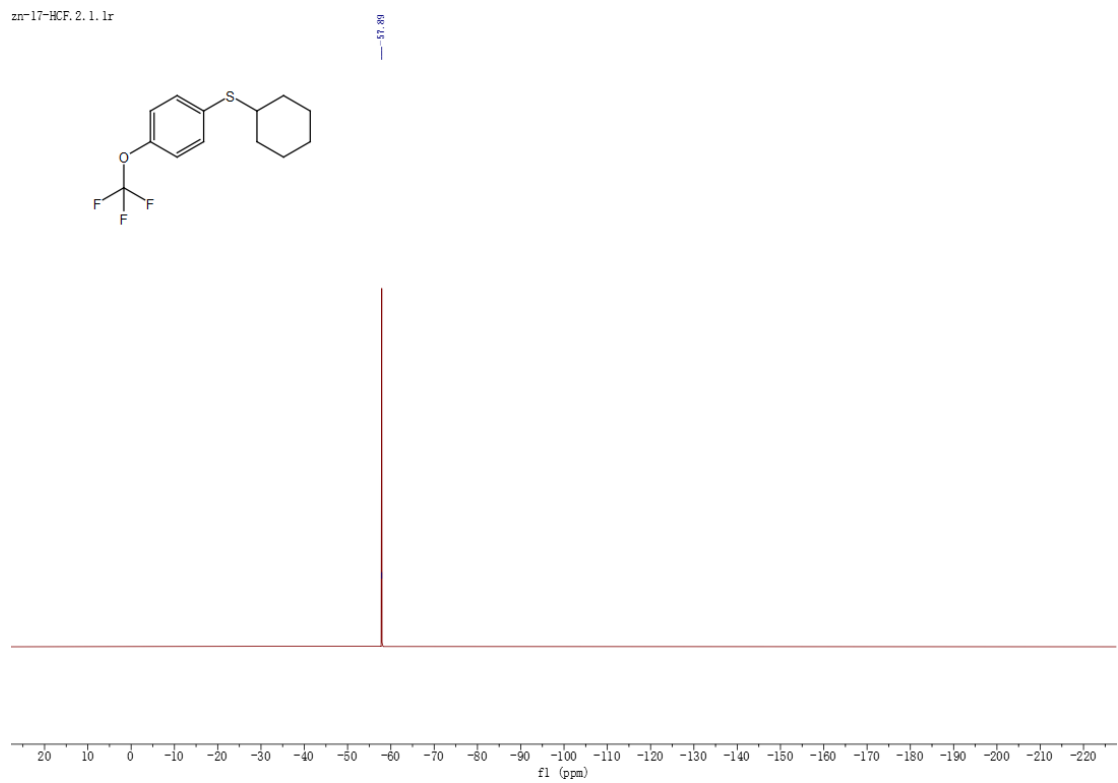
<sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>, 23 °C) of **3h**

zn-17-HCF.3.1.1r



<sup>19</sup>F NMR spectrum (376 MHz, CDCl<sub>3</sub>, 23 °C) of **3h**

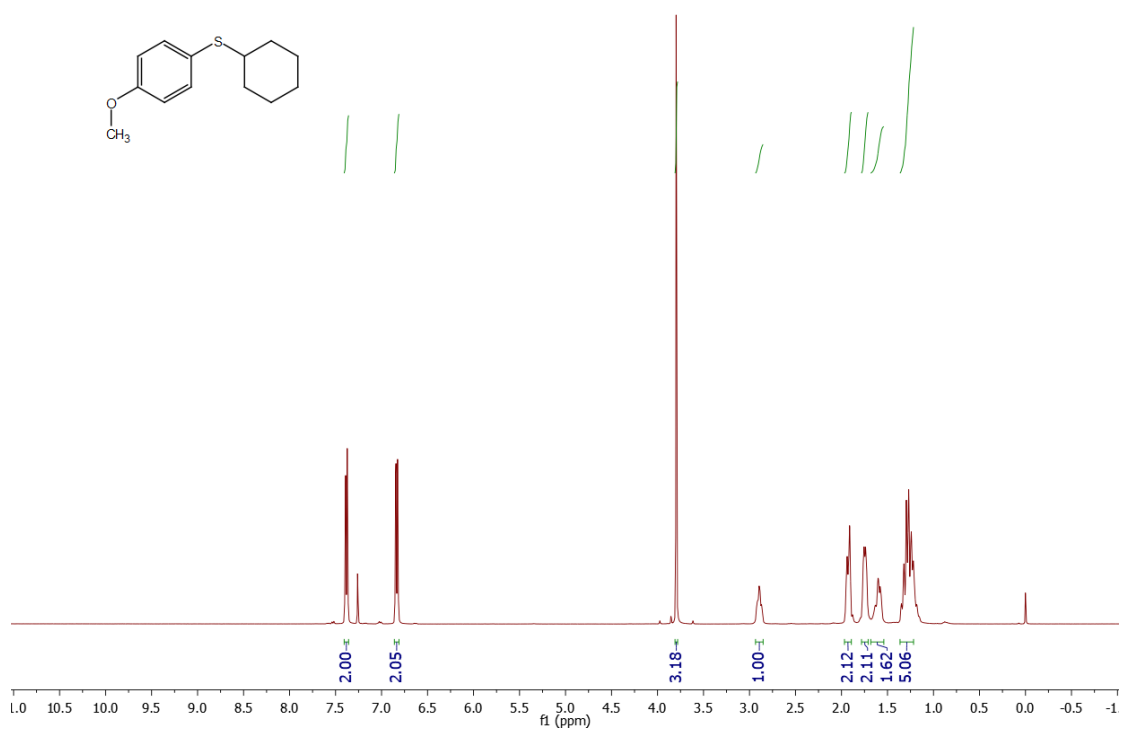
zn-17-HCF.2.1.1r



<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 23 °C) of **3i**

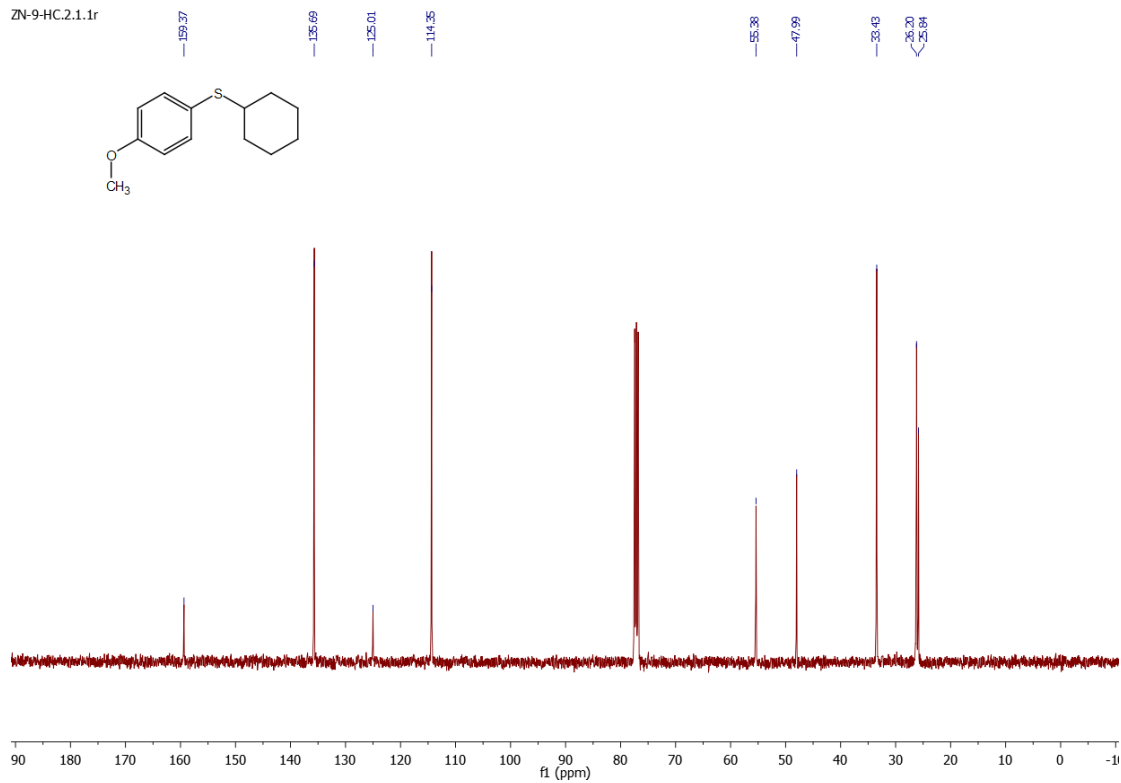


ZN-9-HC.1.1.1r



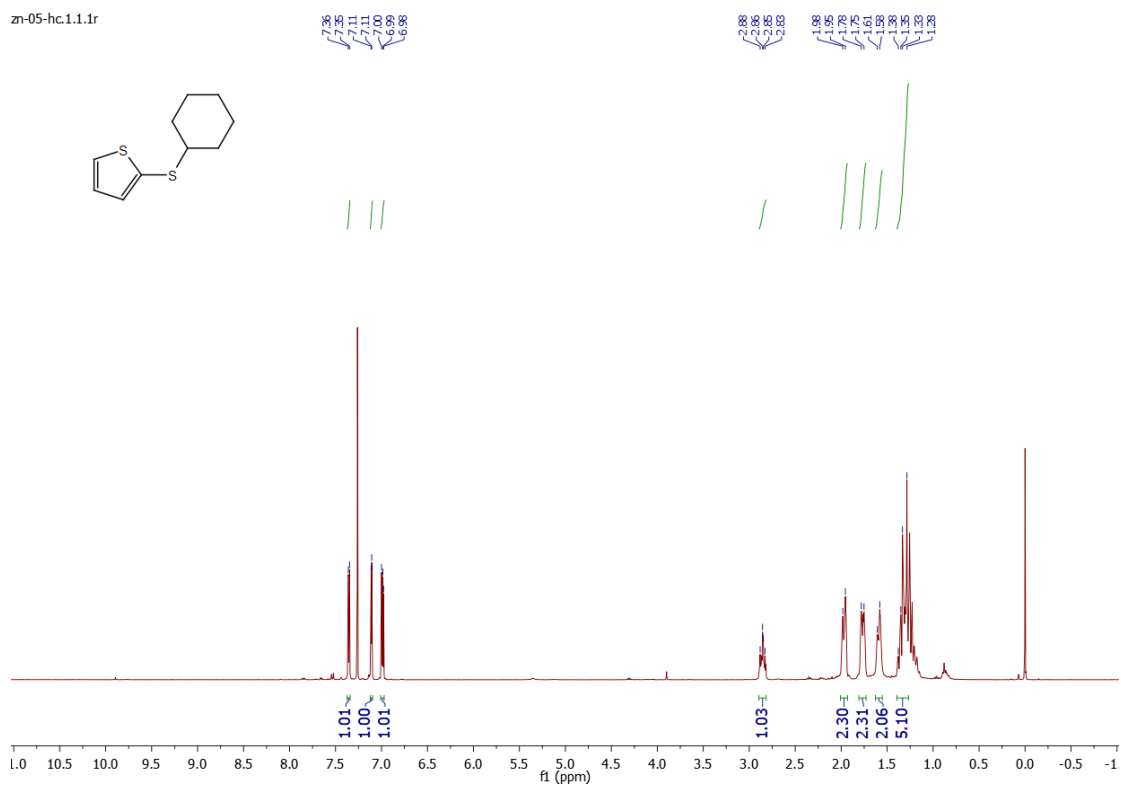
<sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>, 23 °C) of **3i**

ZN-9-HC.2.1.1r



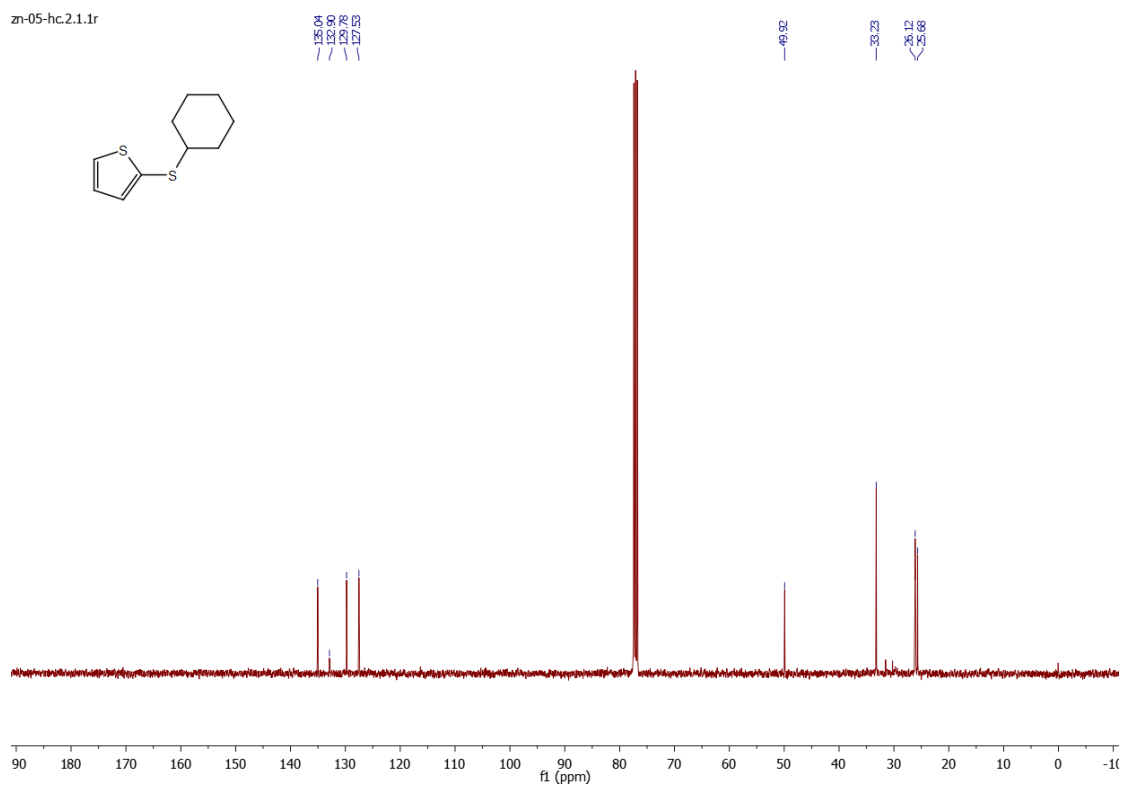
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 23 °C) of **3j**

zn-05-hc.1.1.1r



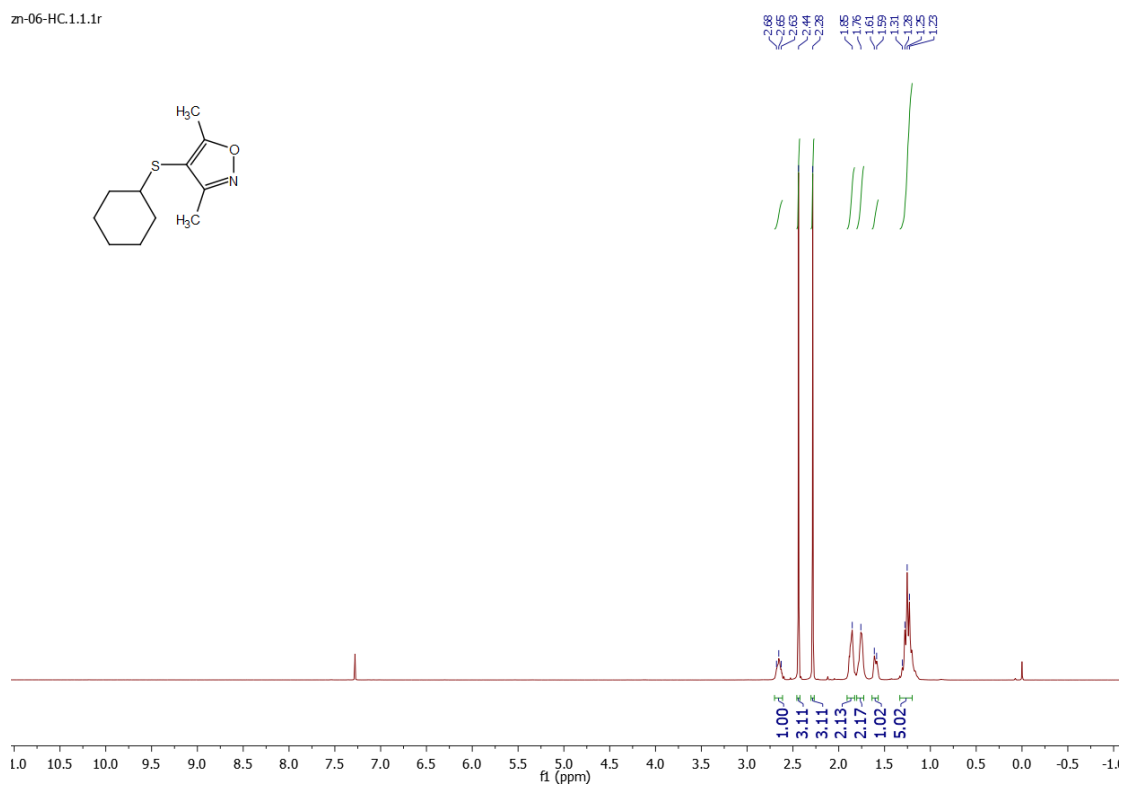
<sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>, 23 °C) of **3j**

zn-05-hc.2.1.1r

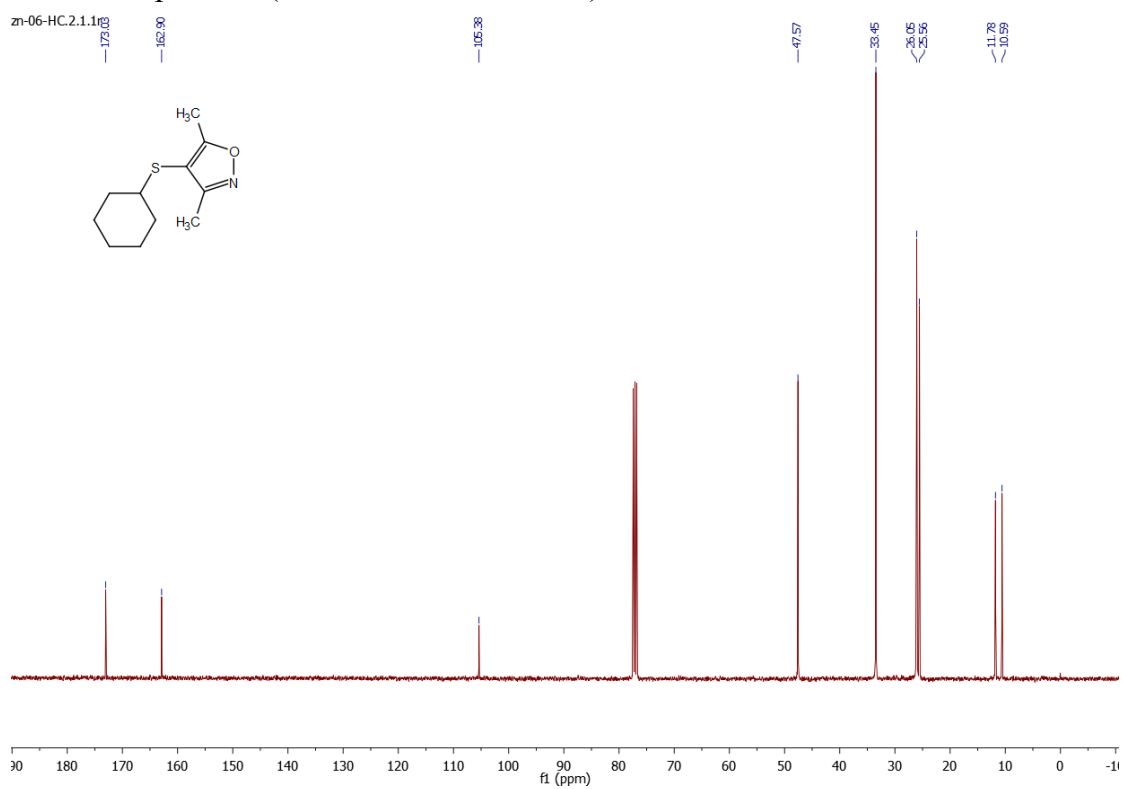


<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 23 °C) of **3k**

zn-06-HC.1.1.1r

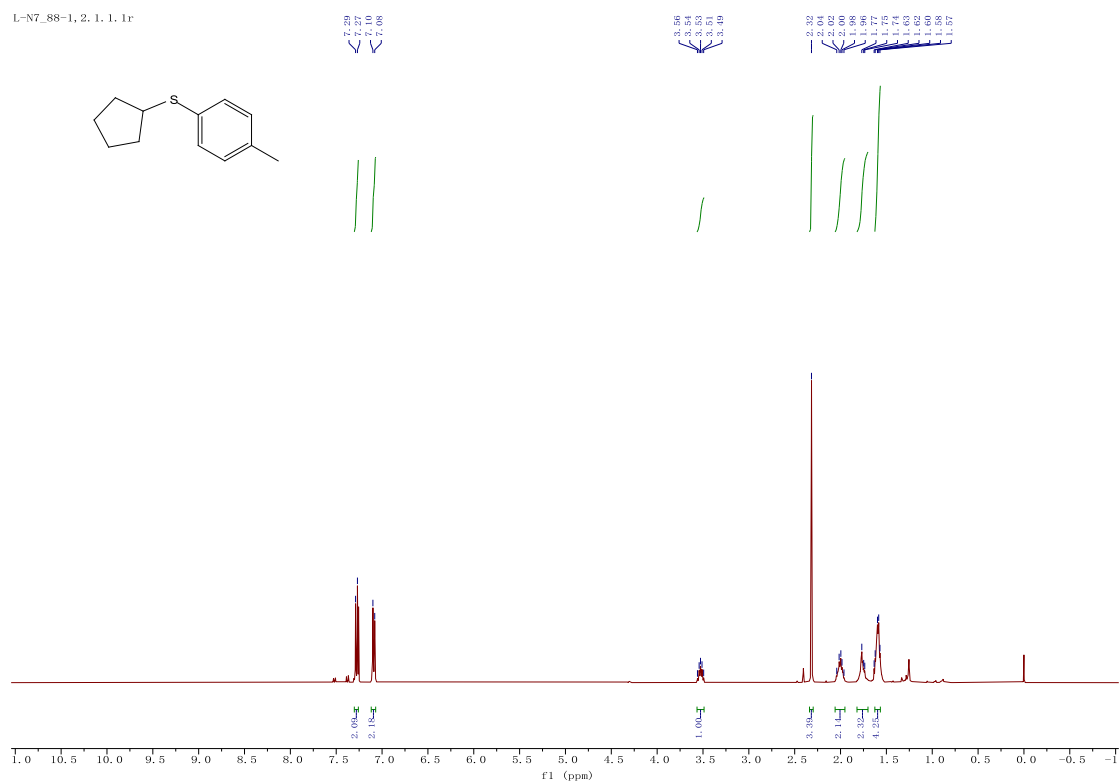


<sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>, 23 °C) of **3k**



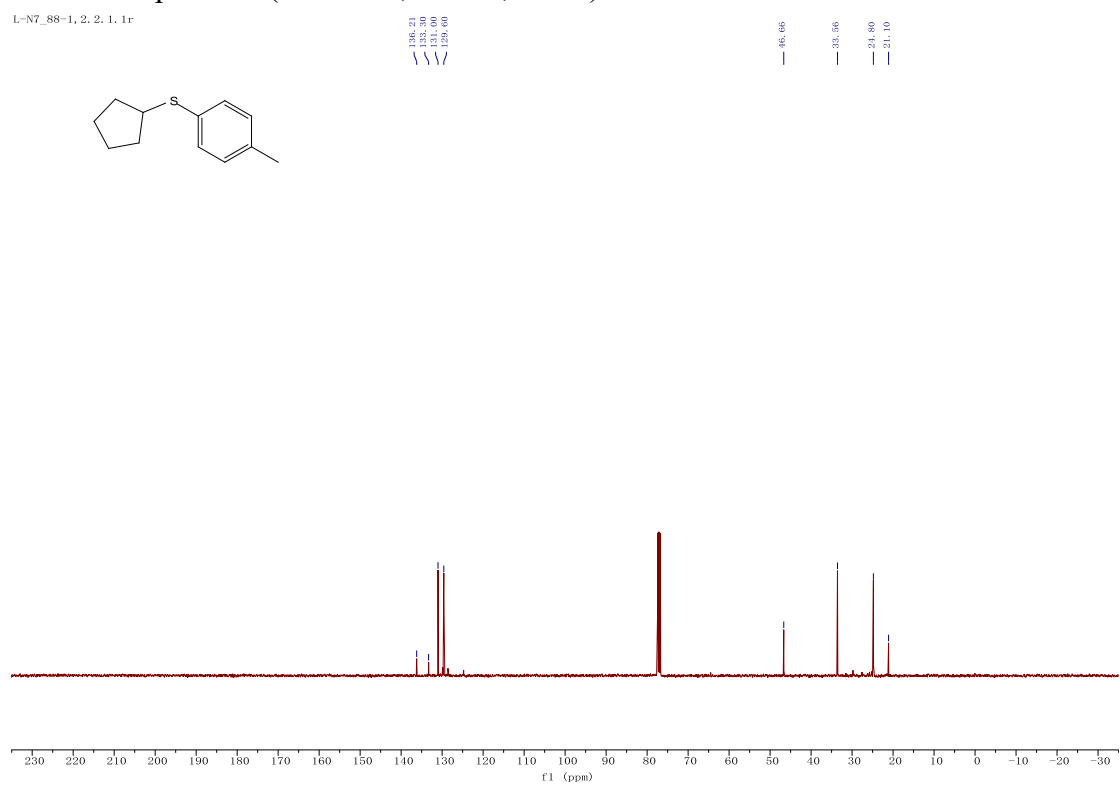
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 23 °C) of **3l**

L-N7\_88-1, 2, 1, 1, 1r



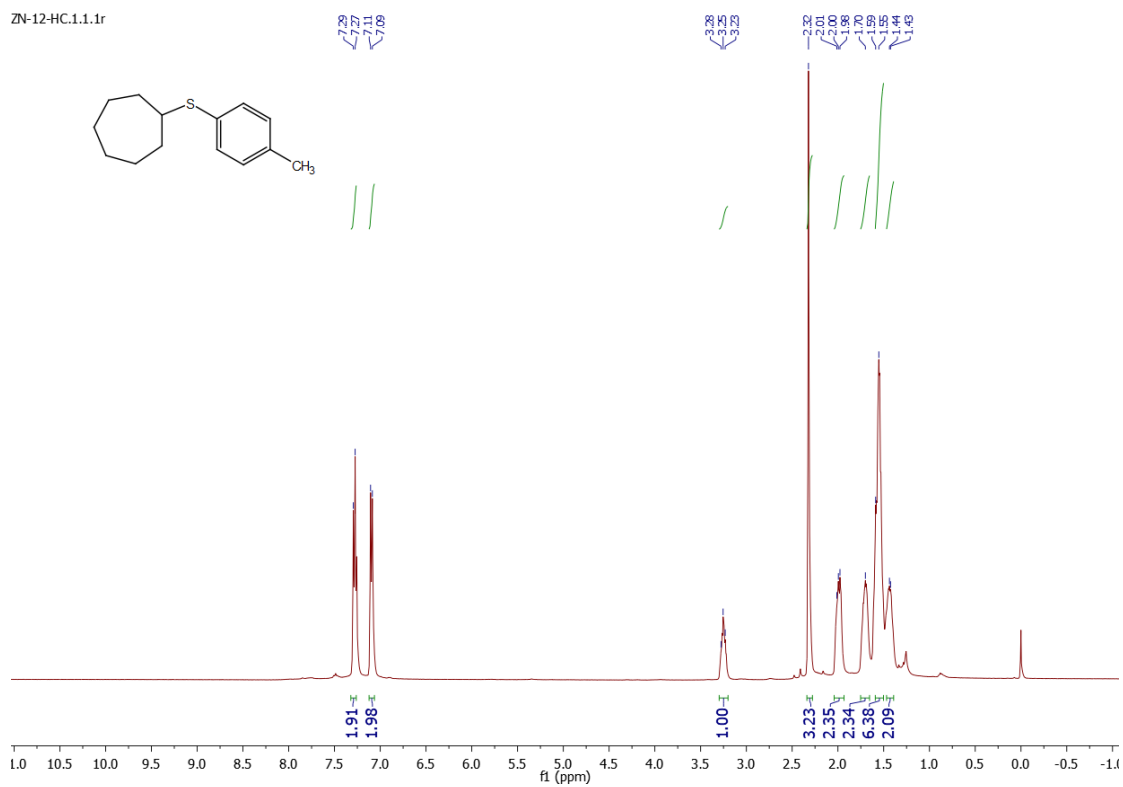
### <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>, 23 °C) of **31**

L-N7\_88-1, 2, 2, 1, 1r



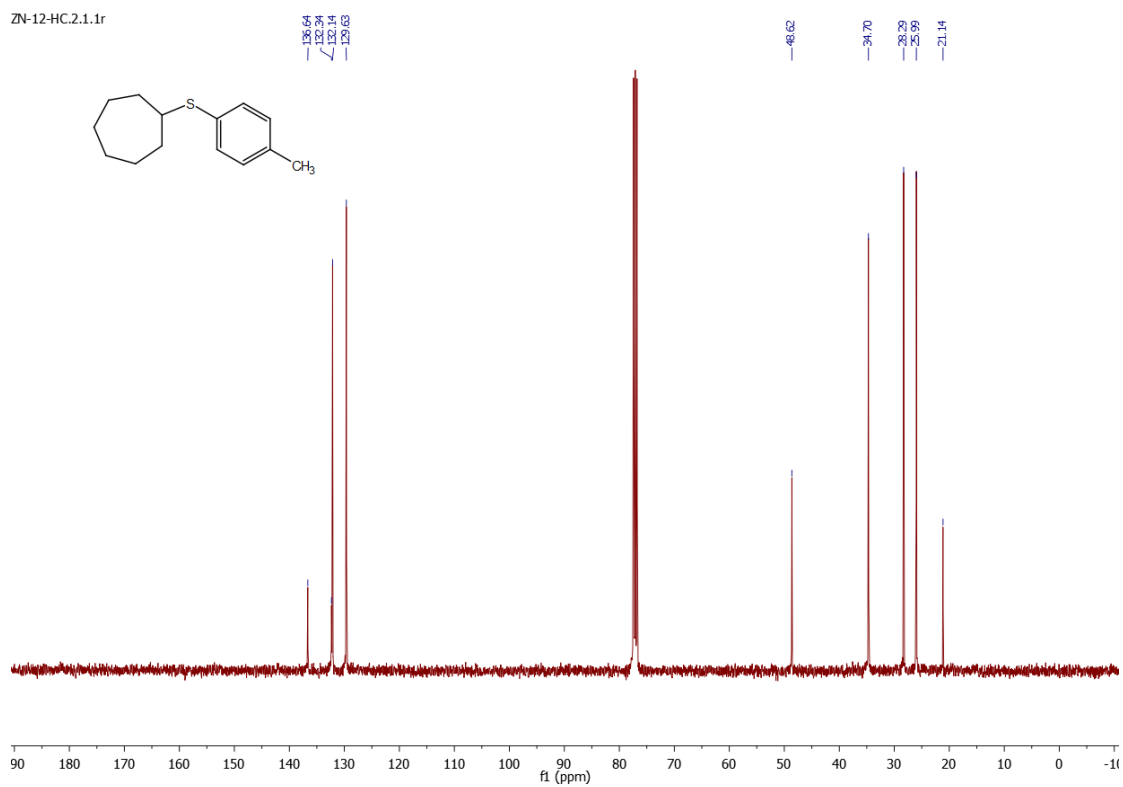
### <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 23 °C) of **3m**

ZN-12-HC.1.1.1r



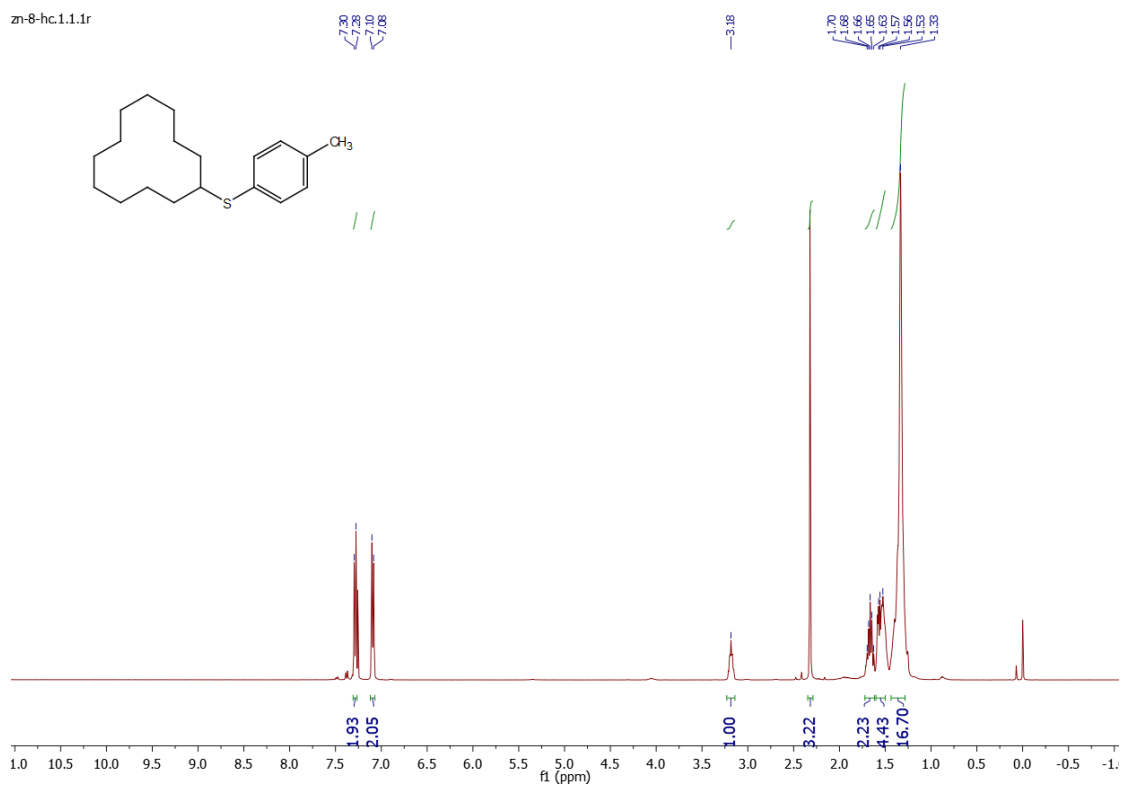
<sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>, 23 °C) of **3m**

ZN-12-HC.2.1.1r



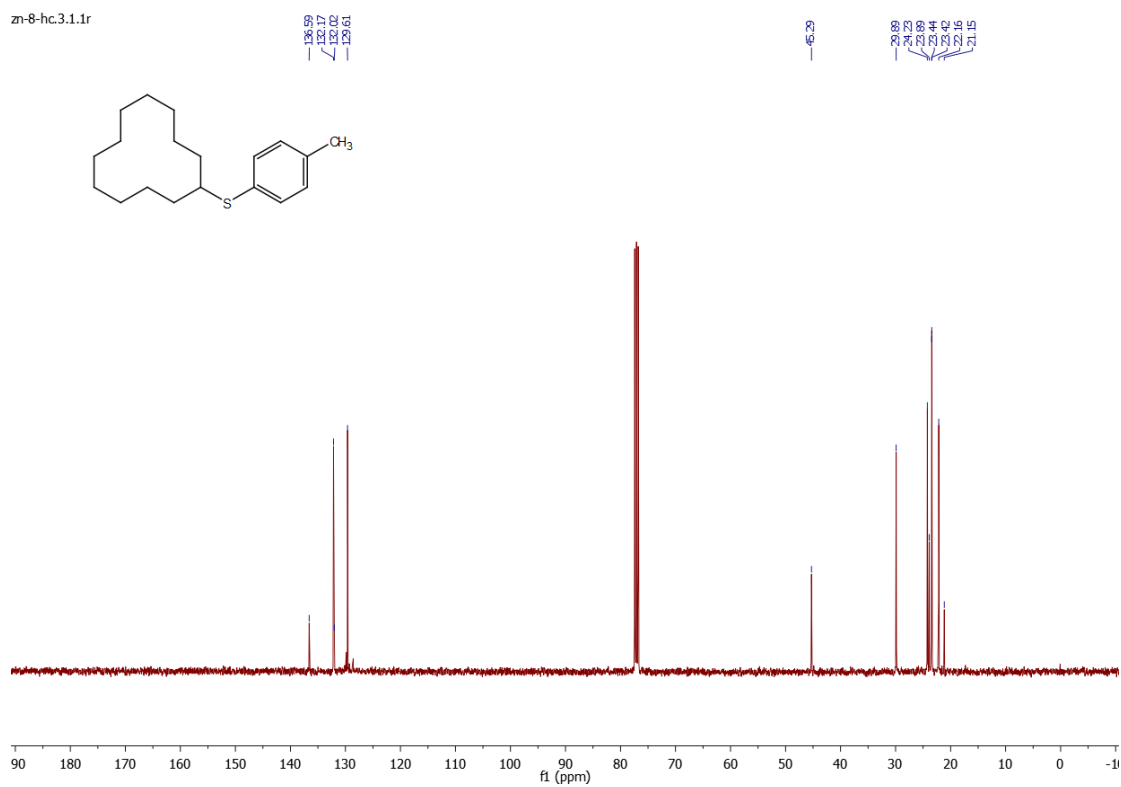
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 23 °C) of **3n**

zn-8-hc.1.1.1r



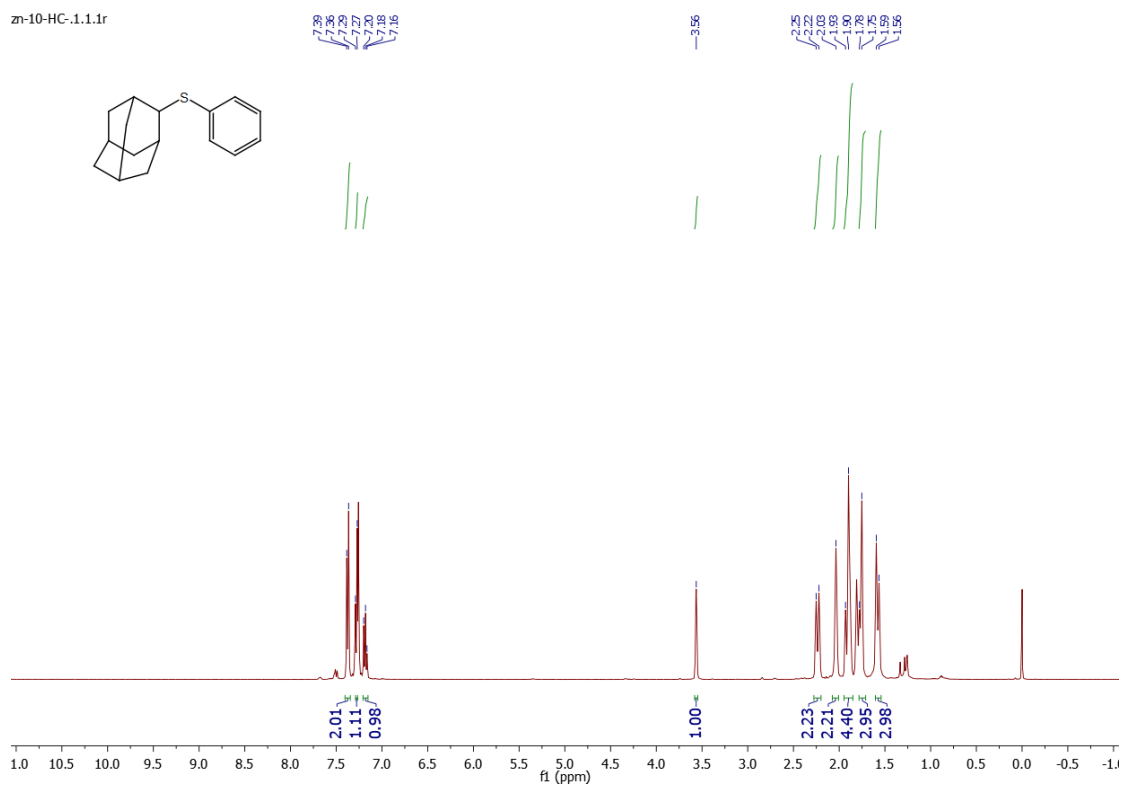
$^{13}\text{C}$  NMR spectrum (100 MHz,  $\text{CDCl}_3$ , 23 °C) of **3n**

zn-8-hc.3.1.1r



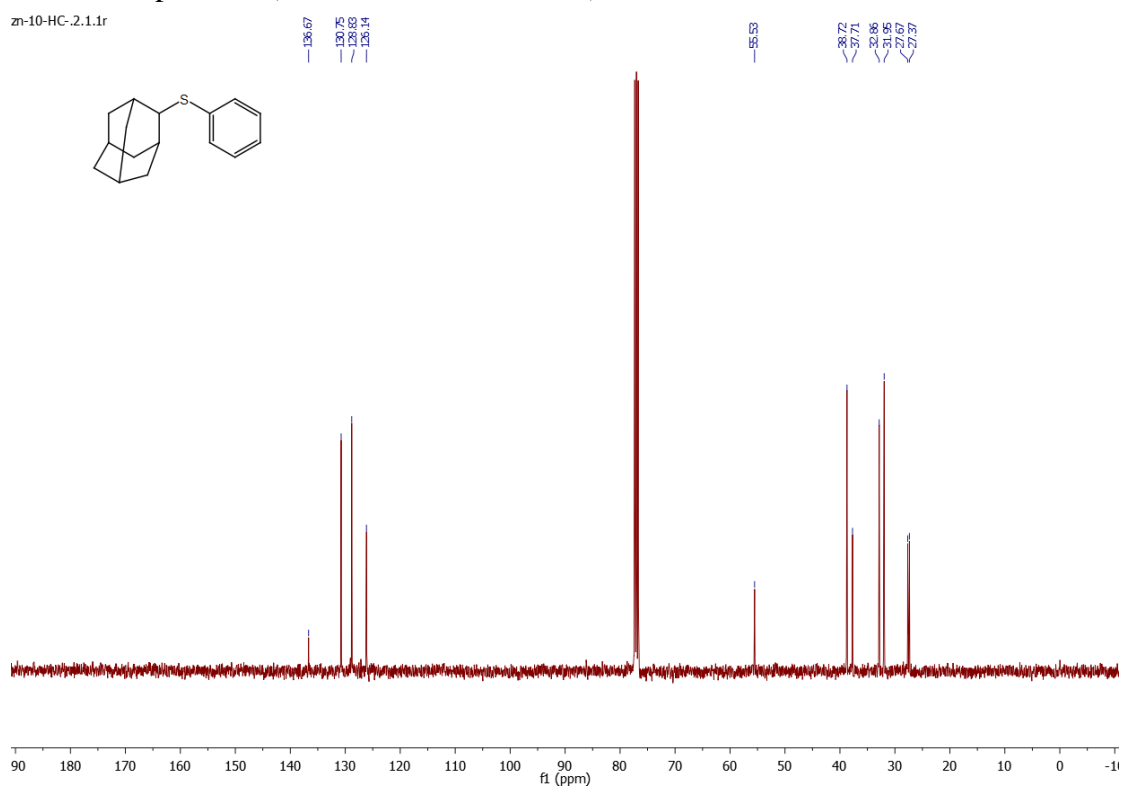
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , 23 °C) of **3o**

zn-10-HC-1.1.1r



<sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>, 23 °C) of **3o**

zn-10-HC-2.1.1r

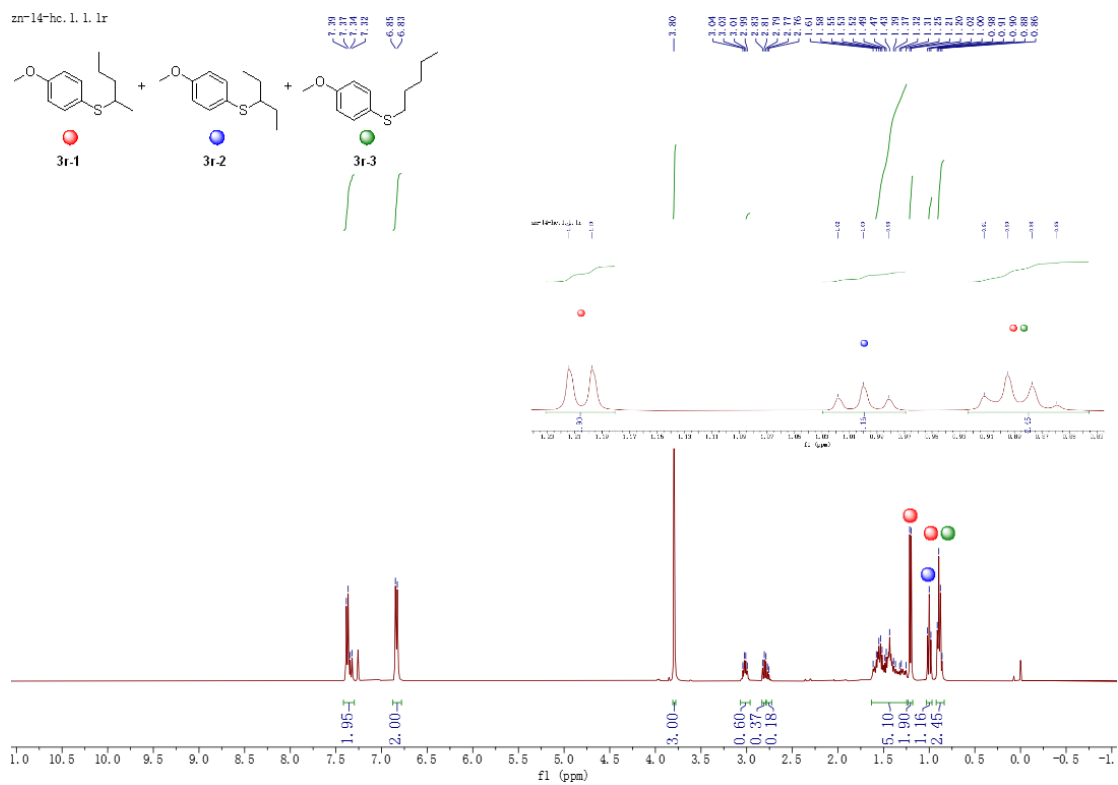


<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 23 °C) of **3p**

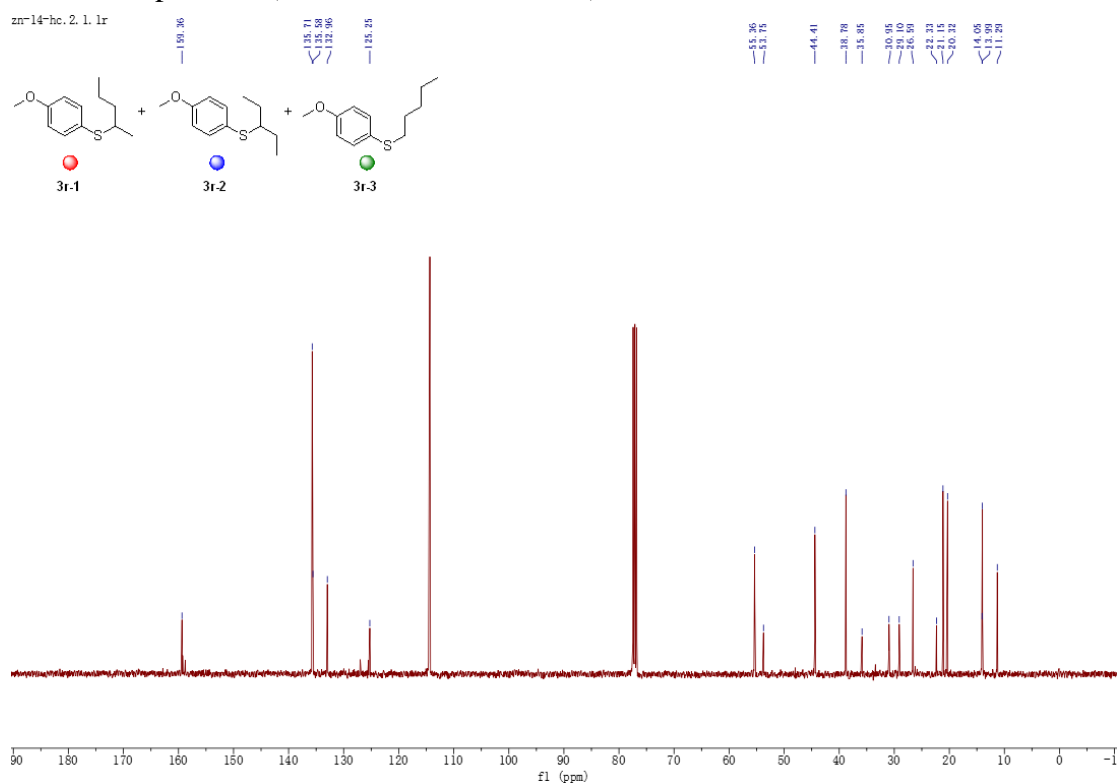






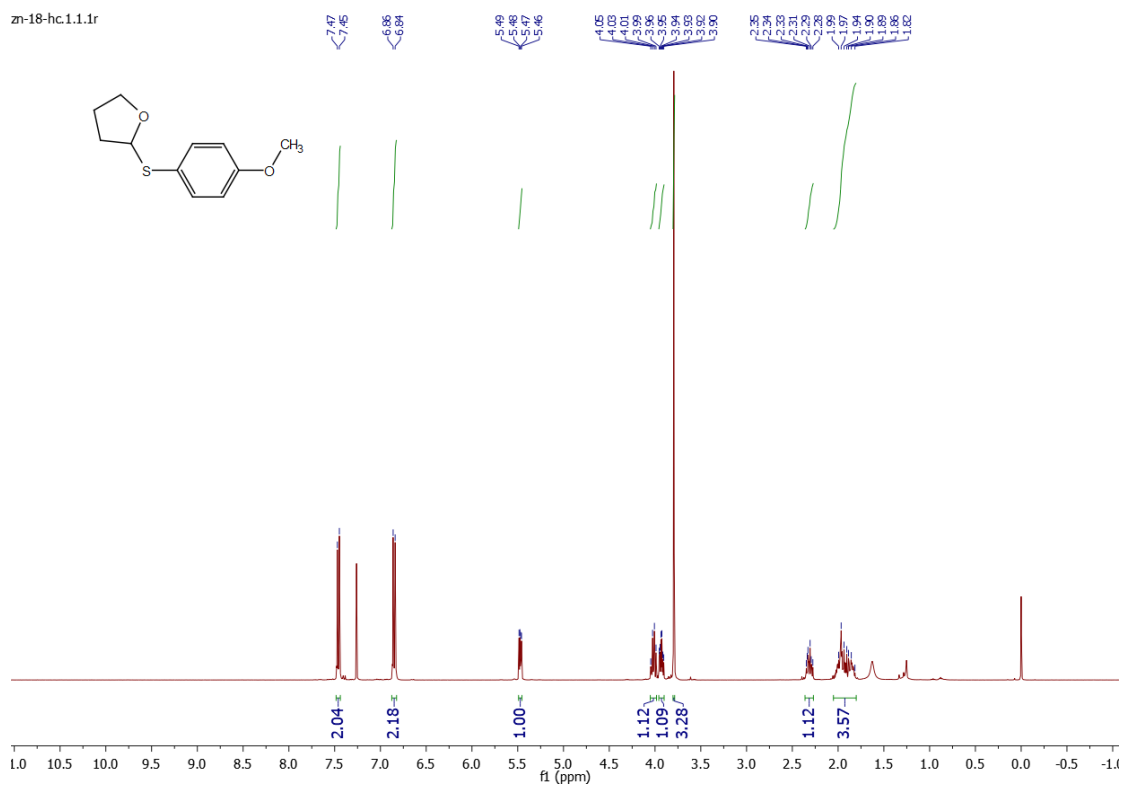


**<sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>, 23 °C) of 3r**



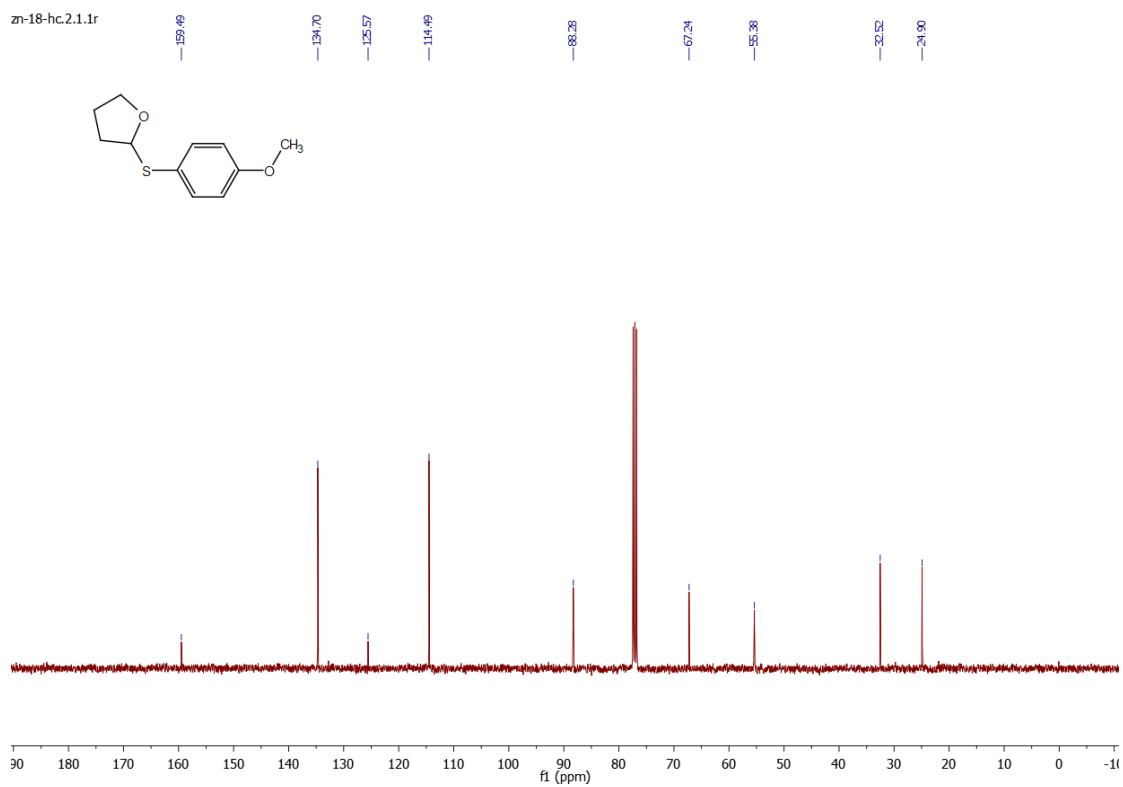
**<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 23 °C) of 3s**

zn-18-hc.1.1.1r



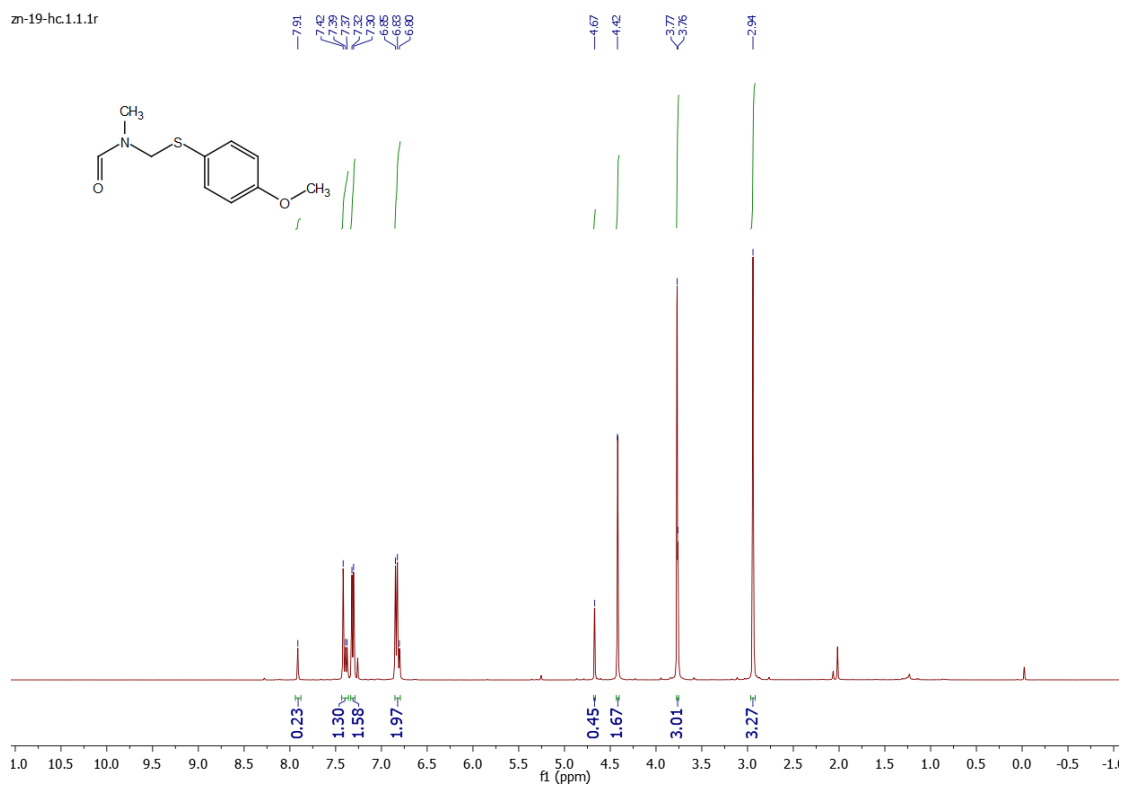
<sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>, 23 °C) of **3s**

zn-18-hc.2.1.1r



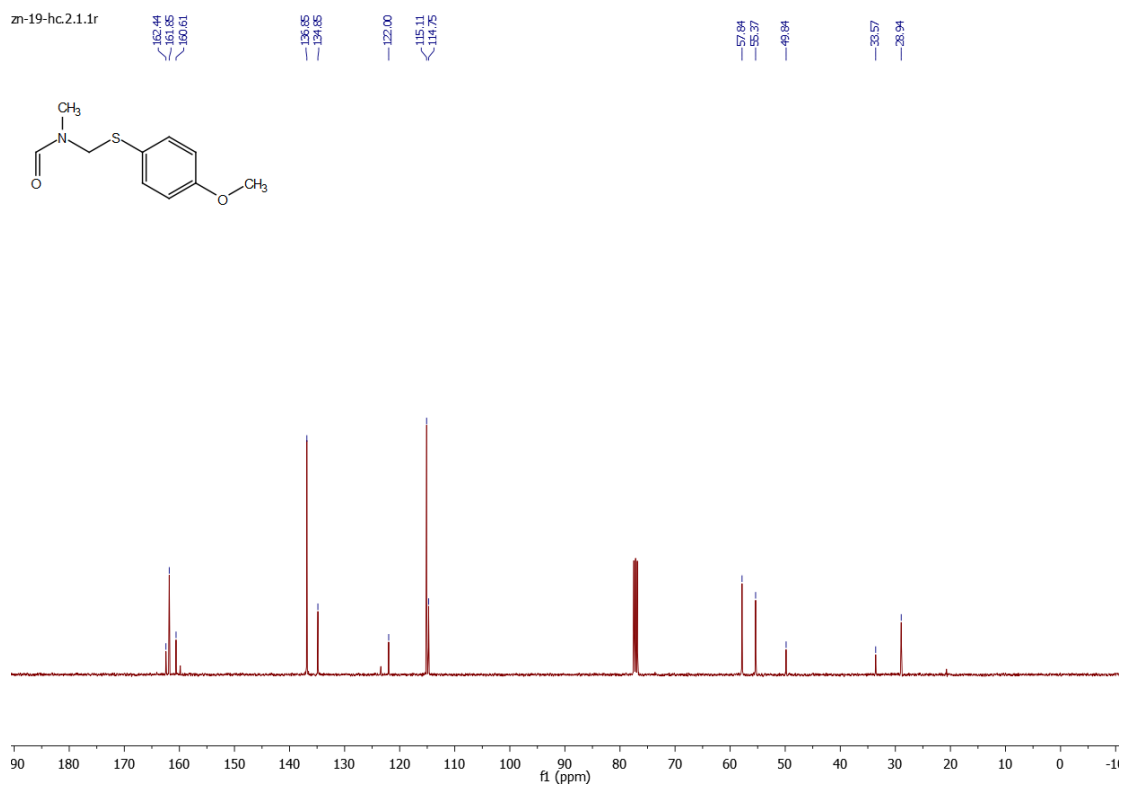
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 23 °C) of **3t**

zn-19-hc.1.1.1r



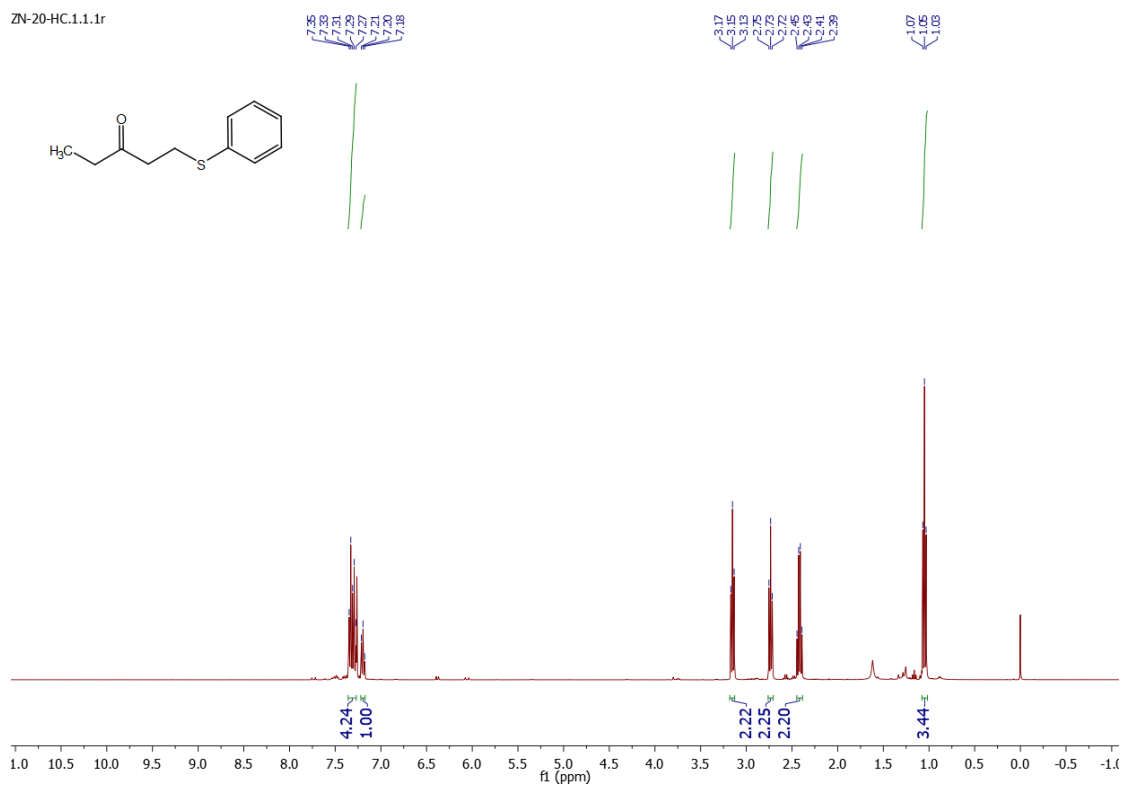
$^{13}\text{C}$  NMR spectrum (100 MHz,  $\text{CDCl}_3$ , 23 °C) of **3t**

zn-19-hc.2.1.1r



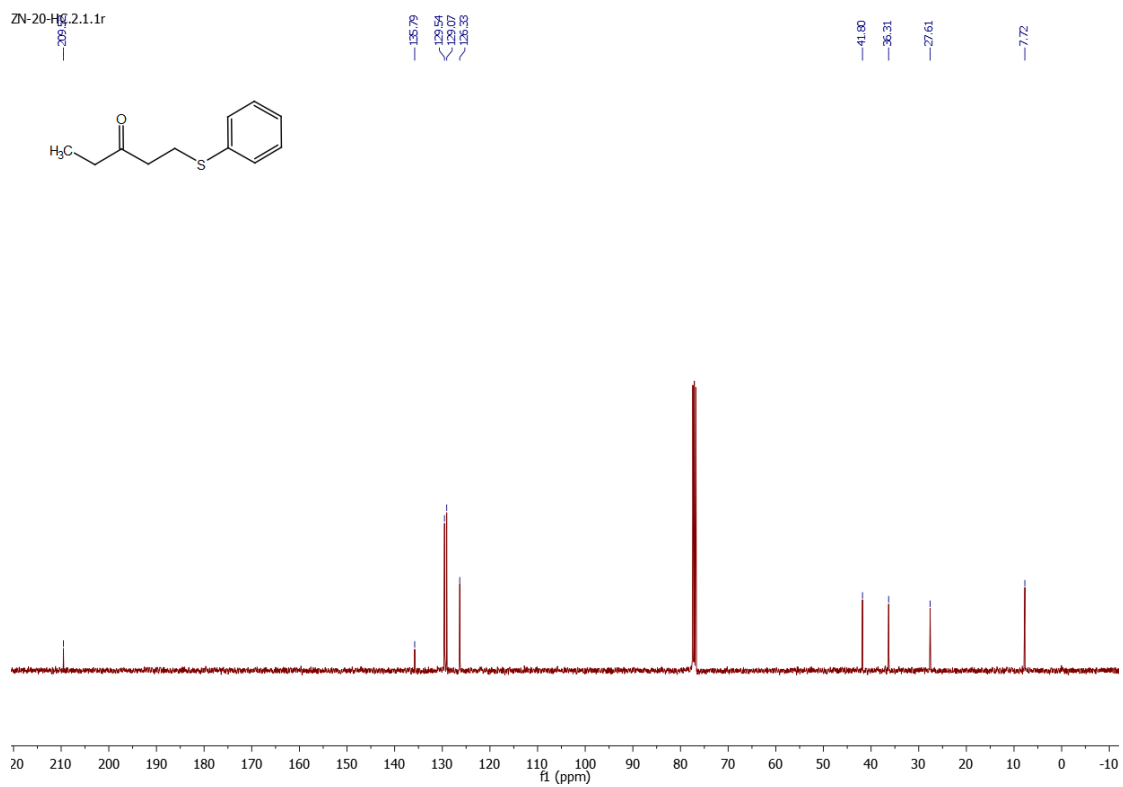
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , 23 °C) of **3u**

ZN-20-HC.1.1.1r



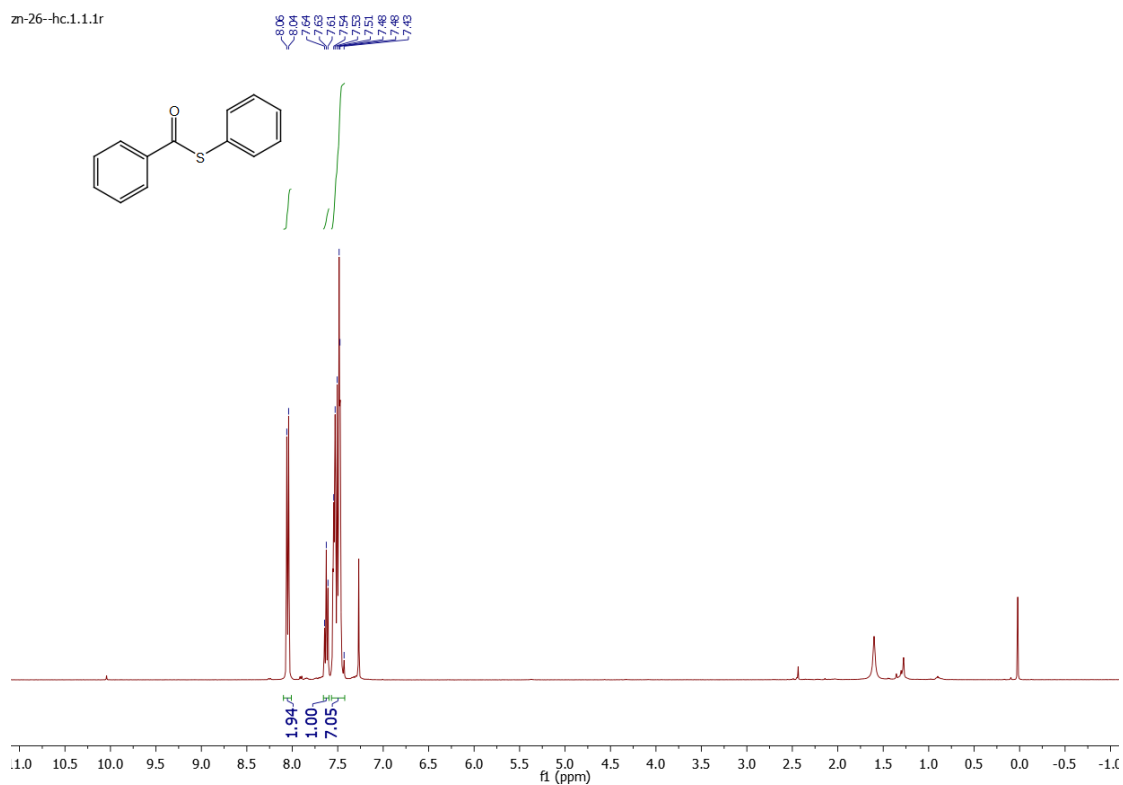
<sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>, 23 °C) of **3u**

ZN-20-HC.2.1.1r



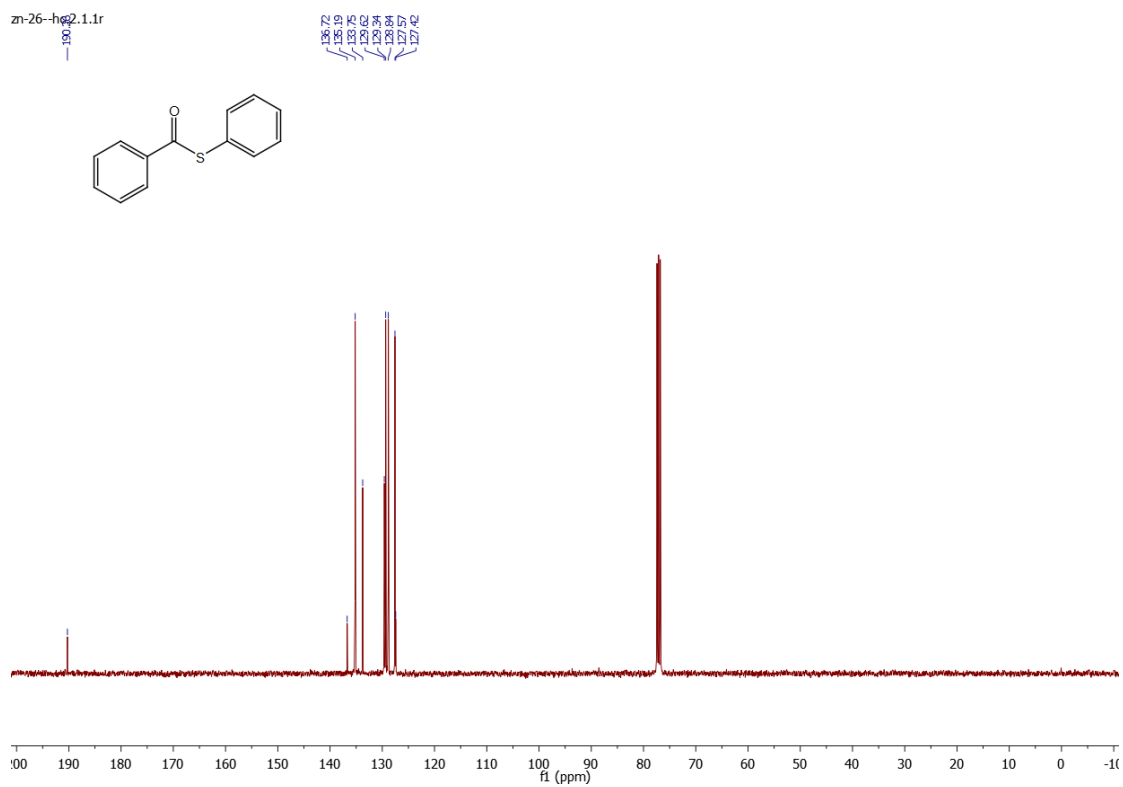
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 23 °C) of **3v**

zn-26-hc.1.1.1r



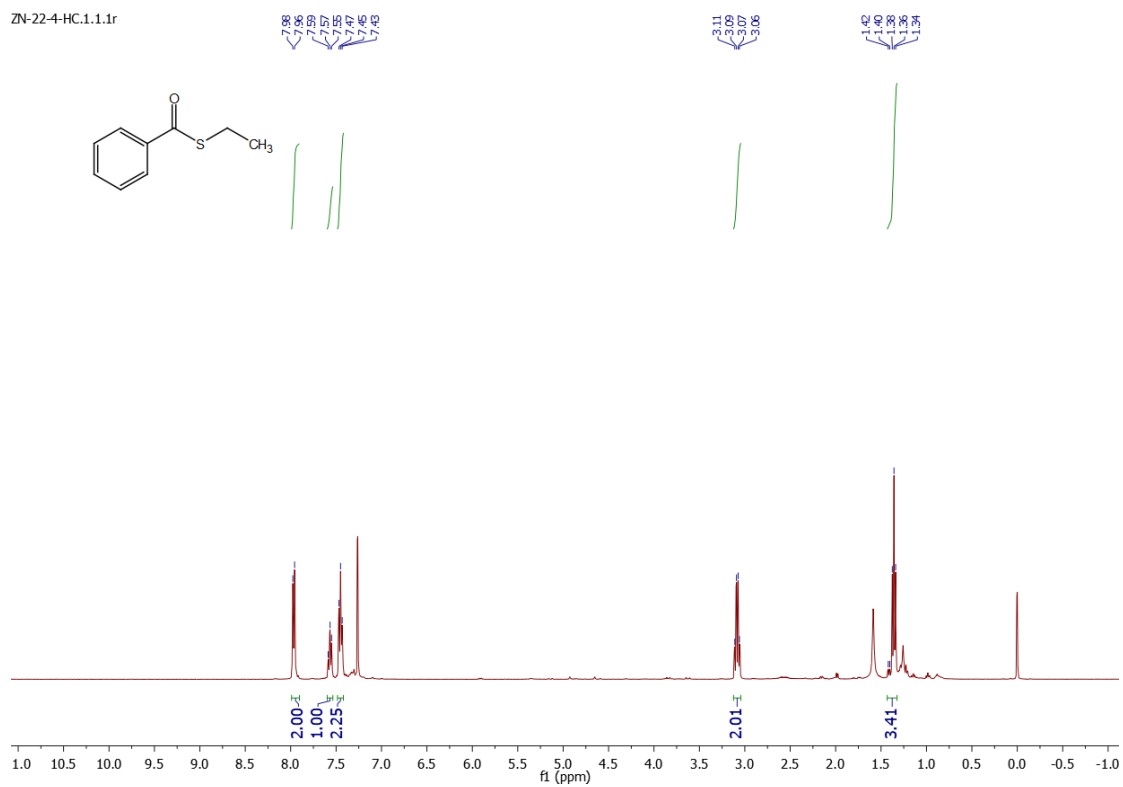
$^{13}\text{C}$  NMR spectrum (100 MHz,  $\text{CDCl}_3$ , 23 °C) of **3v**

zn-26-hc.1.1.1r



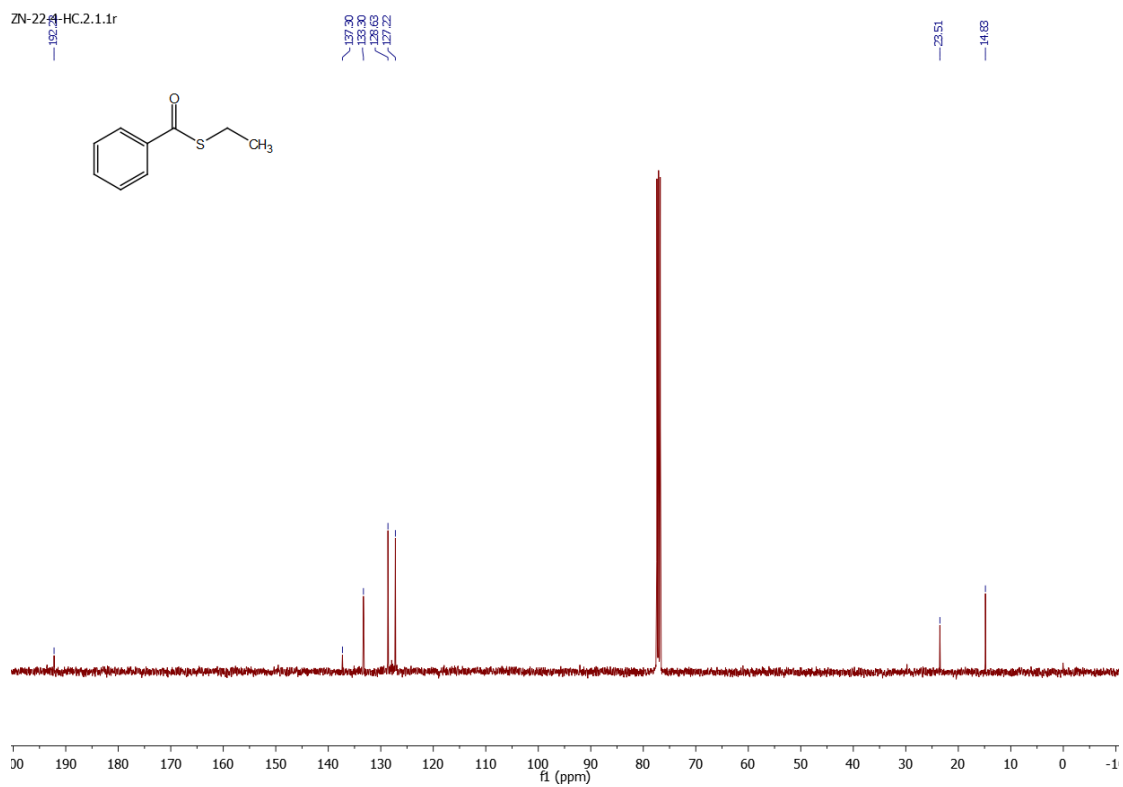
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , 23 °C) of **3w**

ZN-22-4-HC.1.1.1r



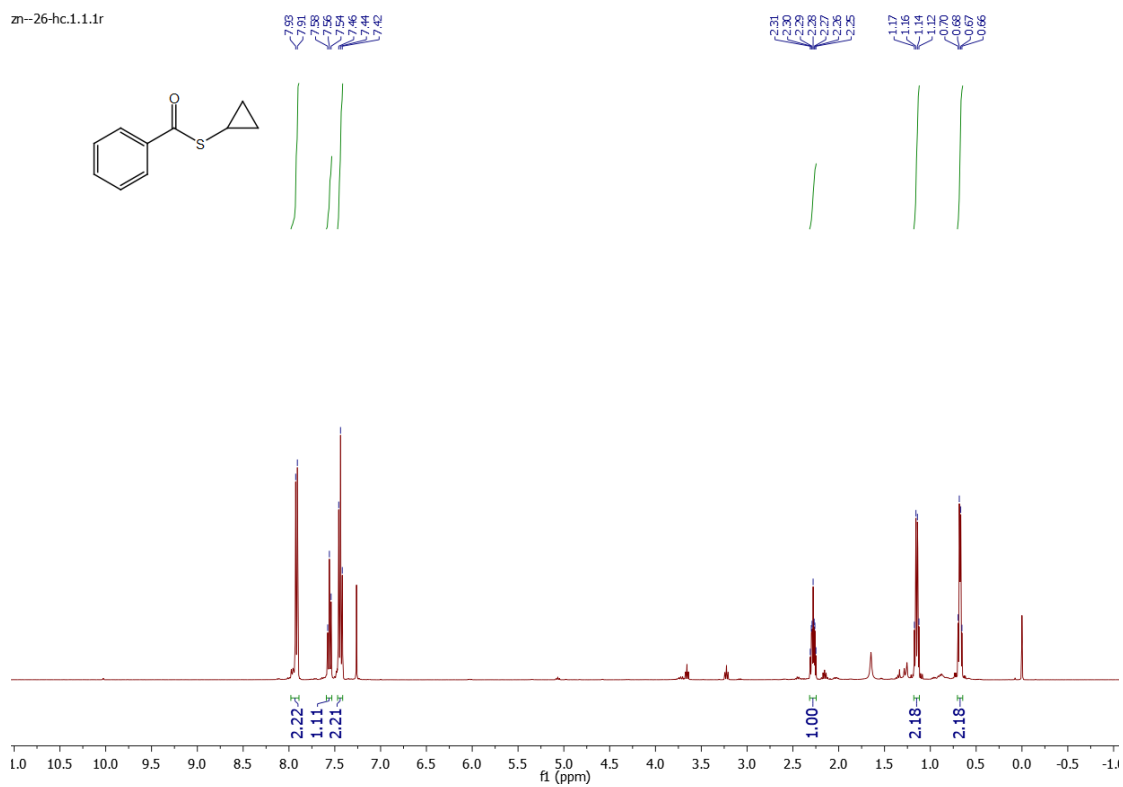
<sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>, 23 °C) of **3w**

ZN-22-4-HC.2.1.1r



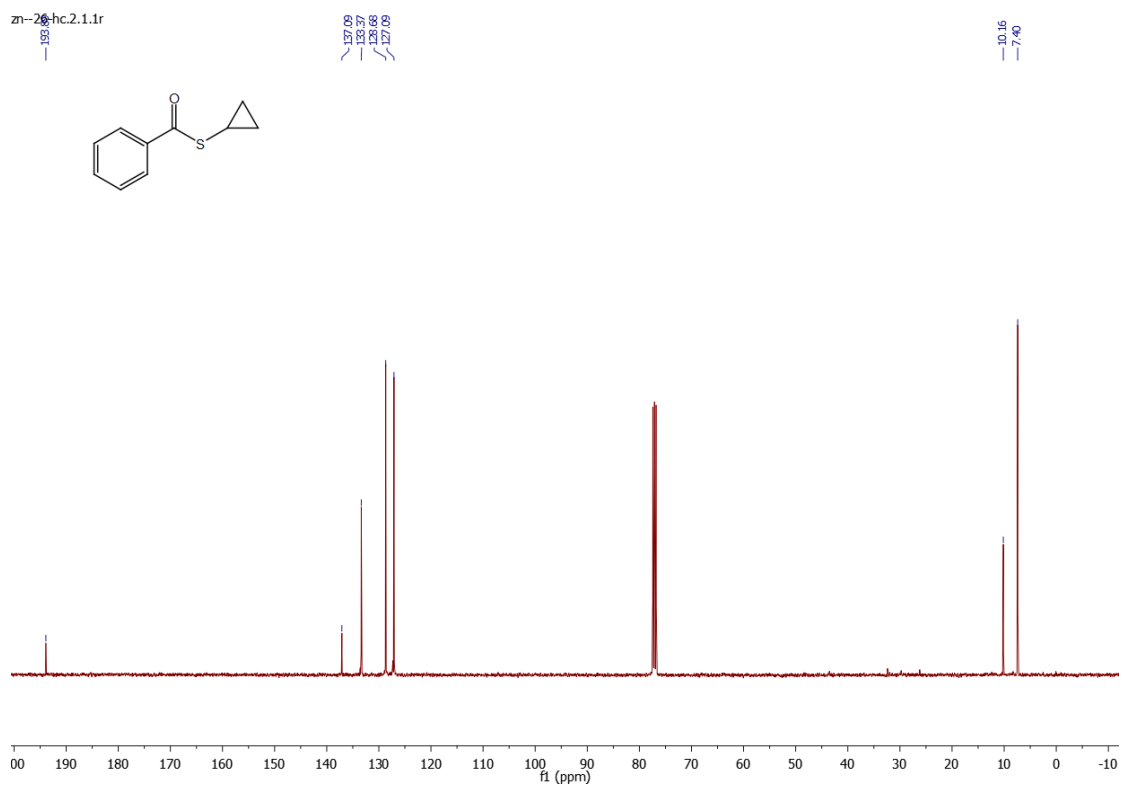
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 23 °C) of **3x**

zn-26-hc.1.1.1r



<sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>, 23 °C) of **3x**

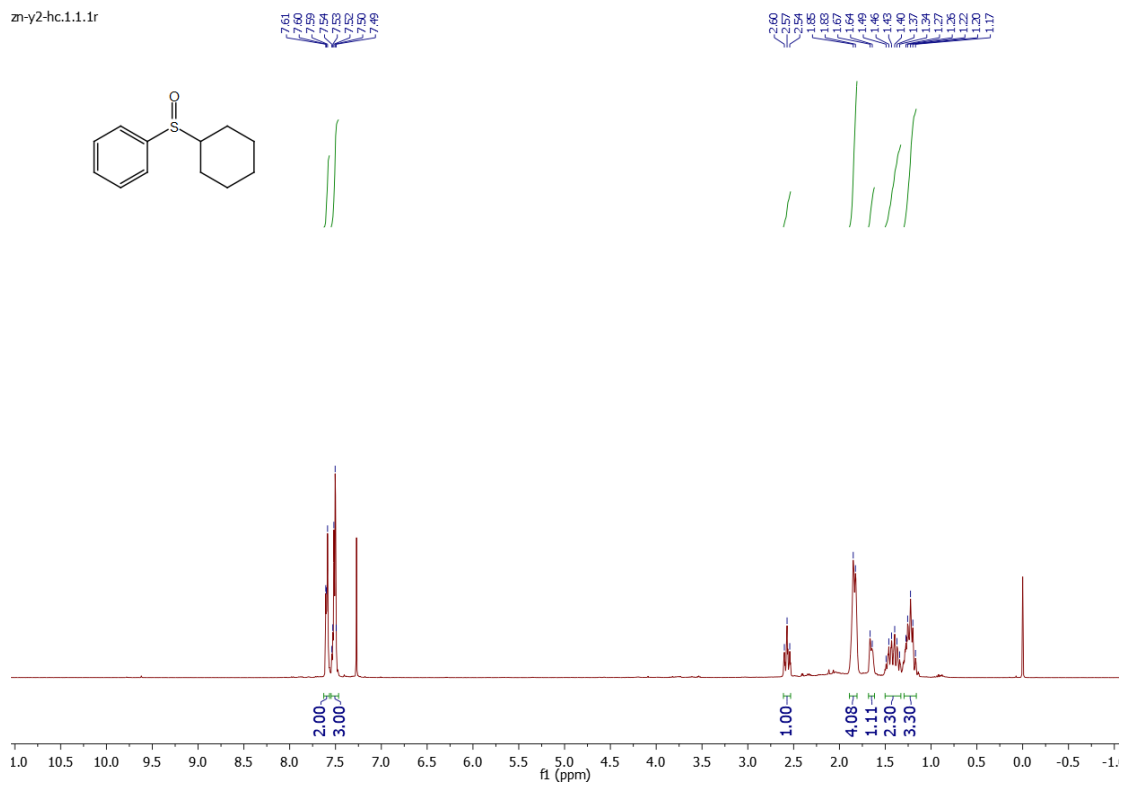
zn-26-hc.2.1.1r



<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 23 °C) of **4a**

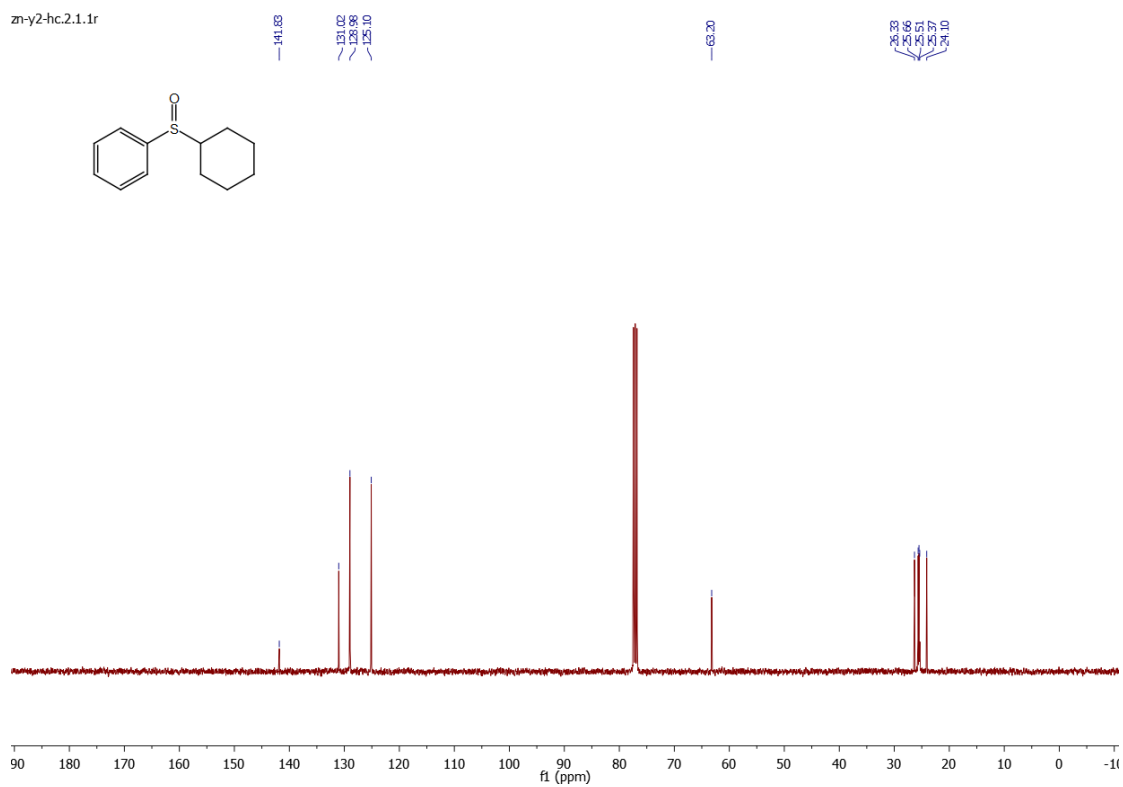


zn-y2-hc.1.1.1r



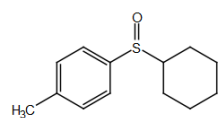
<sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>, 23 °C) of 4a

zn-y2-hc.2.1.1r



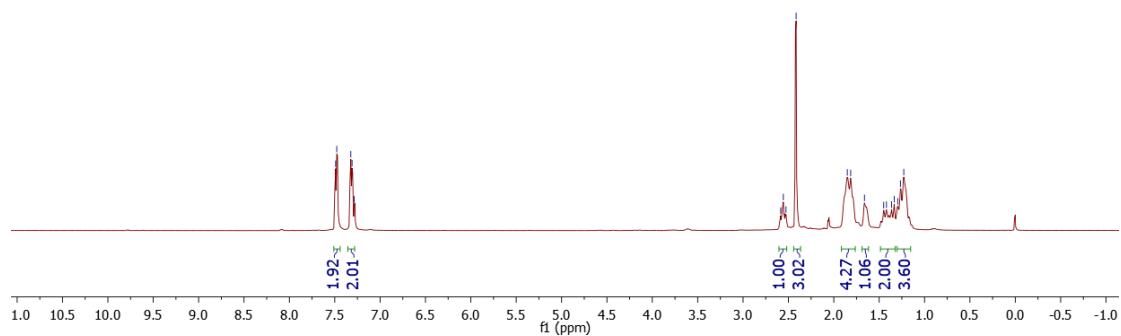
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 23 °C) of 4b

ZN-Y3-HC.1.1.1r



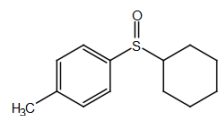
7.49  
7.48  
7.31  
7.29

2.59  
2.55  
2.42  
1.81  
1.66  
1.45  
1.42  
1.39  
1.30  
1.27  
1.23



<sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>, 23 °C) of **4b**

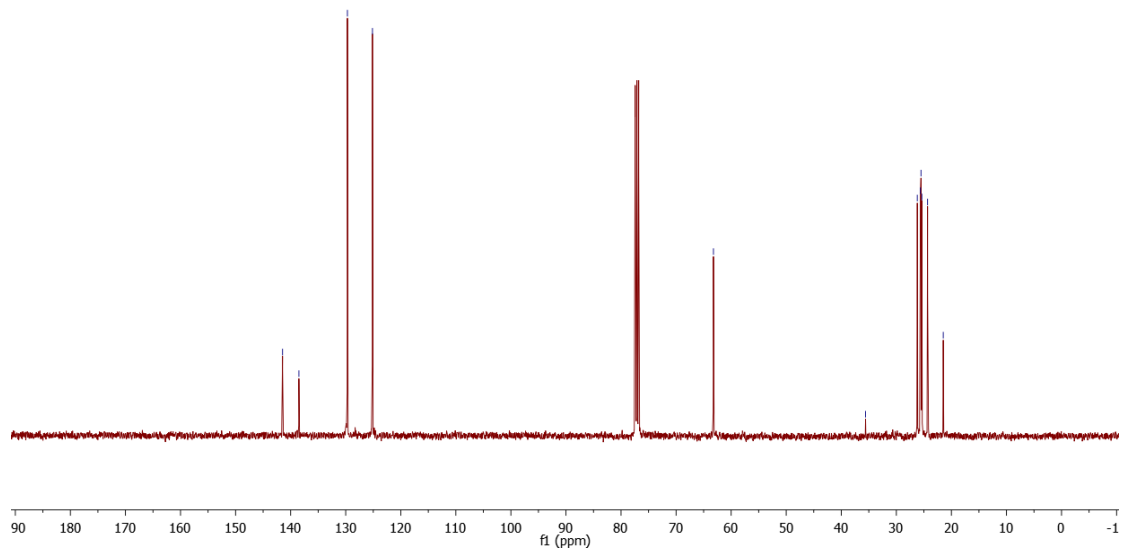
ZN-Y3-HC.2.1.1r



141.47  
138.50  
129.69  
125.14

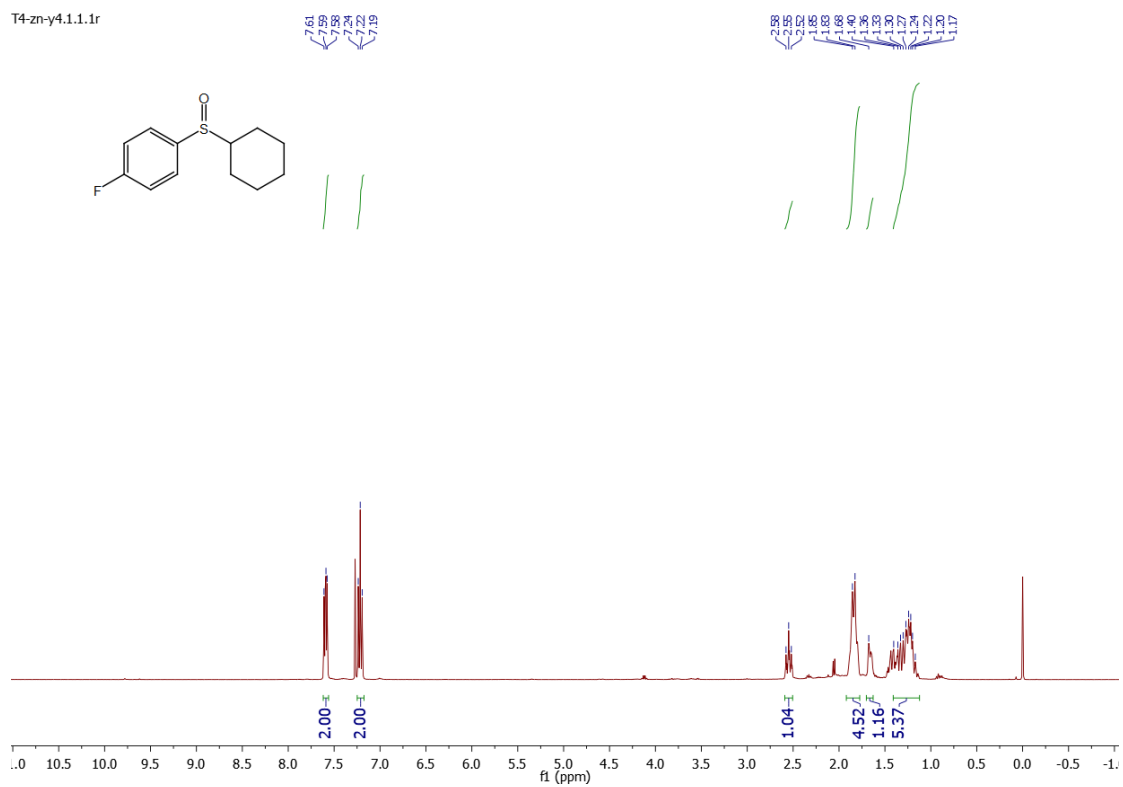
63.21

35.89  
29.19  
28.62  
27.37  
26.98  
21.48

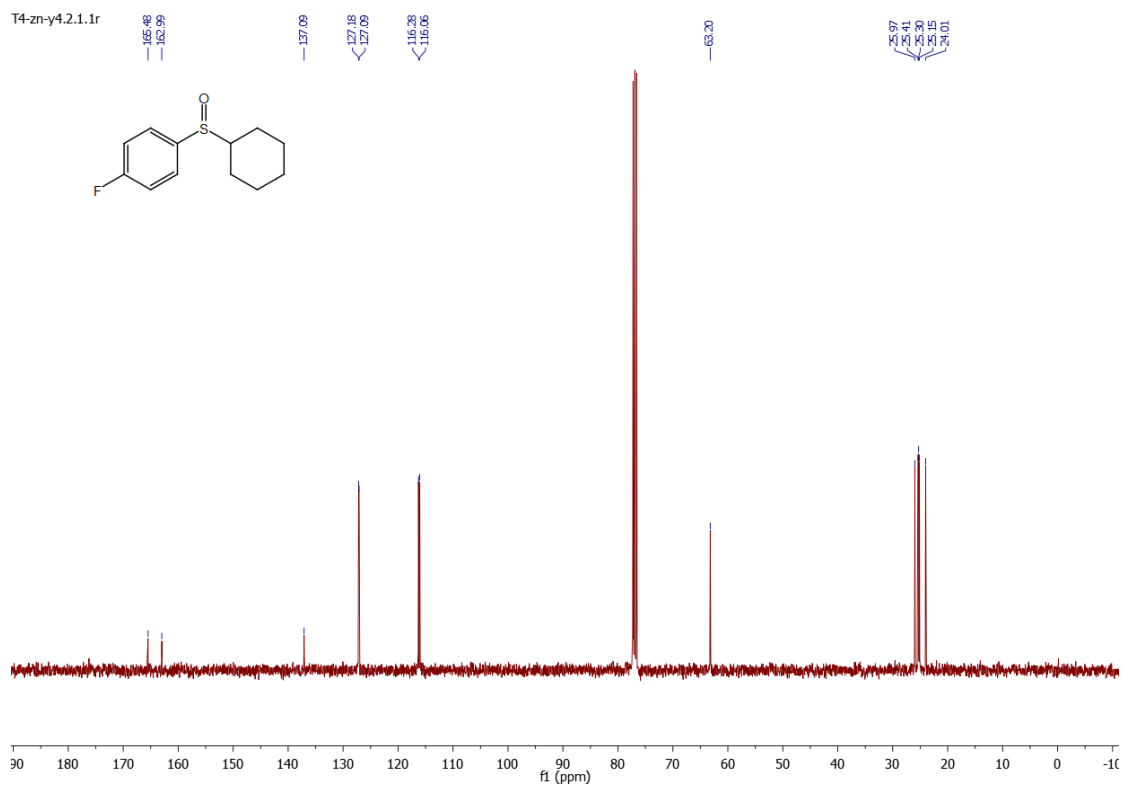


<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 23 °C) of **4c**

T4-zn-y4.1.1.1r



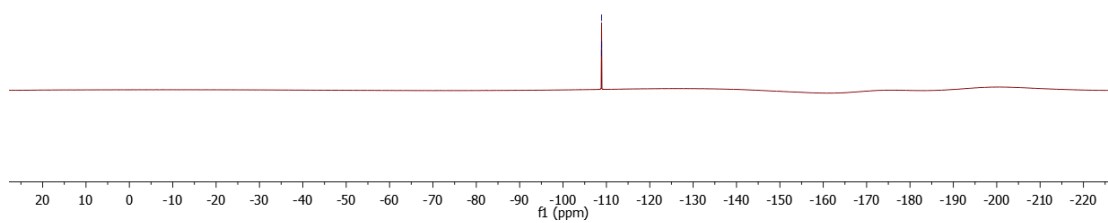
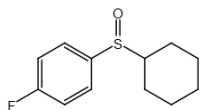
<sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>, 23 °C) of **4c**



<sup>19</sup>F NMR spectrum (376 MHz, CDCl<sub>3</sub>, 23 °C) of **4c**

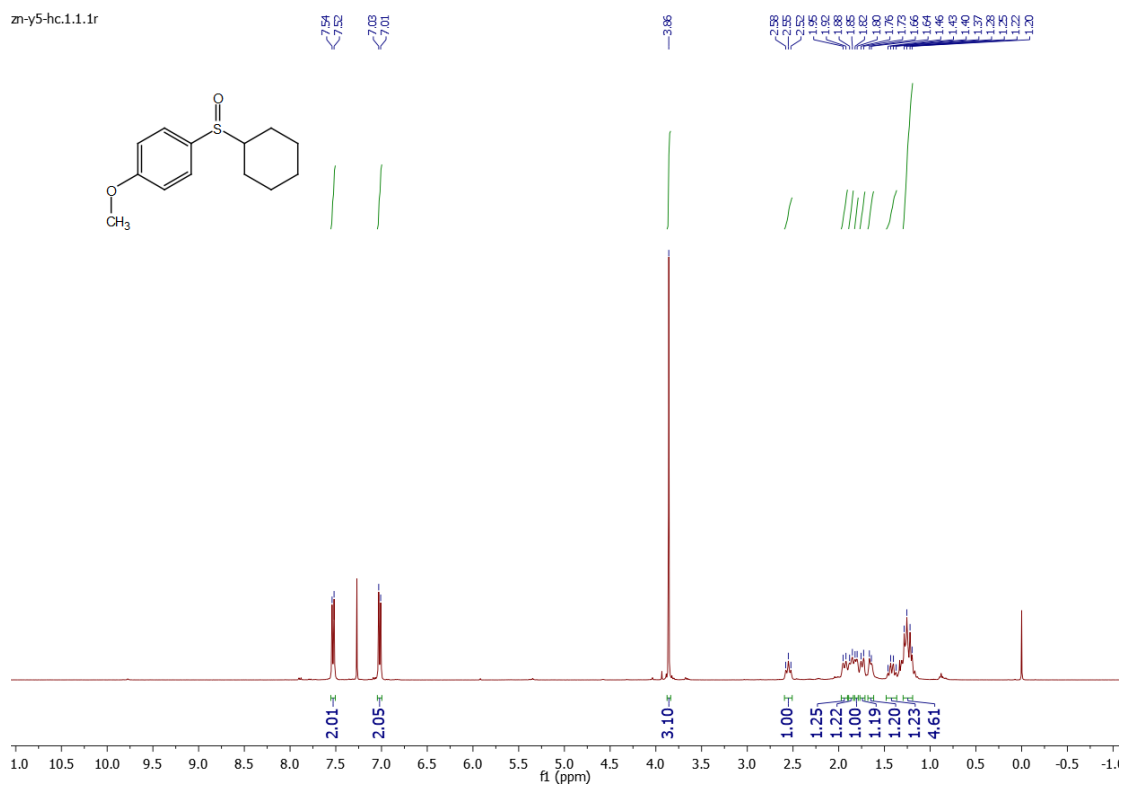
T4-zn-y4.3.1.1r

-108.87  
-108.89  
-108.90



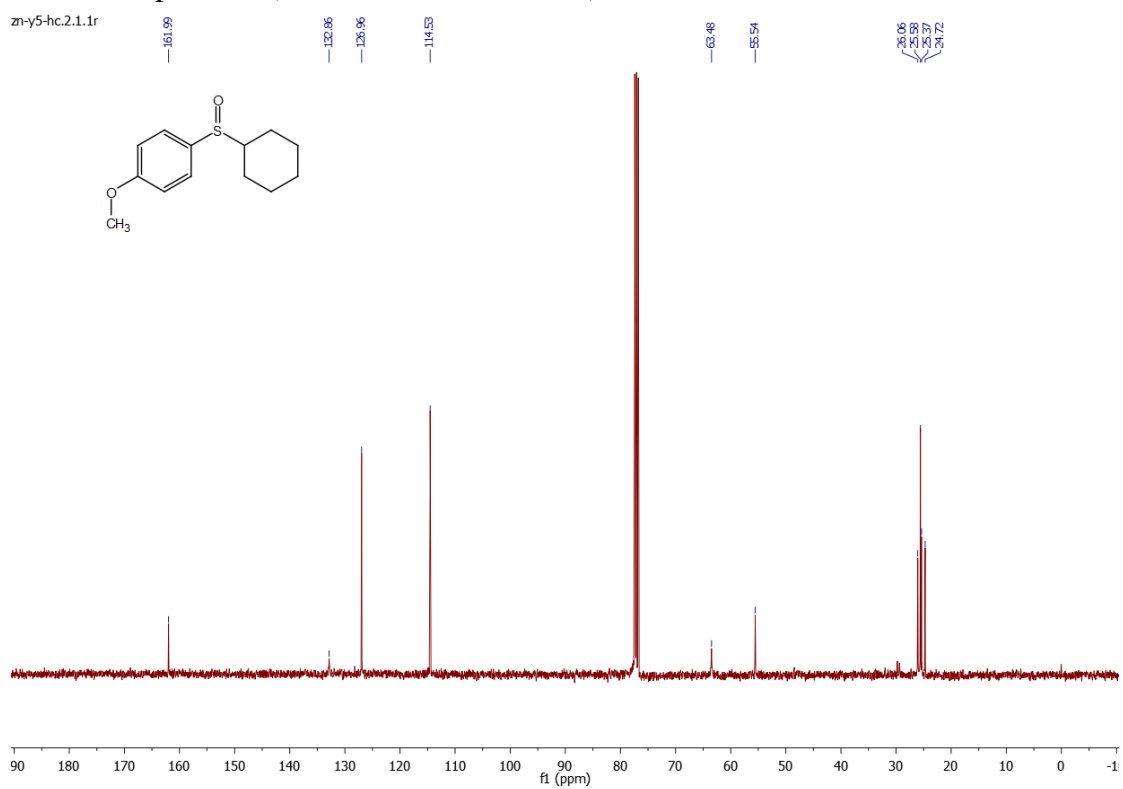
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 23 °C) of **4d**

zn-y5-hc.1.1.1r



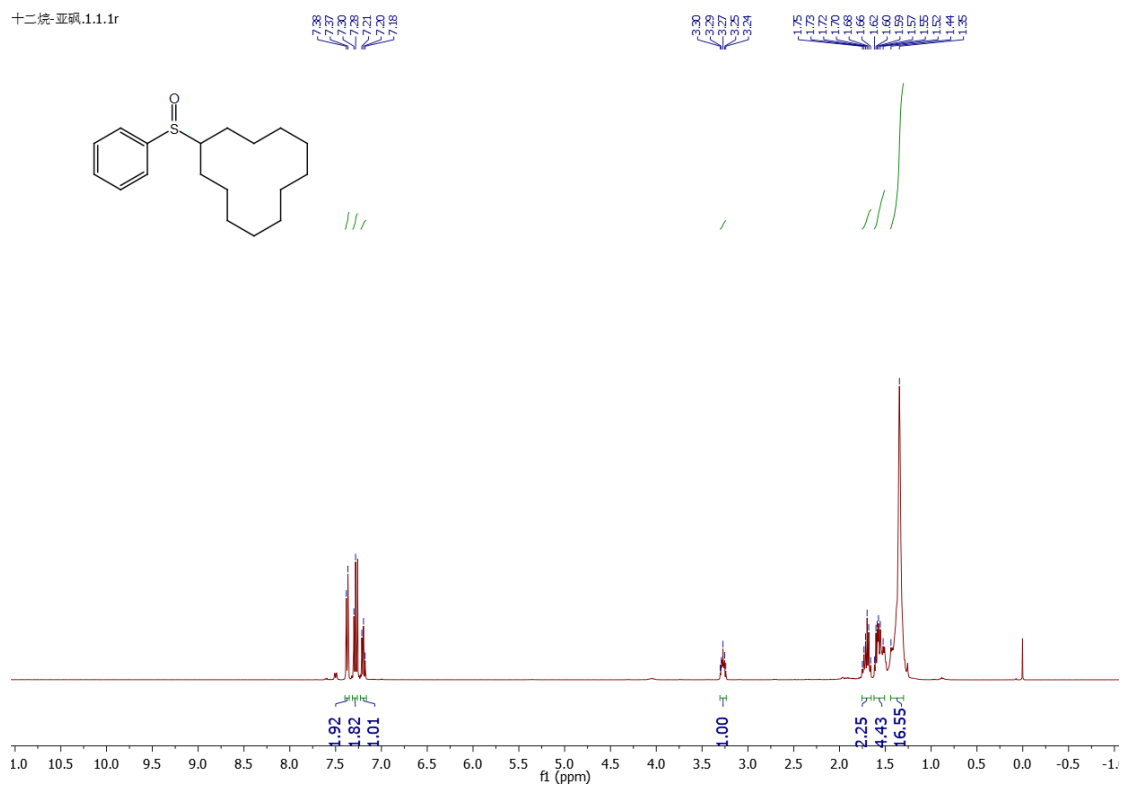
<sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>, 23 °C) of **4d**

zn-y5-hc.2.1.1r



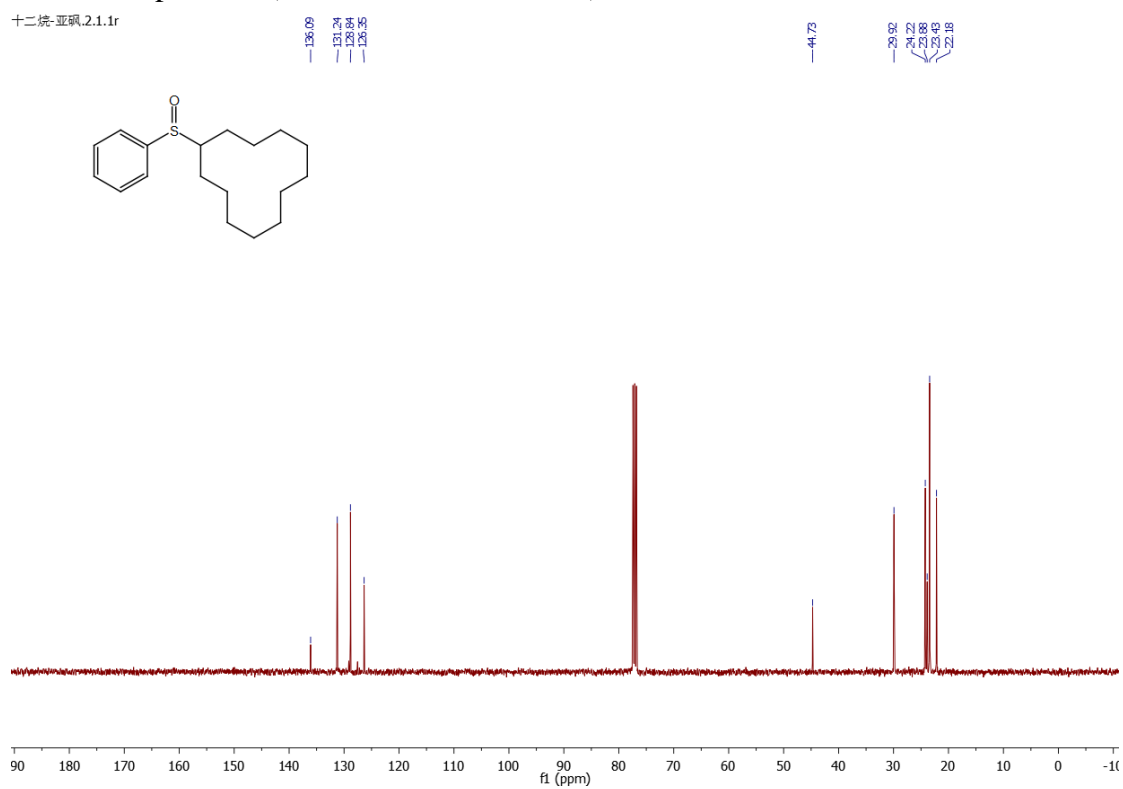
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 23 °C) of **4e**

十二烷-亚磺.1.1.1r



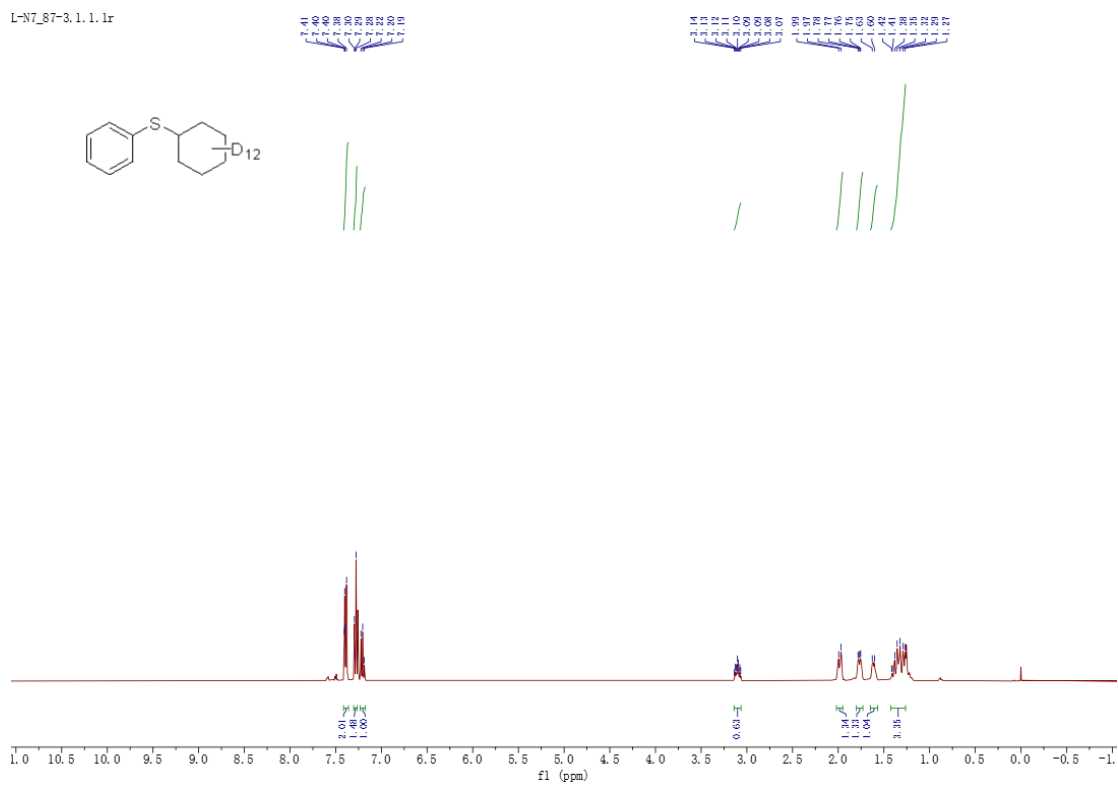
<sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>, 23 °C) of **4e**

十二烷-亚磺.2.1.1r



<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 23 °C) of **3a** and **3a-d<sub>11</sub>**

L-N7\_87-3.1.1.1r



$^{13}C$  NMR spectrum (400 MHz,  $CDCl_3$ , 23 °C) of **3a** and **3a-d<sub>11</sub>**

L-N7\_87-3.2.1.1r

