

## Supporting Information

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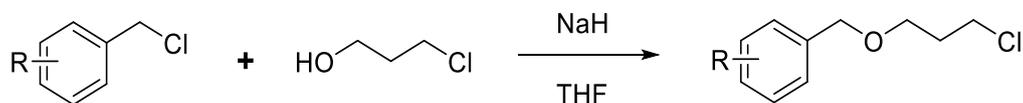
## General Information

Unless otherwise noted, all chemicals used in the preparations of starting materials and in the nickel-catalyzed sulfonylation were commercially available and were used as received without further purifications. All catalytic reactions were carried out under nitrogen in reaction tubes. Column chromatography purifications were carried out using 200-300 mesh silica gel. The eluents for column chromatography and PTLC were presented as ratios of solvent volumes. Nuclear Magnetic Resonance spectra were recorded on a Bruker 400 MHz (100 MHz and 376 MHz for  $^{13}\text{C}$  and  $^{19}\text{F}$ , respectively) instruments at ambient temperature. All  $^1\text{H}$  NMR spectra were measured in part per million (ppm) relative to the signals of tetramethylsilane (TMS, 0.00 ppm) added into the deuterated chloroform ( $\text{CDCl}_3$ , 7.26 ppm) unless otherwise stated. Data for  $^1\text{H}$  NMR were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, and br = broad signal), coupling constants, and integration. All  $^{13}\text{C}$  NMR spectra were reported in ppm relative to tetramethylsilane (0.00 ppm) unless otherwise stated, and were obtained with complete  $^1\text{H}$  decoupling. All GC analyses were performed on a Shimadzu GC-2014C with an FID detector. All GC-MS analyses were performed on a Shimadzu GCMS-QP2020NX. High-resolution mass spectra (HRMS) by electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI), and atmospheric pressure photoionization (APPI) method were performed at the EPFL ISIC Mass Spectroscopy Service.

## Preparation of Alkyl Chlorides

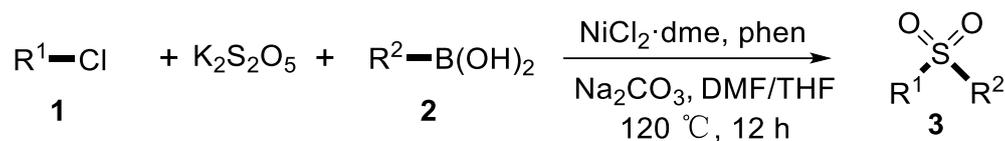
Substrates **1g**<sup>[1]</sup>, **1o**<sup>[2]</sup>, **1p**<sup>[2]</sup>, **1r**<sup>[2]</sup> and **1s**<sup>[2]</sup> were synthesized via known method. **1l**<sup>[2]</sup>, **1q**<sup>[2]</sup>, **1t**<sup>[2]</sup>, **1h**<sup>[3]</sup> and **1u** - **1w**<sup>[3]</sup> were prepared by methods described in the references.

### Preparation of Alkyl Chlorides **1i-1k**, **1m** and **1n**



A flame-dried flask was charged with benzyl chloride (5.0 mmol), 3-Chloro-1-propanol (0.52 g, 5.5 mmol, 1.1 equiv.), and DMF (10 mL) under nitrogen protection. NaH (241 mg (60 % dispersion in mineral oil), 10 mmol, 2 equiv.) was added in batches at 0 °C, and the mixture was stirred for 2 hours. Then the mixture was allowed to warm to room temperature, and stirred for 4h after being added with NaH (0.5 mmol). The mixture was then quenched with ice water and extracted with ethyl acetate (3 x 25 mL). The combined organic phase was washed with water, and brine and dried with anhydrous  $\text{Na}_2\text{SO}_4$ , concentrated in vacuum. Purification by column chromatography affords desired product.

## General Procedure for Nickel-Catalyzed Sulfonation



An oven-dried 15 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was sequentially charged with phenylboronic acids **2** (1.2 equiv.), K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> (1.1 equiv.), Na<sub>2</sub>CO<sub>3</sub> (0.5 equiv.), NiCl<sub>2</sub>·dme (10 mol%), 1,10-phenanthroline (15 mol%) in the glovebox. Then 1.5 mL DMF and 0.5 mL THF, alkyl chlorides **1** (0.2 mmol) were added into the tube in turn. All these procedures were conducted in the glovebox. The vial was sealed with a screw cap and removed from the glove box. Then the vial was placed on a heating base and irradiated at 120 °C for 12 h. After that, the vial was removed from the heating source and cooled to room temperature. The crude reaction mixture was then diluted with water (20 mL) and subsequently extracted with ethyl acetate (EA, 3 x 10 mL). The organic fractions were combined, washed with brine (1 x 10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The crude product residue was purified by flash column chromatography using a solvent mixture (EA, petroleum ether) as an eluent to afford the purified product.

## Summary of the effects of reaction parameters and conditions on the reaction efficiency

Table S1. Screening of Solvents

Entry	Solvent	3a Yield (%) <sup>a</sup>	5 Yield (%) <sup>a</sup>
1	DMF 2 mL	75	9
2	DMA 2 mL	45	4
3	DMSO 2 mL	20	N.D.
4	NMP 2 mL	73	8
5	MeCN 2 mL	33	Trace
6	DCE 2 mL	Trace	N.D.
7	DMF/THF 1.5/0.5 mL	81	12
8	DMF/dioxane 1.5/0.5 mL	79	9

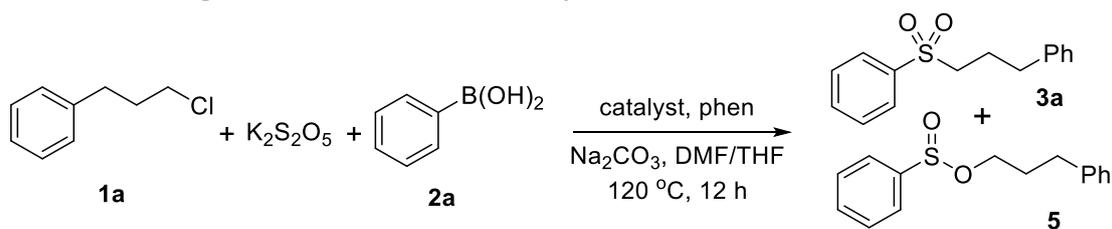
Reaction conditions: **1a** (0.2 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> (1.1 eq.), **2a** (1.5 eq.), NiCl<sub>2</sub>·dme (10 mol%), 1,10-phenanthroline (15 mol%), Na<sub>2</sub>CO<sub>3</sub> (2 eq.) and solvent, 12 h, 120 °C. [a] The yields were detected by GC using naphthalene as an internal standard.

Table S2. Screening of Temperatures

Entry	T / °C	3a Yield (%) <sup>a</sup>	5 Yield (%) <sup>a</sup>
1	100	40	5
2	110	56	7
3	120	78	9

Reaction conditions: **1a** (0.2 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> (1.1 eq.), **2a** (1.5 eq.), NiCl<sub>2</sub>·dme (10 mol%), 1,10-phenanthroline (15 mol%), Na<sub>2</sub>CO<sub>3</sub> (2 eq.) and DMF/THF (1.5/0.5 mL), 12 h, T. [a] The yields were detected by GC using naphthalene as an internal standard.

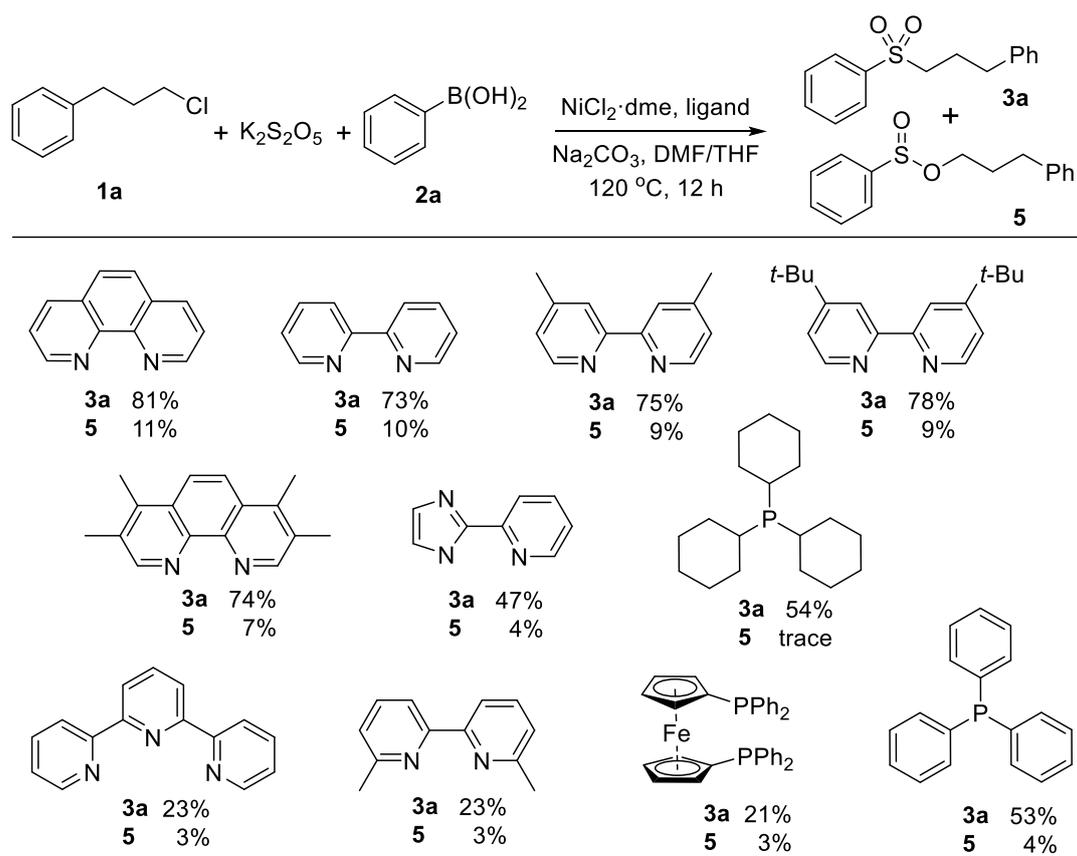
Table S3. Screening of Transition Metal Catalysts



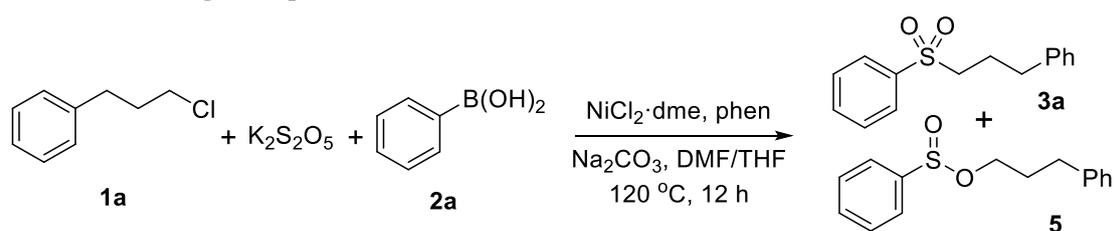
Entry	Catalyst	<b>3a</b> Yield (%) <sup>a</sup>	<b>5</b> Yield (%) <sup>a</sup>
1	$NiCl_2$	82	11
2	$NiCl_2 \cdot dme$	84	11
3	$NiBr_2$	63	7
4	$NiBr_2 \cdot dme$	30	N.D.
5	$NiI_2$	35	N.D.
6	$Ni(acac)_2$	14	2
7	$Co(OAc)_2$	33	3
8	$CoBr_2$	59	2
9	$Cu(OAc)_2$	28	3
10	$CuBr_2$	7	trace
8	$FeBr_3$	36	trace

Reaction conditions: **1a** (0.2 mmol),  $K_2S_2O_5$  (1.1 eq.), **2a** (1.5 eq.), catalyst (10 mol%), 1,10-phenanthroline (15 mol%),  $Na_2CO_3$  (2 eq.) and DMF/THF (1.5/0.5 mL), 12 h,  $120\text{ }^\circ\text{C}$ . [a] The yields were detected by GC using naphthalene as an internal standard.

Table S4. Screening of Ligands

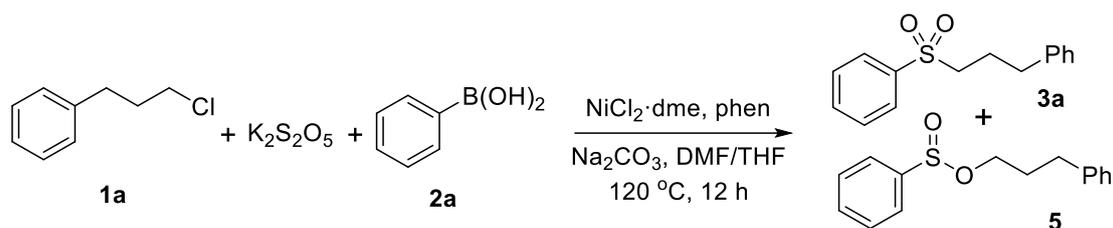


Reaction conditions: **1a** (0.2 mmol),  $K_2S_2O_5$  (1.1 eq.), **2a** (1.5 eq.),  $NiCl_2 \cdot dme$  (10 mol%), ligand (15 mol%),  $Na_2CO_3$  (2 eq.) and DMF/THF (1.5 mL/0.5 mL), 12 h,  $120\text{ }^\circ\text{C}$ . [a] The yields were detected by GC using naphthalene as an internal standard.

Table S5. Screening of Equivalent of  $K_2S_2O_5$ 

Entry	The amount of $K_2S_2O_5$	<b>3a</b> Yield (%) <sup>a</sup>	<b>5</b> Yield (%) <sup>a</sup>
1	1 eq.	66	7
2	1.1 eq.	80	10
3	1.2 eq.	78	9
4	1.5 eq.	79	7

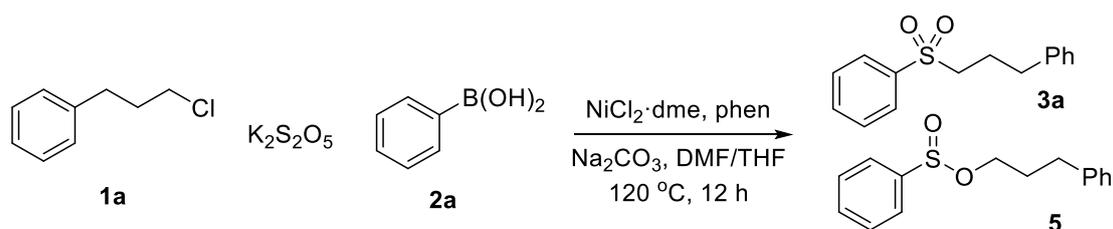
Reaction conditions: **1a** (0.2 mmol),  $K_2S_2O_5$ , **2a** (1.5 eq.),  $NiCl_2 \cdot dme$  (10 mol%), 1,10-phenanthroline (15 mol%),  $Na_2CO_3$  (2 eq.) and DMF/THF (1.5/0.5 mL), 12 h,  $120\text{ }^\circ\text{C}$ . [a] The yields were detected by GC using naphthalene as an internal standard.

Table S6. Screening of Equivalent of **2a**

Entry	The amount of <b>2a</b>	<b>3a</b> Yield (%) <sup>a</sup>	<b>5</b> Yield (%) <sup>a</sup>
1	1 eq.	75	8
2	1.2 eq.	80	10
3	1.5 eq.	83	10

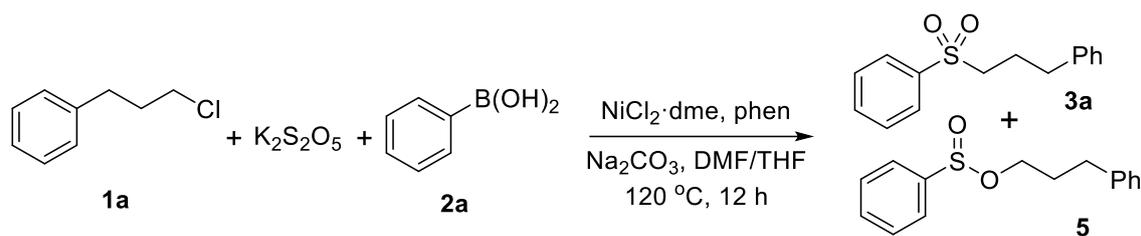
Reaction conditions: **1a** (0.2 mmol),  $\text{K}_2\text{S}_2\text{O}_5$ , **2a** (1.5 eq.),  $\text{NiCl}_2 \cdot \text{dme}$  (10 mol%), 1,10-phenanthroline (15 mol%),  $\text{Na}_2\text{CO}_3$  (2 eq.) and DMF/THF (1.5/0.5 mL), 12 h,  $120\text{ }^\circ\text{C}$ . [a] The yields were detected by GC using naphthalene as an internal standard.

Table S7. Screening of Bases



Entry	Base	<b>3a</b> Yield (%) <sup>a</sup>	<b>5</b> Yield (%) <sup>a</sup>
1	$\text{Na}_2\text{CO}_3$	81	6
2	$\text{K}_2\text{CO}_3$	78	9
3	$\text{Cs}_2\text{CO}_3$	66	8
4	KF	66	5
5	KI	46	Trace
6	NaI	46	Trace
7	<sup>t</sup> BuOLi	39	2
8	<sup>t</sup> BuONa	4	n.d.
9	<sup>t</sup> BuOK	17	Trace

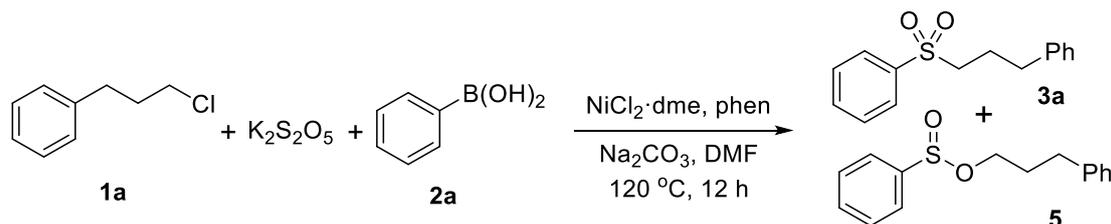
Reaction conditions: **1a** (0.2 mmol),  $\text{K}_2\text{S}_2\text{O}_5$ , **2a** (1.5 eq.),  $\text{NiCl}_2 \cdot \text{dme}$  (10 mol%), 1,10-phenanthroline (15 mol%), base (2 eq.) and DMF/THF (1.5/0.5 mL), 12 h,  $120\text{ }^\circ\text{C}$ . [a] The yields were detected by GC using naphthalene as an internal standard.

Table S8. Screening of Equivalent of Na<sub>2</sub>CO<sub>3</sub>

Entry	The amount of Na <sub>2</sub> CO <sub>3</sub>	<b>3a</b> Yield (%) <sup>a</sup>	<b>5</b> Yield (%) <sup>a</sup>
1	2 equiv	81	9
2	1.5 equiv	79	10
3	1 equiv	80	8
4	0.5 equiv	84(82 <sup>b</sup> )	7

Reaction conditions: **1a** (0.2 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>5</sub>, **2a** (1.5 eq.), NiCl<sub>2</sub>·dme (10 mol%), 1,10-phenanthroline (15 mol%), Na<sub>2</sub>CO<sub>3</sub> and DMF/THF (1.5/0.5 mL), 12 h, 120 °C. [a] The yields were detected by GC using naphthalene as an internal standard. [b] Isolated yield.

Table S9. Screening of Reaction Conditions



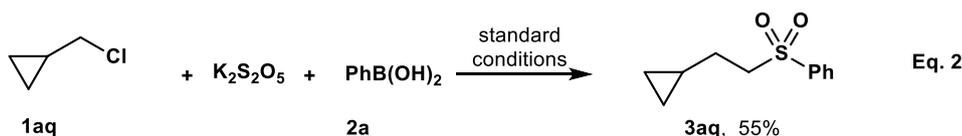
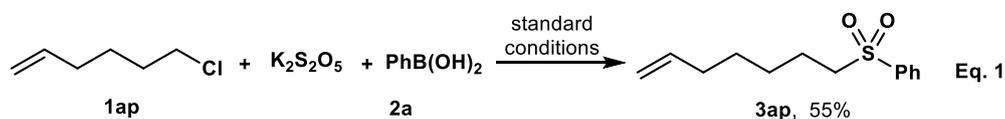
Entry	Deviation from standard conditions	<b>3a</b> Yield (%) <sup>a</sup>	<b>5</b> Yield (%) <sup>a</sup>
1	None	80	9
2	No [Ni]	8	2
3	No 1,10-phenanthroline	36	4
4	No Na <sub>2</sub> CO <sub>3</sub>	69	5

The standard reaction conditions: **1a** (0.2 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> (1.1 eq.), **2a** (1.5 eq.), NiCl<sub>2</sub>·dme (10 mol%), 1,10-phenanthroline (15 mol%), Na<sub>2</sub>CO<sub>3</sub> (2 eq.) and DMF (2 mL), 12 h, 120 °C. [a] The yields were detected by GC using naphthalene as an internal standard.

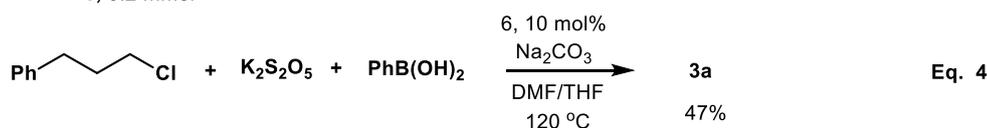
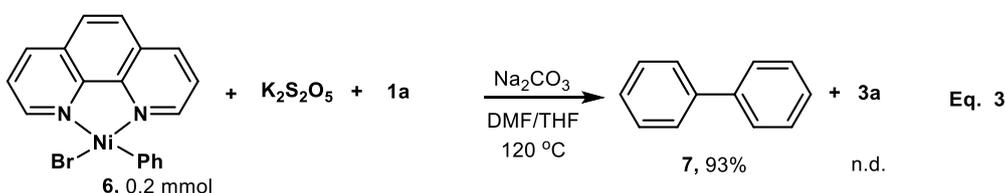
## Control Experiments

Figure S1. Control Experiments

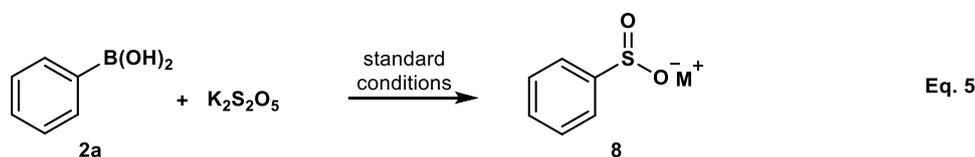
### 1) Reaction of radical clock



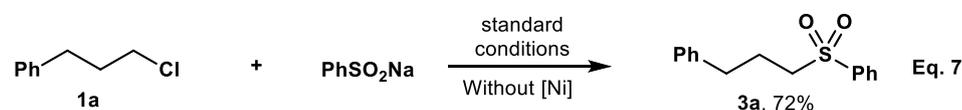
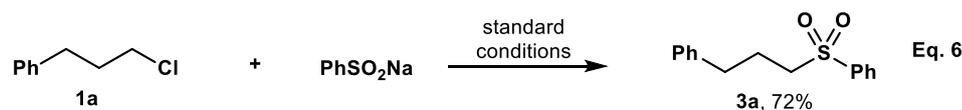
### 2) Pre-synthesis of intermediate **A**



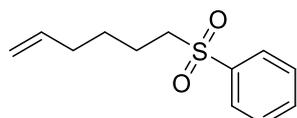
### 3) Aryl sulfinate intermediate trapping experiment



### 4) Alkylation of sodium benzenesulfite



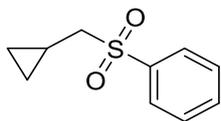
**Equation 1** followed the General Procedure using 6-Chloro-1-hexene (0.2 mmol) and **2a** (1.2 equiv.) as the substrate. After purification, the isolated yield of **3ap** was 55%.



(hex-5-en-1-ylsulfonyl)benzene<sup>[4]</sup> (**3ap**). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.92 – 7.89 (m, 2H), 7.68 – 7.64 (m, 1H), 7.59 – 7.55 (m, 2H), 5.76 – 5.66 (m, 1H), 4.99 – 4.92 (m, 2H), 3.11 – 3.07 (m, 2H), 2.06 – 2.00 (m,

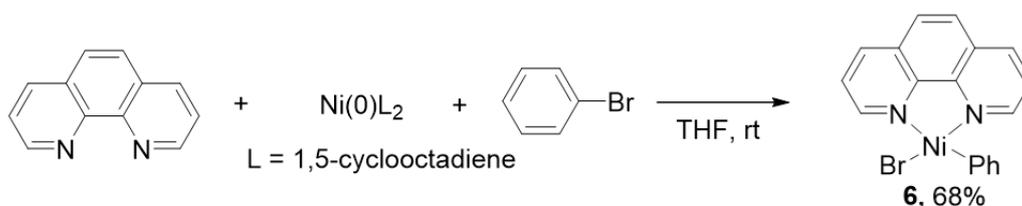
2H), 1.77 – 1.69 (m, 2H), 1.50 – 1.42 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.2, 137.5, 133.7, 129.3, 128.1, 115.4, 56.1, 33.0, 27.4, 22.1.

**Equation 2** followed the General Procedure using (chloromethyl)cyclopropane (0.2 mmol) and **2a** (1.2 equiv.) as the substrate. After purification, the isolated yield of **3aq** was 55%.



**((cyclopropylmethyl)sulfonyl)benzene** <sup>[5]</sup> (**3aq**).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 – 7.92 (m, 2H), 7.67 – 7.63 (m, 1H), 7.58 – 7.54 (m, 2H), 3.01 (d,  $J = 7.2$  Hz, 2H), 1.04 – 0.94 (m, 1H), 0.57 – 0.52 (m, 2H), 0.13 – 0.09 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.3, 133.7, 129.1, 128.4, 61.4, 4.8, 4.4.

The pre-synthesis of nickel catalyst **6**<sup>[6]</sup>:



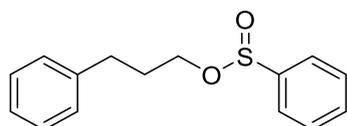
Add phenanthroline (1 mmol), Ni (cod)<sub>2</sub> (1 mmol) and THF (10 mL) to a 50 mL scintillation vial. After stirring the reaction mixture at room temperature for 5 min, add PhBr (1.2 equiv.) and reaction overnight. Concentrate under reduce pressure. Wash the solid several times with dry *n*-pentane and then dry under vacuum for 2 hours to obtain product in 68% yield.

The detection of sulfinate **8**<sup>[7]</sup>:



To a 50 mL Schlenk tube containing phenylboronic acid (**2a**) (0.2 mmol), of NiCl<sub>2</sub>-dme (10 mol%), Na<sub>2</sub>CO<sub>3</sub> (1 equiv), phen (15 mol%), K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> (0.7 equiv), and the tube was purged with N<sub>2</sub> for 3 times, followed by 2 mL of DMF. The resulting mixture was stirred at 120 °C for 16 h. After cooling to room temperature, add ethanol and stir for a while, the mixture was filtered over Celite. The solvent was removed under reduced pressure. Then the remaining solid was extracted and recrystallized by MeCN to get a white solid.  $^1\text{H}$  NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.45 (d,  $J = 7.3$  Hz, 2H), 7.28 (t,  $J = 7.3$  Hz, 2H), 7.21 (t,  $J = 7.2$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  160.1, 128.3, 128.2, 124.7.

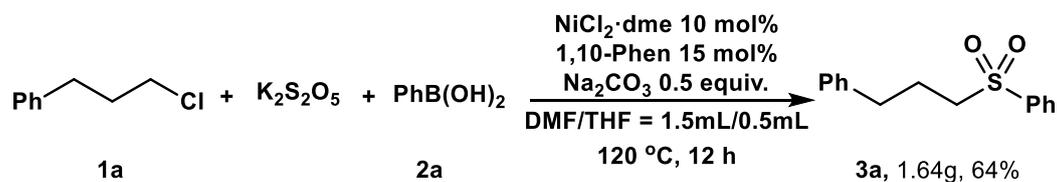
**Equation 6** followed the General Procedure using sodium benzenesulfonate instead of  $K_2S_2O_5$  and **2a** to afford sulfone **3a**. **Equation 7** followed the General Procedure using sodium benzenesulfonate instead of  $K_2S_2O_5$  and **2a** to afford sulfone **3a** under metal-free conditions.



**3-phenylpropyl benzenesulfinate (5):**  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.73 – 7.70 (m, 2H), 7.56 – 7.52 (m, 3H), 7.28 – 7.24 (m, 2H), 7.20 – 7.17 (m, 1H), 7.14 – 7.12 (m, 2H), 4.06 (dt,  $J = 10.0, 6.3$  Hz, 1H), 3.64 (dt,  $J = 10.0, 6.3$  Hz, 1H), 2.69 – 2.65 (m, 2H), 1.98 – 1.91 (m, 2H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  144.5, 140.9, 132.2, 129.1, 128.4, 128.4, 126.0, 125.2, 64.0, 31.9, 31.3.

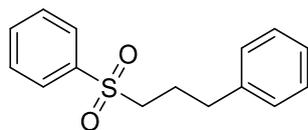
HRMS (ESI/QTOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{15}H_{16}O_2SH^+$  261.0944; Found 261.0949.

### Scale up reaction



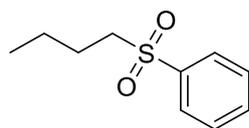
An oven-dried 50 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was sequentially charged with **2a** (1.46 g, 12 mmol, 1.2 equiv.),  $K_2S_2O_5$  (2.44 g, 11 mmol, 1.1 equiv.),  $Na_2CO_3$  (5.3 g, 5 eq, 0.5 equiv.),  $NiCl_2 \cdot dme$  (220 mg, 1 mmol, 10 mol%), 1,10-phenanthroline (252 mg, 1.45 mmol, 15 mol%) under  $N_2$  atmosphere (glovebox). Then 15 mL DMF and 5 mL THF, **1a** (1.54 g, 10 mmol) were added into the tube via syringes in turn. The tube was capped with a pressure screw cap. Then the tube was placed on a heating base and irradiated at 120 °C for 12 h. After which time the tube was removed from the heating source. The crude reaction mixture was then diluted with water, and subsequently extracted with EtOAc (3 x 30 mL). The organic fractions were combined, washed with brine (1 x 30 mL), dried over  $Na_2SO_4$ , filtered, and concentrated under reduced pressure. The crude product residue was purified by flash column chromatography (silica gel; petroleum ether/ethyl acetate), giving the corresponding products **3a** (1.64 g) in 64% yield.

## Analytical Data of Substrates and Products



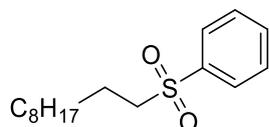
**((3-phenylpropyl)sulfonyl)benzene<sup>[8]</sup> (3a)**: The product was purified by silica gel column chromatography, using petroleum ether/EA = 10/1 (v/v) as an eluent. White solid in 82% yield.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.89 – 7.86 (m, 2H), 7.67 – 7.62 (m, 1H), 7.57 – 7.53 (m, 2H), 7.28 – 7.24 (m, 2H), 7.21 – 7.17 (m, 1H), 7.10 – 7.08 (m, 2H), 3.09 – 3.05 (m, 2H), 2.69 (t, J = 7.4 Hz, 2H), 2.08 – 2.00 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 139.9, 139.1, 133.7, 129.3, 128.7, 128.4, 128.1, 126.5, 55.5, 34.1, 24.2.



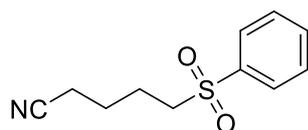
**(butylsulfonyl)benzene<sup>[9]</sup> (3b)**: The product was purified by silica gel column chromatography, using petroleum ether/EA = 20/1 (v/v) as an eluent. Colorless liquid in 75% yield.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.93 – 7.90 (m, 2H), 7.68 – 7.64 (m, 1H), 7.60 – 7.55 (m, 2H), 3.11 – 3.07 (m, 2H), 1.73 – 1.65 (m, 2H), 1.44 – 1.34 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 139.3, 133.7, 129.4, 128.1, 56.2, 24.7, 21.6, 13.6.



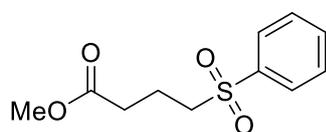
**(decylsulfonyl)benzene<sup>[8]</sup> (3c)**: The product was purified by silica gel column chromatography, using petroleum ether/EA = 20/1 (v/v) as an eluent. Colorless liquid in 68% yield.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.92 – 7.90 (m, 2H), 7.67 – 7.64 (m, 1H), 7.59 – 7.55 (m, 2H), 3.10 – 3.06 (m, 2H), 1.74 – 1.66 (m, 2H), 1.36 – 1.22 (m, 14H), 0.87 (t, J = 6.8 Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 139.2, 133.6, 129.3, 128.1, 56.3, 31.9, 29.4, 29.2, 29.0, 28.3, 22.7 (d, J = 2.7 Hz), 14.1.



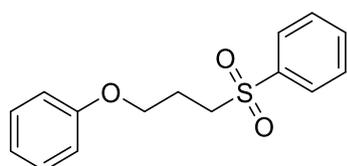
**5-(phenylsulfonyl)pentanenitrile**<sup>[10]</sup> (**3d**): The product was purified by silica gel column chromatography, using petroleum ether/EA = 20/1 (v/v) as an eluent. Colorless liquid in 72% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.91 – 7.88 (m, 2H), 7.69 – 7.64 (m, 1H), 7.60 – 7.55 (m, 2H), 3.14 – 3.10 (m, 2H), 2.39 – 2.34 (m, 2H), 1.90 – 1.76 (m, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.7, 134.0, 129.5, 128.0, 118.9, 55.2, 24.1, 22.0, 16.9.



**methyl-4-(phenylsulfonyl)butanoate**<sup>[8]</sup> (**3e**): The product was purified by silica gel column chromatography, using petroleum ether/EA = 10/1 (v/v) as an eluent. Colorless liquid in 74% yield.

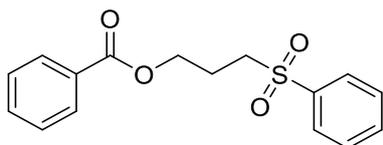
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.96 – 7.93 (m, 2H), 7.72 – 7.67 (m, 1H), 7.62 – 7.58 (m, 2H), 3.68 (s, 3H), 3.23 – 3.19 (m, 2H), 2.49 (t, J = 7.1 Hz, 2H), 2.09 – 2.02 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 172.6, 138.9, 133.9, 129.4, 128.1, 55.1, 51.8, 32.0, 18.3.



**((3-phenoxypropyl)sulfonyl)benzene** (**3f**): The product was purified by silica gel column chromatography, using petroleum ether/EA = 10/1 (v/v) as an eluent. Colorless liquid in 73% yield.

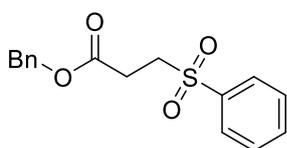
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.72 – 7.66 (m, 2H), 7.54 – 7.48 (m, 3H), 7.26 – 7.21 (m, 2H), 7.17 – 7.09 (m, 3H), 4.04 (dt, J = 9.9, 6.3 Hz, 1H), 3.61 (dt, J = 9.9, 6.3 Hz, 1H), 2.69 – 2.58 (m, 2H), 1.96 – 1.89 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 144.7, 141.0, 132.2, 129.1, 128.5, 126.1, 125.3, 63.9, 31.9, 31.4.

HRMS (ESI/QTOF) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>16</sub>O<sub>3</sub>SNa<sup>+</sup> 299.0712; Found 299.0713.



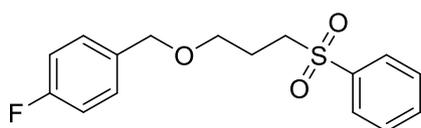
**3-(phenylsulfonyl)propyl benzoate**<sup>[11]</sup> (**3g**): The product was purified by silica gel column chromatography, using petroleum ether/EA = 10/1 (v/v) as an eluent. White solid in 77% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.98 – 7.92 (m, 4H), 7.68 – 7.64 (m, 1H), 7.59 – 7.54 (m, 3H), 7.45 – 7.41 (m, 2H), 4.37 (t, J = 6.2 Hz, 2H), 3.29 – 3.25 (m, 2H), 2.24 – 2.17 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.2, 138.8, 134.0, 133.3, 129.7, 129.6, 129.5, 128.5, 128.1, 62.5, 53.3, 22.6.



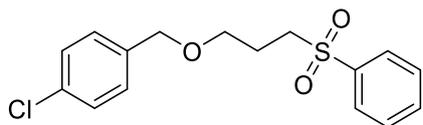
**benzyl-3-(phenylsulfonyl)propanoate**<sup>[12]</sup> (**3h**): The product was purified by silica gel column chromatography, using petroleum ether/EA = 10/1 (v/v) as an eluent. White solid in 61% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.90 – 7.88 (m, 2H), 7.68 – 7.63 (m, 1H), 7.55 (t, J = 7.7 Hz, 2H), 7.38 – 7.29 (m, 5H), 5.06 (s, 2H), 3.46 – 3.42 (m, 2H), 2.80 – 2.77 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 169.9, 138.4, 135.2, 134.1, 129.5, 128.7, 128.6, 128.4, 128.2, 67.2, 51.5, 27.9.



**1-fluoro-4-((3-(phenylsulfonyl)propoxy)methyl)benzene** (**3i**): The product was purified by silica gel column chromatography, using petroleum ether/EA = 10/1 (v/v) as an eluent. White solid in 62% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.91 – 7.89 (m, 2H), 7.67 – 7.63 (m, 1H), 7.58 – 7.54 (m, 2H), 7.26 – 7.21 (m, 2H), 7.04 – 6.99 (m, 2H), 4.39 (s, 2H), 3.51 (t, J = 5.9 Hz, 2H), 3.23 – 3.20 (m, 2H), 2.04 – 1.98 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 162.4 (d, J = 245.8 Hz), 139.1, 133.8, 133.7 (d, J = 3.2 Hz), 129.4 (d, J = 8.1 Hz), 129.3, 128.1, 115.3 (d, J = 21.4 Hz), 72.3, 67.8, 53.5, 23.4. <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -114.43. HRMS (ESI/QTOF) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>17</sub>FO<sub>3</sub>SNa<sup>+</sup> 331.0775; Found 331.0769.

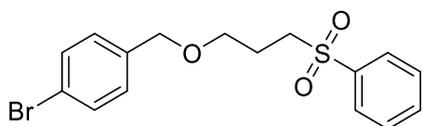


**1-chloro-4-((3-(phenylsulfonyl)propoxy)methyl)benzene (3j):** The product was purified by silica gel column chromatography, using petroleum ether/EA = 10/1 (v/v) as an eluent. White solid in 62% yield.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.92 – 7.89 (m, 2H), 7.68 – 7.64 (m, 1H), 7.58 – 7.54 (m, 2H), 7.31 – 7.27 (m, 2H), 7.21 – 7.18 (m, 2H), 4.40 (s, 2H), 3.51 (t, J = 6.0 Hz, 2H), 3.24 – 3.20 (m, 2H), 2.05 – 1.98 (m, 2H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 139.1, 136.4, 133.8, 133.5, 129.3, 129.0, 128.6, 128.1, 72.2, 67.9, 53.5, 23.4.

HRMS (ESI/QTOF) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>17</sub>ClO<sub>3</sub>SNa<sup>+</sup> 347.0479; Found 347.0479.

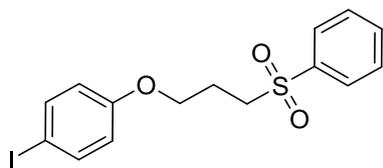


**1-bromo-4-((3-(phenylsulfonyl)propoxy)methyl)benzene (3k):** The product was purified by silica gel column chromatography, using petroleum ether/EA = 10/1 (v/v) as an eluent. White solid in 58% yield.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.91 – 7.88 (m, 2H), 7.67 – 7.63 (m, 1H), 7.58 – 7.54 (m, 2H), 7.46 – 7.42 (m, 2H), 7.15 – 7.11 (m, 2H), 4.37 (s, 2H), 3.50 (t, J = 6.0 Hz, 2H), 3.23 – 3.19 (m, 2H), 2.04 – 1.97 (m, 2H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 139.1, 137.0, 133.8, 131.6, 129.4, 129.3, 128.1, 121.6, 72.2, 67.9, 53.5, 23.4.

HRMS (ESI/QTOF) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>17</sub>BrO<sub>3</sub>SNa<sup>+</sup> 390.9974; Found 390.9976.

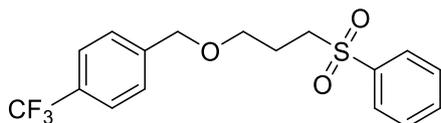


**1-iodo-4-(3-(phenylsulfonyl)propoxy)benzene (3l):** The product was purified by silica gel column chromatography, using petroleum ether/EA = 8/1 (v/v) as an eluent. White solid in 44% yield.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.93 – 7.91 (m, 2H), 7.68 – 7.64 (m, 1H), 7.59 – 7.54 (m, 1H), 7.53 – 7.49 (m, 2H), 6.61 – 6.57 (m, 2H), 3.99 – 3.96 (m, 2H), 3.31 – 3.27 (m, 2H), 2.24 – 2.17 (m, 2H).

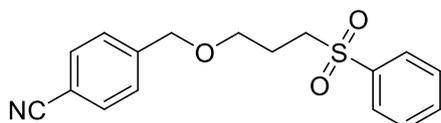
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 158.2, 139.0, 138.3, 133.9, 129.4, 128.0, 116.8, 83.3, 65.5, 53.2, 22.9.

HRMS (ESI/QTOF) m/z: [M + H]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>15</sub>IO<sub>3</sub>SH<sup>+</sup> 402.9859; Found 402.9858.



**1-((3-(phenylsulfonyl)propoxy)methyl)-4-(trifluoromethyl)benzene (3m):** The product was purified by silica gel column chromatography, using petroleum ether/EA = 8/1 (v/v) as an eluent. White solid in 61% yield.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 – 7.89 (m, 2H), 7.68 – 7.63 (m, 1H), 7.59 – 7.54 (m, 4H), 7.37 (d,  $J = 7.9$  Hz, 2H), 4.49 (s, 2H), 3.55 (t,  $J = 6.0$  Hz, 2H), 3.25 – 3.22 (m, 2H), 2.08 – 2.01 (m, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.0, 139.1, 133.8, 129.9 (d,  $J = 32.2$  Hz), 129.4, 128.1, 127.5, 125.4 (q,  $J = 3.8$  Hz), 72.2, 68.1, 53.4, 23.3.  $^{19}\text{F NMR}$  (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.36.

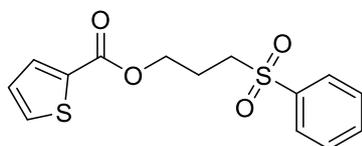
HRMS (ESI/QTOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{17}\text{H}_{17}\text{F}_3\text{O}_3\text{SNa}^+$  381.0743; Found 381.0733.



**4-((3-(phenylsulfonyl)propoxy)methyl)benzonitrile (3n):** The product was purified by silica gel column chromatography, using petroleum ether/EA = 4/1 (v/v) as an eluent. White solid in 47% yield.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 – 7.89 (m, 2H), 7.68 – 7.55 (m, 5H), 7.37 (d,  $J = 8.0$  Hz, 2H), 4.52 (s, 2H), 3.56 (t,  $J = 5.9$  Hz, 2H), 3.25 – 3.21 (m, 2H), 2.08 – 2.01 (m, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  143.5, 139.0, 133.8, 132.3, 129.4, 128.0, 127.7, 118.8, 111.4, 72.0, 68.3, 53.4, 23.3.

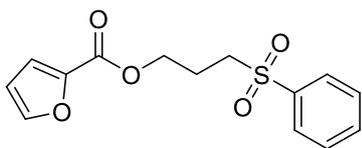
HRMS (ESI/QTOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{17}\text{H}_{17}\text{NO}_3\text{SNa}^+$  338.0821; Found 338.0830.



**3-(phenylsulfonyl)propyl thiophene-2-carboxylate (3o):** The product was purified by silica gel column chromatography, using petroleum ether/EA = 10/1 (v/v) as an eluent. White oil in 42% yield.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 – 7.92 (m, 2H), 7.76 (dd,  $J = 3.8, 1.3$  Hz, 1H), 7.69 – 7.65 (m, 1H), 7.60 – 7.56 (m, 3H), 7.11 – 7.09 (m, 1H), 4.35 (t,  $J = 6.2$  Hz, 2H), 3.27 – 3.23 (m, 2H), 2.22 – 2.15 (m, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.9, 138.8, 134.0, 133.8, 133.1, 132.9, 129.5, 128.1, 127.9, 62.7, 53.2, 22.7.

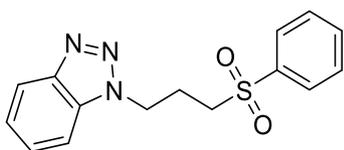
HRMS (ESI/QTOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{14}\text{H}_{14}\text{O}_4\text{S}_2\text{Na}^+$  333.0226; Found 333.0223.



**3-(phenylsulfonyl)propyl furan-2-carboxylate (3p):** The product was purified by silica gel column chromatography, using petroleum ether/EA = 10/1 (v/v) as an eluent. White oil in 56% yield.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.93 – 7.90 (m, 2H), 7.68 – 7.64 (m, 1H), 7.59 – 7.55 (m, 3H), 7.15 (dd, J = 3.5, 0.8 Hz, 1H), 6.50 (dd, J = 3.5, 1.8 Hz, 1H), 4.35 (t, J = 6.2 Hz, 2H), 3.26 – 3.22 (m, 2H), 2.21 – 2.14 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 158.3, 146.6, 144.1, 138.8, 134.0, 129.5, 128.1, 118.4, 112.0, 62.4, 53.1, 22.6.

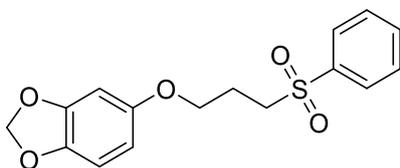
HRMS (ESI/QTOF) m/z: [M + H]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>14</sub>O<sub>5</sub>SH<sup>+</sup> 295.0635; Found 295.0628.



**1-(3-(phenylsulfonyl)propyl)-1H-benzo[d][1,2,3]triazole (3q):** The product was purified by silica gel column chromatography, using petroleum ether/EA = 10/1 (v/v) as an eluent. White solid in 42% yield.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.90 – 7.87 (m, 2H), 7.84 – 7.80 (m, 2H), 7.66 – 7.62 (m, 1H), 7.56 – 7.52 (m, 2H), 7.41 – 7.36 (m, 2H), 4.84 (t, J = 6.5 Hz, 2H), 3.22 – 3.18 (m, 2H), 2.58 – 2.51 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 144.4, 138.7, 134.0, 129.4, 128.1, 126.6, 118.0, 54.5, 53.3, 23.4.

HRMS (ESI/QTOF) m/z: [M + H]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>SH<sup>+</sup> 302.0958; Found 302.0958.

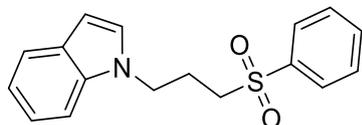


**5-(3-(phenylsulfonyl)propoxy)benzo[d][1,3]dioxole (3r):** The product was purified by silica gel column chromatography, using petroleum ether/EA = 8/1 (v/v) as an eluent. White solid in 64% yield.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.94 – 7.92 (m, 2H), 7.68 – 7.64 (m, 1H), 7.59 – 7.55 (m, 2H), 6.66 (d, J = 8.5 Hz, 1H), 6.40 (d, J = 2.5 Hz, 1H), 6.23 (dd, J = 8.5, 2.5 Hz, 1H), 5.89 (s, 2H), 3.93 (t, J = 5.8 Hz, 2H), 3.31 – 3.28 (m, 2H), 2.21 – 2.14 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 153.8, 148.3, 142.0, 139.0, 133.8,

129.4, 128.1, 108.0, 105.7, 101.2, 98.1, 66.4, 53.3, 23.0.

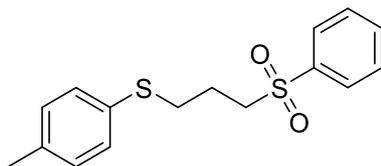
HRMS (ESI/QTOF) m/z:  $[M + Na]^+$  Calcd for  $C_{16}H_{16}O_5SNa^+$  343.0611; Found 343.0618.



**1-(3-(phenylsulfonyl)propyl)-1H-indole (3s):** The product was purified by silica gel column chromatography, using petroleum ether/EA = 10/1 (v/v) as an eluent. White solid in 66% yield.

**$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.85 – 7.83 (m, 2H), 7.65 – 7.60 (m, 2H), 7.54 – 7.50 (m, 2H), 7.29 – 7.25 (m, 1H), 7.20 – 7.16 (m, 1H), 7.12 – 7.05 (m, 2H), 6.49 (d,  $J = 3.1$  Hz, 1H), 4.29 (t,  $J = 6.7$  Hz, 2H), 3.00 – 2.96 (m, 2H), 2.32 – 2.25 (m, 2H).  **$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  138.9, 135.8, 133.9, 129.4, 128.7, 128.0, 127.7, 121.9, 121.2, 119.7, 109.2, 102.0, 53.0, 44.3, 23.6.

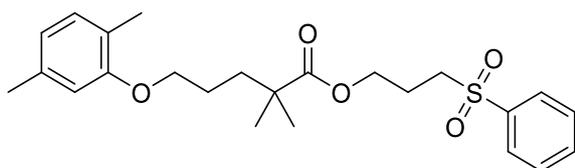
HRMS (ESI/QTOF) m/z:  $[M + H]^+$  Calcd for  $C_{17}H_{17}NO_2SH^+$  300.1053; Found 300.1058.



**(3-(phenylsulfonyl)propyl)(p-tolyl)sulfane (3t):** The product was purified by silica gel column chromatography, using petroleum ether/EA = 15/1 (v/v) as an eluent. White solid in 53% yield.

**$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.88 – 7.86 (m, 2H), 7.68 – 7.63 (m, 1H), 7.57 – 7.53 (m, 2H), 7.19 – 7.17 (m, 2H), 7.06 (d,  $J = 7.9$  Hz, 2H), 3.27 – 3.23 (m, 2H), 2.91 (t,  $J = 6.8$  Hz, 2H), 2.31 (s, 3H), 2.01 – 1.94 (m, 2H).  **$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  139.0, 137.1, 133.8, 131.3, 130.8, 129.9, 129.4, 128.1, 54.6, 33.4, 22.3, 21.1.

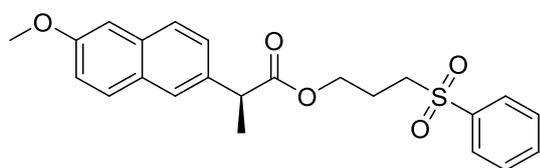
HRMS (ESI/QTOF) m/z:  $[M + H]^+$  Calcd for  $C_{16}H_{18}O_2S_2H^+$  307.0821; Found 307.0829.



**3-(phenylsulfonyl)propyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (3u):** The product was

purified by silica gel column chromatography, using petroleum ether/EA = 5/1 (v/v) as an eluent. White solid in 50% yield.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 – 7.89 (m, 2H), 7.68 – 7.63 (m, 1H), 7.57 – 7.53 (m, 2H), 7.00 (d,  $J = 7.4$  Hz, 1H), 6.67 (d,  $J = 7.4$  Hz, 1H), 6.61 (s, 1H), 4.12 (t,  $J = 6.2$  Hz, 2H), 3.92 – 3.88 (m, 2H), 3.19 – 3.15 (m, 2H), 2.31 (s, 3H), 2.15 (s, 3H), 2.10 – 2.03 (m, 2H), 1.70 – 1.68 (m, 4H), 1.19 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  177.5, 156.9, 138.8, 136.5, 133.9, 130.4, 129.4, 128.1, 123.5, 120.8, 112.0, 67.8, 62.0, 53.2, 42.1, 37.0, 25.2, 25.1, 22.6, 21.4, 15.8.

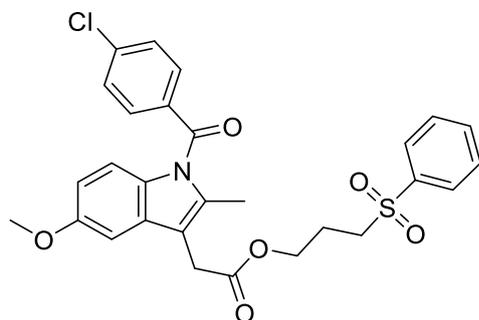
HRMS (ESI/QTOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{24}\text{H}_{32}\text{O}_5\text{SNa}^+$  455.1863; Found 455.1858.



**3-(phenylsulfonyl)propyl (S)-2-(6-methoxynaphthalen-2-yl)propanoate (3v):** The product was purified by silica gel column chromatography, using petroleum ether/EA = 5/1 (v/v) as an eluent. White solid in 56% yield.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 – 7.68 (m, 4H), 7.62 – 7.57 (m, 2H), 7.46 – 7.42 (m, 2H), 7.35 (dd,  $J = 8.5, 1.9$  Hz, 1H), 7.18 – 7.12 (m, 2H), 4.19 – 4.06 (m, 2H), 3.92 (s, 3H), 3.81 (q,  $J = 7.1$  Hz, 1H), 2.95 – 2.91 (m, 2H), 2.02 – 1.95 (m, 2H), 1.54 (d,  $J = 7.1$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.3, 157.7, 138.8, 135.4, 133.7, 129.3, 128.9, 127.8, 127.3, 126.0, 125.9, 119.2, 105.6, 62.2, 55.3, 52.8, 45.3, 22.3, 18.2.

HRMS (ESI/QTOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{23}\text{H}_{24}\text{O}_5\text{SNa}^+$  435.1237; Found 435.1232.

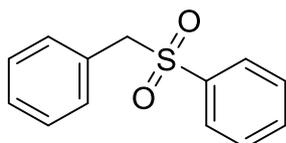


**3-(phenylsulfonyl)propyl-2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (3w):** The product was purified by silica gel column chromatography, using petroleum ether/EA = 3/1 (v/v) as an eluent. White solid in 57% yield.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 – 7.79 (m, 2H), 7.67 – 7.62 (m, 3H), 7.56 – 7.52 (m, 2H), 7.49 – 7.45

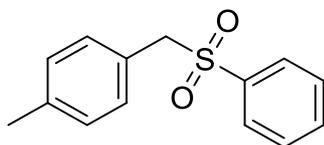
(m, 2H), 6.91 – 6.86 (m, 2H), 6.67 (dd,  $J = 9.0, 2.5$  Hz, 1H), 4.16 (t,  $J = 6.1$  Hz, 2H), 3.81 (s, 3H), 3.64 (s, 2H), 3.03 – 2.99 (m, 2H), 2.35 (s, 3H), 2.07 – 2.01 (m, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.5, 168.3, 156.1, 139.4, 138.8, 136.0, 133.9, 133.8, 131.2, 130.8, 130.5, 129.4, 129.2, 128.0, 115.1, 112.2, 111.7, 101.2, 62.6, 55.7, 53.0, 30.3, 22.4, 13.3.

HRMS (ESI/QTOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{28}\text{H}_{26}\text{ClNO}_6\text{SH}^+$  540.1242; Found 540.1245.



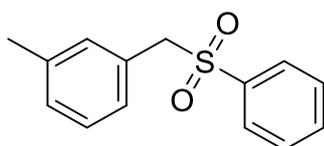
**(benzylsulfonyl)benzene**<sup>[13]</sup> (**3x**): The product was purified by silica gel column chromatography, using petroleum ether/EA = 20/1 (v/v) as an eluent. White solid in 83% yield.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 – 7.58 (m, 3H), 7.44 (t,  $J = 7.8$  Hz, 2H), 7.33 – 7.29 (m, 1H), 7.27 – 7.23 (m, 2H), 7.09 – 7.07 (m, 2H), 4.31 (s, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  137.8, 133.7, 130.8, 128.8, 128.7, 128.6, 128.5, 128.1, 62.8.



**1-methyl-4-((phenylsulfonyl)methyl)benzene**<sup>[8]</sup> (**3y**). The product was purified by silica gel column chromatography, using petroleum ether/EA = 20/1 (v/v) as an eluent. White solid in 87% yield.

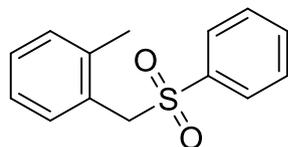
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 – 7.58 (m, 3H), 7.47 – 7.43 (m, 2H), 7.06 (d,  $J = 7.8$  Hz, 2H), 6.96 (d,  $J = 8.1$  Hz, 2H), 4.27 (s, 2H), 2.32 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.7, 138.0, 133.7, 130.7, 129.3, 128.9, 128.7, 125.0, 62.6, 21.2.



**1-methyl-3-((phenylsulfonyl)methyl)benzene**<sup>[14]</sup> (**3z**). The product was purified by silica gel column chromatography, using petroleum ether/EA = 20/1 (v/v) as an eluent. White solid in 86% yield.

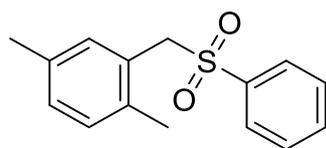
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 – 7.58 (m, 3H), 7.47 – 7.44 (m, 2H), 7.16 – 7.11 (m, 2H), 6.90 (s,

1H), 6.88 – 6.81 (m, 1H), 4.27 (s, 2H), 2.26 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.3, 138.0, 133.7, 131.6, 129.6, 128.9, 128.7, 128.5, 127.9, 127.9, 62.9, 21.3.



**1-methyl-2-((phenylsulfonyl)methyl)benzene**<sup>[15]</sup> (**3aa**). The product was purified by silica gel column chromatography, using petroleum ether/EA = 20/1 (v/v) as an eluent. White solid in 81% yield.

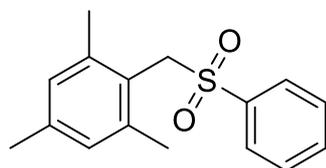
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.66 – 7.60 (m, 3H), 7.46 (t, J = 7.8 Hz, 2H), 7.24 – 7.20 (m, 1H), 7.13 – 7.08 (m, 2H), 7.03 – 7.01 (m, 1H), 4.38 (s, 2H), 2.11 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.3, 138.3, 133.8, 131.9, 130.7, 129.0, 129.0, 128.7, 126.6, 126.1, 60.1, 19.4.



**1,4-dimethyl-2-((phenylsulfonyl)methyl)benzene** (**3ab**). The product was purified by silica gel column chromatography, using petroleum ether/EA = 20/1 (v/v) as an eluent. White solid in 85% yield.

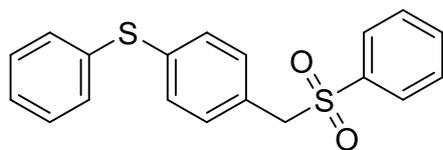
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.67 – 7.60 (m, 3H), 7.56 (t, J = 7.8 Hz, 2H), 7.04 – 6.98 (m, 2H), 6.82 (s, 1H), 4.33 (s, 2H), 2.21 (s, 3H), 2.05 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.4, 135.6, 135.1, 133.8, 132.6, 130.5, 129.7, 128.9, 128.7, 126.2, 60.1, 20.8, 18.9.

HRMS (ESI/QTOF) m/z: [M + H]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>16</sub>O<sub>2</sub>SH<sup>+</sup> 261.0944; Found 261.0953.



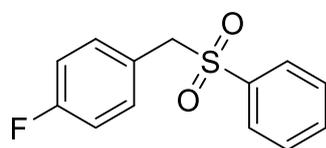
**1,3,5-trimethyl-2-((phenylsulfonyl)methyl)benzene**<sup>[15]</sup> (**3ac**). The product was purified by silica gel column chromatography, using petroleum ether/EA = 20/1 (v/v) as an eluent. White solid in 86% yield;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.78 – 7.76 (m, 2H), 7.67 – 7.63 (m, 1H), 7.53 – 7.49 (m, 2H), 6.85 (s, 2H), 4.47 (s, 2H), 2.27 (s, 3H), 2.17 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 139.6, 139.0, 138.5, 133.8, 129.5, 129.2, 128.5, 122.3, 57.3, 21.0, 20.2.



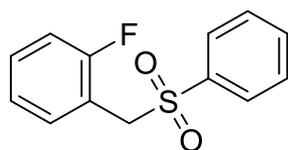
**phenyl(4-((phenylsulfonyl)methyl)phenyl)sulfone**<sup>[16]</sup> (**3ad**). The product was purified by silica gel column chromatography, using petroleum ether/EA = 10/1 (v/v) as an eluent. White solid in 58% yield.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.66 – 7.58 (m, 3H), 7.48 – 7.43 (m, 2H), 7.37 – 7.28 (m, 5H), 7.17 – 7.14 (m, 2H), 7.00 – 6.97 (m, 2H), 4.26 (s, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 137.9, 137.8, 134.4, 133.9, 132.0, 131.5, 130.1, 129.4, 129.0, 128.7, 127.8, 126.4, 62.5.



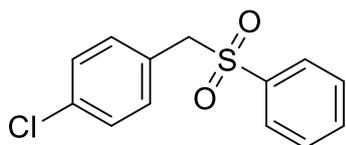
**1-fluoro-4-((phenylsulfonyl)methyl)benzene**<sup>[8]</sup> (**3ae**). The product was purified by silica gel column chromatography, using petroleum ether/EA = 20/1 (v/v) as an eluent. White solid in 79% yield.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.65 – 7.59 (m, 3H), 7.47 (t, J = 7.8 Hz, 2H), 7.07 – 7.04 (m, 2H), 6.97 – 6.93 (m, 2H), 4.28 (s, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 163.1 (d, J = 248.6 Hz), 137.7, 133.9, 132.6 (d, J = 8.4 Hz), 129.1, 128.6, 124.0 (d, J = 3.4 Hz), 115.7 (d, J = 21.8 Hz), 62.0.



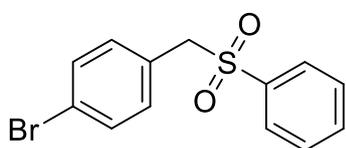
**1-fluoro-2-((phenylsulfonyl)methyl)benzene**<sup>[17]</sup> (**3af**). The product was purified by silica gel column chromatography, using petroleum ether/EA = 20/1 (v/v) as an eluent. White solid in 83% yield.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.68 – 7.60 (m, 3H), 7.46 (t, J = 7.9 Hz, 2H), 7.33 – 7.28 (m, 2H), 7.14 – 7.10 (m, 1H), 6.94 – 6.89 (m, 1H), 4.40 (s, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 161.2 (d, J = 249.8 Hz), 137.9, 133.9, 132.7 (d, J = 2.8 Hz), 131.0 (d, J = 8.3 Hz), 129.0, 128.6, 124.4 (d, J = 3.8 Hz), 115.8 (d, J = 14.6 Hz), 115.5 (d, J = 21.7 Hz), 55.7 (d, J = 2.5 Hz).



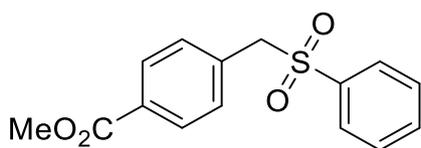
**1-chloro-3-((phenylsulfonyl)methyl)benzene**<sup>[8]</sup> (**3ag**). The product was purified by silica gel column chromatography, using petroleum ether/EA = 20/1 (v/v) as an eluent. White solid in 56% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.66 – 7.61 (m, 3H), 7.48 (t, J = 7.7 Hz, 2H), 7.26 – 7.23 (m, 2H), 7.02 (d, J = 8.4 Hz, 2H), 4.27 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 137.7, 135.1, 134.0, 132.1, 129.1, 128.9, 128.7, 126.7, 62.2.



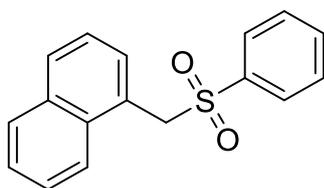
**1-bromo-4-((phenylsulfonyl)methyl)benzene**<sup>[8]</sup> (**3ah**). The product was purified by silica gel column chromatography, using petroleum ether/EA = 20/1 (v/v) as an eluent. White solid in 64% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.66 – 7.61 (m, 3H), 7.50 – 7.46 (m, 2H), 7.42 – 7.38 (m, 2H), 6.97 – 6.94 (m, 2H), 4.26 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 137.7, 134.0, 132.4, 131.9, 129.1, 128.7, 127.2, 123.4, 62.2.



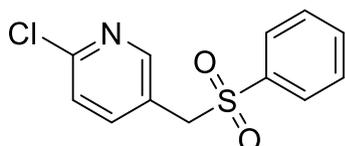
**4-((phenylsulfonyl)methyl)benzoate**<sup>[15]</sup> (**3ai**). The product was purified by silica gel column chromatography, using petroleum ether/EA = 15/1 (v/v) as an eluent. White solid in 60% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93 – 7.90 (m, 2H), 7.63 – 7.59 (m, 3H), 7.47 – 7.43 (m, 2H), 7.15 (d, J = 8.3 Hz, 2H), 4.35 (s, 2H), 3.90 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.6, 137.6, 134.0, 133.1, 130.9, 130.5, 129.8, 129.1, 128.6, 126.5, 62.6, 52.3.



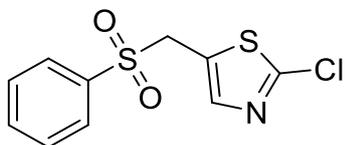
**1-((phenylsulfonyl)methyl)naphthalene<sup>[15]</sup> (3aj)**. The product was purified by silica gel column chromatography, using petroleum ether/EA = 10/1 (v/v) as an eluent White solid in 74% yield.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.84 – 7.81 (m, 3H), 7.61 – 7.59 (m, 2H), 7.54 – 7.50 (m, 1H), 7.47 – 7.39 (m, 2H), 7.35 (t, J = 7.8 Hz, 3H), 7.22 – 7.20 (m, 1H), 4.83 (s, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 138.0, 133.7, 132.1, 130.6, 129.8, 128.9, 128.7, 126.7, 126.0, 125.1, 124.5, 123.6, 59.9.



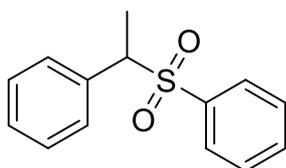
**2-chloro-5-((phenylsulfonyl)methyl)pyridine<sup>[18]</sup> (3ak)**. The product was purified by silica gel column chromatography, using petroleum ether/EA = 10/1 (v/v) as an eluent. White solid in 89% yield.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.96 (d, J = 2.5 Hz, 1H), 7.69 – 7.64 (m, 3H), 7.58 – 7.50 (m, 3H), 7.31 – 7.29 (m, 1H), 4.29 (s, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 152.1, 151.1, 140.8, 137.3, 134.4, 129.4, 128.5, 124.4, 123.5, 59.1.



**2-chloro-5-((phenylsulfonyl)methyl)thiazole<sup>[18]</sup> (3al)**. The product was purified by silica gel column chromatography, using petroleum ether/EA = 15/1 (v/v) as an eluent. White solid in 52% yield.

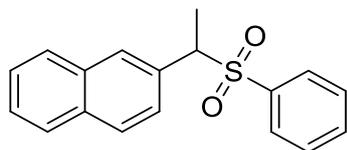
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.78 – 7.75 (m, 2H), 7.70 – 7.66 (m, 1H), 7.56 – 7.52 (m, 2H), 7.17 (s, 1H), 4.45 (s, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 153.8, 143.1, 136.9, 134.6, 129.5, 128.6, 126.4, 54.7.



**((1-phenylethyl)sulfonyl)benzene<sup>[19]</sup> (3am)**. The product was purified by silica gel column chromatography, using petroleum ether/EA = 20/1 (v/v) as an eluent. White solid in 74% yield.

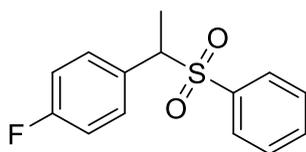
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.57 – 7.52 (m, 3H), 7.41 – 7.37 (m, 2H), 7.31 – 7.21 (m, 3H), 7.14 – 7.11 (m, 2H), 4.23 (q, J = 7.2 Hz, 1H), 1.77 (d, J = 7.2 Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 136.9, 133.8,

133.6, 129.4, 129.2, 128.8, 128.7, 128.4, 66.1, 14.0.



**2-(1-(phenylsulfonyl)ethyl)naphthalene**<sup>[19]</sup> (**3an**). The product was purified by silica gel column chromatography, using petroleum ether/EA = 10/1 (v/v) as an eluent. White solid in 55% yield.

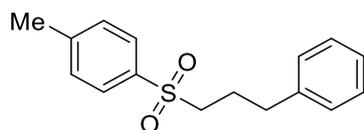
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.80 – 7.78 (m, 1H), 7.73 – 7.68 (m, 2H), 7.55 – 7.43 (m, 6H), 7.36 – 7.32 (m, 2H), 7.27 (dd, J = 8.5, 1.9 Hz, 1H), 4.40 (q, J = 7.1 Hz, 1H), 1.85 (d, J = 7.1 Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 136.8, 133.6, 133.3, 132.9, 131.2, 129.3, 129.1, 128.7, 128.1, 128.1, 127.7, 126.7, 126.6, 126.4, 66.2, 14.3.



**1-fluoro-4-(1-(phenylsulfonyl)ethyl)benzene** (**3ao**). The product was purified by silica gel column chromatography, using petroleum ether/EA = 10/1 (v/v) as an eluent. White solid in 72% yield.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.60 – 7.54 (m, 3H), 7.44 – 7.40 (m, 2H), 7.13 – 7.10 (m, 2H), 6.96 – 6.91 (m, 2H), 4.23 (q, J = 7.2 Hz, 1H), 1.74 (d, J = 7.2 Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 163.0 (d, J = 248.4 Hz), 136.7, 133.7, 131.2 (d, J = 8.4 Hz), 129.6 (d, J = 3.3 Hz), 129.2, 128.8, 115.5 (d, J = 21.6 Hz), 65.3, 14.2. **<sup>19</sup>F NMR** (377 MHz, CDCl<sub>3</sub>) δ -112.47.

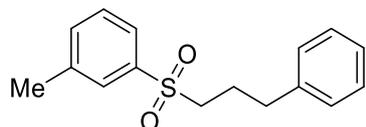
HRMS (ESI/QTOF) m/z: [M + H]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>13</sub>FO<sub>2</sub>SH<sup>+</sup> 265.0693; Found 265.0688.



**1-methyl-4-((3-phenylpropyl)sulfonyl)benzene**<sup>[13]</sup> (**4b**): The product was purified by silica gel column chromatography, using petroleum ether/EA = 10/1 (v/v) as an eluent. White solid in 80% yield.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.75 – 7.73 (m, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.27 – 7.23 (m, 2H), 7.20 – 7.16 (m, 1H), 7.10 – 7.08 (m, 2H), 3.06 – 3.02 (m, 2H), 2.67 (t, J = 7.5 Hz, 2H), 2.43 (s, 3H), 2.06 – 1.98

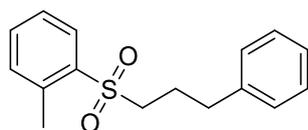
(m, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.7, 140.0, 136.1, 129.9, 128.6, 128.4, 128.1, 126.4, 55.6, 34.1, 24.3, 21.7.



**1-methyl-3-((3-phenylpropyl)sulfonyl)benzene**<sup>[13]</sup> (**4c**): The product was purified by silica gel column chromatography, using petroleum ether/EA = 10/1 (v/v) as an eluent. White solid in 79% yield.

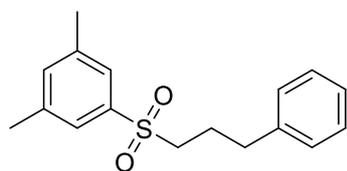
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 – 7.64 (m, 2H), 7.45 – 7.40 (m, 2H), 7.28 – 7.24 (m, 2H), 7.21 – 7.16 (m, 1H), 7.10 – 7.08 (m, 2H), 3.08 – 3.04 (m, 2H), 2.68 (t,  $J = 7.5$  Hz, 2H), 2.42 (s, 3H), 2.07 – 2.00 (m, 2H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.9, 139.6, 138.9, 134.5, 129.2, 128.6, 128.4, 128.3, 126.5, 125.2, 55.4, 34.1, 24.2, 21.4.



**1-methyl-2-((3-phenylpropyl)sulfonyl)benzene**<sup>[13]</sup> (**4d**): The product was purified by silica gel column chromatography, using petroleum ether/EA = 10/1 (v/v) as an eluent. White solid in 25% yield.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (dd,  $J = 8.0, 1.4$  Hz, 1H), 7.50 (td,  $J = 7.5, 1.4$  Hz, 1H), 7.38 – 7.34 (m, 1H), 7.31 – 7.24 (m, 3H), 7.21 – 7.17 (m, 1H), 7.10 – 7.06 (m, 2H), 3.13 – 3.08 (m, 2H), 2.70 (t,  $J = 7.4$  Hz, 2H), 2.59 (s, 3H), 2.07 – 2.00 (m, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.9, 137.9, 137.1, 133.7, 132.8, 130.3, 128.6, 128.4, 126.6, 126.5, 54.3, 34.0, 24.0, 20.3.

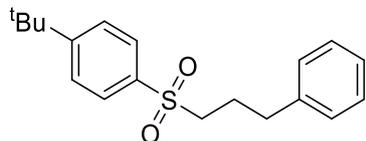


**1,3-dimethyl-5-((3-phenylpropyl)sulfonyl)benzene** (**4e**): The product was purified by silica gel column chromatography, using petroleum ether/EA = 10/1 (v/v) as an eluent. White solid in 78% yield.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (s, 2H), 7.28 – 7.24 (m, 3H), 7.21 – 7.16 (m, 1H), 7.11 – 7.08 (m, 2H), 3.07 – 3.03 (m, 2H), 2.68 (t,  $J = 7.5$  Hz, 2H), 2.37 (s, 6H), 2.07 – 2.00 (m, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )

$\delta$  140.0, 139.4, 138.8, 135.4, 128.6, 128.4, 126.4, 125.5, 55.4, 34.1, 24.2, 21.2.

HRMS (ESI/QTOF) m/z:  $[M + H]^+$  Calcd for  $C_{17}H_{20}O_2SH^+$  289.1257; Found 289.1257.

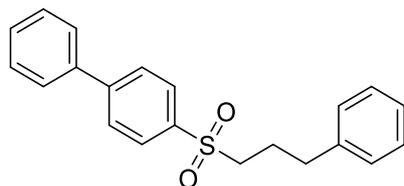


**1-(tert-butyl)-4-((3-phenylpropyl)sulfonyl)benzene (4f):** The product was purified by silica gel column chromatography, using petroleum ether/EA = 10/1 (v/v) as an eluent. White solid in 74% yield.

**$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.80 – 7.77 (m, 2H), 7.56 – 7.52 (m, 2H), 7.27 – 7.23 (m, 2H), 7.20 – 7.16 (m, 1H), 7.11 – 7.08 (m, 2H), 3.08 – 3.04 (m, 2H), 2.69 (t,  $J = 7.5$  Hz, 2H), 2.09 – 2.01 (m, 2H), 1.34 (s, 9H).

**$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  157.6, 134.0, 136.1, 128.6, 128.4, 127.9, 126.4, 126.3, 55.5, 35.3, 34.1, 31.1, 24.2.

HRMS (ESI/QTOF) m/z:  $[M + Na]^+$  Calcd for  $C_{19}H_{24}O_2SNa^+$  339.1389; Found 339.1393.

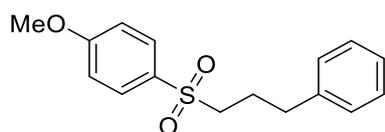


**4-((3-phenylpropyl)sulfonyl)-1,1'-biphenyl (4g):** The product was purified by silica gel column chromatography, using petroleum ether/EA = 10/1 (v/v) as an eluent. White solid in 71% yield.

**$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.92 (d,  $J = 8.0$  Hz, 2H), 7.72 (d,  $J = 8.0$  Hz, 2H), 7.60 – 7.58 (m, 2H), 7.49 – 7.39 (m, 3H), 7.27 – 7.21 (m, 2H), 7.19 – 7.16 (m, 1H), 7.10 – 7.08 (m, 2H), 3.11 – 3.08 (m, 2H), 2.69 (t,  $J = 7.4$  Hz, 2H), 2.11–2.02 (m, 2H).

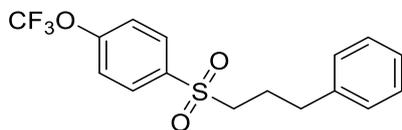
**$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  146.6, 139.9, 139.1, 137.5, 129.1, 128.7, 128.6, 128.6, 128.4, 128.0, 127.4, 126.4, 55.6, 34.1, 24.3.

HRMS (ESI/QTOF) m/z:  $[M + Na]^+$  Calcd for  $C_{21}H_{20}O_2SNa^+$  359.1076; Found 359.1080.



**1-methoxy-4-((3-phenylpropyl)sulfonyl)benzene<sup>[13]</sup> (4h):** The product was purified by silica gel column chromatography, using petroleum ether/EA = 10/1 (v/v) as an eluent. White solid in 71% yield.

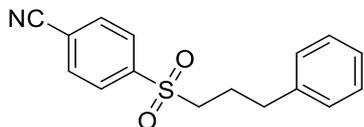
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.81 – 7.77 (m, 2H), 7.28 – 7.24 (m, 2H), 7.21 – 7.17 (m, 1H), 7.11 – 7.08 (m, 2H), 7.01 – 6.98 (m, 2H), 3.87 (s, 3H), 3.06 – 3.02 (m, 2H), 2.68 (t, J = 7.5 Hz, 2H), 2.07 – 1.98 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 163.7, 140.0, 130.6, 130.2, 128.6, 128.4, 126.4, 114.5, 55.8, 55.7, 34.1, 24.4.



**1-((3-phenylpropyl)sulfonyl)-4-(trifluoromethoxy)benzene (4i)**: The product was purified by silica gel column chromatography, using petroleum ether/EA = 10/1 (v/v) as an eluent. White solid in 52% yield.

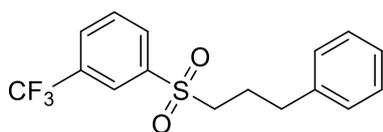
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.94 – 7.90 (m, 2H), 7.38 – 7.35 (m, 2H), 7.29 – 7.25 (m, 2H), 7.22 – 7.18 (m, 1H), 7.11 – 7.09 (m, 2H), 3.10 – 3.05 (m, 2H), 2.70 (t, J = 7.4 Hz, 2H), 2.09 – 2.01 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 153.0 (d, J = 1.9 Hz), 139.7, 137.3, 130.4, 128.7, 128.4, 126.6, 121.1, 120.2 (q, J = 259.8 Hz), 55.5, 34.0, 24.2. **<sup>19</sup>F NMR** (377 MHz, CDCl<sub>3</sub>) δ -57.54.

HRMS (ESI/QTOF) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>15</sub>F<sub>3</sub>O<sub>3</sub>SNa<sup>+</sup> 367.0586; Found 367.0581.



**4-((3-phenylpropyl)sulfonyl)benzonitrile<sup>[13]</sup> (4j)**: The product was purified by silica gel column chromatography, using petroleum ether/EA = 10/1 (v/v) as an eluent. White solid in 65% yield.

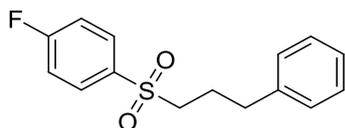
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.00 – 7.98 (m, 2H), 7.86 – 7.84 (m, 2H), 7.29 – 7.25 (m, 2H), 7.23 – 7.18 (m, 1H), 7.10 – 7.08 (m, 2H), 3.11 – 3.07 (m, 2H), 2.71 (t, J = 7.4 Hz, 2H), 2.08 – 2.00 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 143.2, 139.5, 133.1, 128.9, 128.8, 128.4, 126.7, 117.6, 117.1, 55.2, 34.0, 24.1.



**1-((3-phenylpropyl)sulfonyl)-3-(trifluoromethyl)benzene<sup>[20]</sup> (4k)**: The product was purified by silica gel column chromatography, using petroleum ether/EA = 10/1 (v/v) as an eluent. White solid in 66% yield.

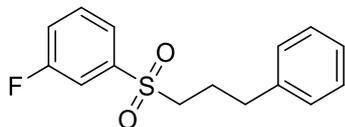
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.15 (s, 1H), 8.16 (d, J = 8.1 Hz, 1H), 7.90 (d, J = 7.9 Hz, 1H), 7.71 (t, J =

7.8 Hz, 1H), 7.29-7.25 (m, 2H), 7.22 – 7.18 (m, 1H), 7.11 – 7.08 (m, 2H), 3.12 – 3.08 (m, 2H), 2.72 (t, J = 7.4 Hz, 2H), 2.11 – 2.03 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.4, 139.6, 132.1 (q, J = 33.6 Hz), 131.5, 130.5 (q, J = 3.6 Hz), 130.2, 128.7, 128.4, 126.6, 125.2 (q, J = 3.9 Hz), 123.1 (q, J = 273.1 Hz), 55.4, 34.0, 24.0.



**1-fluoro-4-((3-phenylpropyl)sulfonyl)benzene<sup>[8]</sup> (4l)**: The product was purified by silica gel column chromatography, using petroleum ether/EA = 10/1 (v/v) as an eluent. White solid in 70% yield.

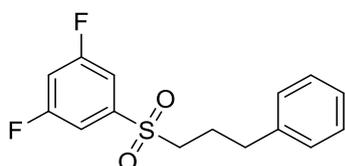
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 – 7.86 (m, 2H), 7.29 – 7.19 (m, 5H), 7.11 – 7.08 (m, 2H), 3.08 – 3.04 (m, 2H), 2.69 (t, J = 7.5 Hz, 2H), 2.07 – 2.00 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.8 (d, J = 256.2 Hz), 139.8, 135.1 (d, J = 3.2 Hz), 131.0 (d, J = 9.7 Hz), 128.7, 128.4, 126.5, 116.7 (d, J = 22.6 Hz), 55.6, 34.1, 24.3.



**1-fluoro-3-((3-phenylpropyl)sulfonyl)benzene (4m)**: The product was purified by silica gel column chromatography, using petroleum ether/EA = 10/1 (v/v) as an eluent. White solid in 70% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 (dt, J = 7.8, 1.3 Hz, 1H), 7.59 – 7.51 (m, 2H), 7.37 – 7.32 (m, 1H), 7.29 – 7.25 (m, 2H), 7.22 – 7.18 (m, 1H), 7.11 – 7.08 (m, 2H), 3.10 – 3.06 (m, 2H), 2.70 (t, J = 7.5 Hz, 2H), 2.08 – 2.01 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.5 (d, J = 252.5 Hz), 141.1 (d, J = 6.4 Hz), 139.7, 131.3 (d, J = 7.7 Hz), 128.7, 128.4, 126.6, 123.9 (d, J = 3.5 Hz), 121.1 (d, J = 21.1 Hz), 115.5 (d, J = 24.2 Hz), 55.3, 34.1, 24.2.  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -109.66.

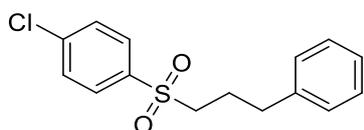
HRMS (ESI/QTOF) m/z:  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{15}\text{FO}_2\text{SH}^+$  279.0850; Found 279.0850.



**1,3-difluoro-5-((3-phenylpropyl)sulfonyl)benzene (4n):** The product was purified by silica gel column chromatography, using petroleum ether/EA = 10/1 (v/v) as an eluent. White solid in 62% yield.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.45 – 7.38 (m, 2H), 7.31 – 7.26 (m, 2H), 7.24 – 7.19 (m, 1H), 7.12 – 7.07 (m, 3H), 3.10 – 3.06 (m, 2H), 2.72 (t, J = 7.4 Hz, 2H), 2.10 – 2.02 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 163.0 (dd, J = 256.0, 11.4 Hz), 142.4 (t, J = 7.9 Hz), 139.5, 128.8, 128.4, 126.7, 111.7 (dd, J = 28.0 Hz), 109.5 (t, J = 25.0 Hz), 55.2, 34.0, 24.1. **<sup>19</sup>F NMR** (377 MHz, CDCl<sub>3</sub>) δ -104.57.

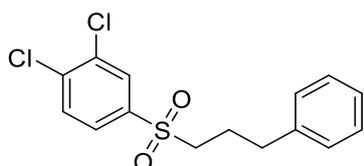
HRMS (ESI/QTOF) m/z: [M + H]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>14</sub>F<sub>2</sub>O<sub>2</sub>SNa<sup>+</sup> 297.0755; Found 297.0752.



**1-chloro-4-((3-phenylpropyl)sulfonyl)benzene (4o):** The product was purified by silica gel column chromatography, using petroleum ether/EA = 10/1 (v/v) as an eluent. White solid in 65% yield.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.82 – 7.79 (m, 2H), 7.54 – 7.50 (m, 2H), 7.29 – 7.25 (m, 2H), 7.22 – 7.18 (m, 1H), 7.14 – 7.08 (m, 2H), 3.08 – 3.04 (m, 2H), 2.70 (t, J = 7.4 Hz, 2H), 2.07 – 2.00 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 140.5, 139.7, 137.5, 129.7, 129.6, 128.7, 128.4, 126.5, 55.5, 34.1, 24.2.

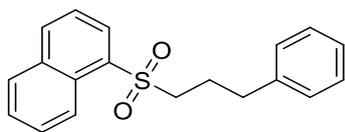
HRMS (ESI/QTOF) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>15</sub>ClO<sub>2</sub>SNa<sup>+</sup> 317.0373; Found 317.0374.



**1,2-dichloro-4-((3-phenylpropyl)sulfonyl)benzene (4p):** The product was purified by silica gel column chromatography, using petroleum ether/EA = 10/1 (v/v) as an eluent. White solid in 50% yield.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.95 (d, J = 2.0 Hz, 1H), 7.70 – 7.67 (m, 1H), 7.64 – 7.61 (m, 1H), 7.29 – 7.25 (m, 2H), 7.22 – 7.18 (m, 1H), 7.11 – 7.08 (m, 2H), 3.09 – 3.05 (m, 2H), 2.71 (t, J = 7.4 Hz, 2H), 2.08 – 2.00 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 139.5, 138.9, 138.8, 134.1, 131.5, 130.1, 128.7, 128.4, 127.2, 126.6, 54.8, 34.0, 24.1.

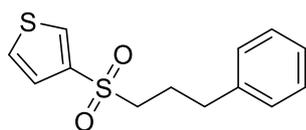
HRMS (ESI/QTOF) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>14</sub>Cl<sub>2</sub>O<sub>2</sub>SNa<sup>+</sup> 350.9984; Found 350.9981.



**1-((3-phenylpropyl)sulfonyl)naphthalene (4q):** The product was purified by silica gel column chromatography, using petroleum ether/EA = 5/1 (v/v) as an eluent. White solid in 33% yield.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.65 (d, J = 8.4 Hz, 1H), 8.28 (dd, J = 7.4, 1.3 Hz, 1H), 8.12 (d, J = 8.3 Hz, 1H), 7.97 – 7.95 (m, 1H), 7.68 – 7.56 (m, 3H), 7.22 – 7.12 (m, 3H), 7.03 – 7.01 (m, 2H), 3.28 – 3.25 (m, 2H), 2.64 (t, J = 7.5 Hz, 2H), 2.07 – 1.99 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 139.9, 135.3, 134.3, 134.1, 130.7, 129.3, 128.9, 128.8, 128.6, 128.4, 127.1, 126.4, 124.5, 124.1, 55.0, 34.0, 24.2.

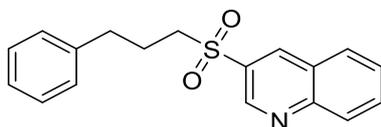
HRMS (ESI/QTOF) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>18</sub>O<sub>2</sub>SNa<sup>+</sup> 333.0920; Found 333.0921.



**3-((3-phenylpropyl)sulfonyl)thiophene (4r):** The product was purified by silica gel column chromatography, using petroleum ether/EA = 8/1 (v/v) as an eluent. White solid in 65% yield.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.05 (dd, J = 3.1, 1.3 Hz, 1H), 7.45 (dd, J = 5.1, 3.1 Hz, 1H), 7.35 (dd, J = 5.1, 1.3 Hz, 1H), 7.30 – 7.25 (m, 2H), 7.22 – 7.18 (m, 1H), 7.12 – 7.10 (m, 2H), 3.12 – 3.08 (m, 2H), 2.71 (t, J = 7.5 Hz, 2H), 2.11 – 2.03 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 139.9, 139.7, 132.7, 128.7, 128.5, 128.4, 126.5, 126.0, 55.8, 34.1, 24.3.

HRMS (ESI/QTOF) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>13</sub>H<sub>14</sub>O<sub>2</sub>S<sub>2</sub>Na<sup>+</sup> 289.0327; Found 289.0334.



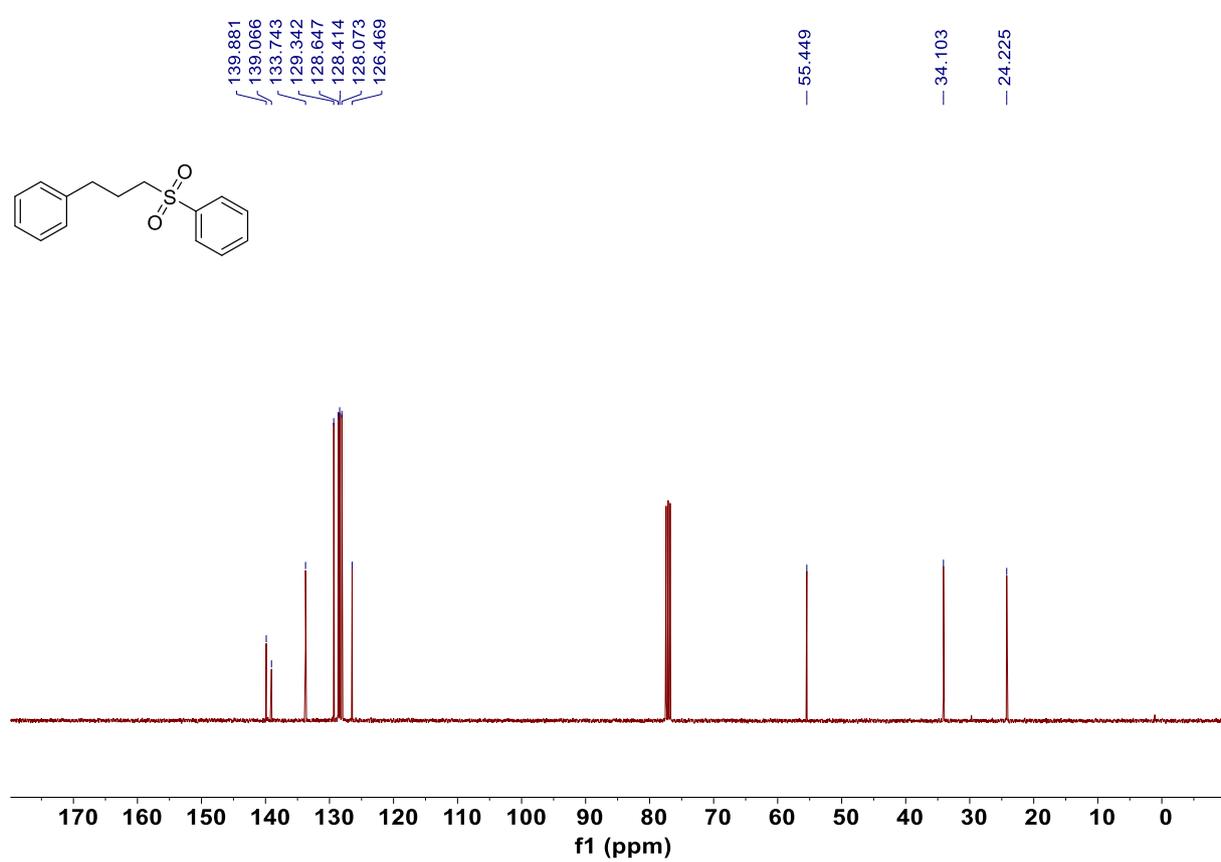
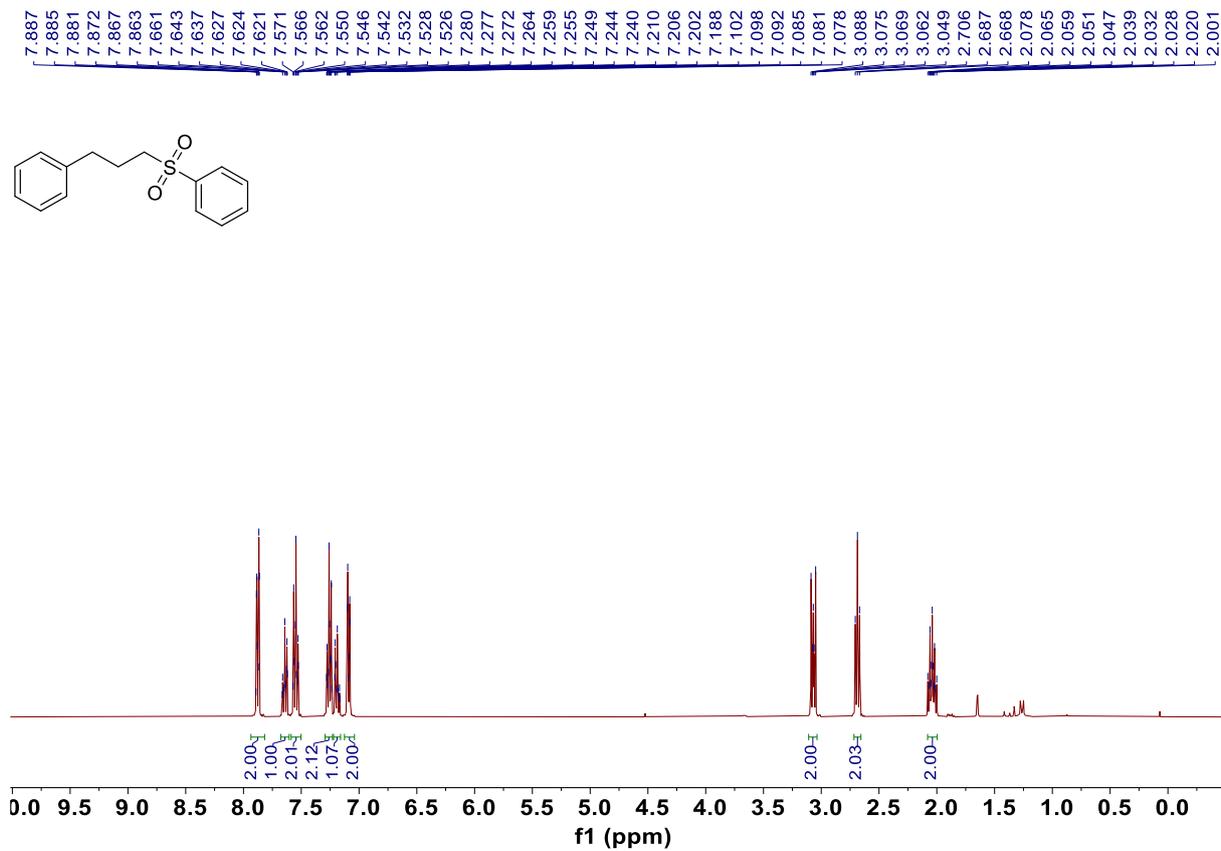
**3-((3-phenylpropyl)sulfonyl)quinoline (4s):** The product was purified by silica gel column chromatography, using petroleum ether/EA = 8/1 (v/v) as an eluent. White solid in 64% yield.

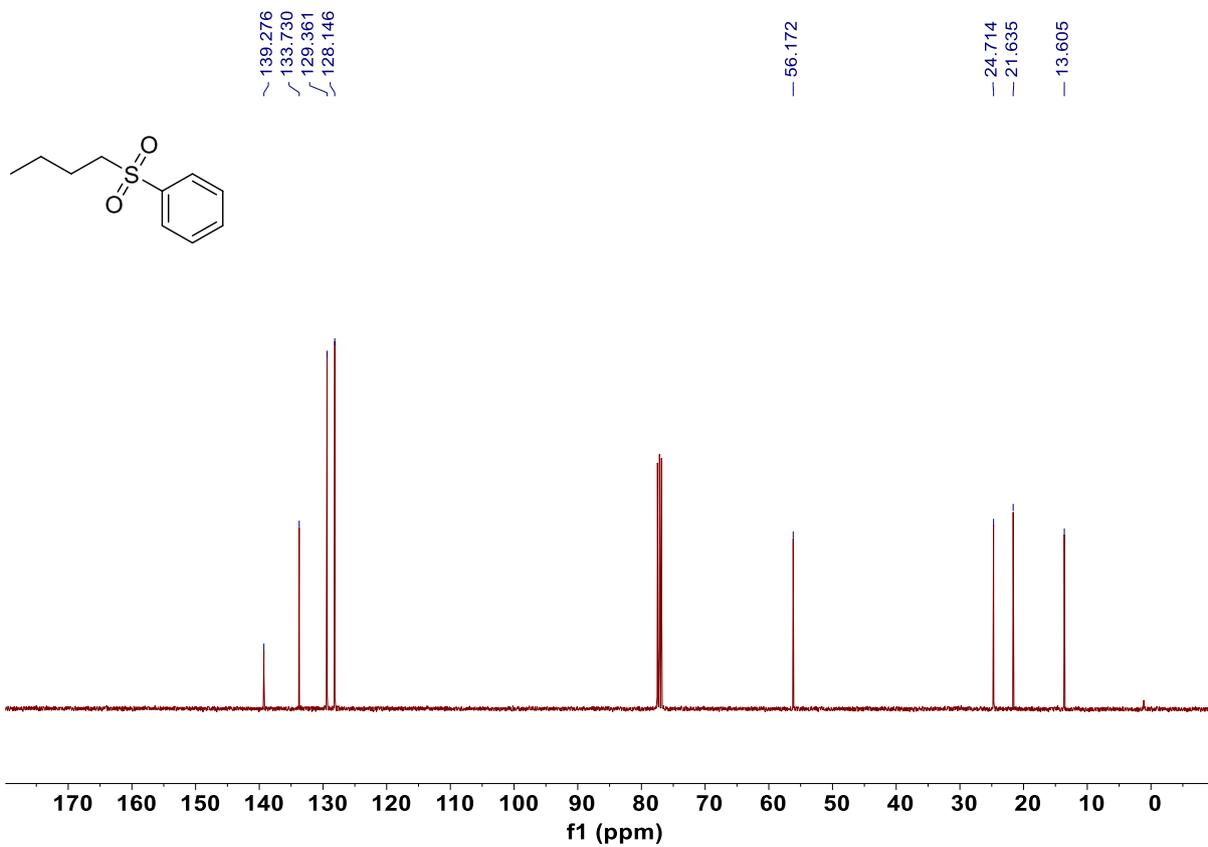
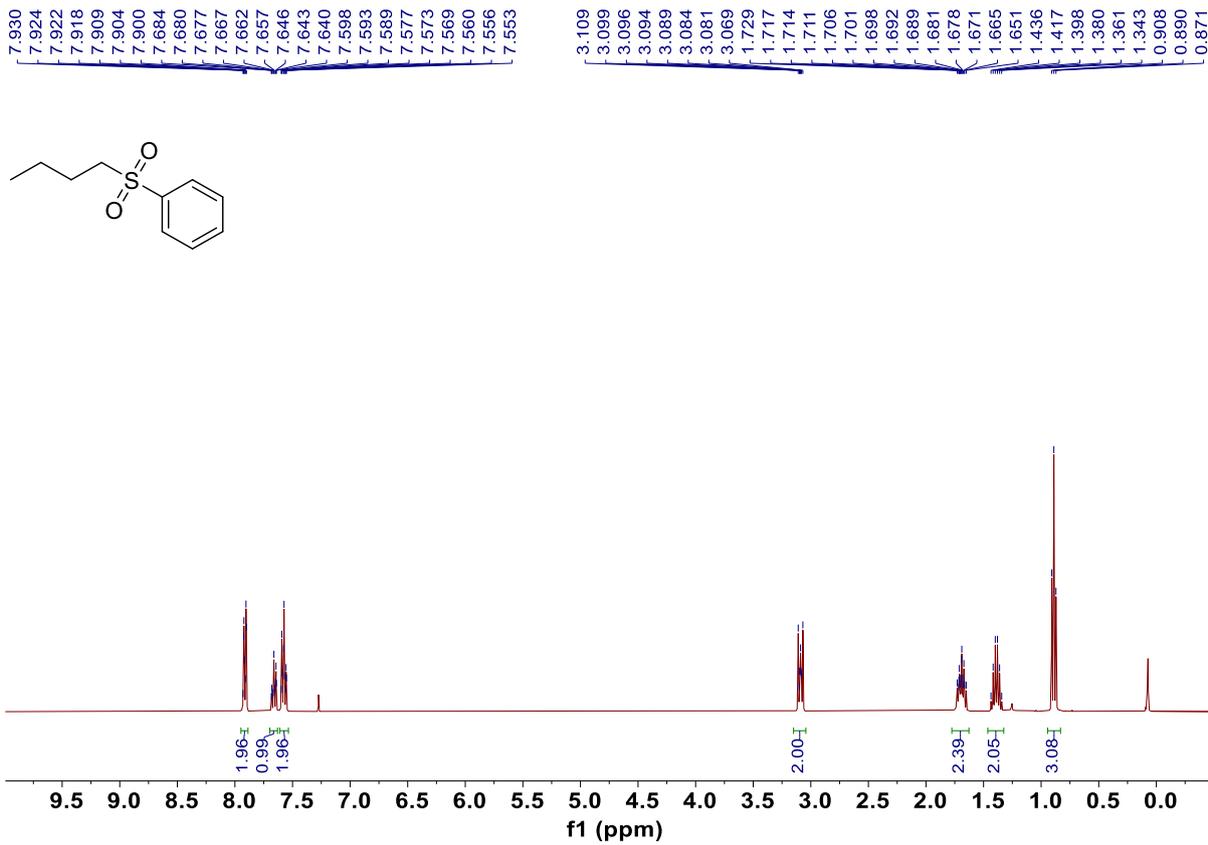
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.24 (d, J = 2.3 Hz, 1H), 8.72 (d, J = 2.3 Hz, 1H), 8.21 (d, J = 8.4 Hz, 1H), 7.97 – 7.89 (m, 2H), 7.72 – 7.68 (m, 1H), 7.25 – 7.14 (m, 3H), 7.09 – 7.06 (m, 2H), 3.21 – 3.17 (m, 2H),

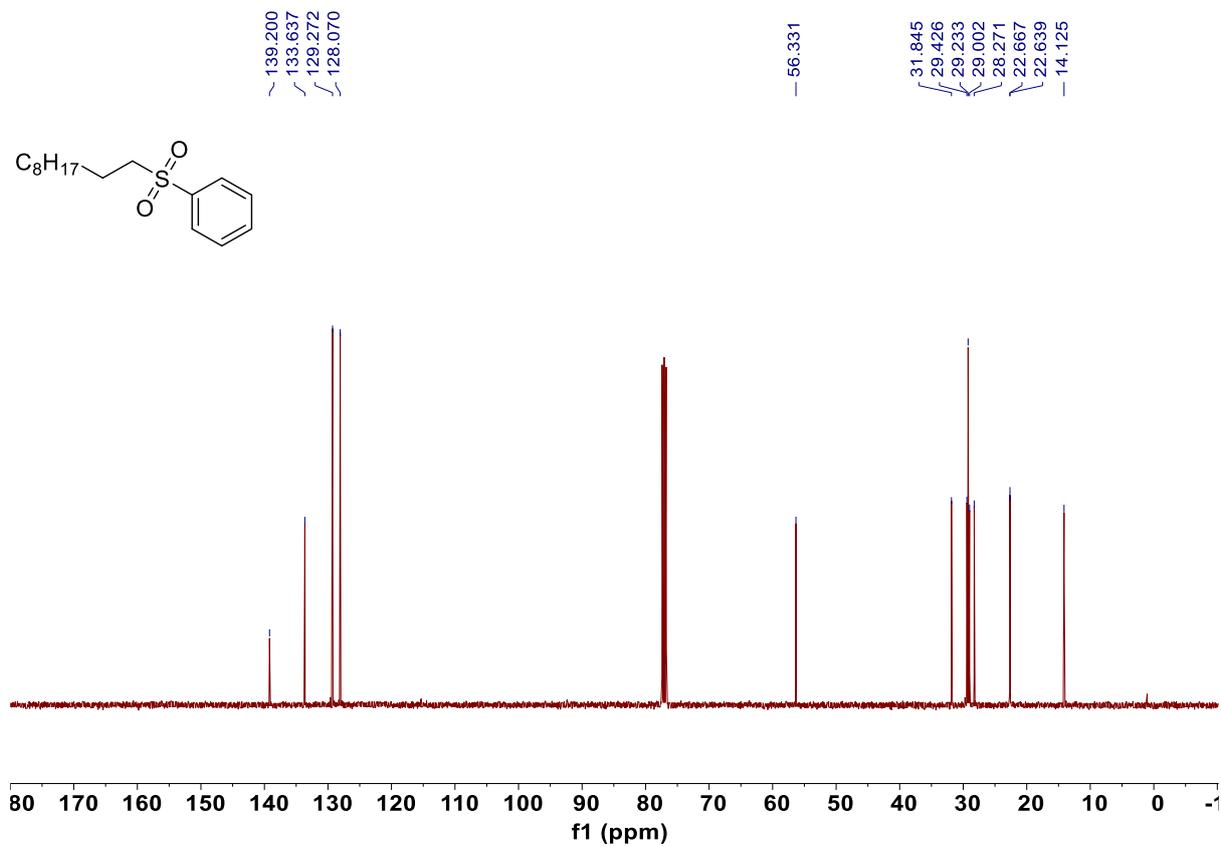
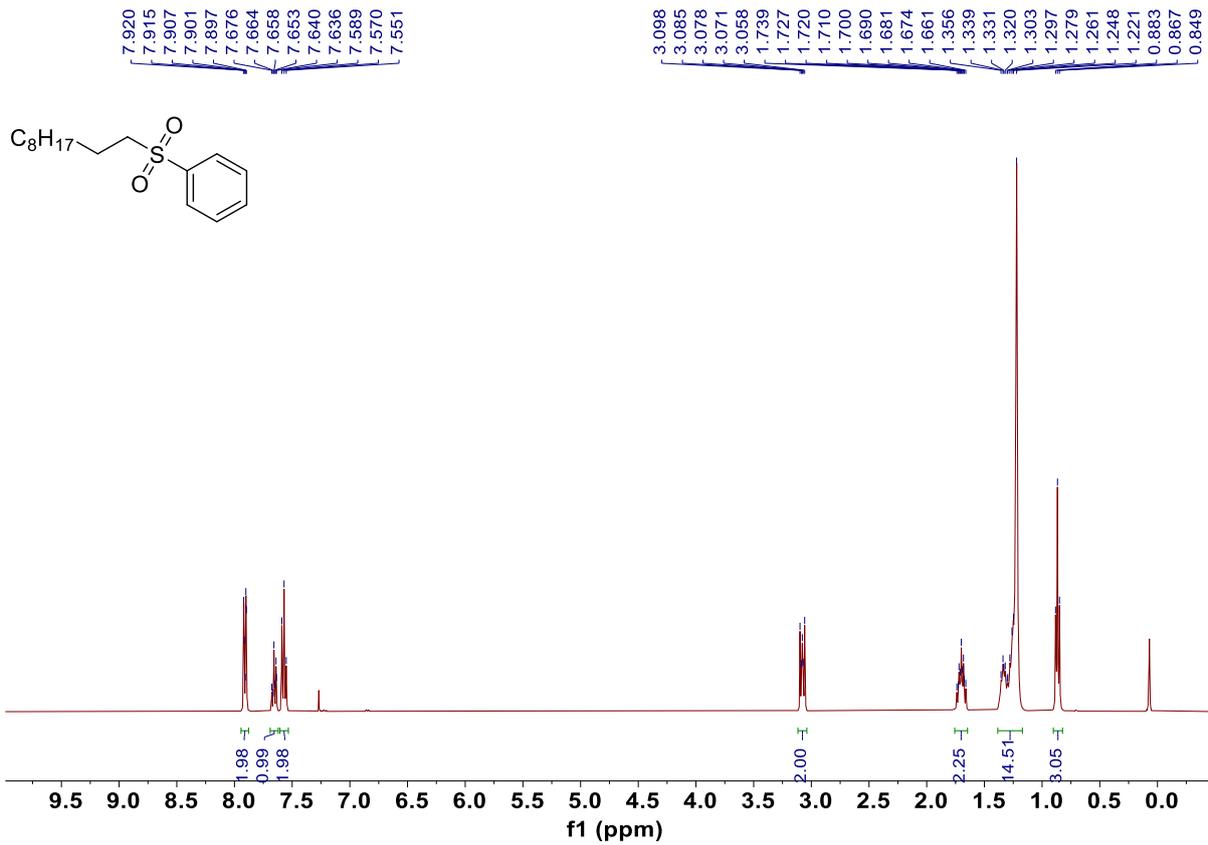
2.71 (t, J = 7.4 Hz, 2H), 2.14 – 2.06 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 149.8, 147.1, 139.5, 138.1, 133.0, 132.1, 129.7, 129.3, 128.7, 128.5, 128.4, 126.6, 126.3, 56.0, 34.1, 24.2.

HRMS (ESI/QTOF) m/z: [M + H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>17</sub>NO<sub>2</sub>SH<sup>+</sup> 312.1053; Found 312.1054.

# NMR Spectra of Substrates and Products

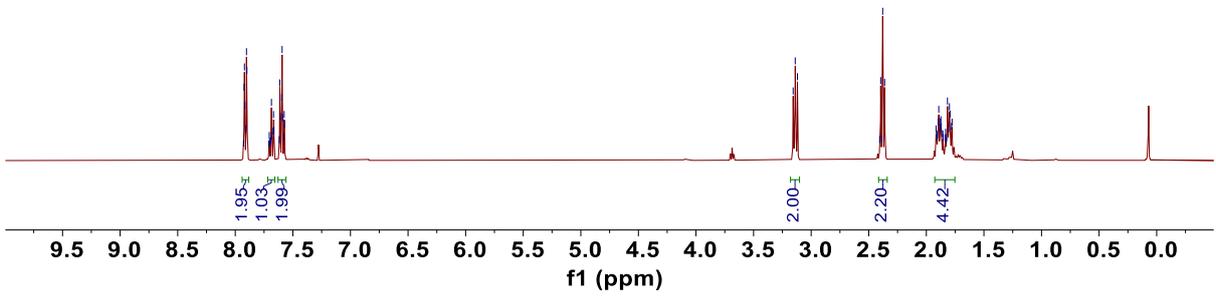
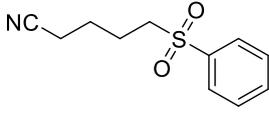






7.928  
7.924  
7.921  
7.917  
7.908  
7.903  
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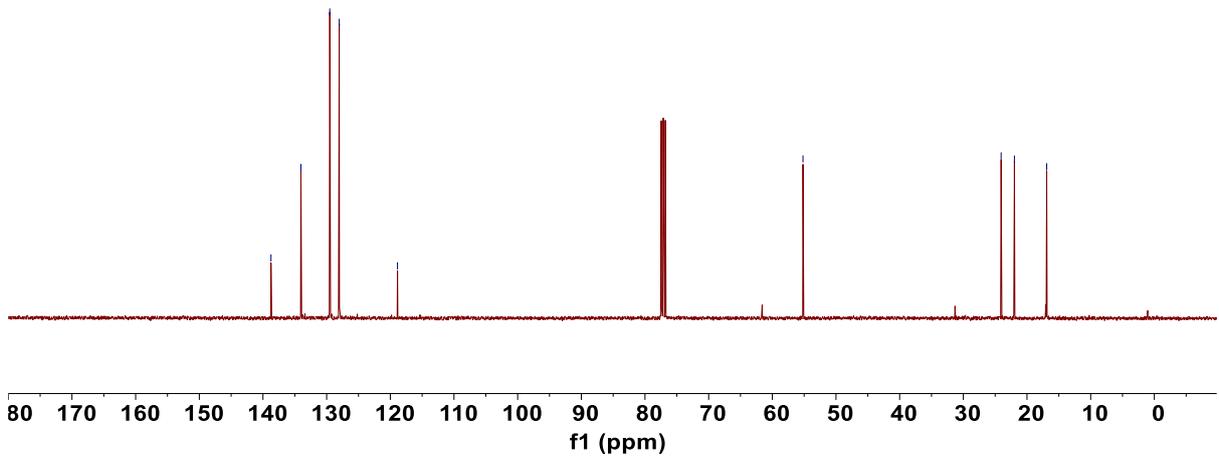
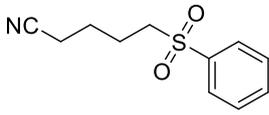


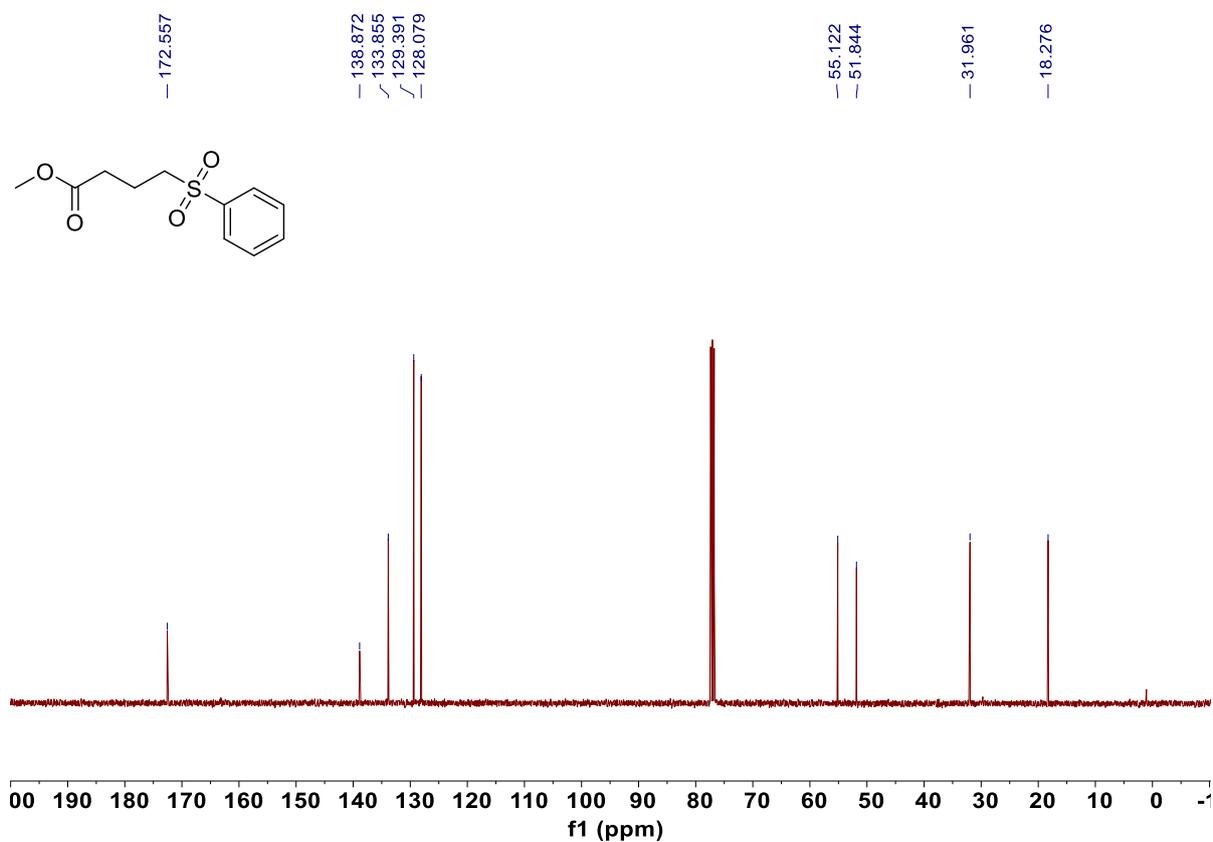
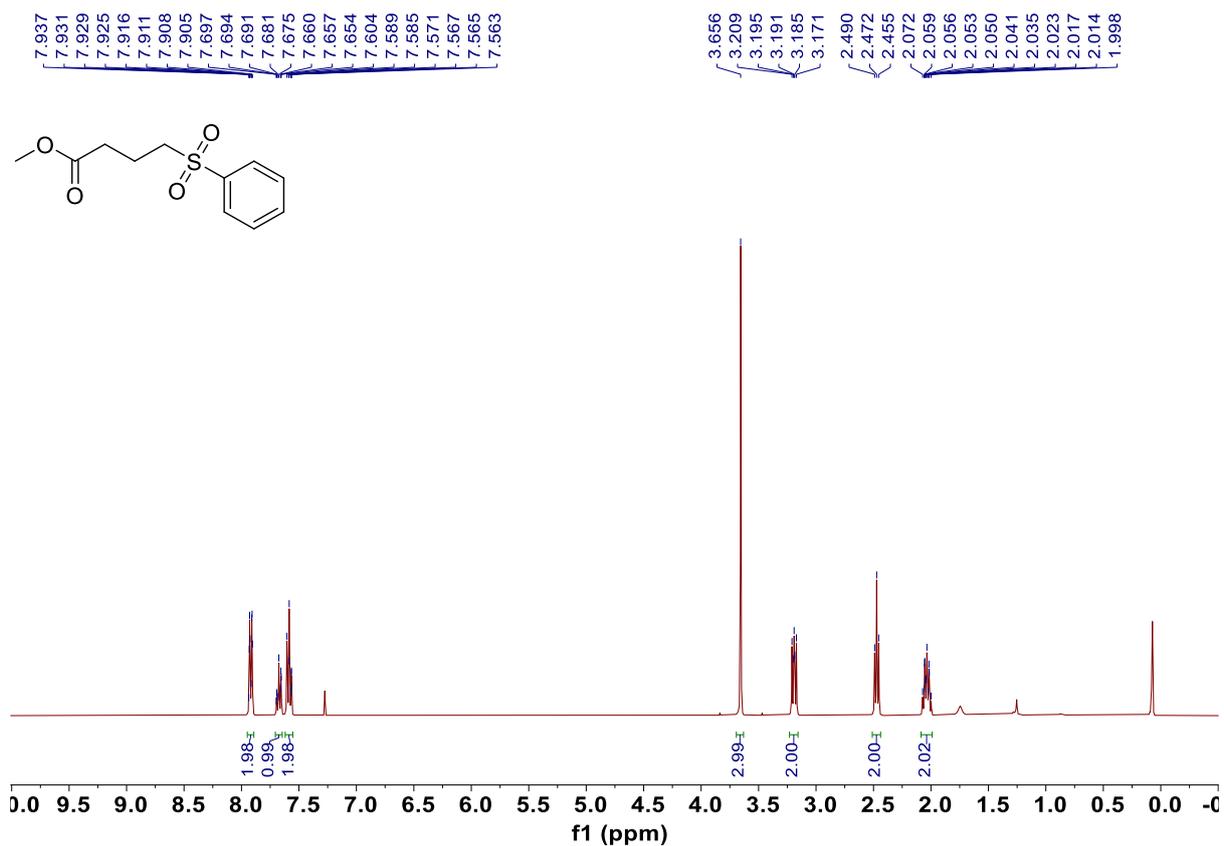
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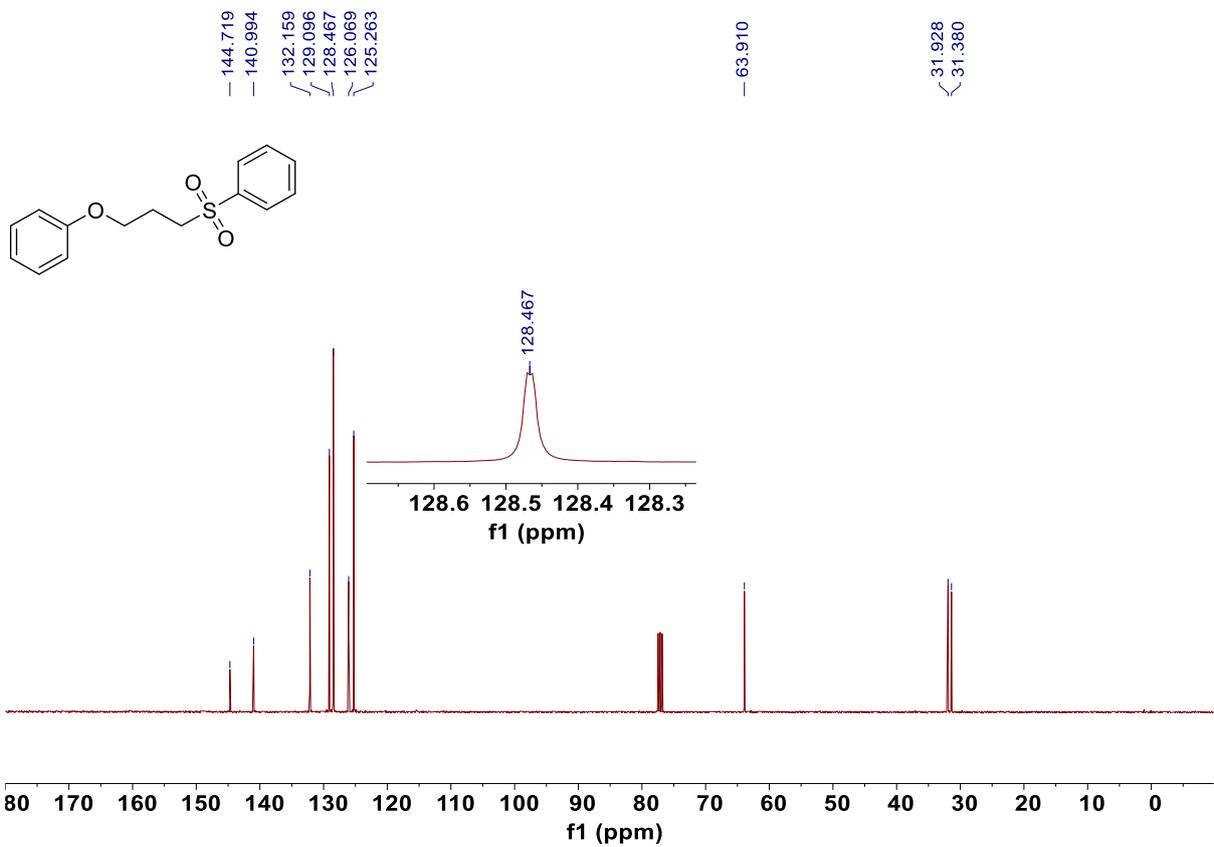
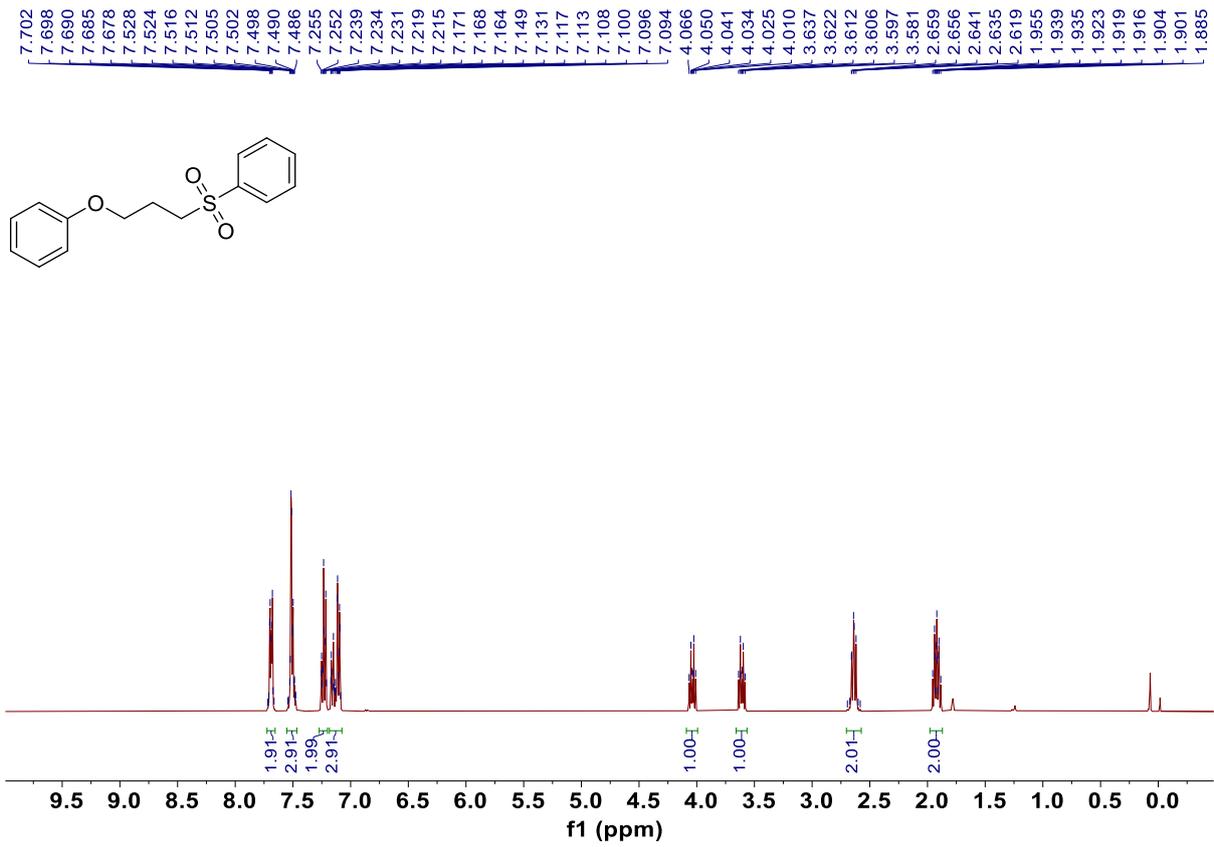
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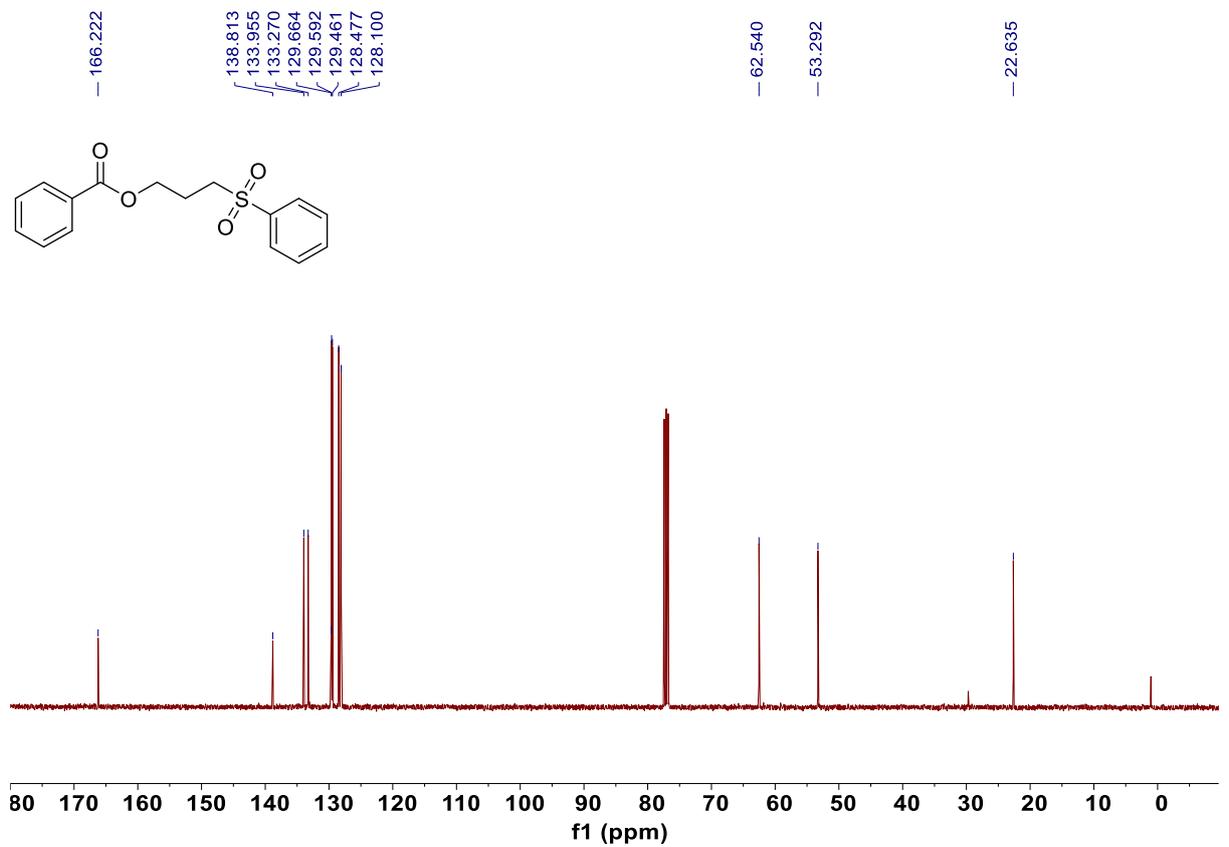
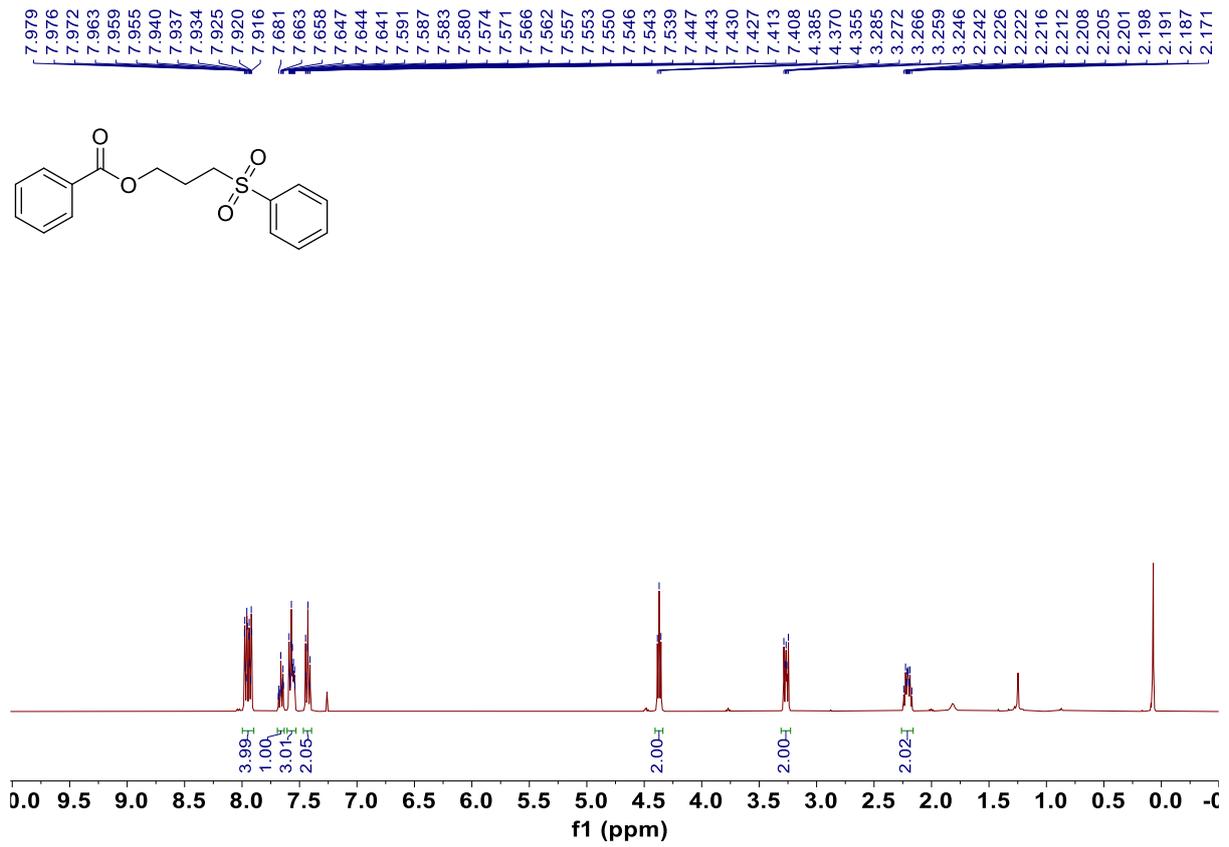
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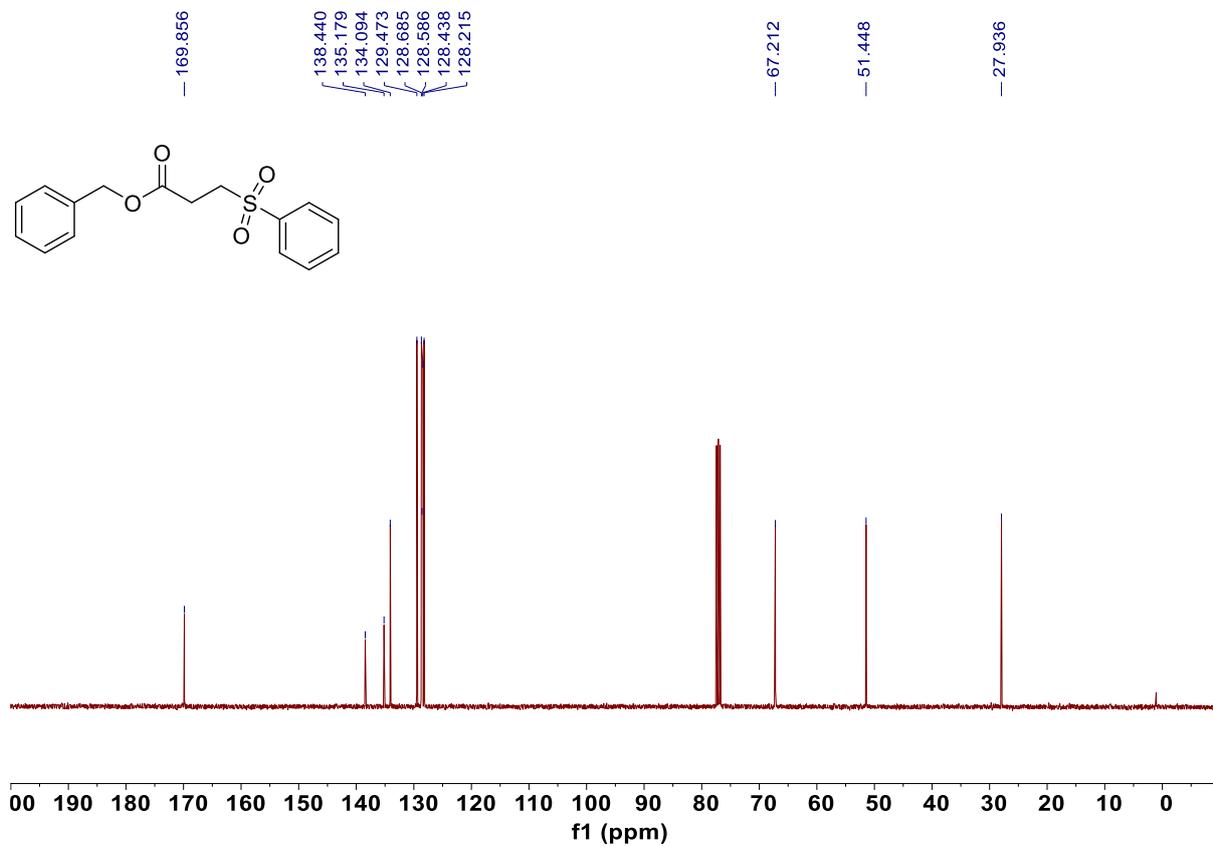
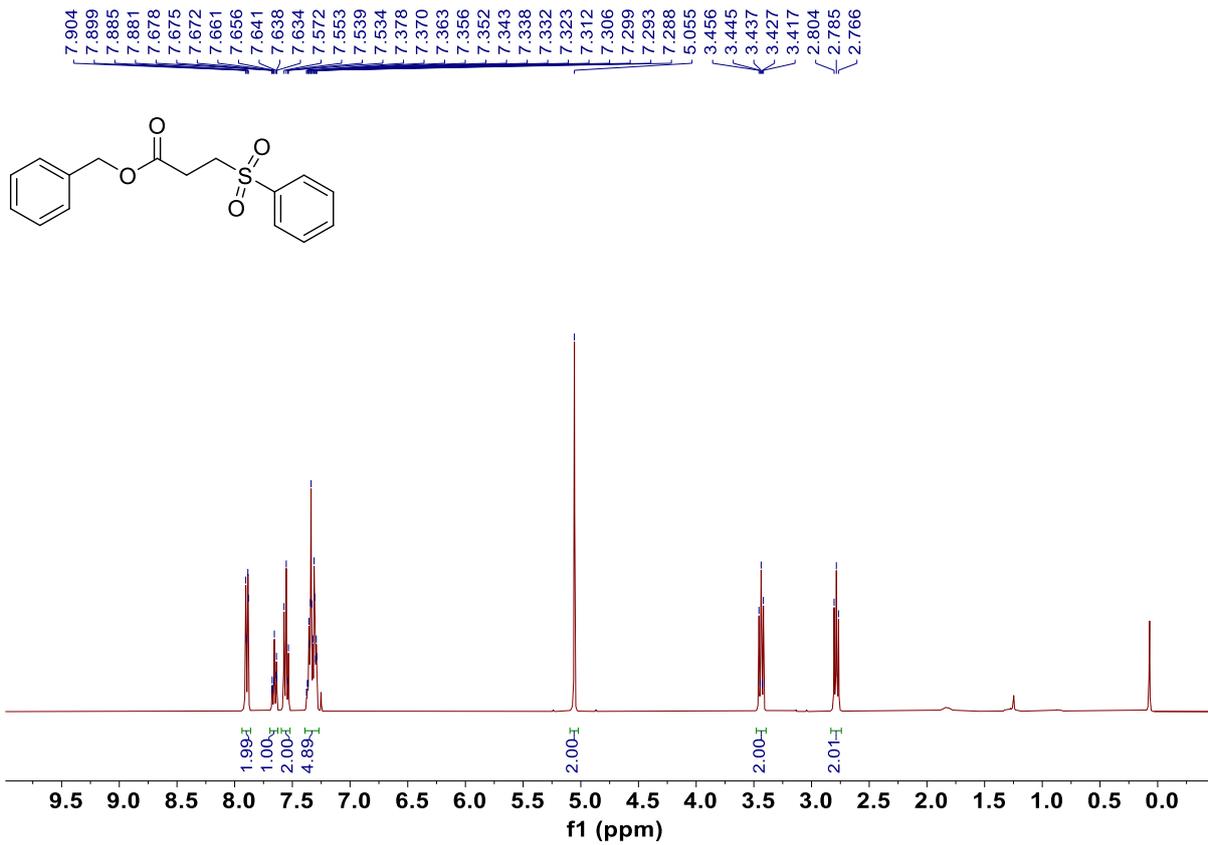
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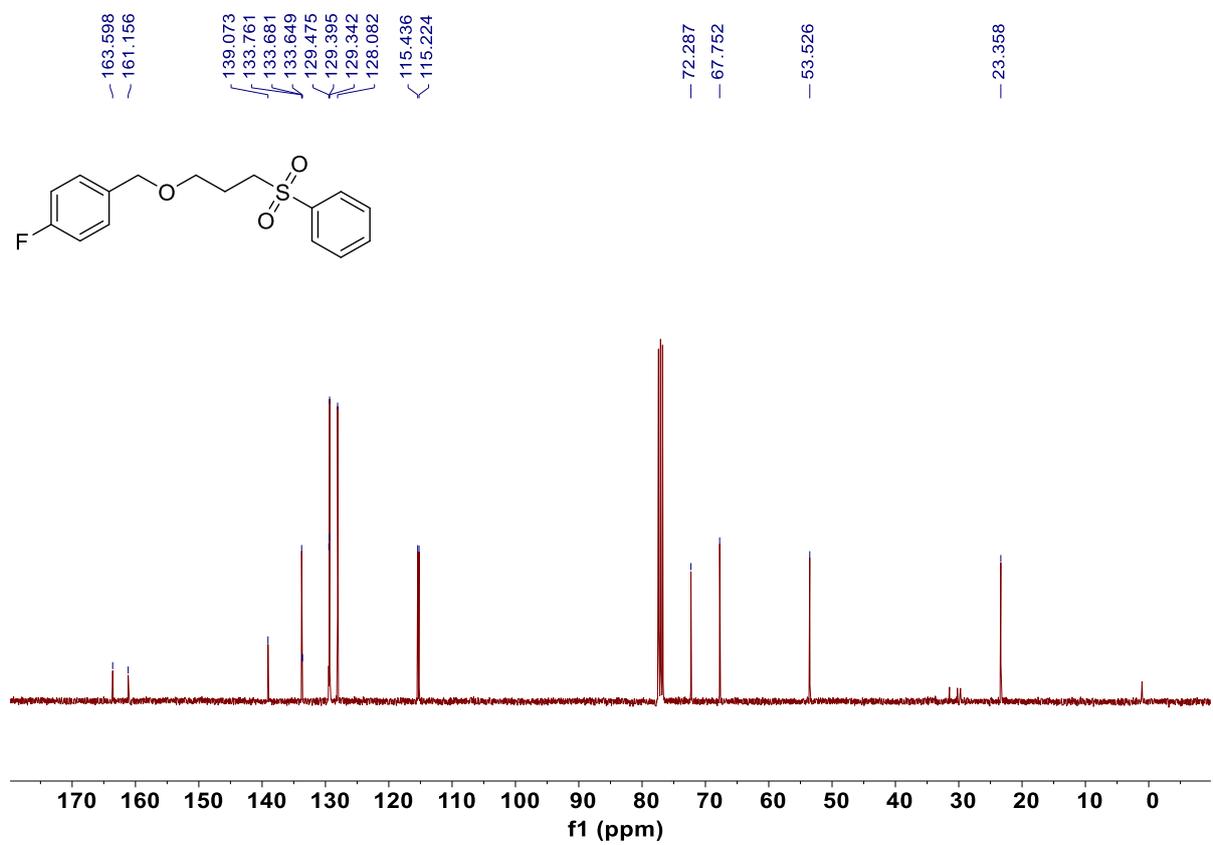
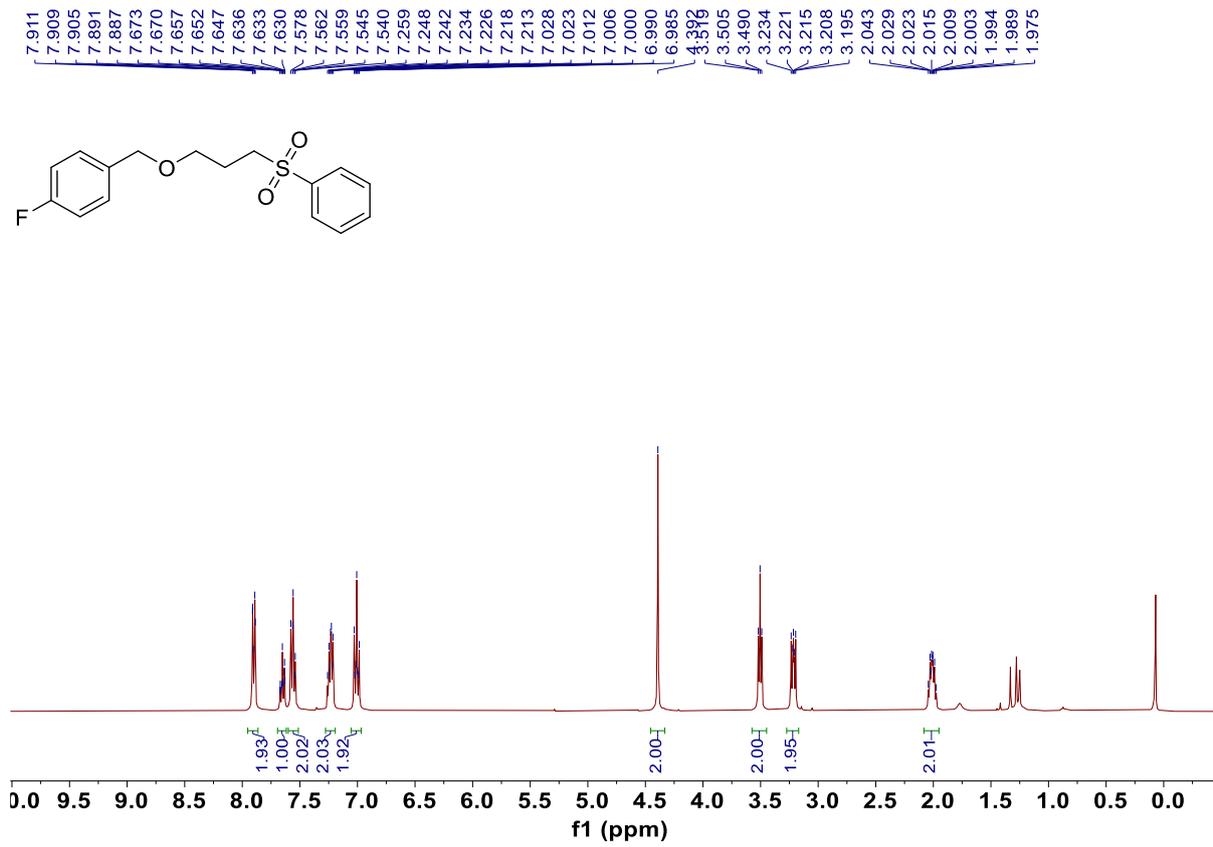


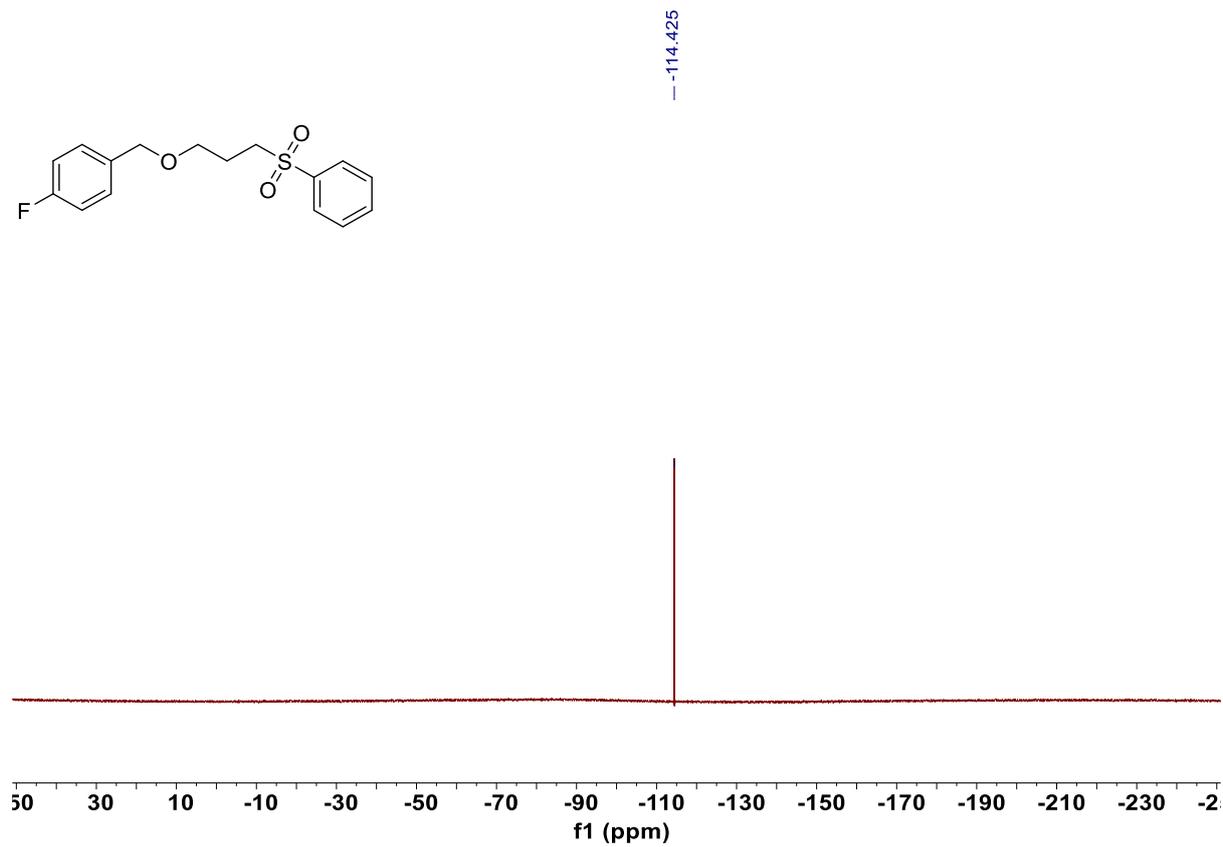
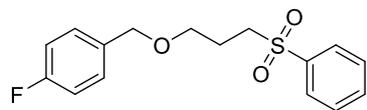




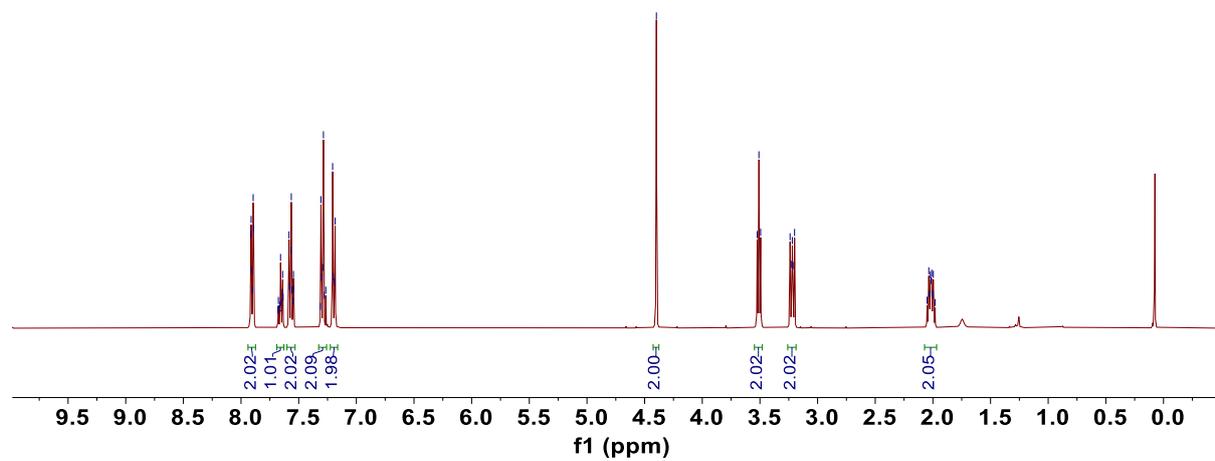
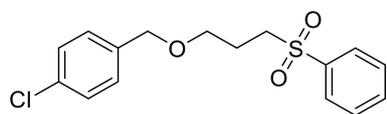




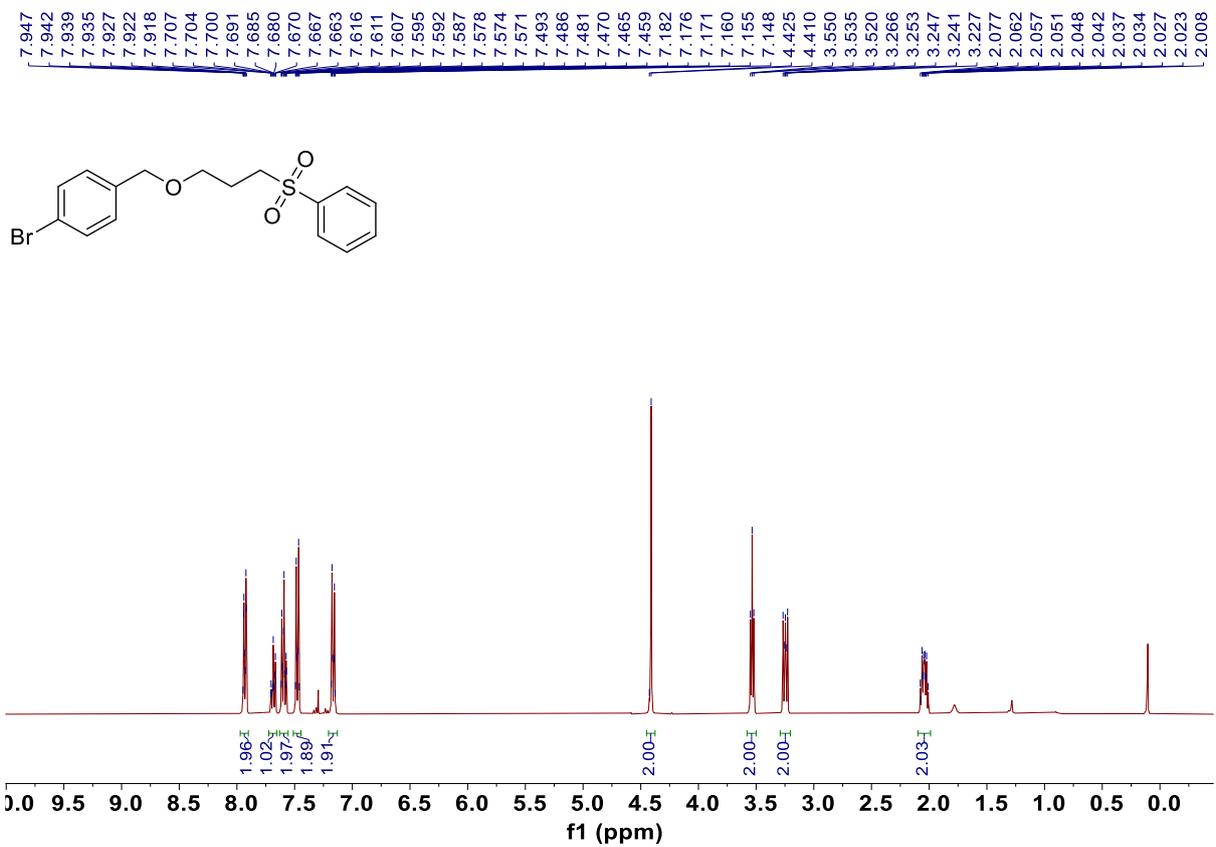
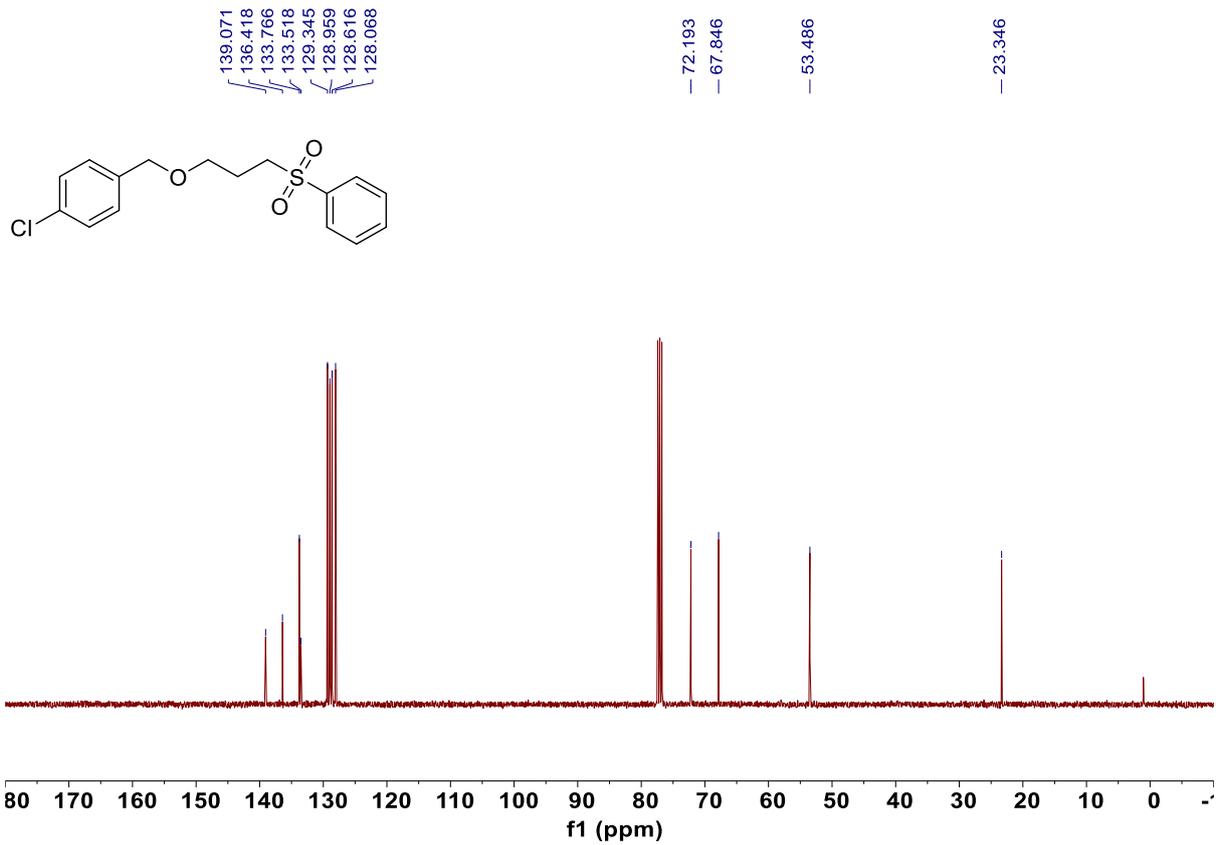


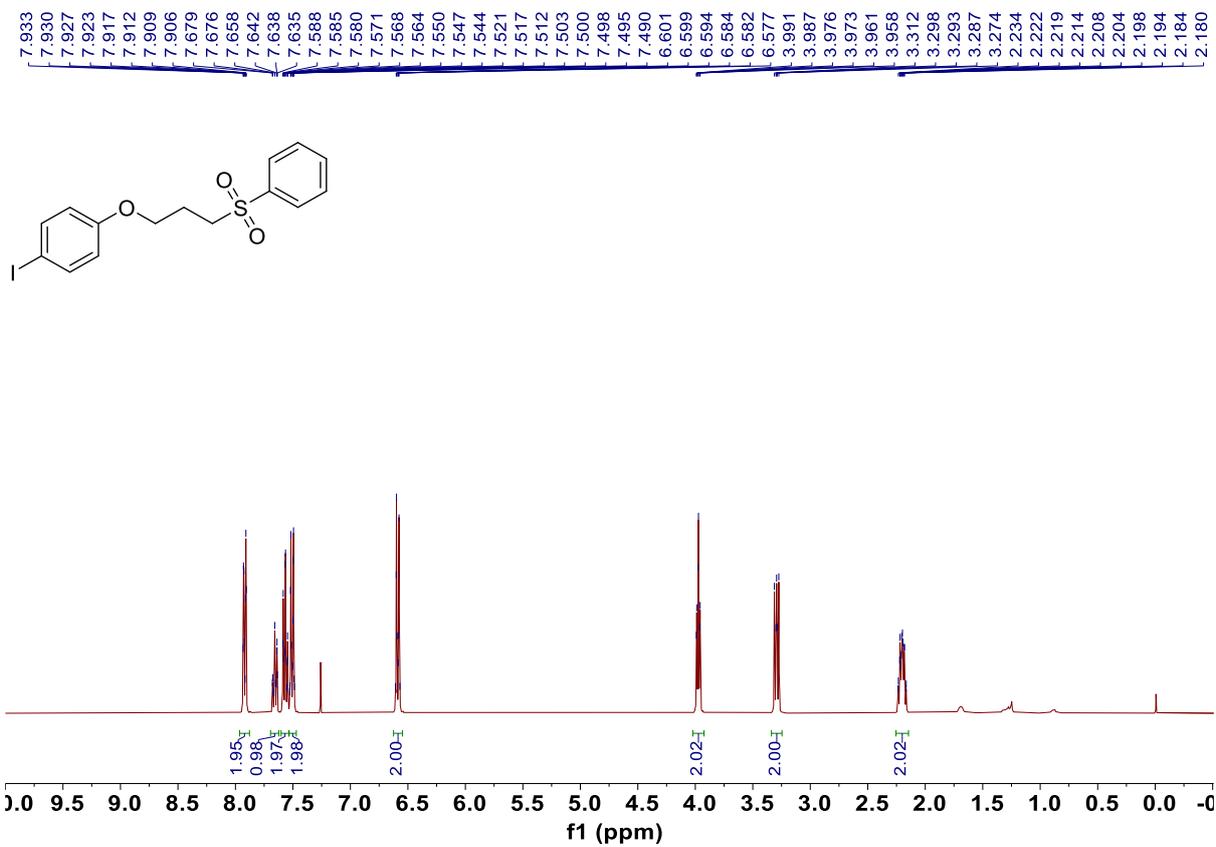
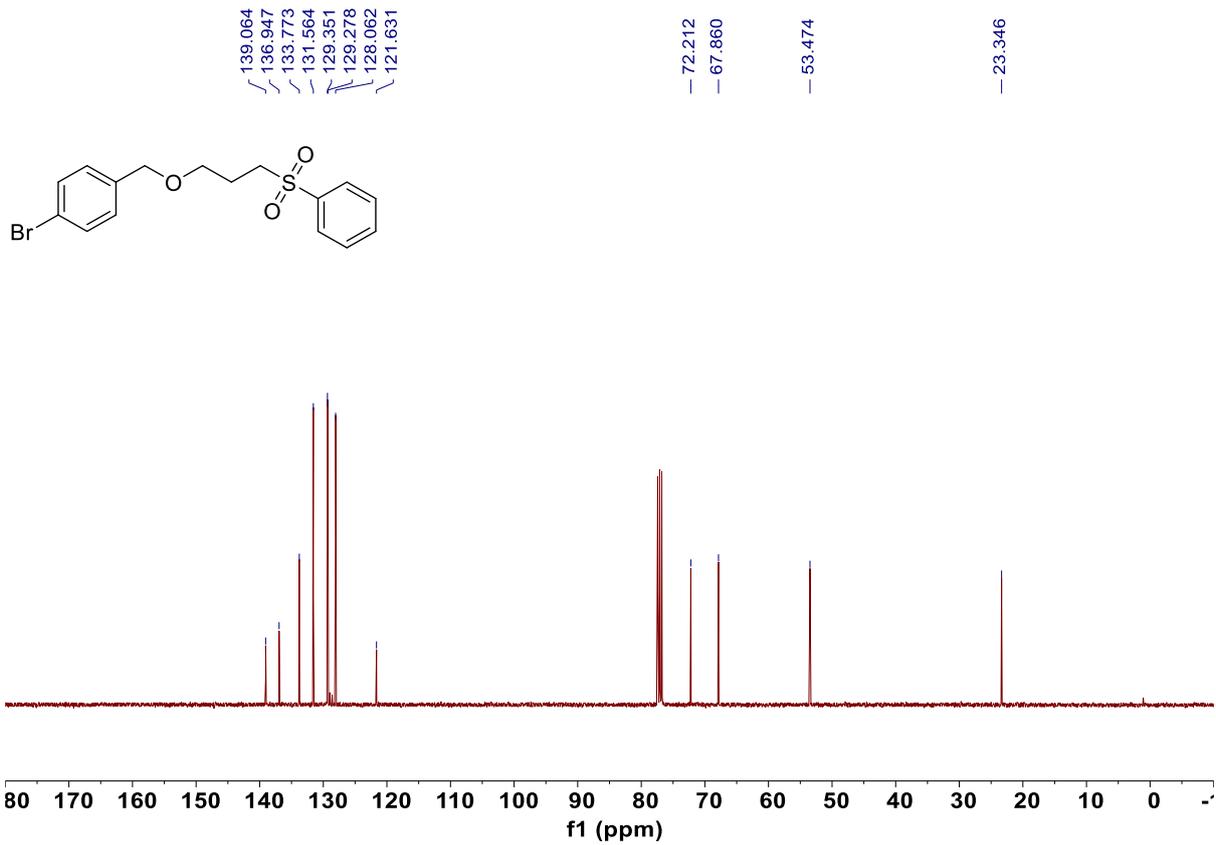


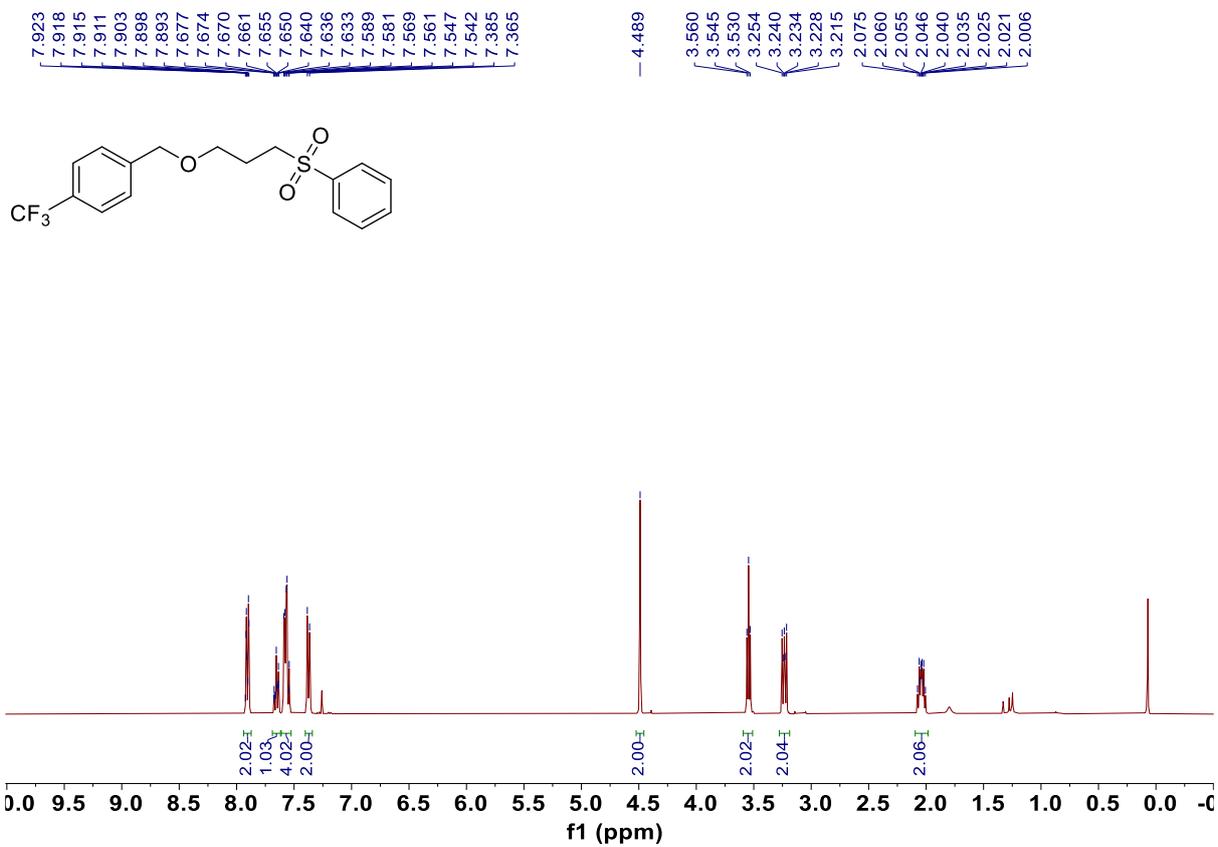
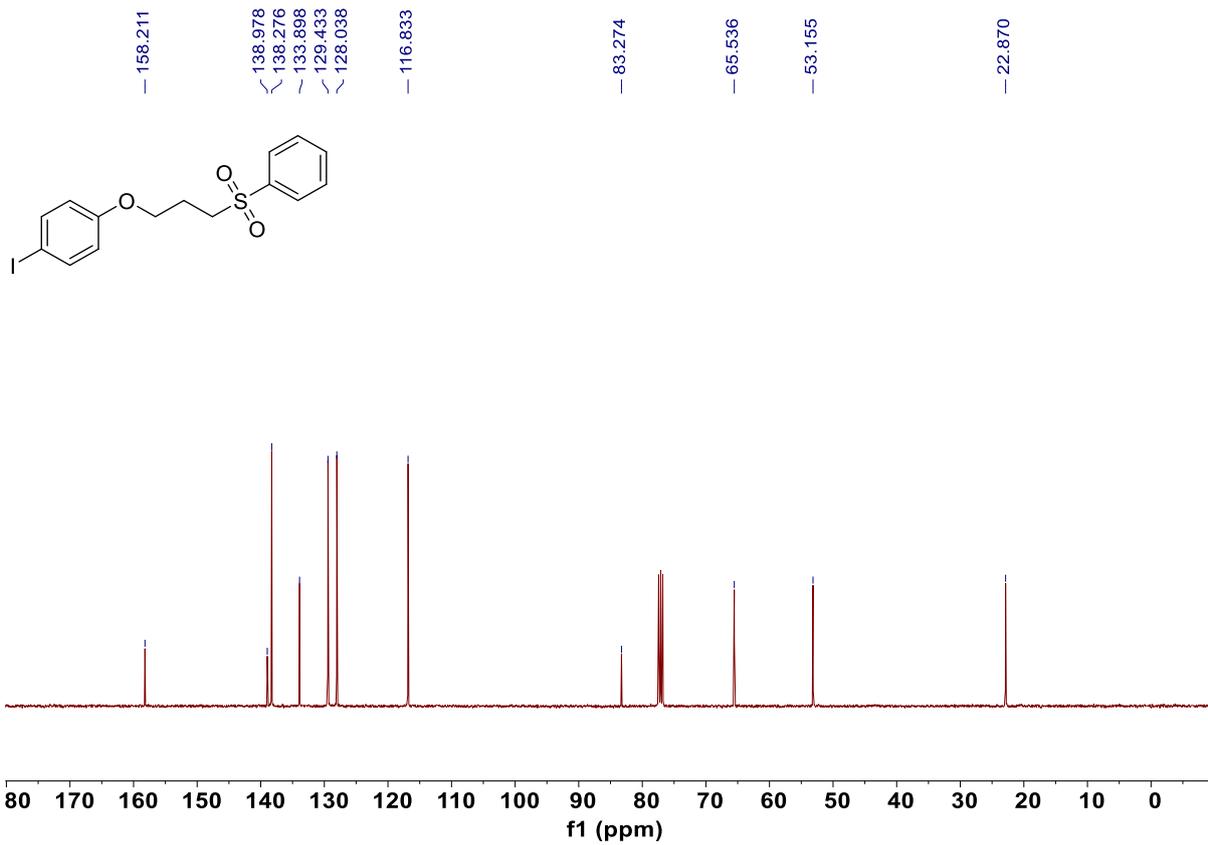
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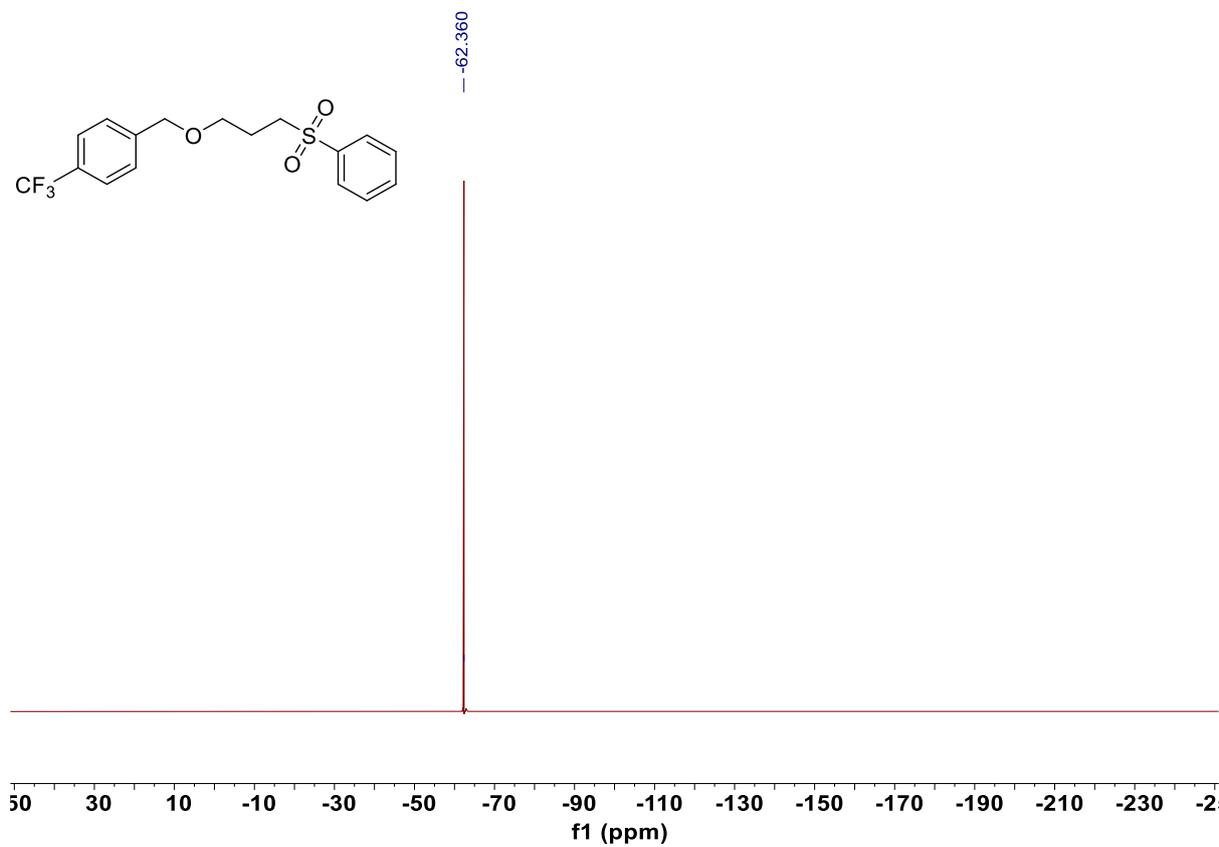
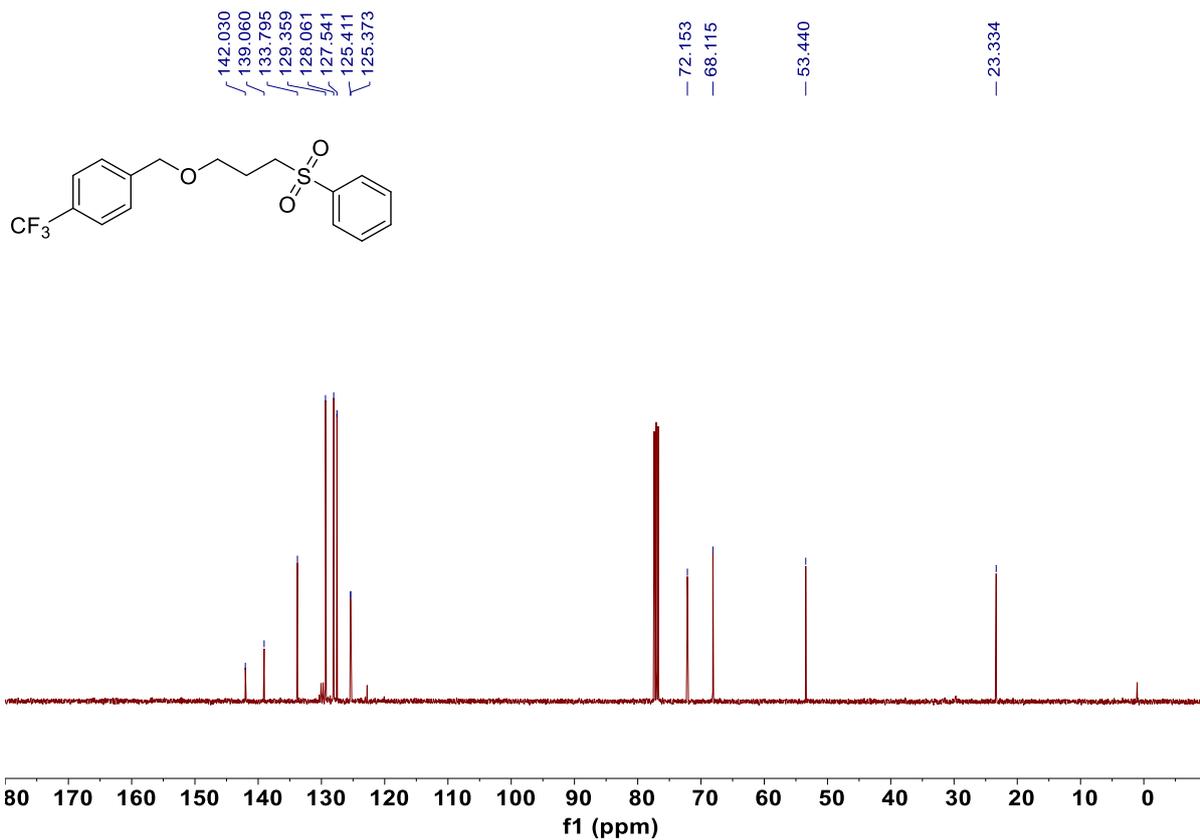


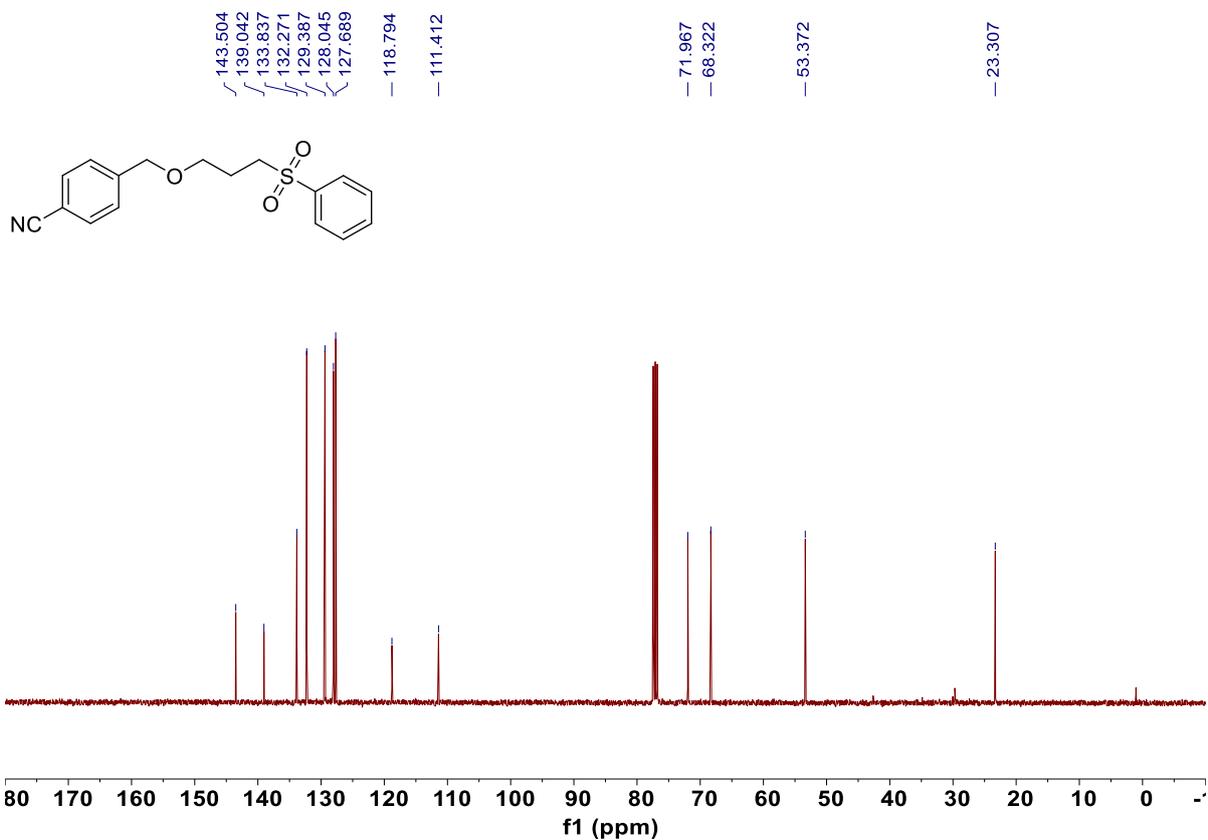
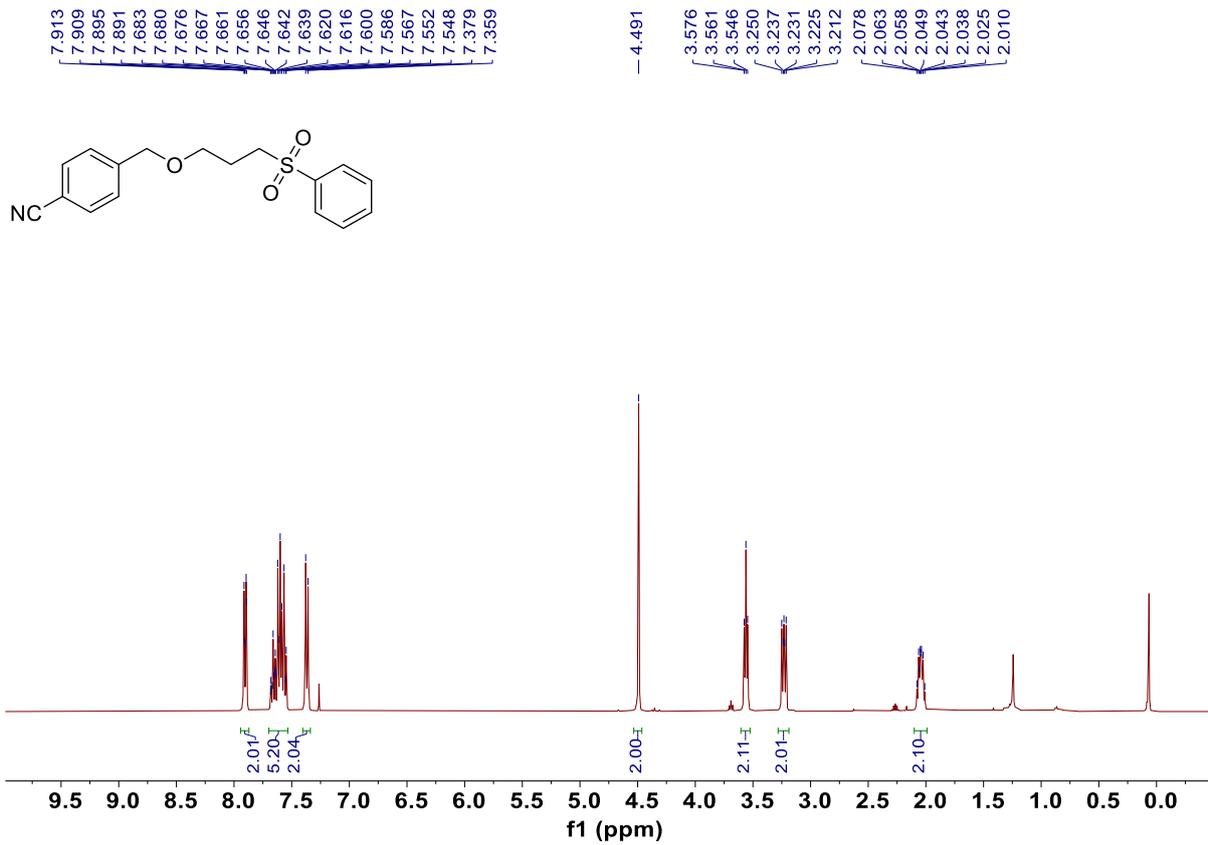
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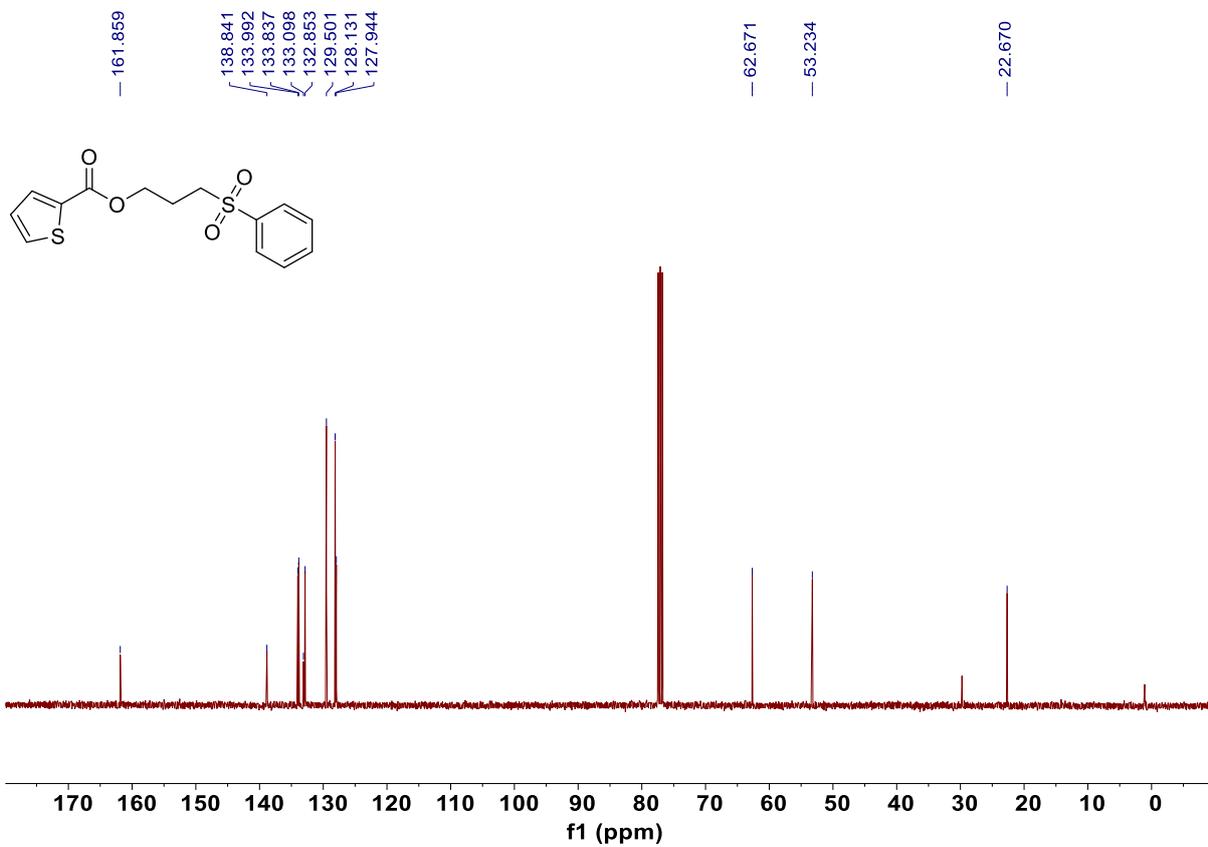
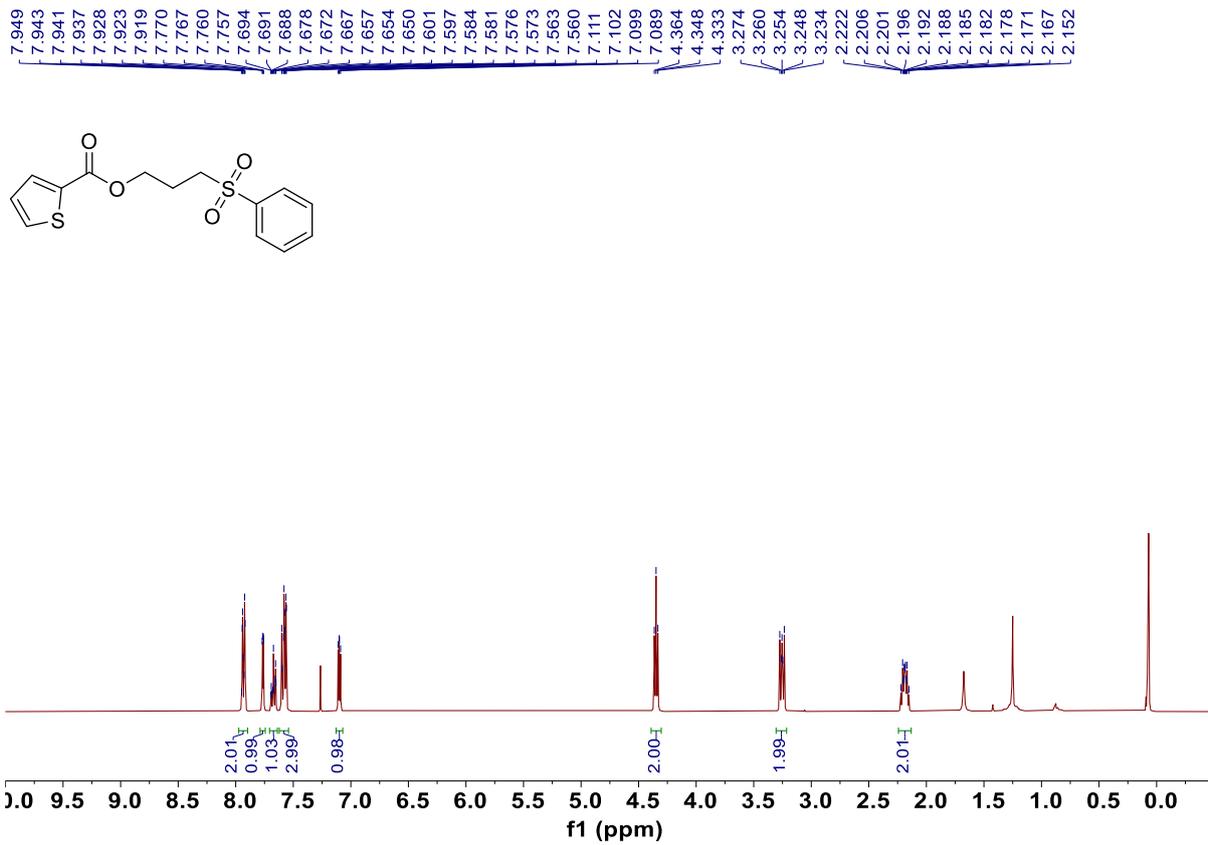


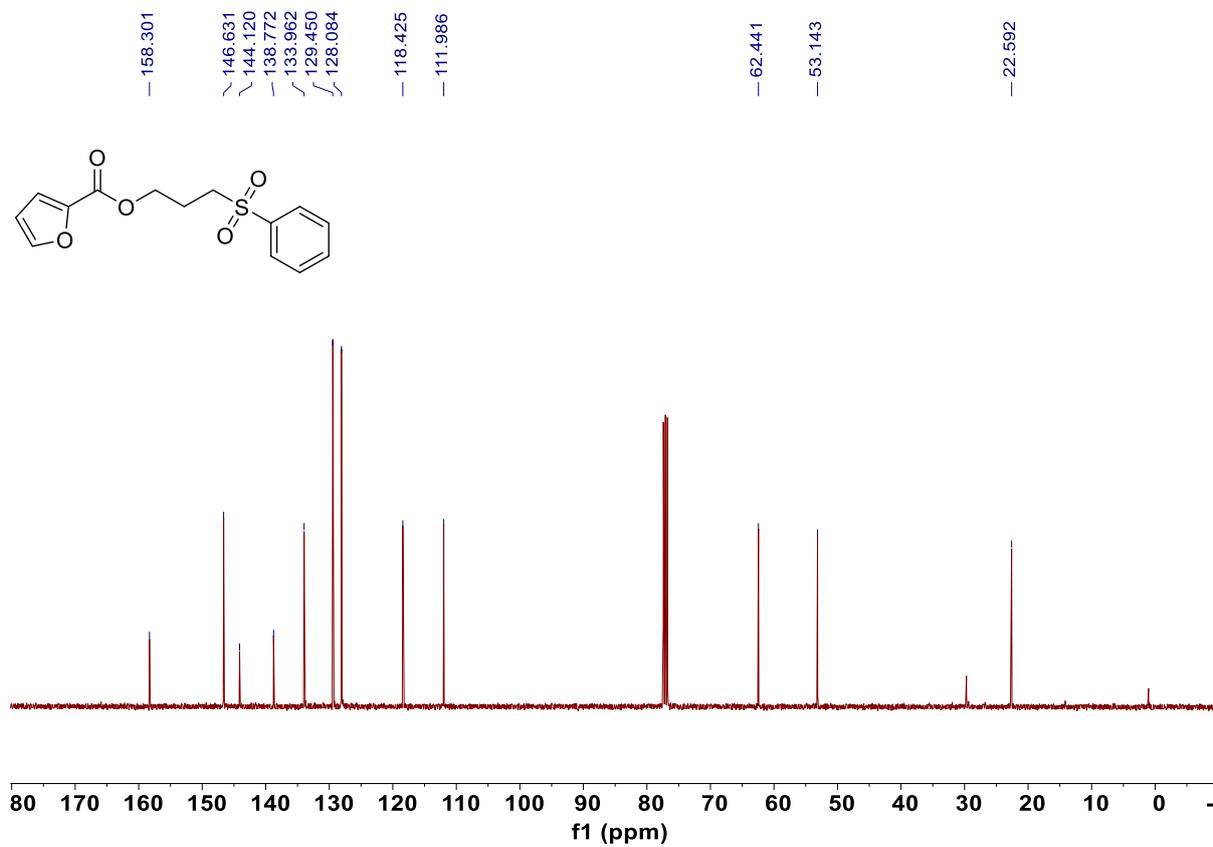
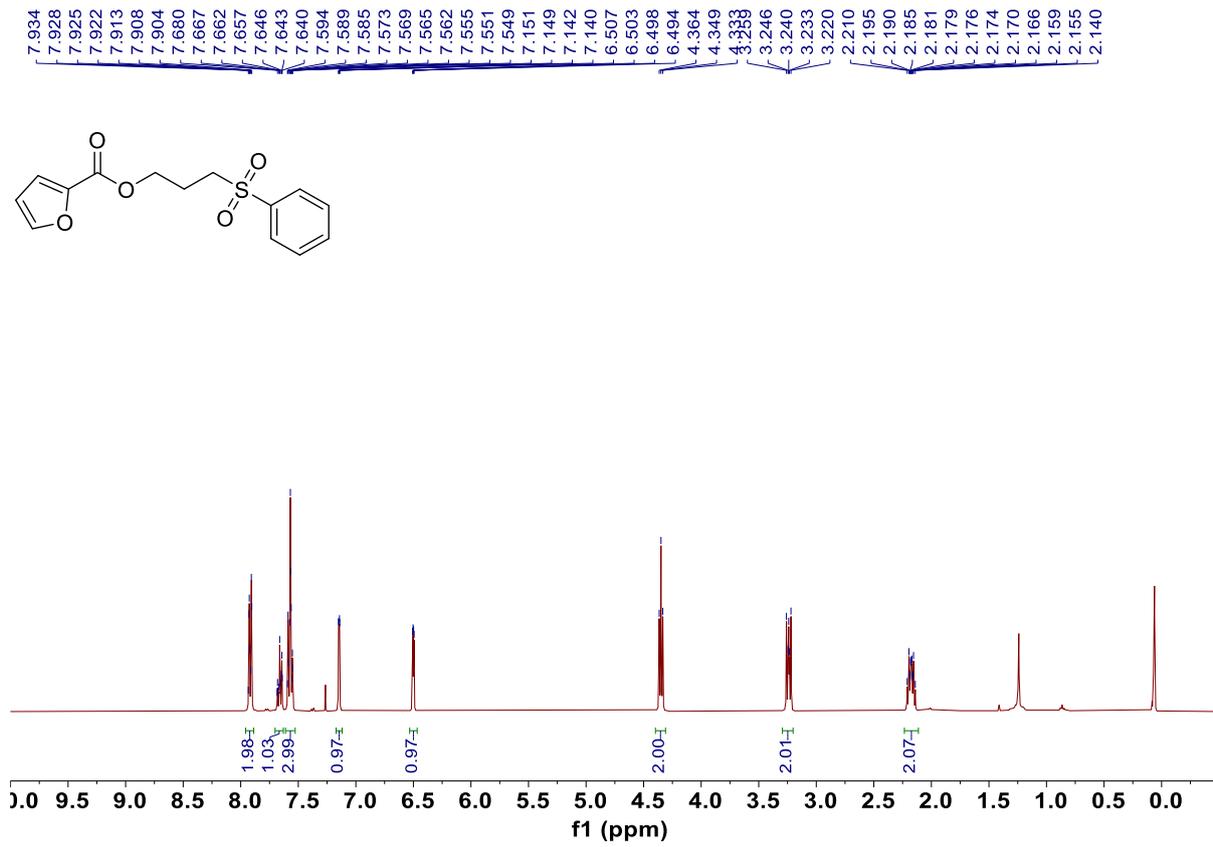


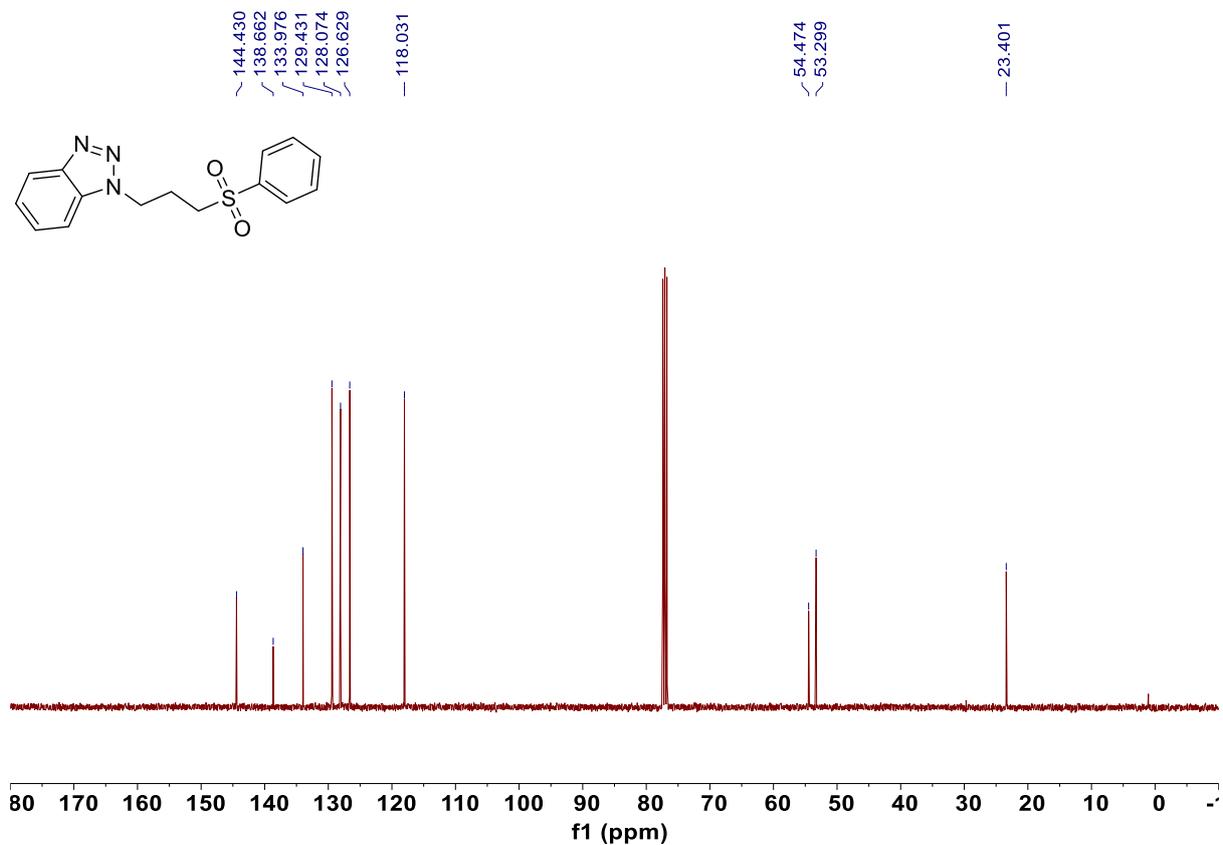
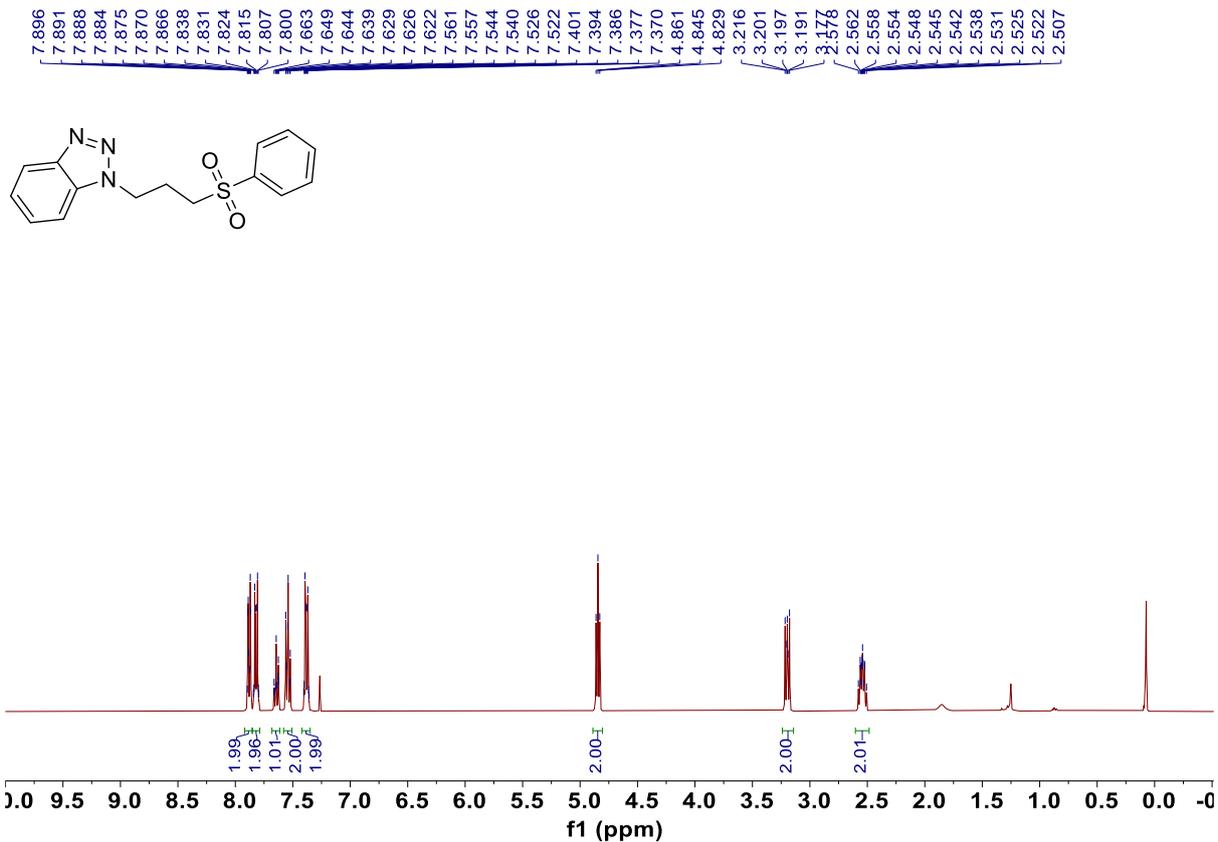


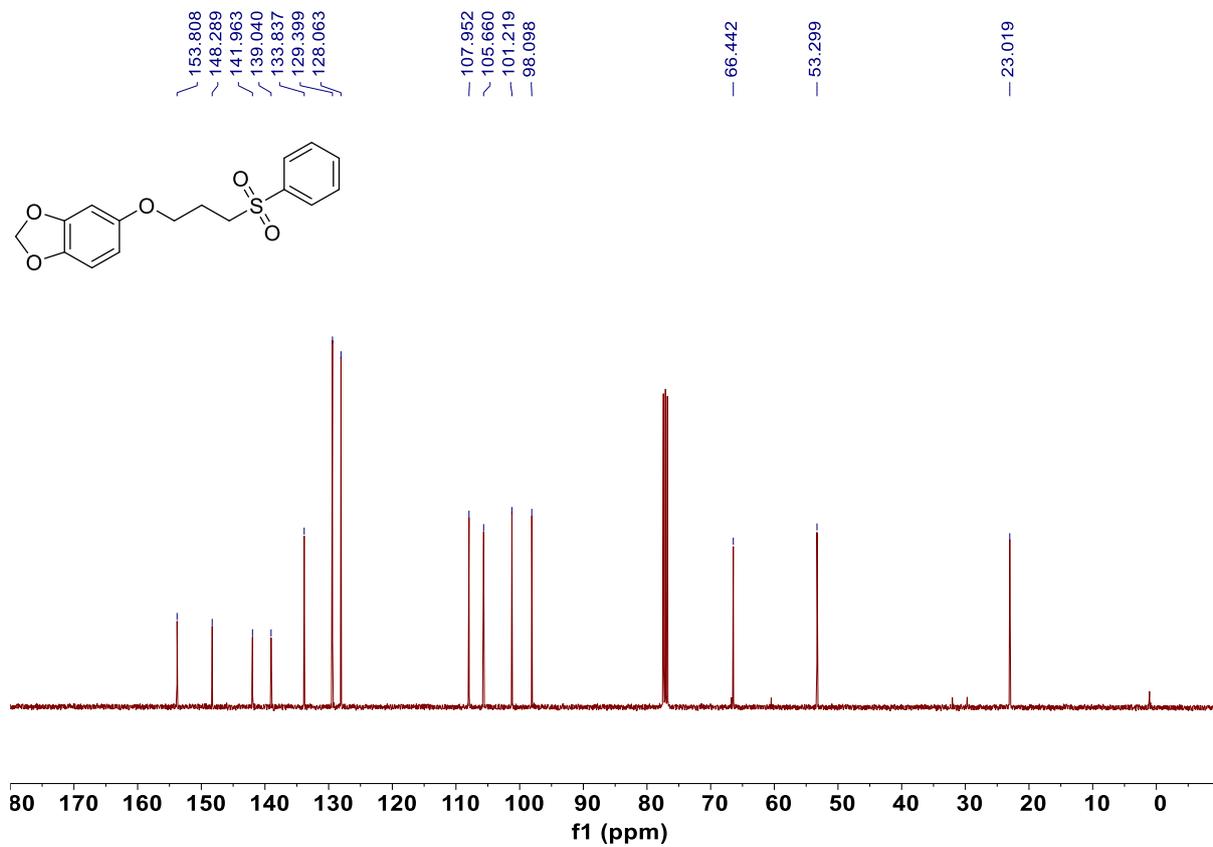
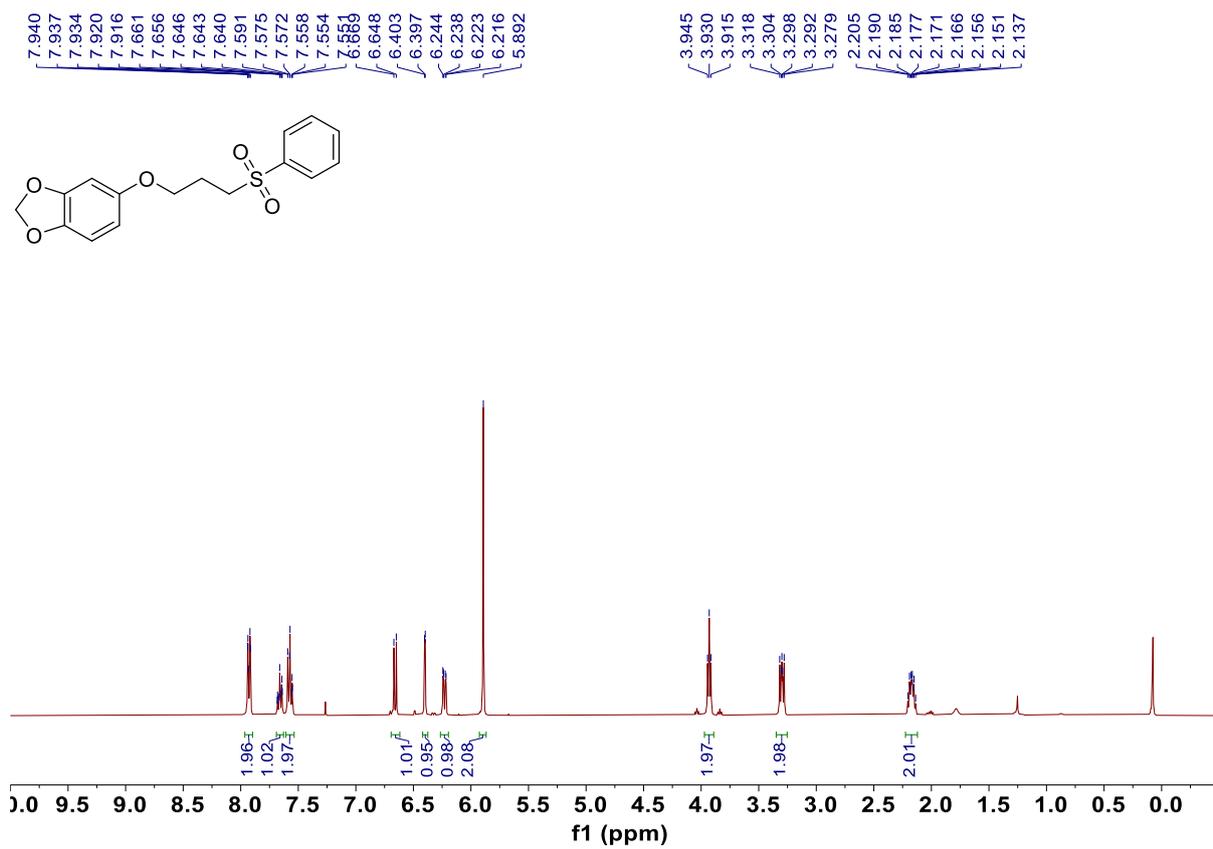


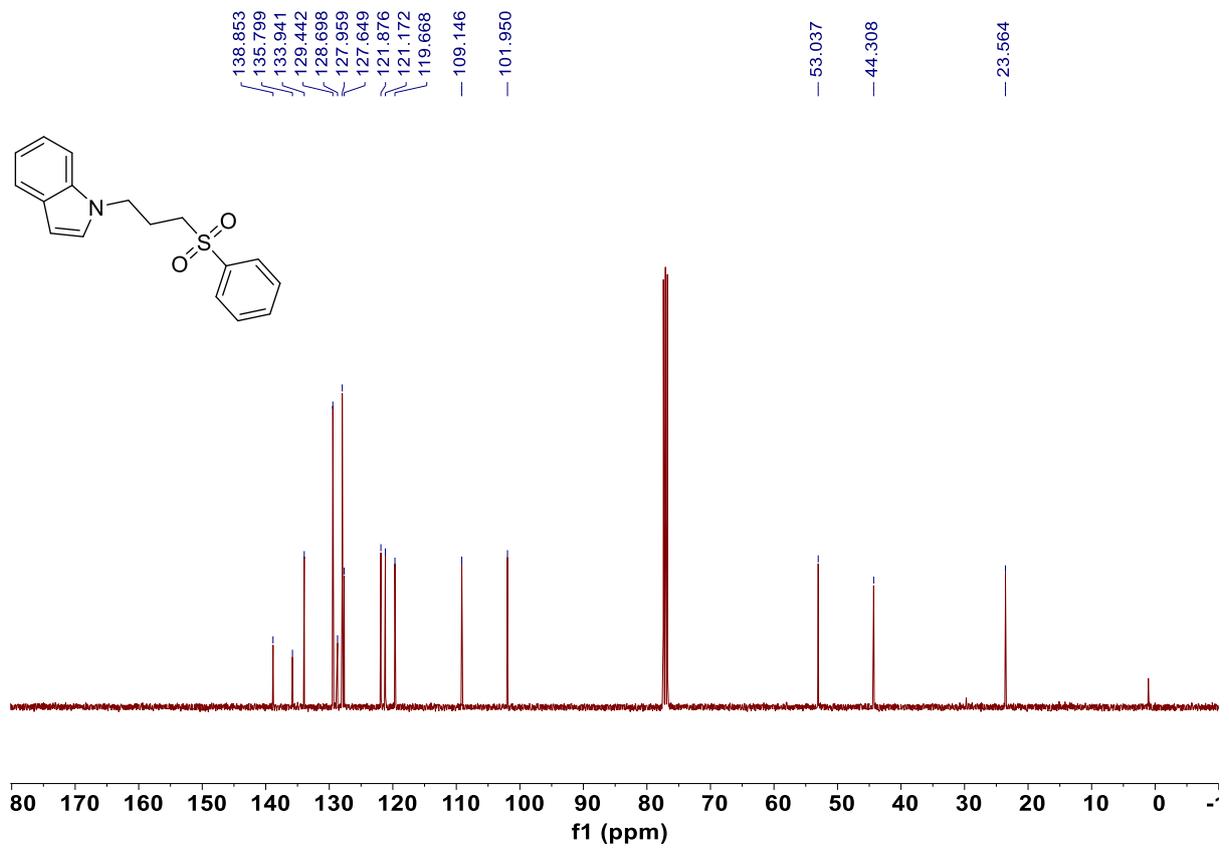
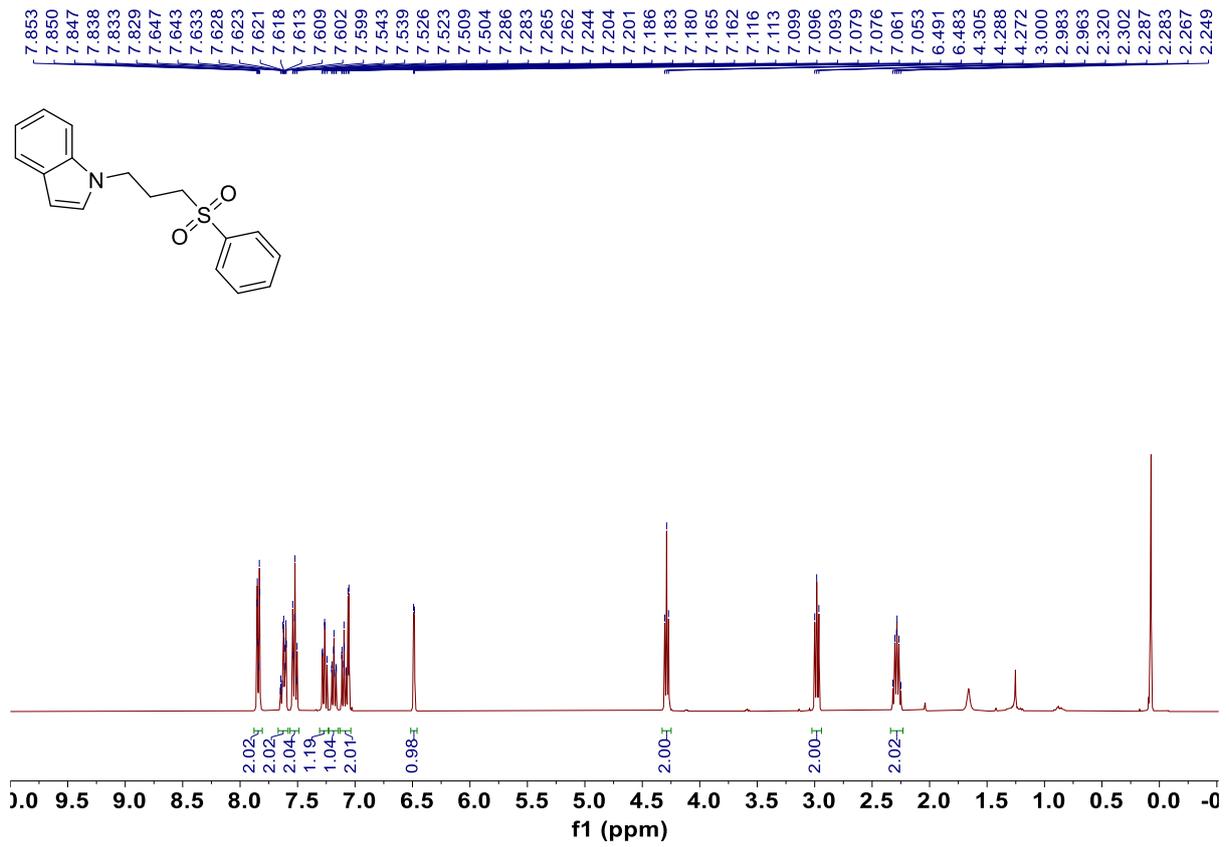


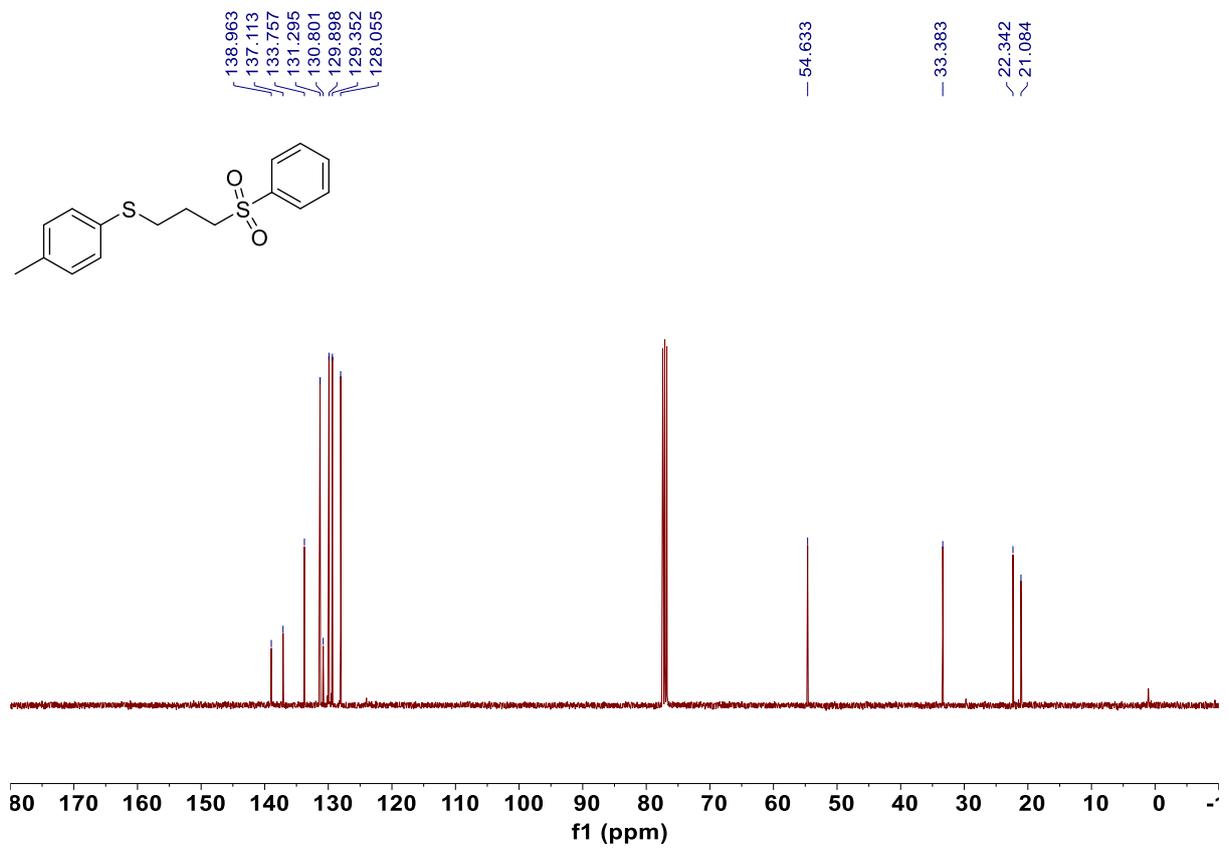
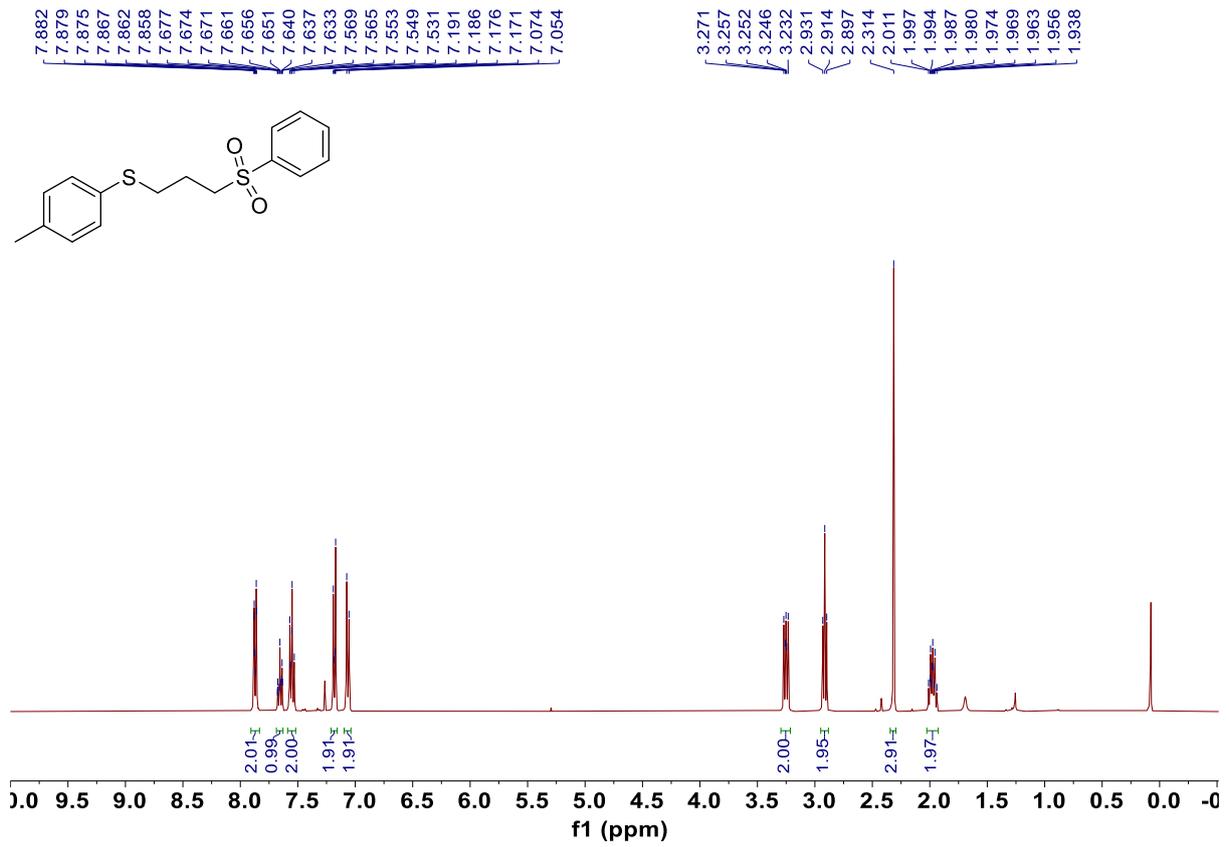


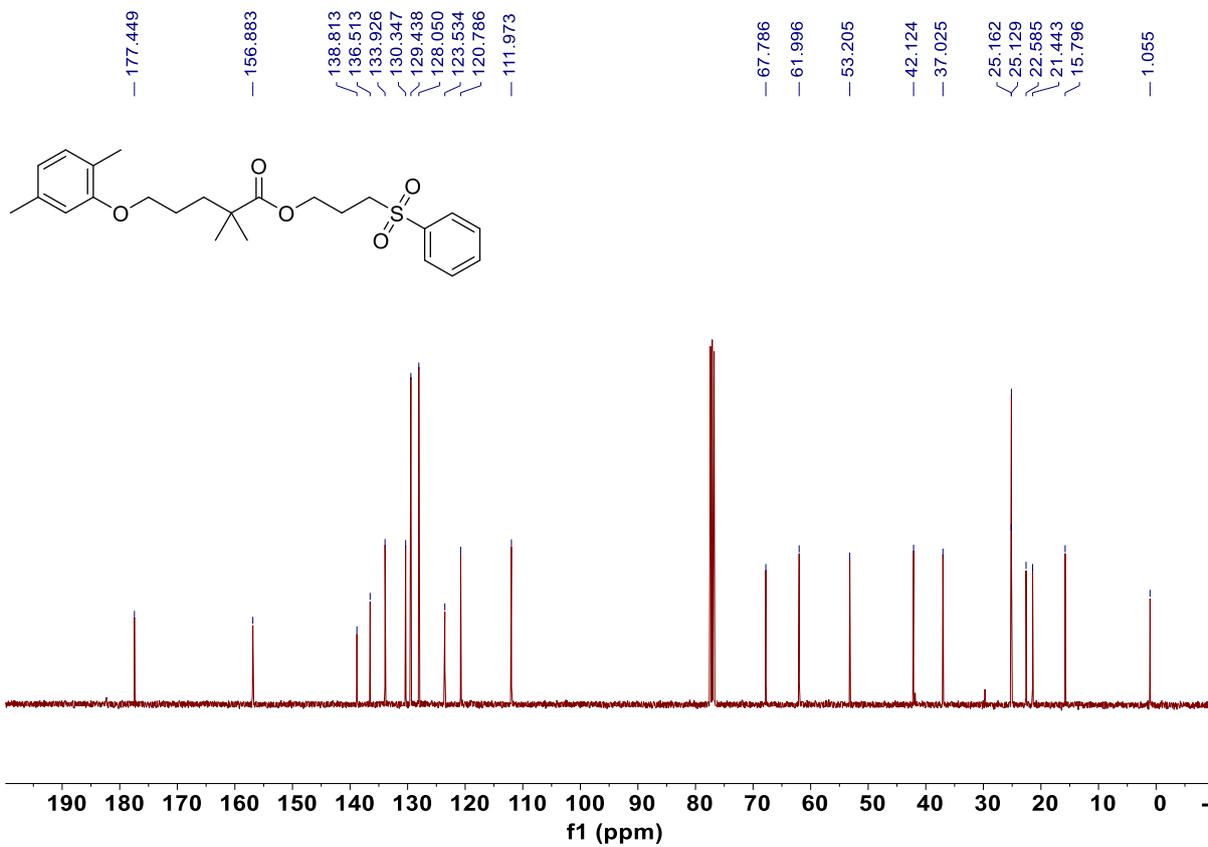
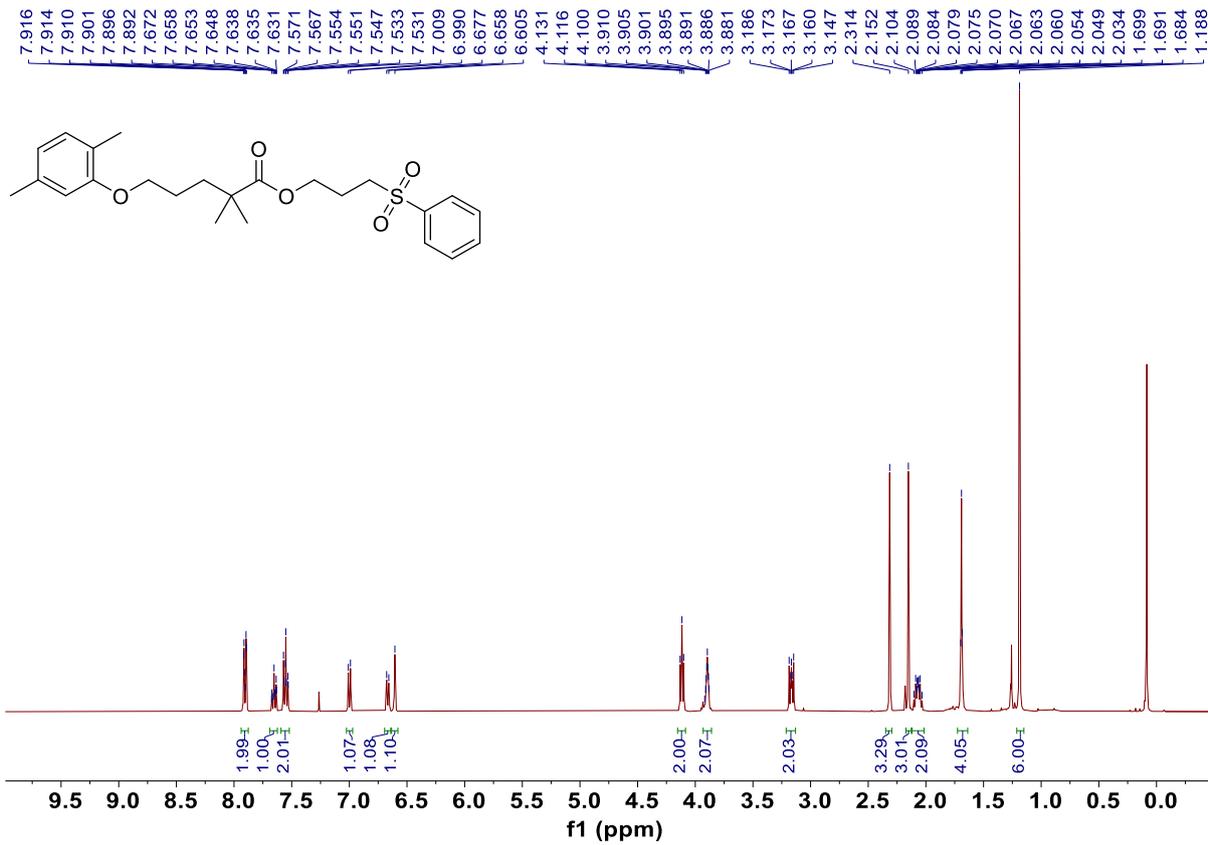


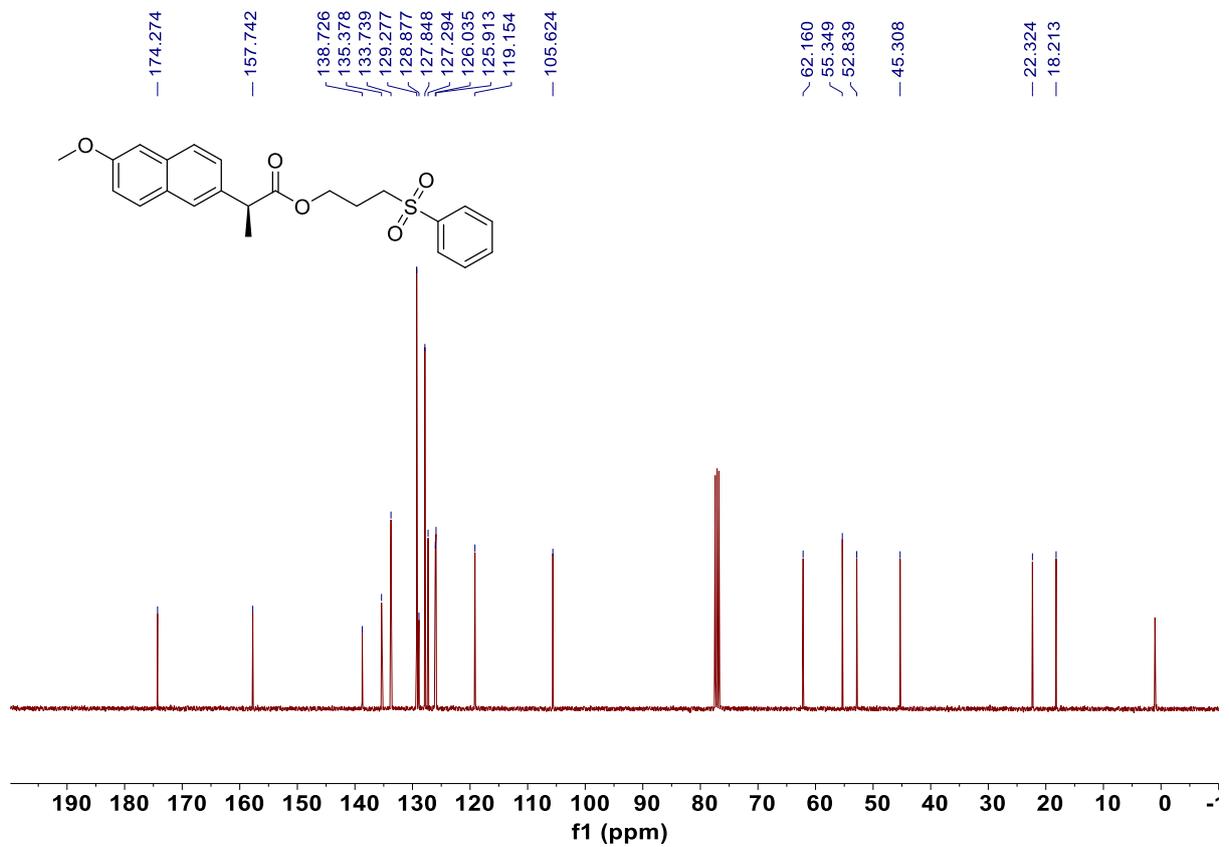
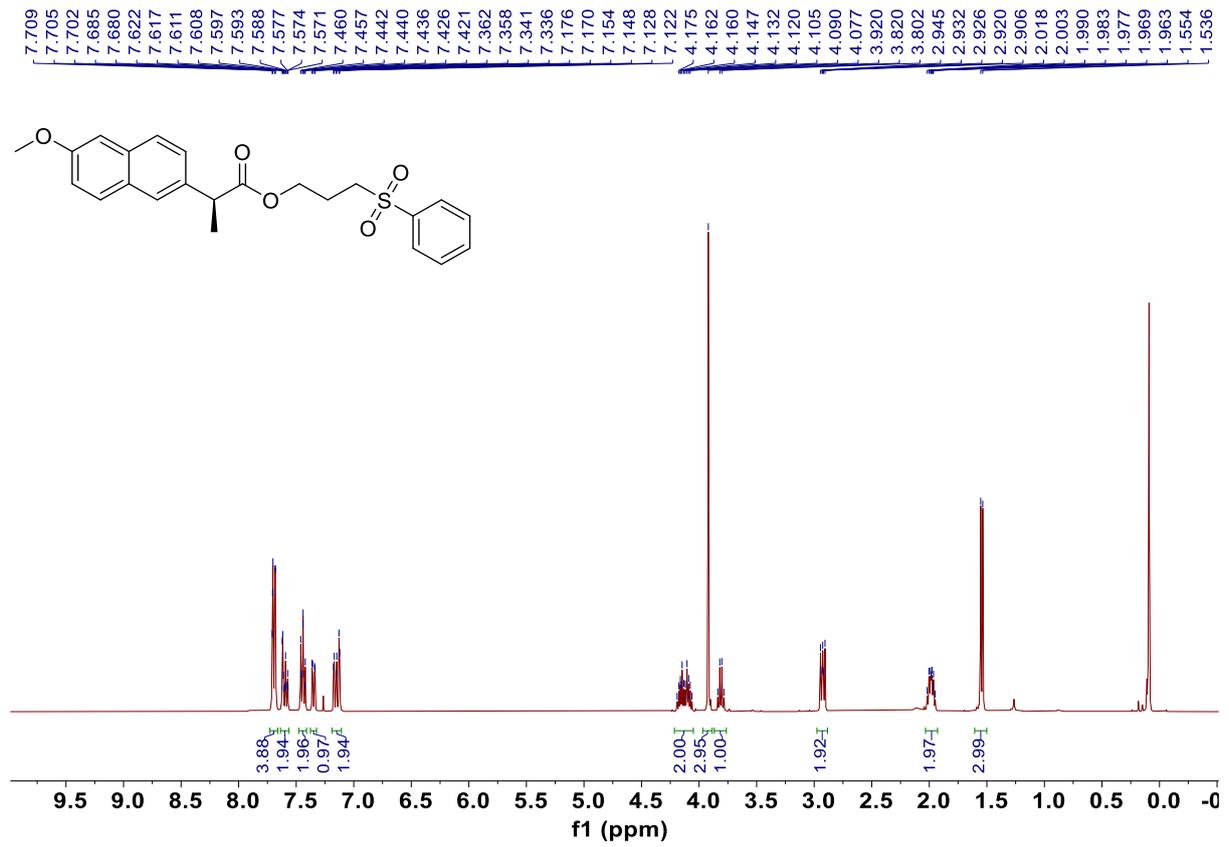


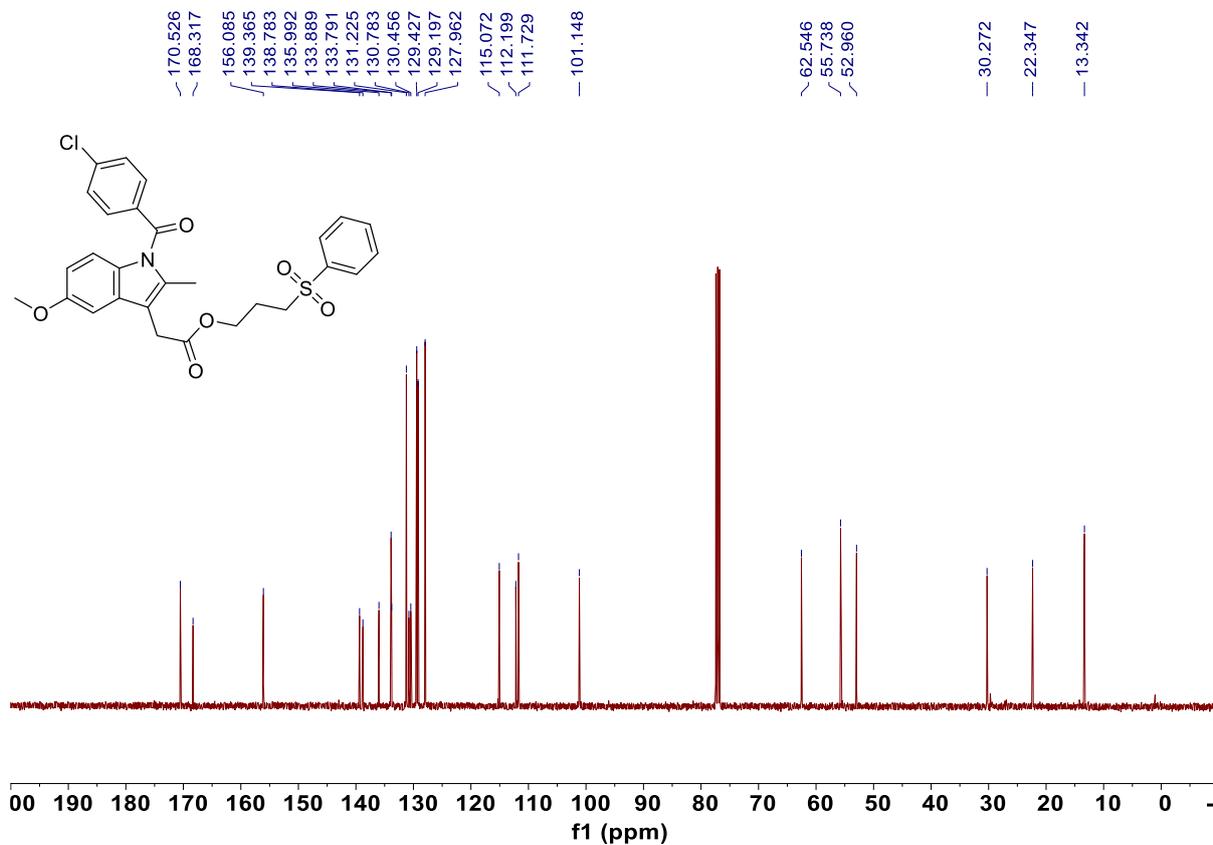
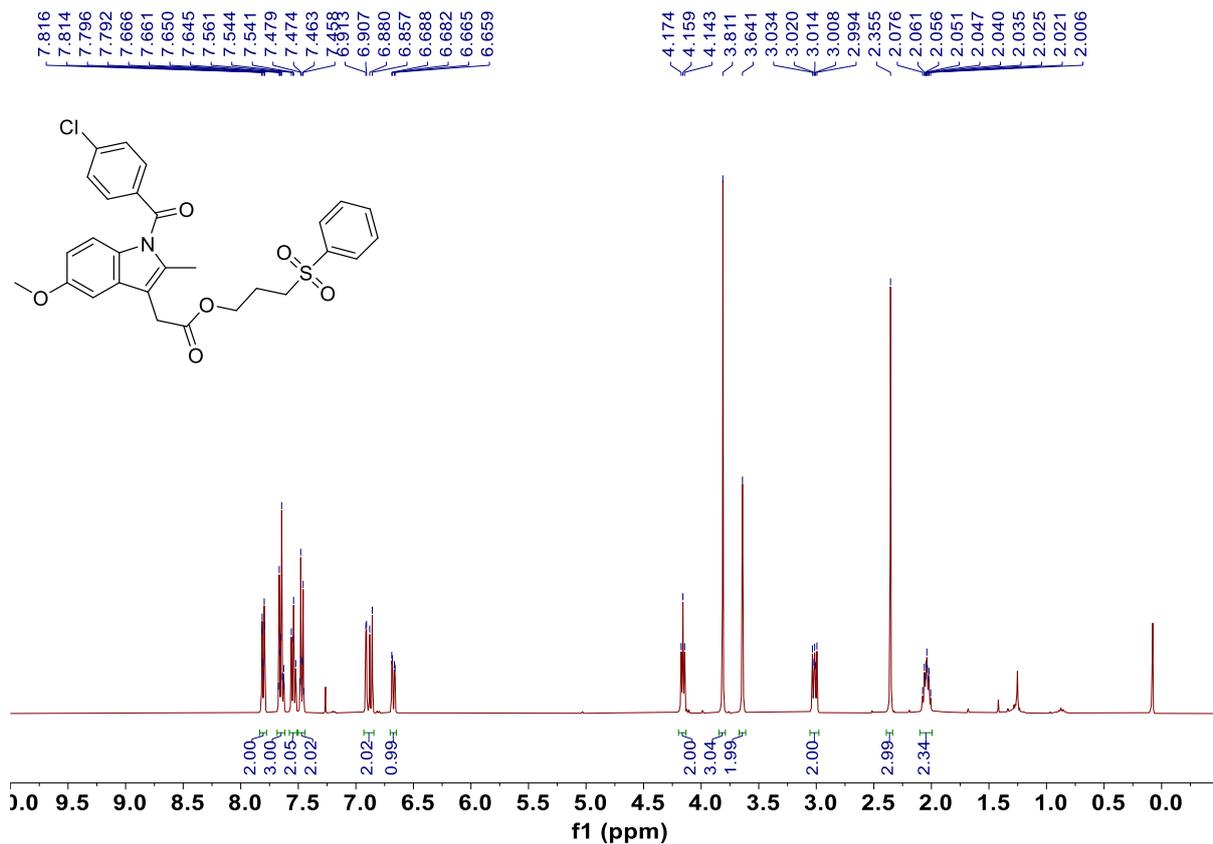


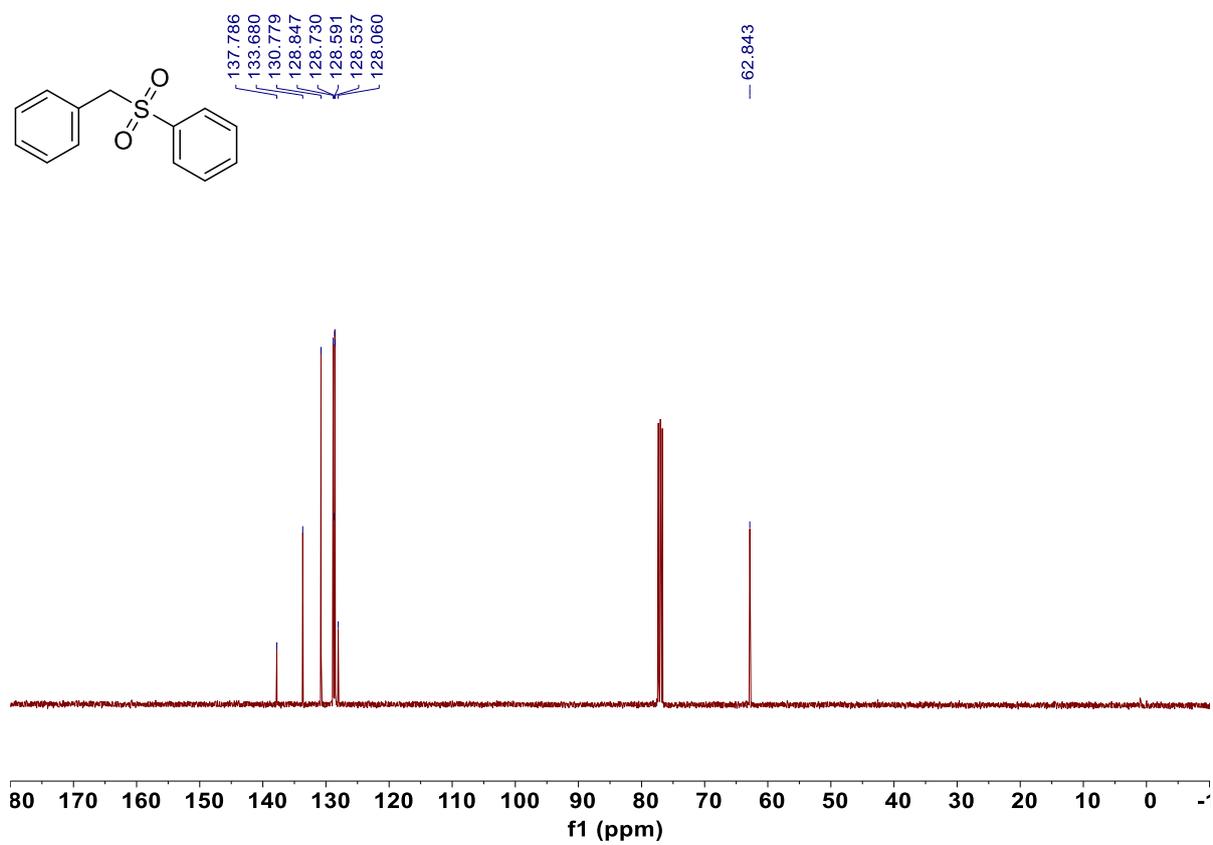
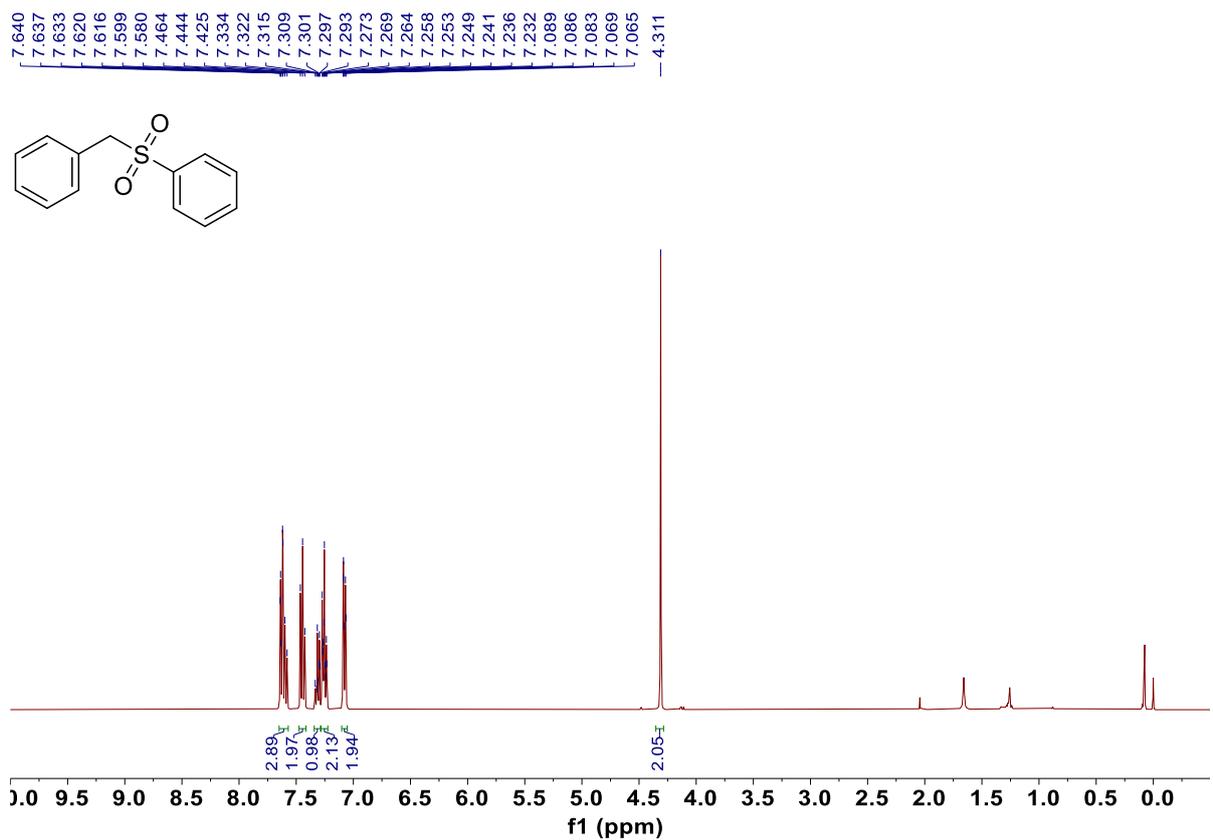


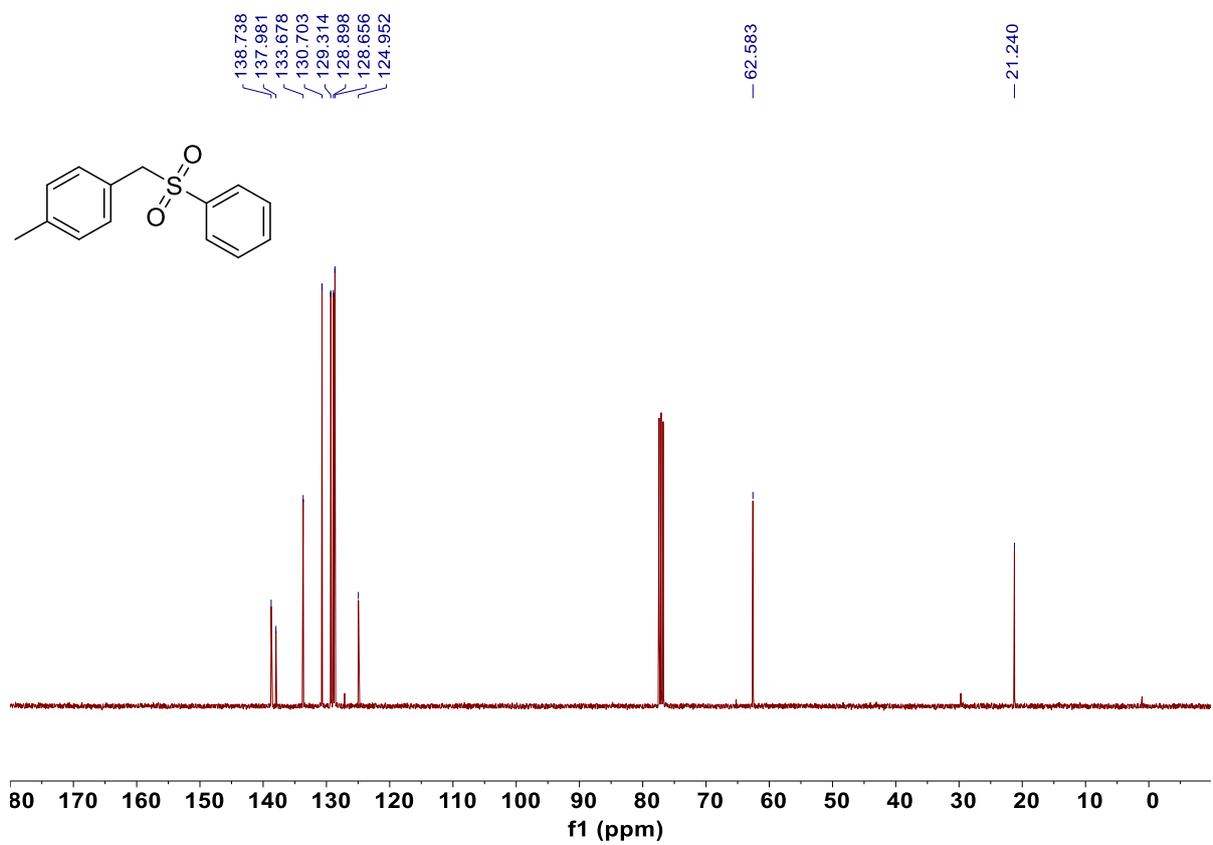
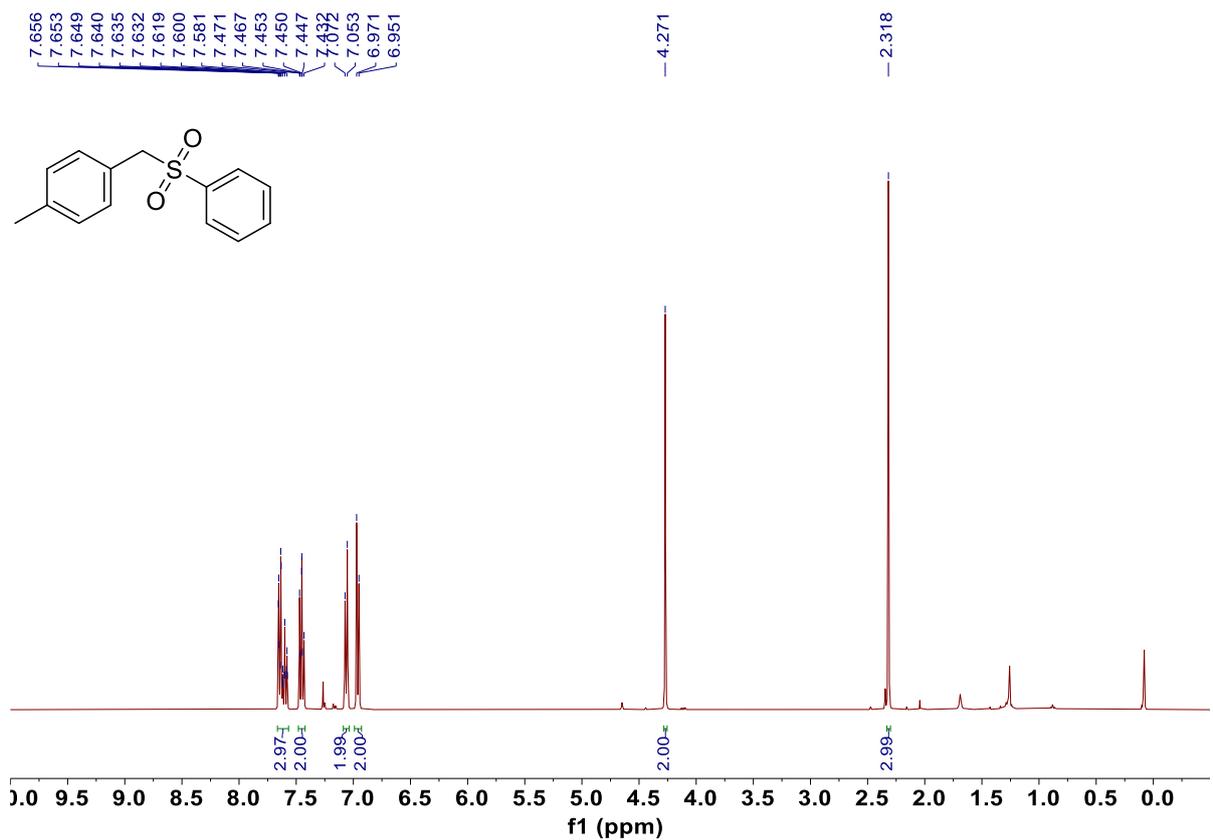


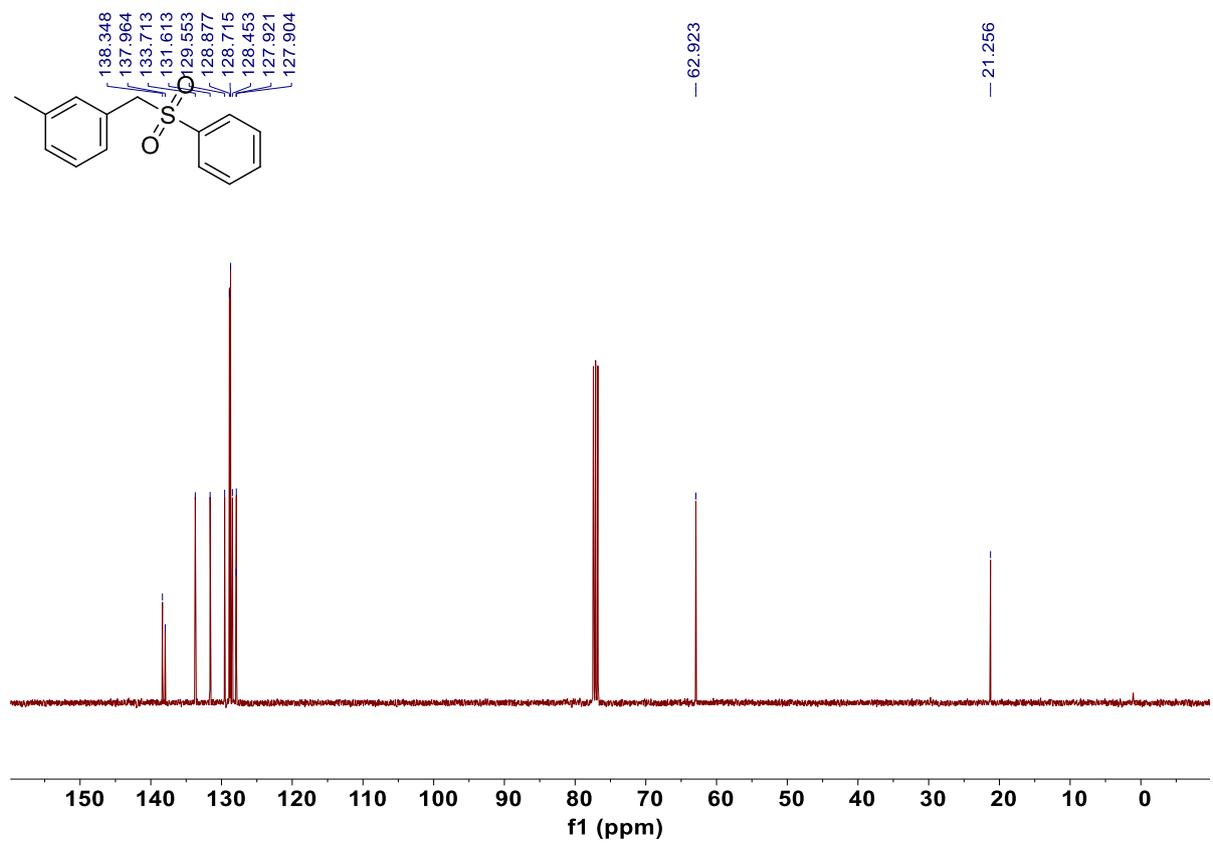
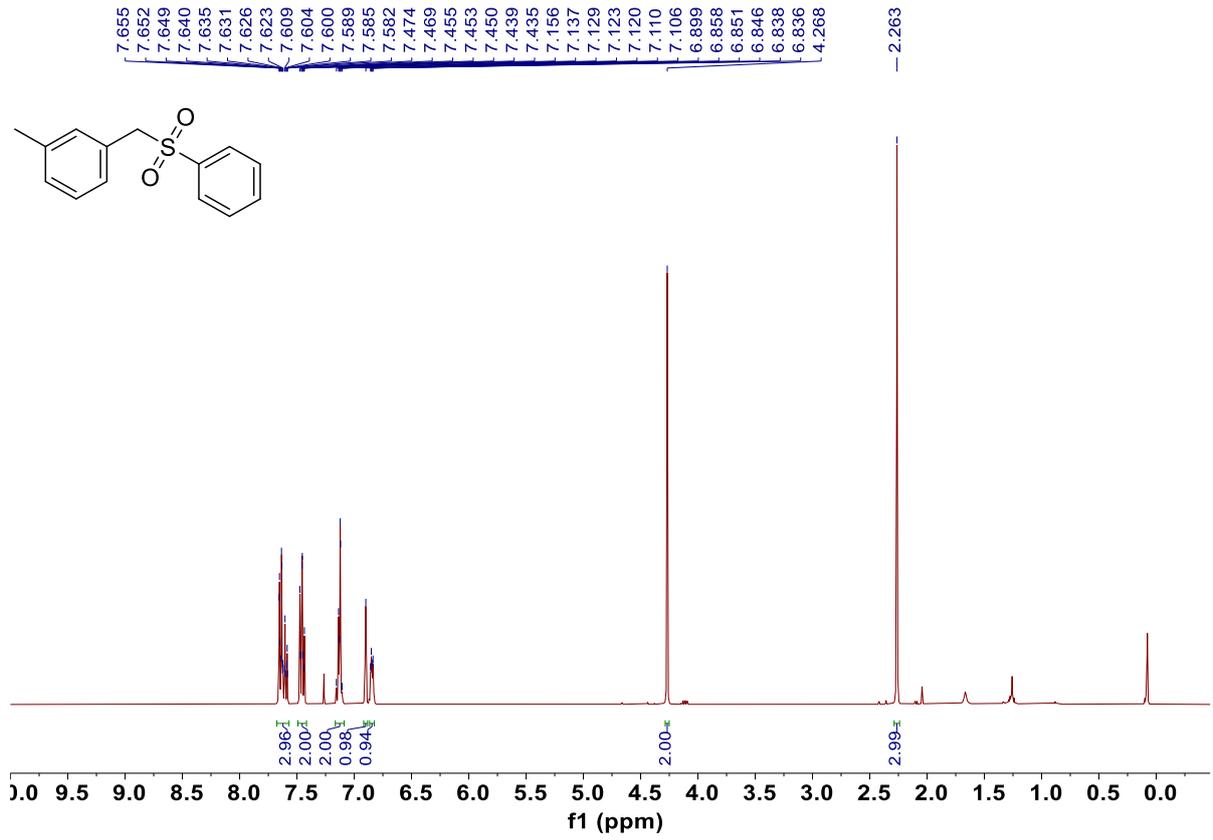


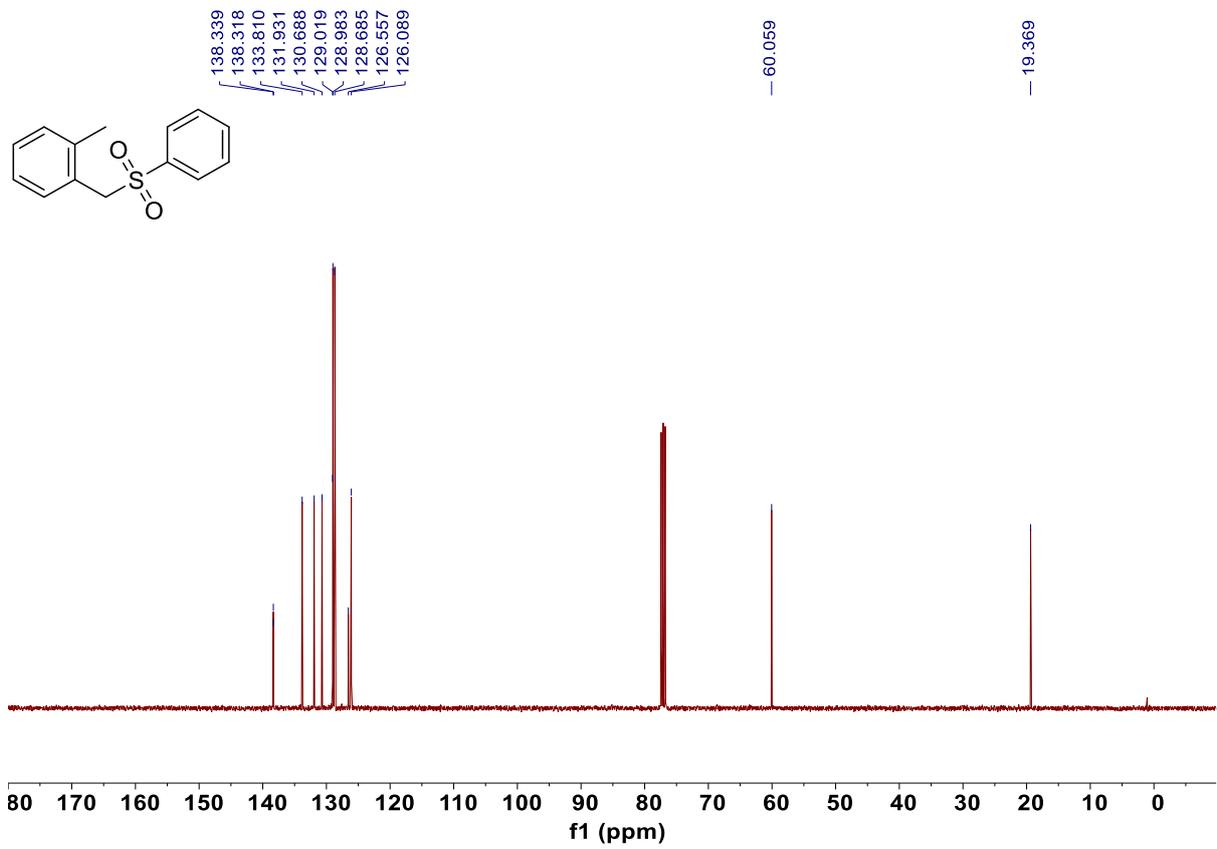
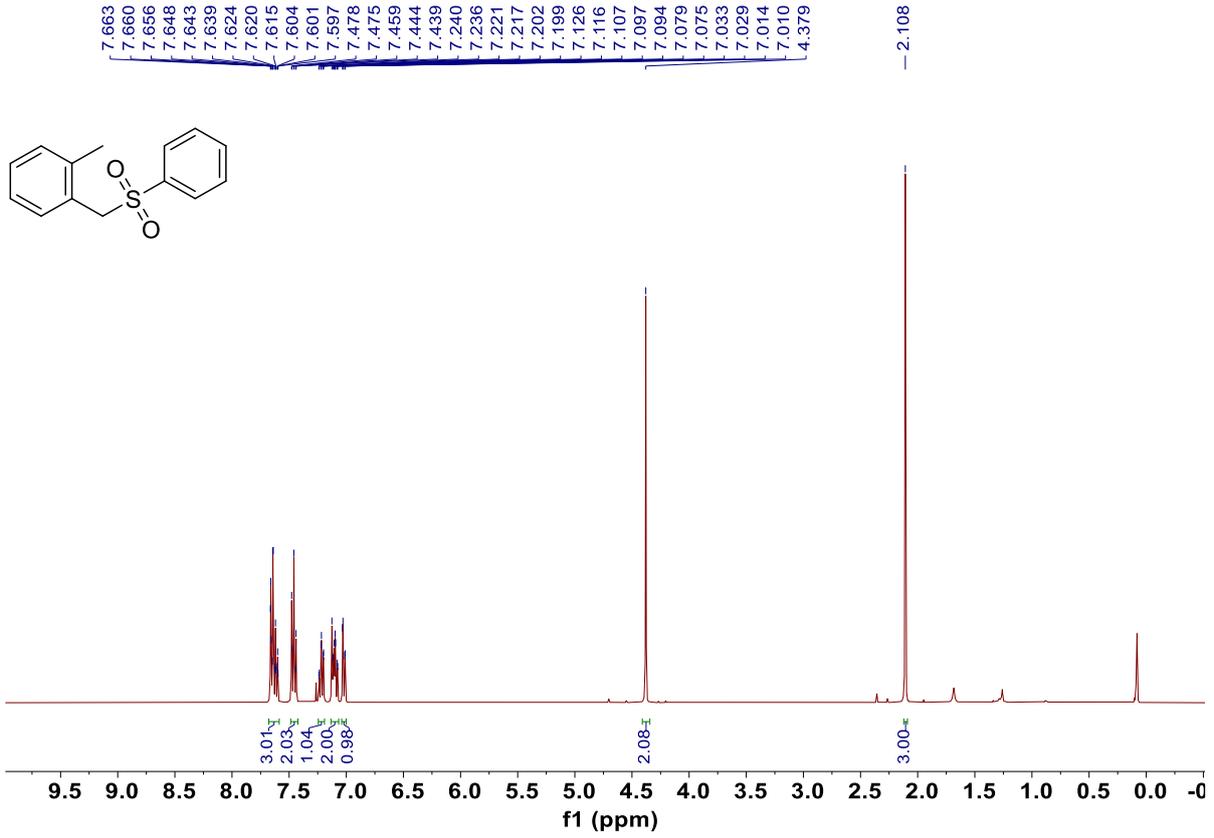


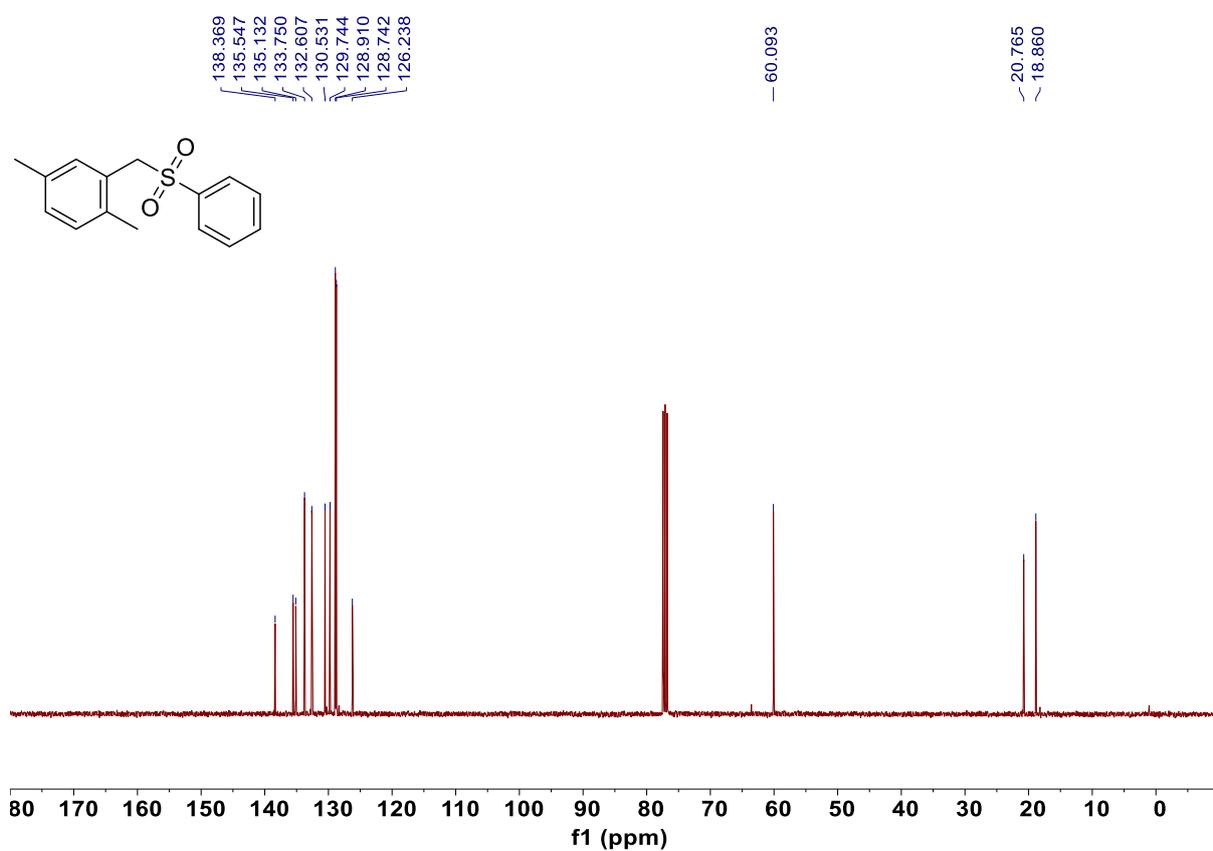
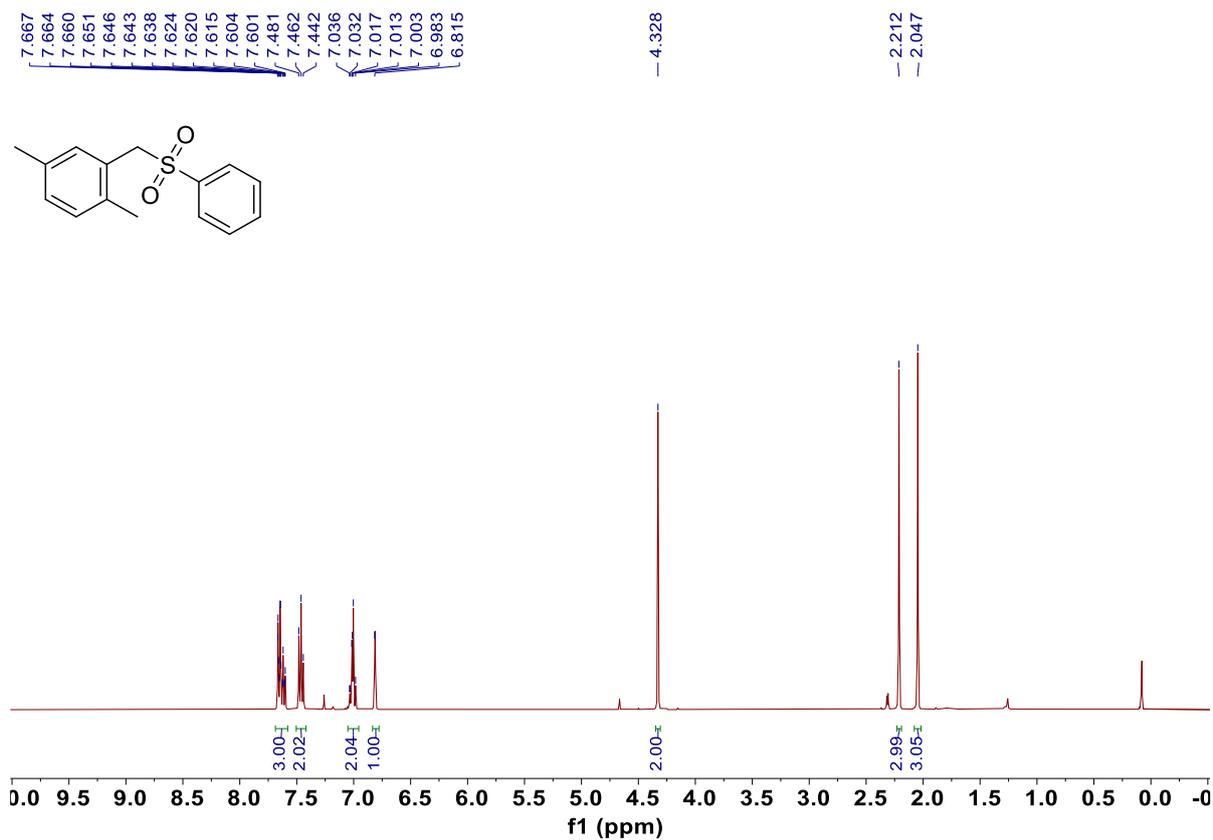


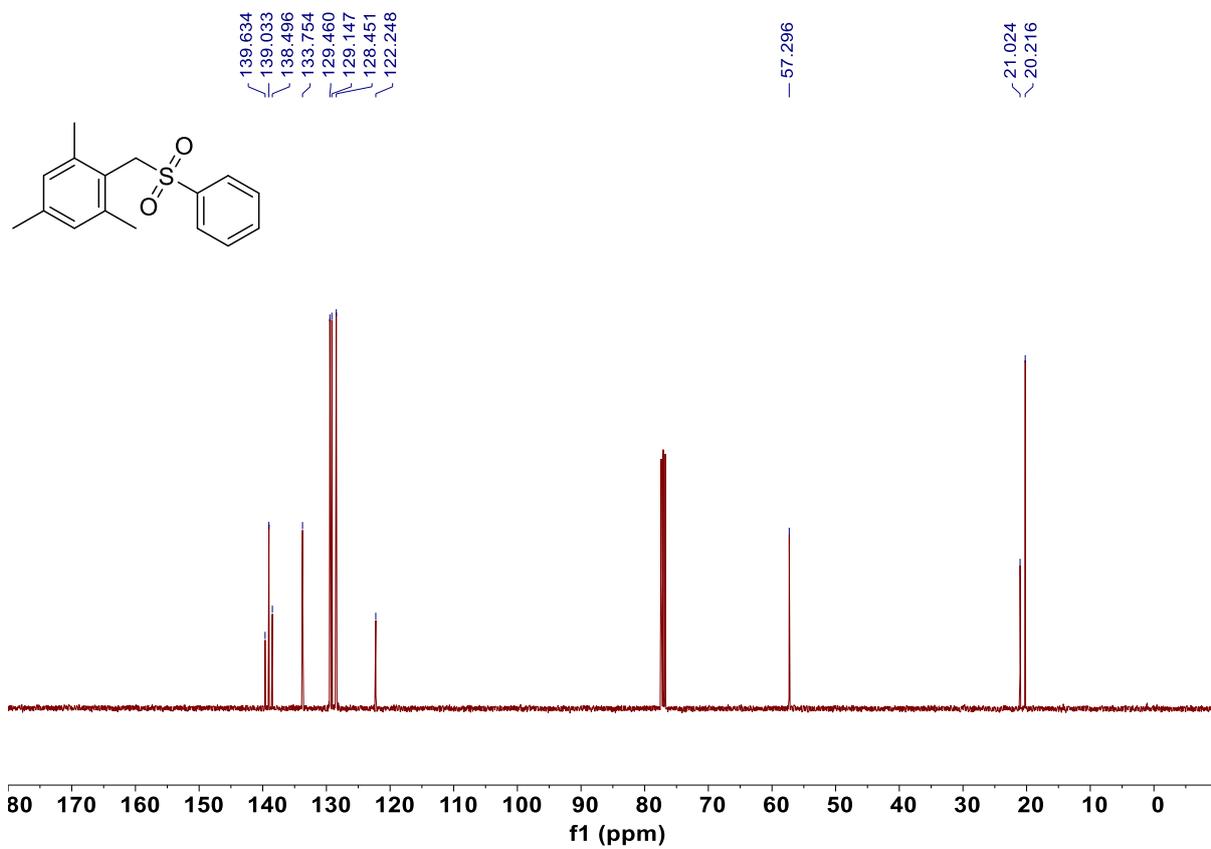
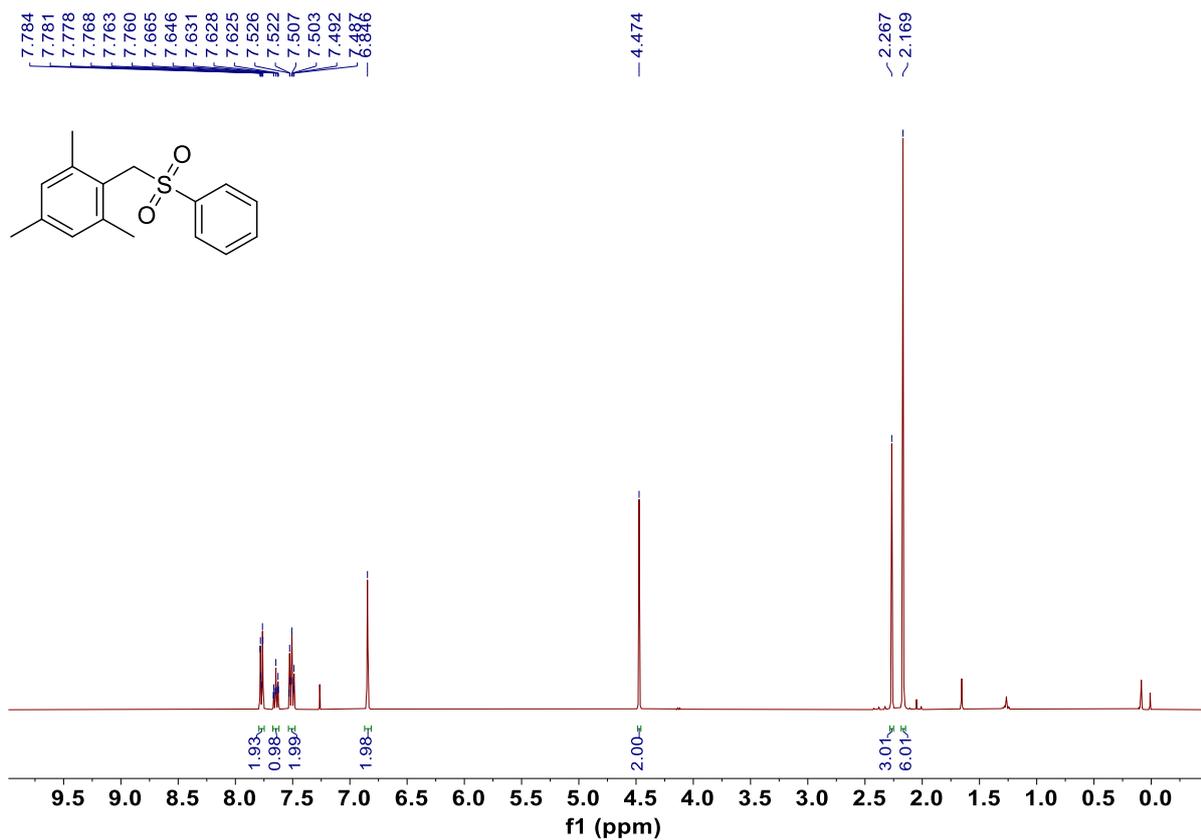




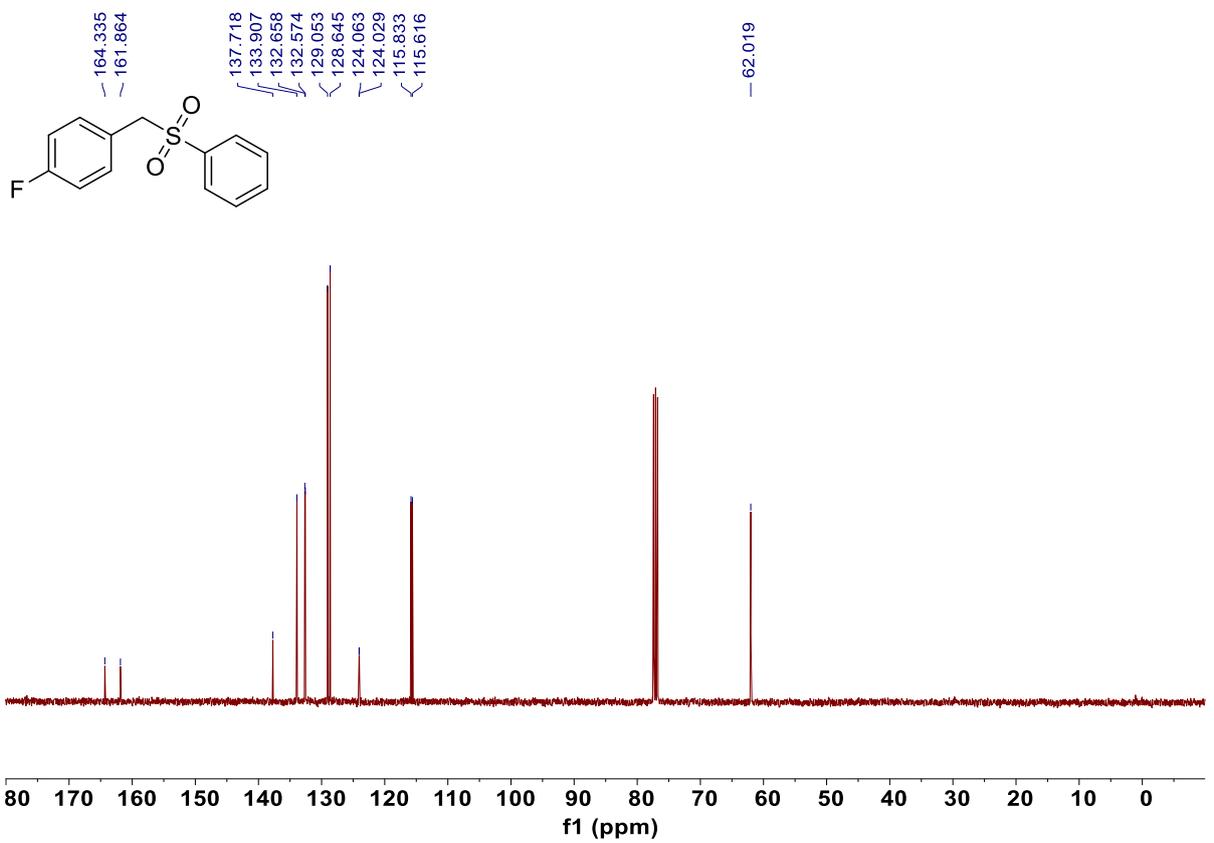
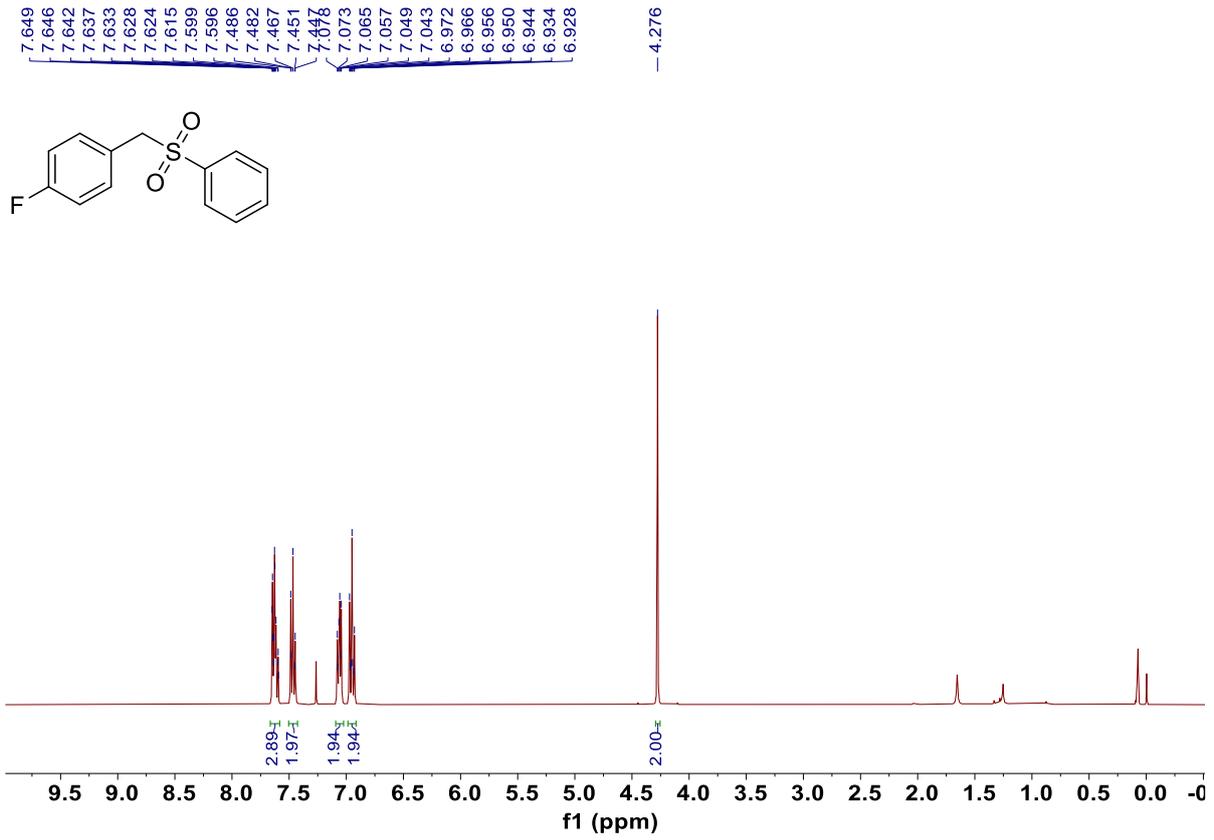


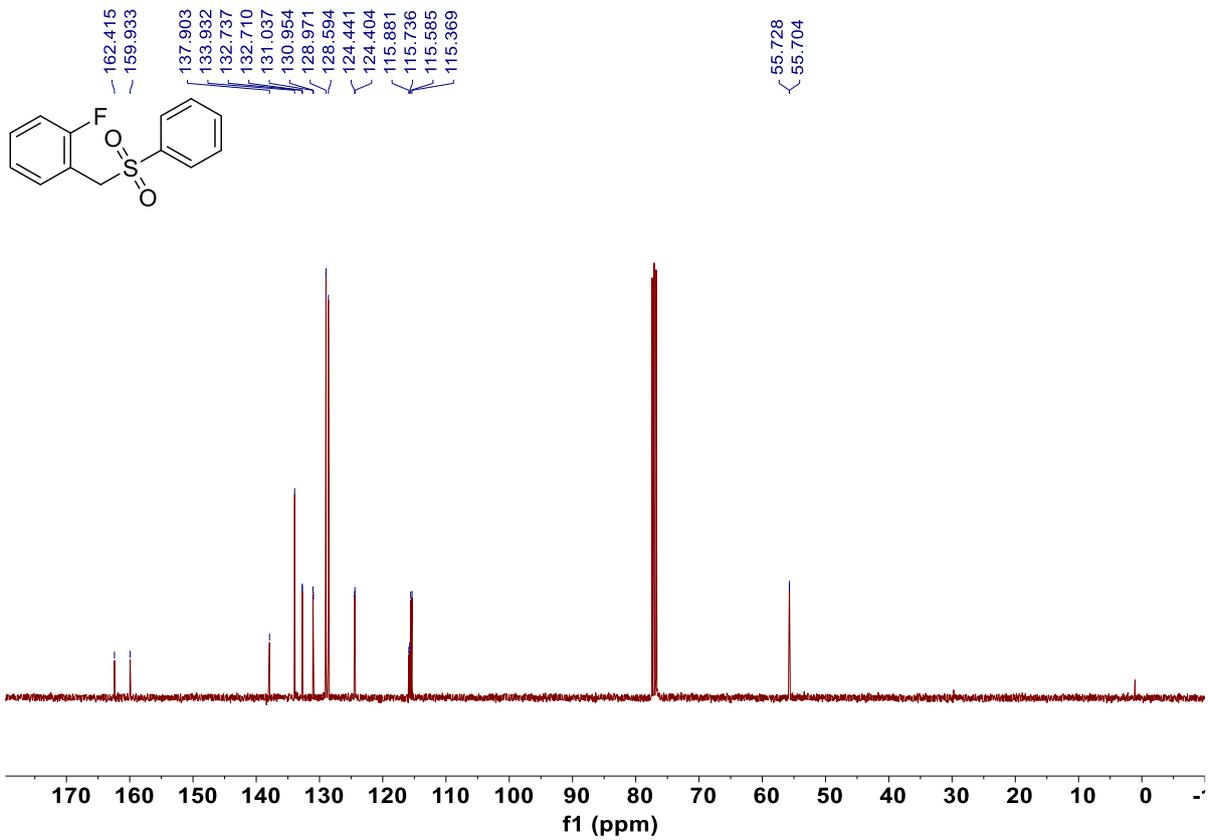
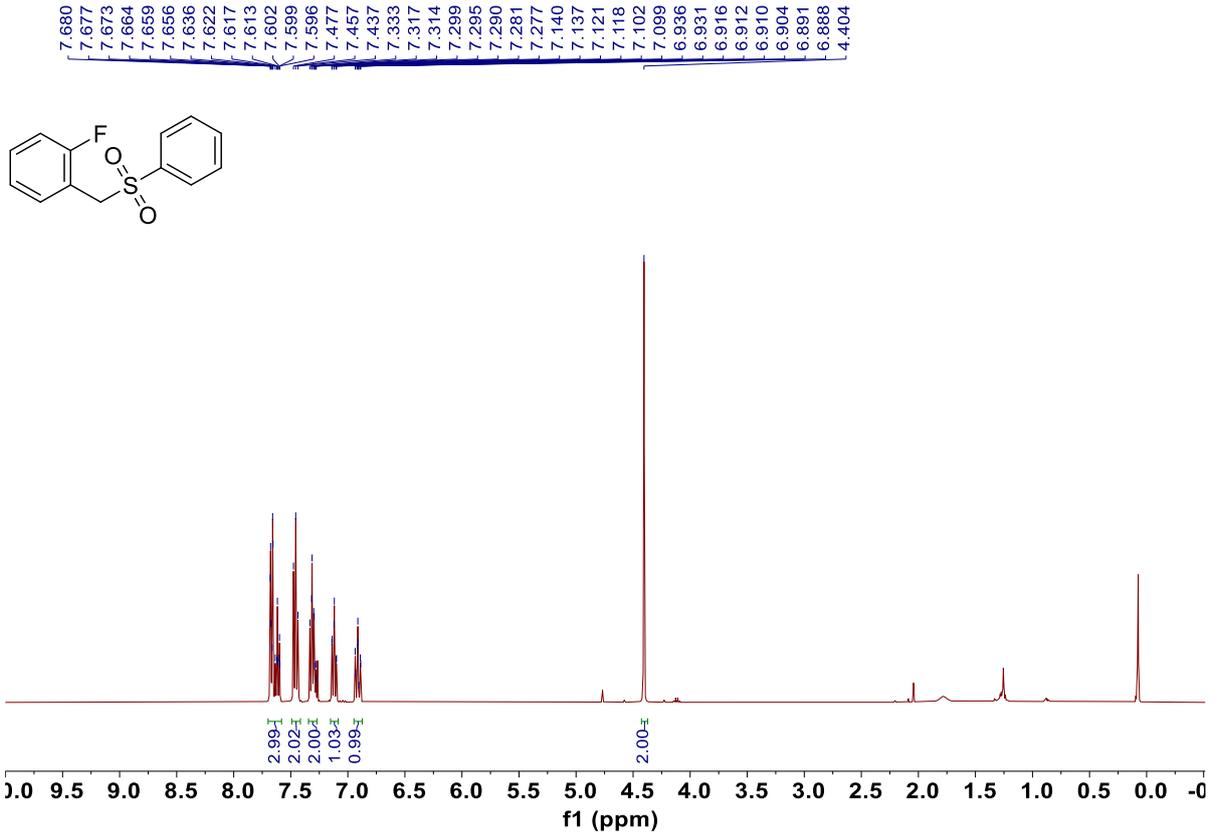


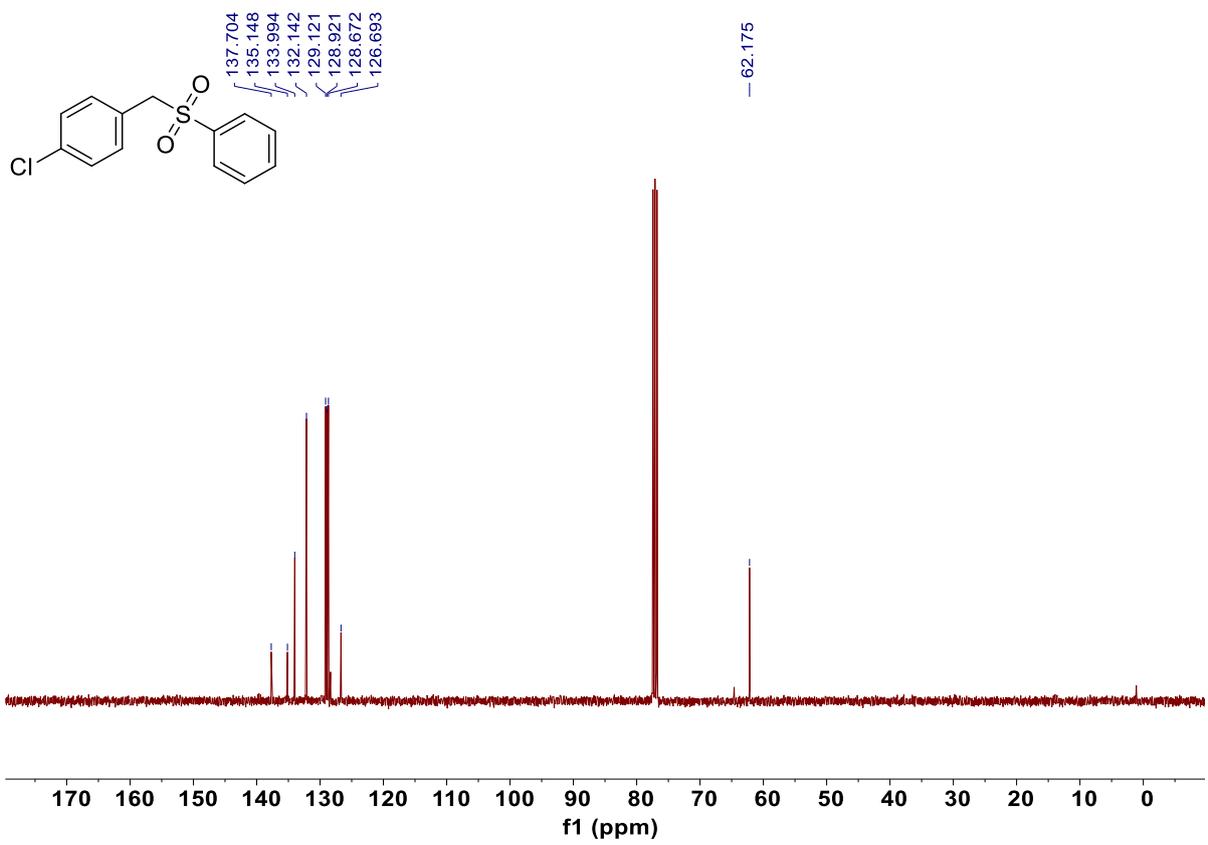
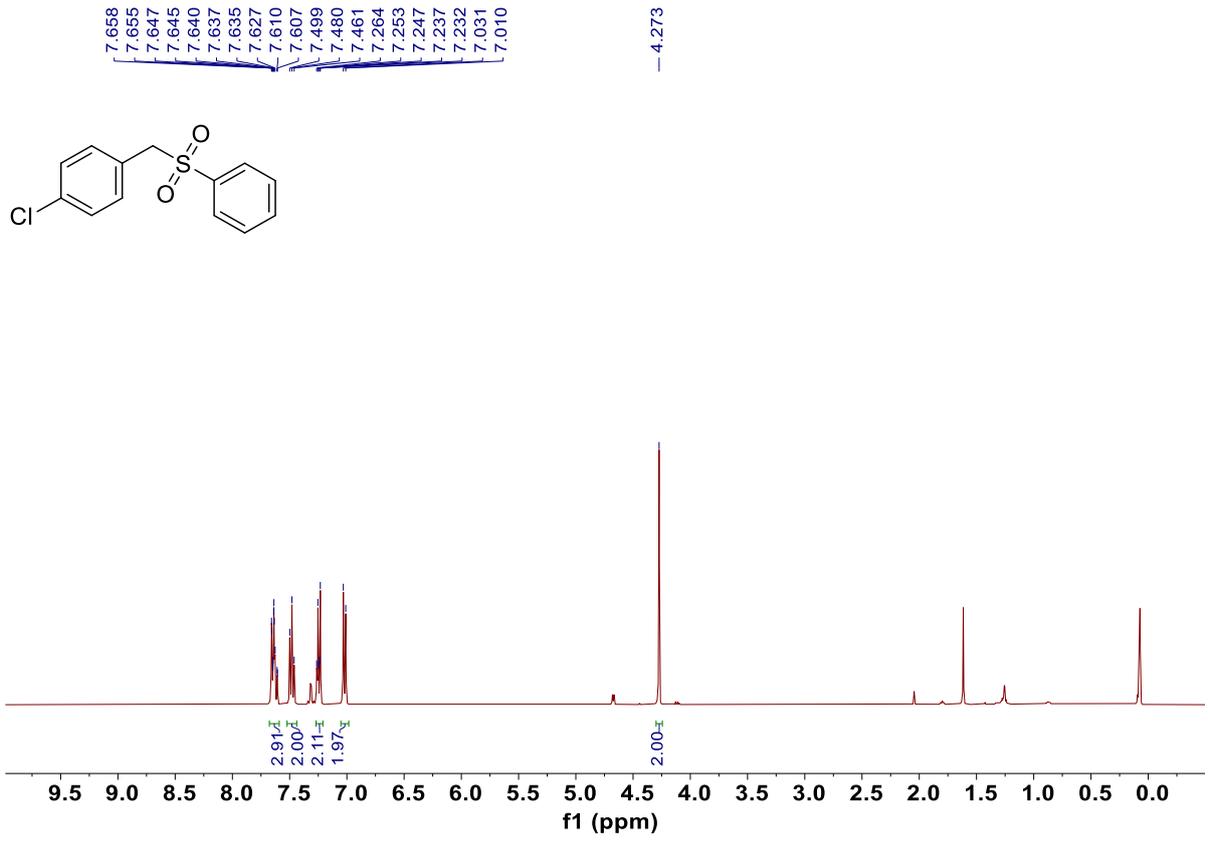


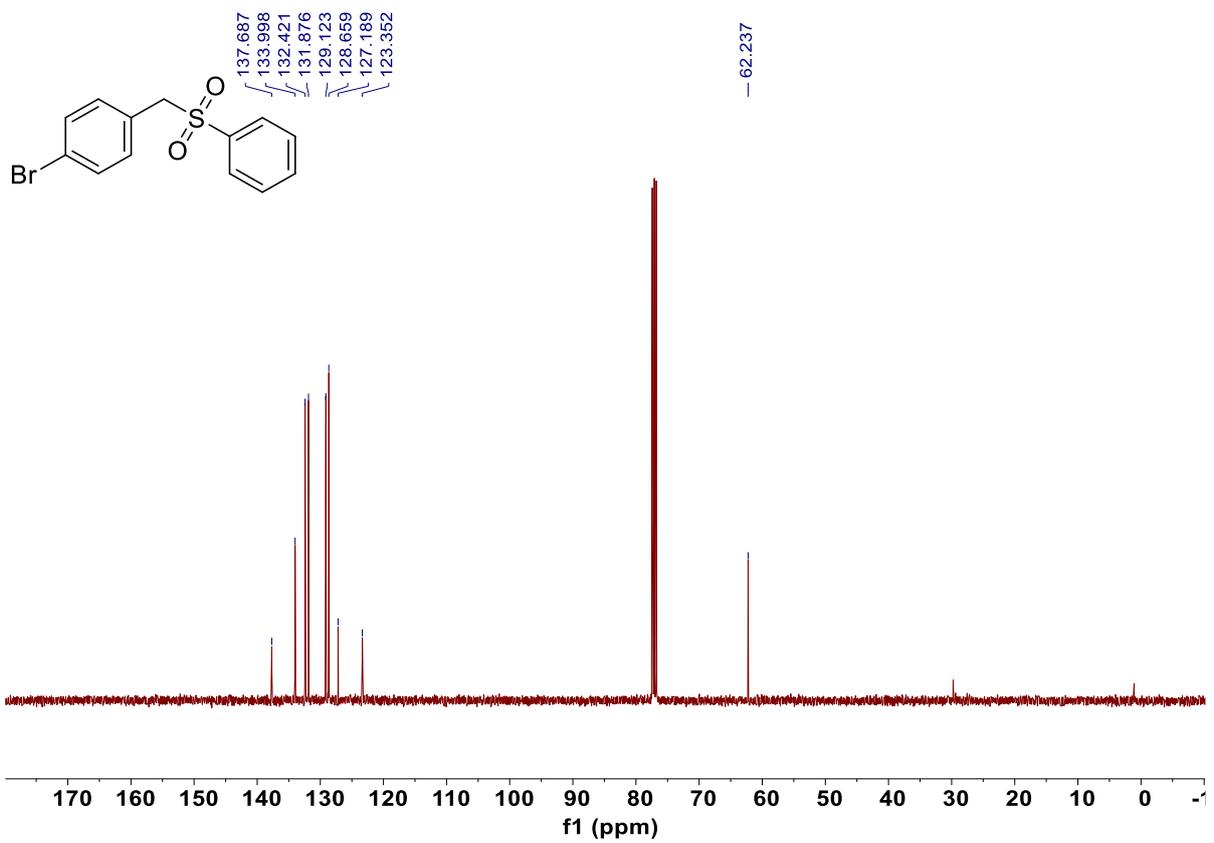
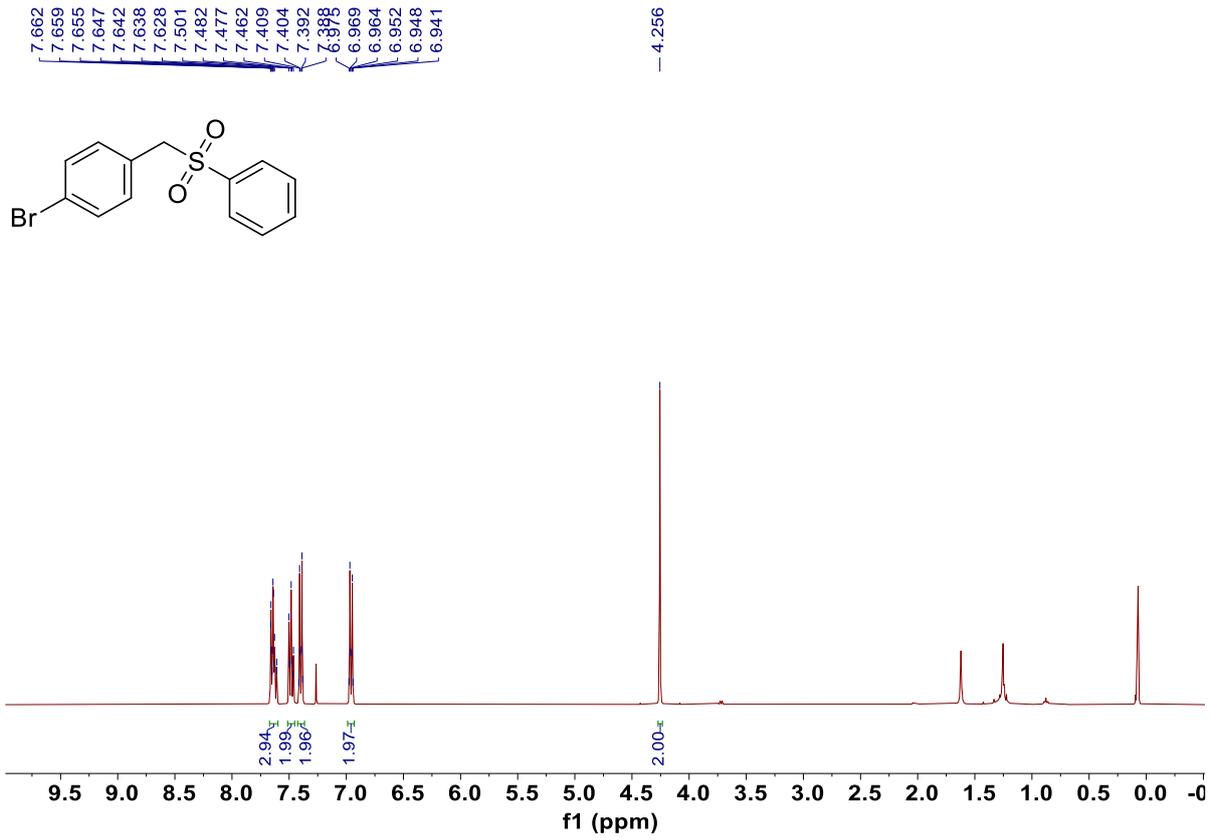


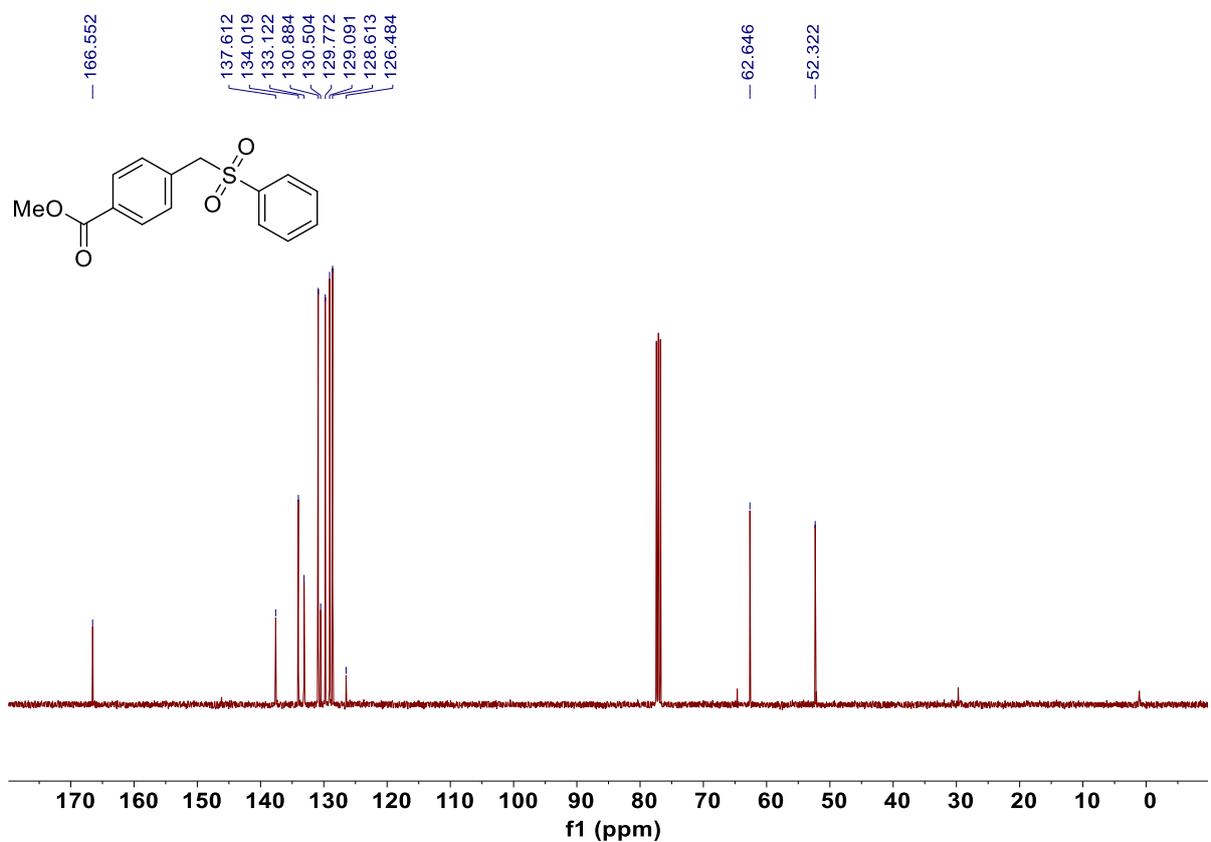
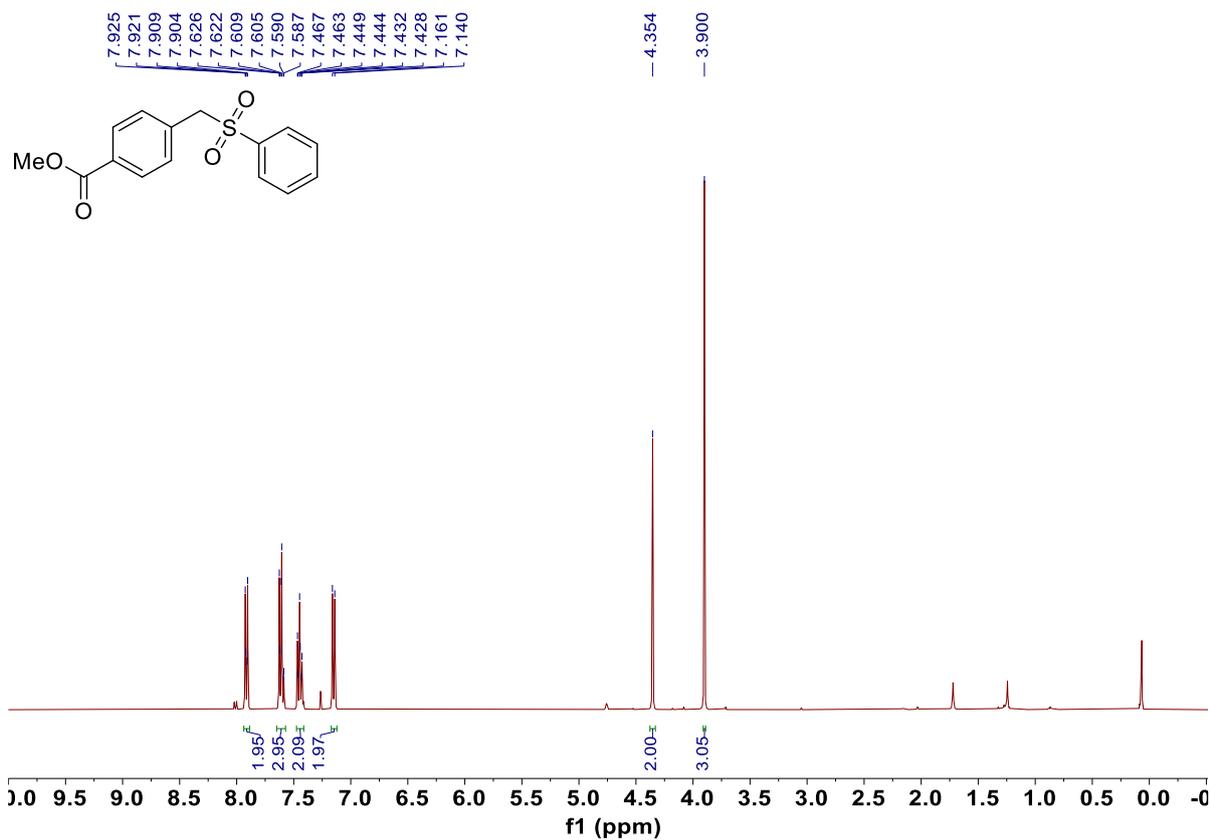


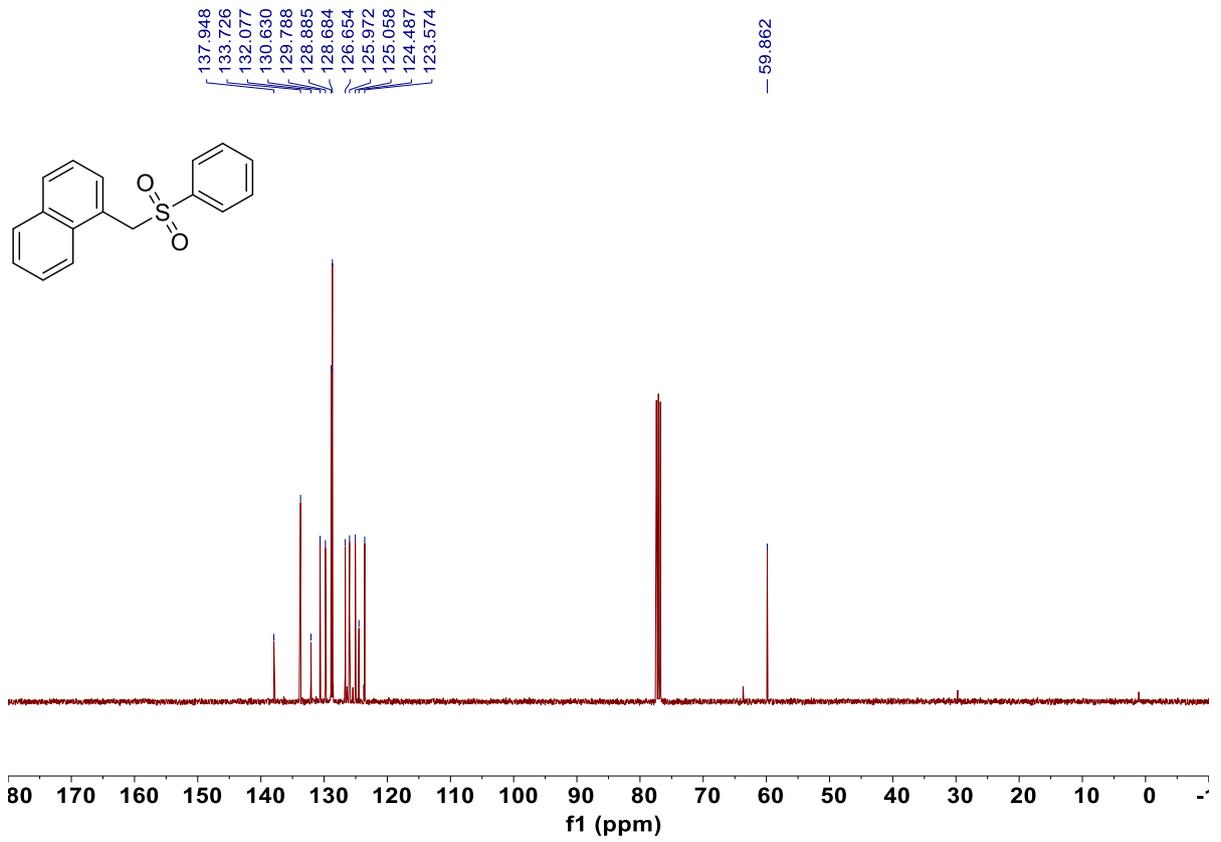
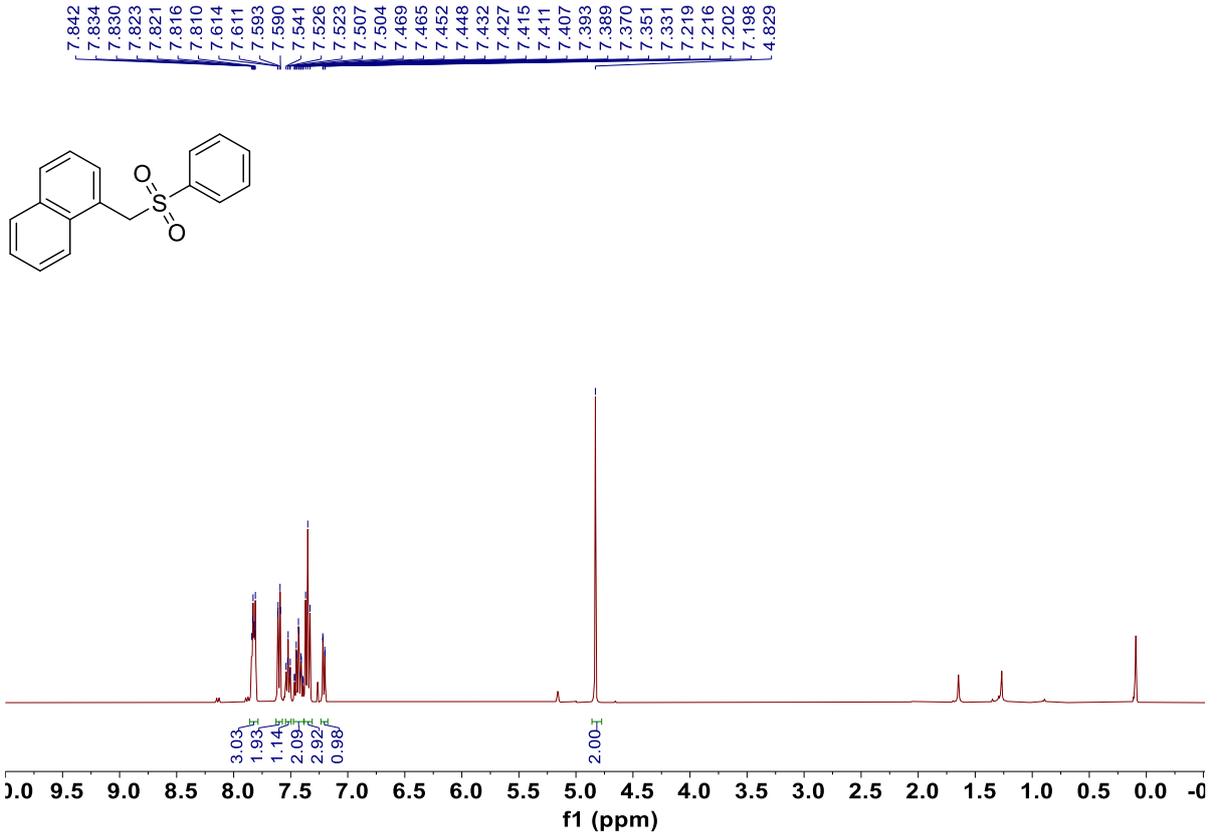


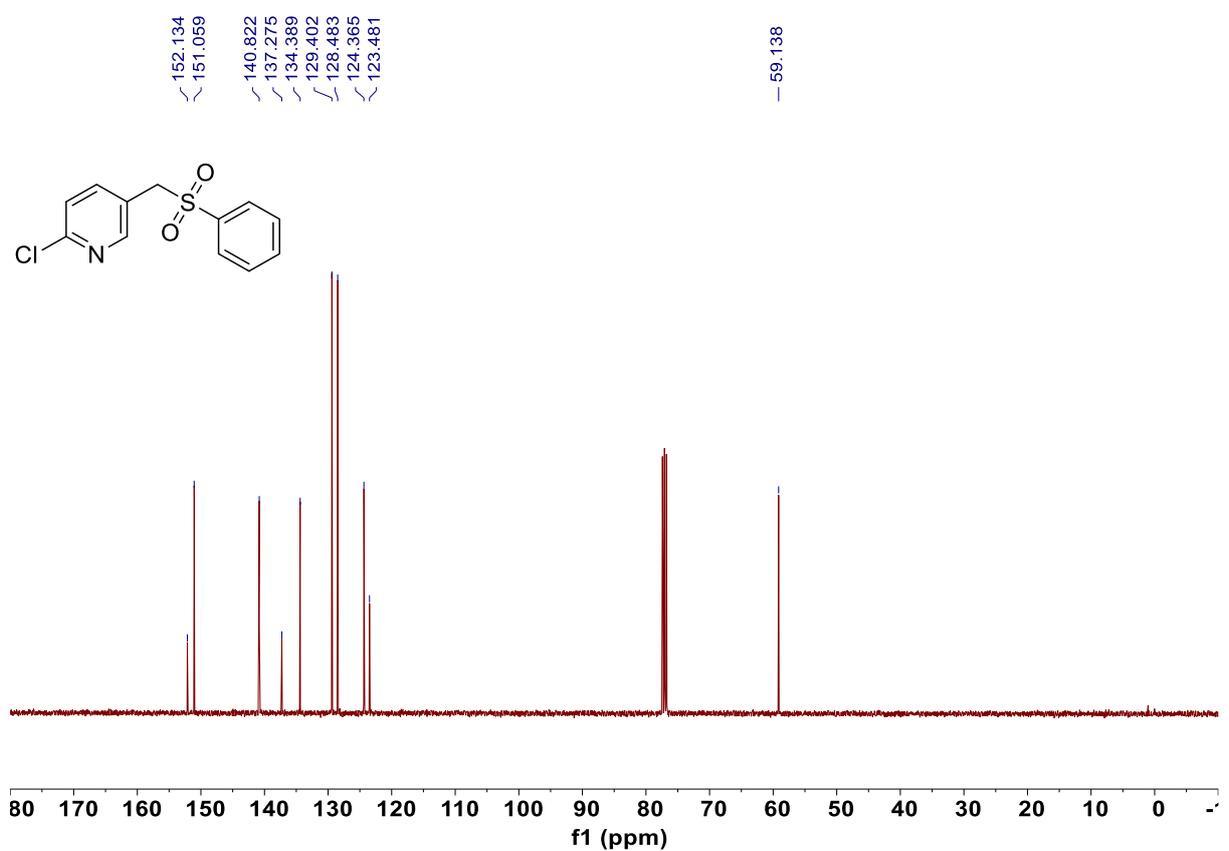
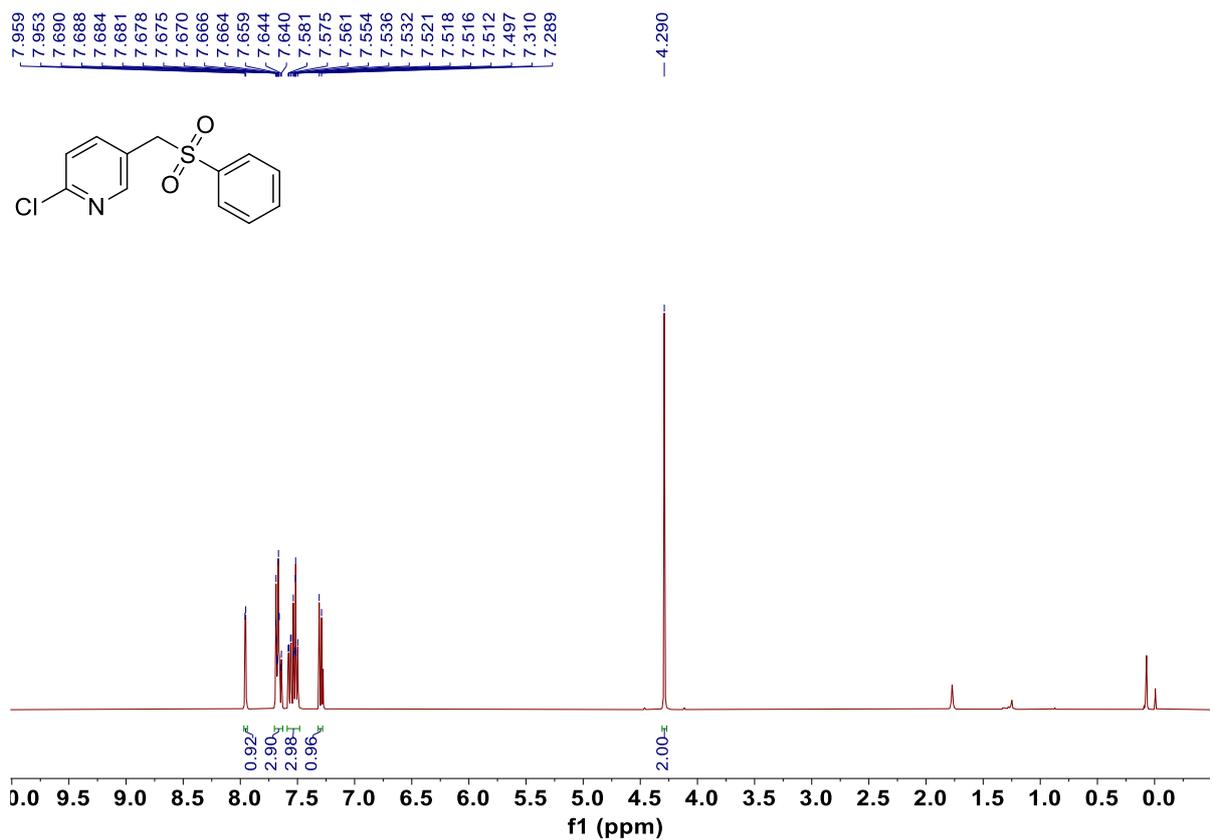


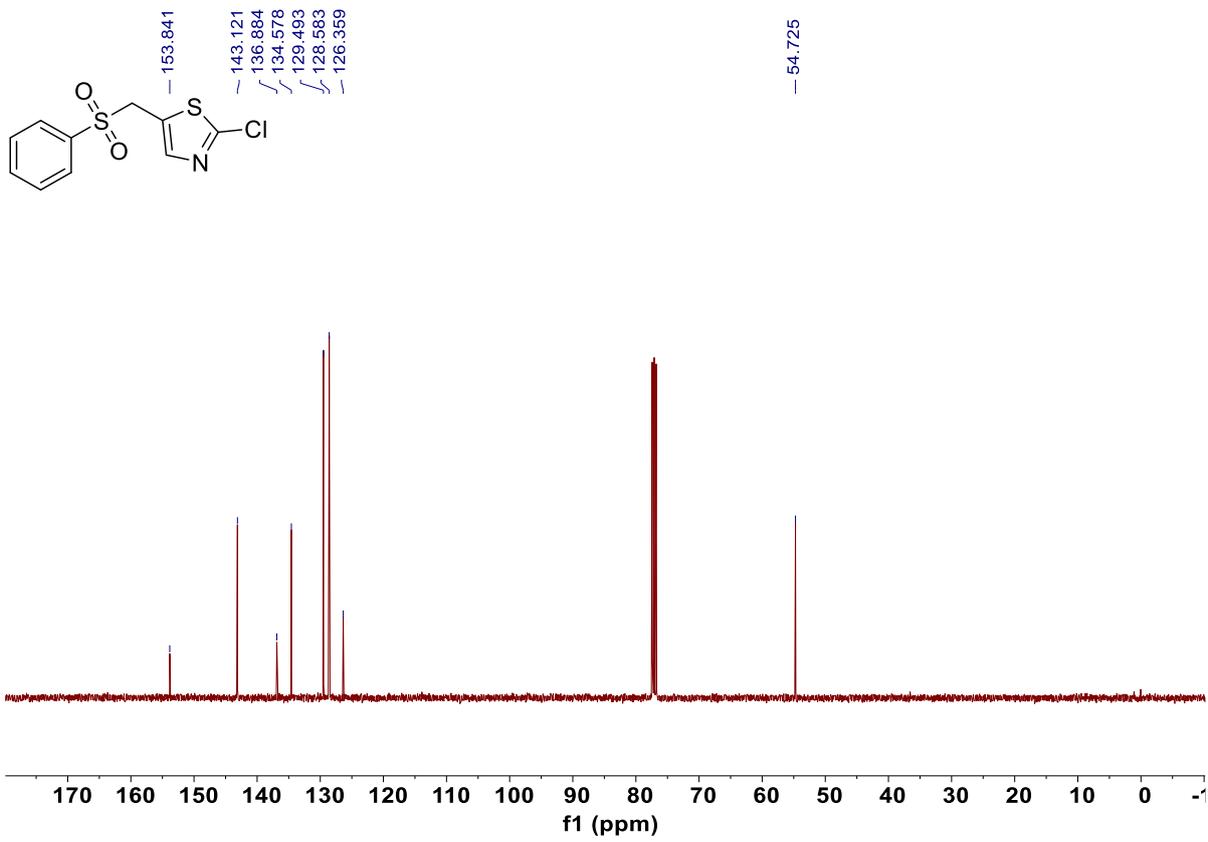
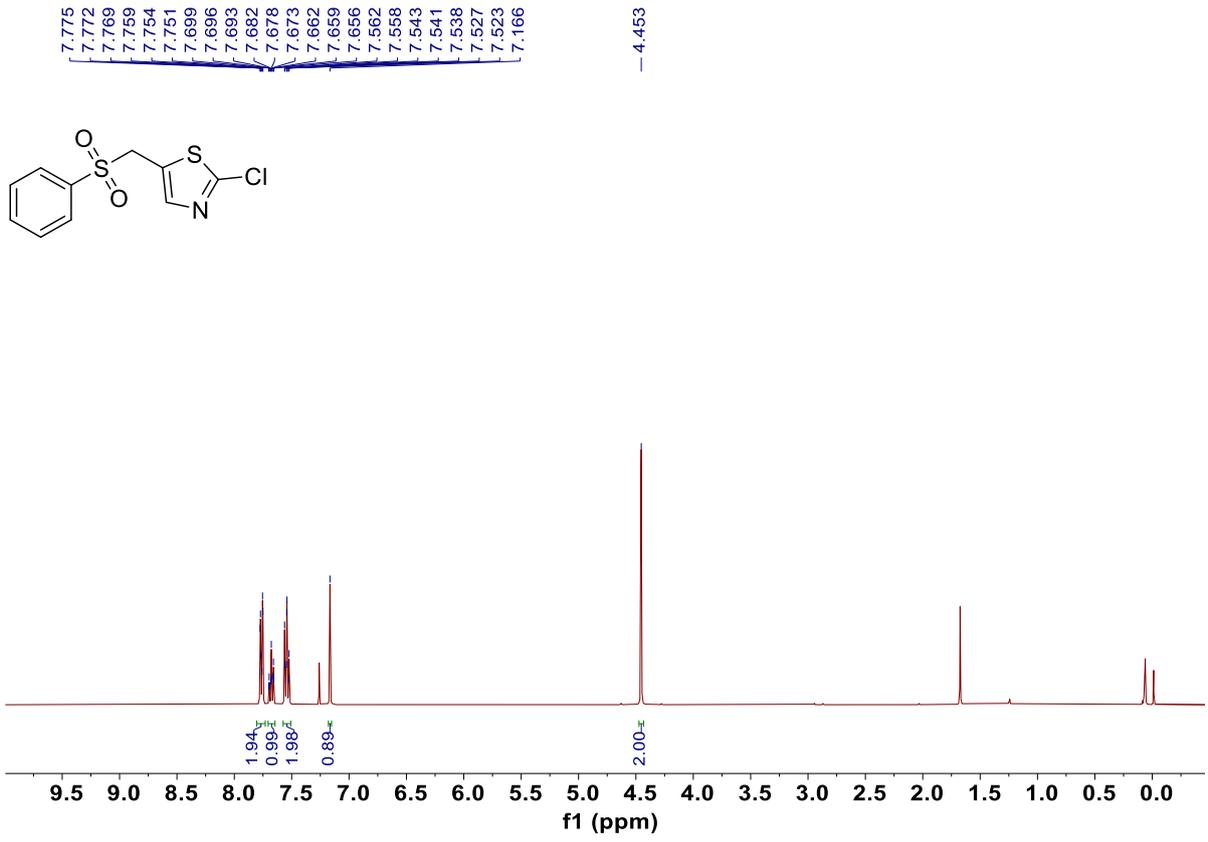


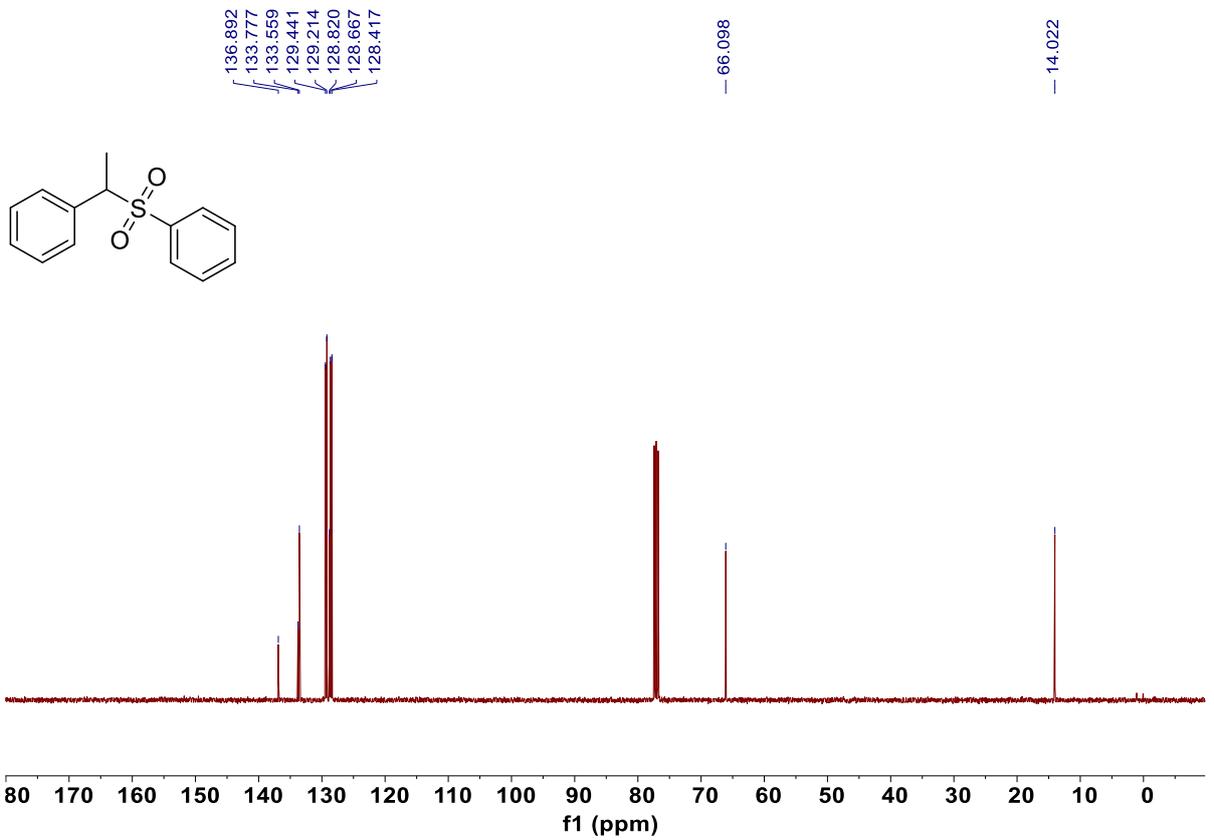
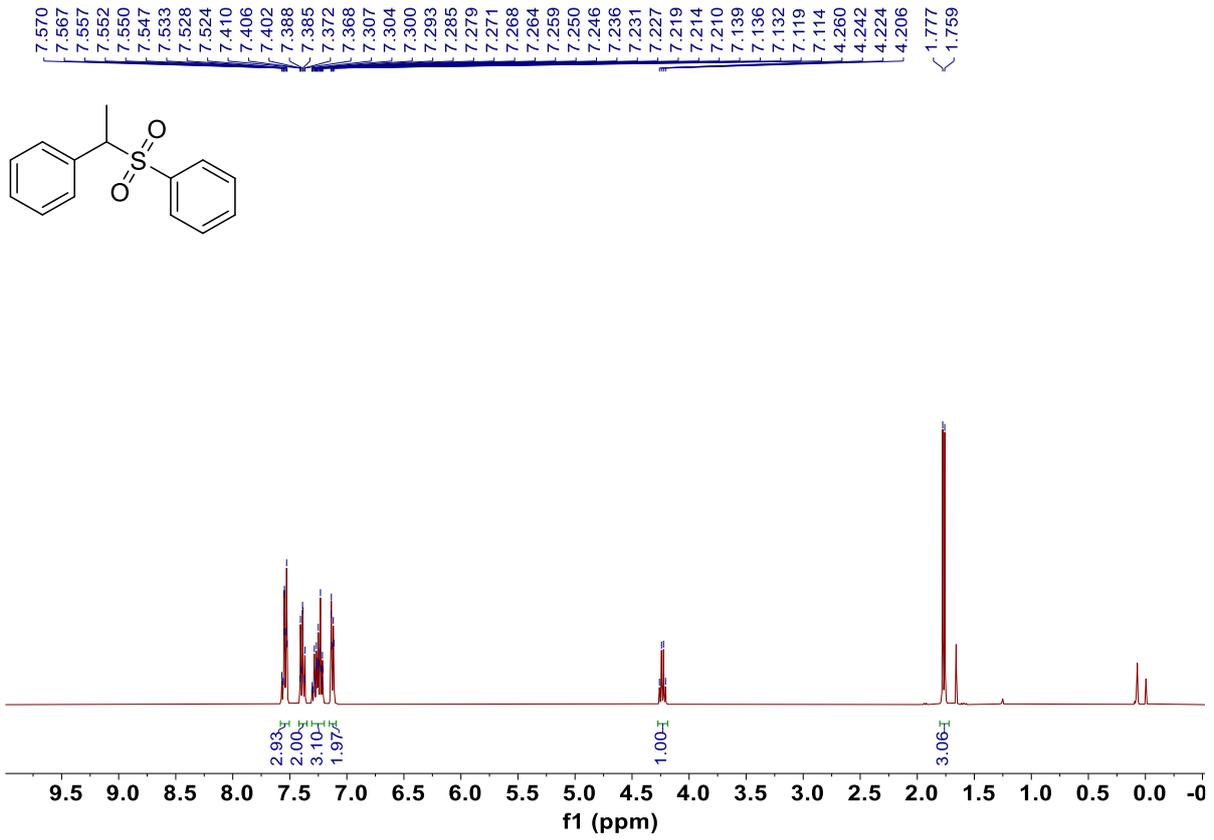


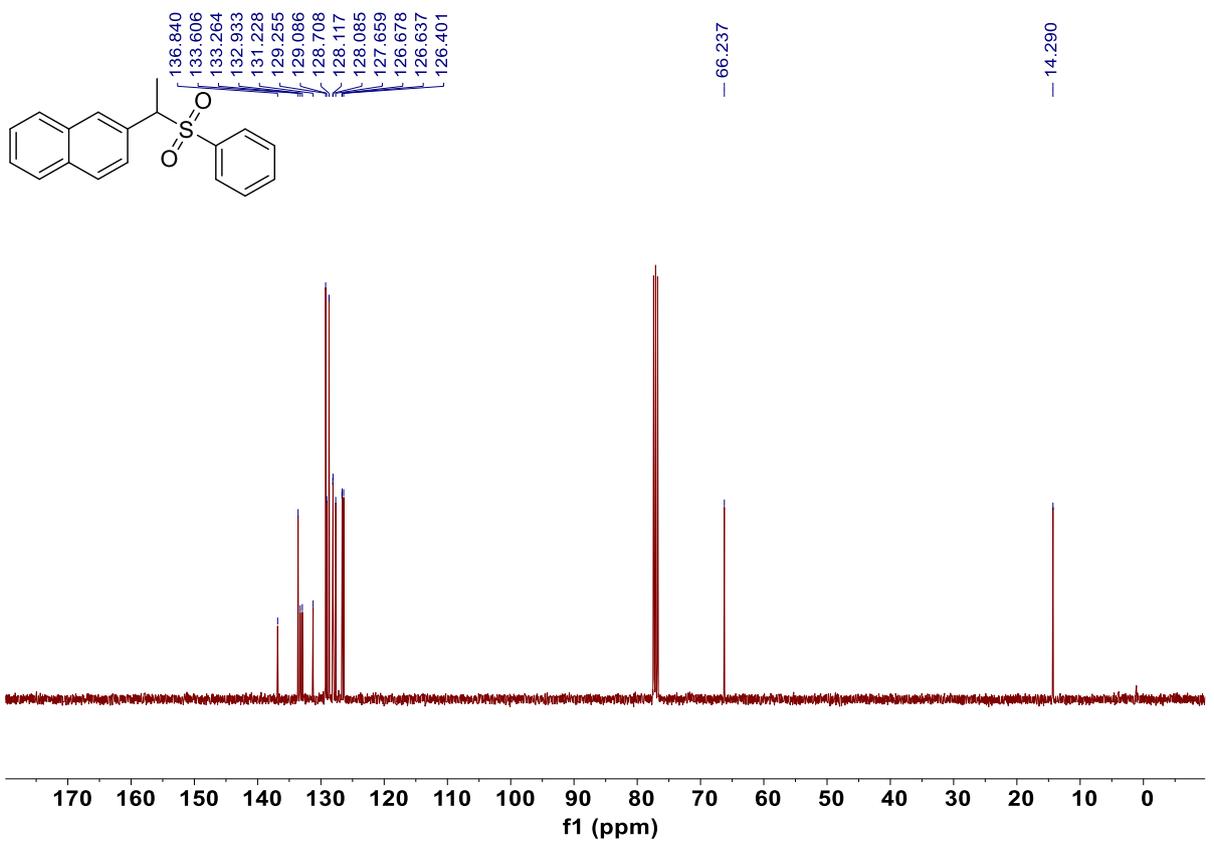
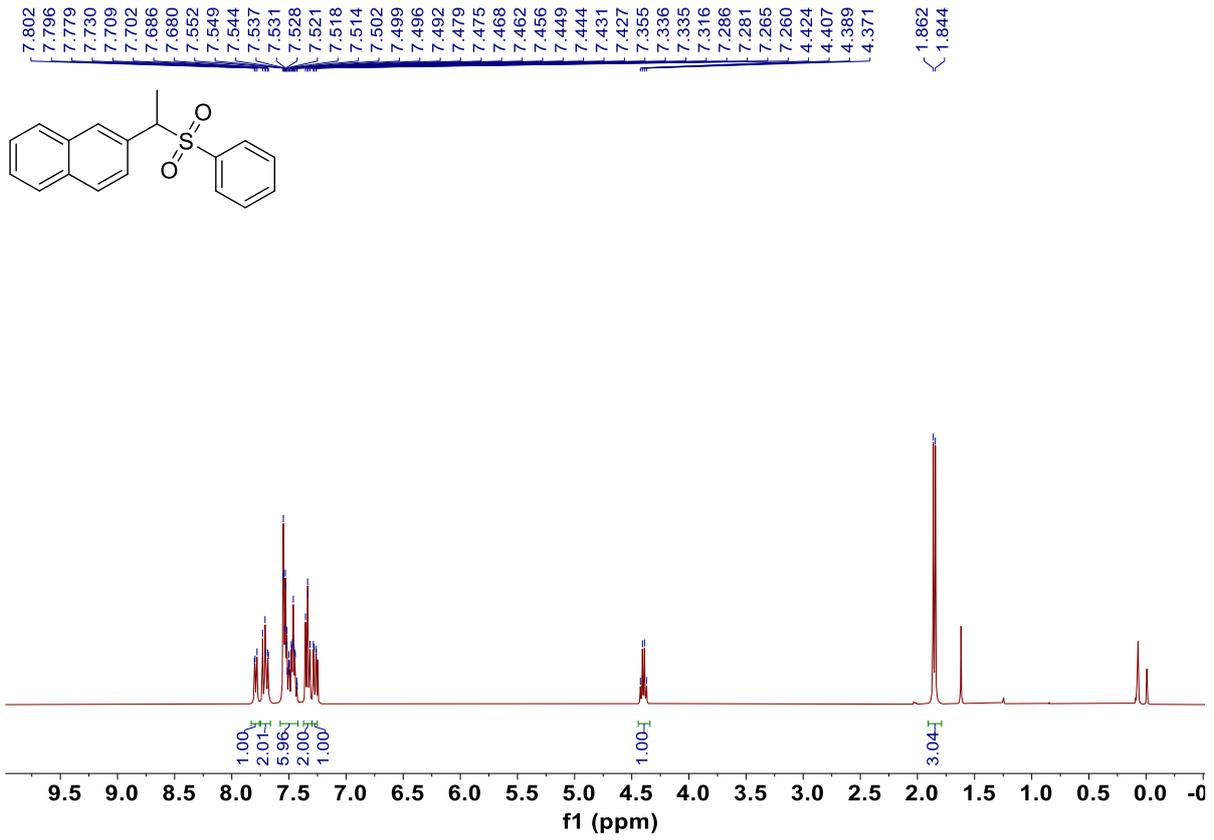


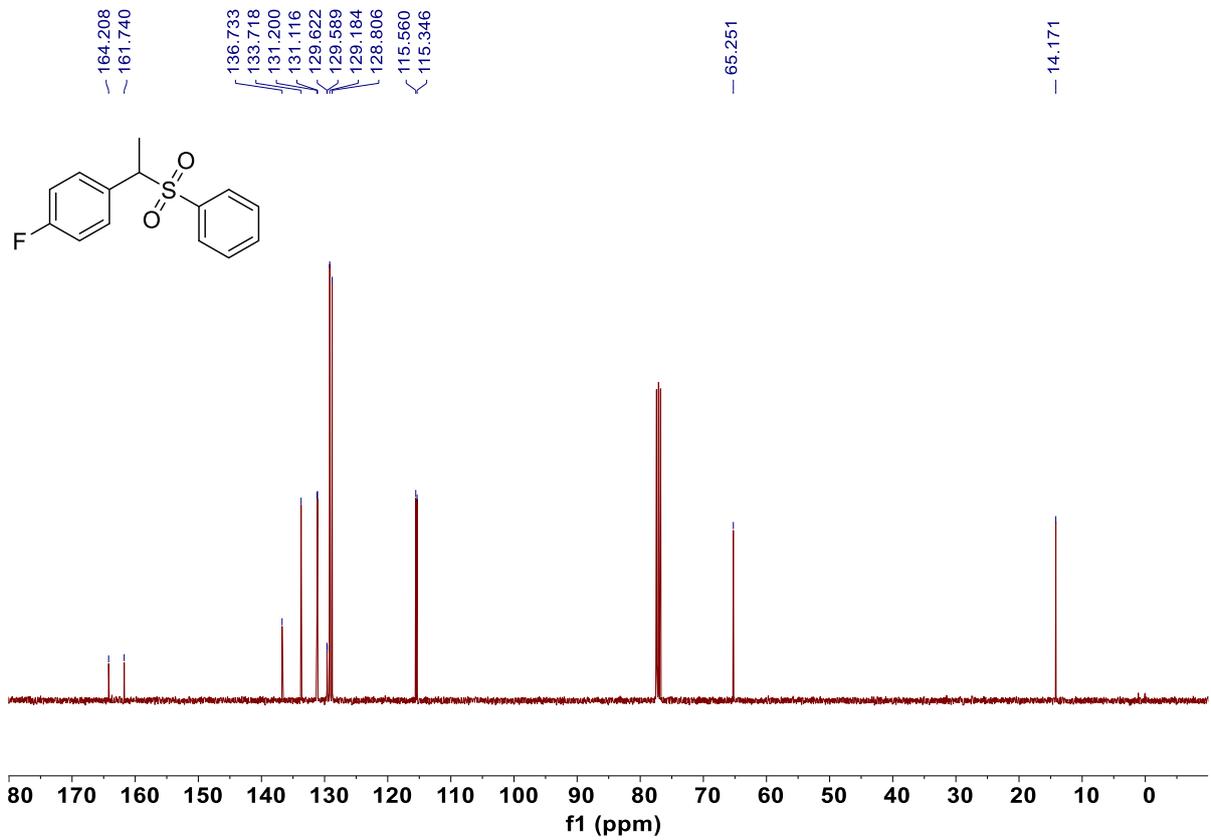
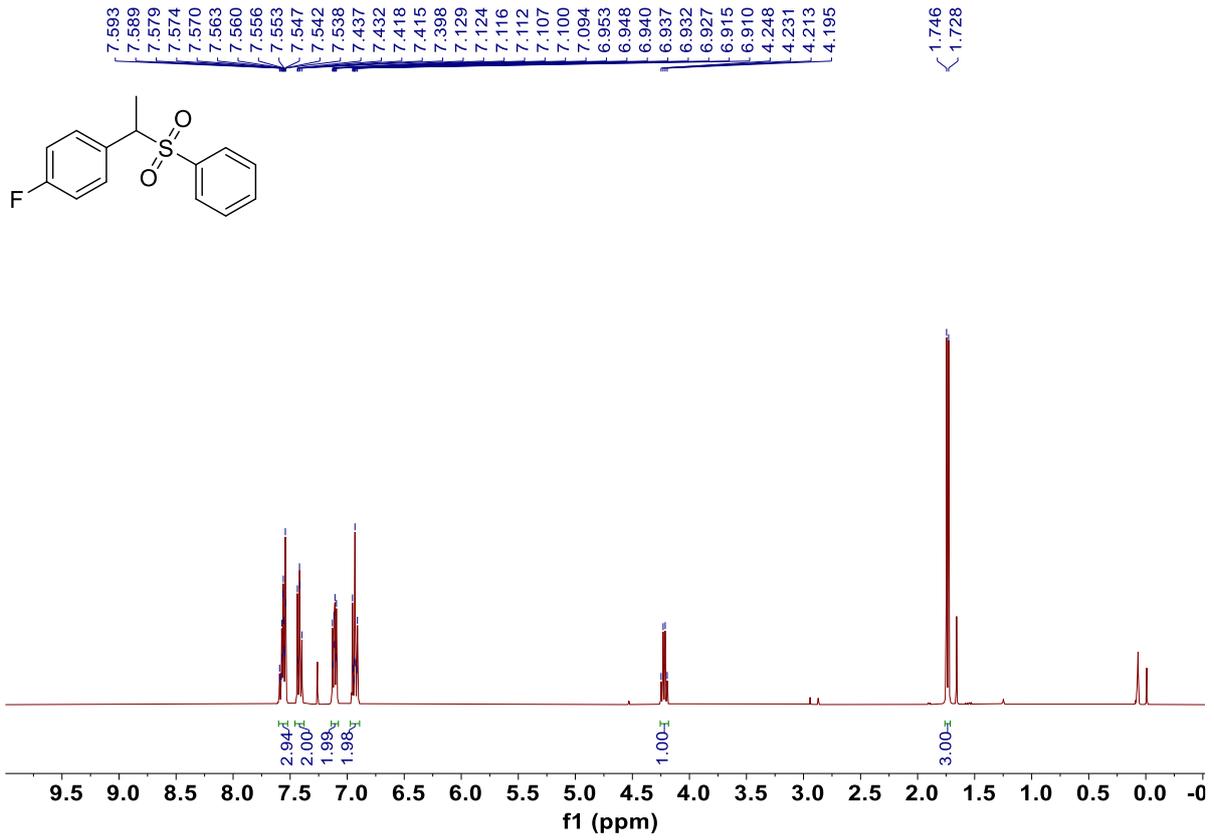


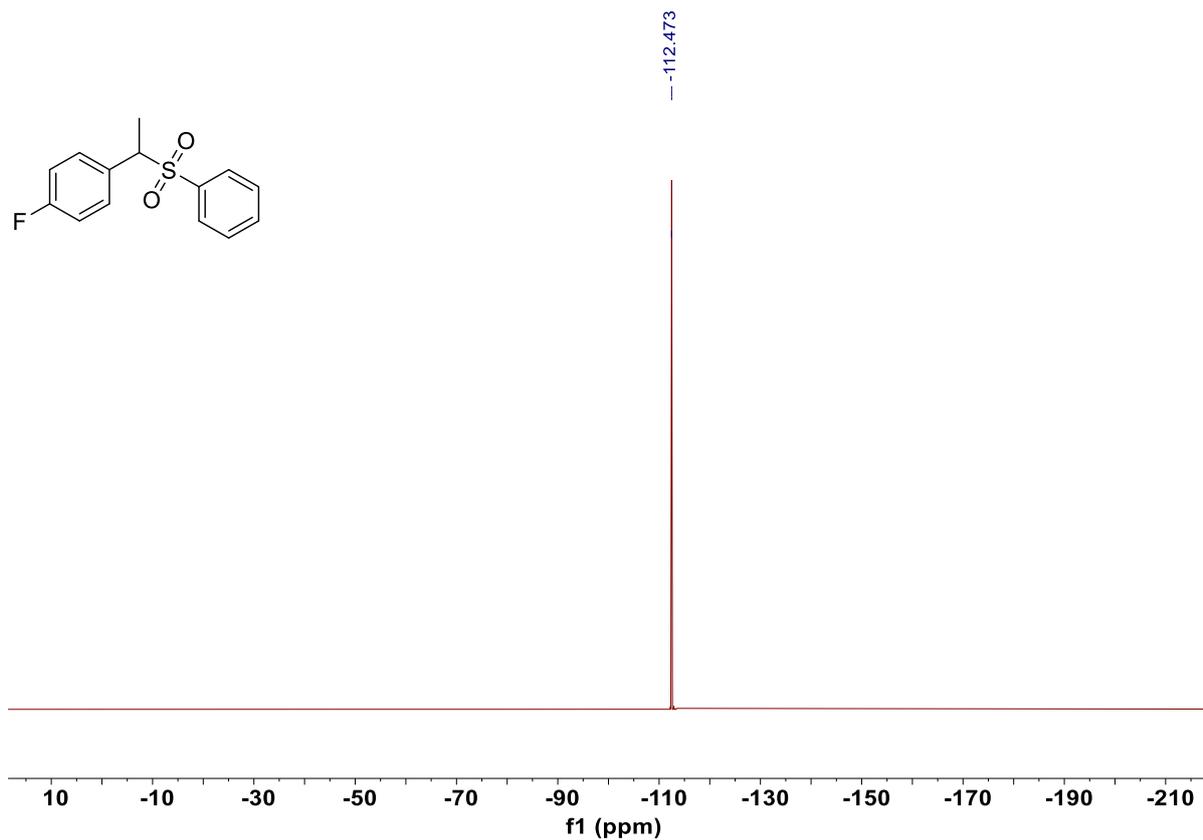
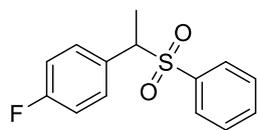




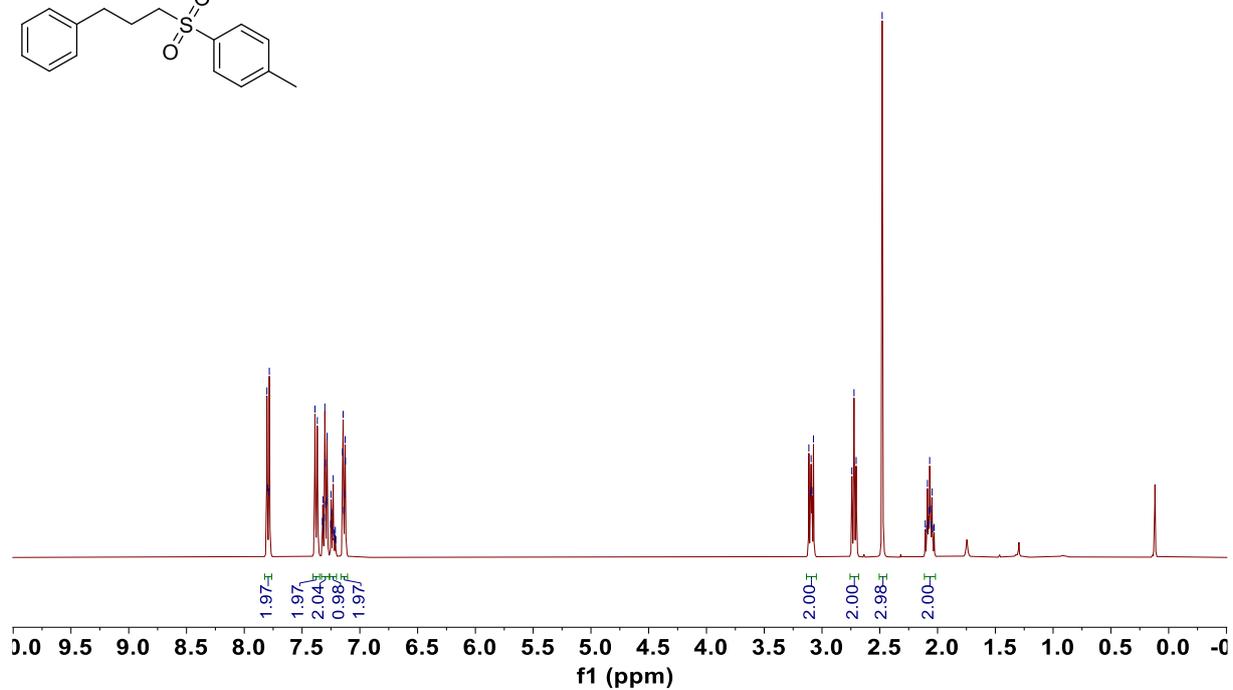
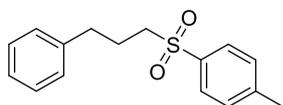




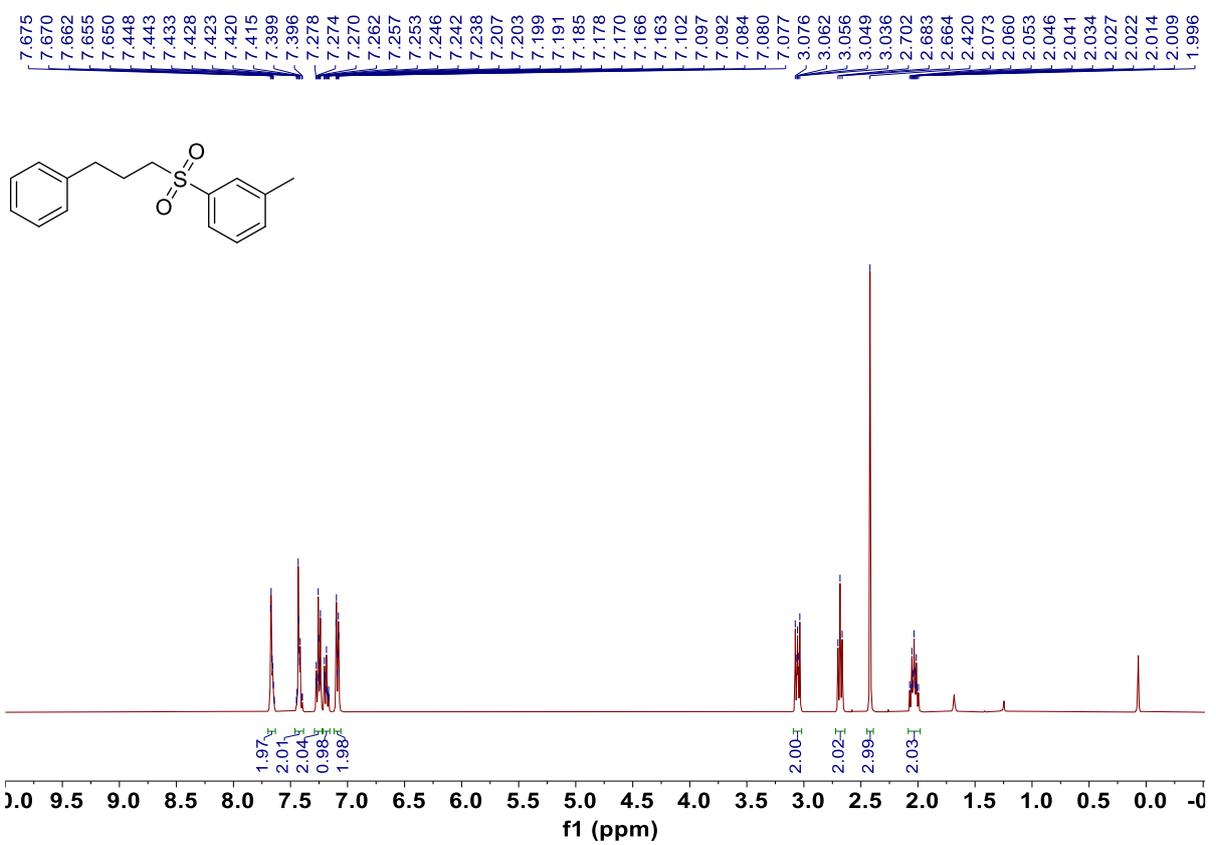
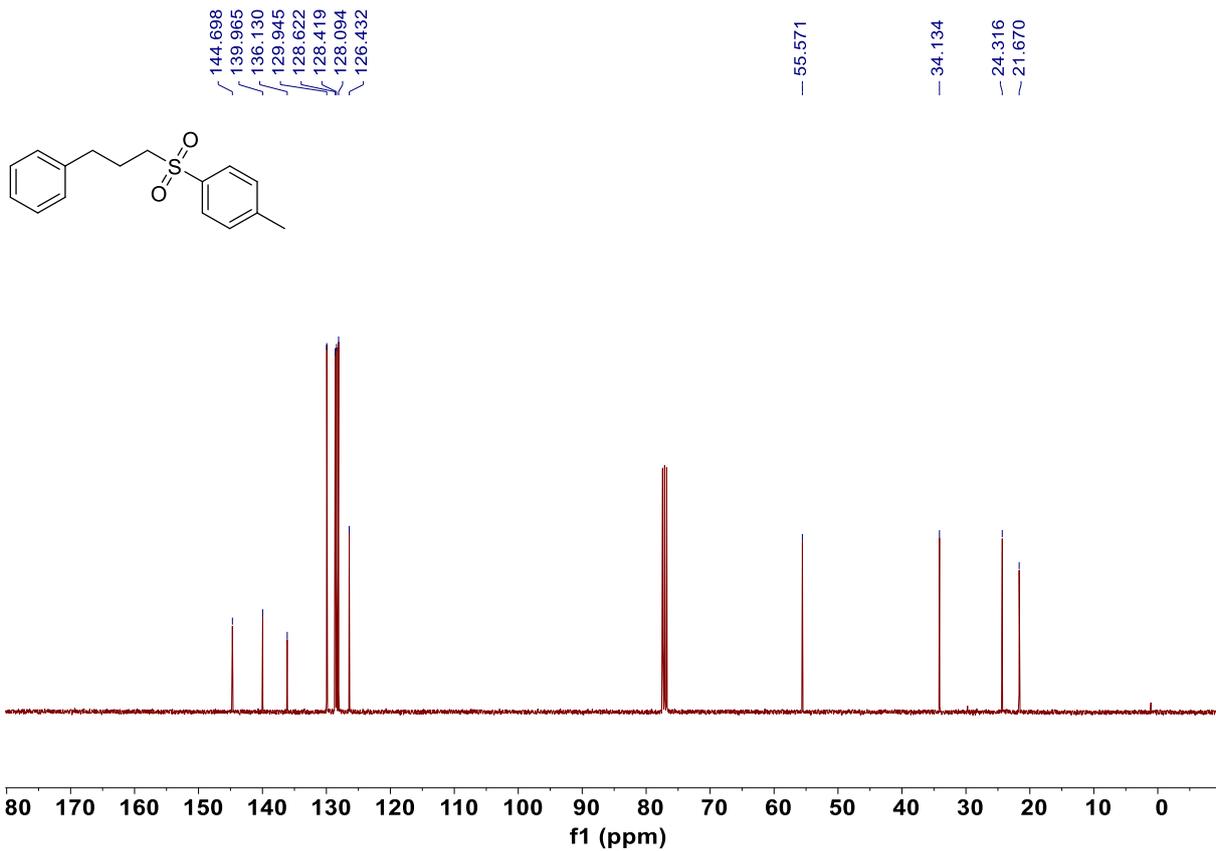


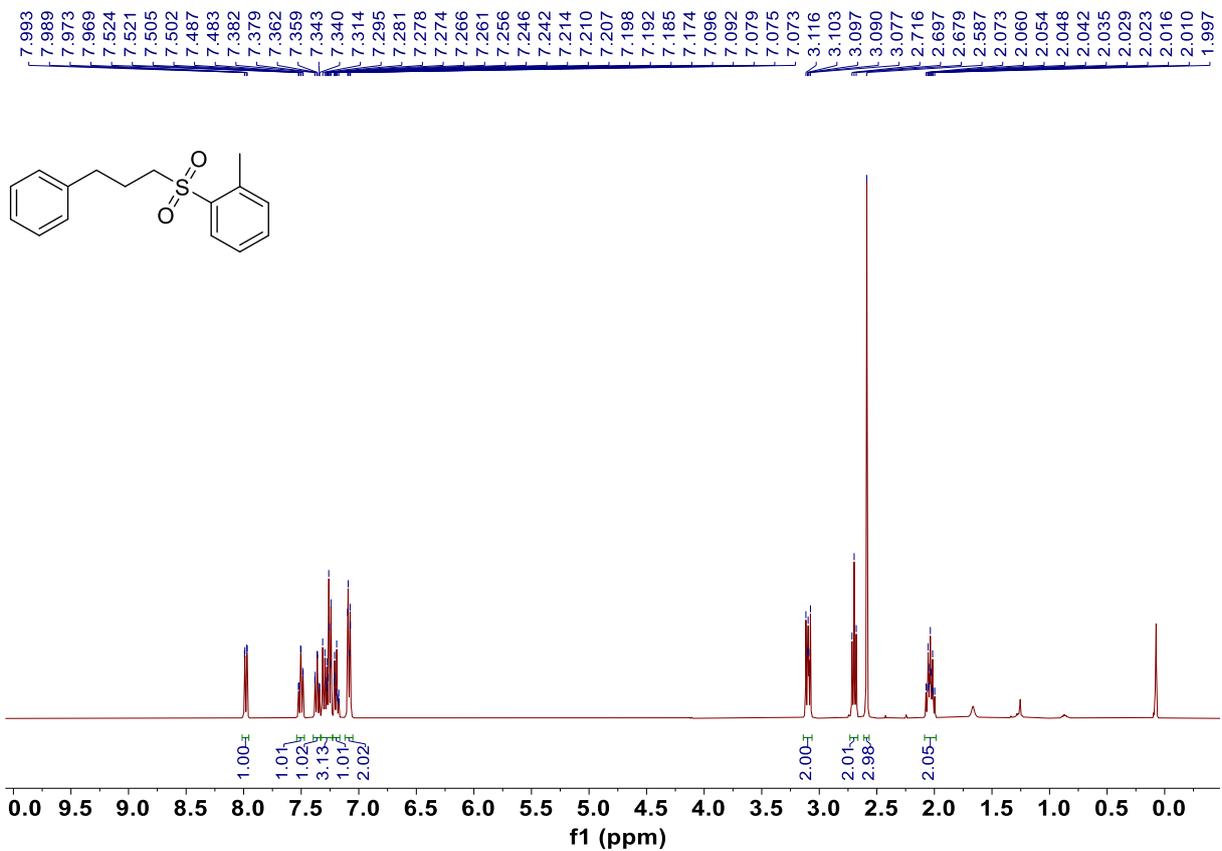
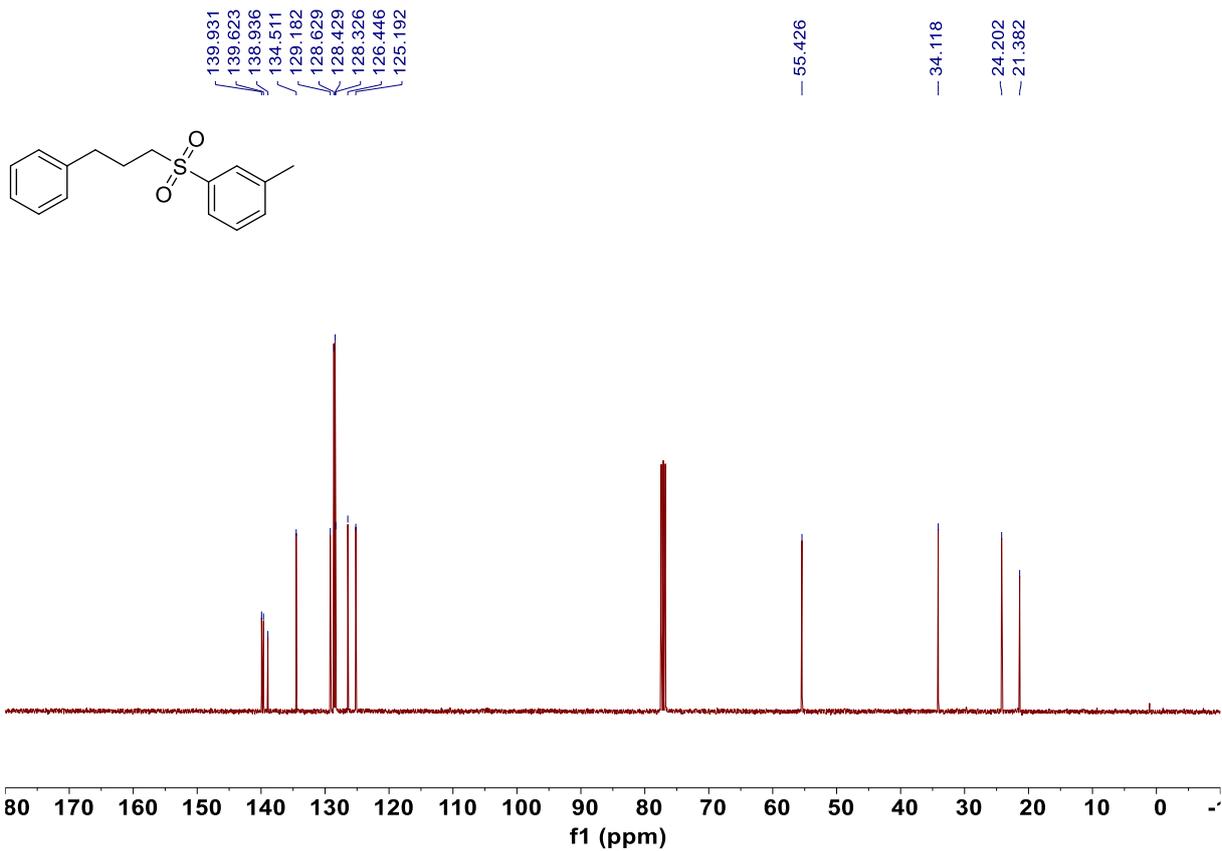


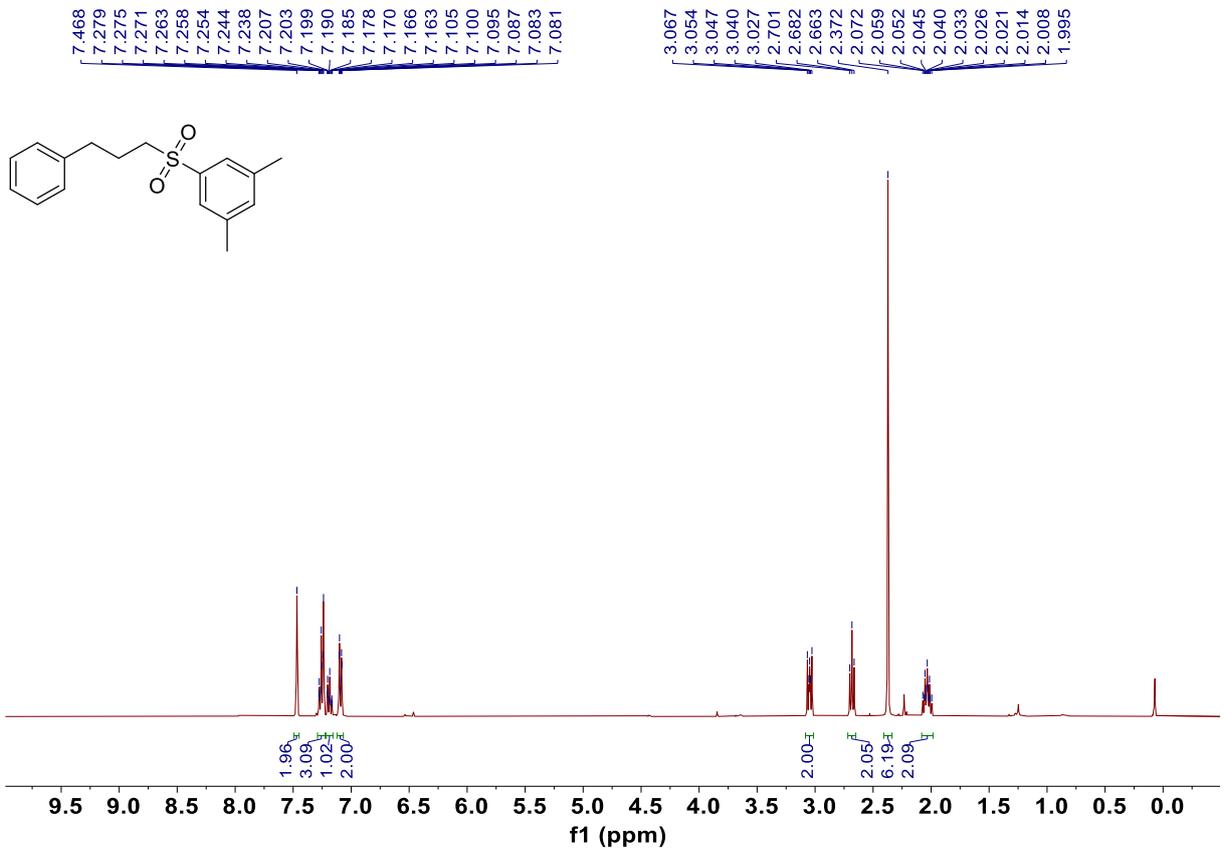
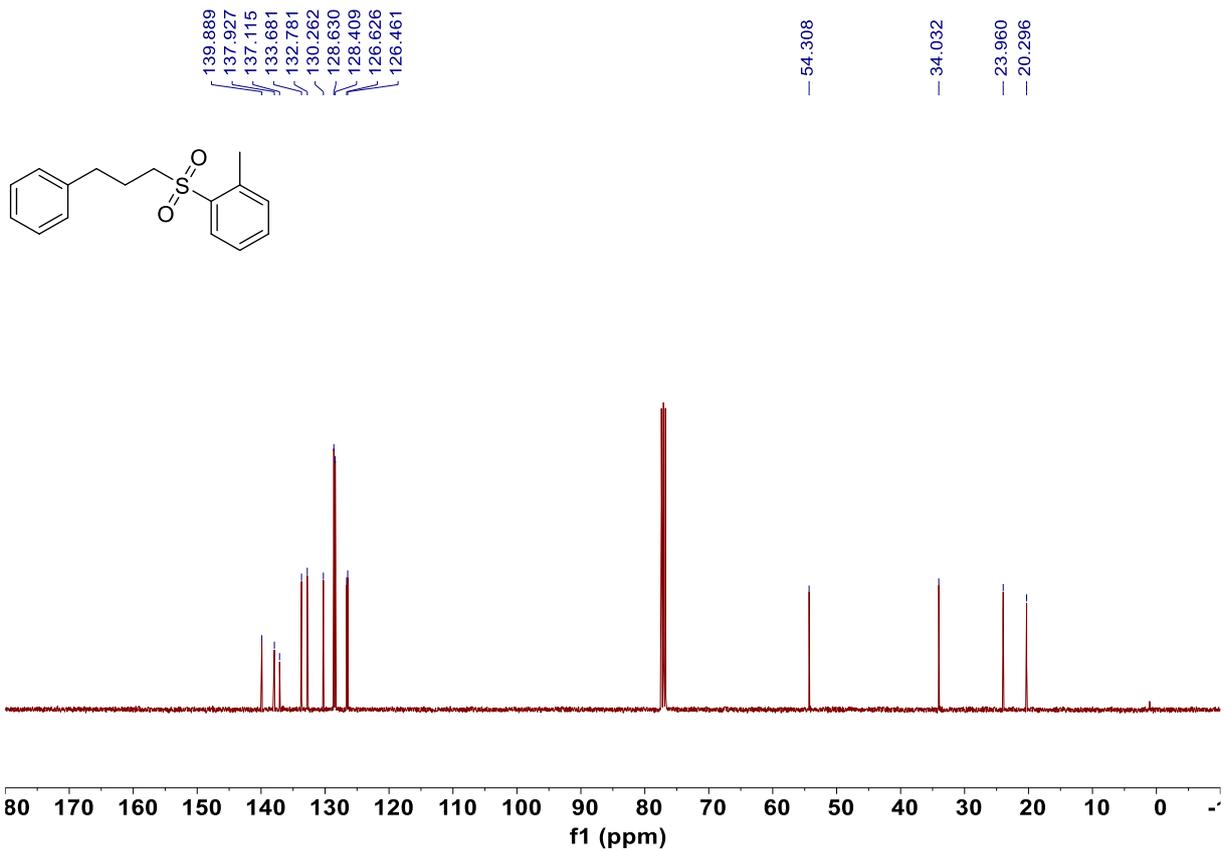
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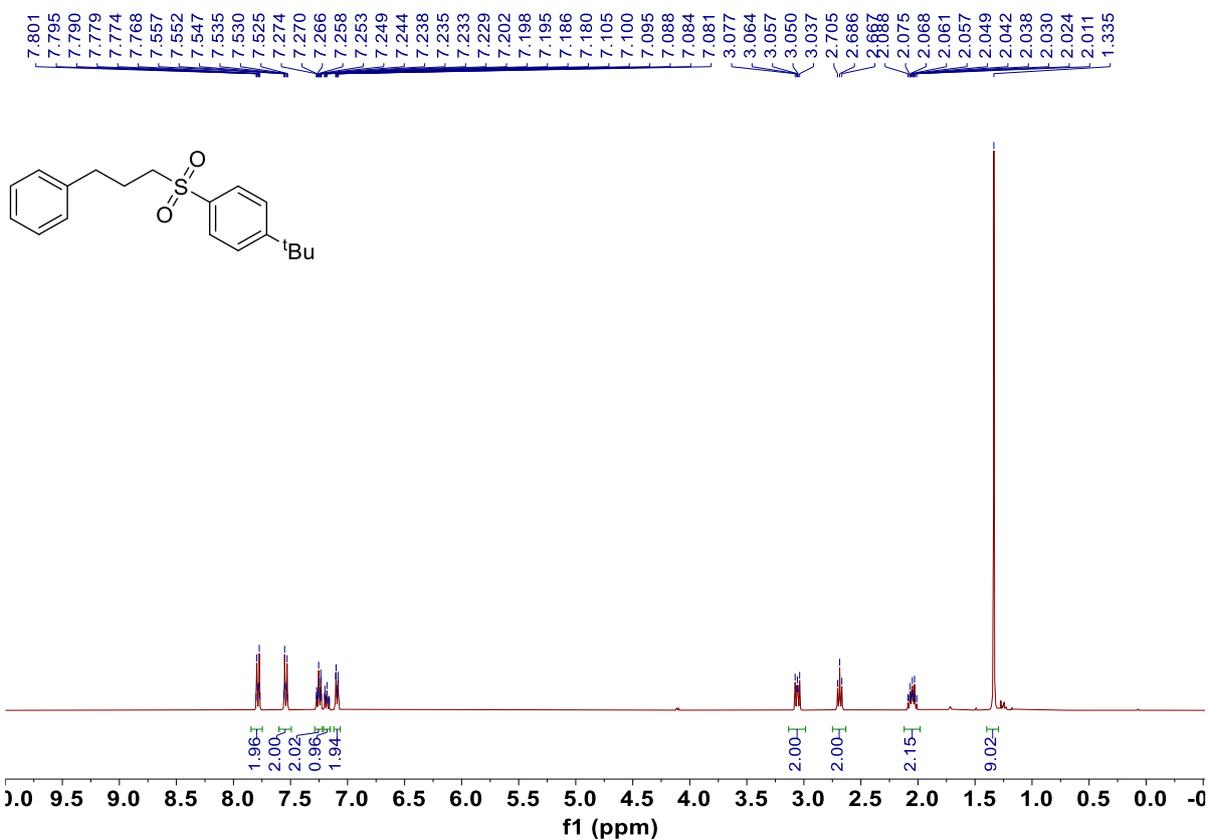
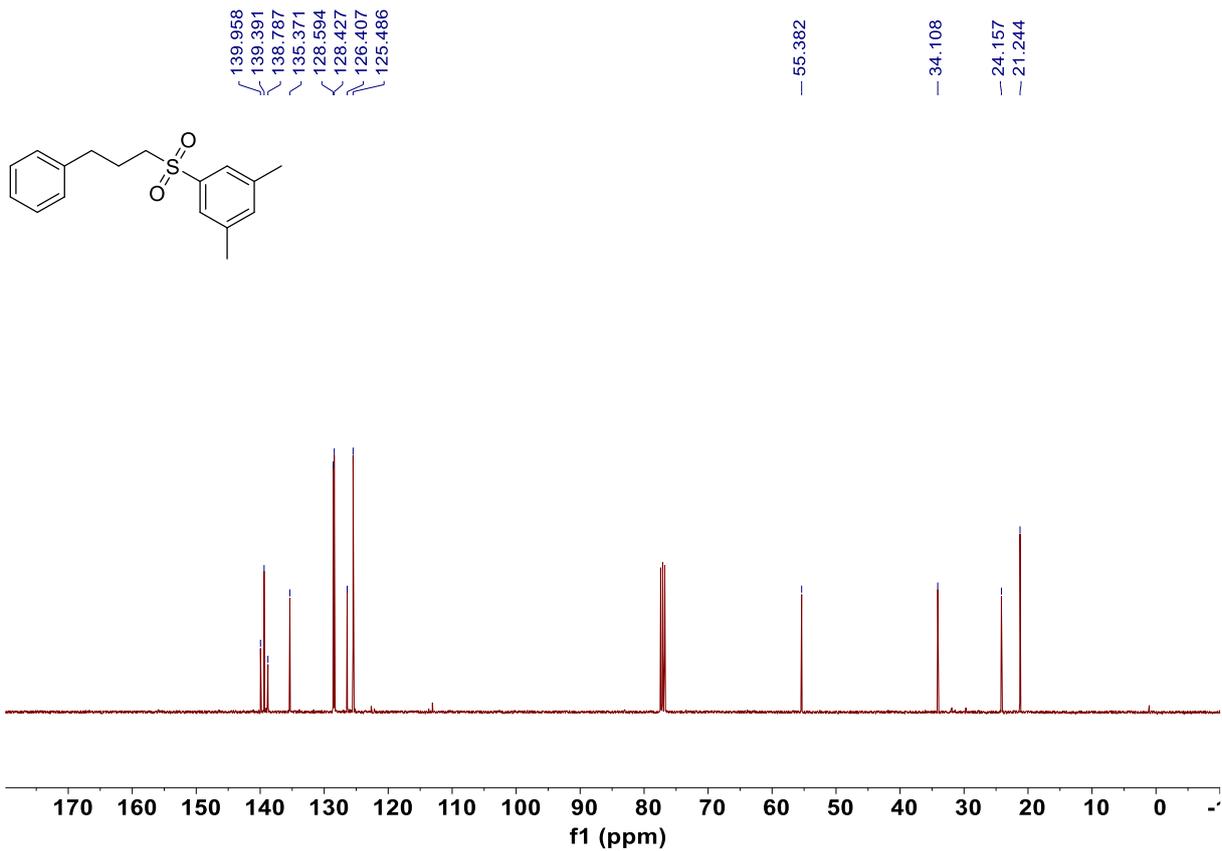


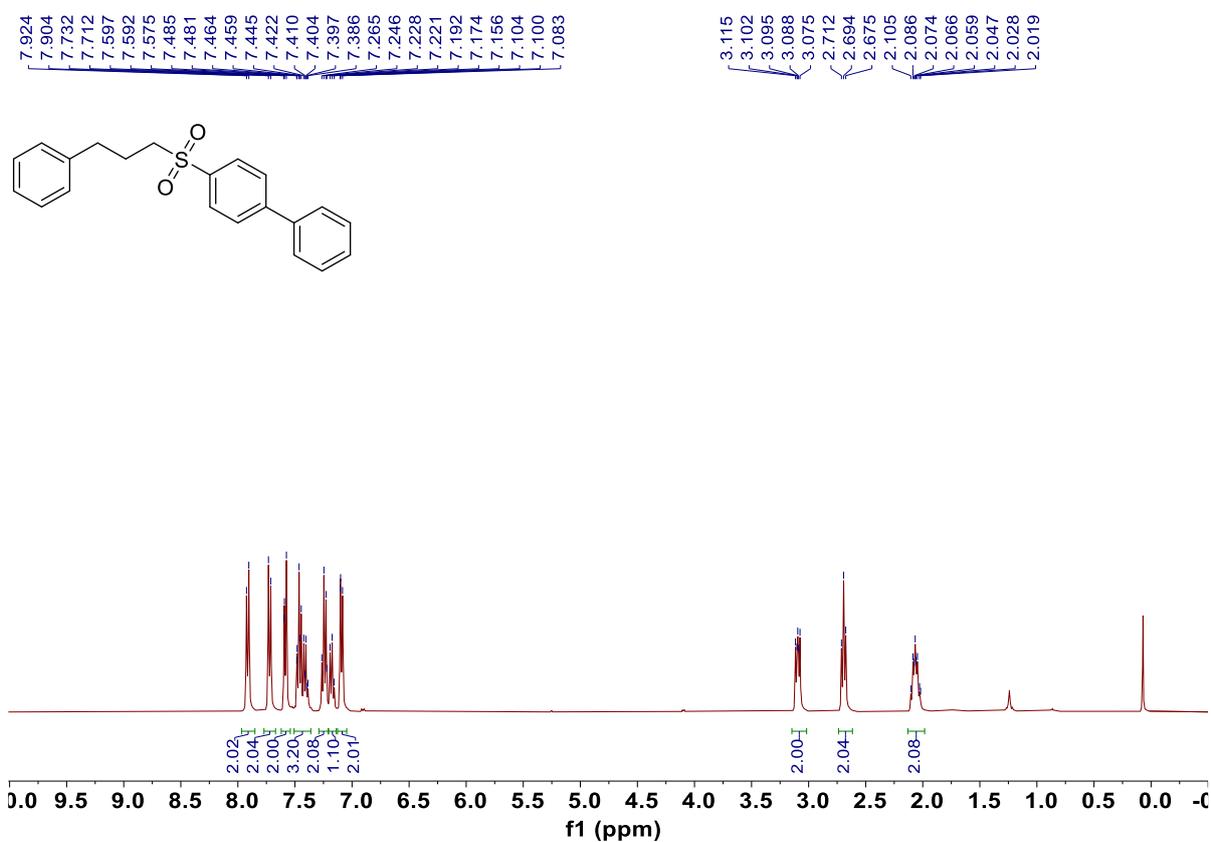
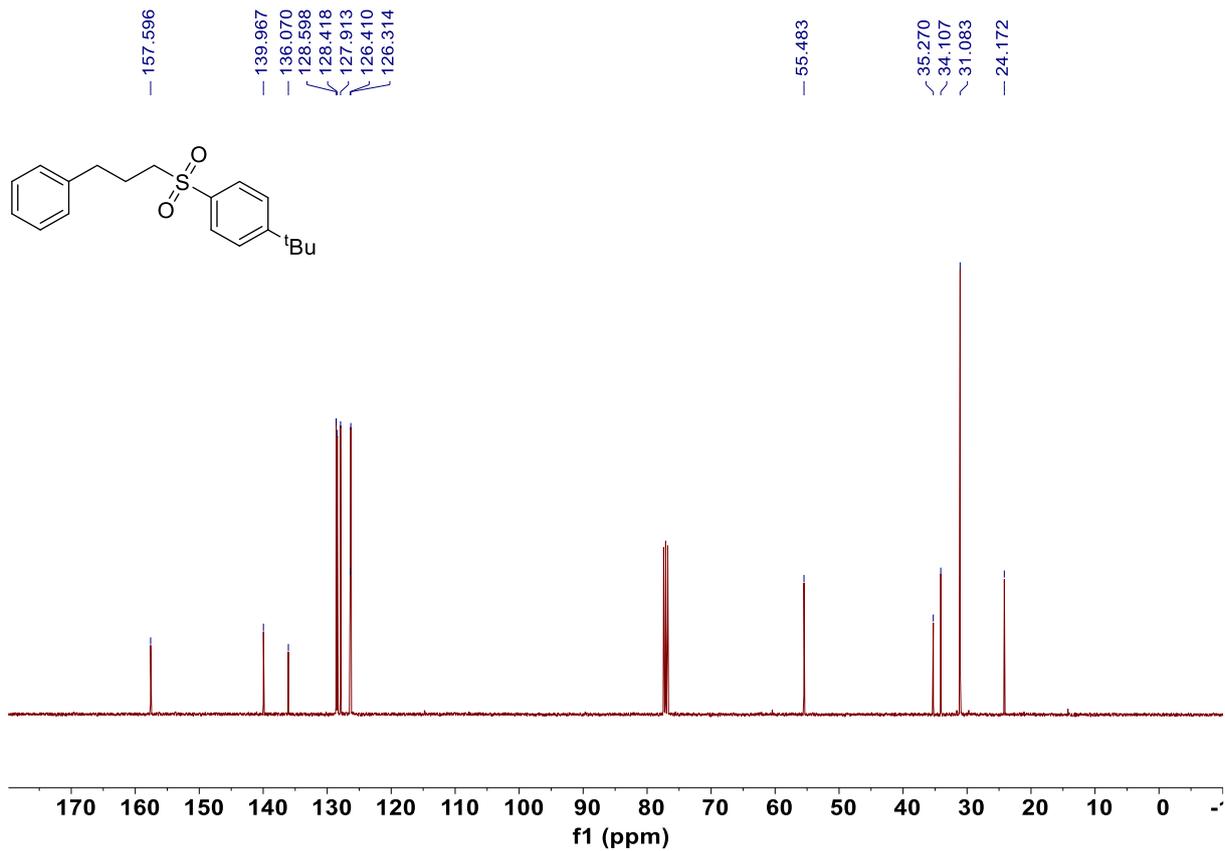
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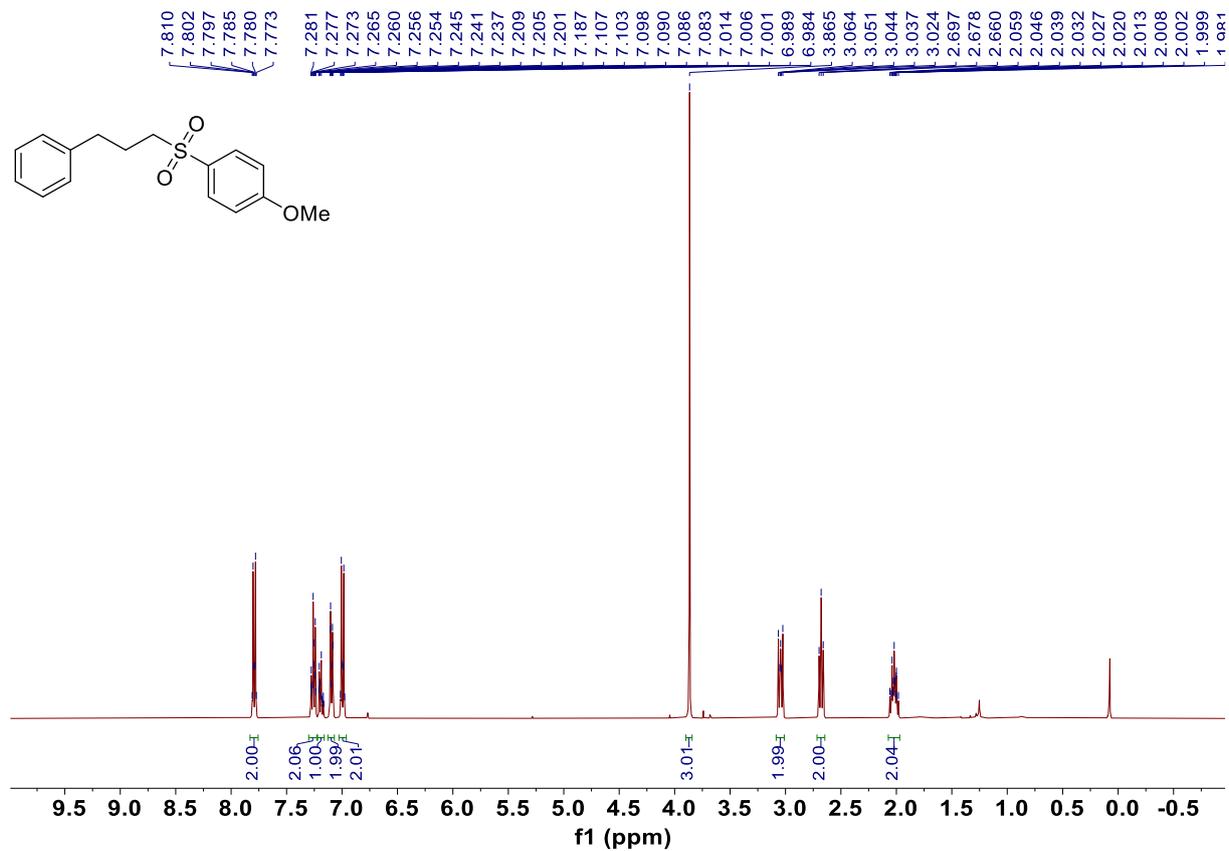
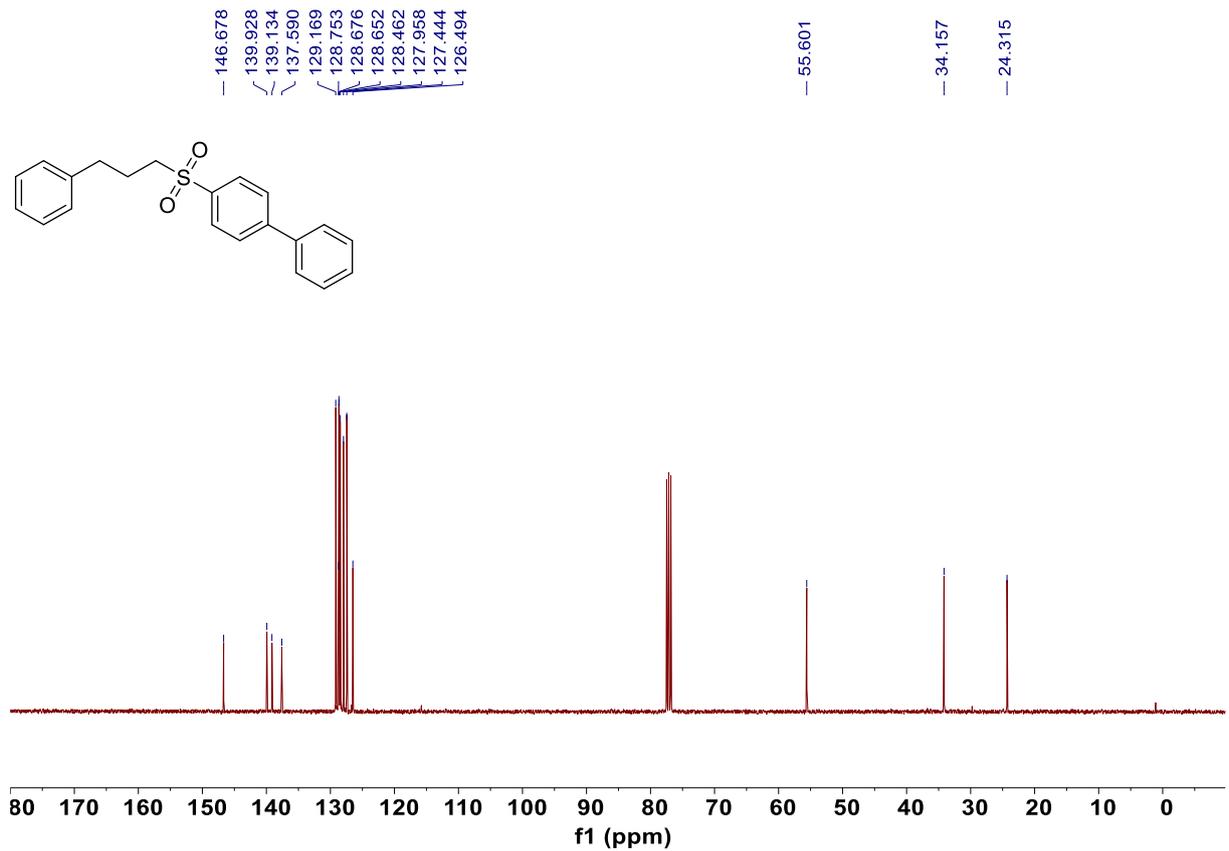


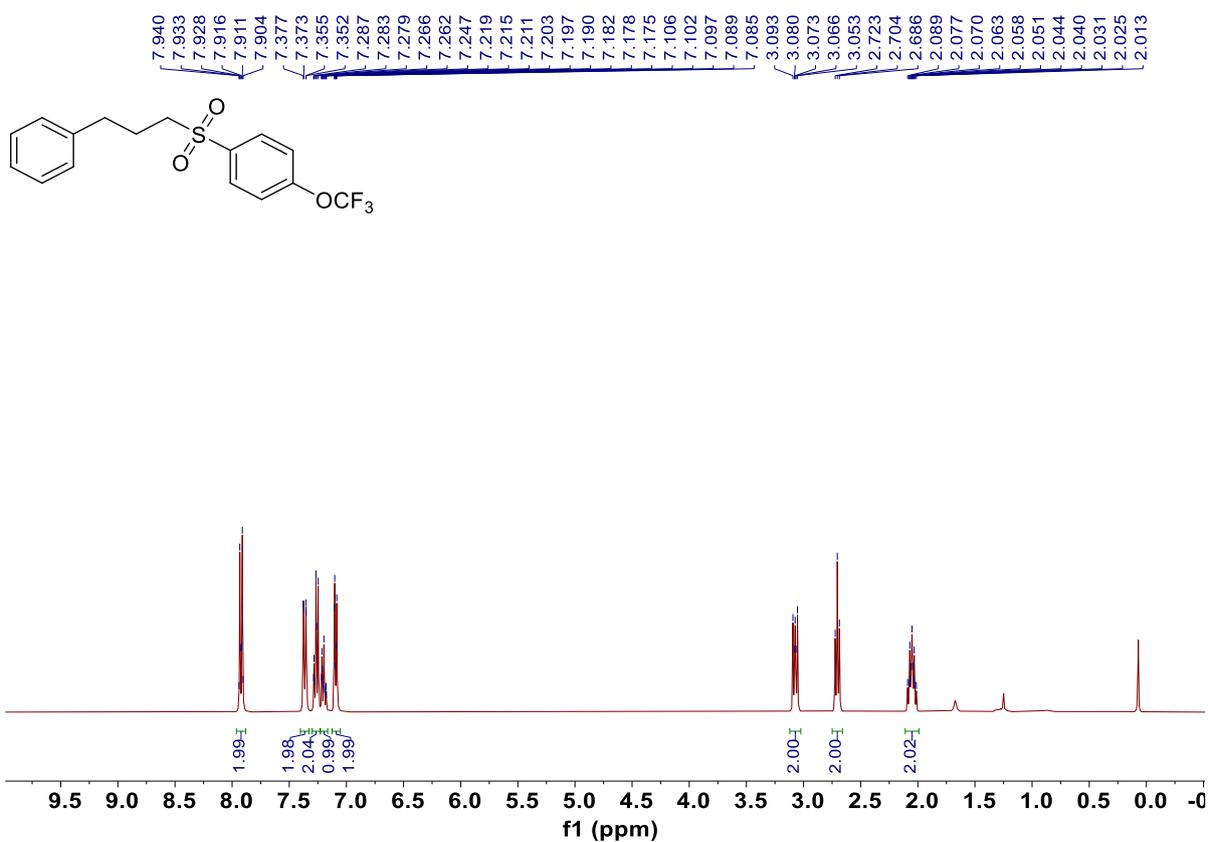
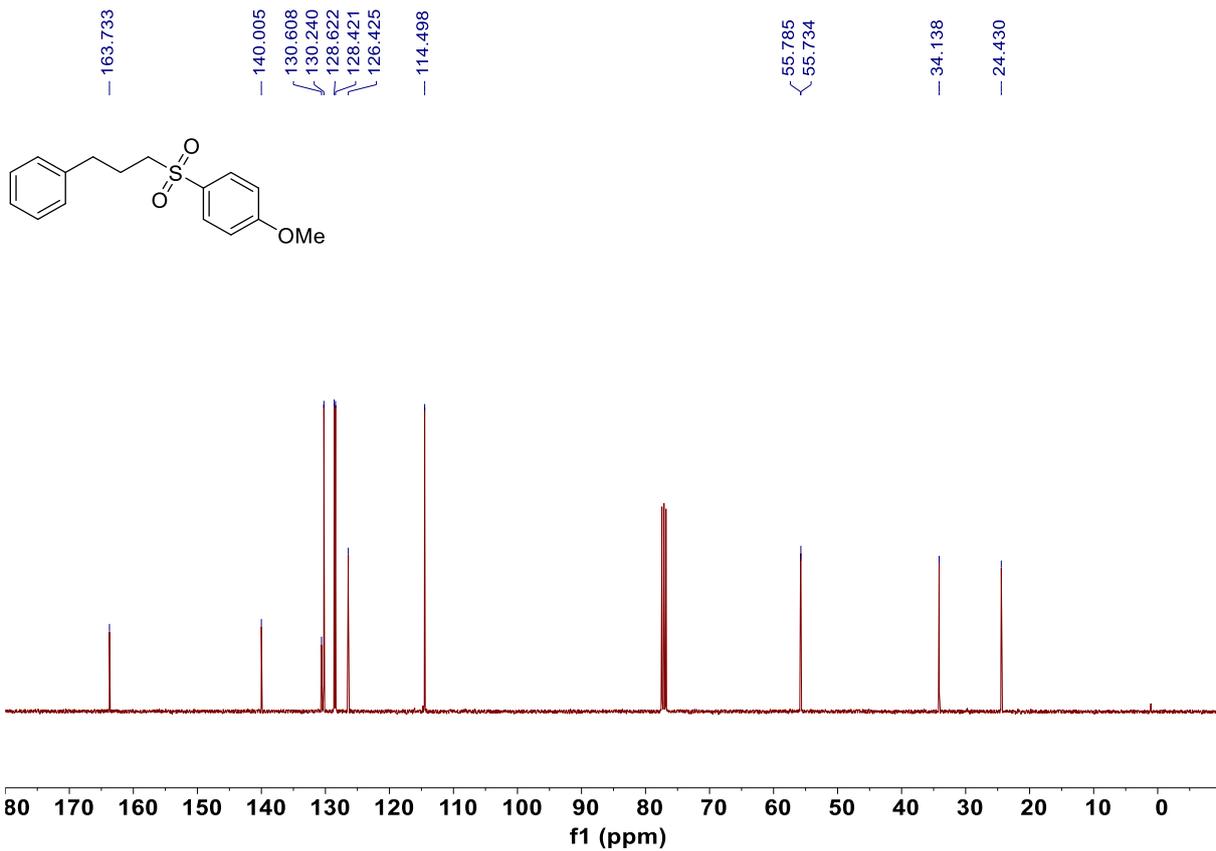


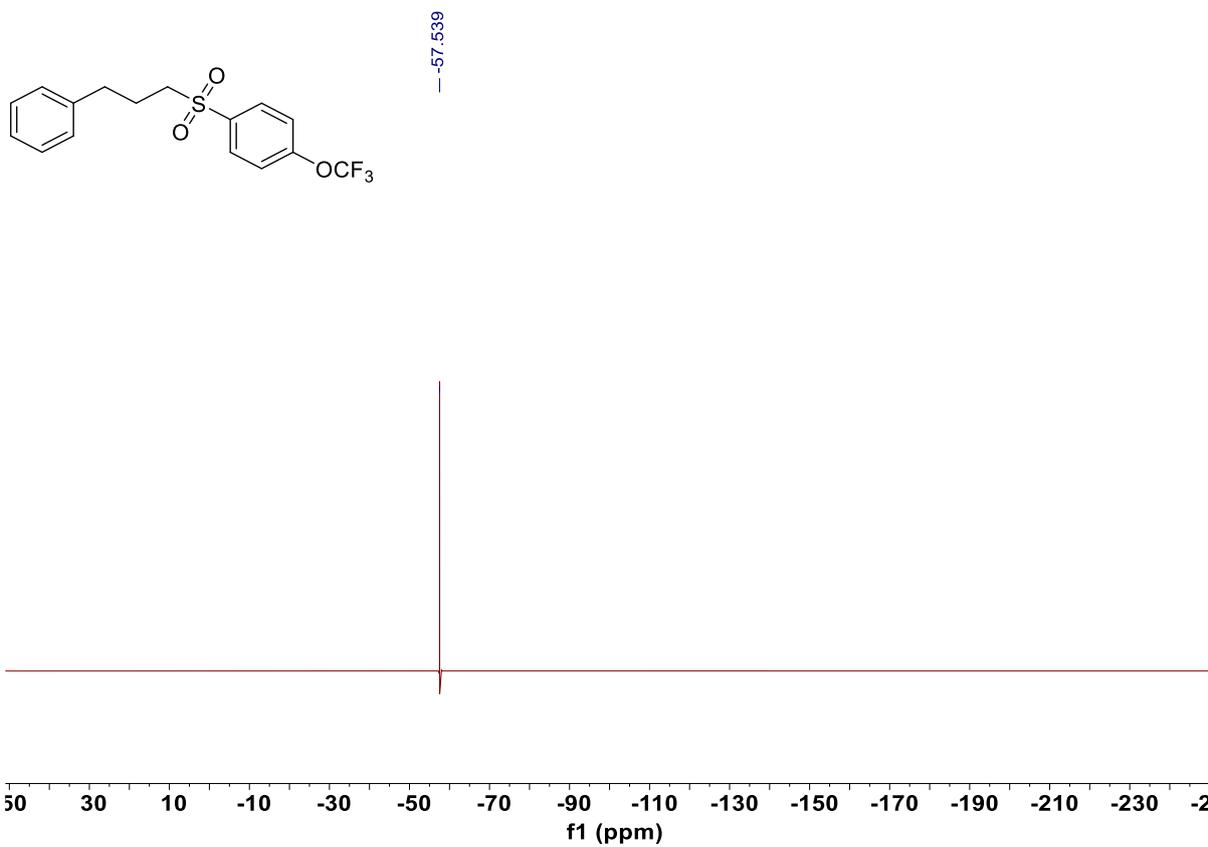
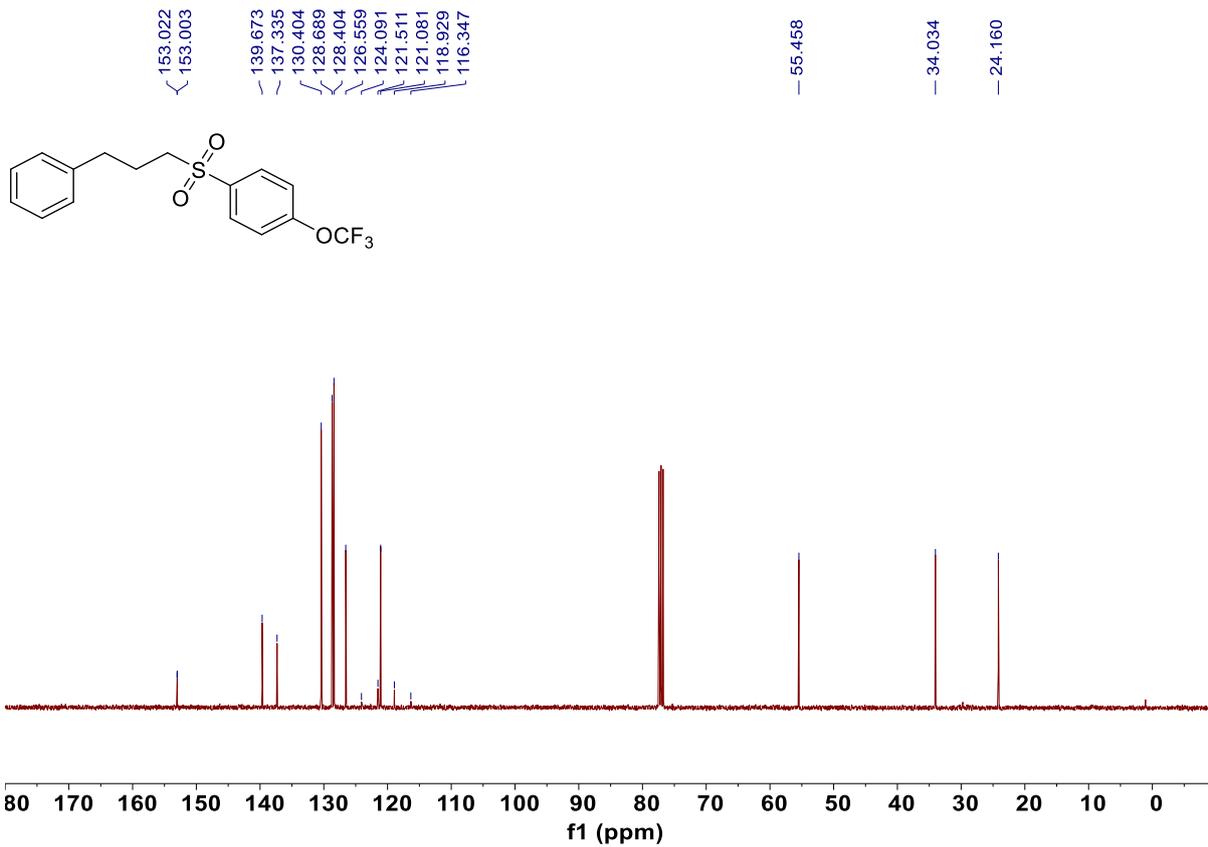


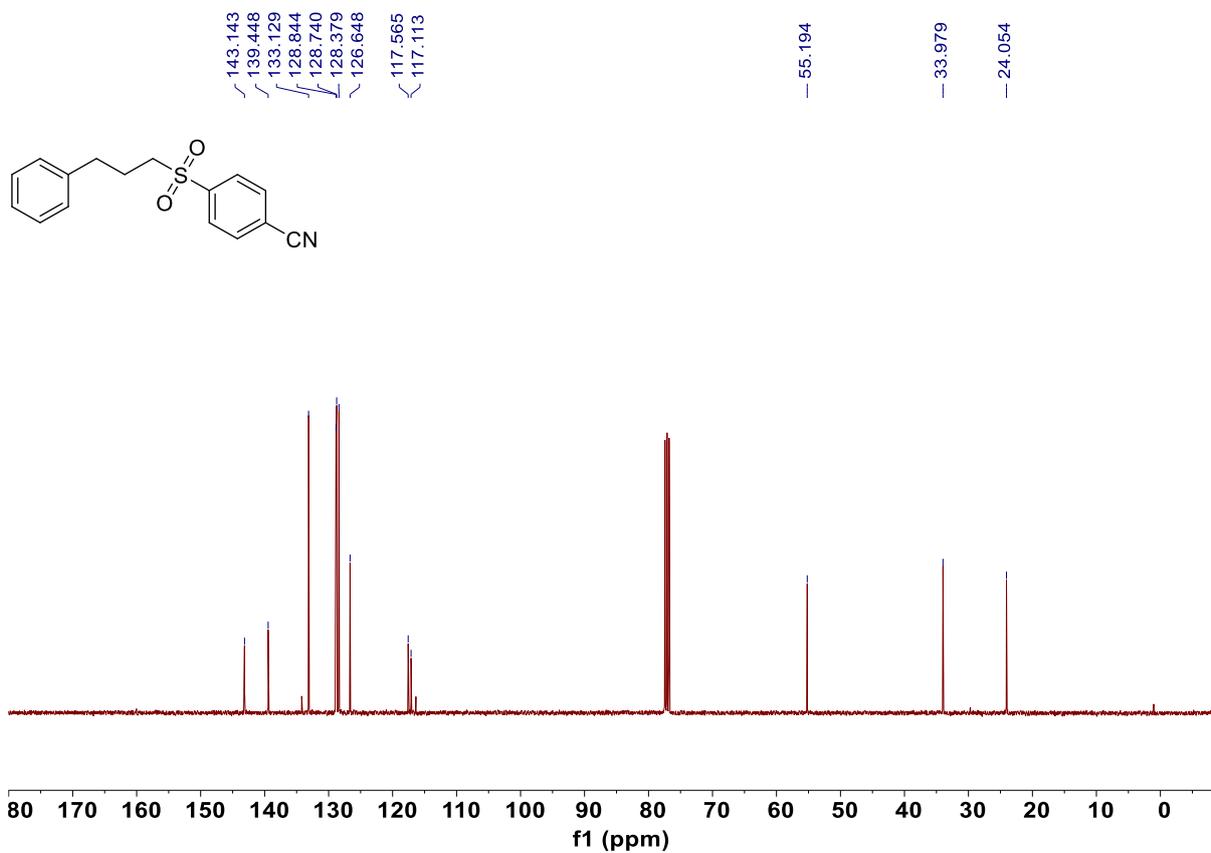
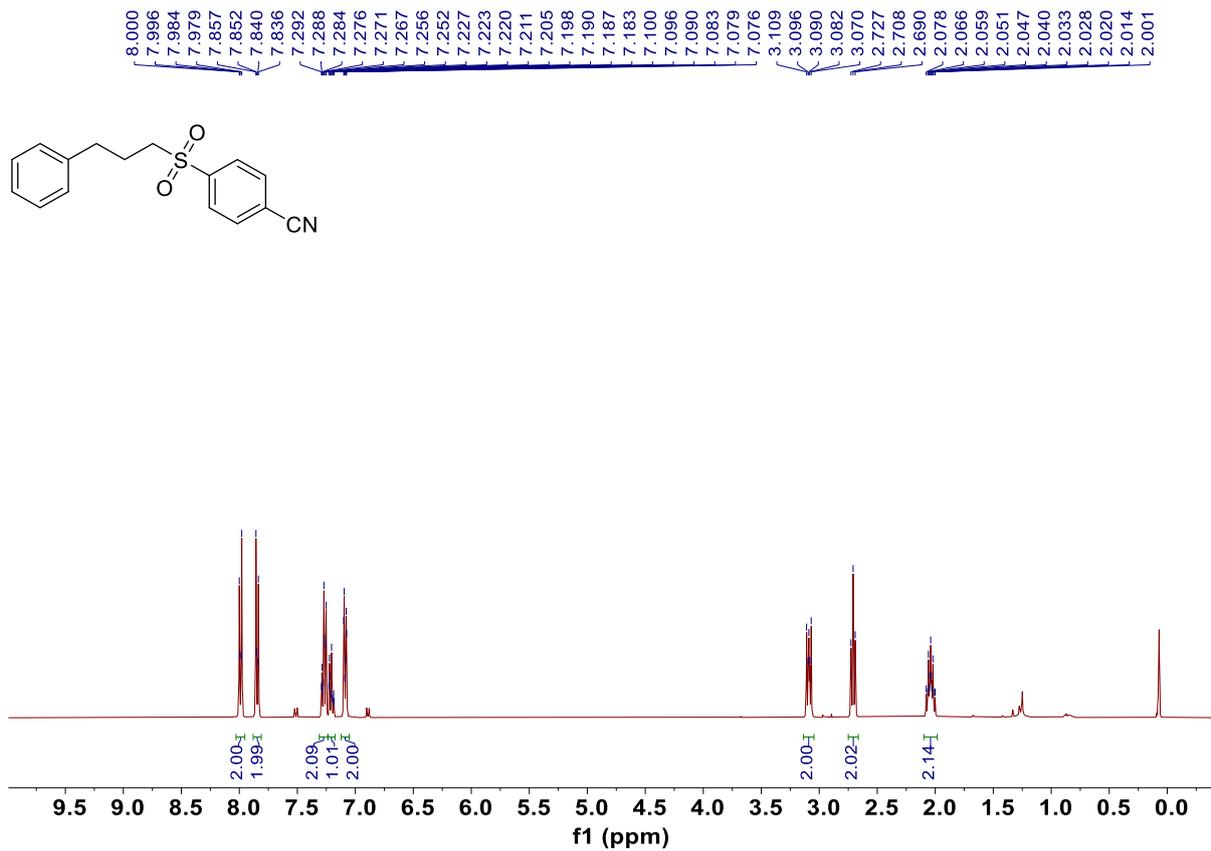


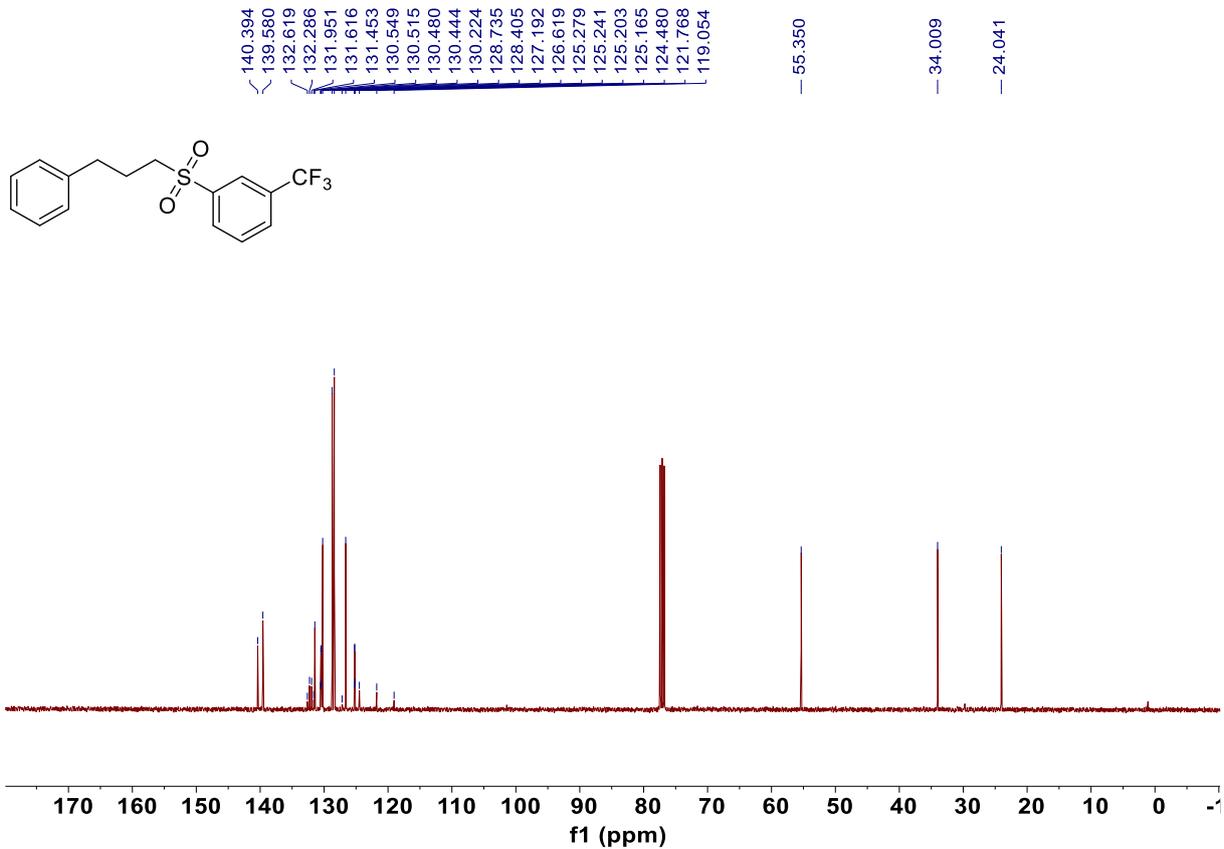
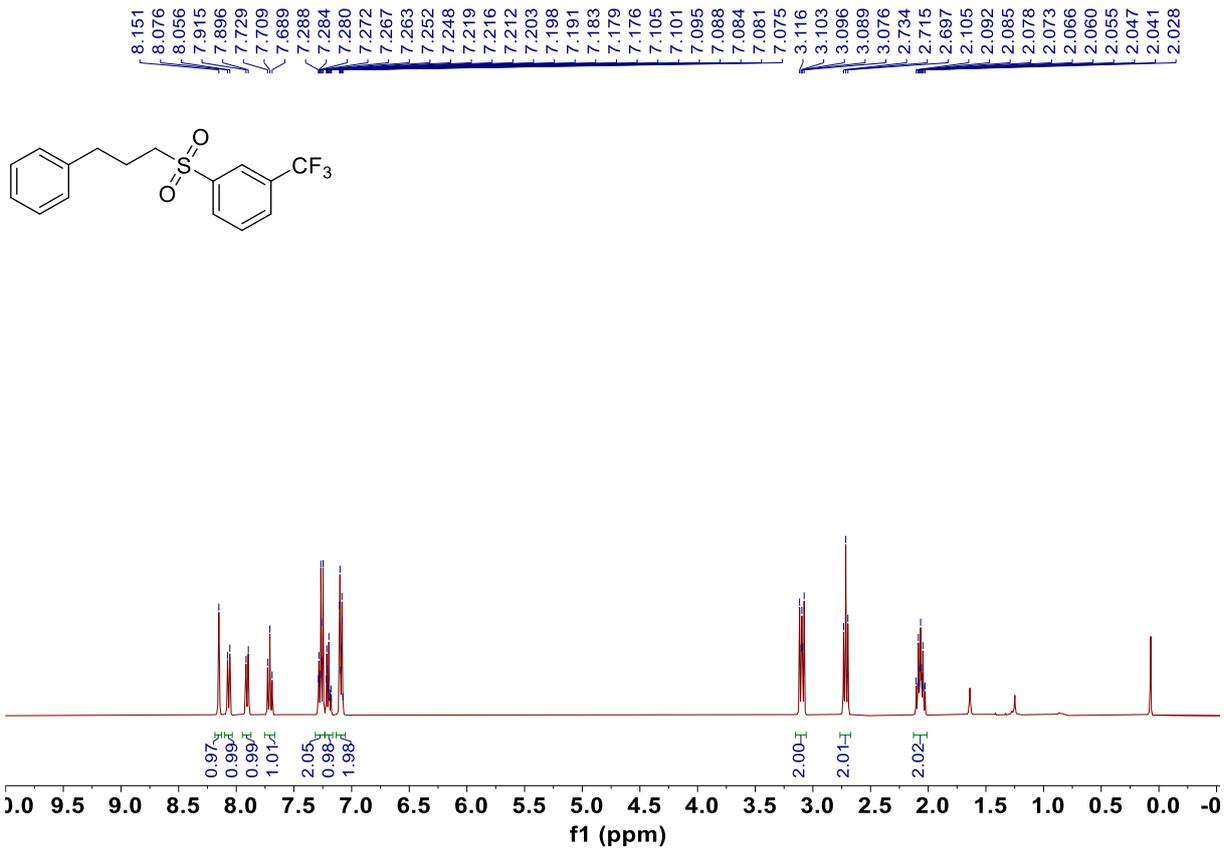


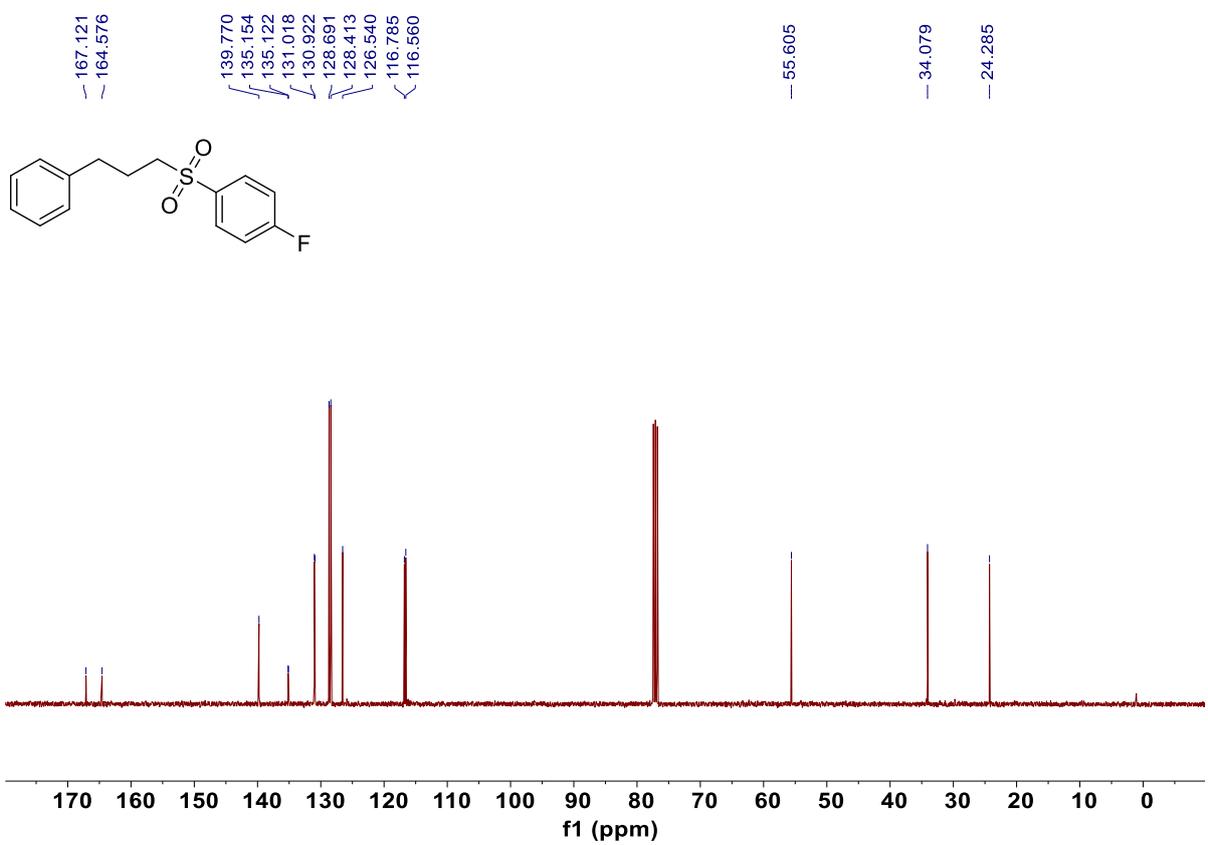
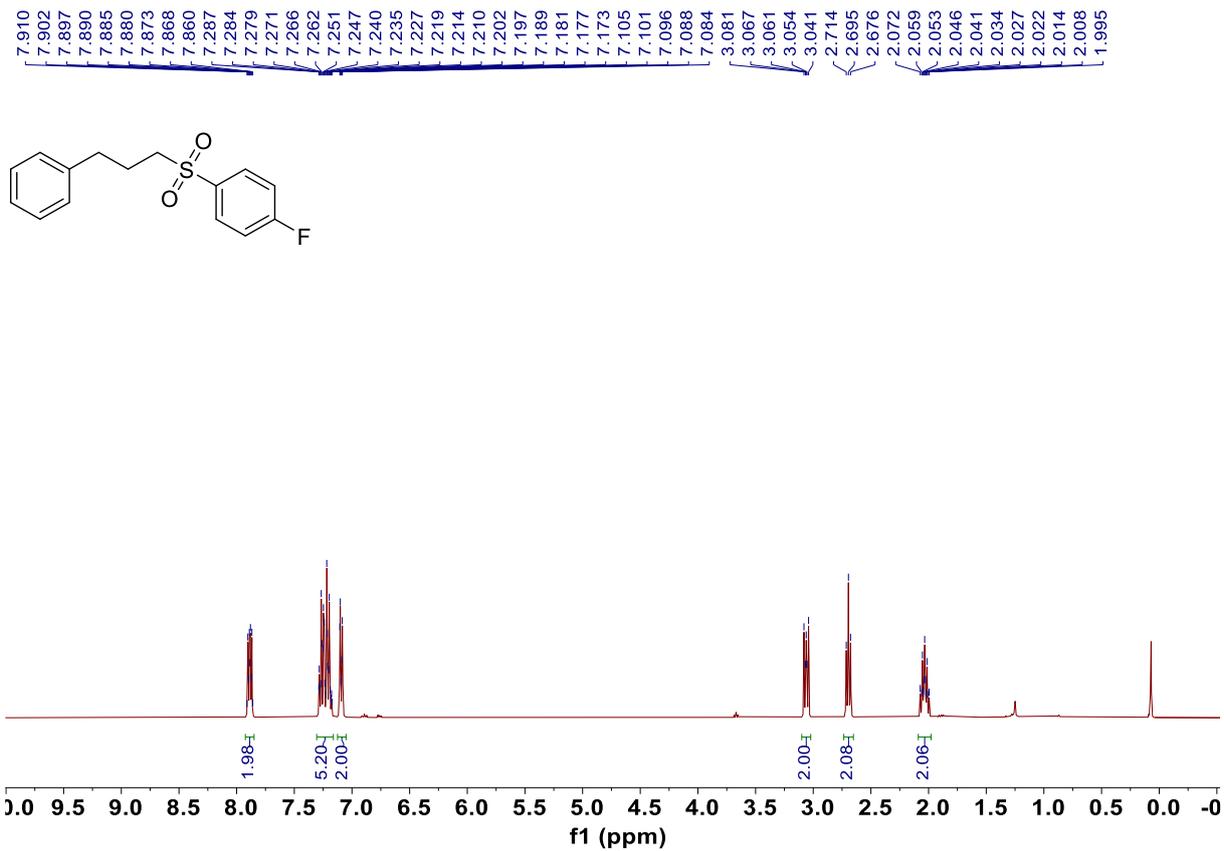


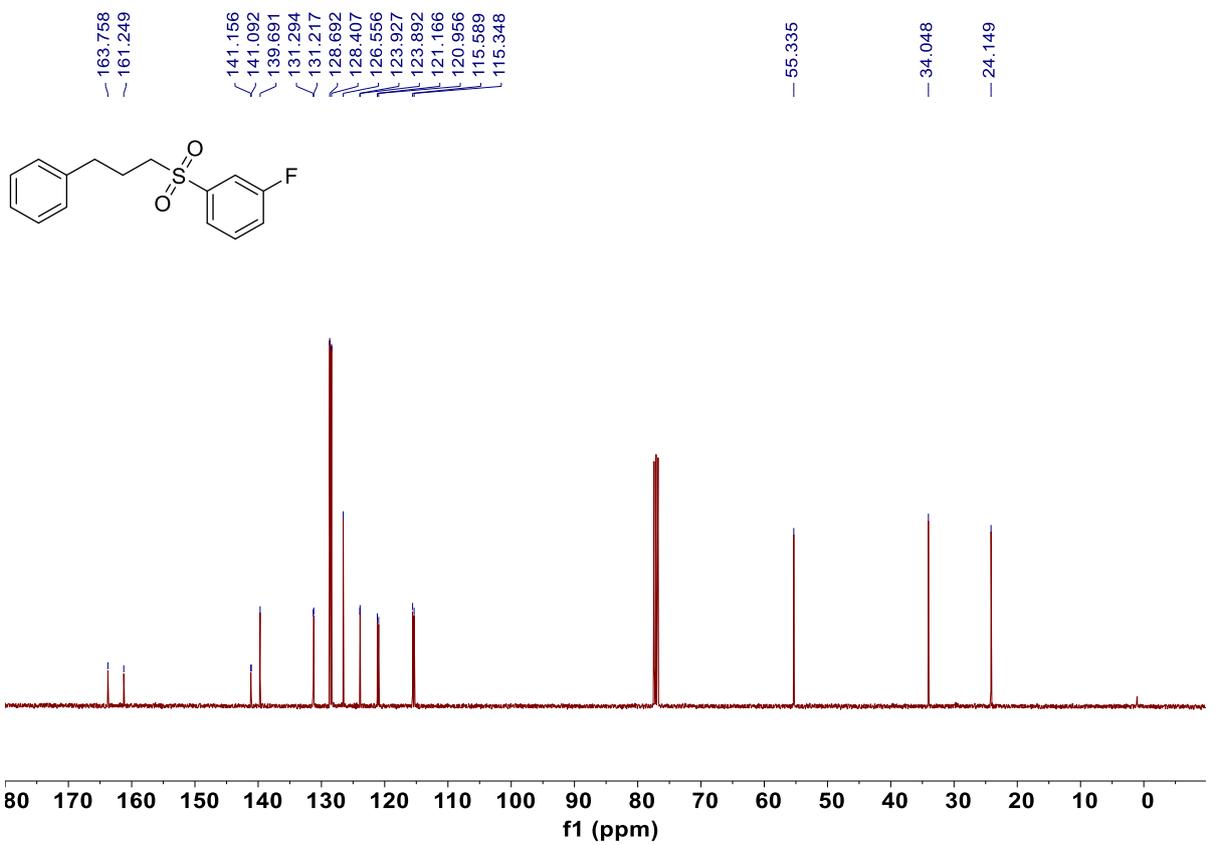
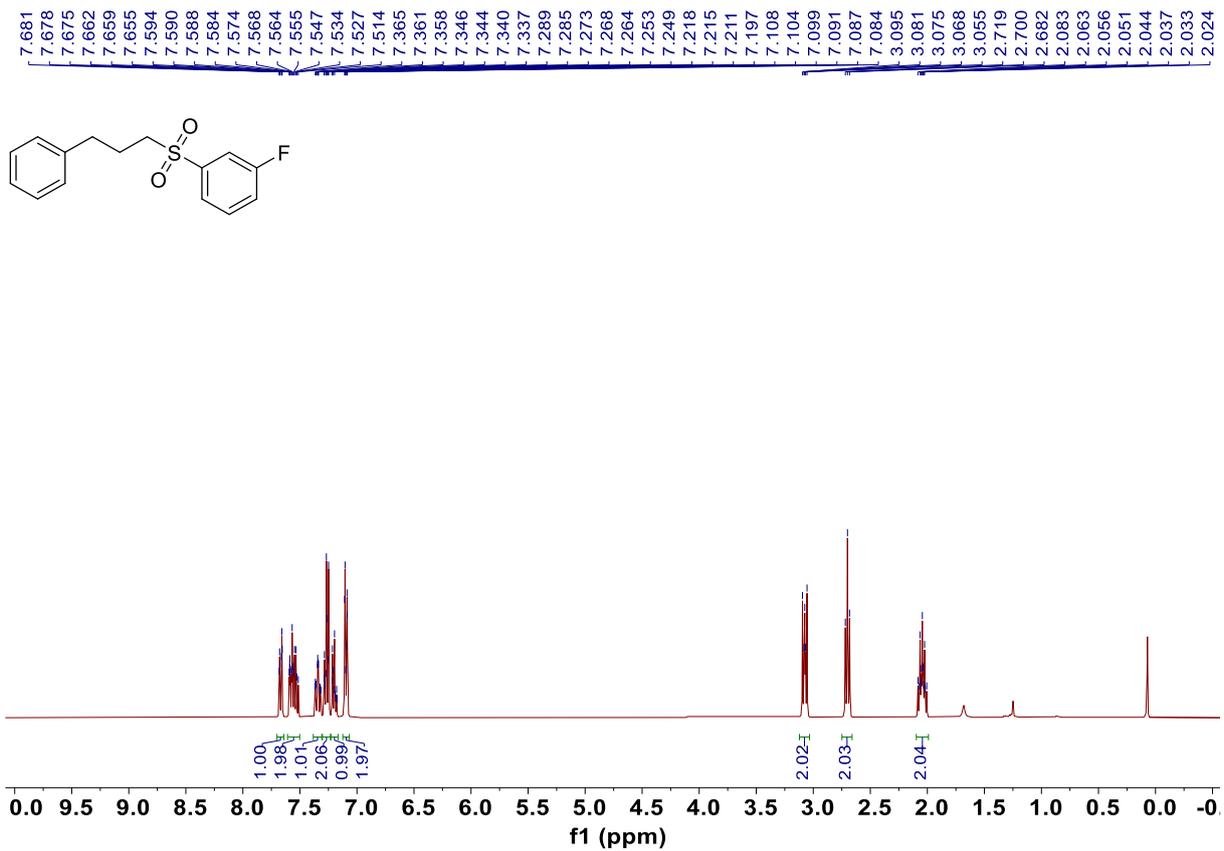


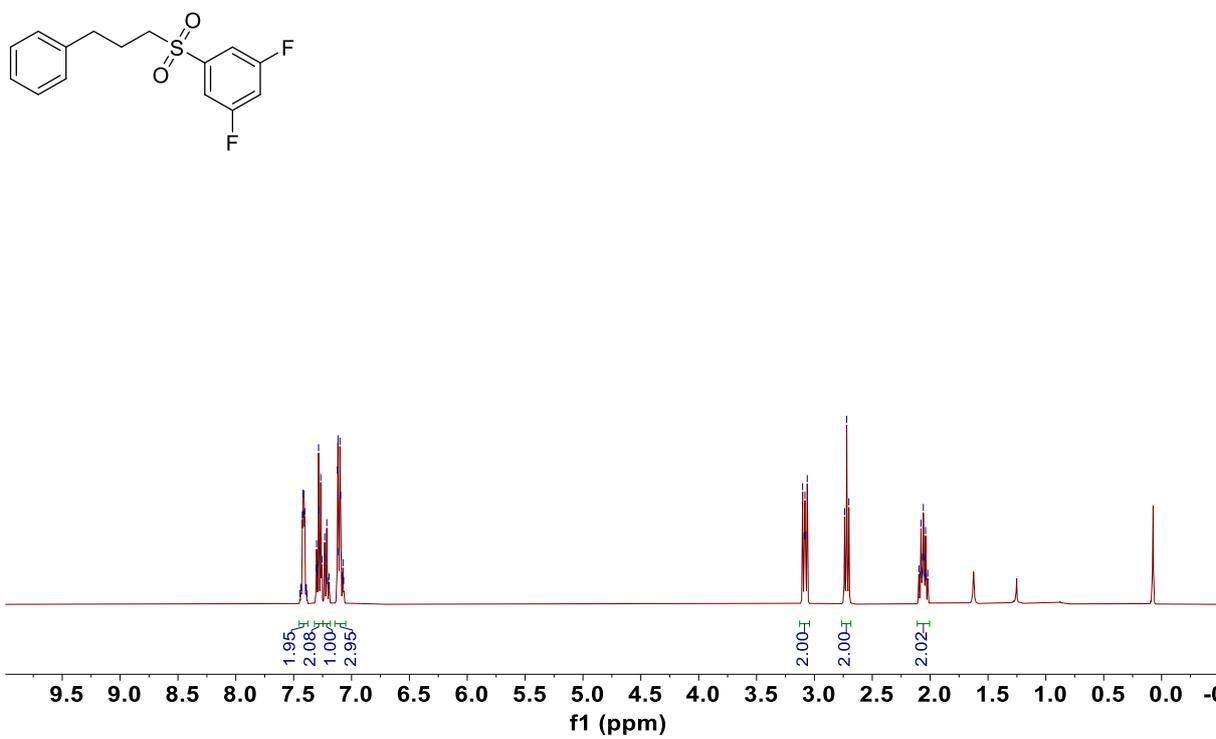
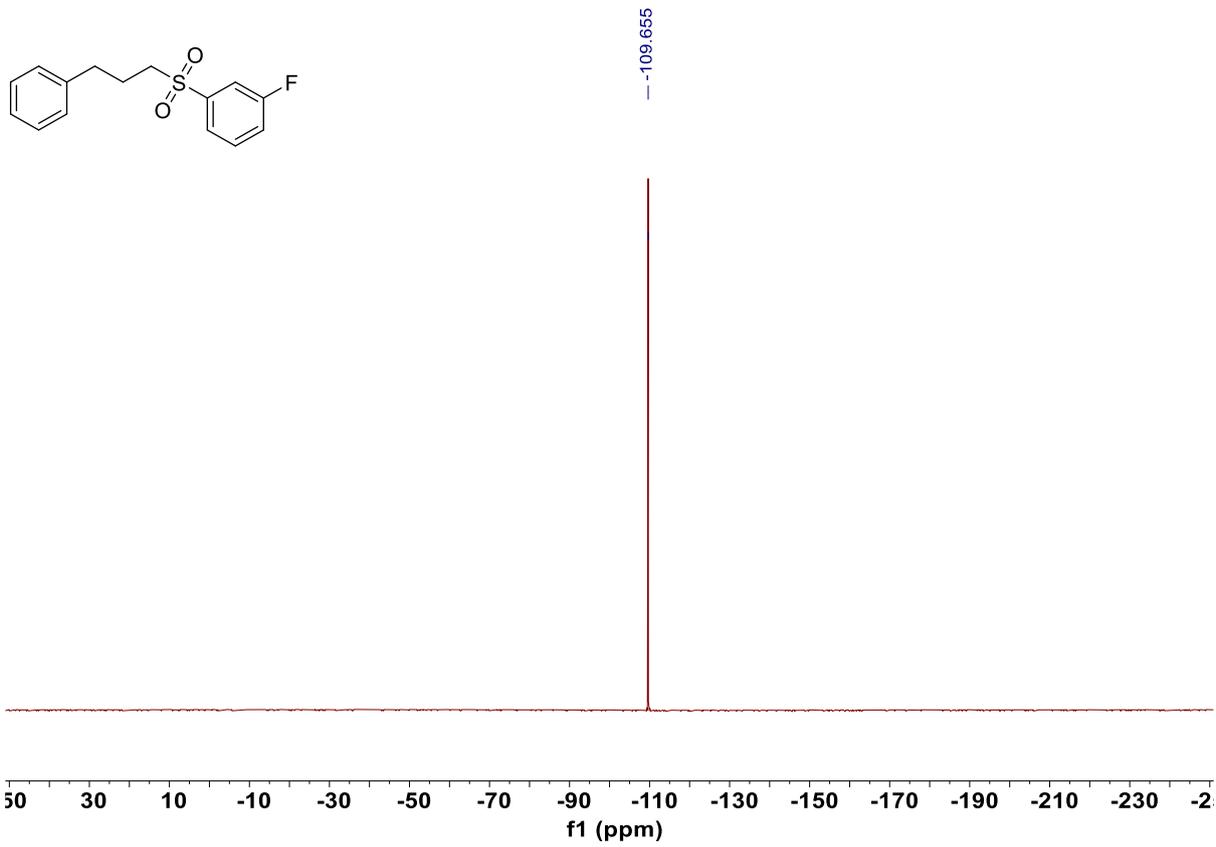


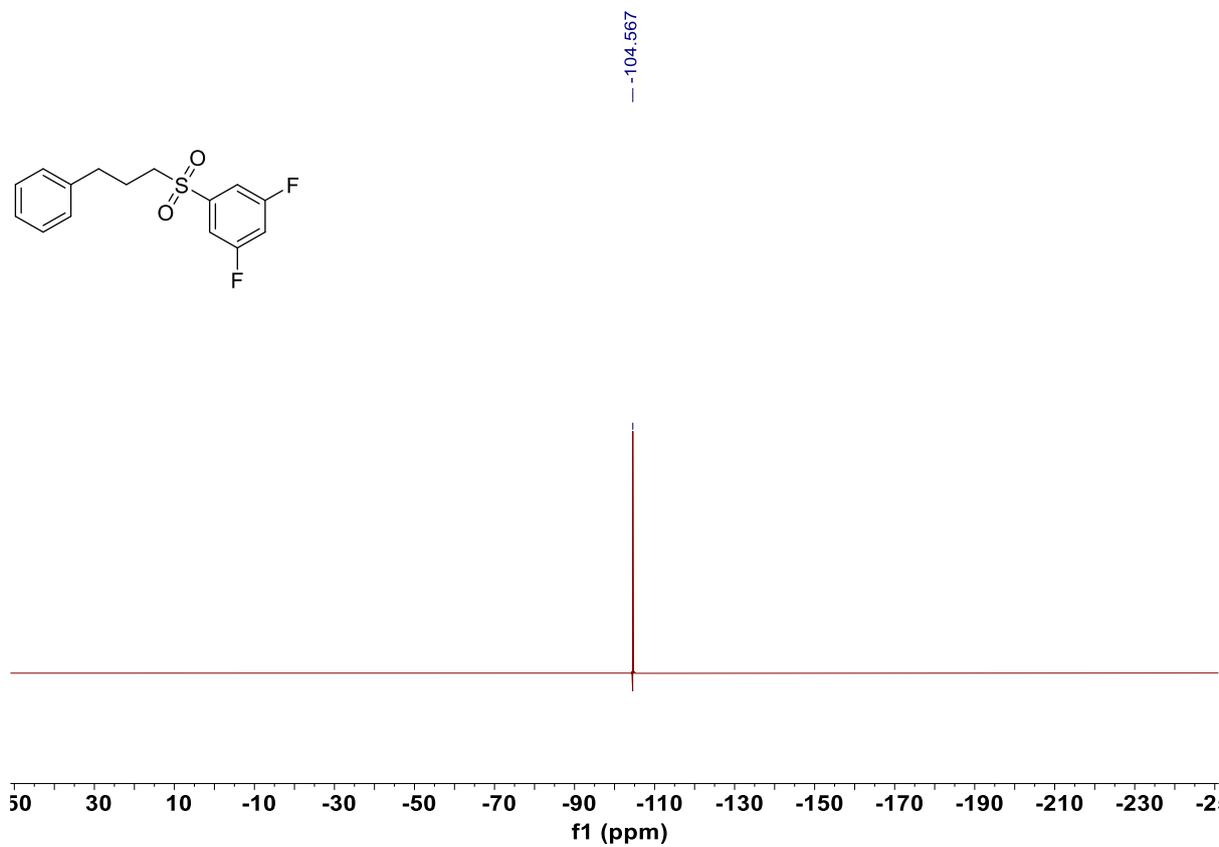
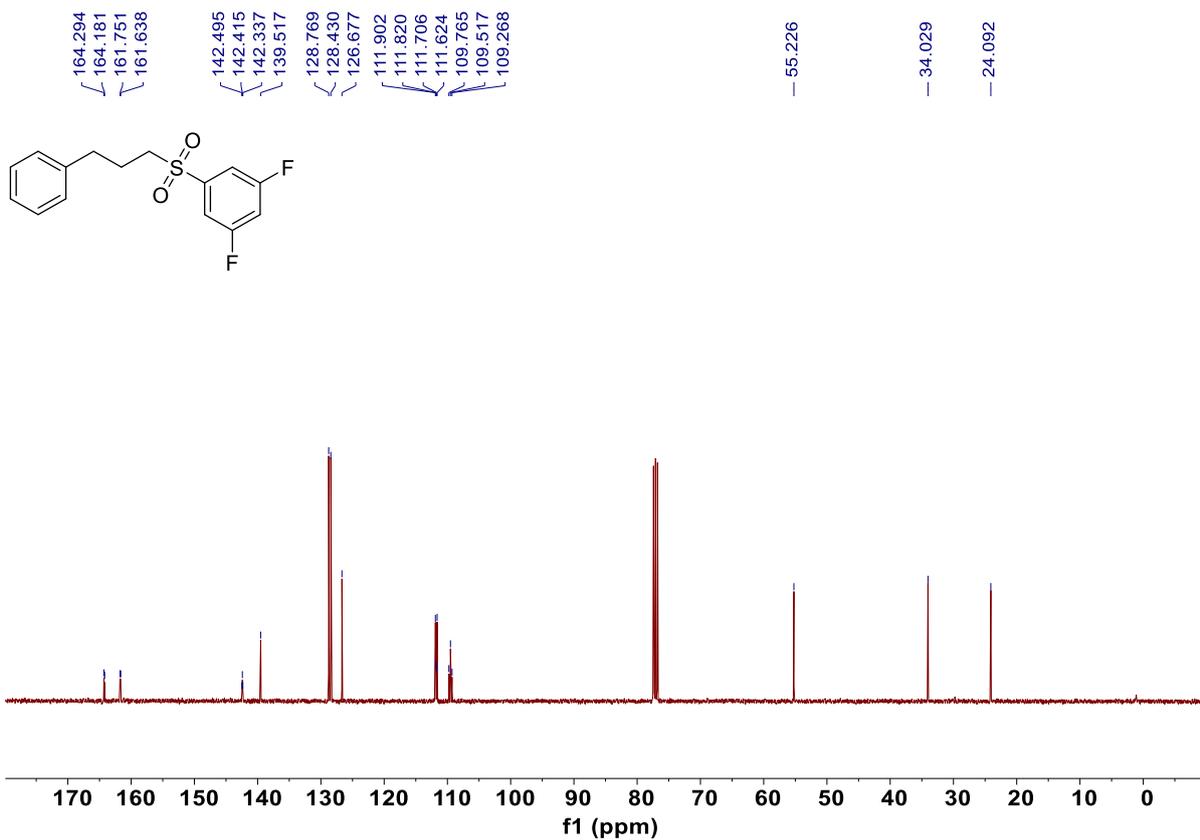




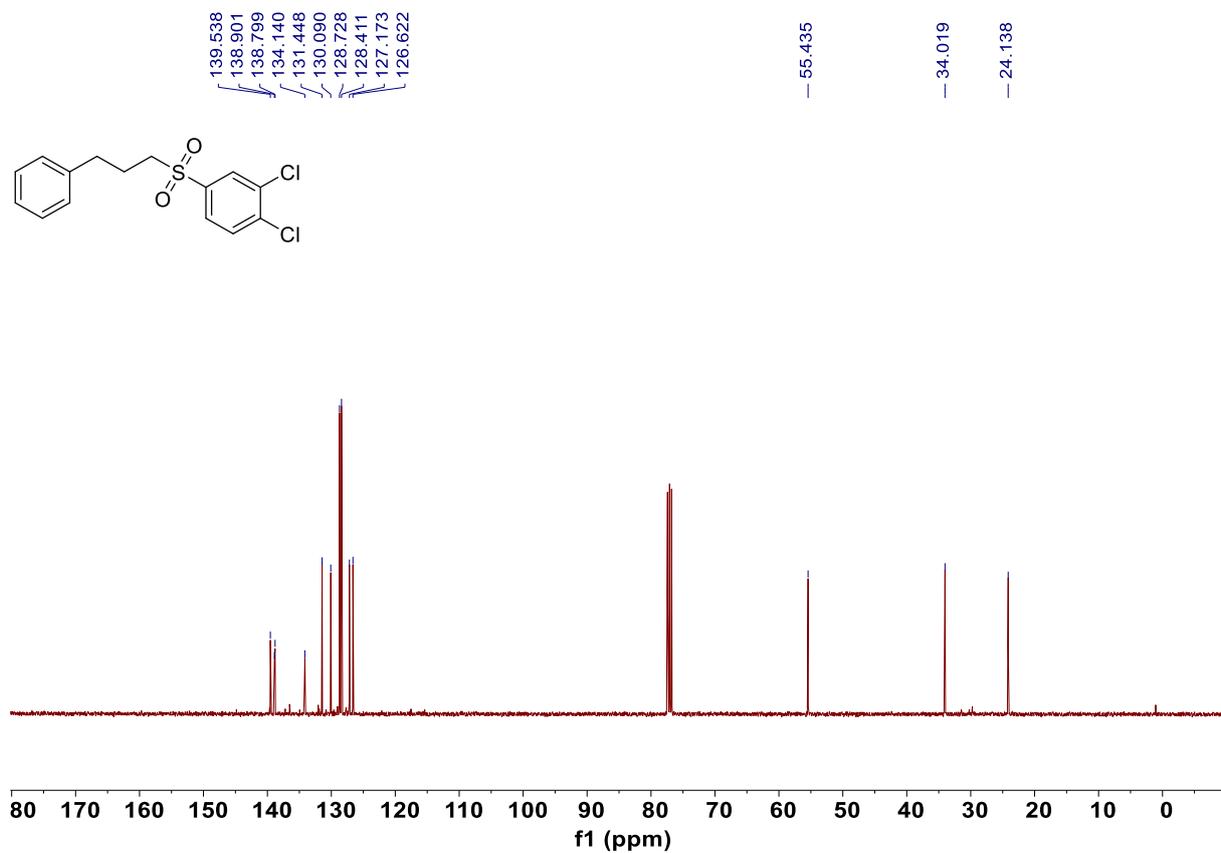
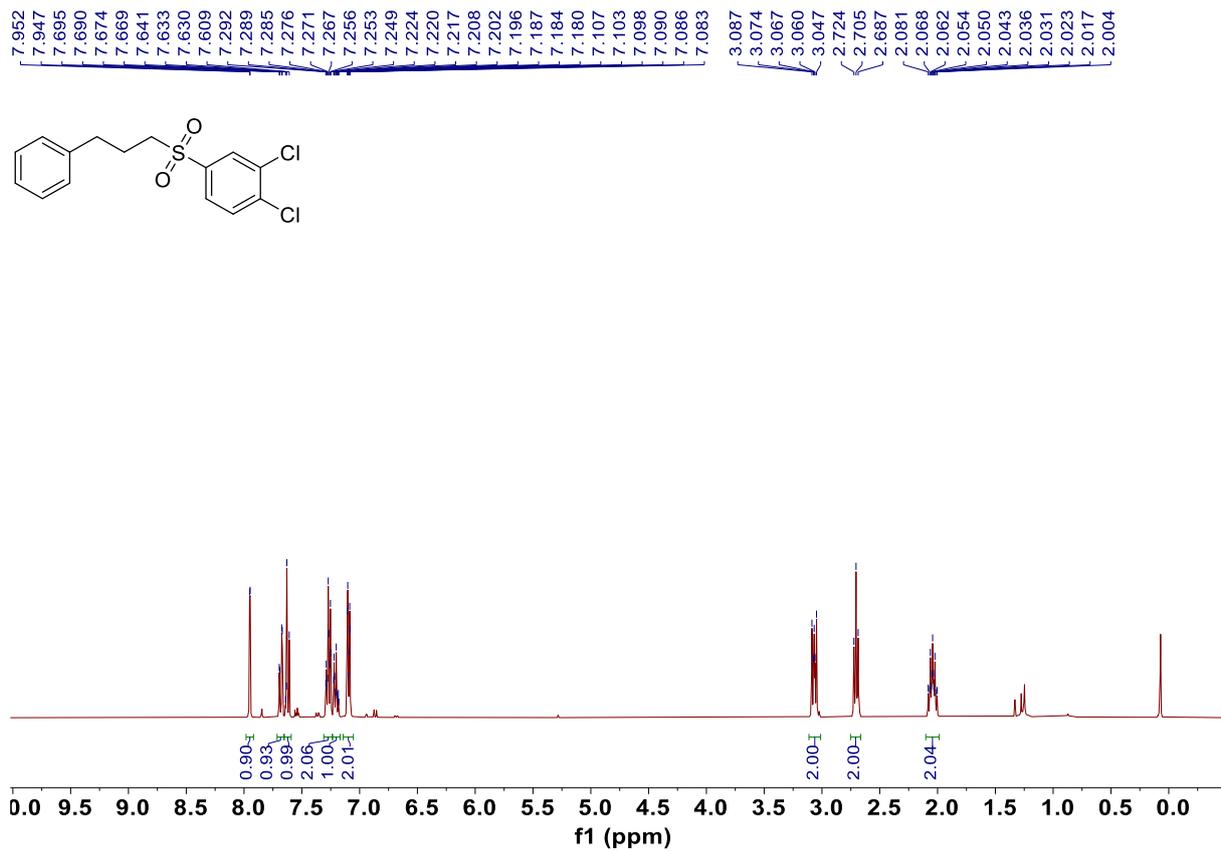


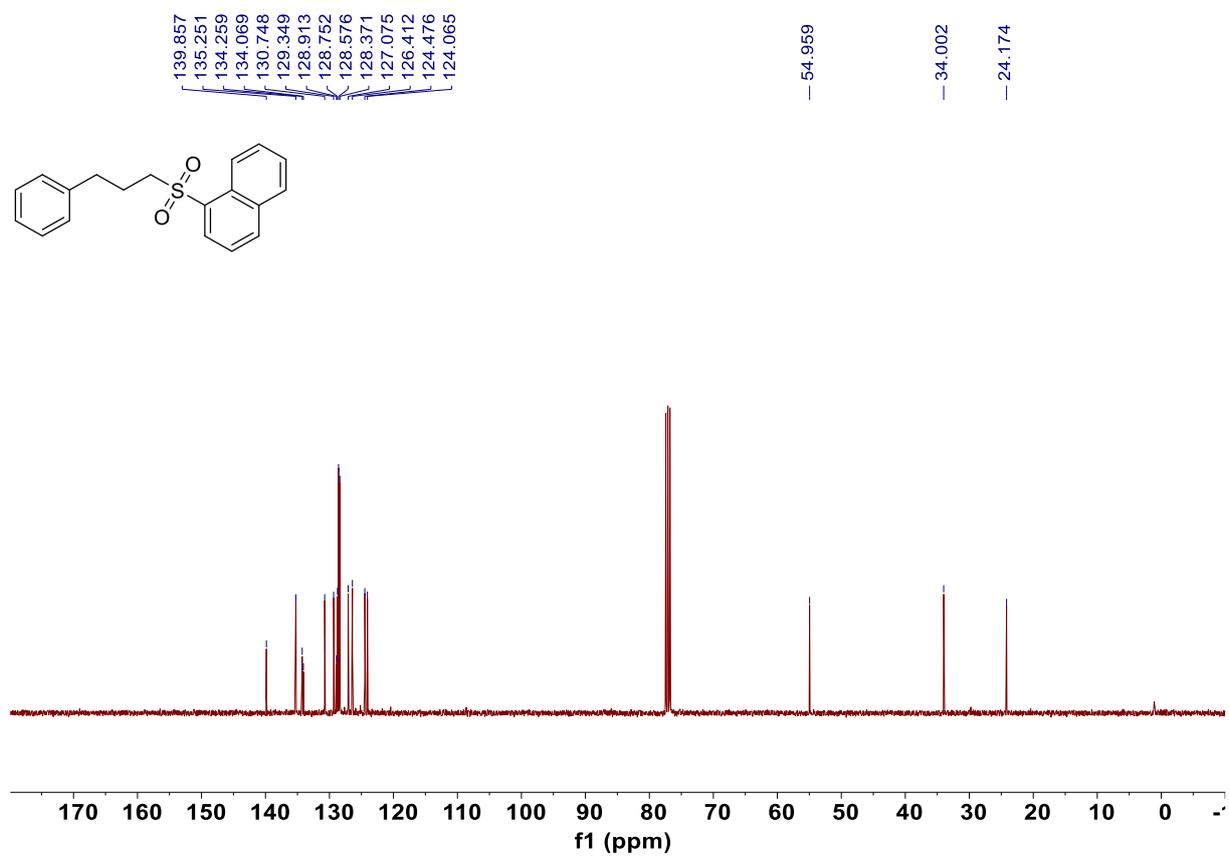
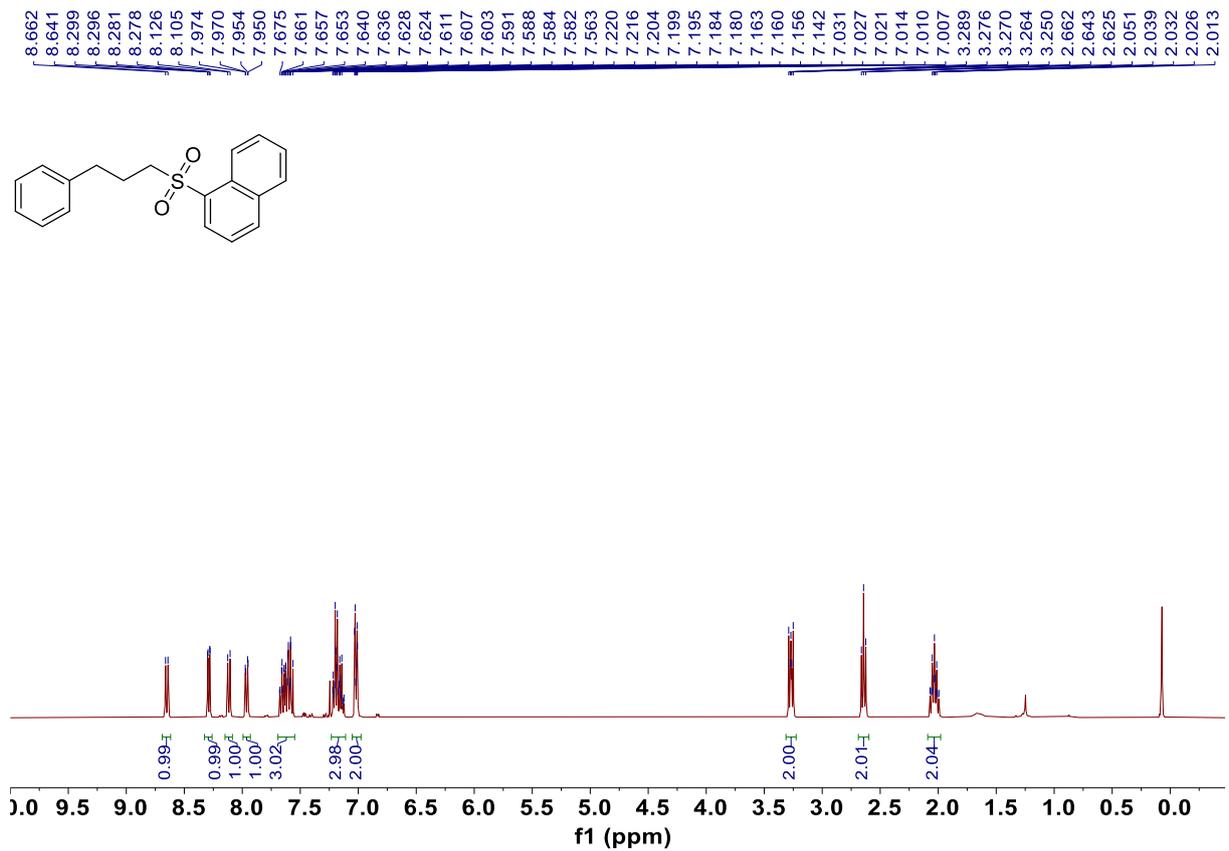


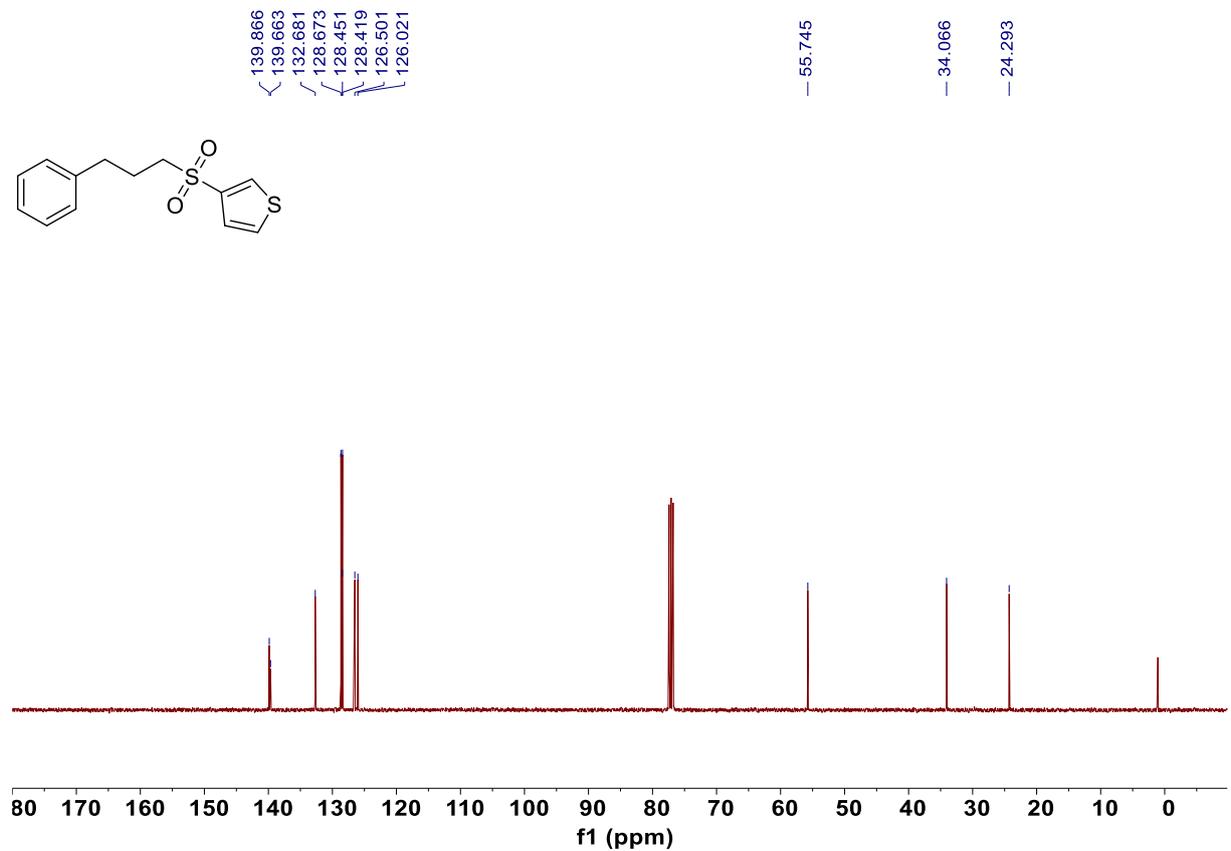
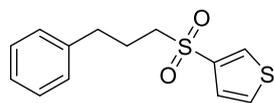
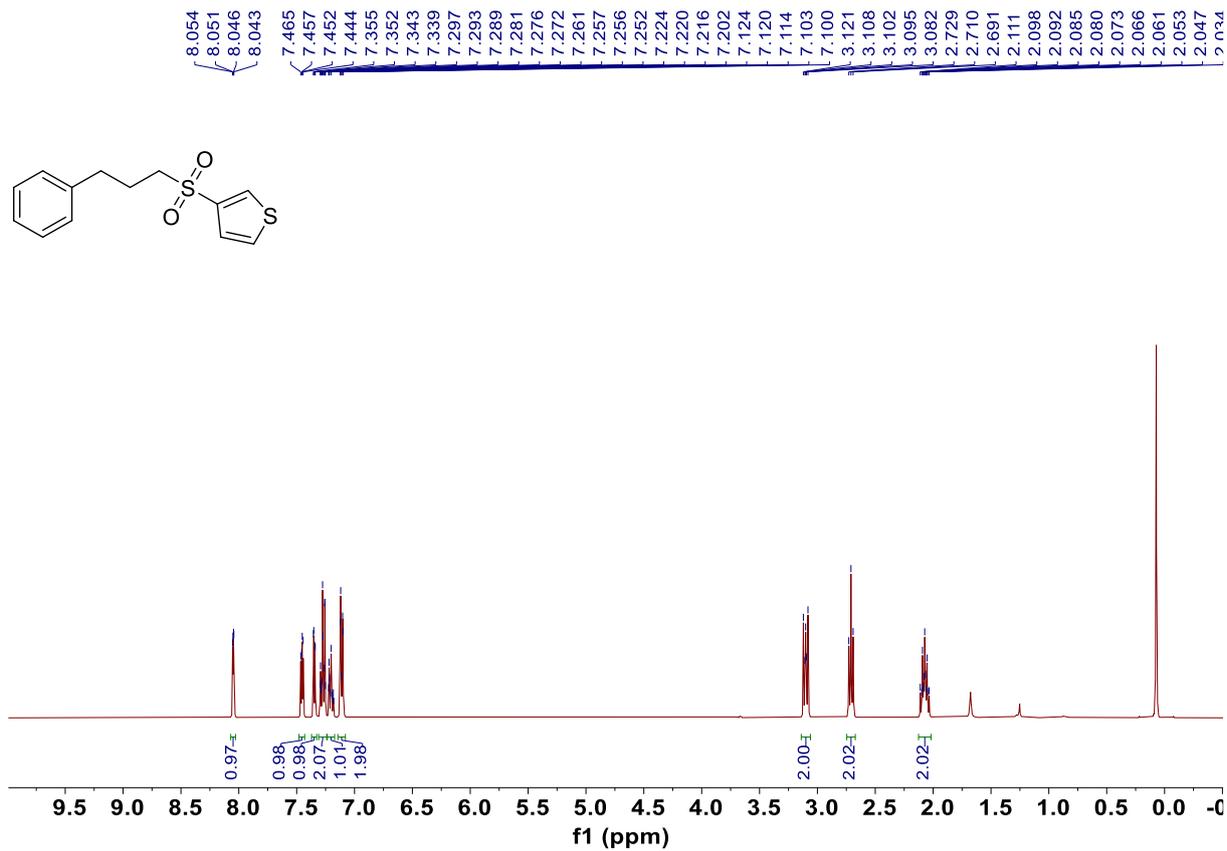
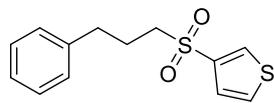


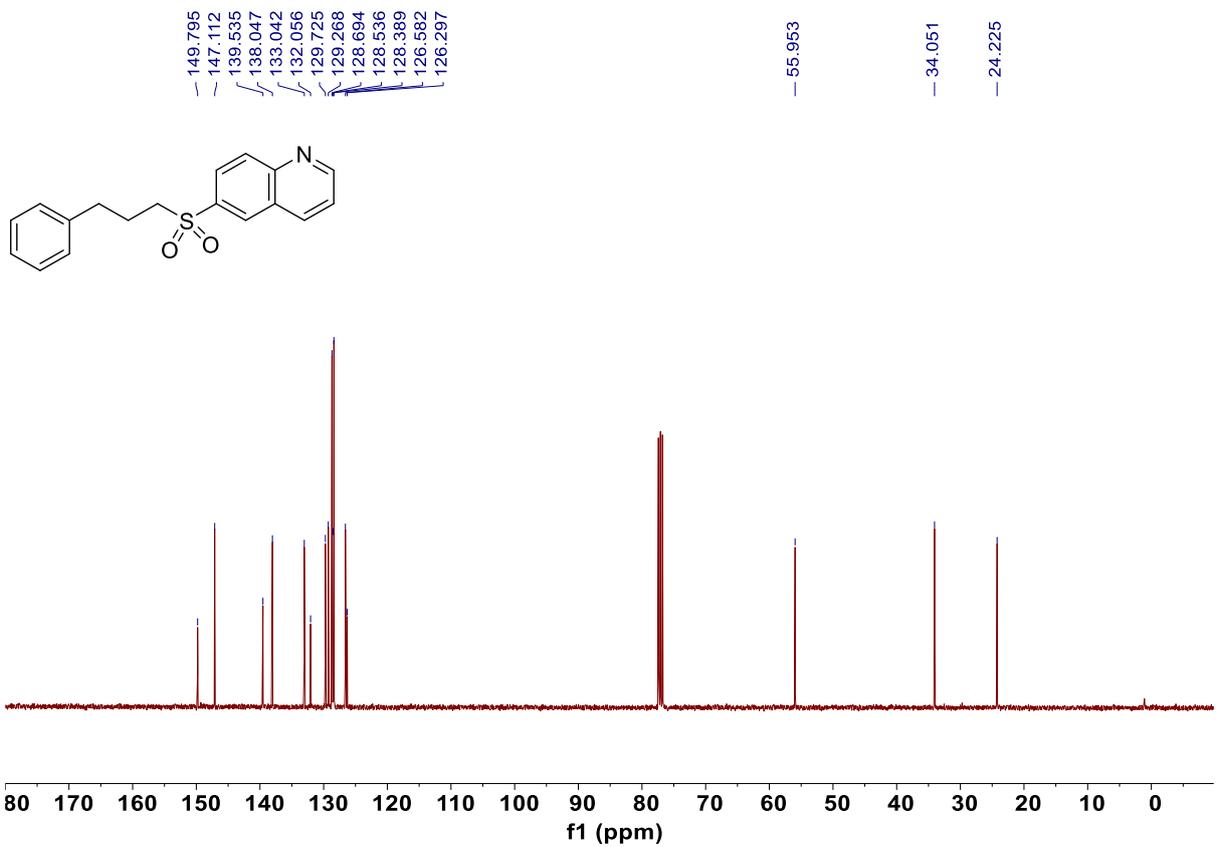
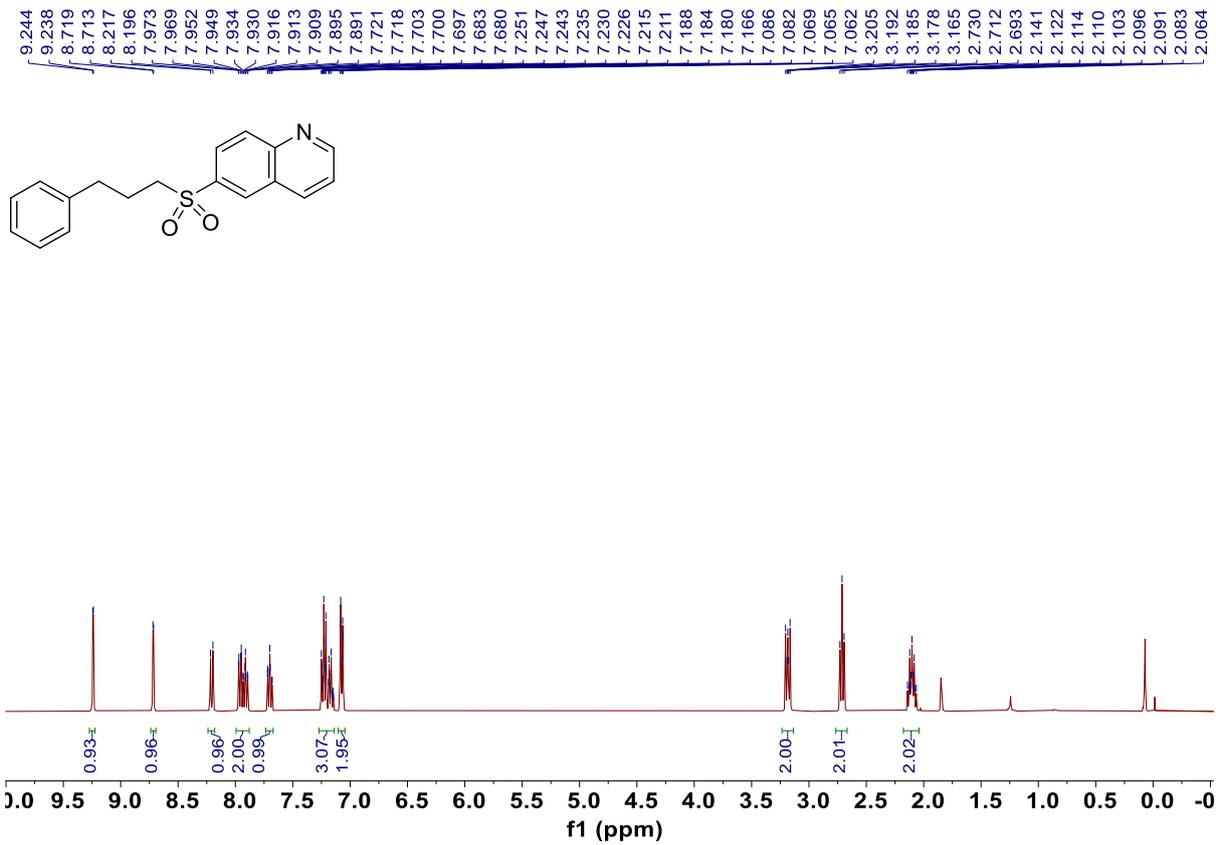


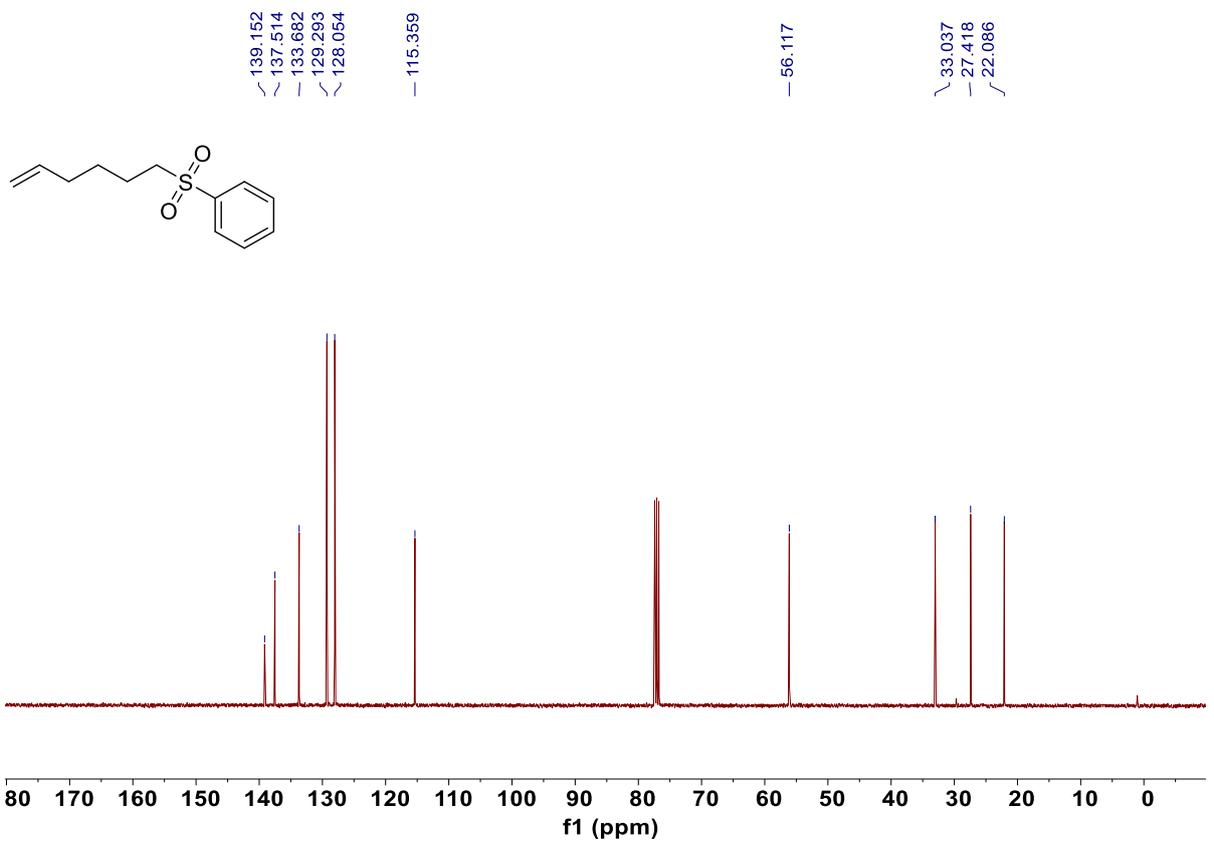
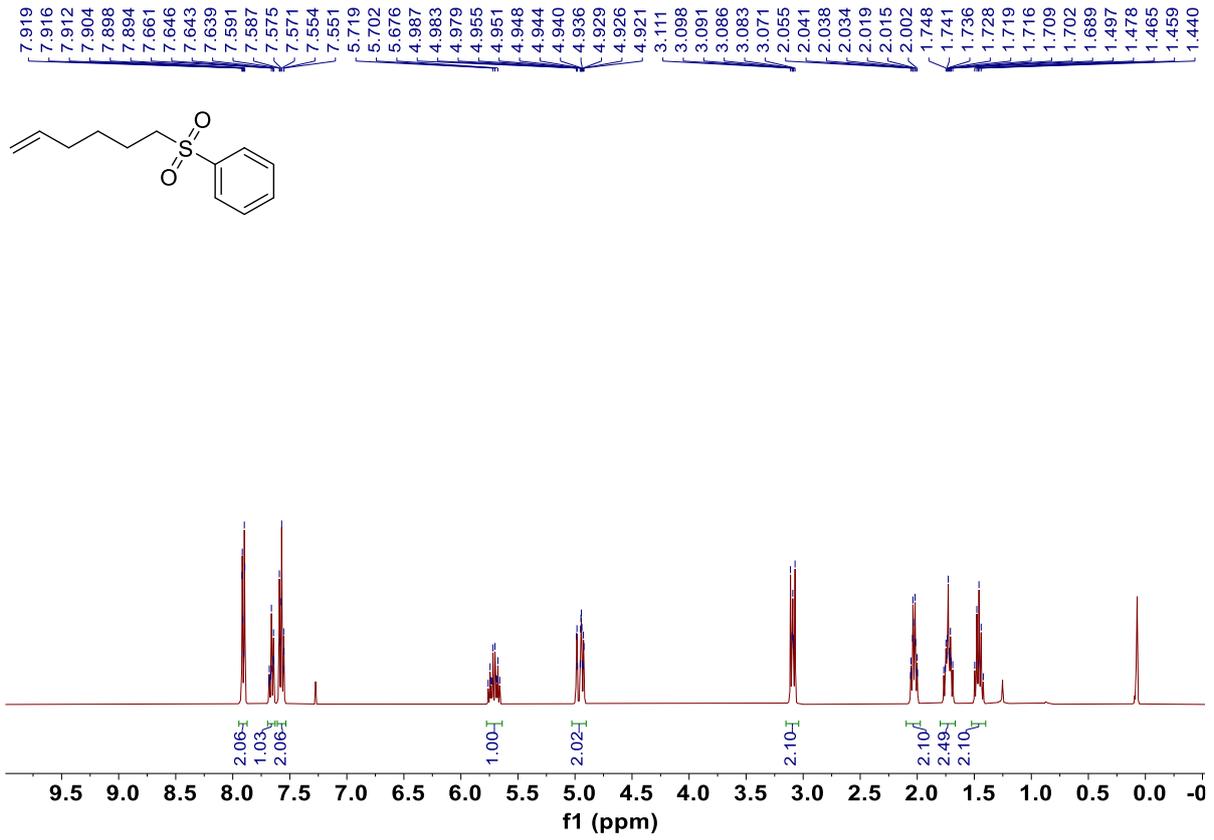


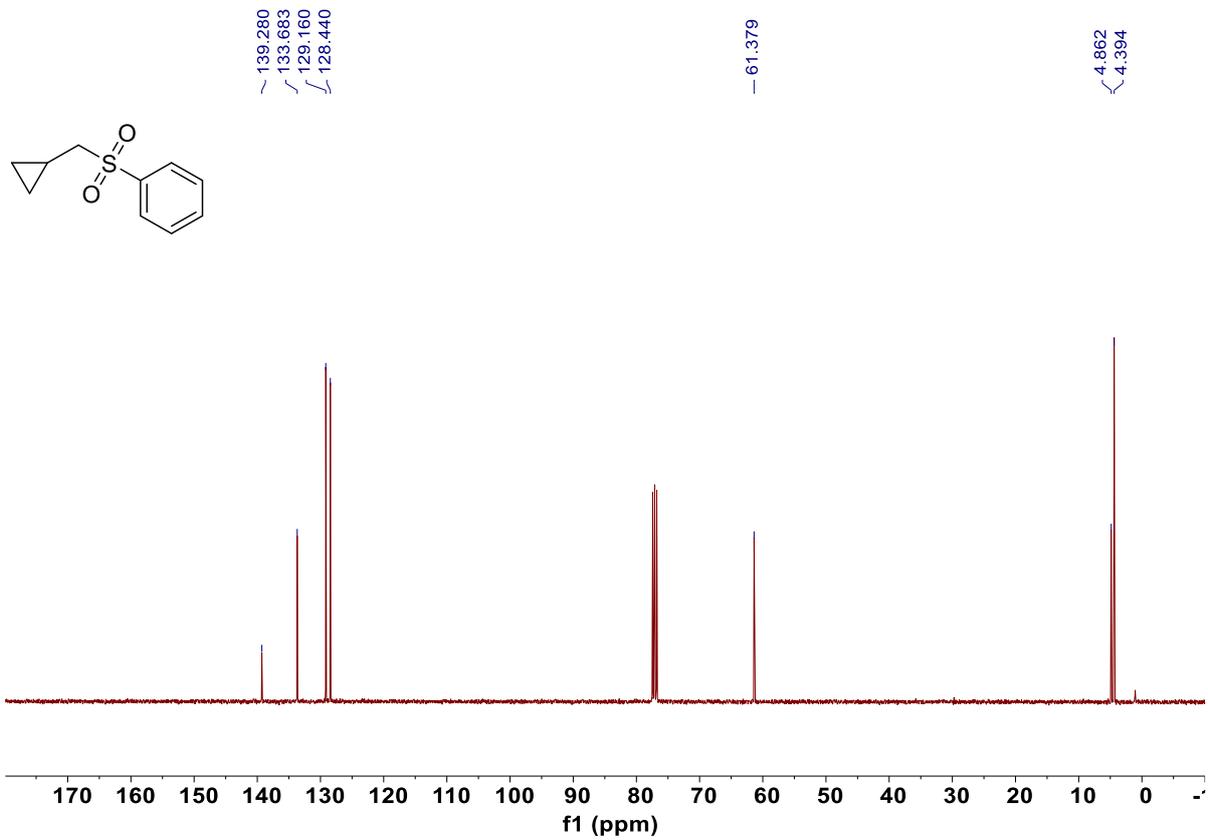
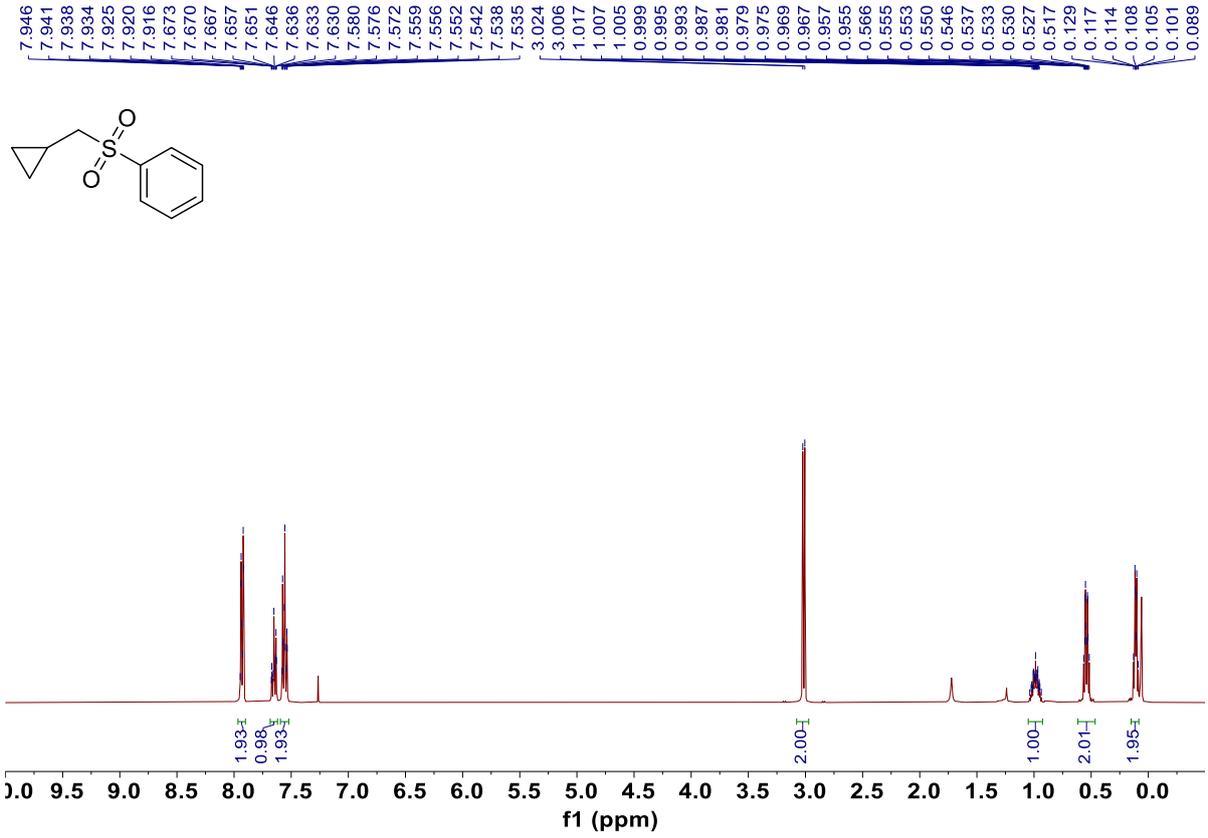


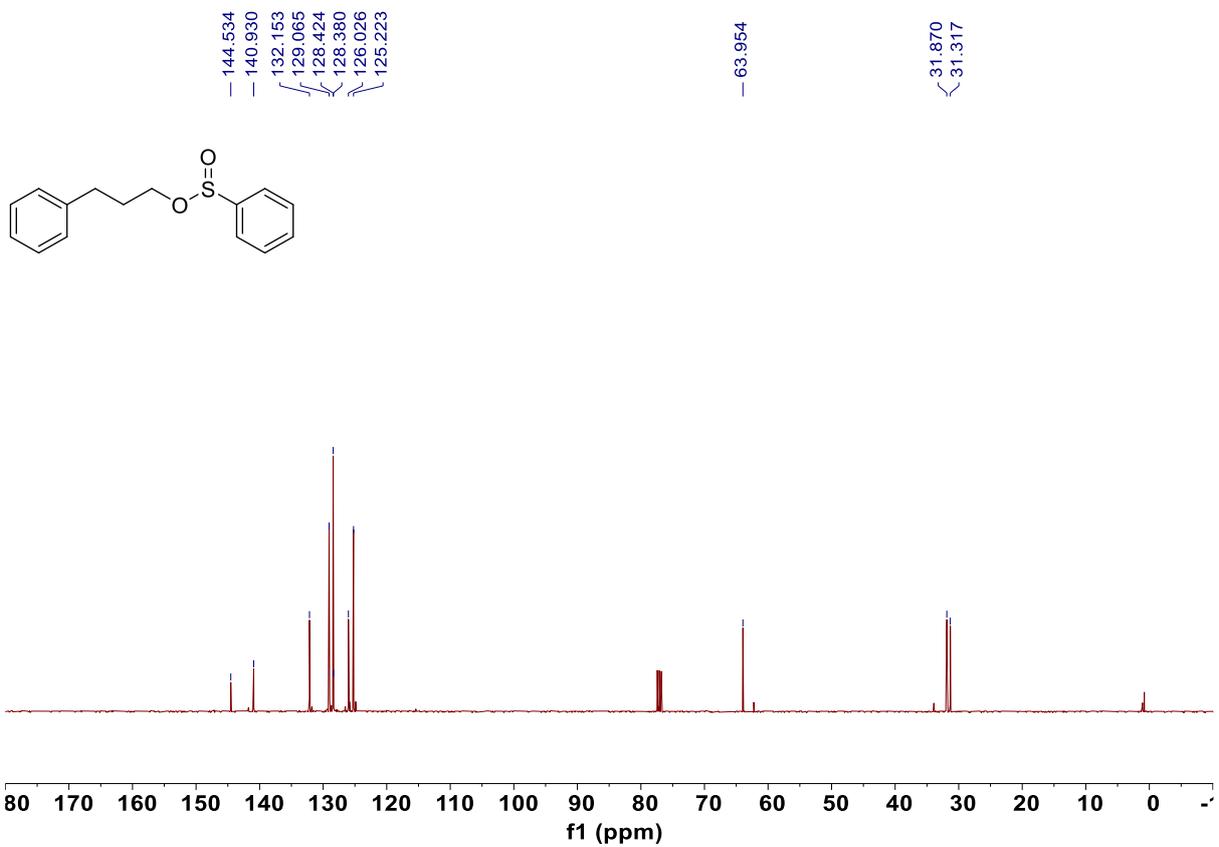
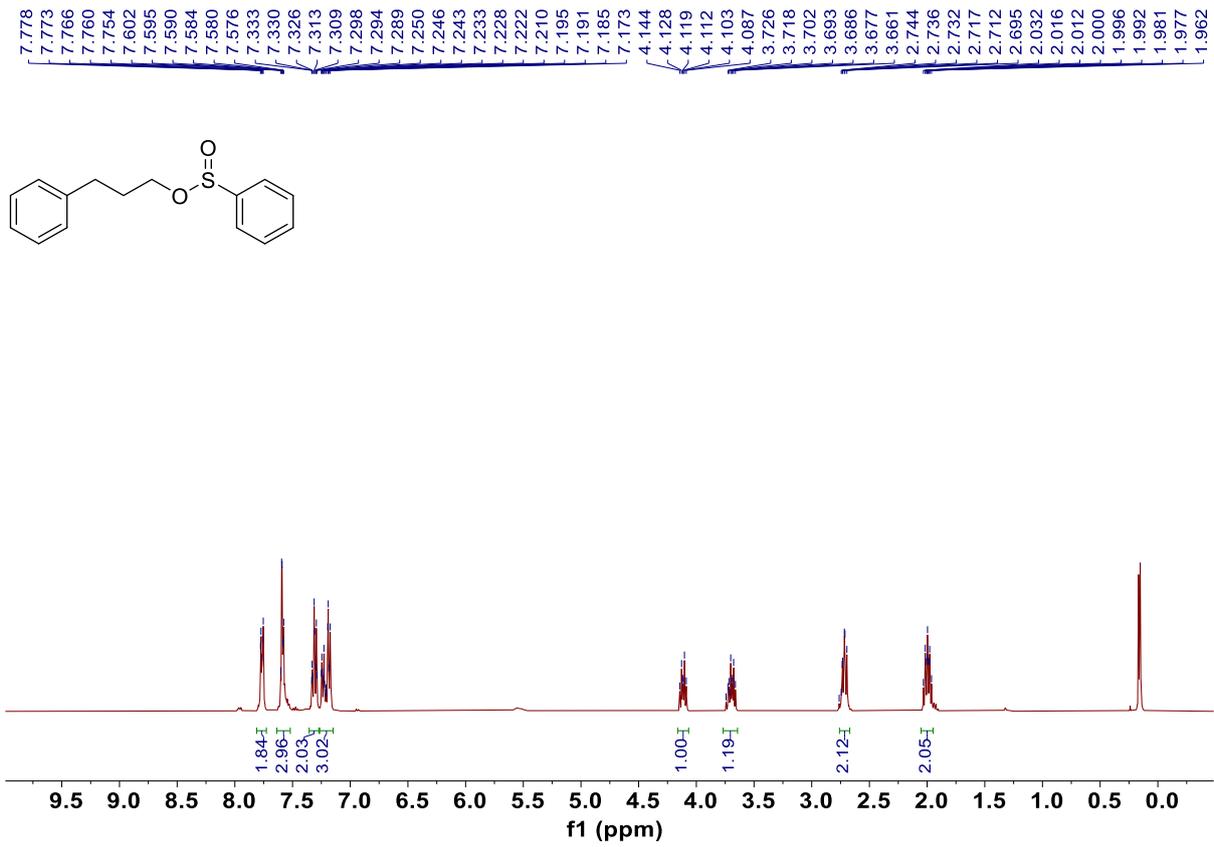


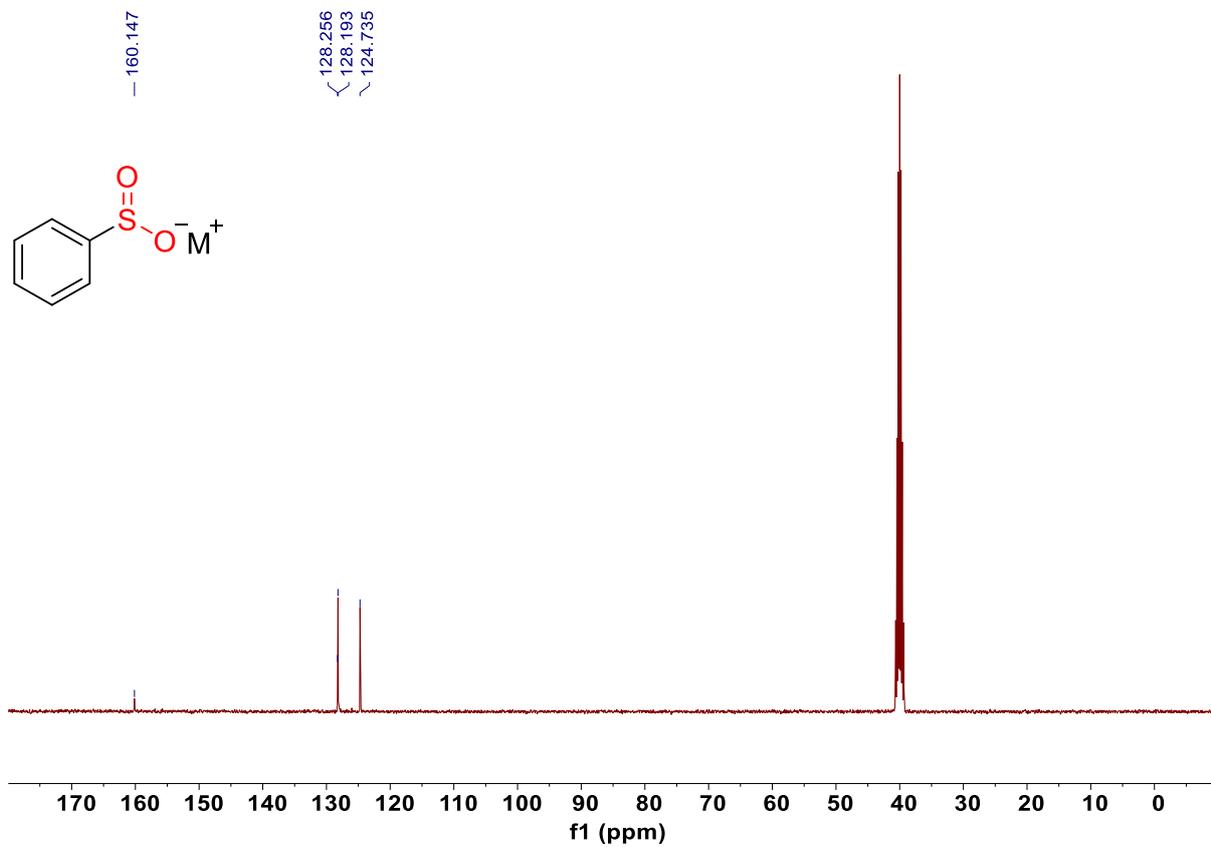
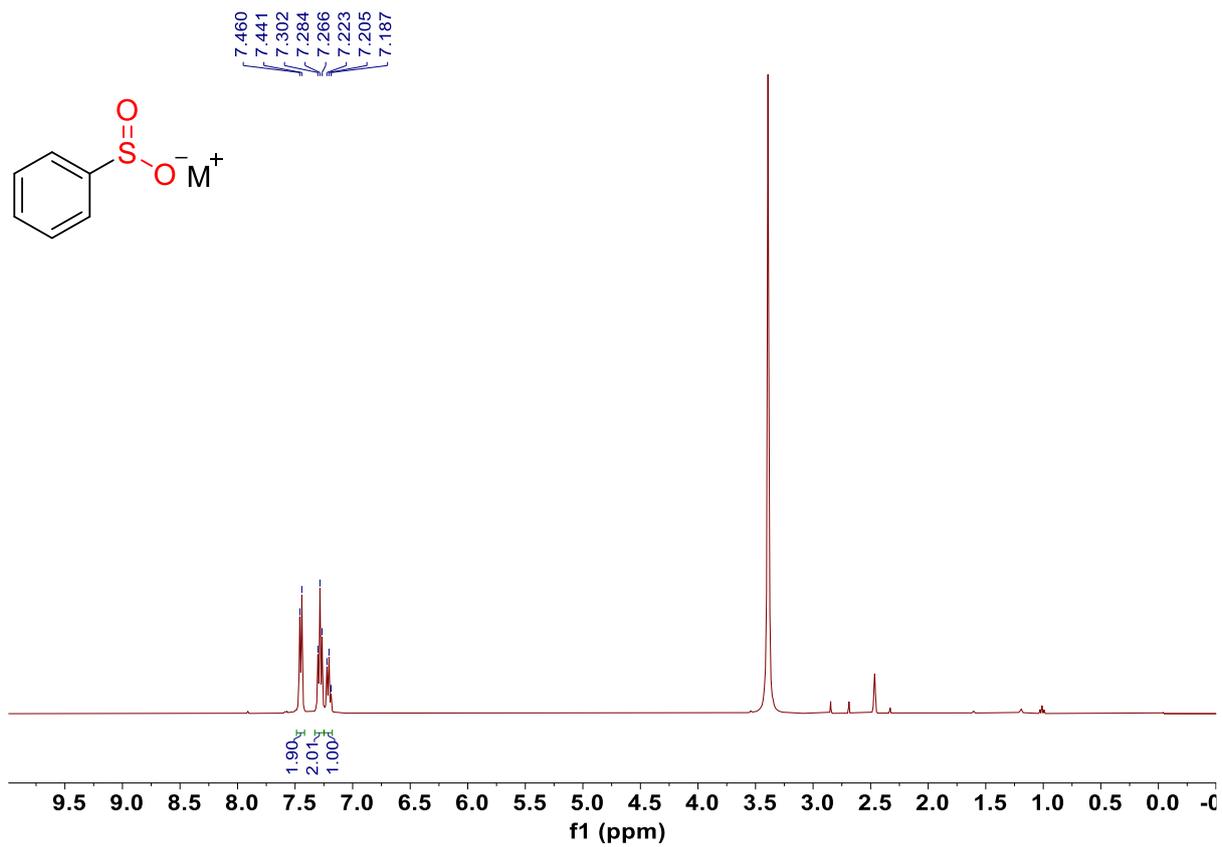












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