

# Electronic Supporting Information

## Trace Water in $\text{BF}_3 \cdot \text{OEt}_2$ System: A Facile Access to Sulfinyl Alkenylsulfone from Alkynes and Sodium Sulfinates

Shi-Wei Yu,<sup>a</sup> Zu-Jia Chen,<sup>a</sup> Zhao-Hua Chen,<sup>a</sup> Si-Hong Chen,<sup>a</sup> Kai Yang,<sup>b,\*</sup> Wen-Jin Xu,<sup>a</sup> and Zhao-Yang Wang<sup>a,\*</sup>

<sup>a</sup> School of Chemistry, South China Normal University; GDMPA Key Laboratory for Process Control and Quality Evaluation of Chiral Pharmaceuticals; Guangzhou Key Laboratory of Analytical Chemistry for Biomedicine; Key Laboratory of Theoretical Chemistry of Environment, Ministry of Education, Guangzhou, Guangdong 510006, P. R. China.

wangzy@sncu.edu.cn

<sup>b</sup> College of pharmacy, Gannan Medical University, Ganzhou 341000, P. R. China

kai\_yangyang@126.com

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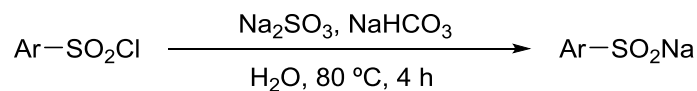
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## General Information

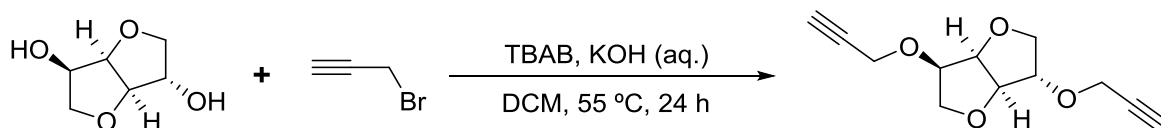
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were collected on an AVANCE NEO-600 in  $\text{CDCl}_3$  using tetramethylsilane (TMS) as an internal standard. Mass spectra were recorded on a Thermo Scientific ISQ gas chromatograph-mass spectrometer. High-resolution mass spectra (HR-MS) were obtained with a MAT 95XP mass spectrometer. Single-crystal X-ray analysis was obtained using Agilent Gemini E. Reactions were monitored using thin-layer chromatography (TLC) and visualized with UV light at 254 nm.

All reagents and solvents, including various alkyne compounds **1** (including **1u**), were purchased from commercial sources and used without further purification. Different sodium sulfonates **2** and isosorbide derived alkyne (**1t**) were synthesized according to the literature procedure.<sup>[1]</sup>

## Preparation of Sodium Sulfonates and Isosorbide Derived Alkyne



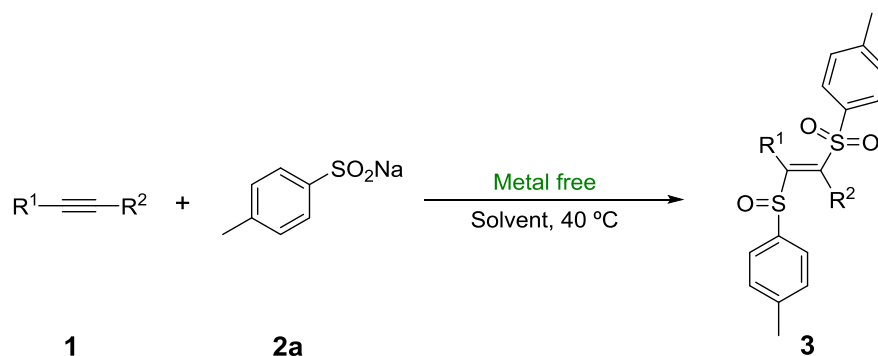
According to the literature,<sup>[1a, 1b]</sup> the mixture of arylsulfonyl chloride (10 mmol), sodium sulfite (20 mmol), sodium bicarbonate (20 mmol) in  $\text{H}_2\text{O}$  (15 mL) was stirred at 80  $^\circ\text{C}$  for 4 h. Water was removed by rotary evaporator. Then, the remaining solid was extracted and recrystallized by ethanol to get the required compound **2**.



According to the literature,<sup>[1c]</sup> isosorbide (1.00 g, 6.8 mmol) was dissolved in KOH solution (4.6 g, 82.0 mmol KOH in 16 mL water), and propargyl bromide (4.7 mL, 54.6 mmol

in 16 mL toluene) was dissolved in 20 mL of DCM. Then, their solution mixture with tetrabutylammonium bromide (220 mg, 0.7 mmol) was stirred at 55 °C for 24 h. After the completion of reaction, EtOAc (15 mL) was poured into the reaction mixture. The organic layers were extracted with the saturated NH<sub>4</sub>Cl (2 × 15 mL) and NaCl (2 × 15 mL). After the organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, the filtration and the evaporation of the solvents under reduced pressure gave the crude product, which was purified by column chromatography on silica gel to afford the required isosorbide derivative **1t**.

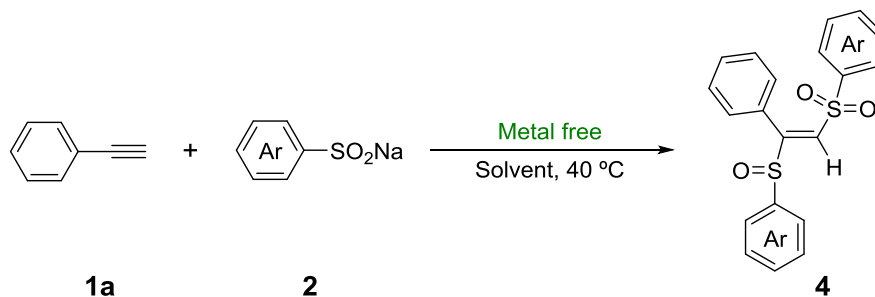
## Experimental Procedure for Compounds 3a-3u



**3a:** R<sup>1</sup> = C<sub>6</sub>H<sub>5</sub>, R<sup>2</sup> = H; **3b:** R<sup>1</sup> = 4-MeC<sub>6</sub>H<sub>4</sub>, R<sup>2</sup> = H; **3c:** R<sup>1</sup> = 4-EtC<sub>6</sub>H<sub>4</sub>, R<sup>2</sup> = H; **3d:** R<sup>1</sup> = 4-OMeC<sub>6</sub>H<sub>4</sub>, R<sup>2</sup> = H; **3e:** R<sup>1</sup> = 4-PhC<sub>6</sub>H<sub>4</sub>, R<sup>2</sup> = H; **3f:** R<sup>1</sup> = 4-FC<sub>6</sub>H<sub>4</sub>, R<sup>2</sup> = H; **3g:** R<sup>1</sup> = 4-ClC<sub>6</sub>H<sub>4</sub>, R<sup>2</sup> = H; **3h:** R<sup>1</sup> = 4-BrC<sub>6</sub>H<sub>4</sub>, R<sup>2</sup> = H; **3i:** R<sup>1</sup> = 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, R<sup>2</sup> = H; **3j:** R<sup>1</sup> = 4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, R<sup>2</sup> = H; **3k:** R<sup>1</sup> = 3-MeC<sub>6</sub>H<sub>4</sub>, R<sup>2</sup> = H; **3l:** R<sup>1</sup> = 3-OMeC<sub>6</sub>H<sub>4</sub>, R<sup>2</sup> = H; **3m:** R<sup>1</sup> = 3-ClC<sub>6</sub>H<sub>4</sub>, R<sup>2</sup> = H; **3n:** R<sup>1</sup> = 2-OMeC<sub>6</sub>H<sub>4</sub>, R<sup>2</sup> = H; **3o:** R<sup>1</sup> = 2-FC<sub>6</sub>H<sub>4</sub>, R<sup>2</sup> = H; **3p:** R<sup>1</sup> = 2-Naphthyl, R<sup>2</sup> = H; **3q:** R<sup>1</sup> = 2-Thienyl, R<sup>2</sup> = H; **3r:** R<sup>1</sup> = Bu, R<sup>2</sup> = H; **3s:** R<sup>1</sup> = C<sub>6</sub>H<sub>5</sub>, R<sup>2</sup> = CH<sub>3</sub>; **3t:** R<sup>1</sup> = Isosorbide, R<sup>2</sup> = H; **3u:** R<sup>1</sup> = Clodinafop-propargyl ester, R<sup>2</sup> = H;

The mixture of alkyne compound **1** (0.30 mmol, 1.0 equiv.), sodium 4-methylbenzenesulfinate **2a** (1.20 mmol, 4.0 equiv.) and BF<sub>3</sub> OEt<sub>2</sub> (0.84 mmol, 2.8 equiv.) in undried DCM (4 mL) under the sealed nitrogen atmosphere was stirred at 40 °C for 1 h. After the completion of reaction, EtOAc (15 mL) was poured into the reaction mixture. The organic layers were extracted with the saturated sodium chloride solution (3 × 15 mL). Then, the organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Finally, after the filtration and the evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel to afford the desired product **3**.

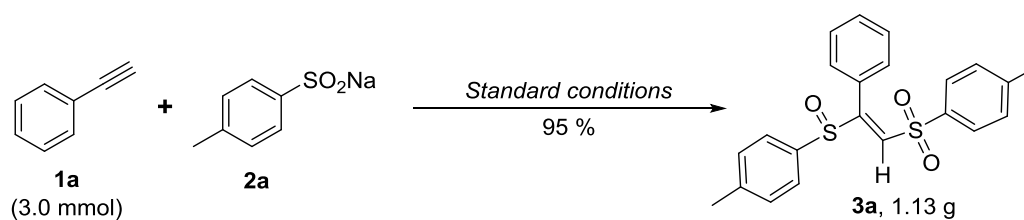
## Experimental Procedure for Compounds 4a-4l



**4a:** Ar = C<sub>6</sub>H<sub>5</sub>; **4b:** Ar = 4-OMeC<sub>6</sub>H<sub>4</sub>; **4c:** Ar = 4-PhC<sub>6</sub>H<sub>4</sub>; **4d:** Ar = 4-FC<sub>6</sub>H<sub>4</sub>; **4e:** Ar = 4-ClC<sub>6</sub>H<sub>4</sub>; **4f:** Ar = 4-BrC<sub>6</sub>H<sub>4</sub>; **4g:** Ar = 4-IC<sub>6</sub>H<sub>4</sub>; **4h:** Ar = 4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>; **4i:** Ar = 3-BrC<sub>6</sub>H<sub>4</sub>; **4j:** Ar = 3-MeC<sub>6</sub>H<sub>4</sub>; **4k:** Ar = 2-Naphthyl; **4l:** Ar = 2-Thienyl.

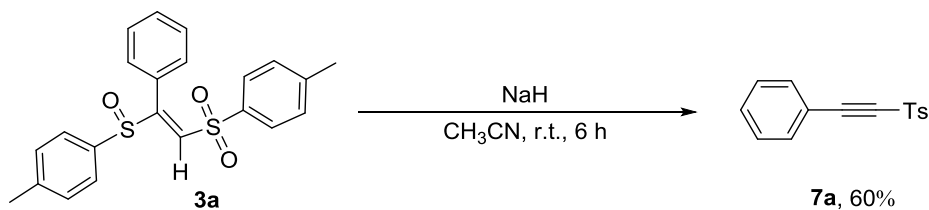
The mixture of phenylacetylene **1a** (0.30 mmol, 1.0 equiv.), sodium sulfinate compound **2** (1.20 mmol, 4.0 equiv.) and  $\text{BF}_3 \cdot \text{OEt}_2$  (0.84 mmol, 2.8 equiv.) in undried DCM (4 mL) under the sealed nitrogen atmosphere was stirred at 40 °C for 1 h. After the completion of reaction, EtOAc (15 mL) was poured into the reaction mixture. The organic layers were extracted with the saturated sodium chloride solution ( $3 \times 15$  mL). Then, the organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ . Finally, after the filtration and the evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel to afford the desired product **4**.

### Gram-scale Experimental Procedure for Compound **3a**

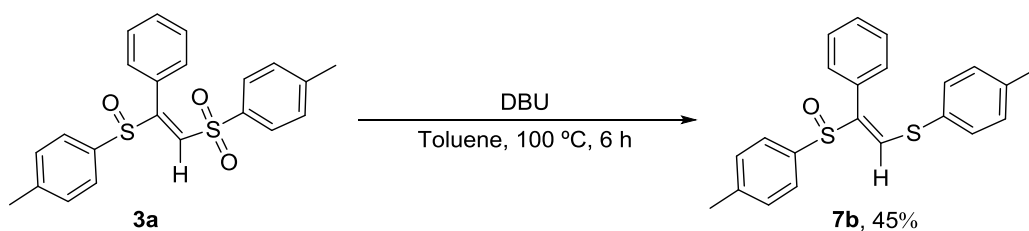


The mixture of phenylacetylene **1a** (3.0 mmol, 0.33 mL), sodium 4-methylbenzenesulfinate **2a** (12.0 mmol, 2.136 g) and  $\text{BF}_3 \cdot \text{OEt}_2$  (8.4 mmol, 2.2 mL) in undried DCM (10 mL) under the sealed nitrogen atmosphere was stirred at 40 °C for 1 h. After the completion of reaction, EtOAc (45 mL) was poured into the reaction mixture. The organic layers were extracted with the saturated sodium chloride solution ( $3 \times 20$  mL). Then, the organic extracts were dried over anhydrous  $\text{Na}_2\text{SO}_4$ . Finally, after the filtration and the evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel (Petroleum ether / Ethyl acetate = 5:1) to afford the desired product of **3a** (yield 95%, 1.13 g).

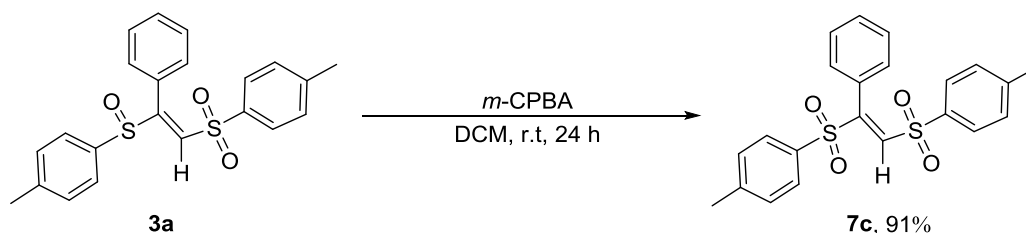
### Experimental Procedure for Compounds **7a-7c**



According to the literature,<sup>[2, 3]</sup> the mixture of compound **3a** (0.30 mmol, 1.0 equiv.), NaH (0.45 mmol, 1.5 equiv.) in anhydrous CH<sub>3</sub>CN (4 mL) was stirred at room temperature for 6 h. After the completion of reaction, EtOAc (15 mL) was poured into the reaction mixture. The organic layers were extracted with the saturated sodium chloride solution (3 × 15 mL). Then, the organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Finally, after the filtration and the evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel to afford the desired product **7a**.



According to the literature,<sup>[2, 3]</sup> the mixture of compound **3a** (0.30 mmol, 1.0 equiv.), DBU (3.0 mmol, 10.0 equiv.) in toluene (4 mL) was stirred at 100 °C for 6 h. After the completion of reaction, the saturated ammonium chloride solution (10 mL) was added to the reaction system to quench the reaction. Then, EtOAc (15 mL) was poured into the reaction mixture. The organic layers were extracted with the saturated sodium chloride solution (3 × 15 mL). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Finally, after the filtration and the evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel to afford the desired product **7b**.

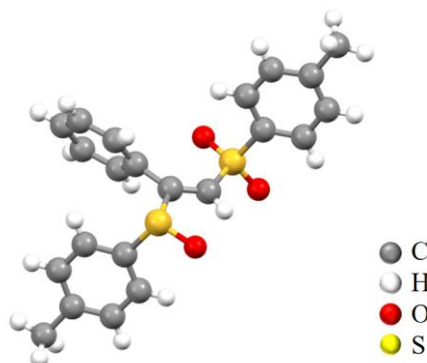


According to the literature,<sup>[2, 3]</sup> the mixture of compound 3a (0.30 mmol, 1.0 equiv.), m-CPBA (0.45 mmol, 1.5 equiv.) in DCM (4 mL) was stirred at room temperature for 24 h. After the completion of reaction, EtOAc (15 mL) was poured into the reaction mixture. The organic layers were extracted with the saturated sodium chloride solution (3 × 15 mL). Then, the organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Finally, after the filtration and the evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel to afford the desired product **7c**.

## Data of Single-crystal X-ray Analysis

**Table S1.** Crystal data and structure refinement for **3a**.

Compound	<b>3a</b>
Empirical formula	C <sub>22</sub> H <sub>20</sub> O <sub>3</sub> S <sub>2</sub>
Formula weight	396.50
Temperature (K)	297
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
Unit cell dimensions (Å, °)	$a = 10.264(3)$ , $b = 8.475(2)$ , $c = 22.934(6)$ $\alpha = 90$ , $\beta = 94.71(3)$ , $\gamma = 90$
Volume (Å <sup>3</sup> )	1988.2(9)
Z	4
Density (calculated) (g/cm <sup>3</sup> )	1.325
Absorption coefficient (mm <sup>-1</sup> )	0.287
F(000)	832.0
Theta range for data collection	3.513 to 29.569
Index ranges	$-11 \leq h \leq 13$ , $-10 \leq k \leq 11$ , $-29 \leq l \leq 28$
Reflections collected	10272
Independent reflections	4692 [R(int) = 0.0392, R(sigma) = 0.0675]
Completeness to theta = 29.569 °	84.1 %
Absorption correction	Multi-Scan
Max. and min. transmission	1.000 and 0.758
Refinement method	Least Squares minimisation
Data / restraints / parameters	4692 / 0 / 246
Goodness-of-fit on F <sup>2</sup>	1.062
Final R indices [I > 2sigma(I)]	R <sub>1</sub> = 0.0718, wR <sub>2</sub> = 0.1360
R indices (all data)	R <sub>1</sub> = 0.1266, wR <sub>2</sub> = 0.1606
Largest diff. peak and hole	0.27 and -0.35 e.Å <sup>-3</sup>

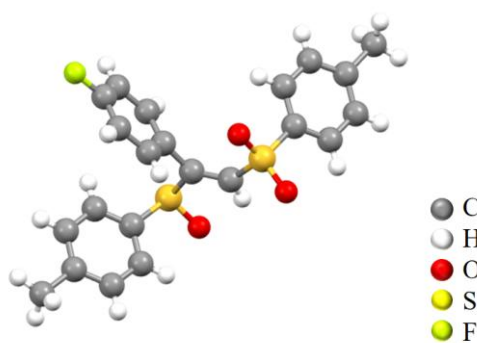


**Fig. S1.** The molecular structure of **3a**.

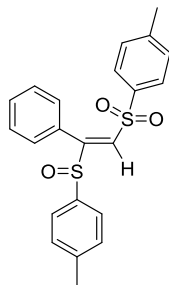


**Table S2.** Crystal data and structure refinement for **3f**.

Compound	<b>3f</b>
Empirical formula	C <sub>22</sub> H <sub>19</sub> FO <sub>3</sub> S <sub>2</sub>
Formula weight	414.49
Temperature (K)	297
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	P-1
Unit cell dimensions (Å, °)	$a = 8.4367(9)$ , $b = 10.2011(7)$ , $c = 24.4853(15)$ $\alpha = 101.895(6)$ , $\beta = 92.033(7)$ , $\gamma = 91.343(7)$
Volume (Å <sup>3</sup> )	2059.7(3)
Z	4
Density (calculated) (g/cm <sup>3</sup> )	1.337
Absorption coefficient (mm <sup>-1</sup> )	0.287
F(000)	864.0
Theta range for data collection	2.041 to 25.000
Index ranges	$-10 \leq h \leq 7$ , $-12 \leq k \leq 11$ , $-29 \leq l \leq 29$
Reflections collected	16406
Independent reflections	7242 [ $R_{\text{int}} = 0.0396$ , $R_{\text{sigma}} = 0.0663$ ]
Completeness to theta = 25.000 °	99.9 %
Absorption correction	Multi-Scan
Max. and min. transmission	1.000 and 0.873
Refinement method	Least Squares minimisation
Data / restraints / parameters	7242 / 0 / 509
Goodness-of-fit on F <sup>2</sup>	1.057
Final R indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0614$ , $wR_2 = 0.1140$
R indices (all data)	$R_1 = 0.0999$ , $wR_2 = 0.1330$
Largest diff. peak and hole	0.19 and -0.34 e.Å <sup>-3</sup>

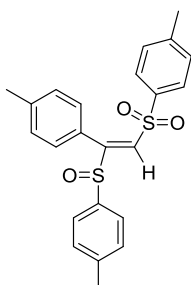
**Fig. S2.** The molecular structure of **3f**.

## Characterization Data for All Products 3a-3u, 4a-4l, 5a and 7a-7c



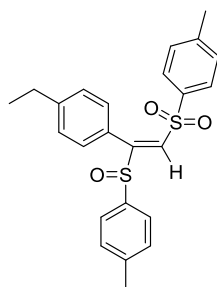
**(E)-1-Methyl-4-((2-phenyl-2-(*p*-tolylsulfinyl)vinyl)sulfonyl)benzene (3a).** The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product **3a** as a white solid (116.4 mg, 98%); m.p.: 166-168 °C (166-167 °C<sup>[2]</sup>); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>),  $\delta$ , ppm: 2.33 (*s*, 3H, CH<sub>3</sub>), 2.40 (*s*, 3H, CH<sub>3</sub>), 6.92 (*d*,  $J = 7.2$  Hz, 2H, ArH), 7.08-7.13 (*m*, 4H, ArH), 7.22 (*d*,  $J = 7.8$  Hz, 2H, ArH), 7.23-7.27 (*m*, 2H, ArH), 7.32 (*s*, 1H, =CH), 7.36 (*t*,  $J = 7.8$  Hz, 1H, ArH), 7.55 (*d*,  $J = 8.4$  Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>),  $\delta$ , ppm: 21.6, 21.8, 125.6, 128.0, 128.2, 182.3, 129.4, 129.6, 129.8, 130.0, 130.2, 137.0, 137.6, 142.9, 144.9, 160.7; ESI-HRMS,  $m/z$ : Calcd for C<sub>22</sub>H<sub>21</sub>O<sub>3</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 397.0927, Found: 397.0920.

The data are in agreement with those previously reported in the literature.<sup>[2]</sup>

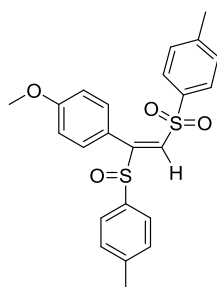


**(E)-1-Methyl-4-((2-(*p*-tolyl)-2-(*p*-tolylsulfinyl)vinyl)sulfonyl)benzene (3b).** The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product **3b** as a white solid (115.6 mg, 94%); m.p.: 165-166 °C (166-167 °C<sup>[2]</sup>); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>),  $\delta$ , ppm: 2.34 (*s*, 3H, CH<sub>3</sub>), 2.35 (*s*, 3H, CH<sub>3</sub>), 2.41 (*s*, 3H, CH<sub>3</sub>), 6.85 (*d*,  $J = 7.8$  Hz, 2H, ArH), 7.07 (*d*,  $J = 8.4$  Hz, 2H, ArH), 7.10-7.15 (*m*, 4H, ArH), 7.23 (*d*,  $J = 7.8$  Hz, 2H, ArH), 7.28 (*s*, 1H, =CH), 7.58 (*d*,  $J = 7.8$  Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>),  $\delta$ , ppm: 21.6, 21.7, 21.8, 125.3, 125.6, 128.1, 129.0, 129.1, 129.3, 129.9, 130.0, 137.2, 137.7, 140.6, 142.8, 144.9, 160.8.

The data are in agreement with those previously reported in the literature.<sup>[2]</sup>

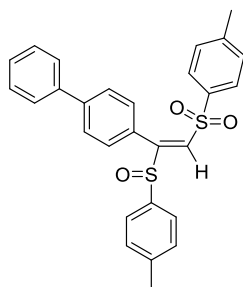


**(E)-1-Ethyl-4-(1-(*p*-tolylsulfinyl)-2-tosylvinyl)benzene (3c).** The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product **3c** as a white solid (117.1 mg, 92%); m.p.: 161-163 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>), δ, ppm: 1.23 (*t*, *J* = 7.2 Hz, 3H, CH<sub>3</sub>), 2.33 (*s*, 3H, CH<sub>3</sub>), 2.40 (*s*, 3H, CH<sub>3</sub>), 2.64 (*q*, *J* = 7.2 Hz, 2H, CH<sub>2</sub>), 6.85 (*d*, *J* = 8.4 Hz, 2H, ArH), 7.07 (*d*, *J* = 8.4 Hz, 2H, ArH), 7.09-7.12 (*m*, 4H, ArH), 7.20 (*d*, *J* = 9.0 Hz, 2H, ArH), 7.30 (*s*, 1H, =CH), 7.55 (*d*, *J* = 8.4 Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>), δ, ppm: 15.4, 21.6, 21.8, 28.8, 125.4, 125.5, 127.7, 128.1, 129.2, 129.4, 129.8, 129.9, 137.2, 137.7, 142.7, 144.8, 146.8, 160.9; ESI-HRMS, *m/z*: Calcd for C<sub>24</sub>H<sub>25</sub>O<sub>3</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 425.1240, Found: 425.1230.



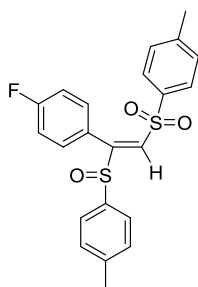
**(E)-1-Methoxy-4-(1-(*p*-tolylsulfinyl)-2-tosylvinyl)benzene (3d).** The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product **3d** as a white solid (121.4mg, 95%); m.p.: 149-151 °C (150-151 °C<sup>[2]</sup>); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>), δ, ppm: 2.34 (*s*, 3H, CH<sub>3</sub>), 2.41 (*s*, 3H, CH<sub>3</sub>), 3.82 (*s*, 3H, OCH<sub>3</sub>), 6.80 (*d*, *J* = 9.0 Hz, 2H, ArH), 6.94 (*d*, *J* = 9.0 Hz, 2H, ArH), 7.11-7.13 (*m*, 4H, ArH), 7.24 (*d*, *J* = 7.8 Hz, 2H, ArH), 7.27 (*s*, 1H, =CH), 7.58 (*d*, *J* = 8.4 Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>), δ, ppm: 21.6, 21.8, 55.4, 113.8, 120.4, 125.5, 128.0, 128.8, 129.9, 130.0, 131.0, 137.5, 137.8, 142.7, 144.9, 160.5, 161.3.

The data are in agreement with those previously reported in the literature.<sup>[2]</sup>



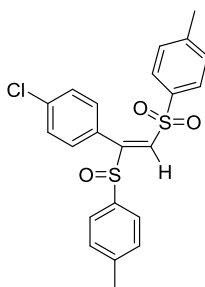
**(E)-4-(1-(*p*-tolylsulfinyl)-2-tosylvinyl)-1,1'-biphenyl (3e).** The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product **3e** as a white solid (120.4 mg, 85%); m.p.: 172-173 °C (162-163 °C<sup>[2]</sup>); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>),  $\delta$ , ppm: 2.34 (*s*, 3H, CH<sub>3</sub>), 2.40 (*s*, 3H, CH<sub>3</sub>), 7.01 (*d*, *J* = 8.4 Hz, 2H, ArH), 7.12-7.16 (*m*, 4H, ArH), 7.22 (*d*, *J* = 7.8 Hz, 2H, ArH), 7.36 (*s*, 1H, =CH), 7.38 (*t*, *J* = 7.8 Hz, 1H, ArH), 7.44-4.47 (*m*, 2H, ArH), 7.49 (*d*, *J* = 8.4 Hz, 2H, ArH), 7.58-7.60 (*m*, 4H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>),  $\delta$ , ppm: 21.6, 21.8, 125.6, 126.7, 127.2, 128.0, 128.1, 129.0, 129.6, 129.8, 130.0, 137.1, 137.6, 139.8, 142.8, 142.9, 145.0, 160.5.

The data are in agreement with those previously reported in the literature.<sup>[2]</sup>



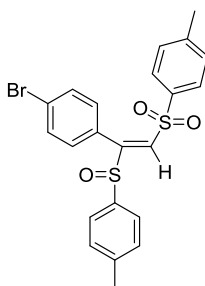
**(E)-1-Fluoro-4-(1-(*p*-tolylsulfinyl)-2-tosylvinyl)benzene (3f).** The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product **3f** as a white solid (110.6 mg, 89%); m.p.: 149-150 °C (148-149 °C<sup>[2]</sup>); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>),  $\delta$ , ppm: 2.35 (*s*, 1H, CH<sub>3</sub>), 2.42 (*s*, 1H, CH<sub>3</sub>), 6.91-6.98 (*m*, 4H, ArH), 7.11-7.15 (*m*, 4H, ArH), 7.26 (*d*, 2H, *J* = 7.2 Hz, ArH), 7.33 (*s*, 1H, =CH), 7.58 (*d*, *J* = 8.4 Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>),  $\delta$ , ppm: 21.6, 21.8, 115.6 (*d*, *J* = 22.5 Hz), 124.3 (*d*, *J* = 3.0 Hz), 125.6, 128.0, 129.9, 130.0, 130.1, 131.5 (*d*, *J* = 9.0 Hz), 136.9, 137.5, 143.1, 145.2, 159.7, 163.8 (*d*, *J* = 249.0 Hz); <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>),  $\delta$ , ppm: -109.3.

The data are in agreement with those previously reported in the literature.<sup>[2]</sup>



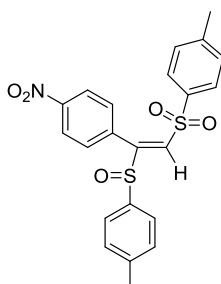
**(E)-1-Chloro-4-(1-(*p*-tolylsulfinyl)-2-tosylvinyl)benzene (3g).** The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product **3g** as a white solid (120.0 mg, 93%); m.p.: 184-185 °C (185-186 °C<sup>[2]</sup>); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>), δ, ppm: 2.35 (*s*, 3H, CH<sub>3</sub>), 2.43 (*s*, 3H, CH<sub>3</sub>), 6.86 (*d*, *J* = 8.4 Hz, 2H, ArH), 7.12-7.16 (*m*, 4H, ArH), 7.23-7.27 (*m*, 4H, ArH), 7.32 (*s*, 1H, =CH), 7.58 (*d*, *J* = 8.4 Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>), δ, ppm: 21.7, 21.8, 125.7, 126.8, 128.1, 128.6, 130.0, 130.2, 130.6, 136.6, 136.7, 137.4, 143.2, 145.3, 159.4.

The data are in agreement with those previously reported in the literature.<sup>[2]</sup>



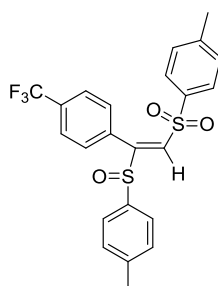
**(E)-1-Bromo-4-(1-(*p*-tolylsulfinyl)-2-tosylvinyl)benzene (3h).** The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product **3h** as a white solid (129.4 mg, 91%); m.p.: 188-190 °C (189-190 °C<sup>[2]</sup>); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>), δ, ppm: 2.36 (*s*, 3H, CH<sub>3</sub>), 2.43 (*s*, 3H, CH<sub>3</sub>), 6.79 (*d*, *J* = 9.0 Hz, 2H, ArH), 7.13-7.17 (*m*, 4H, ArH), 7.26 (*d*, *J* = 7.8 Hz, 2H, ArH), 7.33 (*s*, 1H, =CH), 7.40 (*d*, *J* = 8.4 Hz, 2H, ArH), 7.58 (*d*, *J* = 8.4 Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>), δ, ppm: 21.7, 21.8, 125.0, 125.7, 127.3, 128.1, 130.0, 130.1, 130.2, 130.8, 131.5, 136.7, 137.4, 143.3, 145.3, 159.4.

The data are in agreement with those previously reported in the literature.<sup>[2]</sup>



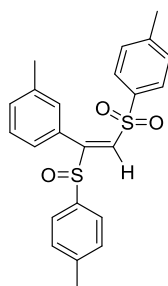
**(E)-1-Methyl-4-((2-(4-nitrophenyl)-2-(*p*-tolylsulfinyl)vinyl)sulfonyl)benzene (3i).** The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product **3i** as a white solid (115.1 mg, 87%); m.p.: 180-182 °C (180-181 °C<sup>[2]</sup>); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>),  $\delta$ , ppm: 2.37 (*s*, 3H, CH<sub>3</sub>), 2.45 (*s*, 3H, CH<sub>3</sub>), 7.09 (*d*, *J* = 9.0 Hz, 1H, ArH), 7.14-7.18 (*m*, 4H, ArH), 7.30 (*d*, *J* = 7.8 Hz, 2H, ArH), 7.37 (*s*, 1H, =CH), 7.62 (*d*, *J* = 8.4 Hz, 2H, ArH), 8.12 (*d*, *J* = 9.0 Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>),  $\delta$ , ppm: 21.7, 21.9, 123.3, 125.8, 128.1, 130.2, 130.3, 130.4, 131.2, 135.2, 136.1, 137.0, 143.8, 145.7, 148.6, 158.3.

The data are in agreement with those previously reported in the literature.<sup>[2]</sup>



**(E)-1-Methyl-4-((2-(*p*-tolylsulfinyl)-2-(4-trifluoromethylphenyl)vinyl)sulfonyl)benzene (3j).** The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product **3j** as a white solid (122.5 mg, 88%); m.p.: 172-174 °C (174-175 °C<sup>[2]</sup>); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>),  $\delta$ , ppm: 2.36 (*s*, 3H, CH<sub>3</sub>), 2.42 (*s*, 3H, CH<sub>3</sub>), 7.00 (*d*, *J* = 7.8 Hz, 2H, ArH), 7.12-7.17 (*m*, 4H, ArH), 7.25 (*d*, *J* = 8.4 Hz, 2H, ArH), 7.38 (*s*, 1H, =CH), 7.50 (*d*, *J* = 8.4 Hz, 2H, ArH), 7.56 (*d*, *J* = 8.4 Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>),  $\delta$ , ppm: 21.7, 21.8, 123.7 (*q*, *J* = 271.5 Hz), 125.1 (*q*, *J* = 3.0 Hz), 125.7, 128.1, 129.7, 130.0, 130.2, 130.9, 132.0 (*q*, *J* = 33.0 Hz), 132.2, 136.4, 137.1, 143.5, 145.4, 159.0; <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>),  $\delta$ , ppm: -62.9.

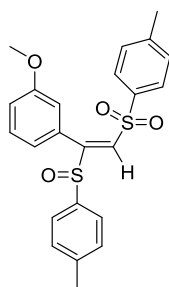
The data are in agreement with those previously reported in the literature.<sup>[2]</sup>



**(E)-1-Methyl-3-(1-(*p*-tolylsulfinyl)-2-tosylvinyl)benzene (3k).** The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product **3k** as a white solid (113.2 mg, 92%); m.p.: 161-162 °C (157-158 °C<sup>[2]</sup>);

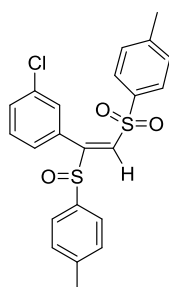
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ),  $\delta$ , ppm: 2.24 (*s*, 3H,  $\text{CH}_3$ ), 2.34 (*s*, 3H,  $\text{CH}_3$ ), 2.40 (*s*, 3H,  $\text{CH}_3$ ), 6.65 (*s*, 1H, ArH), 6.68 (*d*,  $J = 7.8$  Hz, 1H, ArH), 7.08-7.15 (*m*, 6H, ArH), 7.21 (*d*,  $J = 7.8$  Hz, 2H, ArH), 7.30 (*s*, 1H, =CH), 7.54 (*d*,  $J = 8.4$  Hz, 2H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ),  $\delta$ , ppm: 21.4, 21.6, 21.8, 125.6, 126.7, 128.0, 128.1, 129.5, 129.6, 129.8, 129.9, 130.9, 137.1, 137.6, 137.8, 142.8, 144.8, 160.9.

The data are in agreement with those previously reported in the literature.<sup>[2]</sup>



**(E)-1-Methoxy-3-(1-(*p*-tolylsulfinyl)-2-tosylvinyl)benzene (3l).** The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product **3l** as a white solid (115.0 mg, 90%); m.p.: 157-159 °C (153-154 °C<sup>[2]</sup>);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ),  $\delta$ , ppm: 2.34 (*s*, 3H,  $\text{CH}_3$ ), 2.40 (*s*, 3H,  $\text{CH}_3$ ), 3.66 (*s*, 3H,  $\text{OCH}_3$ ), 6.35-6.36 (*m*, 1H, ArH), 6.50 (*d*,  $J = 7.8$  Hz, 1H, ArH), 6.87-6.88 (*dd*,  $J = 2.4$  Hz,  $J = 8.4$  Hz, 1H, ArH), 7.11-7.13 (*m*, 4H, ArH), 7.14-7.17 (*m*, 1H, ArH), 7.22 (*d*,  $J = 7.8$  Hz, 2H, ArH), 7.32 (*s*, 1H, =CH), 7.56 (*d*,  $J = 7.8$  Hz, 2H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ),  $\delta$ , ppm: 21.6, 21.8, 55.4, 114.3, 116.4, 121.7, 125.7, 128.1, 129.3, 129.4, 129.7, 129.8, 130.0, 137.1, 137.6, 142.9, 144.9, 159.1, 160.5.

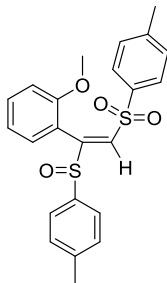
The data are in agreement with those previously reported in the literature.<sup>[2]</sup>



**(E)-1-Chloro-3-(1-(*p*-tolylsulfinyl)-2-tosylvinyl)benzene (3m).** The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product **3m** as a white solid (113.5 mg, 88%); m.p.: 184-186 °C (180-181 °C<sup>[3]</sup>);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ),  $\delta$ , ppm: 2.36 (*s*, 3H,  $\text{CH}_3$ ), 2.42 (*s*, 3H,  $\text{CH}_3$ ), 6.74-6.76 (*m*, 2H, ArH), 7.12-7.19 (*m*, 5H, ArH), 7.24 (*d*,  $J = 7.8$  Hz, 2H, ArH), 7.30-7.32 (*m*, 1H, ArH), 7.35 (*s*, 1H, =CH), 7.55 (*d*,  $J = 8.4$  Hz, 2H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ),  $\delta$ , ppm: 21.7, 21.8,

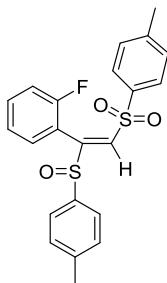
125.7, 127.9, 128.1, 128.8, 129.5, 129.9, 130.0, 130.1, 130.2, 130.7, 134.2, 136.5, 137.3, 143.3, 145.3, 159.1.

The data are in agreement with those previously reported in the literature.<sup>[3]</sup>



**(E)-1-Methoxy-2-(1-(p-tolylsulfinyl)-2-tosylvinyl)benzene (3n).** The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product **3n** as a white solid (109.9 mg, 86%); m.p.: 137-139 °C (138-139 °C<sup>[2]</sup>); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>), δ, ppm: 2.34 (s, 3H, CH<sub>3</sub>), 2.40 (s, 3H, CH<sub>3</sub>), 3.47 (s, 3H, OCH<sub>3</sub>), 6.47-6.61 (m, 1H, ArH), 6.68 (d, *J* = 8.4 Hz, 1H, ArH), 6.77-6.82 (m, 1H, ArH), 7.11-7.14 (m, 4H, ArH), 7.19 (d, *J* = 8.4 Hz, 2H, ArH), 7.28-7.31 (m, 1H, ArH), 7.39 (s, 1H, =CH), 7.53 (d, *J* = 8.4 Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>), δ, ppm: 21.6, 21.8, 55.2, 110.4, 117.0, 120.0, 125.8, 128.2, 129.5, 129.6, 129.9, 131.3, 131.8, 137.5, 142.6, 144.5, 156.5.

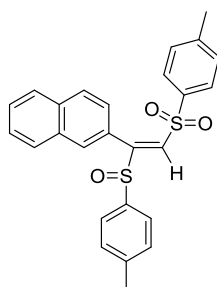
The data are in agreement with those previously reported in the literature.<sup>[2]</sup>



**(E)-1-Fluoro-2-(1-(p-tolylsulfinyl)-2-tosylvinyl)benzene (3o).** The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product **3o** as a white solid (99.3 mg, 80%); m.p.: 157-158 °C (156-157 °C<sup>[3]</sup>); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>), δ, ppm: 2.35 (s, 3H, CH<sub>3</sub>), 2.43 (s, 3H, CH<sub>3</sub>), 6.75-6.82 (m, 1H, ArH), 6.93-6.97 (m, 1H, ArH), 7.03-7.07 (m, 1H, ArH), 7.13-7.16 (m, 4H, ArH), 7.28 (d, *J* = 7.8 Hz, 2H, ArH), 7.33-7.37 (m, 1H, ArH), 7.41 (s, 1H, =CH), 7.64 (d, *J* = 7.8 Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>), δ, ppm: 21.7, 21.8, 115.6 (d, *J* = 21.0 Hz), 116.5 (d, *J* = 16.5 Hz), 123.8 (d, *J* = 3.0 Hz), 125.8, 128.2, 129.9, 130.0, 131.0 (d, *J* = 12.0 Hz), 131.1, 132.3 (d, *J* = 7.5 Hz), 136.6, 137.1, 143.2, 145.2, 155.0, 159.1 (d, *J* = 250.5 Hz); <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>), δ, ppm: -110.74.

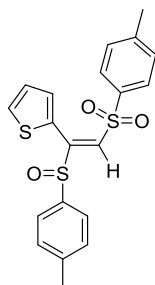


The data are in agreement with those previously reported in the literature.<sup>[3]</sup>



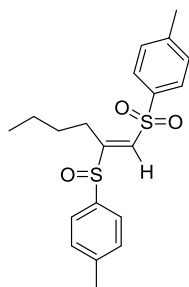
**(E)-2-(1-(p-Tolylsulfinyl)-2-tosylvinyl)naphthalene (3p).** The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product **3p** as a white solid (108.4 mg, 81%); m.p.: 172-174 °C (168-169 °C<sup>[2]</sup>); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>), δ, ppm: 2.31 (s, 3H, CH<sub>3</sub>), 2.33 (s, 3H, CH<sub>3</sub>), 6.93-6.95 (dd, *J* = 8.4 Hz, 1.8 Hz, 1H, ArH), 7.07 (d, *J* = 7.8 Hz, 2H, ArH), 7.10-7.12 (m, 4H, ArH), 7.40-7.43 (m, 2H, =CH, ArH), 7.50-7.56 (m, 4H, ArH), 7.67 (d, *J* = 8.4 Hz, 1H, ArH), 7.73 (d, *J* = 7.8 Hz, 1H, ArH), 7.81 (d, *J* = 7.8 Hz, 1H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>), δ, ppm: 21.6, 21.7, 125.6, 125.9, 126.6, 126.9, 127.6, 127.92, 127.93, 128.1, 128.5, 129.0, 129.7, 129.9, 130.0, 132.3, 133.7, 137.0, 137.5, 142.9, 145.0, 160.6.

The data are in agreement with those previously reported in the literature.<sup>[2]</sup>



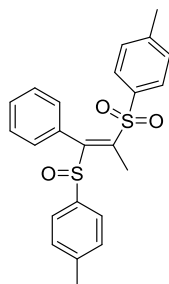
**(E)-2-(1-(p-Tolylsulfinyl)-2-tosylvinyl)thiophene (3q).** The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product **3q** as a white solid (69.9 mg, 58%); m.p.: 156-158 °C (156-157 °C<sup>[2]</sup>); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>), δ, ppm: 2.34 (s, 3H, CH<sub>3</sub>), 2.42 (s, 3H, CH<sub>3</sub>), 7.02-7.04 (m, 1H, ArH), 7.14-7.15 (m, 3H, ArH), 7.21 (d, *J* = 7.8 Hz, 2H, ArH), 7.26 (d, *J* = 7.8 Hz, 2H, ArH), 7.33 (s, 1H, =CH), 7.48 (d, *J* = 5.4 Hz, 1H, ArH), 7.65 (d, *J* = 8.4 Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>), δ, ppm: 21.6, 21.8, 125.5, 127.6, 127.8, 128.0, 129.6, 129.9, 130.1, 130.7, 132.2, 137.4, 137.9, 143.0, 145.1, 154.0.

The data are in agreement with those previously reported in the literature.<sup>[2]</sup>



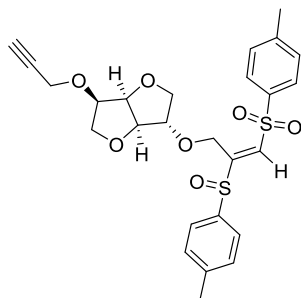
**(E)-1-Methyl-4-((2-(*p*-tolylsulfinyl)hex-1-en-1-yl)sulfonyl)benzene (3r).** The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product **3r** as a white solid (57.5 mg, 51%); m.p.: 151-153 °C (152-153 °C<sup>[2]</sup>); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>),  $\delta$ , ppm: 0.85 (*t*,  $J$  = 7.2 Hz, 3H, CH<sub>3</sub>), 1.25-1.33 (*m*, 2H, CH<sub>2</sub>), 1.49-1.57 (*m*, 2H, CH<sub>2</sub>), 1.97-2.02 (*m*, 1H, CH<sub>2a</sub>), 2.42 (*s*, 3H, CH<sub>3</sub>), 2.47 (*s*, 3H, CH<sub>3</sub>), 2.96-3.01 (*m*, 1H, CH<sub>2b</sub>), 7.13 (*s*, 1H, =CH), 7.30 (*d*,  $J$  = 8.4 Hz, 2H, ArH), 7.37 (*d*,  $J$  = 7.8 Hz, 2H, ArH), 7.47 (*d*,  $J$  = 7.8 Hz, 2H, ArH), 7.82 (*d*,  $J$  = 8.4 Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>),  $\delta$ , ppm: 13.7, 21.7, 21.8, 22.9, 26.7, 31.5, 126.7, 127.7, 127.8, 130.2, 130.5, 137.9, 138.0, 143.7, 145.2, 162.3.

The data are in agreement with those previously reported in the literature.<sup>[2]</sup>

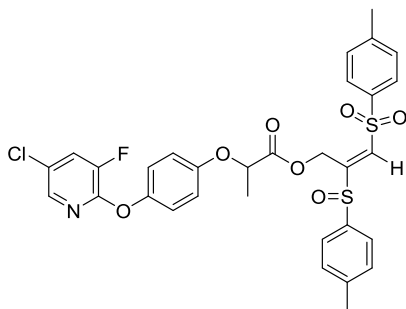


**(E)-1-Methyl-4-((1-phenyl-1-(*p*-tolylsulfinyl)prop-1-en-2-yl)sulfonyl)benzene (3s).** The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product **3s** as a white solid (105.8 mg, 86 %); m.p.: 143-145 °C (143-144 °C<sup>[3]</sup>); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>),  $\delta$ , ppm: 2.37 (*s*, 3H, CH<sub>3</sub>), 2.38 (*s*, 3H, CH<sub>3</sub>), 2.72 (*s*, 3H, CH<sub>3</sub>), 6.21 (*d*,  $J$  = 6.0 Hz, 1H, ArH), 6.76 (*d*,  $J$  = 6.0 Hz, 1H, ArH), 6.99-7.02 (*m*, 3H, ArH), 7.10 (*d*,  $J$  = 7.8 Hz, 2H, ArH), 7.15 (*d*,  $J$  = 8.4 Hz, 2H, ArH), 7.24-7.28 (*m*, 4H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>),  $\delta$ , ppm: 15.8, 21.6, 21.7, 124.4, 126.6, 126.8, 128.1, 128.9, 129.6, 129.8, 131.0, 136.6, 137.9, 142.1, 144.2, 144.6, 153.4.

The data are in agreement with those previously reported in the literature.<sup>[3]</sup>



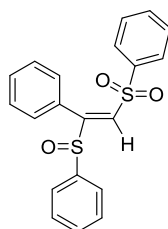
**(3R,3aR,6S,6aR)-3-(Prop-2-yn-1-yloxy)-6-((E)-2-(p-tolylsulfinyl)-3-tosylallyl)oxy-hexahydrofuro[3,2-b]furan (3t).** The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product **3t** as a white waxy solid (94.4 mg, 61 %);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ),  $\delta$ , ppm: 2.40-2.49 (*m*, 6H,  $\text{CH}_3$ ), 3.48-4.04 (*m*, 6H,  $\equiv\text{CH}$ , CH,  $\text{CH}_2$ ), 4.10-4.36 (*m*, 4H,  $\text{CH}_2$ ), 4.50-4.69 (*m*, 2H, CH), 5.22-5.40 (*m*, 1H, CH), 7.17-7.38 (*m*, 5H,  $=\text{CH}$ , ArH), 7.47-7.55 (*m*, 2H, ArH), 7.79-7.83 (*m*, 2H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ),  $\delta$ , ppm: 21.7, 21.9, 56.9, 57.8, 57.9, 63.0, 63.1, 63.7, 64.7, 69.9, 70.3, 70.4, 72.7, 73.2, 73.3, 75.2, 75.3, 75.4, 78.6, 78.9, 79.2, 79.3, 80.26, 80.28, 80.5, 80.58, 80.60, 83.11, 83.12, 84.6, 84.8, 85.3, 85.6, 86.3, 86.33, 126.3, 126.4, 126.44, 126.5, 127.8, 127.93, 127.95, 128.0, 128.3, 128.9, 129.2, 130.3, 130.33, 130.34, 130.36, 130.4, 130.44, 130.5, 137.0, 137.1, 137.14, 137.22, 137.9, 138.0, 138.4, 143.1, 143.2, 143.4, 143.5, 145.5, 145.6, 145.65, 145.7, 158.8, 158.9, 159.5; ESI-HRMS,  $m/z$ : Calcd for  $\text{C}_{26}\text{H}_{29}\text{O}_7\text{S}_2$   $[\text{M}+\text{H}]^+$ : 517.1349, Found: 517.1346.



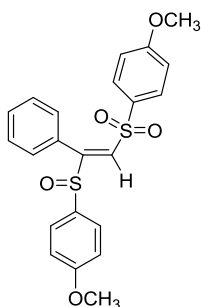
**(E)-2-(p-Tolylsulfinyl)-3-tosylallyl-2-(4-(5-chloro-3-fluoropyridin-2-yl)oxyphenoxy)propanoate (3u).** The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 4:1) to provide the product **3u** as a white waxy solid (108.0 mg, 56 %, dr = 1:1), (76 %, dr = 1:1<sup>[2]</sup>);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ),  $\delta$ , ppm: 1.58 (*d*,  $J$  = 6.6 Hz, 3H,  $\text{CH}_3$ ), 1.63 (*d*,  $J$  = 7.2 Hz, 3H,  $\text{CH}_3$ ), 2.40 (*s*, 3H,  $\text{CH}_3$ ), 2.41 (*s*, 3H,  $\text{CH}_3$ ), 2.47 (*s*, 3H,  $\text{CH}_3$ ), 2.48 (*s*, 3H,  $\text{CH}_3$ ), 4.49 (*d*,  $J$  = 14.4 Hz, 1H, CH), 4.59 (*d*,  $J$  = 14.4 Hz, 1H, CH), 4.72-4.76 (*m*, 2H, CH), 5.80-5.83 (*m*, 1H, CH), 5.86-5.89 (*m*, 1H, CH), 6.90 (*d*,  $J$  = 7.2 Hz, 2H, ArH), 6.91 (*d*,  $J$  = 7.2 Hz, 2H, ArH), 7.08-7.10 (*m*, 4H, ArH), 7.25 (*d*,  $J$  = 9.6 Hz, 2H, ArH), 7.27 (*s*, 1H,  $=\text{CH}$ ), 7.28 (*s*, 1H,  $=\text{CH}$ ), 7.30 (*d*,  $J$  = 8.4 Hz, 2H, ArH), 7.39 (*d*,  $J$  = 8.4 Hz, 4H,

ArH), 7.44-7.50 (*m*, 6H, ArH), 7.80-7.87 (*m*, 6H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ),  $\delta$ , ppm: 18.6, 18.7, 21.7, 21.9, 57.5, 57.8, 72.9, 73.1, 116.2, 116.3, 122.6, 122.7, 125.04 (*d*,  $J = 15.0$  Hz), 125.05 (*d*,  $J = 4.5$  Hz), 125.16 (*d*,  $J = 18.0$  Hz), 125.17 (*d*,  $J = 4.5$  Hz), 126.4, 126.5, 128.16, 128.19, 130.4, 130.6, 130.7, 130.8, 136.69, 136.72, 137.0, 137.1, 140.26 (*d*,  $J = 6.0$  Hz), 140.27 (*d*,  $J = 6.0$  Hz), 144.0, 145.83, 145.84, 147.0 (*d*,  $J = 264.0$  Hz), 147.1 (*d*,  $J = 265.5$  Hz), 147.5, 151.3 (*d*,  $J = 10.5$  Hz), 151.4 (*d*,  $J = 12.0$  Hz), 154.7, 154.8, 155.6, 155.7, 171.2; ESI-HRMS,  $m/z$ : Calcd for  $\text{C}_{31}\text{H}_{28}\text{ClFNO}_7\text{S}_2$   $[\text{M}+\text{H}]^+$ : 644.0974, Found: 644.0966.

The data are in agreement with those previously reported in the literature.<sup>[2]</sup>

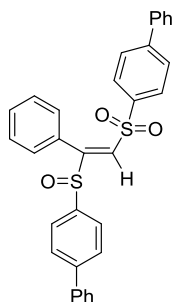


**(E)-((2-Phenyl-2-phenylsulfinylvinyl)sulfonyl)benzene (4a).** The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 5:1) to provide the product **4a** as a white solid (102.7 mg, 93%); m.p.: 183-184 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ),  $\delta$ , ppm: 6.90 (*d*,  $J = 7.2$  Hz, 2H, ArH), 7.20 (*d*,  $J = 7.2$  Hz, 2H, ArH), 7.24-7.27 (*m*, 2H, ArH), 7.31-7.33 (*m*, 2H, ArH), 7.35 (*s*, 1H, =CH), 7.37 (*t*,  $J = 7.8$  Hz, 1H, ArH), 7.41-7.45 (*m*, 3H, ArH), 7.58 (*t*,  $J = 7.2$  Hz, 1H, ArH), 7.68 (*d*,  $J = 7.2$  Hz, 2H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ),  $\delta$ , ppm: 125.5, 128.0, 128.1, 128.3, 129.2, 129.3, 129.4, 129.5, 130.4, 132.2, 133.9, 140.3, 140.5, 161.3; ESI-HRMS,  $m/z$ : Calcd for  $\text{C}_{20}\text{H}_{17}\text{O}_3\text{S}_2$   $[\text{M}+\text{H}]^+$ : 369.0614, Found: 369.0609.

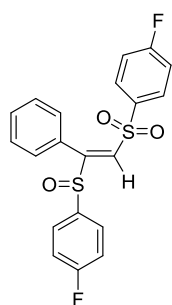


**(E)-1-Methoxy-4-(2-(4-methoxyphenylsulfinyl)-2-phenylvinyl)sulfonylbenzene (4b).** The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 5:1) to provide the product **4b** as a white solid (120.7 mg, 94%); m.p.: 154-156 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ),  $\delta$ , ppm: 3.77 (*s*, 1H,  $\text{OCH}_3$ ), 3.83 (*s*, 1H,  $\text{OCH}_3$ ), 6.80 (*d*,  $J = 9.0$  Hz, 2H, ArH), 6.86 (*d*,  $J = 9.0$  Hz, 2H, ArH), 6.89 (*d*,  $J = 8.4$  Hz, 2H, ArH), 7.16 (*d*,  $J = 9.0$

Hz, 2H, ArH), 7.21-7.25 (*m*, 2H, ArH), 7.31-7.34 (*m*, 2H, =CH, ArH), 7.57 (*d*, *J* = 8.4 Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>), δ, ppm: 55.6, 55.8, 114.4, 114.7, 127.7, 128.1, 128.4, 129.3, 129.9, 130.0, 130.2, 130.9, 132.0, 160.3, 162.7, 163.9; ESI-HRMS, *m/z*: Calcd for C<sub>22</sub>H<sub>21</sub>O<sub>5</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 429.0825, Found: 429.0820.

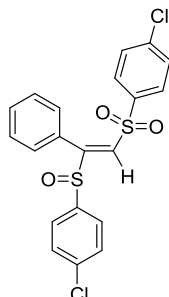


**(E)-4-(2-((1,1'-biphenyl)-4-ylsulfinyl)-2-phenylvinyl)sulfonyl-1,1'-biphenyl (4c).** The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 5:1) to provide the product **4c** as a white solid (109.2 mg, 70%); m.p.: 176-178 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>), δ, ppm: 6.97 (*d*, *J* = 7.2 Hz, 2H, ArH), 7.27-7.29 (*m*, 3H, ArH), 7.37-7.40 (*m*, 2H, ArH), 7.43 (*s*, 1H, =CH), 7.44-7.46 (*m*, 3H, ArH), 7.47-7.50 (*m*, 3H, ArH), 7.53-7.55 (*m*, 4H, ArH), 7.56-7.58 (*m*, 2H, ArH), 7.62 (*d*, *J* = 8.4 Hz, 2H, ArH), 7.73 (*d*, *J* = 8.4 Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>), δ, ppm: 125.9, 127.3, 127.5, 127.8, 127.9, 128.2, 128.3, 128.5, 128.6, 128.8, 129.1, 129.2, 129.4, 129.8, 130.4, 138.8, 138.9, 139.3, 139.4, 145.1, 146.9, 161.0; ESI-HRMS, *m/z*: Calcd for C<sub>32</sub>H<sub>23</sub>O<sub>3</sub>S<sub>2</sub> [M-H]<sup>-</sup>: 519.1094, Found: 519.1093.



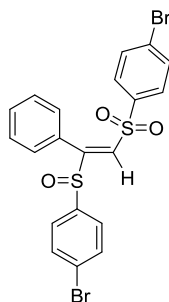
**(E)-1-Fluoro-4-((2-(4-fluorophenylsulfinyl)-2-phenylvinyl)sulfonyl)benzene (4d).** The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 5:1) to provide the product **4d** as a white solid (71.5 mg, 59 %); m.p.: 144-146 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>), δ, ppm: 6.90 (*d*, *J* = 7.2 Hz, 2H, ArH), 7.00-7.04 (*m*, 2H, ArH), 7.07-7.11 (*m*, 2H, ArH), 7.19-7.21 (*m*, 2H, ArH), 7.27-7.30 (*m*, 2H, ArH), 7.34 (*s*, 1H, =CH), 7.39 (*t*, *J* = 7.8 Hz, 1H, ArH), 7.65-7.67 (*m*, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>), δ, ppm: 116.5 (*d*, *J* = 22.5 Hz), 116.7 (*d*, *J* = 22.5 Hz), 127.8 (*d*, *J* = 9.0 Hz), 127.9, 128.5, 129.2,

129.7, 130.6, 131.0 (*d*, *J* = 9.0 Hz), 135.6 (*d*, *J* = 3.0 Hz), 136.3 (*d*, *J* = 3.0 Hz), 161.3, 164.9 (*d*, *J* = 253.0 Hz), 166.0 (*d*, *J* = 255.0 Hz); <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>), δ, ppm: -102.8, -105.9; ESI-HRMS, *m/z*: Calcd for C<sub>20</sub>H<sub>15</sub>F<sub>2</sub>O<sub>3</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 405.0425, Found: 405.0419.

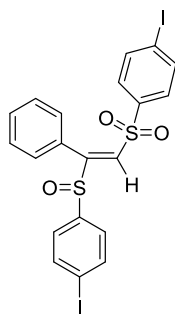


**(E)-1-Chloro-4-((2-(4-chlorophenylsulfinyl)-2-phenylvinyl)sulfonyl)benzene (4e).**

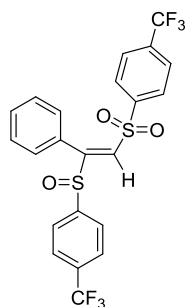
The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 5:1) to provide the product **4e** as a white solid (117.7 mg, 90%); m.p.: 187-189 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>), δ, ppm: 6.91 (*d*, *J* = 7.2 Hz, 2H, ArH), 7.10 (*d*, *J* = 8.4 Hz, 2H, ArH), 7.29-7.31 (*m*, 4H, ArH), 7.32 (*s*, 1H, =CH), 7.38-7.43 (*m*, 3H, ArH), 7.57 (*d*, *J* = 9.0 Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>), δ, ppm: 126.6, 127.7, 128.5, 129.3, 129.4, 129.5, 129.6, 130.7, 138.5, 138.6, 138.7, 140.8, 161.4; ESI-HRMS, *m/z*: Calcd for C<sub>20</sub>H<sub>15</sub>Cl<sub>2</sub>O<sub>3</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 436.9834, Found: 436.9826.



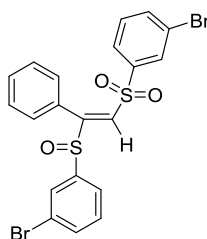
**(E)-1-Bromo-4-(2-(4-bromophenylsulfinyl)-2-phenylvinyl)sulfonylbenzene (4f).** The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 5:1) to provide the product **4f** as a yellow solid (136.7 mg, 87%); m.p.: 190-192 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>), δ, ppm: 6.91 (*d*, *J* = 7.2 Hz, 2H, ArH), 7.03 (*d*, *J* = 9.0 Hz, 2H, ArH), 7.29-7.32 (*m*, 3H, =CH, ArH), 7.42 (*t*, *J* = 7.8 Hz, 1H, ArH), 7.46 (*d*, *J* = 8.4 Hz, 2H, ArH), 7.49 (*d*, *J* = 8.4 Hz, 2H, ArH), 7.56 (*d*, *J* = 9.0 Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>), δ, ppm: 126.7, 127.0, 127.7, 128.6, 129.3, 129.4, 129.5, 129.6, 130.8, 132.5, 132.6, 139.2, 139.3, 161.3; ESI-HRMS, *m/z*: Calcd for C<sub>20</sub>H<sub>15</sub>Br<sub>2</sub>O<sub>3</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 526.8803, Found: 526.8795.



**(E)-1-Iodo-4-(2-(4-iodophenylsulfinyl)-2-phenylvinyl)sulfonylbenzene (4g).** The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 5:1) to provide the product **4g** as a yellow solid (150.7 mg, 81%); m.p.: 187-189 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>), δ, ppm: 6.87 (*d*, *J* = 8.4 Hz, 2H, ArH), 6.91 (*d*, *J* = 7.2 Hz, 2H, ArH), 7.29-7.32 (*m*, 4H, ArH), 7.34 (*s*, 1H, =CH), 7.42 (*t*, *J* = 7.8 Hz, 1H, ArH), 7.66 (*d*, *J* = 8.4 Hz, 2H, ArH), 7.77 (*d*, *J* = 9.0 Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>), δ, ppm: 99.1, 102.1, 126.6, 127.7, 128.5, 129.3, 129.4, 129.5, 130.8, 138.4, 138.5, 139.9, 140.1, 161.3; ESI-HRMS, *m/z*: Calcd for C<sub>20</sub>H<sub>15</sub>I<sub>2</sub>O<sub>3</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 620.8547, Found: 620.8536.

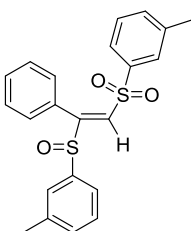


**(E)-1-(2-Phenyl-2-(4-trifluoromethylphenylsulfinyl)vinyl)sulfonyl-4-trifluoromethylbenzene (4h).** The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 5:1) to provide the product **4h** as a white solid (80.1 mg, 53 %); m.p.: 145-146 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>), δ, ppm: 6.92 (*d*, *J* = 7.8 Hz, 2H, ArH), 7.26 (*d*, *J* = 8.4 Hz, 2H, ArH), 7.29-7.33 (*m*, 2H, ArH), 7.36 (*s*, 1H, =CH), 7.44 (*t*, *J* = 7.8 Hz, 1H, ArH), 7.58 (*d*, *J* = 8.4 Hz, 2H, ArH), 7.68 (*d*, *J* = 8.4 Hz, 2H, ArH), 7.78 (*d*, *J* = 8.4 Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>), δ, ppm: 123.1 (*q*, *J* = 271.5 Hz), 123.3 (*q*, *J* = 271.5 Hz), 125.5, 126.2 (*q*, *J* = 3.0 Hz), 126.3 (*q*, *J* = 3.0 Hz), 127.3, 128.7, 129.3, 129.5, 131.1, 134.0 (*q*, *J* = 33.0 Hz), 135.0 (*q*, *J* = 33.0 Hz), 143.5, 144.5, 161.8; <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>), δ, ppm: -63.0, -63.3; ESI-HRMS, *m/z*: Calcd for C<sub>22</sub>H<sub>15</sub>F<sub>6</sub>O<sub>3</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 505.0361, Found: 505.0355.



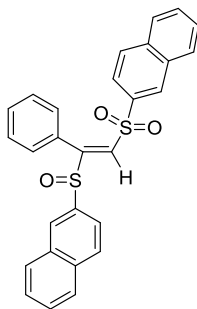
**(E)-1-Bromo-3-(2-((3-bromophenyl)sulfinyl)-2-phenylvinyl)sulfonylbenzene (4i).**

The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 5:1) to provide the product **4i** as a white solid (114.7 mg, 73%); m.p.: 122-124 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>), δ, ppm: 6.90 (*d*, *J* = 7.8 Hz, 2H, ArH), 7.04 (*d*, *J* = 7.8 Hz, 1H, ArH), 7.18 (*t*, *J* = 7.8 Hz, 1H, ArH), 7.26-7.27 (*m*, 1H, ArH), 7.30-7.34 (*m*, 4H, =CH, ArH), 7.44-7.46 (*m*, 1H, ArH), 7.55 (*d*, *J* = 7.2 Hz, 1H, ArH), 7.62 (*d*, *J* = 7.2 Hz, 1H, ArH), 7.68-7.69 (*m*, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>), δ, ppm: 123.2, 123.4, 123.7, 126.6, 127.4, 127.9, 128.6, 129.3, 129.7, 130.6, 130.8, 131.0, 131.1, 135.2, 137.0, 142.0, 142.2, 161.8; ESI-HRMS, *m/z*: Calcd for C<sub>20</sub>H<sub>15</sub>Br<sub>2</sub>O<sub>3</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 524.8658, Found: 524.8650.

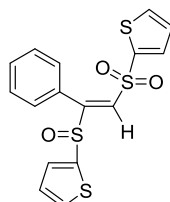


**(E)-1-Methyl-3-(2-phenyl-2-(*m*-tolylsulfinyl)vinyl)sulfonylbenzene (4j).** The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 5:1) to provide the product **4j** as a white solid (97.4 mg, 82%); m.p.: 87-89 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>), δ, ppm: 2.27 (*s*, 3H, CH<sub>3</sub>), 2.34 (*s*, 3H, CH<sub>3</sub>), 6.89 (*d*, *J* = 7.2 Hz, 2H, ArH), 6.91 (*d*, *J* = 7.8 Hz, 1H, ArH), 7.02 (*s*, 1H, ArH), 7.17 (*t*, *J* = 7.8 Hz, 1H, ArH), 7.21 (*d*, *J* = 7.2 Hz, 1H, ArH), 7.25-7.27 (*m*, 2H, ArH), 7.30-7.34 (*m*, 1H, ArH), 7.34 (*s*, 1H, =CH), 7.35-7.38 (*m*, 2H, ArH), 7.43 (*s*, 1H, ArH), 7.48 (*d*, *J* = 7.8 Hz, 1H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>), δ, ppm: 21.3, 21.4, 122.7, 125.1, 125.5, 128.1, 128.2, 128.4, 128.9, 129.1, 129.4, 129.6, 130.2, 133.0, 134.6, 139.5, 139.6, 139.9, 140.3, 161.1; ESI-HRMS, *m/z*: Calcd for C<sub>22</sub>H<sub>19</sub>O<sub>3</sub>S<sub>2</sub> [M-H]<sup>-</sup>: 395.0781, Found: 395.0777.

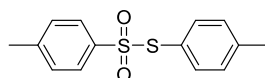




(*E*)-2-(2-(Naphthalen-2-ylsulfinyl)-2-phenylvinyl)sulfonylnaphthalene (**4k**). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 5:1) to provide the product **4k** as a white solid (108.1 mg, 77%); m.p.: 172-174 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>), δ, ppm: 6.86 (*d*, *J* = 7.2 Hz, 2H, ArH), 7.13-7.16 (*m*, 2H, ArH), 7.25-7.27 (*m*, 1H, ArH), 7.28 (*t*, *J* = 7.8 Hz, 1H, ArH), 7.50-7.52 (*m*, 2H, =CH, ArH), 7.55-7.60 (*m*, 2H, ArH), 7.64-7.70 (*m*, 4H, ArH), 7.80-7.83 (*m*, 3H, ArH), 7.87-7.89 (*m*, 2H, ArH), 8.15 (*s*, 1H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>), δ, ppm: 120.4, 122.6, 127.0, 127.5, 127.7, 128.0, 128.1, 128.2, 128.3, 128.5, 128.7, 129.3, 129.4, 129.5, 129.6, 129.7, 130.0, 130.1, 130.4, 132.1, 132.5, 134.8, 135.4, 137.0, 137.1, 161.2; ESI-HRMS, *m/z*: Calcd for C<sub>28</sub>H<sub>21</sub>O<sub>3</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 469.0926, Found: 469.0920.



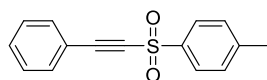
(*E*)-2-(2-Phenyl-2-(thiophen-2-ylsulfinyl)vinyl)sulfonylthiophene (**4l**). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 5:1) to provide the product **4l** as a yellow solid (78.6 mg, 69%); m.p.: 133-134 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>), δ, ppm: 6.91-6.92 (*m*, 1H, ArH), 7.05-7.06 (*m*, 1H, ArH), 7.07-7.08 (*m*, 3H, ArH), 7.29-7.31 (*m*, 2H, ArH), 7.38 (*t*, *J* = 7.2 Hz, 1H, ArH), 7.48-7.49 (*dd*, *J* = 3.6 Hz, 1.2 Hz, 1H, ArH), 7.49 (*s*, 1H, =CH), 7.61-7.62 (*dd*, *J* = 5.4 Hz, 1.2 Hz, 1H, ArH), 7.67-7.68 (*dd*, *J* = 4.8 Hz, 1.2 Hz, 1H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>), δ, ppm: 127.4, 127.9, 128.1, 128.4, 129.1, 130.3, 130.5, 132.8, 133.2, 134.6, 134.9, 141.47, 141.49, 160.2; ESI-HRMS, *m/z*: Calcd for C<sub>16</sub>H<sub>13</sub>O<sub>3</sub>S<sub>4</sub> [M+H]<sup>+</sup>: 380.9742, Found: 380.9734.



*S*-(*p*-Tolyl) 4-methylbenzenesulfonothioate (**5a**). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 15:1) to provide the product **5a** as a white solid (10 mg); m.p.: 73-75 °C (74-75 °C<sup>[4]</sup>); <sup>1</sup>H NMR (600 MHz,

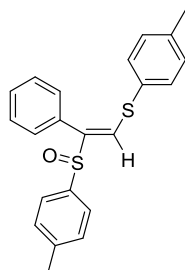
CDCl<sub>3</sub>),  $\delta$ , ppm: 2.38 (*s*, 3H, CH<sub>3</sub>), 2.42 (*s*, 3H, CH<sub>3</sub>), 7.14 (*d*,  $J = 7.8$  Hz 2H, ArH), 7.21 (*d*,  $J = 8.4$  Hz, 2H, ArH), 7.24 (*d*,  $J = 7.8$  Hz, 2H, ArH), 7.46 (*d*,  $J = 8.4$  Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>),  $\delta$ , ppm: 21.6, 21.8, 124.7, 127.7, 129.5, 130.3, 136.6, 140.6, 142.2, 144.7.

The data are in agreement with those previously reported in the literature.<sup>[4]</sup>



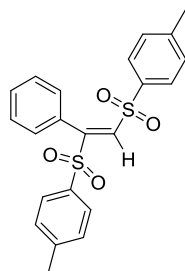
1-Methyl-4-(phenylethynylsulfonyl)benzene (**7a**). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 20:1) to provide the product **7a** as a white solid (46.1 mg, 60%); m.p.: 79-81 °C; (73-74 °C<sup>[2]</sup>); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>),  $\delta$ , ppm: 2.47 (*s*, 3H, CH<sub>3</sub>), 7.35-7.40 (*m*, 4H, ArH), 7.47 (*t*,  $J = 7.8$  Hz, 1H, ArH), 7.51-7.53 (*m*, 2H, ArH), 7.96 (*d*,  $J = 8.4$  Hz, 2H, ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>),  $\delta$ , ppm: 21.9, 85.7, 93.1, 118.2, 127.7, 128.8, 130.1, 131.6, 132.9, 139.1, 145.5; ESI-HRMS,  $m/z$ : Calcd for C<sub>15</sub>H<sub>13</sub>O<sub>2</sub>S [M+H]<sup>+</sup>: 257.0631, Found: 257.0629.

The data are in agreement with those previously reported in the literature.<sup>[2]</sup>



(*E*)-(2-Phenyl-2-(*p*-tolylsulfinyl)vinyl)(*p*-tolyl)sulfane (**7b**). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate = 10:1) to provide the product **7b** as a white solid (45.7 mg, 42%); m.p.: 114-116 °C; (117-118 °C<sup>[2]</sup>); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>),  $\delta$ , ppm: 2.32 (*s*, 3H, CH<sub>3</sub>), 2.36 (*s*, 3H, CH<sub>3</sub>), 7.12 (*d*,  $J = 7.8$  Hz, 2H, ArH), 7.15-7.18 (*m*, 4H, ArH), 7.25-7.27 (*m*, 2H, ArH), 7.29-7.32 (*m*, 3H, ArH), 7.37 (*d*,  $J = 8.4$  Hz, 2H, ArH), 7.41 (*s*, 1H, =CH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>),  $\delta$ , ppm: 21.3, 21.5, 125.2, 128.7, 129.0, 129.1, 129.7, 130.3, 130.6, 131.1, 131.7, 132.3, 138.3, 139.3, 140.0, 141.6; ESI-HRMS,  $m/z$ : Calcd for C<sub>22</sub>H<sub>21</sub>OS<sub>2</sub> [M+H]<sup>+</sup>: 365.1028, Found: 365.1025.

The data are in agreement with those previously reported in the literature.<sup>[2]</sup>



(*E*)-4,4'-(1-Phenylethene-1,2-diyl)disulfonylbis(methylbenzene) (**7c**). The crude product was purified by flash chromatography on silica gel (Petroleum ether / Ethyl acetate/ DCM = 8:1:1) to provide the product **7c** as a white solid (112.5 mg, 91%); m.p.: 148-150 °C (152-153 °C<sup>[2]</sup>); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>),  $\delta$ , ppm: 2.39 (*s*, 3H, CH<sub>3</sub>), 2.40 (*s*, 3H, CH<sub>3</sub>), 6.91 (*d*,  $J = 7.2$  Hz, 2H, ArH), 7.17-7.20 (*m*, 6H, ArH), 7.34-7.37 (*m*, 3H, ArH), 7.45 (*d*,  $J = 8.4$  Hz, 2H, ArH), 7.75 (*s*, 1H, =CH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>),  $\delta$ , ppm: 21.7, 21.8, 127.8, 128.3, 129.3, 129.8, 129.9, 130.1, 130.3, 133.3, 133.9, 136.4, 137.7, 145.5, 145.8, 152.9; ESI-HRMS,  $m/z$ : Calcd for C<sub>22</sub>H<sub>21</sub>O<sub>4</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 413.0876, Found: 413.0873.

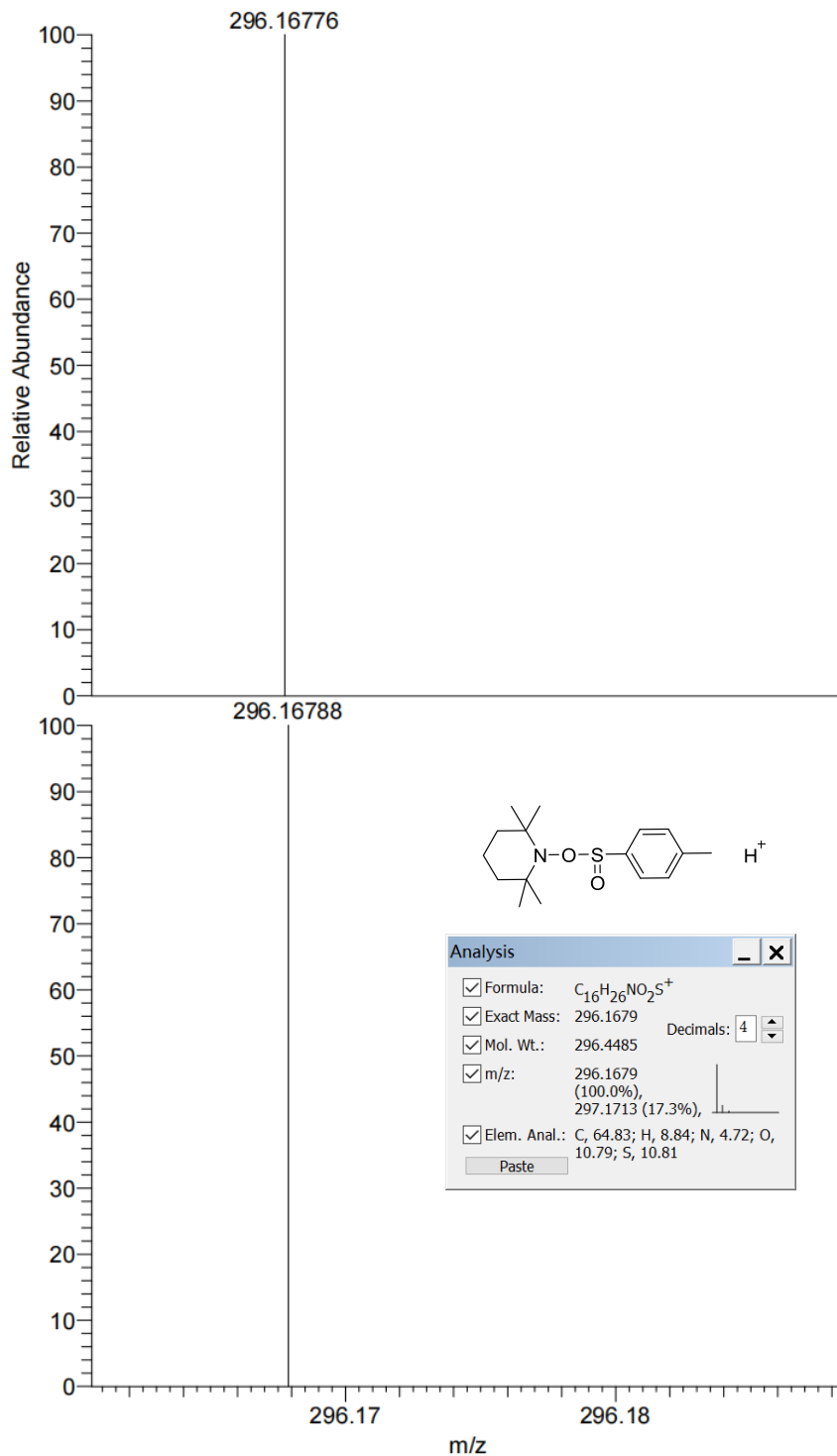
The data are in agreement with those previously reported in the literature.<sup>[2]</sup>

# Experimental Spectra Used in Discussions

(a)

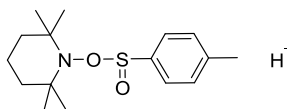
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03/13/23 09:08:53



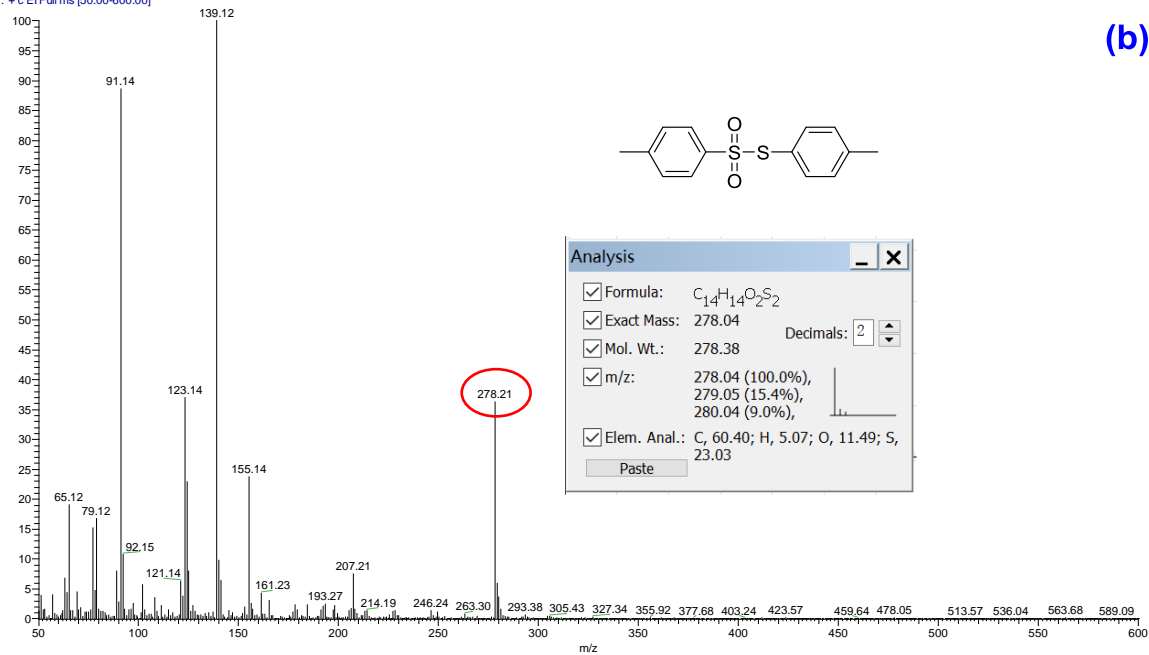
NL:  
6.32E5  
7\_20230313090742#24  
RT: 0.23 AV: 1 SB: 10  
0.97-1.06 T: FTMS + c  
APCI corona Full ms  
[50.0000-750.0000]

NL:  
7.90E5  
C<sub>16</sub> H<sub>25</sub> NO<sub>2</sub> S +H:  
C<sub>16</sub> H<sub>26</sub> N<sub>1</sub> O<sub>2</sub> S<sub>1</sub>  
pa Chrg 1



Analysis	
<input checked="" type="checkbox"/> Formula:	C <sub>16</sub> H <sub>26</sub> NO <sub>2</sub> S <sup>+</sup>
<input checked="" type="checkbox"/> Exact Mass:	296.1679
<input checked="" type="checkbox"/> Mol. Wt.:	296.4485
<input checked="" type="checkbox"/> m/z:	296.1679 (100.0%), 297.1713 (17.3%),
<input checked="" type="checkbox"/> Elem. Anal.:	C, 64.83; H, 8.84; N, 4.72; O, 10.79; S, 10.81
Paste	

wbw-221103-3 #3729 RT: 13.68 AV: 1 NL: 2.36E6  
T: + c EI Full ms [50.00-600.00]



wbw-221103-3 #3371 RT: 12.46 AV: 1 NL: 7.47E5  
T: + c EI Full ms [50.00-600.00]

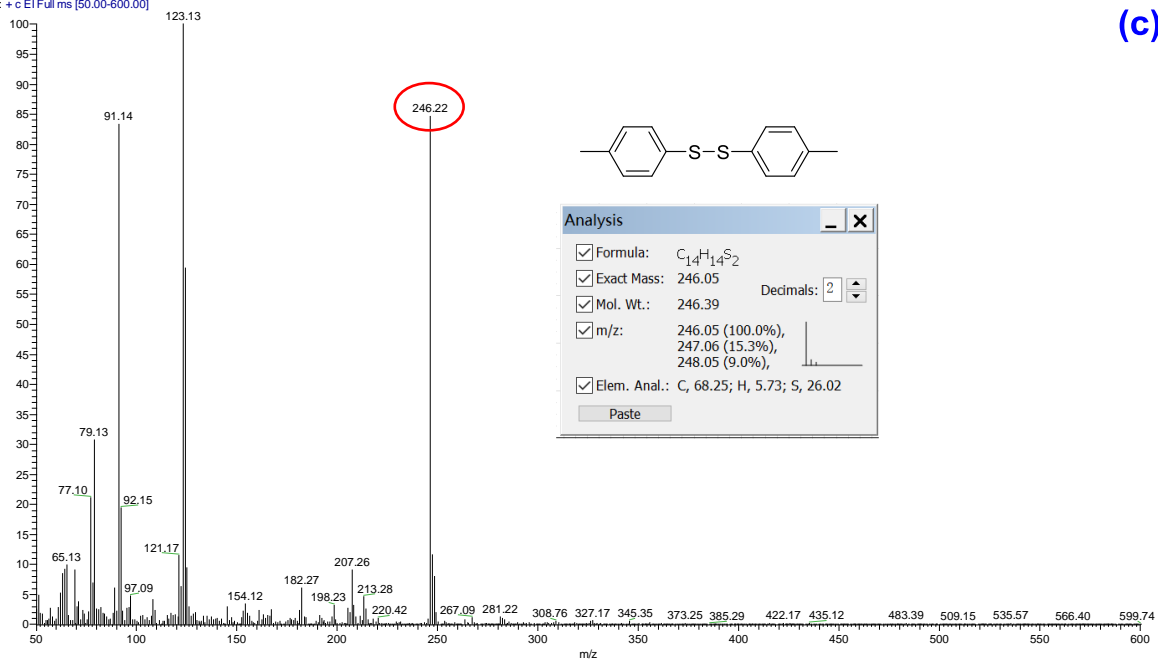
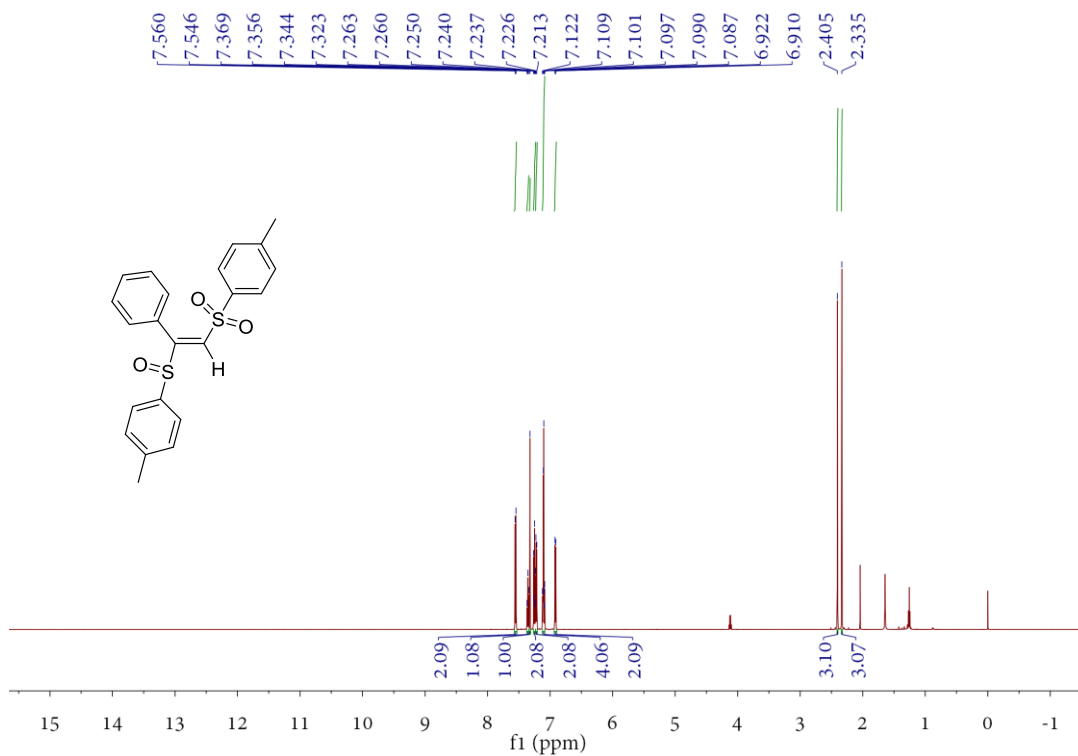
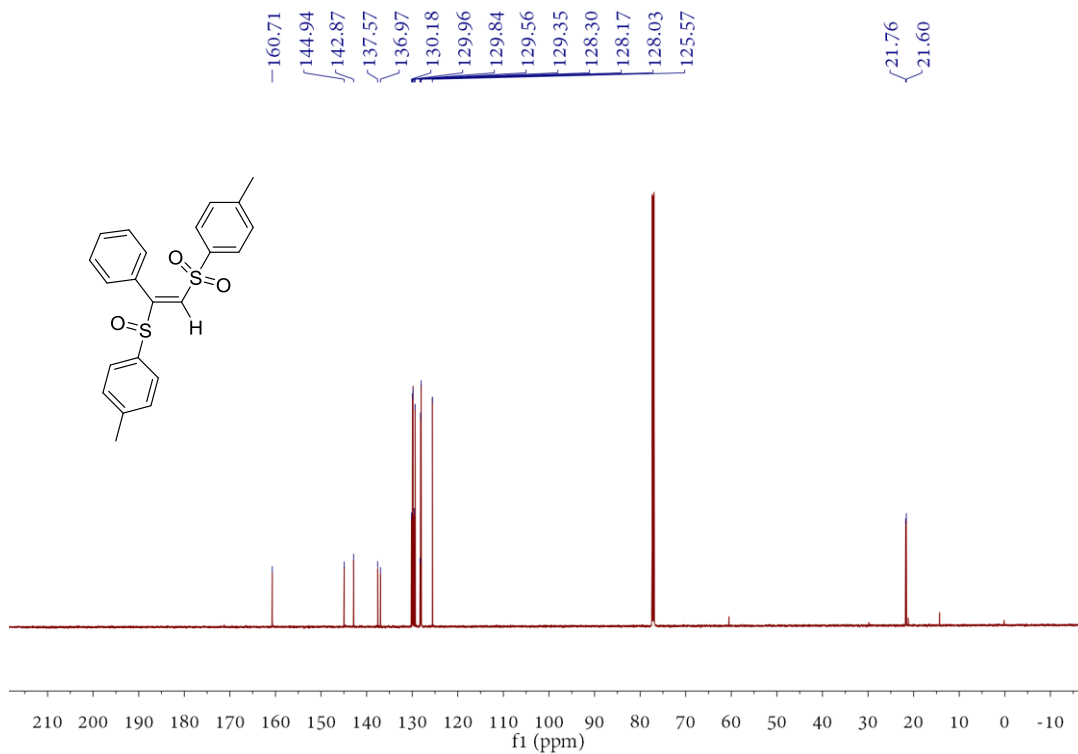


Fig. S3. The HRMS and GC-MS of control experiments.

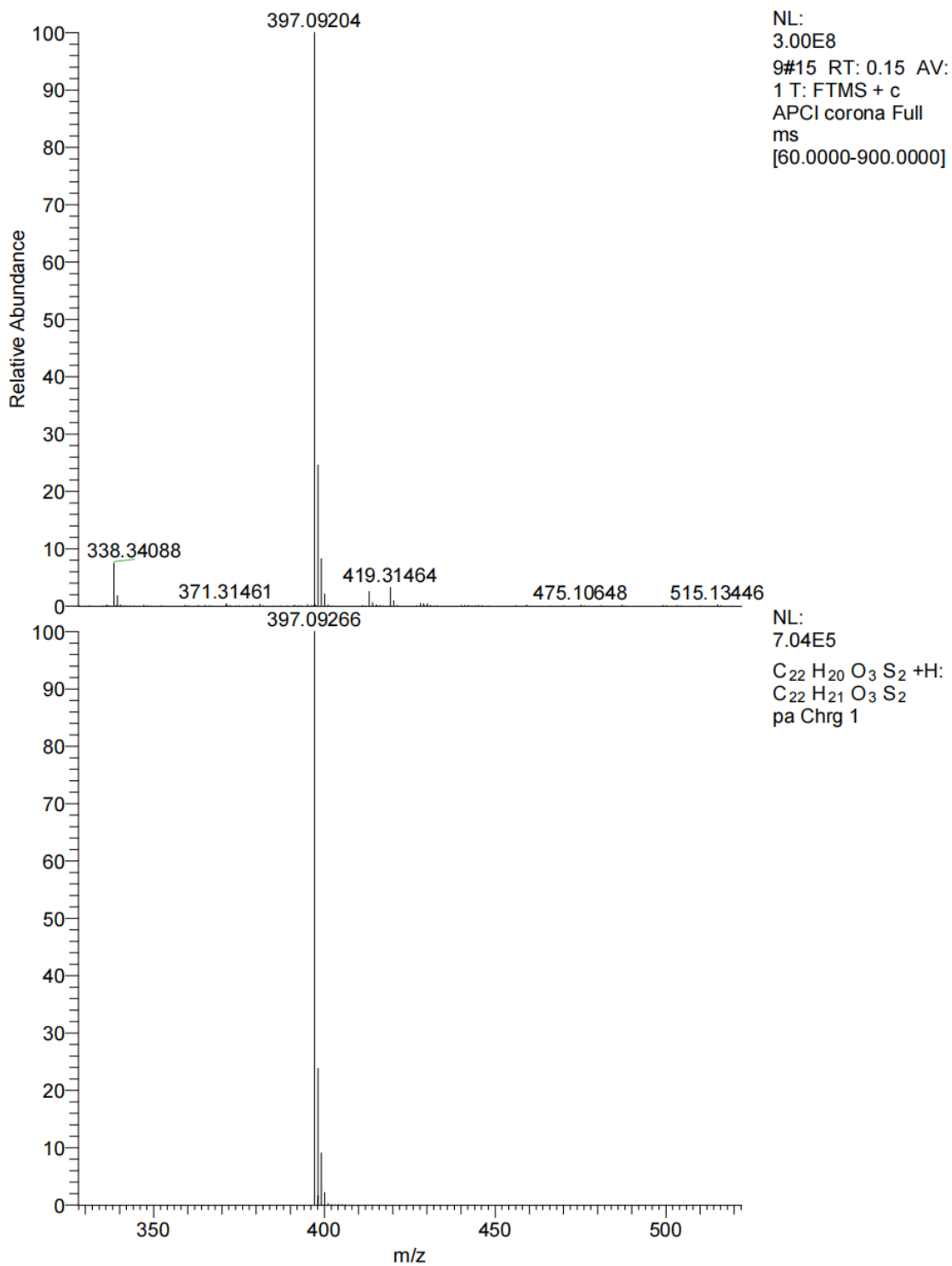
# NMR Spectra and HRMS for All Compounds 3a-3u, 4a-4l, 5a and 7a-7c



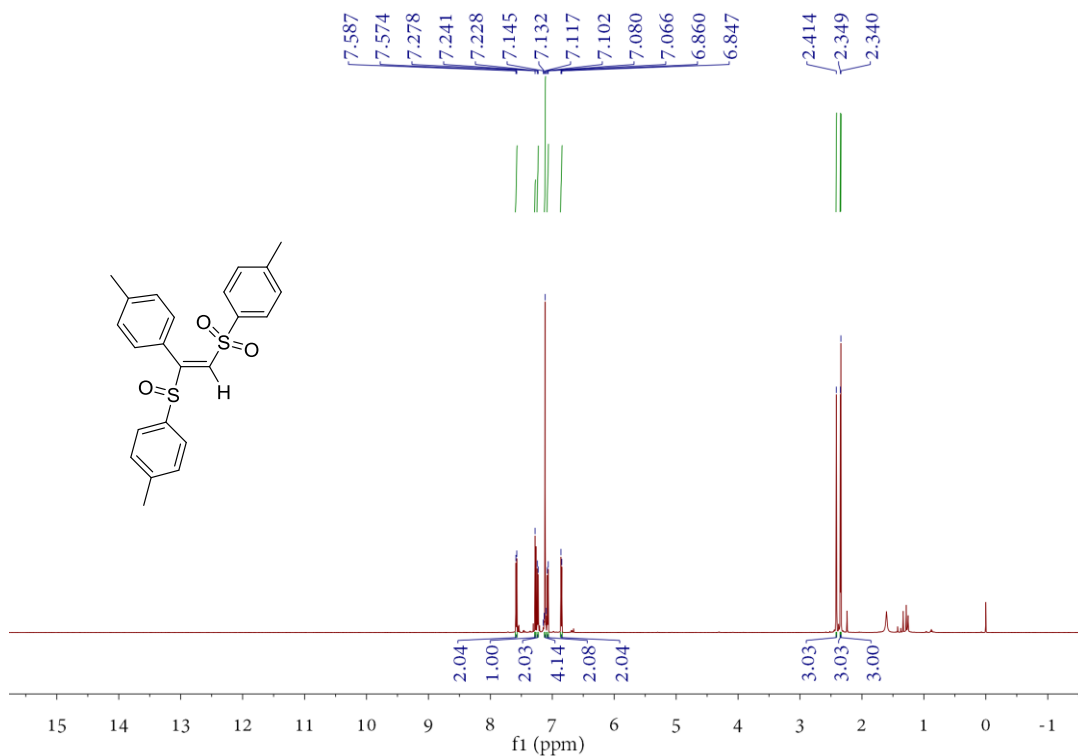
<sup>1</sup>H NMR spectrum of compound 3a



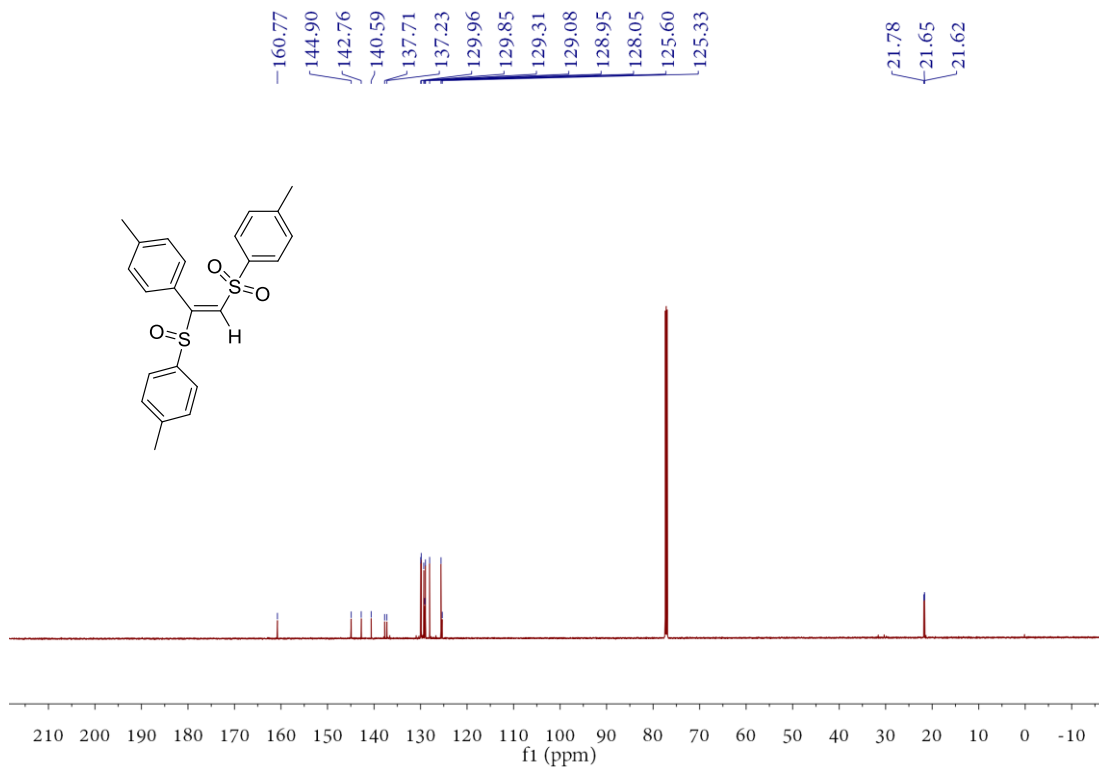
<sup>13</sup>C NMR spectrum of compound 3a



HRMS spectrum of compound **3a**

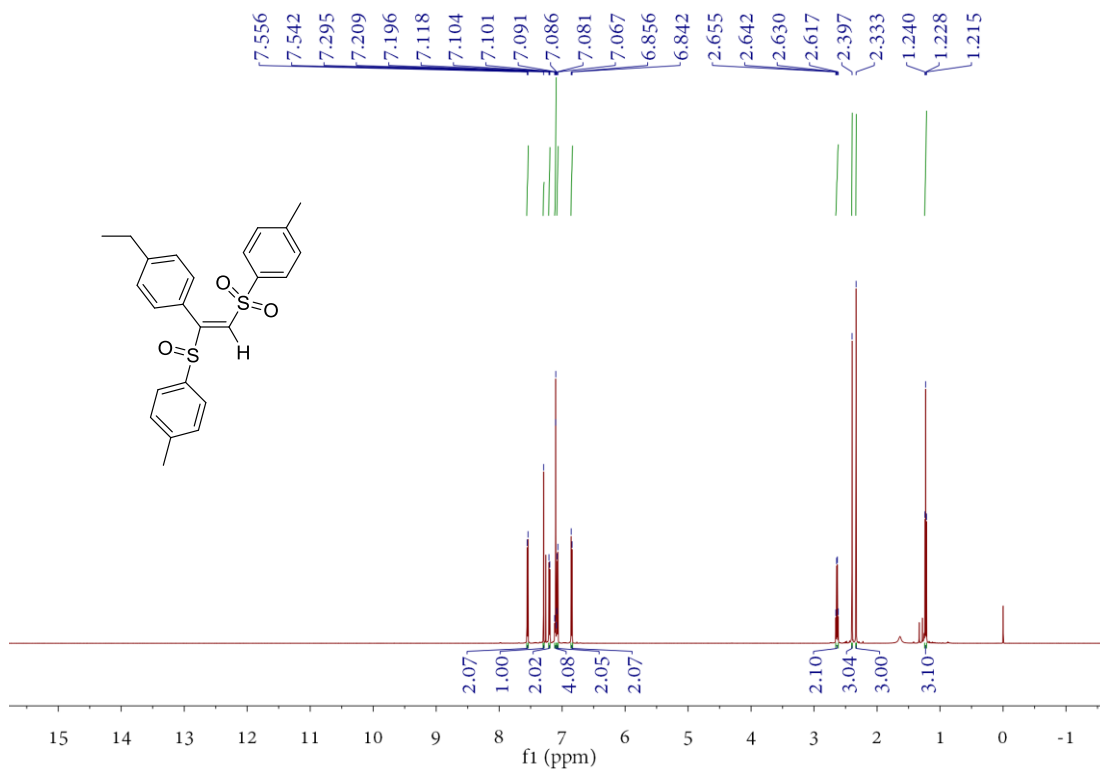


<sup>1</sup>H NMR spectrum of compound **3b**

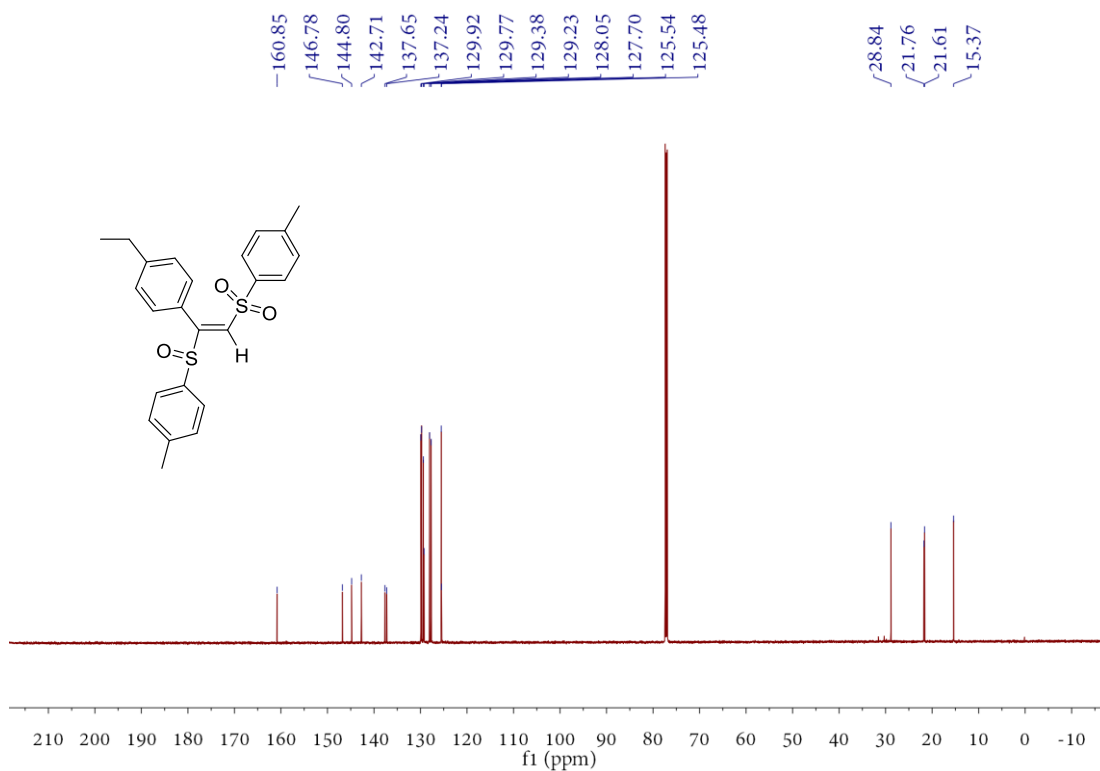


<sup>13</sup>C NMR spectrum of compound **3b**

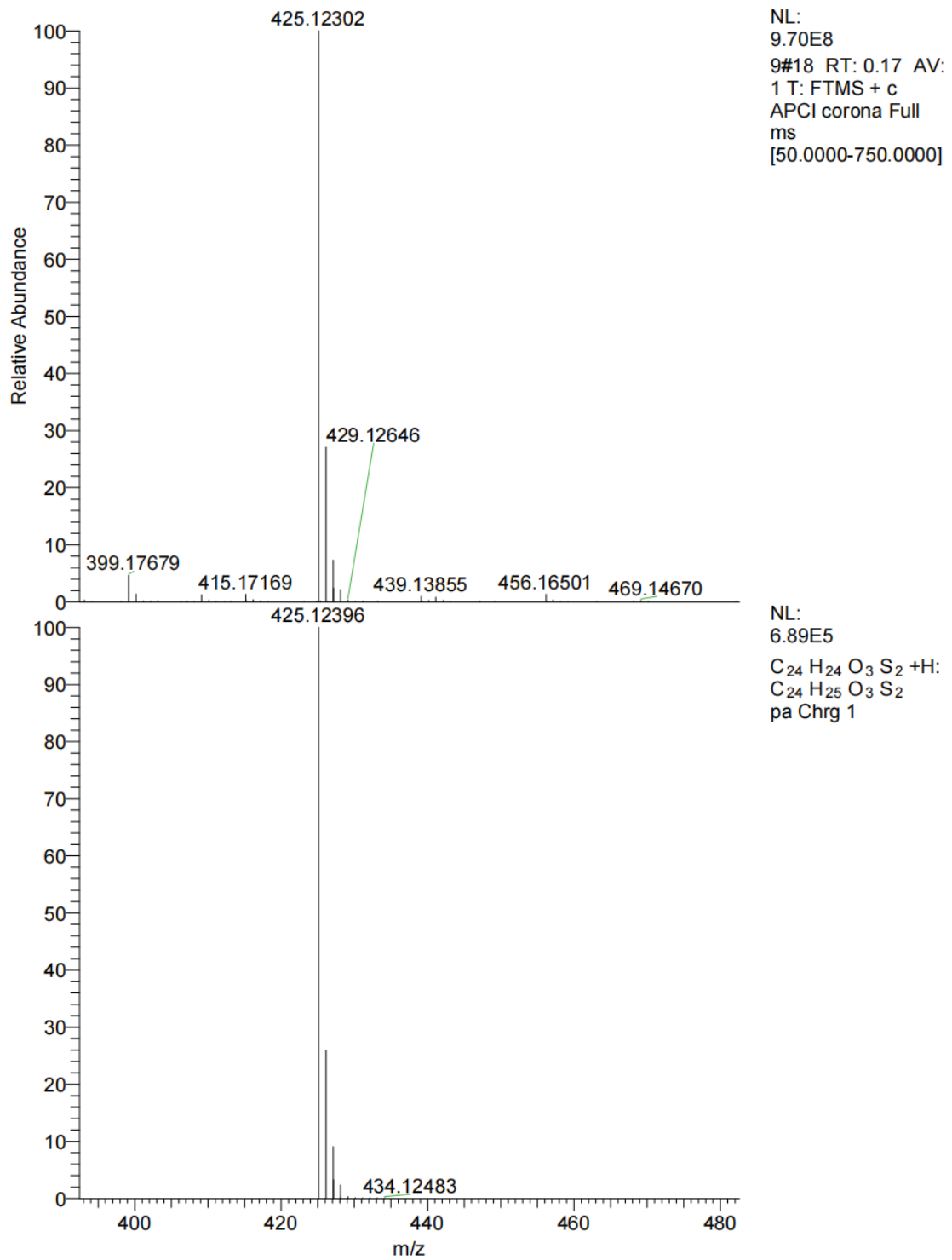




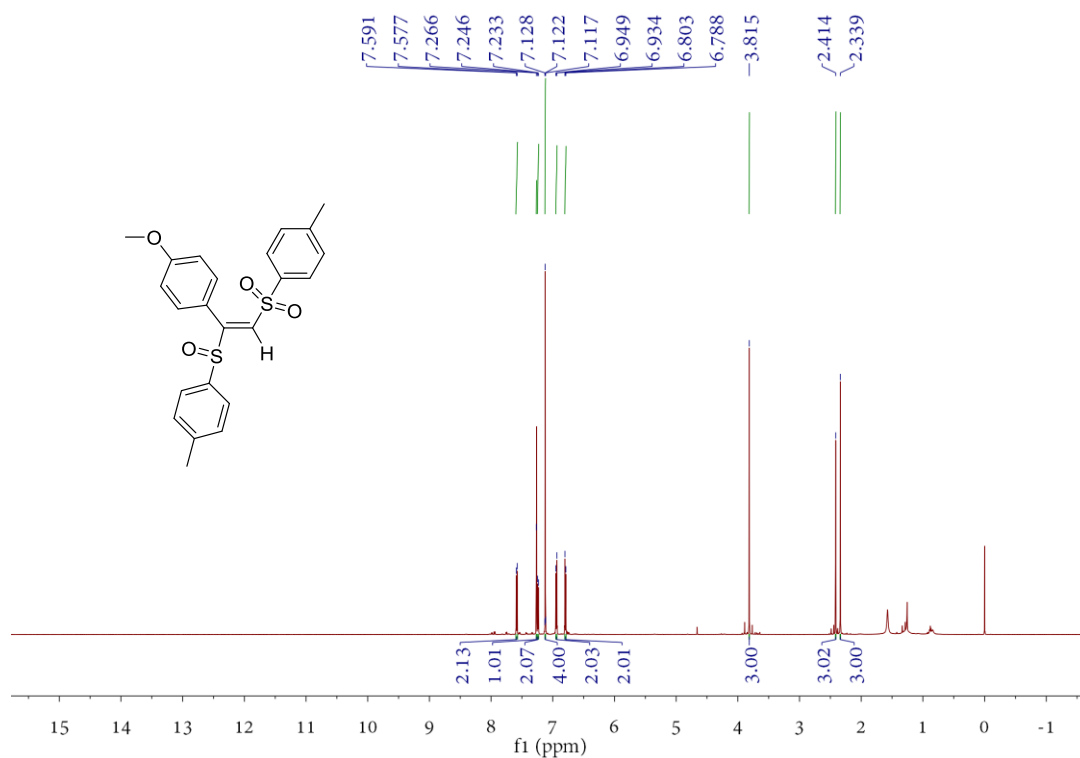
<sup>1</sup>H NMR spectrum of compound 3c



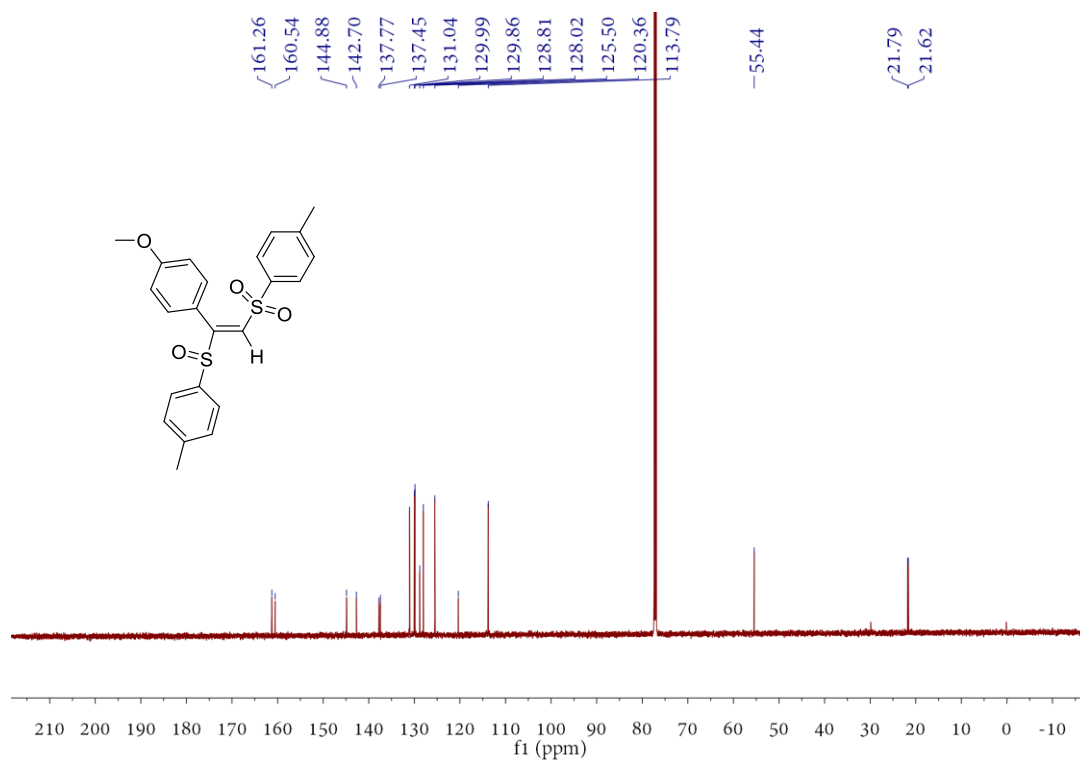
<sup>13</sup>C NMR spectrum of compound 3c



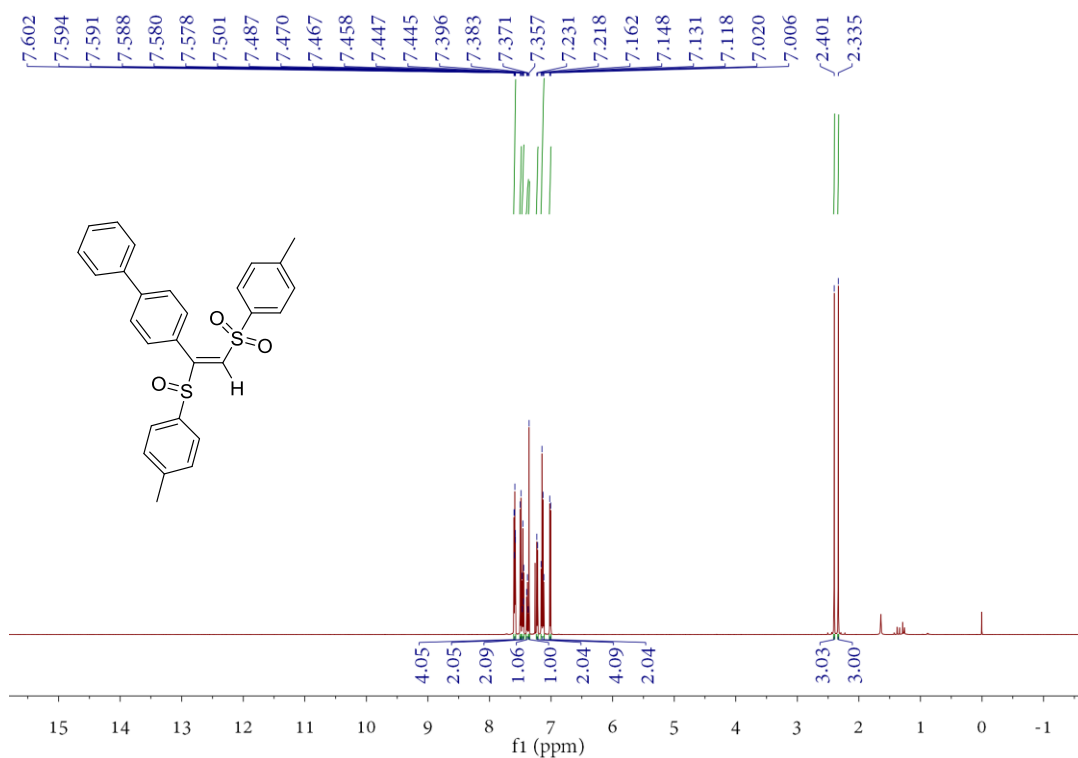
HRMS spectrum of compound **3c**



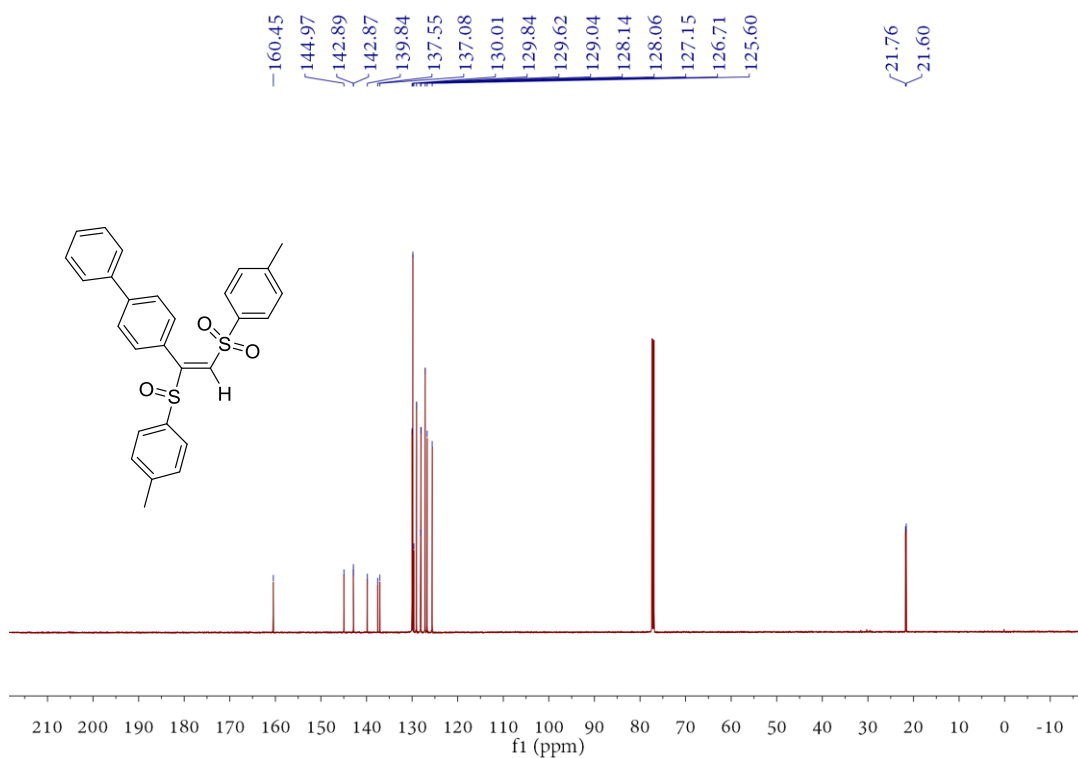
**<sup>1</sup>H NMR spectrum of compound 3d**



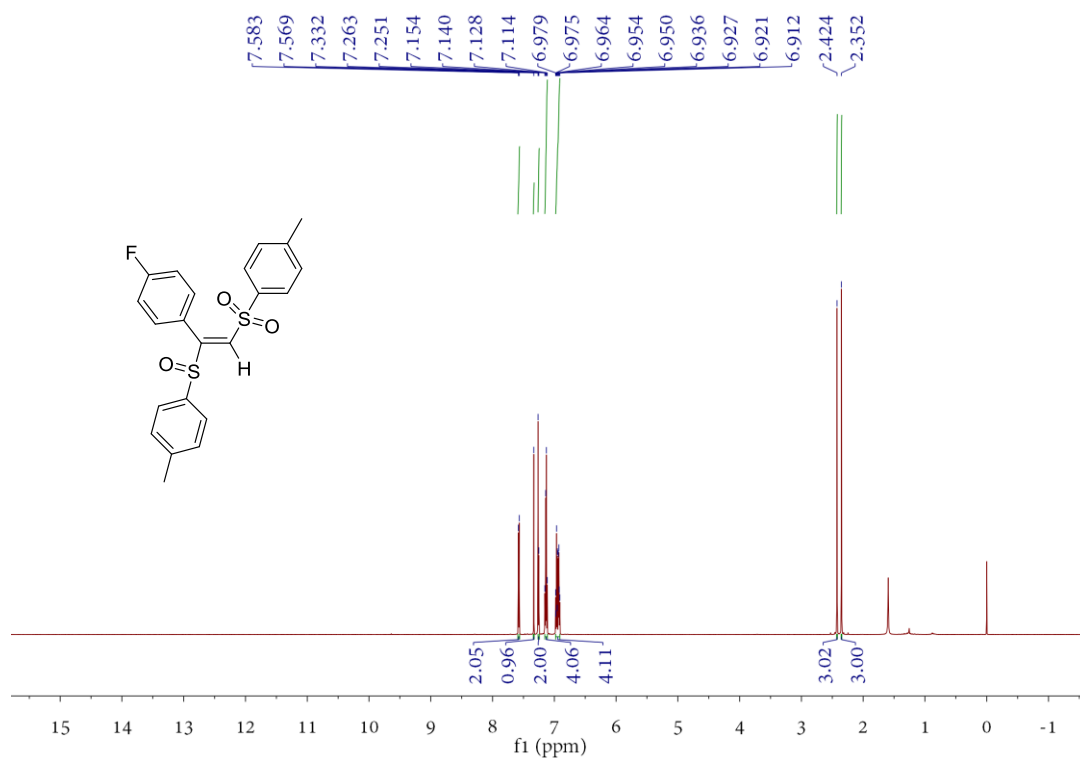
**<sup>13</sup>C NMR spectrum of compound 3d**



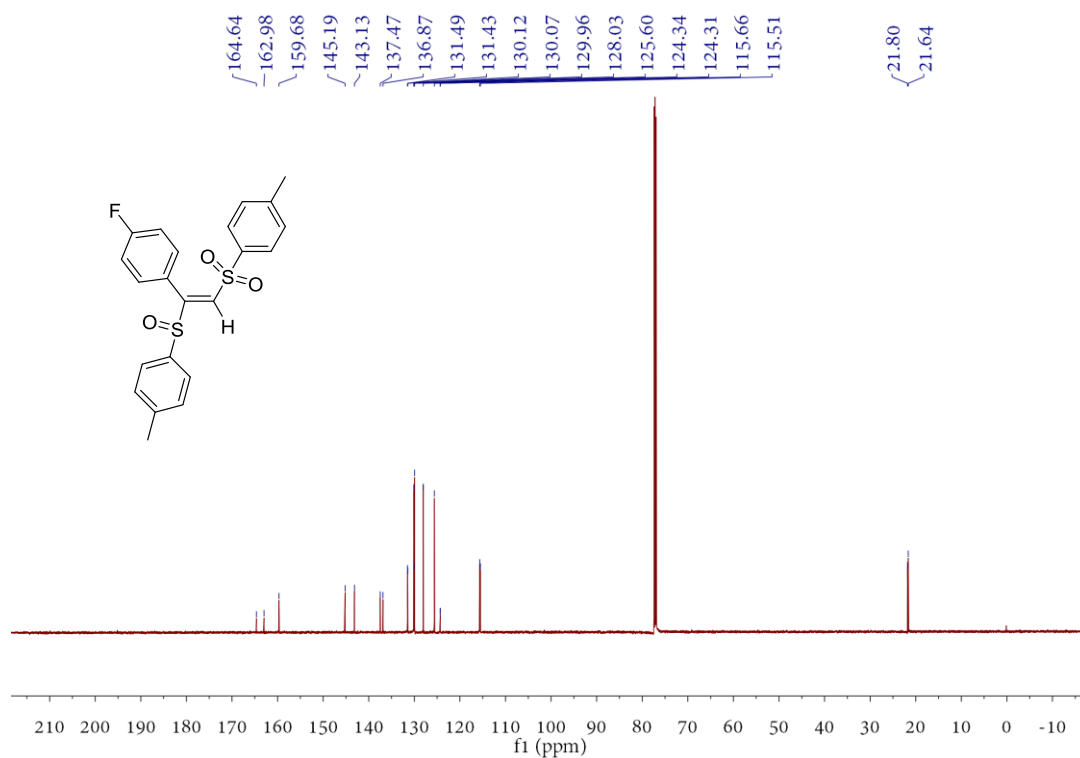
**<sup>1</sup>H NMR spectrum of compound 3e**



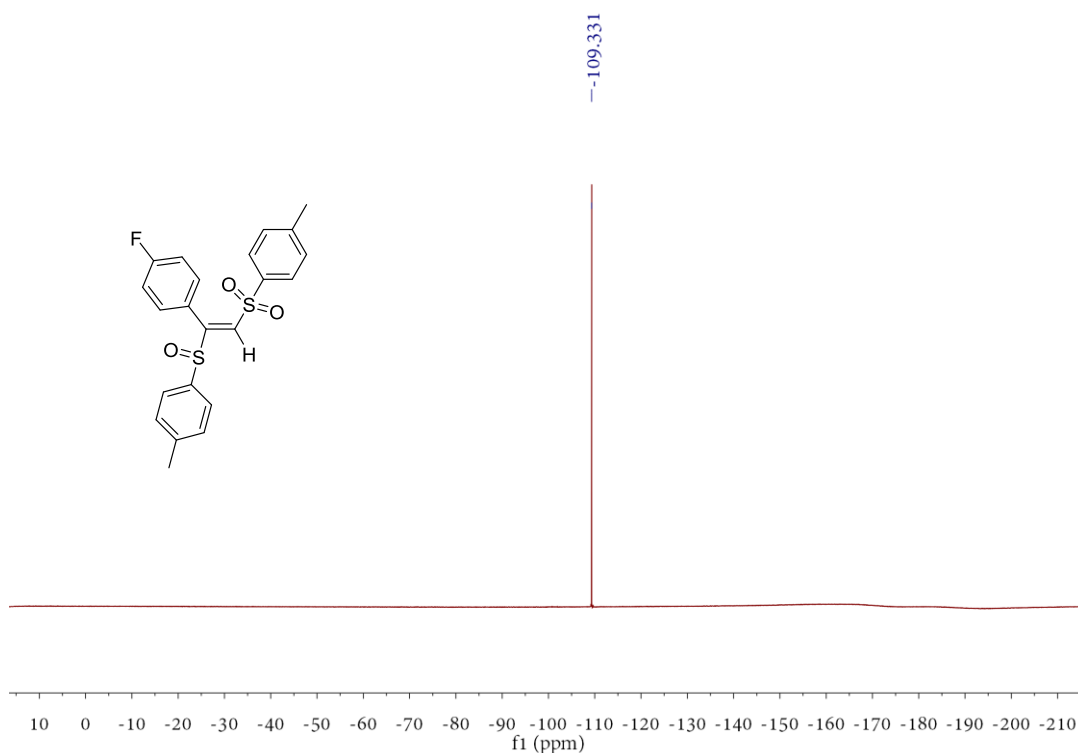
**<sup>13</sup>C NMR spectrum of compound 3e**



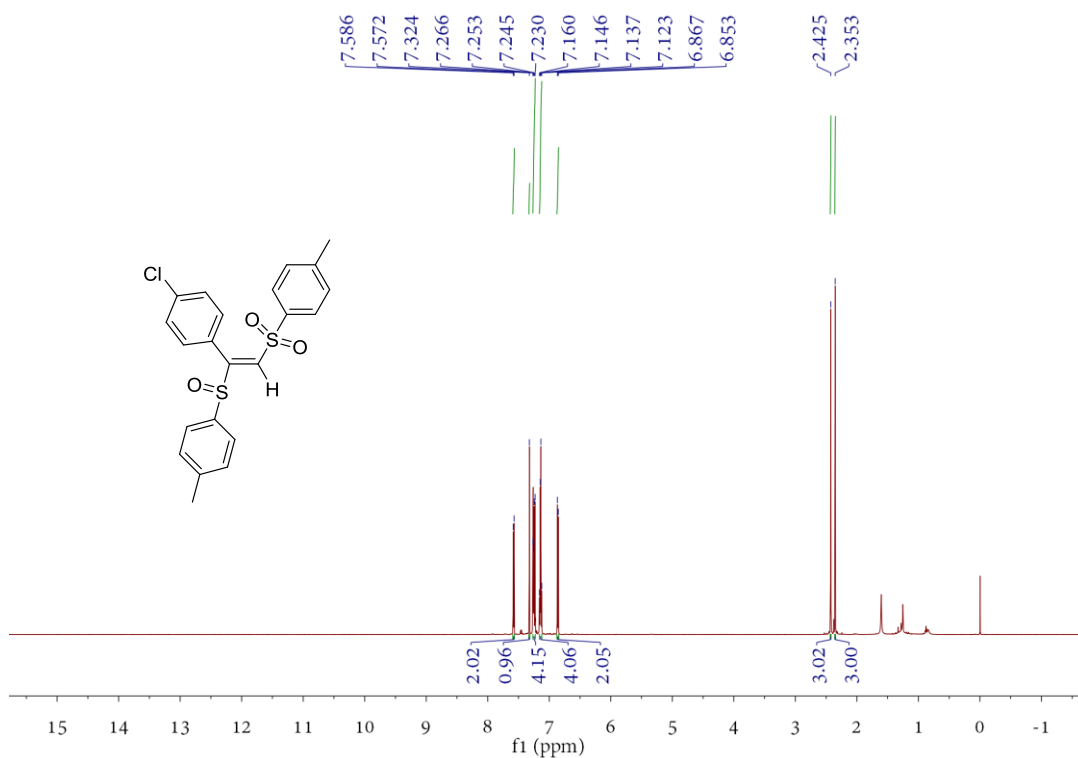
**<sup>1</sup>H NMR spectrum of compound 3f**



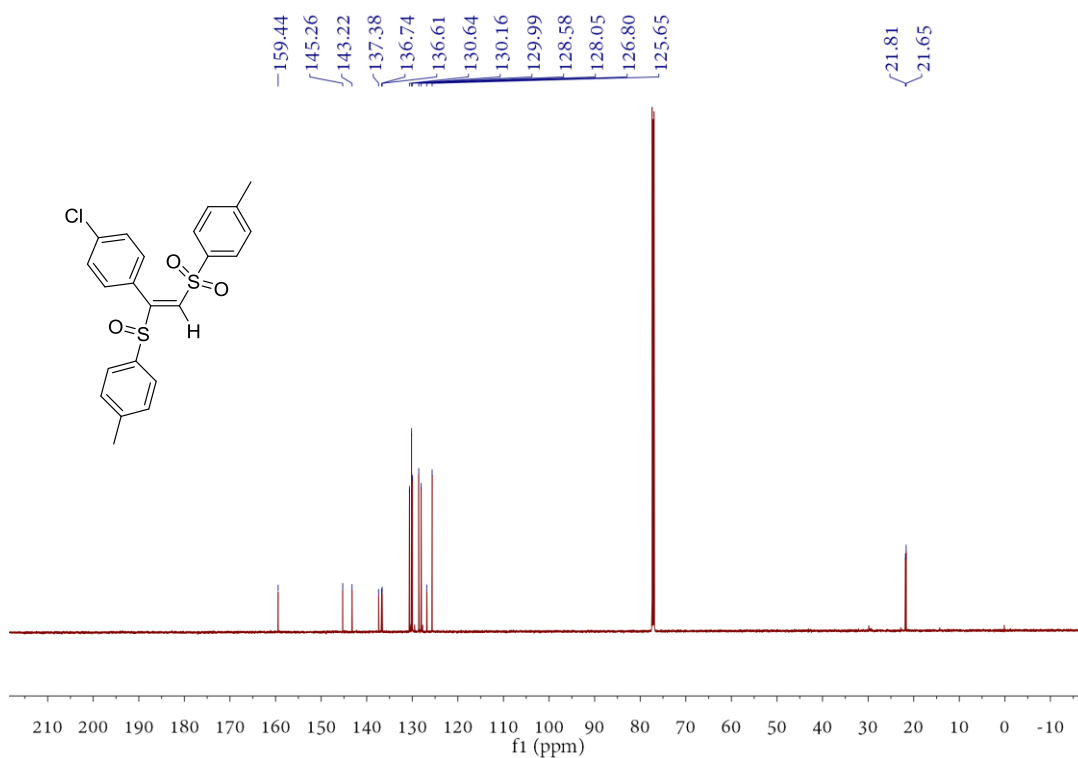
**<sup>13</sup>C NMR spectrum of compound 3f**



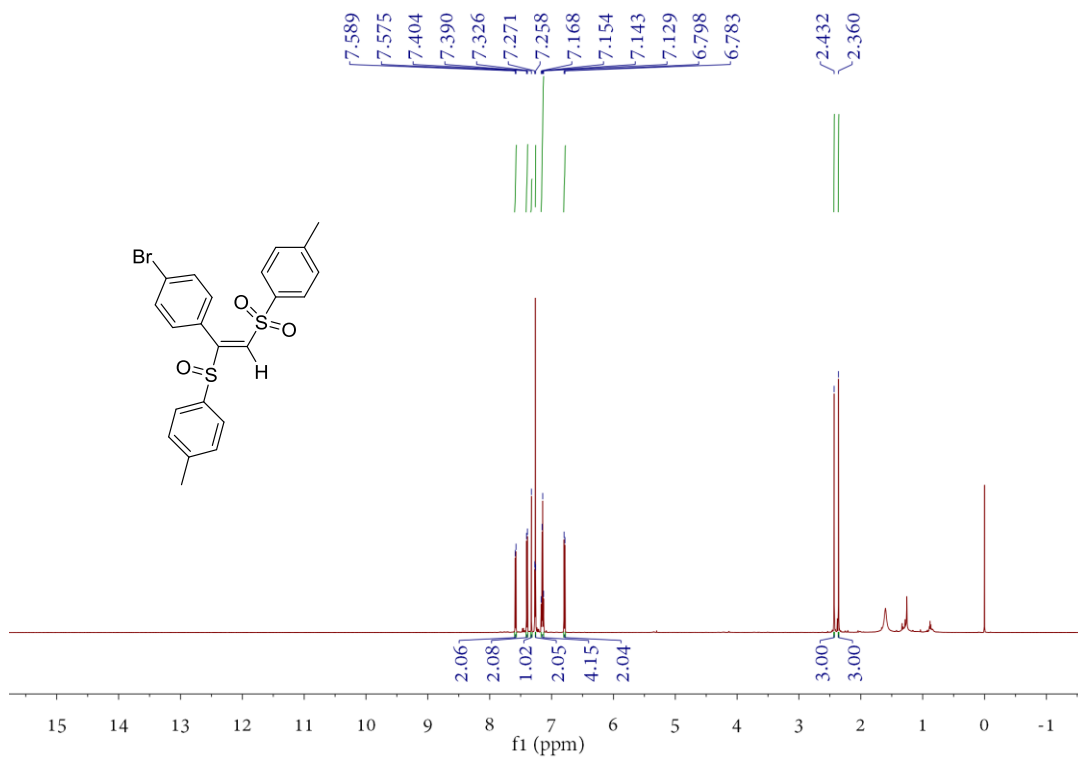
$^{19}\text{F}$  NMR spectrum of compound **3f**



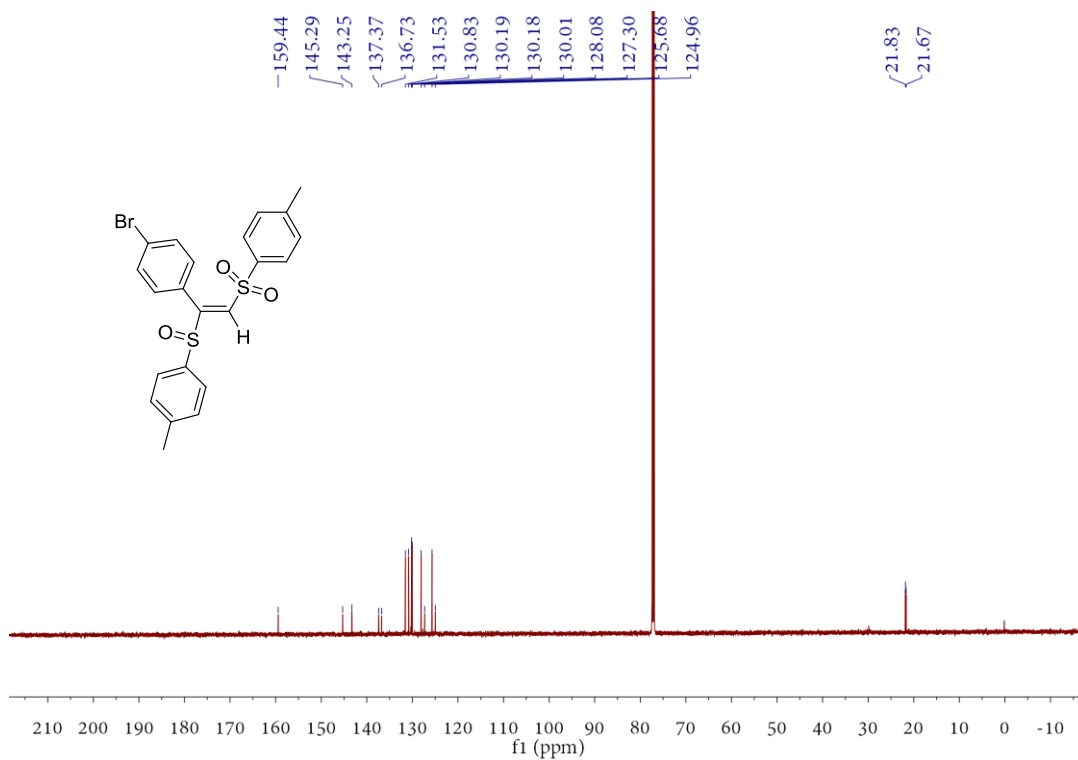
$^1\text{H}$  NMR spectrum of compound **3g**



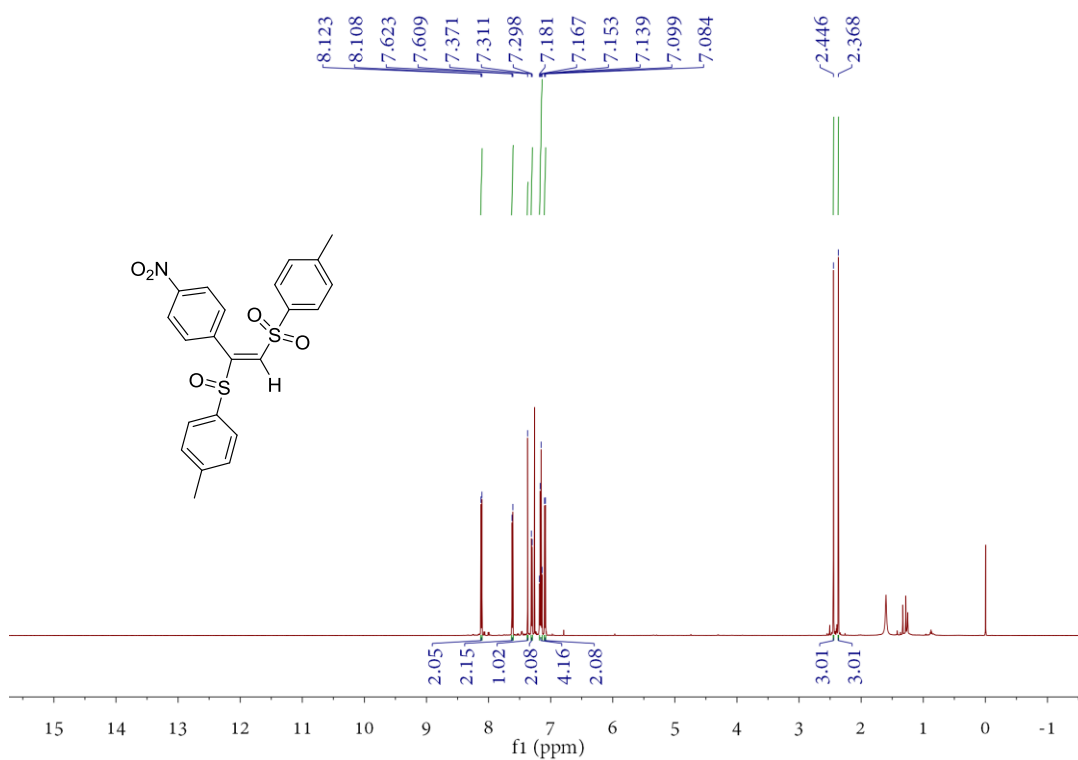
<sup>13</sup>C NMR spectrum of compound **3g**



<sup>1</sup>H NMR spectrum of compound **3h**

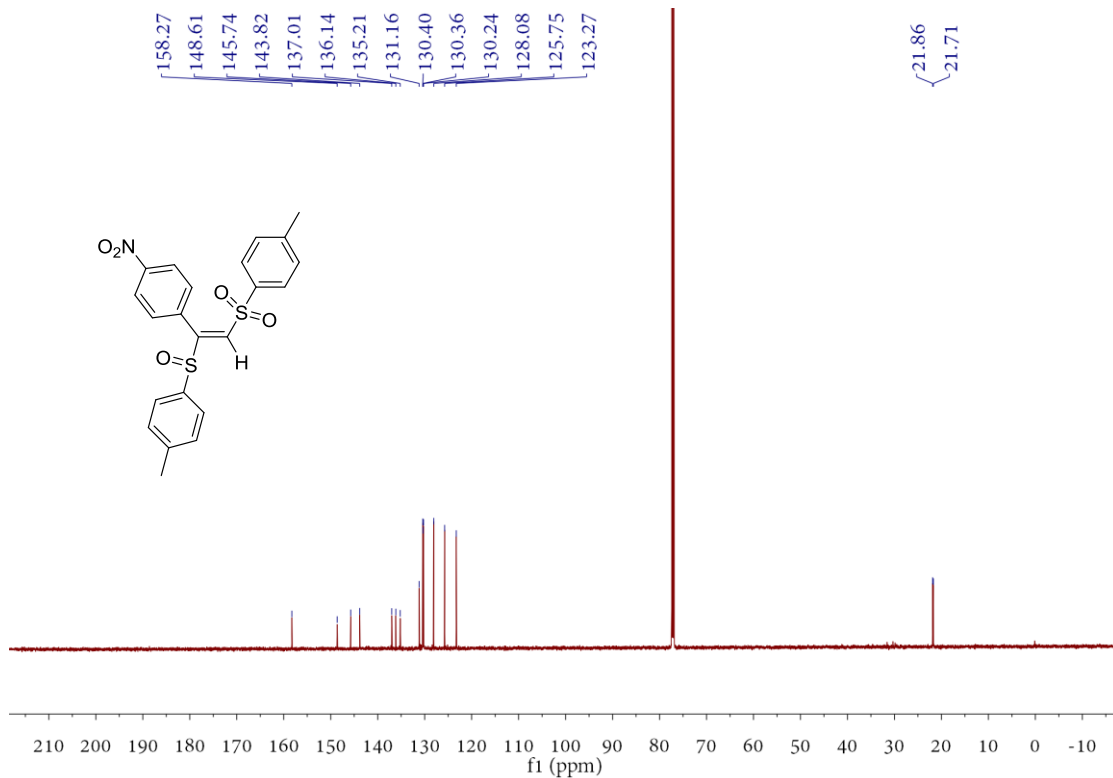


$^{13}\text{C}$  NMR spectrum of compound **3h**

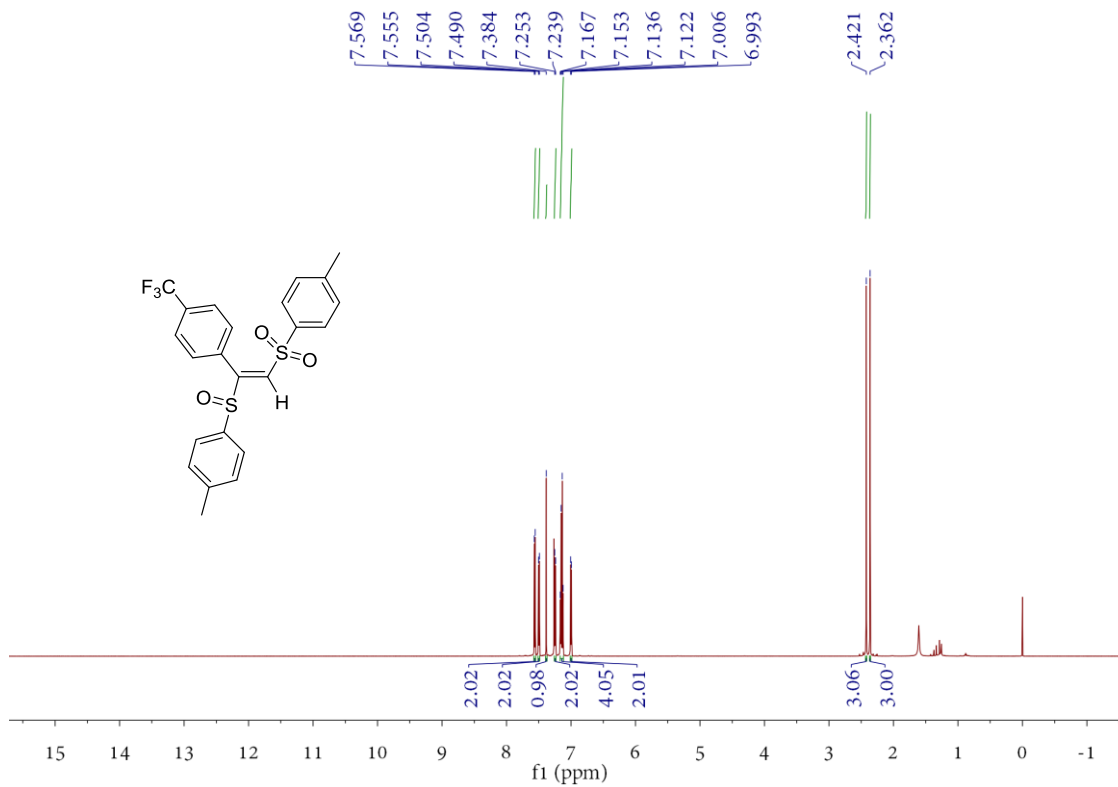


$^1\text{H}$  NMR spectrum of compound **3i**

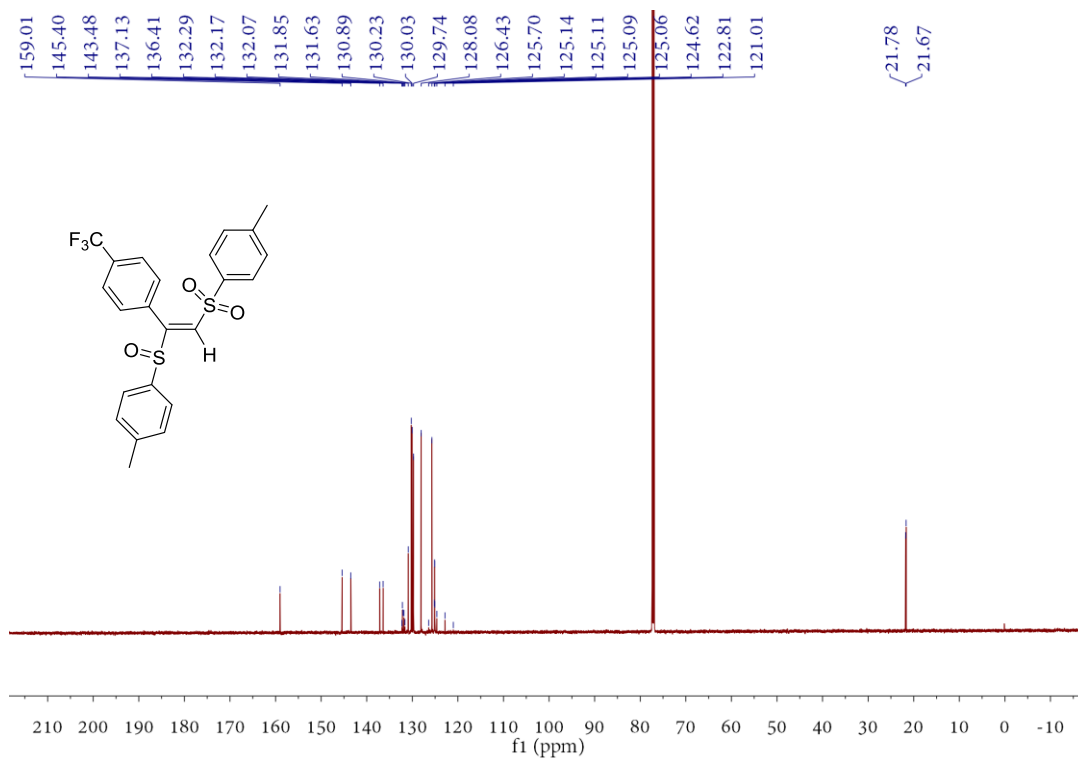




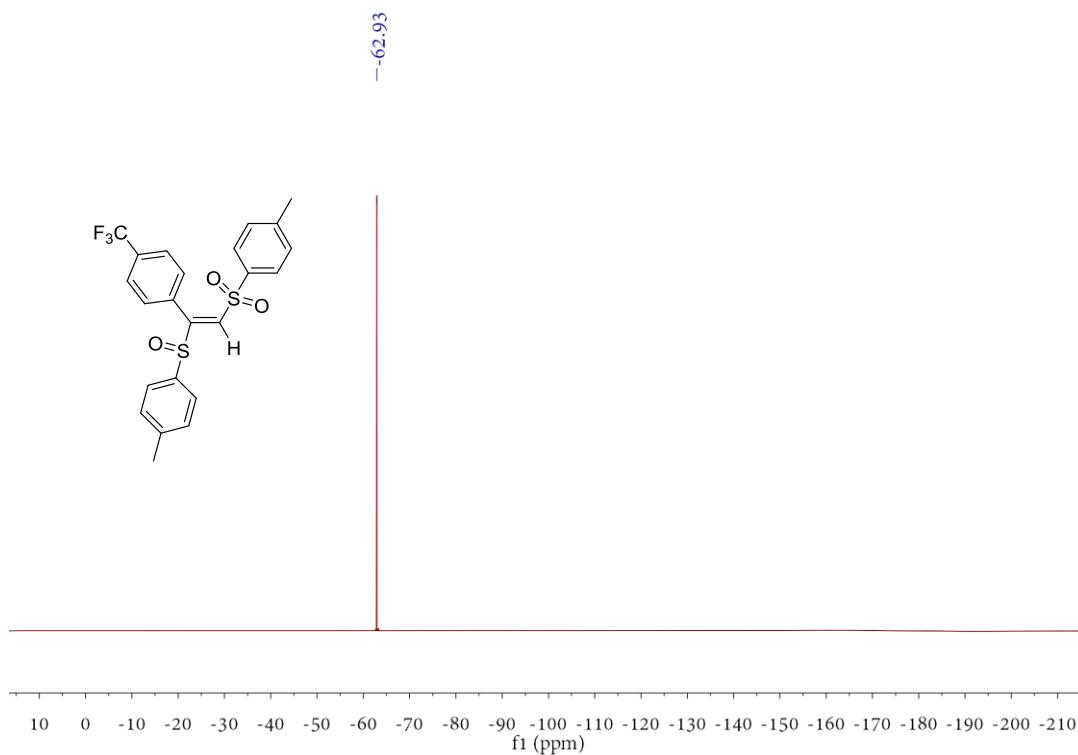
$^{13}\text{C}$  NMR spectrum of compound **3i**



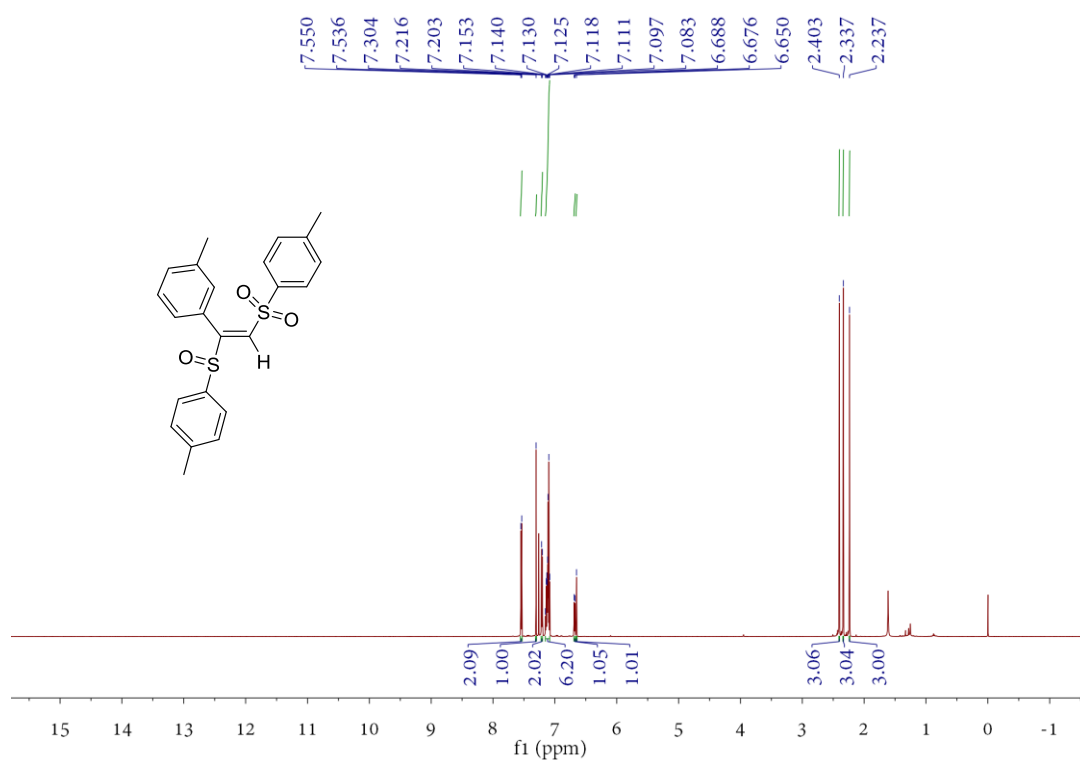
$^1\text{H}$  NMR spectrum of compound **3j**



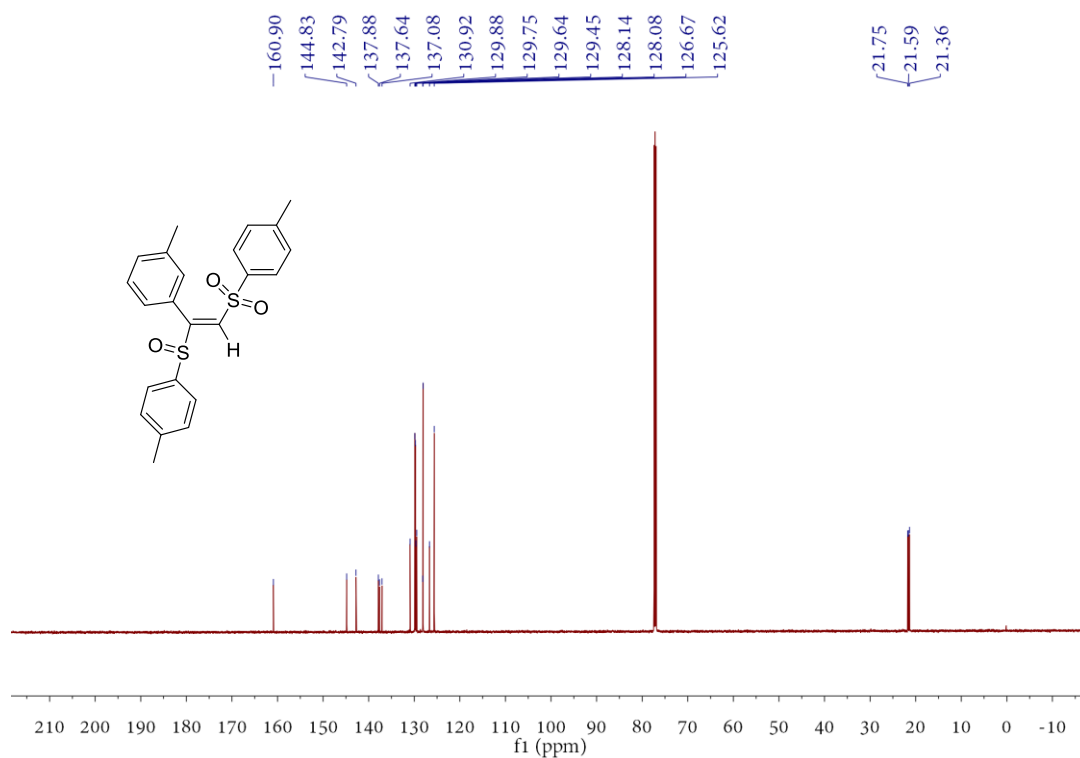
<sup>13</sup>C NMR spectrum of compound **3j**



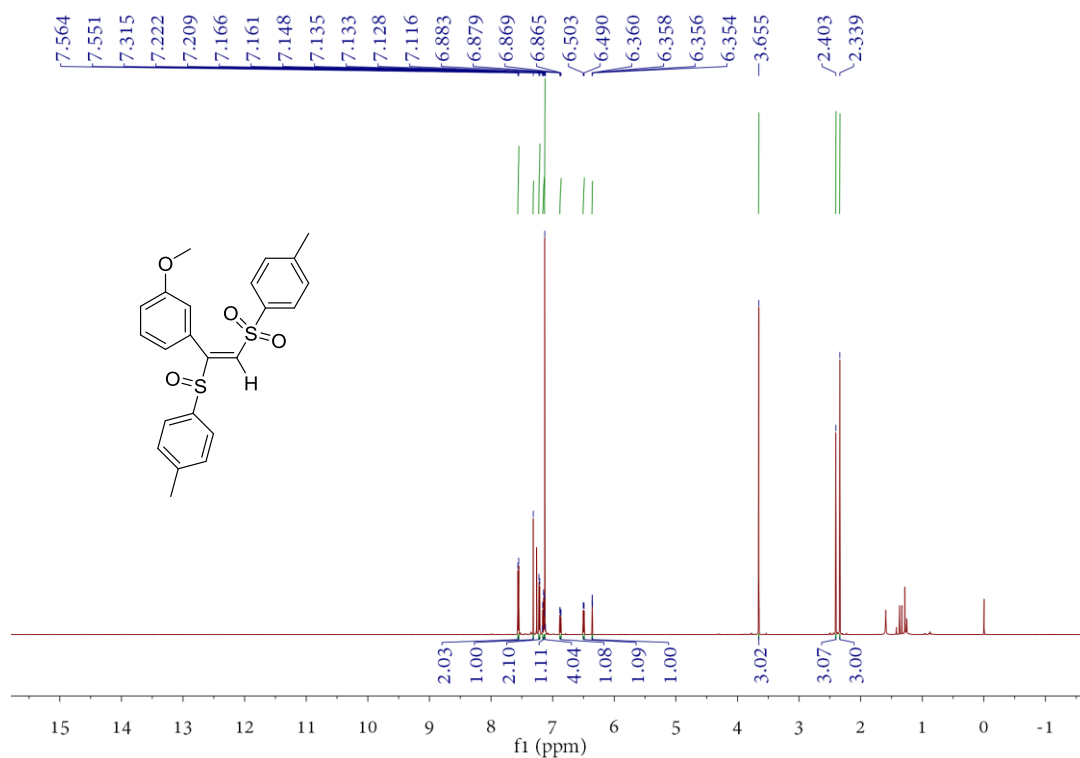
<sup>19</sup>F NMR spectrum of compound **3j**



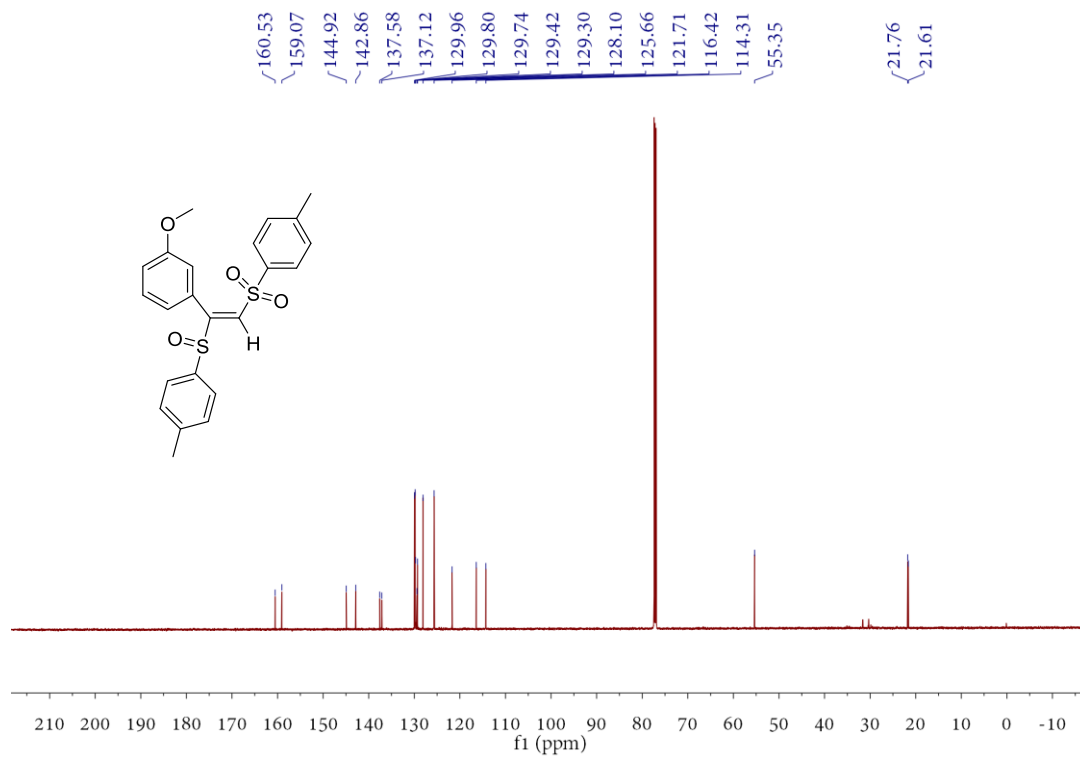
**<sup>1</sup>H NMR spectrum of compound 3k**



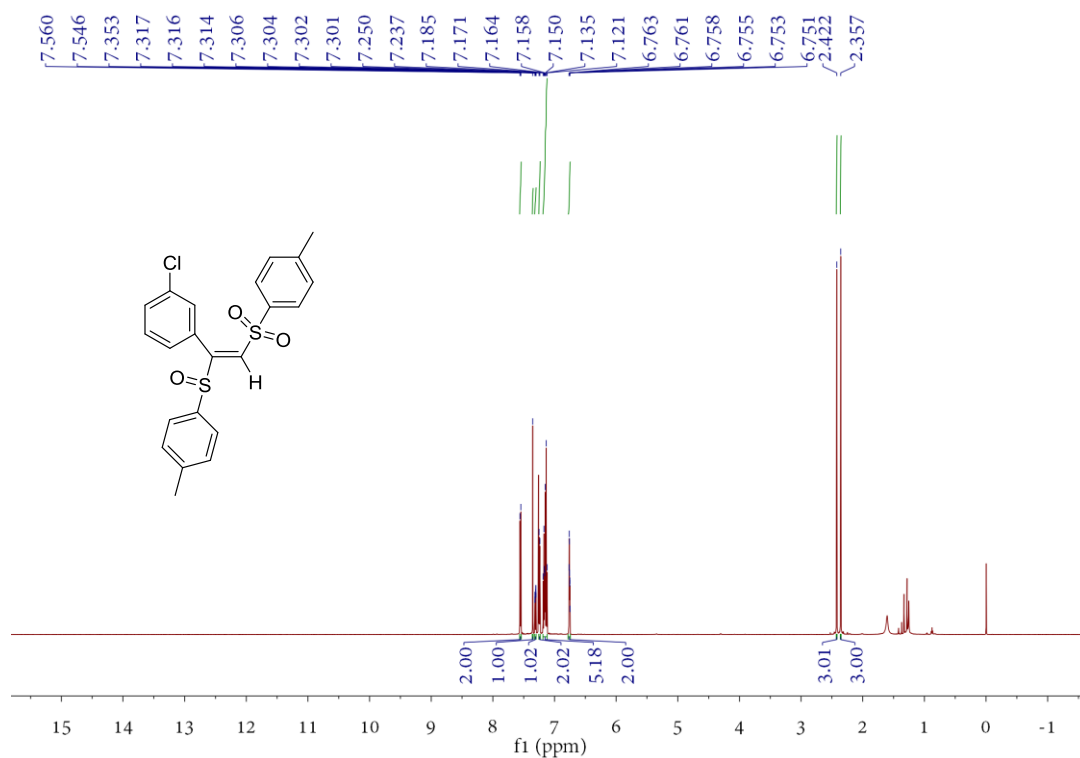
**<sup>13</sup>C NMR spectrum of compound 3k**



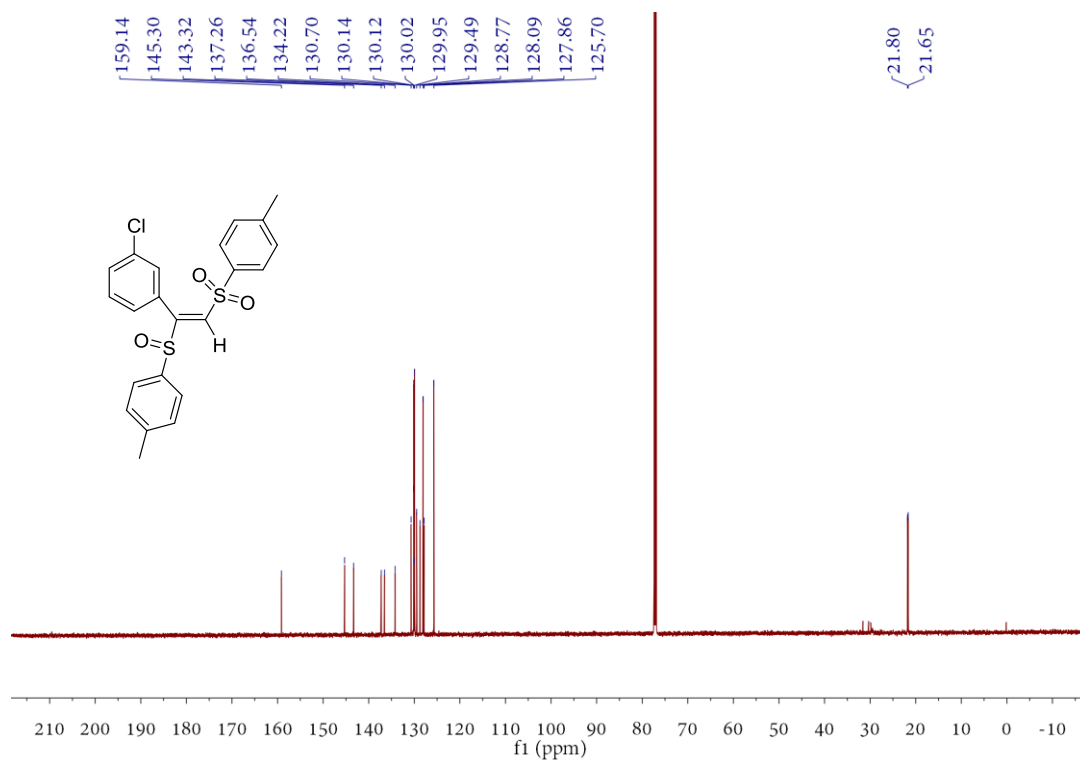
<sup>1</sup>H NMR spectrum of compound 31



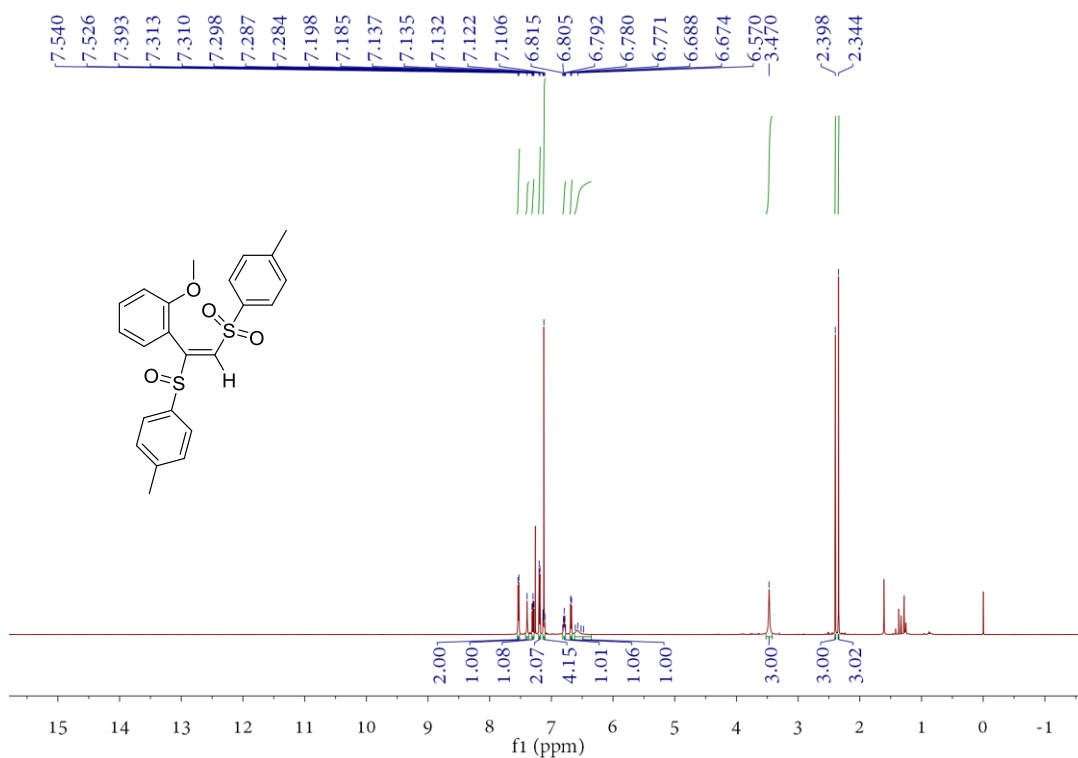
<sup>13</sup>C NMR spectrum of compound 31



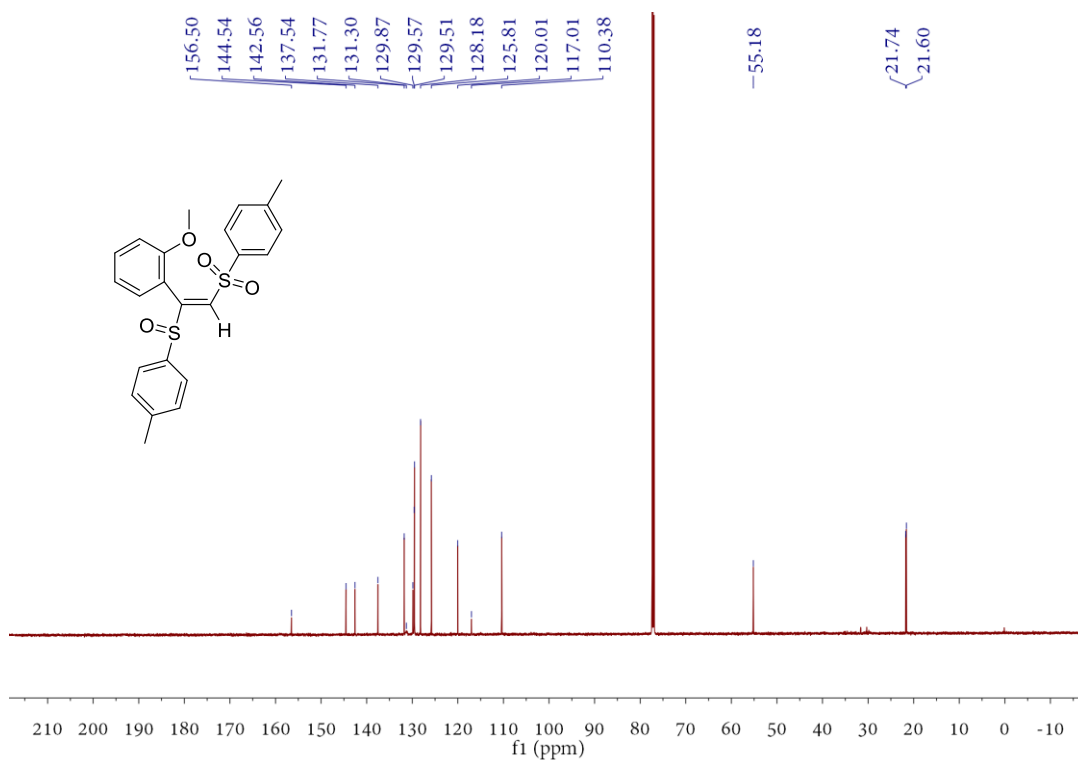
**<sup>1</sup>H NMR spectrum of compound **3m****



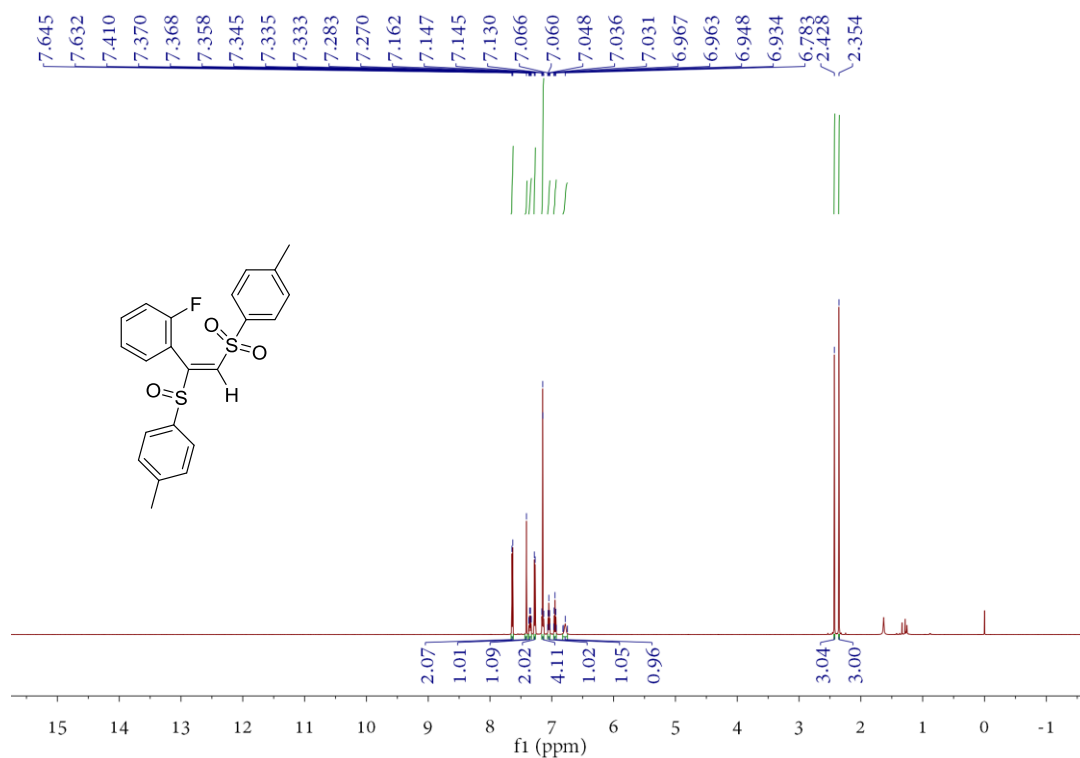
**<sup>13</sup>C NMR spectrum of compound **3m****



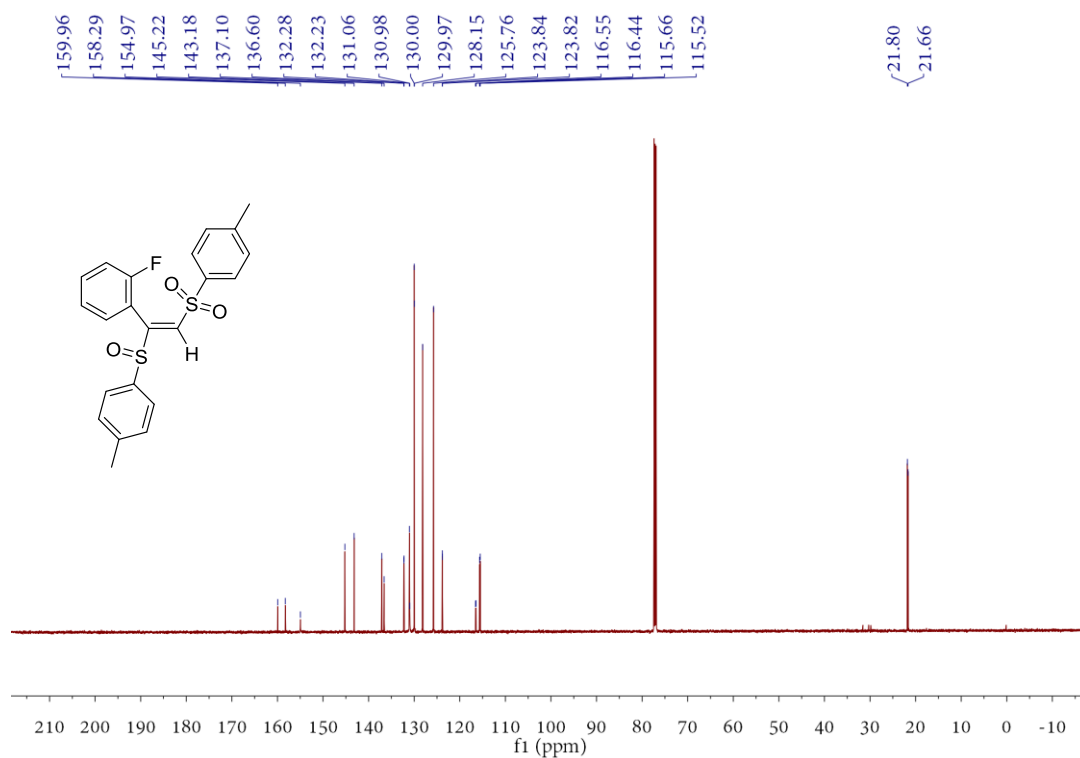
**<sup>1</sup>H NMR spectrum of compound 3n**



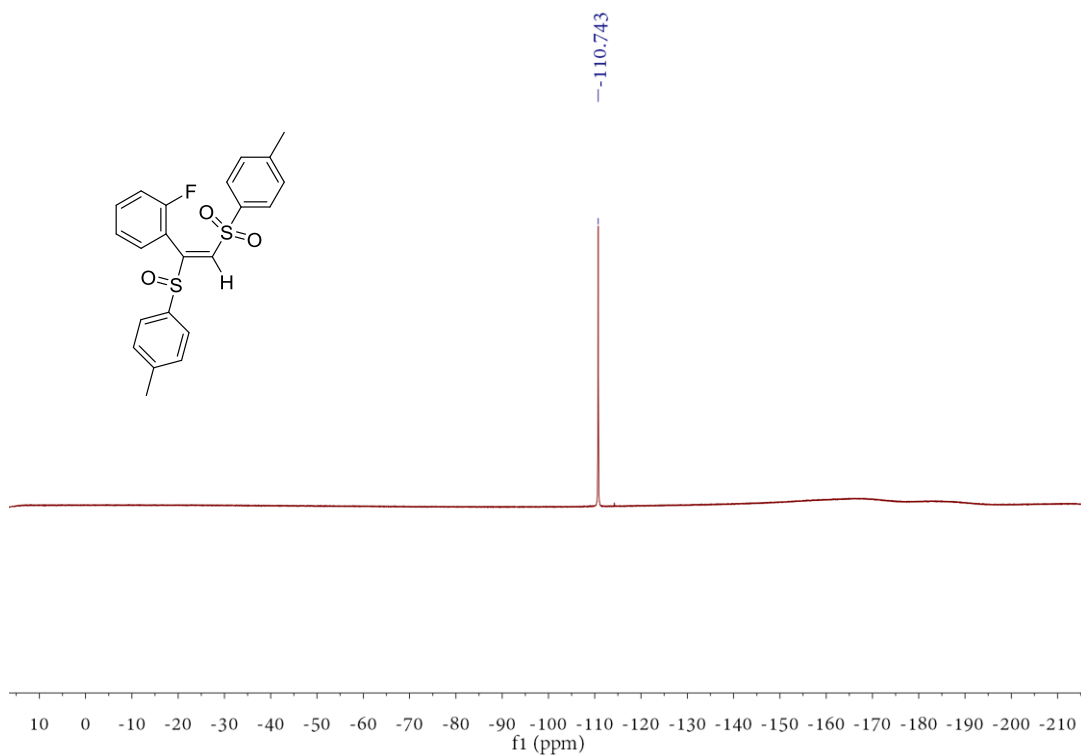
**<sup>13</sup>C NMR spectrum of compound 3n**



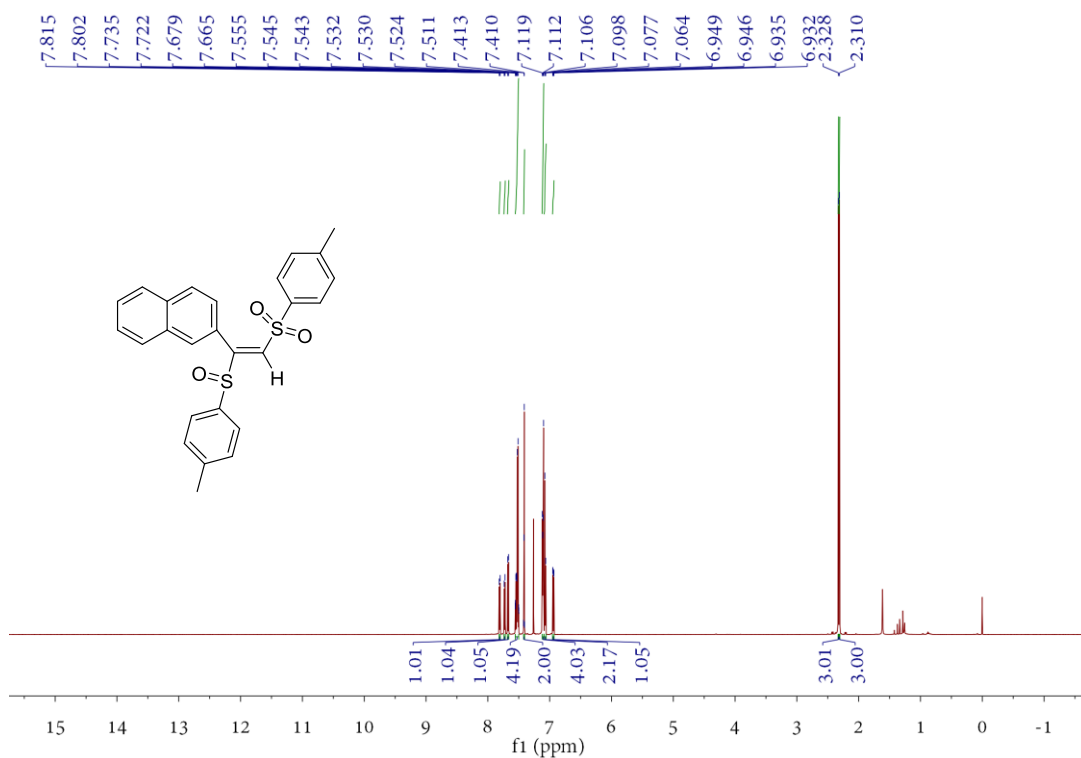
**<sup>1</sup>H NMR spectrum of compound 3o**



**<sup>13</sup>C NMR spectrum of compound 3o**

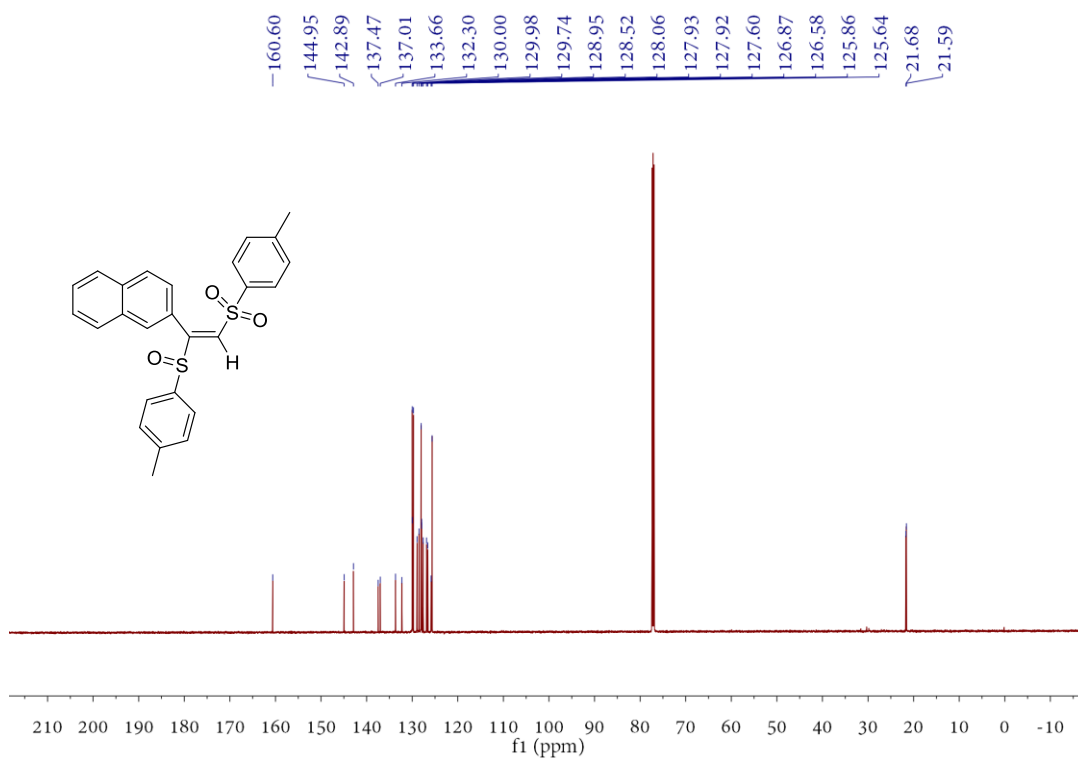


$^{19}\text{F}$  NMR spectrum of compound **3o**

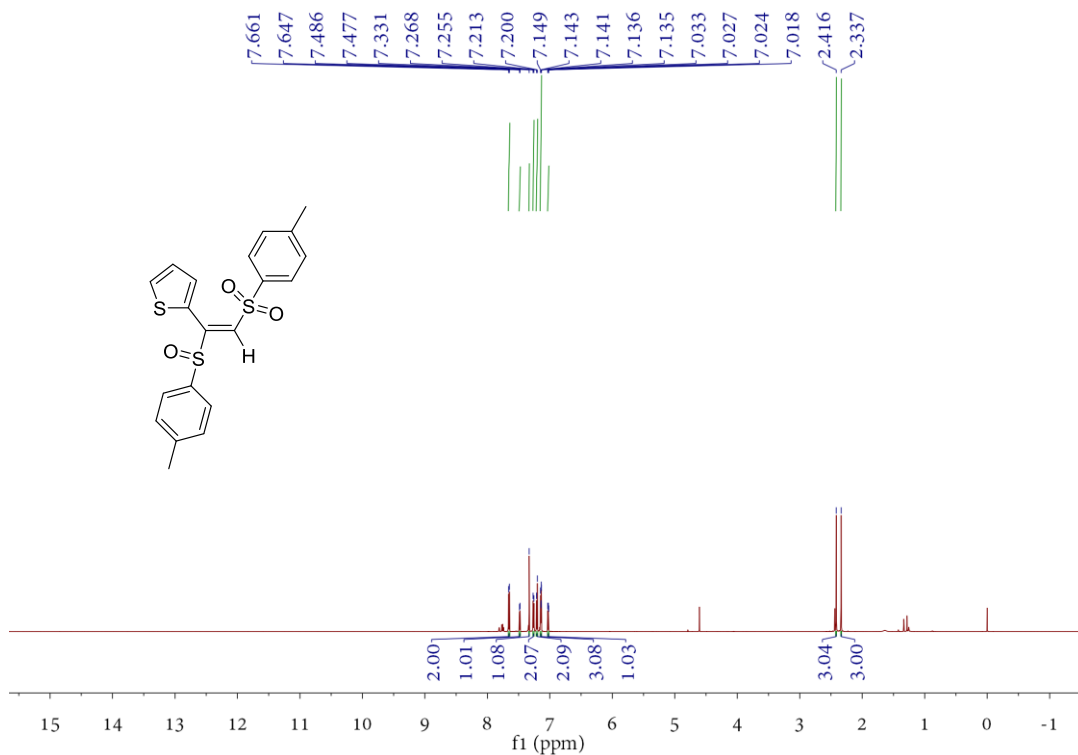


$^1\text{H}$  NMR spectrum of compound **3p**

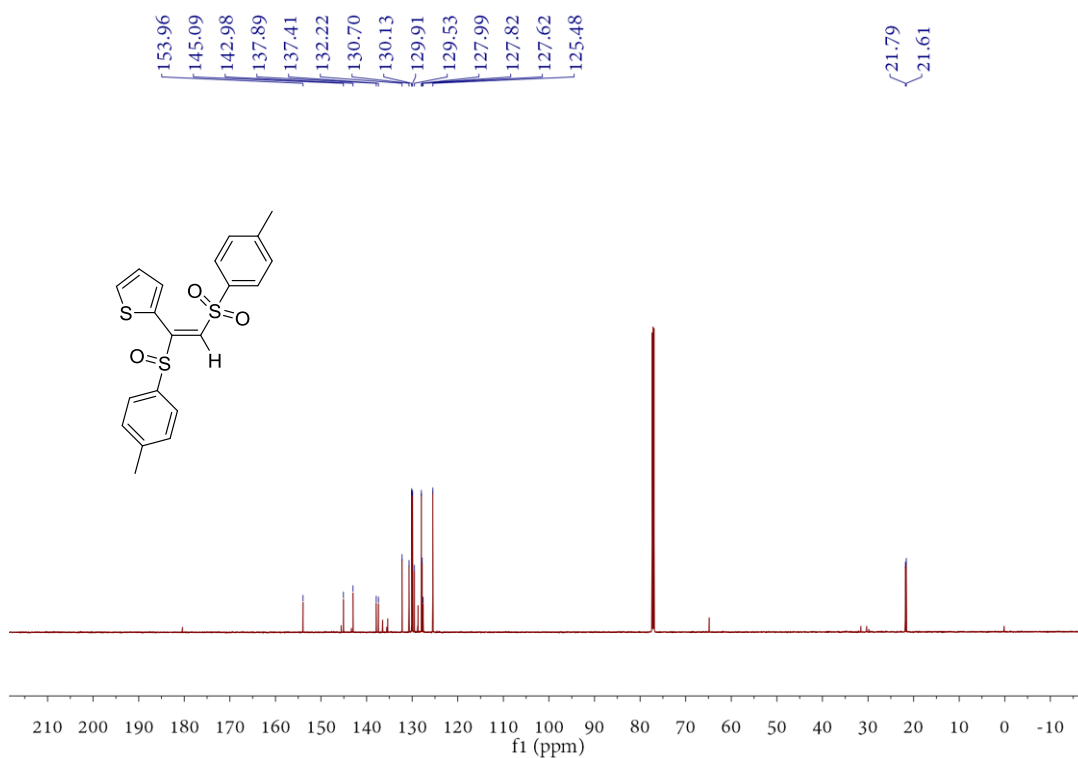




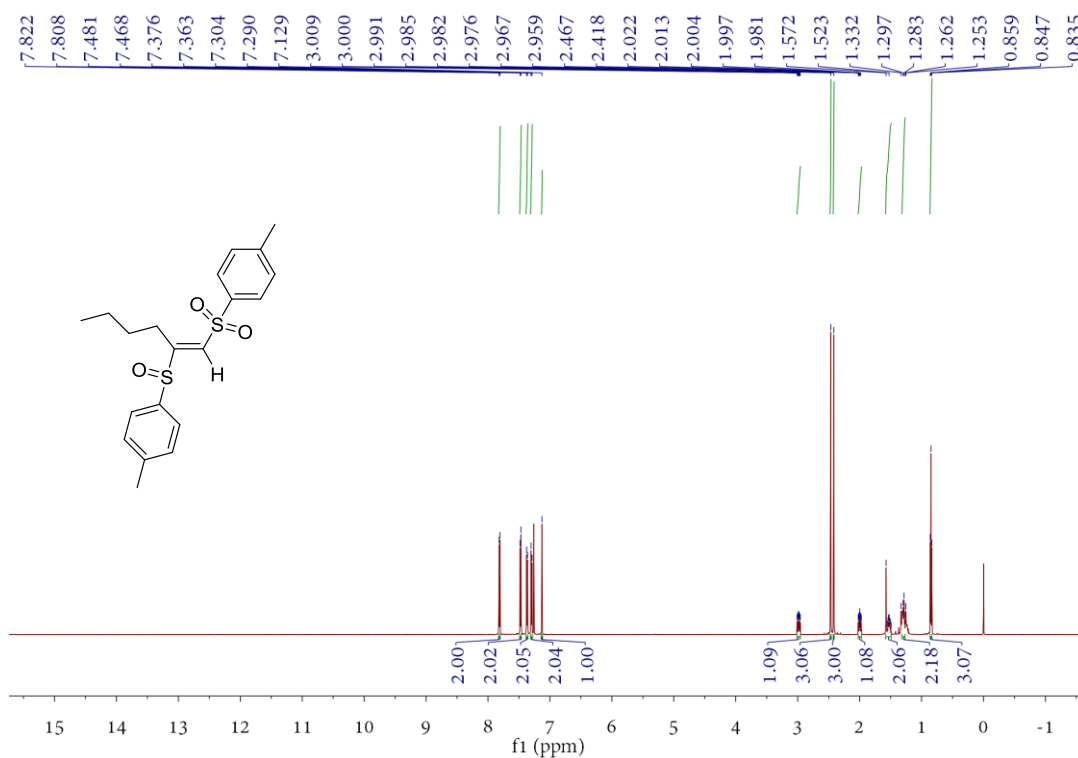
$^{13}\text{C}$  NMR spectrum of compound **3p**



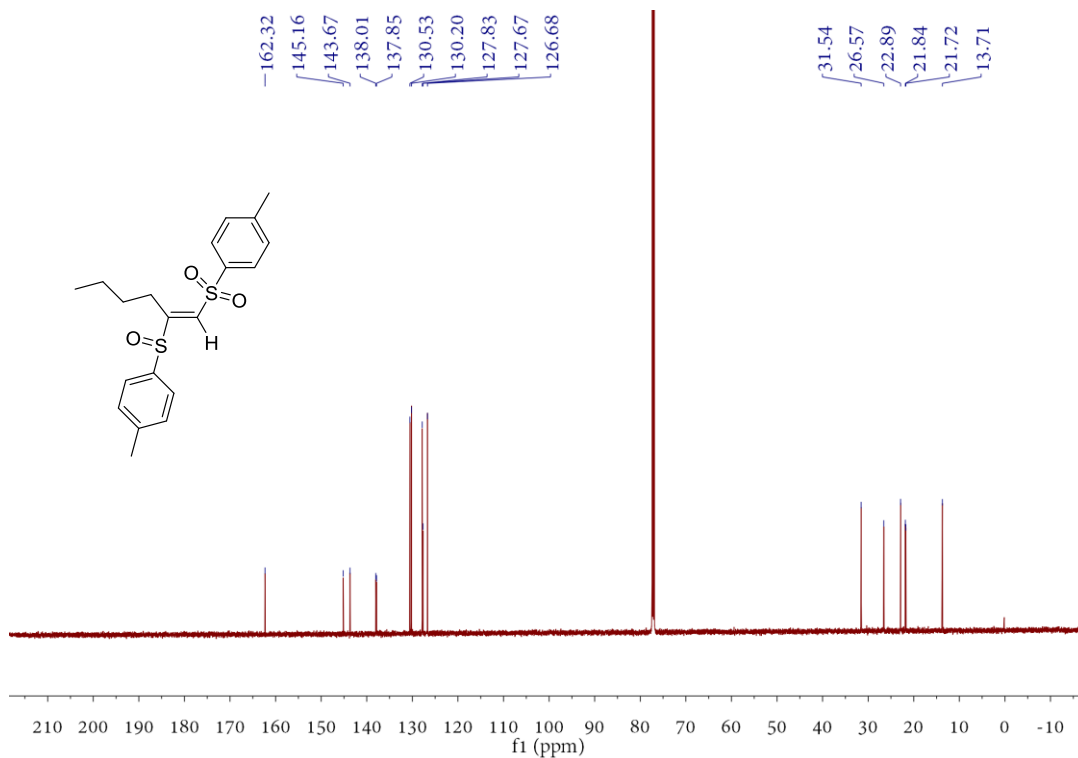
$^1\text{H}$  NMR spectrum of compound **3q**



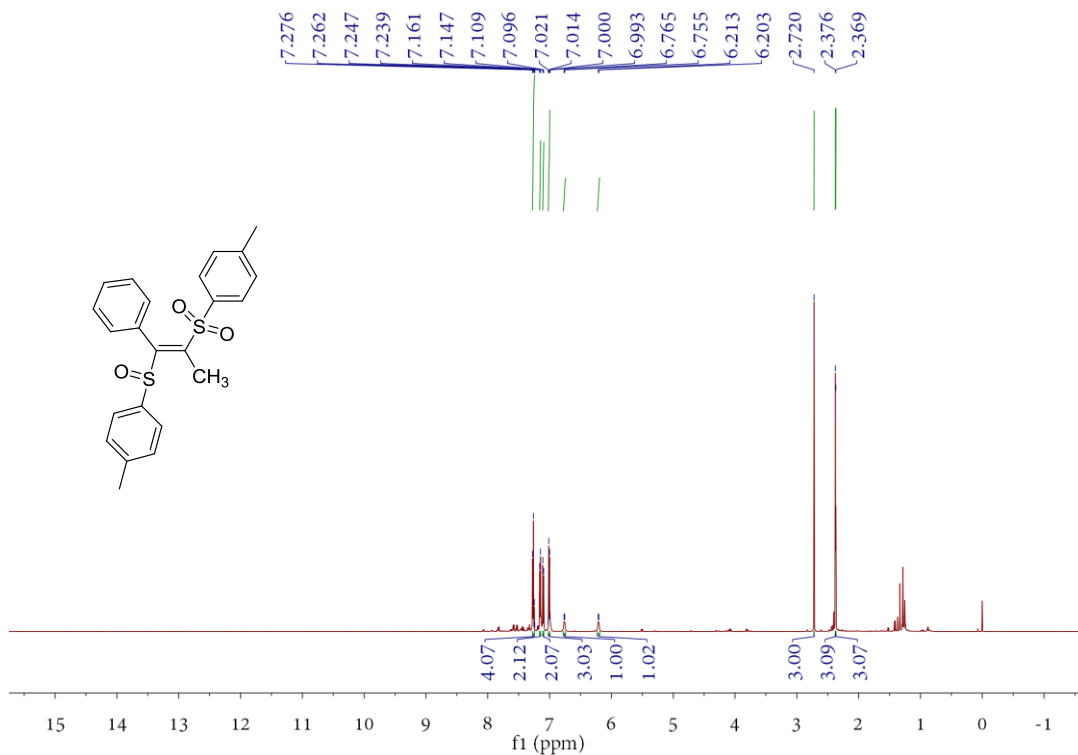
<sup>13</sup>C NMR spectrum of compound **3q**



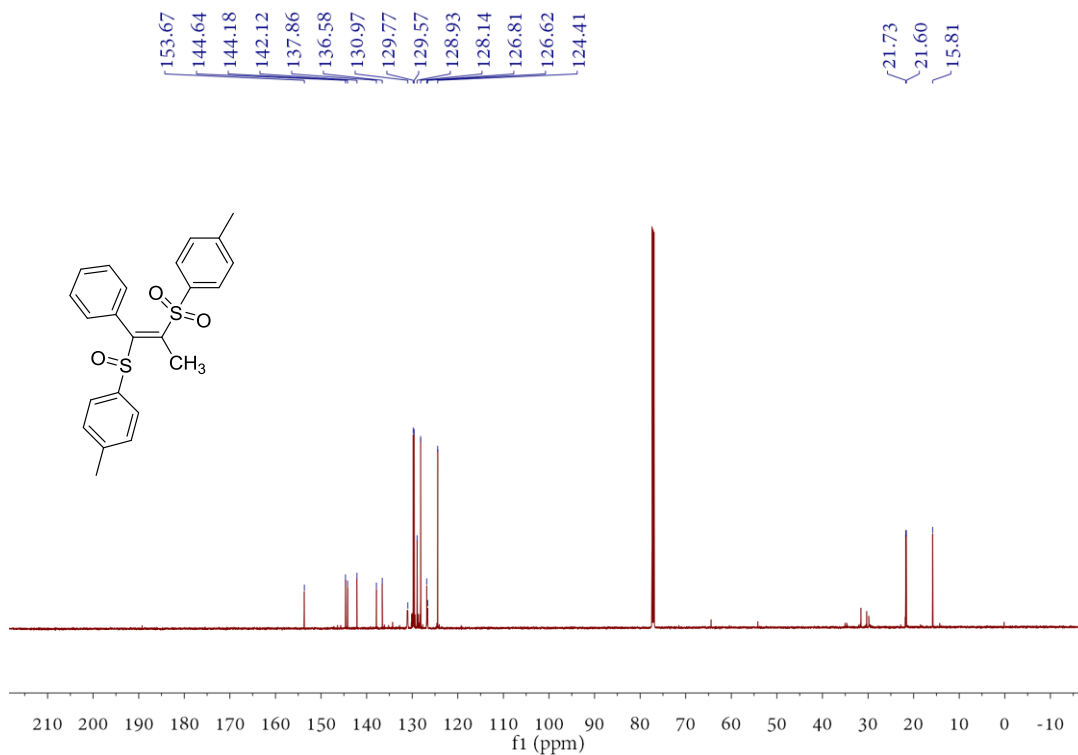
<sup>1</sup>H NMR spectrum of compound **3r**



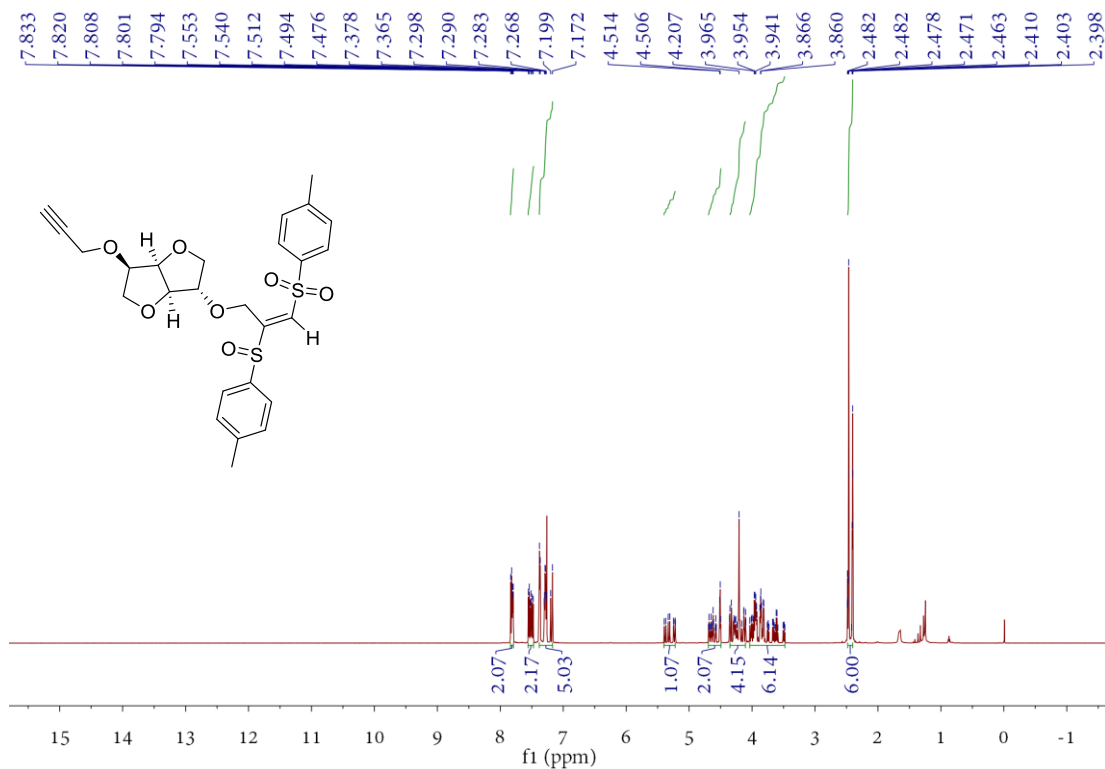
<sup>13</sup>C NMR spectrum of compound **3r**



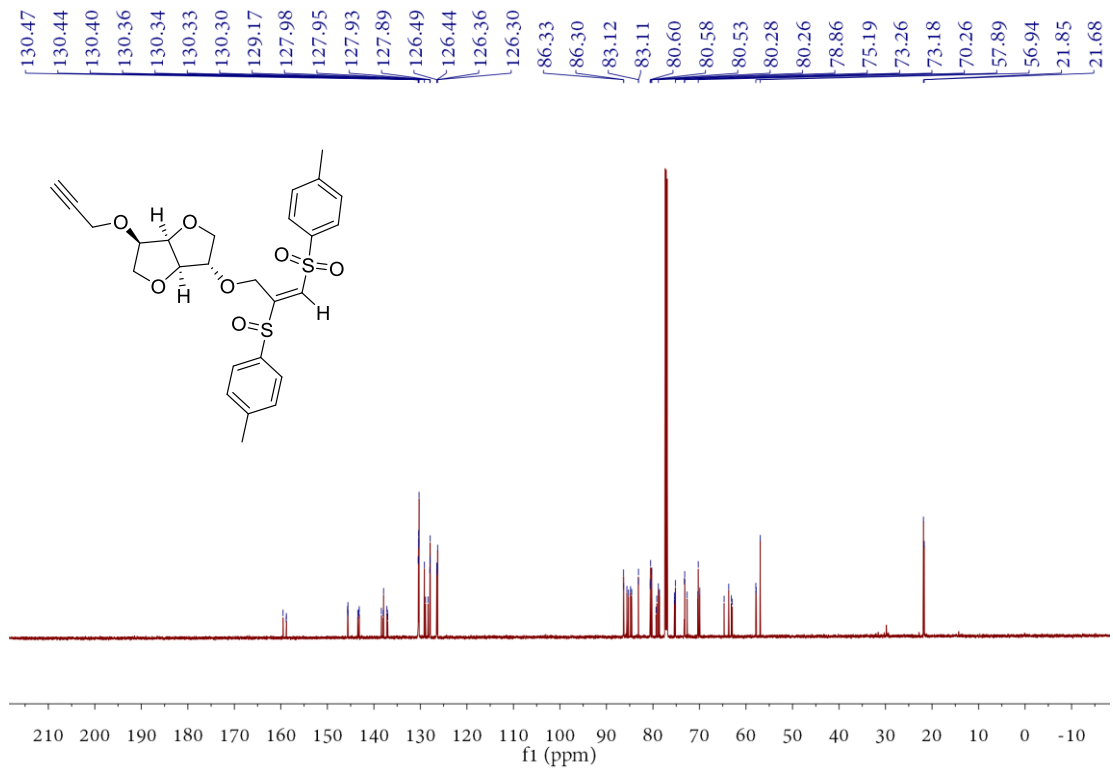
<sup>1</sup>H NMR spectrum of compound **3s**



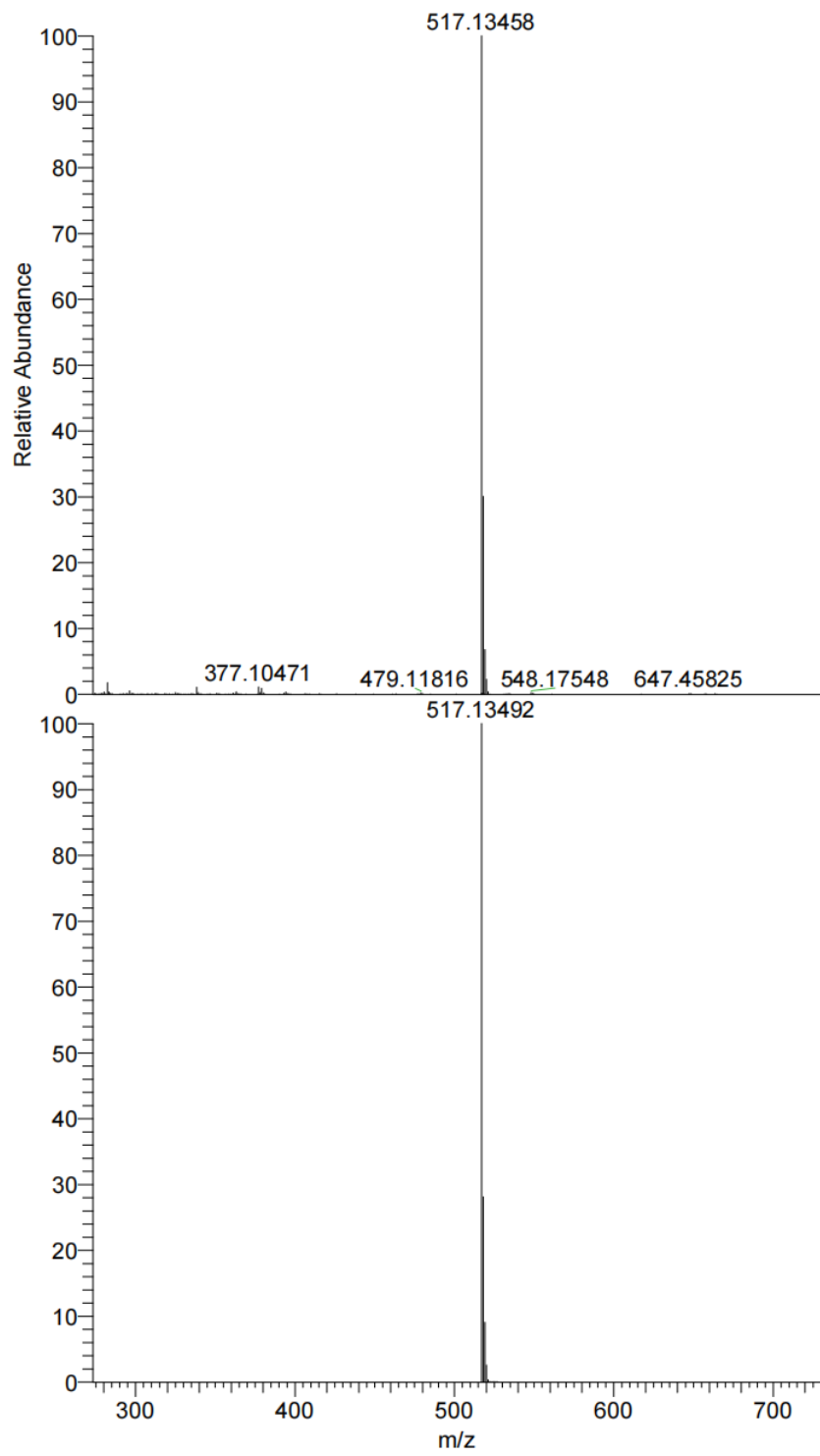
<sup>13</sup>C NMR spectrum of compound **3s**



<sup>1</sup>H NMR spectrum of compound **3t**



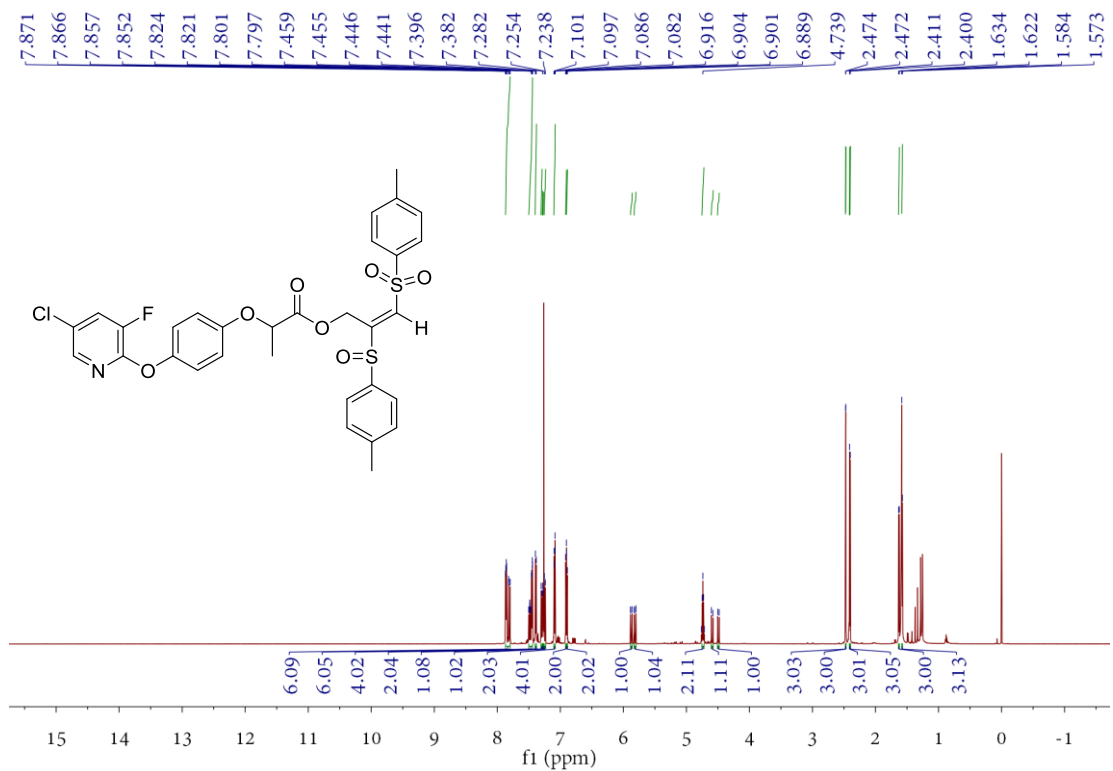
<sup>13</sup>C NMR spectrum of compound **3t**



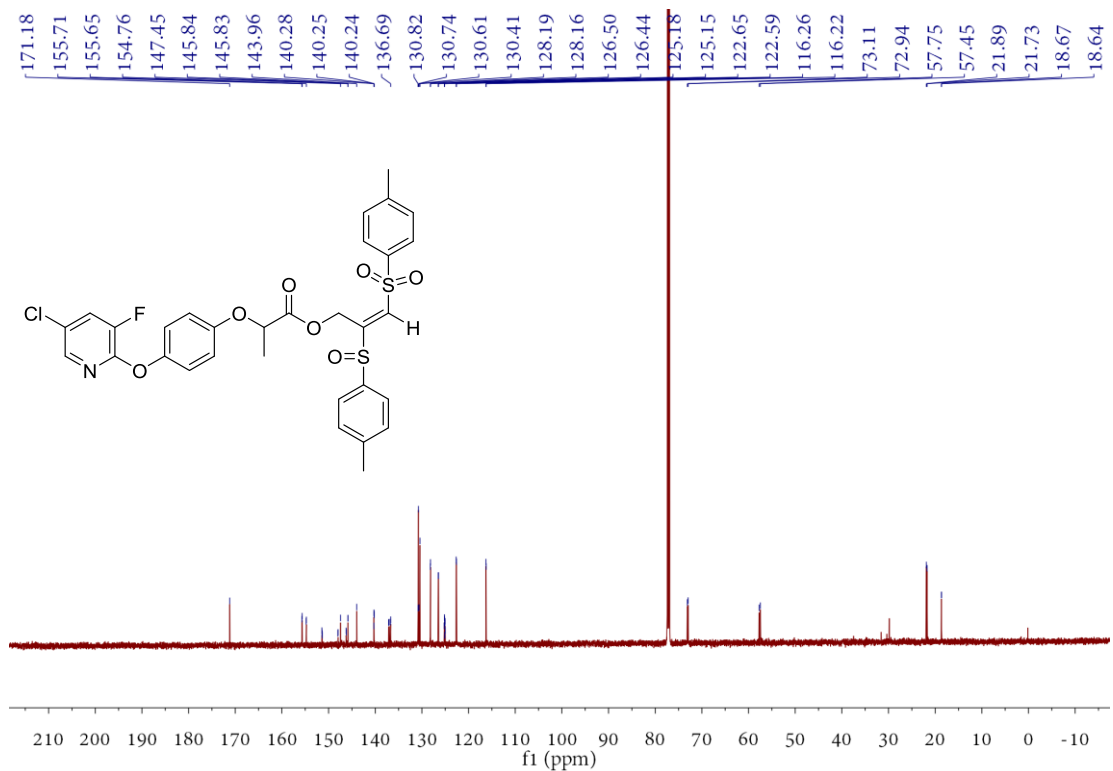
NL:  
8.53E9  
5\_20230313091839#20  
RT: 0.20 AV: 1 T:  
FTMS + c APCI corona  
Full ms  
[66.7000-1000.0000]

NL:  
6.68E5  
C<sub>26</sub>H<sub>28</sub>S<sub>2</sub>O<sub>7</sub> +H:  
C<sub>26</sub>H<sub>29</sub>S<sub>2</sub>O<sub>7</sub>  
pa Chrg 1

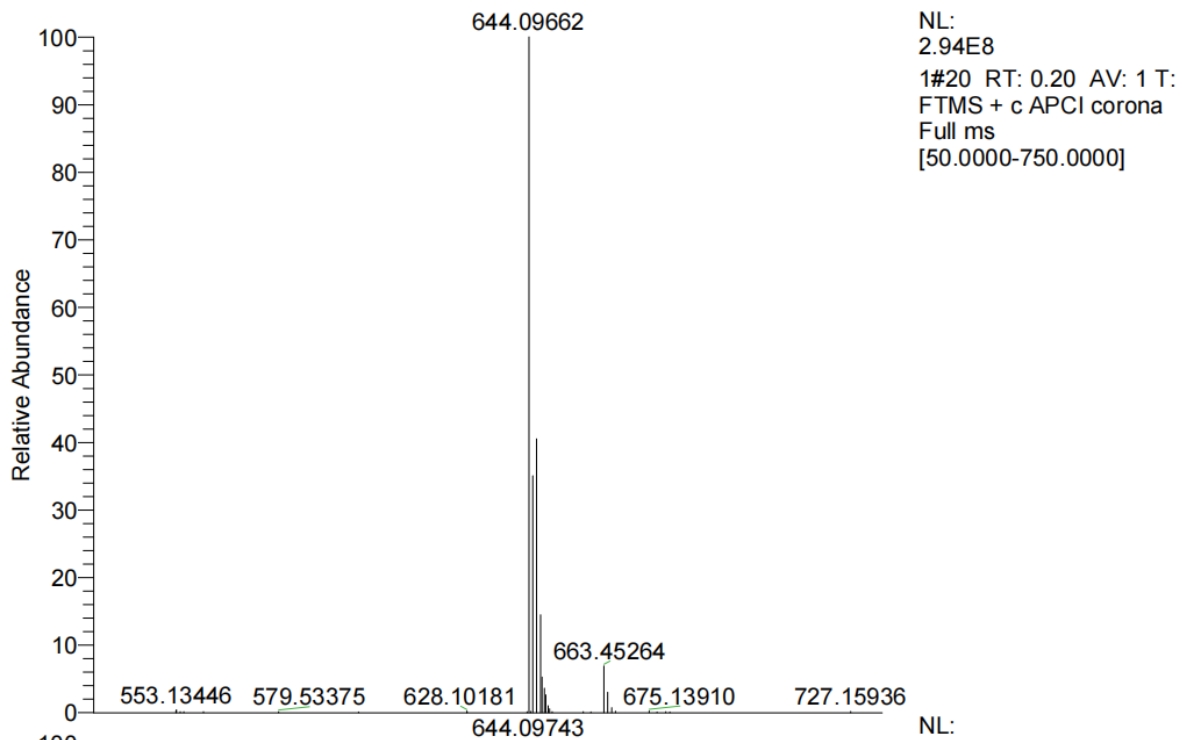
HRMS of compound **3t**



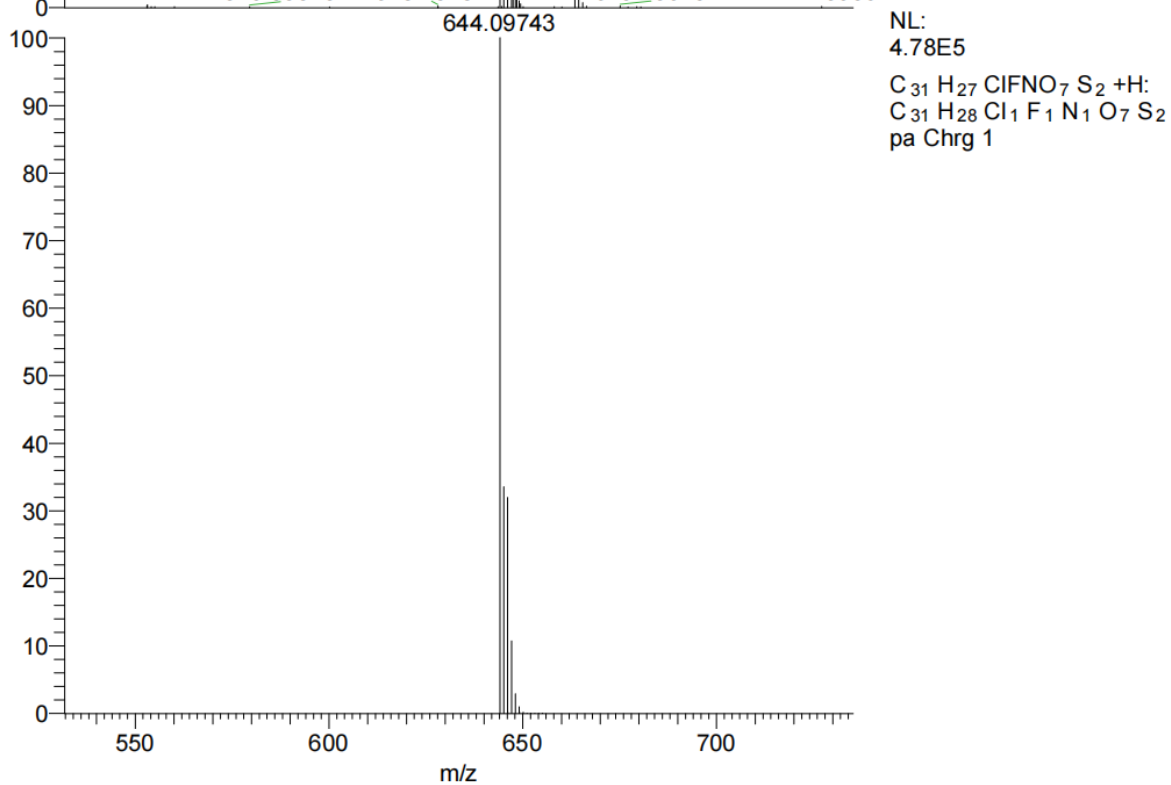
**<sup>1</sup>H NMR spectrum of compound 3u**



**<sup>13</sup>C NMR spectrum of compound 3u**



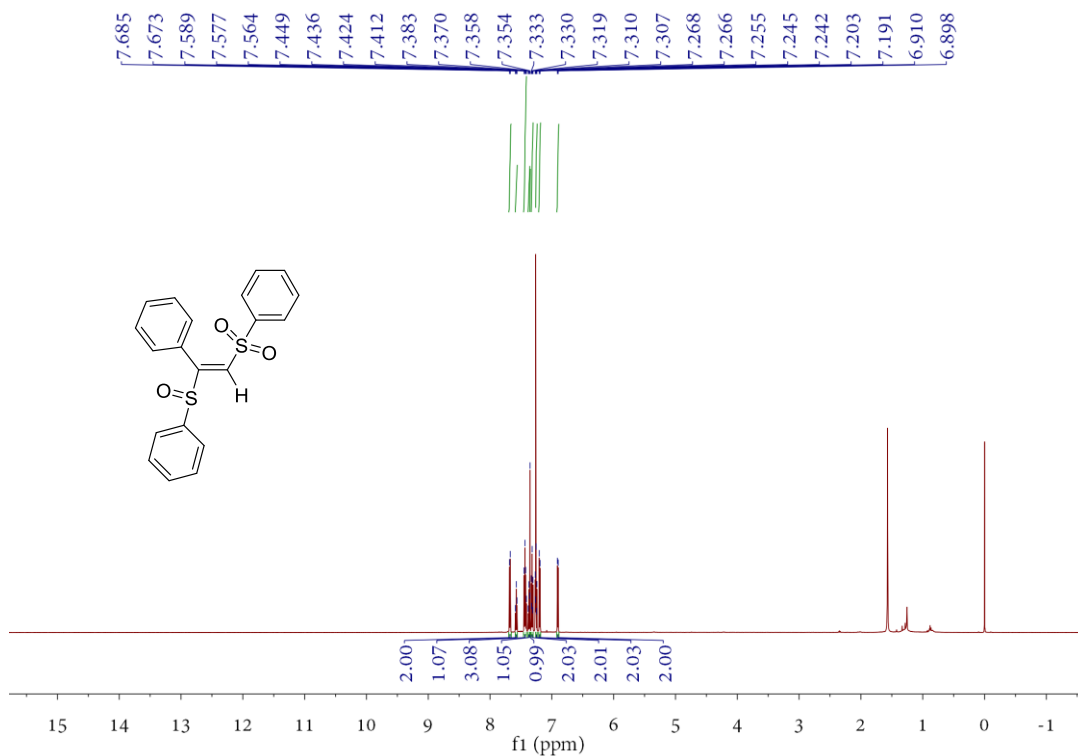
NL:  
2.94E8  
1#20 RT: 0.20 AV: 1 T:  
FTMS + c APCI corona  
Full ms  
[50.0000-750.0000]



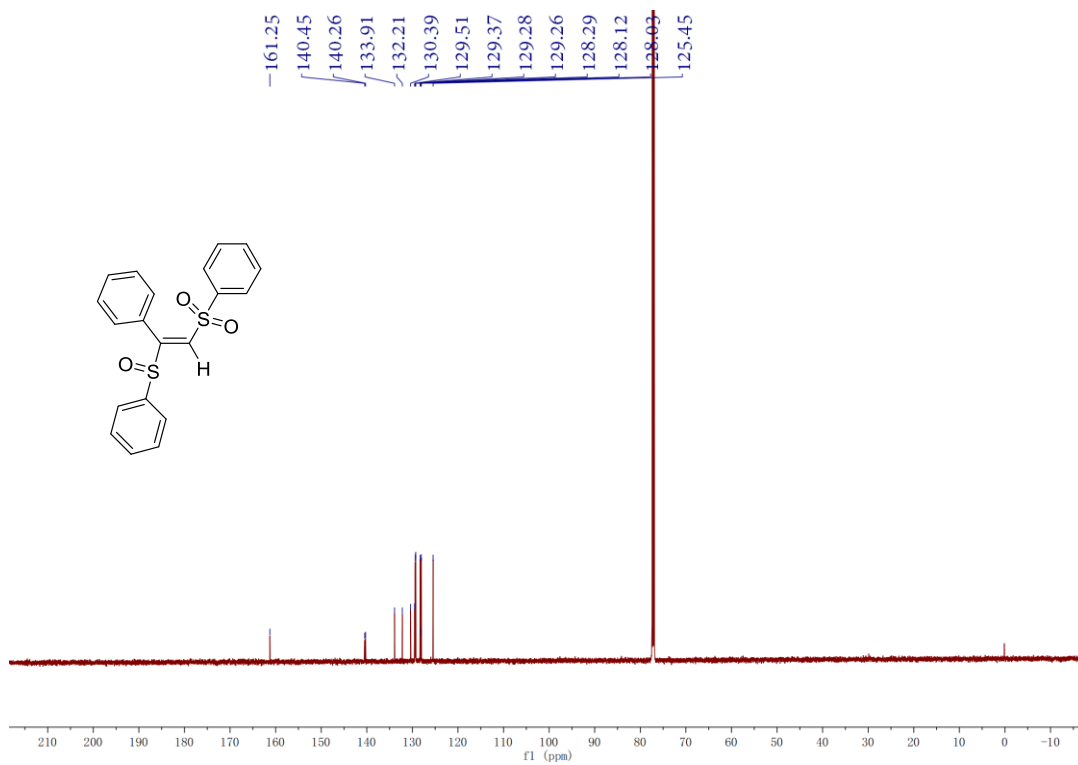
NL:  
4.78E5  
C<sub>31</sub>H<sub>27</sub>ClFNO<sub>7</sub>S<sub>2</sub> +H:  
C<sub>31</sub>H<sub>28</sub>Cl<sub>1</sub>F<sub>1</sub>N<sub>1</sub>O<sub>7</sub>S<sub>2</sub>  
pa Chrg 1

HRMS of compound **3u**

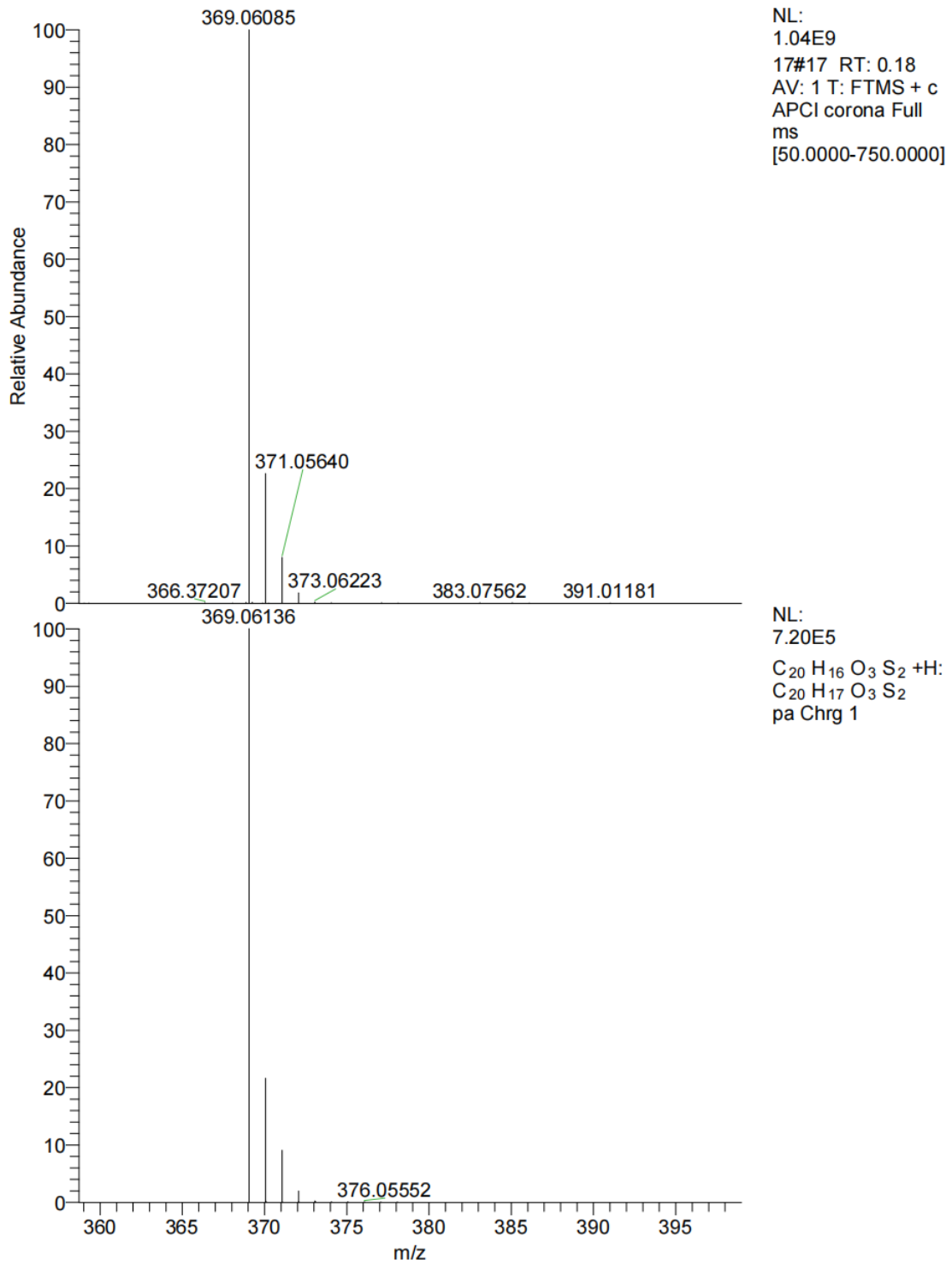




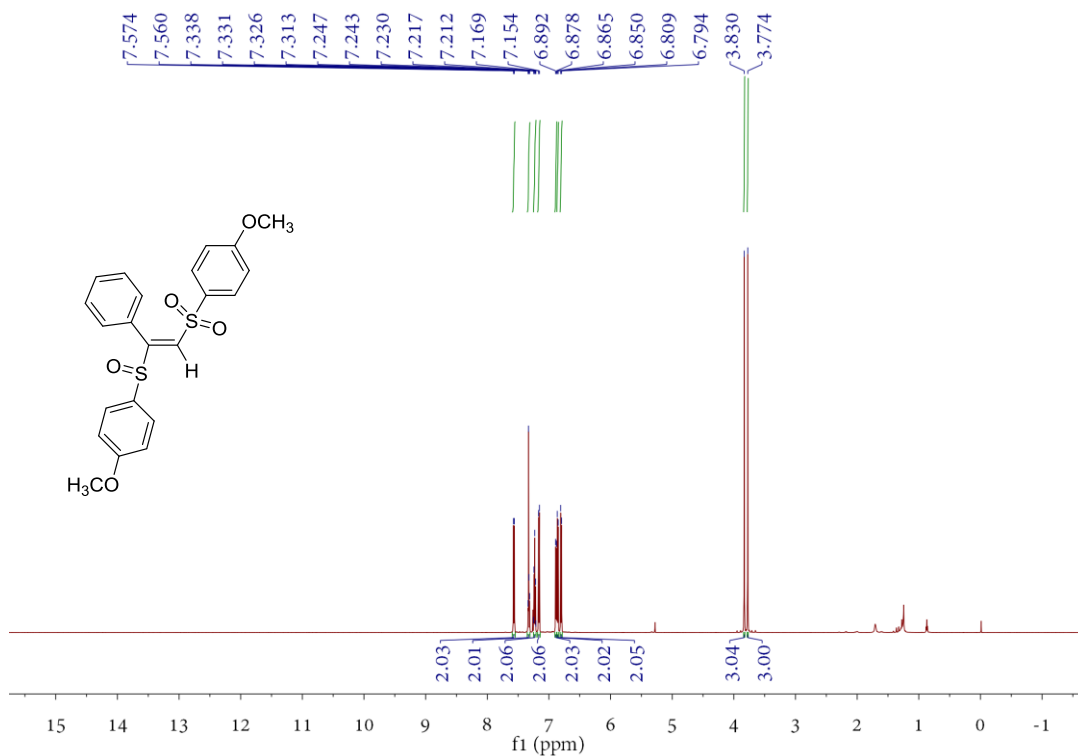
<sup>1</sup>H NMR spectrum of compound 4a



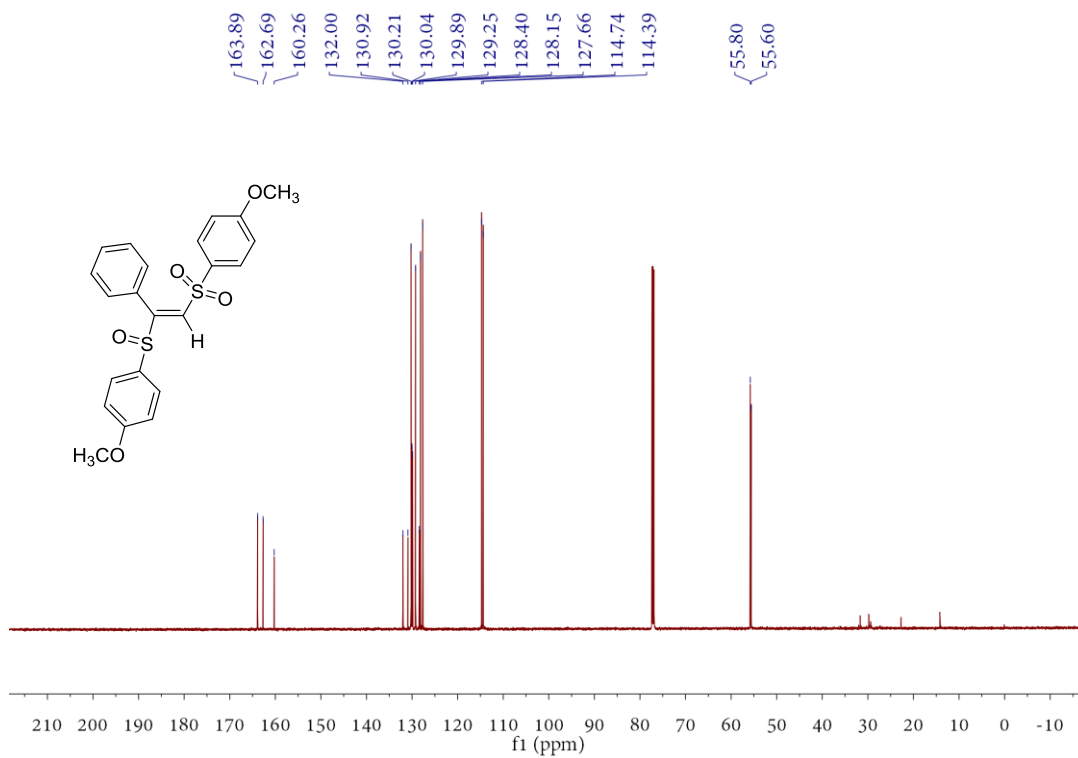
<sup>13</sup>C NMR spectrum of compound 4a



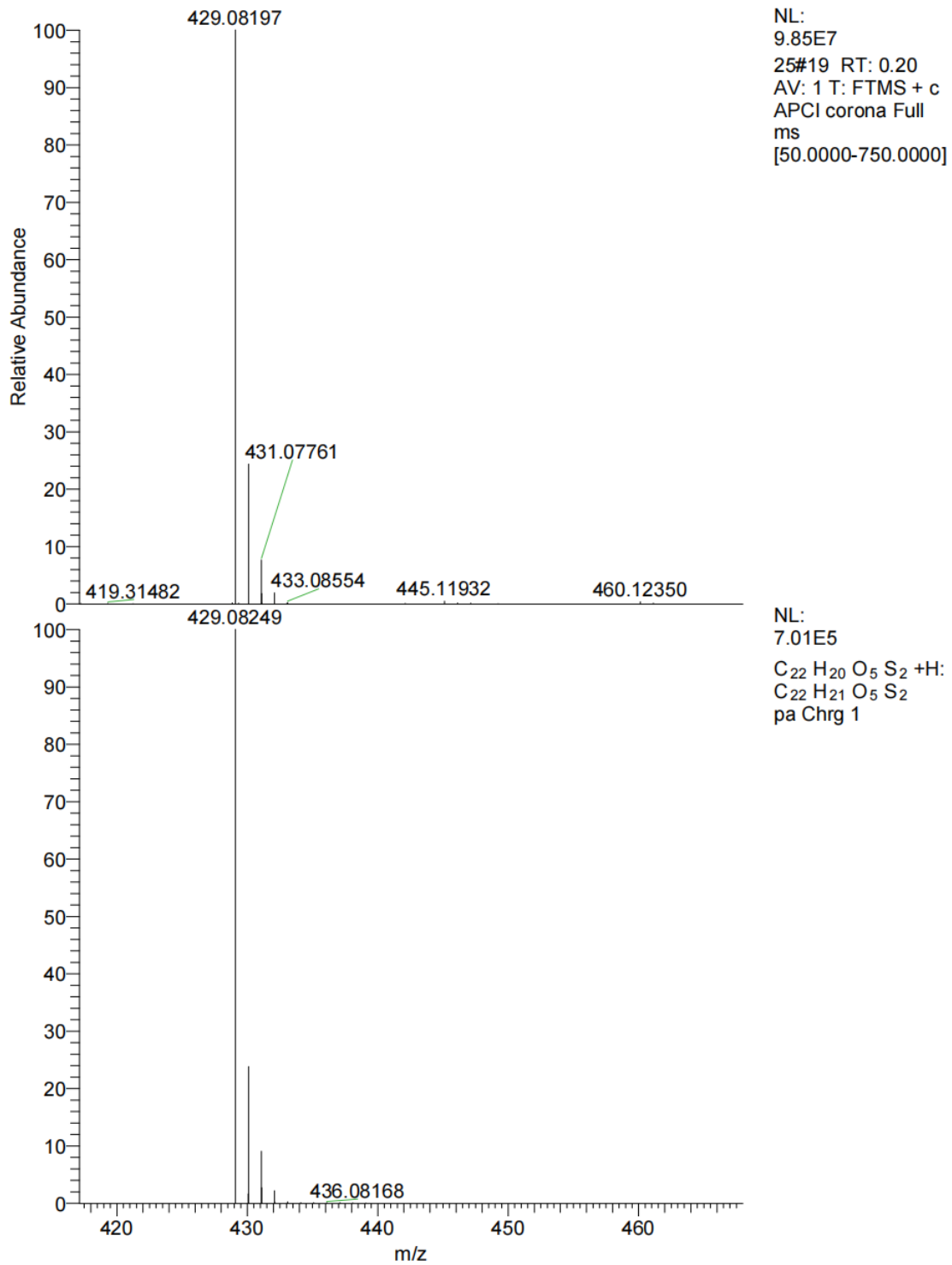
HRMS spectrum of compound **4a**



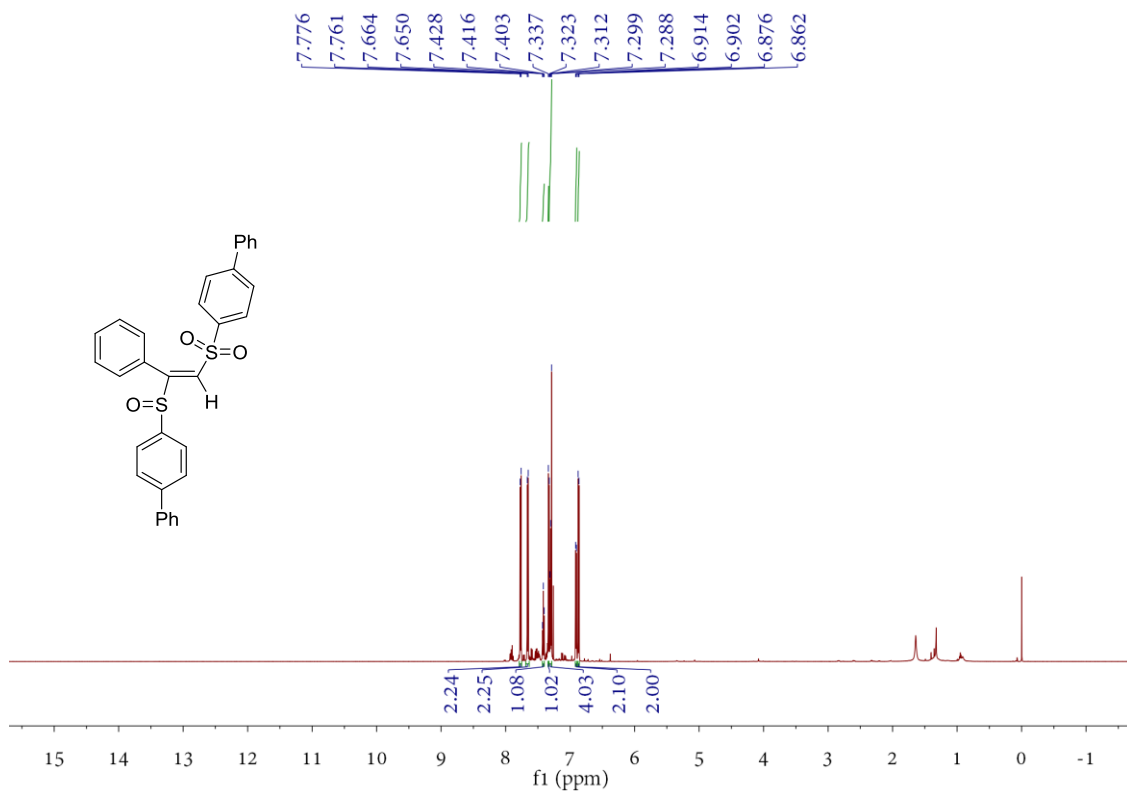
**<sup>1</sup>H NMR spectrum of compound 4b**



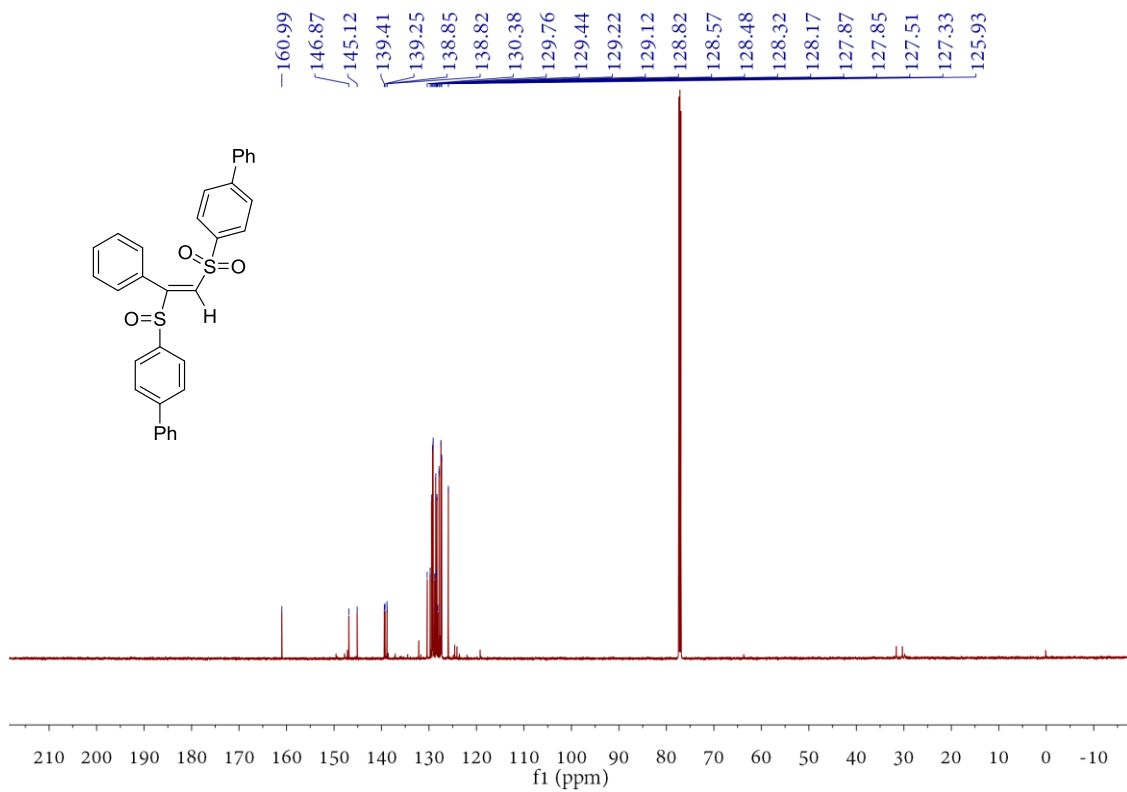
**<sup>13</sup>C NMR spectrum of compound 4b**



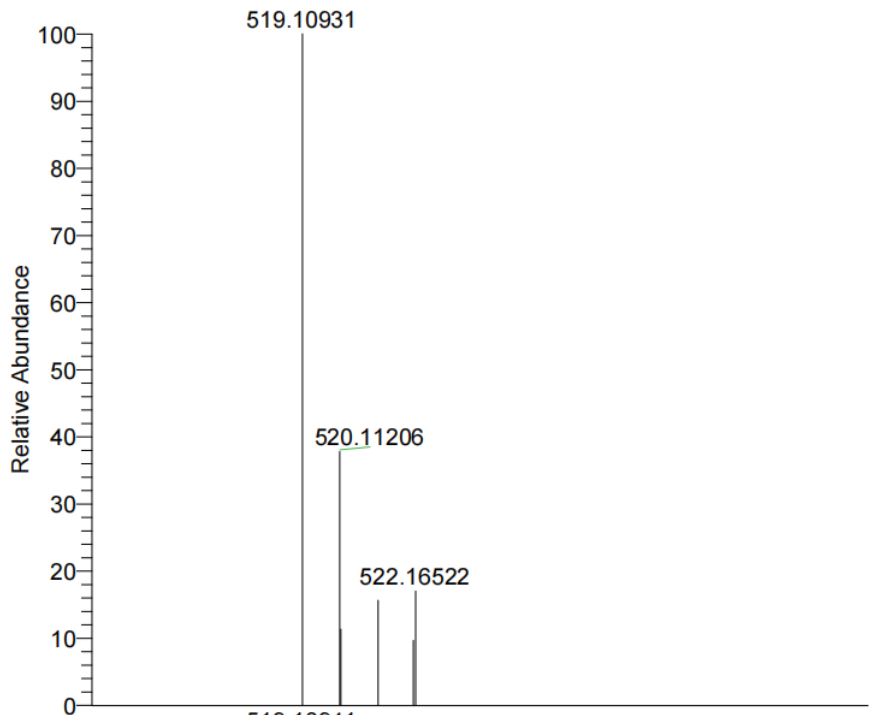
HRMS of compound **4b**



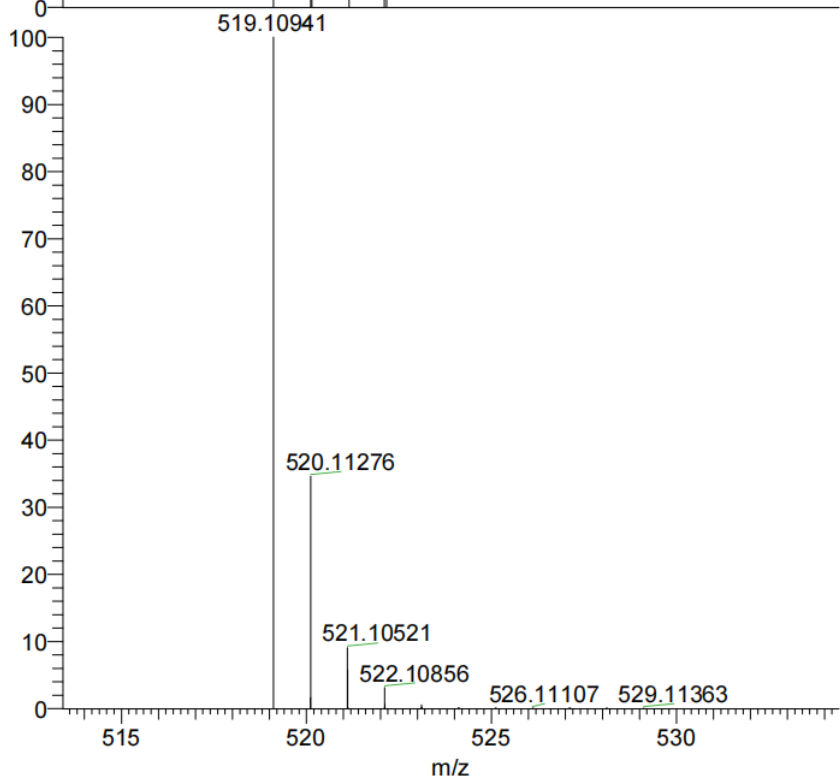
**<sup>1</sup>H NMR spectrum of compound 4c**



**<sup>13</sup>C NMR spectrum of compound 4c**

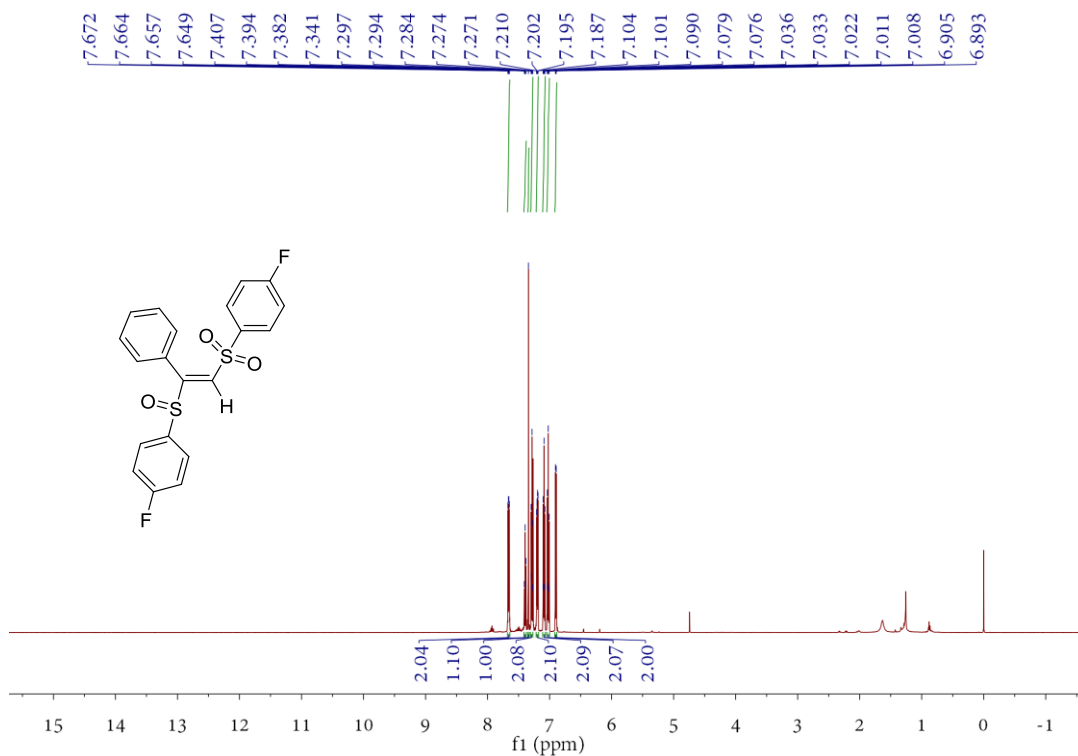


NL:  
6.37E6  
10#15 RT: 0.14  
AV: 1 T: FTMS - c  
APCI corona Full  
ms  
[50.0000-750.0000]

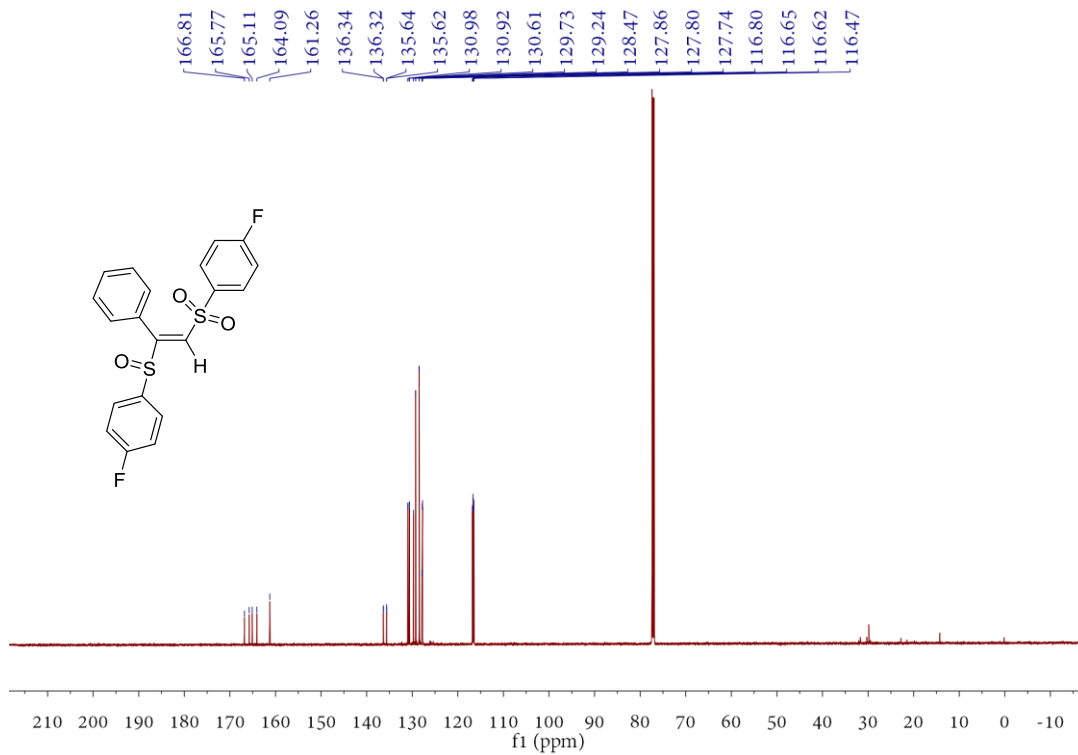


NL:  
6.32E5  
C<sub>32</sub> H<sub>24</sub> O<sub>3</sub> S<sub>2</sub> +H:  
C<sub>32</sub> H<sub>23</sub> O<sub>3</sub> S<sub>2</sub>  
pa Chrg -1

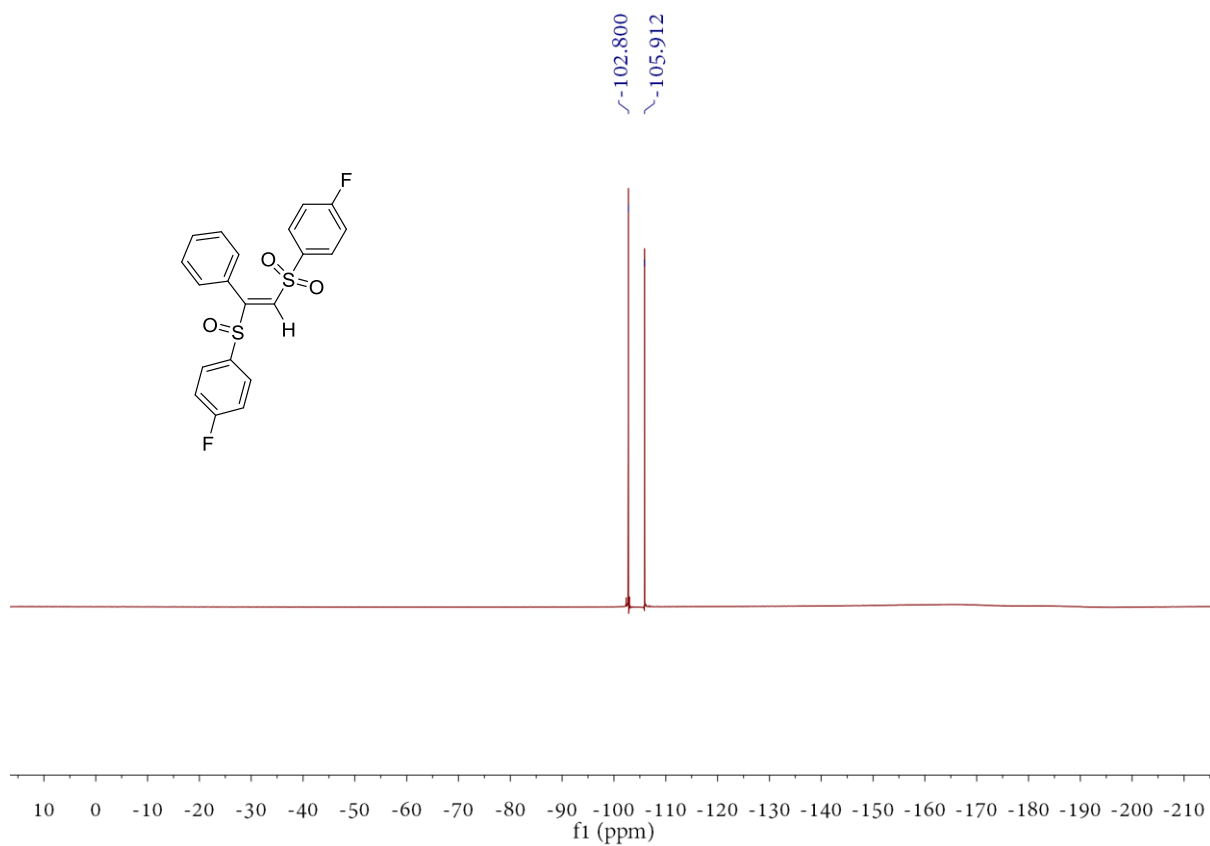
HRMS of compound 4c



<sup>1</sup>H NMR spectrum of compound 4d

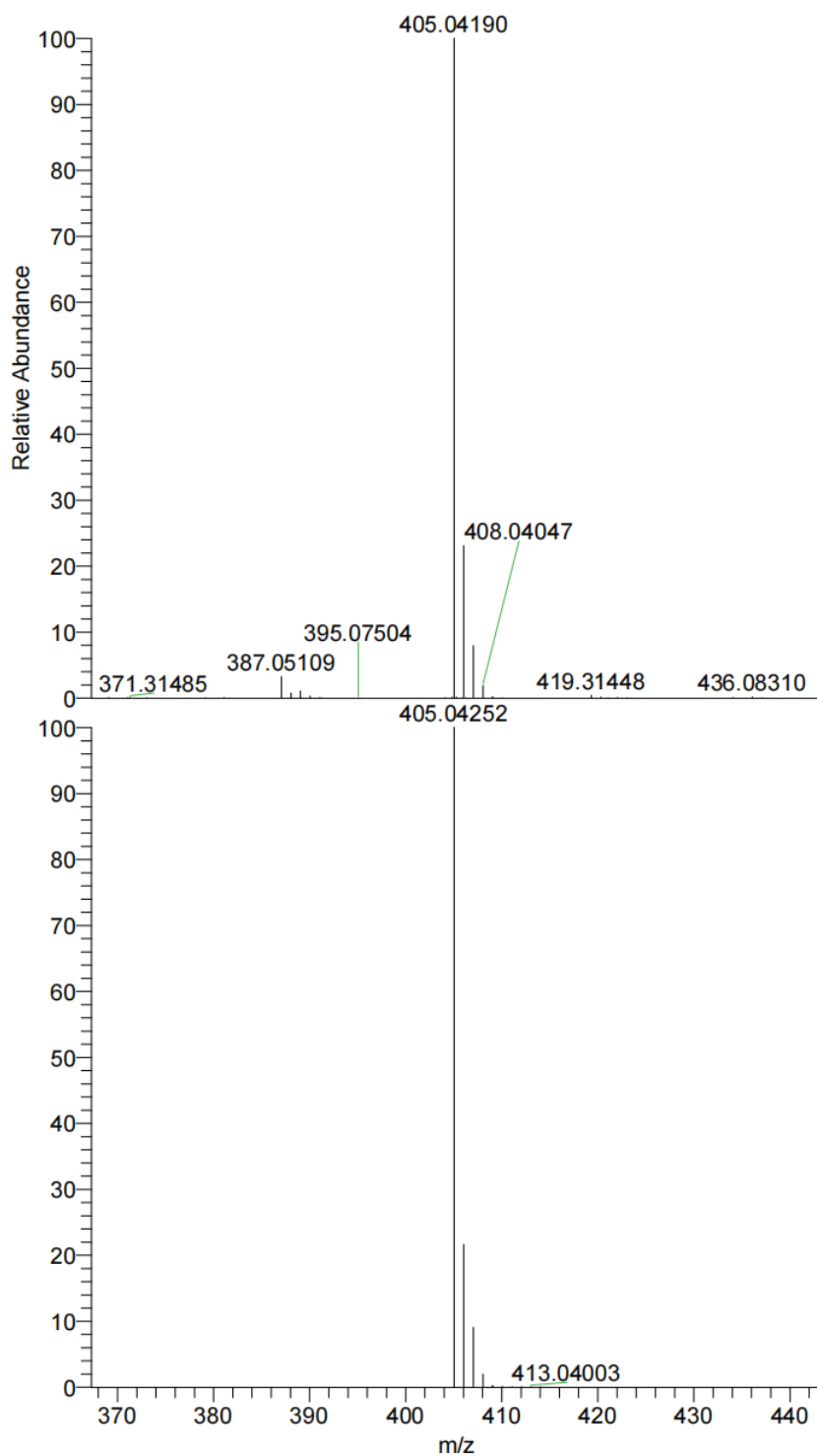


<sup>13</sup>C NMR spectrum of compound 4d



$^{19}\text{F}$  NMR spectrum of compound **4d**

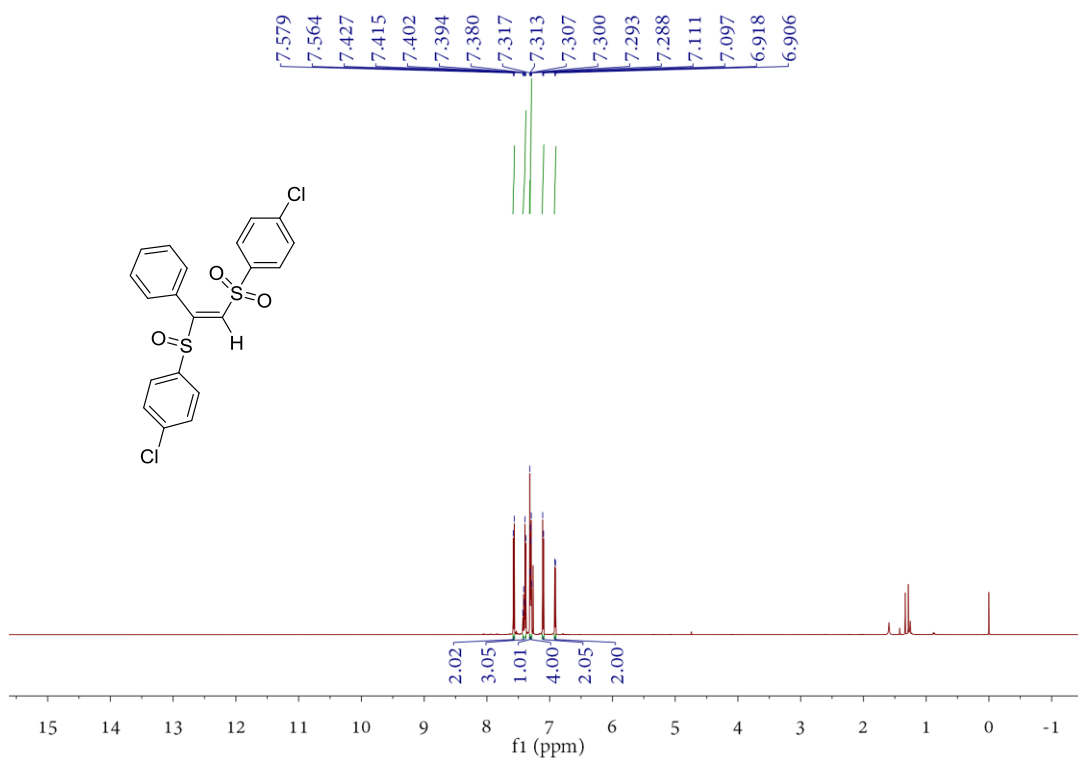




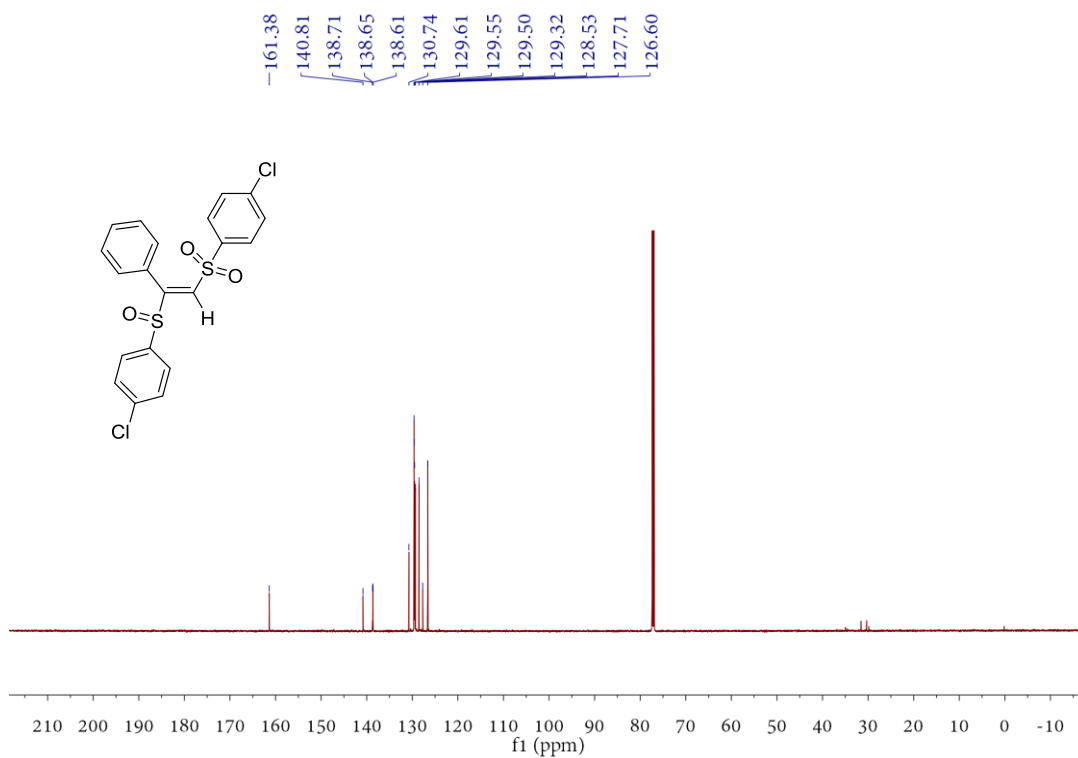
NL:  
1.07E9  
20#17 RT: 0.18 AV: 1  
T: FTMS + c APCI  
corona Full ms  
[50.0000-750.0000]

NL:  
7.20E5  
C<sub>20</sub>H<sub>14</sub>F<sub>2</sub>O<sub>3</sub>S<sub>2</sub>+H:  
C<sub>20</sub>H<sub>15</sub>F<sub>2</sub>O<sub>3</sub>S<sub>2</sub>  
pa Chrg 1

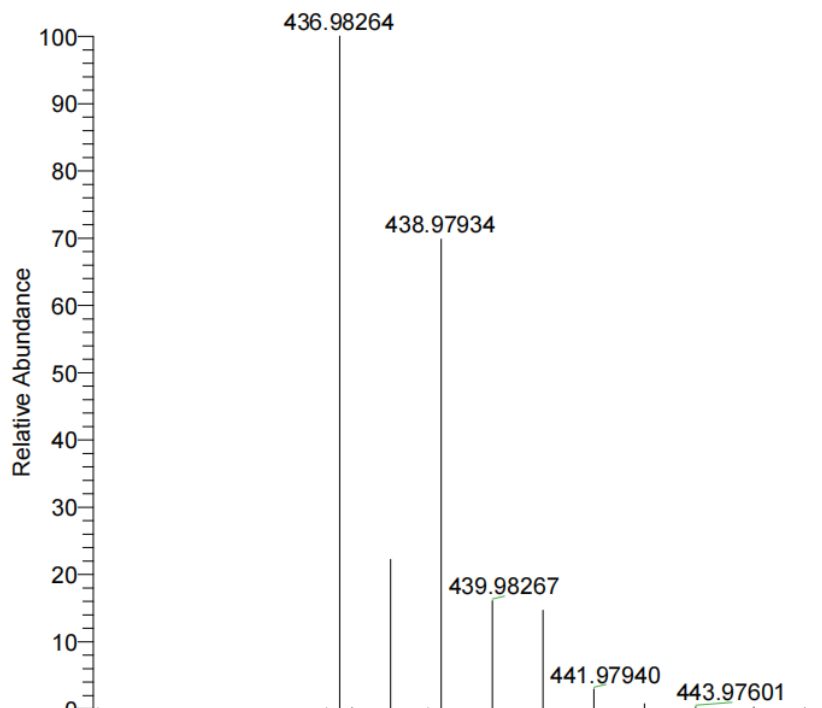
HRMS of compound **4d**



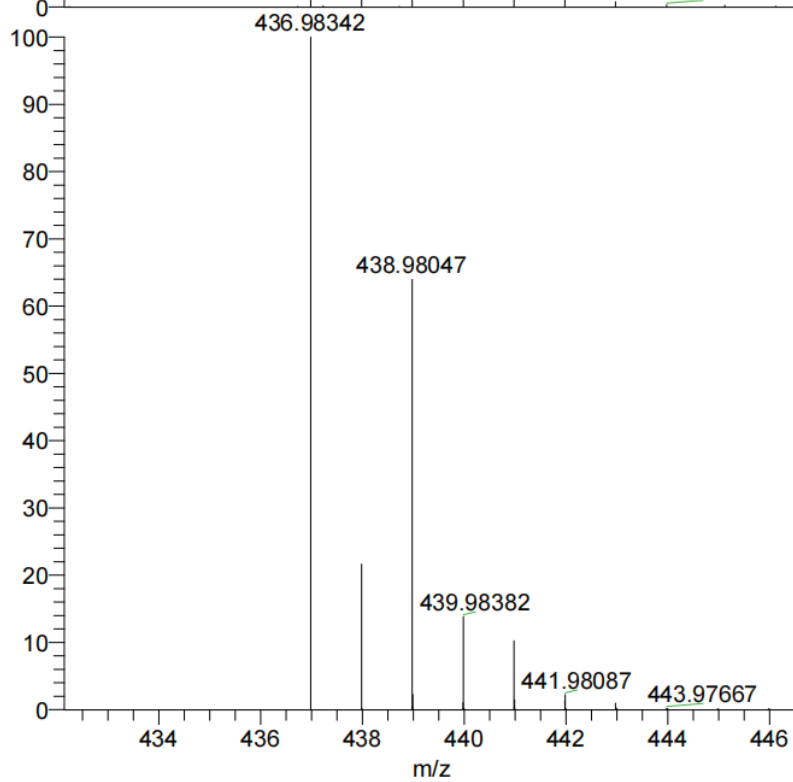
**<sup>1</sup>H NMR spectrum of compound 4e**



**<sup>13</sup>C NMR spectrum of compound 4e**

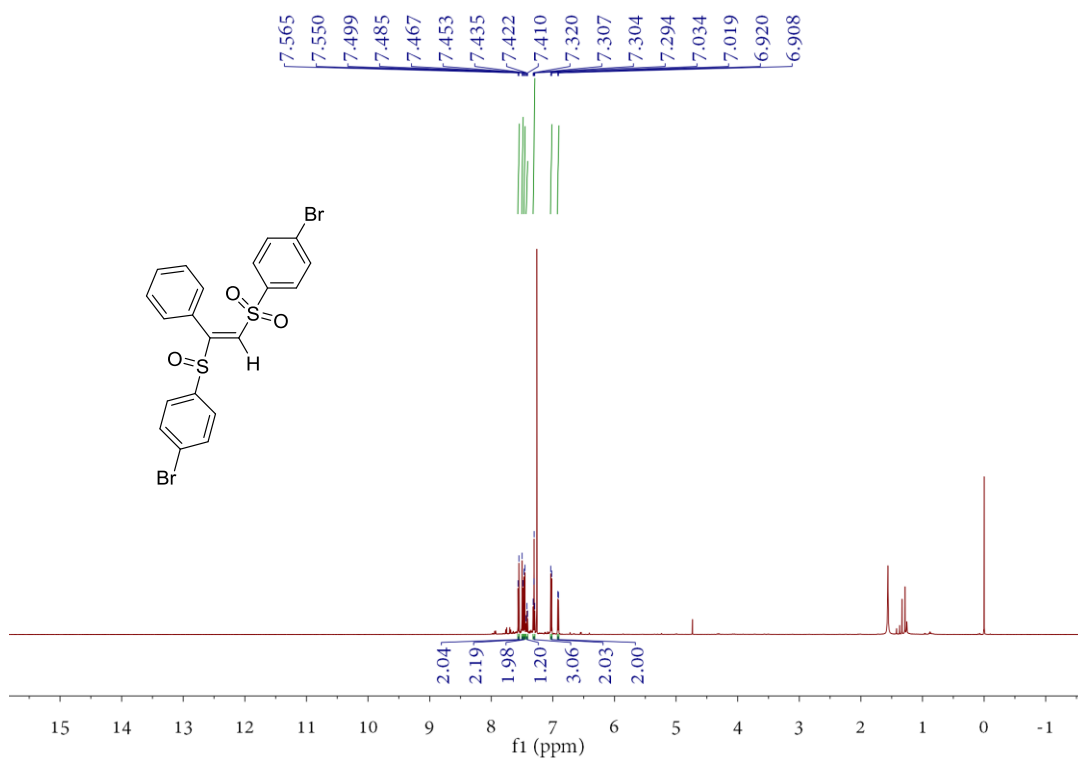


NL:  
3.36E7  
21#17 RT: 0.18 AV: 1  
T: FTMS + c APCI  
corona Full ms  
[50.0000-750.0000]

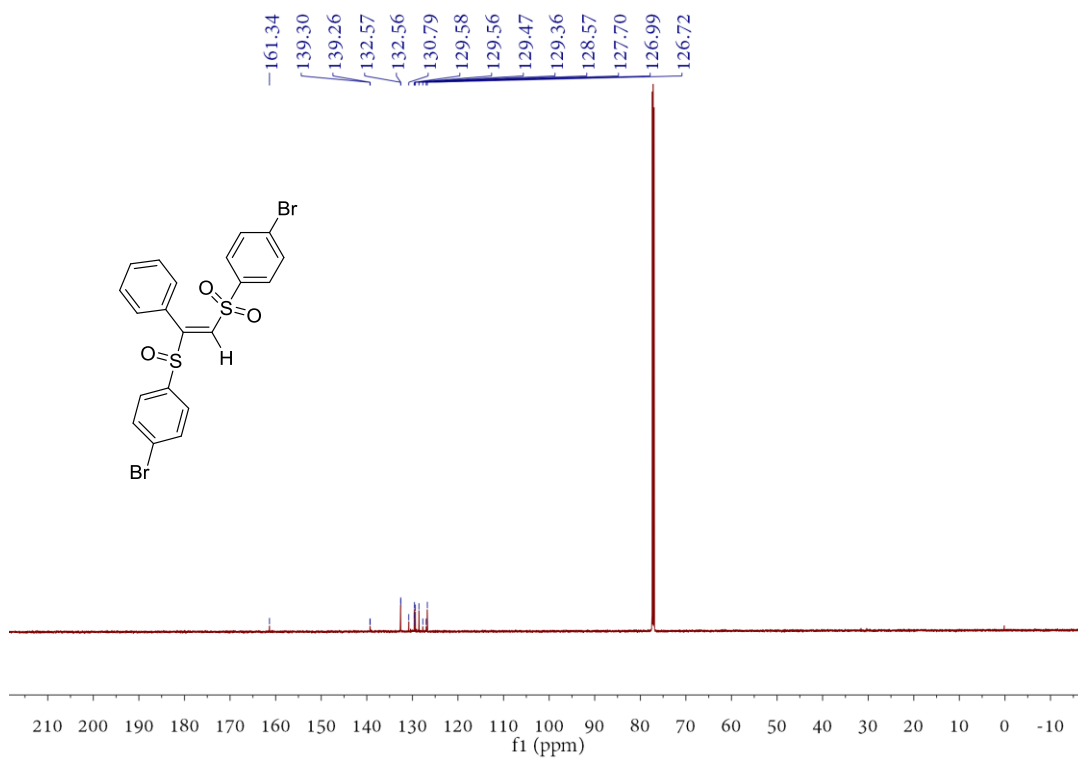


NL:  
4.14E5  
C<sub>20</sub>H<sub>14</sub>Cl<sub>2</sub>O<sub>3</sub>S<sub>2</sub>+H:  
C<sub>20</sub>H<sub>15</sub>Cl<sub>2</sub>O<sub>3</sub>S<sub>2</sub>  
pa Chrg 1

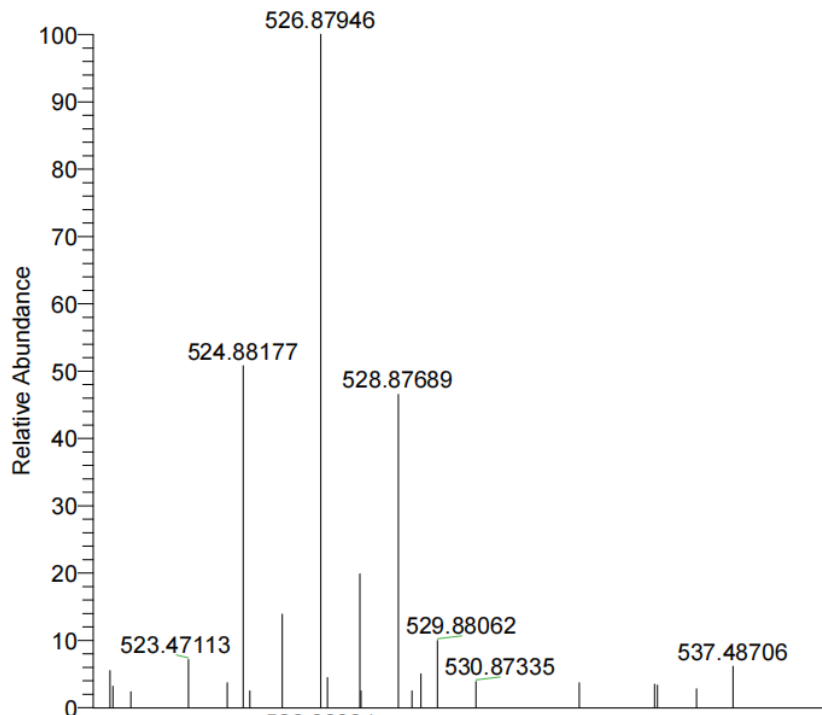
HRMS of compound 4e



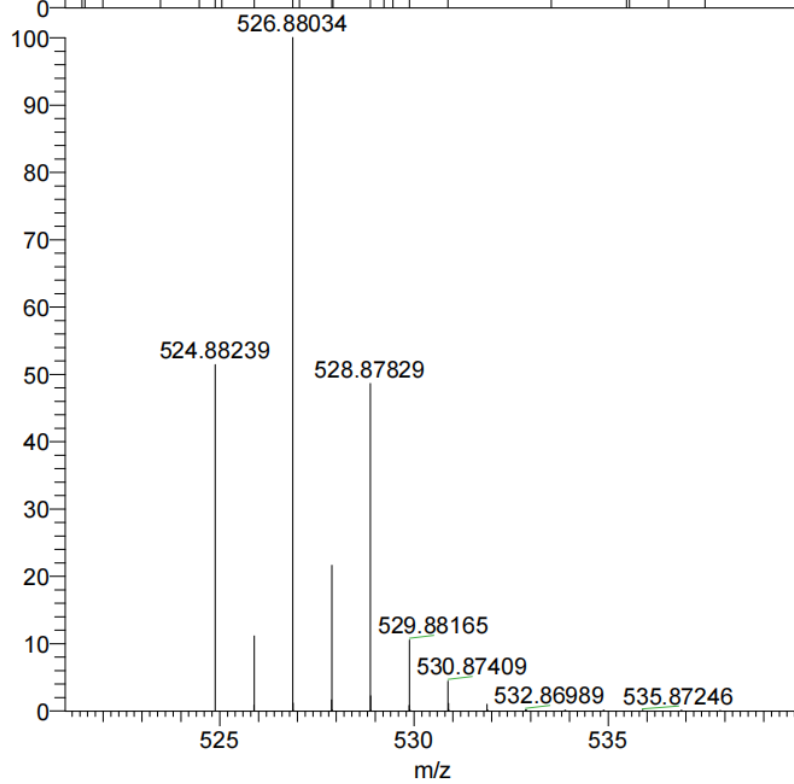
**<sup>1</sup>H NMR spectrum of compound 4f**



**<sup>13</sup>C NMR spectrum of compound 4f**

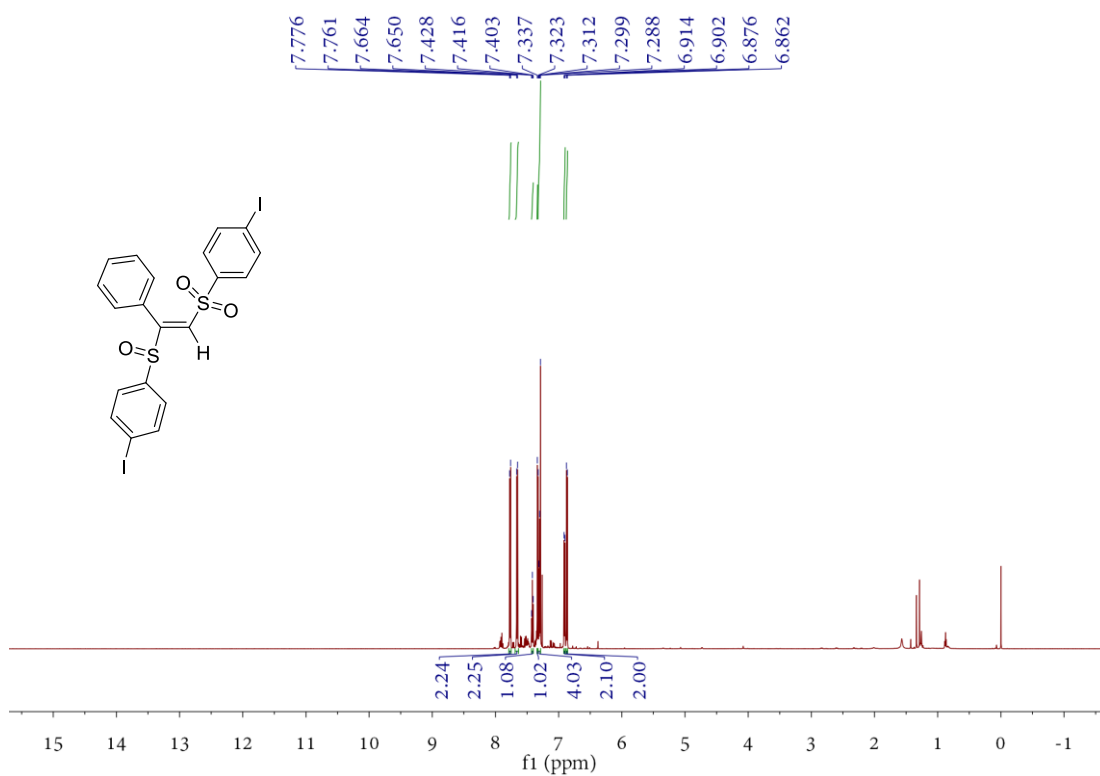


NL:  
 1.40E6  
 22#19 RT: 0.20 AV: 1  
 T: FTMS + c APCI  
 corona Full ms  
 [50.0000-750.0000]

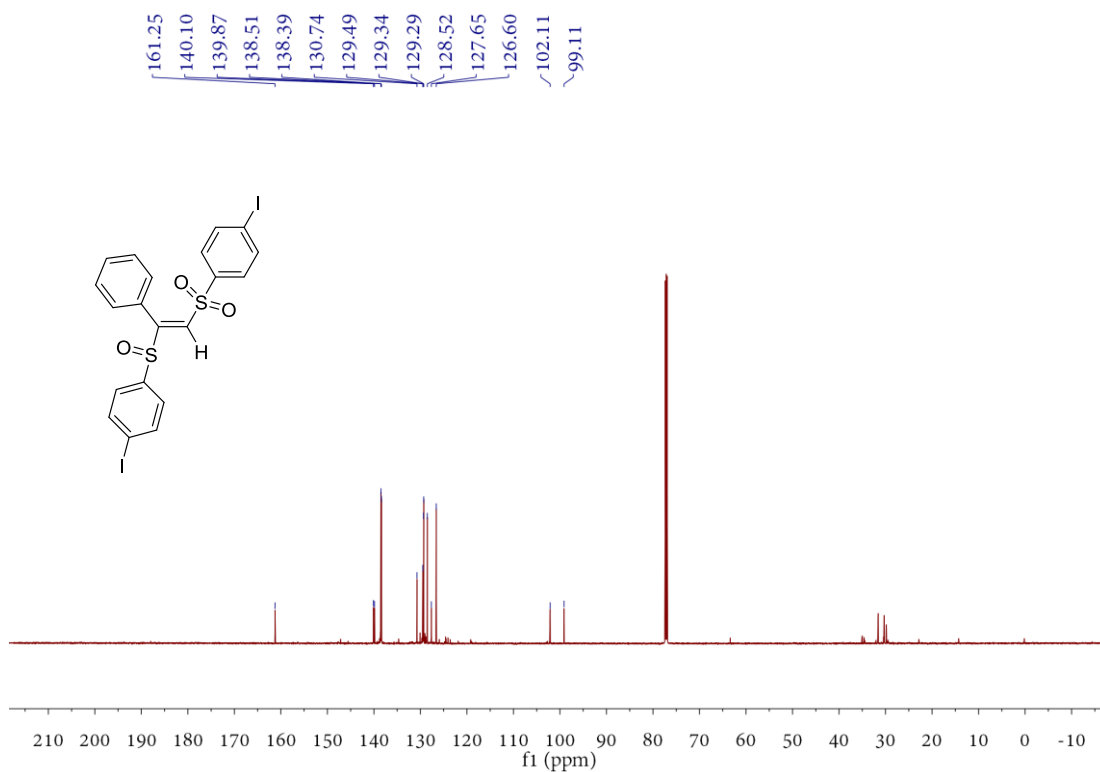


NL:  
 3.60E5  
 $C_{20}H_{14}Br_2O_3S_2 + H$   
 $C_{20}H_{15}Br_2O_3S_2$   
 pa Chrg 1

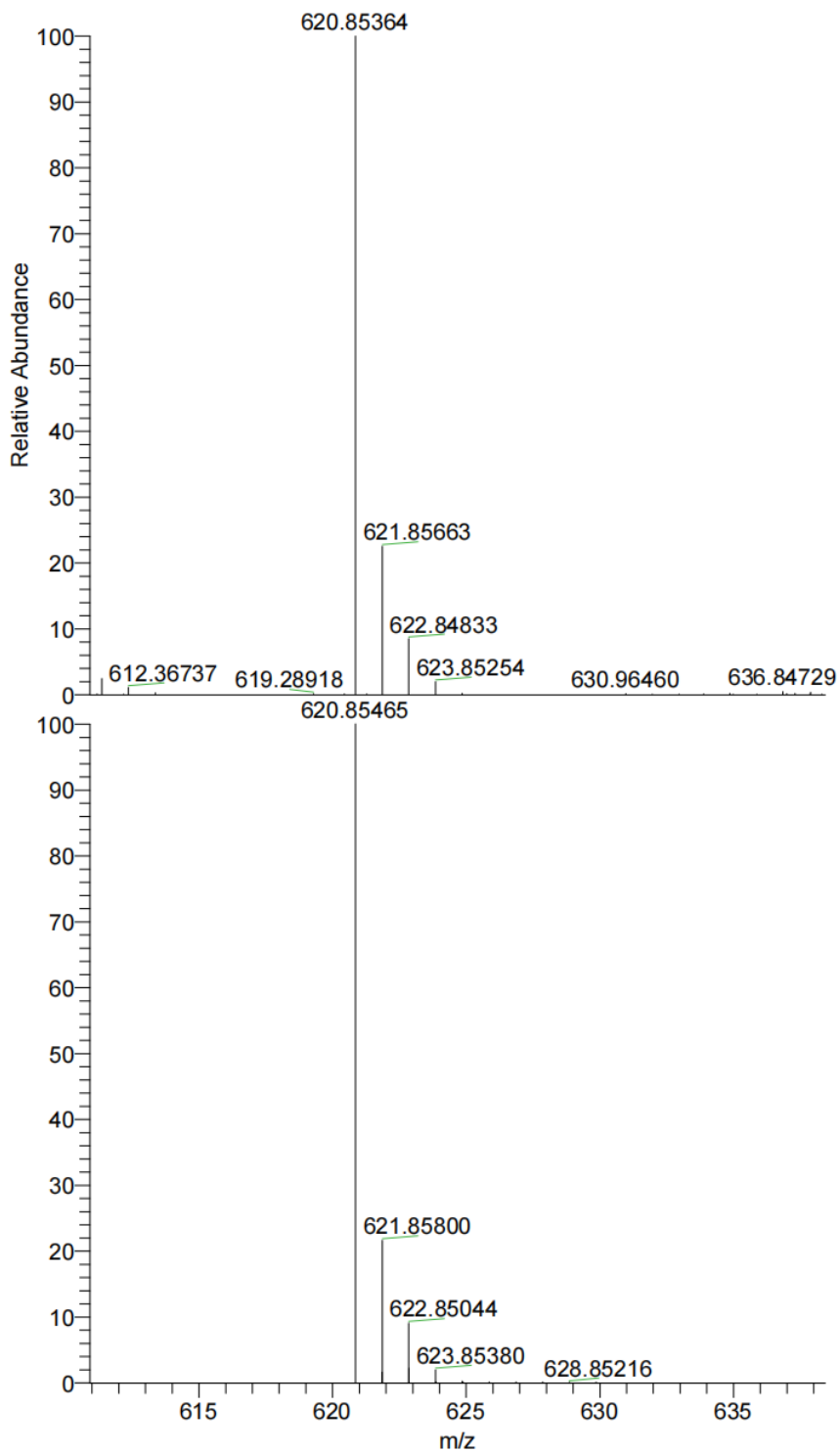
HRMS of compound **4f**



**<sup>1</sup>H NMR spectrum of compound 4g**



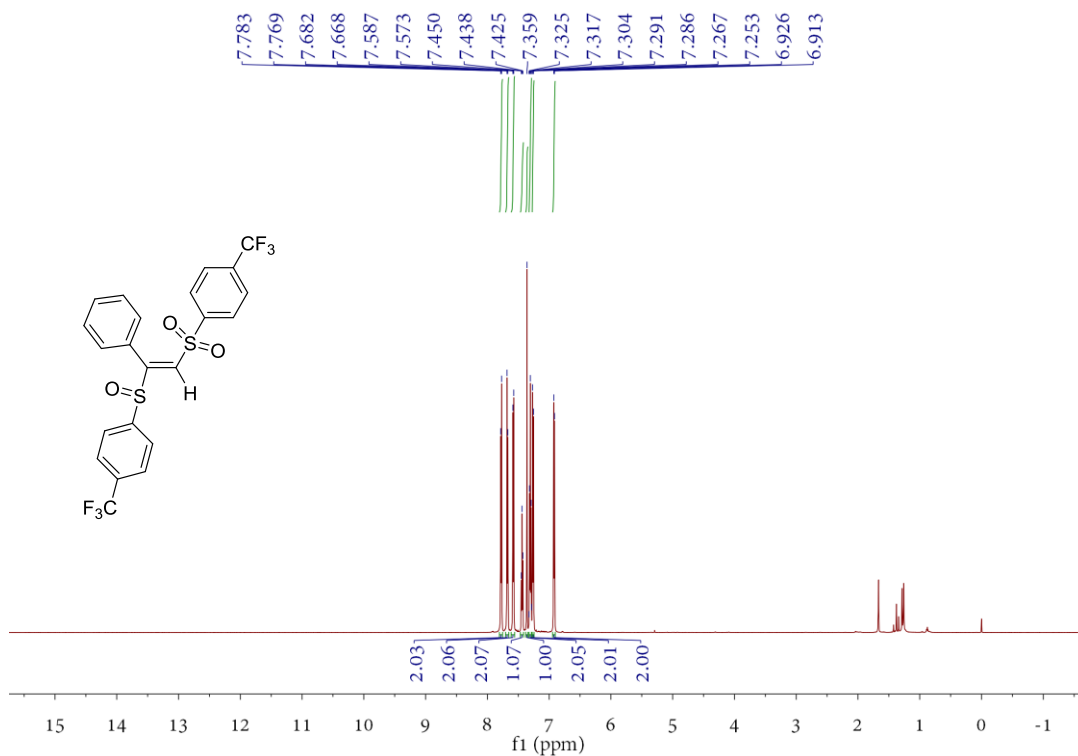
**<sup>13</sup>C NMR spectrum of compound 4g**



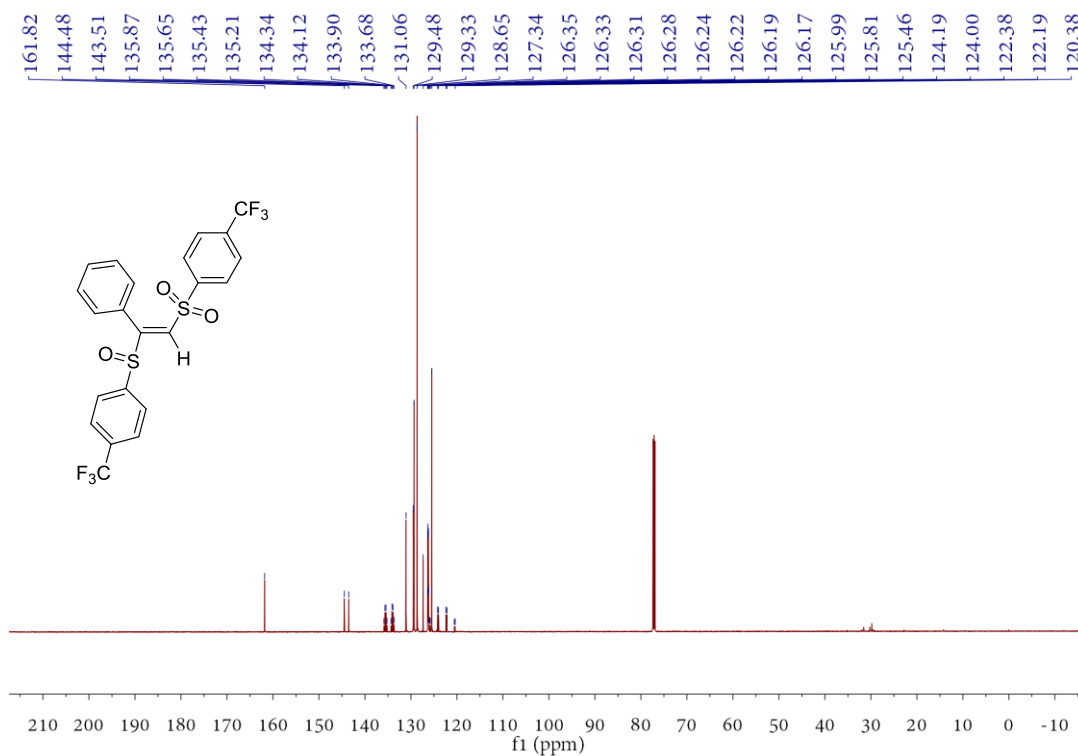
NL:  
 1.05E8  
 23#17 RT: 0.18 AV:  
 1 T: FTMS + c APCI  
 corona Full ms  
 [50.0000-750.0000]

NL:  
 7.20E5  
 $C_{20}H_{14}I_2O_3S_2 + H$   
 $C_{20}H_{15}I_2O_3S_2$   
 pa Chrg 1

HRMS of compound **4g**

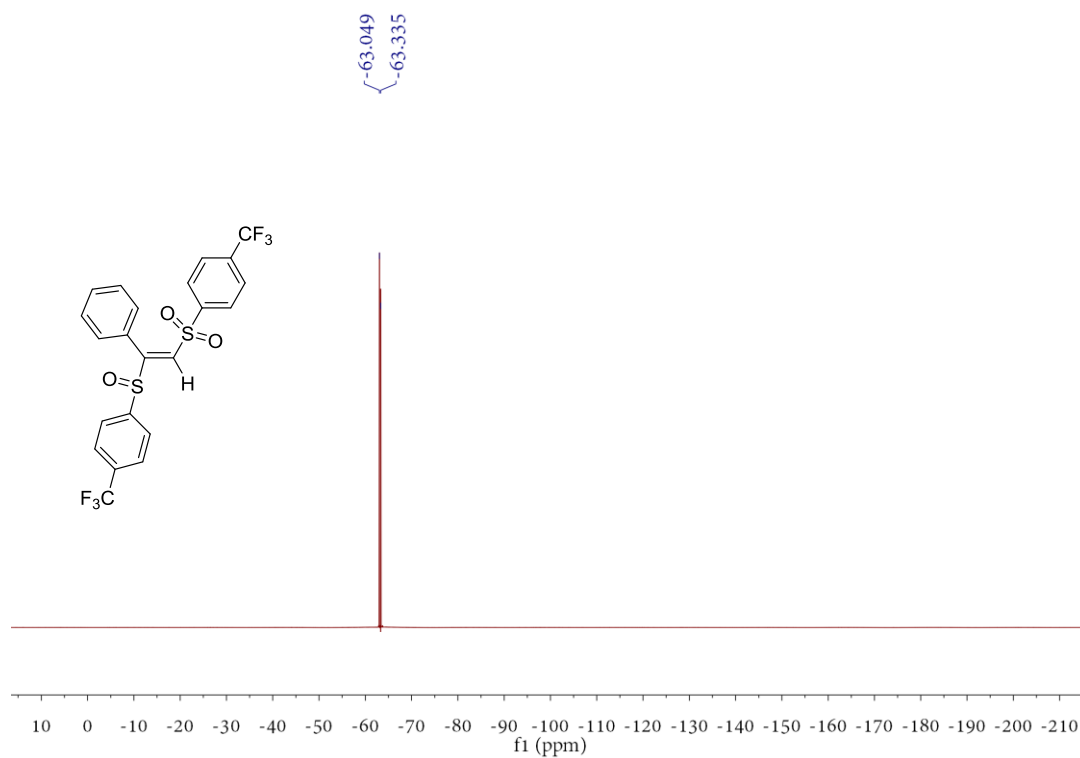


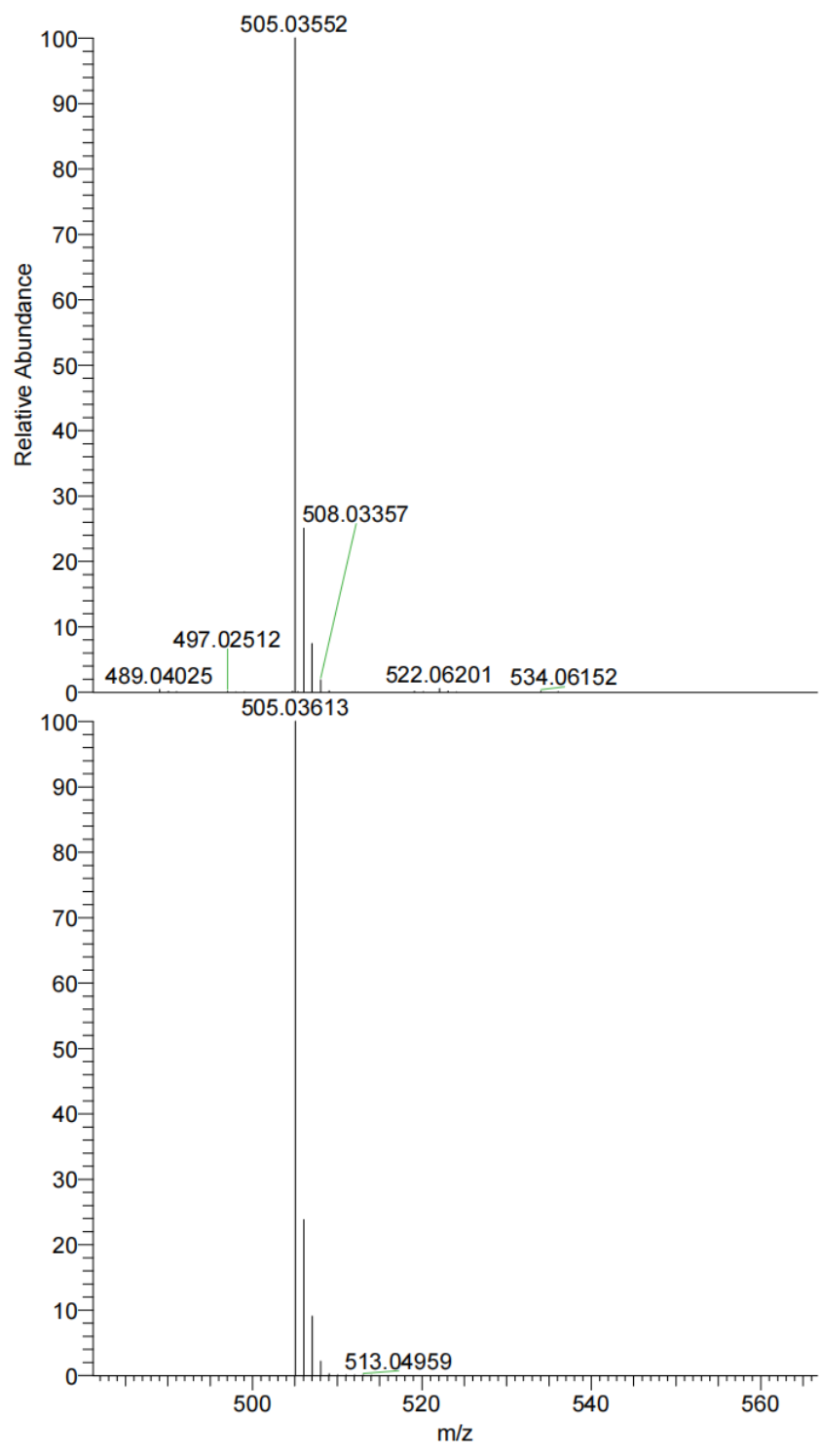
<sup>1</sup>H NMR spectrum of compound **4h**



<sup>13</sup>C NMR spectrum of compound **4h**



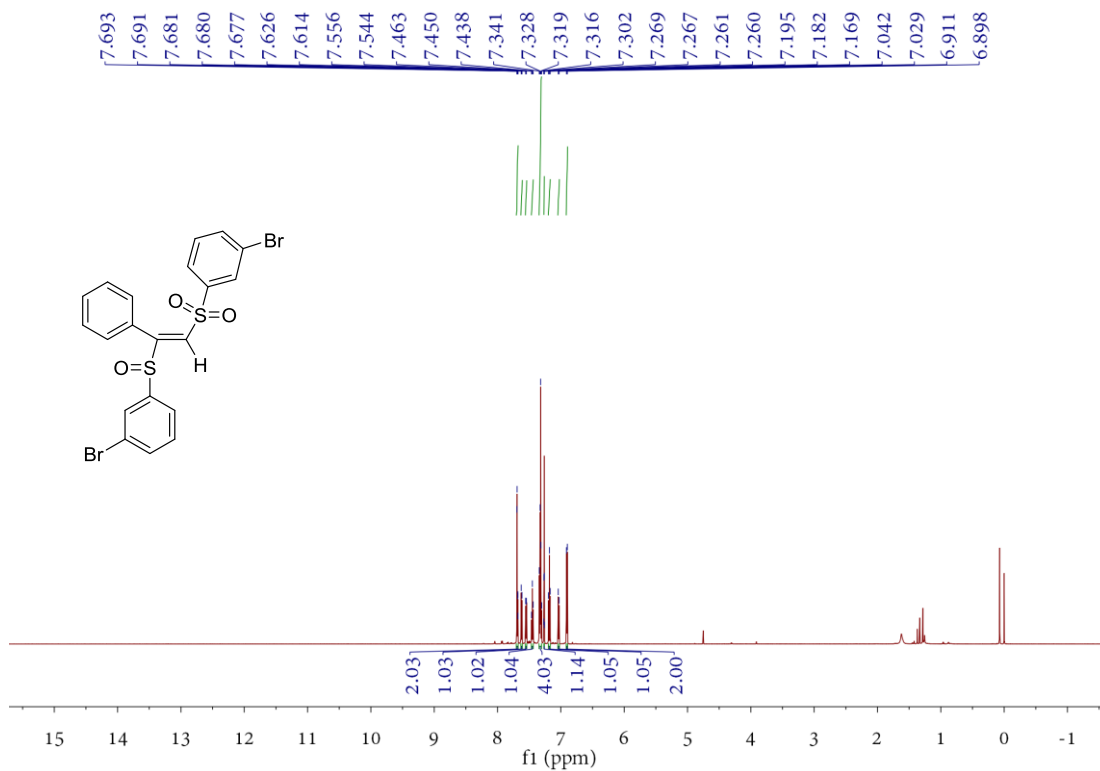




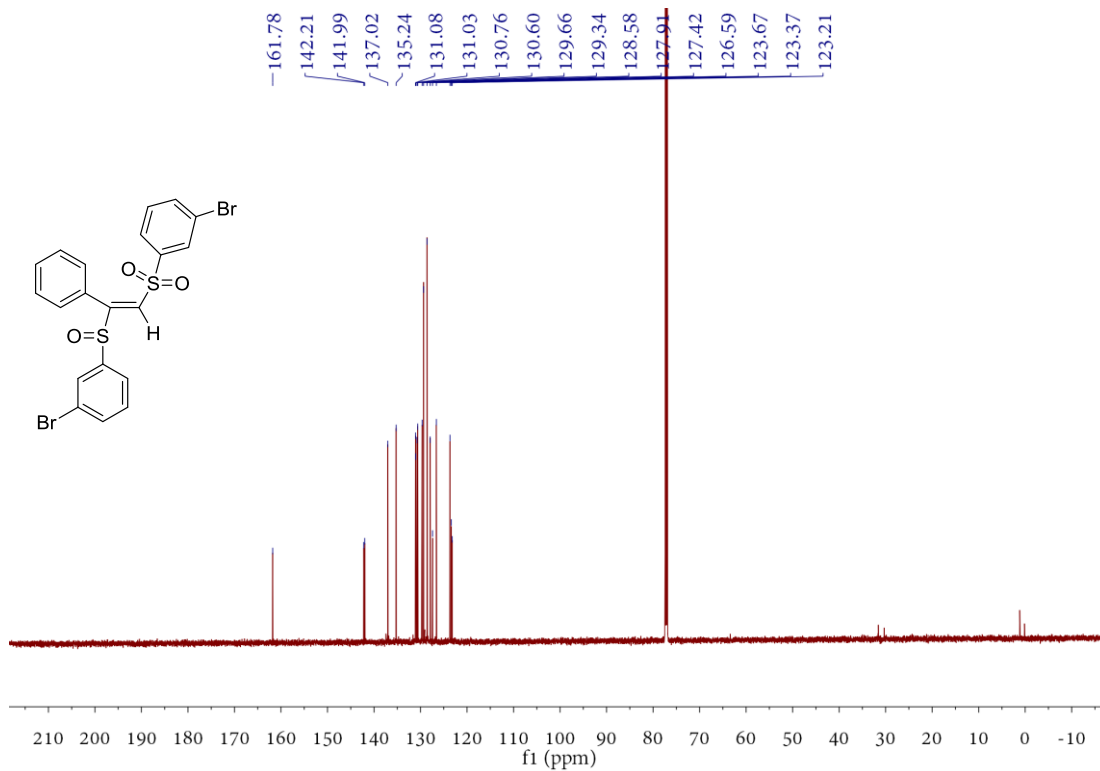
NL:  
2.20E8  
18#17 RT: 0.18 AV: 1  
T: FTMS + c APCI  
corona Full ms  
[50.0000-750.0000]

NL:  
7.05E5  
C<sub>22</sub>H<sub>14</sub>F<sub>6</sub>O<sub>3</sub>S<sub>2</sub>+H:  
C<sub>22</sub>H<sub>15</sub>F<sub>6</sub>O<sub>3</sub>S<sub>2</sub>  
pa Chrg 1

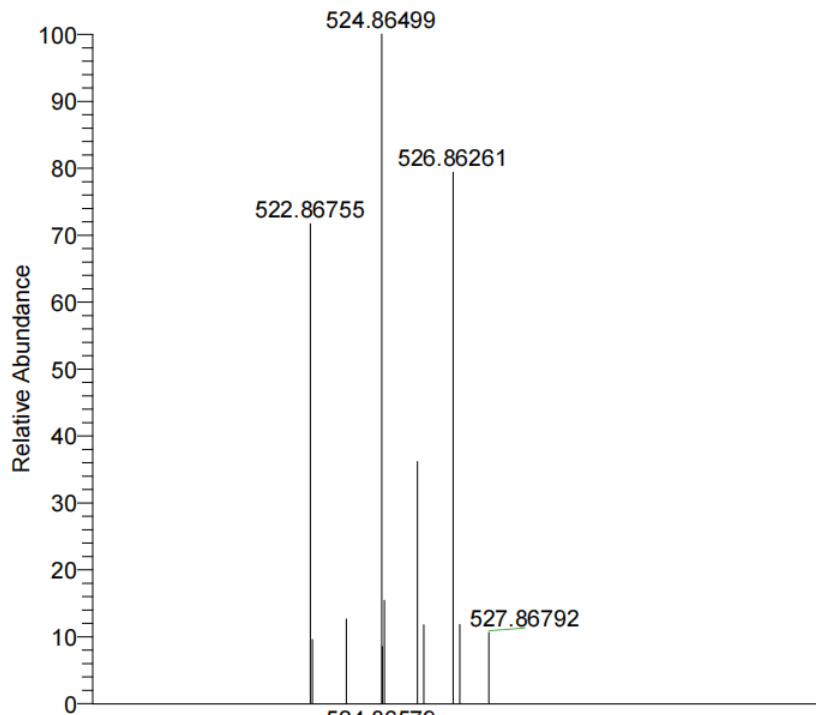
HRMS of compound **4h**



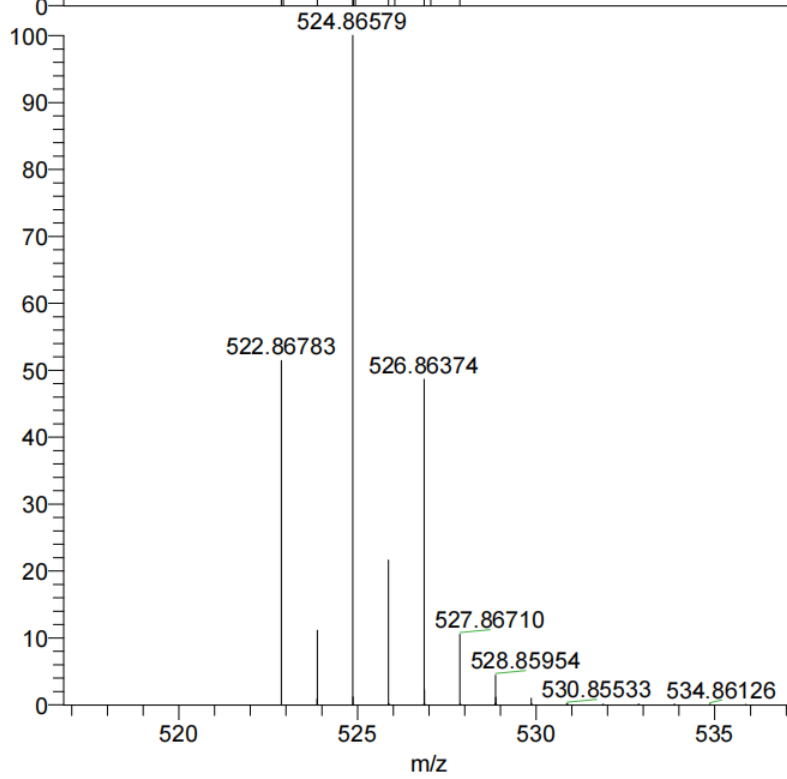
**<sup>1</sup>H NMR spectrum of compound 4i**



**<sup>13</sup>C NMR spectrum of compound 4i**

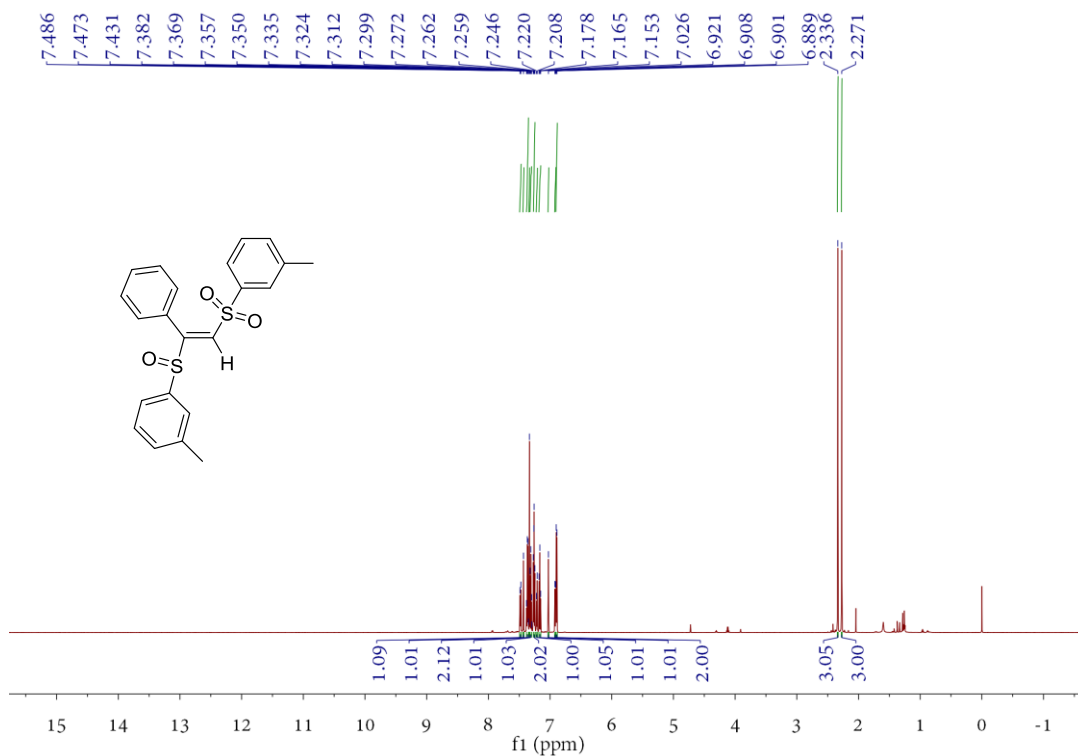


NL:  
 3.61E6  
 12#23 RT: 0.22 AV: 1  
 T: FTMS - c APCI  
 corona Full ms  
 [50.0000-750.0000]

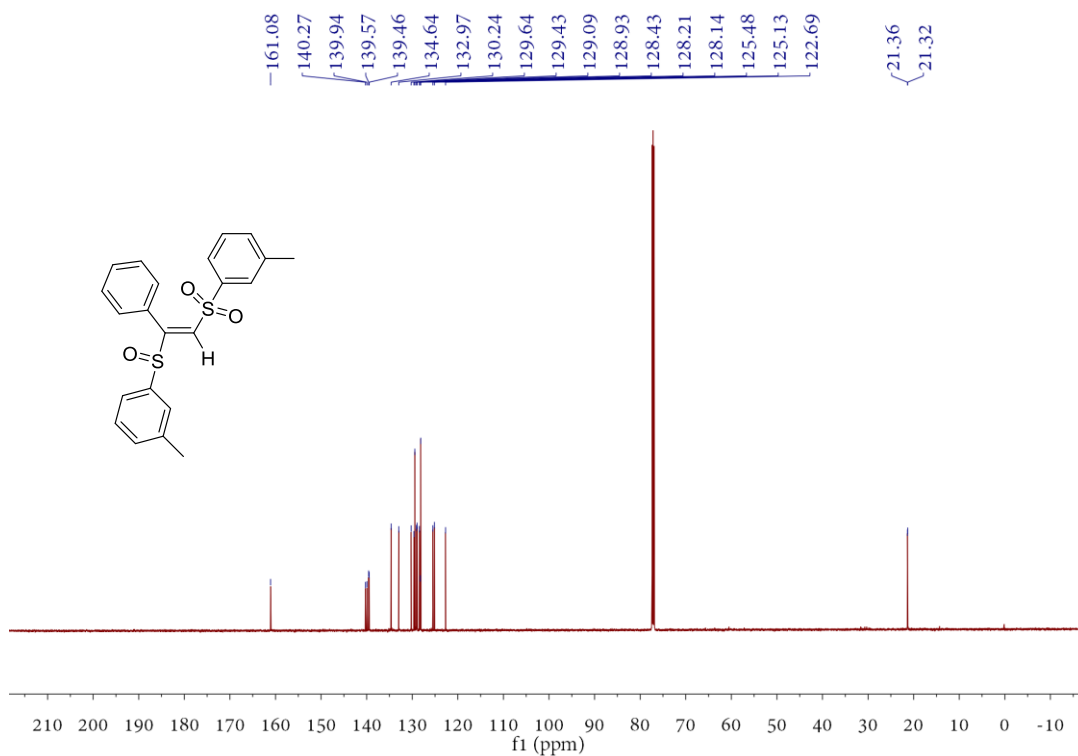


NL:  
 3.60E5  
 $C_{20}H_{14}Br_2O_3S_2 + H^+$   
 $C_{20}H_{13}Br_2O_3S_2$   
 pa Chrg -1

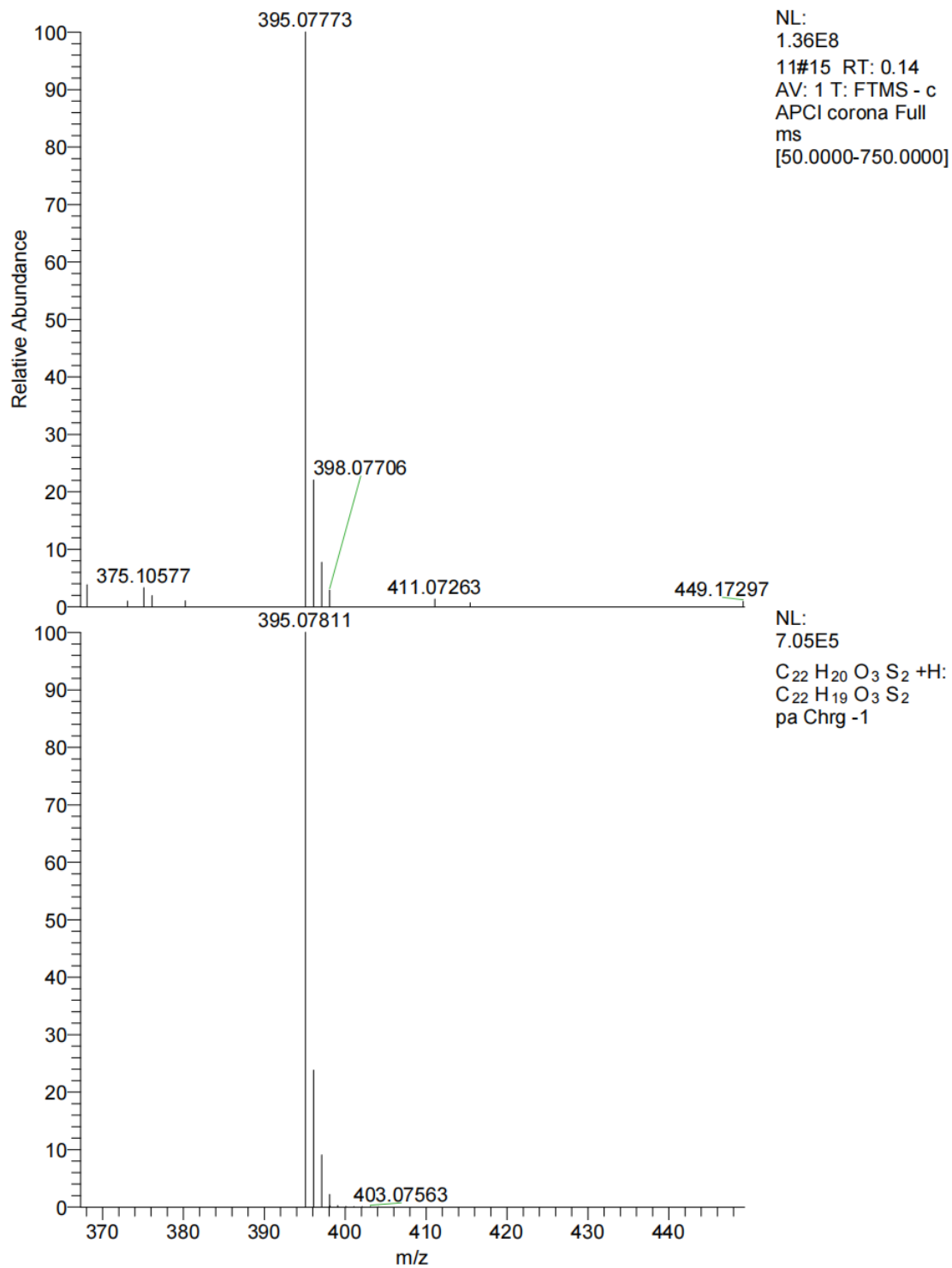
HRMS of compound **4i**



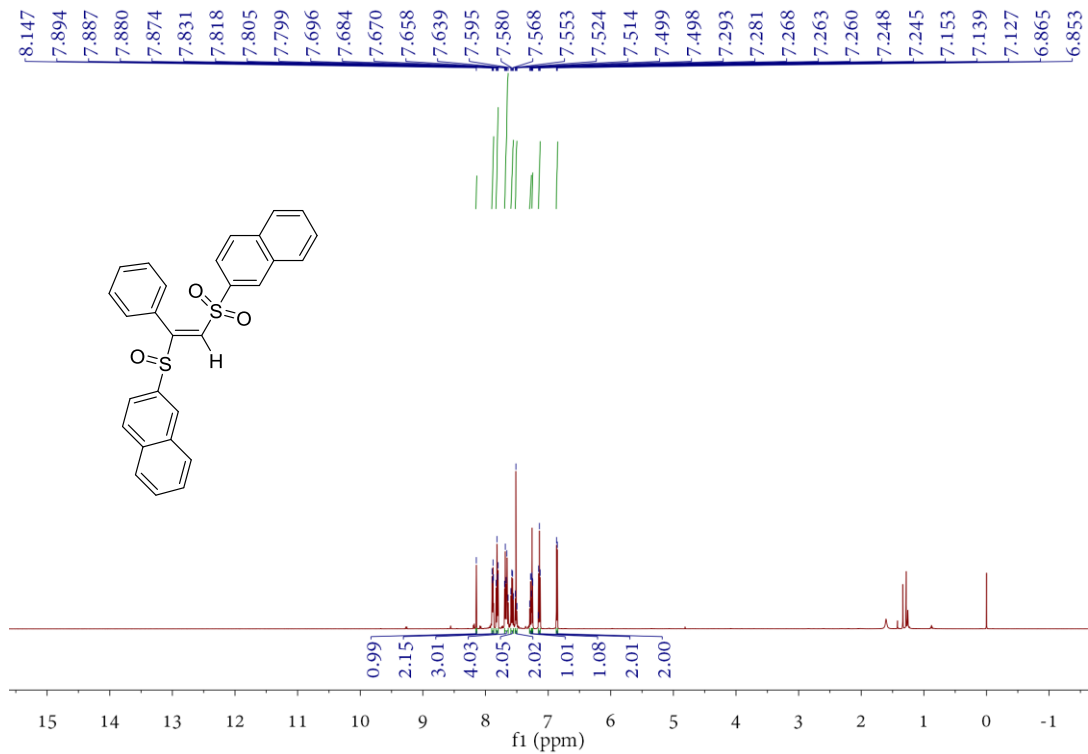
**<sup>1</sup>H NMR spectrum of compound 4j**



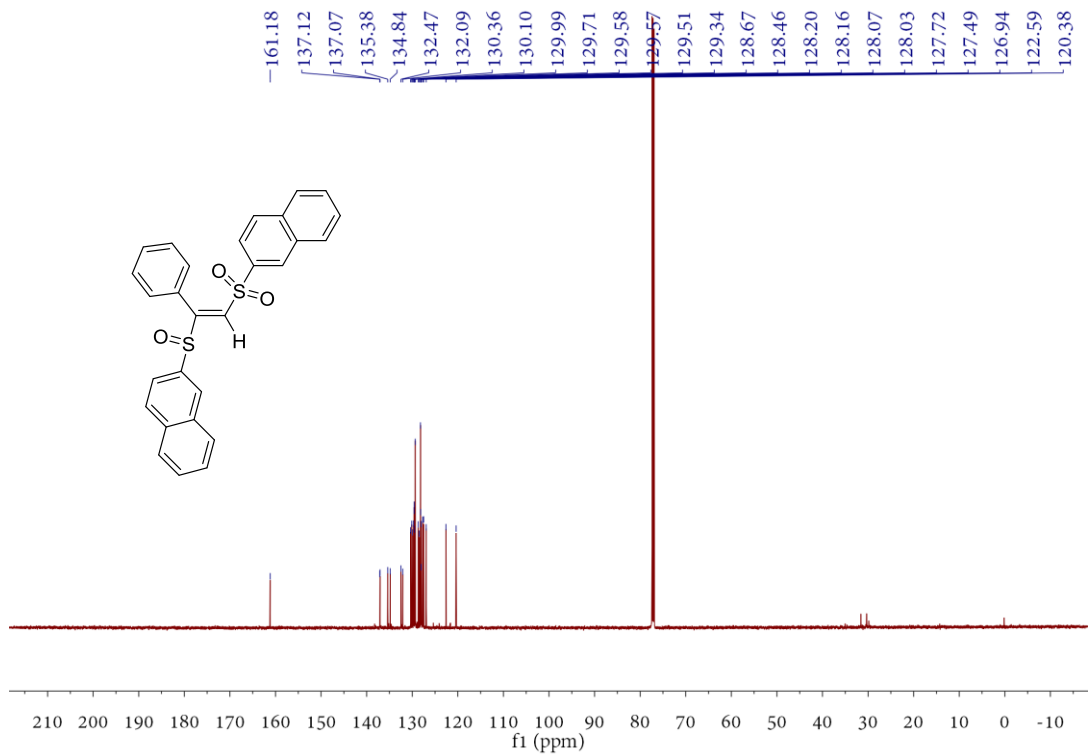
**<sup>13</sup>C NMR spectrum of compound 4j**



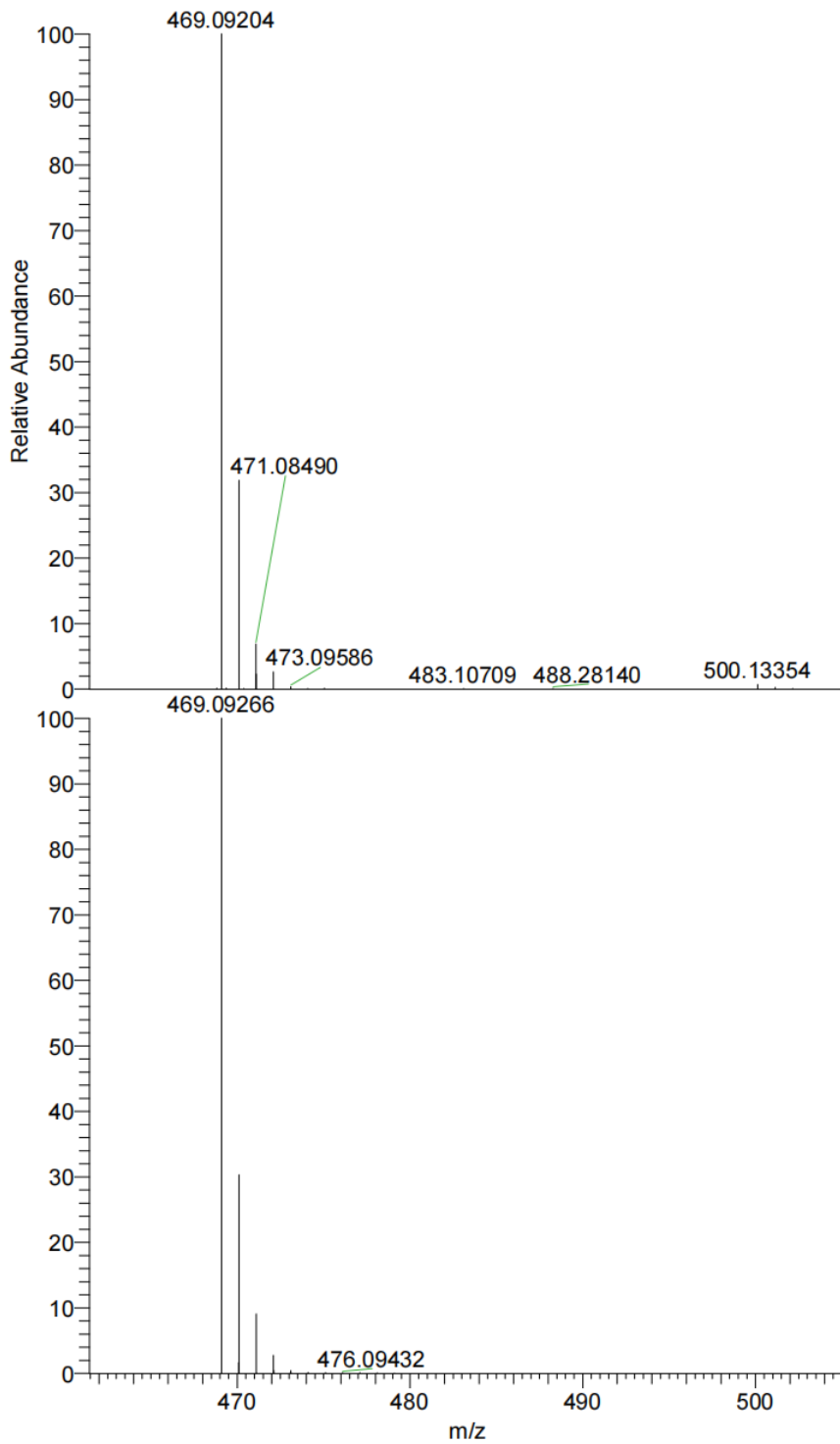
HRMS of compound **4j**



**<sup>1</sup>H NMR spectrum of compound 4k**



**<sup>13</sup>C NMR spectrum of compound 4k**

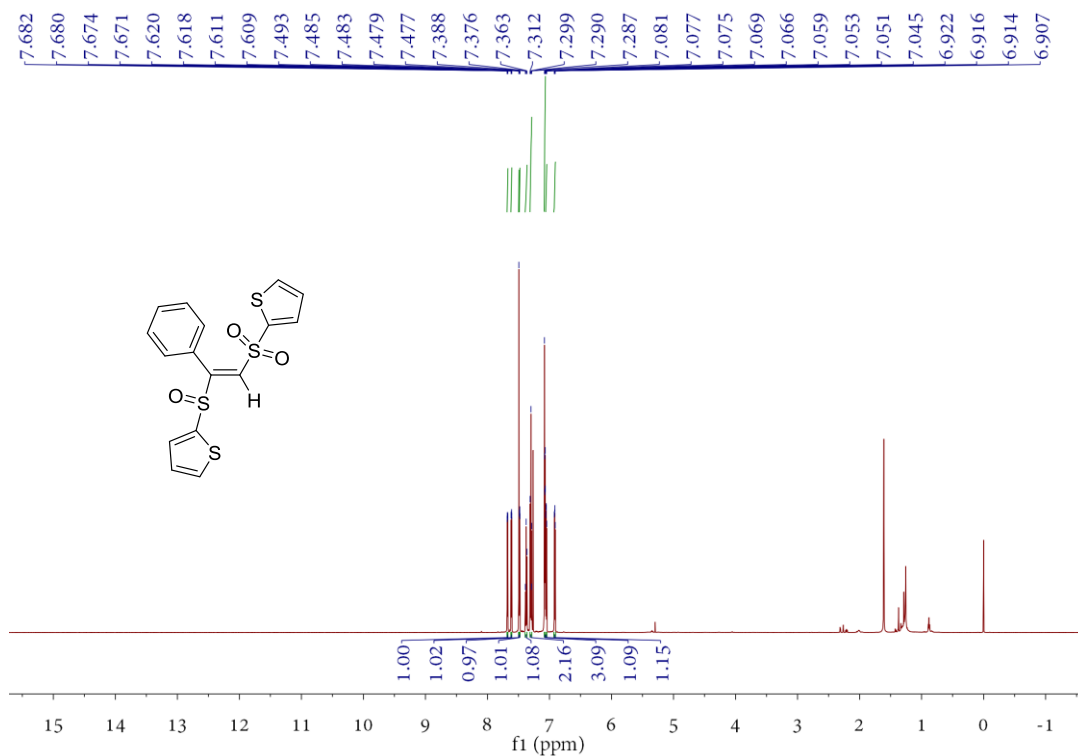


NL:  
 2.31E8  
 24#17 RT: 0.18  
 AV: 1 T: FTMS + c  
 APCI corona Full  
 ms  
 [50.0000-750.0000]

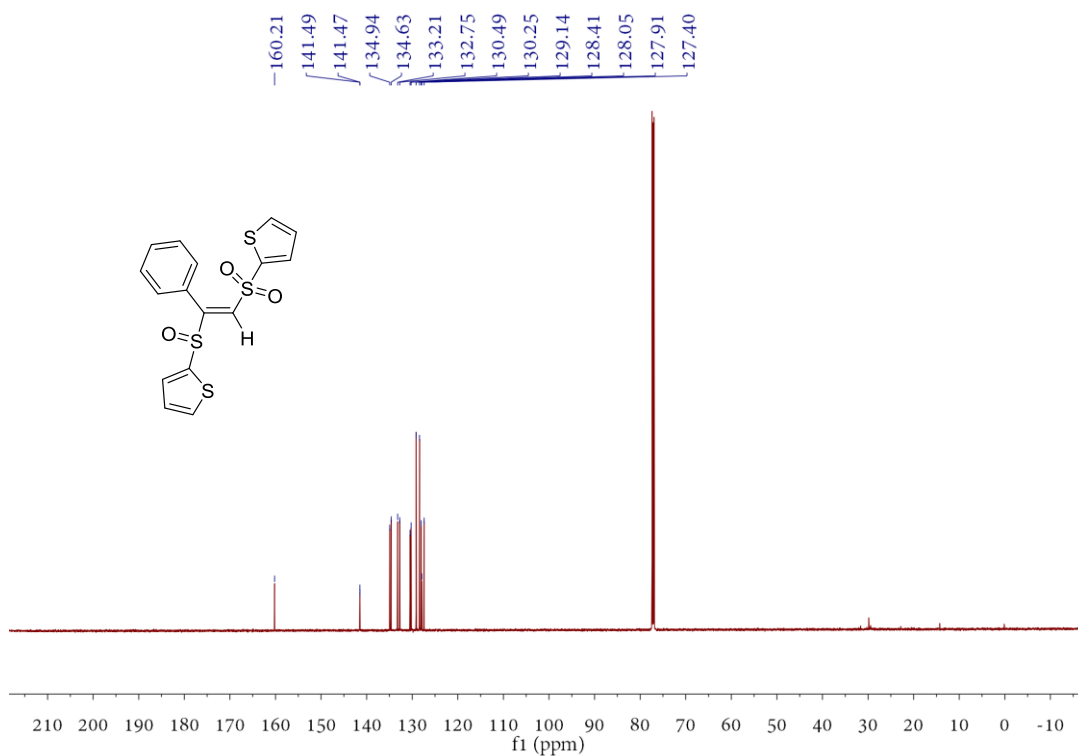
NL:  
 6.60E5  
 $C_{28}H_{20}O_3S_2 + H$   
 $C_{28}H_{21}O_3S_2$   
 pa Chrg 1

HRMS of compound **4k**

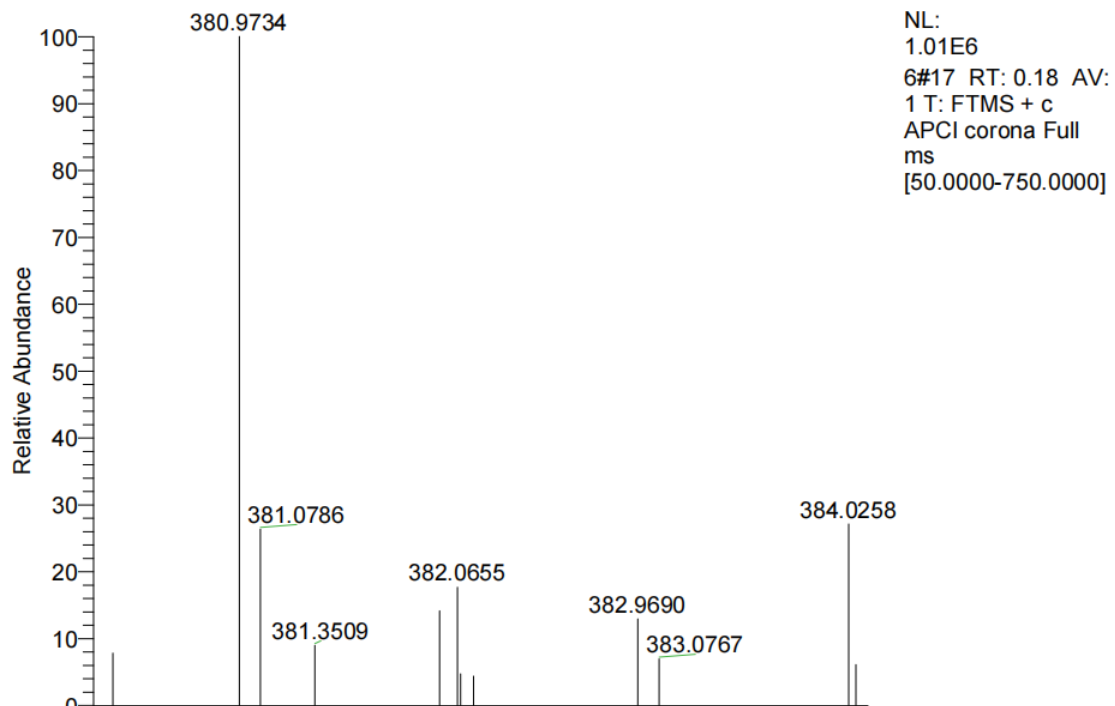




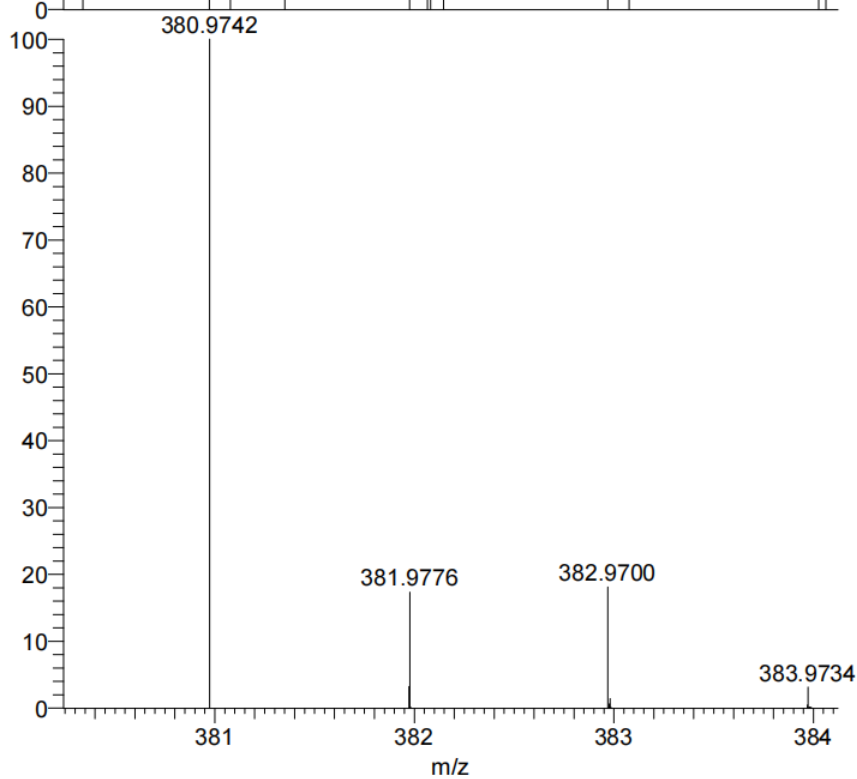
<sup>1</sup>H NMR spectrum of compound **4l**



<sup>13</sup>C NMR spectrum of compound **4l**

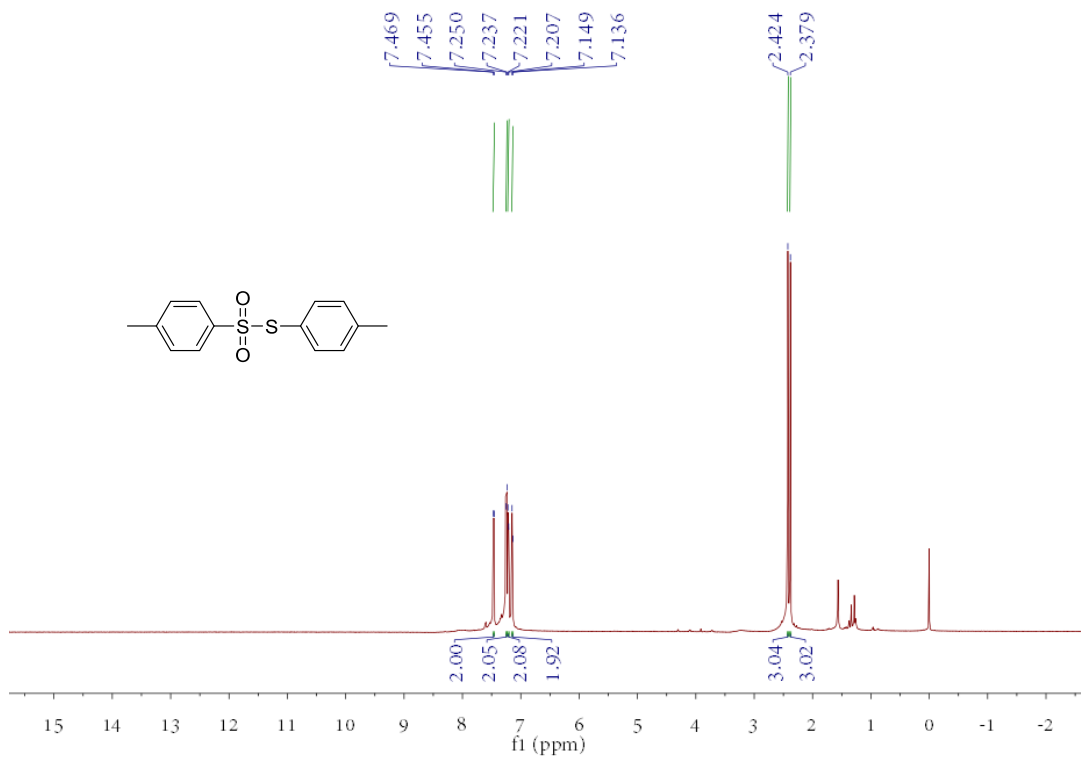


NL:  
1.01E6  
6#17 RT: 0.18 AV:  
1 T: FTMS + c  
APCI corona Full  
ms  
[50.0000-750.0000]

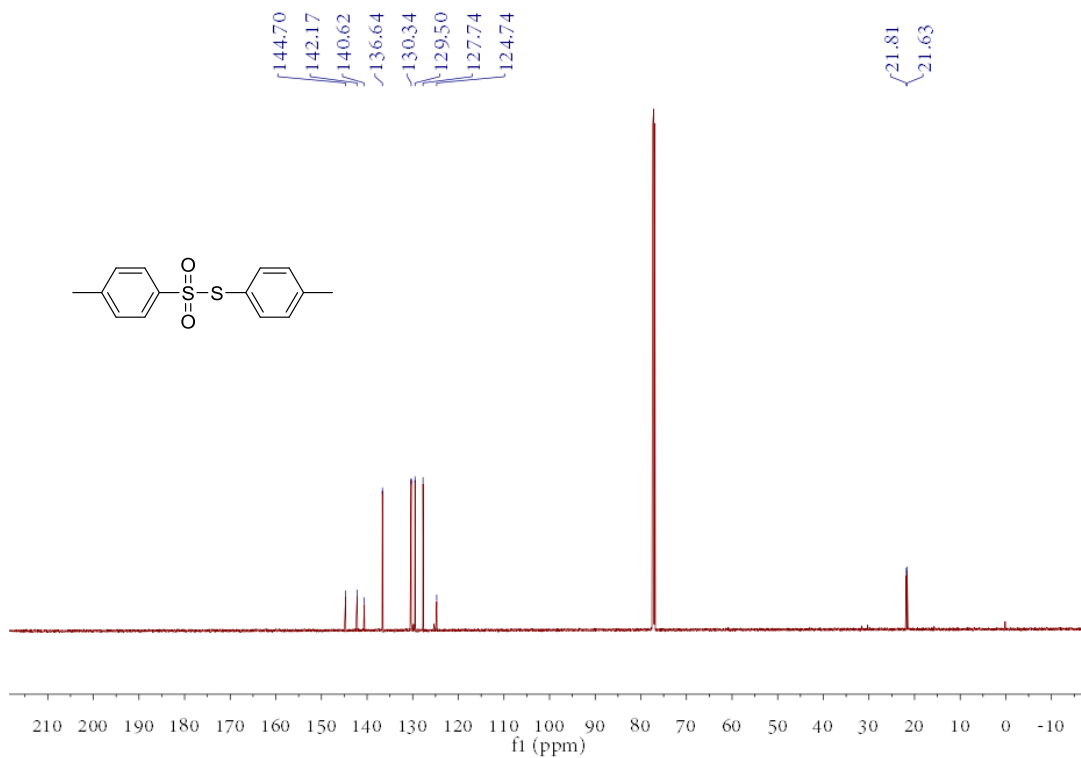


NL:  
6.78E5  
C<sub>16</sub> H<sub>12</sub> O<sub>3</sub> S<sub>4</sub> +H:  
C<sub>16</sub> H<sub>13</sub> O<sub>3</sub> S<sub>4</sub>  
pa Chrg 1

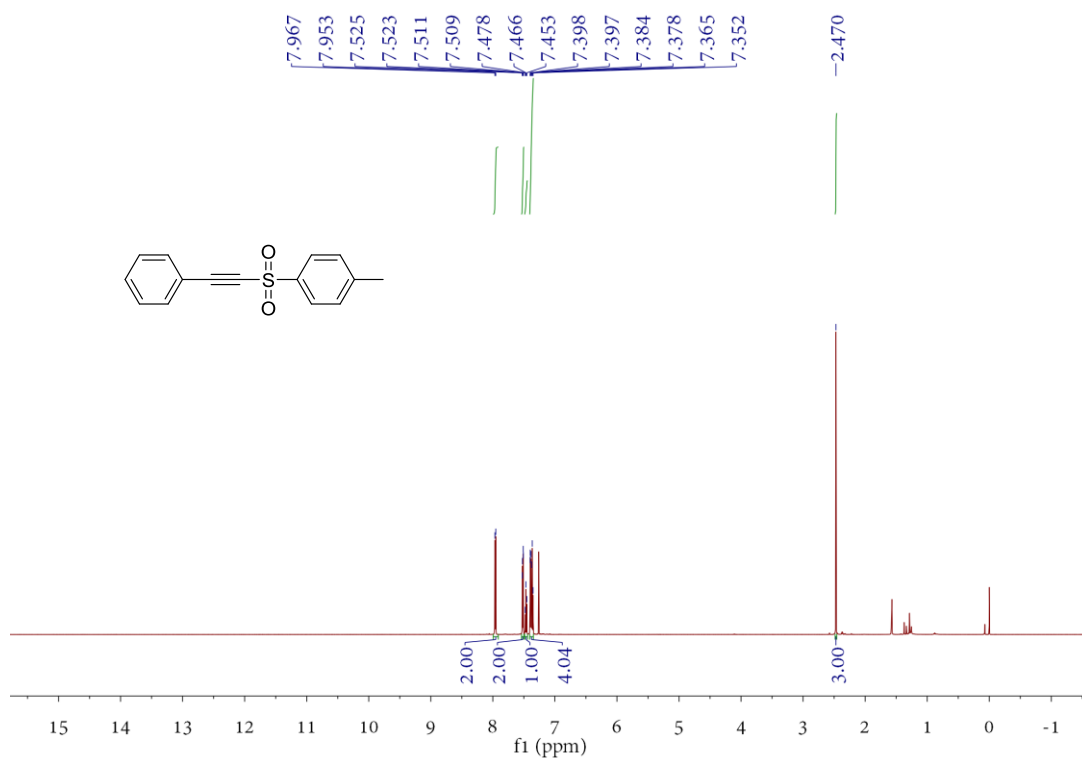
HRMS of compound **41**



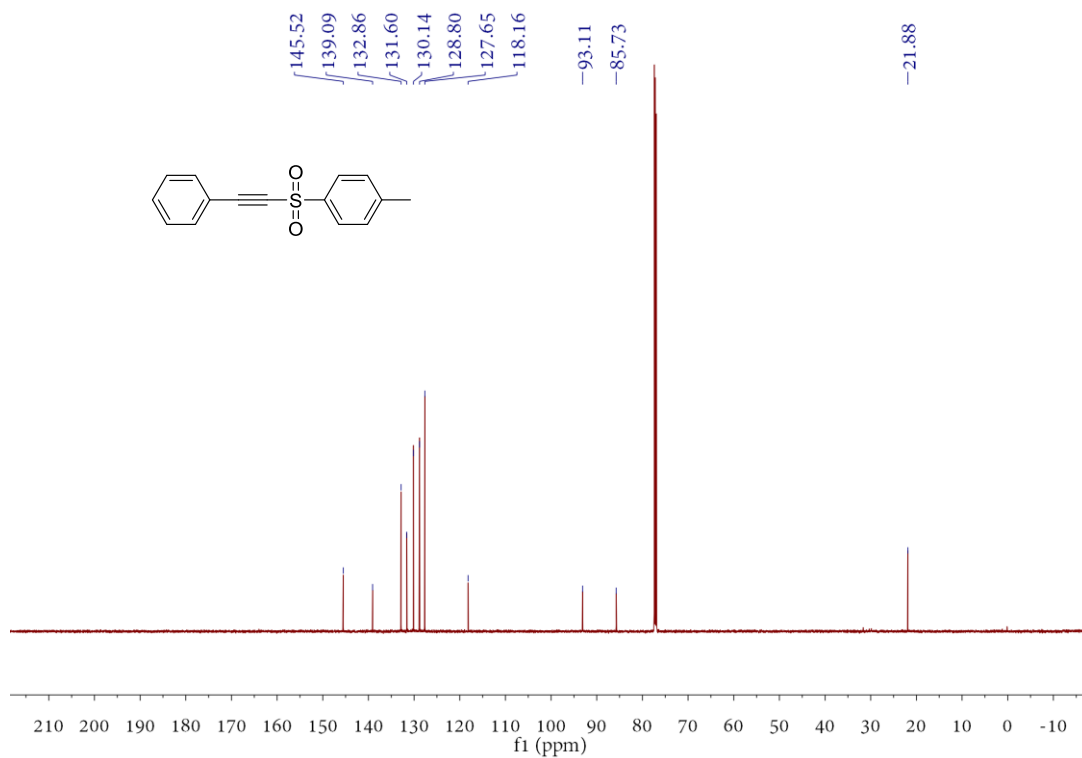
<sup>1</sup>H NMR spectrum of compound 5a



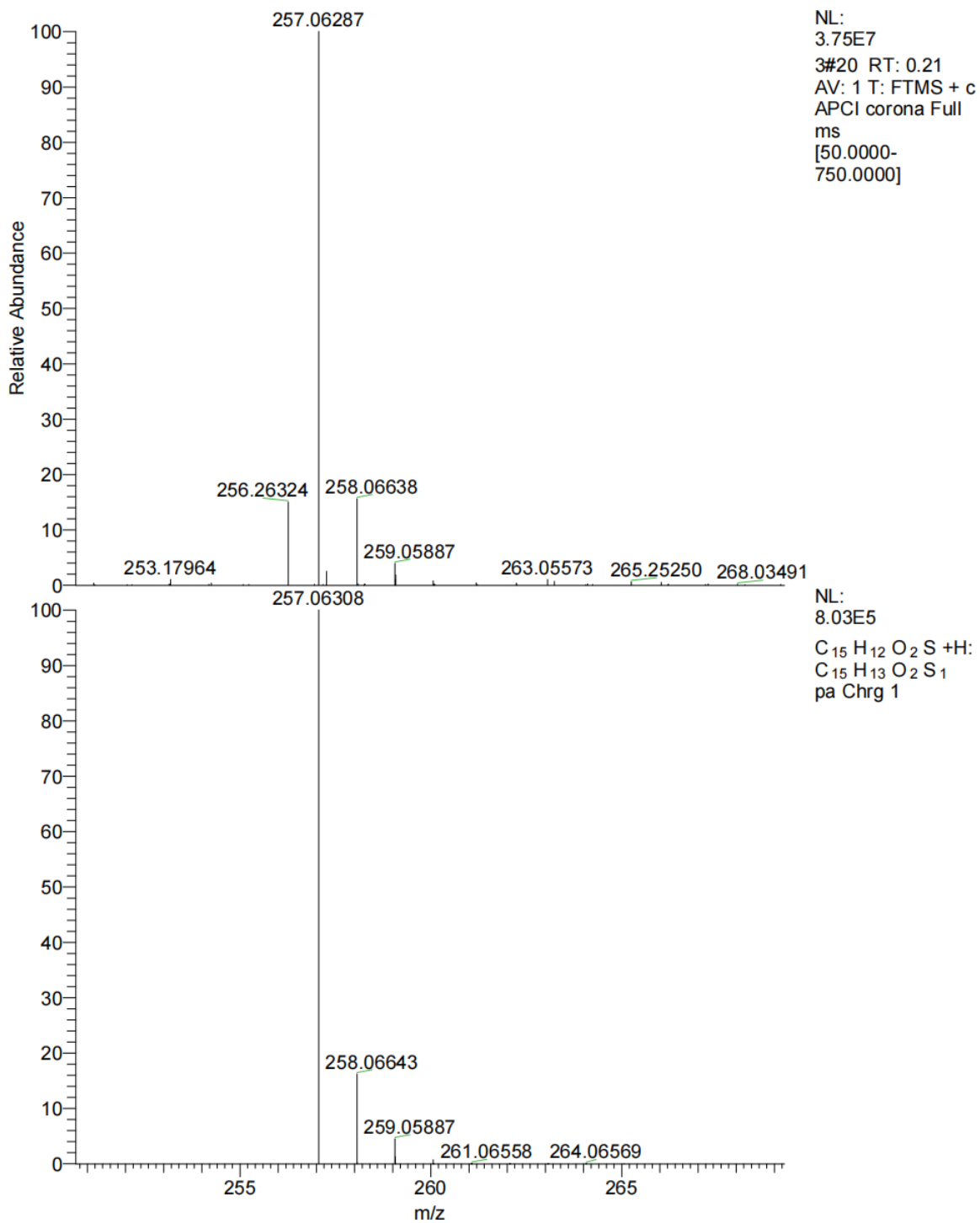
<sup>13</sup>C NMR spectrum of compound 5a



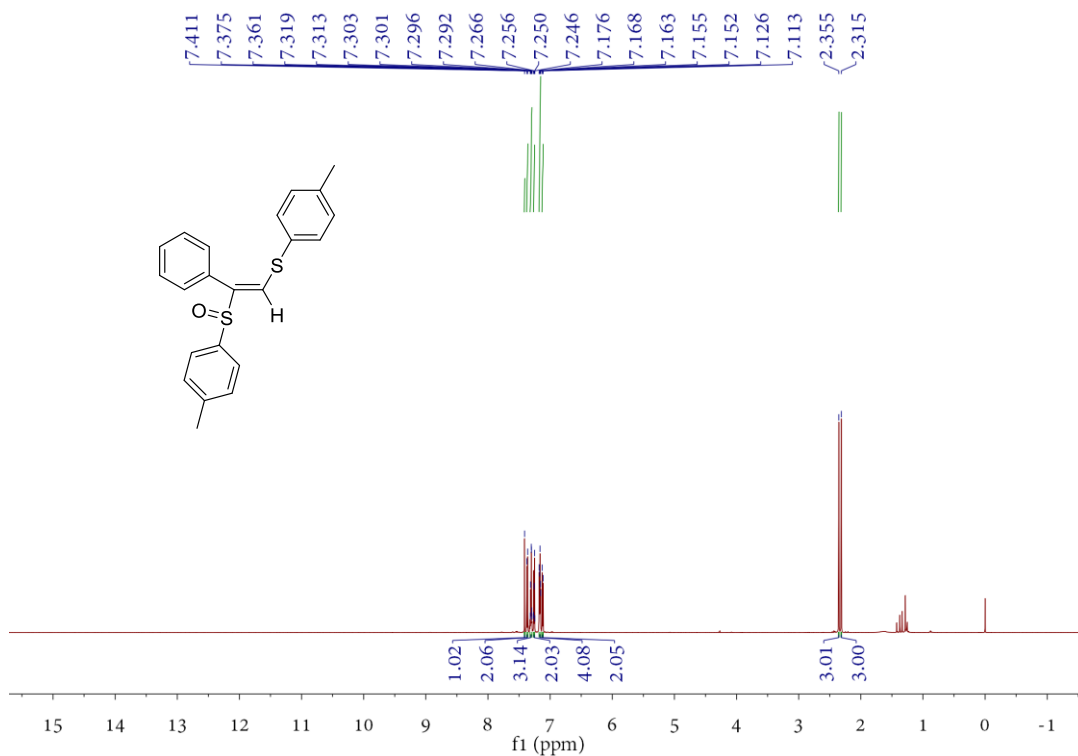
<sup>1</sup>H NMR spectrum of compound 7a



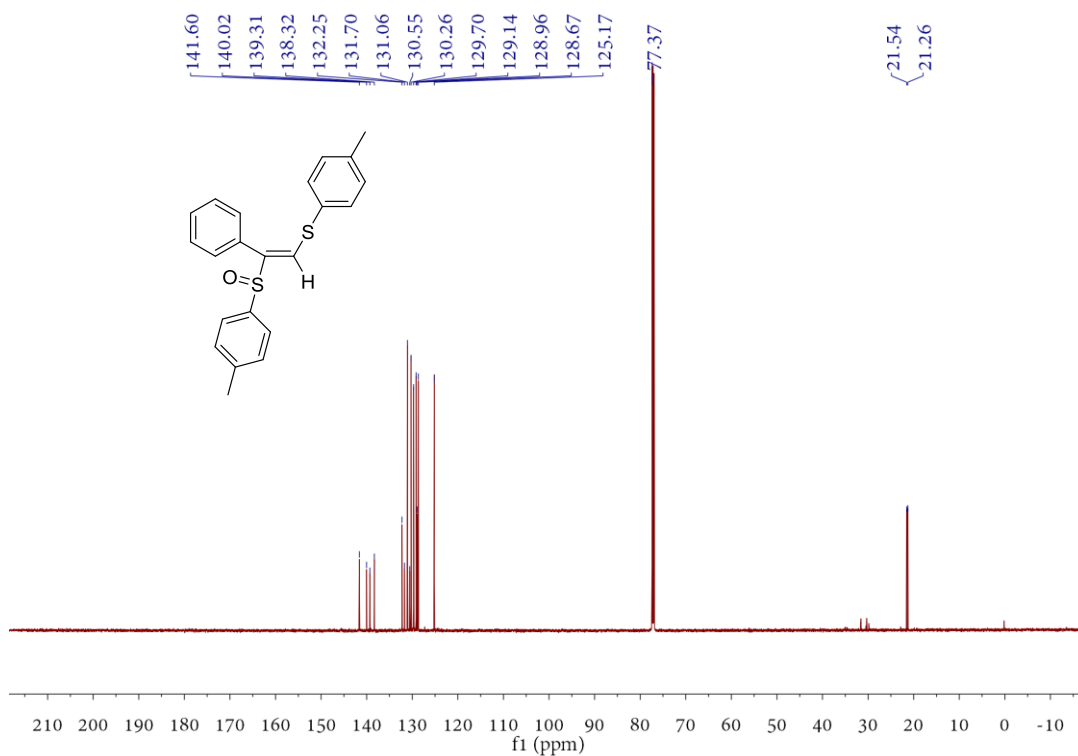
<sup>13</sup>C NMR spectrum of compound 7a



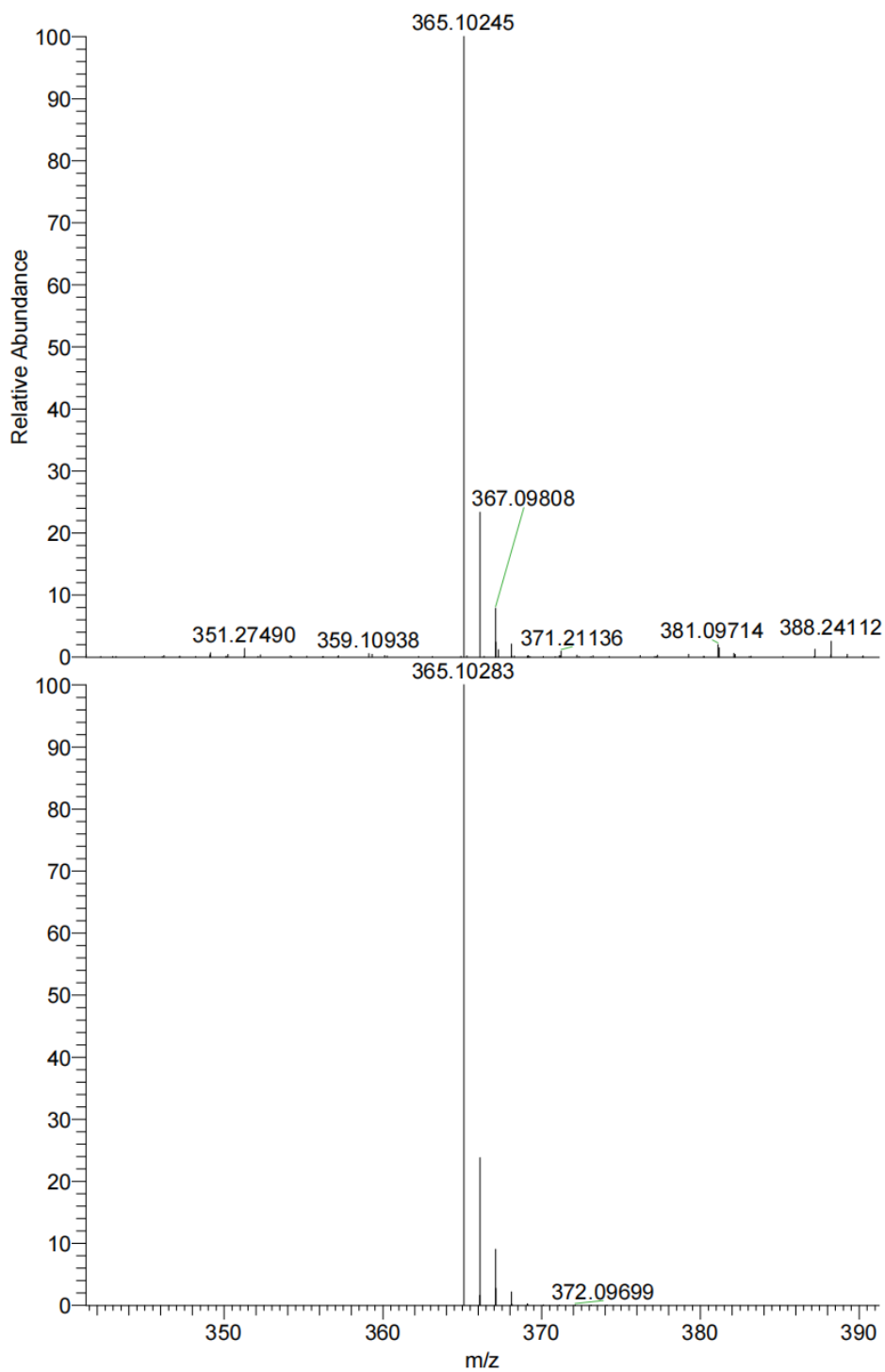
HRMS of compound **7a**



<sup>1</sup>H NMR spectrum of compound **7b**



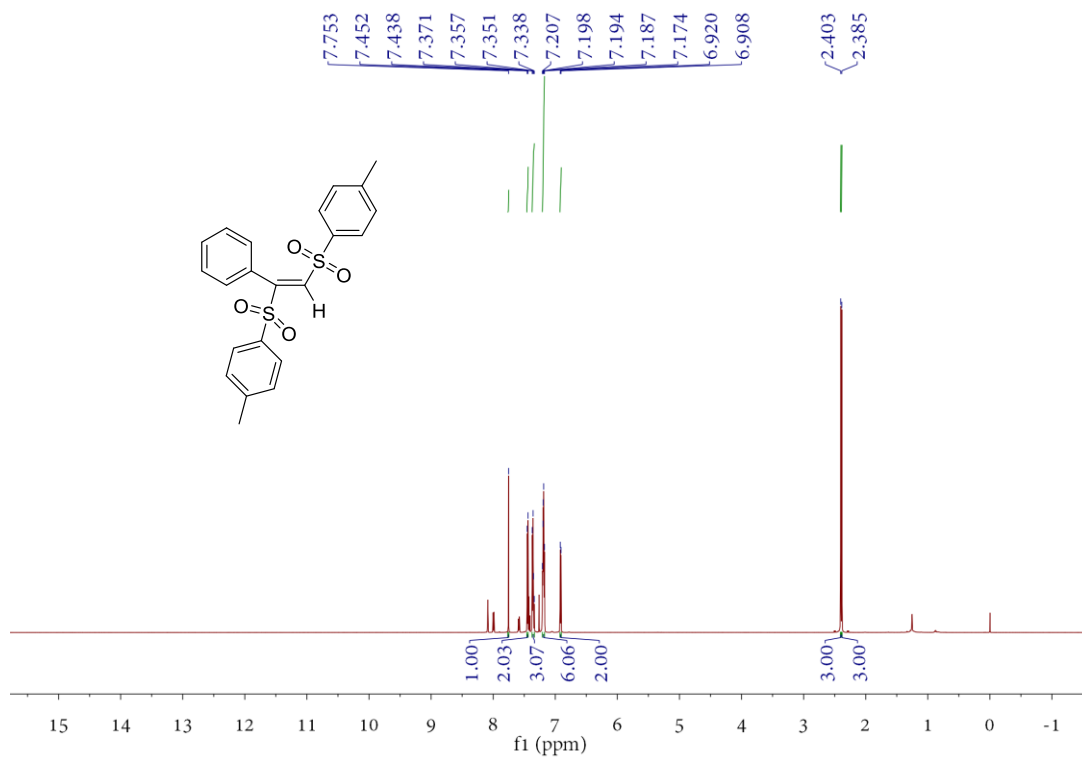
<sup>13</sup>C NMR spectrum of compound **7b**



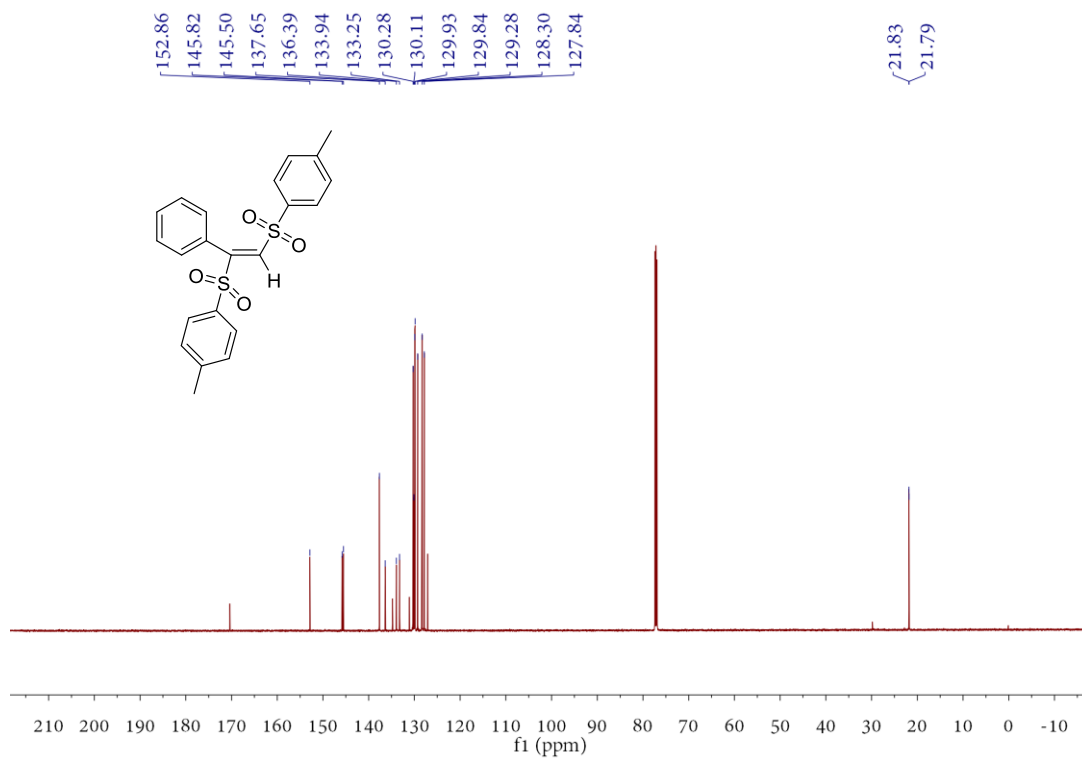
NL:  
1.26E8  
2#20 RT: 0.21  
AV: 1 T: FTMS + c  
APCI corona Full  
ms  
[50.0000-  
750.0000]

NL:  
7.08E5  
C<sub>22</sub>H<sub>20</sub>OS<sub>2</sub>+H:  
C<sub>22</sub>H<sub>21</sub>O<sub>1</sub>S<sub>2</sub>  
pa Chrg 1

HRMS of compound **7b**

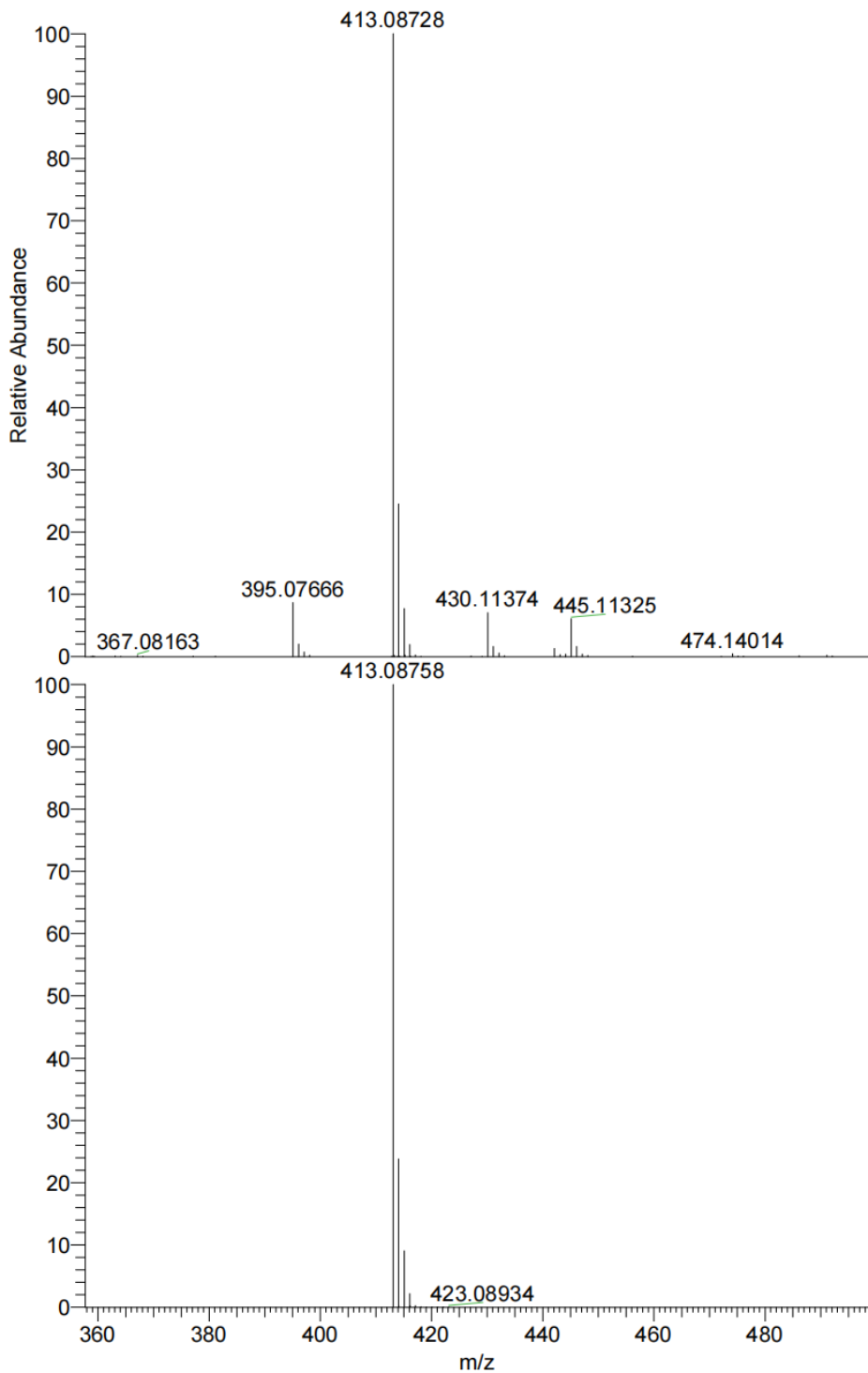


<sup>1</sup>H NMR spectrum of compound 7c



<sup>13</sup>C NMR spectrum of compound 7c





NL:  
1.39E9  
4#20 RT: 0.21 AV:  
1 T: FTMS + c APCI  
corona Full ms  
[50.0000-750.0000]

NL:  
7.03E5  
C<sub>22</sub>H<sub>20</sub>O<sub>4</sub>S<sub>2</sub>+H:  
C<sub>22</sub>H<sub>21</sub>O<sub>4</sub>S<sub>2</sub>  
pa Chrg 1

HRMS of compound 7c

## References

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