

# Palladium-Catalyzed Selective Defluorinative Sulfenylation for the Synthesis of Fluorovinylthioethers

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## Supplementary data

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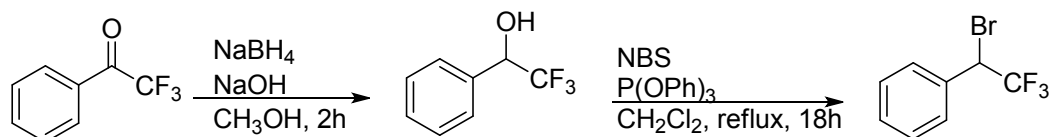
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## 1. General information.

Chemicals were either purchased or purified by standard techniques.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were measured on 500 or 400 MHz spectrometer ( $^1\text{H}$ : 500 or 400 MHz,  $^{13}\text{C}$ : 125 MHz), using DMSO as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. Chemical shifts are given in  $\delta$  relative to TMS, the coupling constants  $J$  are given in Hz. High resolution mass spectra were recorded on an ESI-Q-TOF mass spectrometry. All reactions were conducted under air atmosphere using standard Schlenk techniques. Melting points were measured on X4 melting point apparatus and uncorrected. Column chromatography was performed using EM Silica gel 60 (300-400 mesh).

## 2. General Procedure for Synthesis of 1a.<sup>1</sup>

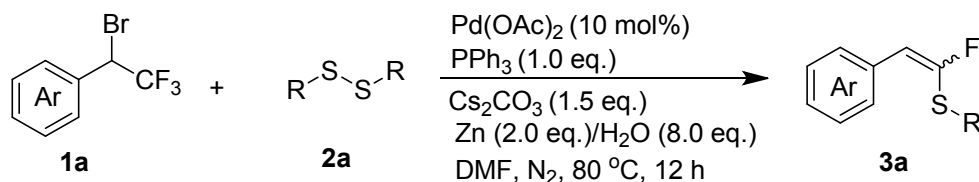


Step 1: 2,2,2-trifluoro-1-phenylethanone (1.74 g, 10 mmol) was dissolved in methyl alcohol (100ml), Then add the sodium borohydride (1.14 g, 30 mmol) and 1 Normal aqueous sodium hydroxide solution ( $\text{NaOH}$ ; 10ml) at 0 °C. The reaction mixture was warmed to 25°C and stirred for 2 hours. After the reaction was deemed completed by thin layer chromatography (TLC), saturated aqueous ammonium chloride ( $\text{NH}_4\text{Cl}$ ) solution was added to the reaction mixture and the mixture was concentrated under reduced pressure. The residue was diluted with diethyl ether ( $\text{Et}_2\text{O}$ ) and washed with water ( $\text{H}_2\text{O}$ ; 3 x 50 ml). The organic layer was dried over sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) and concentrated under reduced pressure to afford the title compound 2,2,2-trifluoro-1-phenylethanol was isolated as color less oil (1.51 g, 86.8%).

Step 2: 2,2,2-trifluoro-1-phenylethanol was dissolved in dichloromethane (50 ml), then N-bromosuccinimide (NBS, 1.78 g, 10 mmol) and triphenyl phosphite ( $\text{P(OPh)}_3$ , 4.65 g, 15 mmol) were dissolved in mixture in stirred. The resultant reaction mixture was heated at reflux for 18 h. After the reaction was deemed complete by TLC, the reaction mixture was cooled to 25 °C, Purification by flash column chromatography

on silica gel, during with Petroleum ether afforded (1-bromo-2,2,2-trifluoroethyl)benzene. Yield 45%.

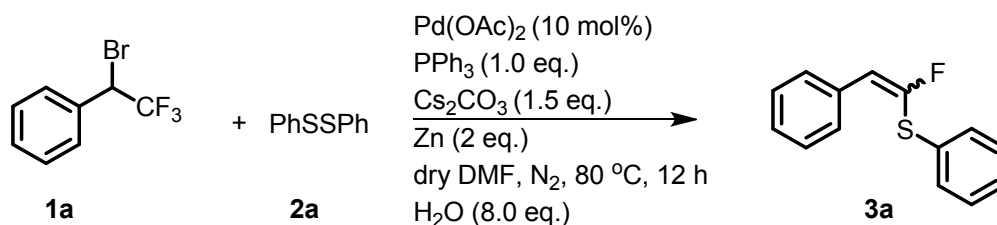
### 3. Typical experimental procedure for the synthesis of fluorovinylthioethers derivatives 3a–3s



To a flame-dried Schlenk tube with a magnetic stirring bar were charged Pd(OAc)<sub>2</sub> (2.2mg, 0.01 mmol), Cs<sub>2</sub>CO<sub>3</sub> (42.4 mg, 0.15 mmol), PhSSPh (0.05 mmol), PPh<sub>3</sub>(0.1 mmol), Zn (13.0 mg, 0.2 mmol), H<sub>2</sub>O(14.4 mg, 0.8 mmol) in dry DMF (2 mL). The mixture was stirred under a nitrogen atmosphere and heated at 80 °C for 12 hours. After the reaction was completed, it was filtered, and the filtrate was washed with a saturated sodium chloride solution and extracted with ethyl acetate, then the solvent was removed by a rotary evaporator to obtain a residue, which was subjected to column separation on a silica gel column and rinsed with an eluent to collect the effluent containing the target product, Finally, the effluent was combined and concentrated in vacuo to remove the solvent to give **3a-3s**.

### 4. Optimization details.

**Table 1** The optimization of H<sub>2</sub>O equivalent <sup>a</sup>

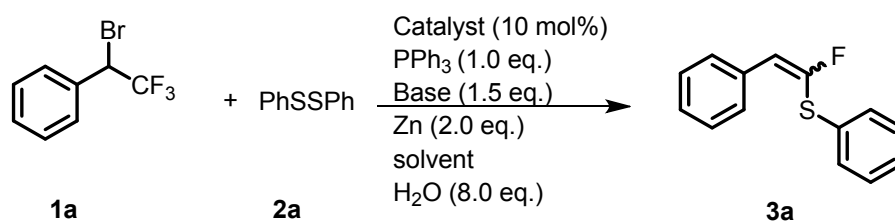


Entry	H <sub>2</sub> O (eq.)	Yield (%)
1	0	45
2	2	55

3	4	61
4	6	69
5	8	82
6	10	73
7 <sup>b</sup>	0	68

<sup>a</sup> Reaction conditions: **1a** (0.1 mmol), **2a** (0.5 equiv.), Pd(OAc)<sub>2</sub> (10 mol%), PPh<sub>3</sub> (1.0 equiv.), Cs<sub>2</sub>CO<sub>3</sub> (1.5 equiv.), Zn (2.0 equiv.), H<sub>2</sub>O (8.0 equiv.), dry DMF (2 mL), 80 °C, 12 h; isolated yield. <sup>b</sup>not dried DMF (2 mL).

**Table 2.** Optimization of reaction conditions. <sup>a</sup>

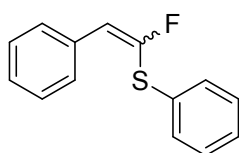


Entry	Catalyst	Base	Solvent	Yield (%)
1.	PdCl <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	MeCN	51
2.	Pd(PPh <sub>3</sub> ) <sub>4</sub>	Cs <sub>2</sub> CO <sub>3</sub>	MeCN	35
3.	Pd <sub>2</sub> (dba) <sub>3</sub>	Cs <sub>2</sub> CO <sub>3</sub>	MeCN	43
4.	Pd(PPh <sub>3</sub> )Cl <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	MeCN	46
5.	Pd(OAc) <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	MeCN	70
6.	CuI	Cs <sub>2</sub> CO <sub>3</sub>	MeCN	ND
7.	Cu(OTf) <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	MeCN	ND
8.	Pd(OAc) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	MeCN	34
9.	Pd(OAc) <sub>2</sub>	t-BuOK	MeCN	42
10.	Pd(OAc) <sub>2</sub>	DBU	MeCN	41
11.	Pd(OAc) <sub>2</sub>	K <sub>3</sub> PO <sub>4</sub>	MeCN	21
12.	Pd(OAc) <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	MeCN	38
13.	Pd(OAc) <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	dioxane	NR
14.	Pd(OAc) <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	Toluene	NR
15.	Pd(OAc) <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	NMP	25
16.	Pd(OAc) <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	DMA	20

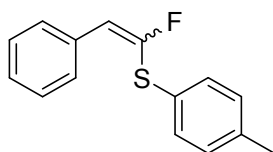
17.	Pd(OAc) <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	THF	NR
18.	Pd(OAc) <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	68
19.	Pd(OAc) <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	DMF	82
20.	-	Cs <sub>2</sub> CO <sub>3</sub>	DMF	ND
21.	Pd(OAc) <sub>2</sub>	-	DMF	NR
22 <sup>c</sup>	Pd(OAc) <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	DMF	70
23 <sup>d</sup>	Pd(OAc) <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	DMF	66
24 <sup>e</sup>	Pd(OAc) <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	DMF	69
25 <sup>f</sup>	Pd(OAc) <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	DMF	71
26 <sup>g</sup>	Pd(OAc) <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	DMF	56

<sup>a</sup> Reaction conditions: **1a** (0.1 mmol), **2a** (0.5 equiv.), Catalyst (10 mol%), PPh<sub>3</sub> (1.0 equiv.), base (1.5 equiv.), Zn (2.0 equiv), H<sub>2</sub>O (8.0 equiv.), dry DMF (2 mL), 80 °C, 12 h. <sup>b</sup> Isolated yields, <sup>c</sup> Cs<sub>2</sub>CO<sub>3</sub> (1.0 equiv), <sup>d</sup> Cs<sub>2</sub>CO<sub>3</sub> (2.0 equiv), <sup>e</sup> At 100 °C, <sup>f</sup> At 60 °C, <sup>g</sup> under air. NR = no reaction, ND = not detected.

## 5. Analytical Data for All Compounds

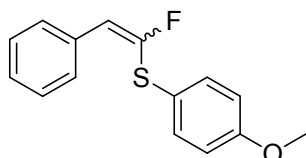


(1-fluoro-2-phenylvinyl)(phenyl)sulfane (**3a**): clear oil (18.9 mg, 82% yield); lit.<sup>2</sup> Both isomers: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62-7.58 (m, 2H), 7.54-7.49 (m, 2H), 7.43-7.39 (m, 4H), 7.37-7.33 (m, 2H), 6.84 (d, *J* = 16.0 Hz, 0.88H), 6.36 (d, *J* = 32.4 Hz, 0.12H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 152.5 (d, *J* = 293.8 Hz), 132.4 (d, *J* = 8.8 Hz), 131.2 (d, *J* = 2.5 Hz), 129.9, 129.3, 129.1, 128.9, 128.8, 128.6, 128.4, 128.0, 127.6, 118.6 (d, *J* = 31.3 Hz); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -80.32 (s, 0.88F), -85.54 (s, 0.12F); LRMS (EI 70 ev) *m/z* (%): 230 (M<sup>+</sup>, 100), 196 (36), 165 (23), 109 (48), 77 (22), 51 (26).

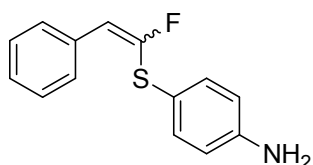


(1-fluoro-2-phenylvinyl)(*p*-tolyl)sulfane (**3b**): clear oil (19.5 mg, 80% yield); lit.<sup>3</sup> Both isomers: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62 (d, *J* = 7.6 Hz, 2H), 7.44-7.40 (m, 4H),

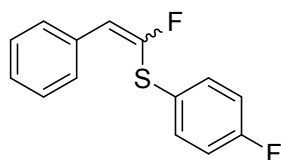
7.36-7.31 (m, 1H), 7.21 (d,  $J = 8.0$  Hz, 2H), 6.77 (d,  $J = 16.4$  Hz, 0.94H), 6.31 (d,  $J = 32.4$  Hz, 0.06H), 2.40 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  153.1 (d,  $J = 293.8$  Hz), 138.0, 132.6 (d,  $J = 8.8$  Hz), 131.1, 130.7, 130.1, 129.9, 128.8 (d,  $J = 2.5$  Hz), 128.7, 128.6, 128.4, 127.8, 127.3, 117.5 (d,  $J = 31.3$  Hz), 21.1;  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -80.48 (s, 0.95F), -85.66 (s, 0.05F); LRMS (EI 70 ev)  $m/z$  (%): 244 ( $\text{M}^+$ , 100), 224 (27), 196 (46), 152 (48), 77 (30), 51 (23).



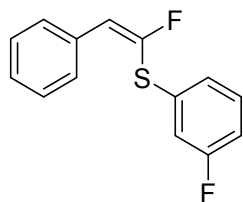
(1-fluoro-2-phenylvinyl)(4-methoxyphenyl)sulfane (**3c**): clear oil (21.8 mg, 84% yield); lit.<sup>2</sup> Both isomers:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 (d,  $J = 7.2$  Hz, 2H), 7.48 (d,  $J = 8.8$  Hz, 2H), 7.44-7.39 (m, 2H), 7.36-7.32 (m, 1H), 6.97-6.92 (m, 2H), 6.68 (d,  $J = 16.8$  Hz, 0.82H), 6.23 (d,  $J = 33.2$  Hz, 0.18H), 3.86 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  160.1, 153.7 (d,  $J = 295.0$  Hz), 133.6, 132.7 (d,  $J = 8.8$  Hz), 128.9 (d,  $J = 3.8$  Hz), 128.7, 128.6, 128.4, 127.8, 127.7, 120.8, 116.1 (d,  $J = 31.3$  Hz), 115.2 (d,  $J = 12.5$  Hz), 115.0, 55.4;  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.22 (s, 0.83F), -86.13 (s, 0.17F); LRMS (EI 70 ev)  $m/z$  (%): 260 ( $\text{M}^+$ , 100), 197 (32), 152 (25), 121 (22), 109 (32), 63(21).



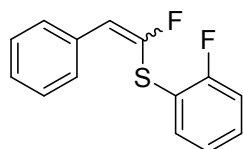
4-((1-fluoro-2-phenylvinyl)thio)aniline (**3d**): pale yellow oil (12.5 mg, 51% yield); lit.<sup>3</sup> Both isomers:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (d,  $J = 8.0$  Hz, 1H), 7.46 (d,  $J = 6.0$  Hz, 1H), 7.37-7.33 (m, 2H), 7.31-7.27 (m, 3H), 6.65-6.61 (m, 2H), 6.54 (d,  $J = 13.6$  Hz, 0.79H), 6.09 (d,  $J = 26.4$  Hz, 0.21H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) 154.3 (d,  $J = 293.8$  Hz), 147.3 (d,  $J = 5.0$  Hz), 134.2, 132.9 (d,  $J = 8.8$  Hz), 132.1 (d,  $J = 10.0$  Hz), 128.9, 128.8, 128.6, 128.5, 128.3, 127.5 (d,  $J = 1.3$  Hz), 115.7, 115.1 (d,  $J = 31.3$  Hz), 114.0 (d,  $J = 11.3$  Hz);  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.37 (s, 0.80F), -86.41 (s, 0.20F); LRMS (EI 70 ev)  $m/z$  (%): 245 ( $\text{M}^+$ , 100), 212 (22), 182 (17), 124 (25), 77 (32), 51 (28).



(*E*)-1-fluoro-2-phenylvinyl(4-fluorophenyl)sulfane (**3e**): clear oil (18.6 mg, 75% yield); Both isomers:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 (d,  $J = 7.6$  Hz, 2H), 7.44-7.40 (m, 2H), 7.38-7.33 (m, 2H), 7.27-7.20 (m, 2H), 7.05-7.00 (m, 1H), 6.91 (d,  $J = 16.0$  Hz, 0.88H), 6.41 (d,  $J = 32.0$  Hz, 0.12H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  163.0 (d,  $J = 248.8$  Hz), 151.5 (d,  $J = 293.8$  Hz), 133.6 (d,  $J = 2.5$  Hz), 132.1 (d,  $J = 8.8$  Hz), 130.6 (d,  $J = 8.8$  Hz), 129.0 (d,  $J = 8.8$  Hz), 128.9 (d,  $J = 3.8$  Hz), 128.7, 128.5, 128.2, 124.9 (d,  $J = 2.5$  Hz), 119.8 (d,  $J = 30.0$  Hz), 116.3 (d,  $J = 23.8$  Hz), 114.6 (d,  $J = 20.0$  Hz);  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -80.62 (s, 0.90F), -85.85 (s, 0.10F), -111.25 (s, 1F); LRMS (EI 70 ev)  $m/z$  (%): 248 ( $\text{M}^+$ , 100), 214 (29), 183 (24), 121 (25), 109 (55), 75 (27). HRMS-ESI ( $m/z$ ) calcd. for  $\text{C}_{14}\text{H}_{10}\text{F}_2\text{S}$  ( $[\text{M} + \text{Na}]^+$ ): 271.0363; found: 271.0368.

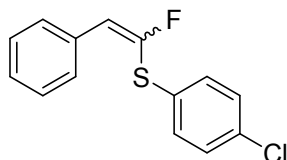


(*Z*)-1-fluoro-2-phenylvinyl(3-fluorophenyl)sulfane (**3f**): clear oil (14.9 mg, 60% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 (d,  $J = 7.6$  Hz, 2H), 7.49 (d,  $J = 7.6$  Hz, 2H), 7.42-7.39 (m, 3H), 7.37-7.34 (m, 2H), 6.83 (d,  $J = 16.0$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  152.5 (d,  $J = 295.0$  Hz), 132.4 (d,  $J = 7.5$  Hz), 131.2, 129.9, 129.3, 128.8 (d,  $J = 2.5$  Hz), 128.4, 127.9, 127.6, 118.6 (d,  $J = 31.3$  Hz);  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -80.35 (s, 1F), -111.31 (s, 1F); LRMS (EI 70 ev)  $m/z$  (%): 248 ( $\text{M}^+$ , 100), 203 (24), 183 (27), 127 (49), 77 (21), 51 (24). HRMS-ESI ( $m/z$ ) calcd. for  $\text{C}_{14}\text{H}_{10}\text{F}_2\text{S}$  ( $[\text{M} + \text{Na}]^+$ ): 271.0363; found: 271.0367.

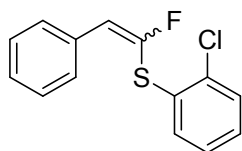


(*E*)-1-fluoro-2-phenylvinyl(2-fluorophenyl)sulfane (**3g**): pale yellow oil (12.9 mg, 52% yield); Both isomers:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 (d,  $J = 7.6$  Hz, 2H), 7.54-7.49 (m, 2H), 7.43-7.39 (m, 3H), 7.37-7.33 (m, 2H), 6.84 (d,  $J = 16.0$  Hz, 0.80H),

6.36 (d,  $J = 32.4$  Hz, 0.20H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  152.5 (d,  $J = 295.0$  Hz), 132.4 (d,  $J = 8.8$  Hz), 131.2, 129.9, 129.3, 129.1, 128.8 (d,  $J = 3.8$  Hz), 128.6, 128.4, 128.2, 127.6, 118.6 (d,  $J = 31.3$  Hz), 116.1 (d,  $J = 22.5$  Hz);  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.81 (s, 0.82F), -86.15 (s, 0.18F), -109.37 (s, 1F); LRMS (EI 70 ev)  $m/z$  (%): 248 ( $\text{M}^+$ , 100), 214 (28), 183 (22), 109 (50), 83 (22), 75 (28). HRMS-ESI ( $m/z$ ) calcd. for  $\text{C}_{14}\text{H}_{10}\text{F}_2\text{S}$  ( $[\text{M} + \text{Na}]^+$ ): 271.0363; found: 271.0366.

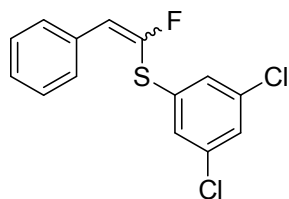


(4-chlorophenyl)(1-fluoro-2-phenylvinyl)sulfane (**3h**): clear oil (19.3 mg, 73% yield); Both isomers:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 (d,  $J = 7.6$  Hz, 2H), 7.45-7.40 (m, 4H), 7.39-7.35 (m, 3H), 6.84 (d,  $J = 16.4$  Hz, 0.88H), 6.36 (d,  $J = 32.4$  Hz, 0.12H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  152.0 (d,  $J = 295.0$  Hz), 134.0, 132.7 (d,  $J = 5.0$  Hz), 132.2 (d,  $J = 8.8$  Hz), 131.3, 131.2, 129.0, 128.8 (d,  $J = 2.5$  Hz), 128.7, 128.5, 128.4 (d,  $J = 1.3$  Hz), 128.1, 118.8 (d,  $J = 31.3$  Hz), 118.2 (d,  $J = 12.5$  Hz);  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.02 (s, 0.90 F), -86.07 (s, 0.10 F); LRMS (EI 70 ev)  $m/z$  (%): 266 ( $\text{M}^+$ , 37), 264 (100), 196 (65), 165 (32), 109 (59), 75 (34). HRMS-ESI ( $m/z$ ) calcd. for  $\text{C}_{14}\text{H}_{10}\text{ClFS}$  ( $[\text{M} + \text{H}]^+$ ): 265.0249; found: 265.0255.

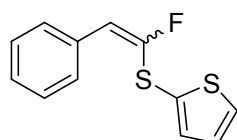


(2-chlorophenyl)(1-fluoro-2-phenylvinyl)sulfane (**3i**): clear oil (13.3 mg, 50% yield); Both isomers:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64-7.60 (m, 2H), 7.53 (d,  $J = 7.6$  Hz, 1H), 7.47-7.35 (m, 4H), 7.32-7.23 (m, 2H), 7.00 (d,  $J = 16.0$  Hz, 0.92H), 6.47 (d,  $J = 32.0$  Hz, 0.08H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.7 (d,  $J = 293.8$  Hz), 133.3, 132.0 (d,  $J = 8.8$  Hz), 131.1 (d,  $J = 3.8$  Hz), 130.1, 129.6, 129.0 (d,  $J = 7.5$  Hz), 128.8 (d,  $J = 3.8$  Hz), 128.7, 128.5, 128.2, 127.5, 120.7 (d,  $J = 31.3$  Hz), 120.3 (d,  $J = 11.3$  Hz);  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -76.69 (s, 0.08 F), -81.31 (s, 0.92 F); LRMS (EI 70 ev)  $m/z$  (%): 266 ( $\text{M}^+$ , 38), 264 (100), 196 (73), 152 (74), 77 (45), 51 (48). HRMS-ESI ( $m/z$ ) calcd. for  $\text{C}_{14}\text{H}_{10}\text{ClFS}$  ( $[\text{M} + \text{H}]^+$ ): 265.0249; found: 265.0253.

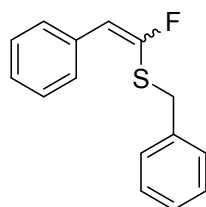




*(3,5-dichlorophenyl)(1-fluoro-2-phenylvinyl)sulfane (3j)*: clear oil (23.0 mg, 77% yield); Both isomers:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62-7.54 (m, 2H), 7.44-7.35 (m, 3H), 7.33-7.30 (m, 3H), 6.95 (d,  $J = 16.0$  Hz, 0.92H), 6.42 (d,  $J = 32.0$  Hz, 0.08H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.4 (d,  $J = 293.8$  Hz), 135.7, 135.0, 131.7 (d,  $J = 8.8$  Hz), 128.9 (d,  $J = 3.8$  Hz), 128.8, 128.5, 128.4, 127.6, 126.9, 120.8 (d,  $J = 31.3$  Hz);  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.28 (s, 0.94F), -86.28 (s, 0.06F); LRMS (EI 70 ev)  $m/z$  (%): 300 ( $\text{M}^+$ , 55), 298 (81), 230 (45), 152 (25), 109 (100), 75 (26). HRMS-ESI ( $m/z$ ) calcd. for  $\text{C}_{14}\text{H}_9\text{Cl}_2\text{FS}$  ( $[\text{M} + \text{H}]^+$ ): 298.9859; found: 298.9841.

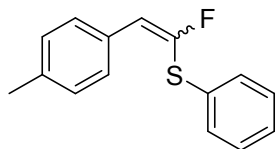


*2-((1-fluoro-2-phenylvinyl)thio)thiophene (3k)*: clear oil (16.6 mg, 70% yield); Both isomers:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 (d,  $J = 6.0$  Hz, 2H), 7.44 (d,  $J = 4.0$  Hz, 1H), 7.40-7.37 (m, 2H), 7.32-7.27 (m, 2H), 7.03-7.01 (m, 1H), 6.55 (d,  $J = 13.2$  Hz, 0.95H), 6.15 (d,  $J = 26.0$  Hz, 0.05H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) 153.0 (d,  $J = 296.3$  Hz), 135.4, 132.4 (d,  $J = 8.8$  Hz), 131.0, 128.9 (d,  $J = 3.8$  Hz), 128.6, 128.5, 127.8, 127.7, 126.7, 115.3 (d,  $J = 30.0$  Hz), 114.5 (d,  $J = 12.5$  Hz);  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -67.26 (s, 0.06F), -82.92 (s, 0.94F); LRMS (EI 70 ev)  $m/z$  (%): 236 ( $\text{M}^+$ , 100), 203 (59), 173 (22), 159(22), 101 (23), 71 (41). HRMS-EI ( $m/z$ ) calcd. for  $\text{C}_{12}\text{H}_9\text{FS}_2$  ( $[\text{M} + \text{H}]^+$ ): 237.0202; found: 237.0201.

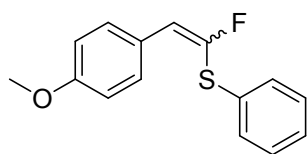


*benzyl(1-fluoro-2-phenylvinyl)sulfane (3l)*: clear oil (11.4 mg, 47% yield); lit.<sup>2</sup> Both isomers:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 (s, 3H), 7.30-7.25 (m, 6H), 7.23-7.19 (m,

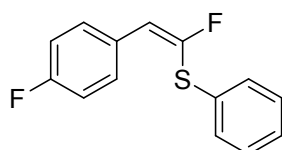
1H), 6.52 (d,  $J = 14.4$  Hz, 0.92H), 5.91 (d,  $J = 27.2$  Hz, 0.08H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) 154.1 (d,  $J = 292.5$  Hz), 136.8, 132.9, 132.7 (d,  $J = 10.0$  Hz), 129.1, 128.9, 128.8, 128.7, 128.6, 128.5, 128.2, 127.5, 127.3, 115.9 (d,  $J = 31.3$  Hz), 36.2 (d,  $J = 2.5$  Hz);  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.28 (s, 0.95 F), -86.28 (s, 0.05 F); LRMS (EI 70 ev)  $m/z$  (%): 244 ( $\text{M}^+$ , 16), 109 (14), 91 (100), 77(31), 65 (11), 51 (21).



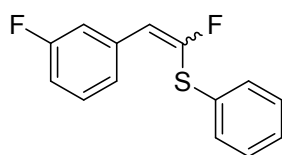
(1-fluoro-2-(*p*-tolyl)vinyl)(phenyl)sulfane (**3m**): clear oil (19.6 mg, 80% yield); lit.<sup>3</sup> Both isomers:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53-7.49 (m, 4H), 7.41-7.31 (m, 3H), 7.22 (d,  $J = 8.0$  Hz, 2H), 6.83 (d,  $J = 16.0$  Hz, 0.90H), 6.35 (d,  $J = 32.4$  Hz, 0.08 H), 2.41 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) 151.8 (d,  $J = 293.8$  Hz), 138.0, 131.5 (d,  $J = 2.5$  Hz), 131.1, 129.7, 129.6, 129.5, 129.4, 129.3, 129.1, 128.9, 128.7 (d,  $J = 3.8$  Hz), 127.5, 118.8 (d,  $J = 32.5$  Hz), 21.2;  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.29 (s, 0.05F), -81.37 (s, 0.95F); LRMS (EI 70 ev)  $m/z$  (%): 244 ( $\text{M}^+$ , 100), 224 (51), 196 (43), 152 (43), 77 (28), 51 (22).



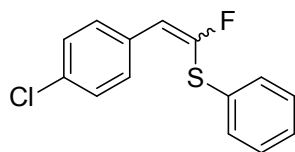
(1-fluoro-2-(4-methoxyphenyl)vinyl)(phenyl)sulfane (**3n**): clear oil (14.3 mg, 55% yield); lit.<sup>2</sup> Both isomers:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (d,  $J = 8.8$  Hz, 2H), 7.46 (d,  $J = 8.0$  Hz, 2H), 7.38-7.32 (m, 3H), 6.92 (d,  $J = 8.8$  Hz, 2H), 6.80 (d,  $J = 16.4$  Hz, 0.93H), 6.31 (d,  $J = 32.8$  Hz, 0.07H), 3.85 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) 158.5, 149.9 (d,  $J = 291.3$  Hz), 130.7, 129.4, 129.1 (d,  $J = 2.5$  Hz), 128.4, 128.3, 128.2, 126.4, 123.7 (d,  $J = 8.8$  Hz), 117.8 (d,  $J = 32.5$  Hz), 113.1, 112.9, 54.3;  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -82.29 (s, 0.93 F), -88.42 (s, 0.07 F); LRMS (EI 70 ev)  $m/z$  (%): 260 ( $\text{M}^+$ , 100), 215 (49), 168 (21), 139 (23), 77 (34), 51 (20).



*(Z)*-(1-fluoro-2-(4-fluorophenyl)vinyl)(phenyl)sulfane (**3o**): clear oil (17.7 mg, 73% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.48 (d, *J* = 4.8 Hz, 4H), 7.35-7.25 (m, 3H), 7.05 (d, *J* = 6.4 Hz, 2H), 6.74 (d, *J* = 12.4 Hz, 0.88H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) 162.3 (d, *J* = 245.0 Hz), 152.4 (d, *J* = 295.0 Hz), 131.0 (d, *J* = 2.5 Hz), 130.6 (d, *J* = 3.8 Hz), 130.5 (d, *J* = 2.5 Hz), 129.8, 129.4, 127.7, 117.6 (d, *J* = 32.5 Hz), 115.4 (d, *J* = 21.3 Hz); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -80.55 (s, 1F), -113.22 (s, 1F); LRMS (EI 70 ev) *m/z* (%): 248 (M<sup>+</sup>, 100), 203 (21), 183 (20), 152 (20), 109 (53), 75 (27). HRMS-ESI (*m/z*) calcd. for C<sub>14</sub>H<sub>10</sub>F<sub>2</sub>S ([M + Na]<sup>+</sup>): 271.0363; found: 271.0370.

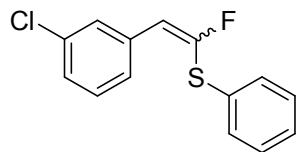


*(1-fluoro-2-(3-fluorophenyl)vinyl)(phenyl)sulfane* (**3p**): clear oil (17.2 mg, 71% yield); Both isomers: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.51-7.44 (m, 2H), 7.36-7.24 (m, 6H), 7.00-6.96 (m, 1H), 6.70 (d, *J* = 12.8 Hz, 0.82H), 6.24 (d, *J* = 25.6 Hz, 0.18H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) 162.7 (d, *J* = 245.0 Hz), 154.8, 152.4, 134.6, 130.4, 130.3, 129.4, 127.9, 124.8, 117.1 (d, *J* = 32.5 Hz), 115.4 (d, *J* = 2.5 Hz), 115.3 (d, *J* = 2.5 Hz), 114.8 (d, *J* = 21.3 Hz); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -78.43 (s, 0.85F), -83.74 (s, 0.15F), -112.89 (s, 1F); LRMS (EI 70 ev) *m/z* (%): 248 (M<sup>+</sup>, 100), 215 (25), 183 (23), 127 (31), 77 (20), 51 (48). HRMS-ESI (*m/z*) calcd. for C<sub>14</sub>H<sub>10</sub>F<sub>2</sub>S ([M + Na]<sup>+</sup>): 271.0363; found: 271.0369.

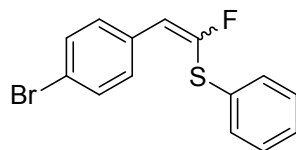


*(2-(4-chlorophenyl)-1-fluorovinyl)(phenyl)sulfane* (**3q**): clear oil (21.2 mg, 80% yield); Both isomers: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.50-7.46 (m, 2H), 7.45-7.42 (m, 2H), 7.35-7.29 (m, 5H), 6.70 (d, *J* = 12.4 Hz, 0.82H), 6.23 (d, *J* = 25.6 Hz, 0.16H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) 153.1 (d, *J* = 296.3 Hz), 133.7, 130.9 (d, *J* = 8.8 Hz), 130.7, 130.2, 130.1, 130.0 (d, *J* = 3.8 Hz), 129.8, 129.4, 129.3, 128.8, 128.6, 127.8, 117.3 (d, *J* = 32.5 Hz); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -66.02 (s, 0.15F) -79.17 (s, 0.85F); LRMS (EI 70 ev) *m/z* (%): 266 (M<sup>+</sup>, 40), 264 (100), 196 (59), 152 (56), 77

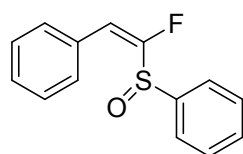
(25), 51 (25). HRMS-ESI (m/z) calcd. for C<sub>14</sub>H<sub>10</sub>ClFS ([M + H]<sup>+</sup>): 265.0249; found: 265.0263.



(2-(3-chlorophenyl)-1-fluorovinyl)(phenyl)sulfane (**3r**): pale yellow oil (19.4 mg, 73% yield); Both isomers: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.52 (d, *J* = 1.2 Hz, 1H), 7.50-7.40 (m, 3H), 7.36-7.25 (m, 5H), 6.67 (d, *J* = 12.0 Hz, 0.73H), 6.19 (d, *J* = 25.2 Hz, 0.27H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) 153.8 (d, *J* = 297.5 Hz), 134.3, 130.4, 129.8, 129.6, 129.4, 128.7 (d, *J* = 3.8 Hz), 128.1, 128.0, 127.9, 127.0 (d, *J* = 3.8 Hz), 126.9 (d, *J* = 8.8 Hz), 116.7 (d, *J* = 32.5 Hz), 115.7 (d, *J* = 12.5 Hz); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -78.24 (s, 0.72F), -83.55 (s, 0.28F); LRMS (EI 70 ev) m/z (%): 266 (M<sup>+</sup>, 36), 264 (100), 196 (67), 109 (62), 75 (38), 51 (14). HRMS-ESI (m/z) calcd. for C<sub>14</sub>H<sub>10</sub>ClFS ([M + H]<sup>+</sup>): 265.0249; found: 265.0262.

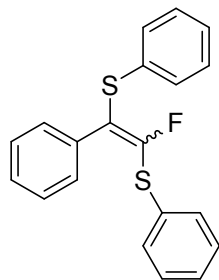


(2-(4-bromophenyl)-1-fluorovinyl)(phenyl)sulfane (**3s**): clear oil (26.2 mg, 86% yield); lit.<sup>4</sup> Both isomers: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.39 (d, *J* = 6.8 Hz, 2H), 7.35-7.33 (m, 3H), 7.30-7.17 (m, 4H), 6.60 (d, *J* = 12.4 Hz, 0.76H), 6.13 (d, *J* = 25.6 Hz, 0.22H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) 153.1 (d, *J* = 296.3 Hz), 131.8, 131.6, 131.4, 131.3, 130.3 (d, *J* = 2.5 Hz), 130.2, 130.1, 129.4, 129.3, 127.9, 122.0, 117.3 (d, *J* = 32.5 Hz), 116.2 (d, *J* = 12.5 Hz); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -78.86 (s, 0.80F), -84.47 (s, 0.20F); LRMS (EI 70 ev) m/z (%): 310 (M<sup>+</sup>, 84), 308 (81), 196 (100), 152 (92), 77 (35), 51(36).

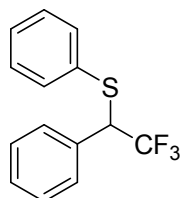


(2-fluoro-2-(phenylsulfinyl)vinyl)benzene (**4**): pale yellow oil (18.0 mg, 78% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.78 (d, *J* = 6.0 Hz, 2H), 7.56-7.54 (m, 5H), 7.39-7.33

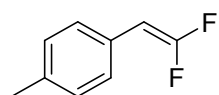
(m, 3H), 6.65 (d,  $J = 29.6$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  158.7 (d,  $J = 317.5$  Hz), 140.7, 132.1, 130.6 (d,  $J = 3.8$  Hz), 129.5 (d,  $J = 6.3$  Hz), 129.3 (d,  $J = 2.5$  Hz), 128.8, 125.4, 111.9;  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -122.4 (s, 1F); LRMS (EI 70 ev)  $m/z$  (%): 246 ( $\text{M}^+$ , 2), 230 (18), 198 (64), 137 (22), 109 (100), 71 (24). HRMS-ESI ( $m/z$ ) calcd. for  $\text{C}_{14}\text{H}_{12}\text{OFS}$  ( $[\text{M} + \text{H}]^+$ ): 247.0587; found: 247.0597.



(*E*)-(1-fluoro-2-phenylethene-1,2-diyl)bis(phenylsulfane) (**5**): pale yellow oil (10.0 mg, 42% yield); lit.<sup>5</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62-7.57 (m, 2H), 7.42-7.36 (m, 4H), 7.32-7.28 (m, 5H), 7.23 (d,  $J = 7.2$  Hz, 2H), 7.16 (d,  $J = 5.2$  Hz, 2H),  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  149.6, 138.1, 135.2, 134.1, 133.5, 133.2, 131.3, 130.5, 129.9, 128.7, 128.5, 127.8, 127.7, 127.5, 127.2, 126.8, 126.7, 124.8 (d,  $J = 260.6$  Hz), 117.4 (d,  $J = 37.5$  Hz).



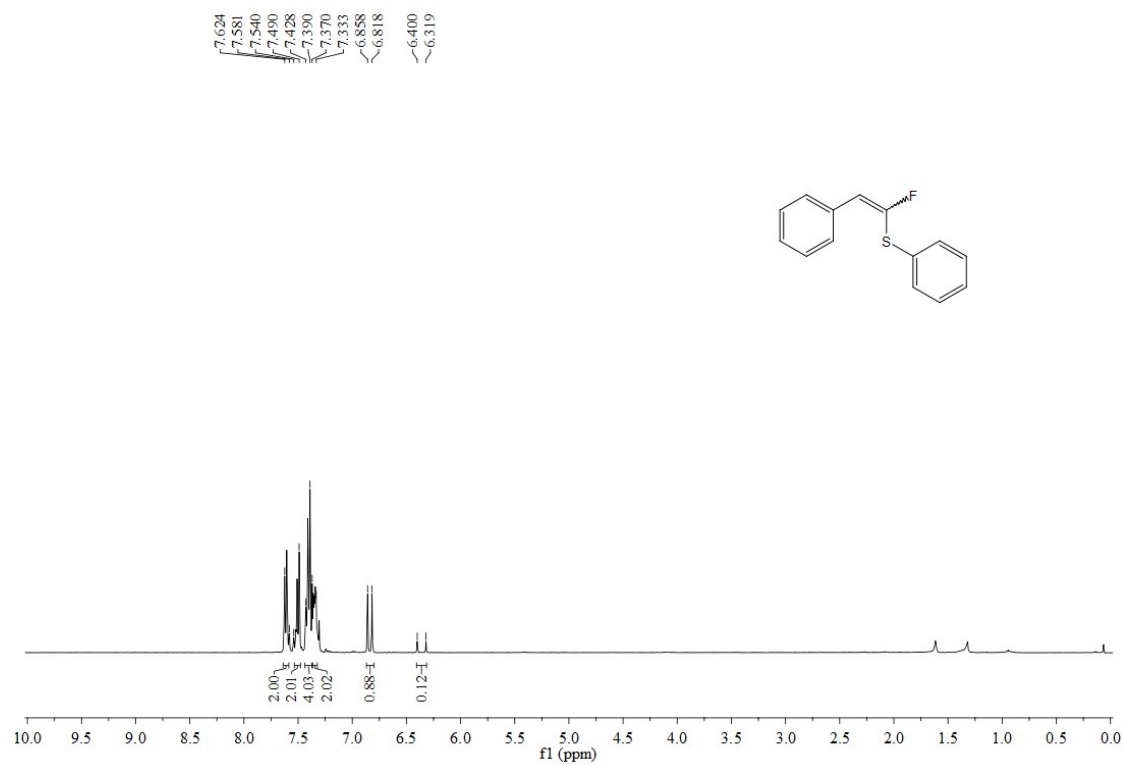
1-phenyl(2,2,2-trifluoro-1-phenylethyl)sulfane (**6**): clear oil (8.3 mg, 31% yield); lit.<sup>6</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48-7.46 (m, 2H), 7.39 (s, 5H), 7.35-7.32 (m, 3H), 4.57 (q,  $J = 8.4$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  133.8, 133.7, 132.8, 129.2, 128.9, 128.8, 128.7, 128.6, 125.6 (q,  $J = 277.5$  Hz), 56.9 (q,  $J = 28.8$  Hz).



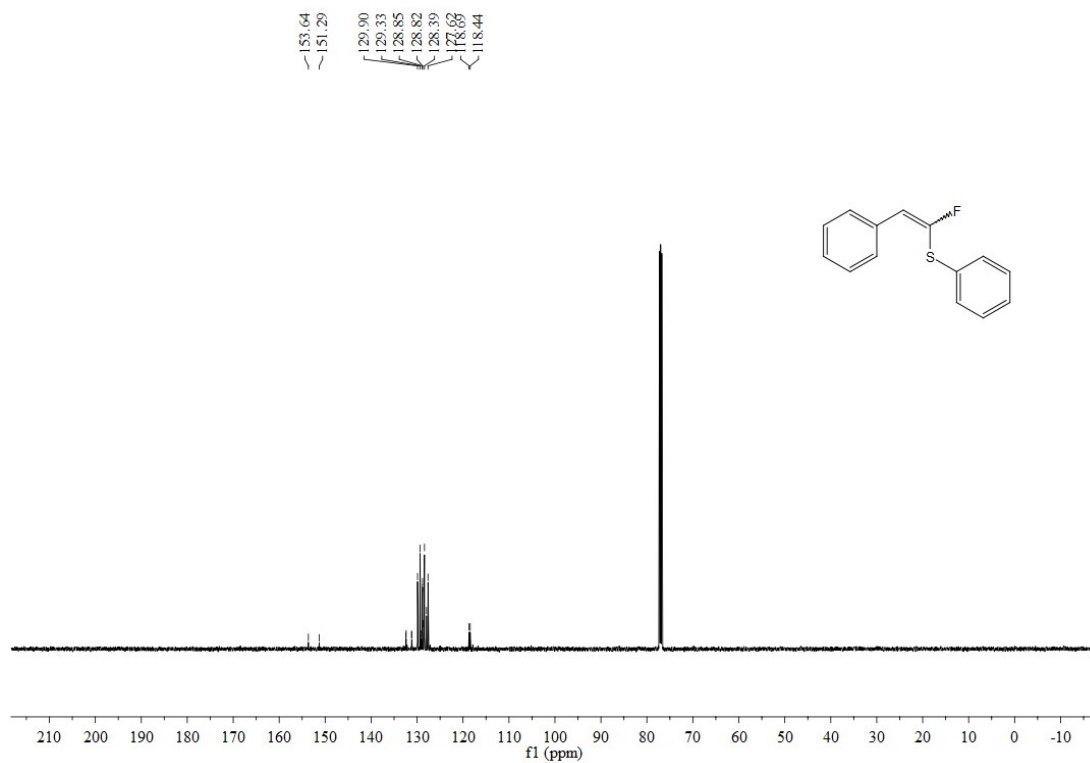
2-(2,2-difluorovinyl)-4-methylbenzene (**7**): clear oil ; lit.<sup>7</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.21 (d,  $J = 6.4$  Hz, 2H), 7.13 (d,  $J = 6.4$  Hz, 2H), 5.23 (dd,  $J = 21.2, 3.2$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  156.1 (dd,  $J = 285.0, 286.3$  Hz), 136.8, 129.4, 127.5 (q,  $J = 2.5$  Hz), 82.0 (dd,  $J = 13.8, 13.8$  Hz), 21.1.

## 6. NMR Spectra for All Compounds

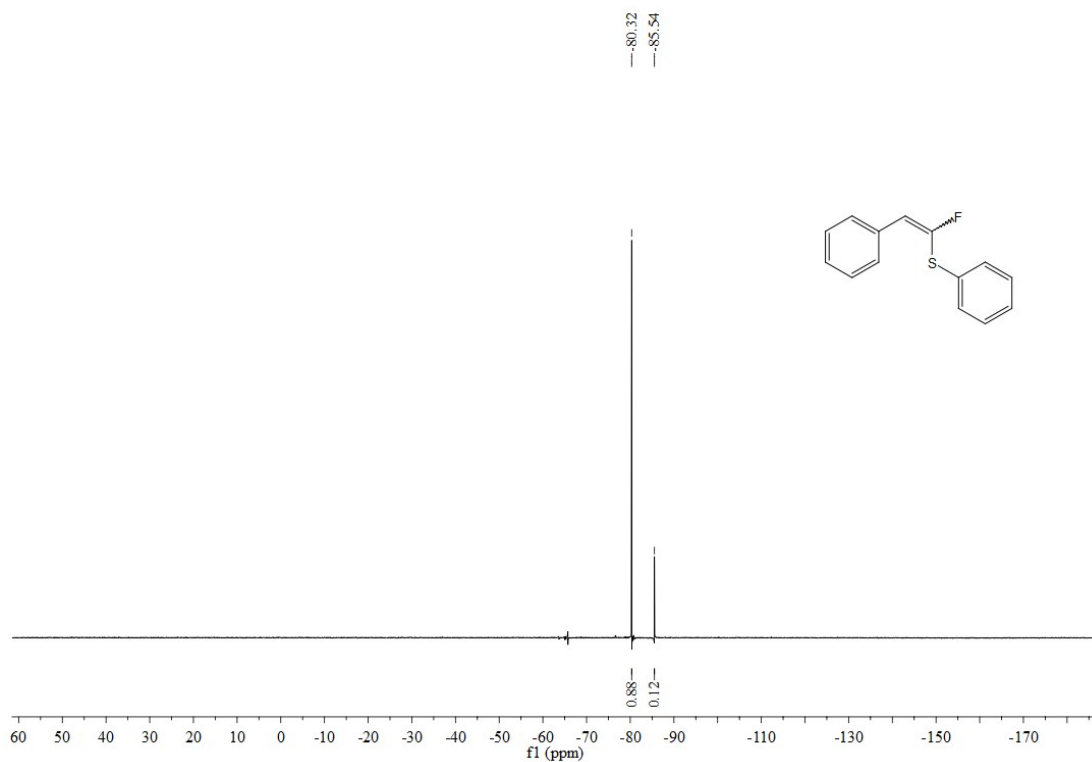
### $^1\text{H}$ NMR: (1-fluoro-2-phenylvinyl)(phenyl)sulfane (3a)



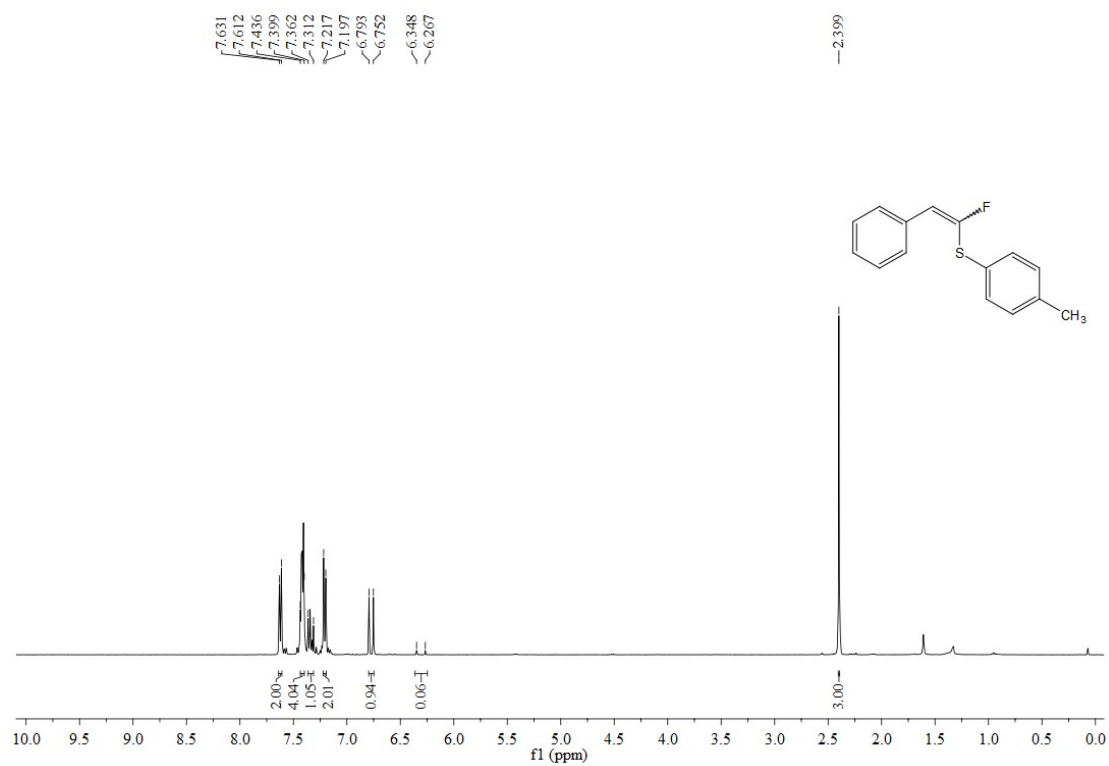
### $^{13}\text{C}$ NMR: (1-fluoro-2-phenylvinyl)(phenyl)sulfane (3a)



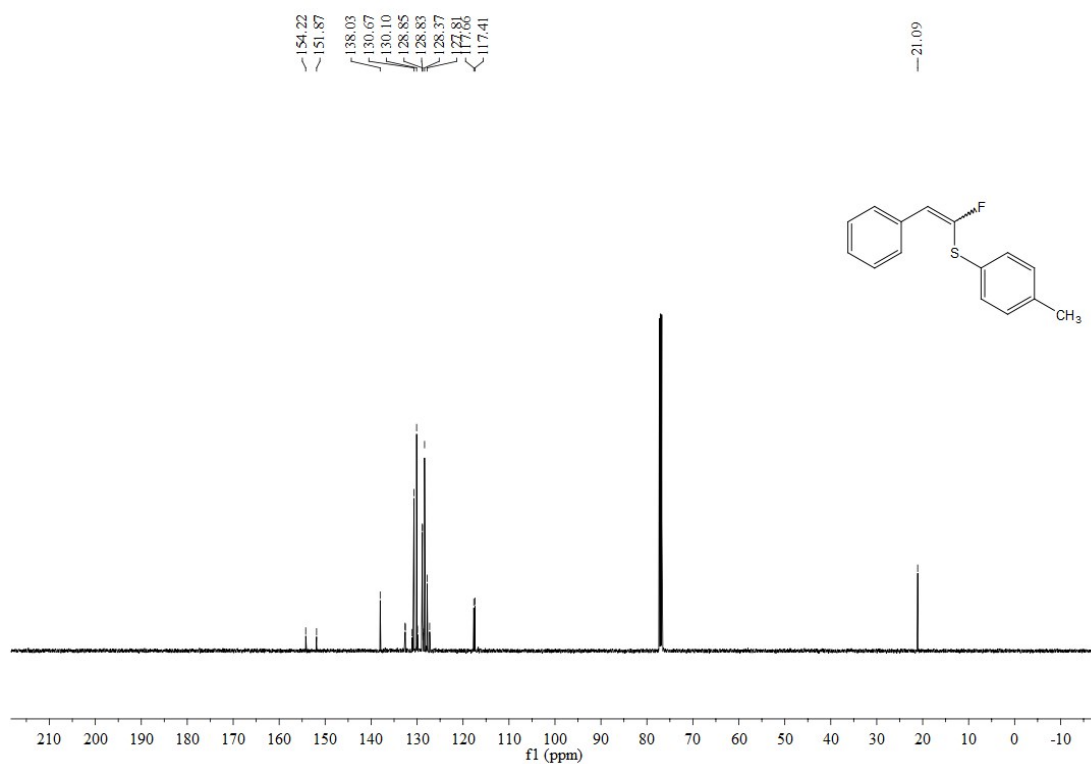
**<sup>19</sup>F NMR: (1-fluoro-2-phenylvinyl)(phenyl)sulfane (3a)**



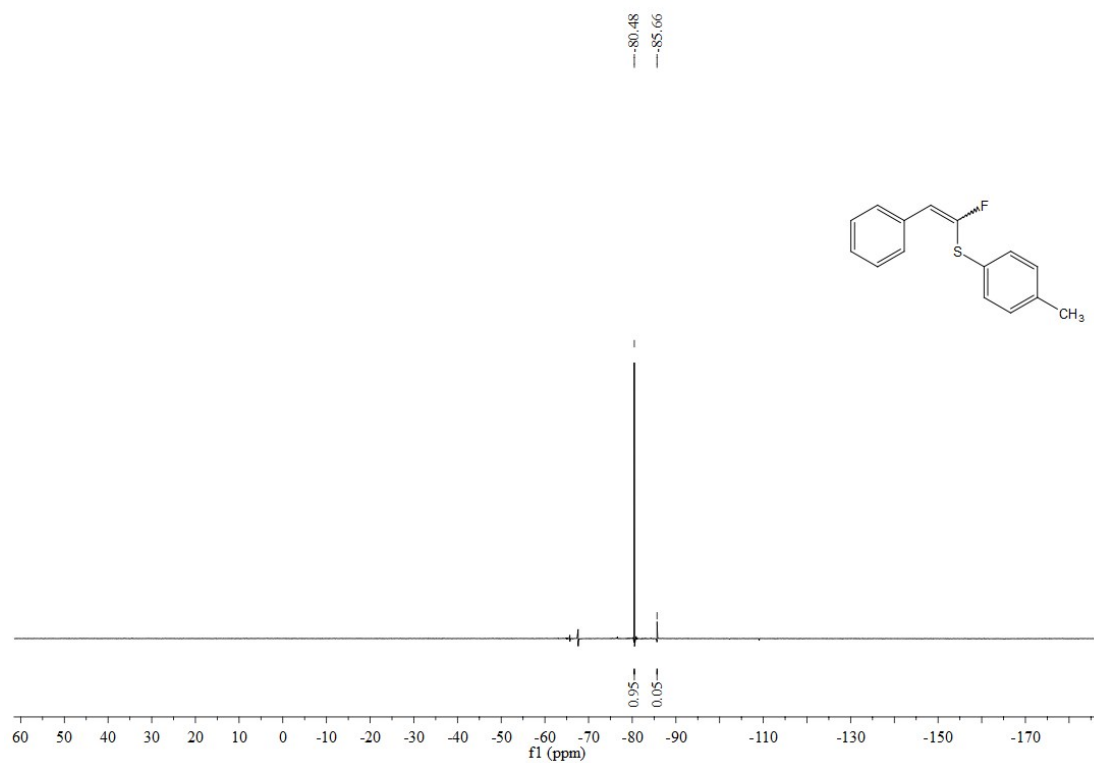
**<sup>1</sup>H NMR: (1-fluoro-2-phenylvinyl)(p-tolyl)sulfane (3b)**



**<sup>13</sup>CNMR: (1-fluoro-2-phenylvinyl)(p-tolyl)sulfane (3b)**

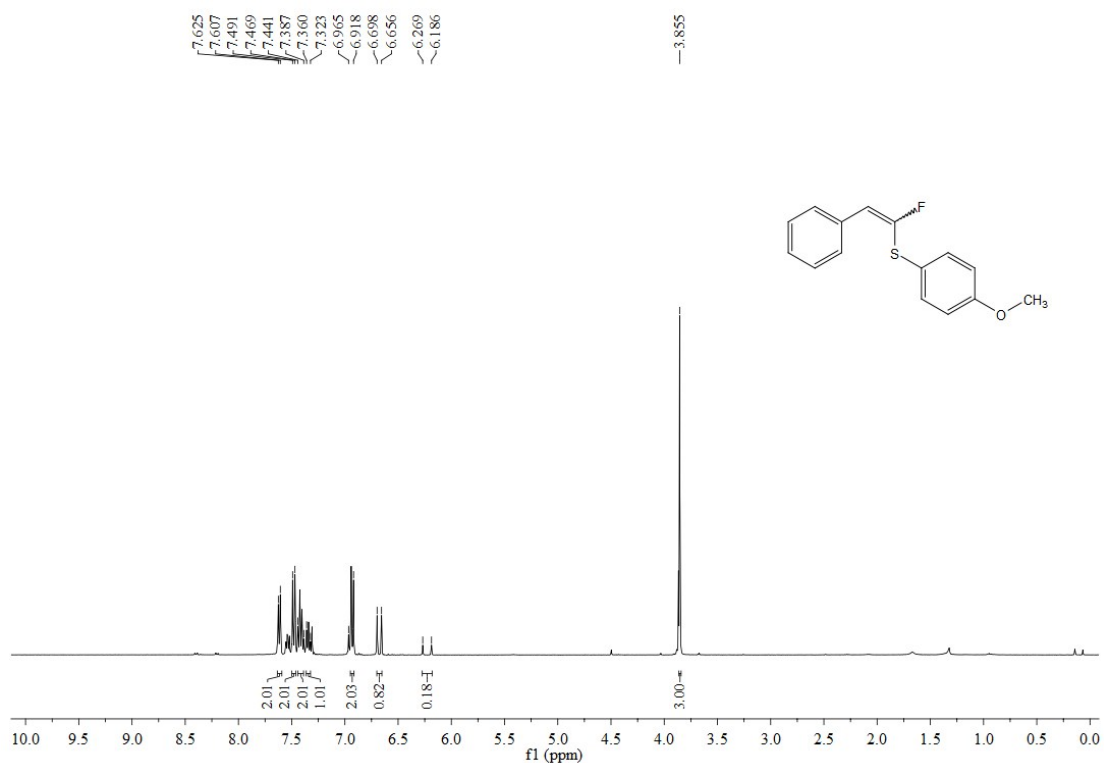


**<sup>19</sup>F NMR: (1-fluoro-2-phenylvinyl)(p-tolyl)sulfane (3b)**

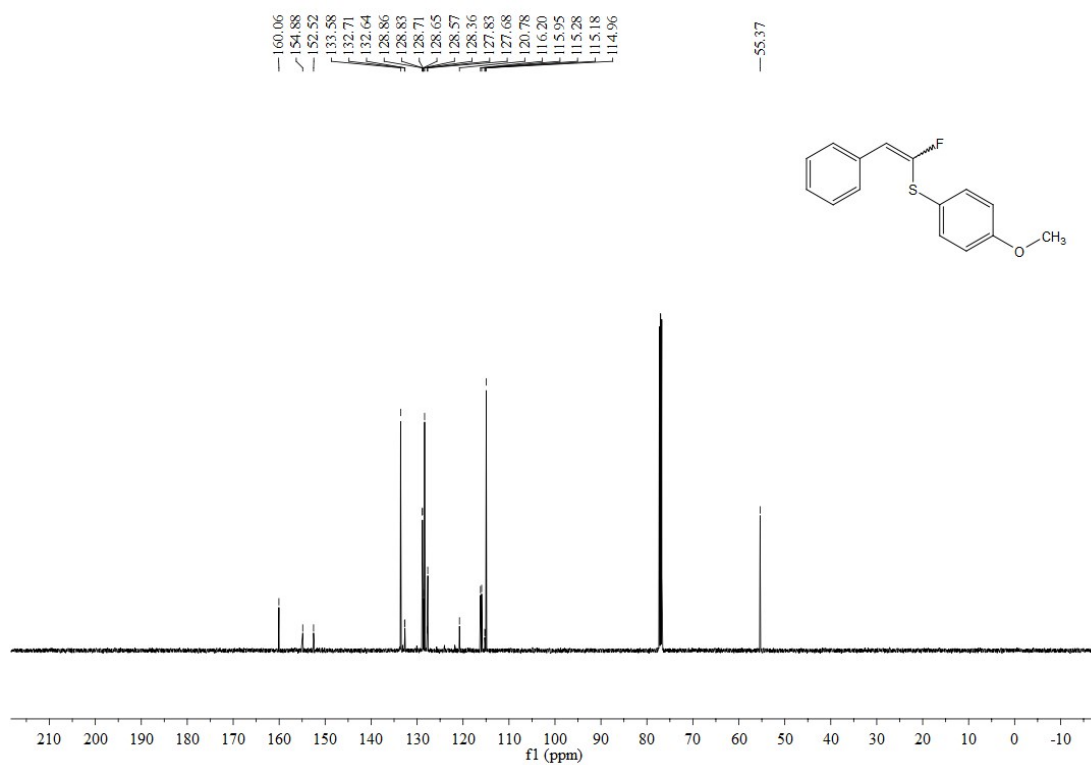




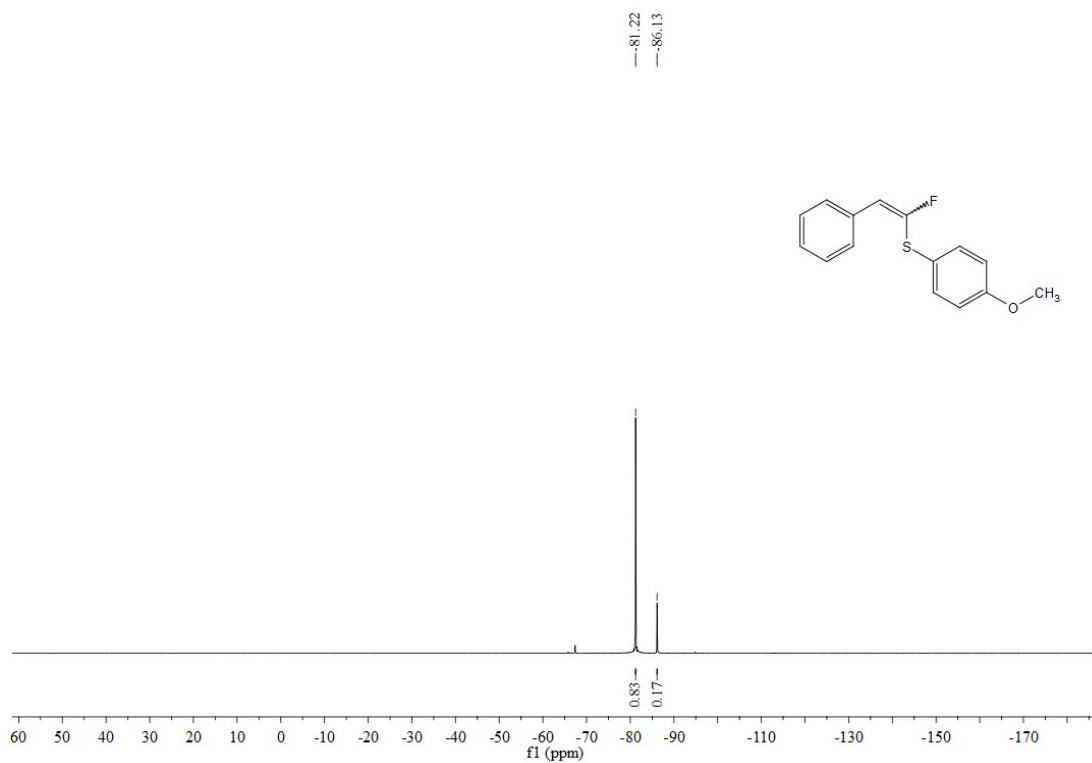
**<sup>1</sup>H NMR: (1-fluoro-2-phenylvinyl)(4-methoxyphenyl)sulfane (3c)**



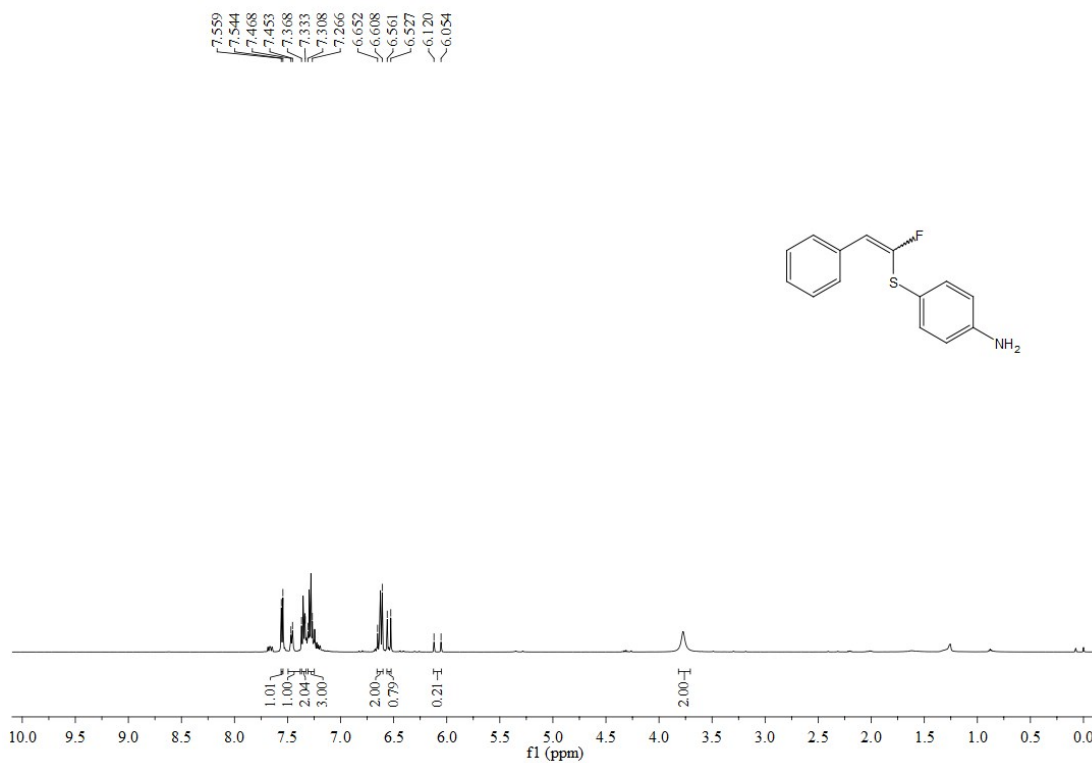
**<sup>13</sup>C NMR: (1-fluoro-2-phenylvinyl)(4-methoxyphenyl)sulfane (3c)**



**<sup>19</sup>F NMR: (1-fluoro-2-phenylvinyl)(4-methoxyphenyl)sulfane (3c)**

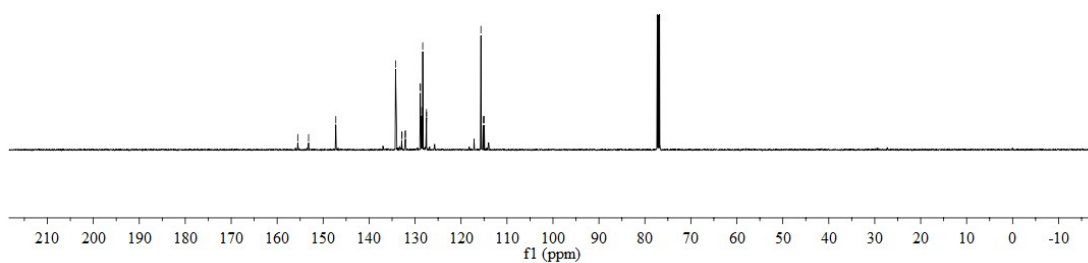
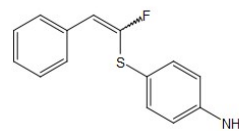


**<sup>1</sup>H NMR: 4-((1-fluoro-2-phenylvinyl)thio)aniline (3d)**



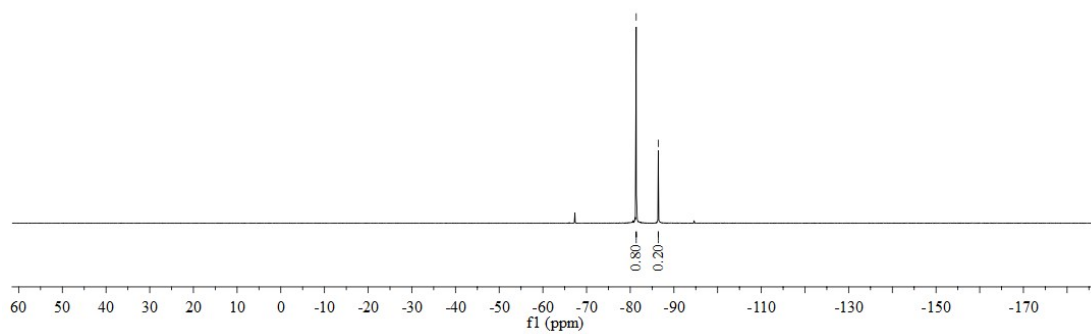
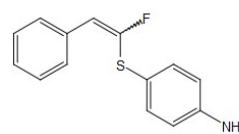
**<sup>13</sup>C NMR: 4-((1-fluoro-2-phenylvinyl)thio)aniline (3d)**

155.52  
153.17  
147.28  
147.24  
134.24  
128.86  
128.84  
128.55  
125.87  
115.20  
114.95

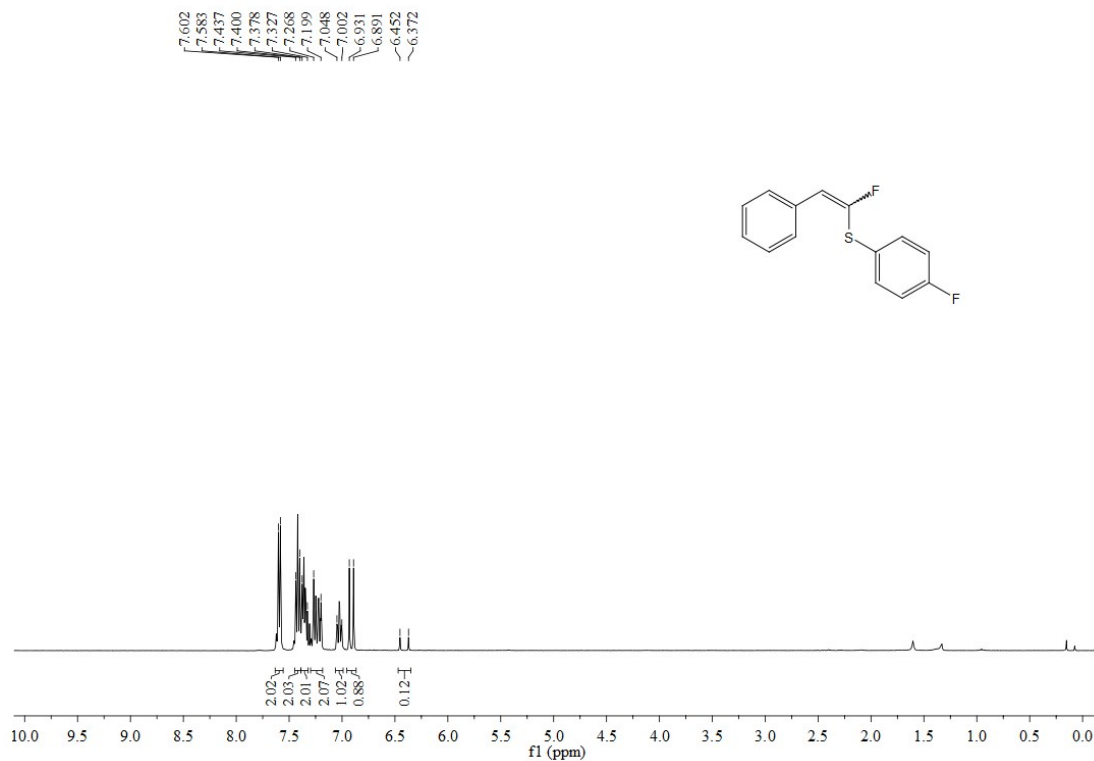


**<sup>19</sup>F NMR: 4-((1-fluoro-2-phenylvinyl)thio)aniline (3d)**

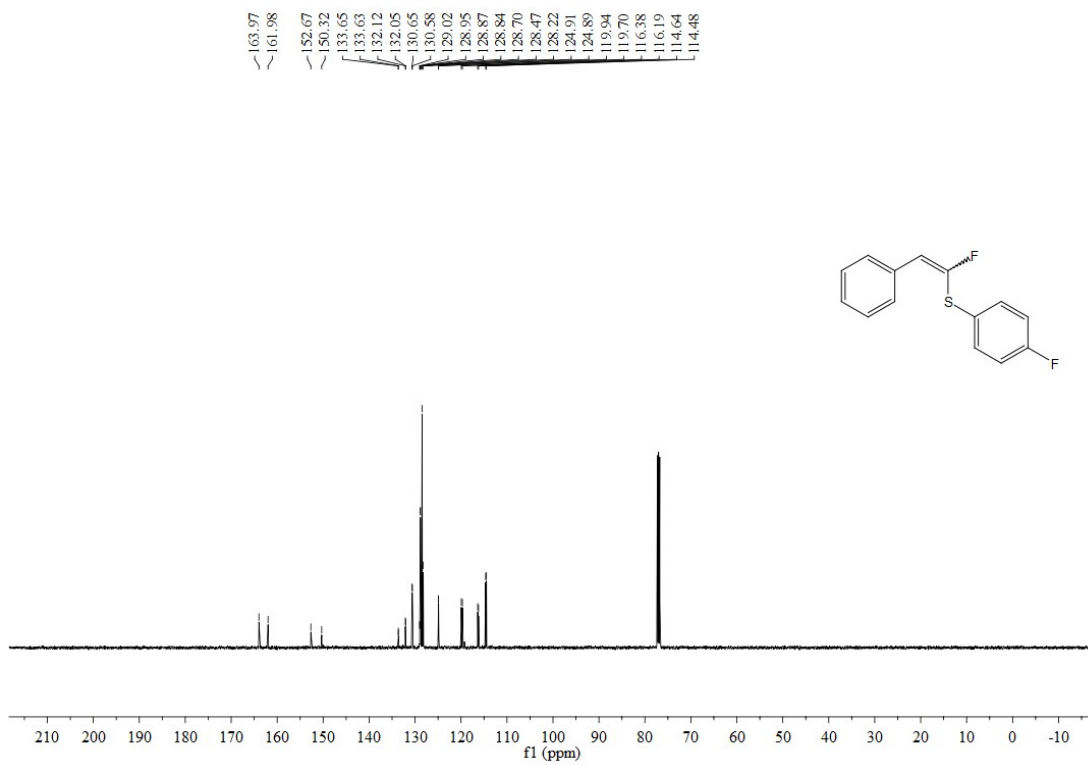
-81.367  
-86.414



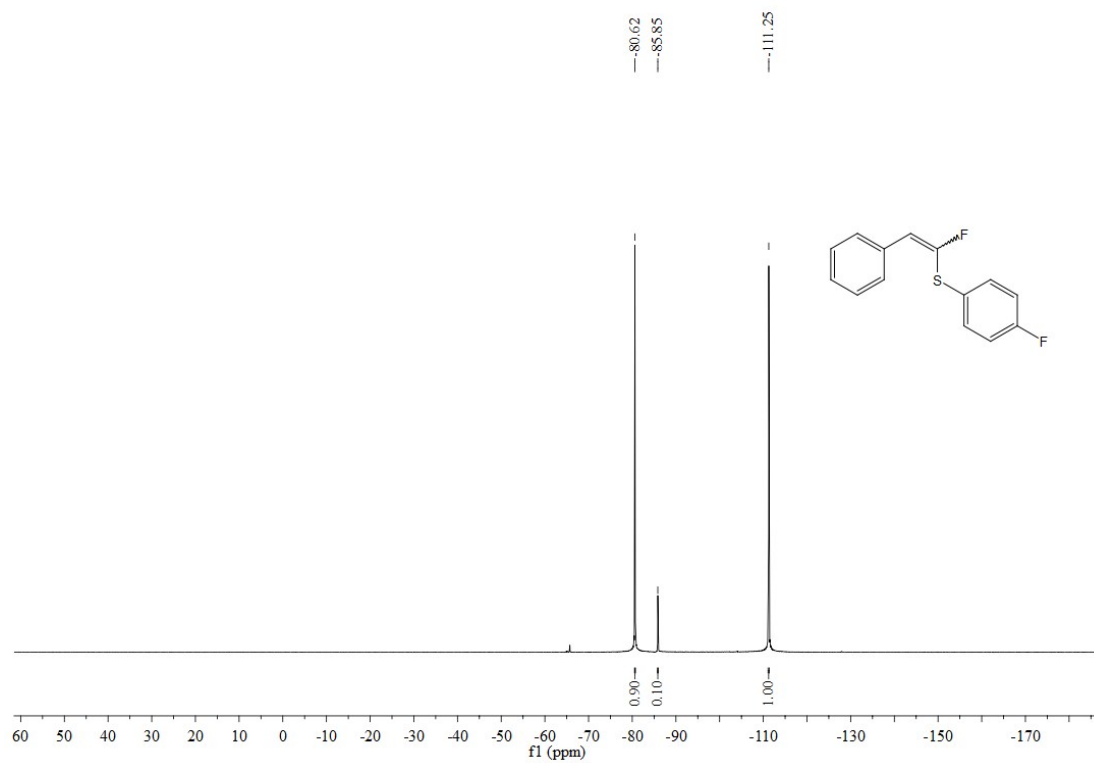
**<sup>1</sup>H NMR: (1-fluoro-2-phenylvinyl)(4-fluorophenyl)sulfane (3e)**



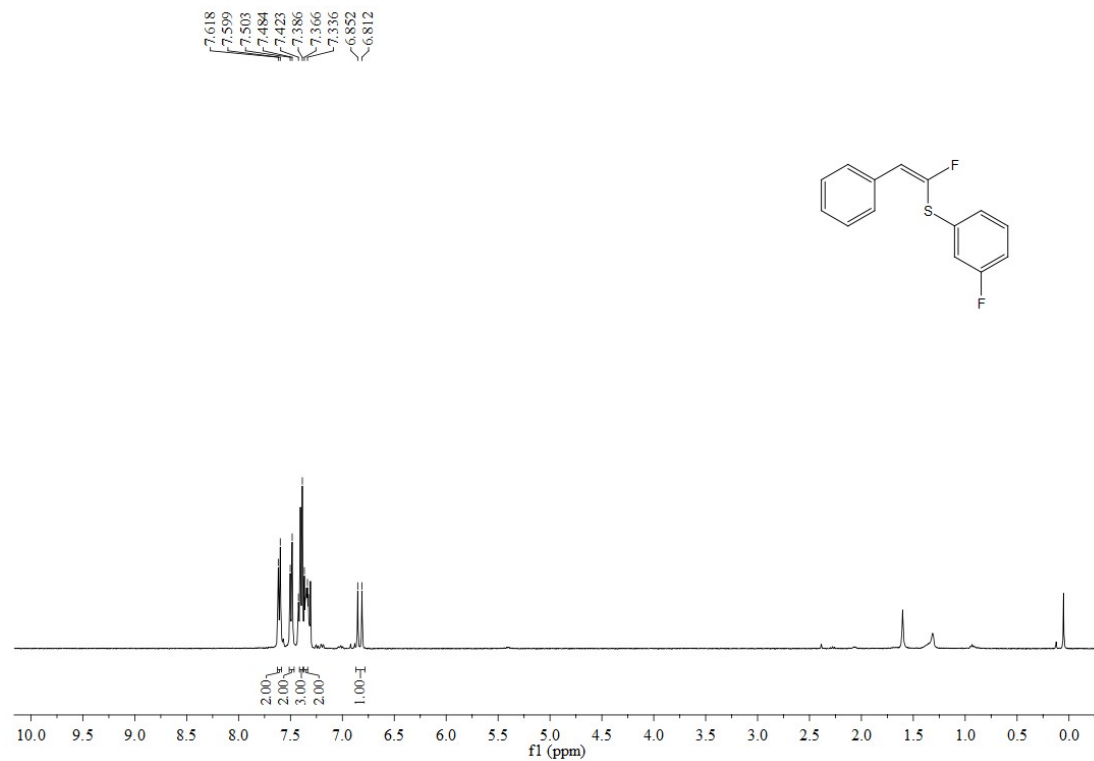
**<sup>13</sup>C NMR: (1-fluoro-2-phenylvinyl)(4-fluorophenyl)sulfane (3e)**



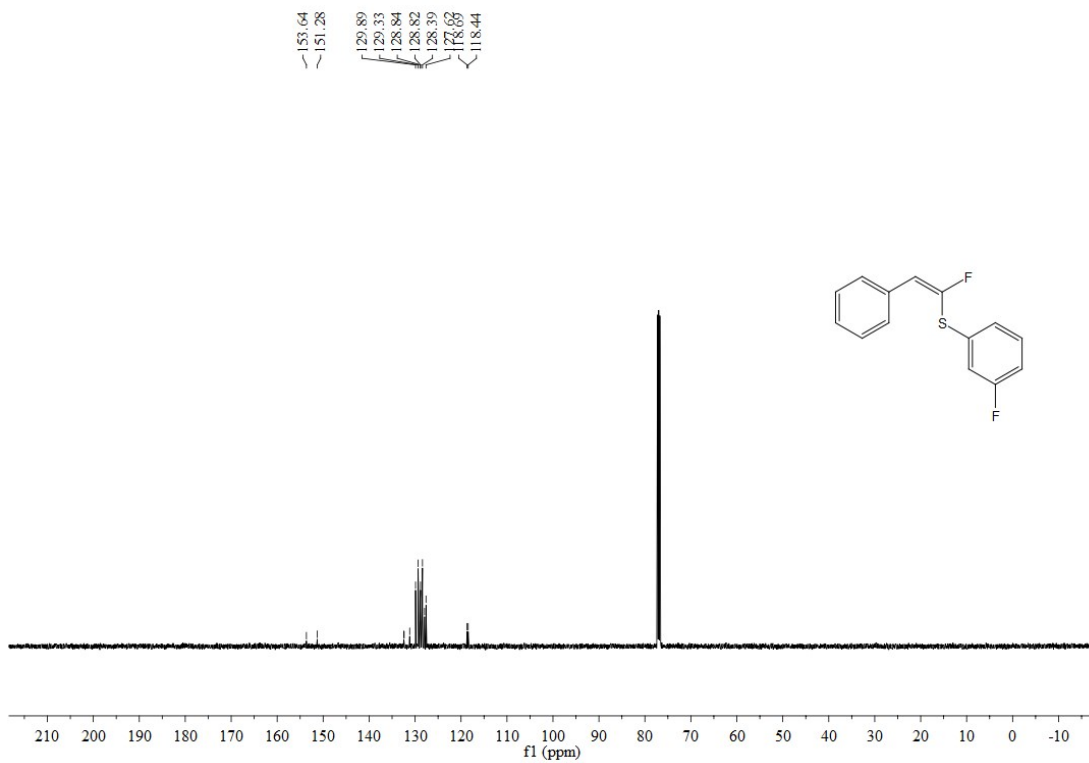
**$^{19}\text{F}$  NMR: (1-fluoro-2-phenylvinyl)(4-fluorophenyl)sulfane (3e)**



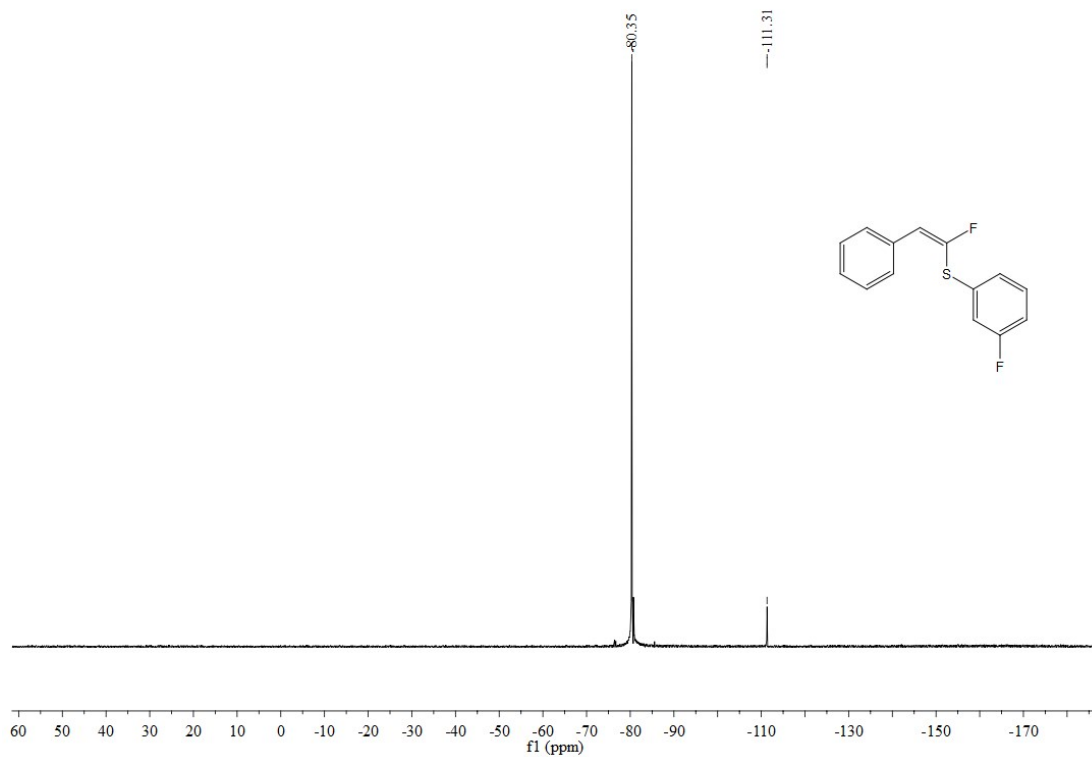
**$^1\text{H}$  NMR: (Z)-(1-fluoro-2-phenylvinyl)(3-fluorophenyl)sulfane (3f)**



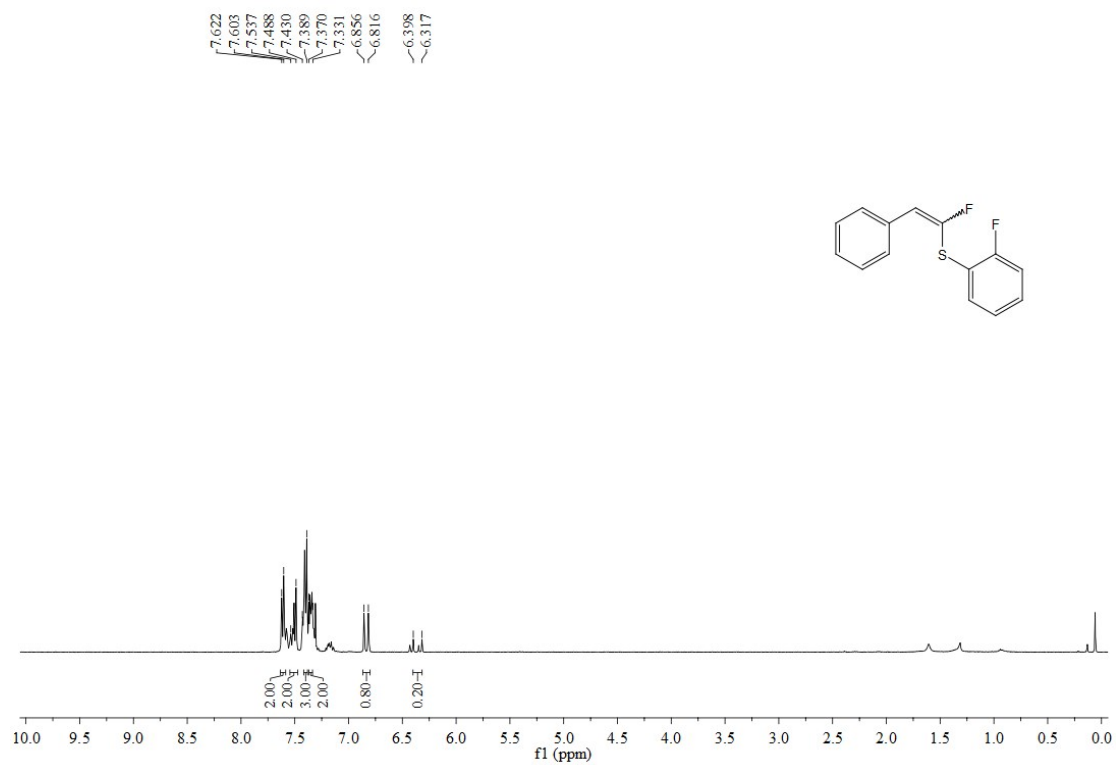
**<sup>13</sup>C NMR: (Z)-(1-fluoro-2-phenylvinyl)(3-fluorophenyl)sulfane (3f)**



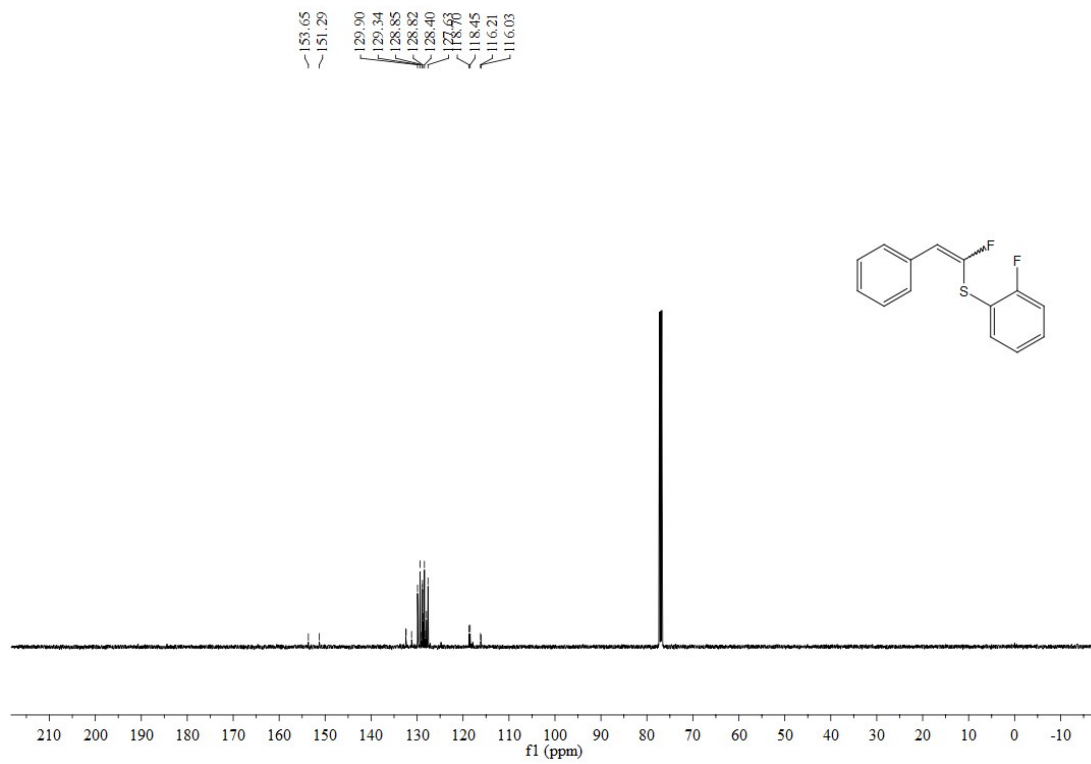
**<sup>19</sup>F NMR: (Z)-(1-fluoro-2-phenylvinyl)(3-fluorophenyl)sulfane (3f)**



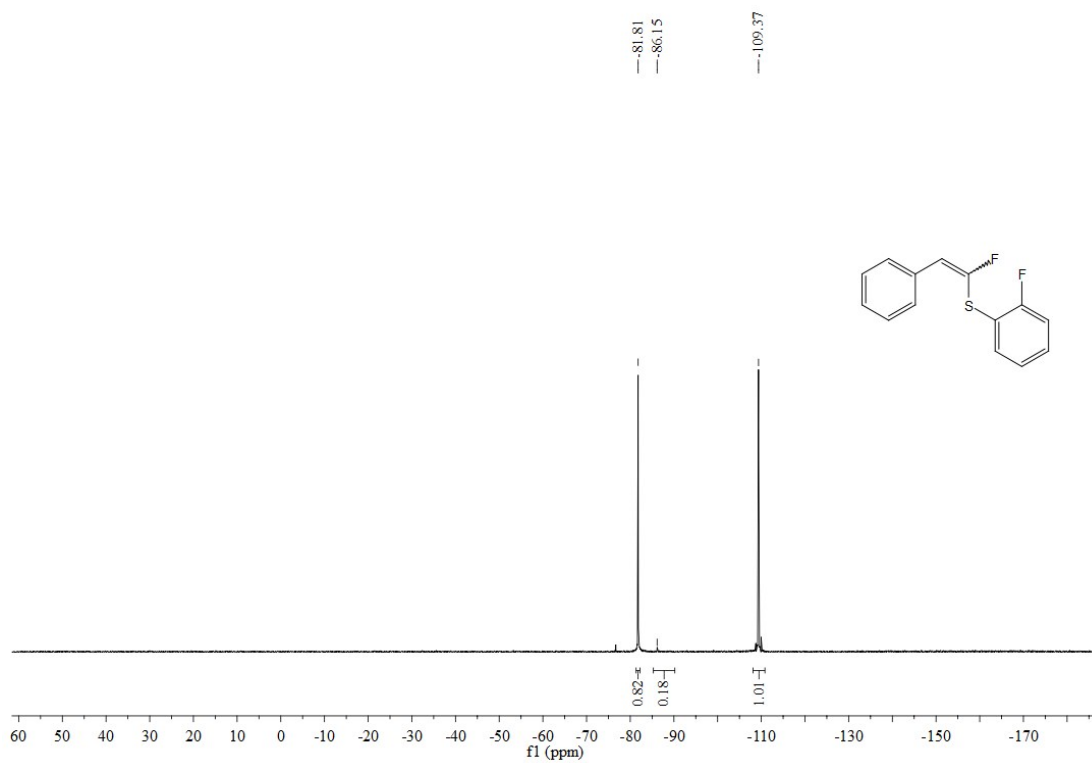
**<sup>1</sup>H NMR: (1-fluoro-2-phenylvinyl)(2-fluorophenyl)sulfane (3g)**



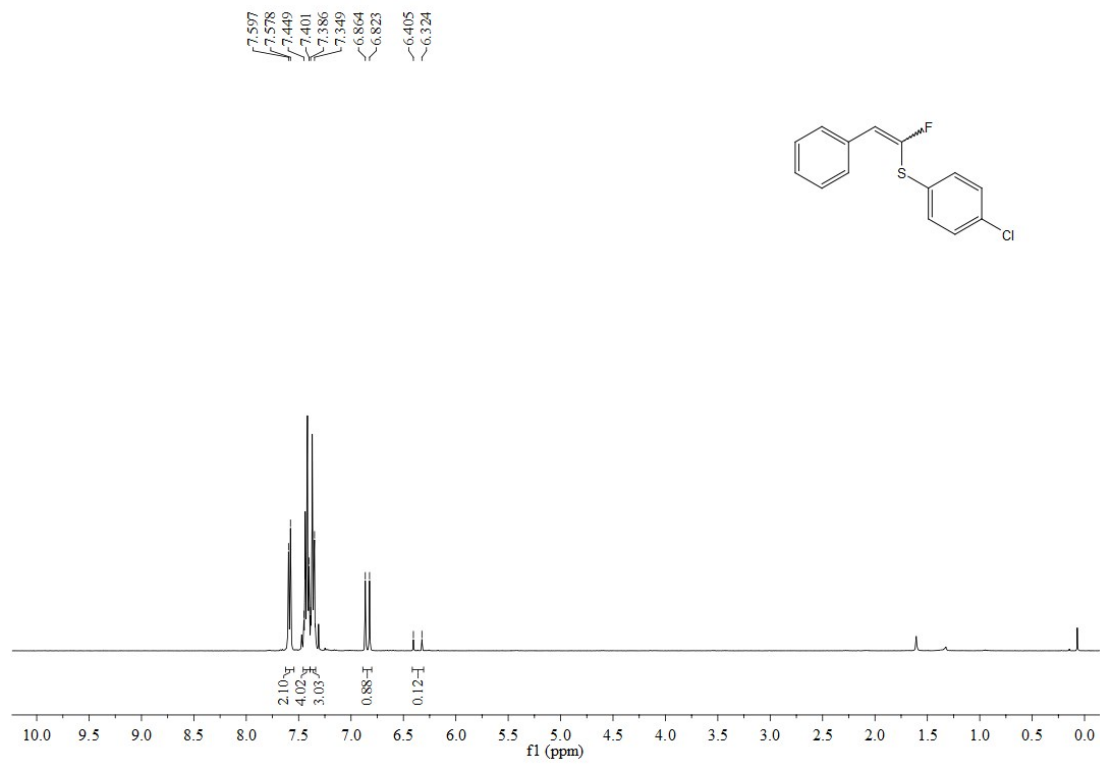
**<sup>13</sup>C NMR: (1-fluoro-2-phenylvinyl)(2-fluorophenyl)sulfane (3g)**



**<sup>19</sup>F NMR: (1-fluoro-2-phenylvinyl)(2-fluorophenyl)sulfane (3g)**

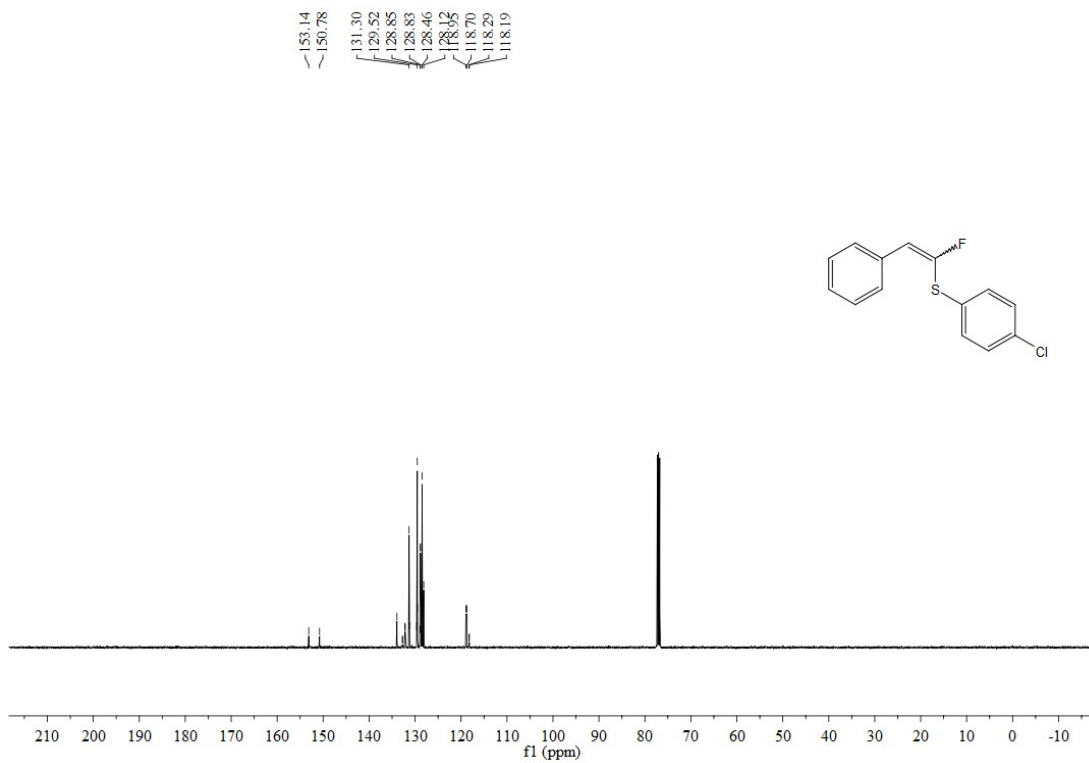


**<sup>1</sup>H NMR: (4-chlorophenyl)(1-fluoro-2-phenylvinyl)sulfane (3h)**

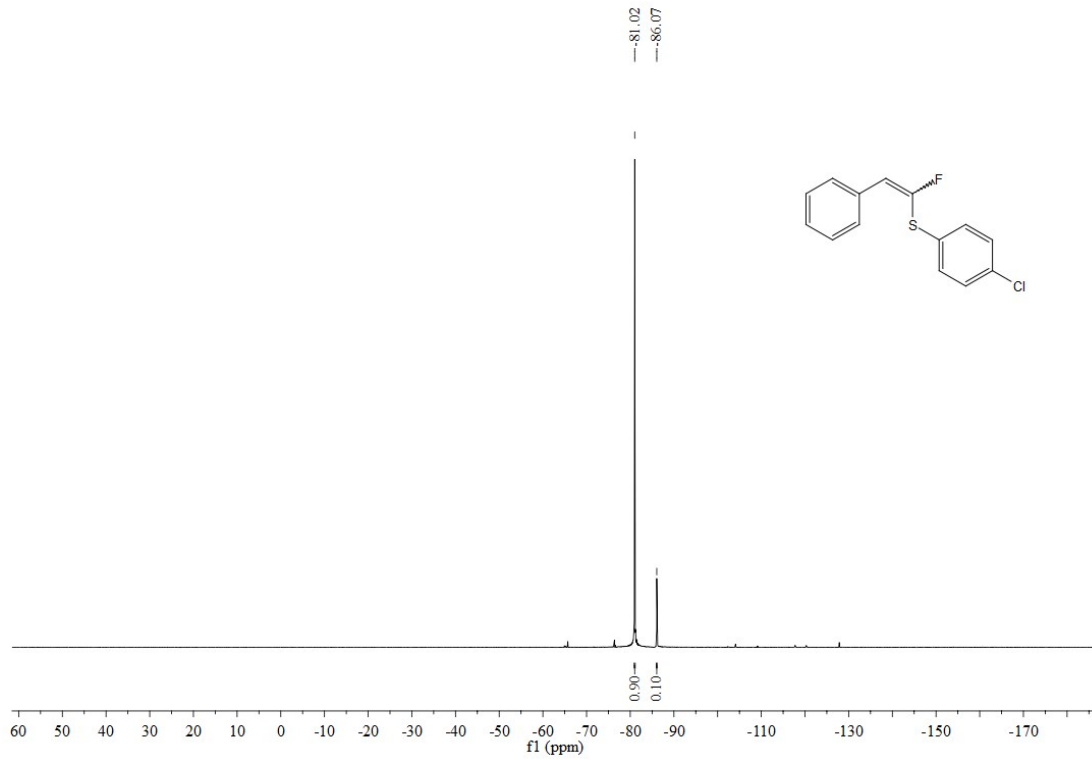




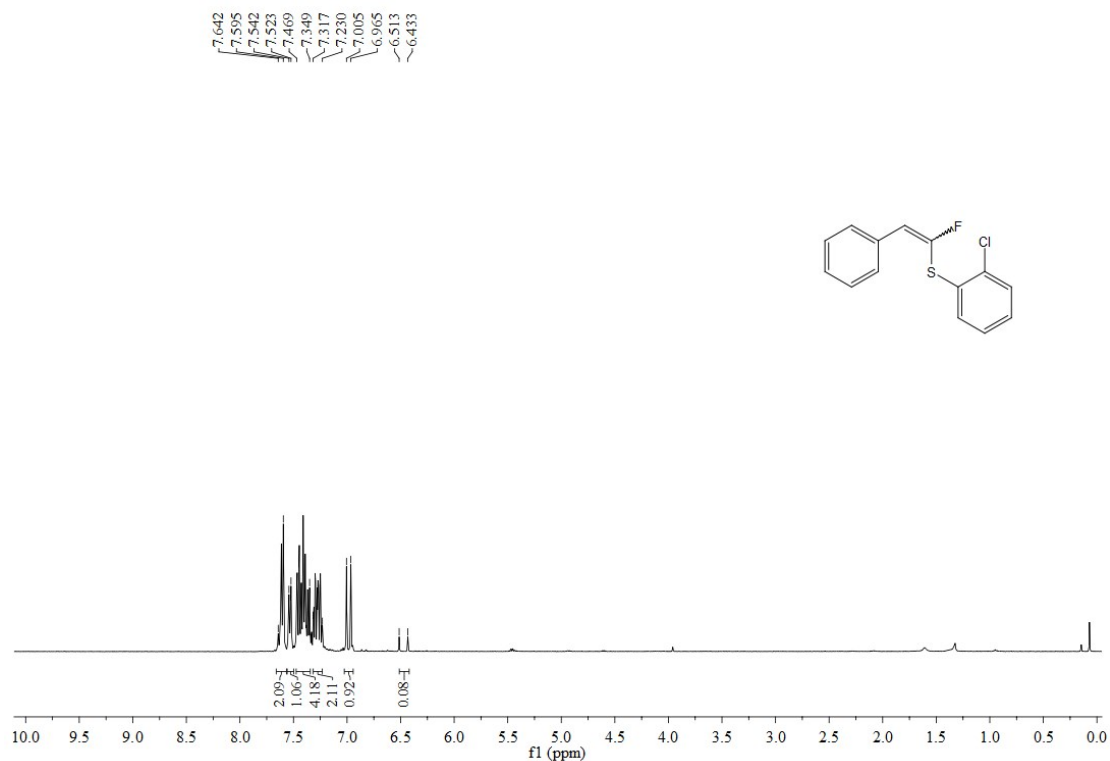
**<sup>13</sup>C NMR: (4-chlorophenyl)(1-fluoro-2-phenylvinyl)sulfane (3h)**



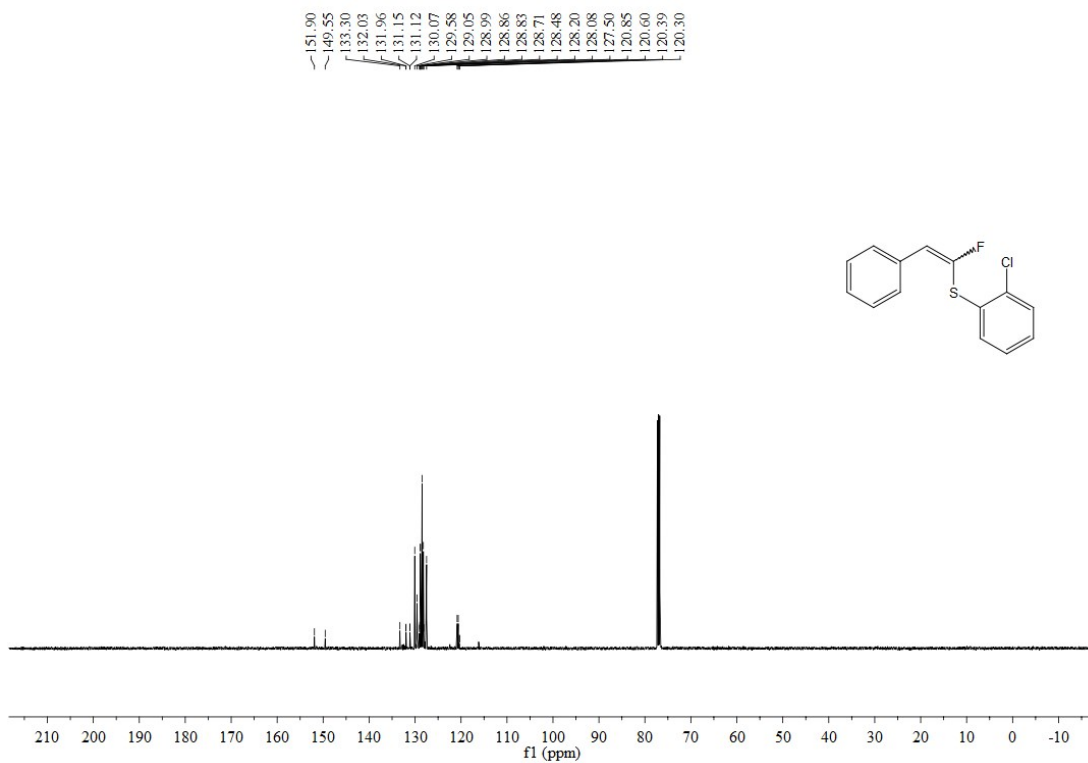
**<sup>19</sup>F NMR: (4-chlorophenyl)(1-fluoro-2-phenylvinyl)sulfane (3h)**



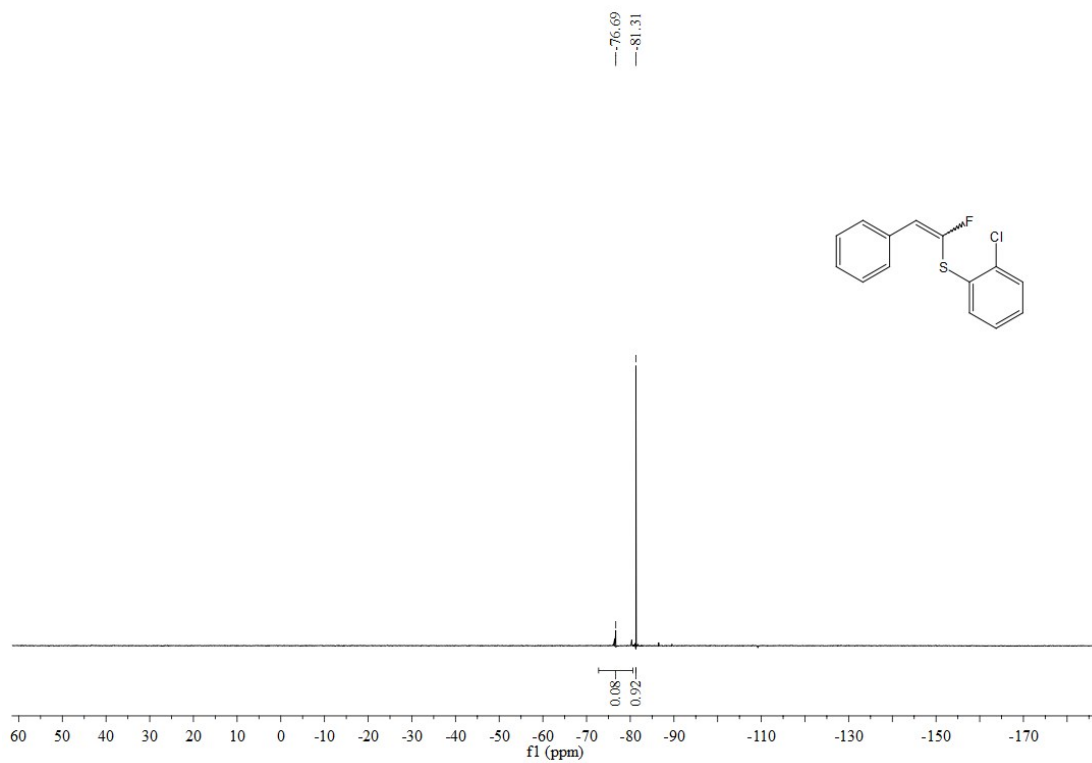
**<sup>1</sup>H NMR: (2-chlorophenyl)(1-fluoro-2-phenylvinyl)sulfane (3i)**



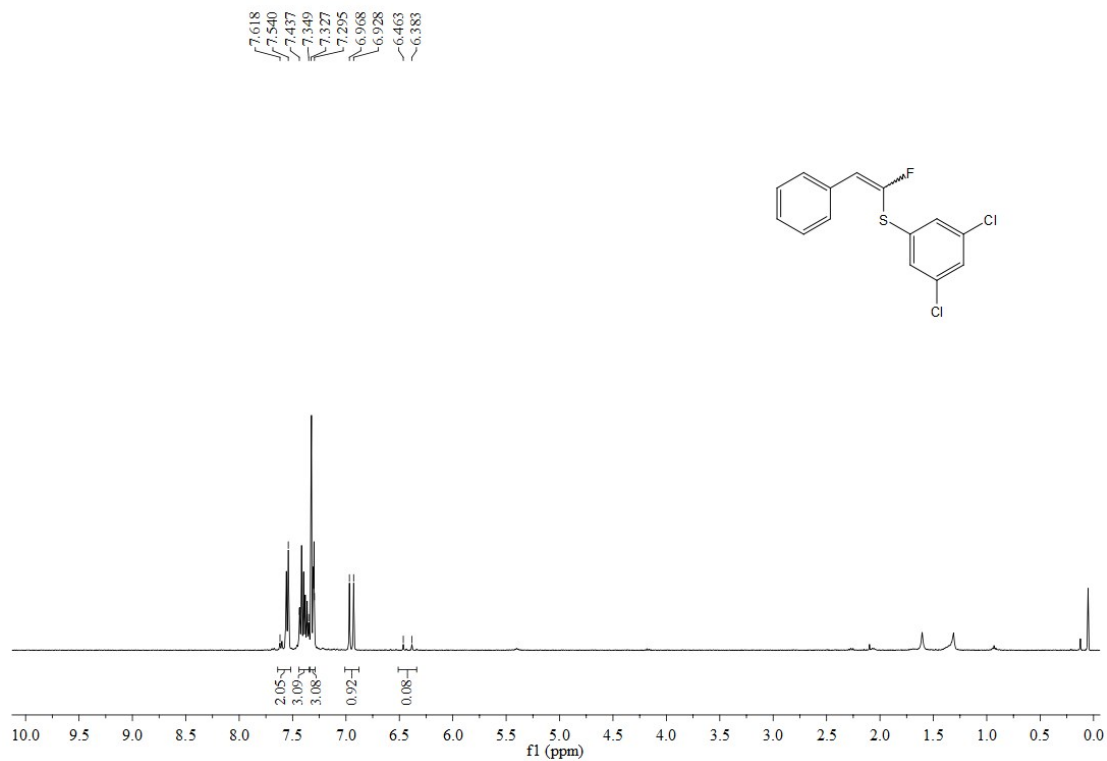
**<sup>13</sup>C NMR: (2-chlorophenyl)(1-fluoro-2-phenylvinyl)sulfane (3i)**



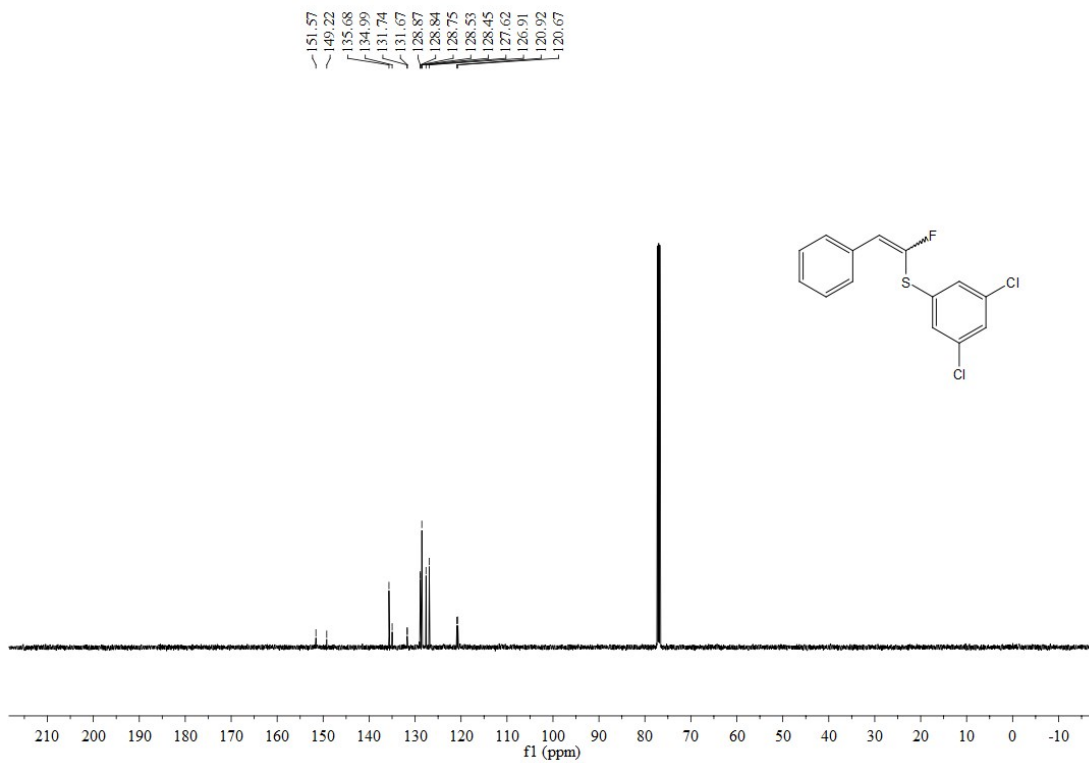
**$^{19}\text{F}$  NMR: (2-chlorophenyl)(1-fluoro-2-phenylvinyl)sulfane (3i)**



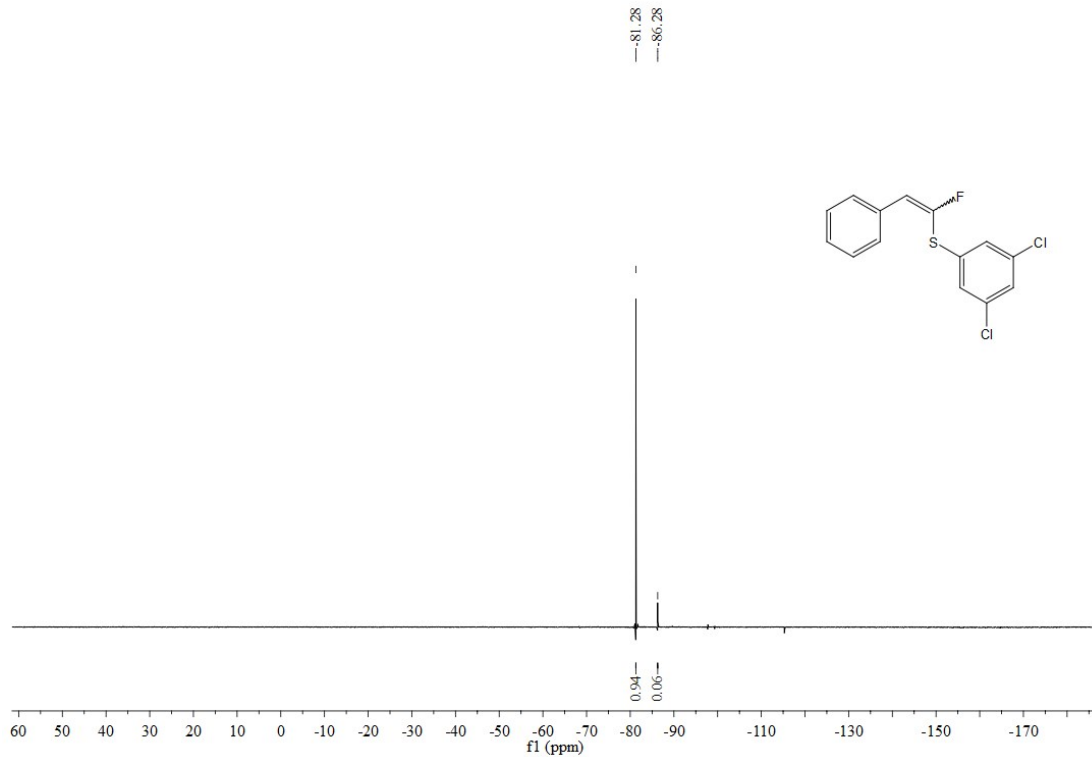
**$^1\text{H}$  NMR: (3,5-dichlorophenyl)(1-fluoro-2-phenylvinyl)sulfane (3j)**



**<sup>13</sup>C NMR: (3,5-dichlorophenyl)(1-fluoro-2-phenylvinyl)sulfane (3j)**

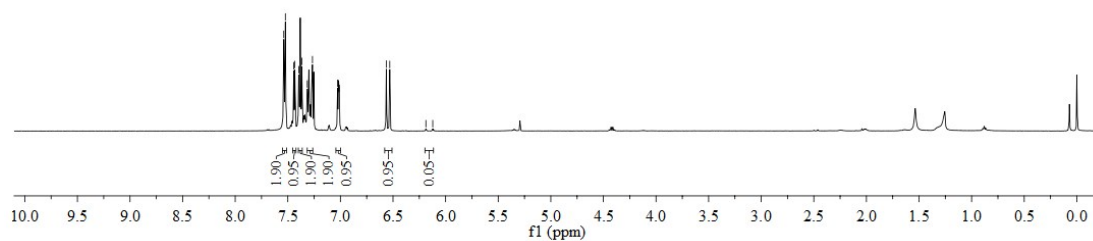
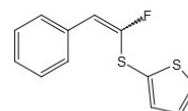


**<sup>19</sup>F NMR: (3,5-dichlorophenyl)(1-fluoro-2-phenylvinyl)sulfane (3j)**



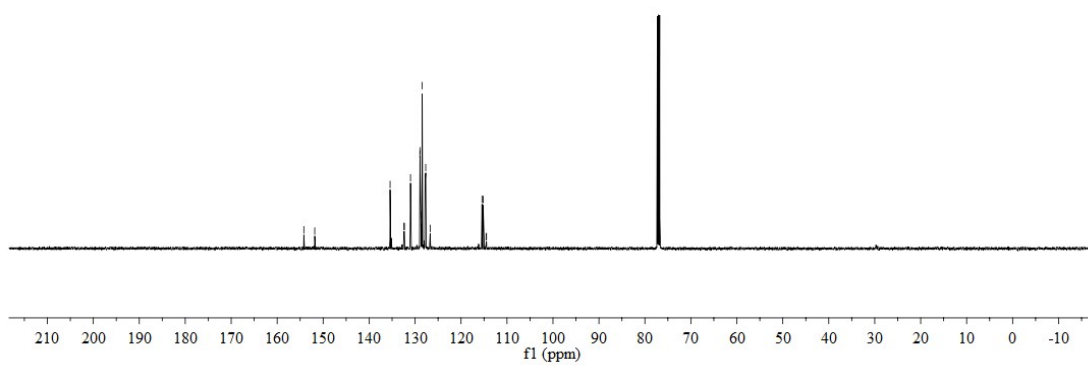
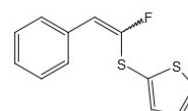
**<sup>1</sup>H NMR: 2-((1-fluoro-2-phenylvinyl)thio)thiophene (3k)**

7.538  
7.523  
7.443  
7.433  
7.396  
7.366  
7.315  
7.266  
7.027  
7.010  
6.564  
6.531  
6.187  
6.122

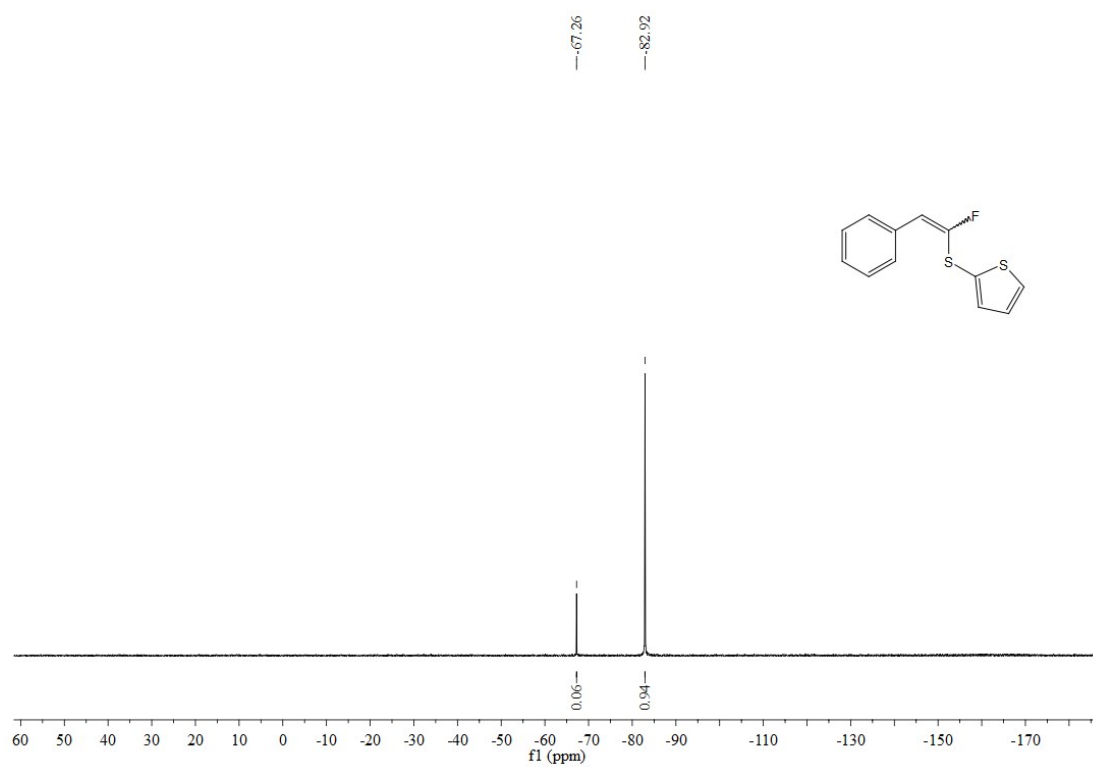


**<sup>13</sup>C NMR: 2-((1-fluoro-2-phenylvinyl)thio)thiophene (3k)**

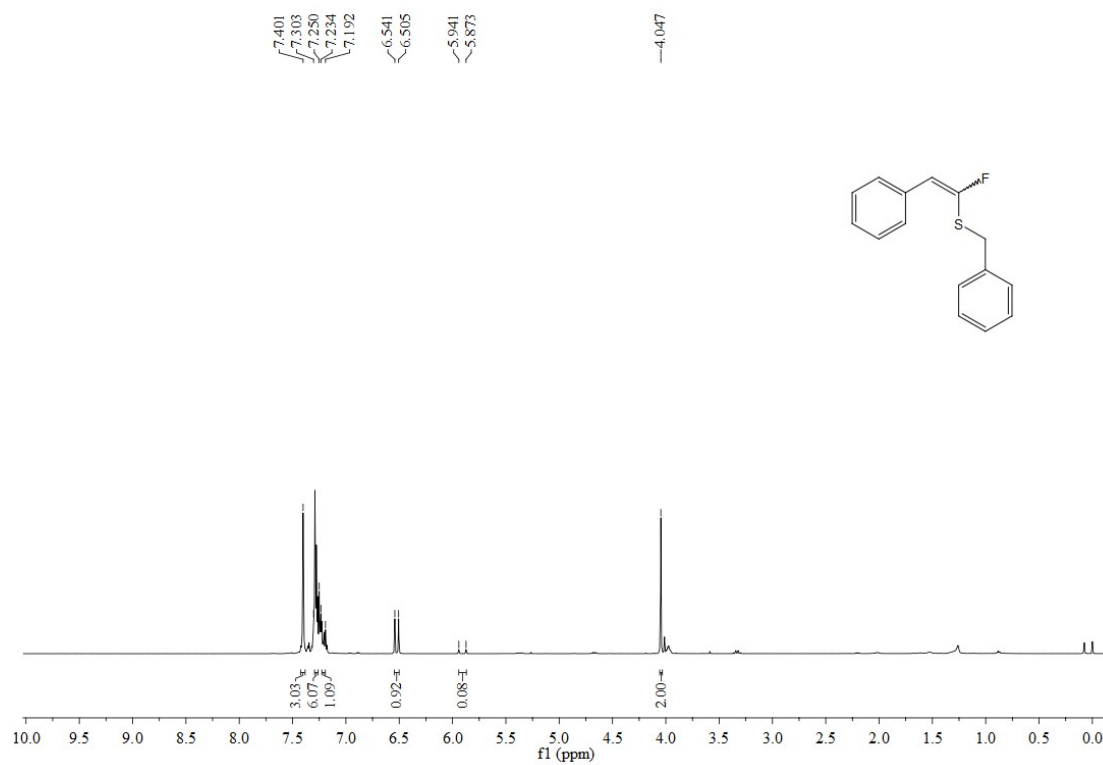
154.20  
151.83  
135.44  
130.99  
128.96  
128.93  
128.45  
127.83  
115.20  
115.07  
114.56  
114.46



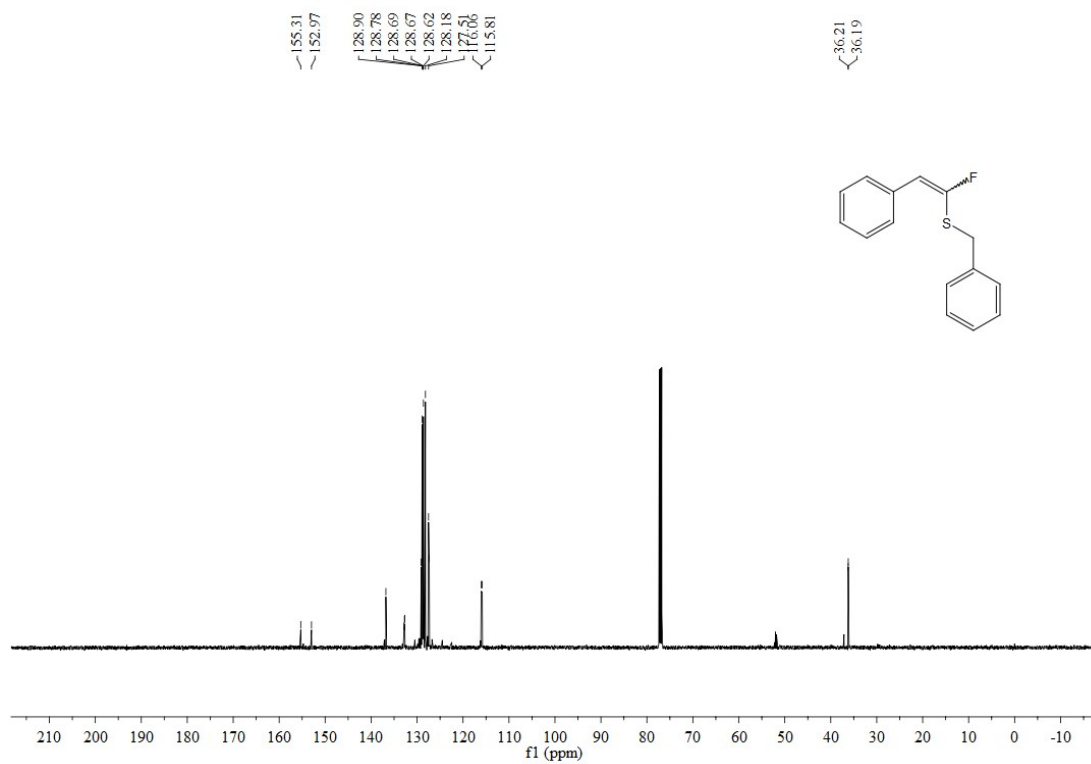
**<sup>19</sup>F NMR: 2-((1-fluoro-2-phenylvinyl)thio)thiophene (3k)**



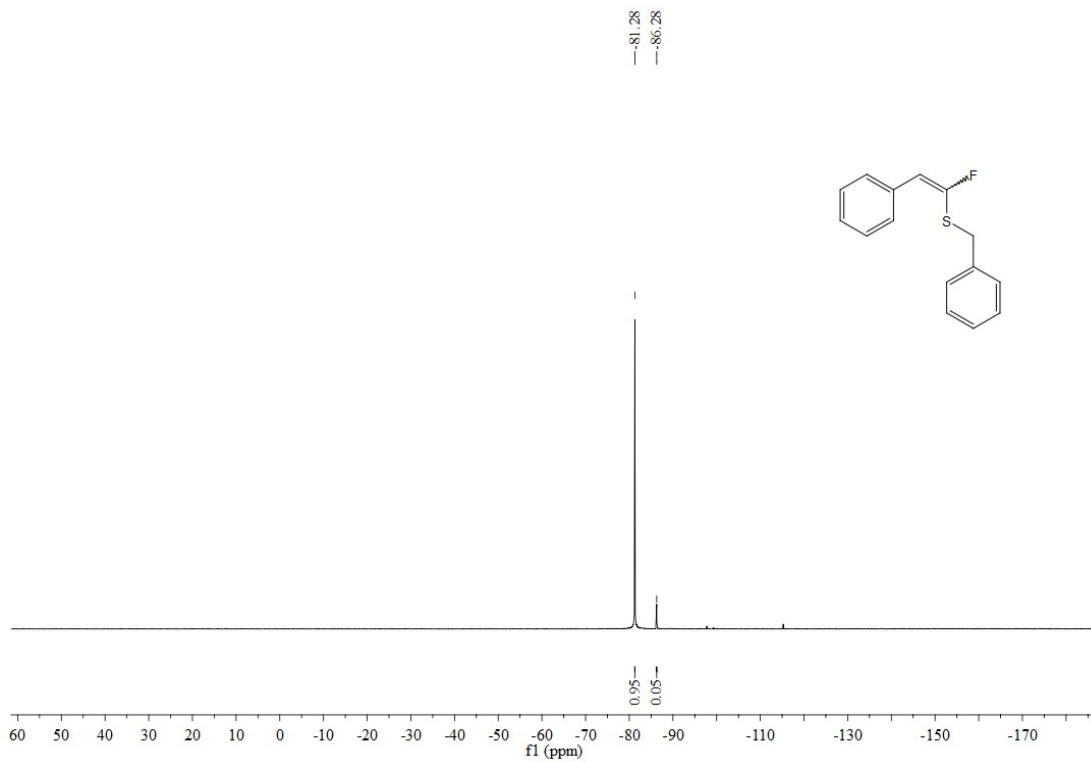
**<sup>1</sup>H NMR: benzyl(1-fluoro-2-phenylvinyl)sulfane (3l)**



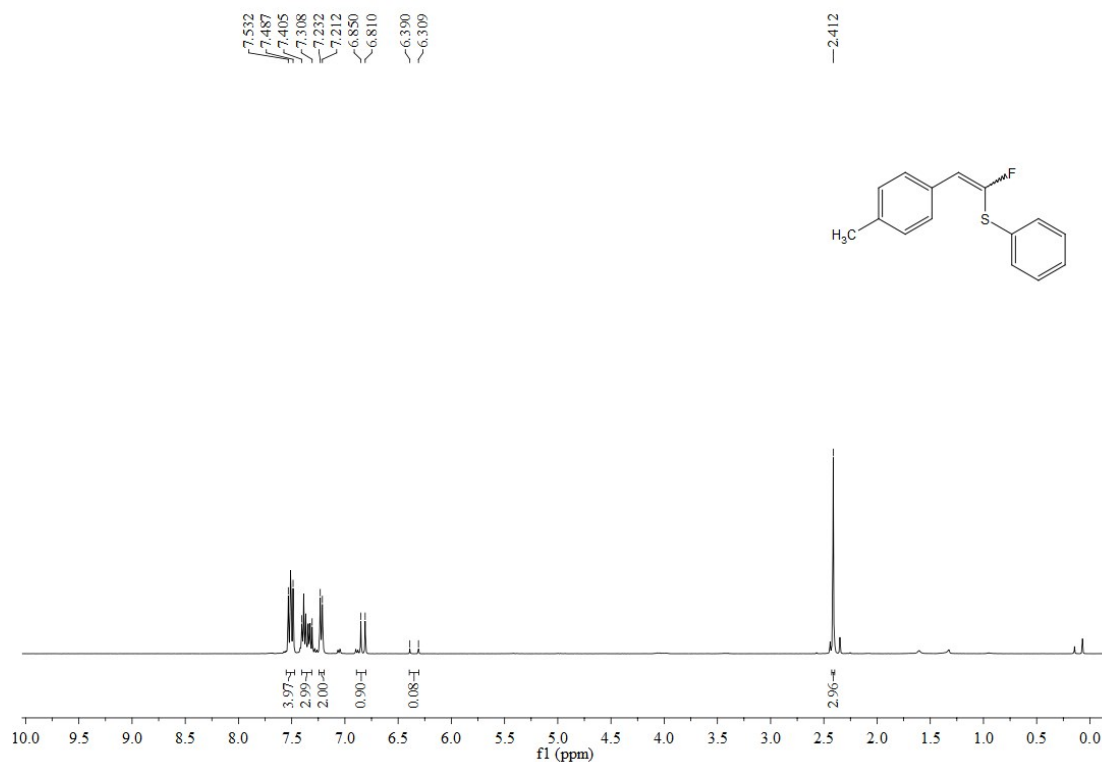
**<sup>13</sup>C NMR: benzyl(1-fluoro-2-phenylvinyl)sulfane (31)**



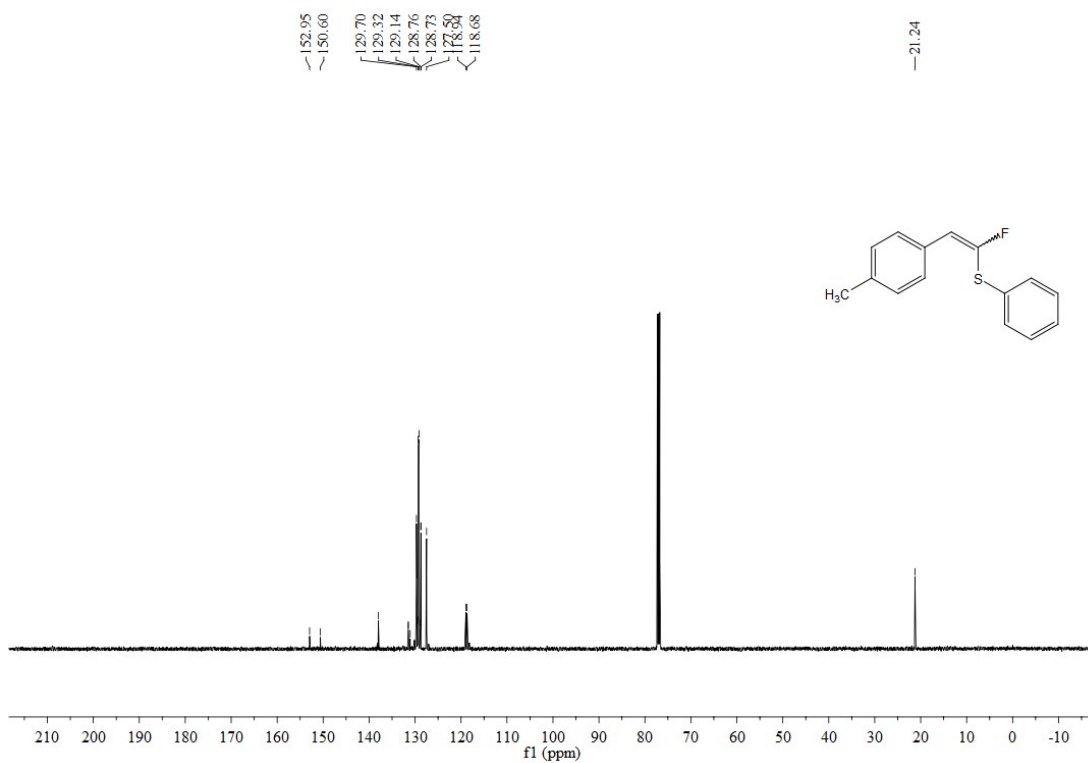
**<sup>19</sup>F NMR: benzyl(1-fluoro-2-phenylvinyl)sulfane (31)**



### <sup>1</sup>H NMR: (1-fluoro-2-(p-tolyl)vinyl)(phenyl)sulfane (3m)

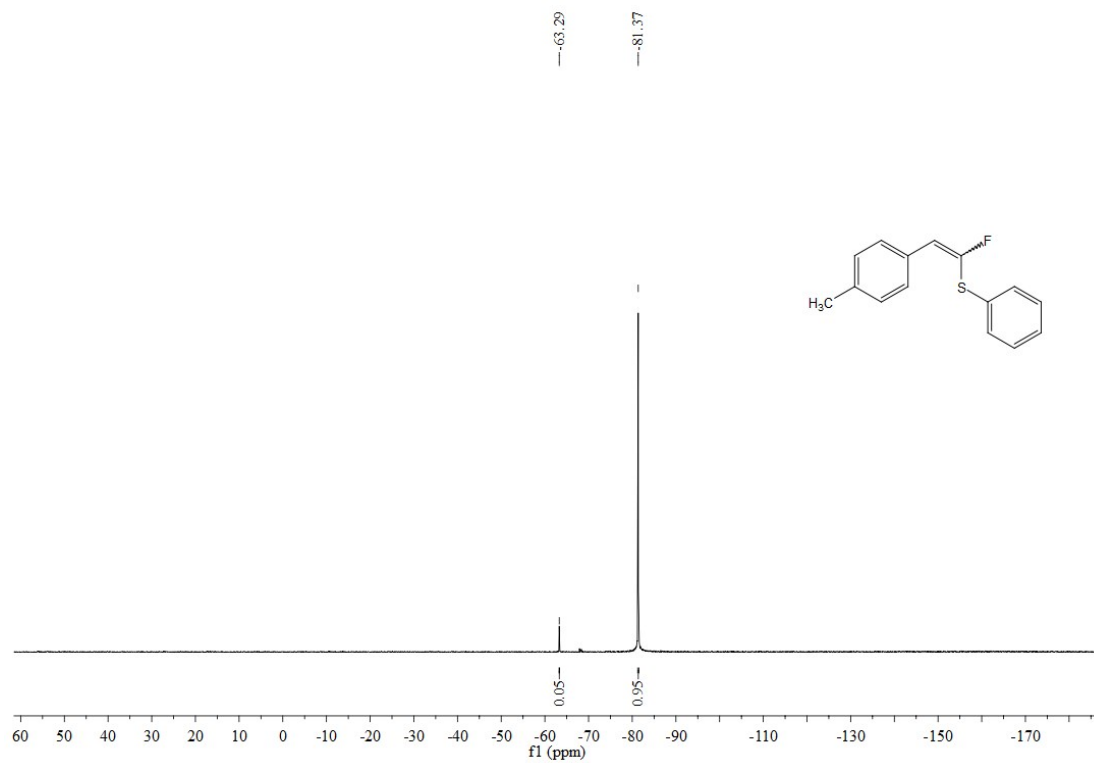


### <sup>13</sup>C NMR: (1-fluoro-2-(p-tolyl)vinyl)(phenyl)sulfane (3m)

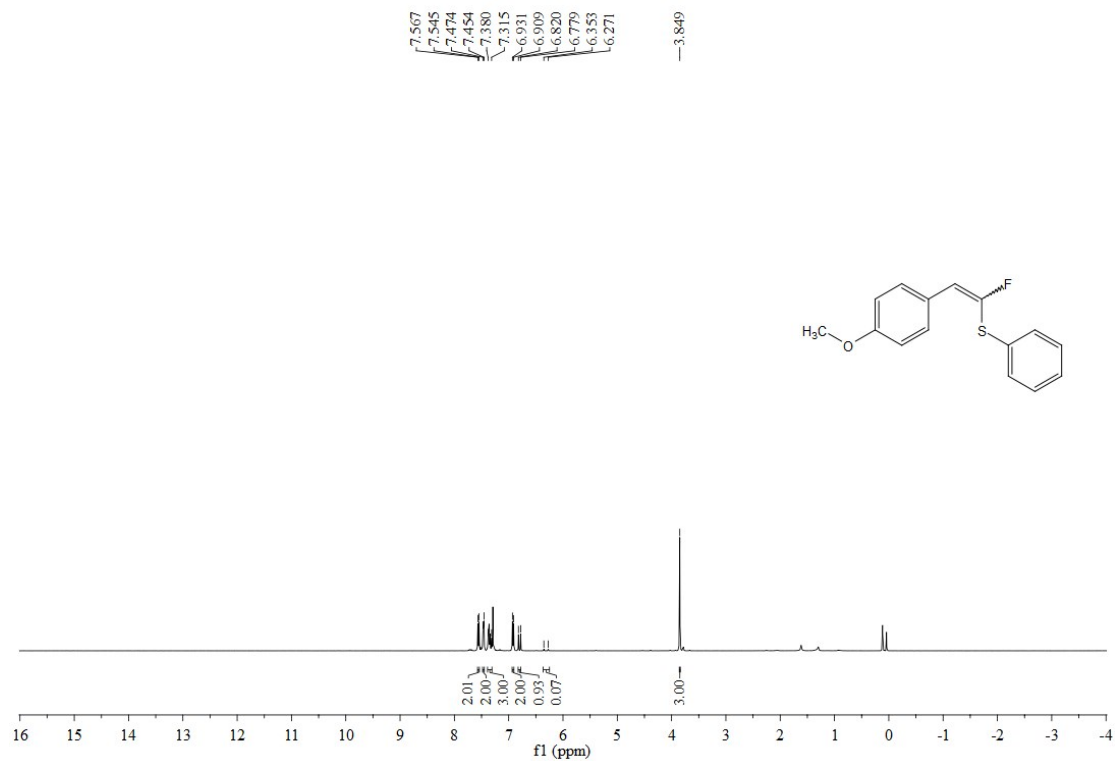




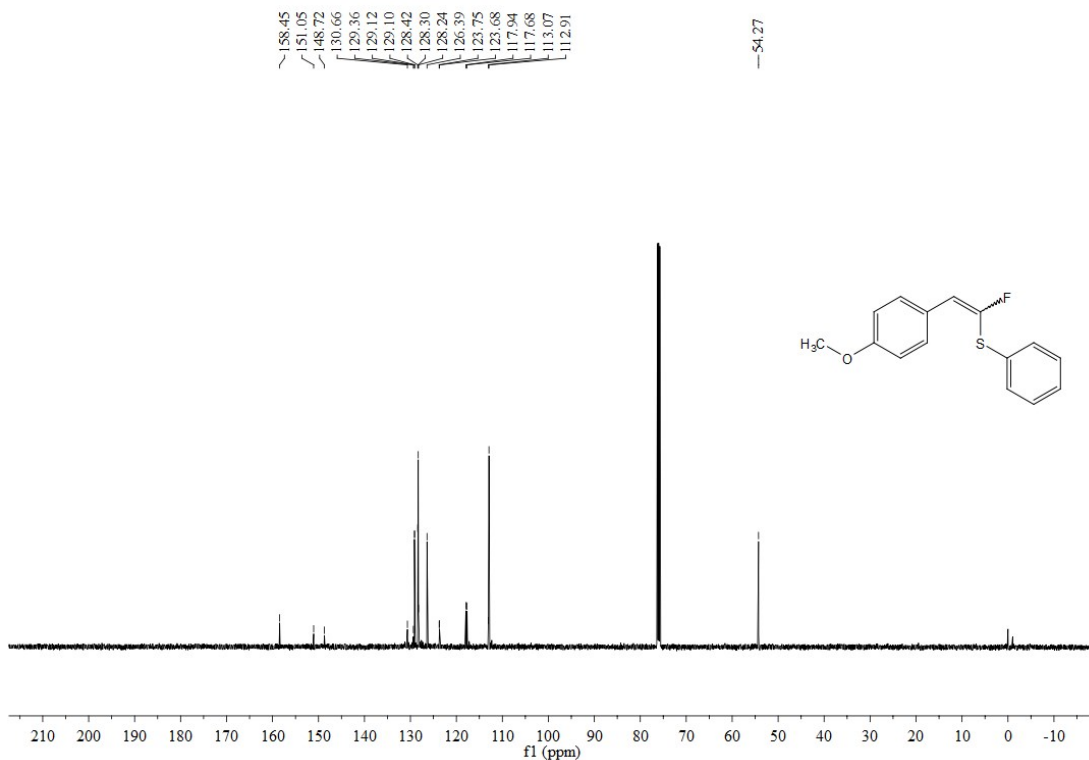
**$^{19}\text{F}$  NMR: (1-fluoro-2-(p-tolyl)vinyl)(phenyl)sulfane (3m)**



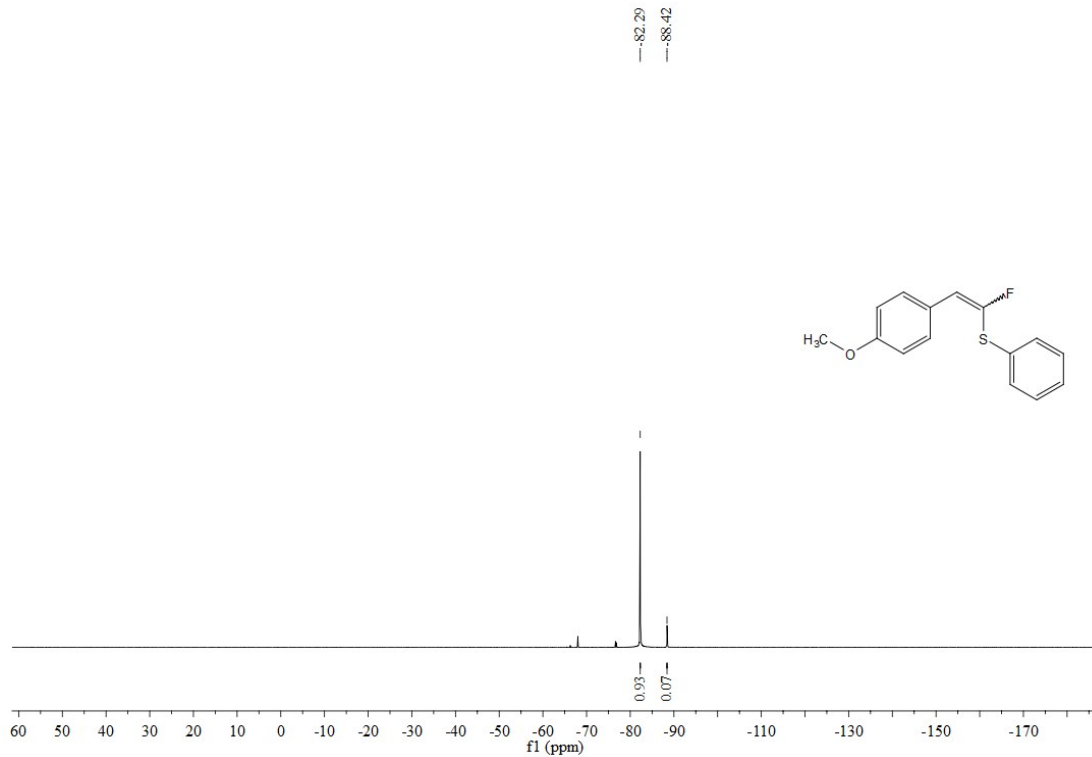
**$^1\text{H}$  NMR: (1-fluoro-2-(4-methoxyphenyl)vinyl)(phenyl)sulfane (3n)**



**<sup>13</sup>C NMR: (1-fluoro-2-(4-methoxyphenyl)vinyl)(phenyl)sulfane (3n)**

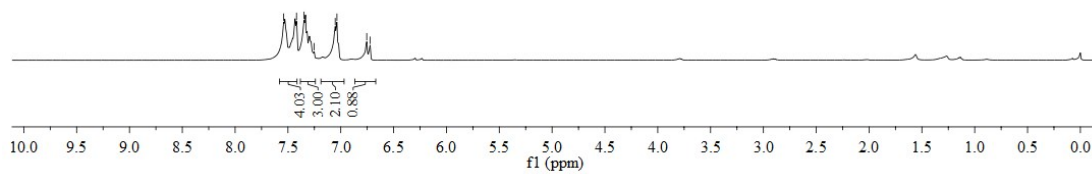
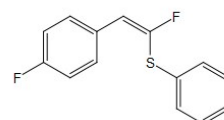


**<sup>19</sup>F NMR: (1-fluoro-2-(4-methoxyphenyl)vinyl)(phenyl)sulfane (3n)**



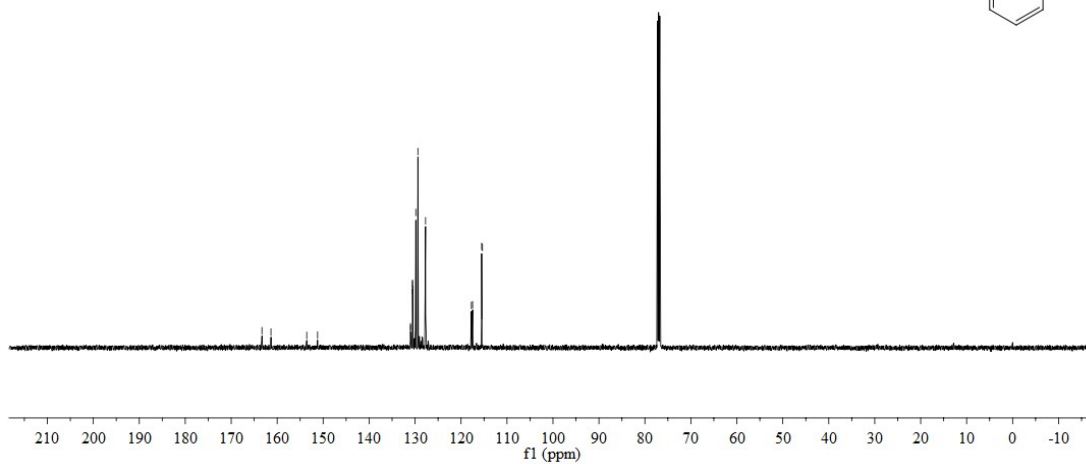
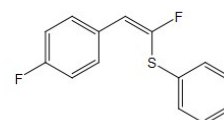
**<sup>1</sup>H NMR: (Z)-(1-fluoro-2-(4-fluorophenyl)vinyl)(phenyl)sulfane (3o)**

7.540  
7.419  
7.347  
7.252  
7.053  
7.037  
6.754  
6.723

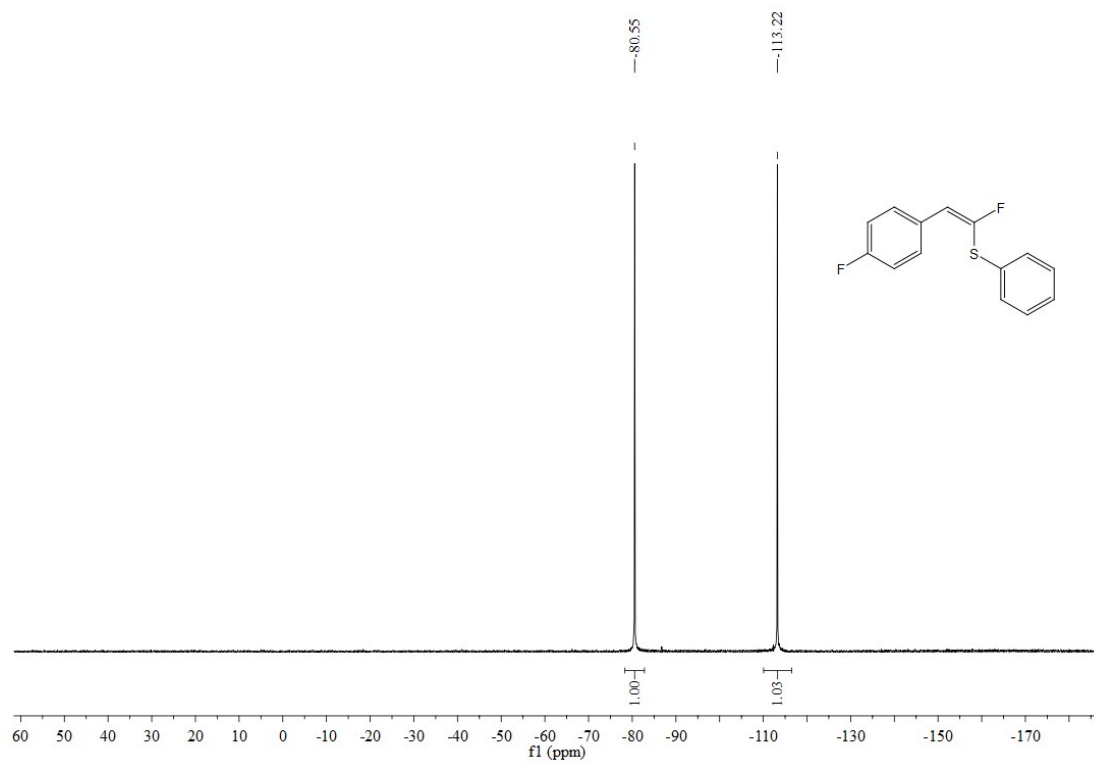


**<sup>13</sup>C NMR: (Z)-(1-fluoro-2-(4-fluorophenyl)vinyl)(phenyl)sulfane (3o)**

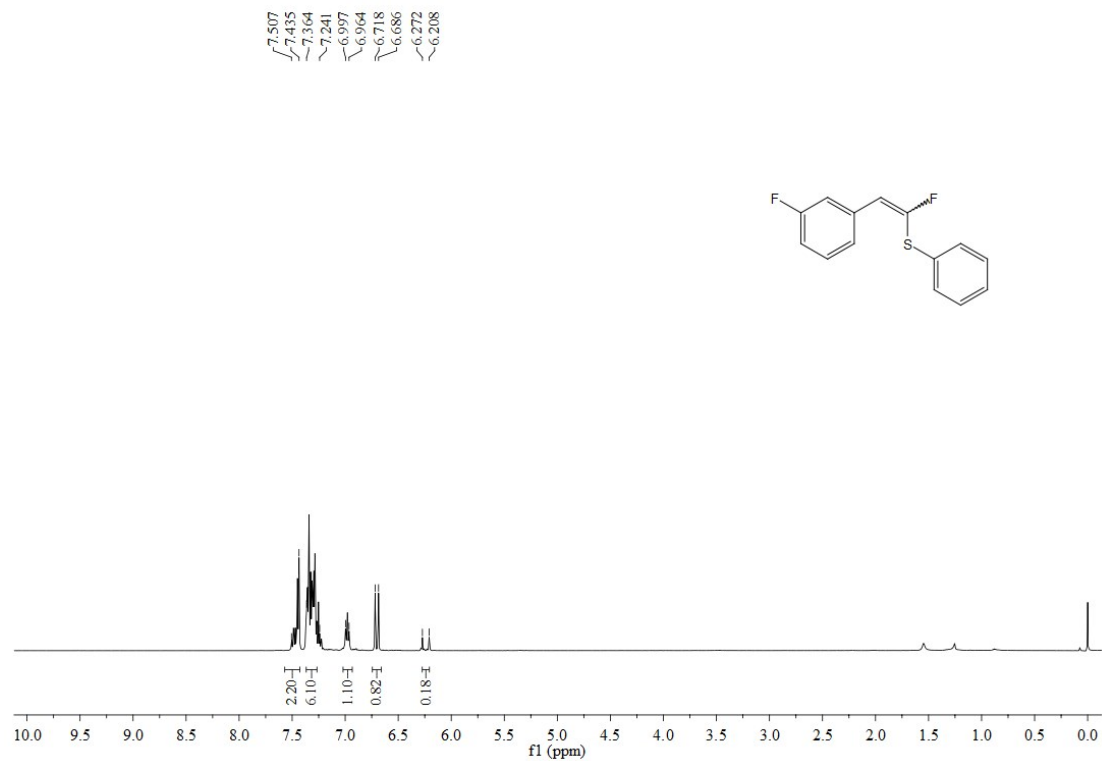
163.31  
161.35  
153.57  
151.21  
130.58  
130.55  
130.51  
129.84  
129.39  
127.73  
117.49  
115.51  
115.34



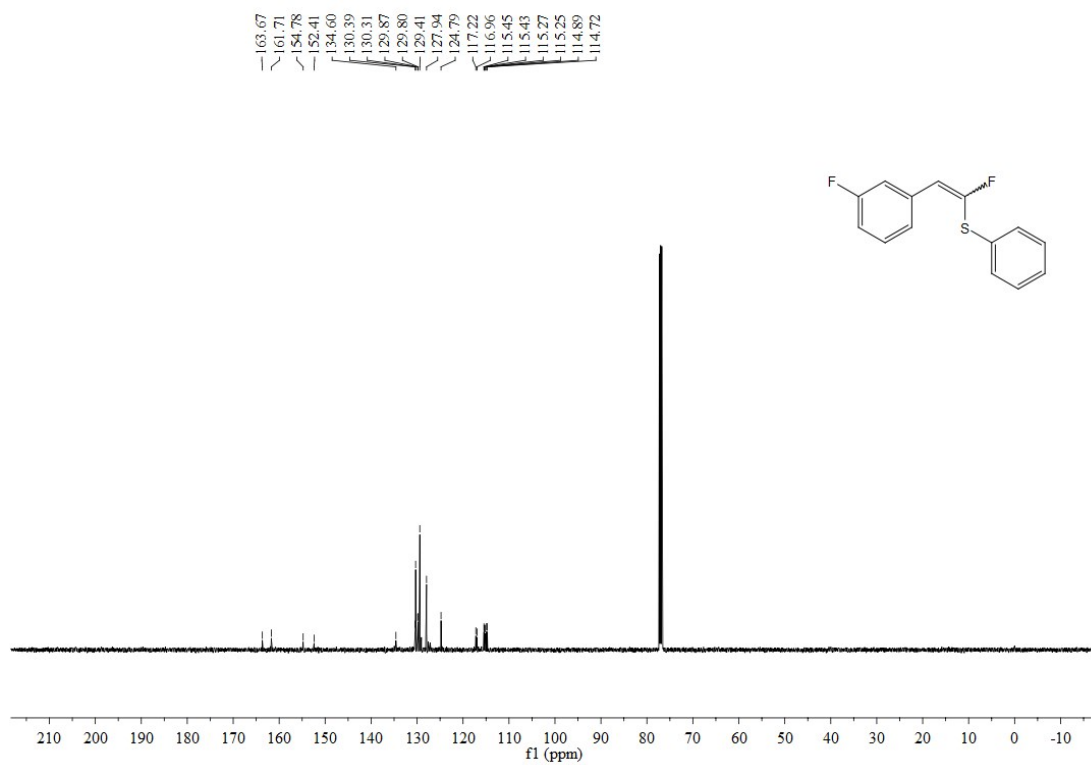
**<sup>19</sup>F NMR: (Z)-(1-fluoro-2-(4-fluorophenyl)vinyl)(phenyl)sulfane (3o)**



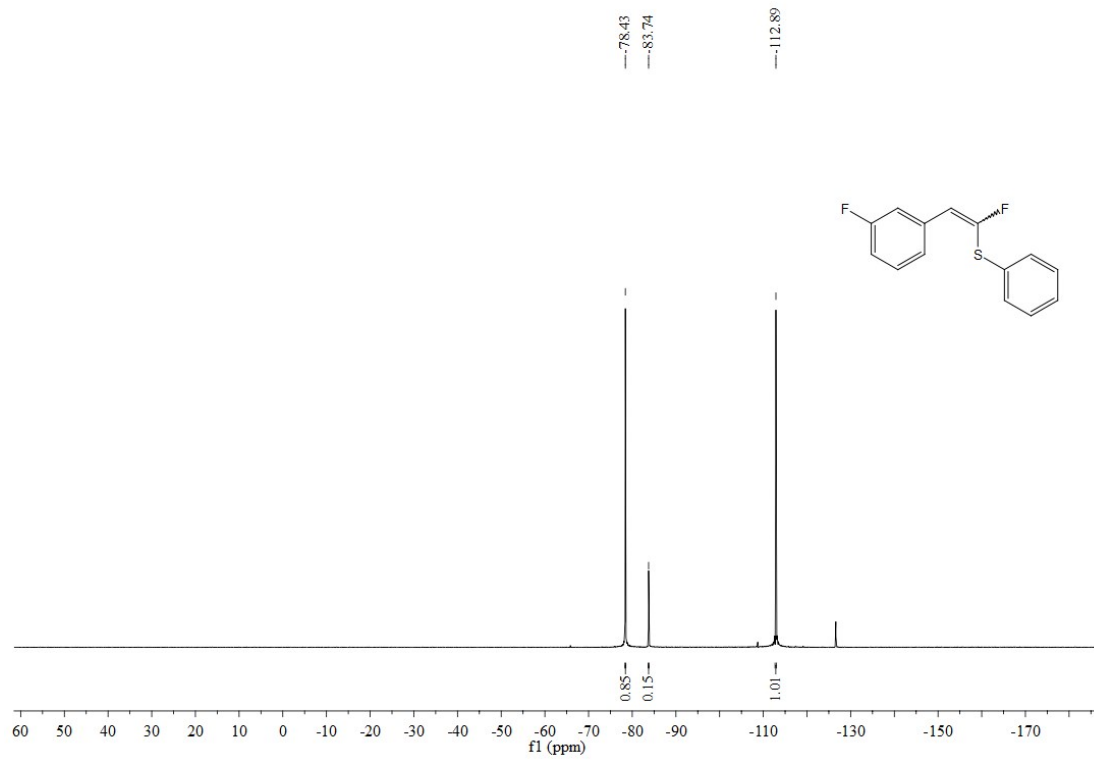
**<sup>1</sup>H NMR: (1-fluoro-2-(3-fluorophenyl)vinyl)(phenyl)sulfane (3p)**



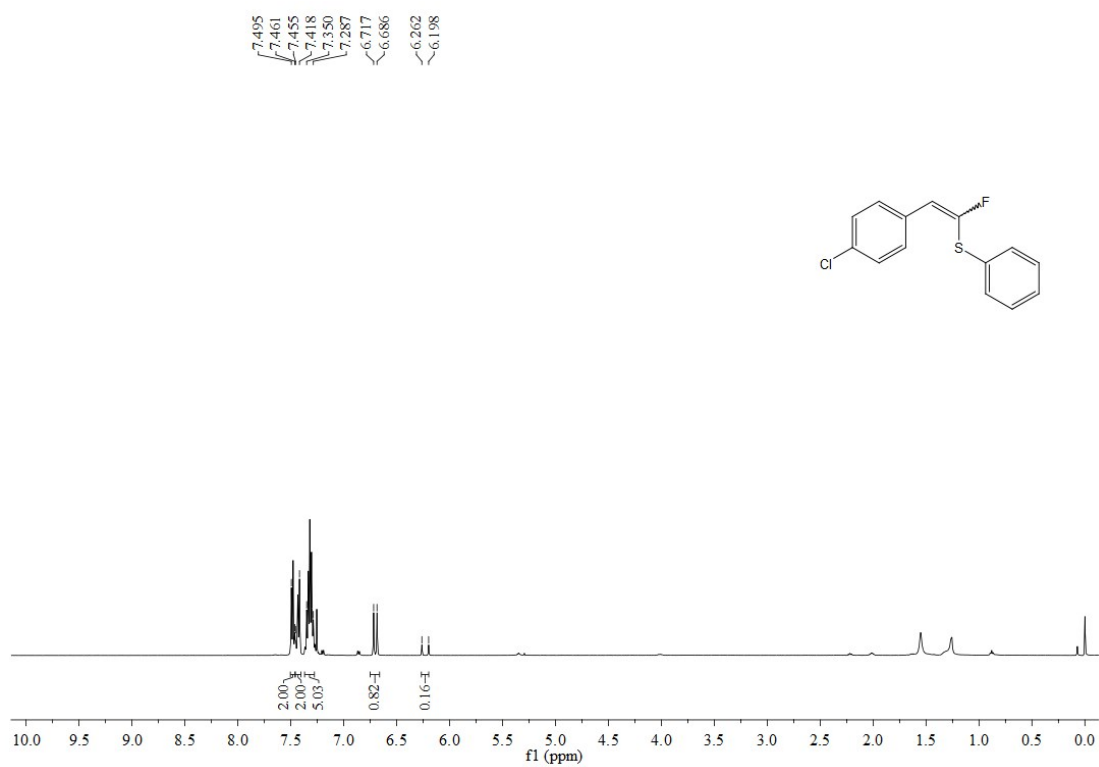
**<sup>13</sup>C NMR: (1-fluoro-2-(3-fluorophenyl)vinyl)(phenyl)sulfane (3p)**



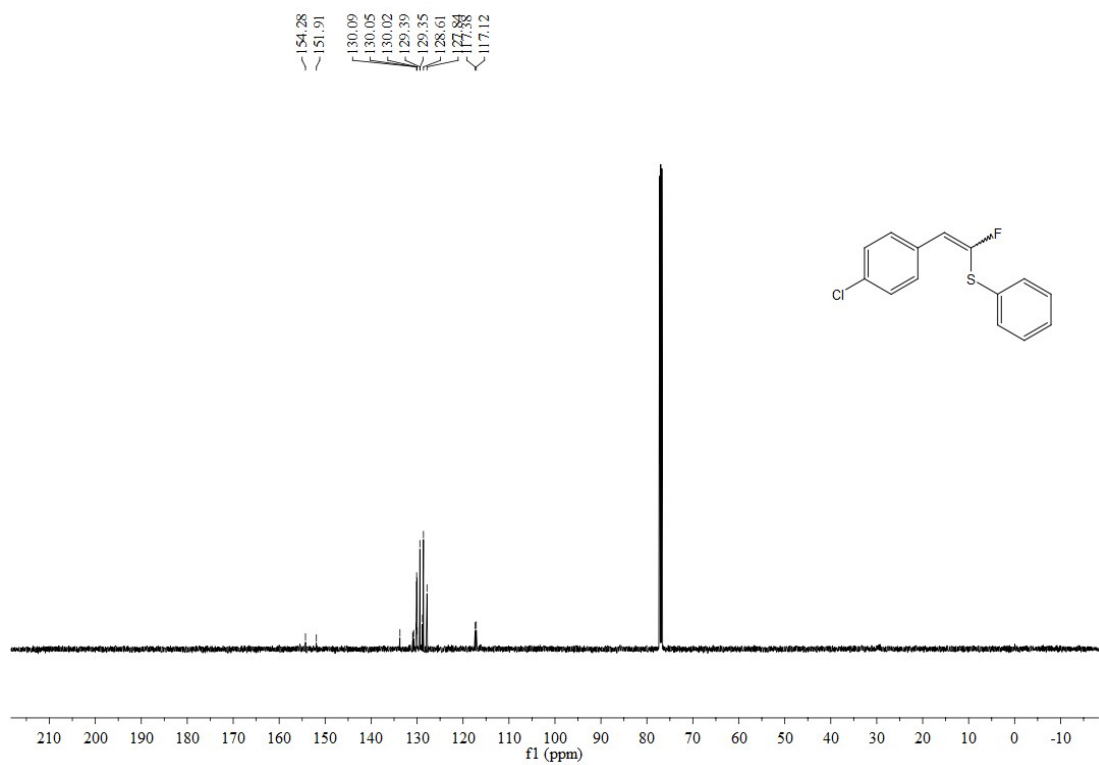
**<sup>19</sup>F NMR: (1-fluoro-2-(3-fluorophenyl)vinyl)(phenyl)sulfane (3p)**



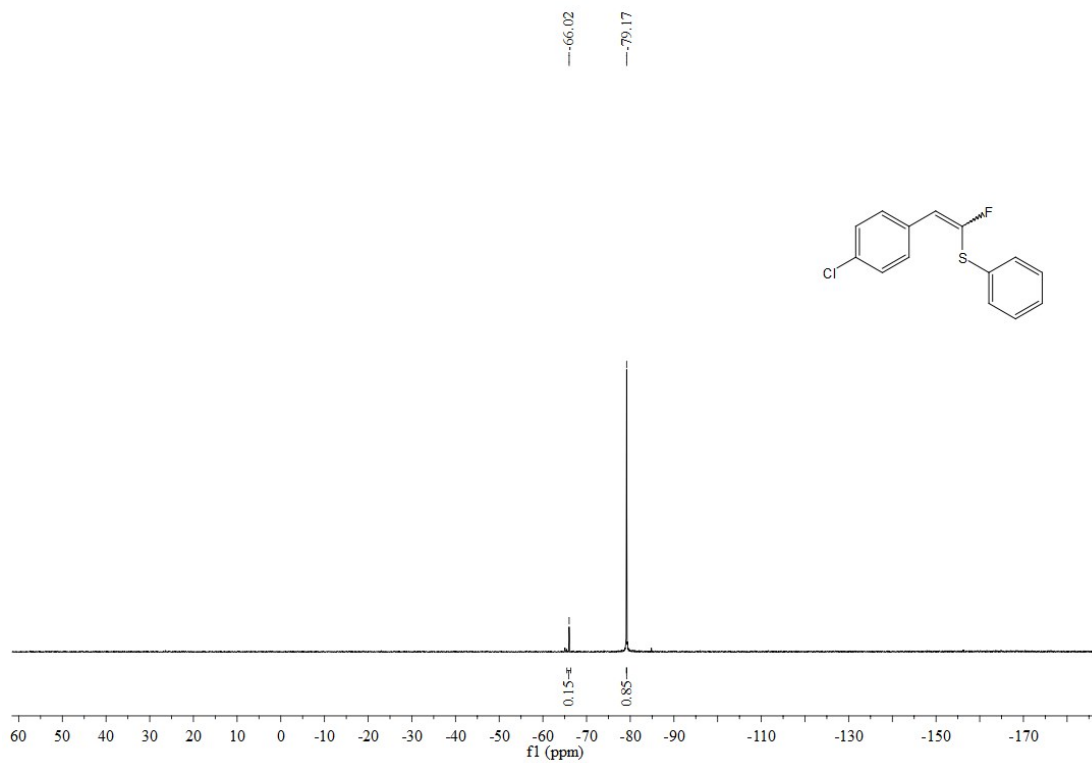
**<sup>1</sup>H NMR: (2-(4-chlorophenyl)-1-fluorovinyl)(phenyl)sulfane (3q)**



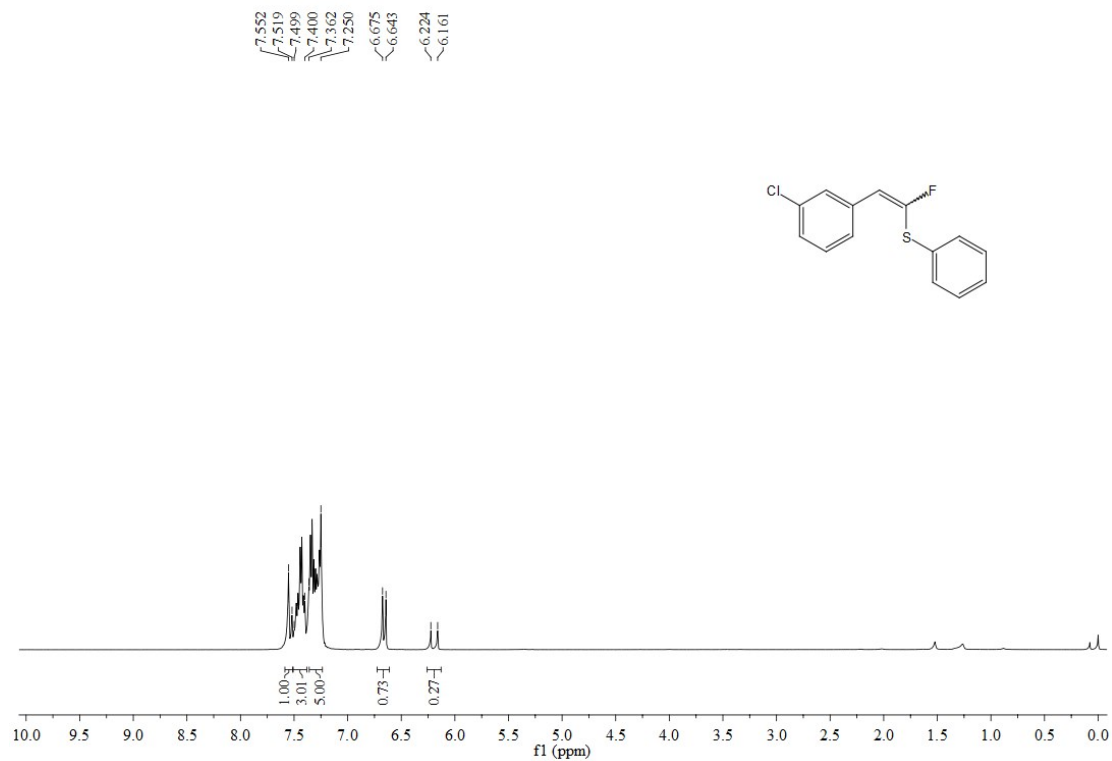
**<sup>13</sup>C NMR: (2-(4-chlorophenyl)-1-fluorovinyl)(phenyl)sulfane (3q)**



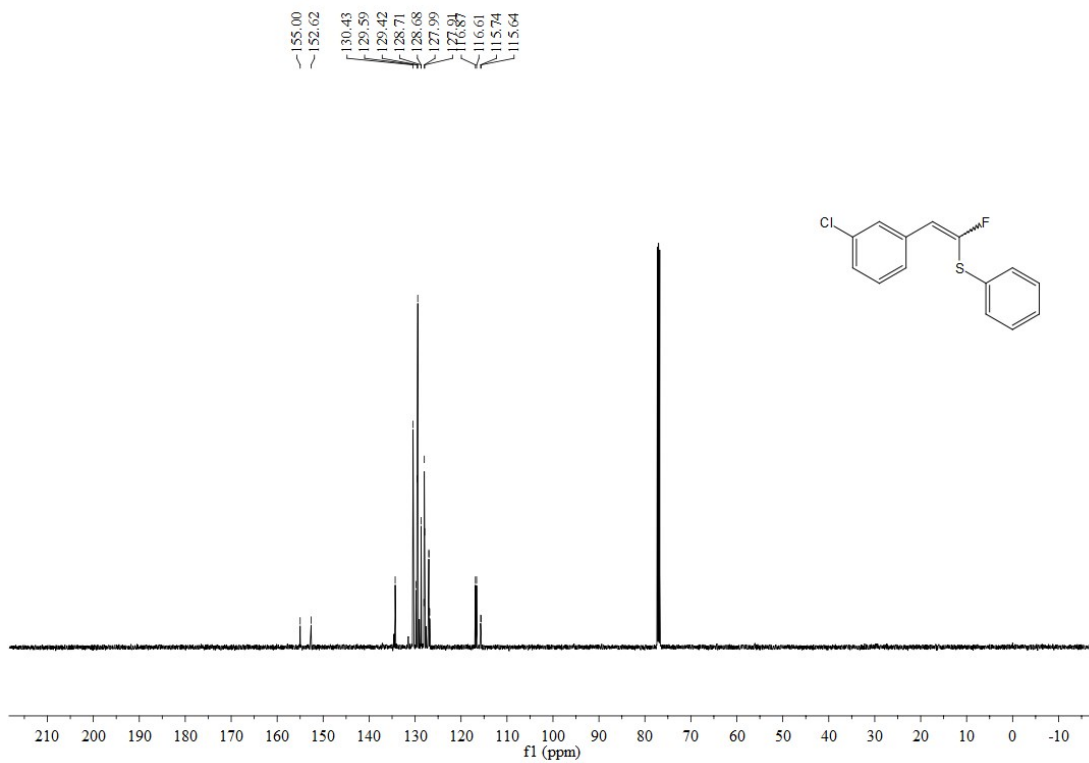
**$^{19}\text{F}$  NMR: (2-(4-chlorophenyl)-1-fluorovinyl)(phenyl)sulfane (3q)**



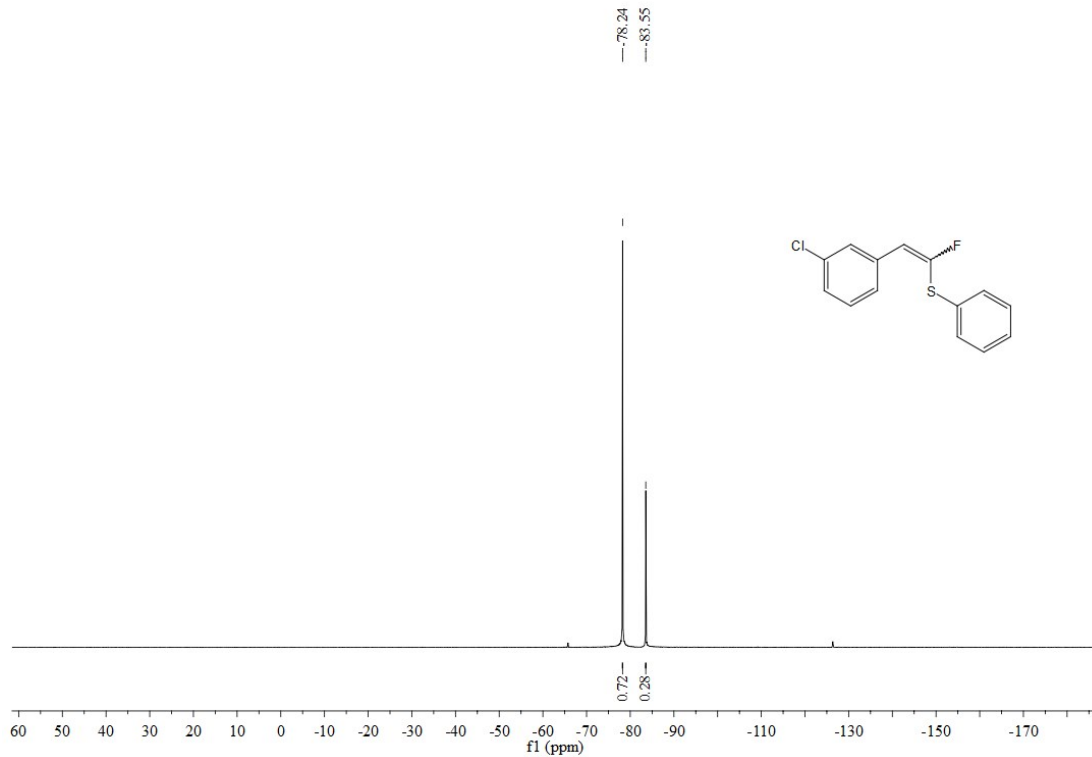
**$^1\text{H}$  NMR: (2-(3-chlorophenyl)-1-fluorovinyl)(phenyl)sulfane (3r)**



**<sup>13</sup>C NMR: (2-(3-chlorophenyl)-1-fluorovinyl)(phenyl)sulfane (3r)**

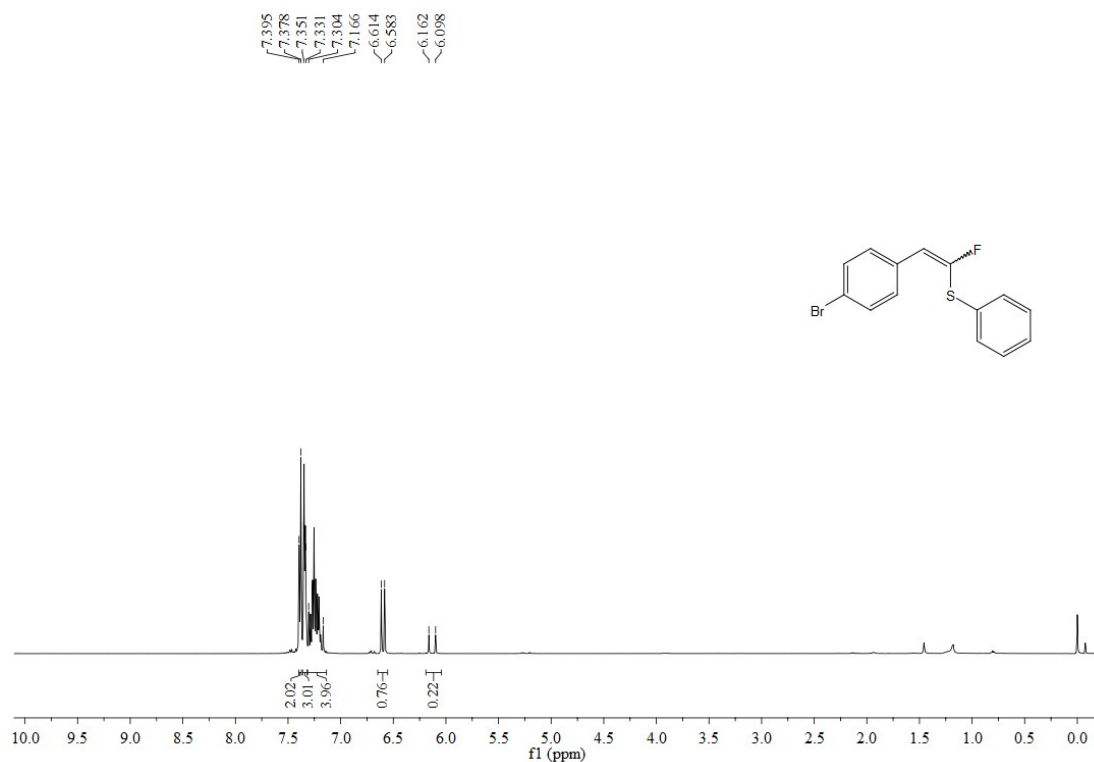


**<sup>19</sup>F NMR: (2-(3-chlorophenyl)-1-fluorovinyl)(phenyl)sulfane (3r)**

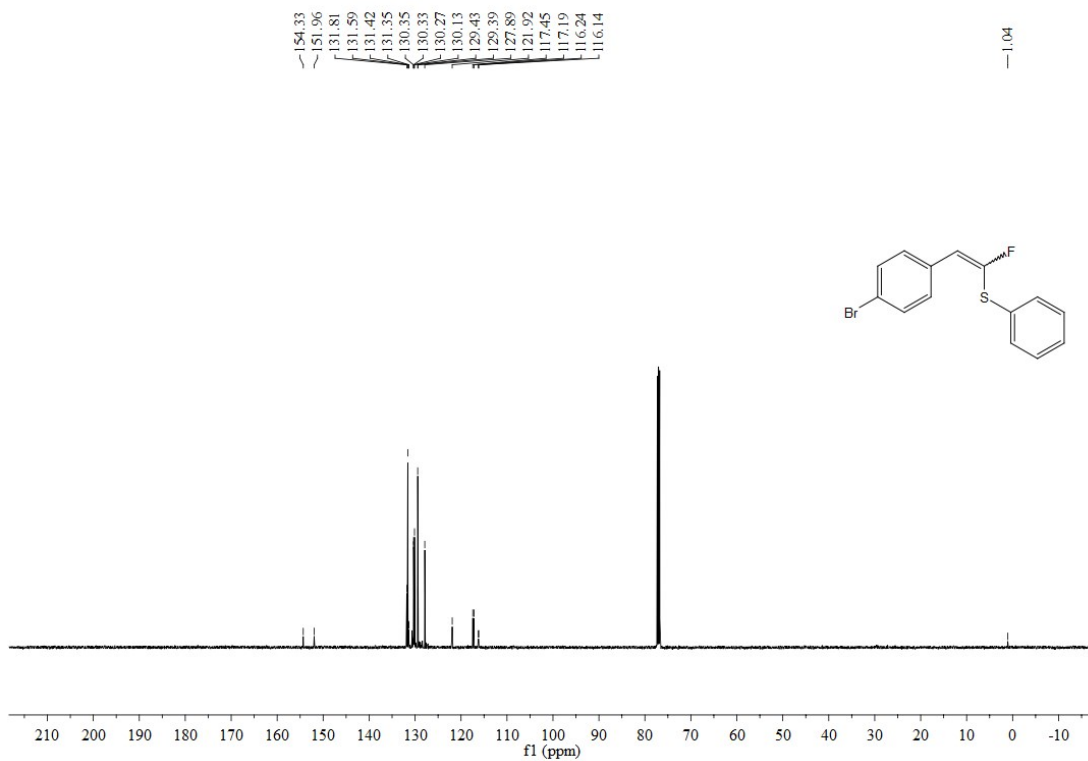




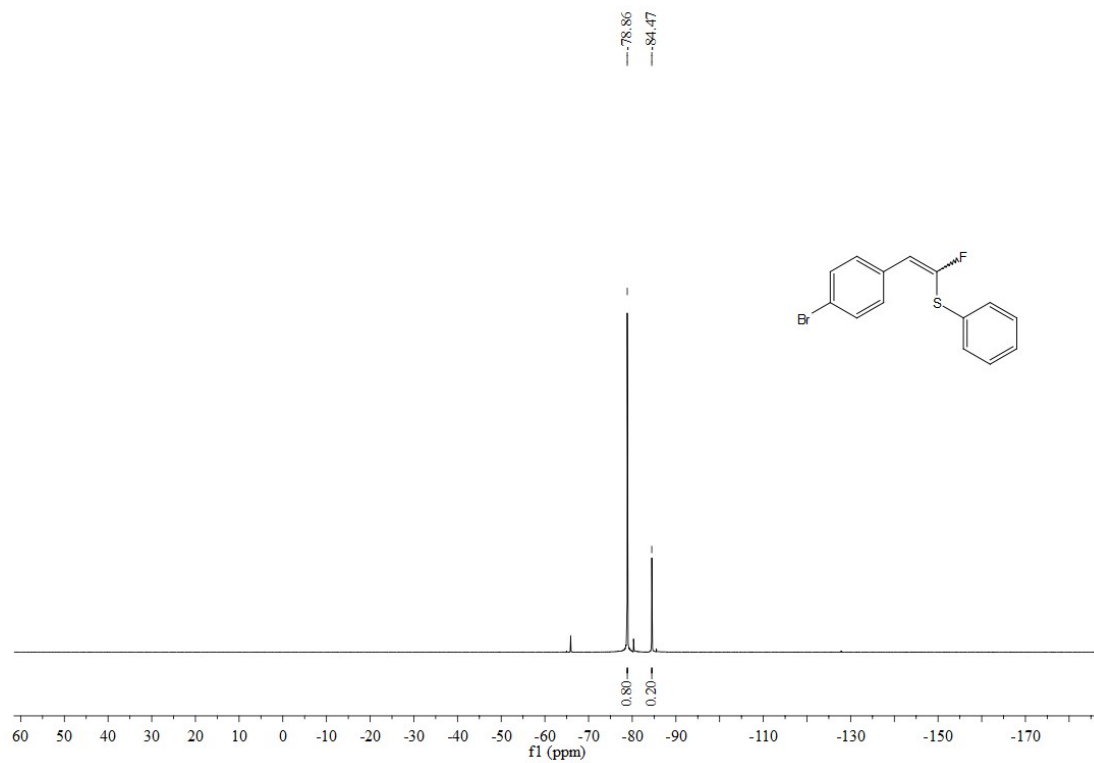
**<sup>1</sup>H NMR: (2-(4-bromophenyl)-1-fluorovinyl)(phenyl)sulfane (3s)**



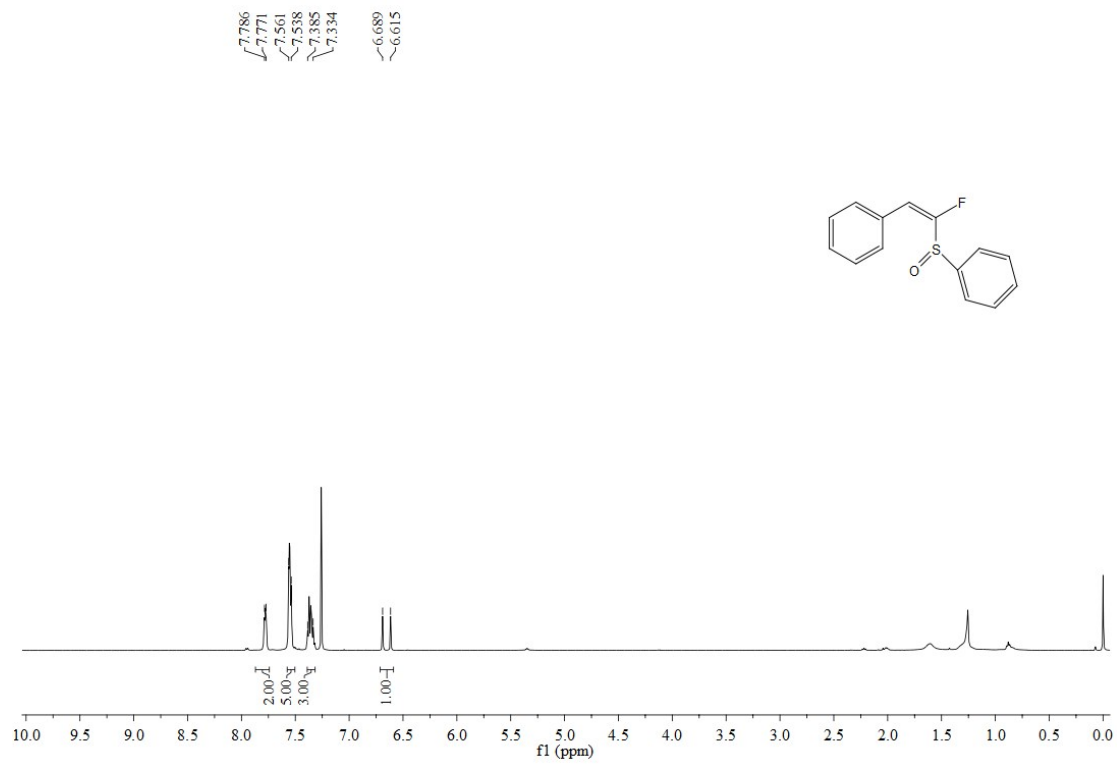
**<sup>13</sup>C NMR: (2-(4-bromophenyl)-1-fluorovinyl)(phenyl)sulfane (3s)**



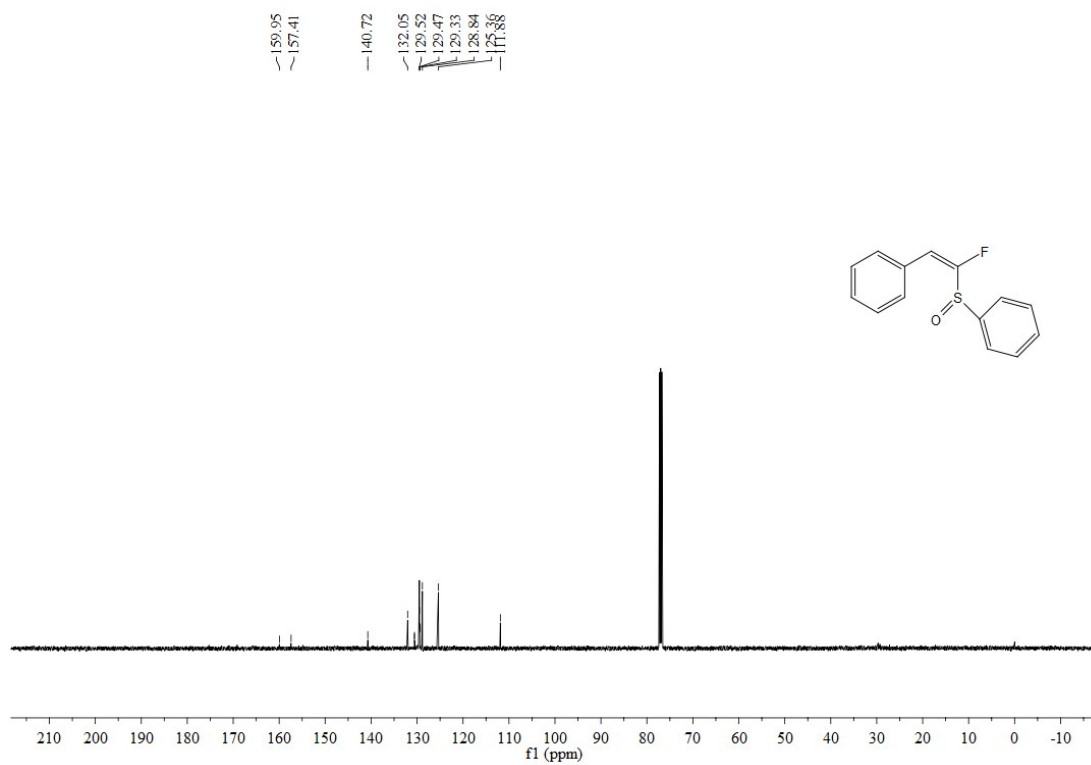
**<sup>19</sup>F NMR: (2-(4-bromophenyl)-1-fluorovinyl)(phenyl)sulfane (3s)**



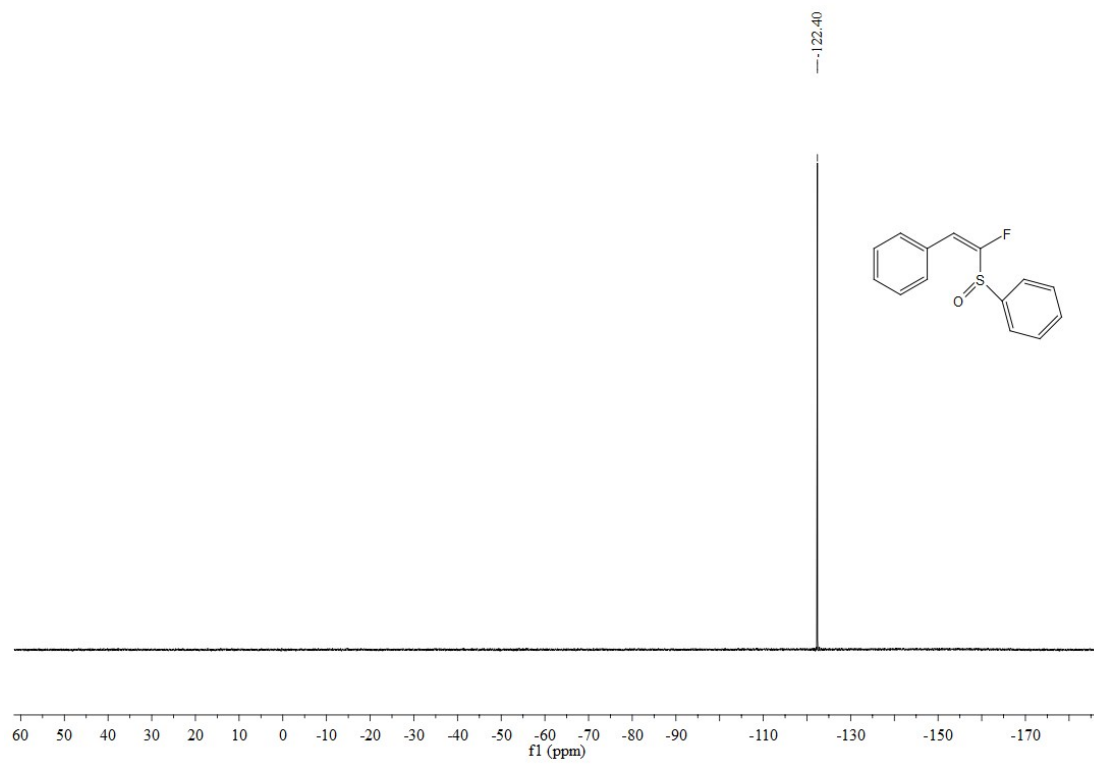
**<sup>1</sup>H NMR: (Z)-2-fluoro-2-(phenylsulfinyl)vinylbenzene (4)**



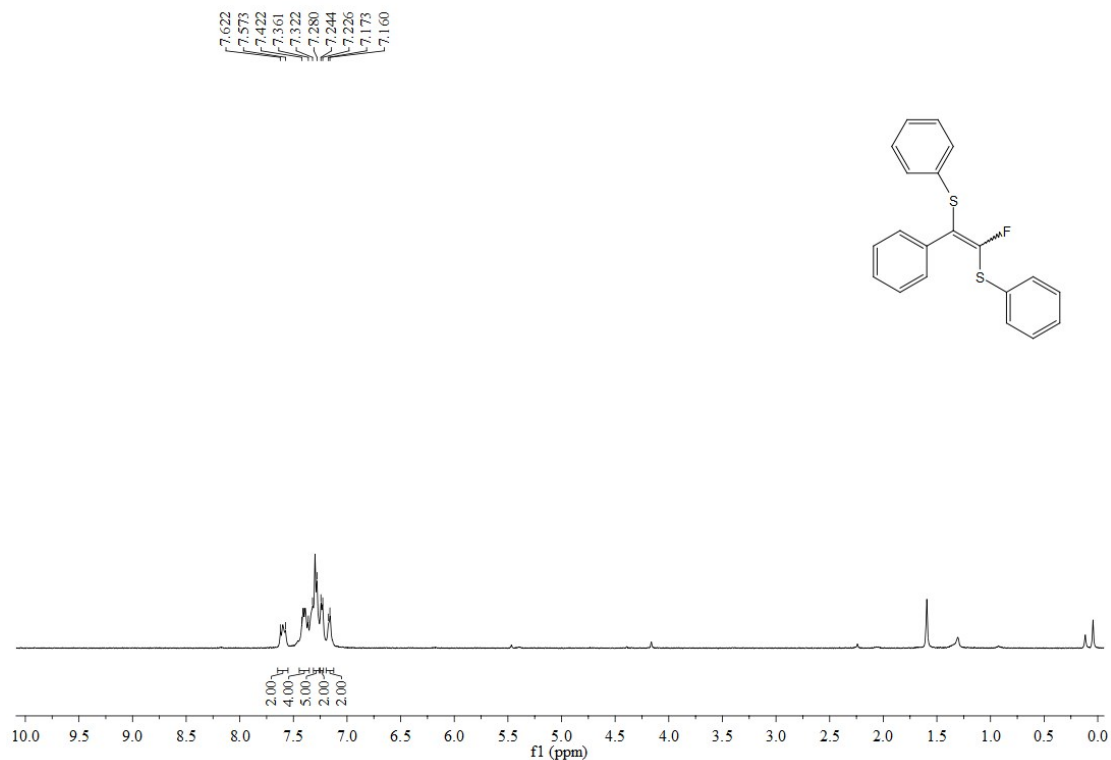
**<sup>13</sup>C NMR: (Z)-(2-fluoro-2-(phenylsulfinyl)vinyl)benzene (4)**



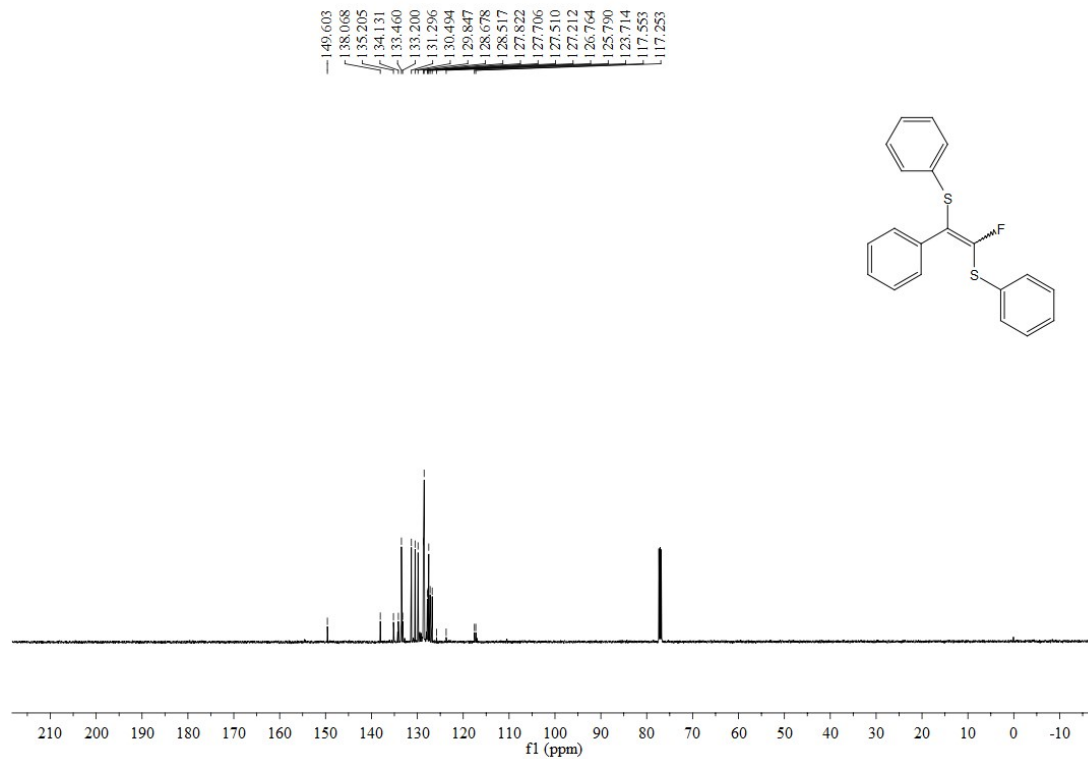
**<sup>19</sup>F NMR: (Z)-(2-fluoro-2-(phenylsulfinyl)vinyl)benzene (4)**



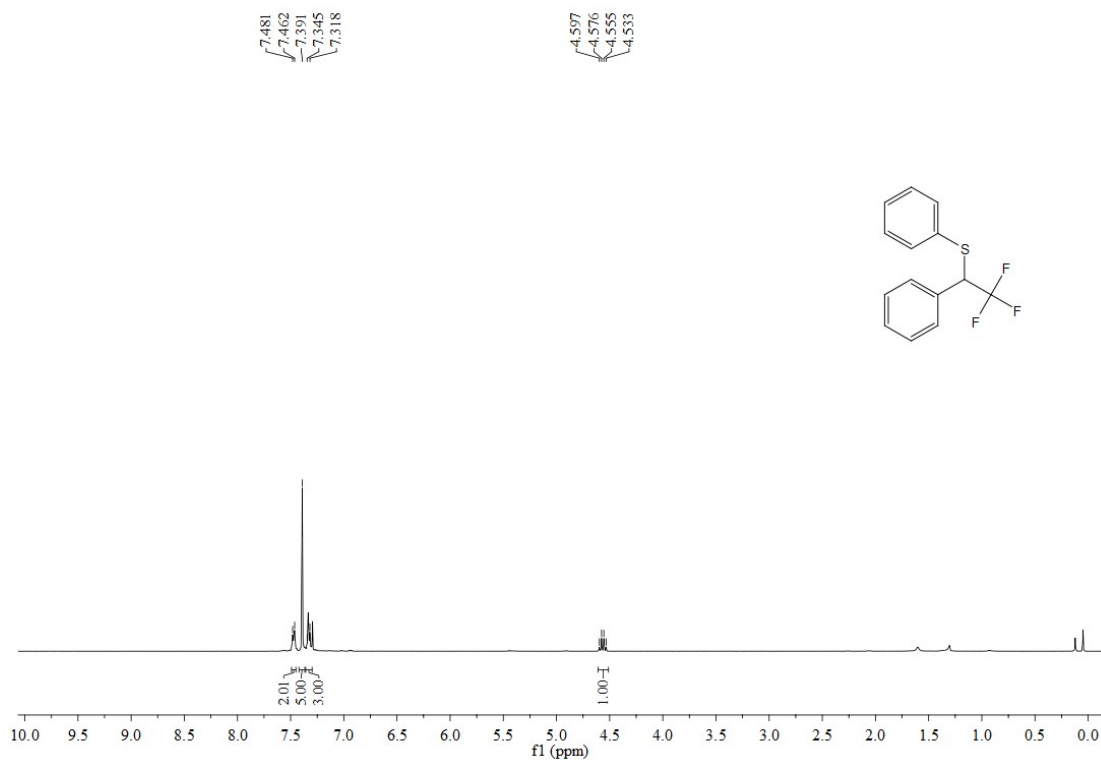
**<sup>1</sup>H NMR: (1-fluoro-2-phenylethene-1,2-diyl)bis(phenylsulfane) (5)**



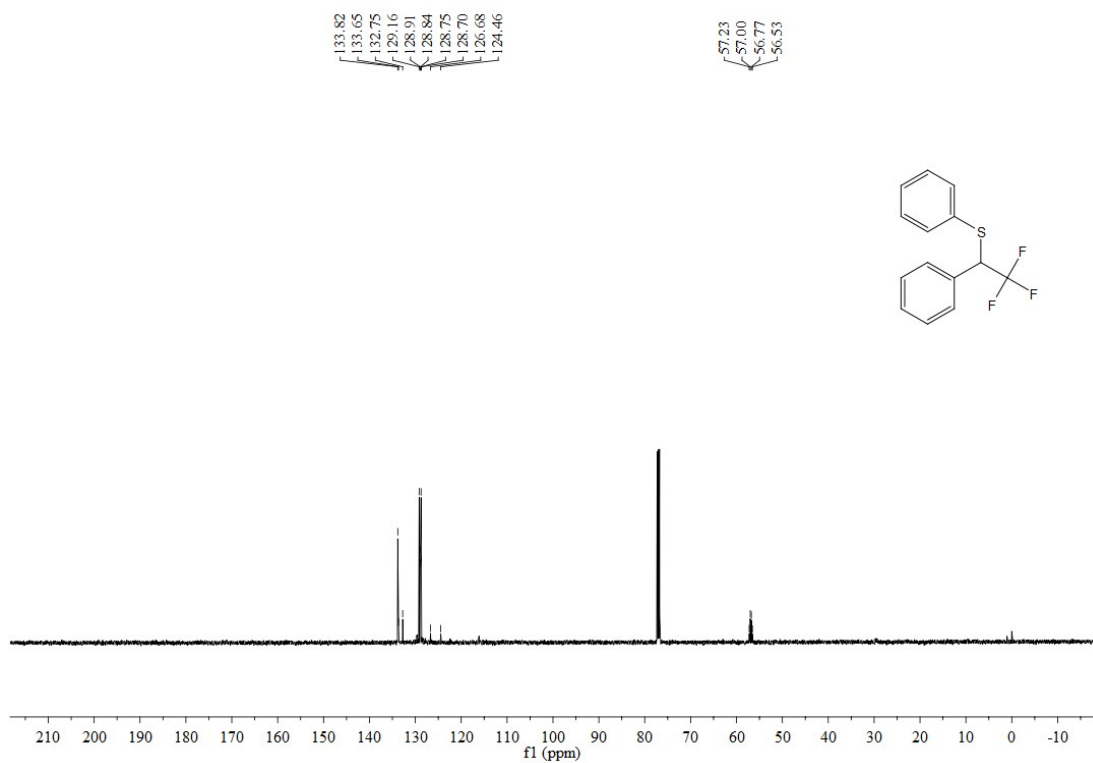
**<sup>13</sup>C NMR: (1-fluoro-2-phenylethene-1,2-diyl)bis(phenylsulfane) (5)**



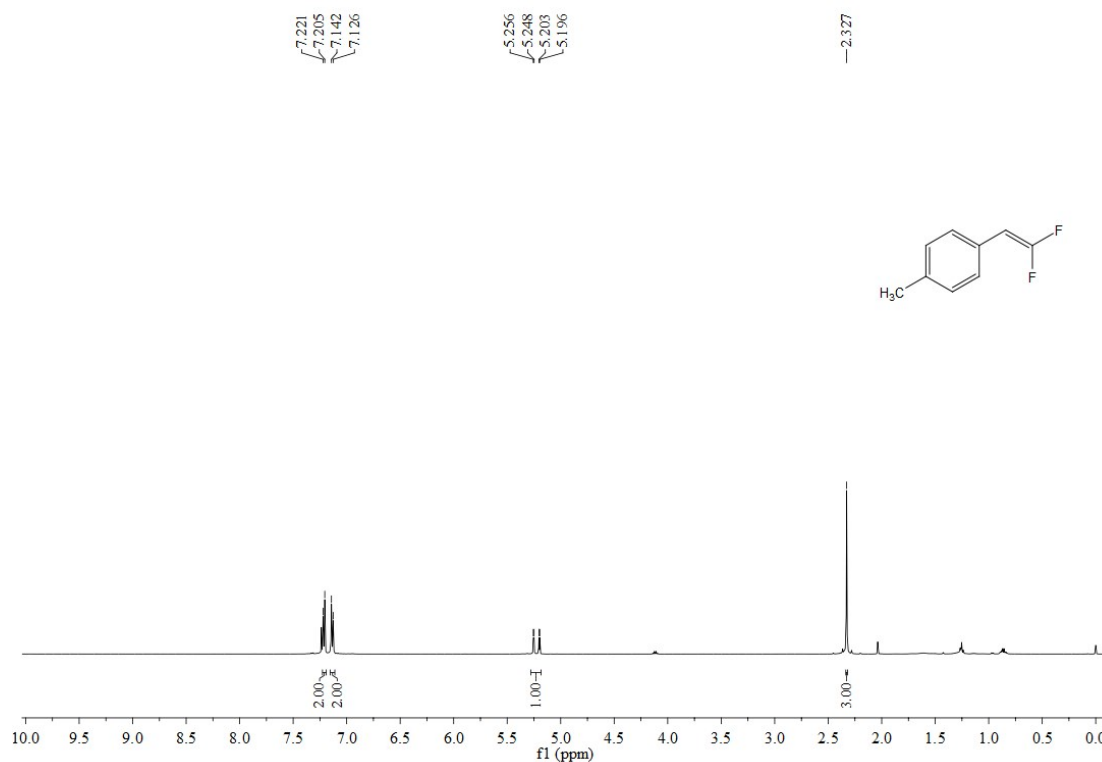
**<sup>1</sup>H NMR: phenyl(2,2,2-trifluoro-1-phenylethyl)sulfane (6)**



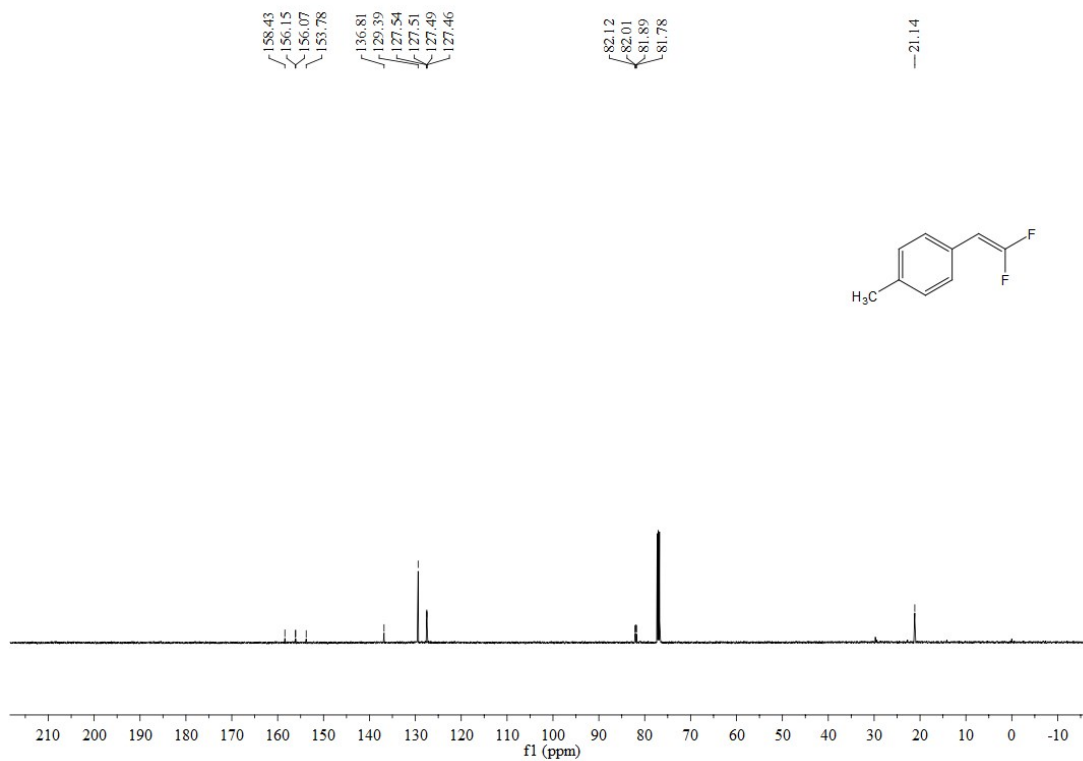
**<sup>13</sup>C NMR: phenyl(2,2,2-trifluoro-1-phenylethyl)sulfane (6)**



### <sup>1</sup>H NMR: 1-(2,2-difluorovinyl)-4-methylbenzene (7)



### <sup>13</sup>C NMR: 1-(2,2-difluorovinyl)-4-methylbenzene (7)



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