

# **Ruthenium-catalyzed highly regio- and stereoselective hydroarylation of aromatic sulfoxides with alkynes via C-H bond activation**

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## **Supporting Information (SI)**

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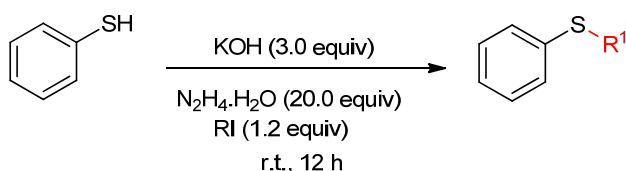
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## Experimental Section

### General procedure for the preparation of aromatic sulfoxides.

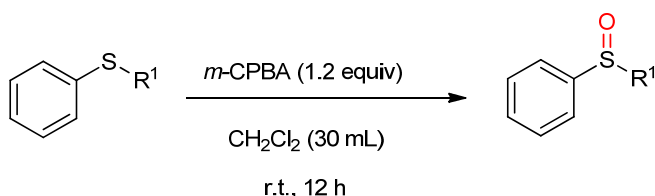
#### Step 1:

In a 100 mL round bottom flask, substituted aromatic thiol (1.0 gm), KOH (3.0 equiv) and hydrazine hydrate (20.0 equiv) were taken. Then, the reaction mixture was cooled for 15 min at 0 °C. The corresponding alkyl iodide was slowly added to the reaction mixture at 0 °C for 5 min and the reaction mixture was stirred at room temperature for 12 h. Later, the reaction mixture was diluted with H<sub>2</sub>O (75 mL) and extracted with EtOAc (3 x 75 mL). The combined organic layer was washed with brine (50 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic layer was concentrated under vacuum and the crude residue was purified through a silica gel column (hexanes and ethyl acetate) to give pure aryl alkyl thioether.



#### Step 2:

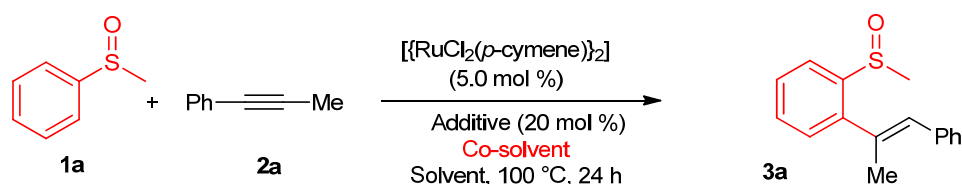
In a 100 mL round bottom flask, aryl alkyl thioether (1.0 gm) and CH<sub>2</sub>Cl<sub>2</sub> (20 mL) were added under the nitrogen atmosphere. In another round bottom flask, *meta*-chloroperoxybenzoic acid (1.2 equiv) was taken in 10 mL CH<sub>2</sub>Cl<sub>2</sub>. At 0 °C, *meta*-chloroperoxybenzoic acid solution was added into the round bottom flask which containing aryl alkyl thioether solution under the nitrogen atmosphere for 5 min. After addition, the resulting mixture was stirred under nitrogen at room temperature for 12 h. The reaction mixture was extracted with saturated sodium bicarbonate and CH<sub>2</sub>Cl<sub>2</sub> (100 mL). The organic layer was dried over NaSO<sub>4</sub>. After evaporation of the solvents under vacuum, the compound purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure aromatic sulfoxide.



**General procedure for the hydroarylation of aromatic sulfoxides with alkynes catalyzed by ruthenium Complex:**

A 15-mL pressure tube with septum containing [ $\text{RuCl}_2(p\text{-cymene})\}_2$ ] (5.0 mol %) and  $\text{AgSbF}_6$  (20 mol %) was evacuated and purged with nitrogen gas three times ( $\text{AgSbF}_6$  was taken inside the glove box). To the tube were then added phenyl sulfoxide **1** (100 mg), alkyne **2** (1.20 equiv), pivalic acid (5.0 equiv) and 1,4-dioxane (2.5 mL) via syringes and again the reaction mixture was evacuated and purged with nitrogen gas three times. After that, the septum was taken out and immediately a screw cap was used to cover the tube under the nitrogen atmosphere. Then, the reaction mixture was allowed to stir at 100 °C for 24 h. After cooling to ambient temperature, the reaction mixture was diluted with  $\text{CH}_2\text{Cl}_2$ , filtered through Celite and silica gel, and the filtrate was concentrated. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure **3**.

**Note:** For the preparation of compounds **3r**, **3s** and **3u**, the reaction was done at 100 °C for 12 h.

**Table S1. Optimization Studies<sup>a</sup>**


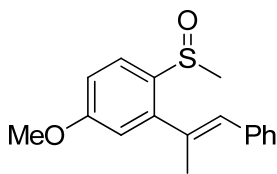
Entry	Solvent	Cosolvent	Additive	Yield of <b>3a</b> (%) <sup>b</sup>
1	1,4-Dioxane	No	AgSbF <sub>6</sub>	5
2	1,4-Dioxane	Pivalic acid (2.0 equiv)	AgSbF <sub>6</sub>	55
3	1,4-Dioxane	Acetic acid (2.0 equiv)	AgSbF <sub>6</sub>	10
4	1,4-Dioxane	Mesitylenic acid (2.0 equiv)	AgSbF <sub>6</sub>	12
5	1,4-Dioxane	1-Adamantane carboxylic acid (2.0 equiv)	AgSbF <sub>6</sub>	20
6	1,4-Dioxane	Acetic acid (5.0 equiv)	AgSbF <sub>6</sub>	18
7	1,4-Dioxane	Acetic acid (10.0 equiv)	AgSbF <sub>6</sub>	25
<b>8</b>	1,4-Dioxane	<b>Pivalic acid (5.0 equiv)</b>	<b>AgSbF<sub>6</sub></b>	<b>80</b>
9	1,4-Dioxane	Pivalic acid (10.0 equiv)	AgSbF <sub>6</sub>	81
10	1,4-Dioxane	Pivalic acid (5.0 equiv)	AgOTf	NR
11	1,4-Dioxane	Pivalic acid (5.0 equiv)	AgBF <sub>4</sub>	52
12	1,4-Dioxane	Pivalic acid (5.0 equiv)	KPF <sub>6</sub>	NR
13	<i>tert</i> -amyl alcohol	Pivalic acid (5.0 equiv)	AgSbF <sub>6</sub>	NR
14	trifluoroethanol	Pivalic acid (5.0 equiv)	AgSbF <sub>6</sub>	NR
15	THF	Pivalic acid (5.0 equiv)	AgSbF <sub>6</sub>	30
16	ClCH <sub>2</sub> CH <sub>2</sub> Cl	Pivalic acid (5.0 equiv)	AgSbF <sub>6</sub>	42
17	DMSO	Pivalic acid (5.0 equiv)	AgSbF <sub>6</sub>	NR
18	Toluene	Pivalic acid (5.0 equiv)	AgSbF <sub>6</sub>	NR
19	DMF	Pivalic acid (5.0 equiv)	AgSbF <sub>6</sub>	NR
20	CH <sub>3</sub> CN	Pivalic acid (5.0 equiv)	AgSbF <sub>6</sub>	NR
21	<i>i</i> -propanol	Pivalic acid (5.0 equiv)	AgSbF <sub>6</sub>	11

<sup>a</sup>All reactions were carried out under the following conditions: **1a** (100 mg), **2a** (1.2 equiv), [ $\{\text{RuCl}_2(p\text{-cymene})\}_2$ ] (5 mol %), additive (20 mol %) and co-solvent (specified) in solvent (2.5 mL) at 100 °C for 24 h under N<sub>2</sub> atmosphere. <sup>b</sup>GC yield.

**Note:** The catalytic reaction was tried without ruthenium and AgSbF<sub>6</sub>. No product **3a** was observed.

## Spectral Data of Compounds 3a-u.

### (*E*)-4-Methoxy-1-(methylsulfinyl)-2-(1-phenylprop-1-en-2-yl)benzene (3a).



Colorless semisolid; eluent (50% ethyl acetate in hexanes). **1a** was taken in 100 mg, yield is 75% (126 mg).

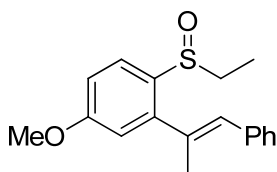
**IR (ATR)**  $\tilde{\nu}$  (cm<sup>-1</sup>): 2390, 1771, 1741, 1084, 734 and 701.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.96 (d, *J* = 8.0 Hz, 1 H), 7.40 – 7.27 (m, 5 H), 7.05 (dd, *J* = 8.0, 4.0 Hz, 1 H), 6.79 (d, *J* = 8.0 Hz, 1 H), 6.43 (s, 1 H), 3.86 (s, 3 H), 2.67 (s, 3 H), 2.22 (s, 3 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  161.6, 144.9, 136.6, 135.2, 134.3, 132.0, 128.8, 128.4, 127.2, 125.4, 114.1, 113.8, 55.5, 43.3, 20.3.

HRMS (ESI): calc. for [(C<sub>17</sub>H<sub>18</sub>O<sub>2</sub>S)H] (M+H) 287.1106, measured 287.1104

### (*E*)-1-(Ethylsulfinyl)-4-methoxy-2-(1-phenylprop-1-en-2-yl)benzene (3b).



Colorless semisolid; eluent (50% ethyl acetate in hexanes). **1b** was taken in 100 mg, yield is 52% (84 mg).

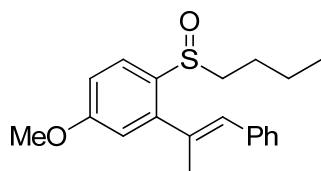
**IR (ATR)**  $\tilde{\nu}$  (cm<sup>-1</sup>): 3058, 2850, 1082, 1048, 757 and 701.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.88 (d, *J* = 12.0 Hz, 1 H), 7.38 (t, *J* = 8.0 Hz, 2 H), 7.32 - 7.27 (m, 3 H), 7.02 (dd, *J* = 12.0, 4.0 Hz, 1 H), 6.80 (d, *J* = 4.0 Hz, 1 H), 6.45 (s, 1 H), 3.85 (s, 3 H), 2.90 – 2.68 (m, 2 H), 2.22 (s, 3 H), 1.16 (t, *J* = 8.0 Hz, 3 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  161.6, 145.3, 136.7, 135.4, 131.9, 131.7, 128.8, 128.4, 127.2, 126.5, 114.3, 113.3, 55.5, 49.2, 20.3, 6.3.

HRMS (ESI): calc. for [(C<sub>18</sub>H<sub>20</sub>O<sub>2</sub>S)H] (M+H) 301.1262, measured 301.1265.

**(E)-1-(Butylsulfinyl)-4-methoxy-2-(1-phenylprop-1-en-2-yl)benzene (3c).**



Colorless semisolid; eluent (50% ethyl acetate in hexanes). **1c** was taken in 100 mg, yield is 47% (73 mg).

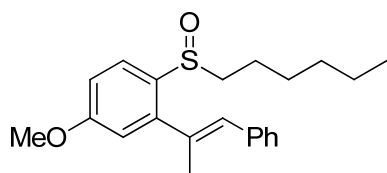
**IR (ATR)**  $\tilde{\nu}$  (cm<sup>-1</sup>): 3055, 2960, 1738, 1496, 1026, 730 and 699.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.90 (d,  $J$  = 8.0 Hz, 1 H), 7.38, (t,  $J$  = 8.0 Hz, 2 H), 7.32 -7.27 (m, 3 H), 7.02 (dd,  $J$  = 8.0,4.0 Hz, 1 H), 6.79 (d,  $J$  = 4.0 Hz, 1 H), 6.45 (s, 1 H), 3.85 (s, 3 H), 2.83 – 2.66 (m, 2 H), 2.21 (s, 3 H), 1.74 -1.52 (m, 2 H), 1.44 -1.28 (m, 2 H), 0.84 (t,  $J$  = 8.0 Hz, 3 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  161.5, 145.1, 136.7, 135.4, 132.6, 131.9, 128.8, 128.4, 127.2, 126.1, 114.3, 113.5, 56.3, 55.5, 24.4, 21.8, 20.3, 13.6.

HRMS (ESI): calc. for [(C<sub>20</sub>H<sub>24</sub>O<sub>2</sub>S)H] (M+H) 329.1575, measured 329.1571.

**(E)-1-(Hexylsulfinyl)-4-methoxy-2-(1-phenylprop-1-en-2-yl)benzene (3d).**



Colorless semisolid; eluent (50% ethyl acetate in hexanes). **1d** was taken in 100 mg, yield is 47% (59 mg).

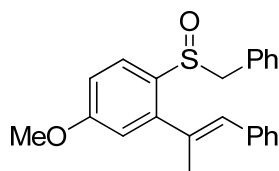
**IR (ATR)**  $\tilde{\nu}$  (cm<sup>-1</sup>): 3058, 2956, 1770, 1042, 726 and 699.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.90 (d,  $J$  = 8.0 Hz, 1 H), 7.37 (t,  $J$  = 8.0 Hz, 2 H), 7.32 - 7.26 (m, 3 H), 7.02 (dd,  $J$  = 8.0,4.0 Hz, 1 H), 6.79 (d,  $J$  = 4.0 Hz, 1 H), 6.45 (s, 1 H), 3.85 (s, 3 H), 2.82 - 2.66 (m, 2 H), 2.22 (s, 3 H), 1.75 - 1.54 (m, 3 H), 1.40 – 1.23 (m, 5 H), 0.78 (t,  $J$  = 8.0 Hz, 3 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  161.5, 145.1, 136.7, 135.4, 132.7, 132.0, 128.8, 128.4, 127.2, 126.1, 114.3, 113.5, 56.7, 55.5, 31.3, 28.3, 22.5, 22.3, 20.2, 13.9.

HRMS (ESI): calc. for [(C<sub>22</sub>H<sub>28</sub>O<sub>2</sub>S)H] (M+H) 357.1888, measured 357.1883.

**(E)-1-(Benzylsulfinyl)-4-methoxy-2-(1-phenylprop-1-en-2-yl)benzene (3e).**



Colorless semisolid; eluent (35% ethyl acetate in hexanes), **1e** was taken in 100 mg, yield is 43% (63 mg).

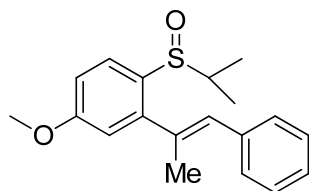
**IR (ATR)**  $\tilde{\nu}$  (cm<sup>-1</sup>): 2985, 1735, 1236, 1098, 1043, 784 and 731.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.58 (d, *J* = 8.0 Hz, 1 H), 7.28 – 7.24 (m, 4 H), 7.22 - 7.19 (m, 3 H), 7.17 - 7.15 (m, 1 H), 7.11 – 7.09 (m, 1 H), 6.96 (dd, *J* = 8.0, 4.0 Hz, 1 H), 6.91 – 6.89 (m, 2 H), 6.53 (s, 1 H), 3.87 (s, 3 H), 3.71 (d, *J* = 12.0 Hz, 1 H), 3.47 (d, *J* = 12.0 Hz, 1 H), 1.26 (s, 3 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  161.6, 144.5, 139.5, 139.2, 136.3, 133.4, 132.2, 132.2, 130.5, 129.5, 128.6, 128.0, 127.4, 127.2, 115.9, 113.9, 61.2, 55.6, 29.7.

HRMS (ESI): calc. for [(C<sub>23</sub>H<sub>22</sub>O<sub>2</sub>S)Na] (M+Na) 385.1238, measured 385.1230.

**(E)-1-(Isopropylsulfinyl)-4-methoxy-2-(1-phenylprop-1-en-2-yl)benzene (3f).**



Colorless semisolid; eluent (40% ethyl acetate in hexanes), **1f** was taken in 100 mg, yield is 56% (88 mg).

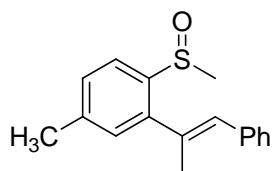
**IR (ATR)**  $\tilde{\nu}$  (cm<sup>-1</sup>): 3057, 2967, 1710, 1046, 732 and 700.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.84 (d, *J* = 8.0 Hz, 1 H), 7.38 (t, *J* = 8.0 Hz, 2 H), 7.32 – 7.25 (m, 3 H), 7.00 (dd, *J* = 8.0, 4.0 Hz, 1 H), 6.80 (s, 1 H), 6.49 (s, 1 H), 3.85 (s, 3 H), 2.90 – 2.81 (m, 1 H), 2.22 (s, 3 H), 1.22 (d, *J* = 8.0 Hz, 3 H), 1.06 (d, *J* = 8.0 Hz, 3 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  161.6, 145.8, 136.9, 135.6, 132.1, 130.8, 128.8, 128.4, 127.14, 127.08, 114.4, 113.1, 55.5, 53.2, 20.3, 17.3, 13.1.

HRMS (ESI): calc. for [(C<sub>19</sub>H<sub>22</sub>O<sub>2</sub>S)H] (M+H) 315.1419, measured 315.1416.

**(E)-4-Methyl-1-(methylsulfinyl)-2-(1-phenylprop-1-en-2-yl)benzene (3g).**



Colorless semisolid; eluent (40% ethyl acetate in hexanes). **1g** was taken in 100 mg, yield is 55% (96 mg).

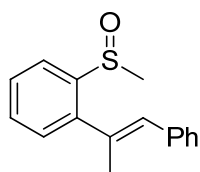
**IR (ATR)**  $\tilde{\nu}$  (cm<sup>-1</sup>): 3055, 2316, 1264, 1031, 734 and 701.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.93 (d, *J* = 8.0 Hz, 1 H), 7.40 -7.35 (m, 3 H), 7.33 -7.29 (m, 3 H), 7.10 (s, 1 H), 6.42 (s, 1 H), 2.67 (s, 3 H), 2.41 (s, 3 H), 2.22 (s, 3 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  143.0, 141.2, 140.2, 136.8, 135.5, 132.0, 129.3, 129.2, 128.8, 128.4, 127.2, 123.5, 43.1, 21.3, 20.3.

HRMS (ESI): calc. for [(C<sub>17</sub>H<sub>18</sub>OS)H] (M+H) 271.1157, measured 271.1161.

**(E)-1-(Methylsulfinyl)-2-(1-phenylprop-1-en-2-yl)benzene (3h).**



Colorless semisolid; eluent (40% ethyl acetate in hexanes). **1h** was taken in 100 mg, yield is 73% (133 mg).

**IR (ATR)**  $\tilde{\nu}$  (cm<sup>-1</sup>): 3055, 1710, 1424, 1264, 1052 and 730.

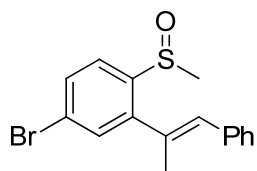
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.09 (d, *J* = 8.0 Hz, 1 H), 7.55 (t, *J* = 8.0 Hz, 1 H), 7.49 (t, *J* = 8.0 Hz, 1 H), 7.42 - 7.38 (m, 2 H), 7.36 - 7.34 (m, 2 H), 7.32 -7.29 (m, 2 H), 6.46 (s, 1 H), 2.71 (s, 3 H), 2.25 (s, 3 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  143.2, 143.0, 136.6, 135.2, 132.2, 130.8, 128.8, 128.5, 128.4, 128.3, 127.2, 123.3, 42.9, 20.2.

HRMS (ESI): calc. for [(C<sub>16</sub>H<sub>16</sub>OS)H] (M+H) 257.1000, measured 257.1001.



**(E)-4-Bromo-1-(methylsulfinyl)-2-(1-phenylprop-1-en-2-yl)benzene (3i).**



Colorless semisolid; eluent (40% ethyl acetate in hexanes). **1i** was taken in 100 mg, yield is 56% (86 mg).

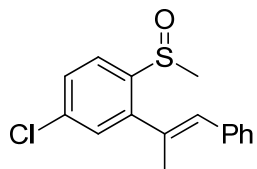
**IR (ATR)**  $\tilde{\nu}$  (cm<sup>-1</sup>): 3057, 2361, 1484, 1031, 744 and 700.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.92 (d,  $J$  = 8.0 Hz, 1 H), 7.66 (dd,  $J$  = 8.0, 4.0 Hz, 1 H), 7.45 (d,  $J$  = 8.0 Hz, 1 H), 7.41 -7.37 (m, 2 H), 7.32 – 7.29 (m, 3 H), 6.46 (s, 1 H), 2.68 (s, 3 H), 2.22 (s, 3 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  144.6, 142.7, 136.2, 134.0, 133.0, 131.6, 131.5, 128.8, 128.5, 127.5, 125.34, 125.28, 42.9, 20.1.

HRMS (ESI): calc. for [(C<sub>16</sub>H<sub>15</sub>BrOS)H] (M+H) 335.0105, measured 335.0104.

**(E)-4-Chloro-1-(methylsulfinyl)-2-(1-phenylprop-1-en-2-yl)benzene (3j).**



Pale yellow solid; eluent (40% ethyl acetate in hexanes). **1j** was taken in 100 mg, yield is 52% (87 mg).

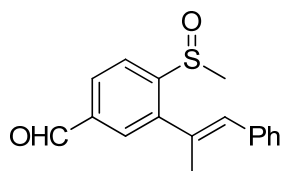
**IR (ATR)**  $\tilde{\nu}$  (cm<sup>-1</sup>): 3055, 2315, 1451, 1057, 730 and 703.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.00 (d,  $J$  = 12.0 Hz, 1 H), 7.50 (dd,  $J$  = 8.0, 4.0 Hz, 1 H), 7.38 (d,  $J$  = 8.0 Hz, 2 H), 7.32 – 7.29 (m, 4 H), 6.46 (s, 1 H), 2.68 (s, 3 H), 2.22 (s, 3 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  144.5, 142.0, 137.0, 136.2, 134.0, 132.9, 128.9, 128.7, 128.6, 128.5, 127.5, 125.2, 43.0, 20.1.

HRMS (ESI): calc. for [(C<sub>16</sub>H<sub>15</sub>ClOS)H] (M+H) 291.0610, measured 291.0610.

**(E)-4-(Methylsulfinyl)-3-(1-phenylprop-1-en-2-yl)benzaldehyde (3k).**



Colorless semisolid; eluent (45% ethyl acetate in hexanes). **1k** was taken in 100 mg, yield is 51% (86 mg).

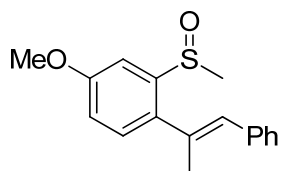
**IR (ATR)**  $\tilde{\nu}$  (cm<sup>-1</sup>): 2962, 2876, 1723, 1037, 743 and 700.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  10.09 (s, 1 H), 8.26 (d,  $J$  = 8.0 Hz, 1 H), 8.03 (dd,  $J$  = 8.0, 4.0 Hz, 1 H) 7.81 (s, 1 H), 7.39 (d,  $J$  = 8.0 Hz, 2 H) 7.34 -7.30 (m, 3 H), 6.51 (s, 1 H), 2.73 (s, 3 H) 2.26 (s, 3 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  191.3, 150.4, 143.8, 138.0, 136.2, 134.1, 133.3, 129.7, 129.2, 128.9, 128.5, 127.6, 124.5, 42.6, 20.0.

HRMS (ESI): calc. for [(C<sub>17</sub>H<sub>16</sub>O<sub>2</sub>S)H] (M+H) 285.0949, measured 285.0951.

**(E)-4-Methoxy-2-(methylsulfinyl)-1-(1-phenylprop-1-en-2-yl)benzene (3l).**



Colorless solid; eluent (40% ethyl acetate in hexanes). **1l** was taken in 100 mg, yield is 57% (95 mg).

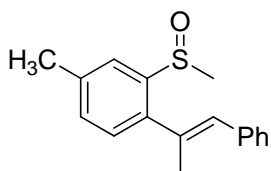
**IR (ATR)**  $\tilde{\nu}$  (cm<sup>-1</sup>): 3052, 1724, 1464, 1052, 723 and 701.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.60 (d,  $J$  = 4.0 Hz, 1 H), 7.37 (d,  $J$  = 8.0 Hz, 2 H), 7.33 - 7.27 (m, 3 H), 7.21 (d,  $J$  = 8.0 Hz, 1 H), 7.00 (dd,  $J$  = 8.0, 4.0 Hz, 1 H), 6.43 (s, 1 H), 3.89 (s, 3 H), 2.70 (s, 3 H), 2.20 (s, 3 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  159.9, 144.4, 136.9, 135.3, 134.9, 132.1, 130.0, 128.8, 128.4, 127.1, 117.8, 107.0, 55.7, 42.8, 20.4.

HRMS (ESI): calc. for [(C<sub>17</sub>H<sub>18</sub>O<sub>2</sub>S)H] (M+H) 287.1106, measured 287.1104.

**(E)-4-Methyl-2-(methylsulfinyl)-1-(1-phenylprop-1-en-2-yl)benzene (3m).**



Pale yellow semisolid; eluent (35% ethyl acetate in hexanes). **1m** was taken in 100 mg, yield is 51% (89 mg).

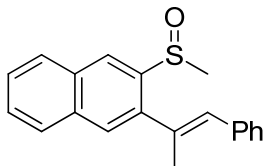
**IR (ATR)**  $\tilde{\nu}$  (cm<sup>-1</sup>): 3024, 2920, 1780, 1055, 760 and 728.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.86 (s, 1 H), 7.38 (t,  $J$  = 8.0 Hz, 2 H), 7.32 (d,  $J$  = 8.0 Hz, 2 H), 7.27 (d,  $J$  = 8.0 Hz, 2 H), 7.18 (d,  $J$  = 8.0 Hz, 1 H), 6.42 (s, 1 H), 2.68 (s, 3 H), 2.44 (s, 3 H), 2.21 (s, 3 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  142.9, 140.2, 138.7, 136.8, 135.3, 132.0, 131.5, 128.8, 128.6, 128.3, 127.1, 123.5, 42.9, 21.2, 20.3.

HRMS (ESI): calc. for [(C<sub>17</sub>H<sub>18</sub>OS)Na] (M+Na) 293.0976, measured 293.0981.

**(E)-2-(Methylsulfinyl)-3-(1-phenylprop-1-en-2-yl)naphthalene (3n).**



Colorless semisolid; eluent (45% ethyl acetate in hexanes). **1n** was taken in 100 mg, yield is 47% (75 mg).

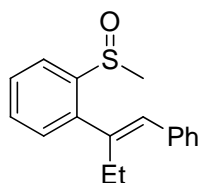
**IR (ATR)**  $\tilde{\nu}$  (cm<sup>-1</sup>): 3056, 2928, 2363, 1646, 1052, 732 and 703.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.56 (s, 1 H), 7.98 (d,  $J$  = 8.0 Hz, 1 H), 7.87 (d,  $J$  = 8.0 Hz, 1 H), 7.76 (s, 1 H), 7.58 - 7.55 (m, 2 H), 7.43 - 7.36 (m, 4 H), 7.30 (d,  $J$  = 8.0 Hz, 1 H), 6.61 (s, 1 H), 2.75 (s, 3 H), 2.32 (s, 3 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  141.8, 139.4, 136.8, 135.3, 134.1, 132.5, 132.3, 128.8, 128.4, 127.9, 127.8, 127.6, 127.2, 126.9, 124.1, 43.1, 20.5.

HRMS (ESI): calc. for [(C<sub>20</sub>H<sub>18</sub>OS)H] (M+H) 307.1157, measured 307.1158.

**(E)-1-(Methylsulfinyl)-2-(1-phenylbut-1-en-2-yl)benzene (3o).**



Colorless semisolid; eluent (35% ethyl acetate in hexanes). **1o** was taken in 100 mg, yield is 71% (136 mg).

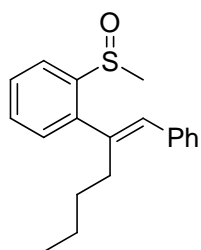
**IR (ATR)**  $\tilde{\nu}$  (cm<sup>-1</sup>): 3058, 2977, 1498, 1040, 736 and 701.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.08 (dd,  $J$  = 8.0, 4.0 Hz, 1 H), 7.55 (t,  $J$  = 8.0 Hz, 1 H), 7.48 (t,  $J$  = 8.0 Hz, 1 H), 7.38 (t,  $J$  = 8.0 Hz, 2 H), 7.31 – 7.25 (m, 4 H), 6.34 (s, 1 H), 2.73 (s, 3 H), 1.23 -1.22 (m, 2 H), 0.99 (t,  $J$  = 8.0 Hz, 3 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  143.9, 141.9, 141.3, 136.6, 131.9, 130.7, 129.4, 128.6, 128.4, 127.2, 123.3, 43.3, 25.7, 12.7.

HRMS (ESI): calc. for [(C<sub>17</sub>H<sub>18</sub>OS)H] (M+H) 271.1157, measured 271.1151.

**(E)-1-(Methylsulfinyl)-2-(1-phenylhex-1-en-2-yl)benzene (3p).**



Colorless semisolid; eluent (35% ethyl acetate in hexanes). **1p** was taken in 100 mg, yield is 67% (142 mg).

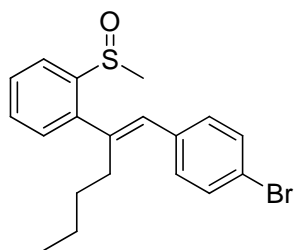
**IR (ATR)**  $\tilde{\nu}$  (cm<sup>-1</sup>): 2985, 1736, 1233, 1099, 1043 and 732.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.08 (dd,  $J$  = 8.0, 4.0 Hz, 1 H), 7.55 (t,  $J$  = 8.0 Hz, 1 H), 7.48 (t,  $J$  = 8.0 Hz, 1 H), 7.38 (t,  $J$  = 8.0 Hz, 2 H), 7.30 – 7.25 (m, 4 H), 6.34 (s, 1 H), 2.72 (s, 3 H), 2.69 -2.53 (m, 2 H), 1.38 – 1.23 (m, 4 H), 0.80 (t,  $J$  = 8.0 Hz, 3 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  143.9, 141.7, 141.1, 136.6, 132.2, 130.7, 129.2, 128.6, 128.5, 128.4, 127.2, 123.3, 43.3, 32.4, 30.3, 22.7, 13.8.

HRMS (ESI): calc. for [(C<sub>19</sub>H<sub>22</sub>OS)H] (M+H) 299.1470, measured 299.1473.

**(E)-1-(1-(4-Bromophenyl)hex-1-en-2-yl)-2-(methylsulfinyl)benzene (3q).**



Light red semisolid; eluent (35% ethyl acetate in hexanes). **1q** was taken in 100 mg, yield is 63% (169 mg).

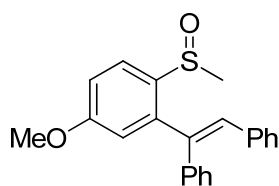
**IR (ATR)**  $\tilde{\nu}$  (cm<sup>-1</sup>): 2984, 2362, 1743, 1462, 1043 and 730.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.03 (dd, *J* = 8.0, 4.0 Hz, 1 H), 7.51 (t, *J* = 8.0 Hz, 1 H), 7.45 -7.41 (m, 3 H), 7.20 (d, *J* = 8.0 Hz, 1 H), 7.10 (d, *J* = 8.0 Hz, 2 H), 6.22 (s, 1 H), 2.66 (s, 3 H), 2.60 – 2.46 (m, 2 H), 1.32 – 1.14 (m, 4 H), 0.75 (t, *J* = 8.0 Hz, 3 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  143.8, 141.8, 141.3, 135.5, 131.5, 130.9, 130.8, 130.2, 129.1, 128.7, 123.3, 121.1, 43.3, 32.4, 30.1, 22.7, 13.7.

HRMS (ESI): calc. for [(C<sub>19</sub>H<sub>21</sub>BrOS)Na] (M+Na) 399.0394, measured 399.0390.

**(E)-1-(1-(5-Methoxy-2-(methylsulfinyl)phenyl)ethene-1,2-diyl)dibenzene (3r).**



Colorless semisolid; eluent (40% ethyl acetate in hexanes). **1r** was taken in 100 mg, yield is 85% (174 mg).

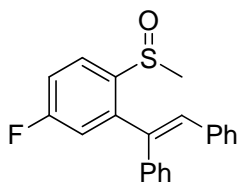
**IR (ATR)**  $\tilde{\nu}$  (cm<sup>-1</sup>): 3054, 2361, 1725, 1453, 1021 and 776.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.94 (d, *J* = 8.0 Hz, 1 H), 7.23 – 7.20 (m, 3 H), 7.18 – 7.16 (m, 3 H), 7.13 – 7.07 (m, 5 H), 6.87 (s, 1 H), 6.68 (s, 1 H), 3.85 (s, 3 H), 2.26 (s, 3 H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  161.6, 143.9, 139.4, 139.3, 136.1, 135.7, 132.2, 130.2, 129.4, 128.5, 128.2, 128.0, 127.5, 125.8, 115.9, 114.4, 55.6, 42.3.

HRMS (ESI): calc. for  $[(\text{C}_{22}\text{H}_{20}\text{O}_2\text{S})\text{H}]$  (M+H) 349.1262, measured 349.1369.

**(E)-1-(5-Fluoro-2-(methylsulfinyl)phenyl)ethene-1,2-diyl)dibenzene (3s).**



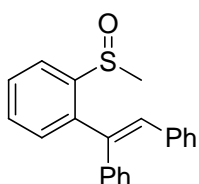
Pale yellow semisolid; eluent (35% ethyl acetate in hexanes). **1s** was taken in 100 mg, yield is 45% (95 mg).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.05 (dd,  $J = 8.0, 4.0$  Hz, 1 H), 7.29 – 7.24 (m, 5 H), 7.21 – 7.19 (m, 3 H), 7.14 – 7.08 (m, 4 H), 6.72 (s, 1 H), 2.35 (s, 3 H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  165.2, 162.7, 144.5 and 144.4 (F coupling), 140.4, 138.8, 138.4, 135.8, 133.0, 130.2, 129.4, 128.7, 128.3 and 128.2 (F coupling), 127.8, 126.5 and 126.4 (F coupling), 117.5 and 117.3 (F coupling), 116.3 and 116.1 (F coupling), 42.4.

HRMS (ESI): calc. for  $[(\text{C}_{21}\text{H}_{17}\text{FOS})\text{H}]$  (M+H) 337.1062, measured 337.1063.

**(E)-1-(2-(Methylsulfinyl)phenyl)ethene-1,2-diyl)dibenzene (3t).**



Colorless semisolid; eluent (35% ethyl acetate in hexanes). **1t** was taken in 100 mg, yield is 83% (188 mg).

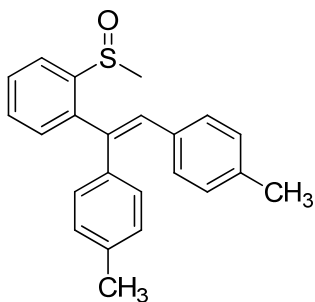
**IR (ATR)**  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ): 3054, 2923, 1708, 1266, 1031, 763 and 732.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.05 (d,  $J = 8.0$  Hz, 1 H), 7.56 (t,  $J = 8.0$  Hz, 1 H), 7.48 (t,  $J = 8.0$  Hz, 1 H), 7.35 (d,  $J = 8.0$  Hz, 1 H), 7.23 - 7.20 (m, 3 H), 7.18 - 7.16 (m, 3 H), 7.13 - 7.10 (m, 4 H), 6.69 (s, 1 H), 2.35 (s, 3 H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  144.9, 142.0, 139.5, 139.3, 136.2, 132.3, 130.8, 130.4, 130.2, 129.4, 129.1, 128.6, 128.2, 128.0, 127.5, 123.8, 42.1.

HRMS (ESI): calc. for  $[(\text{C}_{21}\text{H}_{18}\text{OS})\text{H}]$  (M+H) 319.1157, measured 319.1168.

**(E)-4,4'-(1-(2-(Methylsulfinyl)phenyl)ethene-1,2-diyl)bis(methylbenzene) (3u).**



Colorless semisolid; eluent (40% ethyl acetate in hexanes). **1v** was taken in 100 mg, yield is 66% (163 mg).

**IR (ATR)**  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ): 3050, 2922, 1835, 1032, 756 and 734.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.04 (dd,  $J = 8.0, 4.0$  Hz, 1 H), 7.54 (t,  $J = 8.0$  Hz, 1 H), 7.45 (t,  $J = 8.0$  Hz, 1 H), 7.32 (d,  $J = 8.0$  Hz, 1 H), 7.04 – 6.98 (m, 8 H), 6.61 (s, 1 H), 2.39 (s, 3 H), 2.31 (s, 3 H), 2.29 (s, 3 H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  145.0, 142.4, 138.6, 137.9, 137.4, 136.5, 133.5, 131.8, 130.6, 130.4, 130.1, 129.3, 128.9, 123.6, 42.2, 21.3, 21.2.

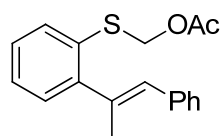
HRMS (ESI): calc. for  $[(\text{C}_{23}\text{H}_{22}\text{OS})\text{H}]$  (M+H) 347.1470, measured 347.1462.

### General Procedure for the Pummerer rearrangement.<sup>1</sup>

A two-neck 50 mL round bottom flask fitted with a condenser containing a mixture of **3h** (100 mg) and AC<sub>2</sub>O (10 equiv). The reaction mixture was refluxed at 140 °C for 4 h. After the reaction, the reaction mixture was allowed to cool to RT. The solvent was removed under reduced pressure and the crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure **4**.

Ref: 1. Padwa, A.; Bur, S. K.; Danca, M. d.; Ginn, J. D.; Lynch, S. M. *Synlett*, **2002**, 6, 851.

### (E)-((2-(1-Phenylprop-1-en-2-yl)phenyl)thio)methyl acetate (**4**).



Colorless semisolid; eluent (45% ethyl acetate in hexanes). **3h** was taken in 100 mg, yield is 87% (101 mg).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.54 (dd, *J* = 8.0, 4.0 Hz, 1 H), 7.38 - 7.37 (m, 4 H), 7.31 - 7.25 (m, 3 H), 7.24 - 7.23 (m, 1 H), 6.41 (s, 1 H), 5.41 (s, 2 H), 2.22 (s, 3 H), 3.07 (s, 3 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 138.0, 137.6, 133.1, 130.7, 129.6, 128.9, 128.7, 128.2, 127.8, 127.0, 126.7, 67.7, 21.0, 19.9.

HRMS (ESI): calc. for [(C<sub>18</sub>H<sub>18</sub>O<sub>2</sub>S)Na] (M+Na) 321.0925, measured 321.0931.

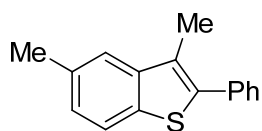
### The preparation of benzothiophene derivative **5**.<sup>2</sup>

A 20 mL two-necked round bottom flask was fitted with a reflux condenser with a nitrogen balloon. In round bottom flask, were added **3m** (100 mg) and CF<sub>3</sub>SO<sub>3</sub>H (0.5 mL). The resulting mixture was stirred under nitrogen at rt for 24 h. Then, the mixture was poured slowly into water/pyridine (9.0 mL of a 9:1 ratio) and stirred at 120 °C for 20 min. After cooling, the reaction mixture was extracted with ethyl acetate (50 mL). The organic layer was dried over NaSO<sub>4</sub>. After evaporation of the solvents under vacuum, the compound purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure **5**.

Ref: 2. K. Nobushige, K. Hirano, T. Satoh, and M. Miura, *Org. Lett.*, 2014, **16**, 1188.



### 3,5-Dimethyl-2-phenylbenzo[b]thiophene (5).



Colorless semisolid; eluent (4% ethyl acetate in hexanes). **3m** was taken in 100 mg, yield is 67% (59 mg).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.69 (s, 1 H), 7.65 - 7.54 (m, 3 H), 7.51 - 7.44 (m, 3 H), 7.29 (dd,  $J = 8.0$ , 4.0 Hz, 1 H), 2.55 (s, 3 H), 2.51 (s, 3 H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  139.1, 134.9, 134.2, 129.6, 128.5, 127.6, 127.2, 125.8, 122.0, 121.7, 21.5, 12.6.

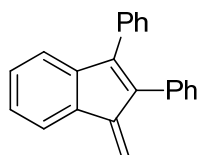
HRMS (ESI): calc. for  $[(\text{C}_{16}\text{H}_{15}\text{S})\text{H}]$  (M+H) 239.0894, measured 239.0885.

### General Procedure for the Cyclization of Aromatic Ketones with Alkynes:<sup>3</sup>

A 15-mL pressure tube with septum containing  $[\{\text{RuCl}_2(p\text{-cymene})\}_2]$  (5.0 mol %) and  $\text{AgSbF}_6$  (20 mol %) was evacuated and purged with nitrogen gas three times ( $\text{AgSbF}_6$  was taken inside the glove box). To the tube were then added acetophenone (100 mg), diphenylacetylene (1.20 equiv), pivalic acid (5.0 equiv) and 1,4-dioxane (2.5 mL) via syringes and again the reaction mixture was evacuated and purged with nitrogen gas three times. After that, the septum was taken out and immediately a screw cap was used to cover the tube under the nitrogen atmosphere. Then, the reaction mixture was allowed to stir at 100 °C for 12 h. After cooling to ambient temperature, the reaction mixture was diluted with  $\text{CH}_2\text{Cl}_2$ , filtered through Celite and silica gel, and the filtrate was concentrated. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure benzofulvene derivative in 45% yield.

Ref: 3. CG. Ravikiran and M. Jeganmohan, *Eur. J. Org. Chem.* 2012, 417.

### 1-Methylene-2,3-diphenyl-1H-indene.



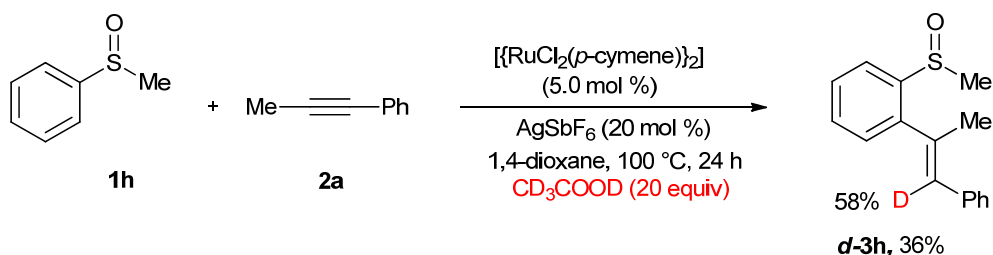
Pale-yellow oil; eluent (hexanes).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.71 (d,  $J = 8.0$  Hz, 1 H), 7.34 (t,  $J = 8.0$  Hz, 1 H), 7.30–7.25 (m, 10 H), 7.20–7.18 (m, 2 H), 6.25 (s, 1 H), 5.72 (s, 1 H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  147.7, 142.8, 140.9, 137.5, 136.3, 134.7, 134.6, 130.8, 129.4, 128.6, 128.3, 128.1, 127.5, 127.0, 125.8, 120.2, 119.9, 114.2.

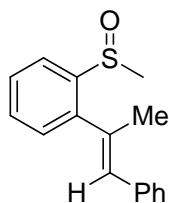
HRMS (ESI): calc. for  $[(\text{C}_{22}\text{H}_{16})\text{H}]$  (M+H) 281.1330, measured 281.1333.

## Mechanistic investigation

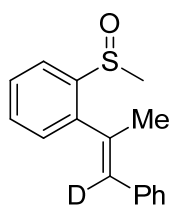


A 15-mL pressure tube with septum containing  $[RuCl_2(p\text{-cymene})]_2$  (5.0 mol %) and  $AgSbF_6$  (20 mol %) was evacuated and purged with nitrogen gas three times ( $AgSbF_6$  was taken inside the glove box). To the tube were then added methyl phenyl sulfoxide **1** (100 mg), 1-phenyl-1-propyne **2** (1.20 equiv),  $CD_3COOD$  (20.0 equiv) and 1,4-dioxane (2.5 mL) via syringes and again the reaction mixture was evacuated and purged with nitrogen gas three times. After that, the septum was taken out and immediately a screw cap was used to cover the tube under the nitrogen atmosphere. Then, the reaction mixture was allowed to stir at 100 °C for 24 h. After cooling to ambient temperature, the reaction mixture was diluted with  $CH_2Cl_2$ , filtered through Celite and silica gel, and the filtrate was concentrated. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure *d-3h* in 36% yield with 58% of deuterium incorporation at the alkene carbon.

### (*E*)-1-(methylsulfinyl)-2-(1-phenylprop-1-en-2-yl)benzene.

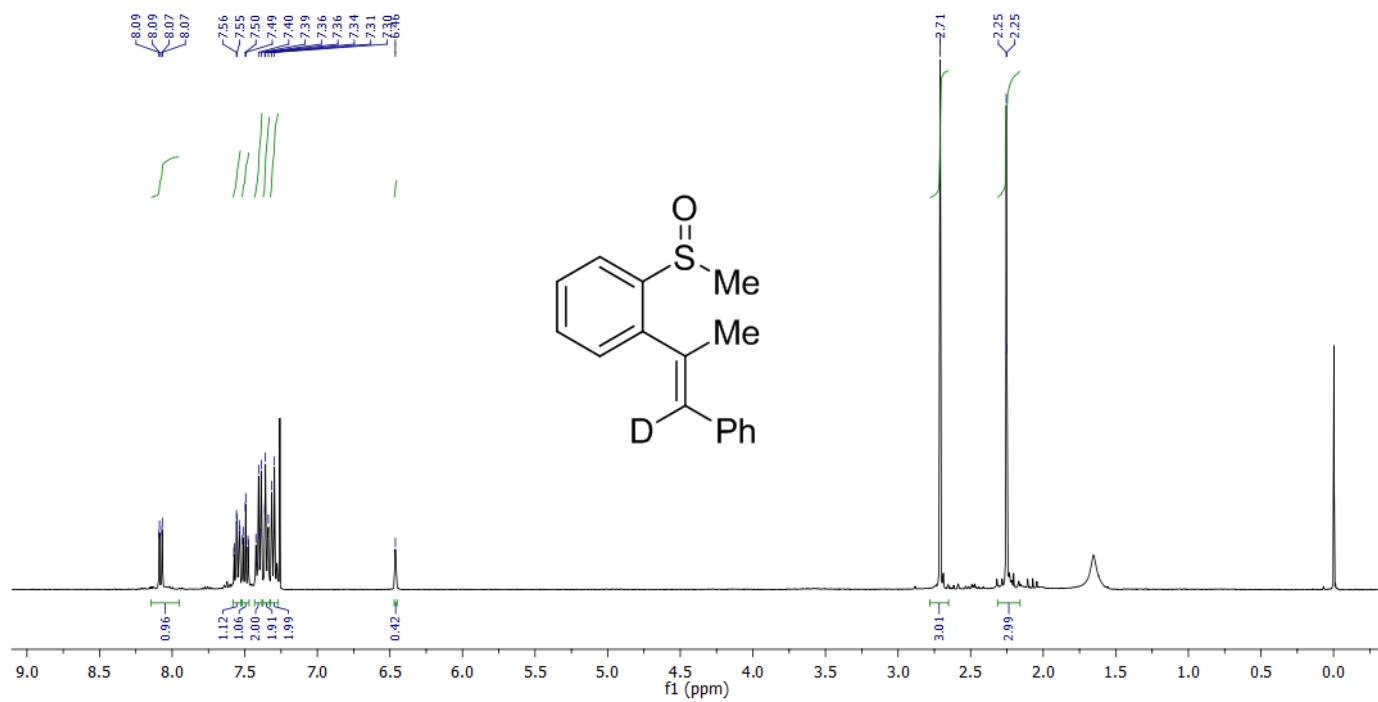


HRMS (ESI): calc. for  $[(C_{16}H_{16}OS)H]$  (M+H) 257.1000, measured 257.1012.

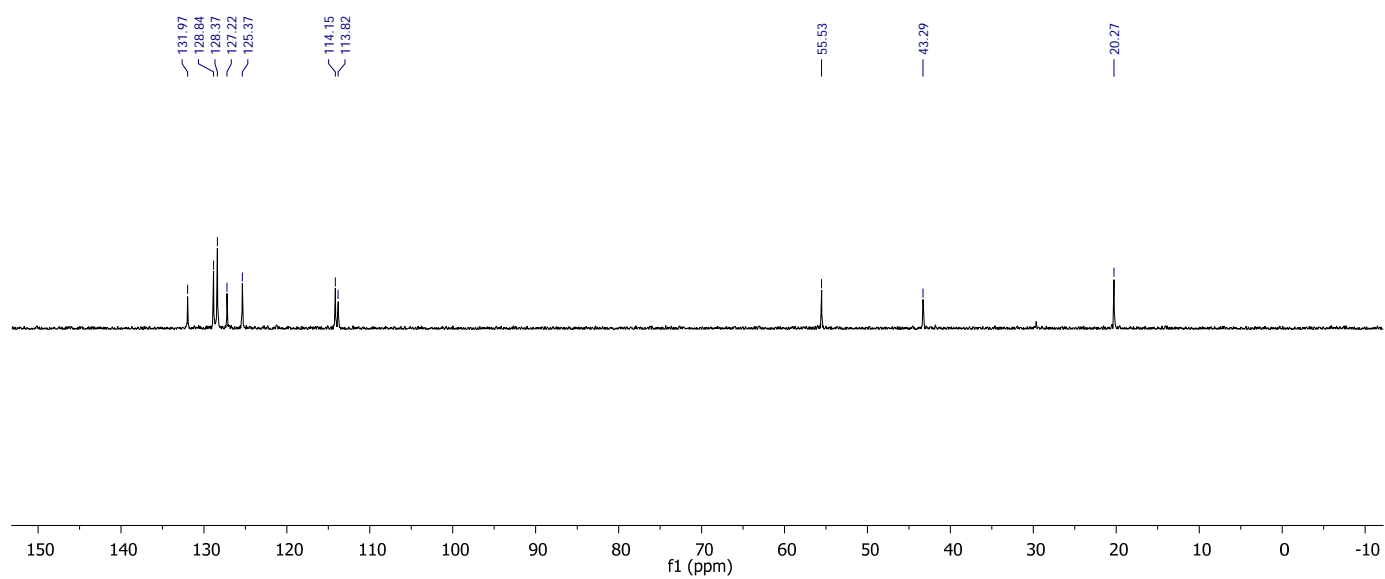
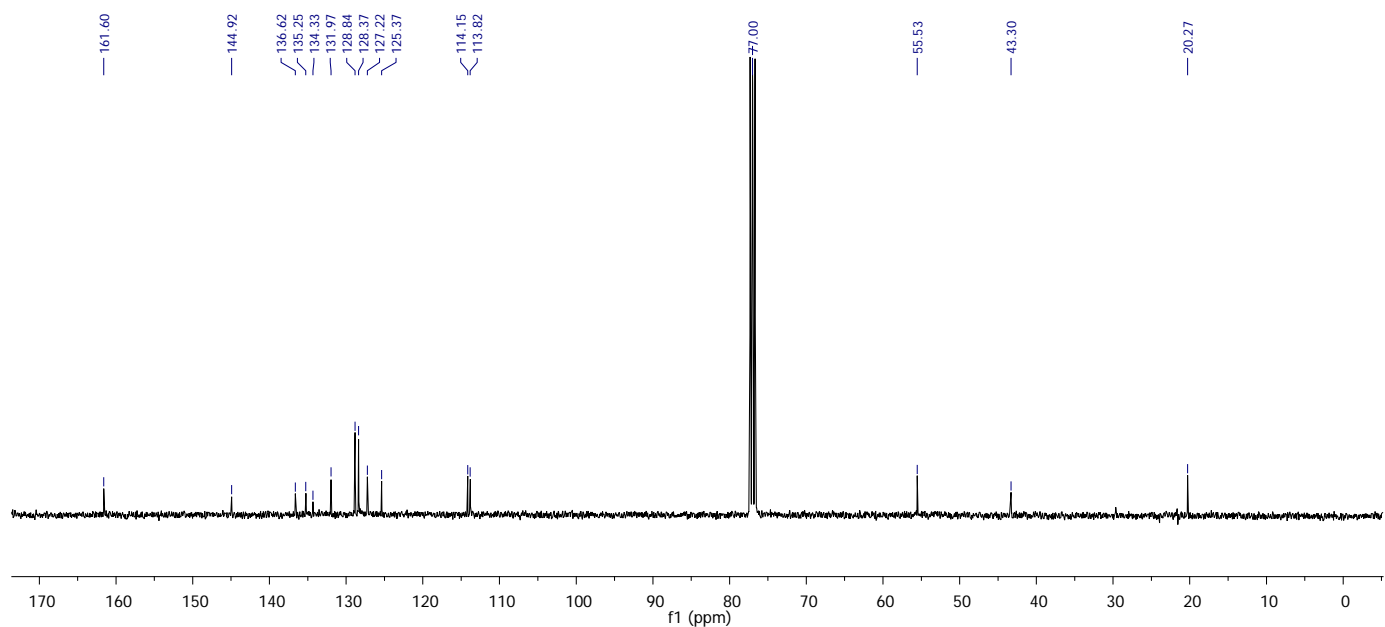
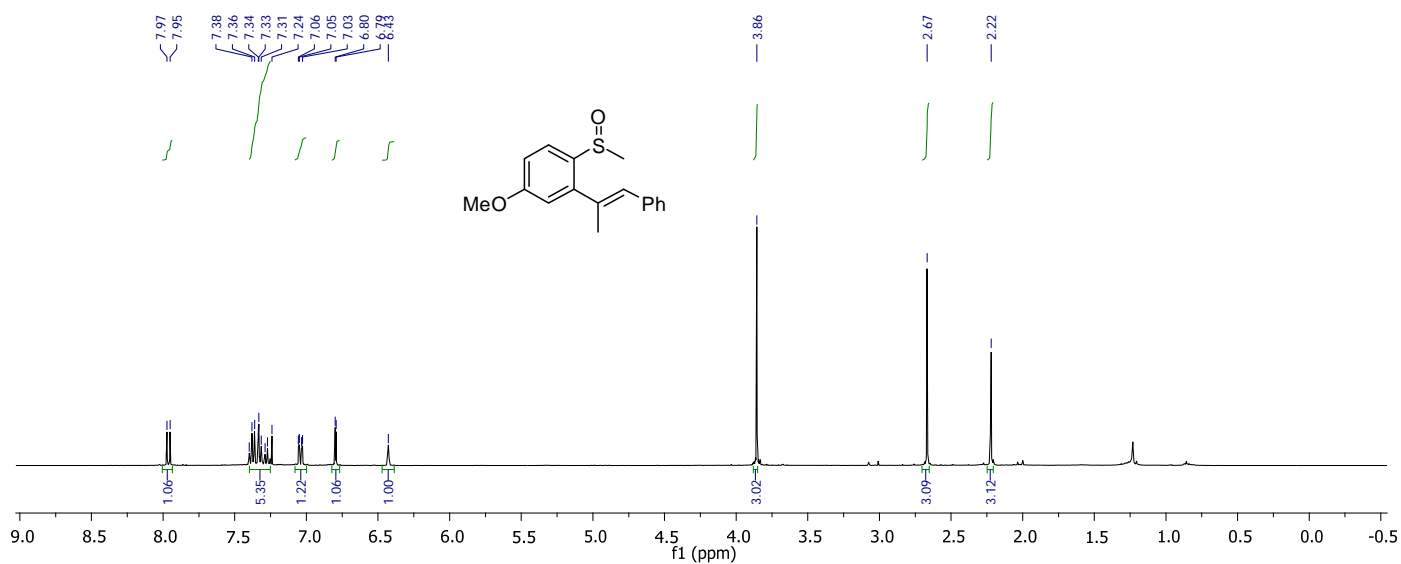


HRMS (ESI): calc. for  $[(C_{16}H_{16}DOS)H]$  (M+H) 258.1063, measured 258.1073.

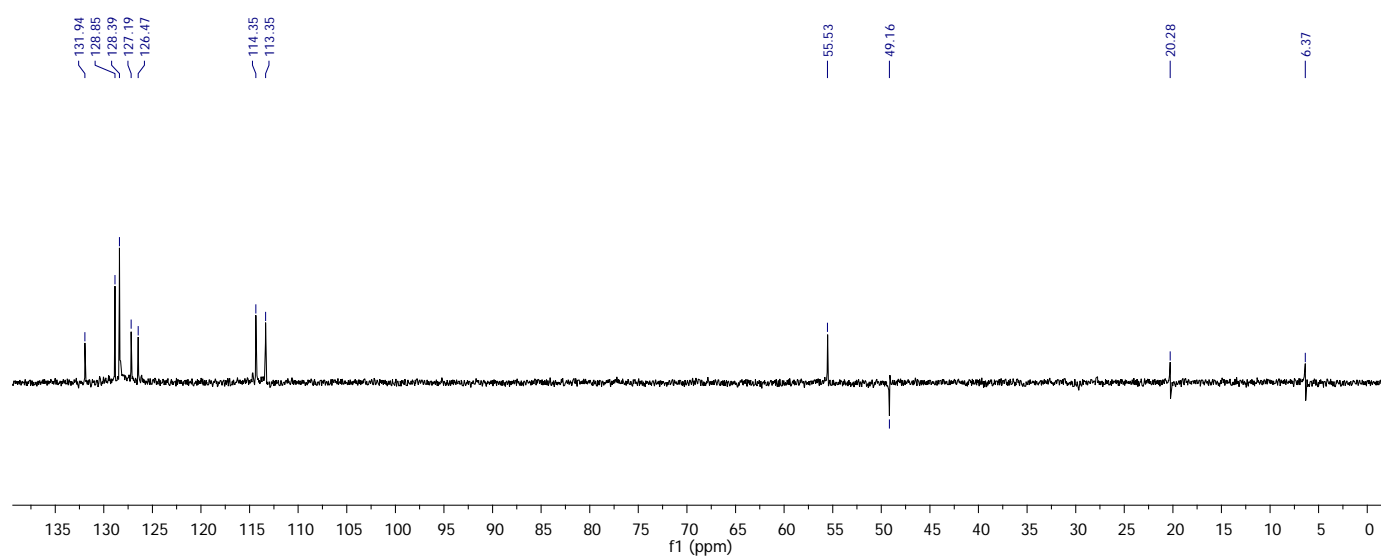
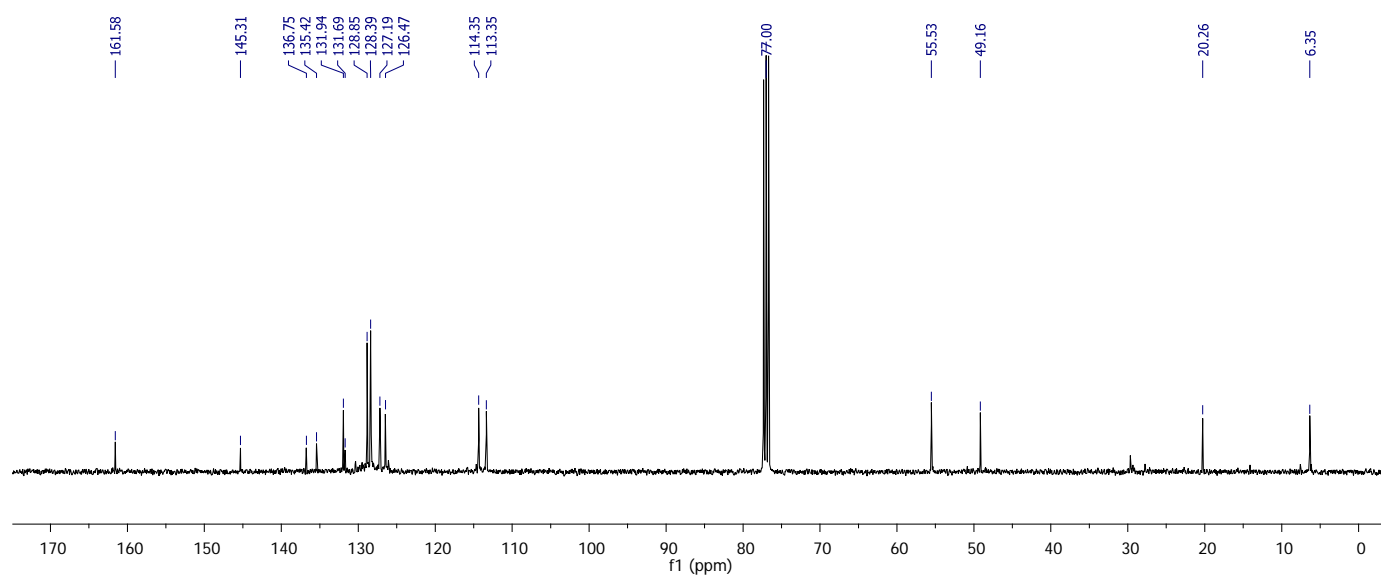
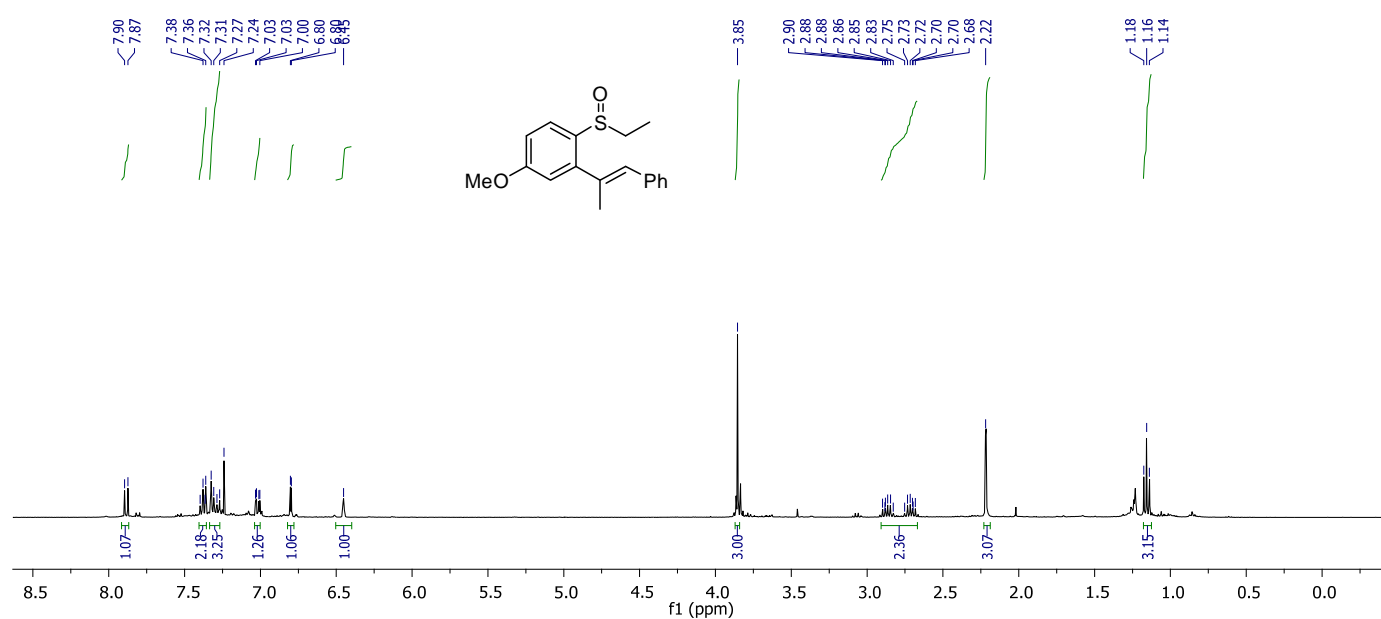
Spectral data of compound *d*-**3h**.



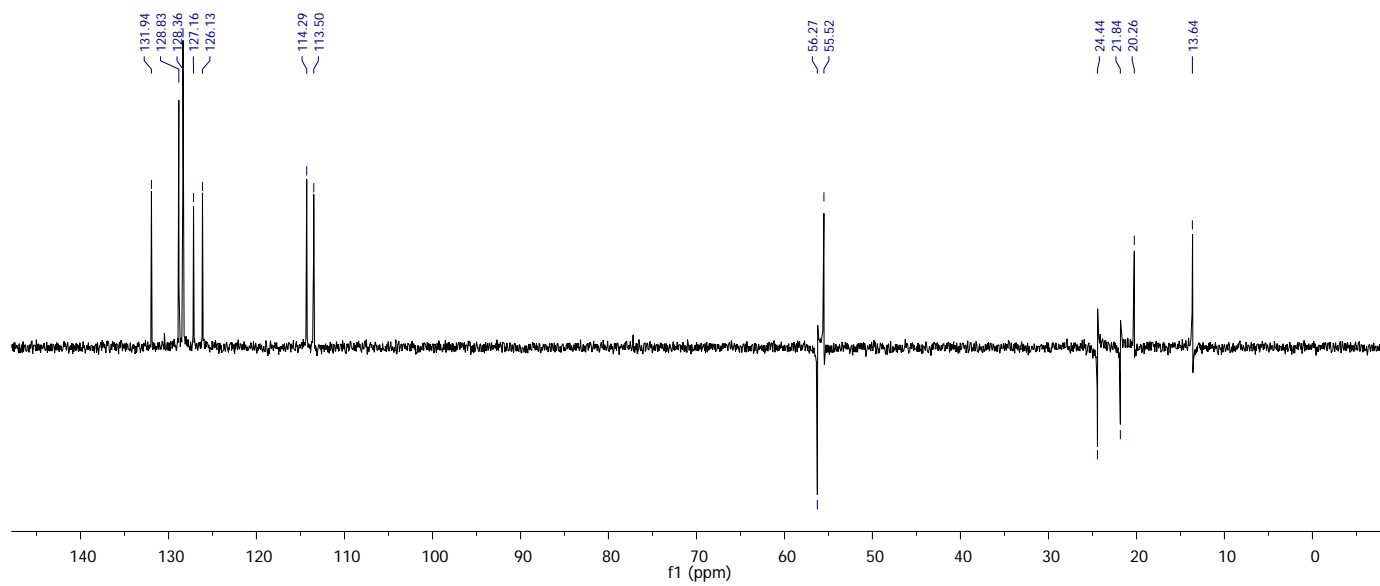
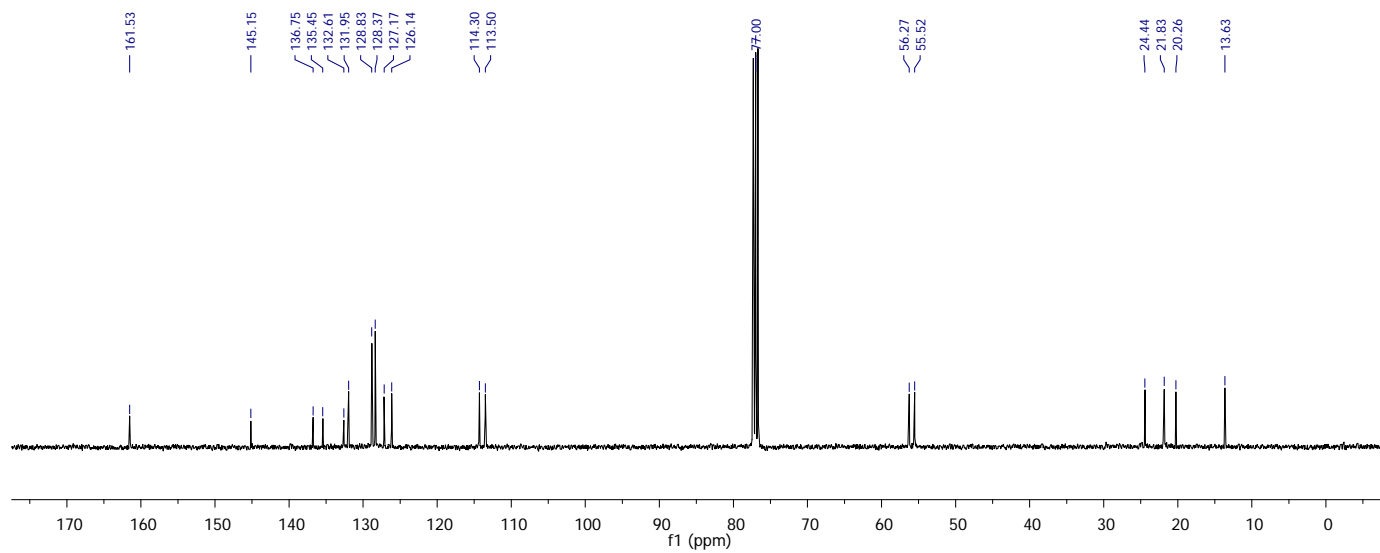
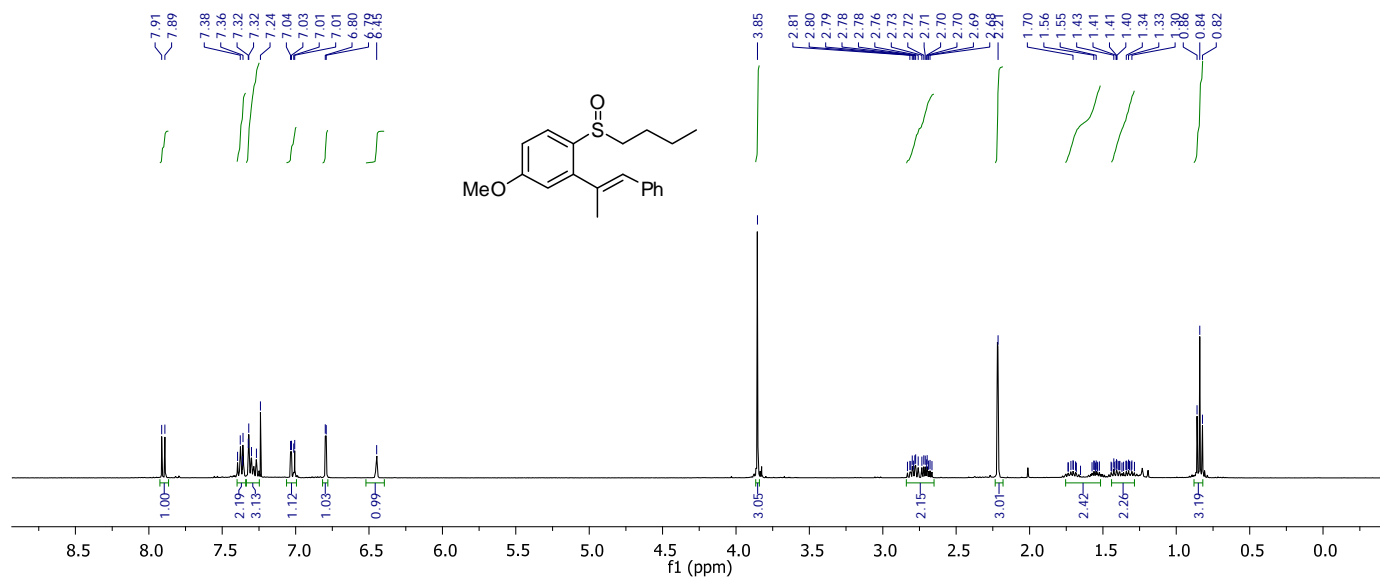
# Spectral data of compound 3a.



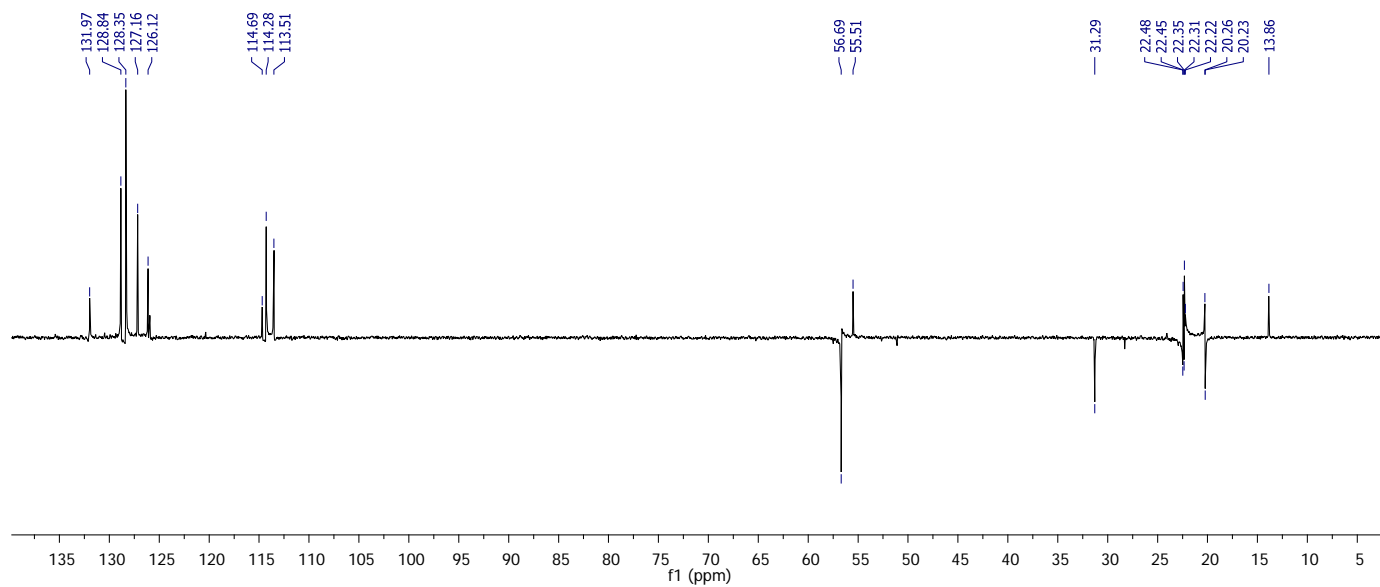
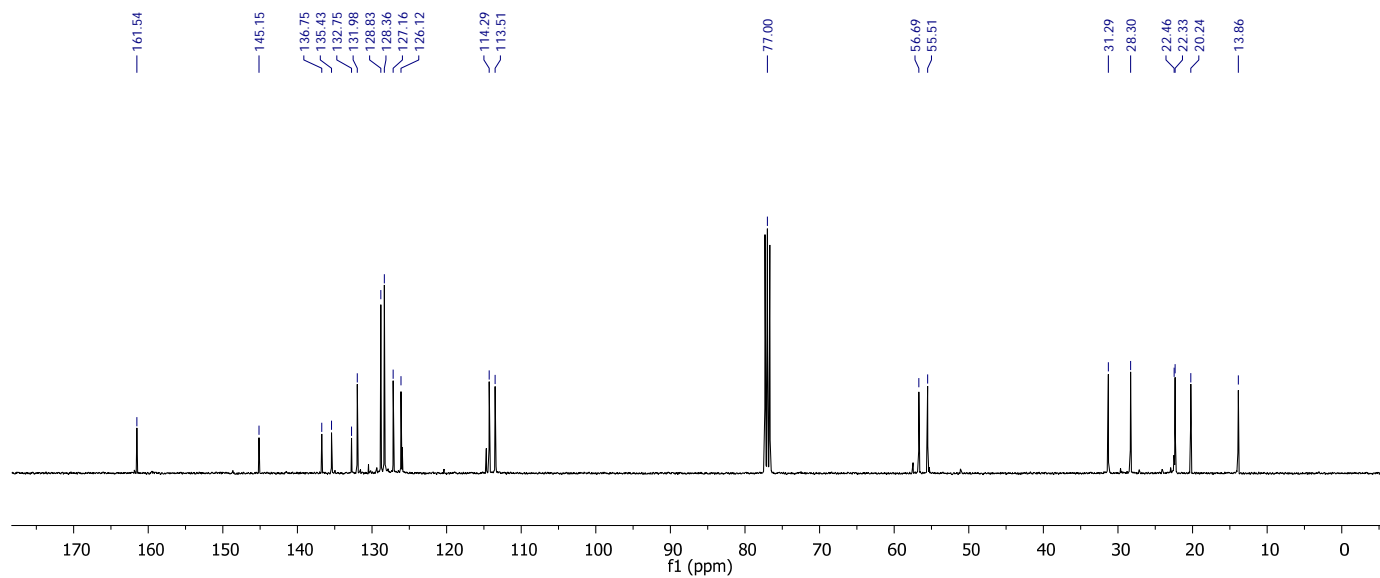
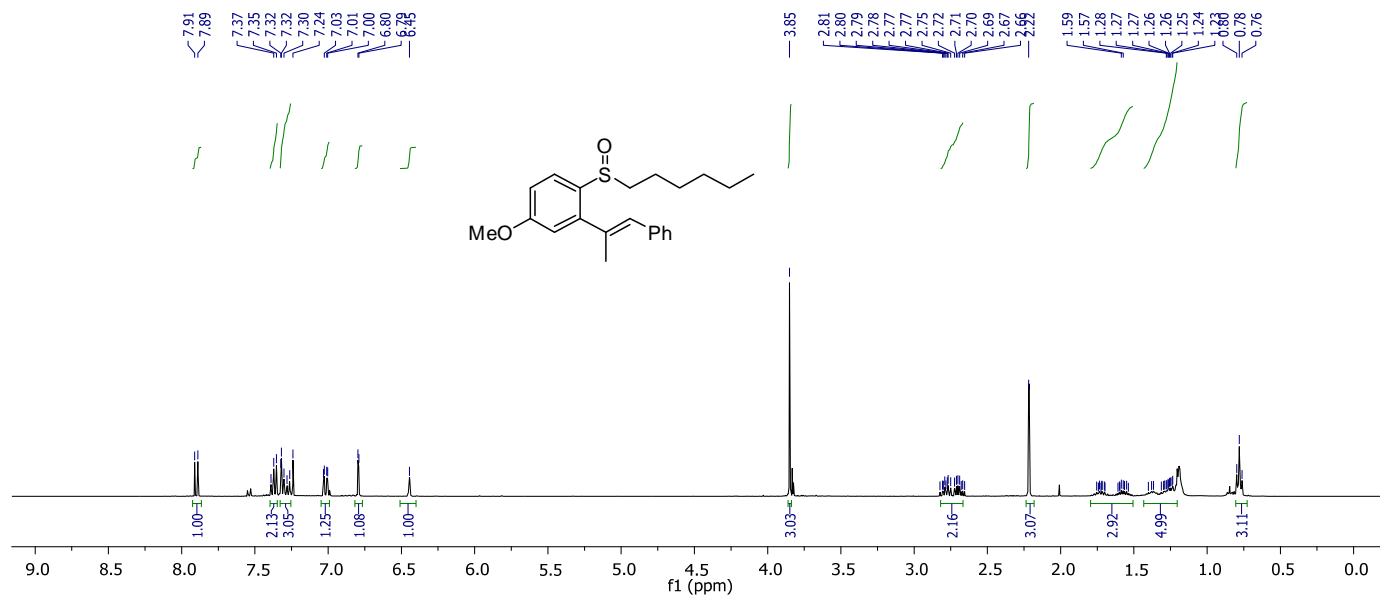
Spectral data of compound **3b**.



Spectral data of compound **3c**.

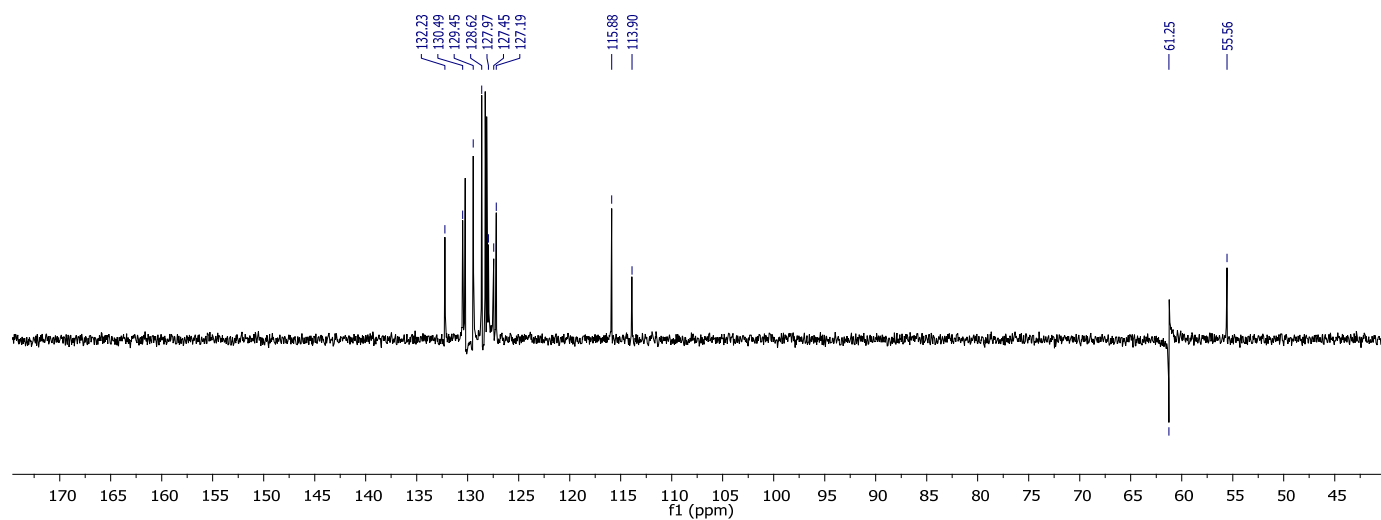
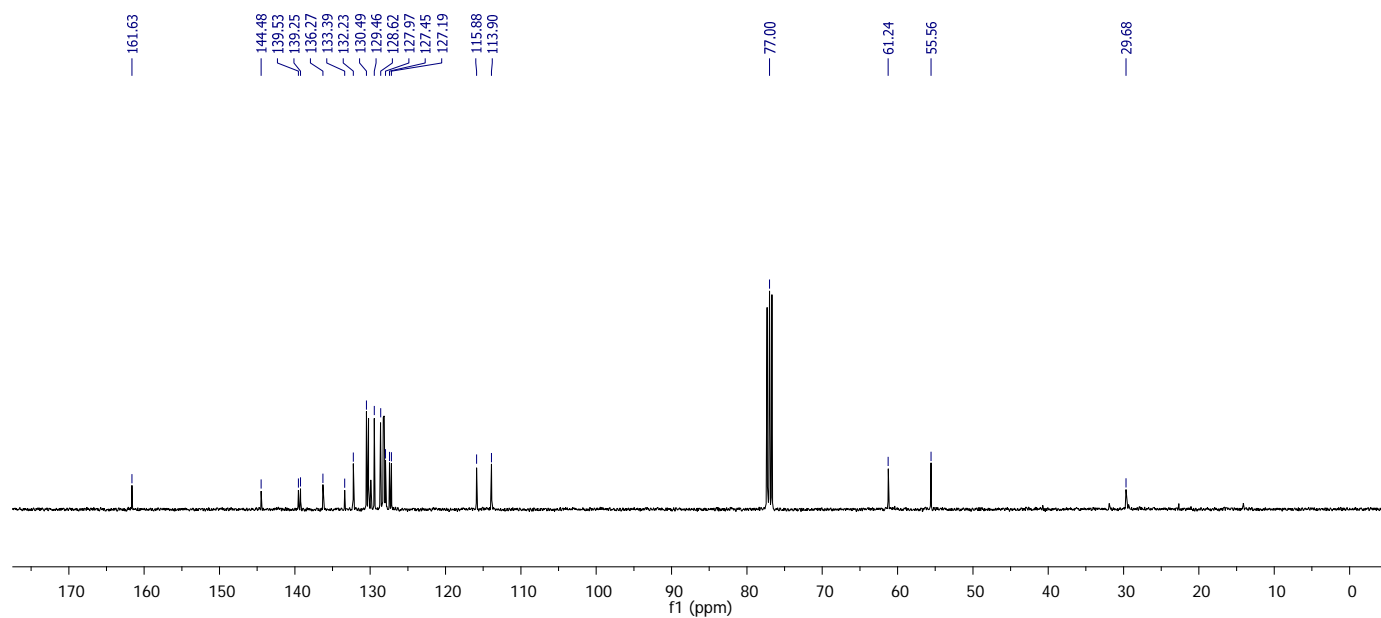
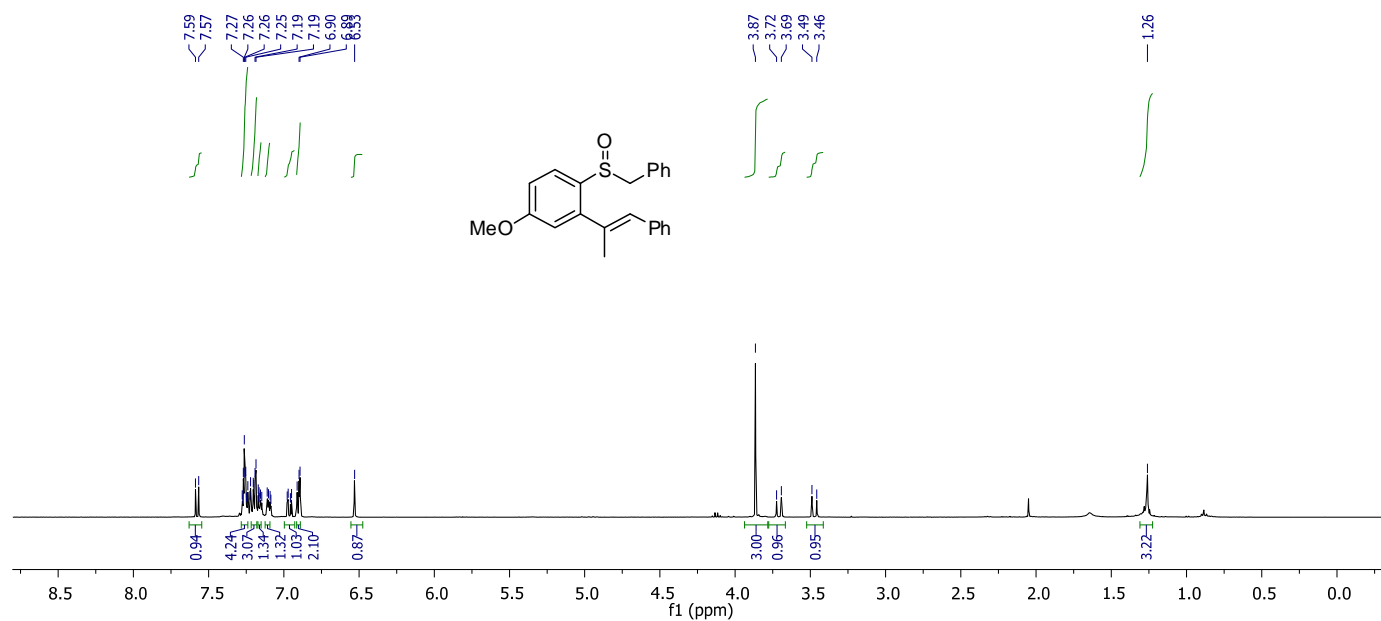


Spectral data of compound **3d**.

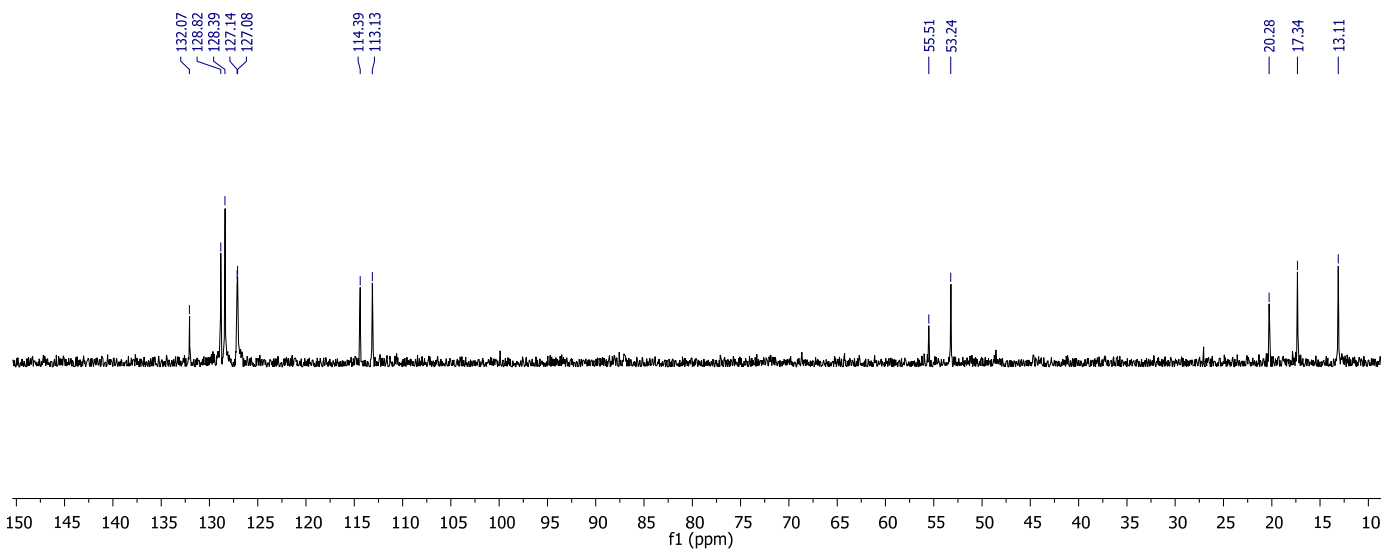
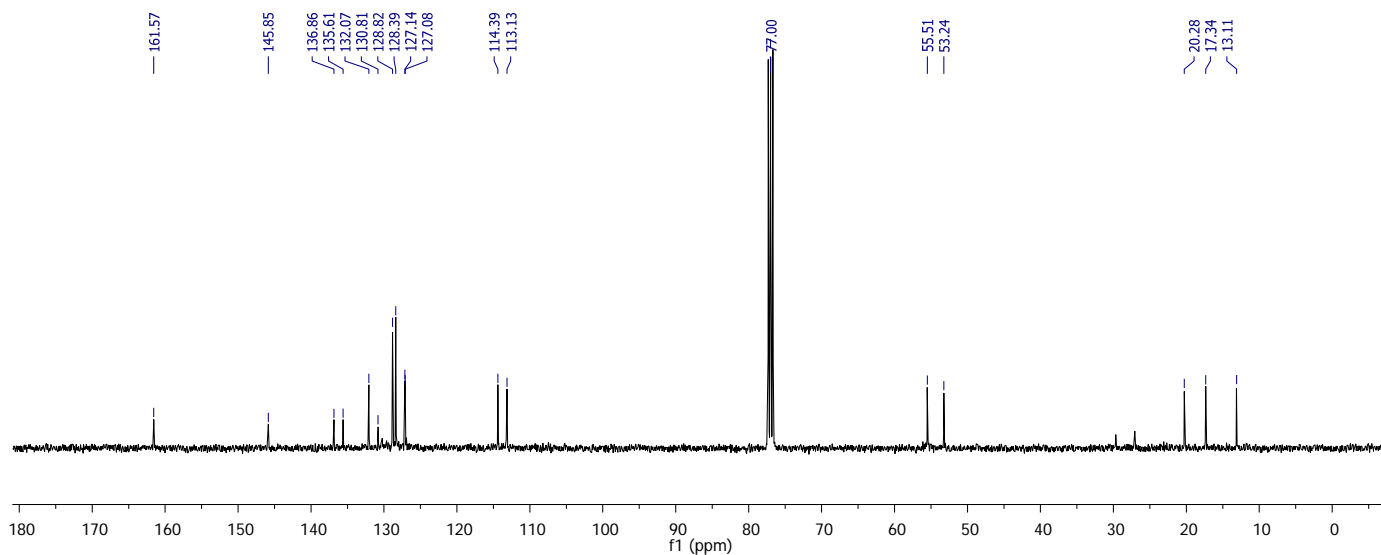
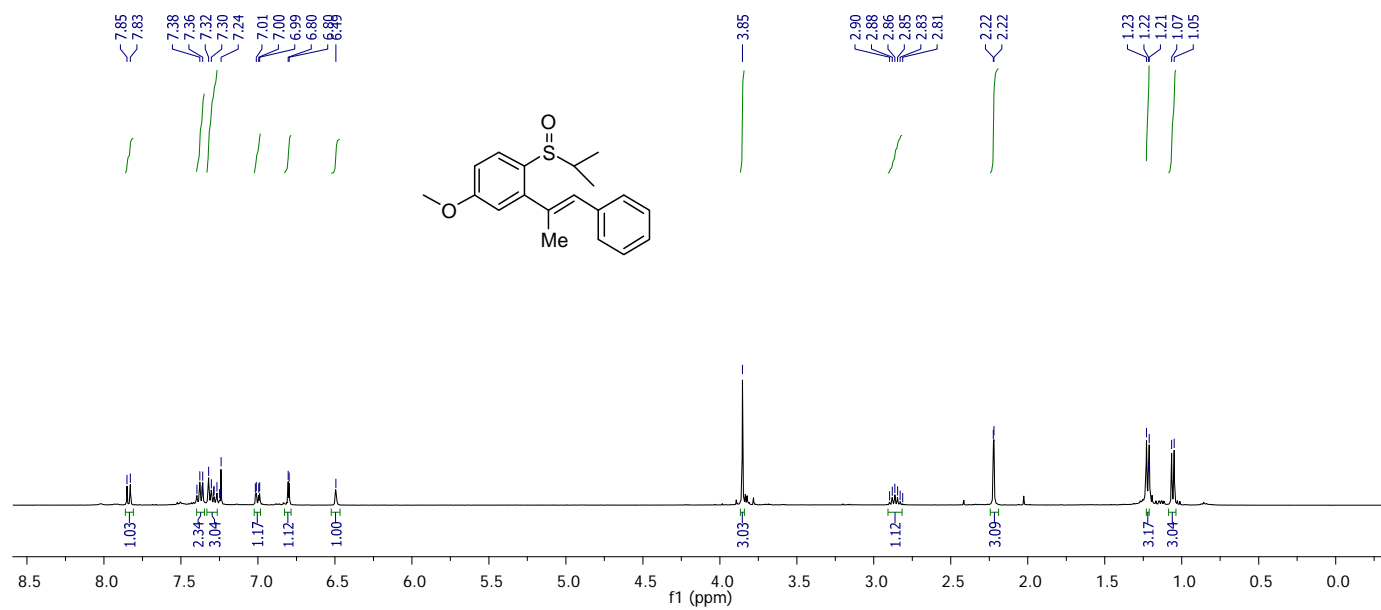




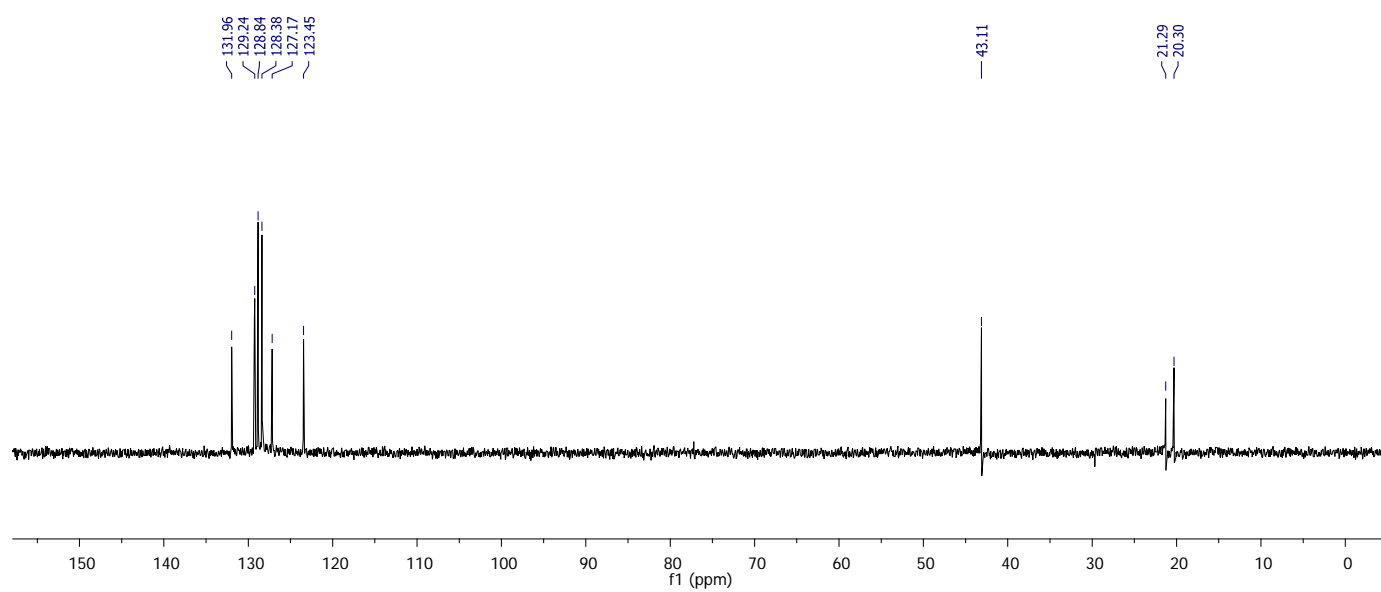
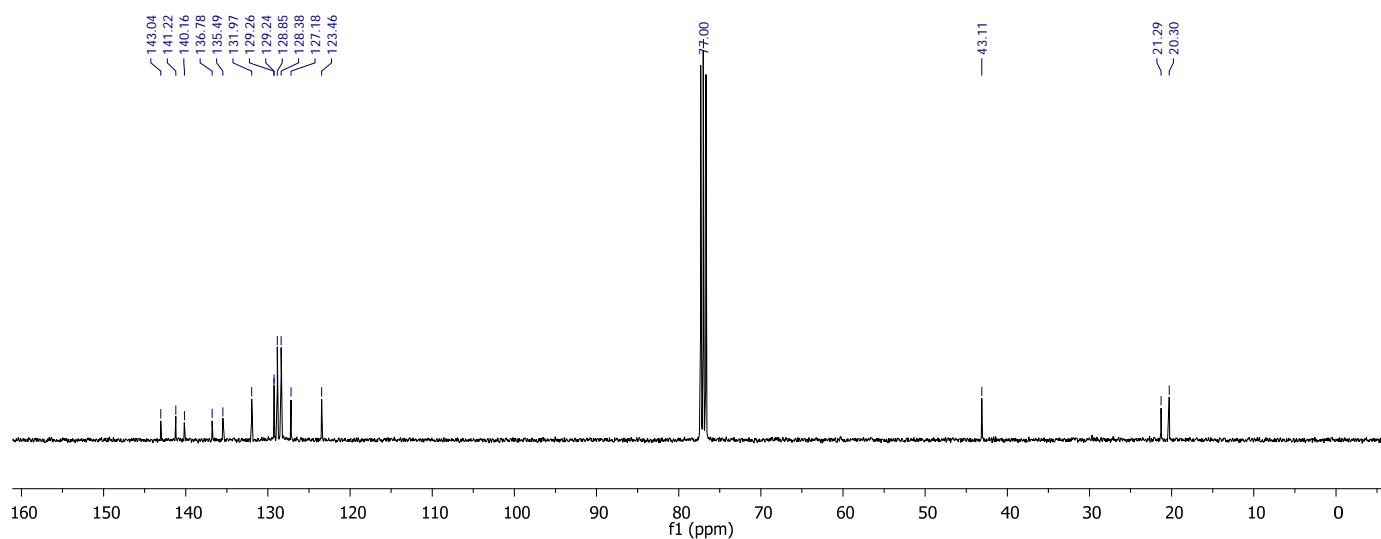
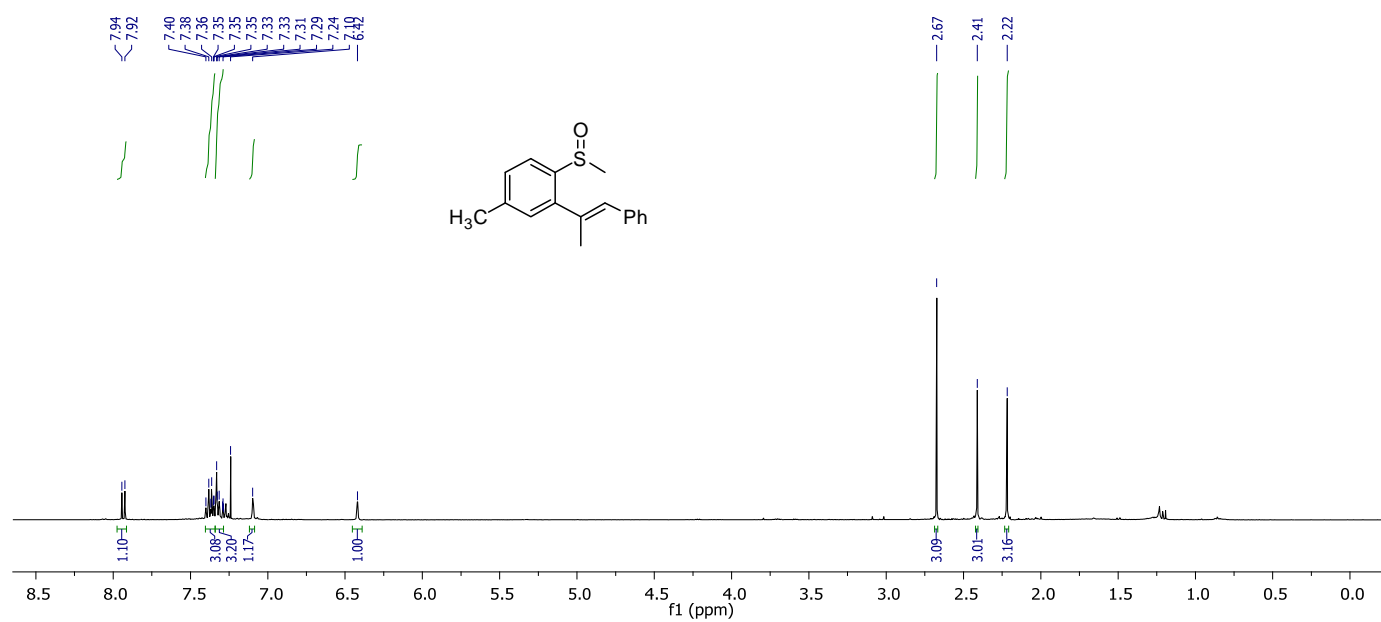
# Spectral data of compound 3e.



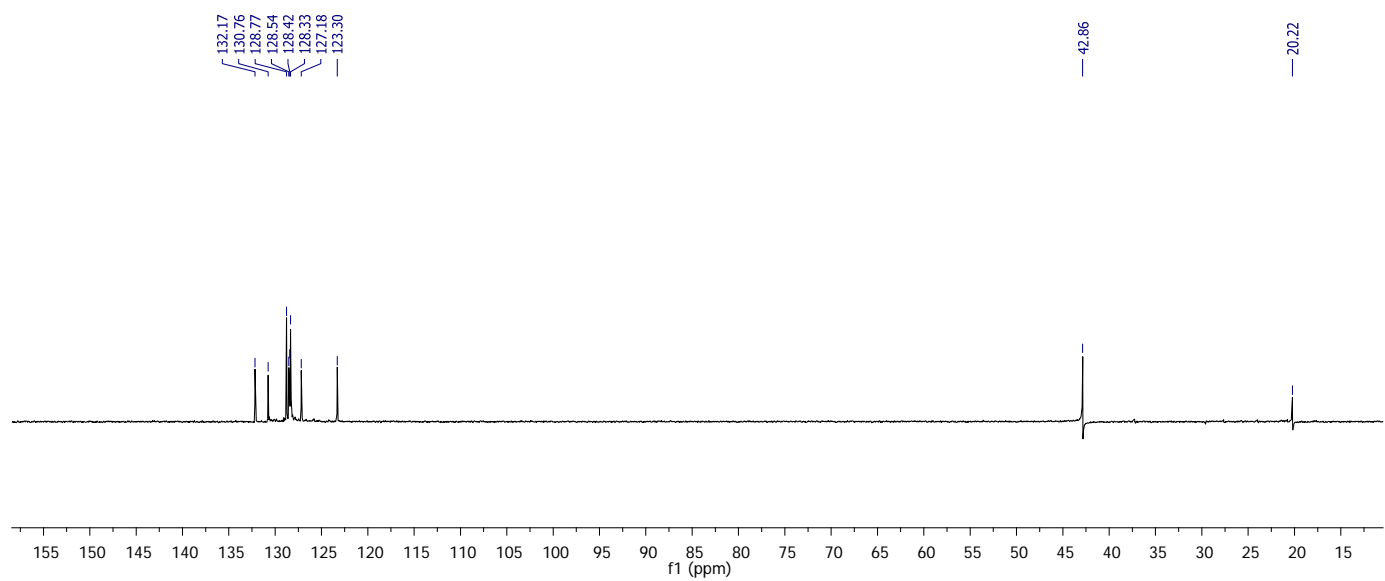
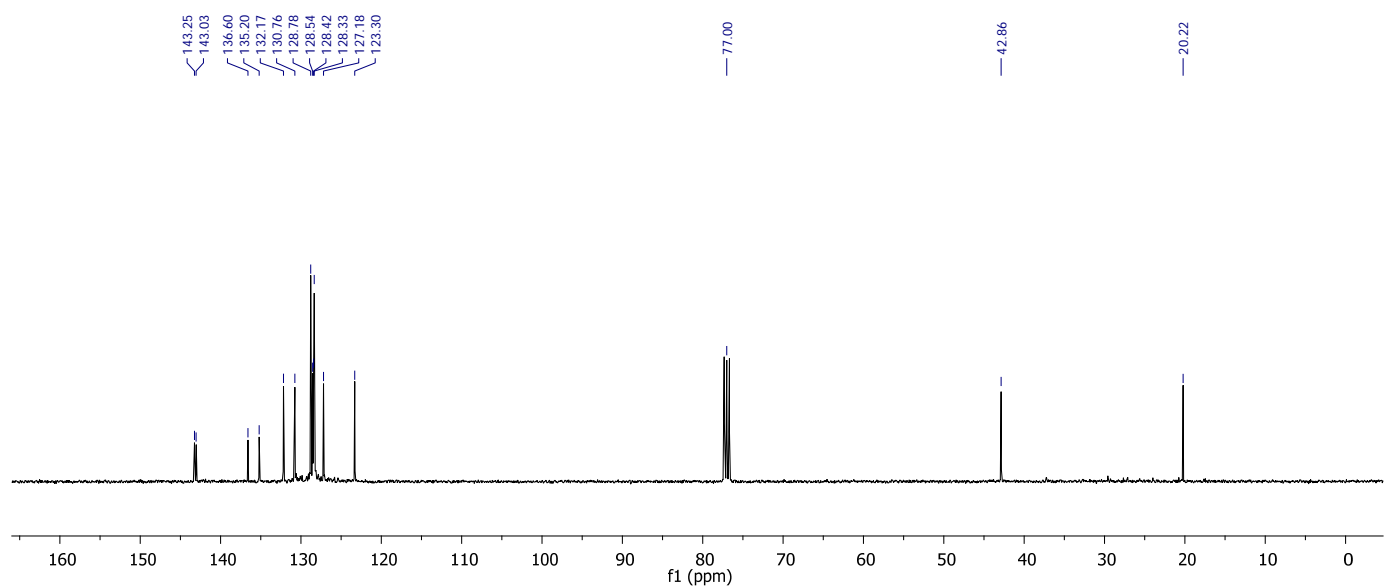
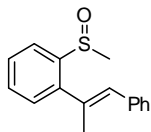
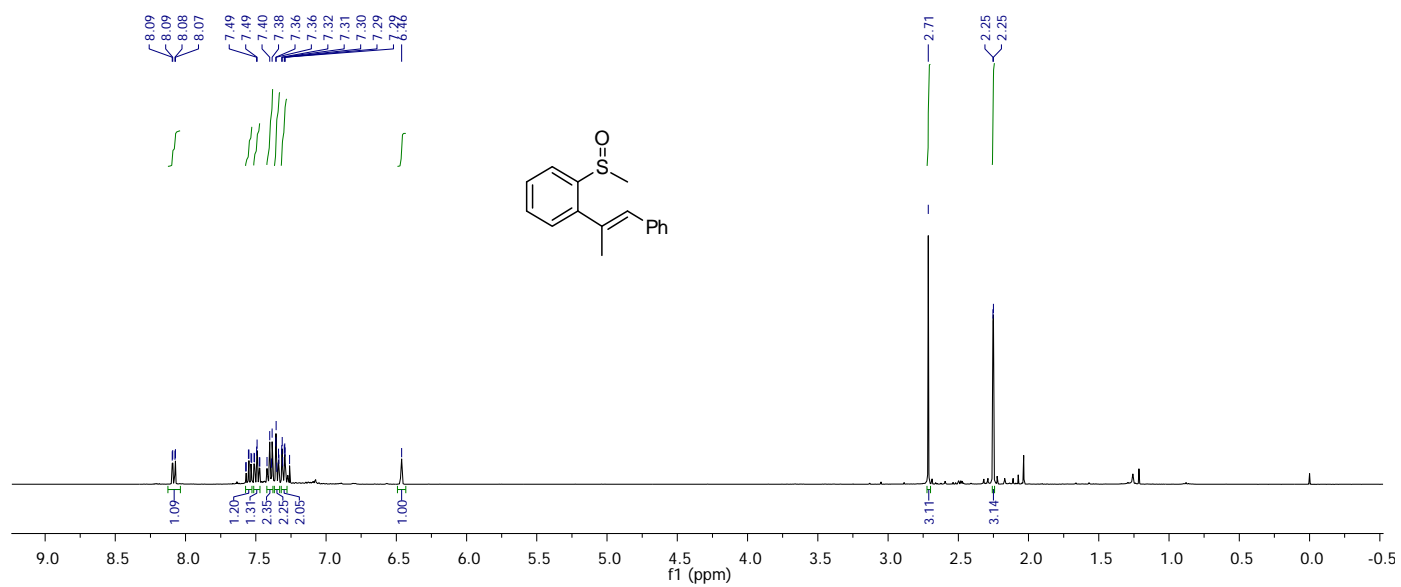
Spectral data of compound **3f**.



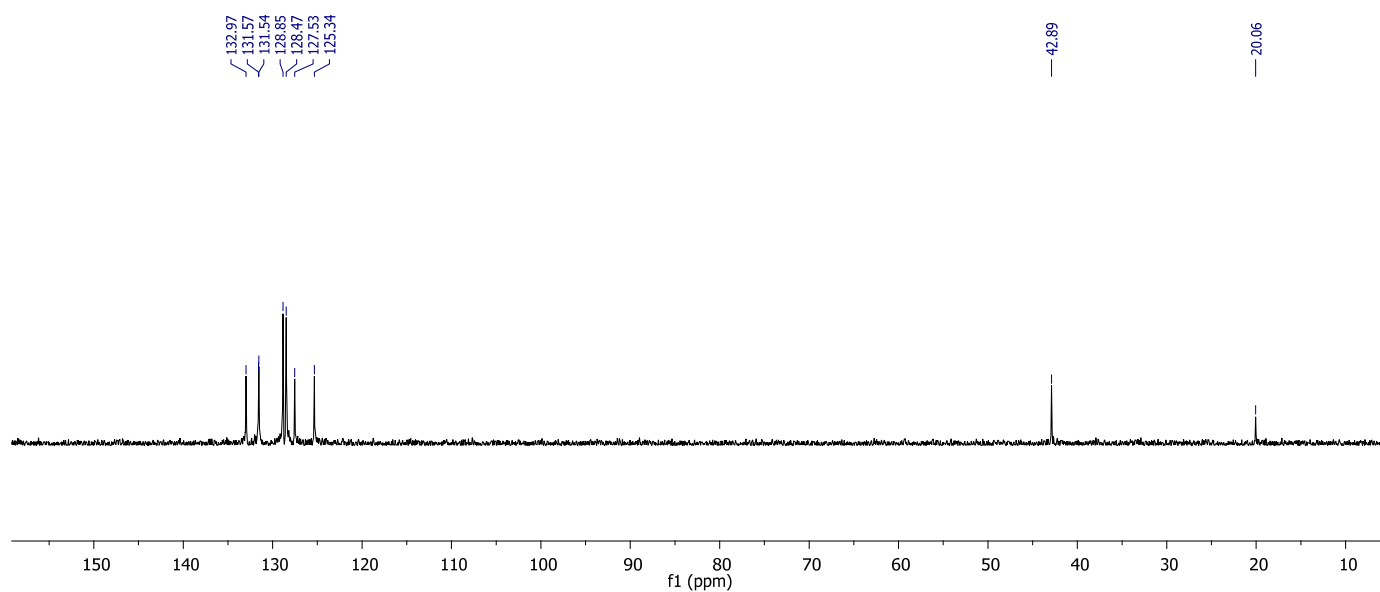
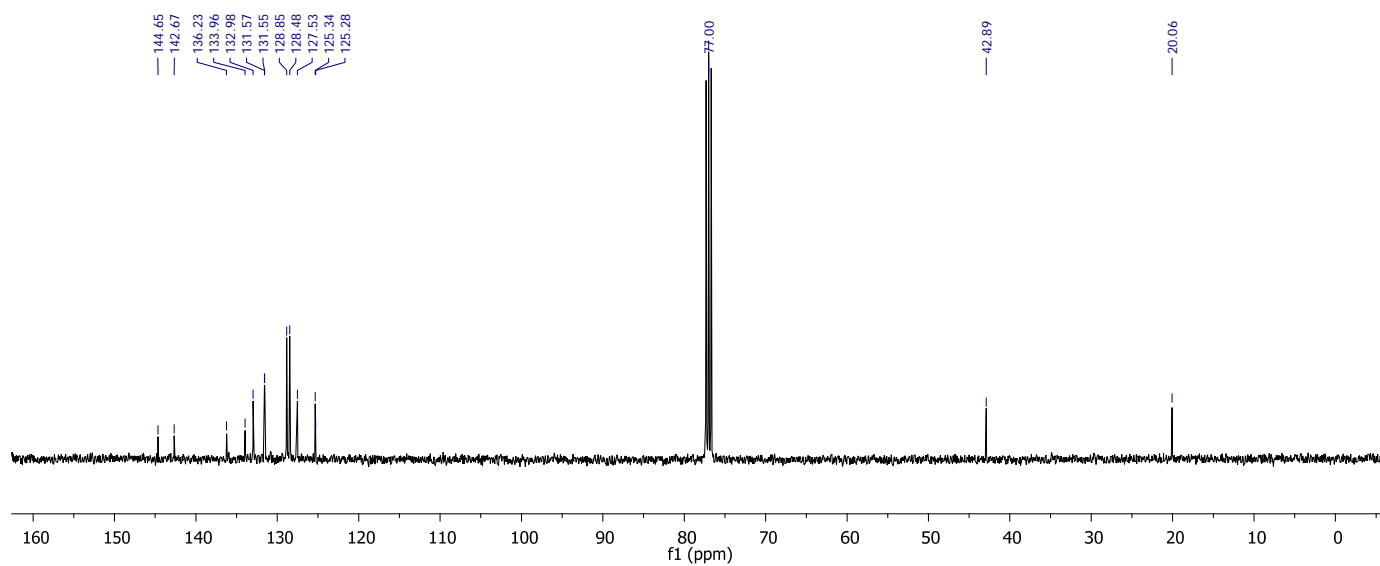
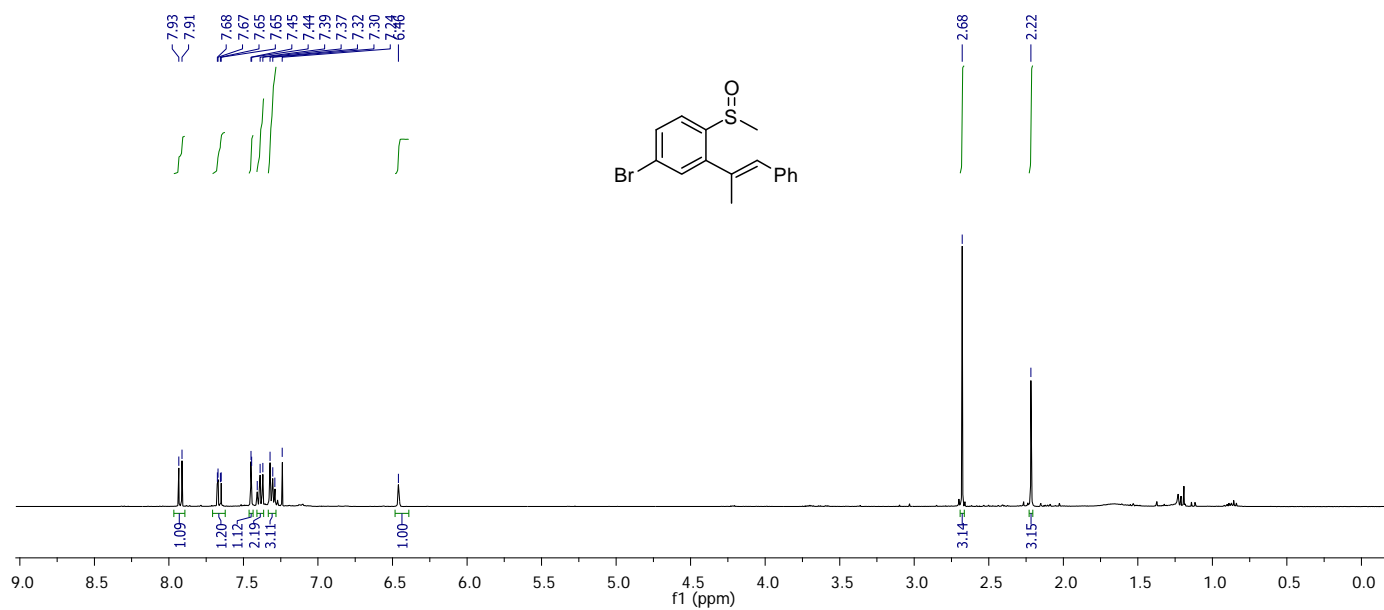
Spectral data of compound **3g**.



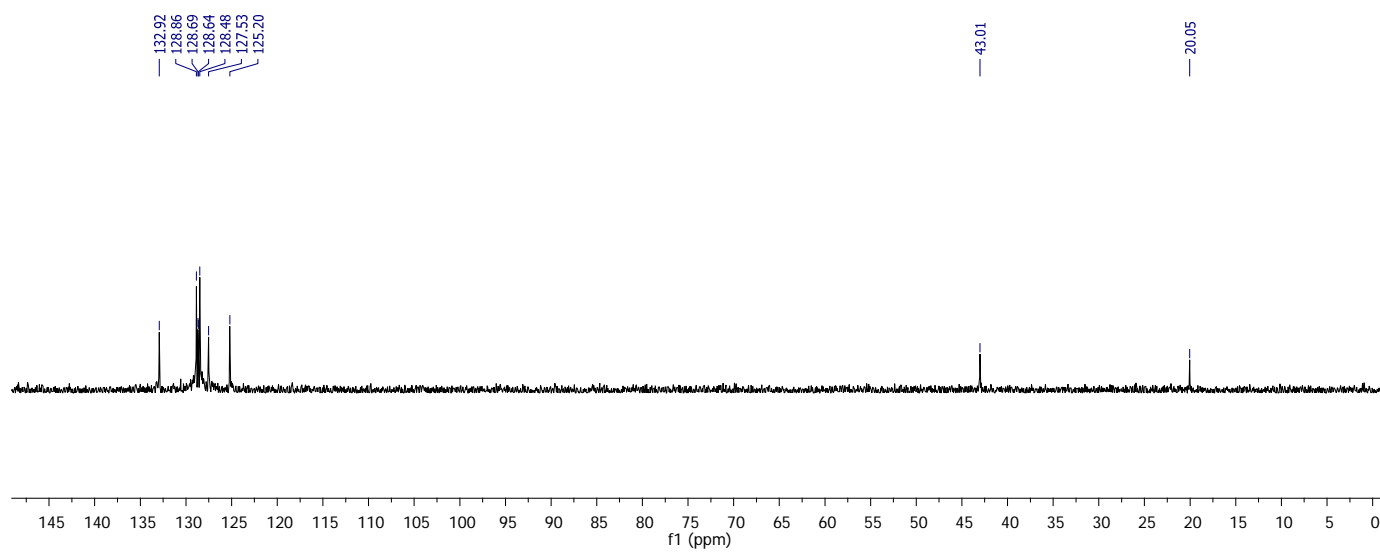
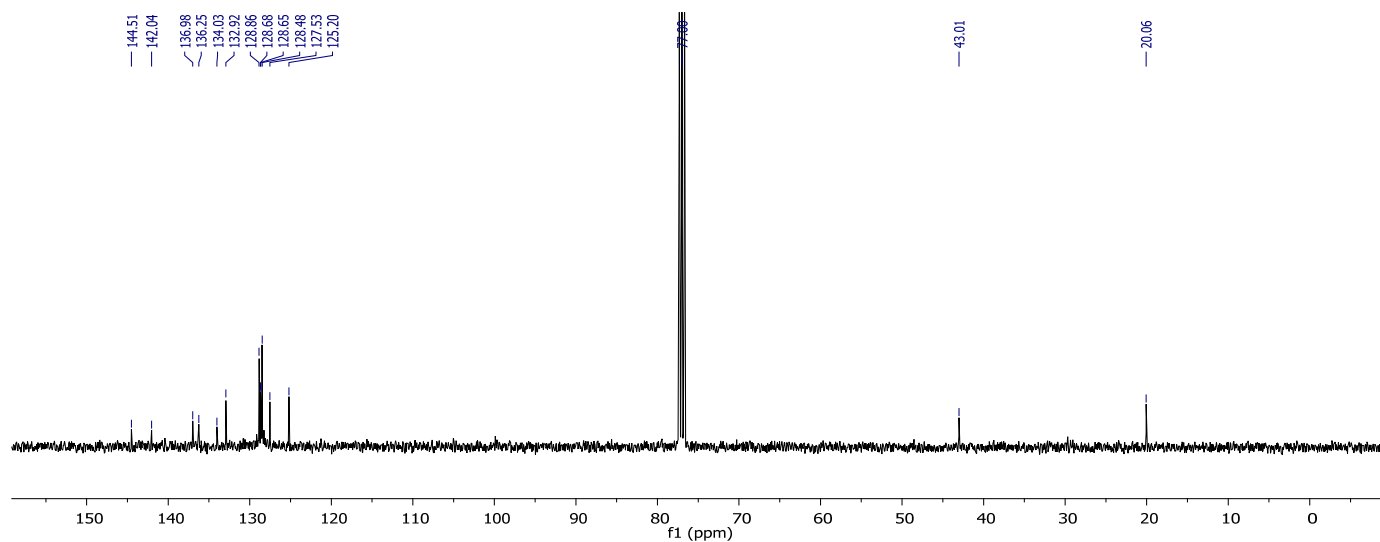
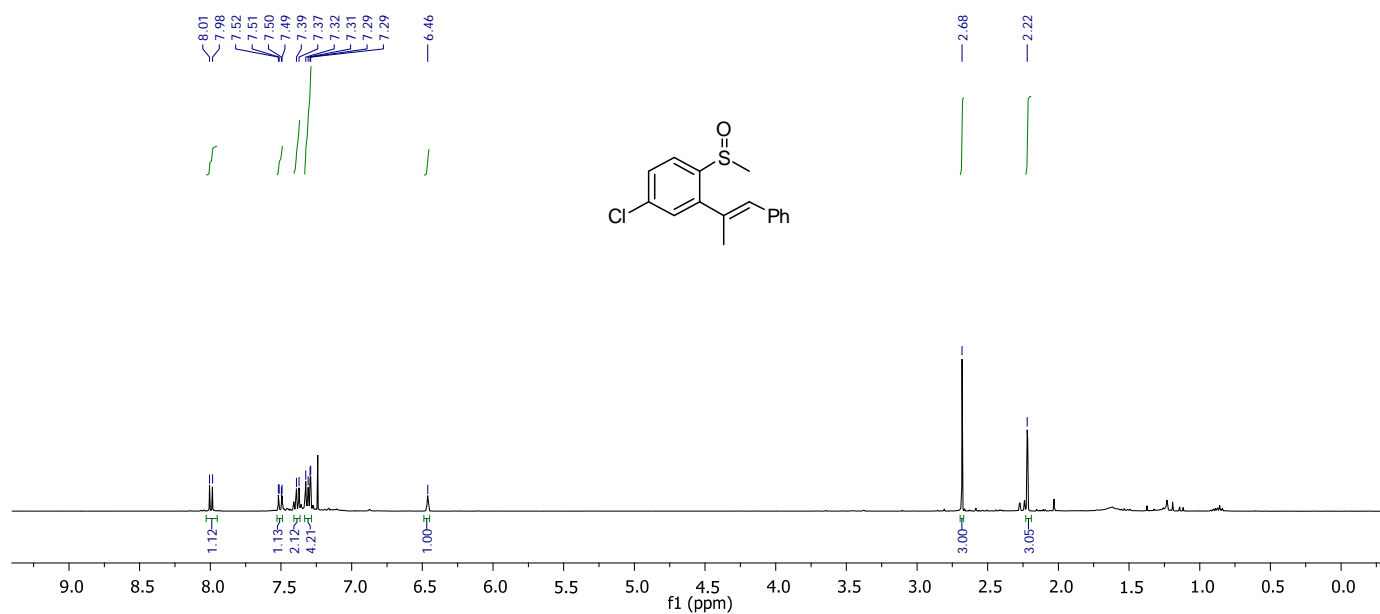
# Spectral data of compound **3h**.



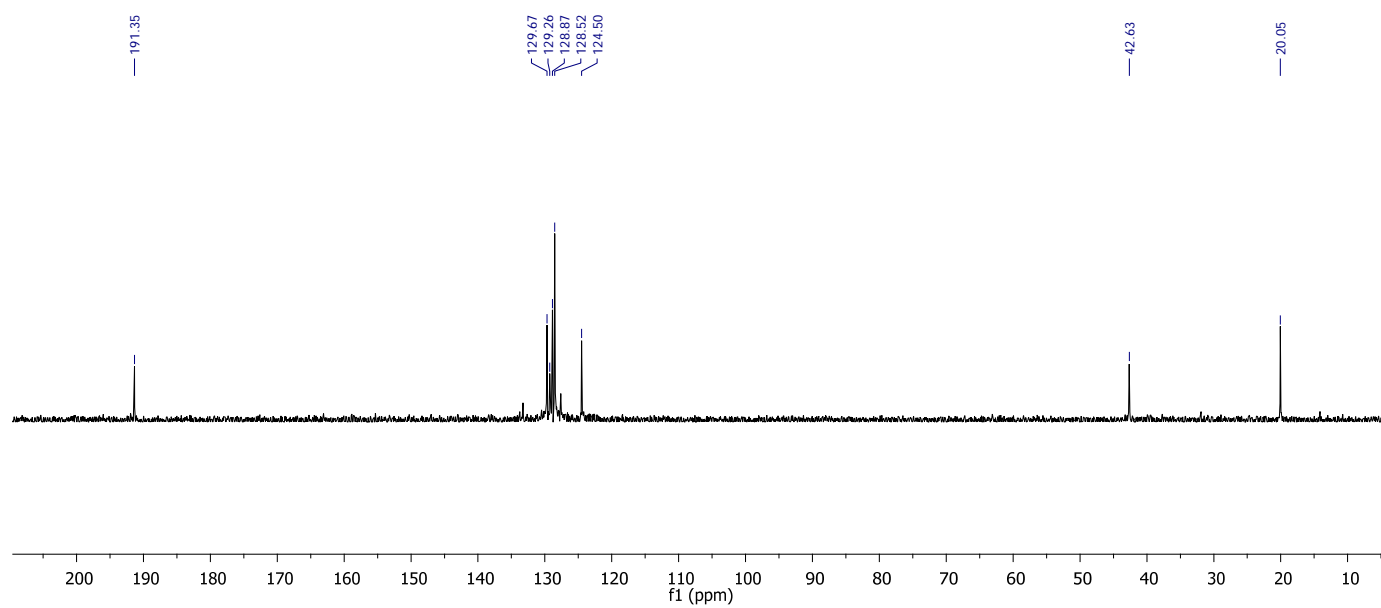
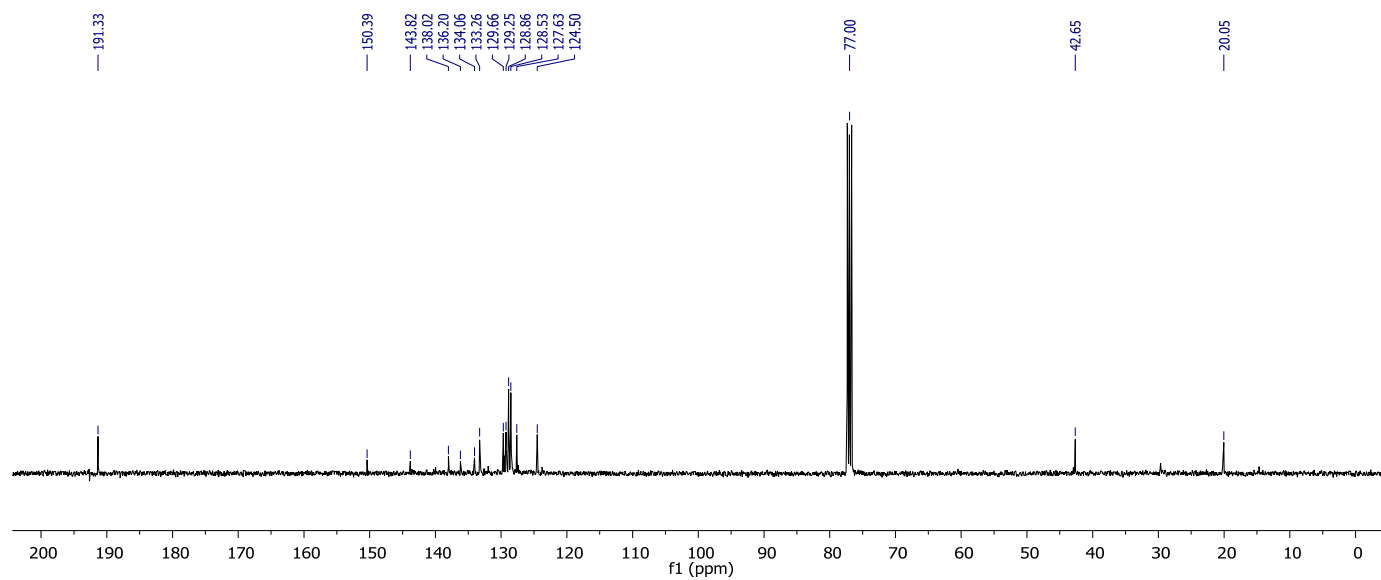
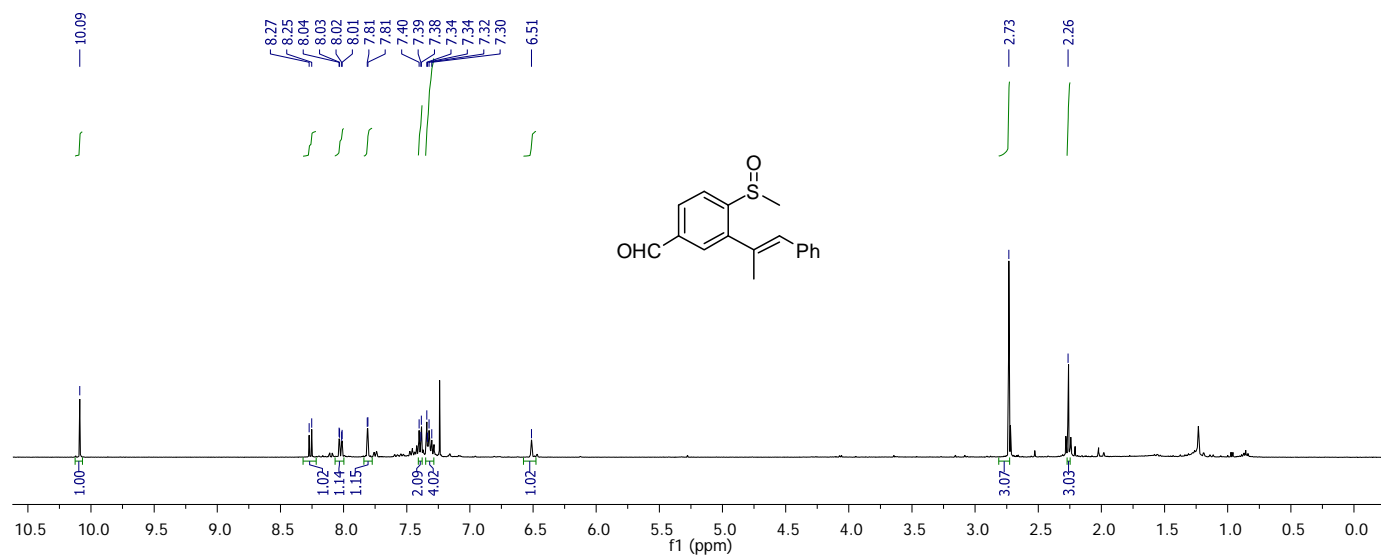
# Spectral data of compound **3i**.



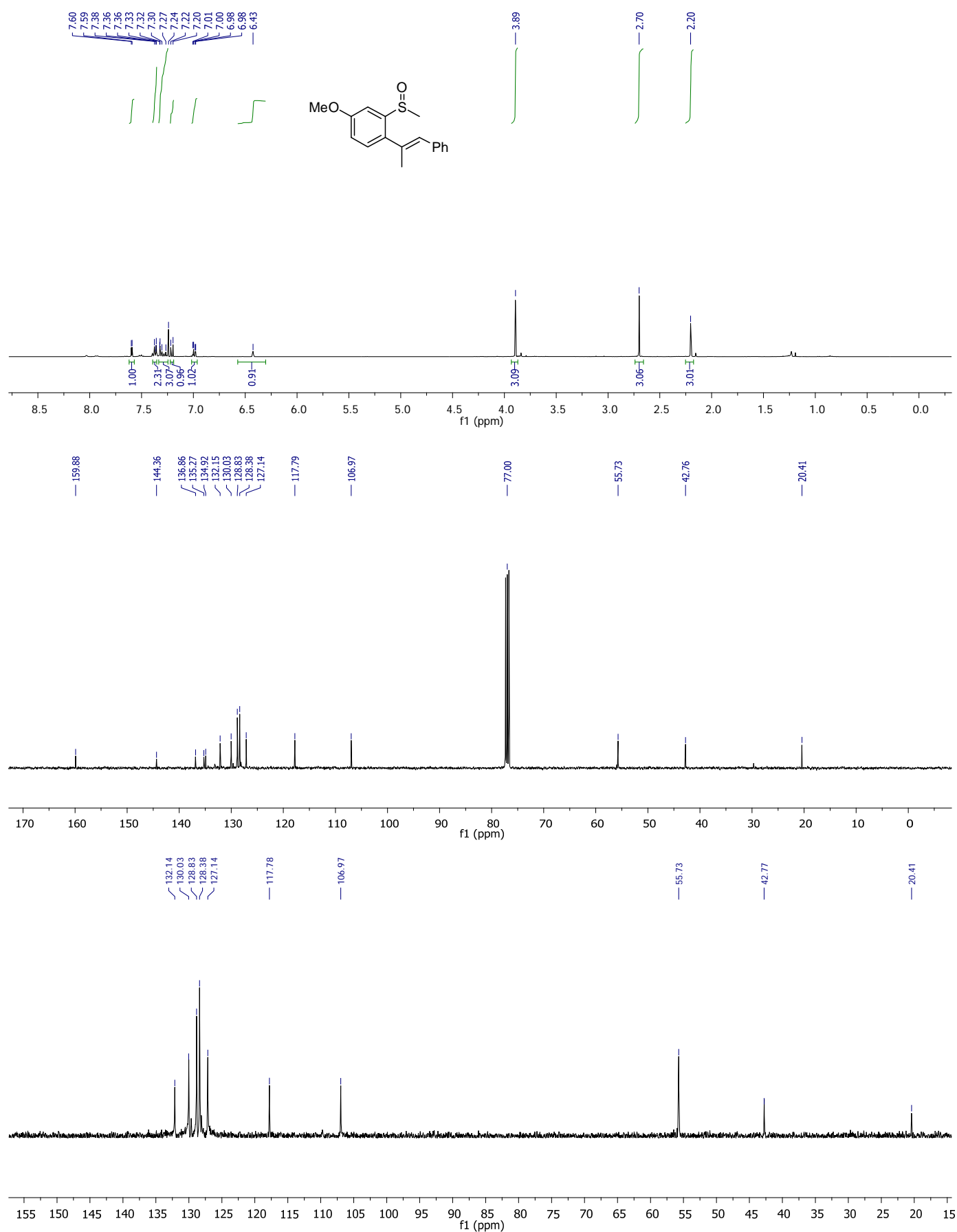
# Spectral data of compound **3j**.



Spectral data of compound **3k**.

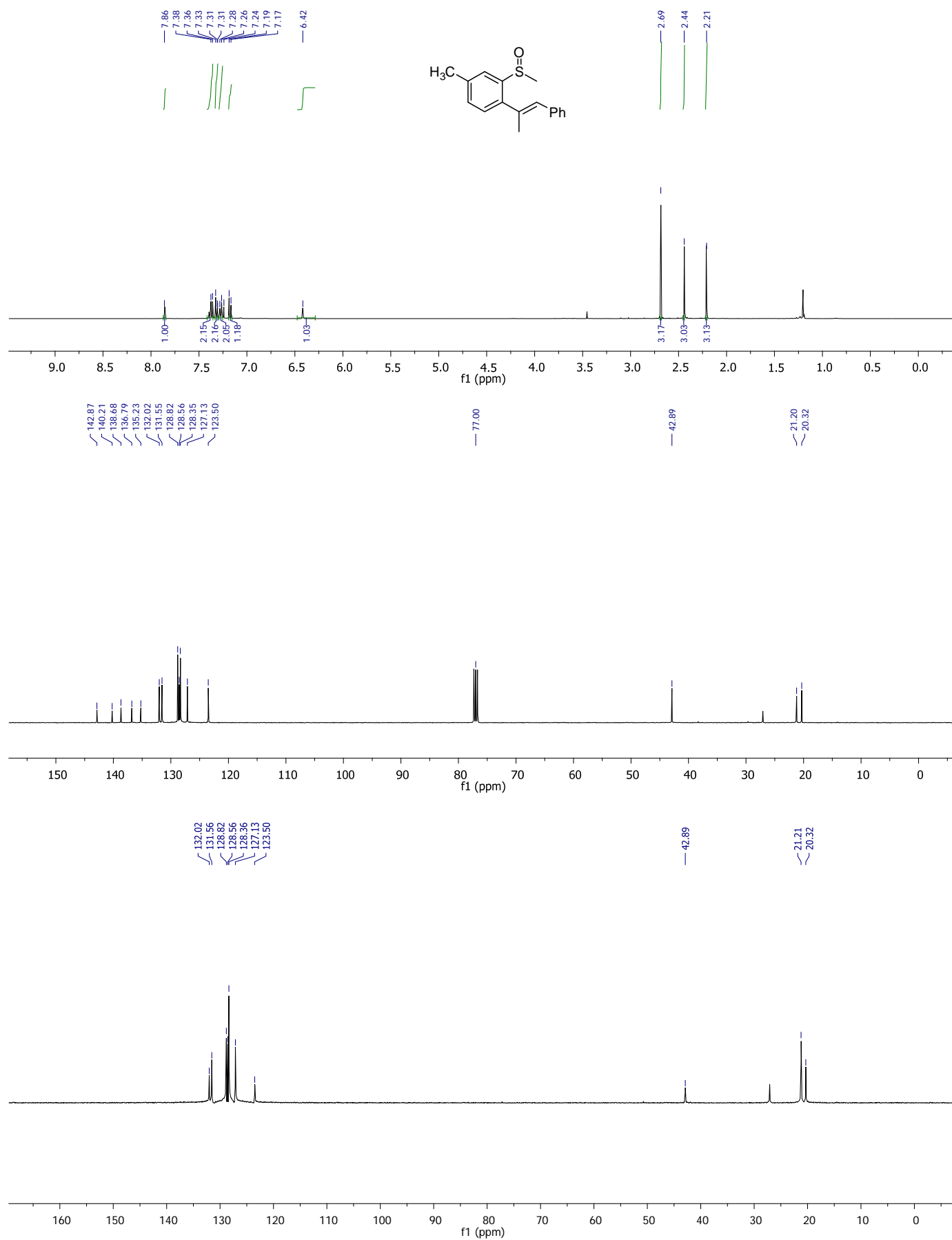


Spectral data of compound **31**.

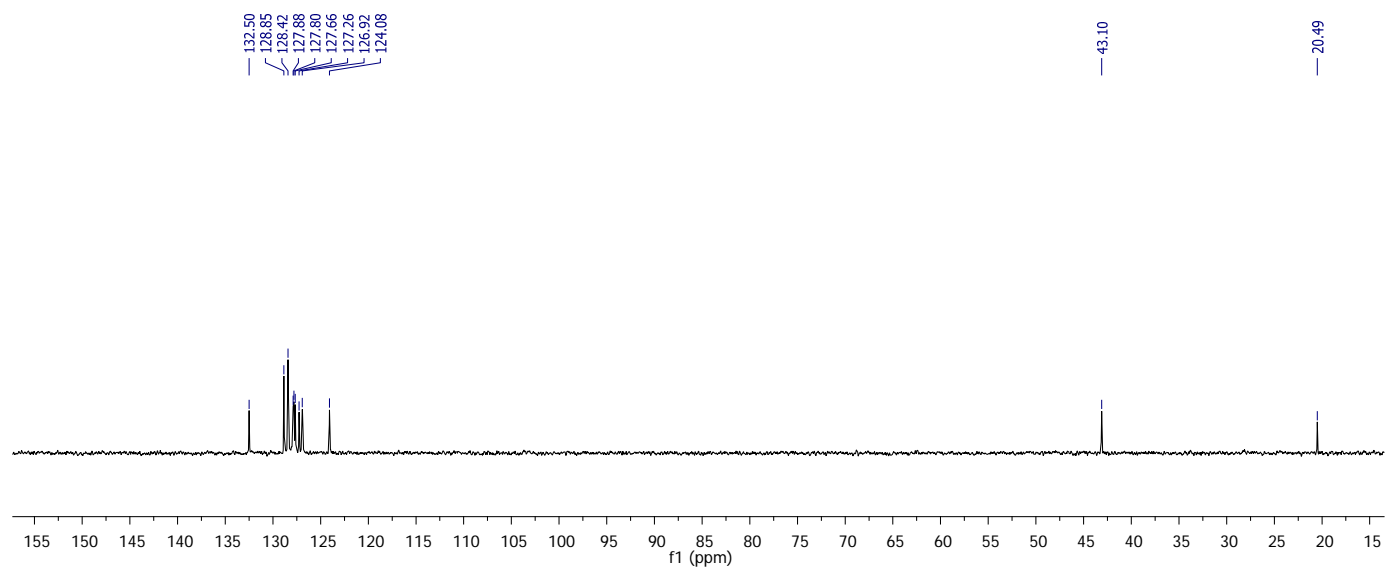
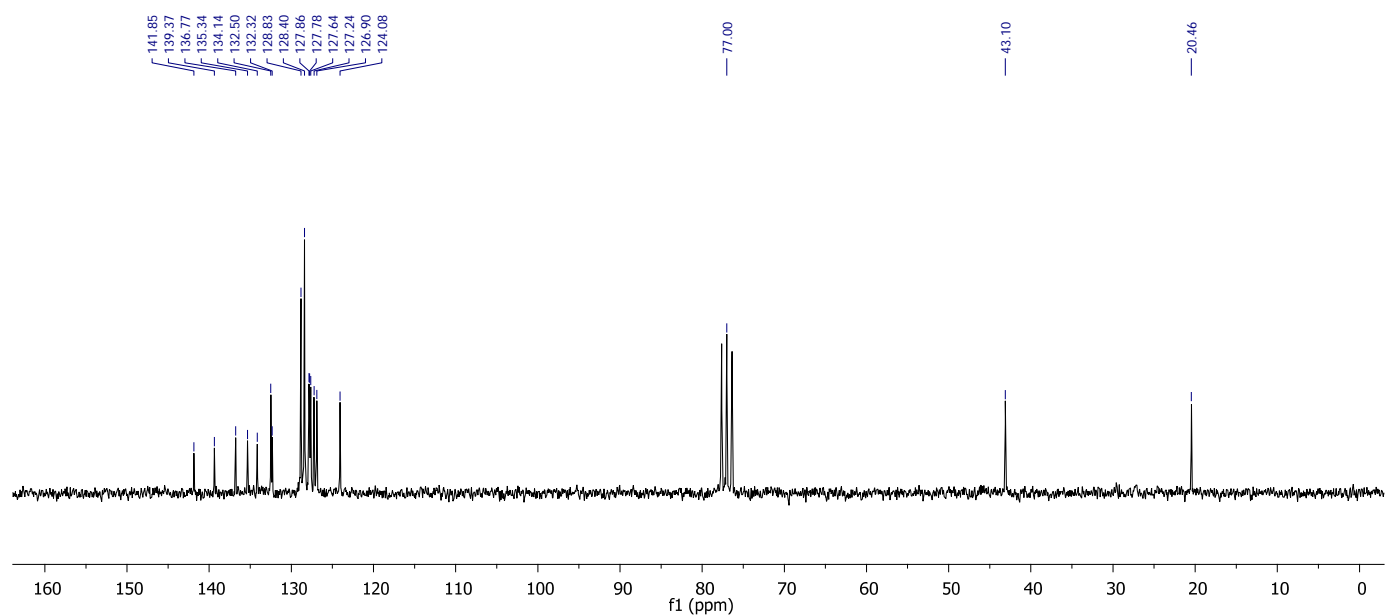
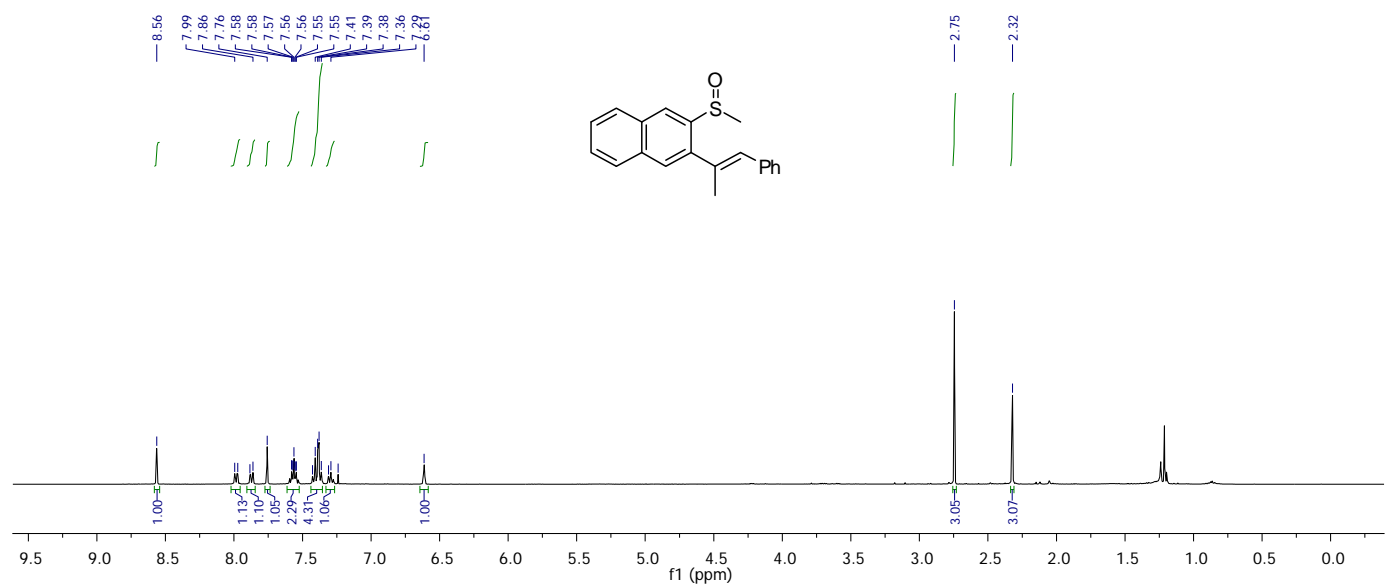




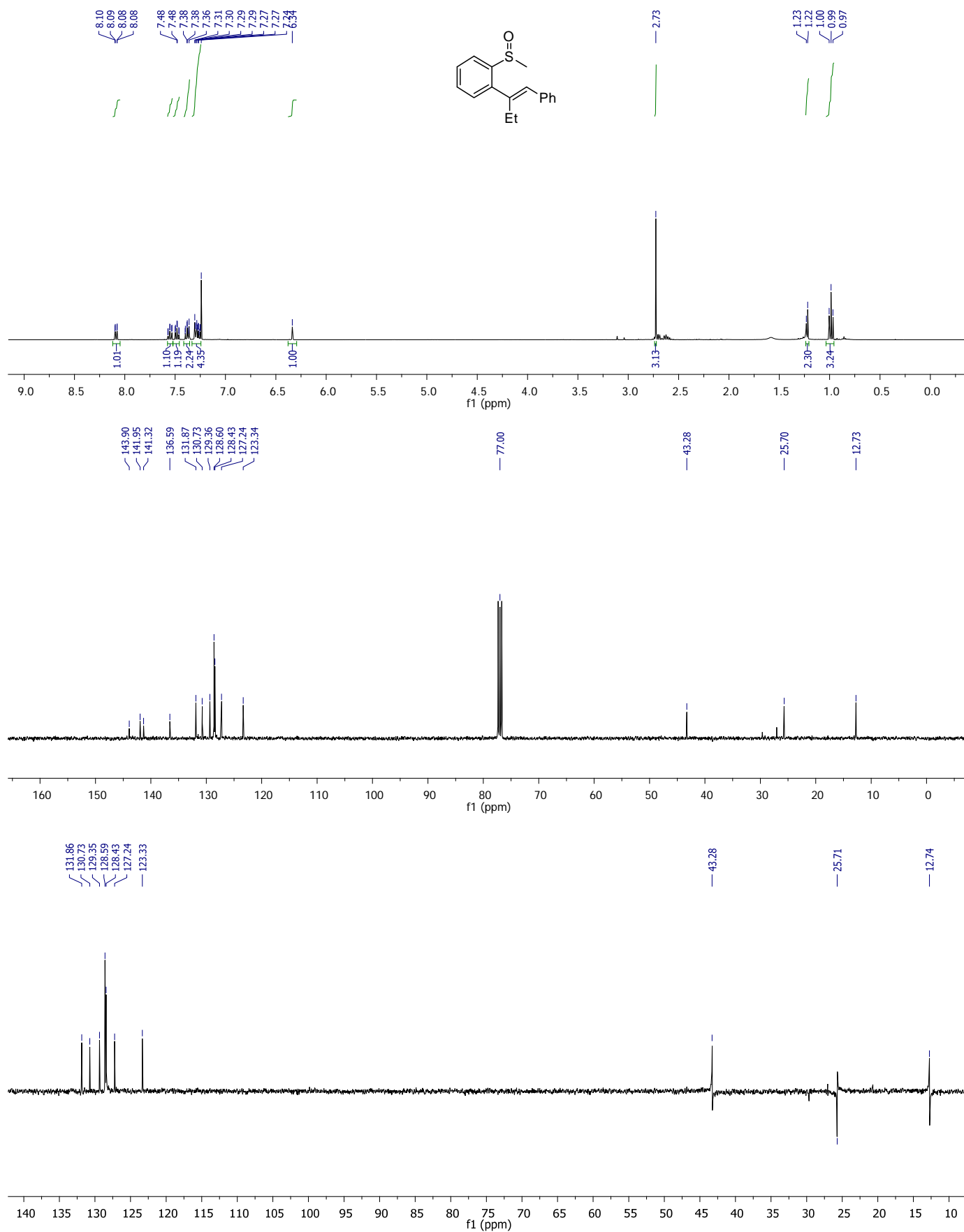
Spectral data of compound **3m**.



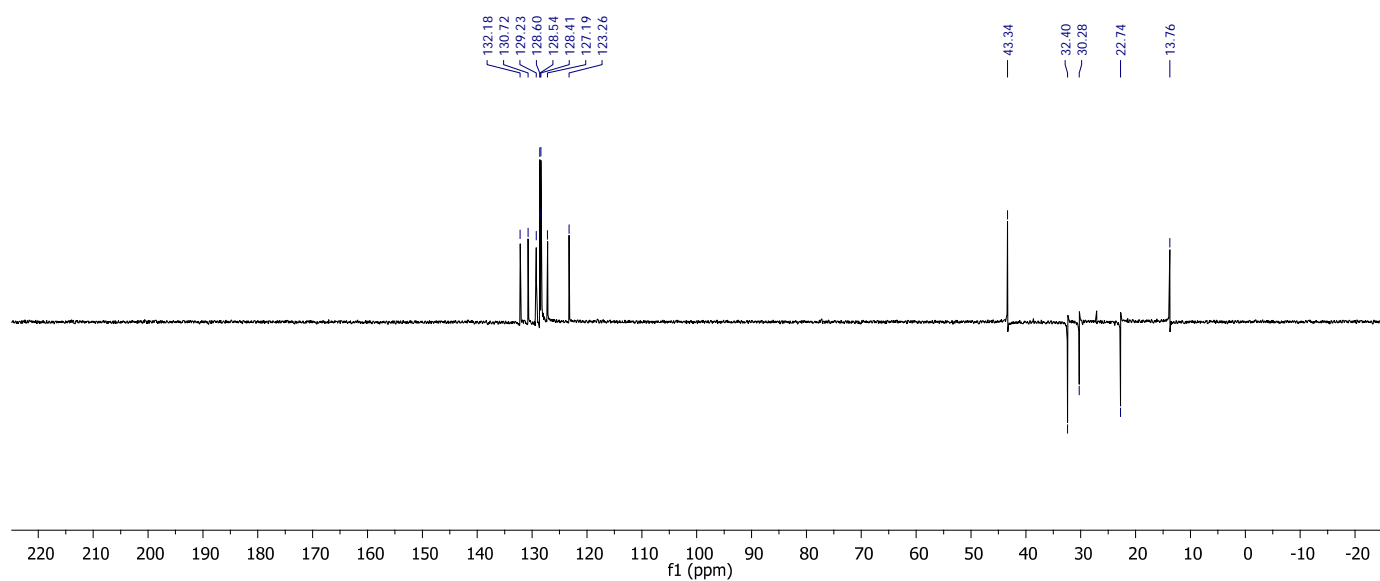
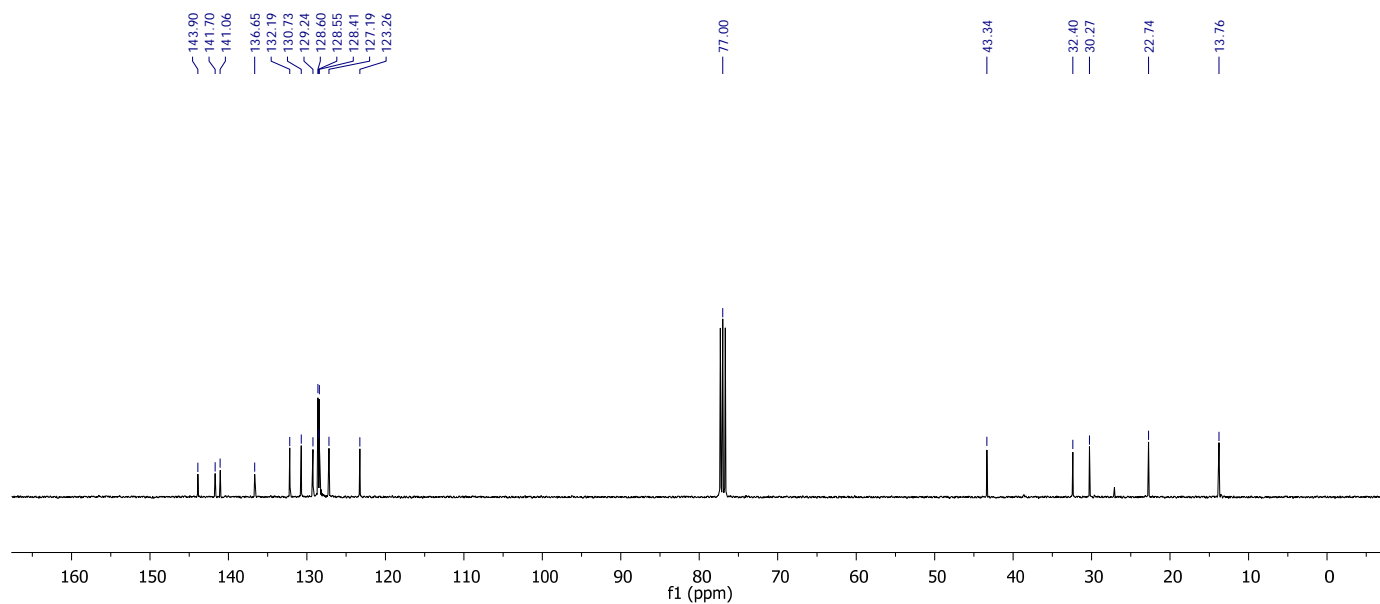
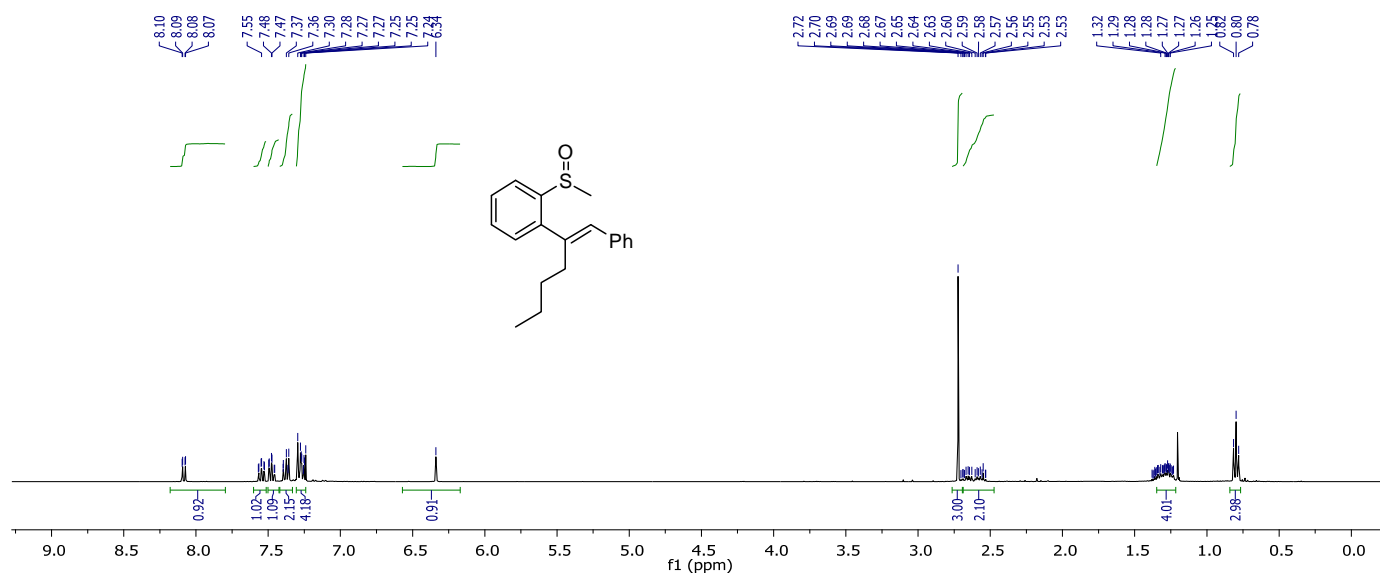
Spectral data of compound **3n**.



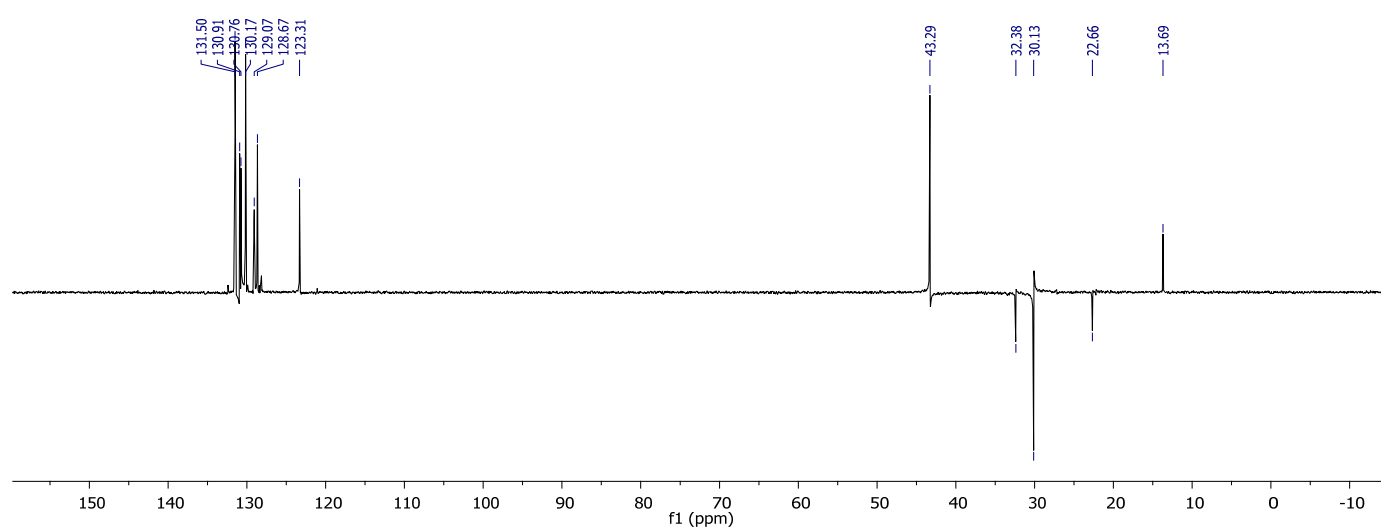
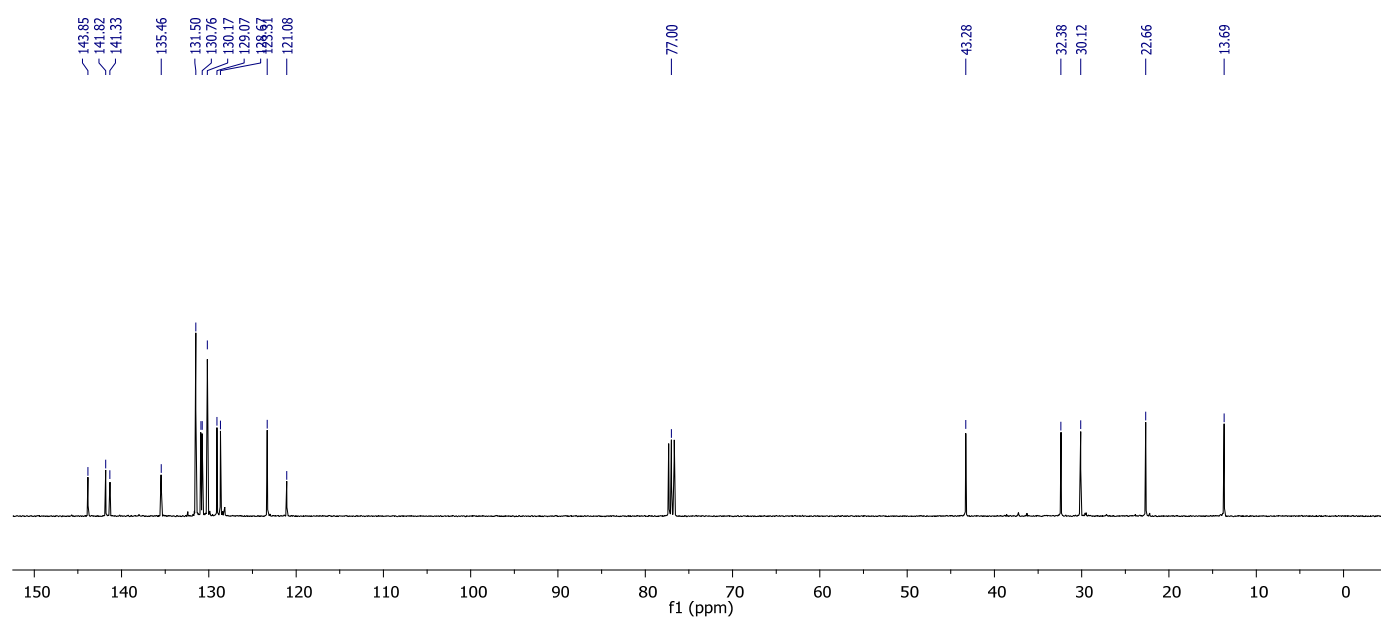
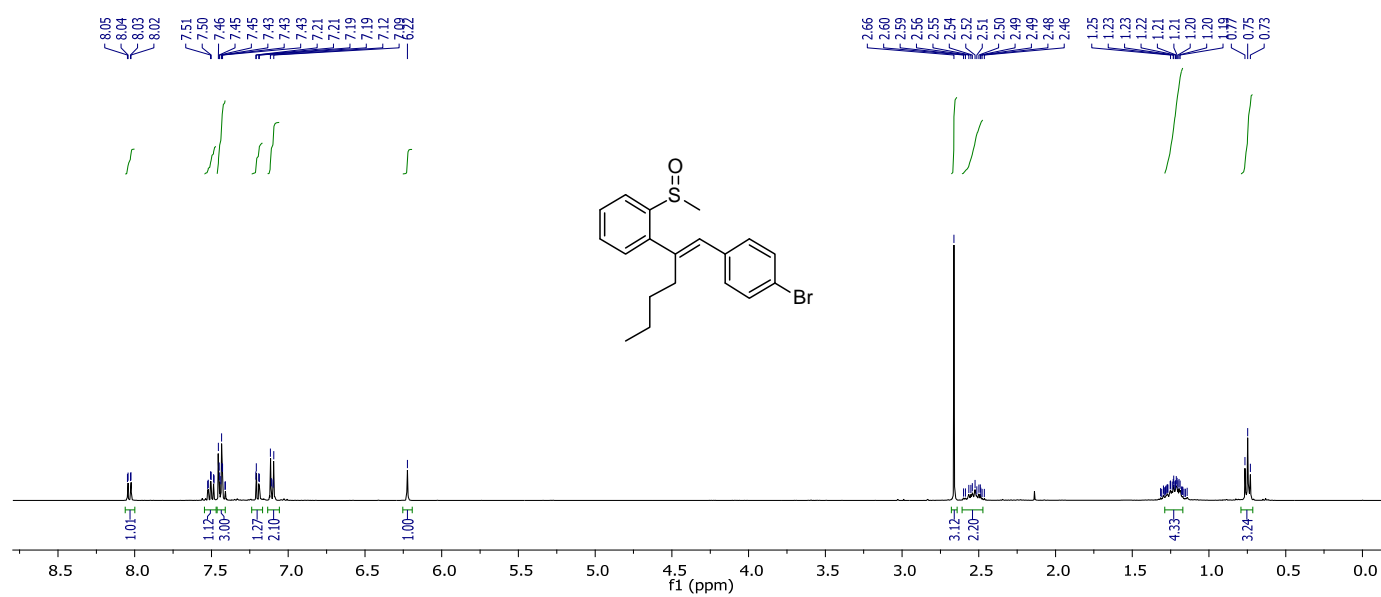
Spectral data of compound **30**.



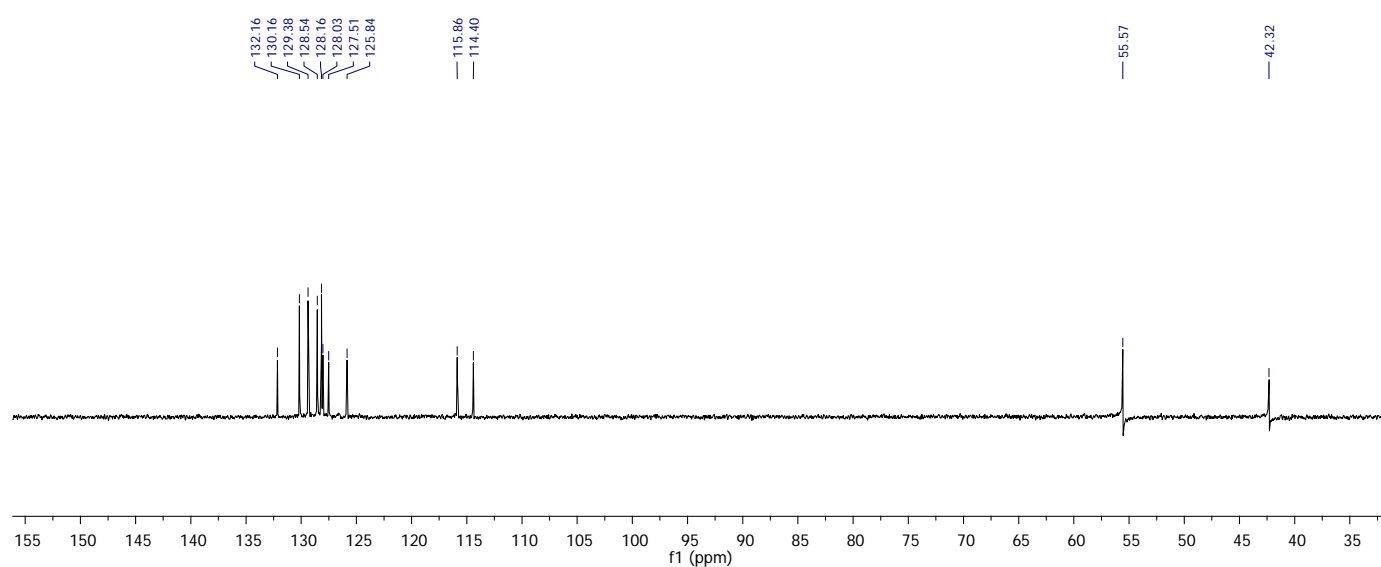
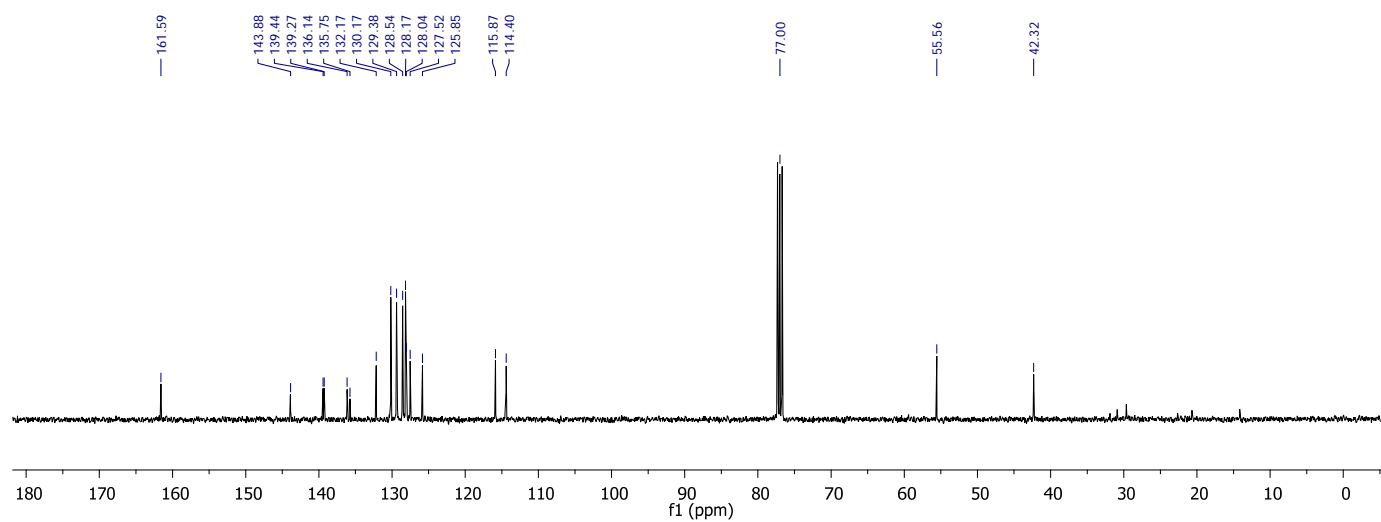
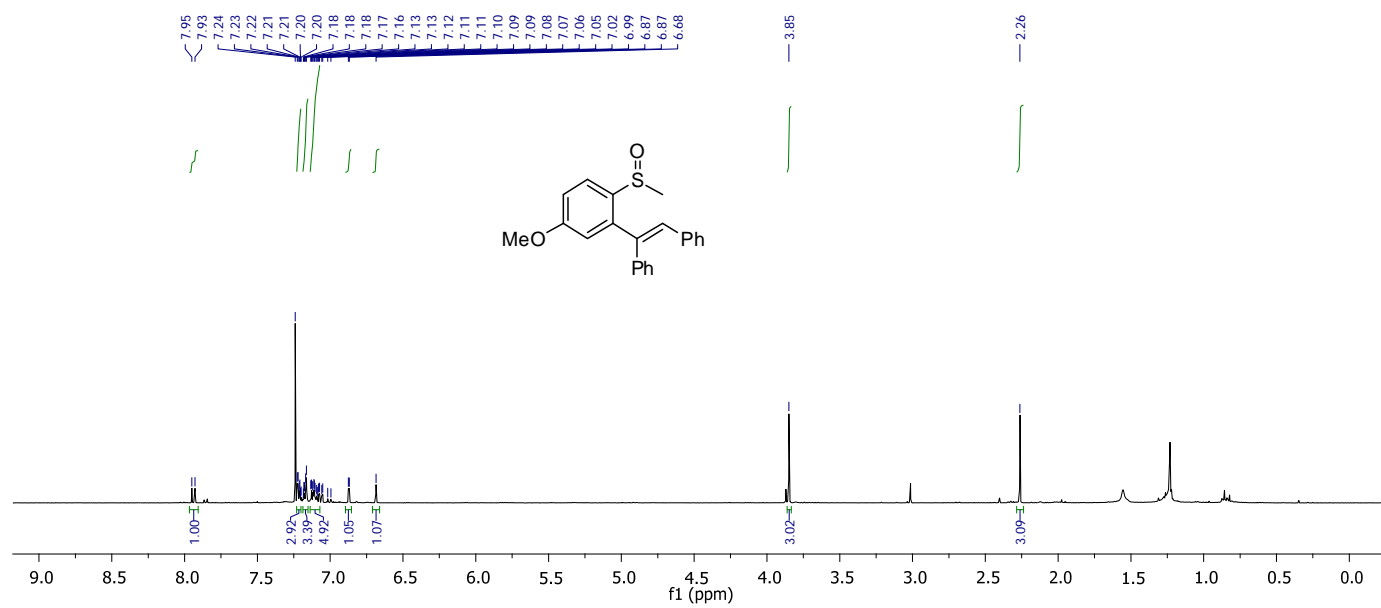
Spectral data of compound **3p**.



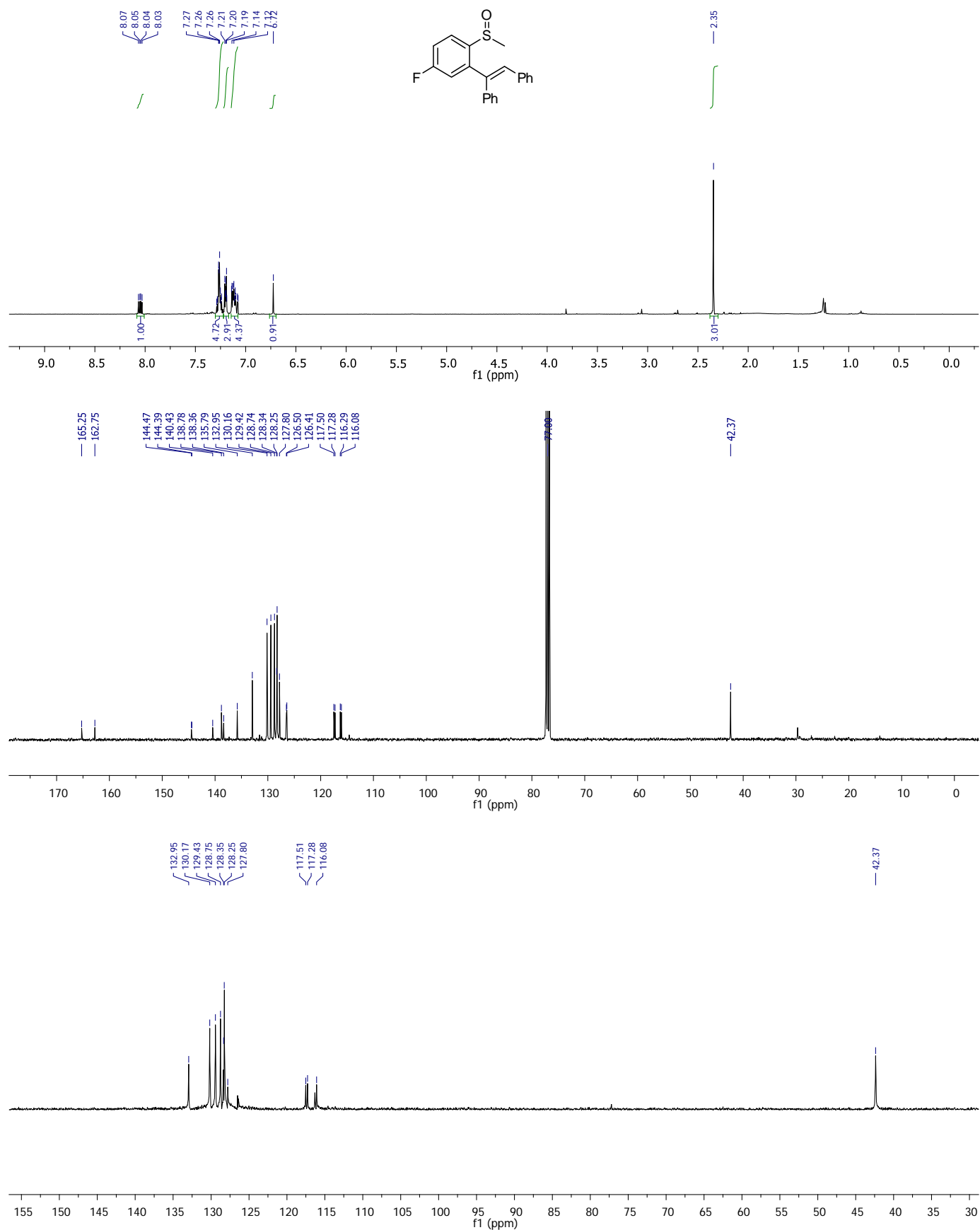
Spectral data of compound **3q**.



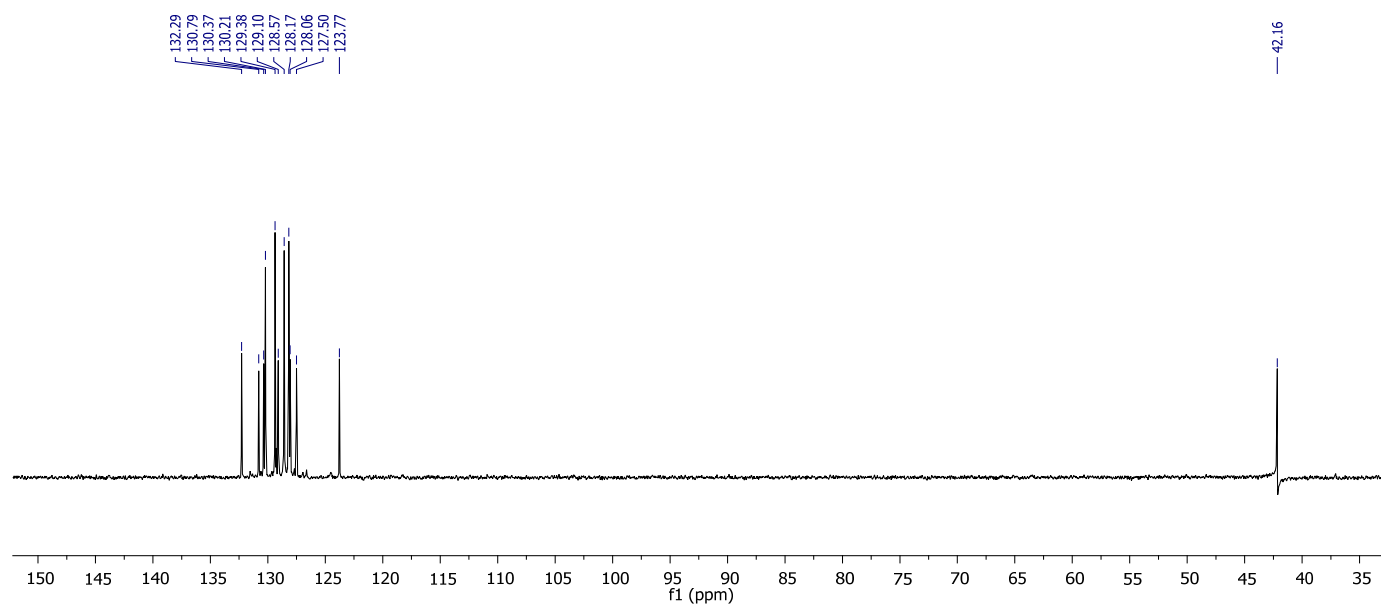
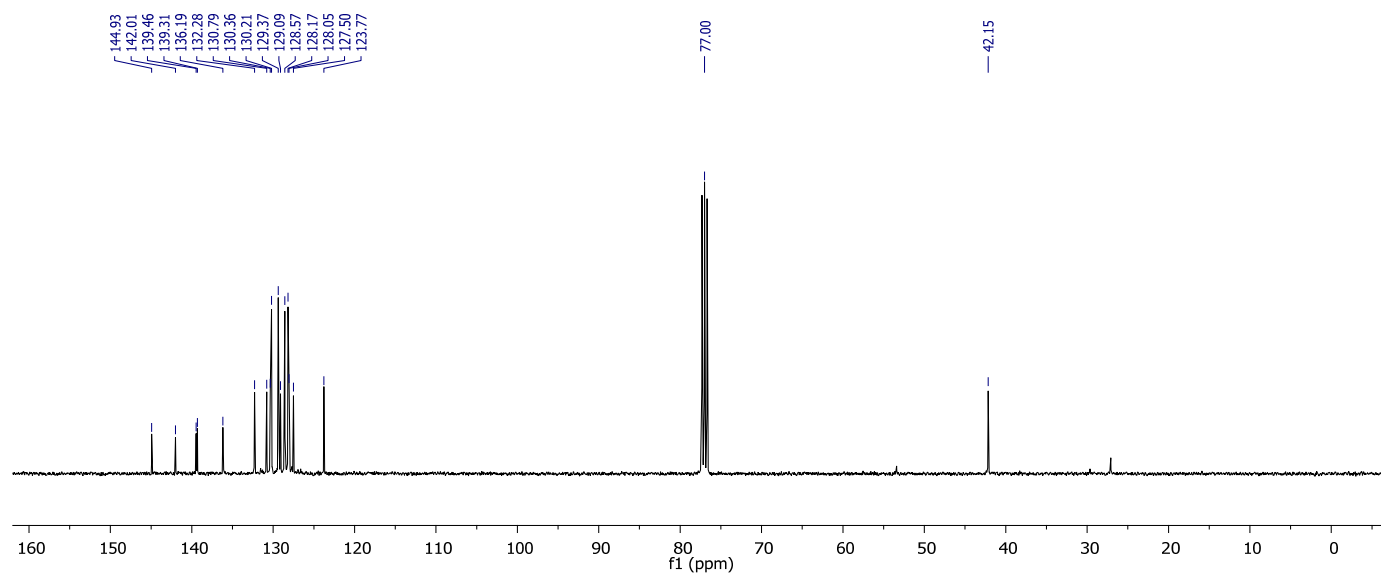
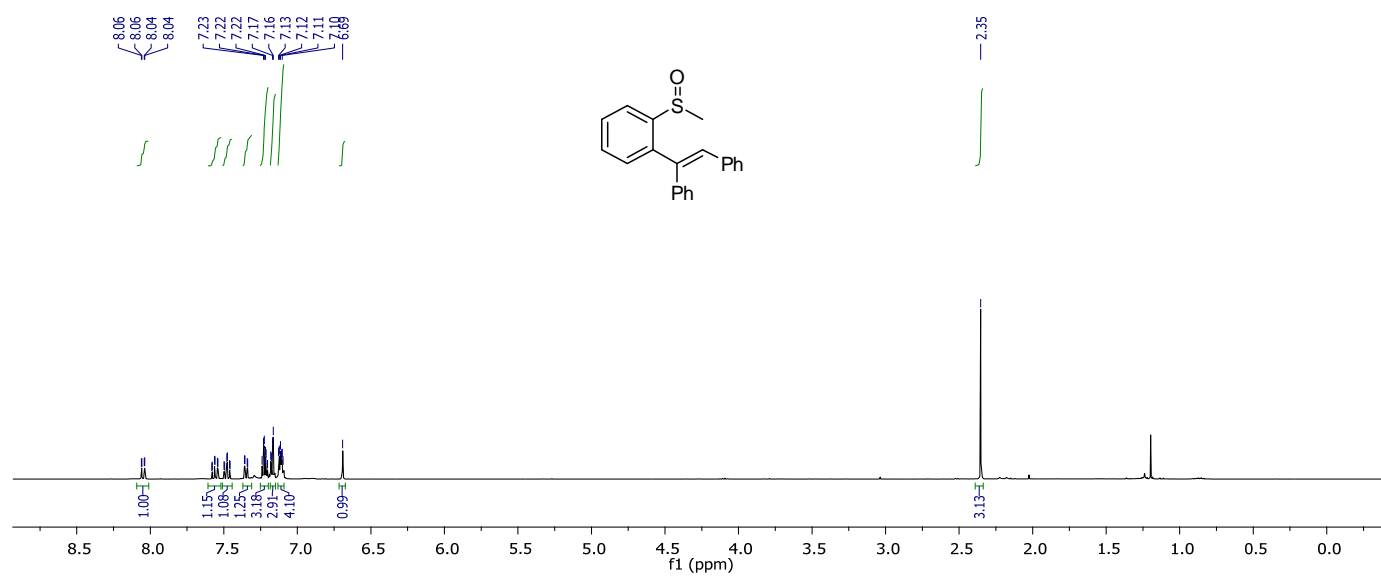
Spectral data of compound **3r**.



Spectral data of compound **3s**.

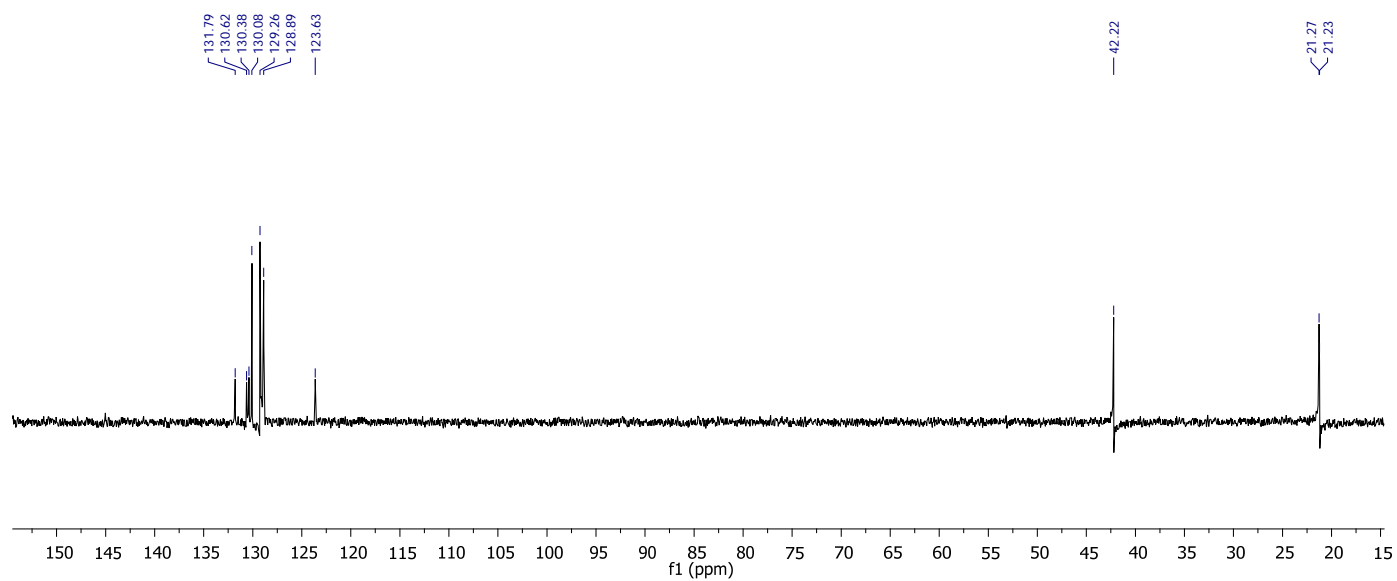
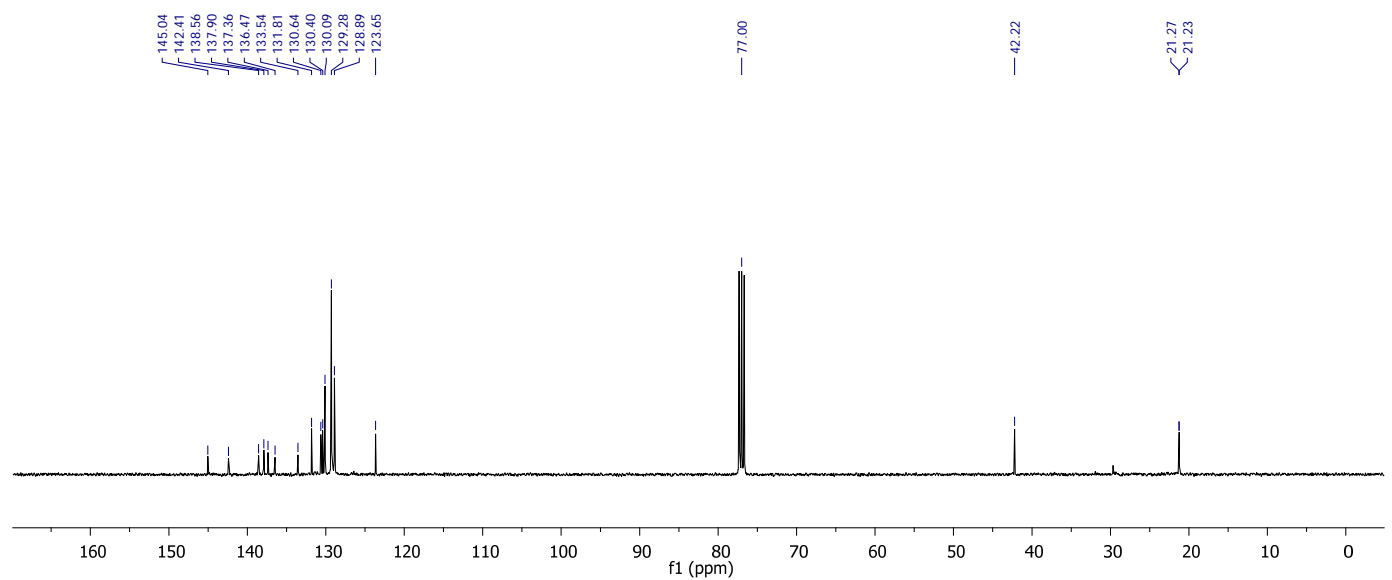
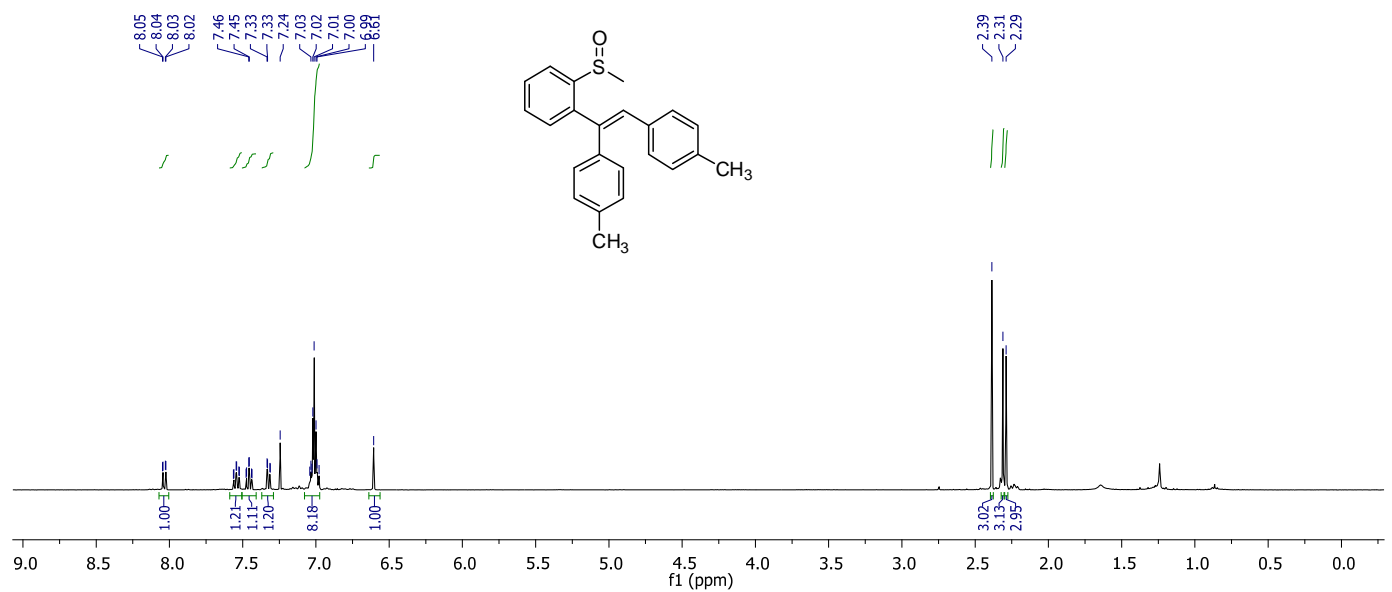


Spectral data of compound **3t**.

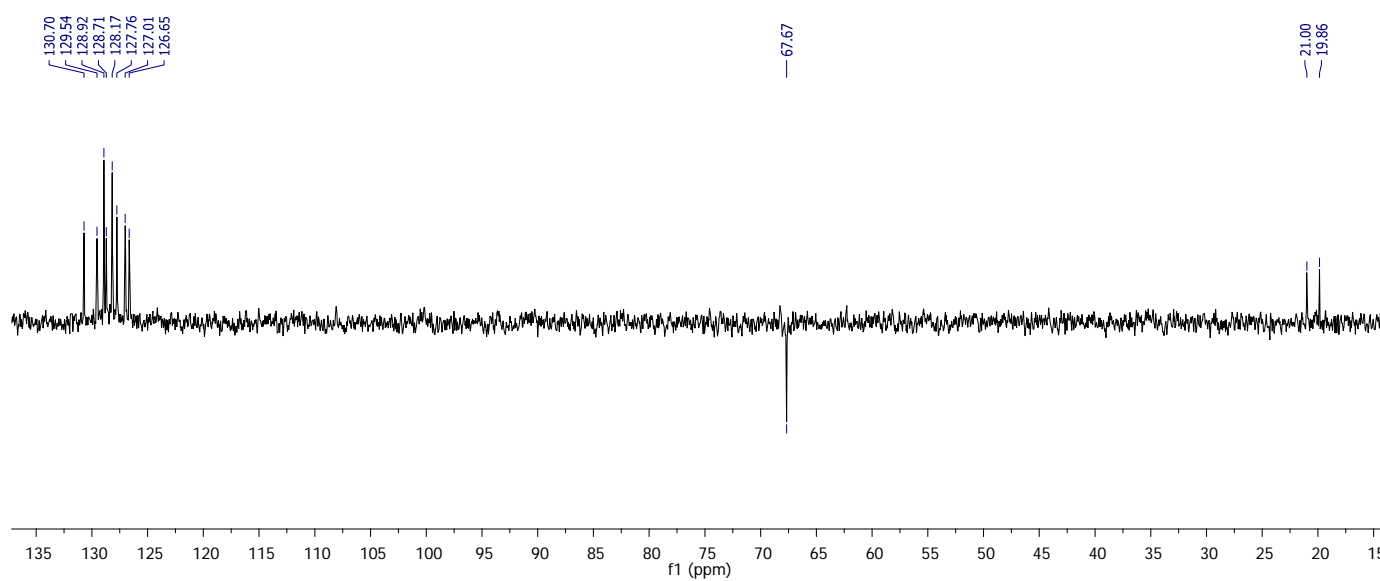
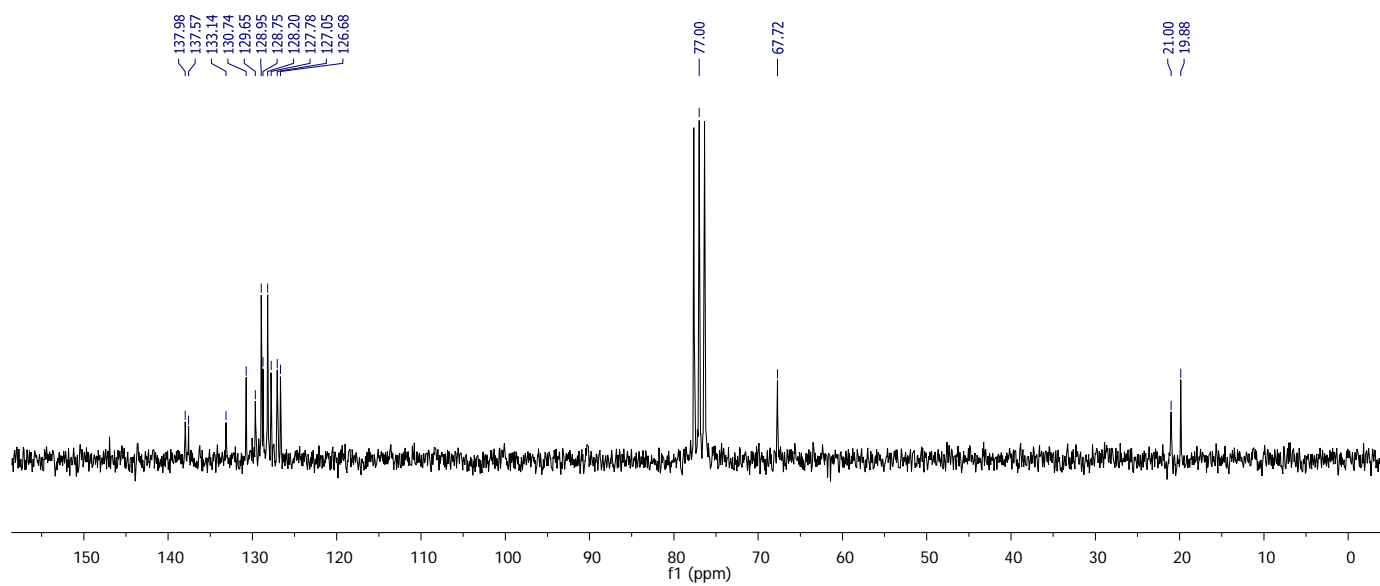
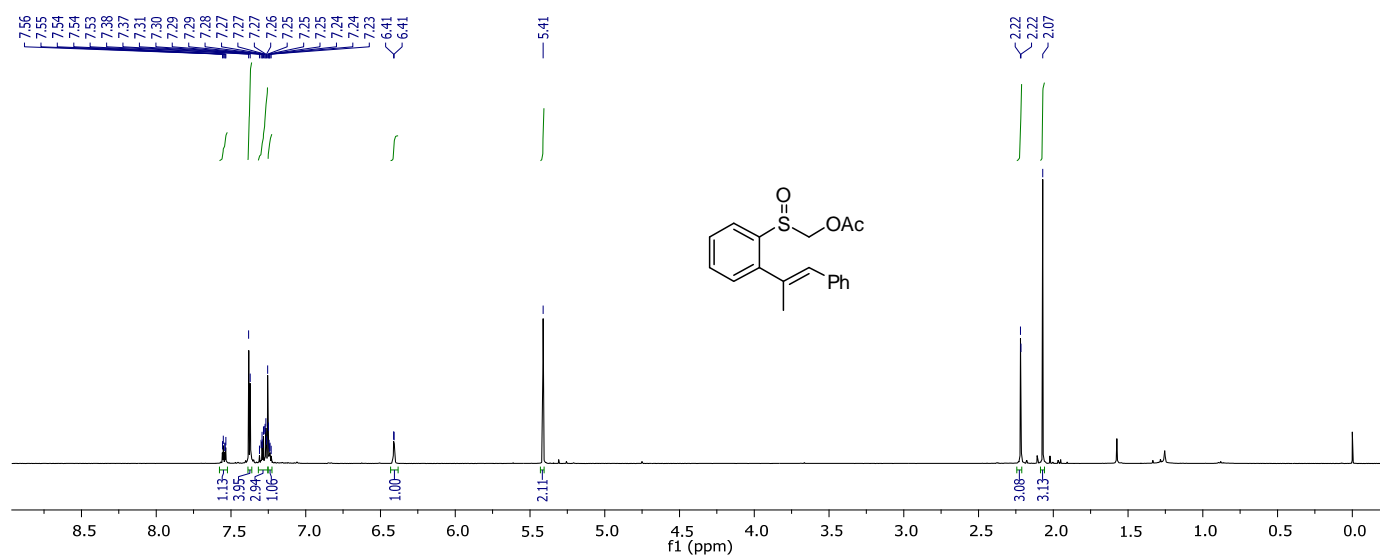




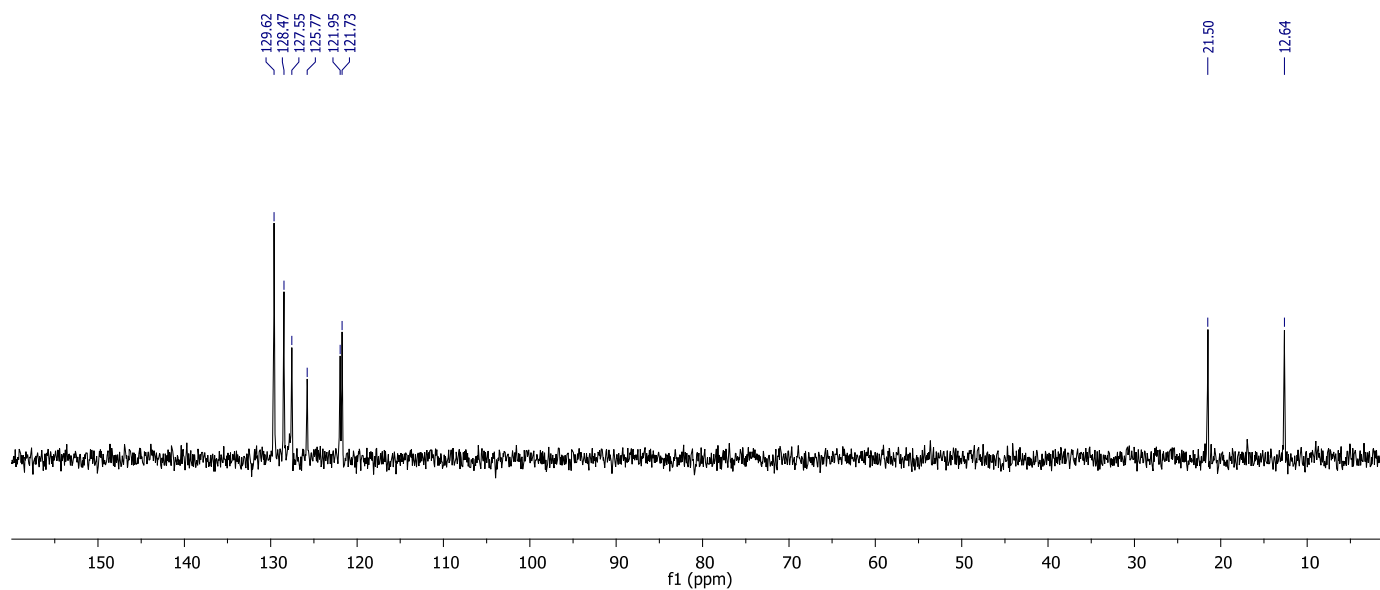
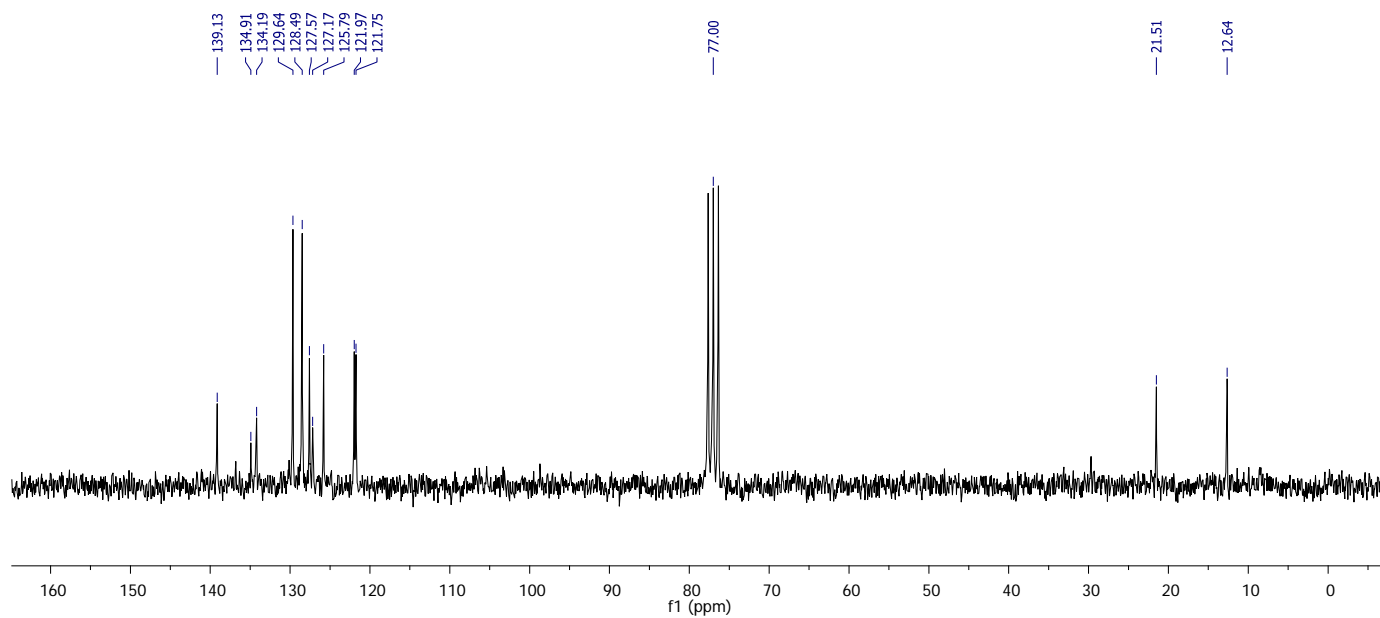
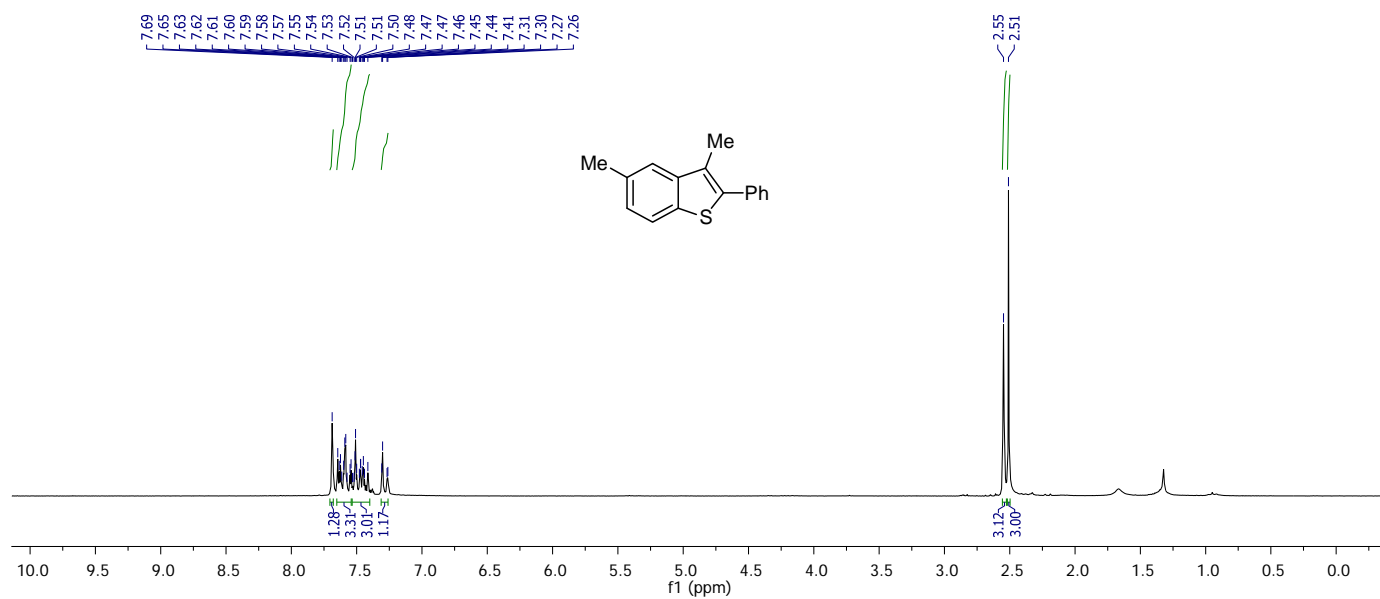
Spectral data of compound **3u**.



# Spectral data of compound 4.



# Spectral data of compound 5.



Spectral data of compound benzofulvene derivative.

