

## Supporting Information

# Catalytic arylsulfonyl radical-triggered 1,5- enyne-bicyclizations and hydrosulfonylation of $\alpha,\beta$ -conjugates

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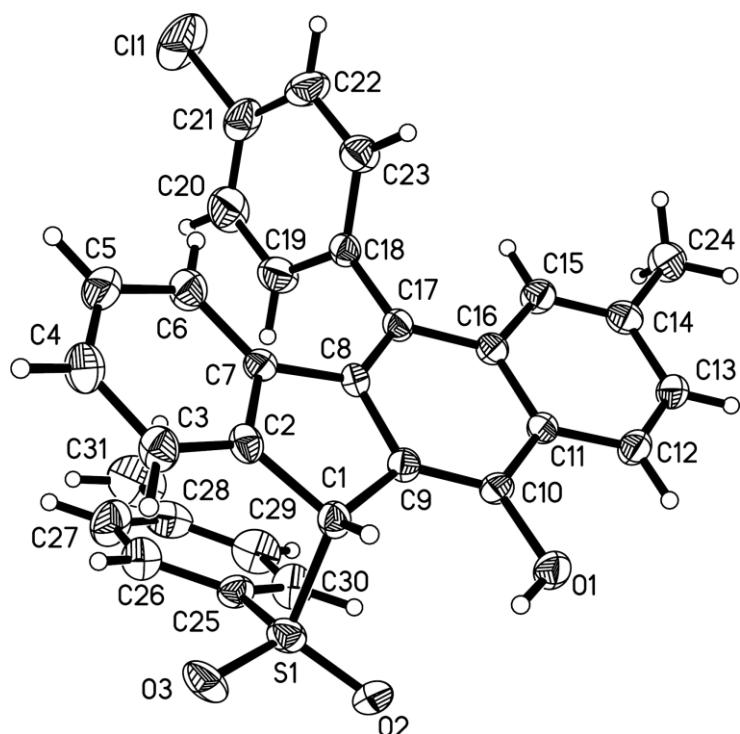
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## Experimental

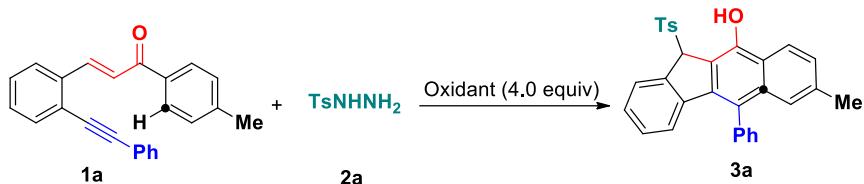
### General Information

Unless otherwise noted all starting materials were either known compounds or were obtained from commercial sources and used without purification. Melting points were determined in open capillaries. IR spectra were taken on a FT-IR-Tensor 27 spectrometer.  $^1\text{H}$  NMR ( $^{13}\text{C}$  NMR) spectra were measured on a Bruker DPX 400 MHz spectrometer in  $\text{CDCl}_3$  (or  $\text{DMSO-d}_6$ ) with chemical shift ( $\delta$ ) given in ppm relative to TMS as internal standard [(*s* = singlet, *d* = doublet, *t* = triplet, *brs* = broad singlet, *m* = multiplet), coupling constant (Hz)]. HRMS (APCI-TOF) was determined by using microTOF-Q II HRMS/MS instrument (BRUKER). X-Ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer.



**Fig 1,** X-ray Structure of **3f**

**Table 1** Optimization of the reaction conditions<sup>a</sup>



Entry	Oxidant (equiv)	Catalyst (mol%)	Additives (equiv)	Solvent	T (°C)	Yield <sup>b</sup> (%)
1	BPO(4.0)	TBAI (20)	-	MeCN	70	18
2	BPO(4.0)	TBAI (20)	-	DCM	70	10
3	BPO(4.0)	TBAI (20)	-	1,4-Dioxane	70	trace
4	BPO(4.0)	TBAI (20)	-	Toluene	70	0
5	BPO(4.0)	TBAI (20)	-	MeCN	100	25
6	BPO(4.0)	I <sub>2</sub> (15)	-	MeCN	100	messy
7	BPO(4.0)	KI (20)	-	MeCN	100	messy
8	BPO(4.0)	CuI (20)	-	MeCN	100	16
9	BPO(4.0)	TBAI (20)	HOAc (1.0)	MeCN	100	28
10	BPO(4.0)	TBAI (20)	L-proline (1.0)	MeCN	100	33
11	BPO(4.0)	TBAI (20)	PivOH (1.0)	MeCN	100	35
12	BPO(4.0)	TBAI (20)/ CuI (5)	PivOH (1.0)	MeCN	100	49
13	BPO(4.0)	TBAI (30)/ Cu(OAc) <sub>2</sub> (5)	PivOH (1.0)	MeCN	100	53
14	BPO(4.0)	TBAI (20)/ Cu(OAc) <sub>2</sub> (5)	PivOH (1.0)	MeCN	100	61
15	BPO(4.0)	TBAI (20)/ Cu(OAc) <sub>2</sub> (5)	PivOH (2.0)	MeCN	100	71
16	BPO(4.0)	TBAI (20)/ Cu(OAc) <sub>2</sub> (10)	PivOH (2.0)	MeCN	100	63
17	TBHP (4.0)	TBAI (20)/ Cu(OAc) <sub>2</sub> (5)	PivOH (2.0)	MeCN	100	64
18	DTBP(4.0)	TBAI (20)/ Cu(OAc) <sub>2</sub> (5)	PivOH (2.0)	MeCN	100	trace
19	H <sub>2</sub> O <sub>2</sub> (4.0)	TBAI (20)/ Cu(OAc) <sub>2</sub> (5)	PivOH (2.0)	MeCN	100	trace
20	BPO(4.0)	Cu(OAc) <sub>2</sub> (5)	PivOH (2.0)	MeCN	100	20
21	BPO(4.0)	TBAI (20)/ Cu(OAc) <sub>2</sub> (5)	-	MeCN	100	33

<sup>a</sup>Reaction conditions: 1,5-conjugated enyne (**1a**, 0.25 mmol), tosylhydrazide (**2a**, 0.50 mmol), Oxidant (1.0 mmol), solvent (2.5 mL), 12 h. <sup>b</sup>Isolated yields based on **1**.

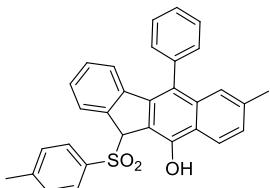
## Experimental Section

### Preparation of Compound 1a:

A mixture of 2-(phenylethynyl)benzaldehyde (5 mmol), *p*-tolylethanone (0.67 g, 5 mmol), NaOH (0.8g, 20 mmol) and EtOH (20.0 mL) were added in a 50-mL reaction vial. Then, the mixture was stirred at 0 °C for 20 min, and the followed reaction system was stirred at room temperature. After completion of the reaction monitored by TLC, the reaction system was poured into the cold water, and the solid product was collected by Büchner filtration. The desired pure 3-(2-(phenylethynyl)phenyl)-1-(*p*-tolyl)prop-2-en-1-one (**1a**) was obtained in 80% yield by recrystallization from 95% EtOH.

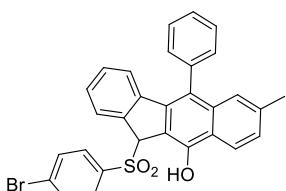
### Preparation of Compound 3a: 7-Methyl-5-phenyl-11H-tosyl-11H-fluoren-10-ol

A mixture of 3-(2-(phenylethynyl)phenyl)-1-(*p*-tolyl)prop-2-en-1-one (**1a**, 0.25 mmol, 1.0 equiv.), tosylhydrazide (**2a**, 0.5 mmol, 2.0 equiv.), BPO (1.0 mmol, 4.0 equiv.), PivOH (0.5 mmol, 2.0 equiv.), TBAI (0.05 mmol, 0.20 equiv.), Cu(OAc)<sub>2</sub> (0.0125 mmol, 0.05 equiv), MeCN (2.0 mL) were added in a sealed 10-mL reaction vial. Then, the mixture was stirred at 100 °C for 12 h until complete consumption of the starting material **1a** as detected by TLC. The mixture was cooled to room temperature and evaporated under vacuum. The crude mixture was purified by flash column chromatography (petroleum ether /ethyl acetate) to afford the desired product 7-methyl-5-phenyl-11-tosyl-11H-fluoren-10-ol (**3a**) in 71% yield.



Red solid, mp 188-189 °C; IR (KBr, v, cm<sup>-1</sup>): 3447, 2917, 1625, 1598, 1586, 1507, 1472, 1301. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>; δ, ppm) 8.29 (d, *J* = 8.4 Hz, 1H, ArH), 7.68 (d, *J* = 7.6 Hz, 1H, ArH), 7.61-7.07 (m, 7H, ArH), 7.07-6.90 (m, 4H, ArH), 6.74 (d, *J* = 8.4 Hz, 2H, ArH), 6.68-6.56 (m, 1H, ArH), 6.44 (s, 1H, CH), 5.85 (d, *J* = 8.0 Hz, 1H, OH), 2.33 (s, 3H, CH<sub>3</sub>), 2.28 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>; δ, ppm) 150.3, 144.9, 142.2, 138.2, 137.3, 136.4, 135.5, 135.3, 130.3, 130.2, 129.9, 129.4, 129.2, 129.1, 128.9, 128.5, 127.7, 127.5, 127.4, 126.8, 126.7, 125.1, 123.7, 123.5, 122.9, 112.9, 70.9, 22.0, 21.5. HRMS (APCI): m/z Calcd. For: C<sub>31</sub>H<sub>24</sub>O<sub>3</sub>S, 475.1367 [M-H]<sup>-</sup>, found: 475.1397.

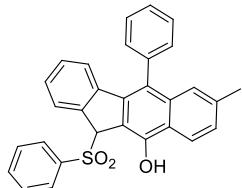
### 11-((4-Bromophenyl)sulfonyl)-7-methyl-5-phenyl-11H-fluoren-10-ol (3b)



Red solid, mp 233-234 °C; IR (KBr, v, cm<sup>-1</sup>): 3466, 2936, 1689, 1565, 1543, 1511, 1488, 1321. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>; δ, ppm) 7.94 (d, *J* = 7.6 Hz, 1H, ArH), 7.53-7.50 (m, 3H, ArH), 7.39-7.37 (m, 1H, ArH), 7.29 (d, *J* = 7.6 Hz, 1H, ArH), 7.25-7.11 (m, 5H, ArH), 7.06-7.02 (m, 1H,

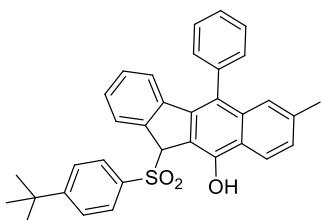
ArH), 6.88 (d,  $J = 8.4$  Hz, 2H, ArH), 6.79-6.75 (m, 1H, ArH), 6.01 (d,  $J = 8.0$  Hz, 1H, CH), 5.78 (s, 1H, OH), 2.39 (s, 3H, CH<sub>3</sub>). HRMS (APCI): m/z Calcd. For: C<sub>31</sub>H<sub>24</sub>O<sub>3</sub>S, 541.0296 [M-H]<sup>-</sup>, found: 541.0281.

### **7-Methyl-5-phenyl-11-(phenylsulfonyl)-11*H*-benzo[*b*]fluoren-10-ol (3c)**



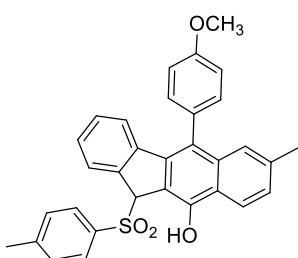
Yellow solid, mp 188-189 °C; IR (KBr, v, cm<sup>-1</sup>): 3448, 2918, 1627, 1613, 1510, 1448, 1302, 1262. <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>; δ, ppm) 8.78 (s, 1H, ArH), 8.34 (d,  $J = 8.4$  Hz, 1H, ArH), 7.88 (d,  $J = 7.6$  Hz, 1H, ArH), 7.51-7.36 (m, 3H, ArH), 7.33-7.29 (m, 2H, ArH), 7.20-7.07 (m, 2H, ArH), 7.06-6.89 (m, 6H, ArH), 6.67 (d,  $J = 7.2$  Hz, 1H, ArH), 5.93 (d,  $J = 8.0$  Hz, 1H, CH), 5.73 (s, 1H, OH), 2.32 (s, 3H, CH<sub>3</sub>). <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>; δ, ppm) 149.2, 141.2, 137.1, 136.3, 135.3, 134.5, 134.1, 132.7, 131.8, 129.2, 129.2, 129.1, 128.4, 128.1, 128.0, 128.0, 126.9, 126.7, 126.5, 126.4, 125.8, 125.7, 124.1, 122.6, 122.4, 121.9, 111.7, 69.8, 20.9. HRMS (APCI): m/z Calcd. For: C<sub>30</sub>H<sub>22</sub>O<sub>3</sub>S, 461.1211 [M-H]<sup>-</sup>, found: 461.1216.

### **11-((4-(Tert-butyl)phenyl)sulfonyl)-7-methyl-5-phenyl-11*H*-benzo[*b*]fluoren-10-ol (3d)**



Yellow solid, mp 208-209 °C; IR (KBr, v, cm<sup>-1</sup>): 3436, 2964, 1628, 1593, 1507, 1463, 1398, 1308. <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>; δ, ppm) 8.29 (d,  $J = 8.4$  Hz, 1H, ArH), 7.72 (d,  $J = 7.6$  Hz, 1H, ArH), 7.69-7.29 (m, 5H, ArH), 7.28-7.24 (m, 1H, ArH), 7.22-7.12 (m, 3H, ArH), 7.03-6.94 (m, 2H, ArH), 6.80-6.72 (m, 2H, ArH), 6.66-6.64 (m, 1H, ArH), 6.44 (s, 1H, CH), 5.81 (d,  $J = 8.0$  Hz, 1H, OH), 2.33 (s, 3H, CH<sub>3</sub>), 1.17 (s, 9H, CH<sub>3</sub>). <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>; δ, ppm) 157.9, 150.3, 142.2, 138.2, 137.2, 136.5, 135.4, 135.4, 130.3, 130.1, 129.6, 129.4, 129.1, 129.0, 128.8, 127.7, 127.5, 127.4, 126.8, 126.7, 125.2, 124.8, 123.7, 123.4, 122.9, 113.1, 70.8, 35.1, 30.9, 22.0. HRMS (APCI): m/z Calcd. For: C<sub>34</sub>H<sub>30</sub>O<sub>3</sub>S, 517.1837 [M-H]<sup>-</sup>, found: 517.1855.

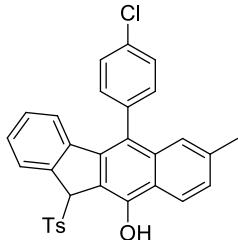
### **5-(4-Methoxyphenyl)-7-methyl-11-tosyl-11*H*-benzo[*b*]fluoren-10-ol (3e)**



Red solid, mp 209-210 °C; IR (KBr, v, cm<sup>-1</sup>): 3483, 2919, 1646, 1577, 1547, 1518, 1457, 1328. <sup>1</sup>HNMR (400 MHz, DMSO-*d*<sub>6</sub>; δ, ppm) 8.33 (d,  $J = 8.4$  Hz, 1H, ArH), 7.86 (d,  $J = 7.6$  Hz, 1H, ArH), 7.29 (d,  $J = 8.4$  Hz, 1H, ArH), 7.19 (s, 1H, ArH), 7.09-7.04 (m, 2H, ArH), 7.00-6.96 (m, 2H, ArH), 6.93-6.88 (m, 3H, ArH), 6.76 (d,  $J = 8.1$  Hz, 2H, ArH), 6.59-6.56 (m, 1H, ArH), 6.07 (d,  $J =$

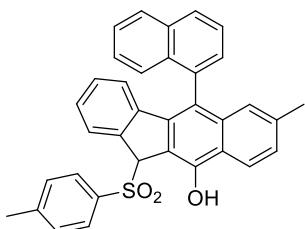
7.8 Hz, 1H, CH), 5.71 (s, 1H, OH), 3.86 (s, 3H, OCH<sub>3</sub>), 2.33 (s, 3H, CH<sub>3</sub>), 2.18 (s, 3H, CH<sub>3</sub>). HRMS (APCI): m/z Calcd. For: C<sub>32</sub>H<sub>26</sub>O<sub>4</sub>S, 505.1474 [M-H]<sup>-</sup>, found: 505.1482.

### **5-(4-Chlorophenyl)-7-methyl-11-tosyl-11*H*-benzo[*b*]fluoren-10-ol (3f)**



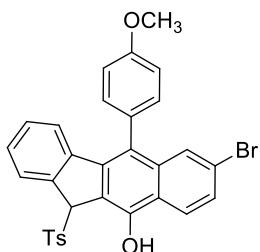
Red solid, mp 194-195 °C; IR (KBr, v, cm<sup>-1</sup>): 3441, 2972, 1627, 1576, 1560, 1446, 1398, 1321. <sup>1</sup>HNMR (400 MHz, DMSO-*d*<sub>6</sub>; δ, ppm) 8.29 (d, *J* = 8.4 Hz, 1H, ArH), 7.69 (d, *J* = 7.6 Hz, 1H, ArH), 7.65-7.56 (m, 2H, ArH), 7.53-7.20 (m, 4H, ArH), 7.11-7.07 (m, 1H, ArH), 7.04-6.86 (m, 3H, ArH), 6.98 (d, *J* = 8.4 Hz, 2H, ArH), 6.66-6.56 (m, 1H, ArH), 6.45 (s, 1H, CH), 5.94 (d, *J* = 8.0 Hz, 1H, OH), 2.35 (s, 3H, CH<sub>3</sub>), 2.27 (s, 3H, CH<sub>3</sub>). <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>; δ, ppm) 150.6, 144.9, 141.9, 137.5, 136.7, 136.5, 135.4, 135.3, 133.7, 131.8, 131.7, 129.9, 129.5, 129.4, 129.3, 129.2, 128.6, 127.6, 127.6, 126.9, 125.2, 124.8, 123.7, 123.3, 123.1, 112.9, 70.8, 22.0, 21.5. HRMS (APCI): m/z Calcd. For: C<sub>31</sub>H<sub>23</sub>ClO<sub>3</sub>S, 509.0977 [M-H]<sup>-</sup>, found: 509.0991.

### **7-Methyl-5-(naphthalen-1-yl)-11-tosyl-11*H*-benzo[*b*]fluoren-10-ol (3g)**



Yellow solid, mp 210-211 °C; IR (KBr, v, cm<sup>-1</sup>): 3442, 2933, 1663, 1586, 1534, 1478, 1397, 1202. <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>; δ, ppm) 9.09 (s, 1H, ArH), 8.46 (d, *J* = 8.4 Hz, 1H, ArH), 8.00-7.94(m, 3H, ArH), 7.68-7.56 (m, 1H, ArH), 7.46-7.42 (m, 1H, ArH), 7.37 (d, *J* = 8.4 Hz, 1H, ArH), 7.31 (d, *J* = 6.8 Hz, 1H, ArH), 7.22-7.19 (m, 1H, ArH), 7.05-7.00 (m, 3H, ArH), 6.95-6.75 (m, 5H, ArH), 6.54 (d, *J* = 8.4 Hz, 1H, ArH), 5.85 (s, 1H, CH), 5.63 (d, *J* = 8.0 Hz, 1H, OH), 2.29 (s, 3H, CH<sub>3</sub>), 2.27 (s, 3H, CH<sub>3</sub>). <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>; δ, ppm) 150.6, 144.8, 141.8, 137.4, 136.1, 135.7, 135.2, 133.8, 132.8, 130.2, 129.5, 129.2, 128.7, 128.3, 128.2, 128.2, 127.7, 127.4, 126.7, 126.1, 125.9, 125.7, 125.3, 125.2, 124.0, 123.8, 123.4, 122.9, 112.6, 70.8, 21.9, 21.8. HRMS (APCI): m/z Calcd. For: C<sub>35</sub>H<sub>25</sub>O<sub>3</sub>S, 525.1524 [M-H]<sup>-</sup>, found: 525.1542.

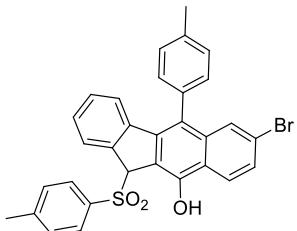
### **7-Bromo-5-(4-methoxyphenyl)-11-tosyl-11*H*-benzo[*b*]fluoren-10-ol (3h)**



Yellow solid, mp 218-219 °C; IR (KBr, v, cm<sup>-1</sup>): 3446, 2943, 622, 581, 1511, 1426, 1363, 1243. <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>; δ, ppm) 8.36 (d, *J* = 8.8 Hz, 1H, ArH), 7.93 (d, *J* = 7.6 Hz, 1H, ArH), 7.60-7.57 (m, 1H, ArH), 7.52 (d, *J* = 1.6 Hz, 1H, ArH), 7.32-7.28 (m, 1H, ArH), 7.16-7.07 (m, 2H,

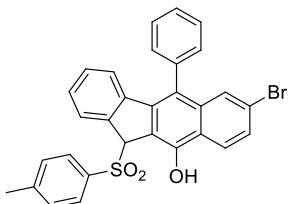
ArH), 7.07-7.05 (m, 2H, ArH), 7.02-6.92 (m, 3H, ArH), 6.84 (d,  $J = 8.0$  Hz, 2H) , ArH, 6.63-6.60 (m, 1H, ArH), 6.16 (d,  $J = 8.0$  Hz, 1H, CH), 5.76 (s, 1H, OH), 3.93 (s, 3H, OCH<sub>3</sub>), 2.26 (s, 3H, CH<sub>3</sub>). <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>;  $\delta$ , ppm) 159.4, 150.2, 145.1, 141.9, 137.9, 136.9, 135.3, 131.3, 131.1, 129.7, 129.6, 129.2, 129.1, 128.6, 128.2, 127.9, 126.8, 126.0, 124.9, 124.0, 123.8, 122.2, 114.7, 114.6, 114.2, 70.9, 55.4, 21.5. HRMS (APCI): m/z Calcd. For: C<sub>31</sub>H<sub>23</sub>BrO<sub>4</sub>S, 569.0421 [M-H]<sup>-</sup>, found: 569.0428.

### **7-Bromo-5-(p-tolyl)-11-tosyl-11*H*-benzo[*b*]fluoren-10-ol (3i)**



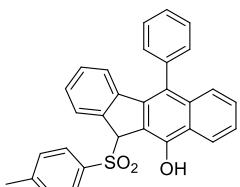
Red solid, mp 176-177 °C; IR (KBr, v, cm<sup>-1</sup>): 3469, 2920, 1621, 1577, 1418, 1354, 1289, 1232. <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>;  $\delta$ , ppm) 8.36 (d,  $J = 8.8$  Hz, 1H, ArH), 7.93 (d,  $J = 7.6$  Hz, 1H, ArH), 7.60-7.57 (m, 1H, ArH), 7.51 (s, 1H, ArH), 7.37-7.26 (m, 3H, ArH), 7.24 (d,  $J = 6.4$  Hz, 1H, ArH), 7.10-7.04 (m, 2H, ArH), 6.94 (d,  $J = 8.0$  Hz, 2H, ArH), 6.84 (d,  $J = 8.0$  Hz, 2H, ArH), 6.57 (d,  $J = 8.0$  Hz, 1H, ArH), 6.11 (d,  $J = 8.0$  Hz, 1H, CH), 5.77 (s, 1H, OH), 2.49 (s, 3H, CH<sub>3</sub>), 2.26 (s, 3H, CH<sub>3</sub>). <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>;  $\delta$ , ppm) 150.3, 144.9, 142.2, 138.2, 137.2, 136.4, 135.4, 135.3, 130.3, 130.2, 129.8, 129.4, 129.1, 129.0, 128.9, 128.5, 127.7, 127.5, 127.4, 126.8, 126.7, 125.1, 123.6, 123.5, 122.9, 70.9, 21.3, 21.5. HRMS (APCI): m/z Calcd. For: C<sub>31</sub>H<sub>23</sub>BrO<sub>3</sub>S, 553.0472 [M-H]<sup>-</sup>, found: 553.0490.

### **7-Bromo-5-phenyl-11-tosyl-11*H*-benzo[*b*]fluoren-10-ol (3j)**



Red solid, mp 200-201 °C; IR (KBr, v, cm<sup>-1</sup>): 3443, 3024, 1623, 1581, 1490, 1447, 1415, 1305, 1215. <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>;  $\delta$ , ppm) 8.37 (d,  $J = 8.8$  Hz, 1H, ArH), 7.93 (d,  $J = 7.6$  Hz, 1H, ArH), 7.65-7.40 (m, 5H, ArH), 7.30 (d,  $J = 7.6$  Hz, 1H, ArH), 7.23-7.16 (m, 1H, ArH), 7.03 (m, 1H, ArH), 6.95 (d,  $J = 8.4$  Hz, 2H, ArH), 6.85 (d,  $J = 8.0$  Hz, 2H, ArH), 6.70 (d,  $J = 7.2$  Hz, 1H, ArH), 6.03 (d,  $J = 8.0$  Hz, 1H, CH), 5.77 (s, 1H, OH), 2.27 (s, 3H, CH<sub>3</sub>). <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>;  $\delta$ , ppm) 150.3, 145.2, 141.7, 137.6, 137.18, 136.5, 135.4, 130.2, 130.1, 129.7, 129.6, 129.3, 129.1, 129.1, 128.7, 128.6, 128.2, 127.9, 126.8, 126.4, 124.9, 123.9, 123.7, 122.3, 114.2, 70.8, 21.5. HRMS (APCI): m/z Calcd. For: C<sub>30</sub>H<sub>21</sub>BrO<sub>3</sub>S, 539.0316 [M-H]<sup>-</sup>, found: 539.0343.

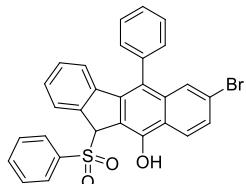
### **5-Phenyl-11-tosyl-11*H*-benzo[*b*]fluoren-10-ol (3k)**



Red solid, mp 212-213 °C; IR (KBr, v, cm<sup>-1</sup>): 3457, 3011, 1624, 1596, 1443, 1422, 1380, 1283.

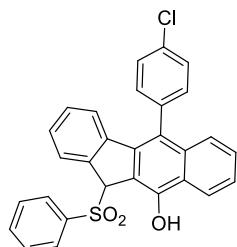
<sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>; δ, ppm) 8.52 (d, *J* = 8.4 Hz, 1H, ArH), 7.93 (d, *J* = 7.6 Hz, 1H, ArH), 7.57-7.39 (m, 6H, ArH), 7.36 (d, *J* = 8.4 Hz, 1H, ArH), 7.28 (d, *J* = 7.6 Hz, 1H, ArH), 7.24-7.20 (m, 1H, ArH), 7.07-6.92 (m, 3H, ArH), 6.83 (d, *J* = 8.0 Hz, 2H, ArH), 6.75 (d, *J* = 7.2 Hz, 1H, ArH), 6.07 (d, *J* = 8.0 Hz, 1H, CH), 5.80 (s, 1H, OH), 2.25 (s, 3H, CH<sub>3</sub>). <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>; δ, ppm) 150.3, 145.0, 142.2, 138.1, 136.3, 135.3, 135.2, 130.3, 130.2, 129.9, 129.5, 129.2, 129.1, 129.0, 128.6, 127.8, 127.5, 127.3, 127.3, 126.8, 126.1, 125.5, 125.3, 123.5, 123.1, 113.7, 70.9, 21.5. HRMS (APCI): m/z Calcd. For: C<sub>30</sub>H<sub>22</sub>O<sub>3</sub>S, 461.1211 [M-H]<sup>-</sup>, found: 461.1219.

### 7-Bromo-5-phenyl-11-(phenylsulfonyl)-11*H*-benzo[*b*]fluoren-10-ol (3l)



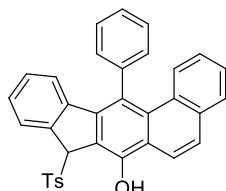
Yellow solid, mp 194-195 °C; IR (KBr, v, cm<sup>-1</sup>): 3449, 2953, 1644, 1578, 1545, 1483, 1324, 1298, 1206. <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>; δ, ppm) 8.38 (d, *J* = 8.8 Hz, 1H, ArH), 7.95 (d, *J* = 7.6 Hz, 1H, ArH), 7.61-7.58 (m, 1H, ArH), 7.55-7.50 (m, 2H, ArH), 7.49-7.28 (m, 5H, ArH), 7.20-7.18 (m, 1H, ArH), 7.11-7.00 (m, 5H, ArH), 6.72 (d, *J* = 7.2 Hz, 1H, ArH), 6.02 (d, *J* = 8.0 Hz, 1H, CH), 5.79 (s, 1H, OH). <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>; δ, ppm) 150.3, 141.7, 137.5, 137.1, 136.5, 135.2, 133.9, 132.7, 130.2, 130.0, 129.6, 129.3, 129.2, 129.1, 128.7, 128.2, 128.2, 128.0, 128.0, 127.0, 126.5, 124.9, 124.0, 123.7, 122.3, 114.0, 70.8. HRMS (APCI): m/z Calcd. For: C<sub>29</sub>H<sub>19</sub>BrO<sub>3</sub>S, 525.0159 [M-H]<sup>-</sup>, found: 525.0163.

### 5-(4-Chlorophenyl)-11-(phenylsulfonyl)-11*H*-benzo[*b*]fluoren-10-ol (3m)



Yellow solid, mp 192-193 °C; IR (KBr, v, cm<sup>-1</sup>): 3444, 2978, 1682, 1598, 1455, 1378, 1289, 1211. <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>; δ, ppm) 8.51 (d, *J* = 8.0 Hz, 1H, ArH), 7.88 (d, *J* = 1.2 Hz, 1H, ArH), 7.56-7.48 (m, 3H, ArH), 7.47-7.40 (m, 2H, ArH), 7.37-7.34 (m, 1H, ArH), 7.21-7.19 (m, 1H, ArH), 7.05-6.94 (m, 3H, ArH), 6.88 (d, *J* = 8.0 Hz, 2H, ArH), 6.76-6.67 (m, 1H, ArH), 5.96 (d, *J* = 8.4 Hz, 1H, CH), 5.74 (s, 1H, OH), 2.27 (s, 3H, CH<sub>3</sub>). <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>; δ, ppm) 150.3, 145.3, 140.6, 137.7, 137.0, 135.2, 133.3, 130.1, 130.0, 129.7, 129.7, 129.2, 129.1, 129.0, 128.7, 128.0, 127.5, 127.4, 126.7, 126.1, 125.6, 124.3, 123.1, 113.4, 70.6, 21.5. HRMS (APCI): m/z Calcd. For: C<sub>29</sub>H<sub>19</sub>ClO<sub>3</sub>S, 481.0664 [M-H]<sup>-</sup>, found: 481.0681.

### 13-Phenyl-8-tosyl-8*H*-indeno[2,1-*b*]phenanthren-7-ol (3n)

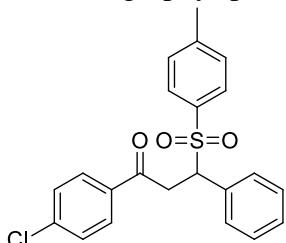


Yellow solid, mp 156-157 °C; IR (KBr, v, cm<sup>-1</sup>): 3445, 2911, 1668, 1599, 1538, 1505, 1373, 1302.

<sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>; δ, ppm) 8.77 (s, 1H, ArH), 8.47 (d, *J* = 8.8 Hz, 1H, ArH), 7.87 (s, 1H, ArH), 7.81-7.65 (m, 2H, ArH), 7.56-7.40 (m, 4H, ArH), 7.40-7.34 (m, 1H, ArH), 7.18-7.10 (m, 2H, ArH), 6.97 (m 1H, ArH), 6.89 (m, 3H, ArH), 6.77 (m, 3H, ArH), 5.71 (s, 1H, CH), 5.55 (d, *J* = 8.0 Hz, 1H, OH), 2.17 (s, 3H, CH<sub>3</sub>). <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>; δ, ppm) 149.4, 144.3, 141.1, 137.0, 136.9, 135.9, 134.6, 133.2, 129.3, 129.3, 129.2, 129.2, 129.1, 129.1, 128.9, 128.8, 128.3, 127.8, 127.8, 127.4, 127.1, 126.0, 125.7, 124.1, 123.2, 123.0, 121.4, 113.5, 70.1, 20.7. HRMS (APCI): m/z Calcd. For: C<sub>34</sub>H<sub>24</sub>O<sub>3</sub>S, 511.1367 [M-H]<sup>-</sup>, found: 511.1375.

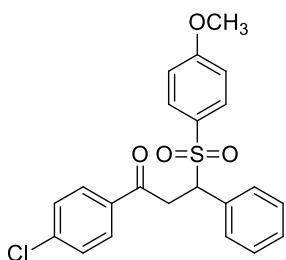
### Preparation of Compound 5a: 1-(4-Chlorophenyl)-3-phenyl-3-tosylpropan-1-one

A mixture of 1-(4-chlorophenyl)-3-phenylprop-2-en-1-one (**4a**, 0.25 mmol, 1.0 equiv.), tosylhydrazide (**2a**, 0.5 mmol, 2.0 equiv.), BPO (0.50 mmol, 2.0 equiv.), TBHP (0.25 mol, 1.0 equiv., 70% in water), TBAI (0.05 mmol, 0.2 equiv.), MeCN (2.5 mL) were added in a sealed 10-mL reaction vial. Then, the mixture was stirred in oil bath at 100 °C for 6 h until complete consumption of the starting material **4a** as detected by TLC. The mixture was cooled to room temperature and evaporated under vacuum. The crude mixture was purified by flash column chromatography (petroleum ether /ethyl acetate) to afford the desired product **5a** in 77% yield.



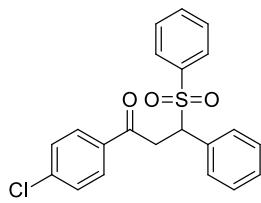
White solid, mp 199-201 °C; IR (KBr, ν, cm<sup>-1</sup>): 2949, 2921, 1689, 1589, 1489, 1311, 1229, 1142, 1086. <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>; δ, ppm) 7.81 (d, *J* = 8.4 Hz, 2H, ArH), 7.42-7.28 (m, 4H, ArH), 7.19-7.05 (m, 7H, ArH), 4.83-4.77 (m, 1H, CH), 4.01 (d, *J* = 3.6 Hz, 1H, CH<sub>2</sub>), 3.82 (d, *J* = 9.6 Hz, 1H, CH<sub>2</sub>), 2.32 (s, 3H, CH<sub>3</sub>). <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>; δ, ppm) 193.9, 144.8, 140.2, 134.5, 133.9, 132.6, 129.7, 129.5, 129.4, 129.1, 128.8, 128.5, 66.4, 37.0, 21.6. HRMS (ESI): m/z Calcd. For: C<sub>22</sub>H<sub>19</sub>ClO<sub>3</sub>S, 399.0821 [M+H]<sup>+</sup>, found: 399.0813.

### 1-(4-Chlorophenyl)-3-((4-methoxyphenyl)sulfonyl)-3-phenylpropan-1-one (**5b**)



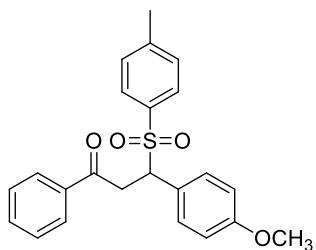
White solid, mp 182-183 °C; IR (KBr, ν, cm<sup>-1</sup>): 3060, 2920, 1689, 1595, 1497, 1314, 1258, 1139, 1089. <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>; δ, ppm) 7.95-7.83 (m, 2H, ArH), 7.43 (d, *J* = 8.4 Hz, 4H, ArH), 7.25-7.14 (m, 5H, ArH), 6.83 (d, *J* = 8.8 Hz, 2H, ArH), 4.88-4.85 (m, 1H, CH), 4.15-4.03 (m, 1H, CH<sub>2</sub>), 3.94-3.86 (m, 1H, CH<sub>2</sub>), 3.83 (s, 3H, OCH<sub>3</sub>). <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>; δ, ppm) 193.9, 163.8, 140.2, 134.5, 133.9, 132.7, 131.2, 129.7, 129.6, 129.1, 128.8, 128.5, 113.9, 66.6, 55.6, 37.0. HRMS (ESI): m/z Calcd. For: C<sub>22</sub>H<sub>19</sub>ClO<sub>4</sub>S, 415.0771 [M+H]<sup>+</sup>, found: 415.0774.

### 1-(4-Chlorophenyl)-3-phenyl-3-(phenylsulfonyl)propan-1-one (**5c**)



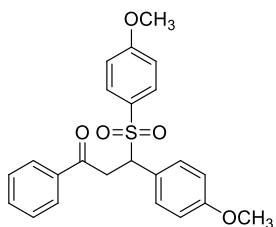
White solid, mp 190-192 °C; IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3063, 2921, 1690, 1588, 1447, 1306, 1226, 1139, 1085. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>;  $\delta$ , ppm) 7.95-7.85 (m, 2H, ArH), 7.58-7.53 (m, 3H, ArH), 7.45-7.37 (m, 4H, ArH), 7.26-7.16 (m, 5H, ArH), 4.93-4.89 (m, 1H, CH), 4.15-4.09 (m, 1H, CH<sub>2</sub>), 3.92-3.85 (m, 1H, CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>;  $\delta$ , ppm) 193.8, 140.3, 136.8, 134.4, 133.8, 132.4, 129.7, 129.6, 129.1, 129.0, 128.9, 128.7, 128.5, 66.4, 36.9. HRMS (ESI): m/z Calcd. For: C<sub>21</sub>H<sub>17</sub>ClO<sub>3</sub>S, 385.0665 [M+H]<sup>+</sup>, found: 385.0650.

### **3-(4-Methoxyphenyl)-1-phenyl-3-tosylpropan-1-one (5d)**



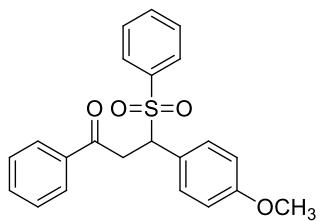
White solid, mp 186-187 °C; IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3071, 2938, 1670, 1601, 1498, 1310, 1243, 1145, 1087. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>;  $\delta$ , ppm) 7.95-7.87 (m, 2H, ArH), 7.42 (d,  $J$  = 8.4 Hz, 2H, ArH), 7.24-7.20 (m, 7H, ArH), 6.98-6.88 (m, 2H, ArH), 4.92-4.89 (m, 1H, CH), 4.09-4.01 (m, 1H, CH<sub>2</sub>), 3.91 (d,  $J$  = 9.6 Hz, 1H, CH<sub>2</sub>), 3.86 (s, 3H, OCH<sub>3</sub>), 2.38 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>;  $\delta$ , ppm) 193.4, 163.9, 144.7, 134.1, 132.7, 130.5, 129.8, 129.4, 129.3, 129.0, 128.7, 128.4, 113.9, 66.6, 55.5, 36.6, 21.6. HRMS (ESI): m/z Calcd. For: C<sub>23</sub>H<sub>22</sub>O<sub>4</sub>S, 395.1317 [M+H]<sup>+</sup>, found: 395.1318.

### **3-(4-Methoxyphenyl)-3-((4-methoxyphenyl)sulfonyl)-1-phenylpropan-1-one (5e)**



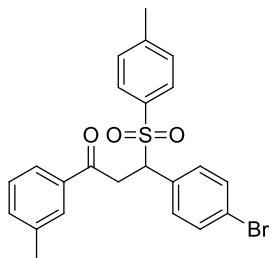
White solid, mp 181-182 °C; IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3061, 2920, 1671, 1598, 1499, 1305, 1238, 1138, 1088. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>;  $\delta$ , ppm) 7.92 (d,  $J$  = 8.8 Hz, 2H, ArH), 7.48-7.36 (m, 2H, ArH), 7.24-7.11 (m, 5H, ArH), 6.92 (d,  $J$  = 8.8 Hz, 2H, ArH), 6.82 (d,  $J$  = 8.8 Hz, 2H, ArH), 4.93 (s, 1H, CH), 4.08-4.00 (m, 1H, CH<sub>2</sub>), 3.90 (d,  $J$  = 9.6 Hz, 1H, CH<sub>2</sub>), 3.86 (s, 3H, OCH<sub>3</sub>), 3.83 (s, 3H, OCH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>;  $\delta$ , ppm) 193.4, 163.9, 163.7, 132.9, 131.2, 130.5, 129.8, 129.3, 128.7, 128.5, 128.4, 113.9, 113.9, 66.8, 55.6, 55.5, 36.6. HRMS (ESI): m/z Calcd. For: C<sub>23</sub>H<sub>22</sub>O<sub>5</sub>S, 411.1266 [M+H]<sup>+</sup>, found: 411.1262.

### **3-(4-Methoxyphenyl)-1-phenyl-3-(phenylsulfonyl)propan-1-one (5f)**



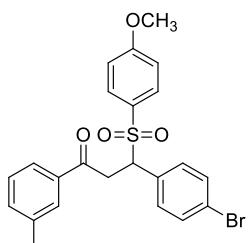
White solid, mp 178-179 °C; IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3060, 2939, 1671, 1598, 1499, 1306, 1256, 1138, 1089. <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>;  $\delta$ , ppm) 7.95 (d,  $J$  = 8.8 Hz, 2H, ArH), 7.61-7.52 (m, 3H, ArH), 7.41 (d,  $J$  = 8.0 Hz, 2H, ArH), 7.26-7.20 (m, 5H, ArH), 6.94 (d,  $J$  = 8.8 Hz, 2H, ArH), 4.97-4.94 (m, 1H, CH), 4.12-4.06 (m, 1H, CH<sub>2</sub>), 3.98-3.90 (m, 1H, CH<sub>2</sub>), 3.88 (s, 3H, CH<sub>3</sub>). <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>;  $\delta$ , ppm) 193.3, 163.9, 137.0, 133.7, 132.6, 130.5, 129.8, 129.2, 129.0, 128.758, 128.7, 128.4, 113.9, 66.6, 55.5, 36.4. HRMS (ESI): m/z Calcd. For: C<sub>22</sub>H<sub>20</sub>O<sub>4</sub>S, 381.1160 [M+H]<sup>+</sup>, found: 381.1161.

### **3-(4-Bromophenyl)-1-(m-tolyl)-3-tosylpropan-1-one (5g)**



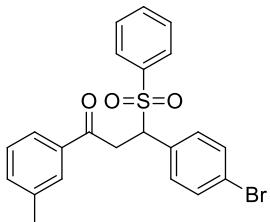
White solid, mp 181-182 °C; IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3073, 2939, 1688, 1595, 1486, 1302, 1286, 1084. <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>;  $\delta$ , ppm) 7.74-7.70 (m, 2H, ArH), 7.45 (d,  $J$  = 8.4 Hz, 2H, ArH), 7.40-7.32 (m, 4H, ArH), 7.22 (d,  $J$  = 8.0 Hz, 2H, ArH), 7.11-7.07 (m, 2H, ArH), 4.87-4.84 (m, 1H, CH), 4.10-4.05 (m, 1H, CH<sub>2</sub>), 3.91-3.84 (m, 1H, CH<sub>2</sub>), 2.40 (d,  $J$  = 2.8 Hz, 6H, CH<sub>3</sub>). <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>;  $\delta$ , ppm) 194.9, 145.0, 138.6, 136.0, 134.5, 133.8, 131.8, 131.6, 131.3, 129.6, 129.0, 128.6, 128.6, 125.3, 123.0, 65.9, 37.0, 21.7, 21.3. HRMS (ESI): m/z Calcd. For: C<sub>23</sub>H<sub>21</sub>BrO<sub>3</sub>S, 457.0473 [M+H]<sup>+</sup>, found: 457.0465.

### **3-(4-Bromophenyl)-3-((4-methoxyphenyl)sulfonyl)-1-(m-tolyl)propan-1-one (5h)**



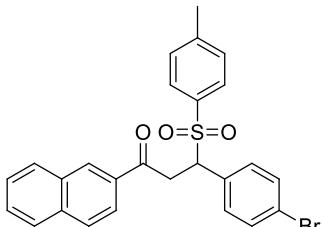
White solid, mp 173-175 °C; IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3079, 2941, 1685, 1596, 1498, 1298, 1261, 1147, 1086, 1008. <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>;  $\delta$ , ppm) 7.72 (s, 2H, ArH), 7.48 (d,  $J$  = 8.8 Hz, 2H, ArH), 7.40-7.32 (m, 4H, ArH), 7.09 (d,  $J$  = 8.4 Hz, 2H, ArH), 6.87 (d,  $J$  = 8.8 Hz, 2H, ArH), 4.86-4.81 (m, 1H, CH), 4.06 (d,  $J$  = 3.2 Hz, 1H, CH<sub>2</sub>), 3.94-3.87 (m, 1H, CH<sub>2</sub>), 3.85 (s, 3H, OCH<sub>3</sub>), 2.40 (s, 3H, CH<sub>3</sub>). <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>;  $\delta$ , ppm) 195.0, 163.9, 138.7, 136.0, 134.6, 133.9, 132.0, 131.7, 131.3, 131.2, 128.7, 128.2, 125.3, 123.0, 114.1, 66.1, 55.7, 37.1, 21.3. HRMS (ESI): m/z Calcd. For: C<sub>23</sub>H<sub>21</sub>BrO<sub>4</sub>S, 473.0422 [M+H]<sup>+</sup>, found: 473.0440.

**3-(4-Bromophenyl)-3-(phenylsulfonyl)-1-(*m*-tolyl)propan-1-one (5i)**



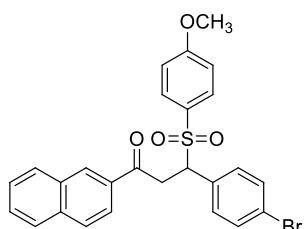
White solid, mp 174-175 °C; IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3064, 2949, 1684, 1585, 1490, 1307, 1255, 1142, 1085. <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>;  $\delta$ , ppm) 7.75-7.70 (m, 2H, ArH), 7.62-7.56 (m, 3H, ArH), 7.46-7.31 (m, 6H, ArH), 7.07 (d,  $J$  = 8.4 Hz, 2H, ArH), 4.90-4.86 (m, 1H, CH), 4.12-4.07 (m, 1H, CH<sub>2</sub>), 3.94-3.83 (m, 1H, CH<sub>2</sub>), 2.40 (s, 3H, CH<sub>3</sub>). <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>;  $\delta$ , ppm) 194.8, 138.7, 136.8, 136.0, 134.6, 133.9, 131.7, 131.3, 129.0, 128.9, 128.7, 128.7, 125.3, 123.1, 65.9, 36.9, 21.3. HRMS (ESI): m/z Calcd. For: C<sub>22</sub>H<sub>19</sub>BrO<sub>3</sub>S, 443.0316 [M+H]<sup>+</sup>, found: 443.0327.

**3-(4-Bromophenyl)-1-(naphthalen-2-yl)-3-tosylpropan-1-one (5j)**



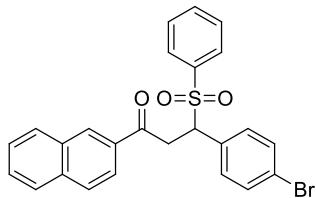
White solid, mp 179-180 °C; IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3068, 2924, 1679, 1598, 1490, 1303, 1256, 1142, 1089. <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>;  $\delta$ , ppm) 8.49 (s, 1H, ArH), 7.99 (d,  $J$  = 8.0 Hz, 1H, ArH), 7.93 (d,  $J$  = 8.4 Hz, 1H, ArH), 7.87 (d,  $J$  = 8.8 Hz, 2H, ArH), 7.65-7.58 (m, 2H, ArH), 7.48 (d,  $J$  = 8.0 Hz, 2H, ArH), 7.35 (d,  $J$  = 8.4 Hz, 2H, ArH), 7.23 (d,  $J$  = 8.0 Hz, 2H, ArH), 7.13 (d,  $J$  = 8.4 Hz, 2H, ArH), 4.94-4.89 (m, 1H, CH), 4.26-7.21 (m, 1H, CH<sub>2</sub>), 4.07-4.00 (m, 1H, CH<sub>2</sub>), 2.41 (s, 3H, CH<sub>3</sub>). <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>;  $\delta$ , ppm) 194.6, 145.1, 135.8, 133.8, 133.3, 132.4, 131.8, 131.7, 131.4, 130.2, 129.7, 129.6, 129.0, 128.9, 128.7, 127.8, 127.1, 123.5, 123.1, 66.0, 37.0, 21.7. HRMS (ESI): m/z Calcd. For: C<sub>25</sub>H<sub>19</sub>BrO<sub>3</sub>S, 493.0473 [M+H]<sup>+</sup>, found: 493.0482.

**3-(4-Bromophenyl)-3-((4-methoxyphenyl)sulfonyl)-1-(naphthalen-2-yl)propan-1-one (5k)**



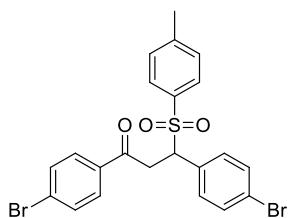
White solid, mp 196-197 °C; IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3059, 2923, 1682, 1594, 1497, 1315, 1259, 1141, 1090. <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>;  $\delta$ , ppm) 8.49 (s, 1H, ArH), 7.99 (d,  $J$  = 8.0 Hz, 1H, ArH), 7.93 (d,  $J$  = 8.8 Hz, 1H, ArH), 7.87 (d,  $J$  = 8.4 Hz, 2H, ArH), 7.64-7.56 (m, 2H, ArH), 7.51 (d,  $J$  = 8.4 Hz, 2H, ArH), 7.36 (d,  $J$  = 8.0 Hz, 2H, ArH), 7.13 (d,  $J$  = 8.4 Hz, 2H, ArH), 6.88 (d,  $J$  = 8.8 Hz, 2H, ArH), 4.92-4.87 (m, 1H, CH), 4.22 (d,  $J$  = 3.2 Hz, 1H, CH<sub>2</sub>), 4.05 (d,  $J$  = 10.0 Hz, 1H, CH<sub>2</sub>), 3.85 (s, 3H, OCH<sub>3</sub>). <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>;  $\delta$ , ppm) 194.5, 144.5, 137.4, 137.1, 136.7, 133.7, 133.6, 131.0, 130.0, 129.5, 129.4, 129.1, 128.7, 128.3, 127.0, 66.2, 36.8, 21.7, 19.7, 19.5. HRMS (ESI): m/z Calcd. For: C<sub>26</sub>H<sub>21</sub>BrO<sub>4</sub>S, 509.0422 [M+H]<sup>+</sup>, found: 509.0426.

**3-(4-Bromophenyl)-1-(naphthalen-2-yl)-3-(phenylsulfonyl)propan-1-one (5l)**



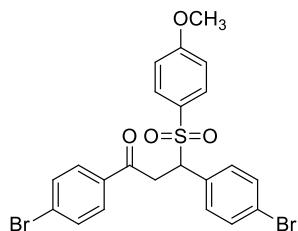
White solid, mp 191-192 °C; IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3065, 2923, 1675, 1589, 1490, 1307, 1225, 1123, 1086. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>;  $\delta$ , ppm) 8.50 (s, 1H, ArH), 7.99 (d,  $J$  = 7.6 Hz, 1H, ArH), 7.95-7.92 (m, 1H, ArH), 7.88 (d,  $J$  = 8.8 Hz, 2H, ArH), 7.65-7.57 (m, 5H, ArH), 7.46-7.42 (m, 2H, ArH), 7.35 (d,  $J$  = 8.4 Hz, 2H, ArH), 7.11 (d,  $J$  = 8.4 Hz, 2H, ArH), 4.96-4.92 (m, 1H, CH), 4.29-4.23 (m, 1H, CH<sub>2</sub>), 4.09-4.02 (m, 1H, CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>;  $\delta$ , ppm) 194.5, 136.8, 135.9, 134.0, 133.3, 132.4, 131.7, 131.3, 130.2, 129.7, 129.0, 128.7, 127.8, 127.1, 123.5, 123.2, 66.1, 36.8. HRMS (ESI): m/z Calcd. For: C<sub>25</sub>H<sub>19</sub>BrO<sub>3</sub>S, 481.0290 [M+H]<sup>+</sup>, found: 481.0302.

**1,3-Bis(4-bromophenyl)-3-tosylpropan-1-one (5m)**



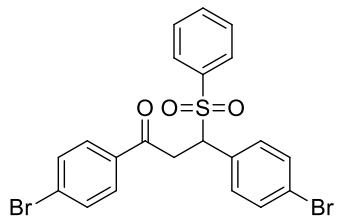
White solid, mp 203-204 °C; IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3068, 2922, 1689, 1584, 1491, 1299, 1227, 1137, 1010. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>;  $\delta$ , ppm) 7.79 (d,  $J$  = 8.4 Hz, 2H, ArH), 7.61 (d,  $J$  = 8.4 Hz, 2H, ArH), 7.44 (d,  $J$  = 8.4 Hz, 2H, ArH), 7.35 (d,  $J$  = 8.4 Hz, 2H, ArH), 7.22 (d,  $J$  = 8.0 Hz, 2H, ArH), 7.07 (d,  $J$  = 8.4 Hz, 2H, ArH), 4.84-4.81 (m, 1H, CH), 4.05 (d,  $J$  = 3.6 Hz, 1H, CH<sub>2</sub>), 3.83 (d,  $J$  = 10.0 Hz, 1H, CH<sub>2</sub>), 2.41 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>;  $\delta$ , ppm) 193.8, 145.1, 134.7, 133.6, 132.2, 131.7, 131.3, 129.6, 129.2, 129.0, 123.2, 65.8, 37.0, 21.7. HRMS (ESI): m/z Calcd. For: C<sub>22</sub>H<sub>18</sub>Br<sub>2</sub>O<sub>3</sub>S, 522.9396 [M+H]<sup>+</sup>, found: 522.9390.

**1,3-Bis(4-bromophenyl)-3-((4-methoxyphenyl)sulfonyl)propan-1-one (5n)**



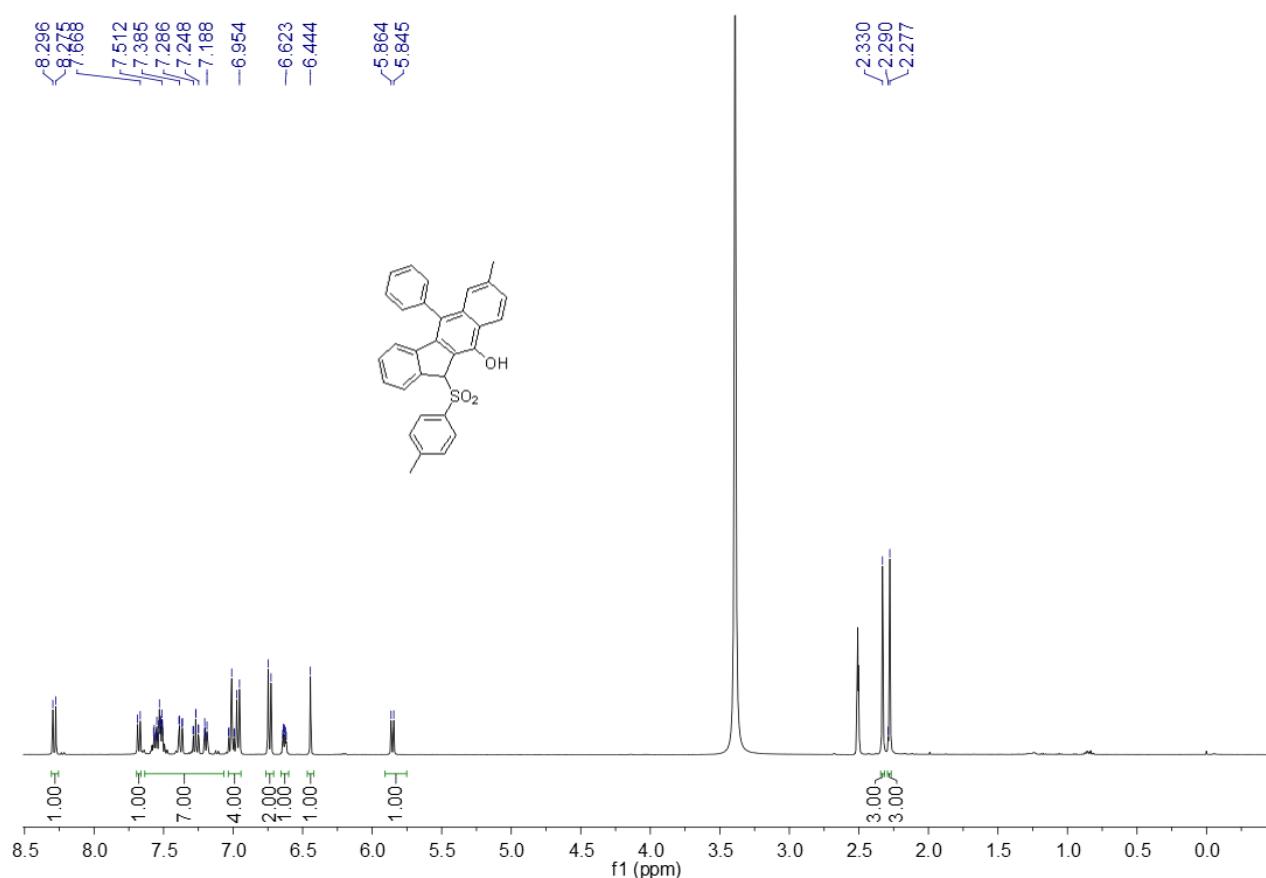
White solid, mp 210-211 °C; IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3093, 2921, 1687, 1595, 1495, 1261, 1226, 1136, 1087. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>;  $\delta$ , ppm) 7.79 (d,  $J$  = 8.4 Hz, 2H, ArH), 7.61 (d,  $J$  = 8.4 Hz, 2H, ArH), 7.47 (d,  $J$  = 8.8 Hz, 2H, ArH), 7.35 (d,  $J$  = 8.4 Hz, 2H, ArH), 7.07 (d,  $J$  = 8.4 Hz, 2H, ArH), 6.87 (d,  $J$  = 8.8 Hz, 2H, ArH), 4.81 (d,  $J$  = 6.0 Hz, 1H, CH), 4.10-4.05 (m, 1H, CH<sub>2</sub>), 3.85 (s, 3H, OCH<sub>3</sub>), 3.82 (d,  $J$  = 10.0 Hz, 1H, CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>;  $\delta$ , ppm) 193.9, 163.9, 134.7, 132.2, 131.9, 131.7, 131.3, 131.2, 129.6, 129.2, 128.0, 123.2, 114.2, 66.0, 55.7, 37.0. HRMS (ESI): m/z Calcd. For: C<sub>22</sub>H<sub>18</sub>Br<sub>2</sub>O<sub>3</sub>S, 538.9345 [M+H]<sup>+</sup>, found: 538.9329.

**1,3-Bis(4-bromophenyl)-3-(phenylsulfonyl)propan-1-one (5o)**

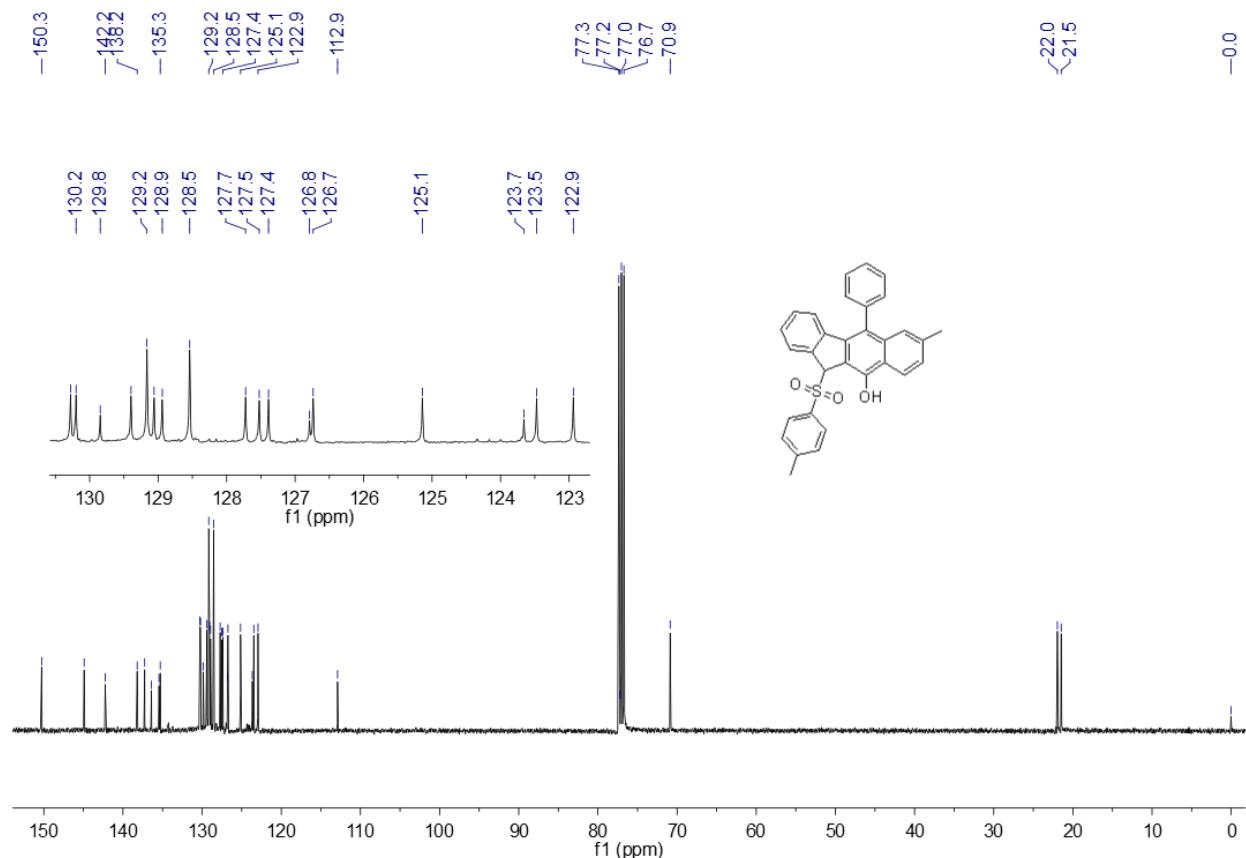


White solid, mp 180-181 °C; IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3059, 2919, 1686, 1584, 1489, 1307, 1227, 1142, 1082. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>;  $\delta$ , ppm) 7.79 (d,  $J$  = 8.4 Hz, 2H, ArH), 7.63-7.55 (m, 5H, ArH), 7.45-7.41 (m, 2H, ArH), 7.34 (d,  $J$  = 8.4 Hz, 2H, ArH), 7.06 (d,  $J$  = 8.4 Hz, 2H, ArH), 4.88-4.83 (m, 1H, CH), 4.13-4.06 (m, 1H, CH<sub>2</sub>), 3.85 (d,  $J$  = 10.0 Hz, 1H, CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>;  $\delta$ , ppm) 193.7, 136.6, 134.7, 134.0, 132.2, 131.7, 131.6, 131.2, 129.6, 129.2, 129.0, 123.3, 65.8, 36.8. HRMS (ESI): m/z Calcd. For: C<sub>21</sub>H<sub>16</sub>Br<sub>2</sub>O<sub>3</sub>S, 508.9240 [M+H]<sup>+</sup>, found: 508.9246.

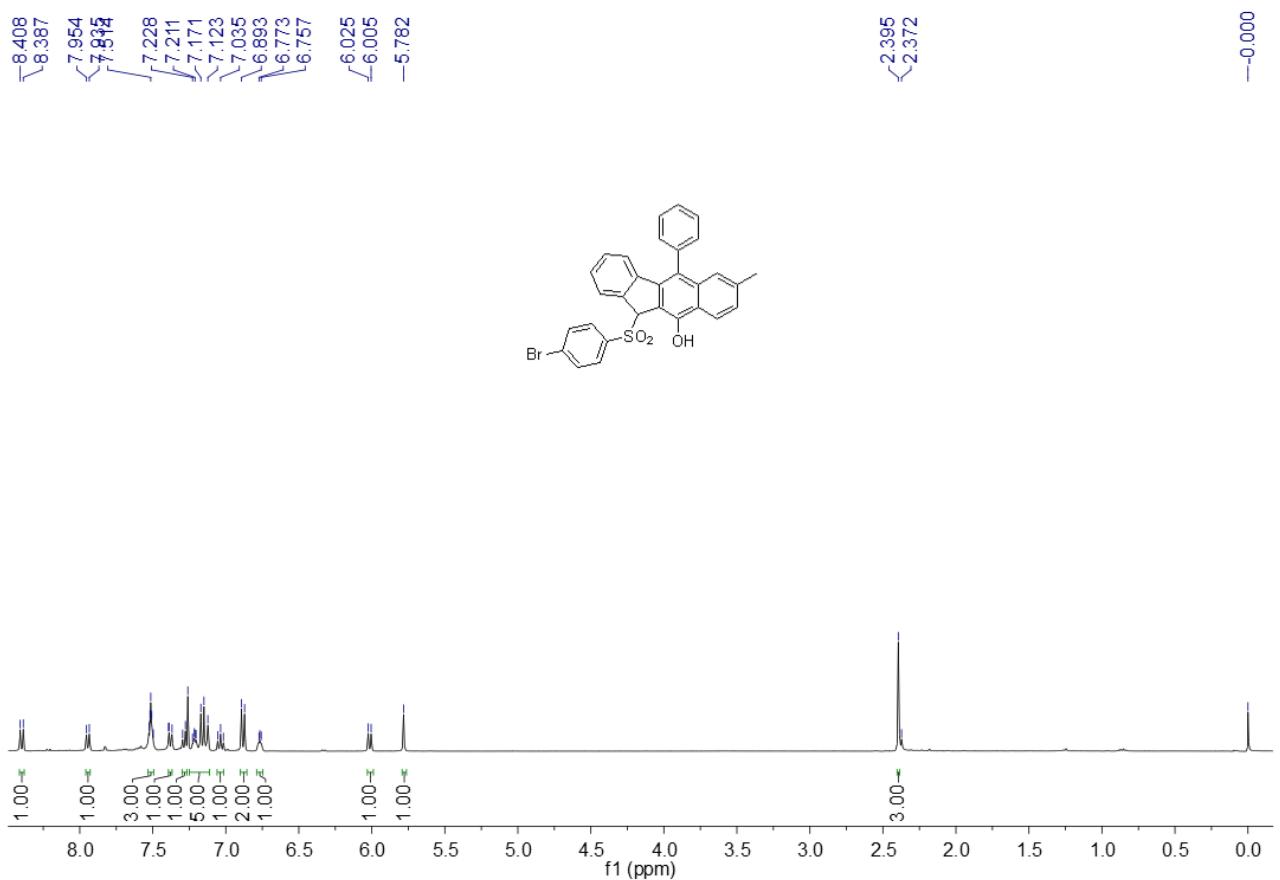
**Copies of  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of Compounds 3 and 5**



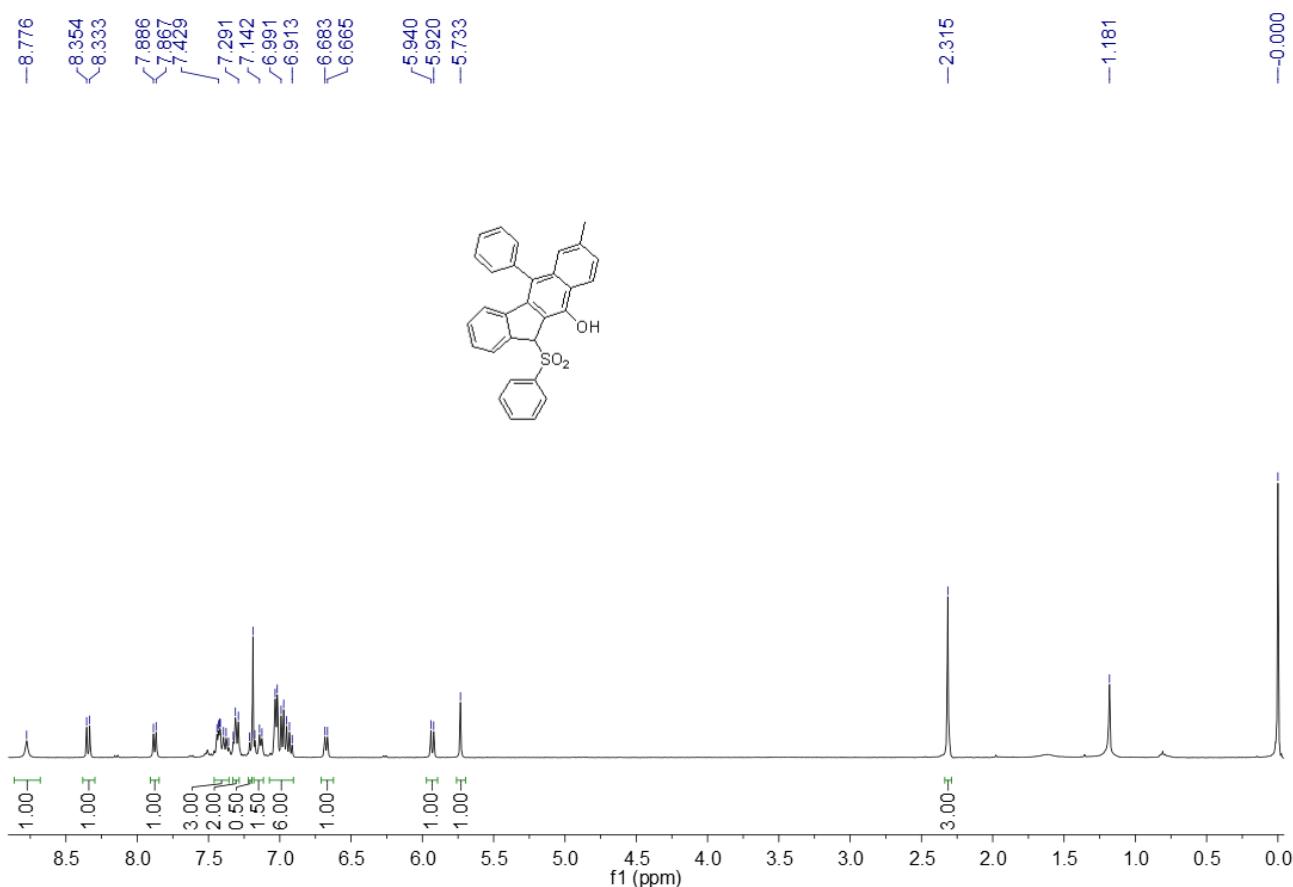
$^1\text{H}$  NMR Spectrum of Compound 3a



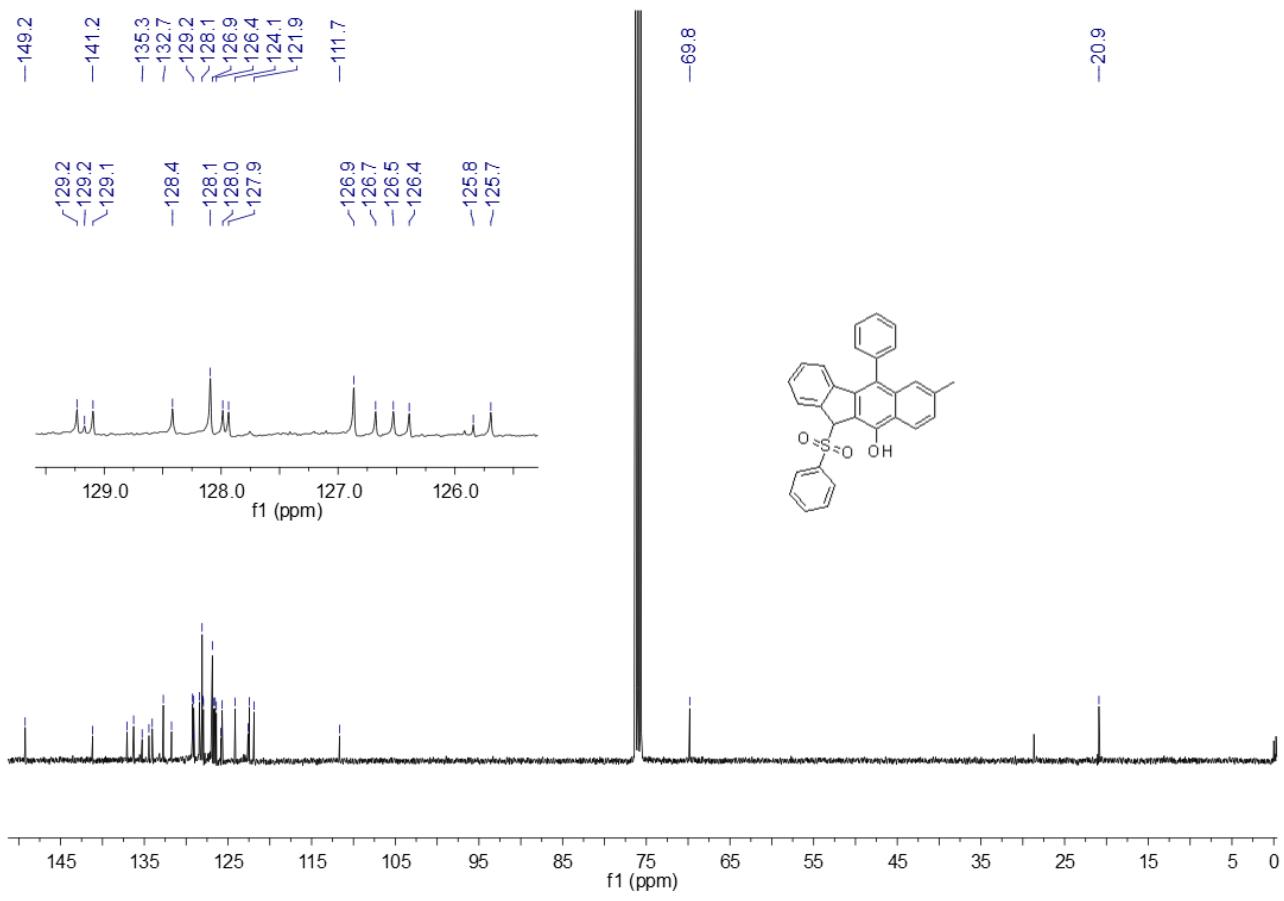
$^{13}\text{C}$  NMR Spectrum of Compound 3a



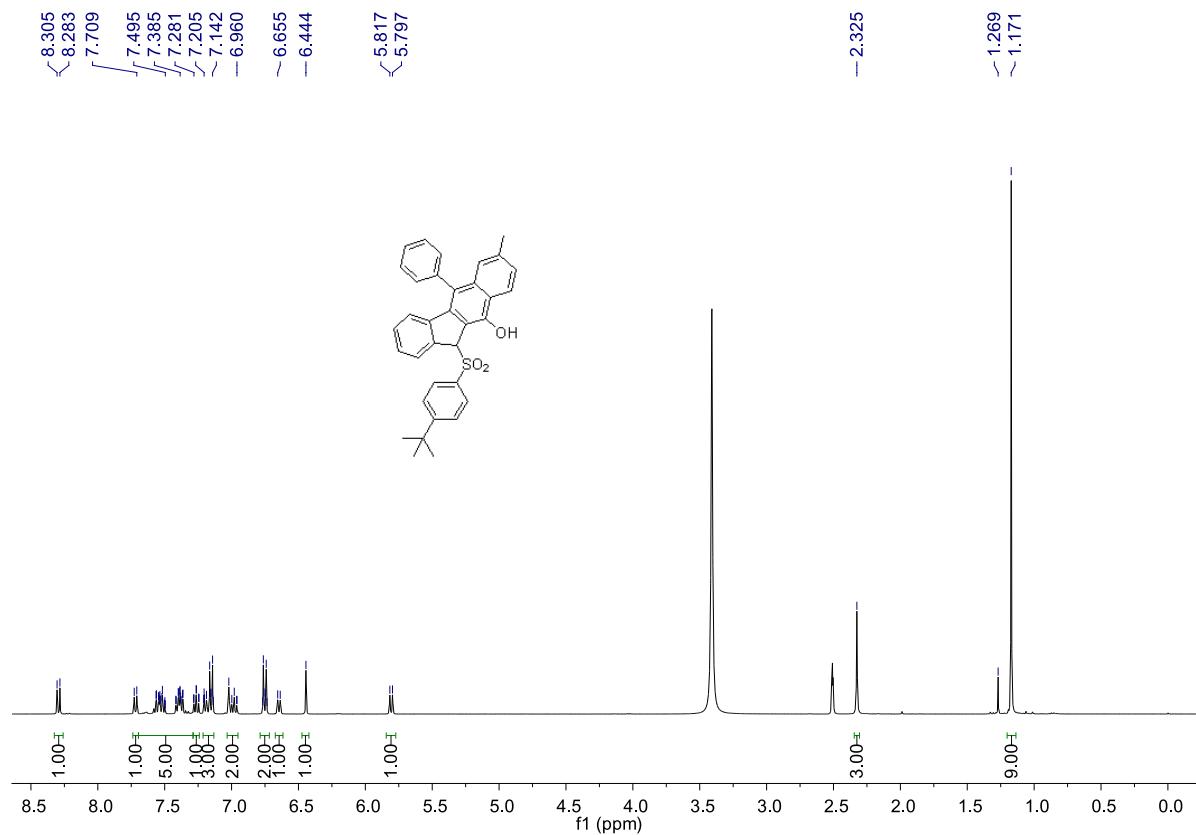
**<sup>1</sup>H NMR Spectrum of Compound 3b**



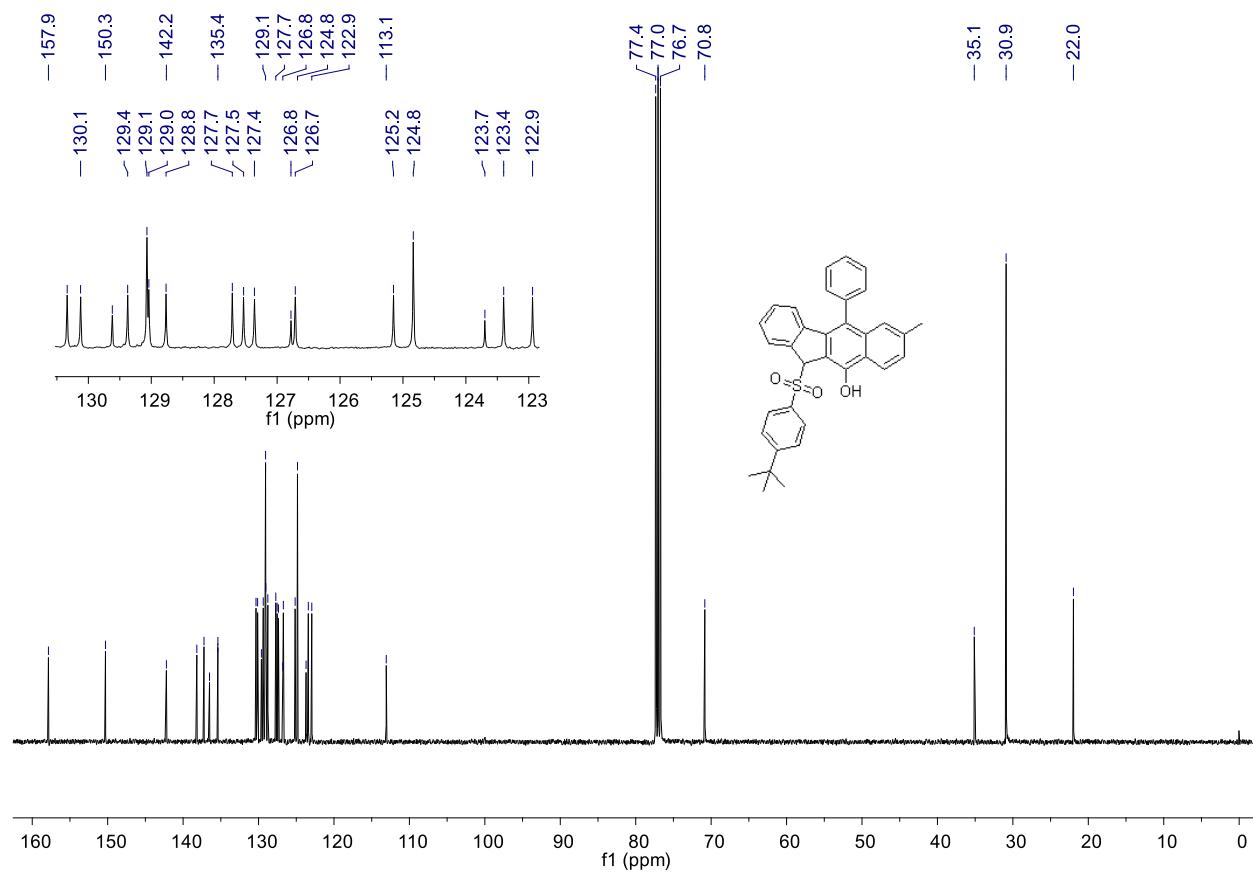
**<sup>1</sup>H NMR Spectrum of Compound 3c**



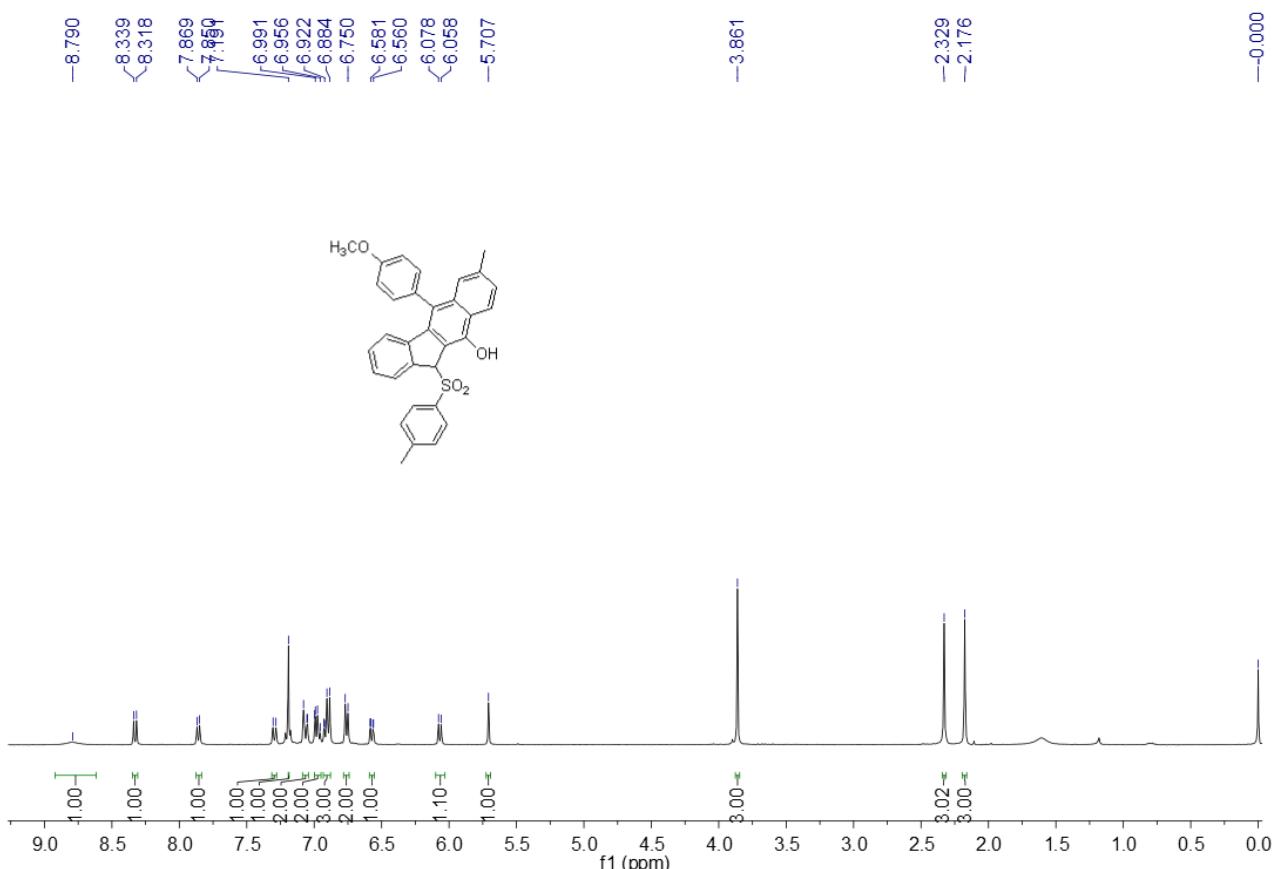
<sup>13</sup>C NMR Spectrum of Compound 3c



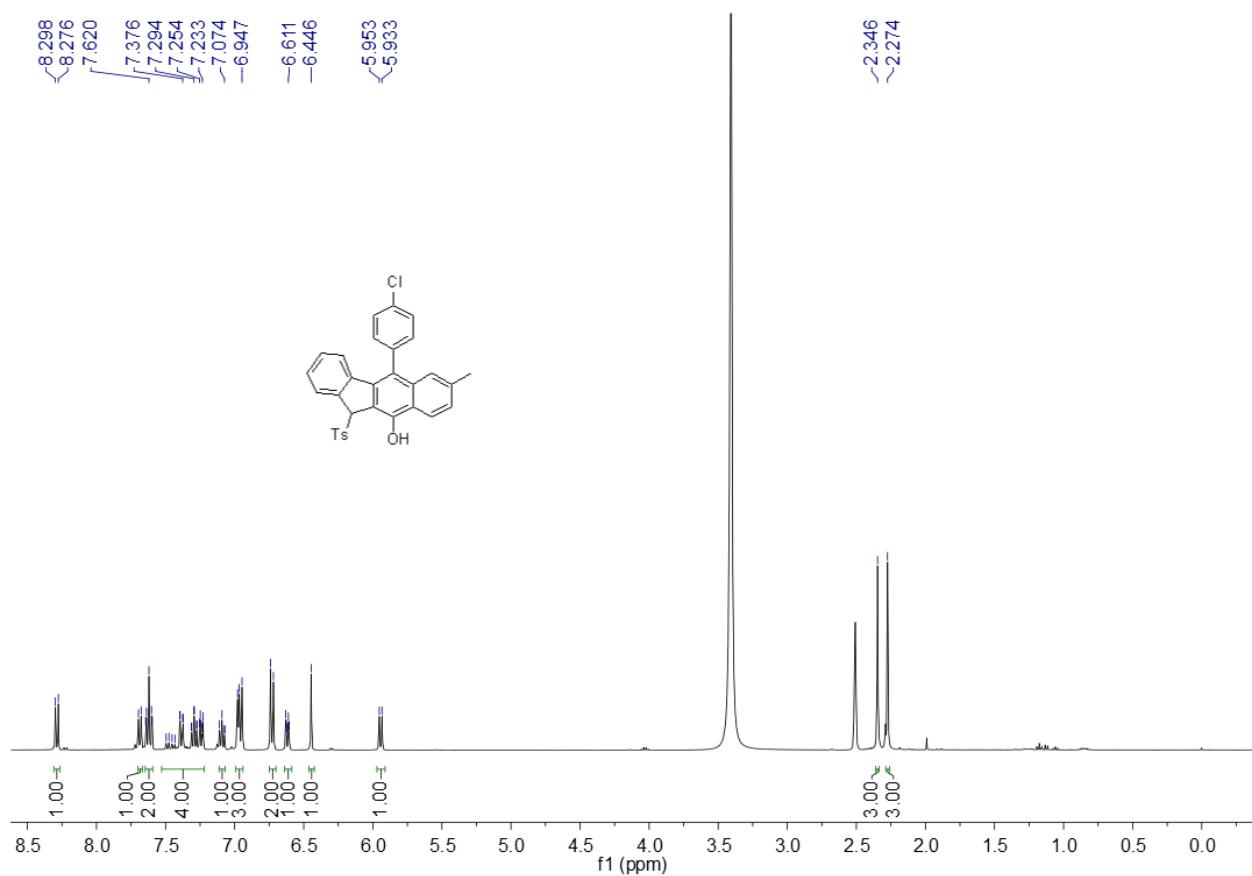
<sup>1</sup>H NMR Spectrum of Compound 3d



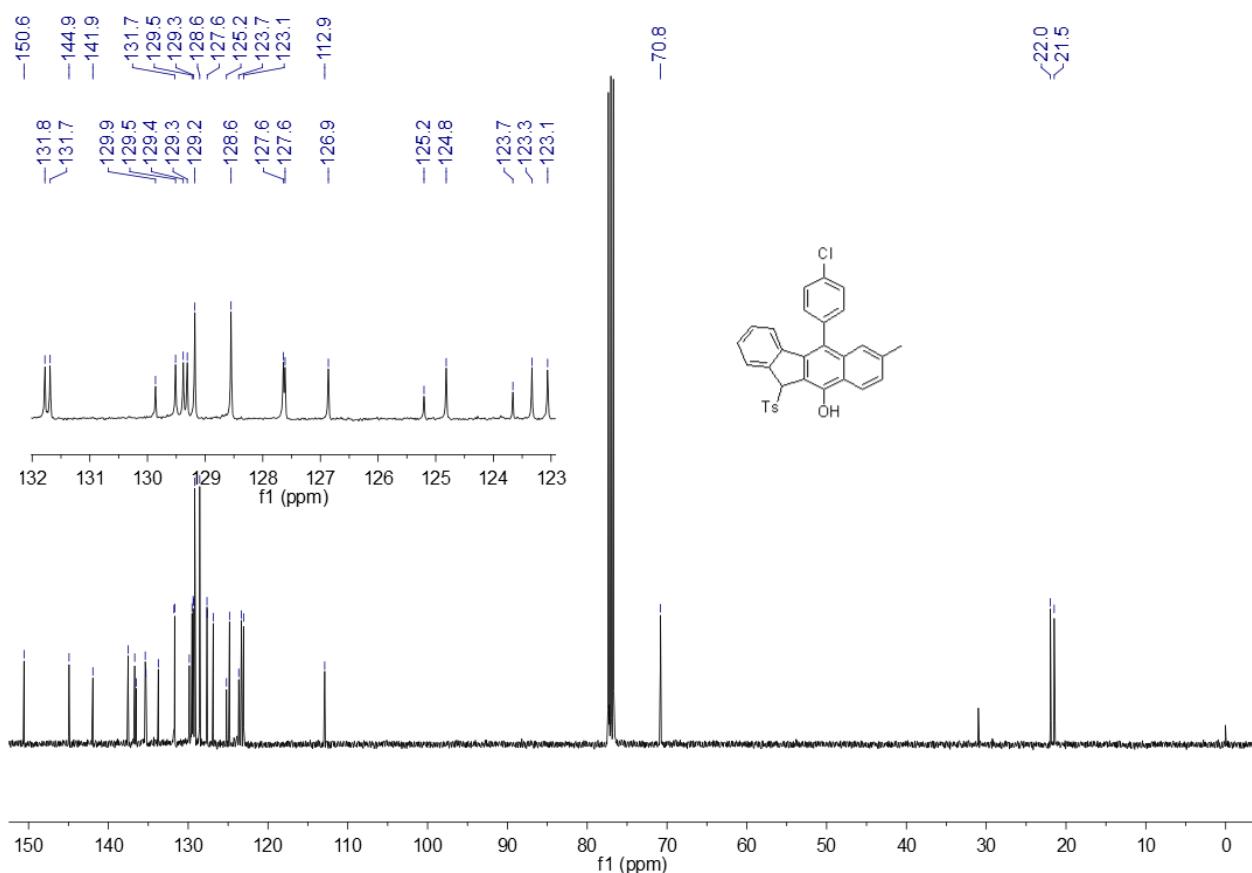
<sup>13</sup>C NMR Spectrum of Compound 3d



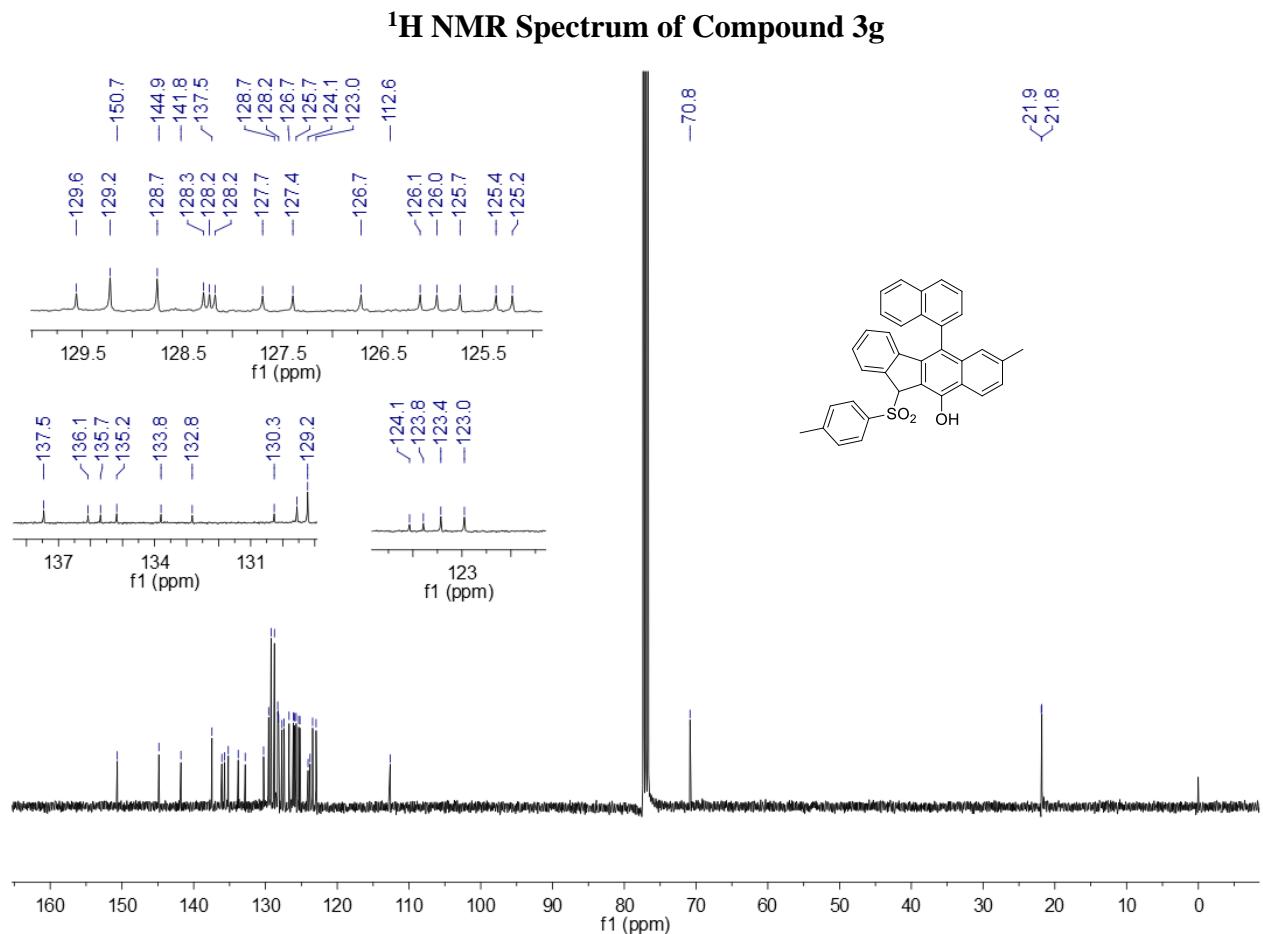
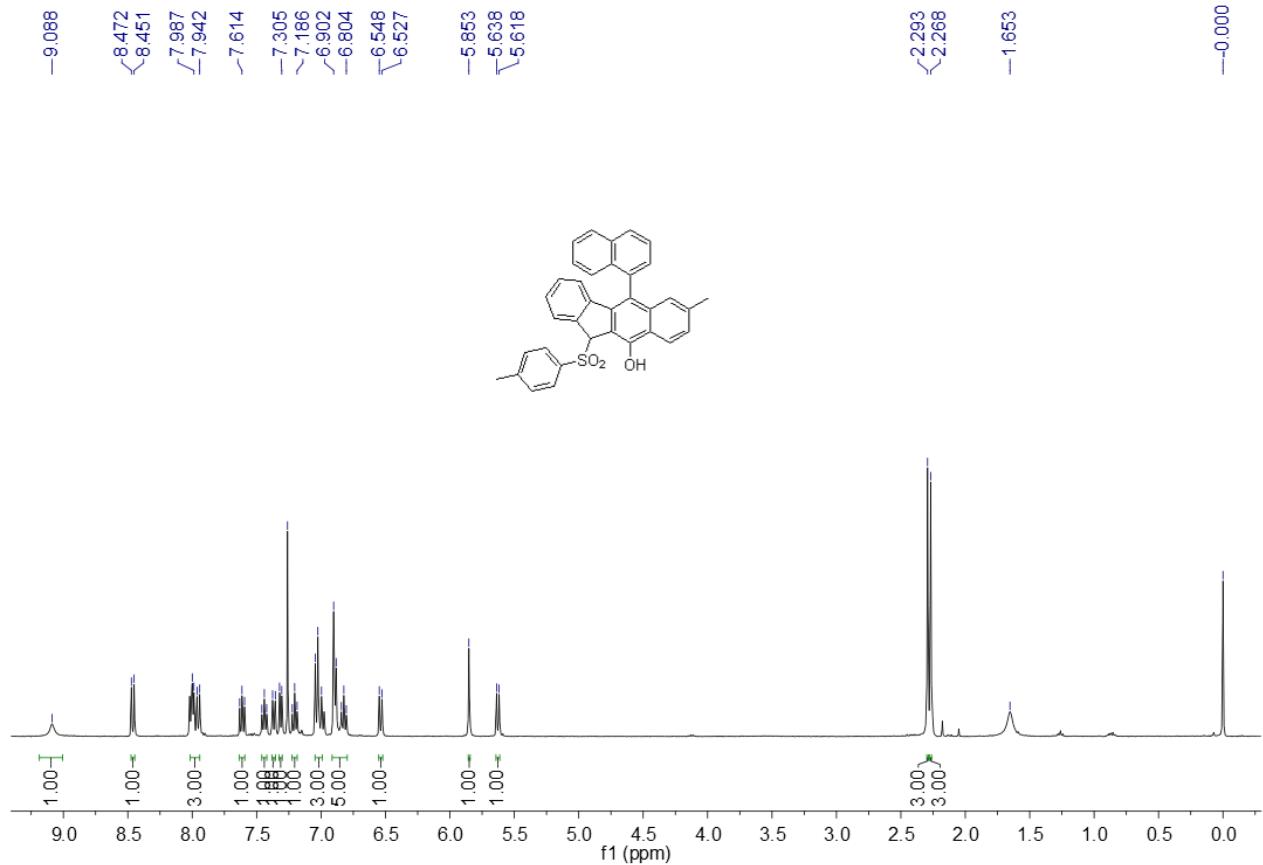
<sup>1</sup>H NMR Spectrum of Compound 3e

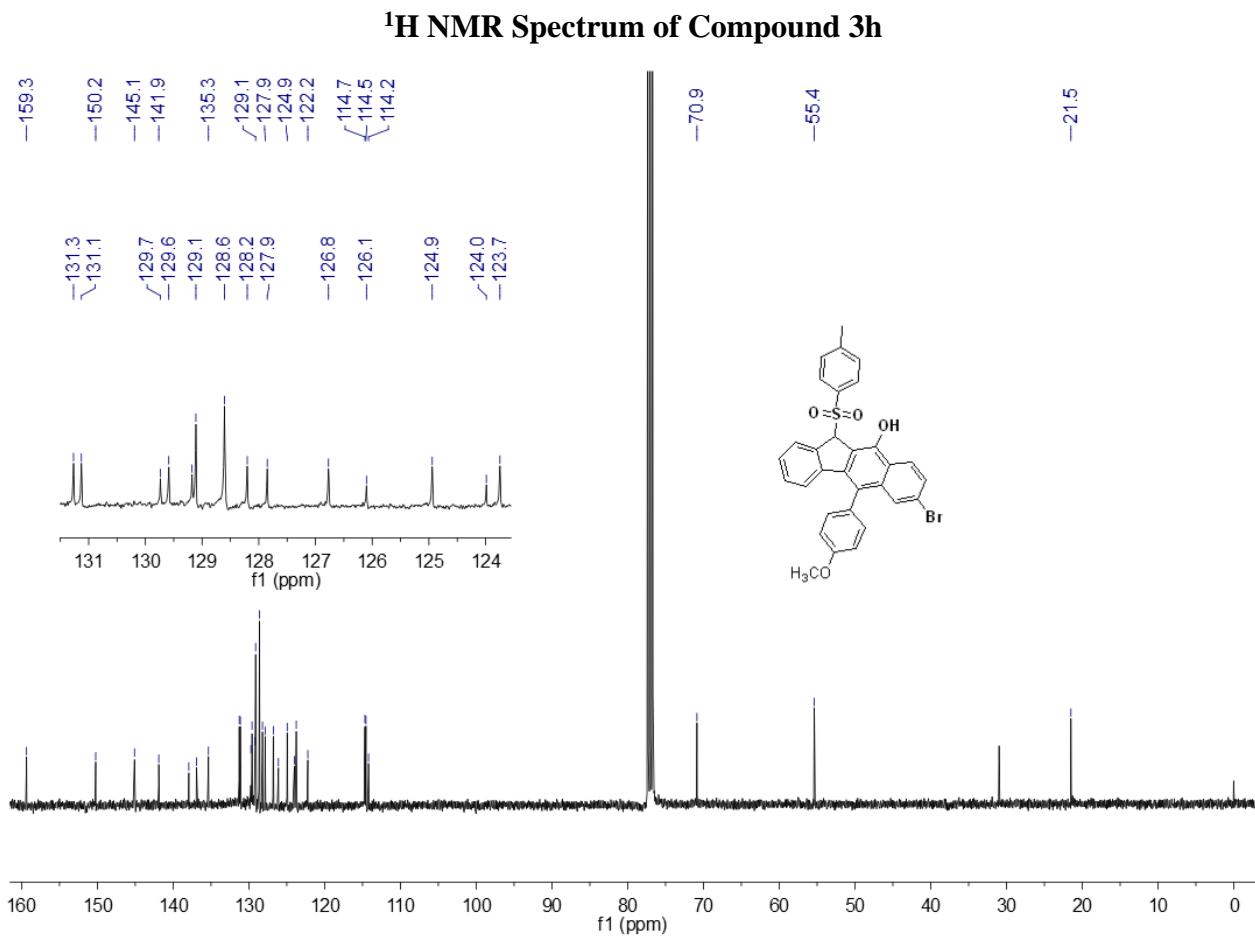
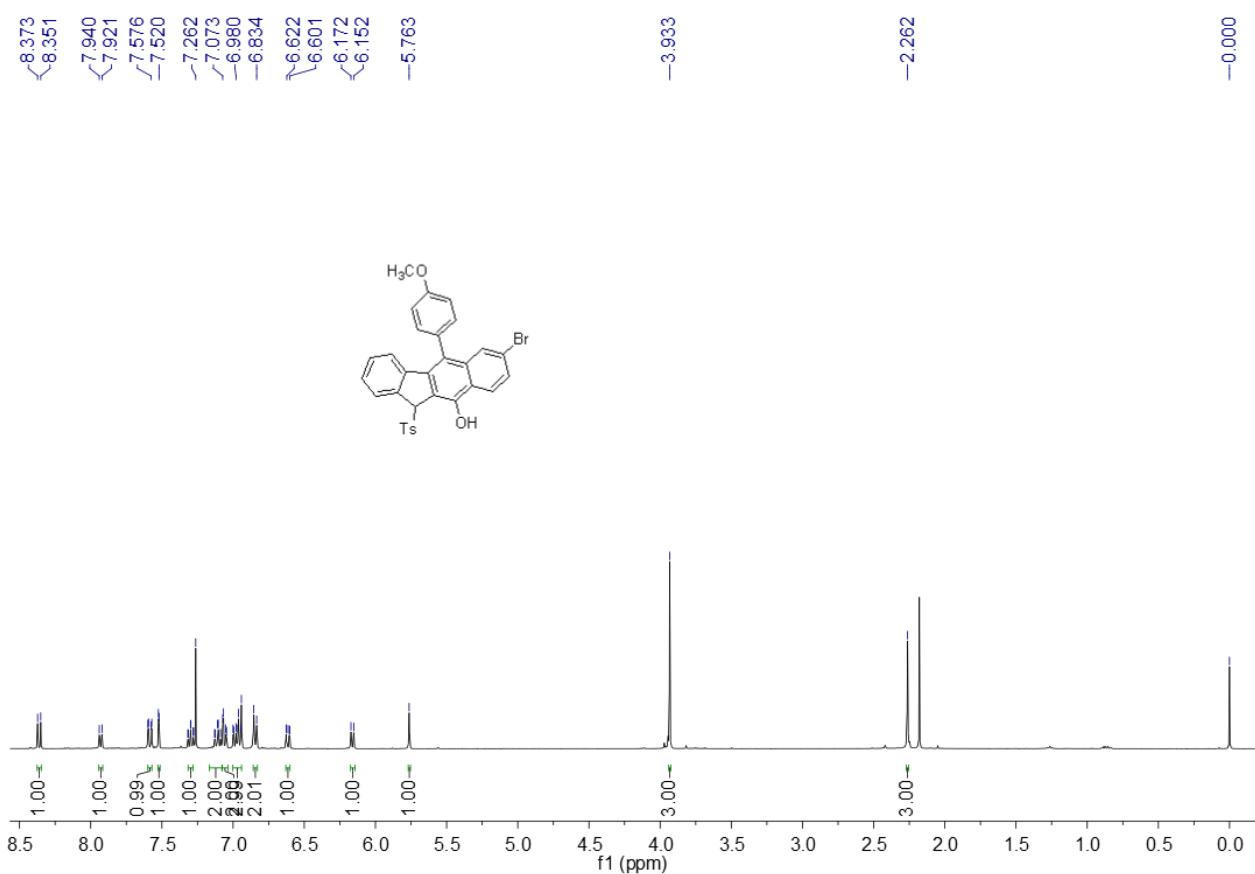


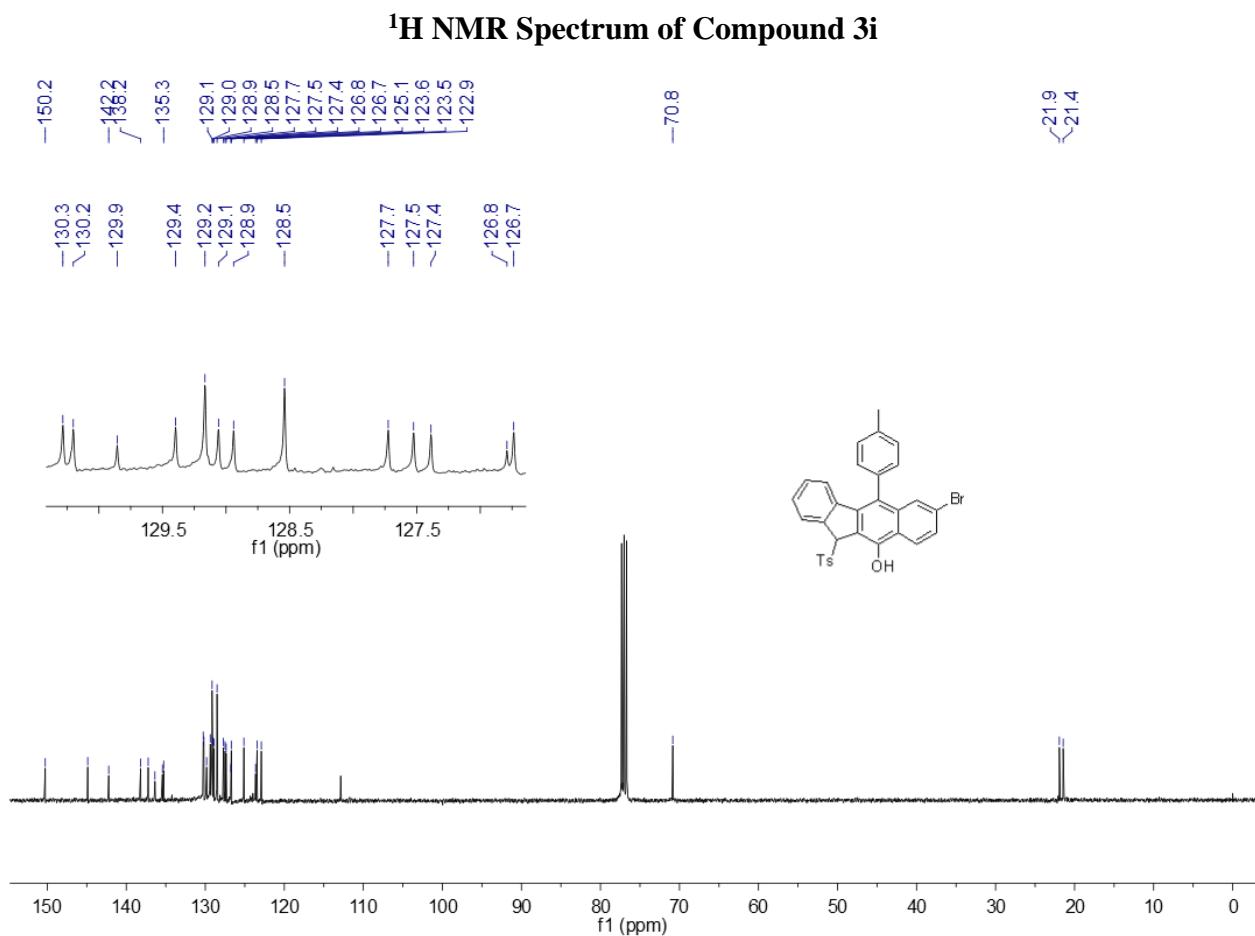
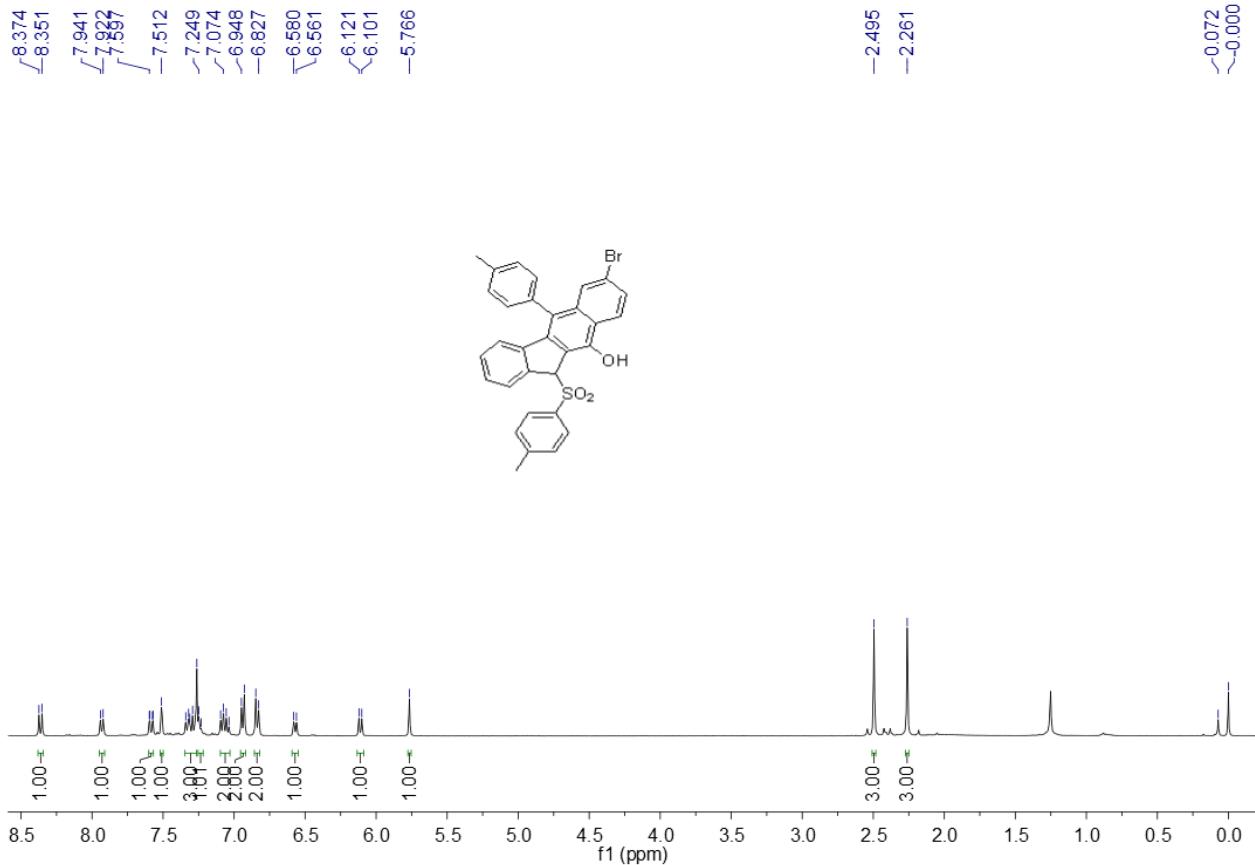
**<sup>1</sup>H NMR Spectrum of Compound 3f**

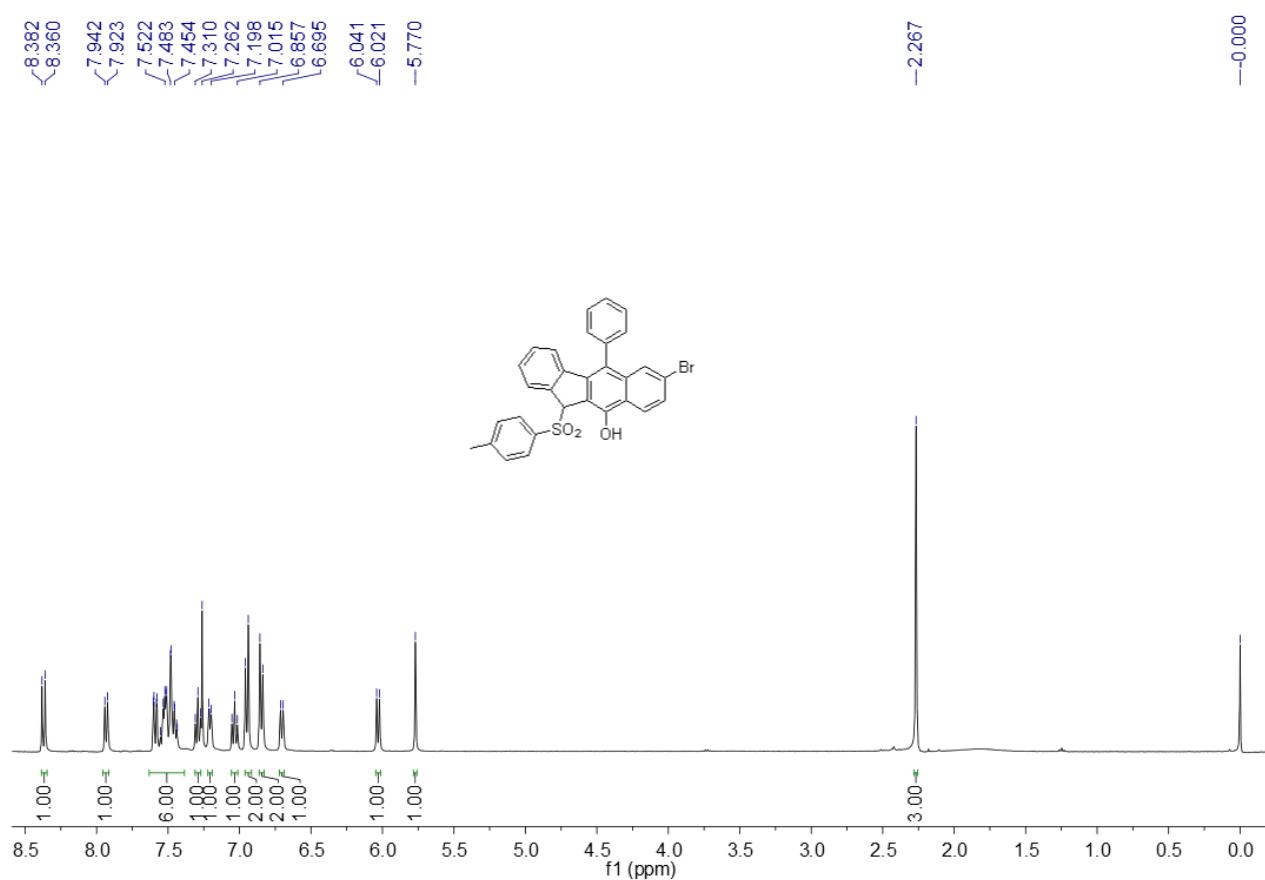


**<sup>13</sup>C NMR Spectrum of Compound 3f**

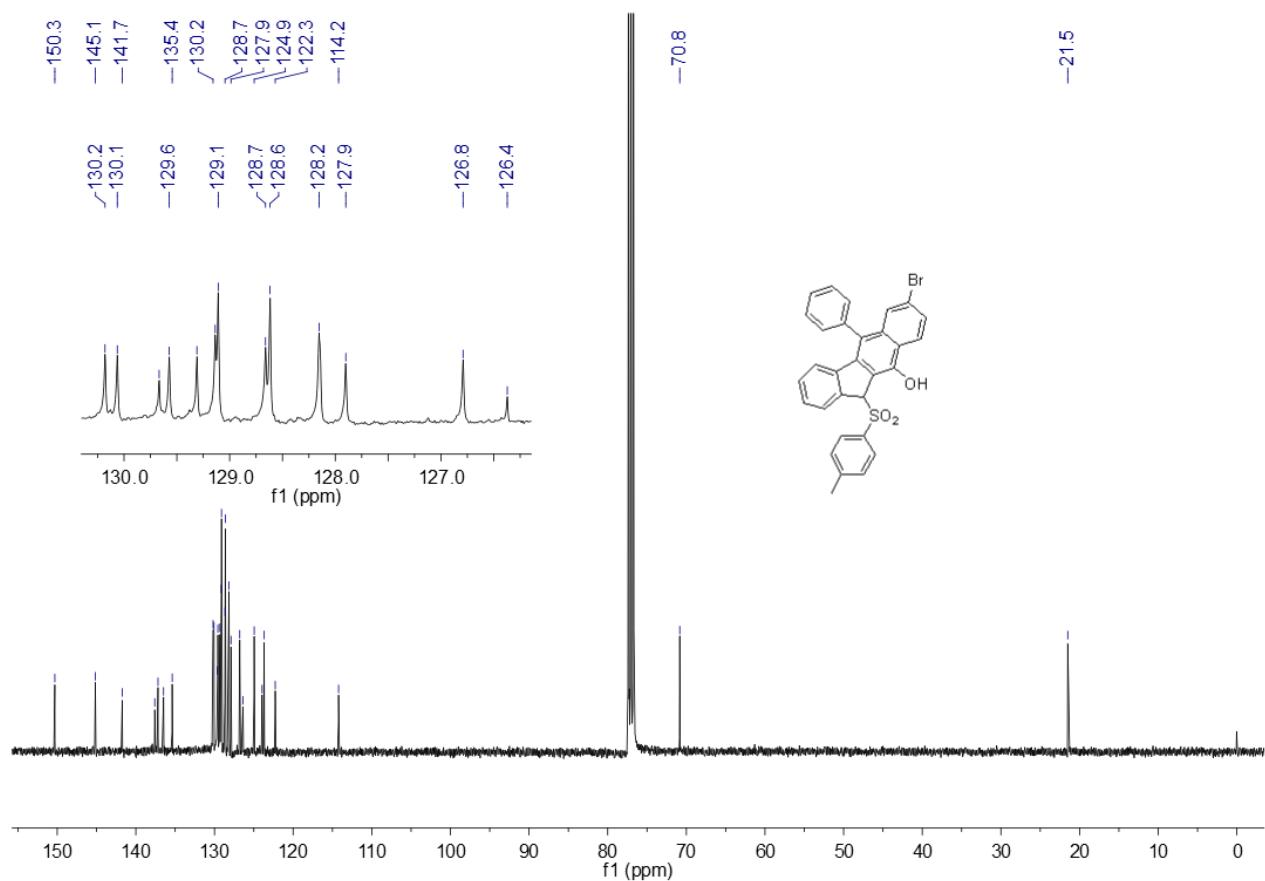




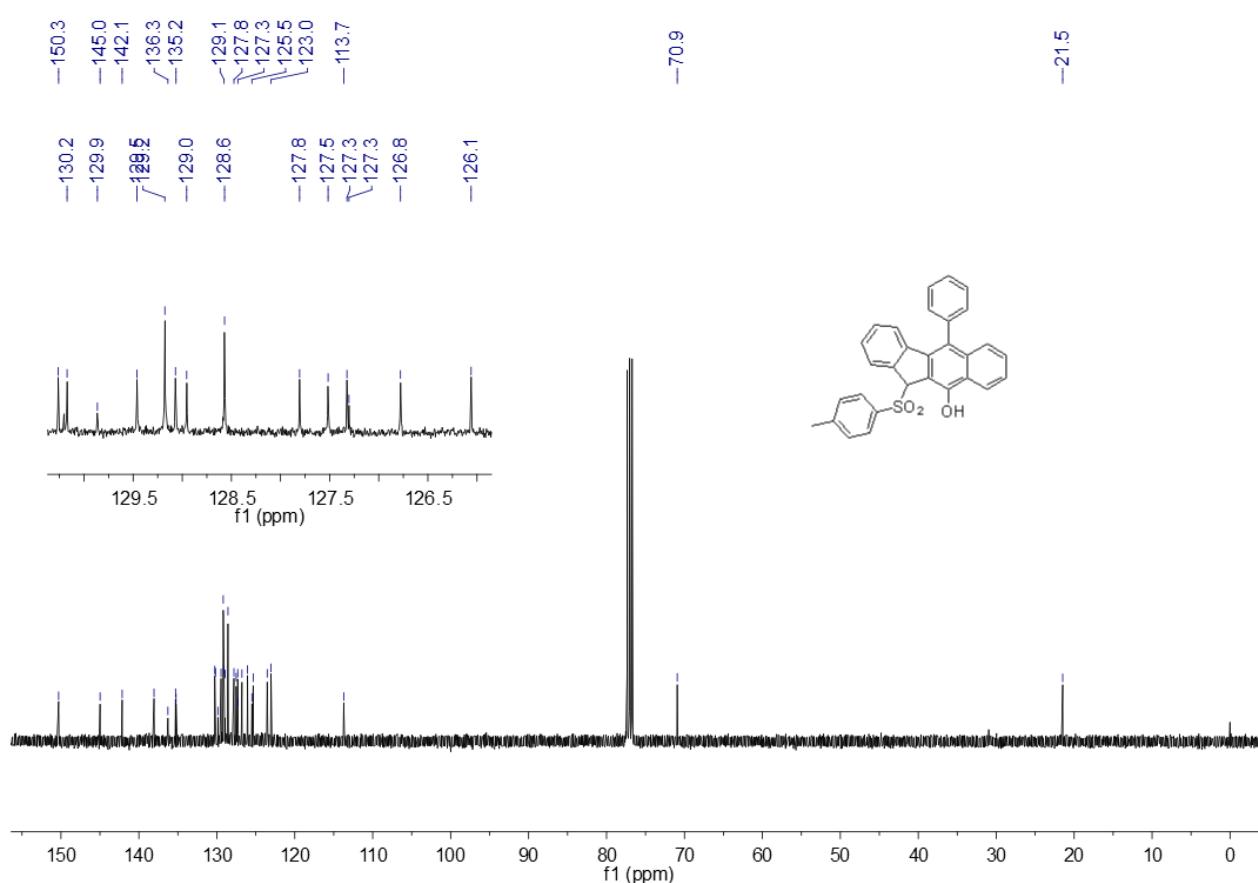
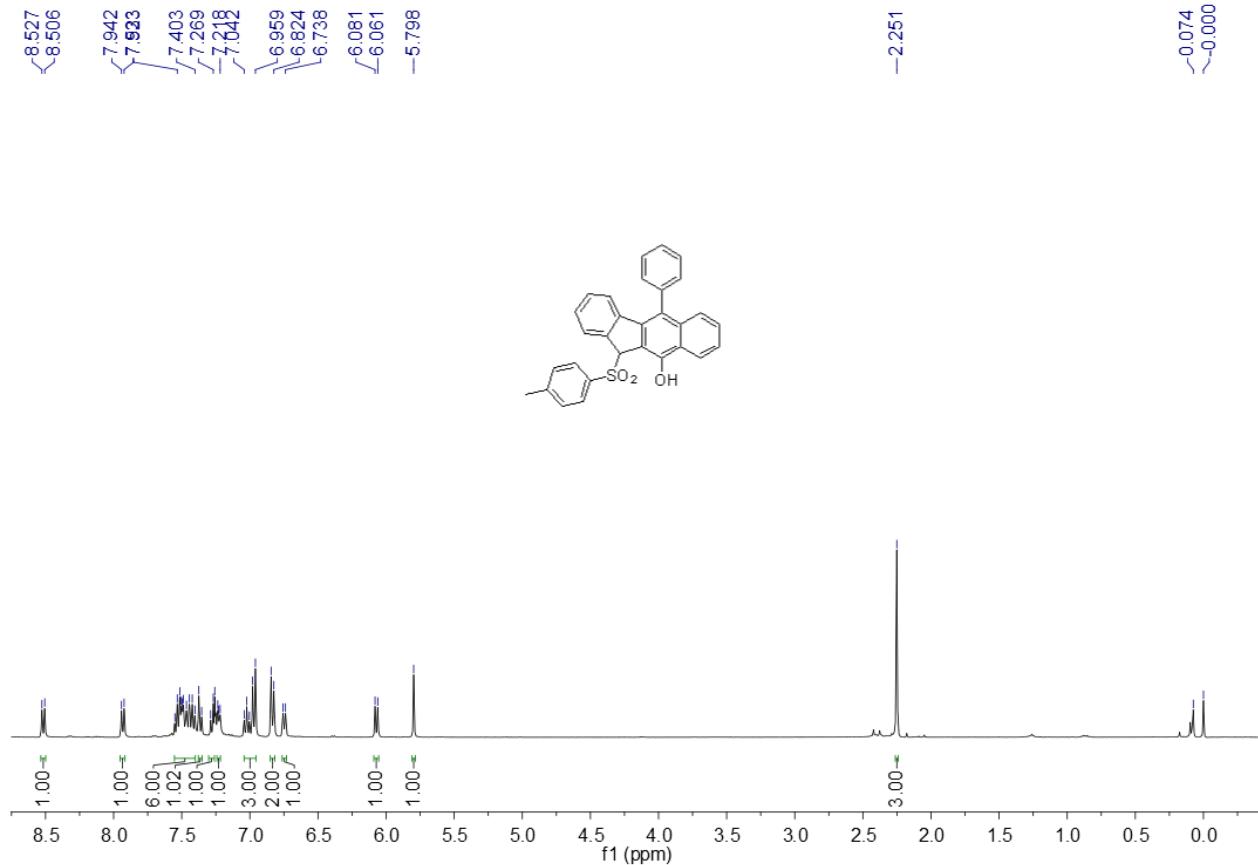


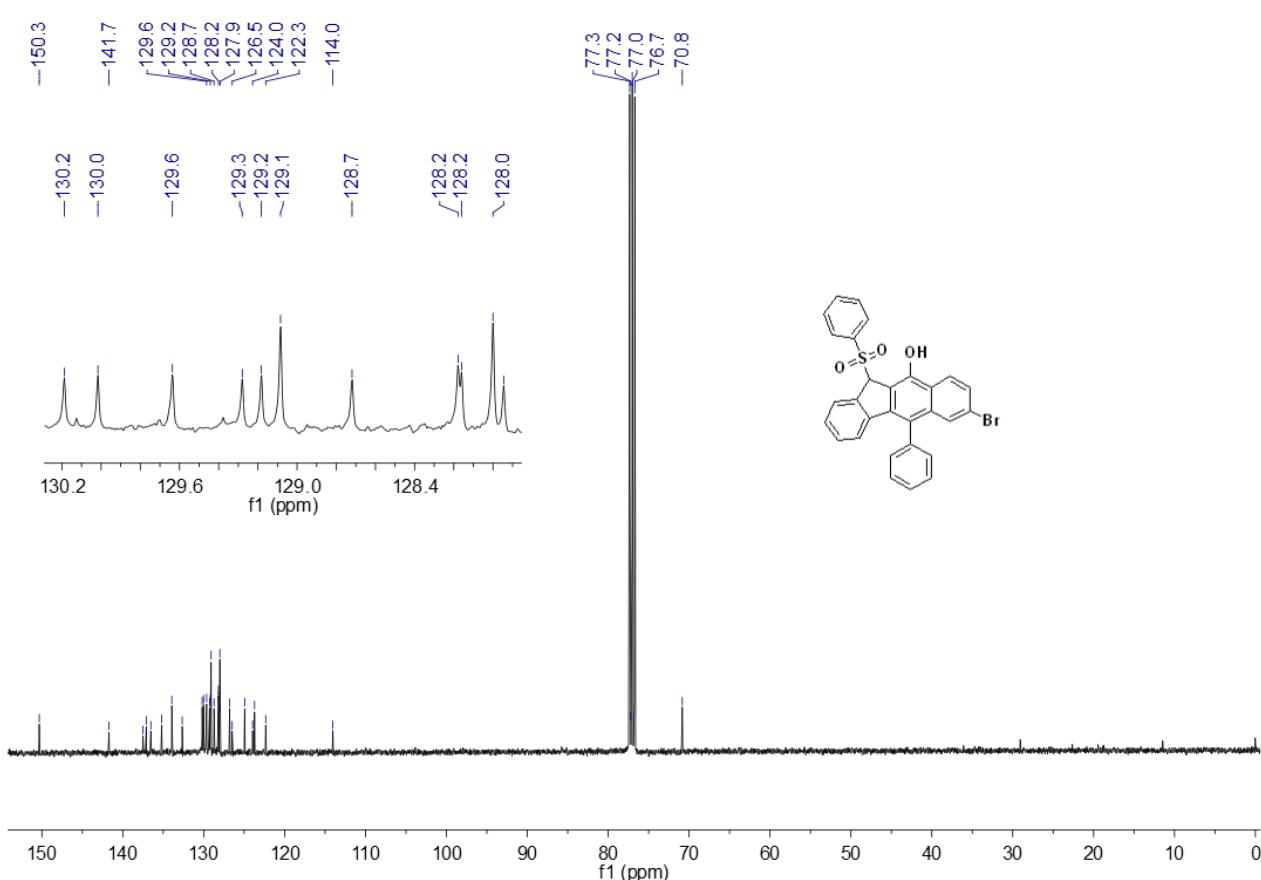
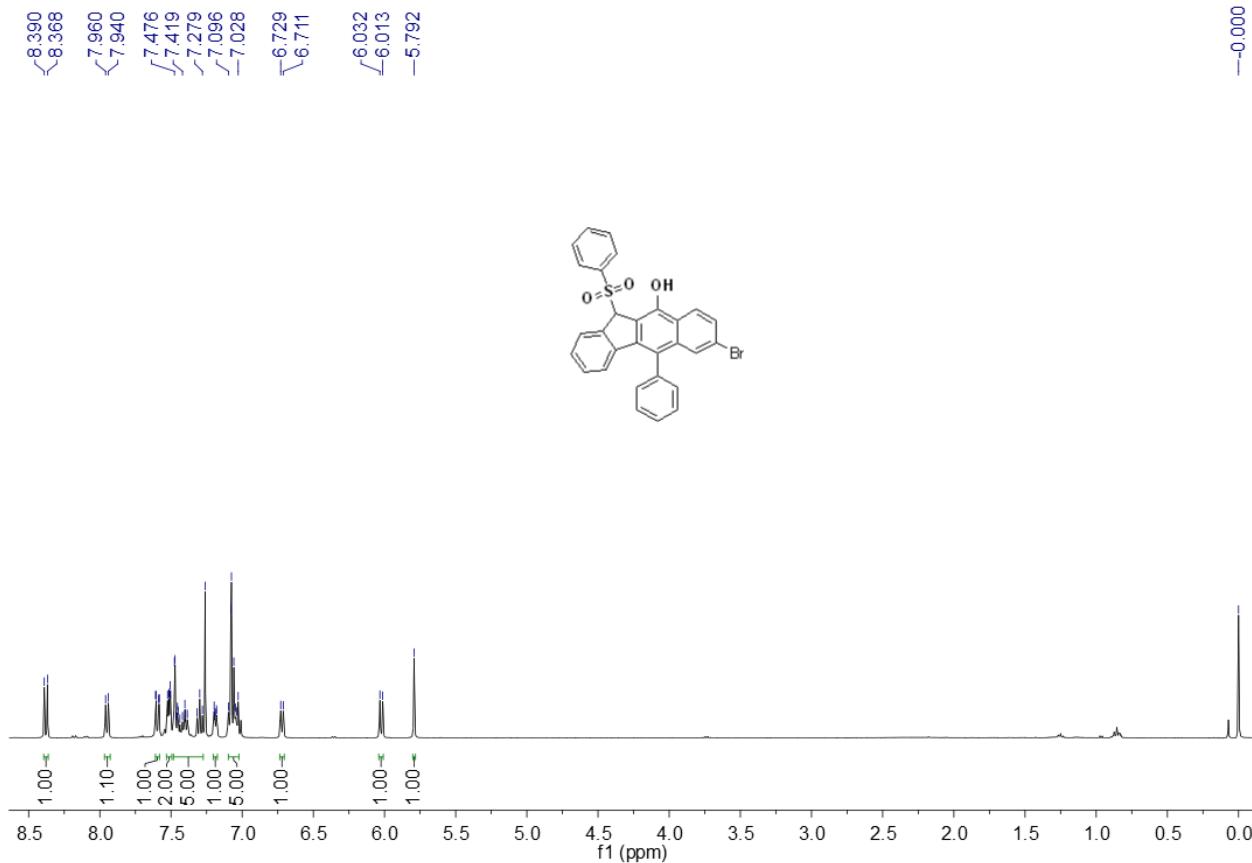


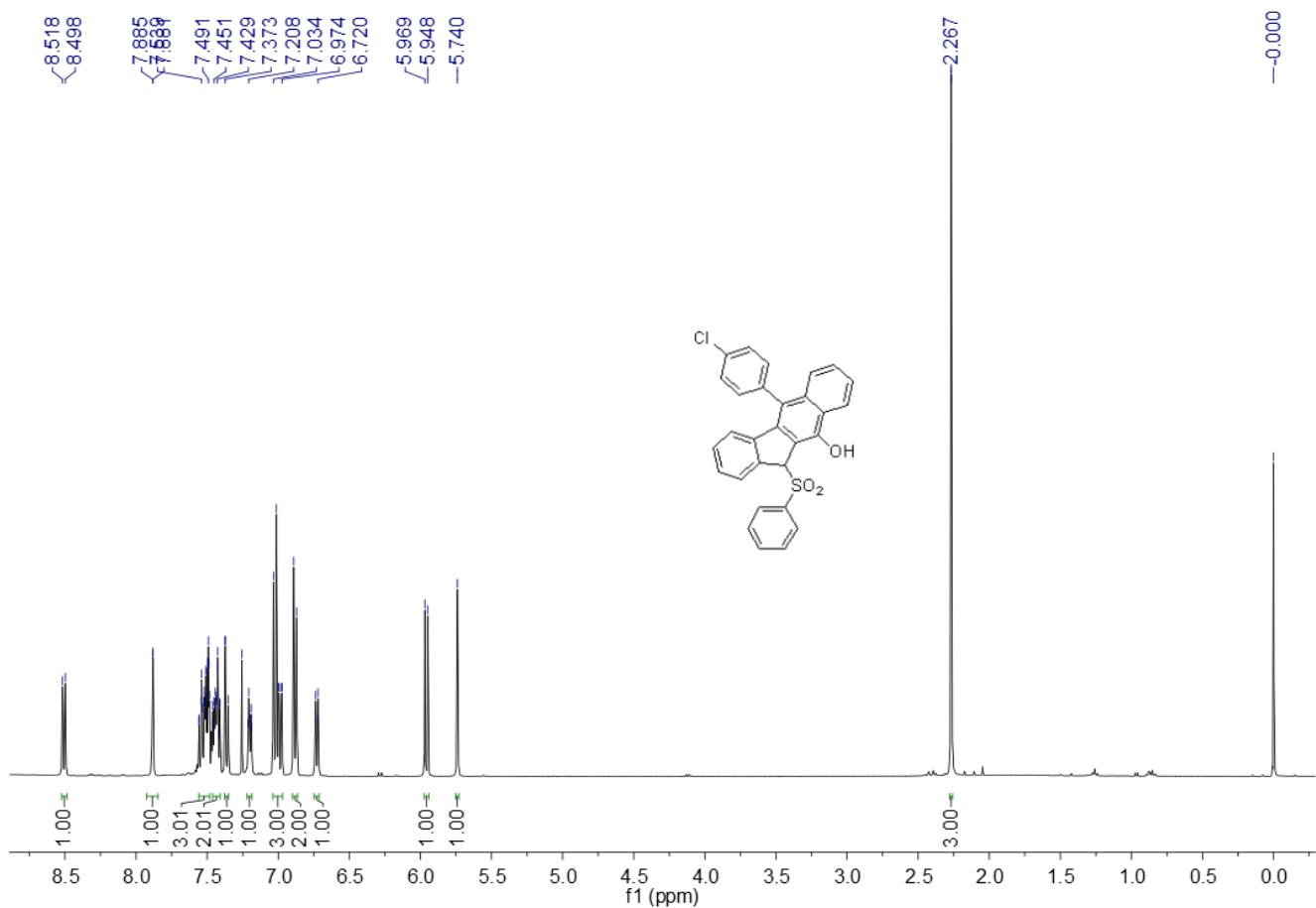
**<sup>1</sup>H NMR Spectrum of Compound 3j**



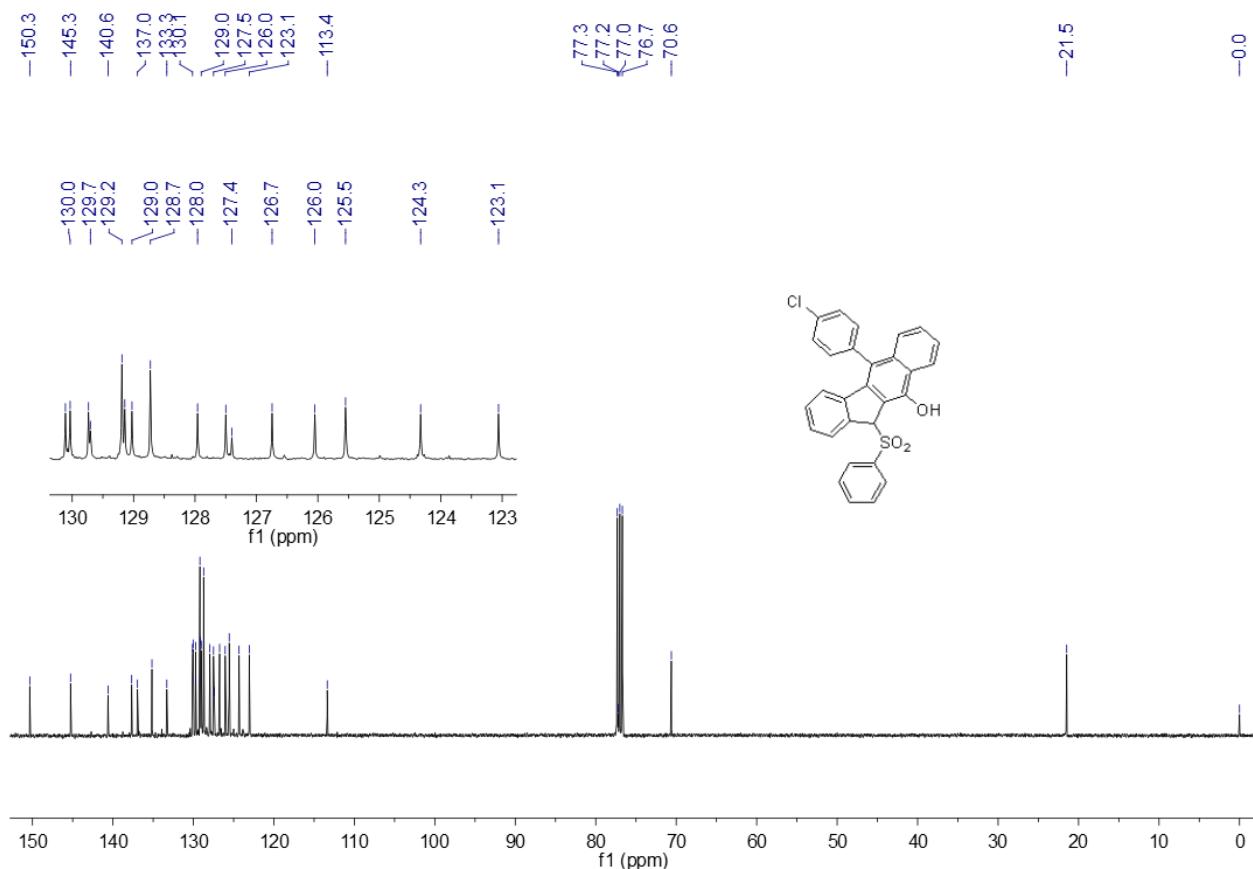
**<sup>13</sup>C NMR Spectrum of Compound 3j**



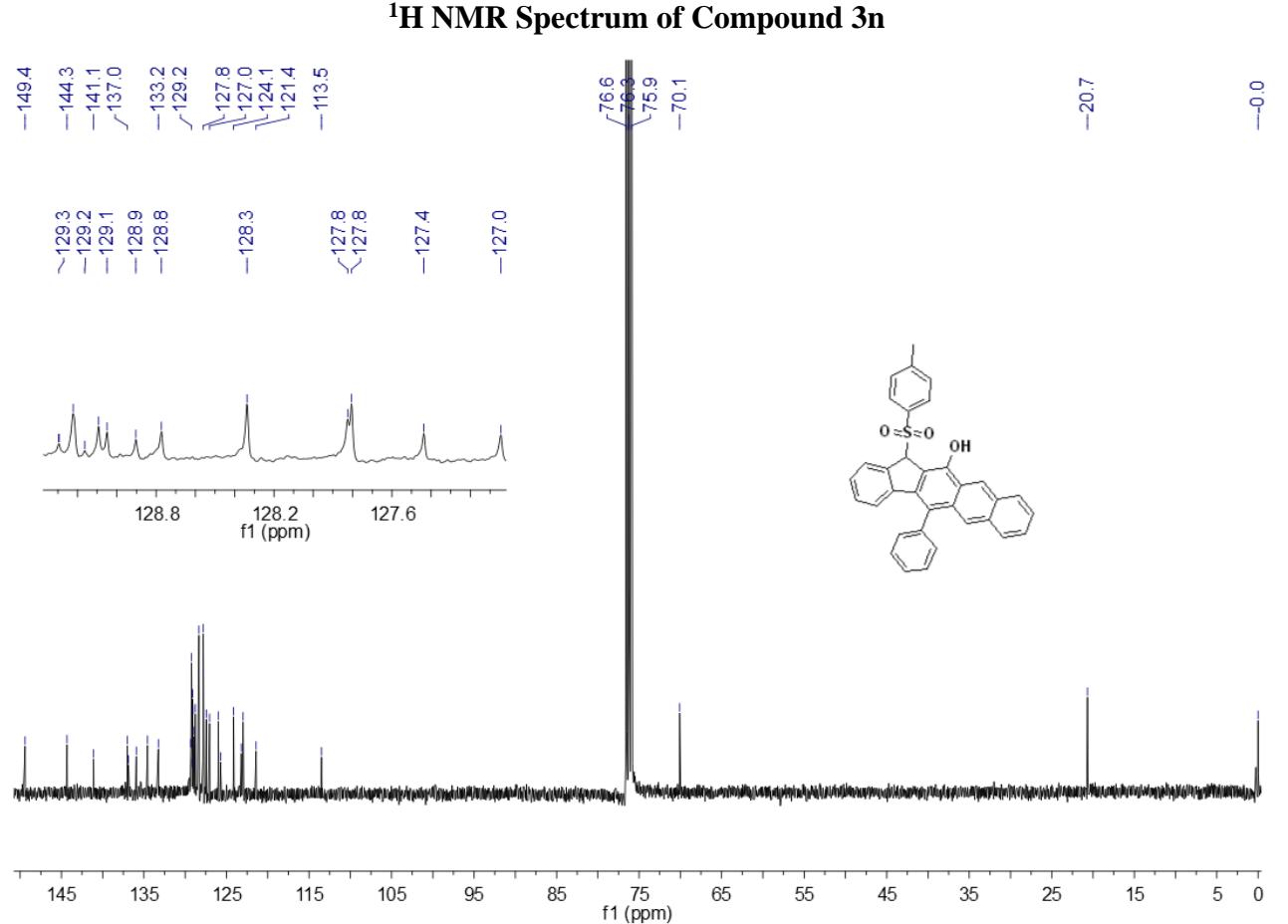
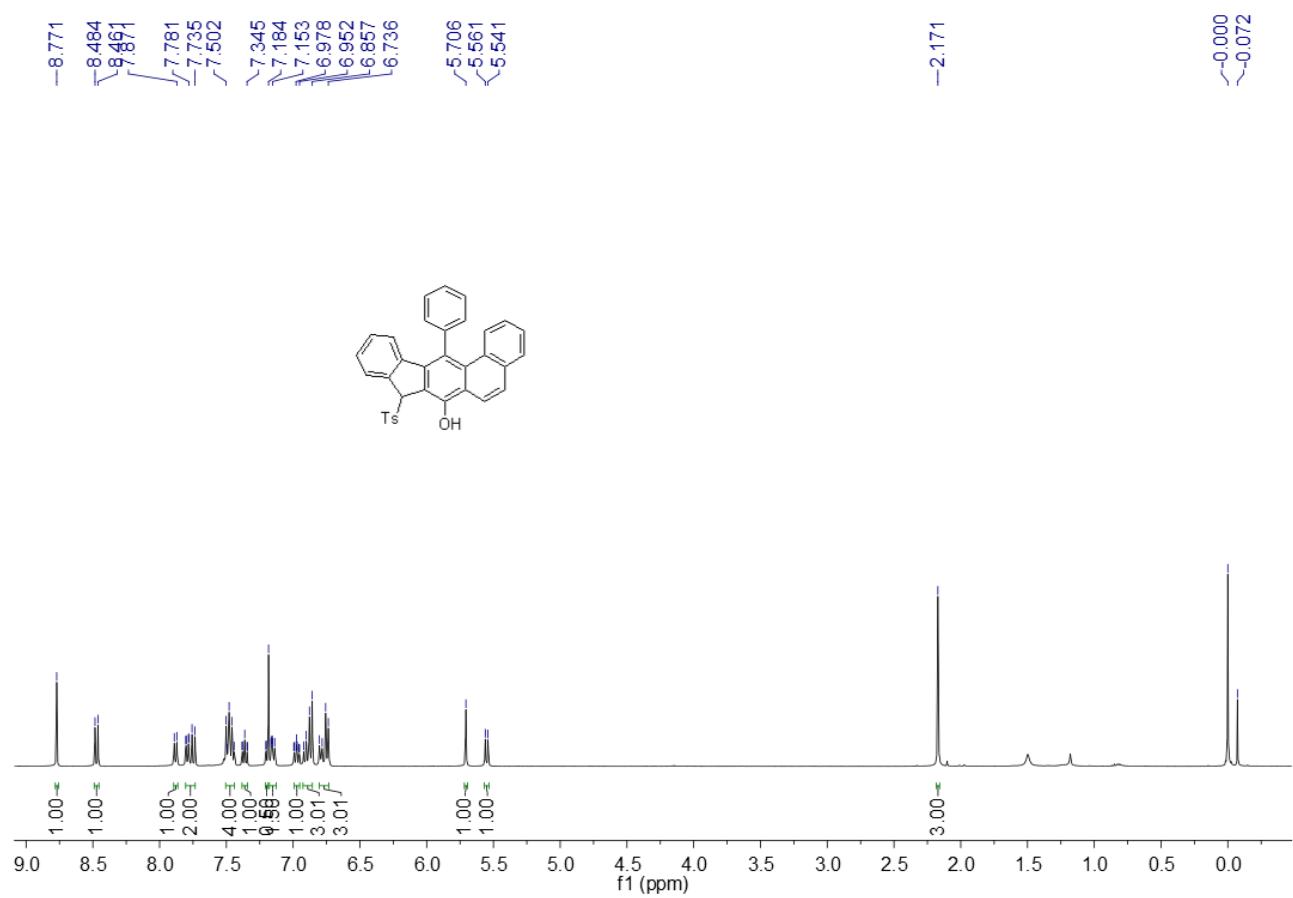


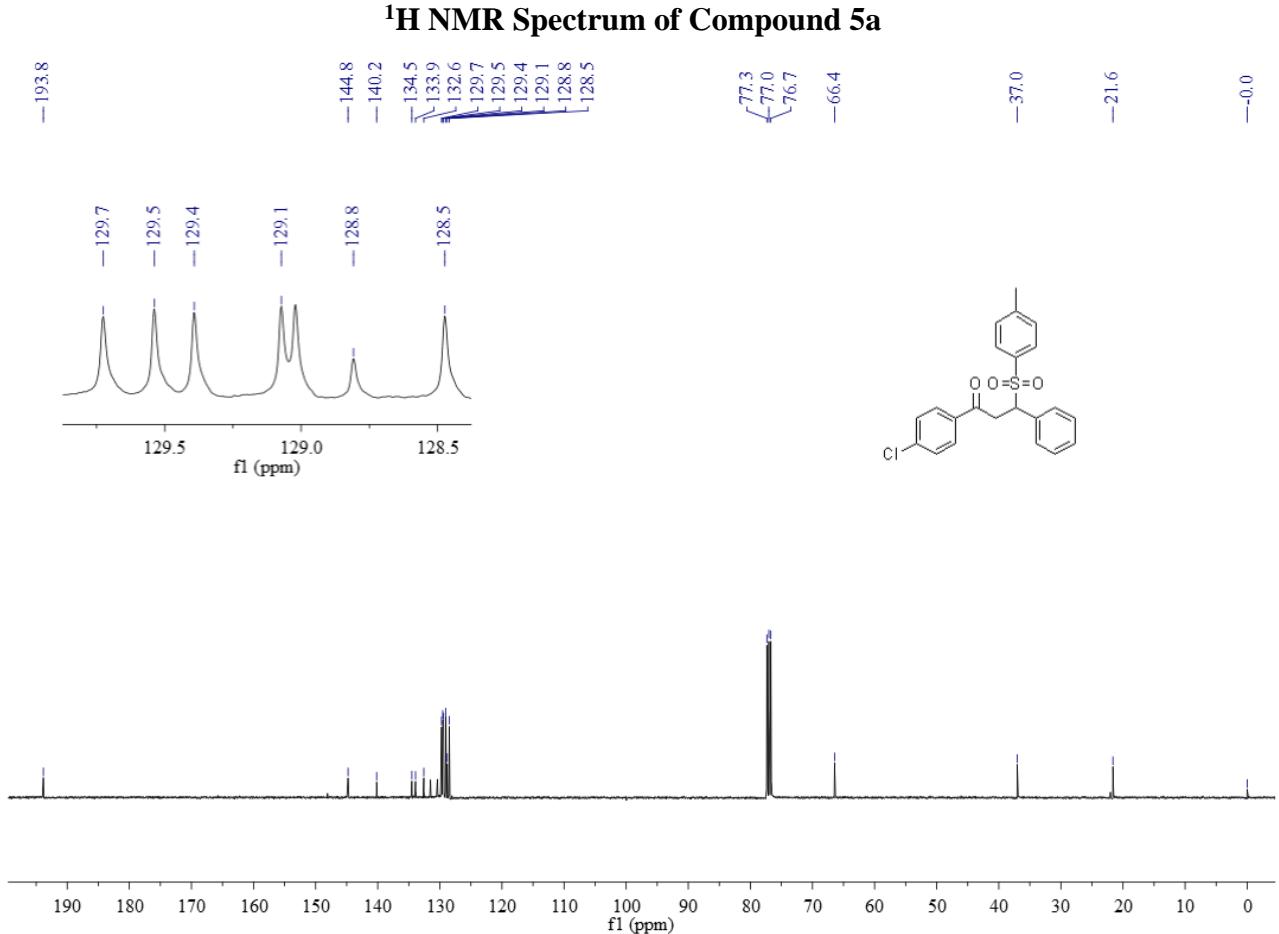
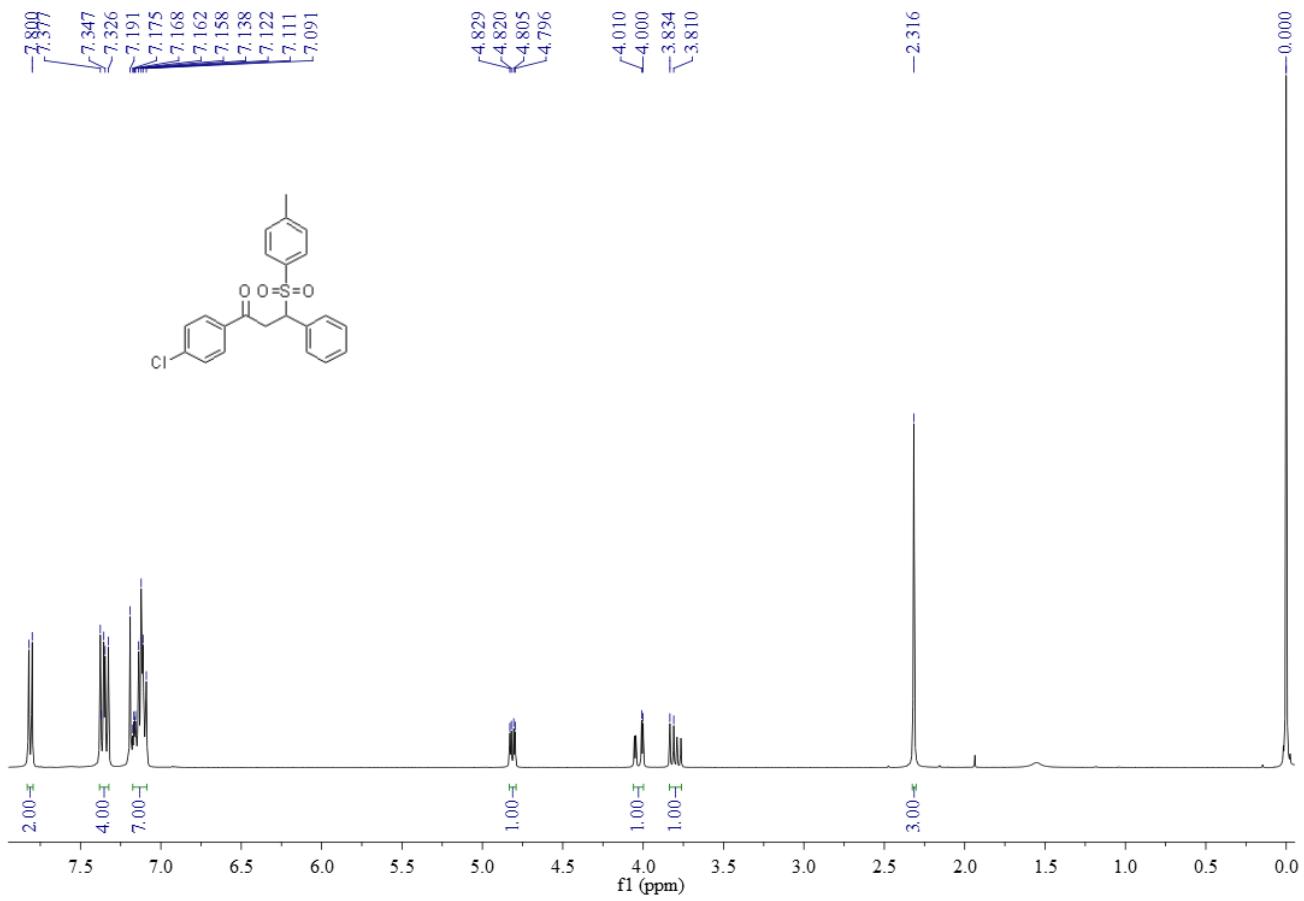


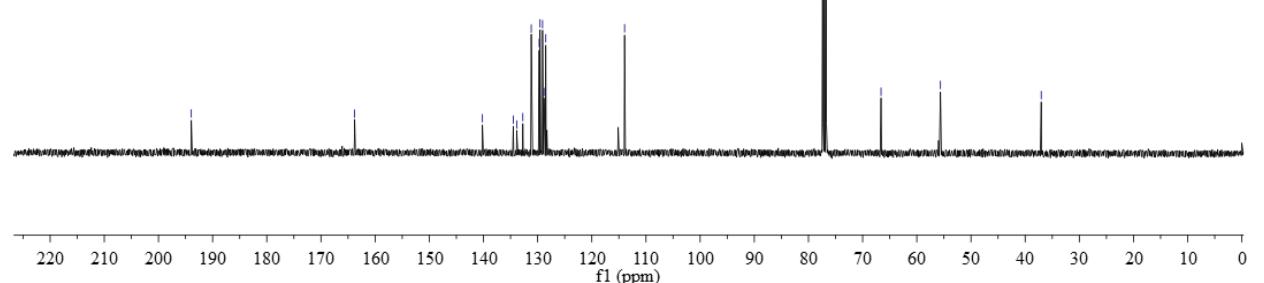
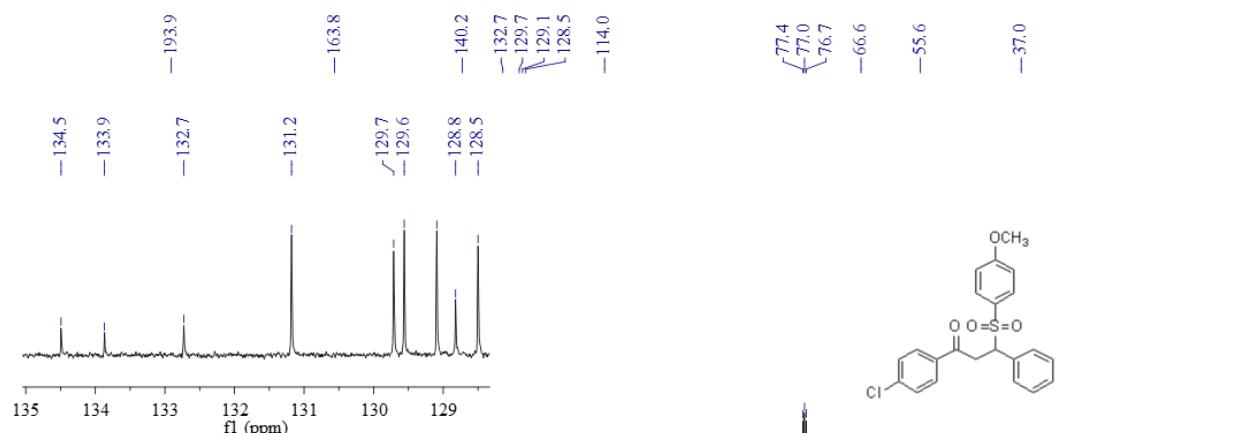
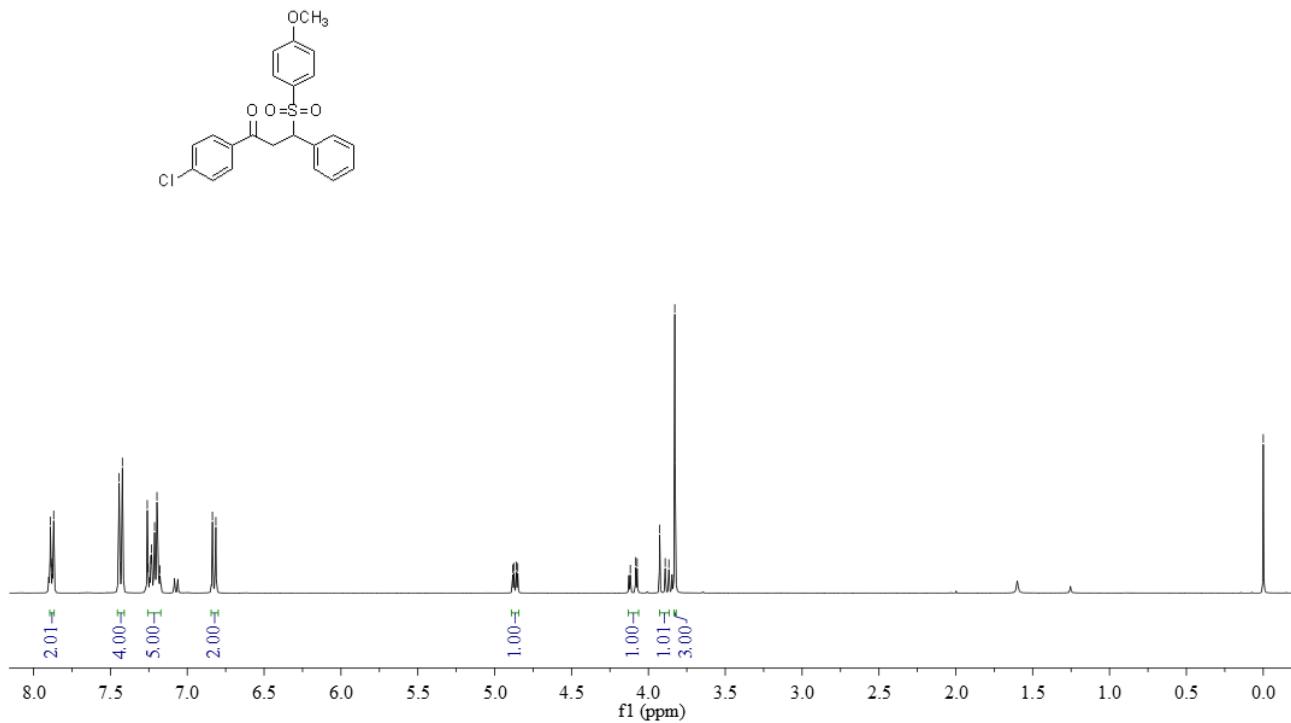
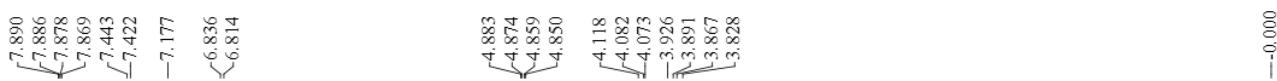
<sup>1</sup>H NMR Spectrum of Compound 3m



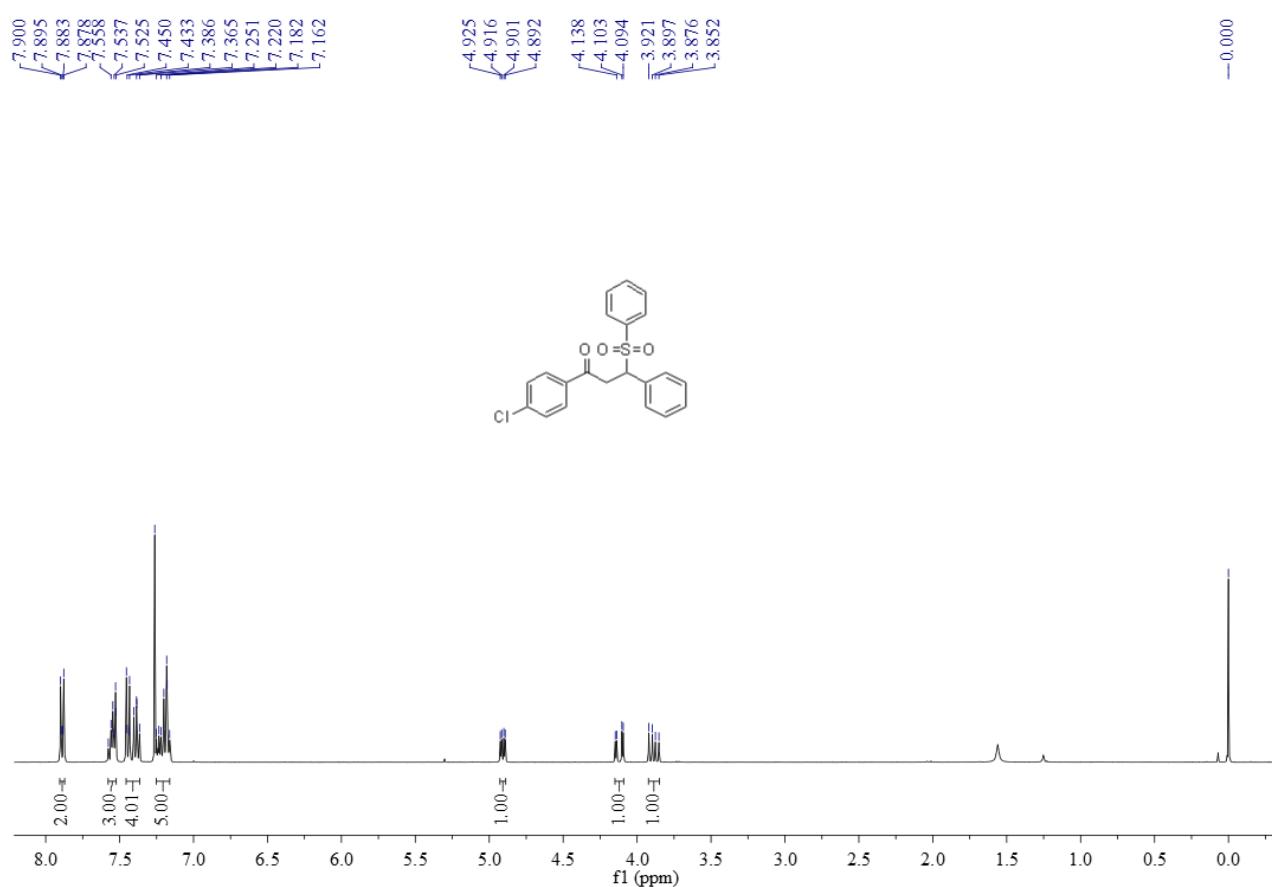
<sup>13</sup>C NMR Spectrum of Compound 3m



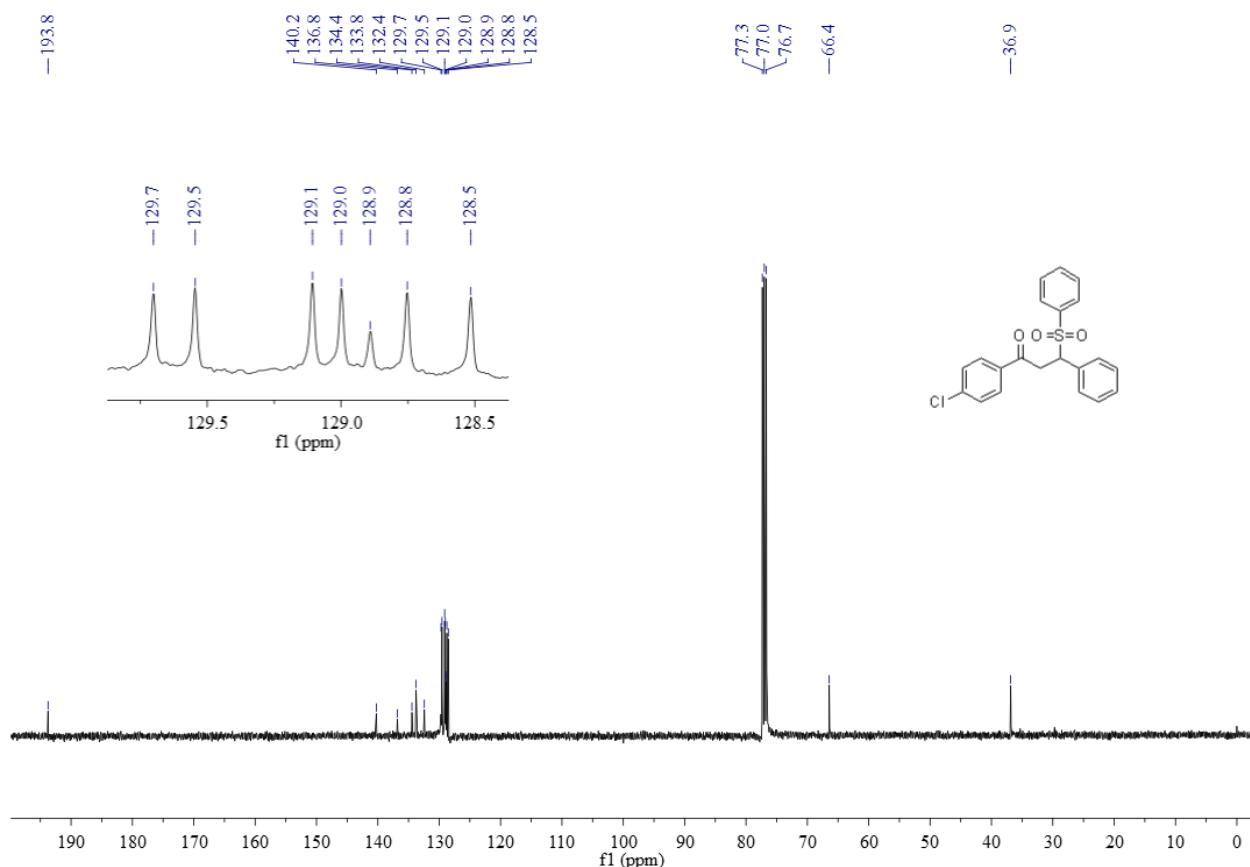




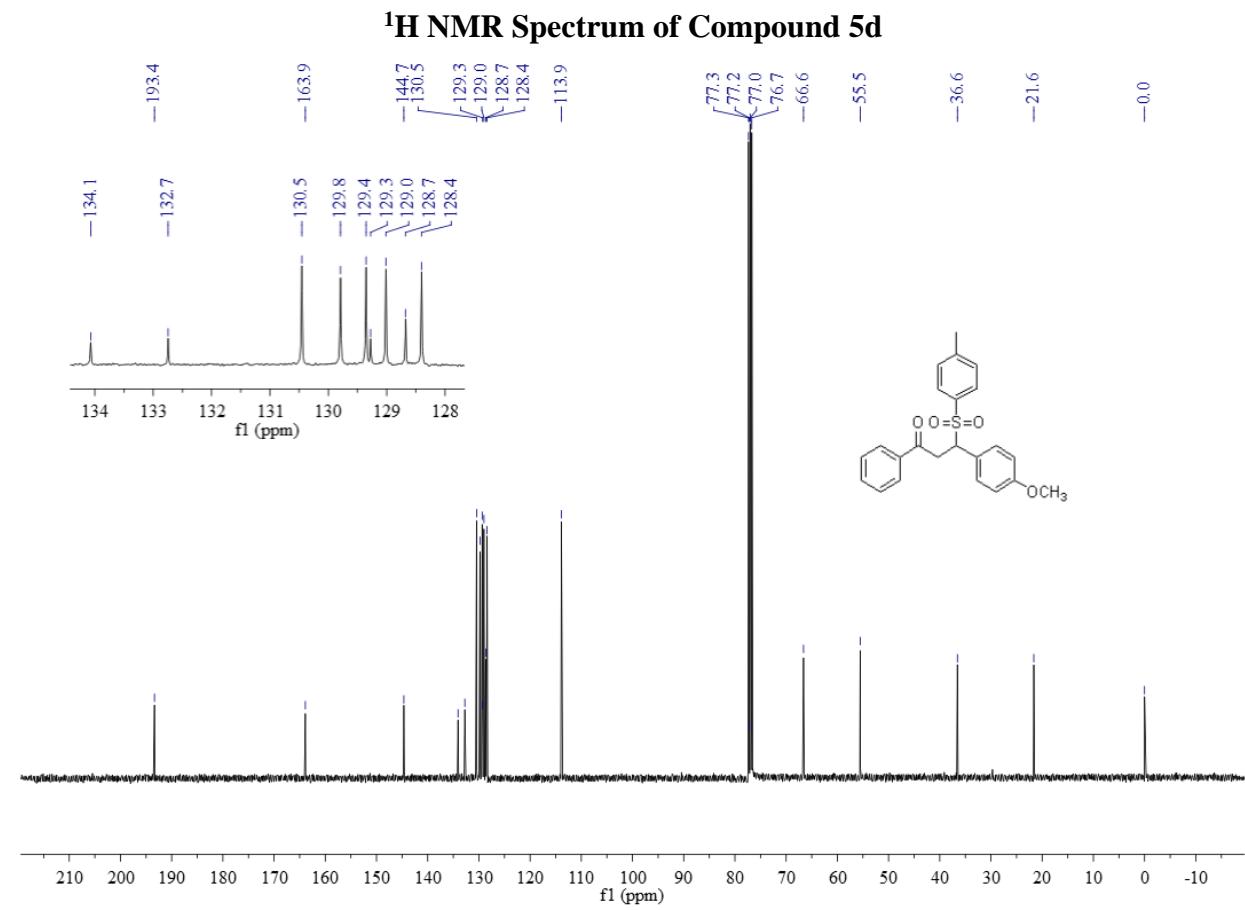
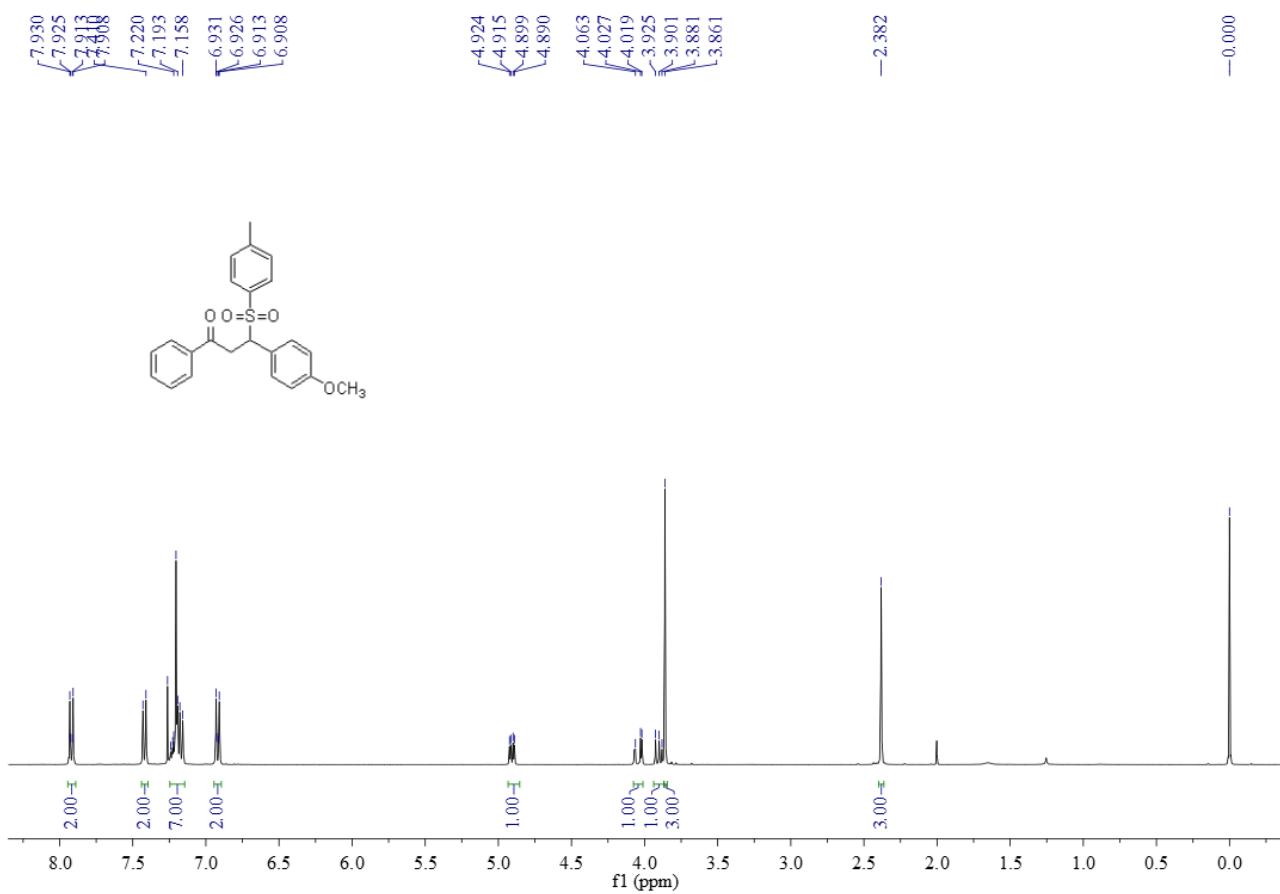
**<sup>13</sup>C NMR Spectrum of Compound 5b**

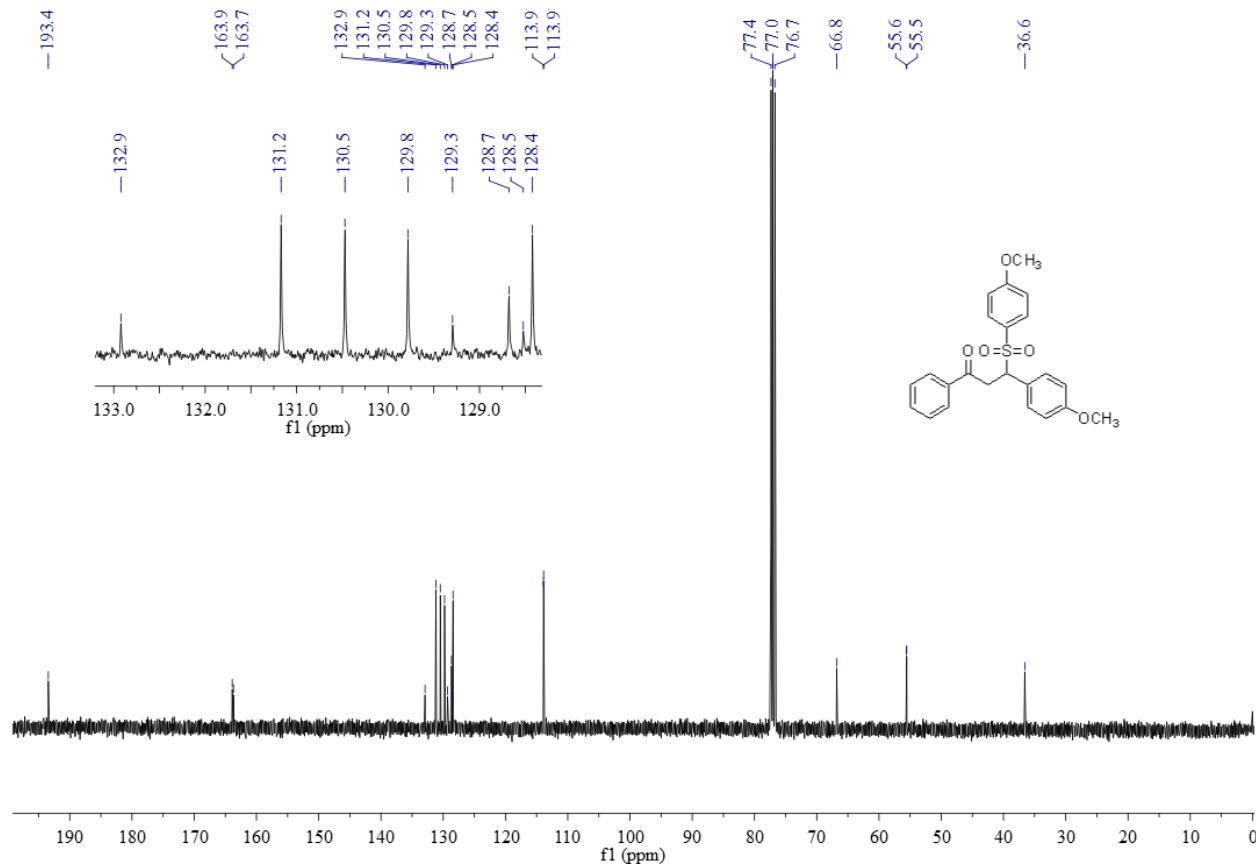
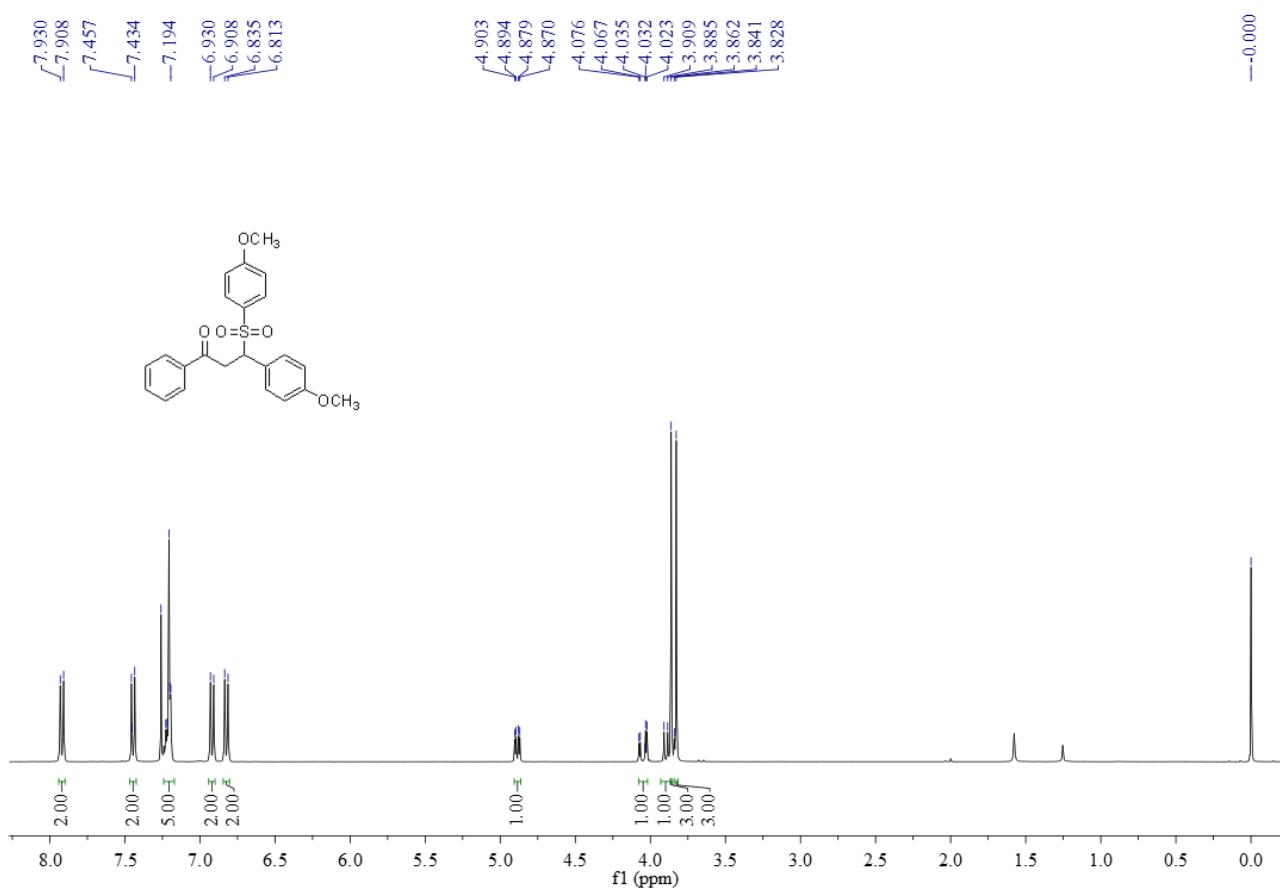


**<sup>1</sup>H NMR Spectrum of Compound 5c**

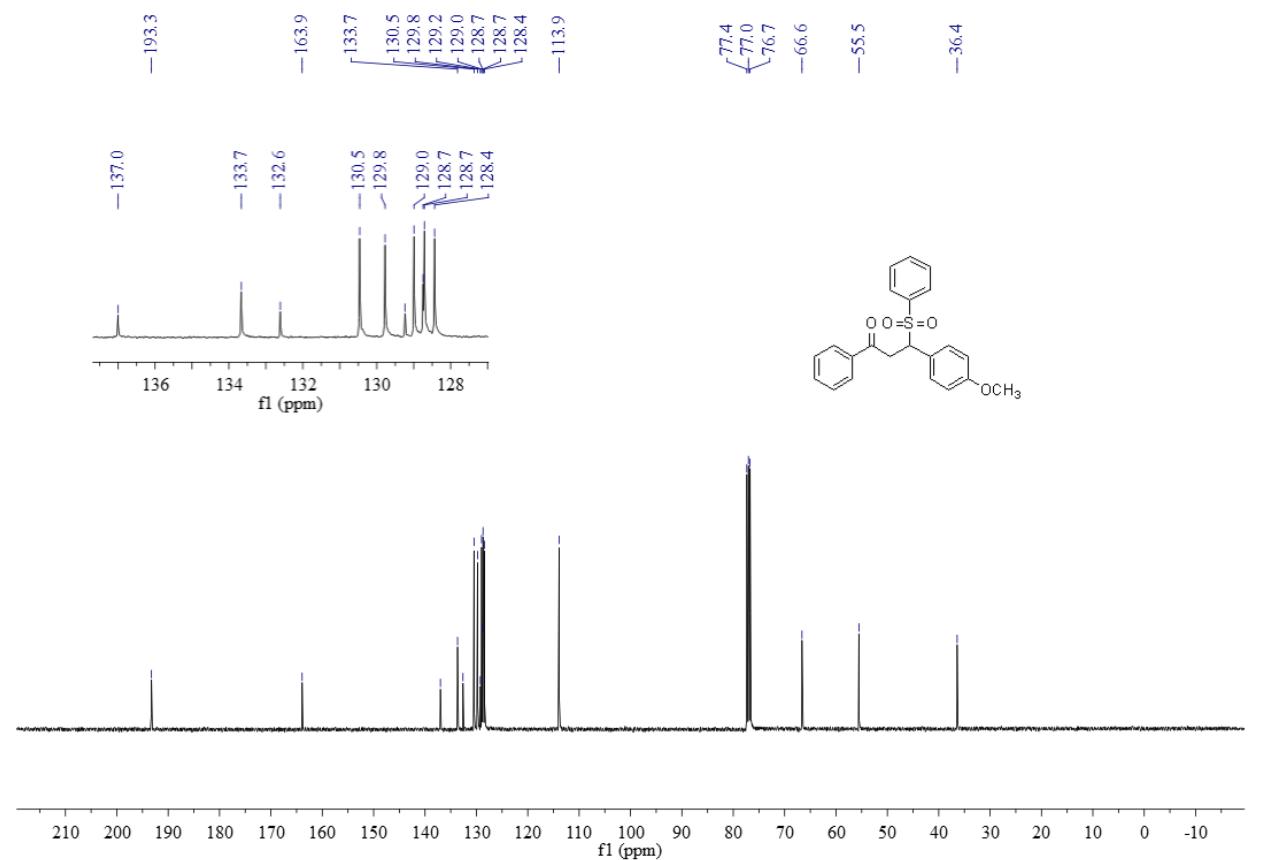
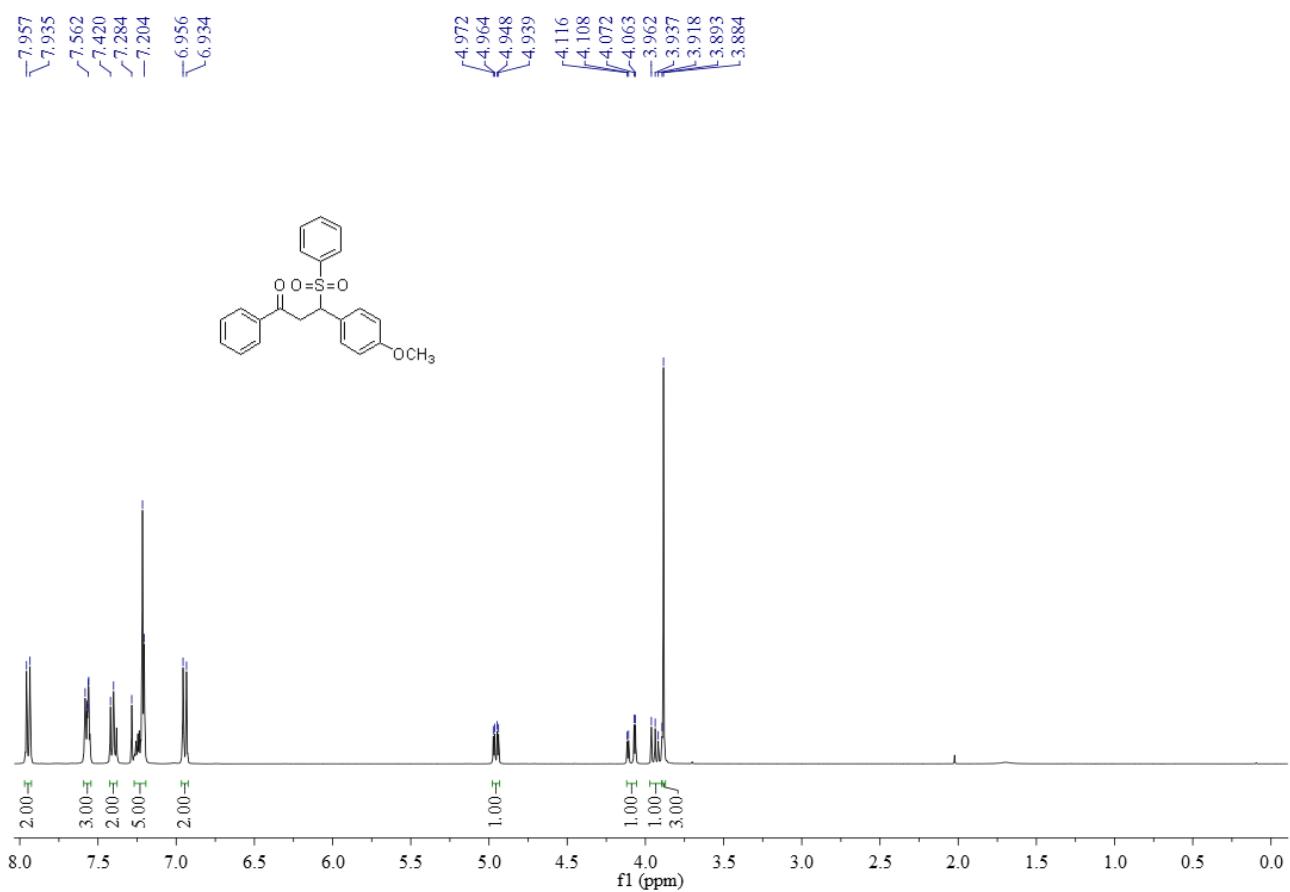


**<sup>13</sup>C NMR Spectrum of Compound 5c**

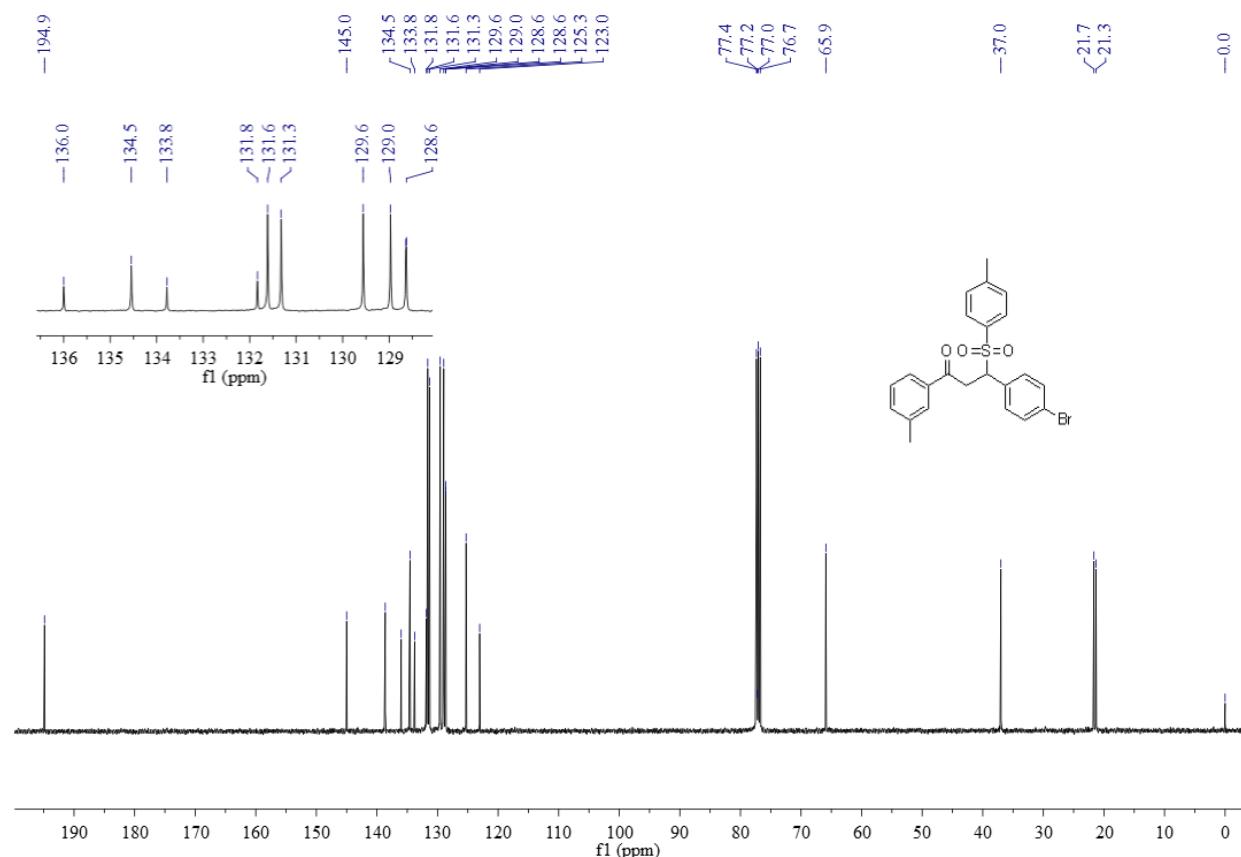
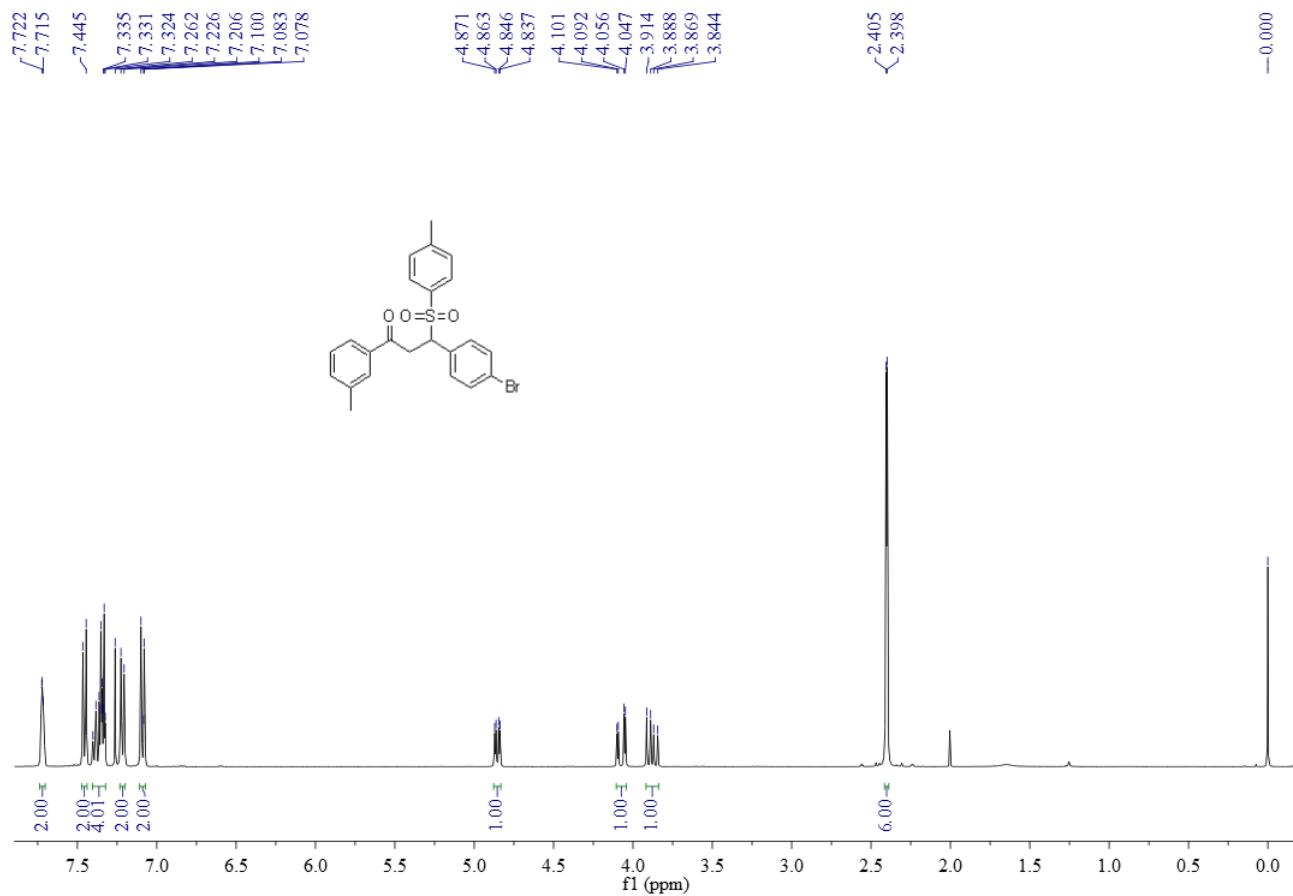


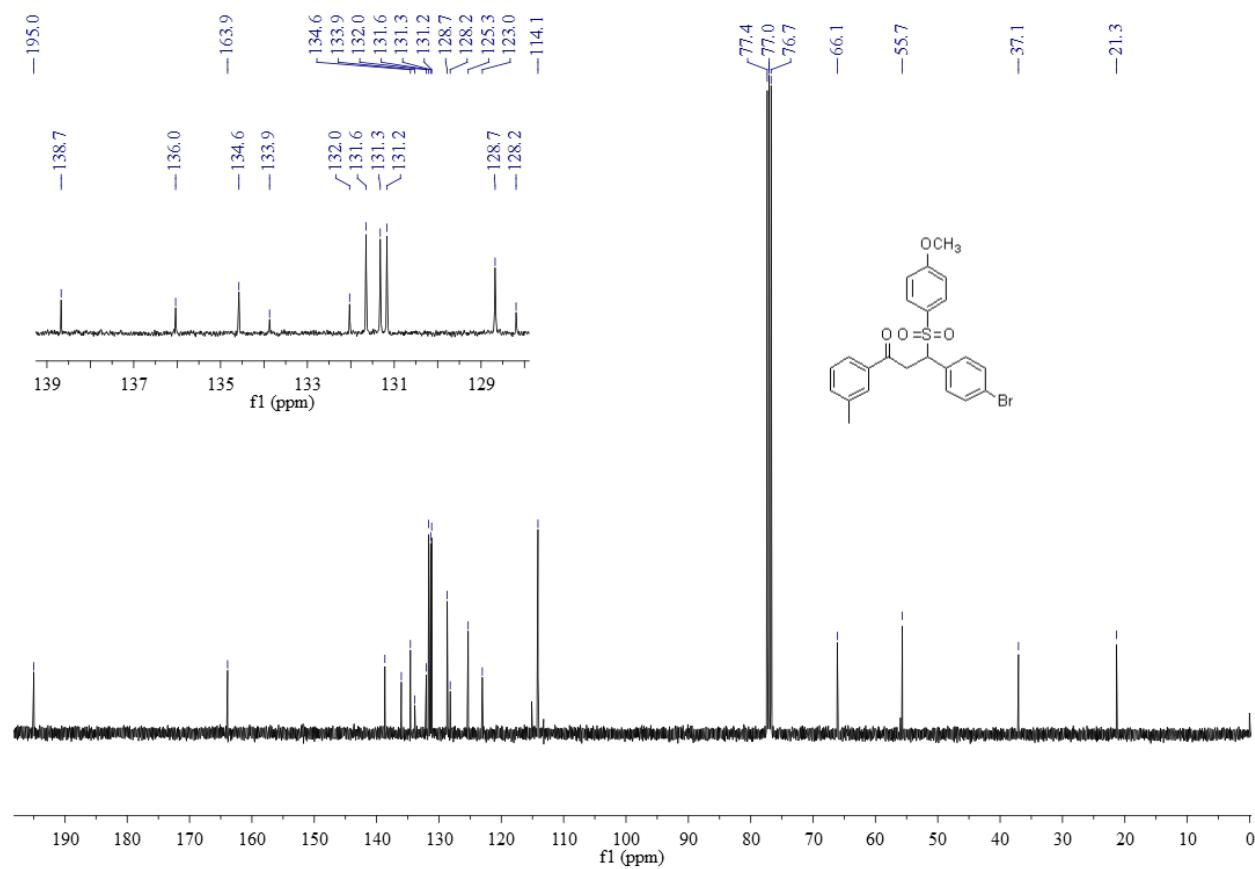
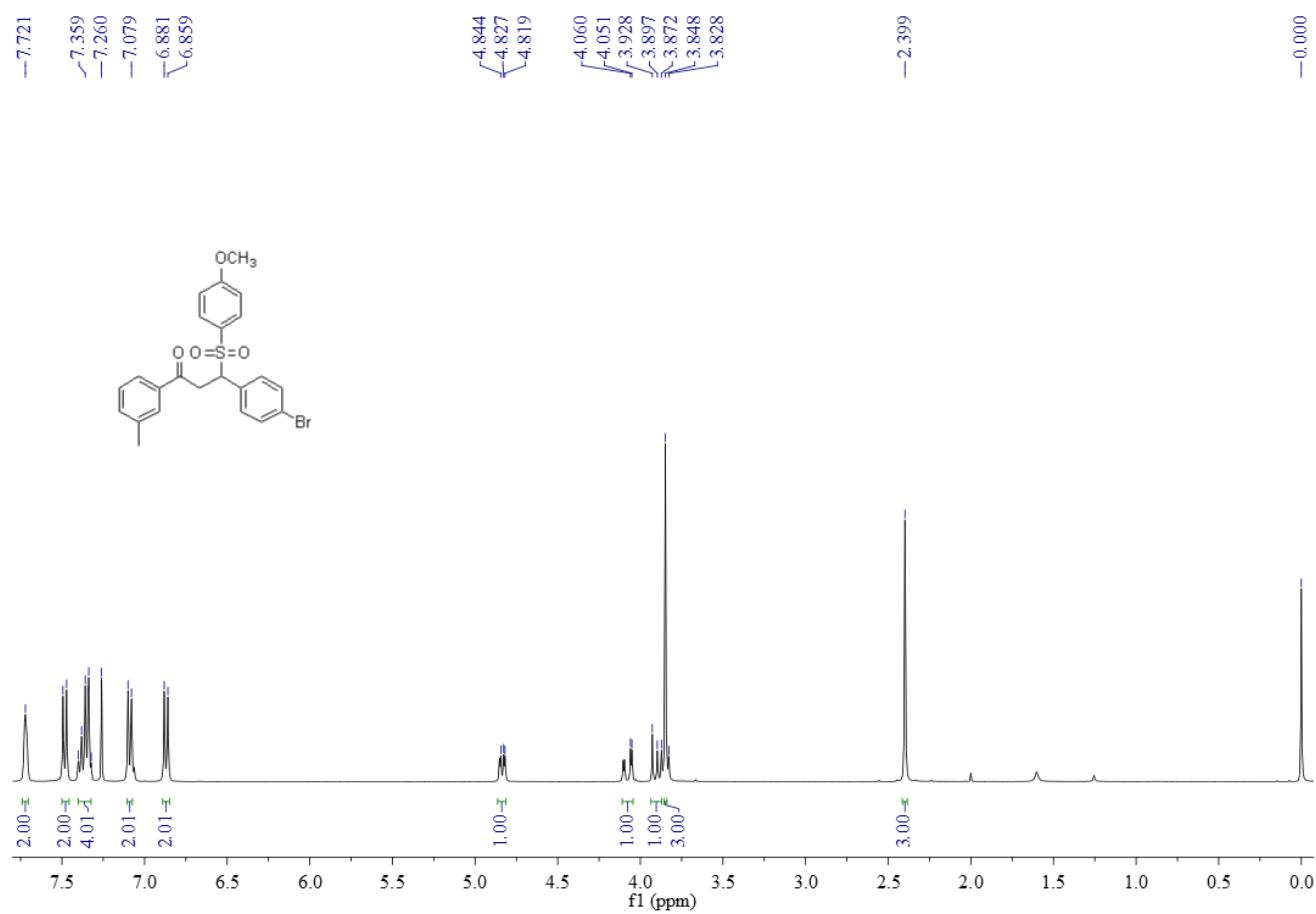


<sup>13</sup>C NMR Spectrum of Compound 5e

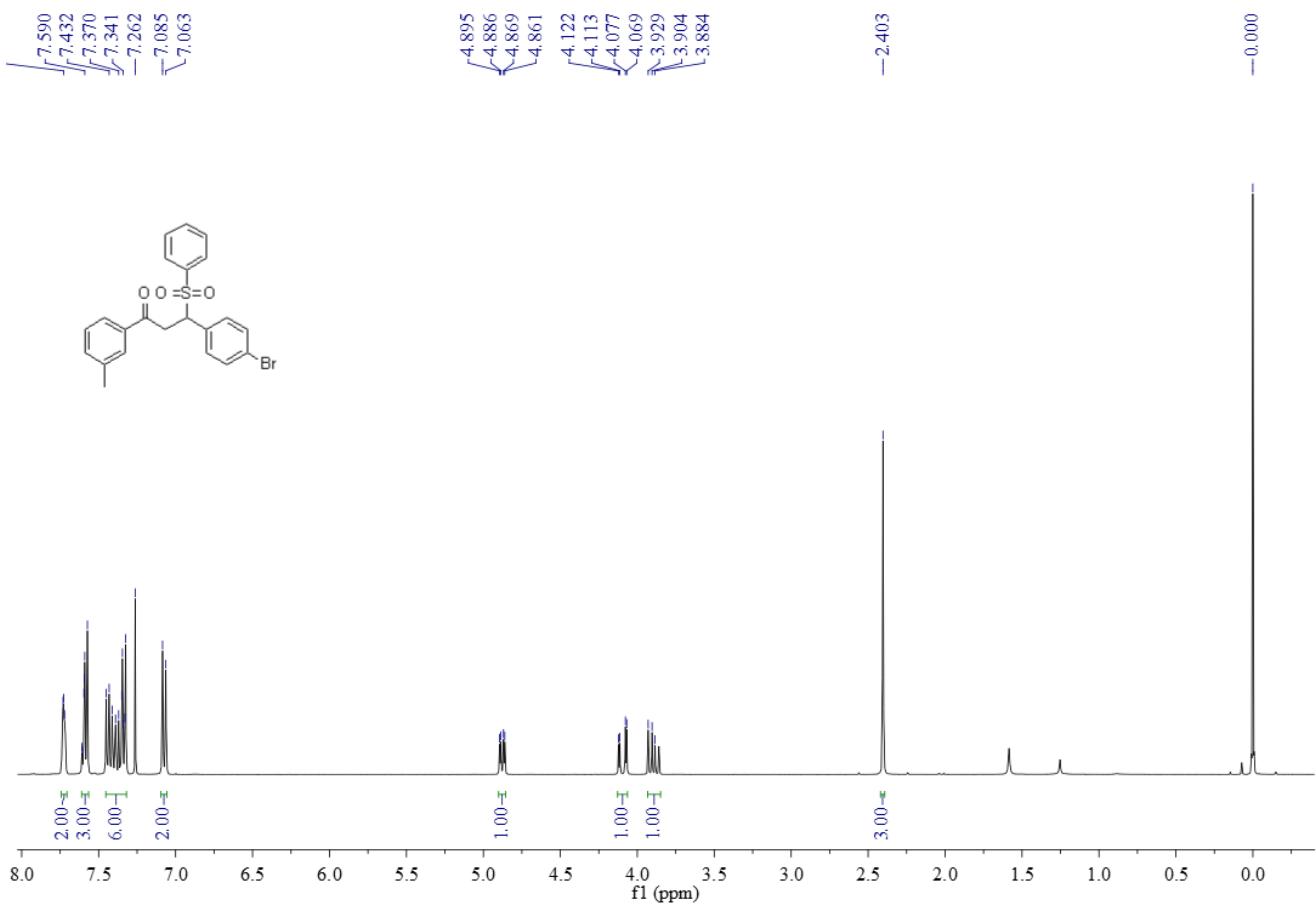


<sup>13</sup>C NMR Spectrum of Compound 5f

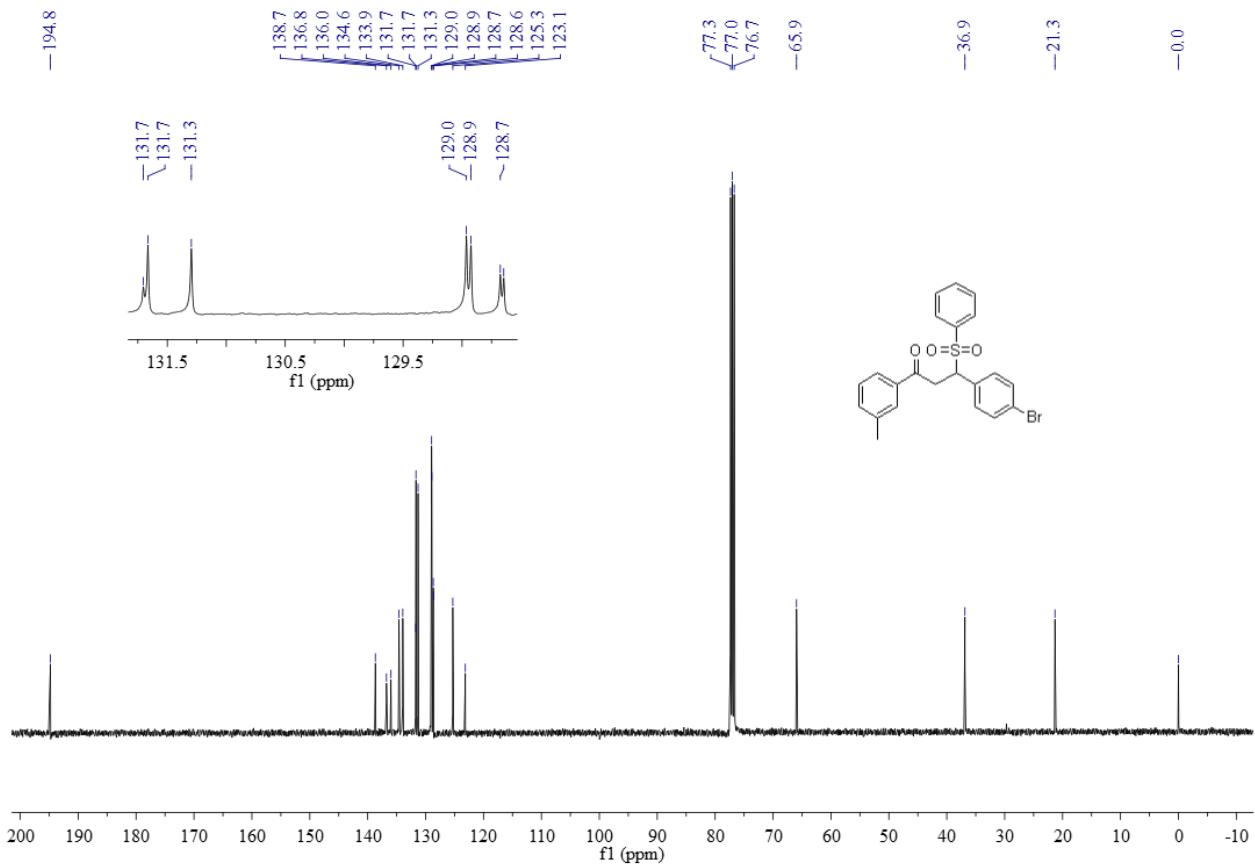




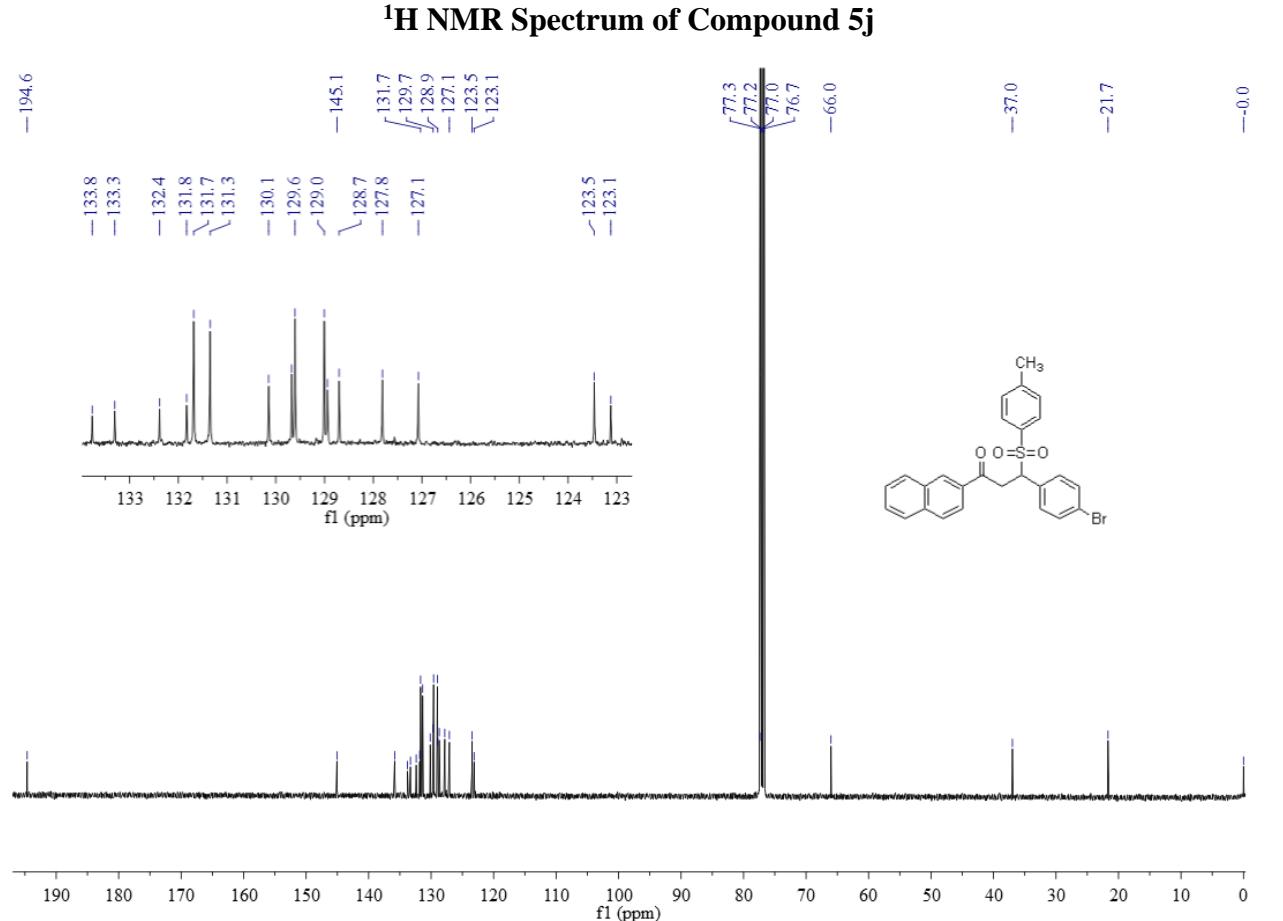
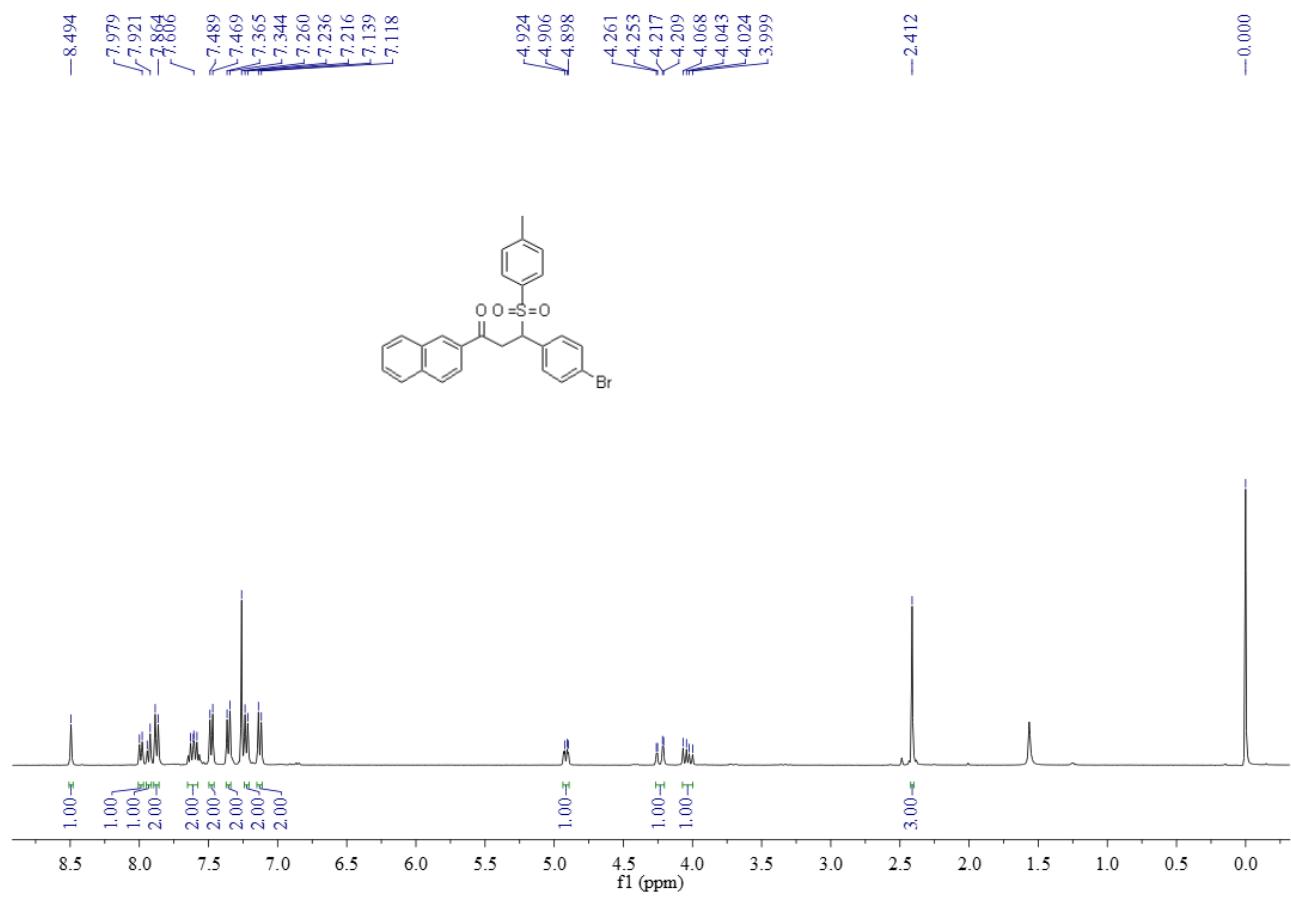
**<sup>13</sup>C NMR Spectrum of Compound 5h**



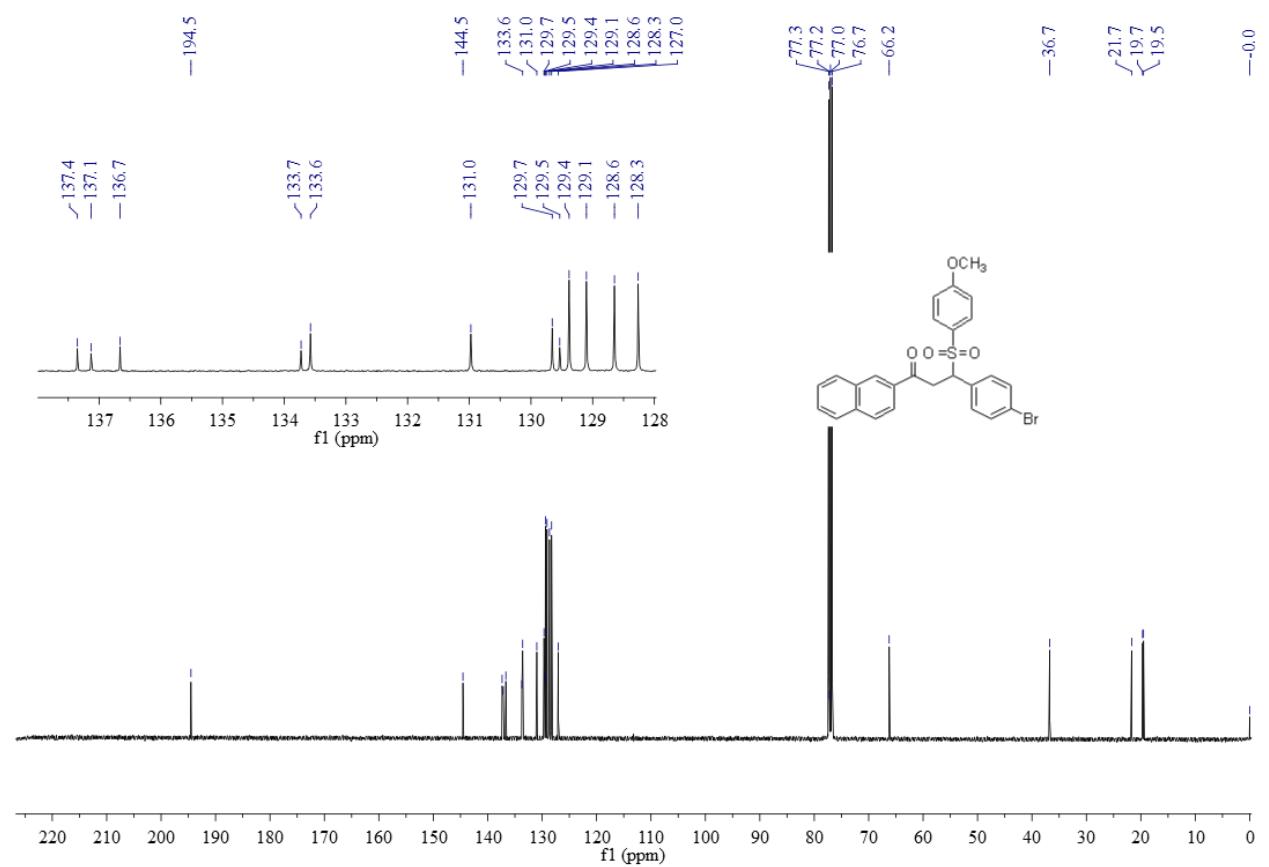
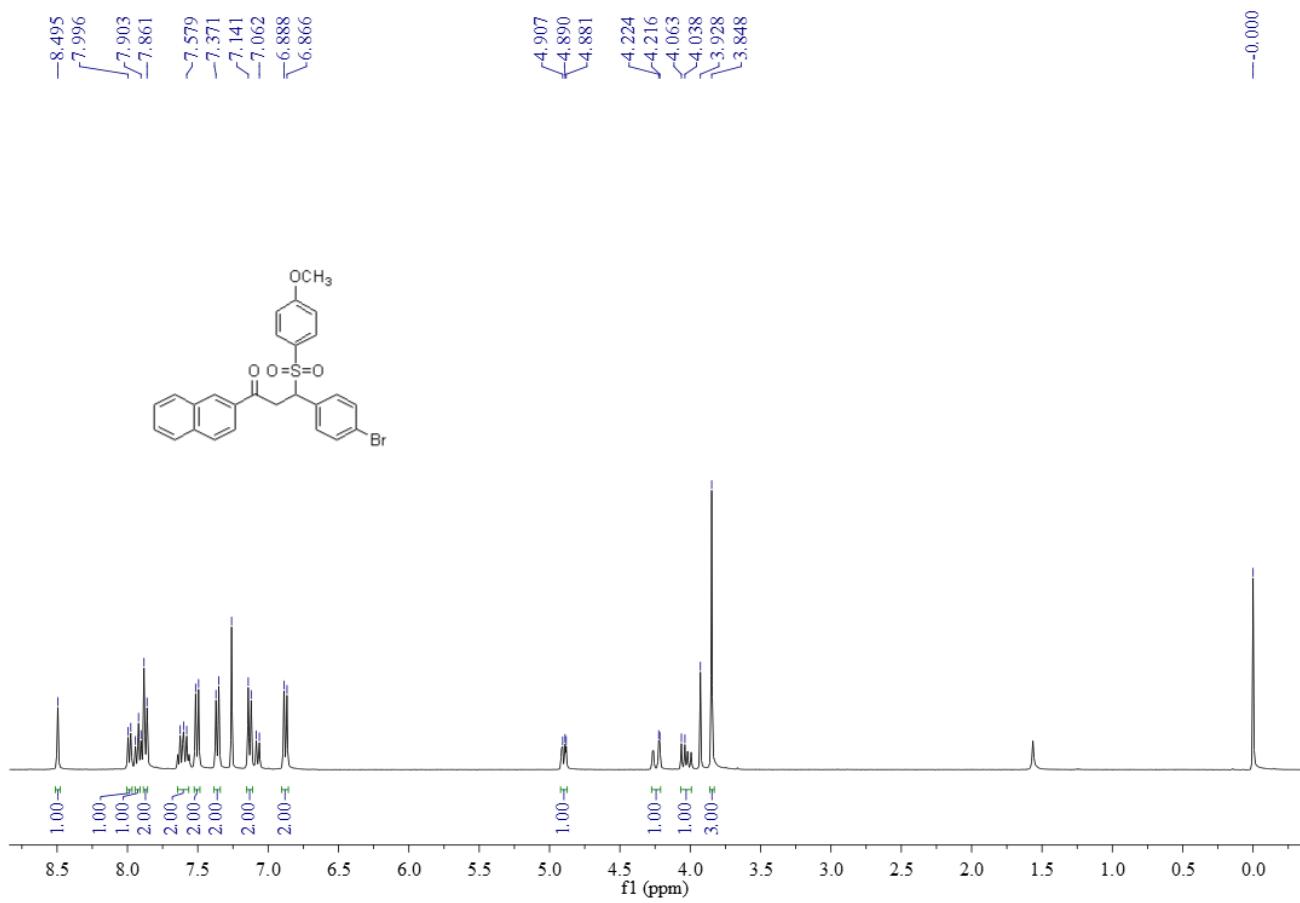
**<sup>1</sup>H NMR Spectrum of Compound 5i**



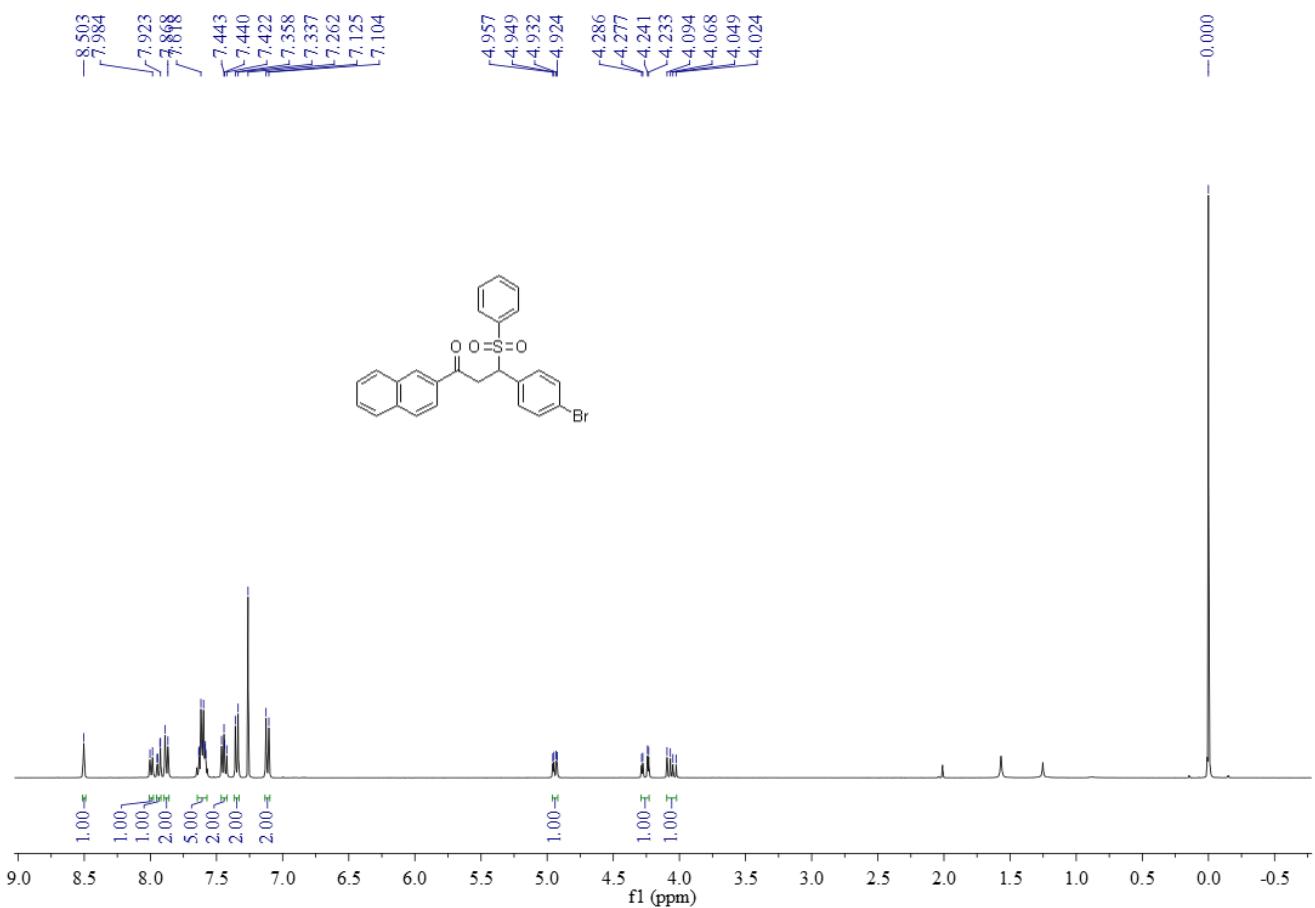
**<sup>13</sup>C NMR Spectrum of Compound 5i**



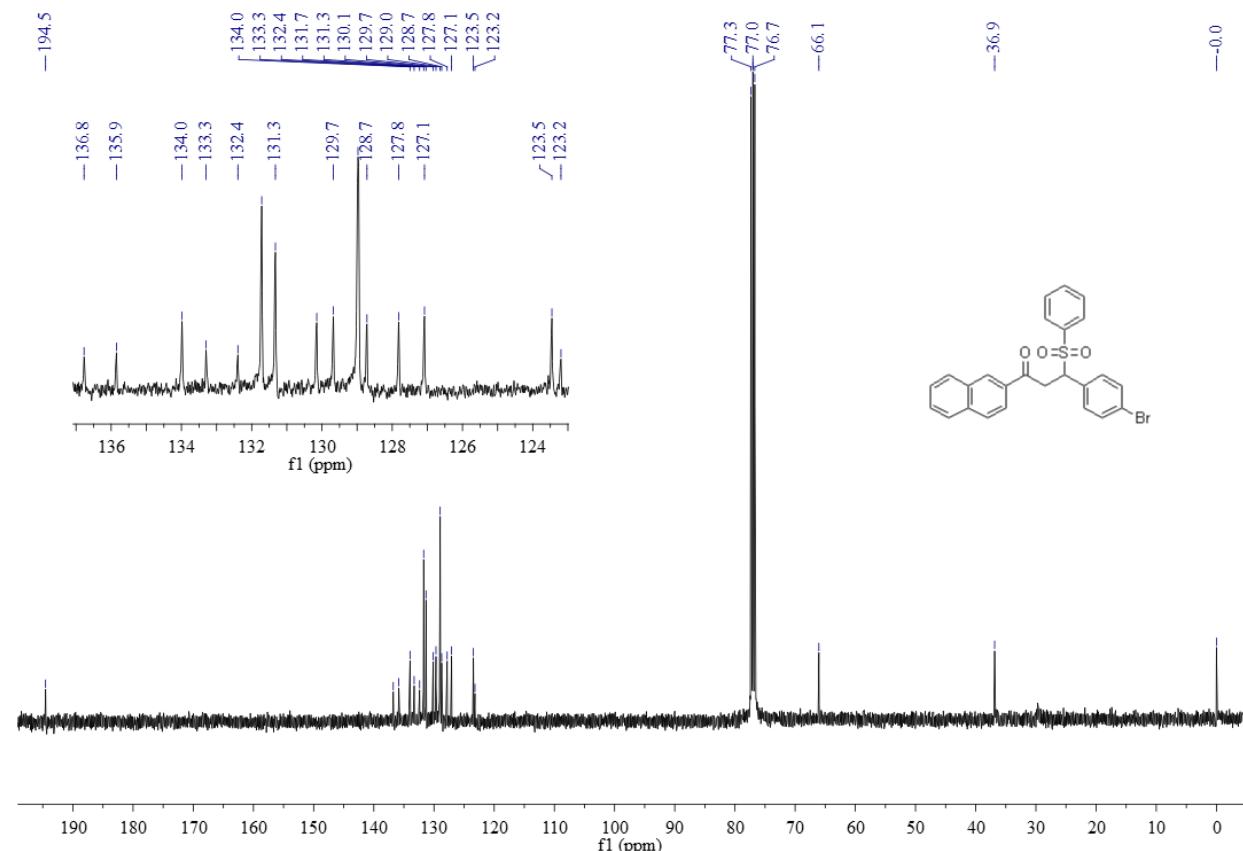
<sup>13</sup>C NMR Spectrum of Compound 5j



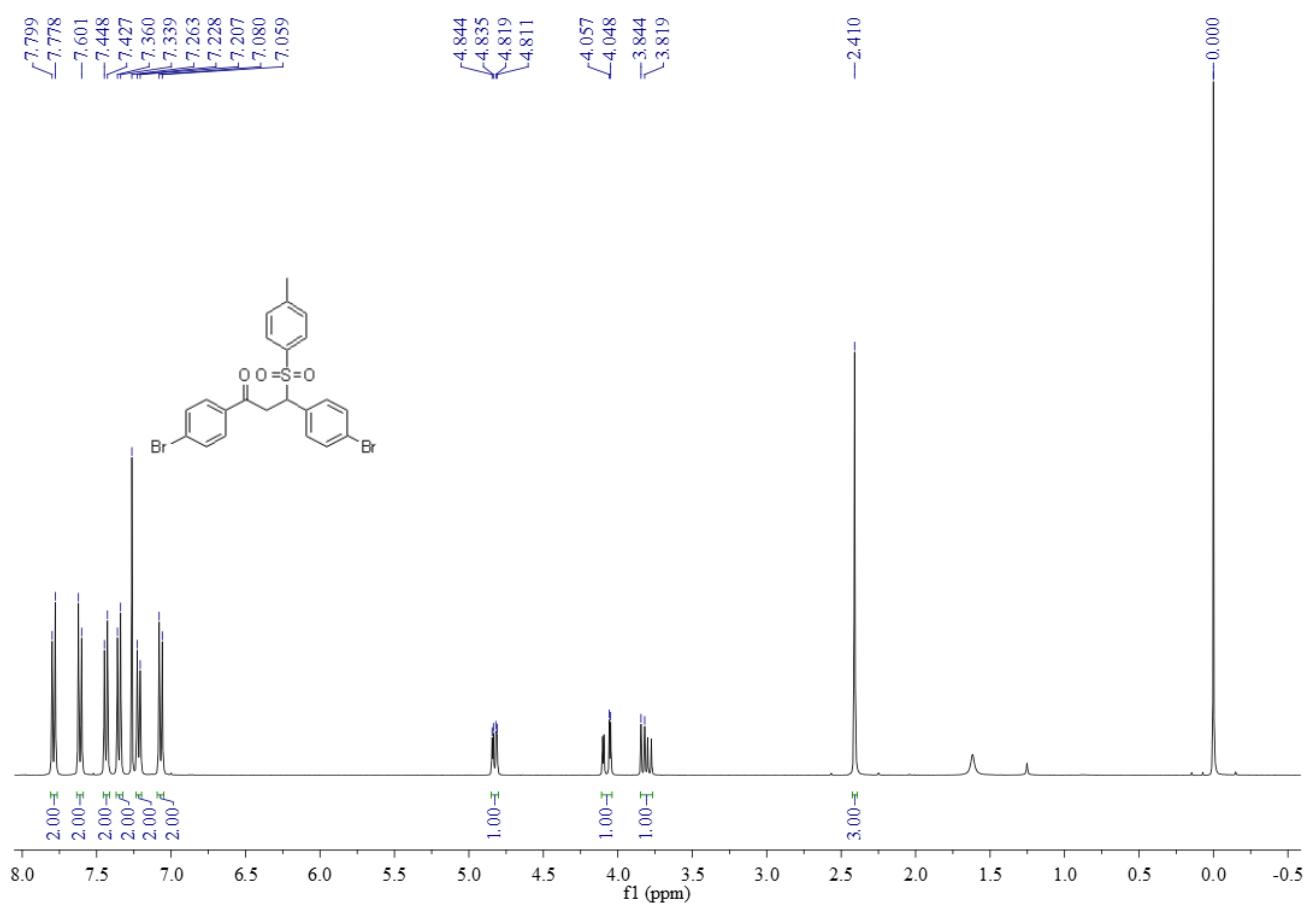
**<sup>13</sup>C NMR Spectrum of Compound 5k**



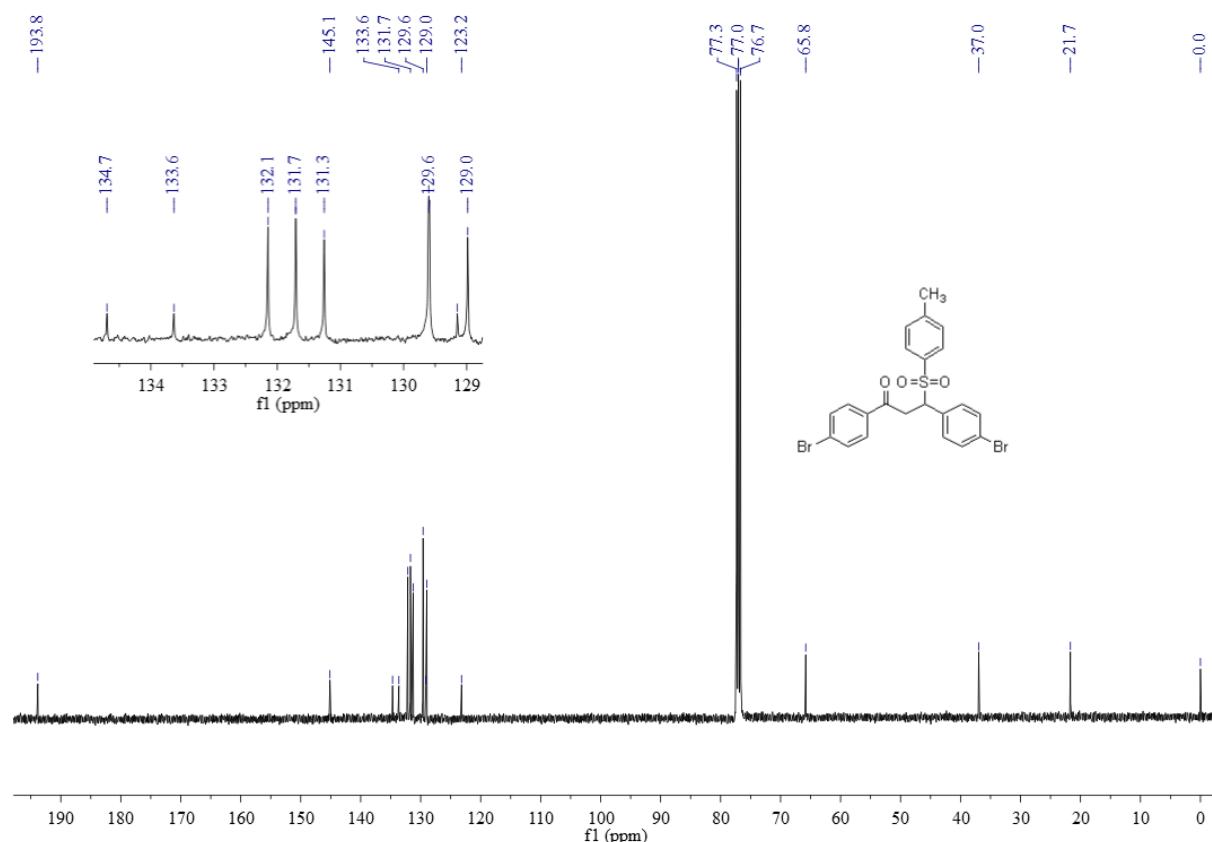
**<sup>1</sup>H NMR Spectrum of Compound 5l**



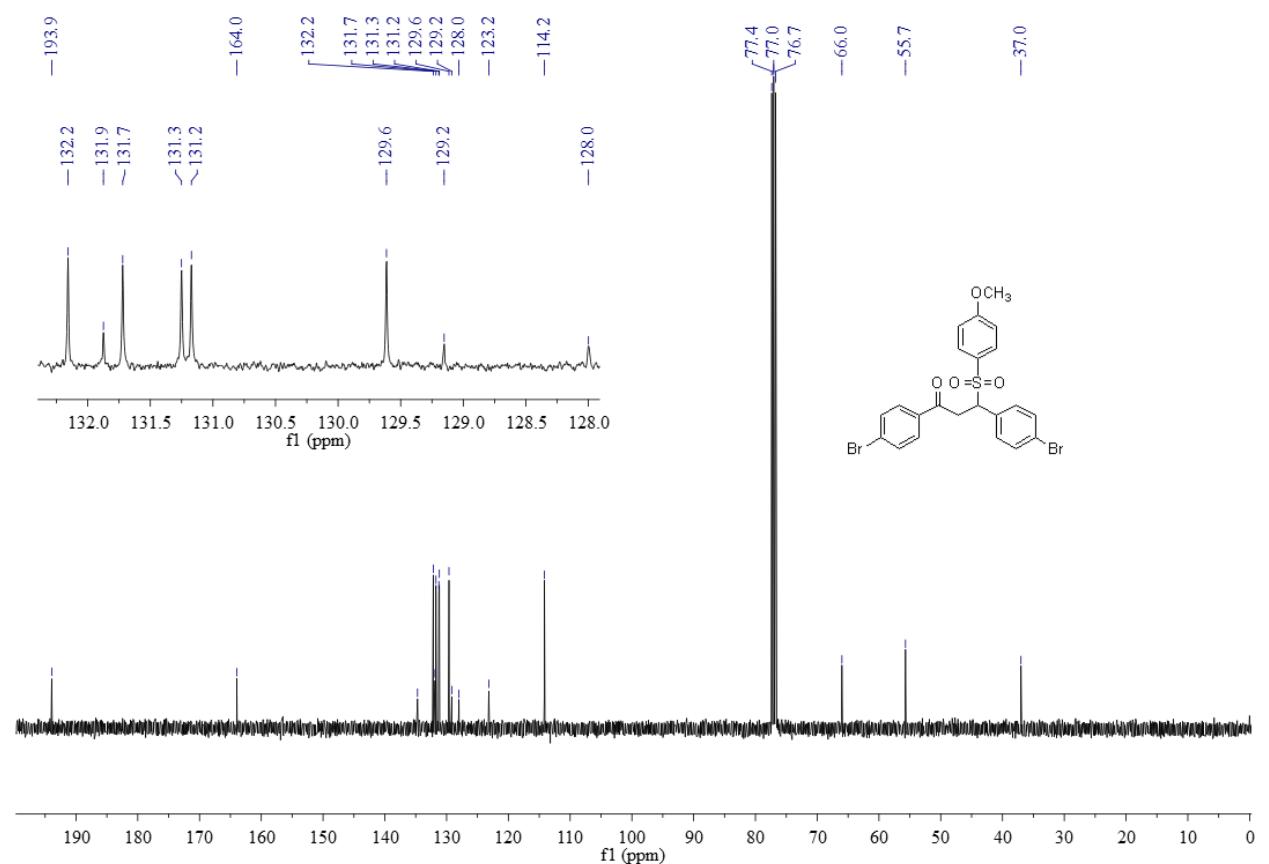
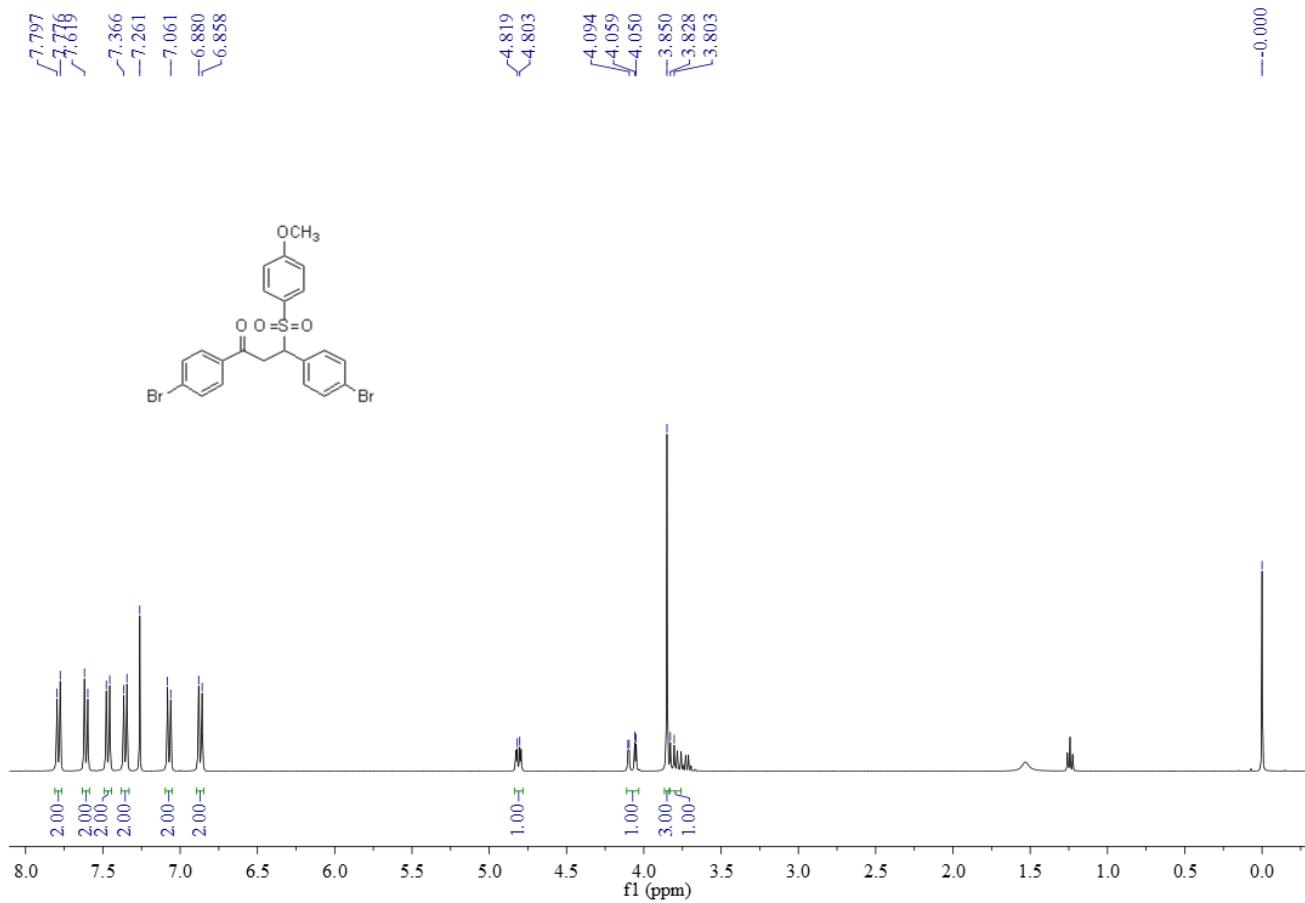
**<sup>13</sup>C NMR Spectrum of Compound 5l**



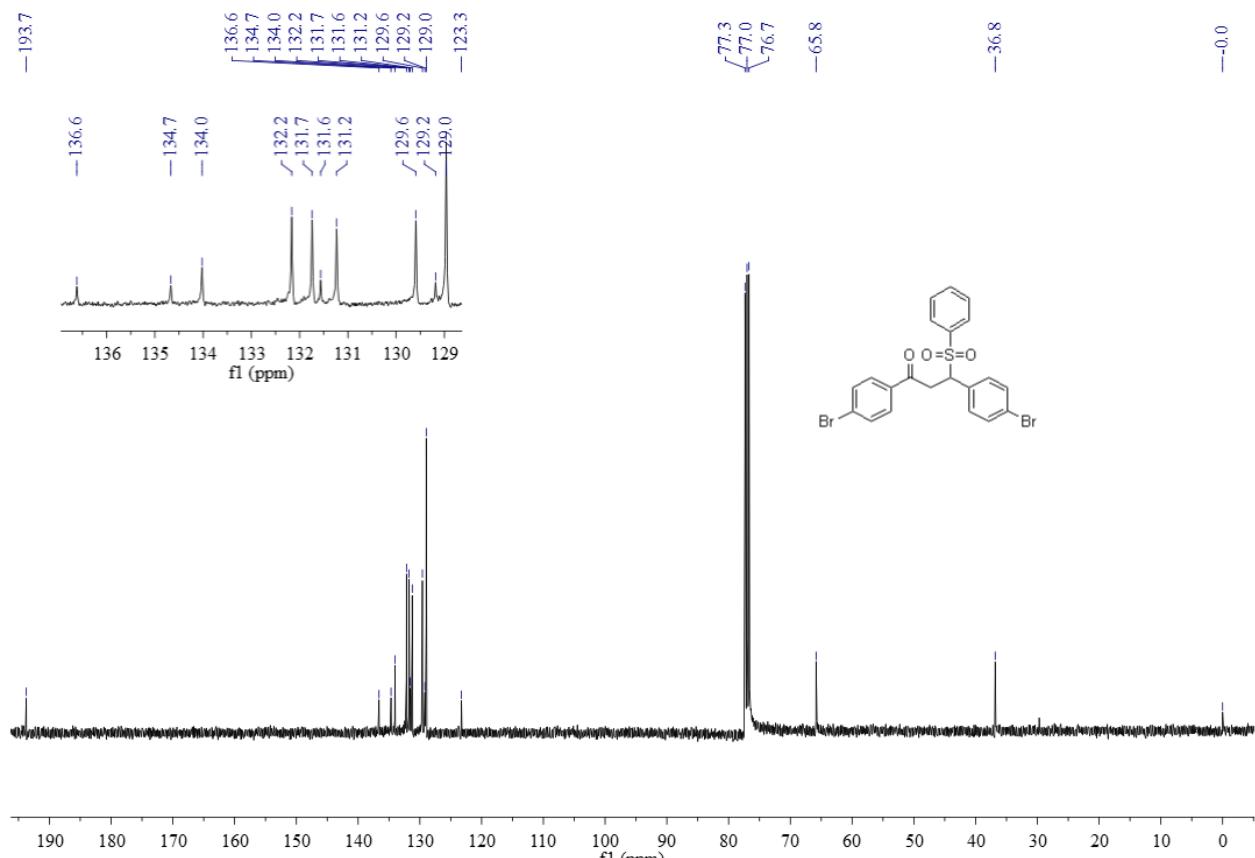
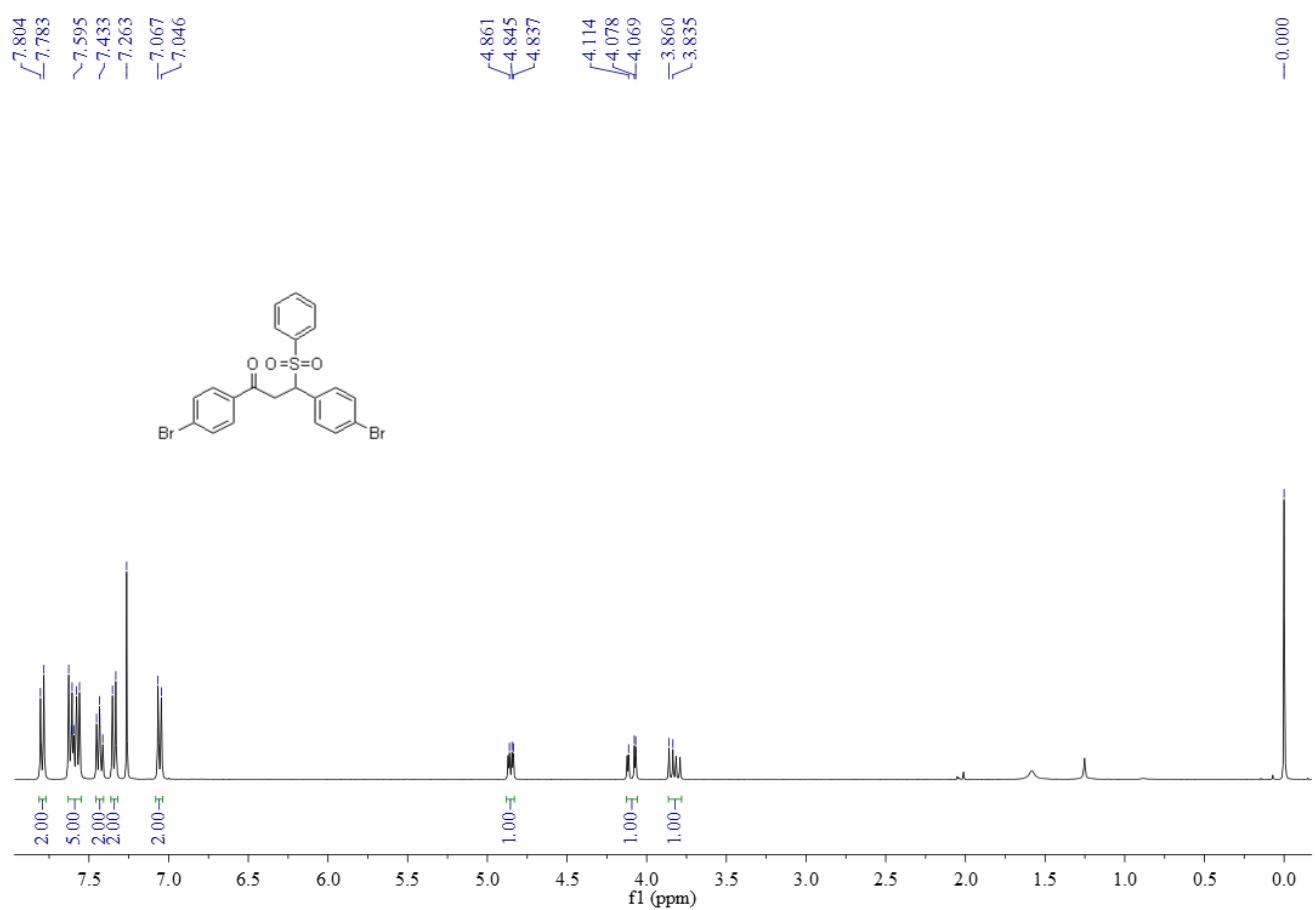
**<sup>1</sup>H NMR Spectrum of Compound 5m**



**<sup>13</sup>C NMR Spectrum of Compound 5m**



**<sup>13</sup>C NMR Spectrum of Compound 5n**



**<sup>13</sup>C NMR Spectrum of Compound 5o**