

Supporting Information

Sulfonyl radical-enabled 6-*endo-trig* cyclization for regiospecific synthesis of unsymmetrical diaryl sulfones

Rong Fu,^a Wen-Juan Hao,^{*,a} Ya-Nan Wu,^a Nan-Nan Wang,^a Shu-Jiang Tu,^{*,a} Guigen Li,^{b,c} and Bo Jiang^{*,a,b}

^aSchool of Chemistry and Chemical Engineering, Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, Jiangsu Normal University, Xuzhou 221116, P. R. China. Email: wjhao@jsnu.edu.cn(WJH); laotu@jsnu.edu.cn (SJT); jiangchem@jsnu.edu.cn (B.J.).

^bDepartment of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX 79409-1061, USA;

^cInstitute of Chemistry & BioMedical Sciences, Nanjing University, Nanjing 210093, P. R. China.

Context

General Information.....	S2
Condition optimization for Product 4a	S2
X-Ray structure of 4a	S3
Condition optimization for Product 6a	S3
X-Ray structure of 6n	S4
Control experiments.....	S4
General Procedure for the Synthesis of Product 4a	S4
Characterization Data of Compounds 4a-4r	S4-S9
General Procedure for the Synthesis of Product 6a	S9
Characterization Data of Compounds 6a-6s	S9-S15
Copies of ¹ H and ¹³ C NMR Spectra for Compounds 4a-4r	S16-S32
Copies of ¹ H and ¹³ C NMR Spectra for Compounds 6a-6s	S33-S50

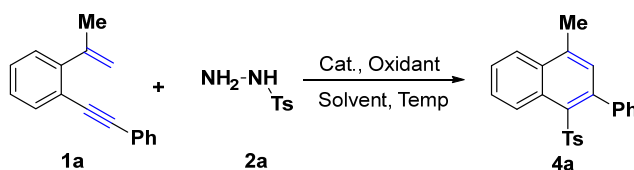
Experimental

General Information

¹H NMR (¹³C NMR) spectra were measured on a Bruker DPX 400 MHz spectrometer in CDCl₃ (DMSO-*d*₆) with chemical shift (δ) given in ppm relative to TMS as internal standard [(s = singlet, d = doublet, t = triplet, brs = broad singlet, m = multiplet), coupling constant (Hz)]. HRMS (ESI) was determined by using microTOF-QII HRMS/MS instrument (BRUKER). X-Ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer.

Condition optimization

Table 1 Screening of Optimal Conditions for Forming **4a**^a



Entry	Oxidant (eq.)	Cat.(mol%)	Additive (eq.)	Solvent	Yield ^b (%)
1	DTBP (4.0)			DCE	29
2	DTBP (4.0)			1,4-dioxane	18
3	DTBP (4.0)			DMF	trace
4	DTBP (4.0)			MeCN	34
5	DTBP (4.0)	FeCl ₂ (10)		MeCN	38
6	DTBP (5.0)	FeCl ₂ (10)		MeCN	43
7	DTBP (6.0)	FeCl ₂ (10)		MeCN	40
8	DTBP (5.0)	Cu(OTf) ₂ (10)		MeCN	30
9	DTBP (5.0)	FeCl ₂ (10)/ Cu(OTf) ₂ (10)		MeCN	50
10	DTBP (5.0)	FeCl ₂ (10)/ Cu(OTf) ₂ (10)	DBU (1.0)	MeCN	66
11	DTBP (5.0)	FeCl ₂ (10)/ Cu(OTf) ₂ (10)	DBU (0.5)	MeCN	77
12	DTBP (5.0)	FeCl ₂ (10)/ Cu(OTf) ₂ (10)	^t BuOLi (0.5)	MeCN	ND ^c
13	DTBP (5.0)	FeCl ₂ (10)/ Cu(OTf) ₂ (10)	Cs ₂ CO ₃ (0.5)	MeCN	30
14	DTBP (5.0)	FeCl ₂ (10)/ Cu(OTf) ₂ (10)	Et ₃ N (0.5)	MeCN	45
15	DTBP (5.0)	FeCl ₂ (10) / Cu(OTf) ₂ (10)	DBU (0.5)	MeCN	68 ^d
16	TBPB (5.0)	FeCl ₂ (10)/ Cu(OTf) ₂ (10)	DBU (0.5)	MeCN	trace
17	DCP (5.0)	FeCl ₂ (10)/ Cu(OTf) ₂ (10)	DBU (0.5)	MeCN	trace
18	TBHP (5.0)	FeCl ₂ (10)/ Cu(OTf) ₂ (10)	DBU (0.5)	MeCN	ND
19	TBHP (5.0)	TBAI (10)	DBU (0.5)	MeCN	ND
20	DTBP (5.0)	FeCl ₂ (10)/ Cu(OTf) ₂ (10)	DBU (0.5)	MeCN	67 ^e
21	DTBP (5.0)	FeCl ₂ (10)/ Cu(OTf) ₂ (10)	DBU (0.5)	MeCN	57 ^f
22	DTBP (5.0)	FeCl ₂ (10)/ Cu(OTf) ₂ (10)	DBU (0.5)	MeCN	70 ^g

^aReaction conditions: **1a** (0.2 mmol, 1.0 equiv.), *p*-toluenesulfonylhydrazine (**2a**, 0.4 mmol, 2.0 equiv.), solvent (1.0 mL), air, 100 °C.

^bIsolated yield based on **1a**. ^cNot detected. ^dUse of 4 Å MS (100 mg). ^eThe mol ratio of **1a**:**2a** was in 1:3. ^fThe reaction was at 90 °C.

^gThe reaction was at 110 °C.

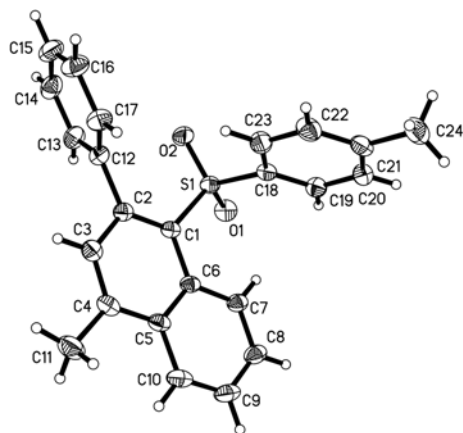
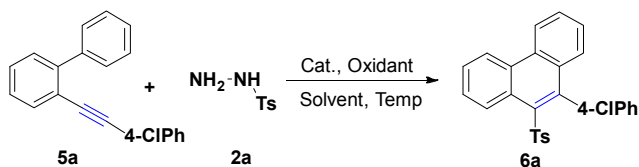


Figure 1 The ORTEP Drawing of **4a** (Thermal ellipsoids are set at 30% probability level)

Table 2 Screening of Optimal Conditions for Forming **6a**^a



Entry	Oxidant (eq.)	Cat. (mol %)	Solvent	Additive (eq.)	T (°C)	Yield ^b (%)
1	DTBP (5.0)	FeCl ₂ (10)/ Cu(OTf) ₂ (10)	MeCN	DBU (0.5)	100	15
2	DTBP (5.0)	Cu(OTf) ₂ (10)	MeCN	DBU (0.5)	100	18
3	DTBP (5.0)	Cu(OTf) ₂ (10)	MeCN		100	25
4	DTBP (5.0)	FeCl ₂ (10)	MeCN		100	20
5	DTBP (5.0)	Cu(OTf) ₂ (10)	MeCN		120	34
6	DTBP (5.0)	Cu(OTf) ₂ (10)	DCE		120	39
7	DTBP (5.0)	Cu(OTf) ₂ (10)	1,4-dioxane		120	18
8	DTBP (5.0)	Cu(OTf) ₂ (10)	toluene		120	28
9	DTBP (5.0)	Cu(OTf) ₂ (10)	DMF		120	trace
10	DTBP (5.0)	FeCl ₃ (10)	DCE		120	18
11	DTBP (5.0)	Pd(OAc) ₂ (10)	DCE		120	trace
12	DTBP (5.0)	CuI(10)	DCE		120	25
13	DTBP (5.0)	Cu(OAc) ₂ (10)	DCE		120	28
14	DTBP (5.0)	Co(acac) ₂ (10)	DCE		120	22
15	DTBP (5.0)	Cu(OTf) ₂ (10)	DCE	4Å MS	120	41 ^c
16	DTBP (6.0)	Cu(OTf) ₂ (10)	DCE	4Å MS	120	50 ^c
16	TBHP (6.0)	Cu(OTf) ₂ (10)	DCE	4Å MS	120	10 ^c
17	TBPB (6.0)	Cu(OTf) ₂ (10)	DCE	4Å MS	120	15 ^c
19	BPO (6.0)	Cu(OTf) ₂ (10)	DCE	4Å MS	120	12 ^c
20	DPO (6.0)	Cu(OTf) ₂ (10)	DCE	4Å MS	120	ND ^c
21	TBHP (5.0)	TBAI (10)	DCE	4Å MS	120	ND ^c

^aReaction conditions: **5a** (0.2 mmol, 1 equiv), *p*-toluenesulfonyl hydrazine (**2a**, 0.8 mmol, 4.0 equiv.), solvent (1.0 mL), air, for 12 h.

^bIsolated yield based on **5a**. ^c4Å MS (100 mg). ND = Not detected

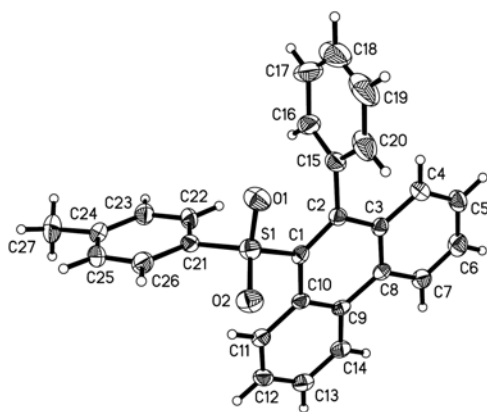
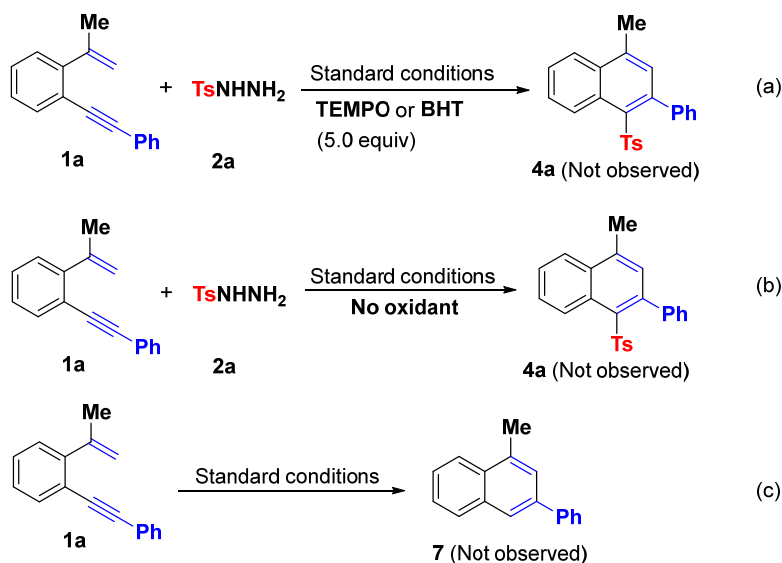


Figure 2 The ORTEP Drawing of **6n** (Thermal ellipsoids are set at 30% probability level)



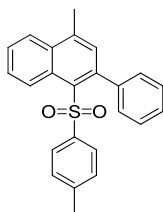
Scheme 1 Control experiments

General Procedure for the Synthesis of Products 4

Example for the synthesis of **4a**:

1-(Phenylethynyl)-2-(prop-1-en-2-yl)benzene **1a** (44 mg, 0.2 mmol, 1.0 equiv), tosylhydrazide (**2a**, 75 mg, 0.4 mmol, 2.0 equiv), Cu(OTf)₂ (7.0 mg, 10 mol%), FeCl₂ (2.5 mg, 10 mol%), and MeCN (1.0 mL) were introduced in a 10-mL reaction tube, DBU (15.2 mg, 0.5 equiv) and DTBP (146.2 mg, 1.0 mmol, 5.0 equiv) were then successively added and sealed. The mixture stirred at 100 °C until complete consumption of the starting material **1a**. After completion of the reaction, the reaction mixture was concentrated in vacuum. The crude product was purified by flash column chromatography (petroleum ether/ethyl acetate) to afford the desired product **4a**.

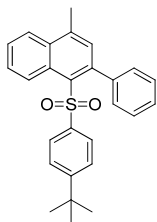
4-Methyl-2-phenyl-1-tosylnaphthalene (4a)



Yellow solid, mp 150-151 °C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) 9.14–9.06 (m, 1H), 8.09–8.00 (m, 1H),

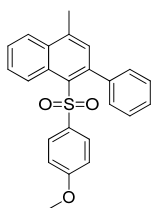
7.63–7.56 (m, 2H), 7.51–7.45 (m, 2H), 7.35–7.28 (m, 3H), 7.26–7.23 (m, 2H), 7.19 (s, 1H), 7.07 (d, $J = 8.0$ Hz, 2H), 2.72 (d, $J = 0.8$ Hz, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 ; δ , ppm) 143.7, 143.0, 141.4, 141.0, 140.4, 132.6, 131.8, 131.0, 130.1, 129.2, 129.0, 127.8, 127.3, 127.2, 126.6, 126.5, 124.6, 21.5, 20.0; HRMS (APCI-TOF) m/z Calcd. For $\text{C}_{24}\text{H}_{21}\text{O}_2\text{S}$, 373.1262 $[\text{M}+\text{H}]^+$, found 373.1263.

1-((4-(tert-Butyl)phenyl)sulfonyl)-4-methyl-2-phenylnaphthalene (4b)



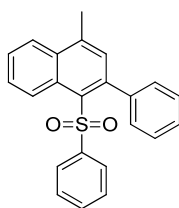
Yellow solid, mp 185–186 °C; ^1H NMR (400 MHz, CDCl_3 ; δ , ppm) 9.18 (d, $J = 8.4$ Hz, 1H), 8.07 (m, 1H), 7.66–7.58 (m, 2H), 7.47 (m, 2H), 7.30–7.24 (m, 5H), 7.23–7.18 (m, 2H), 7.17 (s, 1H), 2.72 (s, 3H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3 ; δ , ppm) 155.84, 143.39, 141.32, 140.70, 140.27, 132.58, 132.10, 130.93, 130.19, 129.08, 127.76, 127.38, 127.16, 126.59, 126.48, 126.46, 125.50, 124.57, 35.01, 31.02, 19.93; HRMS (APCI-TOF) m/z Calcd. For $\text{C}_{27}\text{H}_{27}\text{O}_2\text{S}$ 415.1732 $[\text{M}+\text{H}]^+$, found 415.1728.

1-((4-Methoxyphenyl)sulfonyl)-4-methyl-2-phenylnaphthalene (4c)



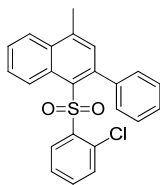
White solid, mp 208–209 °C; ^1H NMR (400 MHz, CDCl_3 ; δ , ppm) 9.18–9.11 (m, 1H), 8.09–8.03 (m, 1H), 7.61 (m, 2H), 7.53–7.48 (m, 2H), 7.36–7.30 (m, 3H), 7.25–7.22 (m, 2H), 7.17 (d, $J = 0.8$ Hz, 1H), 6.76–6.70 (m, 2H), 3.77 (s, 3H), 2.71 (d, $J = 0.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3 ; δ , ppm) 162.45, 143.3, 141.5, 140.2, 135.5, 132.6, 132.3, 131.0, 130.0, 129.0, 128.8, 127.7, 127.4, 127.2, 126.4, 124.6, 113.7, 55.5, 19.9; HRMS (APCI-TOF) m/z Calcd. For $\text{C}_{24}\text{H}_{21}\text{O}_3\text{S}$ 389.1211 $[\text{M}+\text{H}]^+$, found 389.1212.

4-Methyl-2-phenyl-1-(phenylsulfonyl)naphthalene (4d)



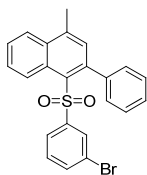
Yellow solid, mp 188–189 °C; ^1H NMR (400 MHz, CDCl_3 ; δ , ppm) 9.17–9.12 (m, 1H), 8.12–8.07 (m, 1H), 7.67–7.59 (m, 4H), 7.47–7.24 (m, 9H), 2.76 (d, $J = 0.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3 ; δ , ppm) 143.9, 143.8, 141.2, 140.6, 132.6, 132.2, 131.5, 131.0, 130.1, 129.1, 128.5, 127.8, 127.4, 127.3, 126.5, 126.5, 126.4, 124.6, 20.0; HRMS (APCI-TOF) m/z Calcd. For $\text{C}_{23}\text{H}_{19}\text{O}_2\text{S}$ 359.1106 $[\text{M}+\text{H}]^+$, found 359.1107.

1-((2-Chlorophenyl)sulfonyl)-4-methyl-2-phenylnaphthalene (4e)



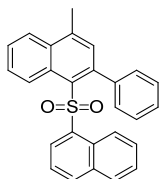
White solid, mp 181-182 °C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) 9.34–9.18 (m, 1H), 8.18–8.07 (m, 1H), 7.72–7.55 (m, 3H), 7.29–7.17 (m, 8H), 7.06 (t, *J* = 7.6 Hz, 1H), 2.77 (s, 3H); ¹³C NMR (100 MHz, CDCl₃; δ, ppm) 142.3, 141.1, 140.5, 140.1, 133.0, 132.5, 131.9, 131.0, 130.7, 130.1, 129.6, 129.5, 127.7, 127.6, 127., 126.5, 126.5, 126.2, 124.6, 20.0; HRMS (APCI-TOF) *m/z* Calcd. For C₂₃H₁₈ClO₂S 393.0716 [M+H]⁺, found 393.0718.

1-((3-Bromophenyl)sulfonyl)-4-methyl-2-phenylnaphthalene (4f)



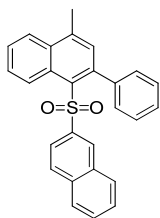
Yellow solid, mp 111-112 °C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) 9.19–9.14 (m, 1H), 8.11–8.07 (m, 1H), 7.65 (m, 2H), 7.57 (t, *J* = 1.6 Hz, 1H), 7.49 (m, 1H), 7.43 (m, 1H), 7.37–7.27 (m, 3H), 7.19–7.10 (m, 4H), 2.74 (d, *J* = 0.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃; δ, ppm) 145.5, 143.6, 141.0, 140.5, 135.2, 132.6, 131.3, 130.8, 130.1, 130.0, 129.7, 129.3, 128.0, 127.7, 127.5, 126.7, 126.2, 125.2, 124.7, 122.4, 20.0; HRMS (APCI-TOF) *m/z* Calcd. For C₂₃H₁₈BrO₂S 437.0211 [M+H]⁺, found 437.0212.

4-Methyl-1-(naphthalen-1-ylsulfonyl)-2-phenylnaphthalene (4g)



Yellow solid, mp 172-173 °C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) 9.25 (m, 1H), 8.30–7.98 (m, 2H), 7.97–7.36 (m, 8H), 7.36–7.00 (m, 6H), 2.73 (d, *J* = 5.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃; δ, ppm) 145.3, 143.2, 143.1, 141.2, 140.7, 139.1, 132.9, 131.8, 130.9, 130.6, 129.9, 129.2, 129.2, 128.4, 128.2, 127.9, 127.4, 127.4, 127.0, 126.8, 126.6, 126.2, 21.5; HRMS (APCI-TOF) *m/z* Calcd. For C₂₇H₂₁O₂S 409.1262 [M+H]⁺, found 409.1270.

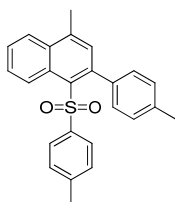
4-Methyl-1-(naphthalen-2-ylsulfonyl)-2-phenylnaphthalene (4h)



Yellow solid, mp 145-146 °C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) 9.24 (d, *J* = 8.4 Hz, 1H), 8.35–7.98 (m, 2H), 7.98–7.42 (m, 9H), 7.42–6.98 (m, 5H), 2.72 (s, 3H); ¹³C NMR (100 MHz, CDCl₃; δ, ppm) 143.7, 141.1, 140.6, 140.5, 134.5, 132.6, 131.8, 131.7, 130.9, 130.2, 129.3, 129.2, 128.8, 128.6, 128.0, 127.9, 127.7, 127.5, 127.3,

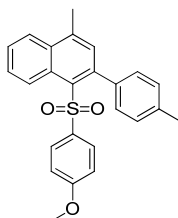
127.2, 126.5, 126.4, 124.6, 121.9, 20.0; HRMS (APCI-TOF) m/z Calcd. For $C_{27}H_{21}O_2S$ 409.1262 $[M+H]^+$, found 409.1250.

4-Methyl-2-(p-tolyl)-1-tosylnaphthalene (4j)



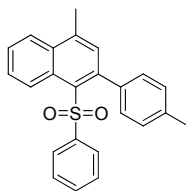
Yellow solid, mp 189-190 °C; 1H NMR (400 MHz, $CDCl_3$; δ , ppm) 9.09 (m, 1H), 8.10–8.04 (m, 1H), 7.65–7.57 (m, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.24–7.05 (m, 7H), 2.74 (s, 3H), 2.43 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ , ppm) 143.8, 142.9, 141.0, 140.3, 138.5, 137.0, 132.5, 131.75, 131.2, 130.1, 129.1, 128.9, 128.1, 127.7, 126.6, 126.4, 126.4, 124.6, 21.5, 21.3, 19.9; HRMS (APCI-TOF) m/z Calcd. For $C_{25}H_{23}O_2S$ 387.1419 $[M+H]^+$, found 387.1428.

1-((4-Methoxyphenyl)sulfonyl)-4-methyl-2-(p-tolyl)naphthalene (4k)



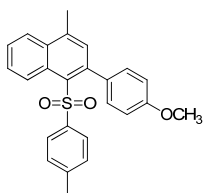
White solid, mp 153-154 °C; 1H NMR (400 MHz, $CDCl_3$; δ , ppm) 9.17–9.08 (m, 1H), 8.04 (m, 1H), 7.63–7.49 (m, 4H), 7.15 (m, 5H), 6.78–6.68 (m, 2H), 3.77 (d, J = 4.0 Hz, 3H), 2.70 (d, J = 3.6 Hz, 3H), 2.40 (d, J = 4.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ , ppm) 162.5, 143.5, 140.1, 138.6, 136.9, 135.6, 132.6, 132.3, 131.2, 130.1, 128.9, 128.8, 128.1, 127.7, 126.5, 126.4, 124.6, 113.6, 55.5, 21.3, 19.9; HRMS (APCI-TOF) m/z Calcd. For $C_{25}H_{23}O_3S$ 403.1368 $[M+H]^+$, found 403.1386.

4-Methyl-1-(phenylsulfonyl)-2-(p-tolyl)naphthalene (4l)



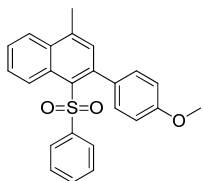
Yellow solid, mp 210-211 °C; 1H NMR (400 MHz, $CDCl_3$; δ , ppm) 9.10–9.04 (m, 1H), 8.08–8.03 (m, 1H), 7.62–7.54 (m, 4H), 7.41–7.36 (m, 1H), 7.29–7.27 (m, 1H), 7.19 (m, 1H), 7.15–7.10 (m, 4H), 2.72 (d, J = 0.4 Hz, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ , ppm) 144.0, 140.5, 138.3, 137.1, 132.5, 132.1, 131.5, 131.1, 130.2, 129.0, 128.4, 128.1, 127.8, 126.5, 126.4, 126.4, 124.6, 21.3, 20.0; HRMS (APCI-TOF) m/z Calcd. For $C_{24}H_{21}O_2S$ 373.1262 $[M+H]^+$, found 373.1258.

2-(4-Methoxyphenyl)-4-methyl-1-tosylnaphthalene (4m)



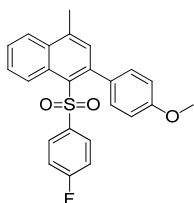
White solid, mp 155-156 °C; ^1H NMR (400 MHz, CDCl_3 ; δ , ppm) 9.11 (m, 1H), 8.08–8.01 (m, 1H), 7.63–7.55 (m, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.20–7.12 (m, 3H), 7.05 (d, J = 8.4 Hz, 2H), 6.87–6.80 (m, 2H), 3.85 (s, 3H), 2.71 (d, J = 0.8 Hz, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 ; δ , ppm) 159.0, 143.4, 142.8, 141.1, 140.2, 133.5, 132.5, 132.0, 131.3, 130.4, 130.3, 129.0, 127.6, 126.5, 126.5, 126.4, 124.5, 112.9, 55.3, 21.5, 19.9; HRMS (APCI-TOF) m/z Calcd. For $\text{C}_{25}\text{H}_{23}\text{O}_3\text{S}$ 403.1368 $[\text{M}+\text{H}]^+$, found 403.1388.

2-(4-Methoxyphenyl)-4-methyl-1-(phenylsulfonyl)naphthalene (4n)



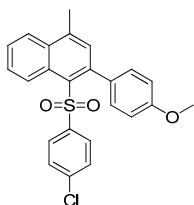
White solid, mp 184-185 °C; ^1H NMR (400 MHz, CDCl_3 ; δ , ppm) 9.13 (m, 1H), 8.05 (m, 1H), 7.63–7.49 (m, 4H), 7.37 (t, J = 7.4 Hz, 1H), 7.25 (t, J = 8.8 Hz, 2H), 7.21–7.09 (m, 3H), 6.88–6.77 (m, 2H), 3.84 (s, 3H), 2.72 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 ; δ , ppm) 162.5, 143.3, 141.5, 140.2, 135.5, 132.6, 132.3, 131.0, 130.0, 129.0, 128.8, 127.7, 127.4, 127.2, 126.5, 126.5, 124.6, 113.7, 55.5, 19.9; HRMS (APCI-TOF) m/z Calcd. For $\text{C}_{24}\text{H}_{21}\text{O}_3\text{S}$ 389.1211 $[\text{M}+\text{H}]^+$, found 389.1205.

1-((4-Fluorophenyl)sulfonyl)-2-(4-methoxyphenyl)-4-methylnaphthalene (4o)



Yellow solid, mp 121-122 °C; ^1H NMR (400 MHz, CDCl_3 ; δ , ppm) 9.16 (m, 1H), 8.07 (m, 1H), 7.66–7.58 (m, 2H), 7.52–7.44 (m, 2H), 7.18–7.09 (m, 3H), 6.94–6.81 (m, 4H), 3.85 (s, 3H), 2.72 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 ; δ , ppm) 164.6 ($^1J_{\text{CF}}$ = 252.0), 159.2, 143.2, 143.2, 140.6, 140.0, 133.1, 132.5, 131.9, 131.2, 130.7, 130.3, 129.2 ($^3J_{\text{CF}}$ = 9.3), 127.8, 126.5, 126.3, 124.6 ($^4J_{\text{CF}}$ = 2.1), 115.5 ($^2J_{\text{CF}}$ = 23.0), 113.0, 77.4, 77.0, 76.7, 55.4, 19.9; HRMS (APCI-TOF) m/z Calcd. For $\text{C}_{24}\text{H}_{20}\text{FO}_3\text{S}$ 407.1117 $[\text{M}+\text{H}]^+$, found 407.1137.

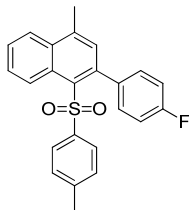
1-((4-Chlorophenyl)sulfonyl)-2-(4-methoxyphenyl)-4-methylnaphthalene (4p)



Yellow solid, mp 141-142 °C; ^1H NMR (400 MHz, CDCl_3 ; δ , ppm) 9.14 (m, 1H), 8.07 (m, 1H), 7.66–7.58 (m,

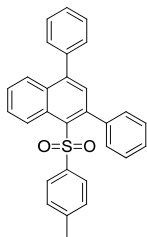
2H), 7.41–7.37 (m, 2H), 7.21–7.15 (m, 3H), 7.12–7.07 (m, 2H), 6.84–6.80 (m, 2H), 3.85 (s, 3H), 2.72 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 ; δ , ppm) 159.3, 143.2, 142.4, 140.7, 138.5, 133.0, 132.5, 131.7, 131.1, 130.7, 130.3, 128.6, 128.0, 127.9, 126.6, 126.3, 124.7, 113.0, 55.4, 20.0; HRMS (APCI-TOF) m/z Calcd. For $\text{C}_{24}\text{H}_{20}\text{ClO}_3\text{S}$ 423.0822 $[\text{M}+\text{H}]^+$, found 423.0823.

2-(4-Fluorophenyl)-4-methyl-1-tosylnaphthalene (4q)



White solid, mp 165-166 °C; ^1H NMR (400 MHz, CDCl_3 ; δ , ppm) 9.11 (m, 1H), 8.06 (m, 1H), 7.64–7.57 (m, 2H), 7.45 (d, $J = 8.0$ Hz, 2H), 7.22–7.18 (m, 2H), 7.16 (s, 1H), 7.09 (d, $J = 8.4$ Hz, 2H), 7.03–6.98 (m, 2H), 2.72 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 ; δ , ppm) 162.2($^1J_{\text{CF}} = 245.1$), 143.1, 142.5, 140.9, 140.6, 137.2, 137.2, 132.6, 132.0, 130.9, 130.7($^3J_{\text{CF}} = 8.1$), 130.1, 129.2, 127.9, 126.6, 126.5($^4J_{\text{CF}} = 4.9$), 124.6, 114.3($^2J_{\text{CF}} = 22.4$), 21.5, 20.0; HRMS (APCI-TOF) m/z Calcd. For $\text{C}_{24}\text{H}_{20}\text{FO}_2\text{S}$ 391.1168 $[\text{M}+\text{H}]^+$, found 391.1170.

2,4-Diphenyl-1-tosylnaphthalene (4r)



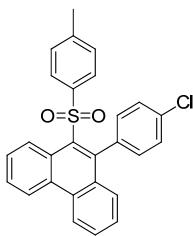
Yellow solid, mp 188-189 °C; ^1H NMR (400 MHz, CDCl_3 ; δ , ppm) 9.17 (d, $J = 8.9$ Hz, 1H), 7.94 (d, $J = 8.4$ Hz, 1H), 7.65–7.60 (m, 1H), 7.54–7.39 (m, 8H), 7.33–7.24 (m, 6H), 7.10 (d, $J = 8.3$ Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 ; δ , ppm) 145.3, 143.2, 143.1, 141.2, 140.7, 139.1, 132.9, 131.84, 130.9, 130.6, 129.9, 129.2, 129.2, 128.4, 128.2, 127.9, 127.4, 127.4, 127.0, 126.8, 126.6, 126.2, 21.5; HRMS (APCI-TOF) m/z Calcd. For $\text{C}_{29}\text{H}_{23}\text{O}_2\text{S}$ 435.1419 $[\text{M}+\text{H}]^+$, found 435.1423.

General Procedure for the Synthesis of Products 6

Example for the synthesis of **6a**:

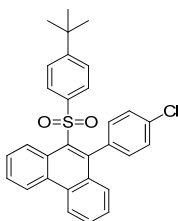
2-((4-Chlorophenyl)ethynyl)-1,1'-biphenyl (**5a**, 58 mg, 0.2 mmol, 1.0 equiv), *p*-toluenesulfonyl hydrazine (**2a**, 149 mg, 0.8 mmol, 4.0 equiv), $\text{Cu}(\text{OTf})_2$ (7.0 mg, 10 mol%), and DCE (1.0 mL) were introduced in a 10-mL reaction tube, 4Å MS (100 mg) and DTBP (175.2 mg, 6.0 equiv) were then successively added and sealed. The mixture stirred at 120 °C until complete consumption of the starting material **5a**. After completion of the reaction, the reaction mixture was concentrated in vacuum. The crude product was purified by flash column chromatography (petroleum ether/ethyl acetate) to afford the desired product **5a**.

9-(4-Chlorophenyl)-10-tosylphenanthrene (6a)



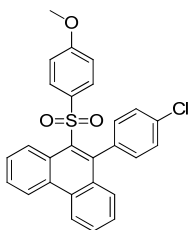
Yellow solid, mp 214-216 °C; ^1H NMR (400 MHz, CDCl_3 ; δ , ppm) 9.03 (d, J = 8.8 Hz, 1H), 8.74 (m, 2H), 7.78–7.67 (m, 2H), 7.63–7.54 (m, 3H), 7.52–7.47 (m, 1H), 7.38 (m, 3H), 7.24–7.19 (m, 2H), 7.15 (d, J = 8.0 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 ; δ , ppm) 143.5, 142.2, 140.6, 136.2, 133.7, 133.06, 132.2, 131.4, 131.3, 130.9, 129.6, 129.4, 129.3, 127.9, 127.5, 127.4, 127.3, 127.1, 126.7, 126.4, 122.9, 122.5, 21.5; HRMS (APCI-TOF) m/z Calcd. For $\text{C}_{27}\text{H}_{20}\text{ClO}_2\text{S}$ 429.0716 $[\text{M}+\text{H}]^+$, found 429.0728.

9-((4-tert-Butylphenyl)sulfonyl)-10-(4-chlorophenyl)phenanthrene (6b)



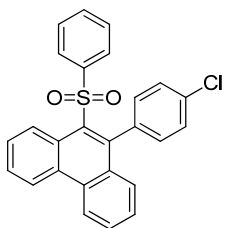
Yellow solid, mp 197-198 °C; ^1H NMR (400 MHz, CDCl_3 ; δ , ppm) 9.13 (d, J = 8.8 Hz, 1H), 8.75 (t, J = 8.8 Hz, 2H), 7.70 (m, 3H), 7.57–7.45 (m, 3H), 7.40–7.28 (m, 5H), 7.19–7.14 (m, 2H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3 ; δ , ppm) 156.4, 141.7, 140.5, 136.0, 133.7, 133.6, 132.2, 131.6, 131.3, 130.9, 129.6, 129.2, 127.9, 127.6, 127.5, 127.3, 127.2, 126.9, 126.3, 125.9, 122.9, 122.6, 35.1, 31.1; HRMS (APCI-TOF) m/z Calcd. For $\text{C}_{30}\text{H}_{26}\text{ClO}_2\text{S}$ 485.1342 $[\text{M}+\text{H}]^+$, found 485.1353.

9-(4-Chlorophenyl)-10-((4-methoxyphenyl)sulfonyl)phenanthrene (6c)



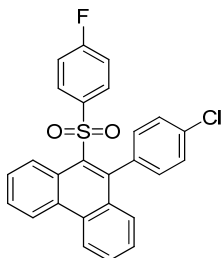
Yellow solid, mp 203-205 °C; ^1H NMR (400 MHz, CDCl_3 ; δ , ppm) 9.10 (dd, J = 8.4, 0.8 Hz, 1H), 8.73 (t, J = 8.0 Hz, 2H), 7.77–7.58 (m, 5H), 7.51–7.46 (m, 1H), 7.42–7.38 (m, 2H), 7.33 (d, J = 8.4 Hz, 1H), 7.22–7.18 (m, 2H), 6.83–6.78 (m, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 ; δ , ppm) 162.8, 141.7, 136.3, 135.2, 133.8, 133.7, 132.2, 131.5, 131.4, 131.0, 129.6, 129.3, 128.8, 127.9, 127.6, 127.5, 127.3, 127.1, 126.8, 122.9, 122.5, 114.0, 55.6; HRMS (APCI-TOF) m/z Calcd. For $\text{C}_{27}\text{H}_{20}\text{ClO}_3\text{S}$ 459.0822 $[\text{M}+\text{H}]^+$, found 459.0829.

9-(4-Chlorophenyl)-10-(phenylsulfonyl)phenanthrene (6d)



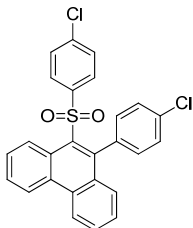
Yellow solid, mp 207-208 °C; ^1H NMR (400 MHz, DMSO; δ , ppm) 9.00 (d, J = 8.4 Hz, 2H), 8.71 (d, J = 8.4 Hz, 1H), 7.91–7.86 (m, 1H), 7.85–7.80 (m, 2H), 7.78–7.73 (m, 1H), 7.69–7.45 (m, 9H), 7.31–7.26 (m, 1H); ^{13}C NMR (100 MHz, DMSO; δ , ppm) 143.3, 142.9, 137.0, 133.6, 132.8, 132.2, 131.9, 131.7, 131.2, 131.0, 130.7, 129.9, 129.4, 128.4, 128.4, 128.1, 126.8, 126.5, 126.1, 124.2, 123.7; HRMS (APCI-TOF) m/z Calcd. For $\text{C}_{26}\text{H}_{18}\text{ClO}_2\text{S}$ 429.0716 $[\text{M}+\text{H}]^+$, found 429.0719.

9-(4-Chlorophenyl)-10-((4-fluorophenyl)sulfonyl)phenanthrene (6e)



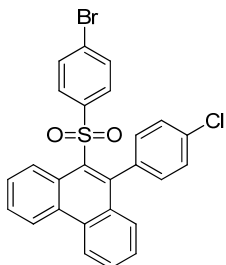
Yellow solid, mp 175-177 °C; ^1H NMR (400 MHz, CDCl_3 ; δ , ppm) 9.03 (d, J = 8.4 Hz, 1H), 8.75 (t, J = 8.4 Hz, 2H), 7.80–7.60 (m, 5H), 7.53–7.34 (m, 4H), 7.23–7.16 (m, 2H), 7.03 (t, J = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3 ; δ , ppm) 164.6 ($^1J_{\text{CF}}$ = 253.9), 142.4, 139.7, 135.9, 134.0, 132.9, 132.3, 131.5, 131.2, 131.0, 129.9, 129.3, 129.2 ($^3J_{\text{CF}}$ = 9.4), 128.0, 127.7, 127.6, 127.5, 126.9, 126.6, 123.0, 122.6, 116.1 ($^2J_{\text{CF}}$ = 22.5); HRMS (APCI-TOF) m/z Calcd. For $\text{C}_{26}\text{H}_{17}\text{ClFO}_2\text{S}$ 447.0622 $[\text{M}+\text{H}]^+$, found 447.0625.

9-(4-Chlorophenyl)-10-((4-chlorophenyl)sulfonyl)phenanthrene (6f)



Yellow solid, mp 212-214 °C; ^1H NMR (400 MHz, DMSO; δ , ppm) 9.01 (d, J = 8.4 Hz, 2H), 8.68 (d, J = 8.0 Hz, 1H), 7.89 (m, 1H), 7.85–7.75 (m, 3H), 7.67 (t, J = 7.6 Hz, 2H), 7.60–7.40 (m, 6H), 7.29 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO; δ , ppm) 143.1, 142.1, 138.5, 136.8, 132.9, 132.3, 131.9, 131.4, 131.2, 131.0, 130.8, 130.0, 129.4, 128.6, 128.5, 128.2, 128.1, 126.6, 125.9, 124.3, 123.7; HRMS (APCI-TOF) m/z Calcd. For $\text{C}_{26}\text{H}_{17}\text{Cl}_2\text{O}_2\text{S}$ 463.0326 $[\text{M}+\text{H}]^+$, found 463.0329.

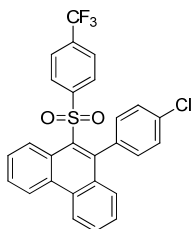
9-((4-Bromophenyl)sulfonyl)-10-(4-chlorophenyl)phenanthrene (6g)



Yellow solid, mp 226-227 °C; ^1H NMR (400 MHz, DMSO; δ , ppm) 9.01 (d, J = 8.4 Hz, 2H), 8.68 (d, J = 8.4 Hz, 1H), 7.90 (s, 1H), 7.81–7.63 (m, 7H), 7.56–7.42 (m, 4H), 7.29 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO; δ , ppm) 143.1, 142.6, 136.8, 132.9, 132.3, 131.9, 131.4, 131.2, 131.0, 130.9, 129.4, 128.6, 128.5, 128.2, 128.1, 127.6,

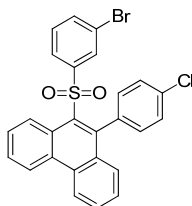
126.6, 125.9, 124.3, 123.7; HRMS (APCI-TOF) m/z Calcd. For $C_{26}H_{17}BrClO_2S$ 506.9821 $[M+H]^+$, found 506.9872.

9-(4-Chlorophenyl)-10-((4-(trifluoromethyl)phenyl)sulfonyl)phenanthrene (6h)



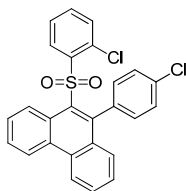
Yellow solid, mp 198-199 °C; 1H NMR (400 MHz, $CDCl_3$; δ , ppm) 9.00 (d, J = 8.8 Hz, 1H), 8.76 (t, J = 9.4 Hz, 2H), 7.75 (m, 4H), 7.63 (m, 3H), 7.51 (t, J = 7.8 Hz, 1H), 7.37 (d, J = 7.2 Hz, 3H), 7.17 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$; δ , ppm) 147.0, 142.7, 135.5, 134.2, 134.1 ($^2J_{CF}$ = 32.8), 132.4, 132.3, 131.7, 131.0, 130.9, 130.1, 129.3, 128.0, 127.9, 127.8, 127.6, 126.8, 126.8, 126.5, 126.0, 126.0 ($^3J_{CF}$ = 3.7), 125.90, 123.2, 123.1 ($^1J_{CF}$ = 271.3), 122.7, 30.96; HRMS (APCI-TOF) m/z Calcd. For $C_{27}H_{17}ClF_3O_2S$ 497.0590 $[M+H]^+$, found 497.0629.

9-((3-Bromophenyl)sulfonyl)-10-(4-chlorophenyl)phenanthrene (6i)



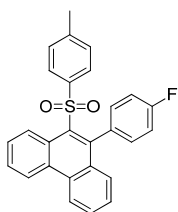
Yellow solid, mp 162-163 °C; 1H NMR (400 MHz, $CDCl_3$; δ , ppm) 9.07 (d, J = 8.4 Hz, 1H), 8.77 (t, J = 9.0 Hz, 2H), 7.81–7.66 (m, 4H), 7.59–7.48 (m, 3H), 7.37 (m, 3H), 7.22 (t, J = 8.0 Hz, 1H), 7.18–7.13 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$; δ , ppm) 145.3, 142.5, 135.6, 135.4, 134.2, 132.69, 132.4, 131.7, 131.1, 130.9, 130.3, 129.9, 129.4, 129.2, 128.0, 127.8, 127.7, 127.5, 126.8, 126.6, 124.9, 123.1, 122.9, 122.6; HRMS (APCI-TOF) m/z Calcd. For $C_{26}H_{17}BrClO_2S$ 506.9821 $[M+H]^+$, found 506.9855.

9-(4-Chlorophenyl)-10-((2-chlorophenyl)sulfonyl)phenanthrene (6j)



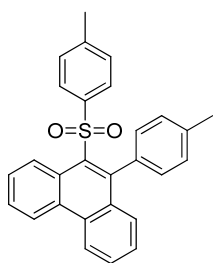
Yellow solid, mp 267-269 °C; 1H NMR (400 MHz, $CDCl_3$; δ , ppm) 9.22 (d, J = 8.8 Hz, 1H), 8.77 (t, J = 9.2 Hz, 2H), 7.78–7.61 (m, 4H), 7.50–7.45 (m, 1H), 7.38–7.32 (m, 2H), 7.25–7.18 (m, 4H), 7.11 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$; δ , ppm) 141.6, 140.7, 134.6, 134.4, 134.2, 133.3, 132.4, 132.3, 131.7, 131.1, 131.0, 130.9, 129.5, 128.9, 128.8, 127.7, 127.6, 127.4, 127.2, 126.8, 126.8, 123.0, 122.7; HRMS (APCI-TOF) m/z Calcd. For $C_{26}H_{17}Cl_2O_2S$ 463.0326 $[M+H]^+$, found 463.0341.

9-(4-Fluorophenyl)-10-tosylphenanthrene (6l)



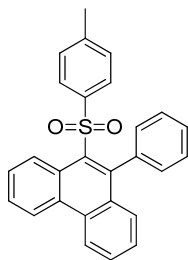
Yellow solid, mp 196-198 °C; ^1H NMR (400 MHz, CDCl_3 ; δ , ppm) 9.04 (d, $J = 8.4$ Hz, 1H), 8.77–8.72 (m, 2H), 7.78–7.67 (m, 2H), 7.61 (m, 1H), 7.56–7.47 (m, 3H), 7.36 (d, $J = 8.4$ Hz, 1H), 7.23 (m, 2H), 7.16–7.10 (m, 4H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 ; δ , ppm) 162.4 ($^1J_{\text{CF}} = 245.5$), 143.4, 142.5, 140.8, 133.4, 133.4, 133.3, 132.3, 131.7 ($^3J_{\text{CF}} = 8.0$), 130.9, 129.6, 129.4, 129.3, 127.5 ($^4J_{\text{CF}} = 4.5$), 127.3, 127.1, 126.9, 126.4, 122.9, 122.5, 114.7 ($^2J_{\text{CF}} = 21.5$), 21.5; HRMS (APCI-TOF) m/z Calcd. For $\text{C}_{27}\text{H}_{20}\text{FO}_2\text{S}$ 427.1168 $[\text{M}+\text{H}]^+$, found 427.1175.

9-(p-Tolyl)-10-tosylphenanthrene (6m)



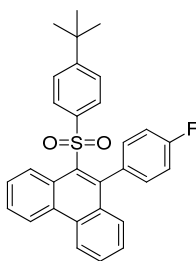
Yellow solid, mp 207-209 °C; ^1H NMR (400 MHz, CDCl_3 ; δ , ppm) 9.01 (dd, $J = 8.4, 0.8$ Hz, 1H), 8.73 (t, $J = 7.6$ Hz, 2H), 7.75–7.65 (m, 2H), 7.61–7.42 (m, 5H), 7.25–7.10 (m, 6H), 2.47 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 ; δ , ppm) 142.7, 142.1, 139.9, 136.2, 133.6, 131.8, 131.1, 130.8, 129.8, 128.9, 128.7, 128.4, 128.2, 127.3, 126.3, 126.2, 126.1, 125.9, 125.5, 125.4, 121.8, 121.3, 29.9, 20.4; HRMS (APCI-TOF) m/z Calcd. For $\text{C}_{28}\text{H}_{23}\text{O}_2\text{S}$ 423.1419 $[\text{M}+\text{H}]^+$, found 423.1451.

9-Phenyl-10-tosylphenanthrene (6n)



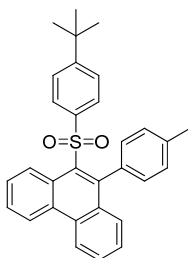
Yellow solid, mp 164-166 °C; ^1H NMR (400 MHz, CDCl_3 ; δ , ppm) 9.08 (d, $J = 8.4$ Hz, 1H), 8.76 (t, $J = 8.2$ Hz, 2H), 7.79–7.60 (m, 5H), 7.49 (m, 4H), 7.41 (d, $J = 8.4$ Hz, 1H), 7.33 (m, 2H), 7.15 (d, $J = 7.2$ Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 ; δ , ppm) 143.6, 143.2, 140.8, 137.7, 132.7, 132.2, 131.7, 130.9, 130.1, 129.6, 129.5, 129.4, 127.5, 127.4, 127.3, 127.2, 127.1, 126.9, 126.4, 122.9, 122.4, 21.5; HRMS (APCI-TOF) m/z Calcd. For $\text{C}_{27}\text{H}_{21}\text{O}_2\text{S}$ 409.1262 $[\text{M}+\text{H}]^+$, found 409.1273.

9-((4-(tert-Butyl)phenyl)sulfonyl)-10-(4-fluorophenyl)phenanthrene (6o)



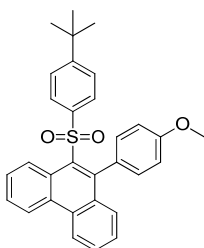
Yellow solid, mp 200-202 °C; ^1H NMR (400 MHz, CDCl_3 ; δ , ppm) 9.17 (d, $J = 8.4$ Hz, 1H), 8.78 (t, $J = 8.8$ Hz, 2H), 7.76 (m, 2H), 7.68 (t, $J = 7.8$ Hz, 1H), 7.58 (d, $J = 8.4$ Hz, 2H), 7.53–7.49 (m, 1H), 7.37 (d, $J = 8.4$ Hz, 3H), 7.25–7.19 (m, 2H), 7.10 (t, $J = 8.6$ Hz, 2H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3 ; δ , ppm) 162.3 ($^1J_{\text{CF}} = 245.7$), 156.3, 142.1, 140.7, 133.7, 133.3, 133.2, 132.2, 132.0 ($^3J_{\text{CF}} = 8.0$), 131.6, 130.9, 129.5, 129.3, 127.5 ($^4J_{\text{CF}} = 4.1$), 127.3, 127.0, 126.2, 125.8, 122.9, 122.5, 114.7 ($^2J_{\text{CF}} = 21.5$), 35.1, 31.0; HRMS (APCI-TOF) m/z Calcd. For $\text{C}_{30}\text{H}_{26}\text{FO}_2\text{S}$ 469.1638 $[\text{M}+\text{H}]^+$, found 469.1631.

9-((4-(tert-Butyl)phenyl)sulfonyl)-10-(p-tolyl)phenanthrene (**6p**)



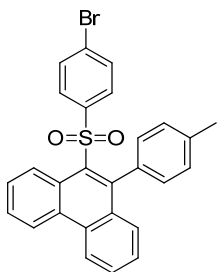
Yellow solid, mp 213-215 °C; ^1H NMR (400 MHz, CDCl_3 ; δ , ppm) 9.12 (d, $J = 8.4$ Hz, 1H), 8.74 (m, 2H), 7.69 (m, 3H), 7.56–7.51 (m, 2H), 7.44 (m, 2H), 7.32–7.28 (m, 2H), 7.15 (m, 4H), 2.45 (s, 3H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3 ; δ , ppm) 156.0, 143.3, 140.8, 137.2, 134.4, 133.3, 132.2, 131.8, 130.8, 130.2, 129.6, 129.4, 128.3, 127.3, 127.3, 127.2, 127.1, 127.1, 126.4, 126.3, 125.6, 122.9, 122.4, 35.0, 31.1, 21.5; HRMS (APCI-TOF) m/z Calcd. For $\text{C}_{31}\text{H}_{29}\text{O}_2\text{S}$ 465.1888 $[\text{M}+\text{H}]^+$, found 4 465.1887.

9-((4-(tert-Butyl)phenyl)sulfonyl)-10-(4-methoxyphenyl)phenanthrene (**6q**)



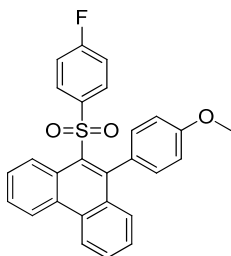
Yellow solid, mp 213-215 °C; ^1H NMR (400 MHz, CDCl_3 ; δ , ppm) 9.16 (d, $J = 9.2$ Hz, 1H), 8.77–8.70 (m, 2H), 7.74–7.62 (m, 3H), 7.52–7.40 (m, 4H), 7.32–7.28 (m, 2H), 7.13–7.09 (m, 2H), 6.90–6.86 (m, 2H), 3.89 (s, 3H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3 ; δ , ppm) 159.1, 155.9, 143.0, 140.9, 133.8, 132.2, 132.0, 131.7, 130.8, 129.4, 129.4, 129.3, 127.3, 127.3, 127.2, 127.1, 126.3, 125.7, 122.9, 122.4, 113.1, 55.3, 35.1, 31.1; HRMS (APCI-TOF) m/z Calcd. For $\text{C}_{31}\text{H}_{29}\text{O}_3\text{S}$ 481.1837 $[\text{M}+\text{H}]^+$, found 481.1883.

9-((4-Bromophenyl)sulfonyl)-10-(p-tolyl)phenanthrene (**6r**)



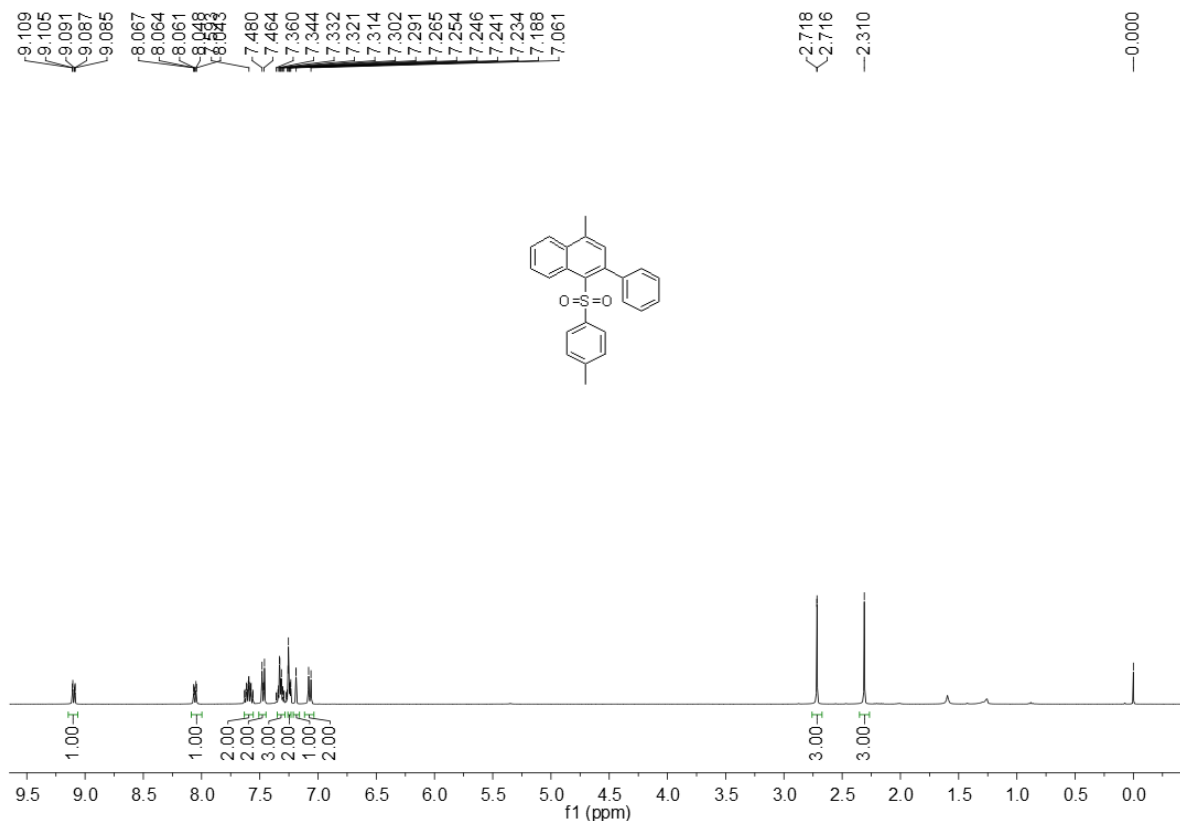
Yellow solid, mp 204-206 °C; ^1H NMR (400 MHz, CDCl_3 ; δ , ppm) 9.05 (d, J = 8.8 Hz, 1H), 8.77 (m, 2H), 7.80–7.71 (m, 2H), 7.67 (m, 1H), 7.51–7.43 (m, 6H), 7.19 (m, 2H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 ; δ , ppm) 143.7, 142.8, 137.7, 134.1, 132.7, 132.3, 131.8, 131.6, 130.8, 130.3, 129.7, 129.6, 128.4, 128.1, 128.0, 127.5, 127.3, 126.9, 126.8, 123.0, 122.4, 21.5; HRMS (APCI-TOF) m/z Calcd. For $\text{C}_{27}\text{H}_{20}\text{BrO}_2\text{S}$ 487.0367 $[\text{M}+\text{H}]^+$, found 487.0404.

9-((4-Fluorophenyl)sulfonyl)-10-(4-methoxyphenyl)phenanthrene (6s)

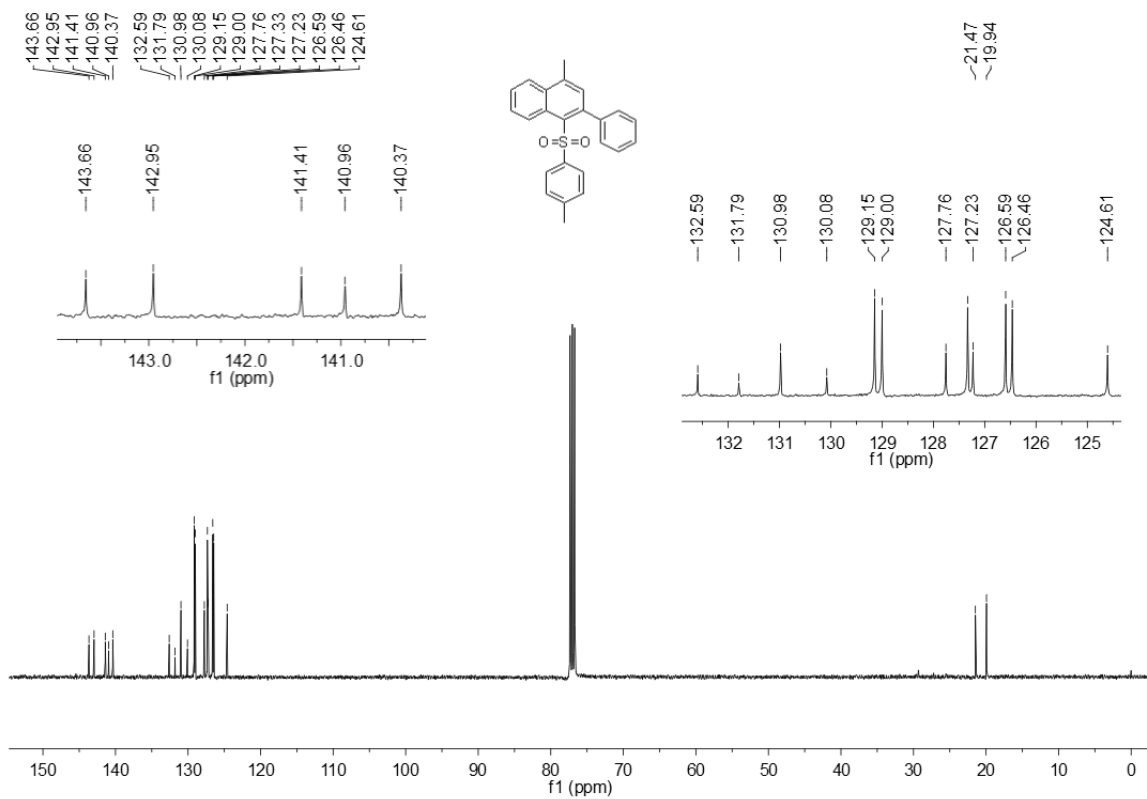


Yellow solid, mp 173-175 °C; ^1H NMR (400 MHz, CDCl_3 ; δ , ppm) 9.14 (d, J = 8.8 Hz, 1H), 8.77 (m, 2H), 7.79–7.66 (m, 3H), 7.62–7.58 (m, 2H), 7.51–7.43 (m, 2H), 7.14–7.10 (m, 2H), 7.01–6.93 (m, 4H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 ; δ , ppm) 164.6 ($^1J_{\text{CF}}$ = 253.1), 159.3, 143.2, 140.0, 139.9, 133.4, 132.2, 131.8, 131.7, 130.8, 129.6, 129.4, 129.1 ($^3J_{\text{CF}}$ = 9.4), 129.0, 127.4, 127.4, 127.2, 126.9, 123.0, 122.5, 115.8 ($^2J_{\text{CF}}$ = 22.5), 113.2, 55.3; HRMS (APCI-TOF) m/z Calcd. For $\text{C}_{27}\text{H}_{20}\text{FO}_3\text{S}$ 443.1117 $[\text{M}+\text{H}]^+$, found 443.1168.

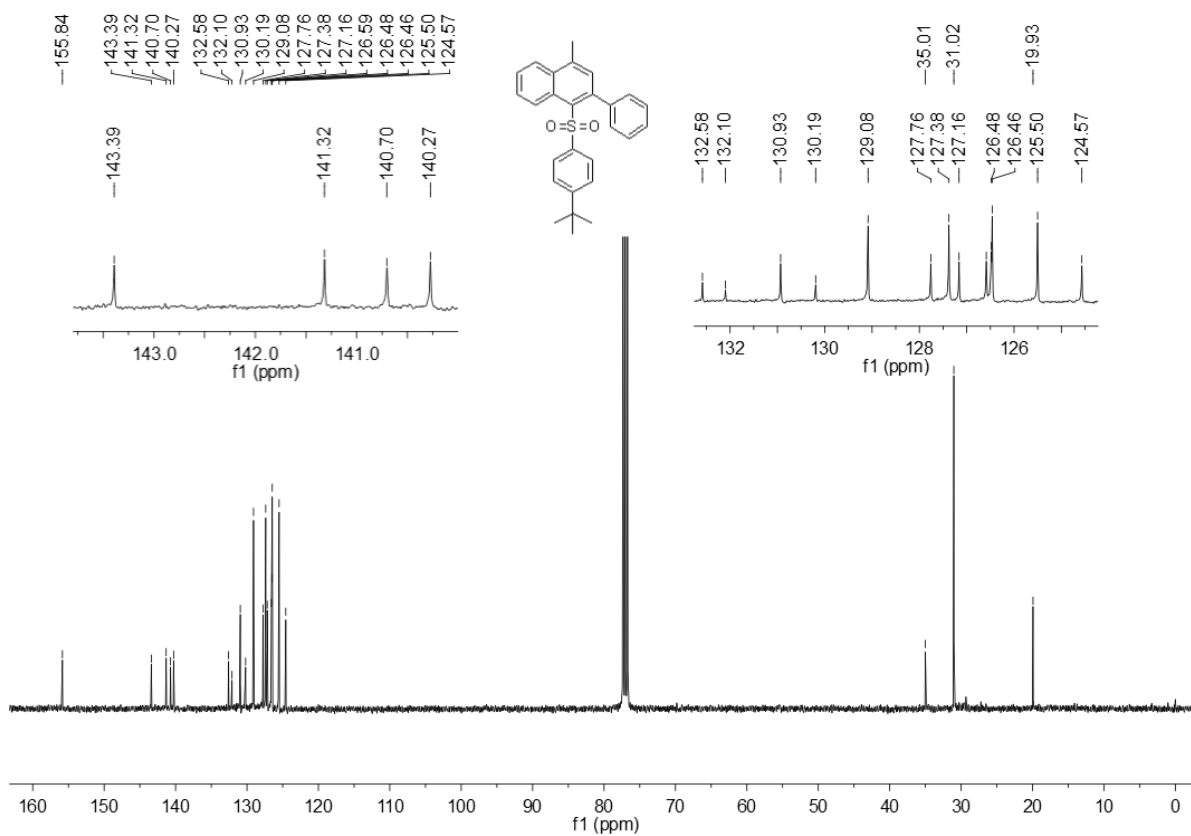
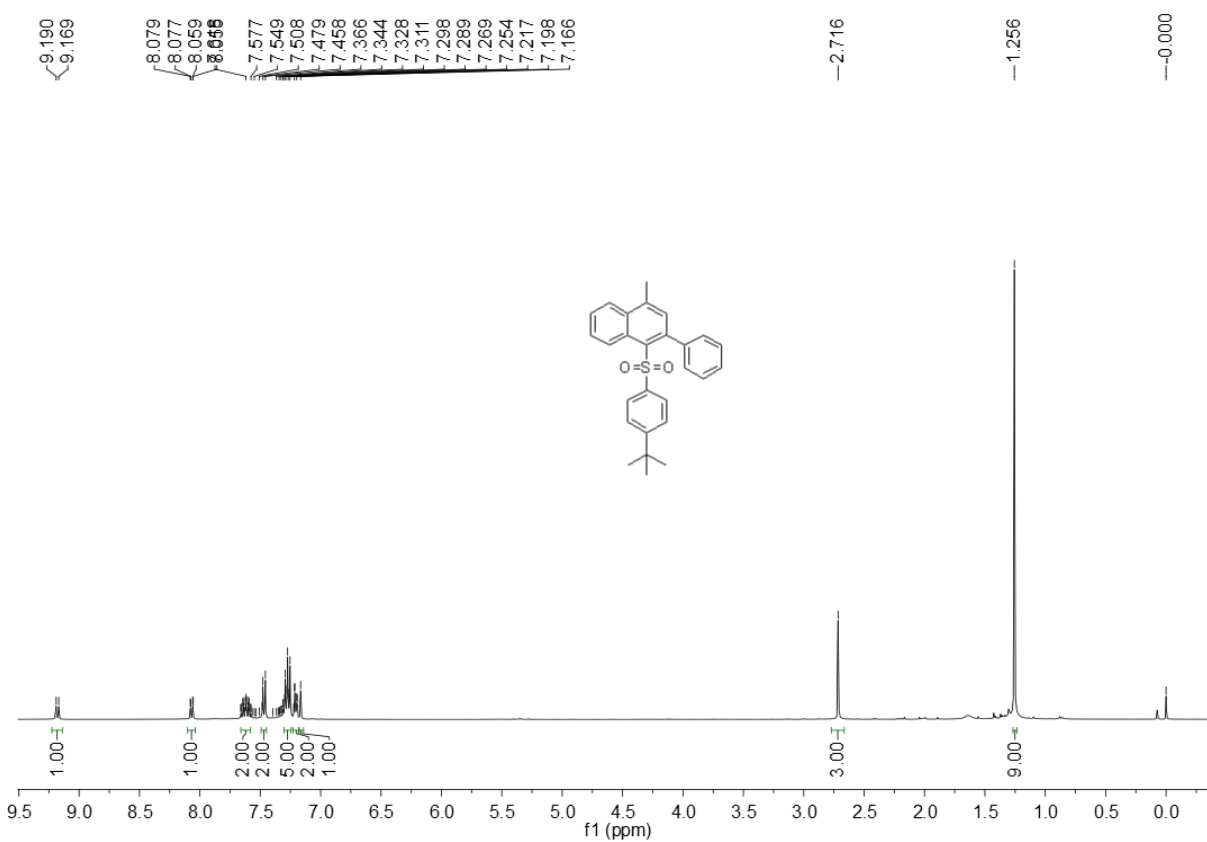
Copies of ^1H NMR and ^{13}C NMR of compounds 4 and 6



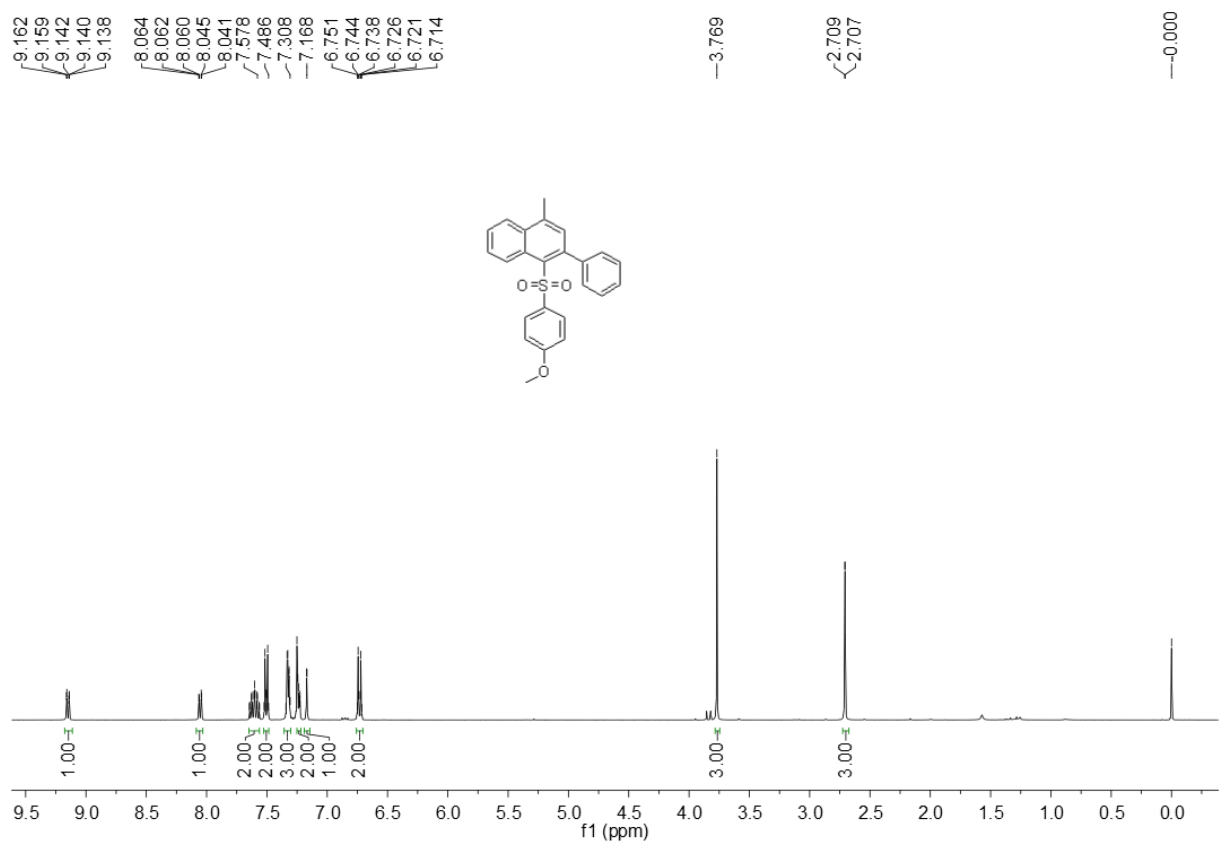
^{13}C NMR Spectrum of Compound 4a



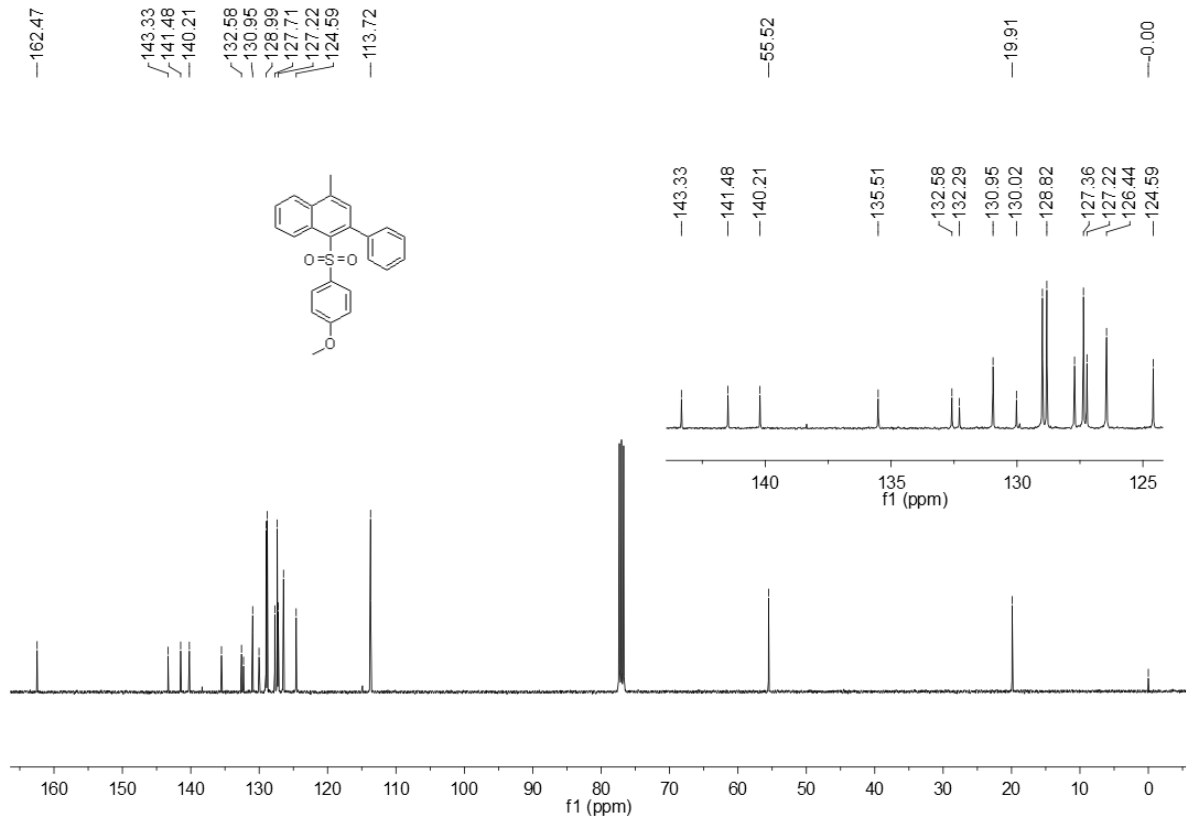
^{13}C NMR Spectrum of Compound 4a



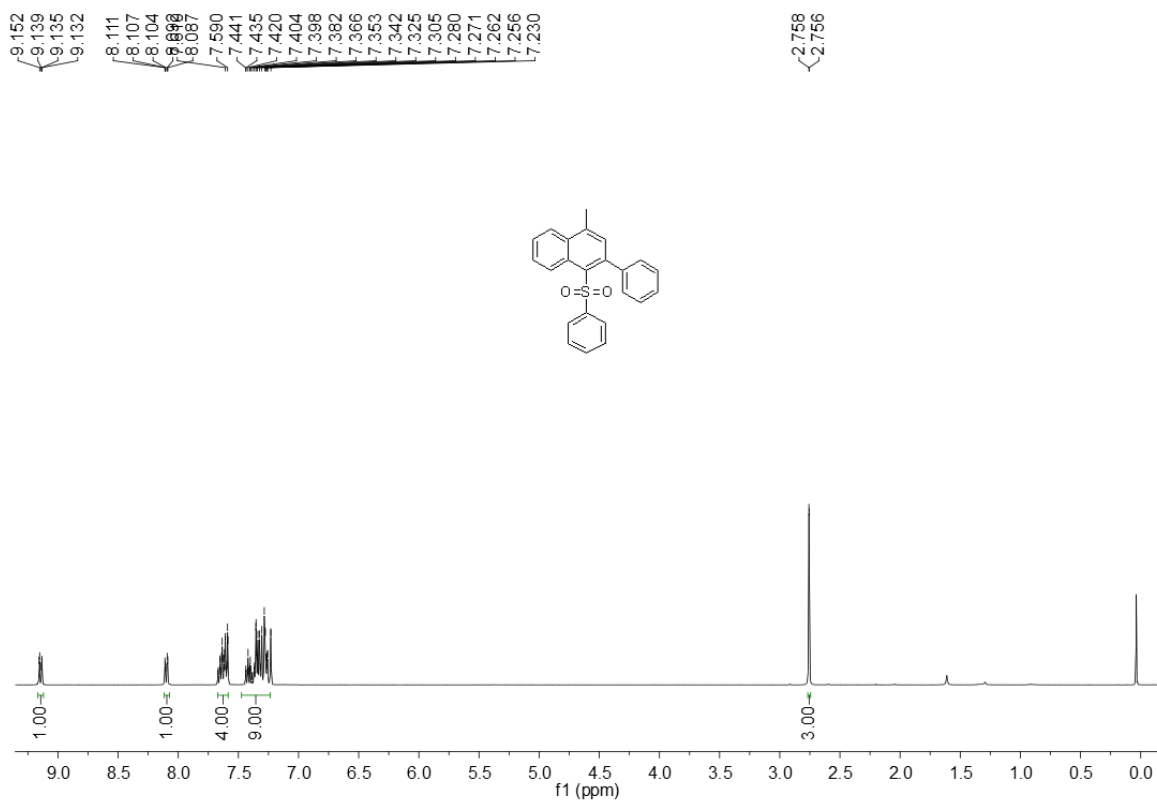
¹³C NMR Spectrum of Compound 4b



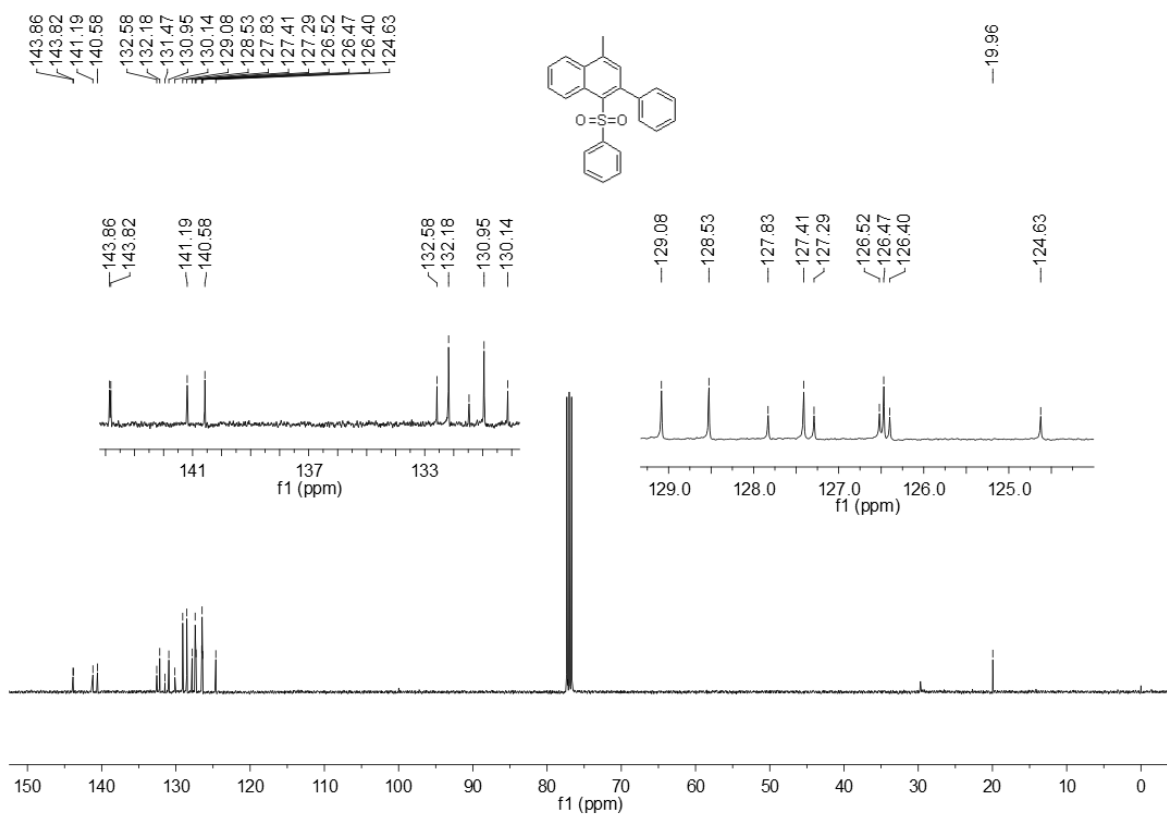
¹H NMR Spectrum of Compound 4c



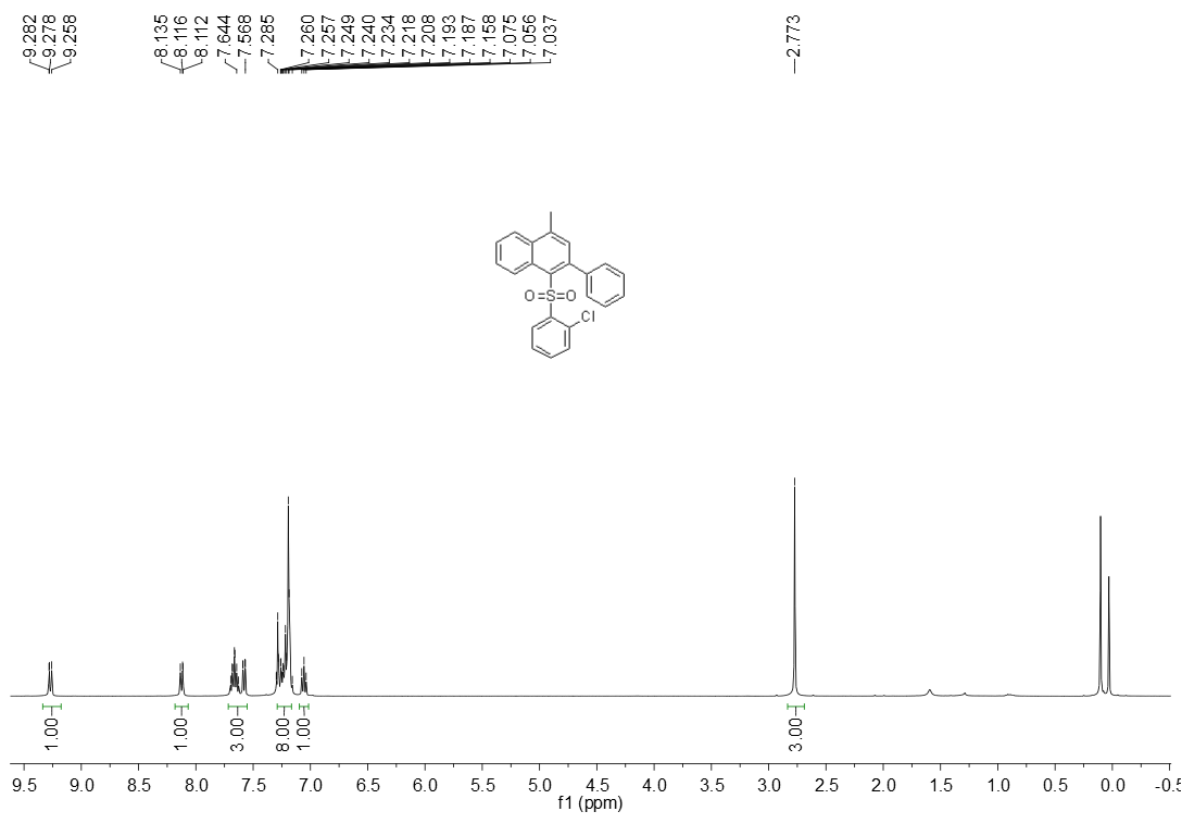
¹³C NMR Spectrum of Compound 4c



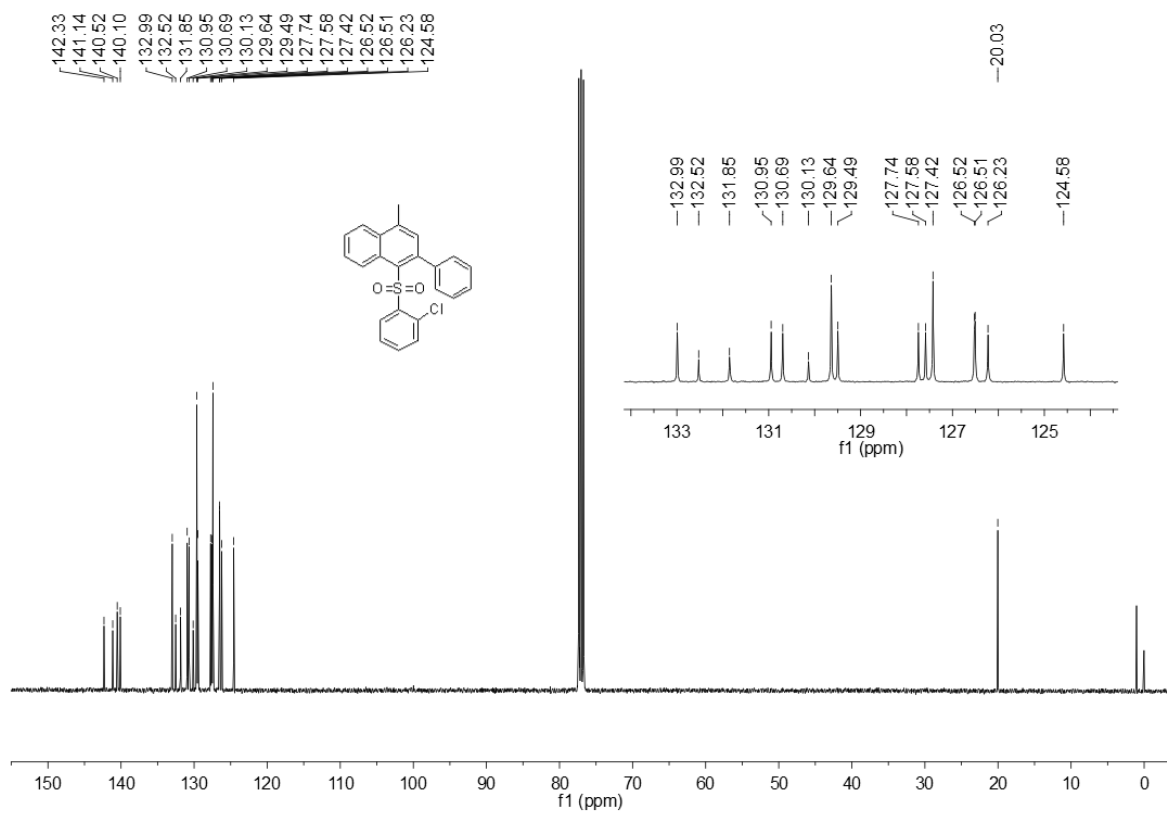
¹H NMR Spectrum of Compound 4d



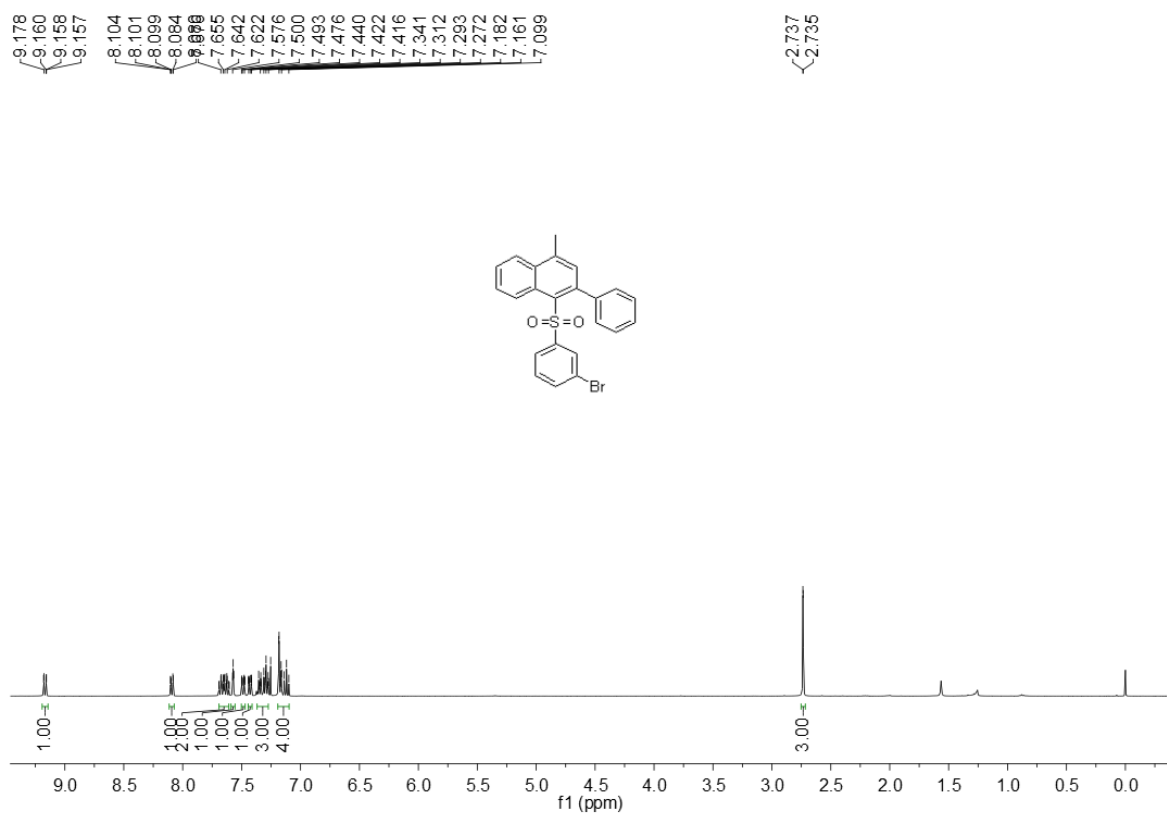
¹³C NMR Spectrum of Compound 4d



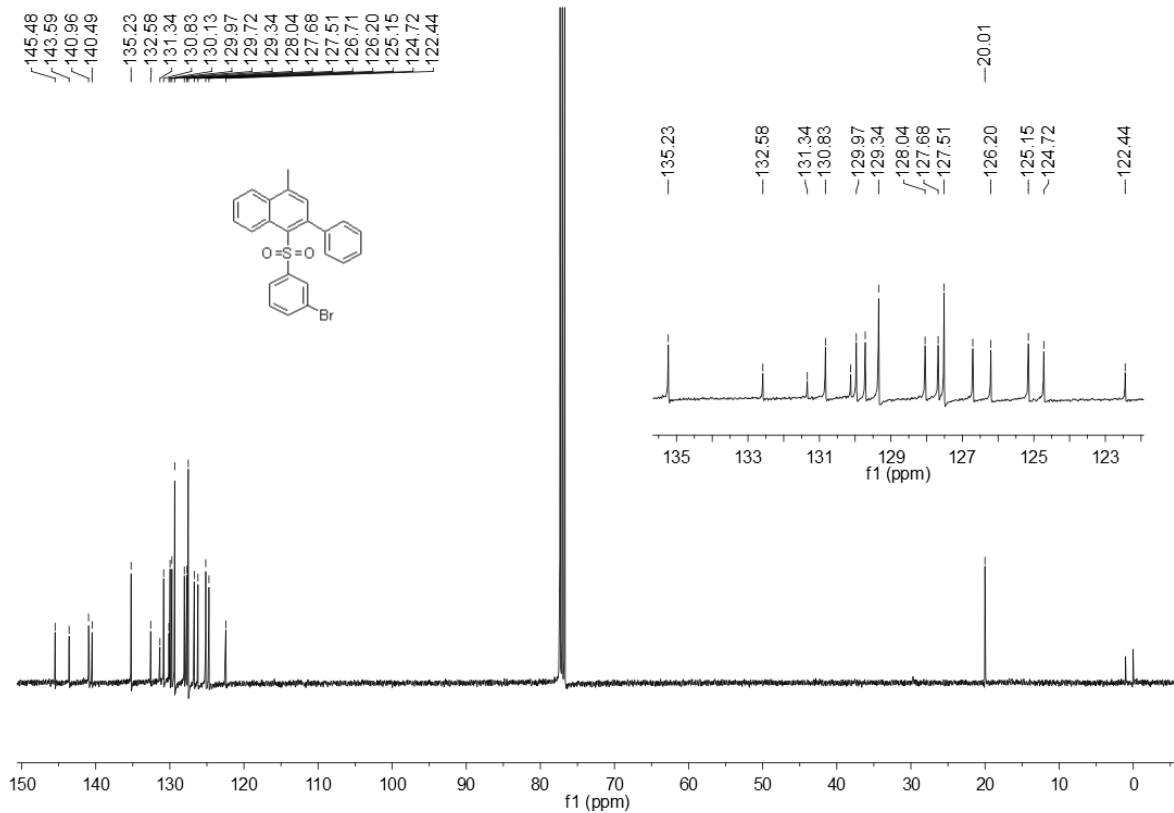
¹H NMR Spectrum of Compound 4e



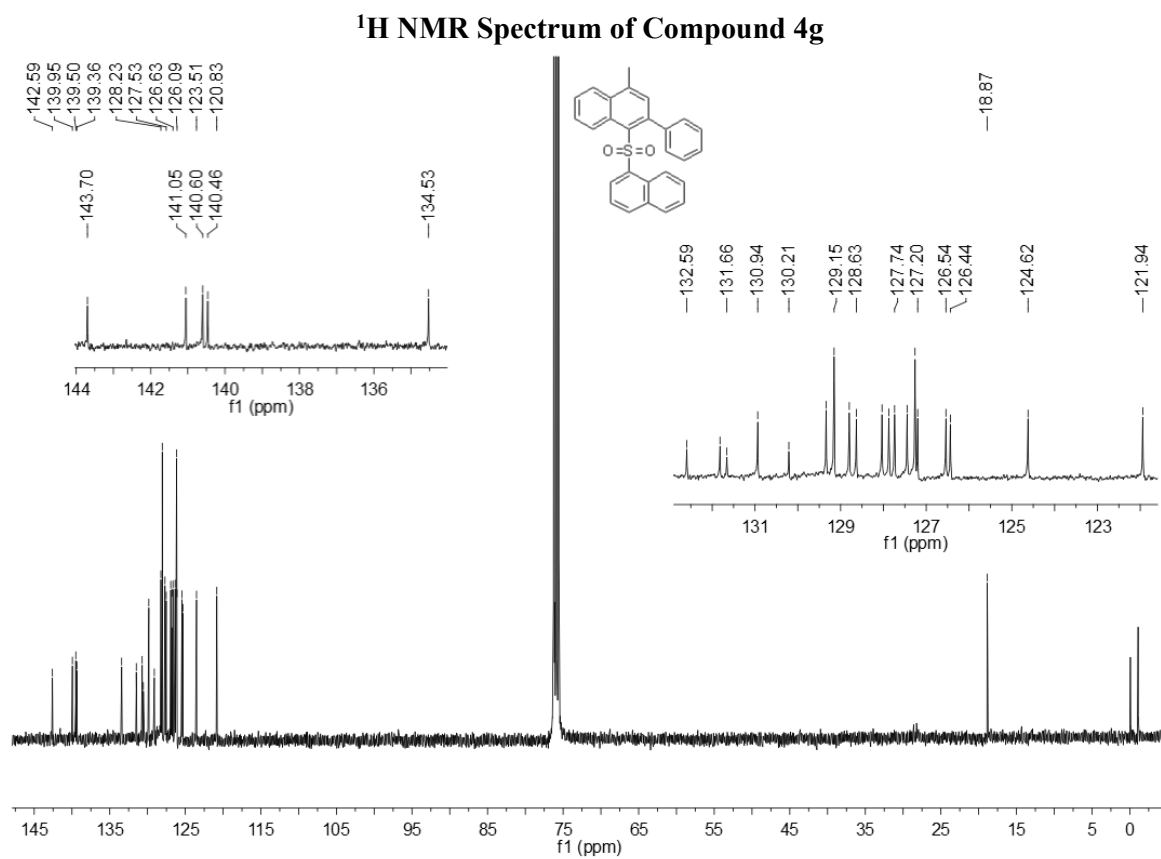
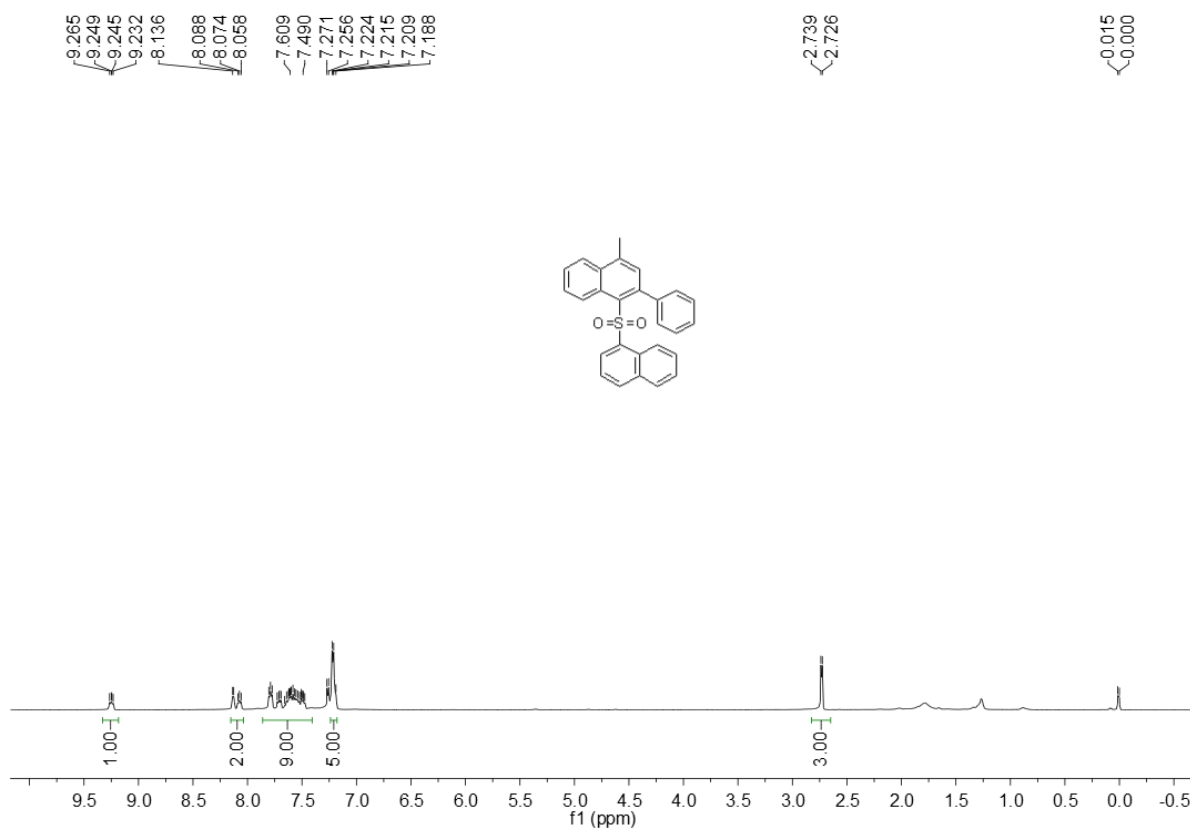
¹³C NMR Spectrum of Compound 4e

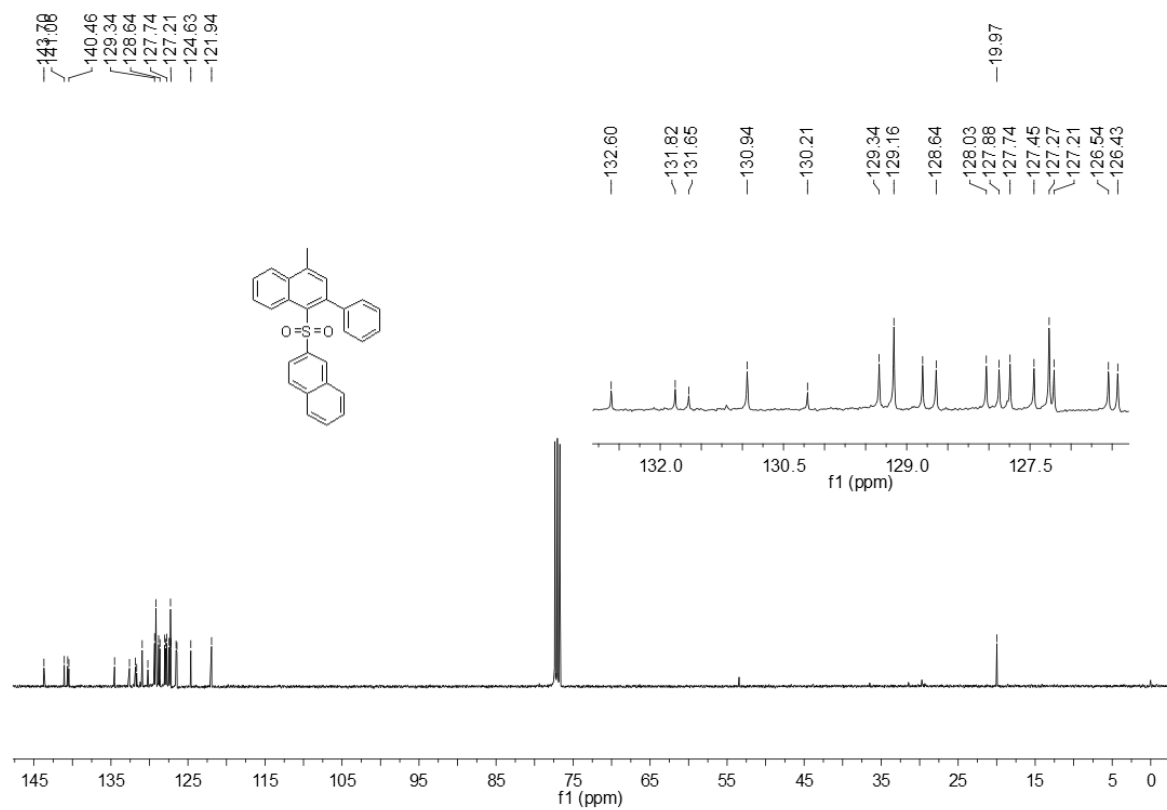
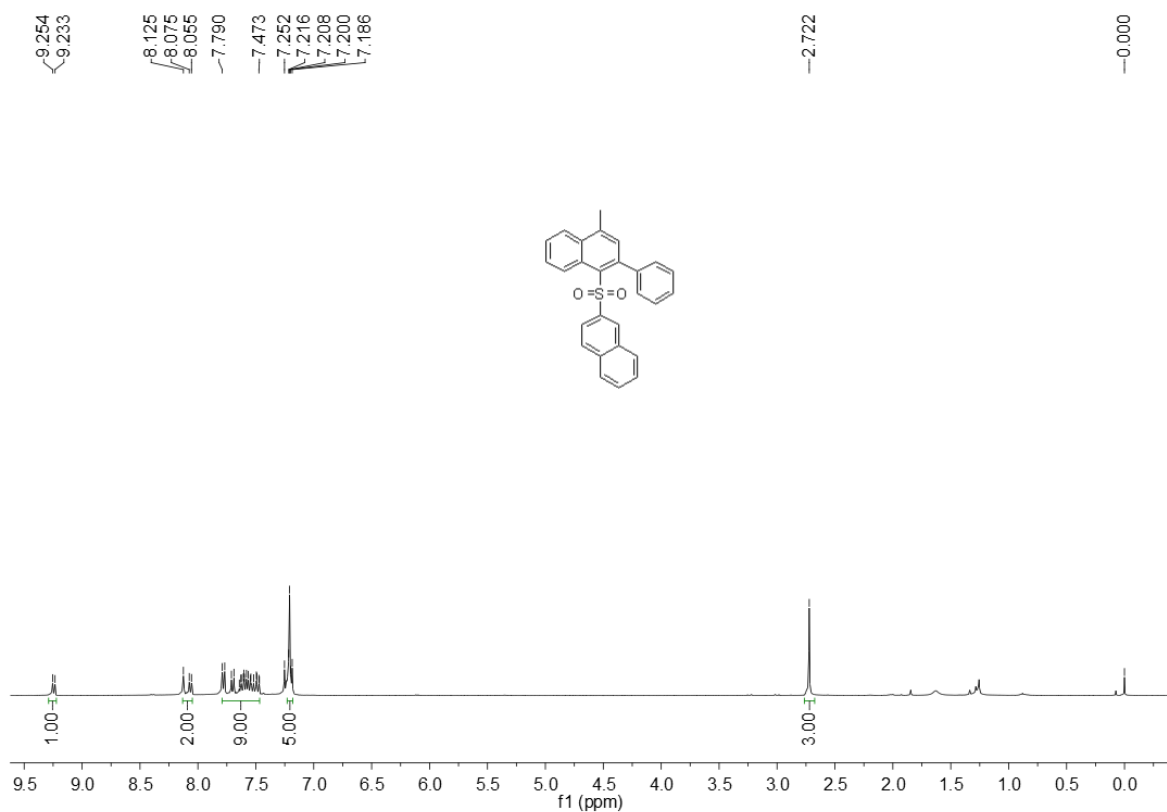


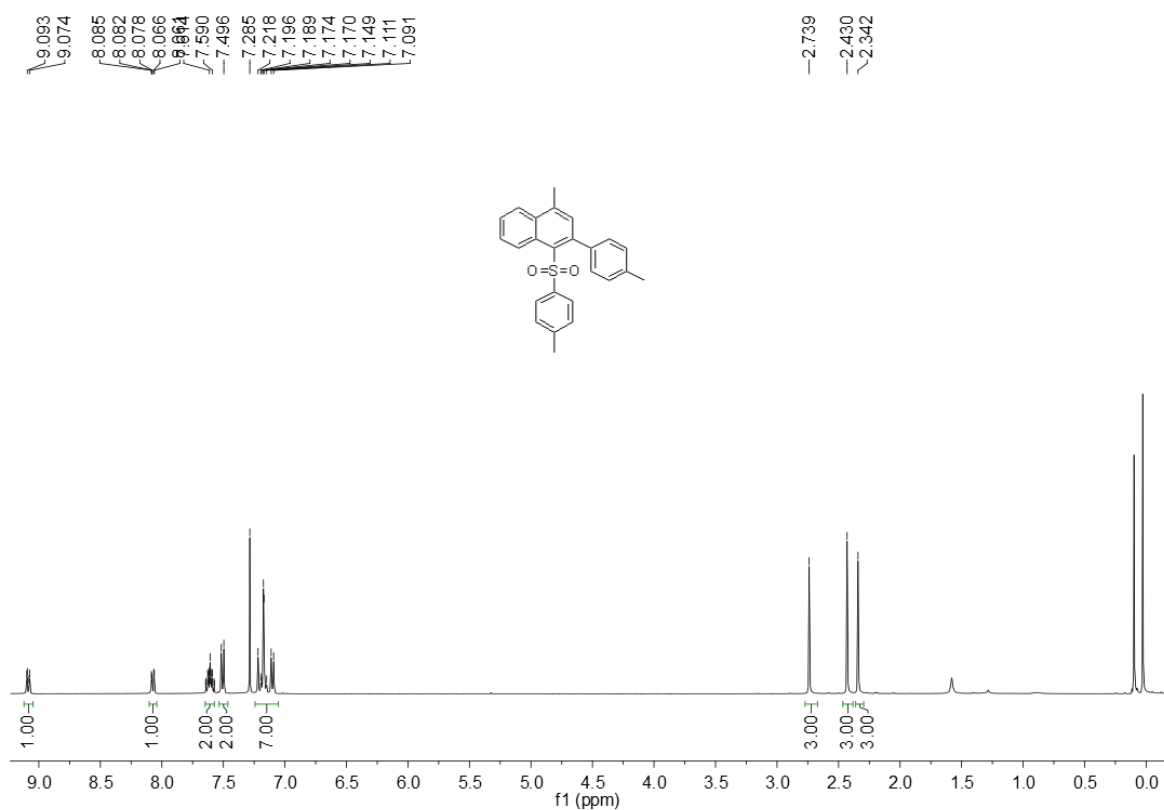
¹H NMR Spectrum of Compound 4f



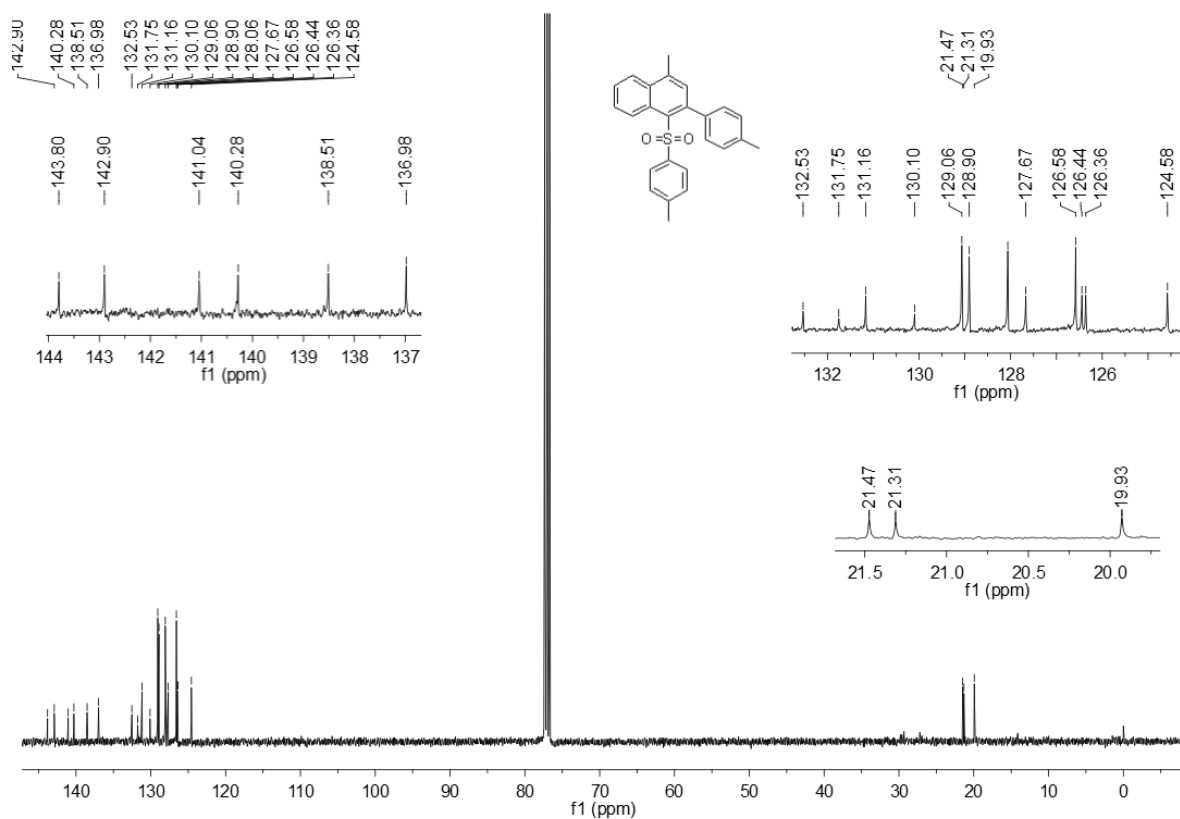
¹³C NMR Spectrum of Compound 4f



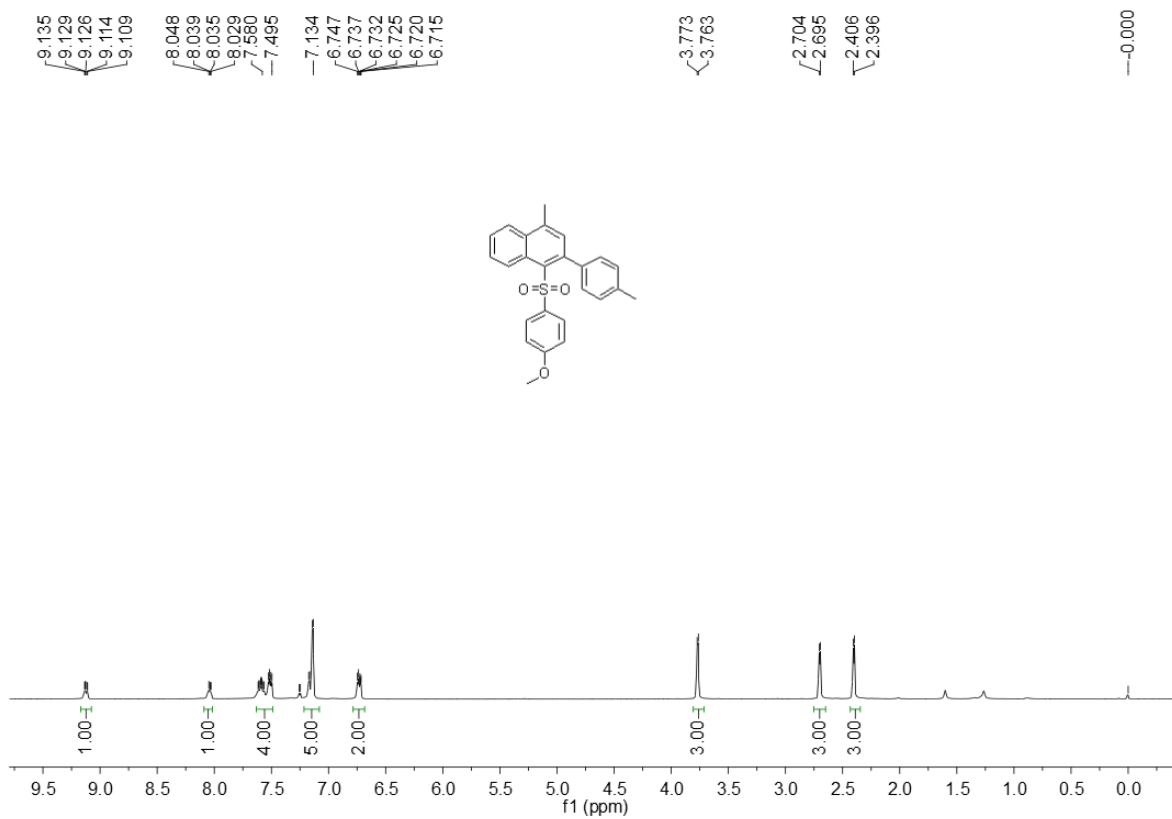




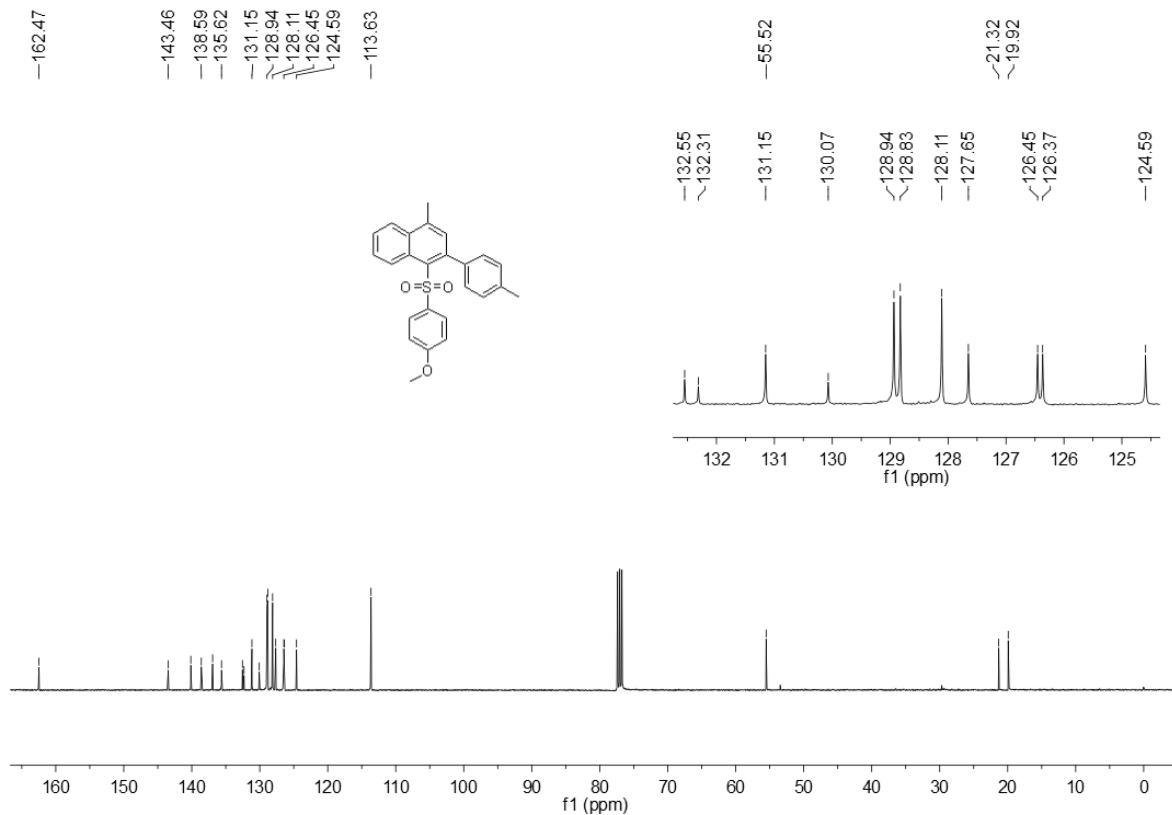
¹H NMR Spectrum of Compound 4j



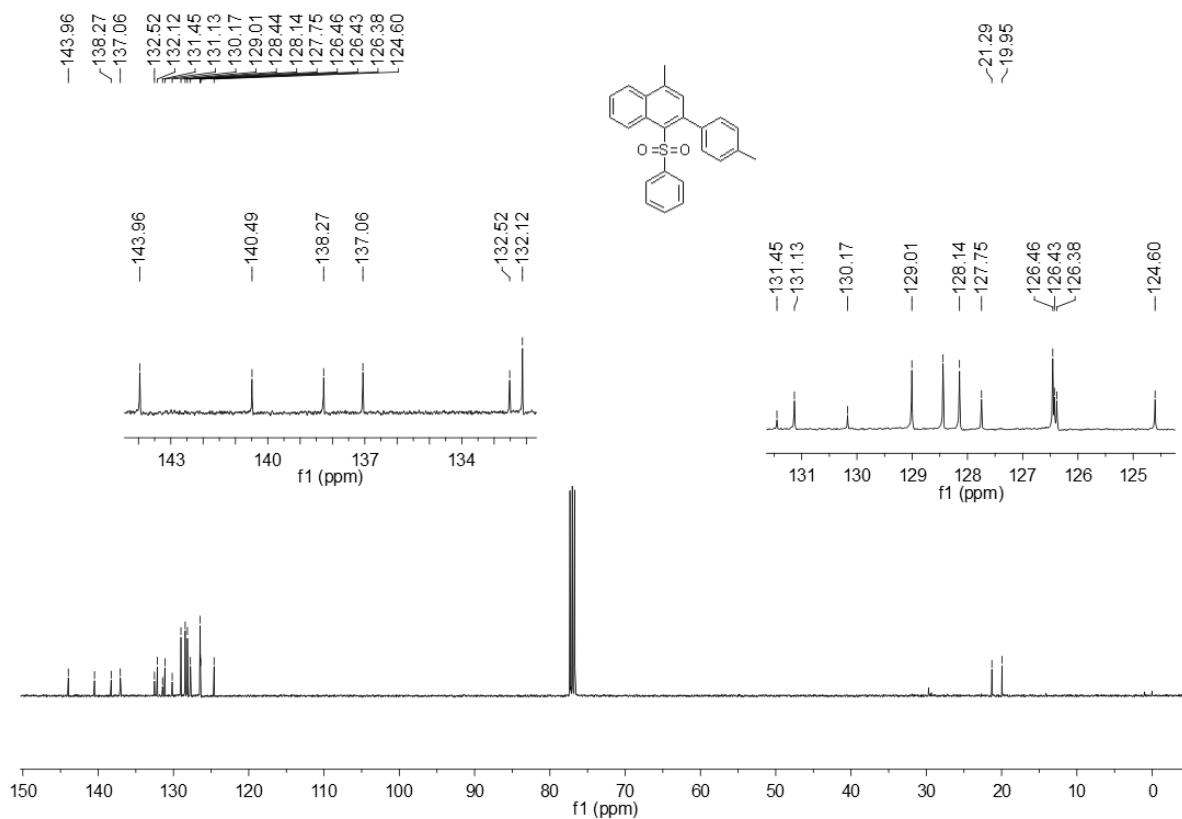
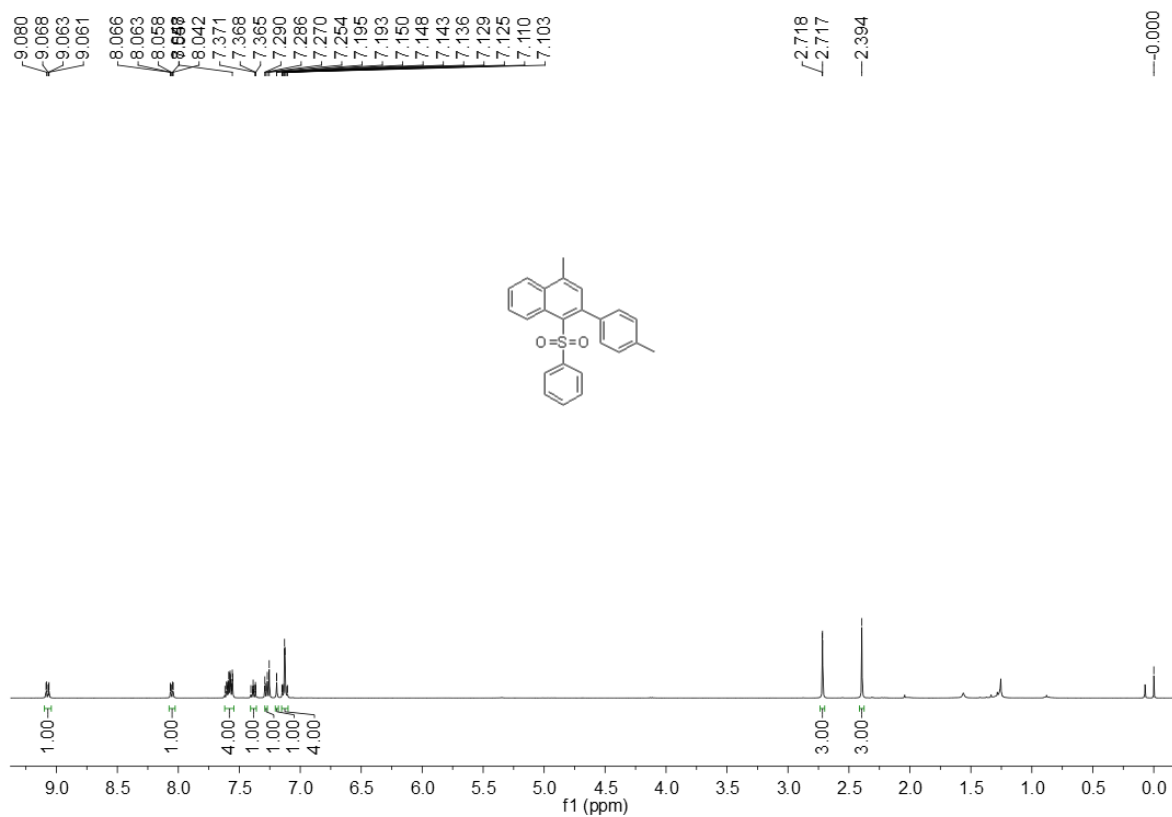
¹³C NMR Spectrum of Compound 4j

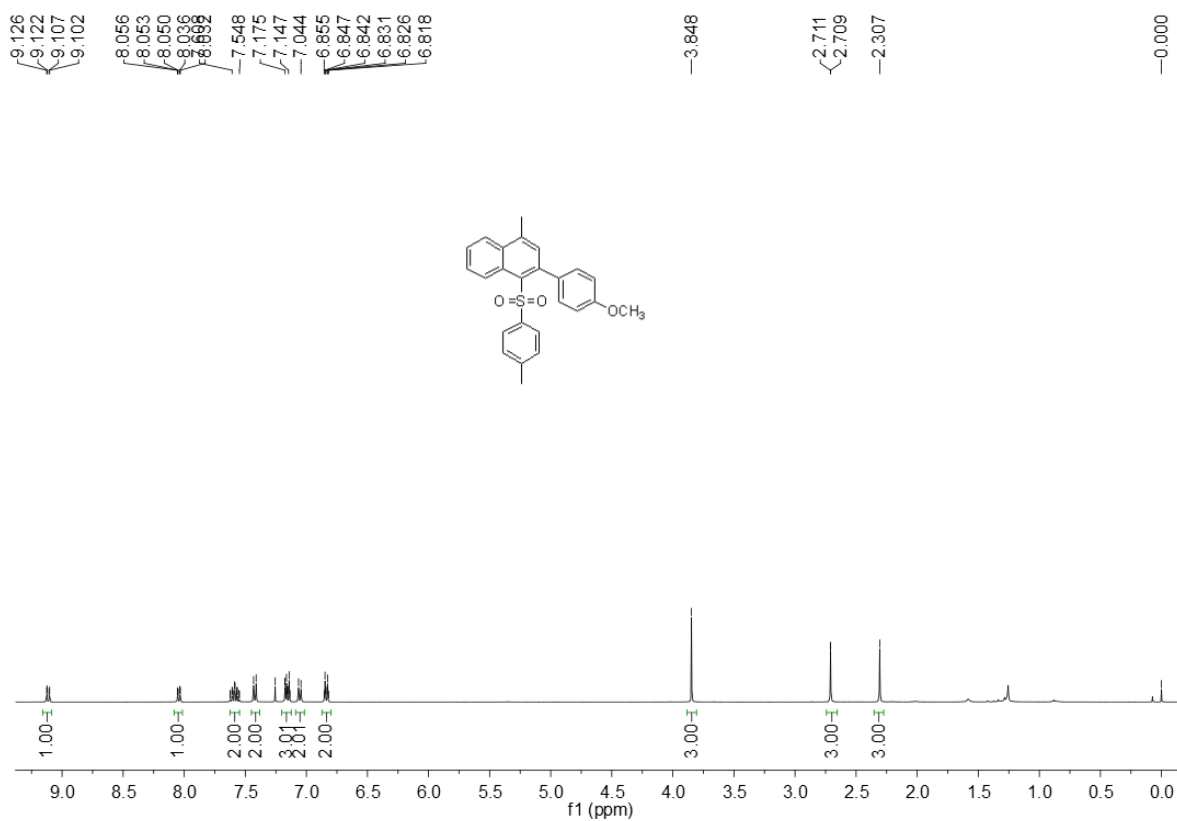


¹H NMR Spectrum of Compound 4k

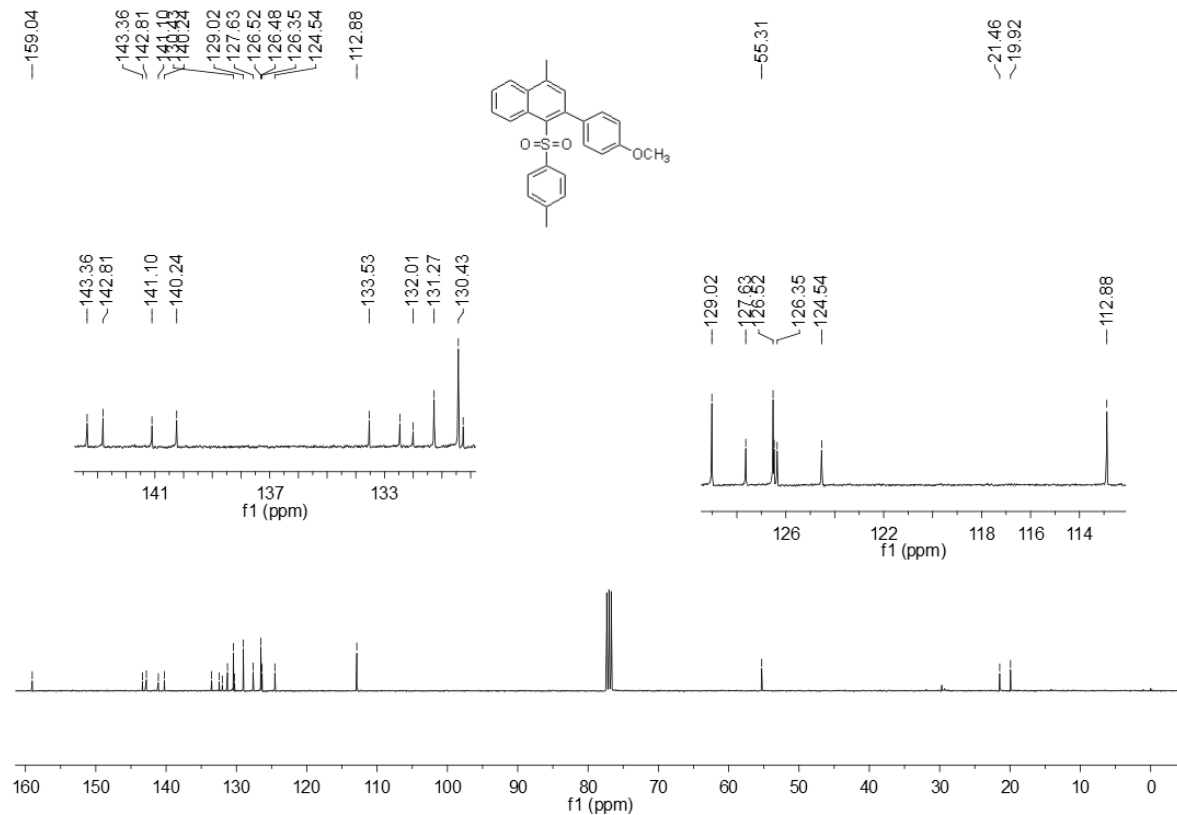


¹³C NMR Spectrum of Compound 4k

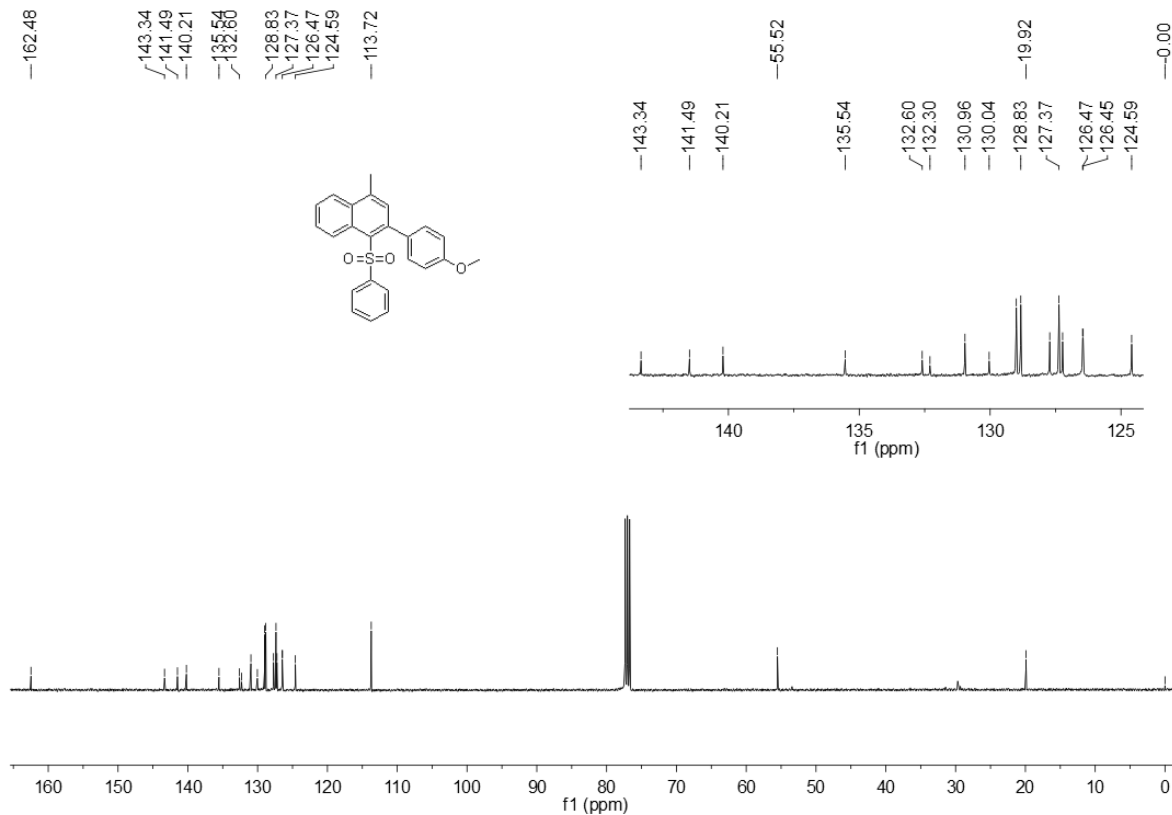
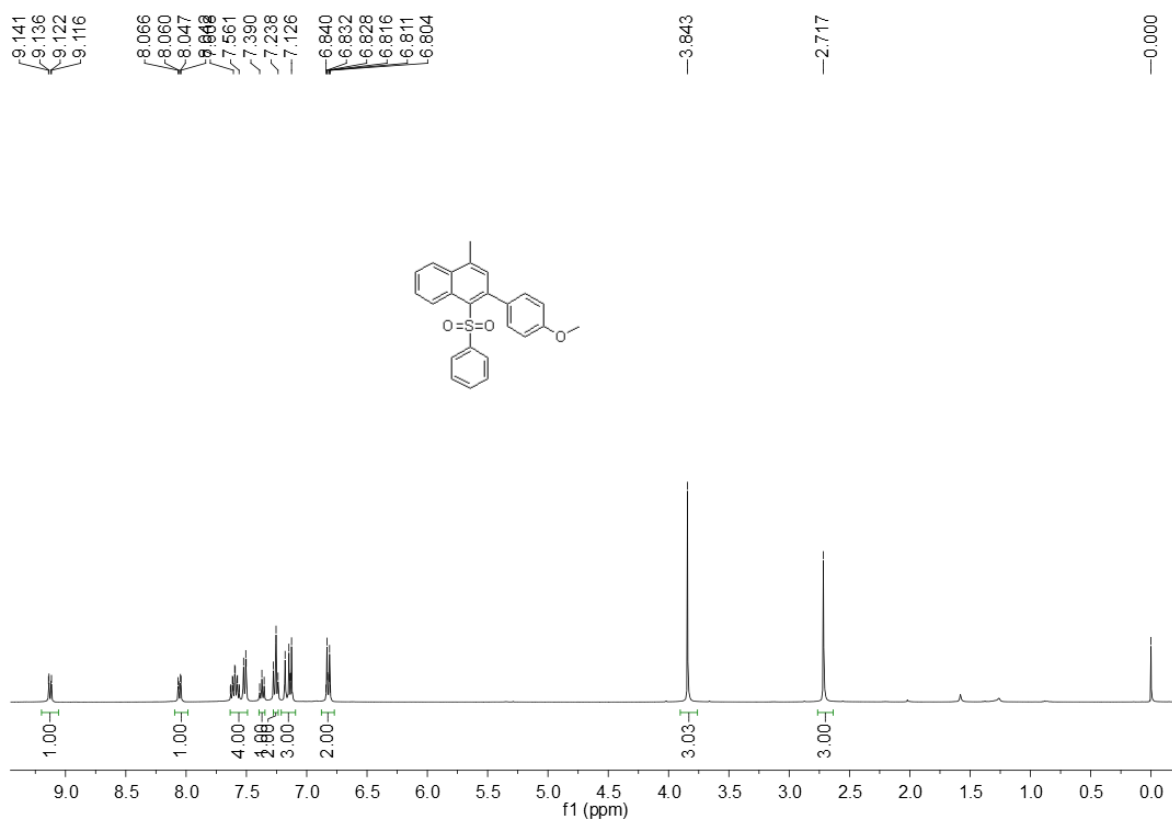




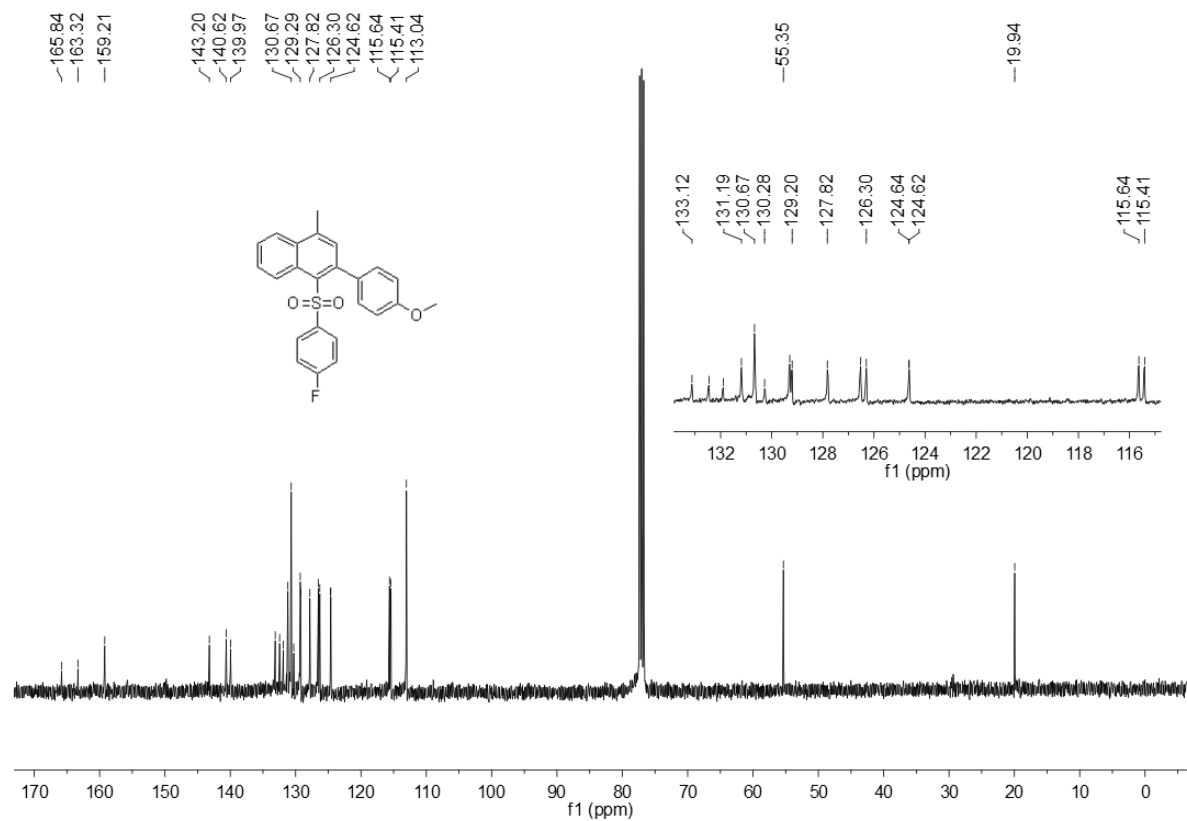
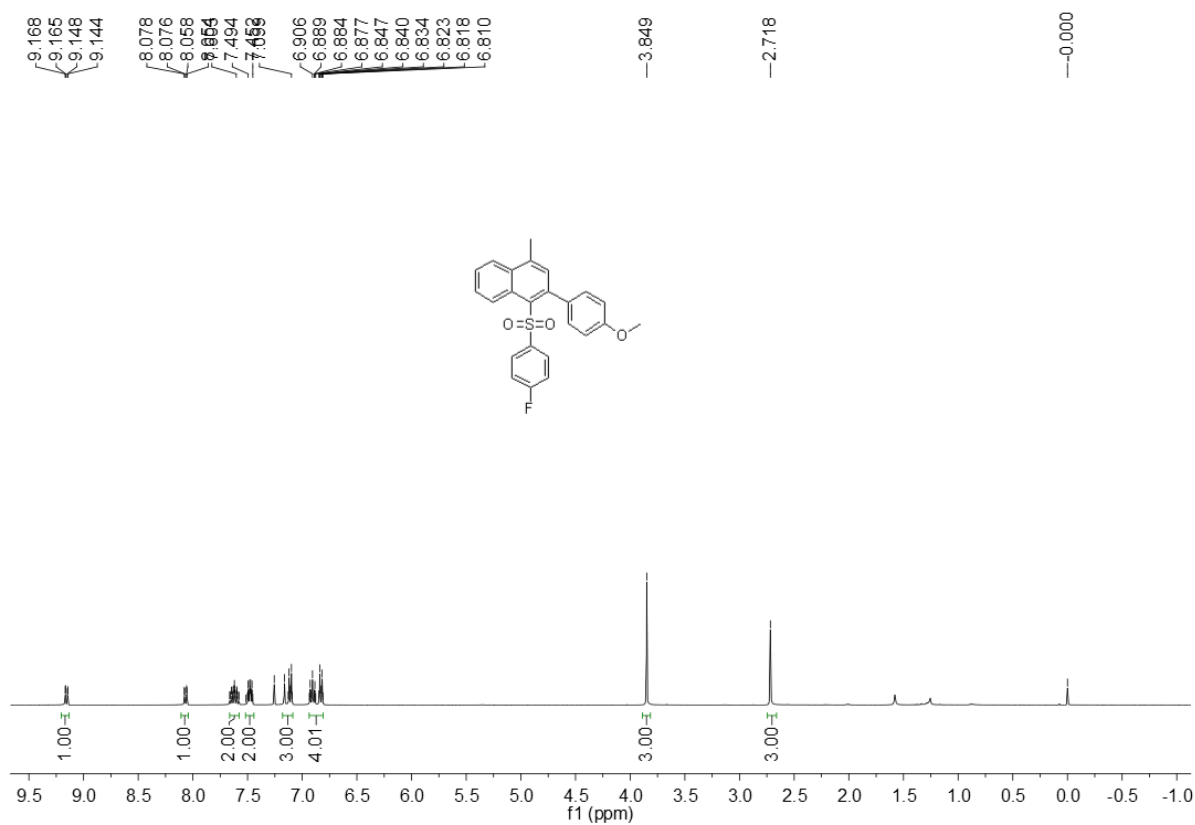
¹H NMR Spectrum of Compound 4m

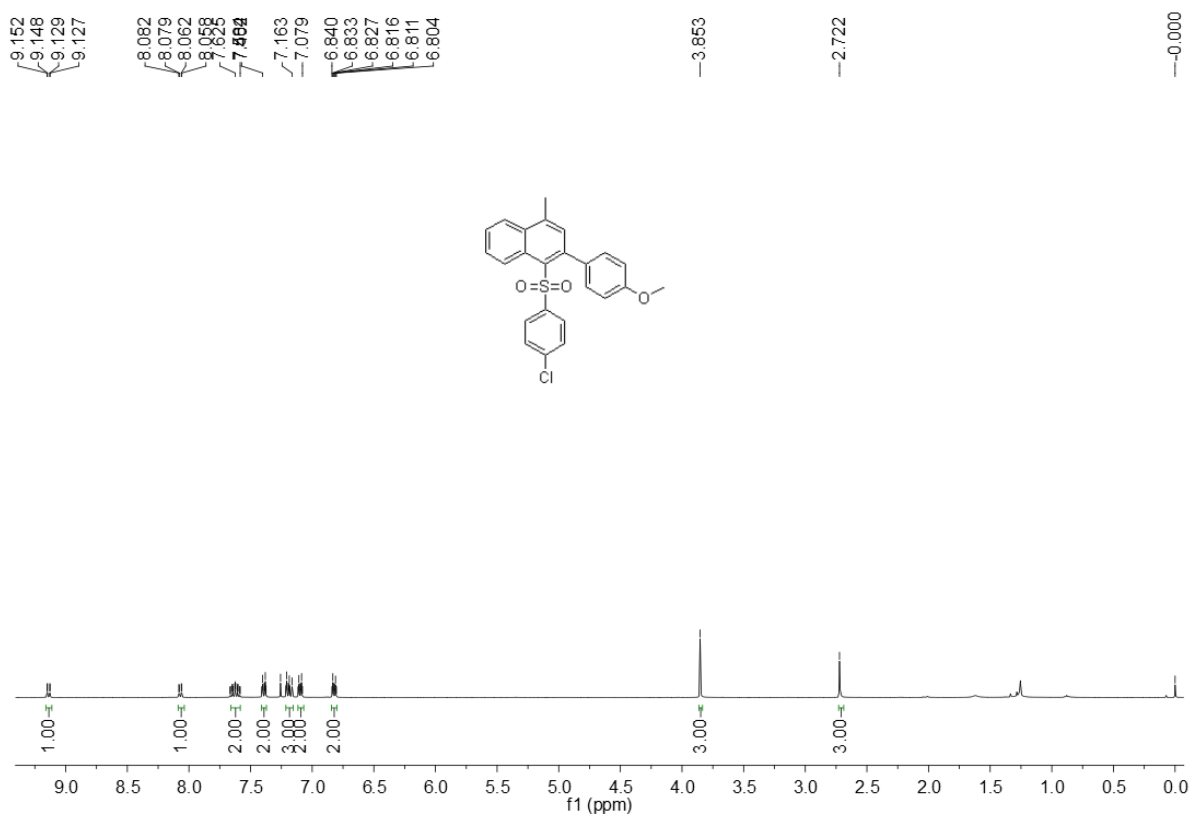


¹³C NMR Spectrum of Compound 4m

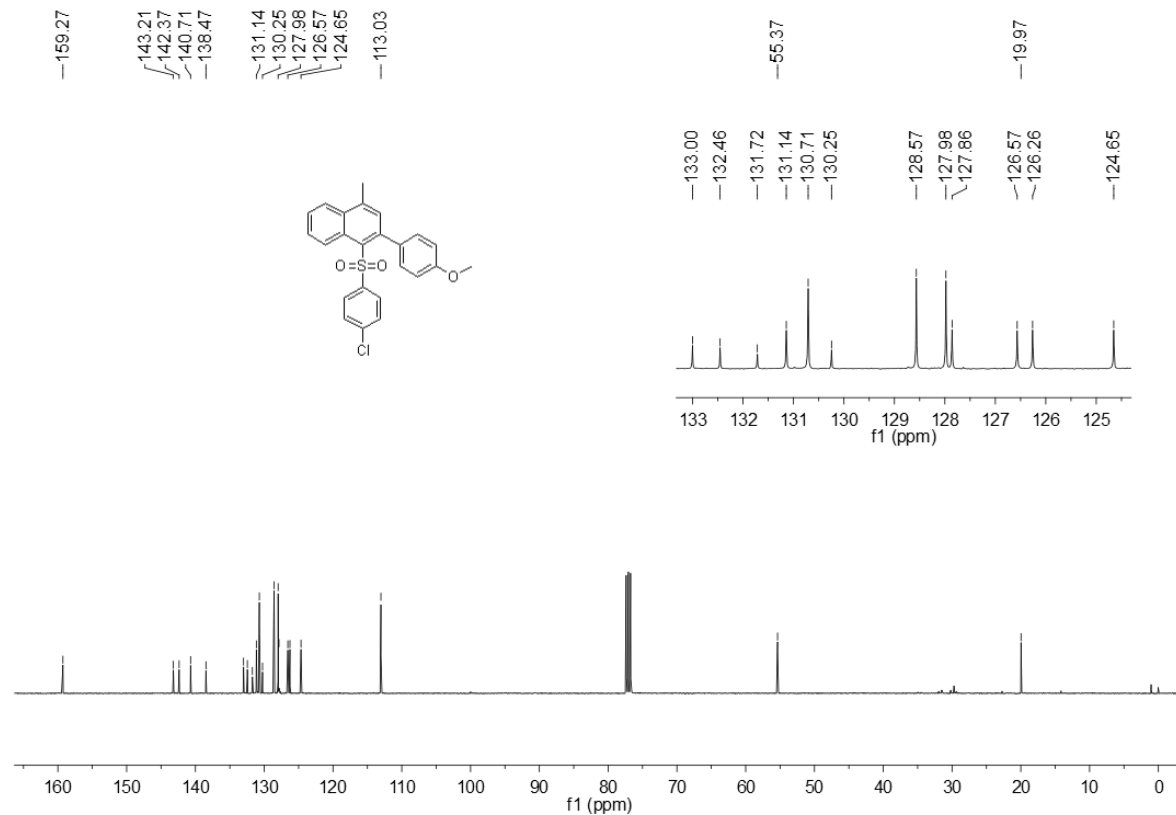


¹³C NMR Spectrum of Compound 4n

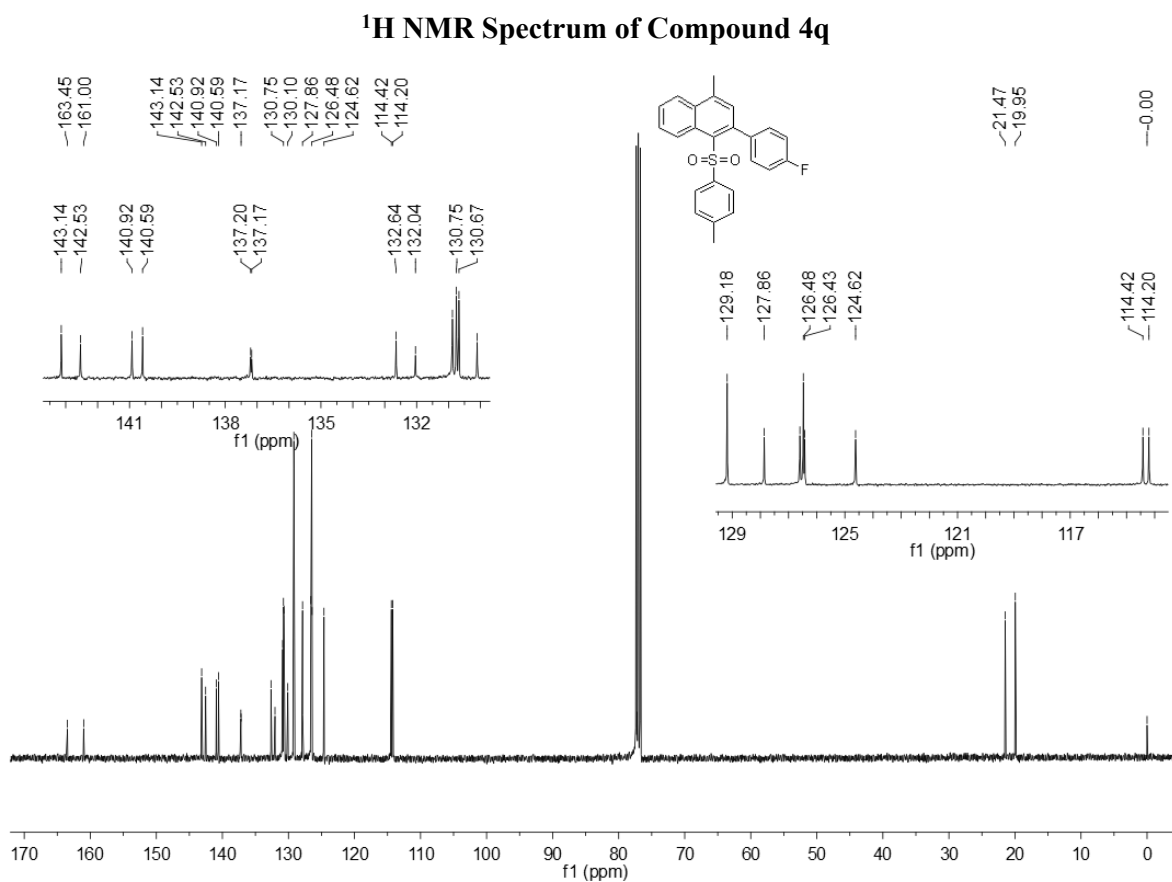
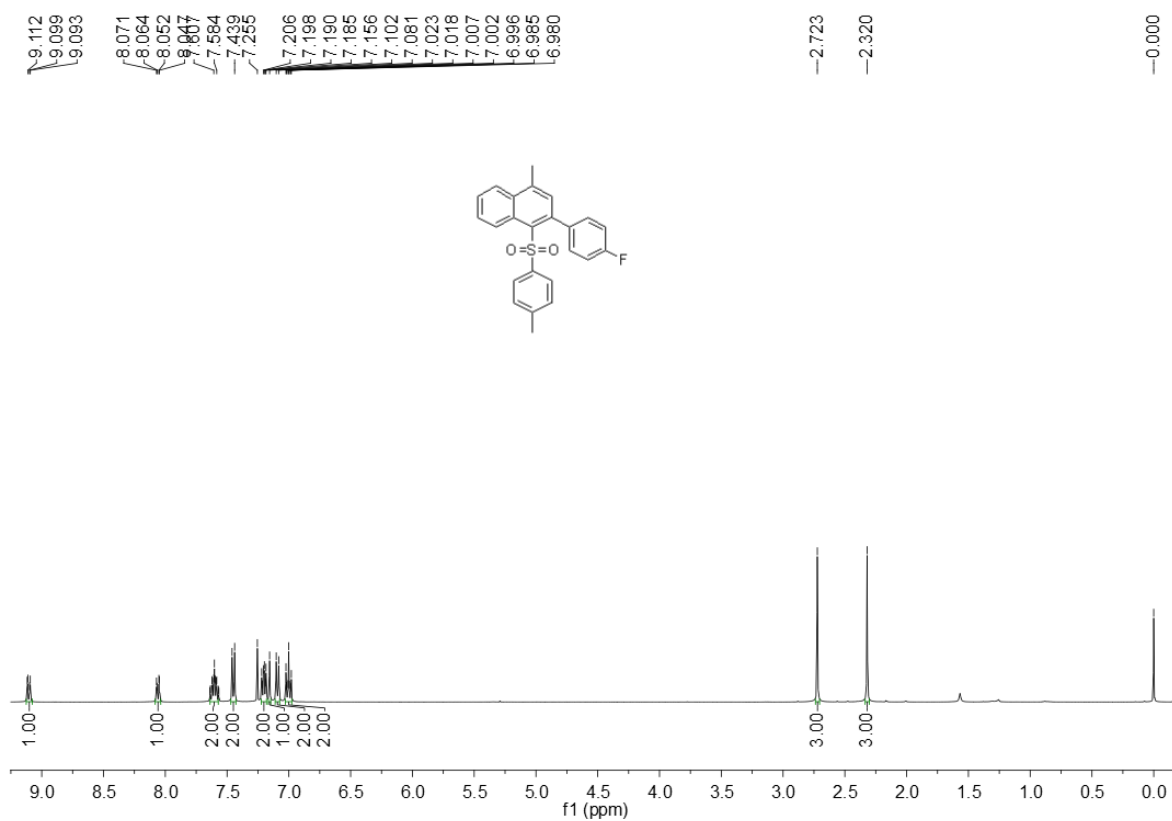


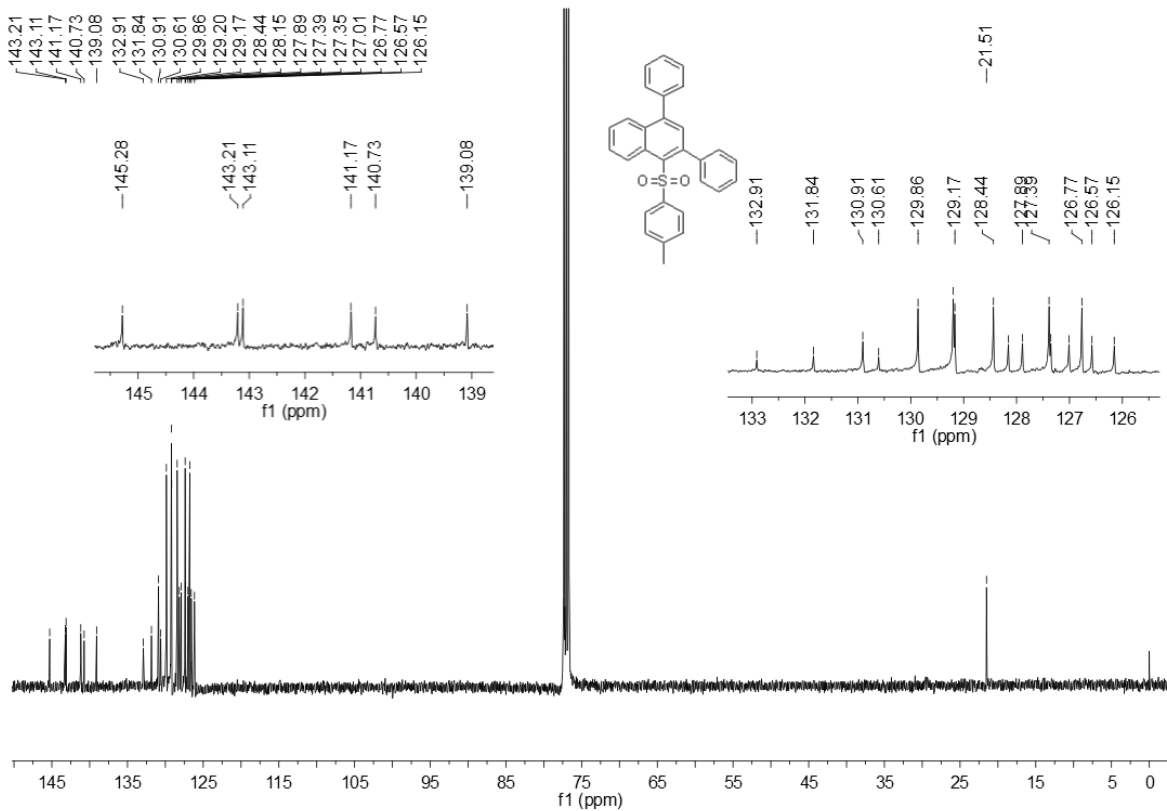
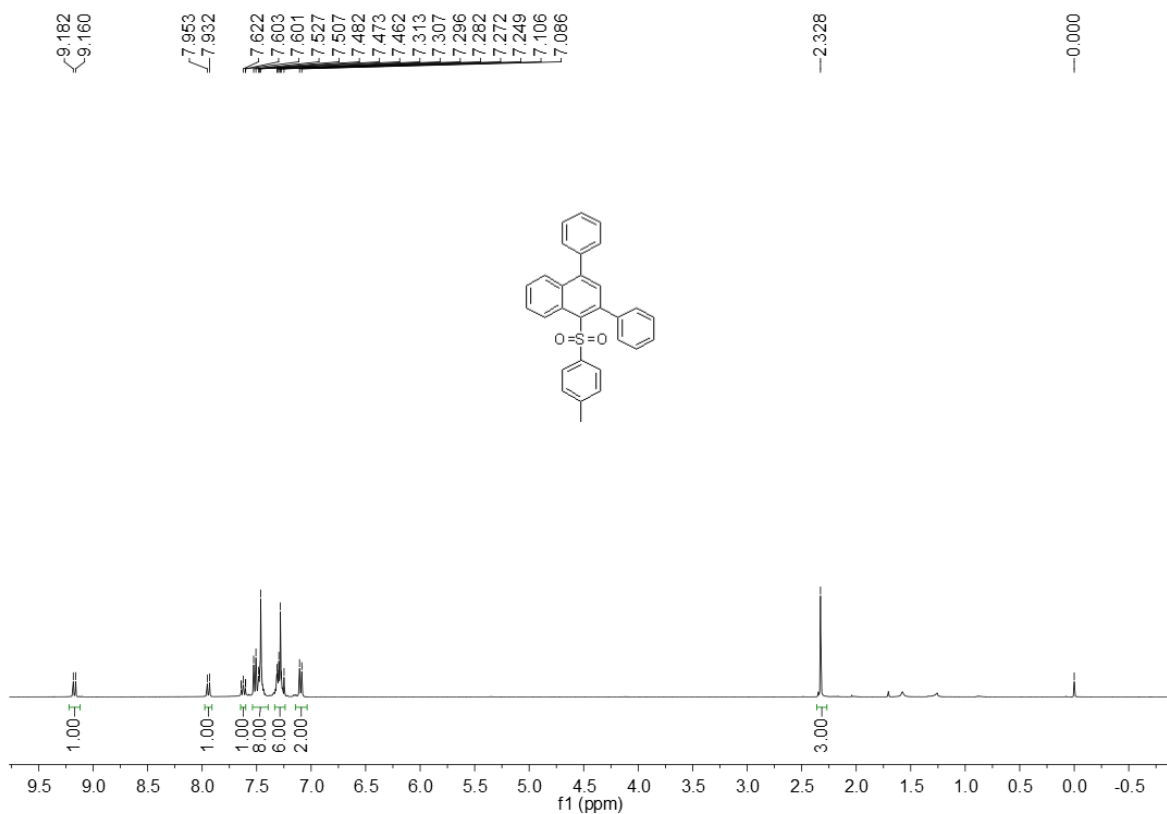


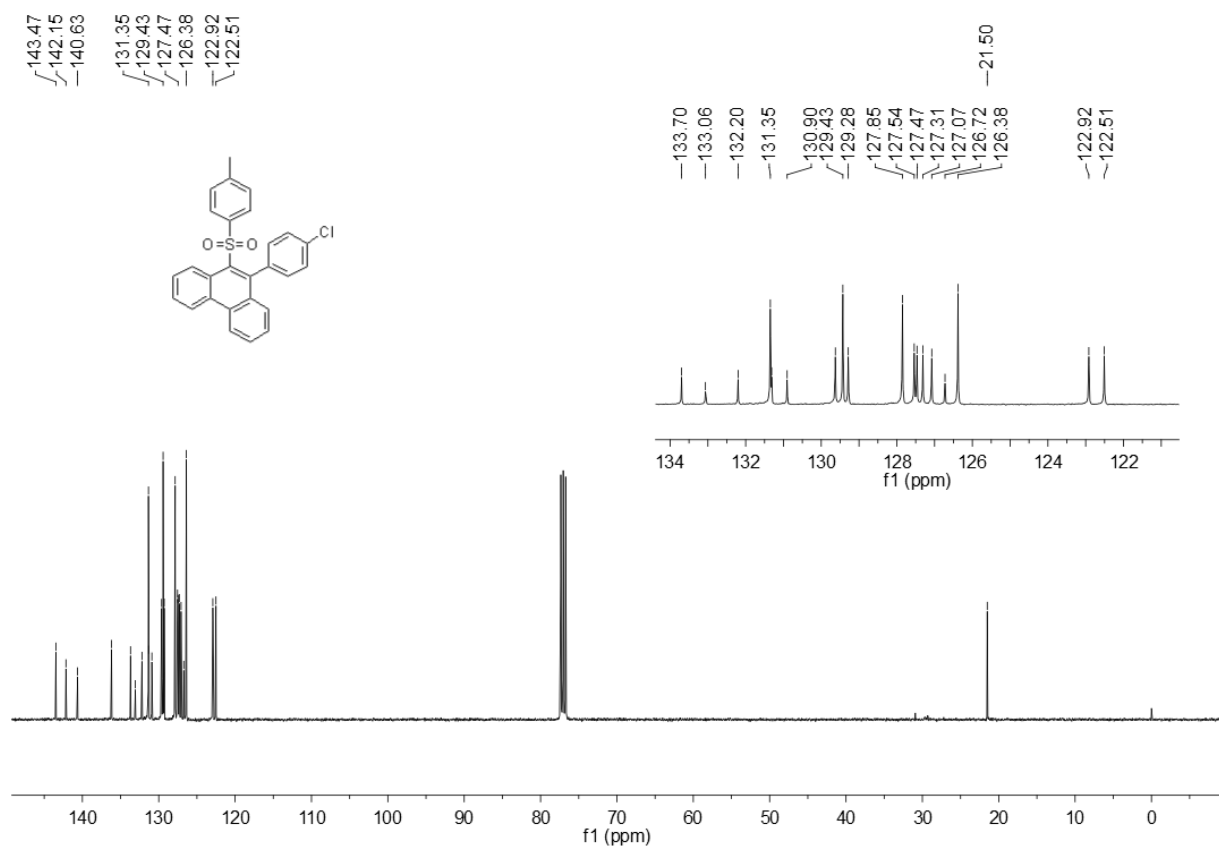
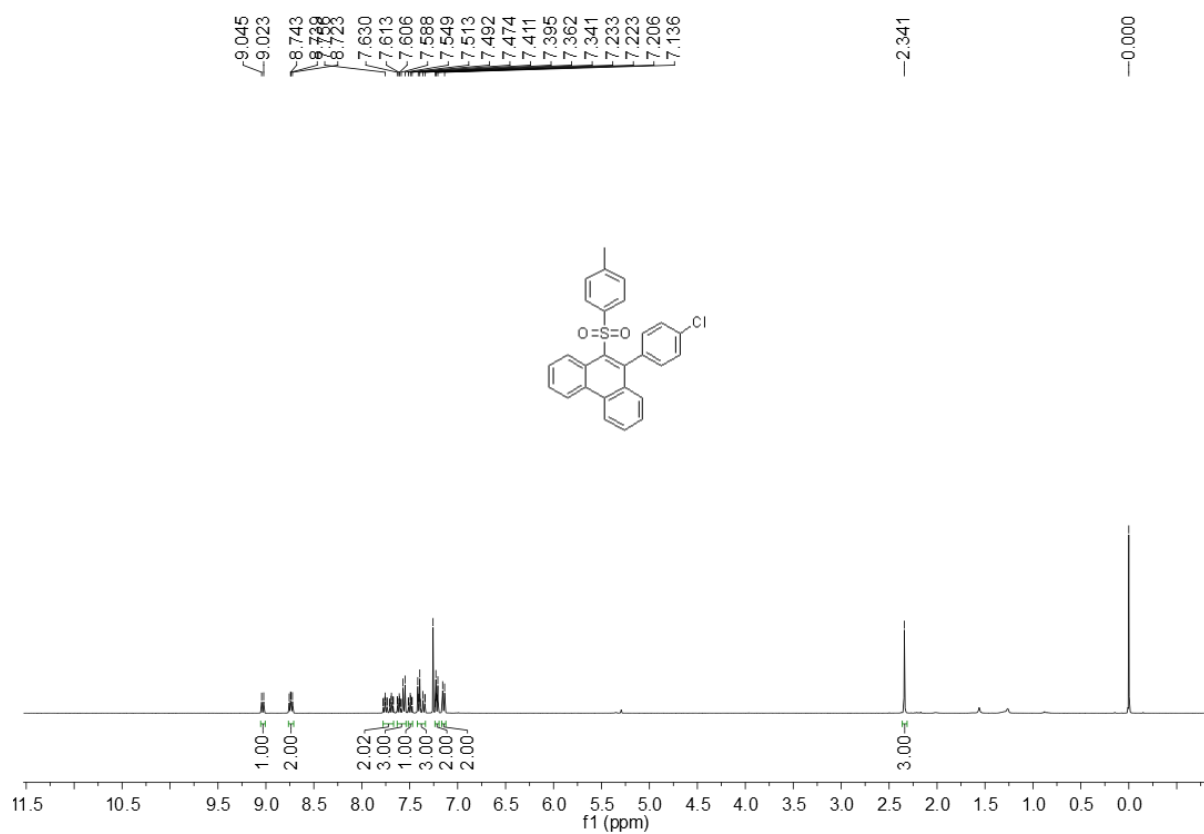
¹H NMR Spectrum of Compound 4p

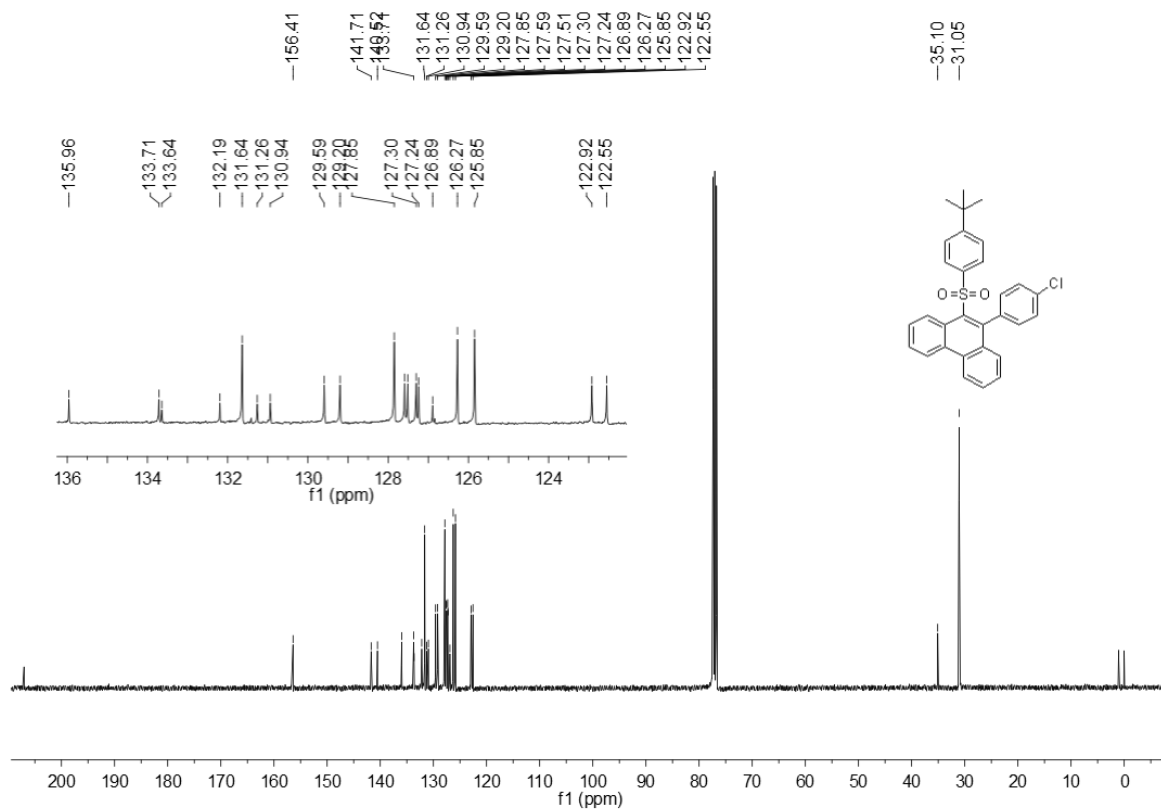
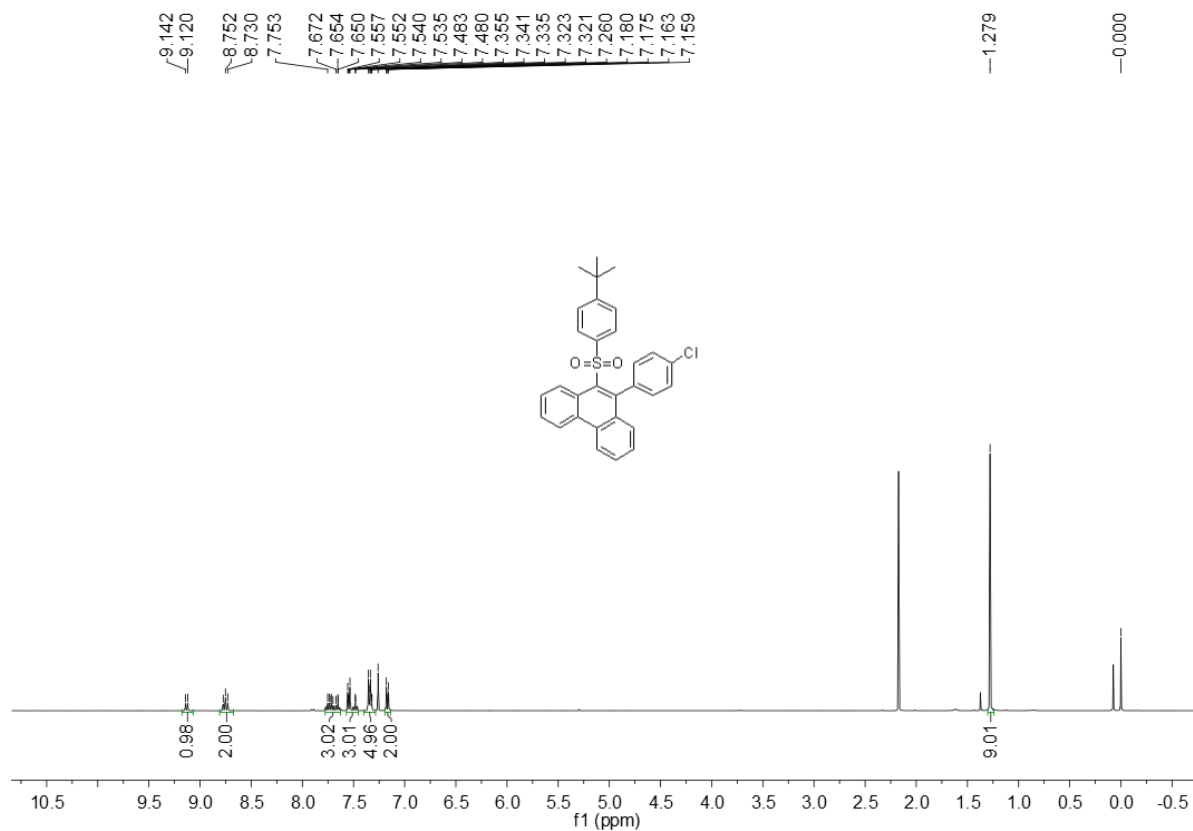


¹³C NMR Spectrum of Compound 4p

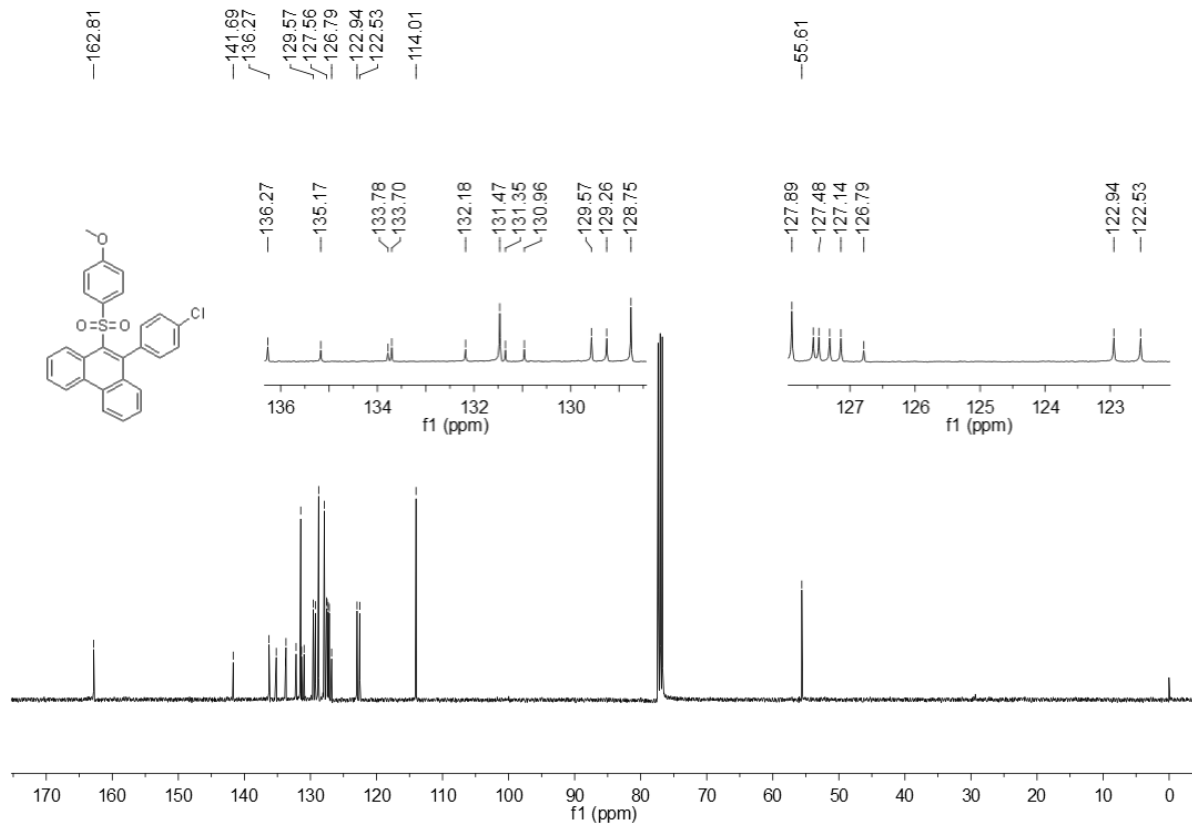
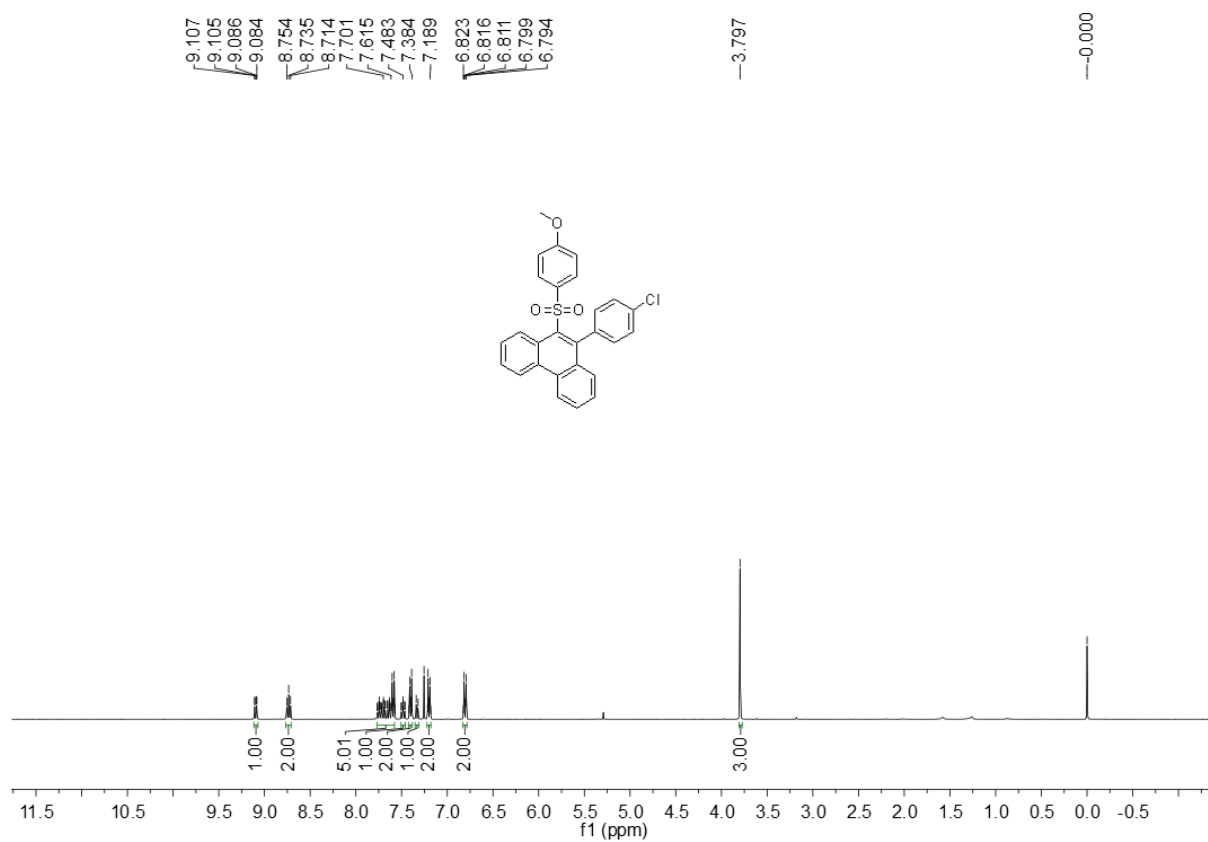


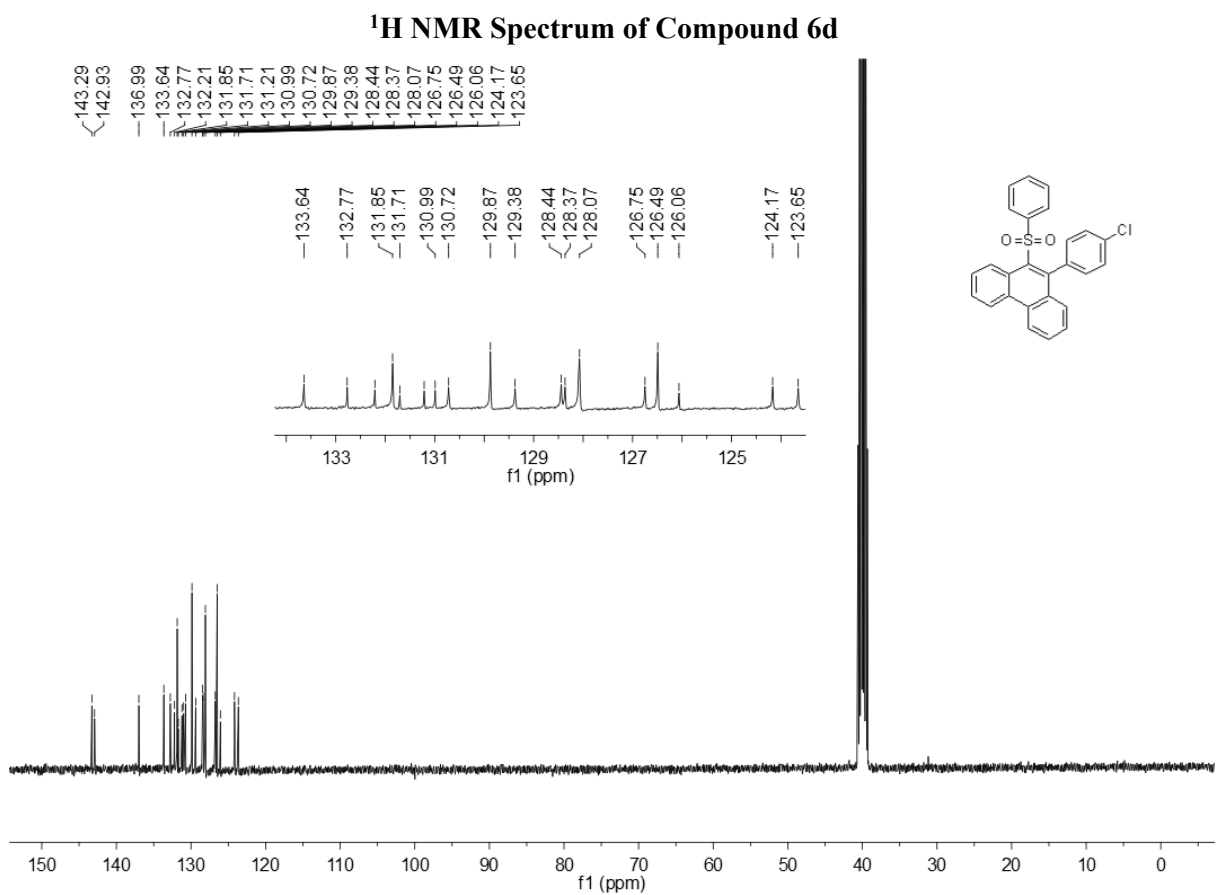
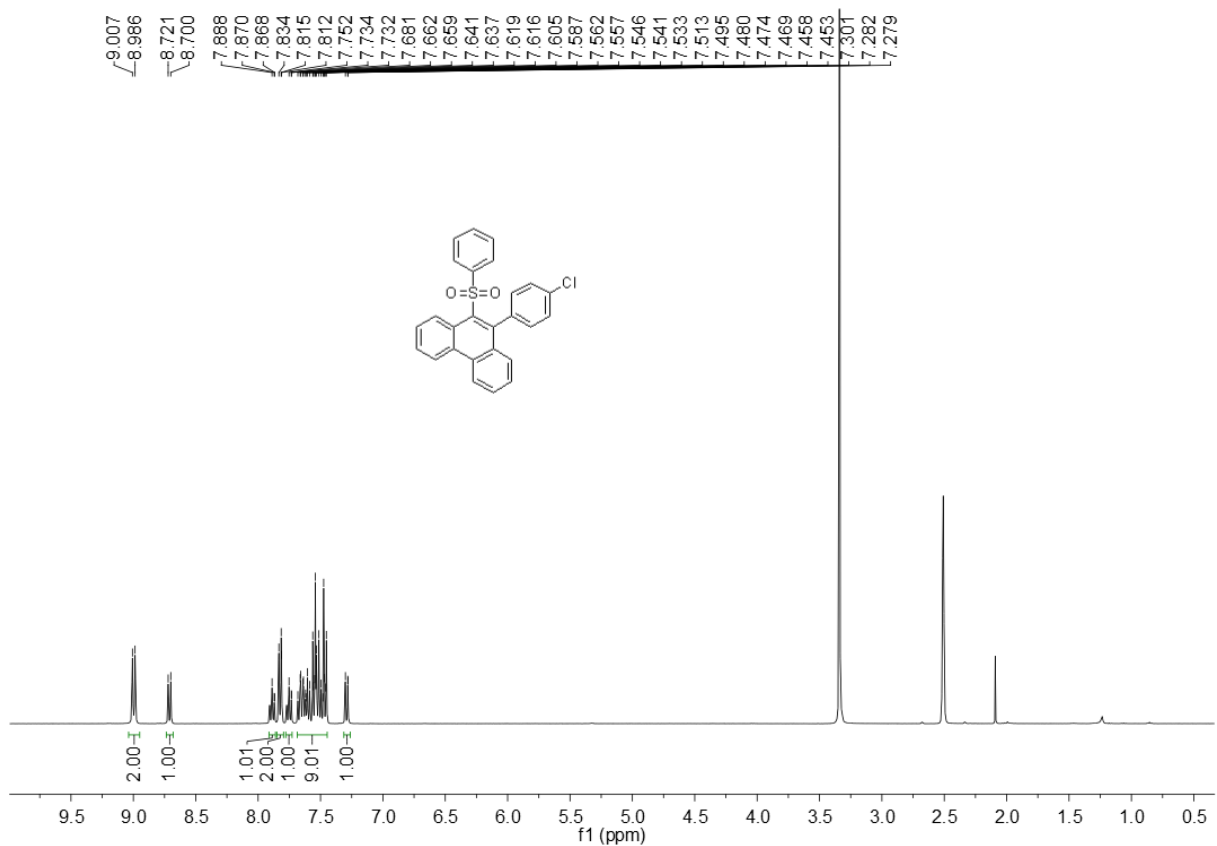


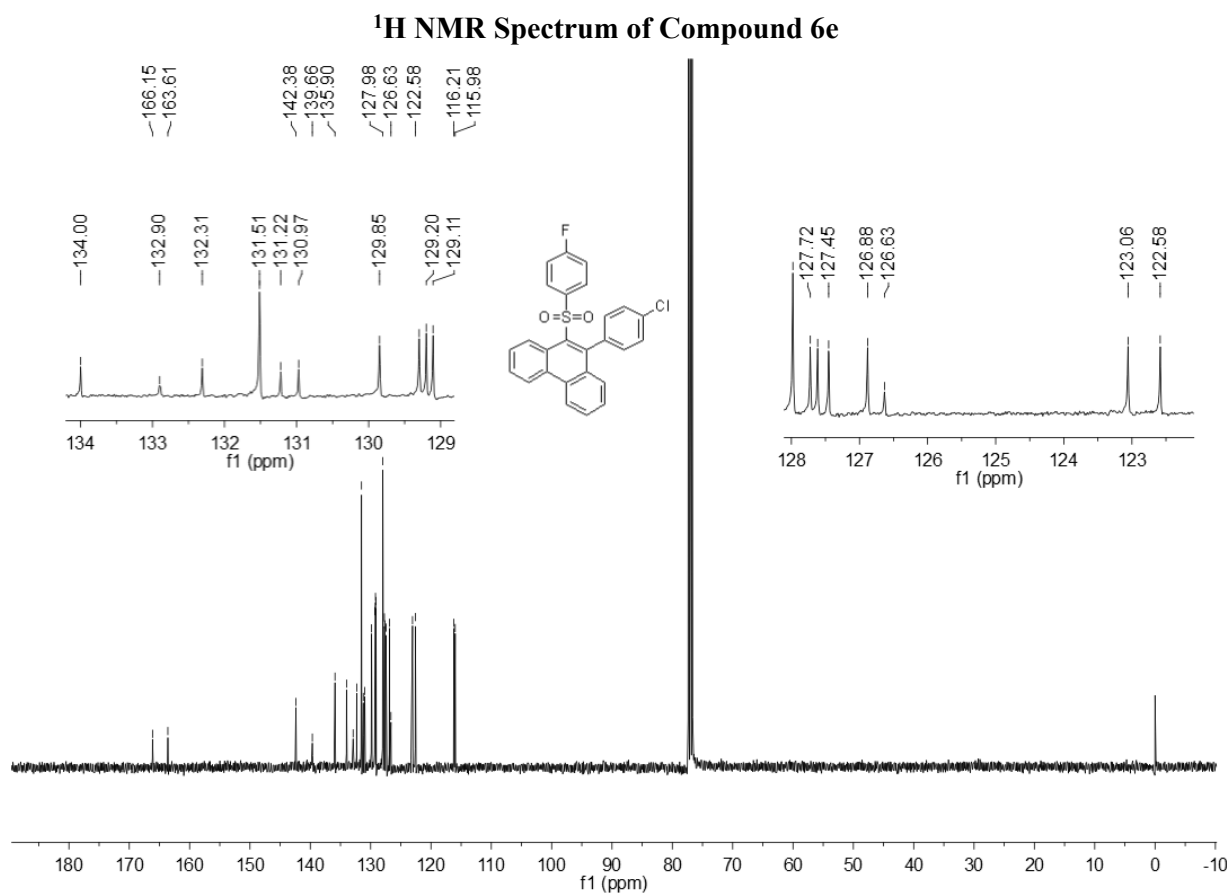
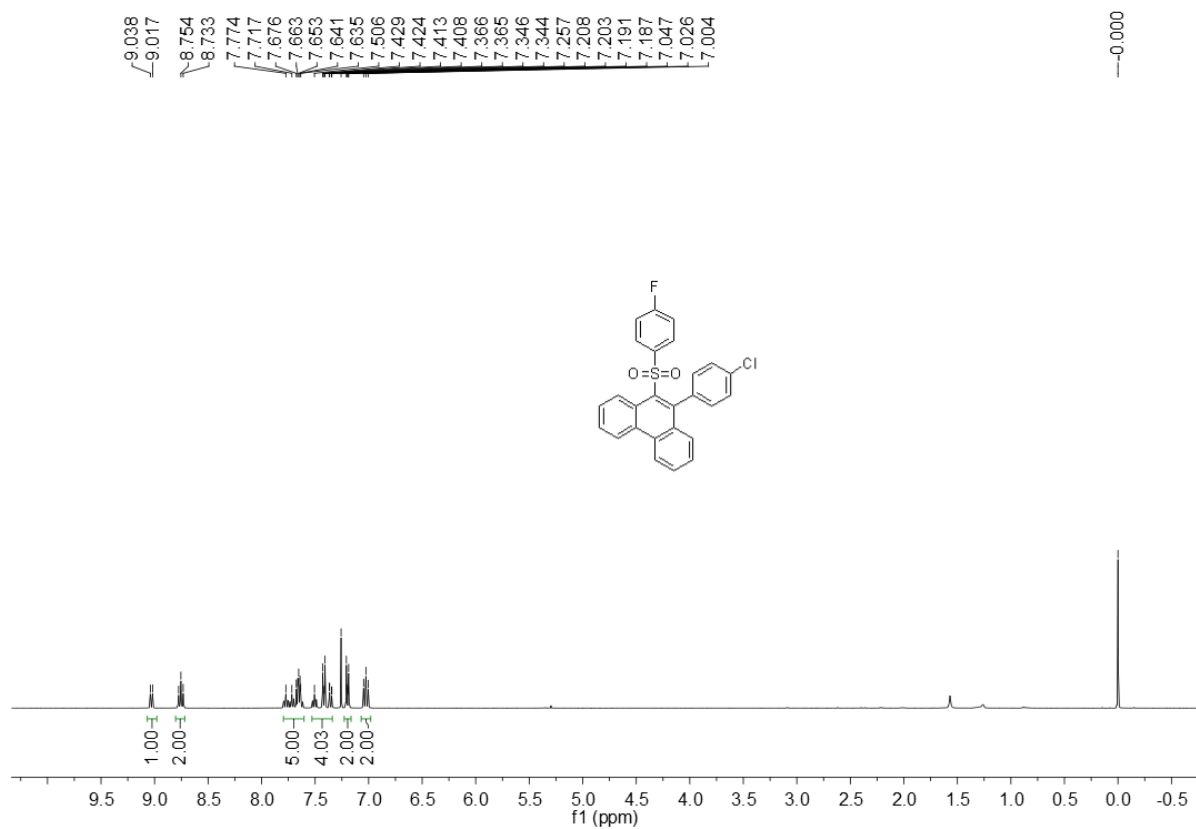


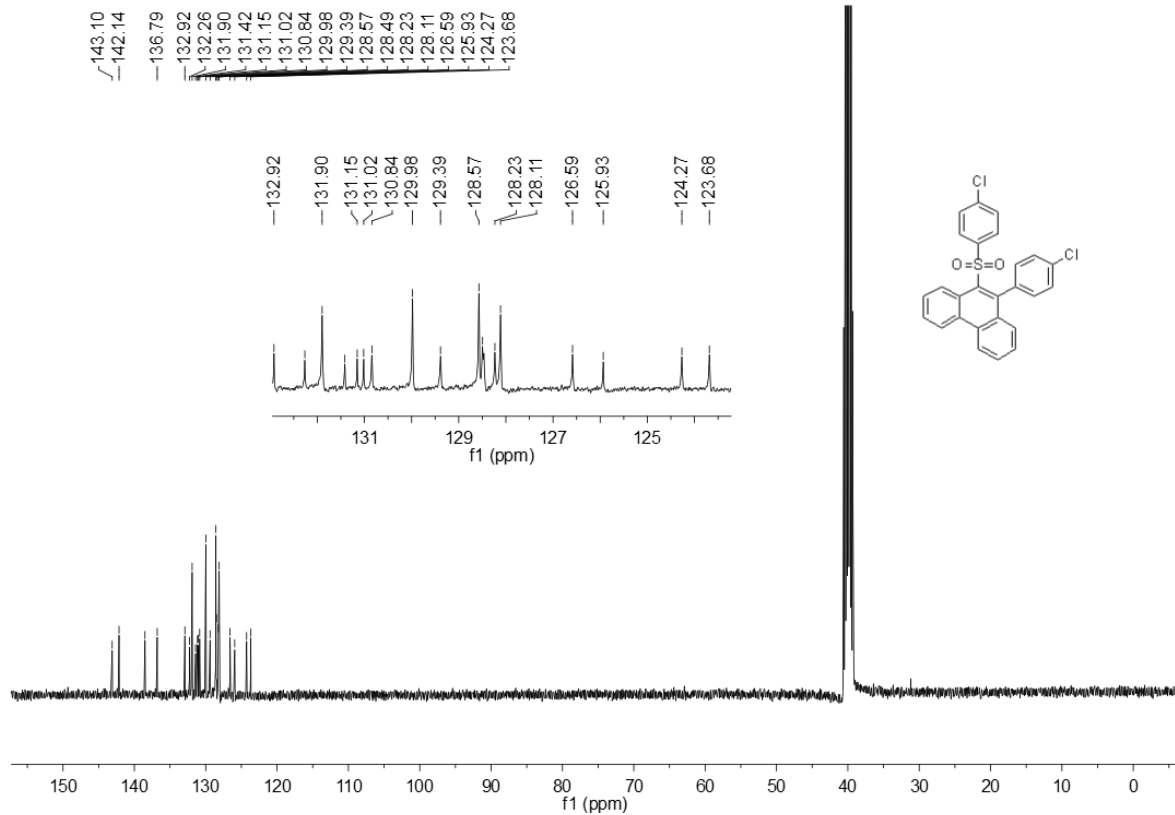
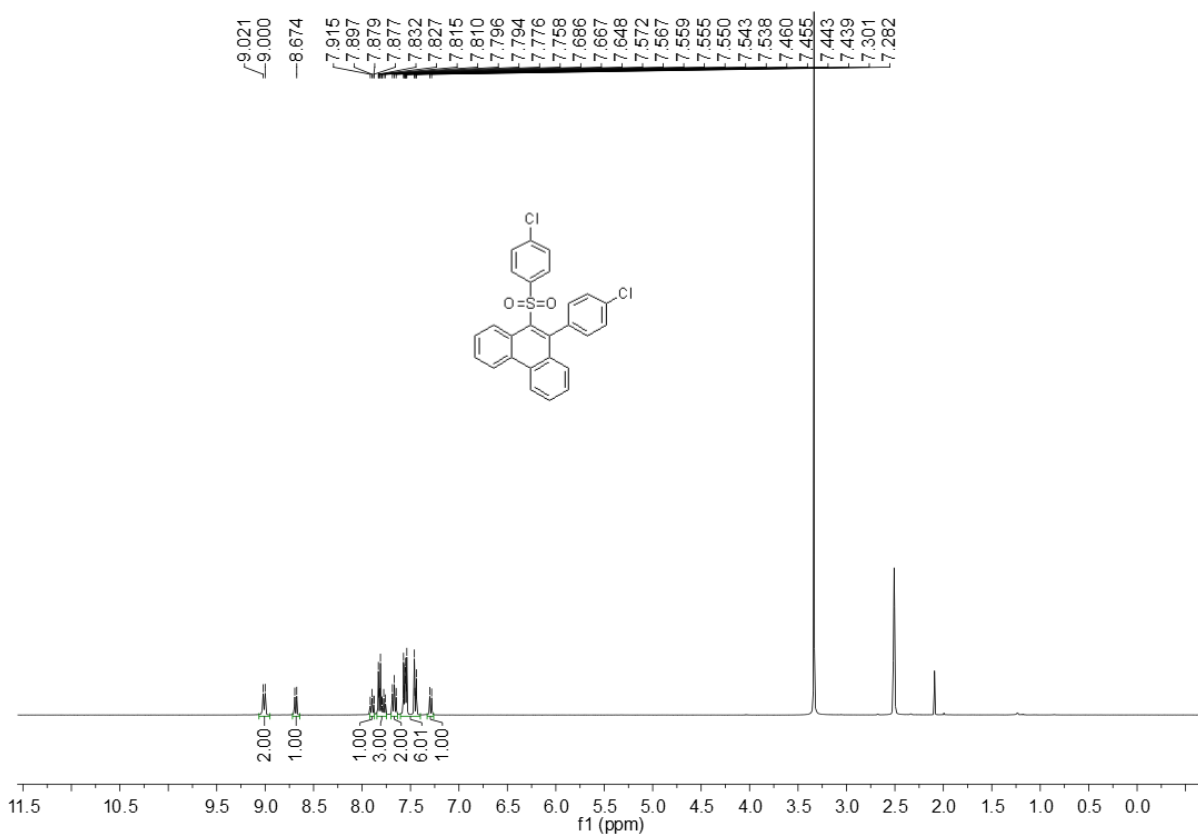


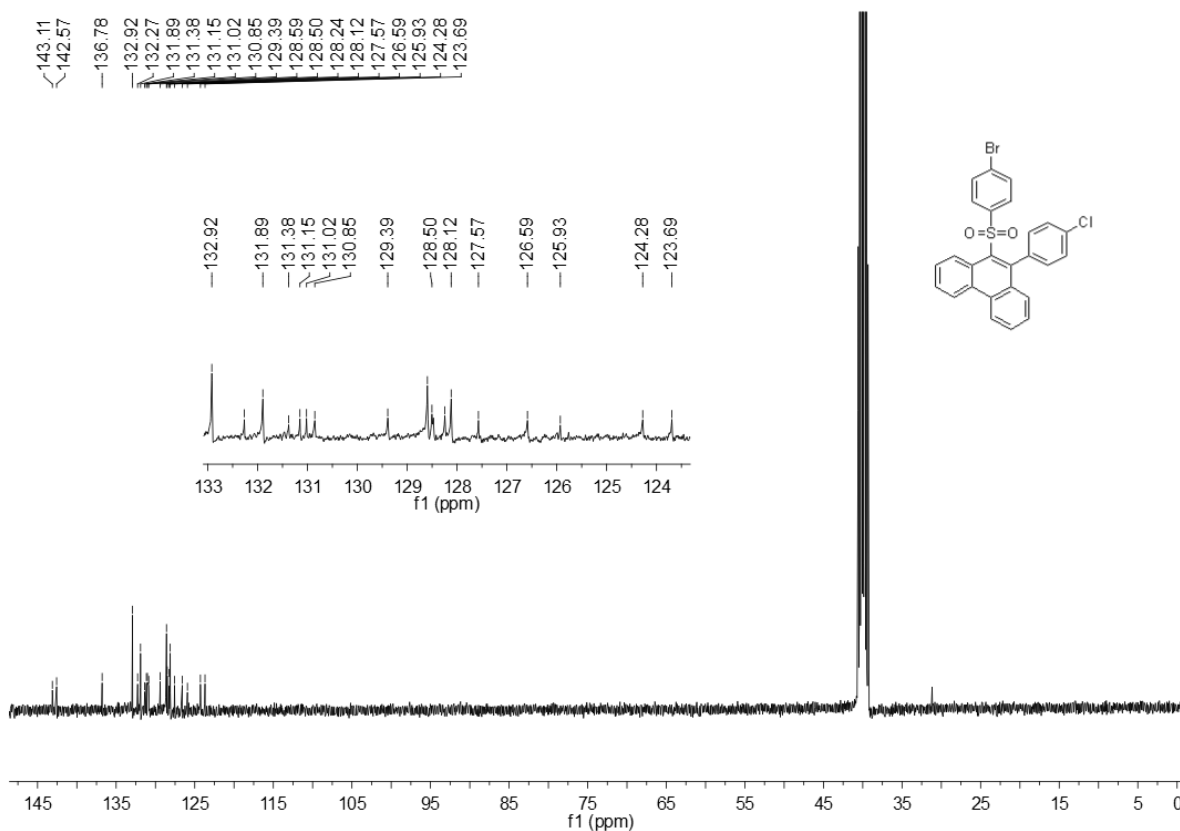
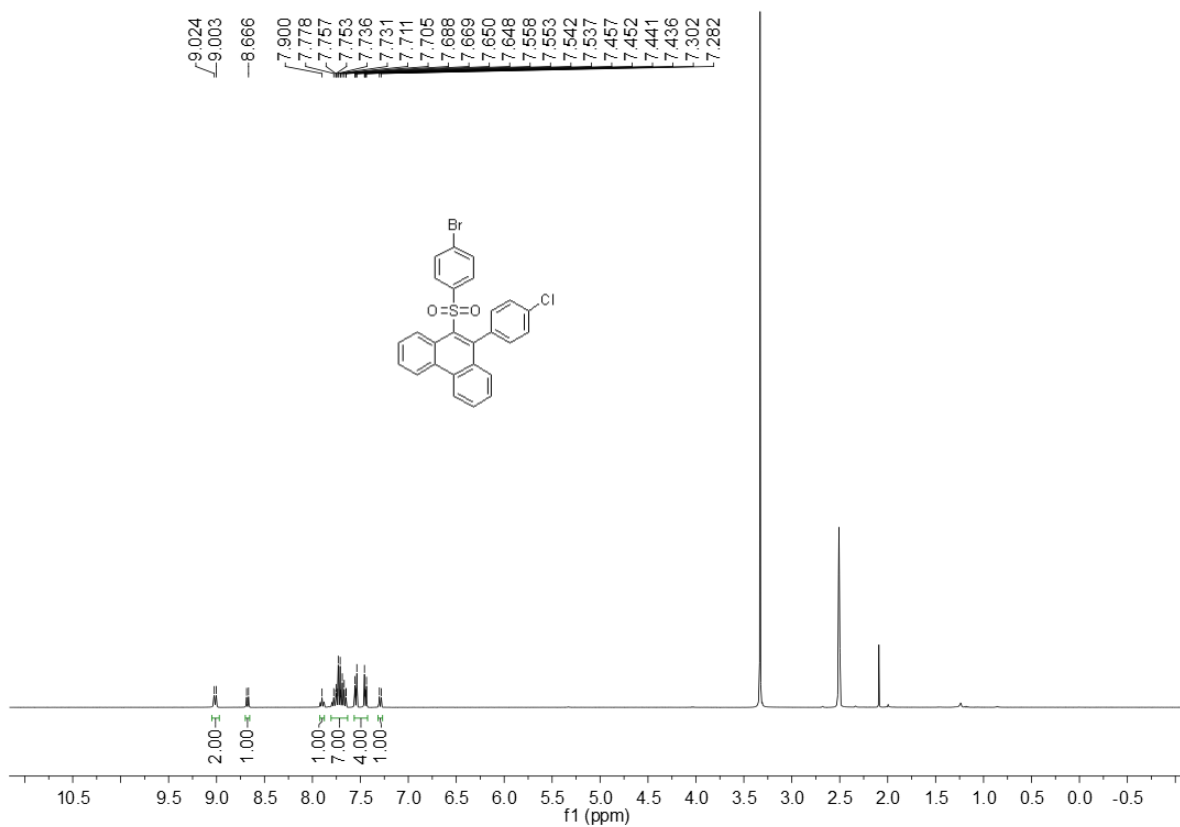
¹³C NMR Spectrum of Compound 6b

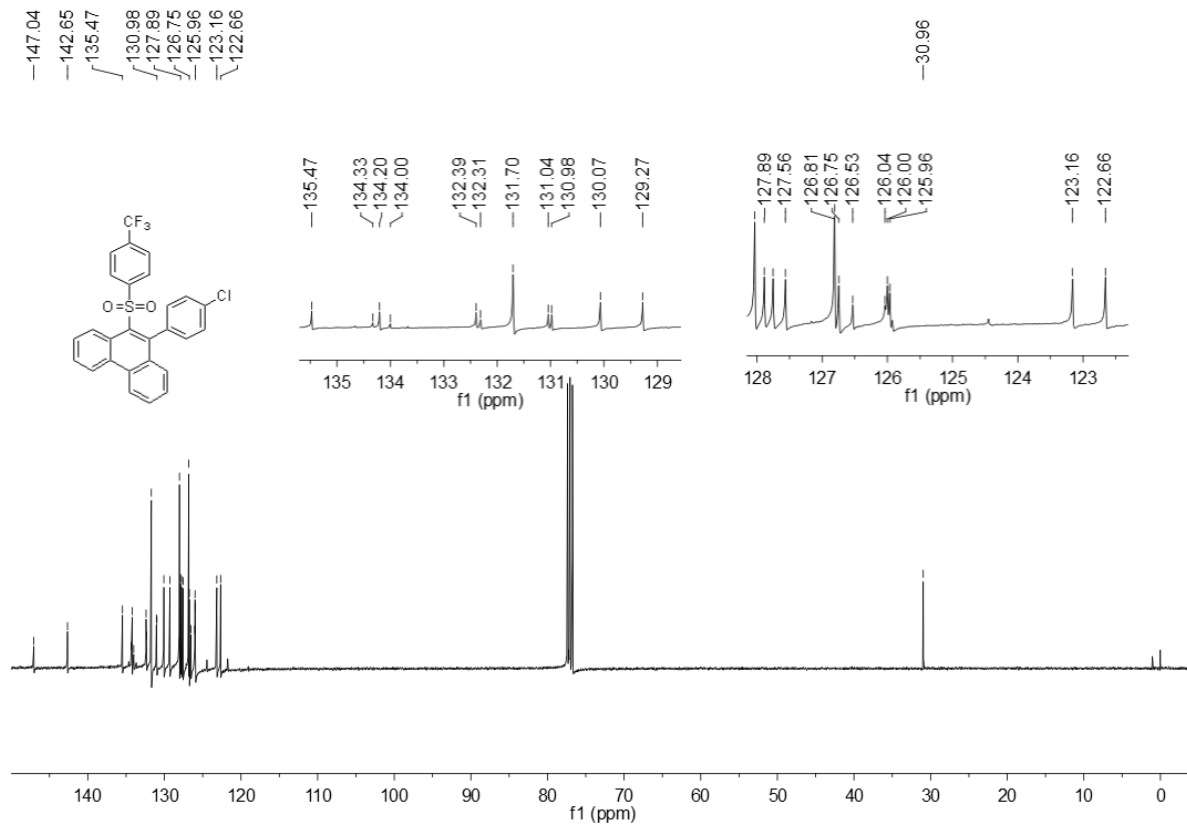
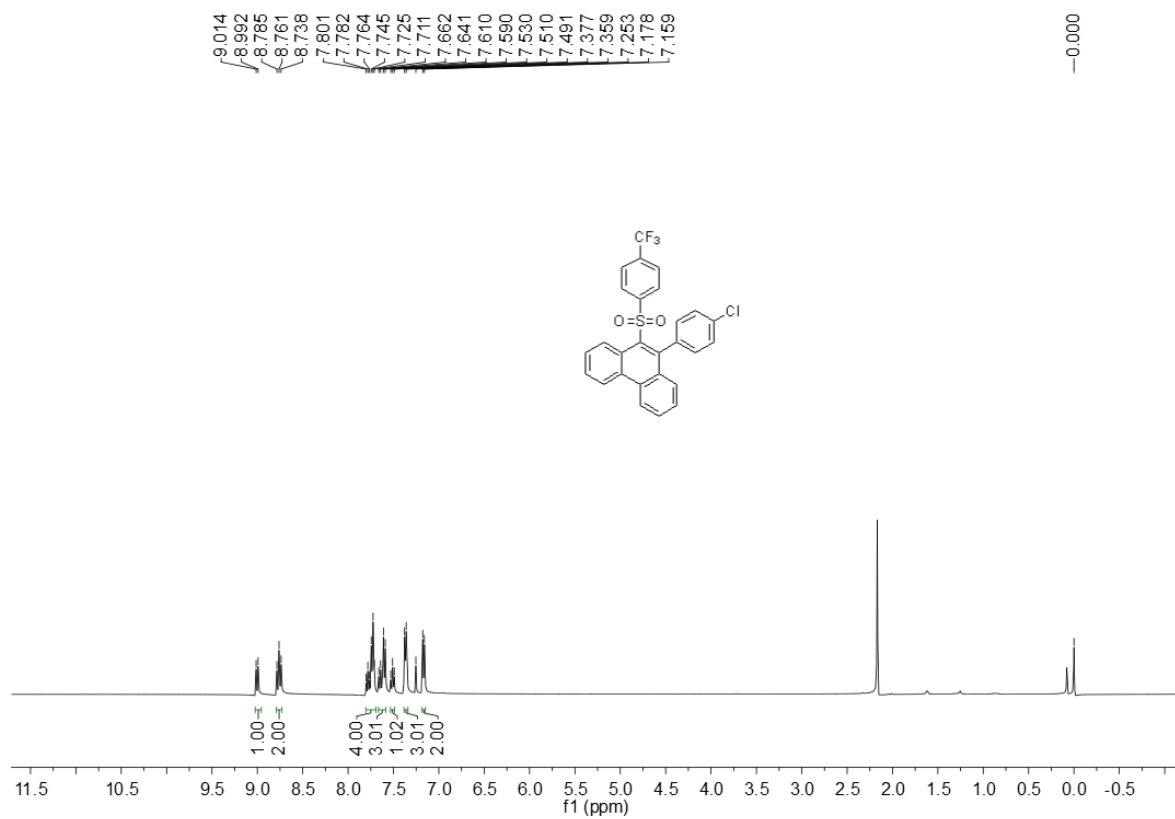


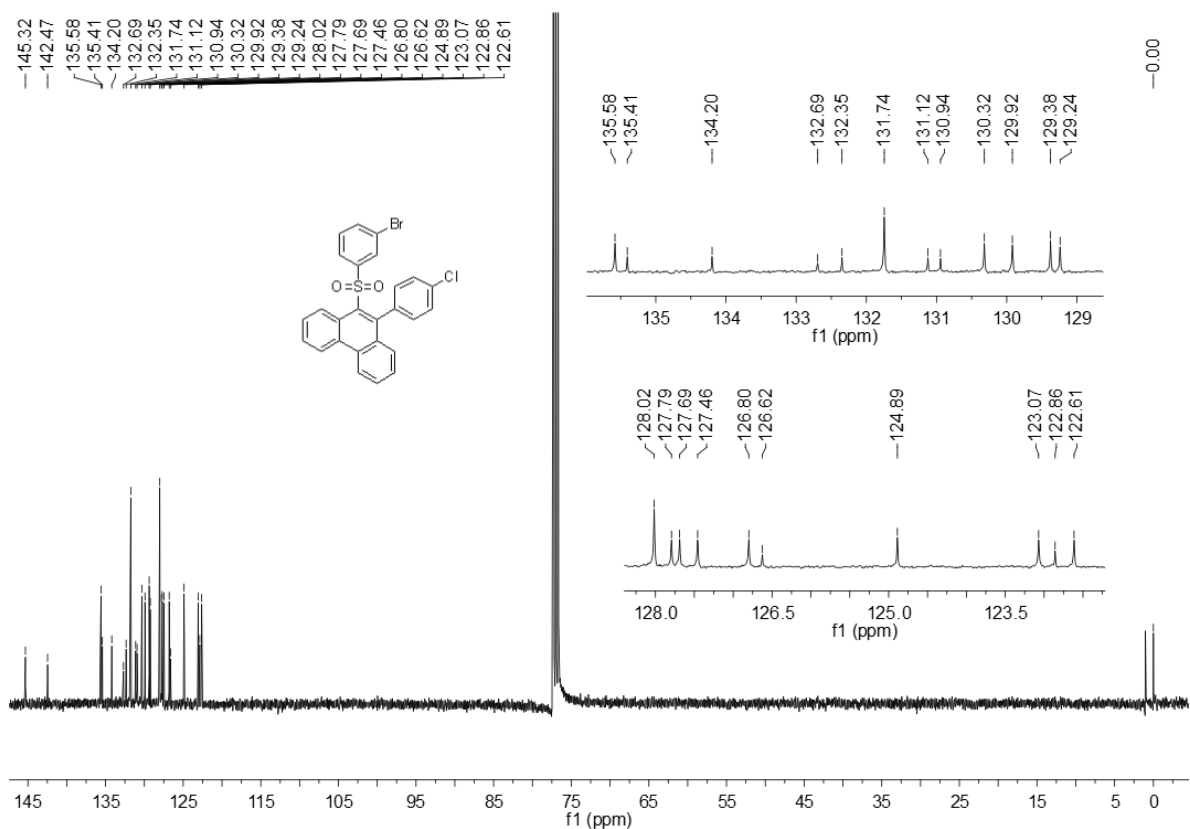
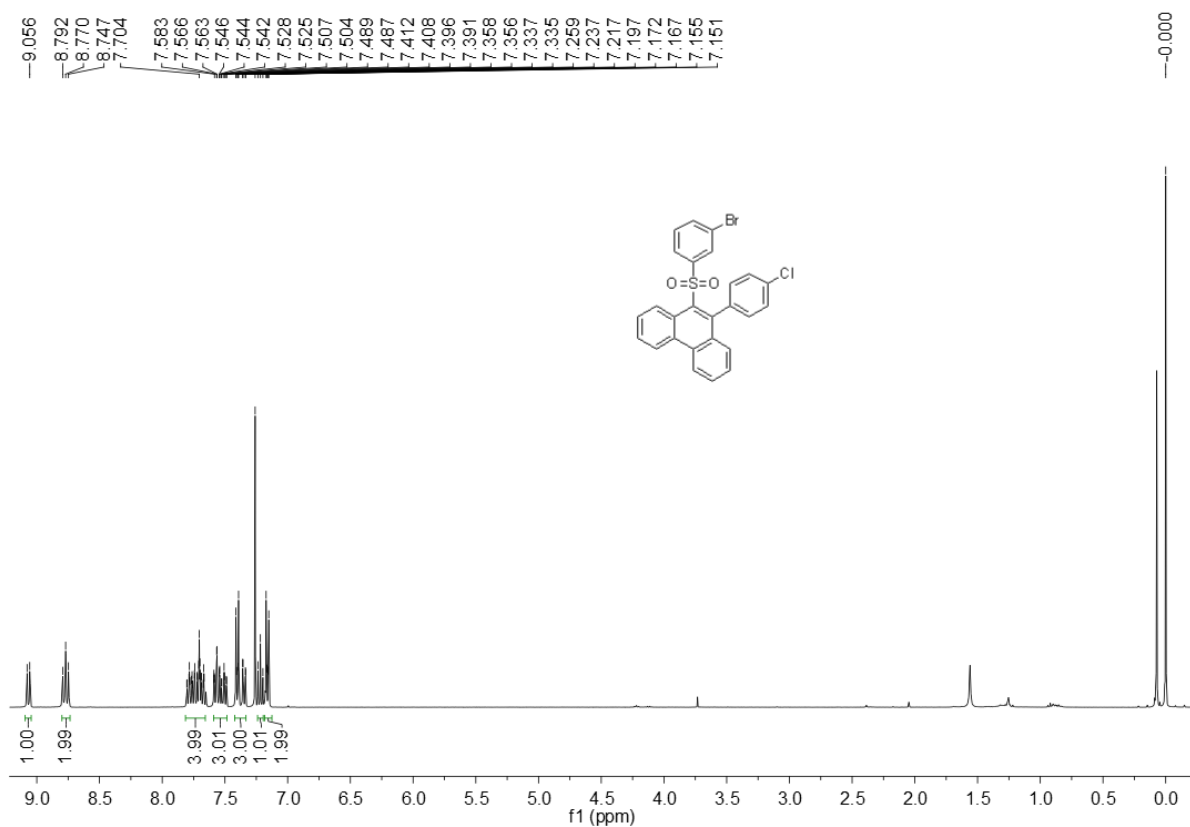


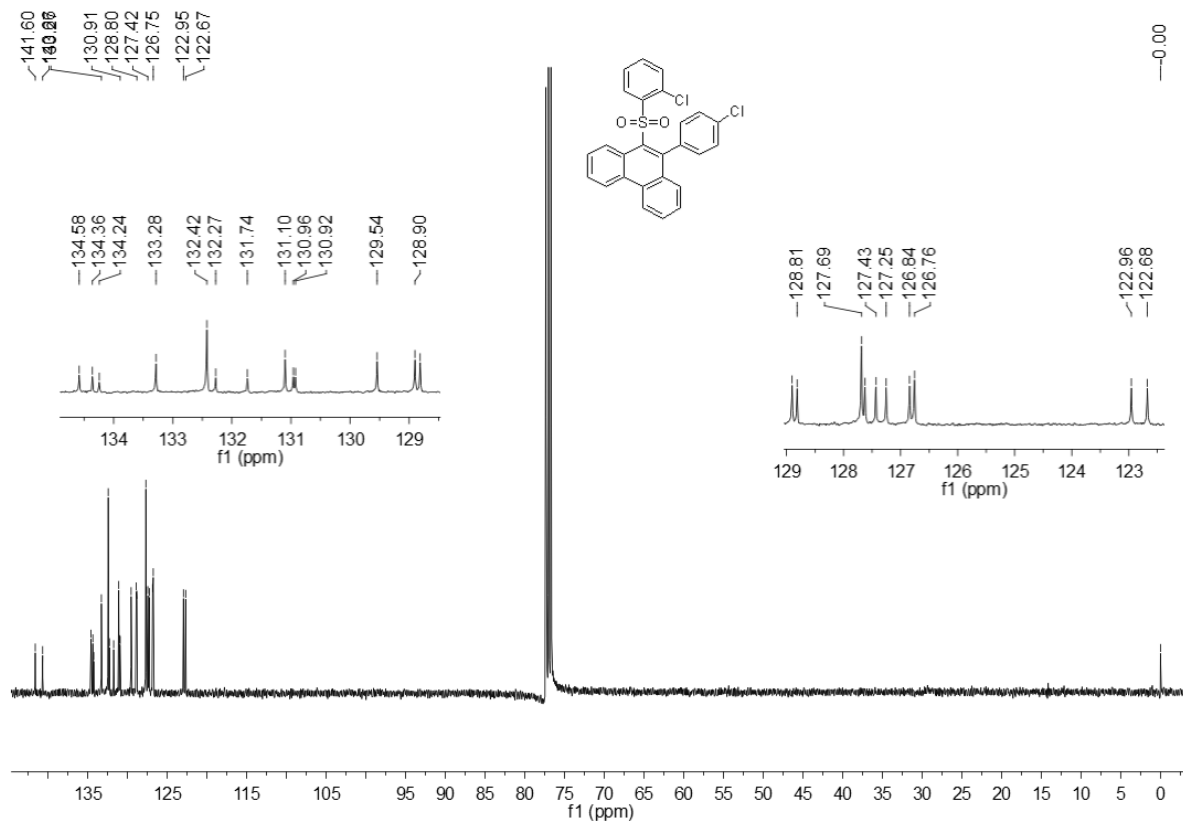
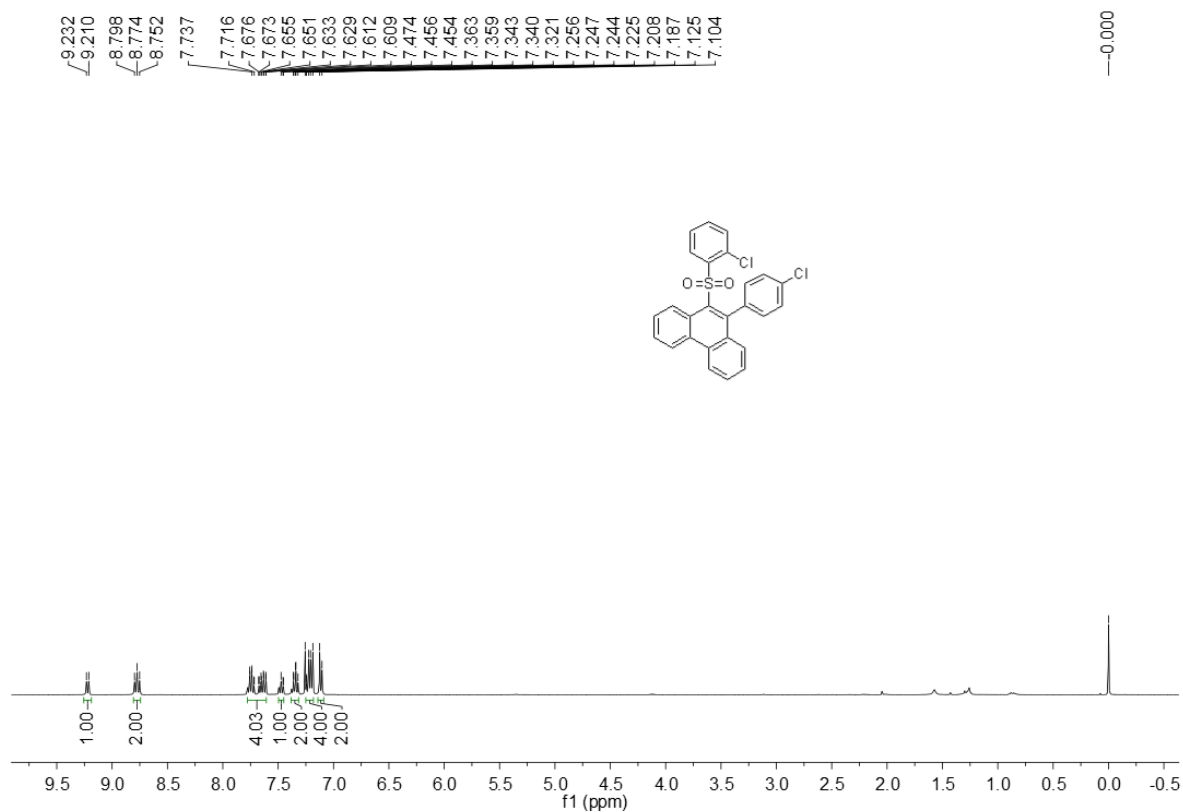


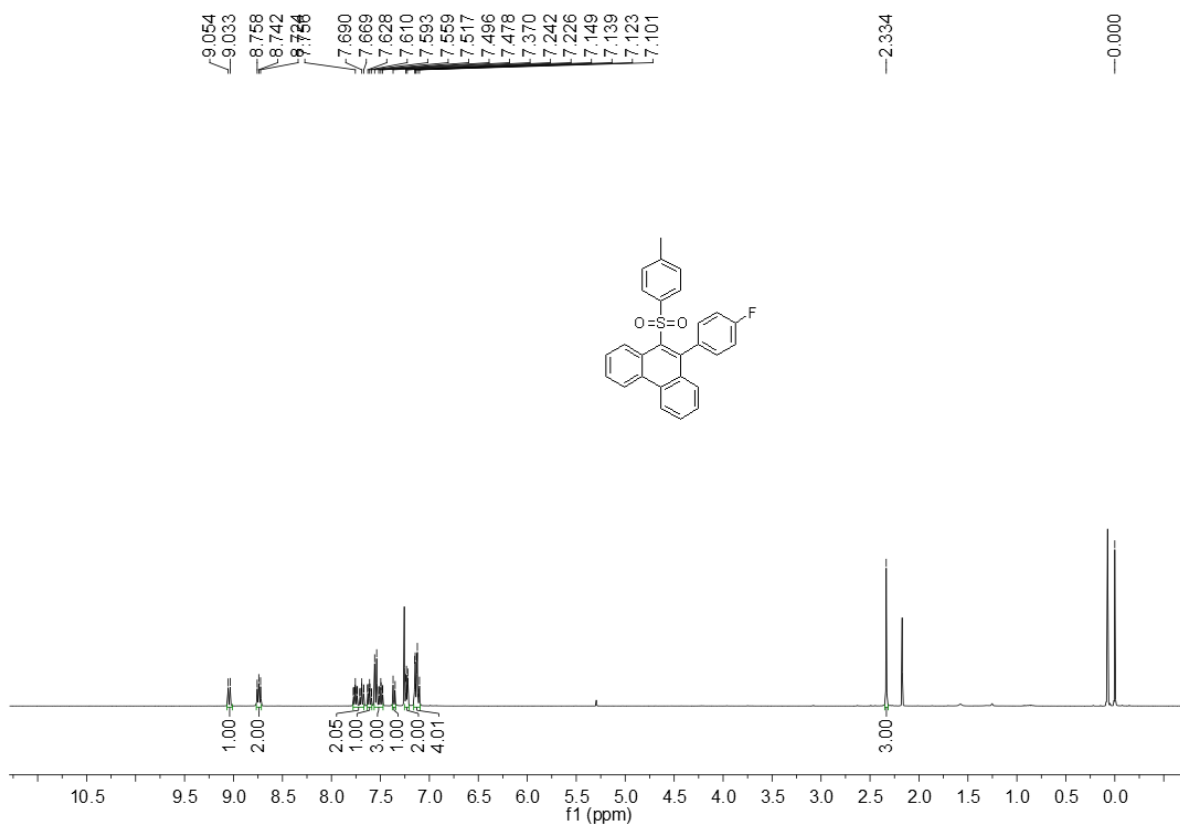




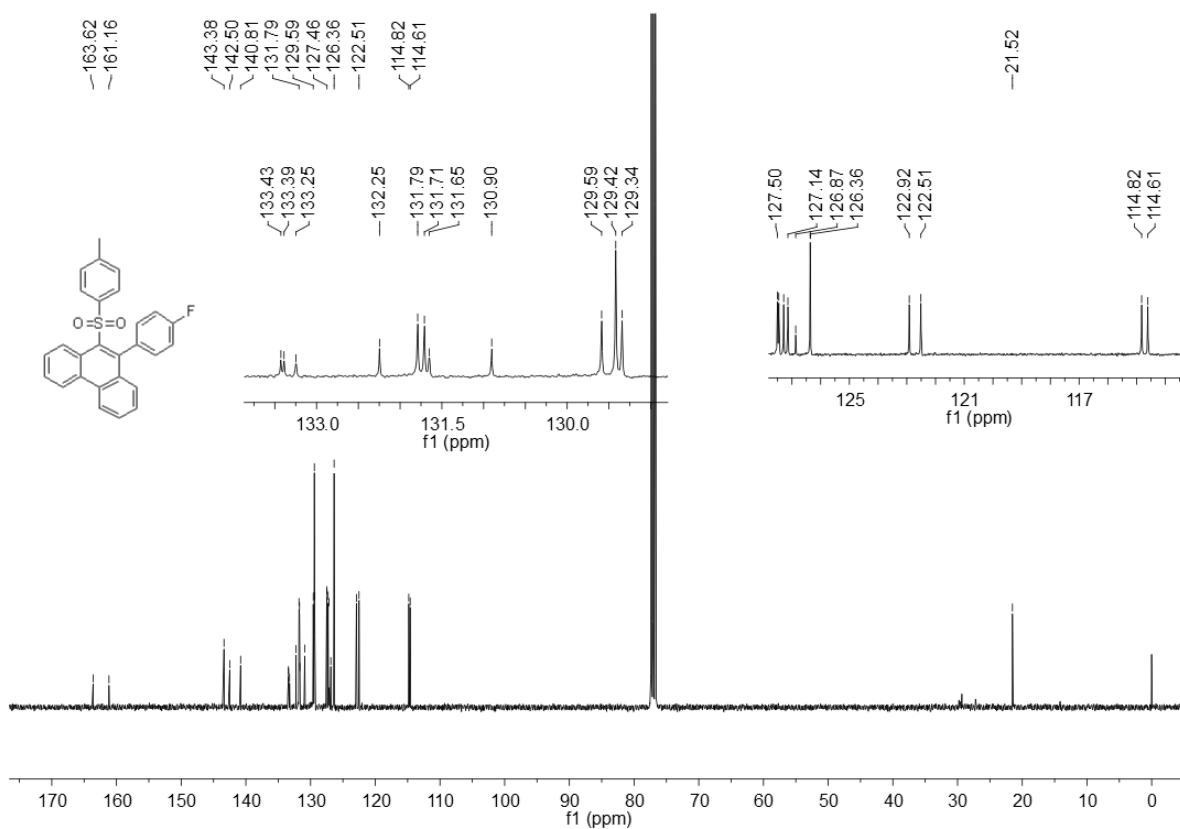




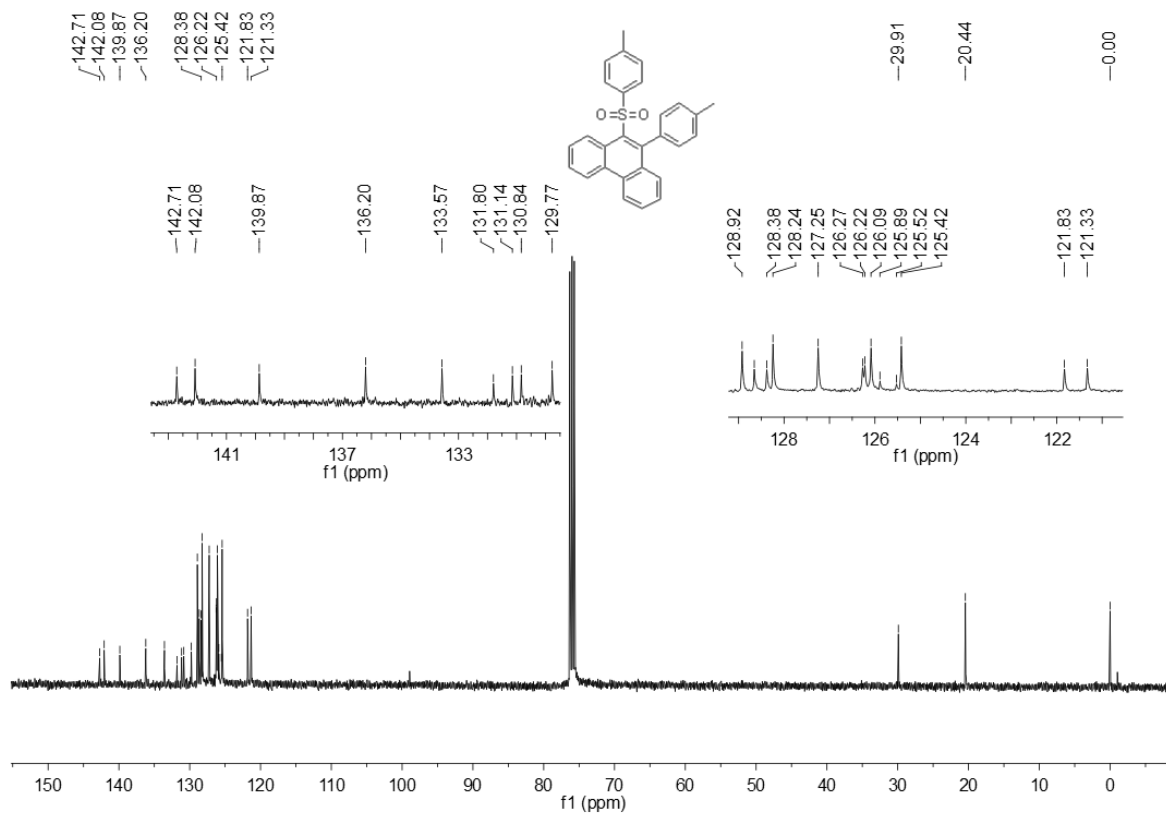
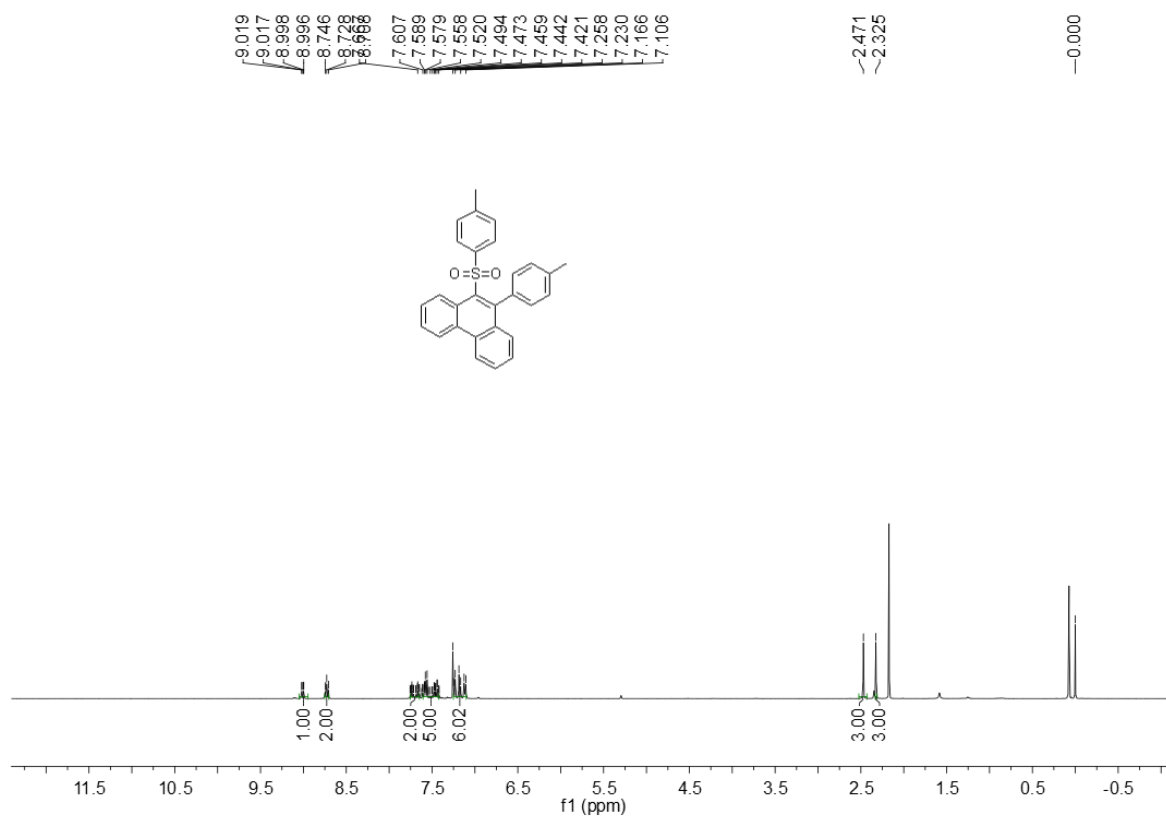


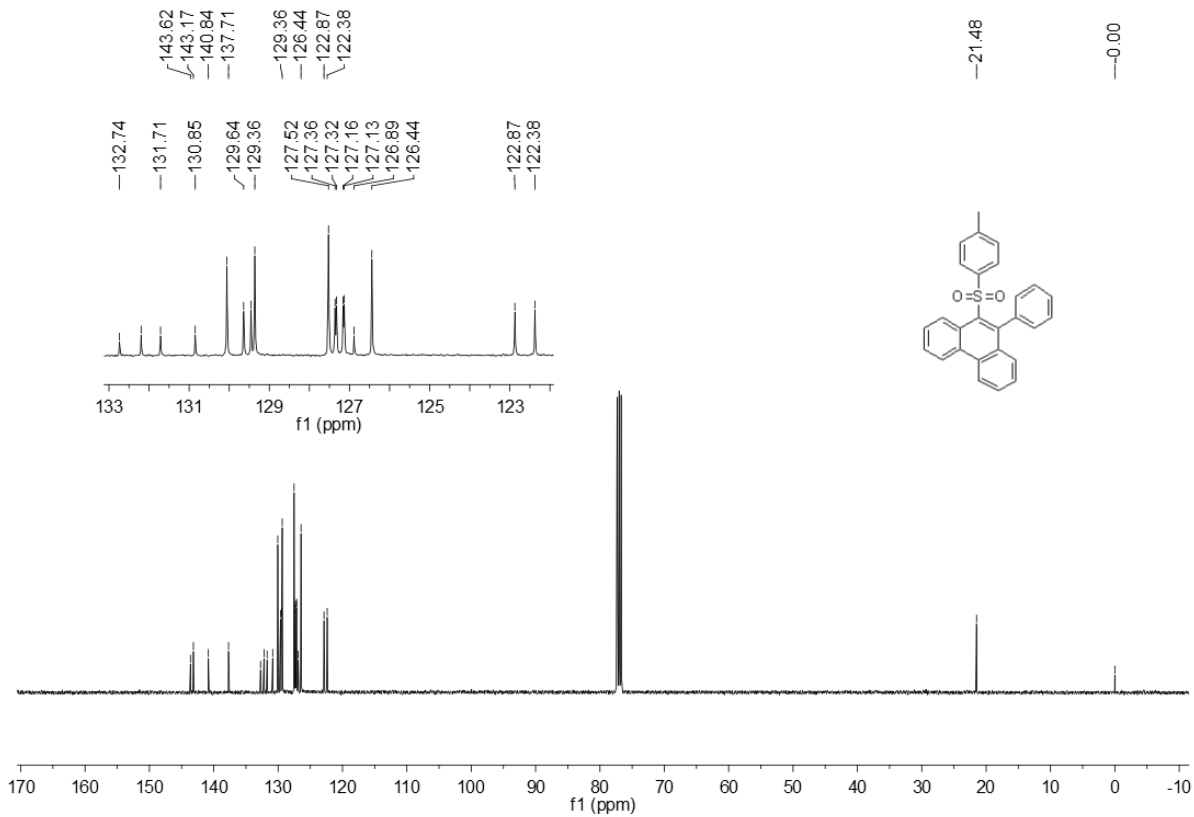
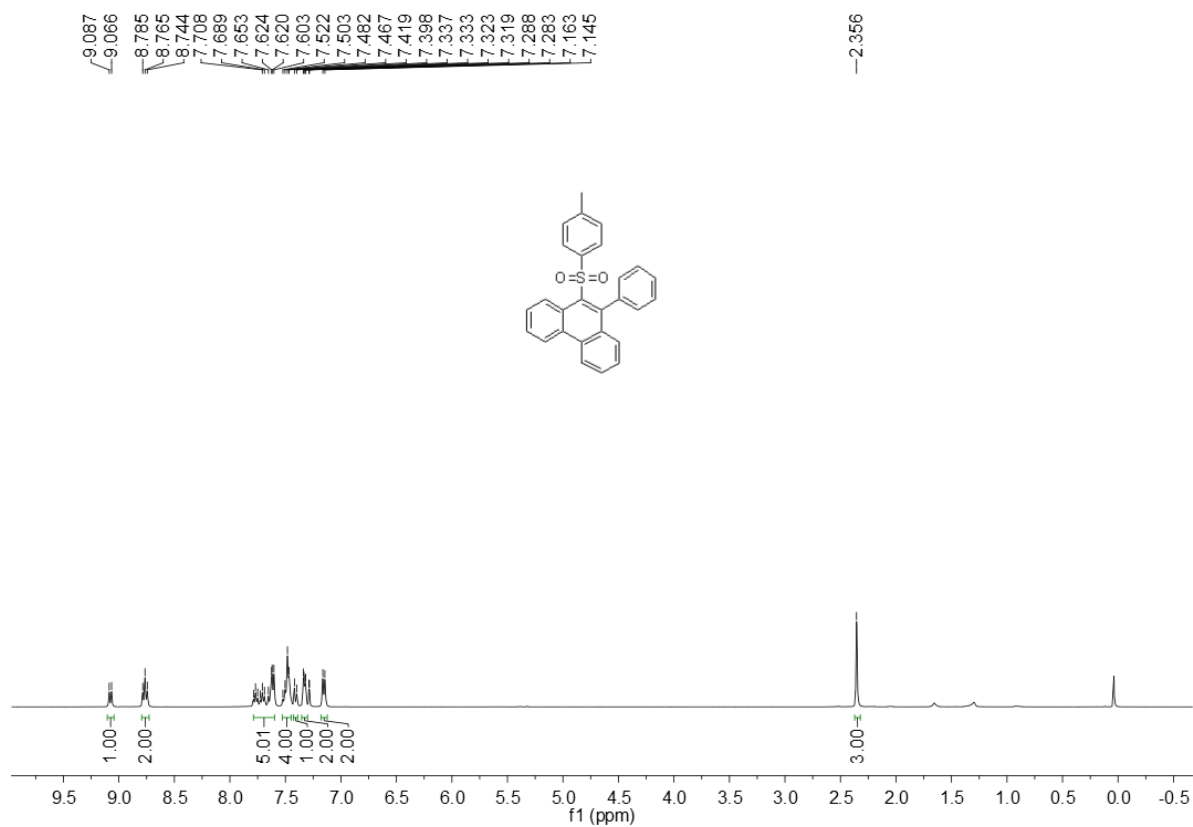


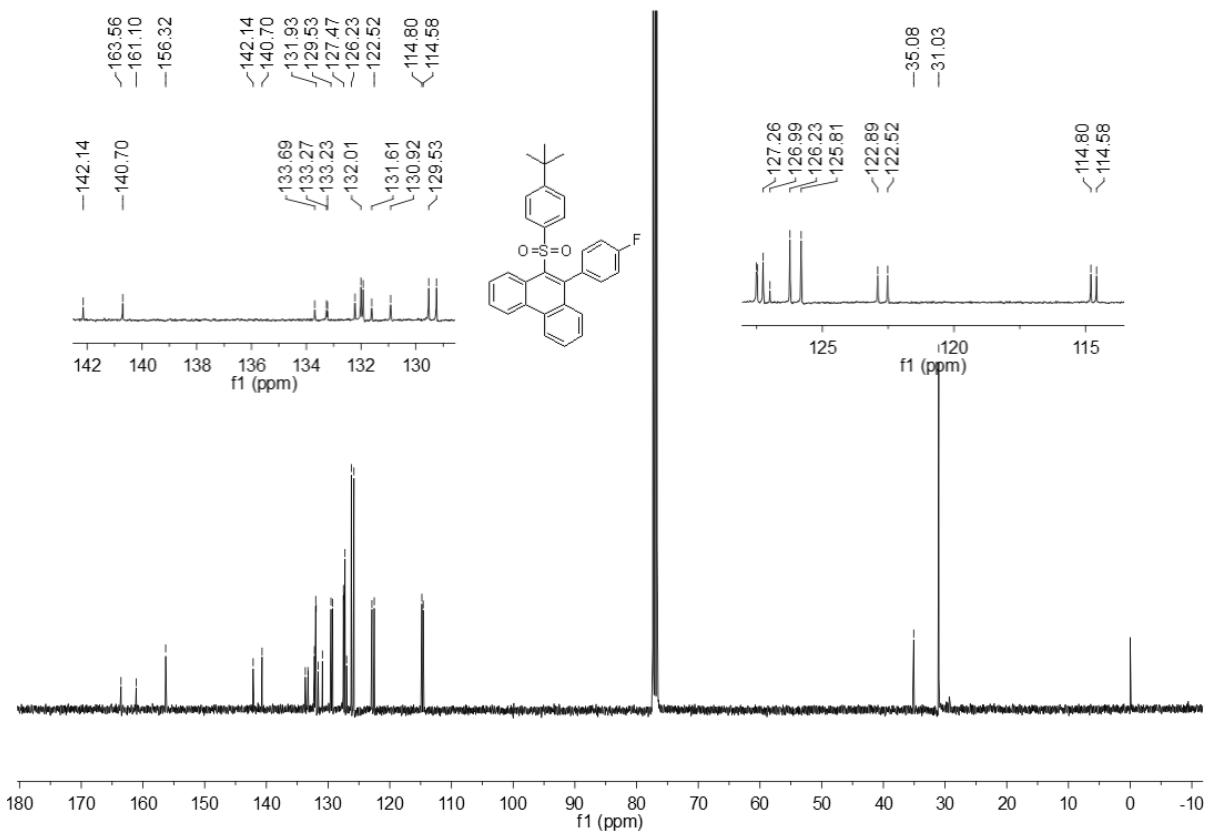
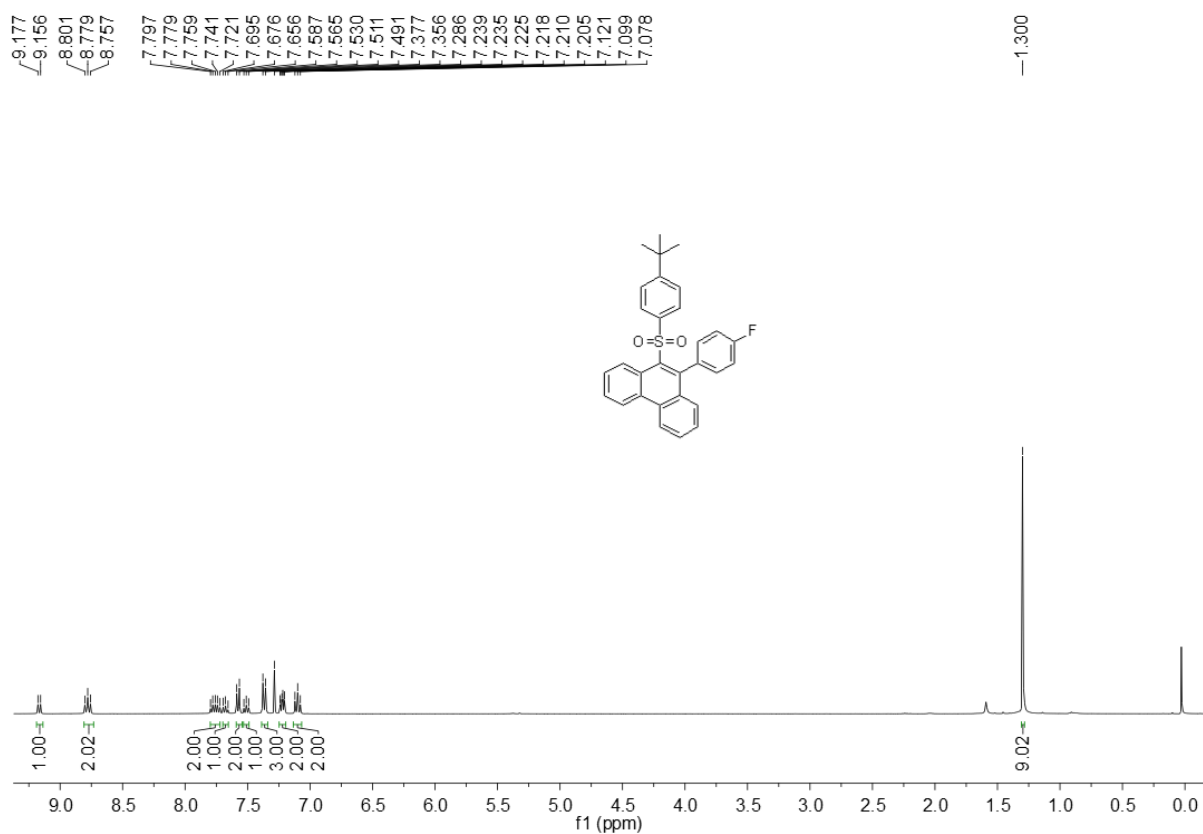
¹H NMR Spectrum of Compound 6l

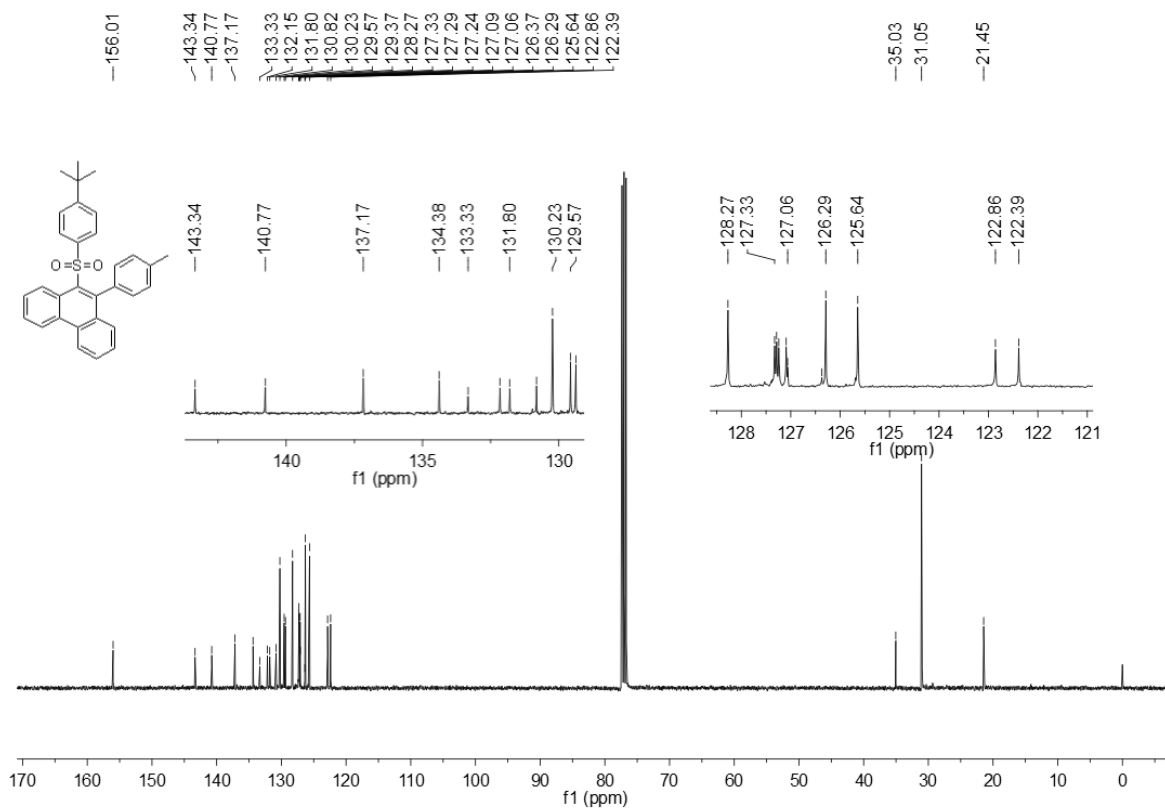
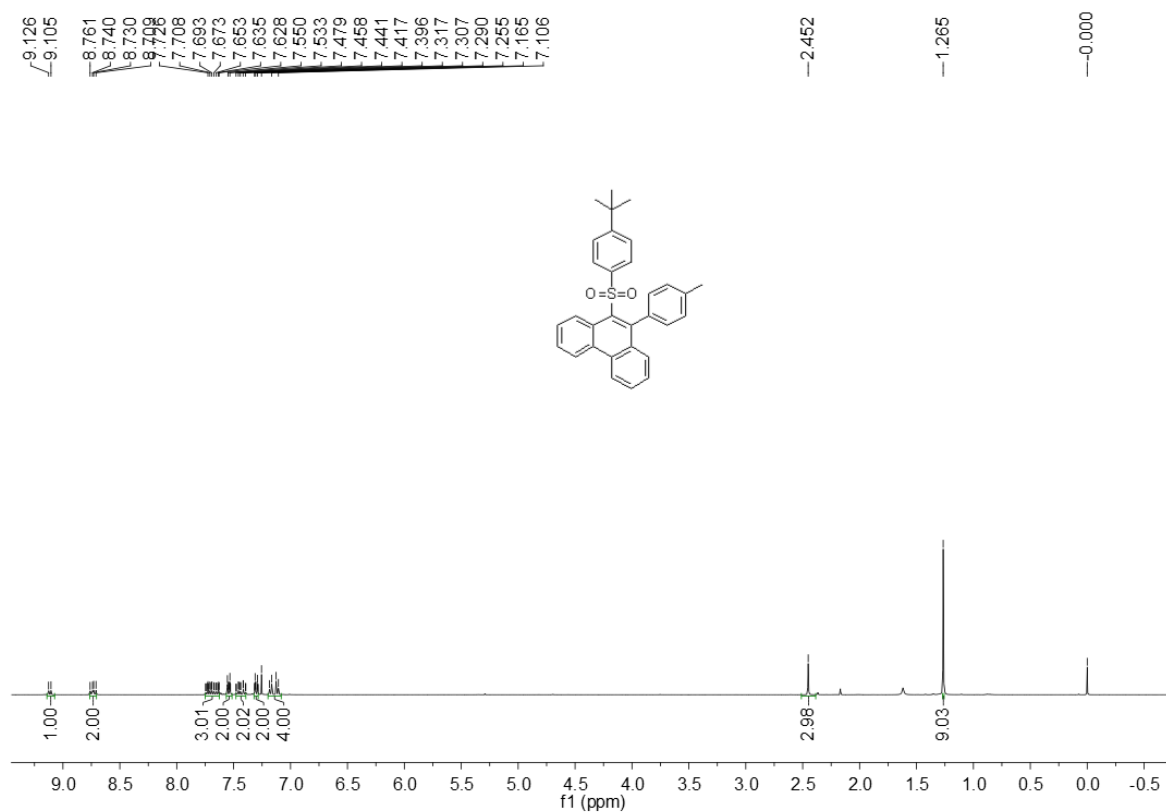


¹³C NMR Spectrum of Compound 6l

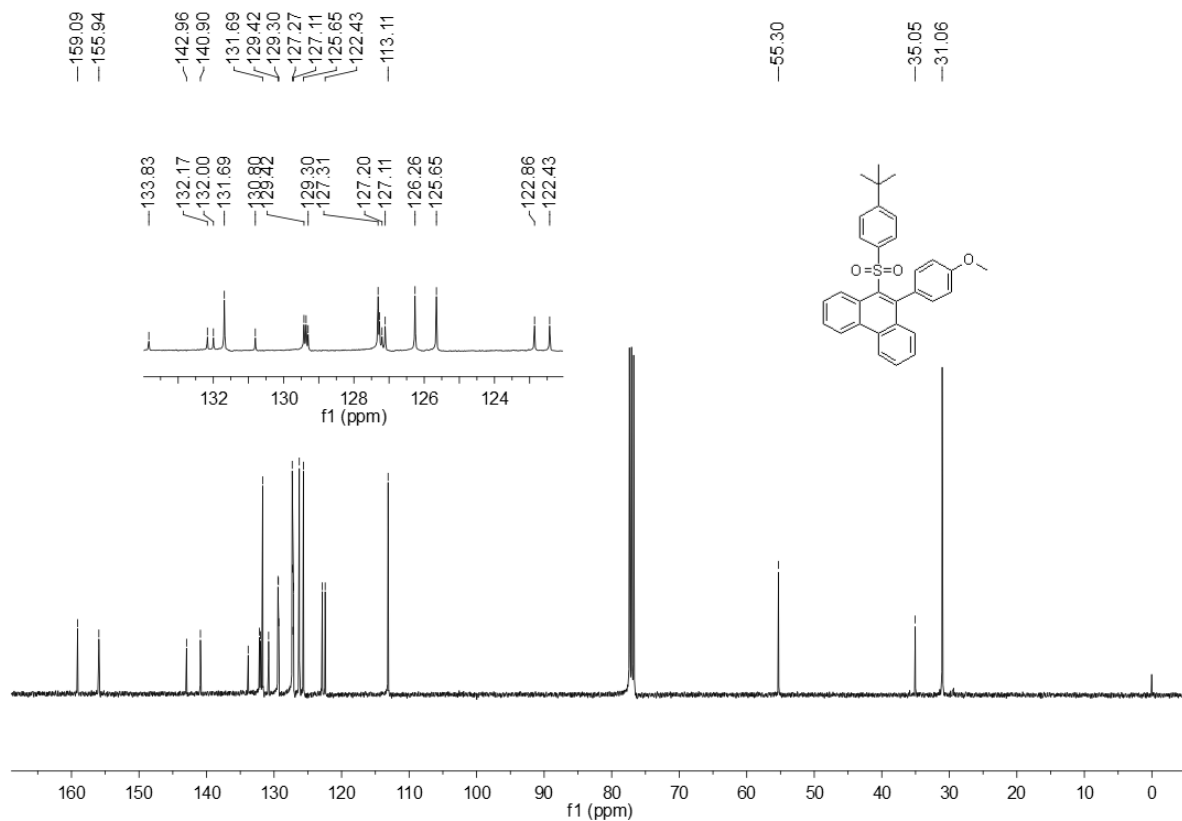
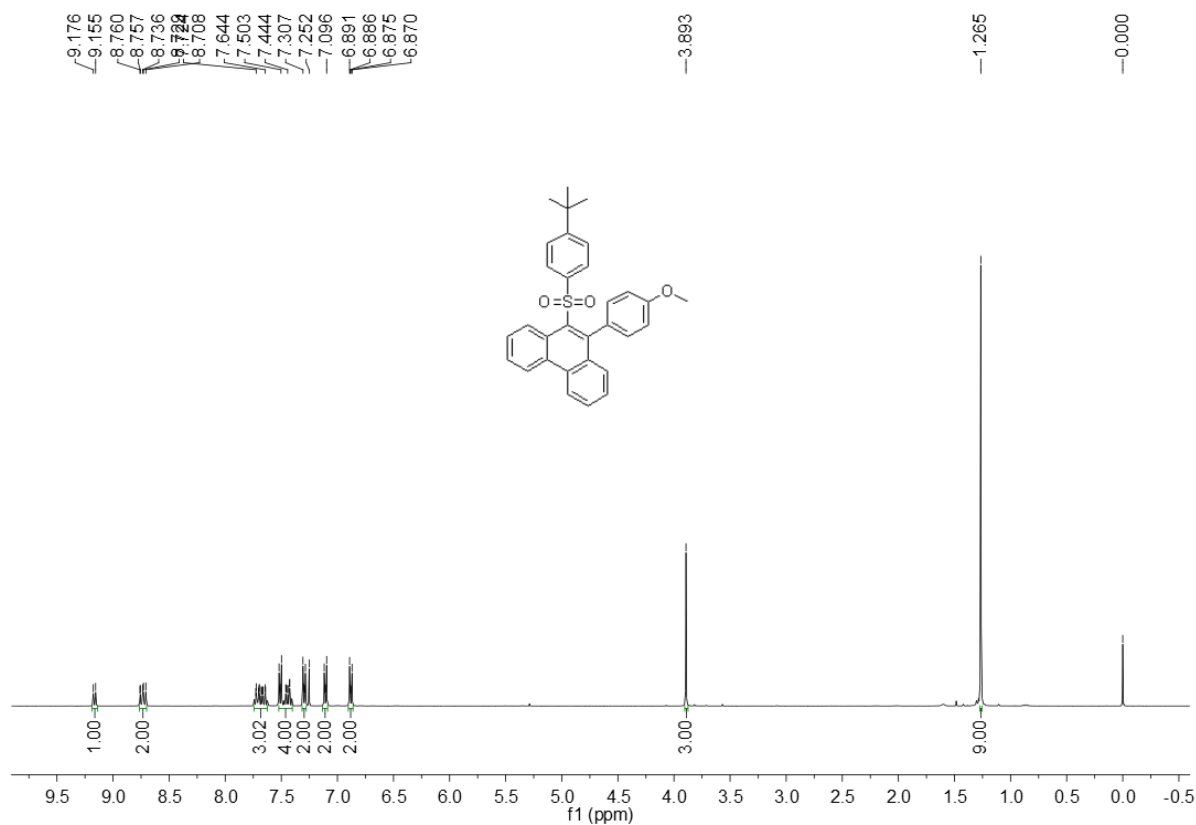


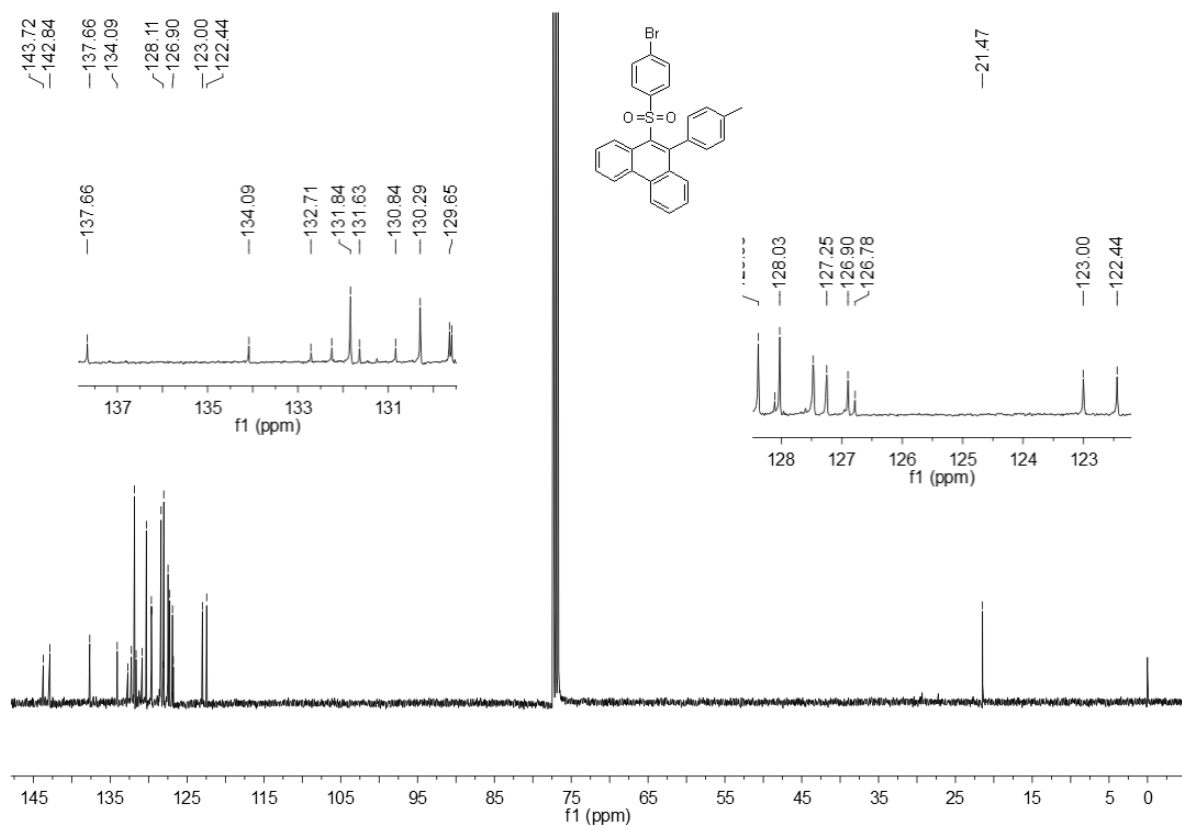
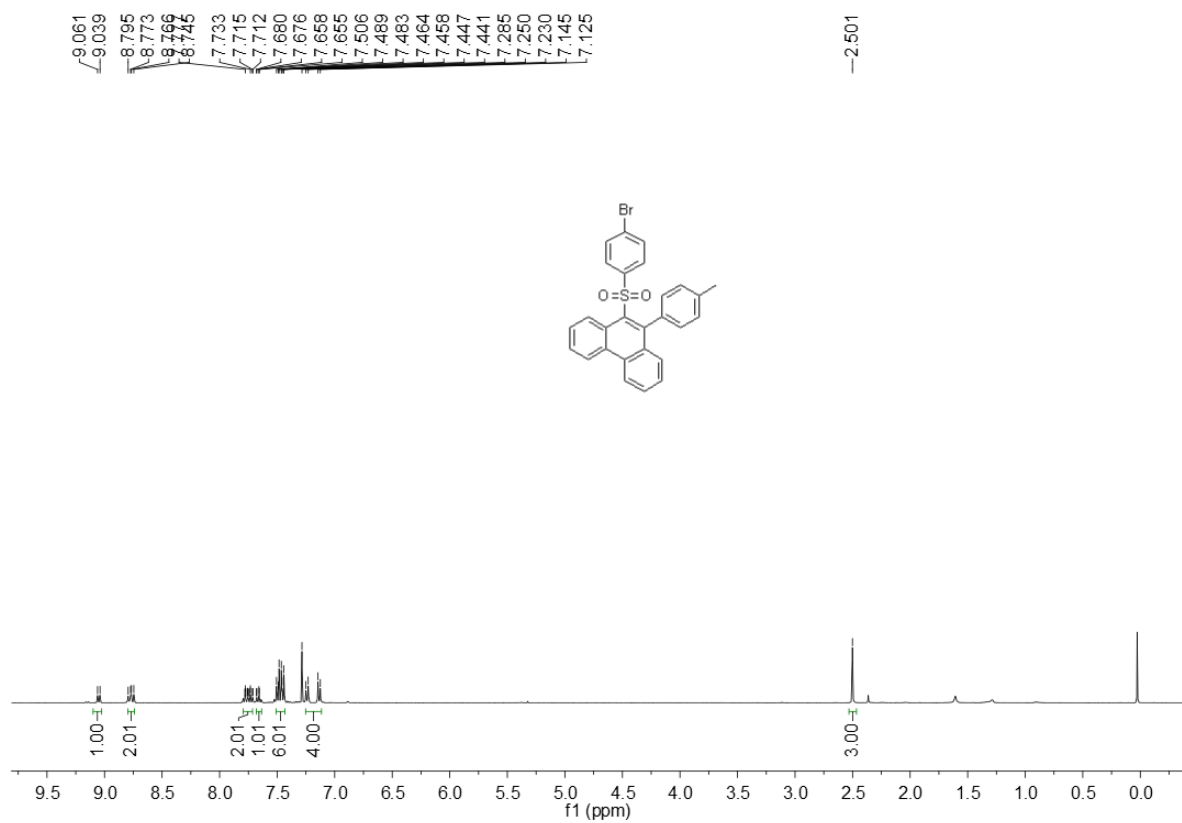


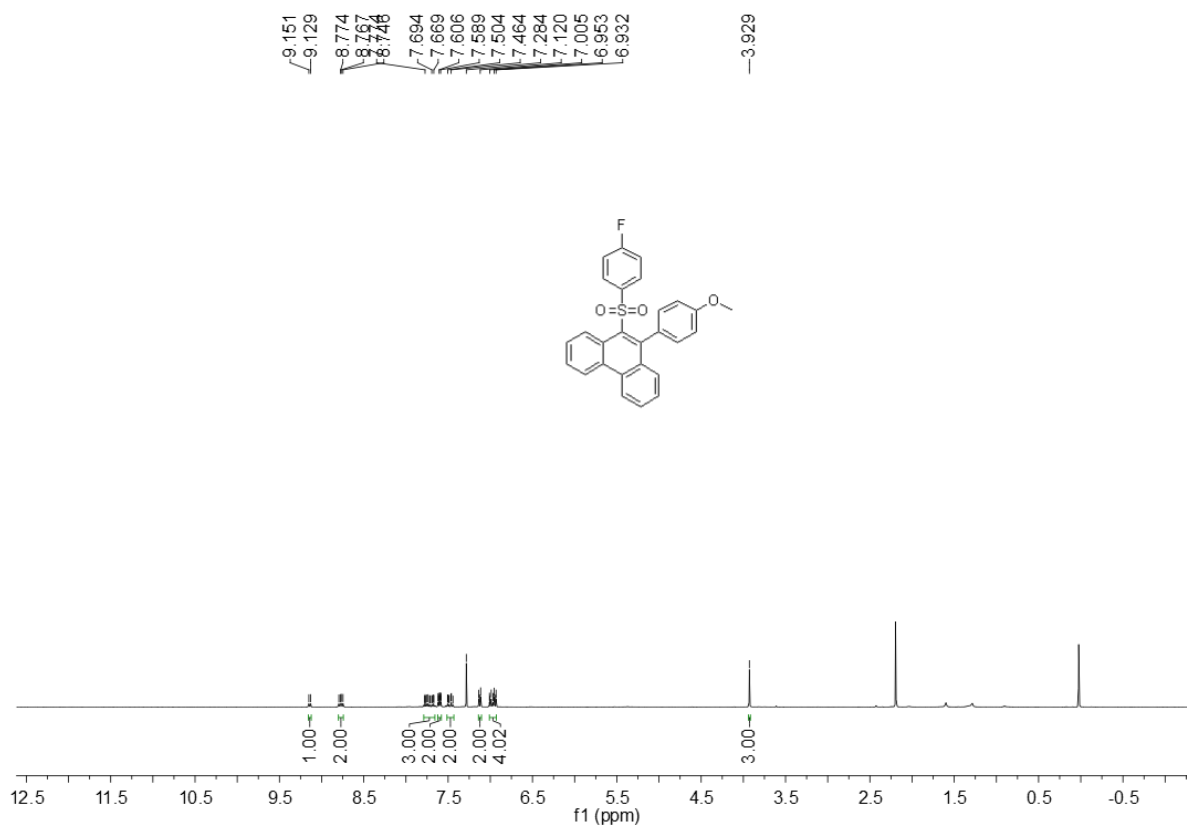




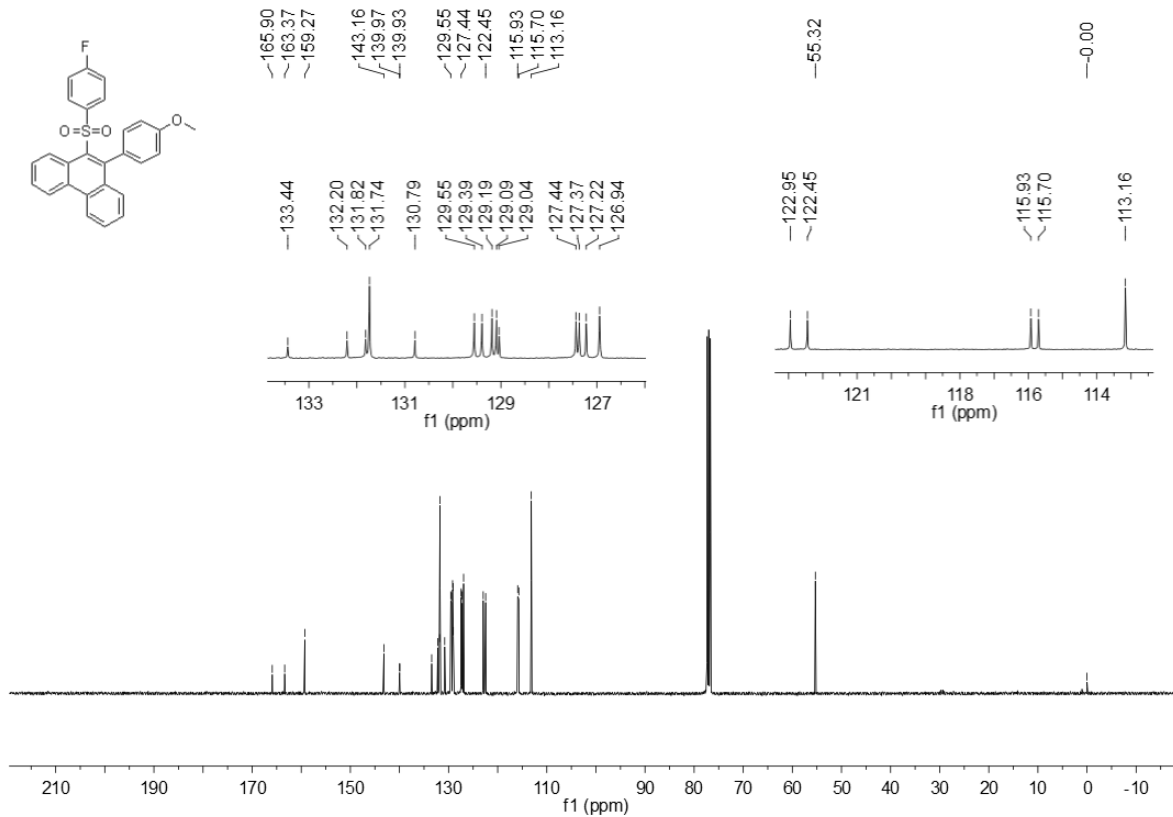
¹³C NMR Spectrum of Compound 6p







¹H NMR Spectrum of Compound 6s



¹³C NMR Spectrum of Compound 6s