Supporting Information for

Photo-induced tandem cyclization of alkynes with sodium sulfinates to access sulfonated exocyclic alkenes

Jiefang Xu[a^], Haoqun Fan[b^], Feng Cao[a], Xiaohu Yang*[b], Chuanyan Huang*[c]

[a] Department of Critical Care Medicine, Zhejiang Hospital, Hangzhou, Zhejiang, 310013, P. R. China.
[b] Department of Pharmacy, Zhejiang Hospital, Hangzhou, Zhejiang, 310013, P. R. China. E-mail: yxh_zjyy@163.com
[c] Department of Thoracic Surgery, Zhejiang Hospital, Hangzhou, Zhejiang, 310013, P. R. China. E-mail: nishengliang@163.com

Table of Contents for Supporting Information

1. General considerations

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Flash column chromatography was performed over silica gel (200-300 mesh). All reactions were carried out under nitrogen atmosphere. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker Avance NMR spectrometer (600 MHz/150 MHz) in $CDCl_3$ as solvent and recorded in ppm relative to internal tetramethylsilane standard. ^{1}H NMR data are reported as follows: δ, chemical shift; coupling constants (J are given in Hertz, Hz) and integration. The high-resolution mass spectra (HRMS) were recorded on a Thermo Fisher Scientific Exactive mass spectrometer using ESI as the ionization method (Analyzer: Orbitrap). Abbreviations to denote the multiplicity of a signal were s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets) and m (multiplet). The X-ray crystal structure was measured on the Agilent Gemini E diffractometer instrument.

Photochemical experiments were performed magnetically stirred in 15 mL glass tubes, sealed with a rubber septum. The tubes were irradiated with blue light (465-480 nm, Cree production) using a LED lamp with a power output of 15 W. This blue LED was purchased from taobao (link: https://shop35740806.taobao.com/?spm=pc_detail.30350276.shop_block.dshopinfo.8d443484yQms3z). The LED's energy peak wavelength is 473.7 nm, the peak width at half-height is 24.5 nm. The distance from the light source to the irradiation vessel is approximately 4 cm.

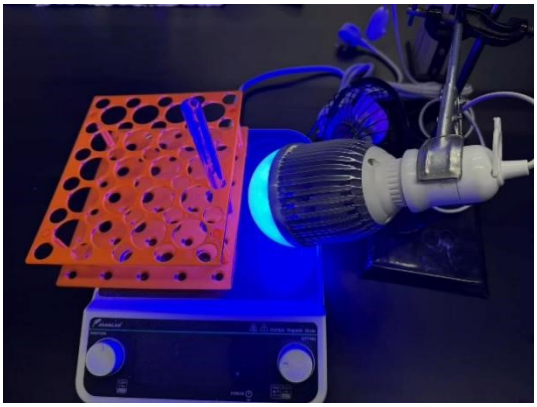


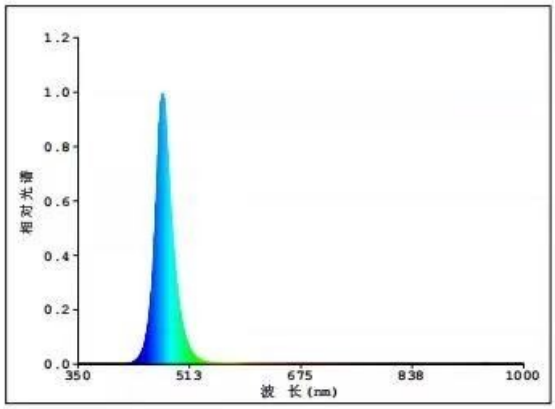
Figure S1. LED reaction setup for photocatalytic reactions

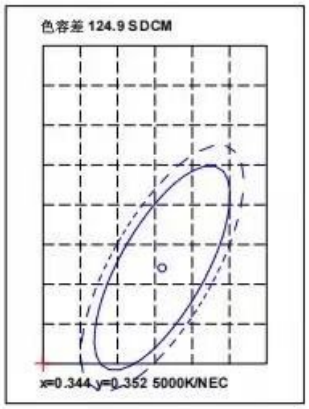
EVERFINE 远方

Test report

远方 (EVERFINE) LEDspec光色电测试报告

光 源 光 谱 测 试 报 告





颜色参数：

色品坐标:x=0.1161 y=0.1168/u'=0.1114 v'=0.2521 duv=1.199e-001
相关色温:Tc=100000K 主波长:λd=477.0nm 色纯度: Purity=94.2%
色比:R=0.4% G=29.1% B=70.5% 峰值波长:λp=473.7nm 半宽度:Δλd=24.5nm
显色指数:Ra=-36.0

R1 =-14	R2 =-27	R3 =-98	R4 =-64	R5 =6	R6 =-39	R7 =-27	
R8 =-24	R9 =-279	R10=-187	R11=-91	R12=-70	R13=-30	R14=-14	R15=-2

光度参数：

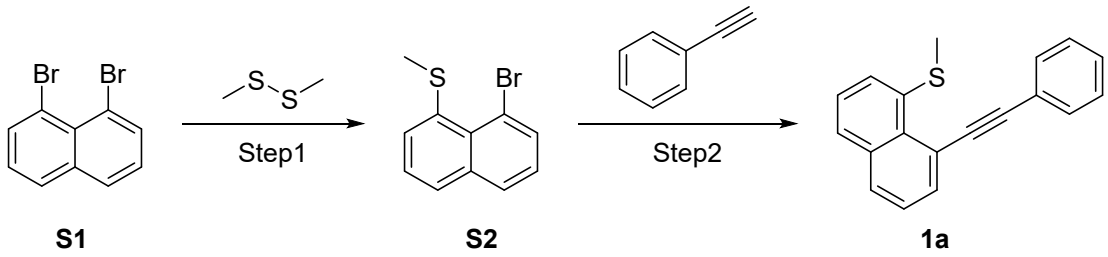
光通量 Φ = 239.4 lm 光效 : 27.67 lm/W Φe = 2296 mW

电参数：

正向电压 VF = 9.612 V 正向电流 IF = 899.9 mA 功率 P = 8651 mW
反向电流 IR = 0 uA (反向电压 VR=7.998V)
分级:*0* 白光分类:OUT

仪器状态: 积分时间 T=0.32ms Ip=53935 (82%) [HAAS1200_V1_USB] V2.00.224

2. General procedure for the synthesis of 1a

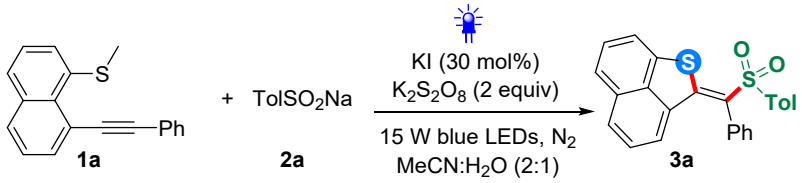


Step 1: A 50 mL double-necked flask containing 1,8-dibromonaphthalene (10.0 mmol) was evacuated and purged with nitrogen. Then, anhydrous THF (15 mL) was added and the mixture was cooled to -78 °C. *n*-BuLi (4.4 mL) was then added dropwise and the reaction was carried out at -78 °C for 30 minutes, followed by 30 minutes at room temperature. Subsequently, dimethyl disulfide (5.0 mmol) was added to the system and the reaction was conducted at -78 °C for 20 minutes, then at room temperature for 2 hours. The reaction was quenched with saturated NH_4Cl aqueous solution (20 mL) and extracted with ethyl acetate (20 mL ×3). The combined organic layers were dried over anhydrous Na_2SO_4. The solvent was then removed under reduced pressure and the residue was used in the next step.

Step 2: To a solution of **S2** (10.0 mmol) and phenylacetylene (12.0 mmol, 1.2 equiv) in DMF (5 mL), $PdCl_2(PPh_3)_2$ (2 mol%), CuI (2 mol%) and Et_3N (20 mL) were added. The reaction mixture was stirred vigorous at 50 °C for 12 h under an N_2 atmosphere. After completion, the mixture was diluted

with water (50 mL), and then extracted with ethyl acetate (3*50 mL), and the combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate (100:1, V/V) as the eluent to afford the corresponding product **1a**.

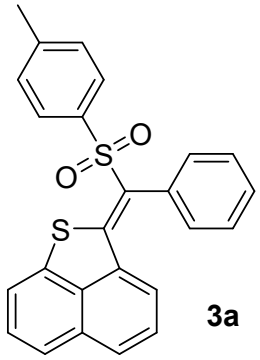
3. General procedure for the synthesis of 3a



General Procedure: To an oven-dried 20 mL Schlenk tube charged with alkyne **1** (0.2 mmol), sodium sulfinate (**2**, 0.4 mmol), $K_2S_2O_8$ (0.4 mmol) and KI (30 mol%). The tube was degassed by alternating vacuum evacuation (3 min) and nitrogen backfill for three times. Then, MeCN:H_2O (2:1, 2 mL) was injected into the tube. The resulting mixture was stirred at room temperature with the irradiation of 15 W blue LED for 10 hours. After completion of reaction as monitored by TLC analysis, the reaction was quenched with saturated NH_4Cl aqueous solution and extracted with EA. The residue was subjected to flash column chromatography on silica gel using petroleum ether as the eluent to afford product **3a**.

4. Characterization data of products

(*Z*)-2-(phenyl(tosyl)methylene)-2*H*-naphtho[1,8-*bc*]thiophene (**3a**)

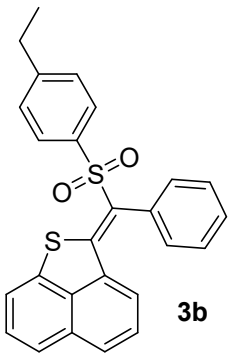


3a

The product purified by flash column chromatography on silica gel (PE) to afford the **3a** as a yellow solid (69 mg, 82% yield, mp 106−109 °C). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.62 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.49 – 7.45 (m, 1H), 7.40 (d, *J* = 4.7 Hz, 3H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 7.03 (t, *J* = 7.9 Hz, 1H), 6.99 (d, *J* = 7.3 Hz, 2H), 6.16 (d, *J* = 7.7 Hz, 1H), 2.30 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 148.4, 143.4, 137.1, 136.0, 135.7, 132.7, 132.7, 130.6, 130.3, 129.2, 128.9, 128.45, 128.3, 128.0, 127.2, 127.1, 126.4, 125.0, 121.9, 117.2, 20.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{19}O_2S_2$ 415.0826, found 415.0820.

(*Z*)-2-(((4-ethylphenyl)sulfonyl)(phenyl)methylene)-2*H*-naphtho[1,8-*bc*]thiophene (**3b**)

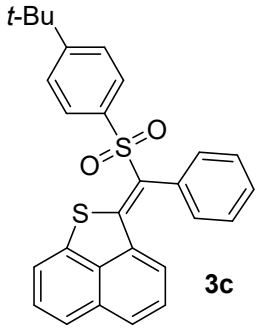


3b

The product purified by flash column chromatography on silica gel (PE) to afford the **3b** as a yellow solid (73 mg, 85% yield, mp 127−131 °C). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.70 (dd, *J* = 8.2, 1.8 Hz, 3H), 7.55 (p, *J* = 3.4 Hz, 1H), 7.52 – 7.47 (m, 3H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.12 (t, *J* = 7.9 Hz, 1H), 7.08 (d, *J* = 7.2 Hz, 2H), 6.24 (d, *J* = 7.7 Hz, 1H), 2.68 (q, *J* = 7.6 Hz, 2H), 1.22 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 150.6, 149.4, 138.1, 137.1, 136.6, 133.8, 133.7, 131.6, 131.3, 130.2, 130.0, 129.5, 129.1, 128.3, 128.2, 128.1, 127.5, 126.0, 122.9, 118.3, 28.9, 15.2.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{21}O_2S_2$ 429.0983, found 429.0979.

(*Z*)-2-(((4-(tert-butyl)phenyl)sulfonyl)(phenyl)methylene)-2*H*-naphtho[1,8-*bc*]thiophene (3c)

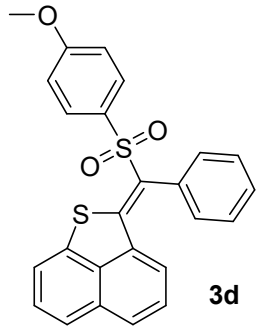


3c

The product purified by flash column chromatography on silica gel (PE) to afford the **3c** as a yellow solid (73 mg, 80% yield, mp 117−120 °C). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.74 – 7.71 (m, 2H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.55 (q, *J* = 4.2, 3.8 Hz, 1H), 7.50 (q, *J* = 5.9, 4.4 Hz, 3H), 7.47 – 7.41 (m, 4H), 7.12 (d, *J* = 7.9 Hz, 1H), 7.09 (t, *J* = 6.0 Hz, 2H), 6.25 (d, *J* = 7.6 Hz, 1H), 1.30 (d, *J* = 1.5 Hz, 9H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 157.5, 149.5, 138.1, 136.9, 136.6, 133.8, 133.8, 131.6, 131.2, 130.3, 123.0, 129.5, 129.0, 128.1, 128.0, 127.5, 126.0, 125.7, 122.9, 118.3, 35.2, 31.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{25}O_2S_2$ 457.1296, found 457.1296.

(*Z*)-2-(((4-methoxyphenyl)sulfonyl)(phenyl)methylene)-2*H*-naphtho[1,8-*bc*]thiophene (3d)

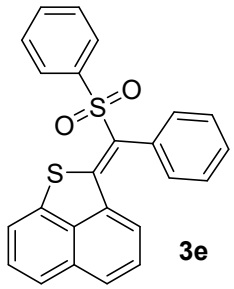


3d

The product purified by flash column chromatography on silica gel (PE) to afford the **3d** as a yellow solid (60 mg, 70% yield, mp 134−136 °C). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.70 (d, *J* = 8.1 Hz, 3H), 7.57 – 7.54 (m, 1H), 7.49 (d, *J* = 5.4 Hz, 3H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.12 (t, *J* = 7.9 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 6.24 (d, *J* = 7.7 Hz, 1H), 3.83 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 163.7, 148.8, 138.2, 136.7, 133.8, 131.7, 131.6, 131.3, 130.6, 130.3, 129.9, 129.5, 128.9, 128.1, 127.5, 125.9, 122.8, 118.2, 113.9, 55.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{19}O_3S_2$ 431.0776, found 431.0767.

(*Z*)-2-(phenyl(phenylsulfonyl)methylene)-2*H*-naphtho[1,8-*bc*]thiophene (3e)

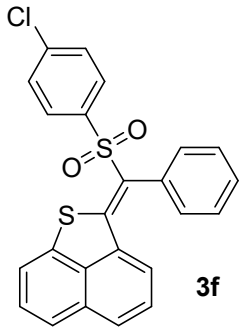


3e

The product purified by flash column chromatography on silica gel (PE) to afford the **3e** as a yellow solid (62mg, 77% yield, mp 132−136 °C). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.79 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.57 (dd, *J* = 11.8, 6.6 Hz, 2H), 7.50 (dd, *J* = 11.0, 5.4 Hz, 3H), 7.43 (dd, *J* = 15.9, 7.9 Hz, 4H), 7.13 (t, *J* = 7.9 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 2H), 6.26 (d, *J* = 7.7 Hz, 1H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 149.92 (s), 139.88 (s), 138.06 (s), 136.60 (s), 133.75 (s), 133.58 (s), 133.43 (s), 131.63 (s), 131.32 (s), 129.96 (s), 129.56 (s), 129.13 (s), 128.70 (s), 128.70 (s), 128.15 (s), 128.12 (s), 127.46 (s), 126.11 (s), 122.95 (s), 118.35 (s).

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{17}O_2S_2$ 401.0670, found 401.0665.

(*Z*)-2-(((4-chlorophenyl)sulfonyl)(phenyl)methylene)-2*H*-naphtho[1,8-*bc*]thiophene (3f)

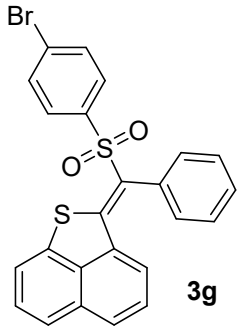


3f

The product purified by flash column chromatography on silica gel (PE) to afford the **3f** as a yellow solid (50 mg, 58% yield, mp 124−126 °C). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.64 (dd, *J* = 14.2, 8.3 Hz, 3H), 7.53 – 7.48 (m, 1H), 7.43 (d, *J* = 4.6 Hz, 3H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.06 (t, *J* = 7.9 Hz, 1H), 7.01 (d, *J* = 7.3 Hz, 2H), 6.20 (d, *J* = 7.7 Hz, 1H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 150.5, 140.1, 138.4, 137., 136.4, 133.7, 133.3, 131.6, 131.3, 130.1, 129.7, 129.5, 129.3, 129.1, 129.0, 128.1, 127.5, 126.2, 123.1, 118.5.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{16}ClO_2S_2$ 435.0280, found 435.0277.

(*Z*)-2-(((4-bromophenyl)sulfonyl)(phenyl)methylene)-2*H*-naphtho[1,8-*bc*]thiophene (3g)

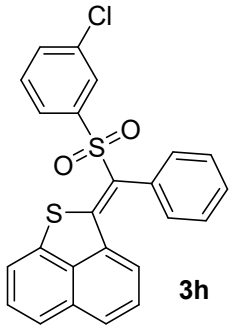


3g

The product purified by flash column chromatography on silica gel (PE) to afford the **3g** as a yellow solid (73mg, 76% yield, mp 158−160 °C). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.65 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.53 – 7.47 (m, 3H), 7.44 (t, *J* = 7.8 Hz, 3H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.06 (t, *J* = 7.8 Hz, 1H), 7.01 (d, *J* = 7.3 Hz, 2H), 6.20 (d, *J* = 7.7 Hz, 1H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 149.6, 137.9, 136.7, 135.4, 132.6, 132.3, 131.3, 130.9, 130.5, 130.3, 129.0, 128.7, 128.5, 128.3, 128.1, 127.6, 127.3, 126.4, 126.0, 125.2, 122.0, 117.4.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{16}BrO_2S_2$ 478.9775, found 478.9767.

(*Z*)-2-(((3-chlorophenyl)sulfonyl)(phenyl)methylene)-2*H*-naphtho[1,8-*bc*]thiophene (3h)

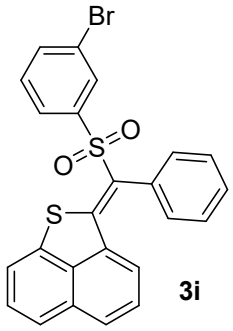


3h

The product purified by flash column chromatography on silica gel (PE) to afford the **3h** as a yellow solid (66mg, 76% yield, mp 137−139 °C). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.79 – 7.72 (m, 2H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.59 (dd, *J* = 6.4, 2.7 Hz, 1H), 7.52 (q, *J* = 4.2, 2.9 Hz, 4H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 2H), 6.30 (d, *J* = 7.6 Hz, 1H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 151.0, 141.5, 137.7, 136.4, 135.0, 133.7, 133.5, 133.2, 131.6, 131.4, 130.1, 123.0, 129.8, 129.5, 128.8, 128.2, 128.1, 127.5, 126.3, 126.2, 123.2, 118.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{16}ClO_2S_2$ 435.0280, found 435.0276.

(*Z*)-2-(((3-bromophenyl)sulfonyl)(phenyl)methylene)-2*H*-naphtho[1,8-*bc*]thiophene (3i)

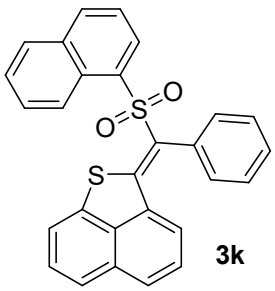


3i

The product purified by flash column chromatography on silica gel (PE) to afford the **3i** as a yellow solid (71mg, 74% yield, mp 132−134 °C). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.90 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 2H), 7.59 (dd, *J* = 6.2, 2.2 Hz, 1H), 7.52 (dd, *J* = 8.8, 6.1 Hz, 3H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.28 (dd, *J* = 18.3, 10.3 Hz, 1H), 7.15 (t, *J* = 7.9 Hz, 1H), 7.09 (d, *J* = 7.3 Hz, 2H), 6.30 (d, *J* = 7.7 Hz, 1H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 150.9, 141.6, 137.7, 136.4, 133.7, 133.2, 131.6, 131.4, 131.2, 130.9, 130.1, 130.1, 129.8, 129.4, 128.8, 128.1, 127.5, 126.6, 126.3, 123., 122.7, 118.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{16}BrO_2S_2$ 478.9775, found 478.9769.

(*Z*)-2-((naphthalen-1-ylsulfonyl)(phenyl)methylene)-2*H*-naphtho[1,8-*bc*]thiophene (3k)

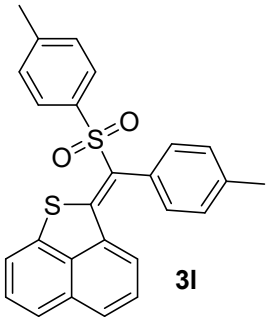


3k

The product purified by flash column chromatography on silica gel (PE) to afford the **3k** as a yellow solid (58mg, 64% yield, mp 148−151 °C). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 8.22 (s, 1H), 7.79 (d, *J* = 8.6 Hz, 3H), 7.72 (dd, *J* = 8.7, 1.4 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.51 – 7.38 (m, 5H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.04 (t, *J* = 7.9 Hz, 1H), 6.98 (d, *J* = 7.3 Hz, 2H), 6.18 (d, *J* = 7.7 Hz, 1H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 150.1, 138.1, 136.8, 136.6, 135.3, 133.8, 133.6, 132.0, 131.6, 131.3, 123.0, 129.8, 129.6, 129.5, 129.2, 129.0, 128.9, 128.1, 127.9, 127.5, 127.4, 126.1, 123.1, 123.0, 118.4.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{19}O_2S_2$ 451.0826, found 451.0825.

(*Z*)-2-(*p*-tolyl(tosyl)methylene)-2*H*-naphtho[1,8-*bc]*thiophene (3l)

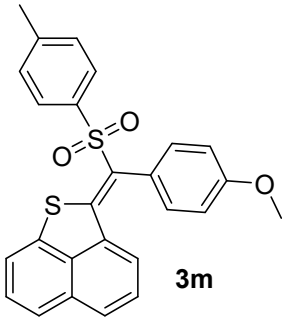


3l

The product purified by flash column chromatography on silica gel (PE) to afford the **3l** as a yellow solid (66mg, 77% yield, mp 145−148 °C). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.71 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 2H), 7.56 (s, 1H), 7.49 (d, *J* = 4.6 Hz, 2H), 7.25 (d, *J* = 7.2 Hz, 3H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 8.2 Hz, 1H), 6.95 (d, *J* = 7.5 Hz, 2H), 6.33 (d, *J* = 7.7 Hz, 1H), 2.45 (s, 3H), 2.40 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 149.3, 144.3, 139.5, 138.2, 137.1, 136.8, 133.8, 131.6, 131.0, 130.7, 130.6, 129.3, 128.9, 128.2, 128.1, 127.5, 126.0, 122.8, 118.2, 21.6, 21.5.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{21}O_2S_2$ 429.0983, found 429.0983.

(*Z*)-2-((4-methoxyphenyl)(tosyl)methylene)-2*H*-naphtho[1,8-*bc*]thiophene (3m)

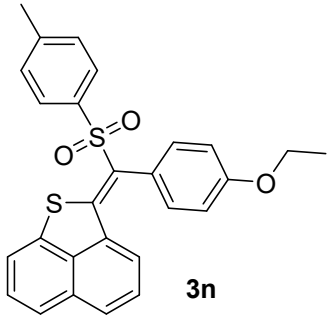


3m

The product purified by flash column chromatography on silica gel (PE) to afford the **3m** as a yellow solid (67mg, 75% yield, mp 117−119 °C). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.62 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 6.5 Hz, 1H), 7.40 (d, *J* = 6.2 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.08 (t, *J* = 7.8 Hz, 1H), 6.89 (s, 4H), 6.30 (d, *J* = 7.7 Hz, 1H), 3.80 (s, 3H), 2.31 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 160.5, 149.5, 144.3, 138.3, 137.1, 136.8, 133.8, 132.6, 131.6, 123.0, 129.4, 128.9, 128.1, 128.1, 127.5, 126.0, 125.5, 122.8, 118.2, 115.4, 55.4, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{21}O_3S_2$ 445.0932, found 445.0924.

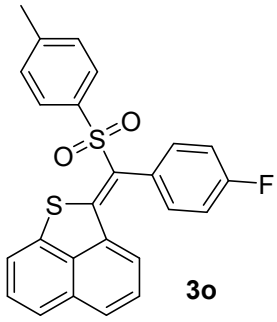
(*Z*)-2-((4-methoxyphenyl)(tosyl)methylene)-2*H*-naphtho[1,8-*bc*]thiophene(3n)



3n

The product purified by flash column chromatography on silica gel (PE) to afford the **3n** as a yellow solid (66mg, 72% yield, mp 154−156 °C). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.57 (dd, *J* = 15.3, 8.1 Hz, 3H), 7.43 (dd, *J* = 6.3, 2.1 Hz, 1H), 7.36 (d, *J* = 6.1 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.05 (t, *J* = 7.9 Hz, 1H), 6.86 (s, 4H), 6.29 (d, *J* = 7.7 Hz, 1H), 4.00 (q, *J* = 6.9 Hz, 2H), 2.28 (s, 3H), 1.37 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 160.0, 149.4, 144.30, 138.2, 137.1, 136.8, 133.8, 132.6, 131.6, 129.4, 128.9, 128.2, 128.1, 127.5, 126.0, 125.3, 122.8, 118.1, 115.9, 114.8, 63.6, 21.6, 14.8. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{23}O_3S_2$ 459.1089, found 459.1086.

(*Z*)-2-((4-fluorophenyl)(tosyl)methylene)-2*H*-naphtho[1,8-*bc*]thiophene (3o)

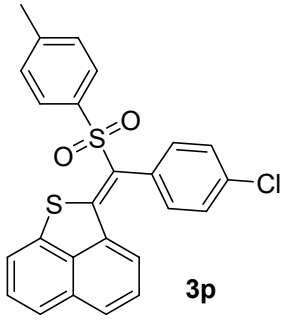


3o

The product purified by flash column chromatography on silica gel (PE) to afford the **3o** as a yellow solid (61mg, 71% yield, mp 111−113 °C). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.73 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 6.8 Hz, 1H), 7.50 (d, *J* = 4.9 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.16 (dt, *J* = 14.1, 8.2 Hz, 3H), 7.09 – 7.02 (m, 2H), 6.32 (d, *J* = 7.7 Hz, 1H), 2.39 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 163.50 (d, *J* = 250.4 Hz), 150.0, 144.6, 138.0, 136.9, 136.5, 133.7, 133.43 (d, *J* = 8.3 Hz), 131.7, 129.6, 129.5, 129.3, 129.0, 128.2, 128.1, 127.45, 125.9, 123.0, 118.4, 117.20 (d, *J* = 21.6 Hz), 21.7. ^{19}F NMR (565 MHz, $CDCl_3$) δ -105.43 (s).

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{18}FO_2S_2$ 433.0732, found 433.0727.

(*Z*)-2-((4-chlorophenyl)(tosyl)methylene)-2*H*-naphtho[1,8-*bc*]thiophene (3p)

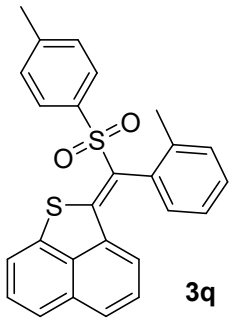


3p

The product purified by flash column chromatography on silica gel (PE) to afford the **3p** as a yellow solid (57mg, 63% yield, mp 99−101 °C). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.74 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.58 (dt, *J* = 5.8, 3.6 Hz, 1H), 7.51 – 7.48 (m, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.20 – 7.17 (m, 1H), 7.03 (d, *J* = 8.2 Hz, 2H), 6.37 (d, *J* = 7.7 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 150.1, 144.6, 137.9, 136.9, 136.4, 135.8, 133.7, 132.9, 132.6, 132.2, 131.7, 130.3, 129.5, 129.3, 128.2, 128.1, 127.5, 125.9, 123.1, 118.5, 21.7.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{18}ClO_2S_2$ 449.0437, found 449.0436.

(*Z*)-2-(o-tolyl(tosyl)methylene)-2*H*-naphtho[1,8-*bc*]thiophene (3q)

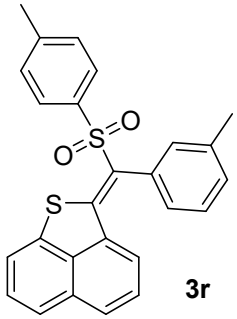


3q

The product purified by flash column chromatography on silica gel (PE) to afford the **3q** as a yellow solid (64mg, 75% yield, mp 121−123 °C). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.58 (t, *J* = 7.8 Hz, 3H), 7.44 (q, *J* = 3.8 Hz, 1H), 7.37 (d, *J* = 4.9 Hz, 2H), 7.21 (q, *J* = 7.7 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.03 (t, *J* = 7.9 Hz, 1H), 6.83 (s, 1H), 6.70 (d, *J* = 6.7 Hz, 1H), 6.19 (d, *J* = 7.7 Hz, 1H), 2.29 (s, 3H), 2.23 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 149.1, 144.4, 139.8, 138.1, 137.1, 136.7, 133.8, 133.6, 131.8, 131.6, 130.4, 130.3, 129.8, 129.3, 129.0, 128.3, 128.1, 127.5, 126.1, 122.9, 118.2, 21.6, 21.4.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{21}O_2S_2$ 429.0983, found 429.0976.

(*Z*)-2-(m-tolyl(tosyl)methylene)-2*H*-naphtho[1,8-*bc*]thiophene (3r)

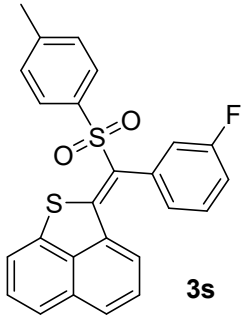


3r

The product purified by flash column chromatography on silica gel (PE) to afford the **3r** as a yellow solid (69mg, 80% yield, mp 113−115 °C). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.60 (dd, *J* = 15.6, 8.0 Hz, 3H), 7.49 – 7.45 (m, 1H), 7.40 (d, *J* = 3.5 Hz, 2H), 7.22 (d, *J* = 7.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.05 (t, *J* = 7.9 Hz, 1H), 6.85 (s, 1H), 6.71 (d, *J* = 6.5 Hz, 1H), 6.20 (d, *J* = 7.7 Hz, 1H), 2.31 (s, 3H), 2.24 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 148.1, 143.3, 138.7, 137.1, 136.0, 135.7, 132.7, 132.5, 130.7, 130.6, 129.2, 128.7, 128.2, 127.9, 127.2, 127.1, 127.0, 126.4, 125.1, 121.8, 117.2, 20.6, 20.4.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{21}O_2S_2$ 429.0983, found 429.0978.

(*Z*)-2-((3-fluorophenyl)(tosyl)methylene)-2*H*-naphtho[1,8-*bc*]thiophene (3s)



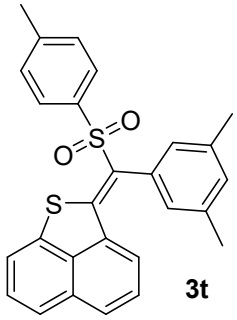
3s

The product purified by flash column chromatography on silica gel (PE) to afford the **3s** as a yellow solid (62mg, 75% yield, mp 150−152 °C). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.74 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.60 – 7.56 (m, 1H), 7.52 – 7.49 (m, 2H), 7.46 – 7.41 (m, 1H), 7.26 – 7.20 (m, 3H), 7.17 (t, *J* = 7.9 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.86 – 6.80 (m, 1H), 6.32 (d, *J* = 7.7 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 164.4, 162.8, 150.2, 144.7, 137.9, 136.8, 136.3, 135.8, 135.7, 133.7, 131.7, 131.6, 131.5, 129.5, 129.4, 128.2, 128.1, 127.5,

127.2, 127.2, 126.0, 125.4, 123.1, 118.5, 118.5, 118.3, 116.7, 116.6, 21.7. ^{19}F NMR (565 MHz, $CDCl_3$) δ -104.61 (s).

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{18}FO_2S_2$ 433.0732, found 433.0729.

(*Z*)-2-((3,5-dimethylphenyl)(tosyl)methylene)-2*H*-naphtho[1,8-*bc*]thiophene (3t)

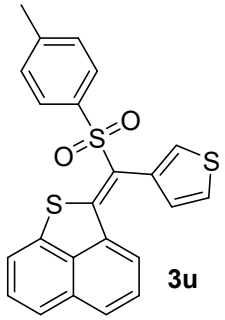


3t

The product purified by flash column chromatography on silica gel (PE) to afford the **3t** as a yellow solid (75 mg, 85% yield, mp 165−167 °C). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.72 – 7.66 (m, 3H), 7.55 (dd, *J* = 6.1, 2.6 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 7.9 Hz, 1H), 7.11 (s, 1H), 6.65 (s, 2H), 6.34 (d, *J* = 7.7 Hz, 1H), 2.40 (s, 3H), 2.27 (s, 6H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 148.9, 144.3, 139.5, 138.2, 137.1, 136.8, 133.8, 133.4, 131.6, 131.1, 130.7, 129.2, 128.9, 128.6, 128.4, 128.0, 127.5, 126.2, 122.8, 118.1, 21.6, 21.3.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{23}O_2S_2$ 443.1139, found 443.1133.

(*Z*)-2-(thiophen-3-yl(tosyl)methylene)-2*H*-naphtho[1,8-*bc*]thiophene (3u)



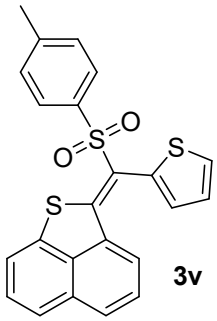
3u

The product purified by flash column chromatography on silica gel (PE) to afford the **3u** as a yellow solid (57mg, 68% yield, mp 188−190 °C). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.74 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 2H), 7.57 (d, *J* = 6.7 Hz, 1H), 7.49 (d, *J* = 4.9 Hz, 2H), 7.45 (s, 1H), 7.22 (t, *J* = 7.6 Hz, 3H), 7.11 (s, 1H), 6.74 (d, *J* = 4.8

Hz, 1H), 6.44 (d, *J* = 7.7 Hz, 1H), 2.39 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 150.0, 144.4, 138.1, 137.0, 136.6, 133.7, 132.9, 131.6, 129.4, 129.2, 129.0, 128.1, 128.0, 127.6, 127.5, 127.4, 125.7, 124.9, 123.0, 118.3, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{17}O_2S_3$ 421.0391, found 421.0387.

(*Z*)-2-(thiophen-2-yl(tosyl)methylene)-2*H*-naphtho[1,8-*bc*]thiophene (3v)



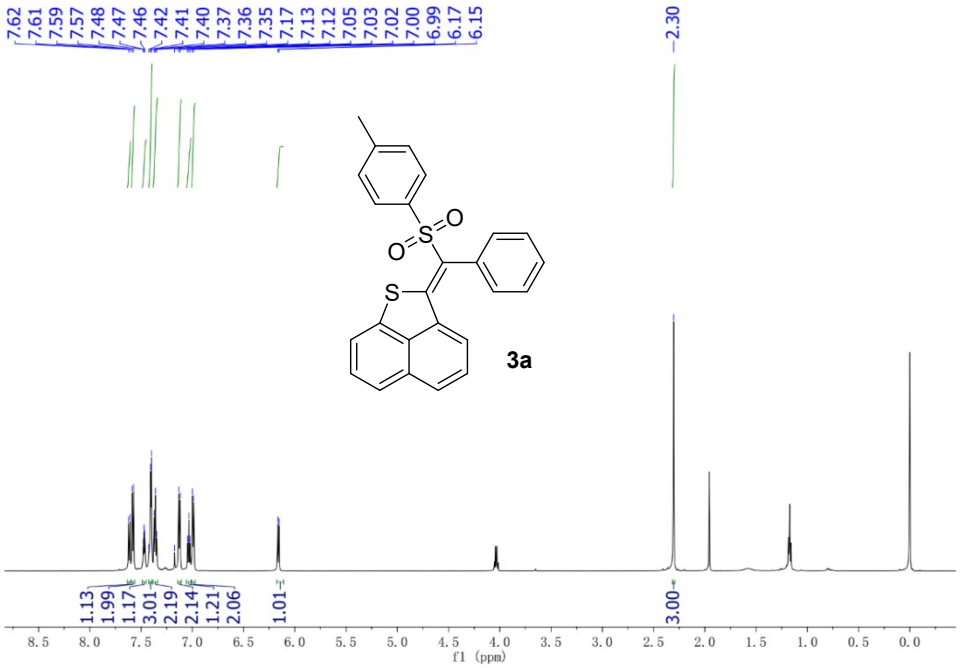
3v

The product purified by flash column chromatography on silica gel (PE) to afford the **3v** as a yellow solid (55mg, 65% yield, mp 173−175 °C). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.70 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.54 – 7.50 (m, 1H), 7.47 (d, *J* = 5.2 Hz, 1H), 7.43 (d, *J* = 4.4 Hz, 2H), 7.19 – 7.15 (m, 3H), 7.09 – 7.05 (m, 1H), 6.76 (d, *J* = 3.3 Hz, 1H), 6.38 (d, *J* = 7.7 Hz, 1H), 2.32 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 151.9, 143.5, 136.7, 135.6, 135.4, 132.8, 132.6, 130.5, 129.4, 128.9, 128.6, 128.4, 127.3, 127.2, 127.1, 126.9, 126.7, 125.4, 122.2, 117.6, 20.6.

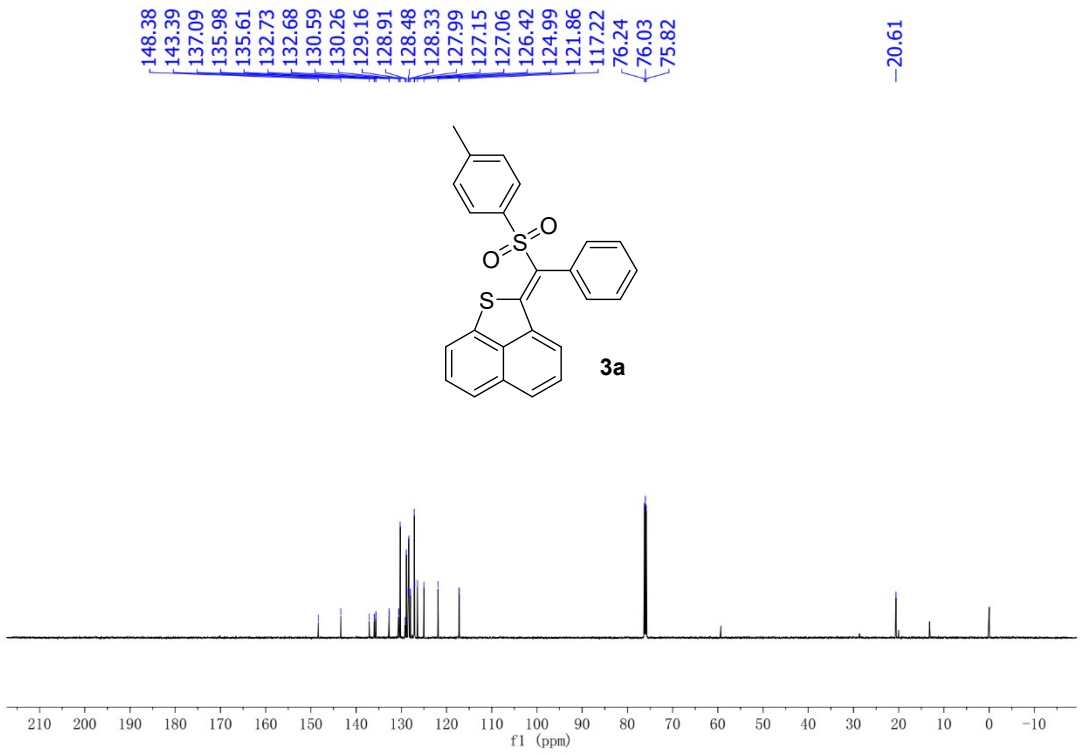
HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{17}O_2S_3$ 421.0391, found 421.0388.

5. NMR spectra of compounds

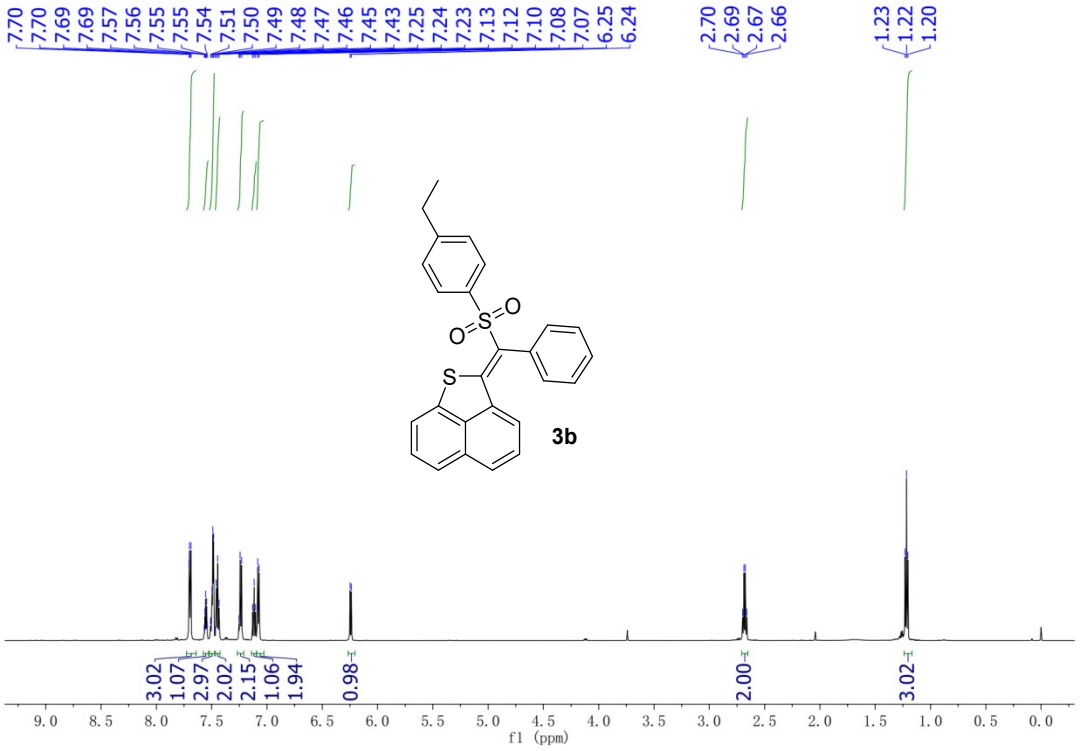
^{1}H NMR of **3a** in $CDCl_3$ (600 MHz, $CDCl_3$)



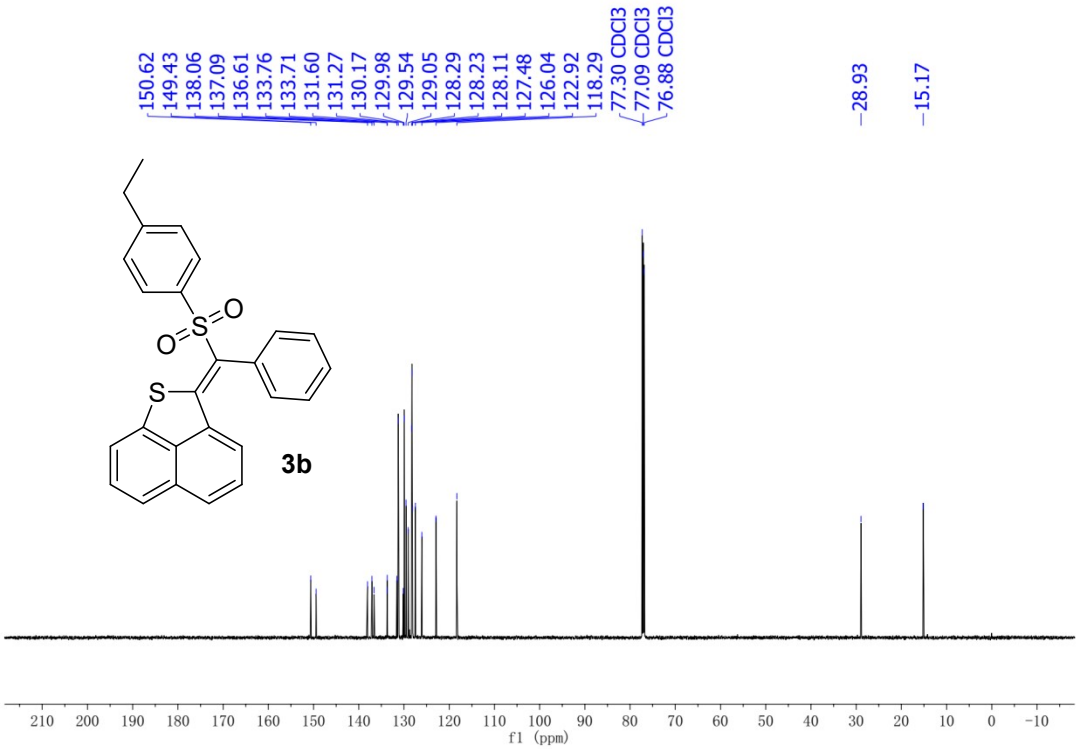
^{13}C NMR of **3a** in $CDCl_3$ (151 MHz, $CDCl_3$)



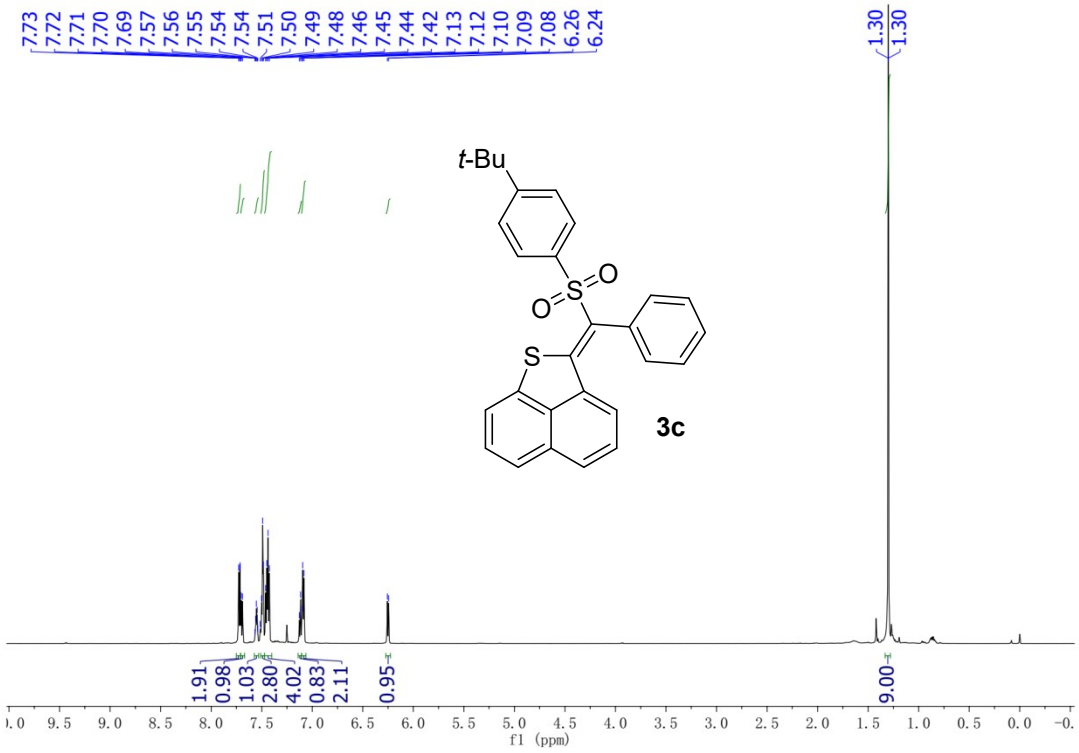
^{1}H NMR of **3b** in $CDCl_3$ (600 MHz, $CDCl_3$)



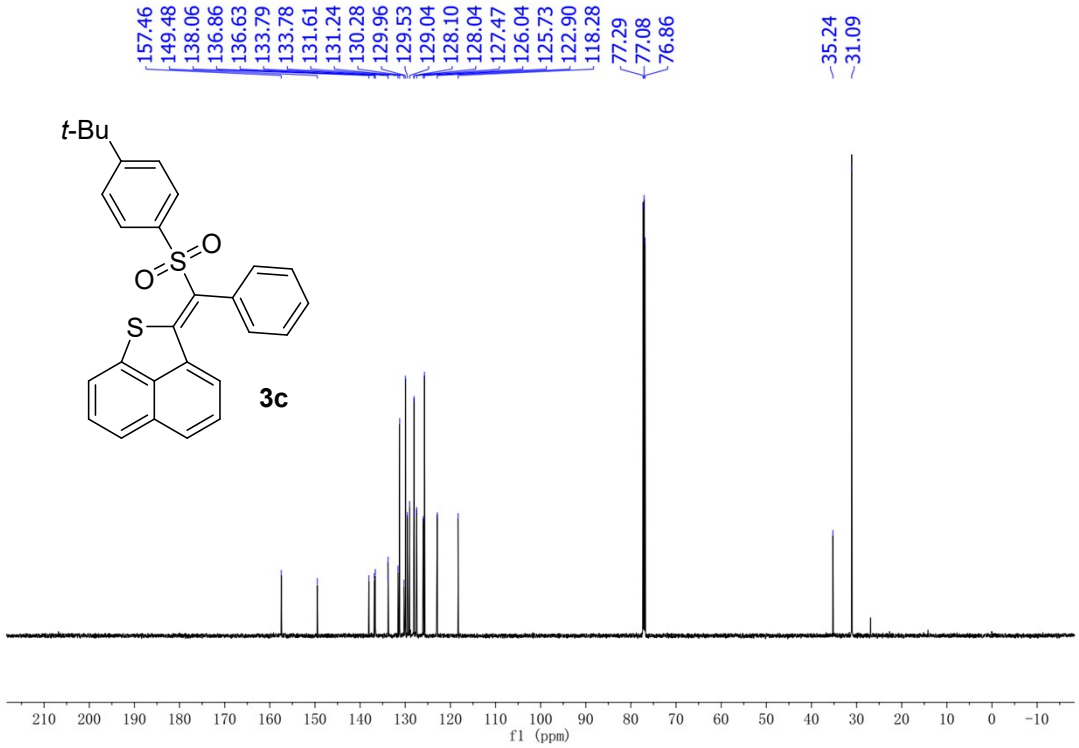
^{13}C NMR of **3b** in $CDCl_3$ (151 MHz, $CDCl_3$)



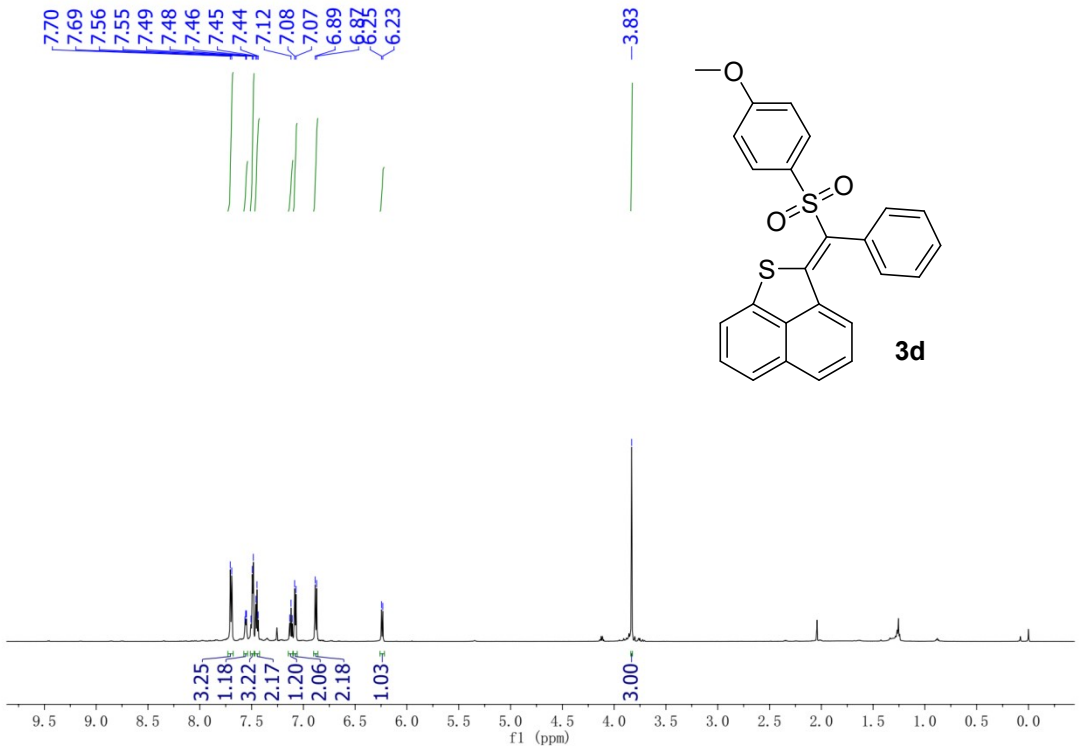
^{1}H NMR of **3c** in $CDCl_3$ (600 MHz, $CDCl_3$)



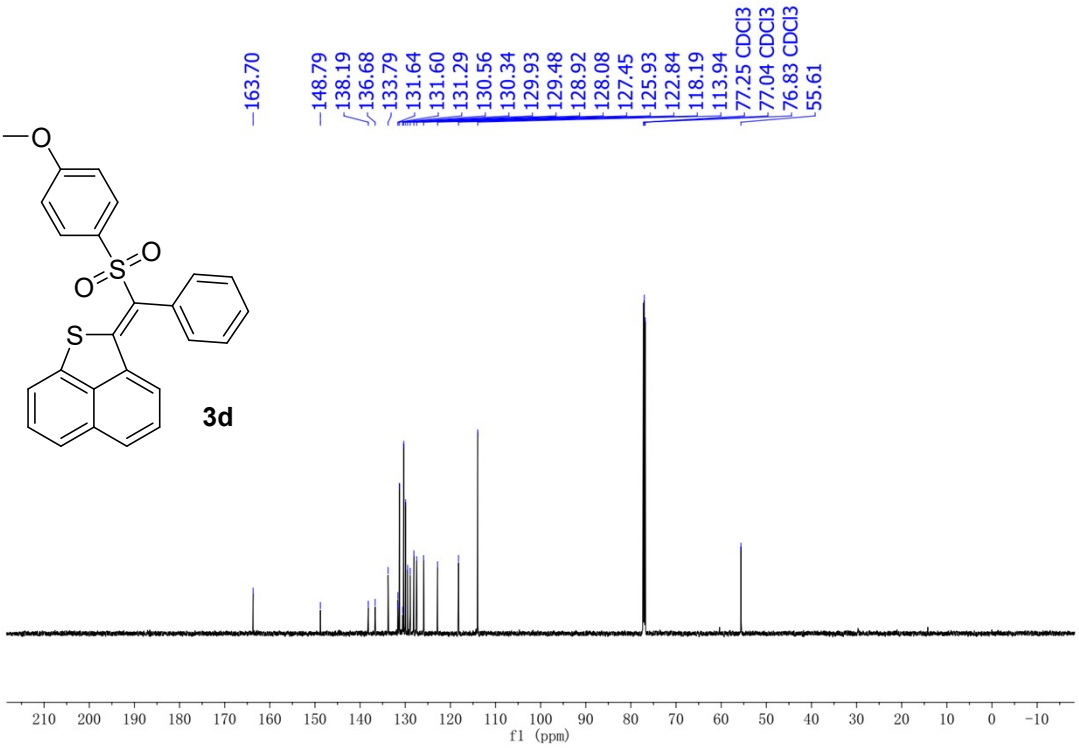
^{13}C NMR of **3c** in $CDCl_3$ (151 MHz, $CDCl_3$)



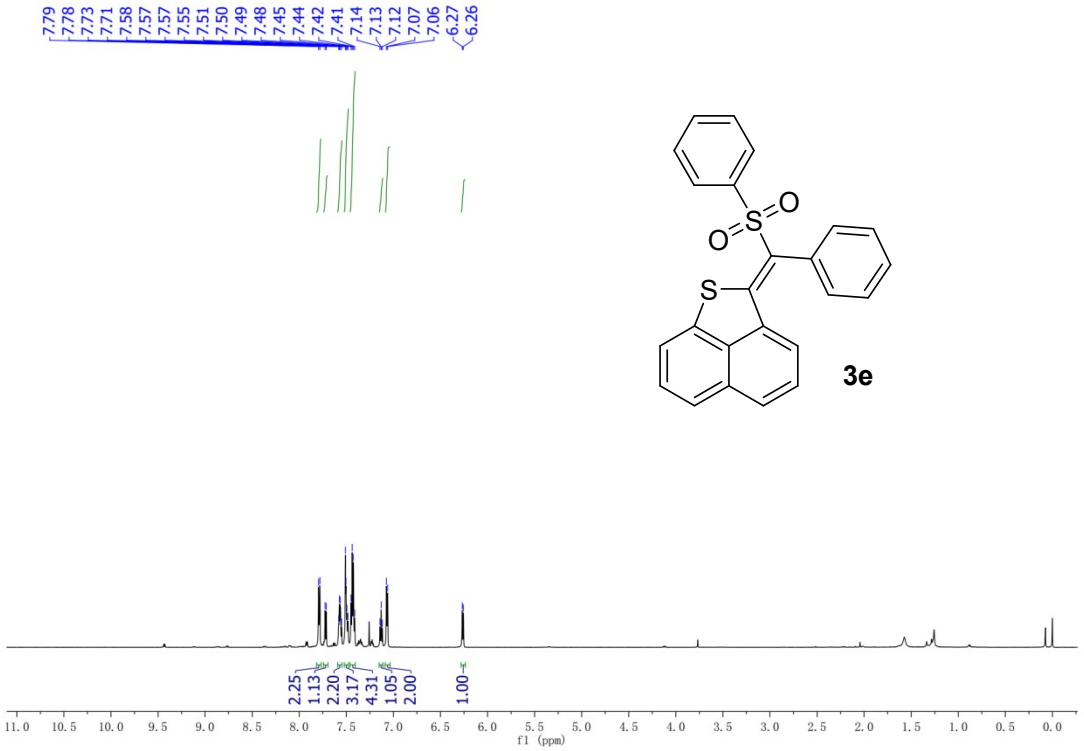
^{1}H NMR of **3d** in $CDCl_3$ (600 MHz, $CDCl_3$)



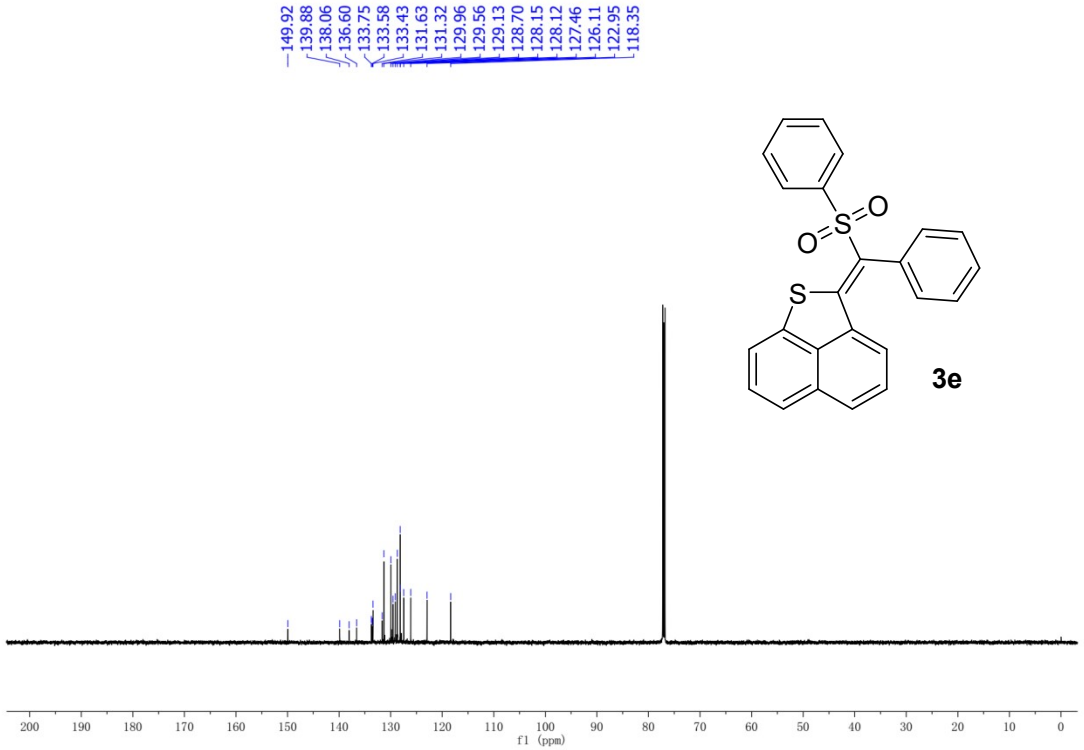
^{13}C NMR of **3d** in $CDCl_3$ (151 MHz, $CDCl_3$)



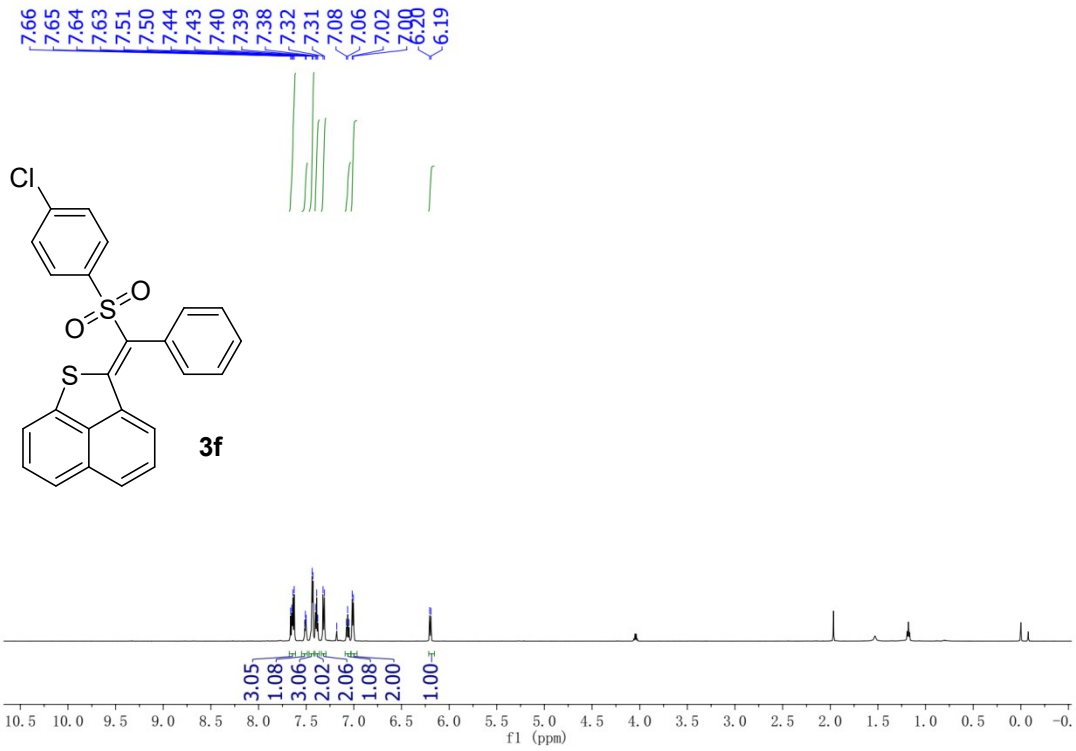
^{1}H NMR of **3e** in $CDCl_3$ (600 MHz, $CDCl_3$)



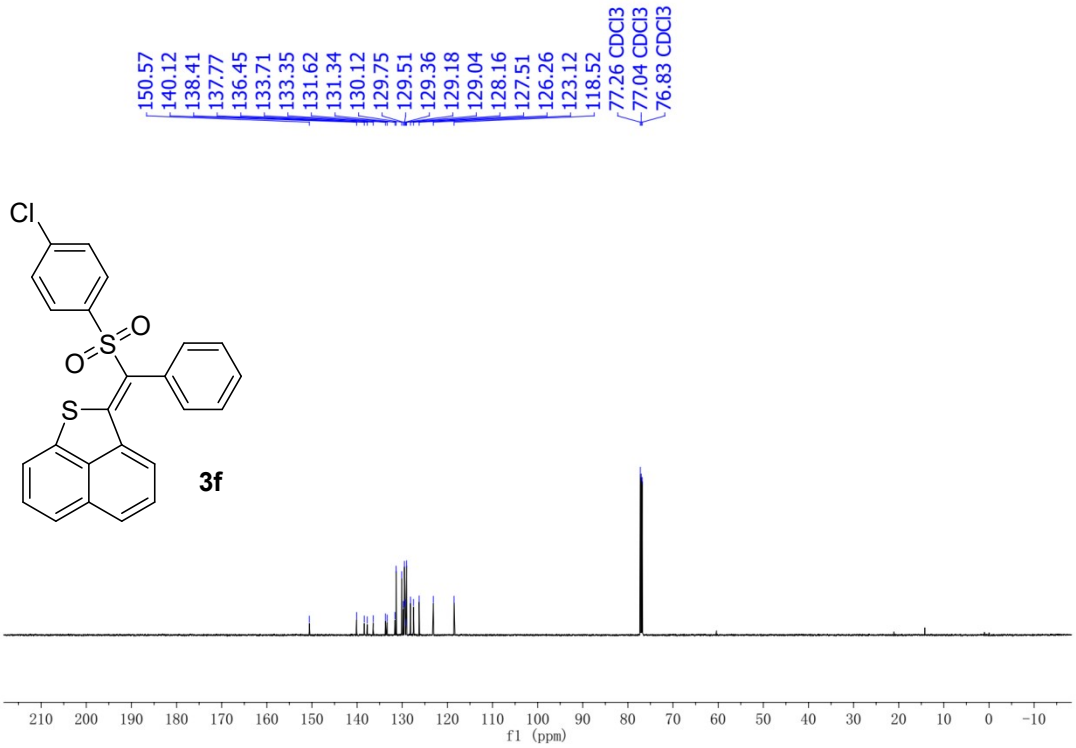
^{13}C NMR of **3e** in $CDCl_3$ (151 MHz, $CDCl_3$)



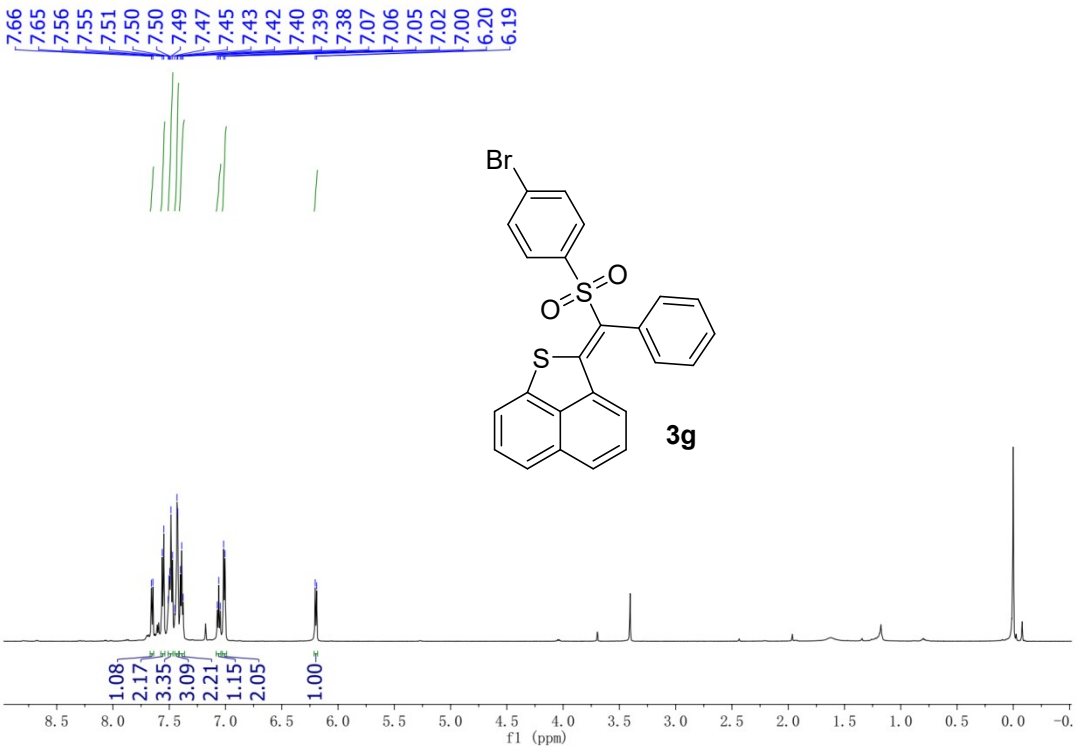
^{1}H NMR of **3f** in $CDCl_3$ (600 MHz, $CDCl_3$)



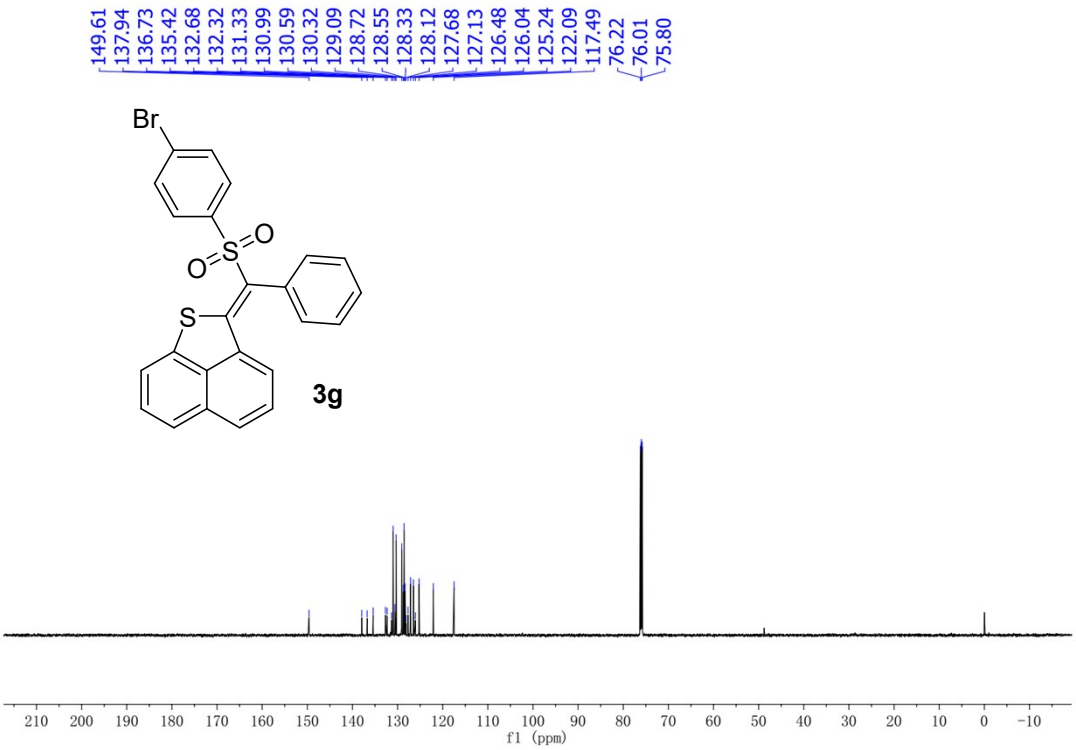
^{13}C NMR of **3f** in $CDCl_3$ (151 MHz, $CDCl_3$)



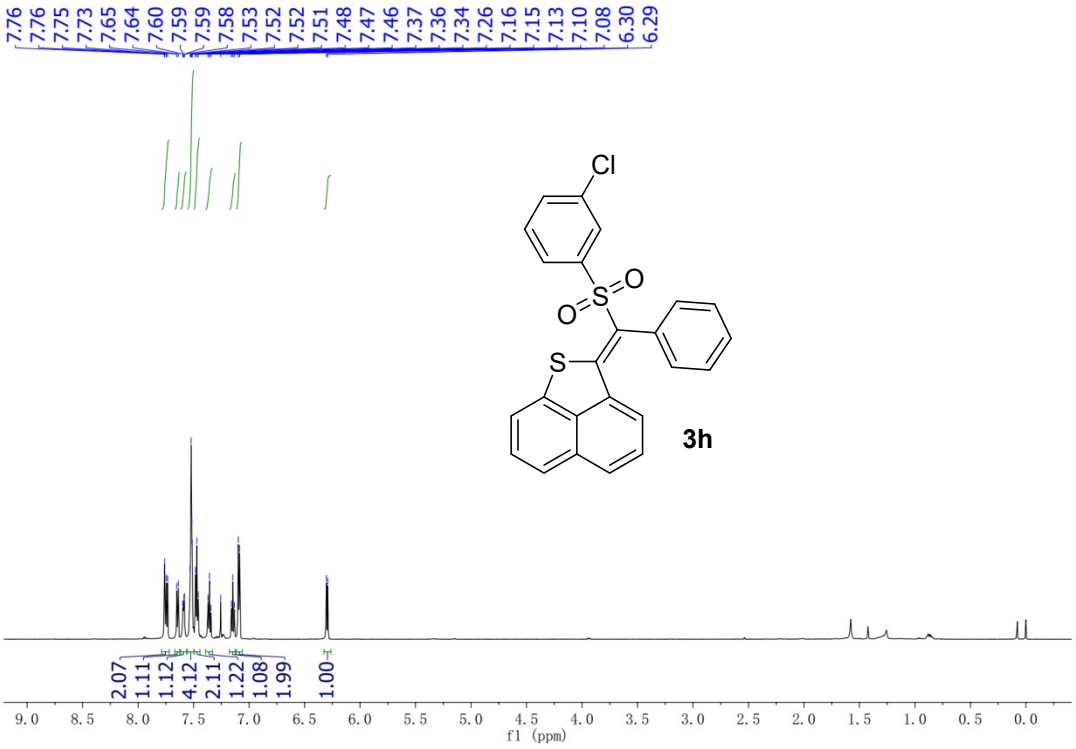
^{1}H NMR of **3g** in $CDCl_3$ (600 MHz, $CDCl_3$)



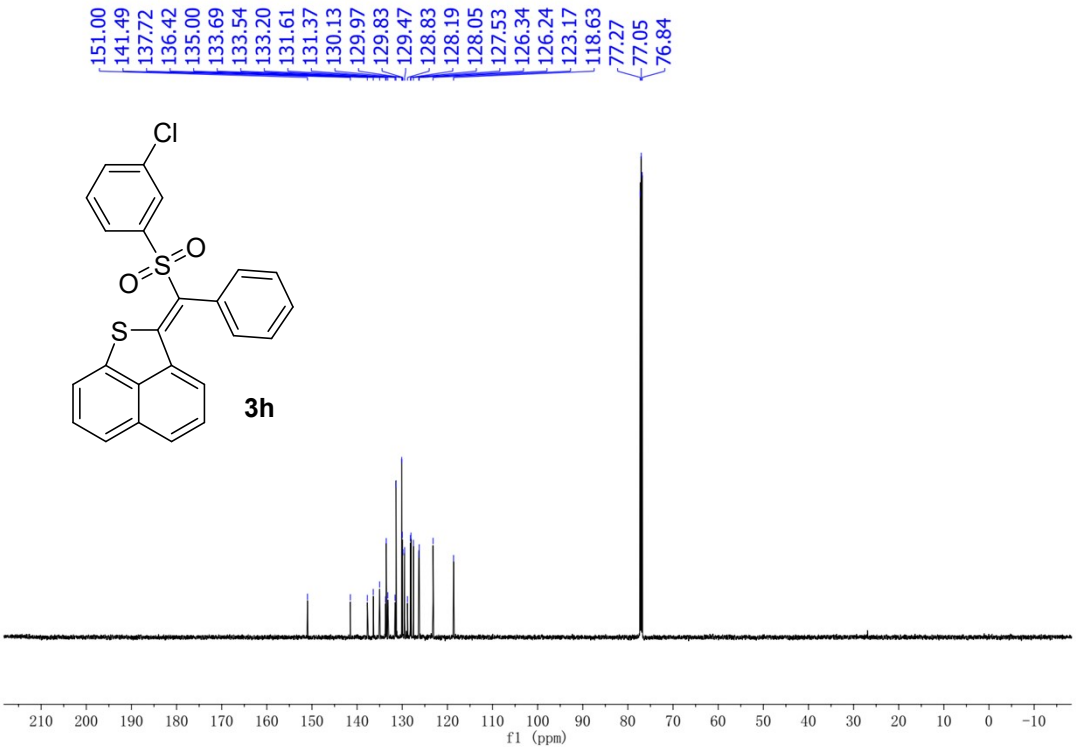
^{13}C NMR of **3g** in $CDCl_3$ (151 MHz, $CDCl_3$)



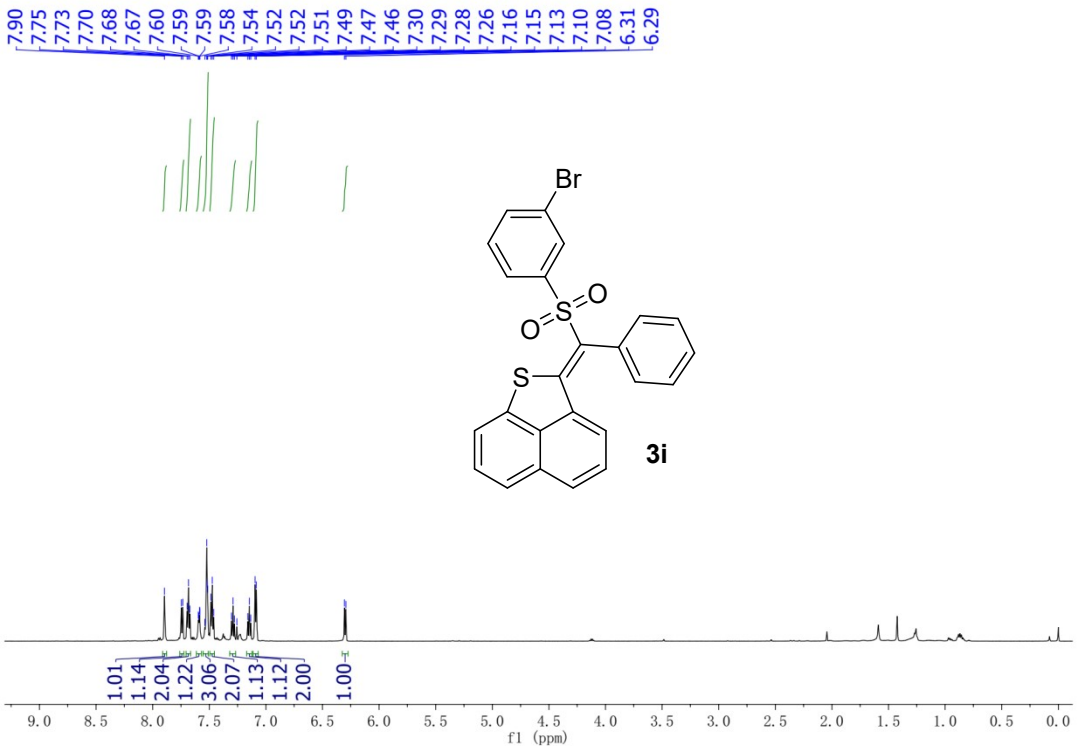
^{1}H NMR of **3h** in $CDCl_3$ (600 MHz, $CDCl_3$)



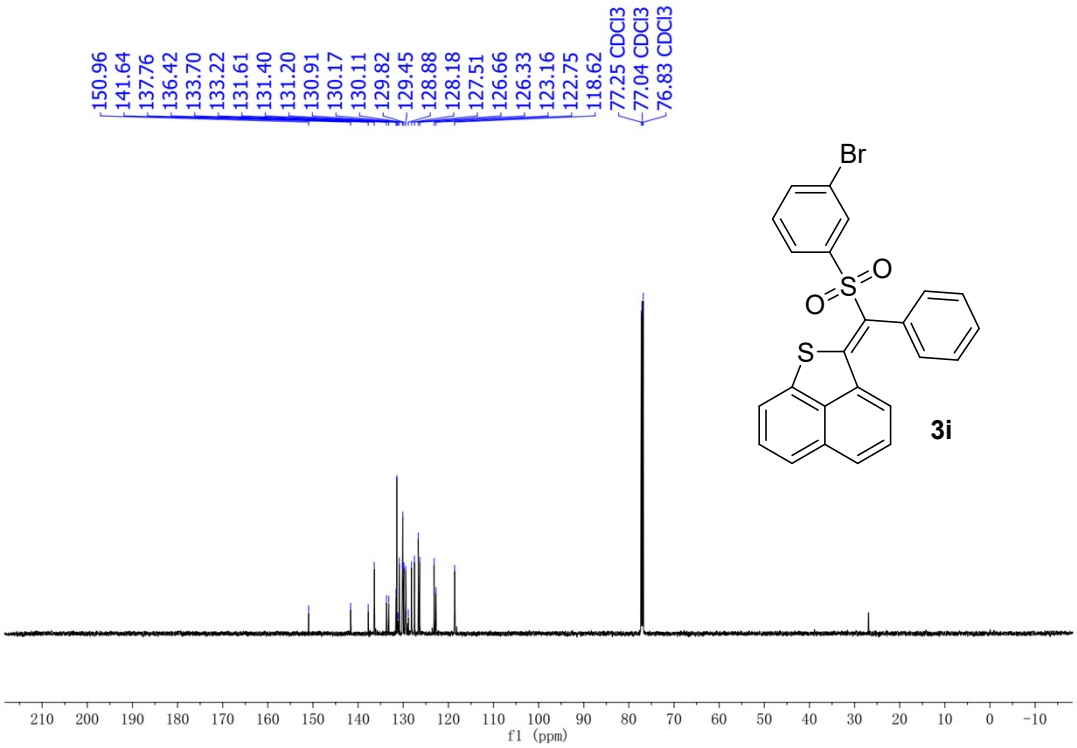
^{13}C NMR of **3h** in $CDCl_3$ (151 MHz, $CDCl_3$)



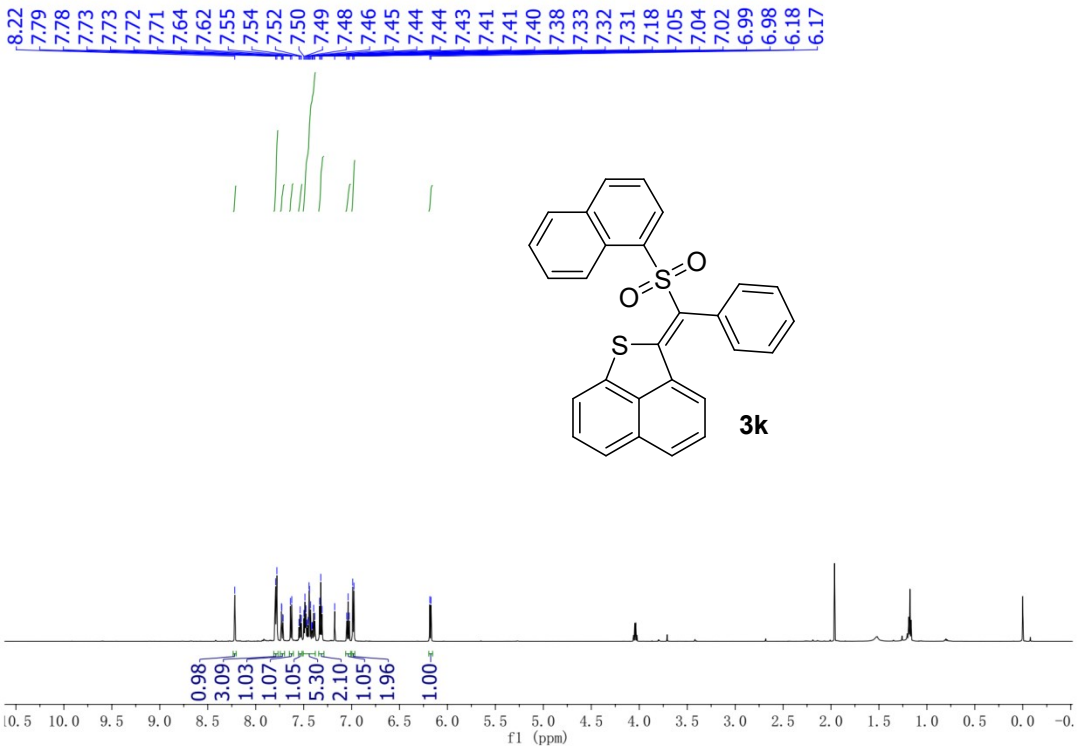
^{1}H NMR of **3i** in $CDCl_3$ (600 MHz, $CDCl_3$)



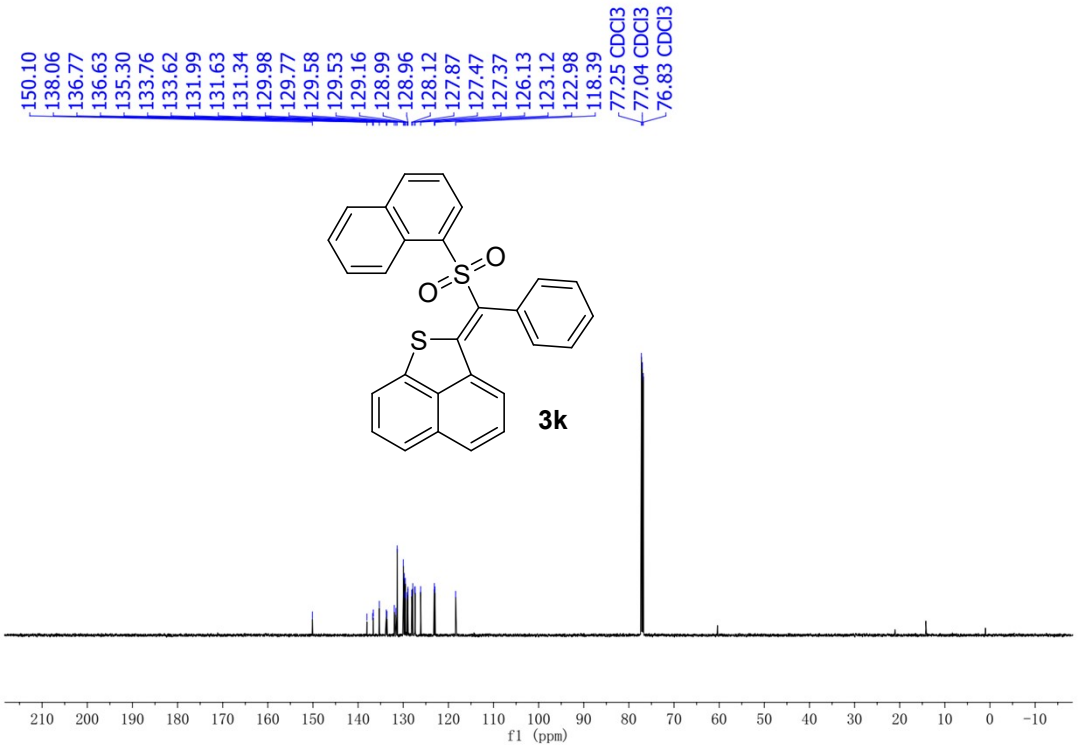
^{13}C NMR of **3i** in $CDCl_3$ (151 MHz, $CDCl_3$)



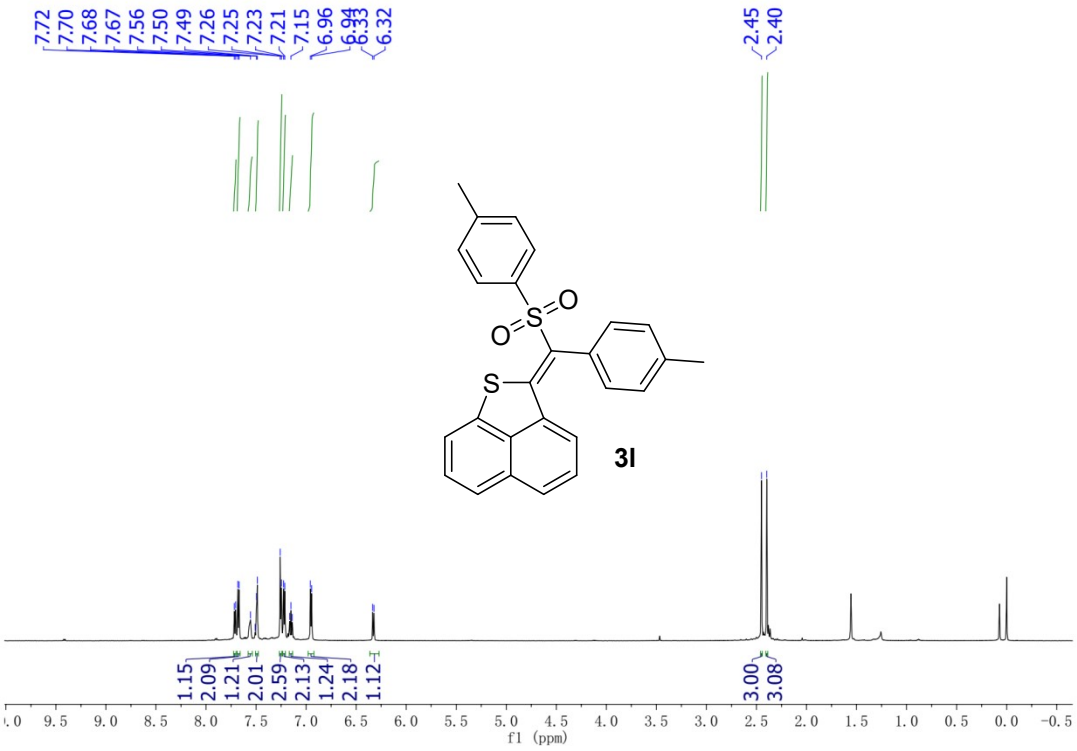
^{1}H NMR of **3k** in $CDCl_3$ (600 MHz, $CDCl_3$)



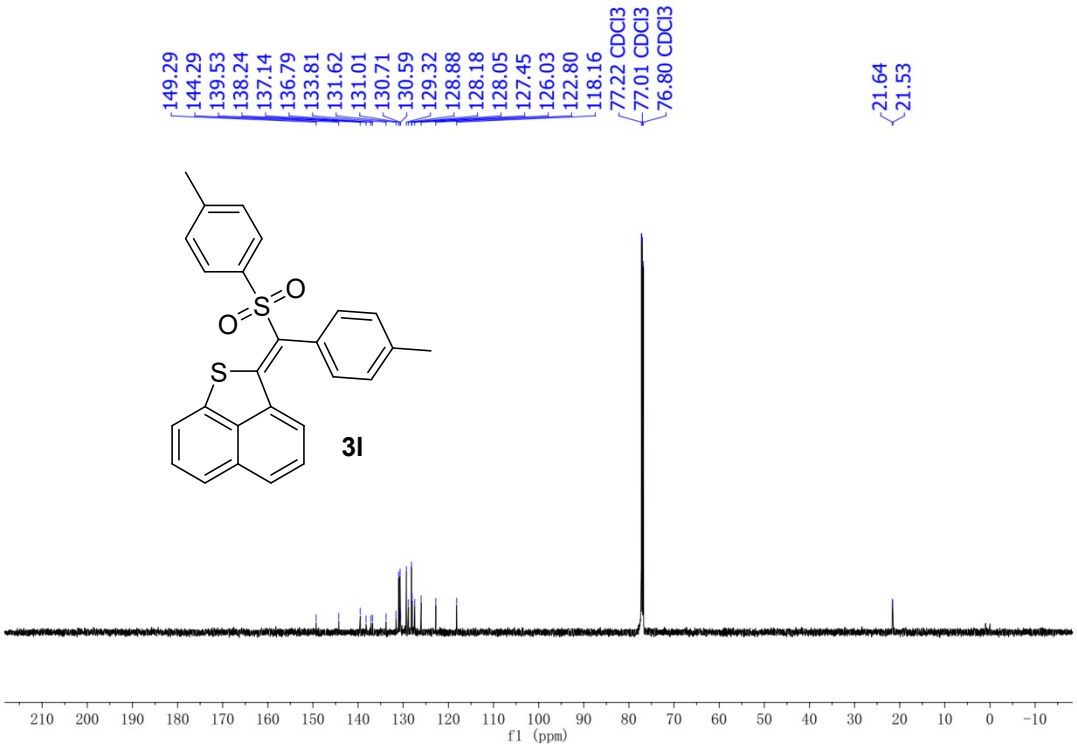
^{13}C NMR of **3k** in $CDCl_3$ (151 MHz, $CDCl_3$)



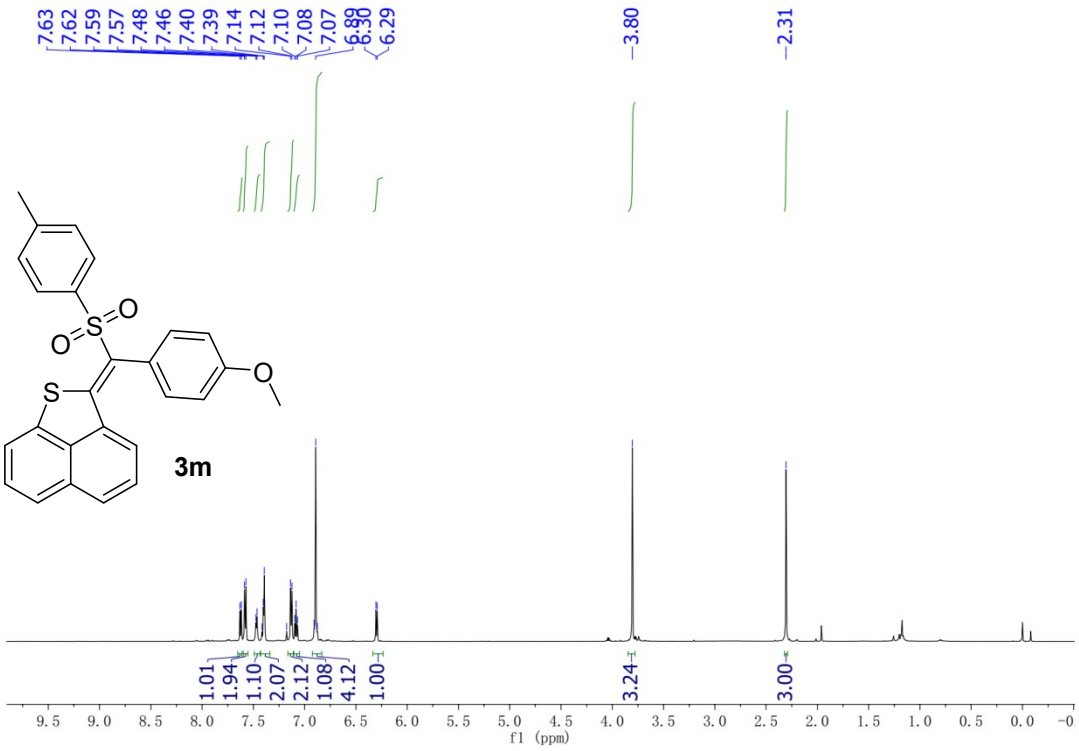
^{1}H NMR of **3l** in $CDCl_3$ (600 MHz, $CDCl_3$)



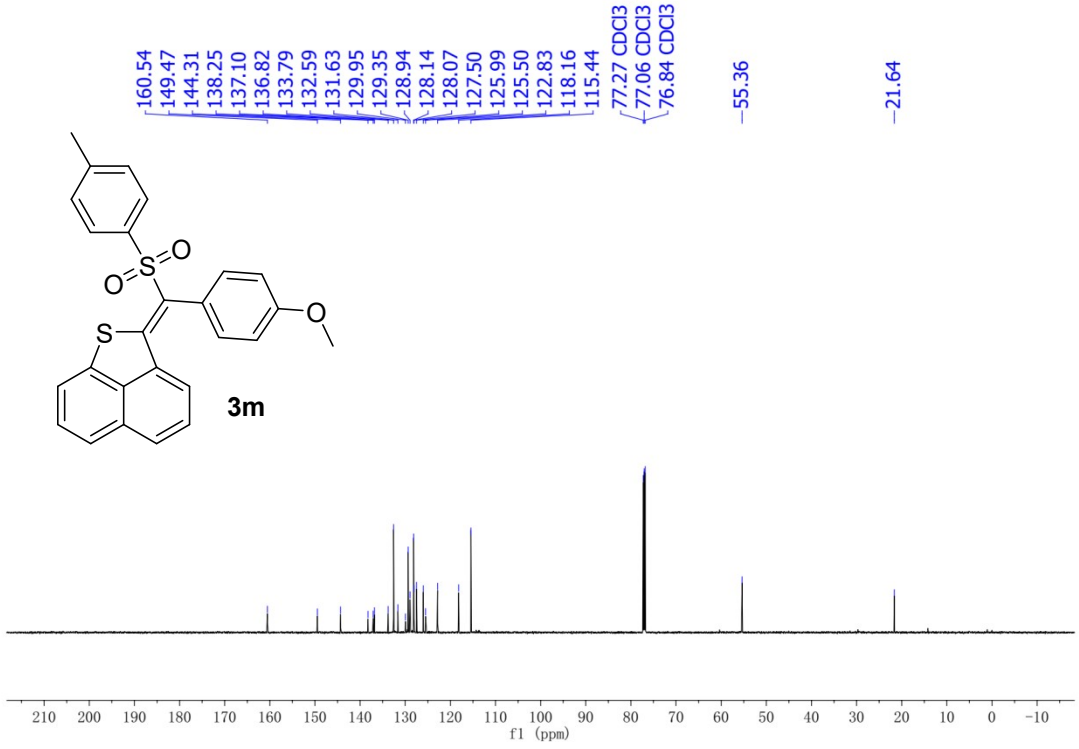
^{13}C NMR of **3l** in $CDCl_3$ (151 MHz, $CDCl_3$)



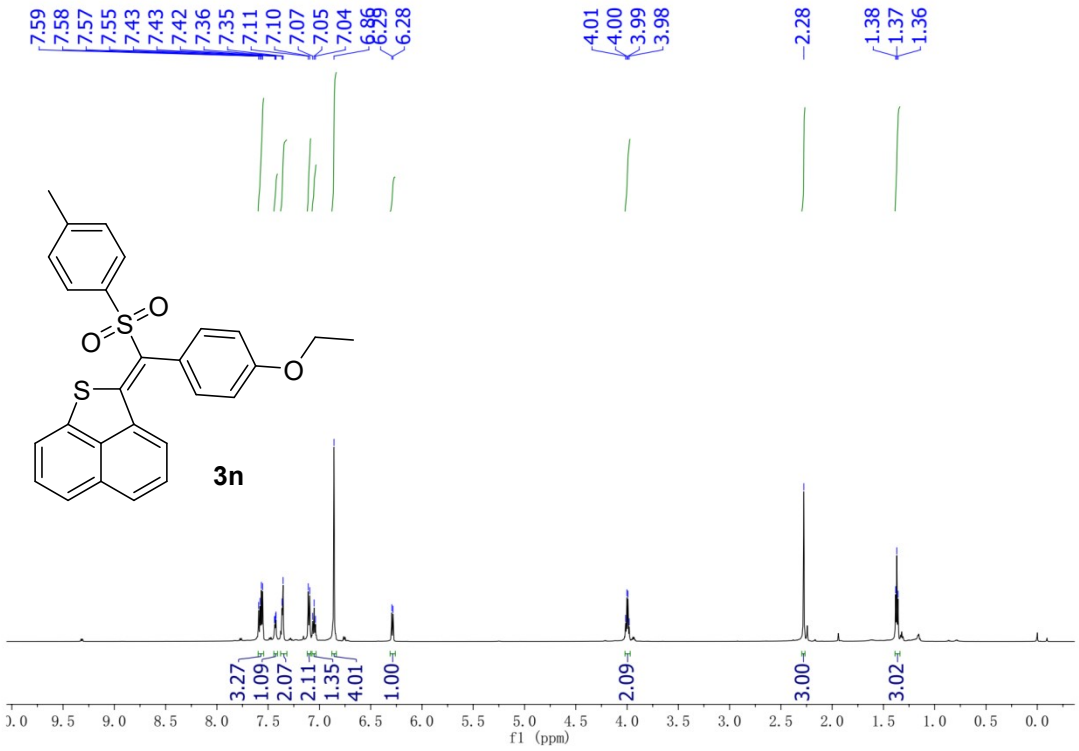
^{1}H NMR of **3m** in $CDCl_3$ (600 MHz, $CDCl_3$)



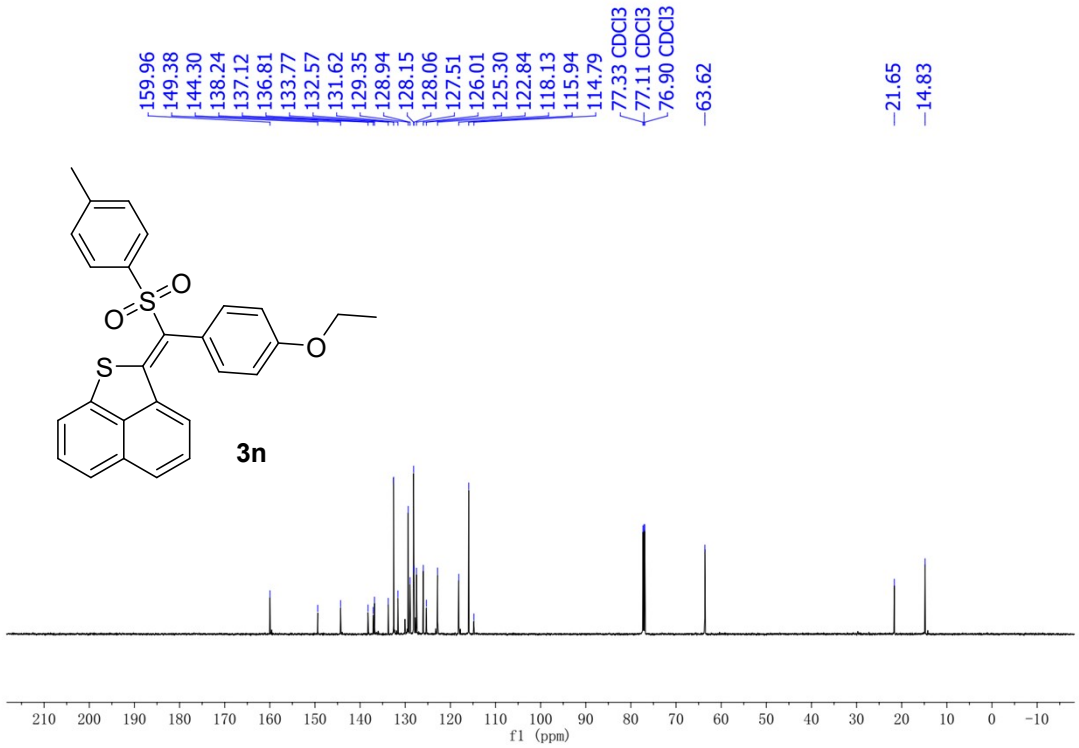
^{13}C NMR of **3m** in $CDCl_3$ (151 MHz, $CDCl_3$)



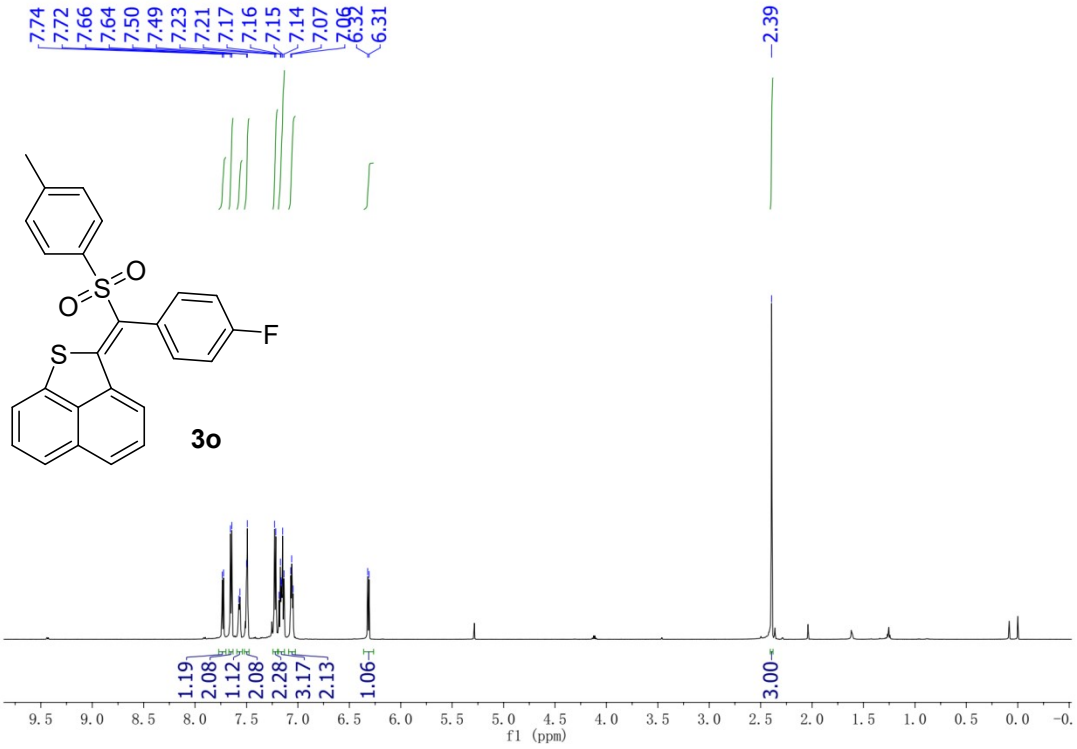
^{1}H NMR of **3n** in $CDCl_3$ (600 MHz, $CDCl_3$)



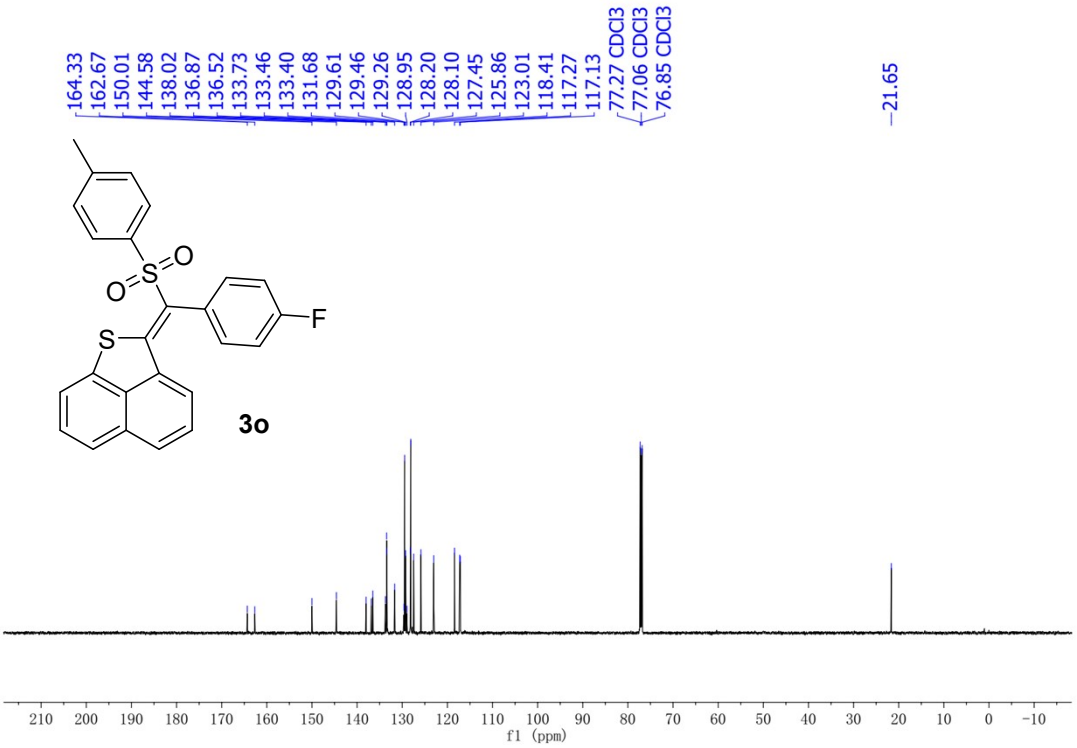
^{13}C NMR of **3n** in $CDCl_3$ (151 MHz, $CDCl_3$)



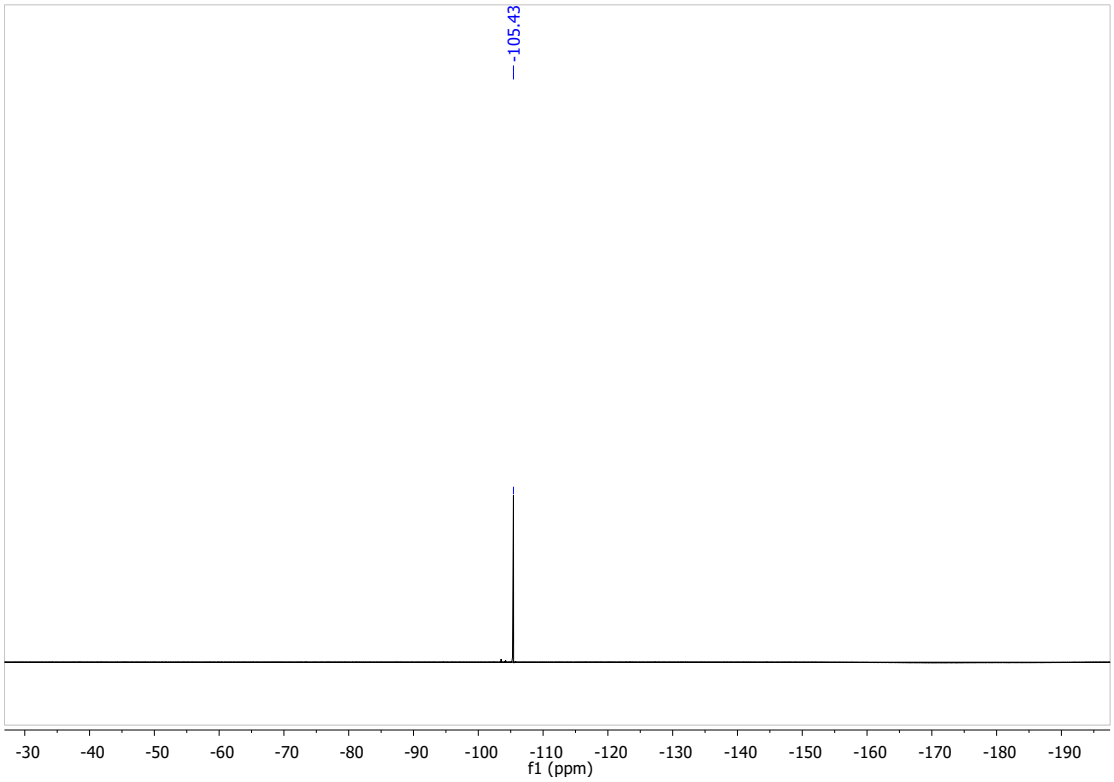
^{1}H NMR of **3o** in $CDCl_3$ (600 MHz, $CDCl_3$)



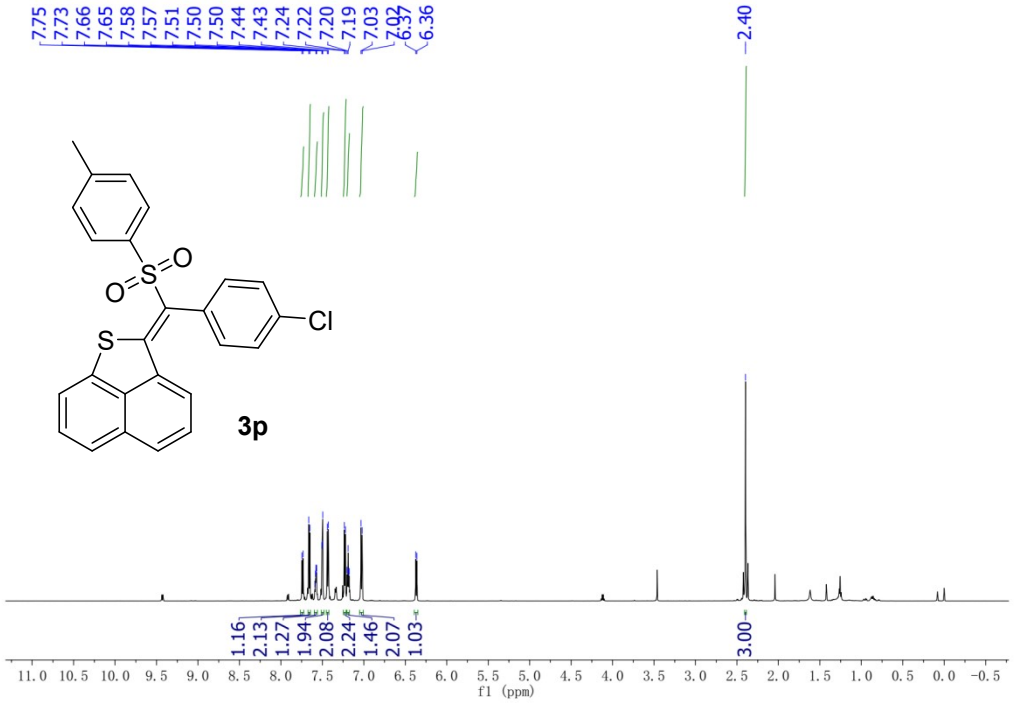
^{13}C NMR of **3o** in $CDCl_3$ (151 MHz, $CDCl_3$)



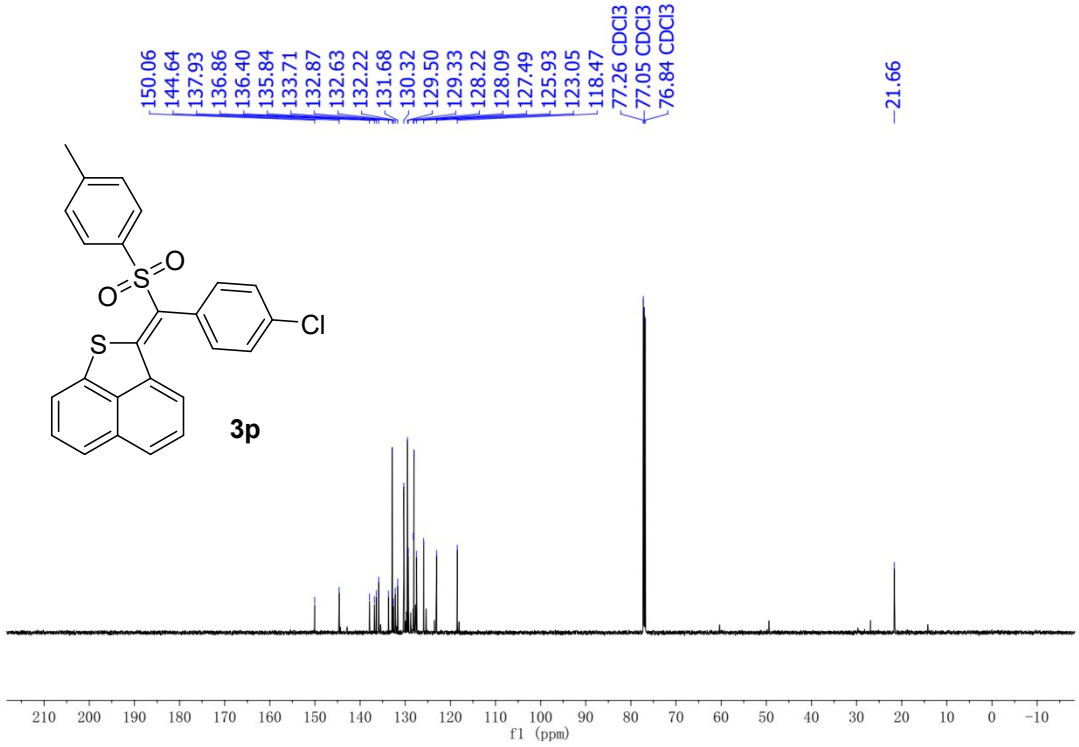
^{19}F NMR of **3o** in $CDCl_3$ (565 MHz, $CDCl_3$)



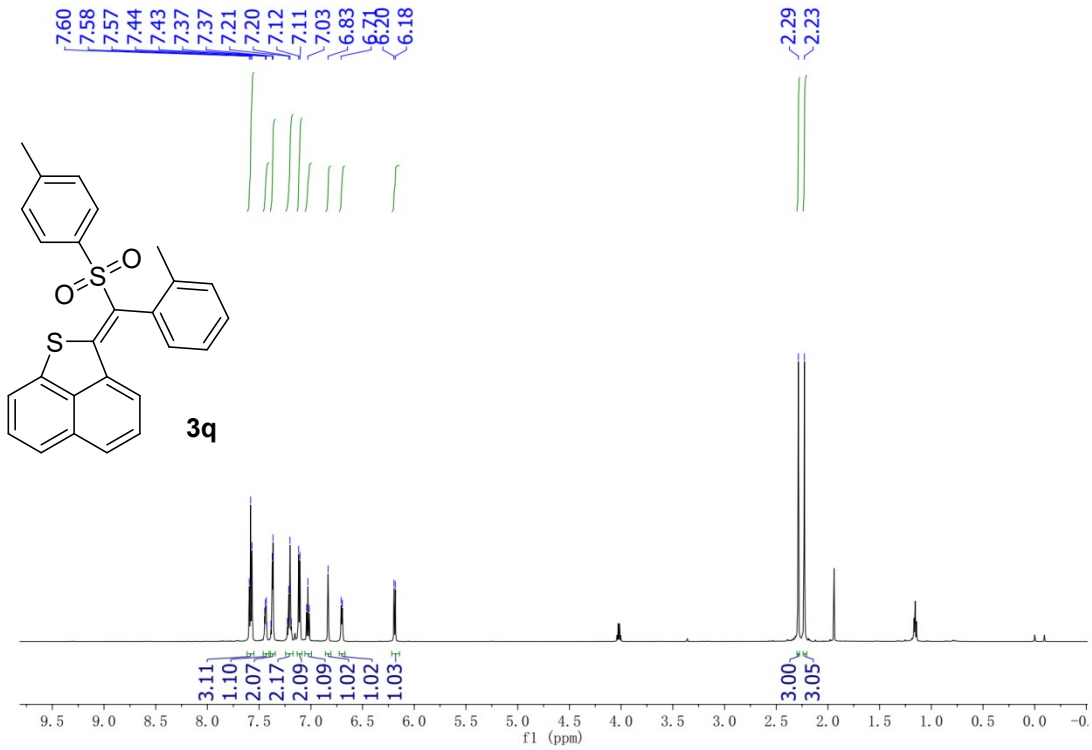
^{1}H NMR of **3p** in $CDCl_3$ (600 MHz, $CDCl_3$)



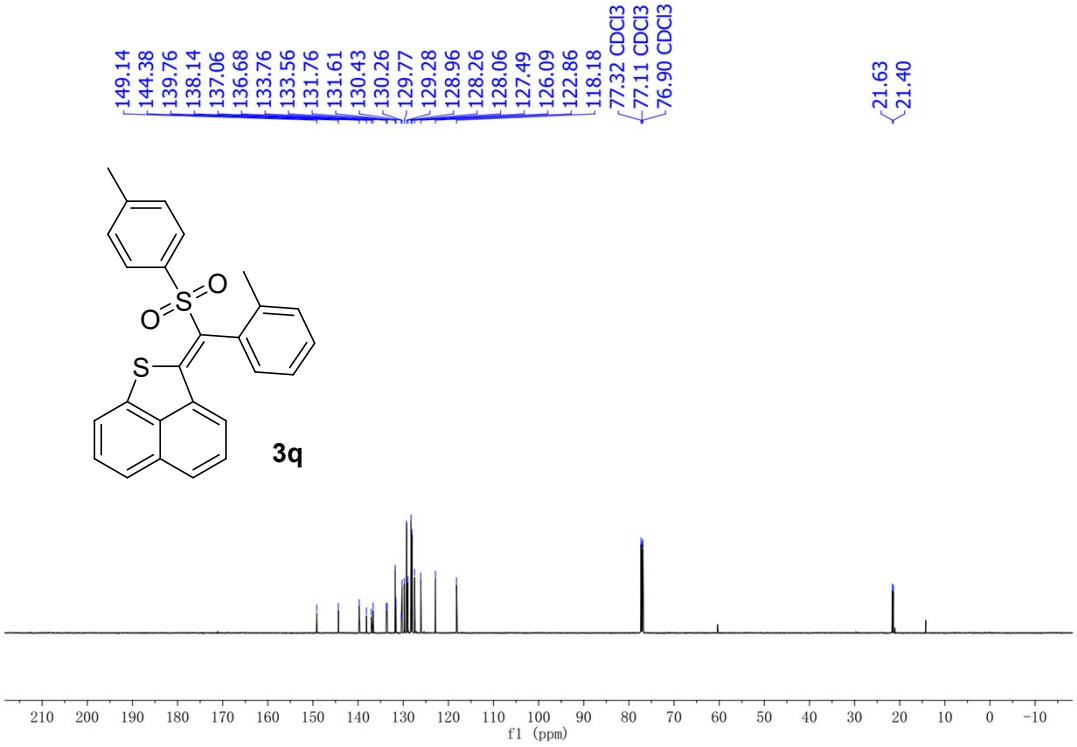
^{13}C NMR of **3p** in $CDCl_3$ (151 MHz, $CDCl_3$)



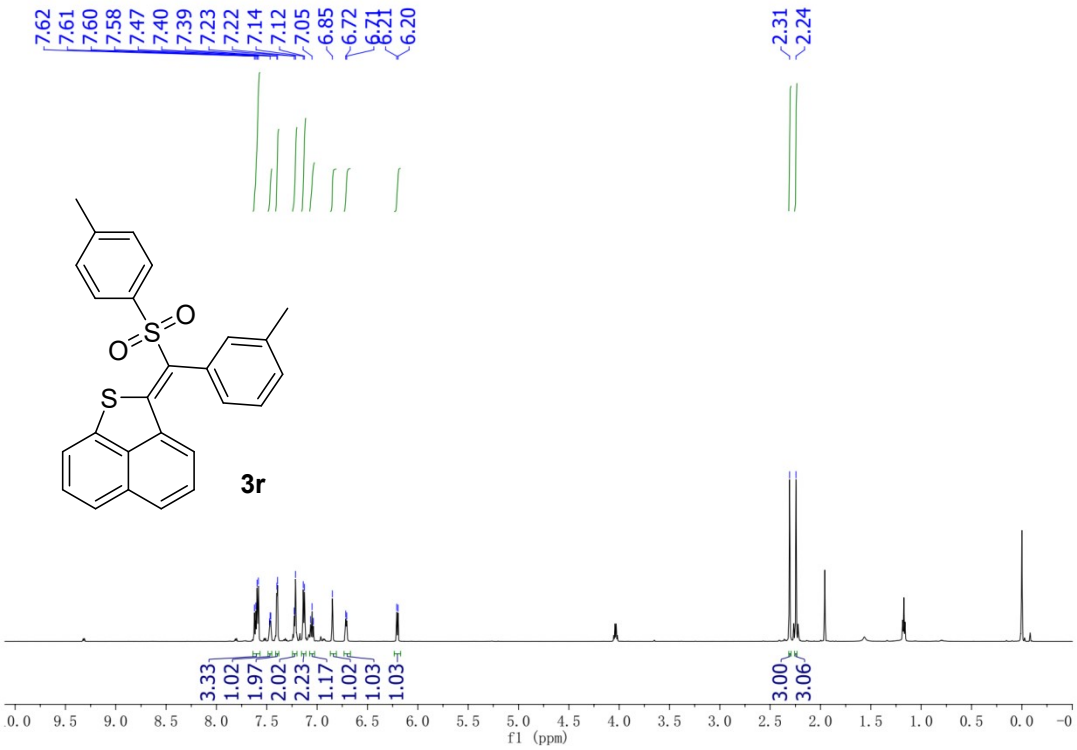
^{1}H NMR of **3q** in $CDCl_3$ (600 MHz, $CDCl_3$)



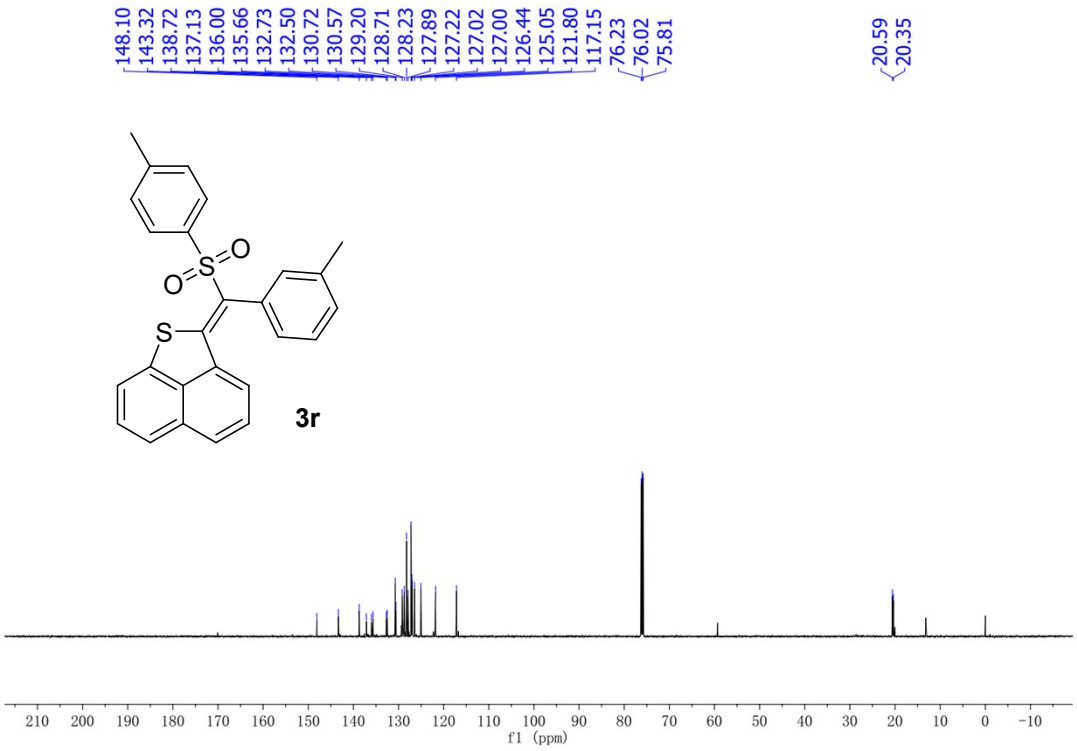
^{13}C NMR of **3q** in $CDCl_3$ (151 MHz, $CDCl_3$)



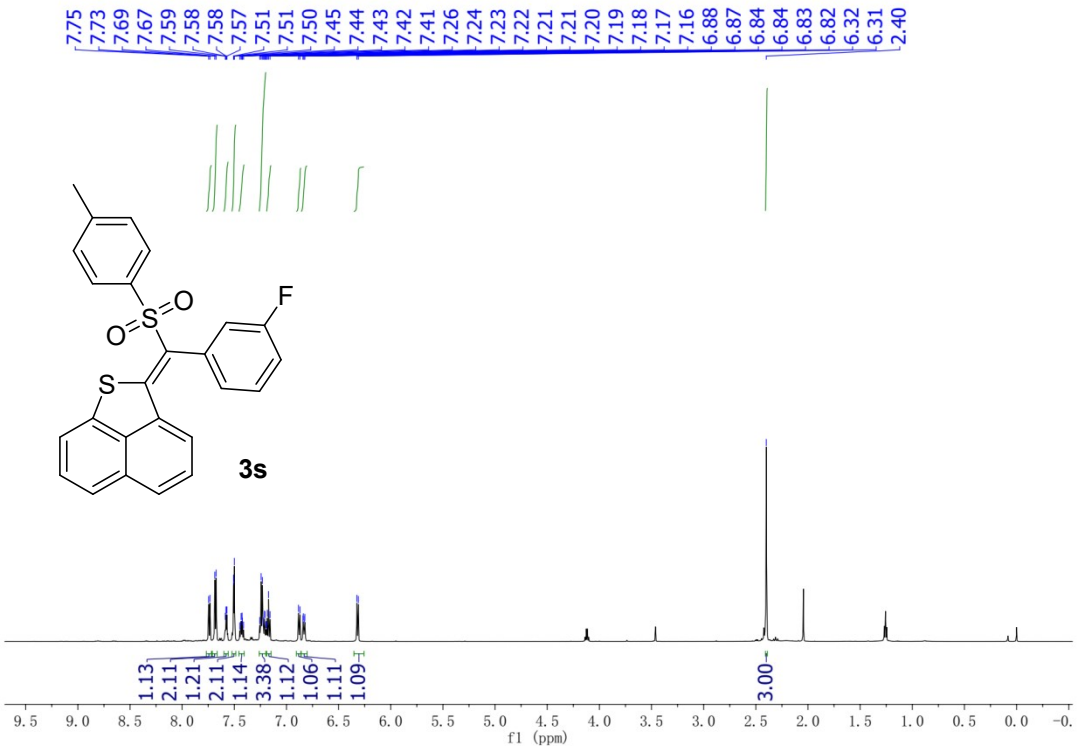
^{1}H NMR of **3r** in $CDCl_3$ (600 MHz, $CDCl_3$)



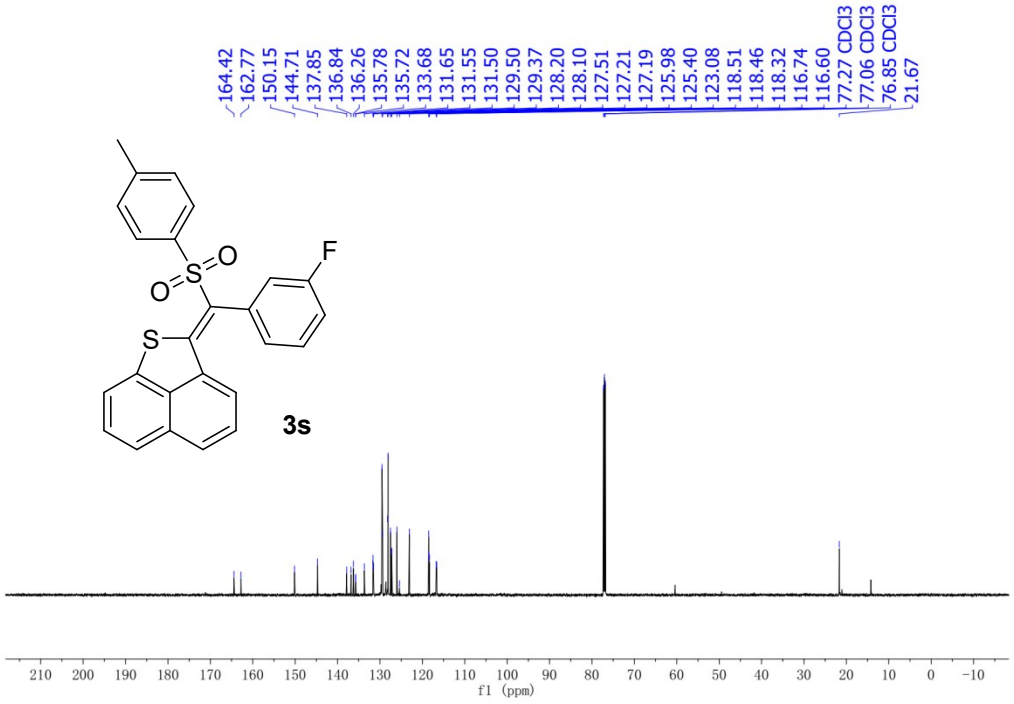
^{13}C NMR of **3r** in $CDCl_3$ (151 MHz, $CDCl_3$)



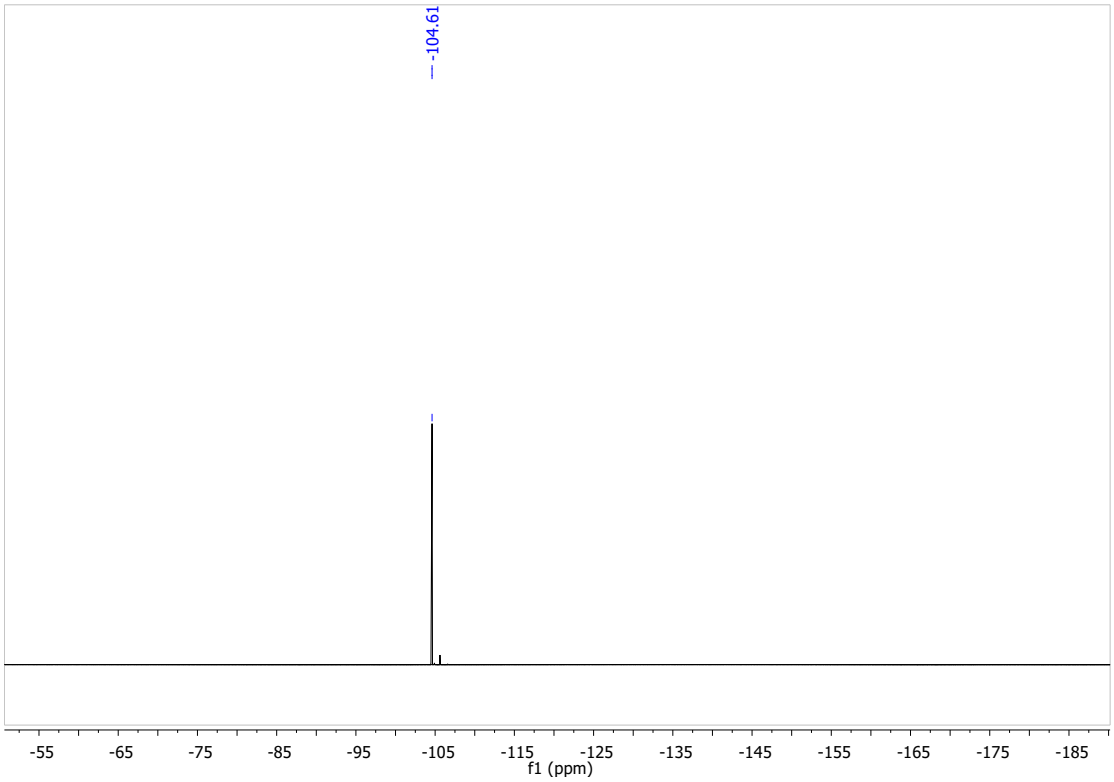
^{1}H NMR of **3s** in $CDCl_3$ (600 MHz, $CDCl_3$)



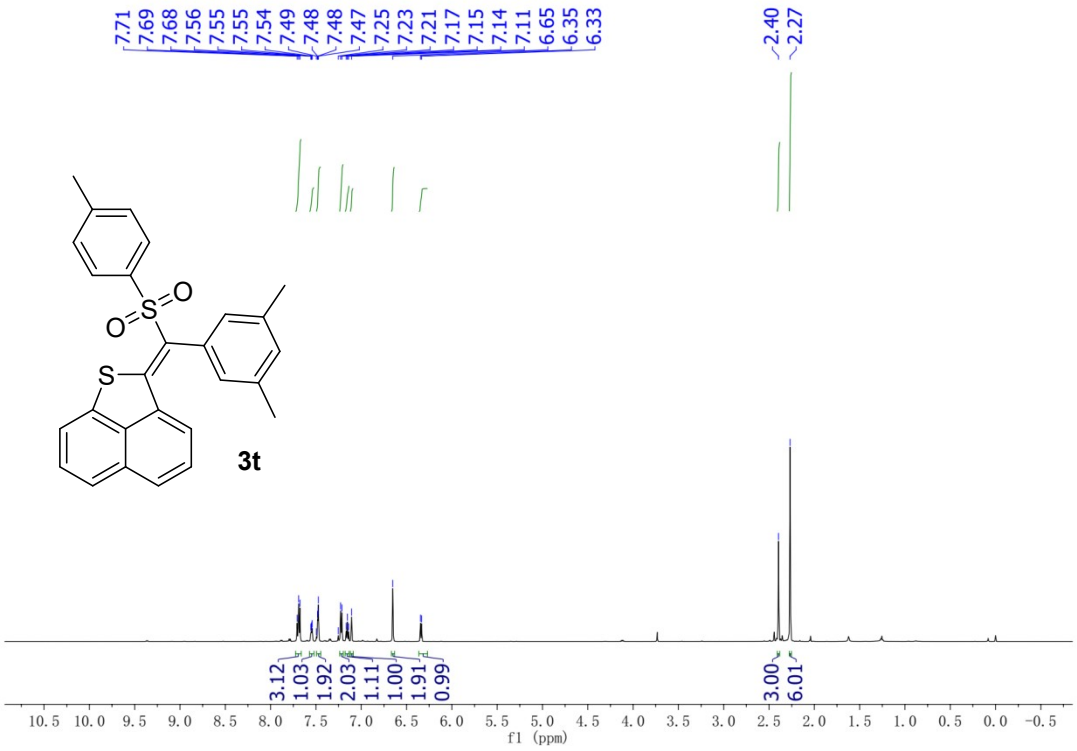
^{13}C NMR of **3s** in $CDCl_3$ (151 MHz, $CDCl_3$)



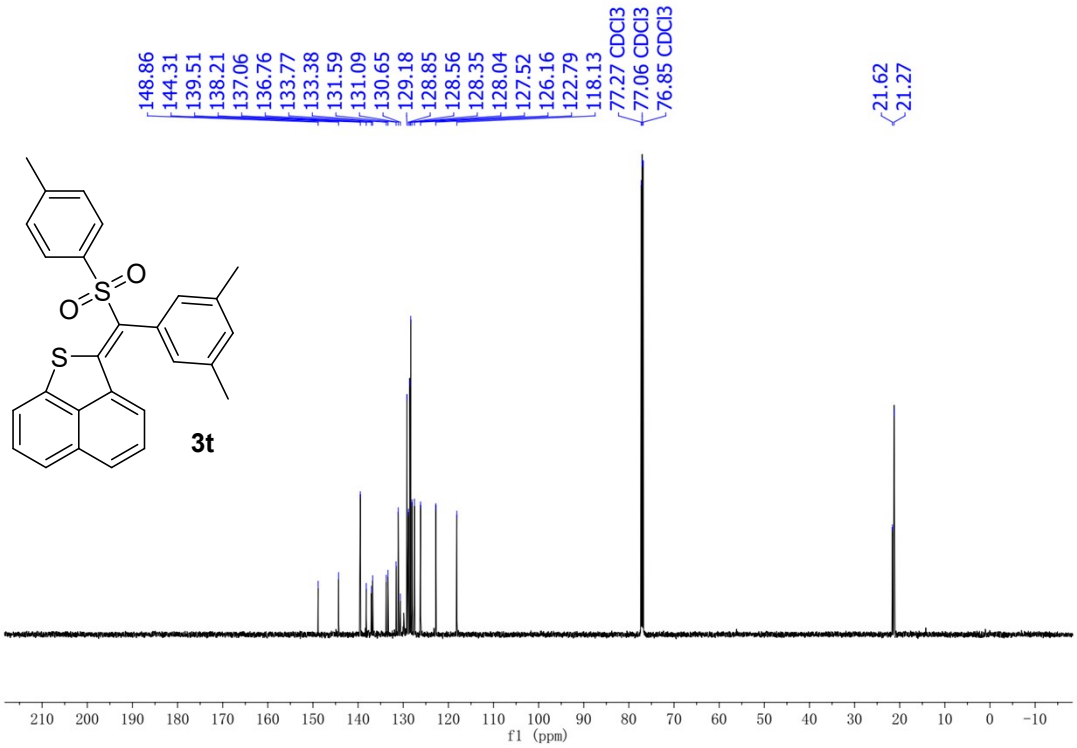
^{19}F NMR of **3s** in $CDCl_3$ (565 MHz, $CDCl_3$)



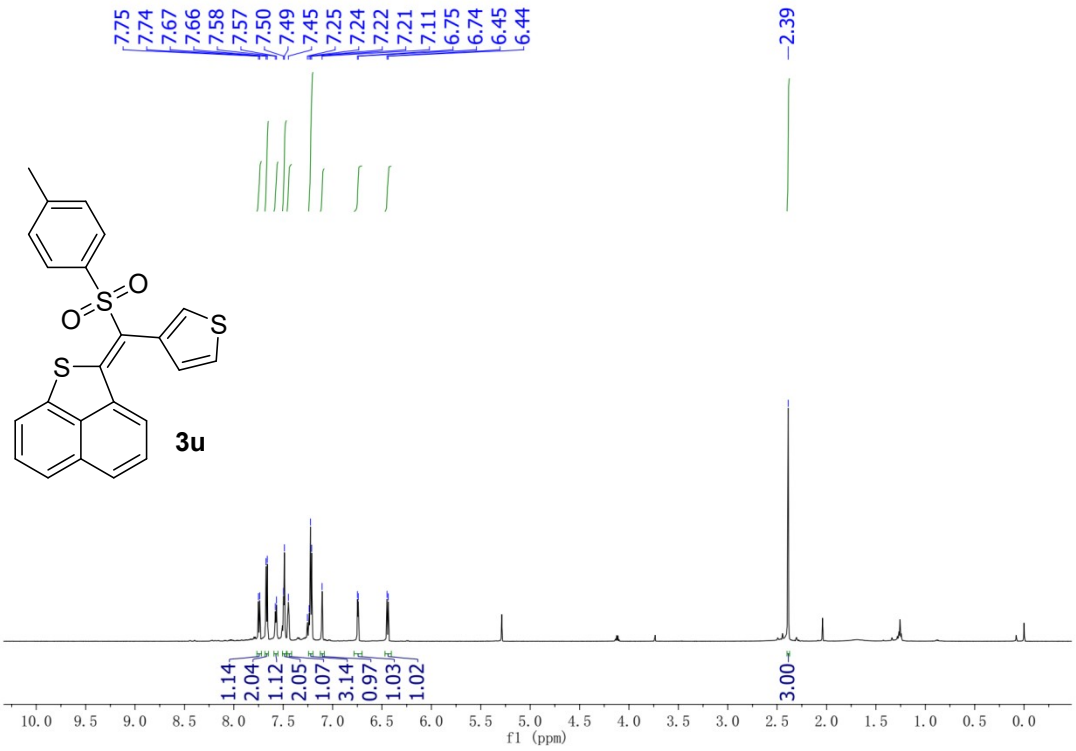
^{1}H NMR of **3t** in $CDCl_3$ (600 MHz, $CDCl_3$)



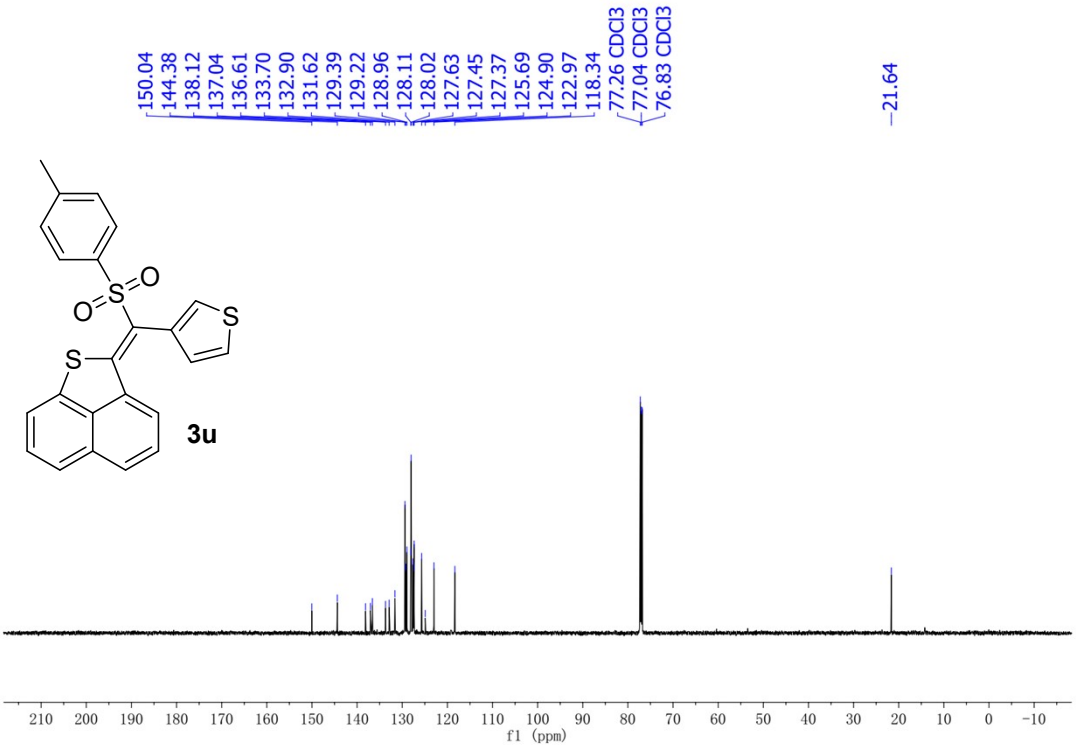
^{13}C NMR of **3t** in $CDCl_3$ (151 MHz, $CDCl_3$)



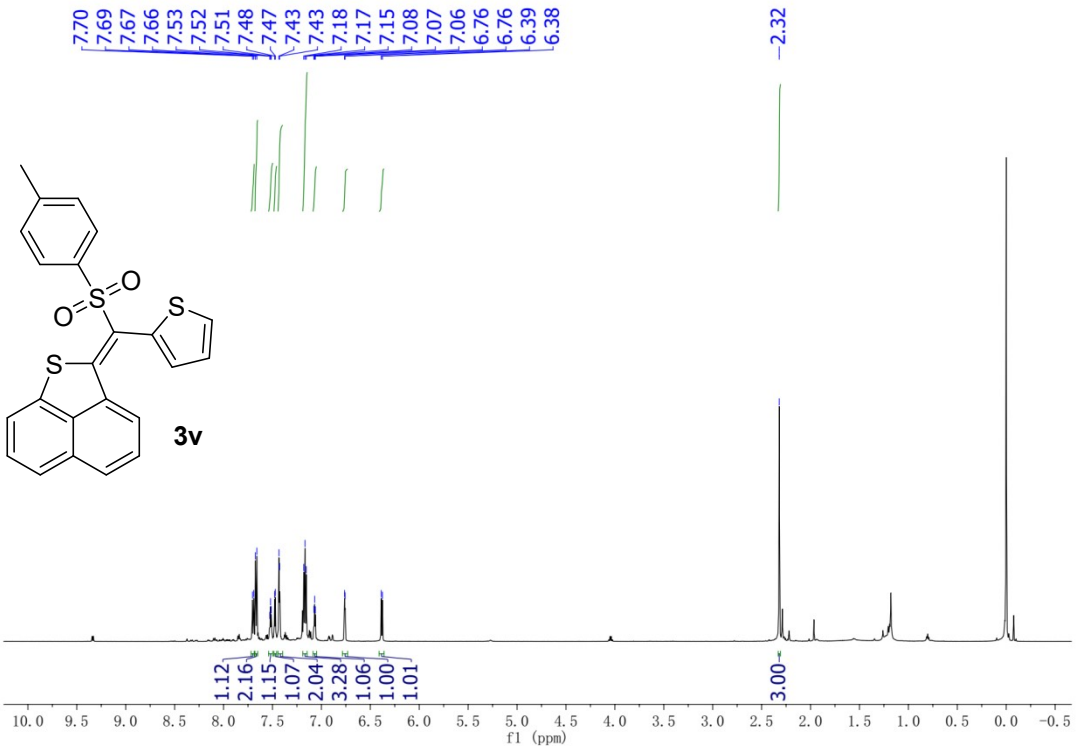
^{1}H NMR of **3u** in $CDCl_3$ (600 MHz, $CDCl_3$)



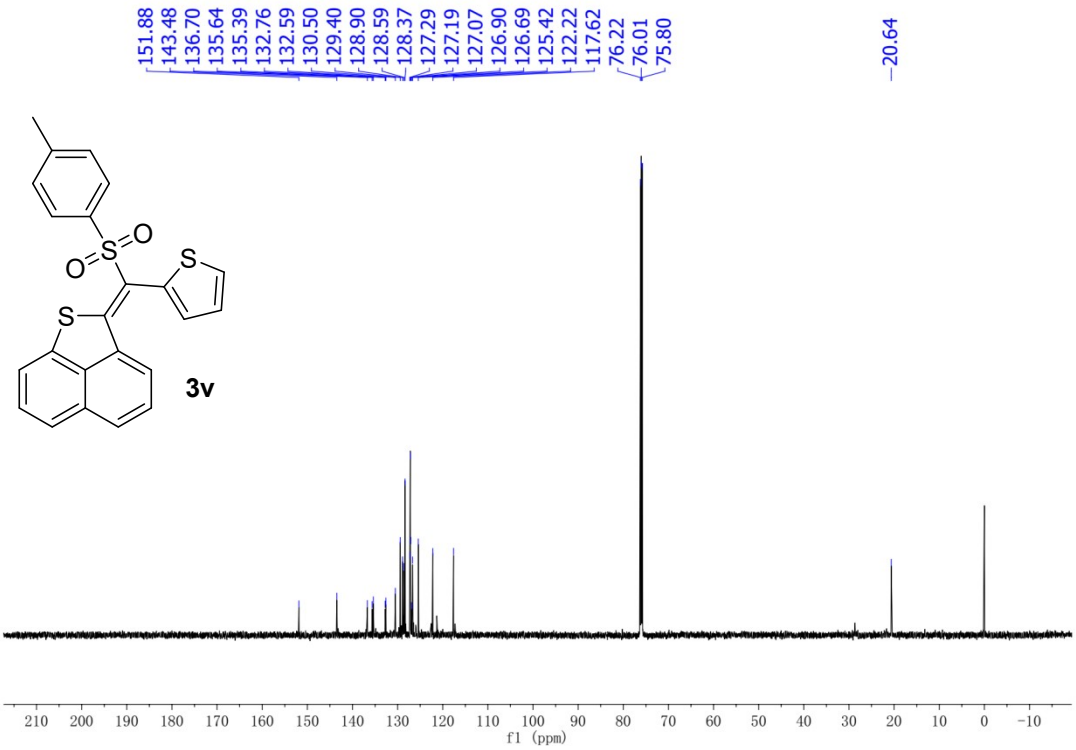
^{13}C NMR of **3u** in $CDCl_3$ (151 MHz, $CDCl_3$)



^{1}H NMR of **3v** in $CDCl_3$ (600 MHz, $CDCl_3$)



^{13}C NMR of **3u** in $CDCl_3$ (151 MHz, $CDCl_3$)



6. X-Ray Cystallographic Data of product

Diffraction was performed on a Bruker D8 VENTURE area detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) for all complexes at 293(2) K, φ and ω scan technique. An empirical absorption correction was applied using the SADABS program. All structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations based on F^2 using the SHELXTL program package. The hydrogen atom coordinates were calculated with SHELXTL by using an appropriate riding model with varied thermal parameters. The residual electron densities of solvents were squeezed by using PLATON. All crystal structural pictures drawn by *OLEX 2* program.

Single crystals of **3g** were grown from slow evaporation of N-hexane and cyclohexane solution at room temperature. The data of the crystal structure **3g** has been deposited at the Cambridge Crystallographic Data Centre and allocated the

deposition number: CCDC 2449196.

Datablock 1_a - ellipsoid plot