Supporting Information

Visible Light-induced Cyclization/aromatization of 2-Vinyloxy Arylalkynes: Synthesis of Thio-substituted Dibenzofuran Derivatives

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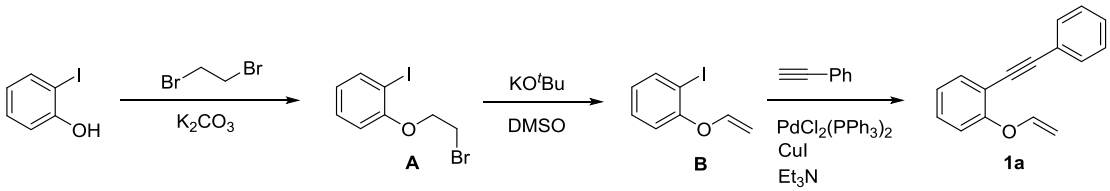
General information.

Column chromatography was performed on silica gel (100-200，300−400 mesh). NMR spectra were obtained using a Bruker Avance 400/600 spectrometer (^{1}H at 400/600 MHz and ^{13}C at 100/150 MHz). Chemical shifts were reported in ppm. ^{1}H NMR spectra were referenced to $CDCl_3$(7.26 ppm), and ^{13}C-NMR spectra were referenced to $CDCl_3$ (77.0 ppm). Peak multiplicities were designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet and J, coupling constant in Hz. High resolution mass spectra (HRMS) were recorded on the Exactive Mass Spectrometer (Agilent Technologies 7250 GCQTOF) equipped with EI ionization source and Exactive Mass Spectrometer (Thermo Scientific, USA) equipped with ESI or APCI ionization source. UV-Vis spectroscopy was performed on a UV-Vis spectrophotometer (Shimadzu UV2700) and all fluorescence spectra were recorded using a spectrofluorometer (Shimadzu RF-6000). Unless stated otherwise, commercial reagents were used without further purification.

General Procedure for the Synthesis of Substrate 1, 2 and 4.

Preparation of Substrate 1 and 4a.[1]



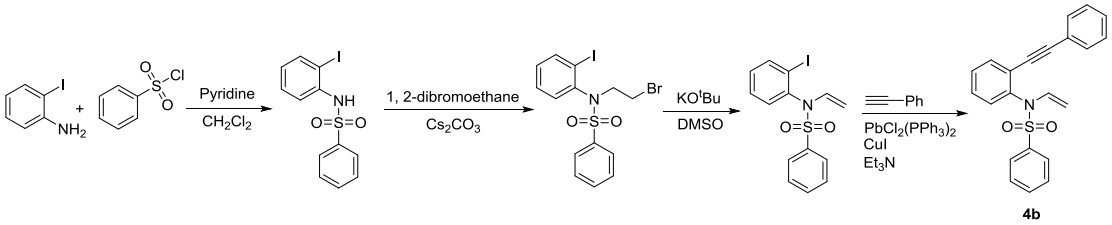
To a stirred solution of 2-iodophenol (20 mmol, 4.4 g) and 1,2-dibromoethane (60 mmol, 11.28 g) in mixture solvent of DMF and acetone (50 mL, V_{DMF} : $V_{acetone}$ = 3 : 2) was added K_2CO_3 (60 mmol, 8.28 g), and the resulting mixture was stirred at 80 ^oC for overnight. Then the reaction was quenched with water (10 mL), and extracted with EtOAc (20 mL x 3). The organic layer was dried with Na_2SO_4, and concentrated by rotary evaporator under reduced pressure. The residue was purified by flash column chromatography to give **A** as colorless oil in 40% yield (2.61 g).

To a stirred solution of **A** (8 mmol, 2.61 g) in DMSO (50 mL) at room temperature at nitrogen atmosphere was added KO^{t}Bu (12 mmol, 1.344 g) in three times. The resulting mixture was stirred for additional 2 h. Then the reaction was quenched with water (10 mL), and extracted with EtOAc (20 mL x 3). The combined organic layer was dried with Na_2SO_4 and concentrated by rotary evaporator under reduced pressure. The residue was purified by flash column chromatography to give **B** as yellow oil in 98% yield (1.97 g).

A solution of **B** (8 mmol, 1.97 g), phenyl acetylene (12 mmol, 1.22 g), $Pd(PPh_3)_2Cl_2$ (0.16 mmol, 112 mg) and CuI (0.4 mmol, 76 mg) in Et_3N (30 mL) was stirrer at room temperature at nitrogen atmosphere for 3 h. The reaction was quenched with water (10 mL) and extracted with EtOAc (20 mL x 3). The combined organic layer was dried

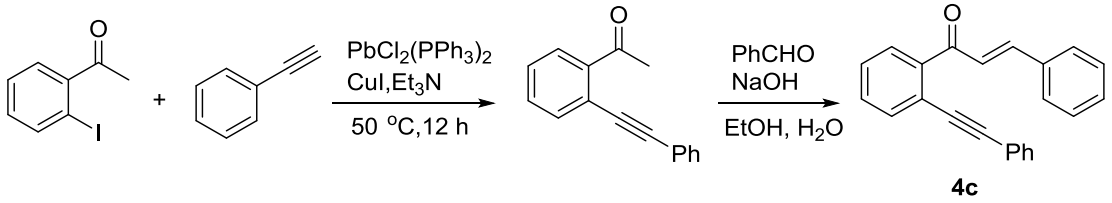
with Na_2SO_4 and concentrated by rotary evaporator under reduced pressure. The residue was purified by flash column chromatography to give **1a** as yellow oil in 98% yield (1.76 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 10.4, 5.5 Hz, 3H), 7.45 – 7.34 (m, 4H), 7.19 – 7.07 (m, 2H), 6.76 (dd, *J* = 13.7, 6.1 Hz, 1H), 4.86 (d, *J* = 13.7 Hz, 1H), 4.54 (d, *J* = 6.1 Hz, 1H). The NMR data are consistent with the reported literature.[1]

Preparation of 4b.[2]



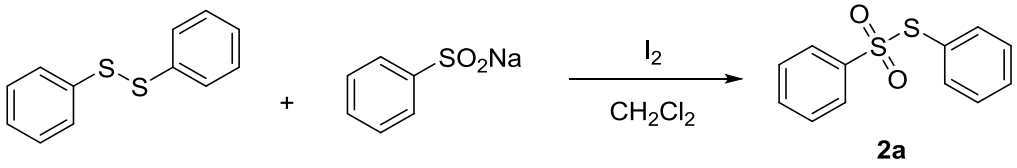
The *N*-(2-(phenylethynyl)phenyl)-*N*-vinylbenzenesulfonamide **4b** was synthesized according to the literature procedures.[2] Yellow oil (2.01g, 56%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.6 Hz, 2H), 7.48 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.29 – 7.18 (m, 9H), 7.12 (dd, *J* = 15.5, 8.9 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 4.23 (d, *J* = 8.9 Hz, 1H), 3.75 (d, *J* = 15.5 Hz, 1H). The NMR data are consistent with the reported literature. [2]

Preparation of 4c.[3]



The (*E*)-3-phenyl-1-(2-(phenylethynyl)phenyl)prop-2-en-1-one **4c** was synthesized according to the literature procedures.[3] Yellow solid (443 mg, 72%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 6.4, 5.5 Hz, 1H), 7.68 (s, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.62 – 7.55 (m, 3H), 7.51 – 7.42 (m, 2H), 7.37 – 7.32 (m, 5H), 7.25 (dd, *J* = 4.8, 2.3 Hz, 1H), 7.20 (t, *J* = 7.3 Hz, 2H). The NMR data are consistent with the reported literature.[3]

Preparation of Substrate 2.[4]



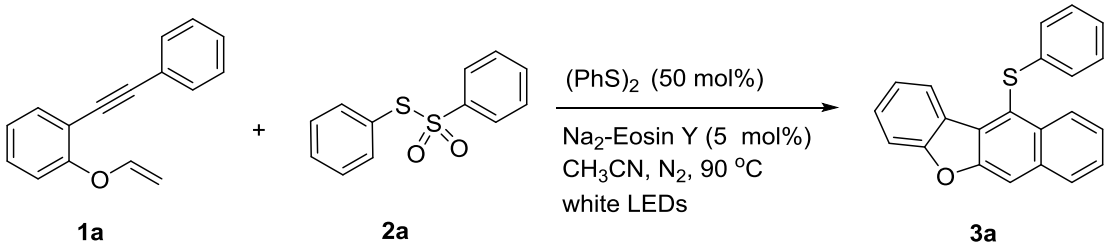
To a stirred solution of sodium sulfinate (6.4 mmol, 1.05 g) and disulfide (2 mmol, 436 mg) in CH_2Cl_2 (20 mL) was added I_2 (4 mmol, 1.02 g) at room temperature. The reaction was detected by TLC until the disulfide was consumed, then CH_2Cl_2 (50 mL)

was added, followed by aqueous $Na_2S_2O_3$ (1 M, 10 mL). The organic layer was washed with H_2O (50 mL x 3) and dried with Na_2SO_4. The organic layer was concentrated under reduced pressure. The residue was purified by flash column chromatography to give **2a** as colorless crystal in 94% yield (470 mg).

Photoreactor configuration

Reactions were irradiated by a simple photoreactor which is consist of a 30 W white LED lamp and heating mantle, and the inside of reaction box was equipped with tin foil to reflect light. The distance between lamp and the quartz tube was 2 cm. And the temperature of reaction box was 90 ^oC measured by a standard alcohol thermometer.

General Procedure for the Synthesis of Compound 3.

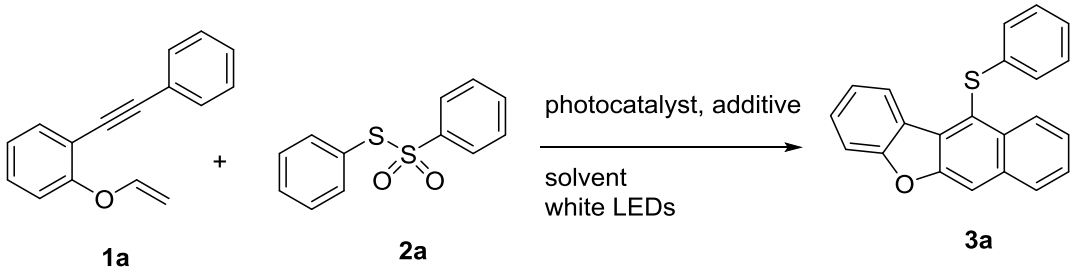


A solution of **1a** (44 mg, 0.2 mmol), **2a** (75 mg, 0.3 mmol), 1,2-diphenyldisulfane (0.1 mmol, 21.8 mg) and Na_2-Eosin Y (0.01 mmol, 7 mg) in CH_3CN (2 mL) in a quartz tube was stirred at 90 ^oC under the irradiation of 30 W white LEDs at nitrogen atmosphere for 12 h. Then the mixture was concentrated under reduced pressure, and the residue was purified by flash column chromatography to give **3a** in 70% yield.

Typical experimental procedure for the synthesis of product 3a in 1mmol scale.

A solution of **1a** (220 mg, 1 mmol), **2a** (375 mg, 1.5 mmol), 1,2-diphenyldisulfane (0.5 mmol, 109 mg) and Na_2-Eosin Y (0.05 mmol, 35 mg) in CH_3CN (5 mL) in a quartz tube was stirred at 90 ^oC under the irradiation of 30 W white LEDs at nitrogen atmosphere for 12 h. Then the mixture was concentrated under reduced pressure, and the residue was purified by flash column chromatography to give **3a** in 59% yield （192 mg）.

Condition Optimization

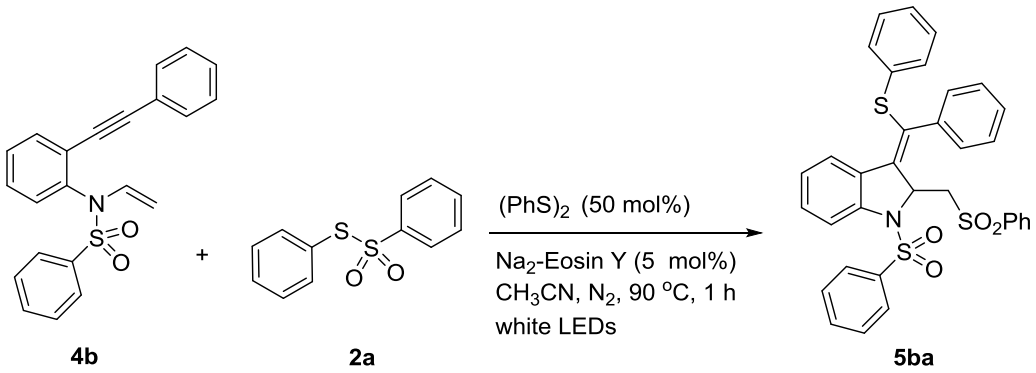


1a 2a 3a

Entry	Photocatalyst	Tem. (^{o}C)	Additive (mol%)	Solvent	Yield (%)
1	Na_2-Eosin Y	80	no	CH_3CN	55
2	no	80	no	CH_3CN	trace
3	Eosin Y	80	no	CH_3CN	31
4	Mes-AcrPh$^+BF_4$	80	no	CH_3CN	trace
5	Rhodamine B	80	no	CH_3CN	50
6	Bengal Rose	80	no	CH_3CN	43
7	$Ru(bpy)_3Cl_2$	80	no	CH_3CN	trace
8	$Ir(ppy)_3$	80	no	CH_3CN	20
9	$Ir(bpy)(ppy)_2PF_6$	80	no	CH_3CN	25
10	Na_2-Eosin Y	80	no	DCE	10
11	Na_2-Eosin Y	80	no	DMF	0
12	Na_2-Eosin Y	80	no	toluene	0
13	Na_2-Eosin Y	80	no	EtOAc	18
14	Na_2-Eosin Y	80	no	1,4-dioxane	16
15	Na_2-Eosin Y	90	no	CH_3CN	60
16	Na_2-Eosin Y	100	no	CH_3CN	56
17	Na_2-Eosin Y	90	$(PhS)_2$ (20 mol%)	CH_3CN	65
18	Na_2-Eosin Y	90	$(PhS)_2$ (50 mol%)	CH_3CN	70
19[b]	Na_2-Eosin Y	90	$(PhS)_2$ (50 mol%)	CH_3CN	trace
20[c]	Na_2-Eosin Y	90	$(PhS)_2$ (50 mol%)	CH_3CN	0

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol) and photocatalyst (5 mol%) in solvent (2.0 mL) under the irradiation of 30 W white LEDs at 80 ^{o}C at nitrogen atmosphere was stirred for 12 h, data in parentheses are the yields of isolated products. [b]The reaction was performed at air atmosphere. [c]The reaction was performed in the dark.

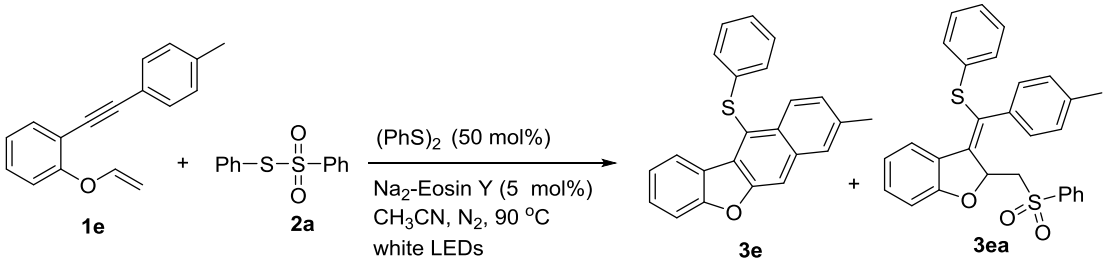
General Procedure for the Synthesis of Compound 5ba.



4b **2a** **5ba**

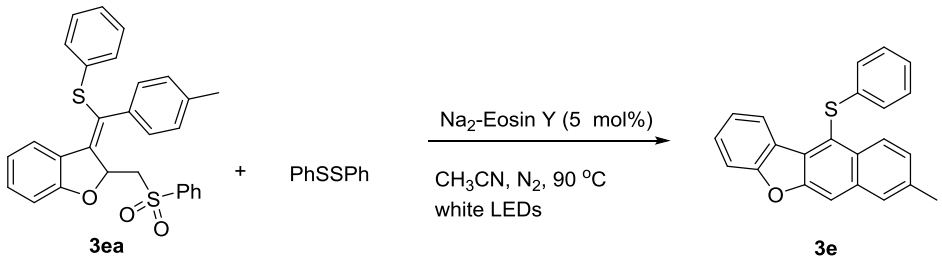
A solution of **4b** (72 mg, 0.2 mmol), **2a** (75 mg, 0.3 mmol), 1,2-diphenyldisulfane (0.1 mmol, 21.8 mg) and Na_2-Eosin Y (0.01 mmol, 7 mg) in CH_3CN (2 mL) in a quartz tube was stirred at 90 ^oC under the irradiation of 30 W white LEDs at nitrogen atmosphere for 1 h. Then the mixture was concentrated under reduced pressure, and the residue was purified by flash column chromatography to give **5ba**. Yellow solid (85.3 mg, 70%); R_f = 0.3 (petroleum ether/ethyl acetate = 10:1); mp: 77-79 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.69 (m, 2H), 7.56 – 7.37 (m, 7H), 7.29 (dd, *J* = 8.2, 7.6 Hz, 3H), 7.22 (d, *J* = 8.1 Hz, 1H), 7.10 – 6.96 (m, 7H), 6.95 – 6.91 (m, 2H), 6.64 – 6.59 (m, 1H), 6.04 (d, *J* = 7.5 Hz, 1H), 5.42 (dd, *J* = 6.0, 3.3 Hz, 1H), 4.09 (dd, *J* = 15.2, 6.0 Hz, 1H), 3.96 (dd, *J* = 15.2, 3.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 140.1, 136.4, 136.3, 135.1, 133.5, 133.4, 132.3, 131.5, 131.0, 130.5, 129.4, 129.1, 129.0, 128.8, 128.4, 128.2, 127.8, 127.5, 125.3, 124.0, 118.6, 63.2, 58.9. HRMS (ESI): m/z $[M+NH_4]^+$ calcd for $C_{34}H_{31}N_2O_4S_3$: 627.1440, found 627.1444.

Controlled experiments

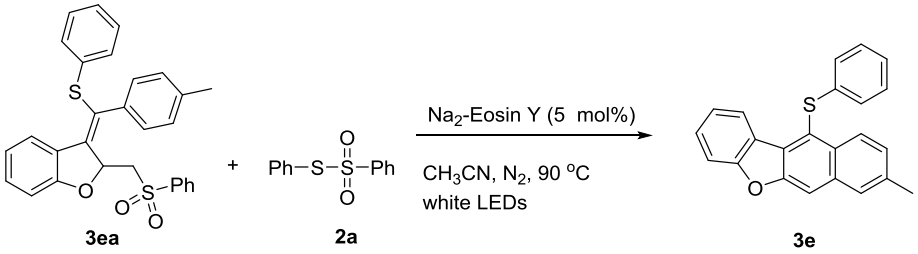


1e **2a** **3e** **3ea**

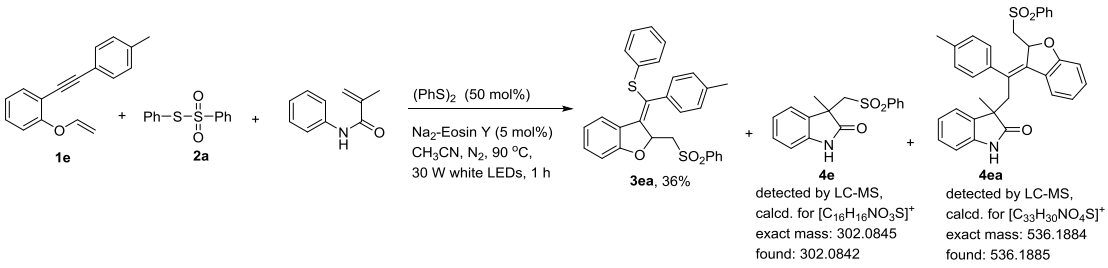
A solution of **1e** (0.2 mmol, 68 mg), **2a** (0.3 mmol, 75 mg), phenyl disulfide (0.1 mmol, 22 mg) and Na_2-Eosin Y (0.01 mmol, 7 mg) in CH_3CN (2 mL) in a quartz tube was stirred at 90 ^oC under the irradiation of 30 W white LEDs at nitrogen atmosphere for 45 min. Then the mixture was concentrated under reduced pressure, and the residue was purified by flash column chromatography to give **3ea** in 81% yield. When the reaction was carried out at 47 ^oC, the yield of **3ea** was 22%.



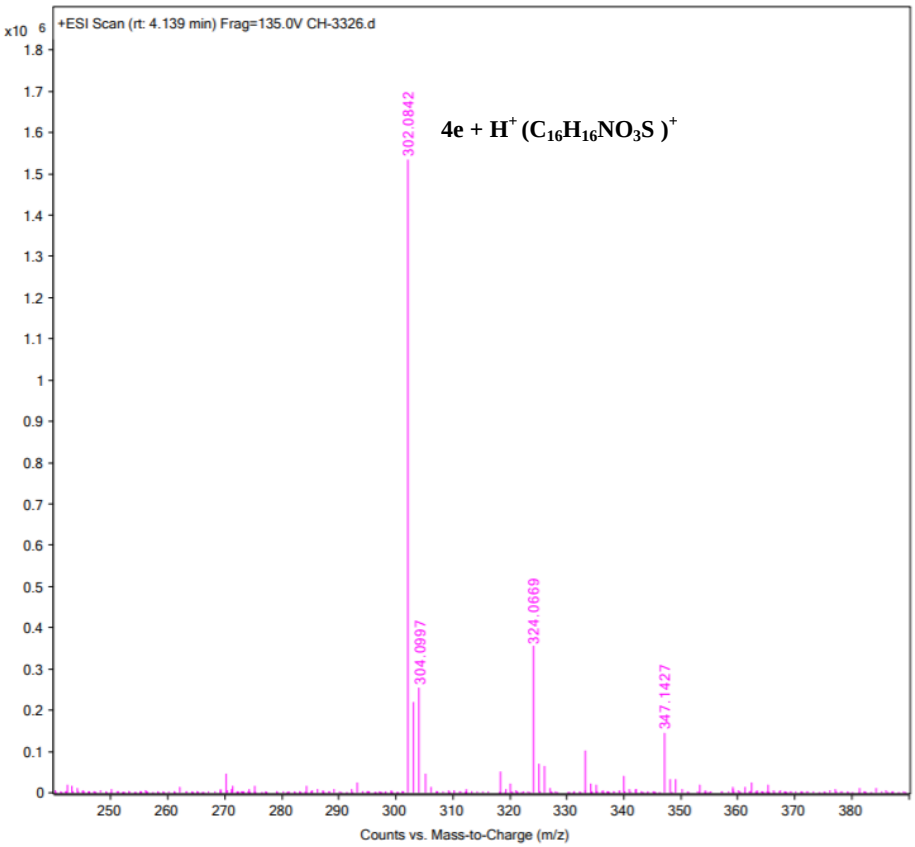
A solution of **3ea** (48 mg, 0.1 mmol), phenyl disulfide (37.5 mg, 0.15 mmol) and Na_2-Eosin Y (0.005 mmol, 3.5 mg) in CH_3CN (1 mL) in a quartz tube was stirred at 90 ^oC under the irradiation of 30 W white LEDs at nitrogen atmosphere for 12 h. Then the mixture was concentrated under reduced pressure, and the residue was purified by flash column chromatography to give **3e** in 69% yield.



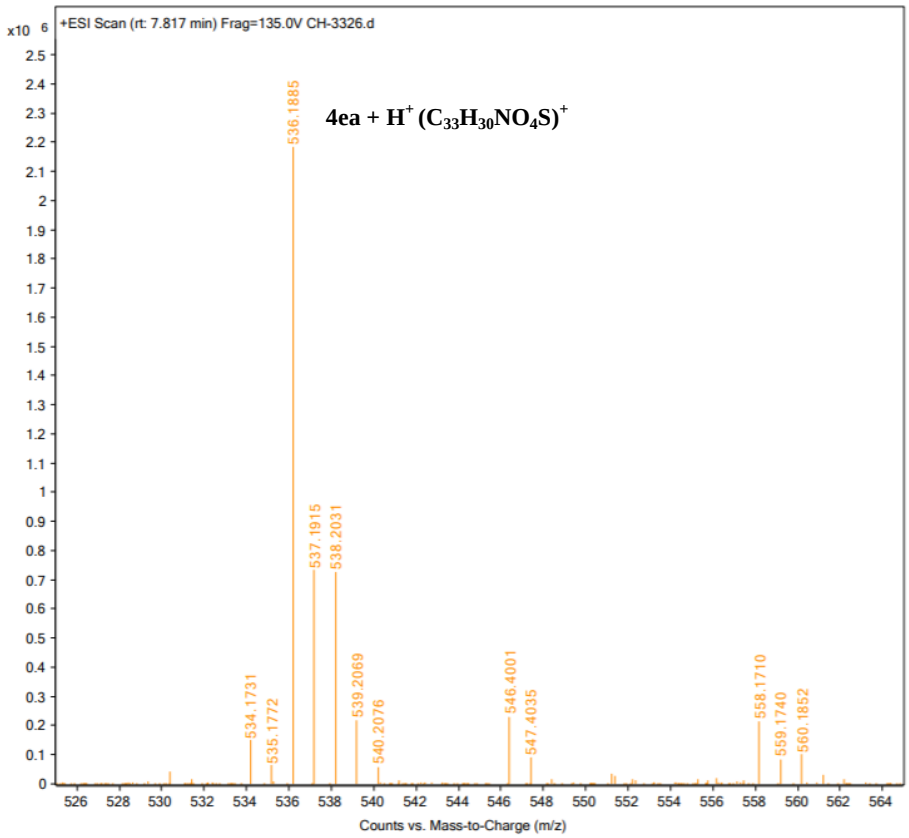
A solution of **3ea** (48.4 mg, 0.1 mmol), **2a** (37.5 mg, 0.15 mmol) and Na_2-Eosin Y (0.005 mmol, 3.5 mg) in CH_3CN (1 mL) in a quartz tube was stirred at 90 ^oC under the irradiation of 30 W white LEDs at nitrogen atmosphere for 12 h. Then the mixture was concentrated under reduced pressure, and the residue was purified by flash column chromatography to give **3e** in 64% yield.



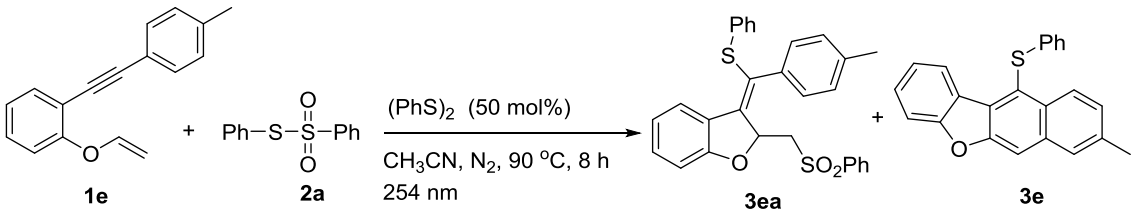
A solution of **1e** (0.2 mmol, 68 mg), **2a** (0.3 mmol, 75 mg), phenyl disulfide (0.1 mmol, 22 mg) and *N*-phenylmethacrylamide (0.6 mmol, 96 mg) in CH_3CN (2 mL) in a quartz tube was stirred at 90 ^oC under the irradiation of 30 W white LEDs at nitrogen atmosphere for 1 h. Then the mixture was analyzed by LC-MS, radical adducts **4e** and **4ea** were detected. The mixture was concentrated under reduced pressure, and the residue was purified by flash column chromatography to give **3ea** in 36% yield



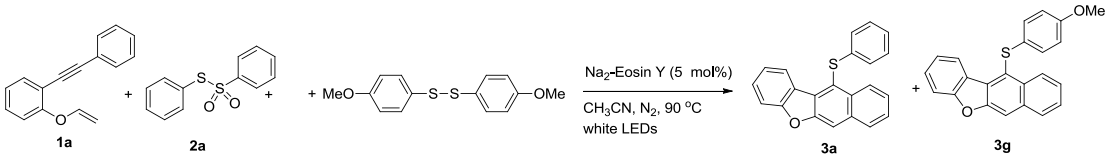
4e + H^+ $(C_{16}H_{16}NO_3S)^+$



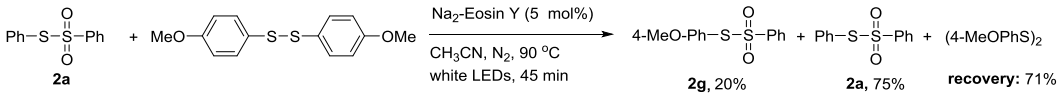
4ea + H^+ $(C_{33}H_{30}NO_4S)^+$



A solution of **1e** (0.2 mmol, 68 mg), **2a** (0.3 mmol, 75 mg), phenyl disulfide (0.1 mmol, 22 mg) in CH_3CN (2 mL) in a quartz tube was stirred at 90 °C under the irradiation of 254 nm light (6 W) at nitrogen atmosphere for 8 h. Then the mixture was concentrated under reduced pressure, and the residue was purified by flash column chromatography to give **3ea** and **3e** in 43% and 14% yield, respectively.



A solution of **1a** (0.2 mmol, 44 mg,), **2a** (0.3 mmol, 75 mg), di(4-methoxyphenyl) persulfide (0.3 mol, 83.4 mg) and Na_2-Eosin Y (0.005 mmol, 7 mg) in CH_3CN (2 mL) in a quartz tube was stirred at 90 °C under the irradiation of 30 W white LEDs at nitrogen atmosphere for 12 h. Then the mixture was concentrated under reduced pressure, and the residue was purified by flash column chromatography to give **3a** in 16% yield and **3g** in 47% yield.



A solution of **2a** (0.2 mmol, 50 mg), di(4-methoxyphenyl) disulfide (0.2 mol, 55.6 mg) and Na_2-Eosin Y (0.005 mmol, 7 mg) in CH_3CN (2 mL) in a quartz tube was stirred at 90 °C under the irradiation of 30 W white LEDs at nitrogen atmosphere for 45 min. Then the mixture was concentrated under reduced pressure, and the residue was purified by flash column chromatography to give **2g** in 20% yield, **2a** and di(4-methoxyphenyl) disulfide were recoveries in 75% and 71%, respectively.

Photophysical Properties

The photophysical properties of compounds **3g, 3i, 3q, 3s, 3u, 3w** and **3y** in DCE.

Compounds	λ_{abs} [a][nm]	λ_{em} [b][nm]	ε [M^{-1} cm^{-1}]
3g	273.5	389.5	2518.0
3i	274.8	442.5	2334.0
3q	268.0	385.5	2012.8
3s	273.5	391.5	2391.0
3u	267.8	382.5	1944.3
3w	273.5	394.5	2364.0
3y	273.5	381.5	2409.0

[a] Absorption maxima in DCE (10^{-5} mol/L). [b] Emission maxima in DCE (10^{-5} mol/L).

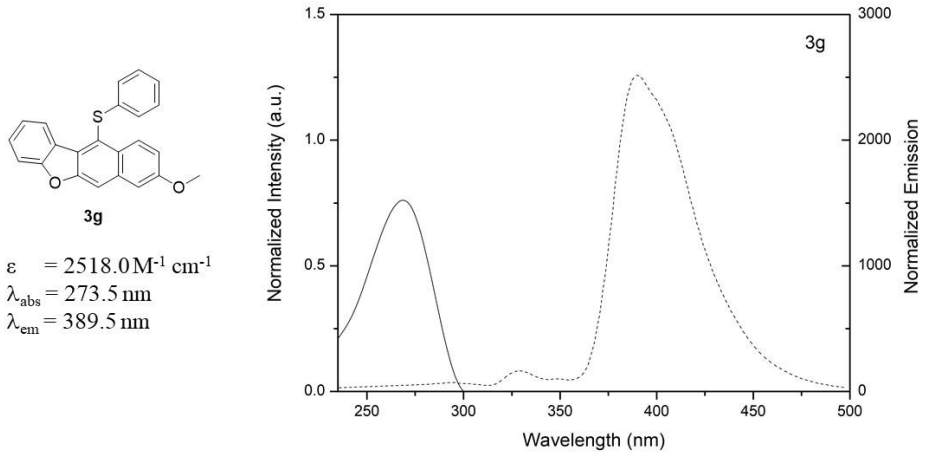


Figure 1. UV/Vis absorption spectra (solid lines) and fluorescence emission spectra (dashed line) obtained for compounds **3g** in DCE.

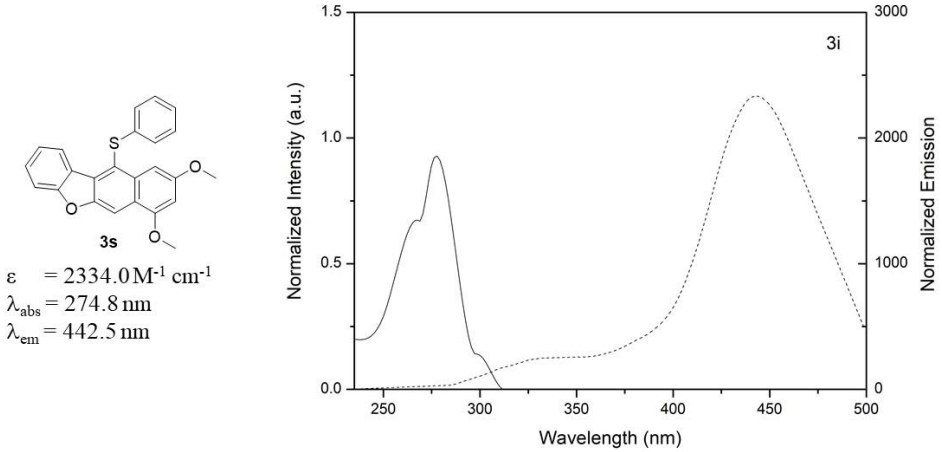


Figure 2. UV/Vis absorption spectra (solid lines) and fluorescence emission spectra (dashed line) obtained for compounds **3i** in DCE.

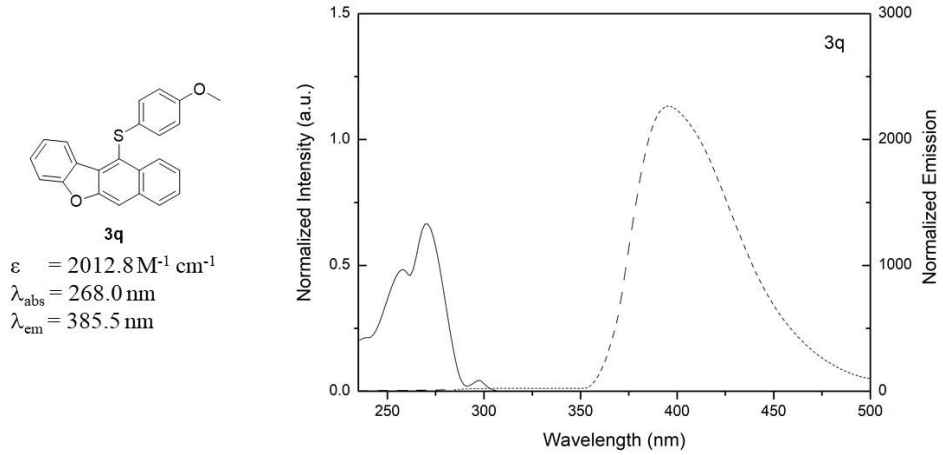


Figure 3. UV/Vis absorption spectra (solid lines) and fluorescence emission spectra (dashed line) obtained for compounds **3q** in DCE.

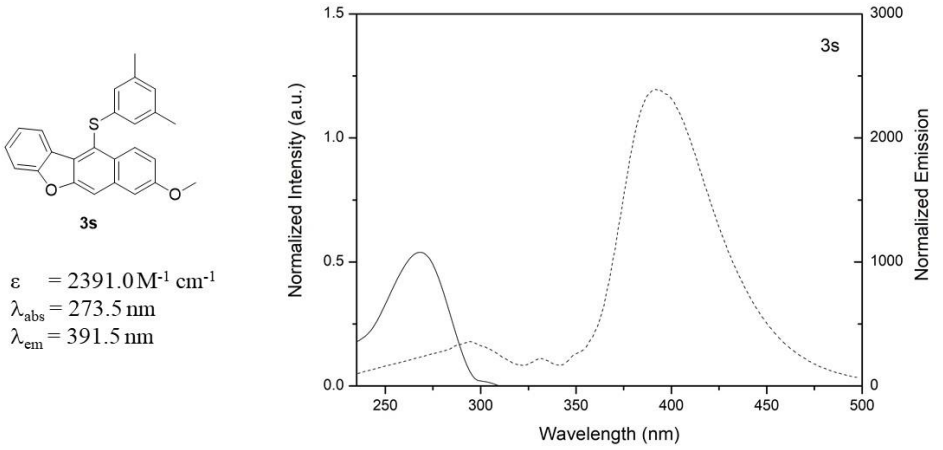


Figure 4. UV/Vis absorption spectra (solid lines) and fluorescence emission spectra (dashed line) obtained for compounds **3s** in DCE.

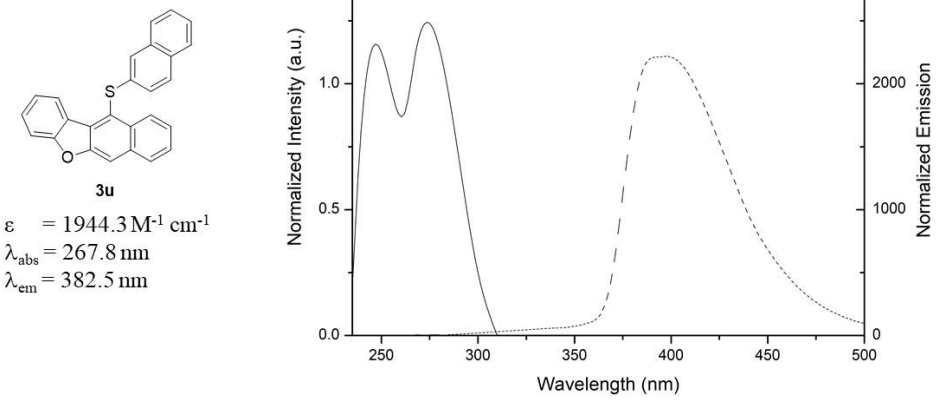


Figure 5. UV/Vis absorption spectra (solid lines) and fluorescence emission spectra (dashed line) obtained for compounds **3u** in DCE.

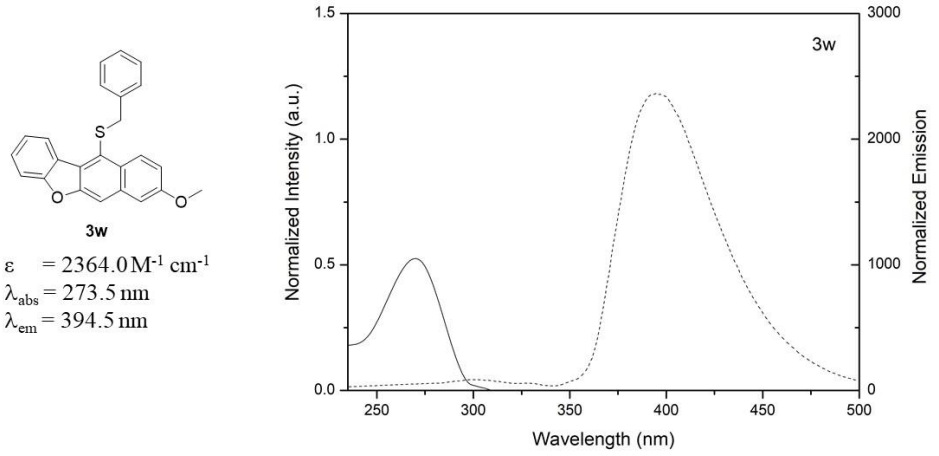


Figure 6. UV/Vis absorption spectra (solid lines) and fluorescence emission spectra (dashed line) obtained for compounds **3w** in DCE.

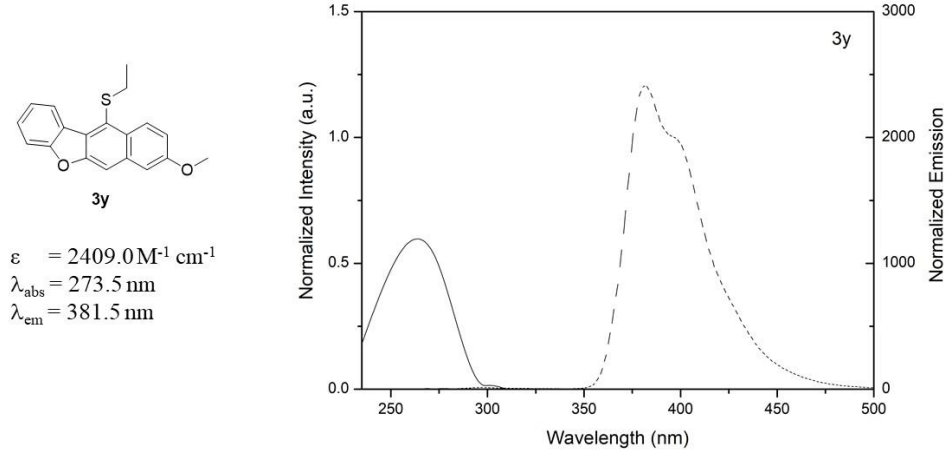


Figure 7. UV/Vis absorption spectra (solid lines) and fluorescence emission spectra (dashed line) obtained for compounds **3y** in DCE.

References

1. Norifumi, S.; Keiichi, N.; Ken, T. Rhodium-Catalyzed Intramolecular Cyclization of Naphthol- or Phenol-Linked 1,6-Enynes Through the Cleavage and Formation of sp^2 C−O Bonds. *Angew. Chem. Int. Ed.* **2012**, *51*, 5976.

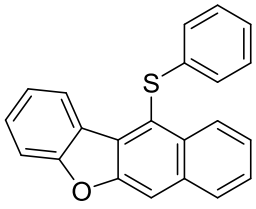
2. Sadhan, J.; Ajay, V.; Rahul, K.; Sangit, K. Visible-light-induced oxidant and metal-free dehydrogenative cascade trifluoromethylation and oxidation of 1,6-enynes with water. *Chem. Sci.* **2017**, *8*, 6633.

3. Wu Y.-N.; Fu R.; Wang N.-N.; Hao W.-J.; Li G.-G.; Tu S.-J.; Jiang B. Catalytic Sulfur-Enabled Dehydrobicyclization of 1,6-Enynes toward Arylated Indeno[1,2-*c*]thiophenes. *J. Org. Chem.* **2016**, *81*, 4762.

4. Fujiki, K.; Tanifuji, N.; Sasaki, Y.; Yokoyama, T. New and Facile Synthesis of Thiosulfonates from Sulfinate/Disulfide/I_2 System. *Synthesis.* **2002**, 343.

Analytical Data of Products

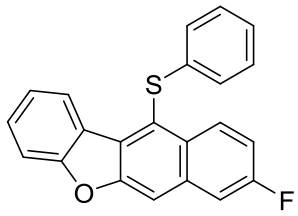
*11-(phenylthio)naphtho[2,3-b]benzofuran (**3a**)*



White solid (45.6 mg, 70%); R_f = 0.6 (petroleum ether); mp: 138-140 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.68 (t, *J* = 7.5 Hz, 2H), 8.01 – 7.94 (m, 2H), 7.53 – 7.45 (m, 4H), 7.27 (dd, *J* = 10.8, 4.1 Hz, 1H), 7.10 – 6.98 (m, 5H). ^{13}C NMR (100 MHz,

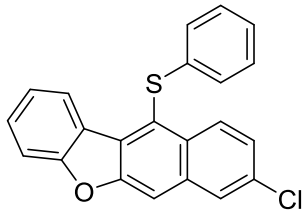
$CDCl_3$) δ 158.0, 154.2, 137.3, 133.4, 132.7, 130.4, 129.1, 129.1, 128.3, 126.5, 126.3, 126.0, 125.7, 125.4, 125.1, 124.0, 123.0, 122.4, 111.3, 109.5. HRMS (EI) m/z: $[M]^+$ calcd for $C_{22}H_{14}OS$, 326.0765; found, 326.0763.

*8-fluoro-11-(phenylthio)naphtho[2,3-b]benzofuran (**3b**)*



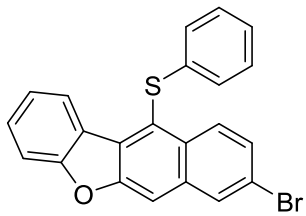
White solid (34 mg, 50%); R_f = 0.6 (petroleum ether); mp: 123-125 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 – 8.57 (m, 2H), 7.93 (s, 1H), 7.60 – 7.46 (m, 3H), 7.31 – 7.23 (m, 2H), 7.11 (t, *J* = 7.4 Hz, 2H), 7.07 – 6.98 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0 (d, C-F, $^1J_{C\text{-}F}$ = 247.8 Hz), 157.8, 155.0, 137.0, 134.3 (d, C-F, $^3J_{C\text{-}F}$ = 9.8 Hz), 129.8 (d, C-F, $^4J_{C\text{-}F}$ = 2.4 Hz), 129.6, 129.2, 129.1, 128.8 (d, C-F, $^3J_{C\text{-}F}$ = 9.2 Hz), 126.5, 125.5, 124.9, 123.8, 123.1, 122.8, 116.08 (d, C-F, $^2J_{C\text{-}F}$ = 25.3 Hz), 111.3, 111.2 (d, C-F, $^2J_{C\text{-}F}$ = 21.5 Hz), 108.9 (d, C-F, $^4J_{C\text{-}F}$ = 5.5 Hz). HRMS (EI) m/z: $[M]^+$ calcd for $C_{22}H_{13}FOS$, 344.0671; found, 344.0674.

*8-chloro-11-(phenylthio)naphtho[2,3-b]benzofuran (**3c**)*



White solid (39.6 mg, 55%); R_f = 0.6 (petroleum ether); mp: 144-146 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (dd, *J* = 16.3, 8.5 Hz, 2H), 7.83 (d, *J* = 2.1 Hz, 1H), 7.77 (s, 1H), 7.45 – 7.37 (m, 2H), 7.31 (dd, *J* = 9.2, 2.1 Hz, 1H), 7.21 – 7.17 (m, 1H), 7.02 (dd, *J* = 10.2, 4.6 Hz, 2H), 6.96 – 6.89 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 154.8, 136.9, 133.9, 132.3, 130.8, 130.5, 129.3, 129.2, 127.8, 126.7, 126.6, 126.5, 125.6, 125.0, 123.6, 123.1, 122.8, 111.3, 108.6. HRMS (EI) m/z: $[M]^+$ calcd for $C_{22}H_{13}ClOS$, 360.0376; found, 360.0379.

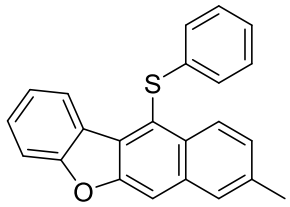
*8-bromo-11-(phenylthio)naphtho[2,3-b]benzofuran (**3d**)*



White solid (47.1 mg, 58%); R_f = 0.6 (petroleum ether); mp: 167-169 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 – 8.51 (m, 1H), 8.41 (d, *J* = 9.1 Hz, 1H), 7.98 (d, *J* = 1.9 Hz,

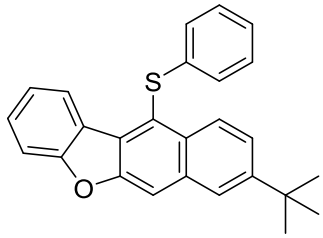
1H), 7.74 (s, 1H), 7.44 – 7.38 (m, 3H), 7.18 (ddd, *J* = 8.1, 6.3, 2.0 Hz, 1H), 7.03 – 6.98 (m, 2H), 6.94 –6.89 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 154.7, 136.9, 134.3, 131.0, 130.6, 130.0, 129.4, 129.2, 129.0, 127.8, 126.6, 125.6, 125.1, 123.6, 123.2, 122.9, 120.7, 111.4, 108.6. HRMS (EI) m/z: $[M]^+$ calcd for $C_{22}H_{13}BrOS$, 405.9850; found, 405.9858.

*8-methyl-11-(phenylthio)naphtho[2,3-b]benzofuran (**3e**)*



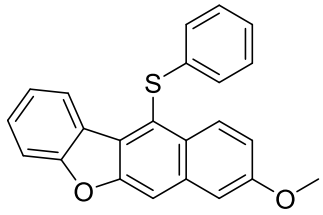
White solid (44.7 mg, 65%); R_f = 0.6 (petroleum ether); mp: 118-120 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.56 (d, *J* = 8.8 Hz, 1H), 7.88 (s, 1H), 7.71 (s, 1H), 7.51 (d, *J* = 8.1 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.32 – 7.20 (m, 3H), 7.08 (dd, *J* = 10.4, 4.4 Hz, 2H), 7.02 (d, *J* = 7.3 Hz, 2H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 154.4, 137.5, 136.2, 133.7, 131.0, 129.5, 129.1, 128.8, 128.1, 127.2, 126.5, 125.8, 125.3, 124.9, 124.1, 122.9, 122.1, 111.2, 108.9, 21.6. HRMS (EI) m/z: $[M]^+$ calcd for $C_{23}H_{16}OS$, 320.0922; found, 340.0929.

*8-(tert-butyl)-11-(phenylthio)naphtho[2,3-b]benzofuran (**3f**)*



White solid (46 mg, 60%); R_f = 0.5 (petroleum ether); mp: 106-108 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (t, *J* = 8.6 Hz, 2H), 7.89 (s, 1H), 7.80 (s, 1H), 7.50 (dd, *J* = 9.1, 1.6 Hz, 1H), 7.44 – 7.39 (m, 1H), 7.37 (dd, *J* = 7.2, 1.0 Hz, 1H), 7.16 (d, *J* = 7.7 Hz, 1H), 7.01 – 6.88 (m, 5H), 1.33 (d, *J* = 2.2 Hz, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.9, 154.4, 149.1, 137.4, 133.5, 131.0, 129.7, 129.1, 128.8, 126.5, 125.7, 125.3, 124.9, 124.9, 124.1, 123.2, 122.9, 121.8, 111.2, 109.6, 34.9, 31.2. HRMS (EI) m/z: $[M]^+$ calcd for $C_{26}H_{22}OS$, 382.1391; found, 382.1400.

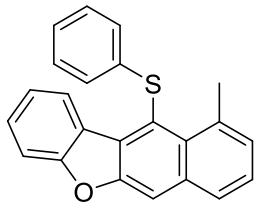
*8-methoxy-11-(phenylthio)naphtho[2,3-b]benzofuran (**3g**)*



Light yellow solid (50.6 mg, 71%); R_f = 0.3 (petroleum ether/ethyl acetate = 200:1);

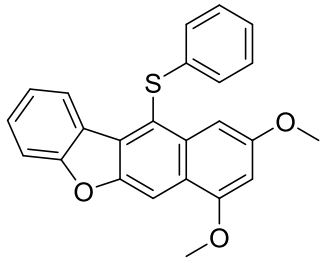
mp: 147-149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (dd, *J* = 12.3, 8.6 Hz, 2H)，7.77 (s, 1H)，7.41 (d, *J* = 8.1 Hz, 1H)，7.36 (dt, *J* = 8.1, 4.1 Hz, 1H)，7.19 – 7.14 (m, 1H)，7.13 (d, *J* = 2.1 Hz, 1H)，7.06 (dd, *J* = 9.3, 2.6 Hz, 1H)，7.02 – 6.97 (m, 2H)，6.96 – 6.89 (m, 3H)，3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 157.6, 154.9, 137.4, 134.9, 129.1, 128.5, 128.2, 128.1, 127.7, 126.4, 125.3, 124.6, 124.2, 122.9, 122.4, 118.8, 111.2, 108.4, 105.9, 55.4. HRMS (EI) m/z: $[M]^+$ calcd for $C_{23}H_{16}O_2S$, 356.0871; found, 356.0878.

*10-methyl-11-(phenylthio)naphtho[2,3-b]benzofuran (**3h**)*



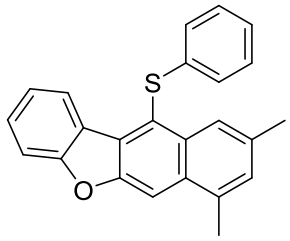
White solid (30 mg, 44%); R_f = 0.6 (petroleum ether); mp: 120-122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.0 Hz, 1H), 7.98 (s, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.47 (dd, *J* = 17.7, 7.5 Hz, 2H), 7.39 – 7.33 (m, 1H), 7.27 (d, *J* = 6.8 Hz, 1H), 7.23 – 7.20 (m, 1H), 7.08 (t, *J* = 7.7 Hz, 2H), 7.00 – 6.86 (m, 3H), 3.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 153.3, 139.5, 136.6, 135.2, 132.7, 132.7, 130.2, 129.2, 128.9, 128.0, 125.8, 125.7, 125.3, 124.8, 124.5, 122.8, 122.2, 111.2, 111.1, 26.6. HRMS (EI) m/z: $[M]^+$ calcd for $C_{23}H_{16}OS$, 340.0922; found, 340.0931.

*7,9-dimethoxy-11-(phenylthio)naphtho[2,3-b]benzofuran (**3i**)*



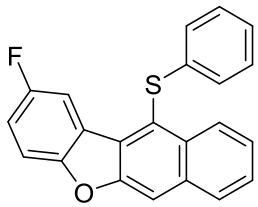
Yellow solid (41.7 mg, 54%); R_f = 0.3 (petroleum ether/ethyl acetate = 200:1); mp: 143-145 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (dd, *J* = 7.9, 0.6 Hz, 1H), 8.31 (s, 1H), 7.48 (dd, *J* = 8.0, 5.1 Hz, 2H), 7.43 – 7.37 (m, 1H), 7.22 – 7.18 (m, 1H), 7.05 – 6.93 (m, 5H), 6.48 (d, *J* = 2.2 Hz, 1H), 3.93 (s, 3H), 3.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 158.0, 156.6, 152.7, 137.2, 134.6, 130.5, 129.0, 128.8, 126.7, 125.3, 124.9, 124.1, 122.7, 121.8, 120.2, 111.3, 104.9, 98.0, 96.0, 55.9, 55.4. HRMS (EI) m/z: $[M]^+$ calcd for $C_{24}H_{18}O_3S$, 386.0977; found, 386.0980.

*7,9-dimethyl-11-(phenylthio)naphtho[2,3-b]benzofuran (**3j**)*



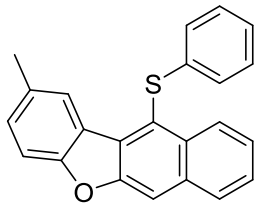
White solid (41 mg, 58%); R_f = 0.6 (petroleum ether); mp: 126-128 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.53 (dd, *J* = 7.8, 0.6 Hz, 1H), 8.30 (s, 1H), 8.06 – 8.01 (m, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.40 – 7.34 (m, 1H), 7.17 (dd, *J* = 11.0, 4.0 Hz, 1H), 7.13 (s, 1H), 7.02 – 6.90 (m, 5H), 2.64 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 153.8, 137.6, 134.9, 134.1, 133.3, 131.0, 129.7, 129.6, 129.1, 128.8, 126.3, 125.2, 125.0, 124.1, 123.1, 122.8, 121.7, 111.2, 106.2, 22.0, 20.1. HRMS (EI) m/z: $[M]^+$ calcd for $C_{24}H_{18}OS$, 354.1078; found, 354.1078.

*2-fluoro-11-(phenylthio)naphtho[2,3-b]benzofuran (**3k**)*



White solid (32.4 mg, 47%); R_f = 0.4 (petroleum ether); mp: 147-149 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.70 (dd, *J* = 8.3, 0.9 Hz, 1H), 8.38 (dd, *J* = 8.9, 2.7 Hz, 1H), 8.06 – 7.98 (m, 2H), 7.60 – 7.47 (m, 2H), 7.49 (dd, *J* = 8.9, 4.1 Hz, 1H), 7.22 (td, *J* = 8.8, 2.8 Hz, 1H), 7.16 – 7.09 (m, 2H), 7.08 – 7.01 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8 (d, C-F, $^1J_{C\text{-}F}$ = 239.2 Hz), 154.9, 154.0, 136.9, 133.6, 132.6, 129.8 (d, C-F, $^4J_{C\text{-}F}$ = 3.8 Hz), 129.2, 128.3, 126.6, 126.5, 126.1, 125.9, 125.5, 124.9 (d, C-F, $^3J_{C\text{-}F}$ = 10.7 Hz), 123.0, 116.3 (d, C-F, $^2J_{C\text{-}F}$ = 25.9 Hz), 111.8 (d, C-F, $^3J_{C\text{-}F}$ = 9.1 Hz), 111.2 (d, C-F, $^2J_{C\text{-}F}$ = 26.6 Hz), 109.8. HRMS (EI) m/z: $[M]^+$ calcd for $C_{22}H_{13}FOS$, 344.0671; found, 344.0668.

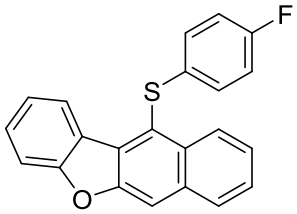
*2-methyl-11-(phenylthio)naphtho[2,3-b]benzofuran (**3l**)*



White solid (35.8 mg, 52%); R_f = 0.6 (petroleum ether); mp: 167-169 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.7 Hz, 1H), 8.41 (d, *J* = 0.4 Hz, 1H), 7.89 (d, *J* = 9.8 Hz, 2H), 7.47 – 7.38 (m, 2H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.21 (d, *J* = 8.3 Hz, 1H), 7.06 – 6.92 (m, 5H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 154.5, 137.5, 133.3, 132.5, 132.4, 130.4, 130.1, 129.1, 128.3, 126.7, 126.2, 126.0, 125.3, 125.4, 125.1, 123.9, 122.3, 110.8, 109.5, 21.5. HRMS (EI) m/z: $[M]^+$ calcd for $C_{23}H_{16}OS$,

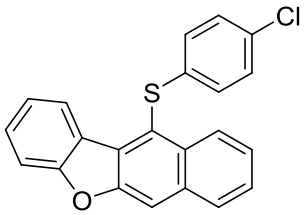
340.0922; found, 340.0929.

*11-((4-fluorophenyl)thio)naphtho[2,3-b]benzofuran (**3m**)*



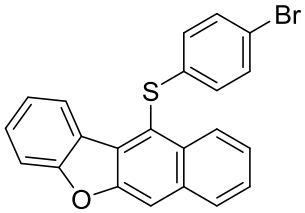
White solid (32 mg, 47%); R_f = 0.5 (petroleum ether); mp: 119-121 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.64 – 8.57 (m, 2H), 7.95 – 7.88 (m, 2H), 7.49 – 7.41 (m, 4H), 7.26 – 7.21 (m, 1H), 6.97 – 6.92 (m, 2H), 6.76 – 6.69 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1 (d, C-F, $^1J_{C-F}$ = 245.1 Hz), 158.0, 154.2, 133.4, 132.4, 132.3 (d, C-F, $^4J_{C-F}$ = 3.1 Hz), 130.3, 129.2, 128.5 (d, C-F, $^3J_{C-F}$ = 8.0 Hz) 128.4, 126.3, 125.8, 125.7, 125.0, 123.9, 123.0, 122.7, 116.4 (d, C-F, $^2J_{C-F}$ = 22.1 Hz), 111.4, 109.7. HRMS (EI) m/z: $[M]^+$ calcd for $C_{22}H_{13}FOS$, 344.0671; found, 344.0676.

*11-((4-chlorophenyl)thio)naphtho[2,3-b]benzofuran (**3n**)*



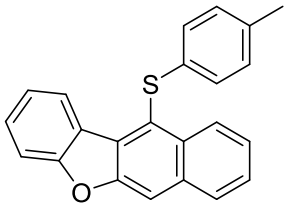
White solid (41.8 mg, 58%); R_f = 0.5 (petroleum ether); mp: 151-153 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.58 – 8.46 (m, 2H), 7.90 – 7.80 (m, 2H), 7.43 – 7.38 (m, 4H), 7.20 – 7.15 (m, 1H), 6.98 – 6.91 (m, 2H), 6.87 – 6.79 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 154.1, 135.9, 133.4, 132.4, 131.2, 130.4, 129.3, 128.4, 127.7, 126.4, 125.9, 125.7, 124.9, 123.8, 123.1, 121.7, 111.4, 109.8. HRMS (EI) m/z: $[M]^+$ calcd for $C_{22}H_{13}ClOS$, 360.0376; found, 360.0373.

*11-((4-bromophenyl)thio)naphtho[2,3-b]benzofuran (**3o**)*



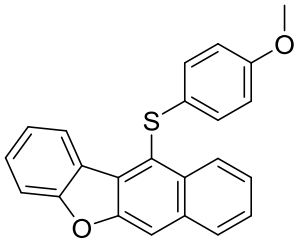
White solid (51.2 mg, 63%); R_f = 0.5 (petroleum ether); mp: 163-165 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.54 – 8.48 (m, 2H), 7.89 (s, 1H), 7.86 (dd, *J* = 7.1, 2.2 Hz, 1H), 7.44 – 7.37 (m, 4H), 7.21 – 7.15 (m, 1H), 7.10 – 7.06 (m, 2H), 6.80 – 6.73 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 154.1, 136.6, 133.4, 132.4, 132.1, 130.4, 129.3, 128.4, 128.0, 126.4, 125.9, 125.7, 124.9, 123.7, 123.1, 121.5, 119.0, 111.4, 109.9. HRMS (EI) m/z: $[M]^+$ calcd for $C_{22}H_{13}BrOS$, 405.9850; found, 405.9854.

*11-(p-tolylthio)naphtho[2,3-b]benzofuran (**3p**)*



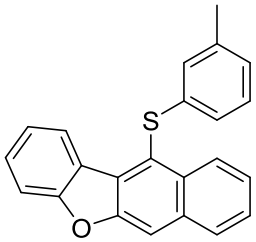
White solid (44.2 mg, 65%); R_f = 0.7 (petroleum ether); mp: 138-140 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 7.6 Hz, 2H), 7.87 – 7.83 (m, 2H), 7.42 – 7.34 (m, 4H), 7.17 (t, *J* = 7.5 Hz, 1H), 6.86 – 6.78 (m, 4H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 154.2, 135.3, 133.8, 133.4, 132.7, 130.3, 129.9, 129.0, 128.3, 126.8, 126.3, 126.1, 125.6, 125.2, 124.1, 123.0, 123.0, 111.3, 109.4, 20.9. HRMS (EI) m/z: $[M]^+$ calcd for $C_{23}H_{16}OS$, 340.0922; found, 340.0928.

*11-((4-methoxyphenyl)thio)naphtho[2,3-b]benzofuran (**3q**)*



Light yellow solid (47 mg, 66%); R_f = 0.3 (petroleum ether/ethyl acetate = 200:1); mp: 132.5-134.1 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.73 – 8.62 (m, 2H), 7.91 – 7.84 (m, 2H), 7.47 – 7.39 (m, 4H), 7.26 – 7.20 (m, 1H), 6.99 – 6.94 (m, 2H), 6.60 – 6.53 (m, 2H), 3.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 158.0, 154.2, 133.4, 132.5, 130.1, 129.0, 128.9, 128.3, 127.9, 126.2, 126.1, 125.5, 125.1, 124.1, 124.0, 123.0, 114.9, 111.3, 109.3, 55.3. HRMS (EI) m/z: $[M]^+$ calcd for $C_{23}H_{16}O_2S$, 356.0871; found, 356.0872.

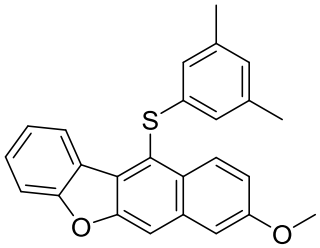
*11-(m-tolylthio)naphtho[2,3-b]benzofuran (**3r**)*



White solid (40.8 mg, 60%); R_f = 0.7 (petroleum ether); mp: 108-110 ^oC.^1H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 7.9 Hz, 2H), 7.95 (s, 1H), 7.94 – 7.89 (m, 1H), 7.49 – 7.41 (m, 4H), 7.23 (t, *J* = 7.5 Hz, 1H), 6.89 (t, *J* = 7.7 Hz, 1H), 6.85 (s, 1H), 6.76 (d, *J* = 7.5 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 2.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 154.2, 138.9, 137.0, 133.4, 132.7, 130.4, 129.0, 129.0, 128.3, 127.0, 126.3, 126.3, 126.1, 125.6, 125.2, 124.0, 123.5, 123.0, 122.5, 111.3, 109.5, 21.4. HRMS (EI)

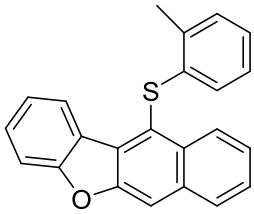
m/z: $[M]^+$ calcd for $C_{23}H_{16}OS$, 340.0922; found, 340.0924.

*11-((3,5-dimethylphenyl)thio)-8-methoxynaphtho[2,3-b]benzofuran (**3s**)*



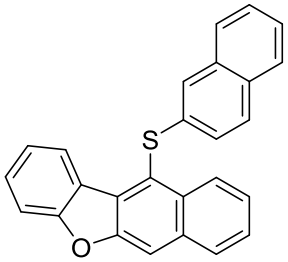
White solid (45.3 mg, 59%); R_f = 0.4 (petroleum ether/ethyl acetate = 250:1); mp: 135-136 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 7.7 Hz, 1H), 8.51 (d, *J* = 9.3 Hz, 1H), 7.85 (s, 1H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.44 – 7.38 (m, 1H), 7.25 – 7.20 (m, 2H), 7.11 (dd, *J* = 9.4, 2.6 Hz, 1H), 6.59 (d, *J* = 4.6 Hz, 3H), 3.90 (s, 3H), 2.03 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 157.6, 154.9, 138.7, 136.9, 134.9, 128.4, 128.3, 128.2, 127.8, 127.4, 124.7, 124.3, 124.0, 122.9, 122.6, 118.6, 111.1, 108.2, 105.9, 55.4, 21.3. HRMS (APCI) m/z: $[M+H]^+$ calcd for $C_{25}H_{21}O_2S$, 385.1257; found, 385.1258.

*11-(o-tolylthio)naphtho[2,3-b]benzofuran (**3t**)*



White solid (41.5 mg, 61%); R_f = 0.7 (petroleum ether); mp: 139-141 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 – 8.52 (m, 2H), 8.06 – 7.98 (m, 2H), 7.56 – 7.46 (m, 4H), 7.27 (ddd, *J* = 8.2, 7.2, 1.1 Hz, 1H), 7.20 (d, *J* = 7.4 Hz, 1H), 6.93 (td, *J* = 7.4, 1.1 Hz, 1H), 6.70 (ddd, *J* = 8.1, 7.4, 0.8 Hz, 1H), 6.31 (dd, *J* = 8.0, 1.0 Hz, 1H), 2.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 154.3, 136.4, 134.7, 133.4, 132.7, 130.5, 130.2, 129.1, 128.3, 126.6, 126.3, 125.9, 125.7, 125.1, 124.9, 124.9, 123.9, 122.9, 122.0, 111.3, 109.5, 20.3. HRMS (EI) m/z: $[M]^+$ calcd for $C_{23}H_{16}OS$, 340.0922; found, 340.0924.

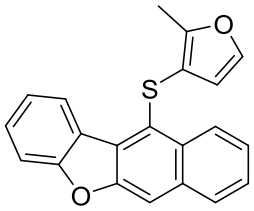
*11-(naphthalen-2-ylthio)naphtho[2,3-b]benzofuran (**3u**)*



White solid (47.4 mg, 63%); R_f = 0.5 (petroleum ether); mp: 204-206 °C. ^{1}H NMR

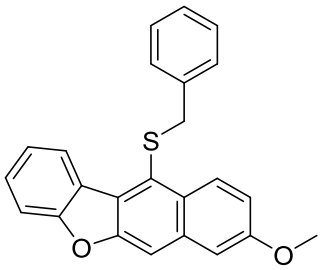
(600 MHz, $CDCl_3$) δ 8.73 (t, *J* = 8.7 Hz, 2H), 8.08 (s, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.69 – 7.65 (m, 1H), 7.60 – 7.54 (m, 3H), 7.52 – 7.47 (m, 3H), 7.42 (s, 1H), 7.35 – 7.30 (m, 2H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.18 (dd, *J* = 8.7, 1.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.0, 154.2, 134.8, 133.8, 133.4, 132.6, 131.4, 130.4, 129.1, 128.7, 128.3, 127.6, 126.9, 126.5, 126.3, 125.9, 125.7, 125.3, 125.0, 124.9, 124.2, 123.9, 123.0, 122.0, 111.3, 109.6. HRMS (EI) m/z: $[M]^+$ calcd for $C_{26}H_{16}OS$, 376.0922; found, 376.0919.

*11-((2-methylfuran-3-yl)thio)naphtho[2,3-b]benzofuran (**3v**)*



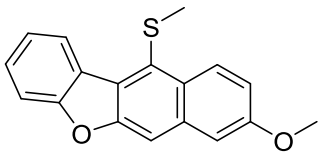
Yellow-green solid (19.8 mg, 30%); R_f = 0.7 (petroleum ether); mp: 119-121 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, *J* = 7.8 Hz, 1H), 8.70 – 8.64 (m, 1H), 7.87 – 7.81 (m, 2H), 7.49 – 7.42 (m, 4H), 7.32 – 7.27 (m, 1H), 6.94 (d, *J* = 1.9 Hz, 1H), 5.89 (d, *J* = 1.9 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 154.0, 151.3, 140.7, 133.4, 132.0, 129.4, 129.0, 128.3, 126.1, 126.0, 125.2, 125.1, 124.2, 122.8, 113.2, 112.0, 111.4, 108.8, 12.3. HRMS (EI) m/z: $[M]^+$ calcd for $C_{21}H_{14}O_2S$, 330.0715; found, 330.0713.

*11-(benzylthio)-8-methoxynaphtho[2,3-b]benzofuran (**3w**)*



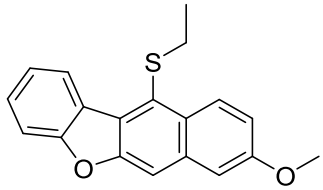
Yellow solid (32.6 mg, 44%); R_f = 0.3 (petroleum ether/ethyl acetate = 200:1); mp: 103-105 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 7.9 Hz, 1H), 8.62 (d, *J* = 9.3 Hz, 1H), 7.81 (s, 1H), 7.51– 7.48 (m, 2H), 7.40 – 7.34 (m, 1H), 7.23 (d, *J* = 2.5 Hz, 1H), 7.16 (dd, *J* = 9.3, 2.6 Hz, 1H), 7.13 – 7.02 (m, 5H), 4.06 (s, 2H), 3.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 157.4, 154.8, 137.5, 134.7, 128.8, 128.3, 128.3, 128.2, 127.7, 127.4, 127.1, 126.0, 124.4, 124.3, 122.7, 118.2, 111.1, 107.5, 105.8, 55.4, 41.0. HRMS (EI) m/z: $[M]^+$ calcd for $C_{24}H_{18}O_2S$, 370.1028; found, 370.1026.

*8-methoxy-11-(methylthio)naphtho[2,3-b]benzofuran (**3x**)*



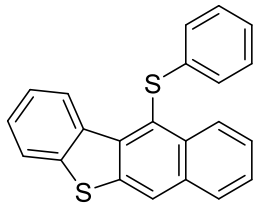
White solid (23.5 mg, 40%); R_f = 0.4 (petroleum ether/ethyl acetate = 250:1); mp: 134-135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (dd, *J* = 29.0, 8.9 Hz, 2H), 7.74 (s, 1H), 7.52 – 7.41 (m, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.18 (d, *J* = 2.5 Hz, 2H), 3.90 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 157.5, 154.9, 134.8, 128.2, 128.1, 127.6, 127.5, 126. 7, 124.4, 122.9, 118.3, 111.2, 107.2, 106.0, 55.5, 19.3. HRMS (EI) m/z: $[M]^+$ calcd for $C_{18}H_{14}O_2S$, 294.0715; found, 294.0711.

*11-(ethylthio)-8-methoxynaphtho[2,3-b]benzofuran (**3y**)*



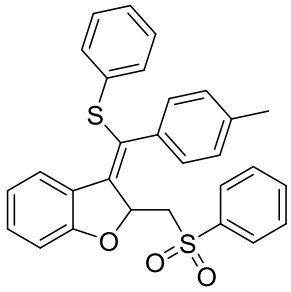
White solid (21.6 mg, 35%); R_f = 0.4 (petroleum ether/ethyl acetate = 250:1); mp: 95-96 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (dd, *J* = 37.4, 8.9 Hz, 2H), 7.71 (s, 1H), 7.49 – 7.39 (m, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.17 – 7.13 (m, 2H), 3.87 (s, 3H), 2.85 (q, *J* = 7.3 Hz, 2H), 1.08 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 157.5, 154.8, 134.7, 128.5, 128.1, 127.9, 127.3, 126.5, 124.6, 124.5, 122.8, 118.1, 111.2, 107.2, 105.8, 55.4, 30.7, 15.2. HRMS (EI) m/z: $[M]^+$ calcd for $C_{19}H_{16}O_2S$, 308.0871; found, 308.0871.

*11-(phenylthio)benzo[b]naphtho[2,3-d]thiophene (**5a**)*



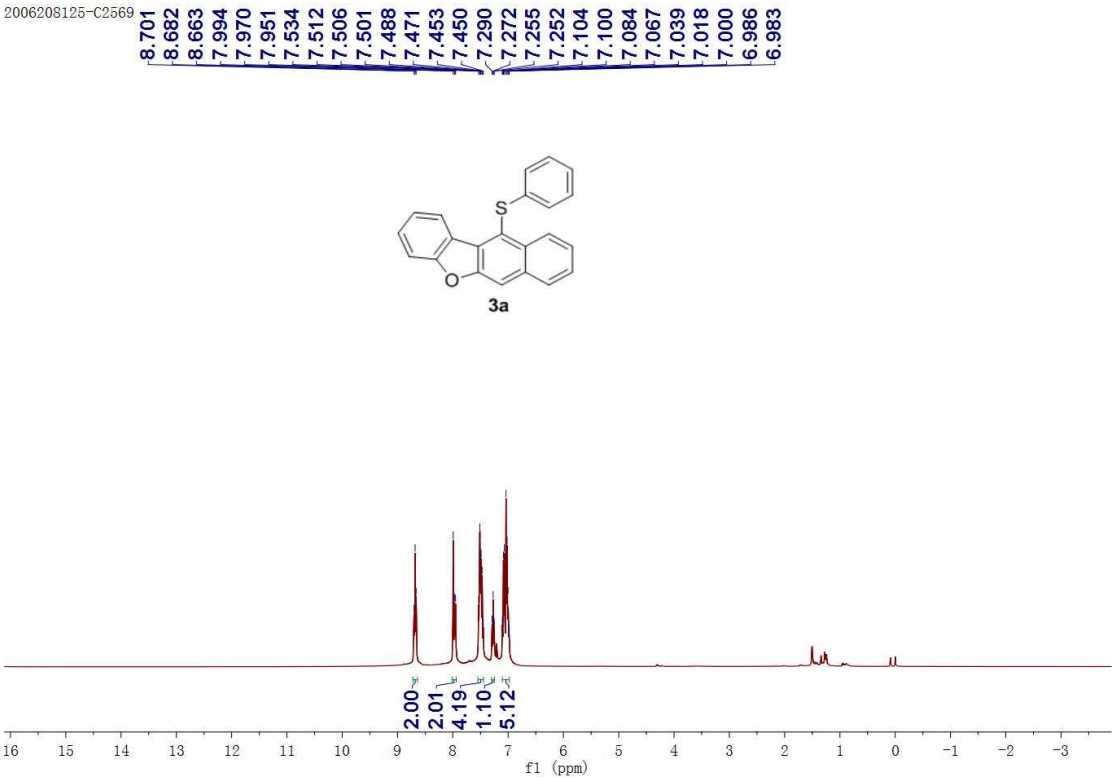
Yellow solid (20.5 mg, 30%); R_f = 0.4 (petroleum ether); mp: 161-162 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.47 (d, *J* = 8.2 Hz, 1H), 8.79 (dd, *J* = 5.7, 4.2 Hz, 1H), 8.37 (s, 1H), 7.87 (dd, *J* = 5.6, 3.9 Hz, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.43 – 7.38 (m, 1H), 7.35 – 7.29 (m, 1H), 7.04 (dd, *J* = 10.5, 4.6 Hz, 2H), 7.00 – 6.89 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 138.6, 138.3, 137.5, 135.5, 134.2, 132.4, 129.1, 128.1, 128.1, 127.4, 126.7, 126.6, 126.5, 126.2, 125.2, 124.5, 124.1, 123.7, 122.5. HRMS (EI) m/z: $[M]^+$ calcd for $C_{22}H_{14}S_2$, 342.0537; found, 342.0536.

*(E)-2-((phenylsulfonyl)methyl)-3-((phenylthio)(p-tolyl)methylene)-2,3-dihydrobenzofuran (**3ea**)*

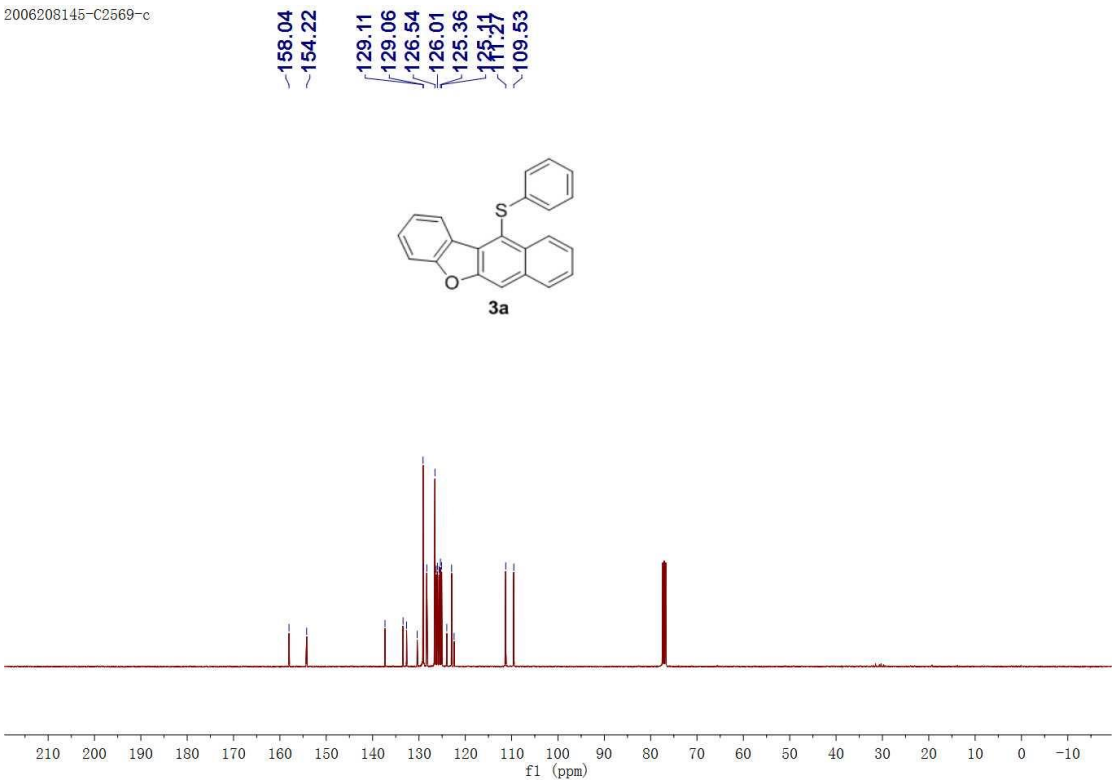


Yellow oil (78.4 mg, 81%); R_f = 0.3 (petroleum ether/ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.84 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.07 – 7.01 (m, 7H), 6.95 (ddd, *J* = 8.6, 4.4, 1.3 Hz, 3H), 6.46 (dd, *J* = 12.5, 4.7 Hz, 2H), 6.30 (d, *J* = 7.6 Hz, 1H), 5.96 (dd, *J* = 9.6, 1.8 Hz, 1H), 3.96 (dd, *J* = 14.7, 1.8 Hz, 1H), 3.55 (dd, *J* = 14.7, 9.6 Hz, 1H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 140.2, 139.1, 138.2, 134.2, 133.6, 132.6, 131.2, 130.6, 129.3, 129.3, 129.0, 128.8, 128.5, 127.4, 127.3, 123.9, 123.8, 121.0, 111.0, 80.6, 59.9, 21.3. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{29}H_{25}O_3S_2$: 485.1240, found 485.1237.

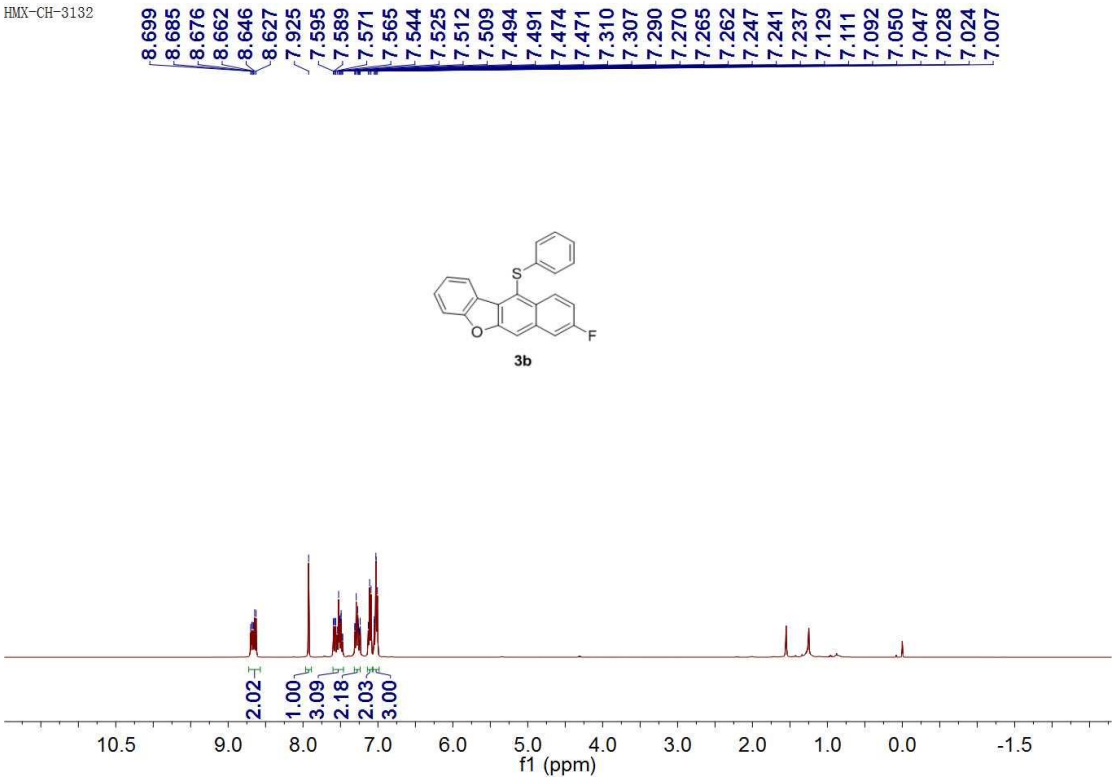
Copies of ^{1}H NMR and ^{13}C NMR spectra of products



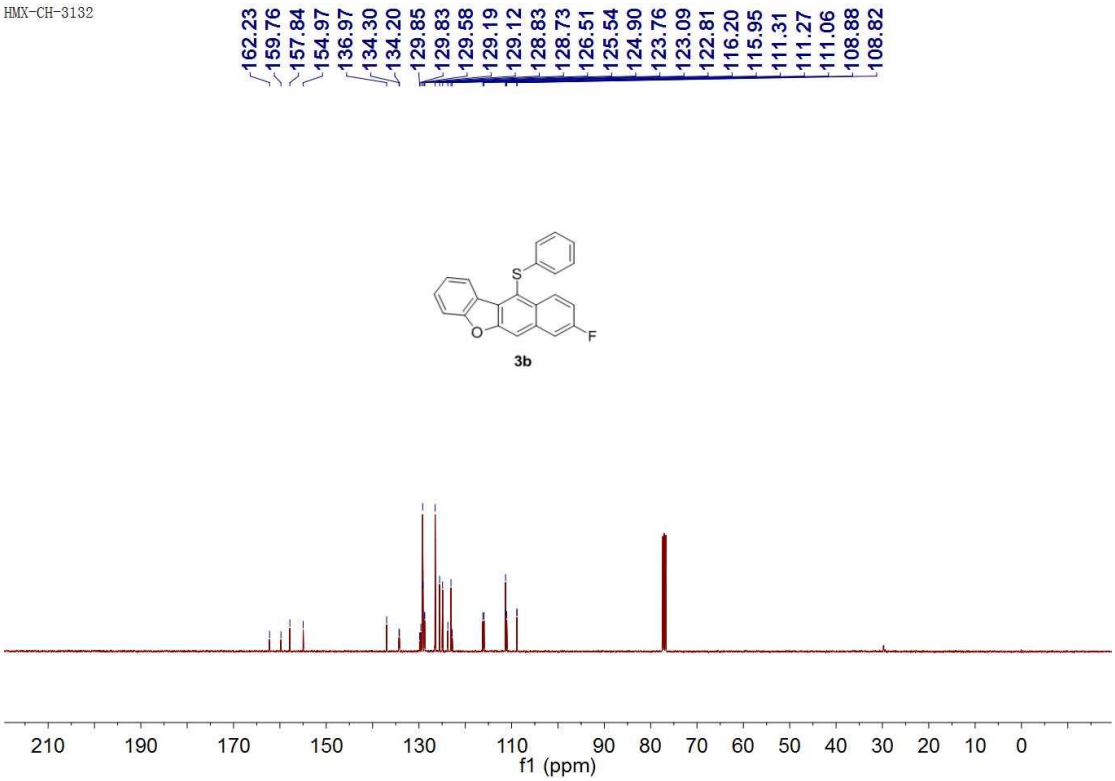
^{1}H NMR of **3a** in $CDCl_3$ (400 MHz)



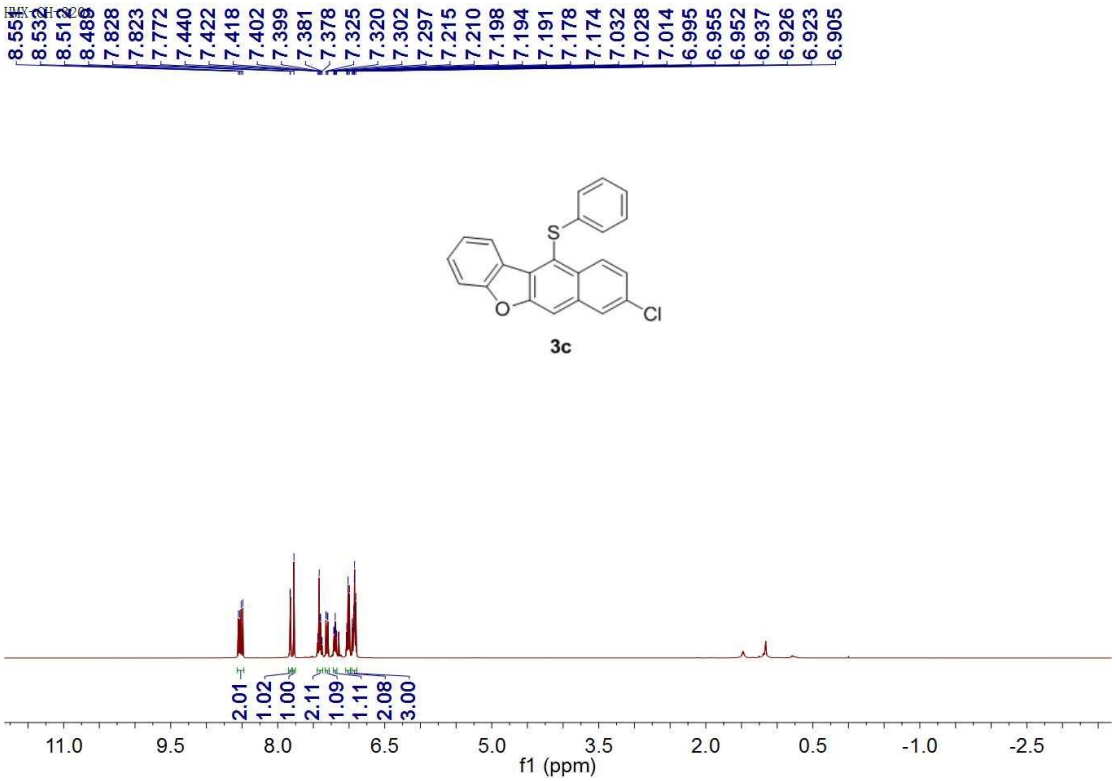
^{13}C NMR of **3a** in $CDCl_3$ (100 MHz)



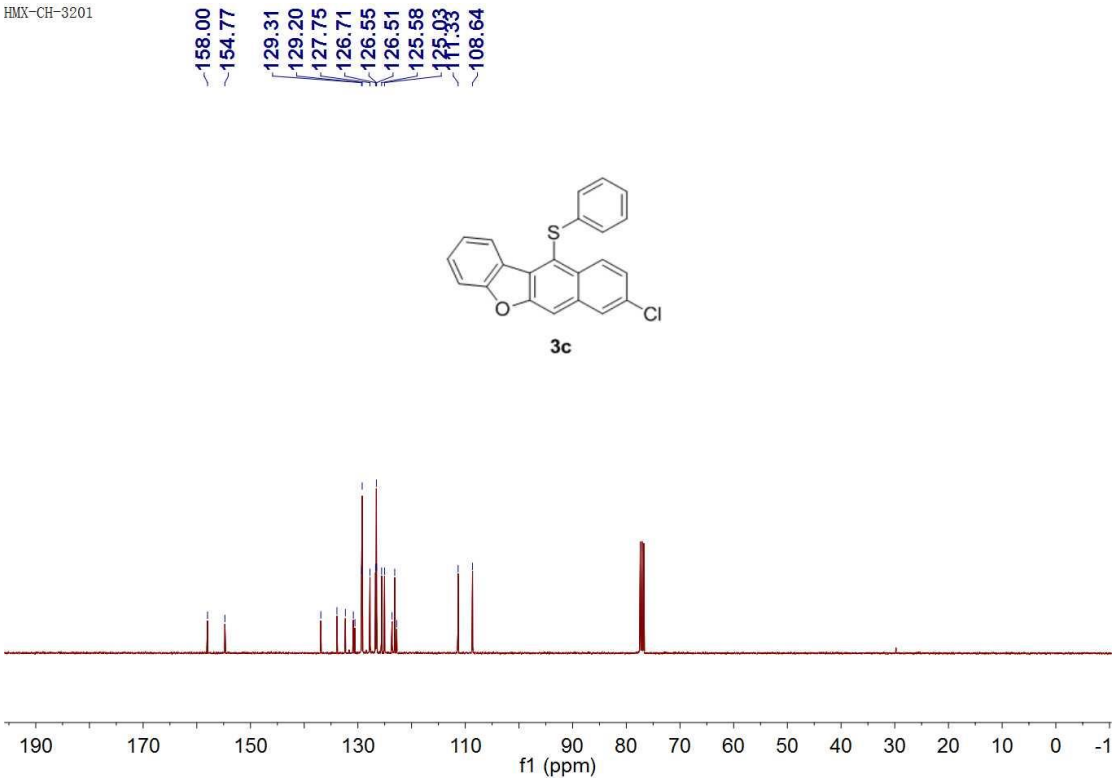
^{1}H NMR of **3b** in $CDCl_3$ (400 MHz)



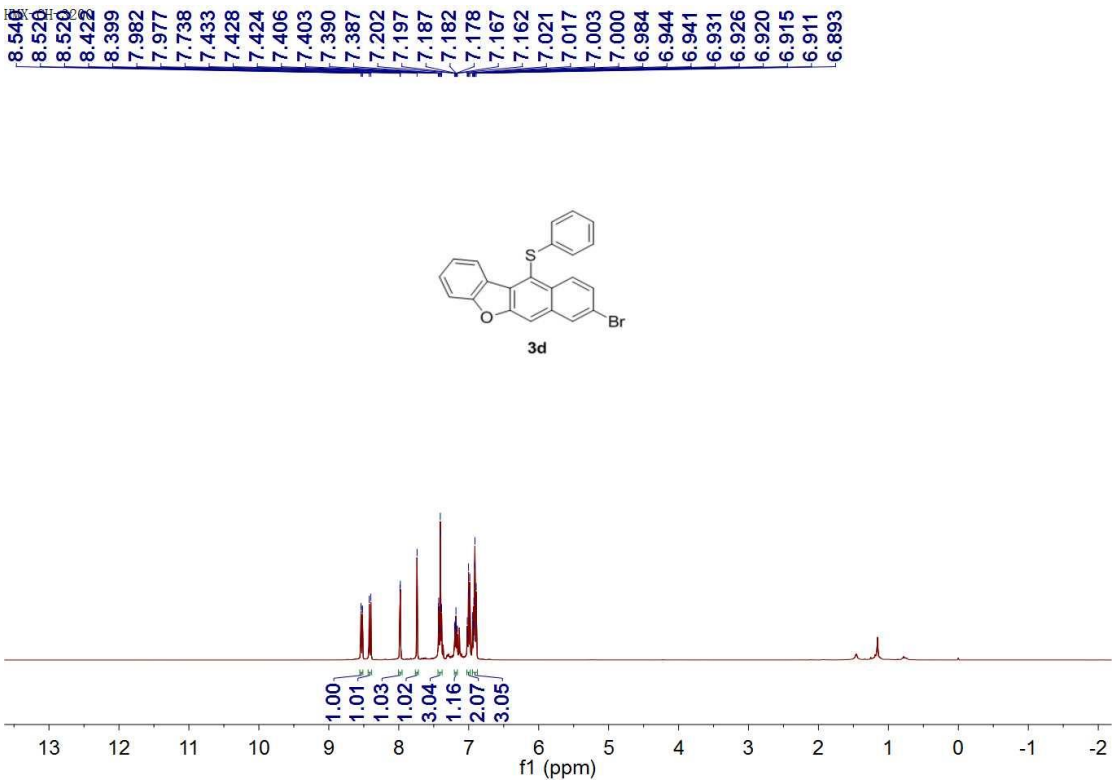
^{13}C NMR of **3b** in $CDCl_3$ (100 MHz)



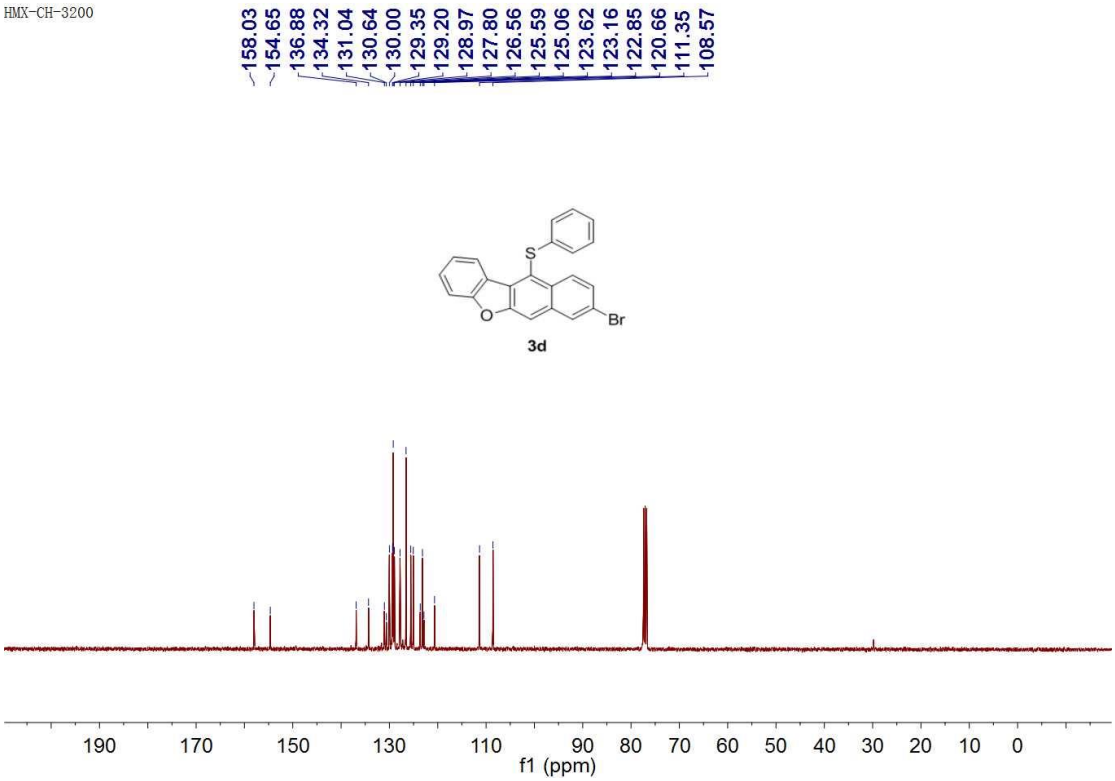
^{1}H NMR of **3c** in $CDCl_3$ (400 MHz)



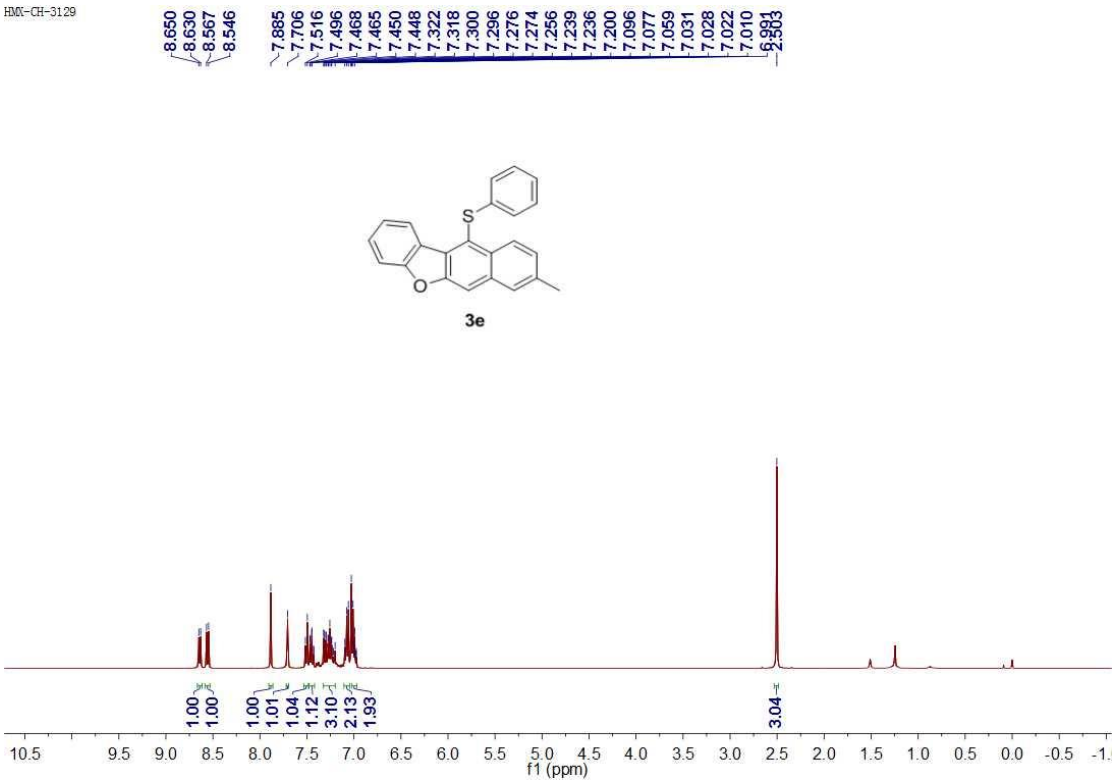
^{13}C NMR of **3c** in $CDCl_3$ (100 MHz)



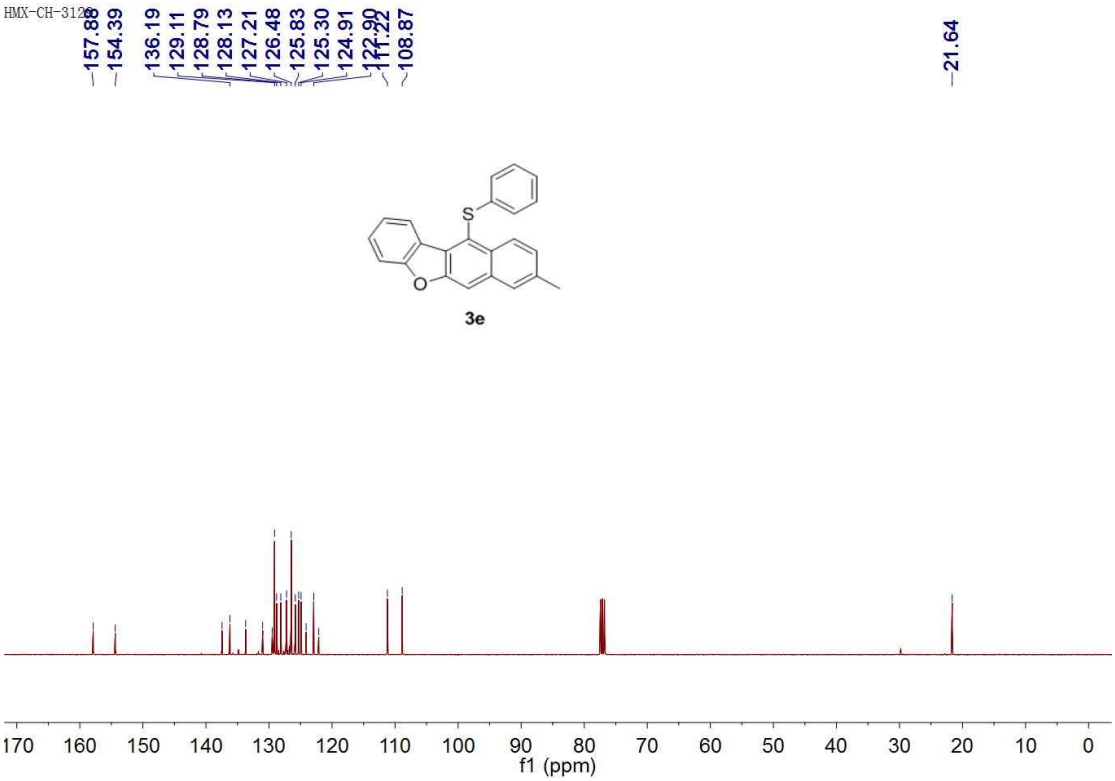
^{1}H NMR of **3d** in $CDCl_3$ (400 MHz)



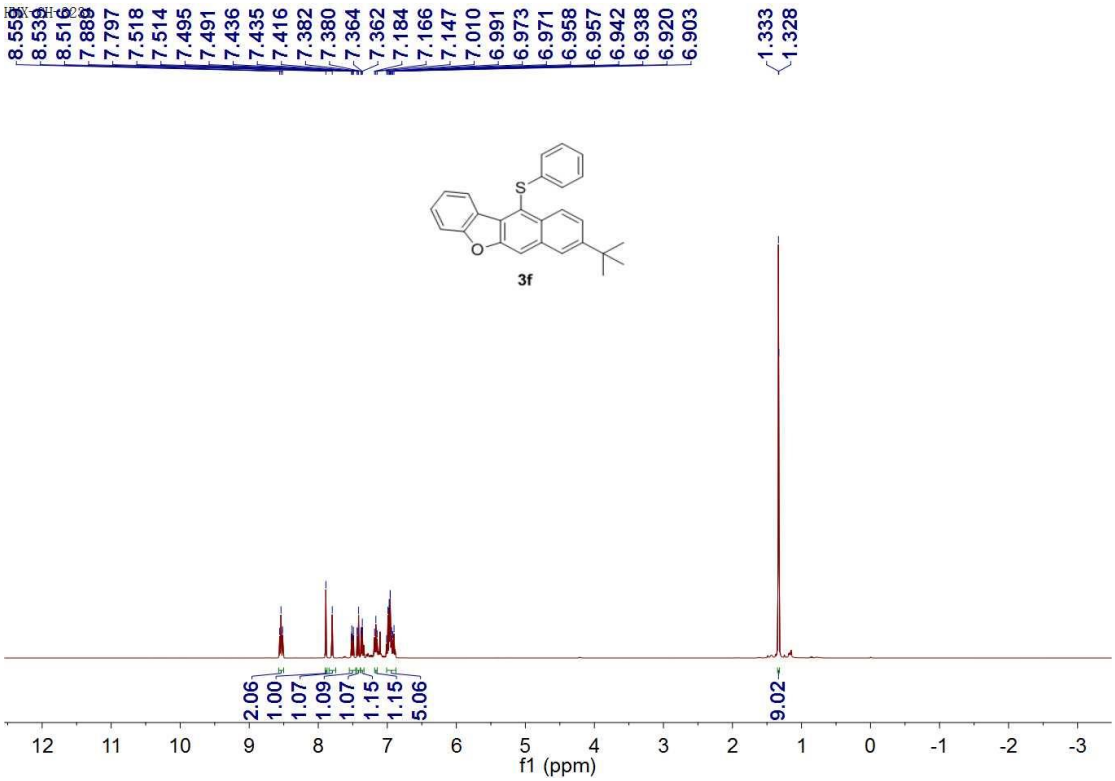
^{13}C NMR of **3d** in $CDCl_3$ (100 MHz)



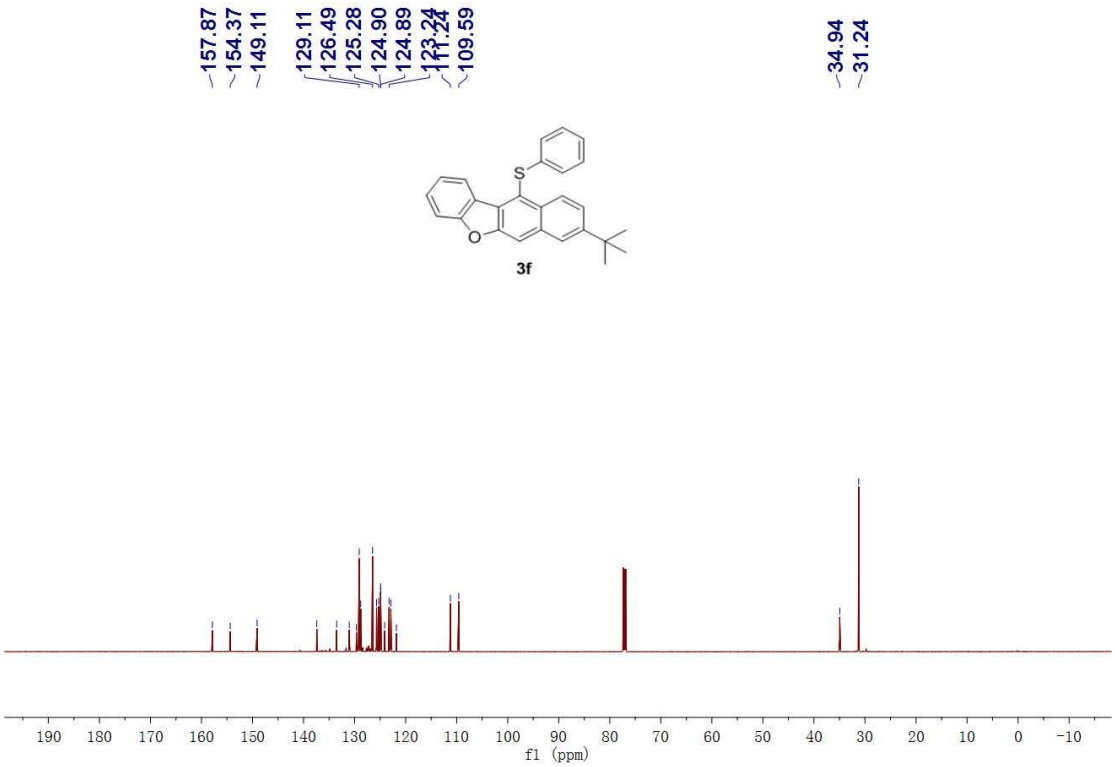
^{1}H NMR of **3e** in $CDCl_3$ (400 MHz)



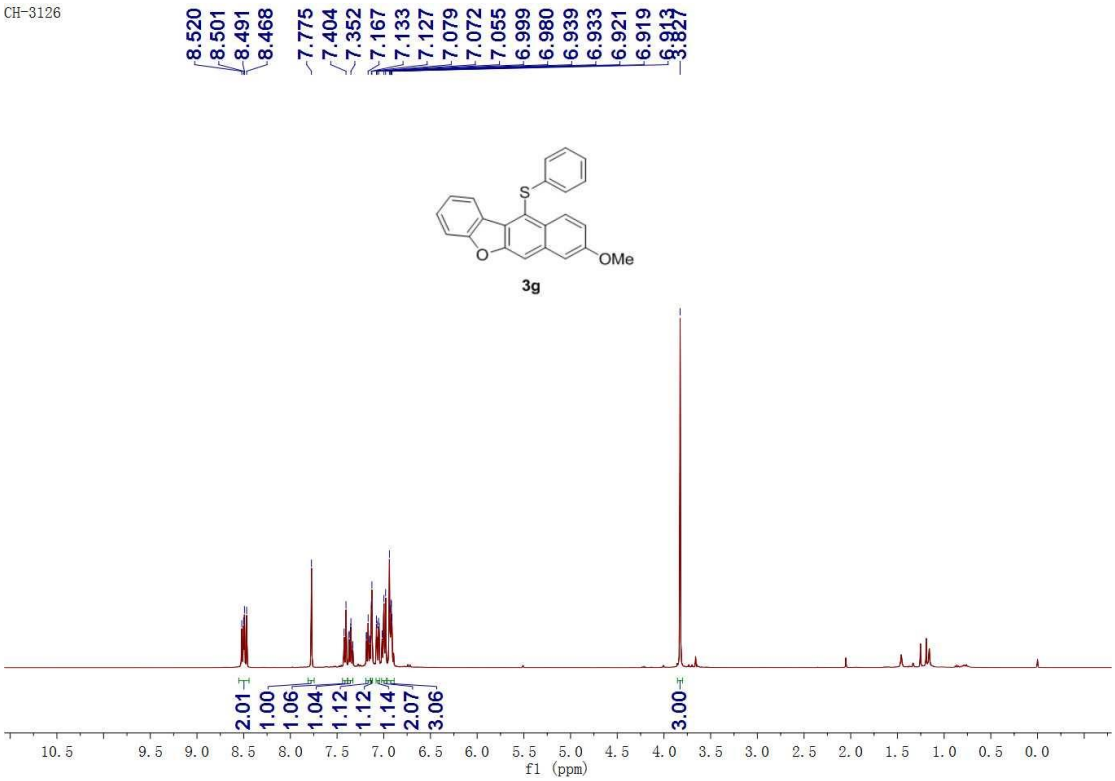
^{13}C NMR of **3e** in $CDCl_3$ (100 MHz)



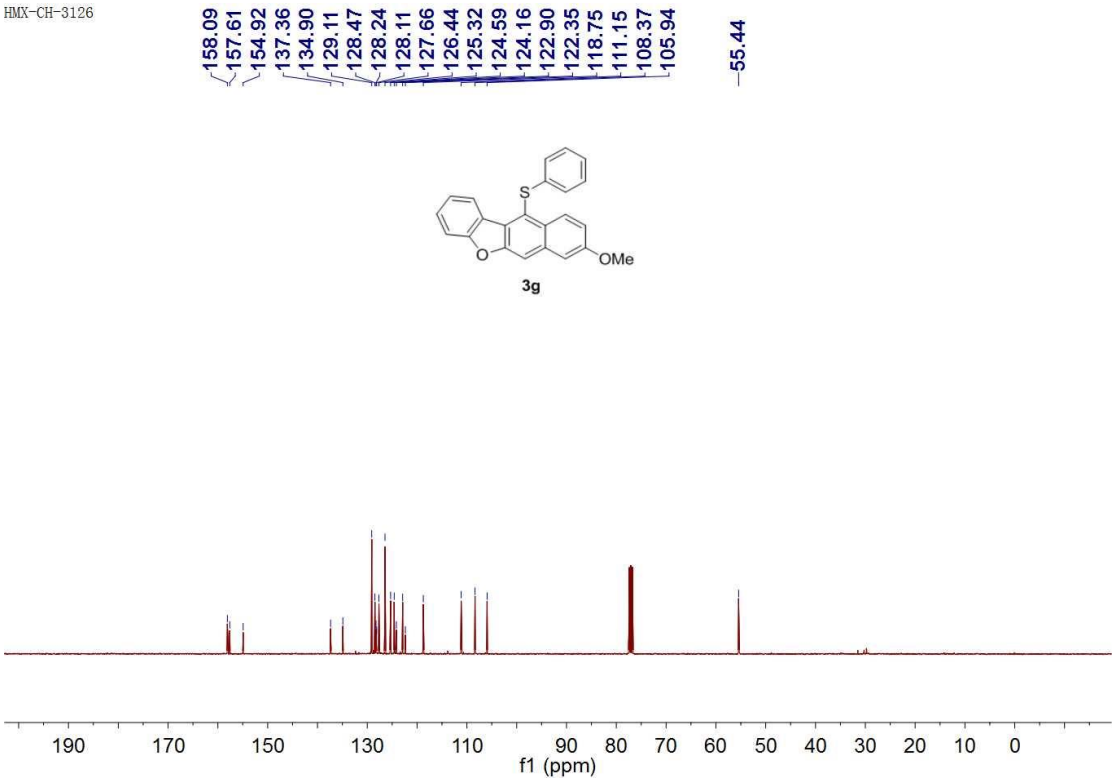
^{1}H NMR of **3f** in $CDCl_3$ (400 MHz)



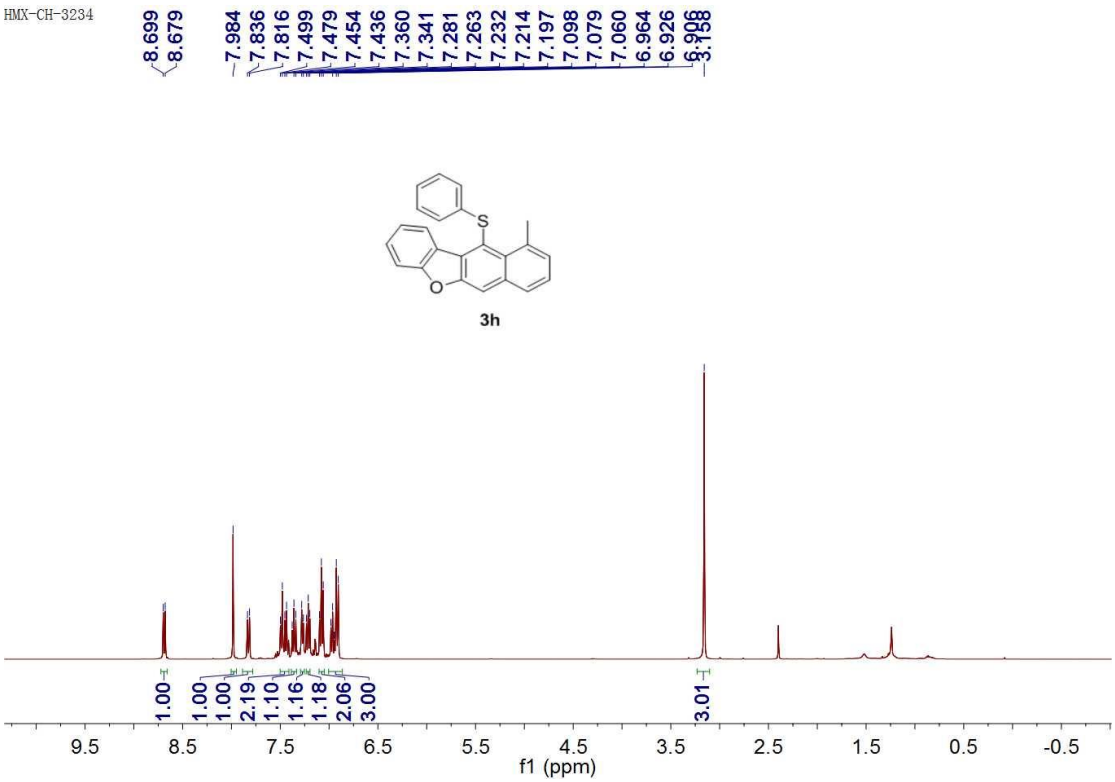
^{13}C NMR of **3f** in $CDCl_3$ (100 MHz)



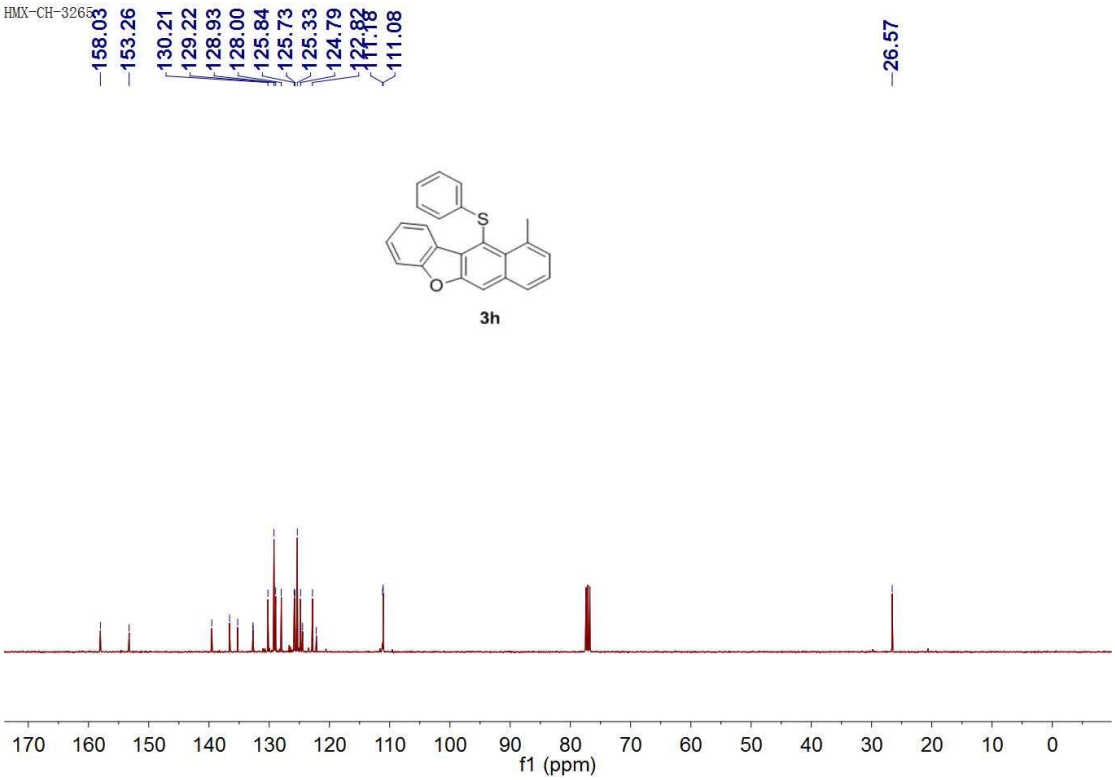
^{1}H NMR of **3g** in $CDCl_3$ (400 MHz)



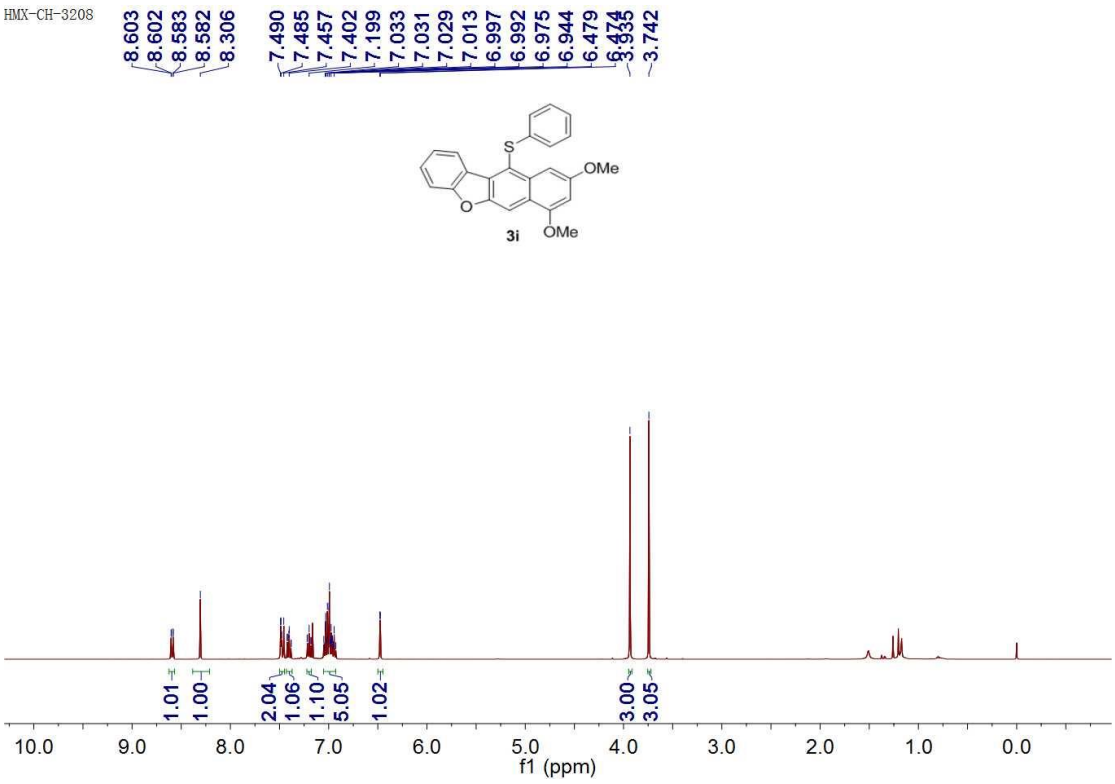
^{13}C NMR of **3g** in $CDCl_3$ (100 MHz)



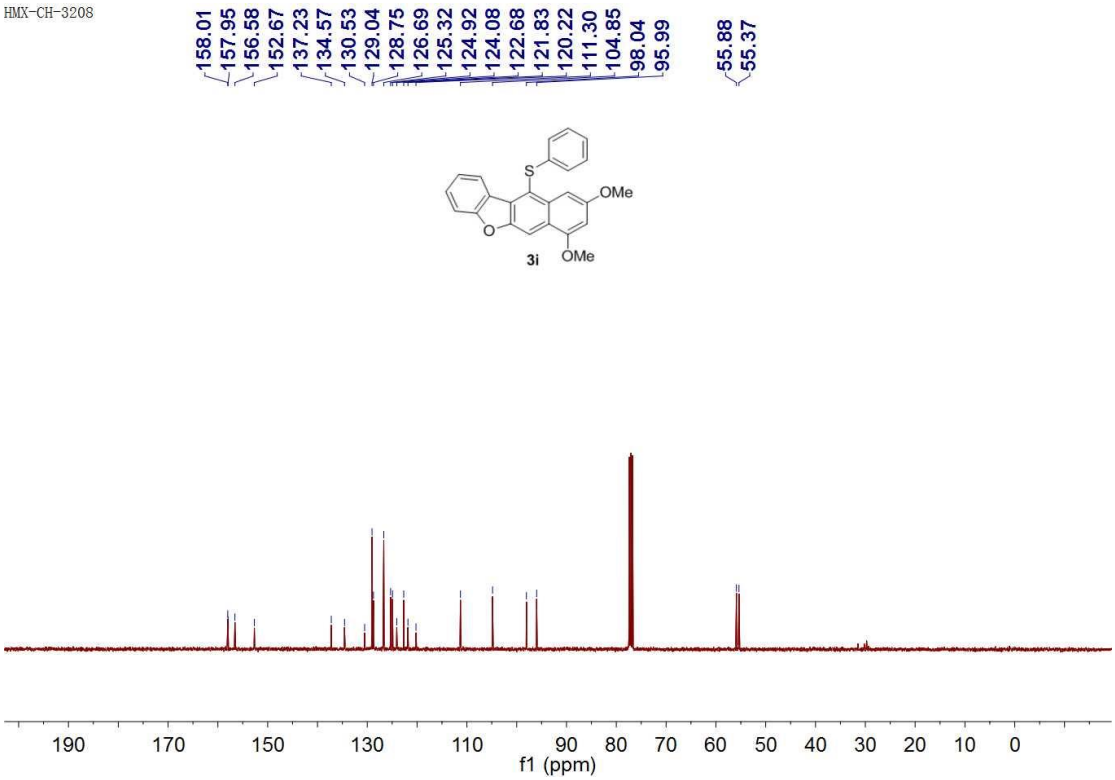
^{1}H NMR of **3h** in $CDCl_3$ (400 MHz)



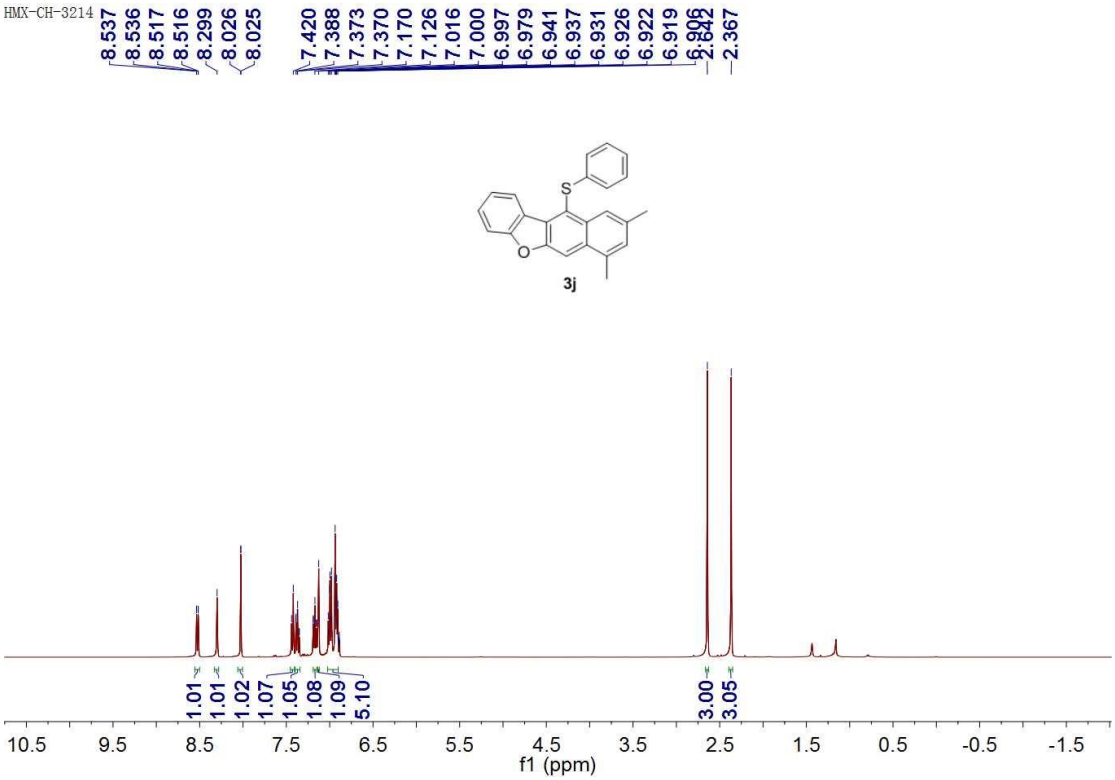
^{13}C NMR of **3h** in $CDCl_3$ (100 MHz)



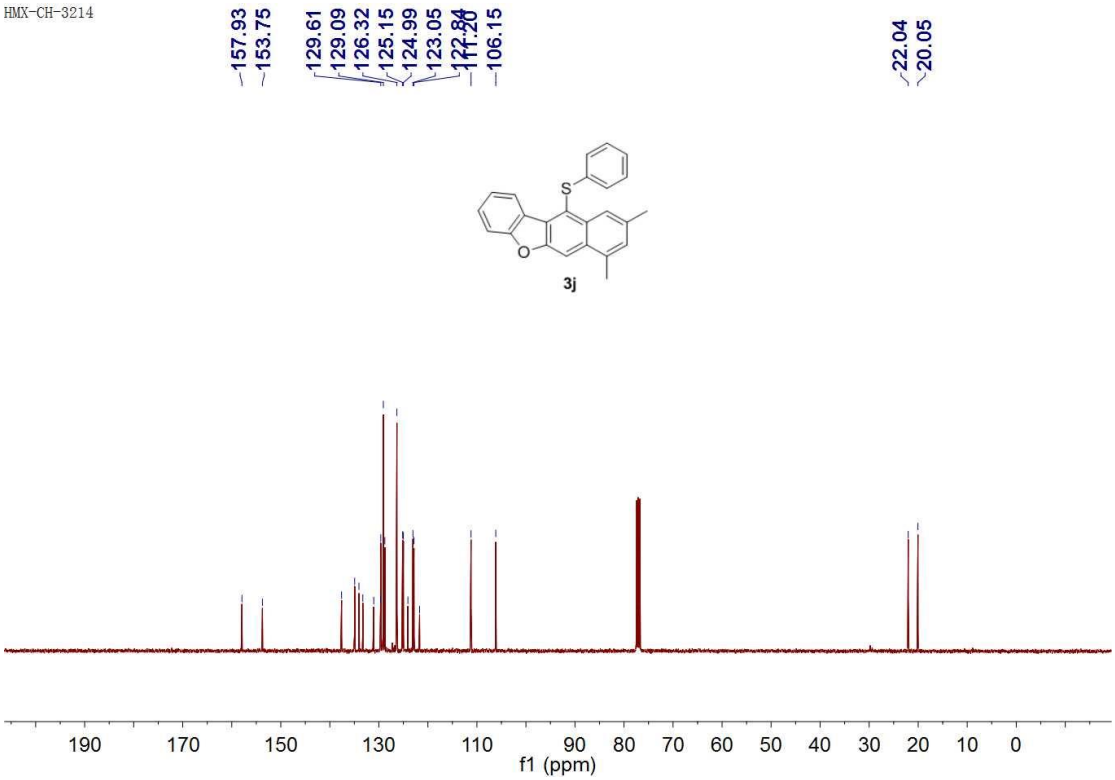
^{1}H NMR of **3i** in $CDCl_3$ (400 MHz)



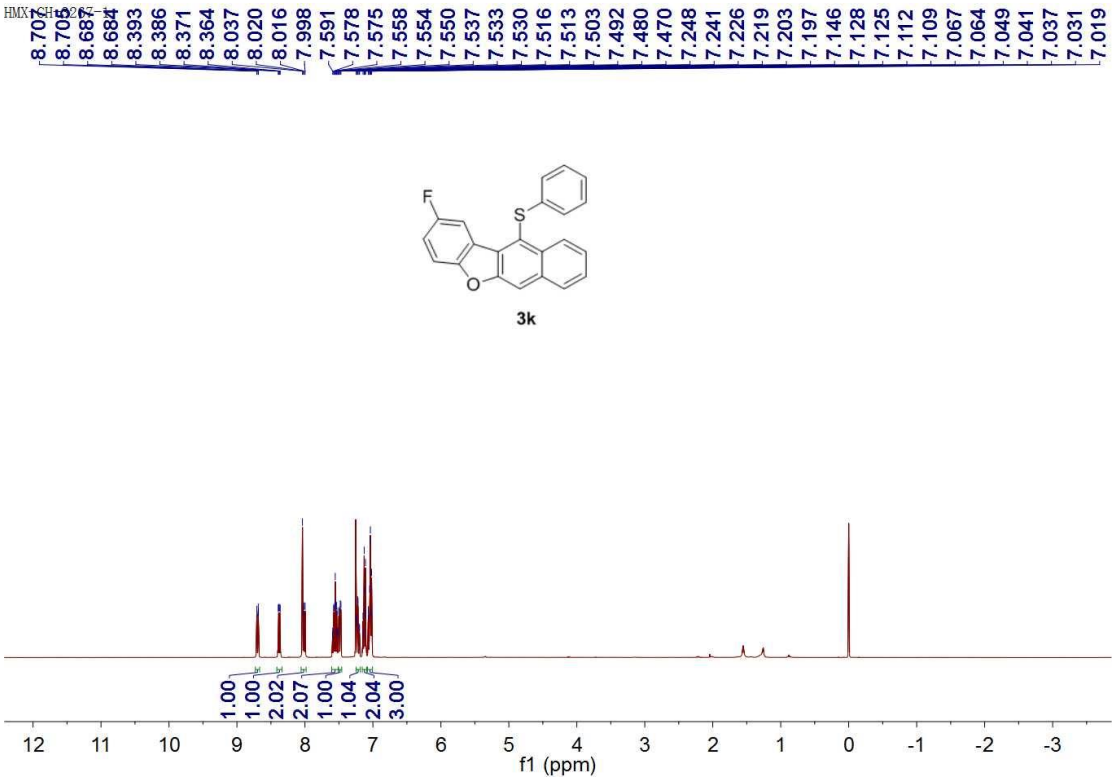
^{13}C NMR of **3i** in $CDCl_3$ (100 MHz)



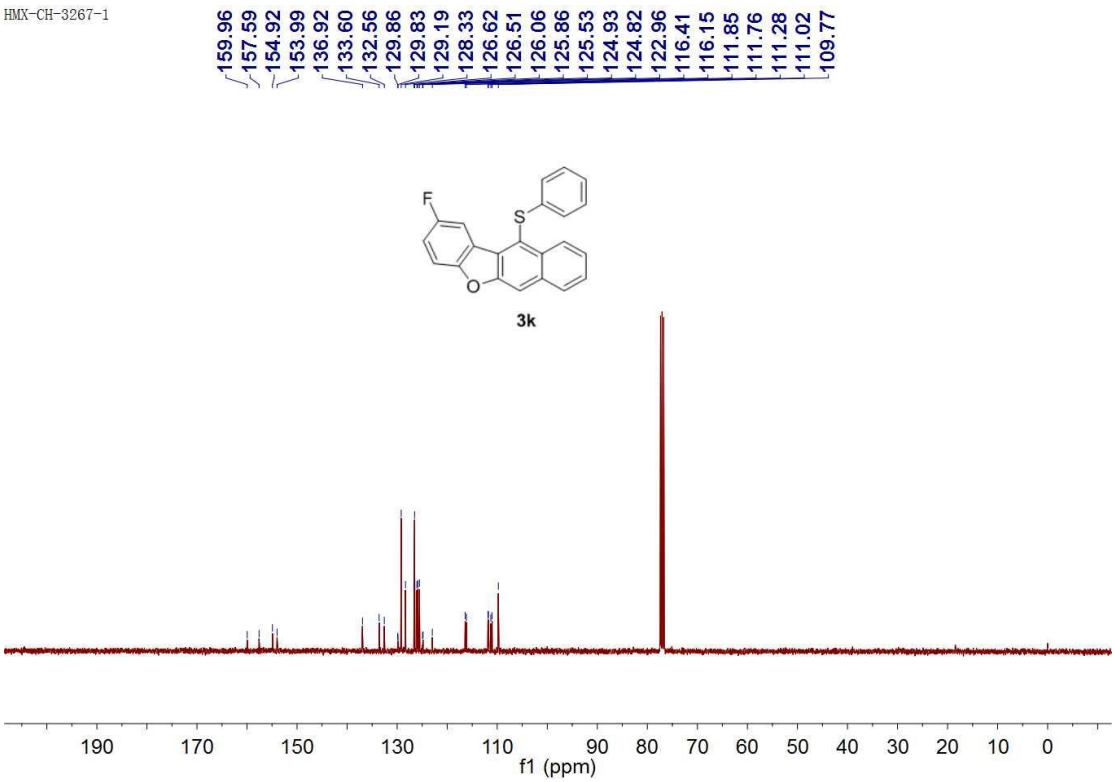
^{1}H NMR of **3j** in $CDCl_3$ (400 MHz)



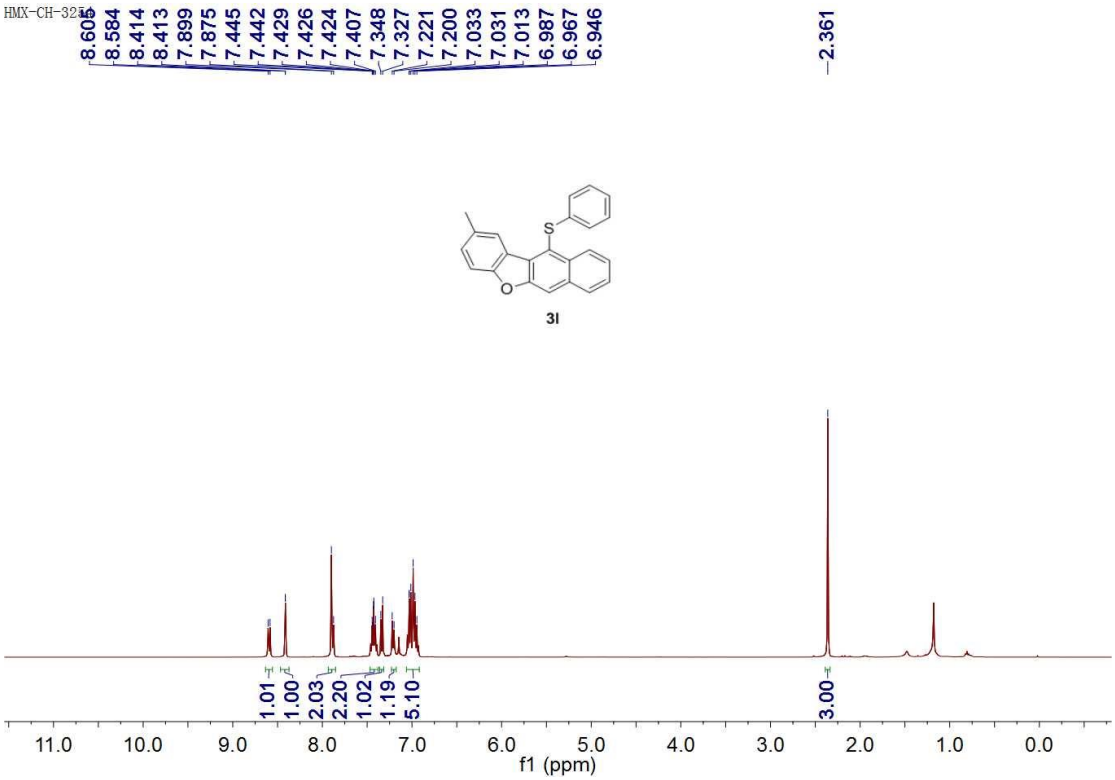
^{13}C NMR of **3j** in $CDCl_3$ (100 MHz)



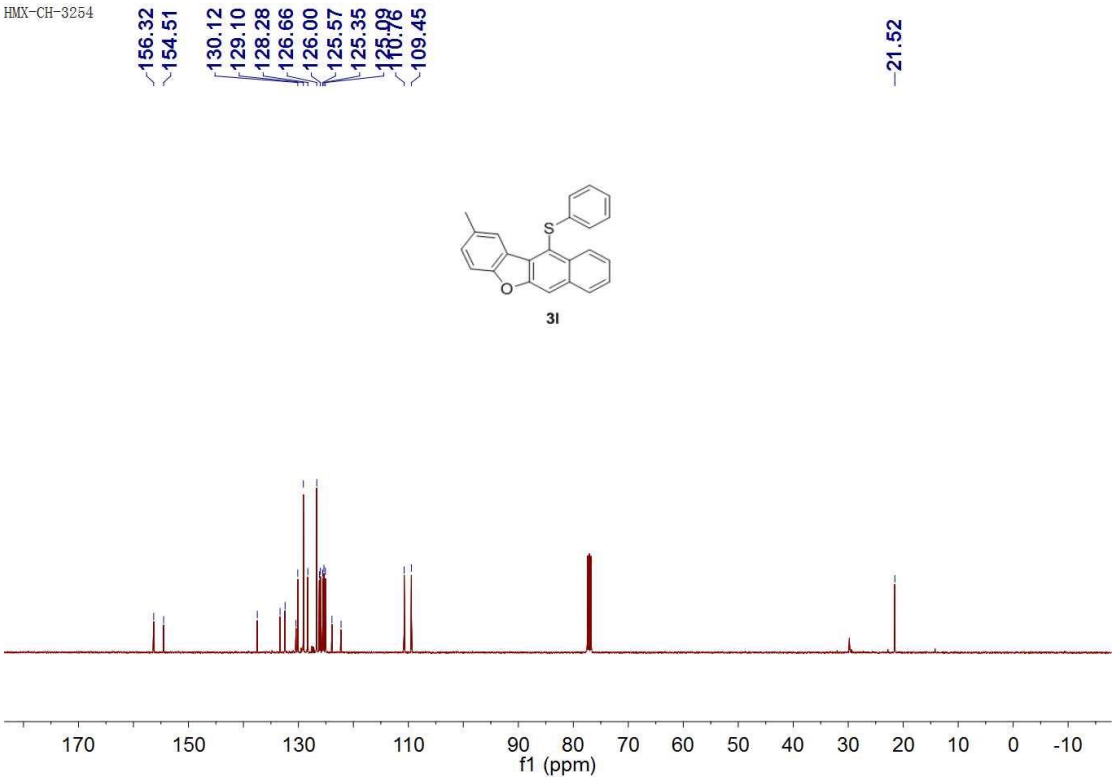
^{1}H NMR of **3k** in $CDCl_3$ (400 MHz)



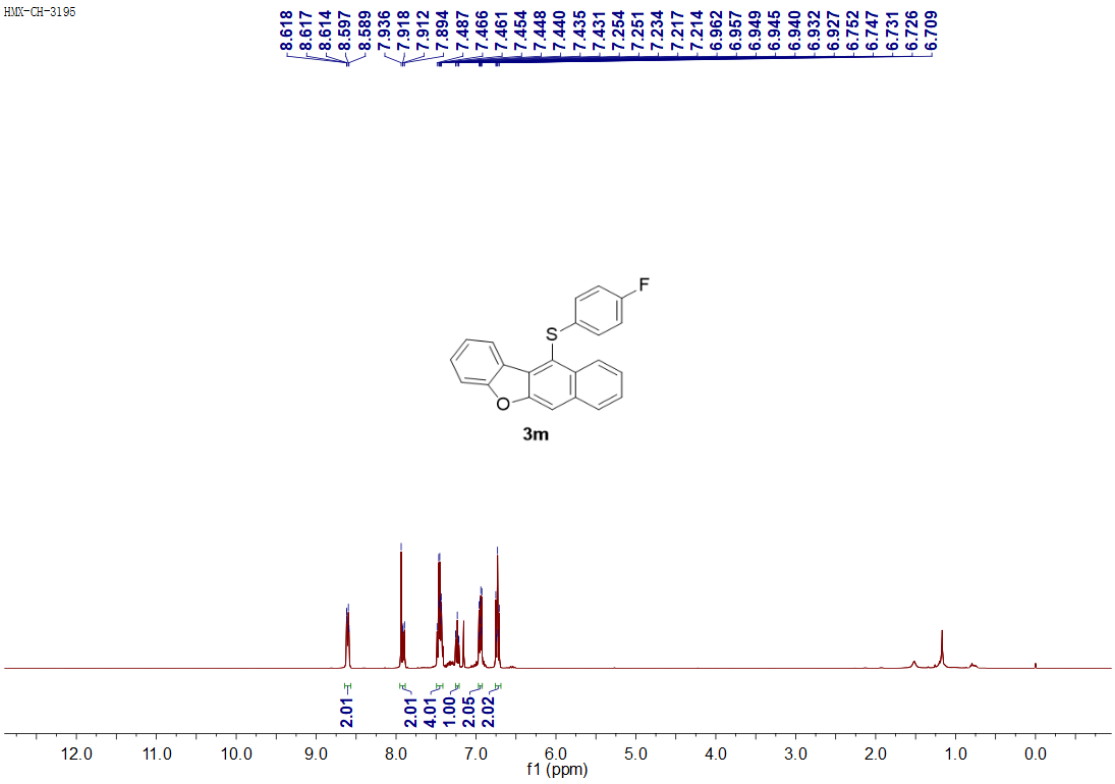
^{13}C NMR of **3k** in $CDCl_3$ (100 MHz)



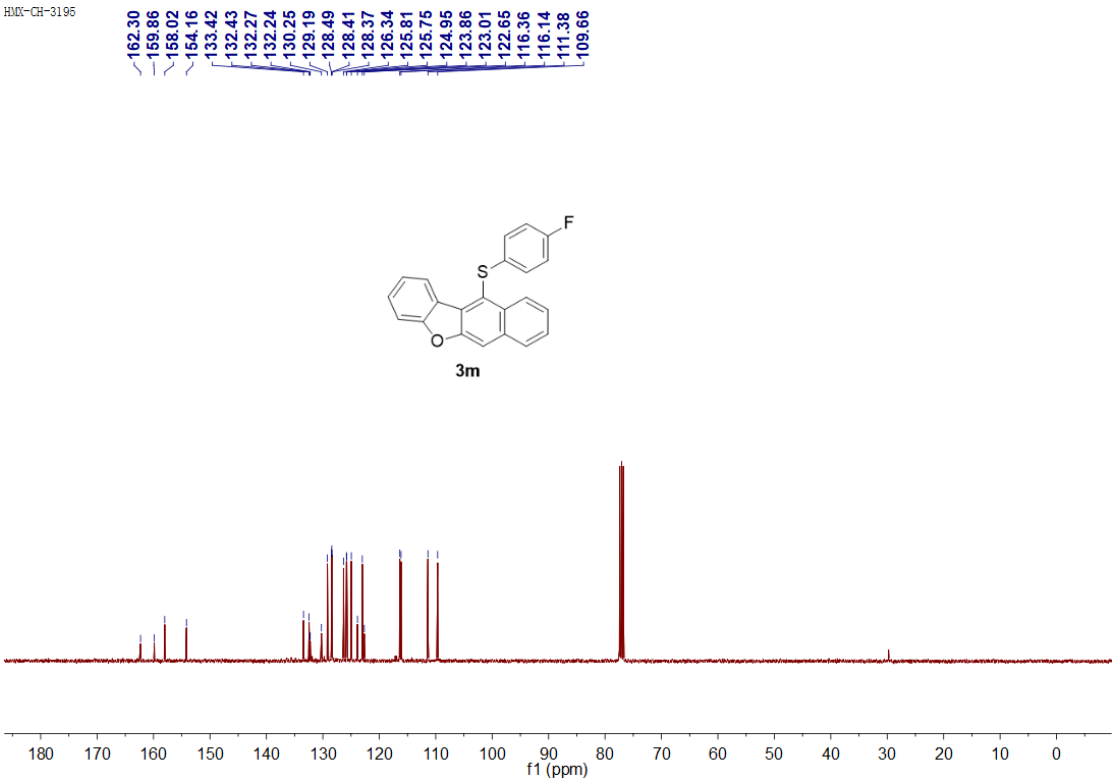
^{1}H NMR of **3l** in $CDCl_3$ (400 MHz)



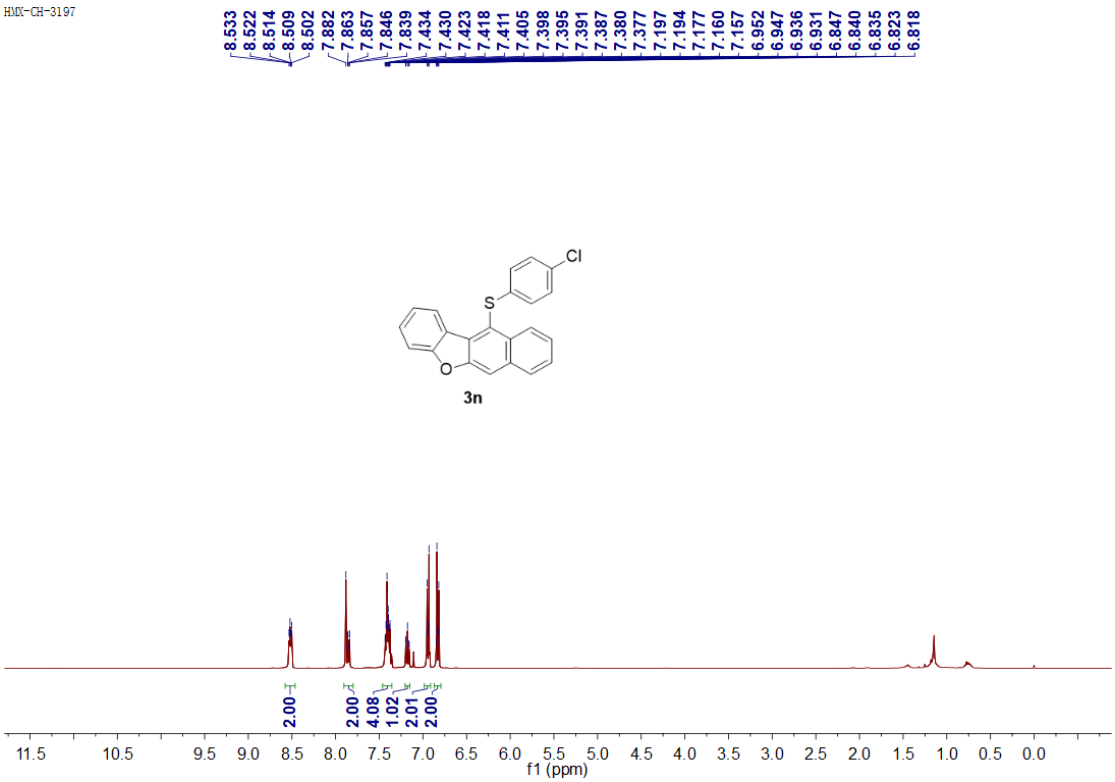
^{13}C NMR of **3l** in $CDCl_3$ (100 MHz)



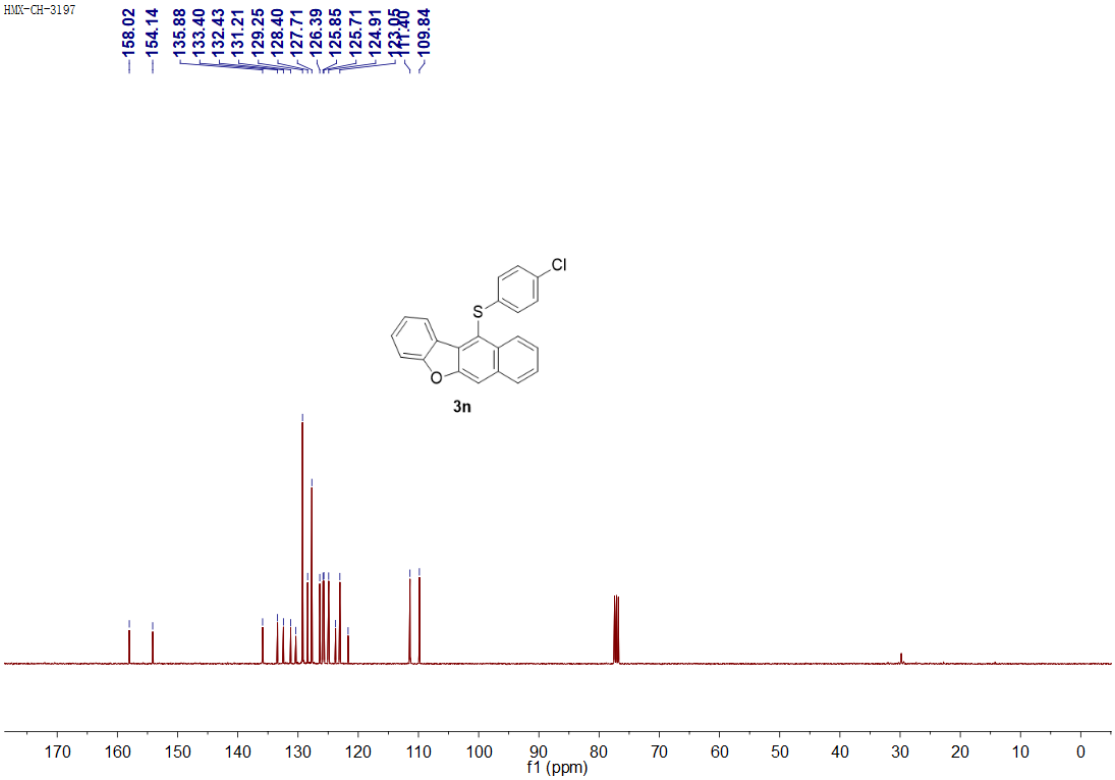
^{1}H NMR of **3m** in $CDCl_3$ (400 MHz)



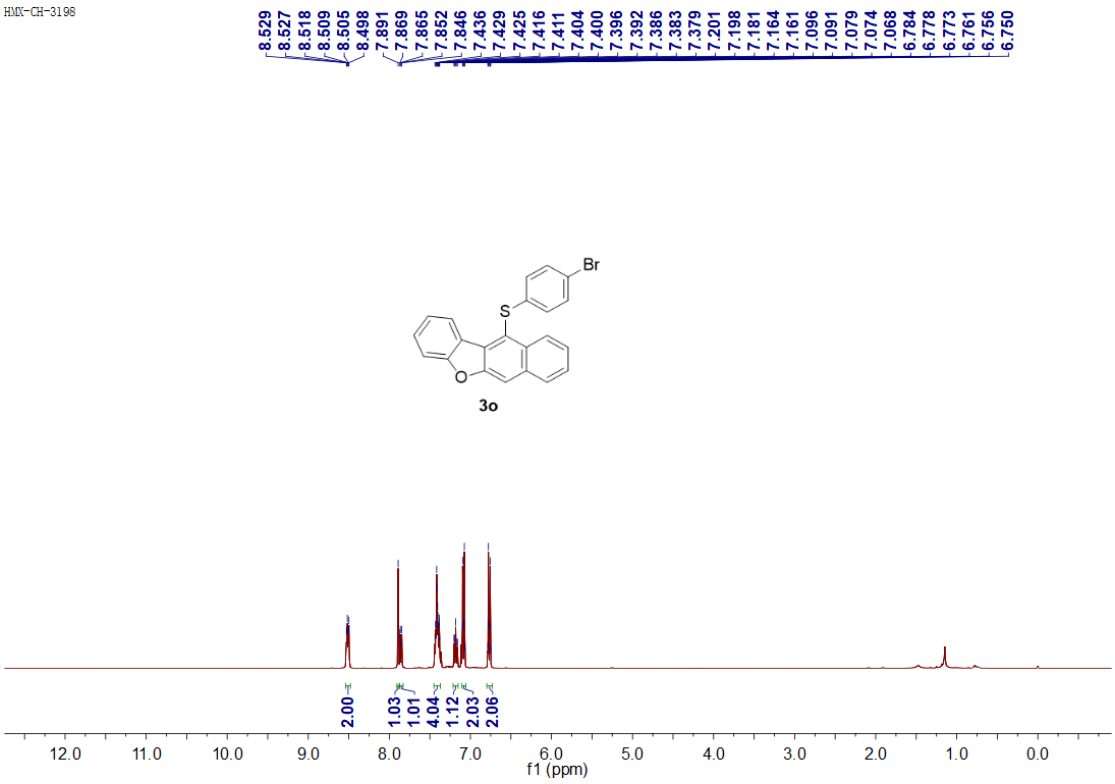
^{13}C NMR of **3m** in $CDCl_3$ (100 MHz)



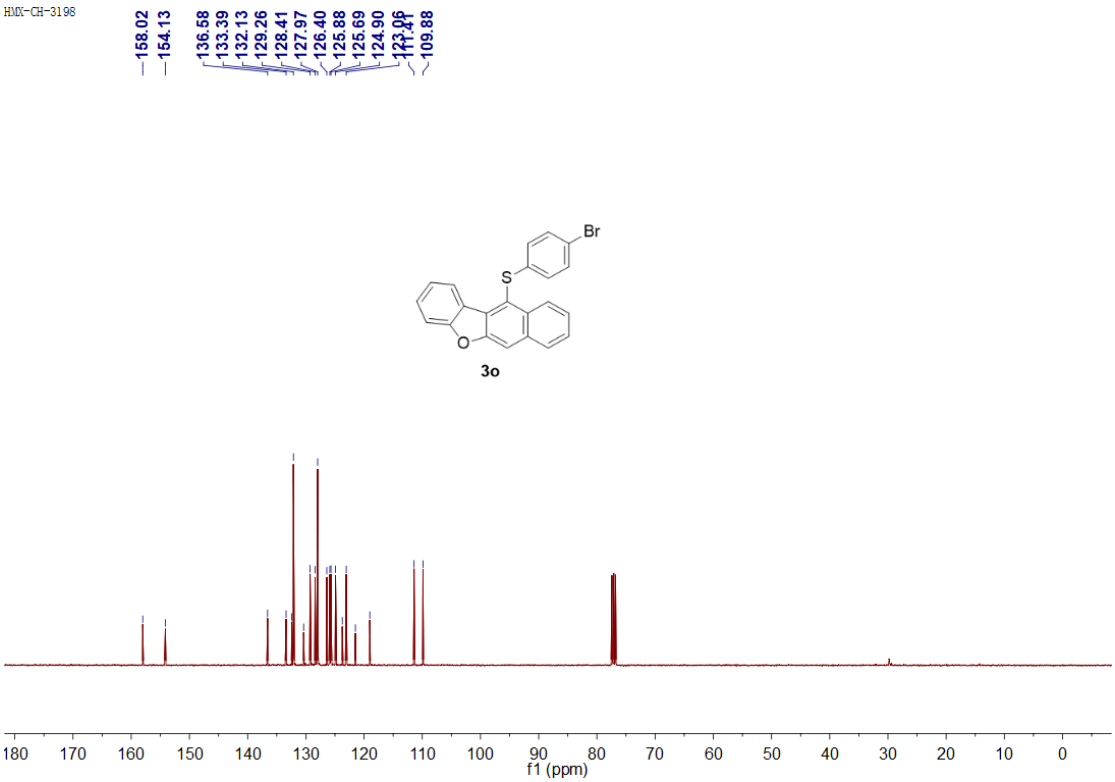
^{1}H NMR of **3n** in $CDCl_3$ (400 MHz)



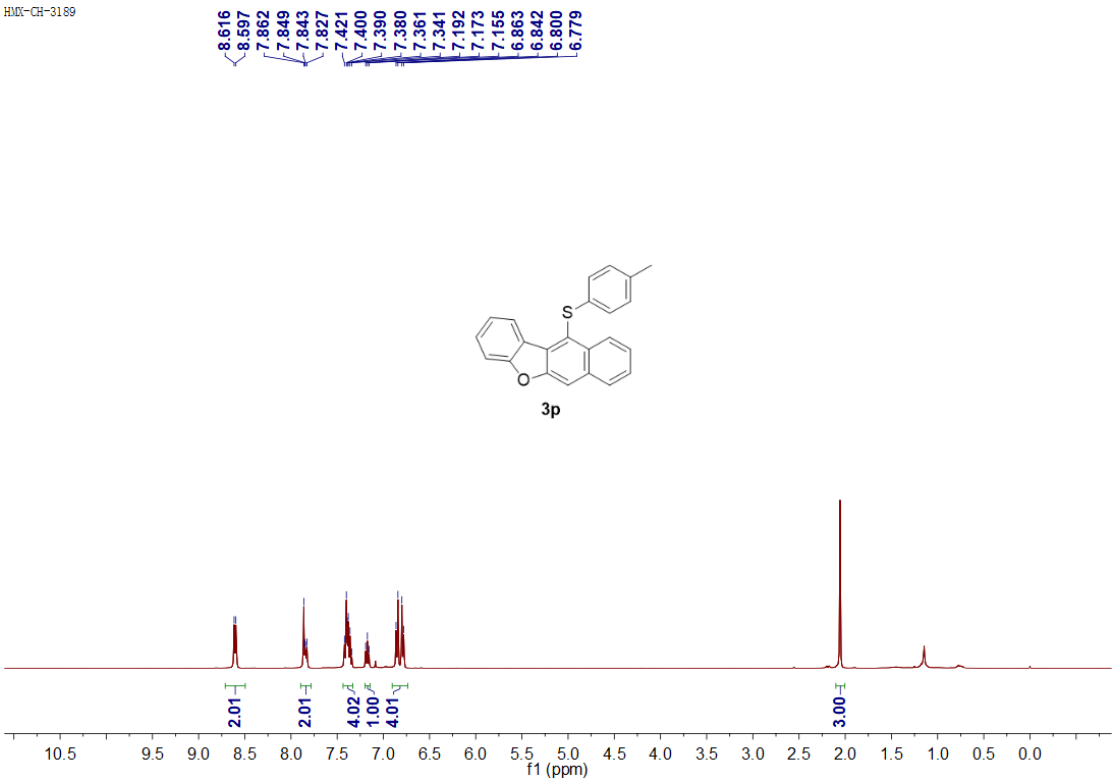
^{13}C NMR of **3n** in $CDCl_3$ (100 MHz)



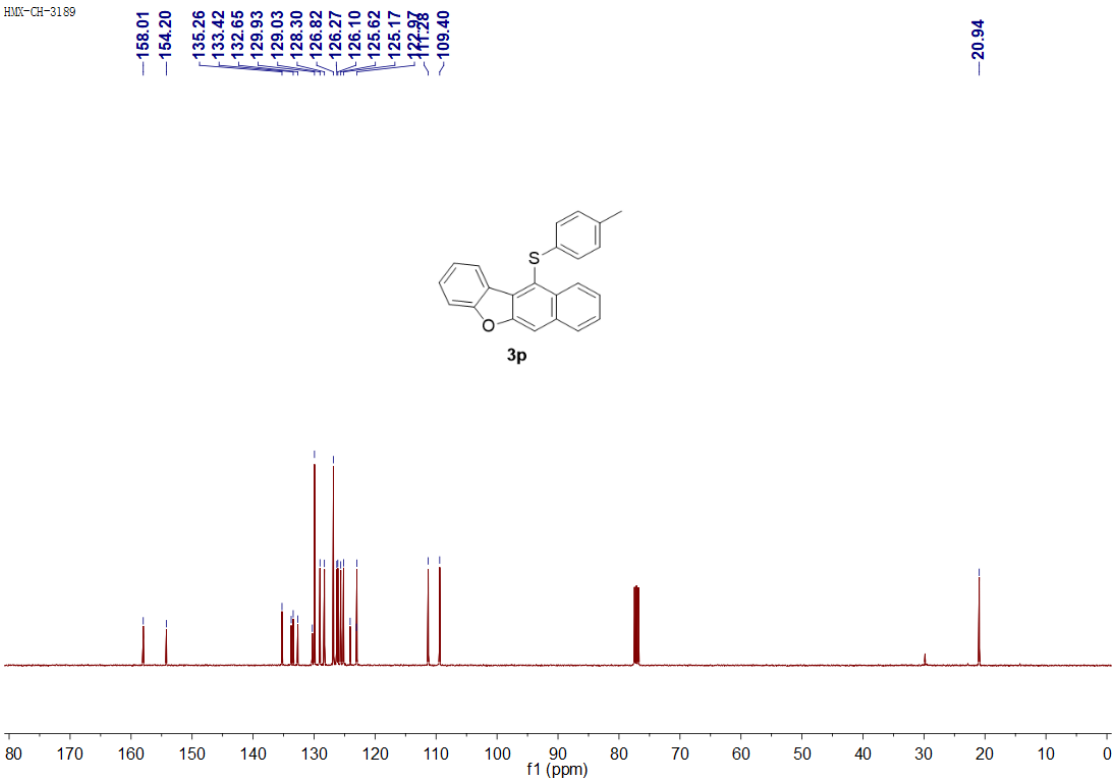
^{1}H NMR of **3o** in $CDCl_3$ (400 MHz)



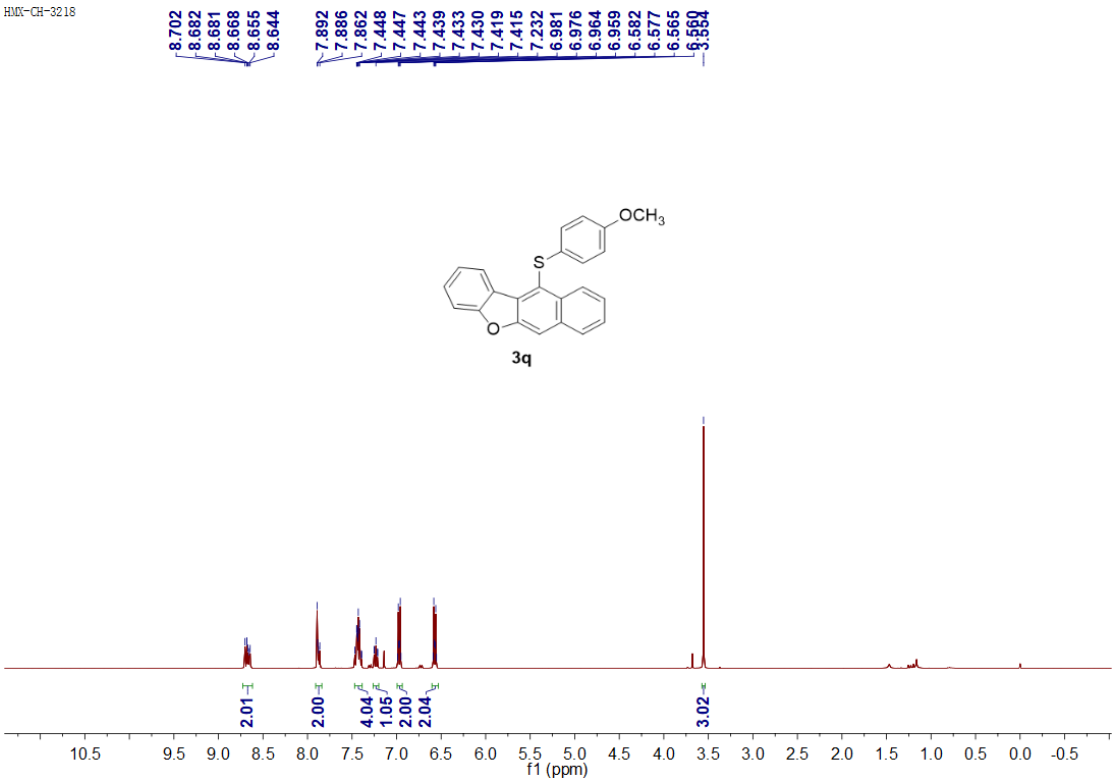
^{13}C NMR of **3o** in $CDCl_3$ (100 MHz)



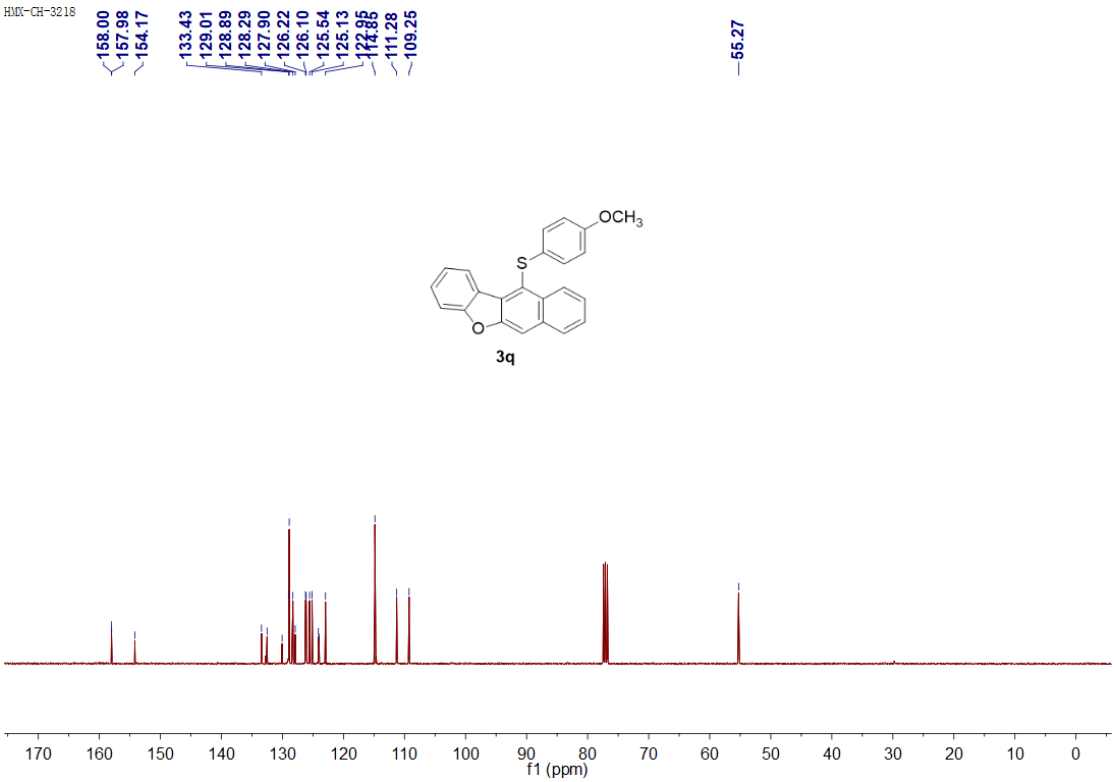
^{1}H NMR of **3p** in $CDCl_3$ (400 MHz)



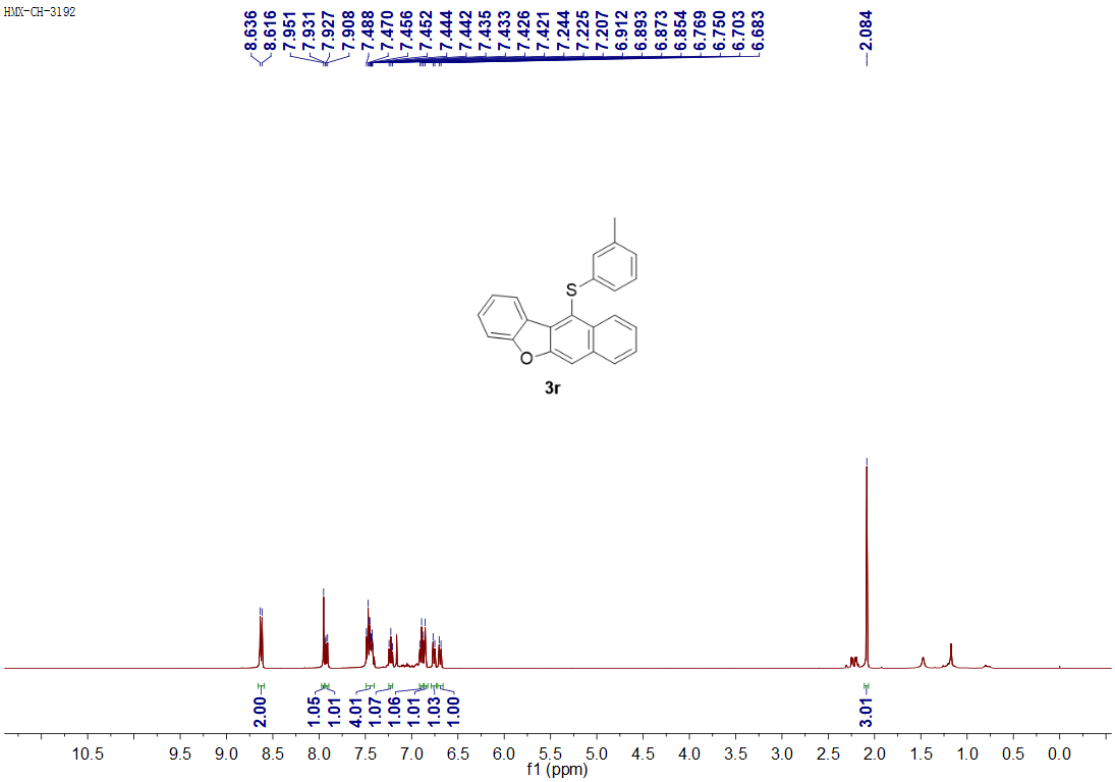
^{13}C NMR of **3p** in $CDCl_3$ (100 MHz)



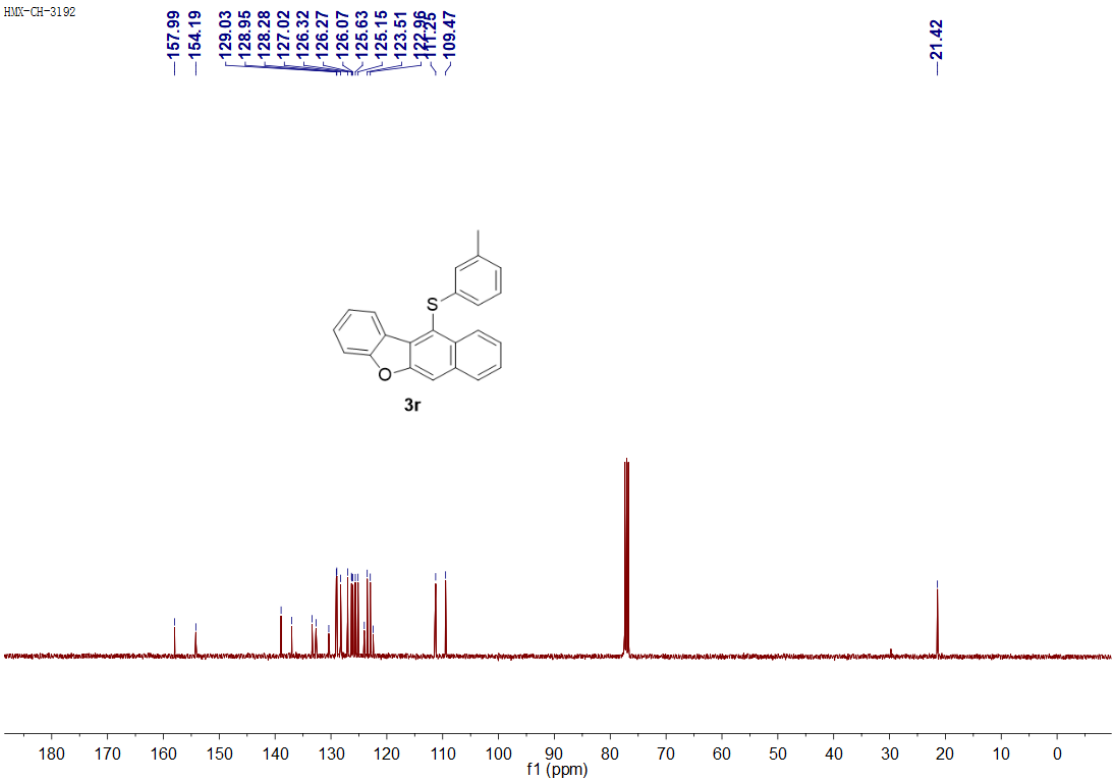
^{1}H NMR of **3q** in $CDCl_3$ (400 MHz)



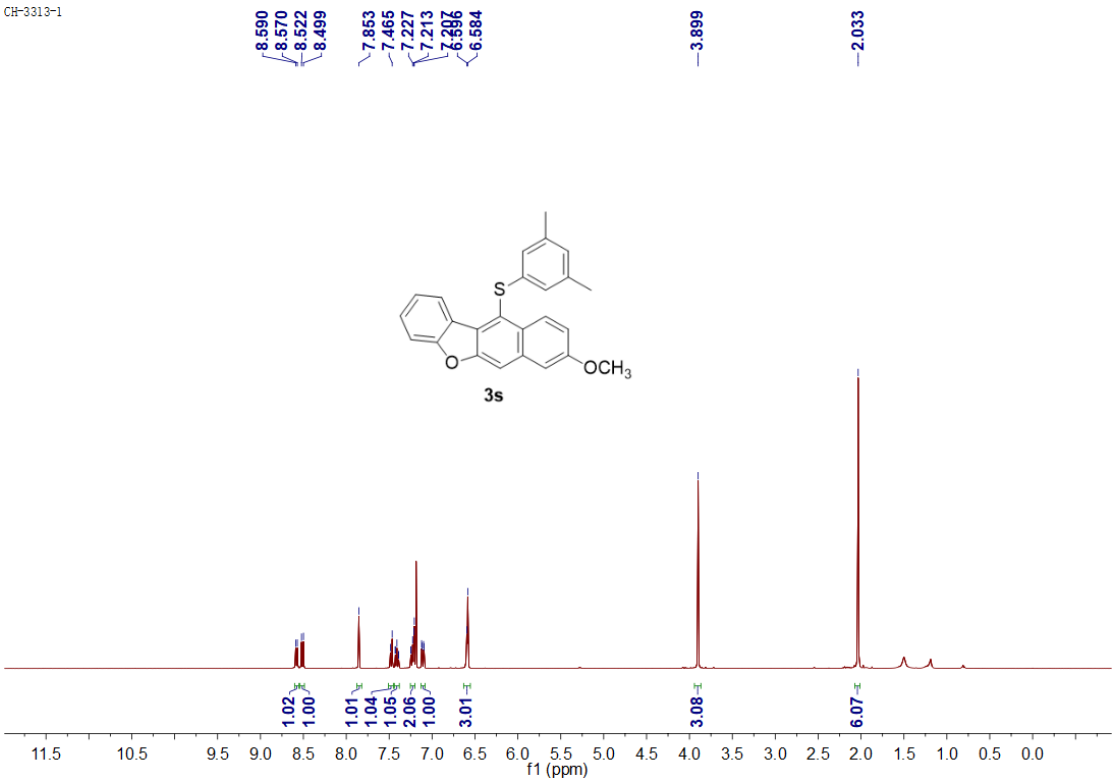
^{13}C NMR of **3q** in $CDCl_3$ (100 MHz)



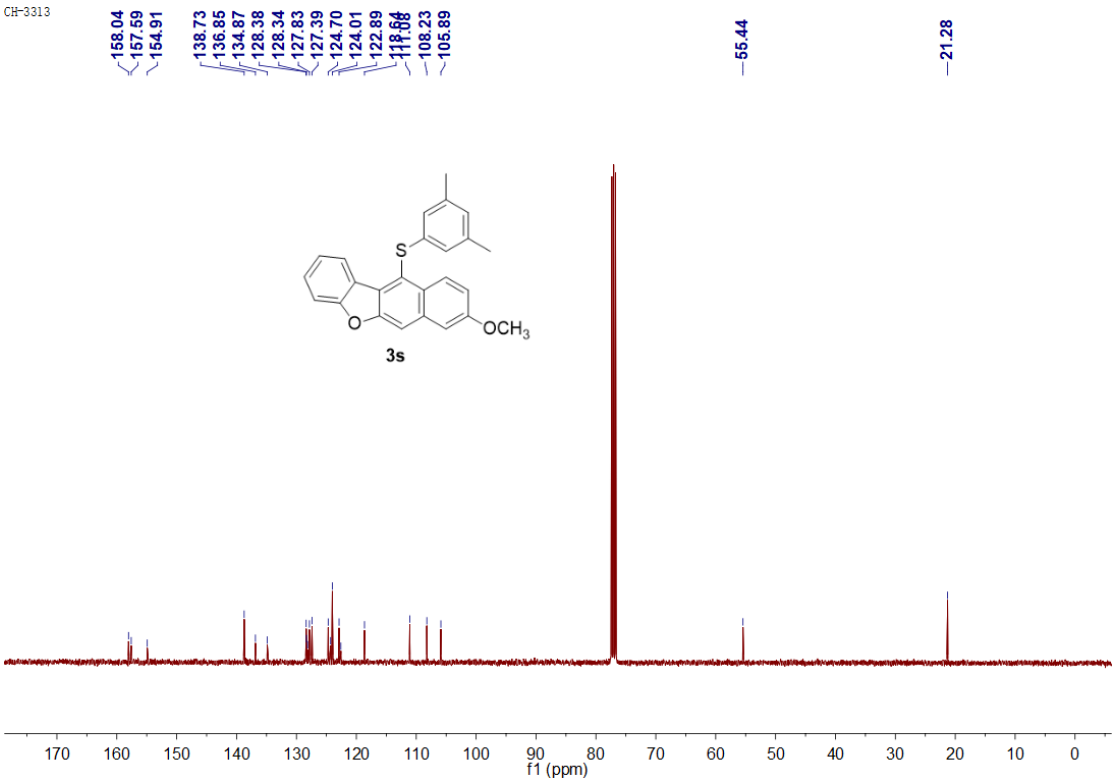
^{1}H NMR of **3r** in $CDCl_3$ (400 MHz)



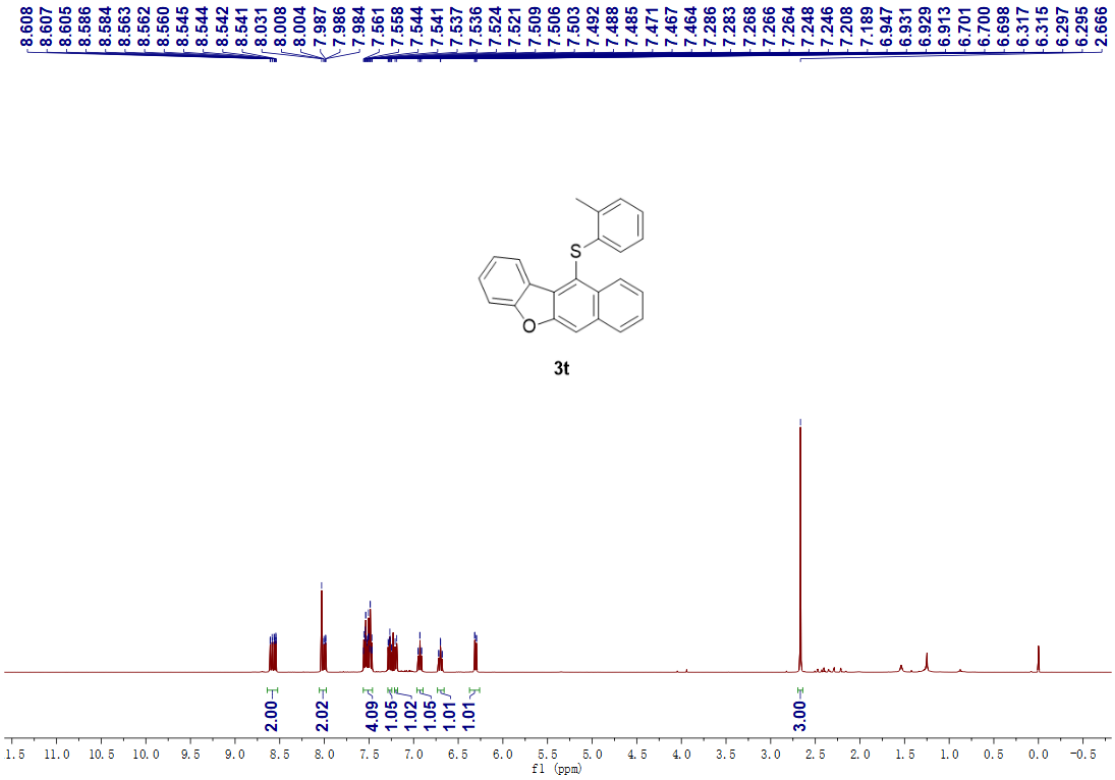
^{13}C NMR of **3r** in $CDCl_3$ (100 MHz)



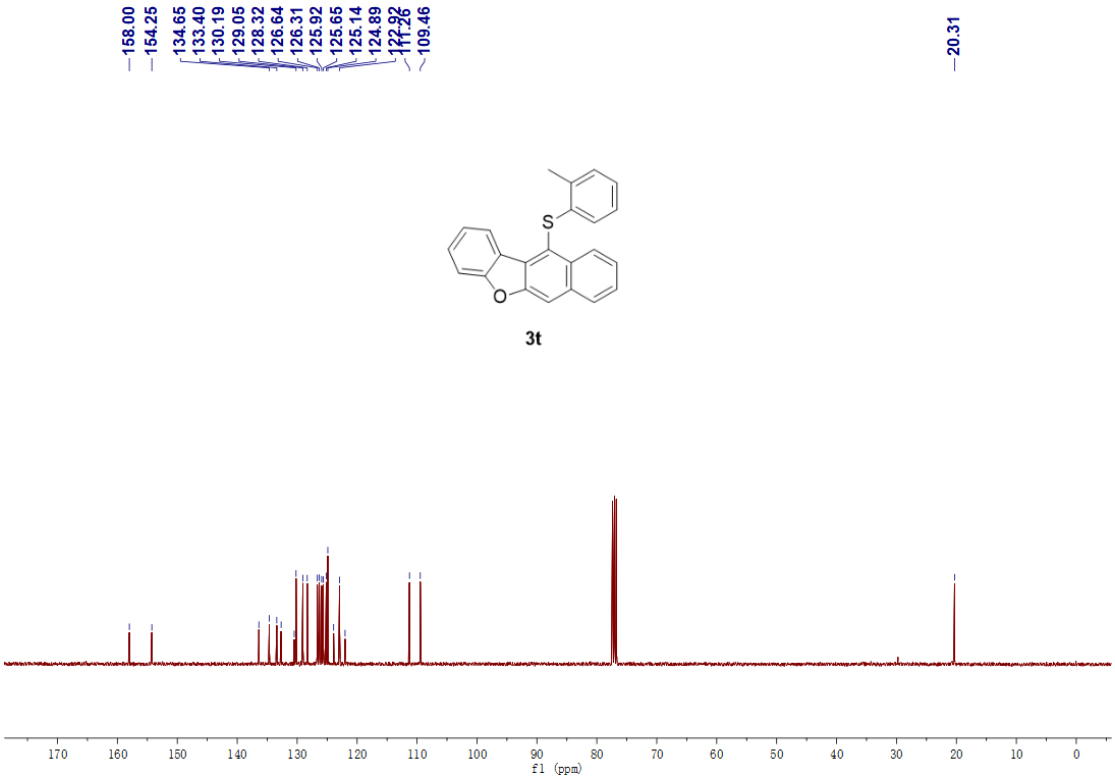
^{1}H NMR of **3s** in $CDCl_3$ (400 MHz)



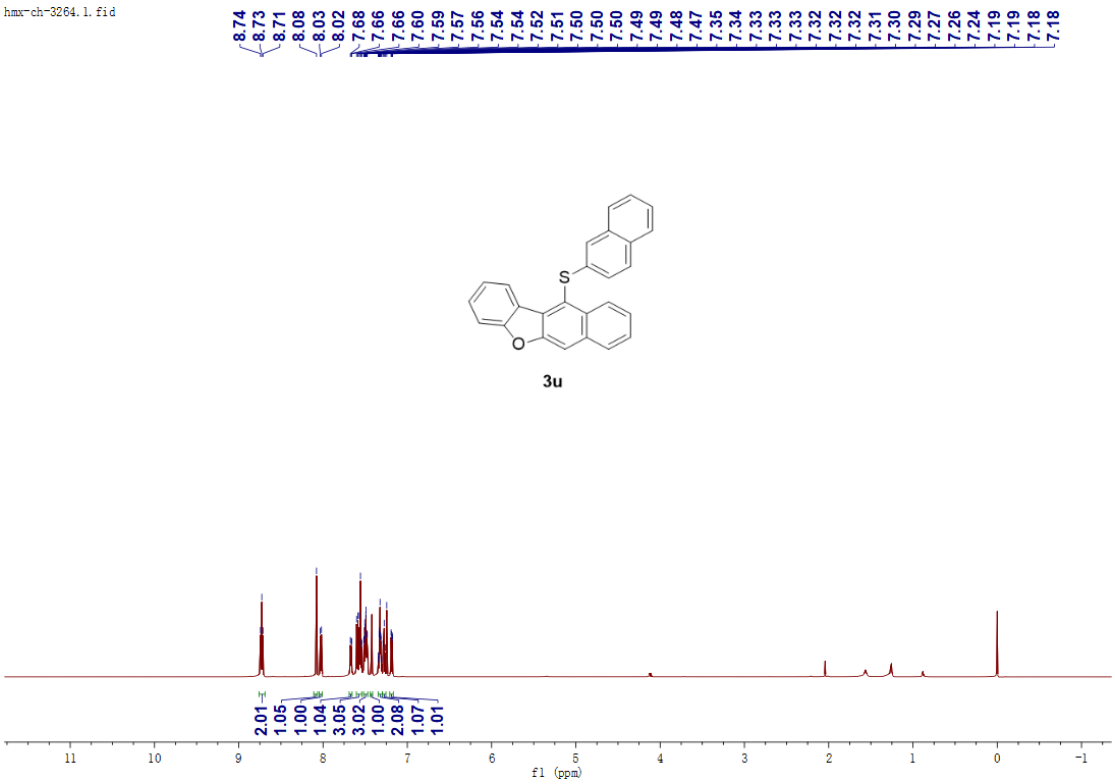
^{13}C NMR of **3s** in $CDCl_3$ (100 MHz)



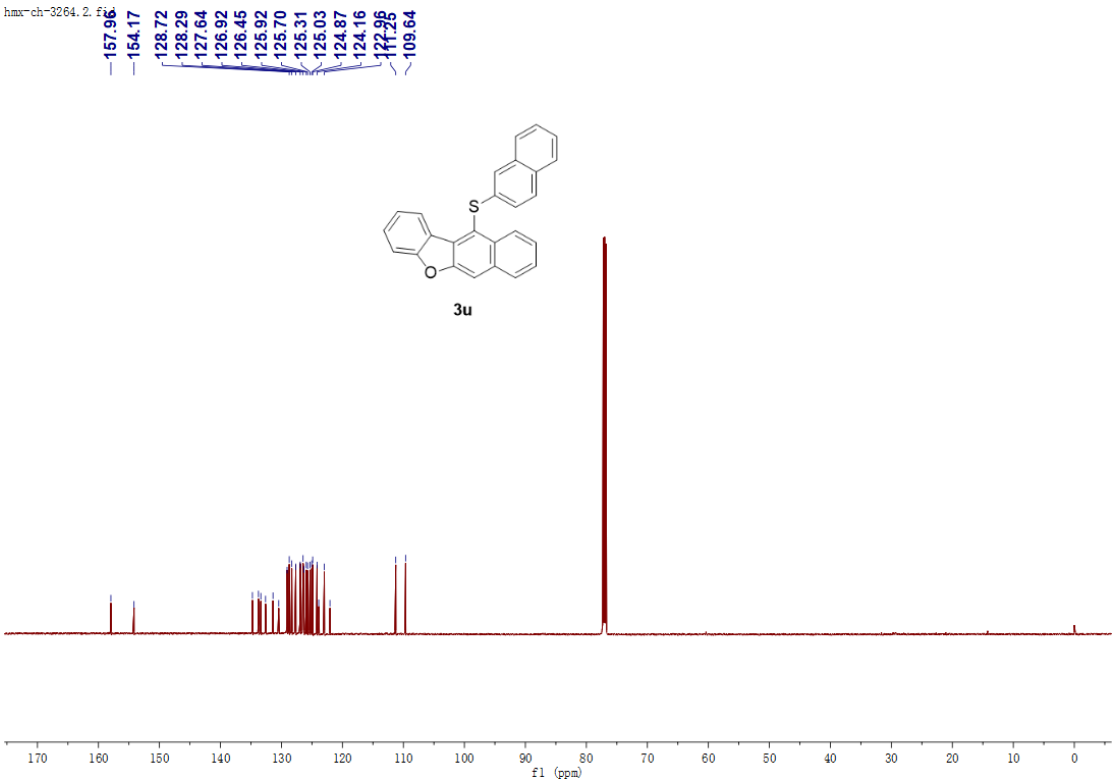
^{1}H NMR of **3t** in $CDCl_3$ (400 MHz)



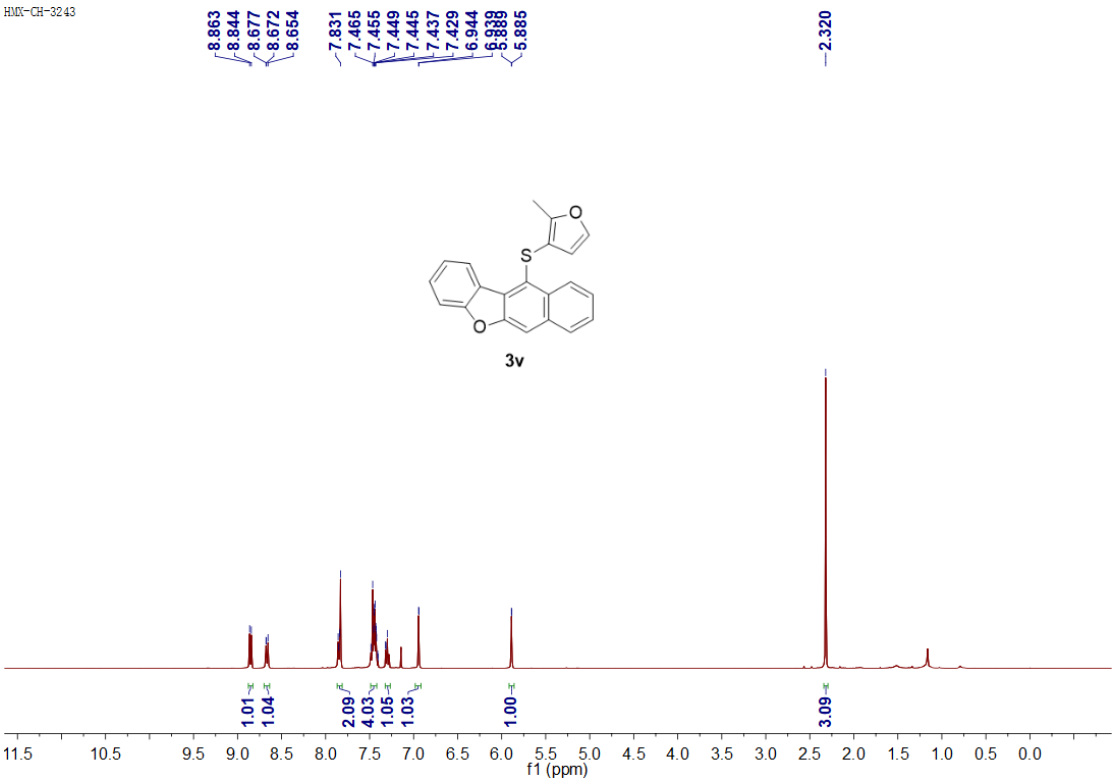
^{13}C NMR of **3t** in $CDCl_3$ (100 MHz)



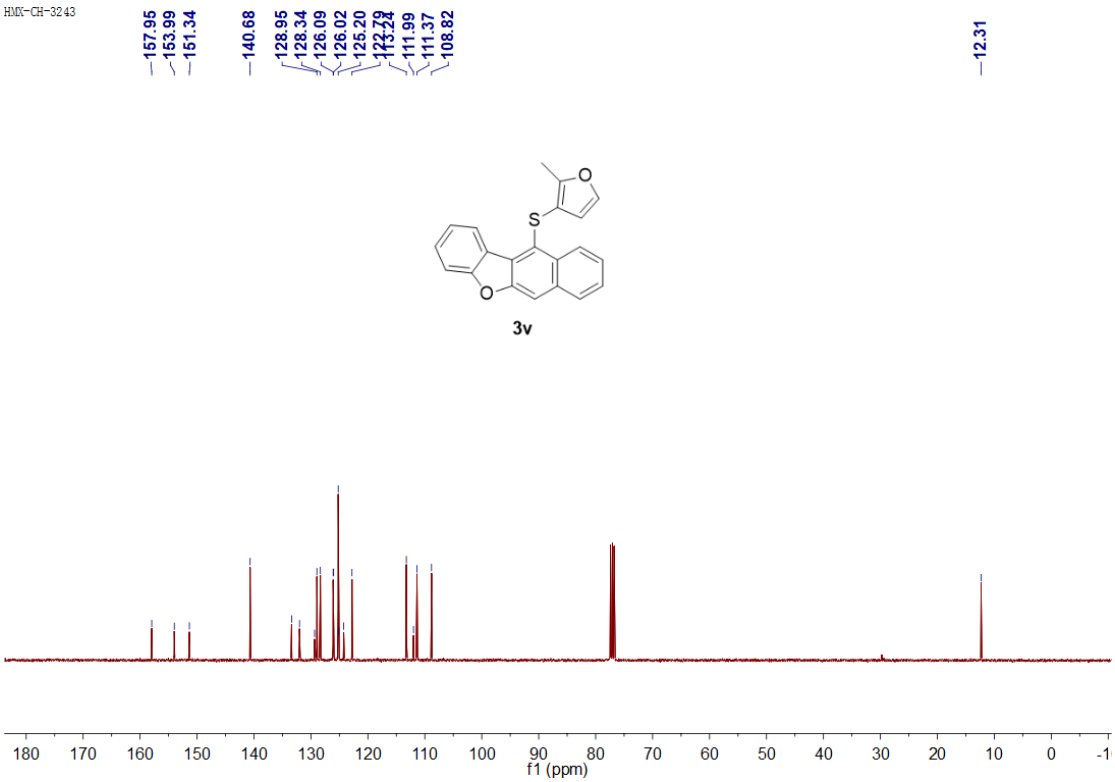
^{1}H NMR of **3u** in $CDCl_3$ (600 MHz)



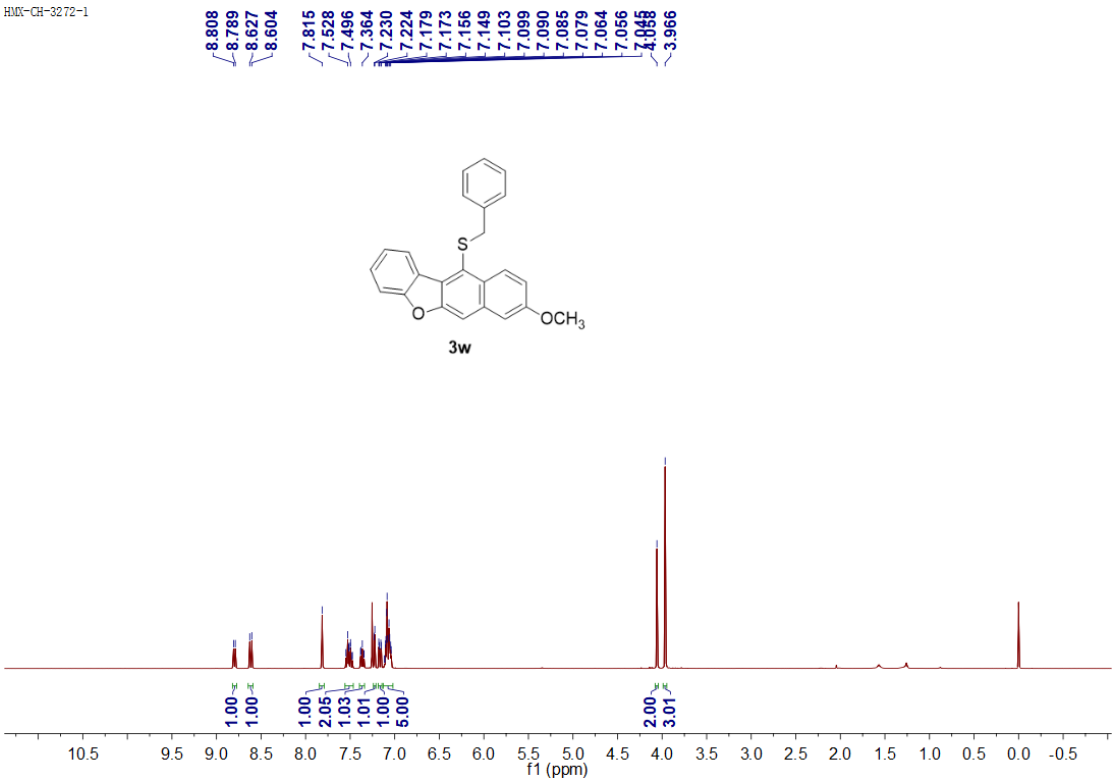
^{13}C NMR of **3u** in $CDCl_3$ (150 MHz)



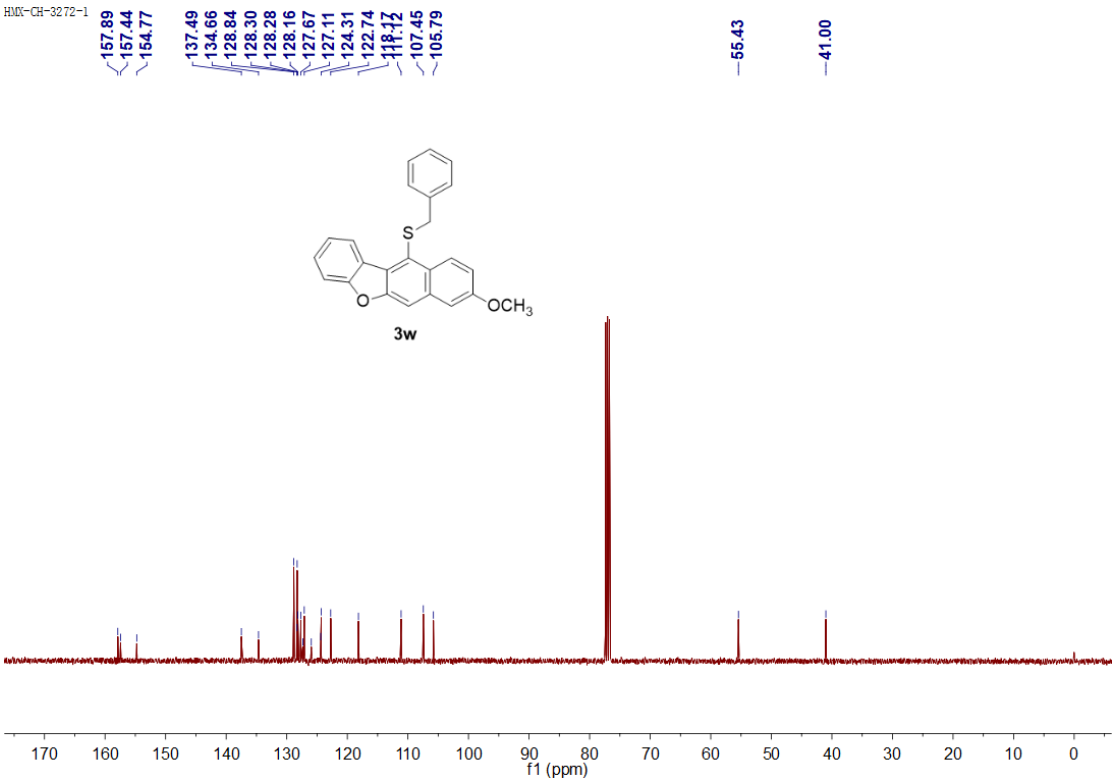
^{1}H NMR of **3v** in $CDCl_3$ (400 MHz)



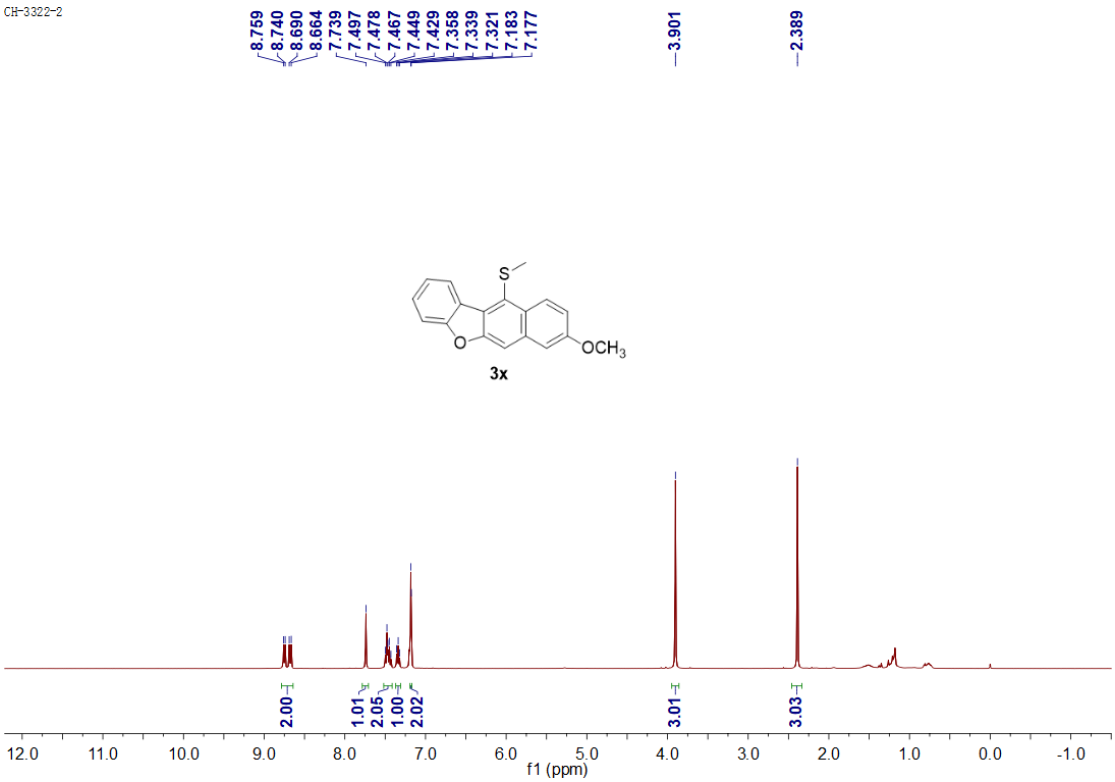
^{13}C NMR of **3v** in $CDCl_3$ (100 MHz)



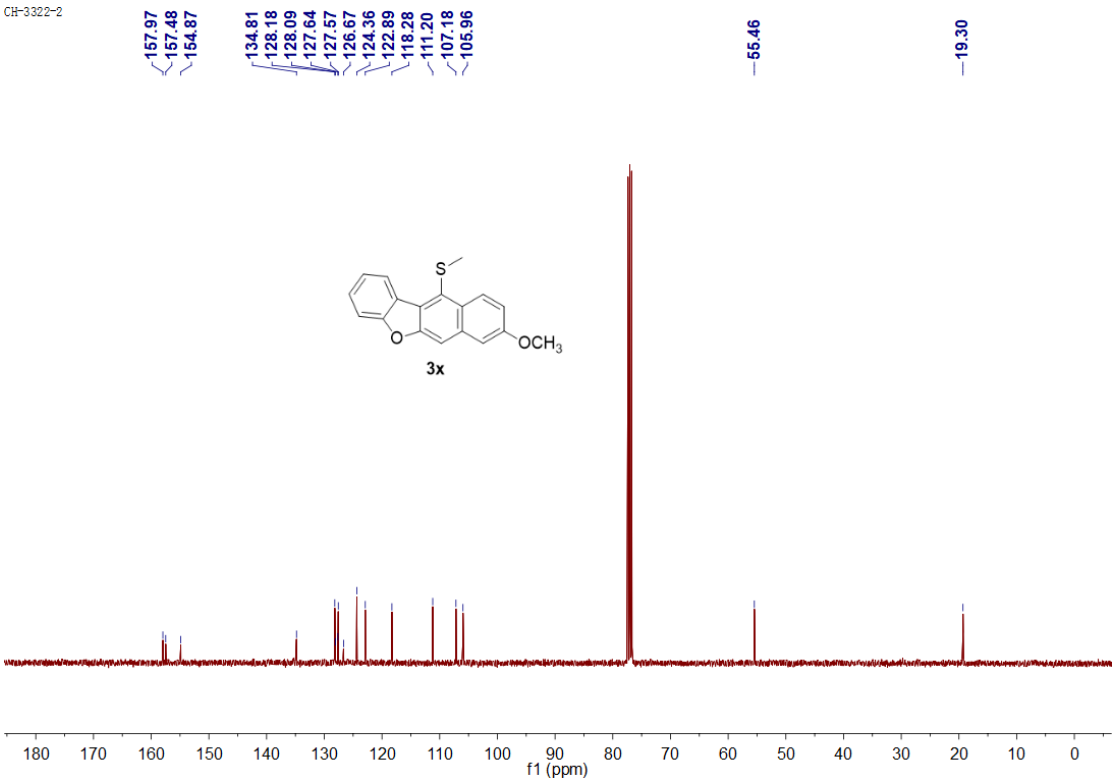
^{1}H NMR of **3w** in $CDCl_3$ (400 MHz)



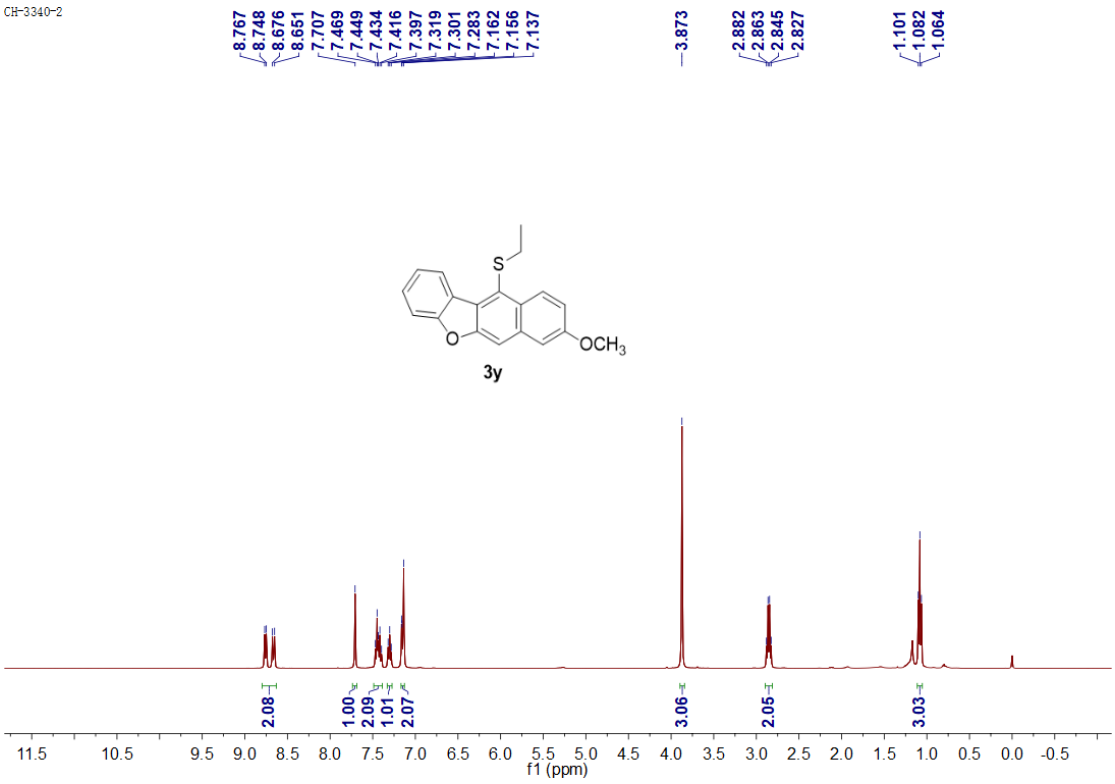
^{13}C NMR of **3w** in $CDCl_3$ (100 MHz)



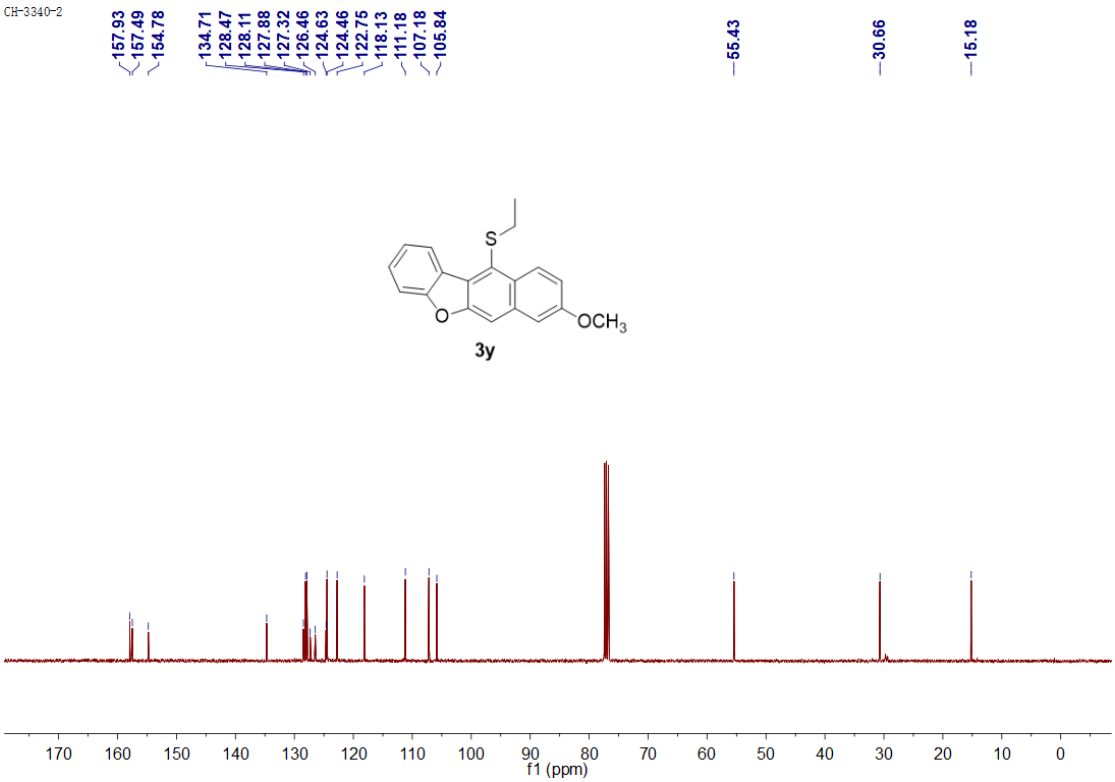
^{1}H NMR of **3x** in $CDCl_3$ (400 MHz)



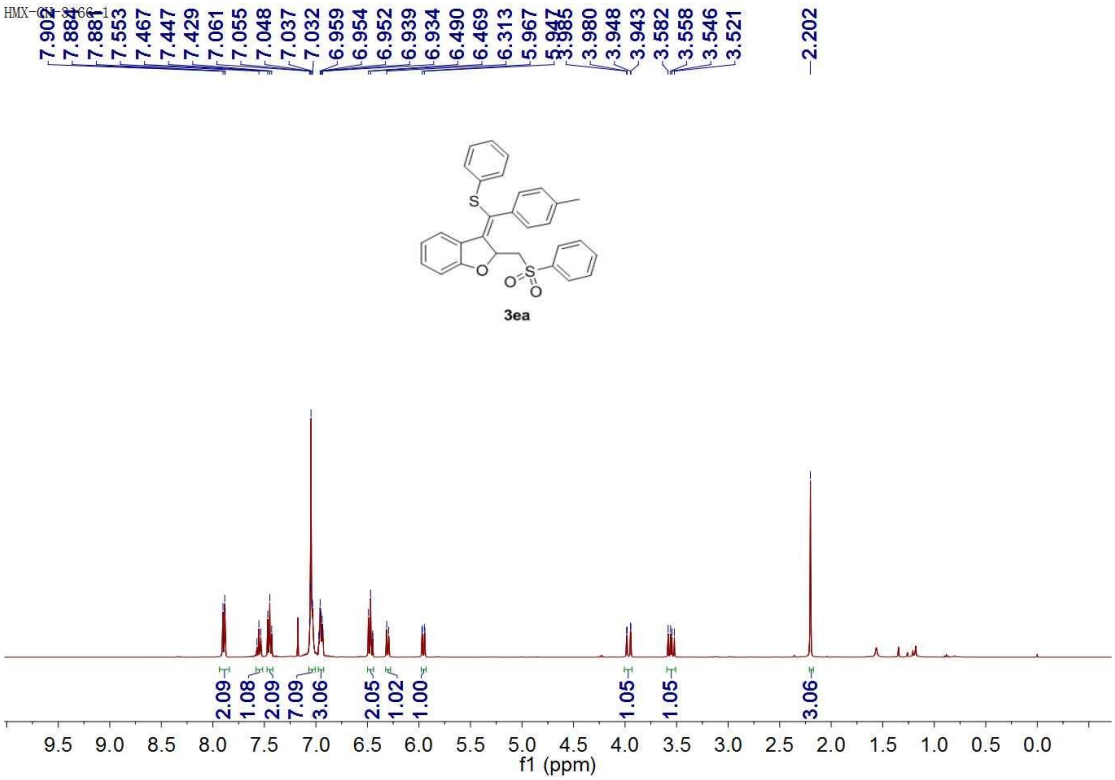
^{13}C NMR of **3x** in $CDCl_3$ (100 MHz)



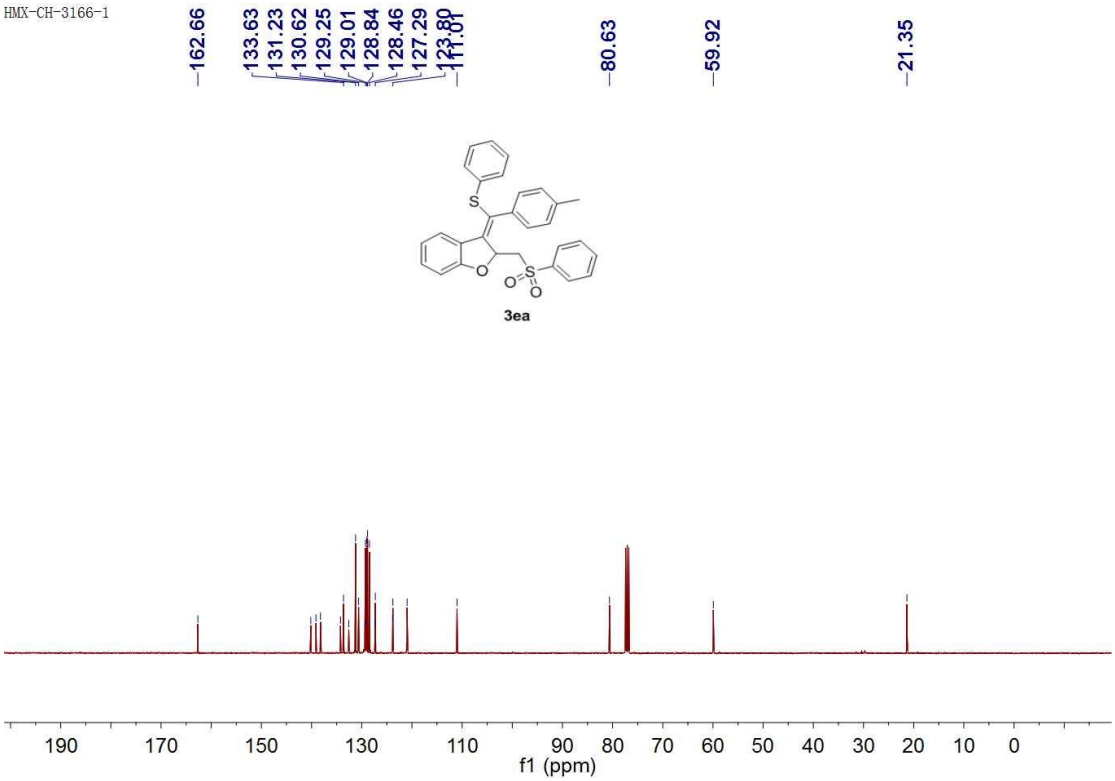
^{1}H NMR of **3y** in $CDCl_3$ (400 MHz)



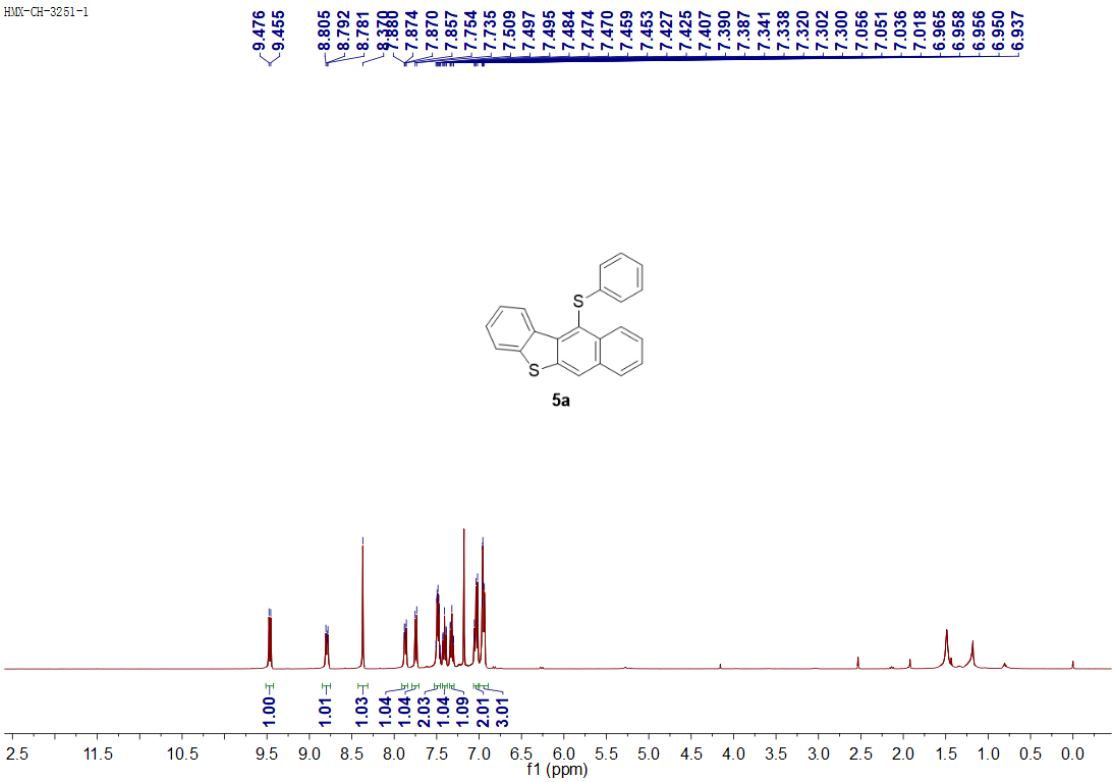
^{13}C NMR of **3y** in $CDCl_3$ (100 MHz)



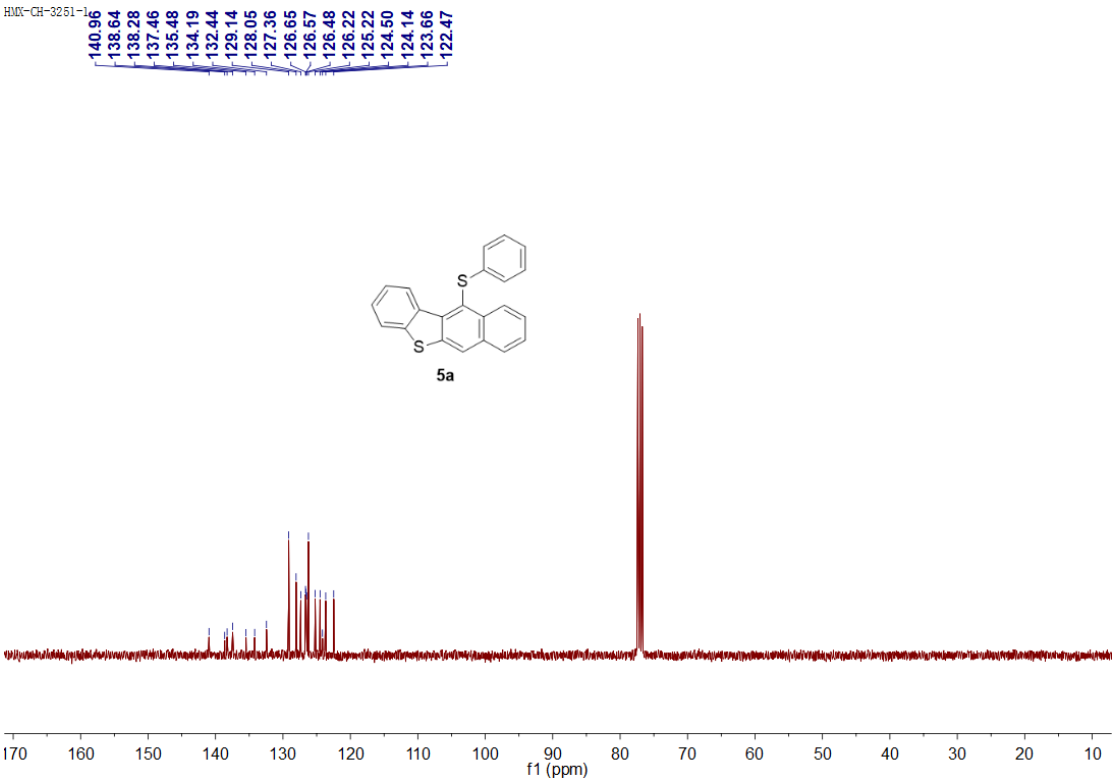
^{1}H NMR of **3ea** in $CDCl_3$ (400 MHz)



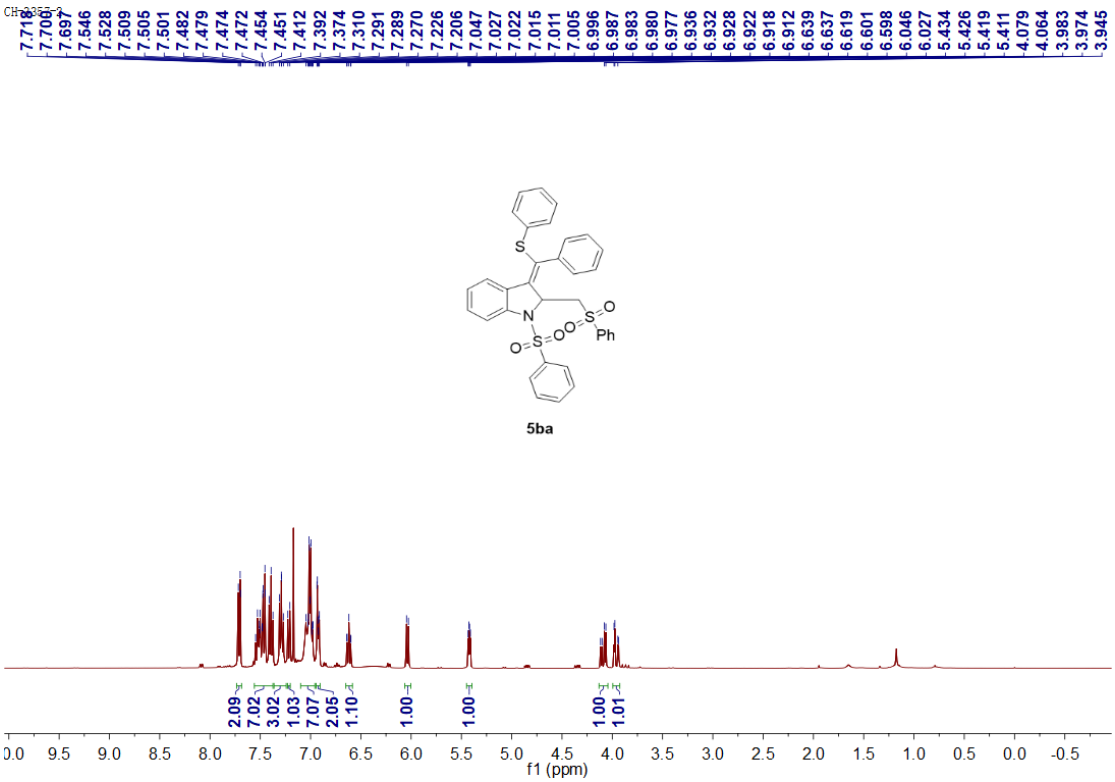
^{13}C NMR of **3ea** in $CDCl_3$ (100 MHz)



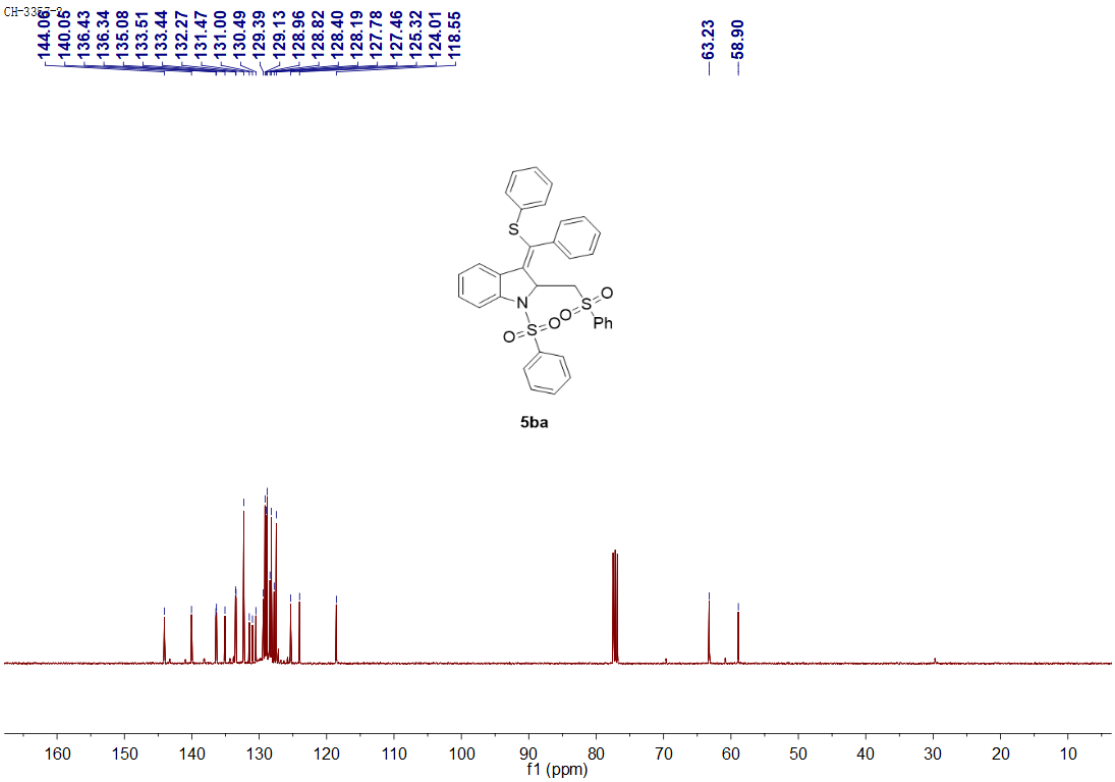
^{1}H NMR of **5a** in $CDCl_3$ (400 MHz)



^{13}C NMR of **5a** in $CDCl_3$ (100 MHz)



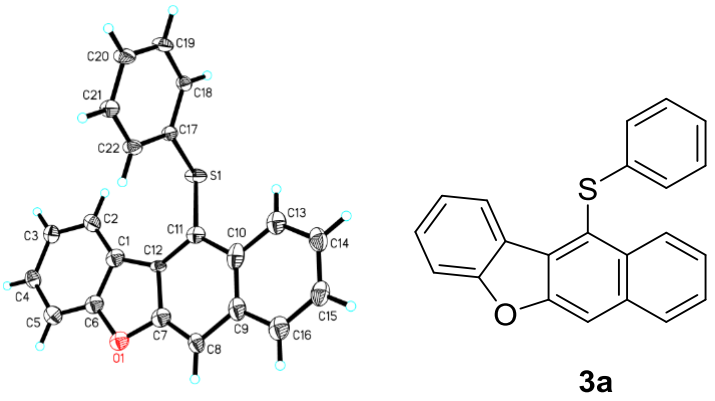
^{1}H NMR of **5ba** in $CDCl_3$ (400 MHz)



^{13}C NMR of **5ba** in $CDCl_3$ (100 MHz)

The X-ray crystal data of 3a

The X-ray crystal structure of **3a** (displacement ellipsoids are drawn at 50% probability level), CCDC: 2032114



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Bond precision:  C-C = 0.0064 A          Wavelength=0.71073

Cell:         a=9.8020(9)        b=9.8192(9)       c=9.9339(10)
              alpha=112.718(9)   beta=105.510(8)   gamma=101.172(8)
Temperature:  100 K

                Calculated                Reported
Volume          800.96(17)                800.96(14)
Space group     P -1                      P -1
Hall group      -P 1                      -P 1
Moiety formula  C22 H14 O S               C22 H14 O S
Sum formula     C22 H14 O S               C22 H14 O S
Mr              326.39                    326.39
Dx,g cm-3       1.353                     1.353
Z               2                         2
Mu (mm-1)       0.206                     0.206
F000            340.0                     340.0
F000'           340.38
h,k,lmax        11,11,11                  11,11,11
Nref            2818                      2818
Tmin,Tmax       0.978,0.984               0.226,1.000
Tmin'           0.978

Correction method= # Reported T Limits: Tmin=0.226 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.000          Theta(max)= 24.999

R(reflections)= 0.0782( 2159)     wR2(reflections)= 0.2202( 2818)

S = 1.182                 Npar= 219
```

Preparation of the crystal

In a test tube, product **3a** was dissolved in CH_3Cl (0.5 mL). Then the closed tube was left at ambient temperature until the well-shaped single crystals formed.

Crystal measurement

3a was collected at 100 K on a Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Cu Kα radiation. Data reduction was carried out with the diffractometer's software.[1] The structure was solved by direct methods using Olex2 software,[2] and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXL-2018[3] using a full-matrix least squares procedure based on F^2. The weighted *R* factor, *wR* and goodness-of-fit *S* values were obtained based on F^2. The hydrogen atom positions were fixed geometrically at the calculated distances and allowed to ride on their parent atoms.

[1] Agilent Technologies, CrysAlisPRO, Version 1.171.36.28, **2013**.

[2] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.

[3] Kratzert, D.; Holstein, J. J.; Krossing, I. *DSR*: enhanced modelling and refinement of disordered structures with *SHELXL*. *J. Appl. Cryst.* **2015**, *48*, 933-938.