

Supporting Information

Electrooxidation-Induced Arylsulfonylation of Xanthene Derivatives with DABSO as an SO₂ Surrogate

Yi Pan,^{#b} Zhenjie Qi,^{#c} Wenxue Li,^b Jingbin Huang,^b Yu Huang,^{*b} Zhenyu An^{*b} and Yafeng Liu^{*a}

^a School of Chemistry and Chemical Engineering, North Minzu University, Yinchuan 750000, Ningxia, China. E-mail: liuyf@nmu.edu.cn

^b Key Laboratory of Protection, Development and Utilization of Medicinal Resources in Liupanshan Area, Ministry of Education, Peptide & Protein Drug Research Center, School of Pharmacy, Ningxia Medical University, Yinchuan 750004, China; E-mail: anzy@nxmu.edu.cn; huangyunxmu@163.com.

^c School of Resource & Environment and Safety Engineering, Jining University, Qufu 273100, Shandong, China.

[#] These authors contributed equally to this work.

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General remark

All the electrochemical reactions were performed in an undivided cell unless otherwise noted. The electrolysis instrument used is an adjustable DC regulated power supply (WANPTEK WPS605B).

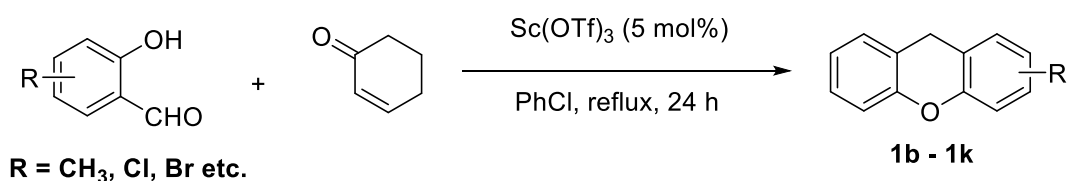
^1H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on Bruker 400M and in CDCl_3 . All ^1H NMR, ^{13}C NMR, and ^{19}F NMR chemical shifts were given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The NMR peak multiplicities identified as s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet; coupling constants (J) were reported in Hz. All compounds were further characterized by HRMS; copies of their ^1H NMR, ^{13}C NMR, and ^{19}F NMR spectra were provided. Cyclic voltammograms were obtained on a CHI 660C potentiostat (CH Instruments, Inc.).

Products were purified by flash chromatography on 200–300 mesh silica gels. Yields refer to chromatographically and spectroscopically pure materials unless otherwise stated. All melting points were determined without correction. All reactions were carried out under air in oven-dried glassware, unless otherwise noted. All reagents were purchased commercially and used as received, unless otherwise noted.

Substrate preparation

1) General procedure for the preparation of xanthene,thioxanthene (1b-1k)

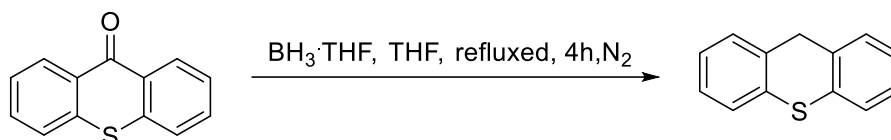
General procedure A^[1]



Salicylaldehyde derivatives (1.1 mmol) and 2-cyclohexene-1-one (1.0 mmol) was quickly added to a suspension of scandium (III) triflate (0.05 mmol) in chlorobenzene (4.0 mL). The reaction mixture was refluxed for 24 hours and allowed to cool to room temperature. DCM (20.0 mL) and saturated aqueous NaHCO_3 (20.0 mL) were added to the reaction mixture and the two layers separated. The aqueous phase was extracted with DCM (3×20.0 mL) and the combined organic layers were dried over Na_2SO_4 ,

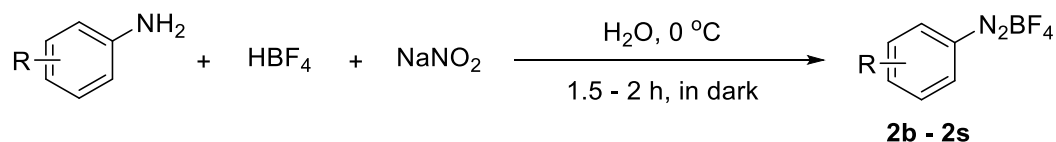
filtered and solvent was removed by rotary evaporator. The crude xanthene products 1 was purified by column chromatography on silica gel using eluent mixtures of petroleum ether and ethyl acetate.

General procedure B^[2]



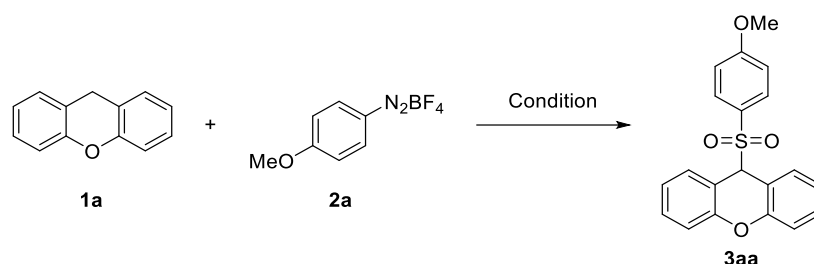
To a slurry of thioxanthone (5.0 mmol) in THF (10 mL), $\text{BH}_3 \cdot \text{THF}$ solution (1.0 M in THF; 10 mL, 10.0 mmol) was added dropwise and the mixture was refluxed for 4 h under N_2 atmosphere. On completion (checked by TLC) the mixture was cooled to 0-5 °C and cautiously quenched by the addition of brine (20 mL) followed by 2 M aq. NaOH (10 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (1 × 20 mL). The collected organic layers were dried over anhydrous Na_2SO_4 and evaporated. The crude product was purified by silica gel column chromatography using 100% petroleum ether as eluent to obtain thioxanthene as a white solid.

2) General procedure for the preparation of benzenediazonium tetrafluoroborate (2b-2s)^[3]



In a round-bottom a pre-cooling sodium nitrite (1.4 g, 20 mmol) in water (5 mL) was added into a mixture solution of HBF_4 (50 wt% in water, 6 mL) and aniline (1.8 mL, 20 mmol) in water (6 mL) in an ice-water bath. After 1.5 h of vigorous stirring, the reaction was at 0 °C in dark, the precipitate was collected by filtration followed by washing with little ice-cold water and the white crystalline was obtained by re-dissolved in acetone and then precipitated with the addition of diethyl ether, then drying to give aryl diazo salt.

Development of the reaction condition



An undivided test column-type electrolysis cell (25 mL) was charged with a stir bar, 9*H*-xanthene **1a** (0.2 mmol, 1.0 equiv.), electrolyte (0.2 mmol), DABSO (0.2 mmol), CH₃CN (4 mL), AcOH (1 mL). Then, add benzenediazonium tetrafluoroborate **2a** (0.3 mmol), and the resulting suspension was stirred for a minute. Then the prepared electrodes were placed into the reaction mixture. The anode and the cathode were placed into reaction system. The mixture was electrolyzed at a constant current of *x* mA at *T* in a N₂ atmosphere until the reagent and its intermediate were consumed entirely (monitored by TLC). The reaction electrodes were taken out, washed twice with ethyl acetate (10 mL) ultrasonically, and the ethyl acetate was combined with the reaction mixture. The combined mixture was washed with H₂O and extracted with ethyl acetate (20 mL × 3), brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography with petroleum ether and ethyl acetate (10:1) as eluents to afford the desired product **3aa**.

(a) Table S1. Survey of solvent^a

Entry	Solvent	Yield of 3aa (%)
1	CH ₃ CN : AcOH = 4 : 1	81
2	CH ₃ CN	55
3	CH ₃ OH	41
4	DCE	18
5	DMSO	11
6	CH ₃ CN : H ₂ O = 4 : 1	45
7	CH ₃ CN : HFIP = 10 : 1	50
8	CH ₃ CN : AcOH = 10 : 1	74
9	CH ₃ CN : AcOH = 2 : 1	65
10	CH ₃ CN : AcOH = 1 : 1	59

^a Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), DABSO (0.2 mmol), *n*Bu₄NPF₆ (0.2 mmol) in an undivided

cell equipped with carbon rod (Φ 6 mm) as anode and Pt plate (1.0 cm \times 1.0 cm \times 0.1 cm) as cathode at a constant current of 10 mA in selected solvent (5 mL), 40 °C, 2 h, N₂.

(b) Table S2. Survey of electrodes^a

Entry	Electrodes	Yield of 3aa (%)
1	C(+)/Pt(-)	81
2	Pt(+)/Pt(-)	61
3	C(+)/Ni(-)	48
4	C(+)/C(-)	45

^a Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), DABSO (0.2 mmol), *n*Bu₄NPF₆ (0.2 mmol) in an undivided cell equipped with selected electrodes at a constant current of 10 mA in CH₃CN : AcOH = 4 : 1 (5 mL), 40 °C, 2 h, N₂.

(c) Table S3. Survey of electrolyte^a

Entry	Electrolyte	Yield of 3aa (%)
1	<i>n</i>Bu₄NPF₆	81
2	<i>n</i> Bu ₄ NBF ₄	68
3	<i>n</i> Bu ₄ NI	53
4	<i>n</i> Bu ₄ NOAc	58
5	<i>n</i> Bu ₄ NCIO ₄	50
6	<i>n</i> Bu ₄ NOH	20
7	Et ₄ NPF ₆	65
8	Me ₄ NPF ₆	57

^a Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), DABSO (0.2 mmol), electrolyte (0.2 mmol) in an undivided cell equipped with carbon rod (Φ 6 mm) as anode and Pt plate (1.0 cm \times 1.0 cm \times 0.1 cm) as cathode at a constant current of 10 mA in CH₃CN : AcOH = 4 : 1 (5 mL), 40 °C, 2 h, N₂.

(d) Table S4. Survey of current intensity and reaction time^a

Entry	Reaction current and time	Yield of 3aa (%)
1	10 mA for 2 h	81
2	10 mA for 3 h	56
3	7 mA for 3.5 h	64
4	5 mA for 5 h	66
5	12 mA for 2 h	60

^a Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), DABSO (0.2 mmol), *n*Bu₄NPF₆ (0.2 mmol) in an undivided cell equipped with carbon rod (Φ 6 mm) as anode and Pt plate (1.0 cm \times 1.0 cm \times 0.1 cm) as cathode at a constant current in CH₃CN : AcOH = 4 : 1 (5 mL), 40 °C, 2 h, N₂.

(e) Table S4. Survey of temperature^a

Entry	Reaction temperature	Yield of 3aa (%)
1	40 °C	81
2	0 °C	43

3	10 °C	51
4	25 °C	66
5	60 °C	64

^a Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), DABSO (0.2 mmol), *n*Bu₄NPF₆ (0.2 mmol) in an undivided cell equipped with carbon rod (Φ 6 mm) as anode and Pt plate (1.0 cm \times 1.0 cm \times 0.1 cm) as cathode at a constant current in CH₃CN : AcOH = 4 : 1 (5 mL), *T*, 2 h, N₂.

General procedures for the electrolysis

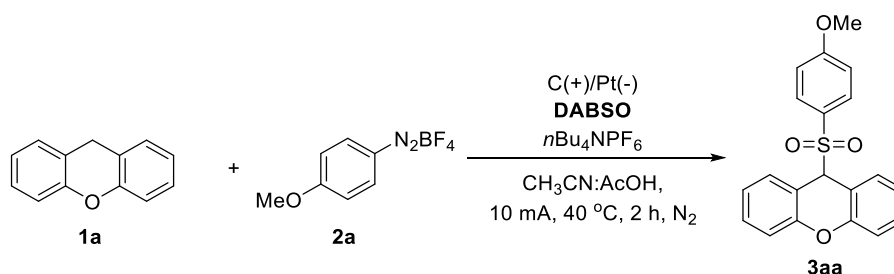
(a) The materials used to make the electrolytic cell

All the materials used to make the electrolytic cell were commercially available (Figure S1). The anode were carbon rod (Φ 6 mm) and the cathode were platinum plate electrode (1.0 cm \times 1.0 cm \times 0.1mm) (Shanghai yueci).



Figure S1. The materials used to make the electrolytic cell for the synthesis of 9-((4-methoxyphenyl)sulfonyl)-9*H*-xanthene

(b) General procedure for the electrosynthesis of 9-((4-methoxyphenyl)sulfonyl)-9*H*-xanthene



An undivided test column-type electrolysis cell (25 mL) was charged with a stir bar, 9*H*-xanthene **1a** (0.2 mmol, 1.0 equiv.), *n*Bu₄NPF₆ (0.2 mmol), DABSO (0.2 mmol), CH₃CN (4 mL), AcOH (1 mL). Then, add benzenediazonium tetrafluoroborate **2a** (0.3

mmol), and the resulting suspension was stirred for a minute. Then the prepared electrodes were placed into the reaction mixture. The anode and the cathode were placed into reaction system. The mixture was electrolyzed at a constant current of 10 mA at 40 °C in a N₂ atmosphere until the reagent and its intermediate were consumed entirely (monitored by TLC). The reaction electrodes were taken out, washed twice with ethyl acetate (10 mL) ultrasonically, and the ethyl acetate was combined with the reaction mixture. The combined mixture was washed with H₂O and extracted with ethyl acetate (20 mL × 3), brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography with petroleum ether and ethyl acetate (10:1) as eluents to afford the desired product **3aa**.

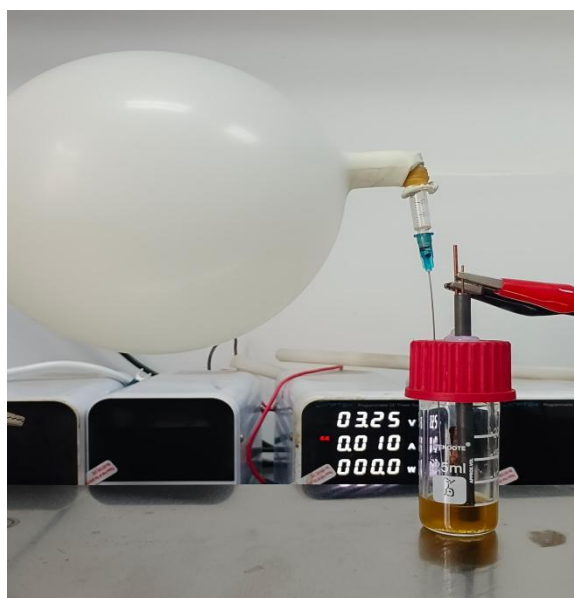


Figure S2. Reaction setup.

Cyclic voltammetry experiments

The cyclic voltammetry experiments were carried out with a computer-controlled electrochemical analyzer for electrochemical measurements. The experiment was performed in a three-electrode cell (volume 20 mL) with CH₃CN = 5 mL as the solvent, *n*Bu₄NPF₆ (0.02 M) as the supporting electrolyte, the tested compound was added respectively, glassy carbon (diameter 3 mm) as the working electrode, Pt plate (1.0 cm × 1.0 cm × 0.1 mm) as the auxiliary electrode, and Ag/AgCl (saturated aqueous KCl) as the reference electrode. The scan speed was 100 mV/s. The potential ranges investigated were 0 V to +4 V, then we performed the experiments.

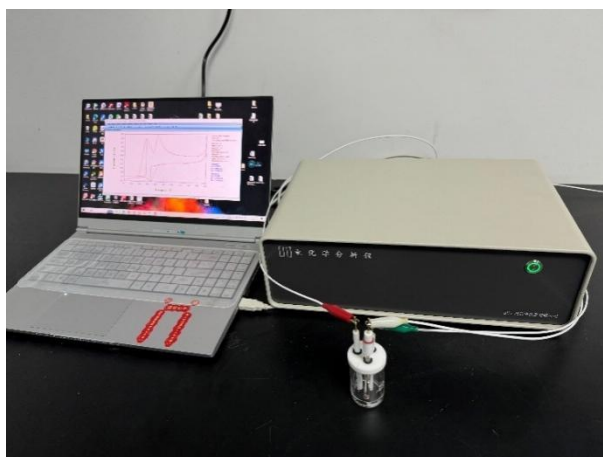


Figure S3. Cyclic voltammograms experiments setup

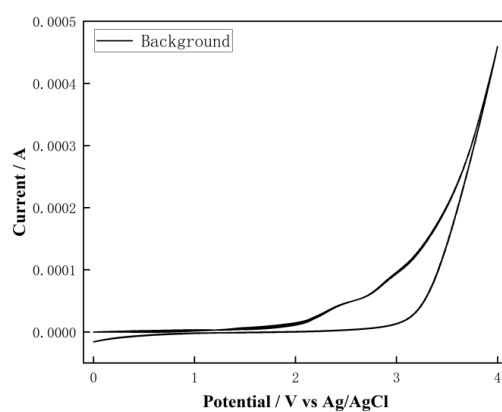


Figure S4. Cyclic voltammogram of $n\text{Bu}_4\text{NPF}_6$ as an electrolyte in $\text{CH}_3\text{CN} = 5 \text{ mL}$.

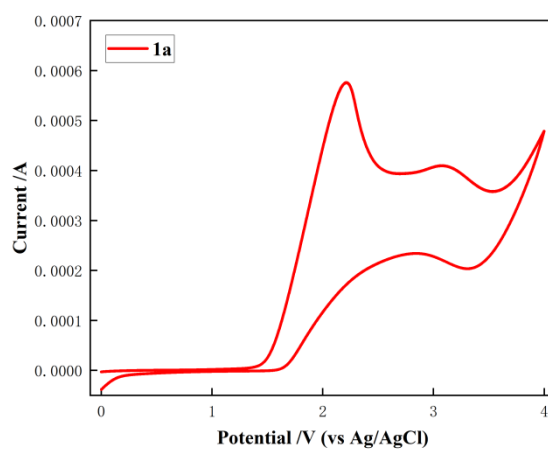


Figure S5. Cyclic voltammogram of electrolyte and **1a** in $\text{CH}_3\text{CN} = 5 \text{ mL}$.

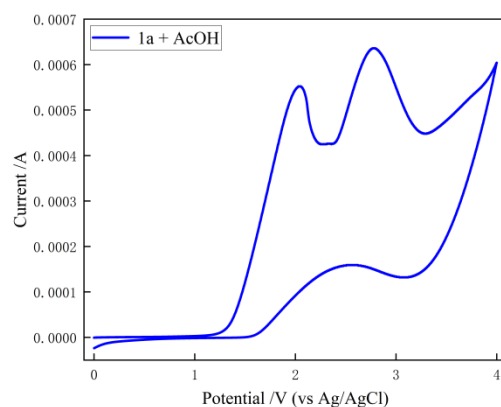


Figure S6. Cyclic voltammogram of electrolyte and **1a** in CH₃CN : AcOH = 5 mL : 1ml.

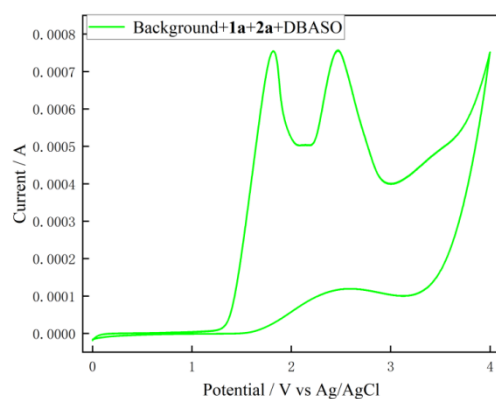


Figure S7. Cyclic voltammogram of *n*Bu₄NPF₆, **1a**, **2a**, DABSO in CH₃CN:AcOH = 5ml : 1ml.

The cyclic voltammetry experiments were carried out with a computer-controlled electrochemical analyzer for electrochemical measurements. The experiment was performed in a three-electrode cell (volume 20 mL) with CH₃CN = 5 mL as the solvent, *n*Bu₄NPF₆ (0.02 M) as the supporting electrolyte, the tested compound was added respectively, glassy carbon (diameter 3 mm) as the working electrode, the platinum wire as the auxiliary electrode, and Ag/AgCl (saturated aqueous KCl) as the reference electrode. The scan speed was 100 mV/s. The potential ranges investigated were -2 V to 0 V, then we performed the experiments.

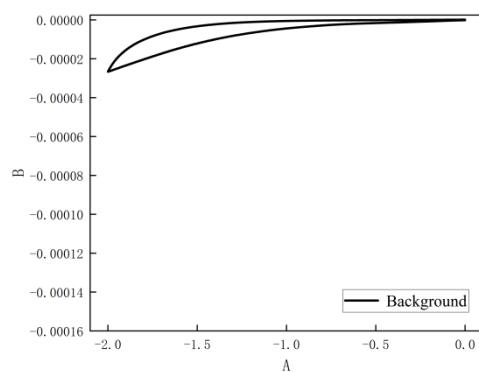


Figure S8. Cyclic voltammogram of $n\text{Bu}_4\text{NPF}_6$ as an electrolyte in $\text{CH}_3\text{CN} = 5 \text{ mL}$.

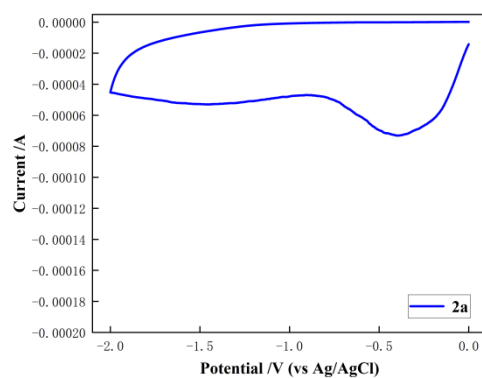


Figure S9. Cyclic voltammogram of electrolyte and **2a** in $\text{CH}_3\text{CN} = 5 \text{ mL}$.

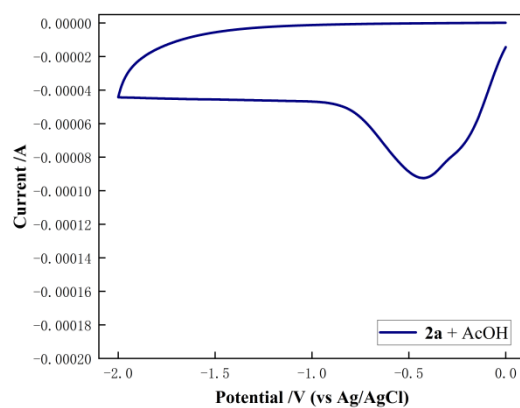


Figure S10. Cyclic voltammogram of electrolyte and **2a** in $\text{CH}_3\text{CN} : \text{AcOH} = 5 \text{ mL} : 1 \text{ mL}$.

Mechanistic experiments

Intermediate trapping experiments

In order to confirm the presence of free radical intermediates during the reaction, we performed HRMS detection. Results possible products and intermediates were detected.

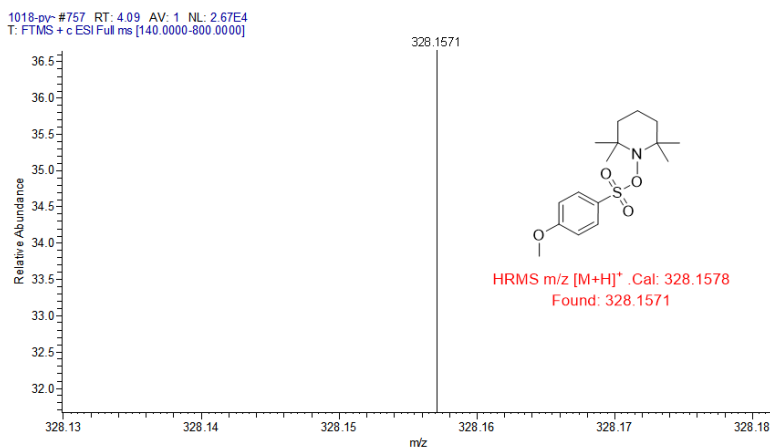


Figure S11 Mass spectrometry (HRMS) data of radical-adduct I

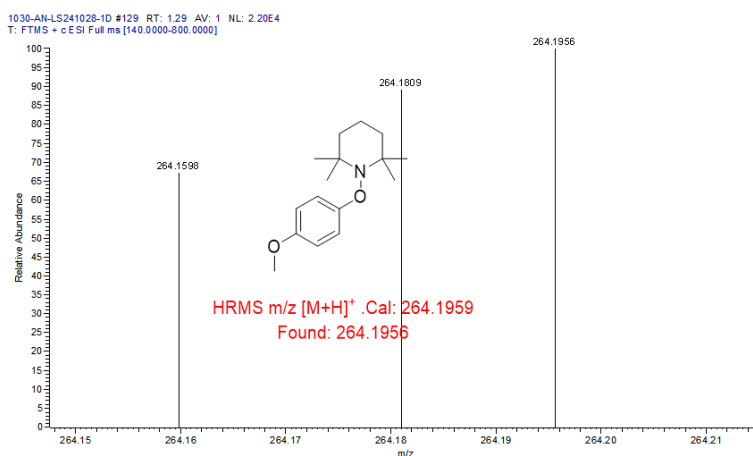


Figure S12 Mass spectrometry (HRMS) data of radical-adduct II

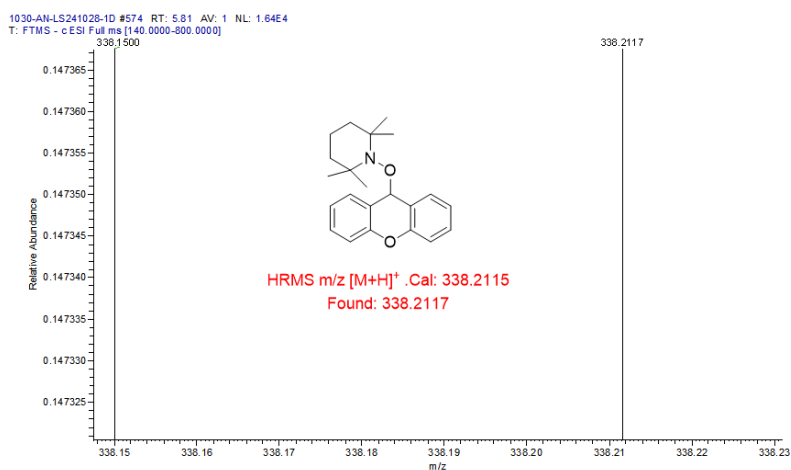


Figure S13 Mass spectrometry (HRMS) data of radical-adduct **III**

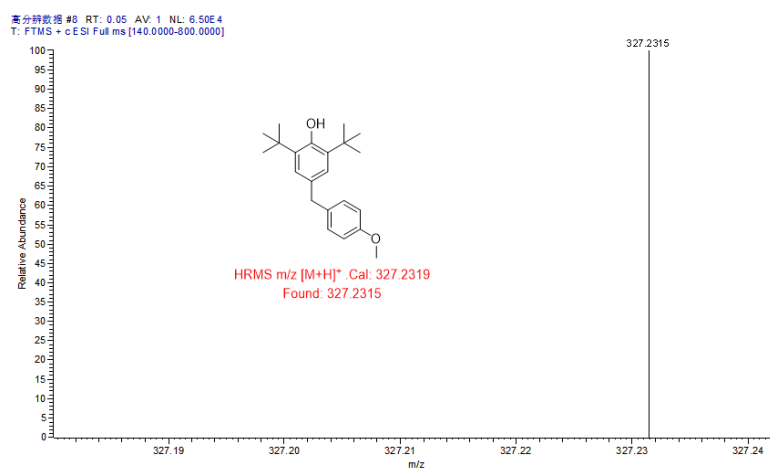


Figure S14 Mass spectrometry (HRMS) data of radical-adduct **IV**

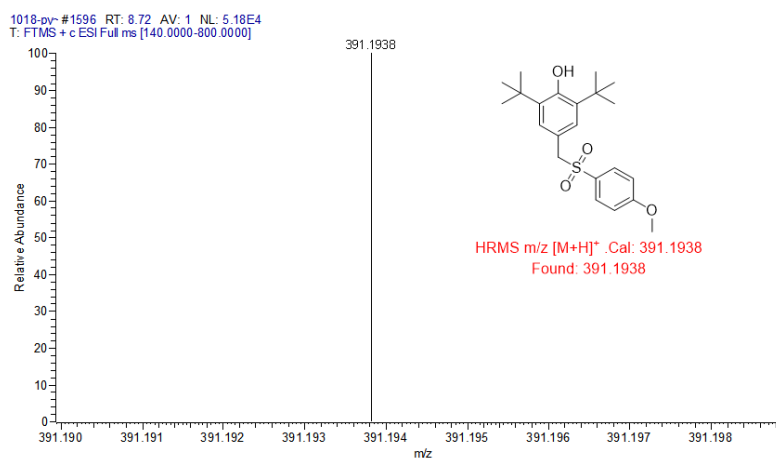


Figure S15 Mass spectrometry (HRMS) data of radical-adduct **V**

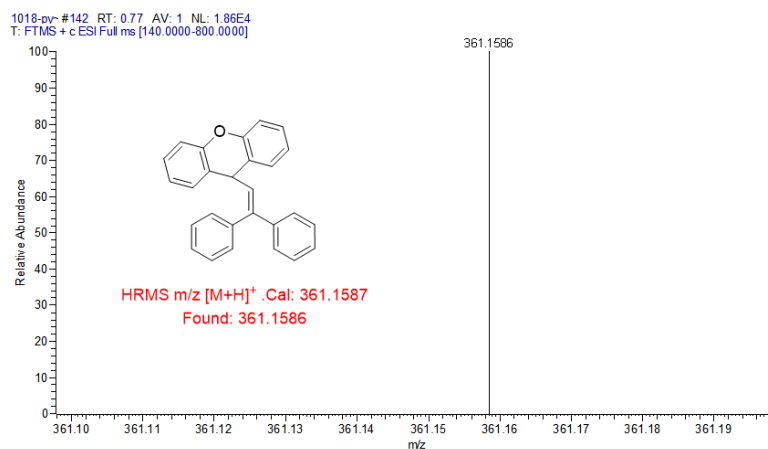


Figure S16 Mass spectrometry (HRMS) data of radical-adduct **VI**

Electricity On-Off Experiment

Electricity on-off experiment was performed on a 0.2 mmol scale. An undivided test column-type electrolysis cell (25 mL) was charged with a stir bar, 9*H*-xanthene **1a** (0.2 mmol, 1.0 equiv.), *n*Bu₄NPF₆ (0.2 mmol), DABSO (0.2 mmol), CH₃CN (4 mL), AcOH (1 mL). Then, add benzenediazonium tetrafluoroborate **2a** (0.3 mmol), and the resulting suspension was stirred for a minute. Then the prepared electrodes were placed into the reaction mixture. The anode and the cathode were placed into reaction system. The mixture was electrolyzed at 40 °C in a N₂ atmosphere. The reaction mixture was then subjected to the following sequence: the reaction protocol involved applying a constant current of 10 mA for 20 minutes, followed by stirring for 20 minutes without electrolysis. This cycle was repeated until the complete consumption of **1a** was achieved. The progress of the reaction was monitored by thin-layer chromatography (TLC) at 254 nm, with the formation of **3aa** indicated by distinct coloration. Results of the experiments are presented on **Figure S17**.

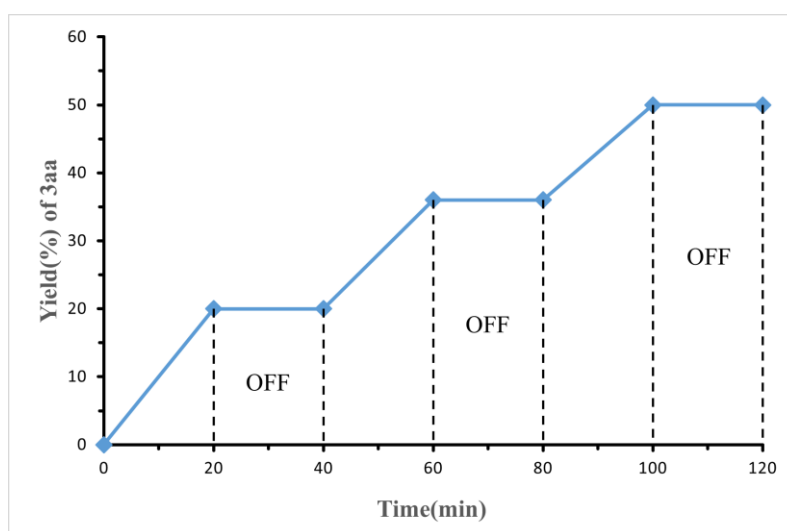


Figure S17 Electricity ON-OFF experiments

Different F/mol reactions experiment

Faraday's constant (FF) is a physical constant that expresses the amount of charge carried per mole of electrons and has a value of approximately 96485.33289 coulombs/mole. Charge (Q) is the amount of charge carried by an object in coulombs (C) and current (I) is the amount of charge passing through the cross-section of a conductor per unit of time in amperes (A). By definition, the relationship between charge and current can be expressed as: $I=Q/t$. Where, *t* denotes time. To relate charge

and current to Faraday's constant, the following equation can be used: $Q=nF$. Where n denotes the number of moles of electrons. Combining the above two equations gives: $I=nF/t$, which shows that the current is related to the number of moles of electrons, Faraday's constant and time. When we fix the time and the amount of reactant moles, changing the current is reacting at different F/mol.

An undivided test column-type electrolysis cell (25 mL) was charged with a stir bar, 9*H*-xanthene **1a** (0.2 mmol, 1.0 equiv.), $n\text{Bu}_4\text{NPF}_6$ (0.2 mmol), DABSO (0.2 mmol), CH_3CN (4 mL), AcOH (1 mL). Then, add benzenediazonium tetrafluoroborate **2a** (0.3 mmol), and the resulting suspension was stirred for a minute. Then the prepared electrodes were placed into the reaction mixture. The anode and the cathode were placed into reaction system. The mixture was electrolyzed at 40 °C in a N_2 atmosphere. It was first electrolyzed at a constant current with a series of different strengths for 15 minutes and then stirred for 45 minutes. We set up six experimental groups with different intensities and one control group. The experimental group was reacted with current intensity of 0 mA, 3 mA, 5 mA, 7 mA, 10 mA, 12 mA for 15 minutes and then stirred for 45 minutes. The control group was reacted continuously at a current intensity of 10 mA for 1 hour. The results of the experiment were determined by monitoring the coloration of **3aa** on a 254 mm thin layer chromatogram by TLC.

As shown in **Fig. S18**, from the experimental results, it is clear that the reaction can proceed at a certain current intensity, but the yield may be different. That is, the reaction can be carried out at different F/mol, but the yield is related to the current F/mol.

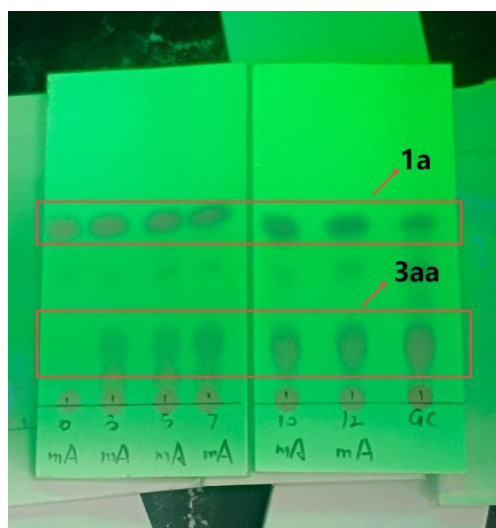


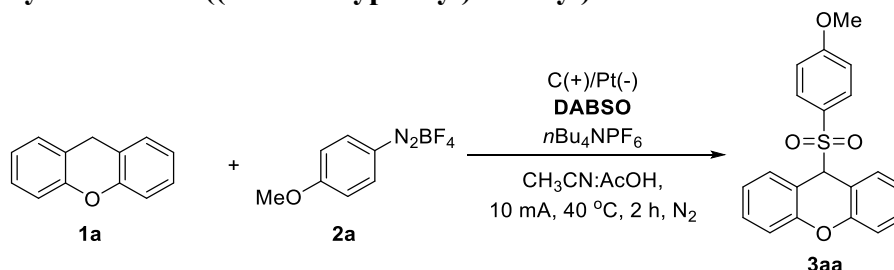
Figure S18 The coloration of **3aa** on a 254 mm thin layer chromatogram

Faradic efficiency calculation

$$\text{Faradaic efficiency} = \frac{Q_{\text{experimental}}}{Q_{\text{theoretical}}} \times 100\%$$

$$= \frac{z \cdot n \cdot e}{Q_{\text{theoretical}}}$$

For the synthesis of 9-((4-methoxyphenyl)sulfonyl)-9H-xanthene



With z = number of electron that the reaction used = 2

n = mol of product that obtained = $0.2 \times 80\% = 0.16 \text{ mmol} = 0.16 \times 10^{-3} \text{ mol}$

F = Faradaic constant (96485 C/mol)

$Q_{\text{theoretical}}$ can be calculated from I (current, Ampere) $\times t$ (reaction time, second)

$$\text{Faradaic efficiency} = \frac{2 \times 0.16 \times 10^{-3} \times 96485}{0.010 \times 2 \times 60 \times 60} \times 100\%$$

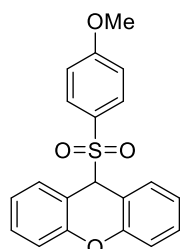
$$= 43\%$$

Reference

- [1] Böß, E.; Hillringhaus, T.; Nitsch, J.; Klussmann, M. Lewis acid-catalysed one pot synthesis of substituted xanthenes. *Org. Biomol. Chem.* **2011**, *9*, 1744-1748.
- [2] Verma, S. K.; Prajapati, A.; Saini, M. K.; Basak, A. K. Lewis Acid Catalyzed Reductive Cyclization of 2-Aryloxybenzaldehydes and 2-(Arylthio) benzaldehydes to Unsubstituted 9H-Xanthenes and Thioxanthenes in Diisopropyl Ether. *Adv. Syn. Catal.* **2021**, *363*, 532-539.
- [3] Moser, D.; Duan, Y.; Wang, F.; Ma, Y.; O'Neill, M. J.; Cornella, J. Selective functionalization of aminoheterocycles by a pyrylium salt. *Angew. Chem. Int. Ed.* **2018**, *57*, 11035-11039.

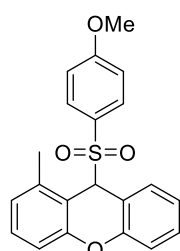
The data of product

9-((4-methoxyphenyl)sulfonyl)-9*H*-xanthene (3aa)



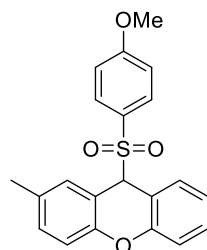
White solid (56.3 mg, 80% yield), melting point: 180-182 °C. **¹H NMR** (400 MHz, CDCl₃, ppm): δ 7.57 (d, *J* = 8.0 Hz, 2 H), 7.34 (t, *J* = 7.8 Hz, 2 H), 7.16 (t, *J* = 7.4 Hz, 2 H), 6.90-6.86 (m, 4 H), 6.68-6.65 (m, 2 H), 5.39 (s, 1 H), 3.80 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃, ppm): δ 164.1, 152.5, 131.8, 131.6, 130.6, 126.3, 123.5, 116.4, 114.1, 113.6, 67.1, 55.7; **HRMS** (ESI) calcd for C₂₀H₁₇O₄S [M+H]⁺ 353.0843, found: 353.0838.

9-((4-methoxyphenyl)sulfonyl)-1-methyl-9*H*-xanthene (3ba)



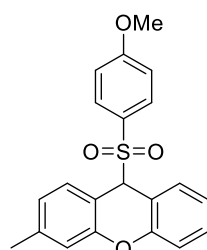
White solid (54.5 mg, 73% yield), melting point: 184-186 °C. **¹H NMR** (400 MHz, CDCl₃, ppm): δ 7.52 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 1 H), 7.37-7.31 (m, 2 H), 7.19-7.12 (m, 2 H), 7.04 (t, *J* = 7.6 Hz, 1 H), 6.93 (dd, *J* = 8.4 Hz, *J* = 1.2 Hz, 1 H), 6.90-6.86 (m, 2 H), 6.67-6.65 (m, 2 H), 5.35 (s, 1 H), 3.80 (s, 3 H), 2.17 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃, ppm): δ 164.1, 152.6, 150.8, 131.9, 131.6, 131.4, 130.4, 129.0, 126.2, 125.6, 123.4, 122.9, 116.5, 114.3, 113.6, 113.4, 67.5, 55.7, 15.8; **HRMS** (ESI) calcd for C₂₁H₁₈NaO₄S [M+Na]⁺ 389.0818, found: 389.0815.

9-((4-methoxyphenyl)sulfonyl)-2-methyl-9*H*-xanthene (3ca)



White solid (54.9 mg, 75% yield), melting point: 150-152 °C. **¹H NMR** (400 MHz, CDCl₃, ppm): δ 7.55 (d, *J* = 7.6 Hz, 1 H), 7.33 (t, *J* = 8.2 Hz, 2 H), 7.14 (t, *J* = 7.4 Hz, 2 H), 6.90-6.88 (m, 2 H), 6.91-6.86 (m, 1 H), 6.79 (dd, *J* = 8.4 Hz, *J* = 2.0 Hz, 1 H), 6.67-6.66 (m, 2 H), 5.34 (s, 1 H), 3.81 (s, 3 H), 2.37 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃, ppm): δ 164.0, 152.6, 150.4, 132.8, 131.8, 131.5, 131.4, 131.2, 130.4, 126.3, 123.1, 116.3, 116.0, 114.0, 113.7, 113.5, 67.1, 55.6, 20.8; **HRMS** (ESI) calcd for C₂₁H₁₈NaO₄S [M+Na]⁺ 389.0818, found: 389.0818.

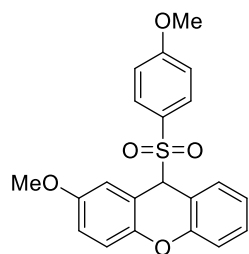
9-((4-methoxyphenyl)sulfonyl)-3-methyl-9*H*-xanthene (3da)



White solid (53.4 mg, 73% yield). melting point: 195-197 °C. **¹H NMR** (400 MHz, CDCl₃, ppm): δ 7.52 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 1 H), 7.42 (d, *J* = 8.0 Hz, 1 H), 7.33-7.29 (m, 1 H), 7.14-7.10 (m, 1 H), 6.96 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1 H), 6.68-6.64 (m, 2 H), 6.87 (d, *J* = 7.6 Hz, 1 H), 6.71 (d, *J* = 8.4 Hz, 1 H), 6.68-6.64 (m, 2 H), 5.34 (s, 1 H), 3.79 (s, 3 H), 2.35 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃, ppm): δ 164.0, 152.6,

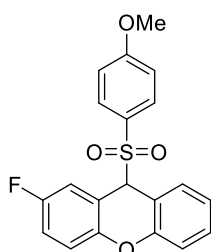
152.3, 141.0, 131.8, 131.5, 131.2, 130.4, 126.4, 124.5, 123.2, 116.6, 116.3, 114.2, 113.5, 111.0, 66.9, 55.7, 21.5; **HRMS** (ESI) calcd for C₂₁H₁₈NaO₄S [M+Na]⁺ 389.0818, found: 389.0817.

9-((4-methoxyphenyl)sulfonyl)-2-methoxy-9H-xanthene (3ea)



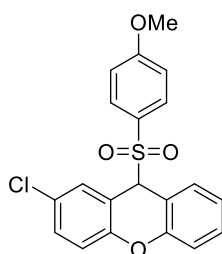
White solid (56.5 mg, 74% yield), melting point: 203-205 °C. **¹H NMR** (400 MHz, CDCl₃, ppm): δ 7.55 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1 H), 7.34-7.30 (m, 1 H), 7.16-7.12 (m, 1 H), 7.05 (d, *J* = 2.8 Hz, 1 H), 6.92-6.89 (m, 3 H), 6.86 (d, *J* = 8.4 Hz, 1 H), 6.82 (d, *J* = 8.8 Hz, 1 H), 6.69-6.65 (m, 2 H), 5.35 (s, 1 H), 3.83 (s, 3 H), 3.80 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃, ppm): δ 164.1, 155.4, 152.7, 146.7, 131.8, 131.5, 130.5, 126.3, 123.2, 117.7, 117.2, 116.3, 114.5, 114.5, 113.6, 113.6, 67.5, 56.0, 55.7; **HRMS** (ESI) calcd for C₂₁H₁₉O₅S [M+H]⁺ 383.0948, found: 383.0943.

9-((4-methoxyphenyl)sulfonyl)-2-fluoro-9H-xanthene (3fa)



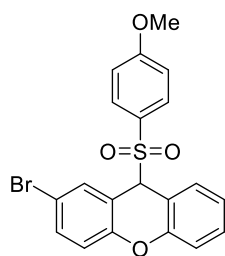
White solid (58.5 mg, 79% yield), melting point: 192-194 °C. **¹H NMR** (400 MHz, CDCl₃, ppm): δ 7.54 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 1 H), 7.37-7.33 (m, 1 H), 7.29 (dd, *J* = 8.4 Hz, *J* = 3.2 Hz, 1 H), 7.19-7.15 (m, 1 H), 7.08-7.03 (m, 1 H), 6.94-6.91 (m, 2 H), 6.90-6.85 (m, 2 H), 6.71-6.67 (m, 2 H), 5.34 (s, 1 H), 3.81 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃, ppm): δ 164.3, 158.3 (d, *J* = 24.1 Hz, 1 C), 152.4, 148.7 (d, *J* = 2.2 Hz, 1 C), 131.8, 131.5, 130.7, 126.1, 123.6, 117.7 (d, *J* = 23.5 Hz, 1 C), 117.6 (d, *J* = 8.1 Hz, 1 C), 117.5 (d, *J* = 24.1 Hz, 1 C), 116.4, 115.4 (d, *J* = 8.1 Hz, 1 C), 113.7, 113.3, 67.0, 55.73; **¹⁹F NMR** (377 MHz, CDCl₃, ppm): δ -119.3; **HRMS** (ESI) calcd for C₂₀H₁₆FO₄S [M+H]⁺ 371.0748, found: 371.0747.

9-((4-methoxyphenyl)sulfonyl)-2-chloro-9H-xanthene (3ga)



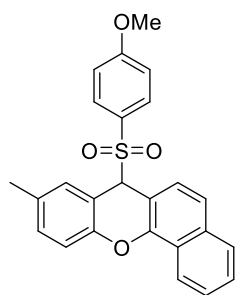
White solid (58.7 mg, 76% yield), melting point: 181-183 °C. **¹H NMR** (400 MHz, CDCl₃, ppm): δ 7.54 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 1 H), 7.50 (d, *J* = 2.8 Hz, 1 H), 7.37-7.33 (m, 1 H), 7.29 (dd, *J* = 8.8 Hz, *J* = 2.8 Hz, 1 H), 7.19-7.15 (m, 1 H), 6.96-6.92 (m, 2 H), 6.90 (d, *J* = 2.8 Hz, 1 H), 6.85 (d, *J* = 8.8 Hz, 1 H), 6.72-6.68 (m, 2 H), 5.31 (s, 1 H), 3.82 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃, ppm): δ 164.3, 152.2, 151.1, 131.9, 131.5, 130.9, 130.8, 130.6, 128.3, 126.0, 123.8, 117.8, 116.4, 115.7, 113.7, 113.5, 66.7, 55.8; **HRMS** (ESI) calcd for C₂₀H₁₆ClO₄S [M+H]⁺ 387.0453, found: 387.0452.

9-((4-methoxyphenyl)sulfonyl)-2-bromo-9H-xanthene (3ha)



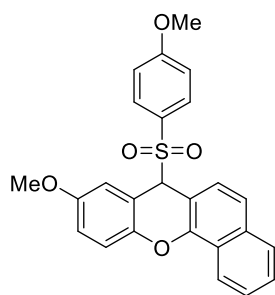
White solid (60.2 mg, 70% yield), melting point: 197-199 °C. **¹H NMR** (400 MHz, CDCl₃, ppm): δ 7.60 (d, *J* = 2.4 Hz, 1 H), 7.53 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 1 H), 7.43 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz, 1 H), 7.37-7.33 (m, 1 H), 7.19-7.15 (m, 1 H), 6.97-6.93 (m, 2 H), 6.92-6.90 (m, 1 H), 6.80 (d, *J* = 8.4 Hz, 1 H), 6.73-6.69 (m, 2 H), 5.30 (s, 1 H), 3.82 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃, ppm): δ 164.3, 152.2, 151.6, 133.8, 133.5, 131.9, 131.5, 130.8, 126.0, 123.8, 118.2, 116.5, 116.2, 115.5, 113.8, 113.5, 66.6, 55.8.; **HRMS** (ESI) calcd for C₂₀H₁₆BrO₄S [M+H]⁺ 430.9948, found: 430.9953.

7-((4-methoxyphenyl)sulfonyl)-9-methyl-7H-benzo[*c*]xanthene (3ia)



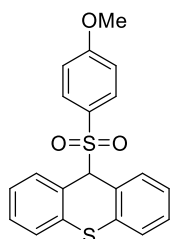
Yellow solid (59.9 mg, 72% yield), melting point: 188-190 °C. **¹H NMR** (400 MHz, CDCl₃, ppm): δ 8.13 (d, *J* = 8.4 Hz, 1 H), 7.83 (d, *J* = 8.0 Hz, 1 H), 7.58 (t, *J* = 8.4 Hz, 2 H), 7.54-7.48 (m, 2 H), 7.39 (d, *J* = 2.0 Hz, 1 H), 7.18-7.15 (m, 1 H), 6.95 (d, *J* = 8.4 Hz, 1 H), 6.83 (d, *J* = 8.4 Hz, 2 H), 6.54 (d, *J* = 8.8 Hz, 2 H), 5.45 (s, 1 H), 3.71 (s, 3 H), 2.40 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃, ppm): δ 164.0, 150.4, 148.5, 134.5, 133.3, 131.7, 131.4, 131.2, 127.7, 127.7, 127.4, 126.1, 126.0, 123.6, 122.6, 121.8, 116.2, 114.0, 113.4, 108.2, 67.6, 55.6, 20.9; **HRMS** (ESI) calcd for C₂₅H₂₁O₄S [M+H]⁺ 417.1156, found: 417.1152.

7-((4-methoxyphenyl)sulfonyl)-9-methoxy-7H-benzo[*c*]xanthene (3ja)



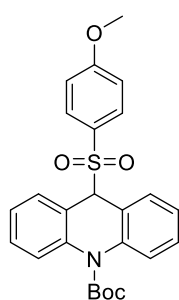
Yellow solid (57.9 mg, 67% yield), melting point: 197-199 °C. **¹H NMR** (400 MHz, CDCl₃, ppm): δ 8.13 (d, *J* = 8.4 Hz, 1 H), 7.84 (d, *J* = 8.0 Hz, 1 H), 7.60 (t, *J* = 6.8 Hz, 2 H), 7.56-7.48 (m, 2 H), 7.12 (d, *J* = 2.8 Hz, 1 H), 6.99 (d, *J* = 8.8 Hz, 1 H), 6.95 (dd, *J* = 9.2 Hz, *J* = 2.8 Hz, 1 H), 6.87-6.84 (m, 2 H), 6.57-6.54 (m, 2 H), 5.50 (s, 1 H), 3.86 (s, 3 H), 3.73 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃, ppm): δ 164.1, 155.7, 148.6, 146.6, 134.5, 131.7, 127.8, 127.7, 127.4, 126.1, 126.0, 123.6, 122.7, 121.8, 117.6, 117.4, 114.8, 114.2, 113.5, 107.7, 67.9, 56.0, 55.7; **HRMS** (ESI) calcd for C₂₅H₂₀NaO₅S [M+Na]⁺ 455.0924, found: 455.0926.

9-((4-methoxyphenyl)sulfonyl)-9H-thioxanthene (3ka)



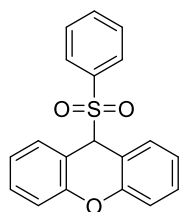
White solid (37.6 mg, 51% yield), melting point: 229-231 °C. **¹H NMR** (400 MHz, CDCl₃, ppm): δ 7.52 (dd, *J* = 7.2 Hz, *J* = 1.6 Hz, 2 H), 7.32-7.26 (m, 4 H), 7.17 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 2 H), 7.05-7.02 (m, 2 H), 6.74-6.70 (m, 2 H), 5.51 (s, 1 H), 3.84 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃, ppm): δ 164.5, 133.7, 133.0, 132.0, 129.1, 128.1, 126.4, 125.8, 124.9, 114.0, 74.7, 55.8; **HRMS** (ESI) calcd for C₂₀H₁₇O₃S₂ [M+H]⁺ 369.0614, found: 369.0620.

tert-butyl 9-((4-methoxyphenyl)sulfonyl)acridine-10(9H)-carboxylate (3ma)



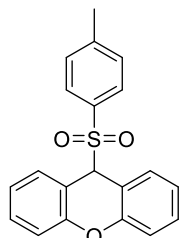
Yellow solid (63.2 mg, 70% yield), melting point: 235-237 °C. **¹H NMR** (400 MHz, CDCl₃, ppm): δ 7.70 (d, *J* = 8.4 Hz, 2 H), 7.47-7.45 (m, 2 H), 7.37-7.32 (m, 2 H), 7.08 (t, *J* = 7.6 Hz, 2 H), 7.01 (d, *J* = 7.6 Hz, 2 H), 6.83 (d, *J* = 7.6 Hz, 2 H), 5.16 (s, 1 H), 3.83 (s, 3 H), 1.54 (s, 9 H); **¹³C NMR** (100 MHz, CDCl₃, ppm): δ 163.8, 152.3, 139.6, 131.7, 130.0, 128.4, 128.3, 126.1, 125.1, 124.2, 114.0, 82.5, 71.1, 55.7, 28.3; **HRMS** (ESI) calcd for C₂₅H₂₆NO₅S [M+H]⁺ 452.1527, found: 452.1524.

9-(phenylsulfonyl)-9H-xanthene (3ab)



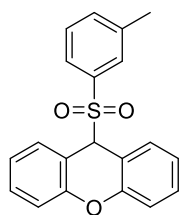
White solid (48.3 mg, 75% yield), melting point: 175-177 °C. **¹H NMR** (400 MHz, CDCl₃, ppm): δ 7.56 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 2 H), 7.53-7.49 (m, 1 H), 7.36-7.31 (m, 2 H), 7.23-7.19 (m, 2 H), 7.18-7.14 (m, 2 H), 6.99 (dd, *J* = 8.4 Hz, *J* = 1.2 Hz, 2 H), 6.87 (dd, *J* = 8.4 Hz, *J* = 1.2 Hz, 2 H), 5.42 (s, 1 H); **¹³C NMR** (100 MHz, CDCl₃, ppm): δ 1152.5, 134.8, 134.0, 131.5, 130.7, 129.7, 128.3, 123.5, 116.4, 113.8, 67.3; **HRMS** (ESI) calcd for C₁₉H₁₄NaO₃S [M+Na]⁺ 345.0556, found: 345.0560.

9-tosyl-9H-xanthene (3ac)



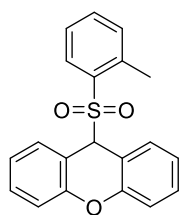
White solid (47.7 mg, 71% yield), melting point: 201-203 °C. **¹H NMR** (400 MHz, CDCl₃, ppm): δ 7.55 (d, *J* = 7.6 Hz, 2 H), 7.34 (t, *J* = 7.8 Hz, 2 H), 7.16 (t, *J* = 7.4 Hz, 2 H), 7.01 (d, *J* = 7.6 Hz, 2 H), 6.90-6.85 (q, 4 H), 5.40 (s, 1 H), 2.36 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃, ppm): δ 152.5, 145.0, 132.0, 131.5, 130.6, 129.7, 129.0, 123.5, 116.4, 114.0, 67.1, 21.8; **HRMS** (ESI) calcd for C₂₀H₁₆NaO₃S [M+Na]⁺ 359.0713, found: 359.0717.

9-(*m*-tolylsulfonyl)-9H-xanthene (3ad)



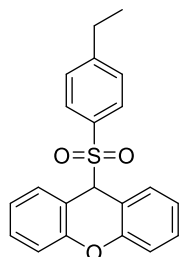
White solid (43.7 mg, 65% yield), melting point: 152-154 °C. **¹H NMR** (400 MHz, CDCl₃, ppm): δ 7.56 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 2 H), 7.36-7.31 (m, 3 H), 7.18-7.14 (m, 2 H), 7.10 (t, *J* = 7.8 Hz, 1 H), 6.87 (dd, *J* = 8.4 Hz, *J* = 1.2 Hz, 2 H), 6.80 (d, *J* = 8.0 Hz, 1 H), 6.71 (s, 1 H), 5.40 (s, 1 H), 2.15 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃, ppm): δ 152.6, 138.5, 134.7, 134.4, 131.5, 130.6, 130.3, 128.1, 126.8, 123.5, 116.3, 113.9, 67.3, 20.9; **HRMS** (ESI) calcd for C₂₀H₁₆NaO₃S [M+Na]⁺ 359.0713, found: 359.0708.

9-(*o*-tolylsulfonyl)-9*H*-xanthene (3ae)



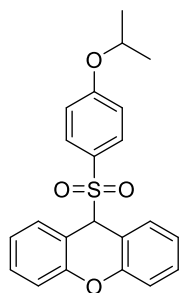
White solid (41.7 mg, 62% yield), melting point: 189-191 °C. **¹H NMR** (400 MHz, CDCl₃, ppm): δ 7.43 (d, *J* = 8.0 Hz, 2 H), 7.39-7.33 (m, 3 H), 7.14-7.09 (m, 4 H), 7.01 (d, *J* = 7.6 Hz, 1 H), 6.97 (d, *J* = 8.4 Hz, 2 H), 5.39 (s, 1 H), 1.94 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃, ppm): δ 153.0, 140.6, 134.0, 133.3, 132.4, 132.3, 131.5, 130.7, 125.8, 123.5, 116.6, 113.9, 67.9, 19.9; **HRMS** (ESI) calcd for C₂₀H₁₆NaO₃S [M+Na]⁺ 359.0713, found: 359.0717.

9-((4-ethylphenyl)sulfonyl)-9*H*-xanthene (3af)



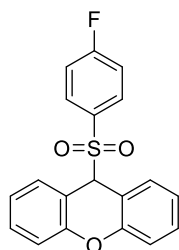
White solid (49.0 mg, 70% yield), melting point: 151-153 °C. **¹H NMR** (400 MHz, CDCl₃, ppm): δ 7.54 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 2 H), 7.36-7.31 (m, 2 H), 7.17-7.13 (m, 2 H), 7.03 (d, *J* = 8.4 Hz, 2 H), 6.91-6.87 (m, 4 H), 5.40 (s, 1 H), 2.65 (dd, *J* = 7.6 Hz, 2 H), 1.20 (d, *J* = 7.4 Hz, 3 H); **¹³C NMR** (100 MHz, CDCl₃, ppm): δ 152.5, 151.2, 132.1, 131.5, 130.6, 129.8, 127.8, 123.4, 116.4, 114.0, 67.2, 29.0, 15.3; **HRMS** (ESI) calcd for C₂₁H₁₈NaO₃S [M+Na]⁺ 373.0869, found: 373.0871.

9-((4-isopropoxyphenyl)sulfonyl)-9*H*-xanthene (3ag)



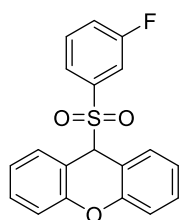
White solid (60.1 mg, 79% yield), melting point: 155-157 °C. **¹H NMR** (400 MHz, CDCl₃, ppm): δ 7.56 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 2 H), 7.35-7.31 (m, 2 H), 7.17-7.13 (m, 2 H), 6.89 (dd, *J* = 1.2 Hz, 2 H), 6.87-6.83 (m, 2 H), 6.65-6.61 (m, 2 H), 5.38 (s, 1 H), 4.59-4.53 (m, 1 H), 1.32 (d, *J* = 6.0 Hz, 6 H); **¹³C NMR** (100 MHz, CDCl₃, ppm): δ 162.6, 152.5, 131.8, 131.5, 130.5, 125.7, 123.4, 116.4, 115.0, 114.2, 70.5, 67.1, 21.8; **HRMS** (ESI) calcd for C₂₂H₂₁O₄S [M+H]⁺ 381.1156, found: 381.1156.

9-((4-fluorophenyl)sulfonyl)-9*H*-xanthene (3ah)



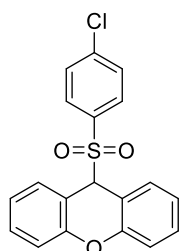
White solid (49.7 mg, 73% yield), melting point: 197-199 °C. **¹H NMR** (400 MHz, CDCl₃, ppm): δ 7.60 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 2 H), 7.38-7.33 (m, 2 H), 7.18 (t, *J* = 7.6 Hz, 2 H), 6.96-6.93 (m, 2 H), 6.88 (t, *J* = 8.4 Hz, 4 H), 5.43 (s, 1 H); **¹³C NMR** (100 MHz, CDCl₃, ppm): δ 166.3 (d, *J* = 255.1 Hz, 1 C), 152.4, 132.5 (d, *J* = 9.8 Hz, 1 C), 131.6, 130.8, 130.7 (d, *J* = 3.1 Hz, 1 C), 123.7, 116.5, 115.7 (d, *J* = 22.4 Hz, 1 C), 113.8, 67.3; **¹⁹F NMR** (377 MHz, CDCl₃, ppm): δ -113.0; **HRMS** (ESI) calcd for C₁₉H₁₄FO₃S [M+H]⁺ 341.0643, found: 341.0649.

9-((3-fluorophenyl)sulfonyl)-9H-xanthene (3ai)



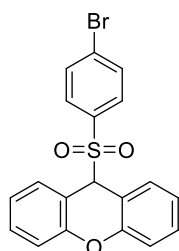
White solid (41.5 mg, 61% yield), melting point: 159-161 °C. **¹H NMR** (400 MHz, CDCl₃, ppm): δ 7.58 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 2 H), 7.39-7.35 (m, 2 H), 7.24-7.17 (m, 4 H), 6.91 (dd, *J* = 8.4 Hz, *J* = 1.2 Hz, 2 H), 6.80-6.77 (m, 1 H), 6.68-6.65 (m, 1 H), 5.45 (s, 1 H); **¹³C NMR** (100 MHz, CDCl₃, ppm): δ 161.9 (d, *J* = 250.3 Hz, 1 C), 152.5, 136.8 (d, *J* = 26.4 Hz, 1 C), 131.5, 130.9, 130.0 (d, *J* = 29.6 Hz, 1 C), 125.6 (d, *J* = 3.4 Hz, 1 C), 123.7, 121.3 (d, *J* = 21.0 Hz, 1 C), 117.0 (d, *J* = 24.4 Hz, 1 C), 116.5, 113.5, 67.5; **¹⁹F NMR** (377 MHz, CDCl₃, ppm): δ -110.9; **HRMS** (ESI) calcd for C₁₉H₁₄FO₃S [M+H]⁺ 341.0643, found: 341.0649.

9-((4-chlorophenyl)sulfonyl)-9H-xanthene (3aj)



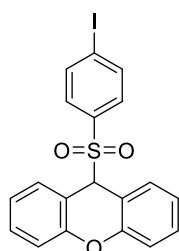
White solid (55.6 mg, 78% yield), melting point: 195-197 °C. **¹H NMR** (400 MHz, CDCl₃, ppm): δ 7.59 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 2 H), 7.38-7.34 (m, 2 H), 7.20-7.16 (m, 4 H), 6.91 (dd, *J* = 1.2 Hz, 2 H), 6.89-6.85 (m, 2 H), 5.44 (s, 1 H); **¹³C NMR** (100 MHz, CDCl₃, ppm): δ 152.4, 141.0, 133.4, 131.6, 131.1, 130.9, 128.7, 123.7, 116.53, 113.6, 67.3; **HRMS** (ESI) calcd for C₁₉H₁₄ClO₃S [M+H]⁺ 357.0347, found: 357.0350.

9-((4-bromophenyl)sulfonyl)-9H-xanthene (3ak)



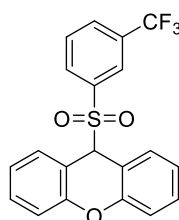
White solid (62.4 mg, 78% yield), melting point: 204-206 °C. **¹H NMR** (400 MHz, CDCl₃, ppm): δ 7.58 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 2 H), 7.38-7.34 (m, 4 H), 7.20-7.16 (m, 2 H), 6.91 (dd, *J* = 8.4 Hz, *J* = 1.2 Hz, 2 H), 6.82-6.79 (m, 2 H), 5.43 (s, 1 H); **¹³C NMR** (100 MHz, CDCl₃, ppm): δ 152.4, 134.0, 131.6, 131.5, 131.1, 130.9, 129.6, 123.7, 116.6, 113.6, 67.3; **HRMS** (ESI) calcd for C₁₉H₁₄BrNaO₃S [M+Na]⁺ 422.9661, found: 422.9666.

9-((4-iodophenyl)sulfonyl)-9H-xanthene (3al)



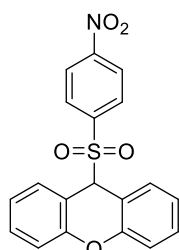
Pale yellow solid (63.7 mg, 71% yield). melting point: 214-216 °C. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 7.57 (dd, $J = 8.4$ Hz, $J = 1.6$ Hz, 4 H), 7.38-7.34 (m, 2 H), 7.19-7.15 (m, 2 H), 6.92 (dd, $J = 8.0$ Hz, $J = 1.6$ Hz, 2 H), 6.66-6.63 (m, 2 H), 5.42 (s, 1 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 152.5, 137.6, 134.7, 131.5, 130.9, 130.9, 123.7, 116.6, 113.6, 102.4, 67.3; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{14}\text{IO}_3\text{S}$ $[\text{M}+\text{H}]^+$ 448.9703, found: 448.9702.

9-((3-(trifluoromethyl)phenyl)sulfonyl)-9H-xanthene (3am)



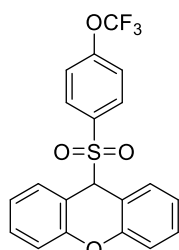
White solid (41.4 mg, 53% yield), melting point: 165-167 °C. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 7.76 (d, $J = 7.6$ Hz, 1 H), 7.61 (d, $J = 7.6$ Hz, 2 H), 7.38-7.33 (m, 3 H), 7.20 (t, $J = 7.4$ Hz, 2 H), 7.13 (t, $J = 8.8$ Hz, 2 H), 6.84 (d, $J = 8.4$ Hz, 2 H), 5.46 (s, 1 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 152.3, 135.6, 135.0, 132.8, 131.5, 131.1, 131.0 (q, $J = 33.4$ Hz, 1 C), 130.6 (q, $J = 3.5$ Hz, 1 C), 129.0, 127.0 (q, $J = 3.9$ Hz, 1 C), 123.8, 116.5, 113.4, 67.5; ^{19}F NMR (377 MHz, CDCl_3 , ppm): δ -63.0; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{14}\text{F}_3\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$ 391.0611, found: 391.0616.

9-((4-nitrophenyl)sulfonyl)-9H-xanthene (3an)



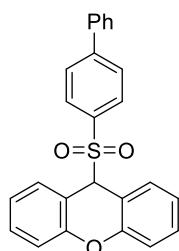
Yellow solid (38.9 mg, 53% yield), melting point: 190-192 °C. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 7.59 (d, $J = 7.6$ Hz, 2 H), 7.38-7.34 (m, 2 H), 7.18 (t, $J = 7.6$ Hz, 2 H), 7.00 (dd, $J = 8.8$ Hz, 4 H), 6.88 (d, $J = 8.0$ Hz, 2 H), 5.44 (s, 1 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 153.4, 152.4, 132.9, 131.9, 131.6, 130.9, 123.7, 120.0, 116.5, 113.7, 67.5; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{14}\text{NO}_5\text{S}$ $[\text{M}+\text{H}]^+$ 368.0588, found: 368.0583.

9-((4-(trifluoromethoxy)phenyl)sulfonyl)-9H-xanthene (3ao)



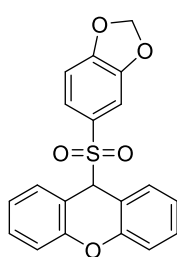
Pale yellow solid (45.5 mg, 56% yield), melting point: 188-190 °C. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 7.58 (dd, $J = 8.0$ Hz, $J = 1.6$ Hz, 2 H), 7.38-7.34 (m, 2 H), 7.20-7.16 (m, 2 H), 7.04-6.97 (m, 4 H), 6.88 (dd, $J = 7.6$ Hz, $J = 1.2$ Hz, 2 H), 5.44 (s, 1 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 153.4, 152.4, 132.9, 131.9, 131.5, 130.9, 123.7, 120.3 (q, $J = 258$ Hz, 1 C), 120.0, 116.5, 113.6, 67.4; ^{19}F NMR (377 MHz, CDCl_3 , ppm): δ -86.0; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{14}\text{F}_3\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$ 407.0560, found: 407.0562.

9-([1,1'-biphenyl]-4-ylsulfonyl)-9H-xanthene (3ap)



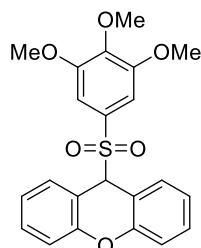
White solid (51.8 mg, 65% yield), melting point: 216-281 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.59 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 2 H), 7.57-7.54 (m, 2 H), 7.49-7.41 (m, 5 H), 7.37-7.33 (m, 2 H), 7.20-7.16 (m, 2 H), 7.05-7.02 (m, 2 H), 6.89 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 2 H), 5.46 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 152.6, 146.8, 139.3, 133.5, 131.6, 130.7, 130.2, 129.2, 128.8, 127.5, 126.9, 123.6, 116.5, 113.9, 67.4; HRMS (ESI) calcd for C₂₅H₁₈NaO₃S [M+Na]⁺ 421.0869, found: 421.0873.

9-(benzo[d][1,3]dioxol-5-ylsulfonyl)-9H-xanthene (3aq)



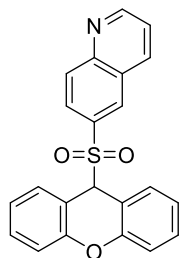
White solid (53.5 mg, 73% yield), melting point: 173-175 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.55 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 2 H), 7.37-7.32 (m, 2 H), 7.18-7.14 (m, 2 H), 6.93 (dd, *J* = 8.4 Hz, *J* = 1.2 Hz, 2 H), 6.59 (d, *J* = 8.0 Hz, 1 H), 6.52 (dd, *J* = 8.4 Hz, *J* = 2.0 Hz, 1 H), 6.35 (d, *J* = 2.0 Hz, 1 H), 5.99 (s, 2 H), 5.38 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 152.5, 152.5, 147.7, 131.5, 130.7, 127.9, 126.0, 123.5, 116.4, 114.0, 109.5, 107.8, 102.3, 67.2; HRMS (ESI) calcd for C₂₀H₁₅O₅S [M+H]⁺ 367.0635, found: 367.0634.

9-((3,4,5-trimethoxyphenyl)sulfonyl)-9H-xanthene (3ar)



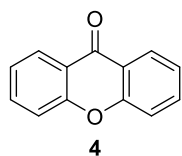
Yellow solid (70.9 mg, 86% yield), melting point: 222-224 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.63 (dd, *J* = 8.0 Hz, *J* = 2.0 Hz, 2 H), 7.36-7.32 (m, 2 H), 7.20-7.16 (m, 2 H), 6.89 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 2 H), 6.11 (s, 2 H), 5.41 (s, 1 H), 3.84 (s, 3 H), 3.47 (s, 6 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 152.7, 152.6, 142.8, 131.6, 130.5, 128.4, 123.5, 116.3, 114.2, 106.9, 67.3, 61.1, 56.1; HRMS (ESI) calcd for C₂₂H₂₁O₆S [M+H]⁺ 413.1054, found: 413.1054.

6-((9H-xanthen-9-yl)sulfonyl)quinoline (3as)



White solid (56.0 mg, 75% yield), melting point: 217-219 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 9.04 (d, *J* = 3.6 Hz, 1 H), 7.95-7.89 (m, 2 H), 7.62 (d, *J* = 8.0 Hz, 2 H), 7.42-7.45 (m, 2 H), 7.36-7.32 (m, 2 H), 7.19 (t, *J* = 7.4 Hz, 3 H), 6.75 (d, *J* = 8.0 Hz, 2 H), 5.51 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 153.7, 152.4, 149.9, 137.3, 132.7, 132.1, 131.6, 130.8, 129.9, 127.8, 126.8, 123.7, 122.6, 116.4, 113.7, 67.5; HRMS (ESI) calcd for C₂₂H₁₆NO₃S [M+H]⁺ 374.0846, found: 374.0841.

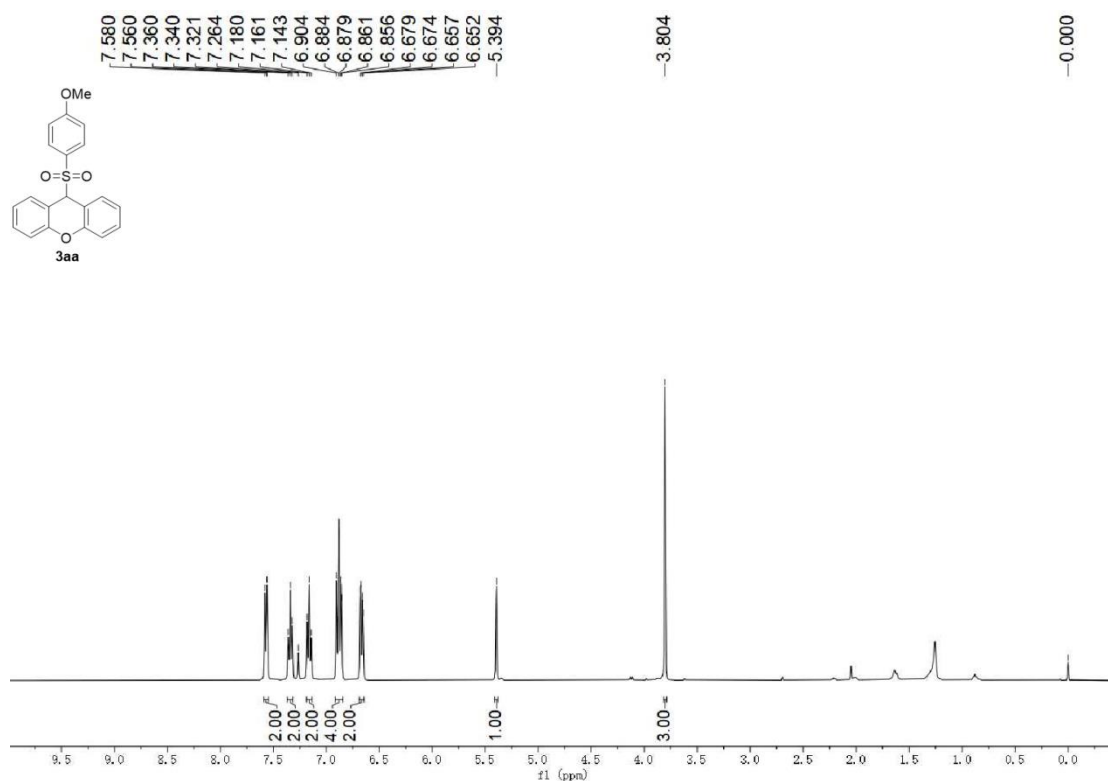
9H-xanthen-9-one (4)



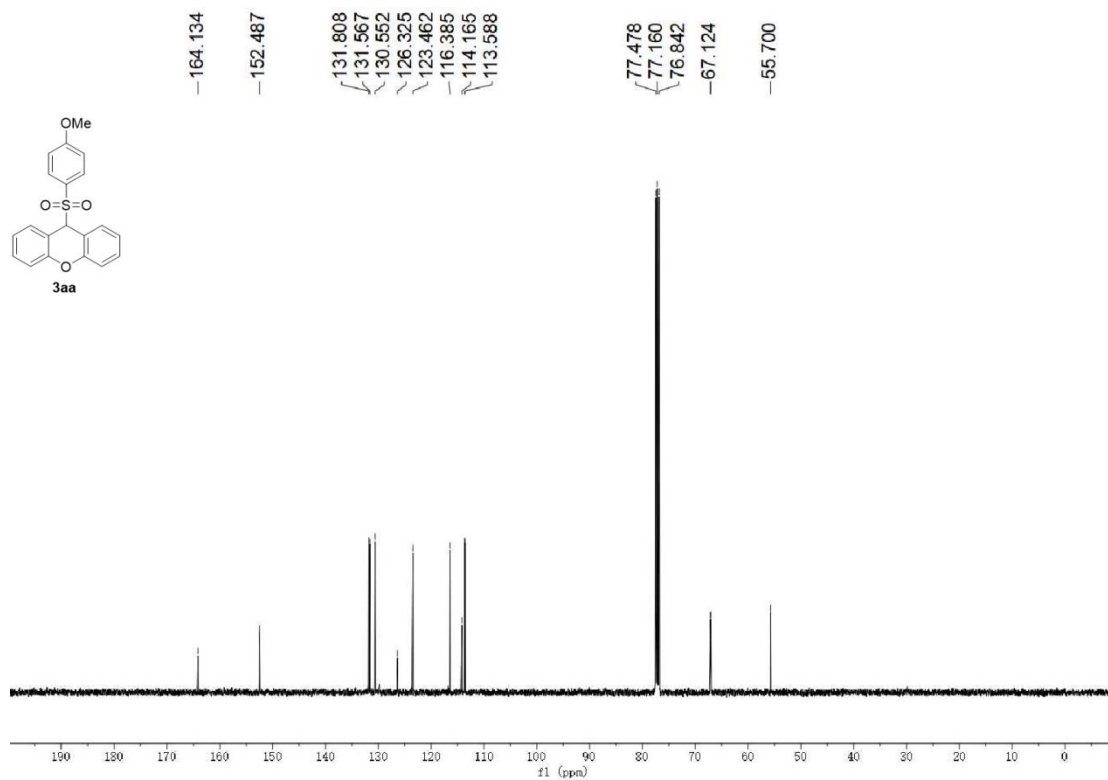
White solid, **¹H NMR** (400 MHz, CDCl₃, ppm): δ 8.33 (dd, *J* = 8.0 Hz, *J* = 2.0 Hz, 2 H), 7.73-7.69 (m, 2 H), 7.47 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 2 H), 7.39-7.35 (m, 2 H); **HRMS** (ESI) calcd for C₂₂H₁₅NO₃S [M+H]⁺ 374.0846, found: 374.0841.

NMR spectra for electrolysis products

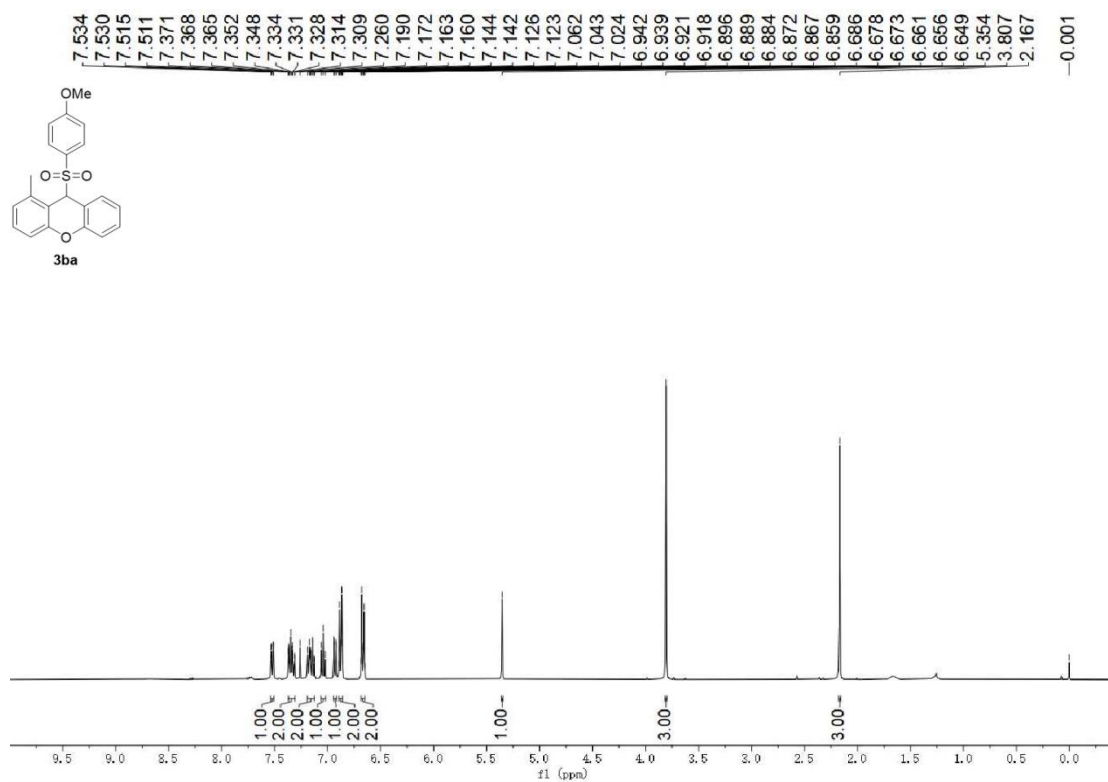
^1H -NMR (400 MHz) spectrum (CDCl_3) of **3aa**



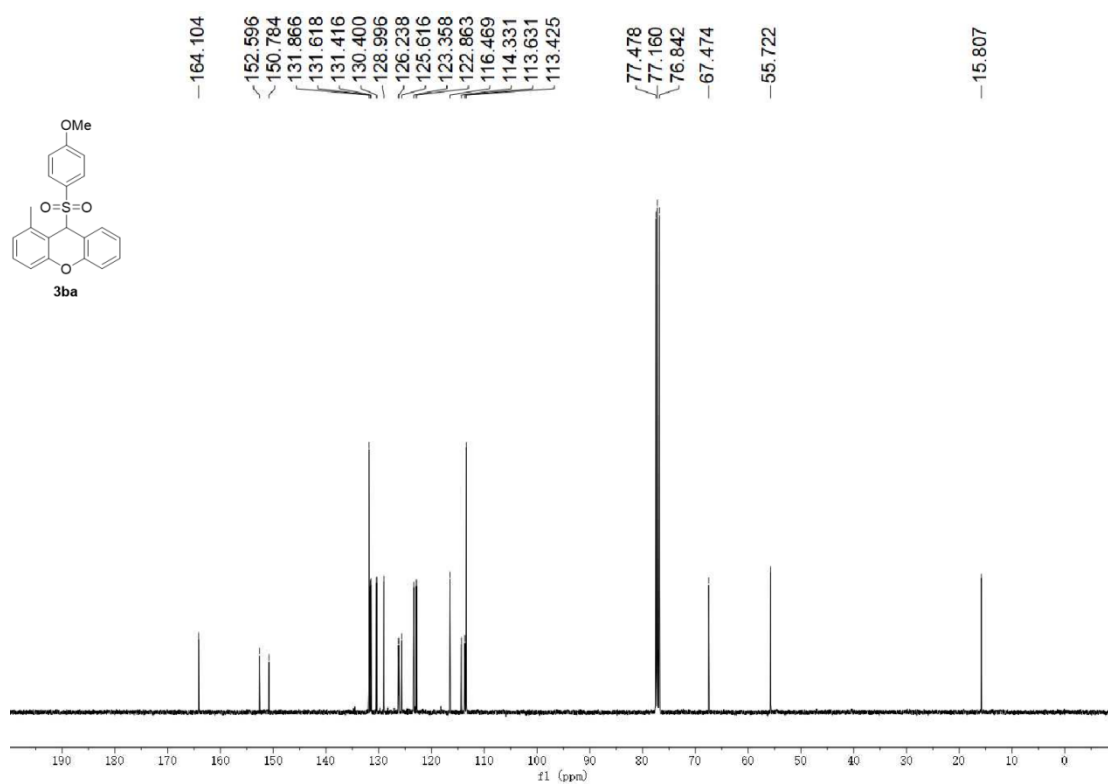
^{13}C -NMR (100 MHz) spectrum (CDCl_3) of **3aa**



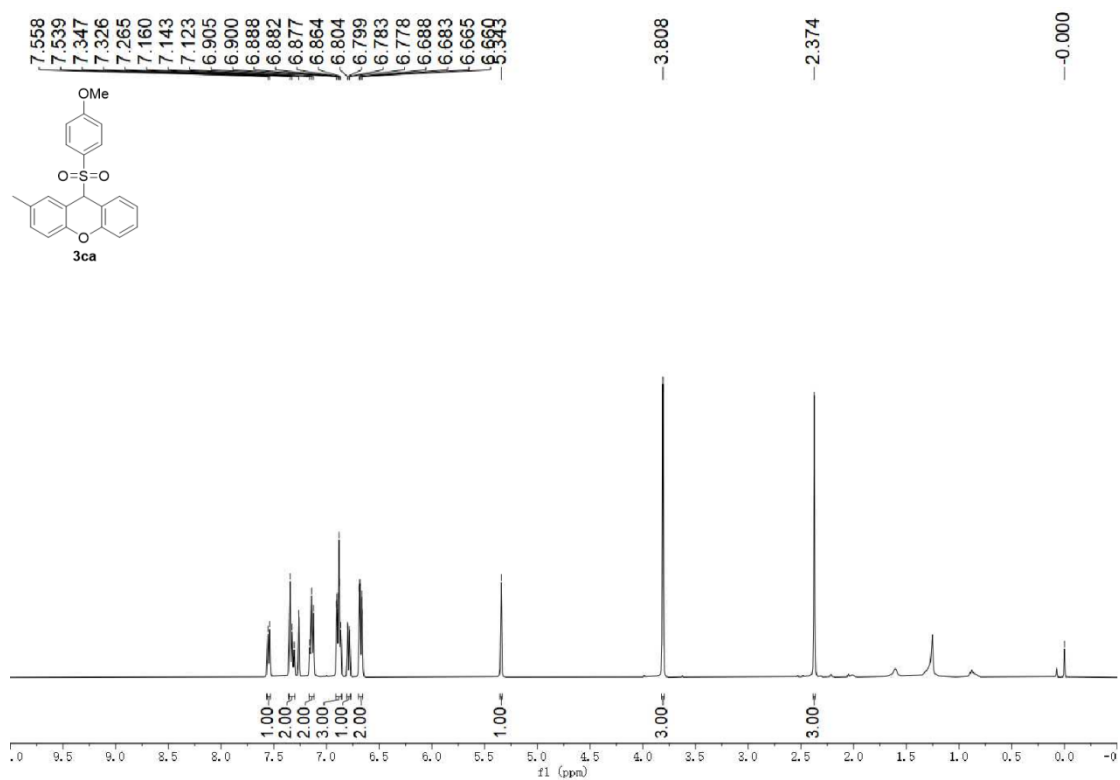
¹H-NMR (400 MHz) spectrum (CDCl₃) of **3ba**



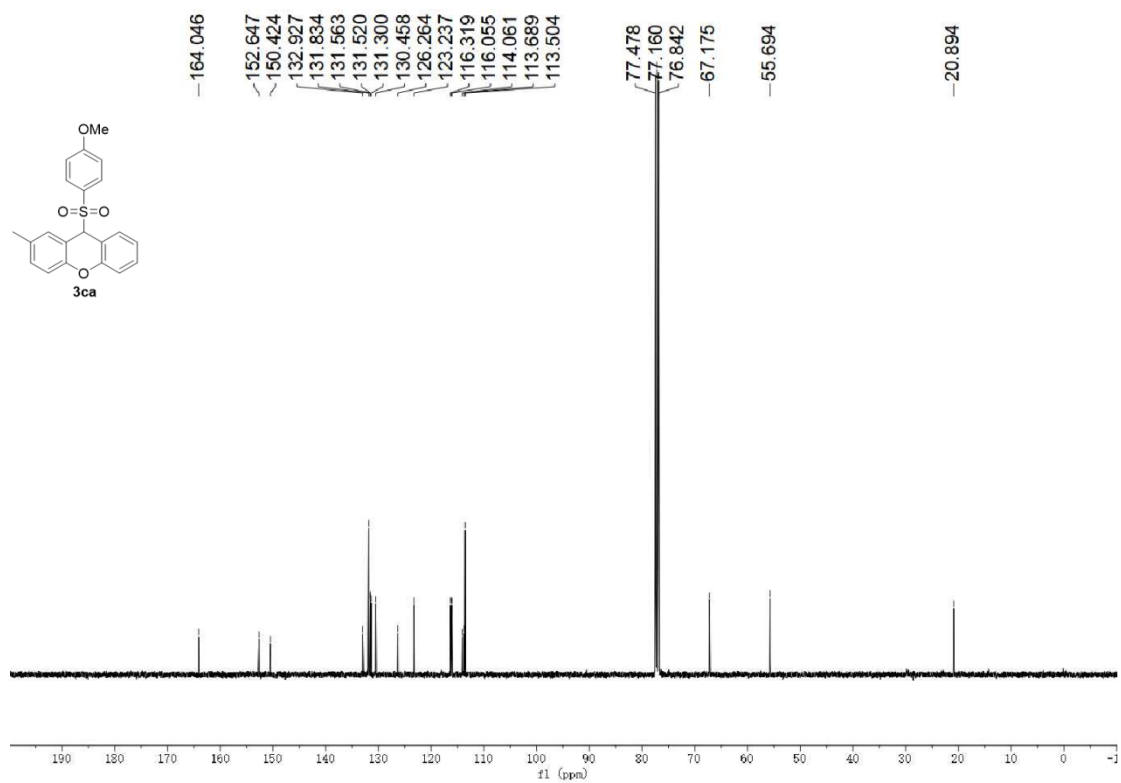
¹³C-NMR (100 MHz) spectrum (CDCl₃) of **3ba**



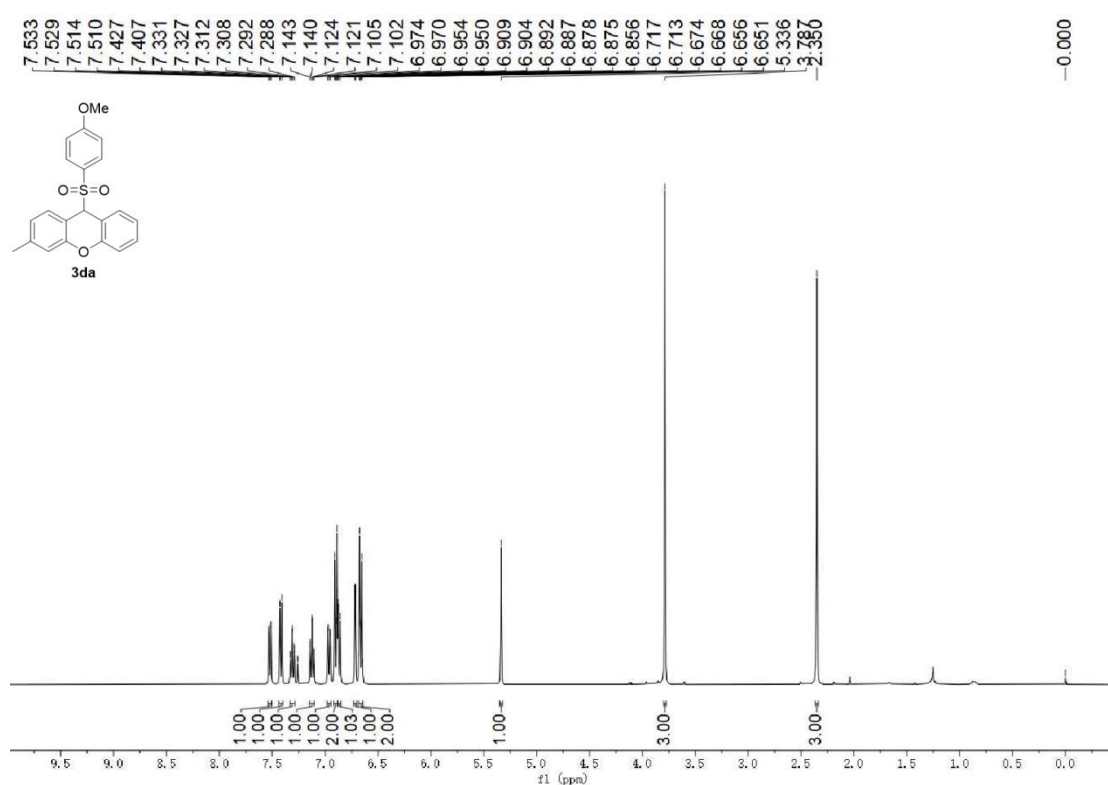
¹H-NMR (400 MHz) spectrum (CDCl₃) of **3ca**



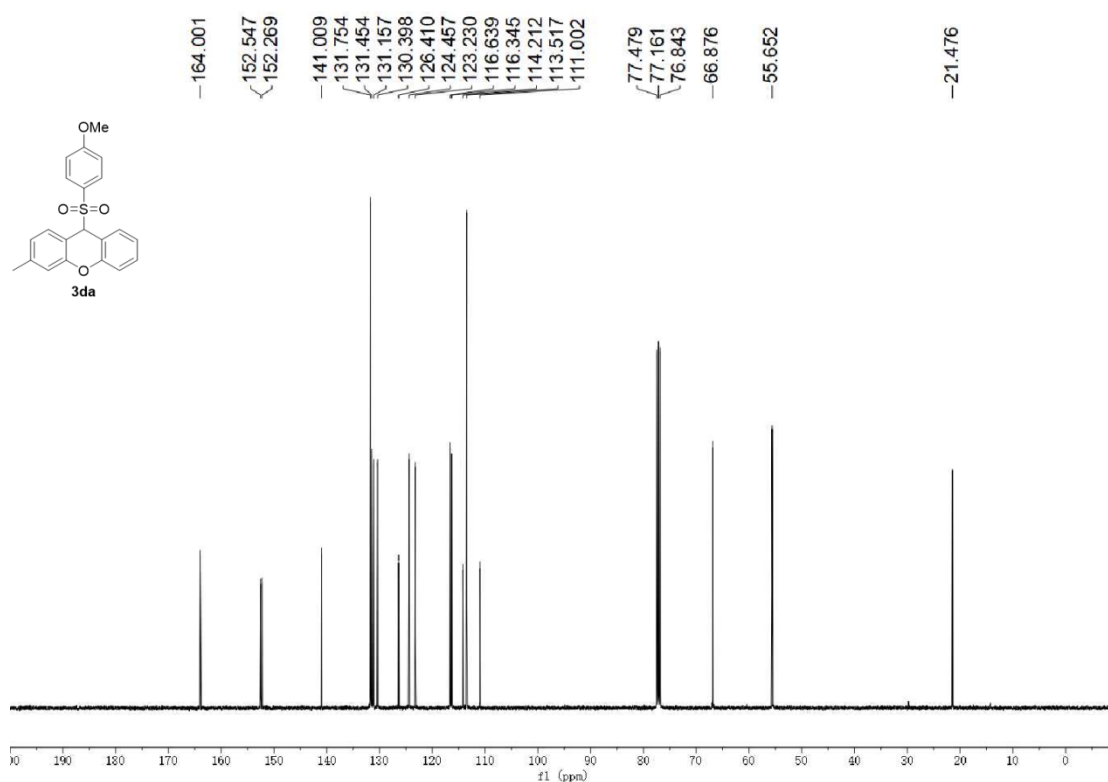
¹³C-NMR (100 MHz) spectrum (CDCl₃) of **3ca**



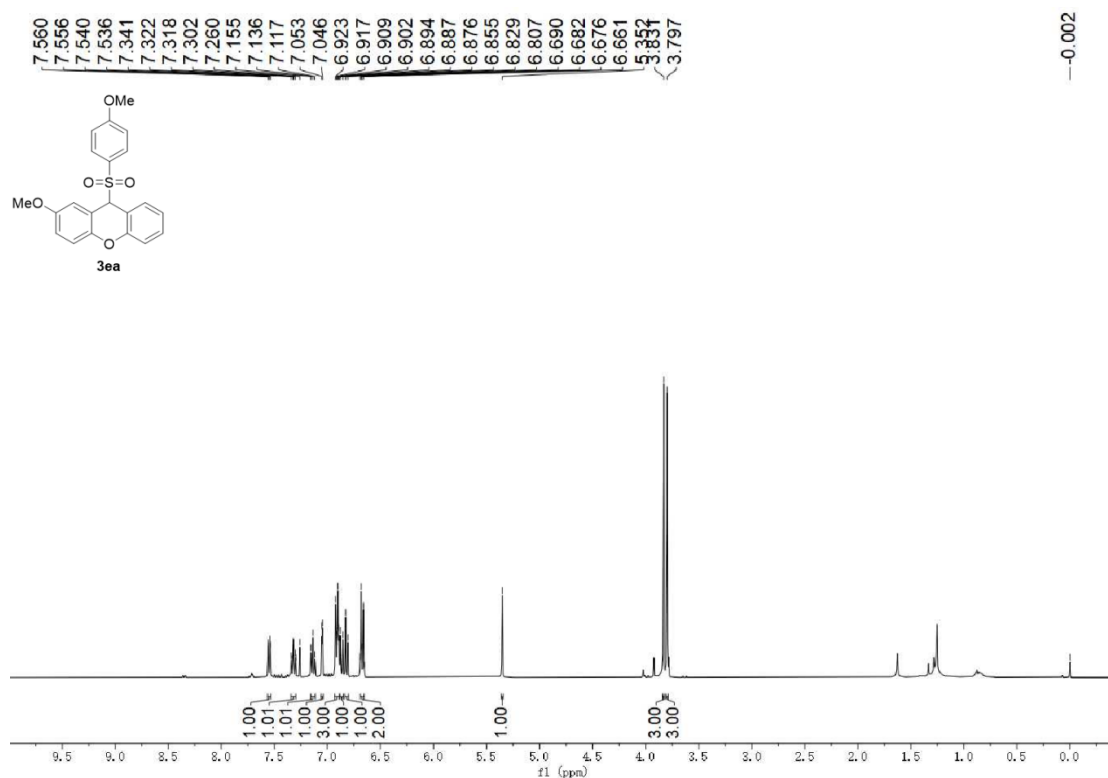
¹H-NMR (400 MHz) spectrum (CDCl₃) of **3da**



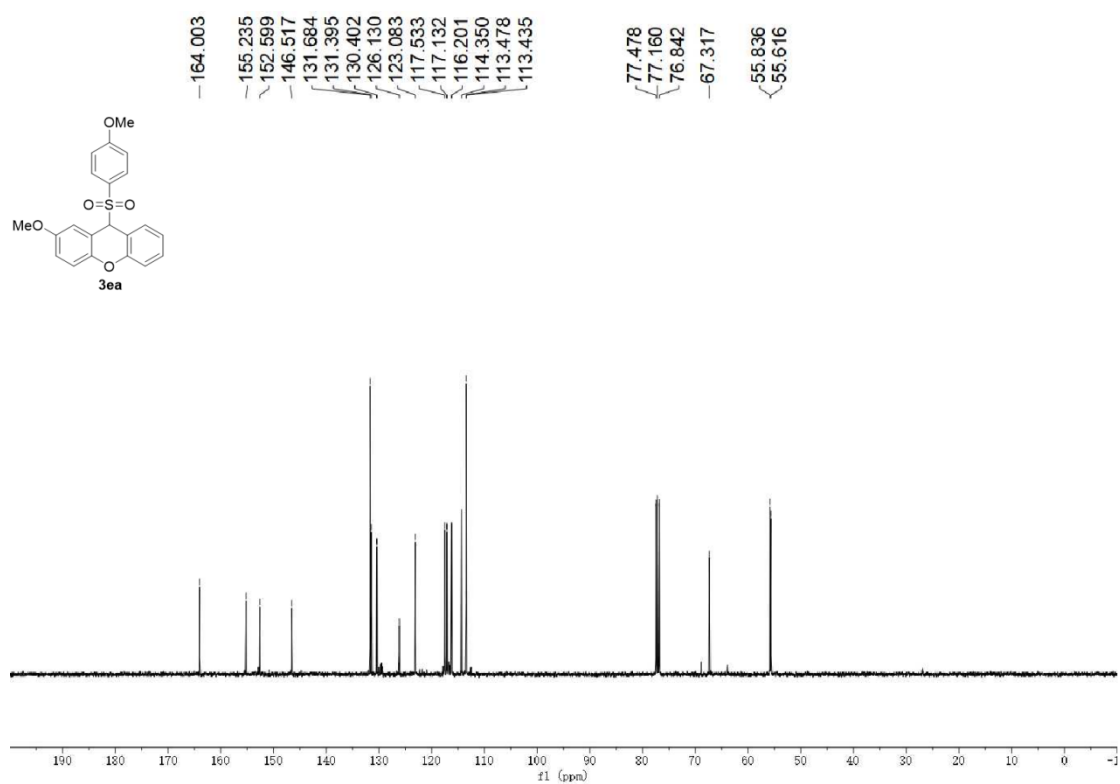
¹³C-NMR (100 MHz) spectrum (CDCl₃) of **3da**



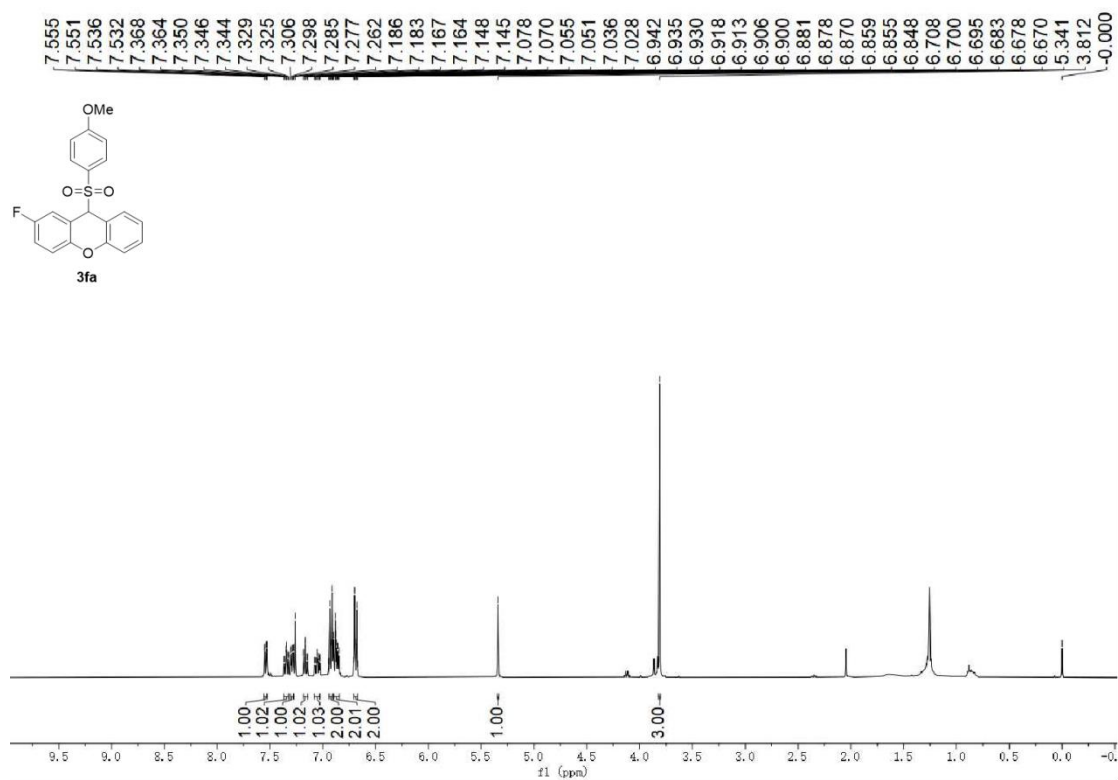
^1H -NMR (400 MHz) spectrum (CDCl_3) of **3ea**



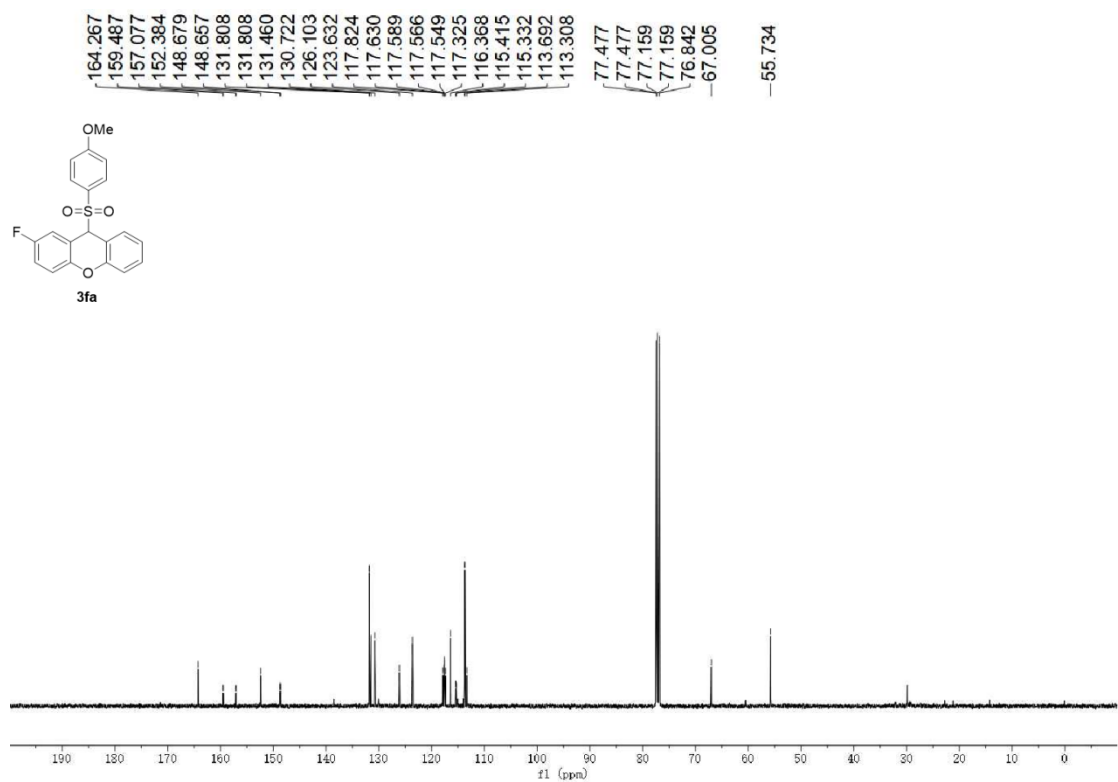
^{13}C -NMR (100 MHz) spectrum (CDCl_3) of **3ea**



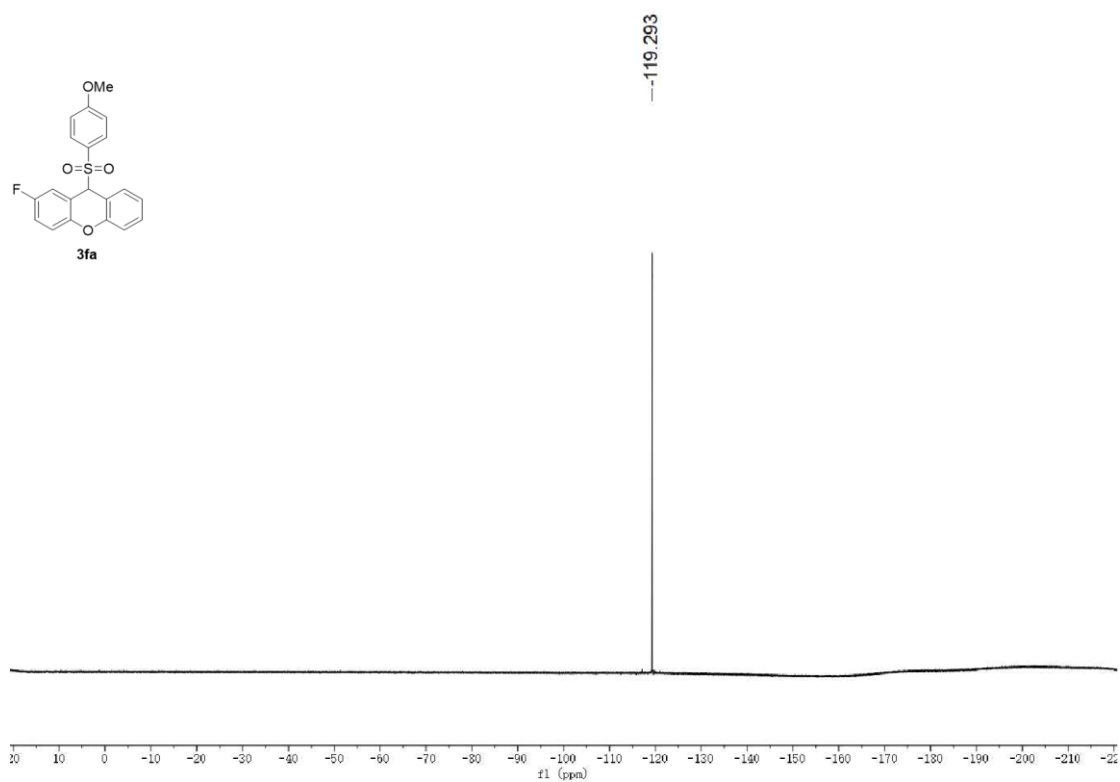
¹H-NMR (400 MHz) spectrum (CDCl₃) of **3fa**



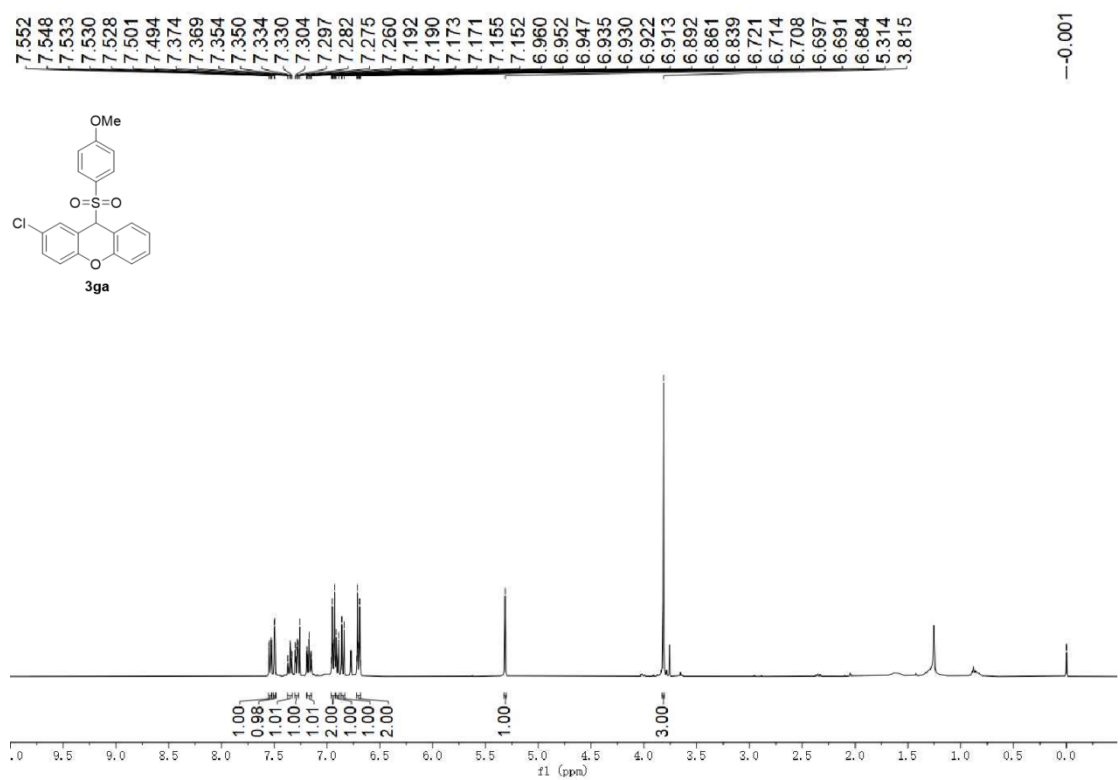
¹³C-NMR (100 MHz) spectrum (CDCl₃) of **3fa**



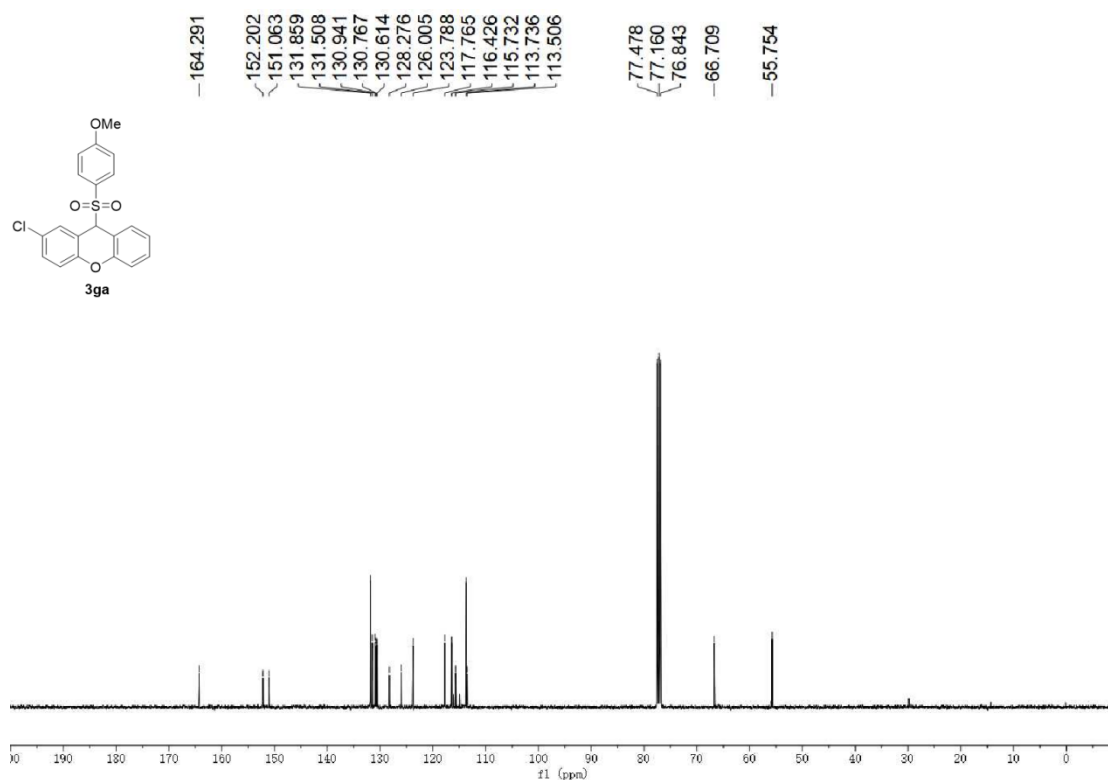
^{19}F -NMR (377 MHz) spectrum (CDCl_3) of **3fa**



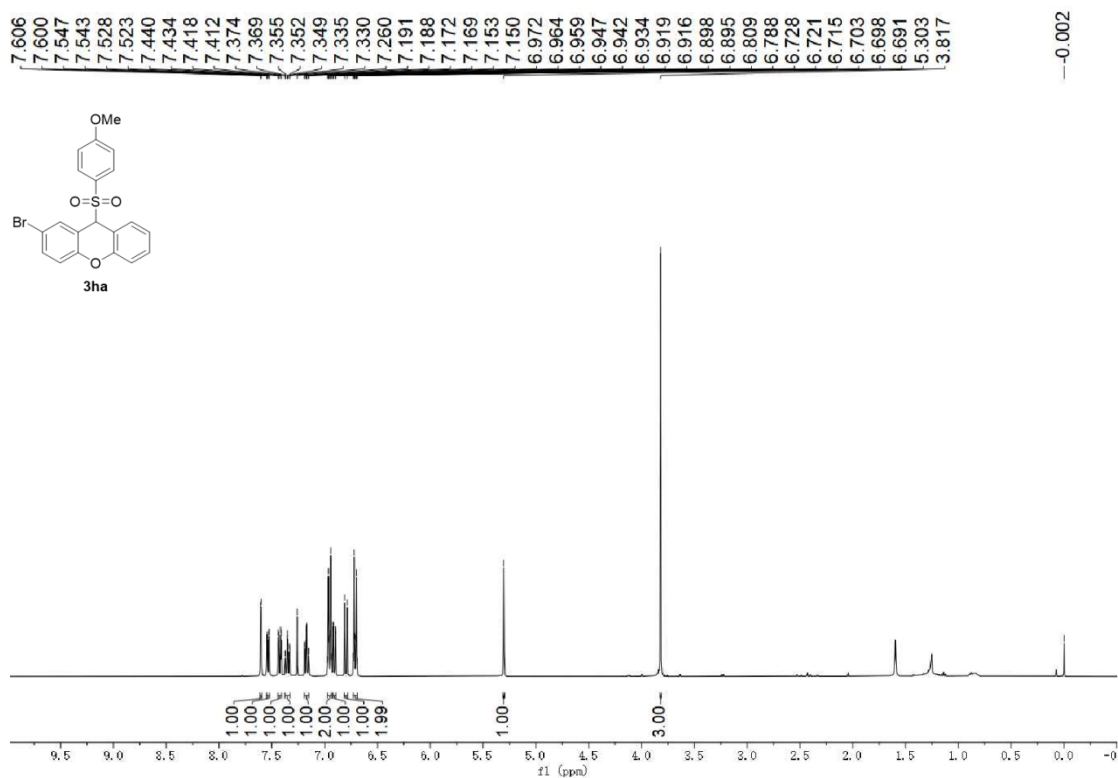
^1H -NMR (400 MHz) spectrum (CDCl_3) of **3ga**



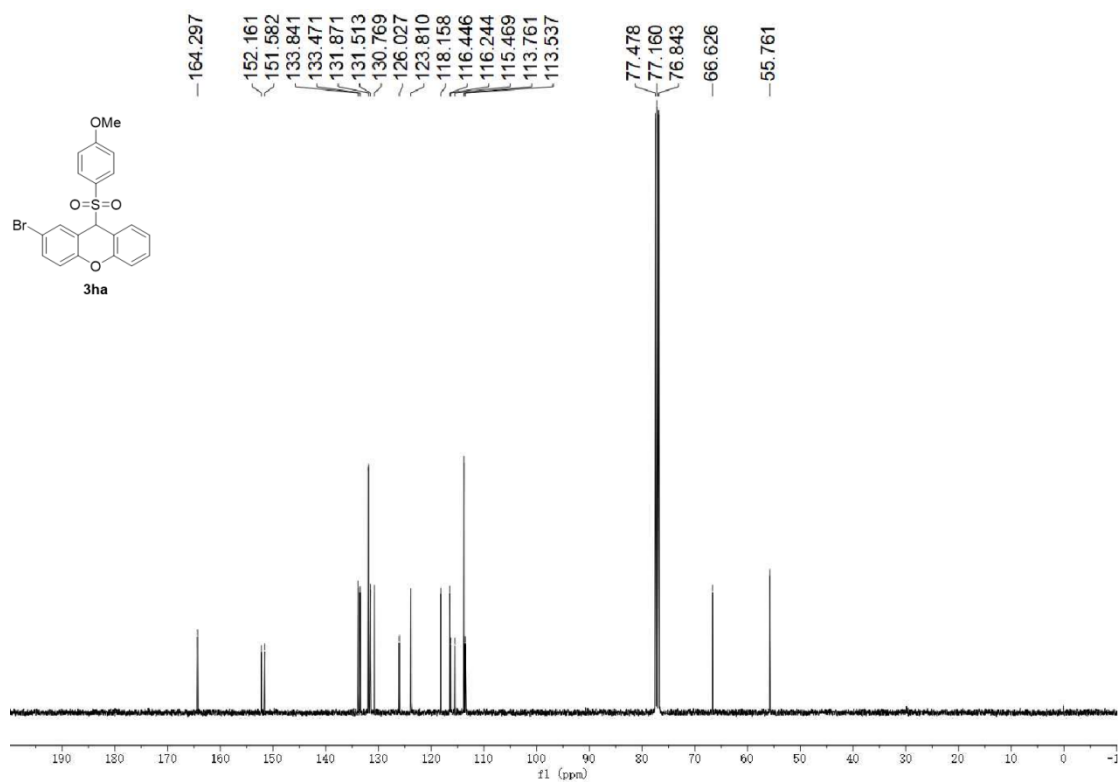
^{13}C -NMR (100 MHz) spectrum (CDCl_3) of **3ga**



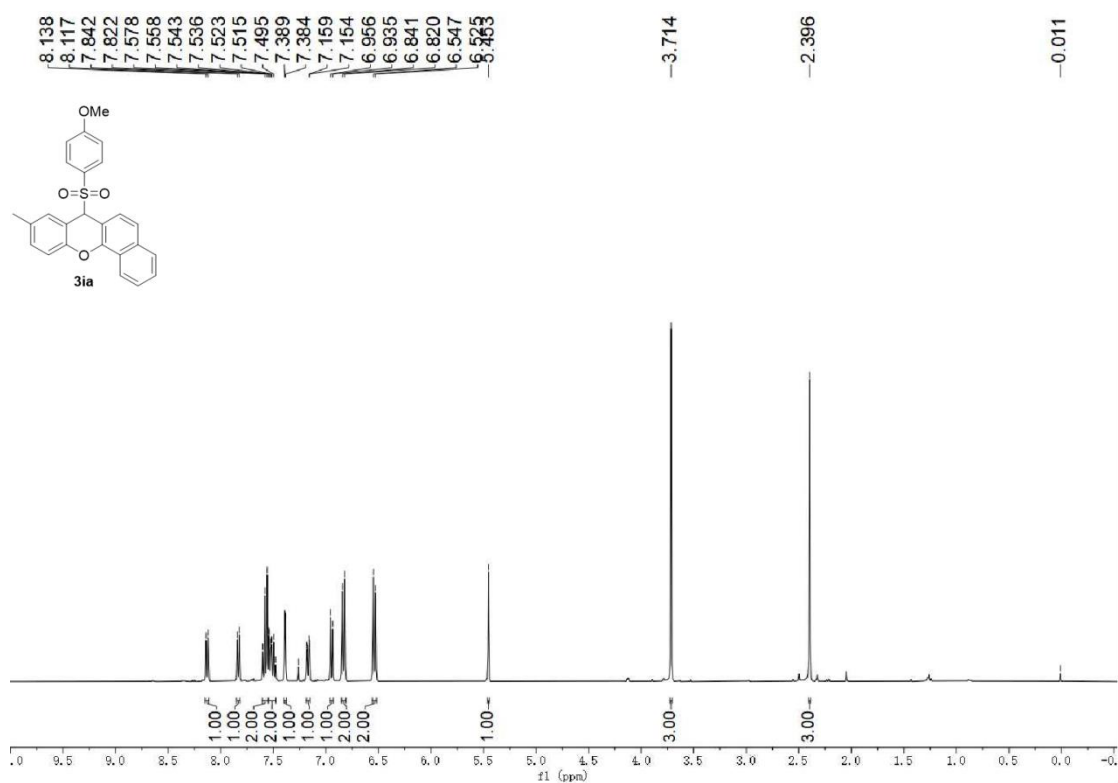
^1H -NMR (400 MHz) spectrum (CDCl_3) of **3ha**



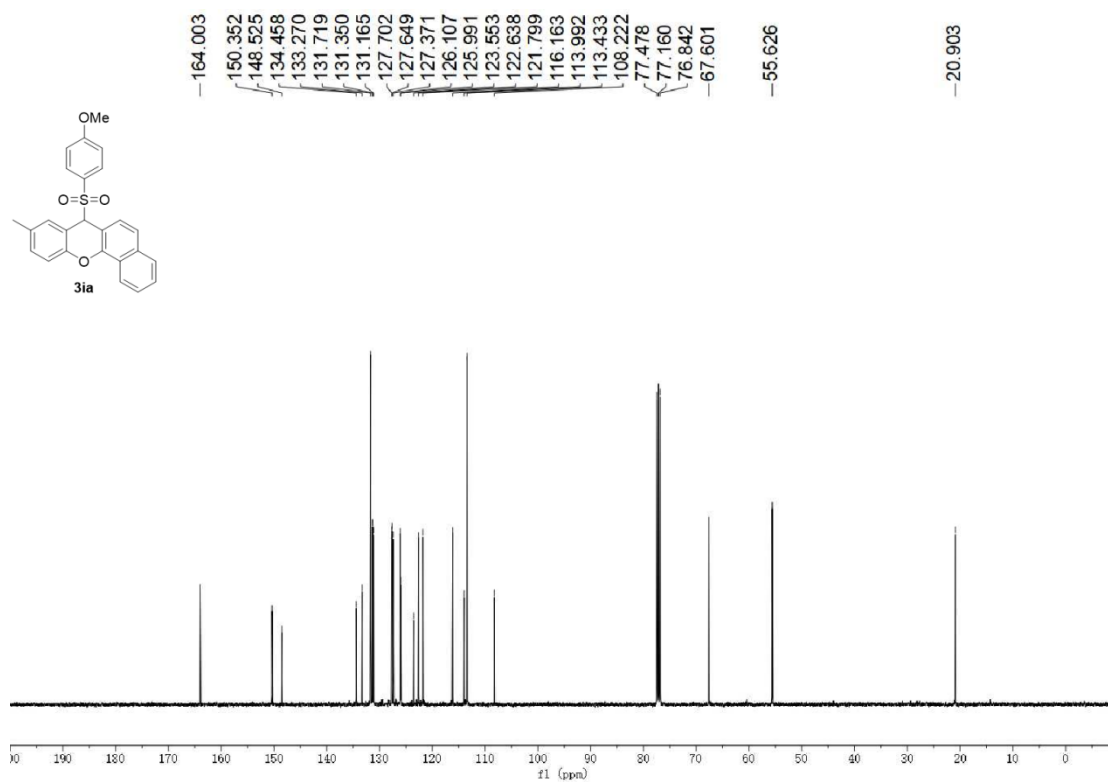
^{13}C -NMR (100 MHz) spectrum (CDCl_3) of **3ha**



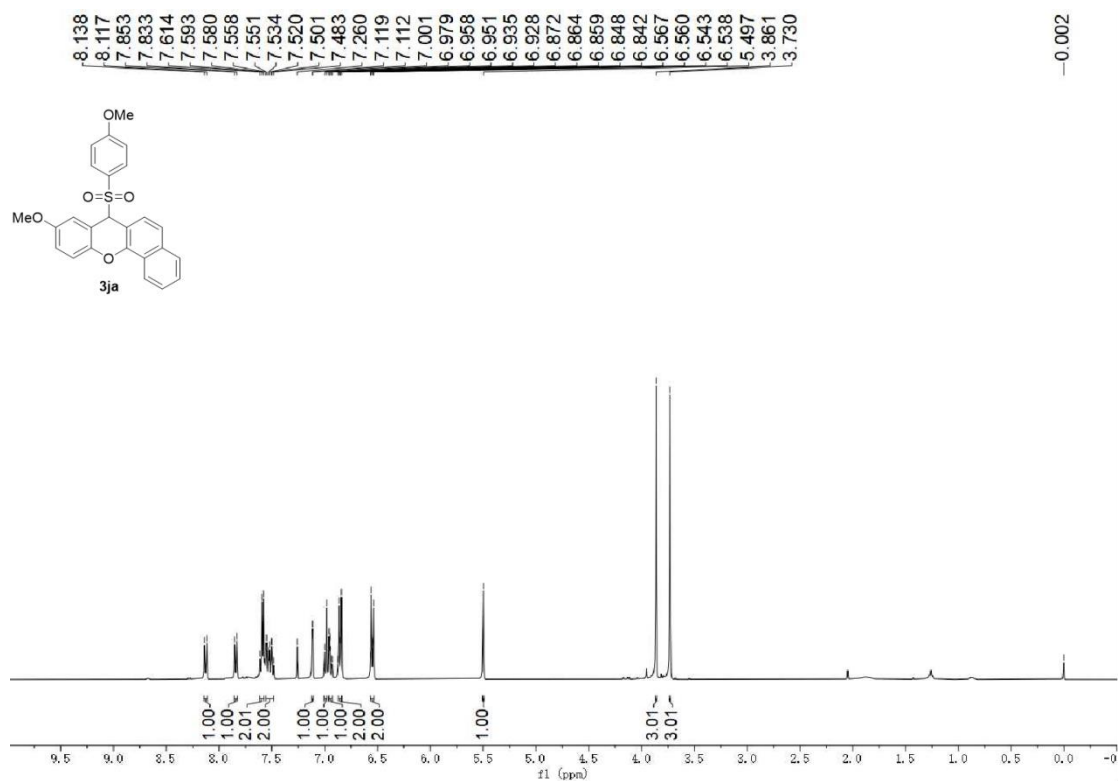
^1H -NMR (400 MHz) spectrum (CDCl_3) of **3ia**



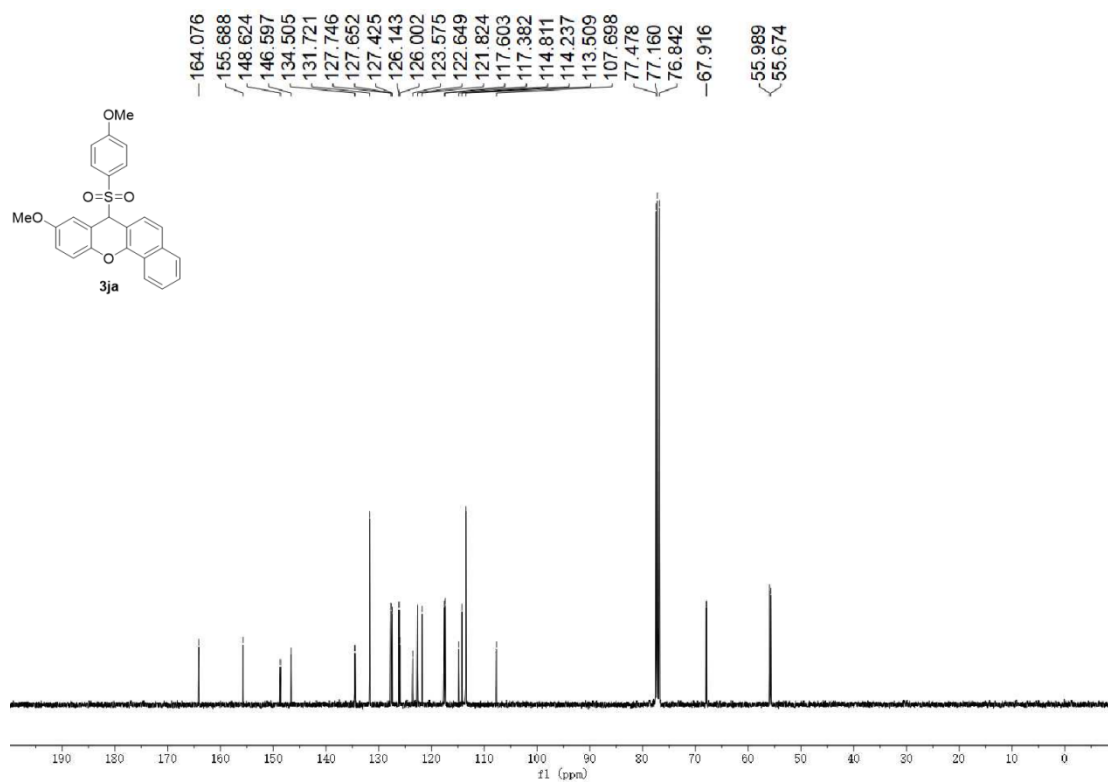
^{13}C -NMR (100 MHz) spectrum (CDCl_3) of **3ia**



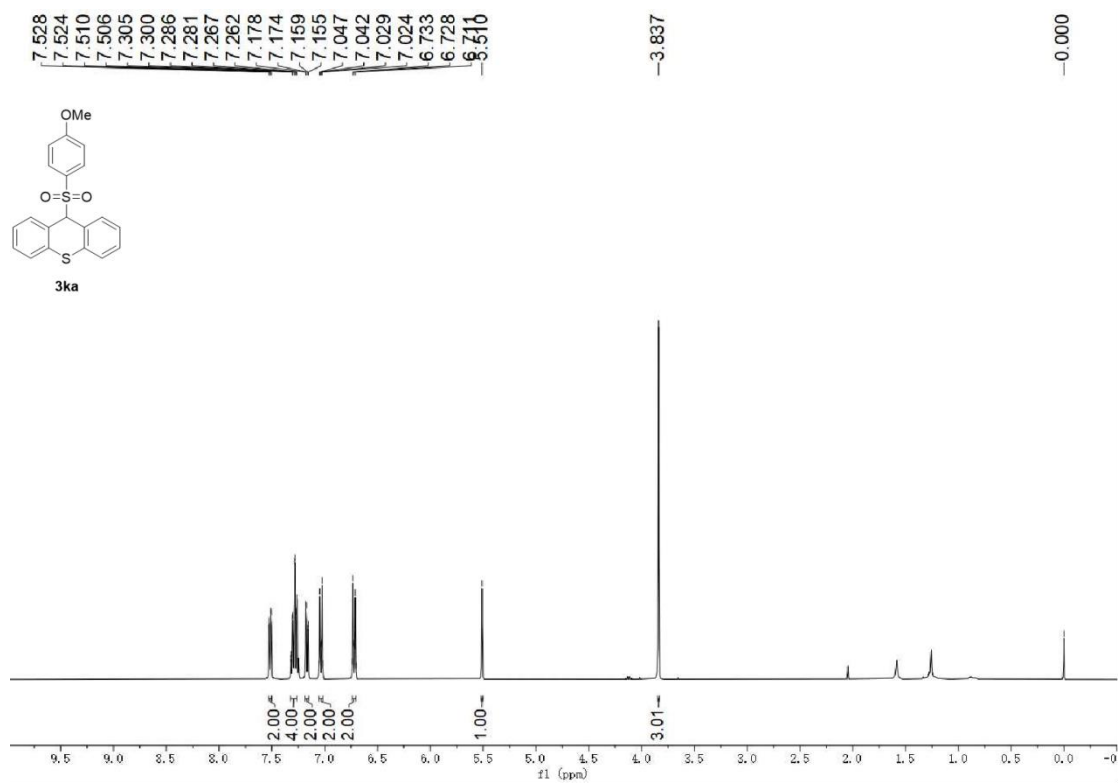
^1H -NMR (400 MHz) spectrum (CDCl_3) of **3ja**



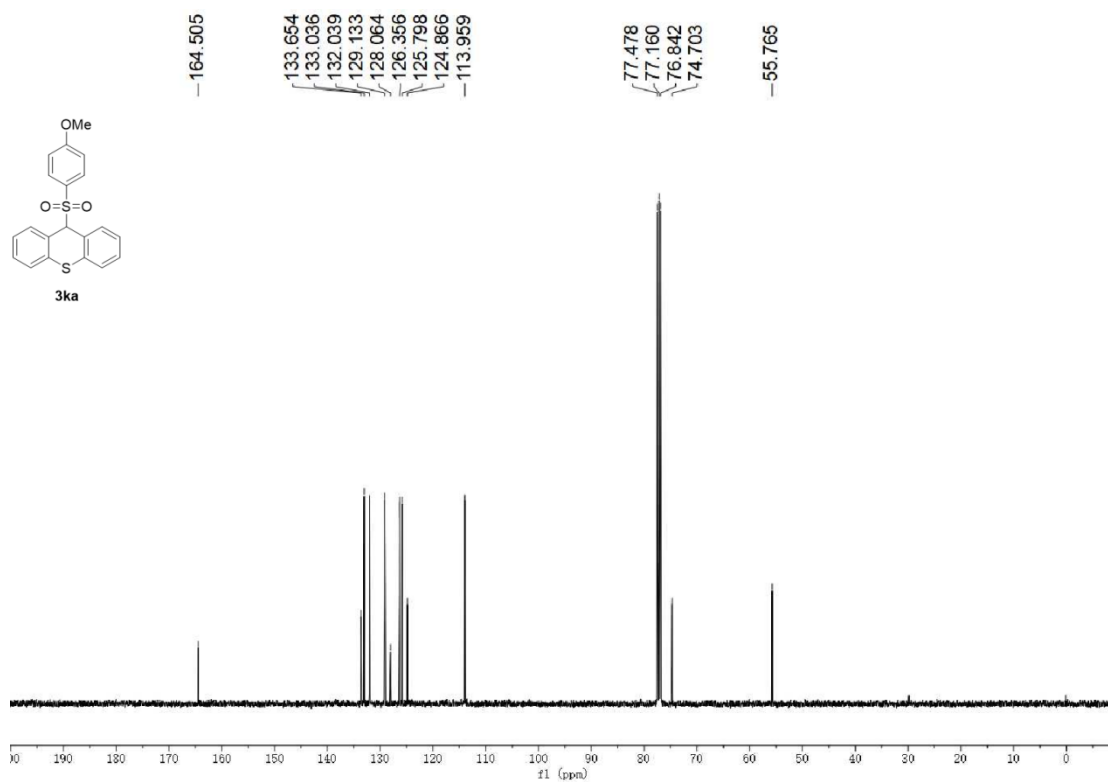
^{13}C -NMR (100 MHz) spectrum (CDCl_3) of **3ja**



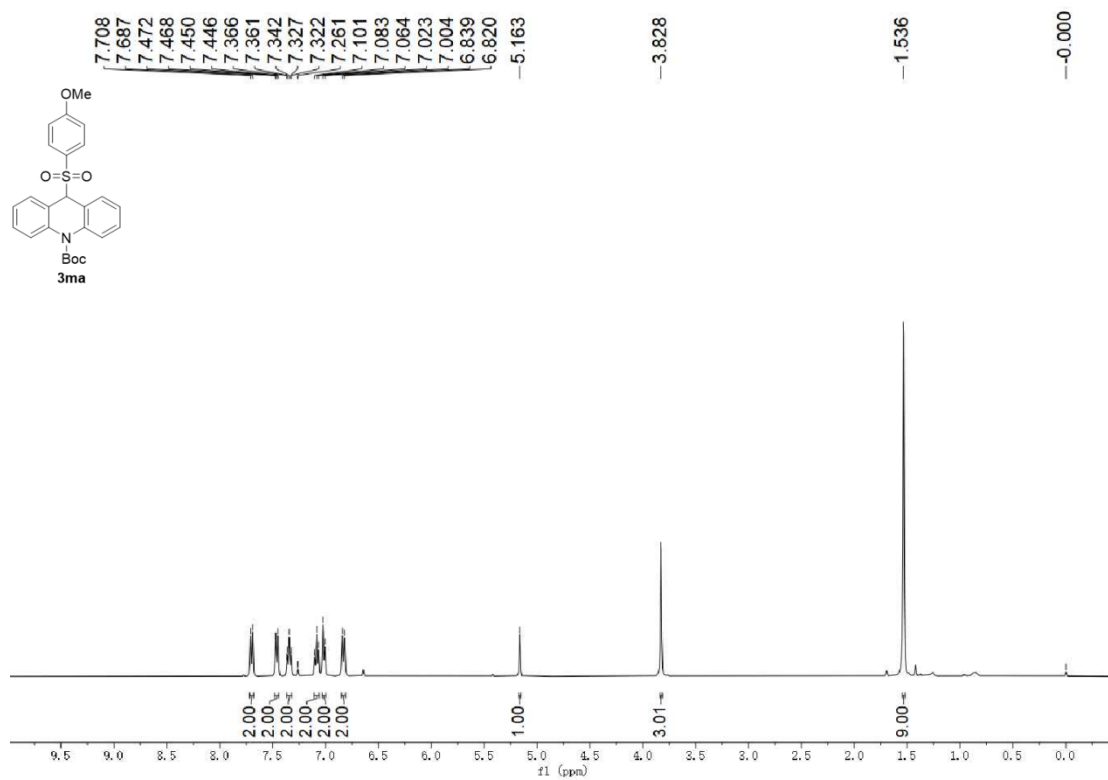
^1H -NMR (400 MHz) spectrum (CDCl_3) of **3ka**



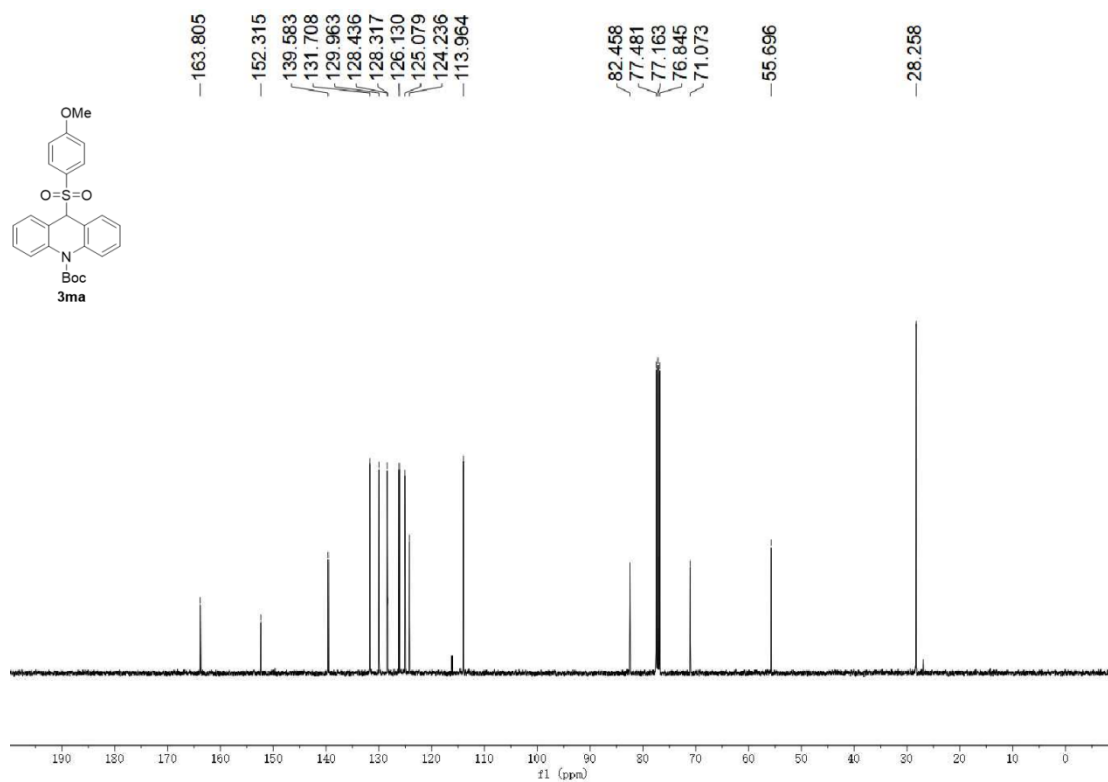
^{13}C -NMR (100 MHz) spectrum (CDCl_3) of **3ka**



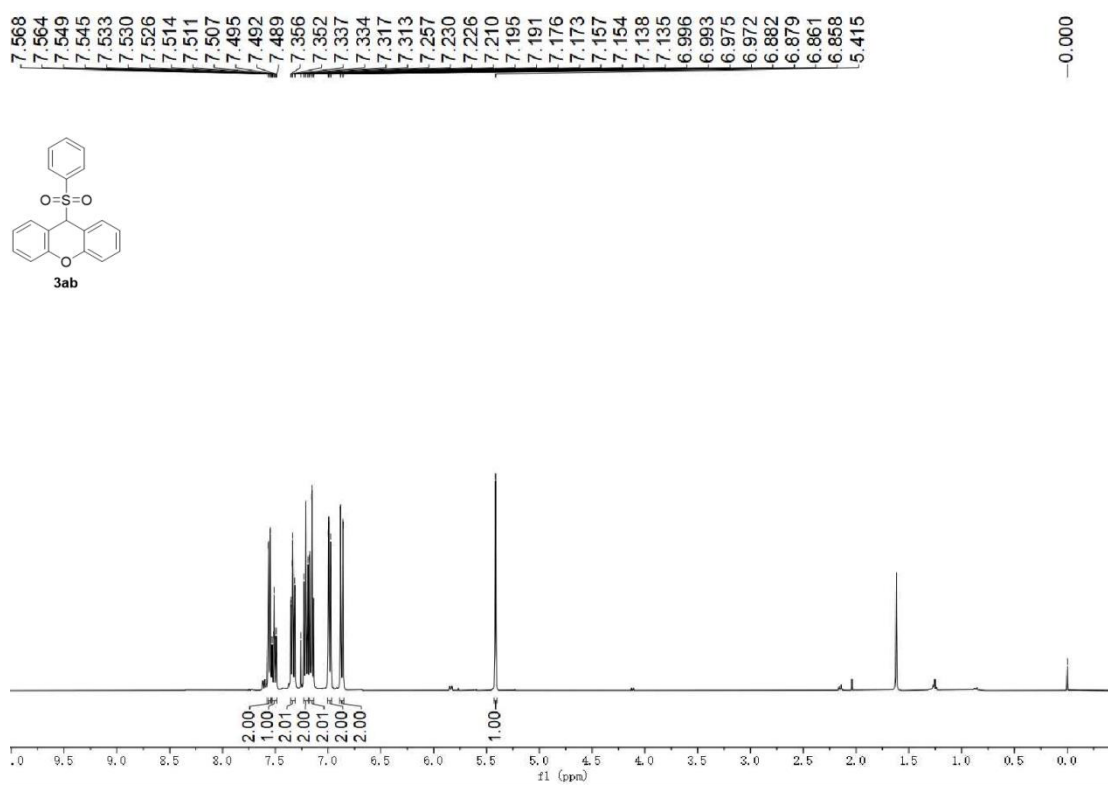
^1H -NMR (400 MHz) spectrum (CDCl_3) of **3ma**



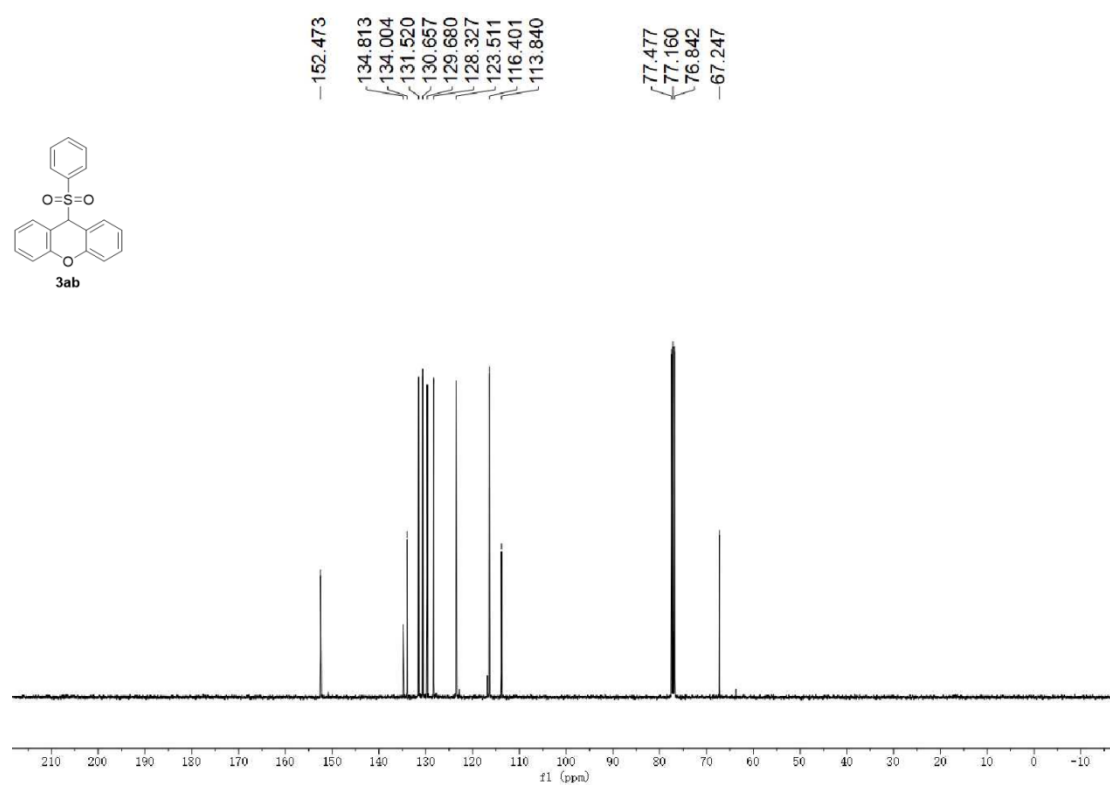
^{13}C -NMR (100 MHz) spectrum (CDCl_3) of **3ma**



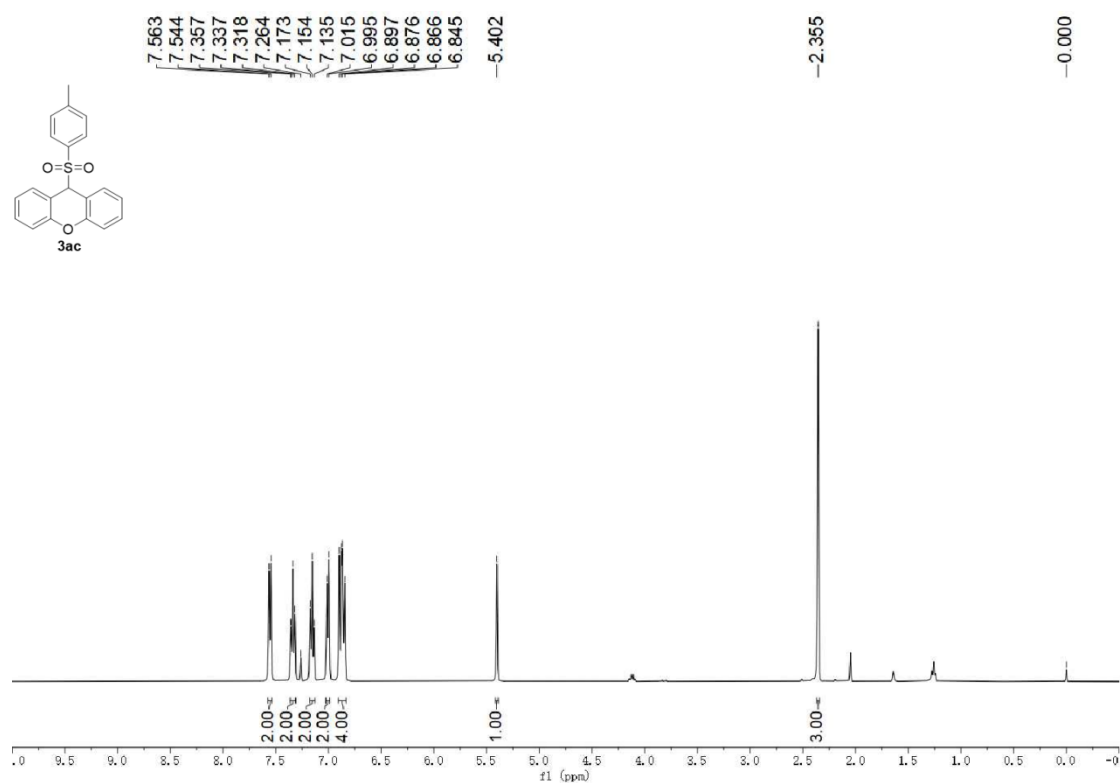
^1H -NMR (400 MHz) spectrum (CDCl_3) of **3ab**



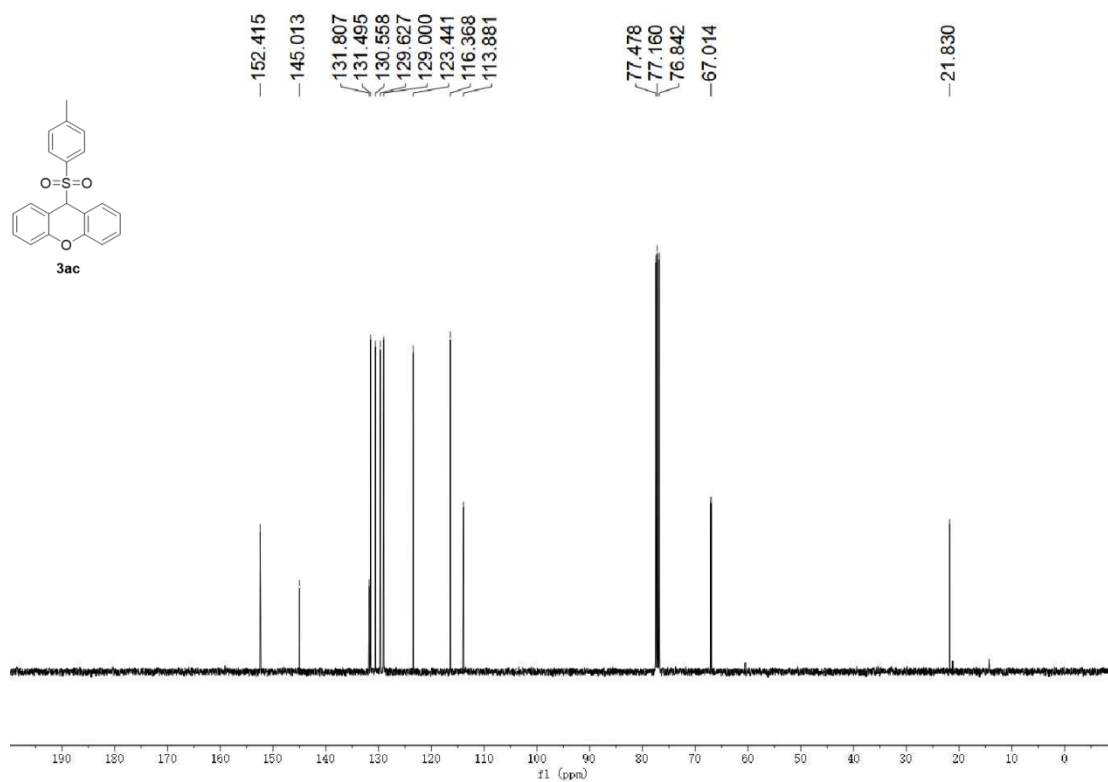
^{13}C -NMR (100 MHz) spectrum (CDCl_3) of **3ab**



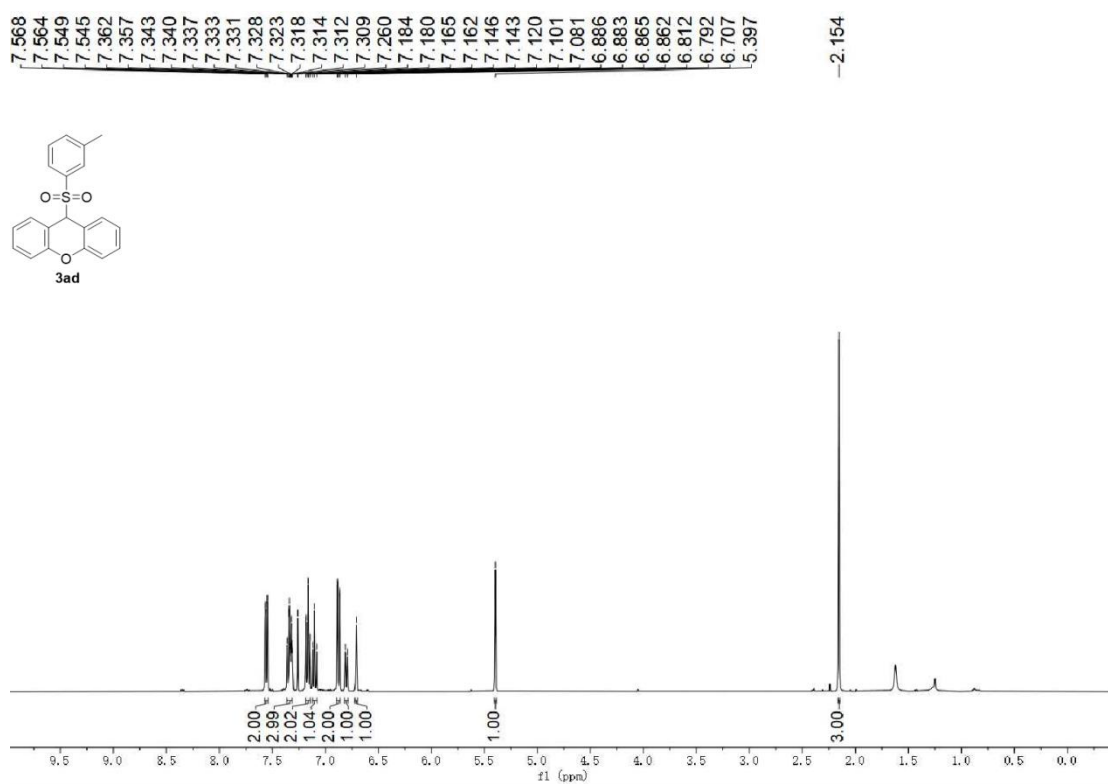
^1H -NMR (400 MHz) spectrum (CDCl_3) of **3ac**



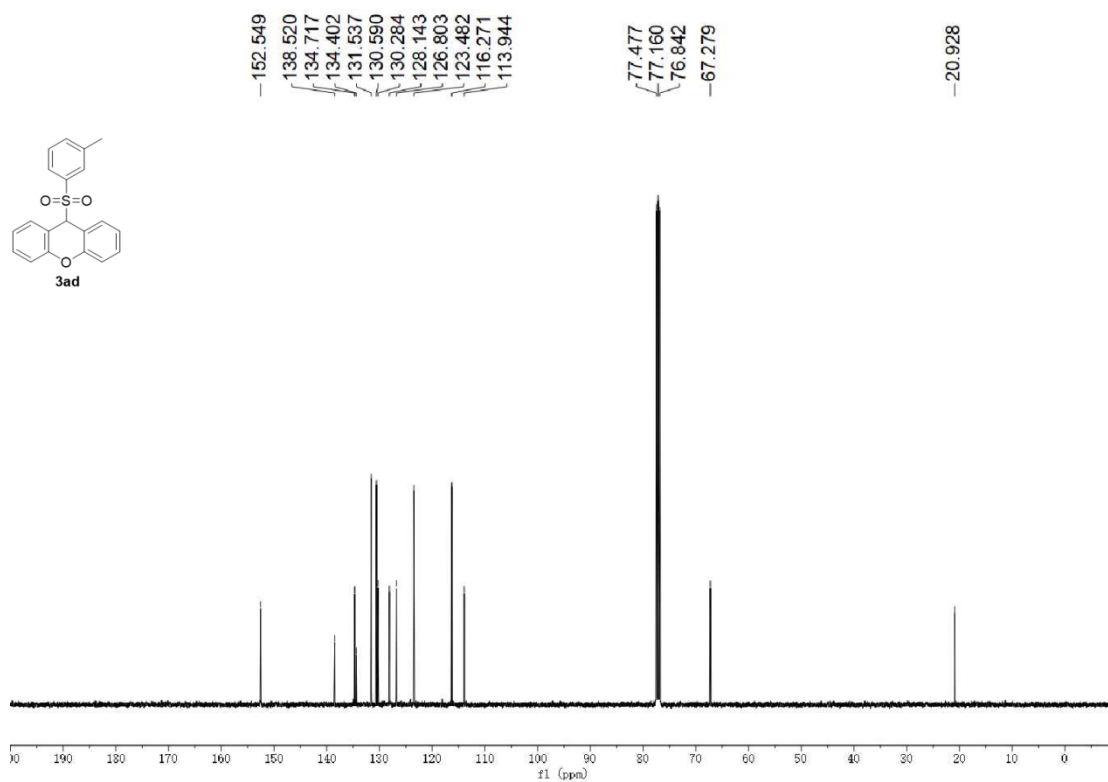
^{13}C -NMR (100 MHz) spectrum (CDCl_3) of **3ac**



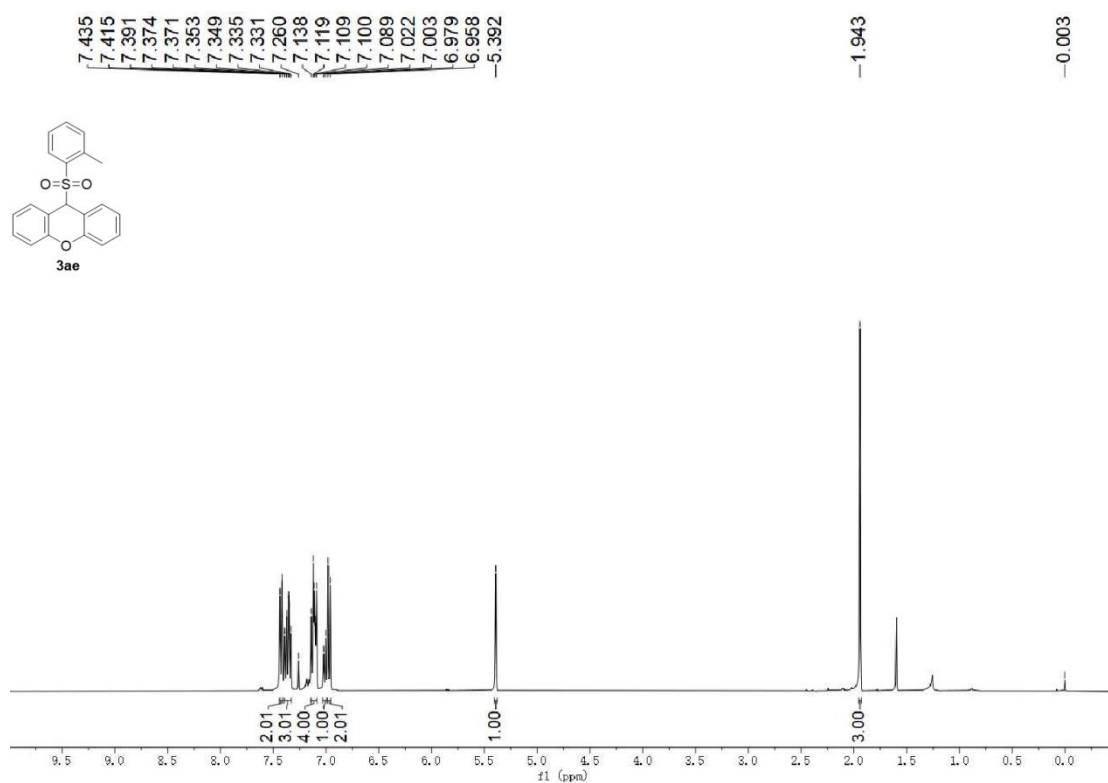
^1H -NMR (400 MHz) spectrum (CDCl_3) of **3ad**



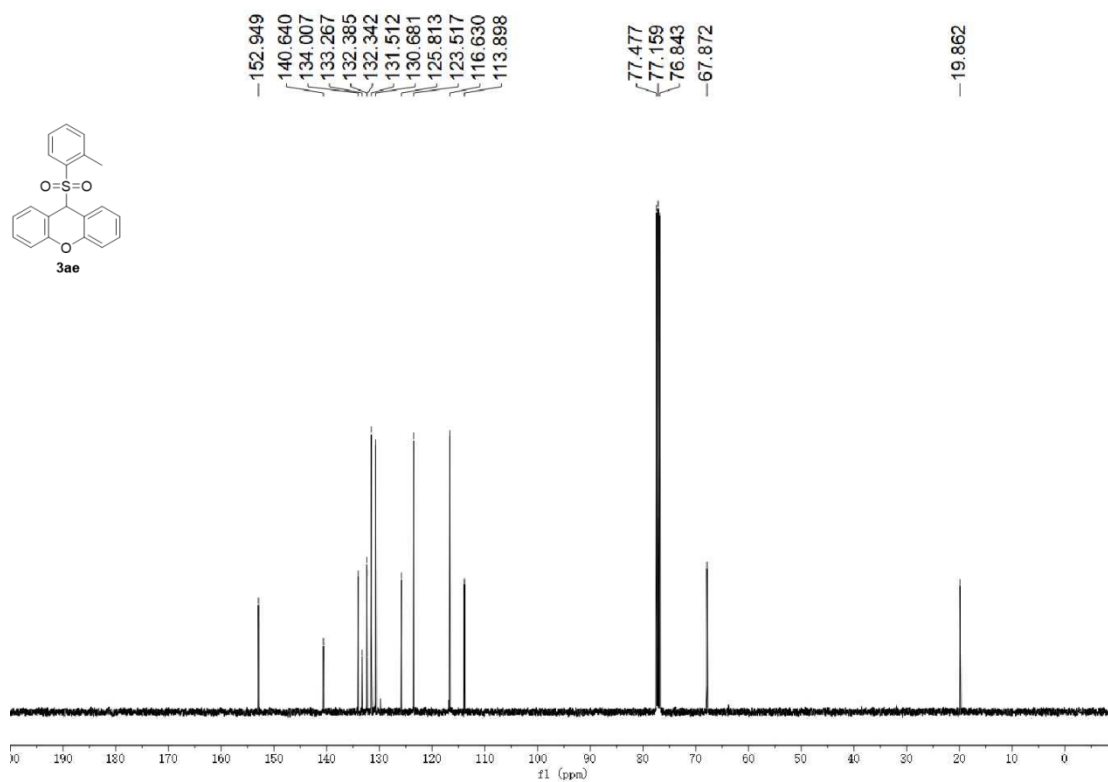
^{13}C -NMR (100 MHz) spectrum (CDCl_3) of **3ad**



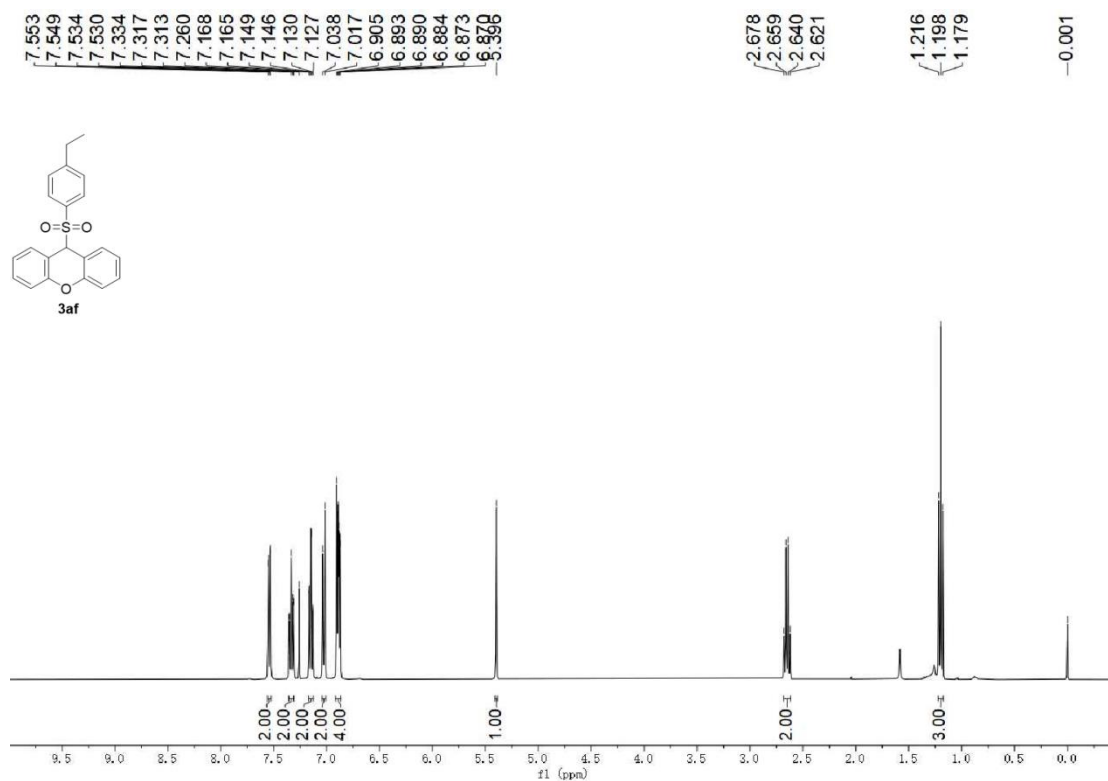
^1H -NMR (400 MHz) spectrum (CDCl_3) of **3ae**



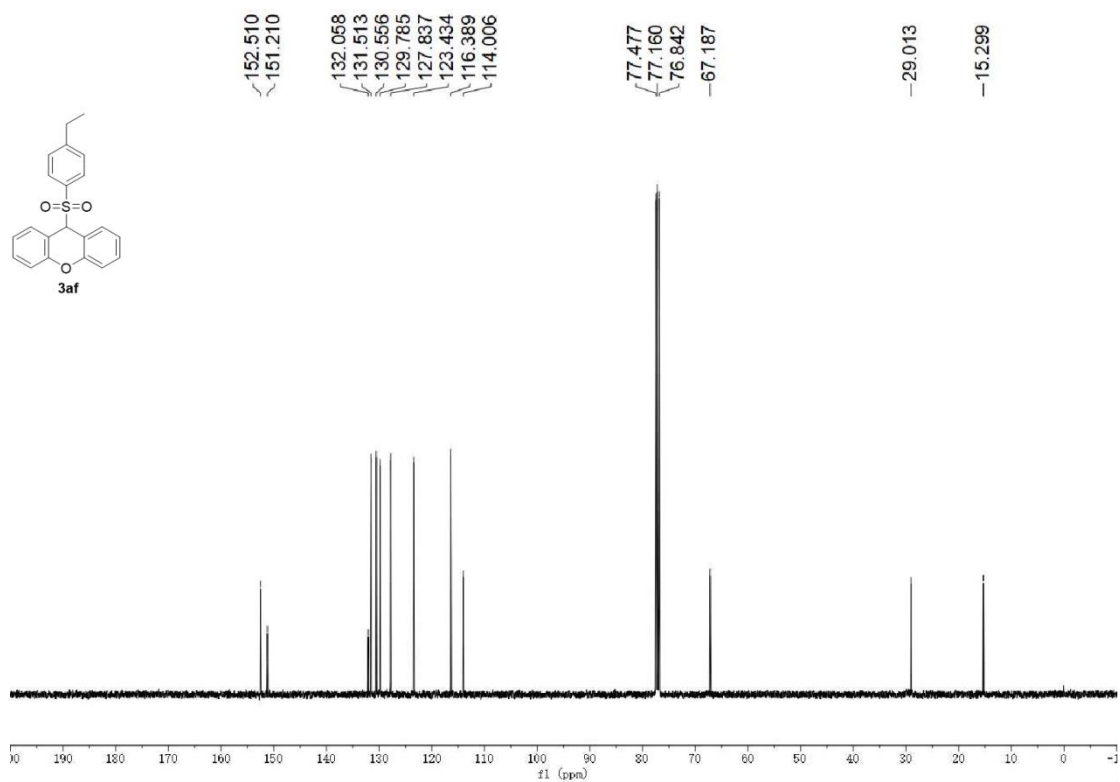
^{13}C -NMR (100 MHz) spectrum (CDCl_3) of **3ae**



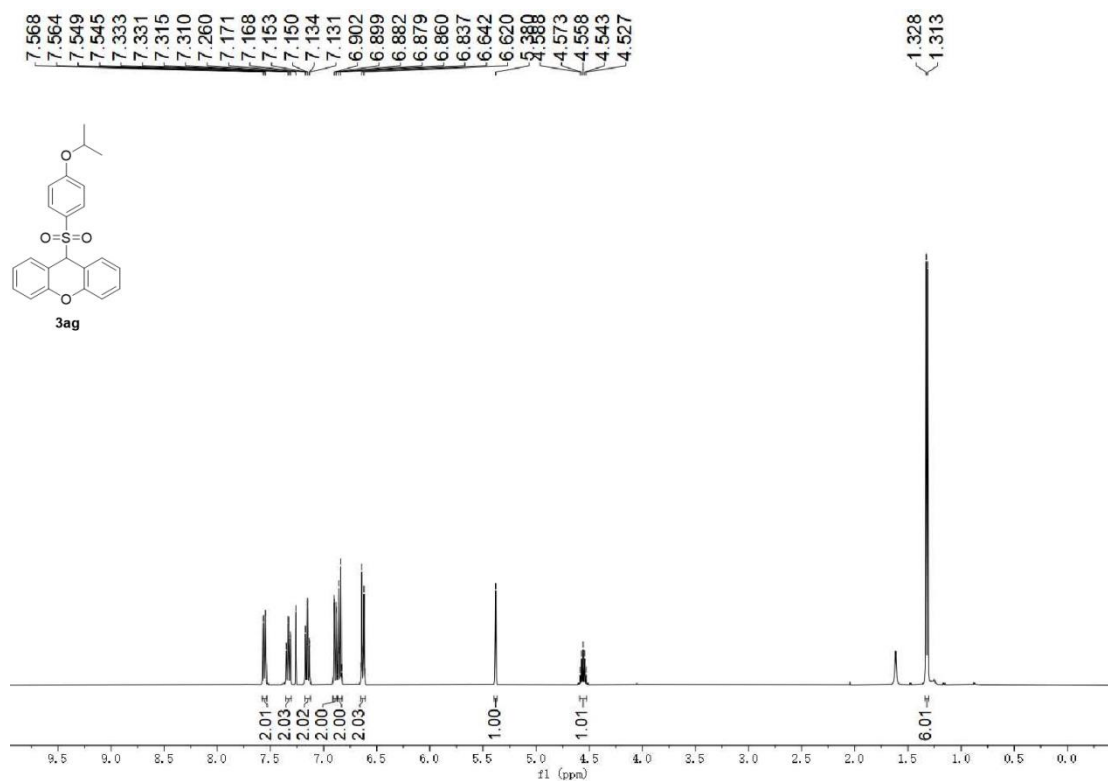
^1H -NMR (400 MHz) spectrum (CDCl_3) of **3af**



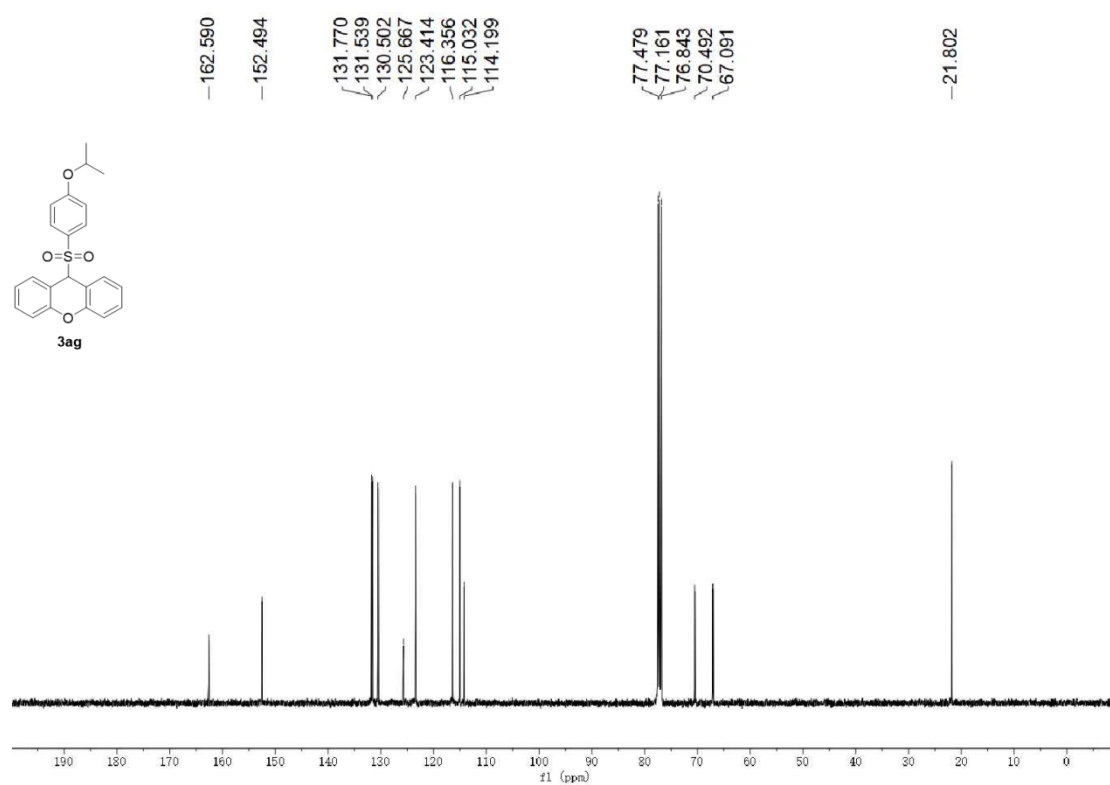
^{13}C -NMR (100 MHz) spectrum (CDCl_3) of **3af**



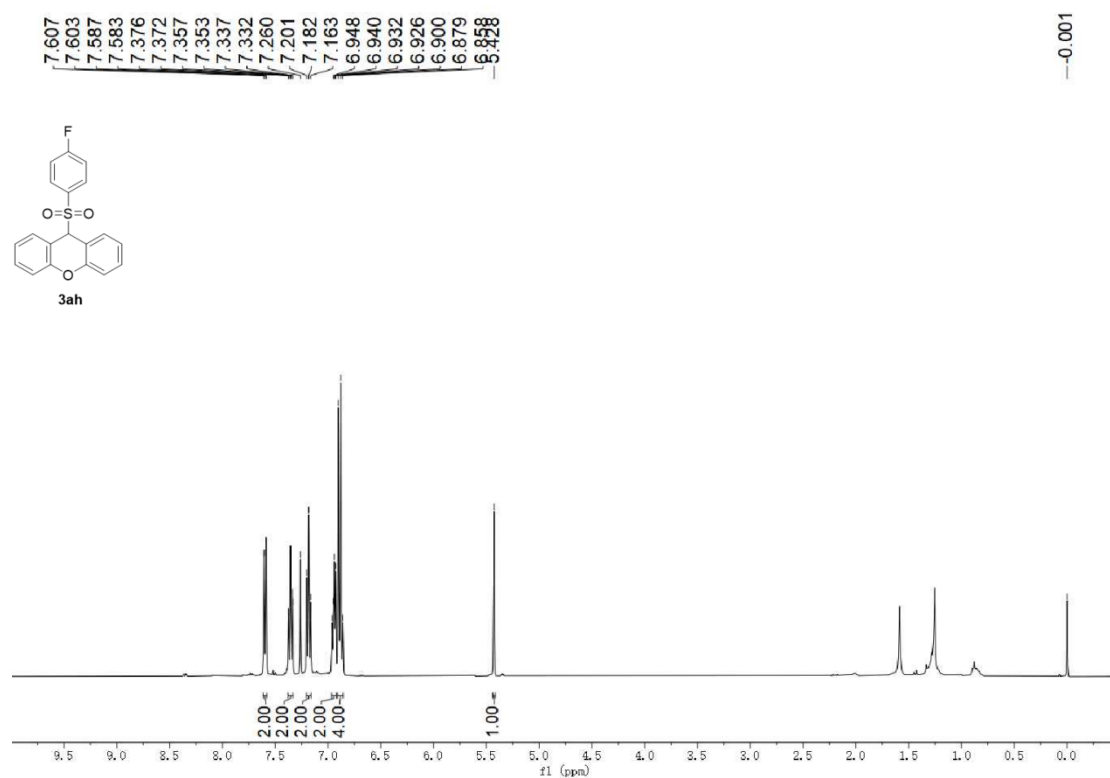
^1H -NMR (400 MHz) spectrum (CDCl_3) of **3ag**



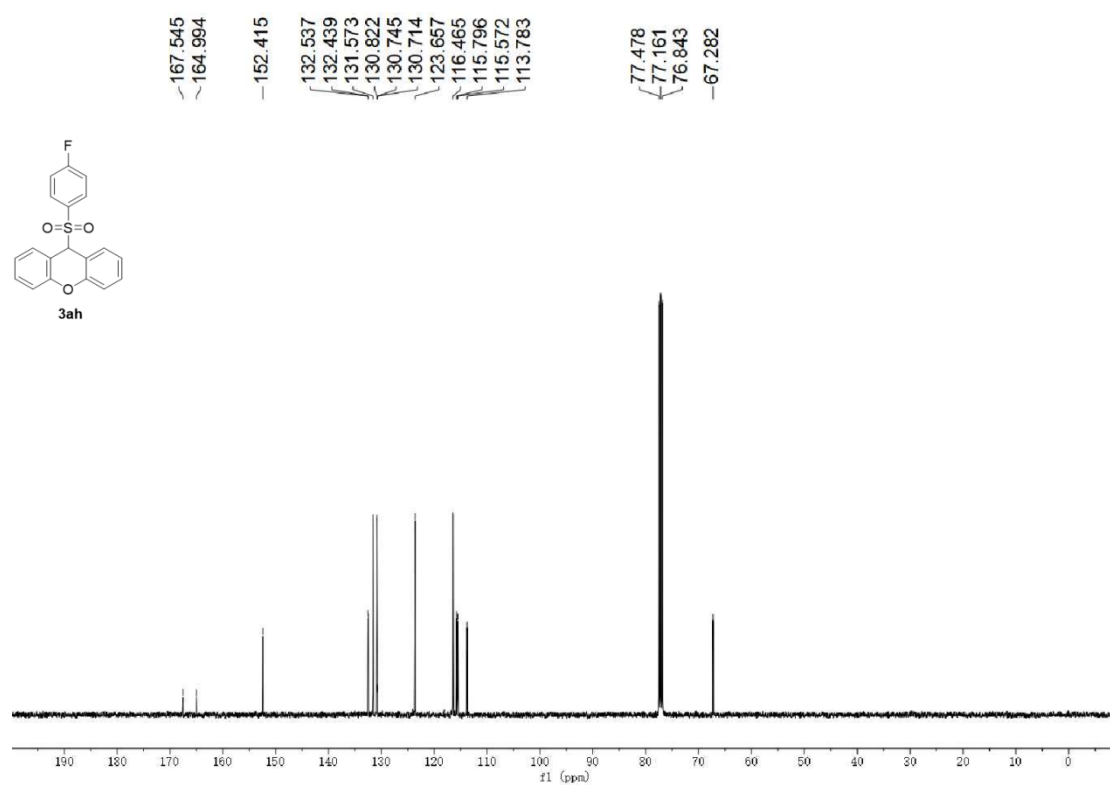
^{13}C -NMR (100 MHz) spectrum (CDCl_3) of **3ag**



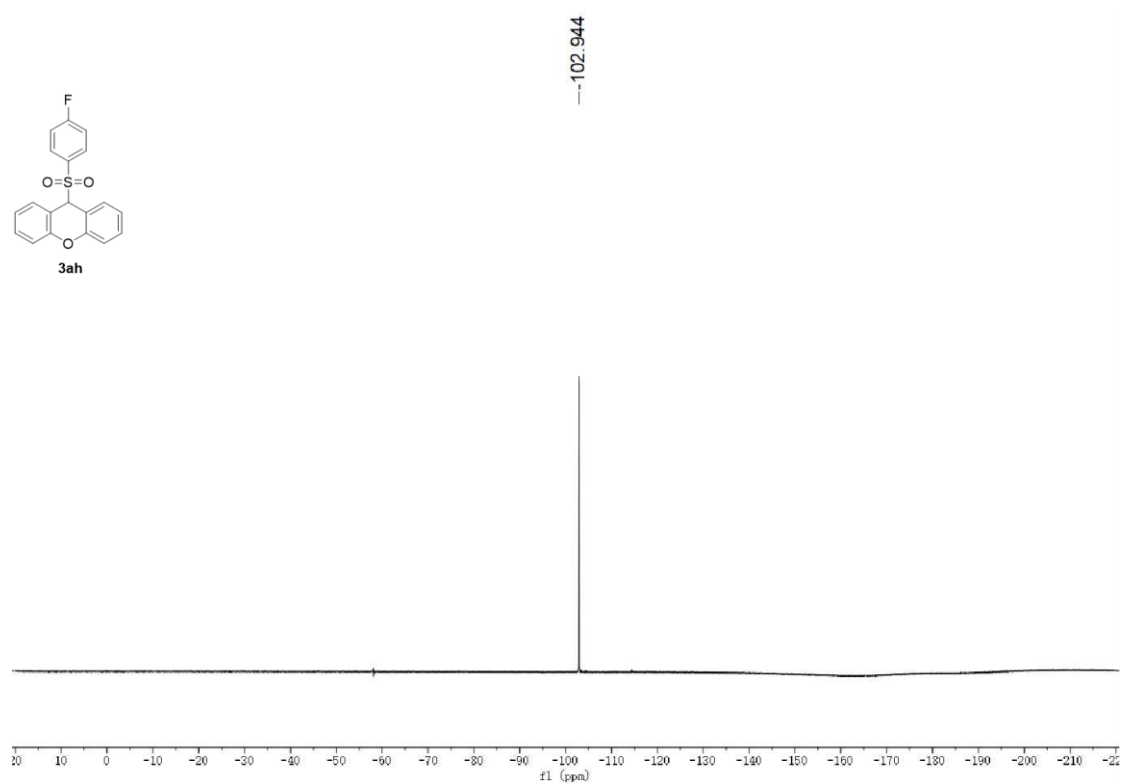
^1H -NMR (400 MHz) spectrum (CDCl_3) of **3ah**



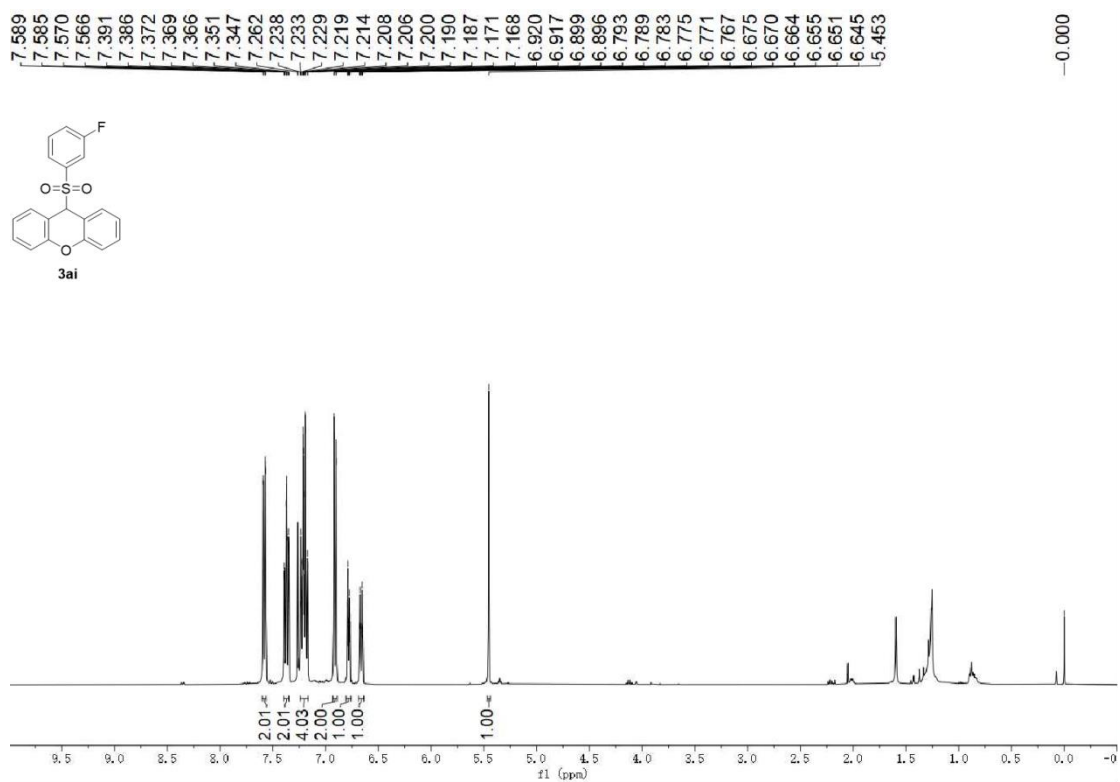
^{13}C -NMR (100 MHz) spectrum (CDCl_3) of **3ah**



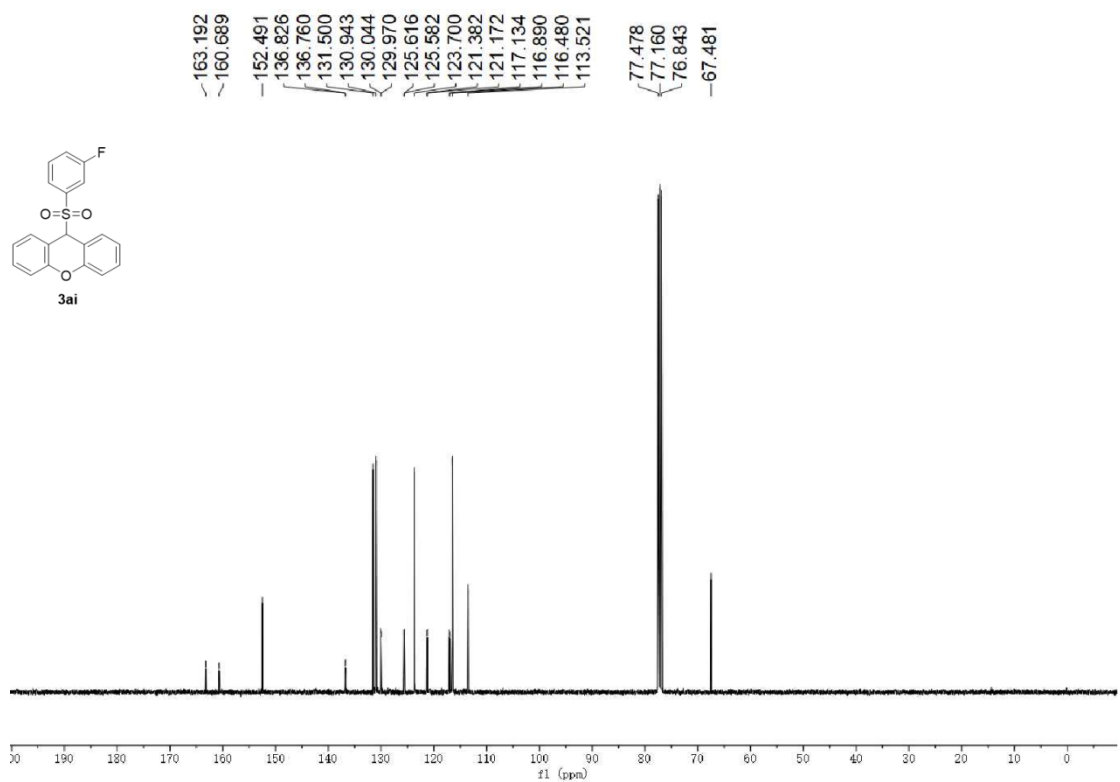
^{19}F -NMR (377 MHz) spectrum (CDCl_3) of **3ah**



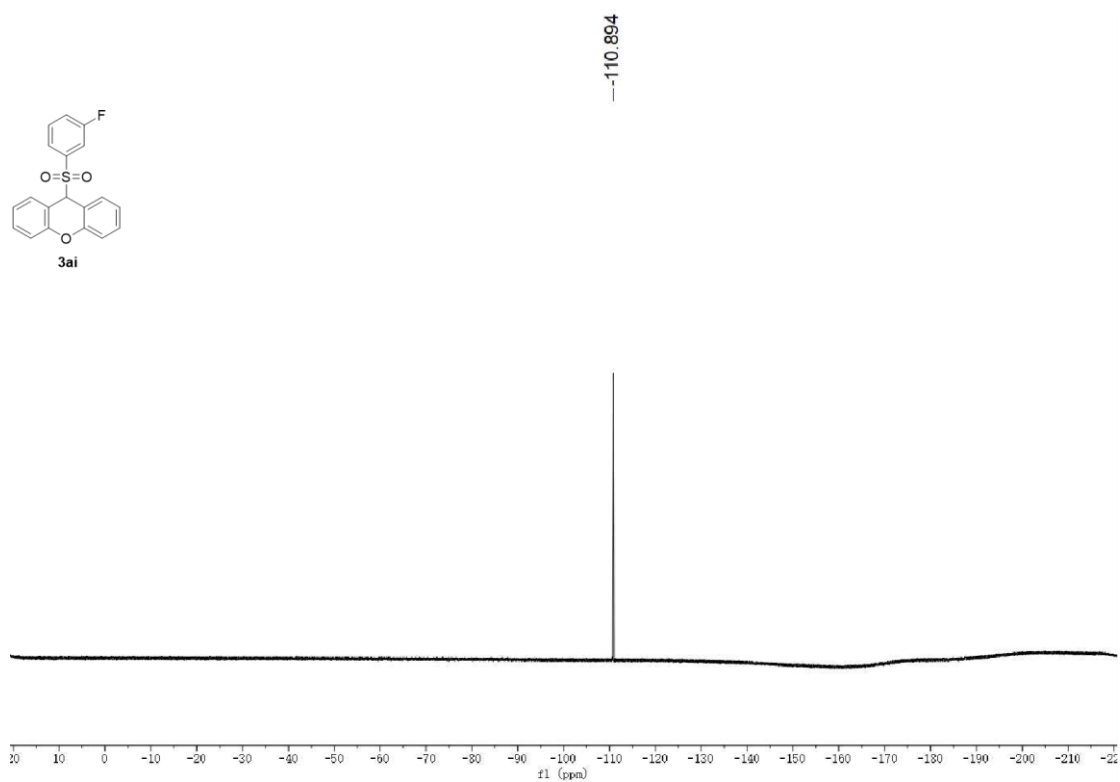
¹H-NMR (400 MHz) spectrum (CDCl₃) of **3ai**



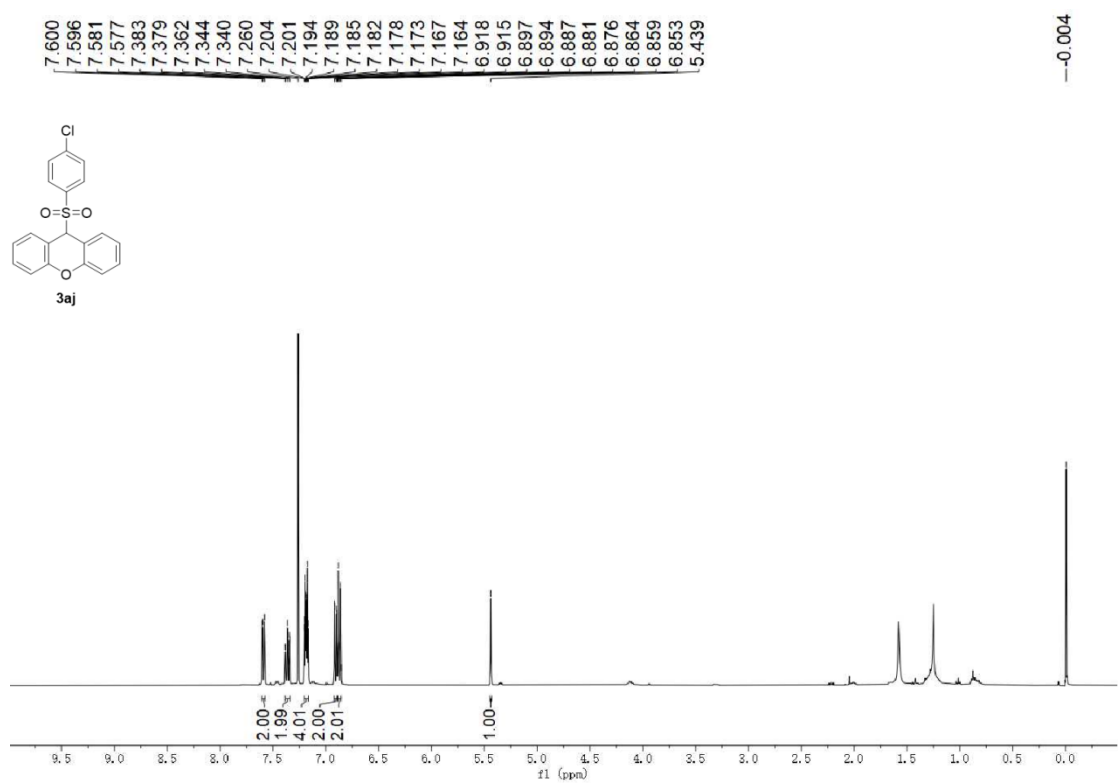
¹³C-NMR (100 MHz) spectrum (CDCl₃) of **3ai**



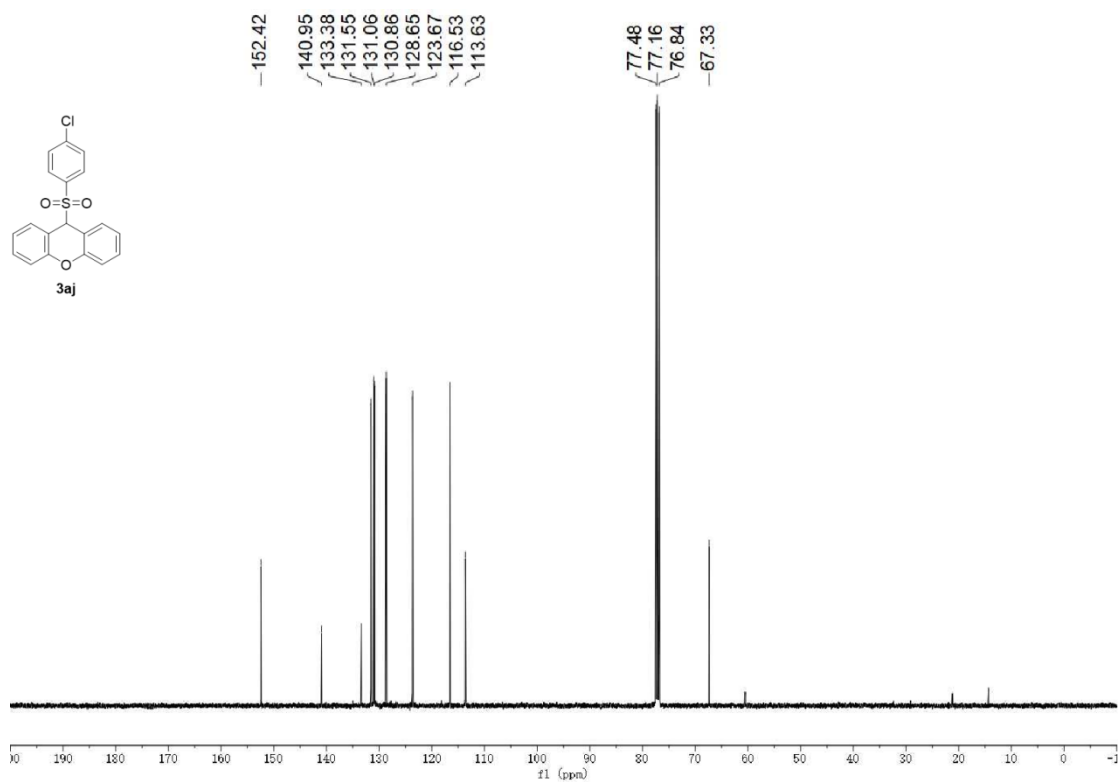
¹⁹F-NMR (377 MHz) spectrum (CDCl₃) of **3ai**



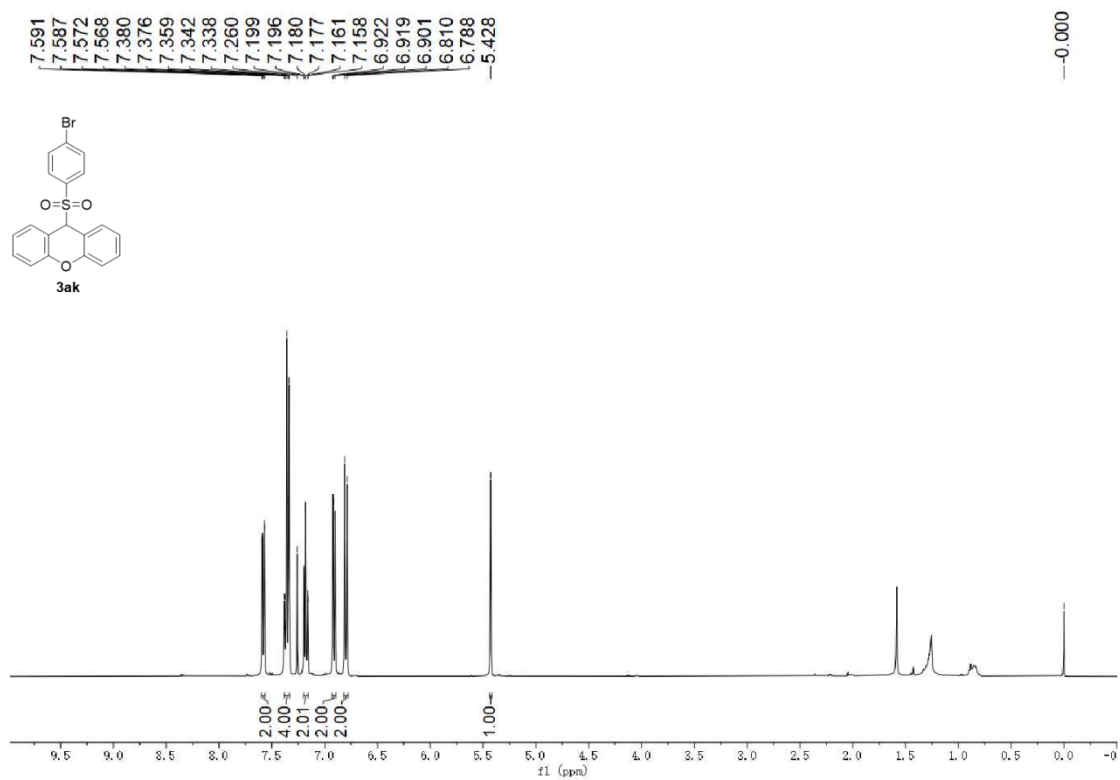
¹H-NMR (400 MHz) spectrum (CDCl₃) of **3aj**



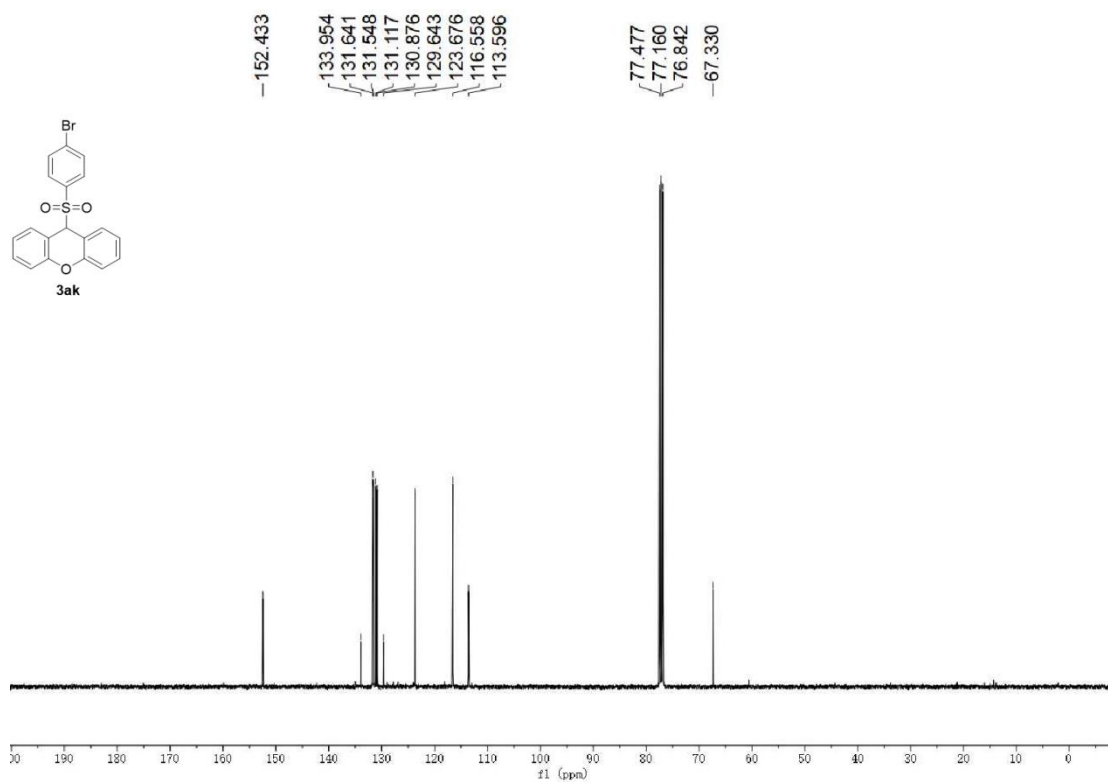
^{13}C -NMR (100 MHz) spectrum (CDCl_3) of **3aj**



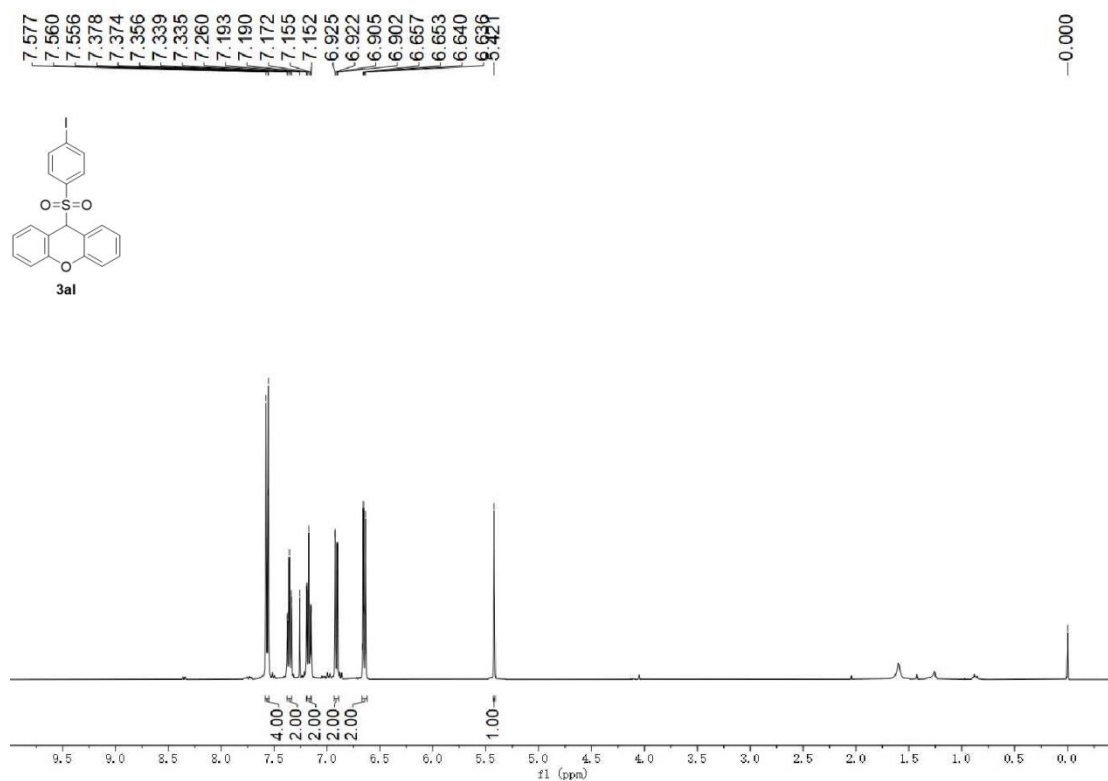
^1H -NMR (400 MHz) spectrum (CDCl_3) of **3ak**



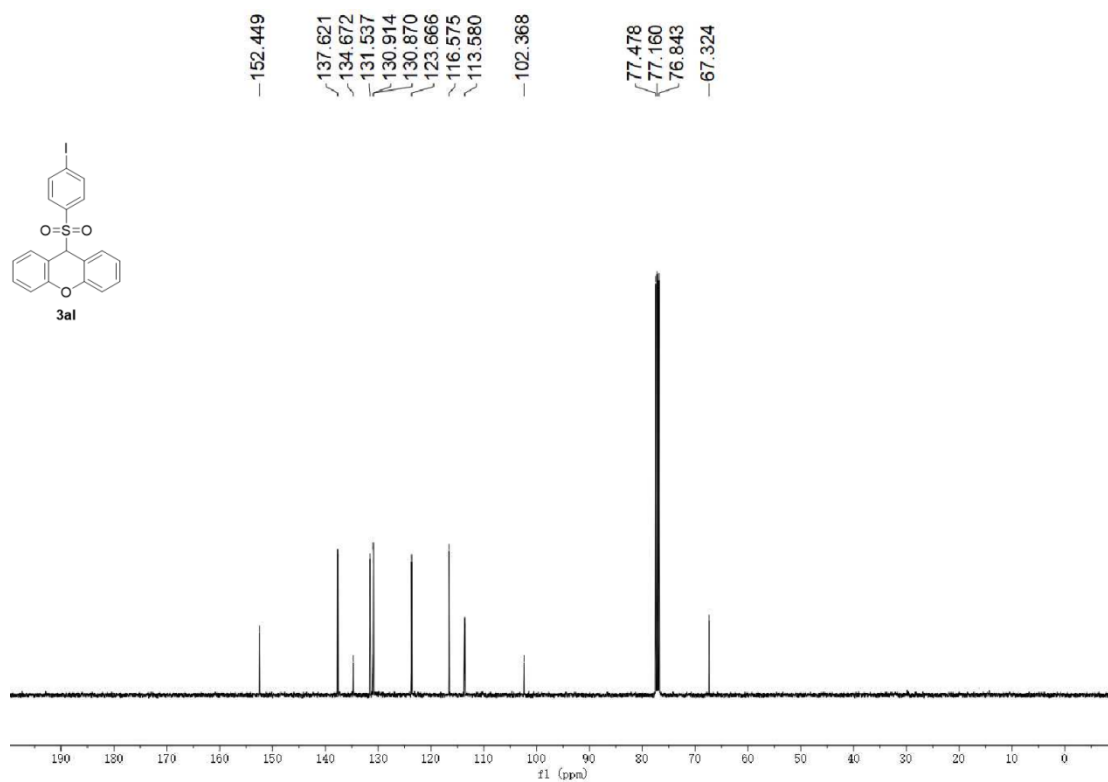
^{13}C -NMR (100 MHz) spectrum (CDCl_3) of **3ak**



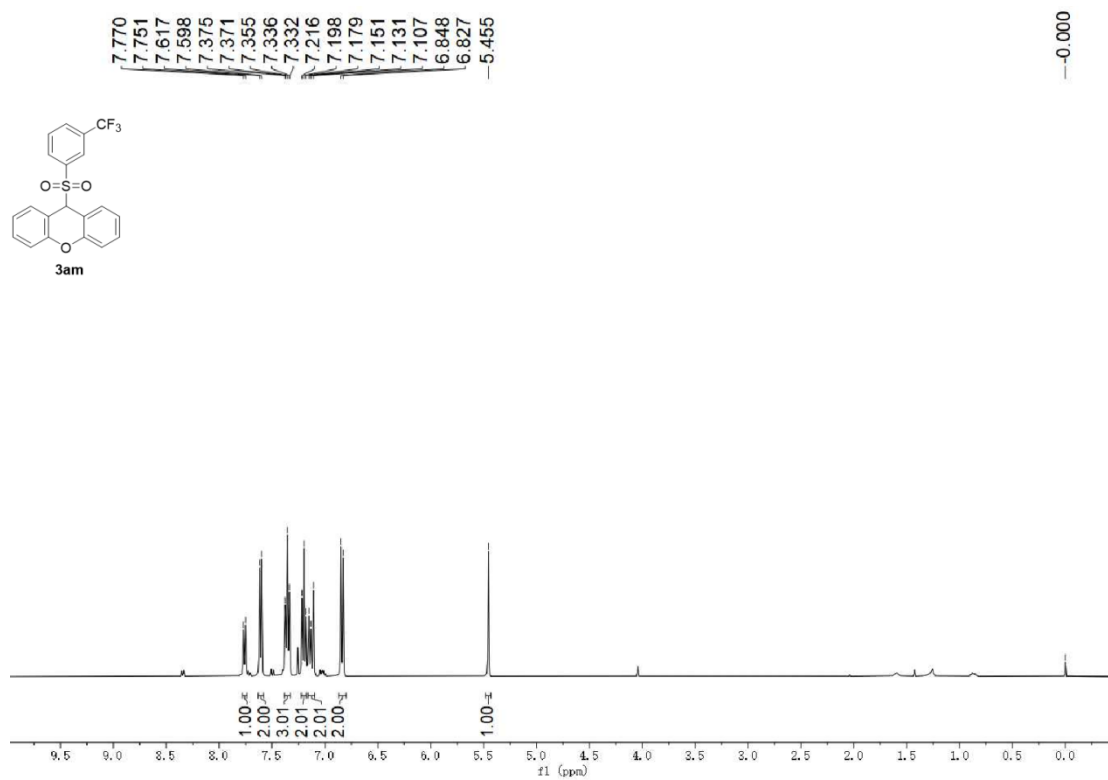
^1H -NMR (400 MHz) spectrum (CDCl_3) of **3al**



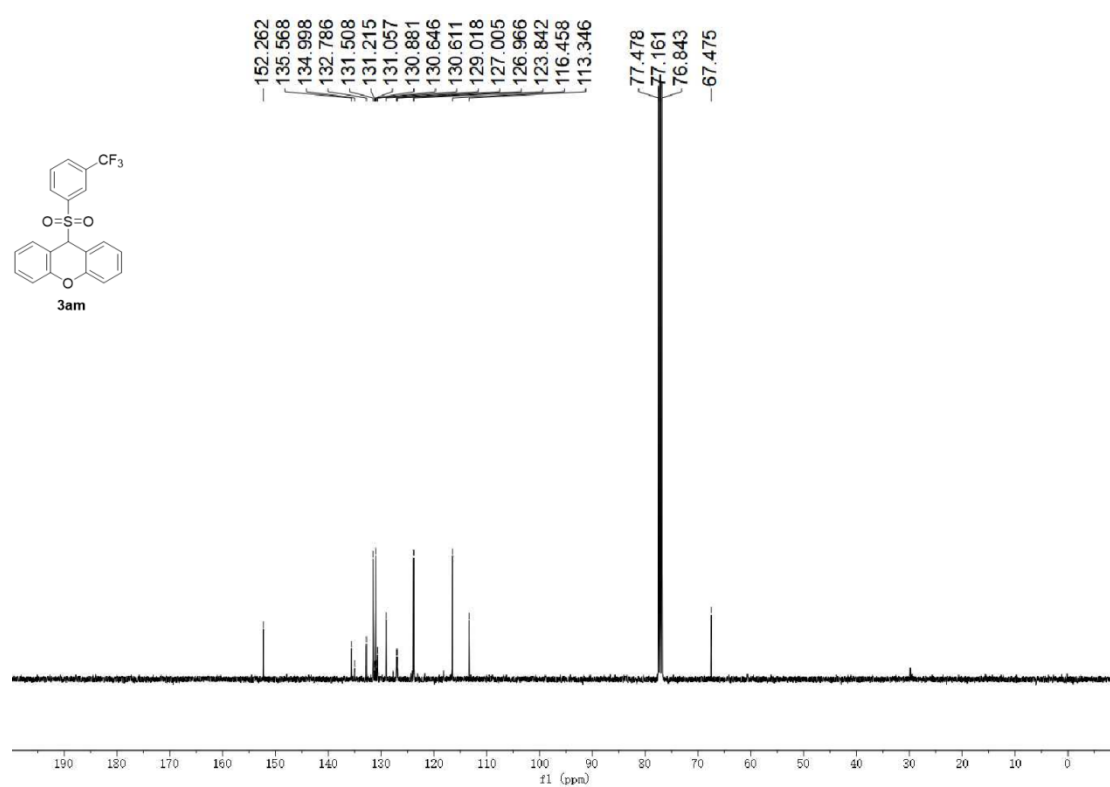
^{13}C -NMR (100 MHz) spectrum (CDCl_3) of **3al**



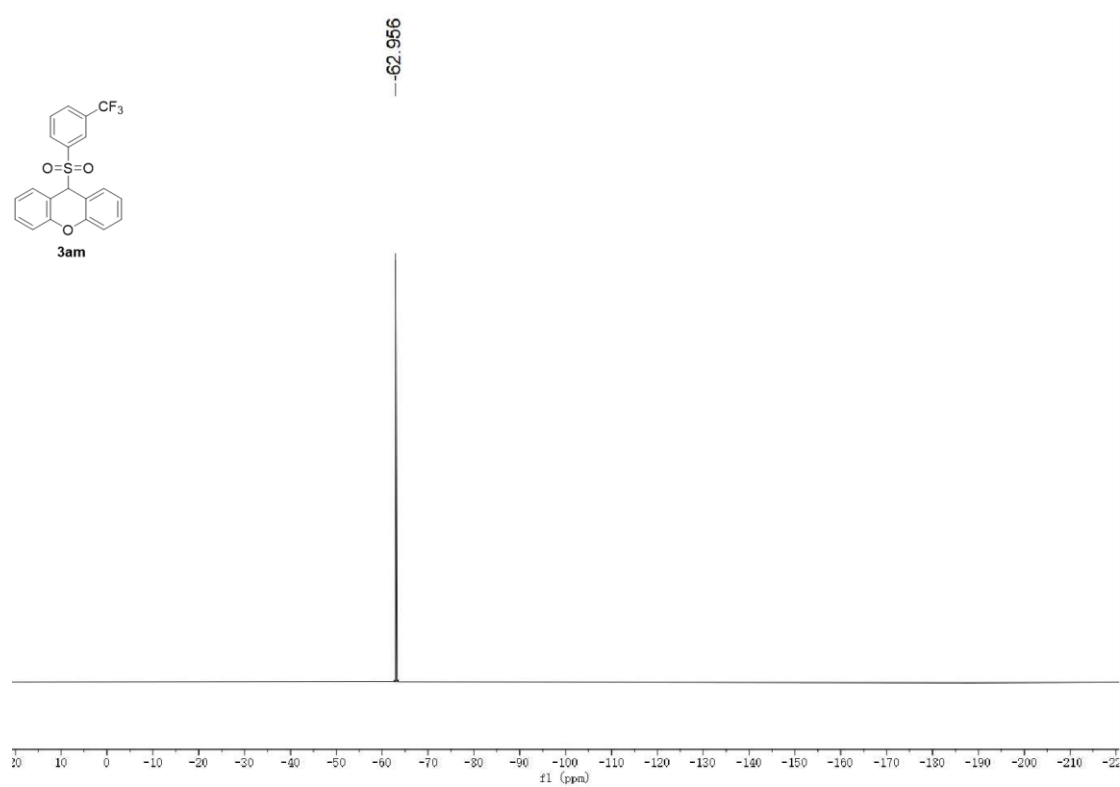
^1H -NMR (400 MHz) spectrum (CDCl_3) of **3am**



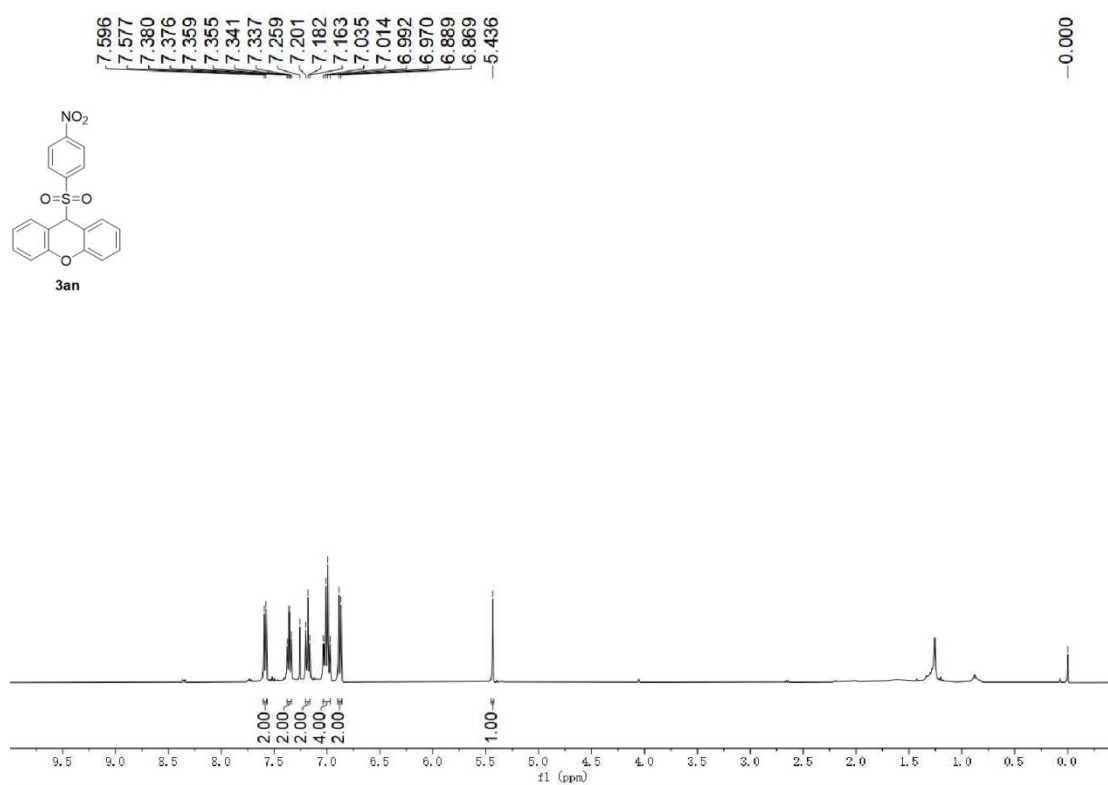
^{13}C -NMR (100 MHz) spectrum (CDCl_3) of **3am**



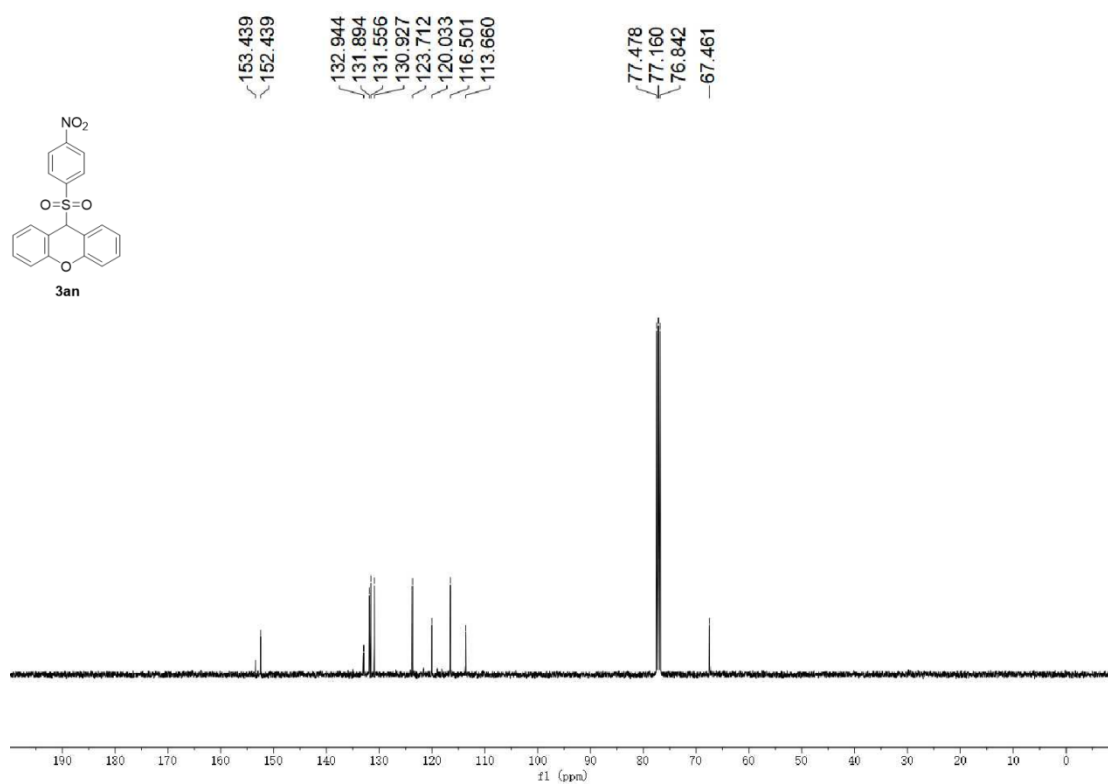
^{19}F -NMR (377 MHz) spectrum (CDCl_3) of **3am**



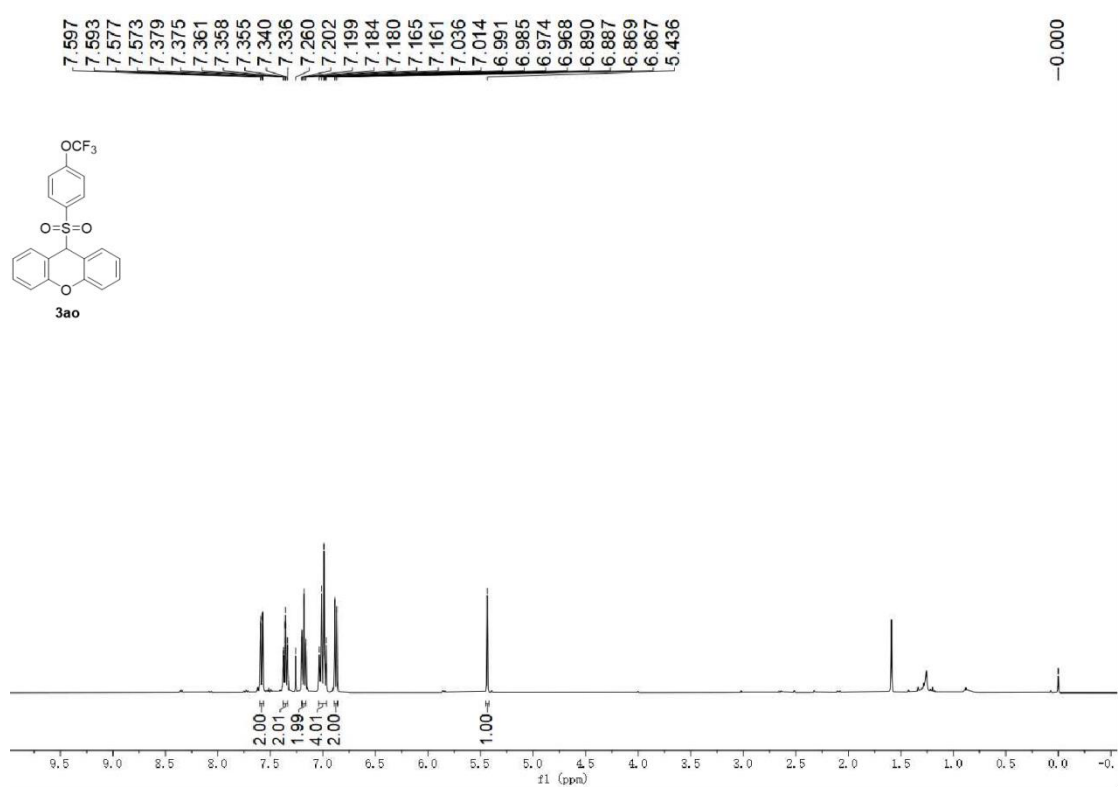
¹H-NMR (400 MHz) spectrum (CDCl₃) of **3an**



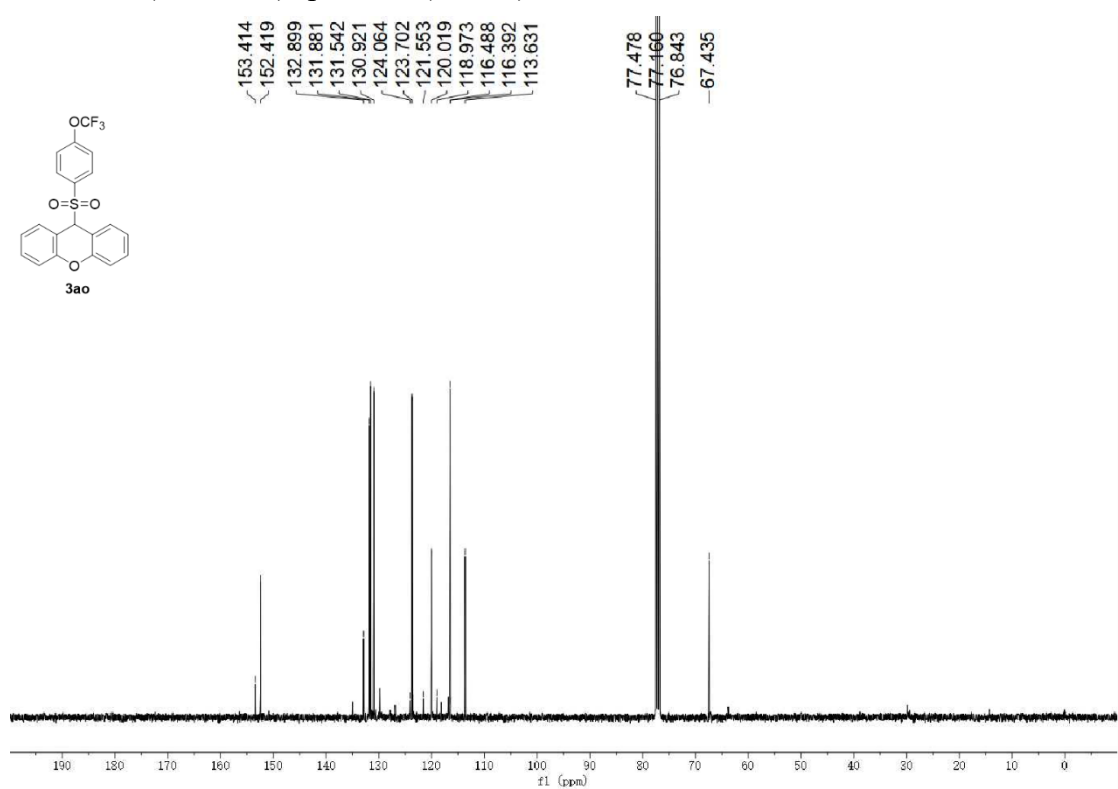
¹³C-NMR (100 MHz) spectrum (CDCl₃) of **3an**



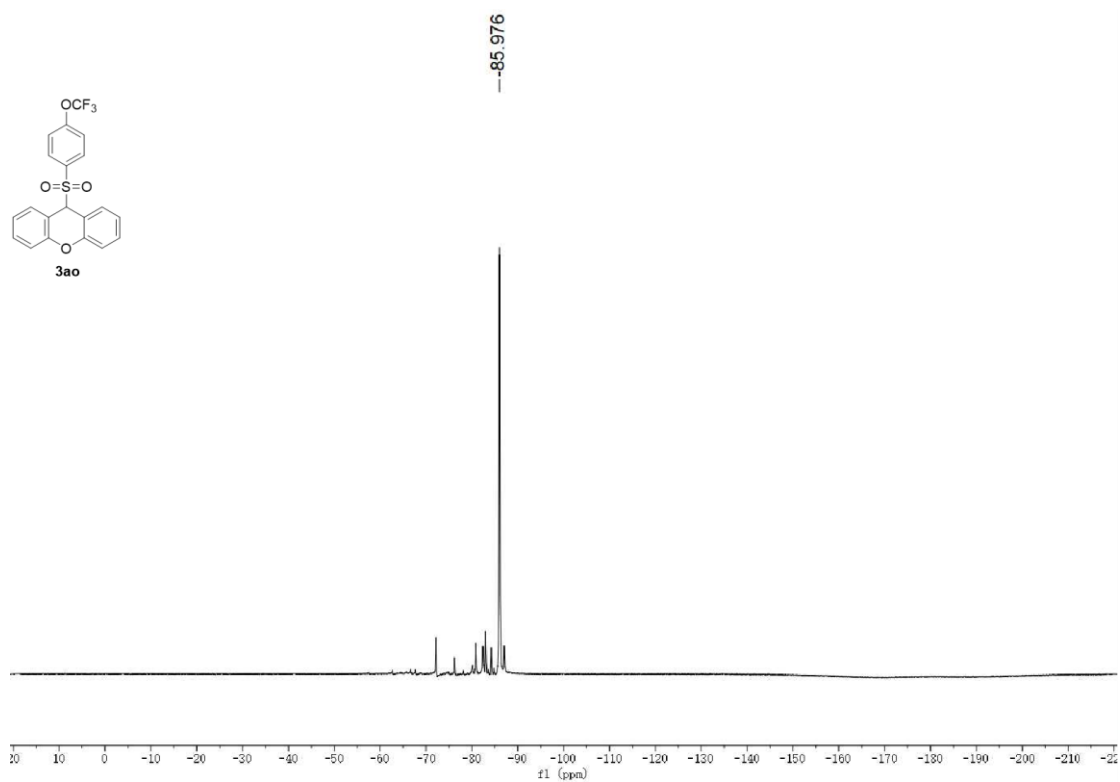
¹H-NMR (400 MHz) spectrum (CDCl₃) of **3ao**



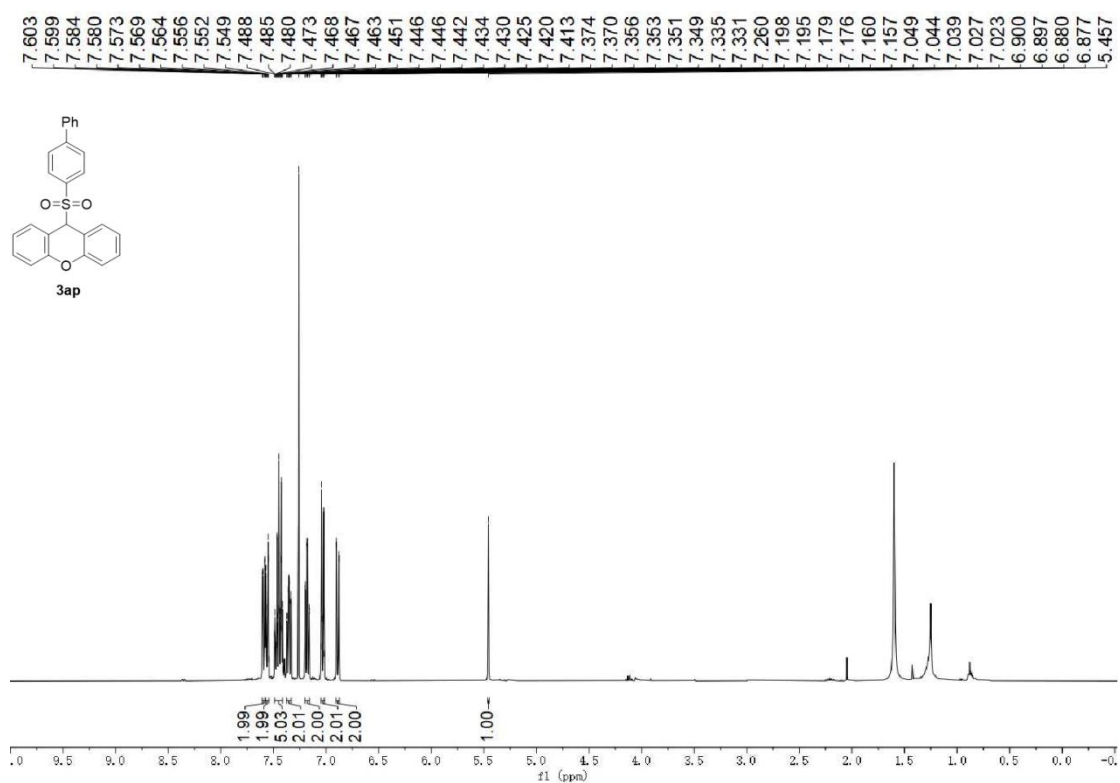
¹³C-NMR (100 MHz) spectrum (CDCl₃) of **3ao**



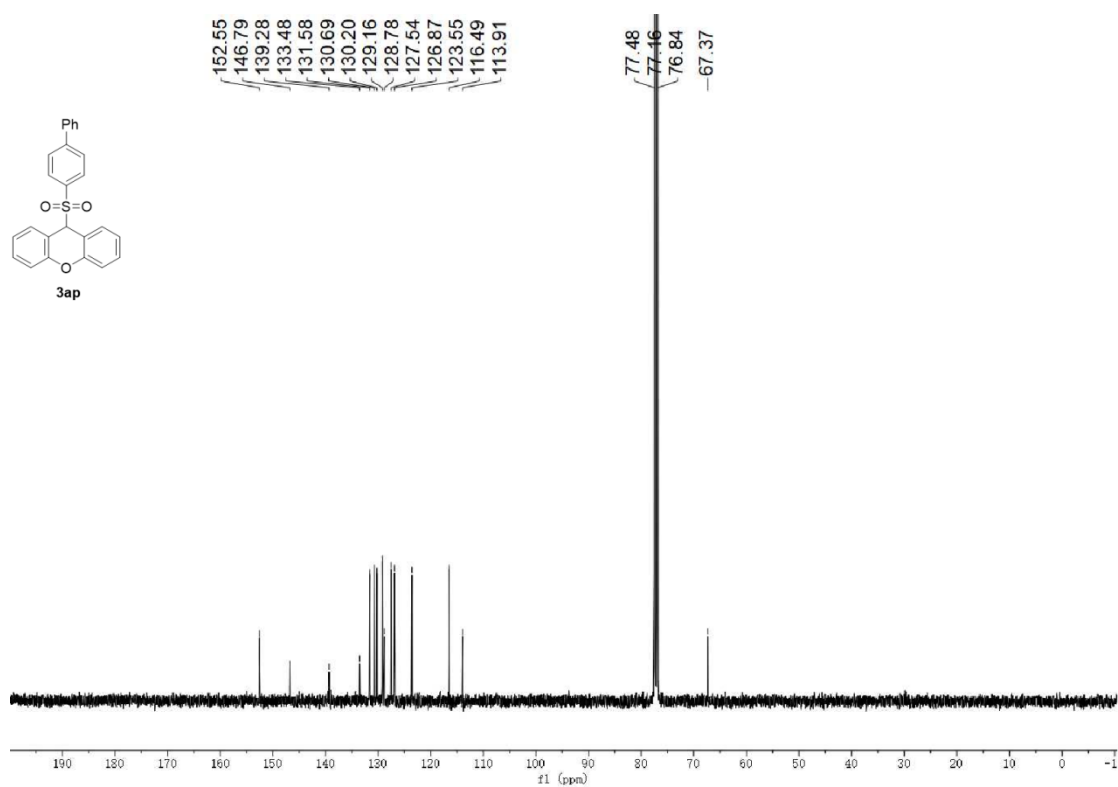
^{19}F -NMR (377 MHz) spectrum (CDCl_3) of **3ao**



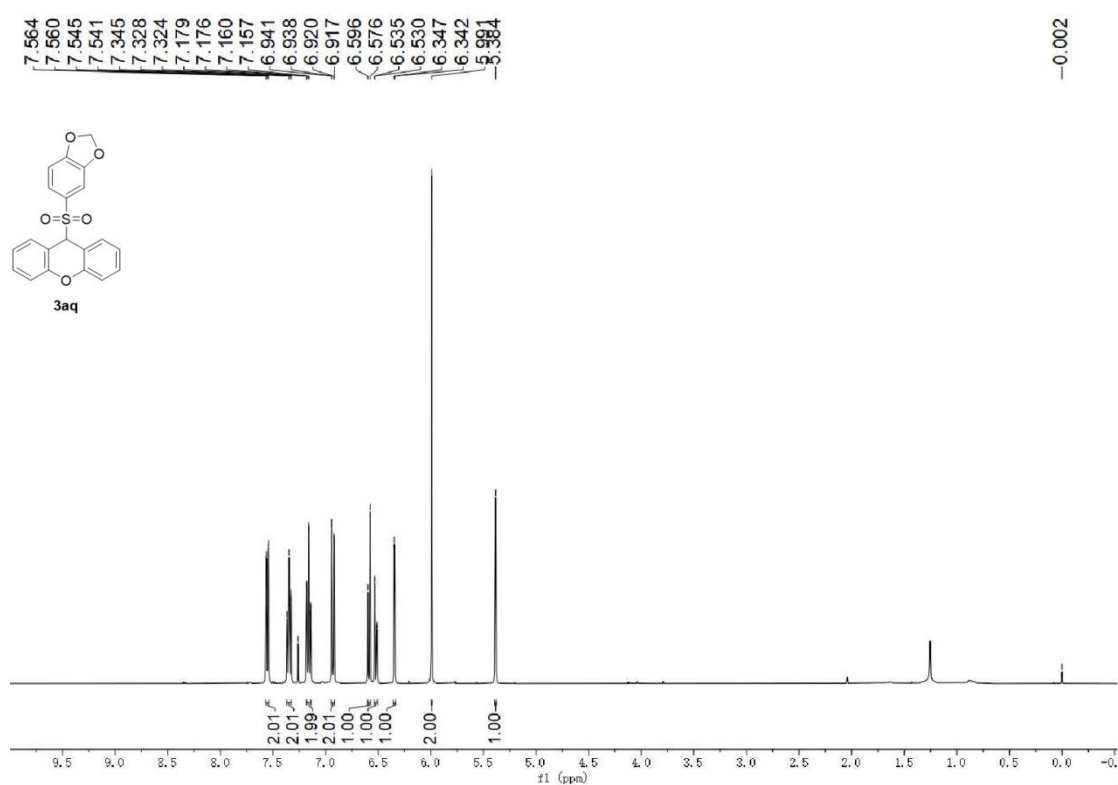
^1H -NMR (400 MHz) spectrum (CDCl_3) of **3ap**



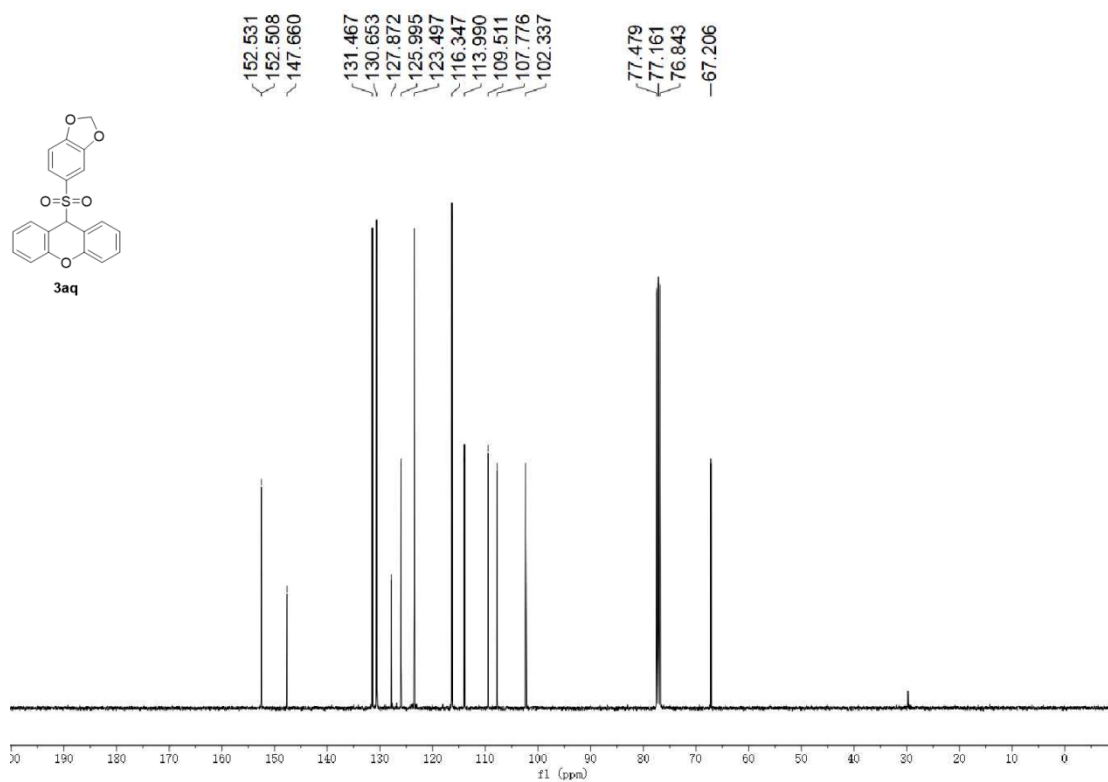
^{13}C -NMR (100 MHz) spectrum (CDCl_3) of **3ap**



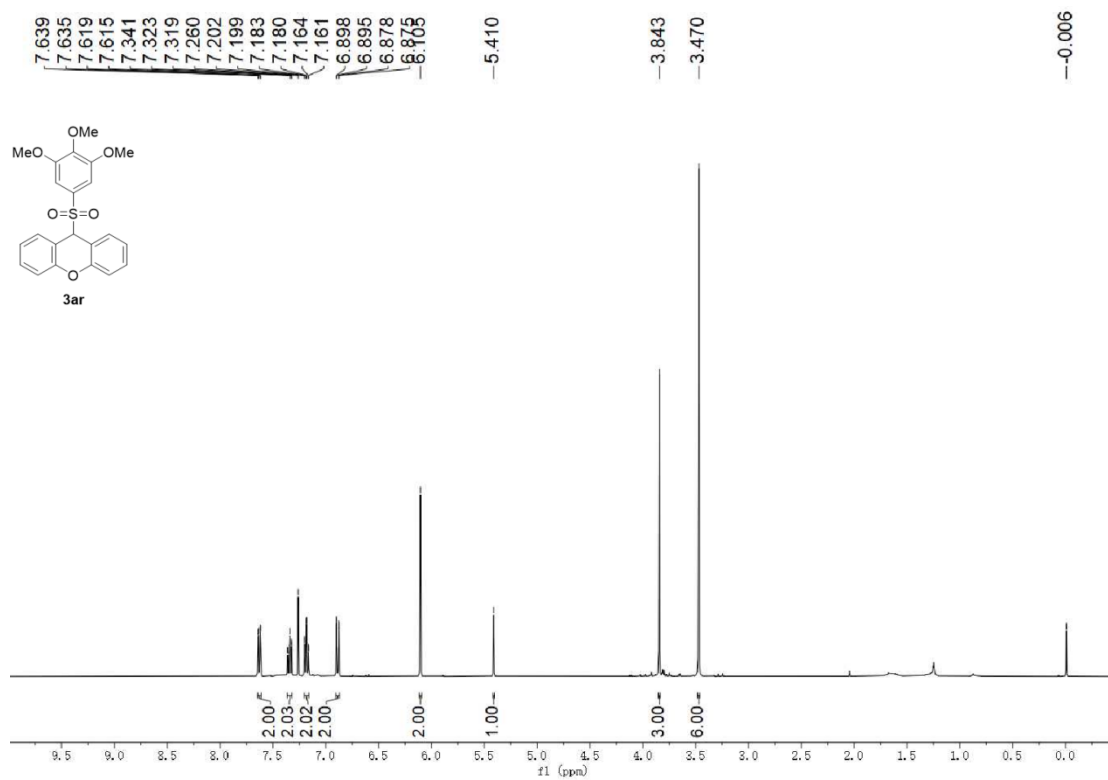
^1H -NMR (400 MHz) spectrum (CDCl_3) of **3aq**



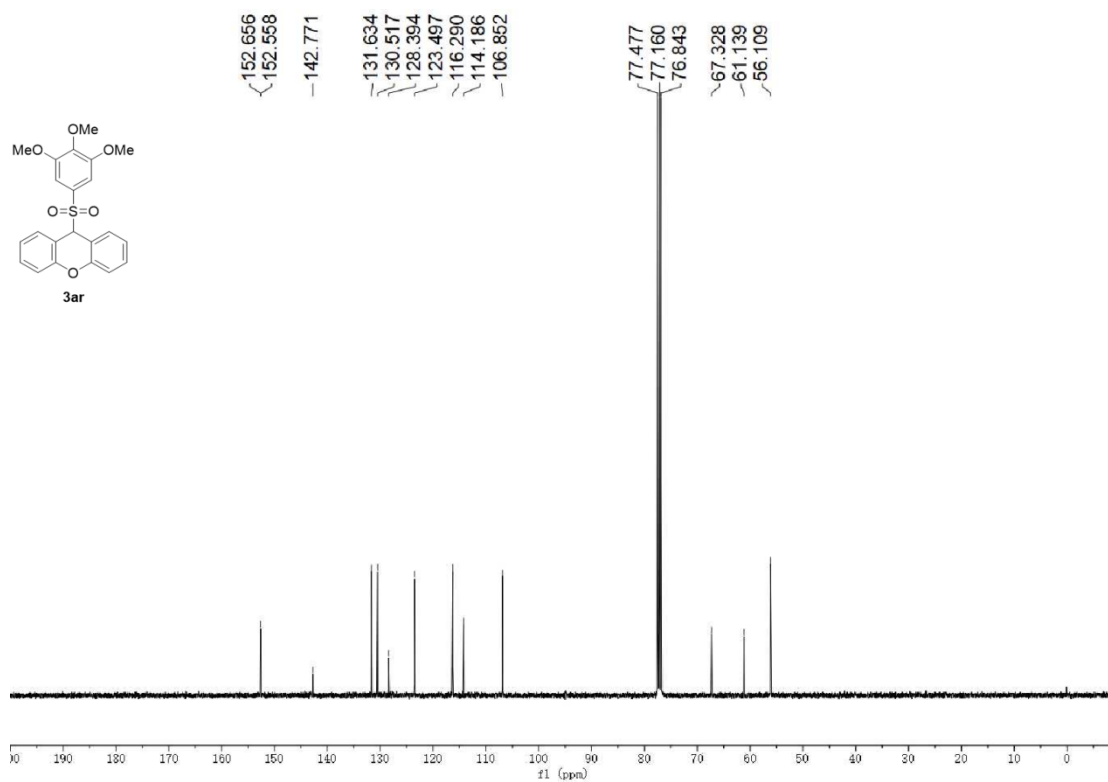
^{13}C -NMR (100 MHz) spectrum (CDCl_3) of **3aq**



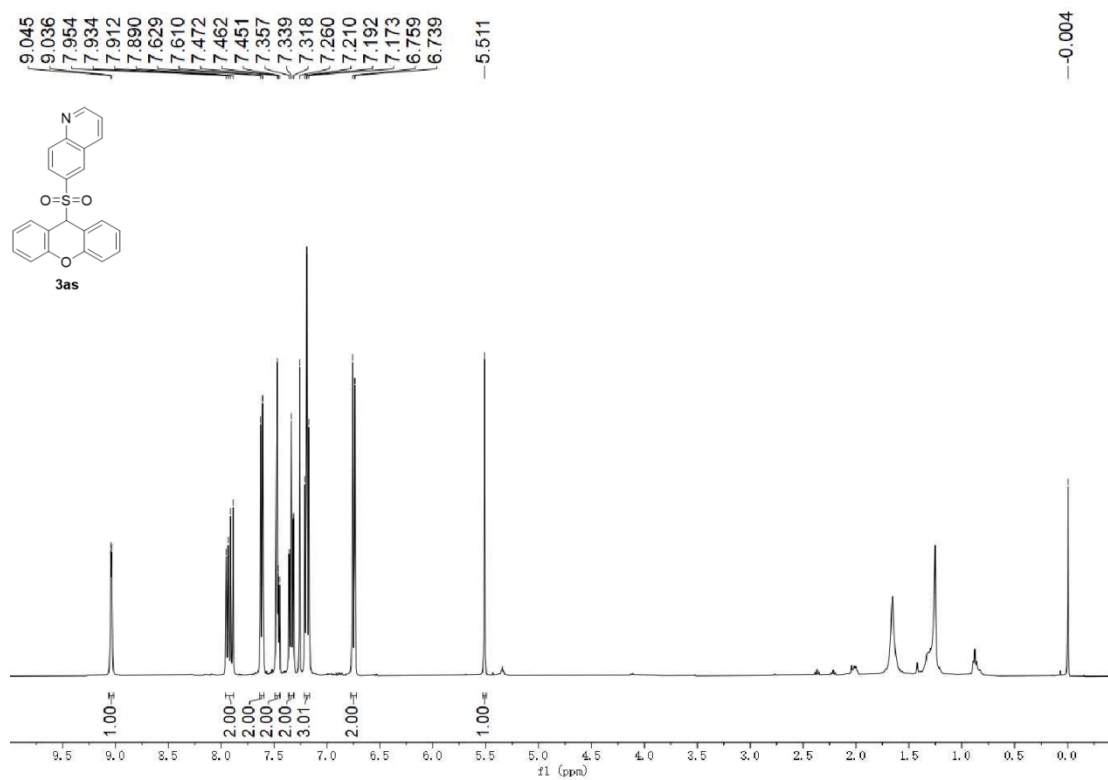
^1H -NMR (400 MHz) spectrum (CDCl_3) of **3ar**



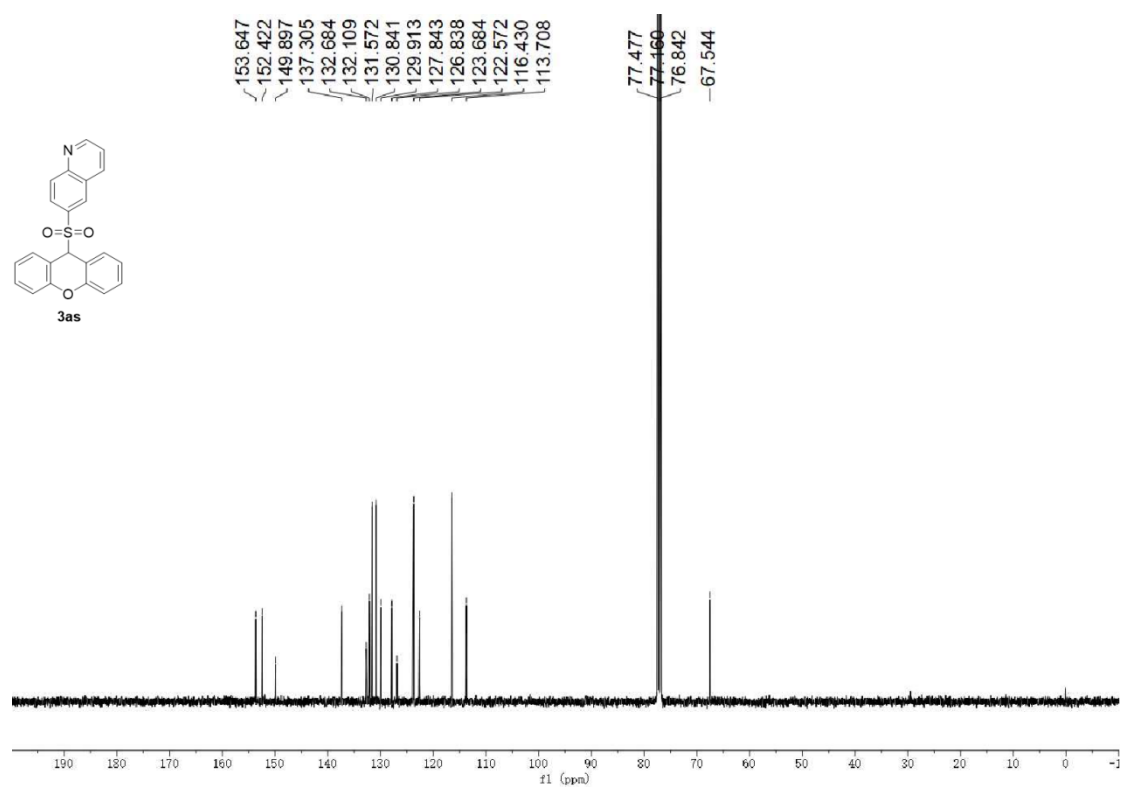
^{13}C -NMR (100 MHz) spectrum (CDCl_3) of **3ar**



^1H -NMR (400 MHz) spectrum (CDCl_3) of **3as**



^{13}C -NMR (100 MHz) spectrum (CDCl_3) of **3as**



^1H -NMR (400 MHz) spectrum (CDCl_3) of **4**

