Supporting Information

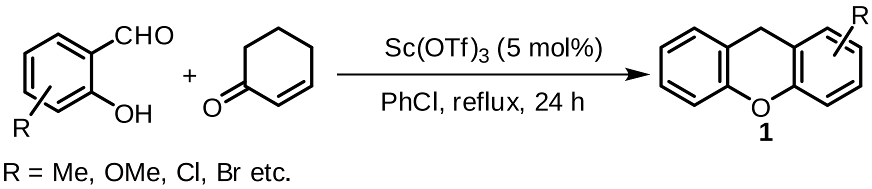
A Radical-Radical Cross-Coupling Reaction of Xanthene with Sulfonyl Hydrazides: Facile Access to Xanthen-9-sulfone Derivatives

General Information:

All reactions were carried out in oven-dried reaction vessels under a nitrogen atmosphere unless otherwise mentioned. TLC analysis was performed on silica gel TLC plates. Column chromatography was done using 230−400 mesh silica gel by applying pressure through an air pump. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on 400 spectrometers and are reported as chemical shifts (δ) in parts per million (ppm), and multiplicities are abbreviated as s = singlet, d = doublet, t = triplet, sep = septet, m = multiplet, comp = complex, app = apparent. Internal standards or residual solvent signals were used as references. HRMS (m/z) was recorded using ESI (Q-Tof and Orbitrap, positive ion) and EI (magnetic sector, positive ion) mode. Melting points were determined in a capillary melting point apparatus and are uncorrected. Single-crystal X-ray diffraction data were collected on Bruker APEX II diffractometer with a graphite monochromator using Mo Kα radiation. The CIF file was submitted to CCDC (2118371) and can be obtained at https://summary.ccdc.cam.ac.uk/structure-summary-form.

Preparation of starting materials:

Preparation of substituted xanthenes 1:[1]

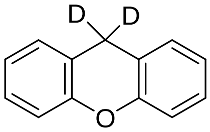


General procedure: Salicylaldehyde derivatives (1.1 mmol) and 2-cyclohexene-1-one (1.0 mmol) was quickly added to a suspension of scandium (III) triflate (0.05 mmol) in chlorobenzene (4.0 mL). The reaction mixture was refluxed for 24 hours and allowed to cool to room temperature. DCM (20.0 mL) and saturated 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 $MgSO_4$, 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 hexane and ethyl acetate.

Preparation of xanthene-*d*$_2$ (Xanthene-*d*$_2$ (**1a**-*d*$_2$) was prepared according to the literature proecudure):[2]

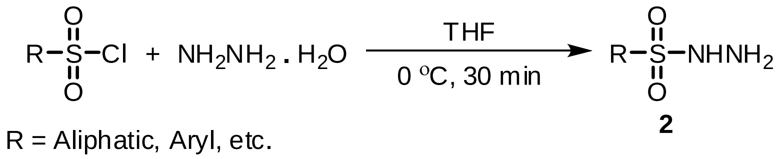
Taking xanthene (0.16 g, 0.87 mmol) in DMSO-*d*$_6$ (5.0 mL) along with NaH (0.10 g, 4.2 mmol) under an inert atmosphere. The reaction mixture was stirred for ~ 8 hours and then quenched with D_2O (5.0 mL). The crude product was filtered and washed thoroughly with distilled H_2O. ^{1}H NMR of the product confirmed the formation of xanthene-*d*$_2$ (99% D).

Xanthene-*d*$_2$ (**1a**-*d*$_2$):



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23-7.19 (comp, 2H), 7.18 (dd, *J* = 7.0 Hz, 0.9 Hz, 2H), 7.08 -7.05 (comp, 2H), 7.04-7.02 (comp, 2H).

Preparation of sulfonyl hydrazides 2:[3]



Hydrazine monohydrate (30.0 mmol) was added drop wise into the solution of corresponding sulfonyl chloride (10.0 mmol) in THF (50.0 mL) under nitrogen at 0 °C. Subsequently, the mixture was further stirred at 0 °C for 30 minutes. After the completion of the reaction, the solvent was removed by evaporation, and the residue was extracted with dichloromethane (3 x 20.0 mL), and the combined organic layer was washed with water, and brine, and dried over Na_2SO_4. Concentration in vacuum followed by silica gel column purification with petroleum ether/ethyl acetate eluent gave the desired product **2** in yields range from 70-95%.

Preparation of Disulfone diphenyl:[4] (Disulfone diphenyl was prepared according to the literature procedure)

To a solution of phenyl sulfonyl chloride (99.0 mg, 0.56 mmol) in freshly distilled CH_3CN (5.0 mL) was added sodium phenyl sulfinate (119.8 mg, 0.73 mmol) in minimum amount of methanol. The reaction was stirred at room temperature, and monitored by TLC. After completion, the solvent was evaporated. The residue was washed with chloroform several times, and the combined mother liquid was evaporated to give a solid. Wash the obtained solid several times with minimum amounts of methanol and then left to dry to give a white solid.

Figure S1. Selected examples of important bioactive xanthene derivatives and sulfones.

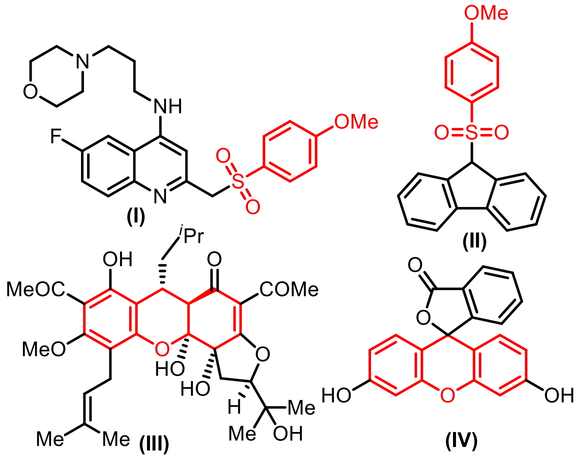
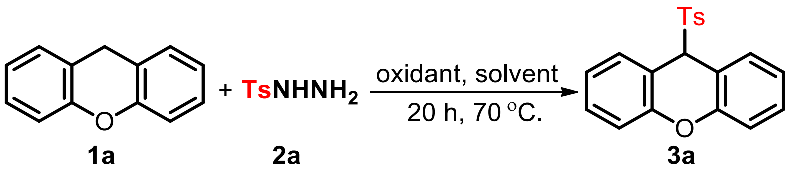


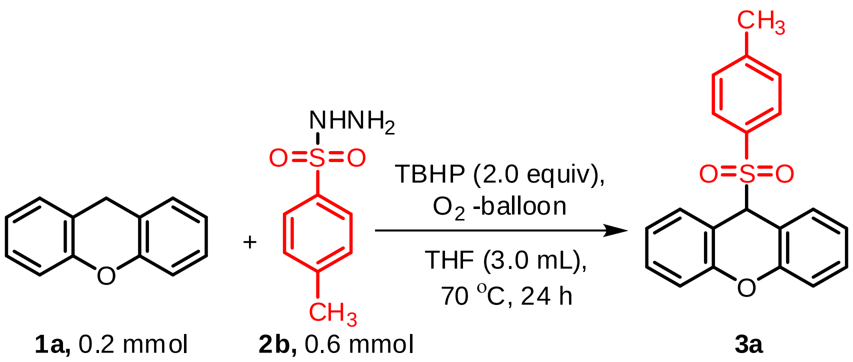
Table S1. Additional Optimizations of Reaction Condition[a]



entry	oxidant	solvent	yield[b]
1	TBHP / Open air	CH_3CN	77
2	TBHP / Open air	DMSO	70
3	TBHP / Open air	H_2O	30
4	TBHP / Open air	MeOH	80
5	TBHP / Open air	EtOH	75
6	TBHP / Open air	DMF	41
7	TBHP / Open air	DCE	66
8	TBHP / Open air	1,4-dioxane	42
9	TBHP / Open air	Toluene	46
10	DTBP/ Open air	THF	42
11 [c,e,f]	TBHP / Open air	THF	88
12 [d]	TBHP (3) / Open air	THF	75
13 [e,f,g]	TBHP / O_2-balloon	THF	90

[a]**Reaction condition: 1a** (0.2 mmol), **2a** (0.6 mmol), oxidant (1.5 equiv), solvent (2.0 mL), at 70 °C for 20 h. TBHP = tert-butyl hydroperoxide (5.0-6.0 M solution in decane), DTBP = di-tert-butyl peroxide; [b]Isolated yield; [c]TBHP (2.0 equiv) was used; [d]TBHP (3.0 equiv) was used; [e]THF (3.0 mL) was used; [f]Reaction time = 24 h; 2.0 equiv of TBHP (70% aqueous) was used.

General Procedure for Sulfonylation of xanthene:



Reaction procedure: A 10 mL oven-dried two-neck round-bottom flask was charged with xanthene **1a** (36.44 mg, 0.2 mmol) *p*-toluenesulfonyl hydrazide **2a** (111.738 mg, 0.6 mmol), and THF (3.0 mL). TBHP (0.4 mmol, 2.0 equiv, 5.0-6.0 M solution in decane) were added by microsyringe. The resulting mixture was stirred and heated to 70 °C temperature for 24 h with O_2-balloon until the reaction was complete as indicated by TLC. After cooled down to room temperature, concentrated in vacuum and the crude product was directly purified by column chromatography using ethyl acetate / petroleum ether (10%) to afford product **3a** (65.94 mg; **yield** = 98%; **R_f** = 0.16).

Gram scale synthetic reaction following the general procedure as above

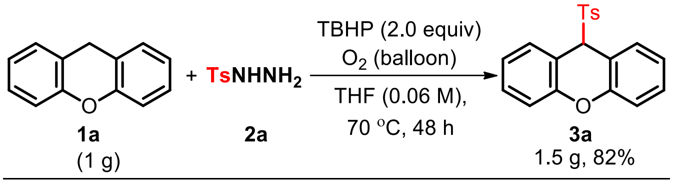
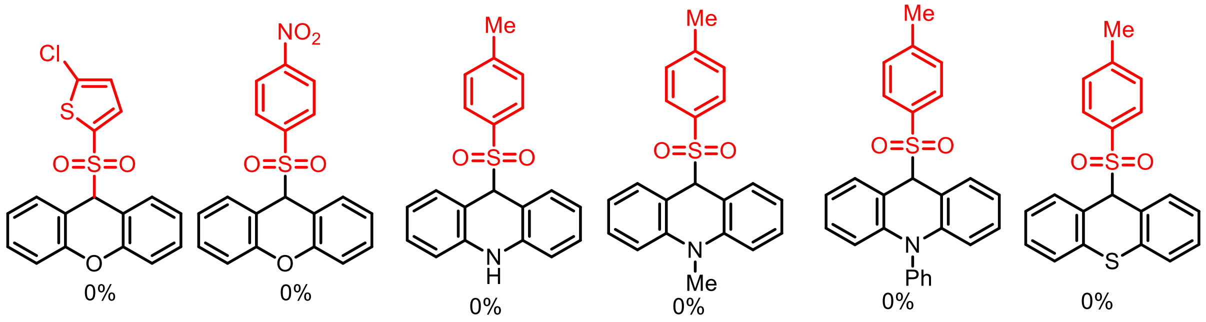
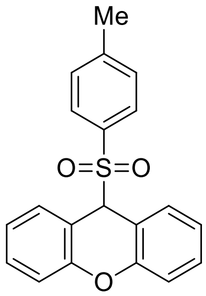


Table S2. Unsuccessful Substrates:



Characterization of xanthene-9-sulfonylation products:

9-tosyl-9*H*-xanthene (3a):



Yield 98% (65.94 mg); colorless solid; **R_f** 0.16 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/ethyl acetate = 9:1; **mp** 184-186 °C (crystallization from $CHCl_3$ and hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.6 Hz, 1.2 Hz, 2H), 7.31-7.36 (comp, 2H), 7.15 (app td, *J* = 7.6 Hz, 0.8 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.85-6.90 (comp, 4H), 5.40 (s, 1H), 2.36 (s, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 152.5 (x 2), 145.0, 132.0, 131.5 (x 2), 130.6 (x 2), 129.7 (x 2), 129.0 (x 2), 123.4 (x 2), 116.4 (x 2), 114.0 (x 2), 67.1, 21.8; **HRMS (ESI-TOF) m/z:** $[M + Na]^+$ Calcd for $C_{20}H_{16}O_3SNa$ 359.0718, found 359.0724.

Figure S2. X-ray crystal structure of **3a** (ellipsoid contour at 50% probability level) (**CCDC -2118371)**

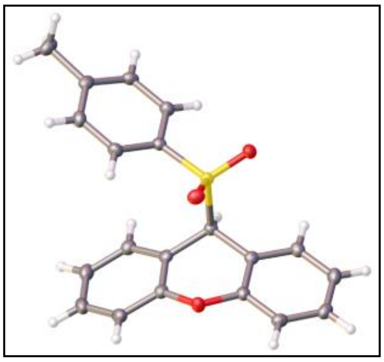
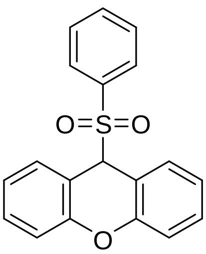


Table S3: Crystal data and structure refinement for 3a

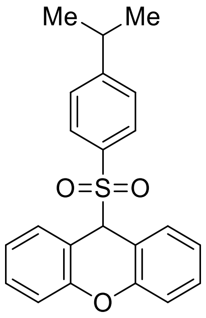
Empirical formula	$C_{20}H_{16}O_3S$
Formula weight	336.39
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.7563(10)
b/Å	5.3376(7)
c/Å	33.444(6)
α/°	90
β/°	94.906(4)
γ/°	90
Volume/Å^3	1557.3(4)
Z	4
ρ_{calc}g/cm^3	1.435
μ/mm^{-1}	1.975
F(000)	704.0
Crystal size/mm^3	0.5 × 0.25 × 0.2
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	5.304 to 133.06
Index ranges	$-10 \leq h \leq 10$, $-5 \leq k \leq 6$, $-39 \leq l \leq 39$
Reflections collected	21860
Independent reflections	2690 [Rint = 0.0447, Rsigma = 0.0285]
Data/restraints/parameters	2690/0/218
Goodness-of-fit on F^2	1.141
Final R indexes [I>=2σ (I)]	$R_1 = 0.0400$, $wR_2 = 0.1164$
Final R indexes [all data]	$R_1 = 0.0402$, $wR_2 = 0.1166$
Largest diff. peak/hole / e Å^{-3}	0.31/-0.40

9-(phenylsulfonyl)-9*H*-xanthene (3b)



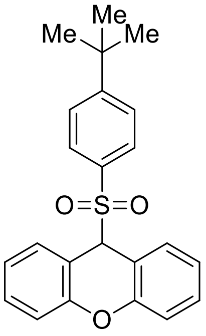
Yield 32% (31.0 mg); colorless solid; **R_f** 0.22 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/ethyl acetate = 9:1; **mp** 162-164 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.7 Hz, 1.4 Hz, 2H), 7.54-7.50 (m, 1H), 7.36-7.32 (comp, 2H), 7.24-7.20 (comp, 2H), 7.16 (td, *J* = 7.6 Hz, 1.1 Hz, 2H), 6.99 (dd, *J* = 8.4 Hz, 1.1 Hz, 2H), 6.91-6.85 (dd, *J* = 8.4 Hz, 0.8 Hz, 2H), 5.42 (s, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 152.3 (x 2), 134.7, 133.9 (x 2), 131.4 (x 2), 130.5 (x 2), 129.6 (x 2), 128.2 (x 2), 123.4 (x 2), 116.3 (x 2), 113.7, 67.1; **HRMS (ESI-TOF) m/z:** $[M + K]^+$ Calcd for $C_{19}H_{14}KO_3S$ 361.0301, found 361.0308.

9-((4-isopropylphenyl)sulfonyl)-9*H*-xanthene (3c):



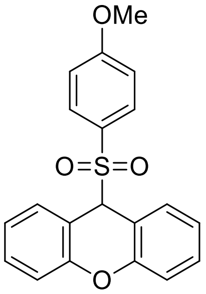
Yield 80% (58.5 mg); colorless solid; **R$_f$** 0.18 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/ethyl acetate = 9:1; **mp** 141-143 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51-7.53 (comp, 2H), 7.31-7.35 (comp, 2H), 7.12-7.16 (comp, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 5.39 (s, 1H), 2.90 (sep, *J* = 6.8 Hz, 1H), 1.22 (s, 3H), 1.21 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 155.7, 152.4 (x 2), 131.9, 131.3 (x 2), 130.4 (x 2), 129.6 (x 2), 126.3 (x 2), 123.2 (x 2), 116.2 (x 2), 113.9 (x 2), 67.1, 34.2, 23.6 (x 2); **HRMS (ESI-TOF) m/z:** [M + Na]$^+$ Calcd for $C_{22}H_{20}O_3SNa$ 387.1031, found 387.1040.

9-((4-(tert-butyl)phenyl)sulfonyl)-9*H*-xanthene (3d):



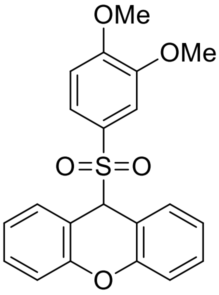
Yield 97% (73.4 mg); colorless solid; **R$_f$** 0.21 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/ethyl acetate = 9:1; **mp** 140-142 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.6 Hz, 2H), 7.31-7.35 (comp, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.11-7.15 (comp, 2H), 6.92 (dd, *J* = 6.8 Hz, 1.6 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 5.38 (s, 1H), 1.28 (s, 9H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 158.1, 152.5 (x 2), 131.7, 131.5 (x 2), 130.5 (x 2), 129.5 (x 2), 125.3 (x 2), 123.4 (x 2), 116.4 (x 2), 114.0 (x 2), 67.3, 35.3, 31.2 (x 3); **HRMS (ESI-TOF) m/z:** [M + Na]$^+$ Calcd for $C_{23}H_{22}O_3SNa$ 401.1187, found 401.1207.

9-((4-methoxyphenyl)sulfonyl)-9*H*-xanthene (3e):



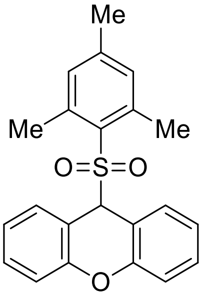
Yield 93% (65.5 mg); colourless solid; **R$_f$** 0.05 (pet ether/ethyl acetate = 8.5:1.5); **eluent composition** pet ether/ethyl acetate = 8.5:1.5; **mp** 150-152 °C ; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.31-7.36 (comp, 2H), 7.16 (app td, *J* = 7.6 Hz, 1.0 Hz, 2H), 6.89 (d, *J* = 5.2 Hz, 2H), 6.87 (dd, *J* = 5.9 Hz, 3.8 Hz, 2H), 6.66 (d, *J* = 8.8 Hz, 2H), 5.39 (s, 1H), 3.80 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ s164.0, 152.3 (x 2), 131.6 (x 2), 131.4 (x 2), 130.4 (x 2), 126.2, 123.3 (x 2), 116.2 (x 2), 114.0 (x 2), 113.4 (x 2), 67.0, 55.5; **HRMS (ESI-TOF) m/z:** [M + Na]$^+$ Calcd for $C_{20}H_{16}O_4SNa$ 375.0667, found 375.0667.

9-((3,4-dimethoxyphenyl)sulfonyl)-9*H*-xanthene (3f):



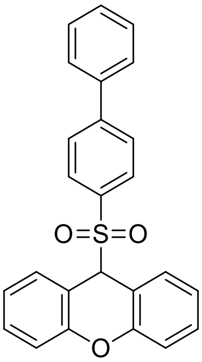
Yield 88% (67.3 mg); colorless solid; **R$_f$** 0.03 (pet ether/ethyl acetate = 8.5:1.5); **eluent composition** pet ether/ethyl acetate = 8.5:1.5; **mp** 176-178 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.60 (dd, *J* = 7.7 Hz, 1.5 Hz, 2H), 7.31-7.35 (comp, 2H), 7.17 (app td, *J* = 7.5 Hz, 1.1 Hz, 2H), 6.88 (dd, *J* = 8.2 Hz, 0.9 Hz, 2H), 6.64 (d, *J* = 8.4 Hz, 1H), 6.60 (dd, *J* = 8.5 Hz, 1.9 Hz, 1H), 6.30 (d, *J* = 2.0 Hz, 1H), 5.40 (s, 1H), 3.87 (s, 3H), 3.49 (s, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 153.5, 152.3 (x 2), 148.2, 131.5 (x 2), 130.3 (x 2), 125.9, 123.7 (x 2), 123.3 (x 2), 116.2 (x 2), 114.1, 111.5, 109.7, 67.0, 56.1, 55.7; **HRMS (ESI-TOF) m/z:** $[M + Na]^+$ Calcd for $C_{21}H_{18}O_5SNa$ 405.0773, found 405.0777.

9-(mesitylsulfonyl)-9*H*-xanthene (3g):



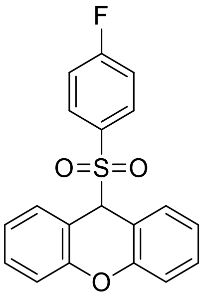
Yield 53% (38.5 mg); colorless solid; **R$_f$** 0.18 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/ethyl acetate = 9:1; **mp** 112-114 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.35-7.39 (comp, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 6.99-7.04 (comp, 4H), 6.86 (s, 2H), 5.34 (s, 1H), 2.31 (s, 3H), 2.21 (s, 6H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 153.4 (x 2), 143.7, 141.9 (x 2), 131.9 (x 2), 130.9 (x 2), 130.4 (x 2), 129.8, 123.1 (x 2), 116.8 (x 2), 113.5 (x 2), 66.8, 22.6 (x 2), 21.1; **HRMS (ESI-TOF) m/z:** $[M + Na]^+$ Calcd for $C_{22}H_{20}O_3SNa$ 387.1031, found 387.1044.

9-([1,1'-biphenyl]-4-ylsulfonyl)-9*H*-xanthene (3h):



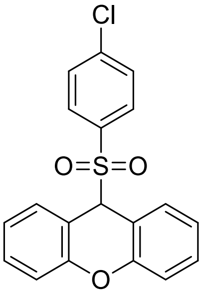
Yield 46% (36.8 mg); colorless solid; **R$_f$** 0.16 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/ethyl acetate = 9:1; **mp** 186-188 °C ; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.59 (dd, *J* = 7.6 Hz, 1.2 Hz, 2H), 7.55-7.57 (comp, 2H), 7.47-7.49 (m, 1H), 7.45-7.46 (comp, 2H), 7.41-7.43 (comp, 2H), 7.33-7.37 (comp, 2H), 7.18 (app td, *J* = 7.5 Hz, 0.9 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 5.45 (s, 1H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): 152.4 (x 2), 146.6, 139.1, 133.3, 131.4 (x 2), 130.5 (x 2), 130.0 (x 2), 129.0 (x 2), 128.6, 127.4 (x 2), 126.7 (x 2), 123.4 (x 2), 116.3 (x 2), 113.7 (x 2), 67.2; **HRMS (ESI-TOF) m/z:** $[M + Na]^+$ Calcd for $C_{25}H_{18}O_3SNa$ 421.0874, found 421.0872.

9-((4-fluorophenyl)sulfonyl)-9*H*-xanthene (3i):



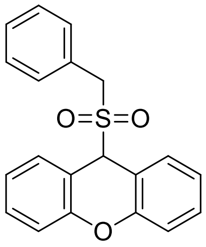
Yield 80% (54.4 mg); colorless solid; **R_f** 0.75 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/ethyl acetate = 9:1; **mp** 188-190 °C; **^{1}H NMR** (400 MHz, $\mathrm{CDCl_3}$): δ 7.59 (dd, *J* = 7.7 Hz, 1.5 Hz, 2H), 7.33-7.38 (comp, 2H), 7.18 (app td, *J* = 7.6 Hz, 1.1 Hz, 2H), 6.92-6.96 (comp, 2H), 6.88-6.90 (comp, 3H), 6.86 (d, *J* = 2.1 Hz, 1H), 5.42 (s, 1H); **^{13}C{^{1}H} NMR** ($\mathrm{CDCl_3}$, 100 MHz): δ 166.1 (d, $^1J_{\text{F-C}}$ = 256.7 Hz), 152.3 (x 2), 132.3 (d, $^3J_{\text{F-C}}$ = 9.7 Hz) (x 2), 131.4 (x 2), 130.7 (x 2), 130.6 (d, $^4J_{\text{F-C}}$ = 2.8 Hz), 123.5 (x 2), 116.3 (x 2), 115.5 (d, $^2J_{\text{F-C}}$ = 22.7 Hz) (x 2), 113.6 (x 2), 67.1; **^{19}F NMR** (376 MHz, $\mathrm{CDCl_3}$) δ -102.87; **HRMS (ESI-TOF) m/z:** $[\mathrm{M + Na}]^+$ Calcd for $\mathrm{C_{19}H_{13}FO_3SNa}$ 363.0467, found 363.0468.

9-((4-chlorophenyl)sulfonyl)-9*H*-xanthene (3j):



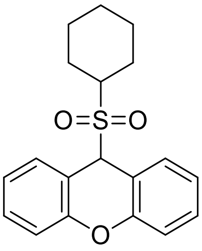
Yield 86% (60.5 mg); colorless solid; **R_f** 0.19 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/ethyl acetate = 9:1; **mp** 173-175 °C; **^{1}H NMR** (400 MHz, $\mathrm{CDCl_3}$): δ 7.58 (dd, *J* = 7.8 Hz, 1.0 Hz, 2H), 7.34-7.38 (comp, 2H), 7.16-7.20 (comp, 4H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.43 (s, 1H); **^{13}C{^{1}H} NMR** ($\mathrm{CDCl_3}$, 100 MHz): δ 152.3 (x 2), 140.8, 133.2, 131.4 (x 2), 130.9 (x 2), 130.7 (x 2), 128.5 (x 2), 123.5 (x 2), 116.4 (x 2), 113.5 (x 2), 67.2; **HRMS (ESI-TOF) m/z:** $[\mathrm{M + Na}]^+$ Calcd for $\mathrm{C_{19}H_{13}ClO_3SNa}$ 379.0172, found 379.0168.

9-(benzylsulfonyl)-9*H*-xanthene (3k):



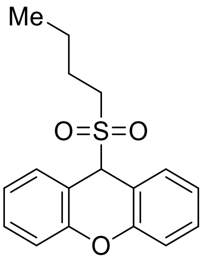
Yield 38% (25.5 mg); colorless solid; **R_f** 0.09 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/ethyl acetate = 9:1; **mp** 158-160 °C; **^{1}H NMR** (400 MHz, $\mathrm{CDCl_3}$): δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.47-7.43 (comp, 2H), 7.27-7.26 (comp, 2H), 7.24-7.21 (comp, 5H), 7.10 (d, *J* = 6.4 Hz, 2H), 5.42 (s, 1H), 3.73 (s, 2H); **^{13}C{^{1}H} NMR** ($\mathrm{CDCl_3}$, 100 MHz): δ 152.2 (x 2), 131.6 (x 2), 131.1 (x 2), 130.9 (x 2), 128.7, 128.5 (x 2), 125.6, 124.0 (x 2), 117.0 (x 2), 114.0 (x 2), 65.6, 53.1; **HRMS (ESI-TOF) m/z:** $[\mathrm{M + Na}]^+$ Calcd for $\mathrm{C_{20}H_{16}O_3SNa}$ 359.0718, found 359.0724.

9-(cyclohexylsulfonyl)-9*H*-xanthene (3l):



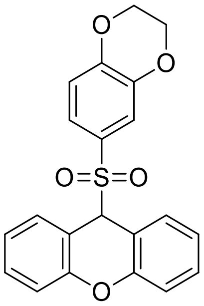
Yield 82% (53.9 mg); colorless solid; **R_f** 0.16 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/ethyl acetate = 9:1; **mp** 108-110 °C ; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 7.4 Hz, 0.6 Hz, 2H), 7.39-7.43 (comp, 2H), 7.19-7.21 (comp, 3H), 7.17 (d, *J* = 1.2 Hz, 1H), 5.38 (s, 1H), 2.73 (tt, *J* = 12.0 Hz, 3.6 Hz, 1H), 1.69-1.77 (comp, 4H), 1.58-1.59 (m, 1H), 1.32-1.43 (comp, 2H), 1.08-1.13 (comp, 3H); **$^{13}C\{^1H\}$ NMR** ($CDCl_3$, 100 MHz): δ 152.6 (x 2), 131.0 (x 2), 130.6 (x 2), 123.7 (x 2), 116.9 (x 2), 114.1 (x 2), 64.3, 57.7, 25.7 (x 2), 25.2 (x 2), 25.0; **HRMS (ESI-TOF) m/z:** $[M + Na]^+$ Calcd for $C_{19}H_{20}O_3SNa$ 351.1031, found 351.1024.

9-(butylsulfonyl)-9*H*-xanthene (3m):



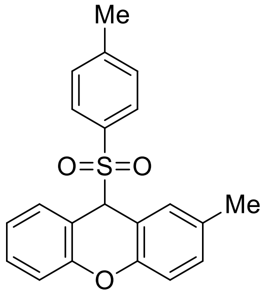
Yield 67% (40.5 mg); colorless solid; **R_f** 0.16 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/ethyl acetate = 9:1; **mp** 112-114 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 7.6 Hz, 2H), 7.43 (app td, *J* = 7.8 Hz, 1.2 Hz, 2H), 7.23 (app s, 1H), 7.19-7.21 (comp, 3H), 5.28 (s, 1H), 2.50 (t, *J* = 8 Hz, 2H), 1.46-154 (comp, 2H), 1.24-1.27 (comp, 2H), 0.77 (t, *J* = 7.2 Hz, 3H); **$^{13}C\{^1H\}$ NMR** ($CDCl_3$, 100 MHz): δ 152.2 (x 2), 131.4 (x 2), 130.7 (x 2), 124.0 (x 2), 116.9 (x 2), 114.1 (x 2), 65.5, 47.0, 22.6, 21.7, 13.4; **HRMS (ESI-TOF) m/z:** $[M + Na]^+$ Calcd for $C_{17}H_{18}O_3SNa$ 325.0874, found 325.0876.

9-((2,3-dihydrobenzo[β][1,4]dioxin-6-yl)sulfonyl)-9*H*-xanthene (3n):



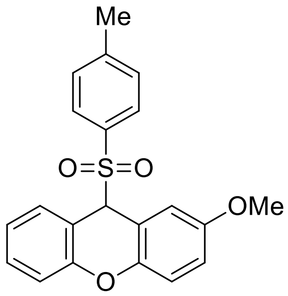
Yield 70% (53.2 mg); colorless solid; **R_f** 0.20 (pet ether/ethyl acetate = 7.5:2.5); **eluent composition** pet ether / ethyl acetate = 4:1; **mp** 166-168 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.53 (dd, *J* = 7.6 Hz, 1.2 Hz, 2H), 7.37-7.32 (comp, 2H), 7.17-7.13 (comp, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.66 (d, *J* = 8.4 Hz, 1H), 6.46-6.51 (app td, *J* = 10.2 Hz, 2.1 Hz, 2H), 5.37 (s, 1H), 4.26 (dd, *J* = 5.0 Hz, 2.9 Hz, 2H), 4.19-4.17 (comp, 2H); **$^{13}C\{^1H\}$ NMR** ($CDCl_3$, 100 MHz): δ 152.4, 148.5, 143.0, 131.3 (x 2), 130.4 (x 2), 126.9, 123.4, 123.3 (x 2), 119.2 (x 2), 116.9 (x 2), 116.2 (x 2), 113.9, 67.1, 64.6, 63.9; **HRMS (ESI-TOF) m/z:** $[M + Na]^+$ Calcd for $C_{21}H_{16}O_5SNa$ 403.0616, found 403.0616.

2-methyl-9-tosyl-9*H*-xanthene (4a):



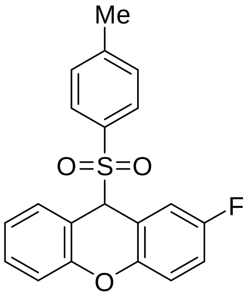
Yield 98% (68.7 mg); colorless solid; **R$_f$** 0.16 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/ ethyl acetate = 9:1; **mp** 170-172 ^{o}C; **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.53 (d, *J* = 7.6 Hz, 1H), 7.30-7.34 (comp, 2H), 7.12-7.15 (comp, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.86 (app s, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 5.34 (s, 1H), 2.36 (s, 6H); **^{13}C{^{1}H} NMR** (CDCl$_3$, 100 MHz): δ 152.7, 150.5, 144.9, 132.9, 132.1, 131.6, 131.5, 131.3, 129.7 (x 2), 129.0 (x 2), 123.2, 116.4, 116.1, 114.0, 113.6, 67.3, 29.8, 21.8, 20.8; **HRMS (ESI-TOF) m/z:** [M + Na]$^+$ Calcd for $C_{21}H_{18}O_3SNa$ 373.0874, found 373.1093.

2-methoxy-9-tosyl-9*H*-xanthene (4b):



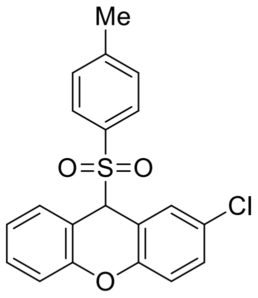
Yield 94% (68.9 mg); colorless solid; **R$_f$** 0.09 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/ethyl acetate = 9:1; **mp** 162-164 ^{o}C ; **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.54 (dd, *J* = 7.7 Hz, 1.3 Hz, 1H), 7.30-7.34 (m, 1H), 7.11-7.15 (m, 1H), 7.02 (d, *J* = 2.8 Hz, 2H), 7.01 (app s, 1H), 6.89-6.92 (comp, 3H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 9.2 Hz, 1H), 5.36 (s, 1H), 3.82 (s, 3H), 2.36 (s, 3H); **^{13}C{^{1}H} NMR** (CDCl$_3$, 100 MHz): δ 155.2, 152.6, 146.5, 144.8, 131.9, 131.3, 130.3, 129.5 (x 2), 128.9 (x 2), 123.0, 117.6, 117.1, 116.2, 114.3, 114.2, 113.3, 67.4, 55.8, 21.7; **HRMS (ESI-TOF) m/z:** [M + Na]$^+$ Calcd for $C_{21}H_{18}O_4SNa$ 389.0823, found 389.0825.

2-fluoro-9-tosyl-9*H*-xanthene (4c):



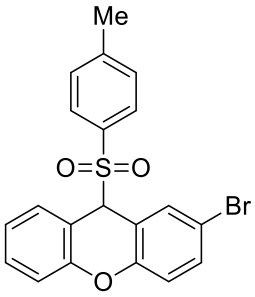
Yield 65% (46.1 mg); colorless solid; **R$_f$** 0.22 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/ethyl acetate = 9:1; **mp** 208-210 ^{o}C; **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.53 (dd, *J* = 7.7 Hz, 1.4 Hz, 1H), 7.37-7.33 (m, 1H), 7.29-7.26 (m, 1H), 7.16 (td, *J* = 7.6 Hz, 1.1 Hz, 1H), 7.07 (dd, *J* = 7.0 Hz, 2.0 Hz, 1H), 7.05-7.03 (comp, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.88-6.85 (comp, 2H), 5.35 (s, 1H), 2.37 (s, 3H); **^{13}C{^{1}H} NMR** (CDCl$_3$, 100 MHz): δ 158.1 (d, ^{1}J = 242.3 Hz), 152.3, 148.6, 145.1, 131.7, 131.3, 130.6, 129.5 (x 2), 129.0, 123.5, 117.7, 117.5, 117.4 (d, ^{4}J = 2.3 Hz), 117.27 (d, ^{2}J = 24.3 Hz), 116.2, 115.06 (d, ^{3}J = 8.6 Hz), 113.0, 66.9, 21.7; **^{19}F NMR** (376 MHz, CDCl$_3$) δ -119.21; **HRMS (ESI-TOF) m/z:** [M + Na]$^+$ Calcd for $C_{20}H_{15}FNaO_3S$ 377.0624, found 377.0640.

2-chloro-9-tosyl-9*H*-xanthene (4d):



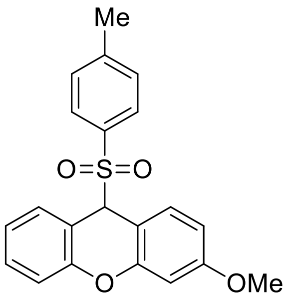
Yield 89% (66.0 mg); colorless solid; **R_f** 0.21 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/ethyl acetate = 9:1; **mp** 177-179 ^{o}C ; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.52 (app d, *J* = 7.6 Hz, 1H), 7.46 (app d, *J* = 2.4 Hz, 1H) , 7.33-7.37 (m, 1H), 7.29 (dd, *J* = 8.8 Hz, 2.4 Hz, 1H), 7.15-7.19 (m, 1H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 1H), 5.32 (s, 1H), 2.37 (s, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 152.1, 150.9, 145.2, 131.6, 131.3, 130.8, 130.6, 130.5, 129.6 (x 2), 129.0 (x 2), 128.1, 123.6, 117.6, 116.31, 115.4, 113.2, 66.6, 21.7; **HRMS (ESI-TOF) m/z:** [M + Na]$^+$ Calcd for $C_{20}H_{15}ClO_3SNa$ 393.0328, found 393.0327.

2-bromo-9-tosyl-9*H*-xanthene (4e):



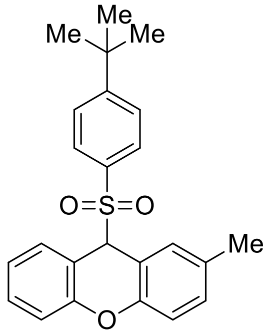
Yield 90% (75.5 mg); colorless solid; **R_f** 0.18 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/EtOAc = 9:1; **mp** 164-166 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56 (app d, *J* = 2.4 Hz, 1H), 7.52 (dd, *J* = 7.8 Hz, 1.4 Hz, 1H), 7.42 (dd, *J* = 8.8 Hz, 2.4 Hz, 1H), 7.33-7.37 (m, 1H), 7.17 (app td, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.91 (dd, *J* = 8.4 Hz, 0.8 Hz, 1H), 6.80 (d, *J* = 8.8 Hz, 1H), 5.31 (s, 1H), 2.38 (s, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 152.0, 151.4, 145.2, 133.6, 133.3, 131.6, 131.3, 130.6, 129.6 (x 2), 129.0 (x 2), 123.7, 118.0, 116.3, 115.9, 115.3, 113.2, 66.5, 21.7; **HRMS (ESI-TOF) m/z:** [M + Na]$^+$ Calcd for $C_{20}H_{15}BrO_3SNa$ 436.9823, found 436.9827.

3-methoxy-9-tosyl-9*H*-xanthene (4f):



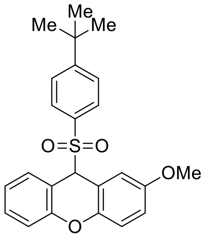
Yield 52% (38.1 mg); colorless solid; **R_f** 0.06 (pet ether/ethyl acetate = 8.5:1.5); **eluent composition** pet ether/ethyl acetate = 9:1; **mp** 148-150 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.54 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H); 7.44 (d, *J* = 8.8 Hz, 1H), 7.32 (app td, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.14 (app td, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.86 (dd, *J* = 8.4 Hz, 0.8 Hz, 1H), 6.73 (dd, *J* = 8.8 Hz, 2.4 Hz, 1H), 6.43 (d, *J* = 2.4 Hz, 1H), 5.34 (s, 1H), 3.81 (s, 3H), 2.36 (s, 3H); **^{13}C{^{1}H} NMR** (CDCl$_3$, 100 MHz): δ 161.4, 153.3, 152.3, 144.7, 132.1, 132.0, 131.4, 130.3, 129.5 (x 2), 128.9 (x 2), 123.2, 116.2, 114.0, 110.3, 105.9, 101.0, 66.6, 55.5, 21.7; **HRMS (ESI-TOF) m/z:** [M + Na]$^+$ Calcd for $C_{21}H_{18}O_4SNa$ 389.0823, found 389.0824.

9-((4-(tert-butyl)phenyl)sulfonyl)-2-methyl-9*H*-xanthene (4g):



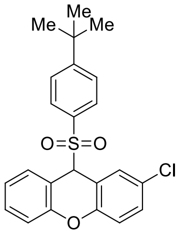
Yield 92% (72.2 mg); colorless solid; **R$_f$** 0.22 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/ethyl acetate = 9:1; **mp** 126-128 ^{o}C; **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.49 (dd, *J* = 7.7 Hz, 1.2 Hz, 1H); 7.30-7.34 (m, 1H), 7.25-7.26 (m, 1H), 7.22-7.23 (m, 1H), 7.18 (d, *J* = 2.0 Hz, 1H), 7.09-7.13 (comp, 2H), 6.97-7.0 (comp, 2H), 6.87 (dd, *J* = 8.2 Hz, 1.0 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 5.32 (s, 1H), 2.33 (s, 3H), 1.29 (s, 9H); **^{13}C{^{1}H} NMR** (CDCl$_3$, 100 MHz): δ 157.9, 152.7, 150.4, 132.6, 131.7, 131.3 (x 2), 131.1, 130.3, 129.4 (x 2), 125.1 (x 2), 123.0, 116.2, 116.0, 113.7, 113.5, 67.3, 35.2, 31.0 (x 3), 20.7; **HRMS (ESI-TOF) m/z:** [M + H] Calcd for $C_{24}H_{25}O_3S$ 393.1524, found 393.1518.

9-((4-(tert-butyl)phenyl)sulfonyl)-2-methoxy-9*H*-xanthene (4h):



Yield 89% (72.7 mg); colorless solid; **R$_f$** 0.12 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/ethyl acetate = 9:1; **mp** 132-134 ^{o}C; **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.50 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.30-7.35 (m, 1H), 7.26 (dd, *J* = 4.1 Hz, 1.7 Hz, 1H), 7.23 (d, *J* = 2.0 Hz, 1H), 7.10-7.14 (m, 1H), 7.00 (dd, *J* = 7.0 Hz, 1.2 Hz, 2H), 6.93 (d, *J* = 2.8 Hz, 1H), 6.85-6.91 (comp, 2H), 6.82 (d, *J* = 8.8 Hz, 1H), 5.35 (s, 1H), 3.79 (s, 3H), 1.29 (s, 9H); **^{13}C{^{1}H} NMR** (CDCl$_3$, 100 MHz): δ 158.0, 155.2, 152.7, 146.6, 131.7, 131.3, 130.3, 129.4 (x 2), 125.2 (x 2), 123.0, 117.6, 117.1, 116.2, 114.2 (x 2), 113.2, 67.5, 55.8, 35.2, 31.0 (x 3); **HRMS (ESI-TOF) m/z:** [M + Na]$^+$ Calcd for $C_{24}H_{24}O_4SNa$ 431.1293, found 431.1286.

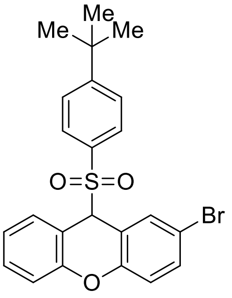
9-((4-(tert-butyl)phenyl)sulfonyl)-2-chloro-9*H*-xanthene (4i):



Yield 90% (74.3 mg); colorless solid; **R$_f$** 0.16 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/ethyl acetate = 9:1; **mp** 178-180 ^{o}C; **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.49 (dd, *J* = 7.7 Hz, 1.3 Hz, 1H), 7.33-7.38 (m, 1H), 7.29-7.30 (comp, 2H), 7.26-7.28 (comp, 2H), 7.13-7.17 (m, 1H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 5.30 (s, 1H),1.30

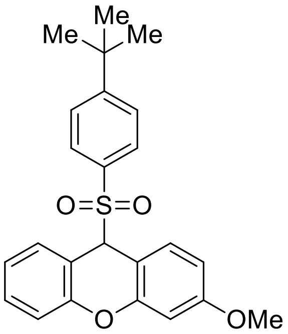
(s, 9H); **^{13}C{^{1}H} NMR** (CDCl$_3$, 100 MHz): δ 158.3, 152.2, 151.0, 131.4, 131.3, 130.6 (x 2), 130.4, 129.4 (x 2), 128.0, 125.4 (x 2), 123.6, 117.6, 116.3, 115.5, 113.1, 66.8, 35.2, 31.0 (x 3); **HRMS (ESI-TOF) m/z:** [M + Na]$^+$ Calcd for $C_{23}H_{21}ClO_3SNa$ 435.0798, found 435.0797.

2-bromo-9-((4-(tert-butyl)phenyl)sulfonyl)-9*H*-xanthene (4j):



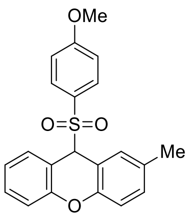
Yield 84% (76.8 mg); colorless solid; **R$_f$** 0.16 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/ethyl acetate = 9:1; **mp** 176-178 ^{o}C; **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.49 (dd, *J* = 7.8 Hz, 1.4 Hz, 1H), 7.39-7.43 (comp, 2H), 7.34-7.38 (m, 1H), 7.28-7.31 (comp, 2H), 7.14-7.18 (m, 1H), 7.04-7.07 (comp, 2H), 6.92 (dd, *J* = 8.2 Hz, 0.9 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 5.29 (s, 1H), 1.31 (s, 9H); **^{13}C{^{1}H} NMR** (CDCl$_3$, 100 MHz): δ 158.3, 152.2, 151.6, 133.5, 133.3, 131.4, 131.3, 130.6, 129.4 (x 2), 125.4 (x 2), 123.6, 118.0, 116.3, 116.0, 115.12, 113.1, 66.6, 35.2, 31.0 (x 3); **HRMS (ESI-TOF) m/z:** [M + Na]$^+$ Calcd for $C_{23}H_{21}BrO_3SNa$ 479.0292, found 479.0294.

9-((4-(tert-butyl)phenyl)sulfonyl)-3-methoxy-9H-xanthene (4k):



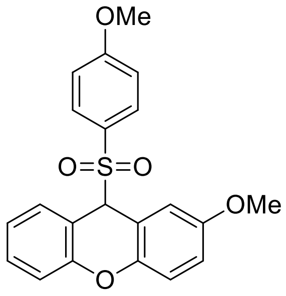
Yield 62% (50.6 mg); colorless solid; **R$_f$** 0.13 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/ethyl acetate = 9:1; **mp** 118-120 ^{o}C; **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.48 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.29-7.33 (m, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.09-7.13 (m, 1H), 6.95 (dd, *J* = 8.6 Hz, 2.2 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 1H), 6.71 (dd, *J* = 8.4 Hz, 2.4 Hz 1H), 6.41 (d, *J* = 2.8 Hz, 1H), 5.32 (s, 1H), 3.81 (s, 3H), 1.29 (s, 9H); **^{13}C{^{1}H} NMR** (CDCl$_3$, 100 MHz): δ 161.4, 157.8, 153.4, 152.3, 132.0, 131.7, 131.3, 130.3, 129.3 (x 2), 125.1 (x 2), 123.2, 116.1, 114.0, 110.2, 105.9, 100.9, 66.7, 55.5, 35.1, 31.0 (x 3); **HRMS (ESI-TOF) m/z:** [M + Na]$^+$ Calcd for $C_{24}H_{24}O_4SNa$ 431.1293, found 431.1297.

9-((4-methoxyphenyl)sulfonyl)-2-methyl-9*H*-xanthene (4l):



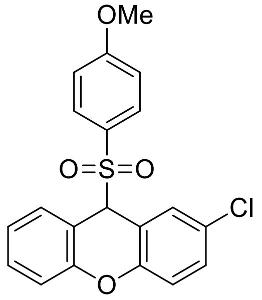
Yield 99% (72.4 mg); colorless solid; **R$_f$** 0.08 (pet ether/ethyl acetate = 8.5:1.5); **eluent composition** pet ether/ethyl acetate = 8.5:1.5; **mp** 148-150 ^{o}C ; **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.54 (d, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 1.2 Hz, 1H), 7.30-7.32 (m, 1H), 7.12-7.15 (comp, 2H), 6.91 (app s, 1H), 6.87 (d, *J* = 10.0 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.67 (d, *J* = 9.2 Hz, 2H), 5.33 (s, 1H), 3.80 (s, 3H), 2.37 (s, 3H); **^{13}C{^{1}H} NMR** (CDCl$_3$, 100 MHz): δ 163.9, 152.5, 150.3, 132.8, 131.7 (x 2), 131.4, 131.4, 131.1, 130.3, 126.3, 123.1, 116.2, 115.9, 114.0, 113.6, 113.4 (x 2), 67.1, 55.5, 20.7; **HRMS (ESI-TOF) m/z:** $[M + Na]^+$ Calcd for $C_{21}H_{18}O_4SNa$ 389.0823, found 389.0838.

2-methoxy-9-((4-methoxyphenyl)sulfonyl)-9H-xanthene (4m):



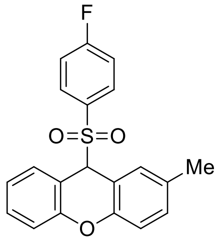
Yield 98% (75.0 mg); colourless solid; **R_f** 0.03 (pet ether/ethyl acetate = 8.5:1.5); **eluent composition** pet ether/ethyl acetate = 8.5:1.5; **mp** 122-124 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55 (dd, *J* = 8 Hz, 1.2 Hz, 1H), 7.30-7.34 (m, 1H), 7.12-7.16 (m, 1H), 7.05 (d, *J* = 2.8 Hz, 1H), 6.89-6.93 (comp, 3H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.82 (d, *J* = 9.2 Hz, 1H), 6.67 (dd, *J* = 7.2 Hz, 1.6 Hz, 2H), 5.35 (s, 1H), 3.83 (s, 3H), 3.80 (s, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 164.0, 155.2, 152.6, 146.5, 131.6 (x 2), 131.4, 130.3, 126.2, 123.0, 117.5, 117.1, 116.1, 114.3 (x 2), 113.4 (x 2), 113.4, 67.4, 55.8, 55.5; **HRMS (ESI-TOF) m/z:** $[M + Na]^+$ Calcd for $C_{21}H_{18}O_5SNa$ 405.0773, found 405.0768.

2-chloro-9-((4-methoxyphenyl)sulfonyl)-9*H*-xanthene (4n):



Yield 99% (75.8 mg); colorless solid; **R_f** 0.08 (pet ether/ethyl acetate = 8.5:1.5); **eluent composition** pet ether/ethyl acetate = 8.5:1.5; **mp** 178-180 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.54 (dd, *J* = 7.7 Hz, 1.4 Hz, 1H); 7.49 (d, *J* = 2.4 Hz, 1H), 7.33-7.37 (m, 1H), 7.29 (dd, *J* = 8.8 Hz, 2.8 Hz, 1H), 7.15-7.19 (m, 1H), 6.93-6.96 (comp, 2H), 6.90 (dd, *J* = 8.0 Hz; 0.6 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 1H), 6.68-6.72 (comp, 2H), 5.31 (s, 1H), 3.81 (s, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 164.1; 152.1, 150.9, 131.7 (x 2), 131.4, 130.8, 130.6, 130.4, 128.1, 125.9, 123.6, 117.6, 116.3, 115.6, 113.6 (x 2), 113.4, 66.6, 55.6; **HRMS (ESI-TOF) m/z:** $[M + Na]^+$ Calcd for $C_{20}H_{15}ClO_4SNa$ 409.0277, found 409.0281.

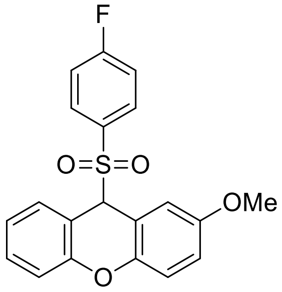
9-((4-fluorophenyl)sulfonyl)-2-methyl-9*H*-xanthene (4o):



Yield 69% (49.0 mg); colorless solid; **R_f** 0.69 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/ethyl acetate = 9:1; **mp** 162-164 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.57 (dd, *J* = 7.7 Hz, 1.2 Hz, 1H), 7.37 (app s, 1H), 7.31-7.36 (m, 1H), 7.14-7.18 (comp, 2H), 6.94-6.98 (comp, 2H), 6.85-6.91 (comp, 3H), 6.78 (d, *J* = 8.3 Hz, 1H), 5.37 (s, 1H), 2.38 (s, 3H);

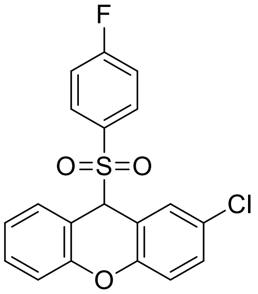
^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ 166.1 (d, $^{1}J_{F\text{-}C}$ = 255.0 Hz), 152.5, 150.2, 133.0, 132.4 (d, $^{3}J_{F\text{-}C}$ = 10.0 Hz), 131.4 (x 3), 130.6 (d, $^{4}J_{F\text{-}C}$ = 3.0 Hz), 130.6 (x 2), 123.3 (x 2), 116.3, 116.0, 115.6, 115.3, 113.4 (d, $^{2}J_{F\text{-}C}$ = 36.0 Hz), 67.3, 20.7; **^{19}F NMR** (376 MHz, CDCl$_3$) δ -103.0; **HRMS (ESI-TOF) m/z:** [M + Na]$^+$ Calcd for $C_{20}H_{15}FO_3SNa$ 377.0624, found 377.0629.

9-((4-fluorophenyl)sulfonyl)-2-methoxy-9*H*-xanthene (4p):



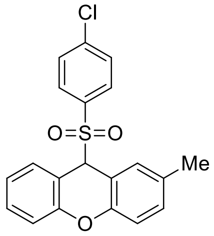
Yield 88% (65.0 mg); colorless solid; **R$_f$** 0.81 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/ethyl acetate = 9:1; **mp** 154-156 °C; **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.58 (dd, *J* = 7.7 Hz, 1.6 Hz, 1H), 7.32-7.36 (m, 1H), 7.14-7.18 (m, 1H), 7.08 (d, *J* = 2.8 Hz, 1H), 6.95-7.0 (comp, 2H), 6.92 (dd, *J* = 8.6 Hz, 2.6 Hz, 2H), 6.88 (d, *J* = 6.7 Hz, 1H), 6.80-6.86 (comp, 2H), 5.39 (s, 1H), 3.85 (s, 3H); **^{13}C{^{1}H} NMR** (CDCl$_3$,100 MHz): δ 166.1 (d, $^{1}J_{F\text{-}C}$ = 255.0 Hz), 155.4, 152.5, 146.4, 132.3 (d, $^{3}J_{F\text{-}C}$ = 9.0 Hz), 131.4 (x 2), 130.6 (x 2), 123.2 (x 2), 117.8, 117.2, 116.2, 115.5 (d, $^{2}J_{F\text{-}C}$ = 23.0 Hz), 114.4, 114.0, 113.1, 67.5, 55.9; **^{19}F NMR** (376 MHz, CDCl$_3$) δ -102.9; **HRMS (ESI-TOF) m/z:** [M + Na]$^+$ Calcd for $C_{20}H_{15}FO_4SNa$ 393.0573, found 393.0578.

2-chloro-9-((4-fluorophenyl)sulfonyl)-9*H*-xanthene (4q):



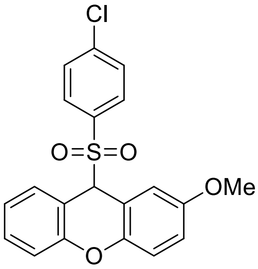
Yield 58% (43.8 mg); colorless solid; **R$_f$** 0.69 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/ethyl acetate = 9:1; **mp** 180-182 °C; **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.57 (dd, *J* = 8.5 Hz, 2.0 Hz, 2H), 7.39-7.35 (m, 1H), 7.31 (dd, *J* = 8.8 Hz, 2.8 Hz, 1H), 7.18-7.22 (m, 1H), 7.03-7.00 (comp, 2H), 6.95-6.90 (comp, 2H), 6.89 (dd, *J* = 4.9 Hz, 1.6 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 1H), 5.36 (s, 1H). **^{13}C{^{1}H} NMR** (CDCl$_3$,100 MHz): δ 152.0, 150.8, 132.4 (d, $^{3}J_{C\text{-}F}$ = 10.0 Hz), 131.4 (x 2), 130.9 (d, $^{3}J_{C\text{-}F}$ = 5.0 Hz), 130.8 (x 2), 130.4 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 128.4, 123.8 (x 2), 117.7, 116.4, 115.8, 115.6, 115.2, 113.0, 66.7; **^{19}F NMR** (376 MHz, CDCl$_3$) δ -102.35; **HRMS (ESI-TOF) m/z:** [M + Na]$^+$ Calcd for $C_{19}H_{12}ClFO_3SNa$ 397.0077, found 397.0078.

2-chloro-9-tosyl-9*H*-xanthene (4r):



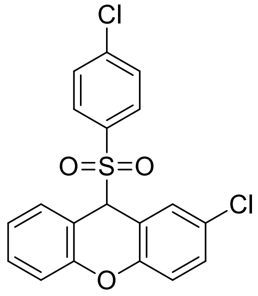
Yield 80% (59.3 mg); colorless solid; **R$_f$** 0.19 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/ethyl acetate = 9:1; **mp** 160-162 °C; **^{1}H NMR** (400 MHz, $\mathrm{CDCl_3}$): δ 7.56 (dd, *J* = 7.7 Hz, 1.5 Hz, 1H), 7.36 (d, *J* = 2.0 Hz, 1H), 7.32-7.35 (m, 1H), 7.18-7.20 (comp, 2H), 7.14-7.17 (comp, 2H), 6.89-6.91 (comp, 2H), 6.87-6.88 (m, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 5.38 (s, 1H), 2.38 (s, 3H); **^{13}C{^{1}H} NMR** ($\mathrm{CDCl_3}$, 100 MHz): δ 152.5, 150.3, 140.7, 133.3, 133.1, 131.5, 131.4 (x 2), 131.0 (x 2), 130.61, 128.4 (x 2), 123.3, 116.3, 116.1, 113.5, 113.1, 67.4, 20.7; **HRMS (ESI-TOF) m/z:** [M + Na]$^+$ Calcd for $\mathrm{C_{20}H_{15}ClO_3SNa}$ 393.0328, found 393.0320.

9-((4-chlorophenyl)sulfonyl)-2-methoxy-9*H*-xanthene (4s):



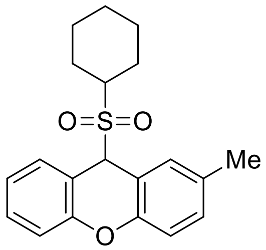
Yield 81% (62.5 mg); colorless solid; **R$_f$** 0.13 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/ethyl acetate = 9:1; **mp** 146-148 °C; **^{1}H NMR** (400 MHz, $\mathrm{CDCl_3}$): δ 7.57 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.32-7.37 (m, 1H), 7.18-7.20 (comp, 2H), 7.14-7.16 (m, 1H), 7.07 (d, *J* = 3.2 Hz, 1H), 6.92-6.94 (comp, 2H), 6.89-6.91 (comp, 2H), 6.82-6.87 (m, 1H), 5.40 (s, 1H), 3.85 (s, 3H); **^{13}C{^{1}H} NMR** ($\mathrm{CDCl_3}$, 100 MHz): δ 155.4, 152.5, 146.4, 140.8, 133.3, 131.4, 130.9 (x 2), 130.6, 128.5 (x 2), 123.2, 117.8, 117.2, 116.3, 114.3, 113.8, 113.0, 67.6, 55.8; **HRMS (ESI-TOF) m/z:** [M + Na]$^+$ Calcd for $\mathrm{C_{20}H_{15}ClO_4SNa}$ 409.0277, found 409.0274.

2-chloro-9-((4-chlorophenyl)sulfonyl)-9*H*-xanthene (4t):



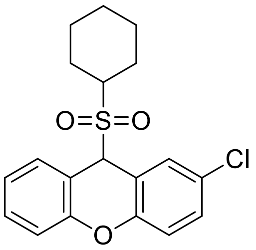
Yield 69% (53.9 mg); colorless solid; **R$_f$** 0.21 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/ethyl acetate = 9:1; **mp** 186-188 °C; **^{1}H NMR** (400 MHz, $\mathrm{CDCl_3}$): δ 7.54-7.56 (comp, 2H), 7.35-7.39 (m, 1H), 7.31 (dd, J = 8.8 Hz, 2.5 Hz, 1H), 7.22 (app s, 1H), 7.21 (d, J = 1.8 Hz, 1H), 7.18 (d, J = 7.6 Hz, 1H), 6.93 (d, J = 8.5 Hz, 2H), 6.91 (d, J = 8.4 Hz, 1H), 6.86 (d, J = 8.8 Hz, 1H), 5.36 (s, 1H); **^{13}C{^{1}H} NMR** ($\mathrm{CDCl_3}$, 100 MHz): δ 152.0, 150.8, 141.1, 133.0, 131.3, 130.9 (x 3), 130.8 (x 2), 128.6 (x 2), 128.4, 123.8, 117.8, 116.4, 115.0, 112.9, 66.7; **HRMS (ESI-TOF) m/z:** [M + Na]$^+$ Calcd for $\mathrm{C_{19}H_{12}Cl_2O_3SNa}$ 412.9782, found 412.9763.

9-(cyclohexylsulfonyl)-2-methyl-9*H*-xanthene (4u):



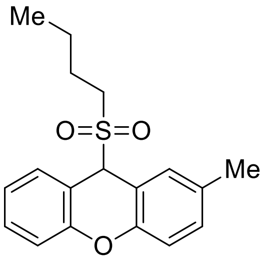
Yield 43% (29.5 mg); colorless solid; **R_f** 0.12 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/ethyl acetate = 9:1; **mp** 78-80 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H); 7.38-7.42 (m, 1H), 7.35 (app s, 1H), 7.15-7.21 (comp, 3H), 7.08 (d, *J* = 8.4 Hz, 1H), 5.33 (s, 1H), 2.72 (tt, *J* = 12.0 Hz, 3.2 Hz, 1H), 2.37 (s, 3H), 1.70-1.75 (comp, 4H), 1.57-1.58 (m, 1H), 1.32-1.41 (comp, 2H), 1.09 (app s, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 152.7, 150.5, 133.2, 131.3, 131.1, 131.0, 130.5, 123.5, 116.9, 116.6, 114.1, 113.7, 64.5, 57.7, 25.7, 25.6, 25.2 (x 2), 25.0, 20.7; **HRMS (ESI-TOF) m/z:** $[M + Na]^+$ Calcd for $C_{20}H_{22}O_3SNa$ 365.1187, found 365.1181.

2-chloro-9-(cyclohexylsulfonyl)-9*H*-xanthene (4v):



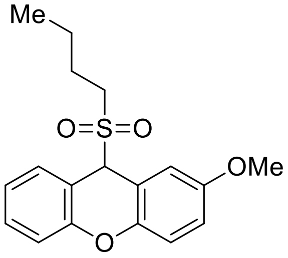
Yield 60% (43.6 mg); colorless solid; **R_f** 0.18 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/ethyl acetate = 9:1; **mp** 156-158 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.53-7.55 (comp, 2H), 7.40-7.44 (m, 1H), 7.36 (dd, *J* = 8.8 Hz, 2.4 Hz, 1H), 7.18-7.22 (comp, 2H), 7.14 (d, *J* = 8.8 Hz, 1H), 5.32 (s, 1H), 2.71-2.78 (m, 1H), 1.76-1.77 (comp, 4H), 1.36-1.42 (comp, 2H), 1.25 (s, 1H), 1.09-1.12 (comp, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 152.3, 151.2, 130.8 (x 2), 130.7, 130.6, 128.6, 124.1, 118.2, 117.0, 115.6, 113.5, 63.6, 57.8, 25.8, 25.5, 25.2 (x 2), 24.9; **HRMS (ESI-TOF) m/z:** $[M + Na]^+$ Calcd for $C_{19}H_{19}ClO_3SNa$ 385.0641, found 385.0642.

9-(butylsulfonyl)-2-methyl-9*H*-xanthene (4w):



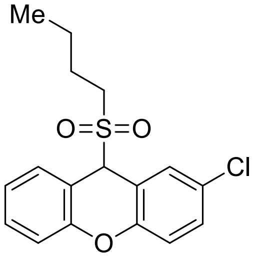
Yield 67% (42.3 mg); colorless solid; **R_f** 0.16 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/ethyl acetate = 9:1; **mp** 88-90 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.6 Hz, 1H); 7.39-7.43 (comp, 2H), 7.08 (d, *J* = 8.4 Hz, 1H), 5.23 (s, 1H), 2.49 (dd, *J* = 9.4 Hz, 6.5 Hz, 2H), 2.38 (s, 3H), 2.16-7.22 (comp, 3H), 1.46-1.54 (comp, 2H), 1.18-1.28 (comp, 2H), 0.78 (t, *J* = 7.4 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 152.4, 150.1, 133.5, 131.5, 131.4 (x 2), 130.6, 123.8, 116.8, 116.5, 114.2, 113.7, 65.7, 46.8, 22.5, 21.7, 20.7, 13.4; **HRMS (ESI-TOF) m/z:** $[M + Na]^+$ Calcd for $C_{18}H_{20}O_3SNa$ 339.1031, found 339.1032.

9-(butylsulfonyl)-2-methoxy-9*H*-xanthene (4x):



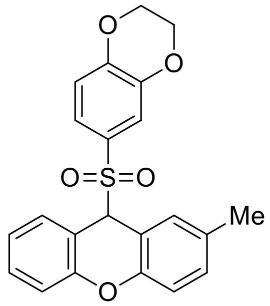
Yield 94% (62.5 mg); colorless solid; **R_f** 0.11 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/ethyl acetate = 9:1; **mp** 78-80 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.59 (dd, *J* = 7.7 Hz, 1.5 Hz, 1H); 7.39-7.43 (comp, 1H), 7.15-7.21 (comp, 2H), 7.09-7.13 (comp, 2H), 6.98 (dd, *J* = 9.0 Hz, 3.0 Hz, 1H), 5.24 (s, 1H), 3.83 (s, 3H), 2.47-2.51 (comp, 2H), 1.46-1.54 (comp, 2H), 1.19-1.29 (comp, 2H), 0.77 (t, *J* = 7.2 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 155.7, 152.4, 146.2, 131.4, 130.6, 123.7, 117.7, 117.6, 116.8, 114.5 (x 2), 113.6, 65.9, 55.8, 46.9, 22.5, 21.7, 13.4; **HRMS (ESI-TOF) m/z:** $[M + Na]^+$ Calcd for $C_{18}H_{20}O_4SNa$ 355.0980, found 355.0987.

9-(butylsulfonyl)-2-chloro-9*H*-xanthene (4y):



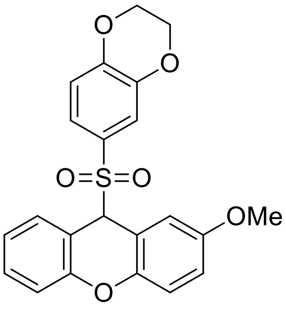
Yield 83% (56.3 mg); colorless solid; **R_f** 0.18 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/ethyl acetate = 9:1; **mp** 156-158 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.59 (dd, *J* = 4.8 Hz, 1.9 Hz, 2H); 7.42-7.46 (m, 1H), 7.38 (dd, *J* = 8.8 Hz, 2.4 Hz, 1H), 7.22-7.25 (m, 1H), 7.18-7.20 (m, 1H), 7.14 (d, *J* = 8.8 Hz, 1H), 5.22 (s, 1H), 2.51 (t, *J* = 8.0 Hz, 2H), 1.49-1.57 (comp, 2H), 1.26 (sextet, *J* = 7.4 Hz, 2H), 0.79 (t, *J* = 7.2 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 151.9, 150.8, 131.3, 130.9, 130.9, 130.9, 128.9, 124.3, 118.2, 116.9, 115.6, 113.5, 65.1, 47.1, 22.6, 21.7, 13.4; **HRMS (ESI-TOF) m/z**: $[M + Na]^+$ Calcd for $C_{17}H_{17}ClO_3SNa$ 359.0485, found 359.0486.

9-((2,3-dihydrobenzo[β][1,4]dioxin-6-yl)sulfonyl)-2-methyl-9*H*-xanthene (4z):



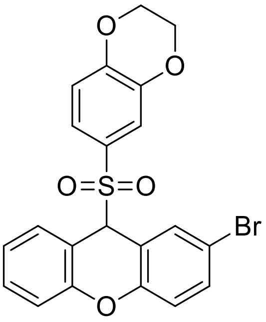
Yield 80% (63.1 mg); colorless solid; **R_f** 0.24 (pet ether/ethyl acetate = 7.5:2.5); **eluent composition** pet ether/ethyl acetate = 4:1; **mp** 136-138 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.50 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.31-7.35 (m, 1H), 7.27 (d, *J* = 7.3 Hz, 1H), 7.11-7.15 (comp, 2H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.83 (d, *J* = 8.3 Hz, 1H), 6.67 (d, *J* = 8.4 Hz, 1H), 6.49-6.54 (comp, 2H), 5.32 (s, 1H), 4.27 (dd, *J* = 5.1 Hz, 2.9 Hz, 2H), 4.18 (dd, *J* = 5.1 Hz, 2.8 Hz, 2H), 2.36 (s, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 152.7, 150.4, 148.4, 143.0, 132.7, 131.3, 131.3, 131.2, 130.3, 127.0, 123.46, 123.1, 119.3, 116.88, 116.16, 115.9, 113.9, 113.5, 67.2, 64.6, 63.9, 20.7; **HRMS (ESI-TOF) m/z:** $[M + Na]^+$ Calcd for $C_{22}H_{18}O_5SNa$ 417.0773, found 417.0775.

9-((2,3-dihydrobenzo[β][1,4]dioxin-6-yl)sulfonyl)-2-methoxy-9*H*-xanthene (4aa):



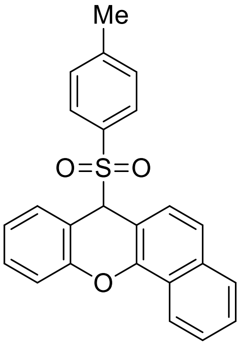
Yield 60% (49.2 mg); colorless solid; **R_f** 0.16 (pet ether/ethyl acetate = 7.5:2.5); **eluent composition** pet ether/ethyl acetate = 7.5:2.5; **mp** 148-150 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 7.0 Hz, 1H), 7.31-7.35 (m, 1H), 7.11-7.15 (m, 1H), 7.00 (d, *J* = 2.7 Hz, 1H), 6.91 (dd, *J* = 8.8 Hz, 2.6 Hz, 2H), 6.86 (d, *J* = 8.9 Hz, 1H), 6.67 (d, *J* = 8.4 Hz, 1H), 6.55-6.51 (comp, 2H), 5.34 (s, 1H), 4.27 (dd, *J* = 5.1 Hz, 2.7 Hz, 2H), 4.18 (dd, *J* = 5.1 Hz, 2.7 Hz, 2H), 3.82 (s, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 155.2, 152.7, 148.5, 146.6, 143.0, 131.3, 130.4, 127.0, 123.4, 123.0, 119.2, 117.6, 117.1, 116.9, 116.1, 114.3, 114.3, 113.3, 67.5, 64.6, 63.9, 55.8; **HRMS (ESI-TOF) m/z:** [M + Na]$^+$ Calcd for $C_{22}H_{18}O_6SNa$ 433.0722, found 433.0723.

2-bromo-9-((2,3-dihydrobenzo[b][1,4]dioxin-6-yl)sulfonyl)-9*H*-xanthene (4ab):



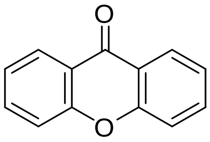
Yield 82% (75.3 mg); colorless solid; **R_f** 0.18 (pet ether/ethyl acetate = 7.5:2.5); **eluent composition** pet ether/ethyl acetate = 7.5:2.5; **mp** 180-182 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.50 (dd, *J* = 8.1 Hz, 1.8 Hz, 2H), 7.43 (dd, *J* = 8.7 Hz, 2.4 Hz, 1H), 7.34-7.40 (m, 1H), 7.16-7.19 (m, 1H), 6.96 (dd, *J* = 8.2 Hz, 0.9 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 1H), 6.71-6.74 (m, 1H), 6.59-6.61 (comp, 2H), 5.28 (s, 1H), 4.29 (td, *J* = 3.3 Hz, 1.5 Hz, 2H), 4.20-4.22 (comp, 2H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 152.2, 151.6, 148.7, 143.2, 133.6, 133.3, 131.3, 130.7, 126.7, 123.7, 123.4, 119.3, 118.0, 117.2, 116.3, 116.0, 115.2, 113.2, 66.6, 64.6, 63.9; **HRMS (ESI-TOF) m/z:** [M + Na]$^+$ Calcd for $C_{21}H_{15}BrO_5SNa$ 480.9721, found 480.9734.

7-tosyl-7H-benzo[χ]xanthenes (4ac):



Yield 98% (75.7 mg); colorless solid; **R_f** 0.23 (pet ether/ethyl acetate = 9:1); **eluent composition** pet ether/ethyl acetate = 9:1; **mp** 160-162 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 7.5 Hz, 1H), 7.55-7.62 (comp, 4H), 7.49-7.54 (m, 1H), 7.36-7.41 (m, 1H), 7.19-7.23 (m, 1H), 7.05-7.07 (m, 1H), 6.81-6.90 (comp, 4H), 5.54 (s, 1H), 2.29 (s, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 152.2, 148.2, 144.8, 134.4, 131.6, 131.2, 130.3, 129.4 (x 2), 128.8 (x 2), 127.6, 127.4, 127.3, 126.1, 123.6, 123.4, 122.8, 121.6, 116.4, 114.1, 108.0, 67.4, 21.6; **HRMS (ESI-TOF) m/z:** $[M + Na]^+$ Calcd for $C_{24}H_{18}O_3SNa$ 409.0874, found 409.0858.

9*H*-xanthen-9-one (5):[11]

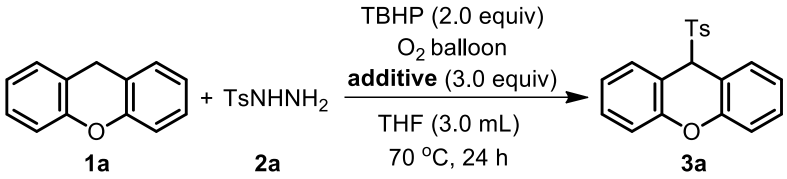


Yield 10% (3.9 mg); colorless solid; **eluent composition** pet ether/ethyl acetate = 9:1; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.35 (dd, *J* = 8.0 Hz, 1.4 Hz, 2H), 7.75-7.71 (comp, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.41-7.37 (comp, 2H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 177.2, 156.2 (x 2), 134.8 (x 2), 126.7 (x 2), 123.9 (x 2), 121.9 (x 2), 118.0 (x 2); **HRMS (ESI-TOF) m/z:** $[M + Na]^+$ Calcd for $C_{13}H_9O_2$ 197.0603, found 197.0605.

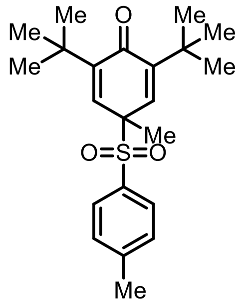
Radical scavenging experiment:

Radical quenching experiments were performed with **1a** under the standard conditions using radical scavengers like TEMPO and BHT, both in the presence and absence of $TsNHNH_2$ (**2a**). In presence of **2a** (procedure A), decreased yields of the sulfonylated product **3a** was observed and the formation of BHT-SO_2Tol adduct was detected in ESI-MS. However, in the absence of **2a** (procedure B), both in the presence of TEMPO and BHT, the formation of xanthene-TEMPO or xanthene-BHT adduct was not detected, but the formation of xanthenes-9-one (**5**) was observed in presence of O_2. These results indicated that the reaction possibly follows a radical mechanism, but in absence of $TsNHNH_2$, the rate of formation of xanthone (**5**) is probably faster than the rate of adduct formation between xanthene and TEMPO/BHT. Also, the tert-butoxy radical or hydroxy radical in addition to O_2 might be the responsible species involved in the abstraction of the C–H bond of **1a** to give xanthyl radical. And the formation of the side-product can be attributed to the participation of O_2.

A: With TsNHNH$_2$



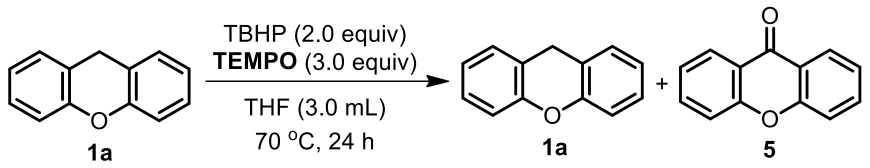
Exp. No.	Additive	Yield (3a)
1	-	97%
2	TEMPO	6%
3	BHT	55%



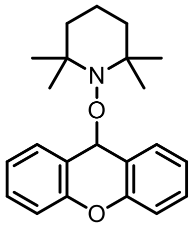
Detected by ESI-MS

[M+Na] = 397.1813

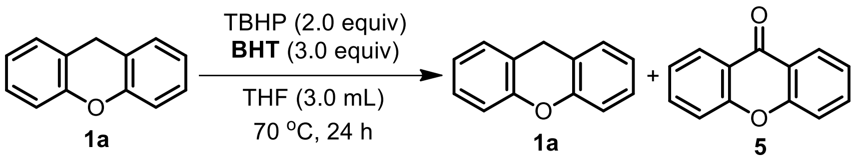
B: Without TsNHNH$_2$



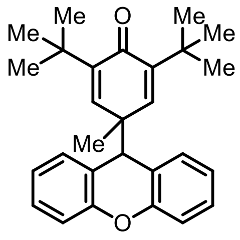
	1a	5
O_2 balloon:	trace	96%
Ar balloon:	70%	trace



Not detected



	1a	5
O_2 balloon:	88%	10%
Ar balloon:	98%	trace

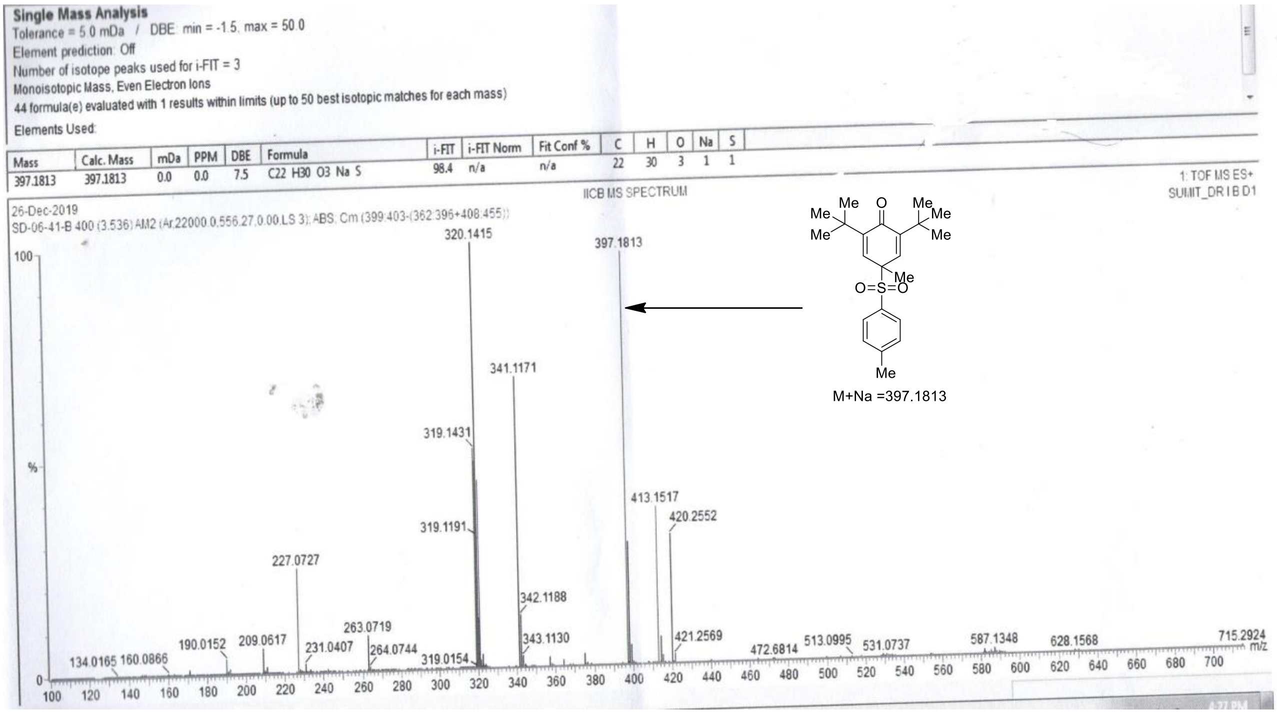


Not detected

Procedure A: A 10 mL oven-dried two-neck round-bottom flask was charged with xanthene **1a** (36.44 mg, 0.2 mmol, 1.0 equiv), *p*-toluenesulfonyl hydrazide **2a** (111.738 mg, 0.6 mmol, 3.0 equiv), additive (0.6 mmol, 3.0 equiv) and THF (3.0 mL) were added. TBHP (0.4 mmol, 2.0 equiv, 5.0-6.0 M solution in decane) were added by microsyringe. The resulting mixture was stirred and heated to 70 °C temperature for 24 h with O_2-balloon in an oil bath. After cooled down to room temperature, concentrated in a vacuum and the crude product was directly purified by column chromatography using ethyl acetate/petroleum ether (10%) to afford product **3a.**

Procedure B: A 10 mL oven-dried two-neck round-bottom flask was charged with xanthene **1a** (36.44 mg, 0.2 mmol, 1.0 equiv), additive (0.6 mmol, 3.0 equiv) and THF (3.0 mL) were added. TBHP (0.4 mmol, 2.0 equiv, 5.0-6.0 M solution in decane) were added by microsyringe. The resulting mixture was stirred and heated to 70 °C temperature for 24 h with O_2-balloon in an oil bath. And directly sample submitted from the crude reaction mixture for ESI-MS

ESI-MS of BHT-SO_2Tol adduct:



Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
44 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:

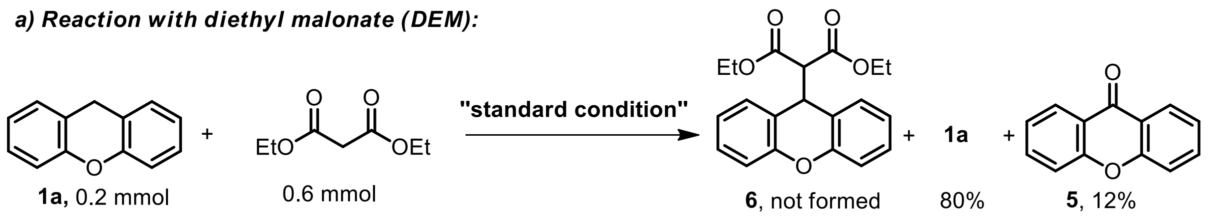
Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	O	Na	S
397.1813	397.1813	0.0	0.0	7.5	C22 H30 O3 Na S	98.4	n/a	n/a	22	30	3	1	1

IICB MS SPECTRUM
26-Dec-2019
SD-06-41-B 400 (3.536) AM2 (Ar,22000.0,556.27,0.00,LS 3); ABS; Cm (399:403-(362:396+408:455))
1: TOF MS ES+
SUMIT_DR I B D1

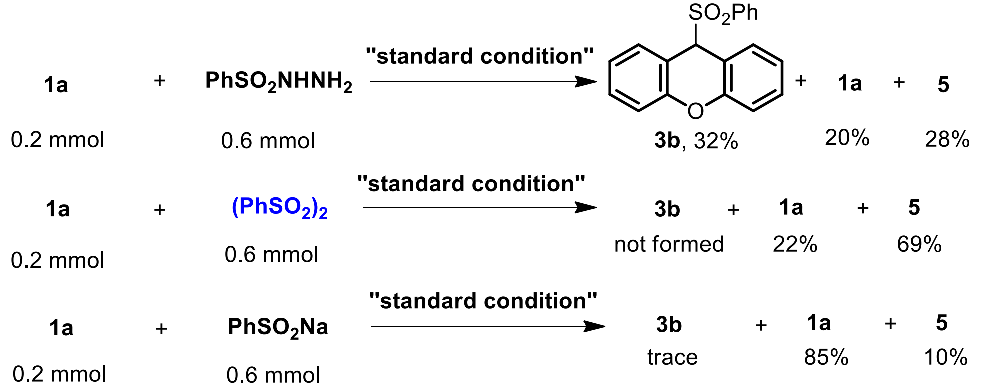
Control experiments with nucleophiles and $(PhSO_2)_2$ dimer:

To check if the reaction goes *via* an ionic mechanism with possible involvement of a xanthene carbocation, we treated xanthene (**1a**) with external nucleophile like diethyl malonate (DEM) under the standard reactions conditions. But the formation of product **6** was not observed. Again **1a** was made to react with $PhSO_2NHNH_2$, $(PhSO_2)_2$ and $PhSO_2Na$ under the standard reaction conditions to check the formation of the sulfonylated product **3b**. The desired product **3b** was formed in the case of $PhSO_2NHNH_2$, but a trace amount of product was formed in case of external nucleophiles like $PhSO_2Na$. These results indicated that the present reaction pathway might not involve an ionic mechanism and a possible involvement of a xanthene carbocation might not be feasible in the reaction pathway. Also, the formation of **3b** was not observed in presence of $(PhSO_2)_2$ dimer which indicated that the dimer species might not be a reaction intermediate of the reaction (see the mechanism in the main text)

a) Reaction with diethyl malonate (DEM):



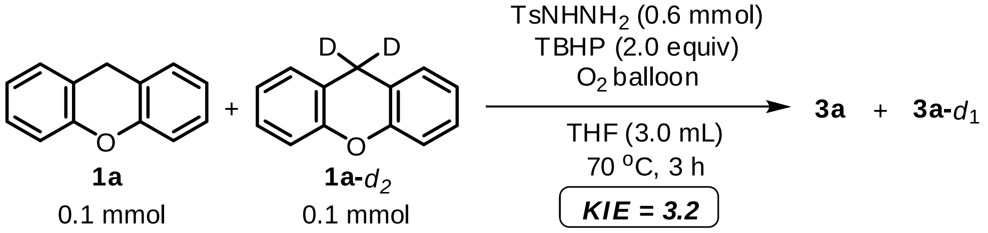
b) Comparison between $PhSO_2NHNH_2$, $(PhSO_2)_2$, and $PhSO_2Na$:



Kinetic isotope effect experiment:

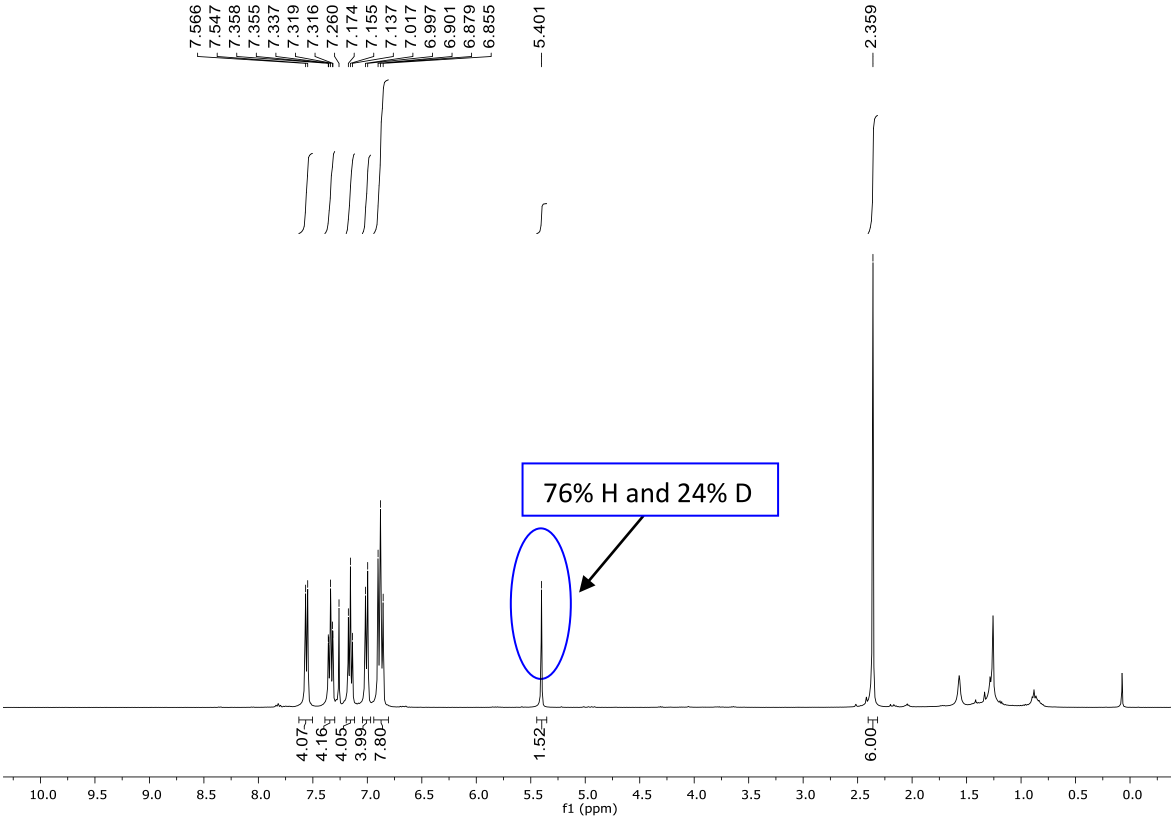
Kinetic isotope experiments (KIE) were performed between xanthene (**1a**) and xanthene-d_2 (**1a**-d_2) to check whether the C–H abstraction step of the reaction is involved in the rate-determining step (rds) of the reaction or not. Intermolecular competitive experiment suggested high k_H/k_D value of 3.2 from ^{1}H NMR spectroscopy. This result indicated that the C–H cleavage step might be involved in the rate-determining step of the reaction.

Procedure for competitive experiment between 1a and 1a-d_2:

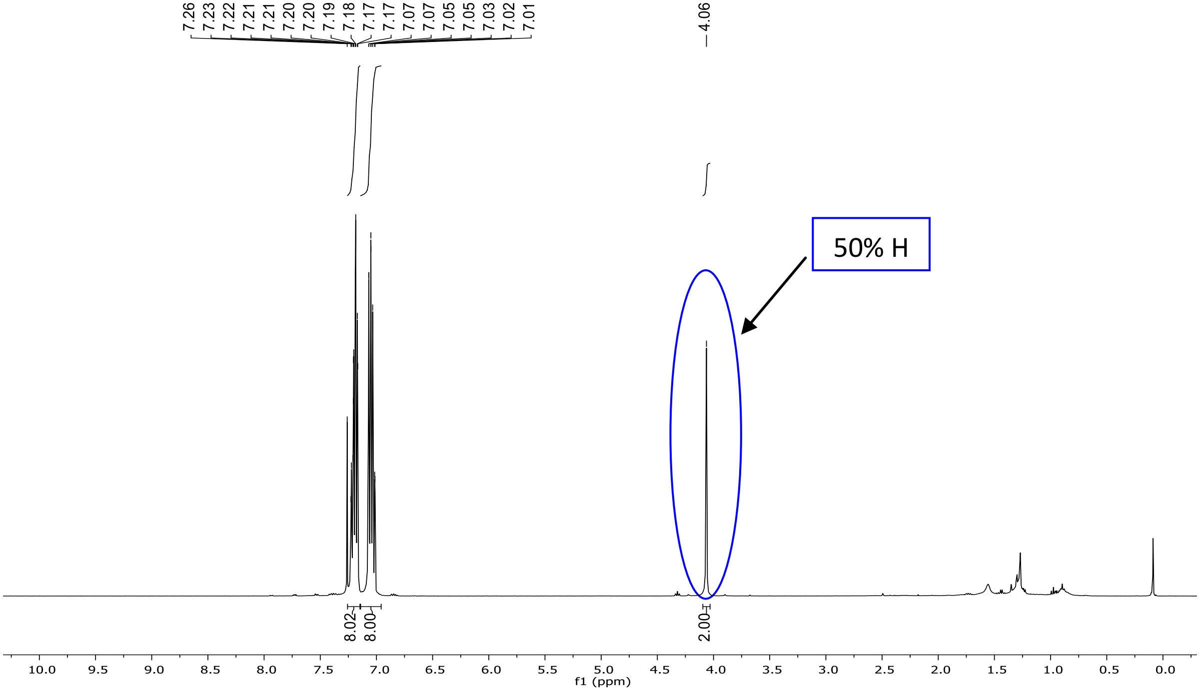


A 10 mL oven-dried two-neck round-bottom flask was charged with xanthene **1a** (18.2 mg, 0.1 mmol), **1a**-d_2 (18.4 mg, 0.1 mmol), *p*-toluenesulfonyl hydrazide **2a** (111.7 mg, 0.6 mmol, 3.0 equiv) and THF (3.0 mL) were added. TBHP (0.4 mmol, 2.0 equiv, 5.0-6.0 M solution in decane) were added by microsyringe. The resulting mixture was stirred and heated to 70 ^{o}C temperature for 3 h with O_2-balloon in an oil bath. After cooled down to room temperature, concentrated in vacuum and the crude product was directly purified by column chromatography using ethyl acetate/petroleum ether (10%) as eluent to afford recovered starting material and product**.** The ratio of **3a** and **3a**-d_1 was determined by ^{1}H NMR spectroscopy. Primary kinetic isotopic effect (KIE) was found be $k_H/k_D \approx 0.76/0.24 \approx 3.2$. ^{1}H NMR spectroscopy of recovered starting material showed that the ratio of **1a**:**1a**-d_2 = 50:50.

^{1}H-NMR of compound (**3a**+**3a**-d_1) (400 MHz, CDCl$_3$):



^{1}H-NMR of recover starting material (**1a**+**1a**-d_2) (400 MHz, CDCl$_3$):



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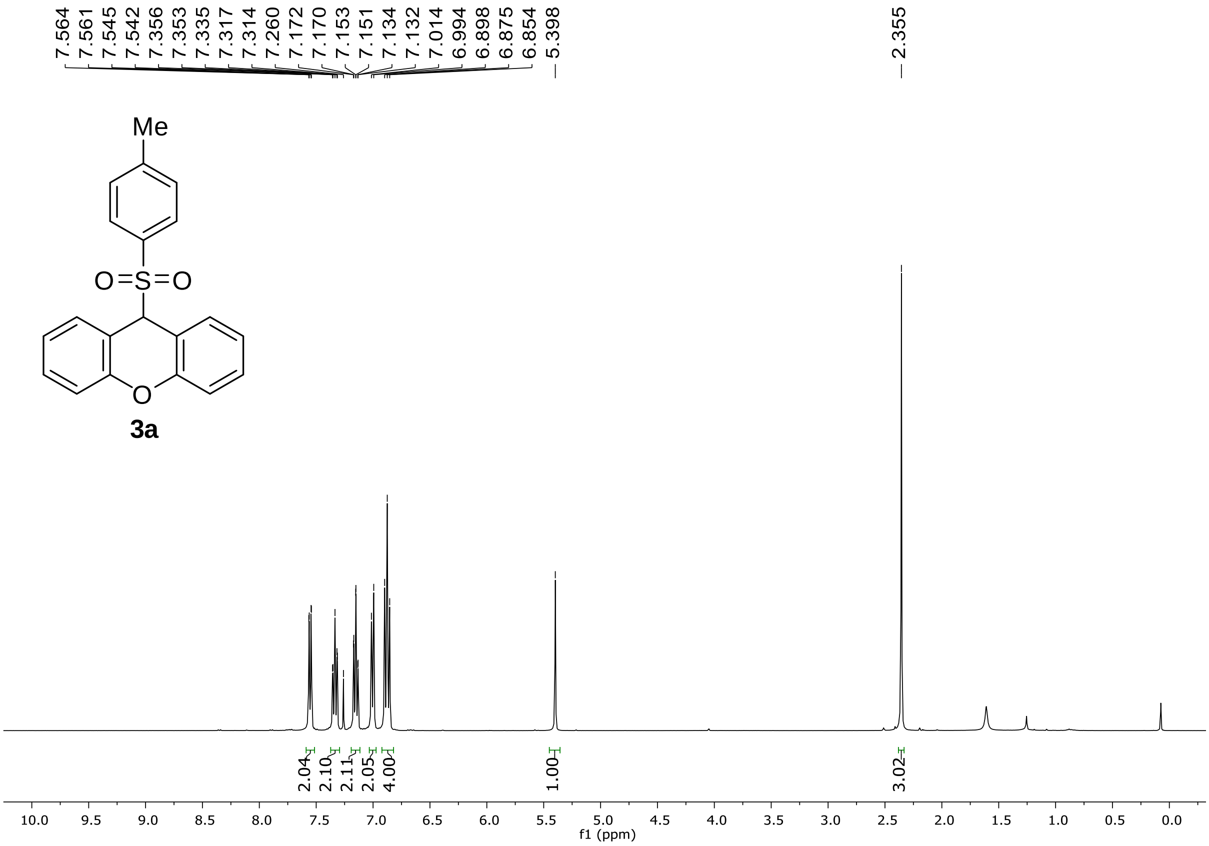
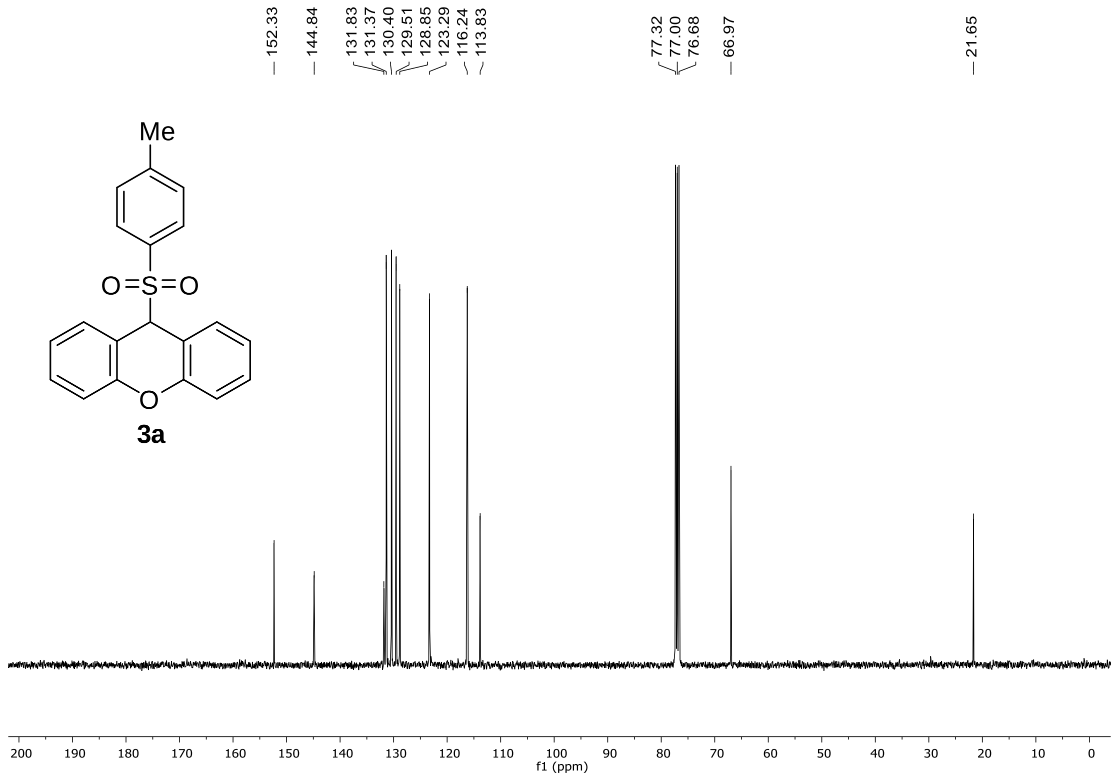
^{1}H, ^{13}C and ^{19}F NMR spectra of 9-sulfonylated xanthene derivatives:

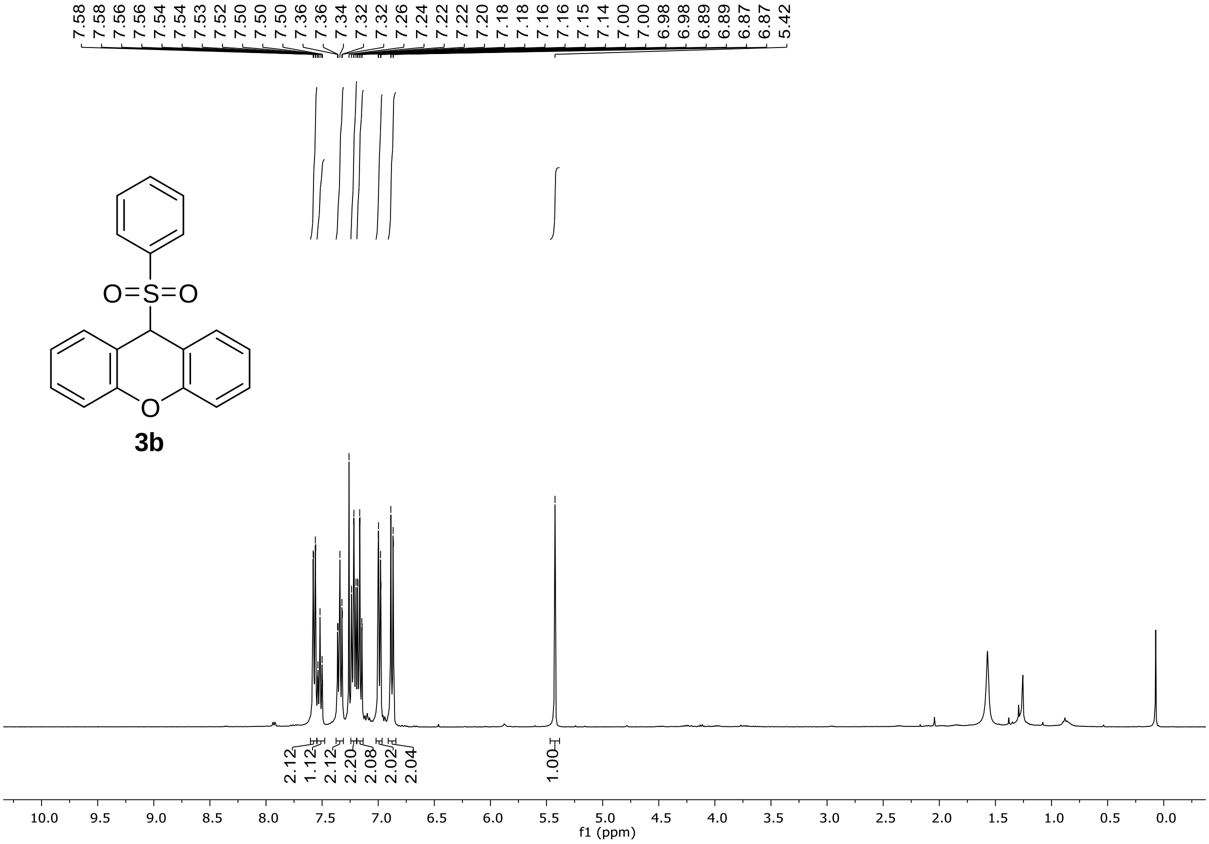
^{1}H NMR spectrum of **3a** (400 MHz, CDCl$_3$):



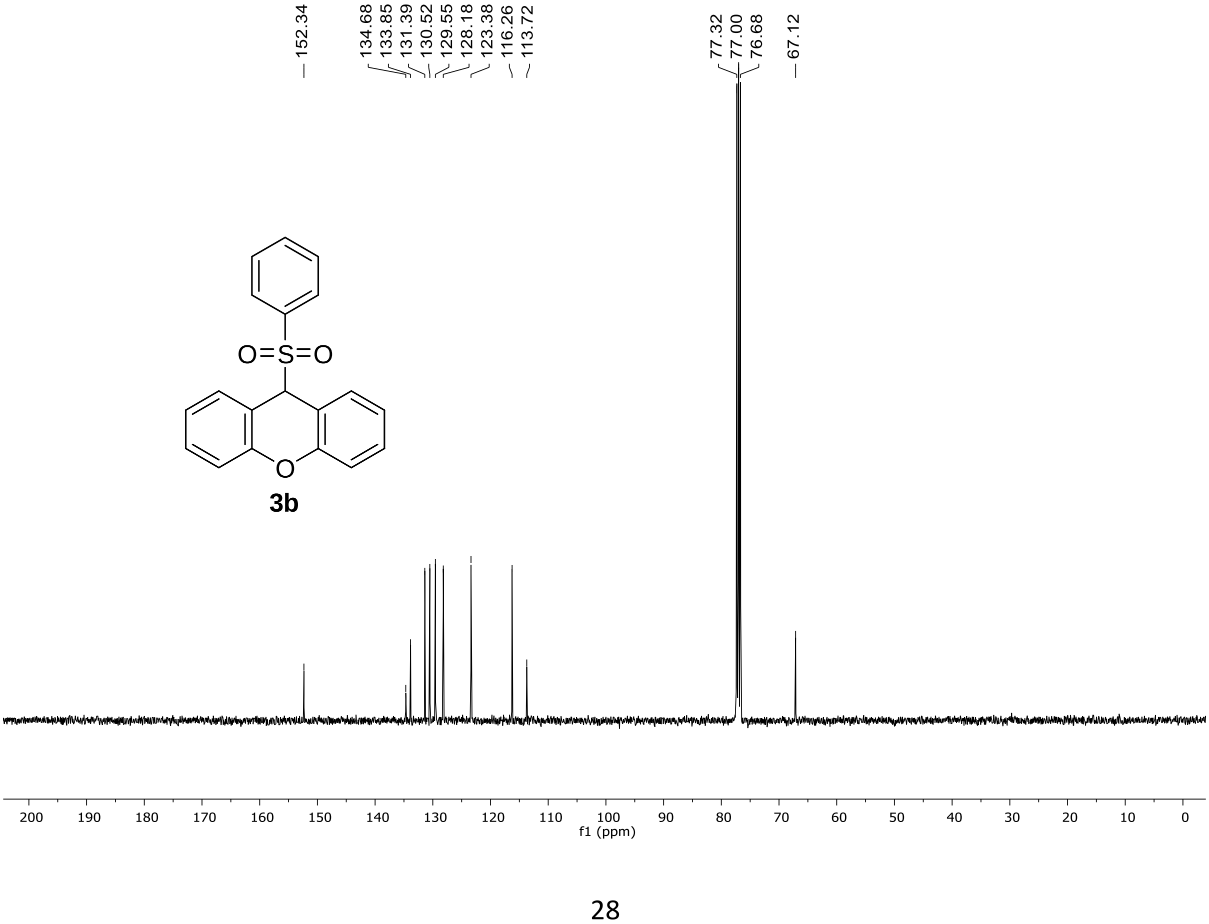
^{13}C {^{1}H} NMR spectrum of **3a** (100 MHz, CDCl$_3$):



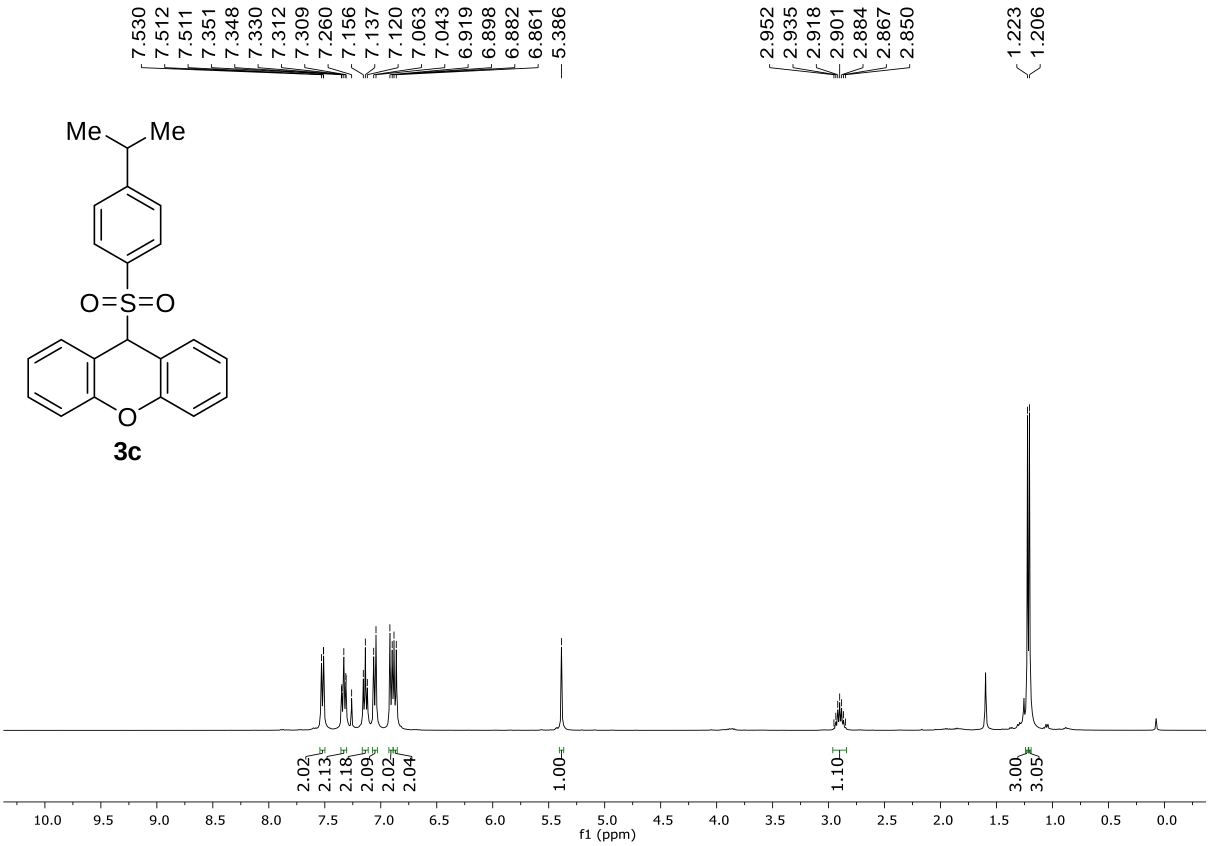
^{1}H NMR spectrum of **3b** (400 MHz, CDCl$_3$):



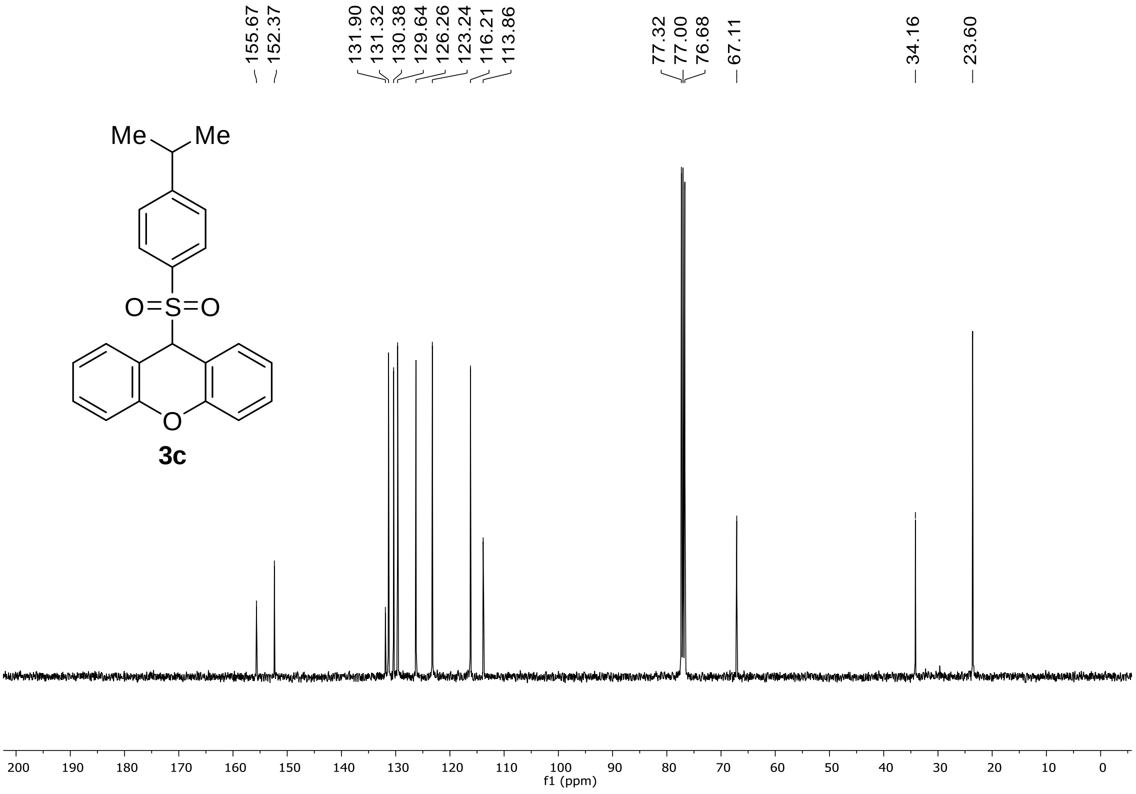
^{13}C {^{1}H} NMR spectrum of **3b** (100 MHz, CDCl$_3$):



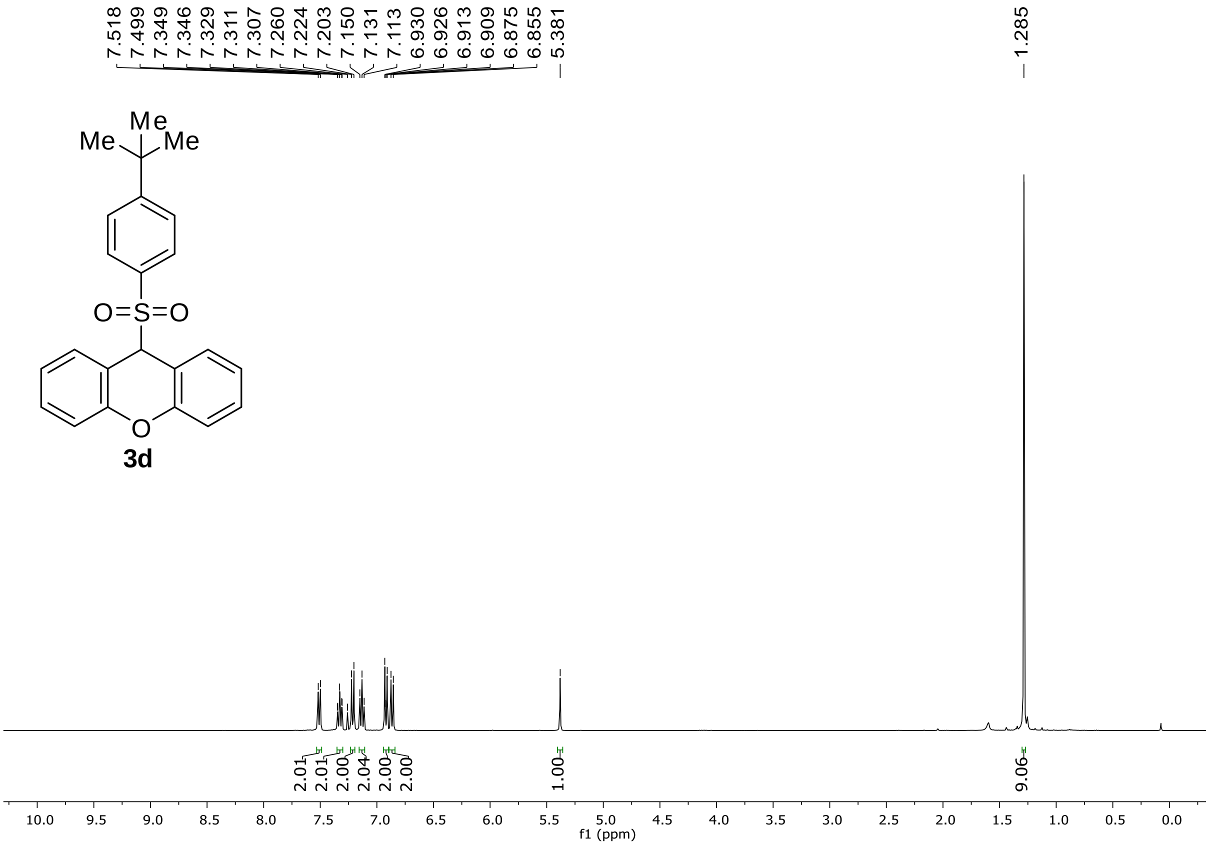
^{1}H NMR spectrum of **3c** (400 MHz, CDCl$_3$):



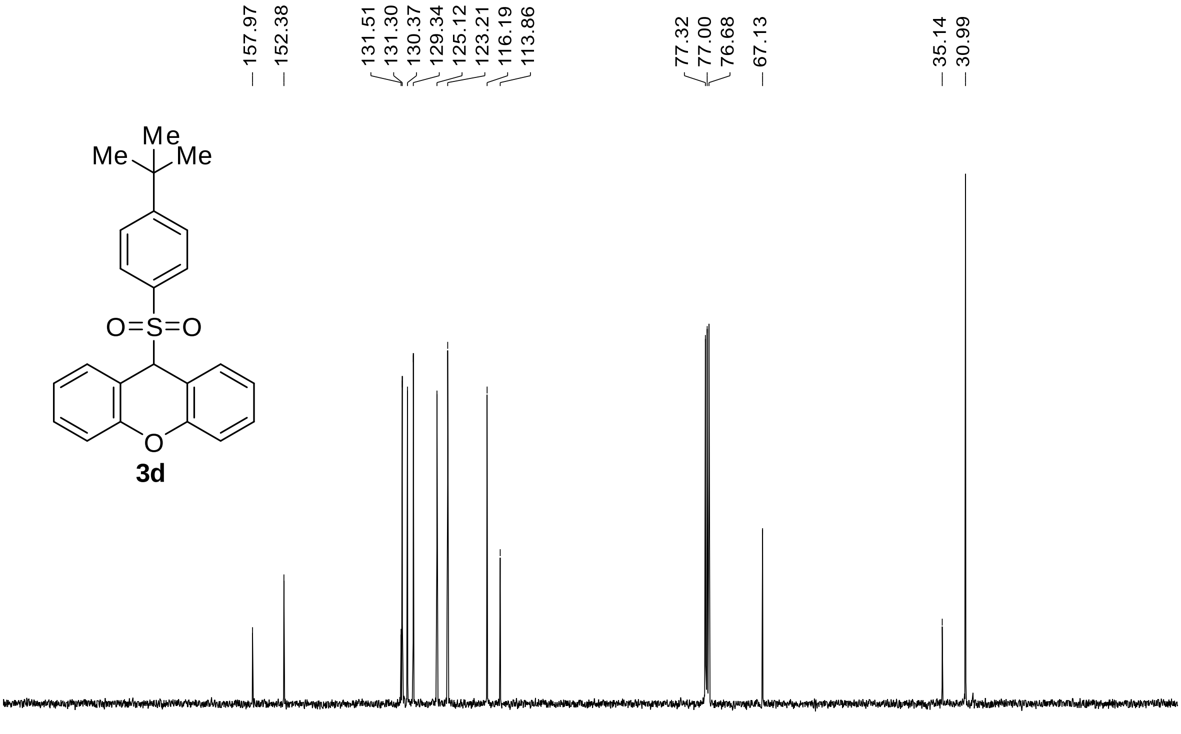
^{13}C {^{1}H} NMR spectrum of **3c** (100 MHz, CDCl$_3$):



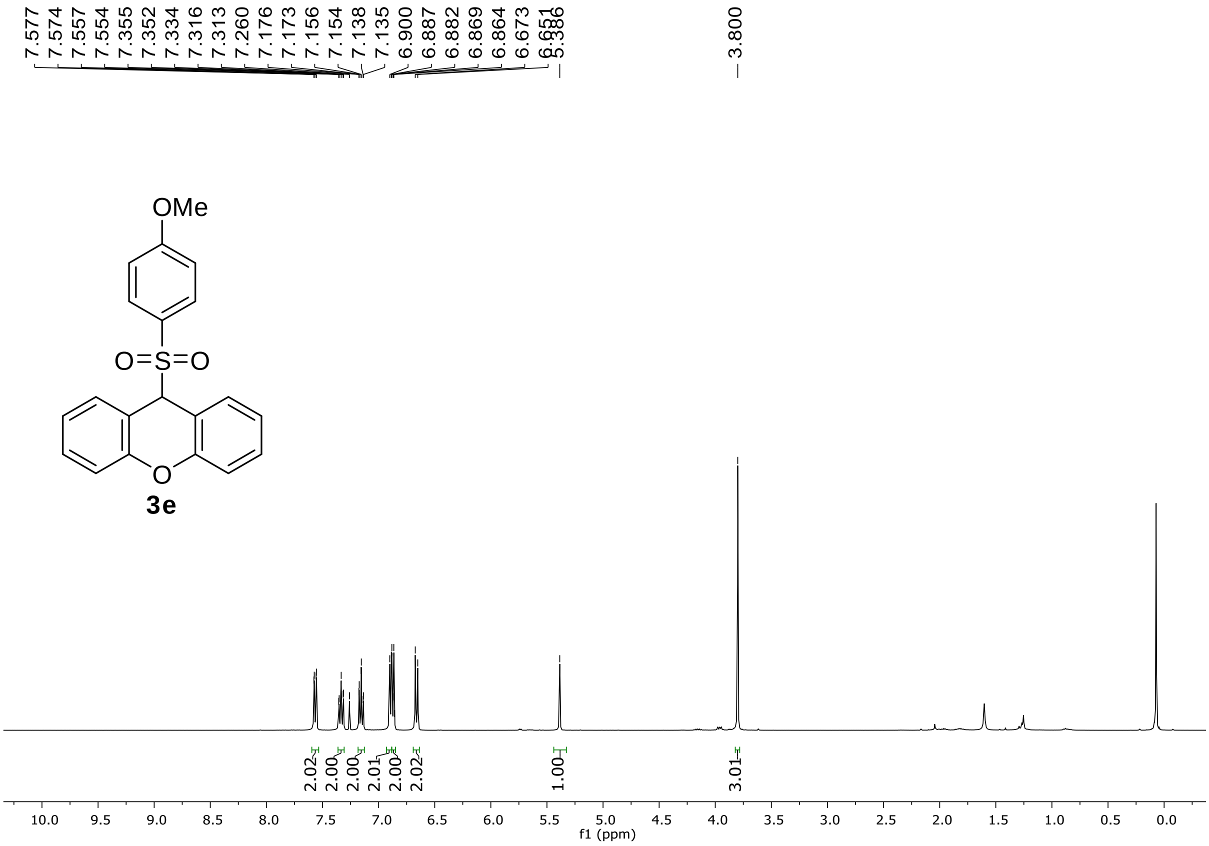
^{1}H NMR spectrum of **3d** (400 MHz, $CDCl_3$):



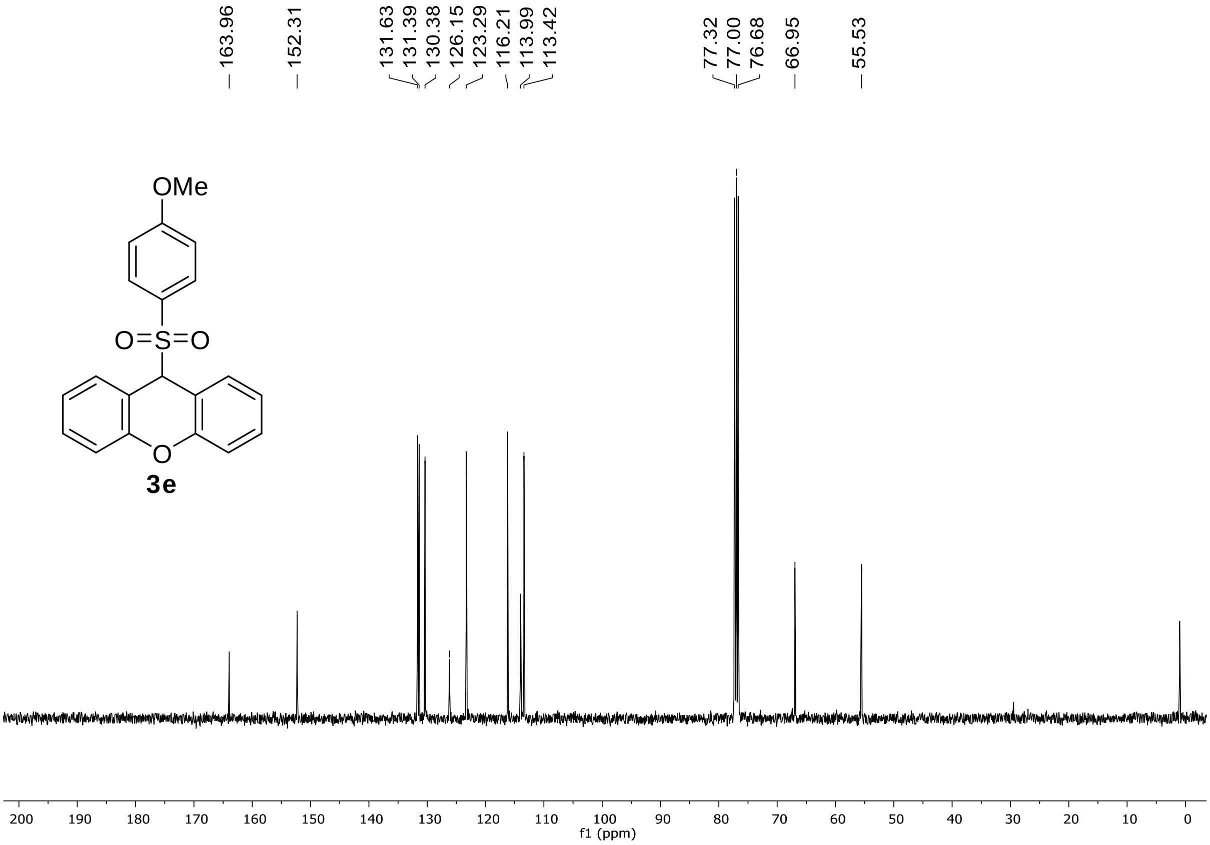
^{13}C {^{1}H} NMR spectrum of **3d** (100 MHz, $CDCl_3$):



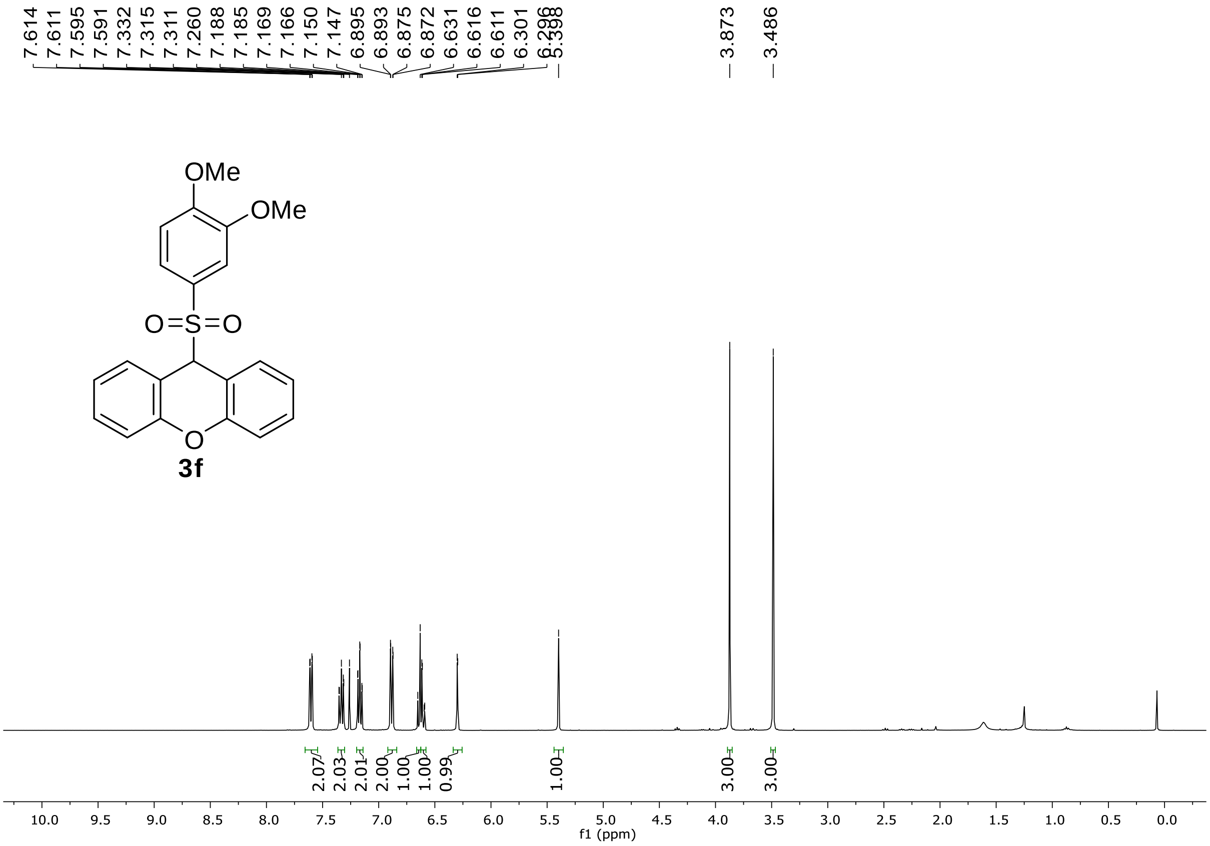
^{1}H NMR spectrum of **3e** (400 MHz, CDCl$_3$):



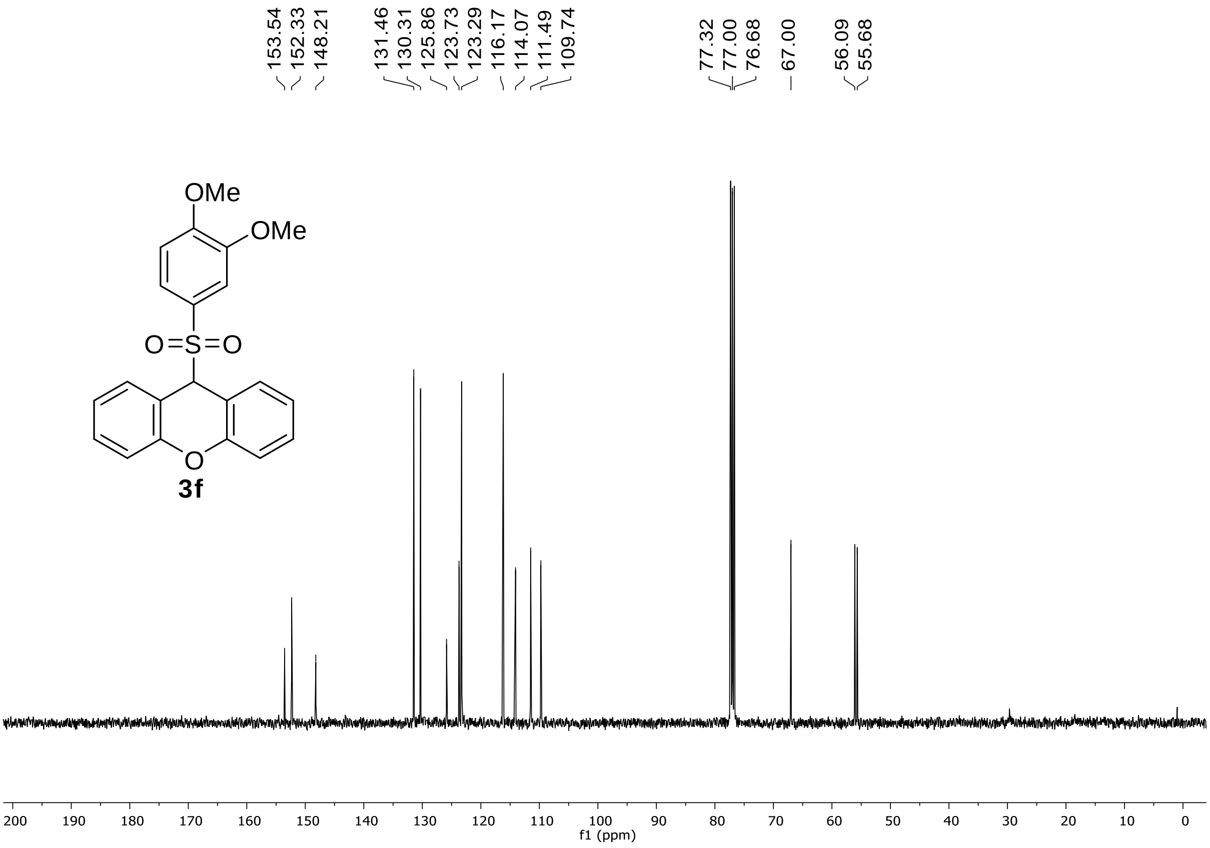
^{13}C {^{1}H} NMR spectrum of **3e** (100 MHz, CDCl$_3$):



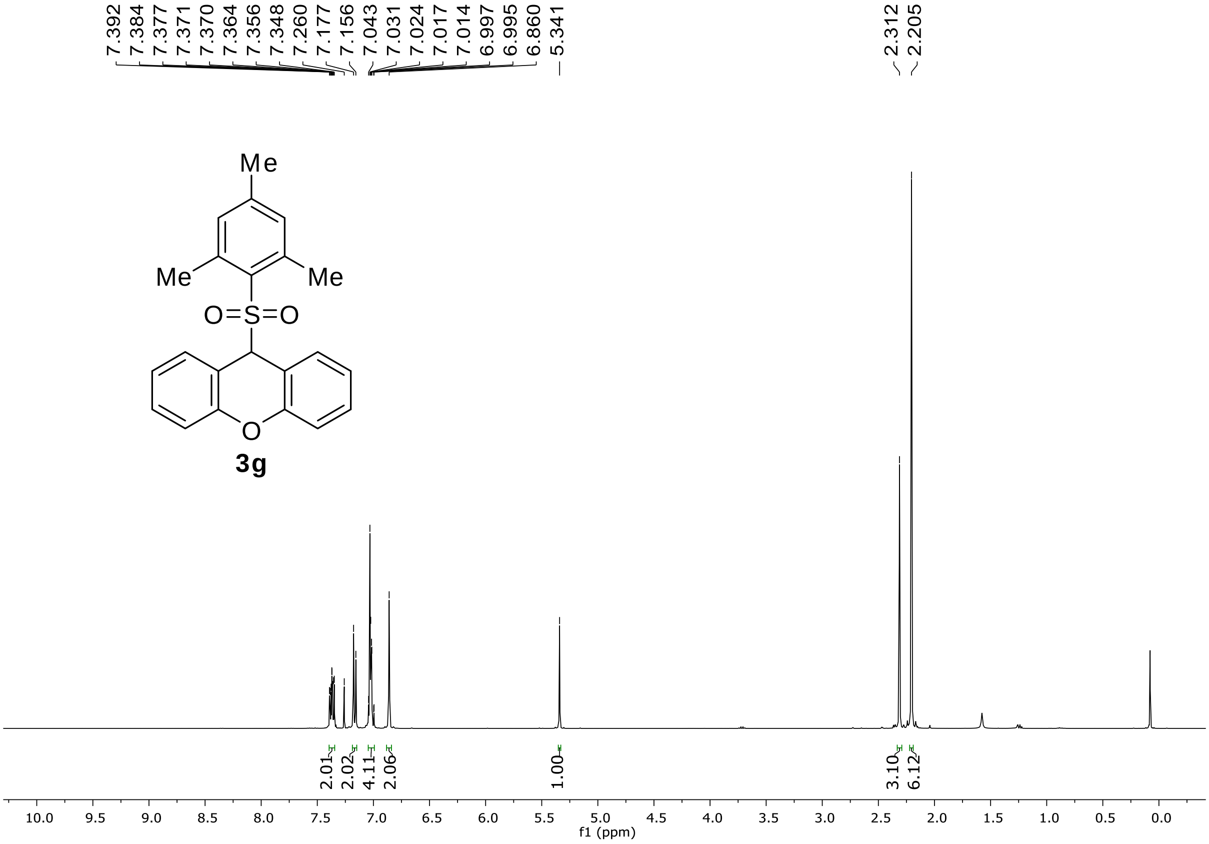
^{1}H NMR spectrum of **3f** (400 MHz, $CDCl_3$):



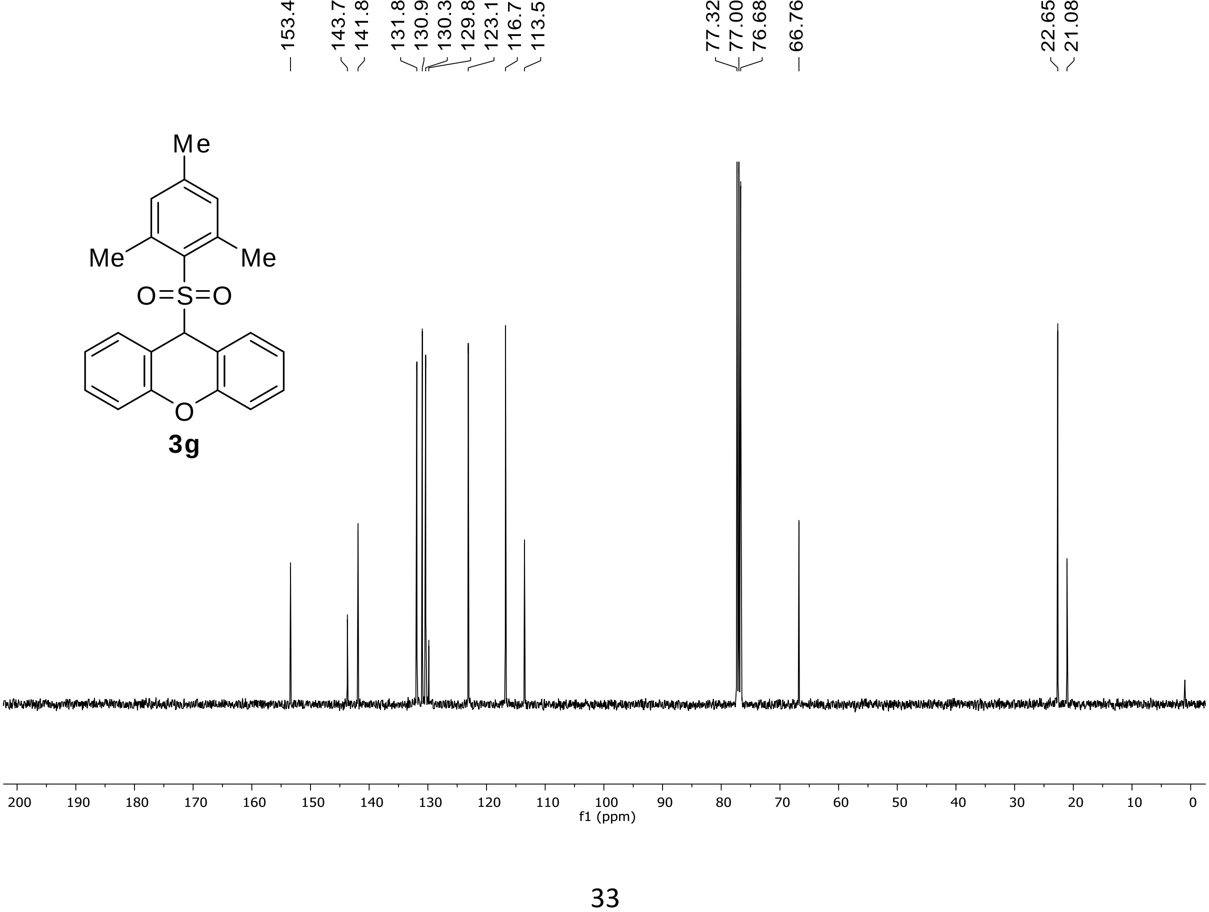
^{13}C {^{1}H} NMR spectrum of **3f** (100 MHz, $CDCl_3$):



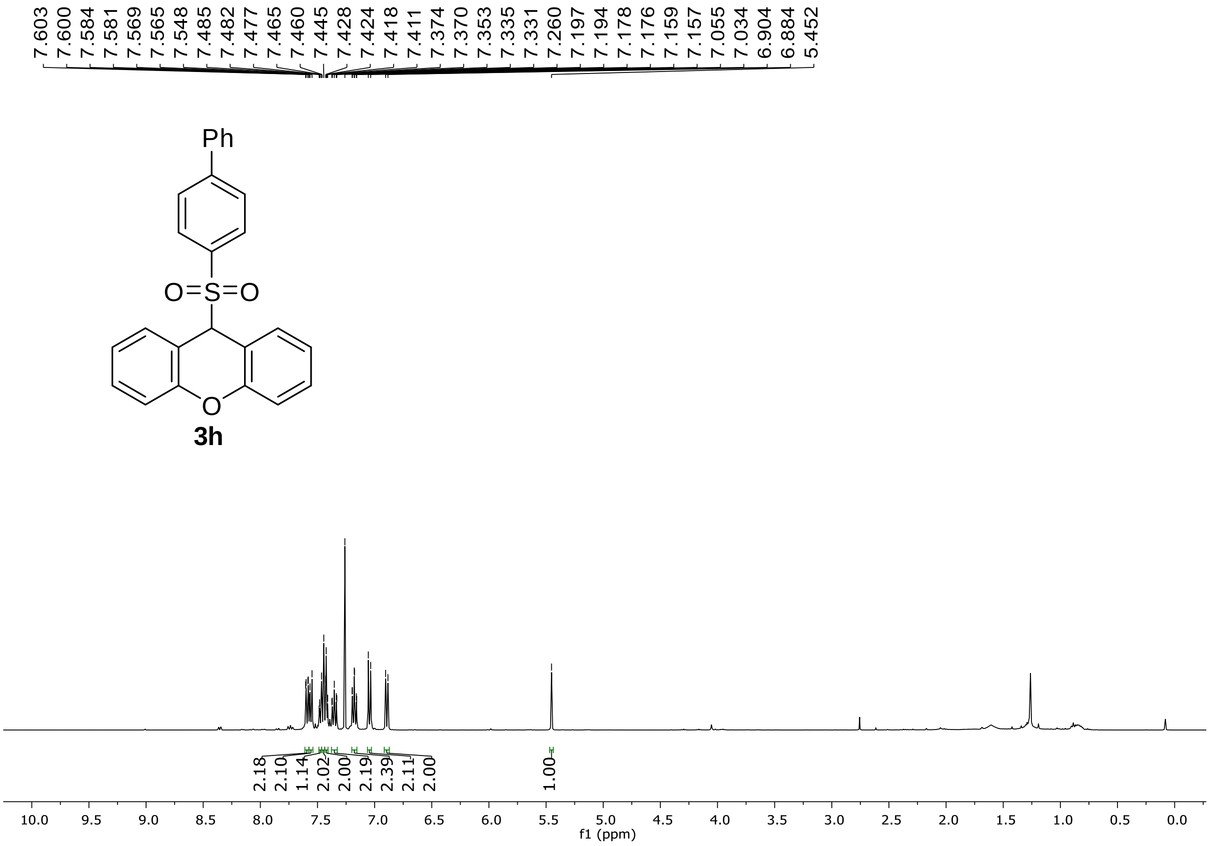
^{1}H NMR spectrum of **3g** (400 MHz, $CDCl_3$):



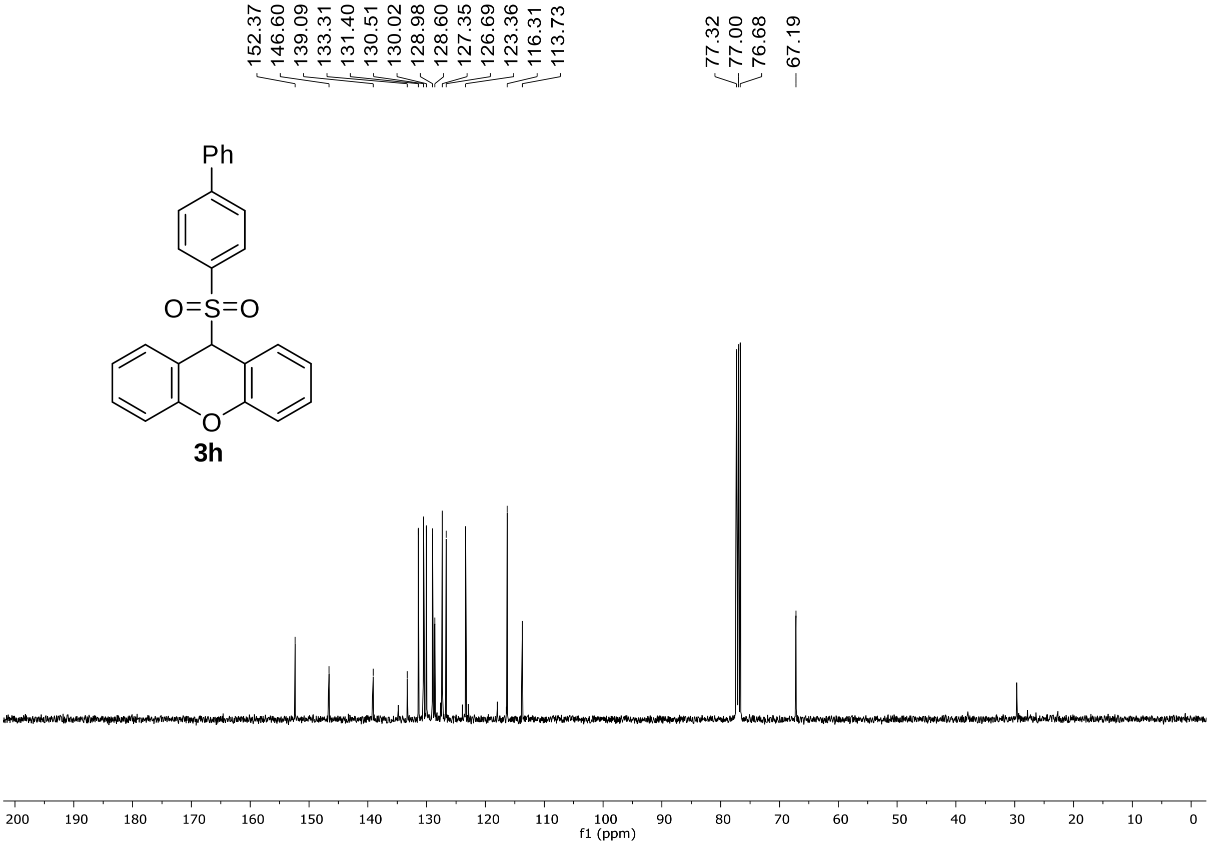
^{13}C {^{1}H} NMR spectrum of **3g** (100 MHz, $CDCl_3$):



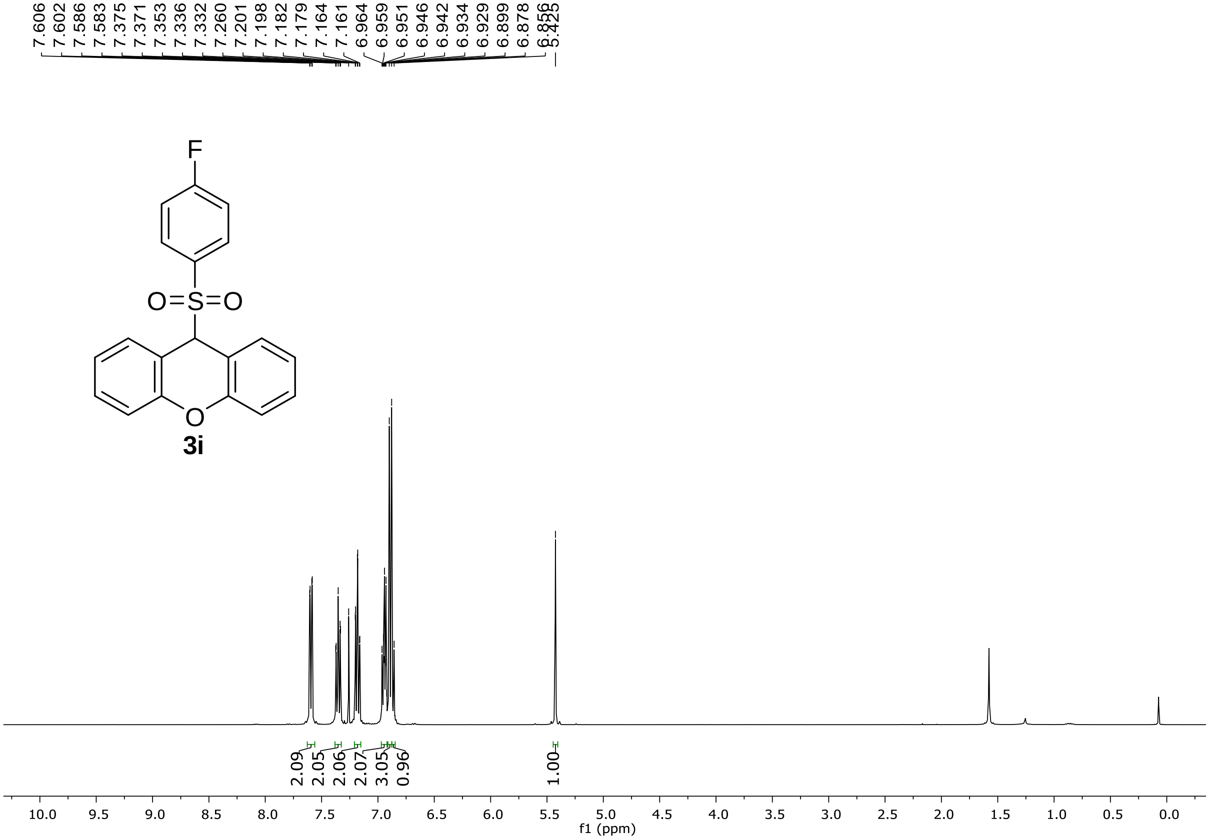
^{1}H NMR spectrum of **3h** (400 MHz, $CDCl_3$):



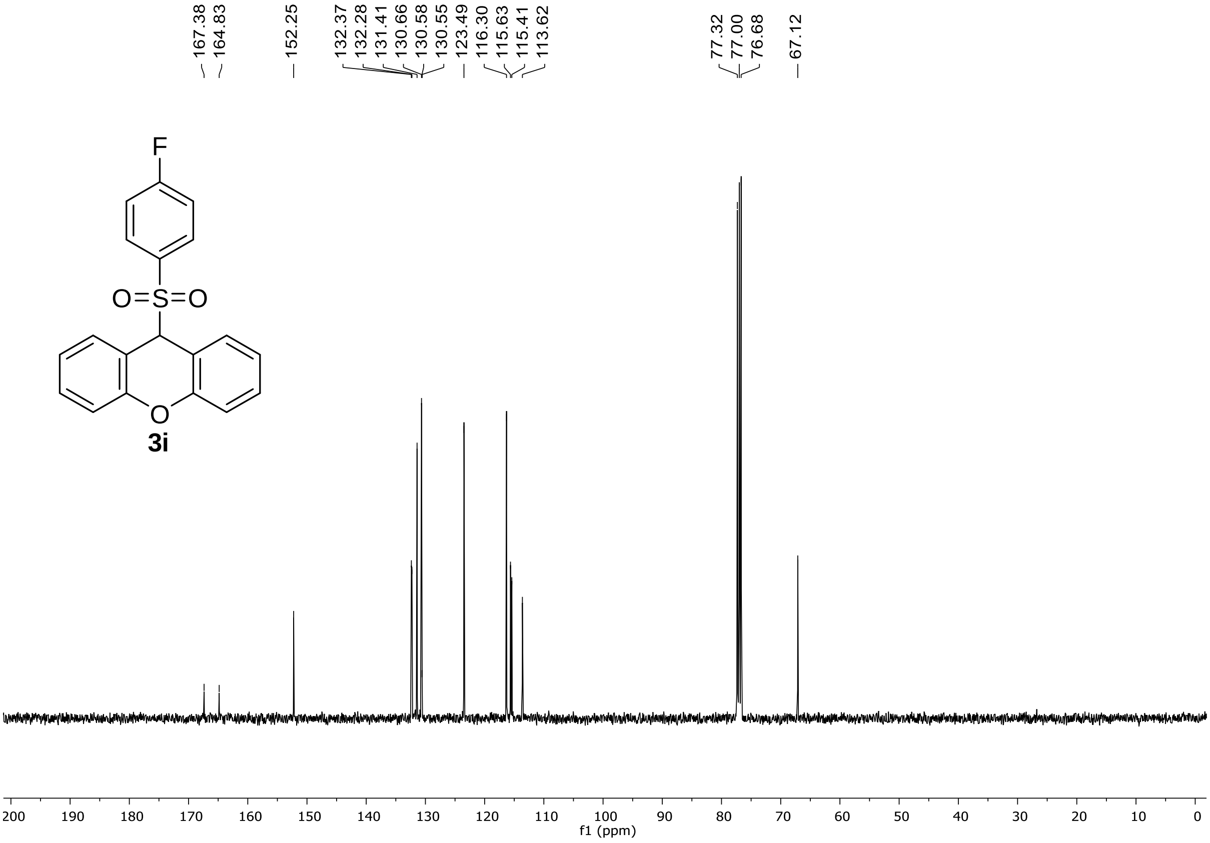
^{13}C {^{1}H} NMR spectrum of **3h** (100 MHz, $CDCl_3$):



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

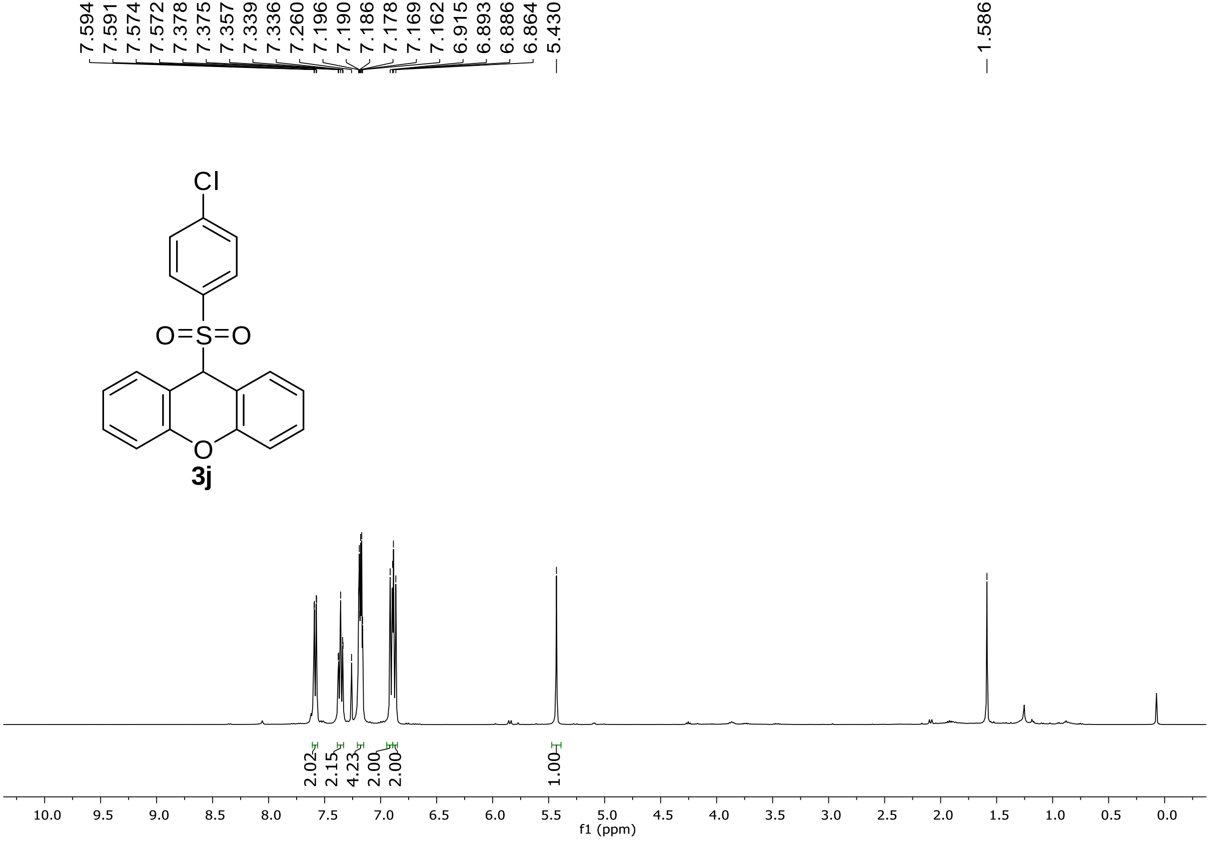


^{13}C {^{1}H} NMR spectrum of **3i** (100 MHz, $CDCl_3$):

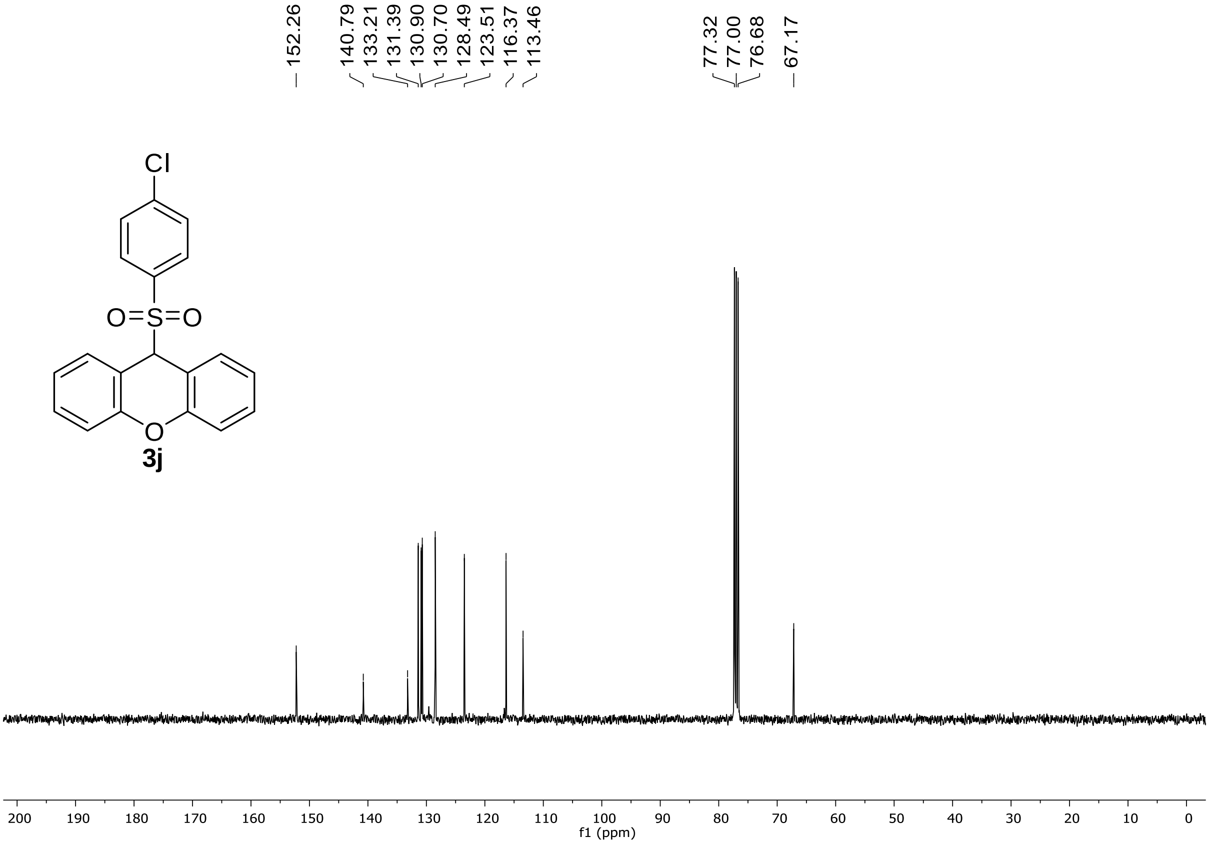


^{19}F NMR spectrum of **3i** (376 MHz, $CDCl_3$):

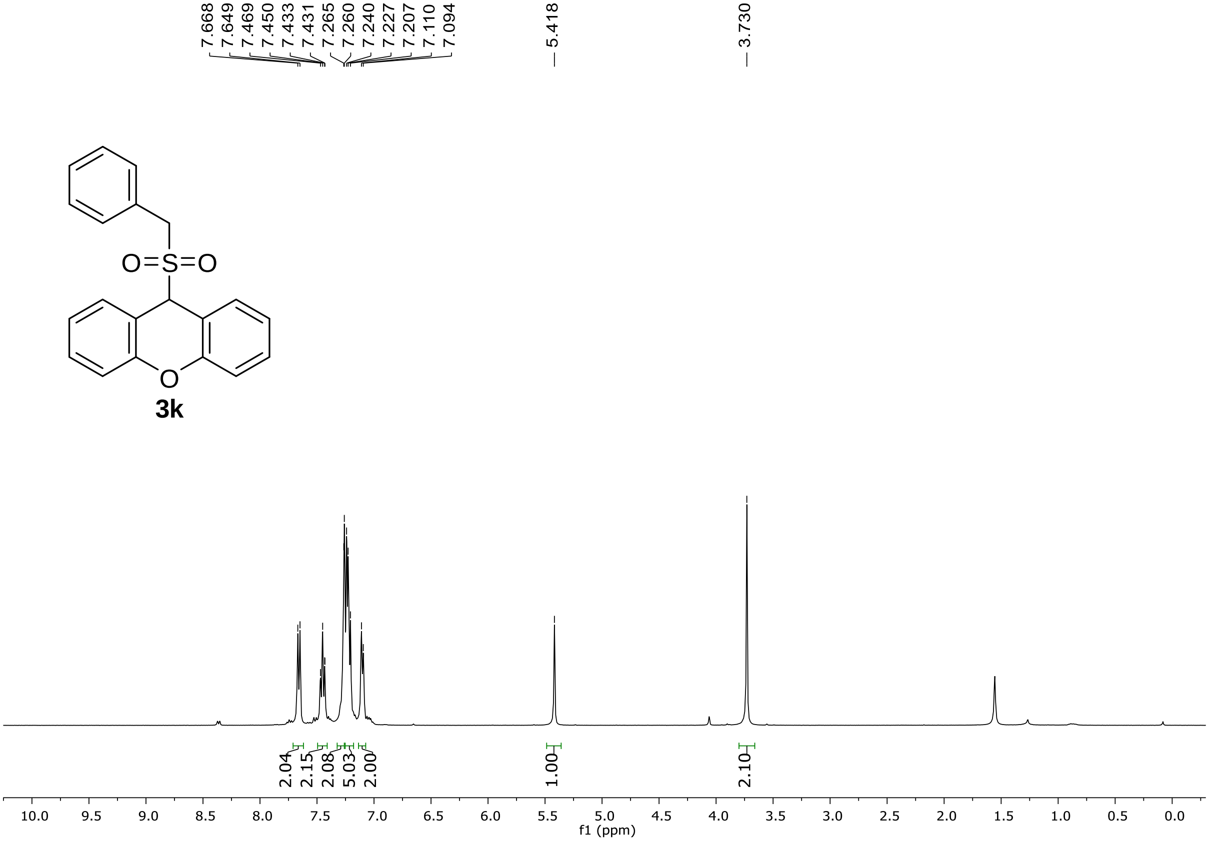
^{1}H NMR spectrum of **3j** (400 MHz, $CDCl_3$):



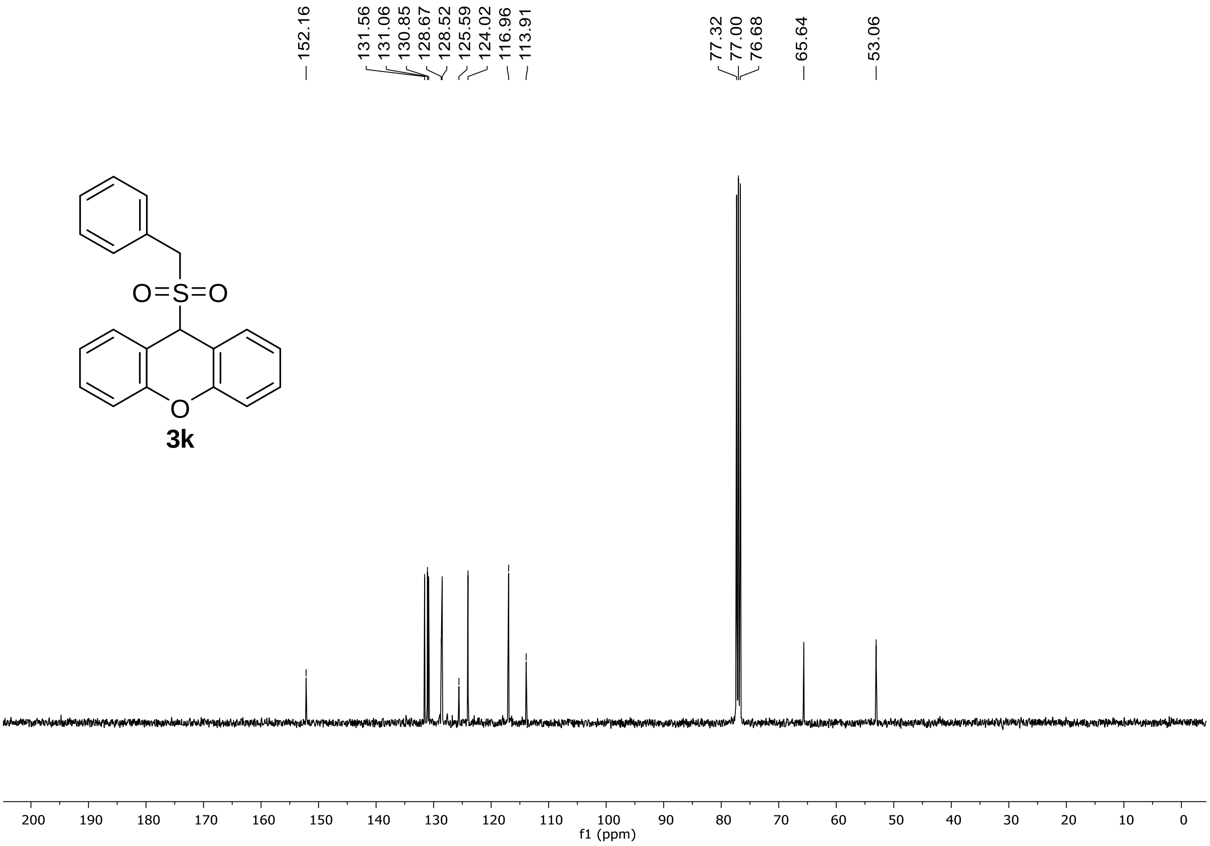
^{13}C {^{1}H} NMR spectrum of **3j** (100 MHz, CDCl$_3$):



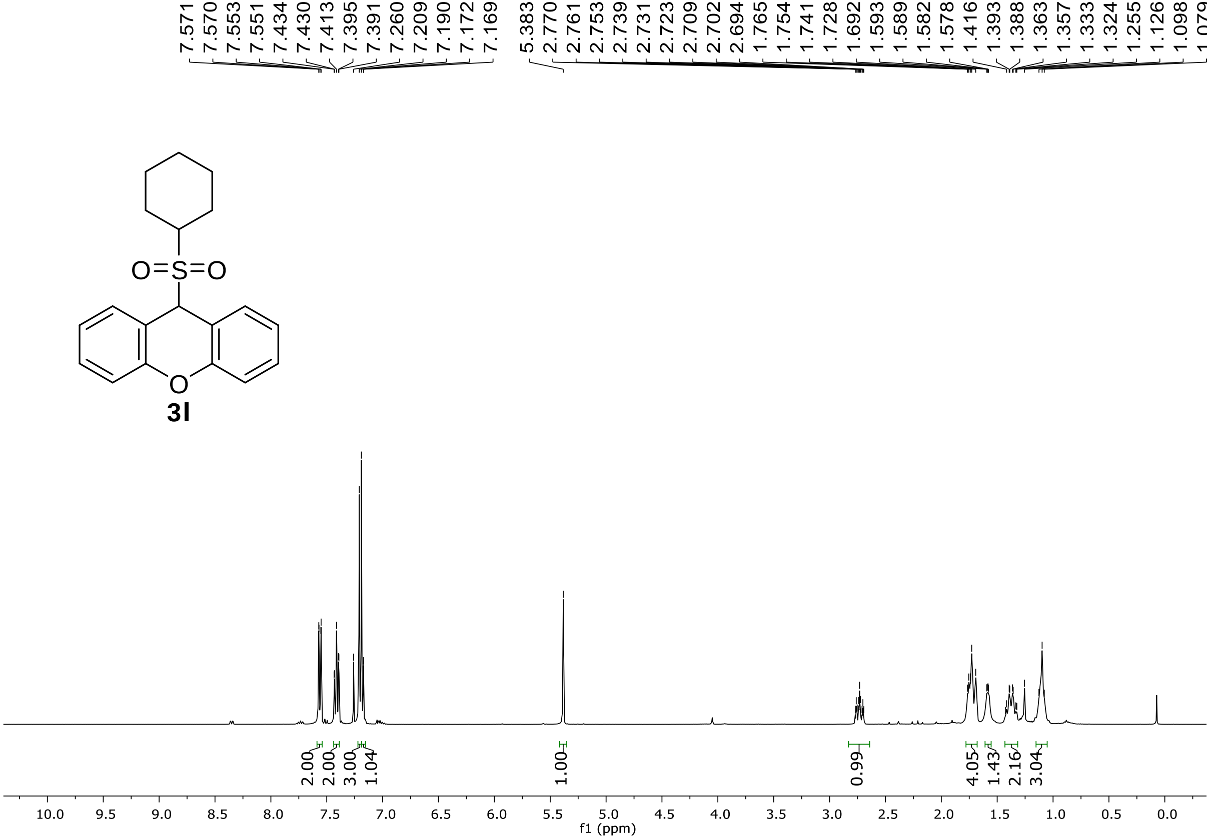
^{1}H NMR spectrum of **3k** (400 MHz, CDCl$_3$):



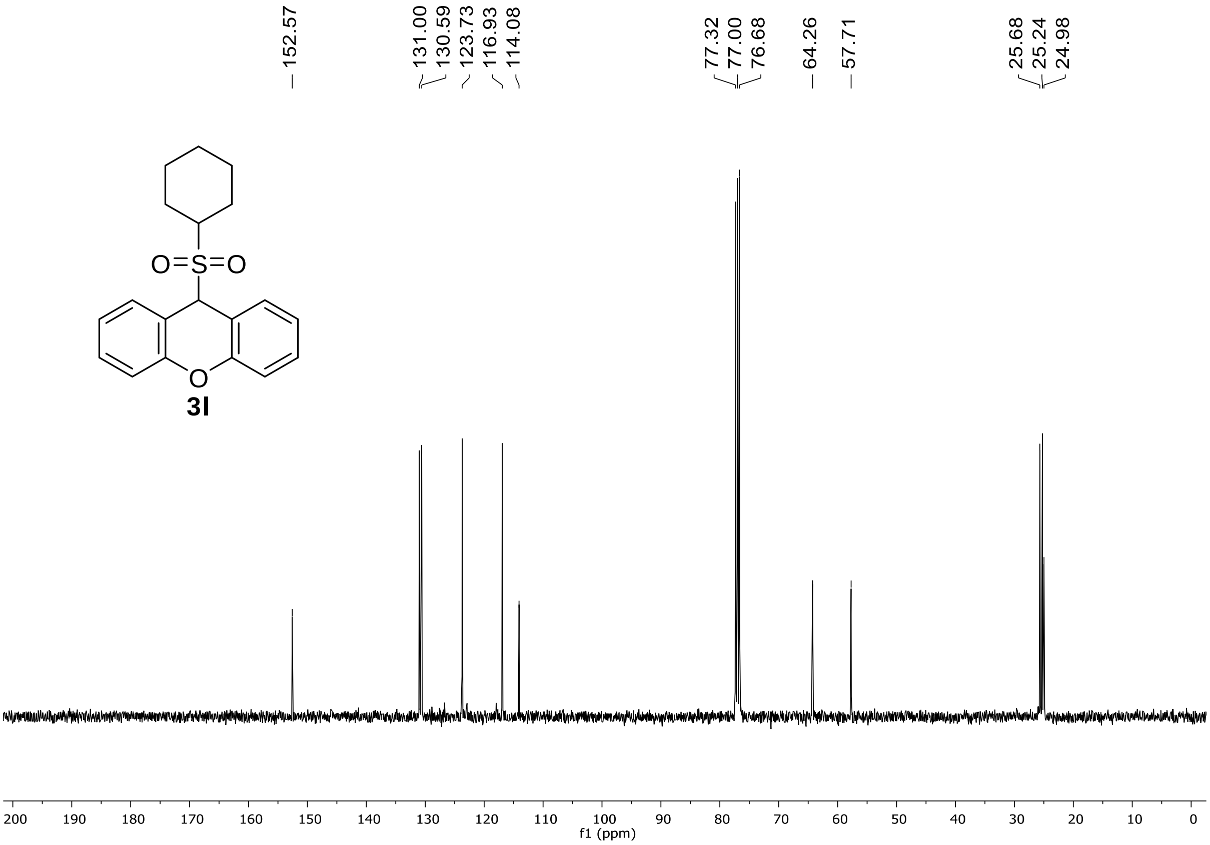
^{13}C {^{1}H} NMR spectrum of **3k**(100 MHz, $CDCl_3$):



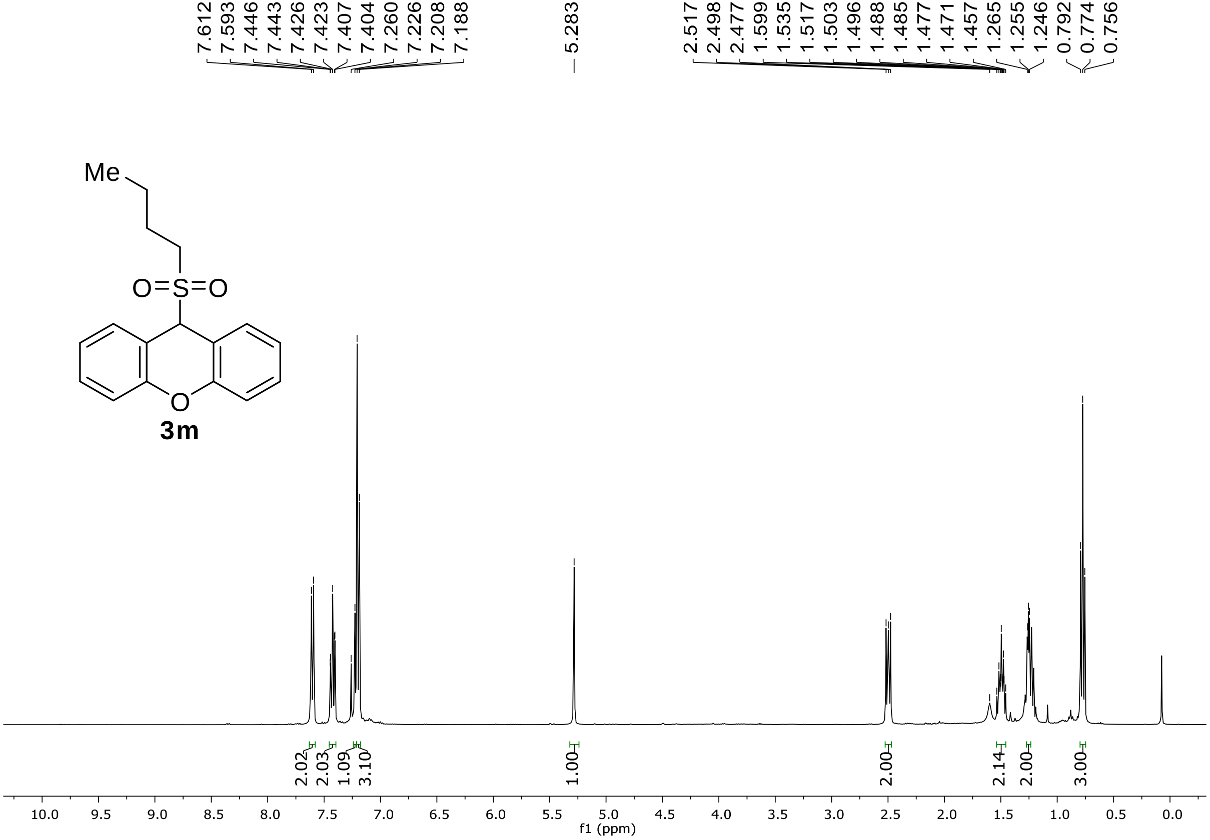
^{1}H NMR spectrum of **3l** (400 MHz, $CDCl_3$):



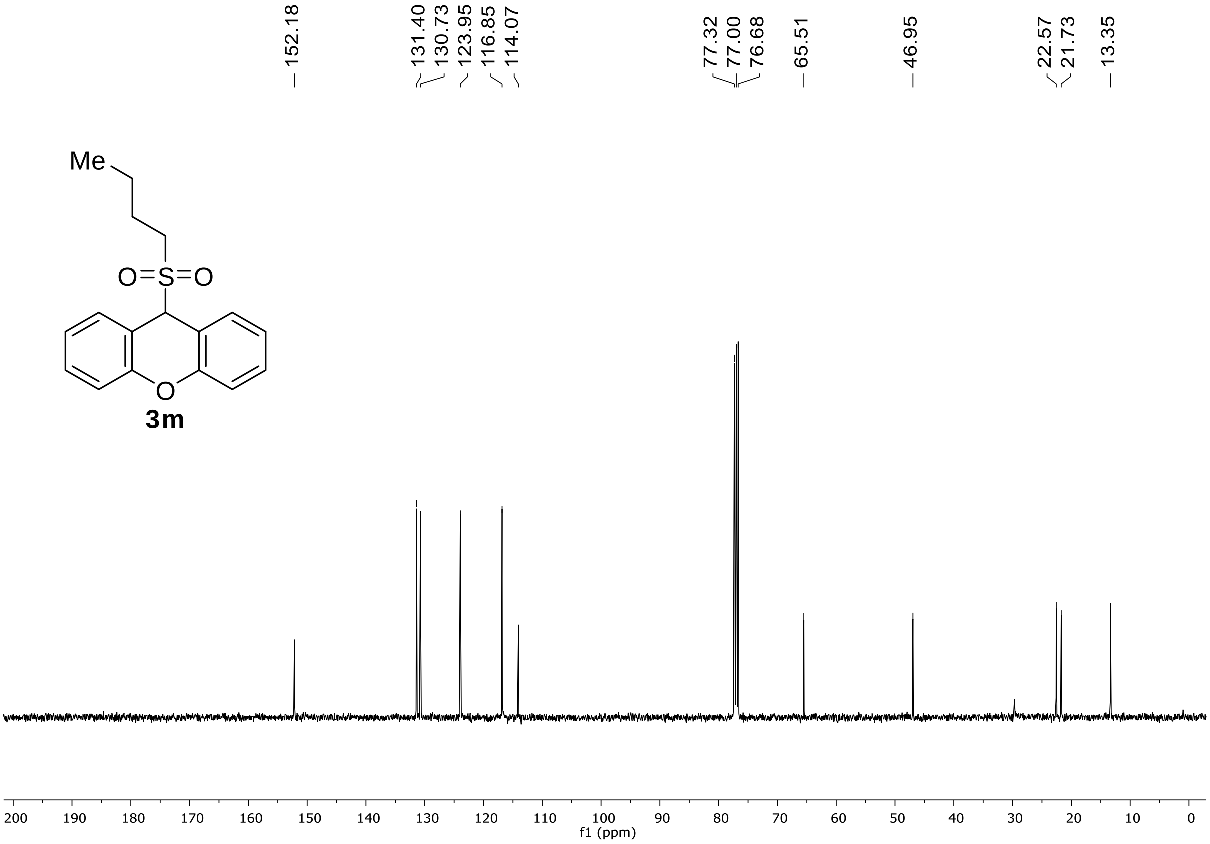
^{13}C {^{1}H} NMR spectrum of **3k** (100 MHz, CDCl$_3$):



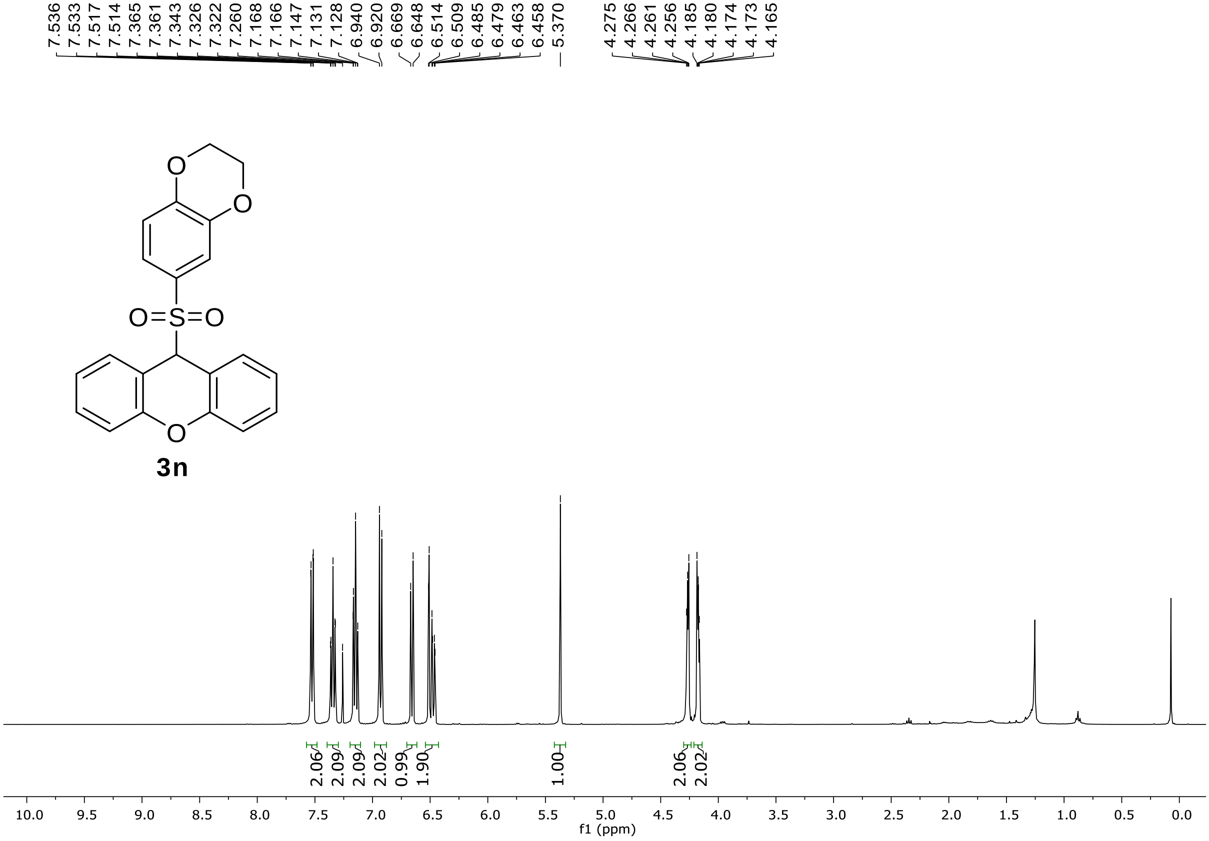
^{1}H NMR spectrum of **3m** (400 MHz, CDCl$_3$):



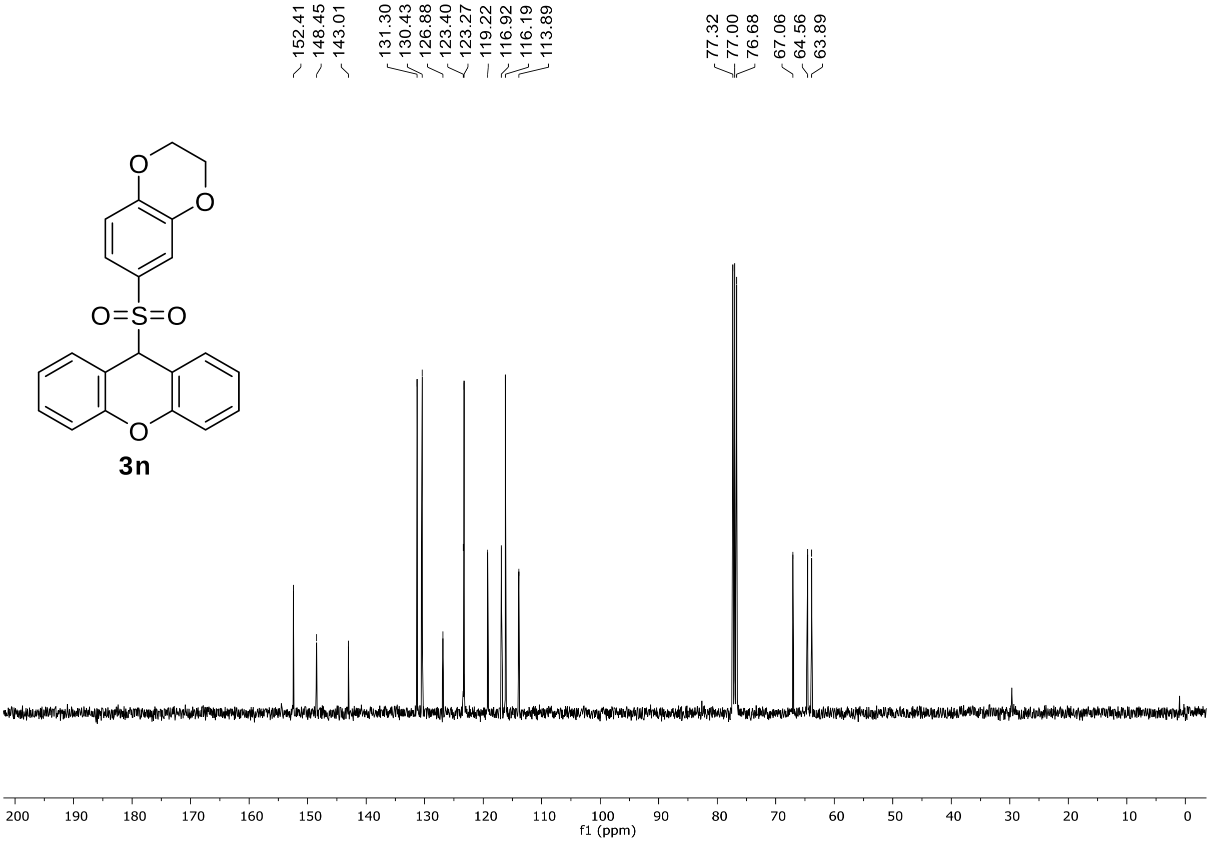
$^{13}C\ \{^1H\}$ NMR spectrum of **3m** (100 MHz, $CDCl_3$):



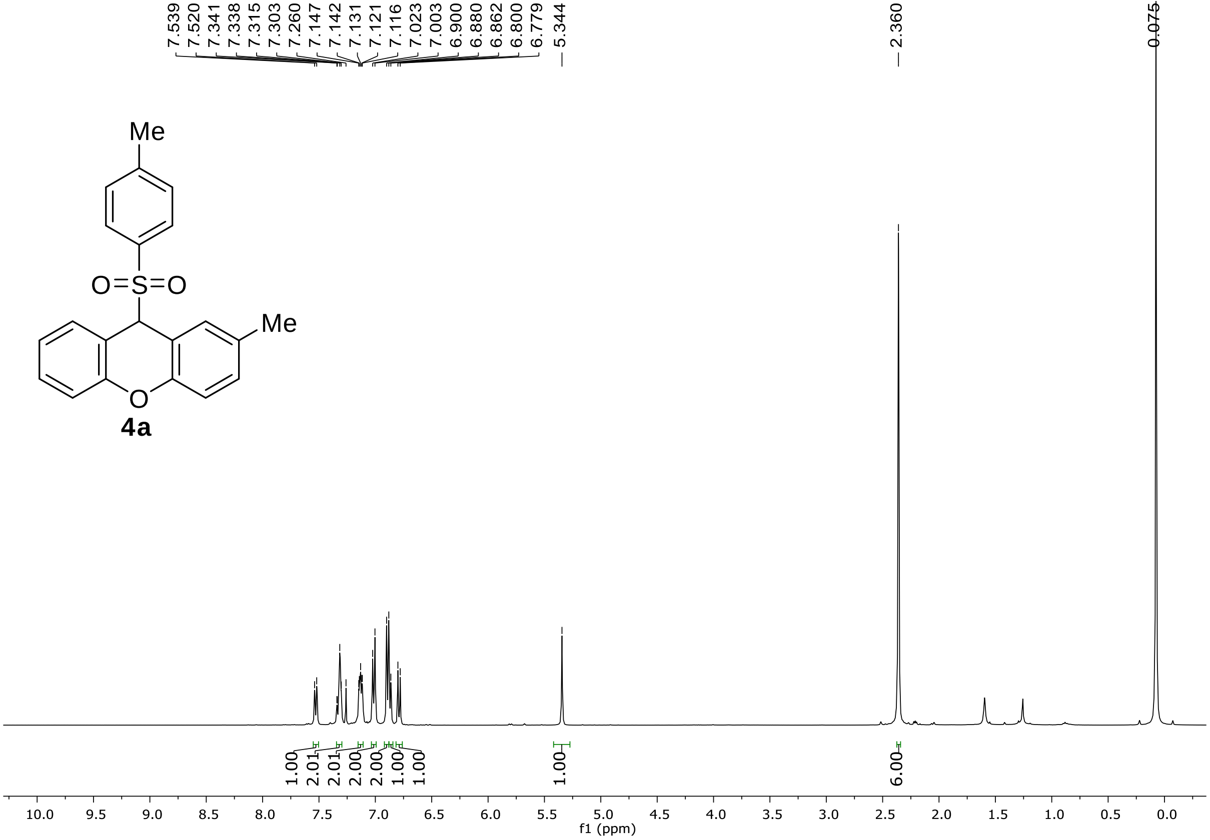
^1H NMR spectrum of **3n** (400 MHz, $CDCl_3$):



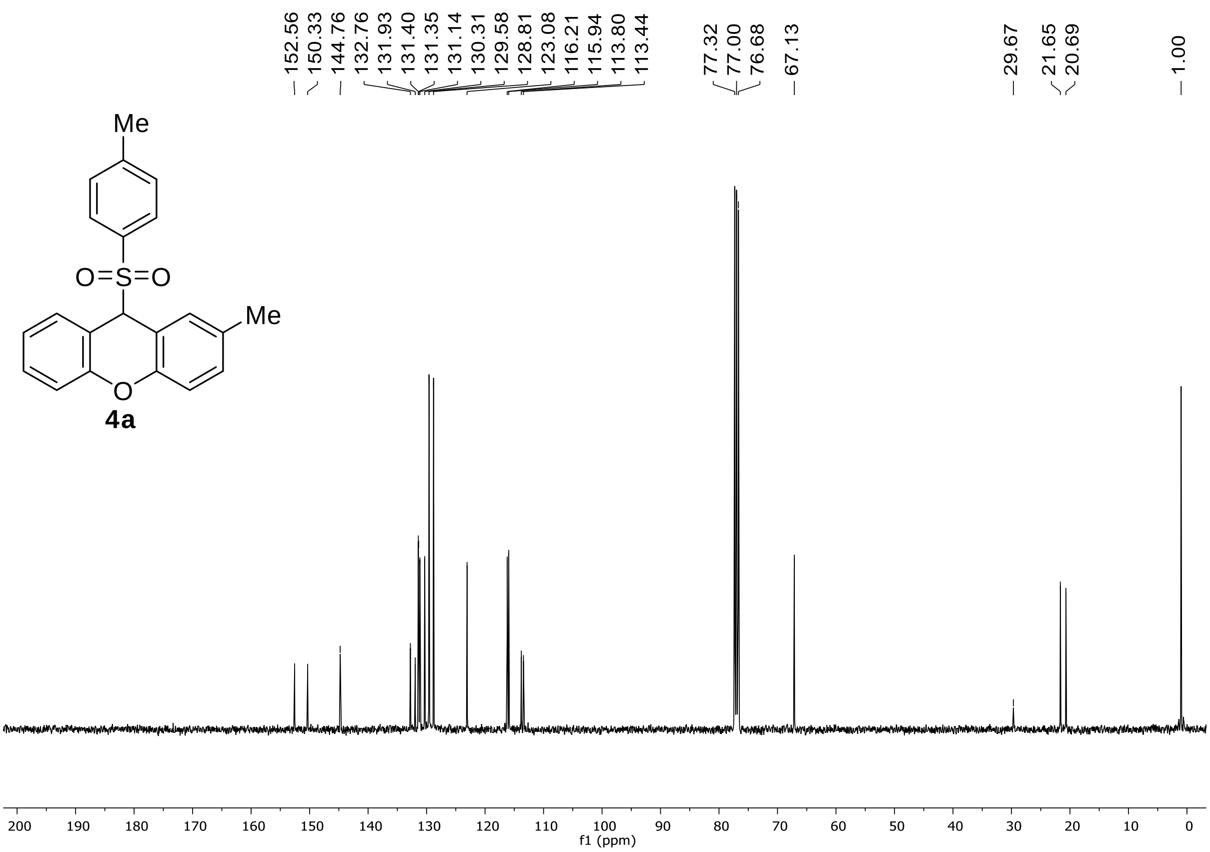
^{13}C {^{1}H} NMR spectrum of **3n** (100 MHz, CDCl$_3$):



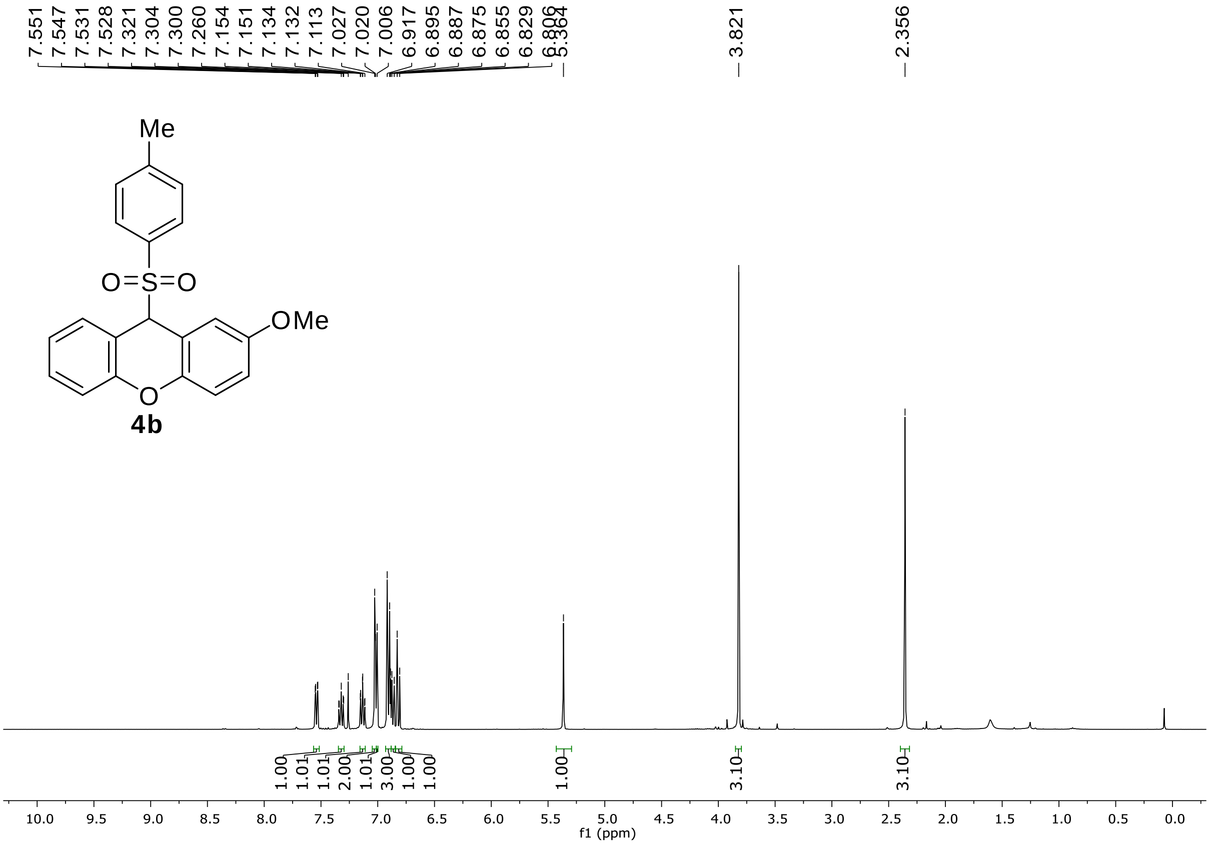
^{1}H NMR spectrum of **4a** (400 MHz, CDCl$_3$):



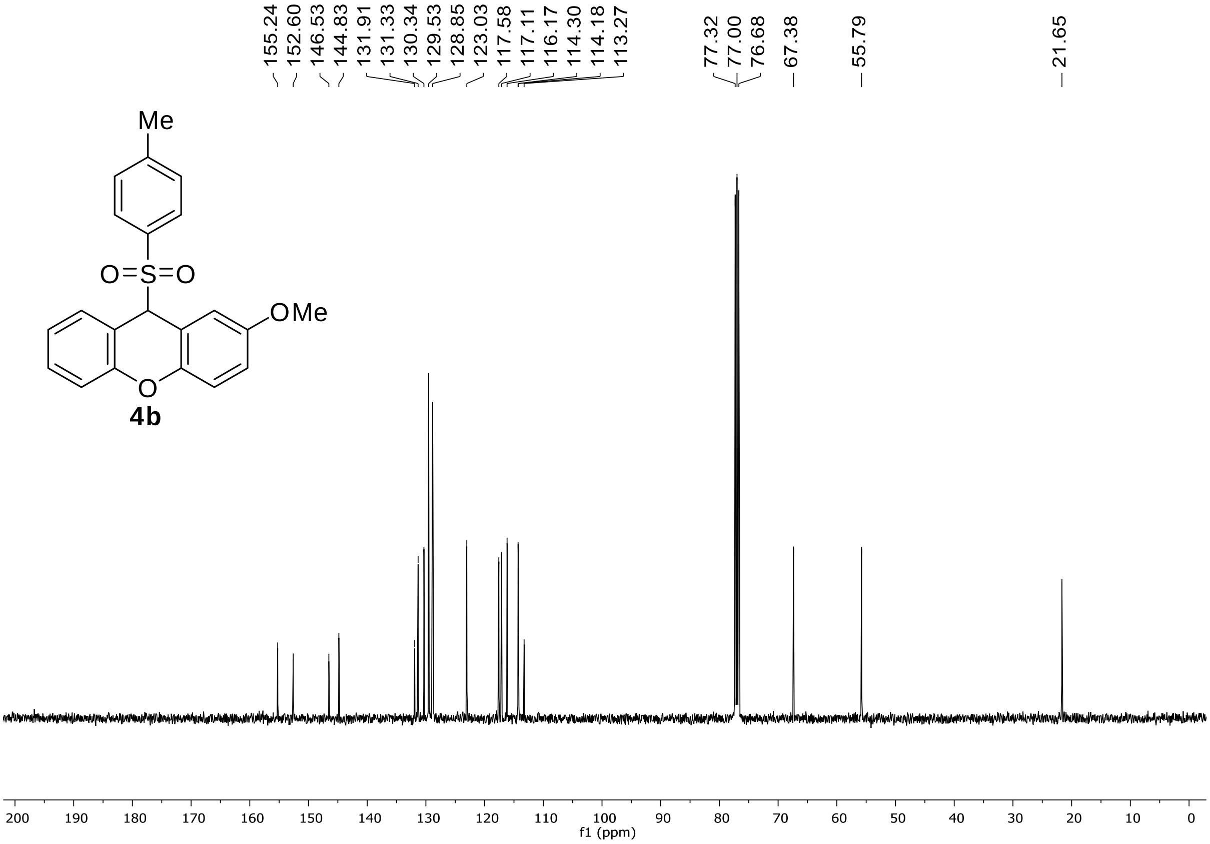
$^{13}C\ \{^{1}H\}$ NMR spectrum of **4a** (100 MHz, $CDCl_3$):



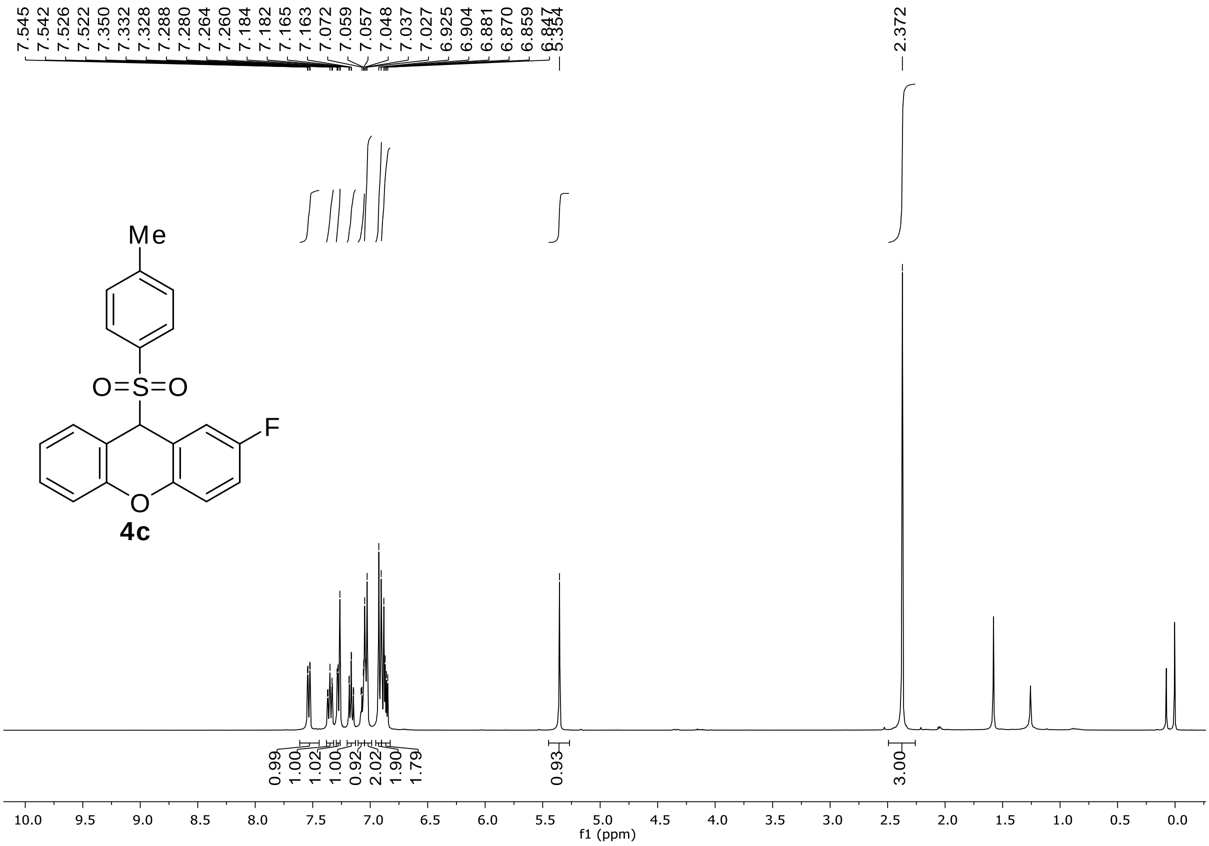
^{1}H NMR spectrum of **4b** (400 MHz, $CDCl_3$):



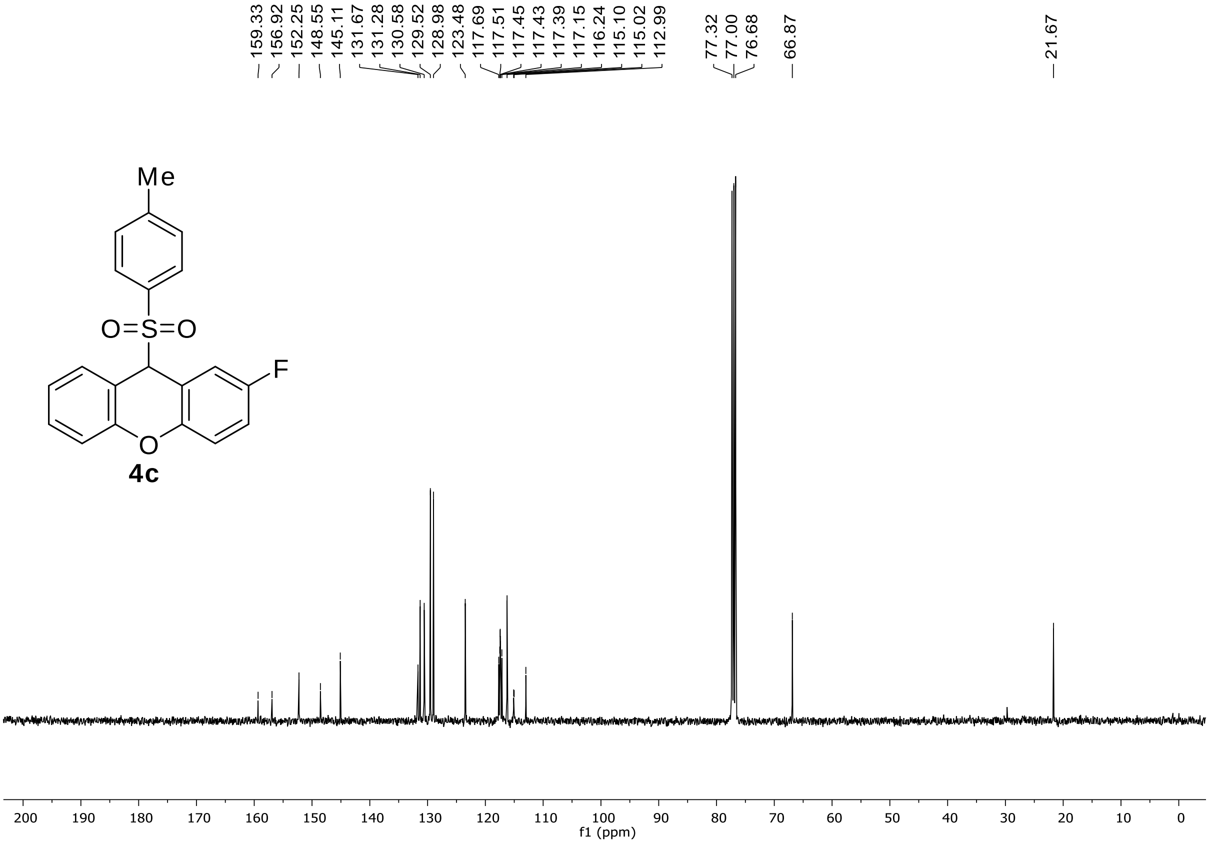
^{13}C {^{1}H} NMR spectrum of **4b** (100 MHz, $CDCl_3$):



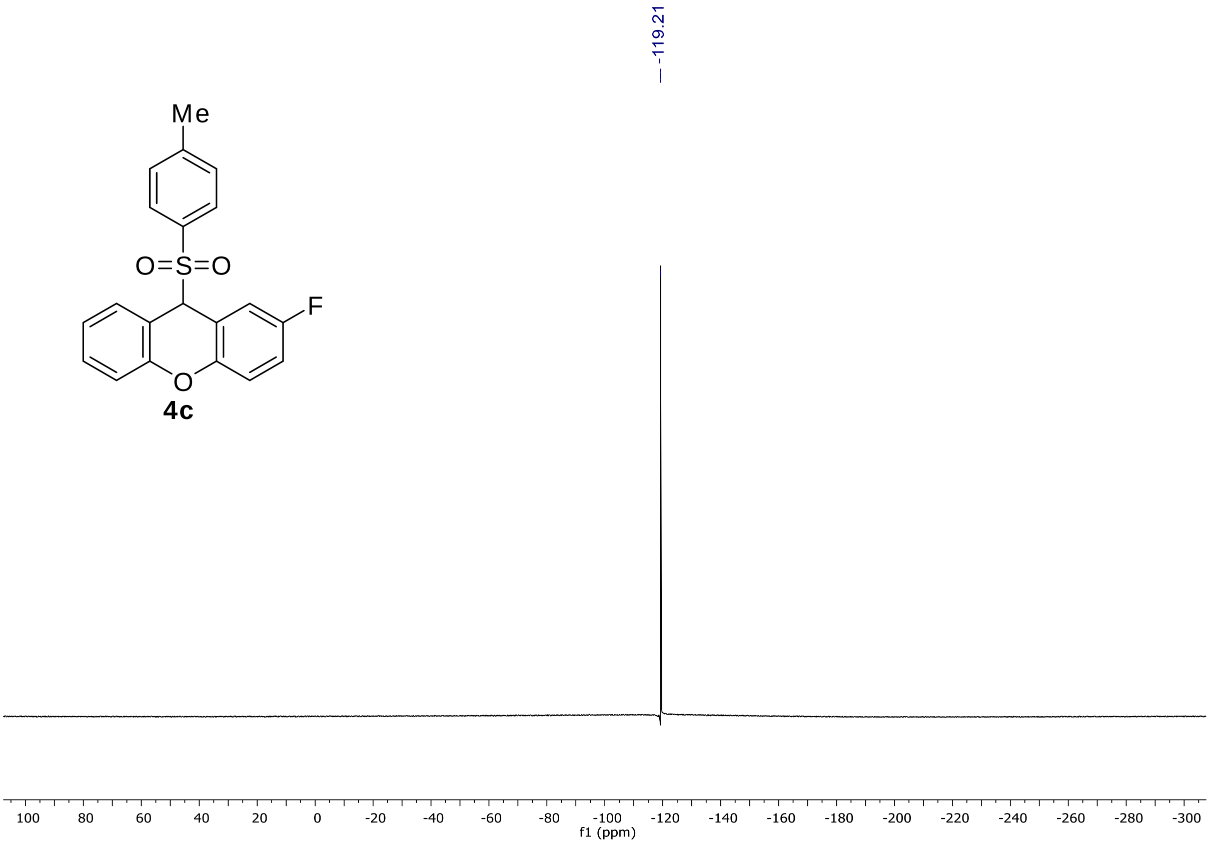
^{1}H NMR spectrum of **4c** (400 MHz, $CDCl_3$):



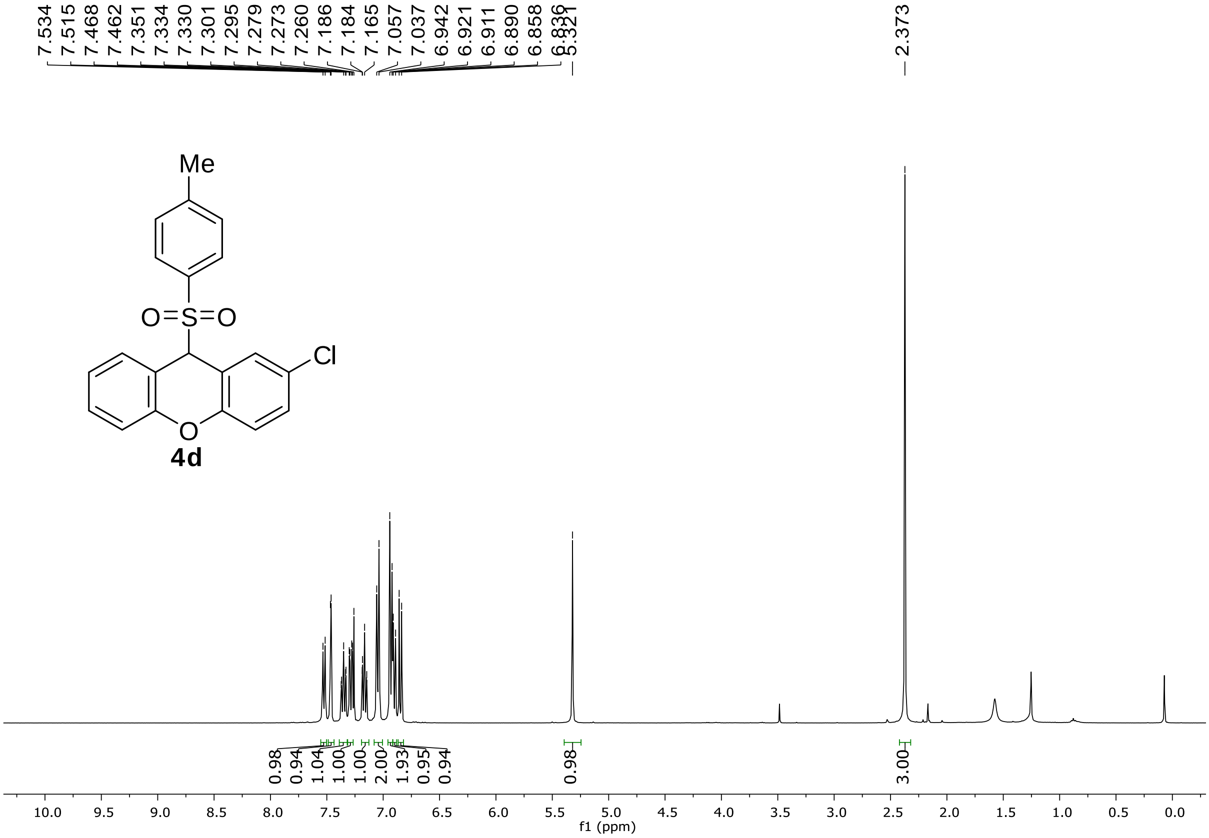
^{13}C {^{1}H} NMR spectrum of **4c** (100 MHz, $CDCl_3$):



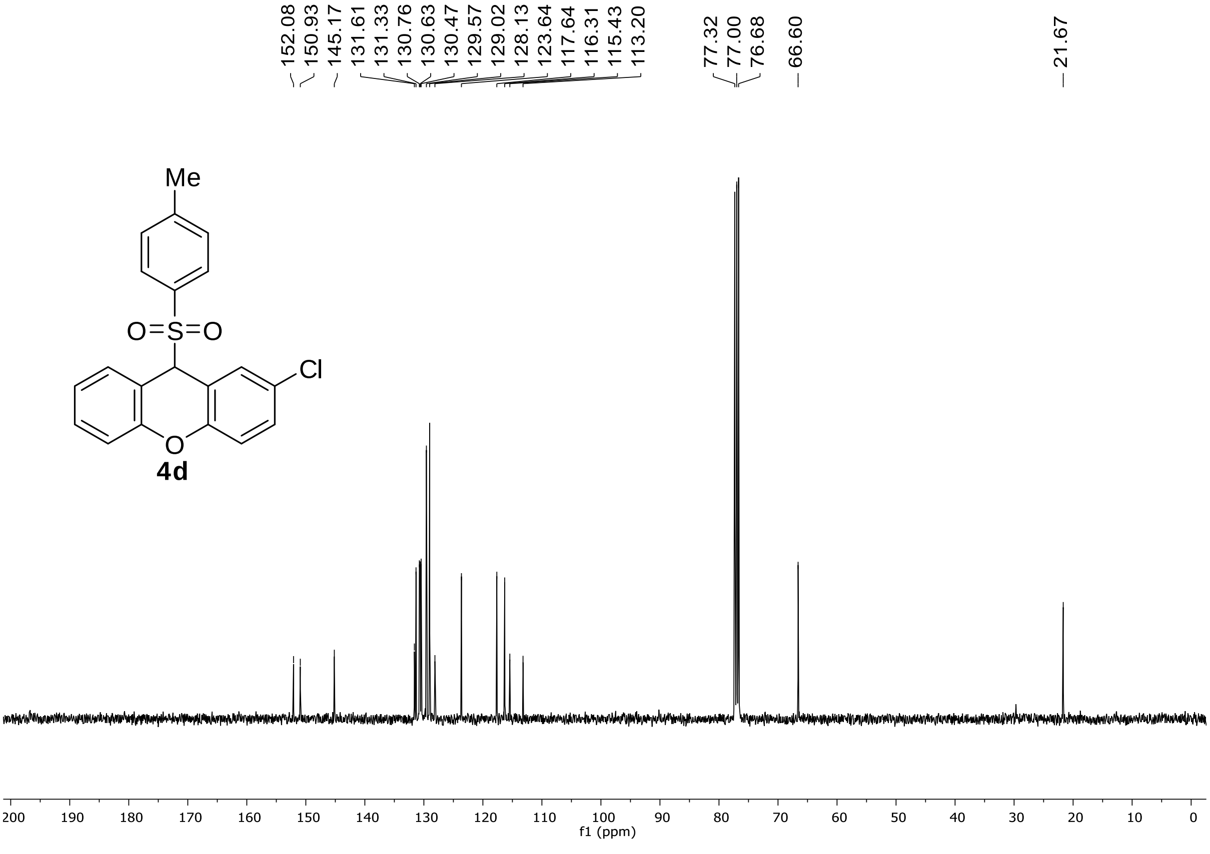
^{19}F NMR spectrum of **4c** (376 MHz, $CDCl_3$):



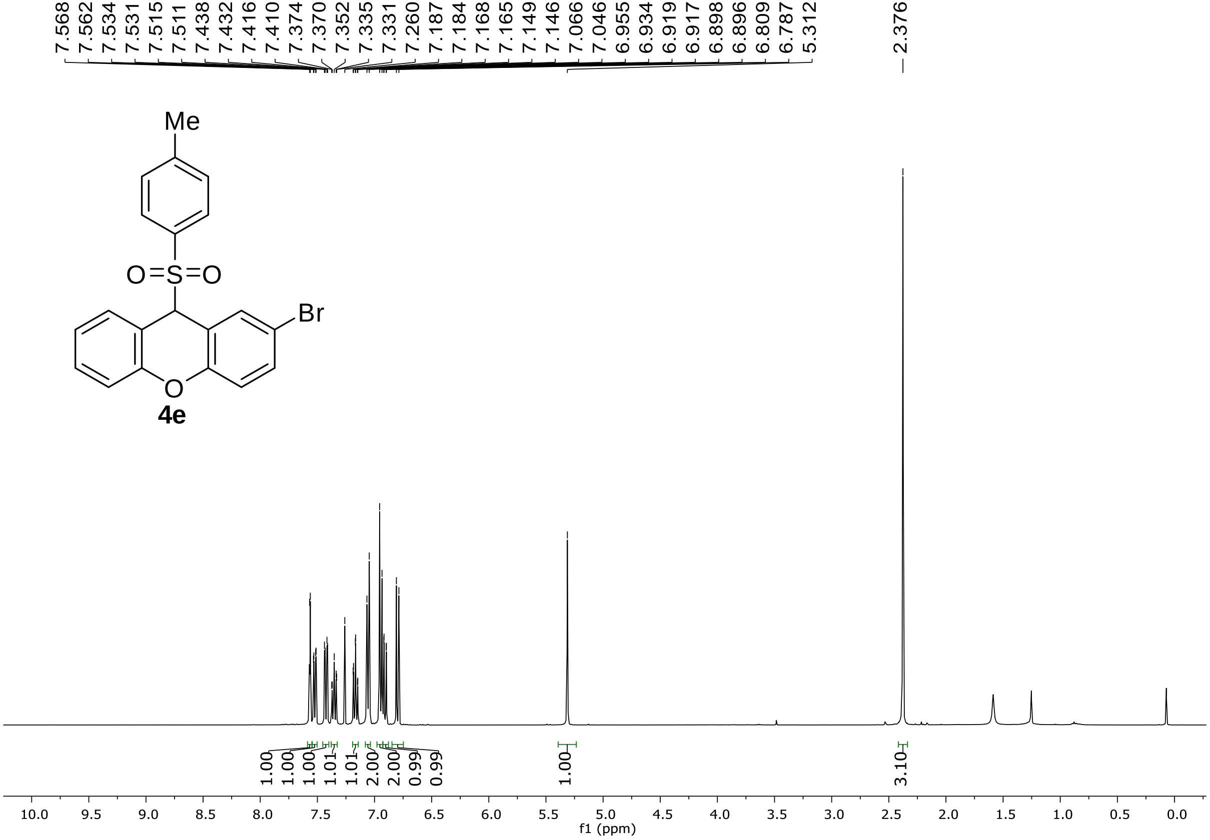
^{1}H NMR spectrum of **4d** (400 MHz, $CDCl_3$):



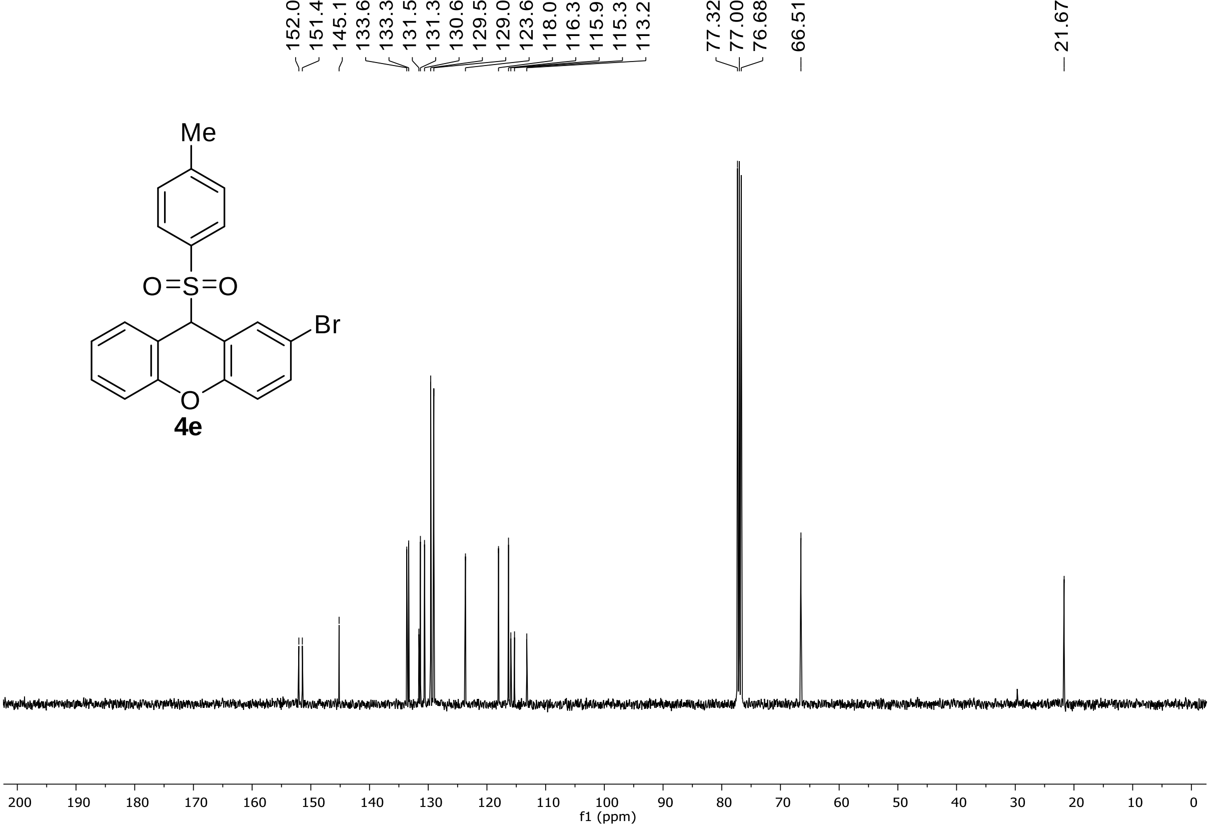
^{13}C {^{1}H} NMR spectrum of **4d** (100 MHz, $CDCl_3$):



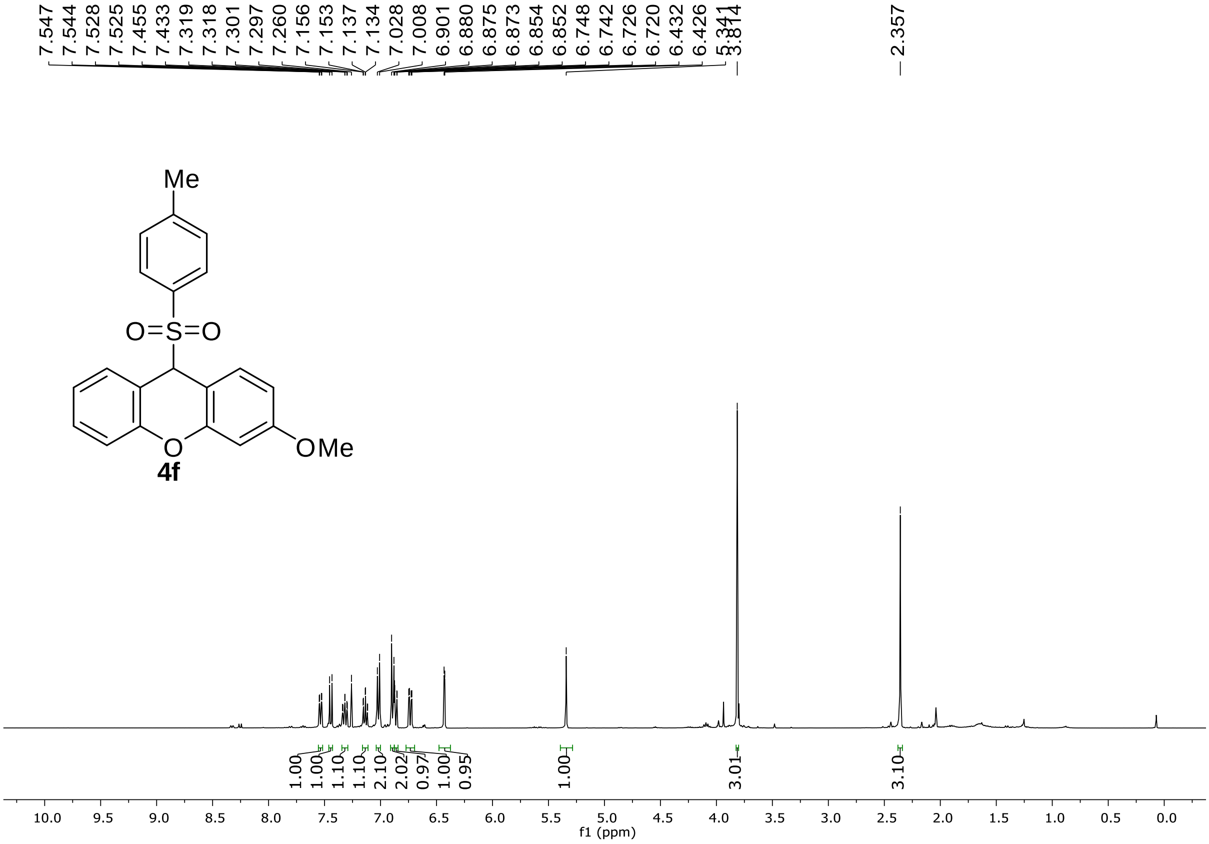
^{1}H NMR spectrum of **4e** (400 MHz, $CDCl_3$):



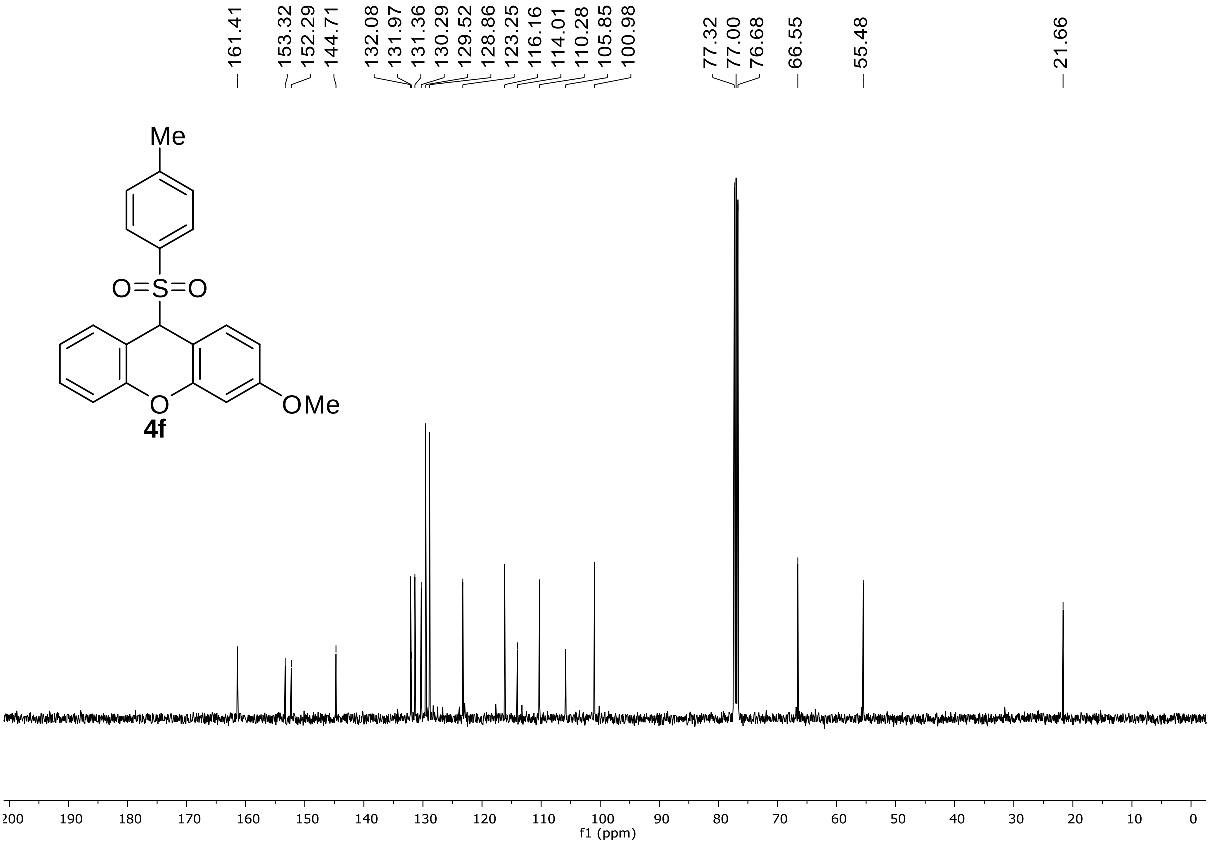
^{13}C {^{1}H} NMR spectrum of **4e** (100 MHz, $CDCl_3$):



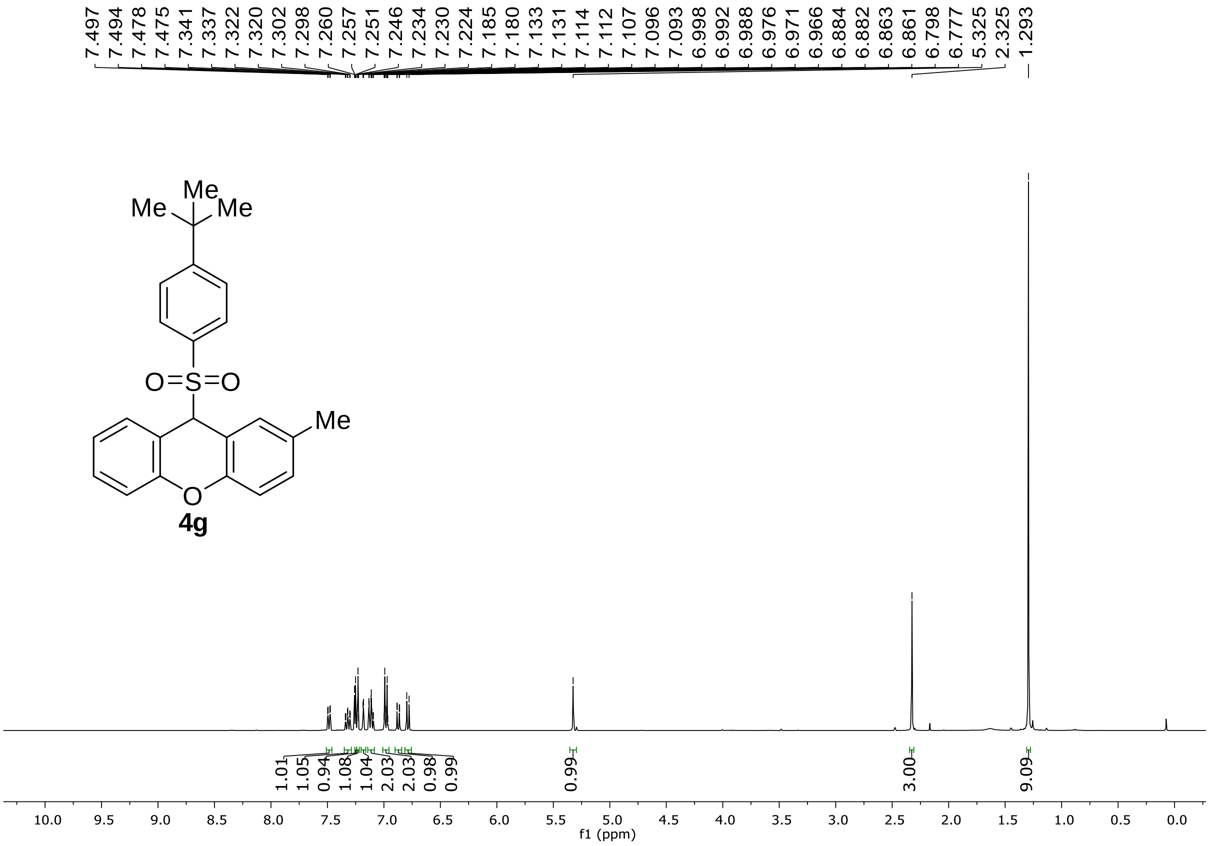
^{1}H NMR spectrum of **4f** (400 MHz, CDCl$_3$):



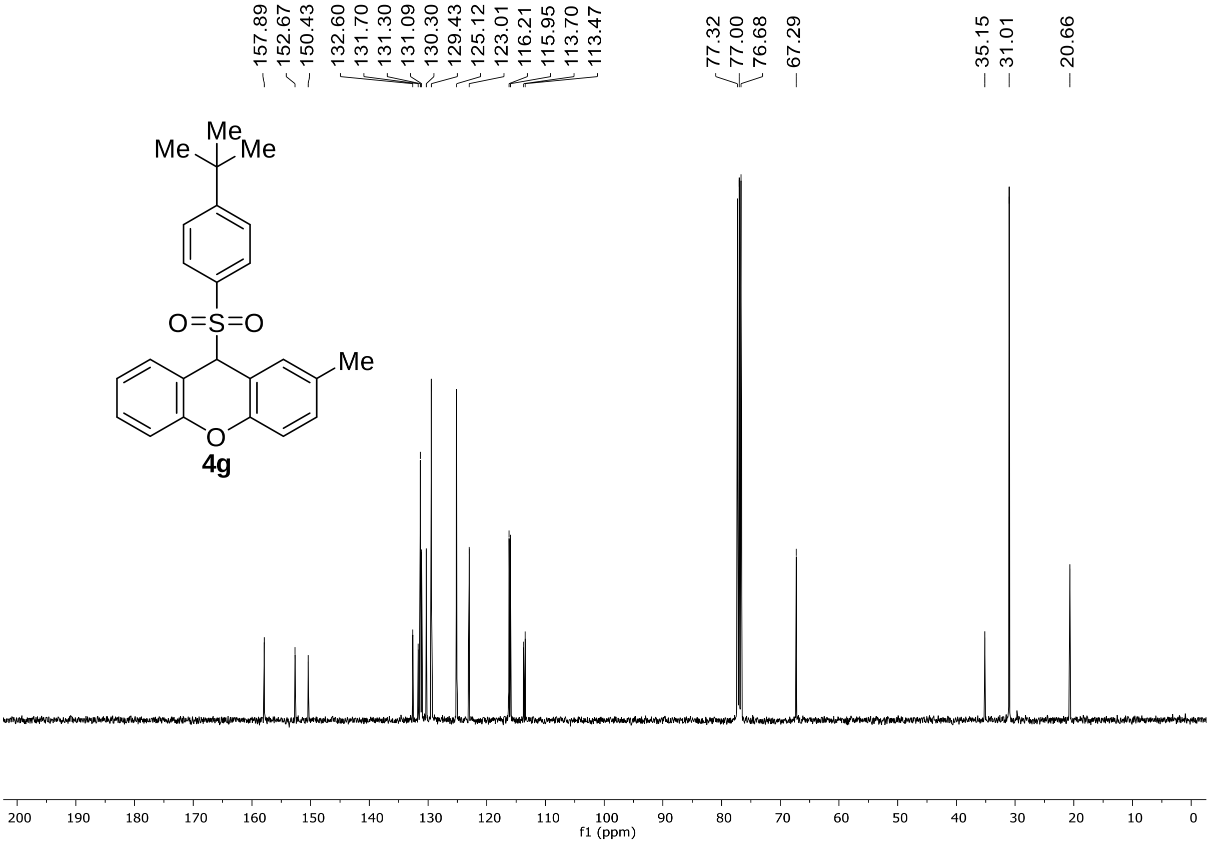
^{13}C {^{1}H} NMR spectrum of **4f** (100 MHz, CDCl$_3$):



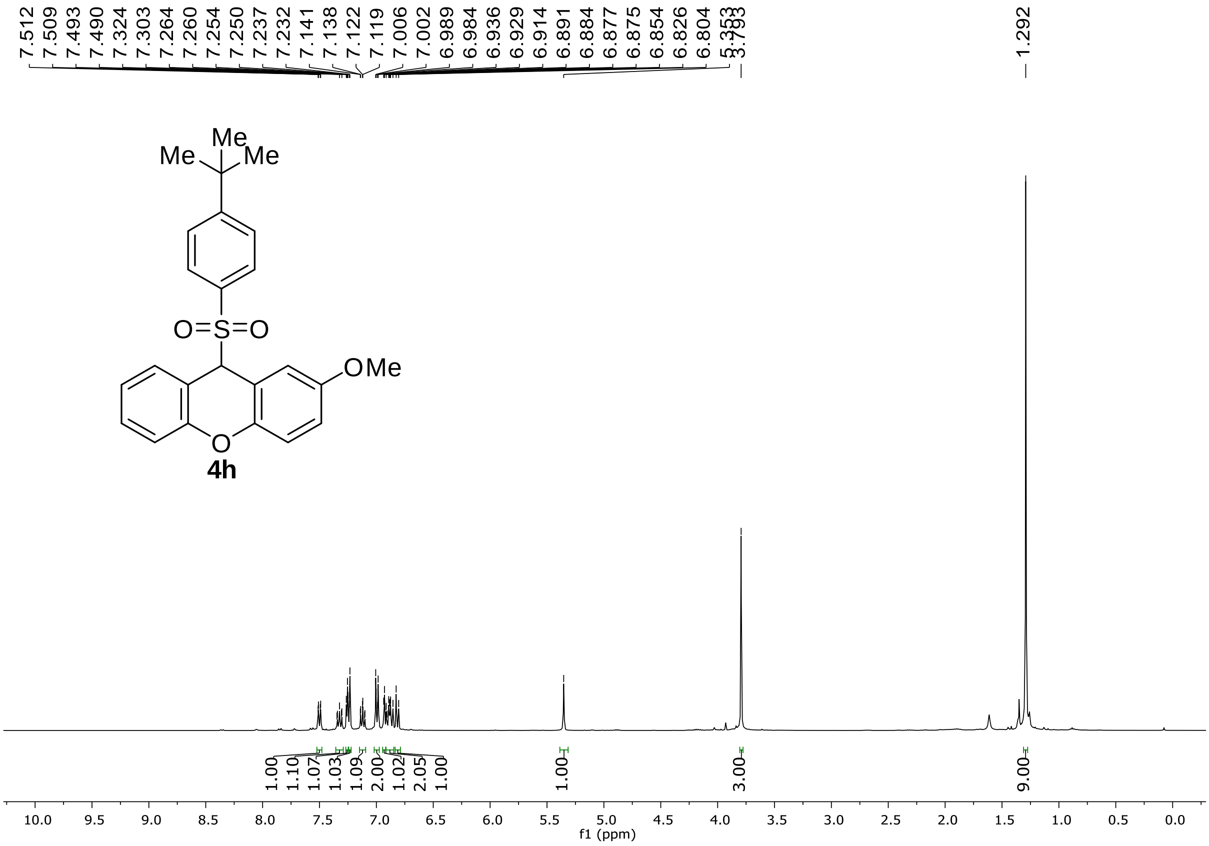
^{1}H NMR spectrum of **4g** (400 MHz, CDCl$_3$):



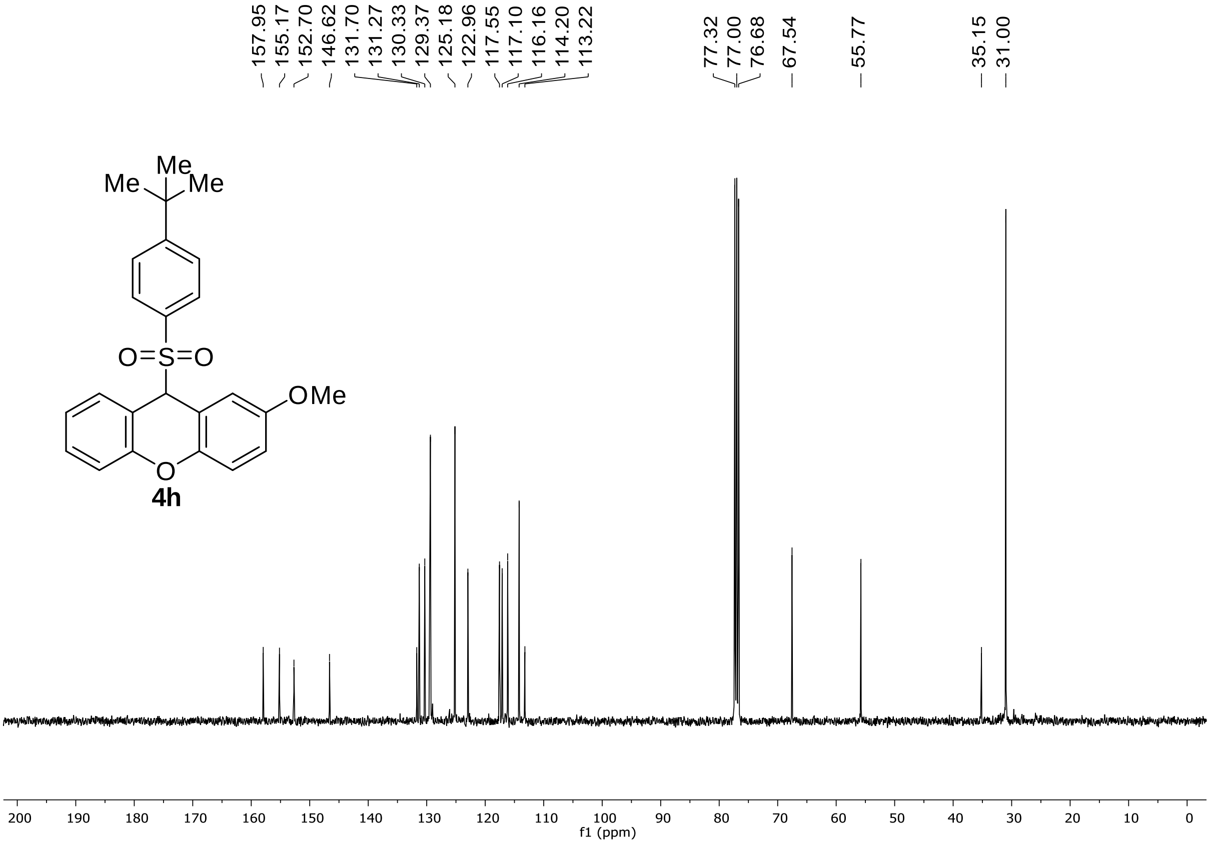
^{13}C {^{1}H} NMR spectrum of **4g** (100 MHz, CDCl$_3$):



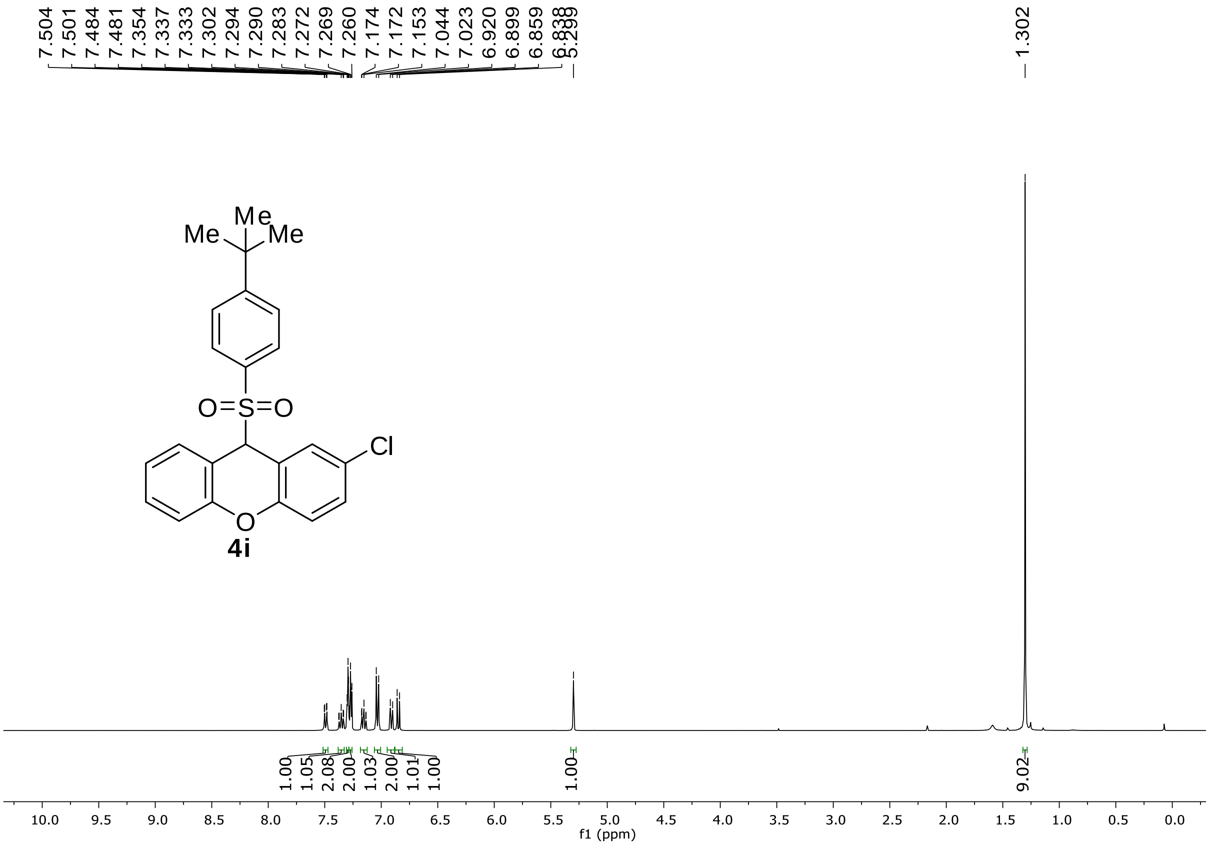
^{1}H NMR spectrum of **4h** (400 MHz, $CDCl_3$):



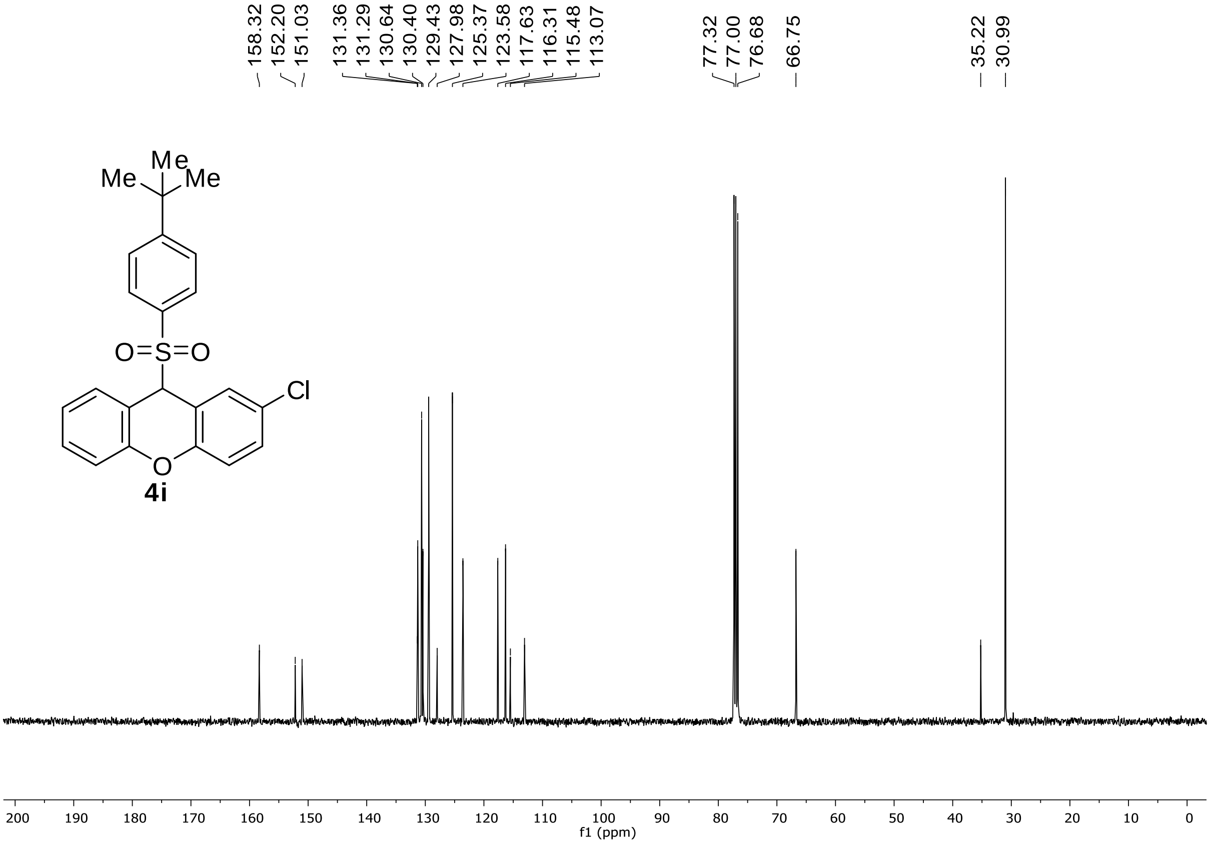
^{13}C {^{1}H} NMR spectrum of **4h** (100 MHz, $CDCl_3$):



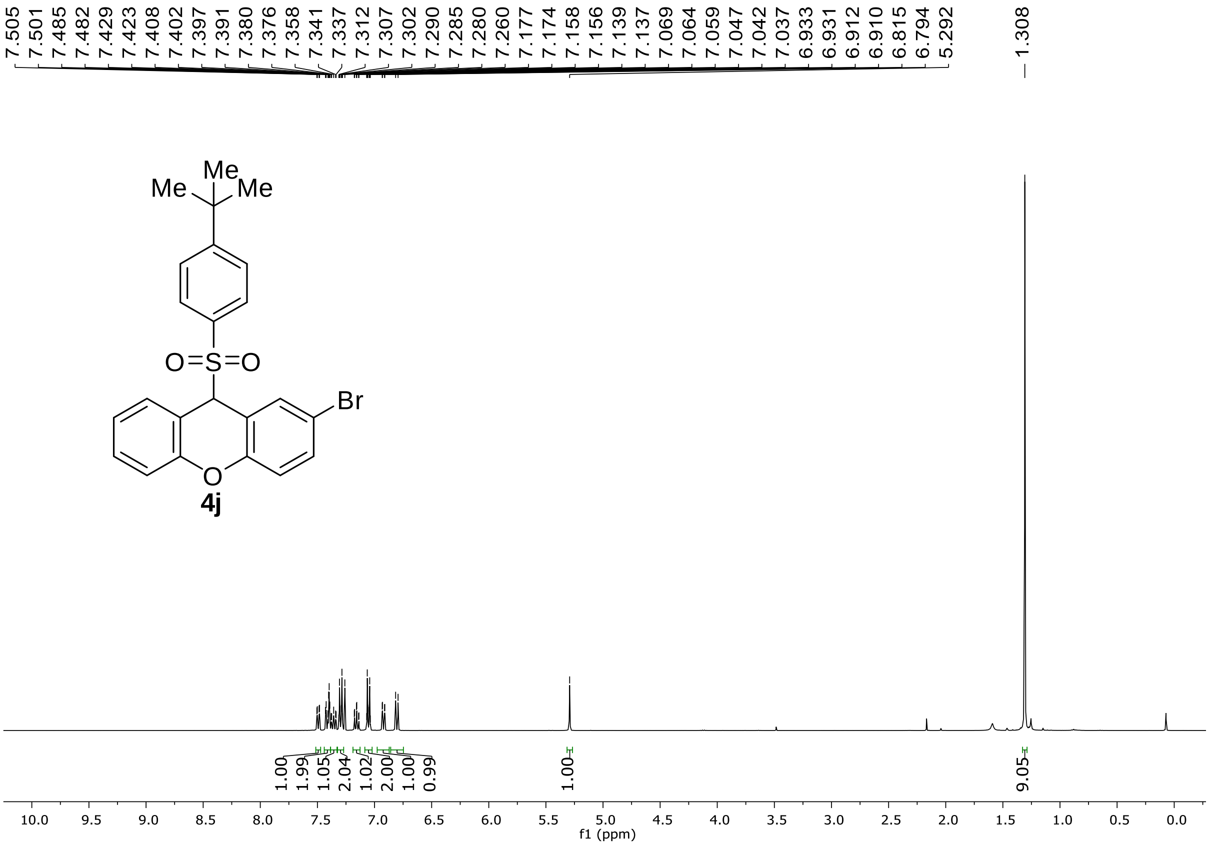
^{1}H NMR spectrum of **4i** (400 MHz, CDCl$_3$):



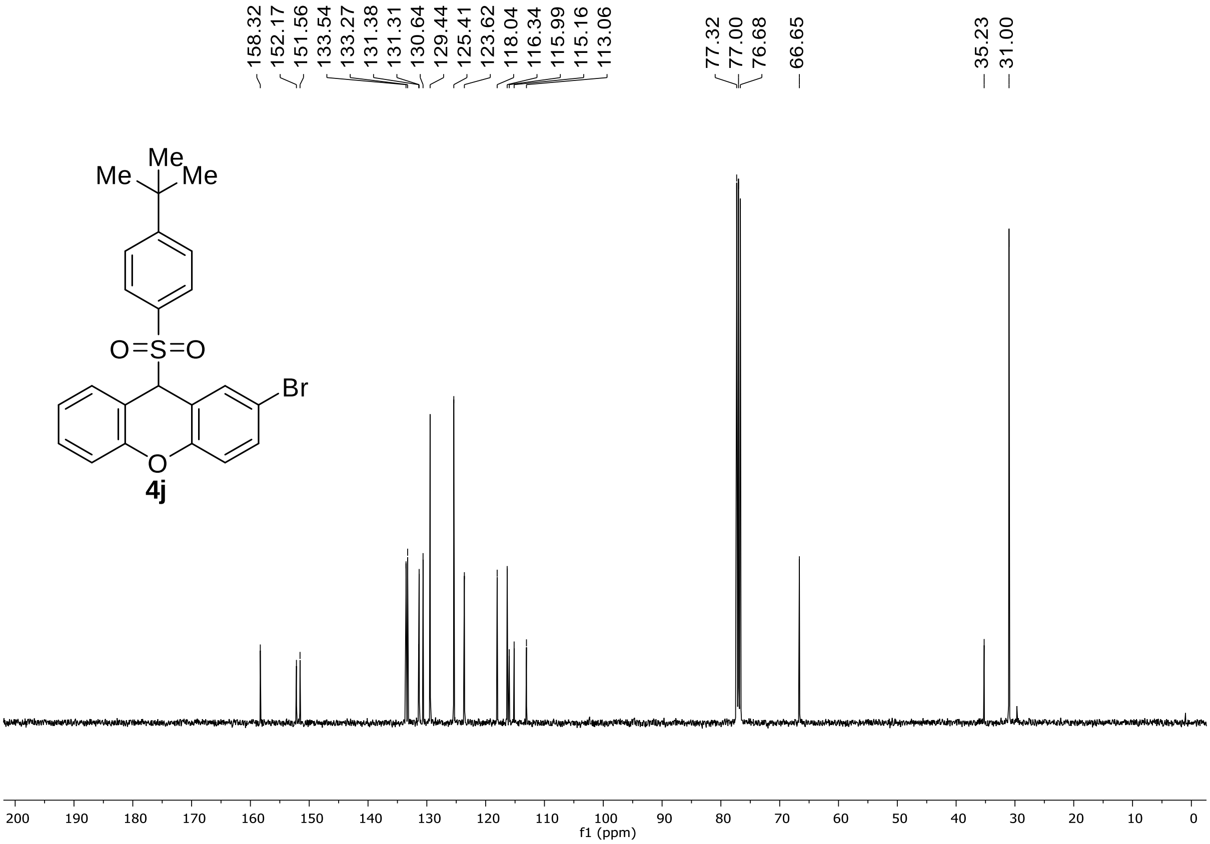
^{13}C {^{1}H} NMR spectrum of **4i** (100 MHz, CDCl$_3$):



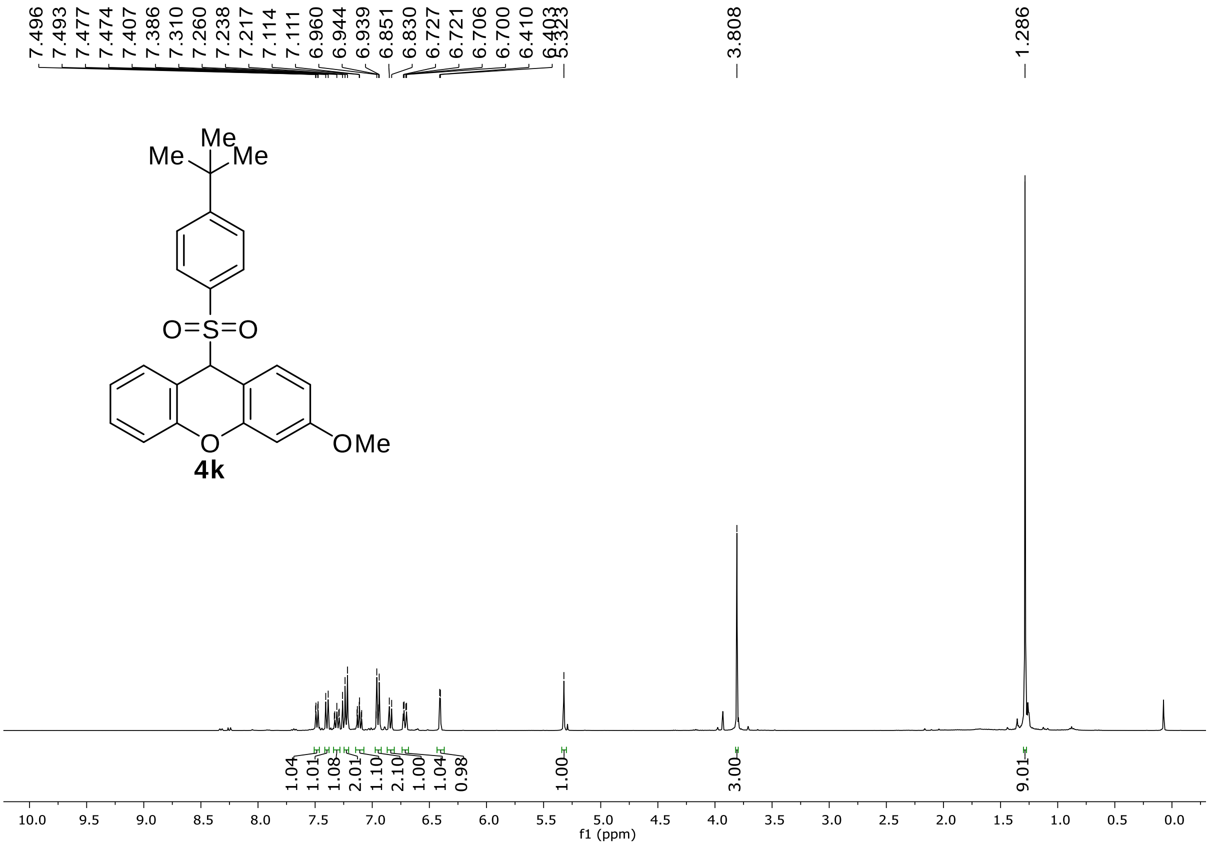
^{1}H NMR spectrum of **4j** (400 MHz, CDCl$_3$):



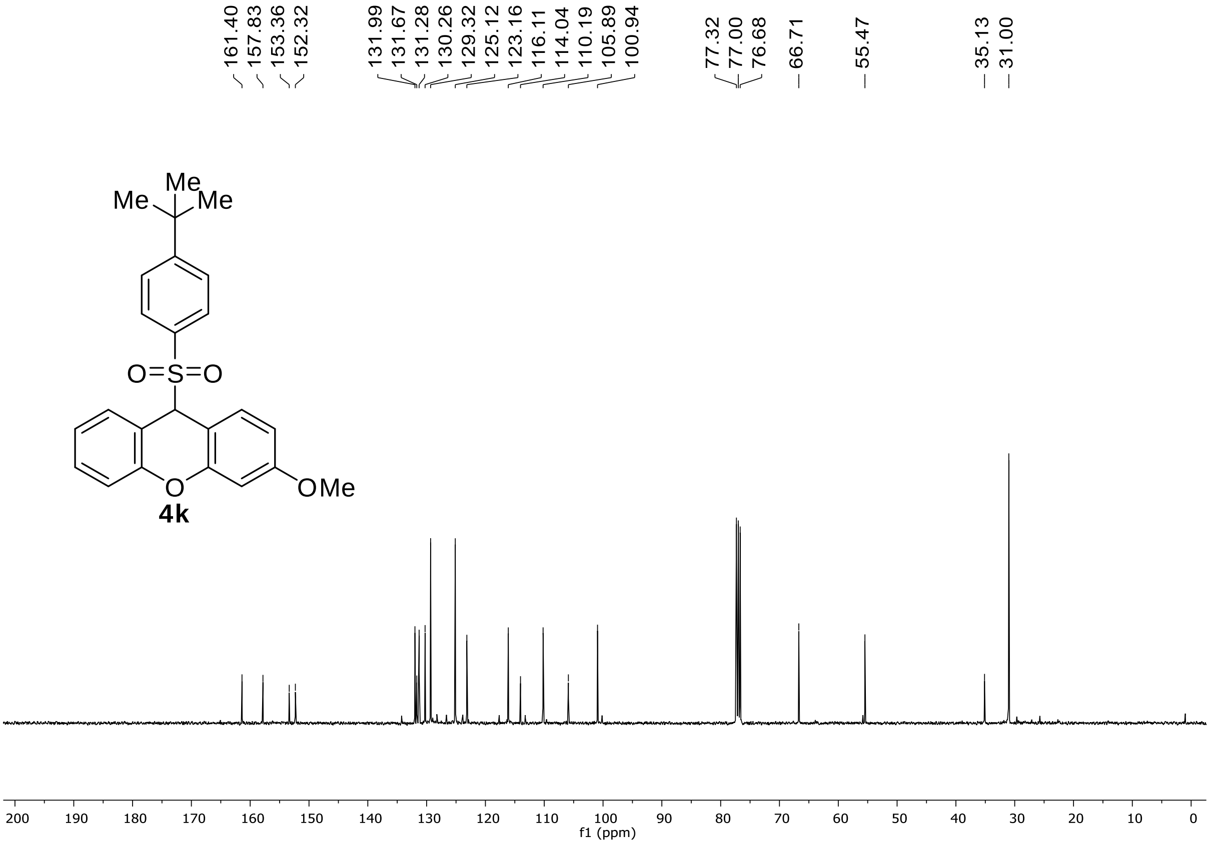
^{13}C {^{1}H} NMR spectrum of **4j** (100 MHz, CDCl$_3$):



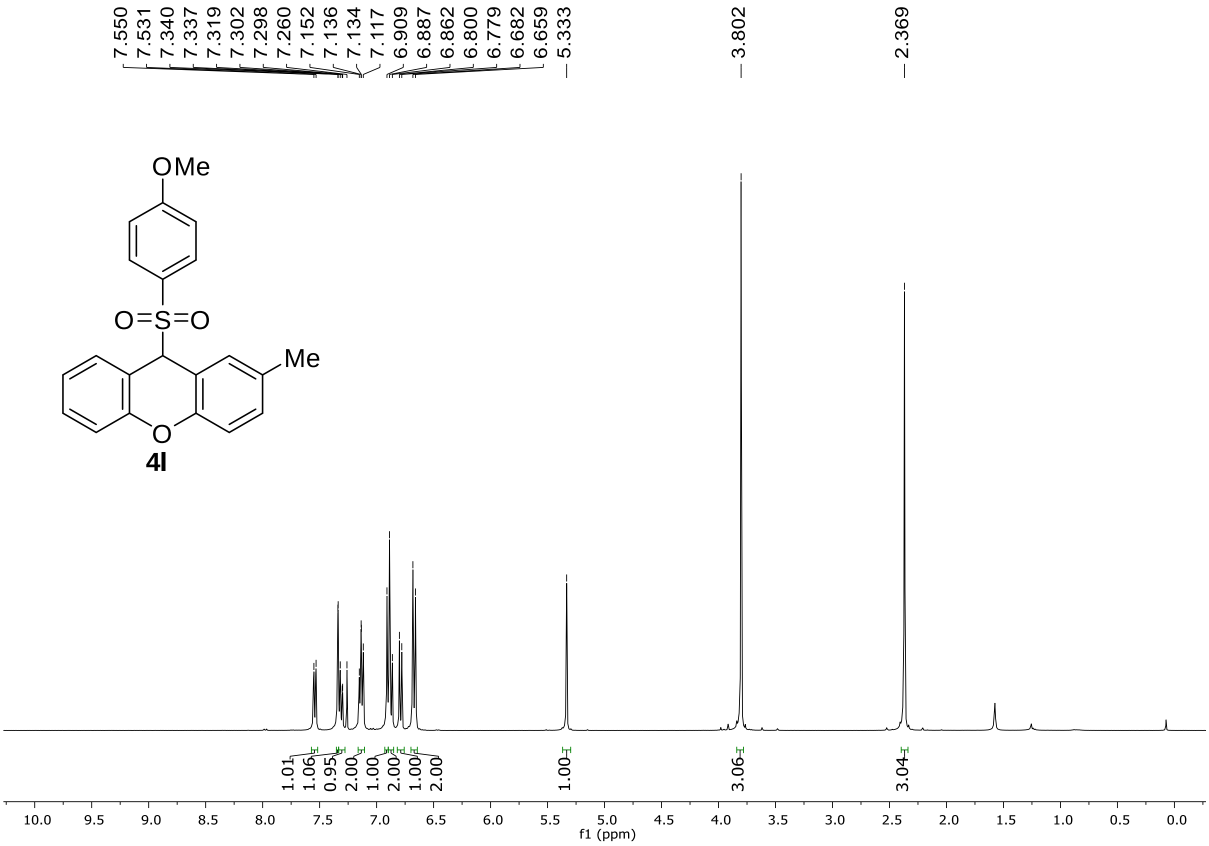
^{1}H NMR spectrum of **4k** (400 MHz, CDCl$_3$):



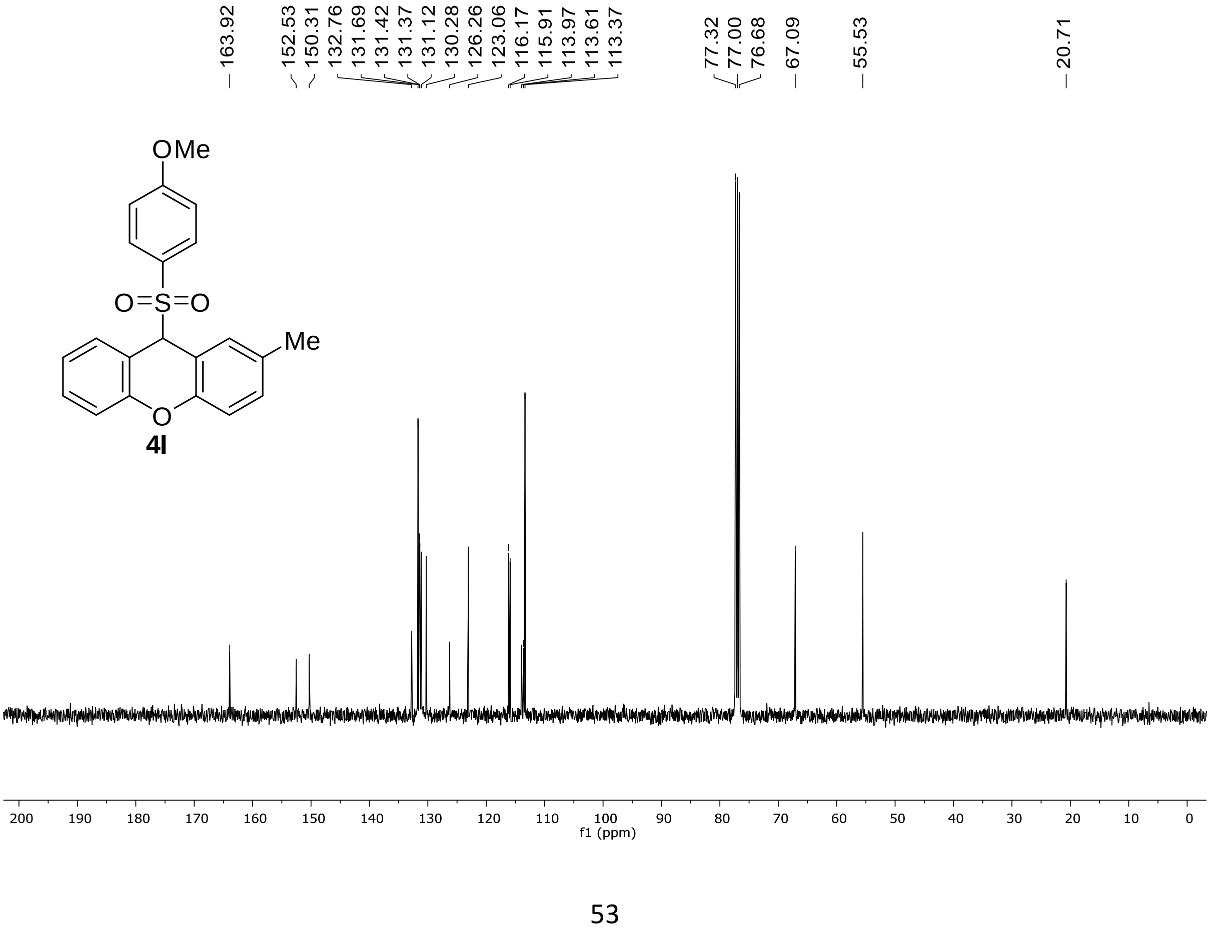
^{13}C {^{1}H} NMR spectrum of **4k** (100 MHz, CDCl$_3$):



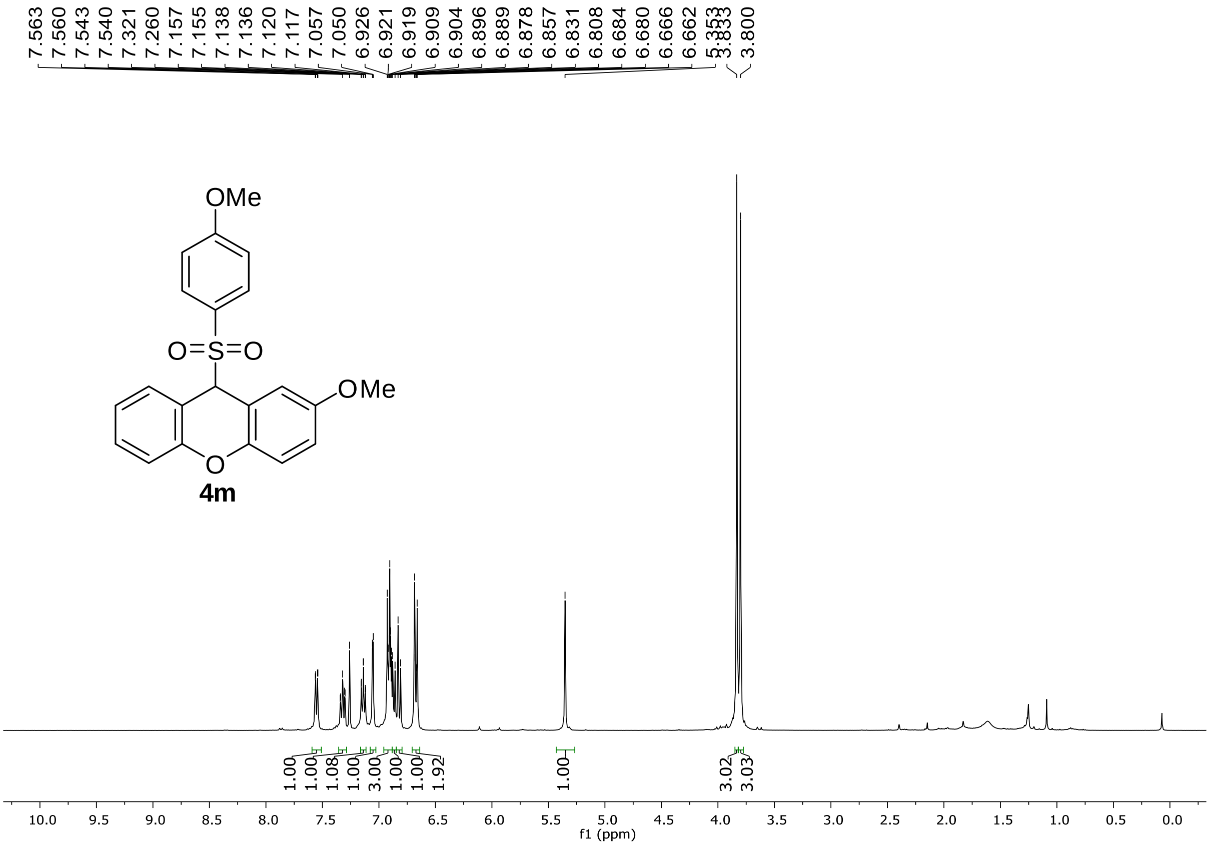
^{1}H NMR spectrum of **4l** (400 MHz, $CDCl_3$):



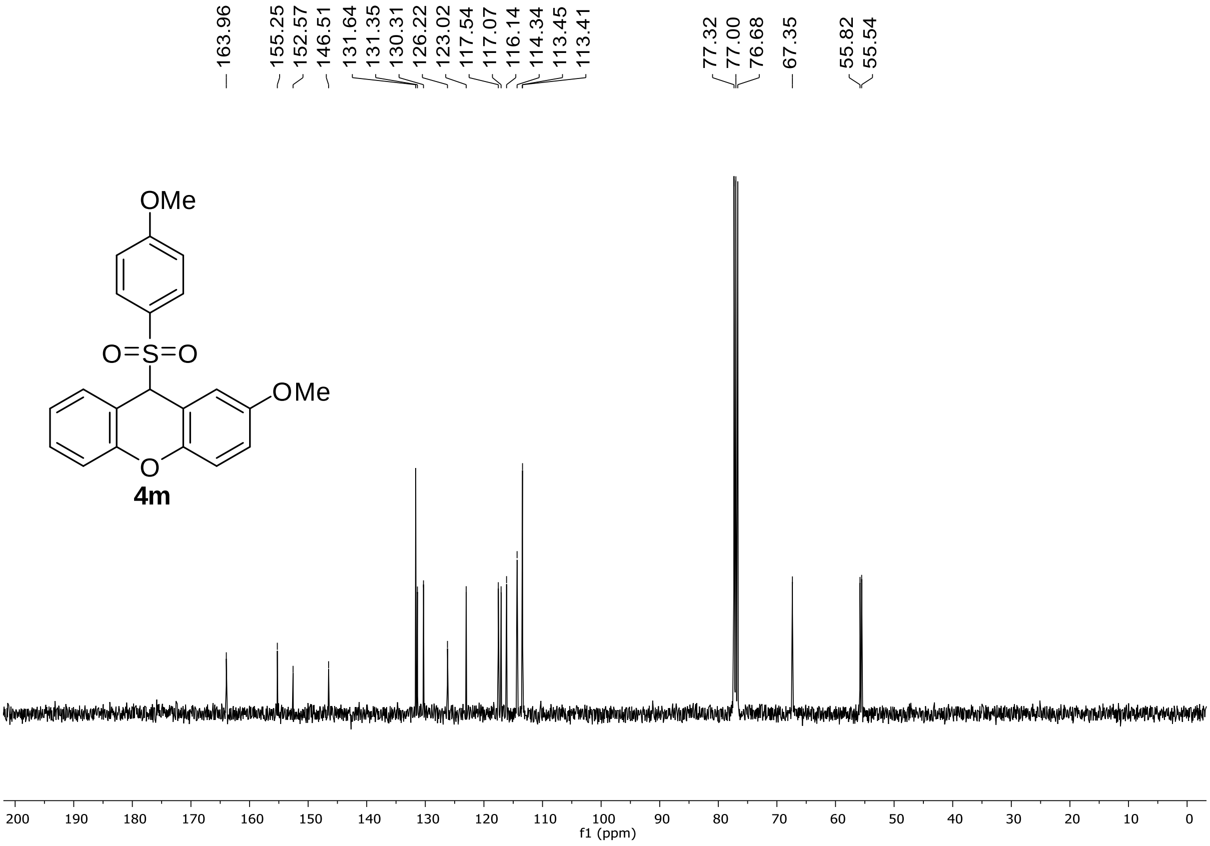
^{13}C {^{1}H} NMR spectrum of **4l** (100 MHz, $CDCl_3$):



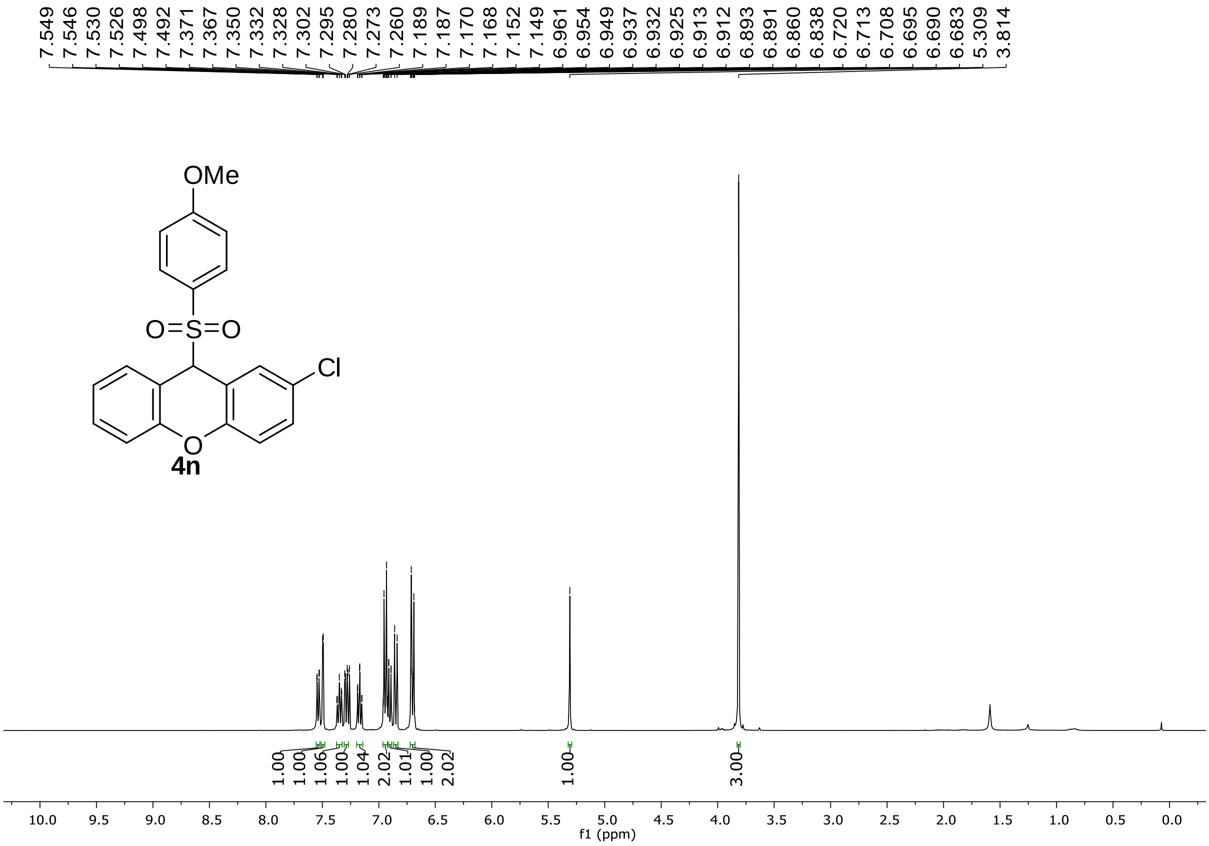
^{1}H NMR spectrum of **4m** (400 MHz, CDCl$_3$):



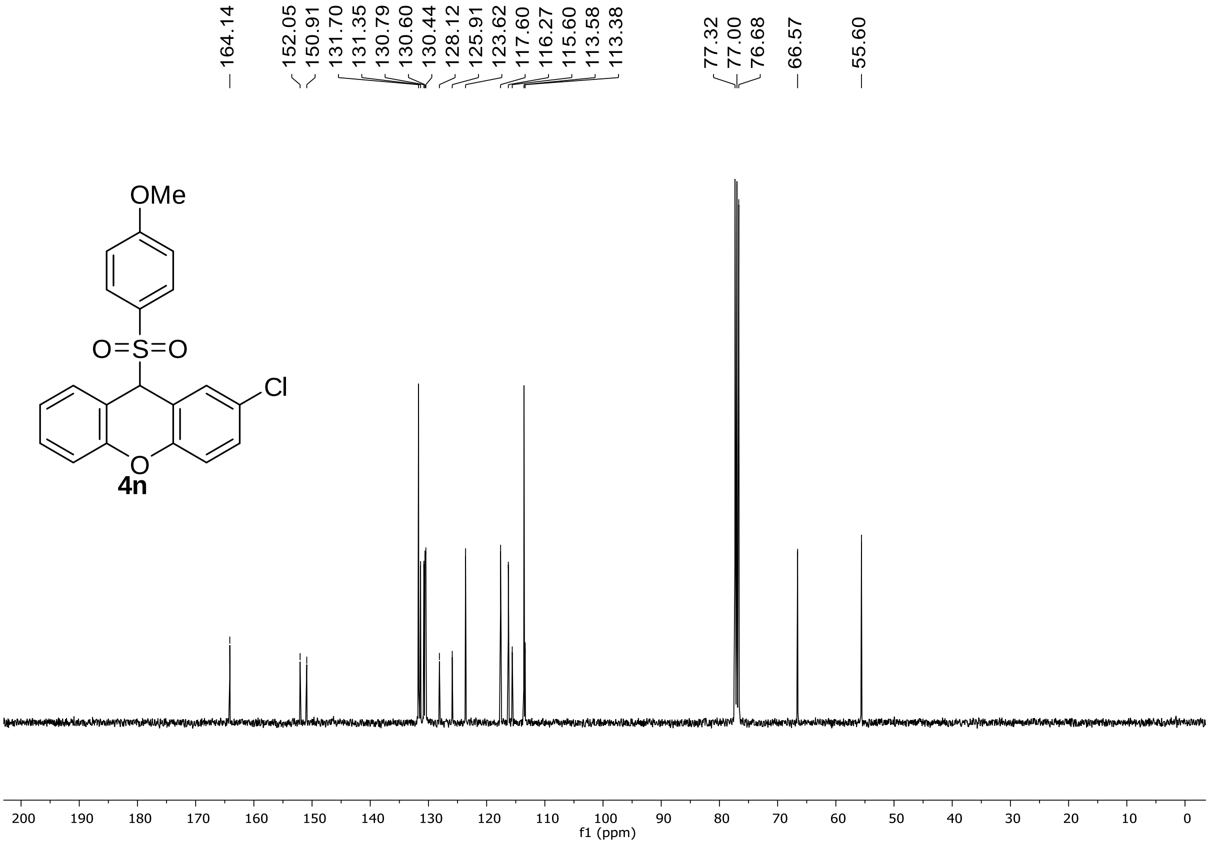
^{13}C {^{1}H} NMR spectrum of **4m** (100 MHz, CDCl$_3$):



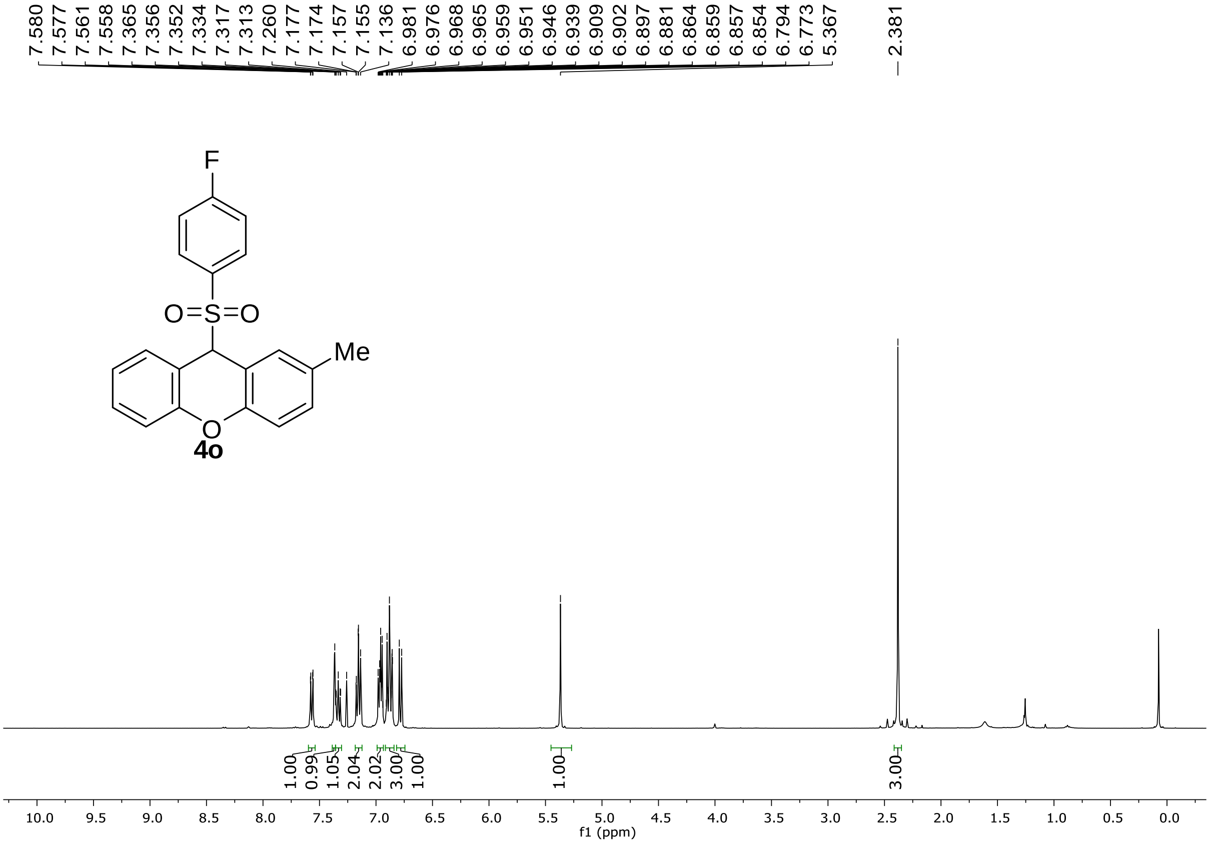
^{1}H NMR spectrum of **4n** (400 MHz, CDCl$_3$):



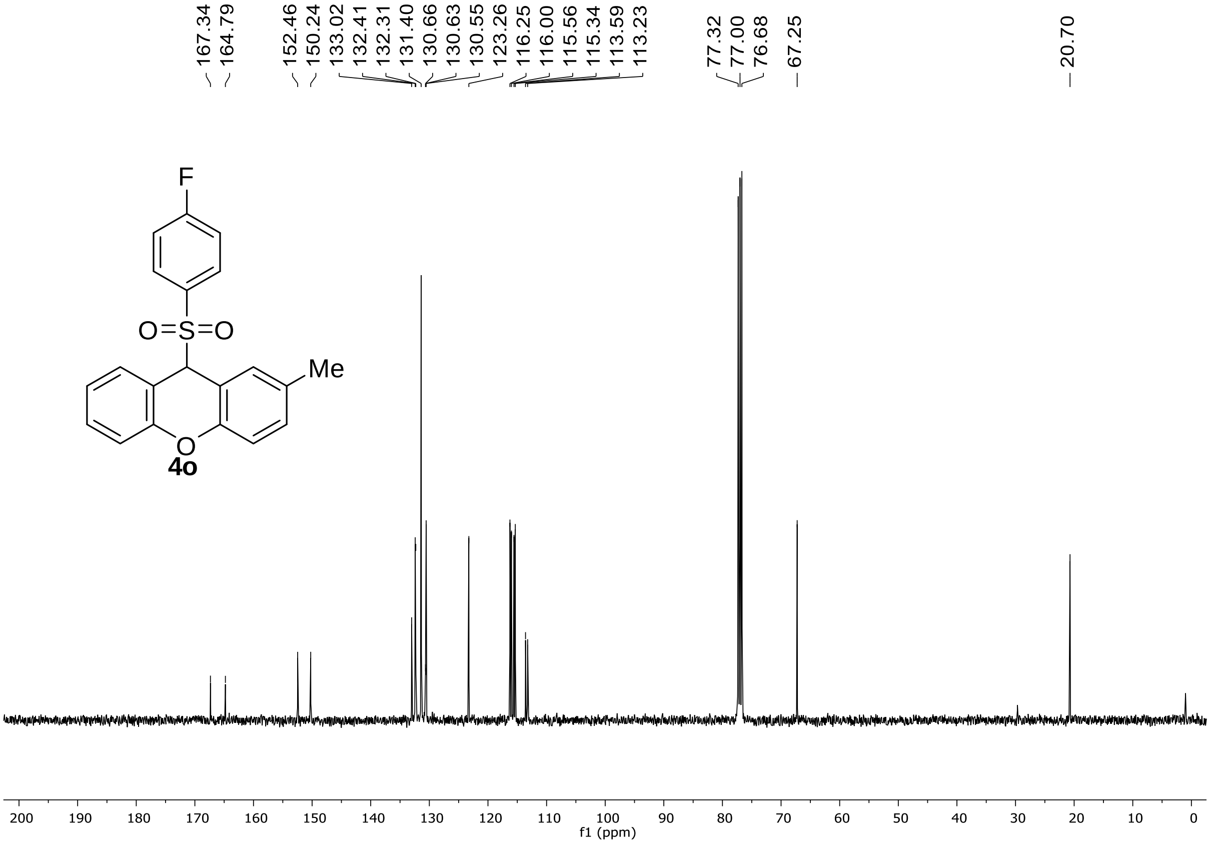
^{13}C {^{1}H} NMR spectrum of **4n** (100 MHz, CDCl$_3$):



^{1}H NMR spectrum of **4o** (400 MHz, $CDCl_3$):



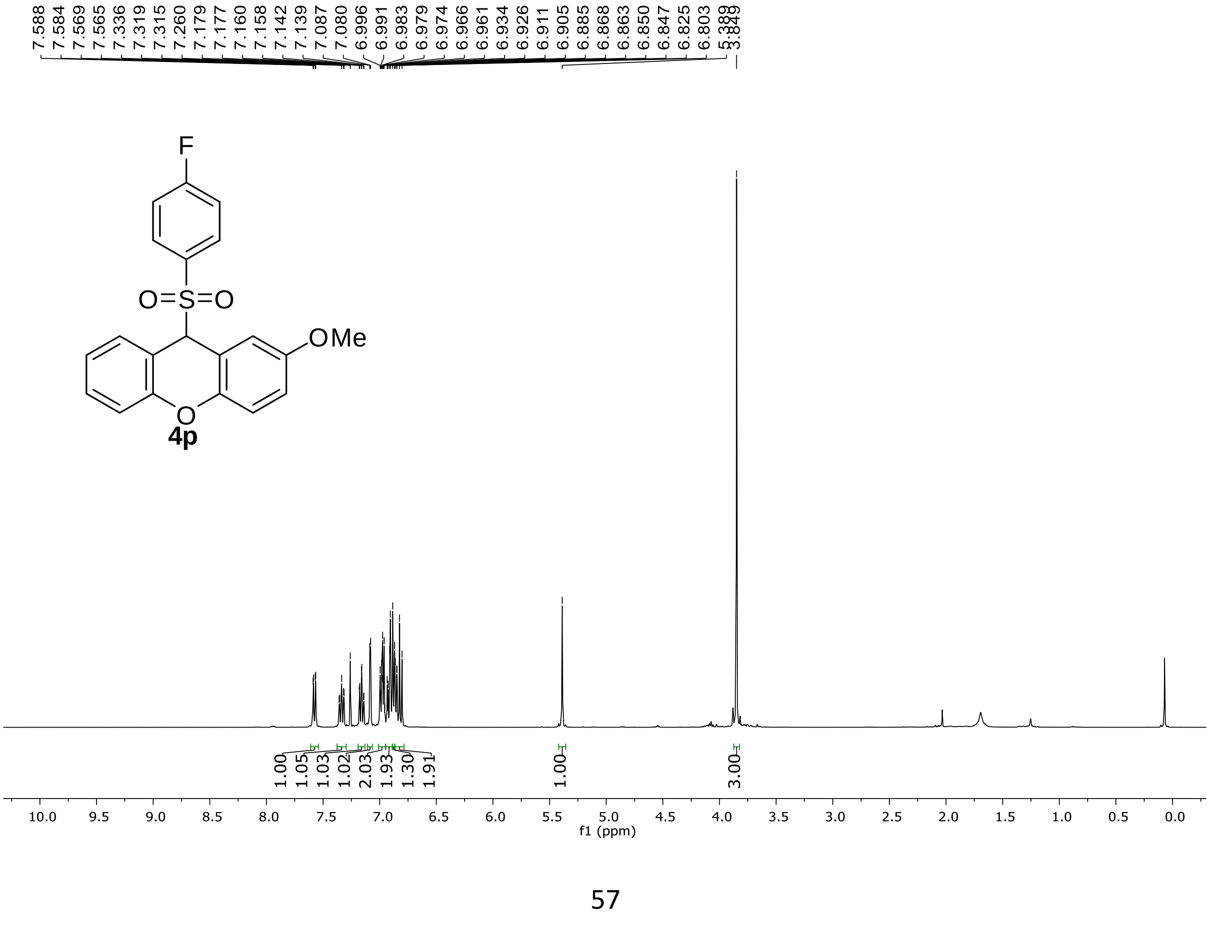
^{13}C {^{1}H} NMR spectrum of **4o** (100 MHz, $CDCl_3$):



^{19}F NMR spectrum of **4n** (376 MHz, $CDCl_3$):

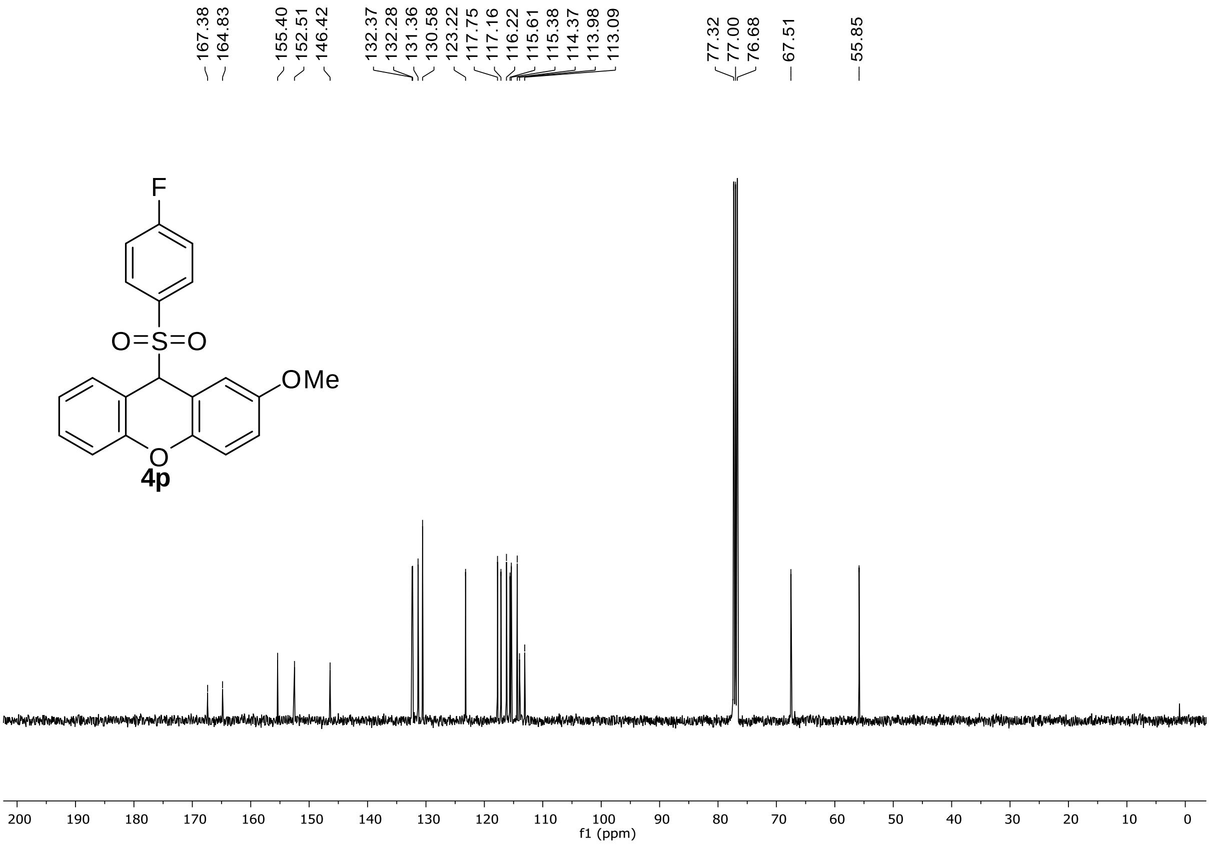
4o

^{1}H NMR spectrum of **4p** (400 MHz, $CDCl_3$):

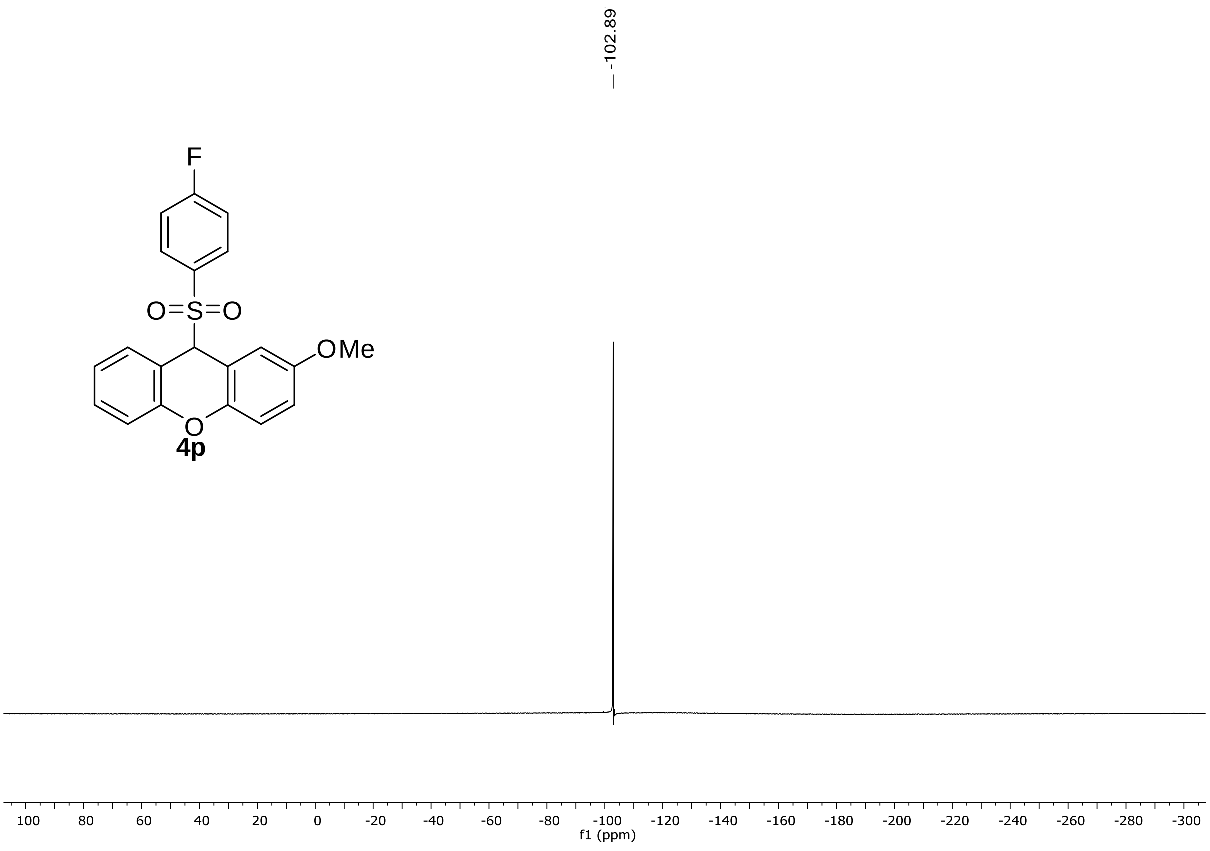


4p

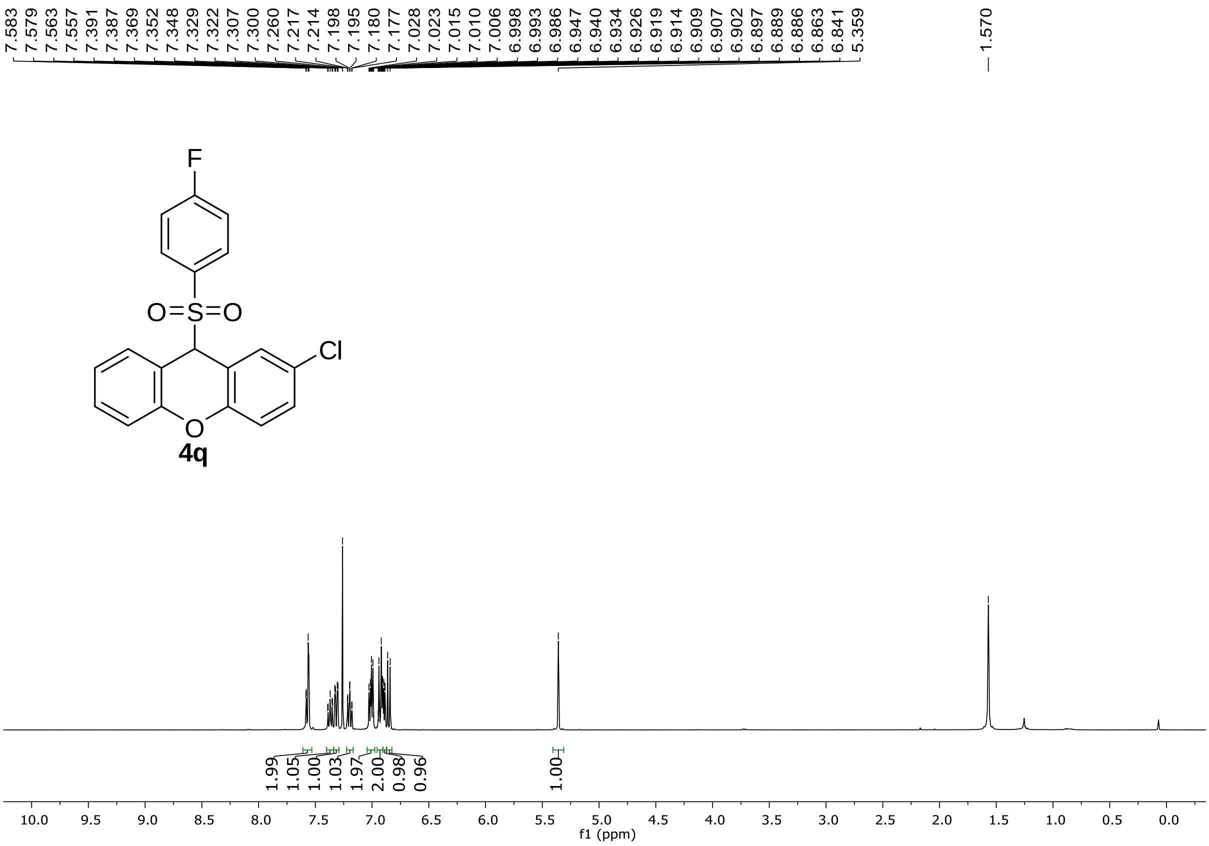
^{13}C {^{1}H} NMR spectrum of **4p** (100 MHz, CDCl$_3$):



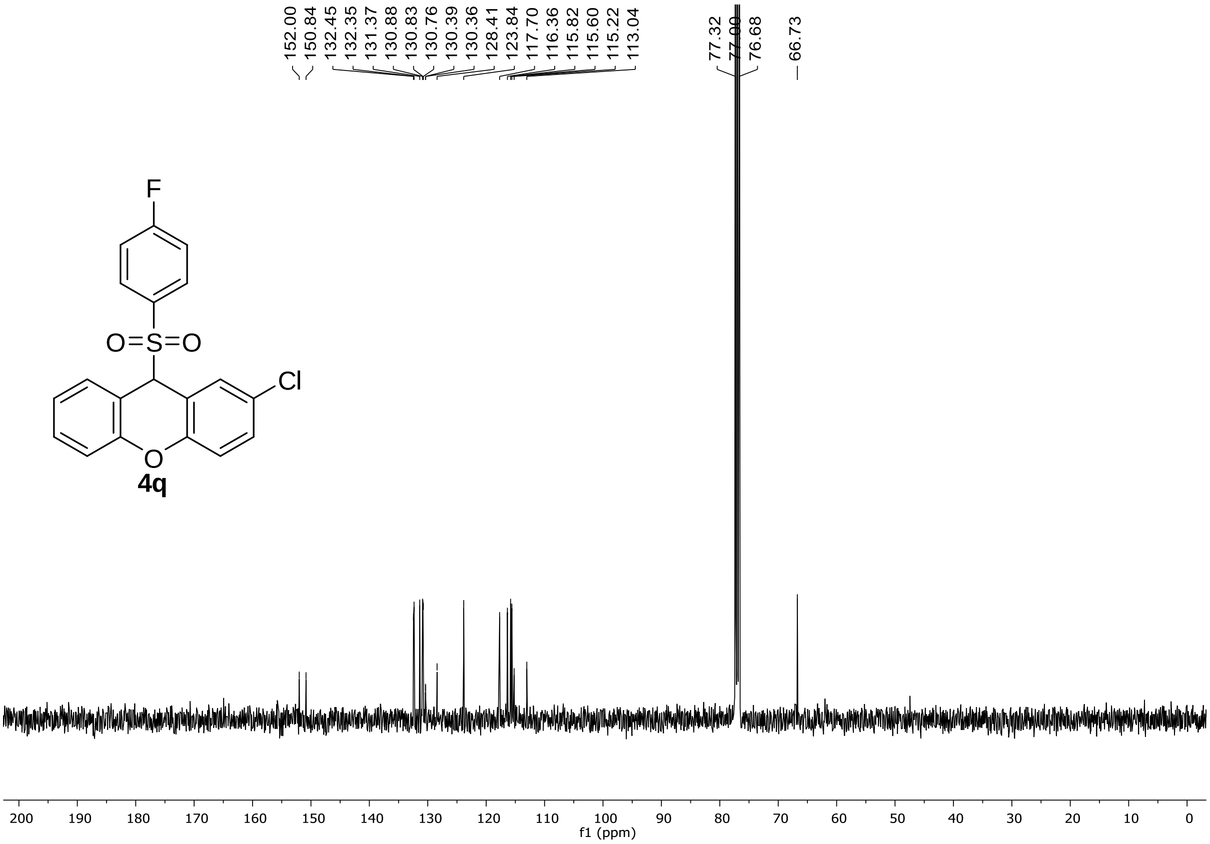
^{19}F NMR spectrum of **4p** (376 MHz, CDCl$_3$):



^{1}H NMR spectrum of **4q** (400 MHz, CDCl$_3$):

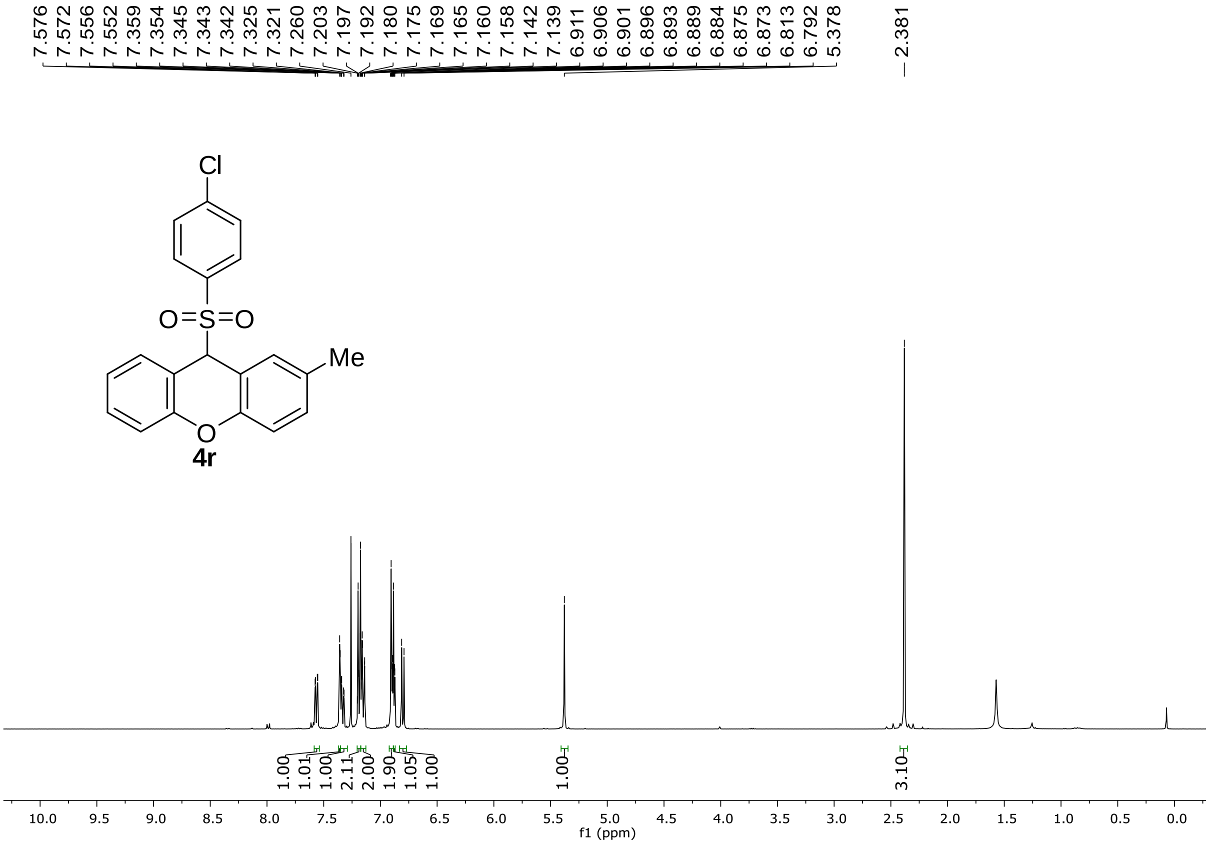


^{13}C {^{1}H} NMR spectrum of **4q** (100 MHz, CDCl$_3$):

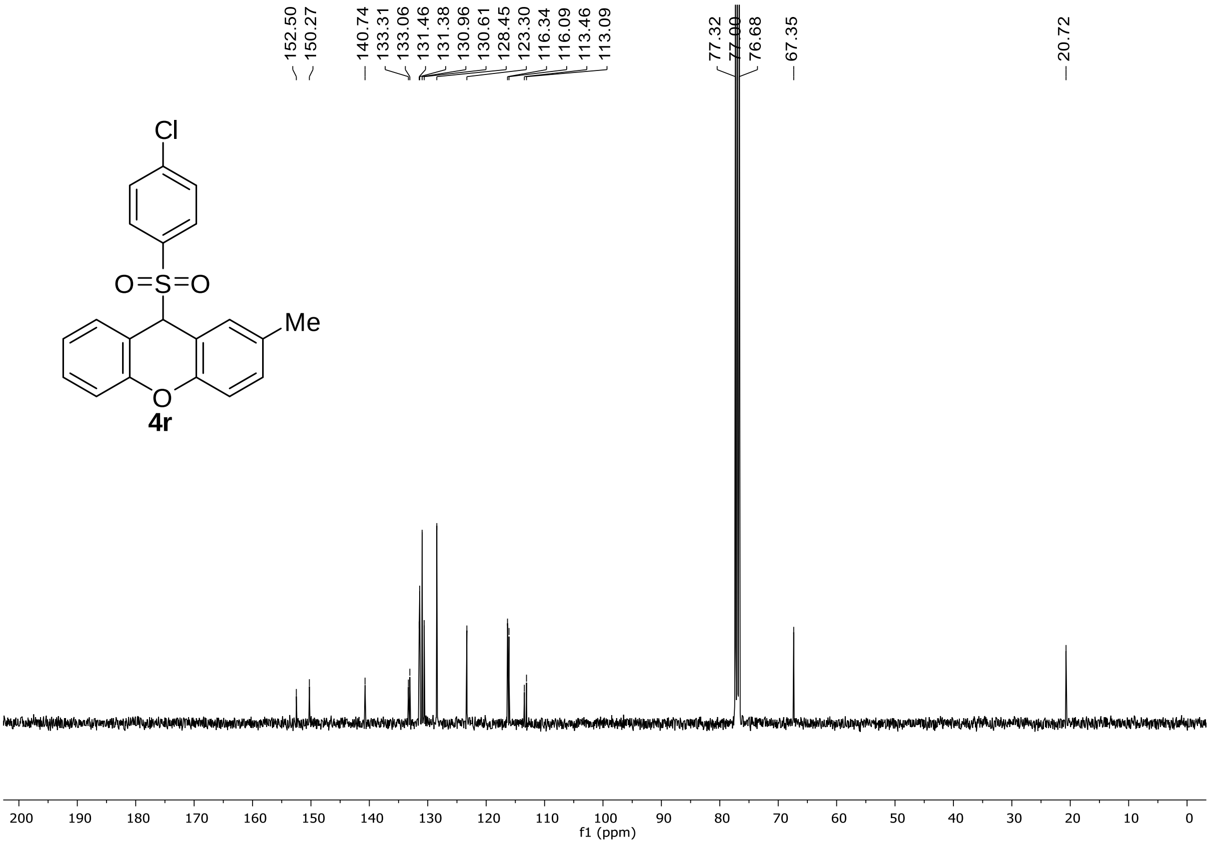


^{19}F NMR spectrum of **4q** (376 MHz, $CDCl_3$):

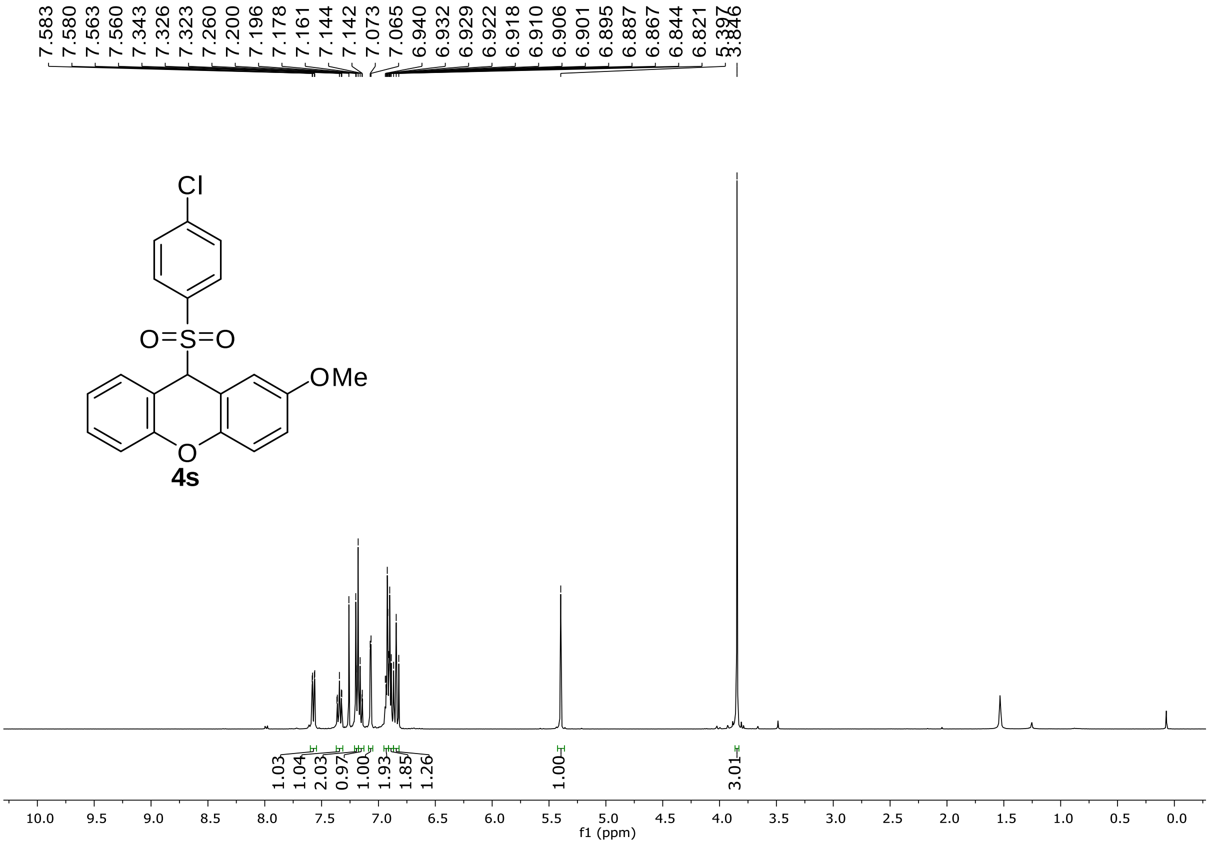
^{1}H NMR spectrum of **4r** (400 MHz, $CDCl_3$):



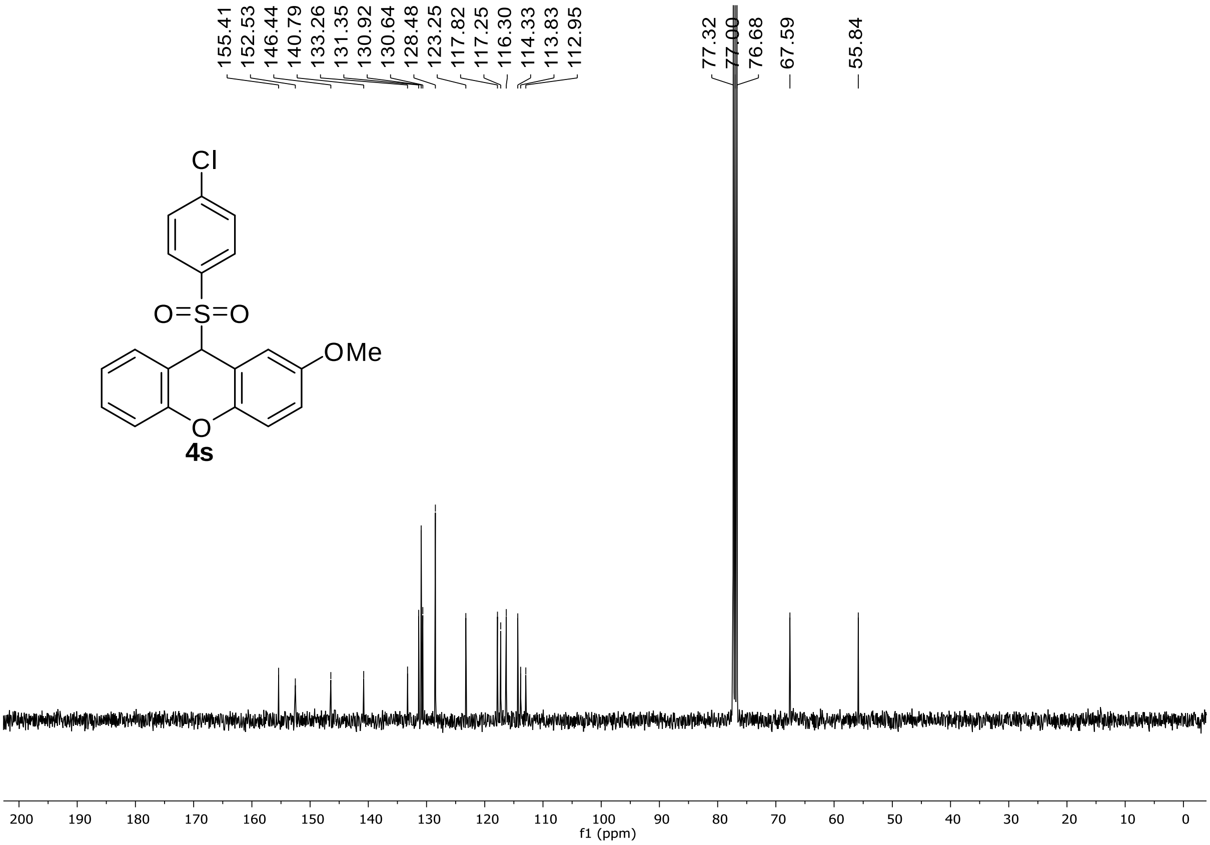
^{13}C {^{1}H} NMR spectrum of **4r** (100 MHz, $CDCl_3$):



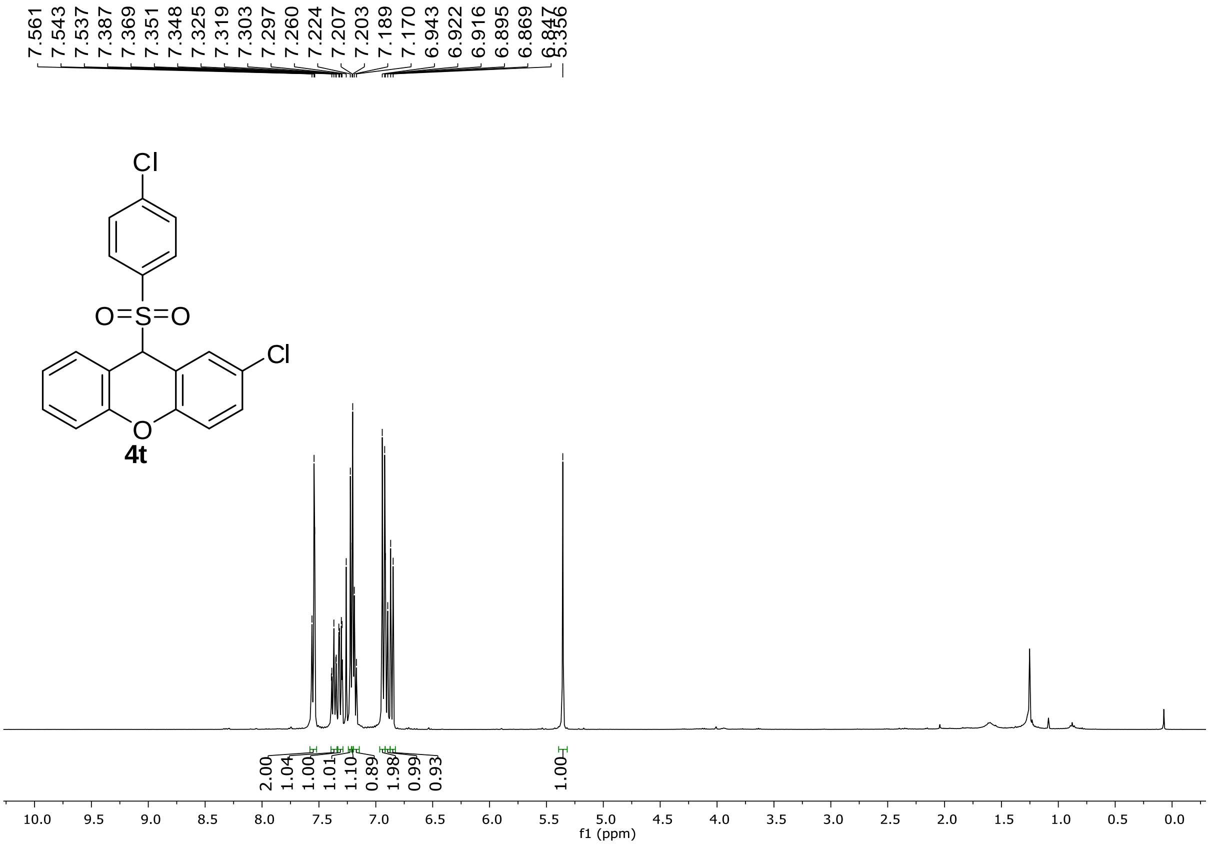
^{1}H NMR spectrum of **4s** (400 MHz, $CDCl_3$):



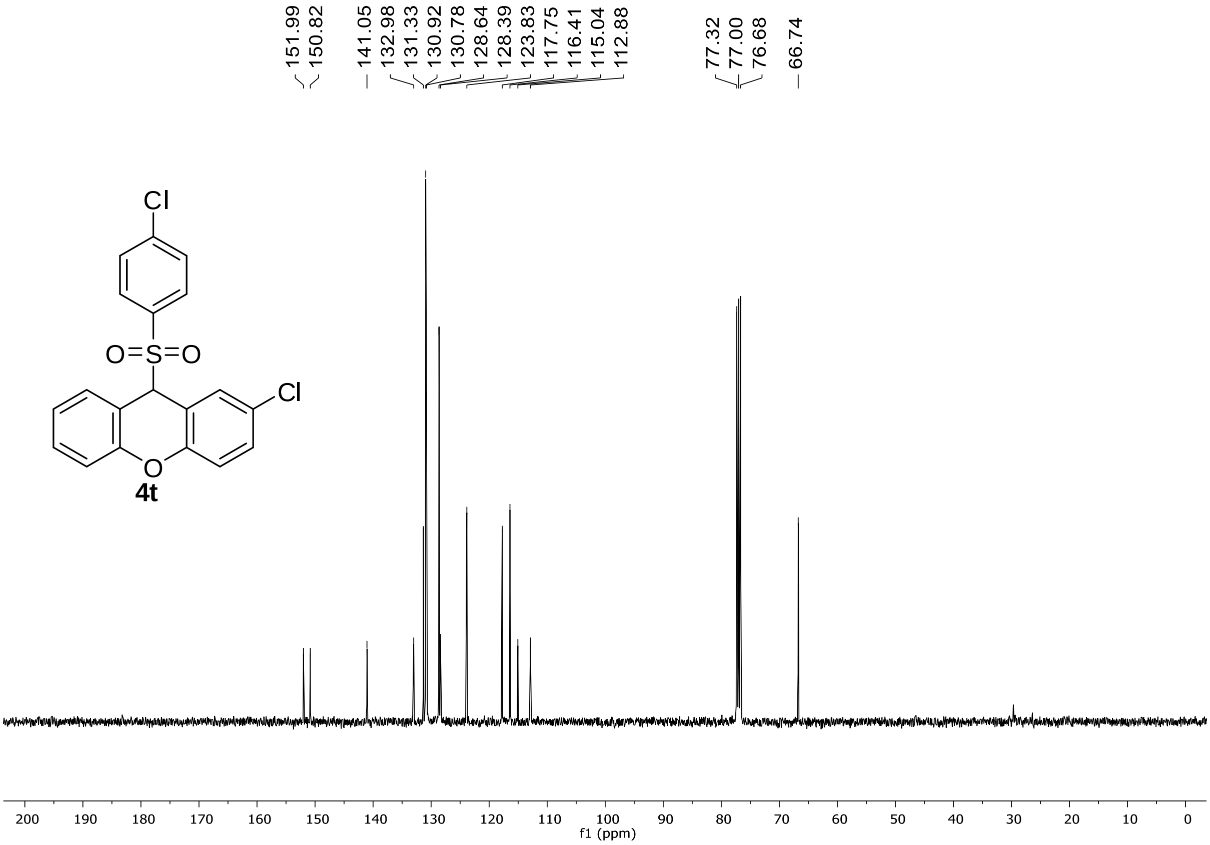
^{13}C {^{1}H} NMR spectrum of **4s** (100 MHz, $CDCl_3$):



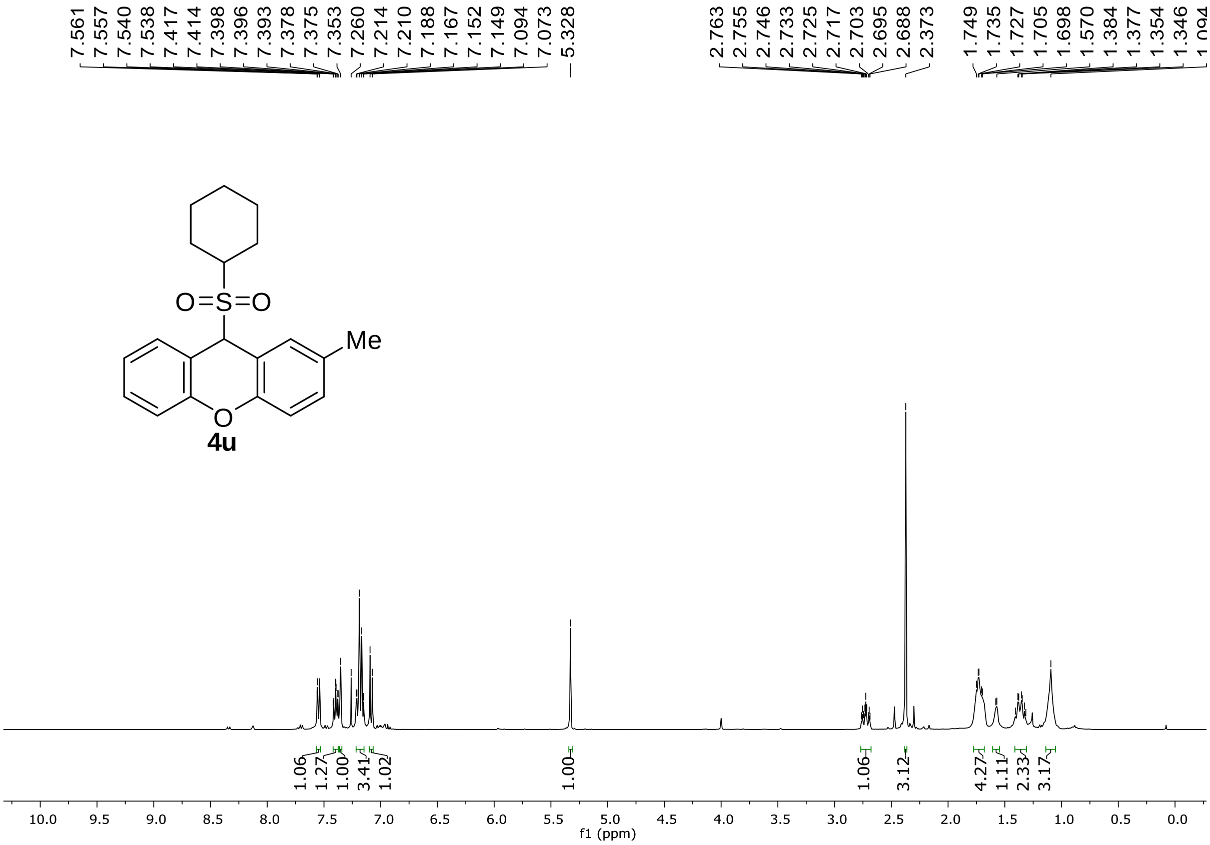
^{1}H NMR spectrum of **4t** (400 MHz, $CDCl_3$):



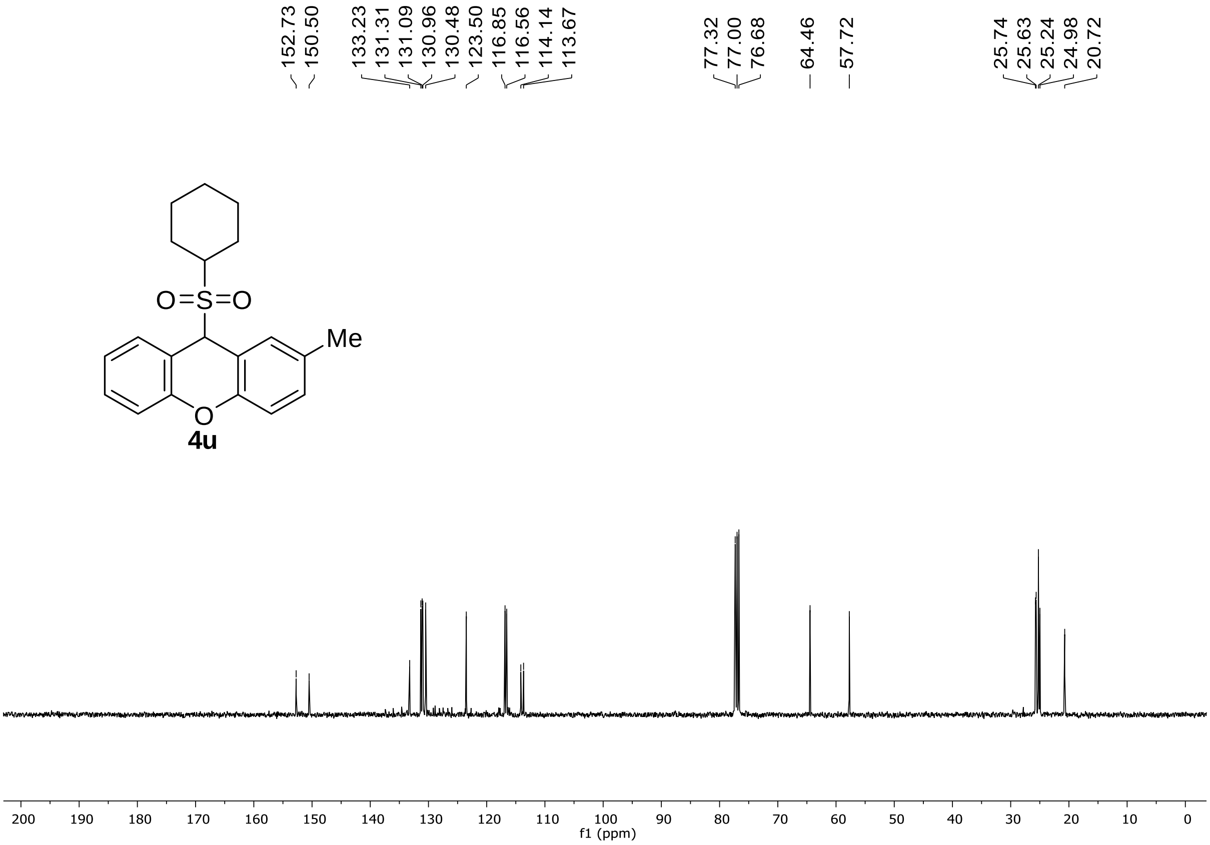
^{13}C {^{1}H} NMR spectrum of **4t** (100 MHz, CDCl$_3$):



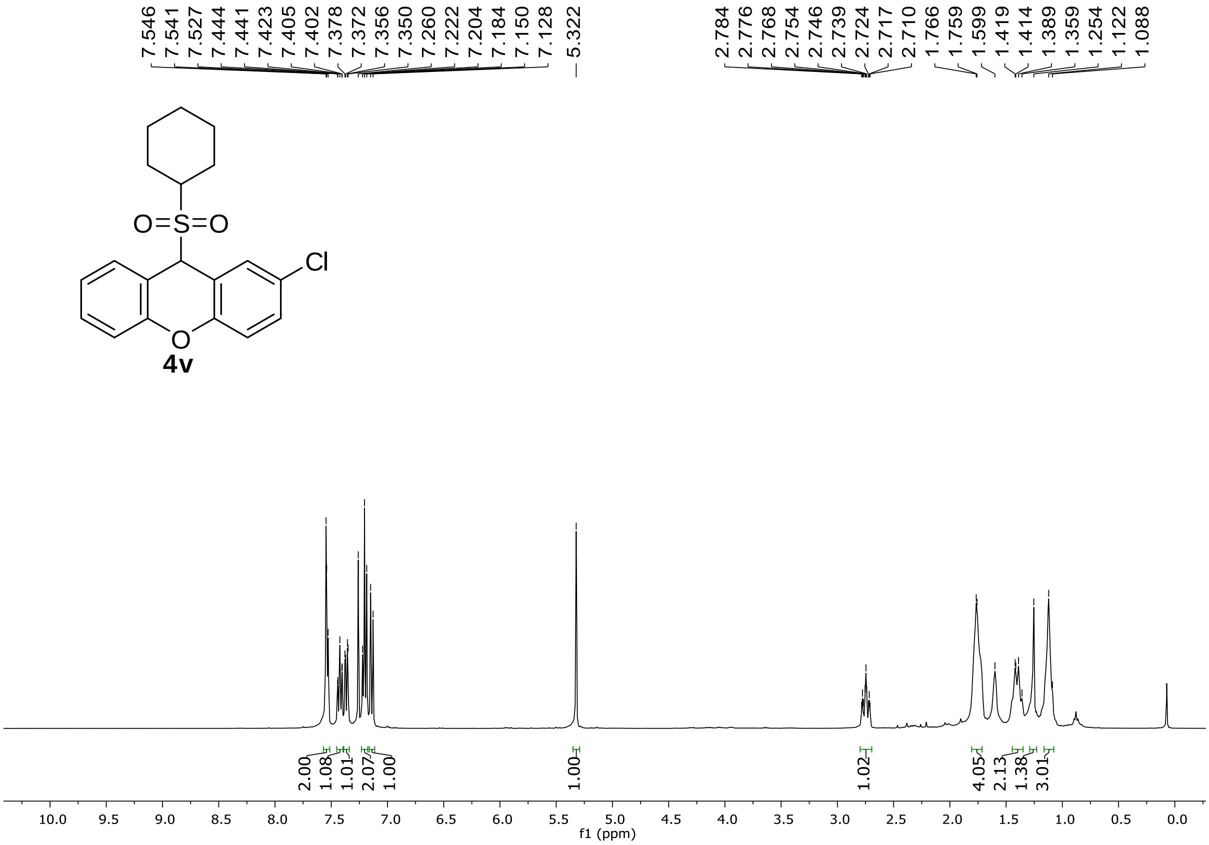
^{1}H NMR spectrum of **4u** (400 MHz, CDCl$_3$):



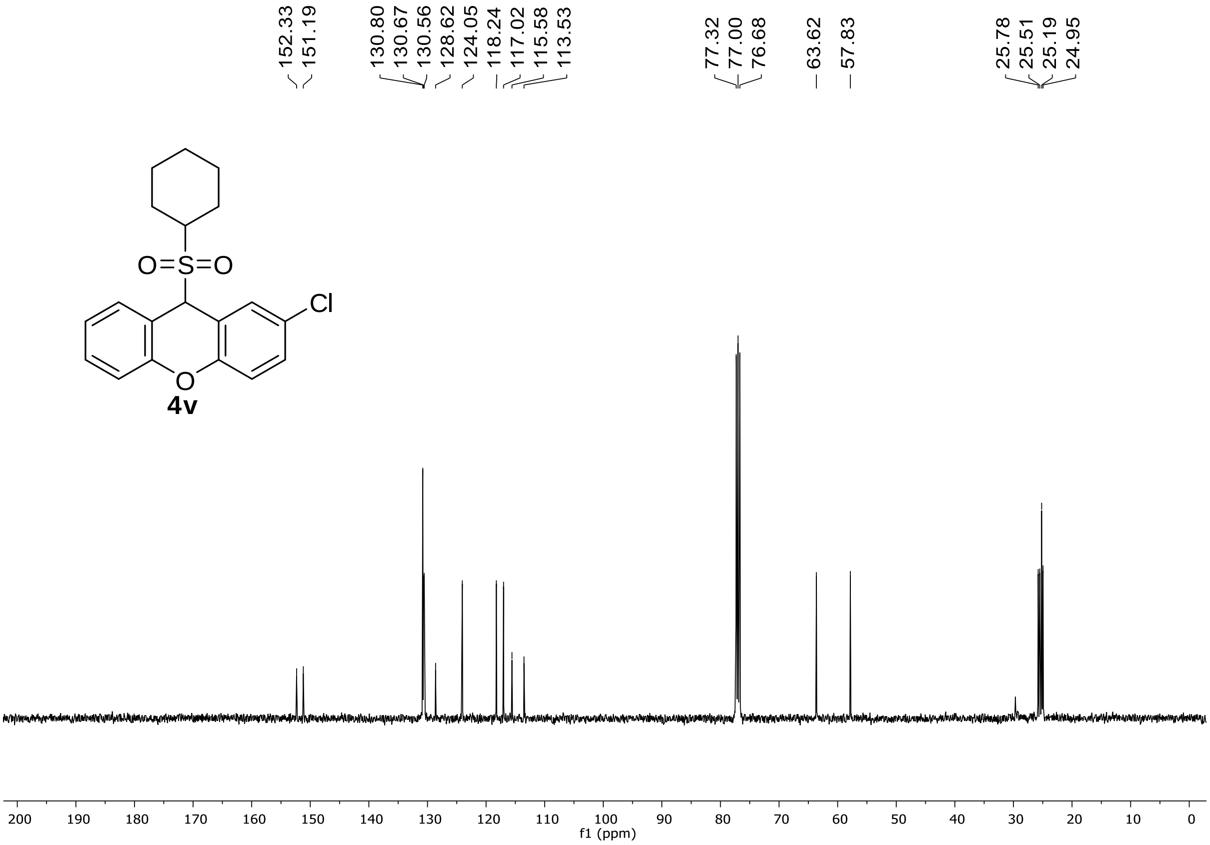
^{13}C {^{1}H} NMR spectrum of **4u** (100 MHz, CDCl$_3$):



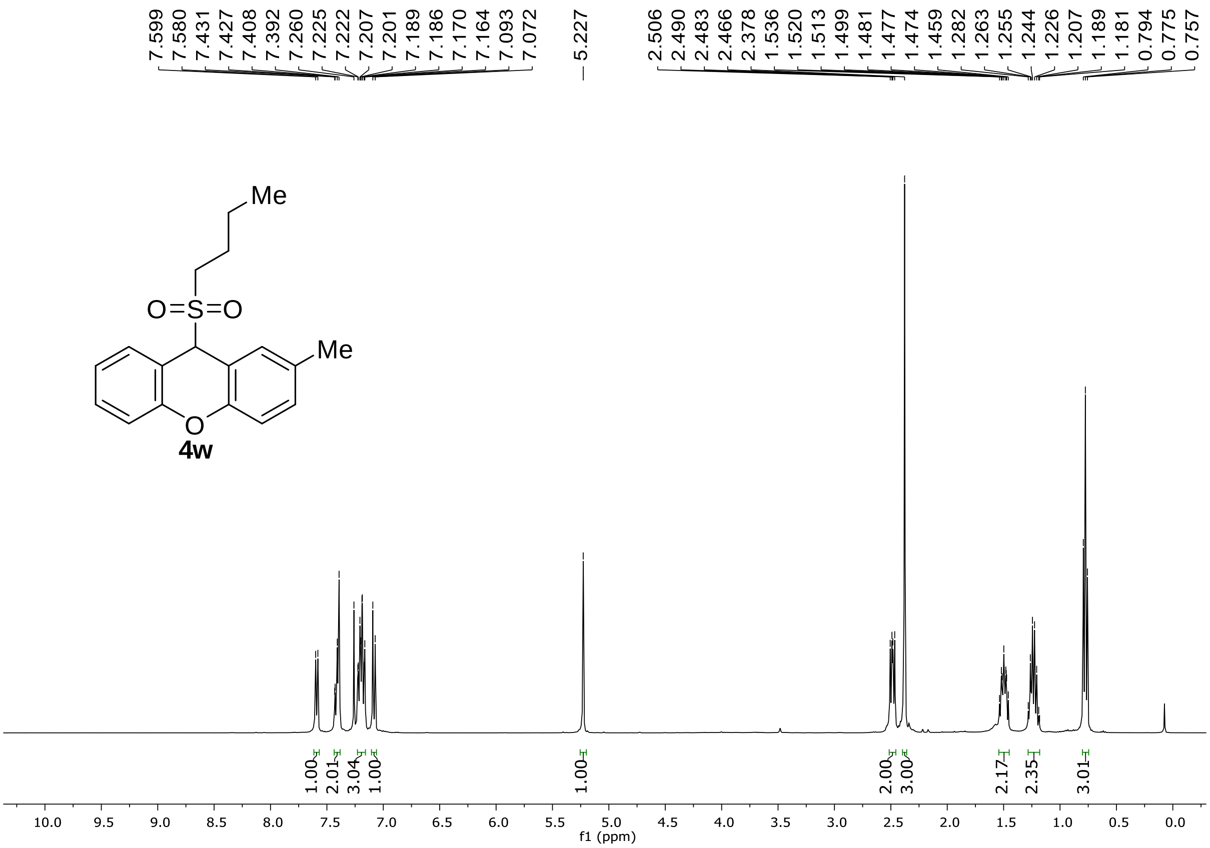
^{1}H NMR spectrum of **4v** (400 MHz, CDCl$_3$):



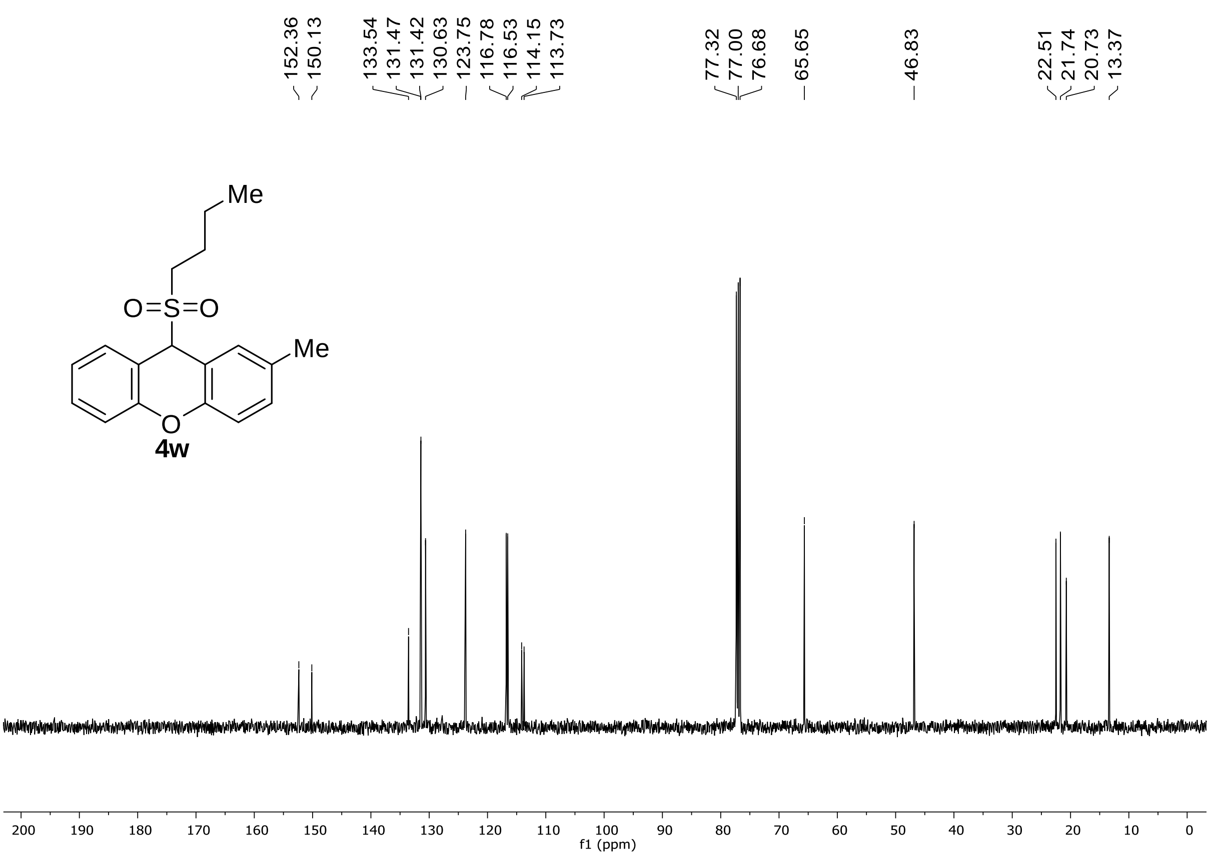
^{13}C {^{1}H} NMR spectrum of **4v** (100 MHz, $CDCl_3$):



^{1}H NMR spectrum of **4w** (400 MHz, $CDCl_3$):

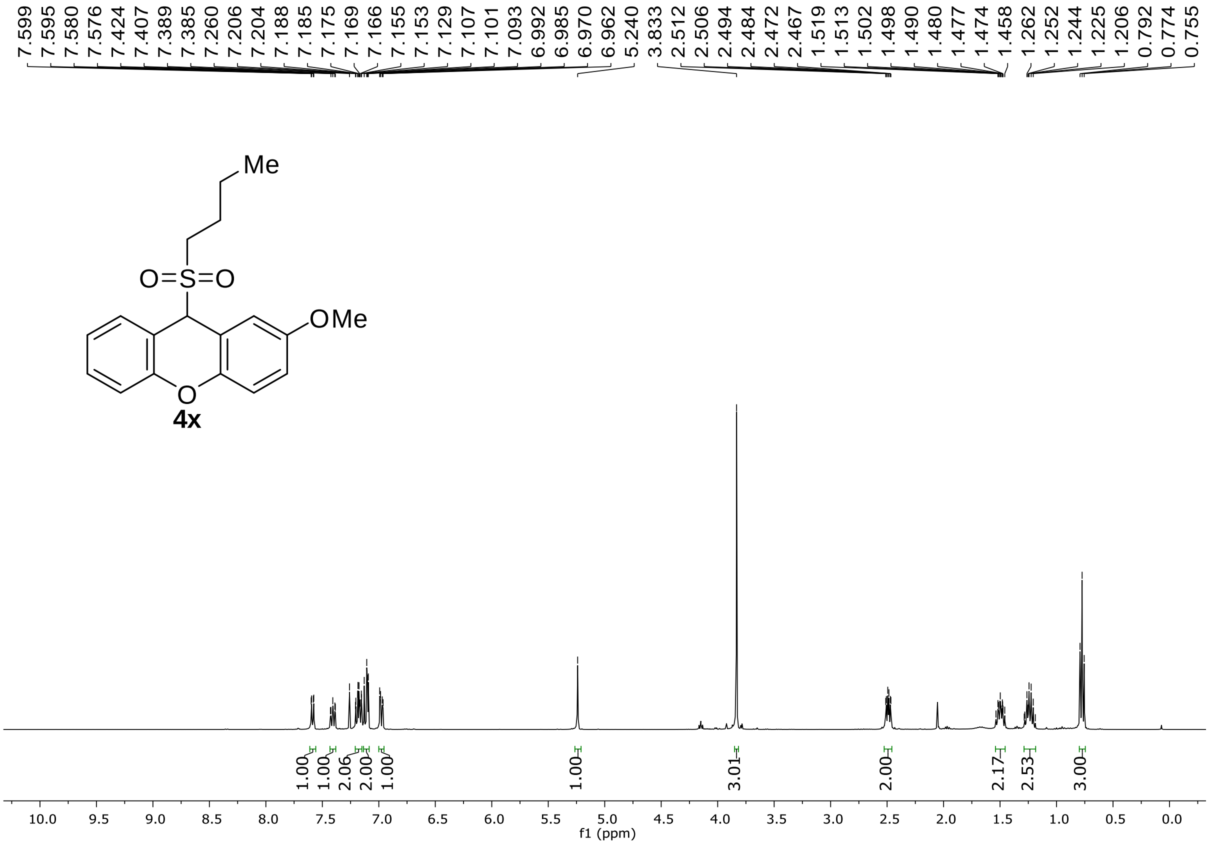


^{13}C {^{1}H} NMR spectrum of **4v** (100 MHz, CDCl$_3$):



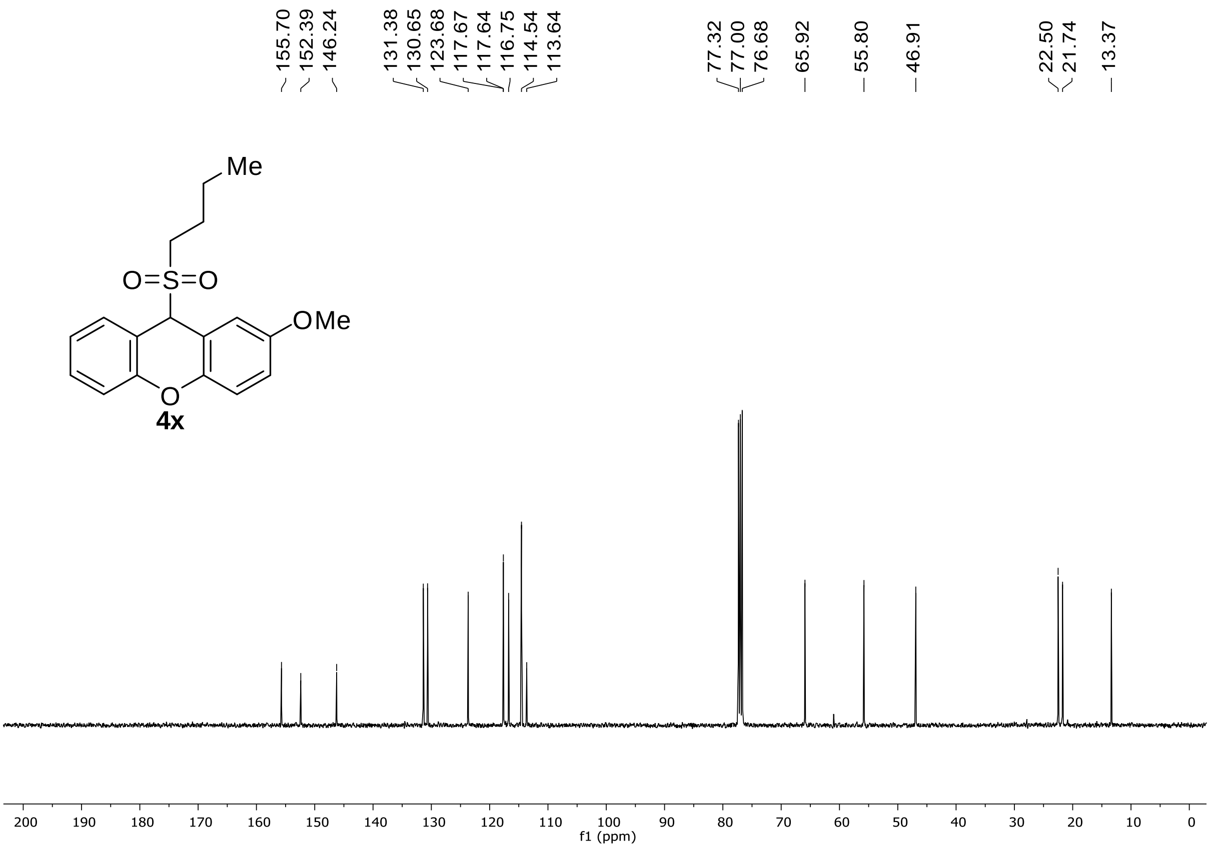
4w

^{1}H NMR spectrum of **4x** (400 MHz, CDCl$_3$):

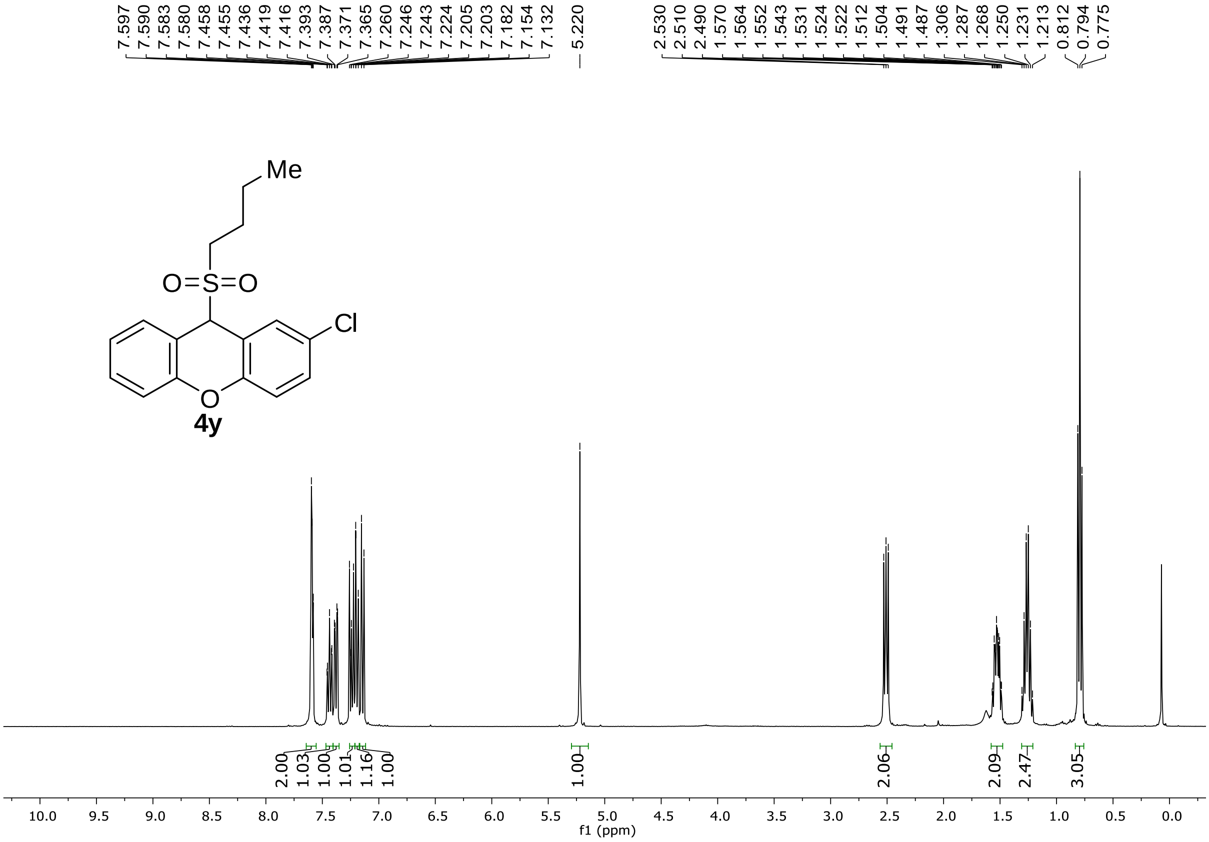


4x

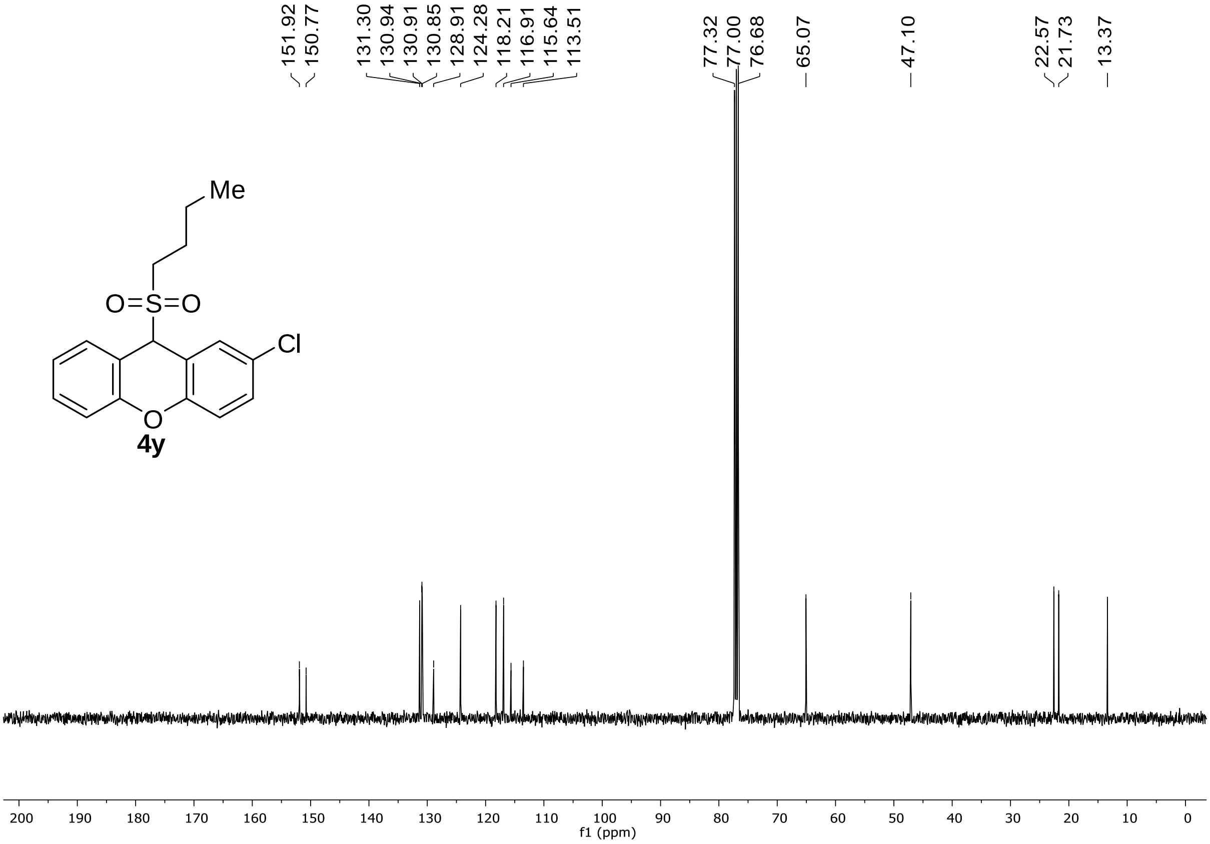
^{13}C {^{1}H} NMR spectrum of **4x** (100 MHz, CDCl$_3$):


4x

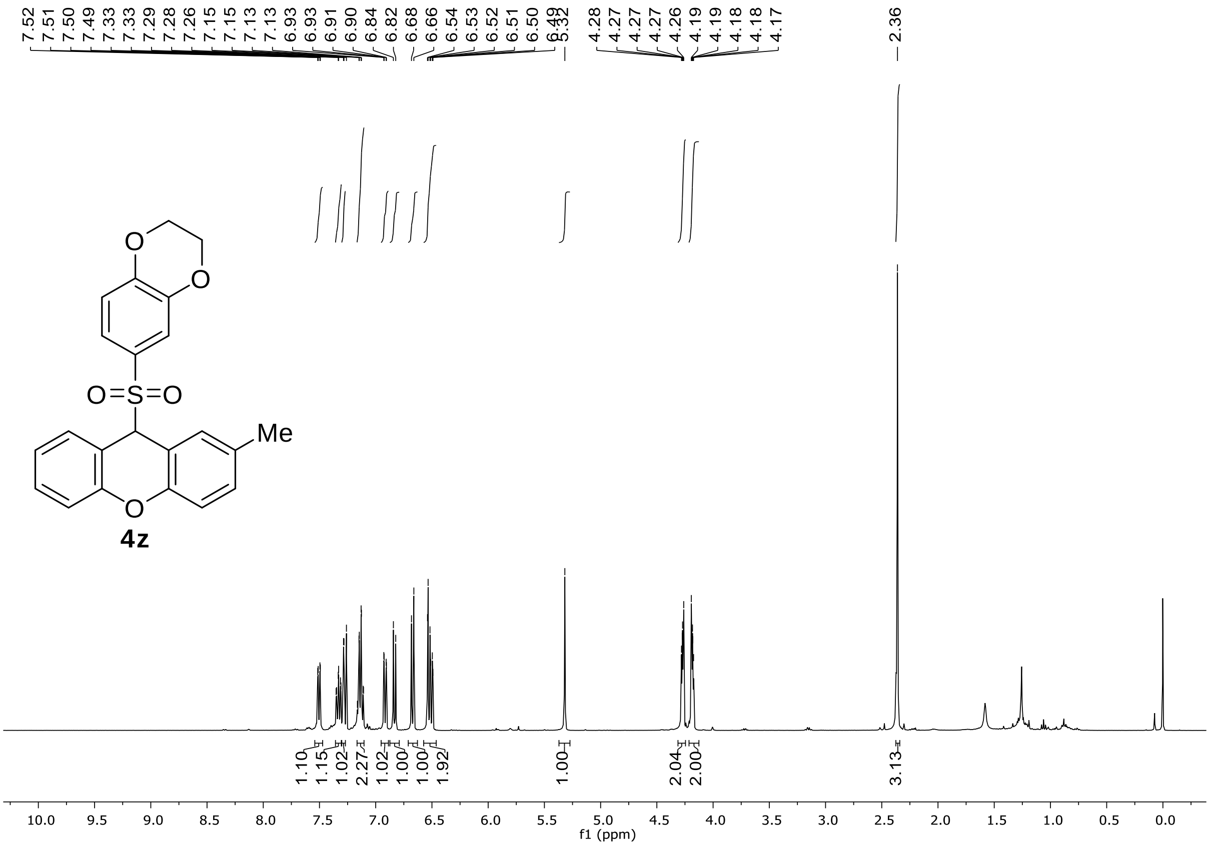
^{1}H NMR spectrum of **4y** (400 MHz, CDCl$_3$):


4y

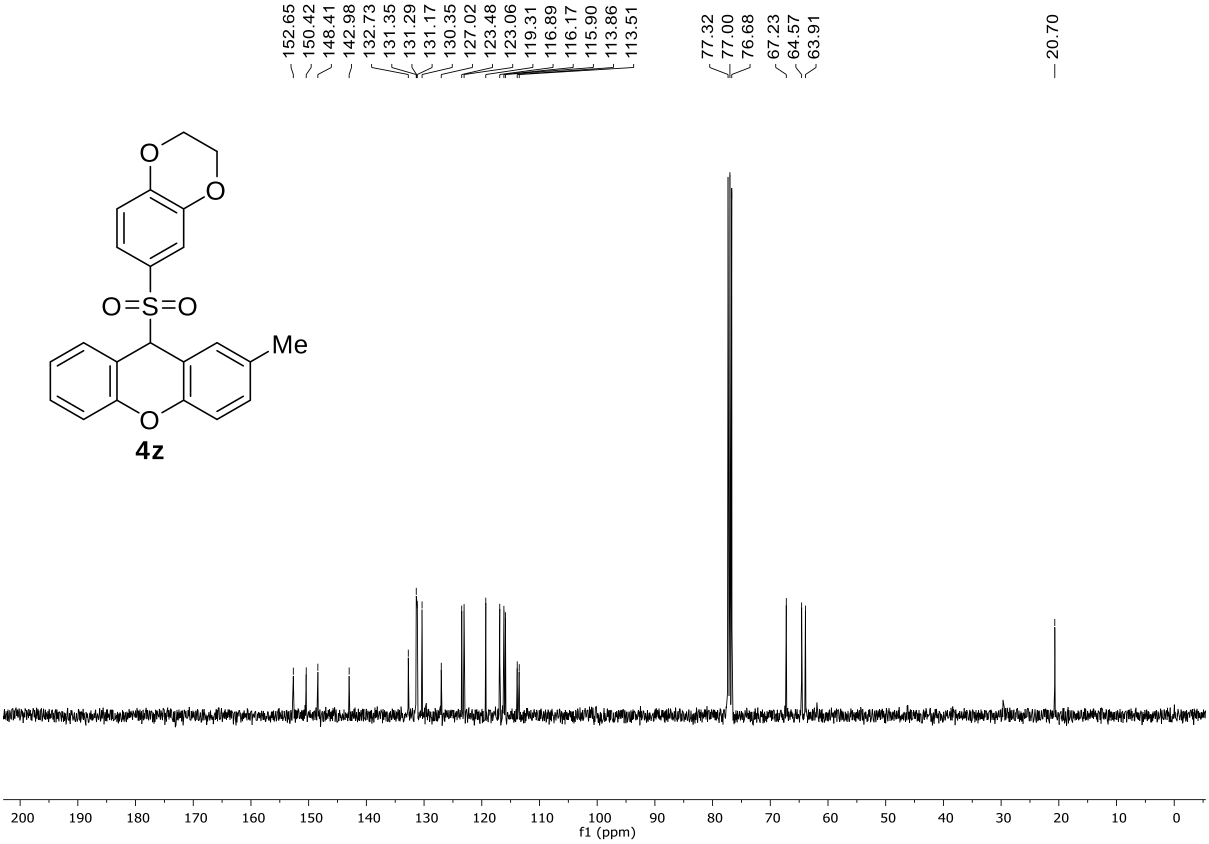
^{13}C {^{1}H} NMR spectrum of **4y** (100 MHz, CDCl$_3$):



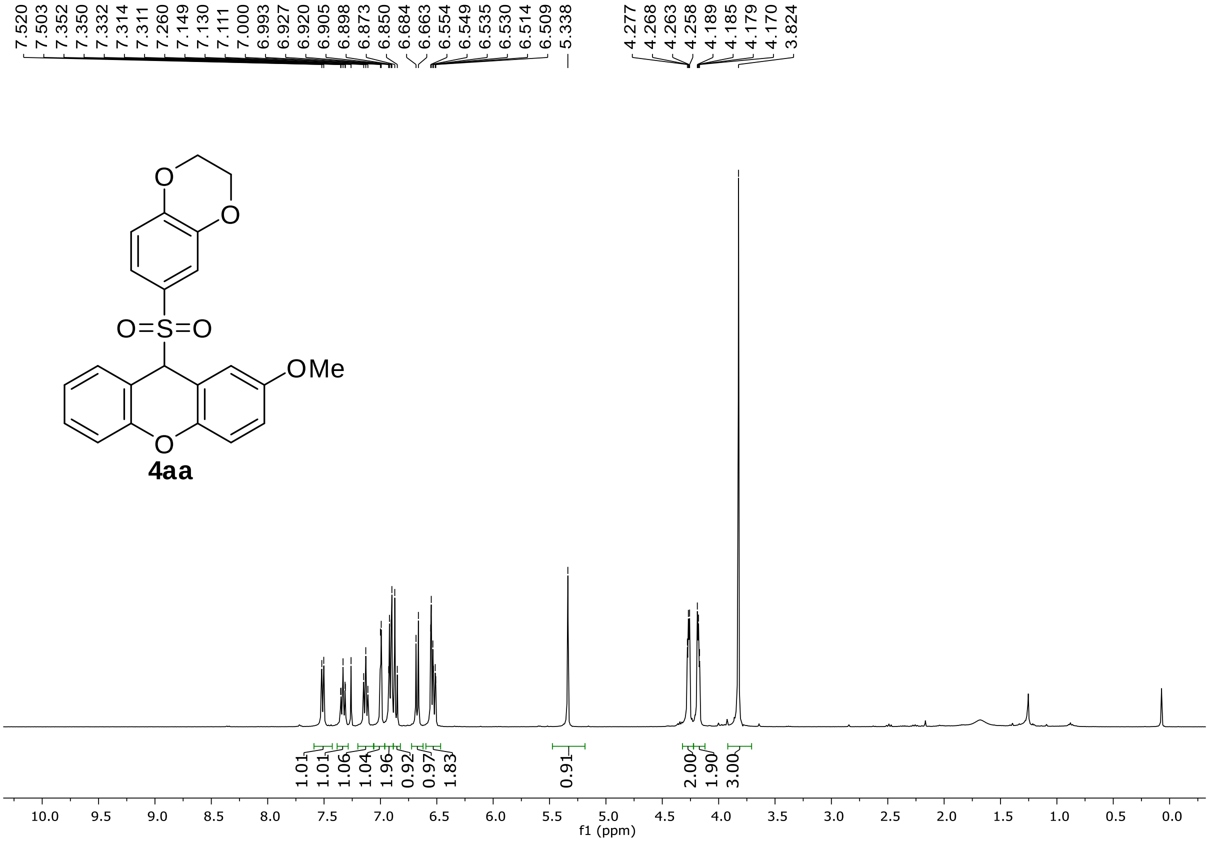
^{1}H NMR spectrum of **4z** (400 MHz, CDCl$_3$):



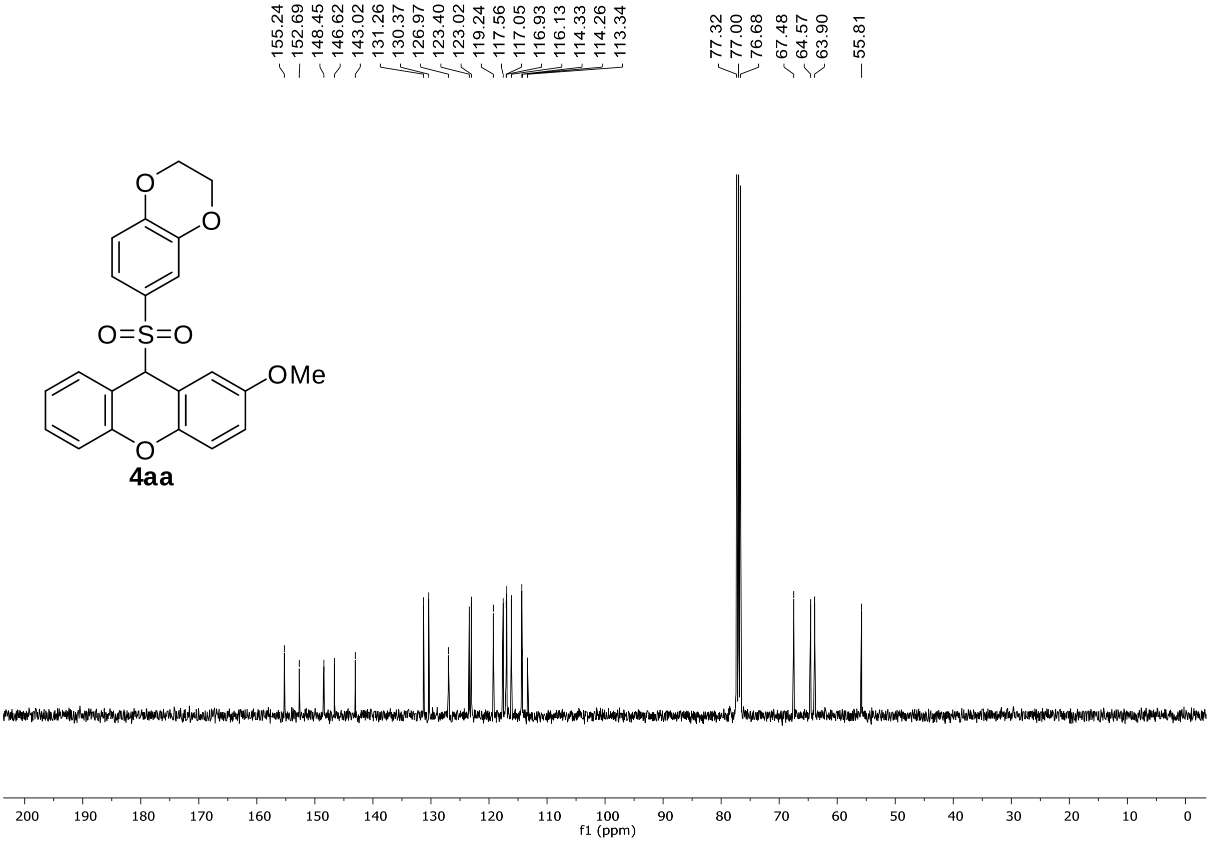
^{13}C {^{1}H} NMR spectrum of **4z** (100 MHz, $CDCl_3$):



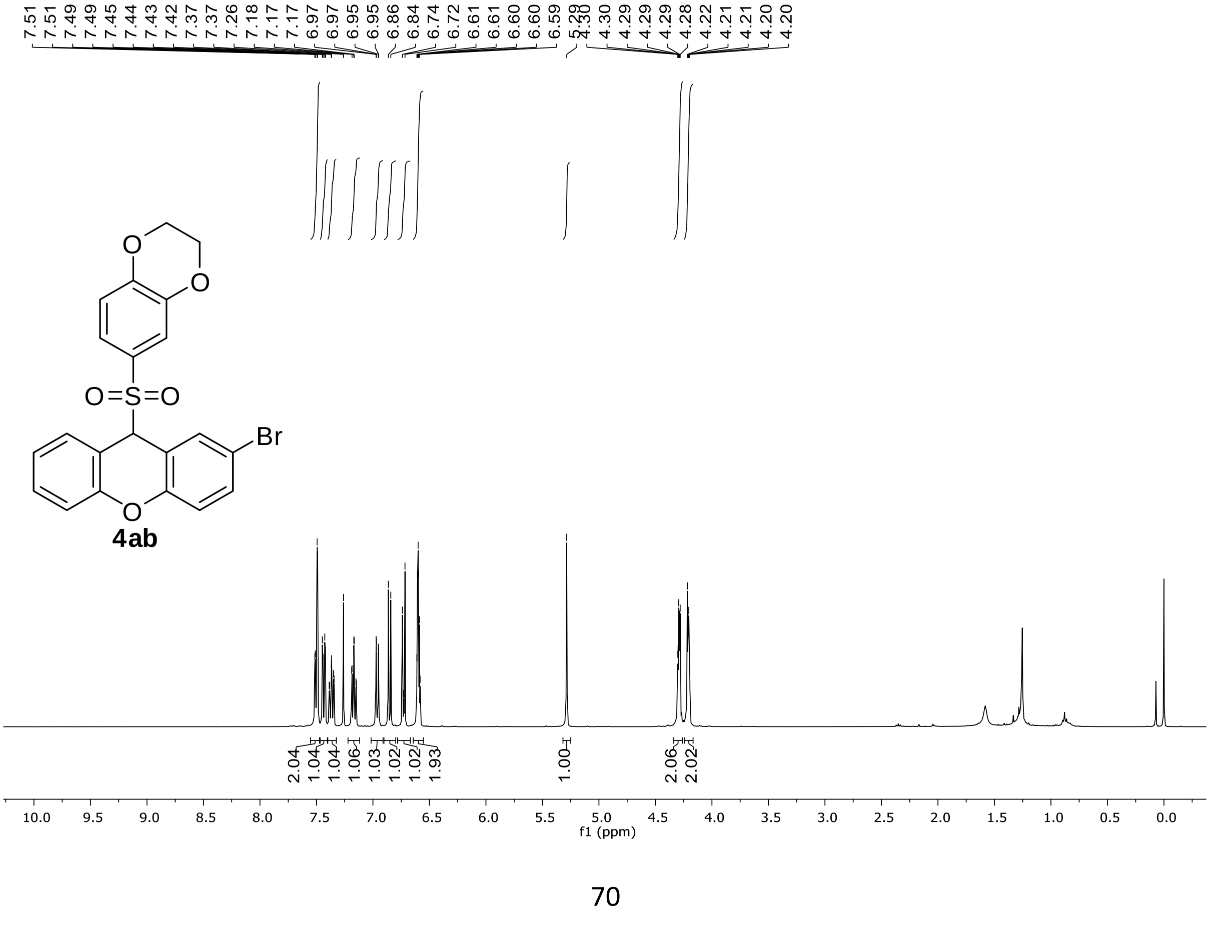
^{1}H NMR spectrum of **4aa** (400 MHz, $CDCl_3$):



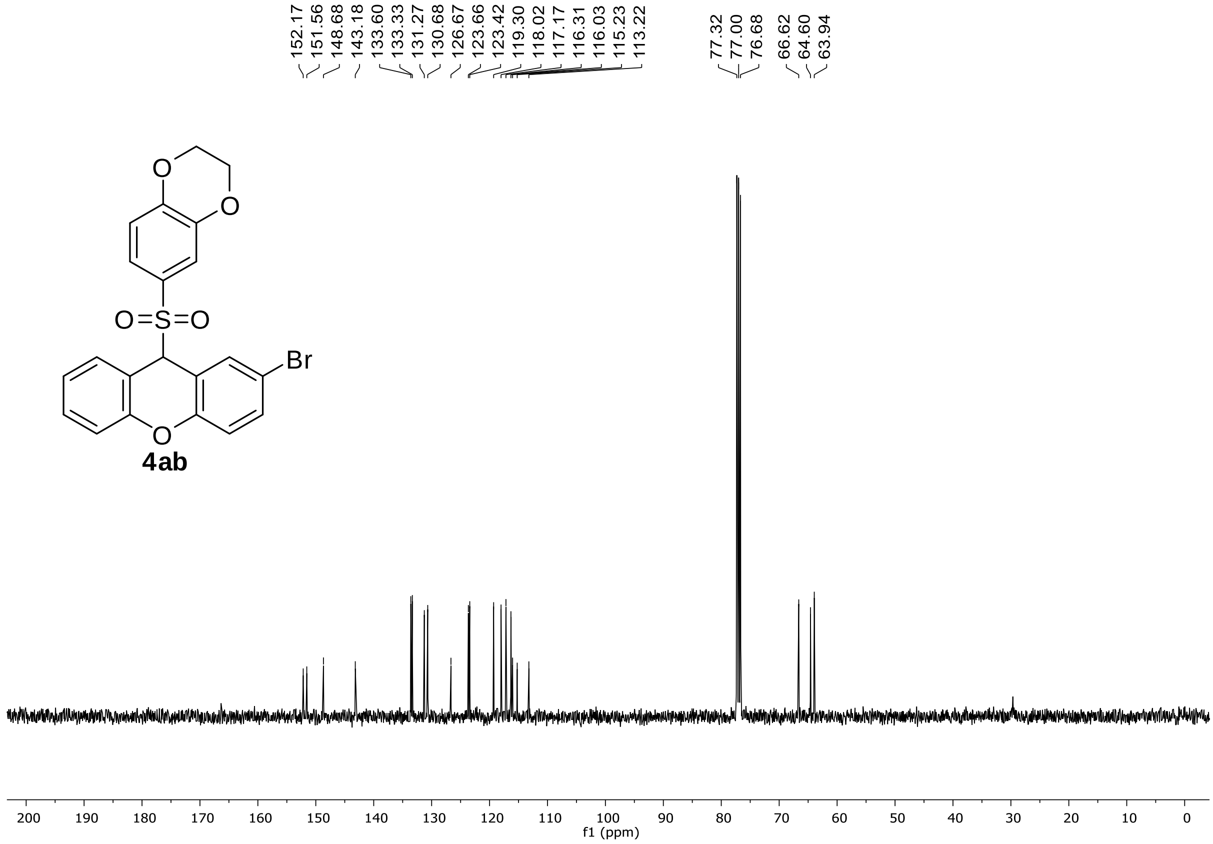
^{13}C {^{1}H} NMR spectrum of **4aa** (100 MHz, $CDCl_3$):



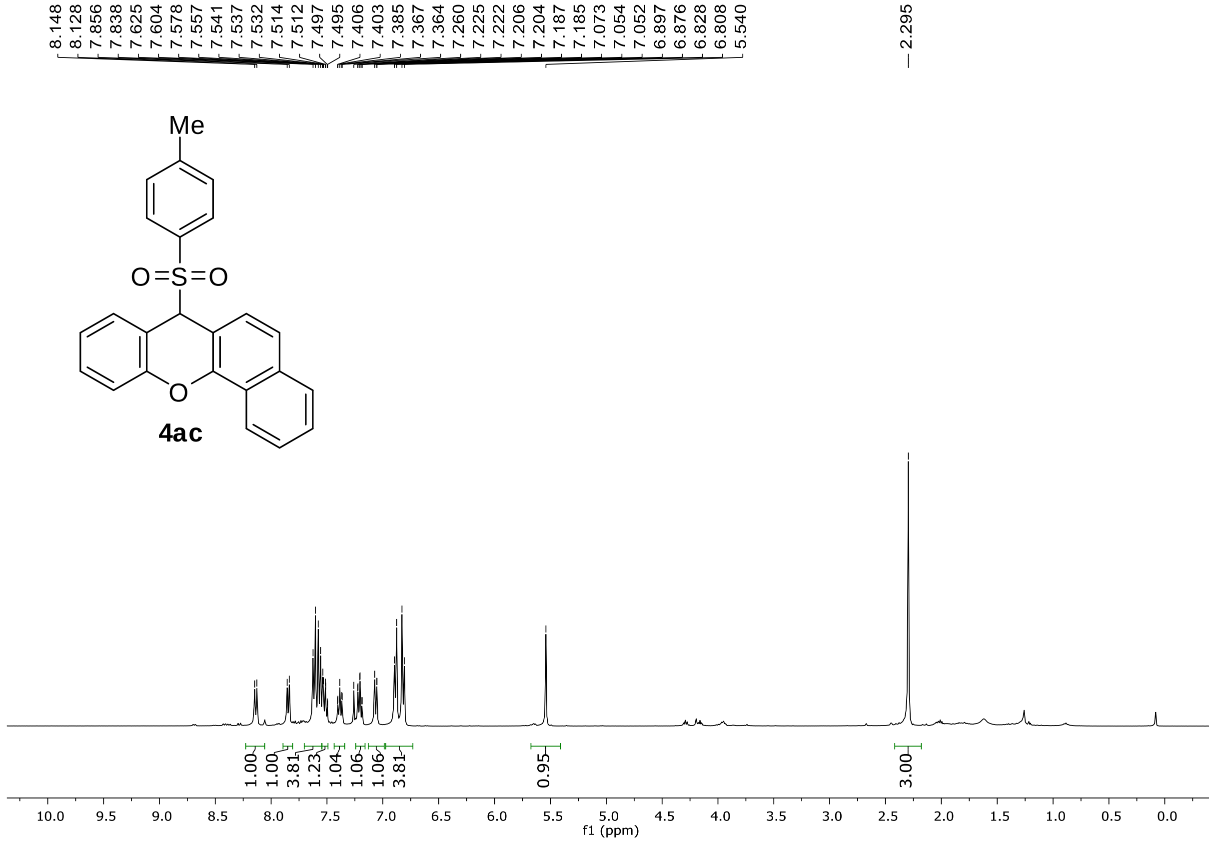
^{1}H NMR spectrum of **4ab** (400 MHz, $CDCl_3$):



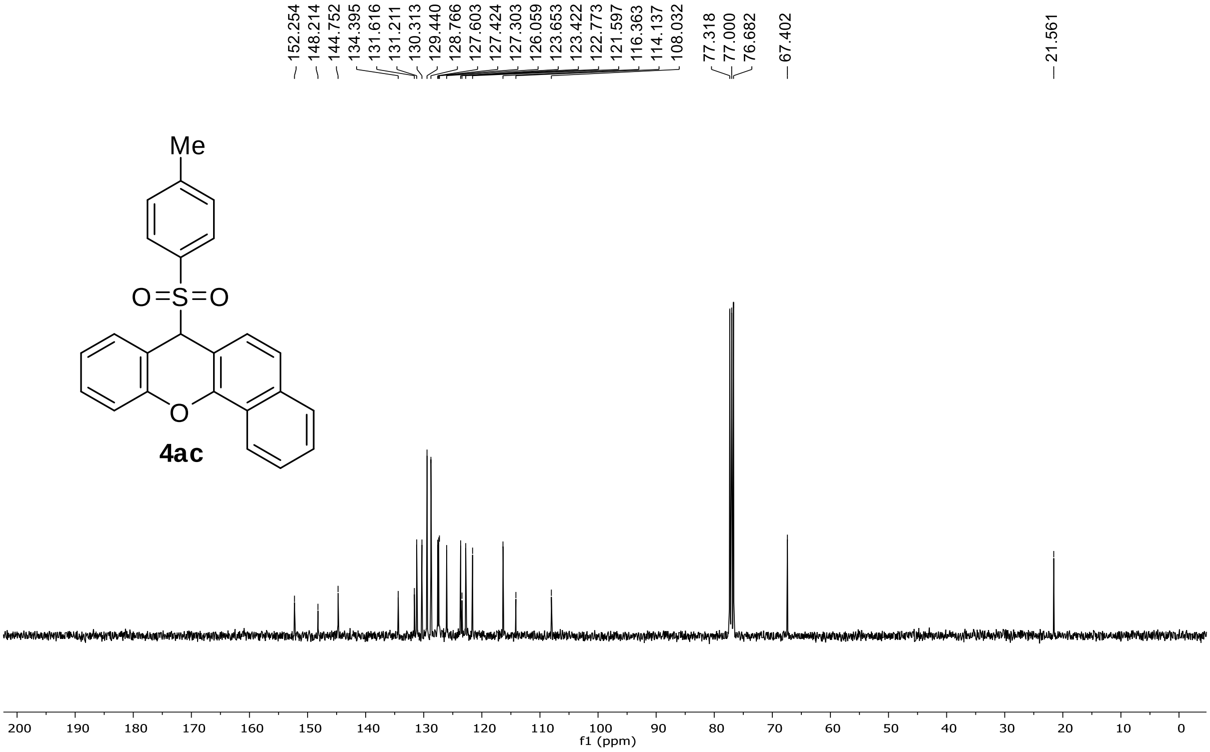
$^{13}C\ \{^1H\}$ NMR spectrum of **4ab** (100 MHz, $CDCl_3$):



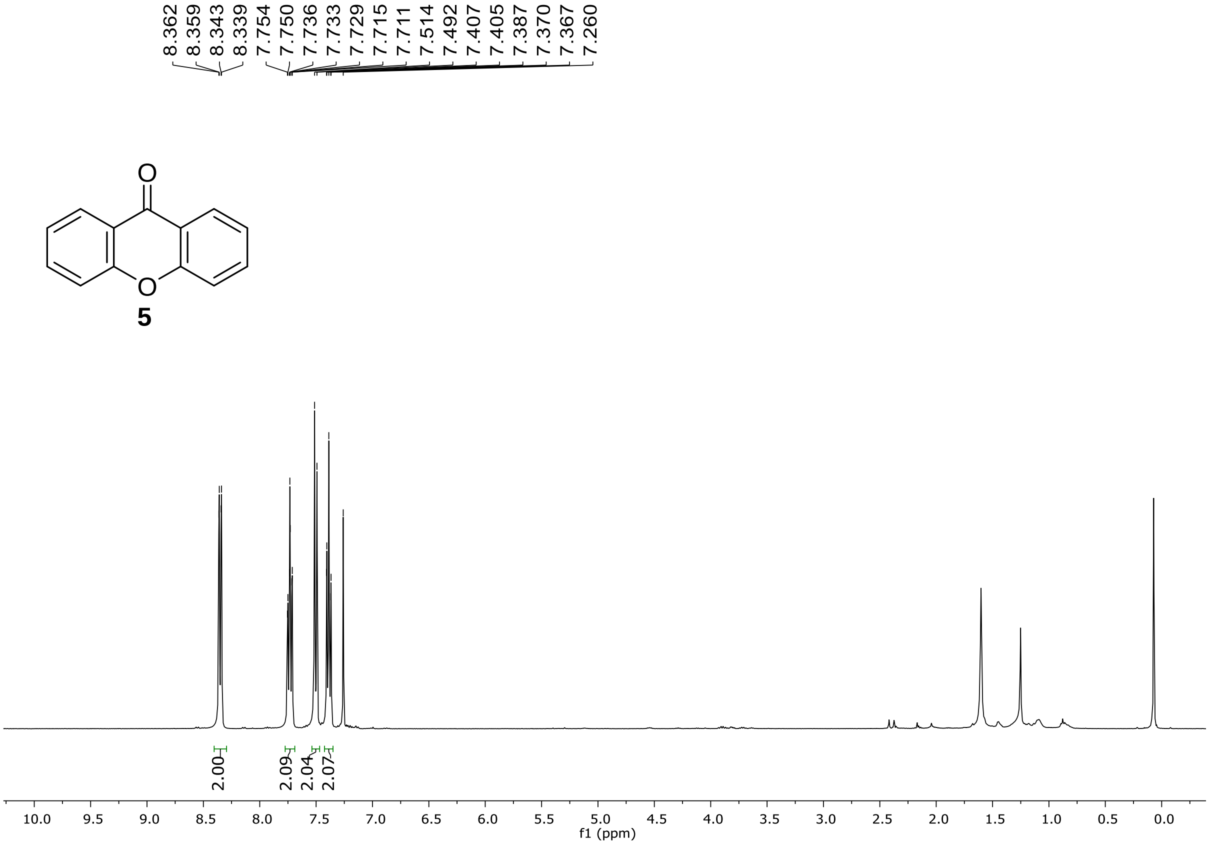
^1H NMR spectrum of **4ac** (400 MHz, $CDCl_3$):



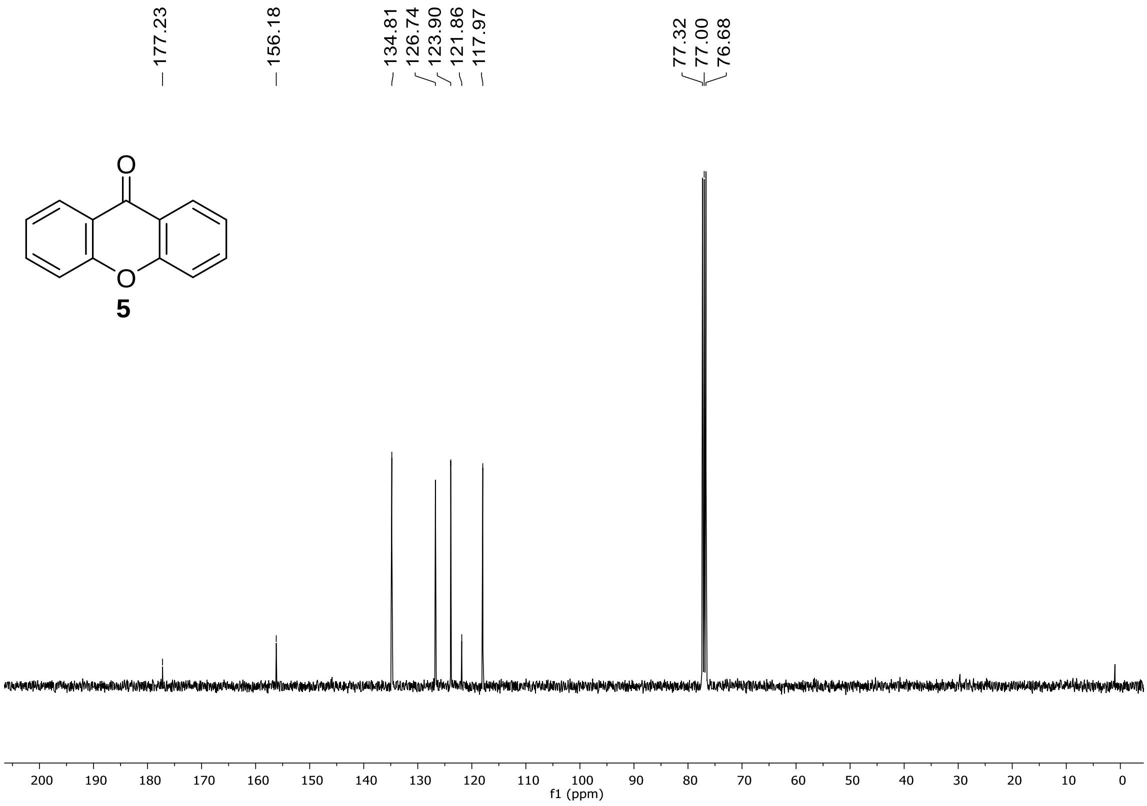
^{13}C {^{1}H} NMR spectrum of **4ab** (100 MHz, CDCl$_3$):



^{1}H NMR spectrum of **5** (400 MHz, CDCl$_3$):



$^{13}C\ \{^1H\}$ NMR spectrum of **5** (100 MHz, $CDCl_3$):



END