Supporting Information

Sulfoximines Assisted Rh(III)-Catalyzed C-H Activation and Intramolecular Annulation for the Synthesis of Fused Isochromeno-1,2-Benzothiazines Scaffolds under Room Temperature

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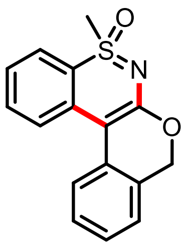
1. X-ray Crystallographic Data of 3aa

1.1 X-ray Single Crystal Diffraction Data of compound 3aa



3aa

Sample preparation: To a solution of compound **3aa** (10 mg) dissolved in EtOAc (1.0 mL) was filtered through a nylon-membrane syringe filter (13 mm*0.22 μm, purchased from ANPEL Laboratory Tech. Shanghai, Inc.) and transferred into a clean 2 mL vial. The vial was sealed with a thin layer of parafilm on top of which 3-5 holes was made with a capillary (0.3 mm) to allow the solvent slowly evaporated at room temperature to afford the single crystal **3aa** in 48 hours.

Single crystal structure of 3aa: X-ray crystal structure of **3aa** was determined at 170 K with the ellipsoid contour at 50% probability levels.

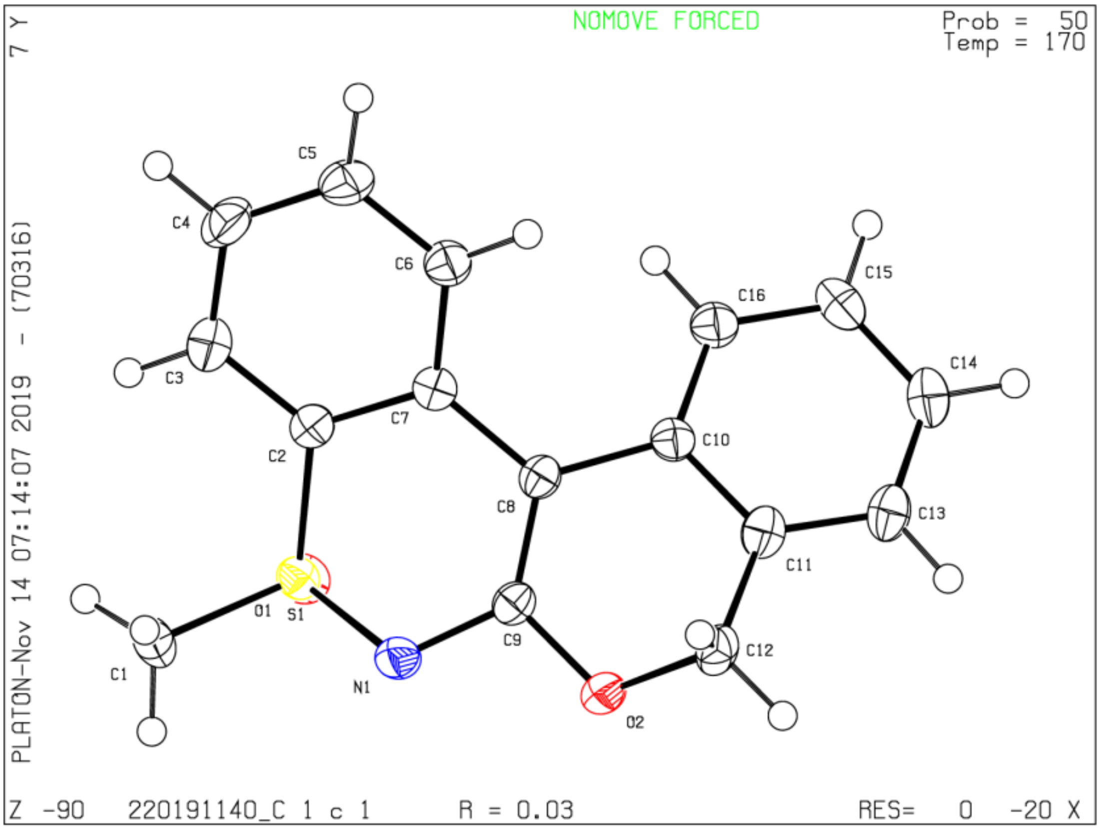


Table 1 Crystal data and structure refinement for 220191140_0m (3aa).

Identification code	220191140_0m
Empirical formula	$C_{16}H_{13}NO_2S$
Formula weight	283.33
Temperature/K	170.0
Crystal system	monoclinic
Space group	Cc
a/Å	14.3267(7)
b/Å	10.2239(6)
c/Å	9.2727(4)
α/°	90
β/°	106.242(2)
γ/°	90
Volume/Å^3	1304.01(12)
Z	4
ρ_{calc}g/cm^3	1.443
μ/mm^{-1}	0.248
F(000)	592.0
Crystal size/mm^3	0.18 × 0.11 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.964 to 54.998
Index ranges	$-18 \leq h \leq 18$, $-12 \leq k \leq 13$, $-12 \leq l \leq 11$
Reflections collected	6706
Independent reflections	2590 [R_{int} = 0.0413, R_{sigma} = 0.0517]
Data/restraints/parameters	2590/2/182
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0344, wR_2 = 0.0804
Final R indexes [all data]	R_1 = 0.0382, wR_2 = 0.0837

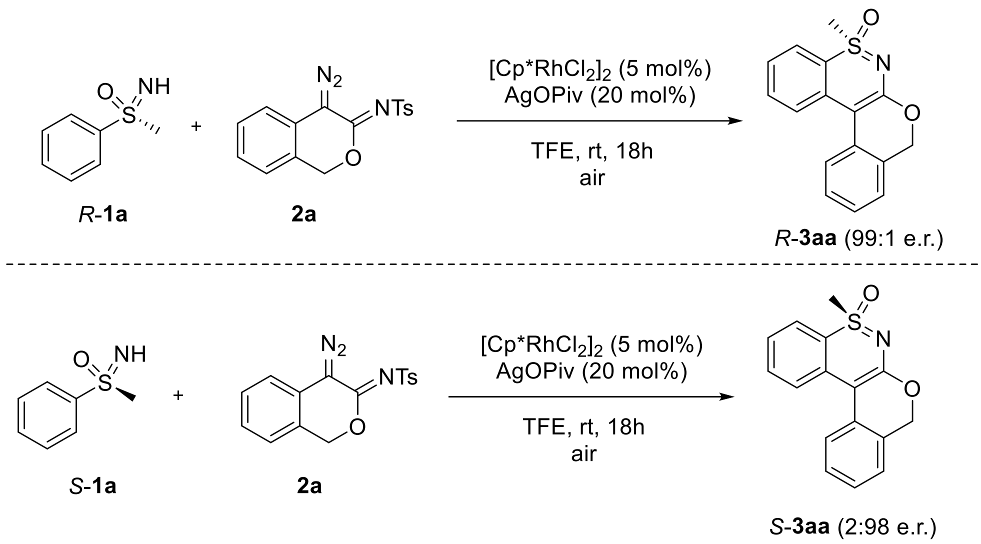
Largest diff. peak/hole / e Å^{-3} 0.25/-0.28

Flack parameter -0.01(6)

Crystal structure determination of [220191140_0m] (3aa)

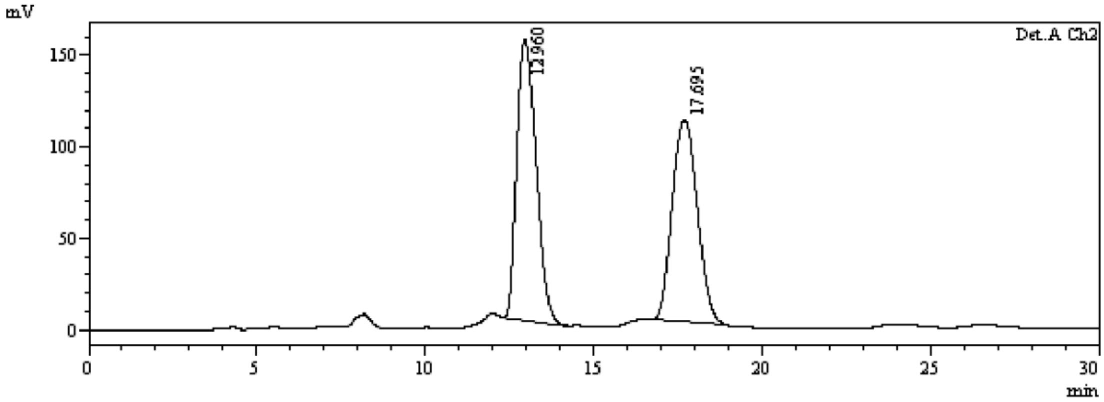
Crystal Data for $C_{16}H_{13}NO_2S$ (M =283.33 g/mol): monoclinic, space group Cc (no. 9), a = 14.3267(7) Å, b = 10.2239(6) Å, c = 9.2727(4) Å, β = 106.242(2)°, V = 1304.01(12) Å^3, Z = 4, T = 170.0 K, μ(MoKα) = 0.248 mm^{-1}, $Dcalc$ = 1.443 g/cm^3, 6706 reflections measured (4.964° ≤ 2Θ ≤ 54.998°), 2590 unique (R_{int} = 0.0413, R_{sigma} = 0.0517) which were used in all calculations. The final R_1 was 0.0344 (I > 2σ(I)) and wR_2 was 0.0837 (all data).

2. Conversion of stereoisomer 1a



5-methyl-8H-5λ^4-isochromeno[3,4-c][1,2]benzothiazine 5-oxide (3aa). (R)-**3aa** Yellow-green solid, yield 93% (39.4 mg), 99:1 e.r. was determined by chiral HPLC (Chiralcel AD-H, n-hexane/i-PrOH = 70/30, 0.8 mL/min, 254 nm, 25 °C): t_R (major) = 13.2 min, t_R (minor) = 17.6 min; (S)-**3aa**, Yellow-green solid, yield 91% (38.6 mg), 2:98 e.r. was determined by chiral HPLC (Chiralcel AD-H, n-hexane/i-PrOH = 70/30, 0.8 mL/min, 254 nm, 25 °C): t_R (minor) = 12.0 min, t_R (major) = 17.4 min; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (d, J = 9.6 Hz, 1H), 7.78 (dd, J = 8.0, 1.3 Hz, 1H), 7.62 – 7.54 (m, 2H), 7.38 – 7.26 (m, 2H), 7.21 – 7.11 (m, 2H), 5.20 – 4.99 (m, 2H), 3.49 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 157.3, 135.0, 132.9, 131.3, 128.8, 128.2, 125.0, 124.8, 124.5, 124.4, 123.2, 122.2, 120.0, 91.9, 70.3, 43.0;

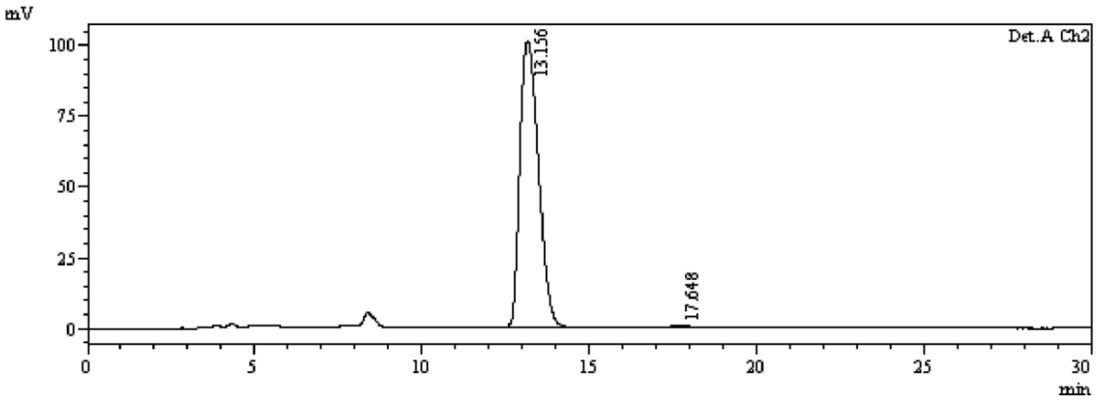
LRMS (ESI): *m/z* 284.1 [M + H]$^+$; HRMS (ESI): calculated for $C_{16}H_{14}NO_2S$ [M + H]$^+$: 284.0740, found: 284.0745.



PeakTable

Detector A Ch2 254nm

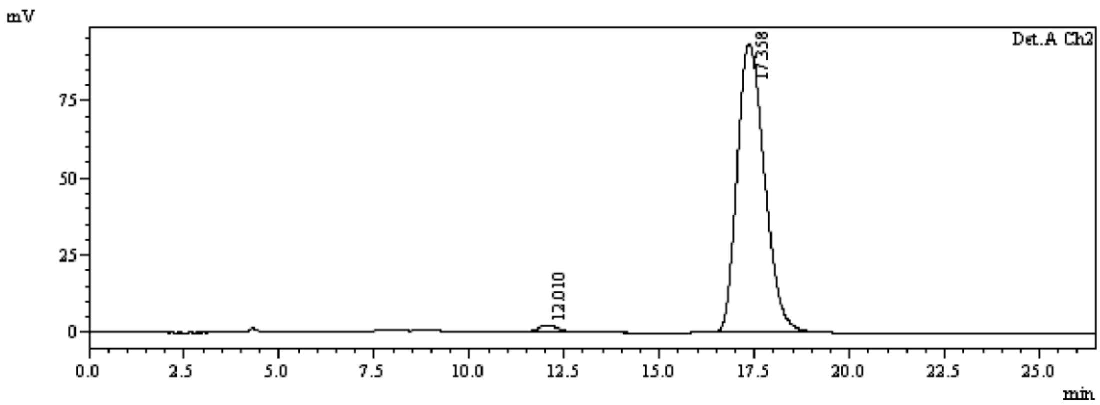
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.960	6107921	152959	51.401	58.021
2	17.695	5774872	110667	48.599	41.979
Total		11882793	263626	100.000	100.000



PeakTable

Detector A Ch2 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.156	3911997	101074	99.243	99.344
2	17.648	29834	668	0.757	0.656
Total		3941832	101742	100.000	100.000



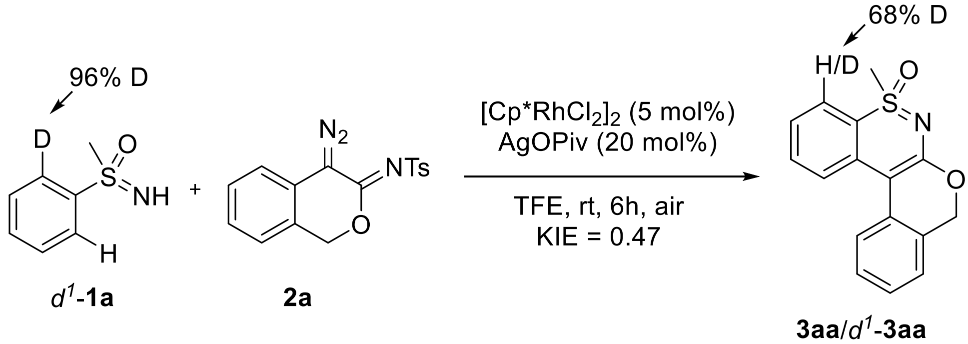
PeakTable

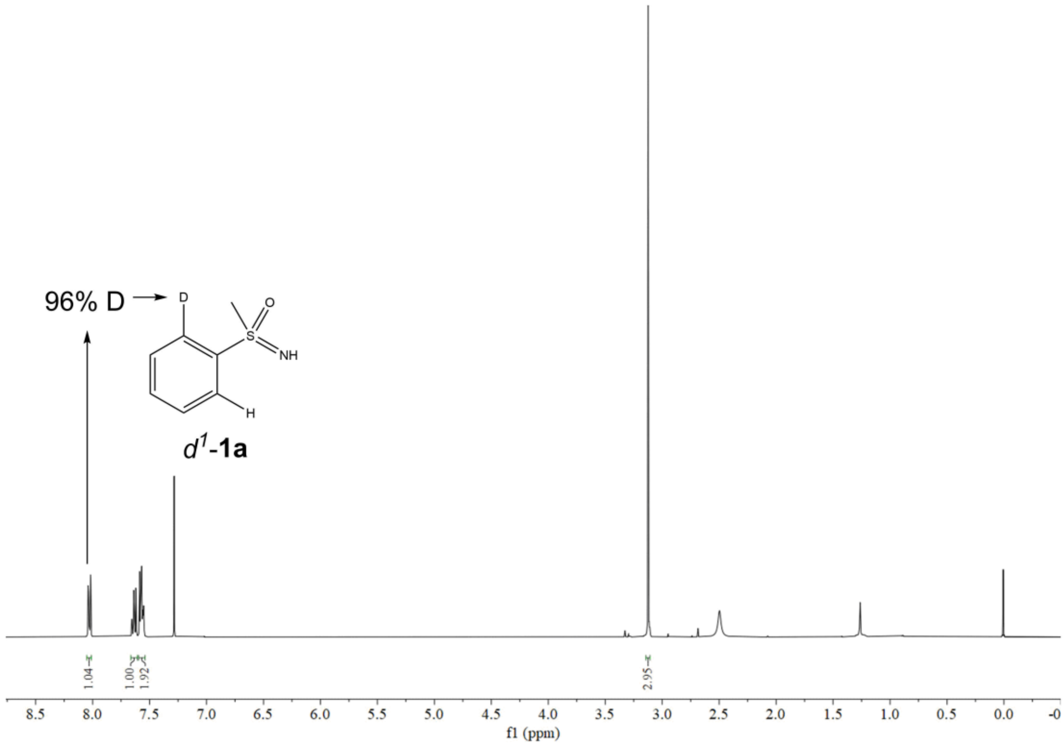
Detector A Ch2 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.010	61014	1919	1.297	2.022
2	17.358	4644479	92999	98.703	97.978
Total		4705493	94918	100.000	100.000

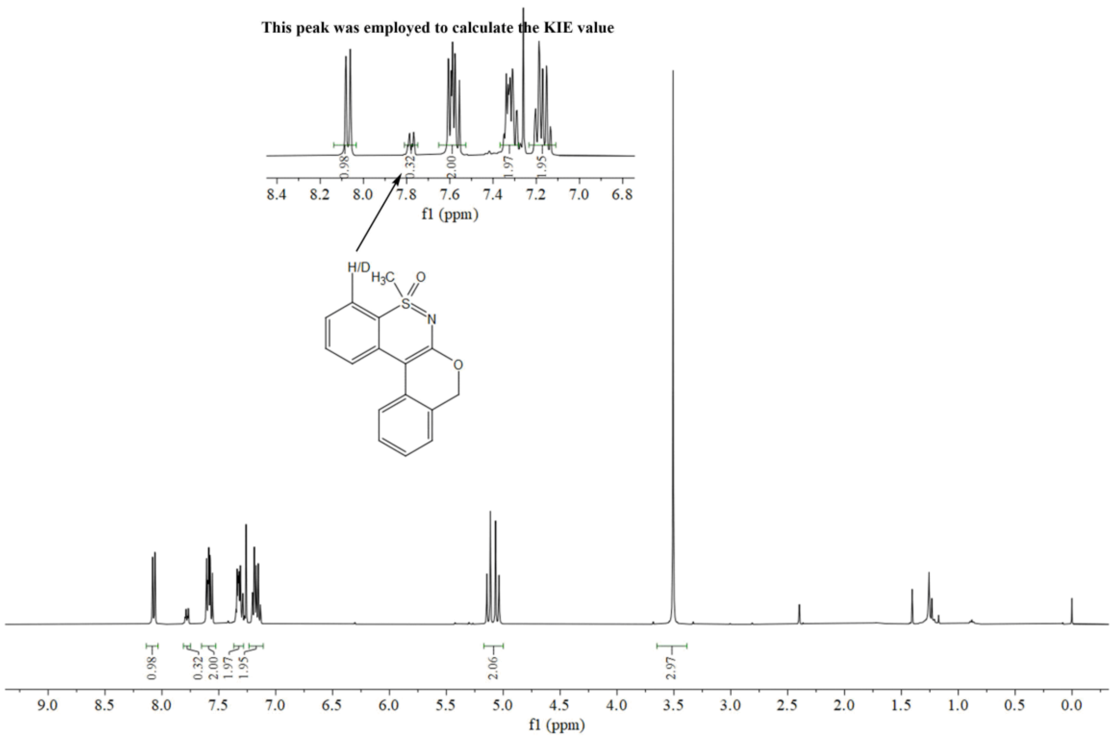
3. Mechanistic Investigations

3.1 Kinetic isotope effect (KIE) experiment



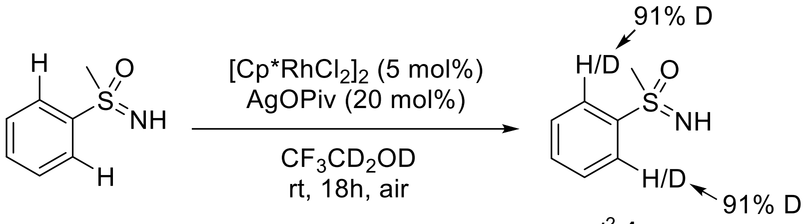


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *d*^{1}**-1a**

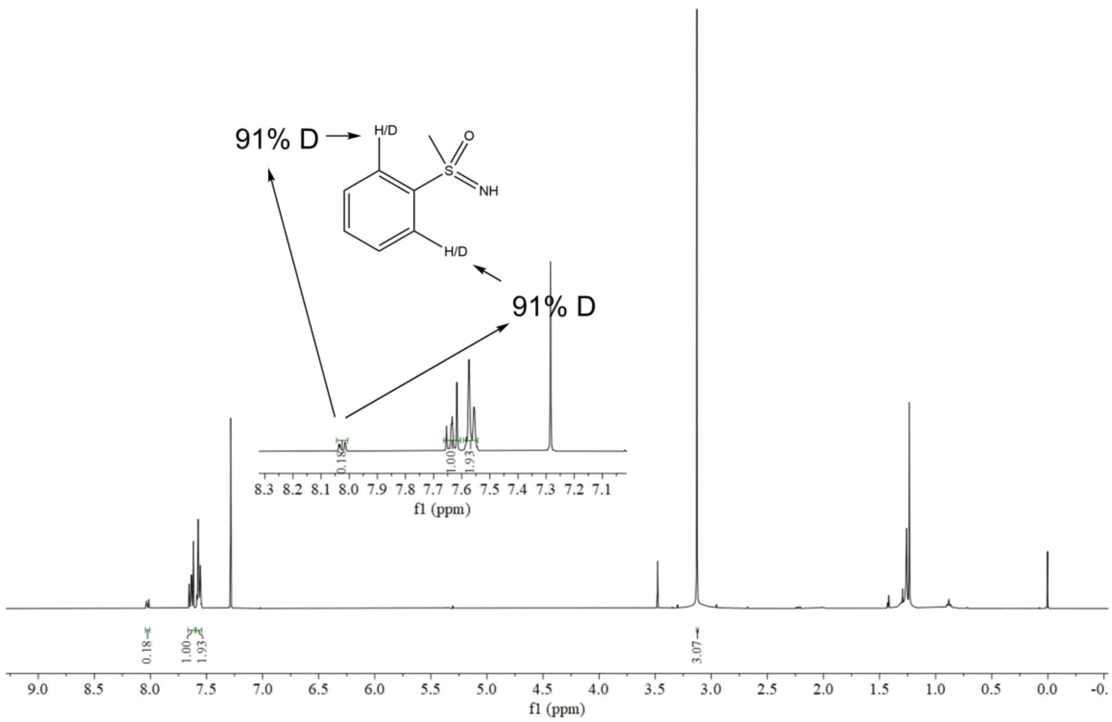


$k_H/k_D = 0.32/0.68 = 0.47$

3.2 H/D exchange experiment

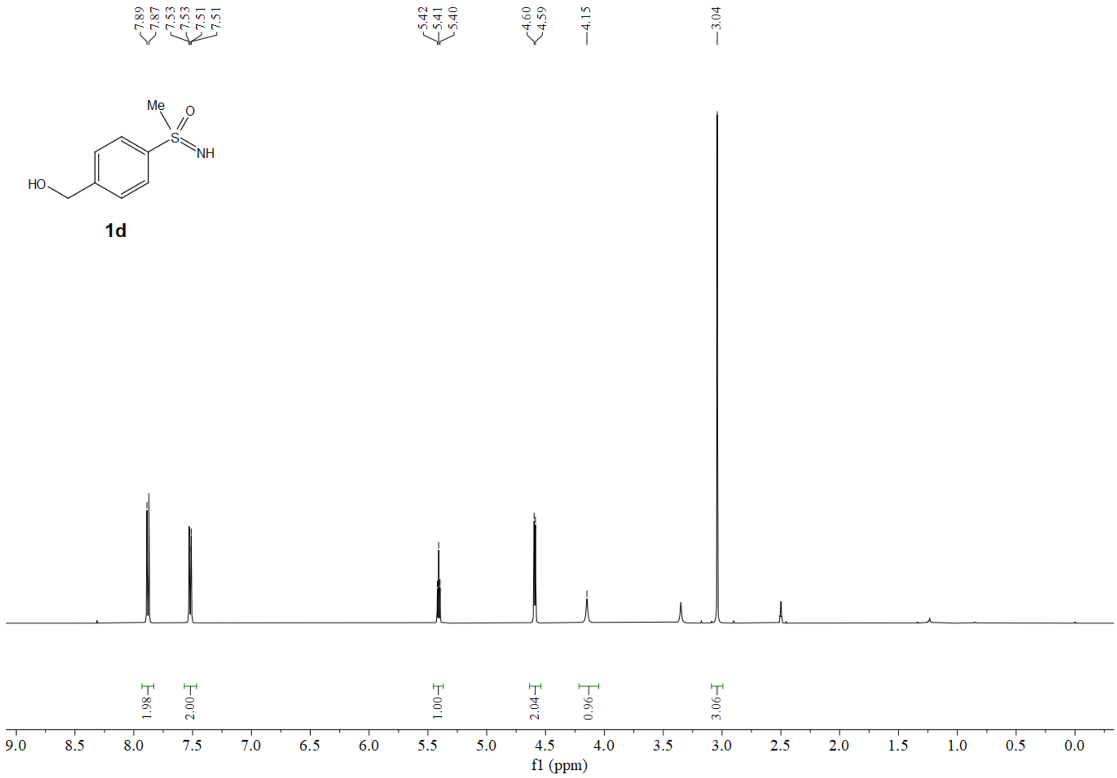


1a d^2-**1a**

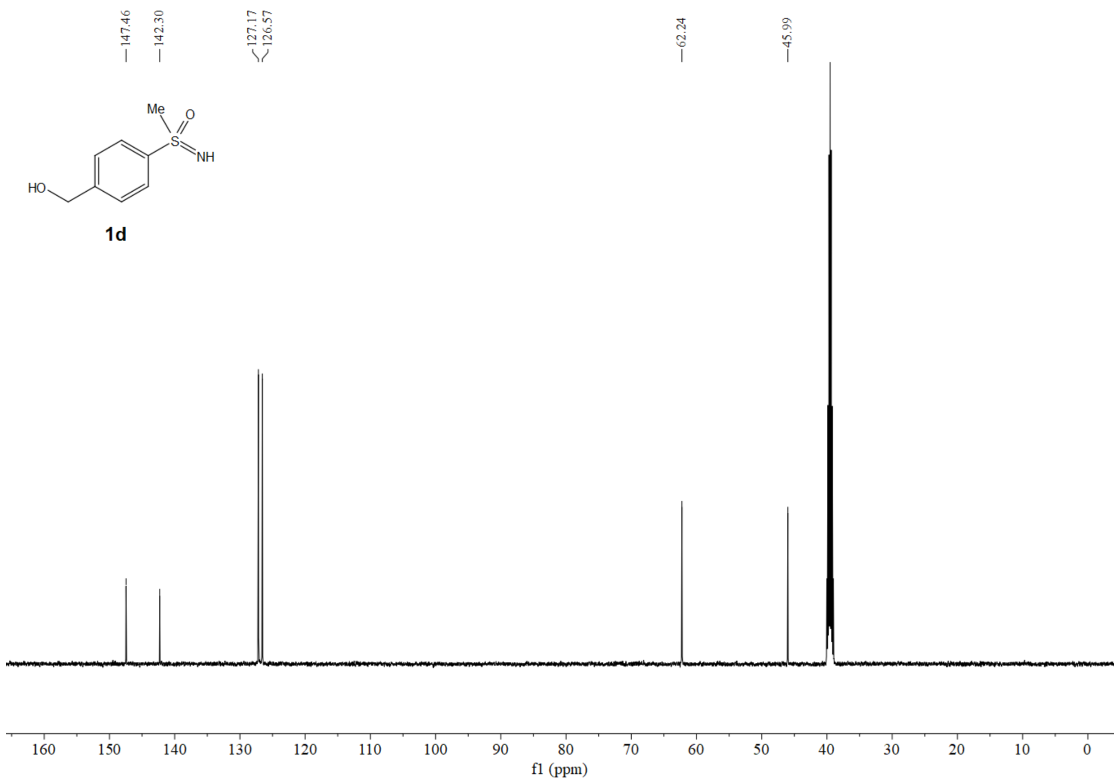


[1]H NMR spectrum (400 MHz, $CDCl_3$) of *d*[2]-**1a**

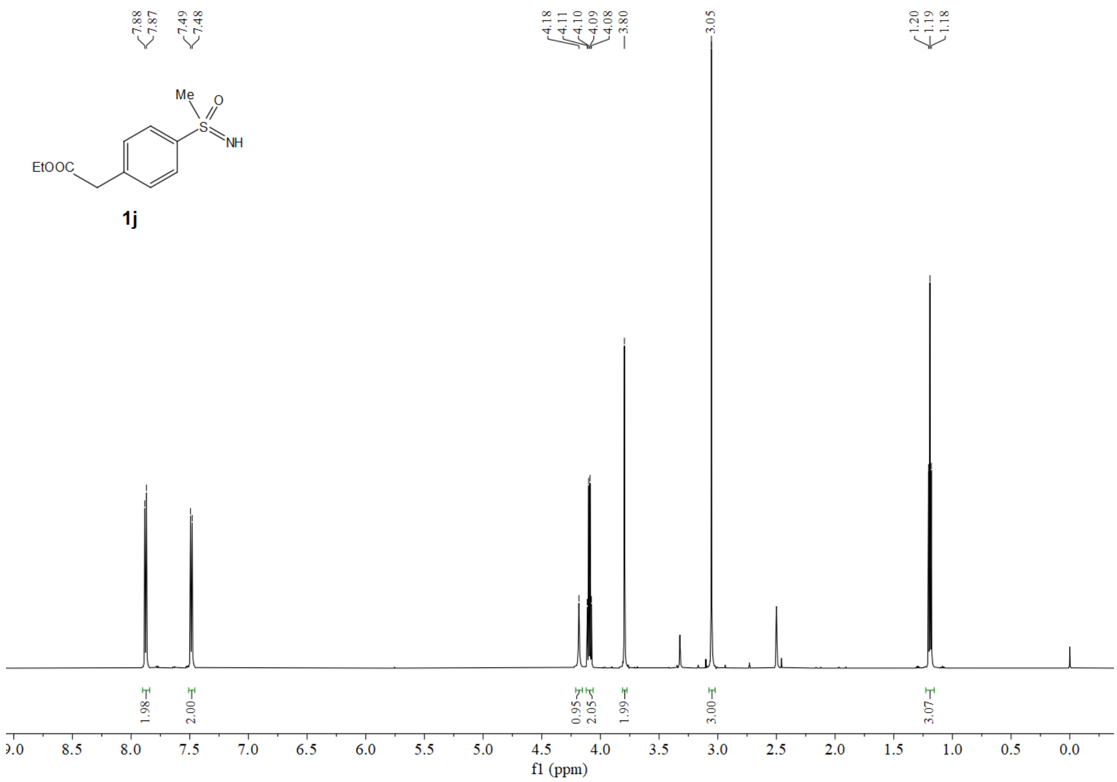
4. NMR Data



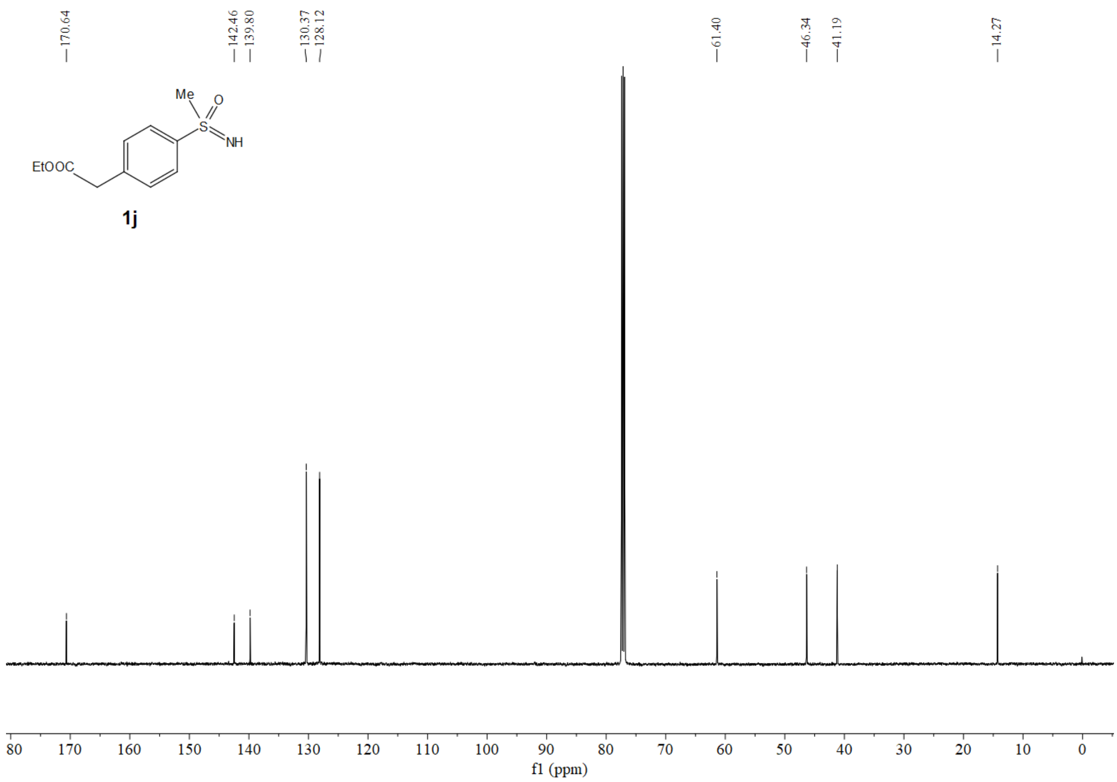
^{1}H NMR spectrum of **1d**



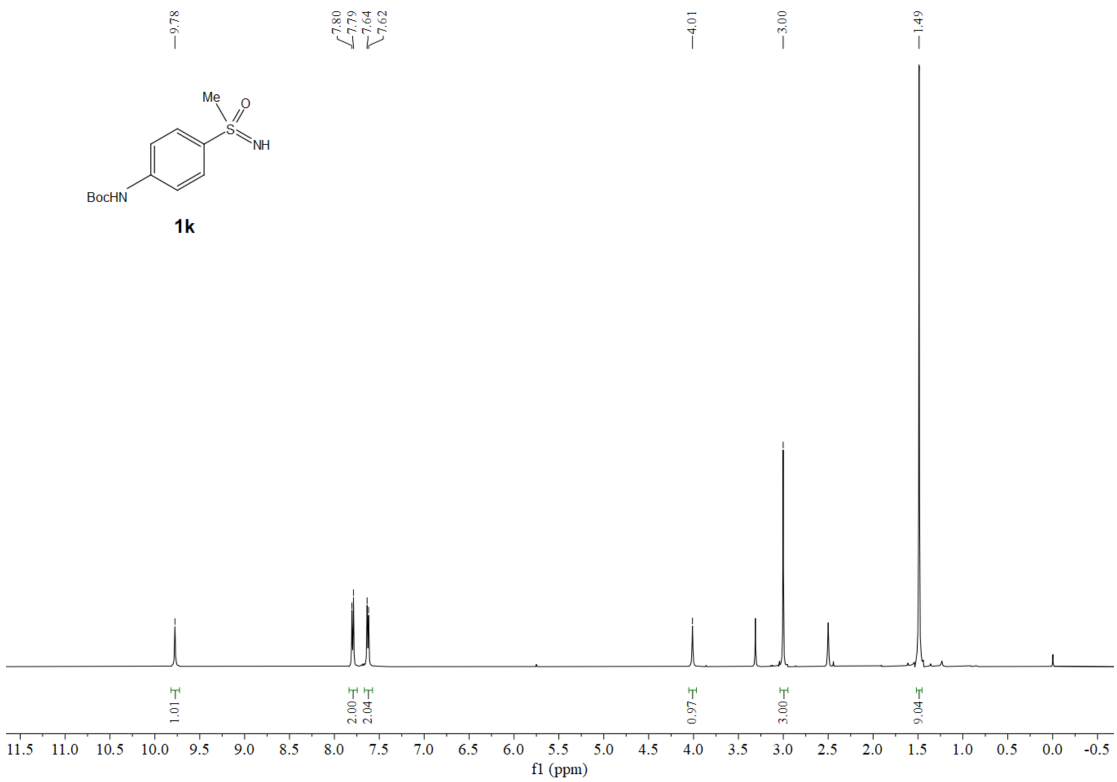
^{13}C NMR spectrum of **1d**



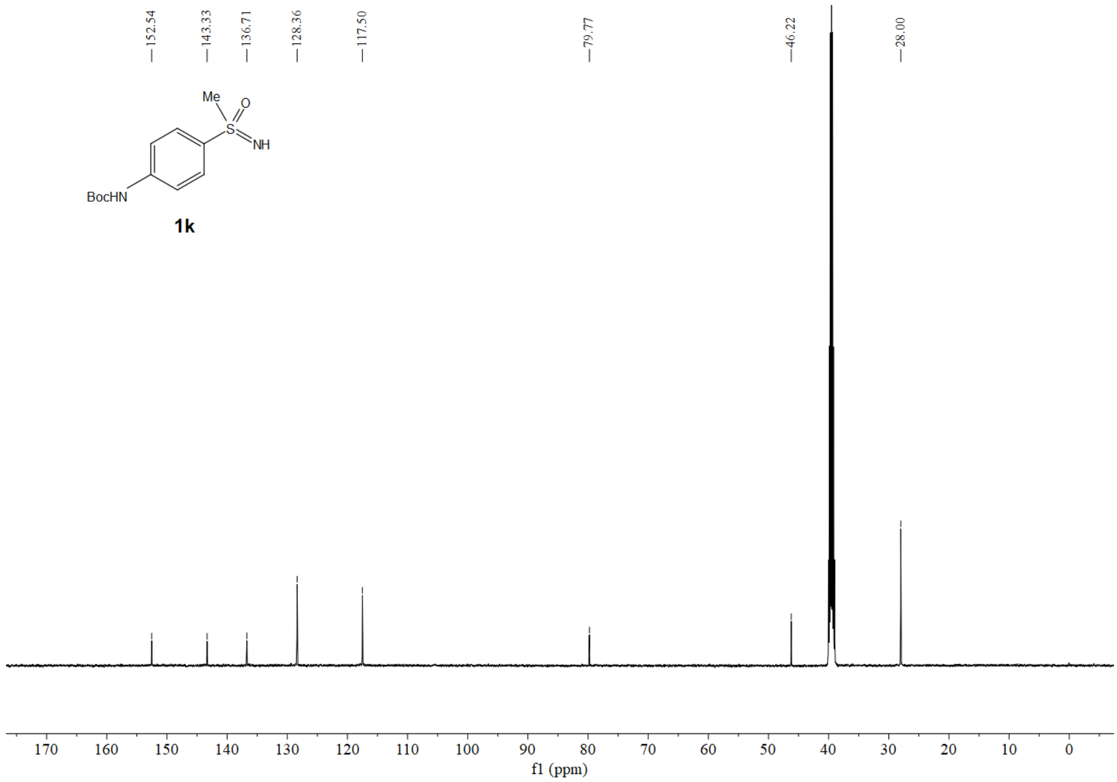
^{1}H NMR spectrum of **1j**



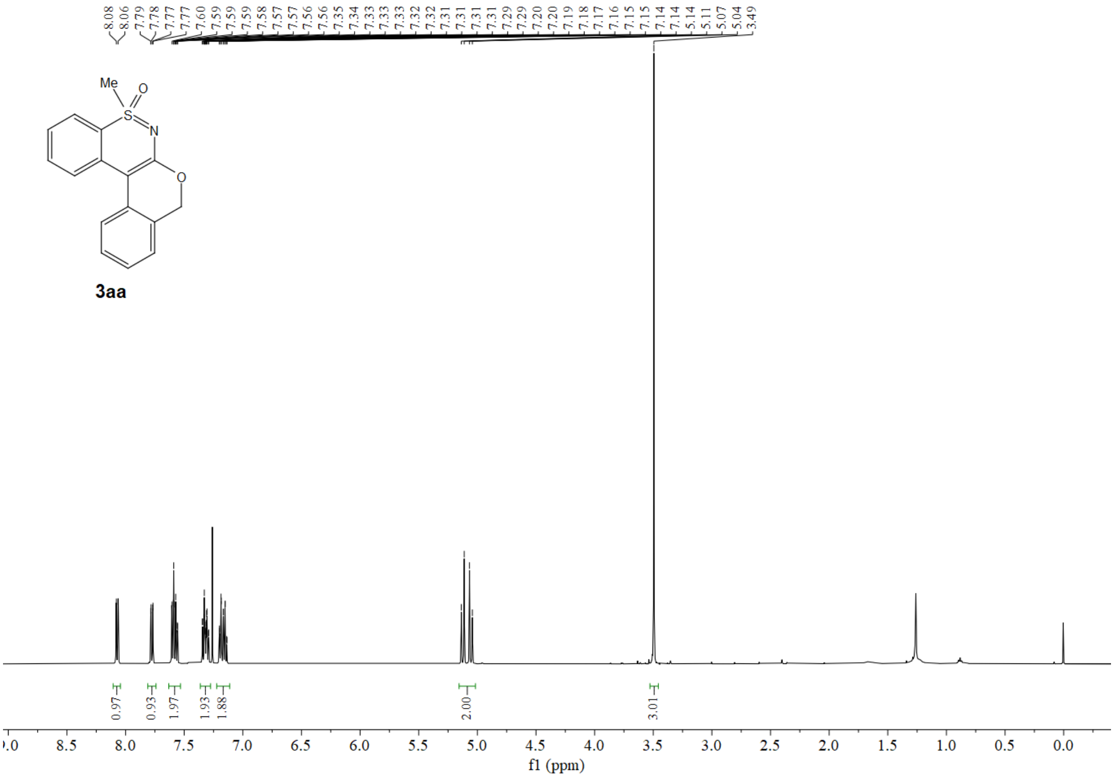
^{13}C NMR spectrum of **1j**



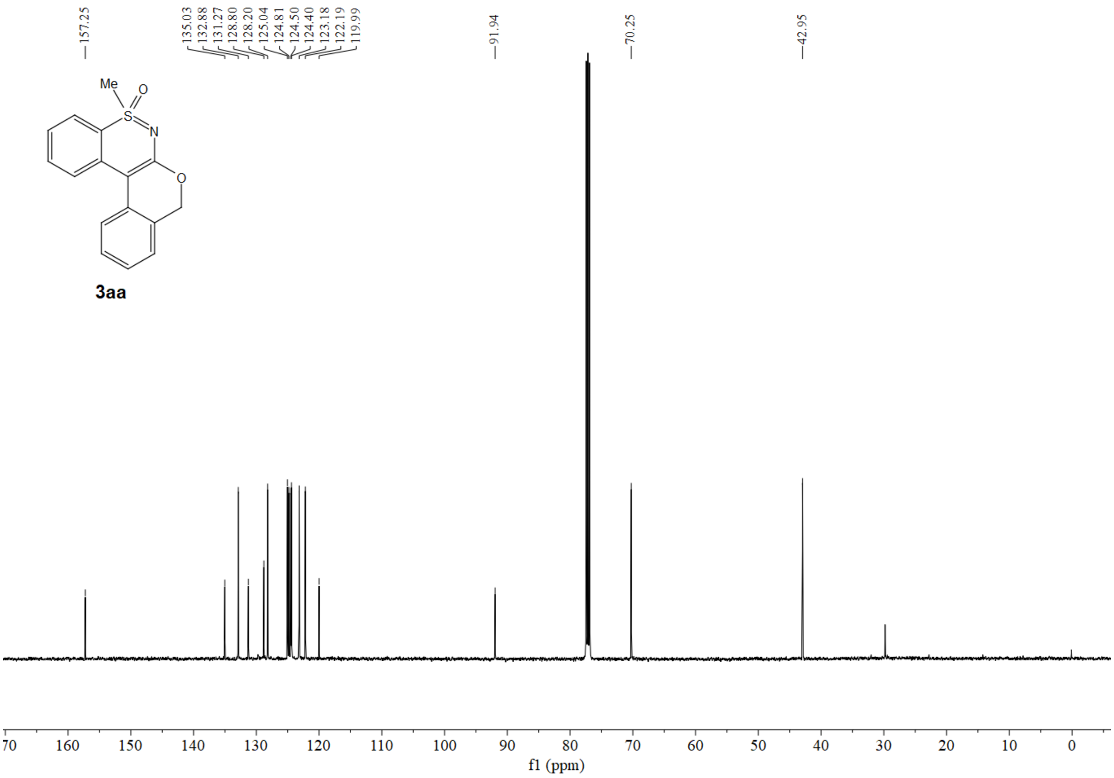
^{1}H NMR spectrum of **1k**



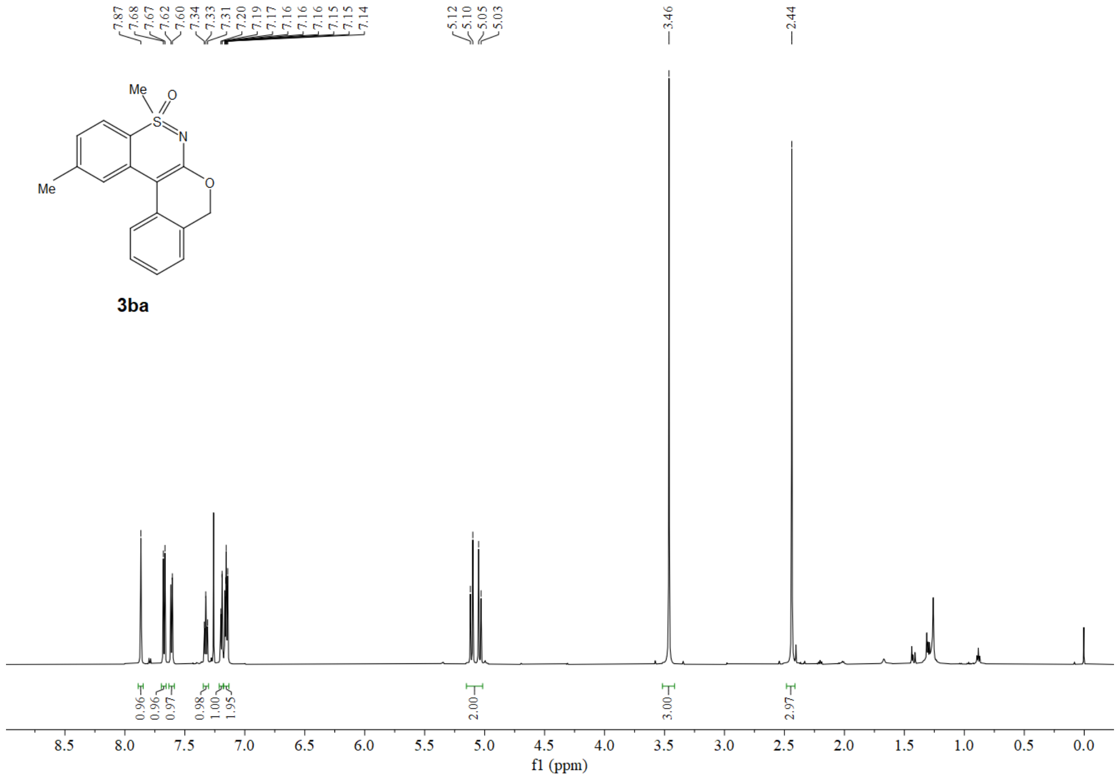
^{13}C NMR spectrum of **1k**



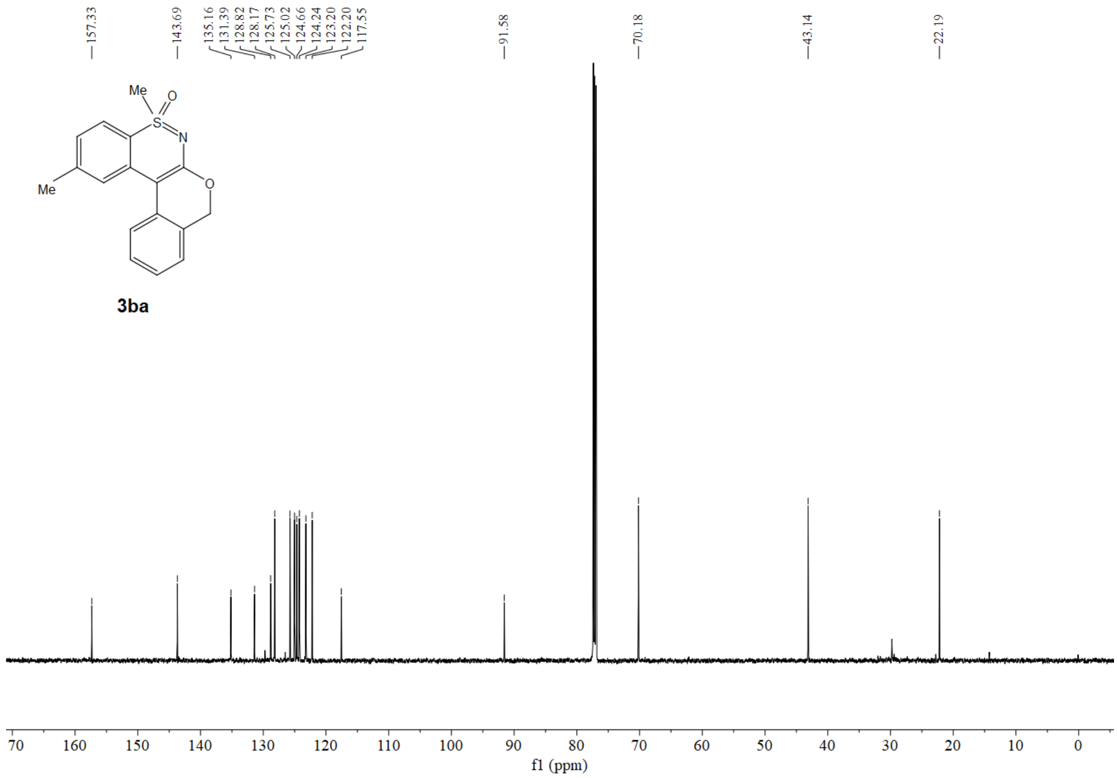
[1]H NMR spectrum of **3aa**



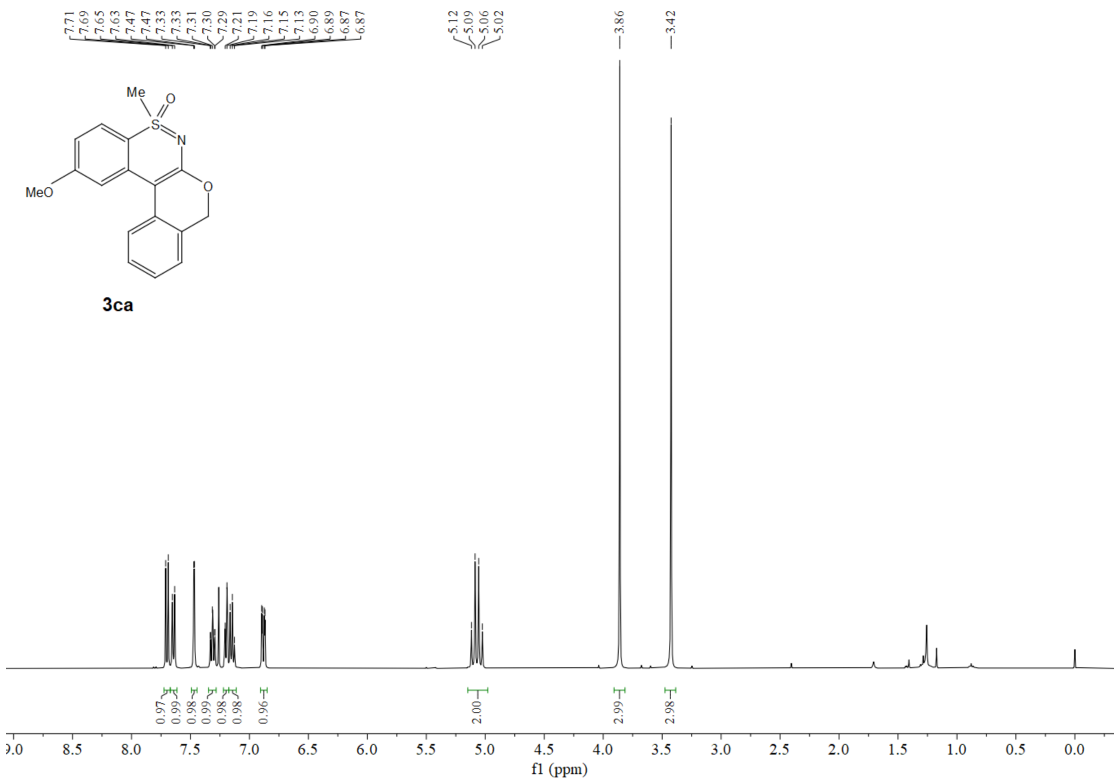
[13]C NMR spectrum of **3aa**



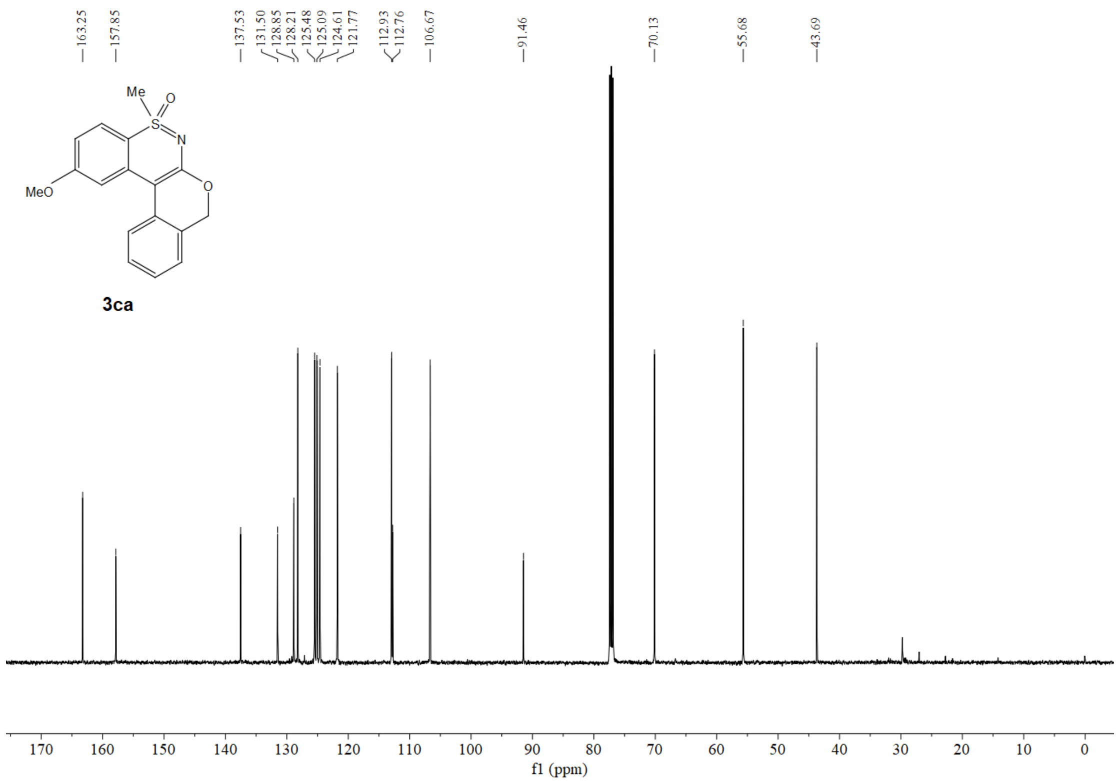
[1]H NMR spectrum of **3ba**



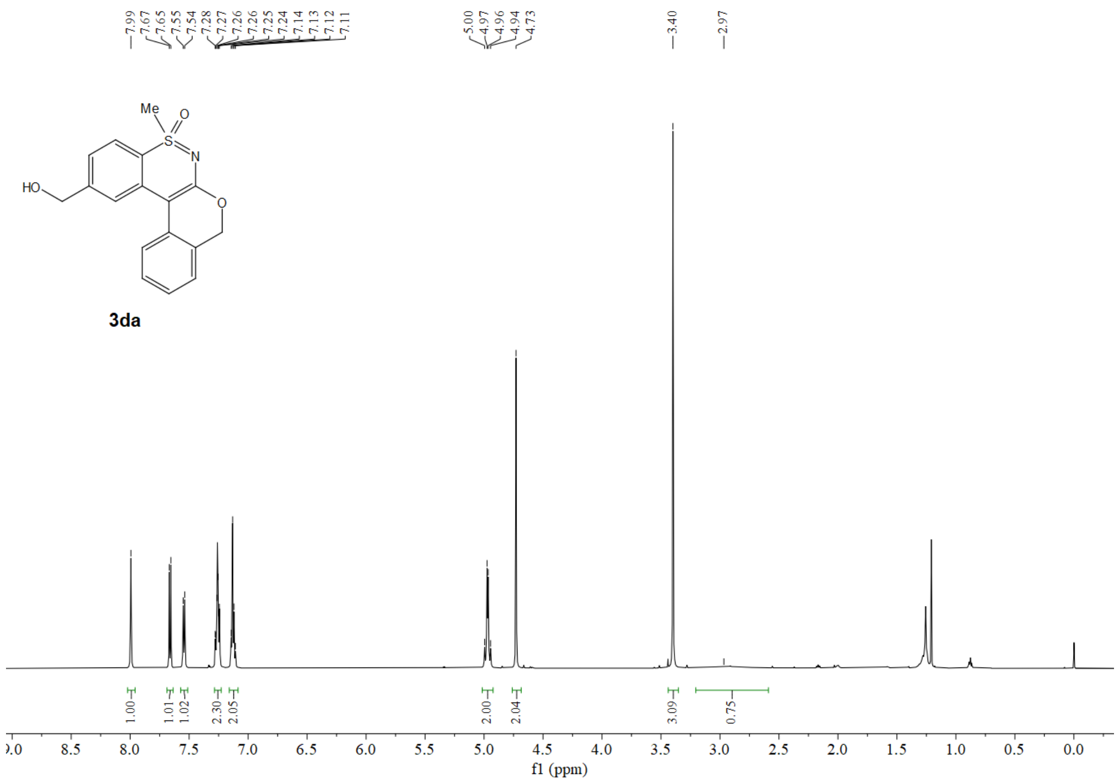
[13]C NMR spectrum of **3ba**



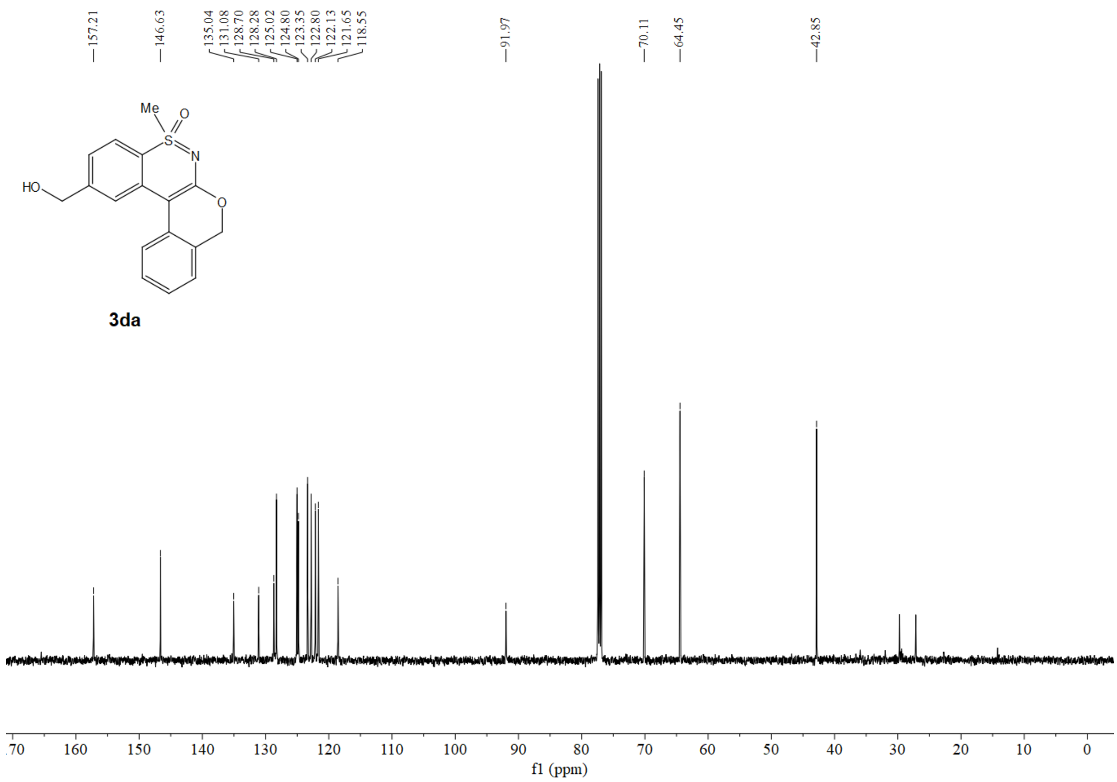
^{1}H NMR spectrum of **3ca**



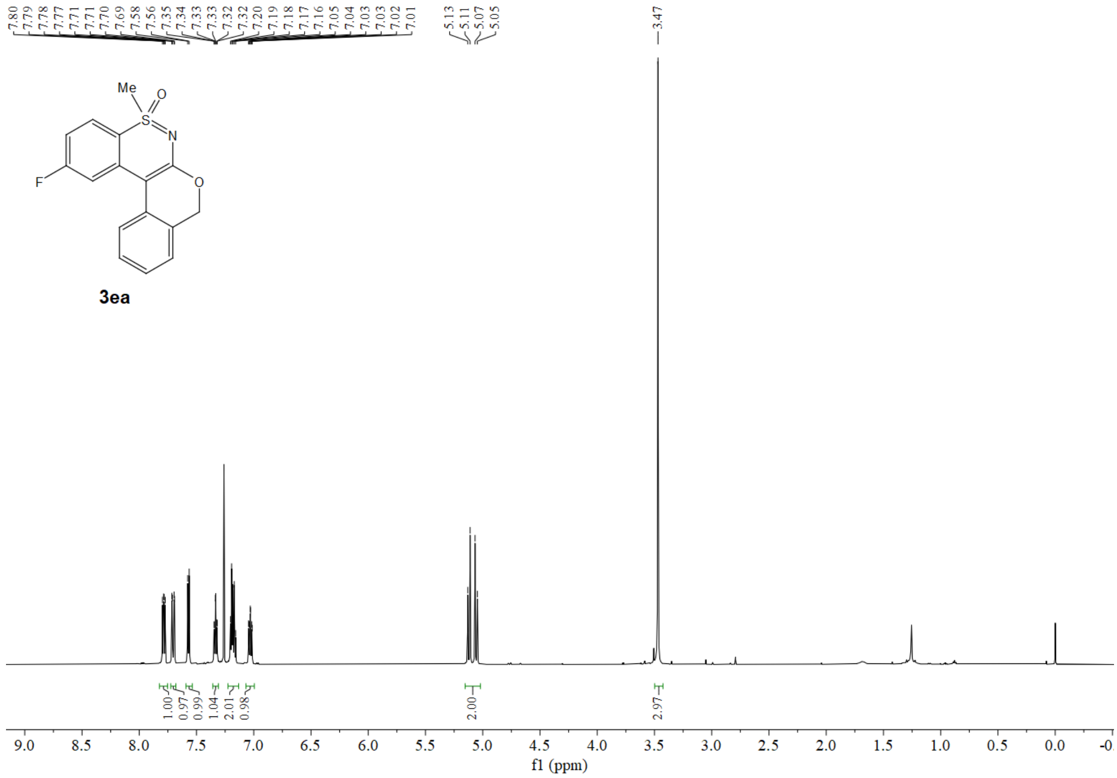
^{13}C NMR spectrum of **3ca**



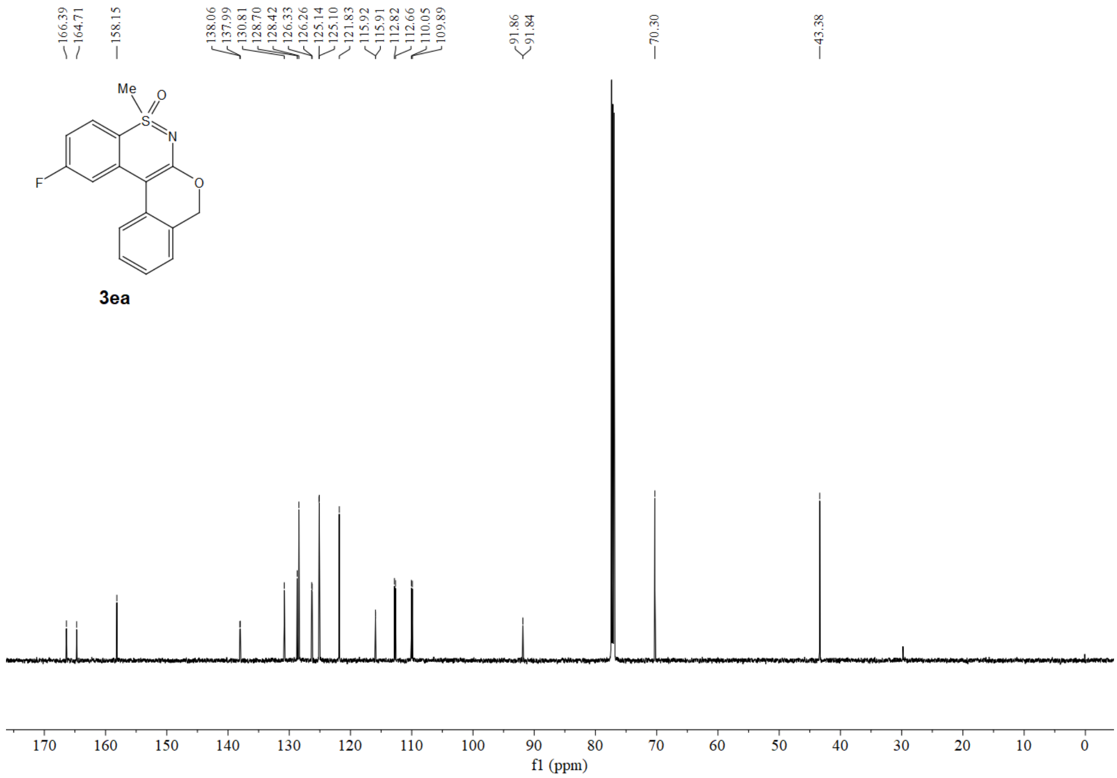
^{1}H NMR spectrum of **3da**



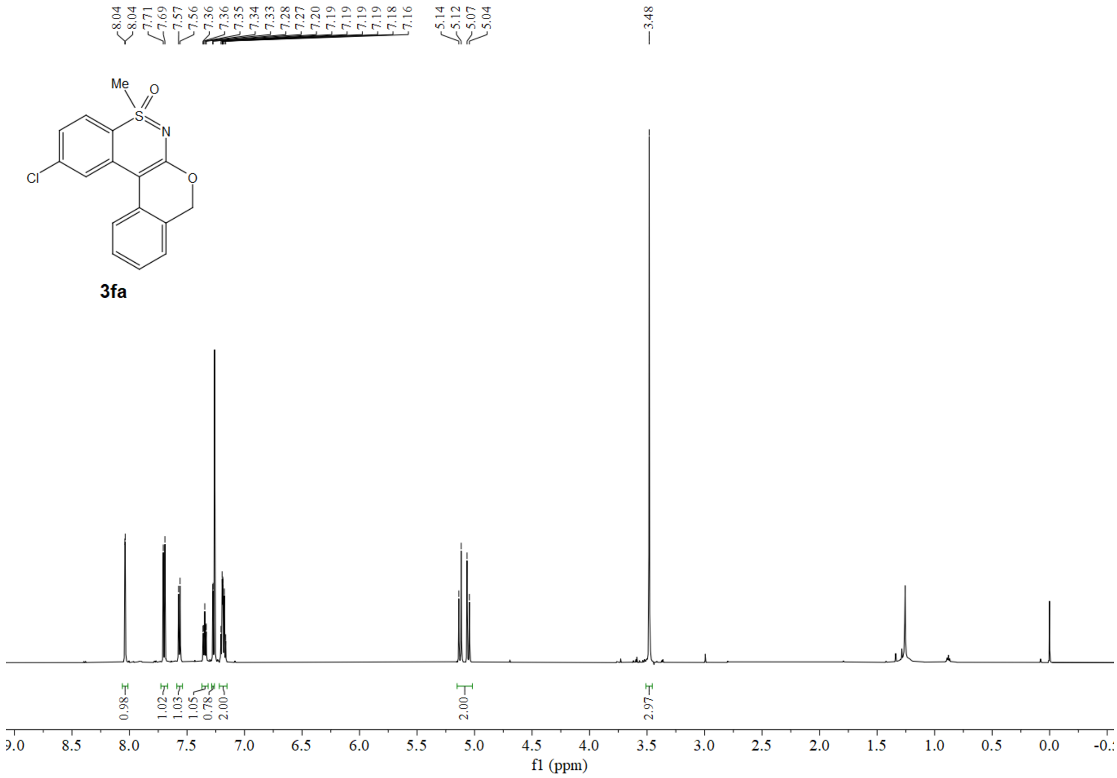
^{13}C NMR spectrum of **3da**



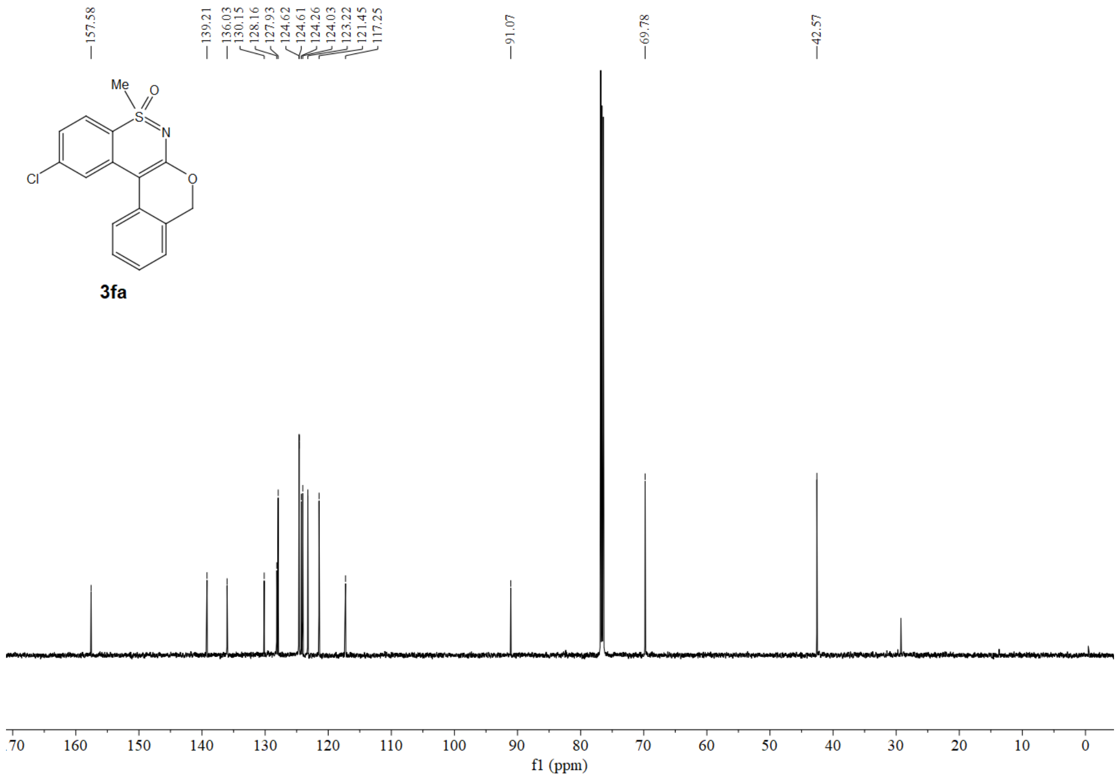
^{1}H NMR spectrum of **3ea**



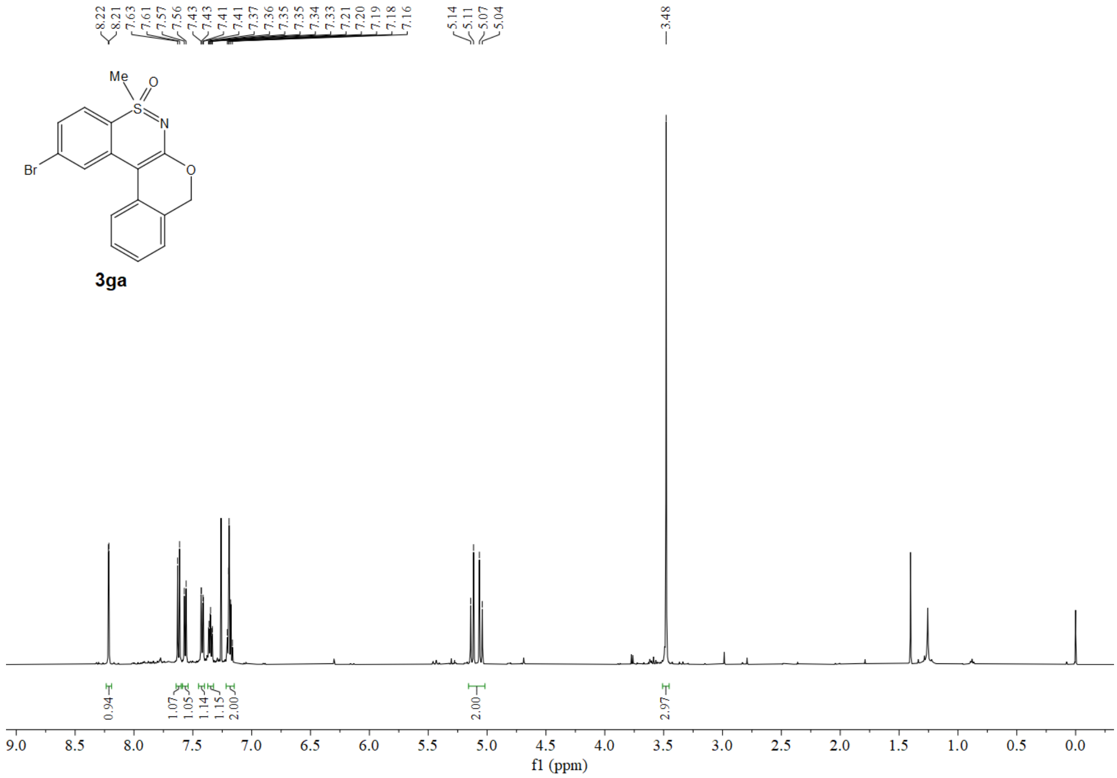
^{13}C NMR spectrum of **3ea**



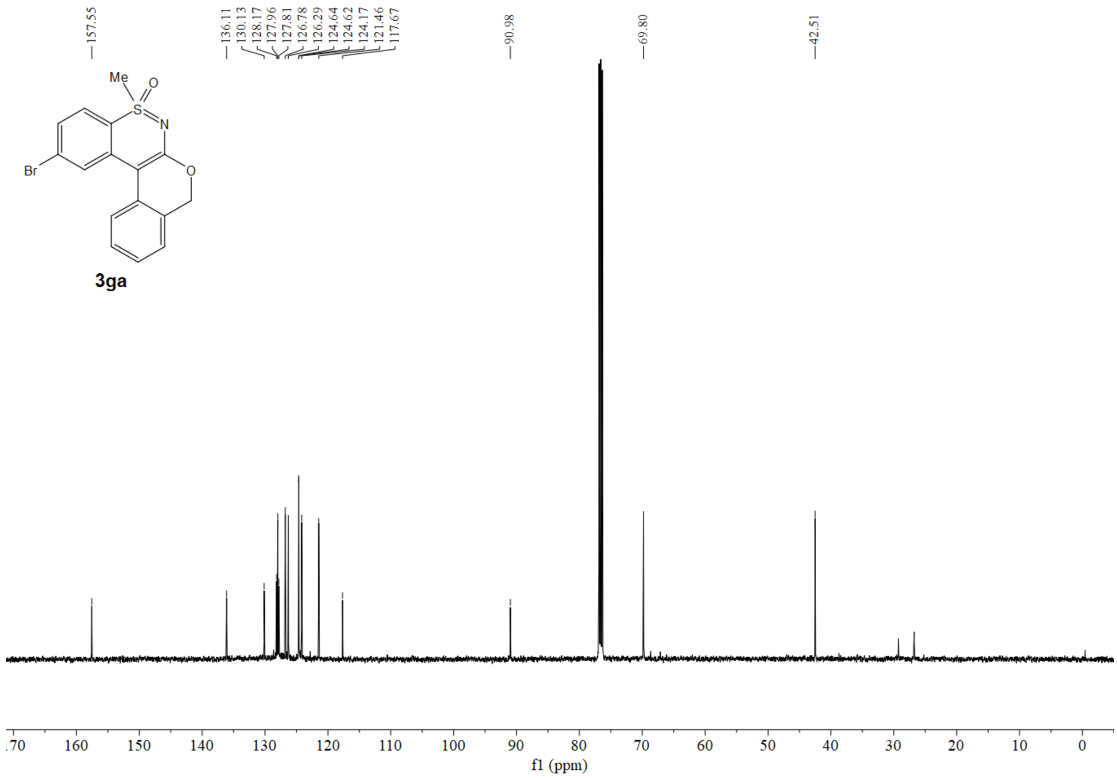
^{1}H NMR spectrum of **3fa**



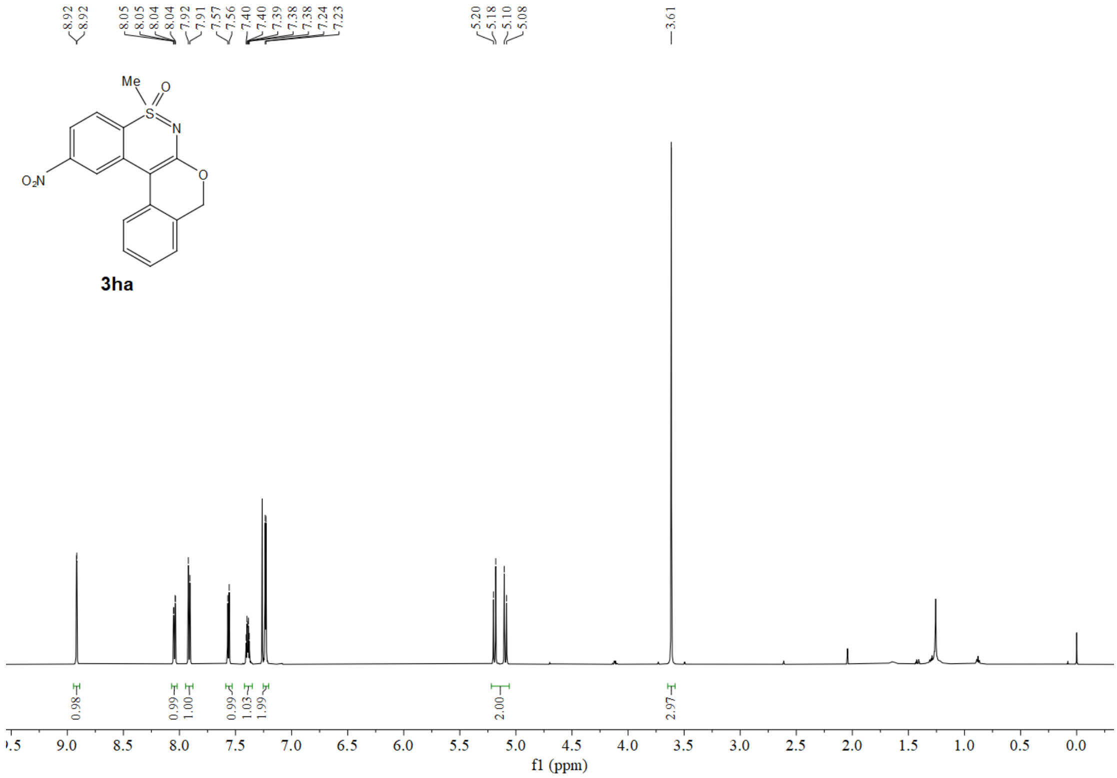
^{13}C NMR spectrum of **3fa**



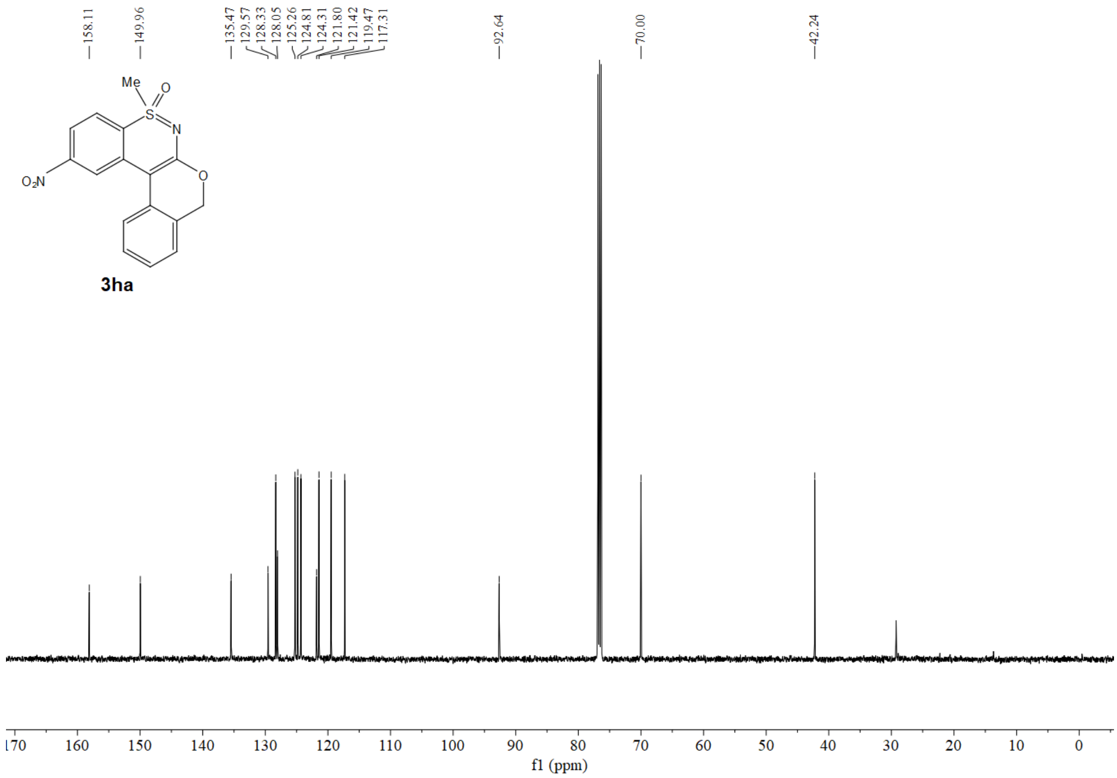
^{1}H NMR spectrum of **3ga**



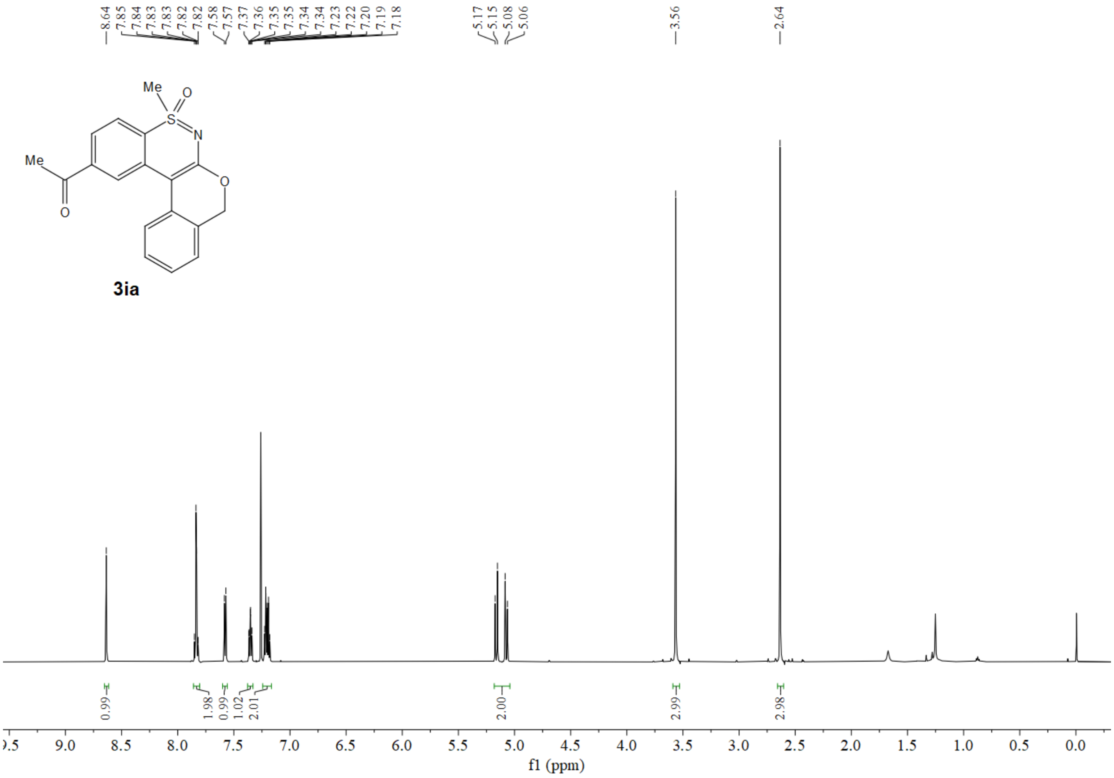
^{13}C NMR spectrum of **3ga**



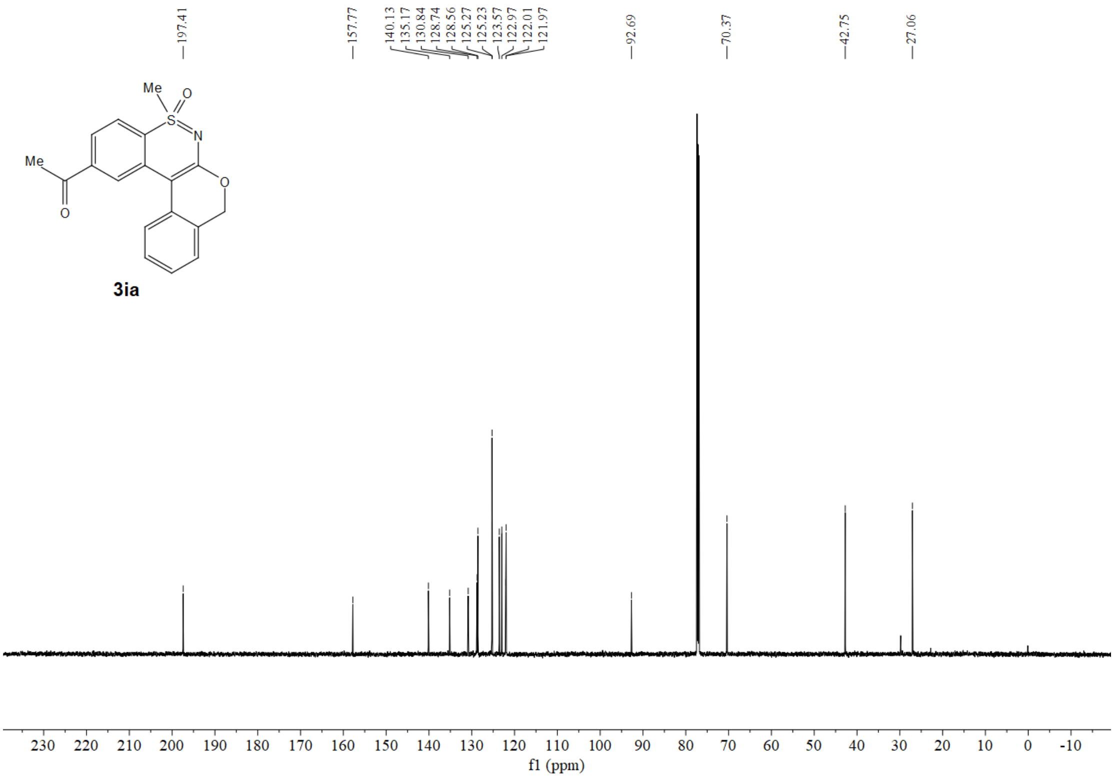
^{1}H NMR spectrum of **3ha**



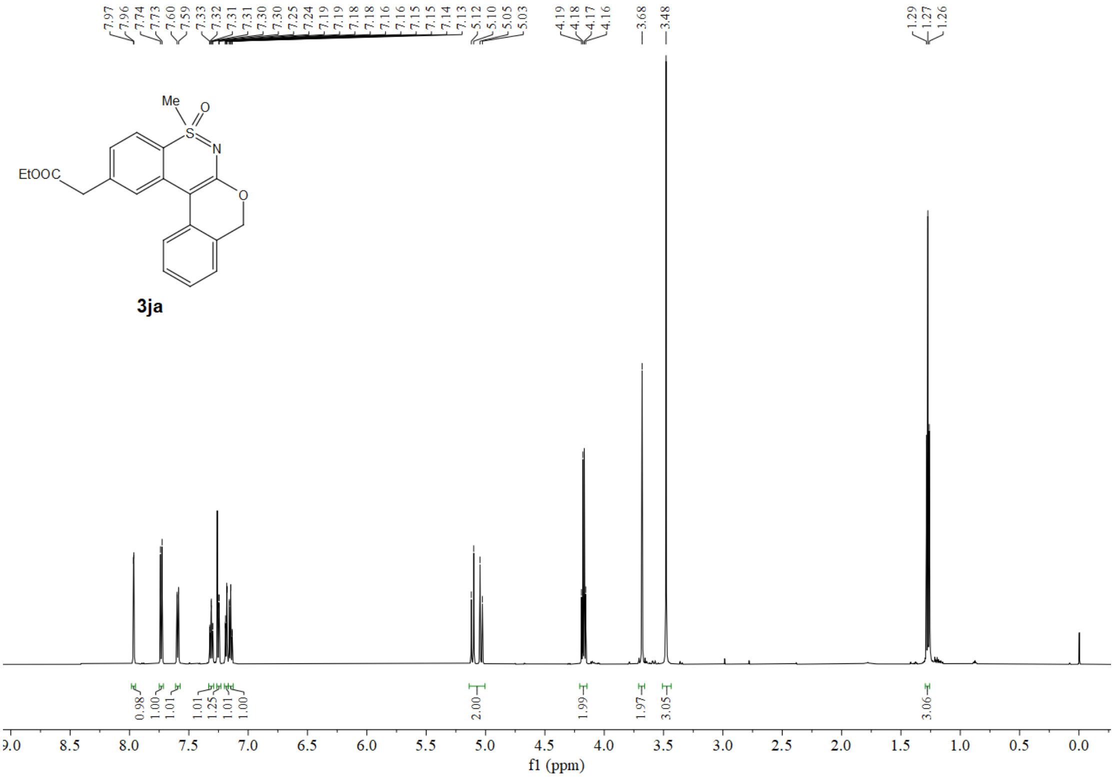
^{13}C NMR spectrum of **3ha**



^{1}H NMR spectrum of **3ia**

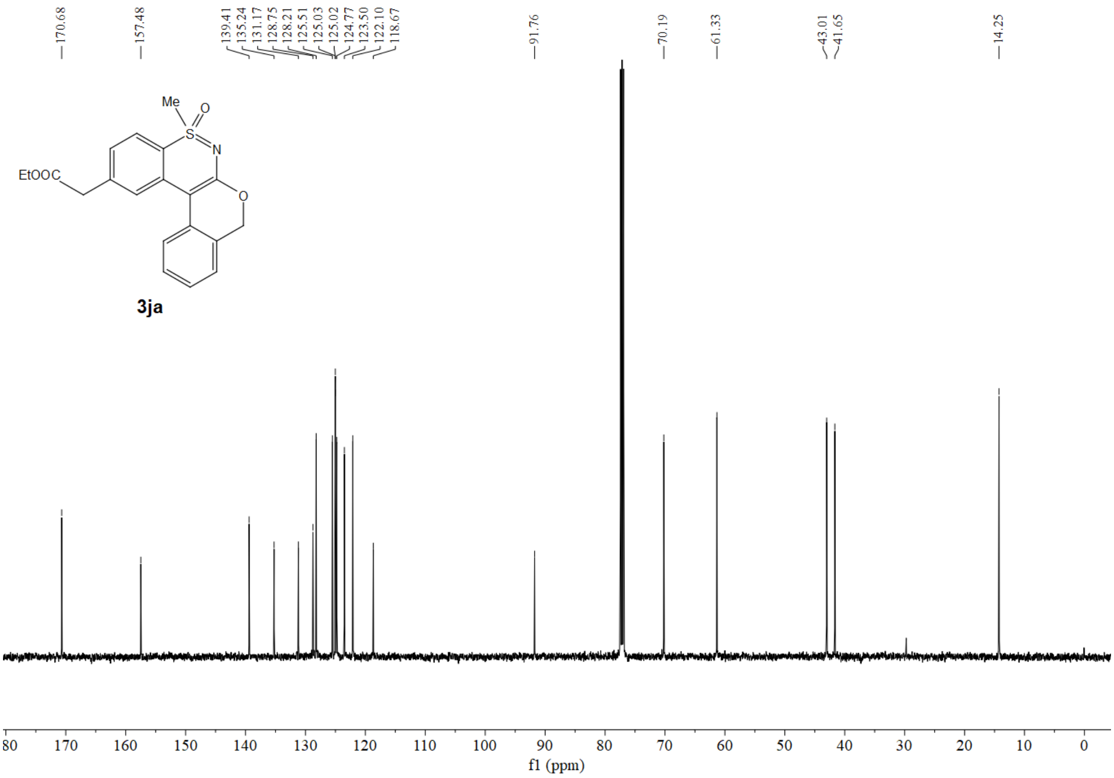


^{13}C NMR spectrum of **3ia**



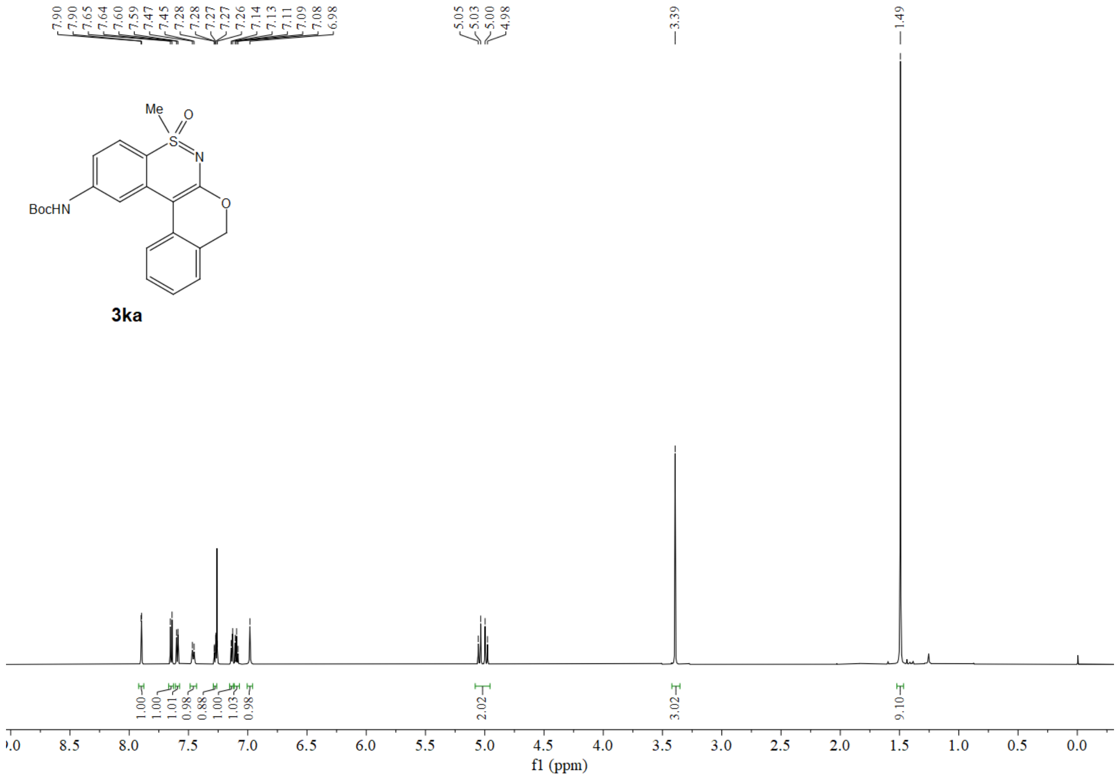
3ja

[1]H NMR spectrum of **3ja**

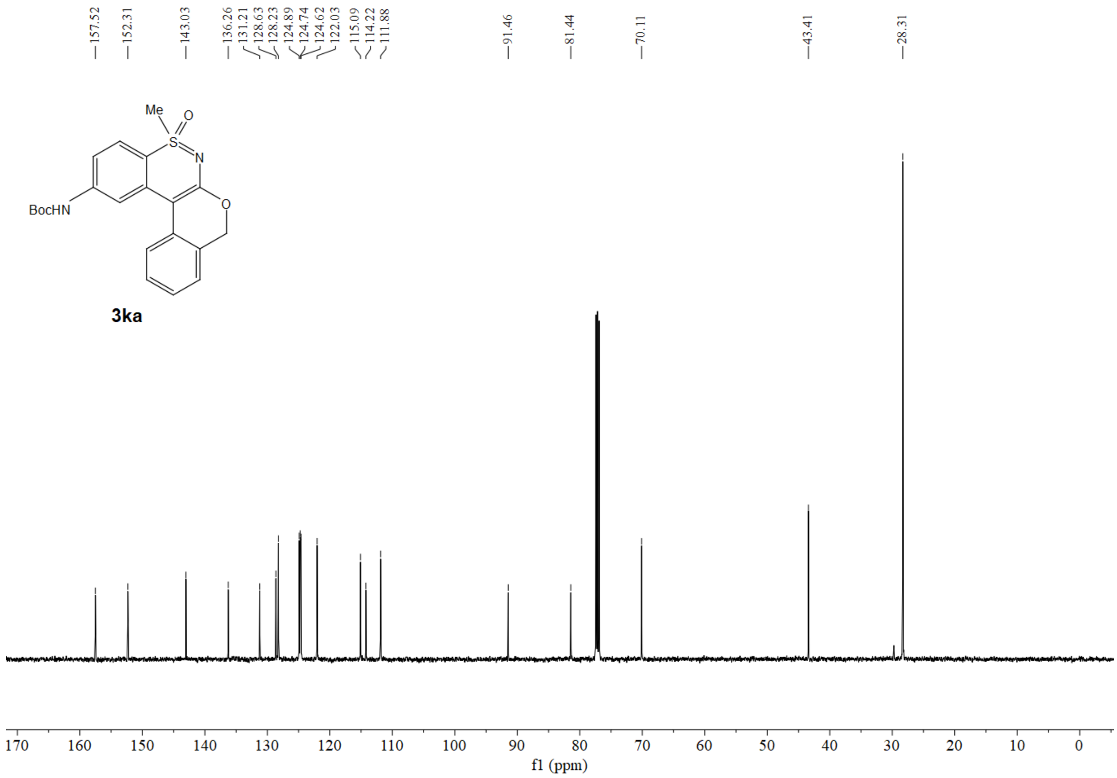


3ja

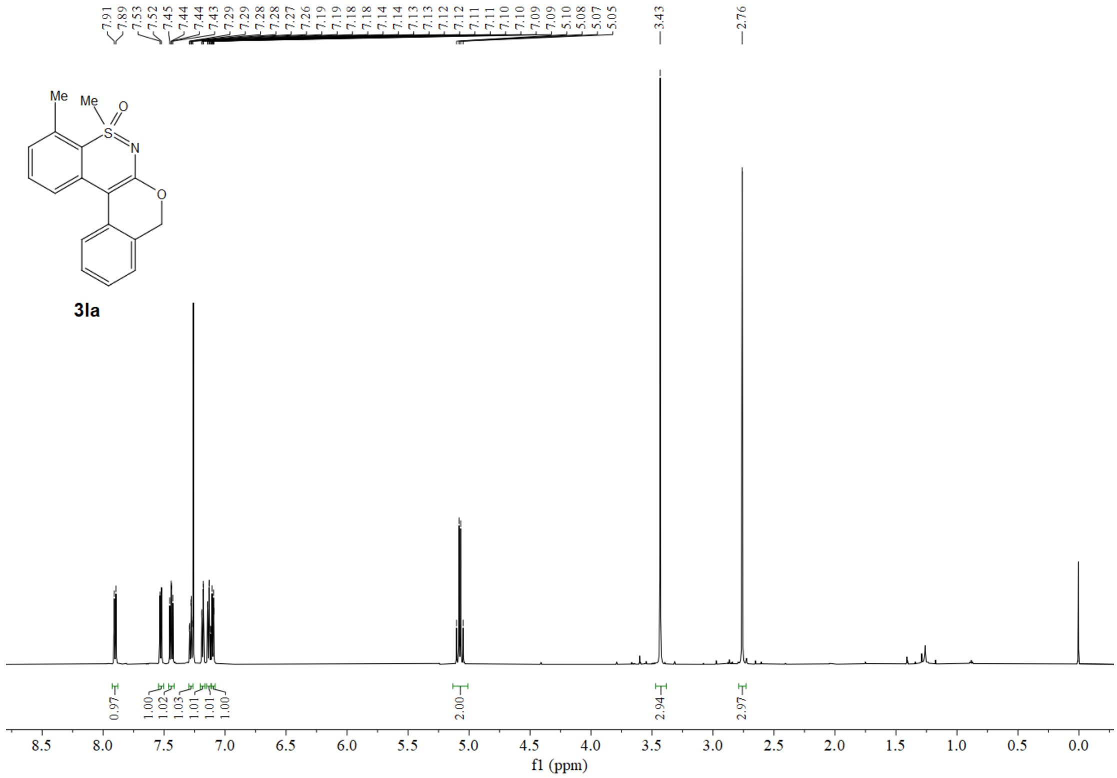
[13]C NMR spectrum of **3ja**



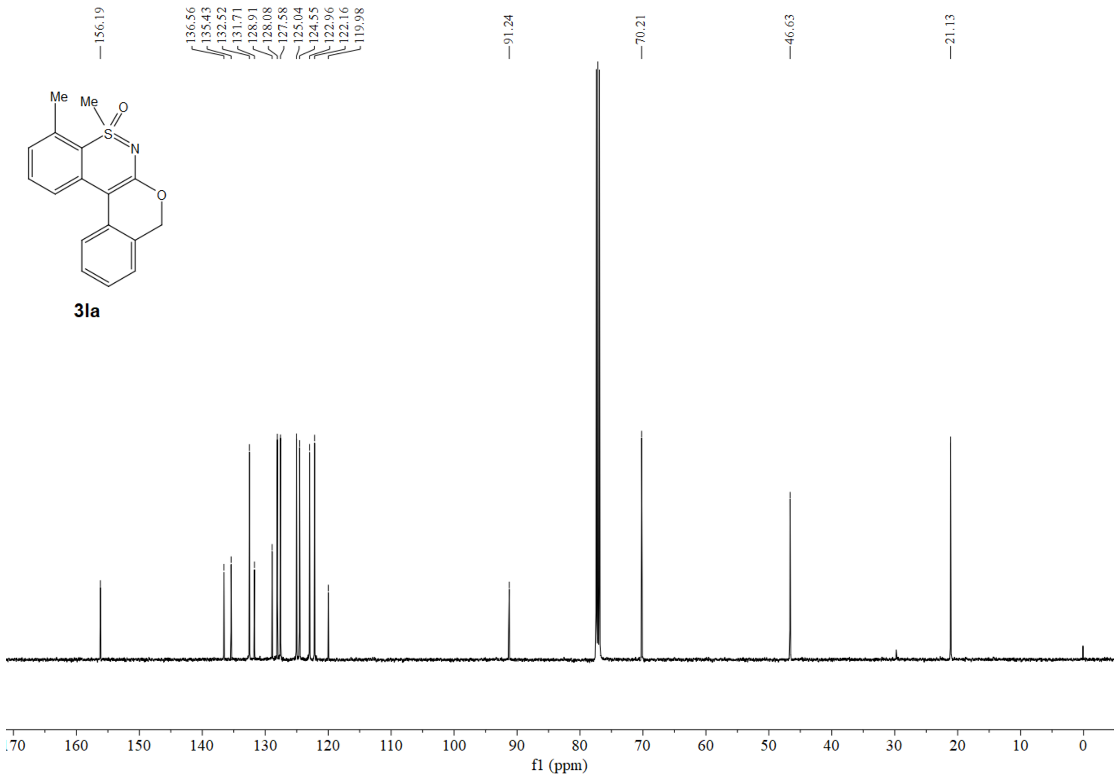
[1]H NMR spectrum of **3ka**



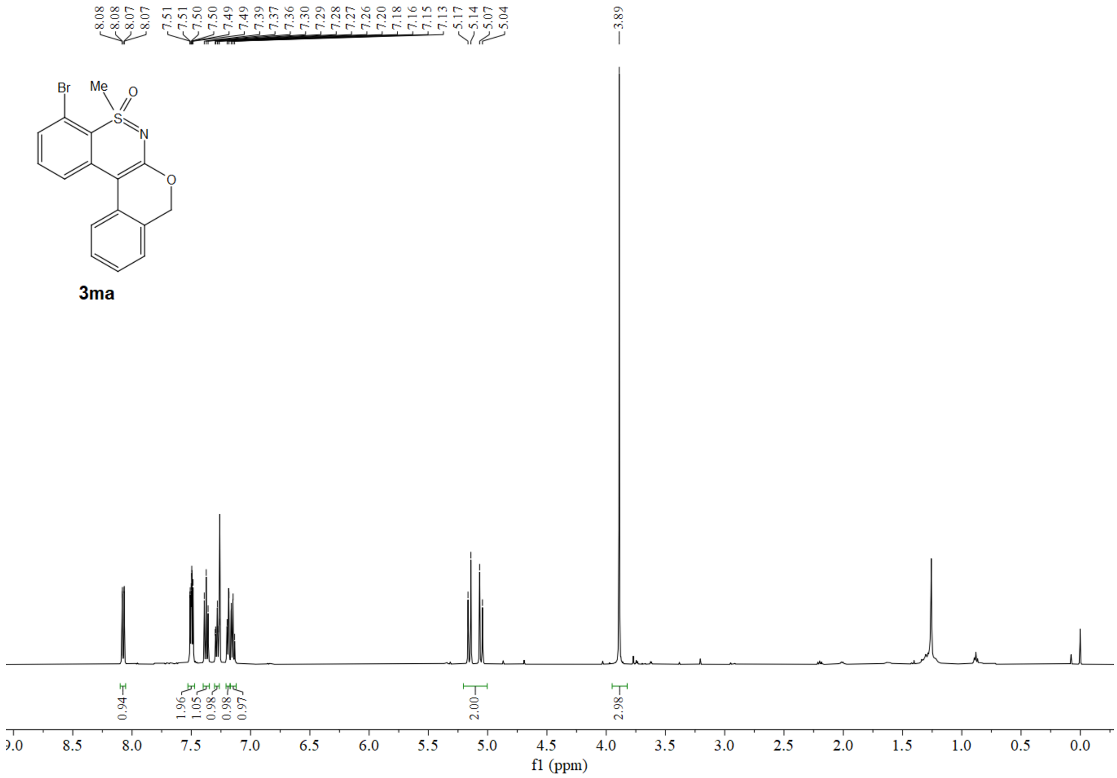
[13]C NMR spectrum of **3ka**



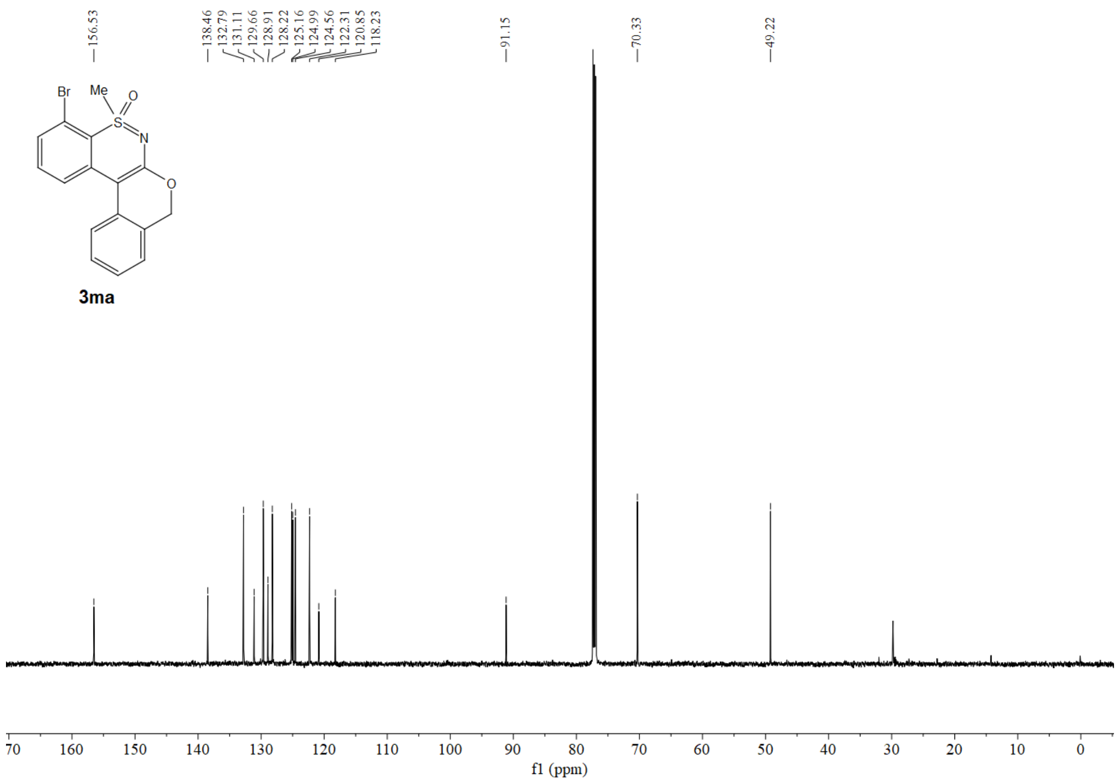
^{1}H NMR spectrum of **3la**



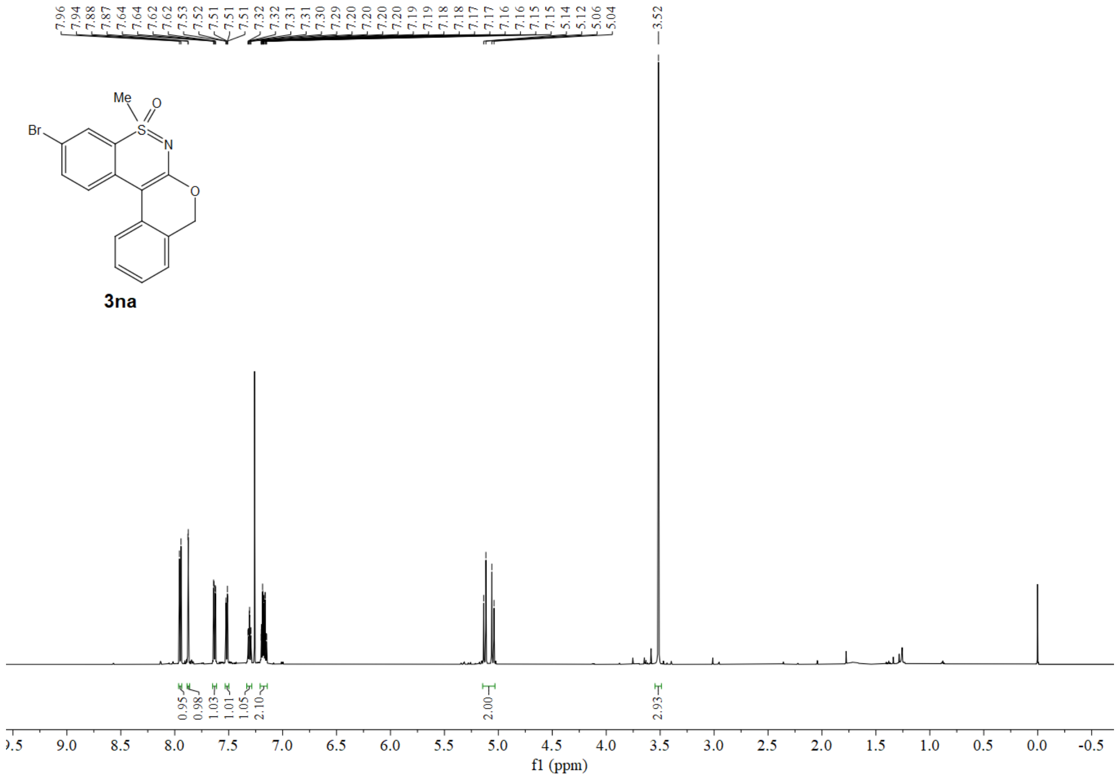
^{13}C NMR spectrum of **3la**



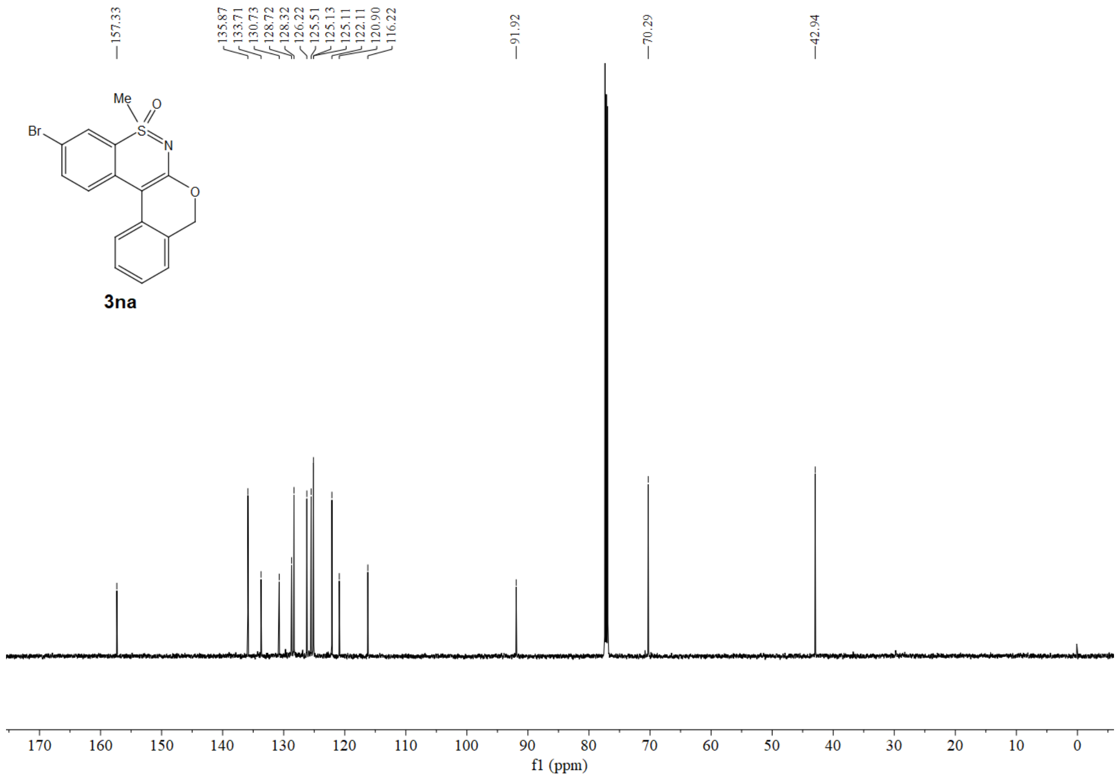
^{1}H NMR spectrum of **3ma**



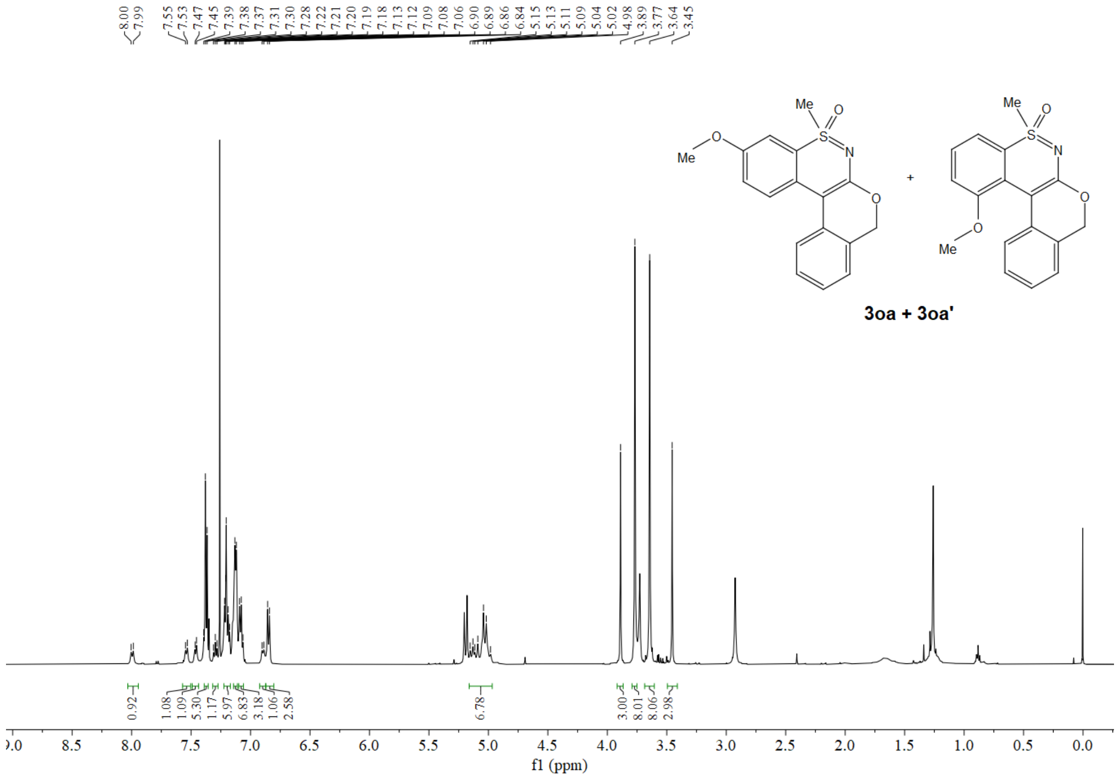
^{13}C NMR spectrum of **3ma**



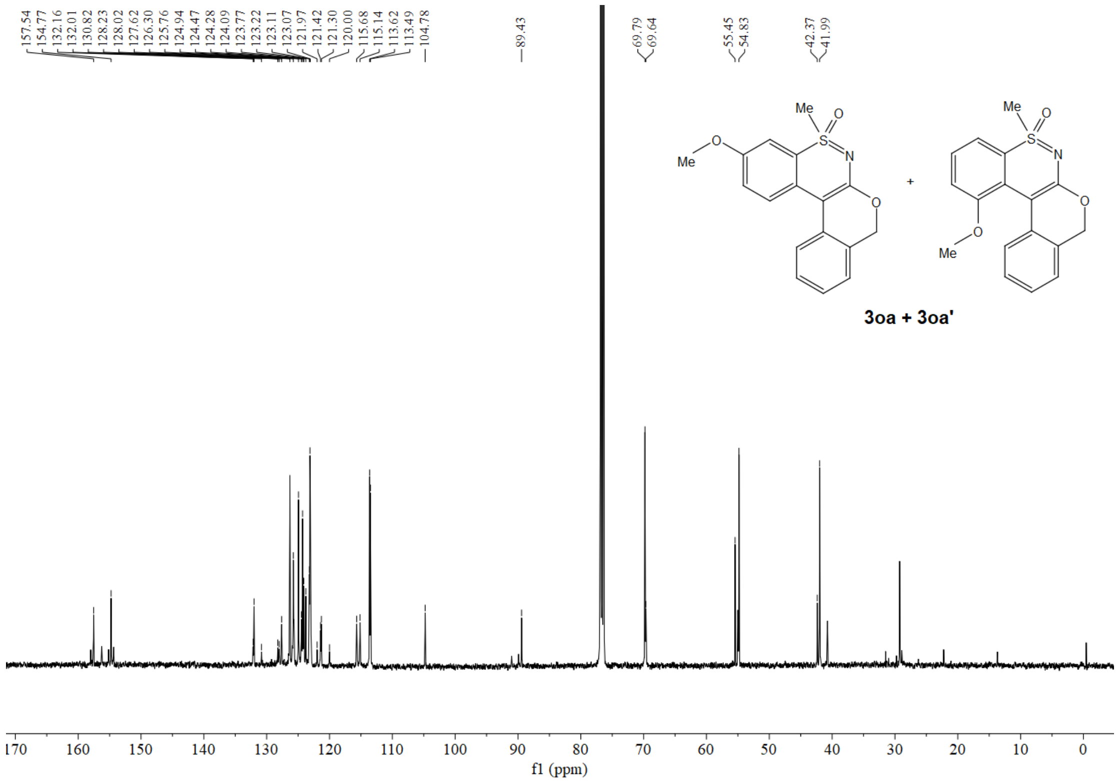
^{1}H NMR spectrum of **3na**



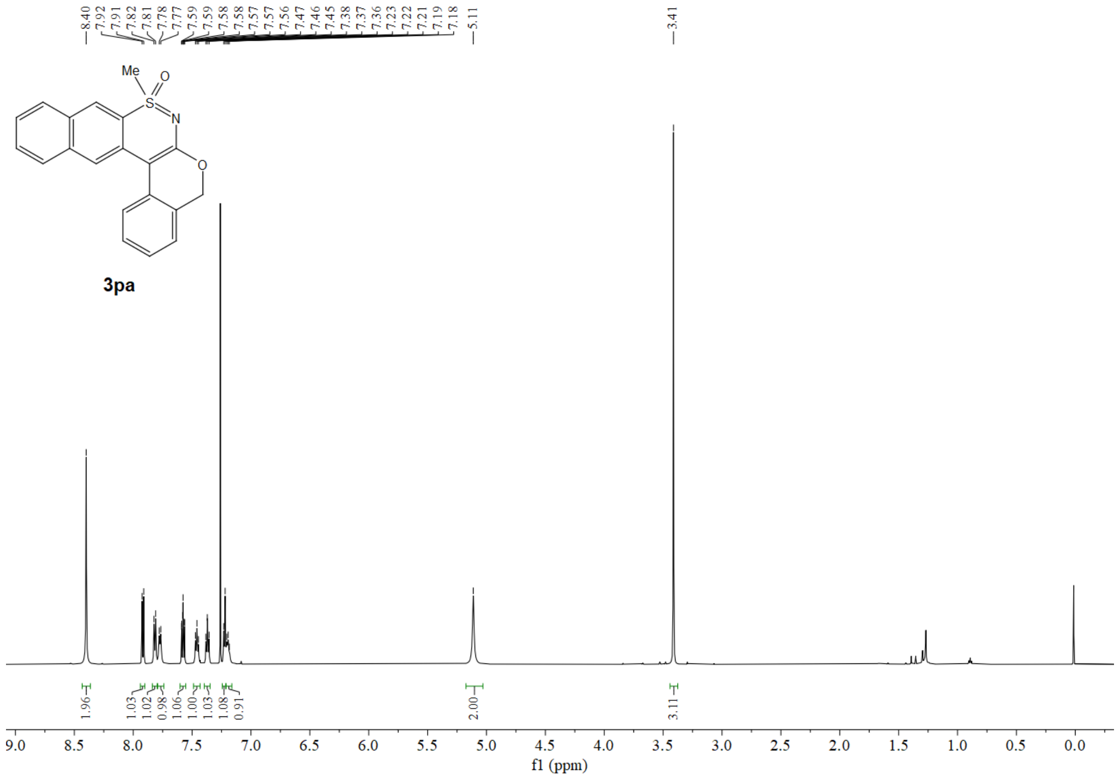
^{13}C NMR spectrum of **3na**



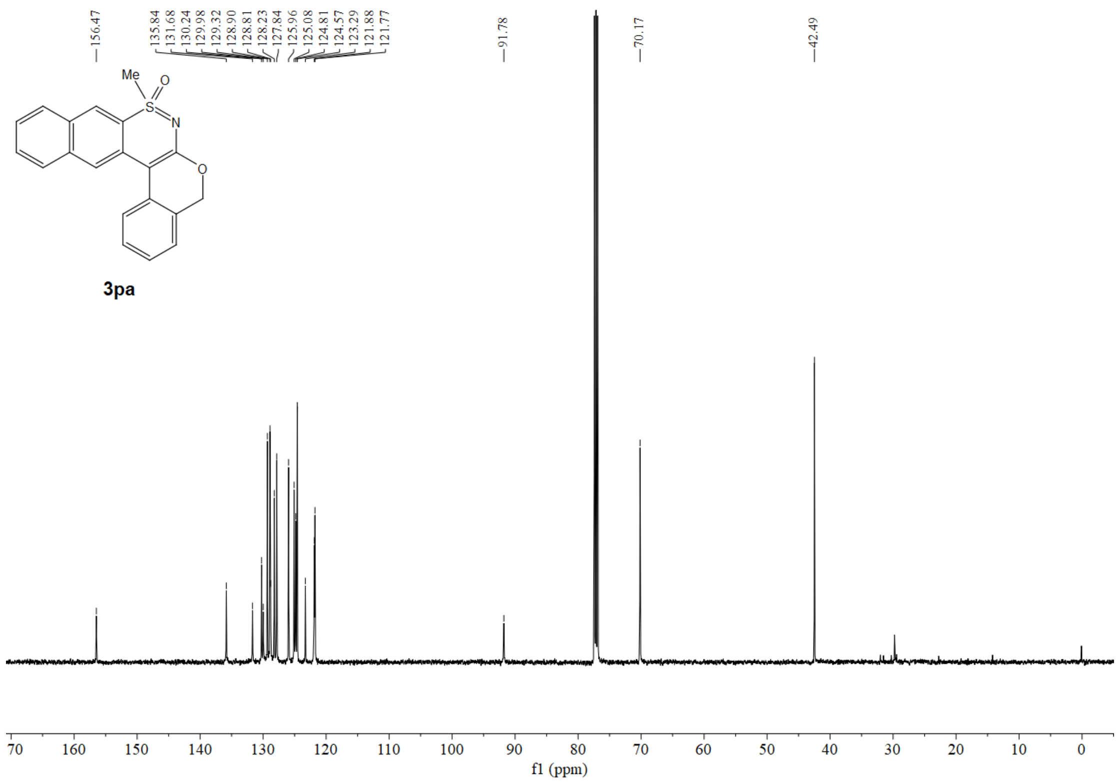
[1]H NMR spectrum of a mixture of **3oa** and **3oa'**



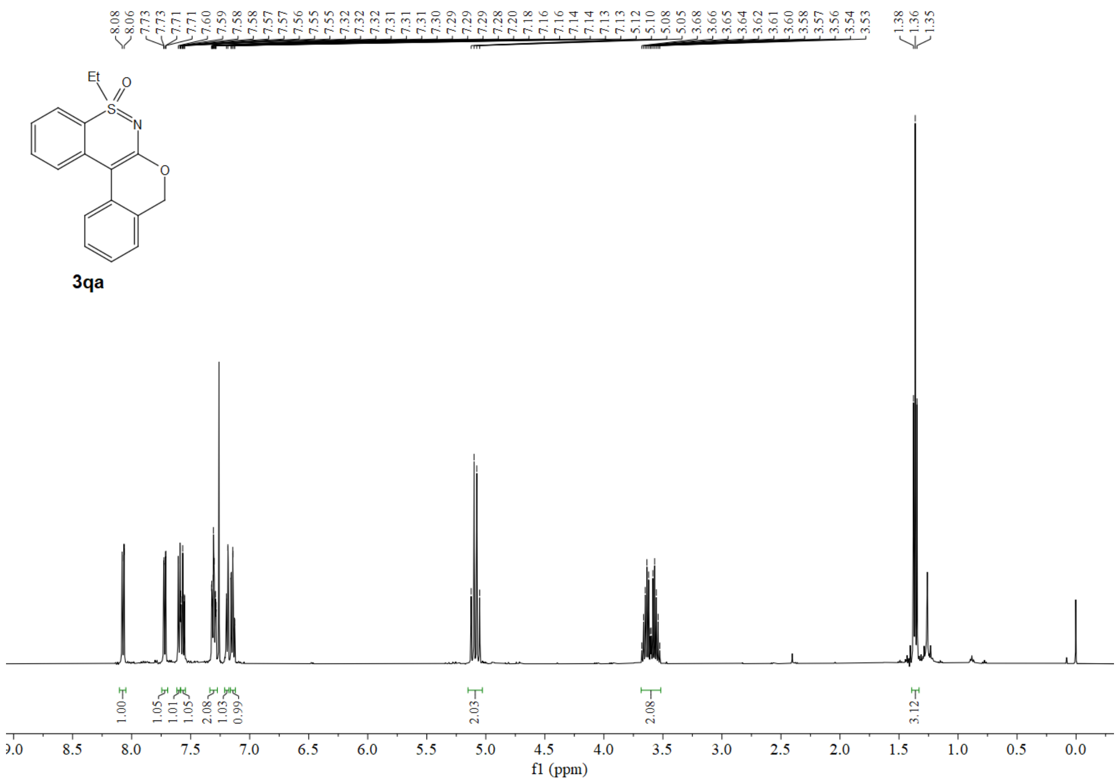
[13]C NMR spectrum of a mixture of **3oa** and **3oa'**



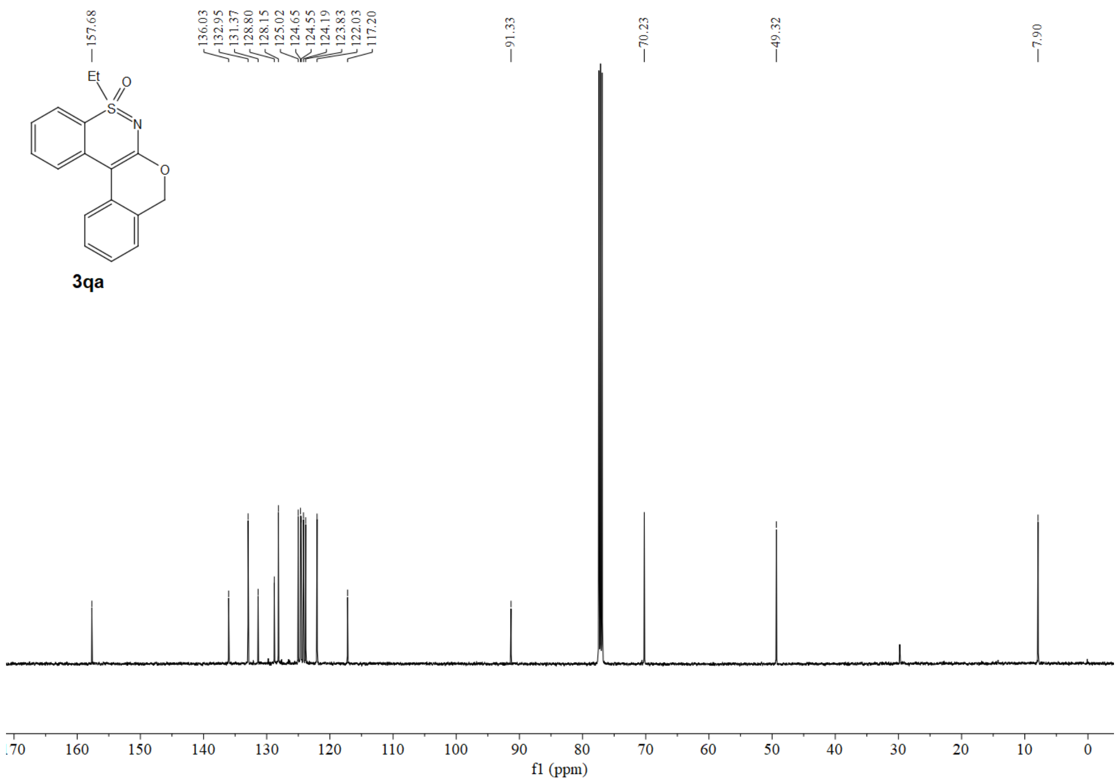
[1]H NMR spectrum of **3pa**



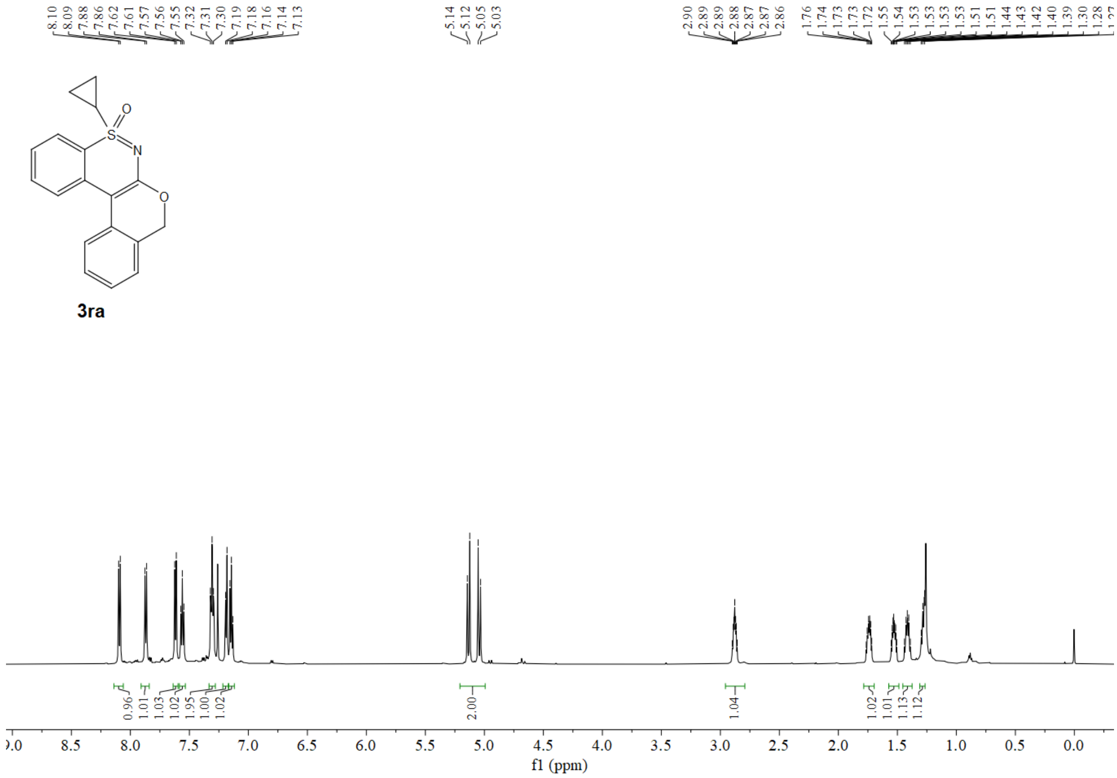
[13]C NMR spectrum of **3pa**



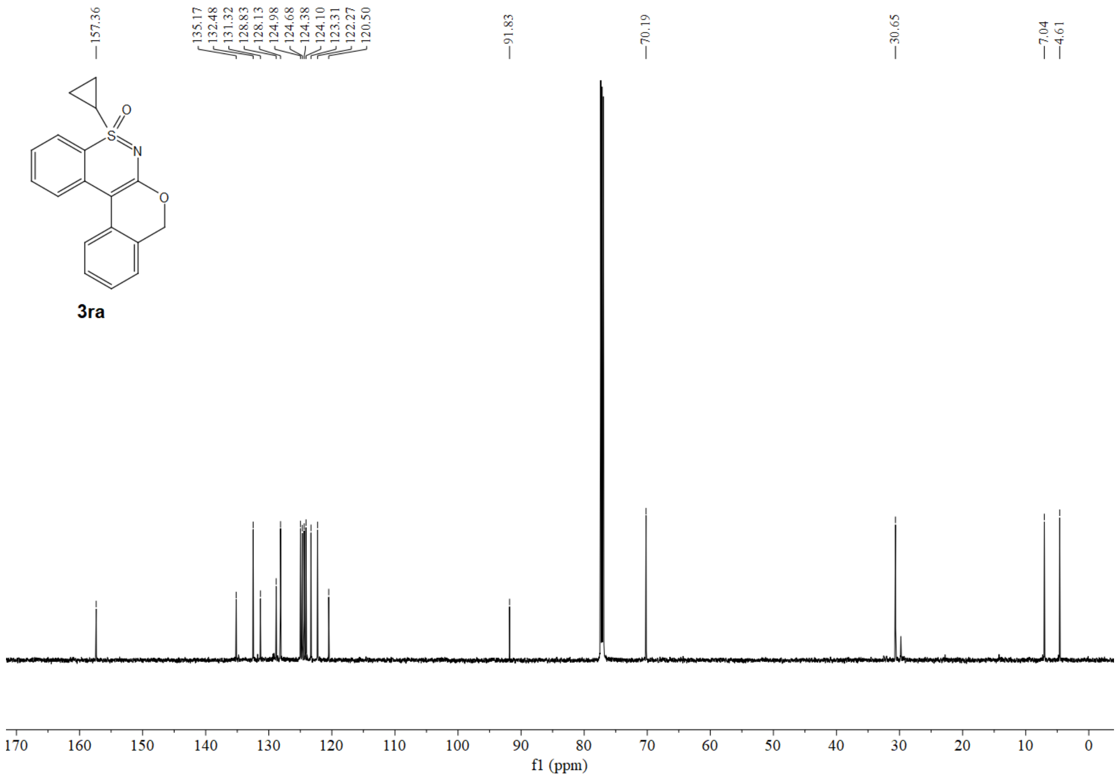
[1]H NMR spectrum of **3qa**



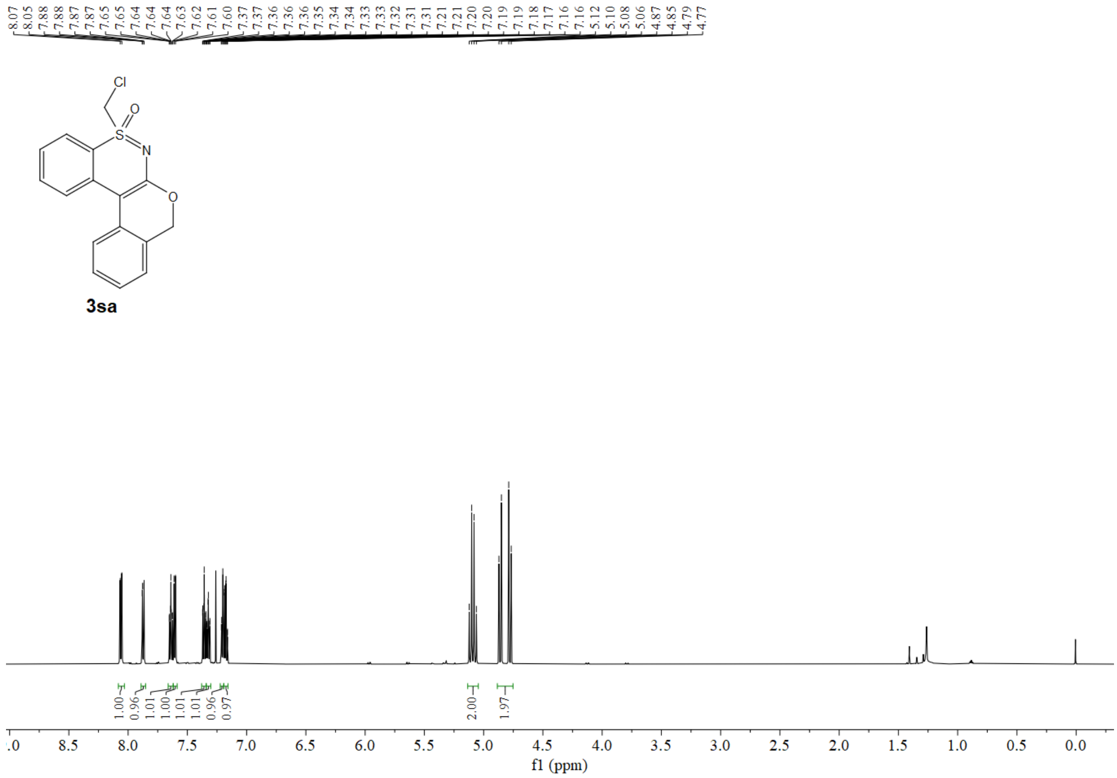
[13]C NMR spectrum of **3qa**



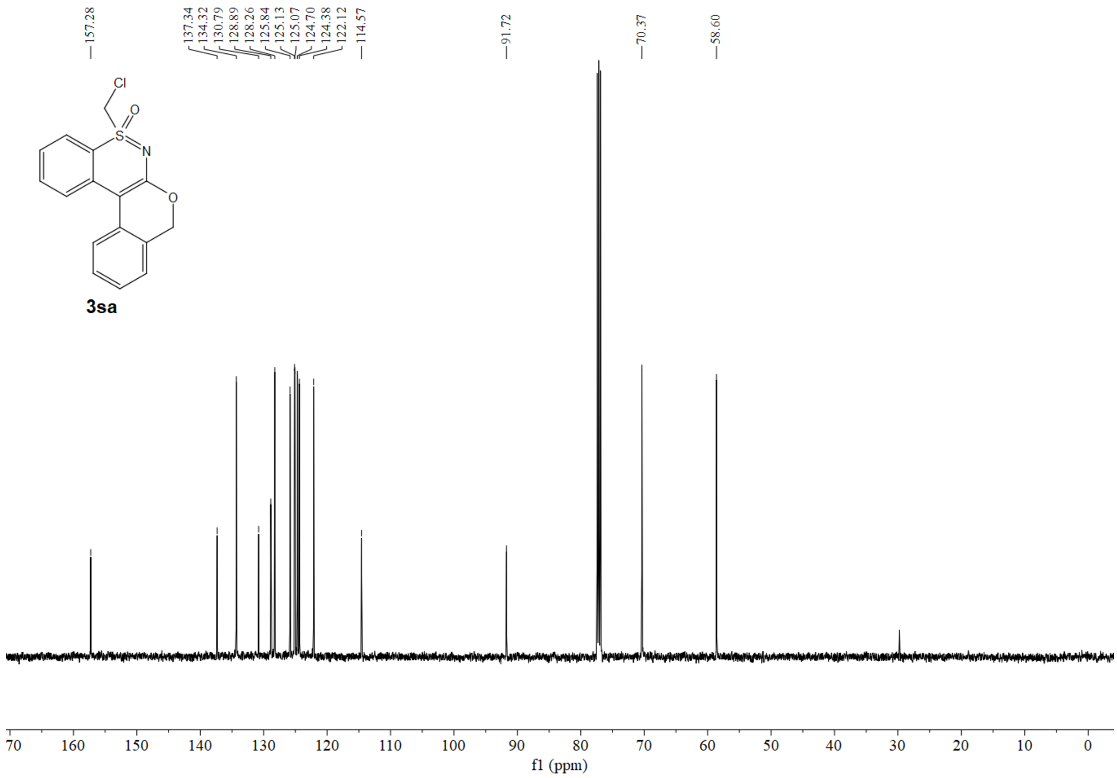
^{1}H NMR spectrum of **3ra**



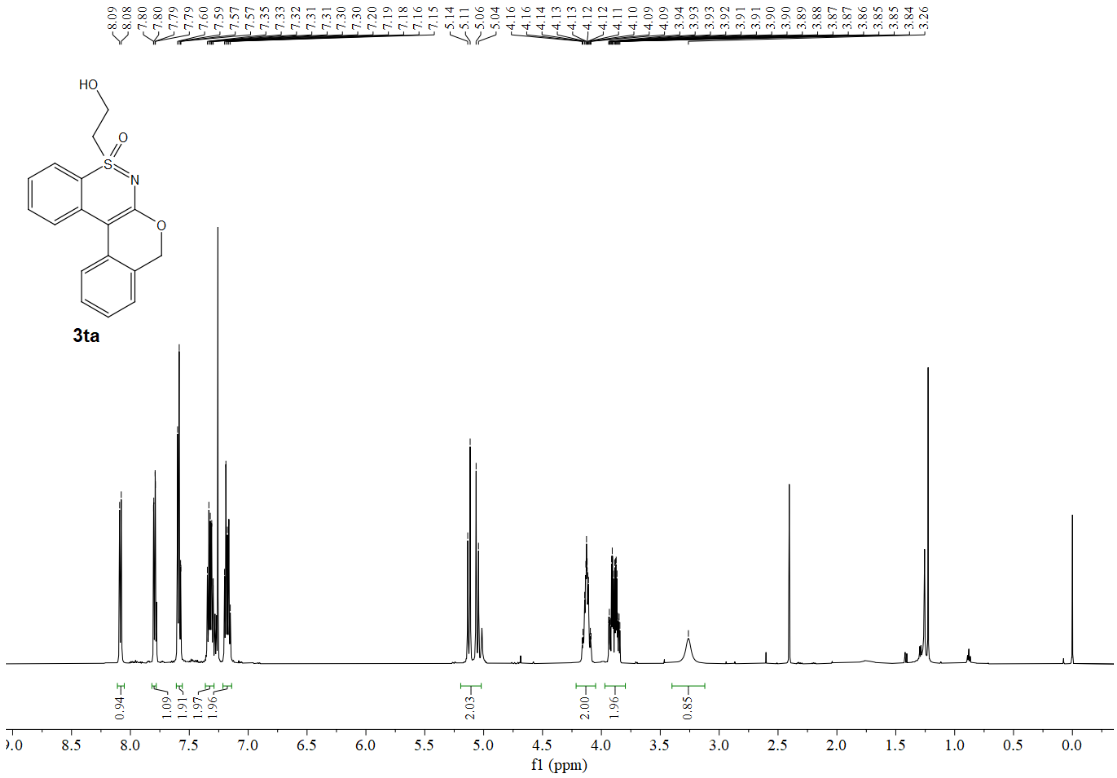
^{13}C NMR spectrum of **3ra**



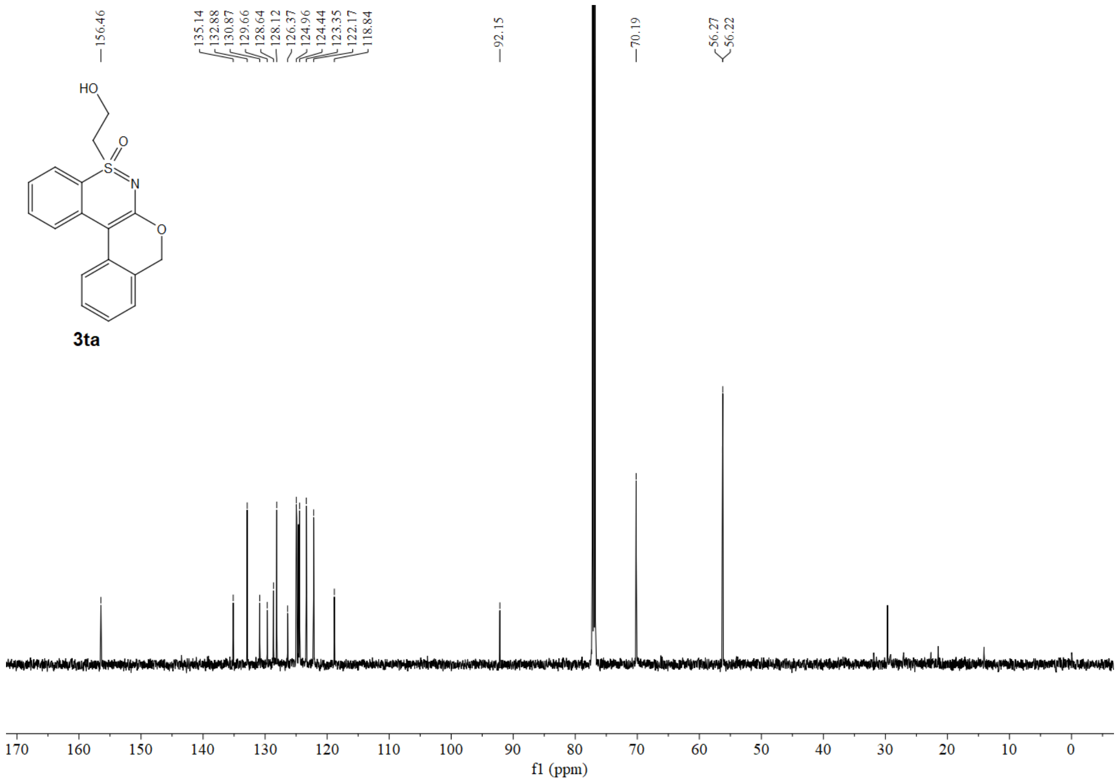
^{1}H NMR spectrum of **3sa**



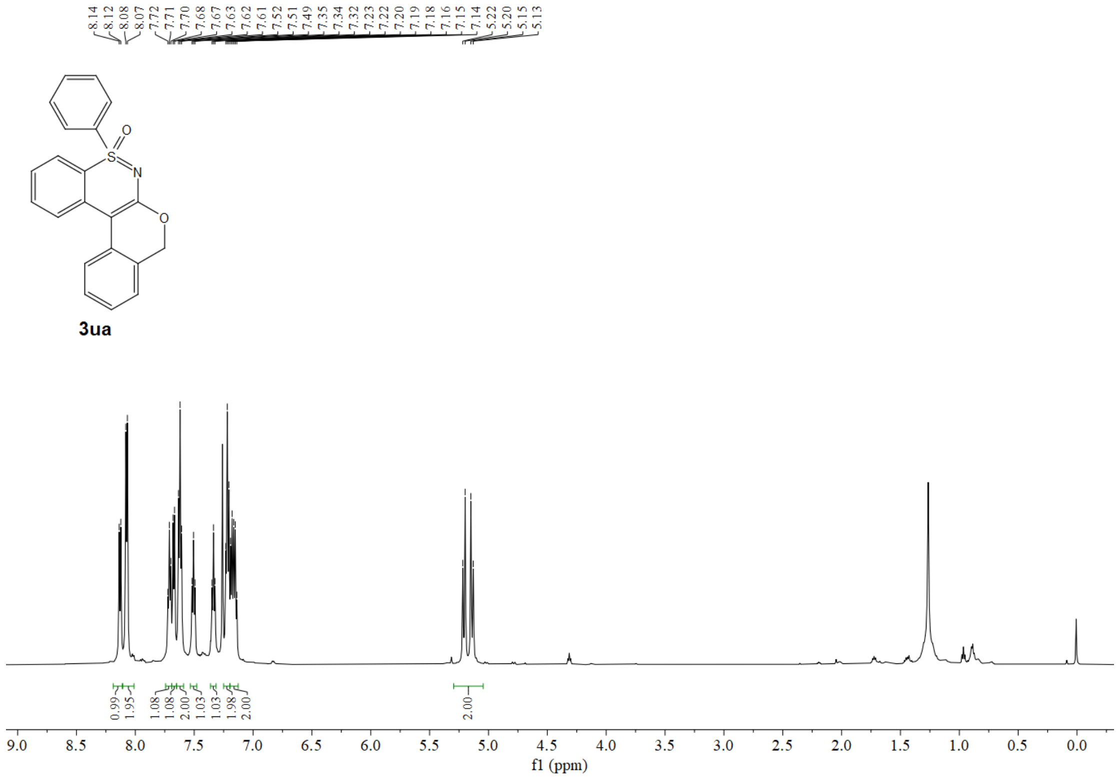
^{13}C NMR spectrum of **3sa**



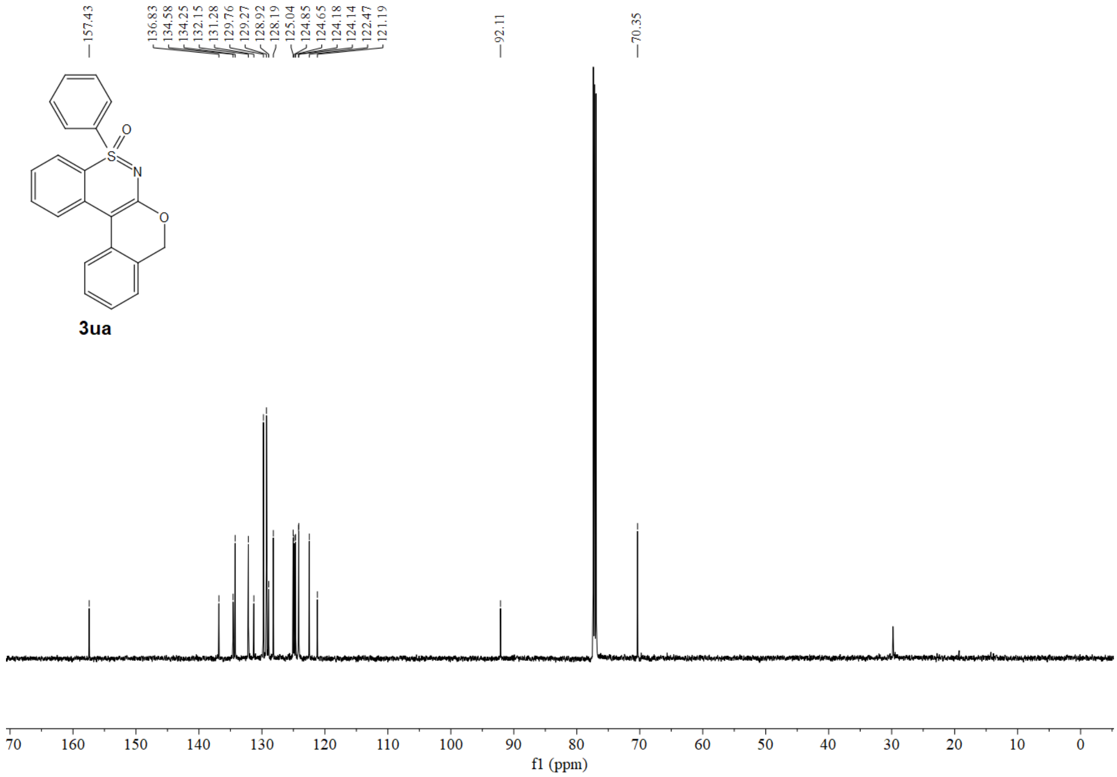
^{1}H NMR spectrum of **3ta**



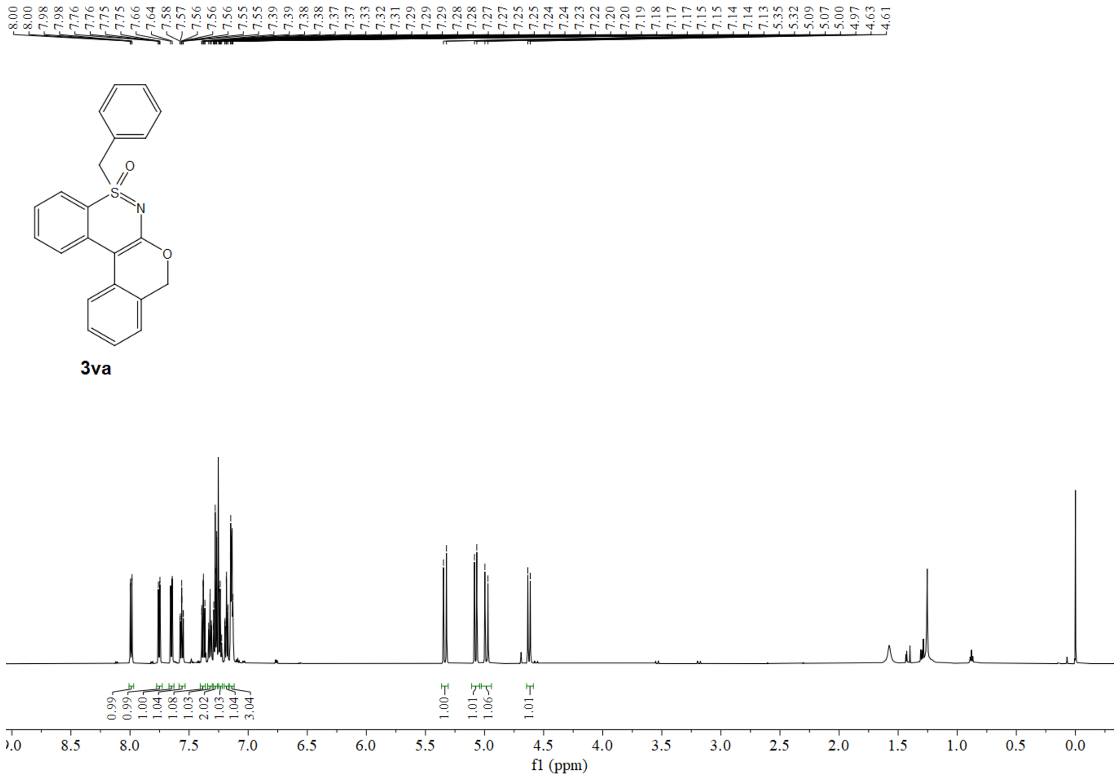
^{13}C NMR spectrum of **3ta**



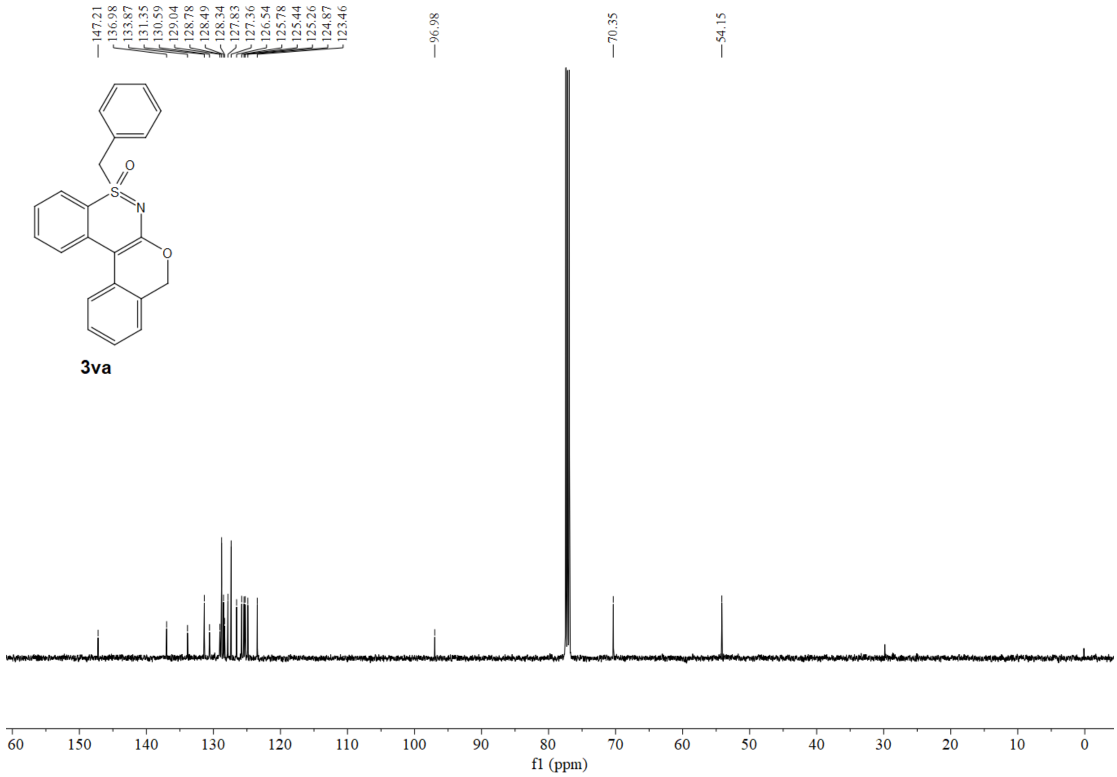
^{1}H NMR spectrum of **3ua**



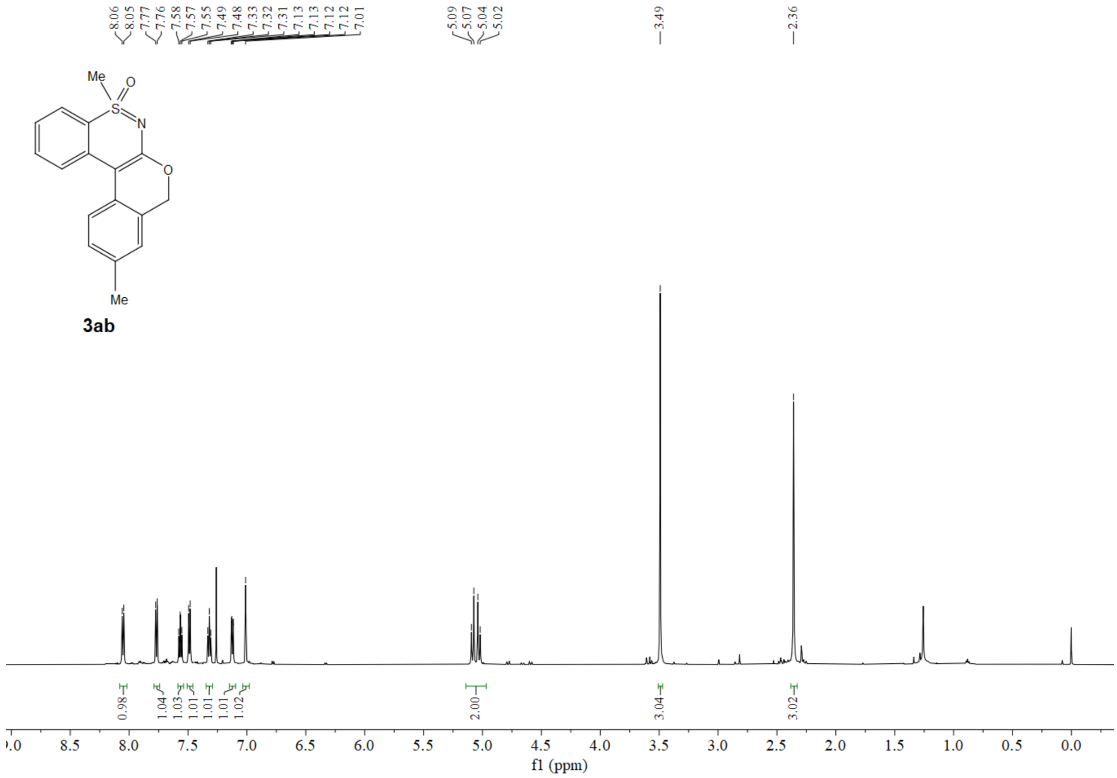
^{13}C NMR spectrum of **3ua**



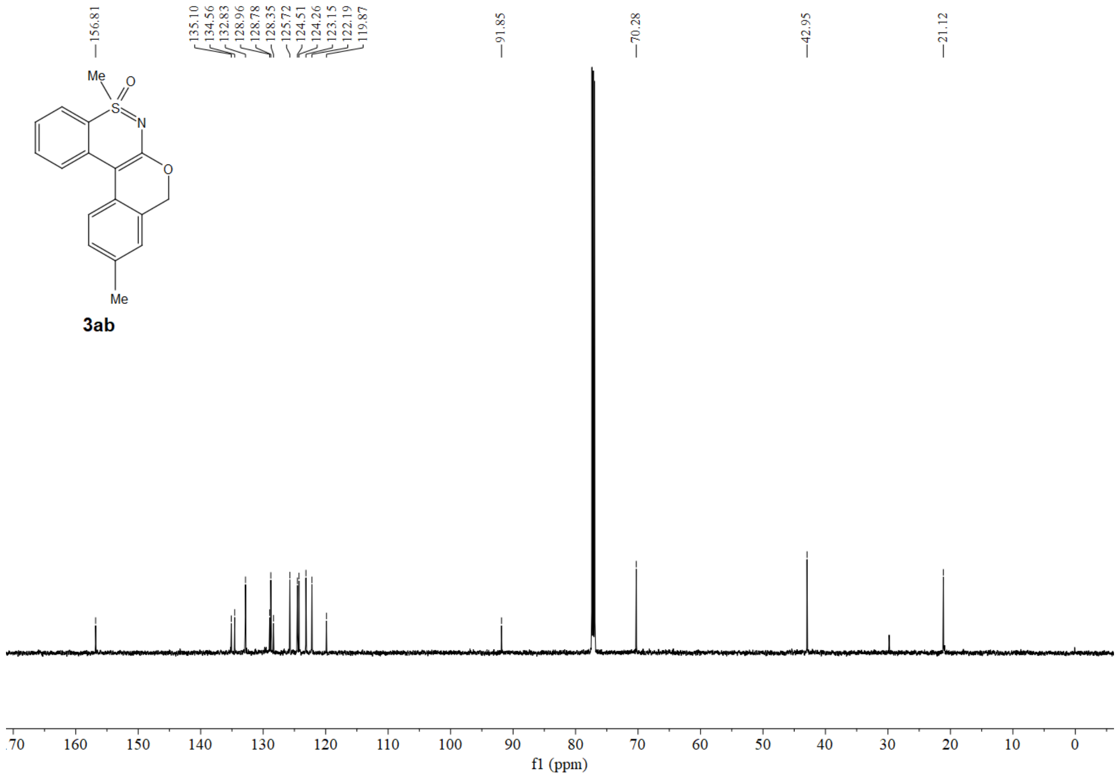
^{1}H NMR spectrum of **3va**



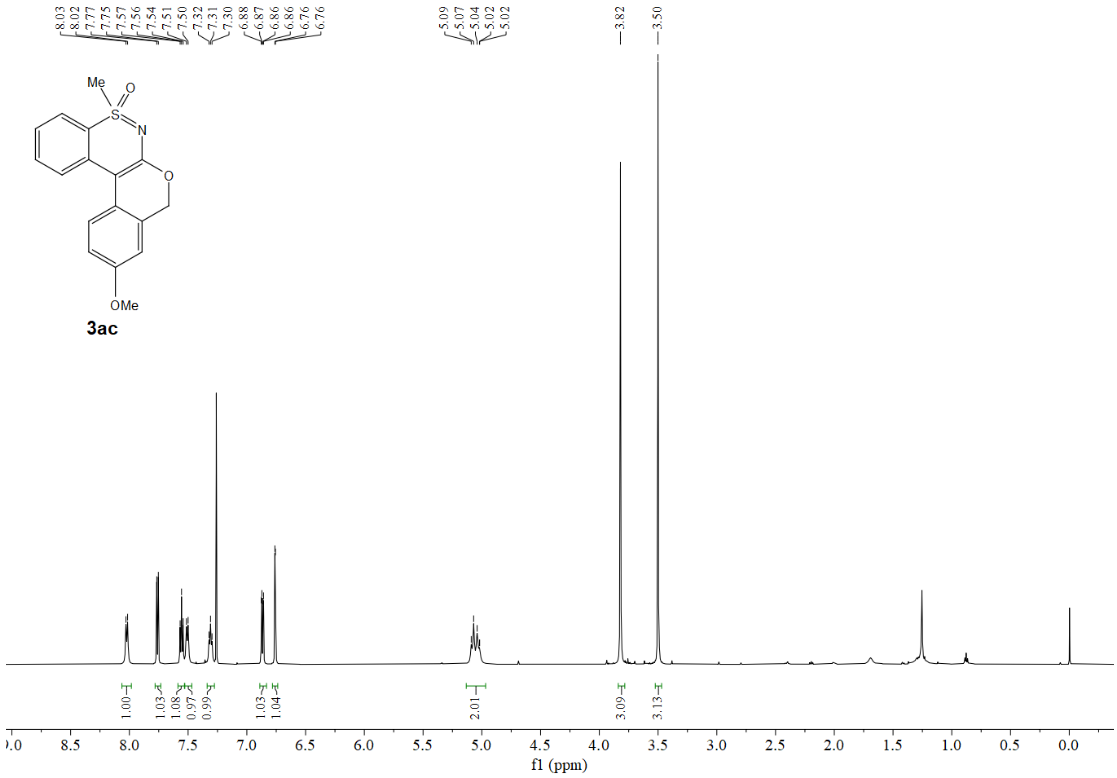
^{13}C NMR spectrum of **3va**



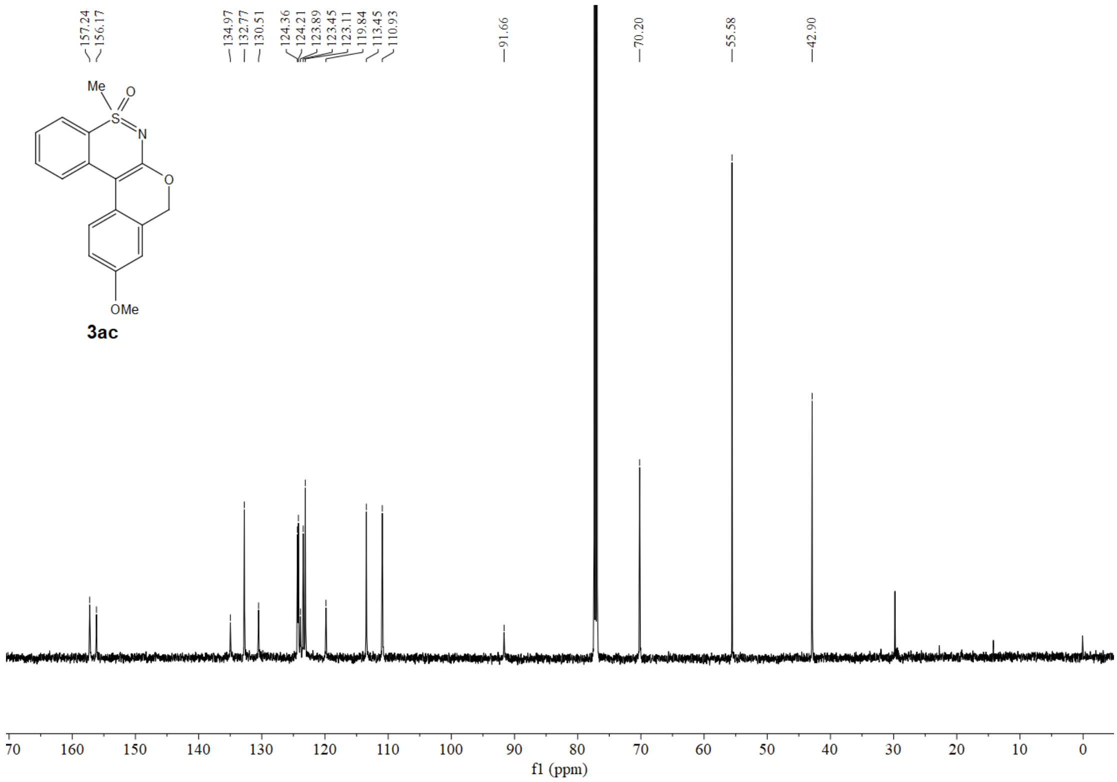
^{1}H NMR spectrum of **3ab**



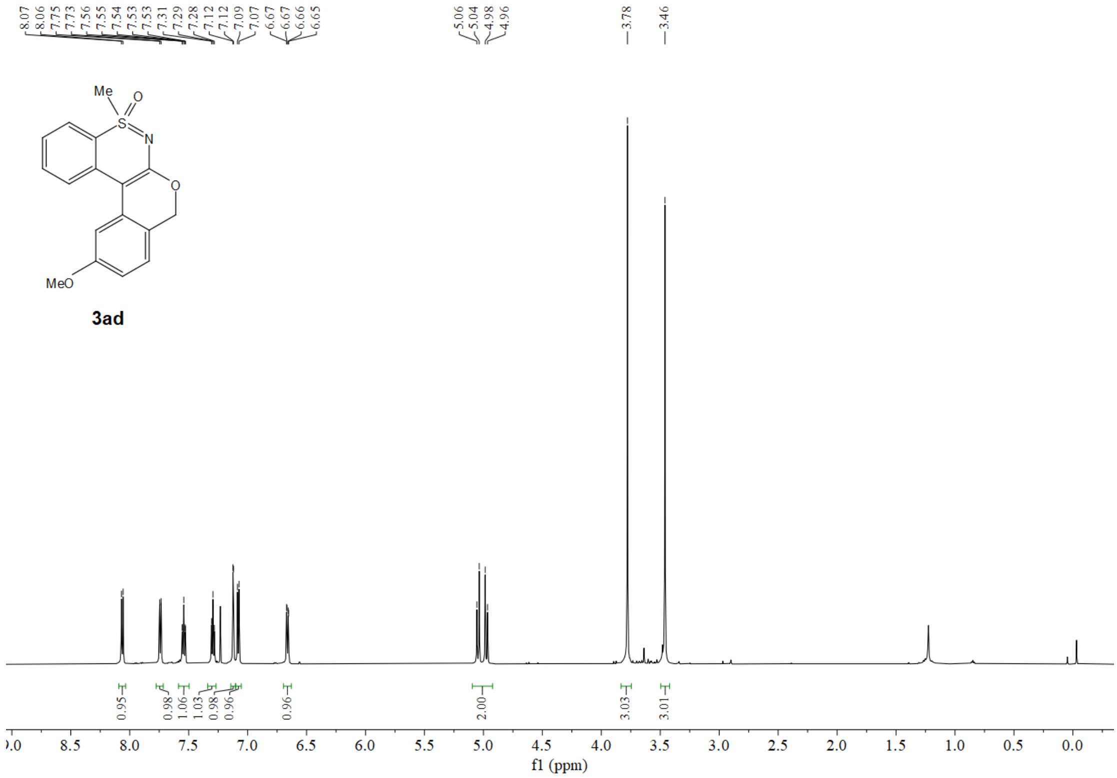
^{13}C NMR spectrum of **3ab**



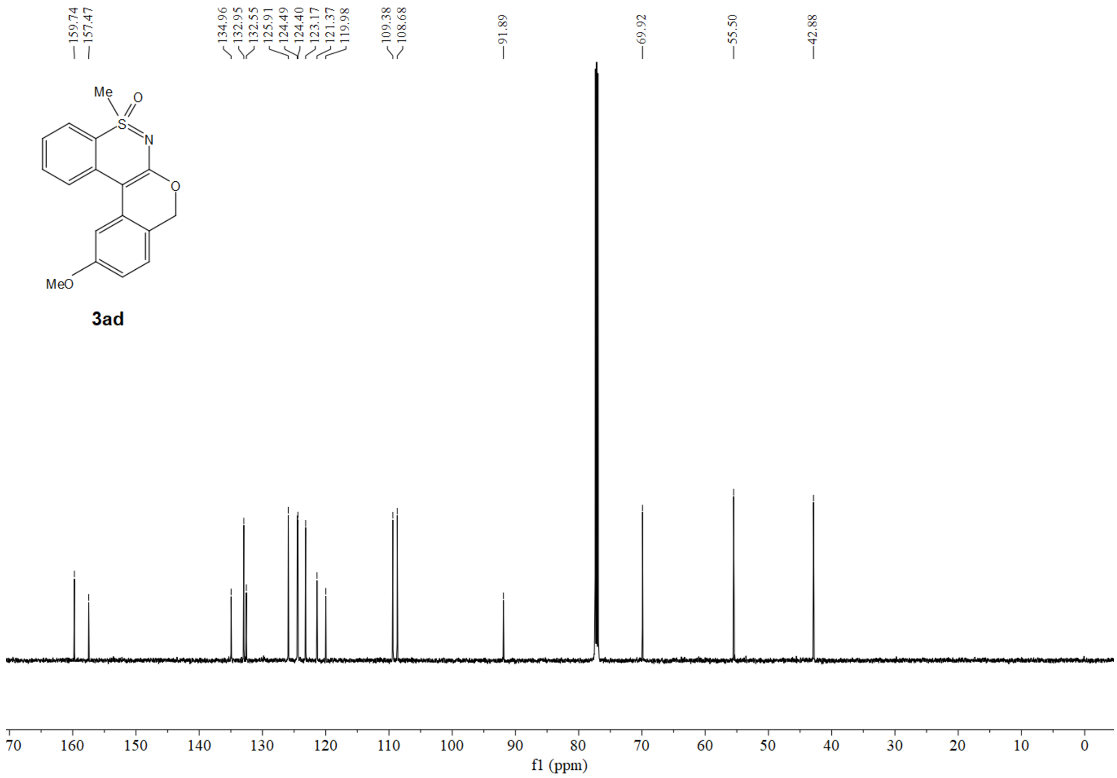
[1]H NMR spectrum of **3ac**



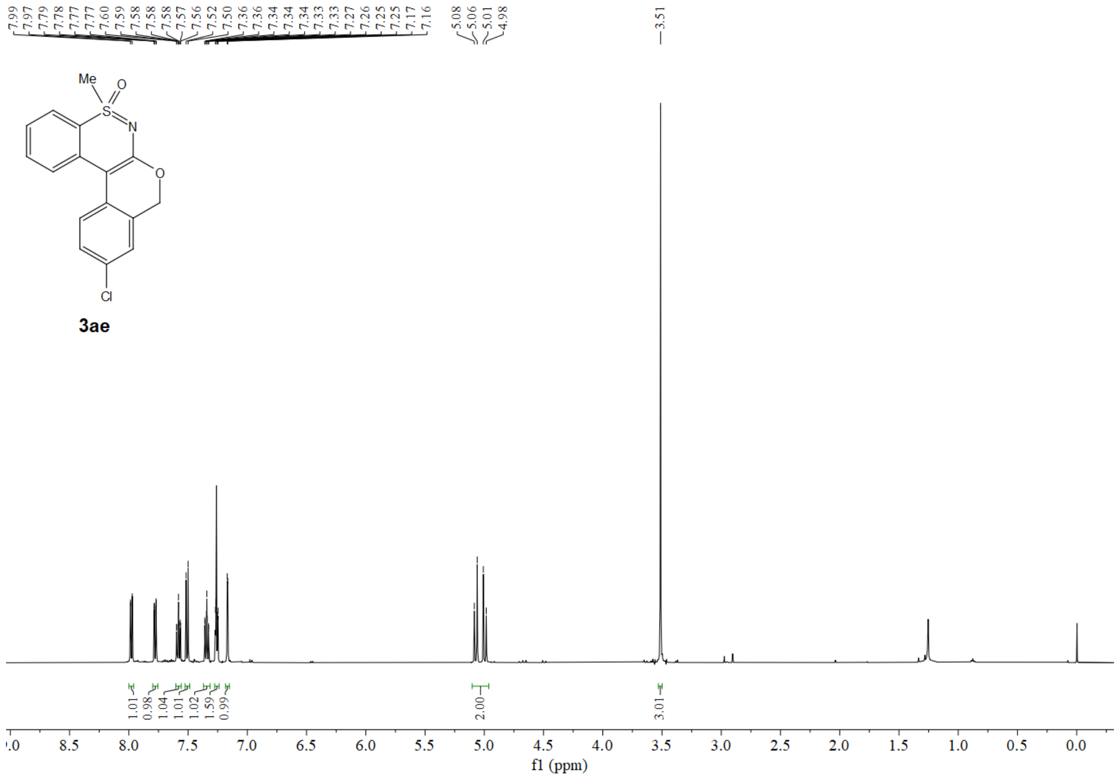
[13]C NMR spectrum of **3ac**



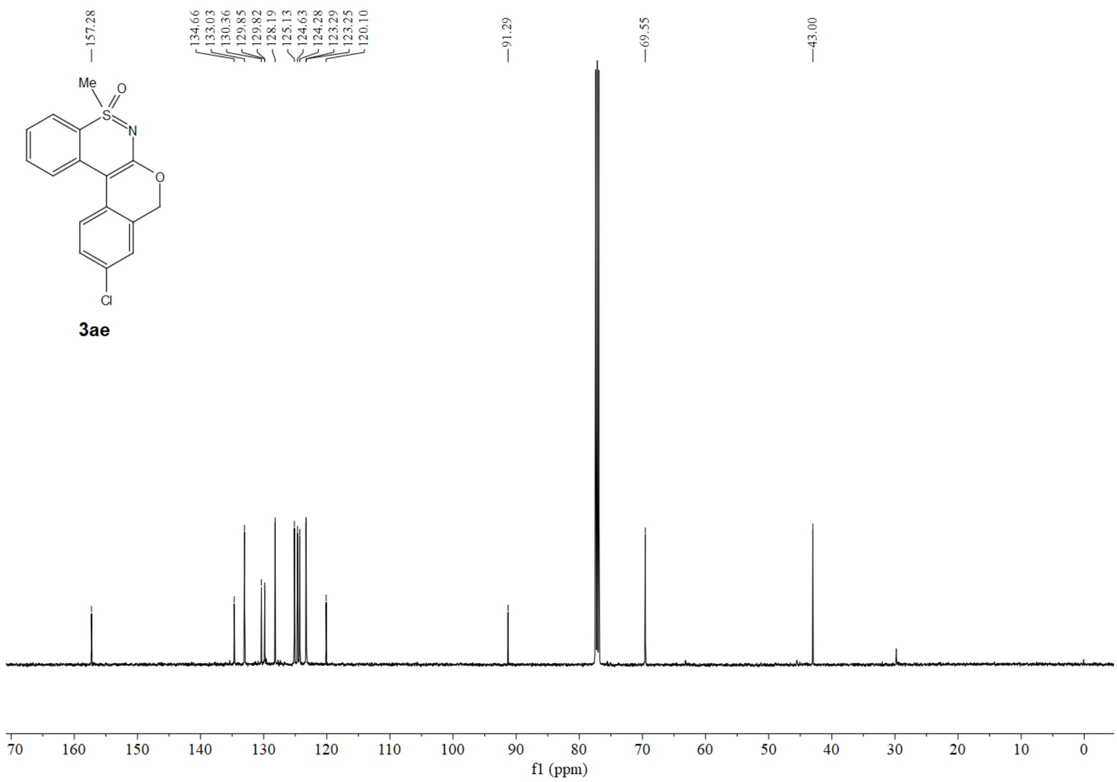
^{1}H NMR spectrum of **3ad**



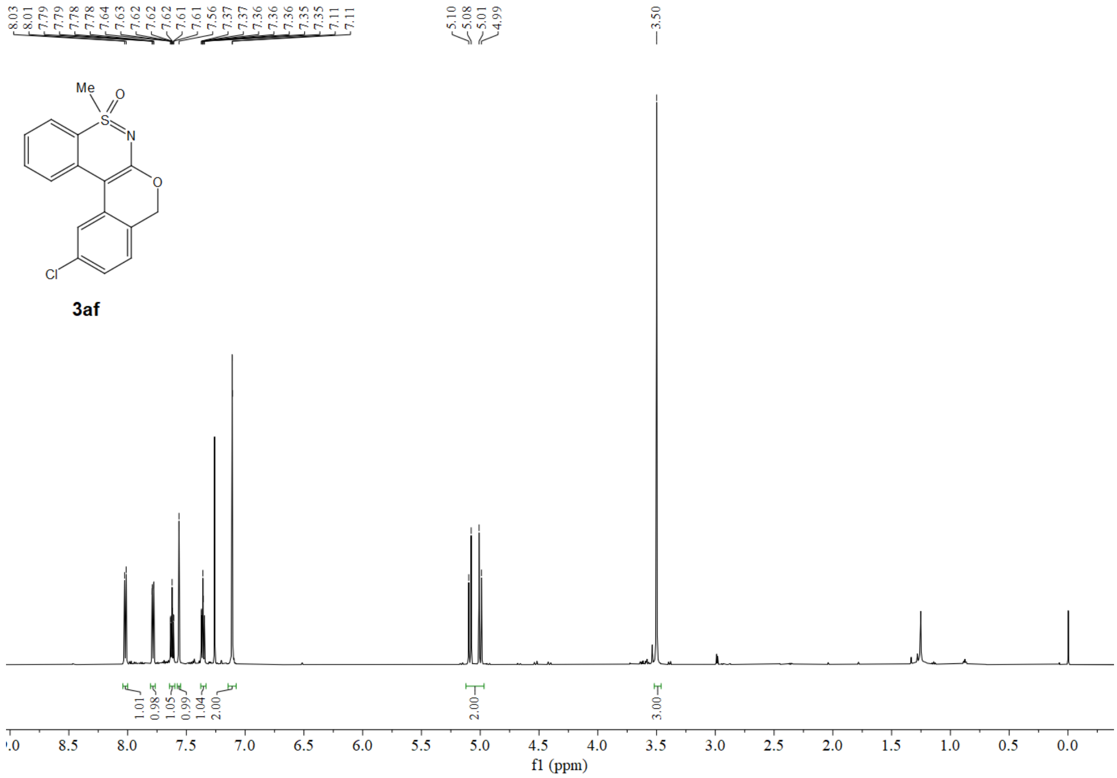
^{13}C NMR spectrum of **3ad**



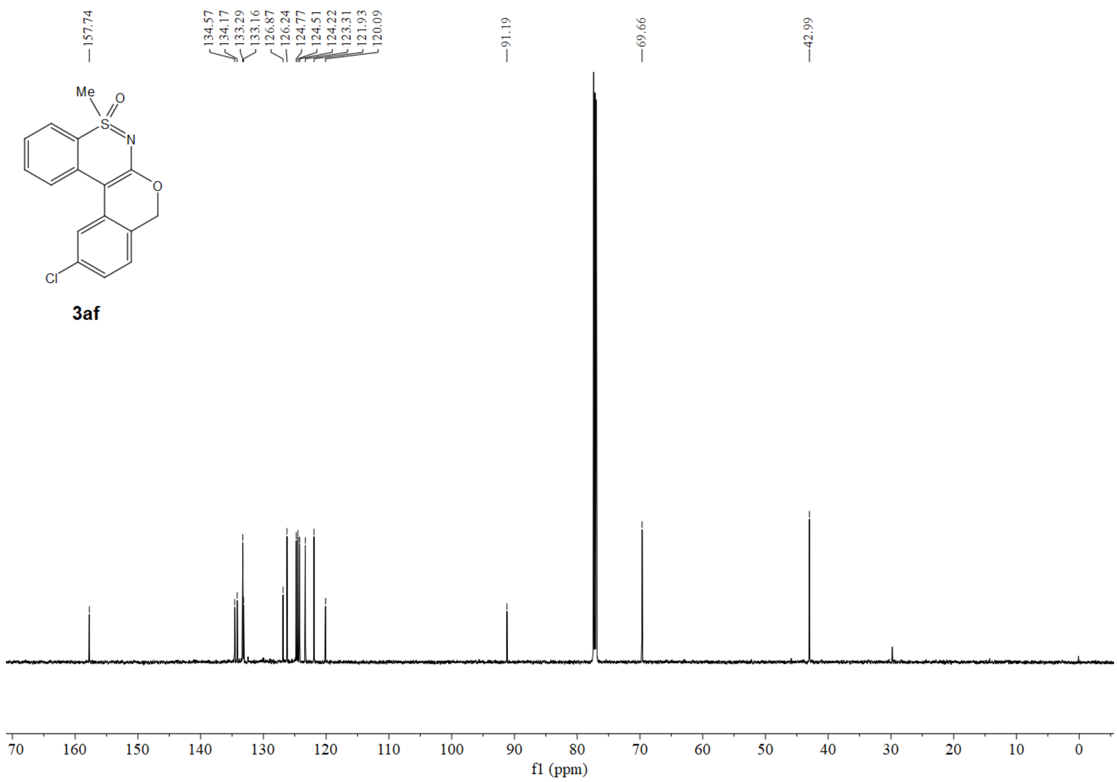
^{1}H NMR spectrum of **3ae**



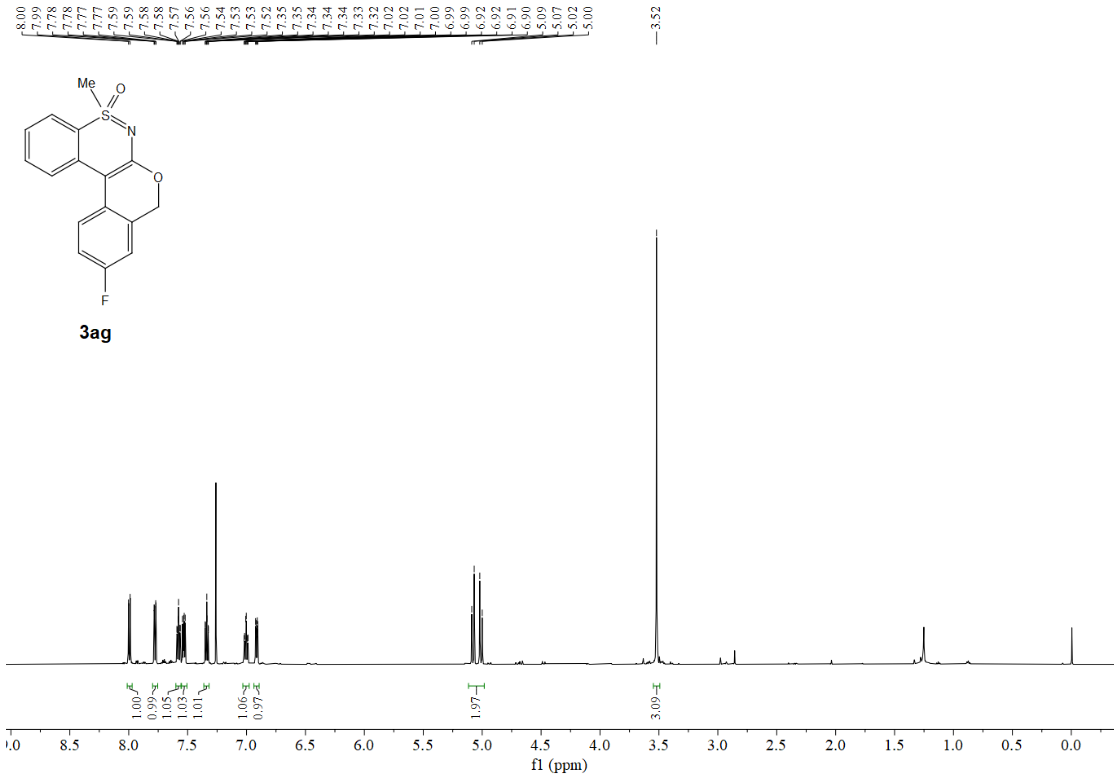
^{13}C NMR spectrum of **3ae**



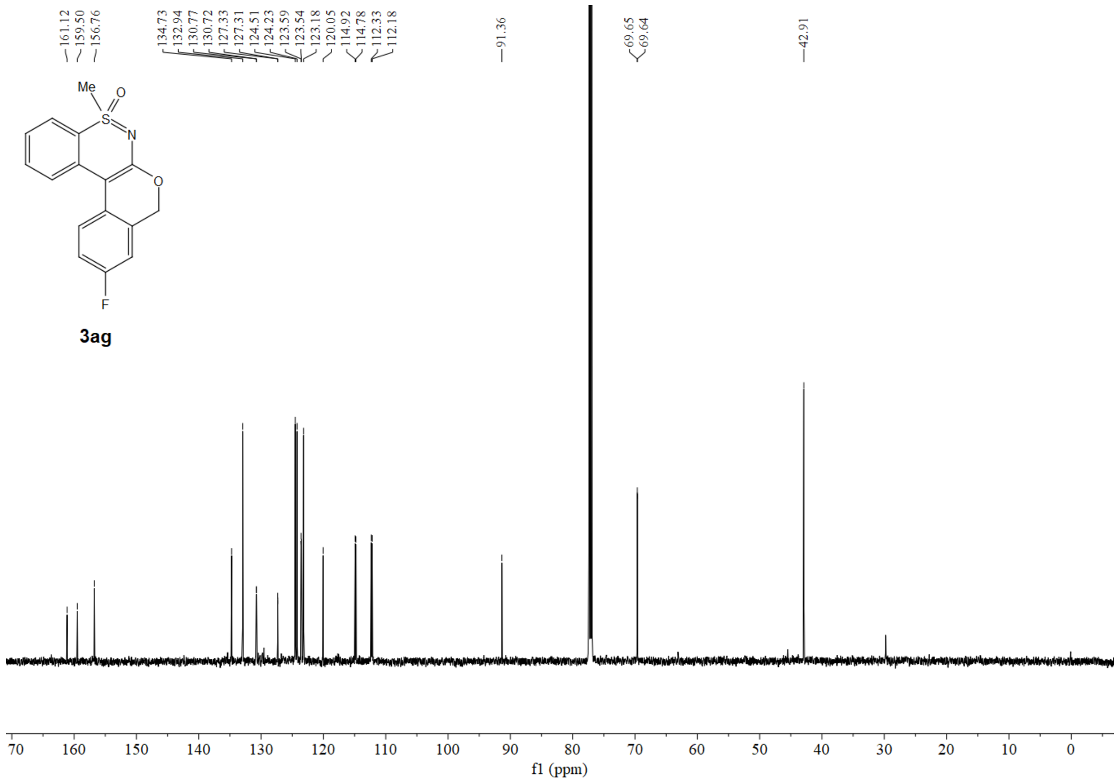
[1]H NMR spectrum of **3af**



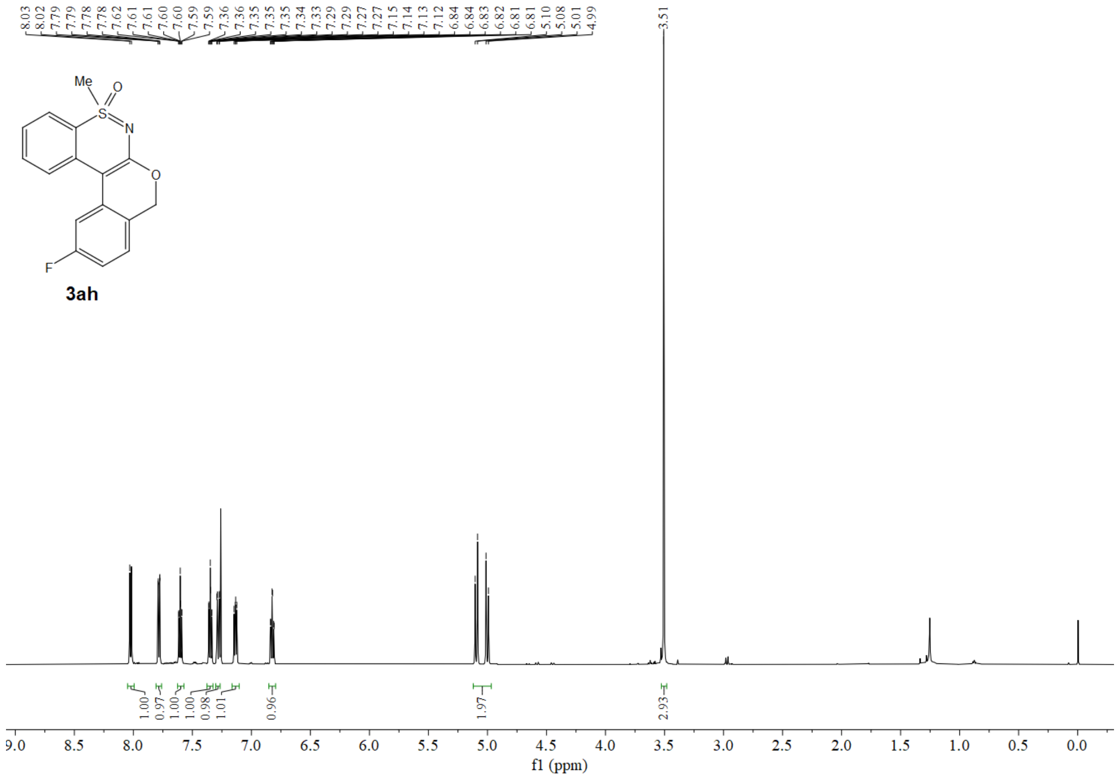
[13]C NMR spectrum of **3af**



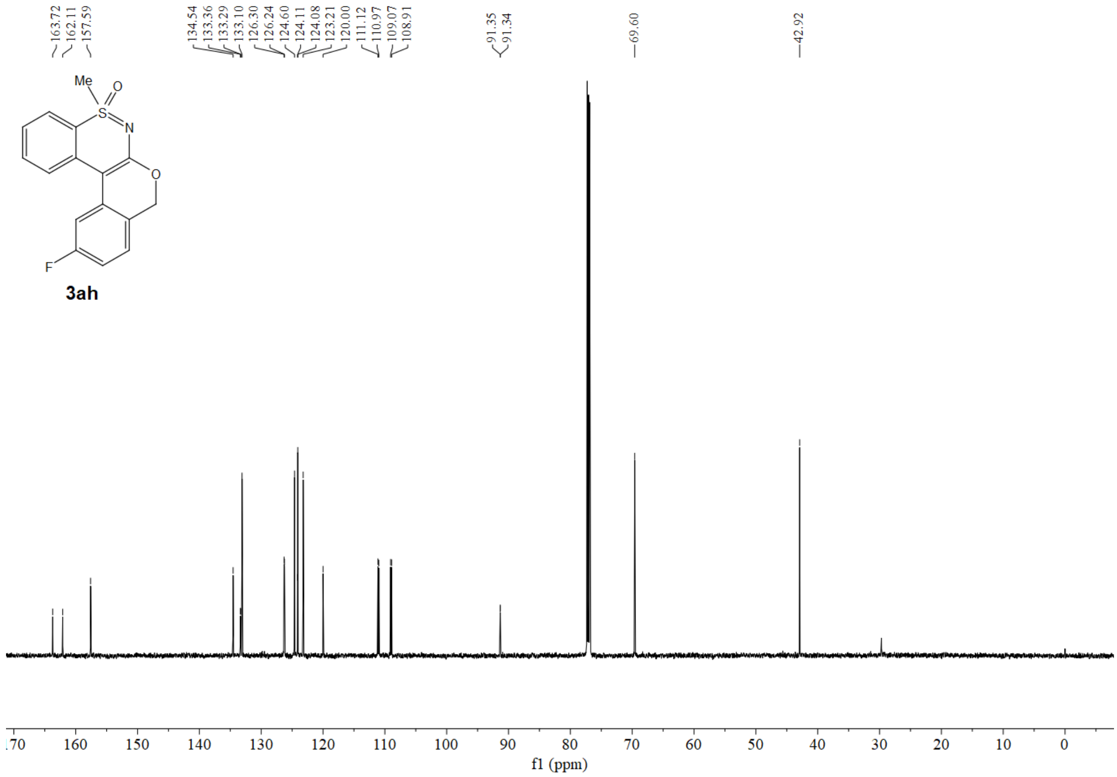
^{1}H NMR spectrum of **3ag**



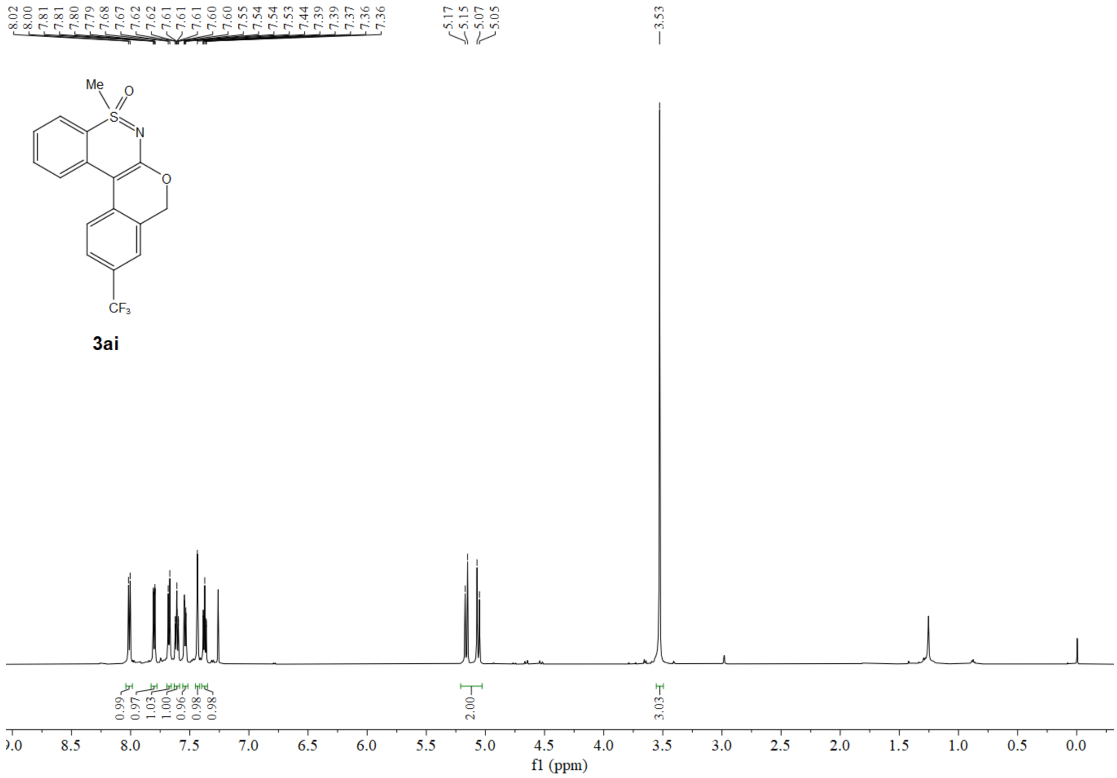
^{13}C NMR spectrum of **3ag**



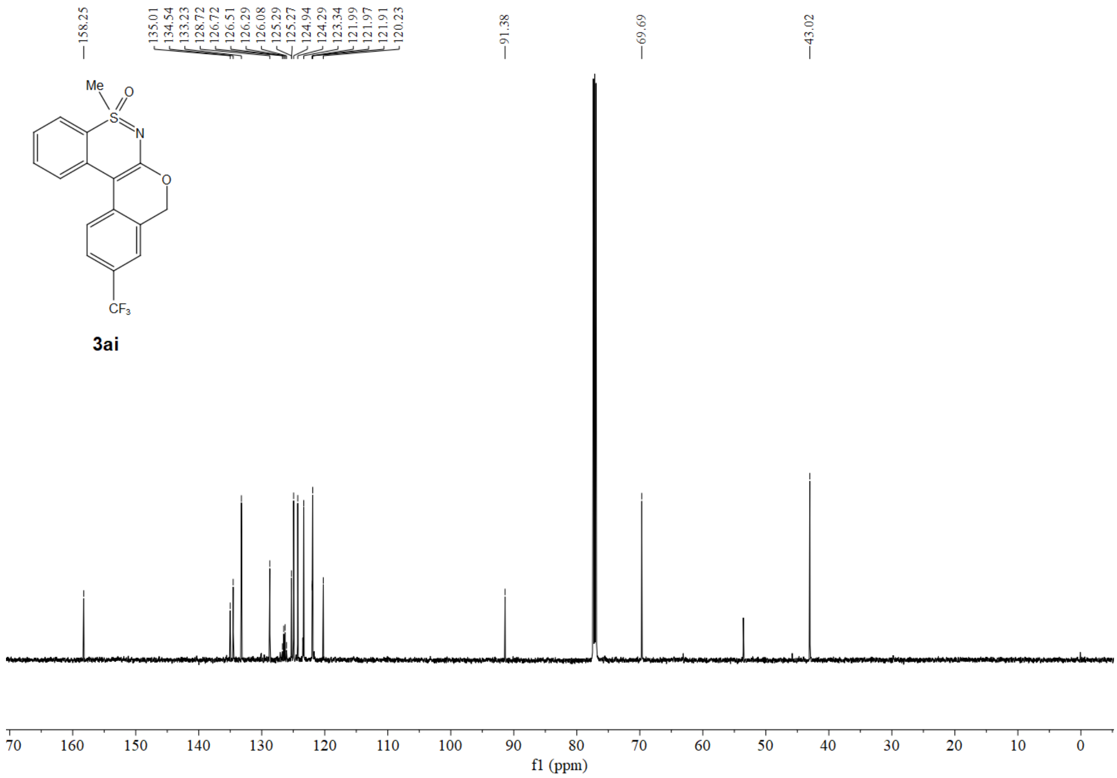
[1]H NMR spectrum of **3ah**



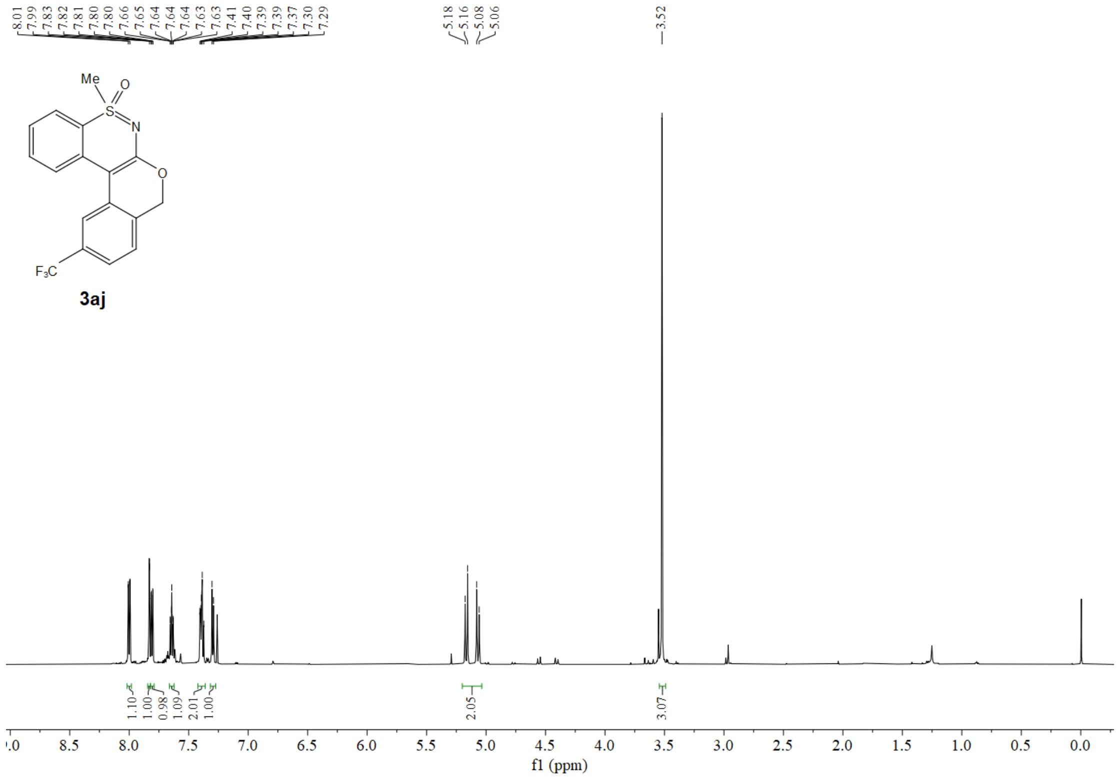
[13]C NMR spectrum of **3ah**



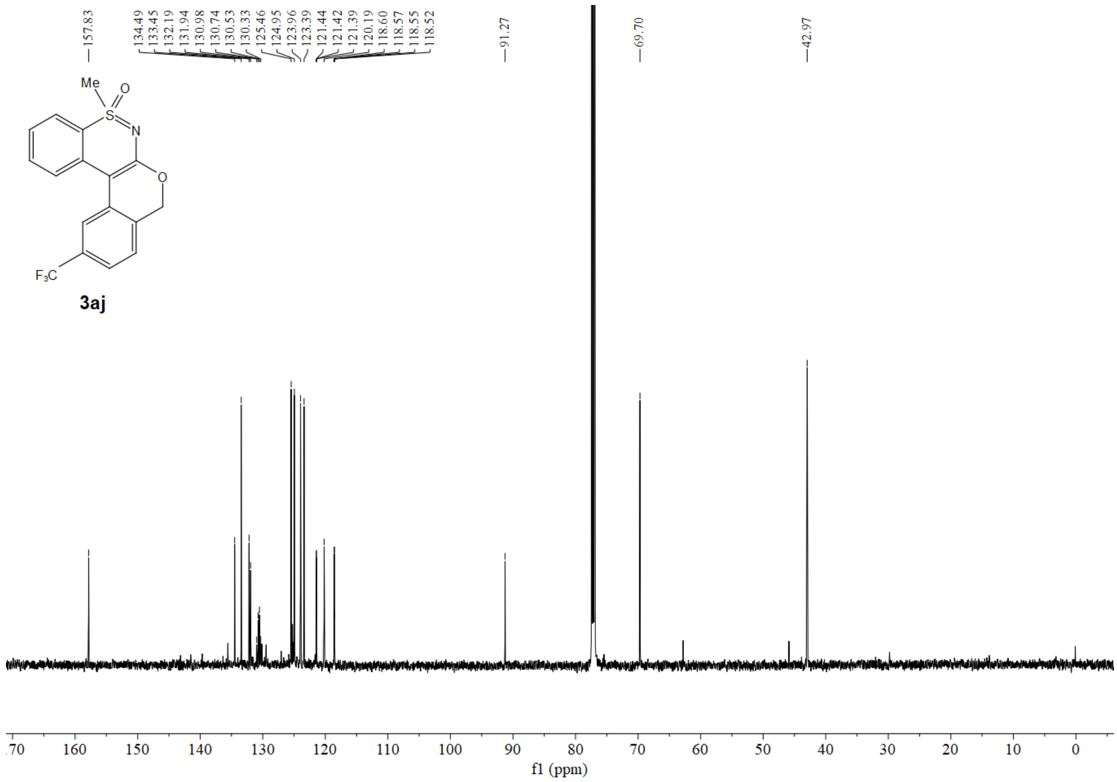
^{1}H NMR spectrum of **3ai**



^{13}C NMR spectrum of **3ai**



^{1}H NMR spectrum of **3aj**



^{13}C NMR spectrum of **3aj**