supporting information

Visible-light-promoted cascade cyclization of N-arylacrylamides with bromomethyl aryl sulfone: Access to sulfonylmethylated phenanthridines

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1. General information

All glassware was thoroughly oven-dried. Unless otherwise stated, all commercial reagents were used without further purification. Column chromatography was performed on silica gel (200-300 mesh) using a proper eluent system. ^{1}H NMR, ^{19}F NMR, and ^{13}C NMR spectra were recorded on a spectrometer at 400, 376 and 101 MHz, respectively, with deuterated chloroform as the solvent. The chemical shifts δ are reported in ppm relative to tetramethylsilane (δ = 0 ppm) or residual $CHCl_3$ (δ = 77.00 ppm). The following abbreviations were used to describe peak splitting patterns when appropriate: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), td (triplet of doublet). Coupling constants *J* are reported in Hertz (Hz). High-resolution mass spectrometry (HRMS) analyses were performed on a Q-TOF spectrometer with an electrospray ionization (ESI) source. Substrates **1**[1-3] and bromomethyl aryl sulfones **2**[4-6] were prepared according to the known literatures.

2. General experimental procedure for the synthesis of sulfonylmethylated phenanthridines 3

Under Ar atmosphere, a 25 mL reaction tube equipped with a magnetic stirrer bar was charged with N-(2-cyano-[1,1′-biphenyl]-3-yl)-N-methylmethacrylamide (**1**, 0.1 mmol), bromomethyl aryl sulfonyl (**2**, 0.2 mmol), $Ir(ppy)_3$ (0.002 mmol, 2 mol%), 2,6-dimethylpyridine (0.2 mmol), and dimethyl sulfoxide (DMSO, 1.0 mL). The reaction mixture was stirred at room temperature for 24 h under 5 W blue LED irradiation. After completion, the reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate (EtOAc, 10 mL × 3). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: EA/PE) to give the desired product **3**.

3. Optimization of the reaction conditions

Table S1. Screening of photocatalyst

Entry	Photocatalyst	Base	Solvent	Yield[a]
1	**$Ir(ppy)_3$**	Na_2HPO_4	DMF	**56%**
2	4CzIPN	Na_2HPO_4	DMF	N.D
3	Rose Bengal	Na_2HPO_4	DMF	N.D
4	EosinY	Na_2HPO_4	DMF	Trace
5	Mes-Acr^+	Na_2HPO_4	DMF	N.D
6	Rhodamine 6G	Na_2HPO_4	DMF	N.D
7	Fluorescent	Na_2HPO_4	DMF	10%
8	$Ru(bpy)_2Cl_2$	Na_2HPO_4	DMF	N.D
9	methylene blue	Na_2HPO_4	DMF	N.D
10	$[Ir(dtbbpy)(ppy)_2][PF_6]$	Na_2HPO_4	DMF	13%
11	$[Ir\{dFCF_3ppy\}_2(bpy)]PF_6$	Na_2HPO_4	DMF	Trace
12	/	Na_2HPO_4	DMF	N.D
13[b]	$Ir(ppy)_3$	Na_2HPO_4	DMF	25%

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), PC. (2 mol%), Na_2HPO_4 (0.2 mmol, 2 equiv), DMF (1 mL), 5 W blue LED, rt, 24 h, Ar. Isolation yields. [b] **1a** (0.2 mmol), **2a** (0.1 mmol)

Table S2. Screening of solvent

Entry	Photocatalyst	Base	Solvent	Yield[a]
1	$Ir(ppy)_3$	Na_2HPO_4	**DMSO**	**68%**
2	$Ir(ppy)_3$	Na_2HPO_4	CH_3CN	10%
3	$Ir(ppy)_3$	Na_2HPO_4	THF	15%
4	$Ir(ppy)_3$	Na_2HPO_4	DCM	45%
5	$Ir(ppy)_3$	Na_2HPO_4	PhMe	17%
6	$Ir(ppy)_3$	Na_2HPO_4	EtOH	N.D
7	$Ir(ppy)_3$	Na_2HPO_4	acetone	Trace
8	$Ir(ppy)_3$	Na_2HPO_4	$CHCl_3$	28%
9	$Ir(ppy)_3$	Na_2HPO_4	MeOH	16%
10	$Ir(ppy)_3$	Na_2HPO_4	EA	13%
11	$Ir(ppy)_3$	Na_2HPO_4	DCE	10%
12	$Ir(ppy)_3$	Na_2HPO_4	DMSO/H_2O (1:1)	N.D
13	$Ir(ppy)_3$	Na_2HPO_4	DMSO/DMF (1:1)	38%
14[b]	$Ir(ppy)_3$	Na_2HPO_4	DMSO	Trace
15[c]	$Ir(ppy)_3$	Na_2HPO_4	DMSO	N.D
16[d]	$Ir(ppy)_3$	Na_2HPO_4	DMSO	65%

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $Ir(ppy)_3$ (2 mol%), Na_2HPO_4 (0.2 mmol, 2 equiv), solvent (1 mL), 5 W blue LED, rt, 24 h, Ar. Isolation yields. [b] In the dark. [c] air. [d] 26 W CFL.

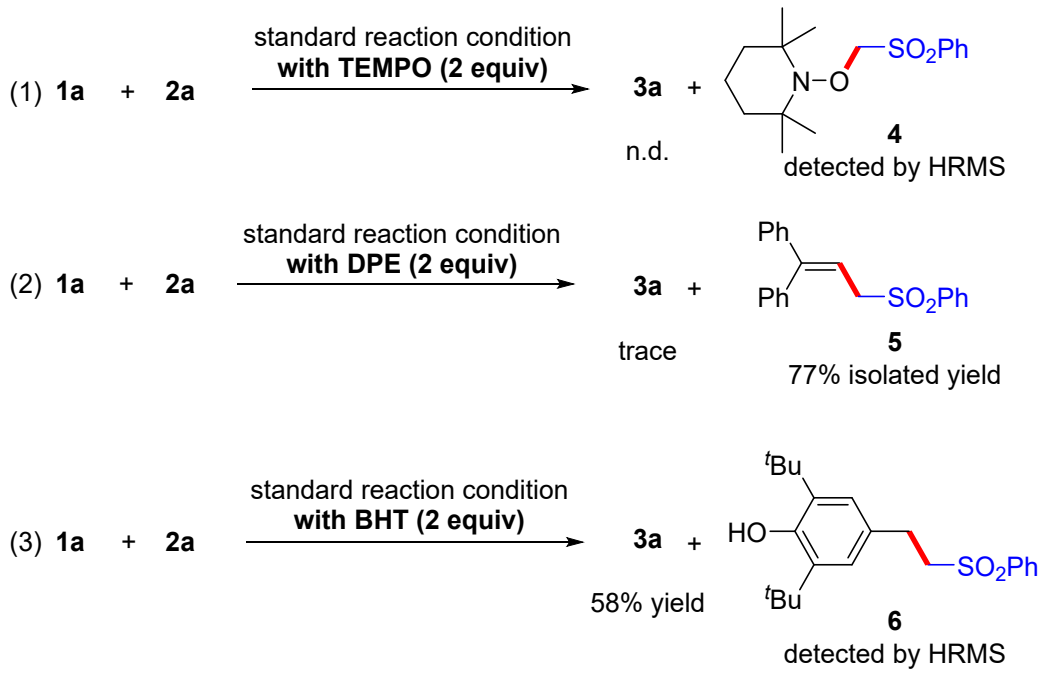
Table S3. Screening of base

Entry	Photocatalyst	Base	Solvent	Yield[a]
1	$Ir(ppy)_3$	Li_2CO_3	DMSO	50%
2	$Ir(ppy)_3$	K_2HPO_4	DMSO	60%
3	$Ir(ppy)_3$	K_2CO_3	DMSO	49%
4	$Ir(ppy)_3$	Na_2CO_3	DMSO	53%
5	$Ir(ppy)_3$	NaOAc	DMSO	52%
6	$Ir(ppy)_3$	Et_3N	DMSO	27%
7	$Ir(ppy)_3$	DBU	DMSO	63%
8	$Ir(ppy)_3$	**2,6-lutidine**	DMSO	**70%**
9	$Ir(ppy)_3$	BDMEP	DMSO	44%
10	$Ir(ppy)_3$	DTBMP	DMSO	40%
11	$Ir(ppy)_3$	2,6-Di-iso-propylpyridine	DMSO	45%
12[b]	$Ir(ppy)_3$	2,6-lutidine	DMSO	40%
13[c]	$Ir(ppy)_3$	2,6-lutidine	DMSO	59%
14[d]	$Ir(ppy)_3$	2,6-lutidine	DMSO	63%

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $Ir(ppy)_3$ (2 mol%), base (0.2 mmol, 2 equiv), DMSO (1 mL), 5 W blue LED, rt, 24 h, Ar. Isolation yields. [b] 2,6-lutidine (0.4 mmol, 4 equiv). [c] 12 h. [d] 36 h.

4. Radical-trapping experiments

Two equivalents of radical scavenger TEMPO (2,2,6,6-tetramethylpiperidinoxy), DPE (1,1-diphenylethylene) or BHT (butylated hydroxytoluene) was added to the reaction of **1a** with **2a** in the standard conditions (Scheme S1). After 24 h, the reaction mixture was cooled to room temperature and was detected by HRMS. The adduct **5** of sulfonylmethyl radical was isolated by column chromatography on silica gel. The results were shown in Figure S1-S5.



Scheme S1. Radical trapping experiments.

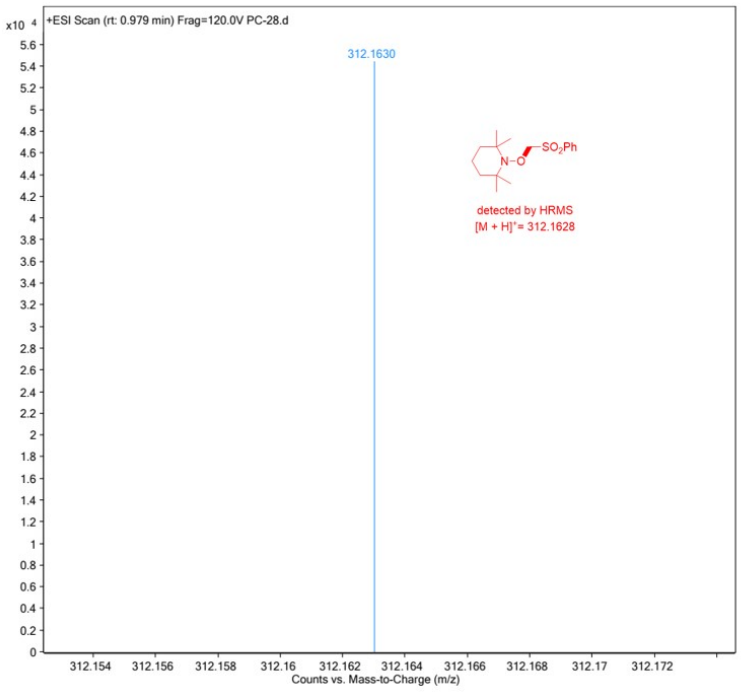


Figure S1. ESI-MS spectrum of the adduct **4**

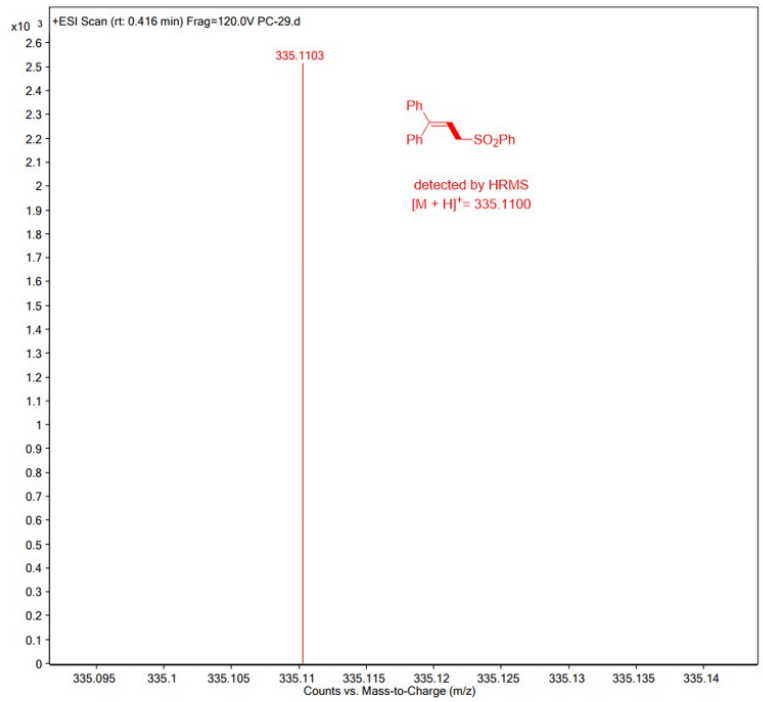


Figure S2. ESI-MS spectrum of the adduct **5**

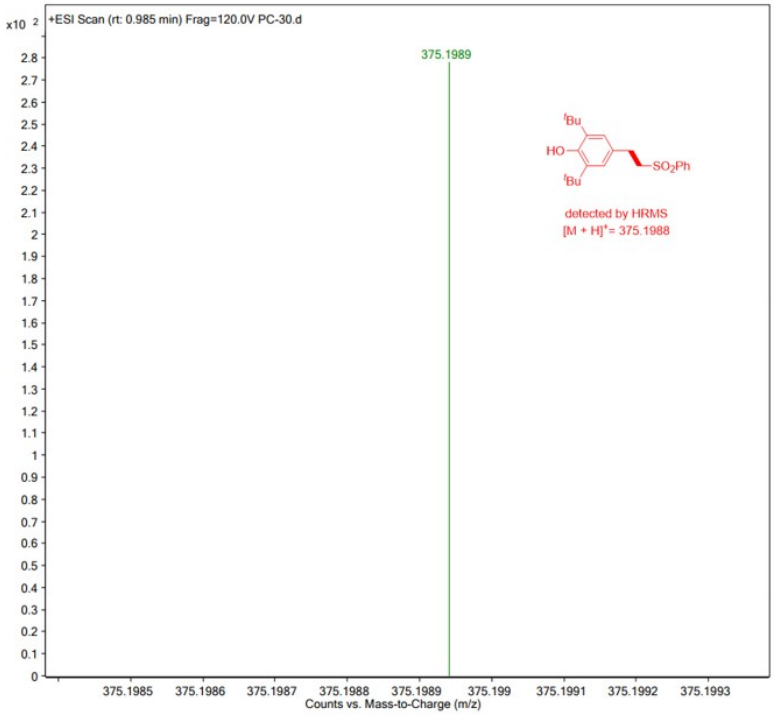


Figure S3. ESI-MS spectrum of the adduct **6**

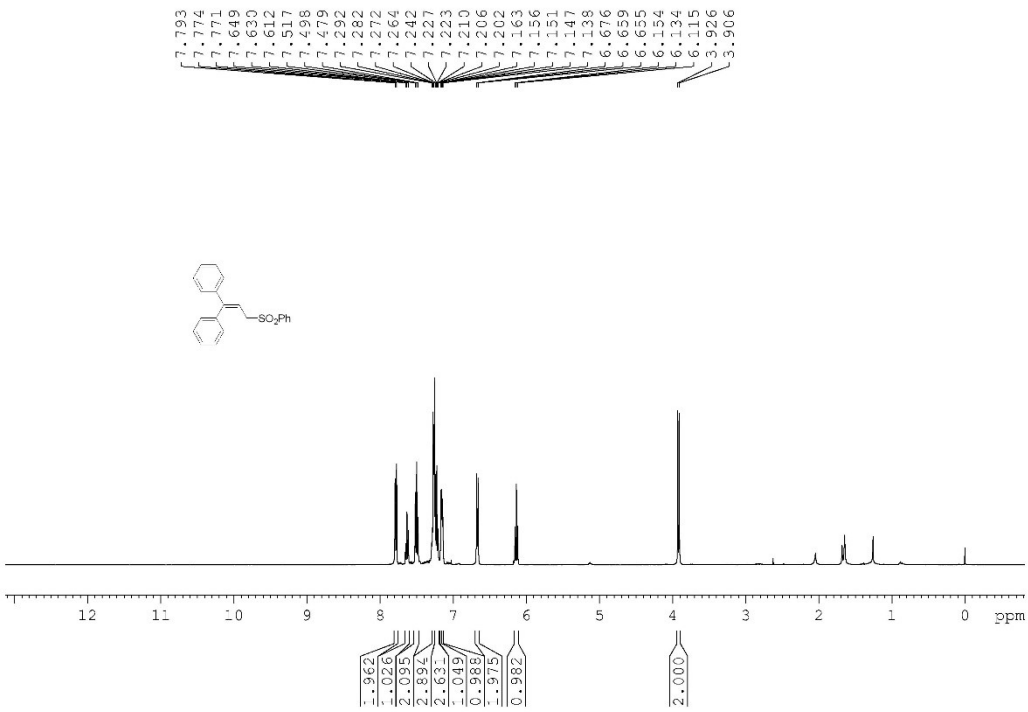


Figure S4. ^{1}H NMR spectrum of the adduct **5**

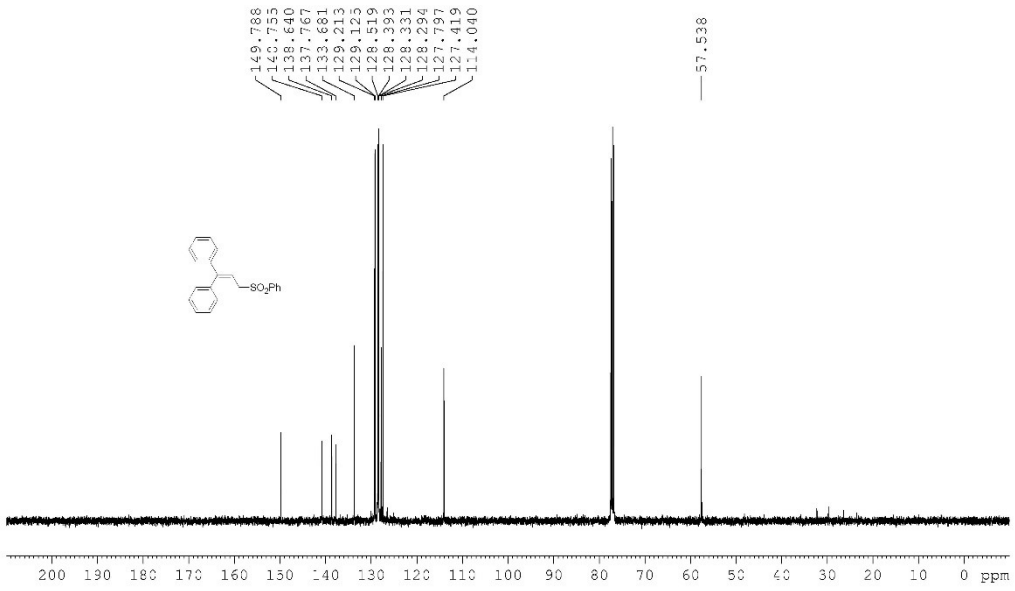


Figure S5. ^{13}C NMR spectrum of the adduct **5**

5. Light ON/OFF experiment

Under standard conditions, eight reactions were carried out, after 6 h, the blue led of one reaction was switched off, and was taken out for yield test, the remaining seven reactions were then continued under dark conditions for 6 h. Then one was taken out for yield test, the remaining six reactions were continued under blue light irradiation for 6 h and so on and so forth.

6. Luminescence quenching experiments

Emission intensities were recorded using an Edinburgh UK F4500 photoluminescence spectrometer from 400 nm to 700 nm. After irradiation of 5×10^{-5} M of $Ir(ppy)_3$ and different concentration of quencher in solvent (CH_2Cl_2) at 380 nm, its fluorescence was measured.

As shown in Figures S6-S8, the emission intensity of the excited state of photocatalyst $Ir(ppy)_3$ is decreased in the presence of **2a**. In contrast, when 2,6 -lutidine solution is adopted there are few effects. The liner relationship between I_0/I and the different concentration of **2a**, 2,6-lutidine, was shown in Figure S8.

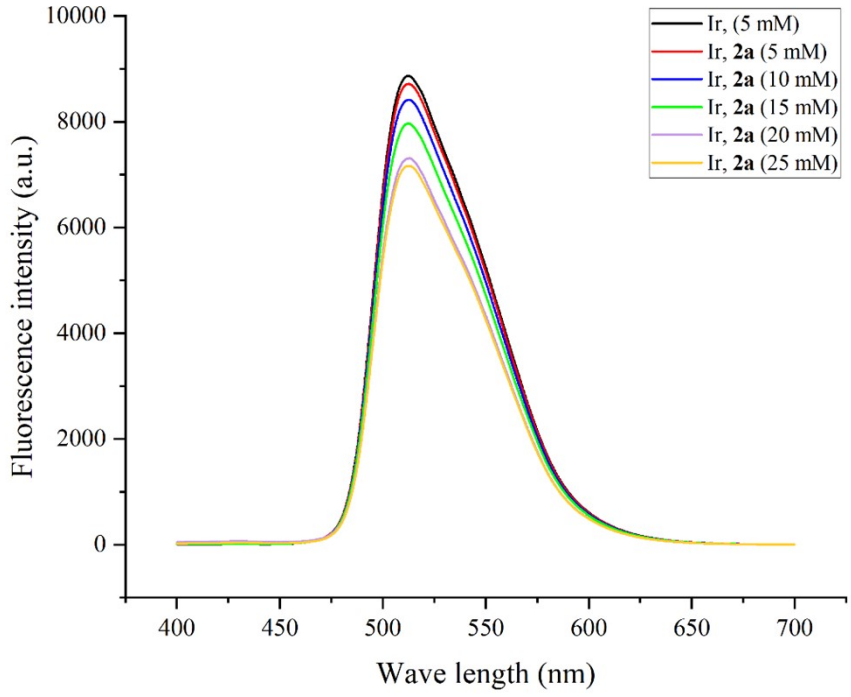


Figure S6. Fluorescence quenching of $Ir(ppy)_3$ with **2a**

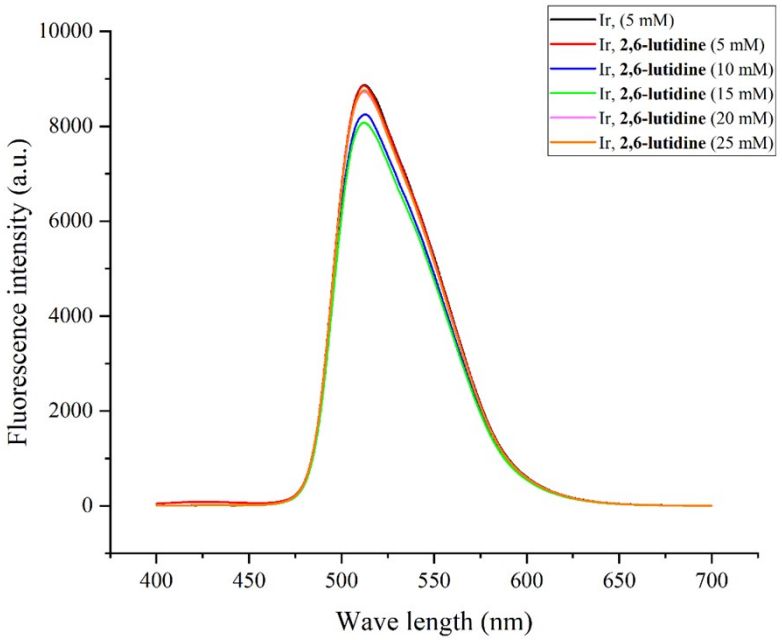


Figure.S7. Fluorescence quenching of $Ir(ppy)_3$ with 2,6-lutidine.

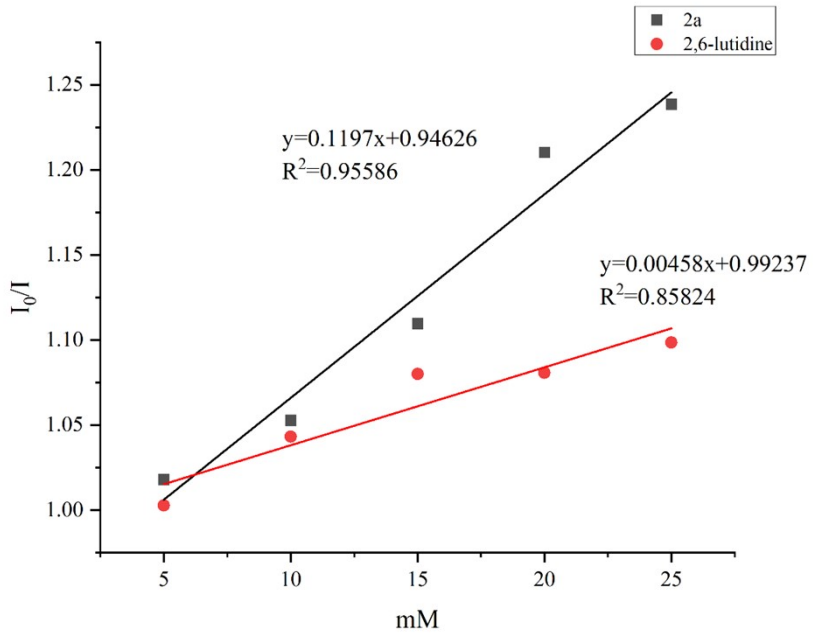
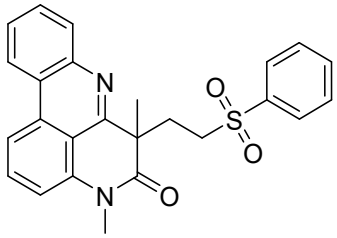
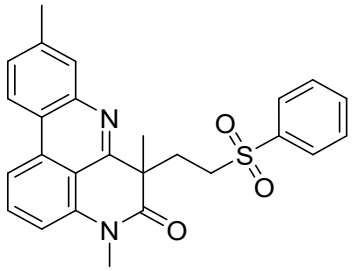


Figure S8. The liner relationship between I_0/I (I_0 and I are the florescence intensities of I $r(ppy)_3$ before and after adding the **2a** and 2,6-lutidine with various concentrations).

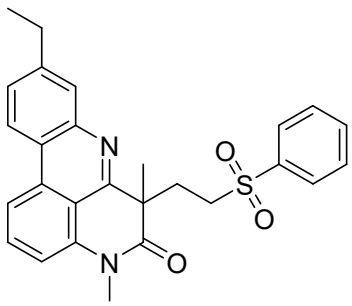
7. Characterization of the products



4,6-dimethyl-6-(2-(phenylsulfonyl)ethyl)-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one (3a) : 30.1 mg, 70% yield, yellow solid; mp 189–194 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.53 (d, *J* = 8.2 Hz, 1H), 8.29 (d, *J* = 8.3 Hz, 1H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.88 – 7.80 (m, 3H), 7.76 (t, *J* = 6.9 Hz, 1H), 7.66 (dt, *J* = 12.0, 7.1 Hz, 2H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 1H), 3.56 (s, 3H), 3.21 – 3.09 (m, 1H), 3.02 (td, *J* = 13.5, 13.0, 3.9 Hz, 1H), 2.89 (td, *J* = 6.5 Hz, 1H), 2.66 (td, *J* = 12.4, 4.6 Hz, 1H), 1.65 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.5, 157.5, 144.7, 138.8, 138.4, 133.6, 133.4, 132.1, 130.0, 129.3, 129.2, 128.1, 127.1, 122.7, 116.5, 111.8, 111.0, 52.5, 50.4, 32.0, 30.0, 29.4. HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{25}H_{23}N_2O_3S$ 431.1424, found 431.1424.

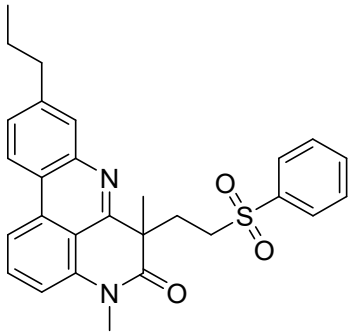


4,6,9-trimethyl-6-(2-(phenylsulfonyl)ethyl)-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one (3b) : 16.1 mg, 44% yield, bright yellow solid; mp 61–65 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.40 (d, *J* = 8.3 Hz, 1H), 8.23 (d, *J* = 8.3 Hz, 1H), 7.88 – 7.77 (m, 3H), 7.75 (s, 1H), 7.64 (d, *J* = 6.2 Hz, 1H), 7.57 – 7.44 (m, 3H), 7.17 (d, *J* = 7.9 Hz, 1H), 3.54 (s, 3H), 3.20 – 3.08 (m, 1H), 2.94 (dtd, *J* = 42.8, 12.6, 3.7 Hz, 2H), 2.70 – 2.62 (m, 1H), 1.63 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.6, 157.4, 144.8, 139.6, 138.8, 138.4, 133.5, 132.0, 129.4, 129.2, 128.9, 128.2, 128.0, 122.3, 120.4, 116.3, 111.5, 110.6, 52.5, 50.4, 31.9, 30.0, 29.5, 21.6. HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{26}H_{25}N_2O_3S$ 445.1580, found 445.1580.

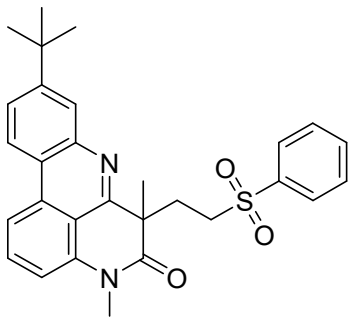


9-ethyl-4,6-dimethyl-6-(2-(phenylsulfonyl)ethyl)-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one (3c) : 22.8 mg, 50% yield, yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.42 (d, *J* = 8.4 Hz, 1H), 8.23 (d, *J* = 8.3 Hz, 1H), 7.91 – 7.76

(m, 3H), 7.74 (s, 1H), 7.69 – 7.61 (m, 1H), 7.52 (t, *J* = 8.5 Hz, 3H), 7.17 (d, *J* = 7.9 Hz, 1H), 3.54 (s, 3H), 3.21 – 3.08 (m, 1H), 3.08 – 2.95 (m, 1H), 2.89 (m, *J* = 12.6, 3.8 Hz, 1H), 2.84 (d, *J* = 7.6 Hz, 2H), 2.72 – 2.59 (m, 1H), 1.82 (h, *J* = 7.4 Hz, 2H), 1.63 (s, 3H), 1.04 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.6, 157.4, 145.8, 144.96, 138.8, 138.3, 133.5, 133.5, 132.0, 129.2, 128.2, 127.8, 122.4, 120.6, 116.3, 111.6, 110.5, 52.5, 50.4, 32.0, 30.0, 29.5, 28.9, 15.5. HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{27}H_{27}N_2O_3S$ 459.1737, found 459.1739.

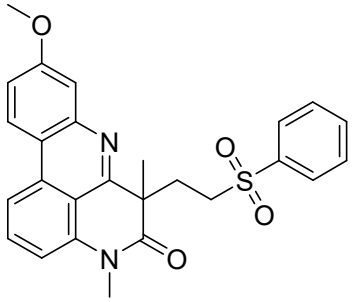


4,6-dimethyl-6-(2-(phenylsulfonyl)ethyl)-9-propyl-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one (3d) : 27.3 mg, 58% yield, yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.42 (d, *J* = 8.4 Hz, 1H), 8.23 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.80 (t, *J* = 8.1 Hz, 1H), 7.74 (s, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 3H), 7.17 (d, *J* = 7.9 Hz, 1H), 3.54 (s, 3H), 3.22 – 3.09 (m, 1H), 3.07 – 2.96 (m, 1H), 2.89 (td, *J* = 12.6, 3.8 Hz, 1H), 2.84 (t, *J* = 7.6 Hz, 2H), 2.65 (td, *J* = 12.6, 4.7 Hz, 1H), 1.82 (h, *J* = 7.4 Hz, 2H), 1.63 (s, 3H), 1.04 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.6, 157.3, 144.9, 144.3, 138.8, 138.3, 133.5, 133.5, 131.9, 129.2, 128.9, 128.2, 128.2, 122.3, 120.7, 116.3, 111.6, 110.5, 52.5, 50.4, 38.0, 31.9, 30.0, 29.5, 24.4, 14.0. HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{28}H_{29}N_2O_3S$ 473.1893, found 473.1890.

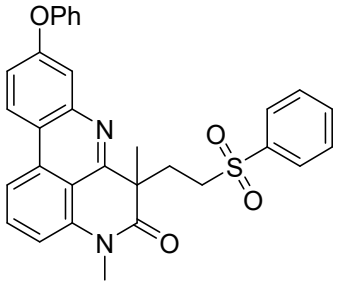


9-(tert-butyl)-4,6-dimethyl-6-(2-(phenylsulfonyl)ethyl)-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one (3e) : 37.1 mg, 76% yield, brown oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.44 (d, *J* = 8.7 Hz, 1H), 8.24 (d, *J* = 8.3 Hz, 1H), 7.93 (d, *J* = 2.1 Hz, 1H), 7.90 – 7.83 (m, 2H), 7.80 (t, *J* = 8.1 Hz, 1H), 7.75 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 1H), 3.54 (s, 3H), 3.21 – 3.08 (m, 1H), 3.08 – 2.99 (m, 1H), 2.86 (td, *J* = 12.6, 4.0 Hz, 1H), 2.74 – 2.60 (m, 1H), 1.64 (s, 3H), 1.47 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.6, 157.3, 152.8, 144.8, 138.8, 138.3, 133.6, 133.4, 132.0, 129.2, 128.1, 125.7, 125.5, 122.3, 120.4, 116.4, 111.6, 110.6, 52.5, 50.3, 35.1, 32.2, 31.4, 29.9, 29.5. HRMS (ESI-

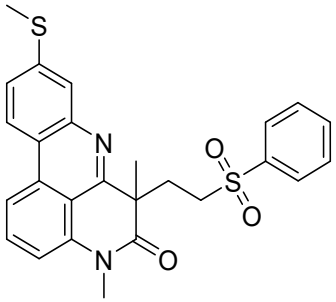
TOF) m/z $[M + H]^+$ calcd for $C_{29}H_{31}N_2O_3S$ 487.2050, found 487.2050.



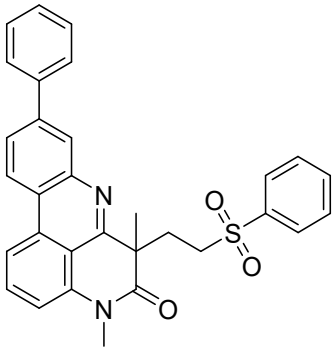
9-methoxy-4,6-dimethyl-6-(2-(phenylsulfonyl)ethyl)-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one (3f) : 28.9 mg, 63% yield, brilliant yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.39 (d, *J* = 9.0 Hz, 1H), 8.16 (d, *J* = 8.3 Hz, 1H), 7.85 (d, *J* = 9.7 Hz, 2H), 7.78 (t, *J* = 8.1 Hz, 1H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.38 (s, 1H), 7.29 (dd, *J* = 9.0, 2.7 Hz, 1H), 7.12 (d, *J* = 7.9 Hz, 1H), 4.01 (s, 3H), 3.53 (s, 3H), 3.20 – 3.07 (m, 1H), 2.95 (dtd, *J* = 49.2, 12.5, 4.0 Hz, 2H), 2.65 (td, *J* = 12.5, 4.7 Hz, 1H), 1.64 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.5, 160.6, 157.9, 146.5, 138.8, 138.4, 133.6, 133.5, 132.1, 129.2, 128.1, 123.7, 118.5, 116.8, 116.0, 111.0, 109.9, 109.4, 52.5, 50.3, 32.0, 29.9, 29.5. HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{26}H_{25}N_2O_4S$ 461.1530, found 461.1535.



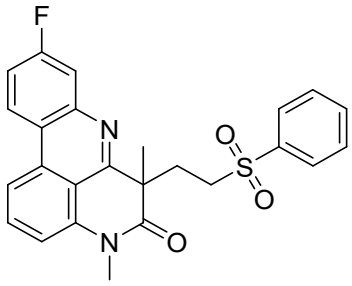
4,6-dimethyl-9-phenoxy-6-(2-(phenylsulfonyl)ethyl)-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one (3g) : 27.5 mg, 53% yield, yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.47 (d, *J* = 9.0 Hz, 1H), 8.19 (d, *J* = 8.3 Hz, 1H), 7.81 (t, *J* = 8.3 Hz, 3H), 7.55 – 7.38 (m, 6H), 7.34 (d, *J* = 2.5 Hz, 1H), 7.26 (d, *J* = 14.9 Hz, 1H), 7.21 – 7.12 (m, 3H), 3.54 (s, 3H), 3.17 – 3.07 (m, 1H), 3.03 – 2.92 (m, 1H), 2.73 (td, *J* = 12.5, 3.9 Hz, 1H), 2.63 (td, *J* = 12.5, 4.8 Hz, 1H), 1.58 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.4, 158.7, 158.4, 156.3, 146.2, 138.6, 138.4, 133.6, 133.4, 132.3, 130.2, 129.1, 128.1, 124.3, 124.2, 120.0, 119.6, 118.4, 116.2, 115.8, 111.3, 52.4, 50.4, 31.9, 30.0, 29.6. HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{31}H_{27}N_2O_4S$ 523.1686, found 523.1681.



4,6-dimethyl-9-(methylthio)-6-(2-(phenylsulfonyl)ethyl)-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one (3h) : 35 mg, 74% yield, orange-yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.36 (d, *J* = 8.7 Hz, 1H), 8.18 (d, *J* = 8.3 Hz, 1H), 7.86 – 7.76 (m, 3H), 7.70 (d, *J* = 2.0 Hz, 1H), 7.68 – 7.59 (m, 1H), 7.56 – 7.46 (m, 3H), 7.16 (d, *J* = 7.9 Hz, 1H), 3.54 (s, 3H), 3.19 – 3.07 (m, 1H), 3.06 – 2.93 (m, 1H), 2.86 (td, *J* = 12.6, 3.9 Hz, 1H), 2.66 (s, 4H), 1.63 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.5, 158.2, 145.3, 140.9, 138.8, 138.4, 133.6, 133.4, 132.2, 129.2, 128.1, 125.8, 124.7, 122.7, 119.8, 116.2, 111.5, 110.6, 52.5, 50.4, 32.0, 30.0, 29.5, 15.3. HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{26}H_{25}N_2O_3S_2$ 477.1301, found 477.1304.

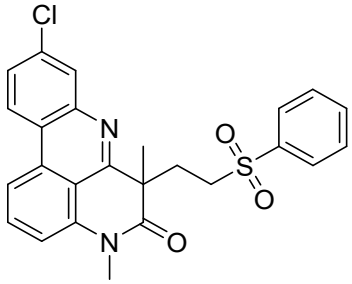


4,6-dimethyl-9-phenyl-6-(2-(phenylsulfonyl)ethyl)-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one (3i) : 27.9 mg, 55% yield, yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.55 (d, *J* = 8.6 Hz, 1H), 8.27 (d, *J* = 8.3 Hz, 1H), 8.15 (d, *J* = 1.9 Hz, 1H), 7.92 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.88 – 7.74 (m, 5H), 7.62 – 7.40 (m, 6H), 7.21 (d, *J* = 7.9 Hz, 1H), 3.55 (s, 3H), 3.24 – 3.11 (m, 1H), 3.09 – 2.96 (m, 1H), 2.90 (td, *J* = 12.6, 3.7 Hz, 1H), 2.69 (td, *J* = 12.5, 4.7 Hz, 1H), 1.65 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.5, 158.0, 145.1, 142.0, 140.0, 138.9, 138.5, 133.6, 133.3, 132.2, 129.2, 129.0, 128.2, 128.0, 127.8, 127.4, 126.2, 123.1, 121.8, 116.5, 111.8, 111.0, 52.5, 50.5, 31.9, 30.0, 29.6. HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{31}H_{27}N_2O_3S$ 507.1737, found 507.1737.

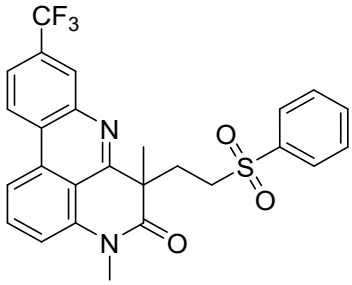


9-fluoro-4,6-dimethyl-6-(2-(phenylsulfonyl)ethyl)-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one (3j) : 29.2 mg, 65% yield, yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.49 (dd, *J* = 9.1, 5.8 Hz, 1H), 8.20 (d, *J* = 8.3 Hz, 1H), 7.90 – 7.80 (m, 3H), 7.71 – 7.63 (m, 1H), 7.54 (t, *J* = 7.7 Hz, 3H), 7.47 – 7.37 (m, 1H), 7.21 (d, *J* = 7.9 Hz, 1H), 3.55 (s, 3H), 3.21 – 3.09 (m, 1H), 3.02 – 2.90 (m, 1H), 2.84 (td, *J* = 12.6, 3.7 Hz, 1H), 2.67 (td, *J* = 14.1, 13.3, 5.5 Hz, 1H), 1.63 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.4, 163.0 (d, *J* = 250.5 Hz), 159.1, 146.0 (d, *J* = 12.0 Hz), 138.7, 138.5, 133.7, 133.3, 132.6, 129.2, 128.2, 124.6 (d, *J* = 9.6 Hz), 119.5 (d, *J* = 1.5

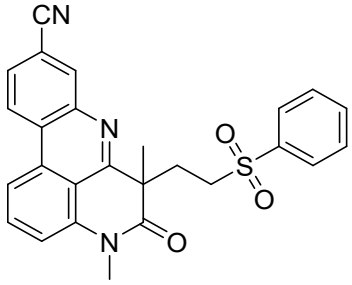
Hz), 116.3 (d, *J* = 24.2 Hz),116.2, 114.3 (d, *J* = 20.5 Hz), 111.5, 110.9, 52.5, 50.5, 31.9, 30.0, 29.6. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -111.01. HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{25}H_{22}FN_2O_3S$ 449.1330, found 449.1332.



9-chloro-4,6-dimethyl-6-(2-(phenylsulfonyl)ethyl)-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one (3k) : 16.1 mg, 35% yield, yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.43 (d, *J* = 8.8 Hz, 1H), 8.21 (d, *J* = 8.3 Hz, 1H), 7.89 – 7.79 (m, 4H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.64 – 7.58 (m, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 1H), 3.55 (s, 3H), 3.21 – 3.10 (m, 1H), 2.97 – 2.89 (m, 1H), 2.85 (td, *J* = 12.6, 3.5 Hz, 1H), 2.68 (td, *J* = 12.5, 4.9 Hz, 1H), 1.62 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.3, 159.0, 145.2, 138.7, 138.6, 135.0, 133.7, 133.1, 132.6, 129.2, 129.1, 128.2, 127.7, 123.9, 121.2, 116.3, 111.8, 111.3, 52.5, 50.5, 31.9, 30.0, 29.7. HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{25}H_{22}ClN_2O_3S$ 465.1034, found 465.1038.

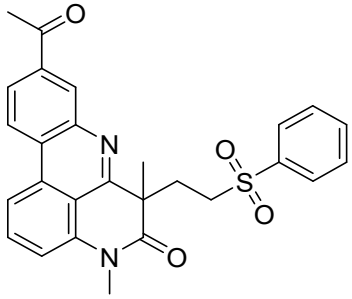


4,6-dimethyl-6-(2-(phenylsulfonyl)ethyl)-9-(trifluoromethyl)-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one (3l) : 27.8 mg, 57% yield, yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.62 (d, *J* = 8.6 Hz, 1H), 8.30 (d, *J* = 8.8 Hz, 1H), 8.09 (s, 1H), 7.91 (t, *J* = 8.1 Hz, 1H), 7.87 – 7.80 (m, 3H), 7.74 – 7.64 (m, 1H), 7.60 – 7.50 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 1H), 3.57 (s, 3H), 3.26 – 3.11 (m, 1H), 2.97 – 2.80 (m, 2H), 2.72 (td, *J* = 12.5, 5.0 Hz, 1H), 1.62 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.2, 159.4, 143.9, 138.7, 138.6, 133.7, 132.8, 132.7, 131.0 (q, *J* = 33 Hz), 129.2, 128.2, 127.4 (q, *J* = 4.4 Hz), 125.4, 124.0 (q, *J* = 272.7 Hz), 123.7,122.8 (q, *J* = 3.7 Hz), 116.7, 112.4, 112.2, 52.4, 50.6, 31.8, 30.0, 29.9. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.26. HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{26}H_{22}F_2N_3O_2S$ 499.1298, found 499.1301.

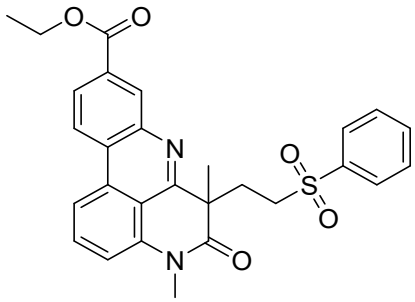


4,6-dimethyl-6-(2-(phenylsulfonyl)ethyl)-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-

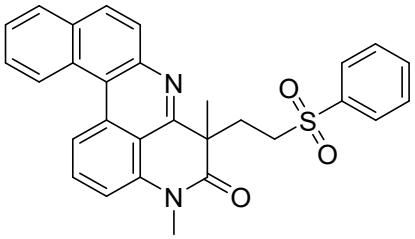
one (3m) : 28 mg, 62% yield, pale yellow solid; mp 150–155 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.59 (d, *J* = 8.5 Hz, 1H), 8.28 (d, *J* = 8.3 Hz, 1H), 8.18 (d, *J* = 1.7 Hz, 1H), 7.94 (t, *J* = 8.1 Hz, 1H), 7.87 – 7.78 (m, 3H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 1H), 3.57 (s, 3H), 3.25 – 3.07 (m, 1H), 2.98 – 2.78 (m, 2H), 2.76 – 2.61 (m, 1H), 1.64 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.1, 160.2, 143.9, 138.8, 138.7, 135.0, 133.8, 133.1, 132.4, 129.3, 128.3, 128.2, 126.0, 124.0, 118.4, 116.8, 112.7, 112.6, 112.5, 52.5, 50.6, 31.8, 30.1, 29.6. HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{26}H_{22}N_3O_3S$ 456.1376, found 456.1379.



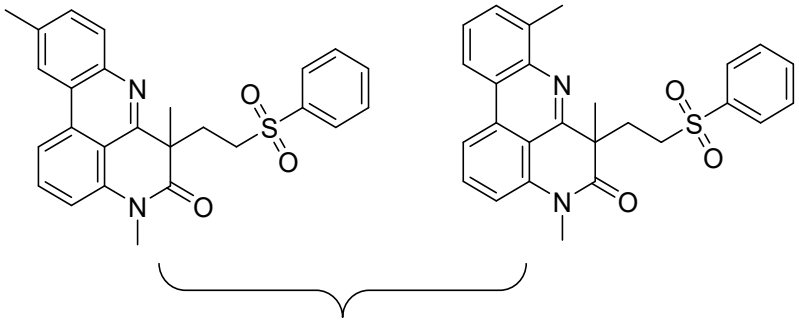
9-acetyl-4,6-dimethyl-6-(2-(phenylsulfonyl)ethyl)-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one (3n) : 17.9 mg, 38% yield, pale yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.58 (d, *J* = 8.6 Hz, 1H), 8.52 (d, *J* = 1.9 Hz, 1H), 8.31 (d, *J* = 8.3 Hz, 1H), 8.24 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.96 – 7.81 (m, 3H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 1H), 3.57 (s, 3H), 3.21 – 3.10 (m, 1H), 2.82 (s, 3H), 2.68 (td, *J* = 12.6, 4.6 Hz, 1H), 1.66 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.8, 172.3, 158.9, 144.3, 138.7, 138.6, 137.4, 133.7, 132.8, 132.6, 131.3, 129.2, 128.2, 126.1, 125.3, 123.2, 117.0, 112.4, 112.2, 52.5, 50.5, 31.9, 30.0, 29.5, 26.9. HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{27}H_{25}N_2O_4S$ 473.1530, found 473.1529.



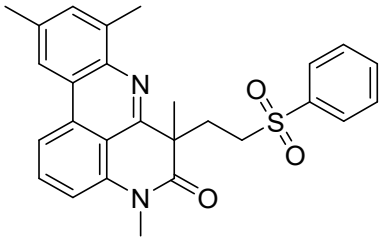
ethyl 4,6-dimethyl-5-oxo-6-(2-(phenylsulfonyl)ethyl)-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridine-9-carboxylate (3o) : 26.8 mg, 55% yield, orange-yellow solid; mp 197–201 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.60 – 8.49 (m, 2H), 8.34 – 8.22 (m, 2H), 7.95 – 7.81 (m, 3H), 7.73 – 7.63 (m, 1H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 1H), 4.52 (q, *J* = 7.1 Hz, 2H), 3.57 (s, 3H), 3.23 – 3.10 (m, 1H), 3.06 – 2.92 (m, 1H), 2.86 (td, *J* = 12.6, 3.7 Hz, 1H), 2.69 (td, *J* = 12.6, 4.7 Hz, 1H), 1.63 (s, 3H), 1.53 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.3, 166.3, 158.7, 144.1, 138.6, 138.6, 133.7, 132.8, 132.5, 131.9, 131.0, 129.2, 128.1, 127.0, 125.9, 122.9, 116.9, 112.4, 112.1, 61.5, 52.4, 50.5, 30.0, 29.7, 14.5. HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{28}H_{27}N_2O_5S$ 503.1653, found 503.1652.



4,6-dimethyl-6-(2-(phenylsulfonyl)ethyl)-4H-benzo[a]pyrido[4,3,2-gh]phenanthridin-5(6H)-one (3p) : 30.2 mg, 63% yield, yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.03 (d, *J* = 8.3 Hz, 1H), 8.77 (d, *J* = 8.6 Hz, 1H), 8.04 (t, *J* = 8.1 Hz, 2H), 7.89 – 7.79 (m, 4H), 7.77 – 7.58 (m, 3H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 1H), 3.59 (s, 3H), 3.22 – 3.11 (m, 1H), 3.10 – 2.99 (m, 1H), 2.91 (td, *J* = 12.6, 3.8 Hz, 1H), 2.70 (td, *J* = 12.5, 4.6 Hz, 1H), 1.66 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.5, 156.7, 144.8, 138.8, 138.1, 133.6, 133.4, 133.3, 131.7, 130.2, 129.7, 129.2, 128.9, 128.2, 128.1, 127.5, 126.8, 126.6, 121.2, 119.4, 113.1, 110.2, 52.6, 50.1, 32.1, 30.1, 29.4. HRMS (ESI-TOF) m/z [M + H]$^{+}$ calcd for $C_{29}H_{25}N_2O_3S$ 481.1580, found 481.1580.

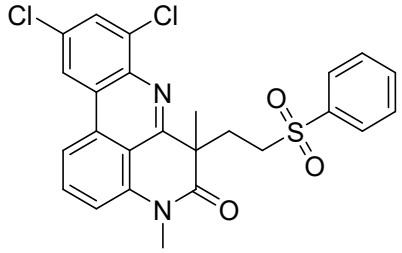


4,6,10-trimethyl-6-(2-(phenylsulfonyl)ethyl)-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one and 4,6,8-trimethyl-6-(2-(phenylsulfnyl)ethyl)-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one (3q:3q' = 3:1) : 19.8 mg, 45% yield, pale yellow solid; mp 158–161 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.38 (d, *J* = 9.7 Hz, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 7.87 – 7.80 (m, 3H), 7.65 – 7.58 (m, 2H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.55 – 7.45 (m, 2H), 7.19 (d, *J* = 7.9 Hz, 1H), 3.55 (s, 3H), 3.21 – 3.08 (td, 1H), 3.06 – 2.90 (m, 2H), 2.70 (td, 3H), 2.69 – 2.64 (m, 1H), 1.64 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.7, 155.9, 143.4, 138.9, 138.3, 137.9, 133.6, 131.8, 131.0, 129.9, 129.2, 128.1, 126.7, 122.5, 120.3, 116.8, 111.6, 110.7, 52.7, 50.6, 32.0, 30.1, 29.9, 18.2. HRMS (ESI-TOF) m/z [M + H]$^{+}$ calcd for $C_{26}H_{25}N_2O_3S$ 445.1580, found 445.1583.

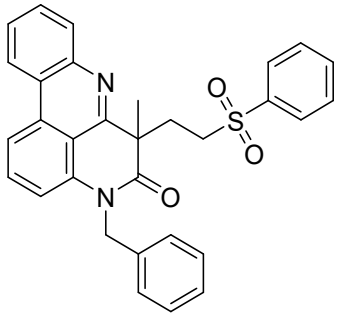


4,6,8,10-tetramethyl-6-(2-(phenylsulfonyl)ethyl)-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one (3r) : 27.2 mg, 60% yield, orange-yellow solid; mp 155–158 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 8.3 Hz, 1H), 8.15 (s, 1H),

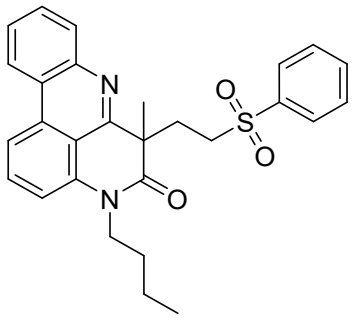
7.83 (d, *J* = 8.1 Hz, 2H), 7.78 (t, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.45 (s, 1H), 7.17 (d, *J* = 7.8 Hz, 1H), 3.54 (s, 3H), 3.14 (td, *J* = 13.0, 4.3 Hz, 1H), 3.07 – 2.88 (m, 2H), 2.67 (td, 1H), 2.66 (s, 3H), 2.58 (s, 3H), 1.63 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.8, 154.8, 141.8, 139.0, 138.3, 137.5, 136.6, 133.6, 133.5, 131.8, 131.5, 129.2, 128.1, 122.4, 119.8, 116.7, 111.7, 110.6, 52.7, 50.5, 32.0, 30.1, 29.9, 22.0, 18.1. HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{27}H_{27}N_2O_3S$ 459.1737, found 459.1739.



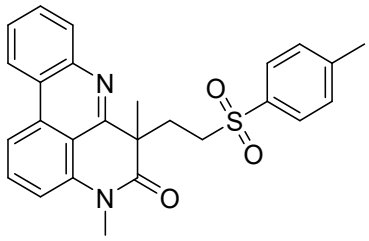
8,10-dichloro-4,6-dimethyl-6-(2-(phenylsulfonyl)ethyl)-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one (3s) : 23.6 mg, 47% yield, orange-yellow solid; mp 204–207 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.39 (d, *J* = 2.2 Hz, 1H), 8.17 (d, *J* = 8.3 Hz, 1H), 7.89 (t, *J* = 8.1 Hz, 1H), 7.85 (s, 1H), 7.82 (dd, *J* = 5.7, 1.9 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 1H), 3.57 (s, 3H), 3.29 – 3.17 (m, 1H), 3.12 (dd, *J* = 12.2, 4.4 Hz, 1H), 2.84 (td, *J* = 12.5, 4.3 Hz, 1H), 2.67 (td, *J* = 12.6, 4.4 Hz, 1H), 1.66 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.3, 158.8, 139.6, 138.8, 138.7, 135.6, 133.6, 132.9, 132.4, 132.3, 129.9, 129.2, 128.1, 124.9, 121.1, 116.6, 112.1, 112.1, 52.4, 50.6, 32.2, 30.1, 29.3. HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{25}H_{21}Cl_2N_2O_3S$ 499.0644, found 499.0648.



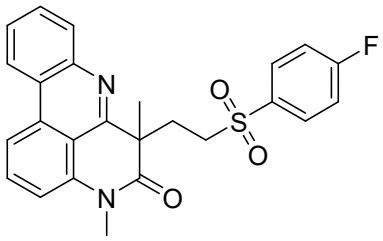
4-benzyl-6-methyl-6-(2-(phenylsulfonyl)ethyl)-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one (3t) : 31.4 mg, 62% yield, yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.49 (d, *J* = 9.6 Hz, 1H), 8.23 (d, *J* = 8.3 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.71 – 7.62 (m, 3H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.32 (d, *J* = 7.1 Hz, 2H), 7.27 (t, 3H), 7.12 (d, *J* = 8.0 Hz, 1H), 5.52 (d, *J* = 16.2 Hz, 1H), 5.23 (d, *J* = 16.0 Hz, 1H), 3.29 – 3.17 (m, 1H), 3.17 – 3.07 (m, 1H), 2.96 (td, *J* = 12.5, 4.0 Hz, 1H), 2.72 (td, *J* = 12.5, 4.7 Hz, 1H), 1.74 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.8, 157.3, 144.7, 138.8, 137.5, 136.1, 133.6, 133.6, 132.0, 123.0, 129.3, 129.2, 129.0, 128.2, 127.5, 127.1, 126.3, 122.8, 122.5, 116.6, 112.1, 112.0, 52.5, 50.6, 46.3, 31.6, 29.7. HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{31}H_{27}N_2O_3S$ 507.1737, found 507.1738.



4-butyl-6-methyl-6-(2-(phenylsulfonyl)ethyl)-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one (3u) : 24.9 mg, 53% yield, yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.51 (d, *J* = 8.8 Hz, 1H), 8.26 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.89 – 7.78 (m, 3H), 7.78 – 7.71 (m, 1H), 7.70 – 7.60 (m, 2H), 7.52 (d, *J* = 15.6 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 1H), 4.12 (ddt, *J* = 34.7, 14.4, 7.7 Hz, 2H), 3.23 – 3.08 (m, 1H), 3.08 – 2.96 (m, 1H), 2.86 (td, *J* = 12.6, 3.9 Hz, 1H), 2.64 (td, *J* = 12.5, 4.6 Hz, 1H), 1.69 (dq, *J* = 15.5, 7.6 Hz, 2H), 1.62 (s, 3H), 1.46 (h, *J* = 7.3 Hz, 2H), 1.01 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.2, 157.6, 138.8, 137.4, 135.2, 133.7, 133.6, 132.1, 129.9, 129.2, 129.2, 128.1, 127.0, 122.8, 122.5, 116.3, 112.1, 111.0, 52.46, 50.3, 42.4, 31.9, 29.4, 28.9, 20.3, 13.9. HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{28}H_{29}N_2O_3S$ 473.1893, found 473.1895.

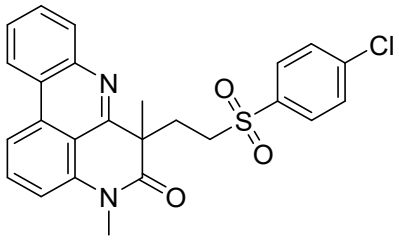


4,6-dimethyl-6-(2-tosylethyl)-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one (3w) : 17.4 mg, 39% yield, yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.52 (d, *J* = 9.7 Hz, 1H), 8.28 (d, *J* = 8.3 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.83 (t, *J* = 8.1 Hz, 1H), 7.78 – 7.72 (m, 1H), 7.72 – 7.61 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 1H), 3.55 (s, 3H), 3.21 – 3.05 (m, 1H), 3.03 – 2.91 (m, 1H), 2.85 (td, *J* = 12.6, 3.8 Hz, 1H), 2.63 (td, *J* = 12.5, 4.6 Hz, 1H), 2.45 (s, 3H), 1.64 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.6, 157.5, 144.7, 144.4, 138.4, 135.8, 133.4, 132.0, 130.0, 129.8, 129.2, 128.1, 127.0, 122.7, 122.5, 116.4, 111.8, 111.0, 52.5, 50.4, 32.3, 30.0, 29.3, 21.7. HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{26}H_{25}N_2O_3S$ 445.1580, found 445.1580.

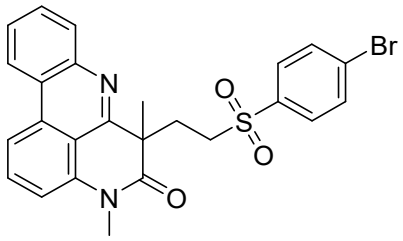


6-(2-((4-fluorophenyl)sulfonyl)ethyl)-4,6-dimethyl-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one (3x) : 23.7 mg, 53% yield, yellow solid; mp 192–197 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.53 (d, *J* = 7.6 Hz, 1H), 8.29 (d, *J* = 8.3 Hz, 1H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.92 – 7.80 (m, 3H), 7.80 – 7.72 (m, 1H), 7.69 (t, *J* = 7.2

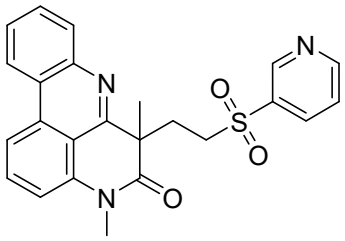
Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.17 (t, *J* = 8.4 Hz, 2H), 3.56 (s, 3H), 3.24 – 3.09 (m, 1H), 3.09 – 2.96 (m, 1H), 2.96 – 2.84 (m, 1H), 2.66 (td, *J* = 12.4, 4.6 Hz, 1H), 1.66 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.4, 165.8 (d, *J* = 255.7 Hz), 157.5, 138.5, 134.8 (d, *J* = 2.9 Hz), 133.5, 132.4, 131.0 (d, *J* = 9.7 Hz), 129.7, 129.5, 127.2, 122.8, 122.6, 116.6, 116.4 (d, *J* = 11.7 Hz), 111.8, 111.1, 52.6, 50.3, 32.0, 30.0, 29.6. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -103.80. HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{25}H_{22}FN_2O_3S$ 449.1330, found 449.1330.



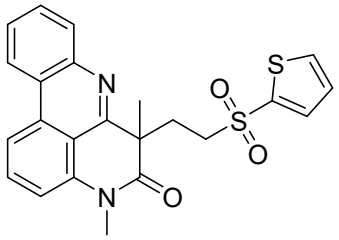
6-(2-((4-chlorophenyl)sulfonyl)ethyl)-4,6-dimethyl-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one (3y) : 34.8 mg, 75% yield, brown yellow solid; mp 191–194 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.52 (d, *J* = 8.3 Hz, 1H), 8.28 (d, *J* = 8.3 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.84 (t, *J* = 8.1 Hz, 1H), 7.79 – 7.71 (m, 3H), 7.67 (td, *J* = 7.6, 6.9, 1.4 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 1H), 3.56 (s, 3H), 3.23 – 3.10 (m, 1H), 3.04 – 2.92 (m, 1H), 2.87 (td, *J* = 12.6, 3.7 Hz, 1H), 2.65 (td, *J* = 12.5, 4.7 Hz, 1H), 1.63 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.5, 157.3, 144.6, 140.3, 138.3, 137.2, 133.4, 132.1, 129.9, 129.6, 129.5, 129.4, 127.1, 122.7, 116.5, 111.8, 111.1, 52.5, 50.4, 31.7, 30.0, 29.7. HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{25}H_{22}ClN_2O_3S$ 465.1034, found 465.1038.



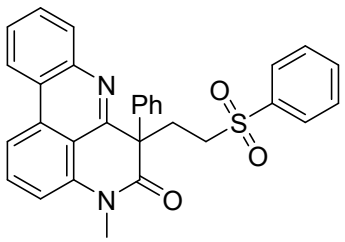
6-(2-((4-bromophenyl)sulfonyl)ethyl)-4,6-dimethyl-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one (3z) : 36 mg, 71% yield, yellow solid; mp 175–177 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.52 (d, *J* = 8.3 Hz, 1H), 8.28 (d, *J* = 8.3 Hz, 1H), 7.89 (d, *J* = 6.8 Hz, 1H), 7.84 (t, *J* = 8.1 Hz, 1H), 7.78 (t, *J* = 7.6 Hz, 1H), 7.66 (p, *J* = 8.4 Hz, 5H), 7.22 (d, *J* = 7.9 Hz, 1H), 3.56 (s, 3H), 3.23 – 3.10 (m, 1H), 3.04 – 2.92 (m, 1H), 2.86 (td, *J* = 12.6, 3.7 Hz, 1H), 2.72 – 2.59 (m, 1H), 1.63 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.5, 157.3, 144.6, 138.4, 137.7, 133.4, 132.5, 132.1, 129.9, 129.7, 129.4, 128.9, 127.1, 122.7, 122.6, 116.5, 111.8, 111.1, 52.4, 50.4, 31.7, 30.0, 29.7. HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{25}H_{22}BrN_2O_3S$ 509.0529, found 509.0529.



4,6-dimethyl-6-(2-(pyridin-3-ylsulfonyl)ethyl)-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one (3aa) : 29 mg, 69% yield, white solid; mp 161–165 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.08 (s, 1H), 8.90 (d, *J* = 6.6 Hz, 1H), 8.52 (d, *J* = 8.2 Hz, 1H), 8.29 (d, *J* = 8.3 Hz, 1H), 8.14 (d, *J* = 8.1 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.85 (t, *J* = 8.1 Hz, 1H), 7.76 (t, *J* = 6.9 Hz, 1H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.49 (dd, *J* = 8.0, 4.8 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 3.56 (s, 3H), 3.28 – 3.16 (m, 1H), 3.16 – 3.04 (m, 1H), 2.93 (td, *J* = 12.5, 3.9 Hz, 1H), 2.71 (td, *J* = 12.4, 4.7 Hz, 1H), 1.61 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.4, 157.3, 154.1, 149.2, 144.7, 138.3, 136.0, 135.3, 133.5, 132.2, 129.9, 129.4, 127.2, 123.8, 122.8, 122.6, 116.5, 111.8, 111.1, 52.9, 50.5, 31.1, 30.2, 30.0. HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{24}H_{22}N_3O_3S$ 432.1376, found 432.1378.

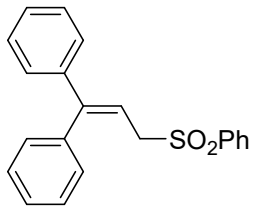


4,6-dimethyl-6-(2-(thiophen-2-ylsulfonyl)ethyl)-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one (3ab) : 26.5 mg, 62% yield, white solid; mp 177–179 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.53 (d, *J* = 8.2 Hz, 1H), 8.29 (d, *J* = 8.3 Hz, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.85 (t, *J* = 8.1 Hz, 1H), 7.80 – 7.72 (m, 1H), 7.71 – 7.63 (m, 3H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.19 – 7.13 (m, 1H), 3.56 (s, 3H), 3.31 – 3.17 (m, 1H), 3.16 – 3.05 (m, 1H), 2.98 (td, *J* = 12.5, 3.8 Hz, 1H), 2.74 (td, *J* = 12.4, 4.7 Hz, 1H), 1.67 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.5, 157.5, 139.8, 138.5, 134.3, 133.9, 133.5, 132.2, 129.8, 129.4, 127.8, 127.2, 122.8, 122.6, 116.5, 111.8, 111.1, 54.0, 50.3, 32.3, 30.0, 29.6. HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{23}H_{21}N_2O_3S_2$ 437.0988, found 437.0988.



4-methyl-6-phenyl-6-(2-(thiophen-2-ylsulfonyl)ethyl)-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one (3ac) : 16 mg, 33% yield, yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.54 (d, *J* = 8.1 Hz, 1H), 8.27 (d, *J* = 8.3 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.93 (d, *J* = 7.4 Hz, 2H), 7.79 (q, *J* = 8.1 Hz, 2H), 7.69 (q, *J* = 6.9 Hz, 2H),

7.58 (t, *J* = 7.7 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 1H), 7.12 – 7.06 (m, 3H), 7.00 – 6.89 (m, 2H), 3.56 (s, 3H), 3.41 – 3.28 (m, 3H), 3.18 – 3.09 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.4, 155.4, 142.0, 139.1, 138.3, 133.5, 133.3, 132.1, 130.4, 129.4, 129.2, 128.7, 128.3, 127.6, 127.4, 126.4, 122.9, 122.6, 116.5, 113.0, 111.2, 58.8, 53.2, 30.6, 30.4. HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{30}H_{25}N_2O_3S$ 493.1580, found 493.1583.



(3-(phenylsulfonyl)prop-1-ene-1,1-diyl)dibenzene (5) : 25.8 mg, 77% yield, colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.74 (m, 2H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.27 (t, *J* = 3.6 Hz, 3H), 7.25 – 7.19 (m, 3H), 7.16 (d, *J* = 2.5 Hz, 1H), 7.15 – 7.13 (m, 1H), 6.71 – 6.61 (m, 2H), 6.13 (t, *J* = 7.9 Hz, 1H), 3.92 (d, *J* = 7.9 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.8, 140.8, 138.6, 137.8, 133.7, 129.2, 129.1, 128.5, 128.4, 128.3, 128.3, 127.8, 127.4, 114.0, 57.5. HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{21}H_{19}O_2S$ 335.1100, found 335.1103.

8. References

[1] Chen, M.; Chen, J.-Q.; Chen, Z.; Wu, J., Synthesis of ester-containing phenanthridinesviaphotoredox-catalyzed radical cascade cyclization of N-arylacrylamides with alkyloxalyl chlorides. *Org. Chem. Front* **2023,** *10*, 3995.

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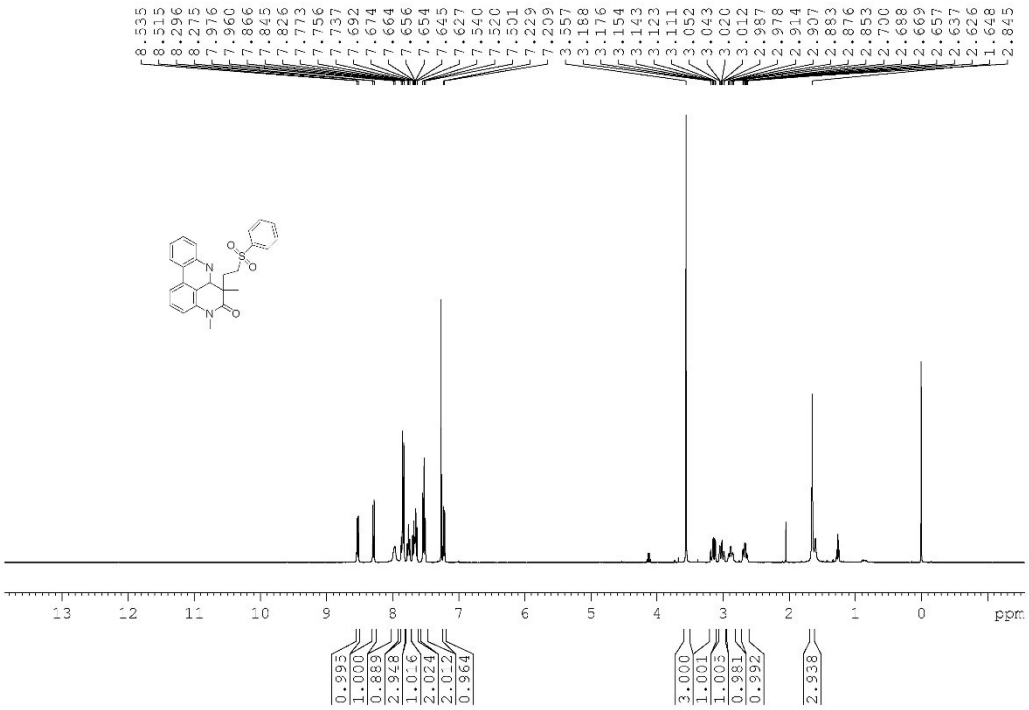
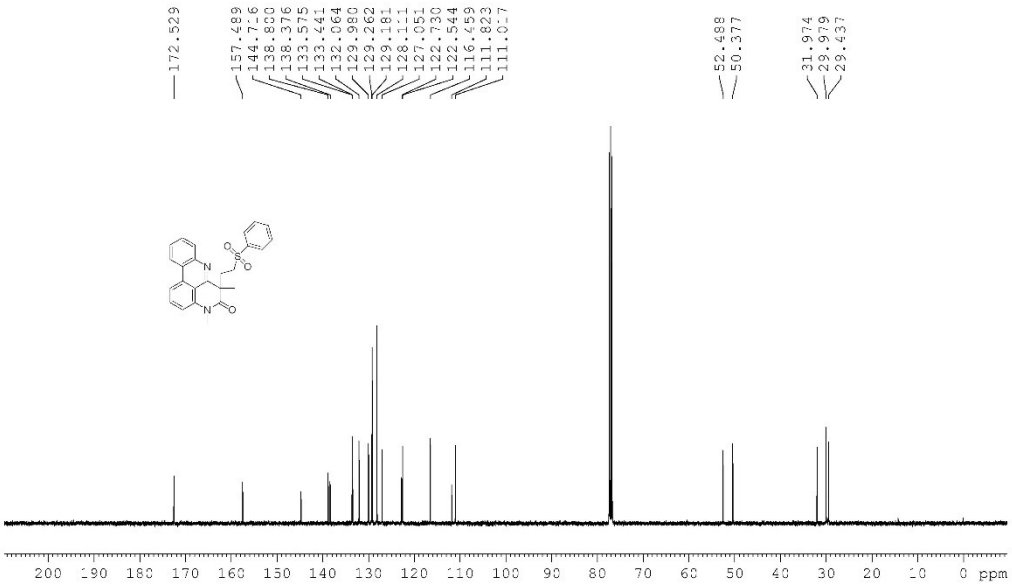
[6] Frederick, G.-B.; Anthony, H.-C.; Donald, E.-Smith.; John, B., Reactions of Carbanions with Electron Acceptors. *J. Org. Chem.* **1985**, *50*, 1151.

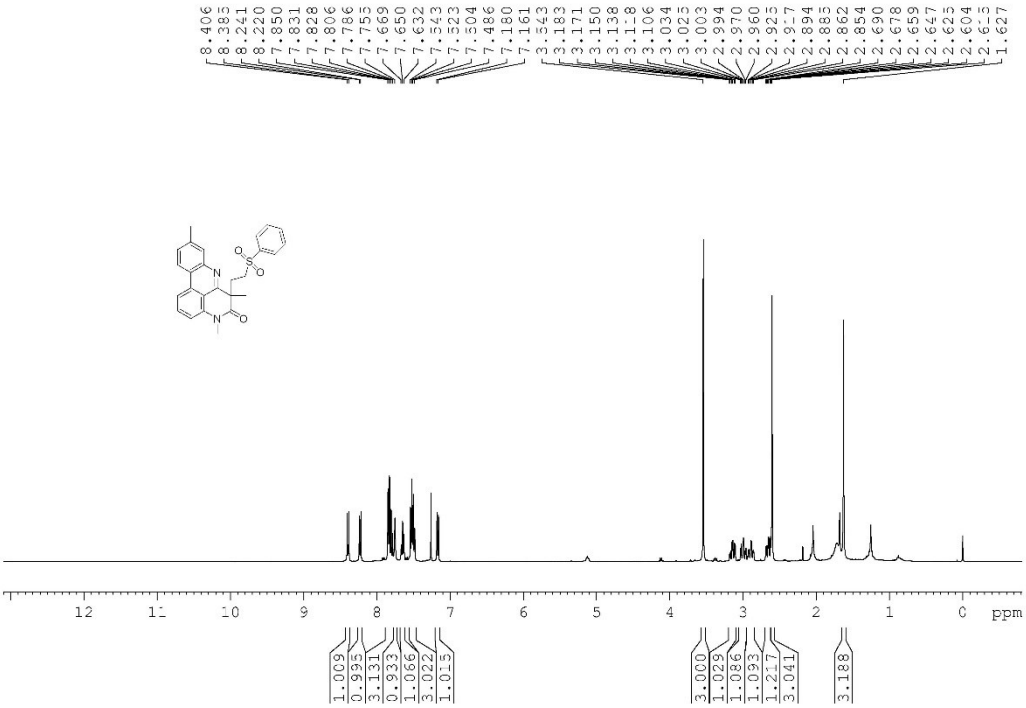
9. Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra



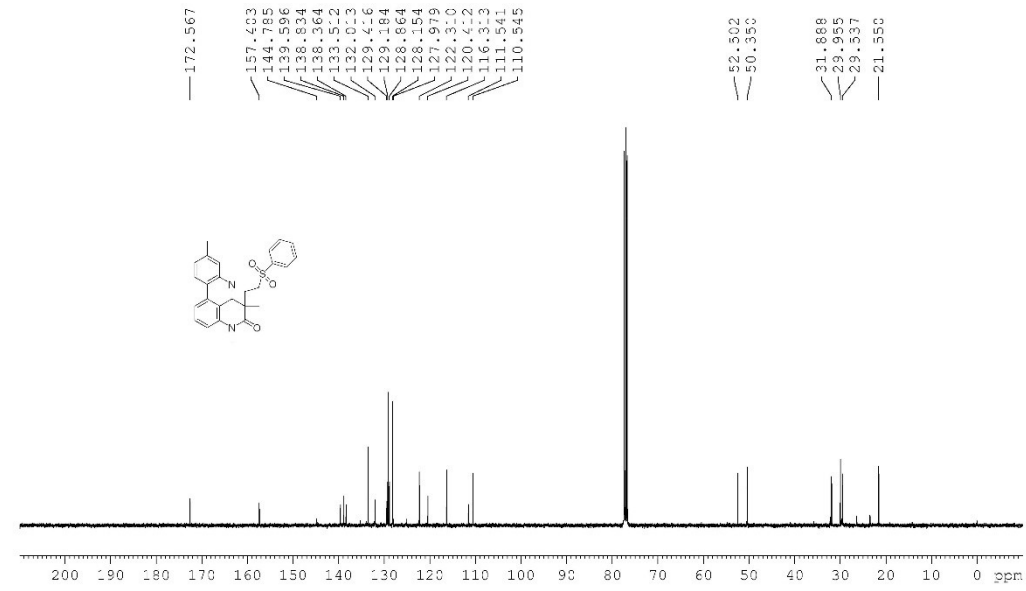
^{1}H NMR spectrum of compound **3a**



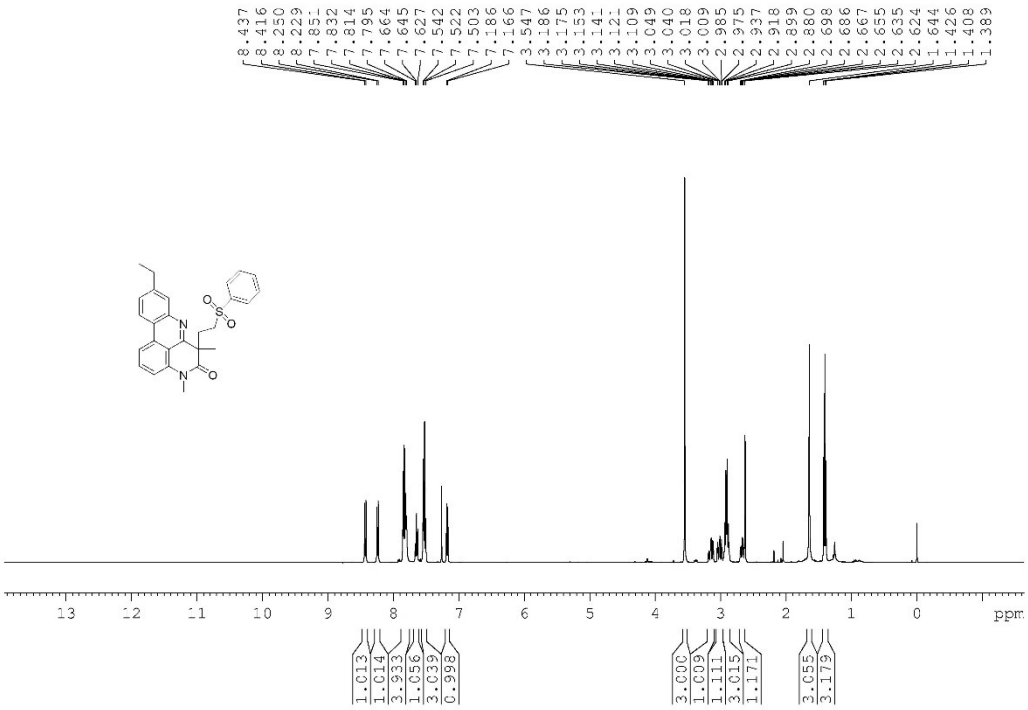
^{13}C NMR spectrum of compound **3a**



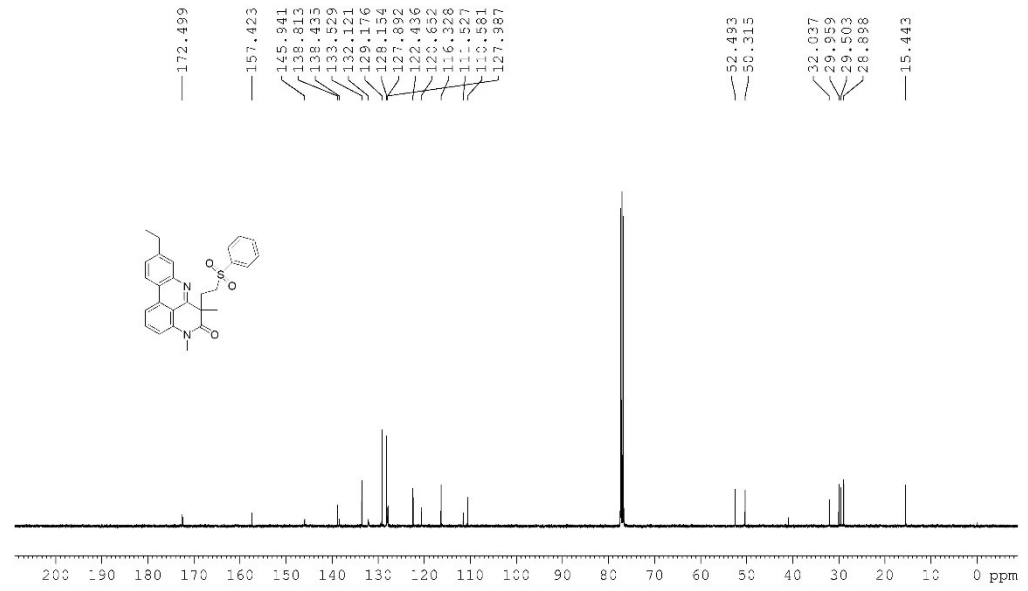
^{1}H NMR spectrum of compound **3b**



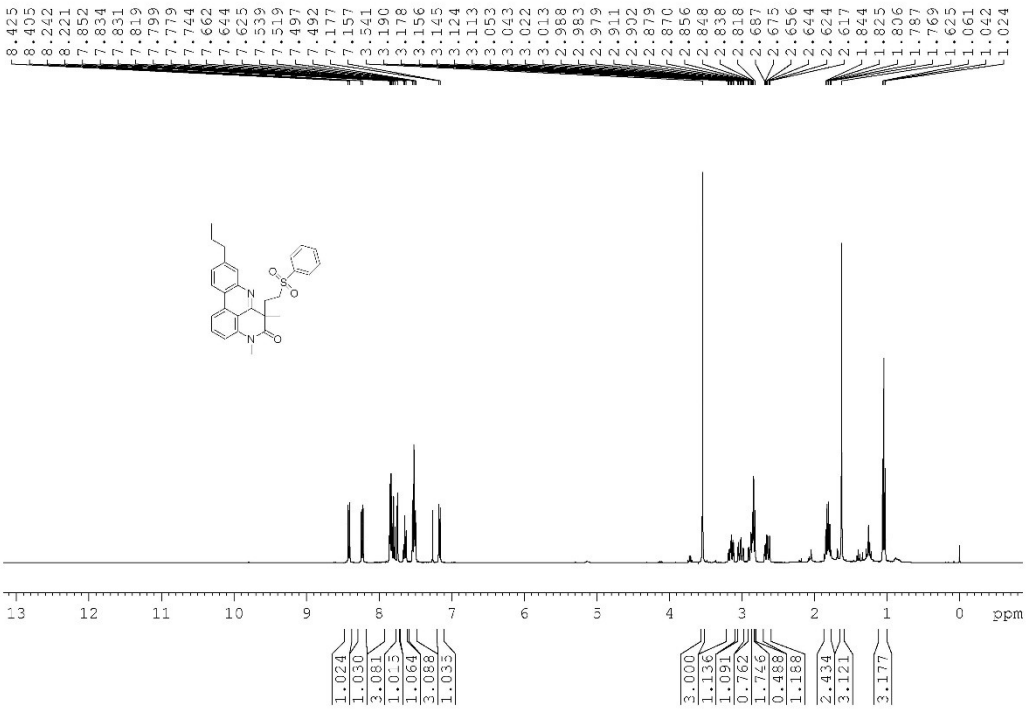
^{13}C NMR spectrum of compound **3b**



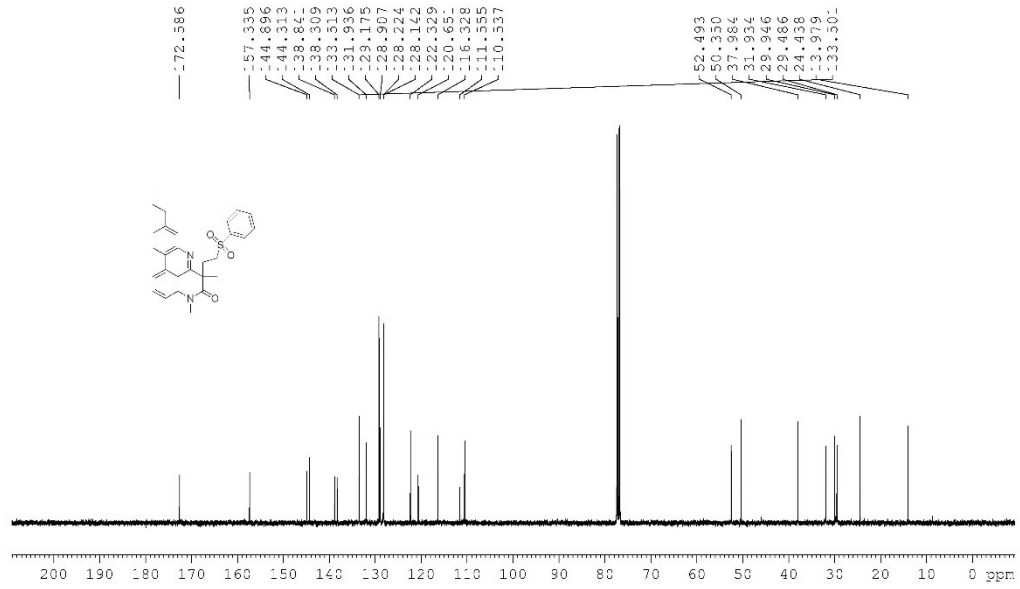
^{1}H NMR spectrum of compound **3c**



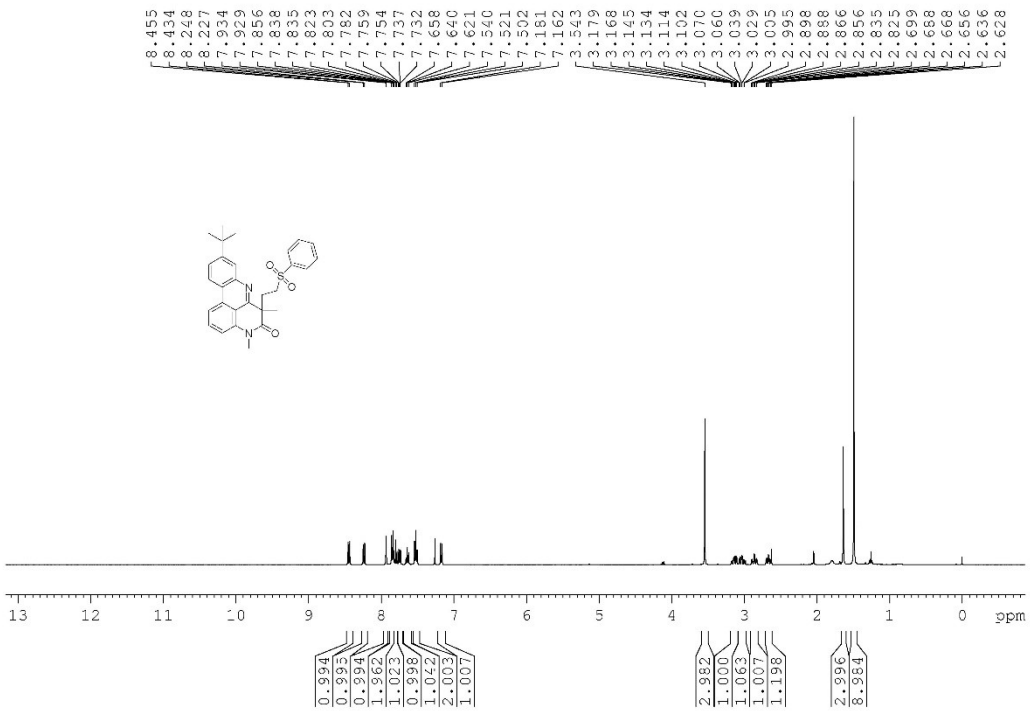
^{13}C NMR spectrum of compound **3c**



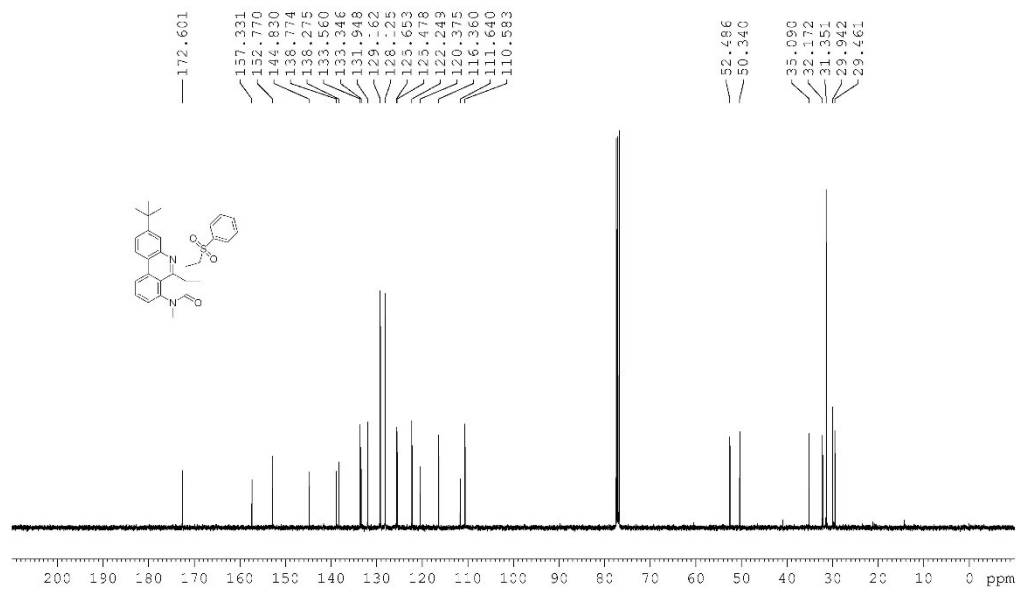
^{1}H NMR spectrum of compound **3d**



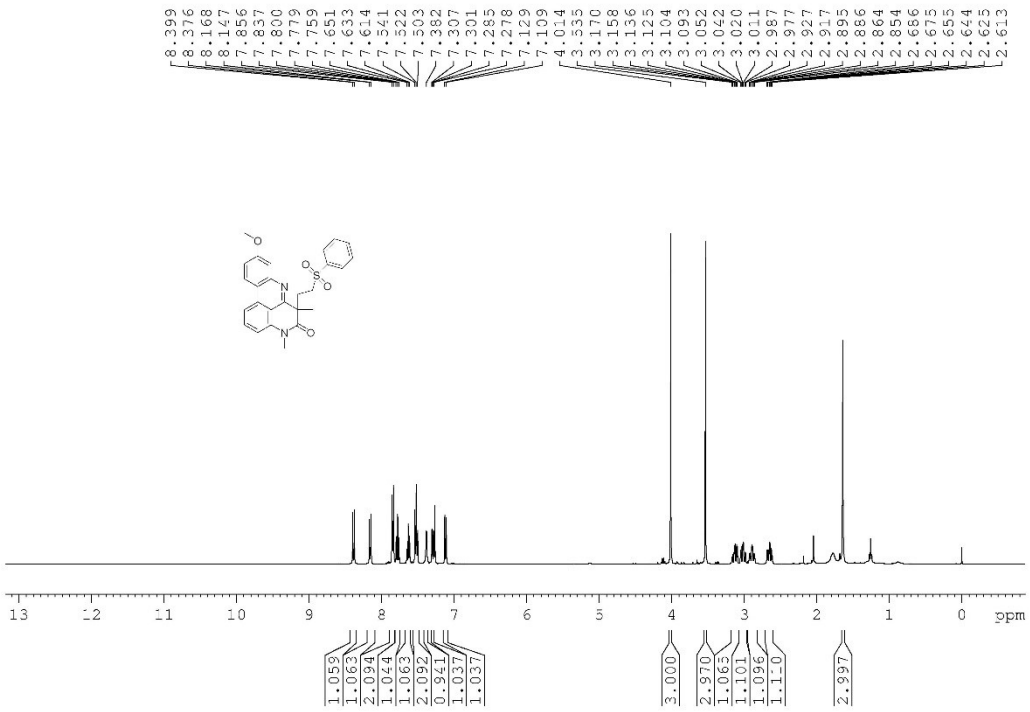
^{13}C NMR spectrum of compound **3d**



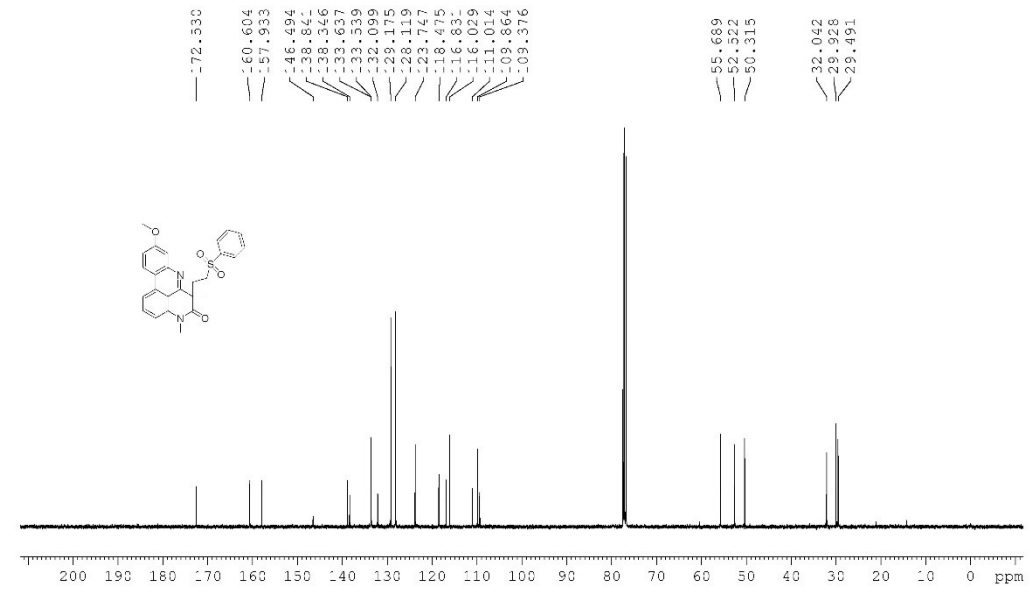
^{1}H NMR spectrum of compound **3e**



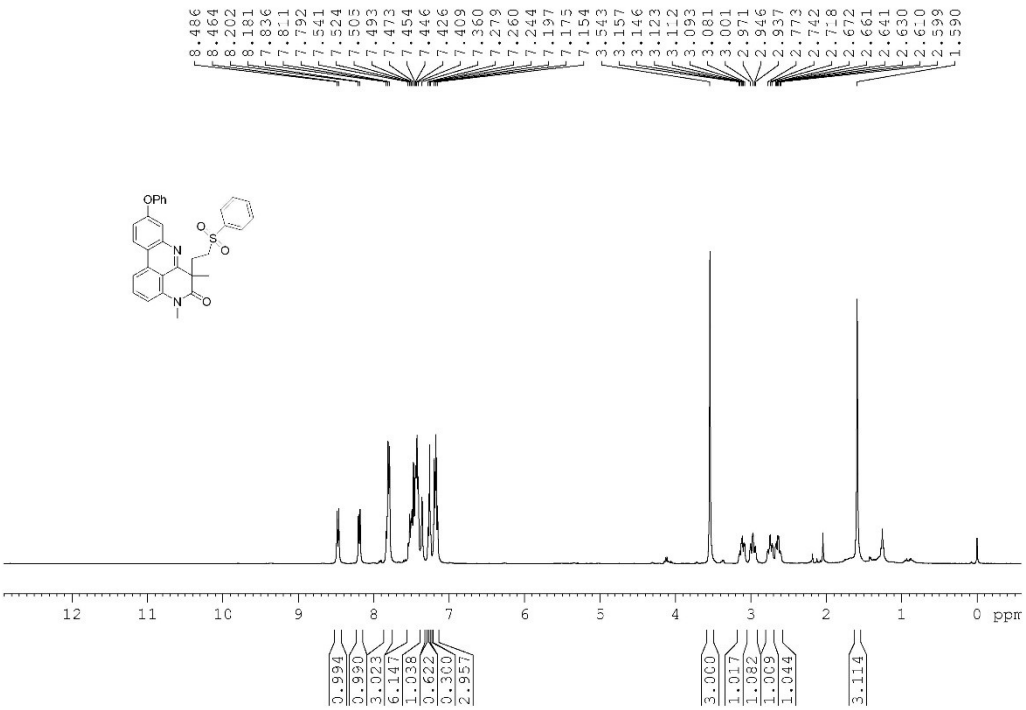
^{13}C NMR spectrum of compound **3e**



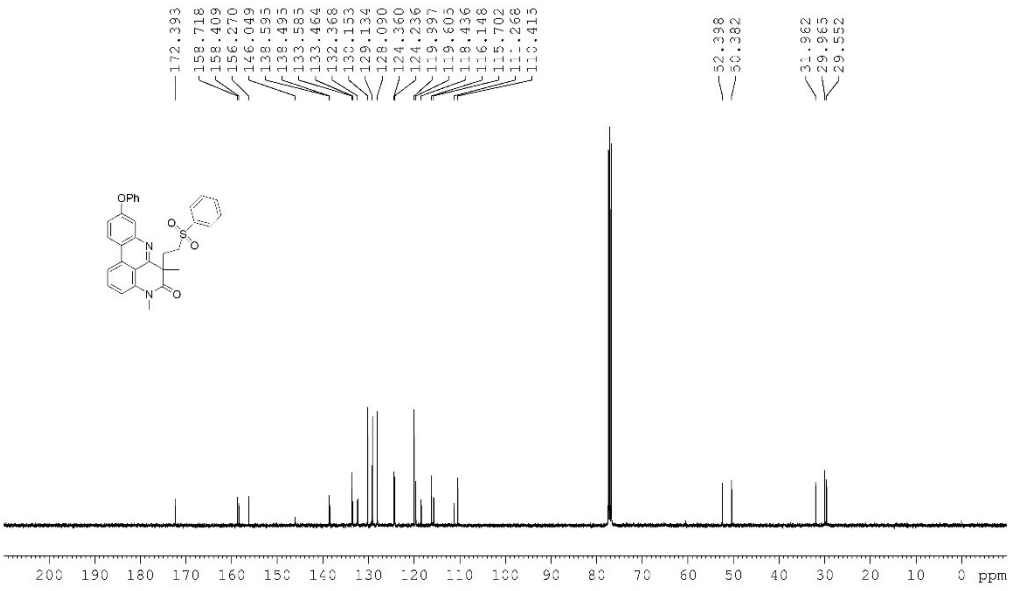
^{1}H NMR spectrum of compound **3f**



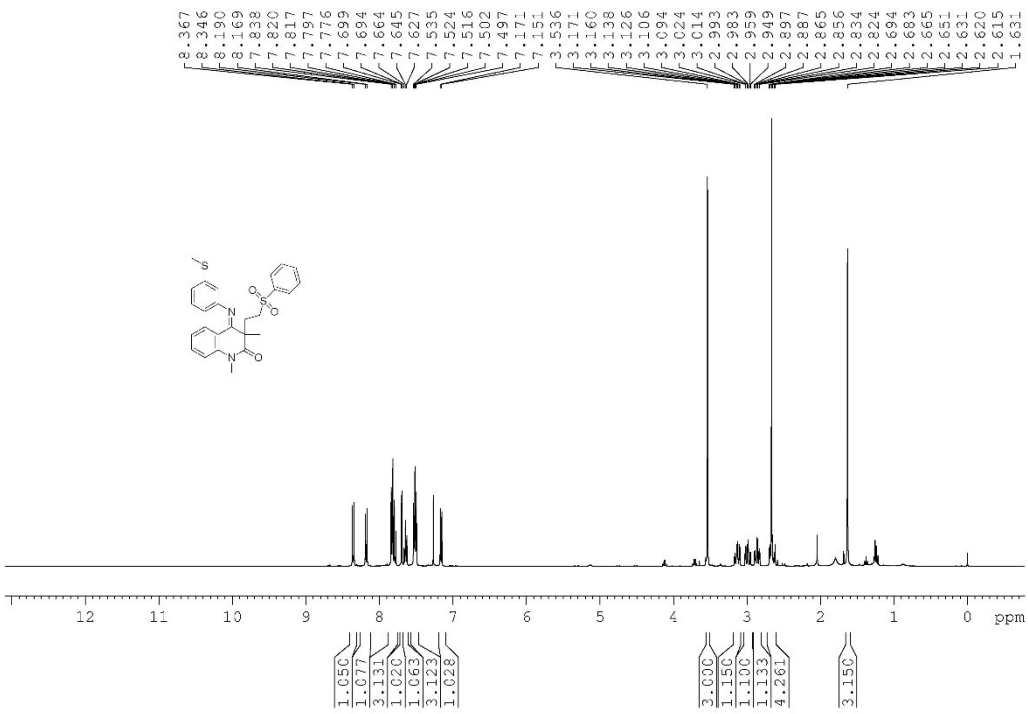
^{13}C NMR spectrum of compound **3f**



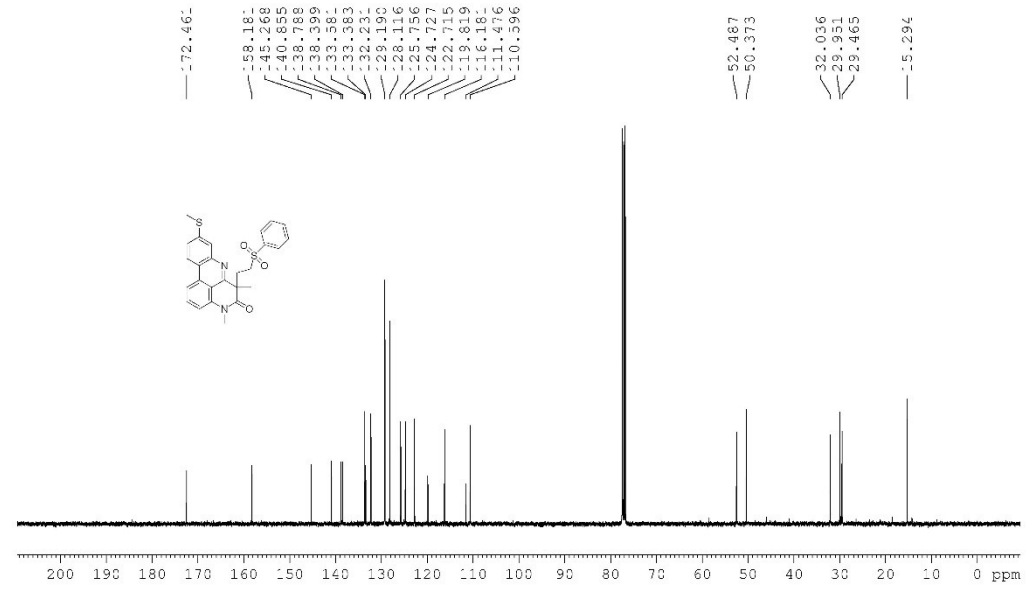
^{1}H NMR spectrum of compound **3g**



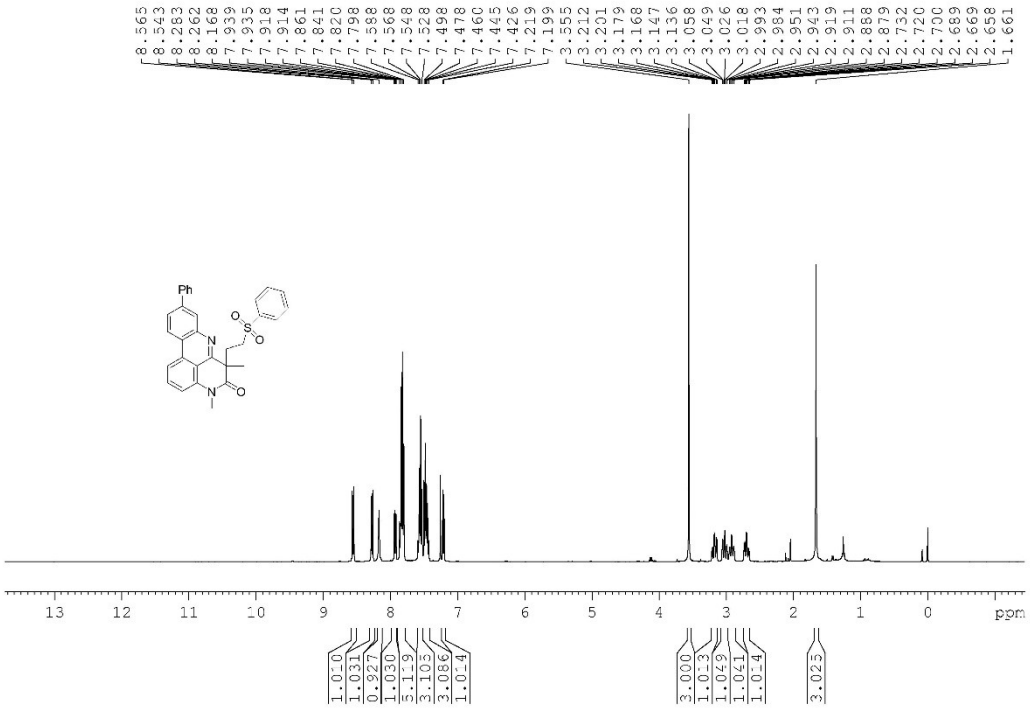
^{13}C NMR spectrum of compound **3g**



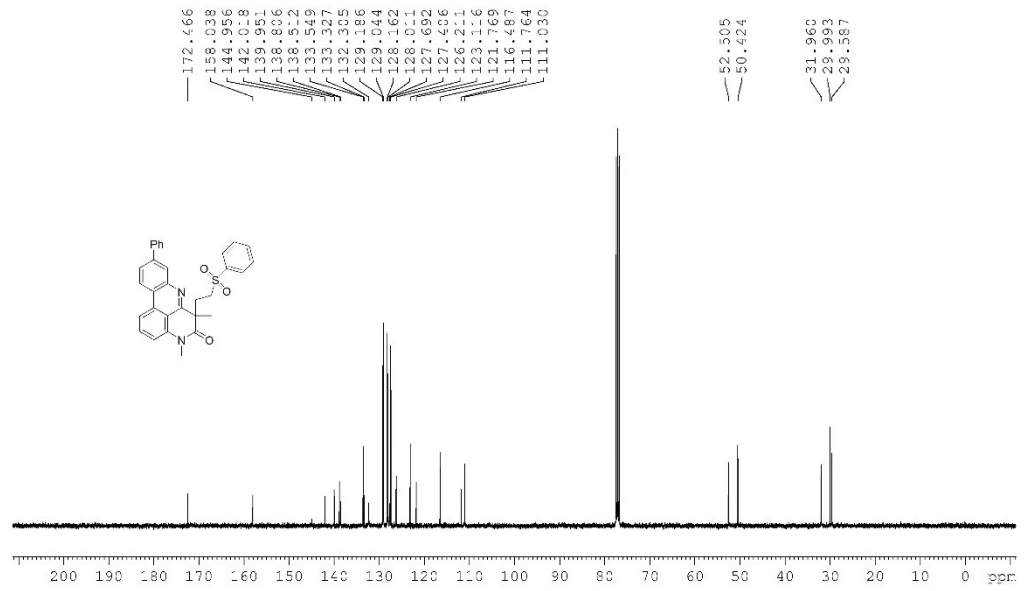
^{1}H NMR spectrum of compound **3h**



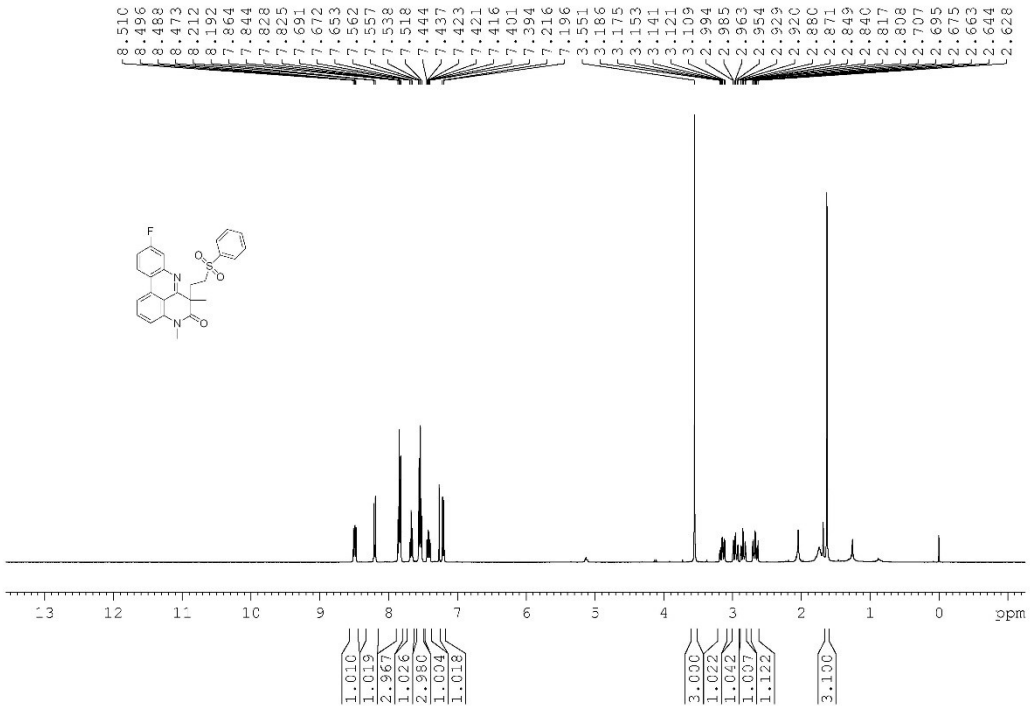
^{13}C NMR spectrum of compound **3h**



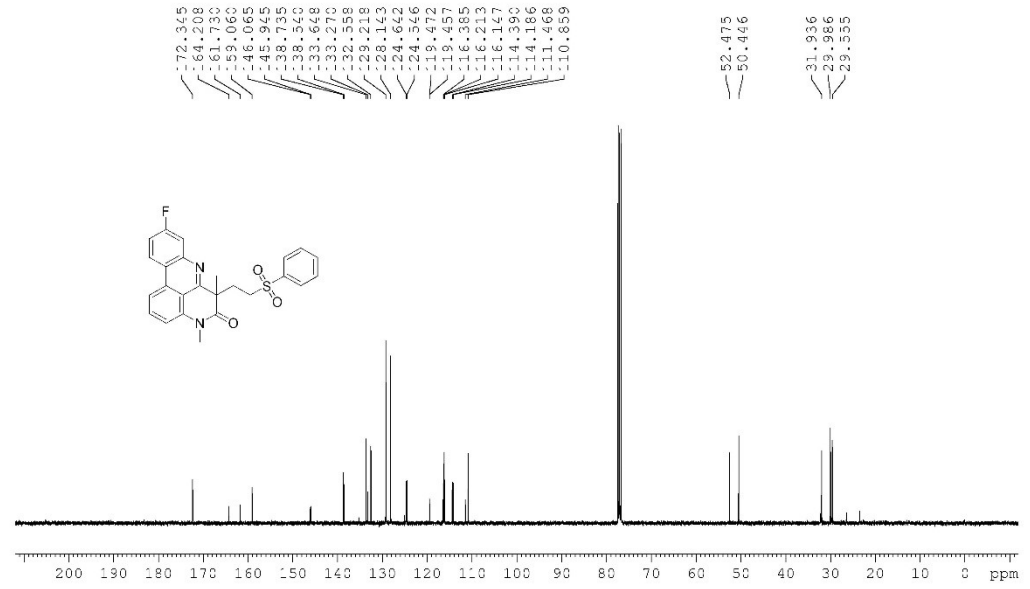
^{1}H NMR spectrum of compound **3i**



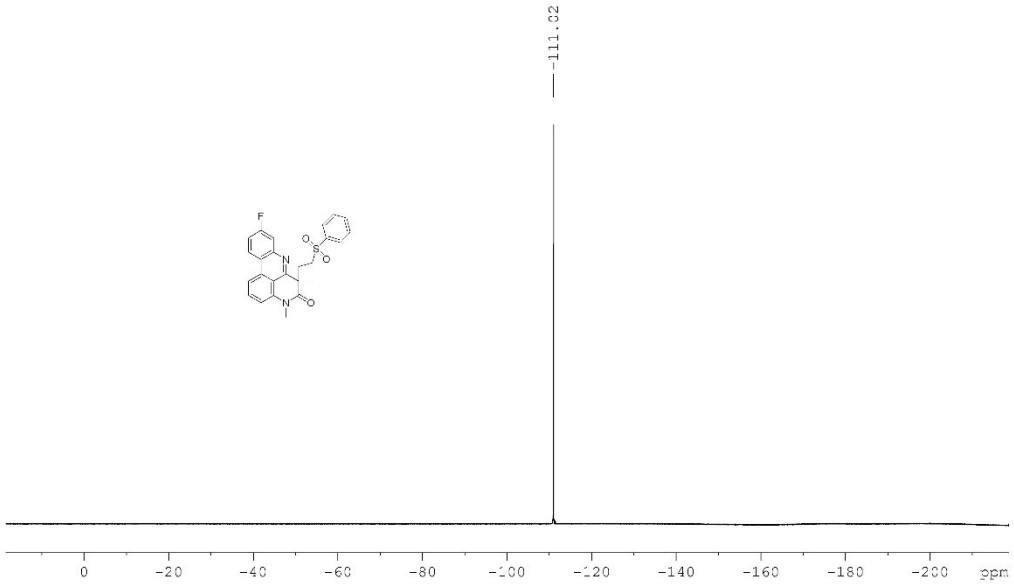
^{13}C NMR spectrum of compound **3i**



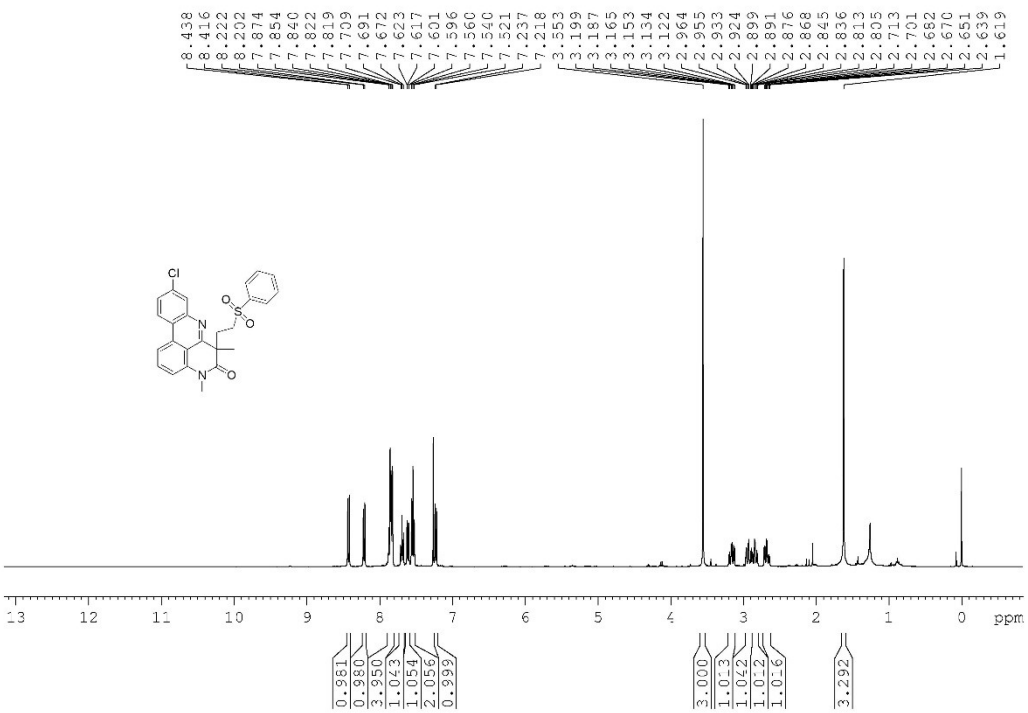
^{1}H NMR spectrum of compound **3j**



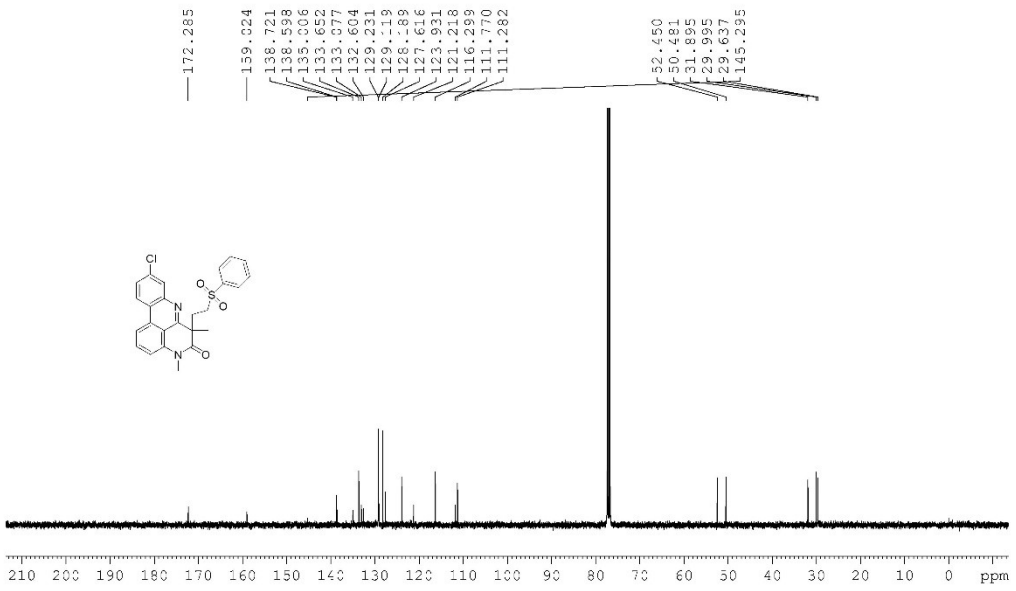
^{13}C NMR spectrum of compound **3j**



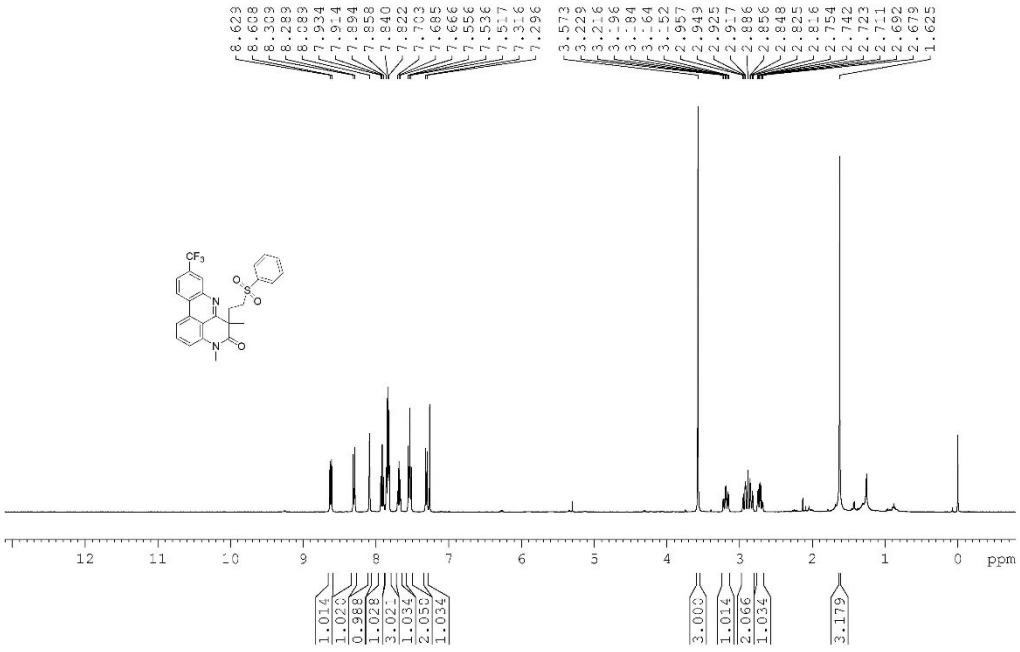
^{19}F NMR spectrum of compound **3j**



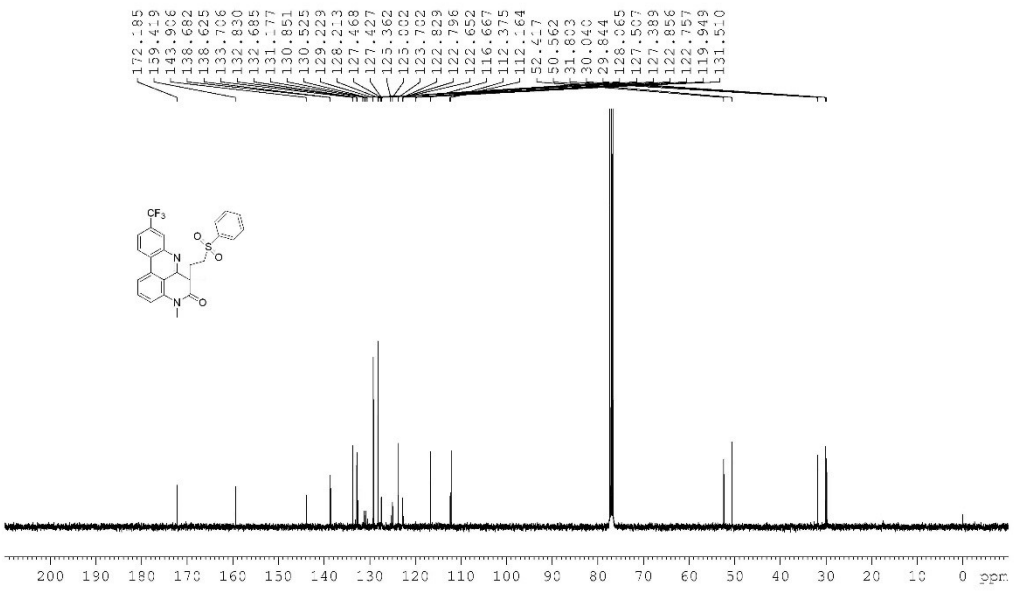
^{1}H NMR spectrum of compound **3k**



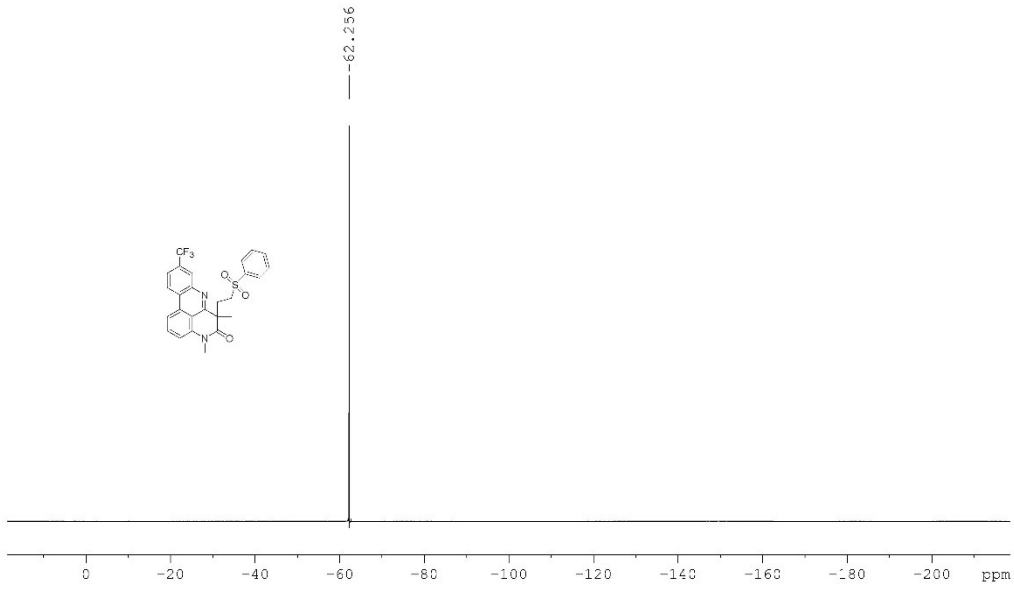
^{13}C NMR spectrum of compound **3k**



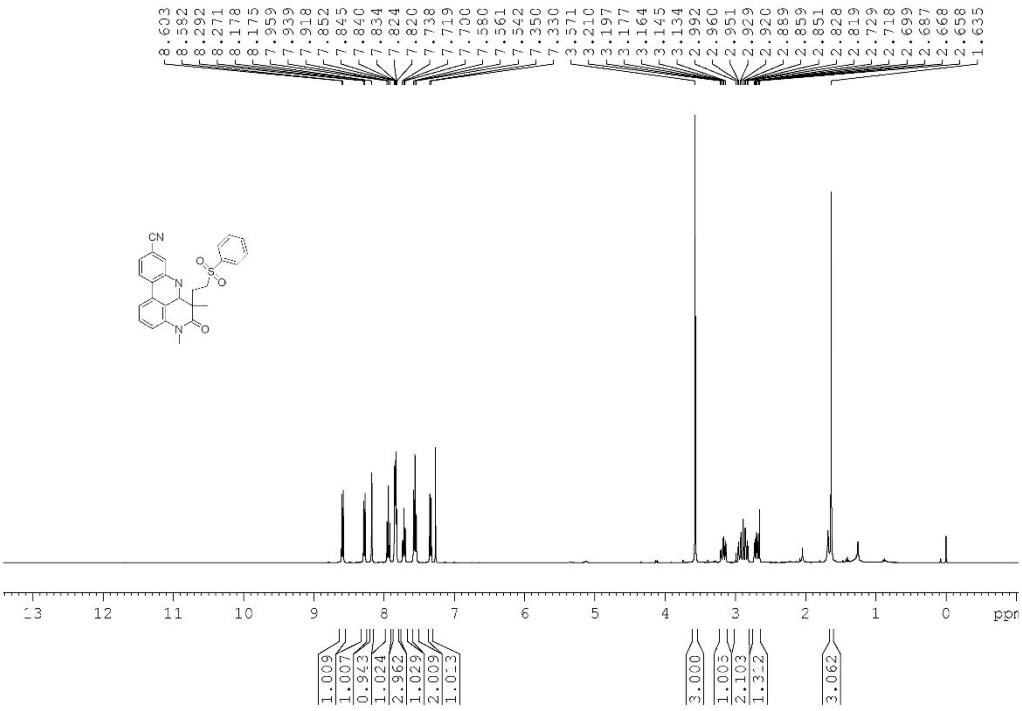
^{1}H NMR spectrum of compound **3l**



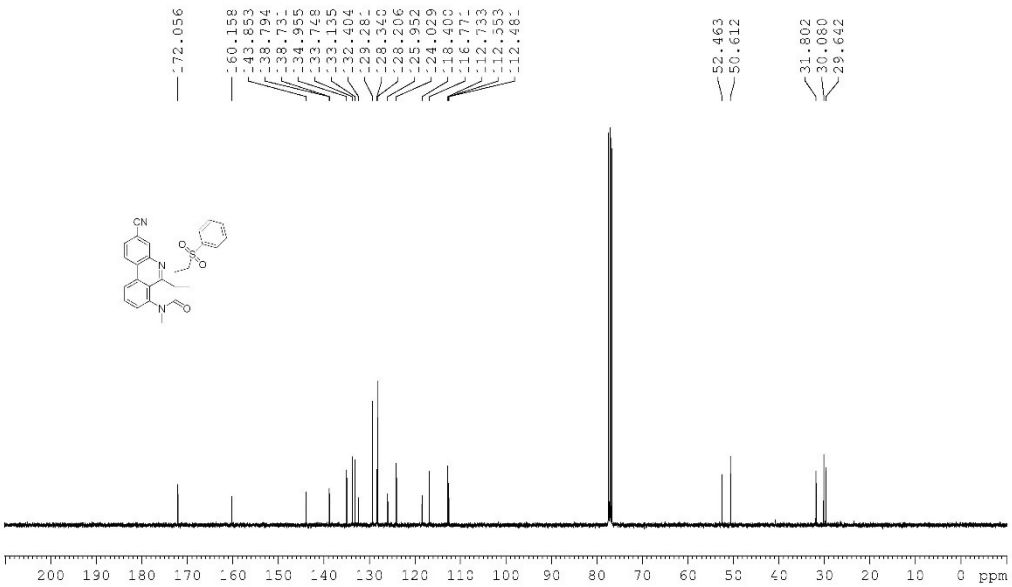
^{13}C NMR spectrum of compound **3l**



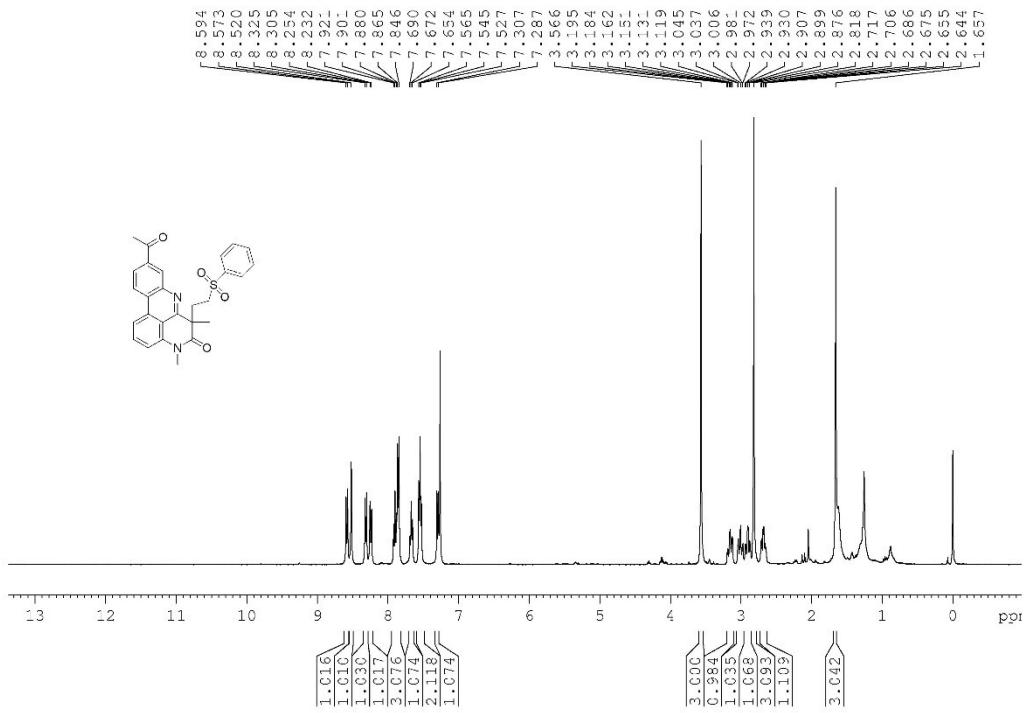
^{19}F NMR spectrum of compound **3l**



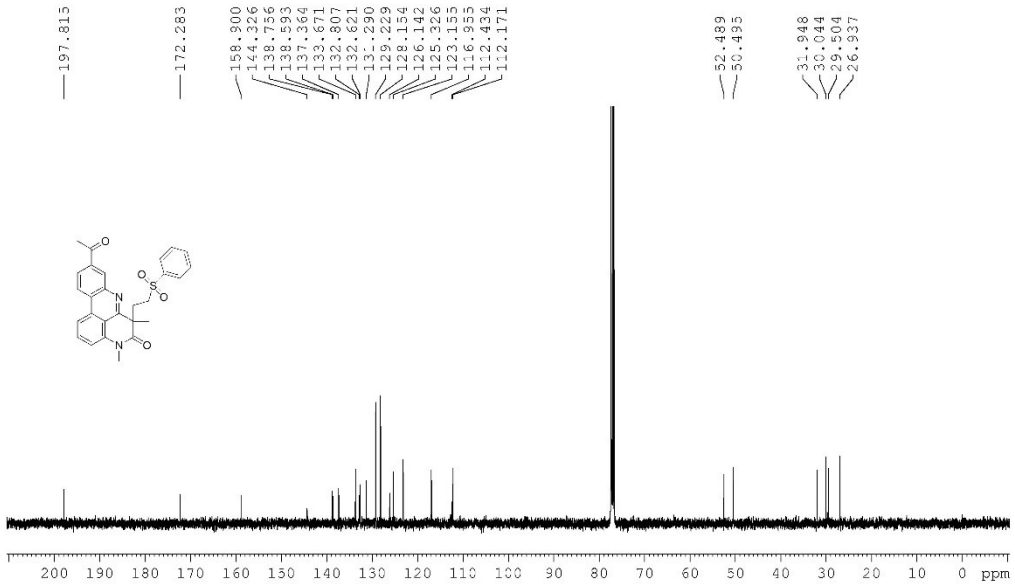
^{1}H NMR spectrum of compound **3m**



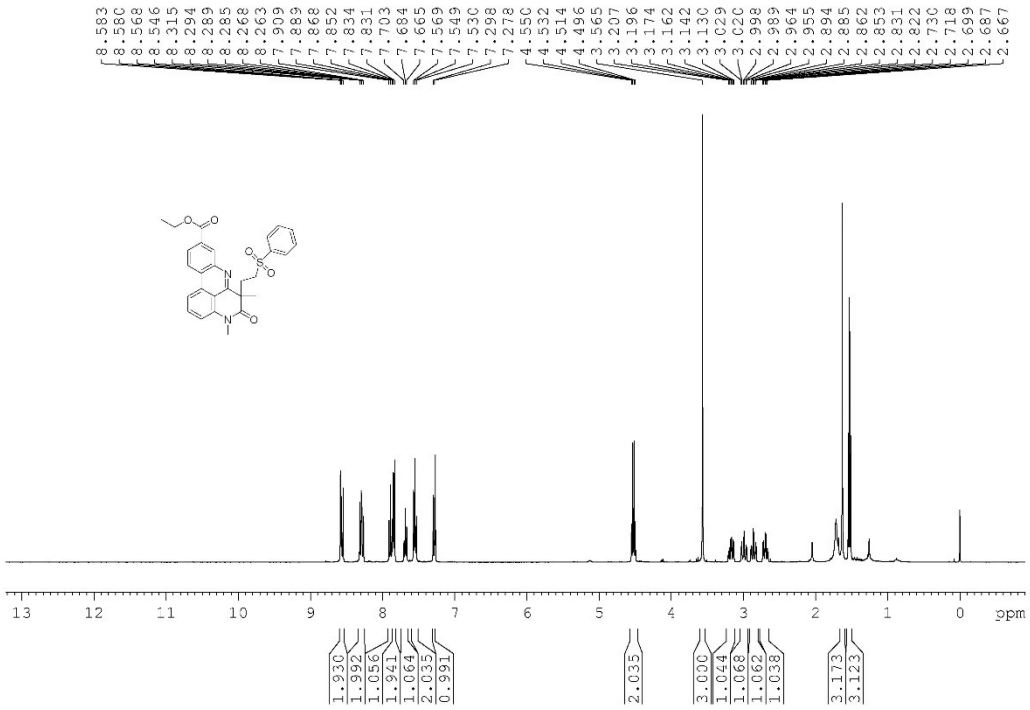
^{13}C NMR spectrum of compound **3m**



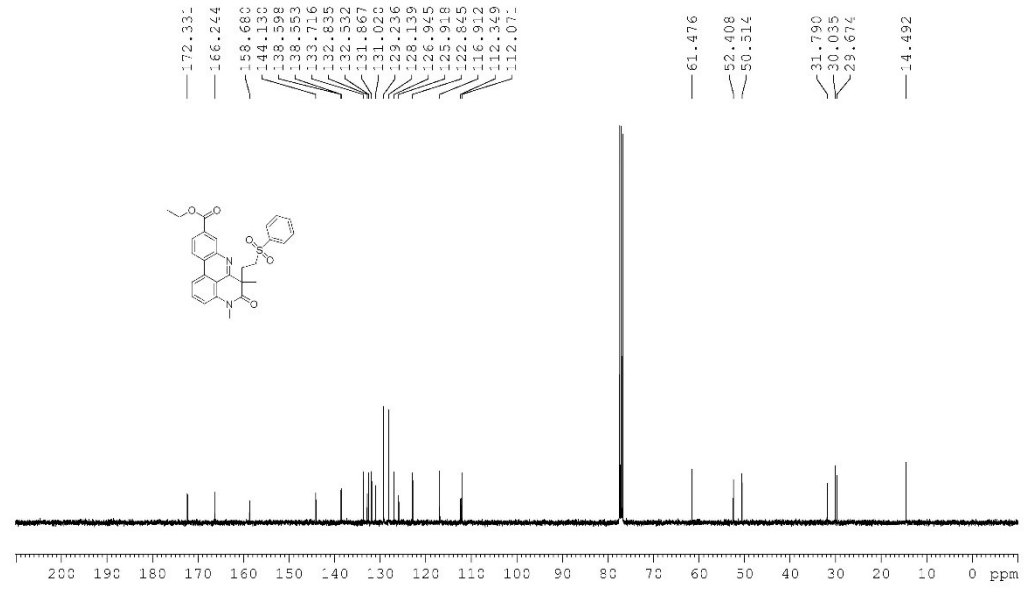
^{1}H NMR spectrum of compound **3n**



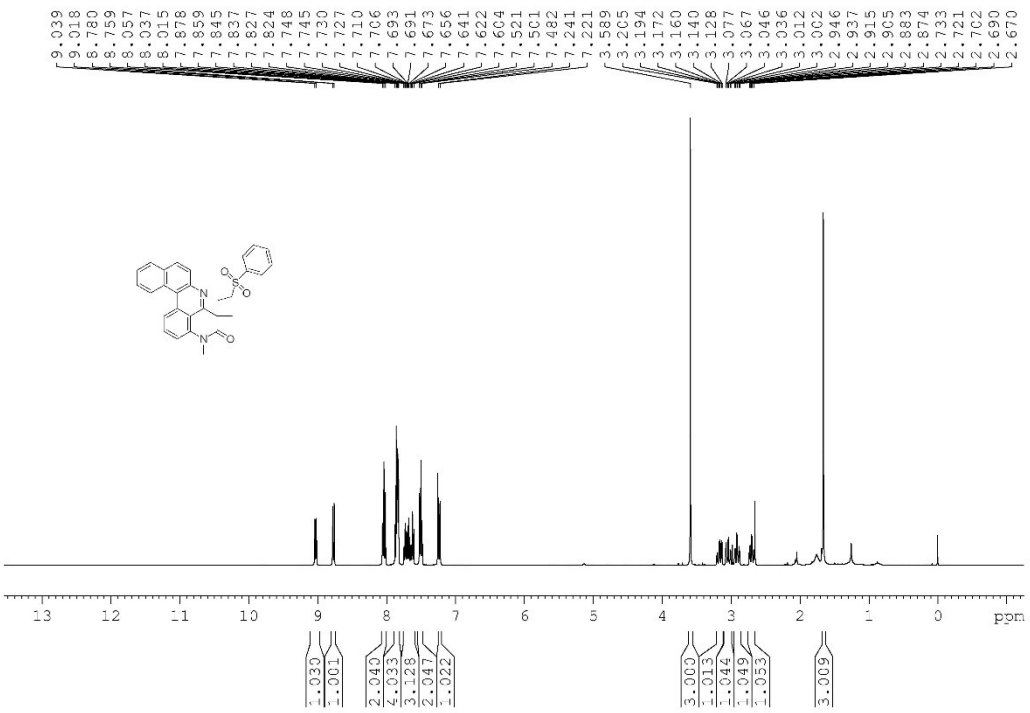
^{13}C NMR spectrum of compound **3n**



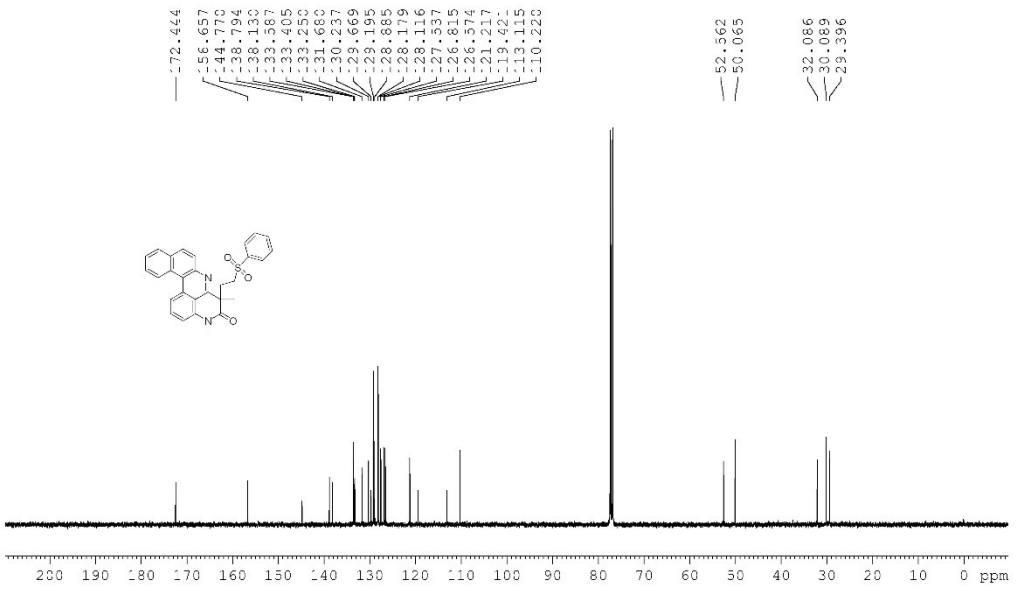
^{1}H NMR spectrum of compound **3o**



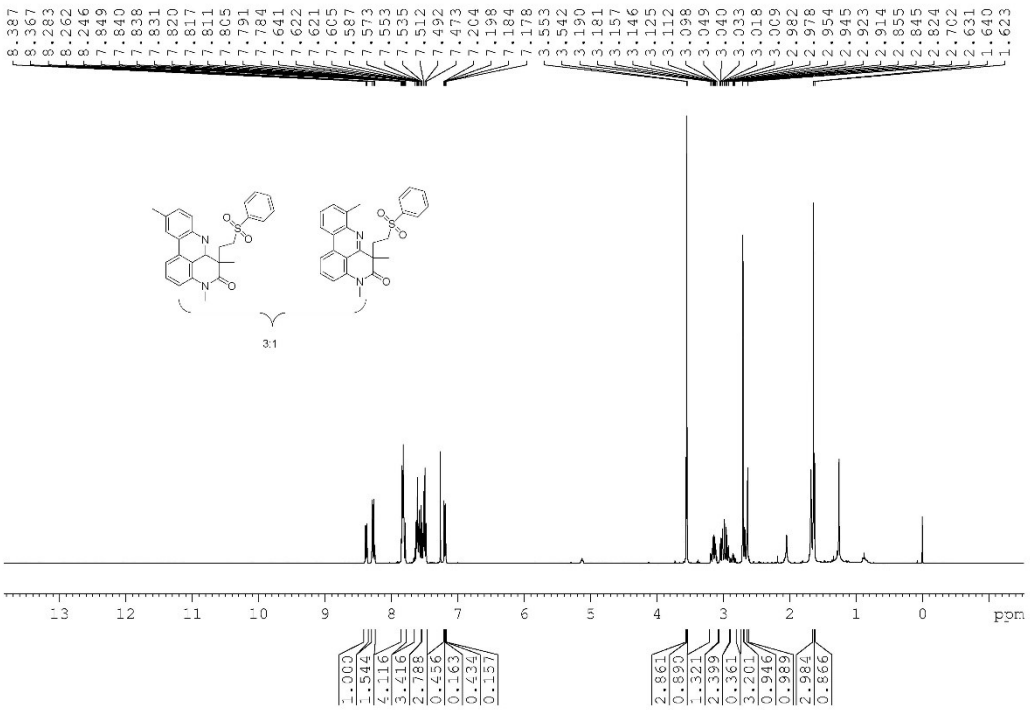
^{13}C NMR spectrum of compound **3o**



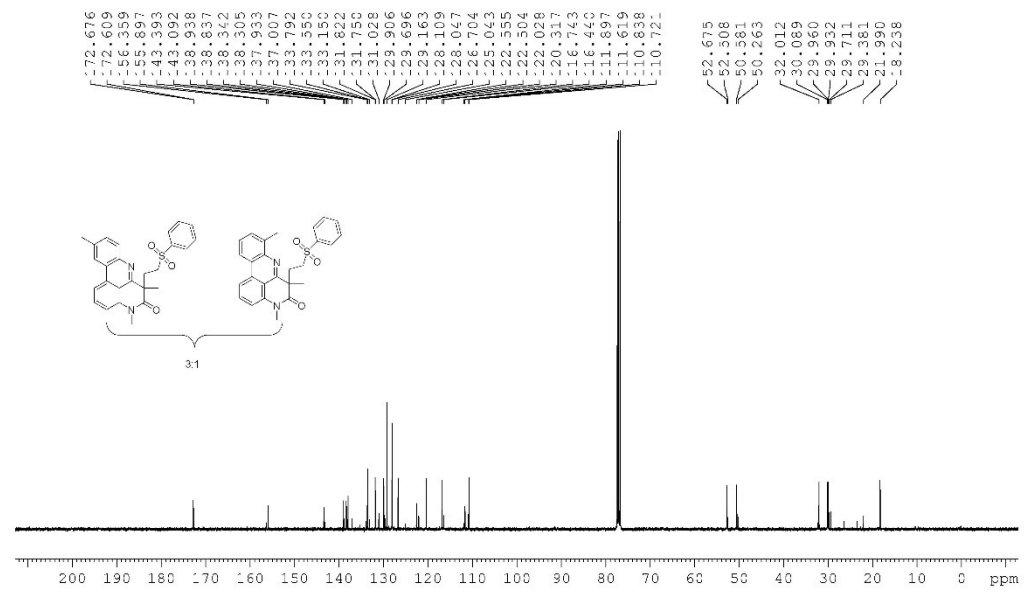
^{1}H NMR spectrum of compound **3p**



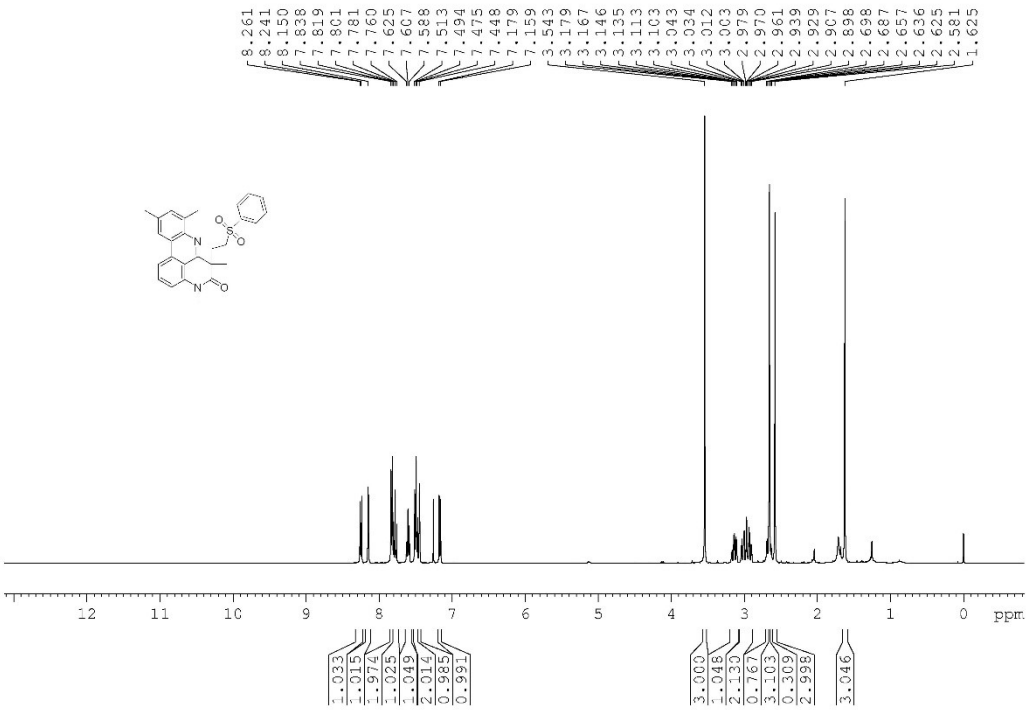
^{13}C NMR spectrum of compound **3p**



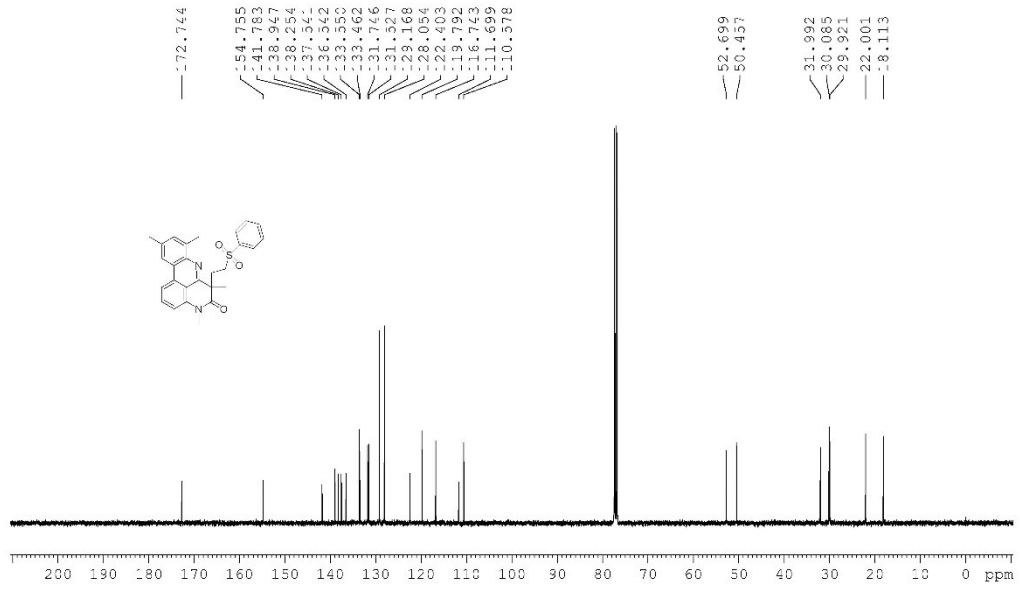
^{1}H NMR spectrum of compound **3q and 3q'**



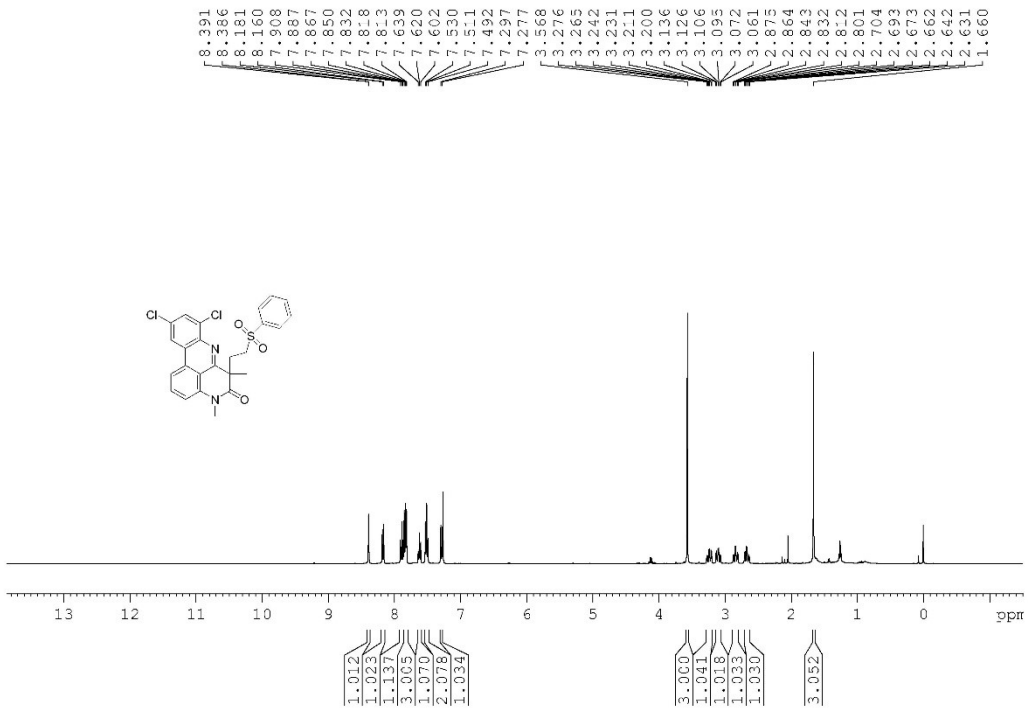
^{13}C NMR spectrum of compound **3q and 3q'**



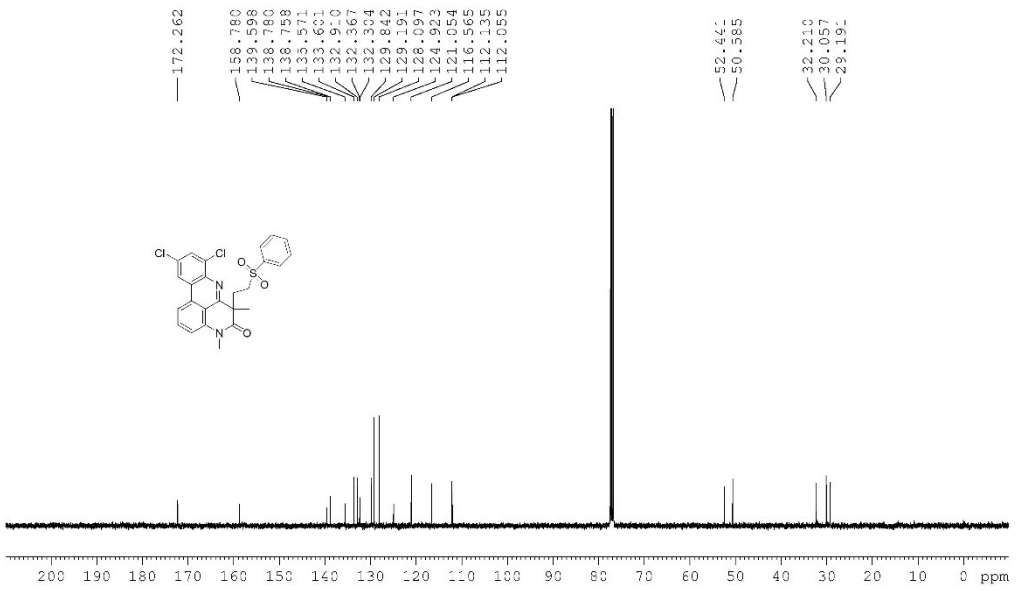
^{1}H NMR spectrum of compound **3r**



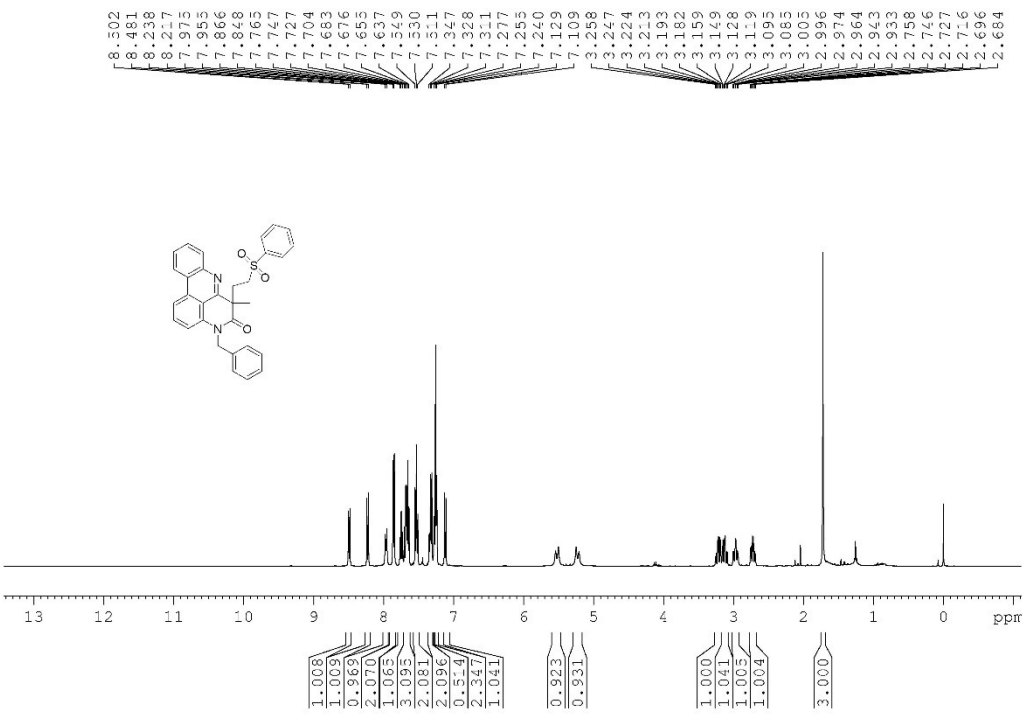
^{13}C NMR spectrum of compound **3r**



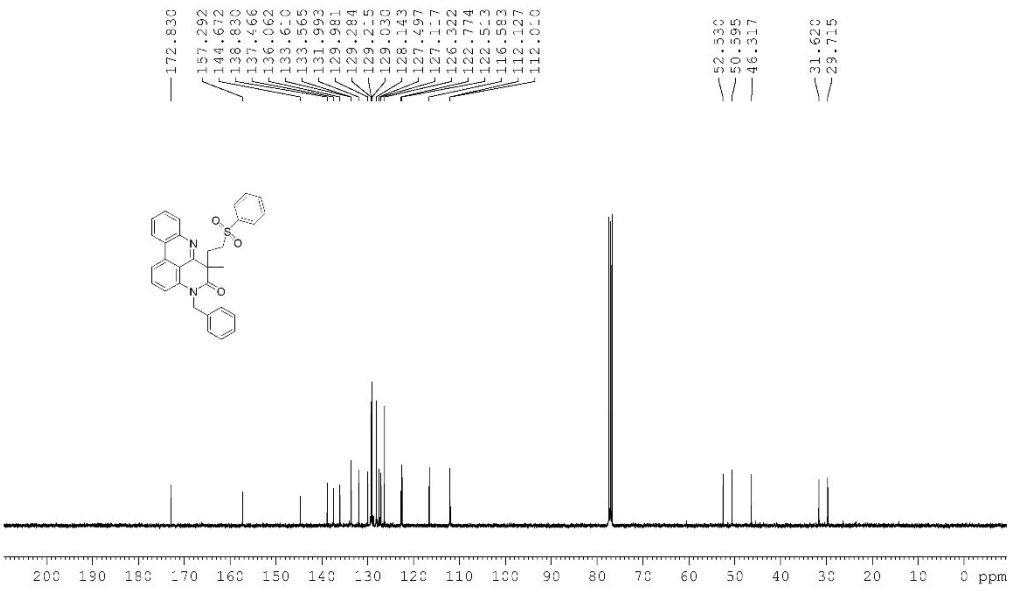
^{1}H NMR spectrum of compound **3s**



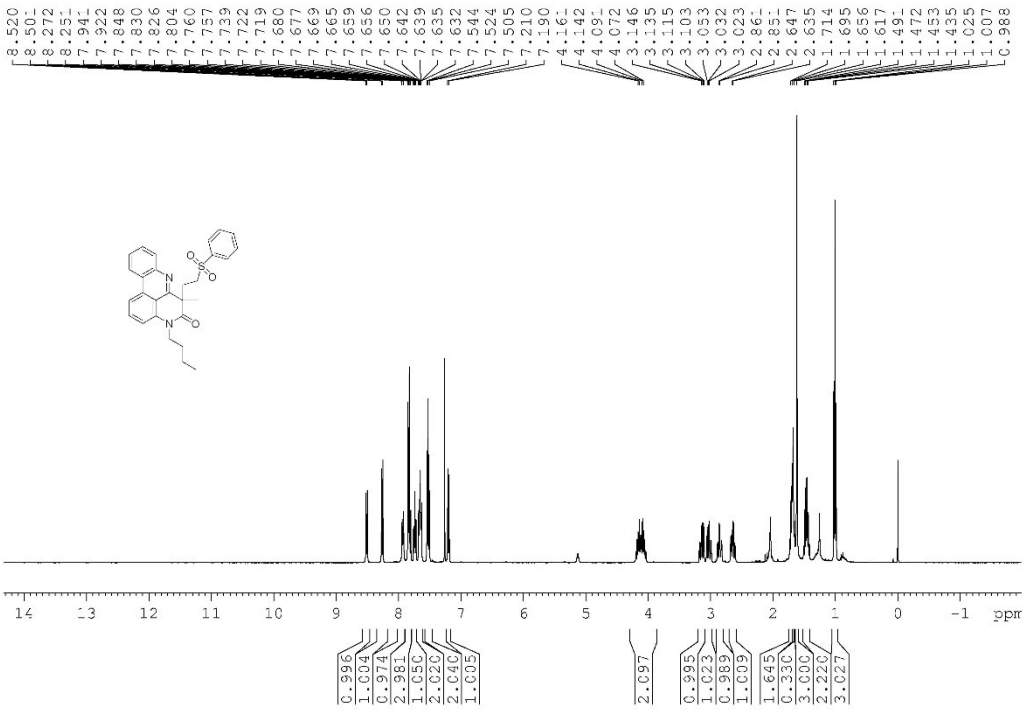
^{13}C NMR spectrum of compound **3s**



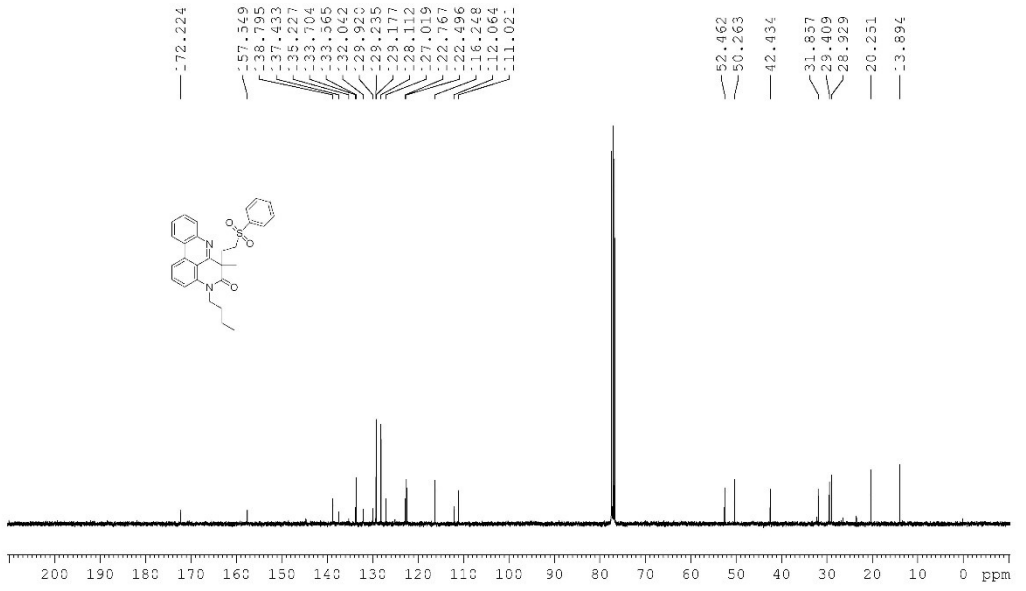
^{1}H NMR spectrum of compound **3t**



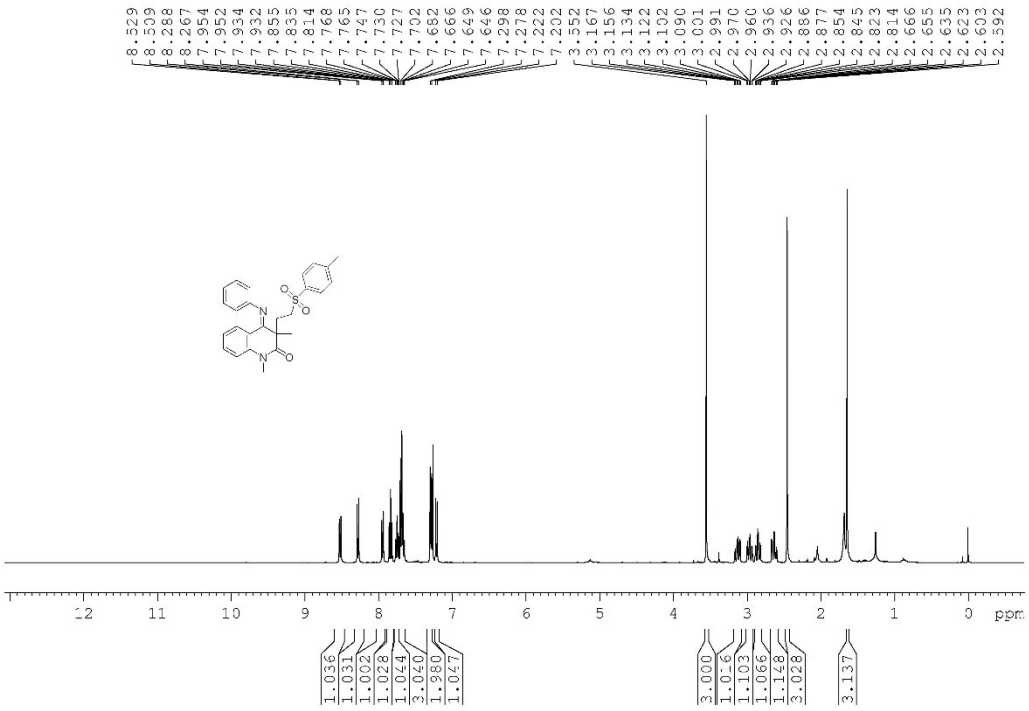
^{13}C NMR spectrum of compound **3t**



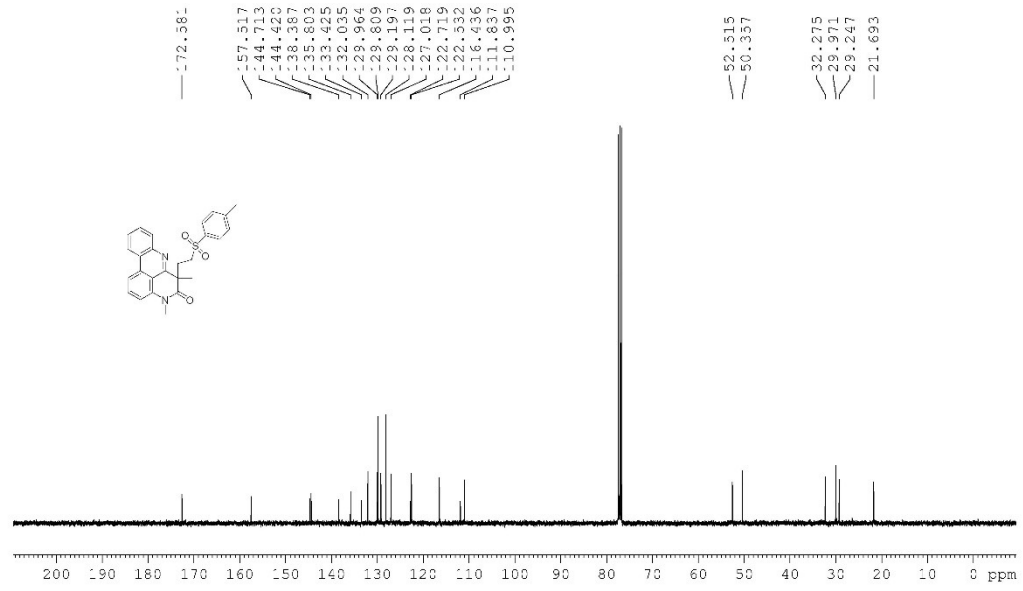
^{1}H NMR spectrum of compound **3u**



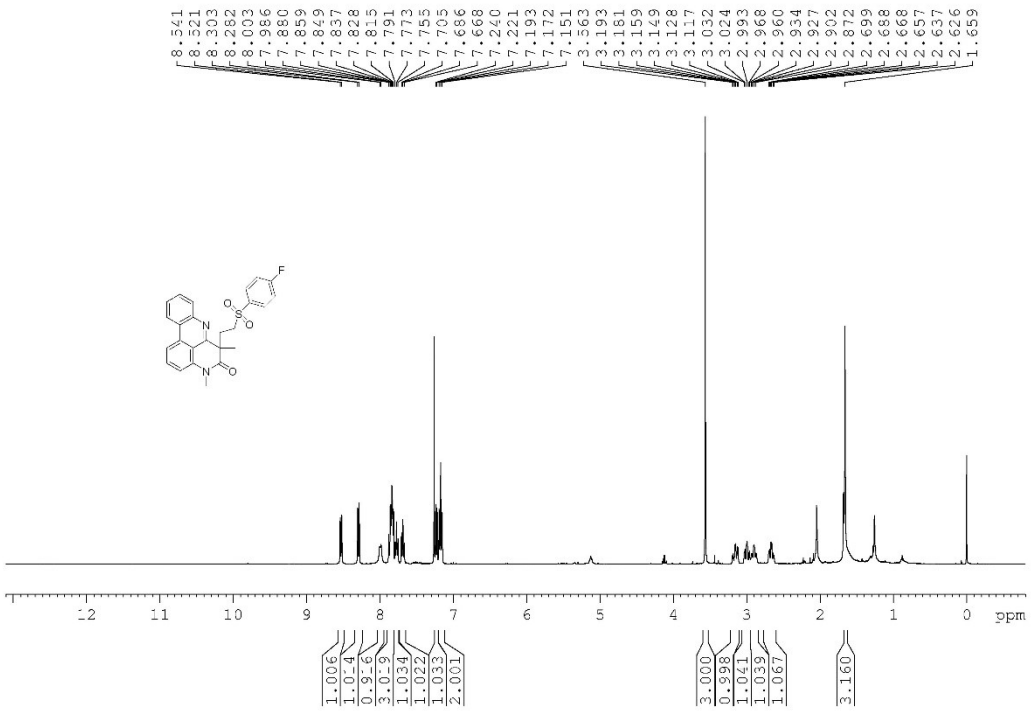
^{13}C NMR spectrum of compound **3u**



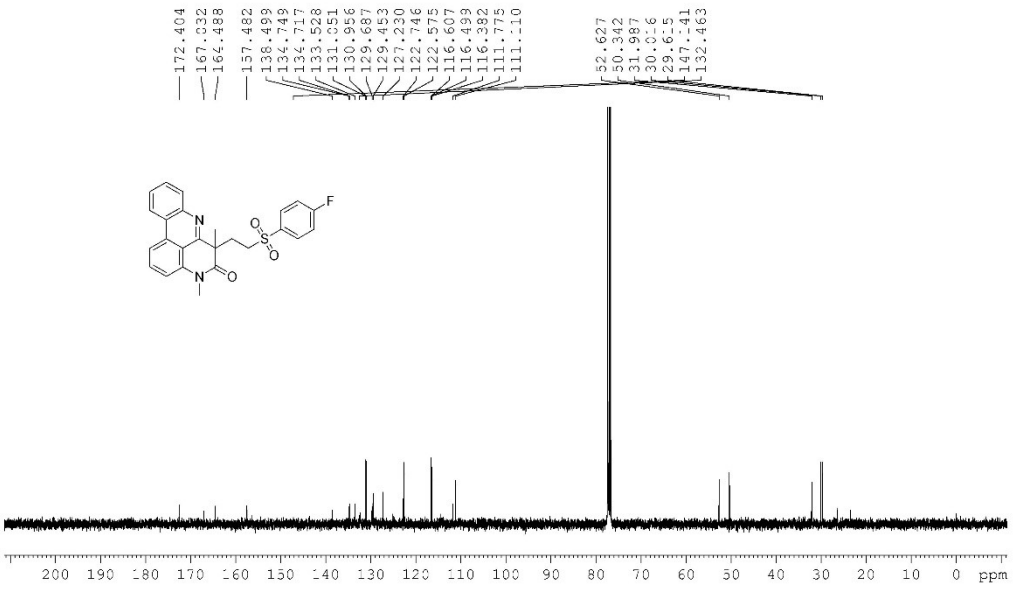
^{1}H NMR spectrum of compound **3w**



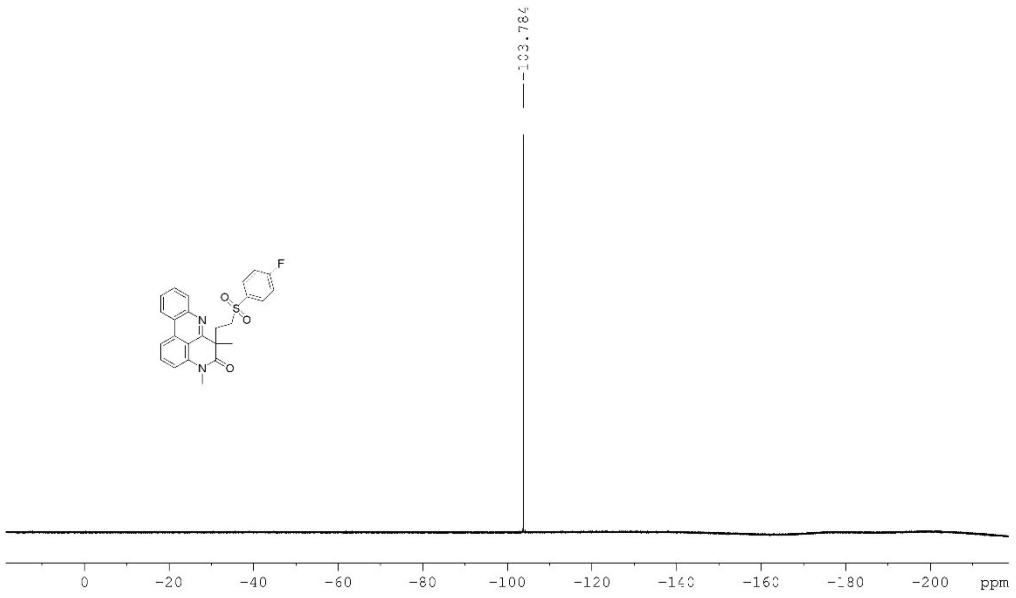
^{13}C NMR spectrum of compound **3w**



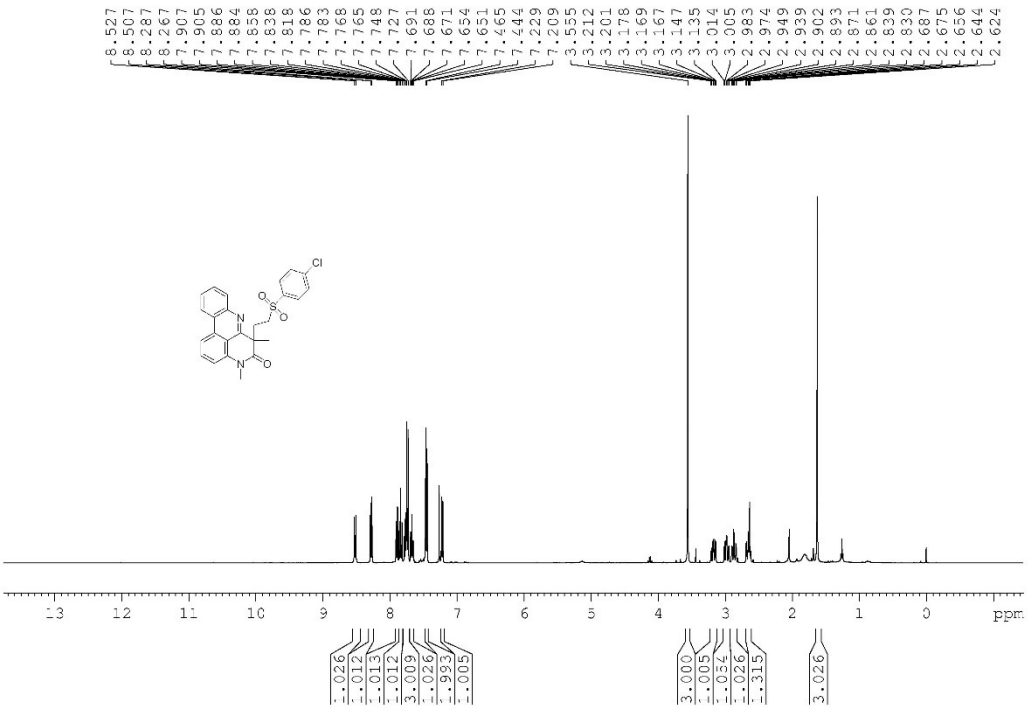
^{1}H NMR spectrum of compound **3x**



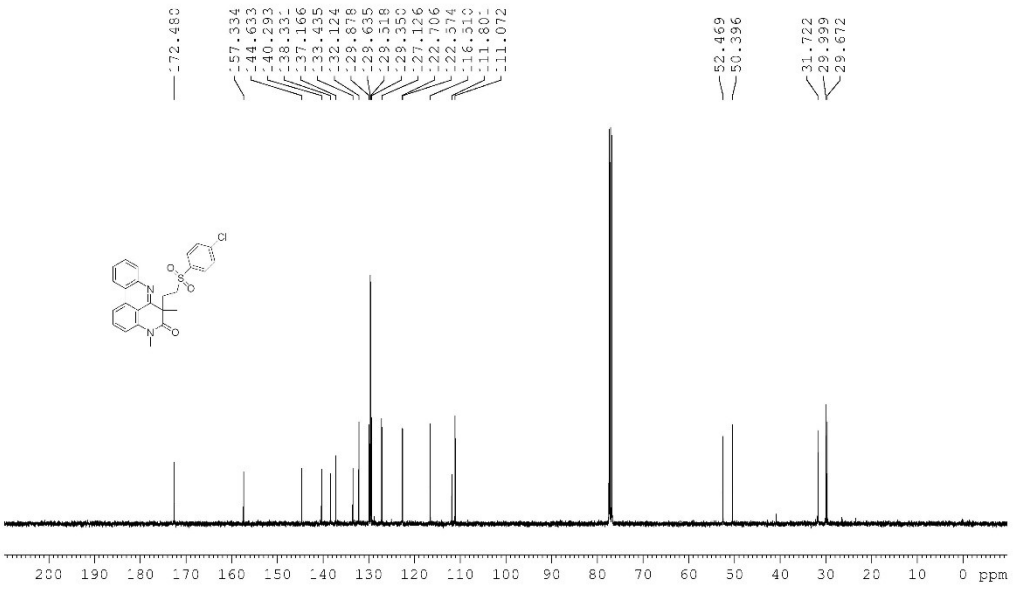
^{13}C NMR spectrum of compound **3x**



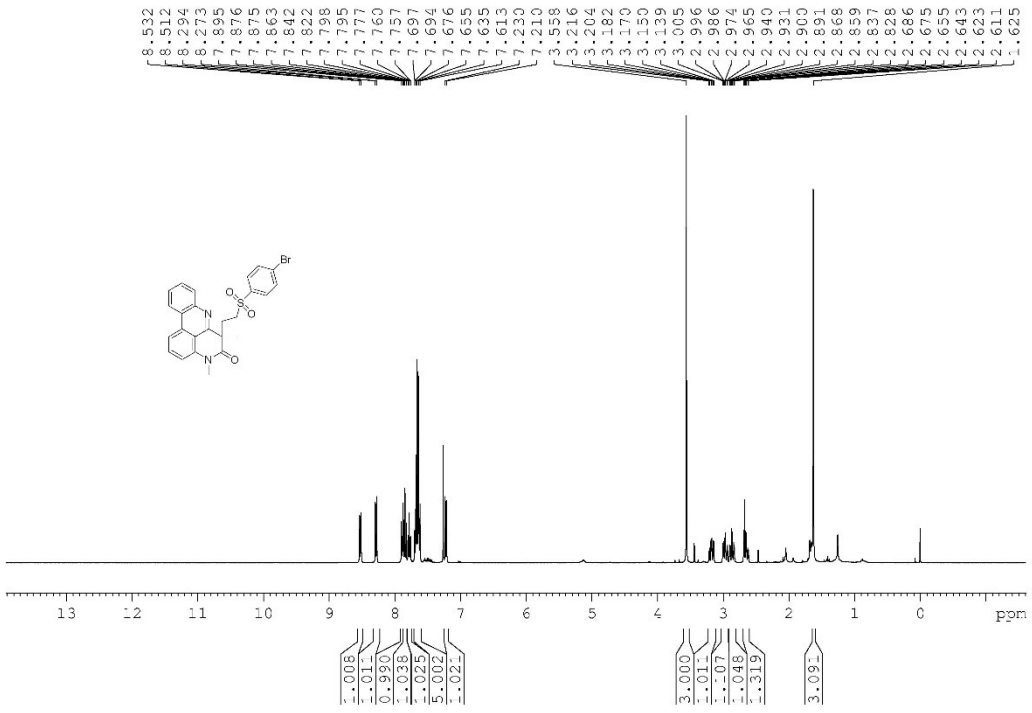
^{19}F NMR spectrum of compound **3x**



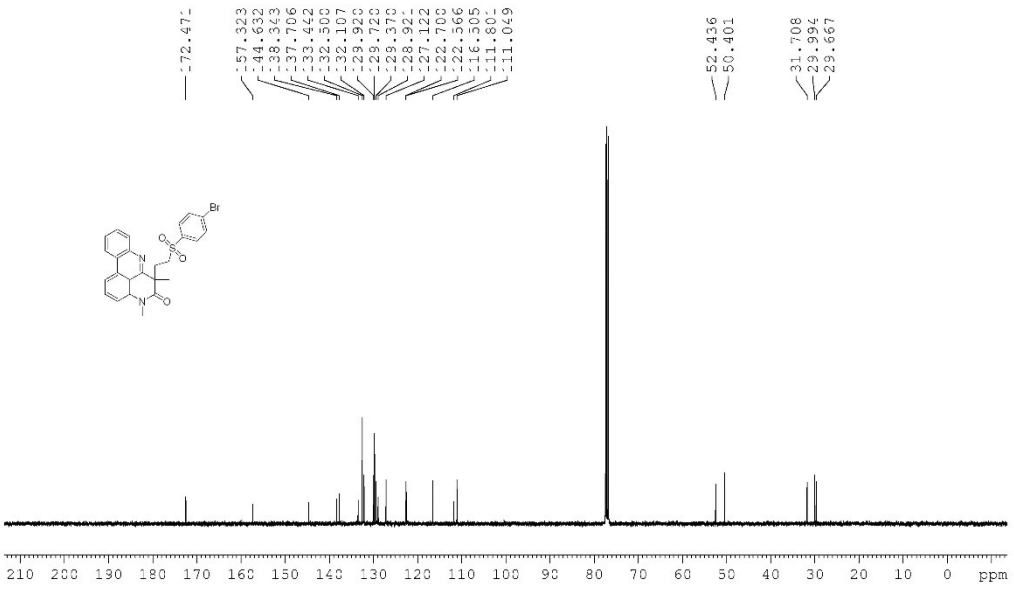
^{1}H NMR spectrum of compound **3y**



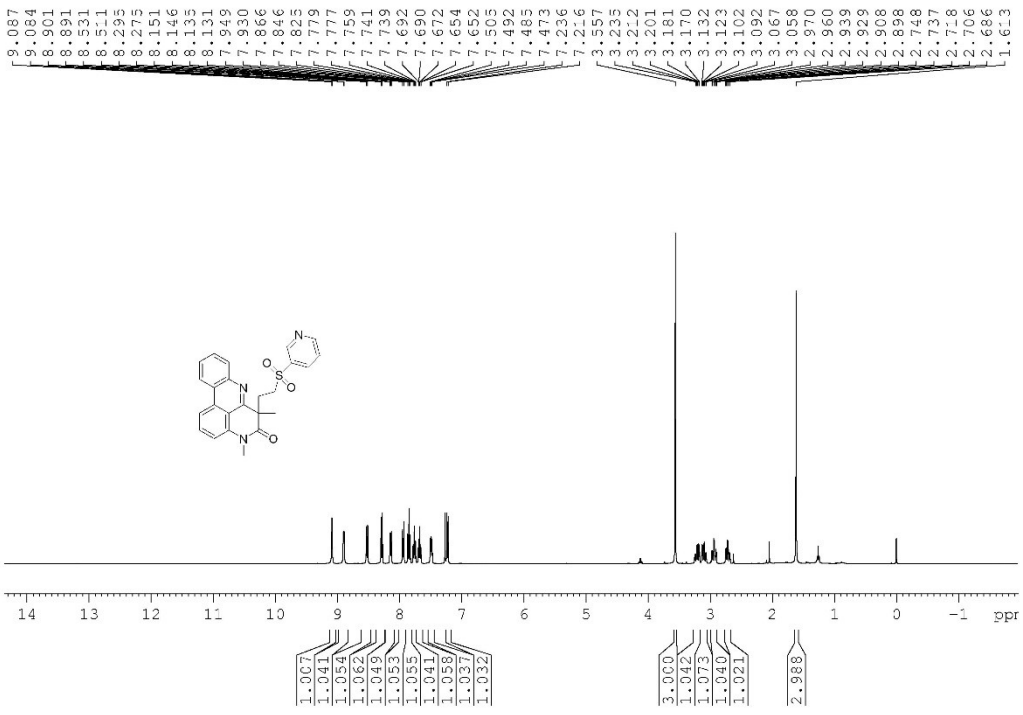
^{13}C NMR spectrum of compound **3y**



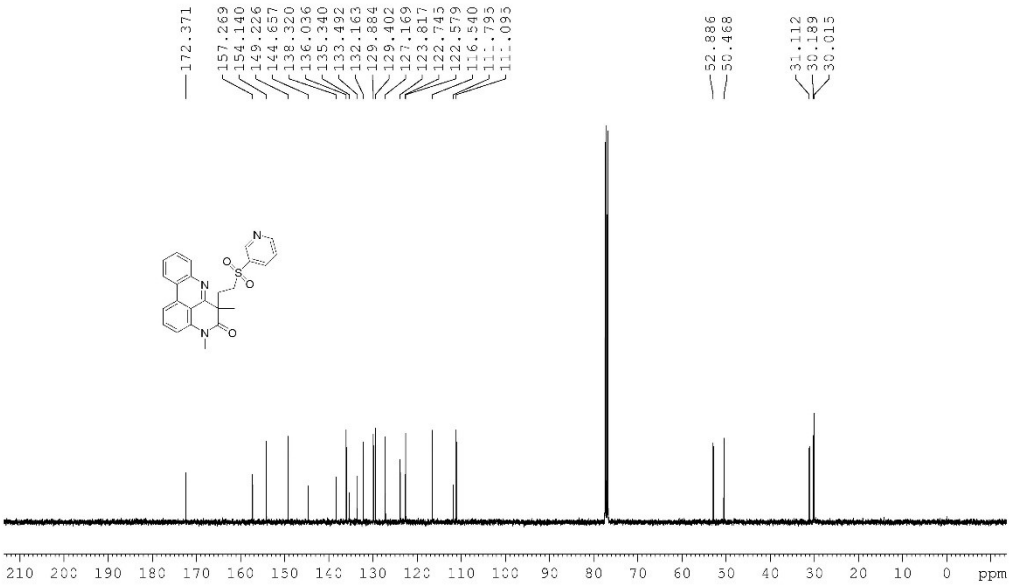
^{1}H NMR spectrum of compound **3z**



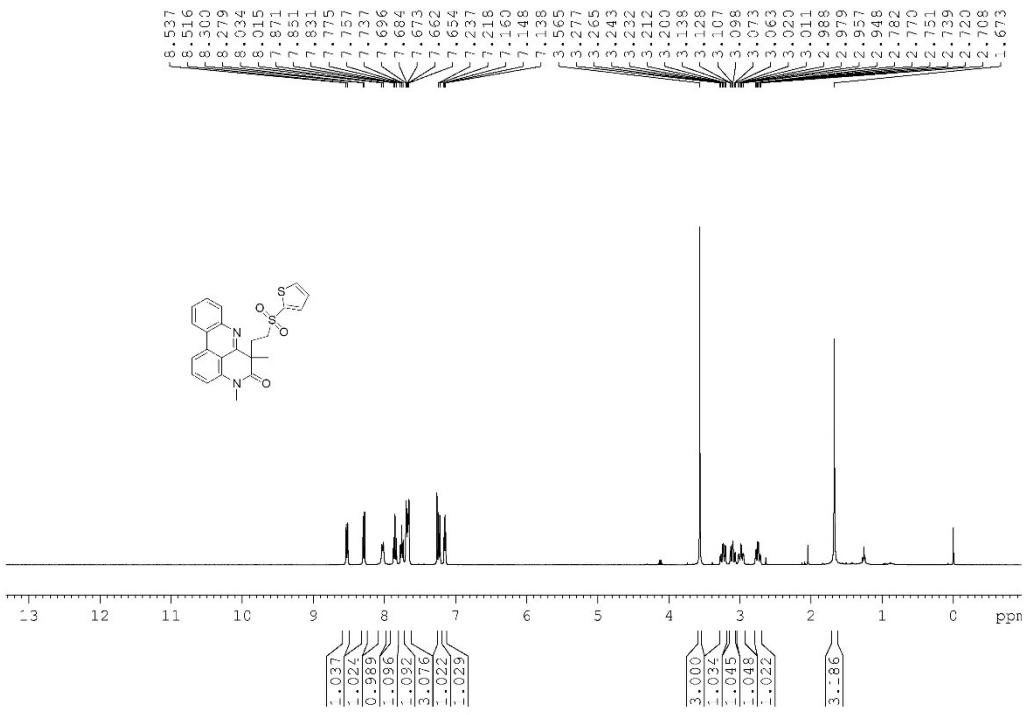
^{13}C NMR spectrum of compound **3z**



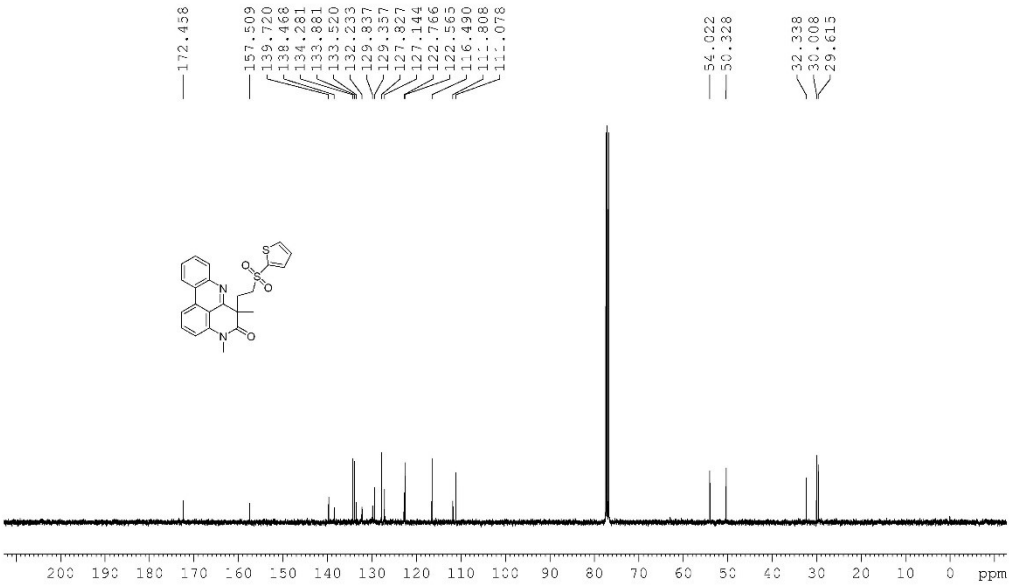
^{1}H NMR spectrum of compound **3aa**



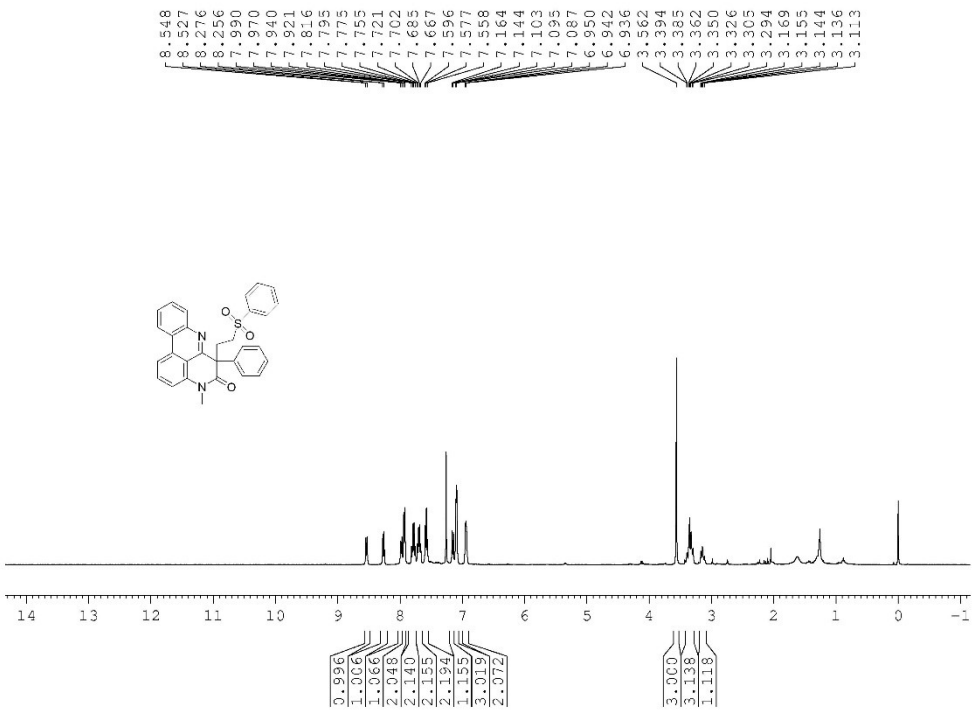
^{13}C NMR spectrum of compound **3aa**



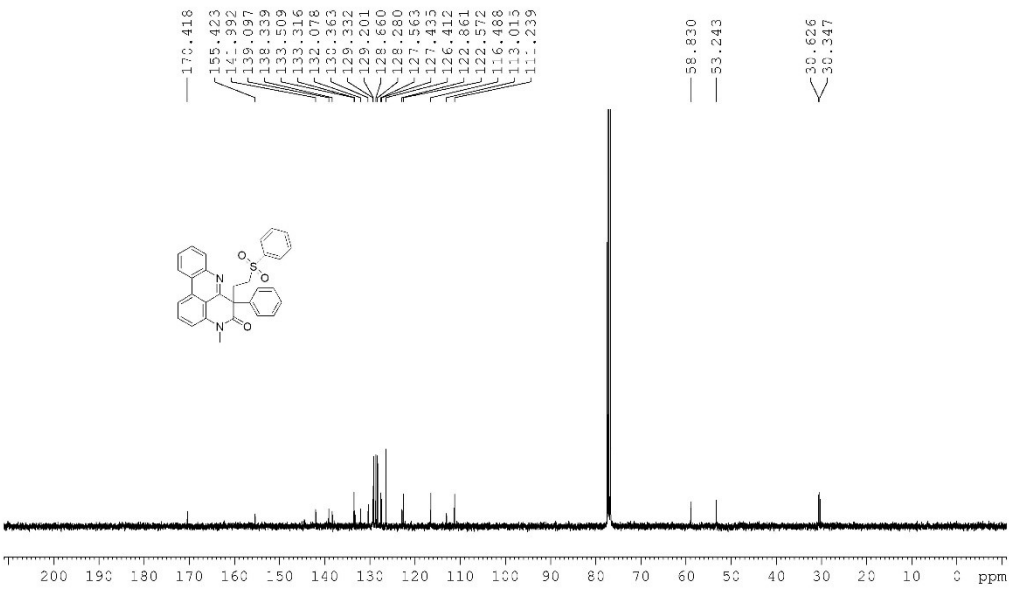
^{1}H NMR spectrum of compound **3ab**



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



^{1}H NMR spectrum of compound **3ac**



^{13}C NMR spectrum of compound **3ac**