

Supporting Information

**Synthesis of 5,6-Dihydrophenanthridines via Palladium Catalyzed
Intramolecular Dehydrogenative Coupling of Two Aryl C–H Bonds**

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1. General information

All reactions were carried out under an air atmosphere. Unless noted otherwise, commercially available chemicals were used without further purification. Flash chromatography was performed with silica gel (200-300 mesh). Oil bath served as the heat source. NMR spectra were acquired on Bruker 400 MHz (^1H at 400 MHz, ^{13}C at 101 MHz) or Jeol 400 MHz (^1H at 400 MHz, ^{13}C at 100 MHz). NMR spectra were recorded in CDCl_3 (TMS, $\delta = 0.00$ ppm for ^1H NMR and $\delta = 77.10$ ppm for ^{13}C NMR) or DMSO-d_6 ($\delta = 2.50$ ppm for ^1H NMR and $\delta = 39.52$ ppm for ^{13}C NMR) or CD_3OD ($\delta = 3.31$ ppm for ^1H NMR and $\delta = 49.00$ ppm for ^{13}C NMR) using the solvent residue peaks as the internal references. Coupling constants were reported in Hertz (Hz). Data for ^1H NMR spectra were reported as follows: chemical shift (ppm, referenced to protium, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet, coupling constant (Hz), and integration). Infrared (IR) data were acquired on a Bruker Invenio-RFT-IR spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). Mass spectra were acquired on a BrukerDaltonics S2 MicroTof-Q II mass spectrometer. X-ray crystal structure analyses were measured on Bruker Smart APEXIICCD instrument using $\text{Mo-K}\alpha$ radiation. The structures were solved and refined using the SHELXTL software package.

2. Condition optimization for preparation of product 2

Table S1. Optimization of conditions for the synthesis of 5,6-dihydrophenanthridine

Reaction scheme: **1** $\xrightarrow[\text{solvent, } T/^{\circ}\text{C}]{[\text{Pd}], \text{additive}}$ **2**

	R ¹	R ²	Pd cat. (equiv)	Additive (equiv)	T /°C	Solvent	Yield (%) ^a
1	-H	Ac	Pd(OAc) ₂ (0.1)	/	70	DMSO	0
2	-CONMe ₂	Ac	Pd(OAc) ₂ (0.1)	/	70	DMSO	trace
3	-CO(2-Py)	Ac	Pd(OAc) ₂ (0.1)	/	70	DMSO	trace
4	-SO ₂ (2-Py)	Ac	Pd(OAc) ₂ (0.1)	/	70	DMSO	9
5	-SO ₂ (2-Py)	Ac	Pd(OAc) ₂ (0.1)	/	70	DCE	5
6	-SO ₂ (2-Py)	Ac	Pd(OAc) ₂ (0.1)	/	70	HFIP	11
7	-SO ₂ (2-Py)	Ac	Pd(OAc) ₂ (0.1)	/	70	CF ₃ CH ₂ OH	12
8	-SO ₂ (2-Py)	Ac	Pd(OAc) ₂ (0.1)	/	70	CF ₂ HCF ₂ CH ₂ OH	4
9	-SO ₂ (2-Py)	Ac	Pd(OAc) ₂ (0.1)	/	70	CF ₂ HCH ₂ OH	5
10	-SO ₂ (2-Py)	Ac	Pd(OAc) ₂ (0.1)	/	70	EA	2
11	-SO ₂ (2-Py)	Ac	Pd(OAc) ₂ (0.1)	/	70	PhMe	3
12	-SO ₂ (2-Py)	Ac	Pd(OAc) ₂ (0.1)	/	70	Other solvents	N.R.
13	-SO ₂ (2-Py)	Ac	Pd(OAc) ₂ (0.1)	Cu(TFA) ₂ ·H ₂ O (1.1)	70	CF ₃ CH ₂ OH	31
14	-SO ₂ (2-Py)	Ac	Pd(OAc) ₂ (0.1)	Cu(OAc) ₂ ·H ₂ O (1.1)	70	CF ₃ CH ₂ OH	22
15	-SO ₂ (2-Py)	Ac	Pd(OAc) ₂ (0.1)	Cu(OAc) ₂ (1.1)	70	CF ₃ CH ₂ OH	21
16	-SO ₂ (2-Py)	Ac	Pd(OAc) ₂ (0.1)	CuOAc (1.1)	70	CF ₃ CH ₂ OH	11
17	-SO ₂ (2-Py)	Ac	Pd(OAc) ₂ (0.1)	CuI (1.1)	70	CF ₃ CH ₂ OH	10
18	-SO ₂ (2-Py)	Ac	Pd(OAc) ₂ (0.1)	CuO (1.1)	70	CF ₃ CH ₂ OH	12
19	-SO ₂ (2-Py)	Ac	Pd(OAc) ₂ (0.1)	CuSO ₄ (1.1)	70	CF ₃ CH ₂ OH	18
20	-SO ₂ (2-Py)	Ac	Pd(OAc) ₂ (0.1)	CuF ₂ ·2H ₂ O (1.1)	70	CF ₃ CH ₂ OH	29
21	-SO ₂ (2-Py)	Ac	Pd(OAc) ₂ (0.1)	AgTFA (1.1)	70	CF ₃ CH ₂ OH	9
22	-SO ₂ (2-Py)	Ac	Pd(OAc) ₂ (0.1)	AgNO ₃ (1.1)	70	CF ₃ CH ₂ OH	8

23	-SO ₂ (2-Py)	Ac	Pd(OAc) ₂ (0.1)	Other additives	70	CF ₃ CH ₂ OH	N.R.
24 ^b	-SO ₂ (2-Py)	Ac	Pd(OAc) ₂ (0.1)	-	70	CF ₃ CH ₂ OH	8
25	-SO ₂ (2-Py)	Ac	Pd(OAc) ₂ (0.1)	Cu(TFA) ₂ ·H ₂ O (1.1)	40	CF ₃ CH ₂ OH	N.R.
26	-SO ₂ (2-Py)	Ac	Pd(OAc) ₂ (0.1)	Cu(TFA) ₂ ·H ₂ O (1.1)	60	CF ₃ CH ₂ OH	23
27	-SO ₂ (2-Py)	Ac	Pd(OAc) ₂ (0.1)	Cu(TFA) ₂ ·H ₂ O (1.1)	80	CF ₃ CH ₂ OH	35
28	-SO ₂ (2-Py)	Ac	Pd(OAc) ₂ (0.1)	Cu(TFA) ₂ ·H ₂ O (1.1)	100	CF ₃ CH ₂ OH	45
29	-SO ₂ (2-Py)	Ac	Pd(OAc) ₂ (0.1)	Cu(TFA) ₂ ·H ₂ O (1.1)	120	CF ₃ CH ₂ OH	46
30	-SO ₂ (2-Py)	Ts	Pd(OAc) ₂ (0.1)	Cu(TFA) ₂ ·H ₂ O (1.1)	100	CF ₃ CH ₂ OH	trace
31	-SO ₂ (2-Py)	Boc	Pd(OAc) ₂ (0.1)	Cu(TFA) ₂ ·H ₂ O (1.1)	100	CF ₃ CH ₂ OH	trace
32	-SO ₂ (2-Py)	Me	Pd(OAc) ₂ (0.1)	Cu(TFA) ₂ ·H ₂ O (1.1)	100	CF ₃ CH ₂ OH	3
33	-SO ₂ (2-Py)	Ph	Pd(OAc) ₂ (0.1)	Cu(TFA) ₂ ·H ₂ O (1.1)	100	CF ₃ CH ₂ OH	18
34	-SO ₂ (2-Py)	Ac	Pd(PPh ₃) ₄ (0.1)	Cu(TFA) ₂ ·H ₂ O (1.1)	100	CF ₃ CH ₂ OH	53
35	-SO ₂ (2-Py)	Ac	Pd(TFA) ₂ (0.1)	Cu(TFA) ₂ ·H ₂ O (1.1)	100	CF ₃ CH ₂ OH	62
36	-SO ₂ (2-Py)	Ac	Pd ₂ (dba) ₃ (0.1)	Cu(TFA) ₂ ·H ₂ O (1.1)	100	CF ₃ CH ₂ OH	trace
37	-SO ₂ (2-Py)	Ac	Pd(OH) ₂ (0.1)	Cu(TFA) ₂ ·H ₂ O (1.1)	100	CF ₃ CH ₂ OH	N.R.
38	-SO ₂ (2-Py)	Ac	PdI ₂ (0.1)	Cu(TFA) ₂ ·H ₂ O (1.1)	100	CF ₃ CH ₂ OH	N.R.
39	-SO ₂ (2-Py)	Ac	Pd(PPh ₃) ₂ Cl ₂ (0.1)	Cu(TFA) ₂ ·H ₂ O (1.1)	100	CF ₃ CH ₂ OH	36
40	-SO ₂ (2-Py)	Ac	Pd(TFA) ₂ (0.15)	Cu(TFA) ₂ ·H ₂ O (1.1)	100	CF ₃ CH ₂ OH	74
41	-SO ₂ (2-Py)	Ac	Pd(TFA) ₂ (0.3)	Cu(TFA) ₂ ·H ₂ O (1.1)	100	CF ₃ CH ₂ OH	75
42	-SO ₂ (2-Py)	Ac	/	Cu(TFA) ₂ ·H ₂ O (1.1)	100	CF ₃ CH ₂ OH	/
43	-SO ₂ (2-Py)	Ac	Pd(TFA) ₂ (0.15)	Cu(TFA) ₂ ·H ₂ O (0.5)	100	CF ₃ CH ₂ OH	16
44	-SO ₂ (2-Py)	Ac	Pd(TFA) ₂ (0.15)	Cu(TFA) ₂ ·H ₂ O (2.2)	100	CF ₃ CH ₂ OH	83
45	-SO ₂ (2-Py)	Ac	Pd(TFA) ₂ (0.15)	Cu(TFA) ₂ ·H ₂ O (4.0)	100	CF ₃ CH ₂ OH	82
46 ^b	-SO ₂ (2-Py)	Ac	Pd(TFA) ₂ (0.15)	Cu(TFA) ₂ ·H ₂ O (2.2)	100	CF ₃ CH ₂ OH	83

^a Isolated yield. ^b Under argon atmosphere.

3. Experimental procedure for the KIE study

3.1 Starting material: The synthesis of [D₇]-benzyl bromide was synthesized according to the literature [59]. The synthesis of [D₇]-**1a** and [D₆]-**2a** were the same as the synthesis of above mentioned materials **1a** and **2a**.

KIE experiment: We use **1a** and [D₇]-**1a** as starting materials and two parallel reacting at standard conditions. The conversion was measured by ¹H NMR analysis for three times (1.5 h, 2.0 h, 3.0 h) to compare the initial reaction rates.

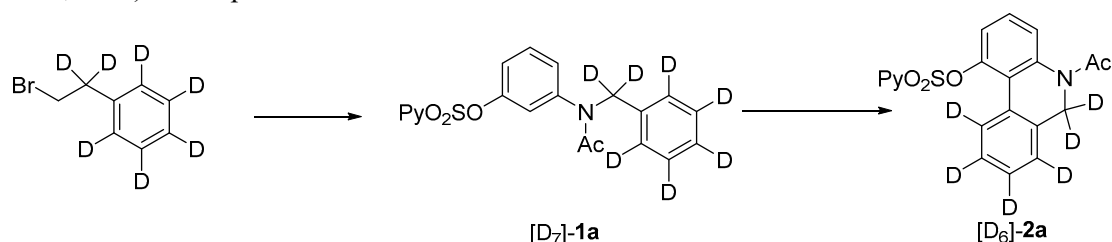


Table S2 Conversion (%) of the reaction of **1a** (7-H or 7-D).

BrC1(C)C(C)C(C)C(C)C1 $\xrightarrow[\text{K}_H / \text{K}_D = 3.04]{\text{standard condition}}$ CC(=O)N1C(C)C(C)C(C)C1
1a, [D₇]-**1a** **2a**, [D₆]-**2a**

reaction time (h)	H-Conversion (%)	D-Conversion (%)
0	0	0
1.5	3.18	1.47
2.0	3.66	2.91
3.0	9.09	3.67

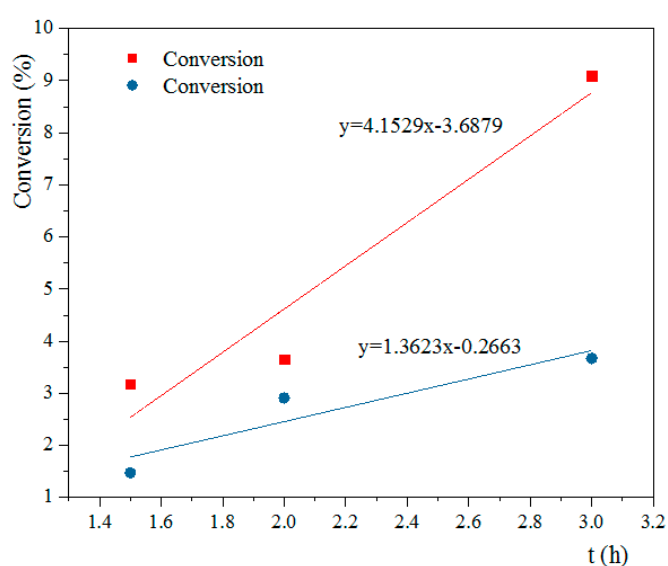
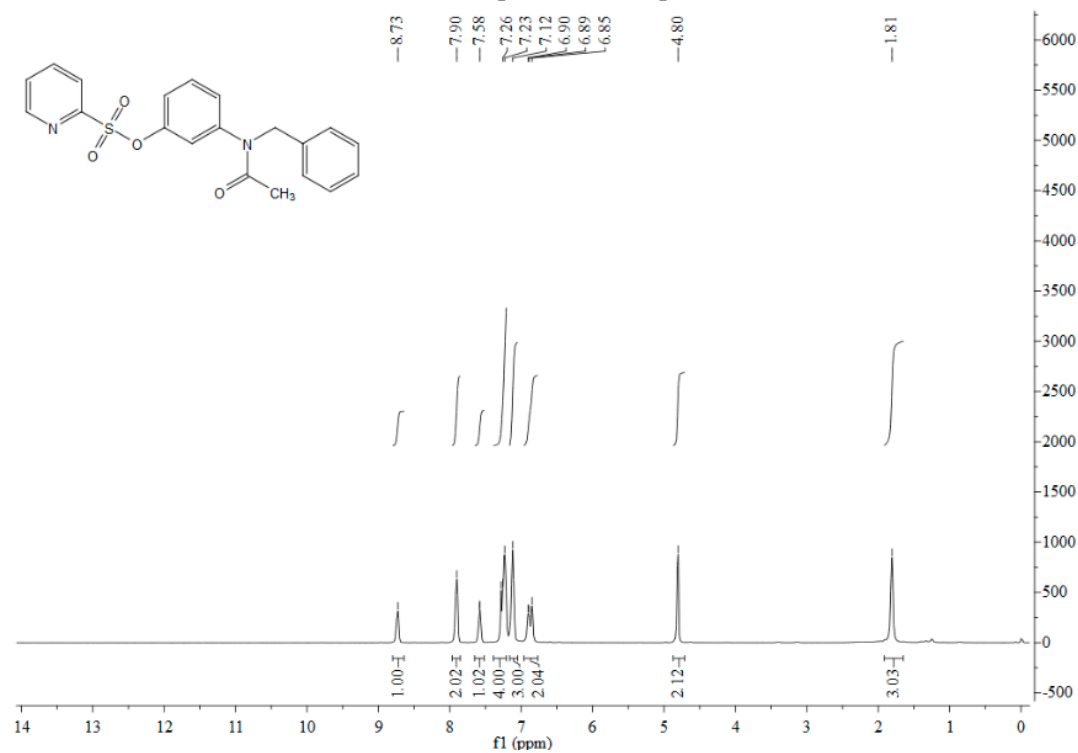


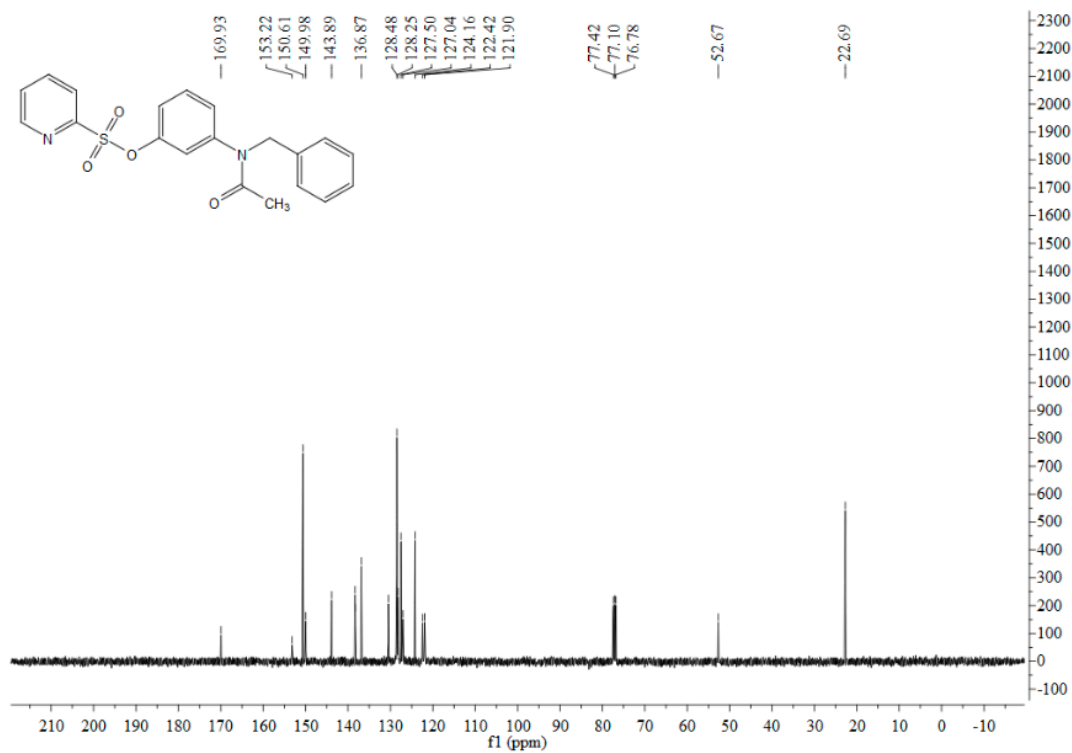
Figure S1. Conversion (%) of the reaction of **1a** (7-H or 7-D).

4. Spectral copies of substrates ^1H NMR and ^{13}C NMR

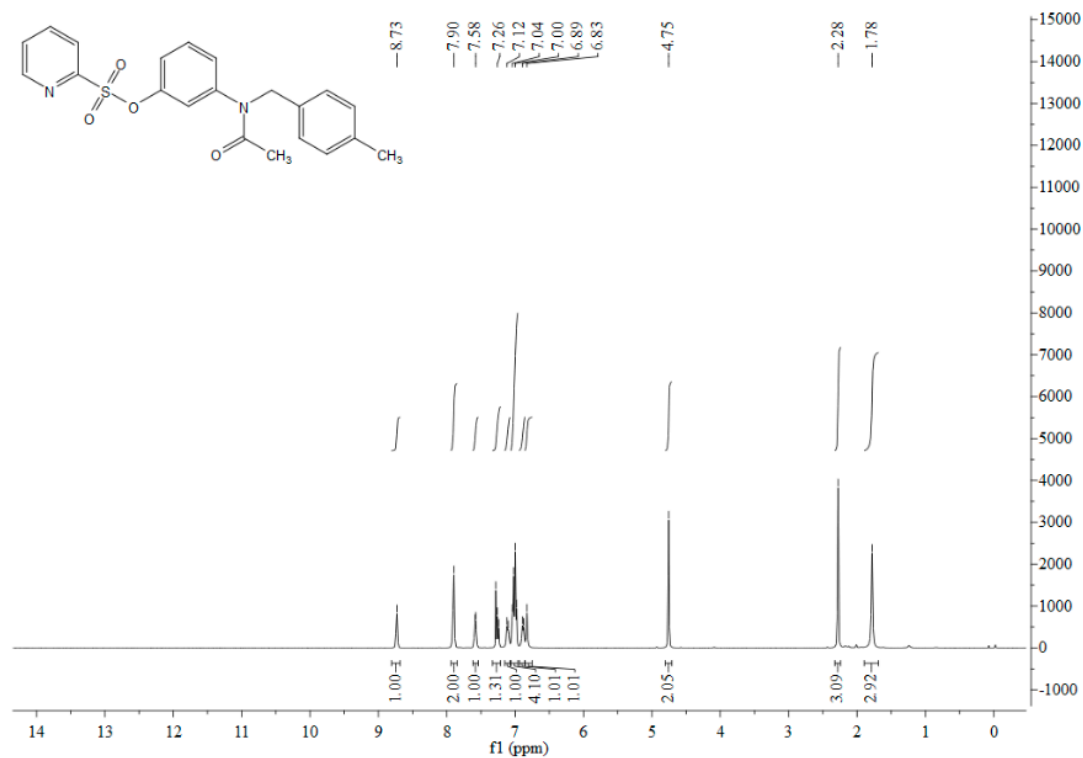
^1H NMR spectra of compound **1a**



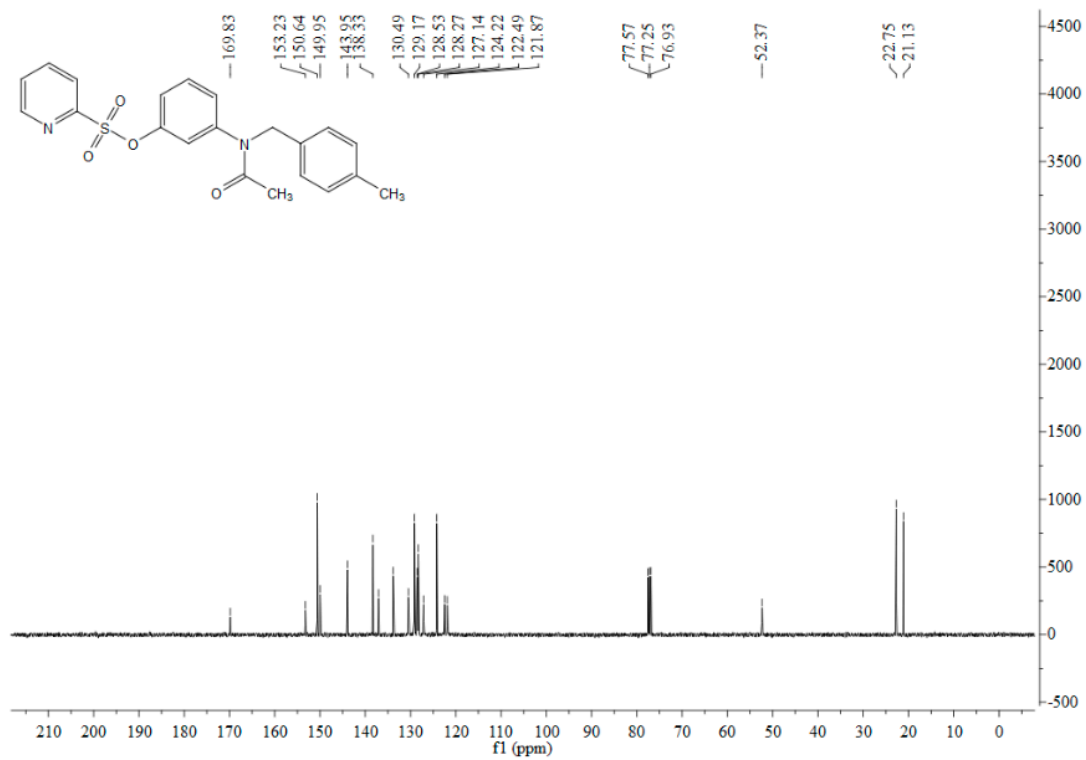
^{13}C NMR spectra of compound **1a**



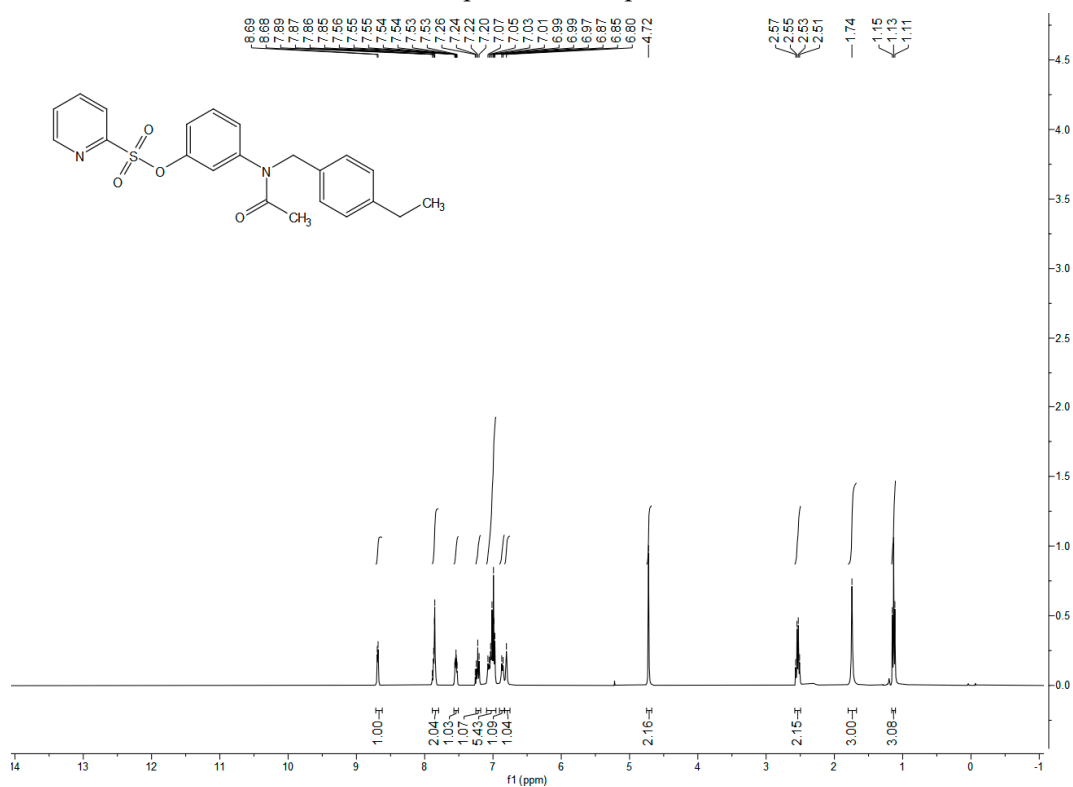
¹H NMR spectra of compound **1b**



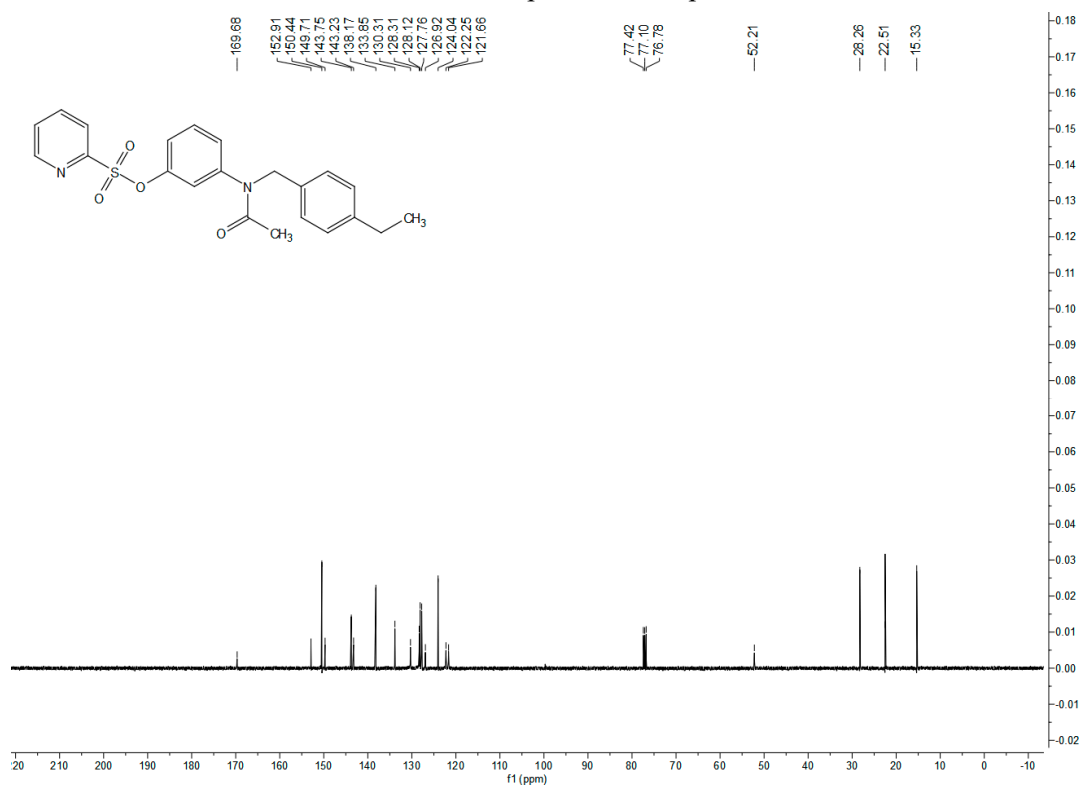
¹³C NMR spectra of compound **1b**



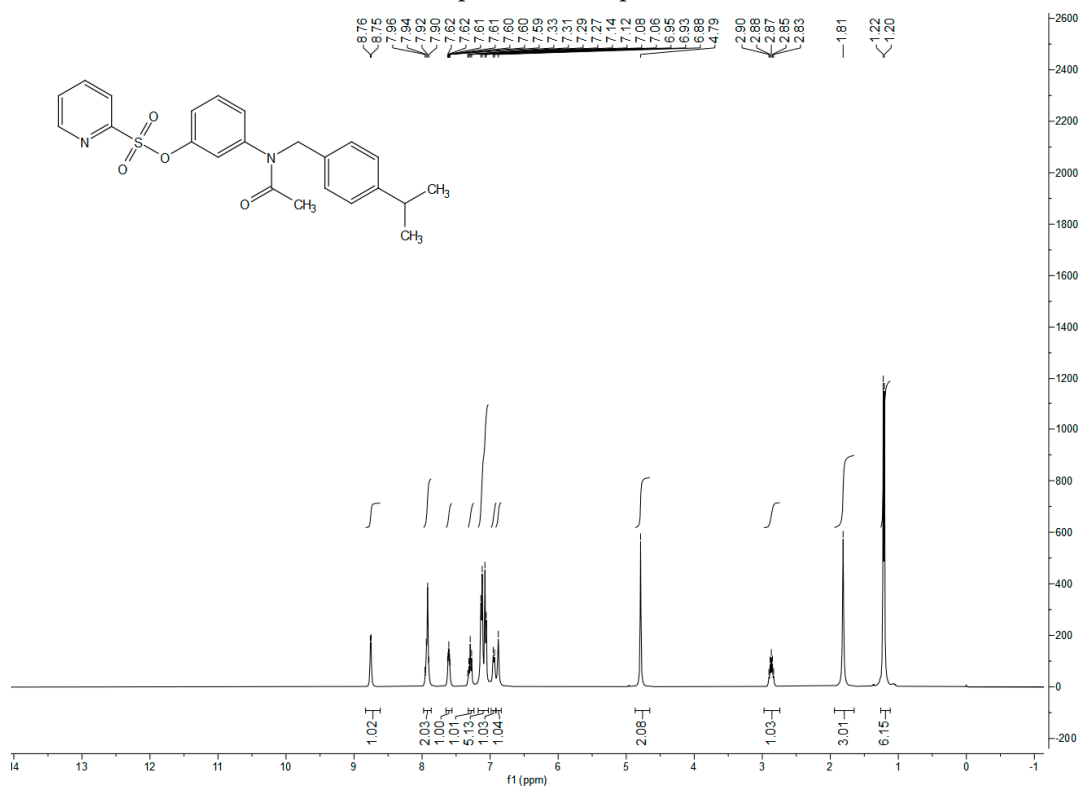
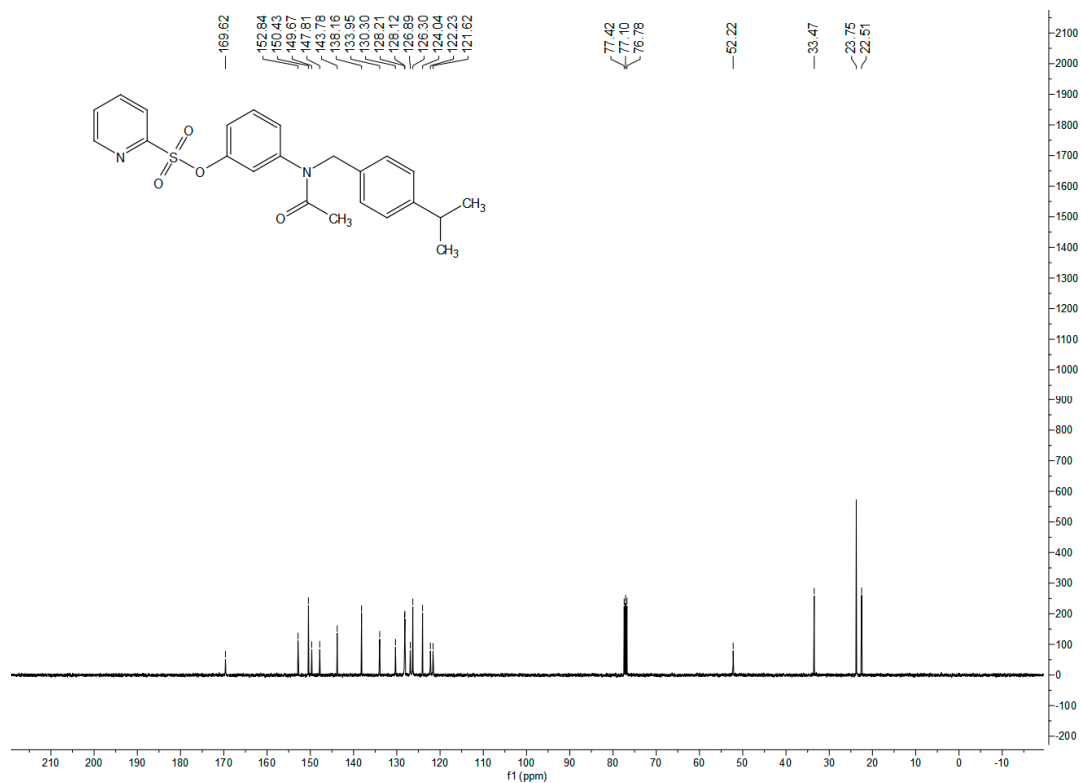
¹³C NMR spectra of compound 1c



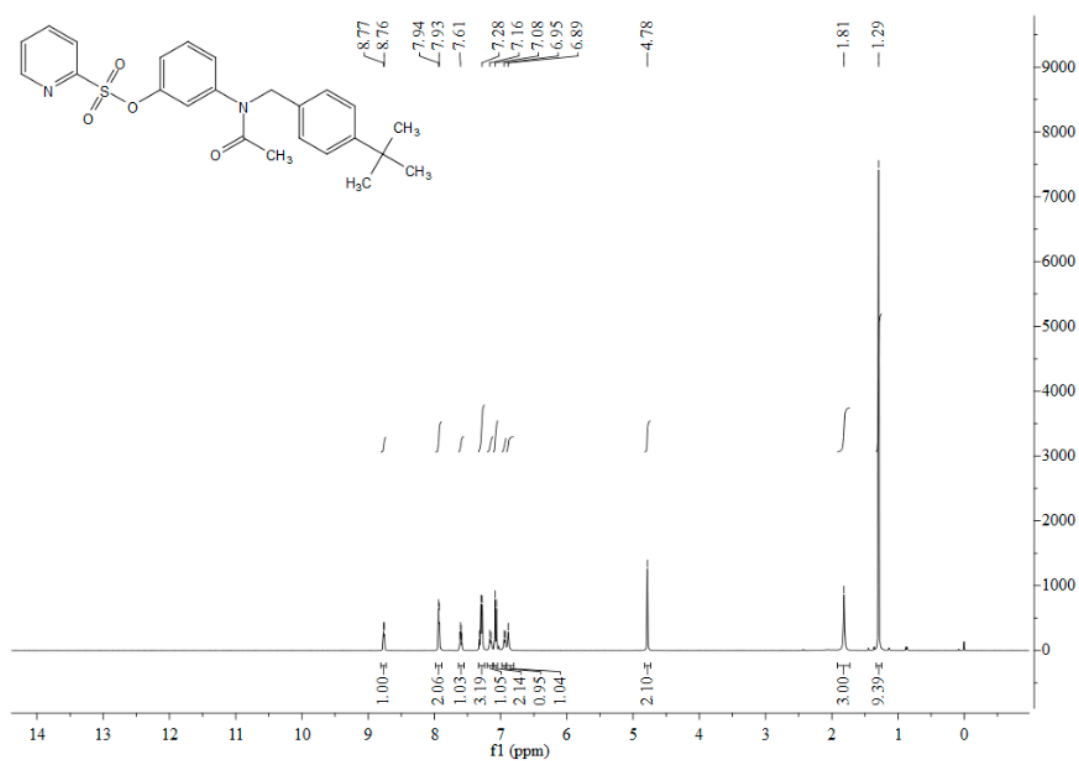
¹³C NMR spectra of compound 1c



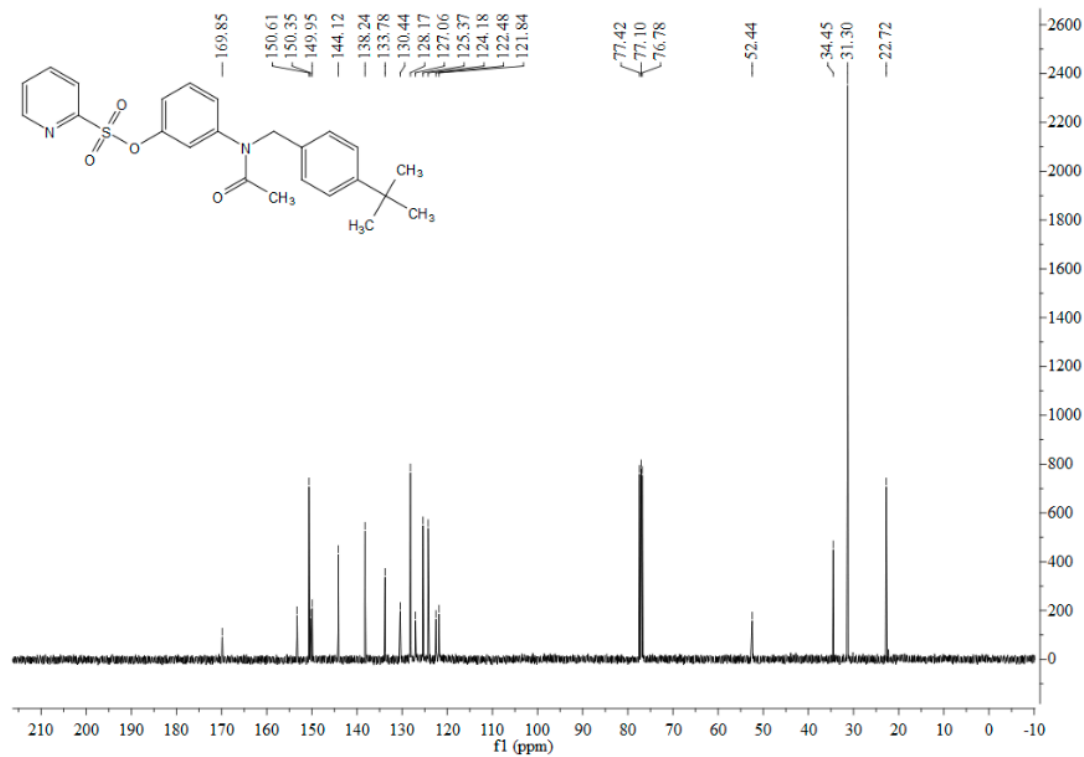
¹H NMR spectra of compound **1d**

 ^{13}C NMR spectra of compound **1d**

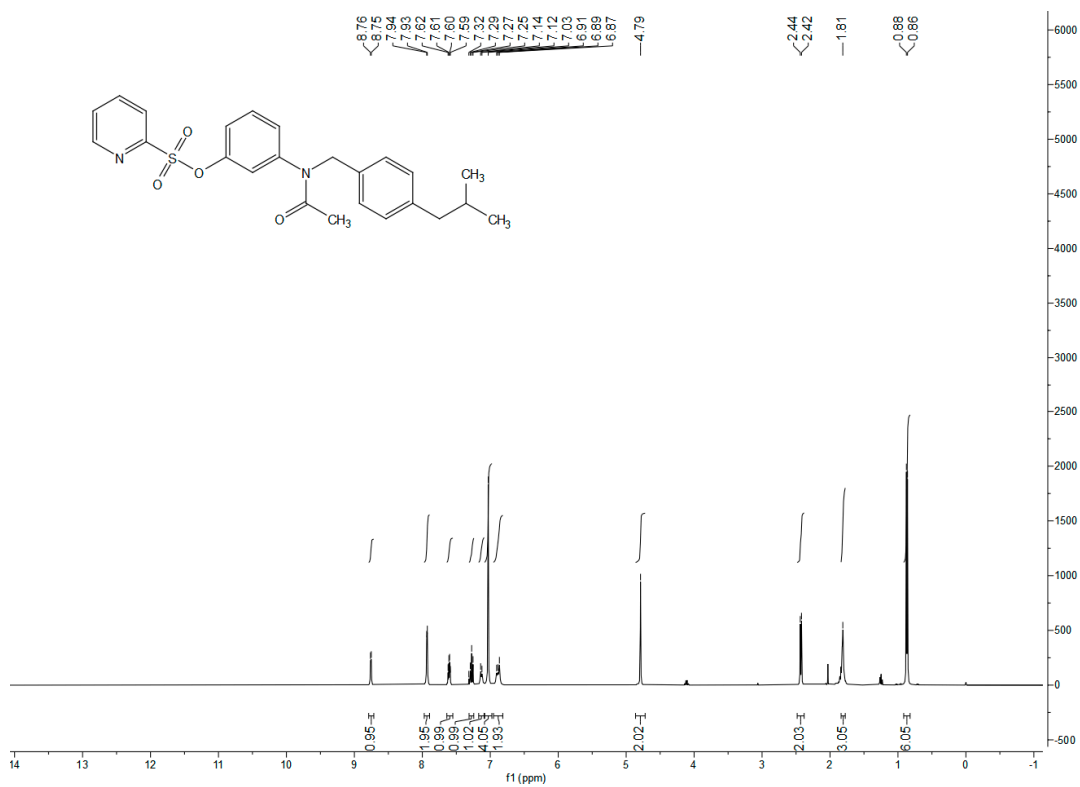
¹H NMR spectra of compound **1e**



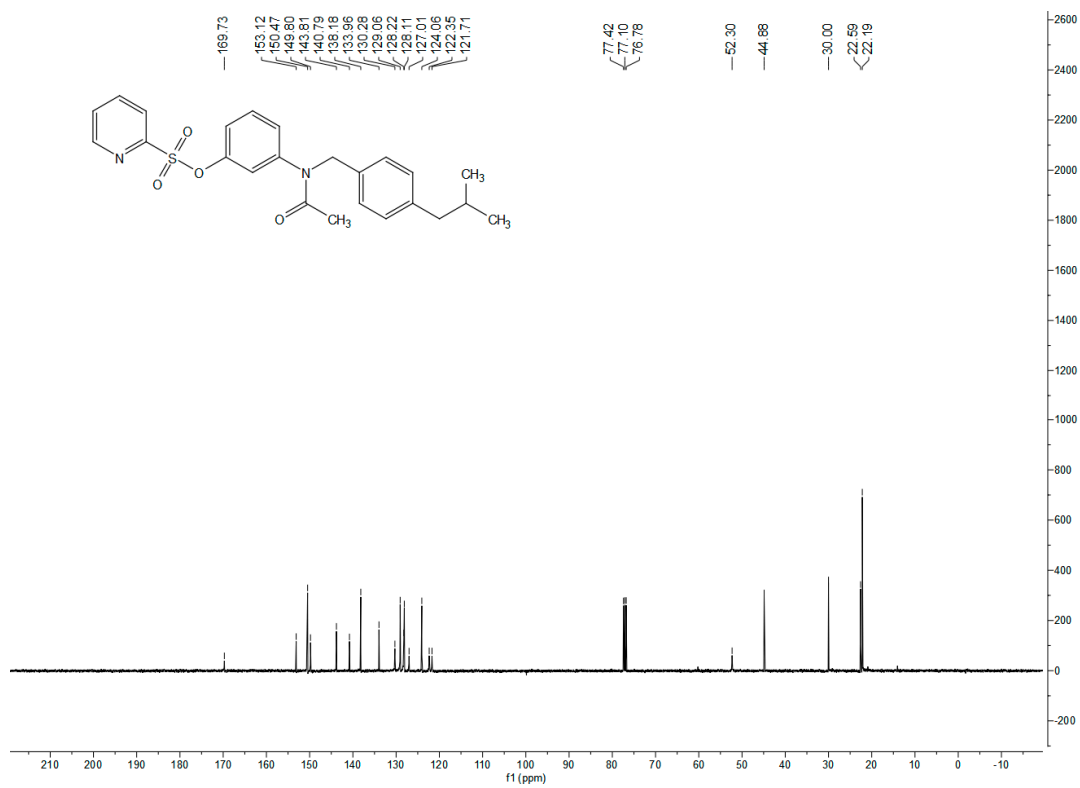
¹³C NMR spectra of compound **1e**



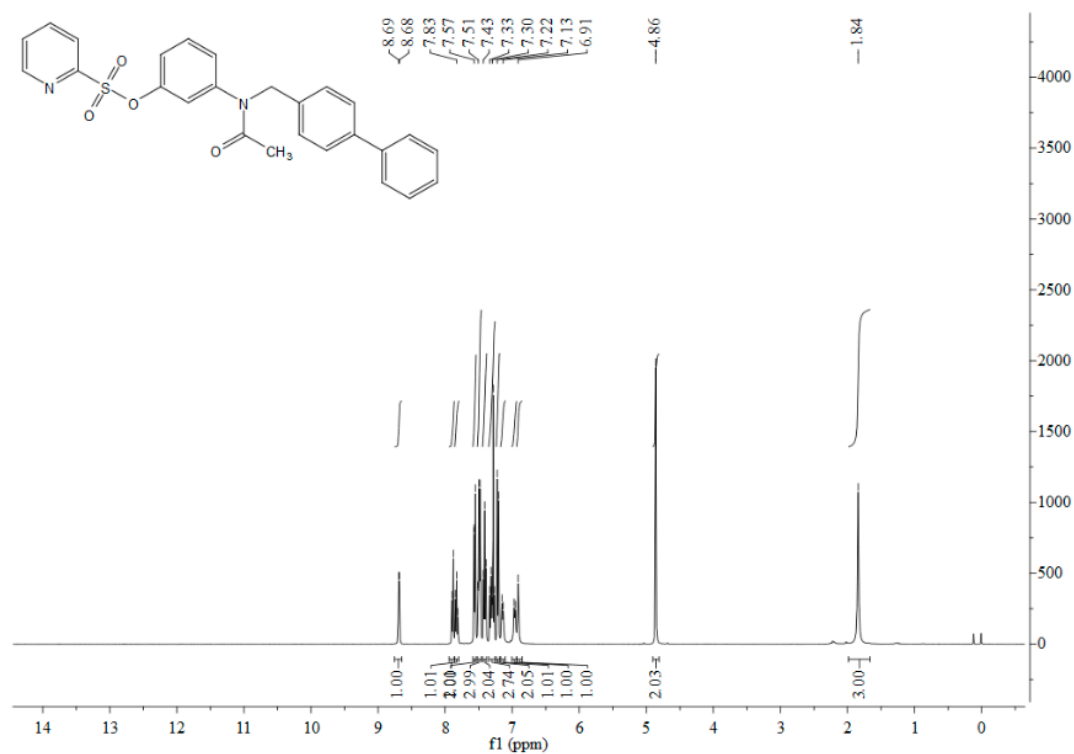
¹H NMR spectra of compound **1f**



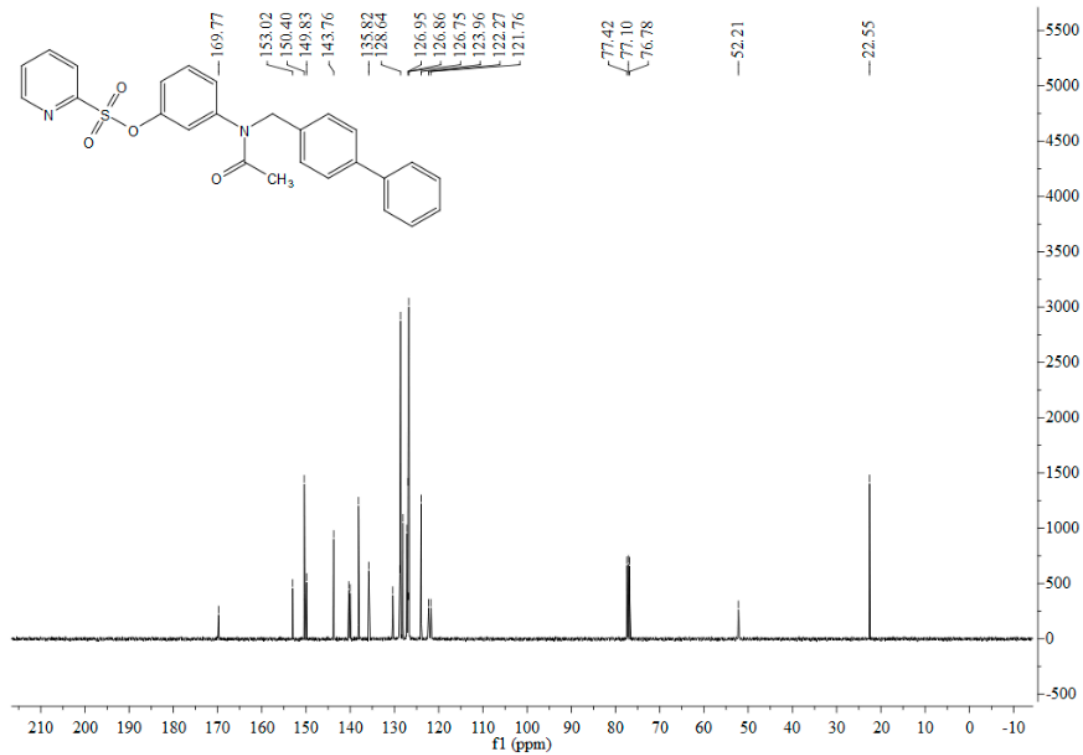
¹³C NMR spectra of compound **1f**



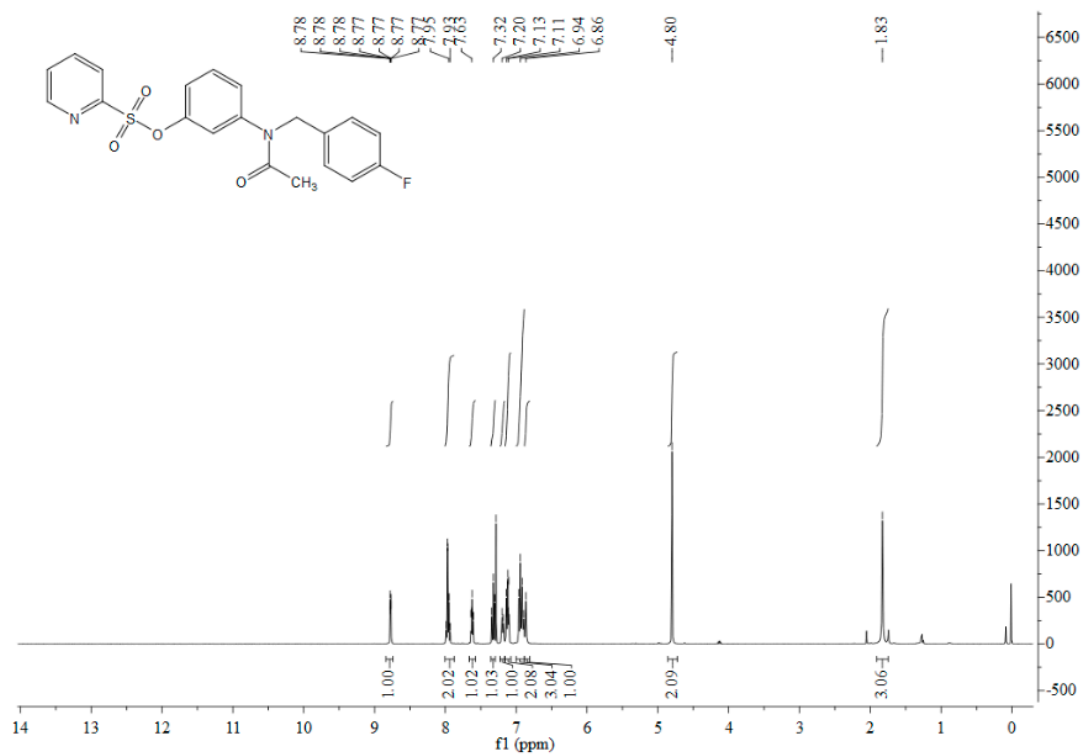
¹H NMR spectra of compound **1g**



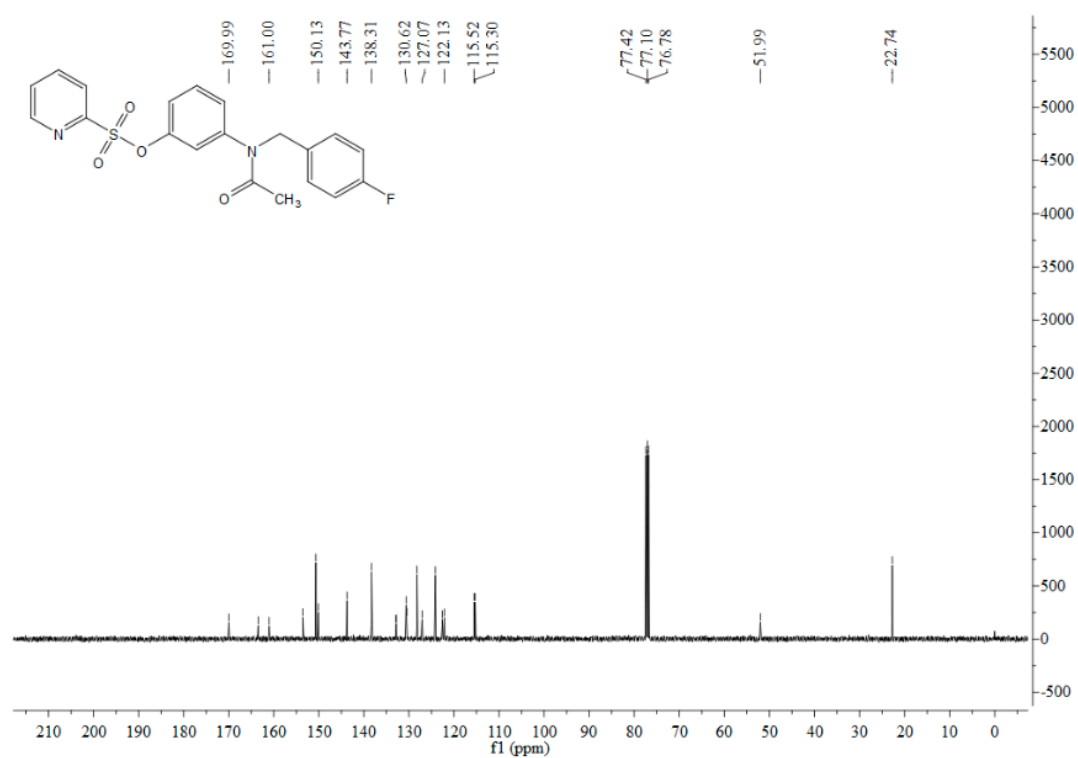
¹³C NMR spectra of compound **1g**



¹H NMR spectra of compound **1h**

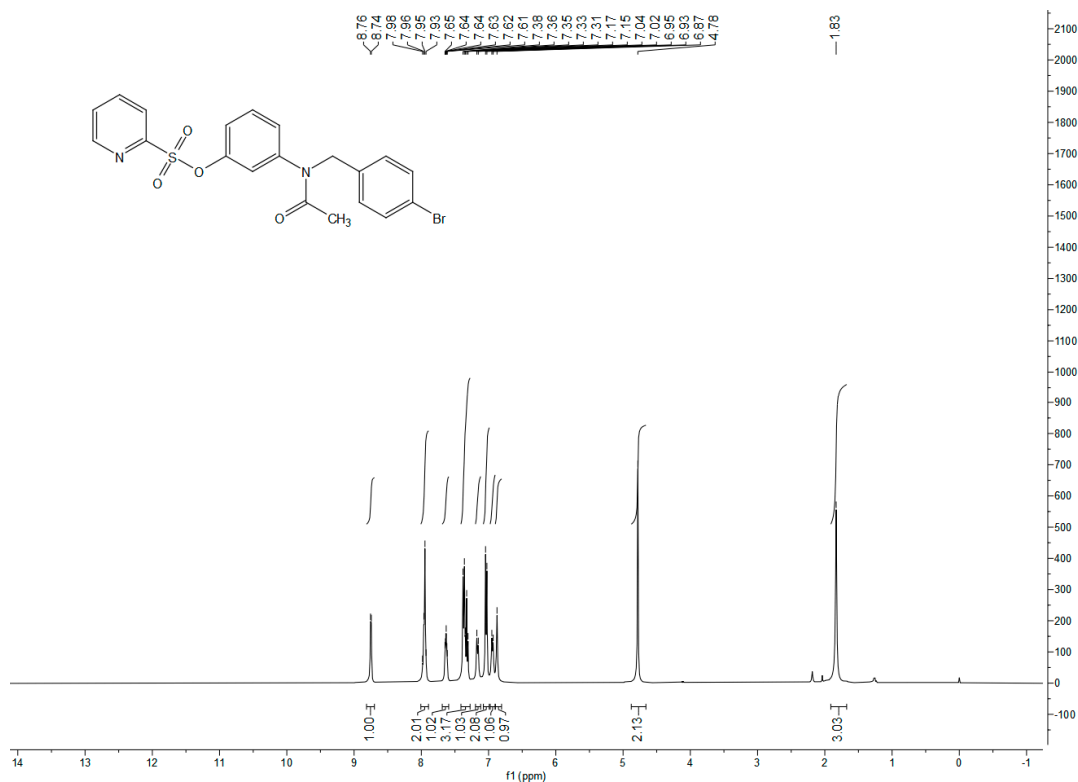


¹³C NMR spectra of compound **1h**

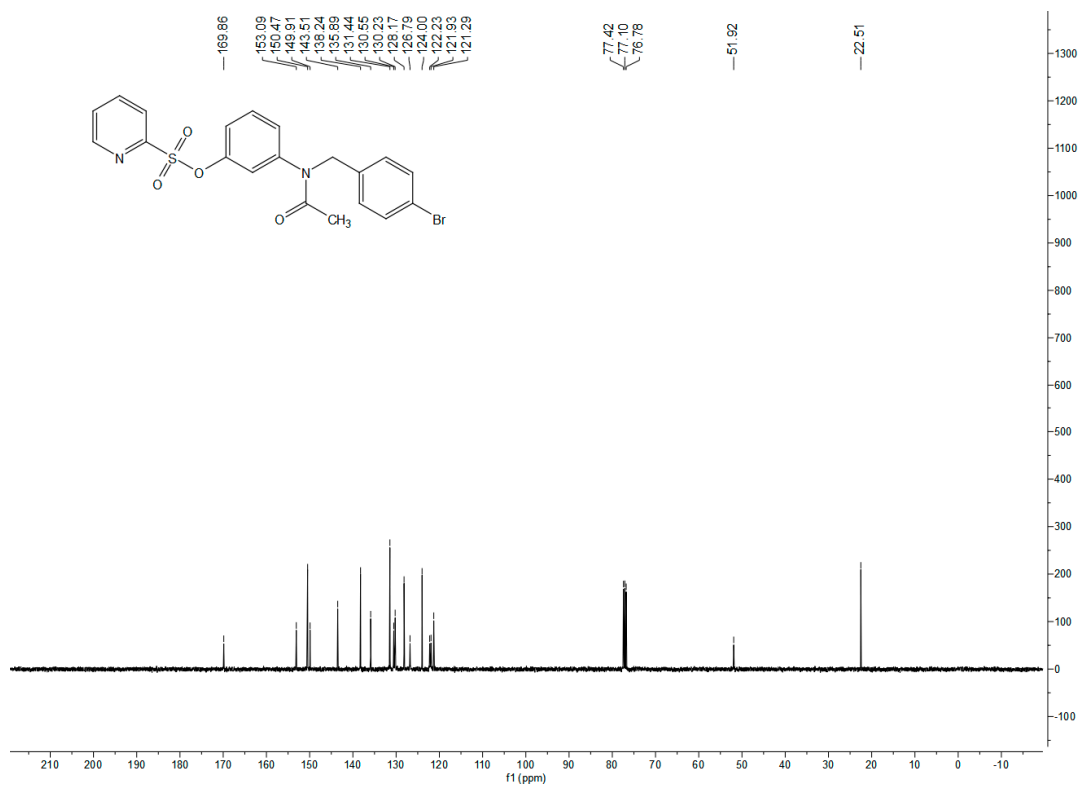


Chemical structure of compound 10 is shown above the spectrum. The spectrum displays peaks corresponding to the following chemical shifts (ppm): 169.94, 153.28, 150.55, 150.01, 143.64, 138.27, 130.60, 130.00, 128.59, 128.19, 126.88, 124.06, 122.36, 122.03, 77.42, 77.10, 76.78, 51.95, and 22.60.

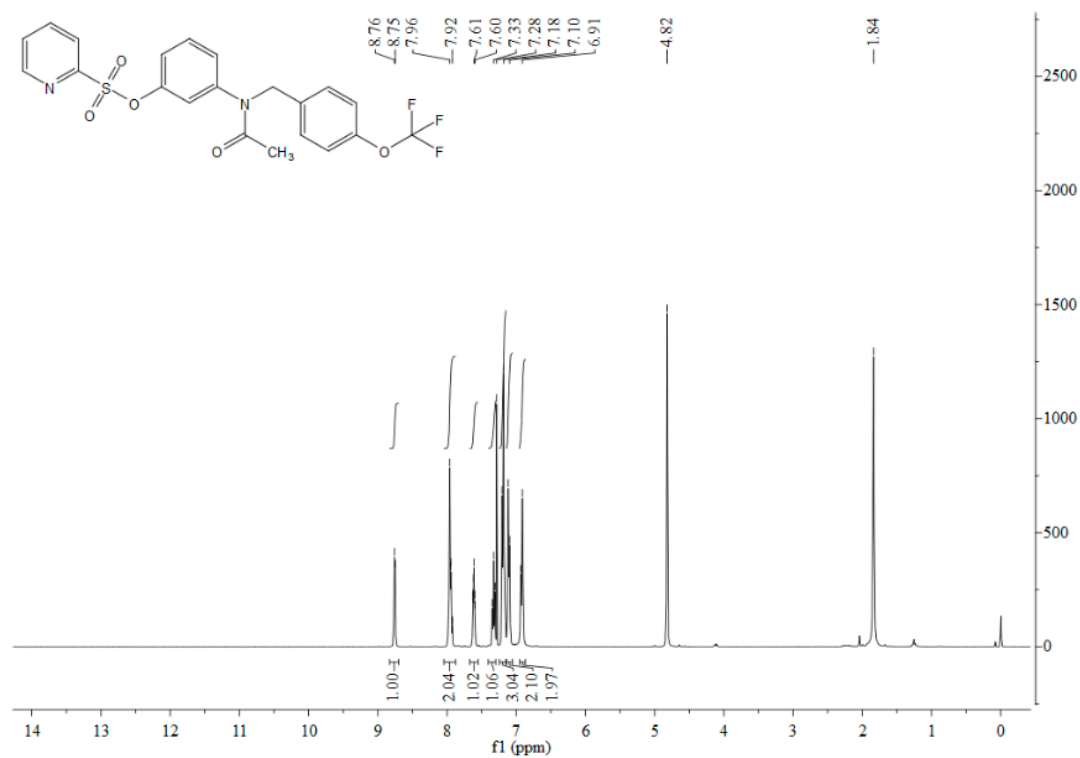
¹H NMR spectra of compound **1j**



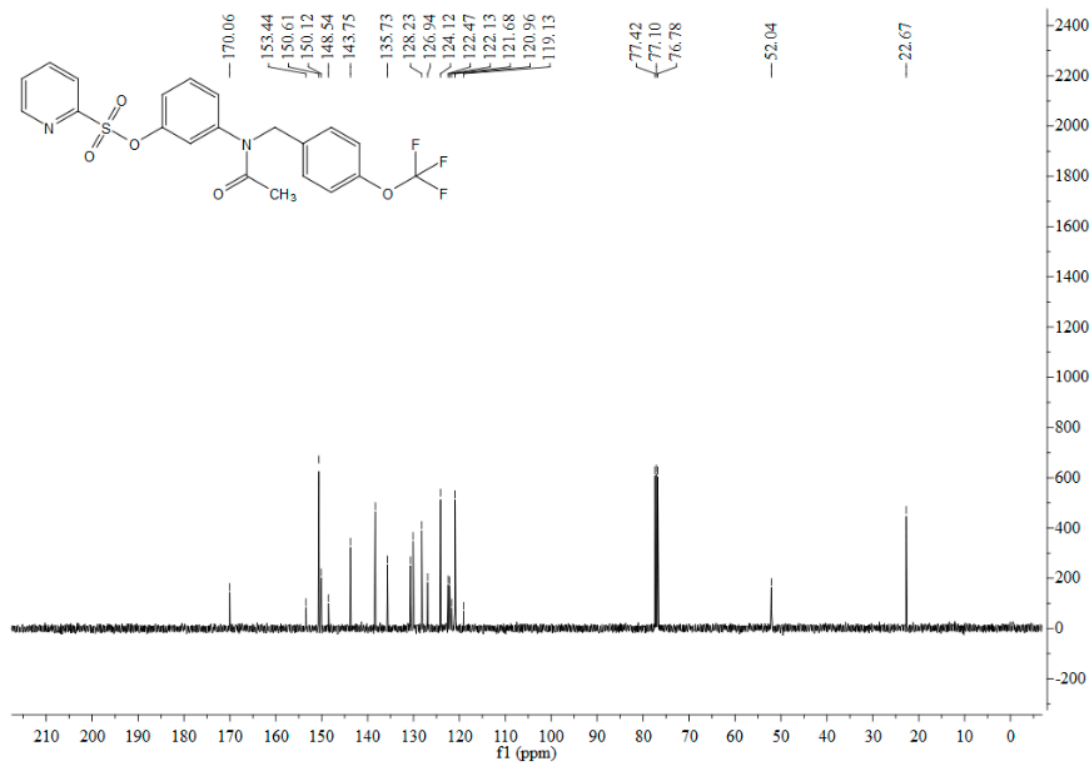
¹³C NMR spectra of compound **1j**



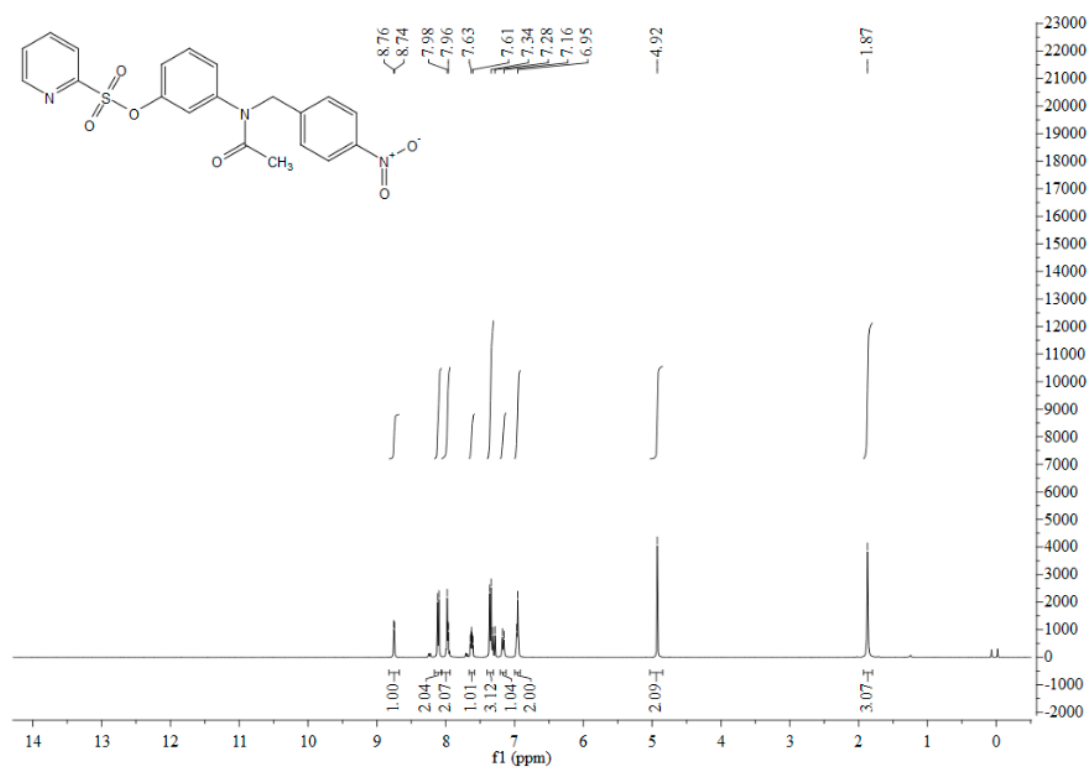
¹H NMR spectra of compound **1k**



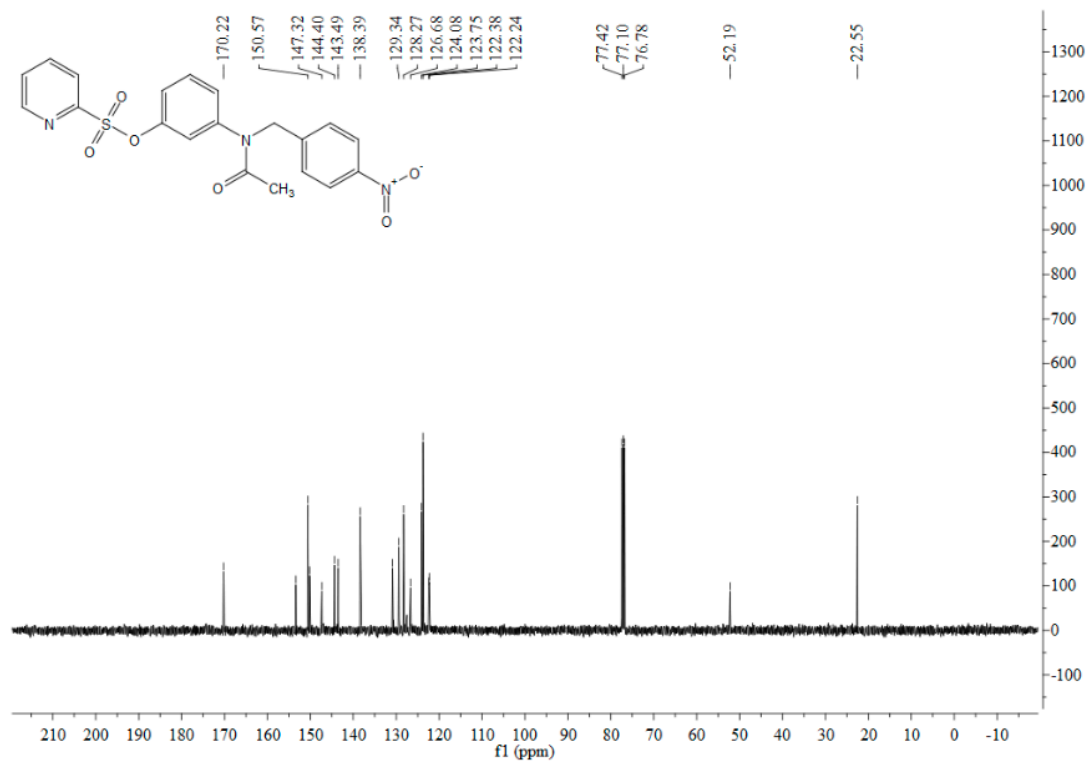
¹³C NMR spectra of compound **1k**



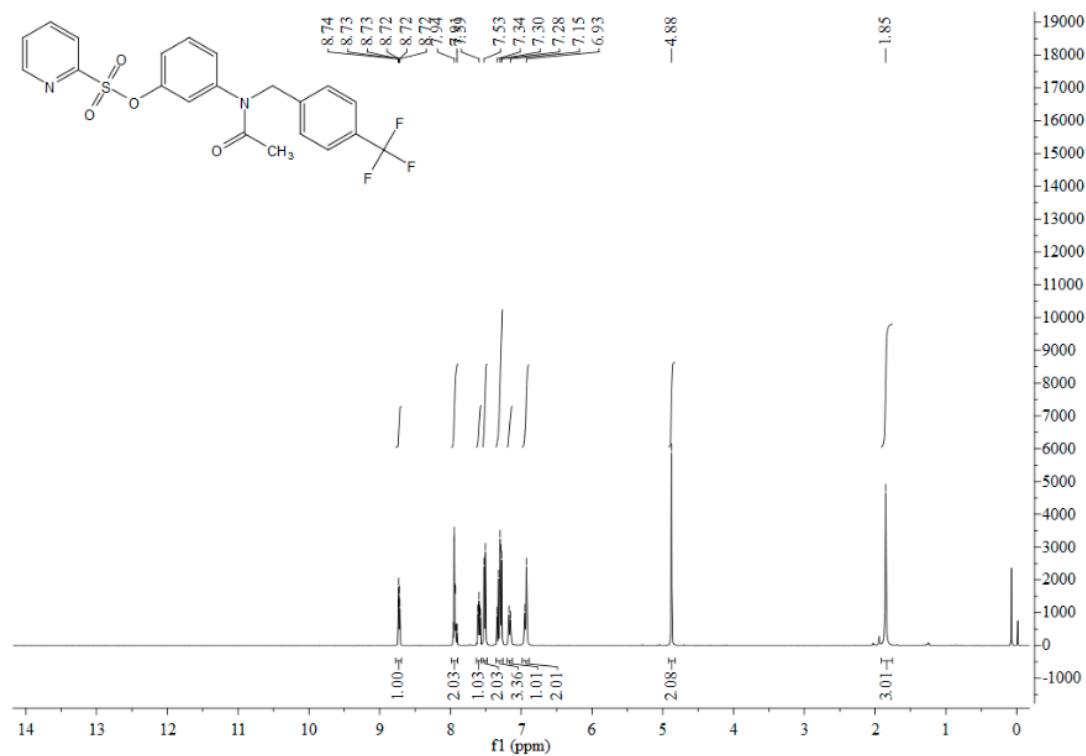
¹H NMR spectra of compound **11**



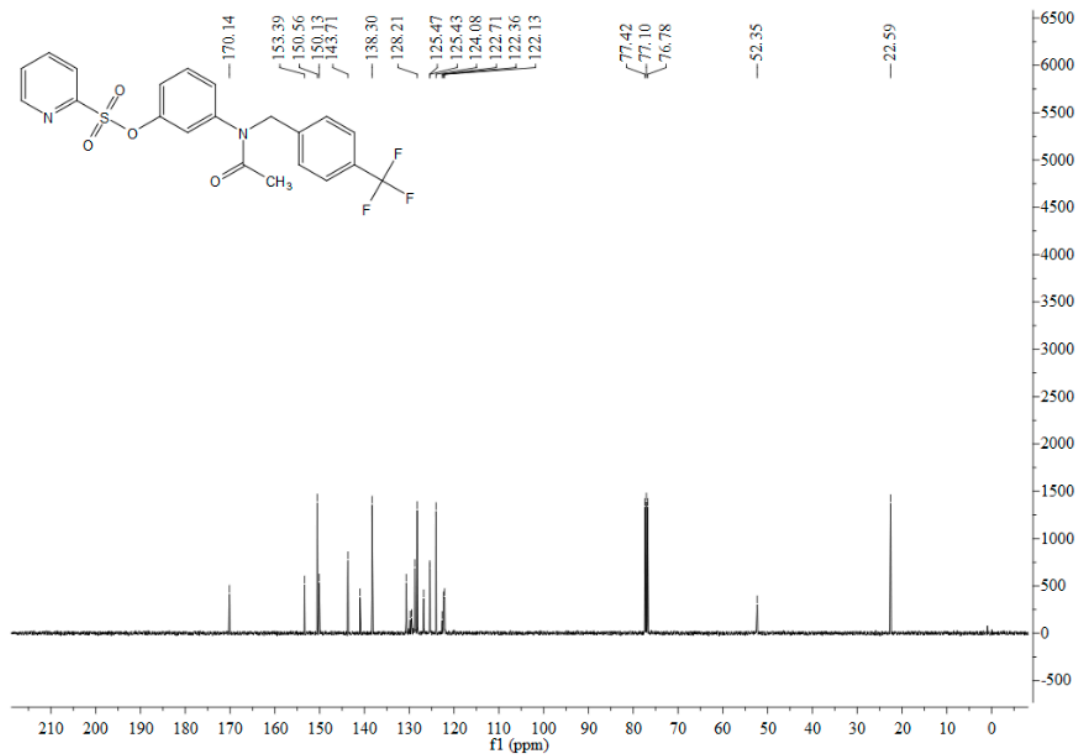
¹³C NMR spectra of compound **11**



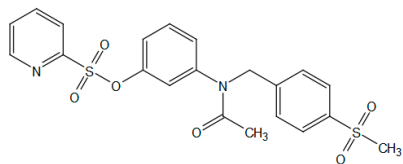
¹H NMR spectra of compound **1m**



¹³C NMR spectra of compound **1m**

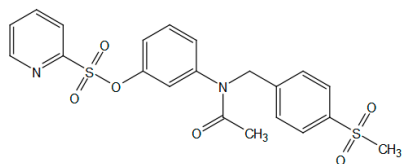


8.75
8.74
7.98
7.97
7.97
7.96
7.96
7.96
7.87
7.85
7.65
7.64
7.63
7.62
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7.27
7.19
7.17
6.99
6.97
6.91
4.93

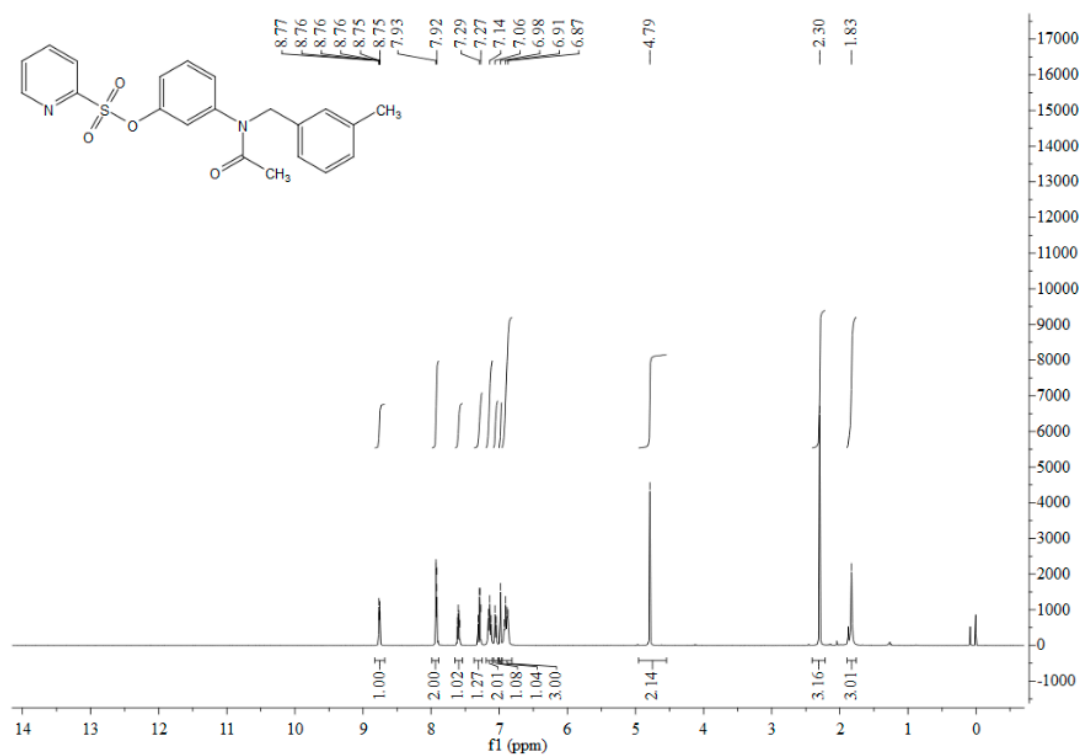


— 169.95

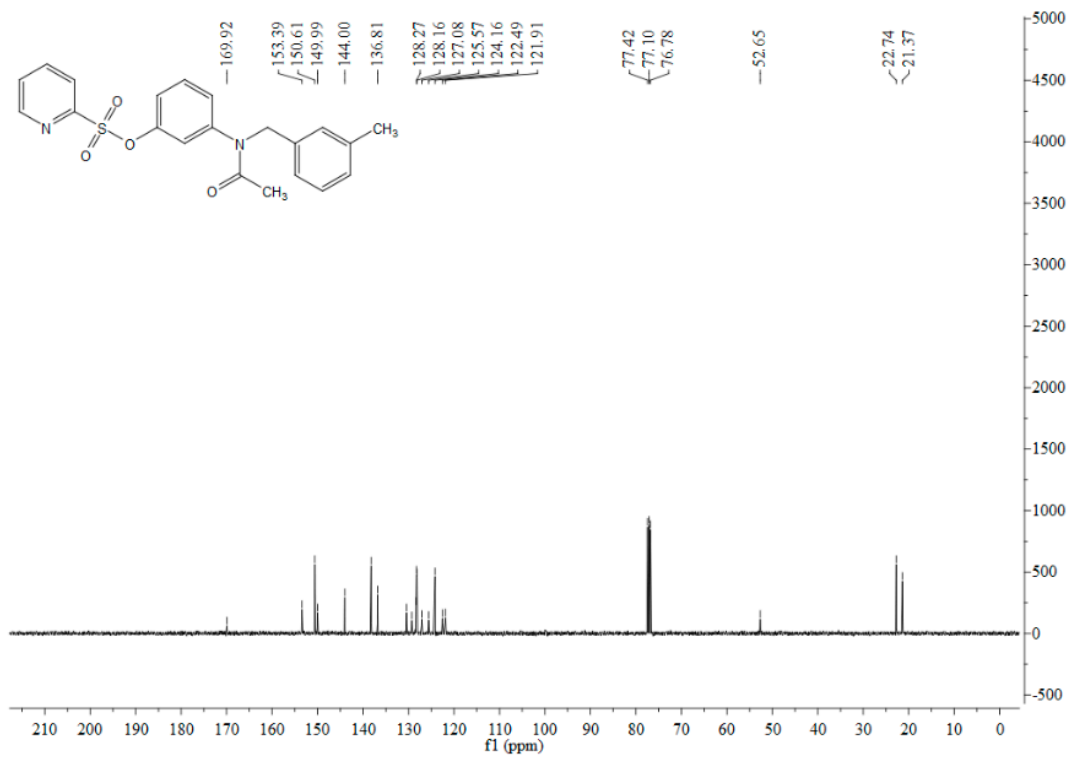
152.73
150.37
149.73
143.24
143.02
139.31
138.30
130.64
128.98
128.26
127.34
126.48
123.90
122.09
121.85



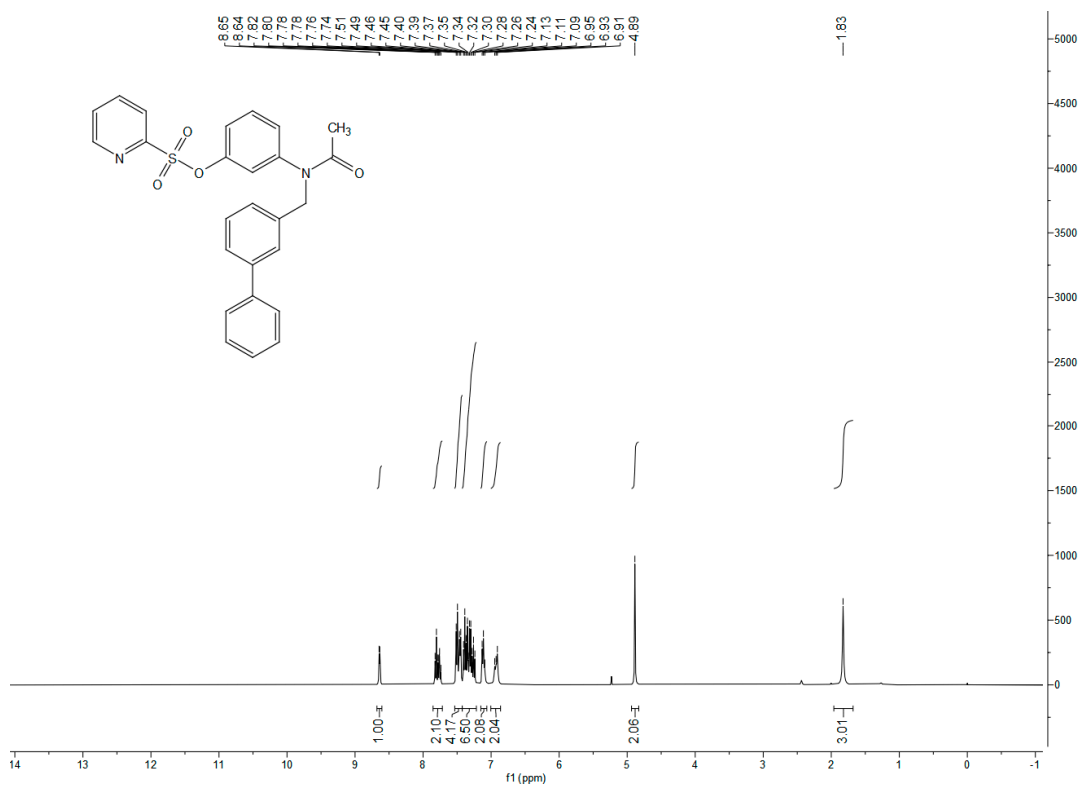
¹H NMR spectra of compound **1o**



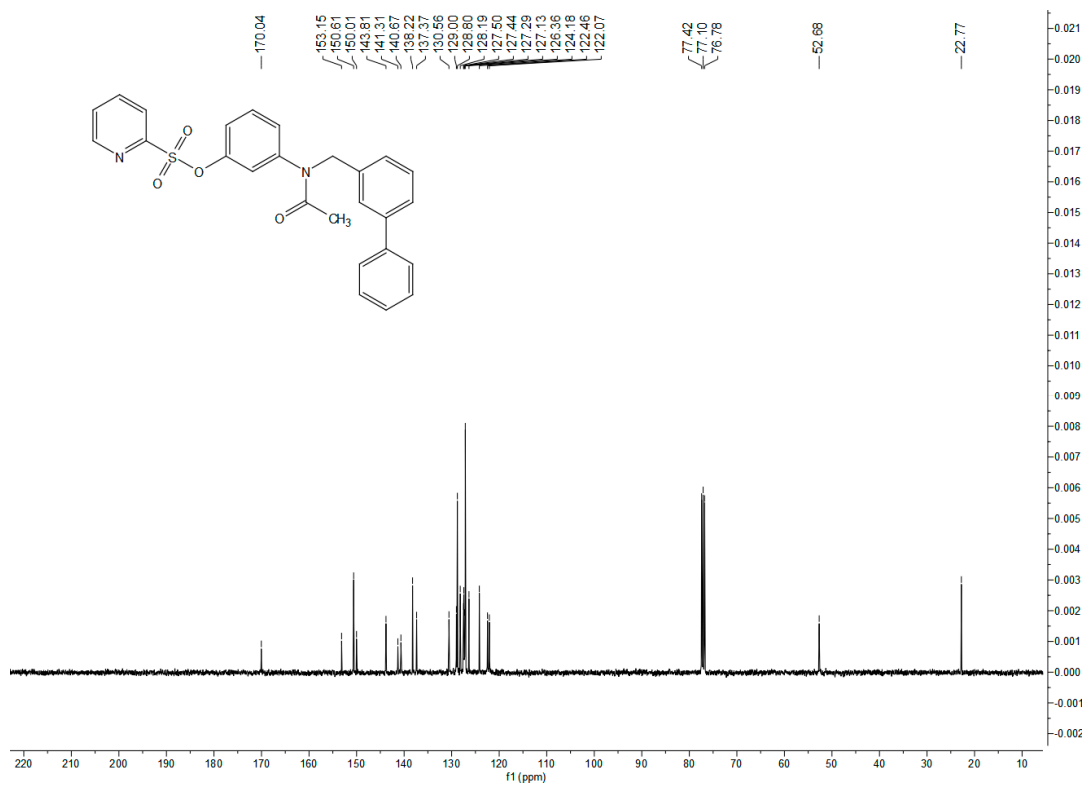
¹³C NMR spectra of compound **1o**



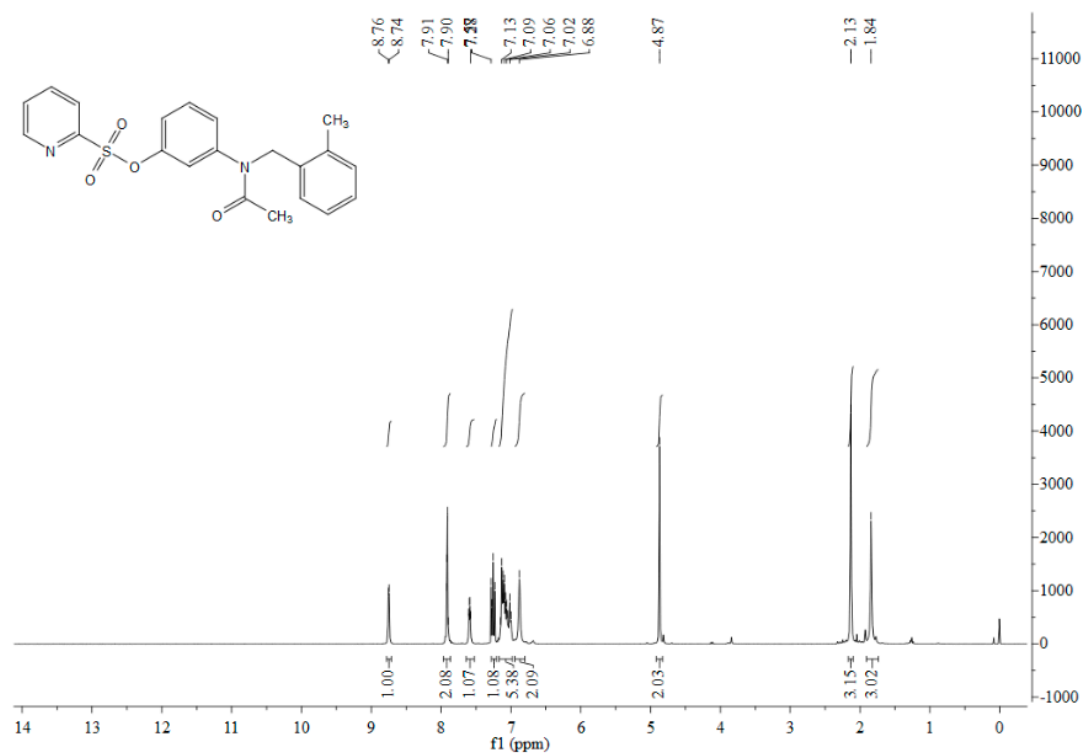
¹H NMR spectra of compound **1p**



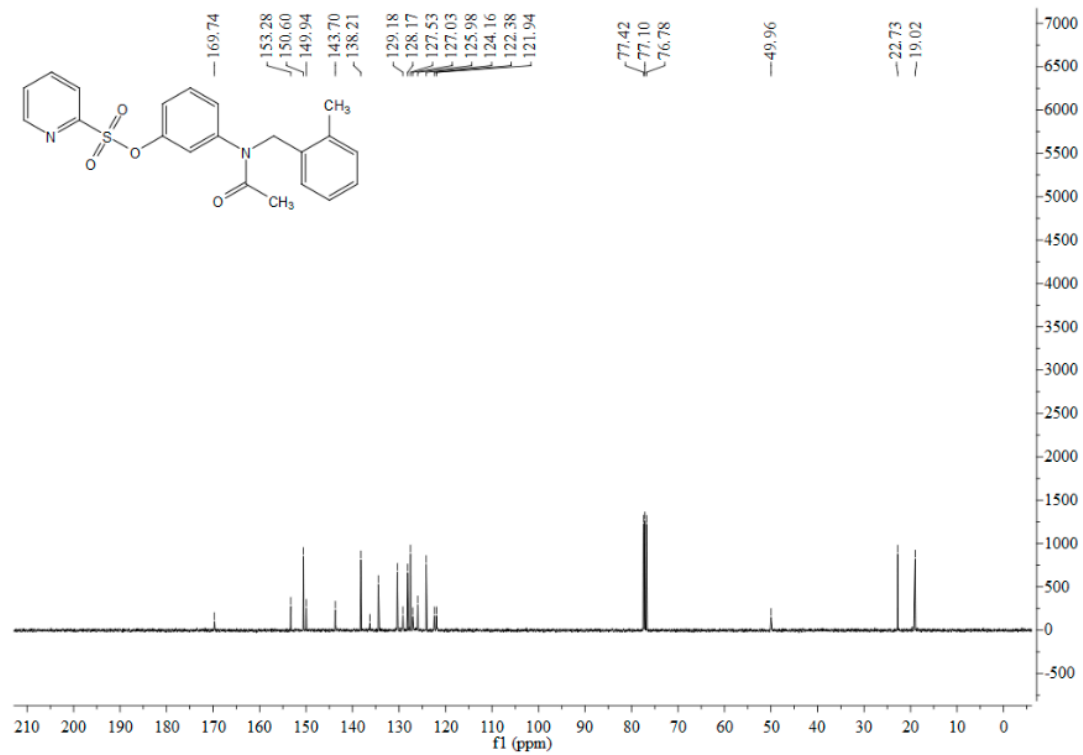
¹³C NMR spectra of compound **1p**



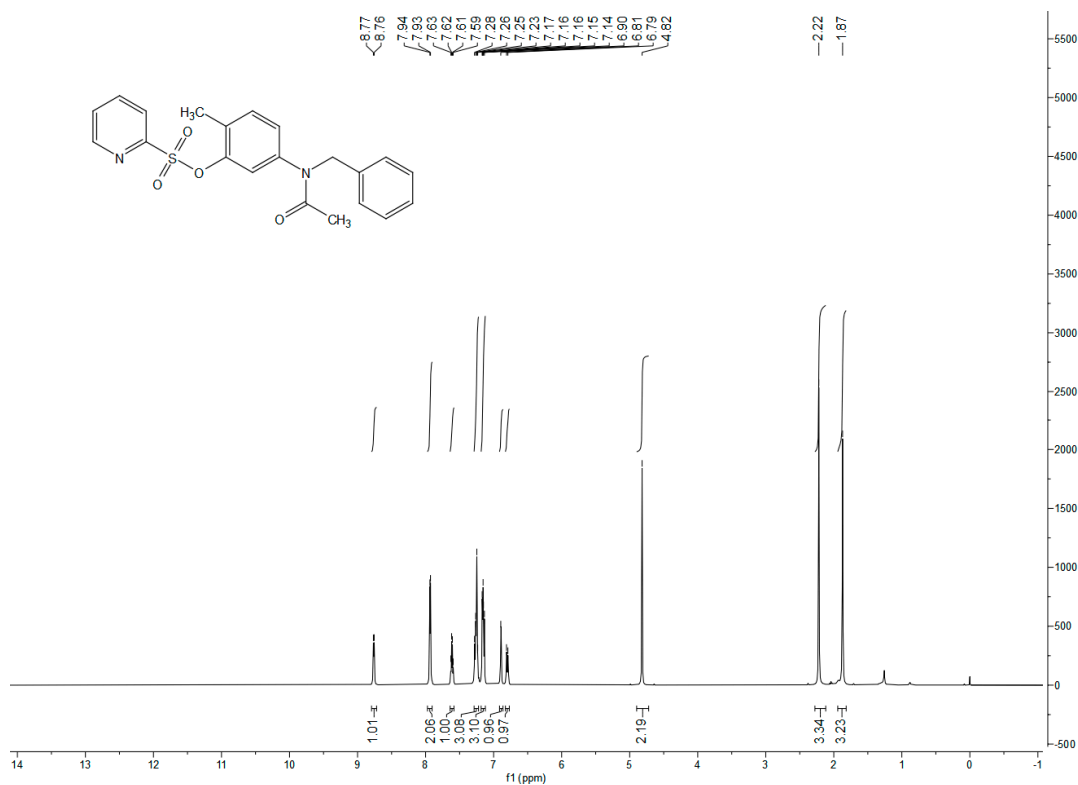
¹H NMR spectra of compound **1q**



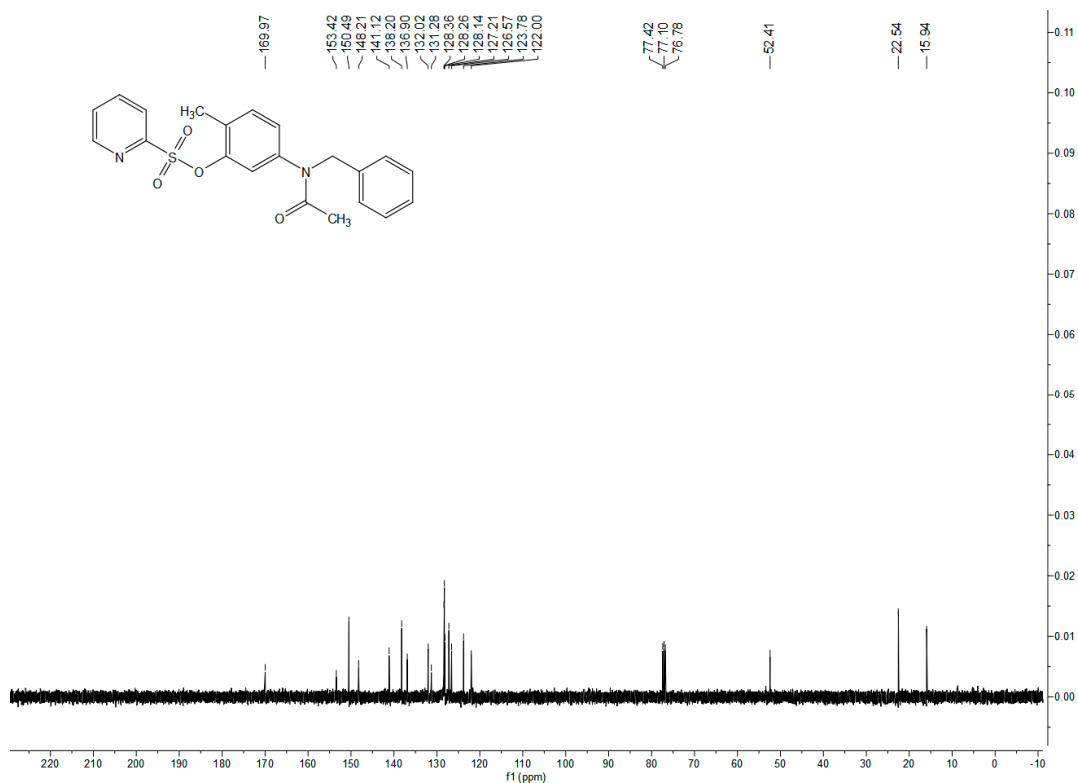
¹³C NMR spectra of compound **1q**



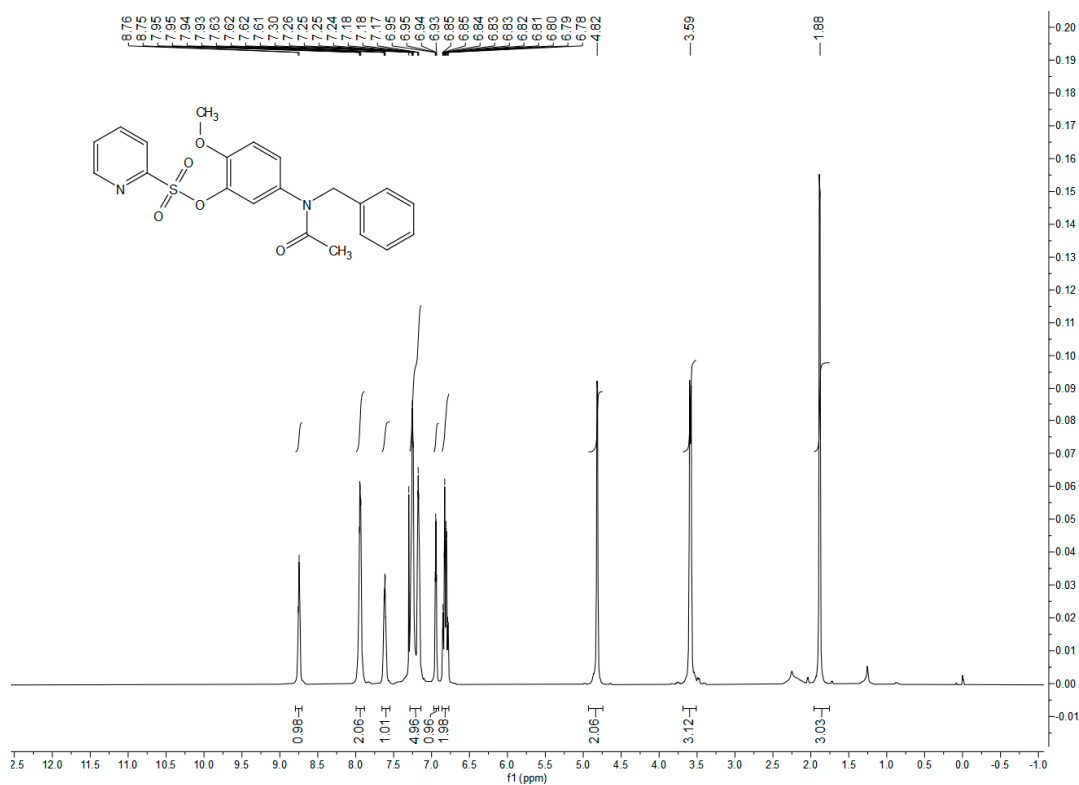
¹H NMR spectra of compound 1r



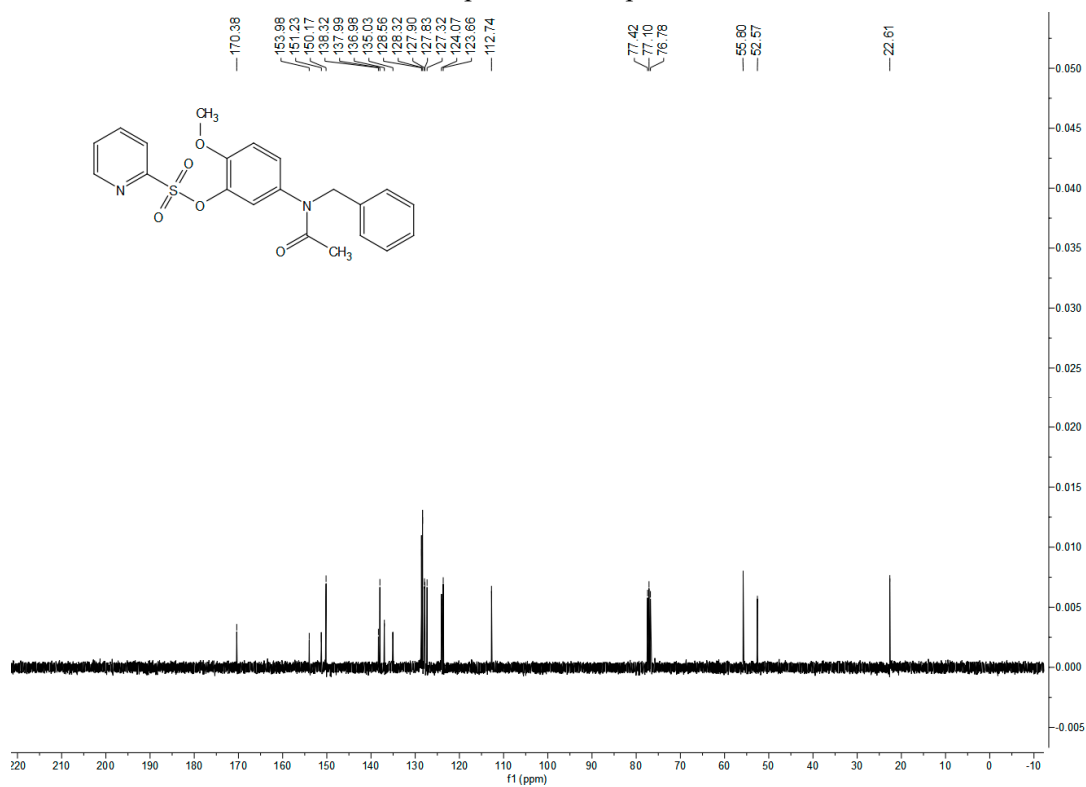
¹³C NMR spectra of compound 1r



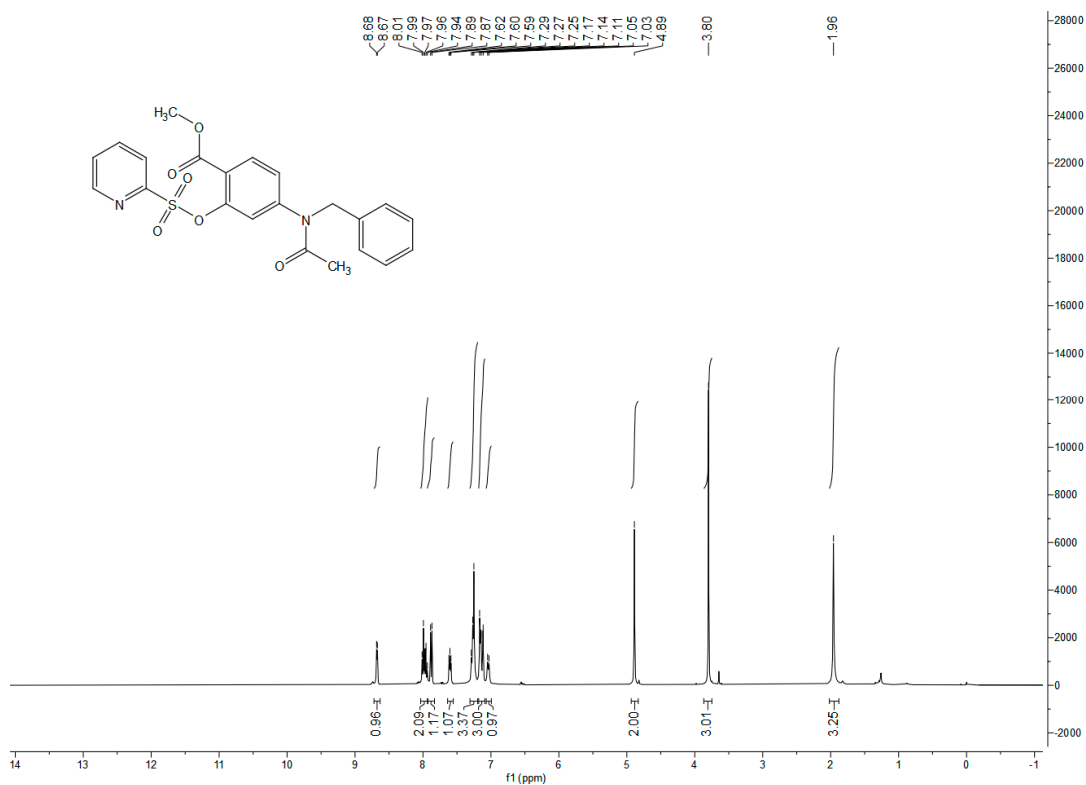
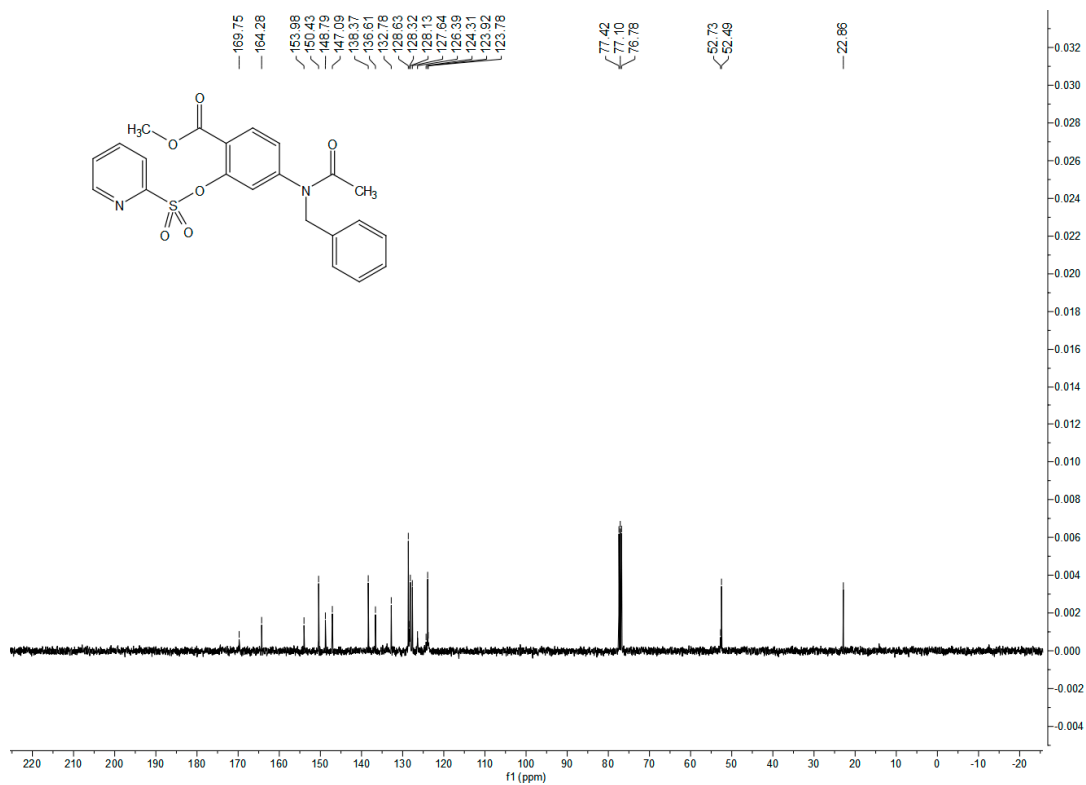
¹H NMR spectra of compound **1s**



¹³C NMR spectra of compound **1s**

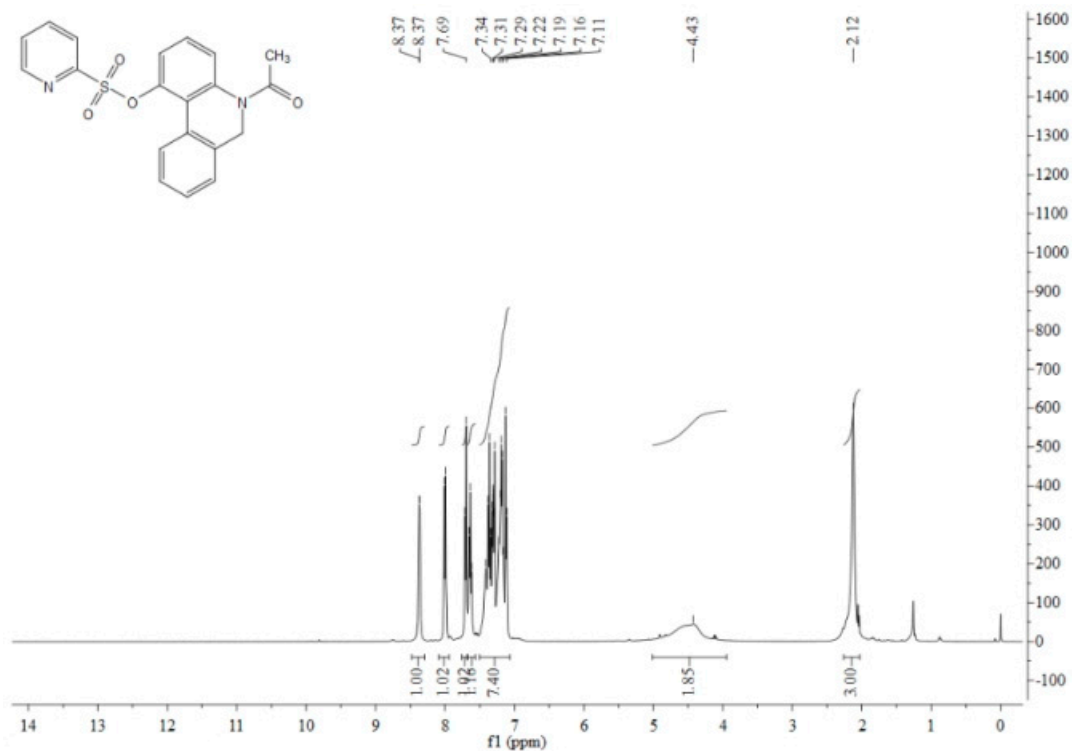


¹H NMR spectra of compound **1t**

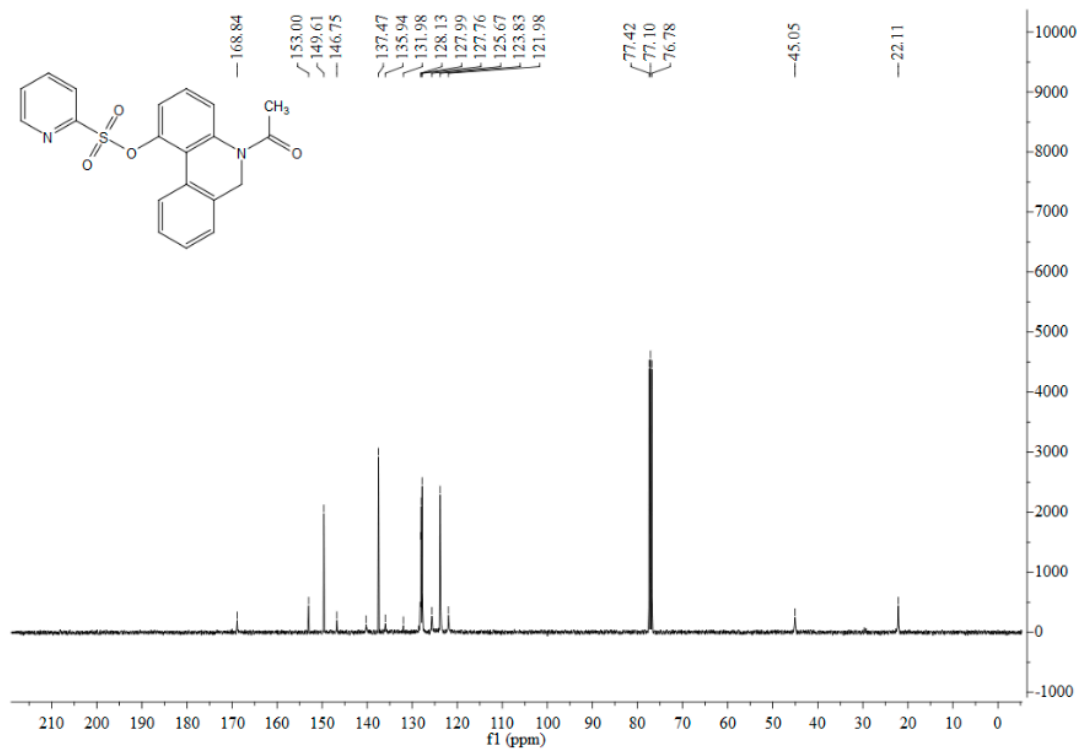
¹³C NMR spectra of compound **1t**

5. Spectral copies of products ^1H NMR and ^{13}C NMR

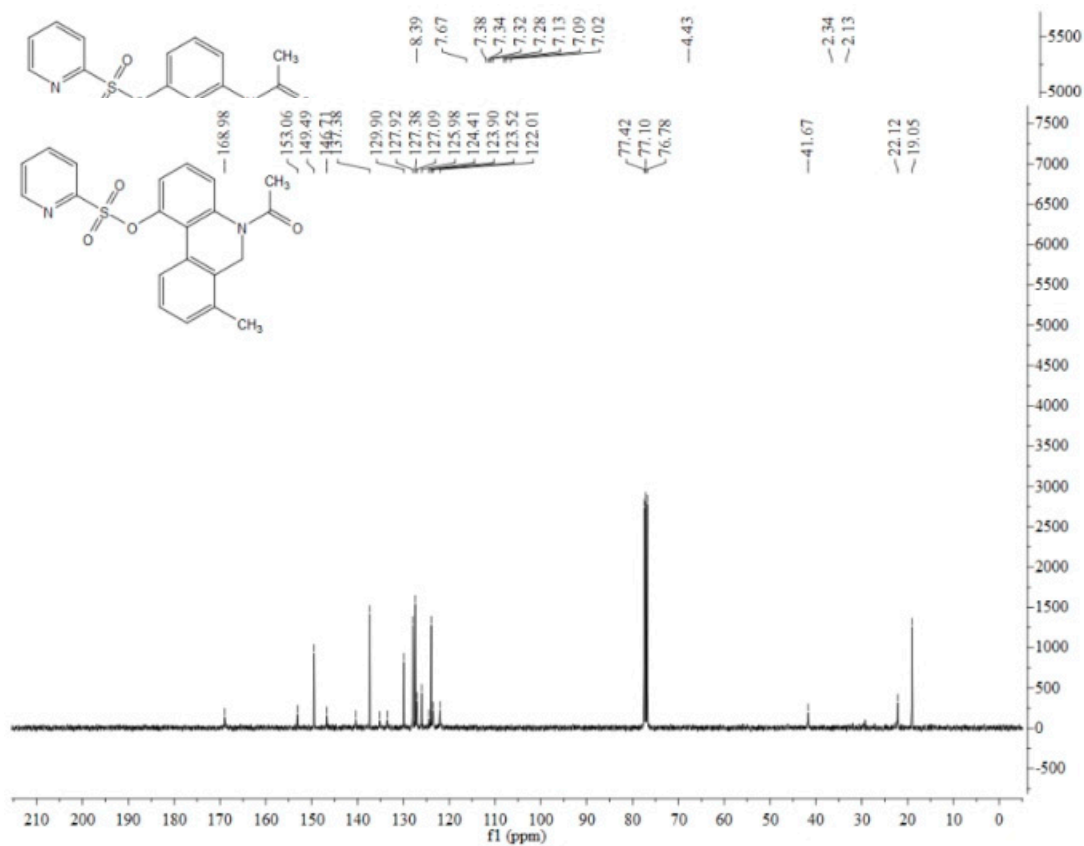
^1H NMR spectra of compound **2a**



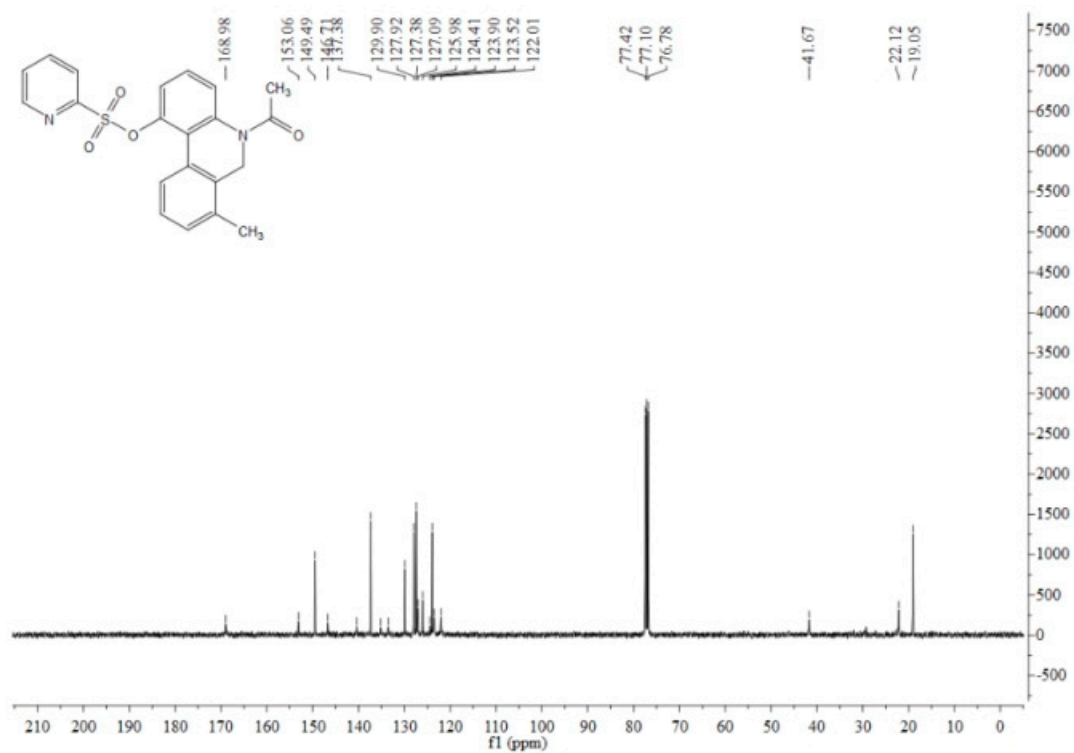
^{13}C NMR spectra of compound **2a**



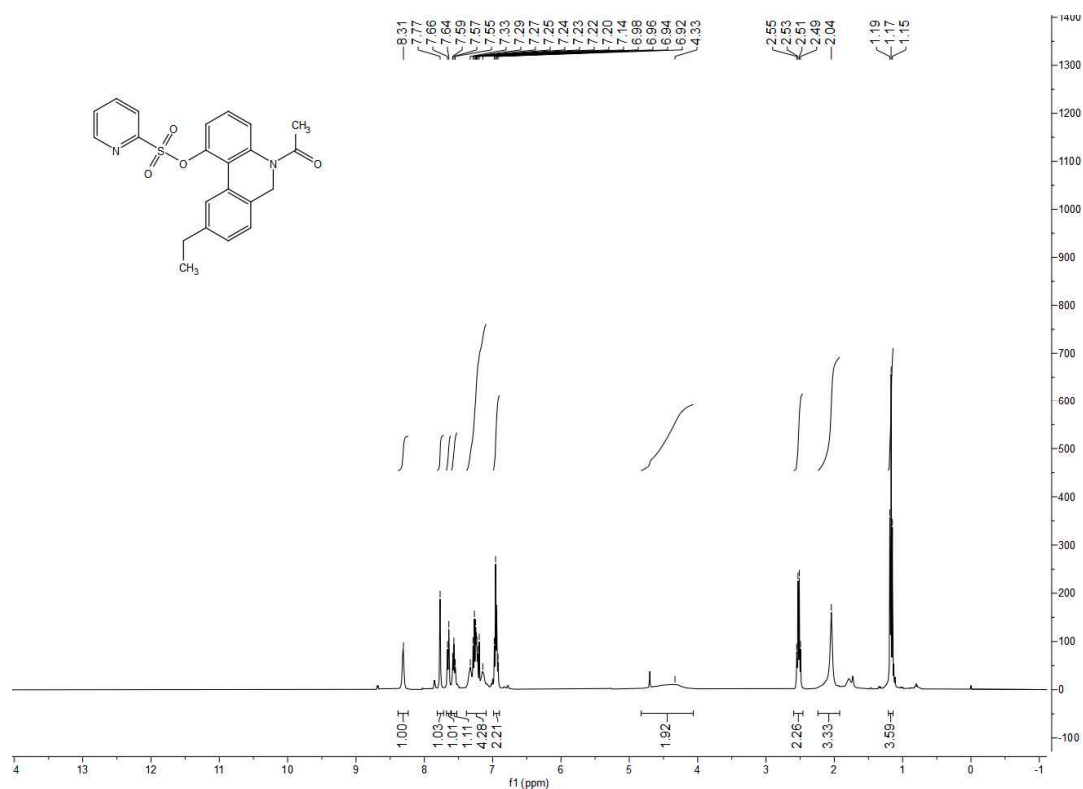
¹H NMR spectra of compound **2b**



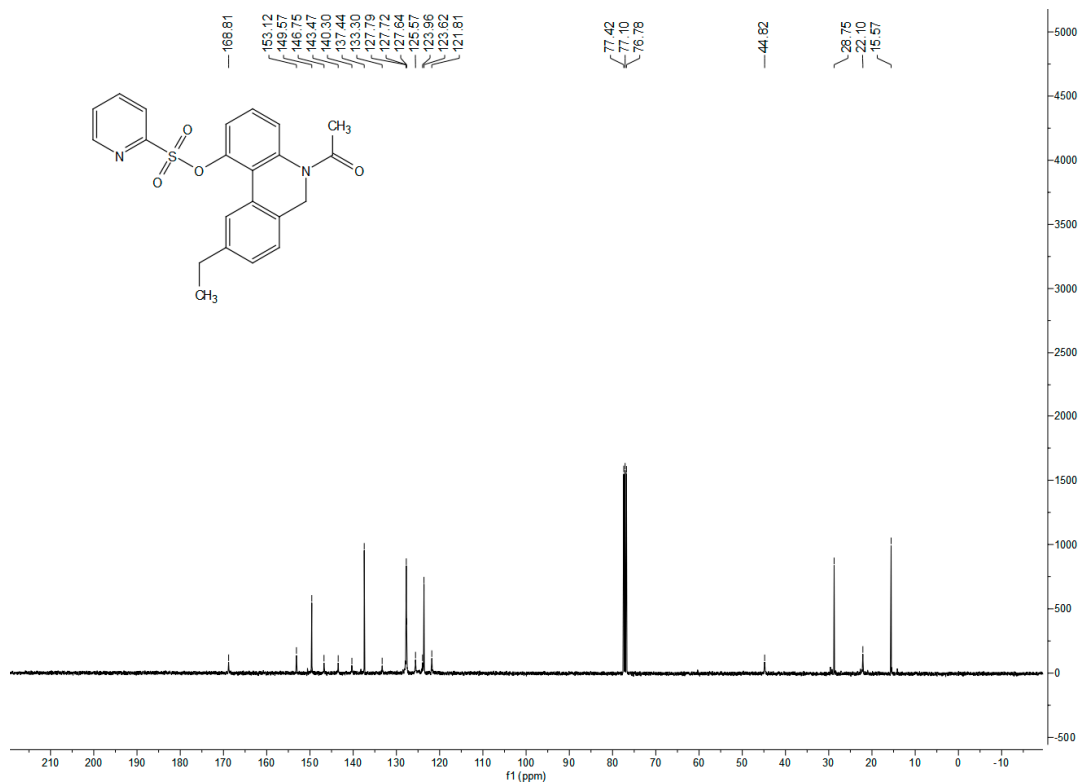
¹³C NMR spectra of compound **2b**



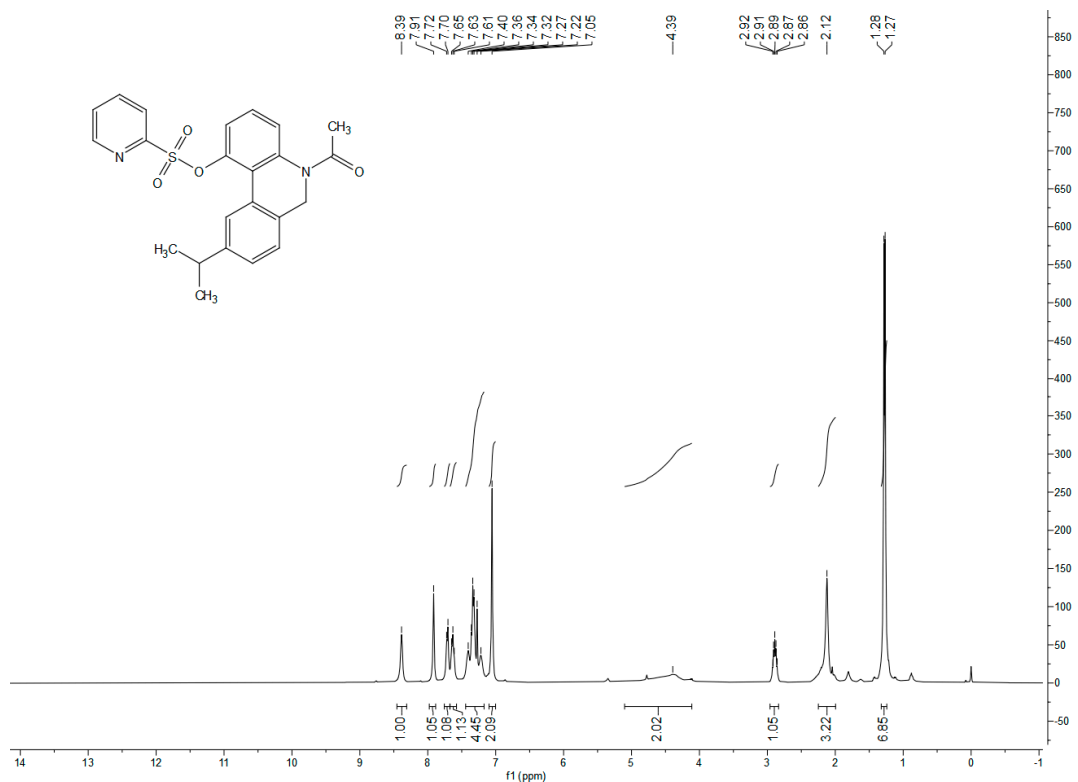
¹H NMR spectra of compound **2c**



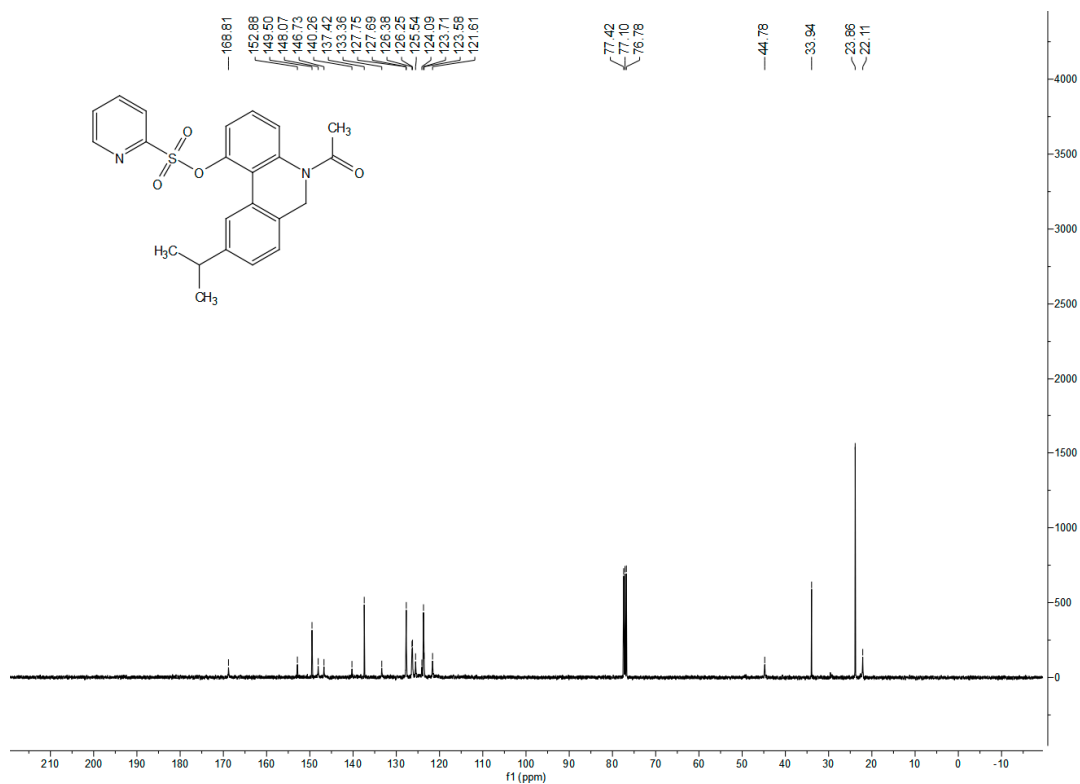
¹³C NMR spectra of compound **2c**



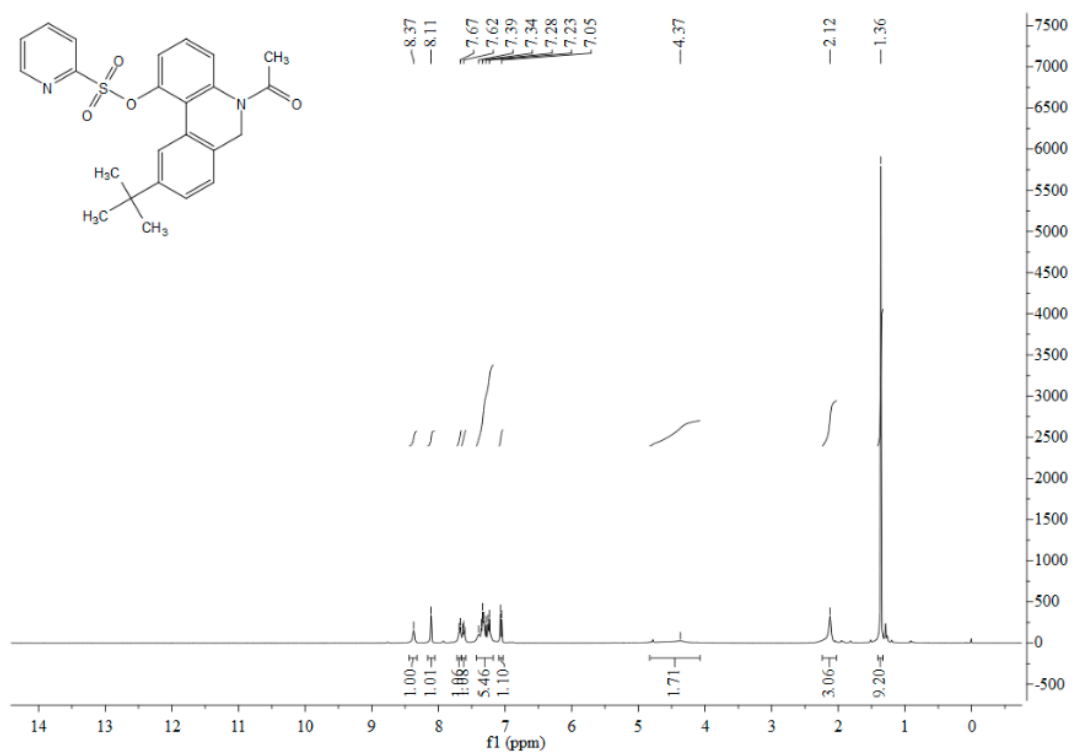
¹H NMR spectra of compound **2d**



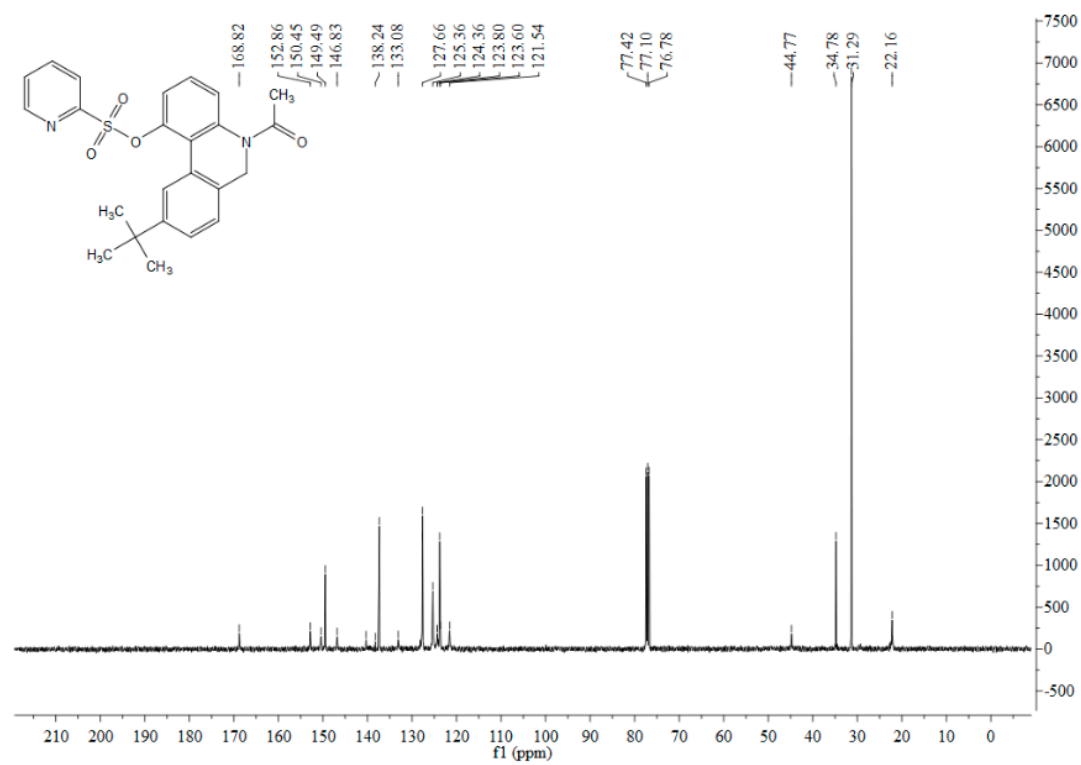
¹³C NMR spectra of compound **2d**



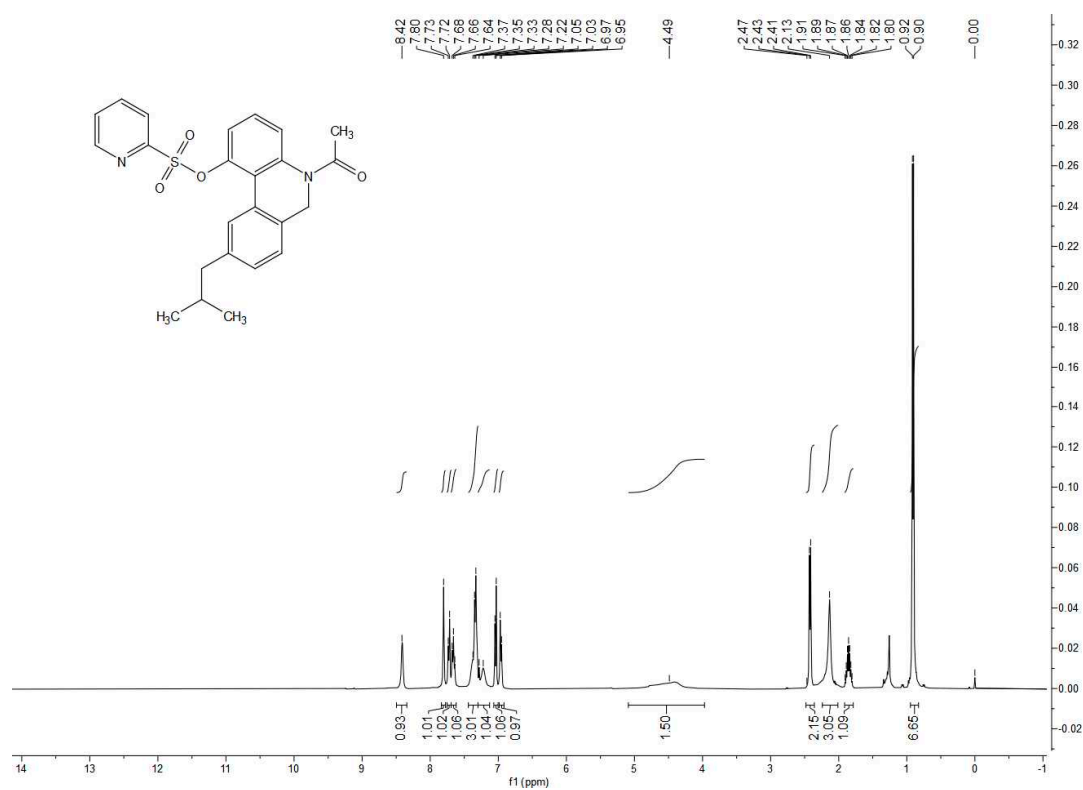
¹H NMR spectra of compound 2e



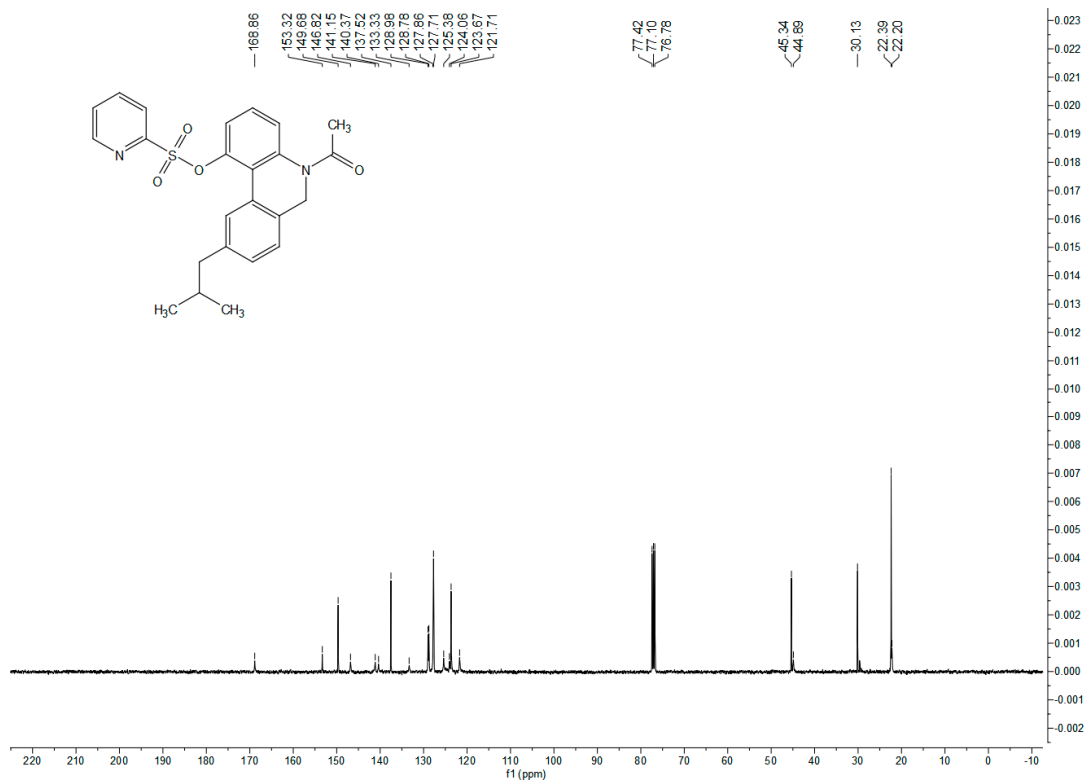
¹³C NMR spectra of compound 2e



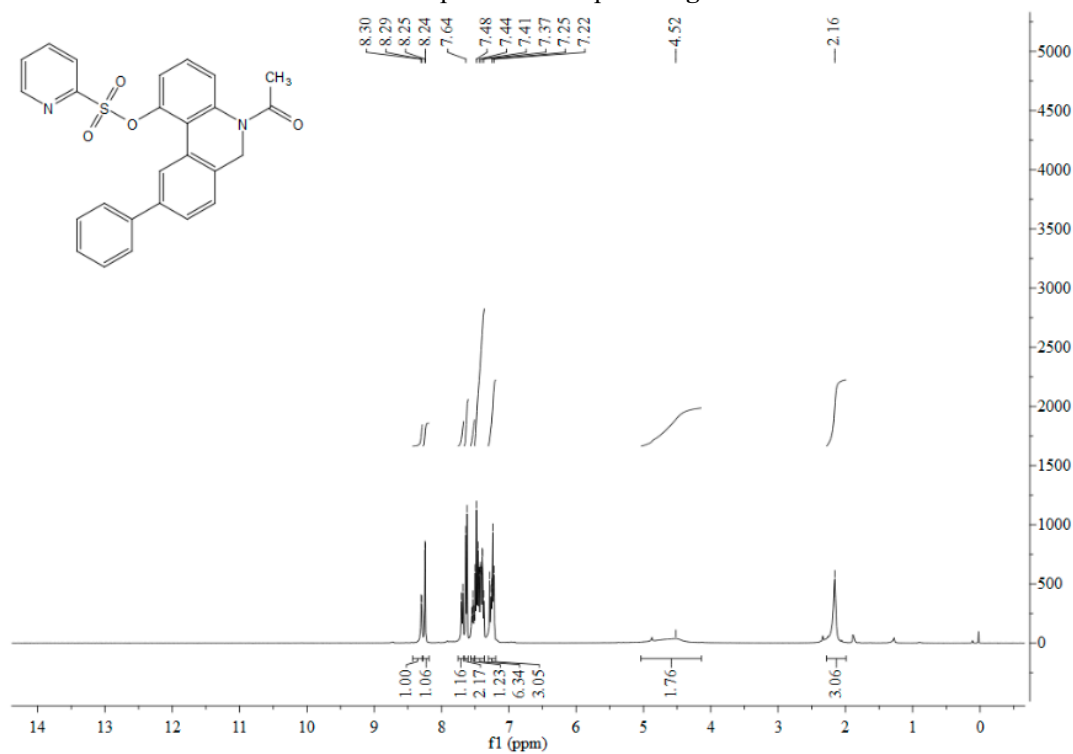
¹H NMR spectra of compound **2f**



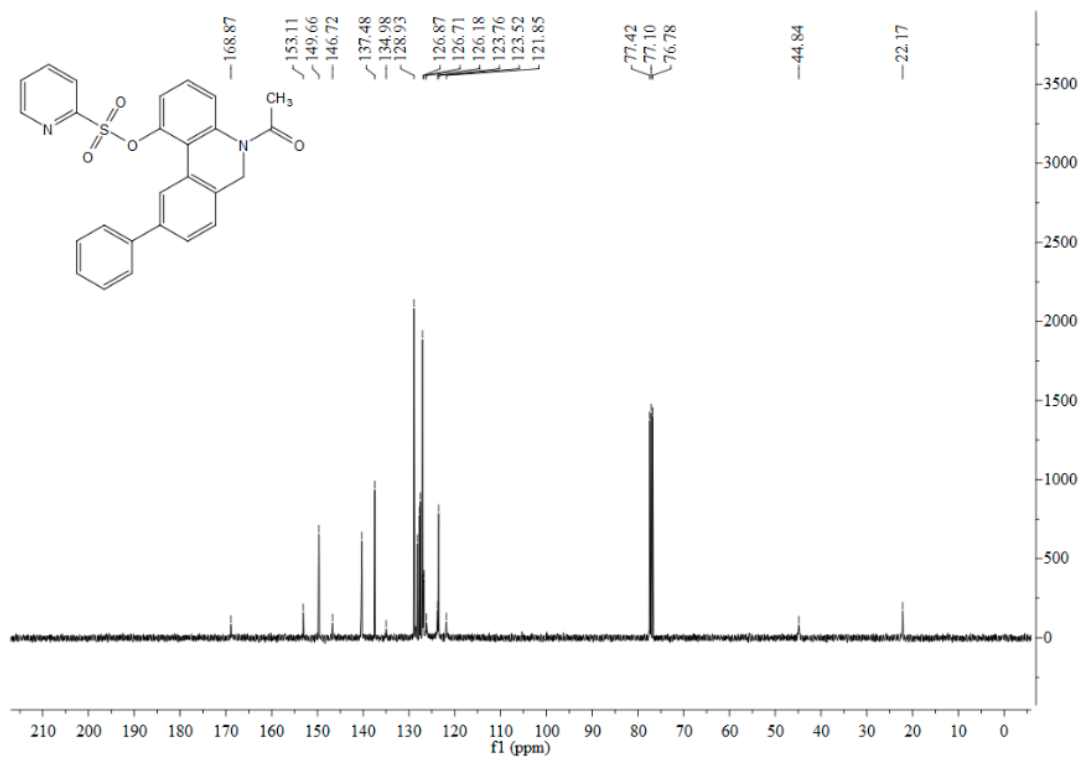
¹³C NMR spectra of compound **2f**



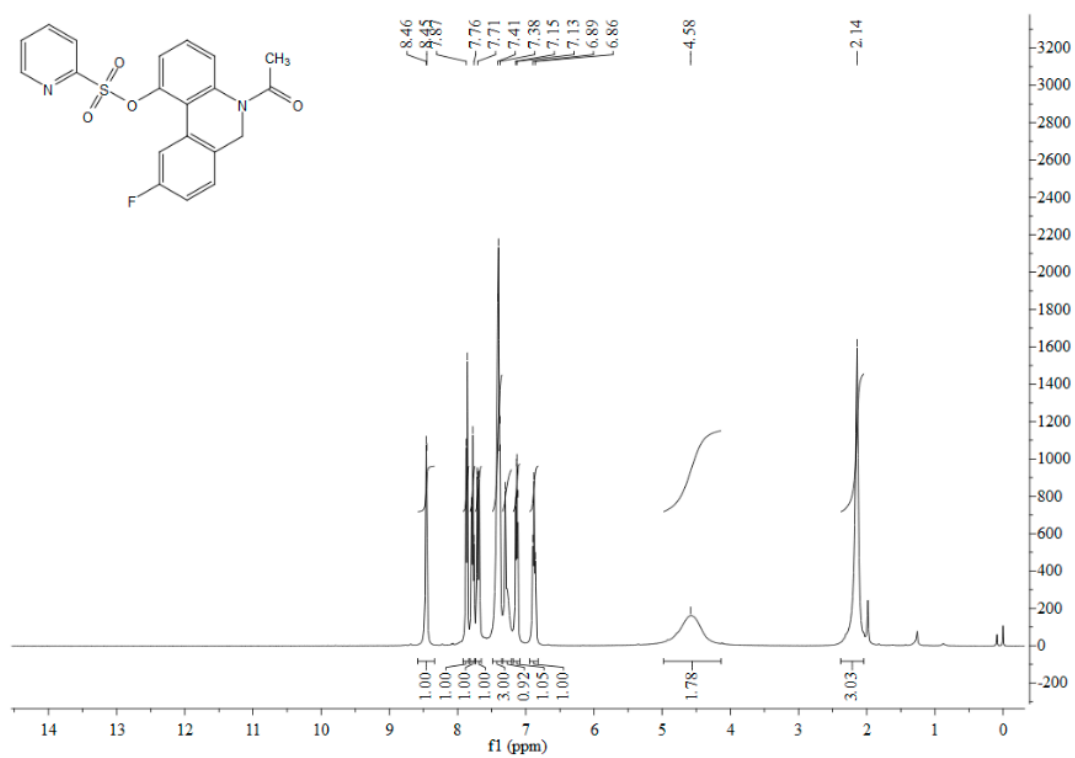
¹H NMR spectra of compound **2g**



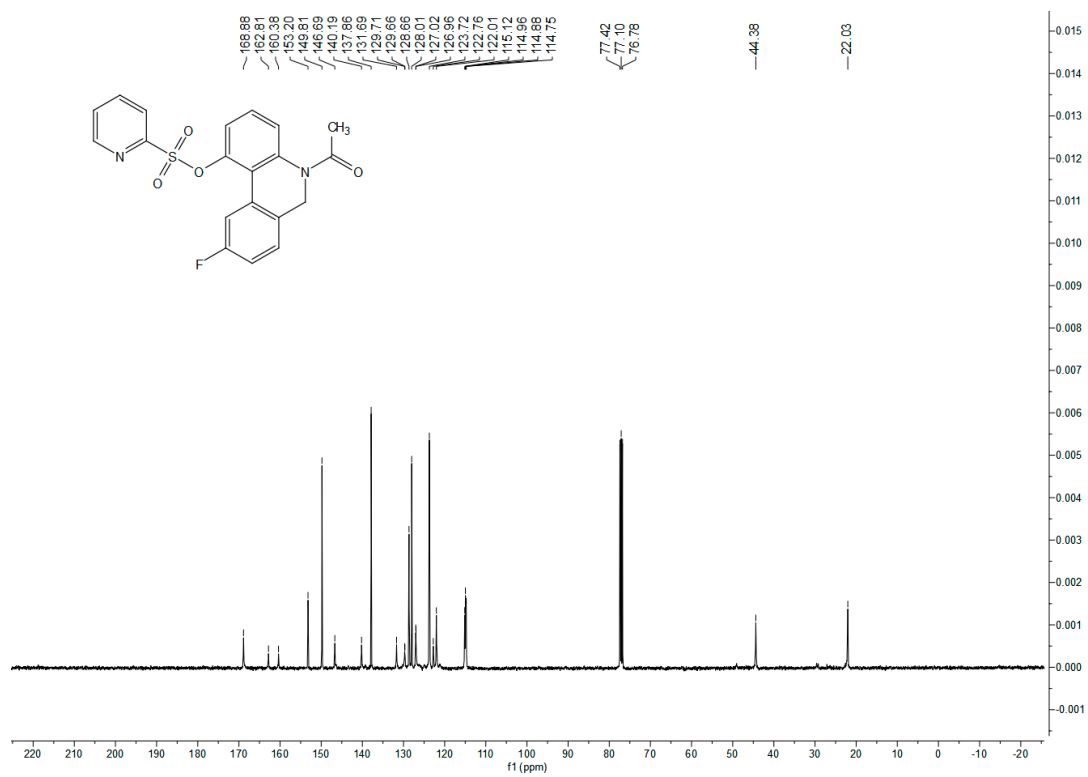
¹³C NMR spectra of compound **2g**



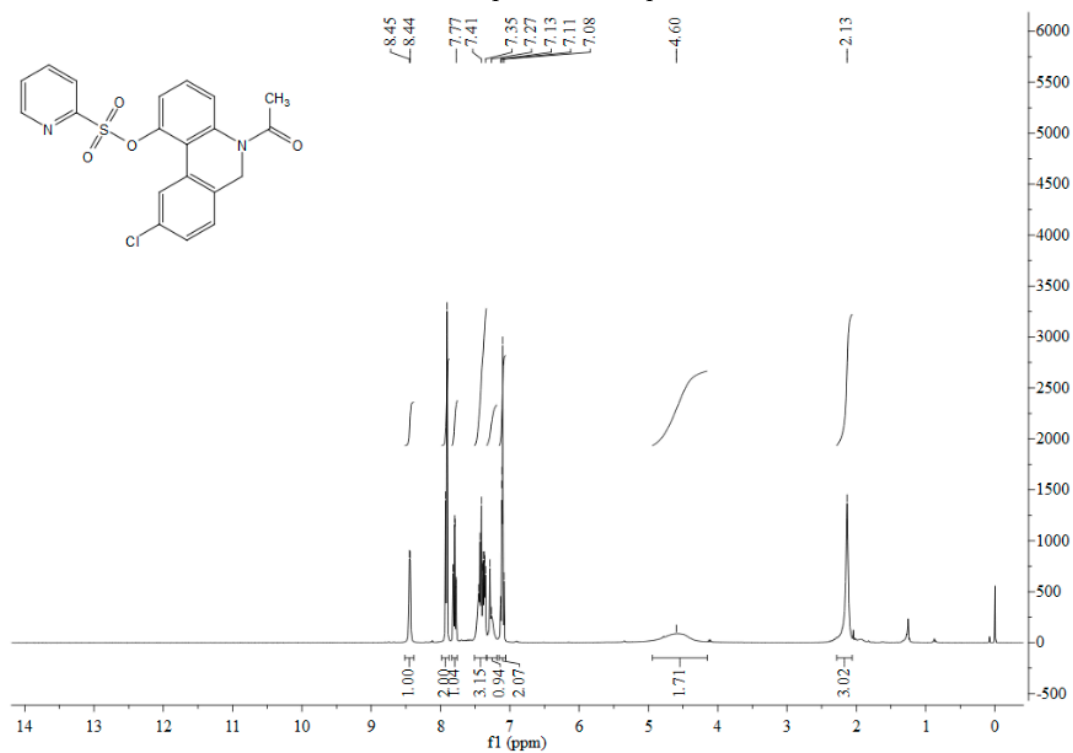
¹H NMR spectra of compound **2h**



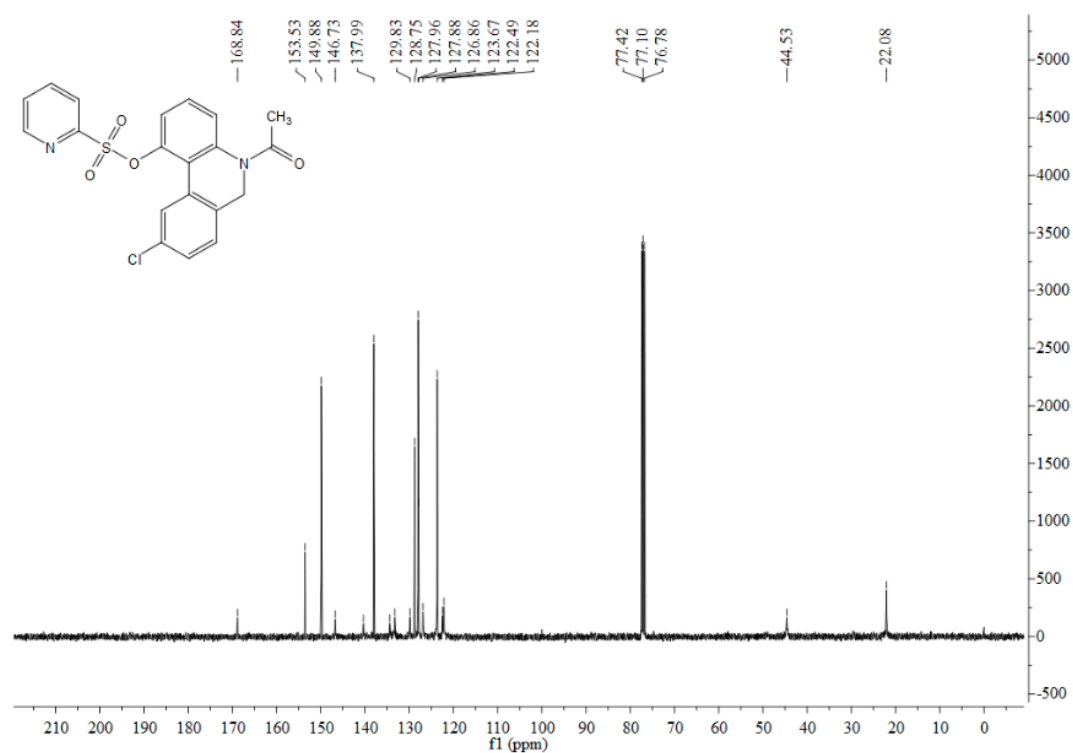
¹³C NMR spectra of compound **2h**



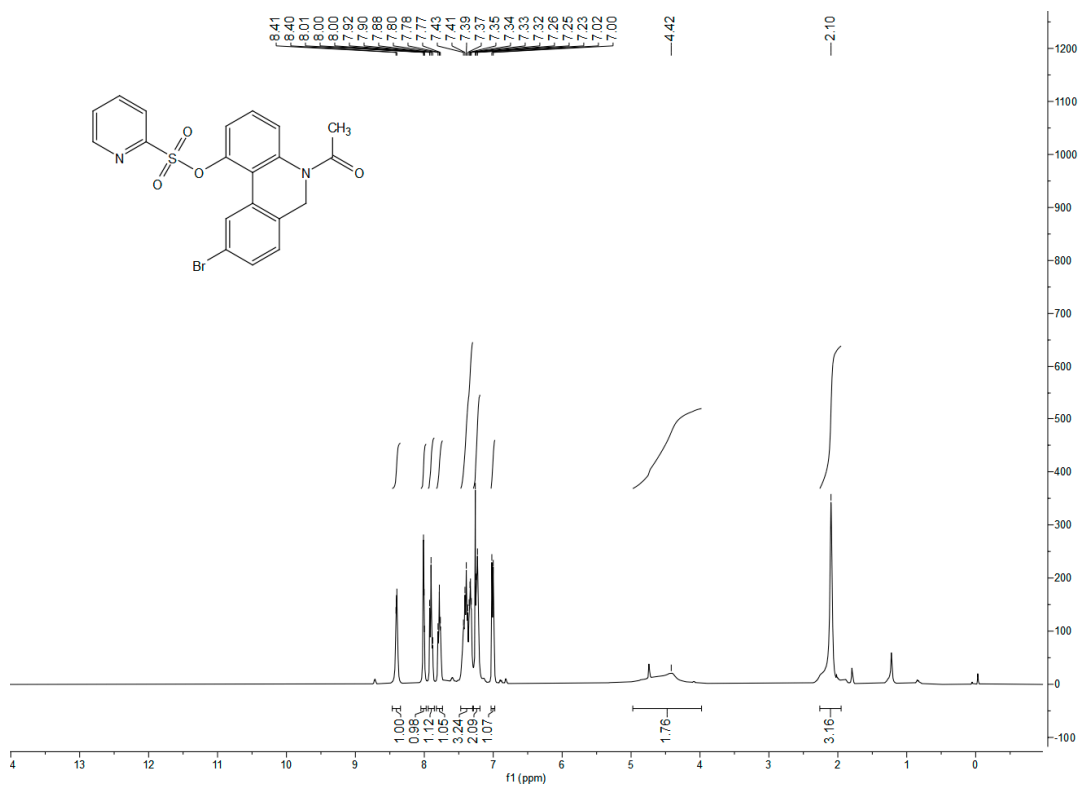
¹H NMR spectra of compound **2i**



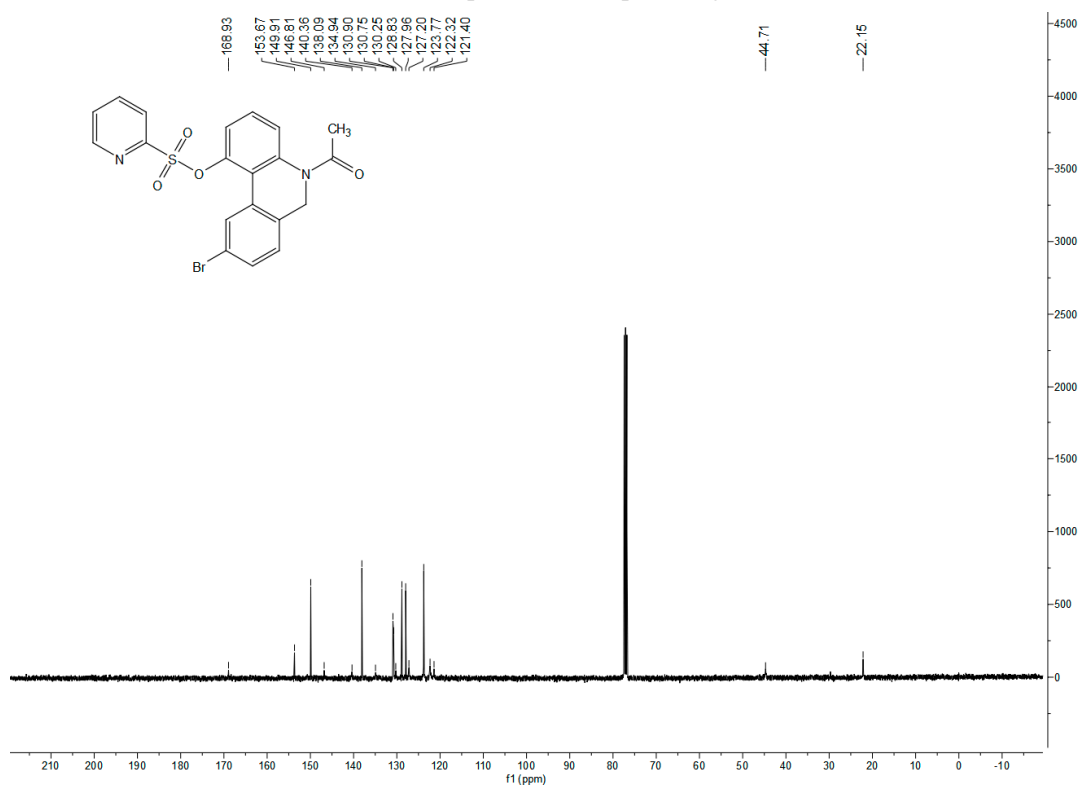
¹³C NMR spectra of compound **2i**



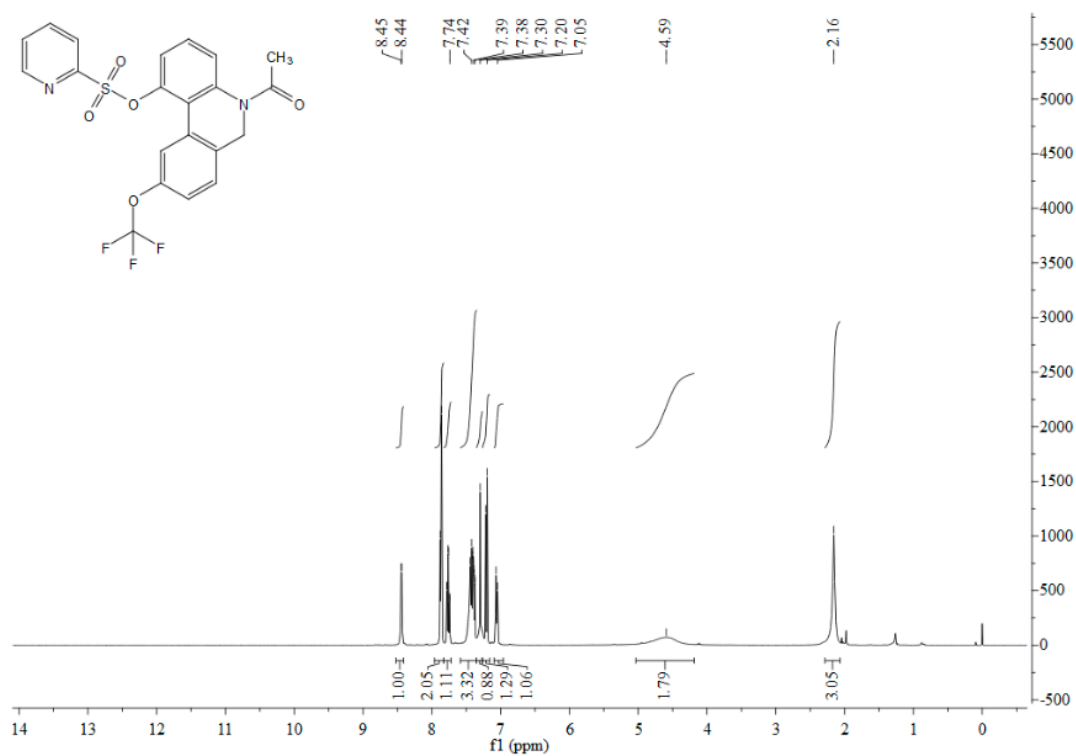
¹H NMR spectra of compound **2j**



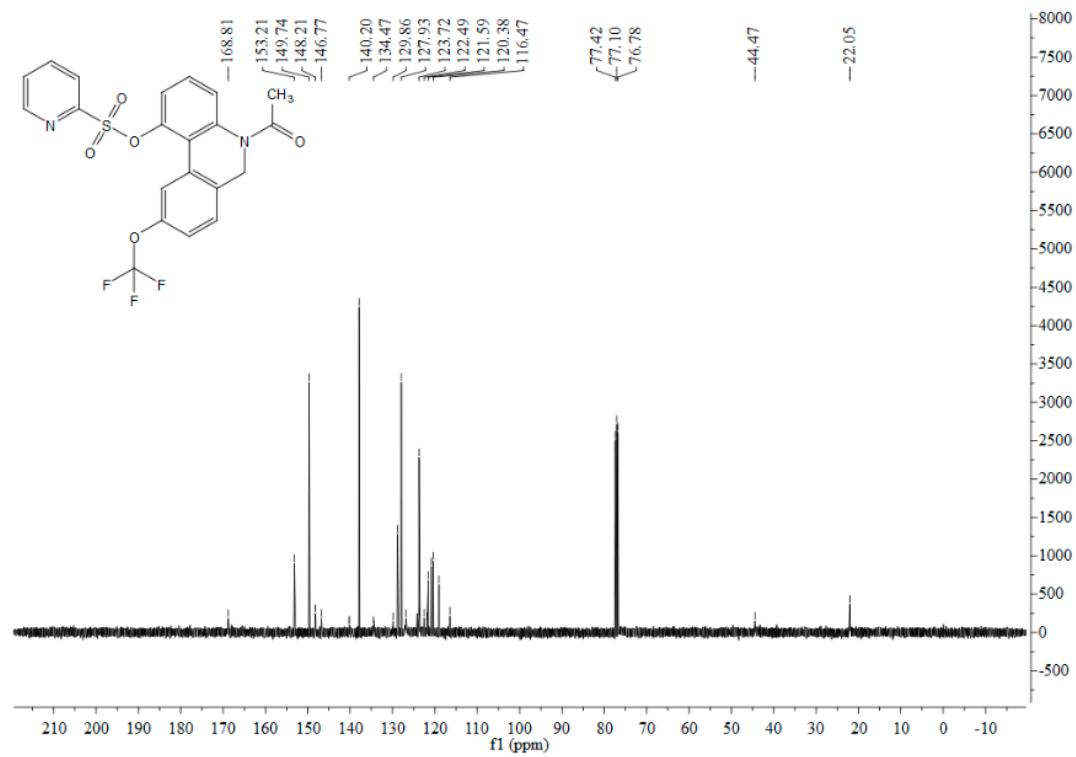
¹³C NMR spectra of compound **2j**



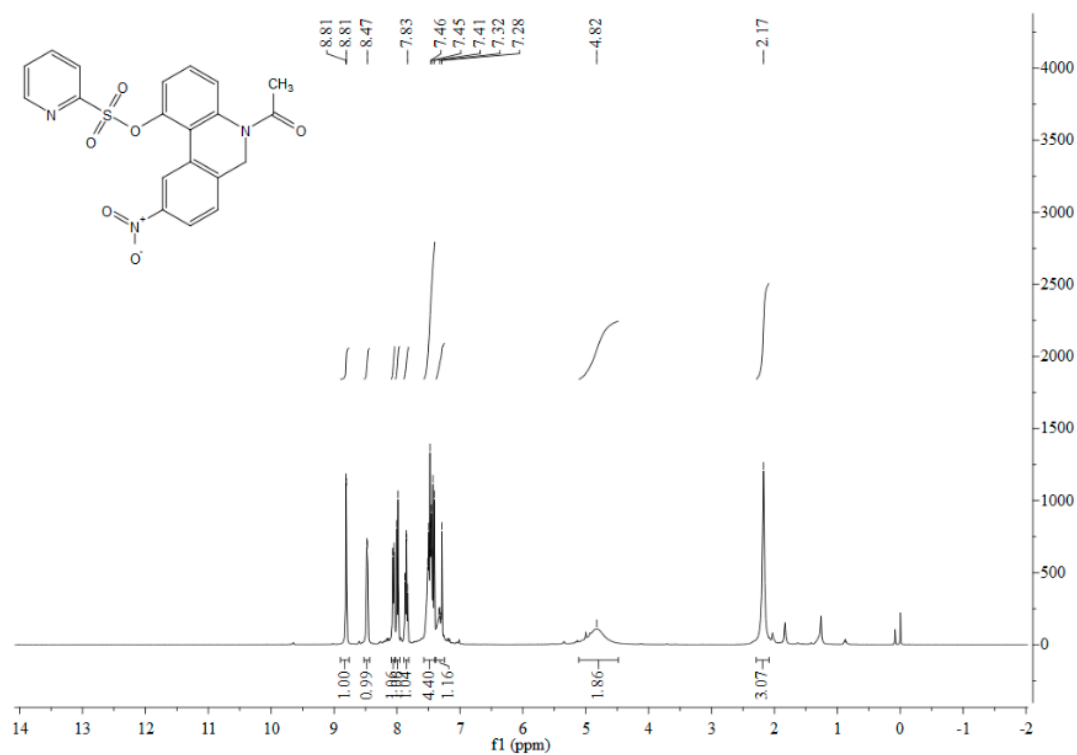
¹H NMR spectra of compound **2k**



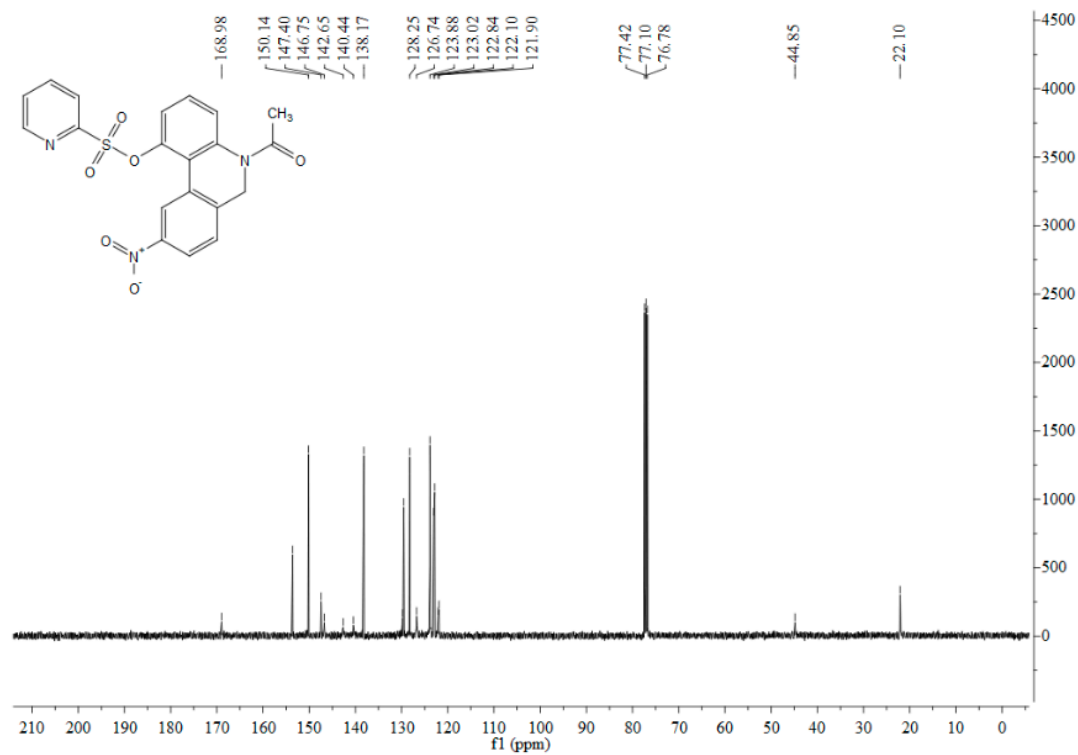
¹³C NMR spectra of compound **2k**



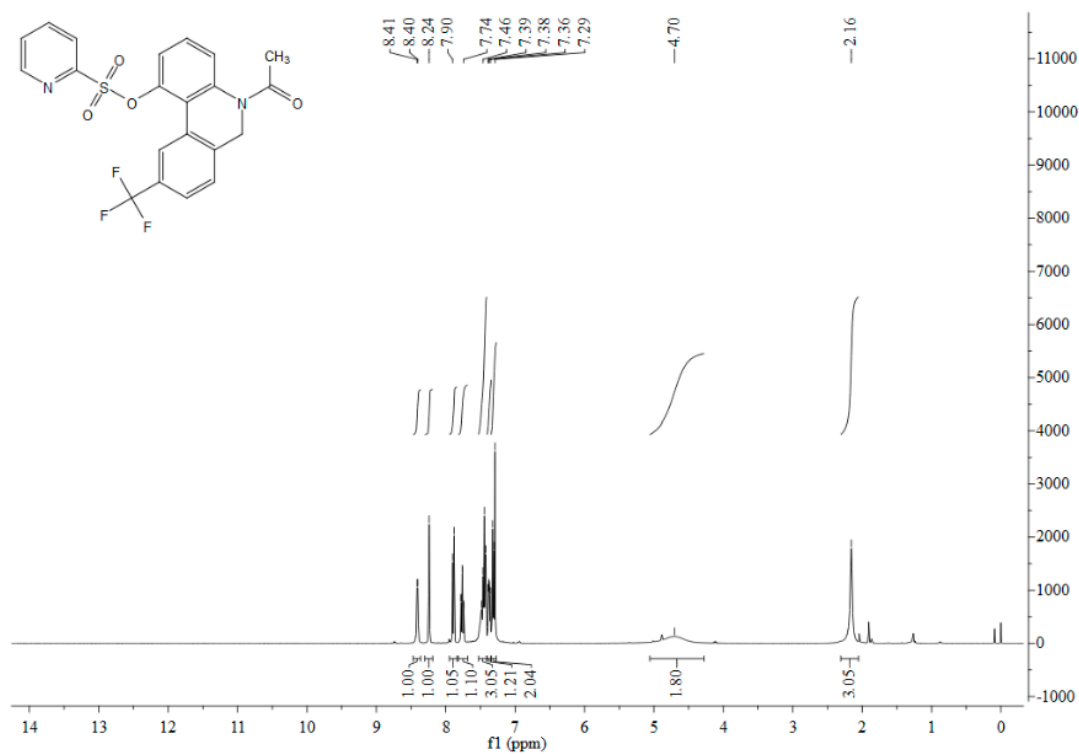
¹H NMR spectra of compound **2I**



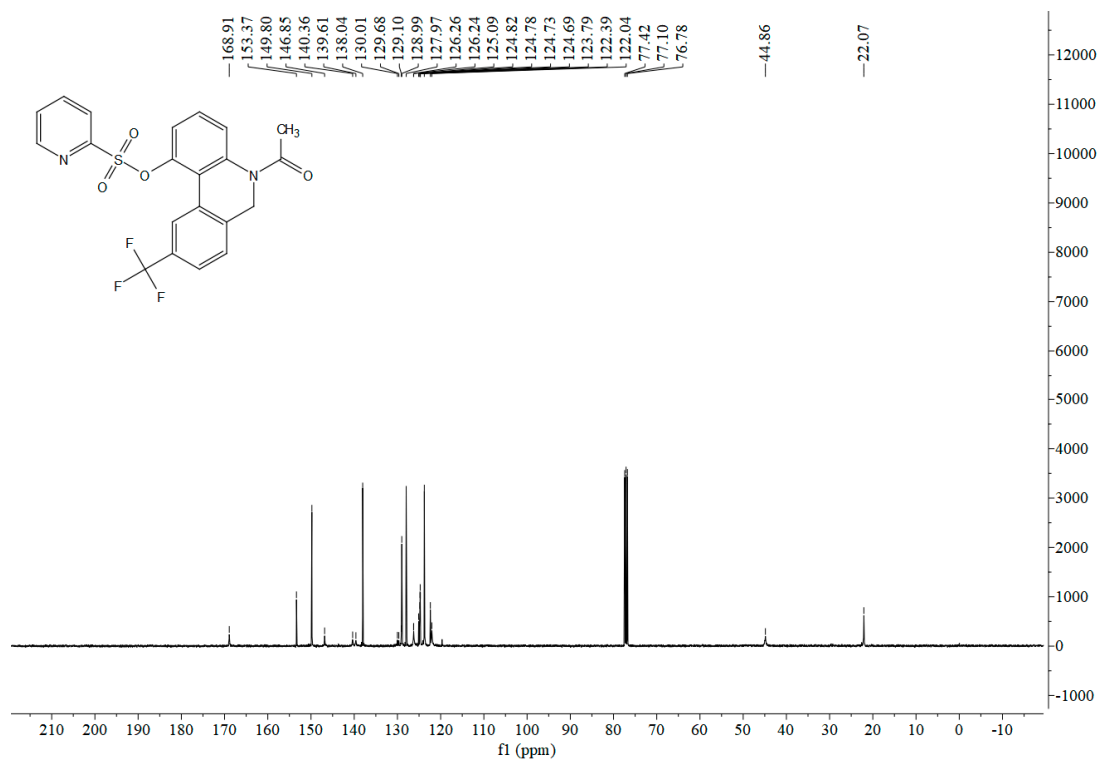
¹³C NMR spectra of compound **2I**



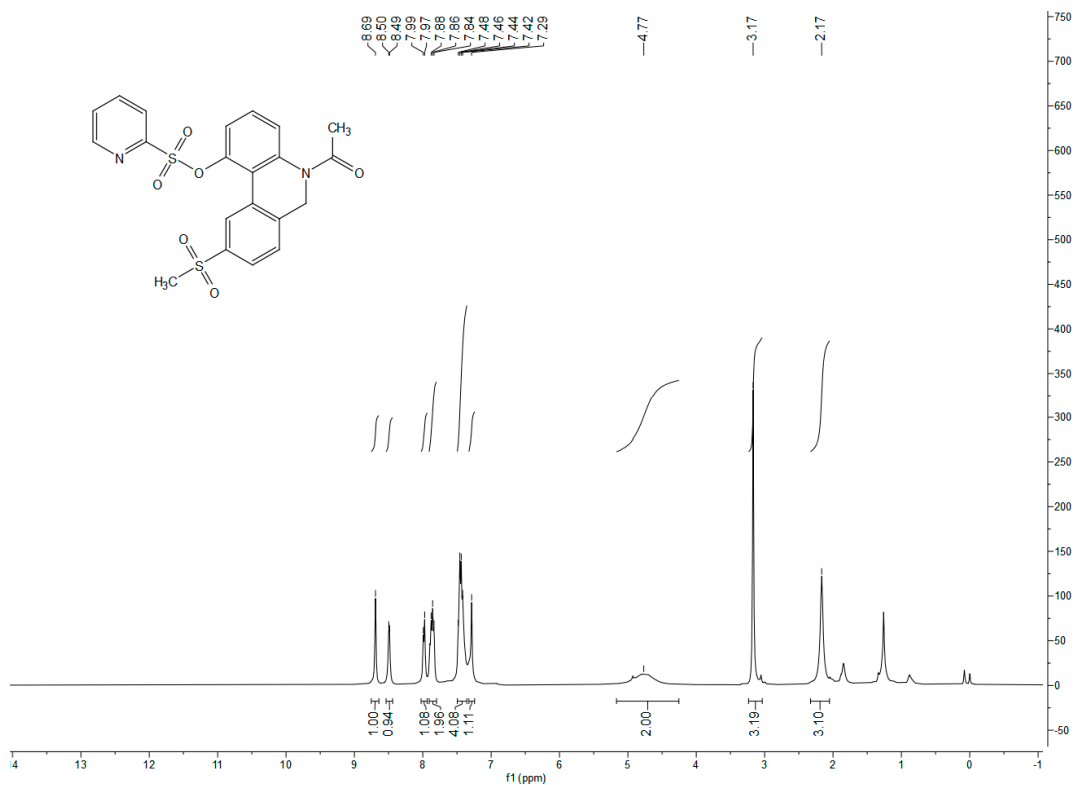
¹H NMR spectra of compound **2m**



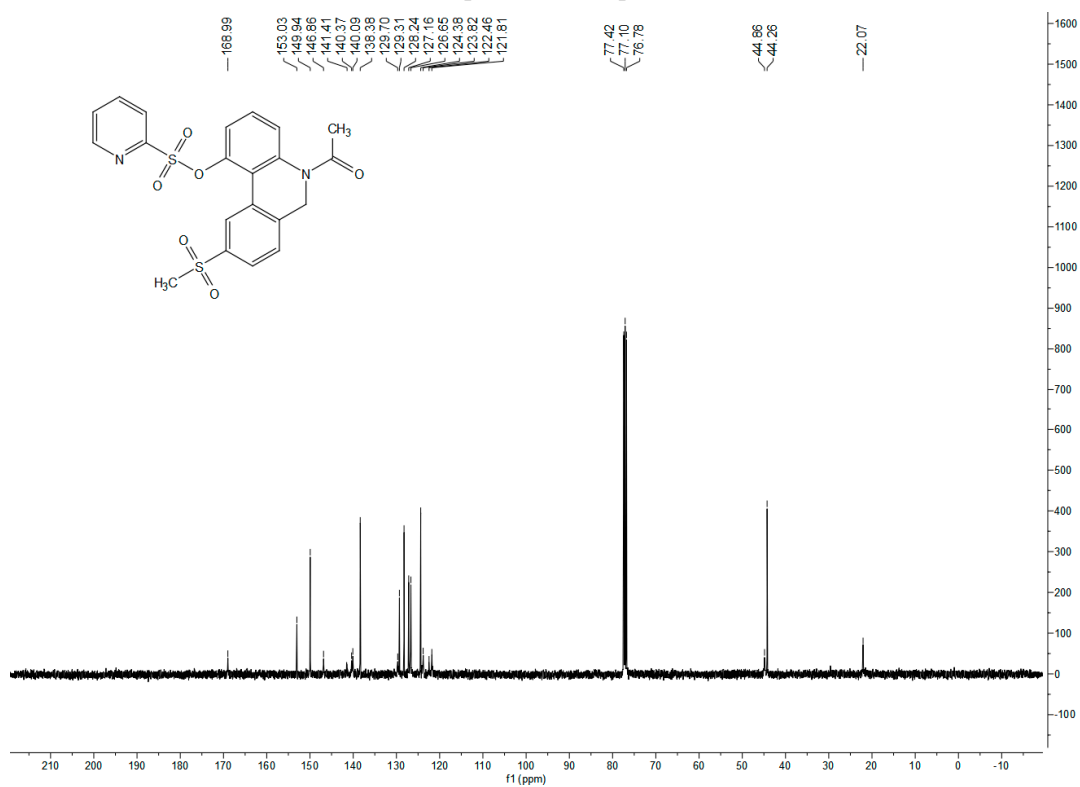
¹³C NMR spectra of compound **2m**



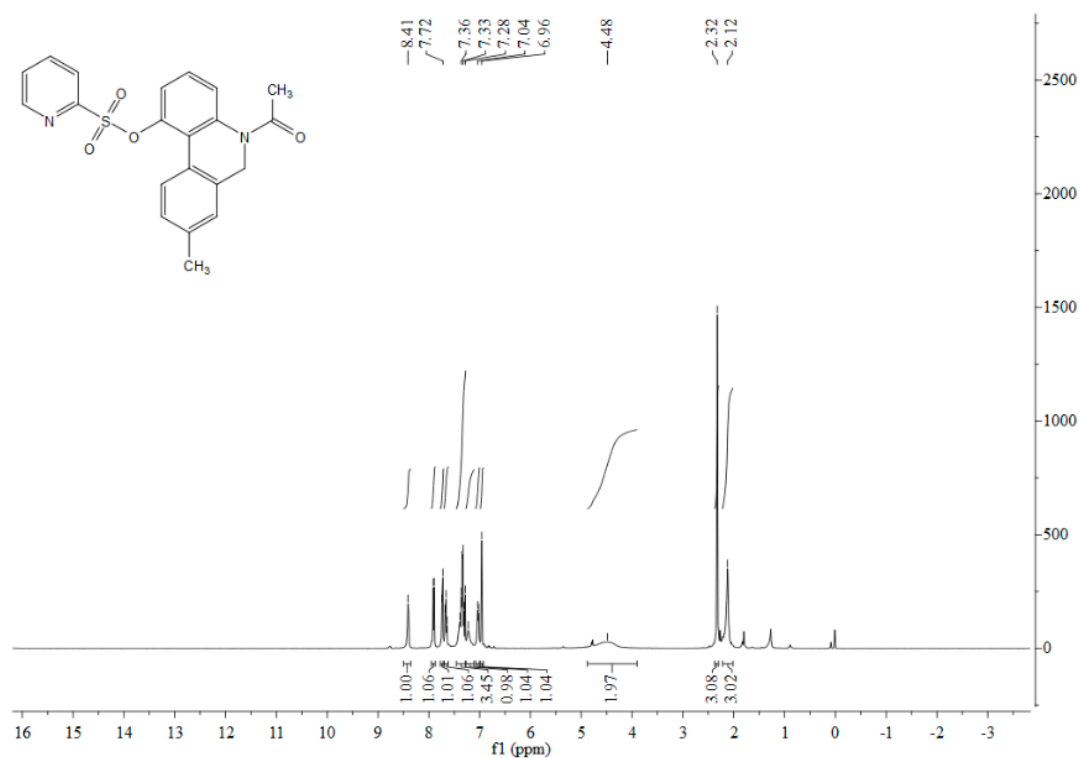
¹H NMR spectra of compound **2n**



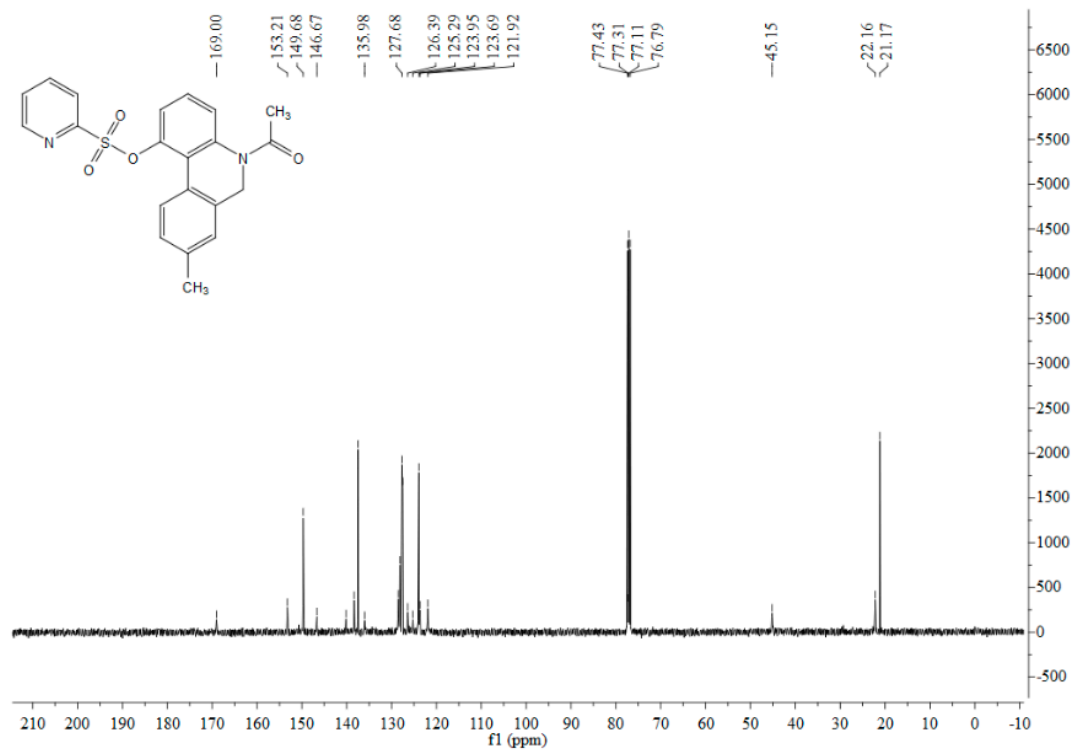
¹³C NMR spectra of compound **2n**



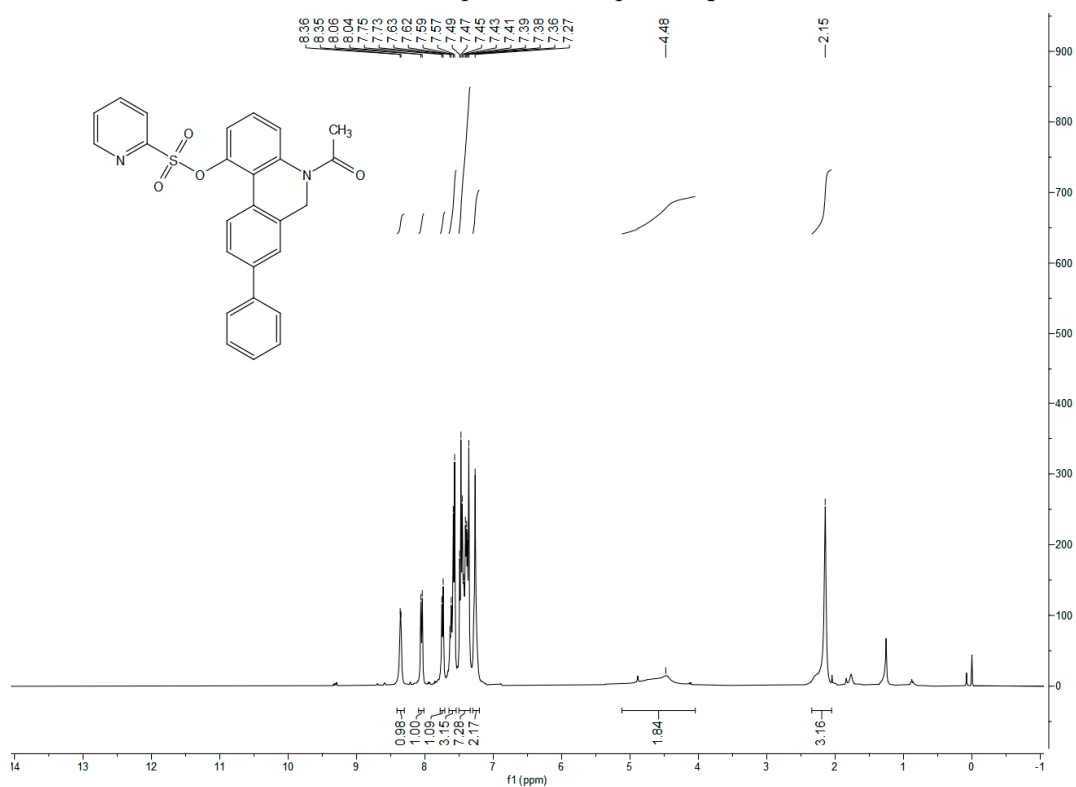
¹H NMR spectra of compound **2o**



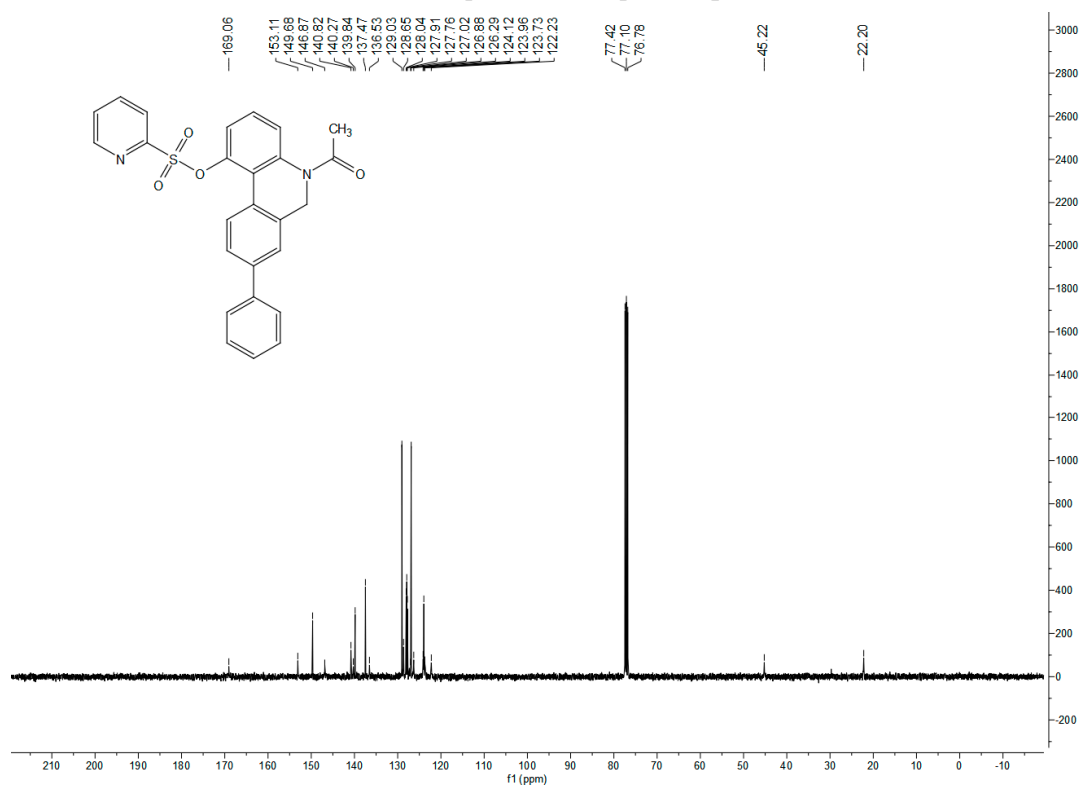
¹³C NMR spectra of compound **2o**



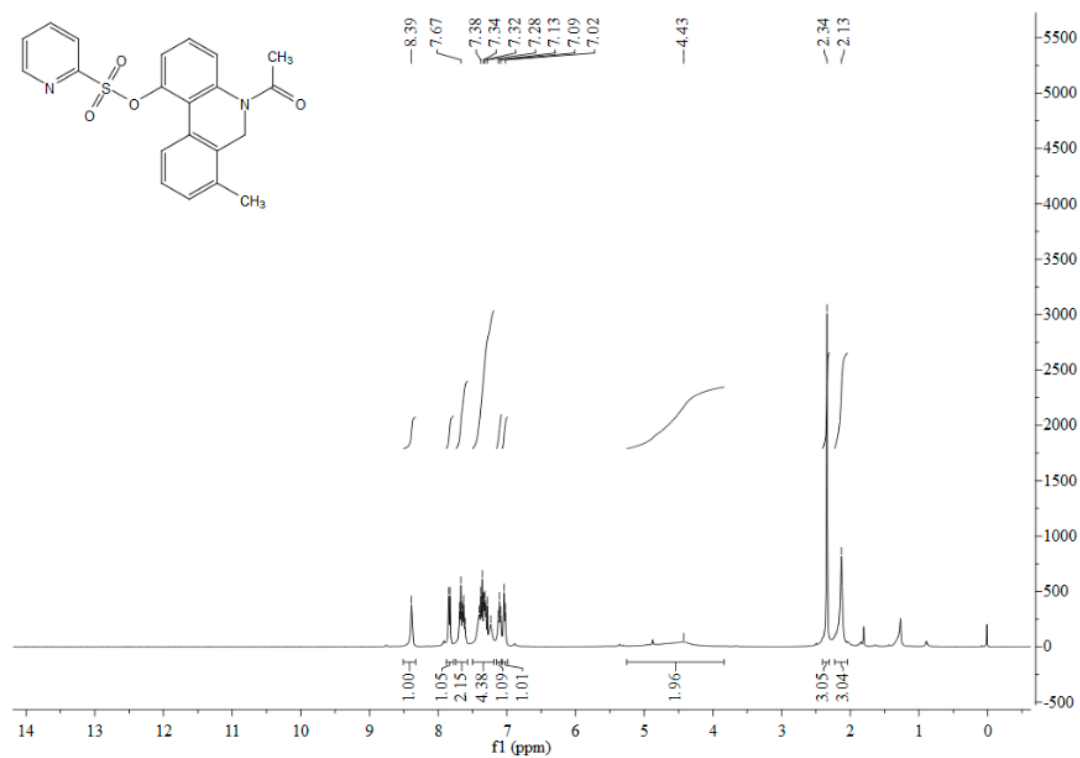
¹H NMR spectra of compound **2p**



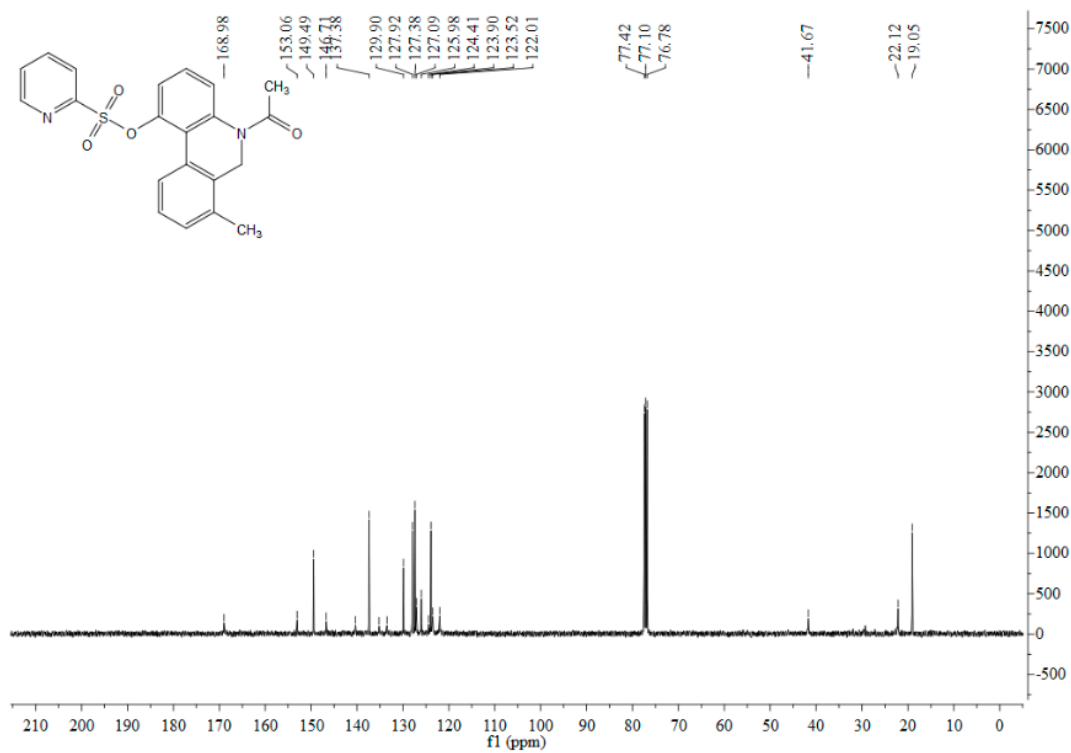
¹³C NMR spectra of compound **2p**



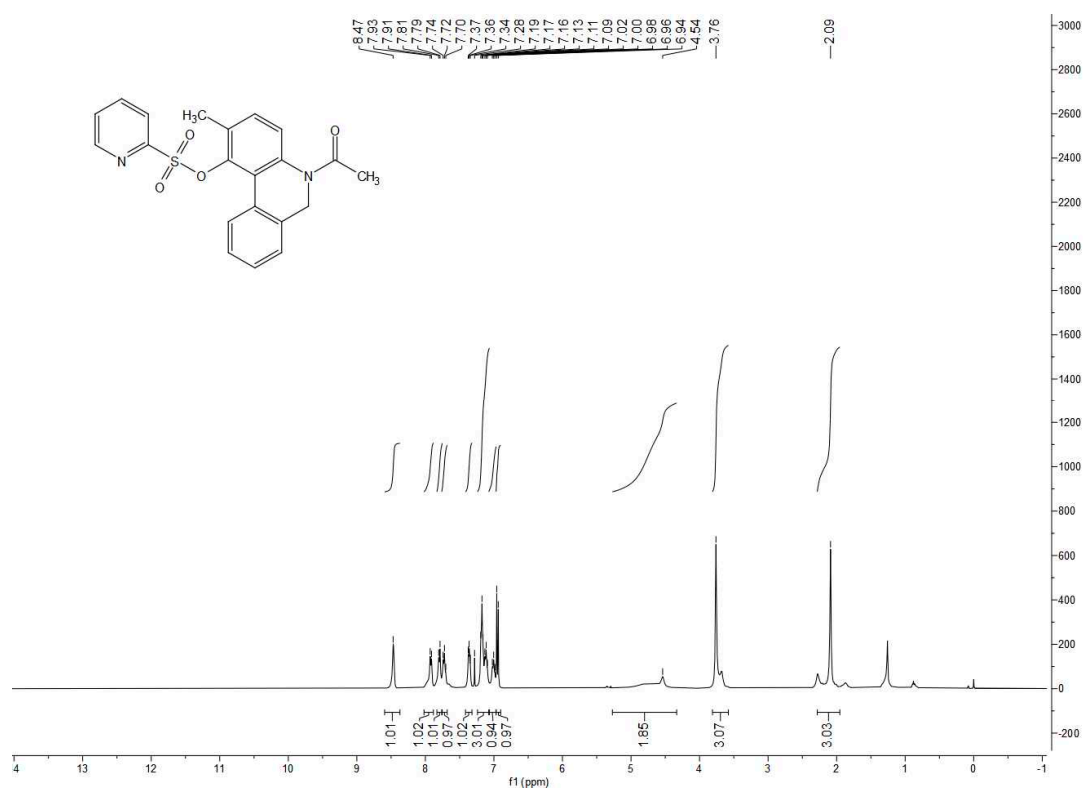
¹H NMR spectra of compound **2q**



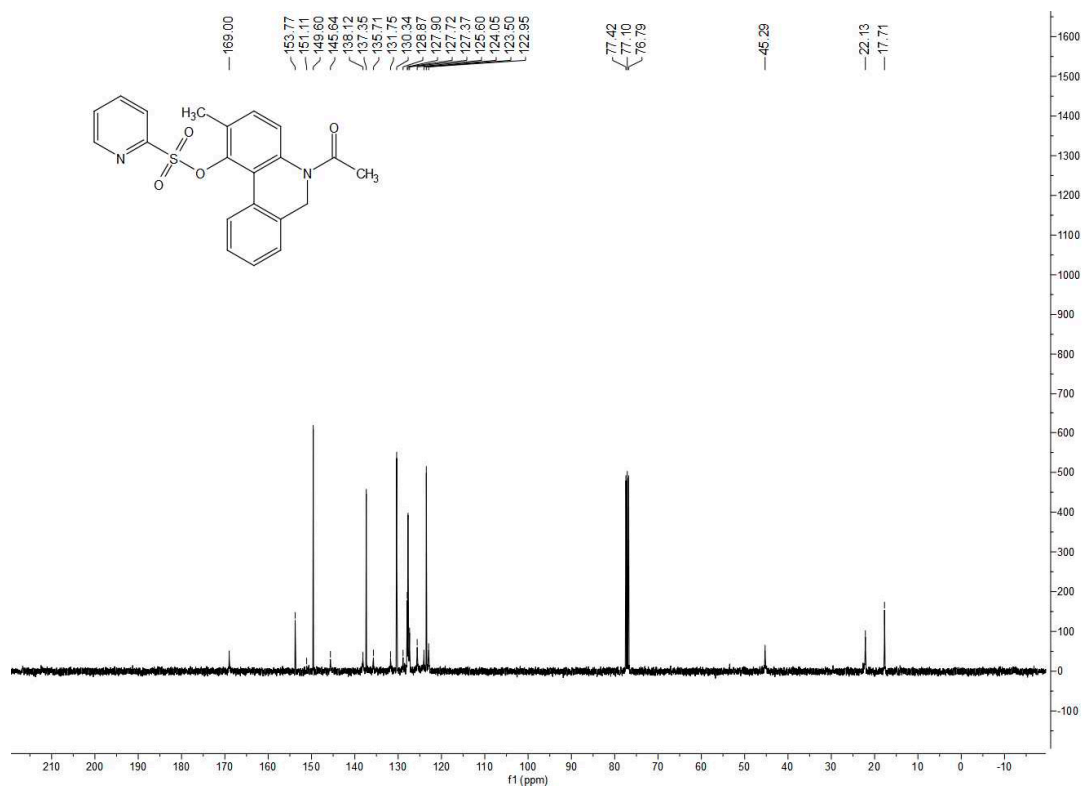
¹³C NMR spectra of compound **2q**



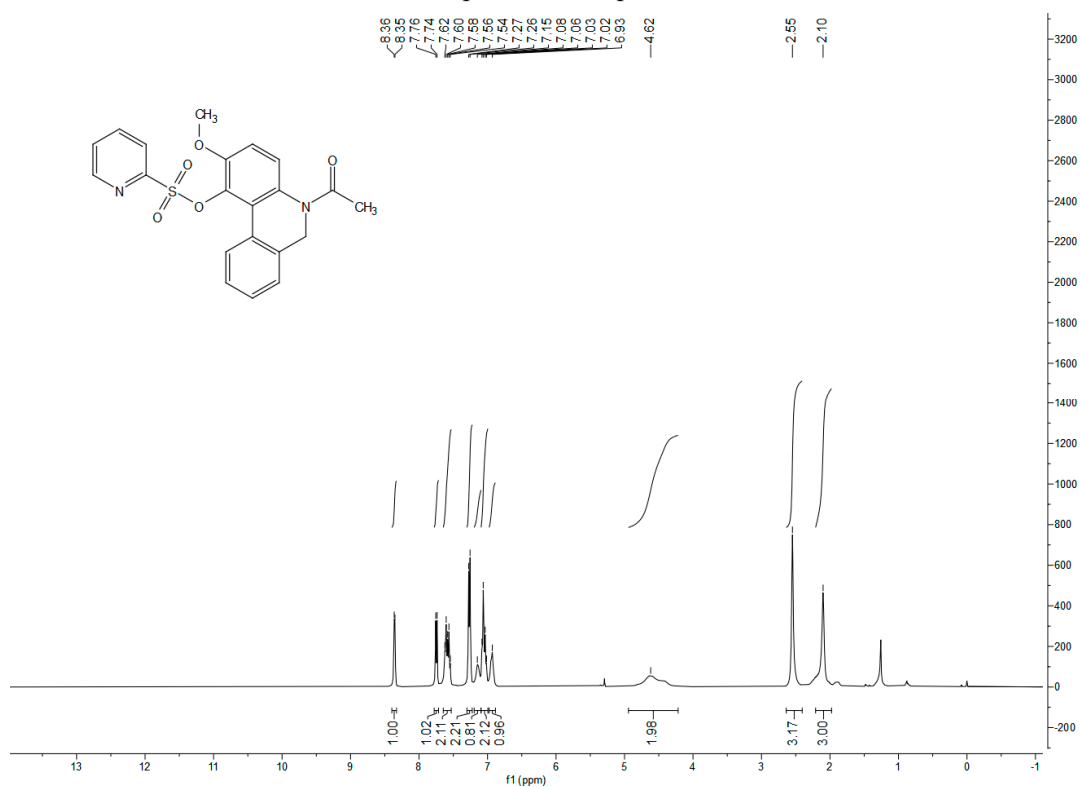
¹H NMR spectra of compound 2r



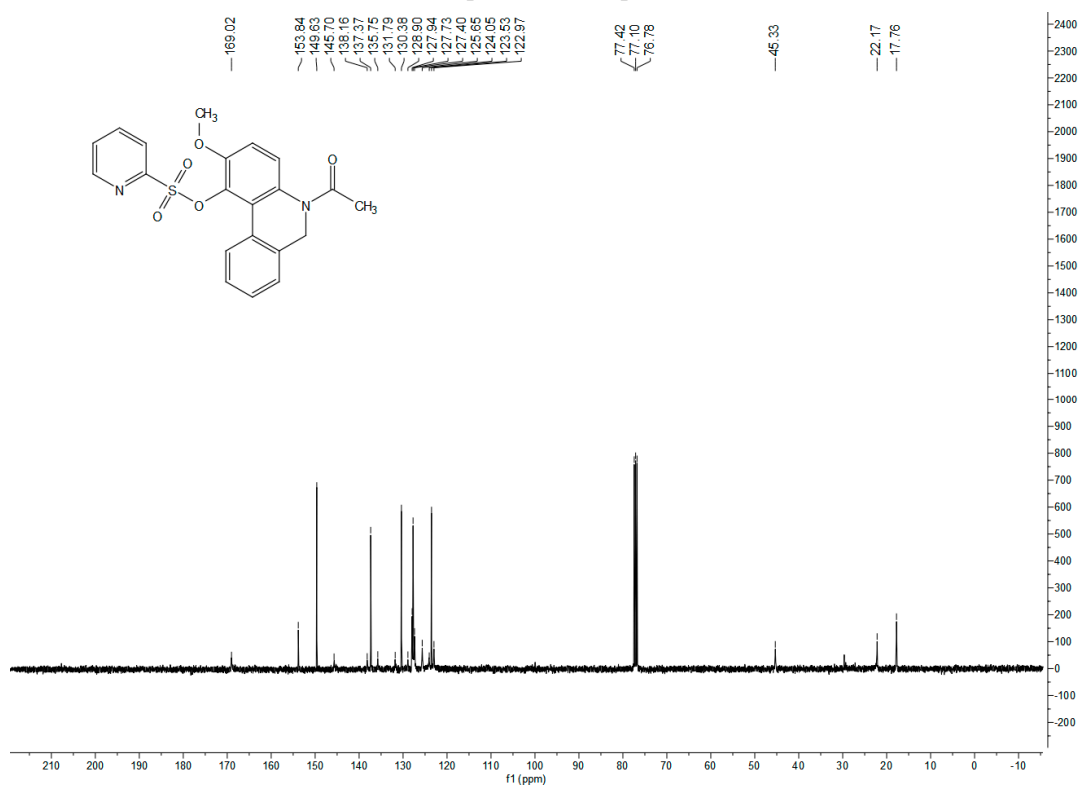
¹³C NMR spectra of compound 2r



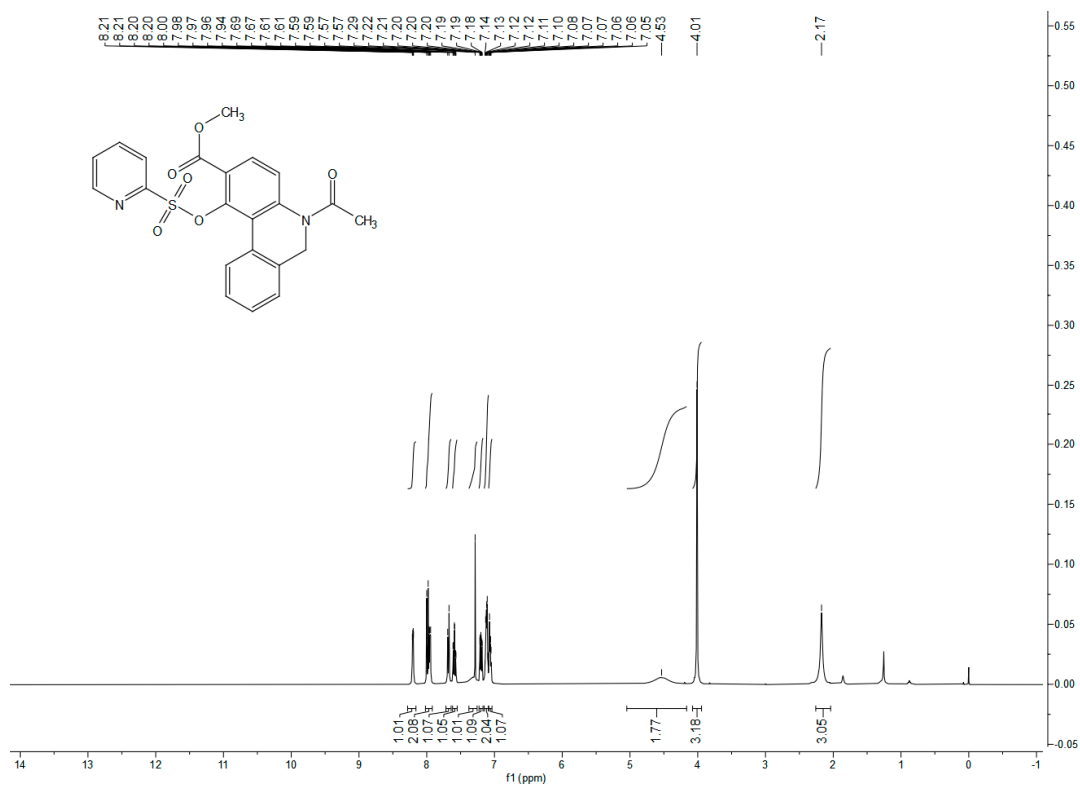
¹H NMR spectra of compound 2s



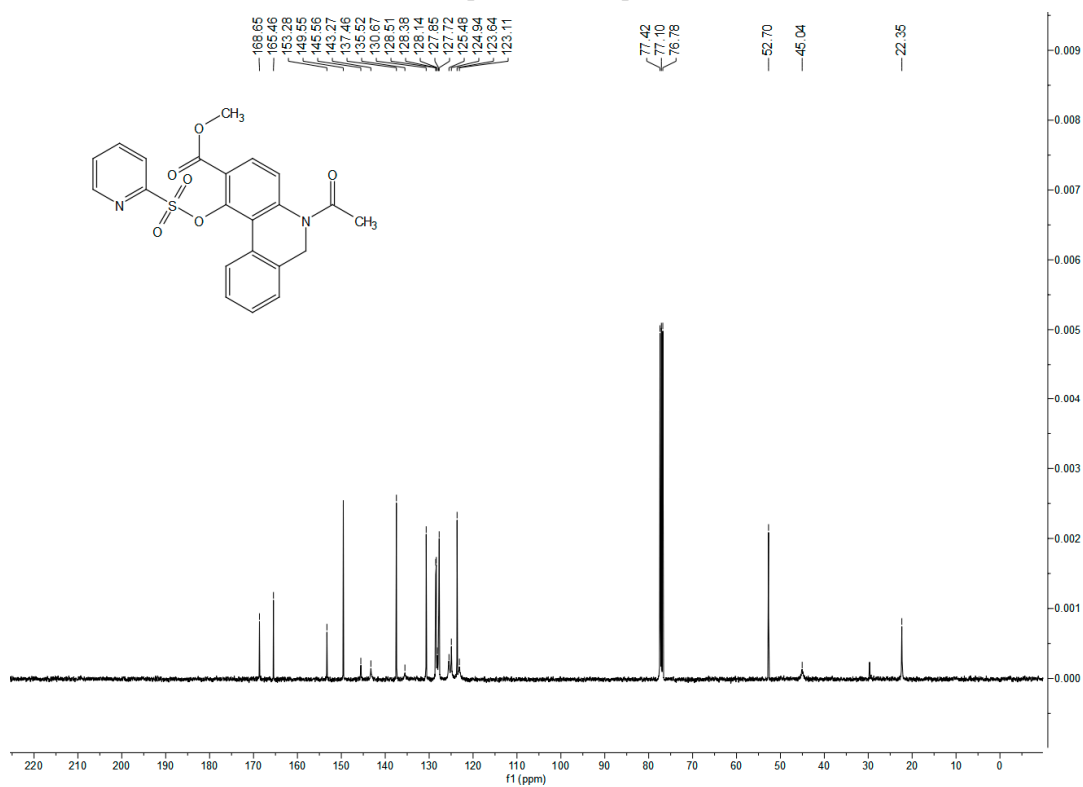
¹³C NMR spectra of compound 2s



¹H NMR spectra of compound 2t

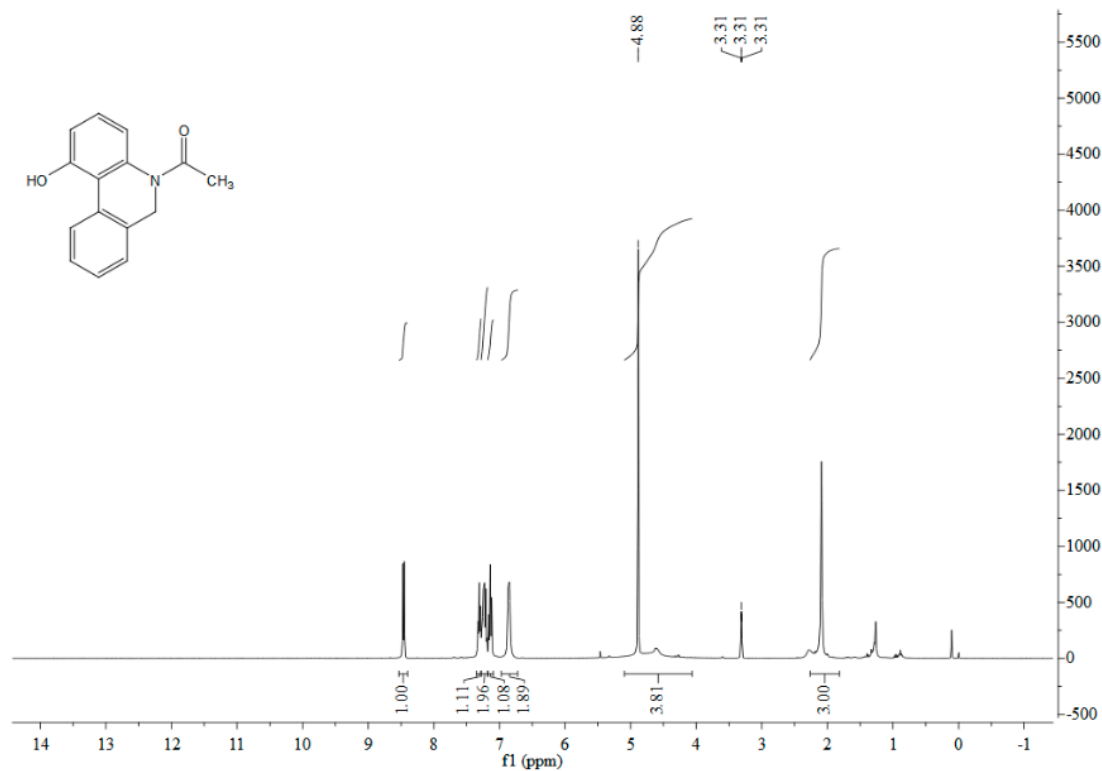


¹³C NMR spectra of compound 2t

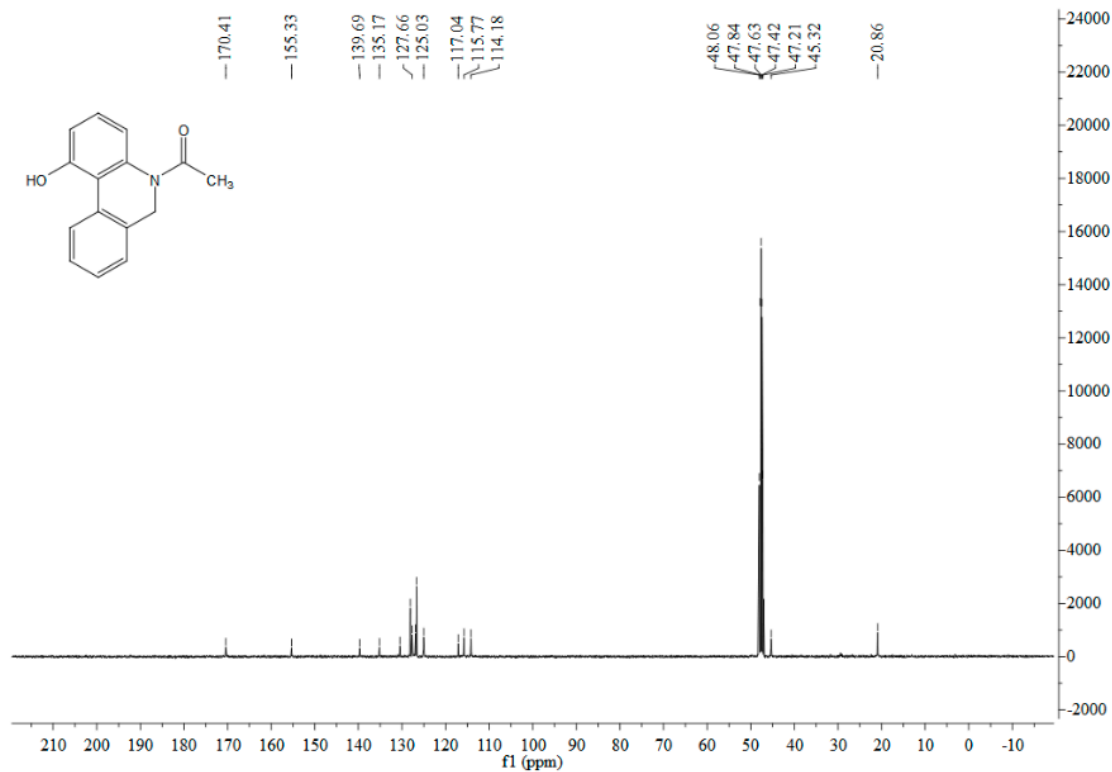


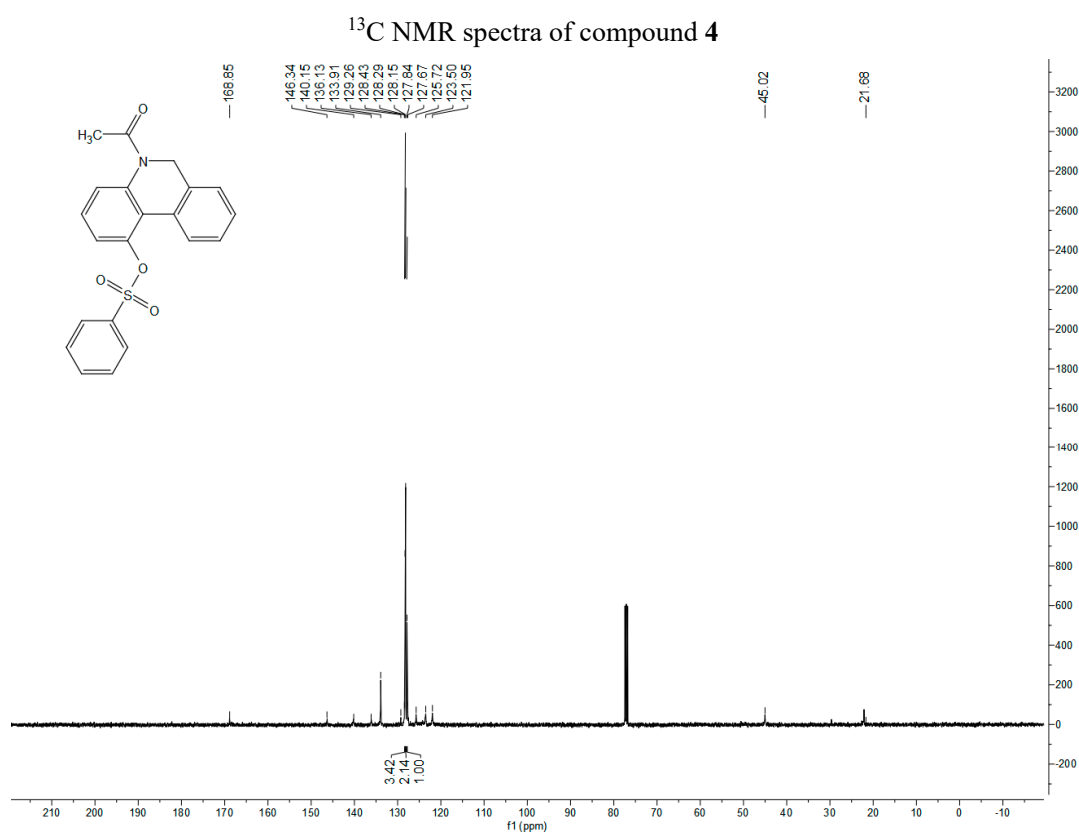
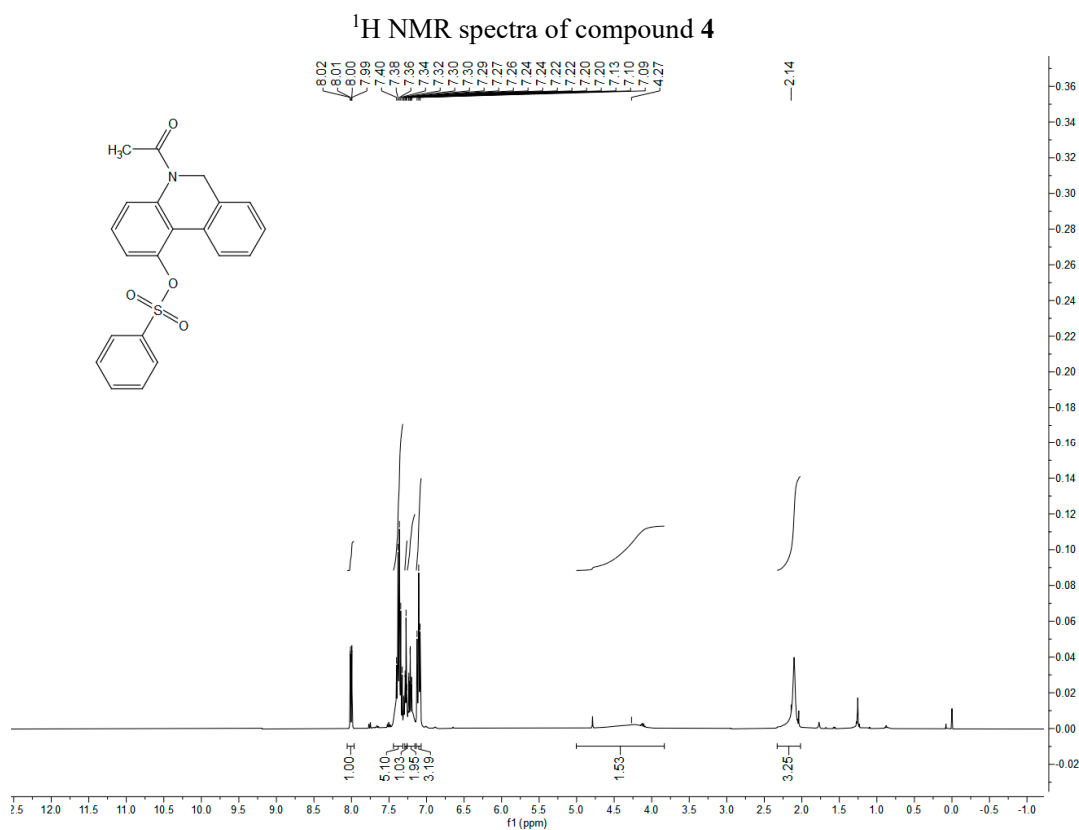
6. Spectral copies of **3-7** ^1H NMR and ^{13}C NMR

^1H NMR spectra of compound **3**

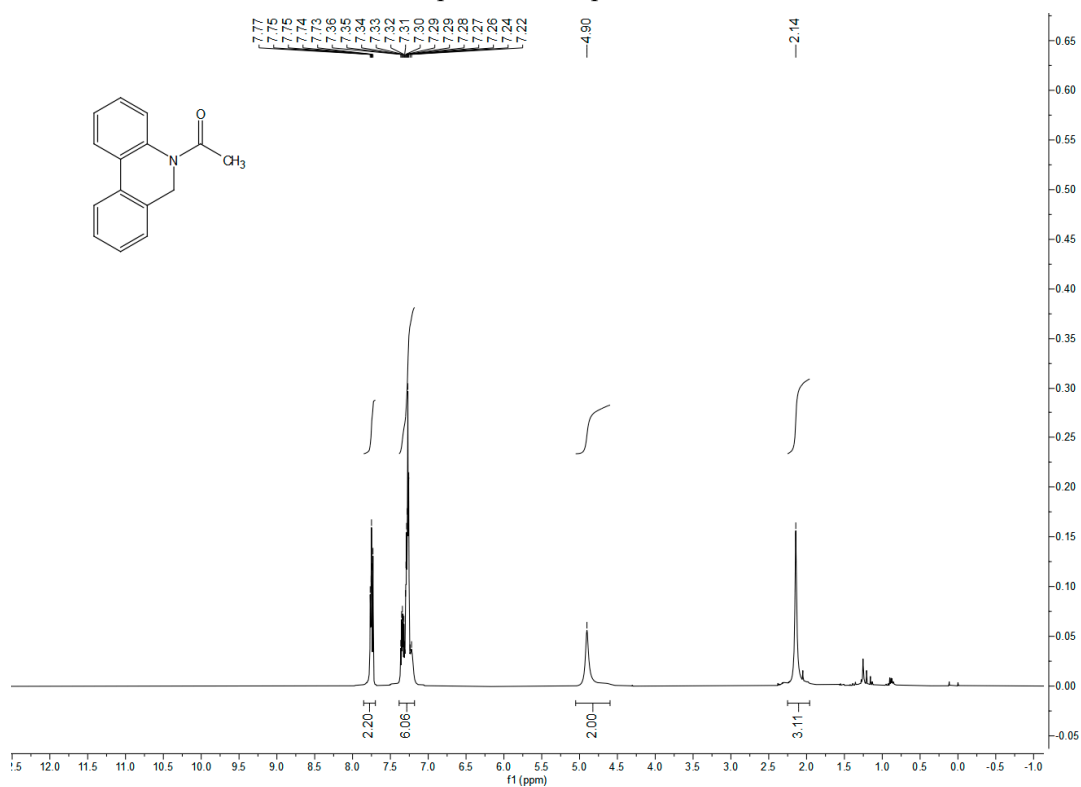


^{13}C NMR spectra of compound **3**

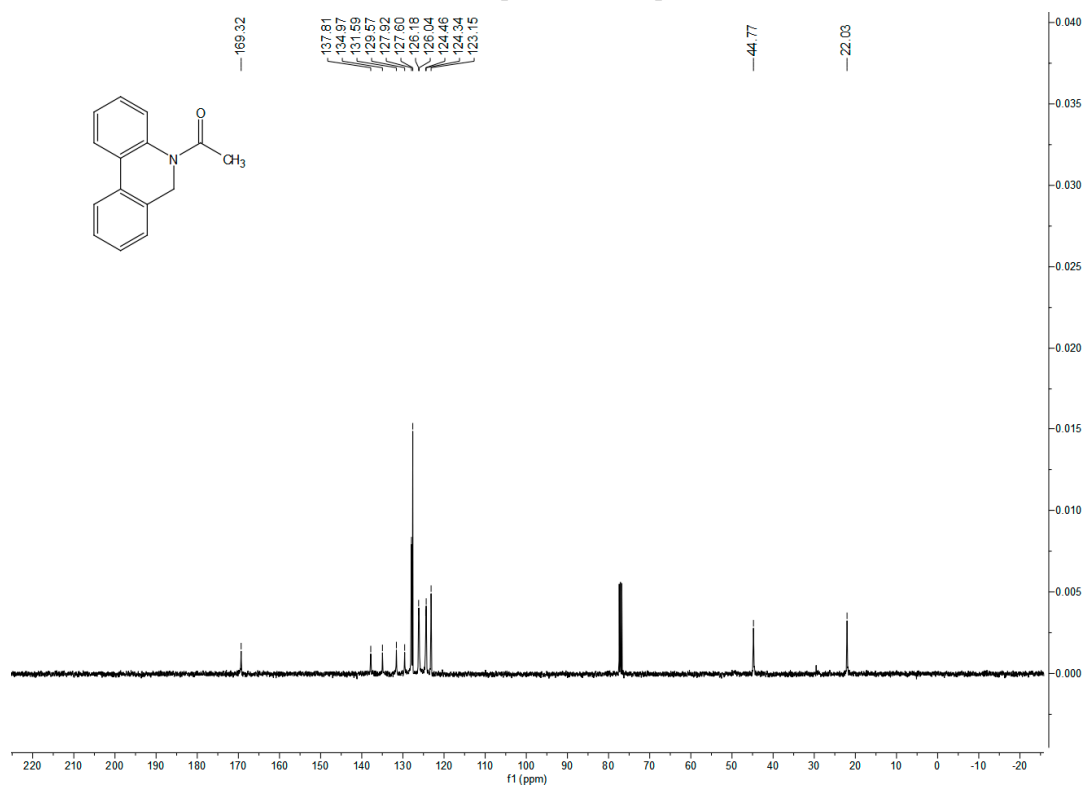


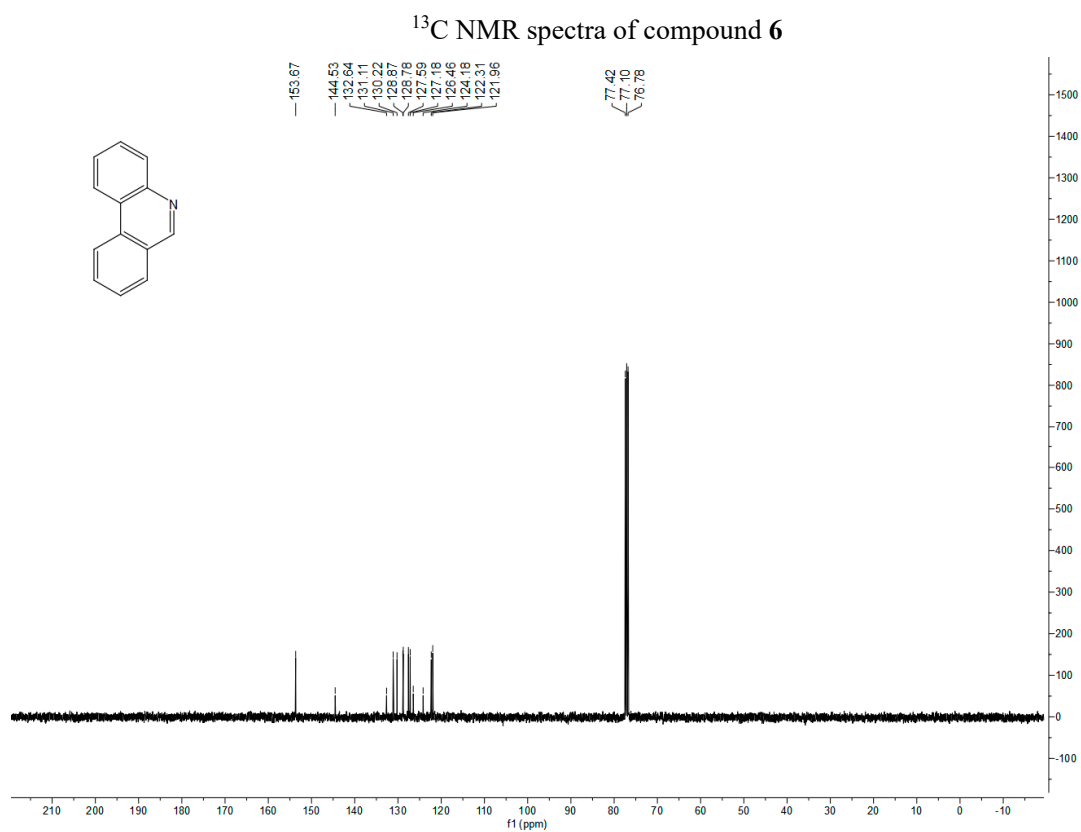
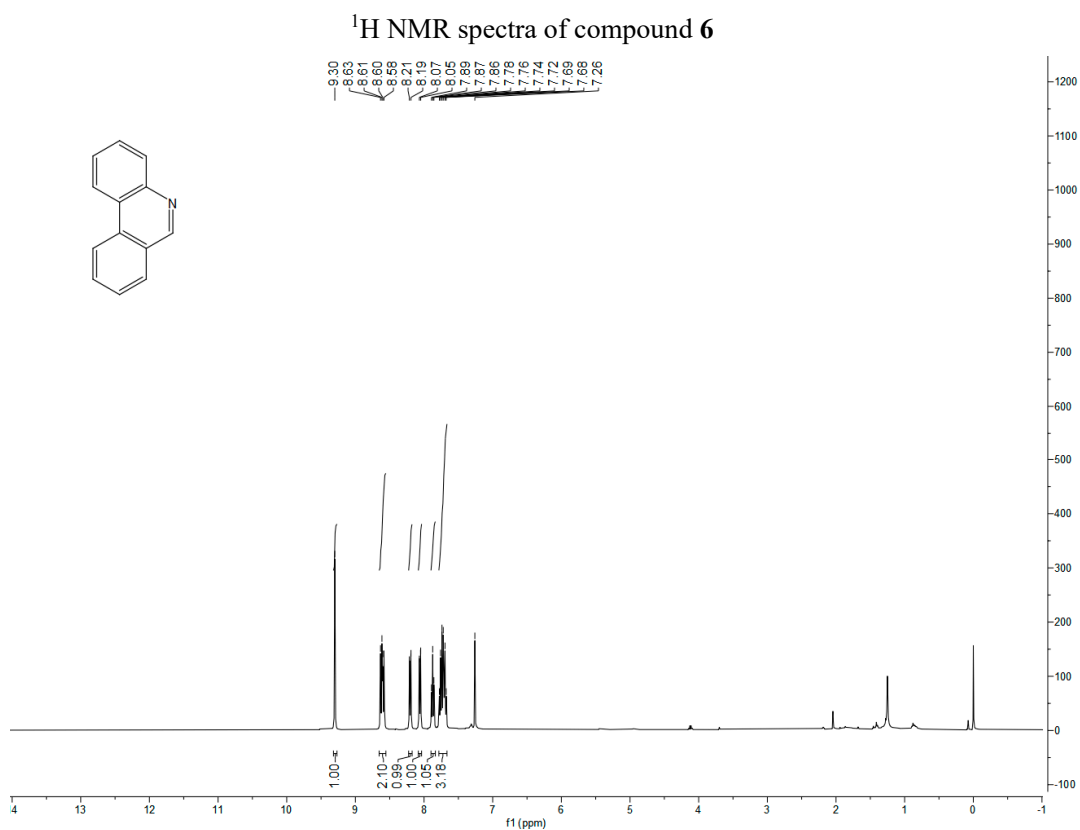


¹H NMR spectra of compound **5**

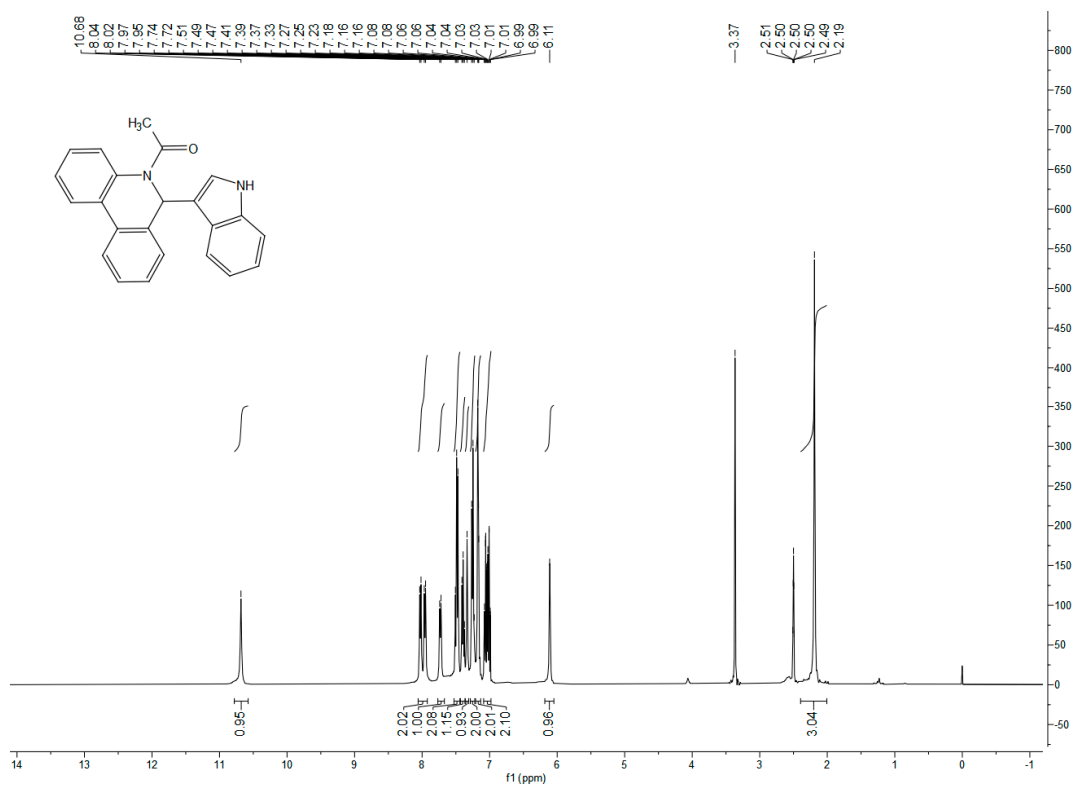


¹³C NMR spectra of compound **5**

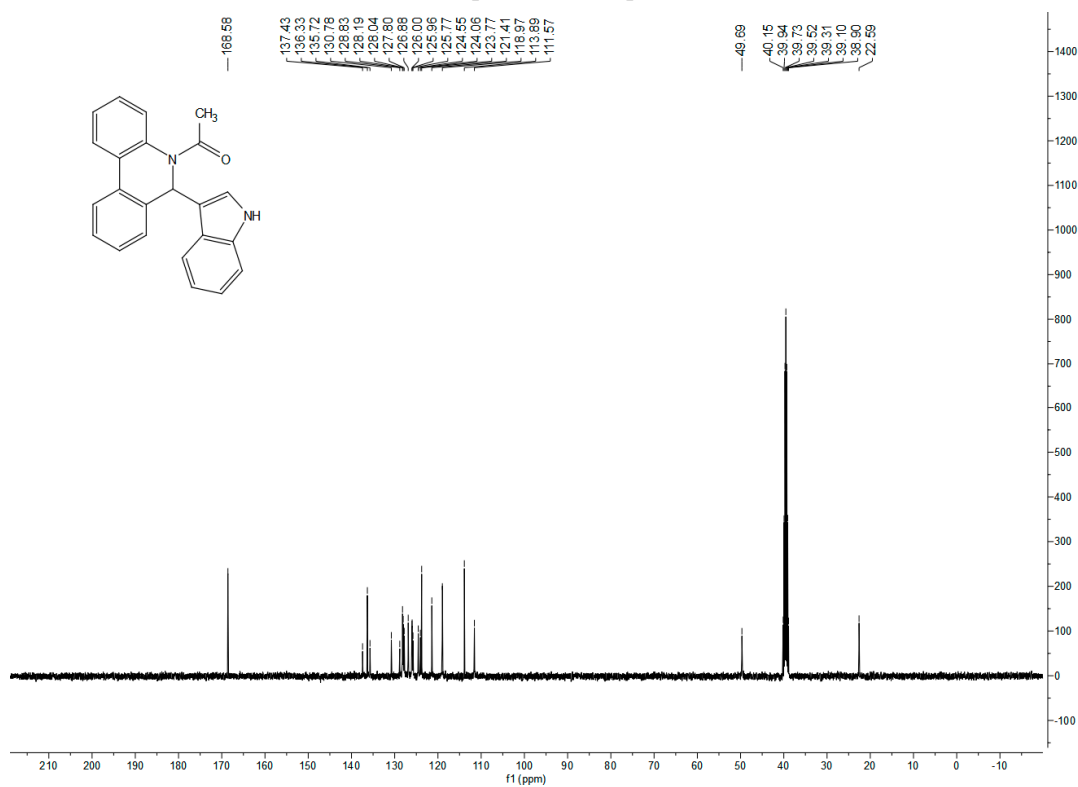




¹H NMR spectra of compound 7



¹³C NMR spectra of compound 7



7. X-ray Crystal Structure of Compounds **2a** (CCDC: 1985688)

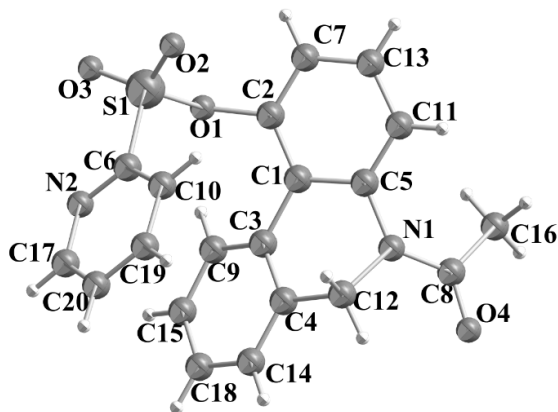


Figure S2. Crystallographic structure data parameters of 2a

Identification code	2a
Empirical formula	C ₂₀ H ₁₆ N ₂ O ₄ S
Formula weight	380.41
Temperature	296.15 K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P 1 2 ₁ /c 1
Unit cell dimensions	a = 7.5334(15) Å alpha = 90 deg. b = 20.396(4) Å beta = 105.500(4) deg c = 12.054(2) Å gamma = 90 deg.
Volume	1784.8(6) Å ³
Z, Calculated density	4, 1.416 Mg/m ³
Absorption coefficient	0.211 mm ⁻¹
F(000)	792
Crystal size	0.52 x 0.43 x 0.40 mm
Theta range for data collection	1.997 to 25.497 deg.
Limiting indices	-9 ≤ h ≤ 8, -22 ≤ k ≤ 24, -11 ≤ l ≤ 14
Reflections collected / unique	9383 / 3308 [R(int) = 0.1193]
Completeness to theta = 25.242	99.7 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²

Data / restraints / parameters	3308 / 0 / 245
Goodness-of-fit on F^2	0.918
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0558$, $wR_2 = 0.1340$
R indices (all data)	$R_1 = 0.0915$, $wR_2 = 0.1526$
Largest diff. peak and hole	0.789 and -0.372 e. \AA^{-3}