Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Photocatalyst-, metal-free visible-light-induced thiolation/pyridylation of styrenes using electron donor-acceptor complex as bifunctional reagents

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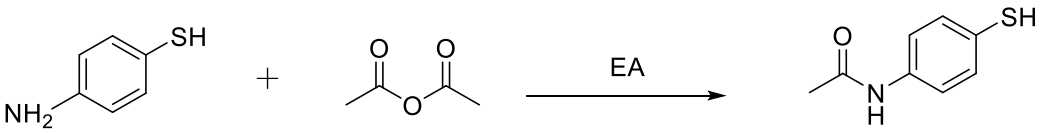
Table of contents

1. General experimental information

Commercial reagents were used without further purification. All the reactions were carried out under nitrogen atmosphere using standard Schlenk technique unless otherwise noted. Substrates were prepared according to literature procedures, respectively. The photochemical reactions were carried out under visible light irradiation by a blue LED at 25^{o}C. RLH-18 8-position Photo Reaction System manufactured by Beijing Roger Tech Ltd. Was used in this system. Eight 10 W blue LEDs were equipped in this Photo reactor. The blue LED's energy peak wavelength is 455 nm, peak width at half-height is 22.9 nm, irradiance@10W is 172.29 Mw/cm^2. The ^{1}H NMR spectra were recorded at 400 MHz or 600 MHz. The ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz The ^{19}F NMR spectra were recorded at 565 MHz. Chemical shifts were expressed in parts per million (δ), and were reported as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), m (multiplet), etc. The coupling constants *J* were given in Hz. High resolution mass spectra (HRMS) were obtained *via* ESI mode by using a MicrOTOF mass spectrometer. UV-vis absorption spectra were obtained on a Cary 100 UV-Vis spectrophotometer (Agilent Technologies). The conversion of starting materials was monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm). Column chromatography was performed on silica gel (200-300 mesh) using petroleum ether (PE)/ethyl acetate (EA).

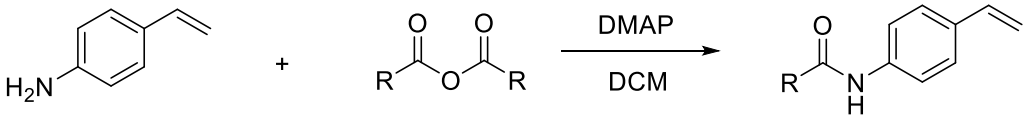
2. substrate preparations and spectroscopic data.

Procedure for the preparation of 1d, 2k, 2l

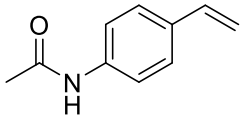


4-aminobenzenethiol (1.3g, 10 mmol) was dissolved in ethyl acetate (50 mL) and cooled to 0℃.Acetic anhydride(1.0 mL 11 mmol) was added carefully and the reaction mixture was allowed to warm to room temperature within 1h. The reaction mixture was diluted with ethyl acetate (50 mL) then washed with aqueous hydrochloric acid (1 N, 50mL) and brine (50 mL). After drying over sodium sulfate the product was purified by flash chromatography onsilica (petroleum ether/ethyl acetate 1:1)[1]. Off-white solid, yield 78% (1.01 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 4.4 Hz, 2H), 7.23 (s, 1H), 3.42 (s, 1H), 2.16 (s, 3H).

Procedure for the preparation of 2k, 2l



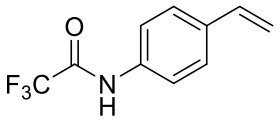
4-Vinylaniline (357.5 mg, 3.0 mmol)was added to a round-bottom flask via syringe and fitted with a rubber septum. The flask was purged with argon and dry DCM (7.5 mL,0.4 M) was added. Acetic anhydride (0.4 mL, 3.6 mmol, 1.2 eq) or trifluoroacetic anhydride was added, DMAP (20 mg) was added and the reaction was stirred at room temperature and monitored by TLC. Upon completion, the reaction mixture was washed with a saturated solution of sodium carbonate. the organic lavers dried with Na_2SO_4 and the solvent removed under reduced pressure. The crude product was purified by chromatographyon silica gel(hexane/AcOEt=1/2) to give the product as a yellow solid(473.9 mg98%).The spectral data of the product were identical with those reported in the literature[2].



N-(4-vinylphenyl)acetamide

White solid; yield: 232 mg, 48%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.29 (s, 1H), 6.67 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.68 (d, *J* = 17.6 Hz, 1H), 5.19 (d, *J* = 10.9 Hz, 1H), 2.17 (s, 3H).

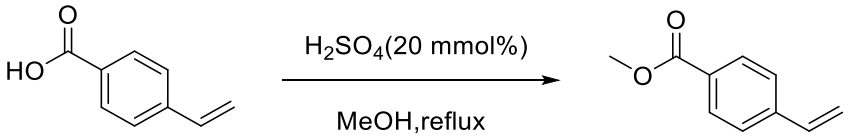


2,2,2-trifluoro-N-(4-vinylphenyl)acetamide

White solid; yield: 555 mg, 85%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.48 (ddd, *J* = 41.3, 8.6, 2.1 Hz, 3H), 6.69 (ddd, *J* = 17.5, 10.9, 2.1 Hz, 1H), 5.74 (dd, *J* = 17.6, 2.0 Hz, 1H), 5.27 (dd, *J* = 10.9, 2.1 Hz, 1H).

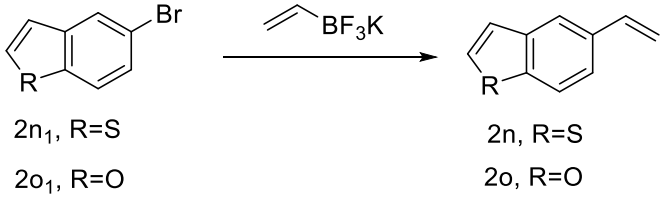
Procedure for the preparation of 2j



To a 50 mL round-bottom flask was added the solution of compound 1-(4-vinylphenyl)ethan-1-one (0.74 g, 5.0 mmol) in MeOH (20 mL). The mixture was stirred at 0 ℃ and added sulfuric acid (0.10g, 1.0 mmol, 20 mol%) slowly. Then the reaction mixture was refluxed at 70℃ for 4 h. Afterwards, the solution was neutralized and the solvent was removed under reduced pressure. The residue was diluted with H_2O (30 mL) and DCM (15 mL), extracted with DCM (15 mL X 3). The combined organic laver was washed with brine (15 mL X 3), dried over Na_2SO_4, and the solvent was removed under reduced pressure to give substrate **2j** (0.75 g, 4.6 mmol, 92%) as a white solid[3].

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 6.75 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.86 (d, *J* = 17.6 Hz, 1H), 5.38 (d, *J* = 10.9 Hz, 1H), 3.91 (s, 3H).

Procedure for the preparation of 2n, 2o



$2n_1$, R=S

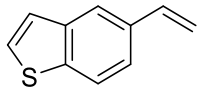
$2o_1$, R=O

2n, R=S

2o, R=O

A 50 mL Schlenk flask equipped with a stir bar was set under an atmosphere of nitrogen and charged with 5-bromobenzo[b]thiophene (2 mmol, 426 mg), potassium

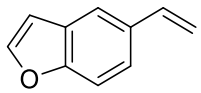
vinyltriflouroborate(1.20 equiv, 2.4 mmol, 320 mg), palladium chloride (2.0 mol% 40.0 umol, 7 mg). triphenylphosphine (1equiv, 2 mmol, 52.5 mg), and cesium carbonate (3.0 equiv, 6.0 mmol, 1.94 g) dissolved in THF/H_2O (20 mL/9:1).The vial was sealed with a septum and heated at 80℃ for 15 h. The reaction mixture was filtered through celite and washed with THF (20 mL). All volatiles were evaporated under reduced pressure and flash column chromatography (SiO_2,PE)afforded the title compound as a white solid[4].



5-vinylbenzo[b]thiophene

White solid; yield: 260 mg, 81%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.79 (m, 2H), 7.47 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.44 (d, *J* = 5.5 Hz, 1H), 7.32 (d, *J* = 5.0 Hz, 1H), 6.84 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.81 (dd, *J* = 17.6, 0.7 Hz, 1H), 5.28 (dd, *J* = 10.9, 0.7 Hz, 1H).

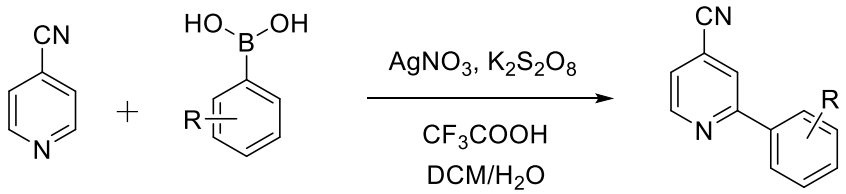


5-vinylbenzofuran

Colorless liquid; yield: 168 mg, 58%.

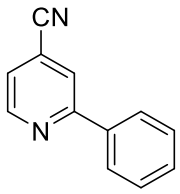
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.59 (m, 2H), 7.47 (d, *J* = 8.6 Hz, 1H), 7.41 (dd, *J* = 8.6, 1.7 Hz, 1H), 6.84 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.76 (dd, *J* = 2.2, 0.9 Hz, 1H), 5.75 (dd, *J* = 17.6, 0.8 Hz, 1H), 5.24 (dd, *J* = 10.9, 0.8 Hz, 1H).

Procedure for the preparation of 3e-3l



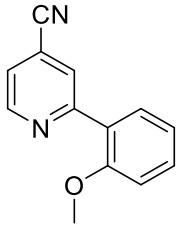
To a solution of 4-cyanopyridine (416.0 mg, 4.0 mmol) in dichloromethane(15 mL) was added trifluoroacetic acid (456.0 mg, 4.0 mmol) followed by arylboronic acid (732.0 mg, 6.0 mmol). Water (15 mL) was then added, followed by silver nitrate(136.0 mg, 0.80 mmol), Potassium persulfate (3.24 g, 12.0 mmol) was then added and the solution was stirred vigorously at room temperature and monitored by thin-layer chromatography analysis of the organic layer. After 3 hours a second addition of solid silver nitrate (136.0 mg, 0.08mmol) and potassium persulfate (3.24 g,

12.0 mmol) was added. The reaction was allowed to proceed for another 12h, and was worked up. The layers were separated, and the aqueous layer was extracted with dichloromethane for three times, dried over Na_2SO_4. After removal of the solvent under reduced pressure to afford the crude product, which was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate(20:1) to give pure product as a white solid (374.5 mg, 52%)[5].



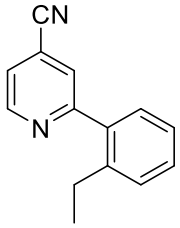
2-phenylisonicotinonitrile

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, *J* = 4.9 Hz, 1H), 8.00 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.95 (s, 1H), 7.57 – 7.47 (m, 3H), 7.45 (dd, *J* = 5.0, 1.4 Hz, 1H).



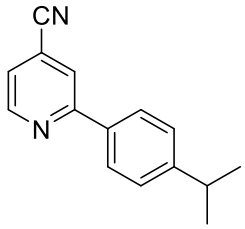
2-(2-methoxyphenyl)isonicotinonitrile

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (dd, *J* = 5.0, 0.7 Hz, 1H), 8.17 (s, 1H), 7.87 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.47 – 7.38 (m, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 3.90 (s, 3H).



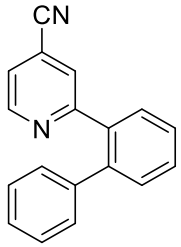
2-(2-ethylphenyl)isonicotinonitrile

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (dd, *J* = 5.0, 0.8 Hz, 1H), 7.64 – 7.60 (m, 1H), 7.48 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.44 – 7.27 (m, 4H), 2.71 (q, *J* = 7.5 Hz, 2H), 1.12 (t, *J* = 7.5 Hz, 3H).



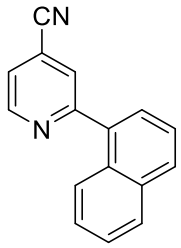
2-(4-isopropylphenyl)isonicotinonitrile

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 4.9 Hz, 1H), 7.93 (d, *J* = 8.5 Hz, 3H), 7.41 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 2H), 3.05 – 2.91 (m, 1H), 1.30 (d, *J* = 6.9 Hz, 6H).



2-([1,1'-biphenyl]-2-yl)isonicotinonitrile

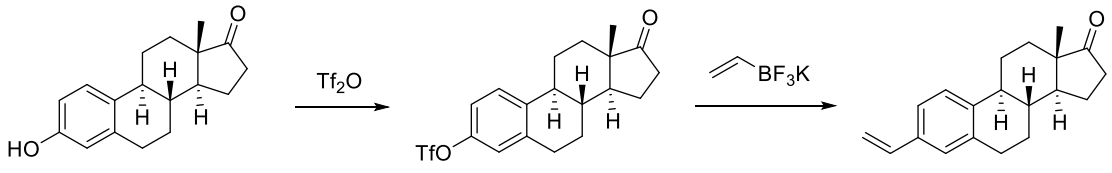
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (dd, *J* = 5.0, 0.8 Hz, 1H), 7.72 – 7.65 (m, 1H), 7.56 – 7.45 (m, 3H), 7.34 – 7.27 (m, 4H), 7.16 – 7.09 (m, 2H), 7.09 – 7.03 (m, 1H).



2-(naphthalen-1-yl)isonicotinonitrile

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (dd, *J* = 5.0, 0.8 Hz, 1H), 8.05 – 7.90 (m, 3H), 7.85 – 7.81 (m, 1H), 7.62 – 7.51 (m, 5H).

Procedure for the preparation of 7

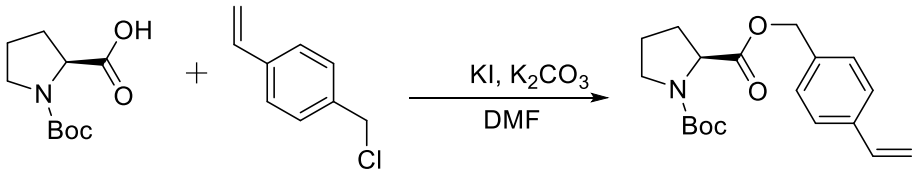


A 50 mL Schlenk flask equipped with a stir bar was set under an atmosphere of nitrogen and charged with estrone (1.0 equiv., 1.48 mmol, 0.40 g), triethylamine (1.50 equiv., 2.22 mmol, 0.31 mL) dissolved in DCM (20 mL). The reaction mixture was cooled to 0 ℃ and trifluoromethanesulfonic anhydride (1.5 equiv., 2.22 mmol, 0.37

mL). The solution was stirred for 1.5 h at 0 ℃ and afterwards extracted with a saturated $NaHCO_3$ solution (3 × 20 mL). All volatiles were evaporated under reduced pressure and flash column chromatography (SiO_2, PE/EA, gradient 0% → 50% EtOAc) afforded the title compound (480 mg, 1.19 mmol, 81%) as a yellow oil A nitrogen-flushed 10 mL vial equipped with a stir bar was charged with estrone triflate (1.0 equiv, 0.99 mmol, 0.40 g), potassium vinyltriflouroborate (1.20 equiv, 1.19 mmol, 160 mg), palladium chloride (2.0 mol%, 20.0 μmol, 3.5 mg), triphenylphosphine (6.0 mol%, 60.0 μmol, 15.7 mg), and cesium carbonate (3.0 equiv, 3.0 mmol, 970 mg) dissolved in THF/H_2O (4 mL, 9:1). The vial was sealed with a septum and heated at 80 ℃ for 15 h. The reaction mixture was filtered through celite and washed with THF (20 mL). All volatiles were evaporated under reduced pressure and flash column chromatography (SiO2, PE/EA, gradient 0% → 40% EA) afforded the title compound (213 mg, 0.76 mmol, 77%) as a white solid[6].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.18 (m, 2H), 7.15 (s, 1H), 6.67 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.71 (d, *J* = 17.6 Hz, 1H), 5.20 (d, *J* = 10.9 Hz, 1H), 2.98 – 2.87 (m, 2H), 2.56 – 2.39 (m, 2H), 2.35 – 2.24 (m, 1H), 2.16 – 1.95 (m, 4H), 1.63 – 1.49 (m, 6H), 0.91 (s, 3H).

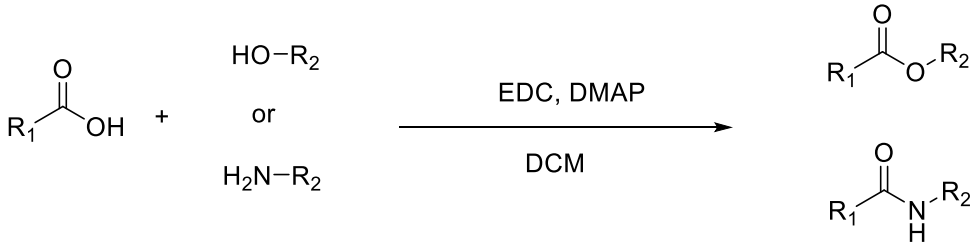
Procedure for the preparation of 8



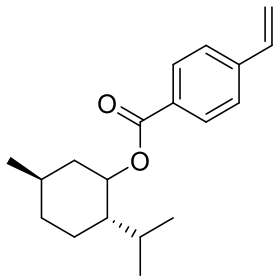
In a dry round-bottomed flask, the L-proline (2 mmol, 430.5 mg) was placed and DMF (10 mL) was added. Then K_2CO_3 (414.6 mg, 3.0 mmol) and KI (498 mg, 3 mmol) were added and stirred. To this stirring suspension, 4-vinylbenzyl chloride (335.8 mg, 2.2 mmol) was added, and the reaction was allowed to proceed overnight at rt. Upon completion of the reaction, 20 mL of EtOAc were added, followed by 20mL of H_2O. The reaction mixture was then extracted and washed three times with H_2O (20mL).The organic layer was washed with sat. NaCl solvent (20mL), dried ($NaSO_4$) and the volatiles were removed under reduced pressure. The crude mixture was subjected to purification by automated flash column chromatography (from hexanes to 15% EtOAc in hexanes). The compound was obtained as a colorless, iscous oil (430 mg, 1.3 mmol, 65%)[4].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.28 (m, 4H), 6.69 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.74 (d, *J* = 17.6 Hz, 1H), 5.31 – 4.99 (m, 3H), 4.31 (ddd, *J* = 48.7, 8.6, 3.6 Hz, 1H), 3.64 – 3.31 (m, 2H), 2.30 – 2.11 (m, 1H), 1.96 – 1.83 (m, 3H), 1.45 (s, 3H), 1.33 (s, 6H).

Procedure for the preparation of 9-13



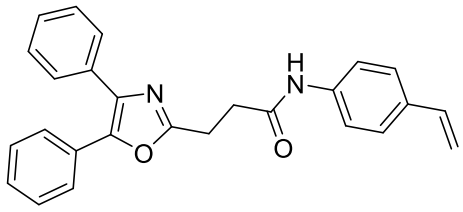
According to the previous reference, a mixture of Carboxylic acid compound (1.0mmol), a hydroxyl or an amino compound (1.02 mmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (287.6 mg, 1.5 mmol), and DMAP (2.5 mg, 0.02 mmol) in CH_2Cl_2 (20.0 mL) was stirred at room temperature for 2.5 h. The reaction mixture was added to H_2O and extracted with CH_2Cl_2. The organic layers were washed with brine, dried over $MgSO_4$, filtered, concentrated in vacuo, and flash chromatographed to afford the product[7].



(2S,5R)-2-isopropyl-5-methylcyclohexyl 4-vinylbenzoate

Yellow oil liquid; yield: 214 mg, 74%.

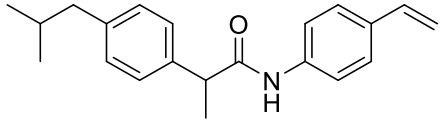
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 6.75 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.85 (d, *J* = 17.6 Hz, 1H), 5.37 (d, *J* = 11.3 Hz, 1H), 4.93 (td, *J* = 10.9, 4.4 Hz, 1H), 2.17 – 2.08 (m, 1H), 1.96 (tt, *J* = 11.2, 3.5 Hz, 1H), 1.78 – 1.68 (m, 2H), 1.60 – 1.48 (m, 2H), 1.20 – 1.04 (m, 2H), 0.92 (dd, *J* = 6.8, 5.1 Hz, 6H), 0.79 (d, *J* = 7.0 Hz, 3H).



3-(4,5-diphenyloxazol-2-yl)-N-(4-vinylphenyl)propanamide

Yellow solid; yield: 340 mg, 86%.

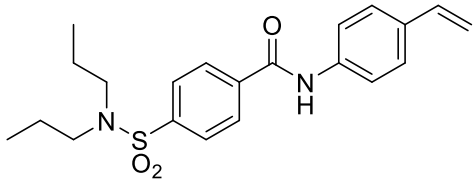
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.64 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.61 – 7.52 (m, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.44 – 7.29 (m, 8H), 6.65 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.66 (d, *J* = 17.6 Hz, 1H), 5.18 (d, *J* = 10.9 Hz, 1H), 3.28 (t, *J* = 6.8 Hz, 2H), 2.96 (t, *J* = 6.8 Hz, 2H).



2-(4-isobutylphenyl)-N-(4-vinylphenyl)propanamide

White solid; yield: 250 mg, 83%.

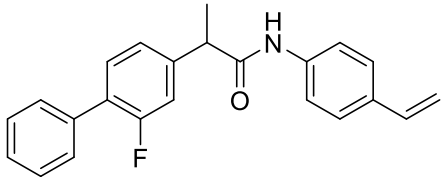
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.24 (m, 6H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.02 (s, 1H), 6.64 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.65 (d, *J* = 17.6 Hz, 1H), 5.17 (d, *J* = 10.9 Hz, 1H), 3.69 (q, *J* = 7.1 Hz, 1H), 2.48 (d, *J* = 7.2 Hz, 2H), 1.86 (td, *J* = 13.6, 6.8 Hz, 1H), 1.59 (d, *J* = 7.2 Hz, 3H), 0.91 (d, *J* = 6.6 Hz, 6H).



4-(N,N-dipropylsulfamoyl)-N-(4-vinylphenyl)benzamide

Yellow solid; yield: 125 mg, 32%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 6.71 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.73 (d, *J* = 17.6 Hz, 1H), 5.24 (d, *J* = 10.9 Hz, 1H), 3.13 – 3.06 (m, 4H), 1.57 – 1.50 (m, 4H), 0.87 (t, *J* = 7.4 Hz, 6H).



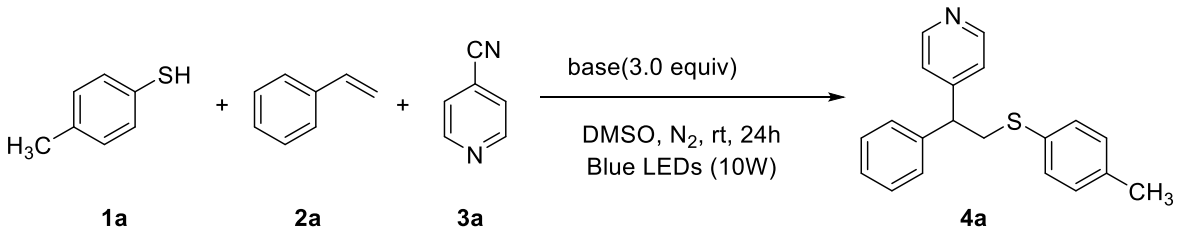
2-(2-fluoro-[1,1'-biphenyl]-4-yl)-N-(4-vinylphenyl)propanamide

White solid; yield: 294 mg, 85%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.50 (m, 2H), 7.45 (dd, *J* = 11.6, 4.4 Hz, 5H), 7.41 – 7.31 (m, 3H), 7.25 – 7.16 (m, 2H), 7.10 (s, 1H), 6.65 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.67 (d, *J* = 17.5 Hz, 1H), 5.19 (d, *J* = 10.9 Hz, 1H), 3.73 (q, *J* = 7.0 Hz, 1H), 1.63 (d, *J* = 7.1 Hz, 3H).

3. Optimization of reaction conditions

Table S1 Effect of base on template reaction

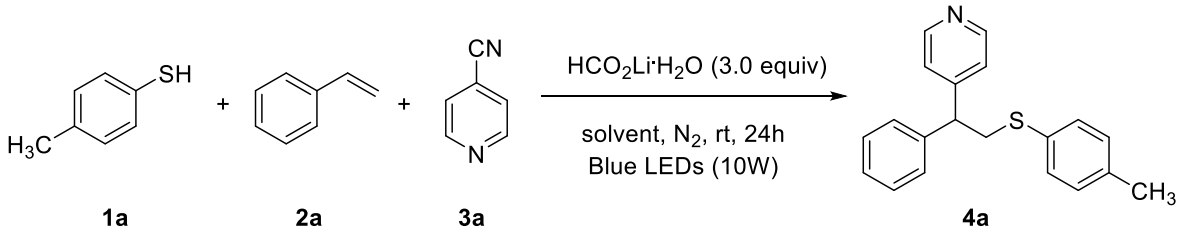


1a **2a** **3a** **4a**

entry	**base**	**Time(h)**	**Yield(%)**
1	$HCO_2Li{\cdot}H_2O$	24	79
2	HCO_2K	24	65
3	CH_3CO_2Na	24	56
4	$HCO_2Cs{\cdot}H_2O$	24	52
5	Et_3N	24	61
6	DIPEA	24	56
7	Na_2CO_3	24	58
8	DBU	24	25

Reaction conditions: **1a** (0.2 mmol), **2a** (0.8 mmol), **3a** (0.3 mmol), base (0.6mmol), N_2, solvent (4.0 mL), 10W blue LEDs (455nm LEDs), 24 h. isolation yield.

Table S2 Effect of solvent on template reaction

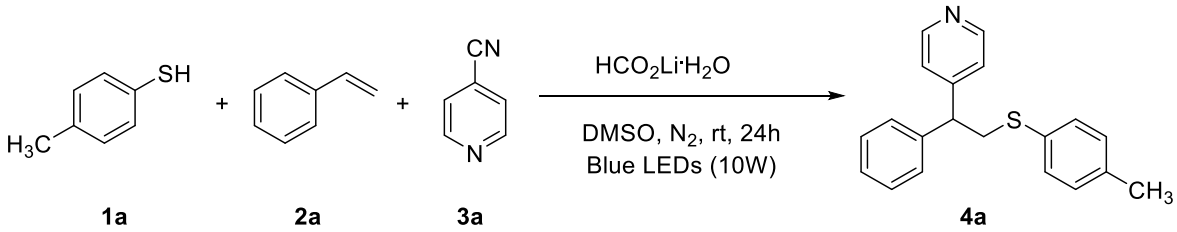


1a **2a** **3a** **4a**

entry	solvent	Time(h)	Yield(%)
1	DCM	24	trace
2	CH_3CN	24	trace
3	MeOH	24	trace
4	DMF	24	36
5	DMA	24	38
6	DCE	24	trace
7	THF	24	trace
8	DMSO	24	79

Reaction conditions: **1a** (0.2 mmol), **2a** (0.8 mmol), **3a** (0.3 mmol), base (0.6mmol), N_2, solvent (4.0 mL), 10W blue (455nm LEDs), 24 h. isolation yield.

Table S3 Effect of reaction charge ratio on template reaction

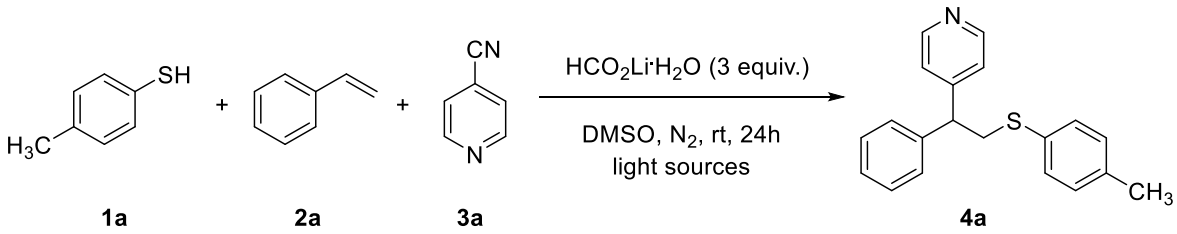


1a **2a** **3a** **4a**

entry	**1a** (mmol)	**2a** (mmol)	**3a** (mmol)	base(mmol)	Time (h)	Yield (%)
1	0.2	0.6	0.3	0.6	24	72
2	0.2	0.8	0.3	0.6	24	79
3	0.2	1.0	0.3	0.6	24	72
4	0.2	1.2	0.3	0.6	24	70
5	0.3	0.2	0.3	0.6	24	5
6	0.4	0.2	0.3	0.6	24	trace
7	0.5	0.2	0.3	0.6	24	trace
8	0.6	0.2	0.3	0.6	24	trace
9	0.2	0.8	0.3	0.2	24	40
10	0.2	0.8	0.3	0.4	24	64
11	0.2	0.8	0.3	0.8	24	68
12	0.2	0.8	0.3	1.0	24	65

Reaction conditions: N_2, DMSO (4.0 mL), 10W blue (455nm LEDs), 24 h. isolation yield.

Table S4 Effect of light sources

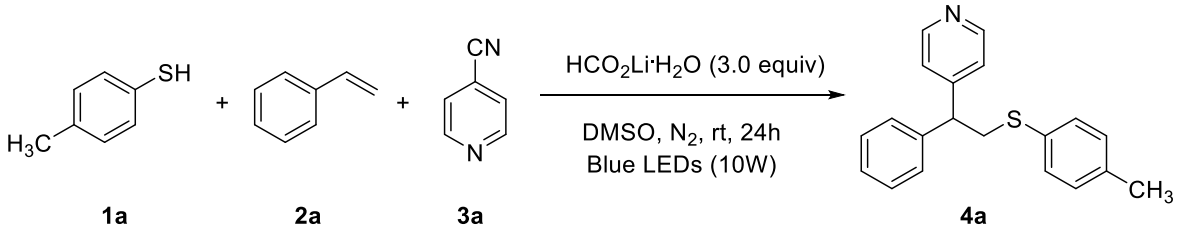


1a **2a** **3a** **4a**

entry	light sources	yield(%)
1	365 nm LEDs	41
2	380 nm LEDs	43
3	395 nm LEDs	42
4	410 nm LEDs	50
5	425 nm LEDs	67
6	480 nm LEDs	25
7	520 nm LEDs	0
8	23 W CFL	0

Reaction conditions: **1a** (0.2 mmol), **2a** (0.8 mmol), **3a** (0.3 mmol), base (0.6mmol), N_2, DMSO (4.0 mL), 24 h. isolation yield.

Table S5 Effect of various factors of photocatalytic system on template reaction



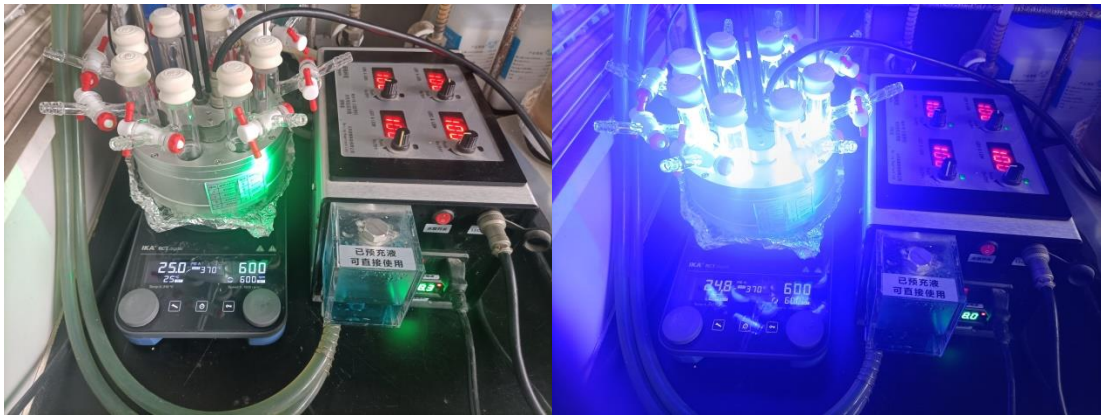
1a **2a** **3a** **4a**

entry	light	base	atmosphere	Yield (%)
1[a]	×	√	N_2	0
2	√	×	N_2	0
3	√	√	air	38
4	√	√	O_2	0

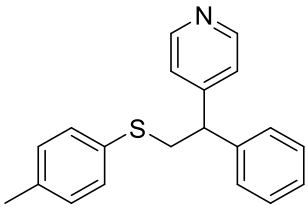
Reaction conditions: **1a** (0.2 mmol), **2a** (0.8 mmol), **3a** (0.3 mmol), base (0.6mmol), DMSO (4.0 mL), 10W blue (455nm LEDs), 24 h. isolation yield. [a] 60 ^{o}C

4. Experimental procedure

A 10 mL Schlenk reaction tube equipped with a magnetic stir bar charged with 4-cyanopyridine (0.3 mmol, 1.5 equiv.), HCO_2Li H_2O (0.6 mmol, 3 equiv.). The tube was capped. After evacuated and backfilled nitrogen three times, styrene (0.8 mmol, 4 equiv.), thiolphenol (0.2 mmol, 1 equiv.), dry DMSO (4 mL) were added via a syringe. The reaction mixture irritated with 10W 455nm blue LEDs at 25 ^oC. After 24h, 10 mL H_2O was added, and extracted with EtOAc (10 mL) three times, the combined organic solvents were collected and washed with brine and then dried over $NaSO_4$, concentrated in vacuo. The crude material was purified by silica gel colum chromatography (PE/EA=4/1~3/1) to afford the products **4**.



Analytical Date of Compounds



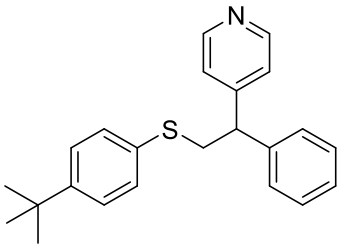
4-(1-phenyl-2-(p-tolylthio)ethyl)pyridine(4a)

Colorless oil liquid; Yield: 42 mg, 79%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 6.0 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.27 – 7.15 (m, 5H), 7.13 (d, *J* = 6.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 4.11 (t, *J* = 7.8 Hz, 1H), 3.51 (dd, *J* = 7.8, 1.5 Hz, 2H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.85 , 150.00 , 141.64 , 136.92 , 131.95 , 130.89 , 129.95 , 128.90 , 128.00 , 127.32 , 123.46 , 50.14 , 39.81 , 21.14.

HRMS(ESI): (m/z) Calcd. for $C_{20}H_{30}NS[M+H]^+$, 306.1311, found 306.1312.



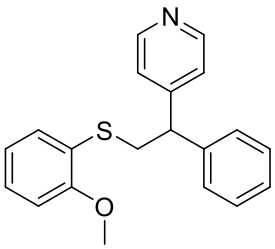
4-(2-((4-(tert-butyl)phenyl)thio)-1-phenylethyl)pyridine(4b)

Yellow oil liquid; Yied: 51 mg, 73%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 4.9 Hz, 2H), 7.33 – 7.27 (m, 4H), 7.27 – 7.22 (m, 3H), 7.18 (d, *J* = 7.1 Hz, 2H), 7.14 (d, *J* = 5.8 Hz, 2H), 4.15 (t, *J* = 7.8 Hz, 1H), 3.53 (dd, *J* = 7.8, 1.6 Hz, 2H), 1.30 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.93, 150.01, 141.66, 132.18, 130.32, 128.90, 128.00, 127.33, 126.21, 123.47, 50.29, 39.60, 34.60, 31.36.

HRMS(ESI): (m/z) Calcd. for $C_{23}H_{26}NS[M+H]^+$, 348.1780, found 348.1789.



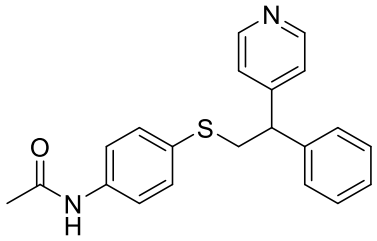
4-(2-((2-methoxyphenyl)thio)-1-phenylethyl)pyridine(4c)

Yellow oil liquid; Yied: 47 mg, 73%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 5.7 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.27 – 7.21 (m, 3H), 7.20 (d, *J* = 1.5 Hz, 1H), 7.18 (s, 1H), 7.15 (d, *J* = 6.0 Hz, 2H), 6.89 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 4.15 (t, *J* = 7.7 Hz, 1H), 3.85 (s, 3H), 3.53 (d, *J* = 7.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.09, 151.96, 149.93, 141.81, 131.38, 128.85, 128.28, 127.95, 127.25, 123.43, 121.10, 110.82, 76.84, 55.84, 50.30, 37.44.

HRMS(ESI): (m/z) Calcd. for $C_{20}H_{20}NOS[M+H]^+$, 322.1260, found 322.1259.



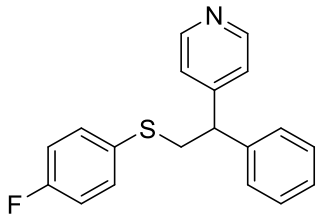
N-(4-((2-phenyl-2-(pyridin-4-yl)ethyl)thio)phenyl)acetamide(4d)

Yellow solid; Yield: 25 mg, 36%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 2H), 7.61 (br, 1H), 7.44 (t, *J* = 9.3 Hz, 3H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.27 (t, *J* = 6.5 Hz, 3H), 7.19 (s, 1H), 7.18 – 7.14 (m, 2H), 4.12 (t, *J* = 7.6 Hz, 1H), 3.52 (d, *J* = 7.7 Hz, 2H), 2.18 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.61, 152.11, 149.80, 141.48, 137.24, 131.91, 130.44, 128.99, 128.00, 127.45, 123.61, 120.58, 50.28, 40.05, 24.69.

HRMS(ESI): (m/z) Calcd. for $C_{21}H_{21}N_2OS[M+H]^+$, 349.1369, found 349.1367.



4-(2-((4-fluorophenyl)thio)-1-phenylethyl)pyridine(4e)

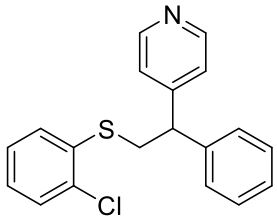
Yellow oil liquid; Yied: 42 mg, 68%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 5.0 Hz, 2H), 7.34 – 7.26 (m, 4H), 7.25 (dd, *J* = 5.3, 1.9 Hz, 1H), 7.18 (d, *J* = 1.5 Hz, 1H), 7.16 (s, 1H), 7.13 (d, *J* = 6.0 Hz, 2H), 6.98 (t, *J* = 8.7 Hz, 2H), 4.09 (t, *J* = 7.8 Hz, 1H), 3.50 (d, *J* = 7.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.11 (d, *J* = 247.1 Hz), 151.60, 150.05, 141.37, 133.16 (d, *J* = 8.3 Hz), 130.61 (d, *J* = 3.1 Hz), 128.92, 127.95, 127.39, 123.34, 116.27 (d, *J* = 21.8 Hz), 50.24, 40.37.

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.54.

HRMS(ESI): (m/z) Calcd. for $C_{19}H_{17}FNS[M+H]^+$, 310.1060, found 310.1064.



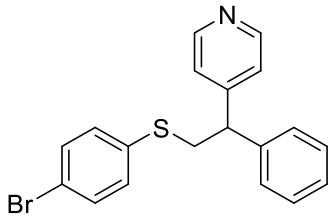
4-(2-((2-chlorophenyl)thio)-1-phenylethyl)pyridine(4f)

Yellow oil liquid; Yied: 47 mg, 72%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 5.1 Hz, 2H), 7.36 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.31 (t, *J* = 7.3 Hz, 2H), 7.26 (t, *J* = 7.1 Hz, 2H), 7.22 (s, 1H), 7.20 (s, 1H), 7.14 (ddd, *J* = 9.1, 8.4, 3.8 Hz, 4H), 4.19 (t, *J* = 7.7 Hz, 1H), 3.57 (d, *J* = 7.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.53, 150.06, 141.36, 134.99, 134.81, 130.25, 130.01, 128.98, 127.92, 127.53, 127.48, 127.26, 123.34 (s), 50.09, 37.95.

HRMS(ESI): (m/z) Calcd. for $C_{19}H_{17}ClNS[M+H]^+$, 326.0765, found 326.0765.



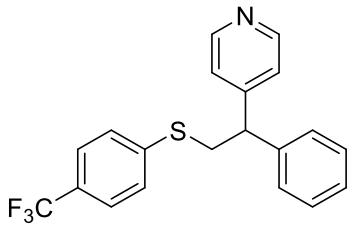
4-(2-((4-bromophenyl)thio)-1-phenylethyl)pyridine(4g)

Yellow oil liquid; Yied: 42 mg, 57%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 7.5 Hz, 2H), 7.27 – 7.24 (m, 1H), 7.19 (s, 1H), 7.17 (s, 1H), 7.16 – 7.12 (m, 4H), 4.12 (t, *J* = 7.8 Hz, 1H), 3.54 (d, *J* = 7.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.55, 150.09, 141.28, 135.04, 132.22, 131.53, 129.00, 127.95, 127.51, 123.35, 120.58, 50.09, 39.15.

HRMS(ESI): (m/z) Calcd. for $C_{19}H_{17}BrNS[M+H]^+$, 370.0260, found 370.0237.



4-(1-phenyl-2-((4-(trifluoromethyl)phenyl)thio)ethyl)pyridine(4h)

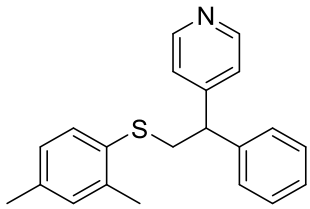
Colorless oil liquid; Yied: 57 mg, 79%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 6.0 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.36 – 7.30 (m, 4H), 7.28 (d, *J* = 7.3 Hz, 1H), 7.23 (d, *J* = 1.5 Hz, 1H), 7.21 (s, 1H), 7.17 (d, *J* = 6.0 Hz, 2H), 4.19 (t, *J* = 7.8 Hz, 1H), 3.63 (dd, *J* = 7.8, 2.3 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.43, 150.18, 141.47, 141.15, 129.09, 128.28, 128.14 (q, *J* = 33.2 Hz), 127.95, 127.67 125.95 (q, *J* = 3.7 Hz), 124.17 (q, *J* = 271.8 Hz), 123.31, 50.00, 37.91.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.44.

HRMS(ESI): (m/z) Calcd. for $C_{20}H_{17}F_3NS[M+H]^+$, 360.1028, found 360.1043.



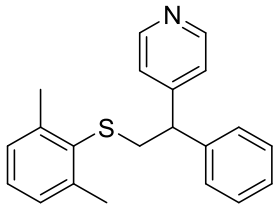
4-(2-((2,4-dimethylphenyl)thio)-1-phenylethyl)pyridine(4i)

Yellow oil liquid; Yied: 40 mg, 63%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 5.4 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 2H), 7.26 (s, 1H), 7.18 (dd, *J* = 14.8, 6.8 Hz, 5H), 7.01 (s, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 4.13 (t, *J* = 7.8 Hz, 1H), 3.48 (d, *J* = 6.8 Hz, 2H), 2.28 (d, *J* = 17.7 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.00, 149.98, 141.76, 139.10, 136.88, 131.40, 131.21, 130.67, 128.92, 128.00, 127.40, 127.34, 123.48, 50.19, 39.09, 21.05, 20.53.

HRMS(ESI): (m/z) Calcd. for $C_{21}H_{22}NS[M+H]^+$, 320.1467, found 320.1482.



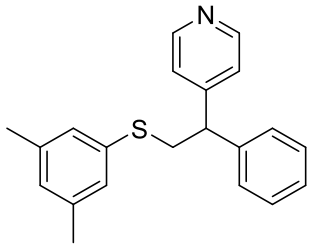
4-(2-((2,6-dimethylphenyl)thio)-1-phenylethyl)pyridine(4j)

Yellow oil liquid; Yied: 35 mg, 55%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 5.8 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.17 (d, *J* = 1.5 Hz, 1H), 7.14 (d, *J* = 6.1 Hz, 3H), 7.11 (d, *J* = 5.7 Hz, 1H), 7.09 (s, 1H), 7.07 (d, *J* = 2.4 Hz, 1H), 4.05 (t, *J* = 7.8 Hz, 1H), 3.31 (d, *J* = 7.8 Hz, 2H), 2.39 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.08, 149.97, 143.01, 141.78, 133.39, 128.90, 128.48, 128.28, 127.93, 127.31, 123.39, 50.98, 39.78, 22.02.

HRMS(ESI): (m/z) Calcd. for $C_{21}H_{22}NS[M+H]^+$, 320.1467, found 320.1481.



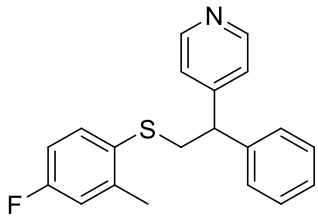
4-(2-((3,5-dimethylphenyl)thio)-1-phenylethyl)pyridine(4k)

Yellow oil liquid; Yied: 55 mg, 86%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.6 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 2H), 7.25 (dt, *J* = 4.6, 1.9 Hz, 1H), 7.21 (d, *J* = 1.5 Hz, 1H), 7.19 (s, 1H), 7.16 (d, *J* = 5.9 Hz, 2H), 6.91 (s, 2H), 6.83 (s, 1H), 4.16 (t, *J* = 7.8 Hz, 1H), 3.54 (dd, *J* = 7.8, 1.5 Hz, 2H), 2.27 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.87, 149.96, 141.70, 138.73, 135.31, 128.88, 128.47, 127.99, 127.58, 127.32, 123.44, 50.23, 39.00, 21.29.

HRMS(ESI): (m/z) Calcd. for $C_{21}H_{22}NS[M+H]^+$, 320.1467, found 320.1474.



4-(2-((4-fluoro-2-methylphenyl)thio)-1-phenylethyl)pyridine(4l)

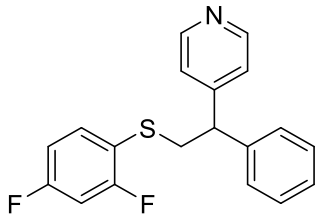
Yellow oil liquid; Yied: 38 mg, 59%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 2H), 7.34 – 7.28 (m, 2H), 7.28 – 7.21 (m, 2H), 7.18 (d, *J* = 1.4 Hz, 1H), 7.16 (s, 1H), 7.14 (d, *J* = 5.8 Hz, 2H), 6.94 – 6.81 (m, 2H), 4.09 (t, *J* = 7.8 Hz, 1H), 3.45 (d, *J* = 7.8 Hz, 2H), 2.28 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.01 (d, *J* = 246.6 Hz), 151.78, 150.02, 142.17 (d, *J* = 7.8 Hz), 141.48, 133.14 (d, *J* = 8.3 Hz), 129.73 (d, *J* = 3.2 Hz), 128.95, 127.95, 127.42, 123.40, 117.37 (d, *J* = 21.2 Hz), 113.59 (d, *J* = 21.8 Hz), 50.29, 39.57, 20.85.

^{19}F NMR (565 MHz, $CDCl_3$) δ -115.21.

HRMS(ESI): (m/z) Calcd. for $C_{20}H_{19}FNS[M+H]^+$, 324.1217, found 324.1241.



4-(2-((2,4-difluorophenyl)thio)-1-phenylethyl)pyridine(4m)

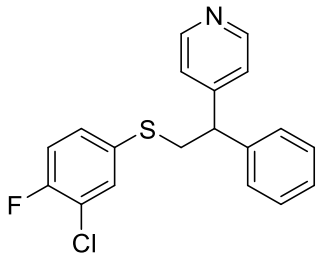
Yellow oil liquid; Yied: 39 mg, 60%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.4 Hz, 2H), 7.33 – 7.21 (m, 4H), 7.17 (d, *J* = 7.1 Hz, 2H), 7.14 (d, *J* = 5.8 Hz, 2H), 6.88 – 6.76 (m, 2H), 4.09 (t, *J* = 7.8 Hz, 1H), 3.50 (d, *J* = 7.8 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.63 (dd, *J* = 57.8, 11.6 Hz), 161.98 (dd, *J* = 55.7, 11.7 Hz), 151.52, 150.07, 141.22, 135.57 (dd, *J* = 9.6, 2.4 Hz), 128.96, 127.96, 127.46, 123.34, 117.52 (dd, *J* = 18.6, 4.2 Hz), 111.95 (dd, *J* = 21.4, 3.8 Hz), 104.75 (d, *J* = 26.4 Hz), 50.76, 39.39.

^{19}F NMR (565 MHz, $CDCl_3$) δ -102.88 (d, *J* = 9.1 Hz), -109.11 (d, *J* = 9.6 Hz).

HRMS(ESI): (m/z) Calcd. for $C_{19}H_{16}F_2NS[M+H]^+$, 328.0966, found 328.0967.



4-(2-((3-chloro-4-fluorophenyl)thio)-1-phenylethyl)pyridine(4n)

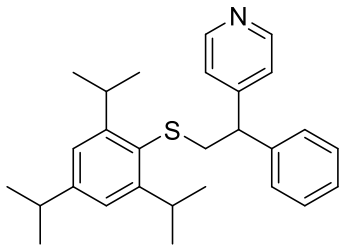
Yellow oil liquid; Yied: 35 mg, 51%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 2H), 7.33 (d, *J* = 2.4 Hz, 1H), 7.31 (d, *J* = 7.3 Hz, 2H), 7.25 (d, *J* = 2.3 Hz, 1H), 7.18 (d, *J* = 7.4 Hz, 2H), 7.15 (d, *J* = 4.4 Hz, 3H), 7.04 (t, *J* = 8.7 Hz, 1H), 4.12 (t, *J* = 7.8 Hz, 1H), 3.53 (d, *J* = 7.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.32 (d, *J* = 249.5 Hz), 151.46, 150.11 141.11, 132.71, 132.26 (d, *J* = 4.1 Hz), 130.68 (d, *J* = 7.0 Hz), 129.01, 127.96, 127.57, 123.31, 121.66 (d, *J* = 18.2 Hz), 117.22 (d, *J* = 21.4 Hz), 50.33, 40.08.

^{19}F NMR (565 MHz, $CDCl_3$) δ -117.06.

HRMS(ESI): (m/z) Calcd. for $C_{19}H_{16}ClFNS[M+H]^+$, 344.0671, found 344.0677.



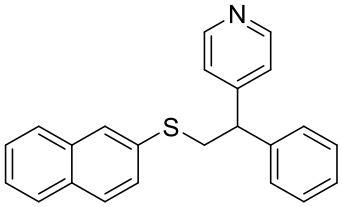
4-(1-phenyl-2-((2,4,6-triisopropylphenyl)thio)ethyl)pyridine(4o)

Yellow solid; Yied: 17 mg, 20%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 5.7 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 2H), 7.26 – 7.14 (m, 5H), 7.00 (s, 2H), 4.16 (t, *J* = 7.8 Hz, 1H), 3.71 (dt, *J* = 13.7, 6.9 Hz, 2H), 3.26 (d, *J* = 7.4 Hz, 2H), 2.88 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.25 (d, *J* = 6.9 Hz, 6H), 1.18 (d, *J* = 6.9 Hz, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.05, 152.33, 149.91, 141.94, 128.87, 128.66, 127.92, 127.30, 123.40, 121.98, 50.81, 42.85, 34.37, 31.65, 24.63, 24.03.

HRMS(ESI): (m/z) Calcd. for $C_{28}H_{36}NS[M+H]^+$, 418.2563, found 418.2556.



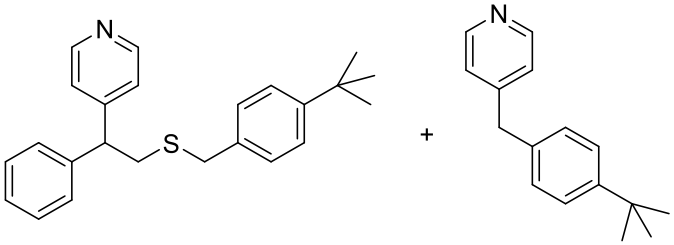
4-(2-(naphthalen-2-ylthio)-1-phenylethyl)pyridine(4p)

Yellow oil liquid; Yied: 37 mg, 54%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 5.4 Hz, 2H), 7.82 – 7.68 (m, 4H), 7.52 – 7.41 (m, 2H), 7.38 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.31 (t, *J* = 7.3 Hz, 2H), 7.27 – 7.18 (m, 3H), 7.15 (d, *J* = 5.9 Hz, 2H), 4.19 (t, *J* = 7.8 Hz, 1H), 3.65 (dd, *J* = 7.8, 3.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.75, 150.07, 141.54, 133.83, 133.22, 132.05, 128.97, 128.76, 128.02, 127.98, 127.84, 127.78, 127.44, 127.23, 126.79, 126.06, 123.42, 50.08, 38.89.

HRMS(ESI): (m/z) Calcd. for $C_{23}H_{20}NS[M+H]^+$, 342.1311, found 342.1309.



4q:4q' = 4:1

4-(2-((4-(tert-butyl)benzyl)thio)-1-phenylethyl)pyridine (4q)

4-(4-(tert-butyl)benzyl)pyridine (4q')

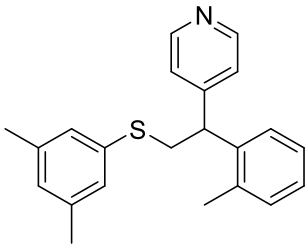
Yellow oil liquid; Yied: 38 mg, 55%

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 – 8.45 (m, 2.5H), 7.36 – 7.32 (m, 2.5H), 7.31 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 7.13 – 7.08 (m, 3H), 7.07 – 7.04 (m, 2H), 3.98 (t, *J* = 7.8 Hz, 1H), 3.93 (s, 0.5H), 3.62 (s, 2H), 3.08 (d, *J* = 7.8 Hz, 2H), 1.32 (s, 9H), 1.31 (s, 2.25H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.28, 150.55, 150.33, 149.89, 149.76, 149.72, 141.88, 135.87, 135.10, 128.85, 128.78, 128.74, 128.73, 128.05, 127.28, 125.76, 125.64, 123.46, 50.80, 40.88, 36.85, 36.38, 34.66, 34.57, 31.50, 31.21.

HRMS(ESI): (m/z) Calcd. for $C_{24}H_{28}NS[M+H]^+$, 362.1937, found 162.1947.

HRMS(ESI): (m/z) Calcd. for $C_{16}H_{20}N[M+H]^+$, 226.1590, found 226.1600.



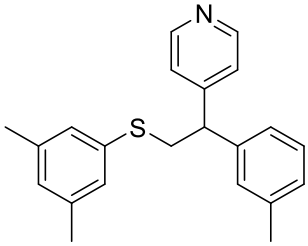
4-(2-((3,5-dimethylphenyl)thio)-1-(o-tolyl)ethyl)pyridine(5a)

Yellow oil liquid; Yied: 55 mg, 82%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 6.0 Hz, 2H), 7.24 (t, *J* = 8.3 Hz, 2H), 7.16 (dd, *J* = 6.4, 1.7 Hz, 2H), 7.11 (d, *J* = 6.1 Hz, 2H), 6.91 (s, 2H), 6.83 (s, 1H), 4.36 (t, *J* = 7.7 Hz, 1H), 3.50 (qd, *J* = 13.0, 7.7 Hz, 2H), 2.26 (s, 6H), 2.17 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.72, 149.89, 139.57, 138.73, 136.36, 135.31, 130.95, 128.53, 127.76, 127.22, 126.96, 126.45, 123.71, 45.86, 39.25, 21.27, 19.72.

HRMS(ESI): (m/z) Calcd. for $C_{22}H_{24}NS[M+H]^+$, 334.1624, found 334.1619.



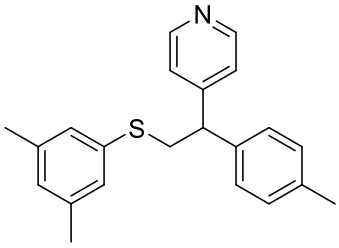
4-(2-((3,5-dimethylphenyl)thio)-1-(m-tolyl)ethyl)pyridine(5b)

Yellow oil liquid; Yied: 47 mg, 70%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 2H), 7.24 – 7.15 (m, 3H), 7.10 – 6.98 (m, 3H), 6.92 (s, 2H), 6.84 (s, 1H), 4.13 (t, *J* = 7.8 Hz, 1H), 3.55 (dd, *J* = 7.8, 3.2 Hz, 2H), 2.32 (s, 3H), 2.28 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.01, 149.97, 141.68, 138.73, 138.57, 135.42, 128.77, 128.45, 128.12, 127.58, 124.96, 123.47, 50.26, 38.99, 21.58, 21.31.

HRMS(ESI): (m/z) Calcd. for $C_{22}H_{24}NS[M+H]^+$, 334.1624, found 334.1629.



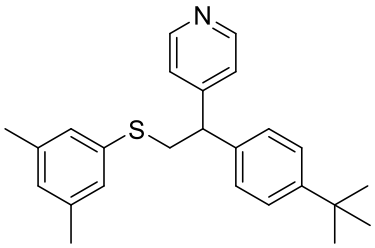
4-(2-((3,5-dimethylphenyl)thio)-1-(p-tolyl)ethyl)pyridine(5c)

Colorless oil liquid; Yied: 54 mg, 81%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 3.9 Hz, 2H), 7.16 (d, *J* = 5.3 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 2H), 6.92 (s, 2H), 6.84 (s, 1H), 4.14 (t, *J* = 7.8 Hz, 1H), 3.53 (dd, *J* = 7.8, 1.9 Hz, 2H), 2.33 (s, 3H), 2.28 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.23, 149.97, 138.76, 138.75, 137.08, 135.44, 129.63, 128.45, 127.88, 127.55, 123.44, 77.48, 77.16, 76.84, 49.89, 39.09, 21.33, 21.16.

HRMS(ESI): (m/z) Calcd. for $C_{22}H_{24}NS[M+H]^+$, 334.1624, found 334.1643.



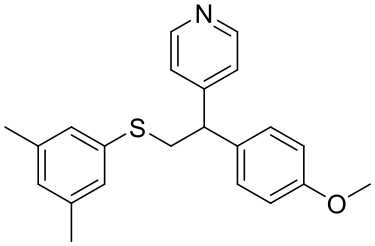
4-(1-(4-(tert-butyl)phenyl)-2-((3,5-dimethylphenyl)thio)ethyl)pyridine(5d)

Yellow oil liquid; Yied: 55 mg, 73%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 4.5 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 5.9 Hz, 2H), 7.14 (d, *J* = 8.3 Hz, 2H), 6.92 (s, 2H), 6.83 (s, 1H), 4.15 (t, *J* = 7.2 Hz, 1H), 3.63 – 3.47 (m, 2H), 2.28 (s, 6H), 1.30 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.06, 150.20, 149.93, 138.73, 135.48, 128.41, 127.54, 127.49, 125.80, 123.55, 49.88, 39.03, 34.56, 31.42, 21.32.

HRMS(ESI): (m/z) Calcd. for $C_{25}H_{30}NS[M+H]^+$, 376.2093, found 376.2089.



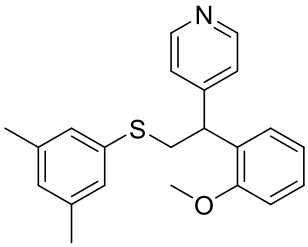
4-(2-((3,5-dimethylphenyl)thio)-1-(4-methoxyphenyl)ethyl)pyridine(5e)

Yellow oil liquid; Yied: 50 mg, 72%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.2 Hz, 2H), 7.15 (d, *J* = 5.9 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 6.92 (s, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.84 (s, 1H), 4.13 (t, *J* = 7.8 Hz, 1H), 3.78 (s, 3H), 3.52 (d, *J* = 7.8 Hz, 2H), 2.28 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.76, 152.31, 149.93, 138.72, 135.42, 133.73, 129.00, 128.41, 127.51, 123.35, 114.24, 55.31, 49.43, 39.19, 21.29.

HRMS(ESI): (m/z) Calcd. for $C_{22}H_{24}NOS[M+H]^+$, 350.1573, found 350.1574.



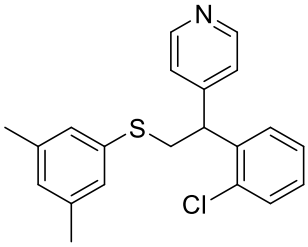
4-(2-((3,5-dimethylphenyl)thio)-1-(2-methoxyphenyl)ethyl)pyridine(5f)

Colorless oil liquid; Yied: 55 mg, 79%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 5.8 Hz, 2H), 7.23 (dt, *J* = 8.2, 1.7 Hz, 1H), 7.17 (d, *J* = 6.0 Hz, 2H), 7.12 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.92 (t, 3H,*J* = 7.6 Hz), 6.84 (d, *J* = 8.2 Hz, 1H), 6.81 (s, 1H), 4.61 (dd, *J* = 8.5, 7.0 Hz, 1H), 3.74 (s, 3H), 3.53 (ddd, *J* = 21.7, 12.9, 7.8 Hz, 2H), 2.26 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.01, 151.92, 149.70, 138.55, 135.80, 130.11, 128.44, 128.28, 128.18, 127.34, 123.81, 120.75, 110.97, 55.41, 43.65, 37.55, 21.32.

HRMS(ESI): (m/z) Calcd. for $C_{22}H_{24}NOS[M+H]^+$, 350.1573, found 350.1562.



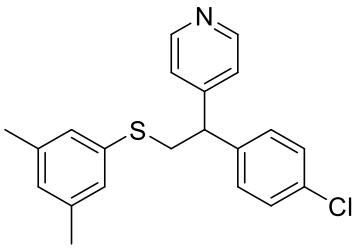
4-(1-(2-chlorophenyl)-2-((3,5-dimethylphenyl)thio)ethyl)pyridine(5g)

Brown oil liquid; Yied: 45 mg, 64%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 2H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.25 (d, *J* = 4.0 Hz, 2H), 7.20 (dd, *J* = 8.0, 4.7 Hz, 1H), 7.15 (d, *J* = 5.9 Hz, 2H), 6.93 (s, 2H), 6.84 (s, 1H), 4.72 (t, *J* = 7.8 Hz, 1H), 3.51 (ddd, *J* = 21.4, 13.1, 7.8 Hz, 2H), 2.27 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.72, 149.95, 138.97, 138.76, 134.86, 134.41, 130.15, 128.84, 128.74, 128.58, 128.13, 127.26, 123.73, 46.17, 38.44, 21.29.

HRMS(ESI): (m/z) Calcd. for $C_{21}H_{21}ClNS[M+H]^+$, 354.1078, found 354.1075.



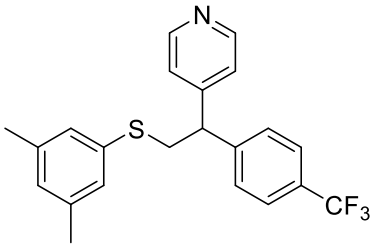
4-(1-(4-chlorophenyl)-2-((3,5-dimethylphenyl)thio)ethyl)pyridine(5h)

Yellow oil liquid; Yied: 31 mg, 44%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 5.8 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 6.7 Hz, 4H), 6.90 (s, 2H), 6.85 (s, 1H), 4.13 (t, *J* = 7.7 Hz, 1H), 3.50 (dd, *J* = 7.8, 2.2 Hz, 2H), 2.27 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.55, 150.11, 140.05, 138.86, 135.00, 133.25, 129.47, 129.06, 128.70, 127.84, 123.31, 49.70, 39.09, 21.32.

HRMS(ESI): (m/z) Calcd. for $C_{21}H_{21}ClNS[M+H]^+$, 354.1078, found 354.1069.



4-(2-((3,5-dimethylphenyl)thio)-1-(4-(trifluoromethyl)phenyl)ethyl)pyridine(5i)

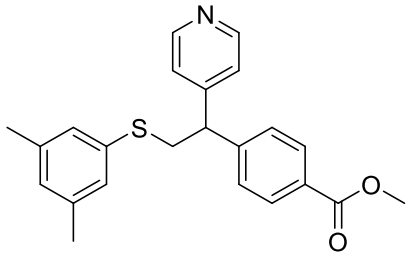
Brown oil liquid; Yied: 45 mg, 58%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 5.7 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 5.9 Hz, 2H), 6.91 (s, 2H), 6.85 (s, 1H), 4.22 (t, *J* = 7.7 Hz, 1H), 3.55 (dd, *J* = 7.7, 1.7 Hz, 2H), 2.27 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.05, 150.22, 145.52, 138.91, 134.79, 129.67 (q, *J* = 32.7 Hz), 128.83, 128.56, 127.95, 125.85 (q, *J* = 3.7 Hz), 124.12 (q, *J* = 407.7 Hz), 123.31, 50.17, 38.96, 21.29.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.54.

HRMS(ESI): (m/z) Calcd. for $C_{22}H_{21}F_3NS[M+H]^+$, 388.1341, found 388.1338.



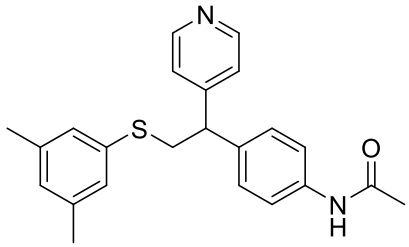
methyl 4-(2-((3,5-dimethylphenyl)thio)-1-(pyridin-4-yl)ethyl)benzoate(5j)

Yellow oil liquid; Yied: 43 mg, 57%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 5.9 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 6.0 Hz, 2H), 6.91 (s, 2H), 6.84 (s, 1H), 4.21 (t, *J* = 7.7 Hz, 1H), 3.90 (s, 3H), 3.54 (d, *J* = 7.8 Hz, 2H), 2.27 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.73, 151.13, 150.12, 146.65, 138.82, 134.86, 130.16, 129.25, 128.72, 128.15, 127.87, 123.32, 52.21, 50.22, 38.87, 21.26.

HRMS(ESI): (m/z) Calcd. for $C_{23}H_{24}NO_2S[M+H]^+$, 378.1522, found 378.1523.



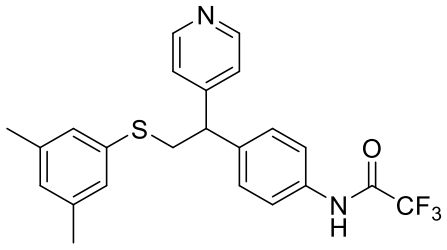
N-(4-(2-((3,5-dimethylphenyl)thio)-1-(pyridin-4-yl)ethyl)phenyl)acetamide(5k)

Yellow solid; Yied: 51 mg, 68%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 5.8 Hz, 2H), 8.41 (s, 1H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.14 (d, *J* = 6.1 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.90 (s, 2H), 6.83 (s, 1H), 4.12 (t, *J* = 7.7 Hz, 1H), 3.50 (d, *J* = 7.7 Hz, 2H), 2.26 (s, 6H), 2.12 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.92, 152.22, 149.69, 138.75, 137.49, 137.17, 135.15, 128.50, 128.43, 127.52, 123.51, 120.35, 49.62, 38.93, 24.42, 21.26.

HRMS(ESI): (m/z) Calcd. for $C_{23}H_{25}N_2OS[M+H]^+$, 377.1682, found 377.1680.

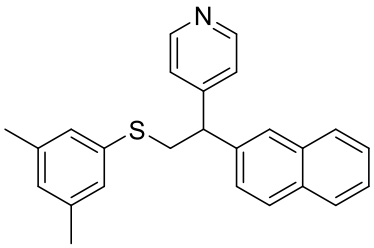


N-(4-(2-((3,5-dimethylphenyl)thio)-1-(pyridin-4-yl)ethyl)phenyl)-2,2,2-trifluoroacetamide(5l)

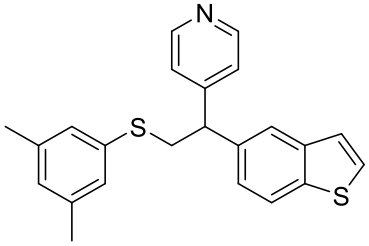
Brown oil liquid; Yied: 61 mg, 71%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 1H), 8.48 (d, *J* = 6.0 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.16 (d, *J* = 6.1 Hz, 2H), 6.91 (s, 2H), 6.85 (s, 1H), 4.16 (t, *J* = 7.7 Hz, 1H), 3.52 (d, *J* = 7.8 Hz, 2H), 2.27 (s, 6H).

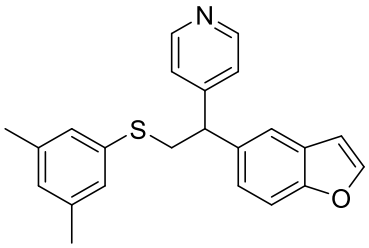
^{13}C NMR (151 MHz, $CDCl_3$) δ 155.15 (q, *J* = 37.5 Hz), 152.64, 149.24, 139.34, 138.92, 134.88, 134.81, 128.96, 128.78, 127.82, 123.69, 121.17, 115.88 (q, *J* = 288.4 Hz), 49.79, 39.00, 21.32.
^{19}F NMR (565 MHz, $CDCl_3$) δ -75.32.
HRMS(ESI): (m/z) Calcd. for $C_{23}H_{22}F_3N_2OS[M+H]^+$, 431.1399, found 431.1399.



4-(2-((3,5-dimethylphenyl)thio)-1-(naphthalen-2-yl)ethyl)pyridine(5m)
Yellow oil liquid; Yied: 49 mg, 66%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 5.9 Hz, 2H), 7.82 (d, *J* = 2.9 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.69 (s, 1H), 7.51 – 7.45 (m, 2H), 7.28 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.22 (d, *J* = 6.0 Hz, 2H), 6.94 (s, 2H), 6.84 (s, 1H), 4.35 (t, *J* = 7.7 Hz, 1H), 3.74 – 3.58 (m, 2H), 2.27 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 151.87, 150.02, 139.00, 138.78, 135.30, 133.49, 132.62, 128.69, 128.54, 127.91, 127.76, 127.73, 126.71, 126.49, 126.16, 123.55, 50.38, 38.98, 21.30.
HRMS(ESI): (m/z) Calcd. for $C_{25}H_{24}NS[M+H]^+$, 370.1624, found 370.1617.

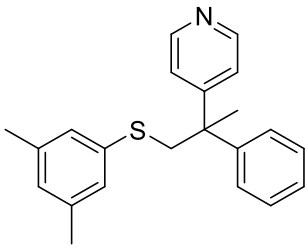


4-(1-(benzo[b]thiophen-5-yl)-2-((3,5-dimethylphenyl)thio)ethyl)pyridine(5n)
Yellow oil liquid; Yied: 46 mg, 61%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 5.9 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 1.5 Hz, 1H), 7.45 (d, *J* = 5.4 Hz, 1H), 7.29 (d, *J* = 5.5 Hz, 1H), 7.20 (d, *J* = 6.0 Hz, 2H), 7.17 (dd, *J* = 8.4, 1.7 Hz, 1H), 6.93 (s, 2H), 6.84 (s, 1H), 4.31 (t, *J* = 7.7 Hz, 1H), 3.62 (dd, *J* = 7.7, 2.0 Hz, 2H), 2.27 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.09, 150.01, 140.06, 138.75, 138.72, 137.87, 135.32, 128.49, 127.64, 127.37, 124.51, 123.83, 123.43, 122.92, 122.85, 50.21, 39.21, 21.28.
HRMS(ESI): (m/z) Calcd. for $C_{23}H_{22}NS_2[M+H]^+$, 376.1188, found 376.1187.



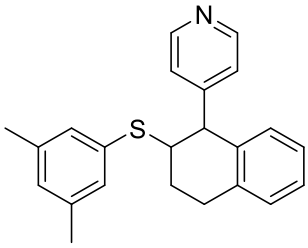
4-(1-(benzofuran-5-yl)-2-((3,5-dimethylphenyl)thio)ethyl)pyridine(5o)
Yellow oil liquid; Yied: 39 mg, 54%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 5.9 Hz, 2H), 7.61 (d, *J* = 2.2 Hz, 1H), 7.44 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.19 (d, *J* = 6.0 Hz, 2H), 7.12 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.92 (s, 2H), 6.83 (s, 1H), 6.72 (dd, *J* = 2.2, 0.8 Hz, 1H), 4.28 (t, *J* = 7.8 Hz, 1H), 3.60 (d, *J* = 7.7 Hz, 2H), 2.27 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.17, 152.38, 149.99, 145.77, 138.77, 136.34, 135.41, 128.49, 127.94, 127.61, 124.48, 123.43, 120.45, 111.75, 106.69, 50.19, 39.44, 21.31.
HRMS(ESI): (m/z) Calcd. for $C_{23}H_{22}NOS[M+H]^+$, 360.1417, found 360.1418.



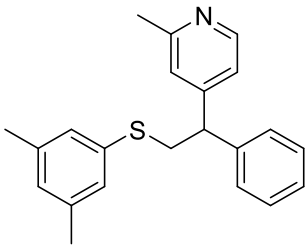
4-(1-((3,5-dimethylphenyl)thio)-2-phenylpropan-2-yl)pyridine(5p)

Colorless oil liquid; Yied: 58 mg, 86%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 5.6 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 2H), 7.25 – 7.16 (m, 3H), 7.14 (d, *J* = 6.0 Hz, 2H), 6.83 (s, 2H), 6.78 (s, 1H), 3.65 (s, 2H), 2.23 (s, 6H), 1.83 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.76, 149.67, 146.23, 138.58, 136.66, 128.42, 128.33, 127.77, 127.33, 126.85, 122.82, 47.39, 47.18, 27.05, 21.25.
HRMS(ESI): (m/z) Calcd. for $C_{22}H_{24}NS[M+H]^+$, 334.1624, found 334.1624.



4-(2-((3,5-dimethylphenyl)thio)-1,2,3,4-tetrahydronaphthalen-1-yl)pyridine(5q)

White solid; Yied: 30 mg, 21%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 2H), 7.18 (d, *J* = 4.0 Hz, 2H), 7.07 (dt, *J* = 8.5, 4.2 Hz, 1H), 6.98 (s, 4H), 6.89 (s, 1H), 6.75 (d, *J* = 7.7 Hz, 1H), 4.15 (d, *J* = 6.0 Hz, 1H), 3.62 – 3.49 (m, 1H), 3.18 – 3.00 (m, 1H), 2.98 – 2.79 (m, 1H), 2.28 (s, 6H), 2.19 – 2.12 (m, 1H), 1.96 – 1.84 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.42, 149.77, 138.71, 136.41, 135.52, 133.77, 130.64, 130.30, 129.38, 129.08, 126.93, 126.40, 50.99, 50.21, 27.15, 26.00, 21.29.
HRMS(ESI): (m/z) Calcd. for $C_{23}H_{24}NS[M+H]^+$, 346.1624, found 346.1625.



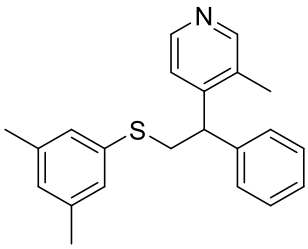
4-(2-((3,5-dimethylphenyl)thio)-1-phenylethyl)-2-methylpyridine(6a)

Colorless oil liquid; Yied: 55 mg, 82%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 5.1 Hz, 1H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.25 (d, *J* = 5.0 Hz, 1H), 7.20 (d, *J* = 7.0 Hz, 2H), 7.01 (s, 1H), 6.98 (d, *J* = 5.2 Hz, 1H), 6.91 (s, 2H), 6.83 (s, 1H), 4.12 (t, *J* = 7.8 Hz, 1H), 3.53 (d, *J* = 7.8 Hz, 2H), 2.51 (s, 3H), 2.27 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.65, 152.18, 149.31, 141.91, 138.74, 135.47, 128.89, 128.46, 128.00, 127.60, 127.30, 123.01, 120.52, 50.37, 39.05, 24.56, 21.32.

HRMS(ESI): (m/z) Calcd. for $C_{22}H_{24}NS[M+H]^+$, 334.1624, found 334.1625.



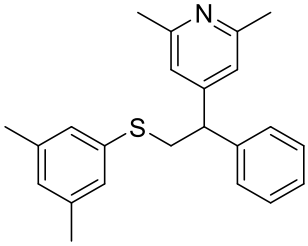
4-(2-((3,5-dimethylphenyl)thio)-1-phenylethyl)-3-methylpyridine(6b)

Colorless oil liquid; Yied: 57 mg, 85%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 5.1 Hz, 1H), 8.34 (s, 1H), 7.32 – 7.19 (m, 4H), 7.15 (d, *J* = 7.0 Hz, 2H), 6.91 (s, 2H), 6.84 (s, 1H), 4.32 (t, *J* = 7.7 Hz, 1H), 3.51 (d, *J* = 7.7 Hz, 2H), 2.27 (s, 6H), 2.12 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.31, 149.50, 147.84, 141.22, 138.77, 135.35, 132.20, 128.85, 128.57, 128.27, 127.82, 127.23, 121.67, 76.84, 46.32, 39.37, 21.31, 16.51.

HRMS(ESI): (m/z) Calcd. for $C_{22}H_{24}NS[M+H]^+$, 334.1624, found 334.1616.



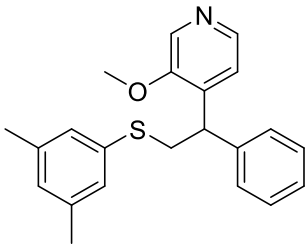
4-(2-((3,5-dimethylphenyl)thio)-1-phenylethyl)-2,6-dimethylpyridine(6c)

Colorless oil liquid; Yied: 68 mg, 95%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.3 Hz, 2H), 7.24 (d, *J* = 6.0 Hz, 1H), 7.20 (d, *J* = 7.1 Hz, 2H), 6.91 (s, 2H), 6.82 (s, 3H), 4.09 (t, *J* = 7.8 Hz, 1H), 3.52 (d, *J* = 7.8 Hz, 2H), 2.47 (s, 6H), 2.27 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.94, 152.39, 142.06, 138.68, 135.60, 128.83, 128.38, 127.97, 127.54, 127.2, 119.97, 50.41, 39.03, 24.58, 21.31.

HRMS(ESI): (m/z) Calcd. for $C_{23}H_{26}NS[M+H]^+$, 348.1780, found 348.1773.



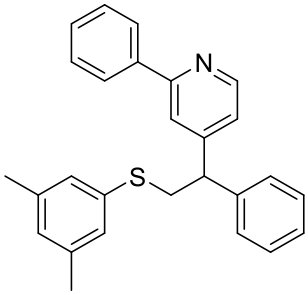
4-(2-((3,5-dimethylphenyl)thio)-1-phenylethyl)-3-methoxypyridine(6d)

Yellow oil liquid; Yied: 29 mg, 41%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 5.1 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.24 (d, *J* = 7.1 Hz, 3H), 7.11 (d, *J* = 4.8 Hz, 1H), 6.92 (s, 2H), 6.82 (s, 1H), 4.63 (t, *J* = 7.9 Hz, 1H), 3.86 (s, 3H), 3.53 (ddd, *J* = 44.4, 12.9, 7.9 Hz, 2H), 2.28 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.85, 141.33, 139.88, 138.58, 135.83, 133.60, 128.65, 128.34, 128.25, 127.49, 127.09, 56.20, 43.61, 37.98, 21.35.

HRMS(ESI): (m/z) Calcd. for $C_{22}H_{24}NOS[M+H]^+$, 350.1573, found 350.1576.



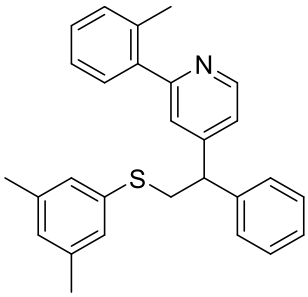
4-(2-((3,5-dimethylphenyl)thio)-1-phenylethyl)-2-phenylpyridine(6e)

Clorless oil liquid; Yied: 38 mg, 48%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 5.1 Hz, 1H), 7.92 (d, *J* = 7.0 Hz, 2H), 7.56 (s, 1H), 7.48 – 7.37 (m, 3H), 7.36 – 7.28 (m, 2H), 7.28 – 7.20 (m, 3H), 7.10 (dd, *J* = 5.1, 1.4 Hz, 1H), 6.93 (s, 2H), 6.82 (s, 1H), 4.23 (t, *J* = 7.7 Hz, 1H), 3.59 (d, *J* = 7.7 Hz, 2H), 2.25 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.82, 152.60, 149.88, 141.82, 139.50, 138.77, 135.36, 129.06, 128.94, 128.79, 128.54, 128.02, 127.71, 127.36, 127.13, 121.87, 120.58, 50.62, 39.13, 21.31.

HRMS(ESI): (m/z) Calcd. for $C_{27}H_{26}NS[M+H]^+$, 396.1780, found 396.1782.



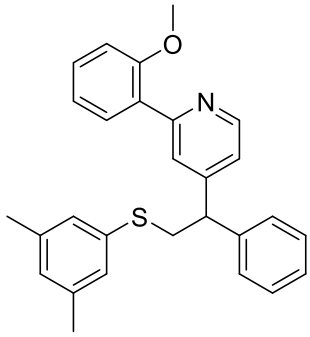
4-(2-((3,5-dimethylphenyl)thio)-1-phenylethyl)-2-(o-tolyl)pyridine(6f)

Yellow oil liquid; Yied: 66 mg, 80%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 5.1 Hz, 1H), 7.37 (d, *J* = 7.3 Hz, 1H), 7.34 – 7.29 (m, 2H), 7.29 – 7.20 (m, 7H), 7.11 (dd, *J* = 5.2, 1.6 Hz, 1H), 6.92 (s, 2H), 6.82 (s, 1H), 4.21 (t, *J* = 7.7 Hz, 1H), 3.58 (d, *J* = 7.7 Hz, 2H), 2.31 (s, 3H), 2.26 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.18, 152.00, 149.43, 141.84, 140.48, 138.75, 135.85, 135.37, 130.83, 129.76, 128.93, 128.50, 128.37, 128.01, 127.62, 127.35, 125.94, 123.88, 121.45, 76.84, 50.40, 39.11, 21.31, 20.41.

HRMS(ESI): (m/z) Calcd. for $C_{28}H_{28}NS[M+H]^+$, 410.1937, found 410.1936.



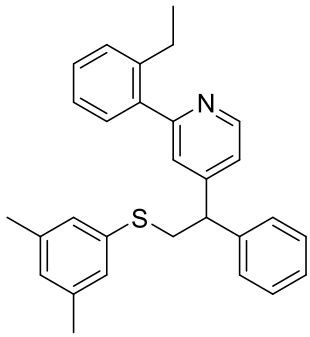
4-(2-((3,5-dimethylphenyl)thio)-1-phenylethyl)-2-(2-methoxyphenyl)pyridine(6g)

Colorless oil liquid; Yied: 65 mg, 76%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 5.1 Hz, 1H), 7.77 – 7.70 (m, 2H), 7.36 – 7.22 (m, 6H), 7.09 – 7.01 (m, 2H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.93 (s, 2H), 6.81 (s, 1H), 4.22 (t, *J* = 7.7 Hz, 1H), 3.77 (s, 3H), 3.58 (dd, *J* = 7.7, 2.3 Hz, 2H), 2.25 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.98, 156.25, 151.35, 149.49, 141.91, 138.67, 135.58, 131.22, 130.01, 129.16, 128.79, 128.35, 128.11, 127.46, 127.20, 124.76, 121.52, 121.11, 111.55, 55.67, 50.41, 39.13, 21.28.

HRMS(ESI): (m/z) Calcd. for $C_{28}H_{28}NOS[M+H]^+$, 426.1886, found 426.1890.



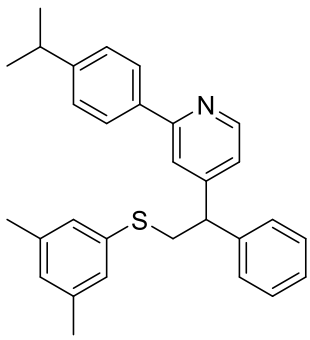
4-(2-((3,5-dimethylphenyl)thio)-1-phenylethyl)-2-(2-ethylphenyl)pyridine(6h)

Colorless oil liquid; Yied: 72 mg, 84%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 5.1 Hz, 1H), 7.36 – 7.27 (m, 5H), 7.27 – 7.19 (m, 5H), 7.12 (dd, *J* = 5.1, 1.6 Hz, 1H), 6.92 (s, 2H), 6.82 (s, 1H), 4.21 (t, *J* = 7.7 Hz, 1H), 3.58 (d, *J* = 7.2 Hz, 2H), 2.65 (q, *J* = 7.5 Hz, 2H), 2.26 (s, 6H), 1.05 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.31, 152.00, 149.39, 142.06, 141.85, 140.21, 138.75, 135.38, 129.81, 129.08, 128.92, 128.54, 128.49, 127.99, 127.60, 127.33, 125.82, 123.83, 121.50, 50.33, 39.09, 26.16, 21.30, 15.66.

HRMS(ESI): (m/z) Calcd. for $C_{29}H_{30}NS[M+H]^+$, 424.2093, found 424.2090.



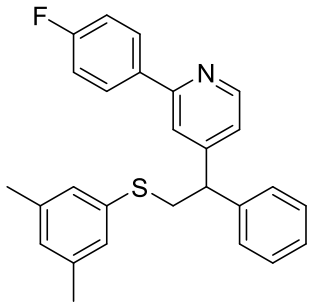
4-(2-((3,5-dimethylphenyl)thio)-1-phenylethyl)-2-(4-isopropylphenyl)pyridine(6i)

Colorless oil liquid; Yied: 76 mg, 87%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 5.1 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.54 (s, 1H), 7.31 (d, *J* = 7.9 Hz, 4H), 7.28 – 7.18 (m, 3H), 7.07 (dd, *J* = 5.1, 1.5 Hz, 1H), 6.93 (s, 2H), 6.82 (s, 1H), 4.22 (t, *J* = 7.7 Hz, 1H), 3.59 (d, *J* = 7.7 Hz, 2H), 2.95 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.26 (s, 6H), 1.27 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.89, 152.50, 150.02, 149.82, 141.86, 138.77, 137.12, 135.43, 128.93, 128.53, 128.05, 127.69, 127.34, 127.11, 126.90, 121.57, 120.34, 50.60, 39.16, 34.04, 24.05, 21.32.

HRMS(ESI): (m/z) Calcd. for $C_{30}H_{32}NS[M+H]^+$, 438.2250, found 438.2252.



4-(2-((3,5-dimethylphenyl)thio)-1-phenylethyl)-2-(4-fluorophenyl)pyridine(6j)

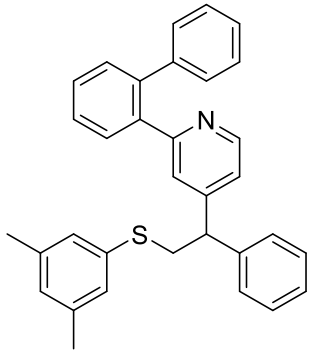
Yellow oil liquid; Yied: 63 mg, 76%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 5.1 Hz, 1H), 7.90 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.51 (s, 1H), 7.39 – 7.28 (m, 2H), 7.25 (t, *J* = 6.7 Hz, 3H), 7.17 – 7.04 (m, 3H), 6.92 (s, 2H), 6.82 (s, 1H), 4.23 (t, *J* = 7.7 Hz, 1H), 3.59 (d, *J* = 8.3 Hz, 2H), 2.25 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.60 (d, *J* = 248.4 Hz), 156.77, 152.69, 149.88, 141.80, 138.78, 135.64 (d, *J* = 3.0 Hz), 135.34, 128.97, 128.88, 128.56, 128.00, 127.71, 127.40, 121.83, 120.25, 115.68 (d, *J* = 21.6 Hz), 50.63, 39.11, 21.31.

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.01.

HRMS(ESI): (m/z) Calcd. for $C_{27}H_{25}FNS[M+H]^+$, 414.1686, found 414.1688.



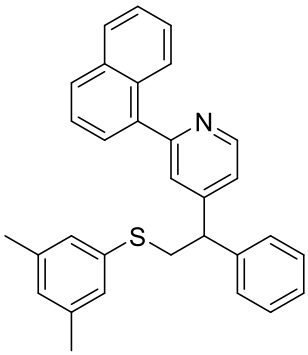
2-([1,1'-biphenyl]-2-yl)-4-(2-((3,5-dimethylphenyl)thio)-1-phenylethyl)pyridine(6k)

Colorless oil liquid; Yied: 46 mg, 49%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 5.1 Hz, 1H), 7.78 – 7.69 (m, 1H), 7.47 – 7.40 (m, 3H), 7.26 – 7.17 (m, 6H), 7.17 – 7.11 (m, 2H), 6.91 (dd, *J* = 5.2, 1.6 Hz, 1H), 6.85 (dd, *J* = 7.7, 1.6 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 3H), 6.74 (s, 1H), 3.88 (t, *J* = 7.7 Hz, 1H), 3.12 (ddd, *J* = 49.0, 12.9, 7.8 Hz, 2H), 2.26 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.16, 151.01, 149.64, 141.62, 141.34, 140.76, 139.45, 138.63, 135.49, 130.54, 129.86, 128.74, 128.65, 128.33, 127.94, 127.82, 127.42, 127.09, 126.85, 125.04, 121.70, 49.94, 38.72, 21.31.

HRMS(ESI): (m/z) Calcd. for $C_{33}H_{30}NS[M+H]^+$, 472.2093, found 472.2086.



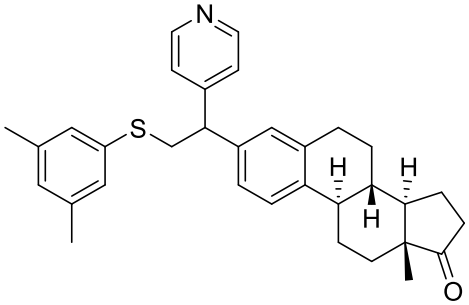
4-(2-((3,5-dimethylphenyl)thio)-1-phenylethyl)-2-(naphthalen-1-yl)pyridine(6l)

Colorless oil liquid; Yied: 66 mg, 74%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 5.2 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 2H), 7.61 – 7.40 (m, 5H), 7.37 – 7.29 (m, 2H), 7.29 – 7.22 (m, 3H), 7.20 (dd, *J* = 5.2, 1.6 Hz, 1H), 6.94 (s, 2H), 6.82 (s, 1H), 4.26 (t, *J* = 7.8 Hz, 1H), 3.61 (d, *J* = 7.8 Hz, 2H), 2.25 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.36, 152.37, 149.76, 141.89, 138.80, 138.50, 135.32, 134.04, 131.25, 129.05, 129.00, 128.57, 128.47, 128.02, 127.71, 127.66, 127.41, 126.61, 125.97, 125.73, 125.38, 124.90, 121.89, 50.51, 39.15, 21.33.

HRMS(ESI): (m/z) Calcd. for $C_{31}H_{28}NS[M+H]^+$, 446.1937, found 446.1942.



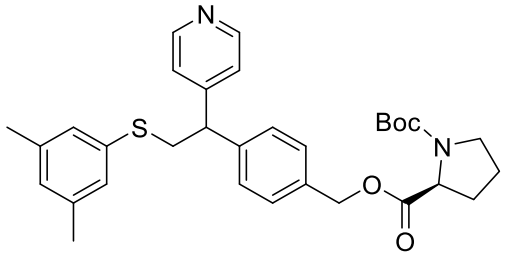
(8R,9S,13S,14S)-3-(2-((3,5-dimethylphenyl)thio)-1-(pyridin-4-yl)ethyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one(7)

White solid; Yied: 65 mg, 66%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 2H), 7.21 (dd, *J* = 21.0, 6.4 Hz, 3H), 7.00 (d, *J* = 7.0 Hz, 1H), 6.91 (s, 3H), 6.83 (s, 1H), 4.11 (t, *J* = 7.7 Hz, 1H), 3.53 (t, *J* = 7.9 Hz, 2H), 2.92 – 2.78 (m, 2H), 2.55 – 2.36 (m, 2H), 2.27 (s, 7H), 2.14 – 1.81 (m, 5H), 1.66 – 1.40 (m, 6H), 0.90 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 220.95, 152.33, 149.77, 139.15, 138.95, 138.75, 137.11, 135.42, 128.53, 128.45, 127.54, 125.93, 125.24, 123.57, 50.62, 49.99, 48.08, 44.41, 38.98, 38.15, 35.96, 31.69, 29.56, 26.56, 25.73, 21.69, 21.34, 13.96.

HRMS(ESI): (m/z) Calcd. for $C_{33}H_{38}NOS[M+H]^+$, 496.2669, found 496.2668.



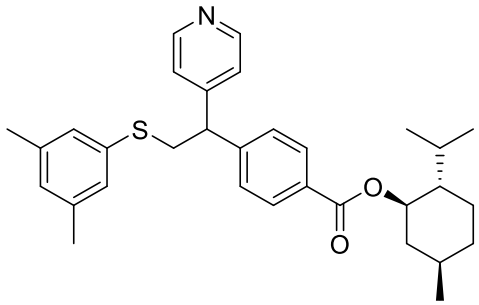
1-(tert-butyl) 2-(4-(2-((3,5-dimethylphenyl)thio)-1-(pyridin-4-yl)ethyl)benzyl) (2S)-pyrrolidine-1,2-dicarboxylate(8)

Yellow solid; Yied: 49 mg, 45%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 5.5 Hz, 2H), 7.30 (t, *J* = 7.0 Hz, 2H), 7.19 (t, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 6.0 Hz, 2H), 6.90 (s, 2H), 6.83 (s, 1H), 5.25 – 4.99 (m, 2H), 4.30 (ddd, *J* = 49.4, 8.6, 3.6 Hz, 1H), 4.15 (t, *J* = 7.7 Hz, 1H), 3.52 (d, *J* = 7.7 Hz, 2H), 3.51 – 3.32 (m, 2H), 2.32 – 2.13 (m, 8H), 1.99 – 1.80 (m, 3H), 1.43 (s, 3H), 1.29 (s, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.12, 172.89, 154.48, 153.84, 151.71, 151.64, 149.99, 141.91, 141.57, 138.78, 135.13, 135.02, 134.79, 128.94, 128.56, 128.52, 128.23, 128.13, 127.61, 123.40, 123.35, 79.93, 79.87, 66.26, 59.24, 58.96, 49.98, 46.64, 46.40, 38.93, 30.97, 29.98, 28.50, 28.30, 24.40, 23.69 , 21.28.

HRMS(ESI): (m/z) Calcd. for $C_{32}H_{38}N_2NaO_4S[M+Na]^+$, 569.2444, found 569.2442.



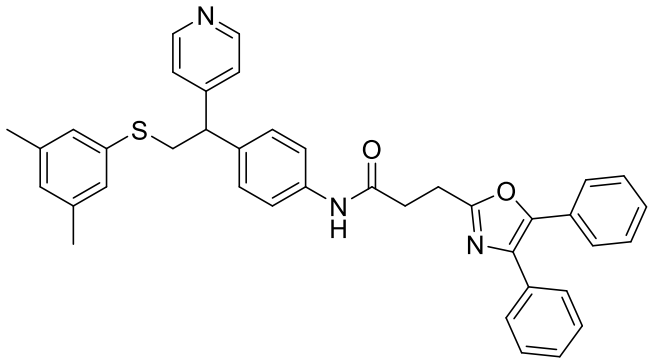
(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 4-(2-((3,5-dimethylphenyl)thio)-1-(pyridin-4-yl)ethyl)benzoate(9)

Colorless oil liquid; Yied: 46 mg, 46%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 4.1 Hz, 2H), 7.99 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 4.1 Hz, 2H), 6.90 (s, 2H), 6.84 (s, 1H), 4.92 (td, *J* = 10.9, 4.4 Hz, 1H), 4.21 (t, *J* = 7.7 Hz, 1H), 3.55 (d, *J* = 7.7 Hz, 2H), 2.27 (s, 6H), 2.10 (d, *J* = 11.3 Hz, 1H), 2.00 – 1.88 (m, 1H), 1.80 (s, 1H), 1.72 (d, *J* = 11.6 Hz, 2H), 1.60 – 1.47 (m, 2H), 1.10 (dd, *J* = 20.8, 10.7 Hz, 2H), 0.91 (m, 6H), 0.78 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.77, 151.30, 150.15, 146.42, 138.87, 134.92, 130.20, 130.03, 128.75, 128.14, 127.91, 123.35, 75.03, 50.30, 47.39, 41.08, 38.95, 34.43, 31.56, 26.60, 23.72, 22.16, 21.32, 20.90, 16.61.

HRMS(ESI): (m/z) Calcd. for $C_{32}H_{40}NO_2S[M+H]^+$, 502.2774, found 502.2767.



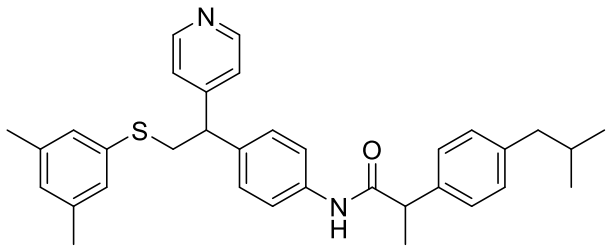
N-(4-(2-((3,5-dimethylphenyl)thio)-1-(pyridin-4-yl)ethyl)phenyl)-3-(4,5-diphenyloxazol-2-yl) propanamide(10)

Yellow solid; Yied: 64 mg, 52%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 8.49 (d, *J* = 5.7 Hz, 2H), 7.62 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.54 (dd, *J* = 7.5, 2.2 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.39 – 7.29 (m, 6H), 7.10 (dd, *J* = 9.0, 7.4 Hz, 4H), 6.90 (s, 2H), 6.83 (s, 1H), 4.10 (t, *J* = 7.7 Hz, 1H), 3.49 (d, *J* = 7.8 Hz, 2H), 3.25 (t, *J* = 6.9 Hz, 2H), 2.93 (t, *J* = 6.9 Hz, 2H), 2.26 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.05, 162.55, 152.16, 149.80, 145.77, 138.75, 137.44, 137.17, 135.22, 134.84, 132.29, 128.76, 128.71, 128.49, 128.32, 127.93, 127.55, 126.56, 123.44, 120.15, 49.63, 38.96, 34.02, 24.08, 21.28.

HRMS(ESI): (m/z) Calcd. for $C_{39}H_{36}N_3O_2S[M+H]^+$, 610.2523, found 610.2521.



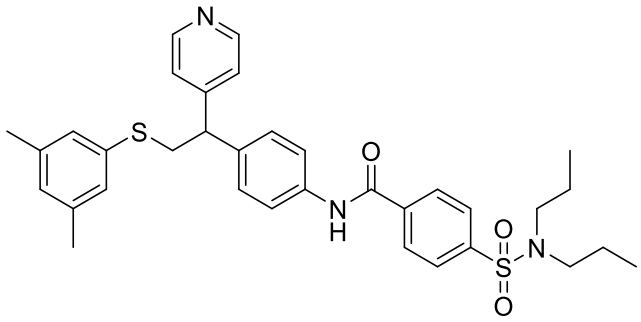
N-(4-(2-((3,5-dimethylphenyl)thio)-1-(pyridin-4-yl)ethyl)phenyl)-2-(4-isobutylphenyl)propan amide(11)

White solid; Yied: 88 mg, 84%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 5.3 Hz, 2H), 7.71 (s, 1H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.11 (dd, *J* = 10.7, 7.7 Hz, 6H), 6.90 (s, 2H), 6.83 (s, 1H), 4.10 (t, *J* = 7.7 Hz, 1H), 3.69 (q, *J* = 7.1 Hz, 1H), 3.49 (d, *J* = 7.8 Hz, 2H), 2.46 (d, *J* = 7.2 Hz, 2H), 2.26 (s, 6H), 1.85 (dp, *J* = 13.6, 6.8 Hz, 1H), 1.56 (d, *J* = 7.1 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.85, 152.10, 149.79, 141.02, 138.72, 138.18, 137.36, 137.14, 135.18, 129.82, 128.47, 128.42, 127.54, 127.38, 123.37, 120.07, 49.58, 47.59, 45.05, 38.95, 30.22, 22.43, 21.25, 18.62.

HRMS(ESI): (m/z) Calcd. for $C_{34}H_{39}N_2OS[M+H]^+$, 523.2778, found 523.2777.



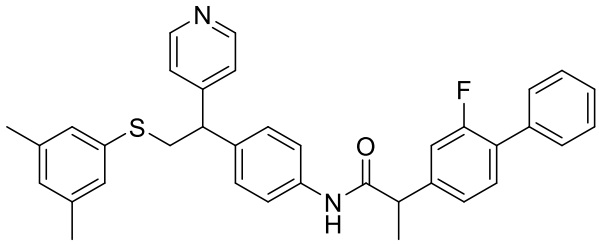
N-(4-(2-((3,5-dimethylphenyl)thio)-1-(pyridin-4-yl)ethyl)phenyl)-4-(N,N-dipropylsulfamoyl)benzamide(12)

Yellow oil liquid; Yied: 80 mg, 66%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 8.46 (d, *J* = 5.6 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.74 – 7.62 (m, 4H), 7.18 (d, *J* = 8.6 Hz, 2H), 7.15 (d, *J* = 6.0 Hz, 2H), 6.91 (s, 2H), 6.83 (s, 1H), 4.15 (t, *J* = 7.7 Hz, 1H), 3.53 (d, *J* = 7.8 Hz, 2H), 3.12 – 2.99 (m, 4H), 2.26 (s, 6H), 1.58 – 1.43 (m, 4H), 0.83 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.06, 152.10, 149.75, 142.57, 138.86, 138.76, 137.89, 137.22, 135.14, 128.57, 128.52, 128.18, 127.57, 127.17, 123.46, 120.85, 50.01, 49.64, 38.94, 21.95, 21.27, 11.20.

HRMS(ESI): (m/z) Calcd. for $C_{34}H_{40}N_3O_3S[M+H]^+$, 602.2506, found 602.2513.



N-(4-(2-((3,5-dimethylphenyl)thio)-1-(pyridin-4-yl)ethyl)phenyl)-2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanamide(13)

Colorless oil liquid; Yied: 82 mg, 73%.

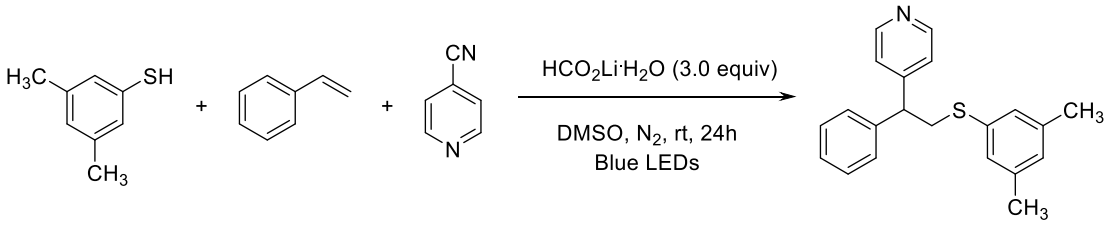
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 5.6 Hz, 2H), 8.03 (s, 1H), 7.58 – 7.32 (m, 8H), 7.22 – 7.07 (m, 6H), 6.91 (s, 2H), 6.84 (s, 1H), 4.12 (t, *J* = 7.7 Hz, 1H), 3.74 (q, *J* = 7.0 Hz, 1H), 3.49 (d, *J* = 7.7 Hz, 2H), 2.27 (s, 6H), 1.59 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.97, 159.88 (d, *J* = 249.2 Hz), 152.16, 149.78, 142.47 (d, *J* = 7.3 Hz), 138.77, 137.34 (d, *J* = 17.1 Hz), 135.36, 135.16, 131.23 (d, *J* = 4.0 Hz), 128.98 (d, *J* = 2.9 Hz), 128.57, 128.52, 127.86, 127.57, 123.60 (d, *J* = 3.3 Hz), 123.45, 120.28, 115.37 (d, *J* = 23.4 Hz), 49.60, 47.40, 38.94, 21.27, 18.74.

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.86.

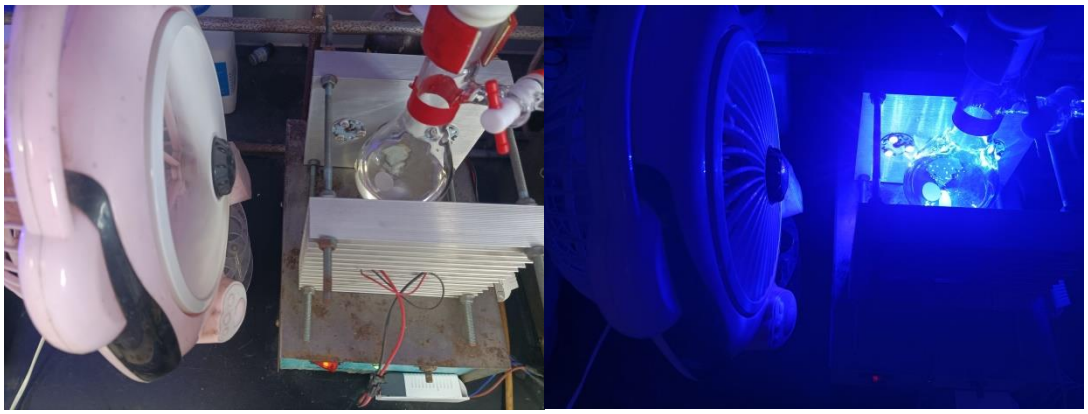
HRMS(ESI): (m/z) Calcd. for $C_{35}H_{34}FN_2OS[M+H]^+$, 561.2370, found 561.2370.

5. Gram-scale synthesis



1k, 5 mmol **2a,** 20 mol **3a,** 7.5 mmol **4k**, 1.15g, 72% yield

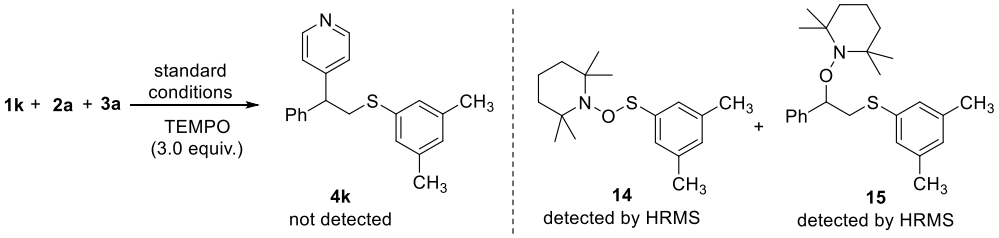
A 200 mL Schlenk reaction bottle equipped with a magnetic stir bar charged with 4-cyanopyridine (7.5 mmol, 1.5 equiv.), $HCO_2Li·H_2O$ (15 mmol, 3 equiv.). The bottle was capped. After evacuated and backfilled nitrogen three times, styrene (20 mmol, 4 equiv.), 3,5-dimethylbenzenethiol (5 mmol, 1 equiv.), dry DMSO (100 mL) were added via a syringe. The reaction mixture irritated with 3W blue LEDs, with colling from a fan. After 48h, 70 mL H_2O was added, and extracted with EtOAc (50 mL) three times, the combined organic solvents were collected and washed with brine and then dried over $NaSO_4$, concentrated in vacuo. The crude material purified by silica gel colum chromatography (PE/EA=4/1~3/1) to afford the products **4k** (1.15g, 72%).



6. Mechanistic Studies

6.1 Radical inhibition experiment

A 10 mL Schlenk reaction tube equipped with a magnetic stir bar charged with 4-cyanopyridine 3 (0.3 mmol, 1.5 equiv.), HCO_2Li H_2O (0.6mmol, 3equiv.), TEMPO (0.6 mmol, 3equiv.). The tube was capped. After evacuated and backfilled nitrogen three times, styrene (0.8mmol, 4equiv.), 3,5-dimethylbenzenethiol (0.2 mmol, 1 equiv.), dry DMSO (4 mL) were added via a syringe. The reaction mixture irritated with 10W 455nm blue LEDs at 25 ^oC. After 24h, the reaction mixtures were analyzed by high resolution mass spectra (HRMS).



1-(((3,5-dimethylphenyl)thio)oxy)-2,2,6,6-tetramethylpiperidine (14)

HRMS(ESI): (m/z) Calcd. for $C_{17}H_{28}NOS[M+H]^+$, 294.1886, found 294.1874.

1-(2-((3,5-dimethylphenyl)thio)-1-phenylethoxy)-2,2,6,6-tetramethylpiperidine(15)

HRMS(ESI): (m/z) Calcd. for $C_{25}H_{36}NOS[M+H]^+$, 398.2512, found 398.2498.

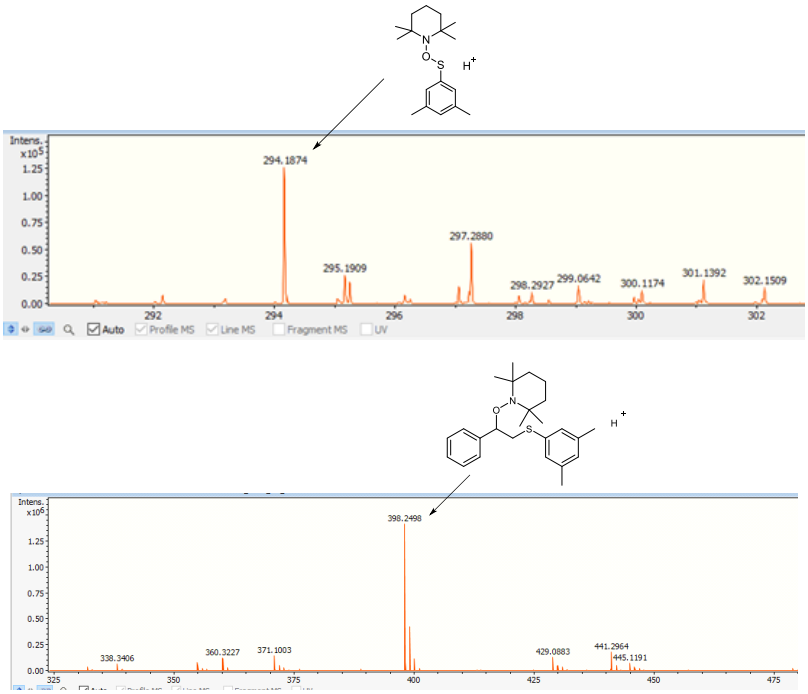
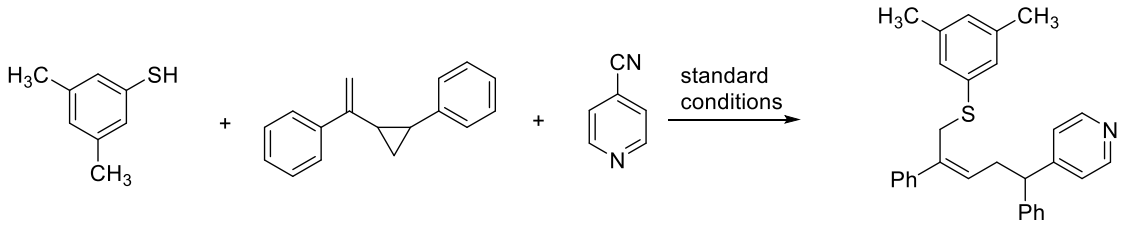


Figure S1. HRMS of **14** and **15**.

6.2 Radical clock experiments



1k **16** **3a** **17**, 55%(E/Z=1/4)

A 10 mL Schlenk reaction tube equipped with a magnetic stir bar charged with 4-cyanopyridine 3 (0.3 mmol, 1.5 equiv.), $HCO_2Li·H_2O$ (0.6mmol, 3equiv.). The tube was capped. After evacuated and backfilled nitrogen three times, styrene **16** (0.4 mmol, 2 equiv.), 3,5-dimethylbenzenethiol (0.2 mmol, 1 equiv.), dry DMSO (4 mL) were added via a syringe. The reaction mixture irritated with 10W 455nm blue LEDs at 25 ^oC. After 24h, 10 mL H_2O was added, and extracted with EtOAc (10 mL) three times, the combined organic solvents were collected and washed with brine and then dried over $NaSO_4$, concentrated in vacuo. The crude material was purified by silica gel colum chromatography (PE/EA=4/1~3/1) to afford the products (48 mg, 55%, E/Z = 1/4).

4-(5-((3,5-dimethylphenyl)thio)-1,4-diphenylpent-3-en-1-yl)pyridine (17)

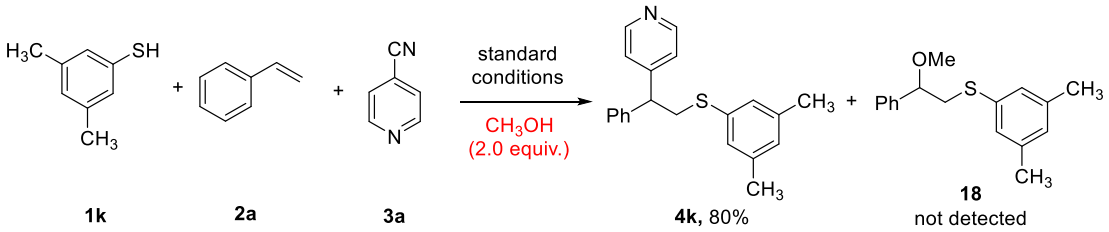
Yellow oil liquid; Yied: 48 mg, 55%

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.49 (d, *J* = 5.1 Hz, 1.6H), 8.40 (d, *J* = 5.1 Hz, 0.4H), 7.34 – 7.19 (m, 8H), 7.19 – 7.15 (m, 1.6H), 7.13 – 7.09 (m, 1.6H), 7.09 – 6.98 (m, 0.8H), 6.98 (s, 1.6H), 6.94 – 6.91 (m, 0.4H), 6.85 (s, 0.8H), 6.80 (s, 0.2H), 5.67 (t, *J* = 7.0 Hz, 0.8H), 5.51 (t, *J* = 7.2 Hz, 0.2H), 3.93 – 3.70 (m, 3H), 2.81 (t, *J* = 7.5 Hz, 1.6H), 2.66 (t, *J* = 7.5 Hz, 0.4H), 2.26 (s, 4.8H), 2.24 (s, 1.2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.33, 153.17, 149.95, 149.77, 142.58, 141.63, 138.65, 138.38, 138.19, 136.82, 136.02, 135.91, 129.63, 128.85, 128.71, 128.65, 128.58, 128.45, 128.36, 128.17, 128.11, 128.02, 127.90, 127.66, 127.43, 127.04, 126.86, 126.38, 123.47, 50.89, 50.61, 42.77, 34.97, 34.49, 34.07, 21.34, 21.30.

HRMS(ESI): (m/z) Calcd. for $C_{30}H_{30}NS[M+H]^+$, 436.2093, found .436.2061

6.3 Cation trap experiment



A 10 mL Schlenk reaction tube equipped with a magnetic stir bar charged with 4-cyanopyridine 3 (0.3 mmol, 1.5 equiv.), $HCO_2Li·H_2O$ (0.6mmol, 3equiv.). The tube was capped. After evacuated and backfilled nitrogen three times, styrene (0.8mmol, 4equiv.), 3,5-dimethylbenzenethiol (0.2 mmol, 1 equiv.), methanol (0.4 mmol, 2 equiv.), dry DMSO (4 mL) were added via a syringe. The reaction mixture irritated with 10W 455nm blue LEDs at 25 ^oC. After 24h, 10 mL H_2O was added, and extracted with EtOAc (10 mL) three times, the combined organic solvents were collected and washed with brine and then dried over $NaSO_4$, concentrated in vacuo. The crude material was analyzed by high resolution mass spectra (HRMS), the product **16** was not detected. The crude material was purified by silica gel colum chromatography (PE/EA=4/1~3/1) to afford the products (51 mg, 80%).

6.4 Light/dark experiments

Six standard reaction mixtures in 10 mL Schlenk reaction tube equipped with a magnetic stir bar charged with 4-cyanopyridine (0.3 mmol, 1.5 equiv.), $HCO_2Li \cdot H_2O$ (0.6mmol, 3equiv.). The tube was capped. After evacuated and backfilled nitrogen three times, styrene (0.4 mmol, 2 equiv.), 3,5-dimethylbenzenethiol (0.2 mmol, 1 equiv.), dry DMSO (4 mL) were added via a syringe. The reaction mixture irritated with 10W 455nm blue LEDs at 25 ^{o}C. After 2 hours, the lamps were turned off, and one vial was removed from the irradiation setup for analysis. The remaining five vials were stirred in the absence of light for an additional 2 hours. Then, one vial was removed for analysis, and the lamps were turned back on to irradiate the remaining for reaction mixtures. After an additional 2 hours of irradiation, the lamps were turned off, and one vial was removed for analysis. The remaining three vials were stirred in the absence of light for an additional 2 hours. Then, a vial was removed for analysis, and the lamps were turned back on to irradiate the remaining two vials. After 2 hours, the lamps were turned off, and one vial was removed for analysis. The remaining one vial was stirred in the absence of light for an additional 2 hours, and the last vial was removed for analysis. The reaction mixtures were analyzed by ^{1}H NMR using CH_2Br_2 as internal.

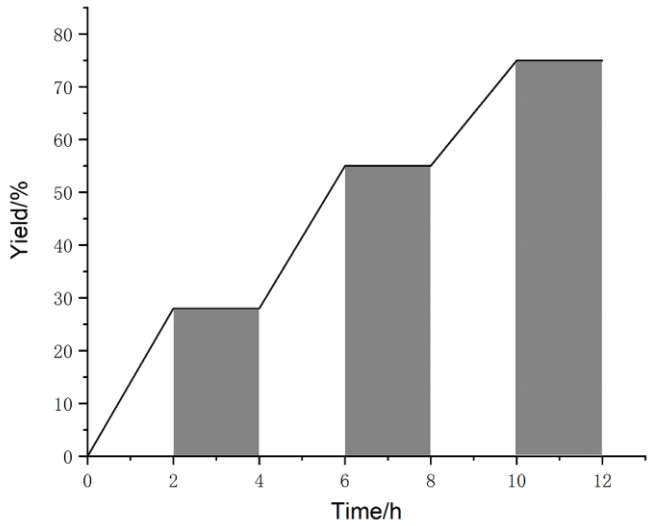


Figure S2. Light on/off experiments.

6.5 UV-vis absorption spectra

The UV-vis absorption spectra of 3,5-dimethylbenzenethiol **1k** (0.05 M), styrene **2a** (0.2 M), isonicotinonitrile **3a** (0.075 M), and $HCO_2Li{\cdot}H_2O$ (0.15 M) in DMSO were recored in 1 cm path quartz cuvettes by using a Cary 100 UV-Vis spectrophotometer (Agilent Technologies).

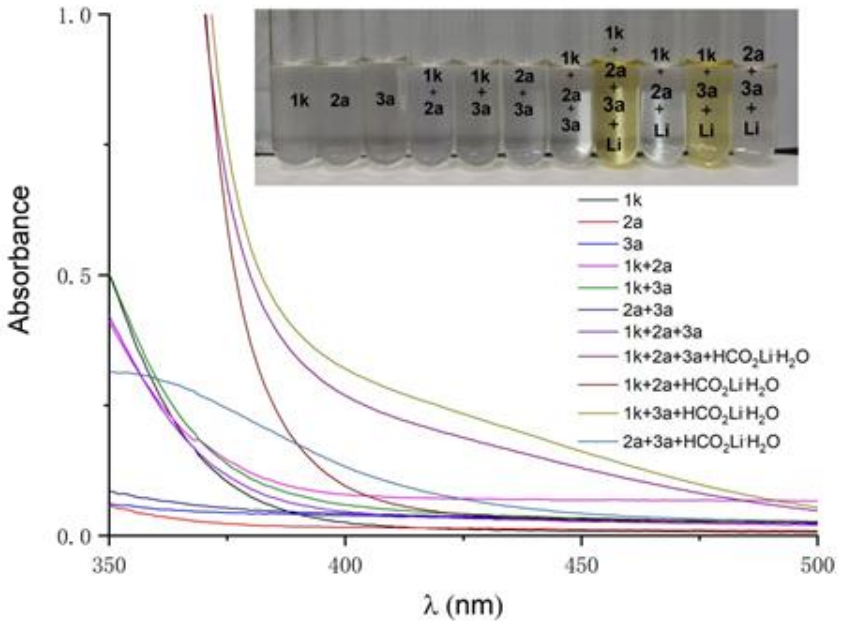


Figure S3. UV−vis spectroscopic measurements on various combinations of **1k**, **2a**, **3a**, and $HCO_2Li{\cdot}H_2O$ in DMSO.

7. references

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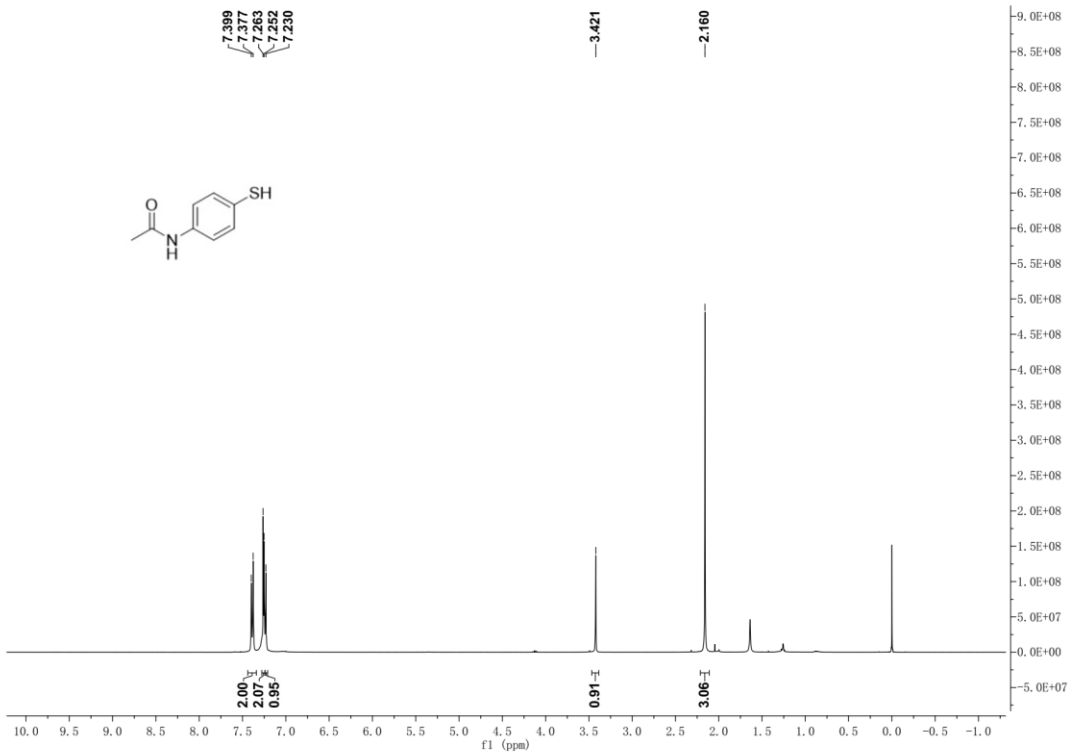
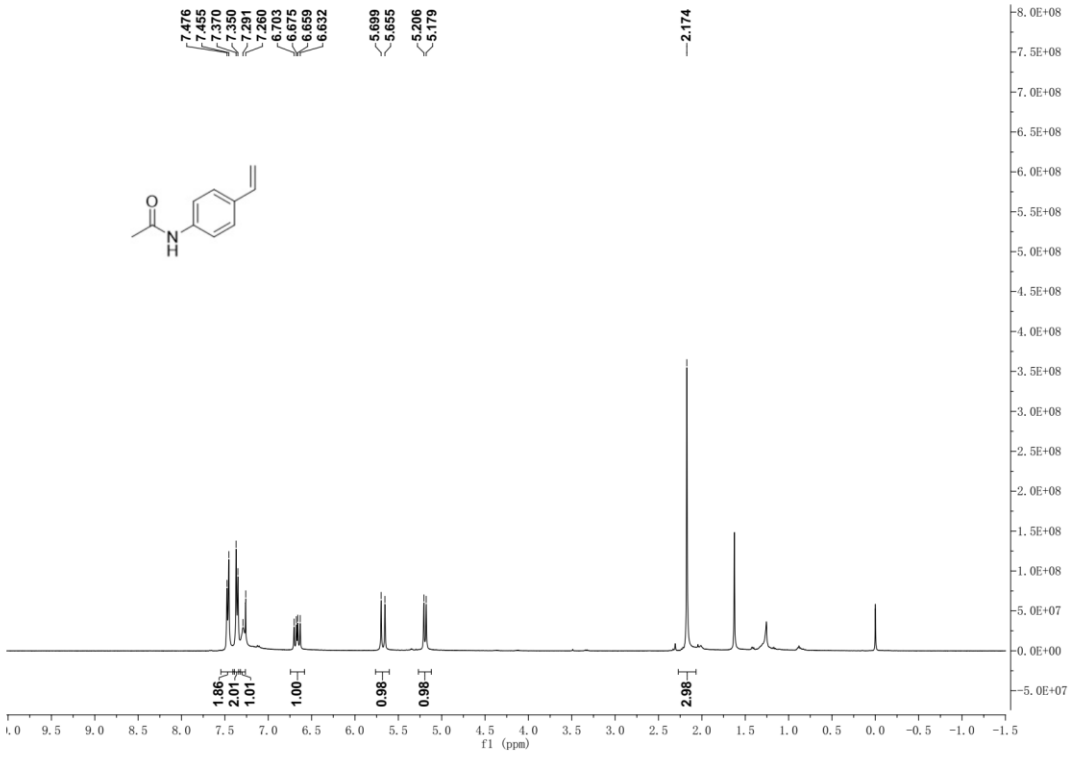
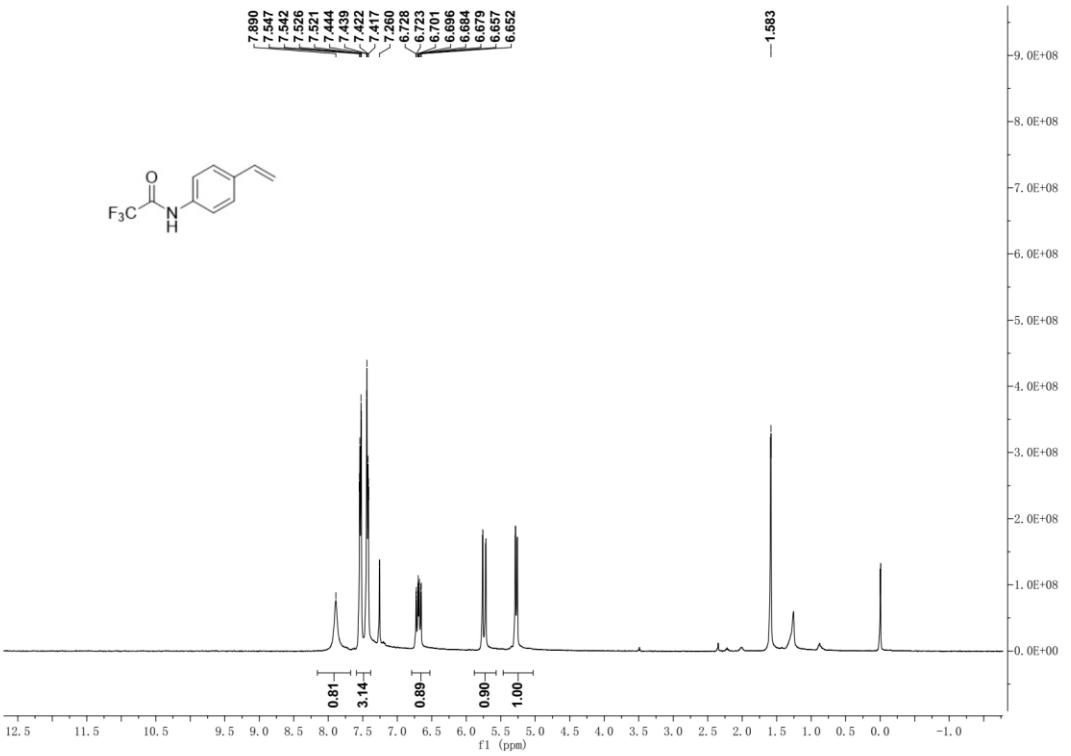
8. Copies of the NMR spectra of



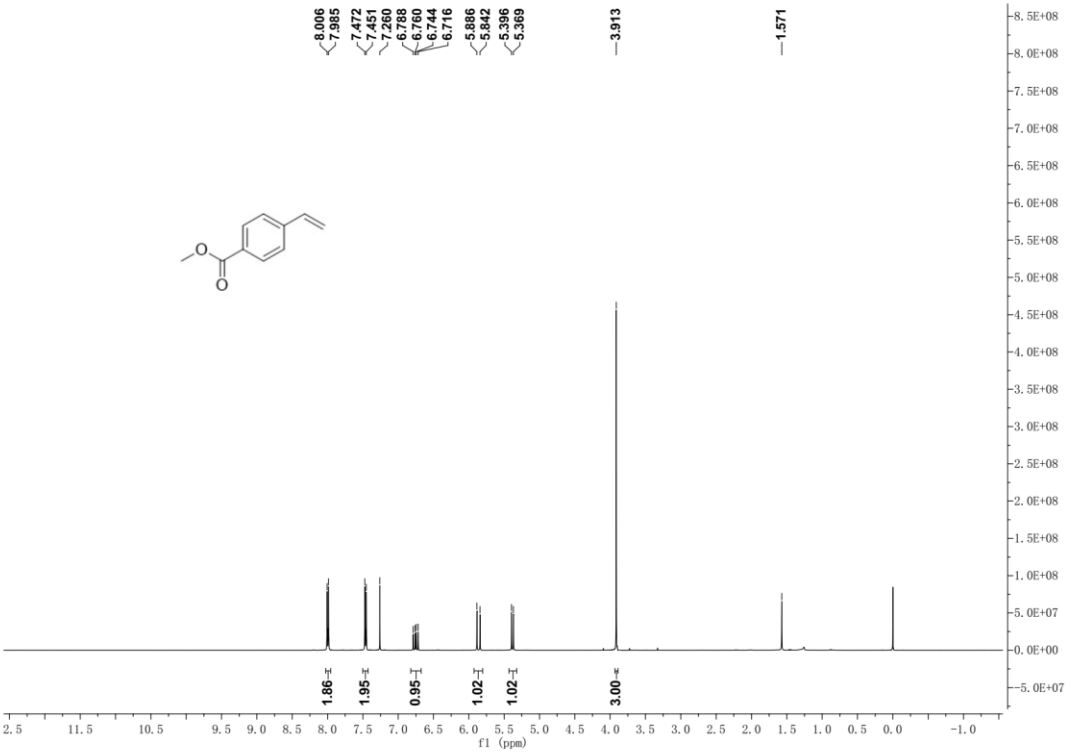
^{1}H NMR of compound 1d



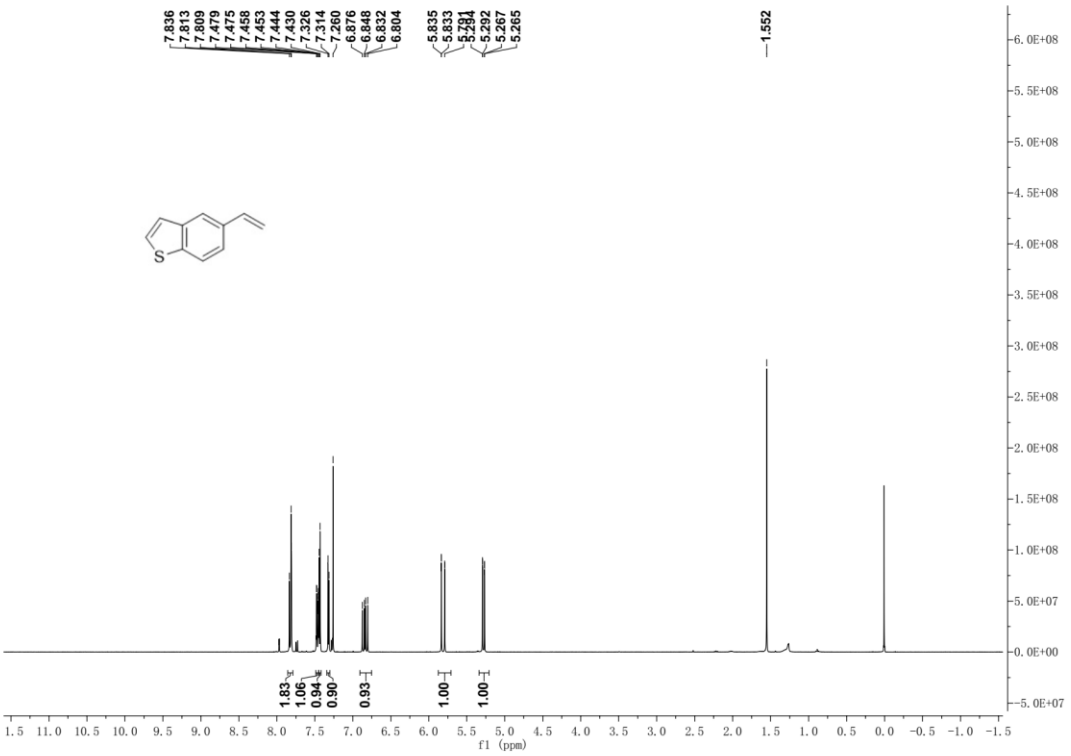
^{1}H NMR of compound 2k



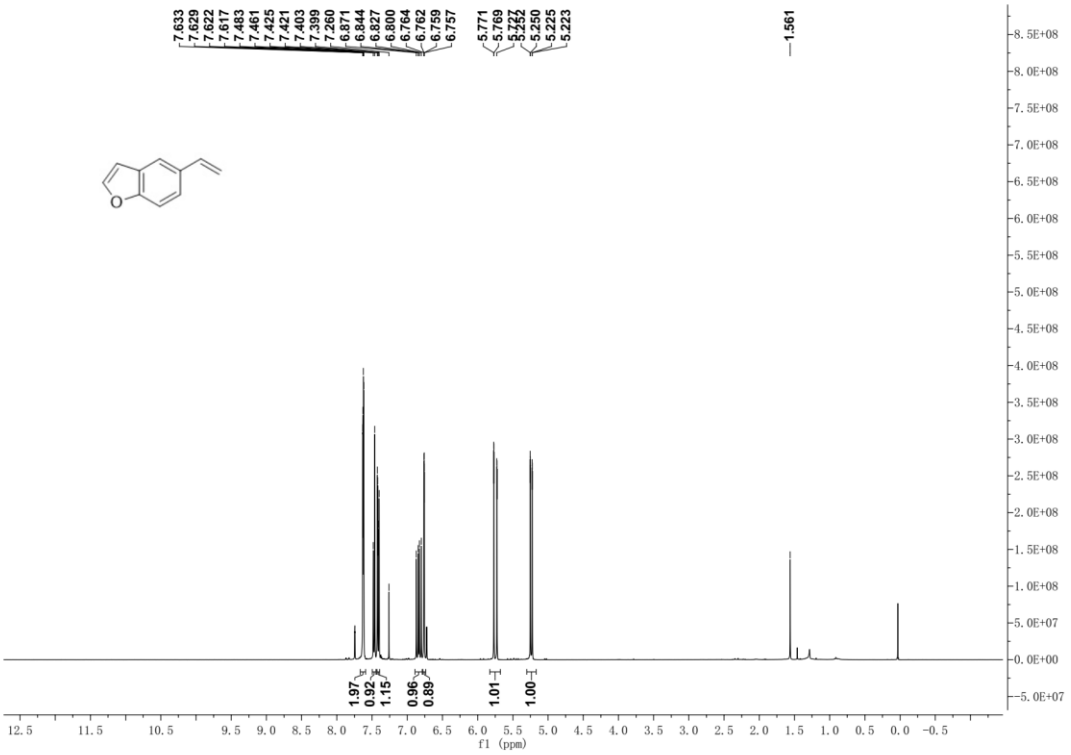
^{1}H NMR of compound 2l



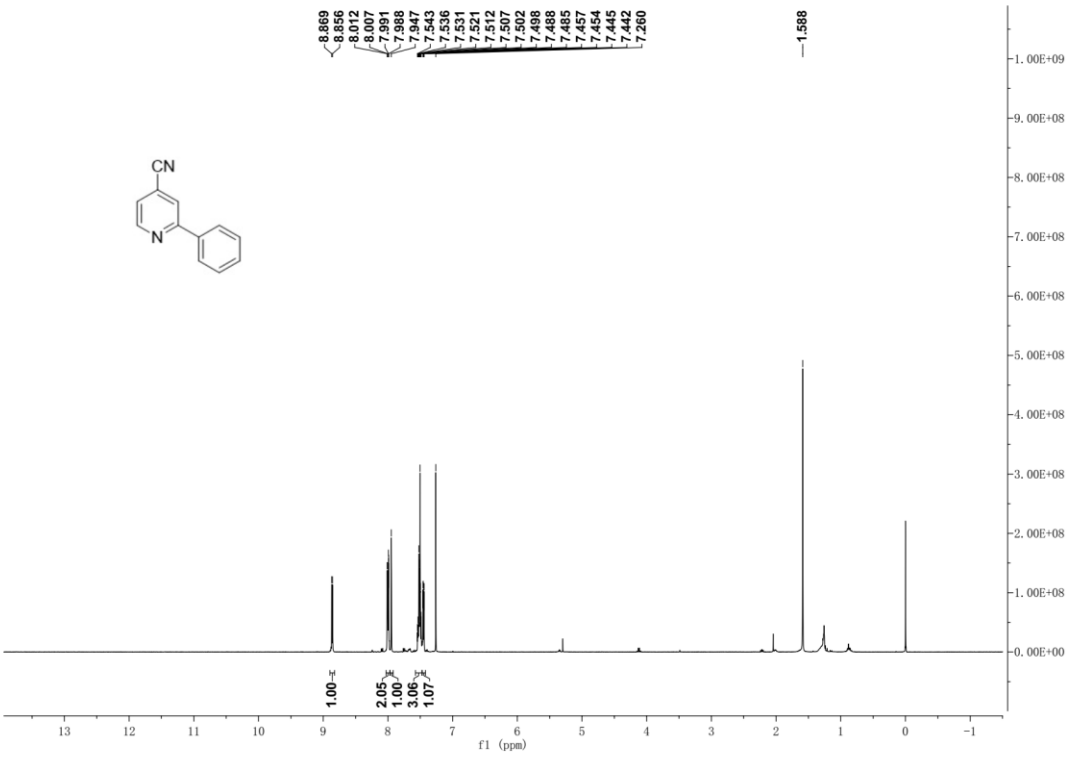
^{1}H NMR of compound 2j



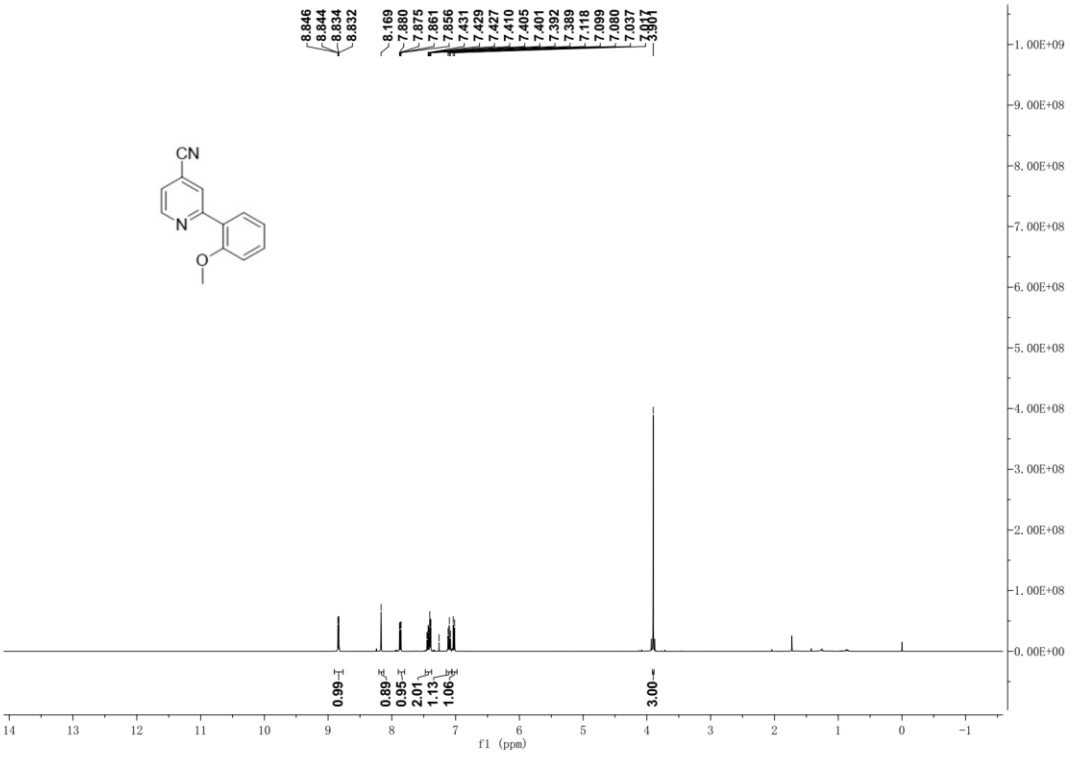
^{1}H NMR of compound 2n



^{1}H NMR of compound 2o



[1]H NMR of compound 3e



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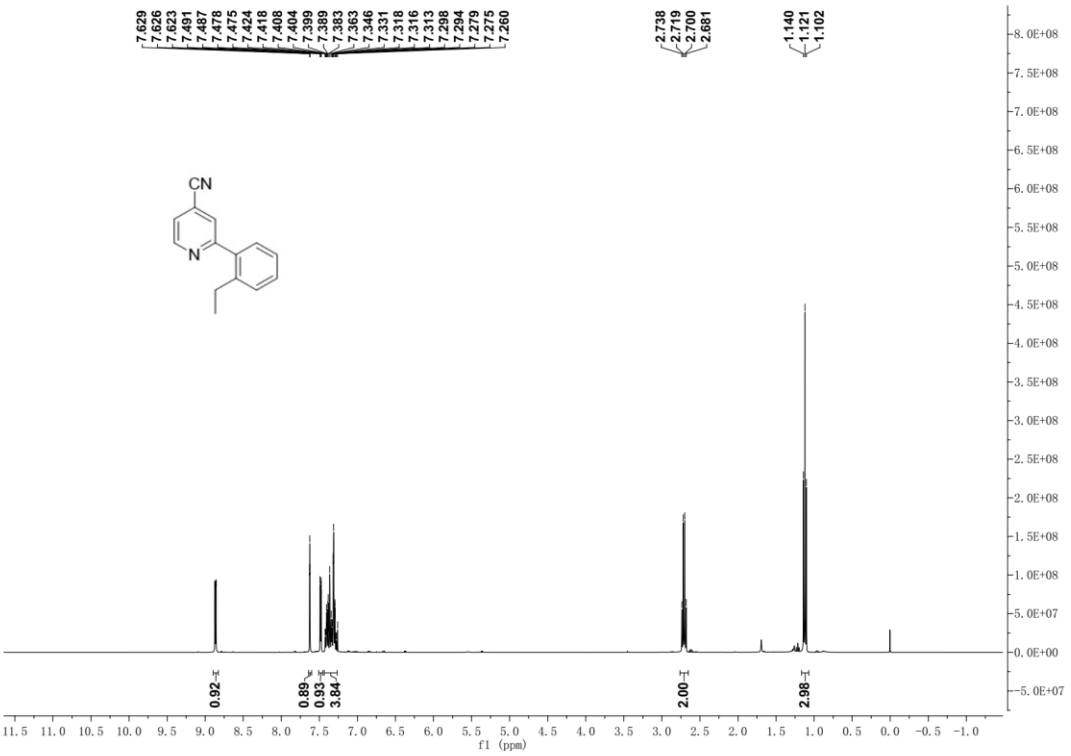
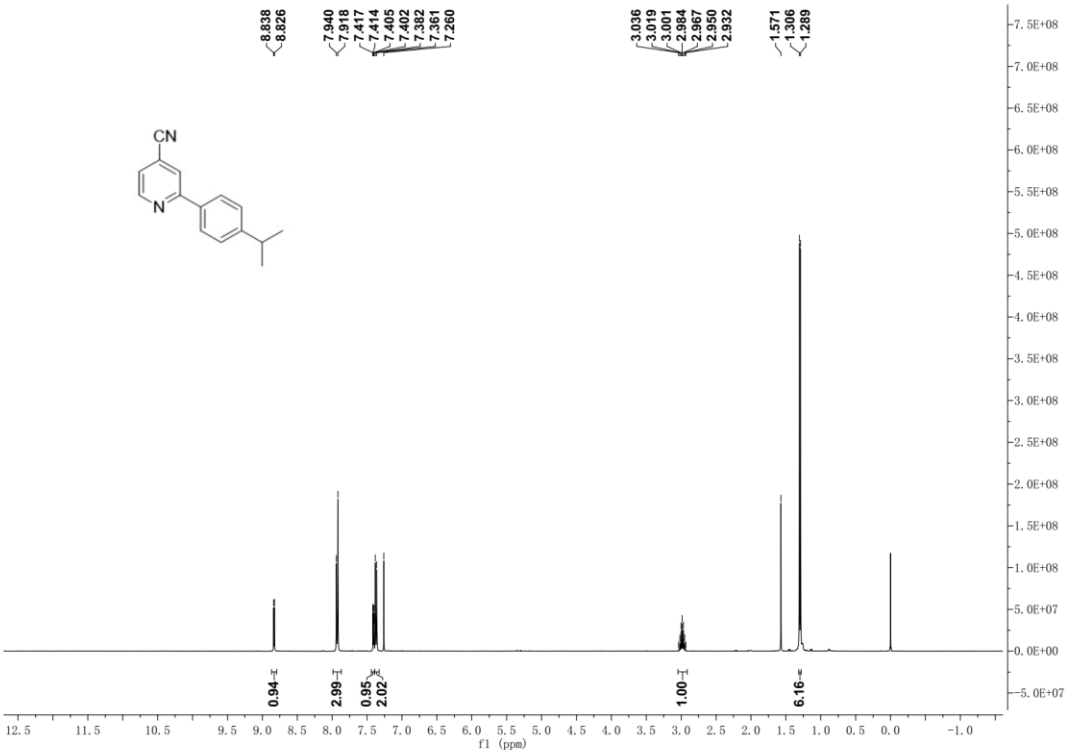
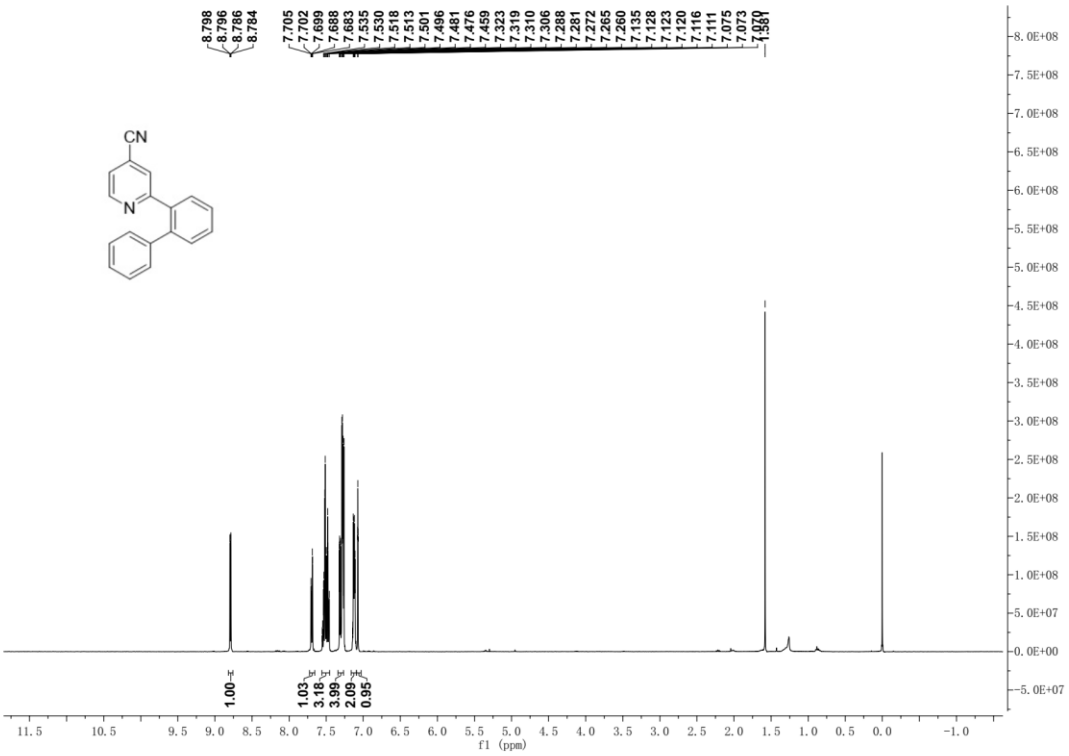


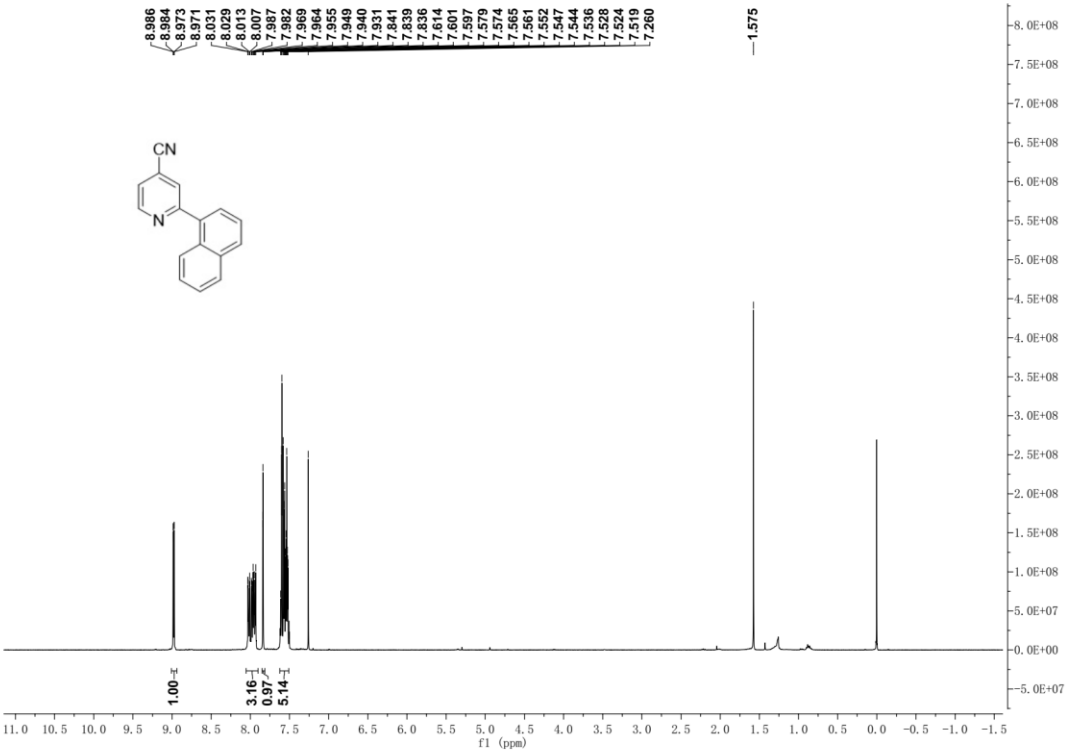
^{1}H NMR of compound 3h



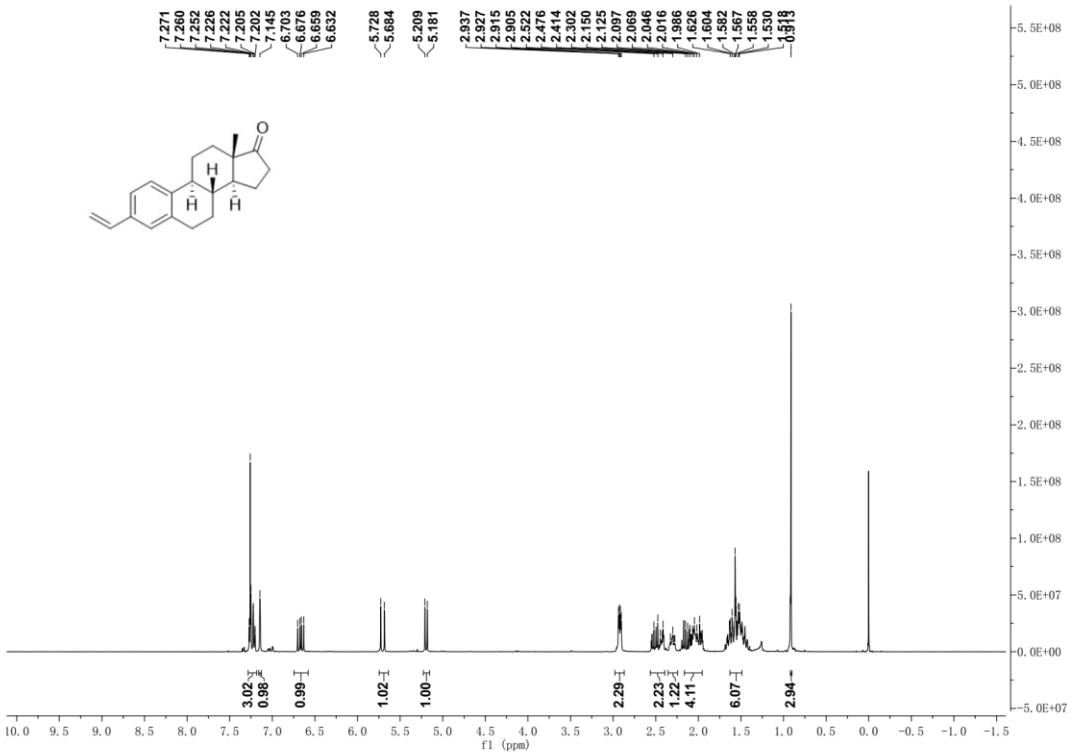
^{1}H NMR of compound 3i



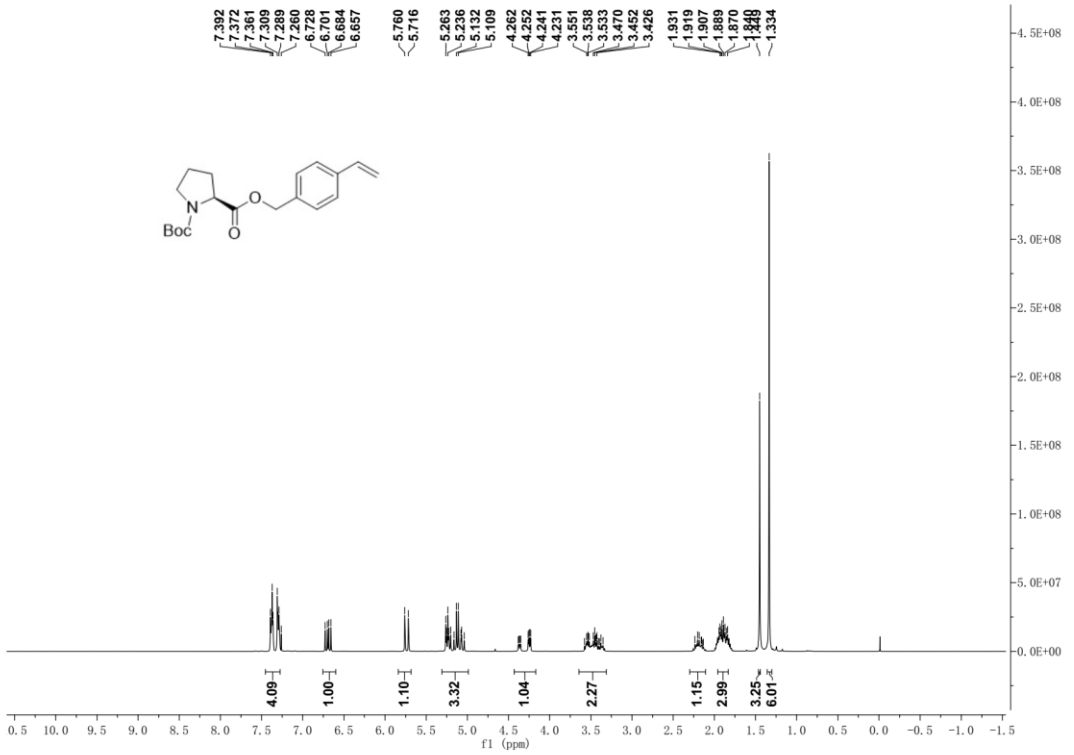
^{1}H NMR of compound 3k



^{1}H NMR of compound 3l



[1]H NMR of compound alkene 7



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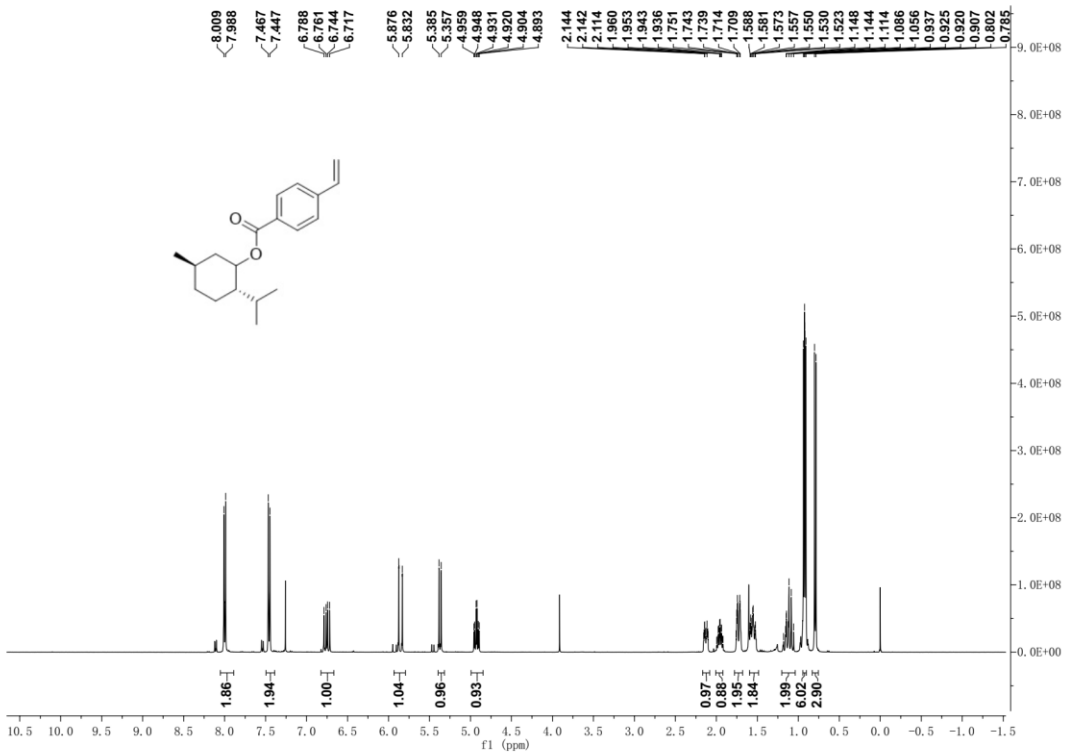

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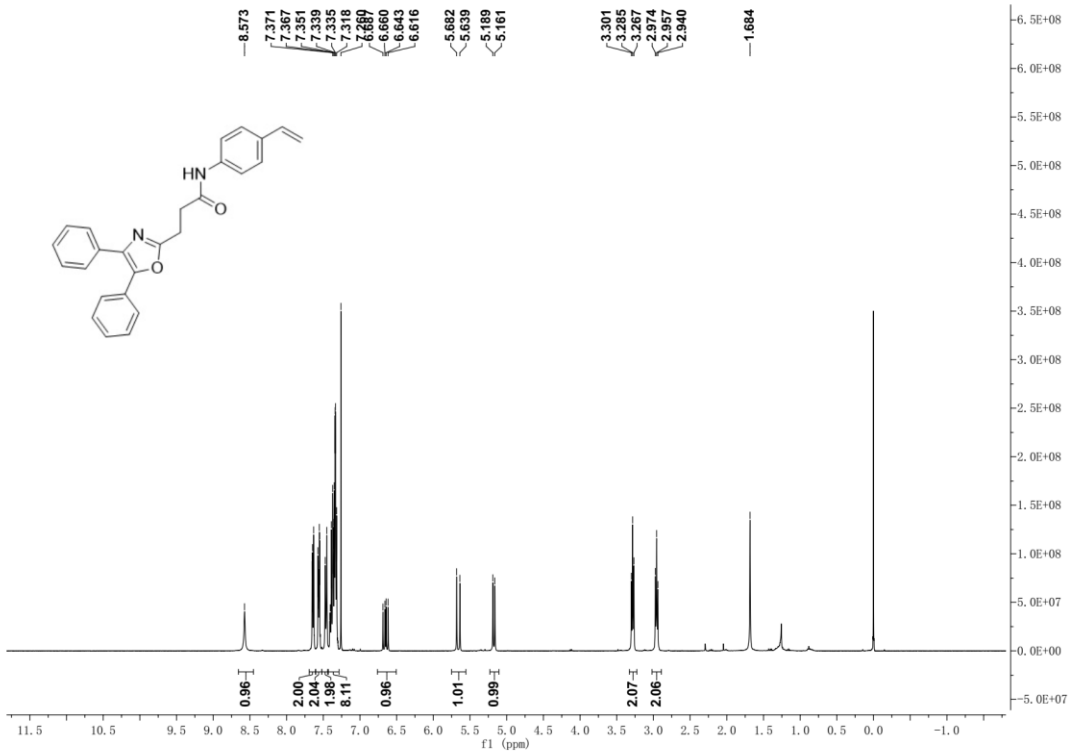

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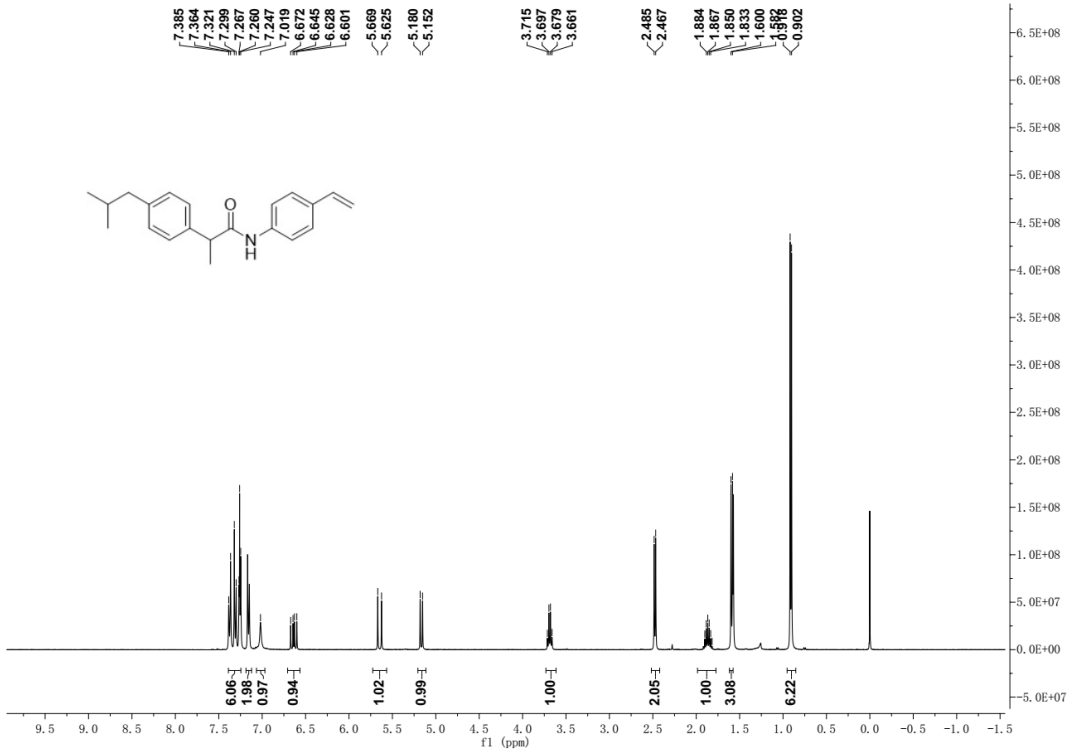
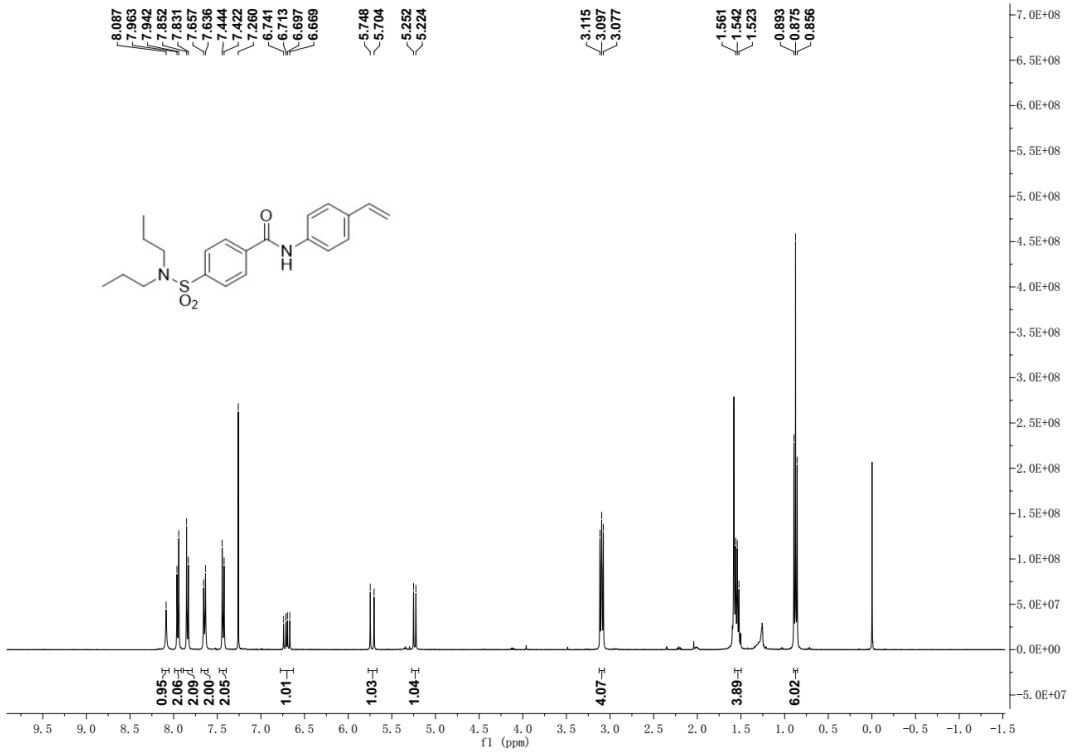
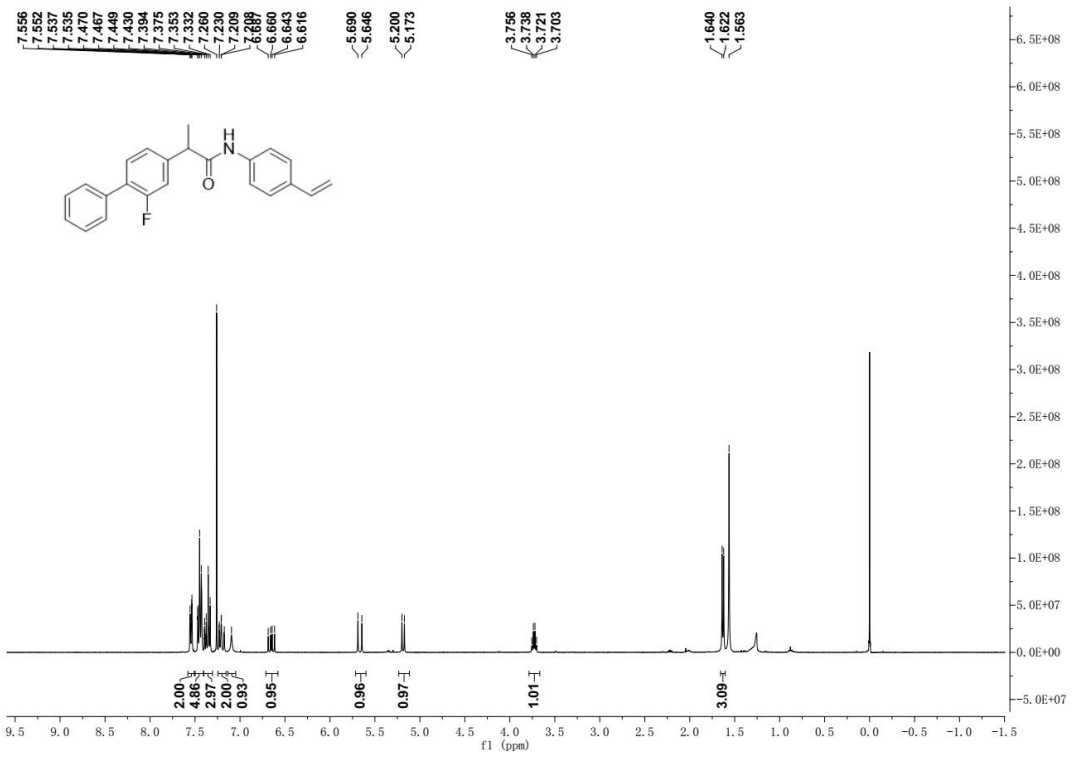


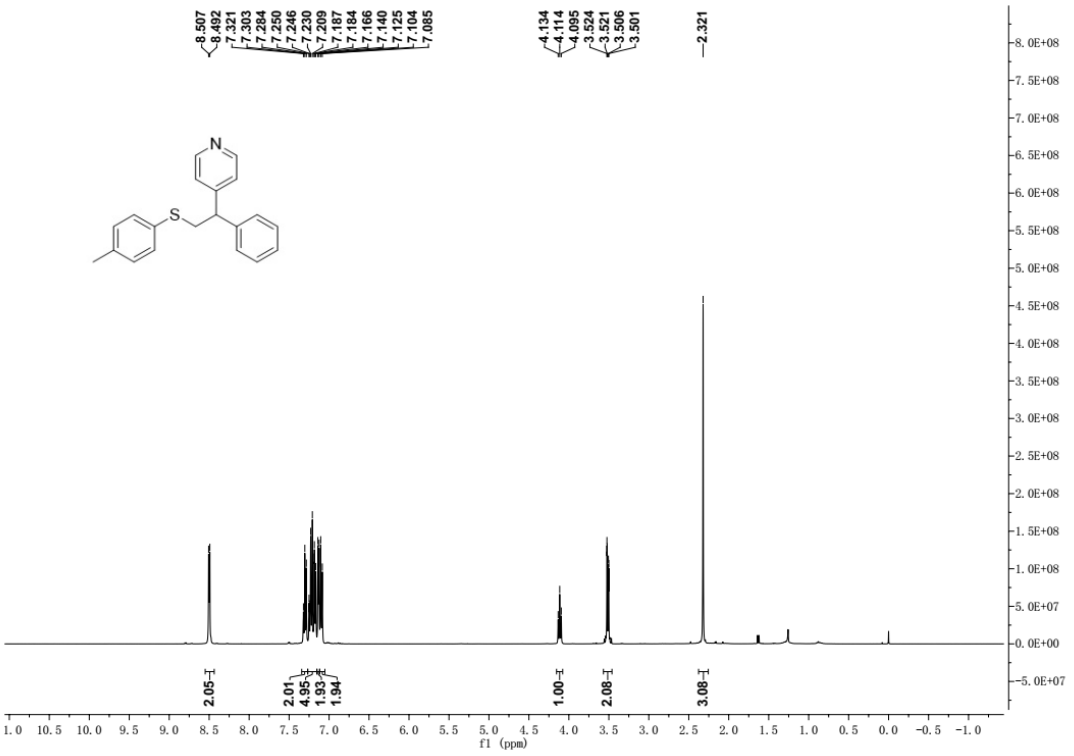
^{1}H NMR of compound alkene 11



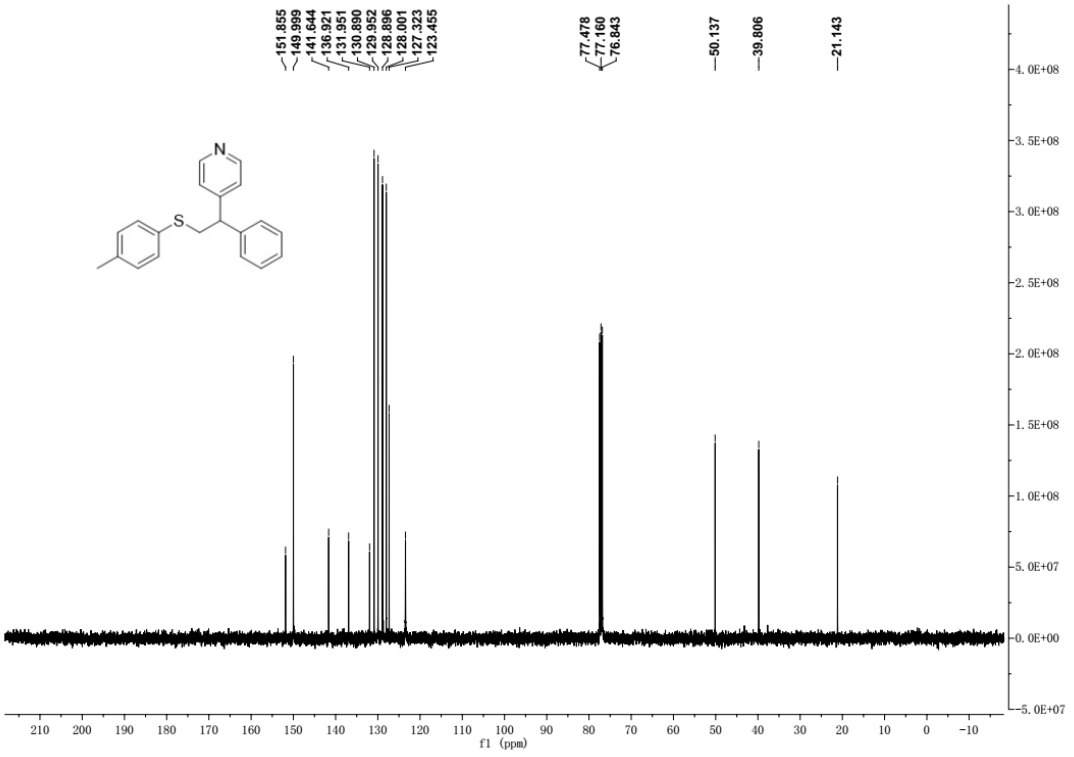
^{1}H NMR of compound alkene 12



[1]H NMR of compound alkene 13

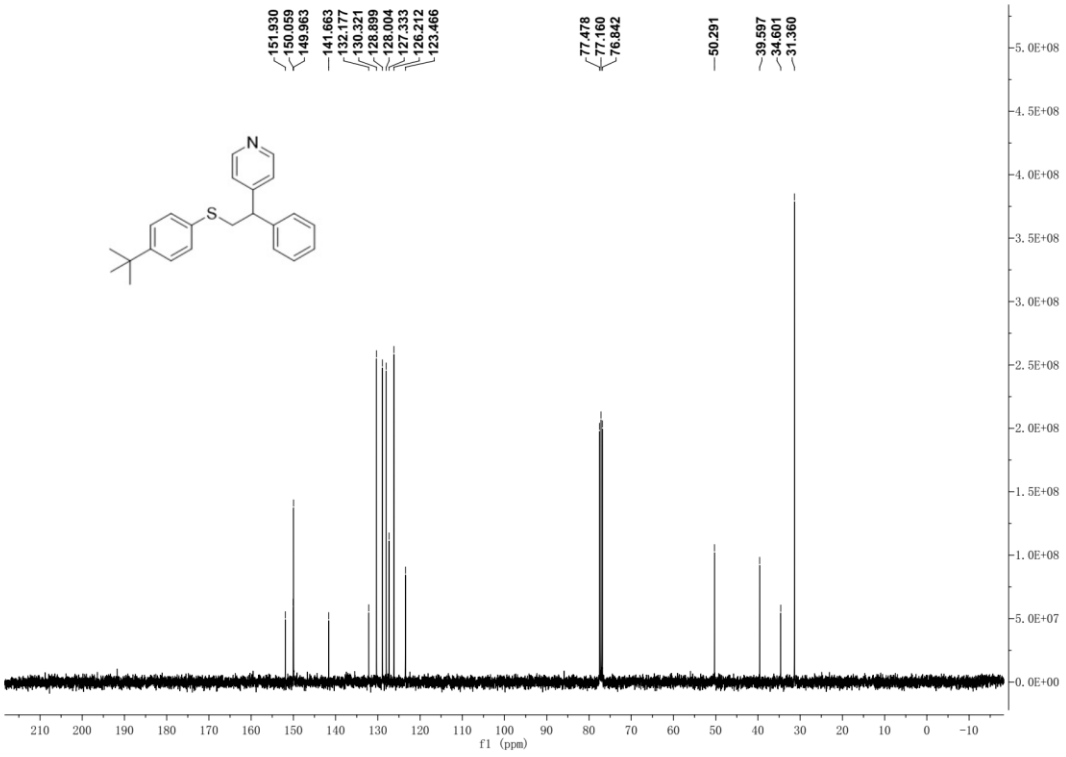


^{1}H NMR of compound 4a



^{13}C NMR of compound 4a

^{1}H NMR of compound 4b



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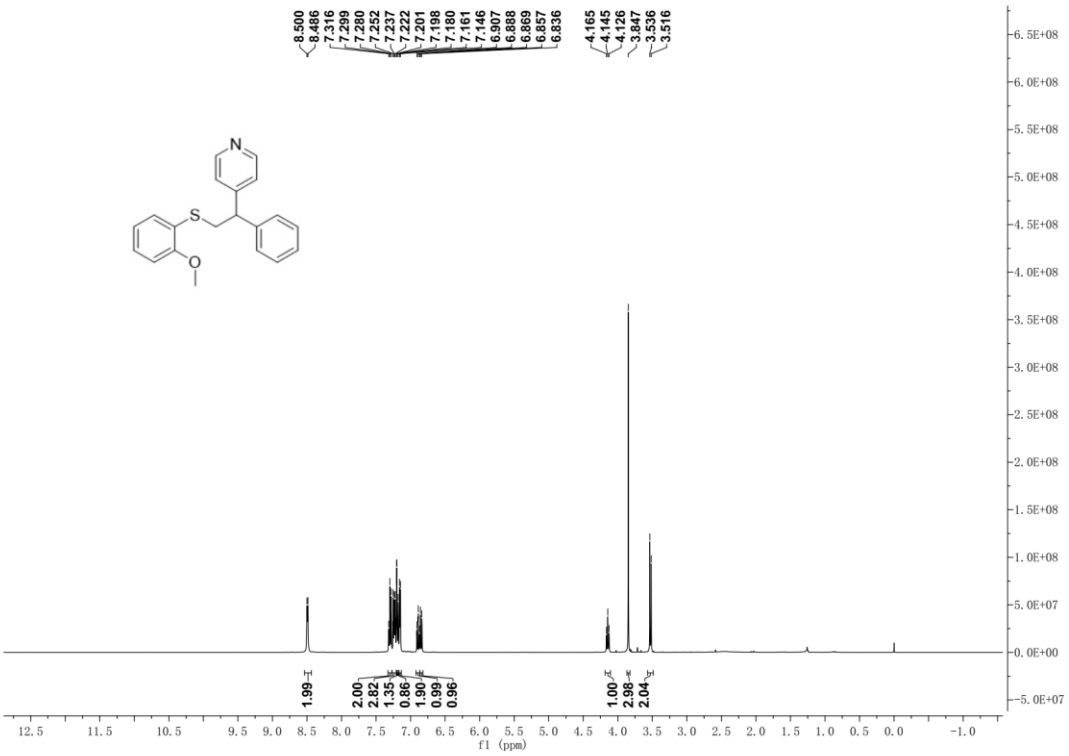
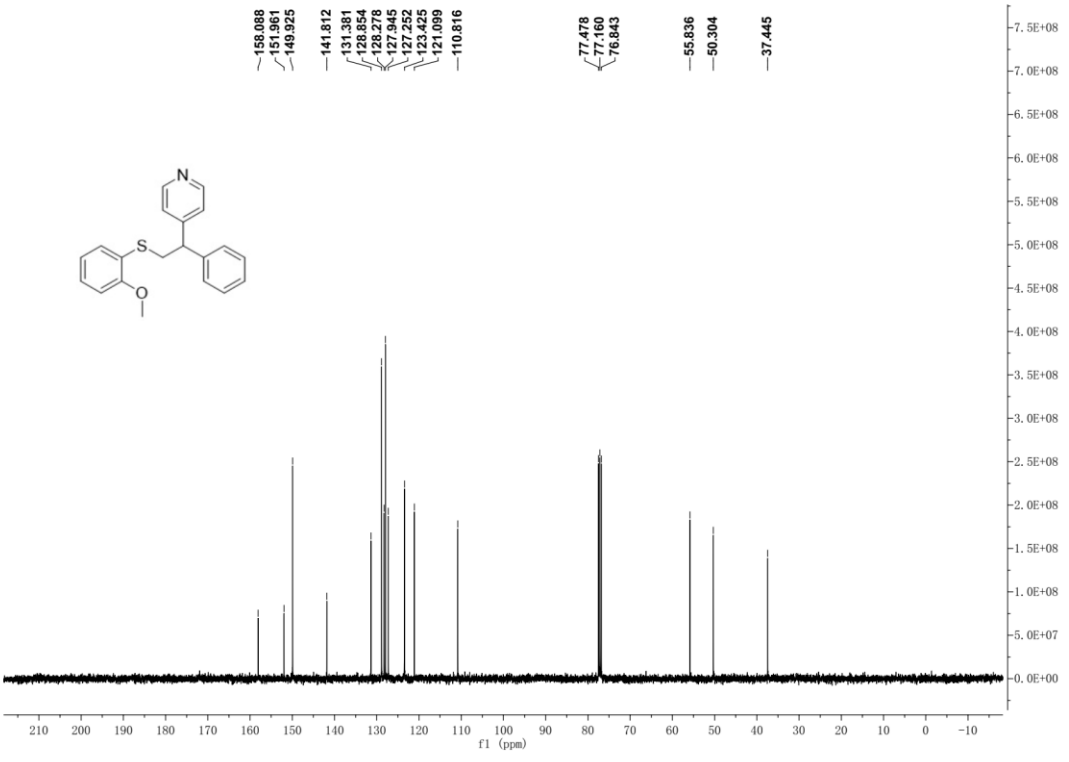


^{1}H NMR of compound 4c



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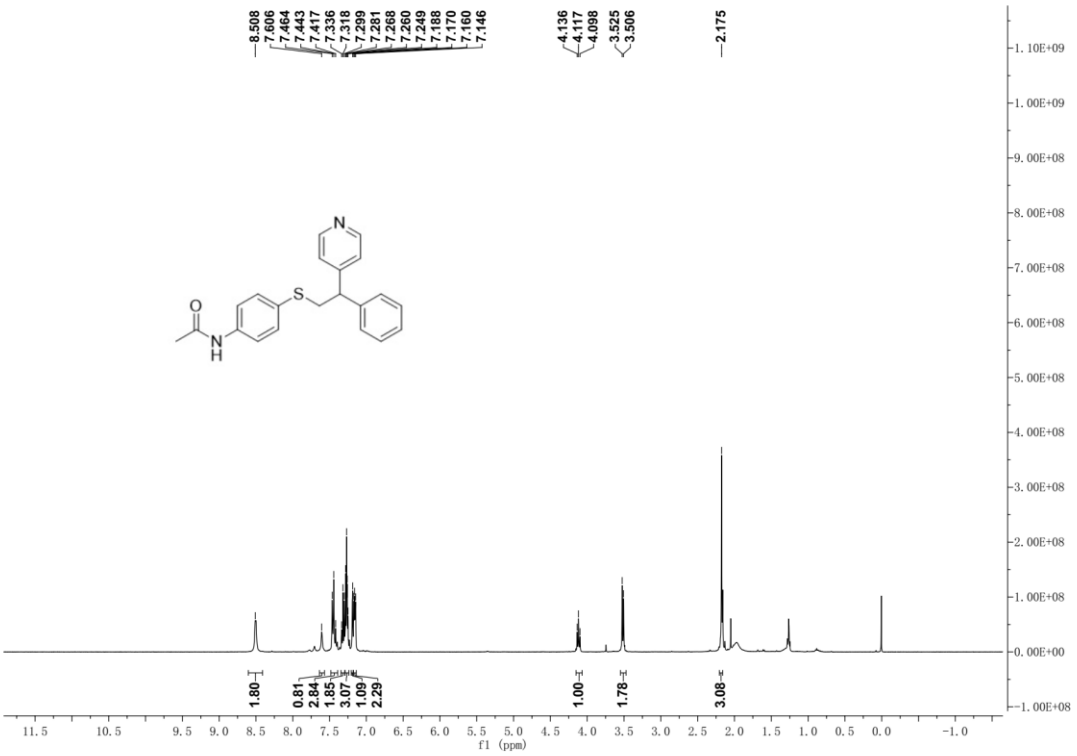

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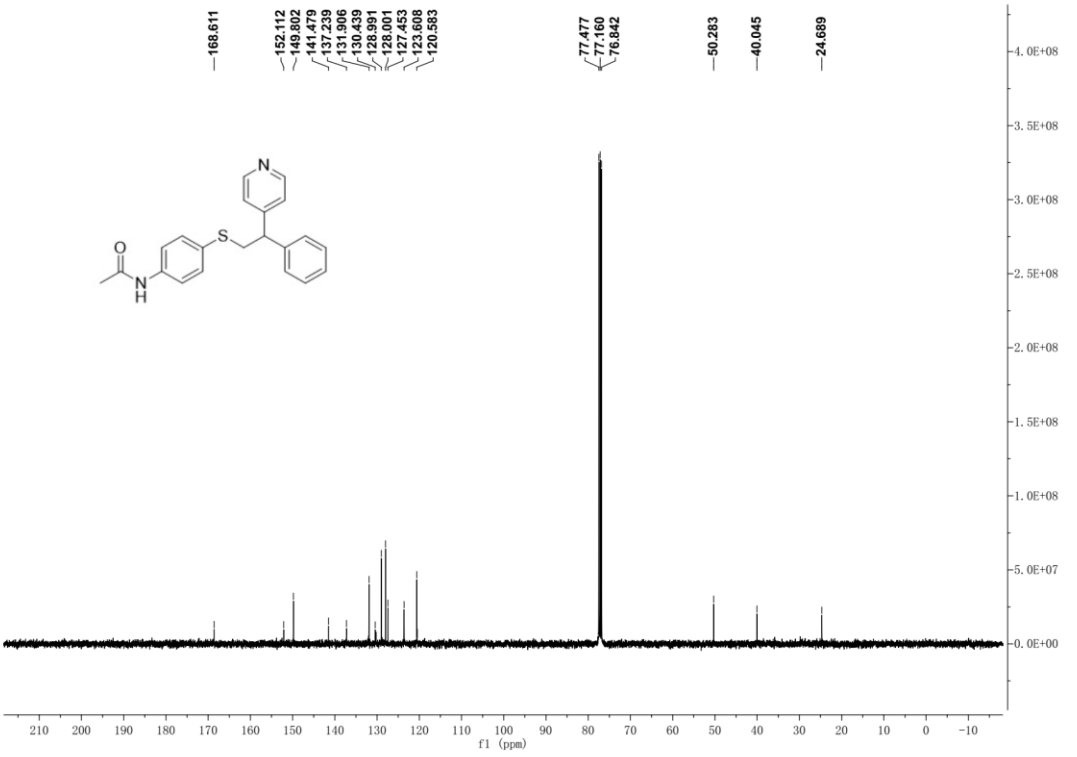

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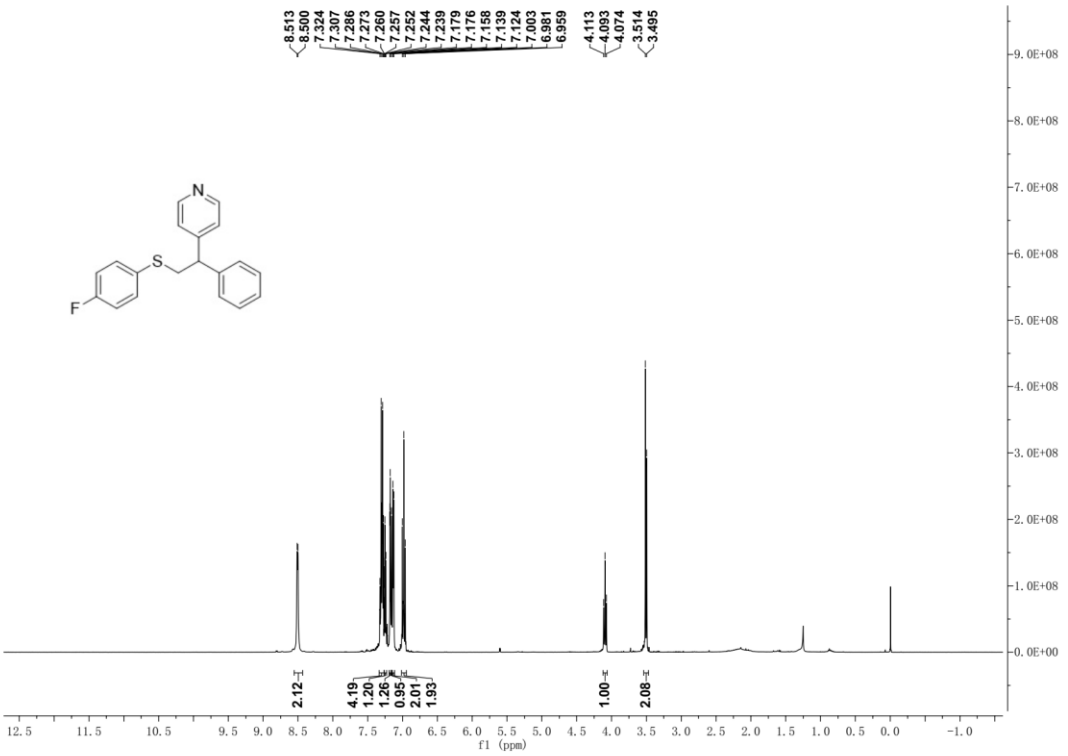
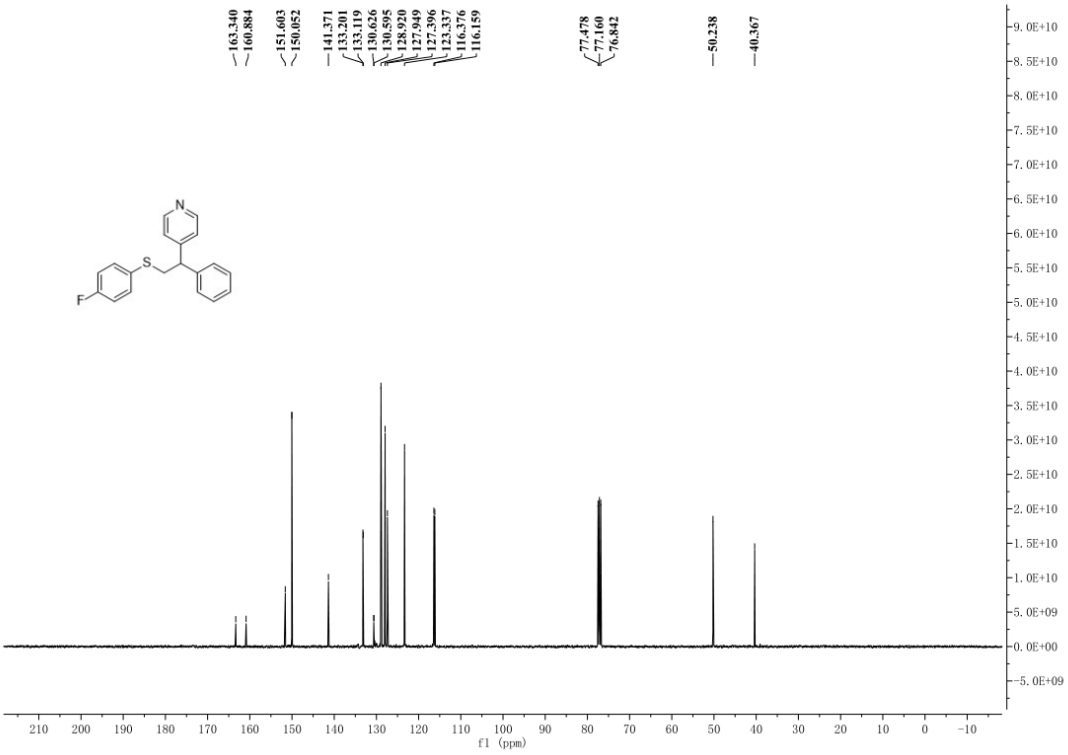
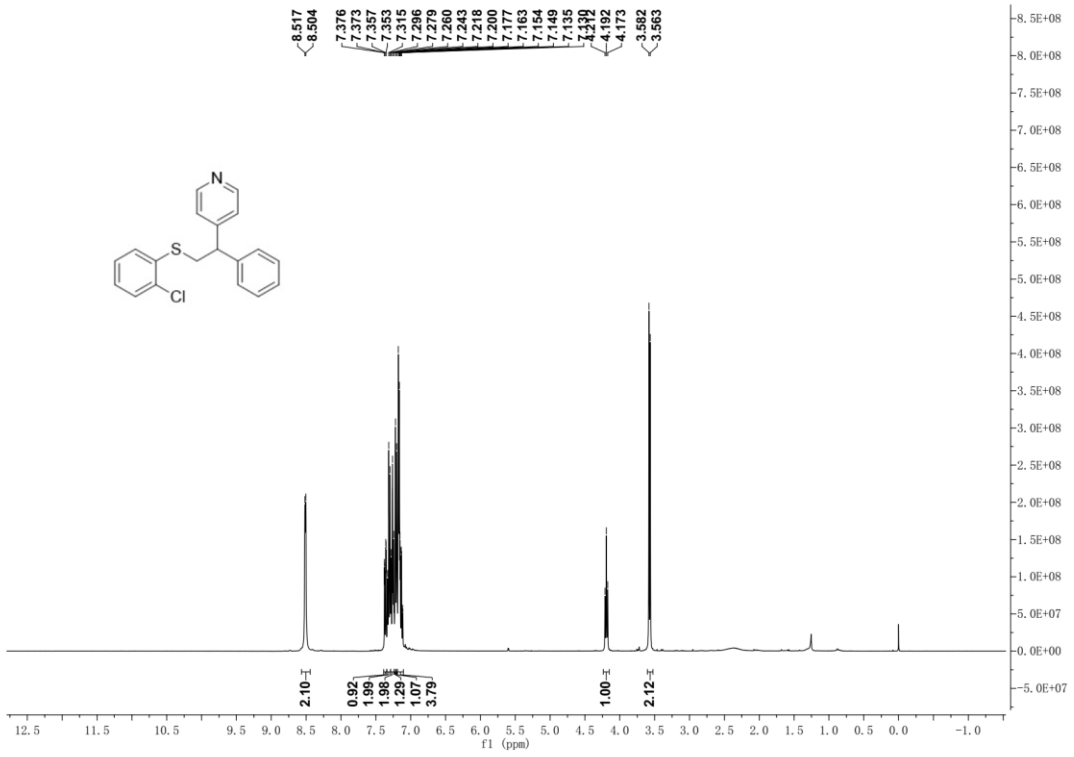


^{1}H NMR of compound 4e



^{13}C NMR of compound 4e

^{19}F NMR of compound 4e



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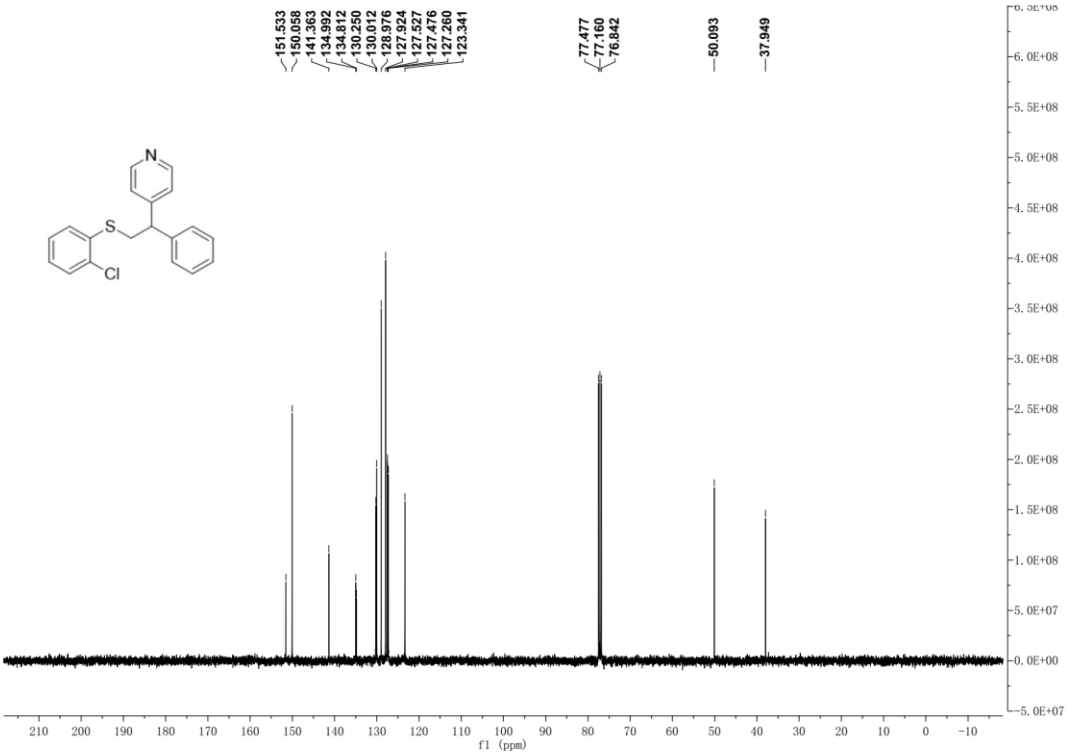

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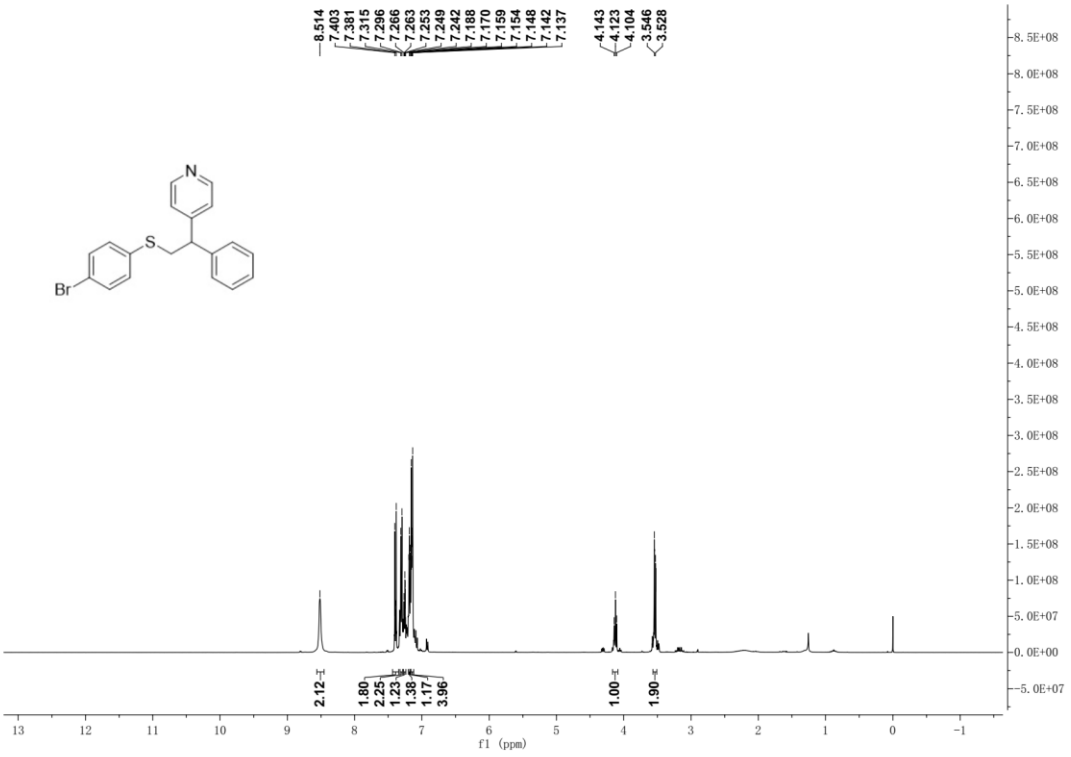
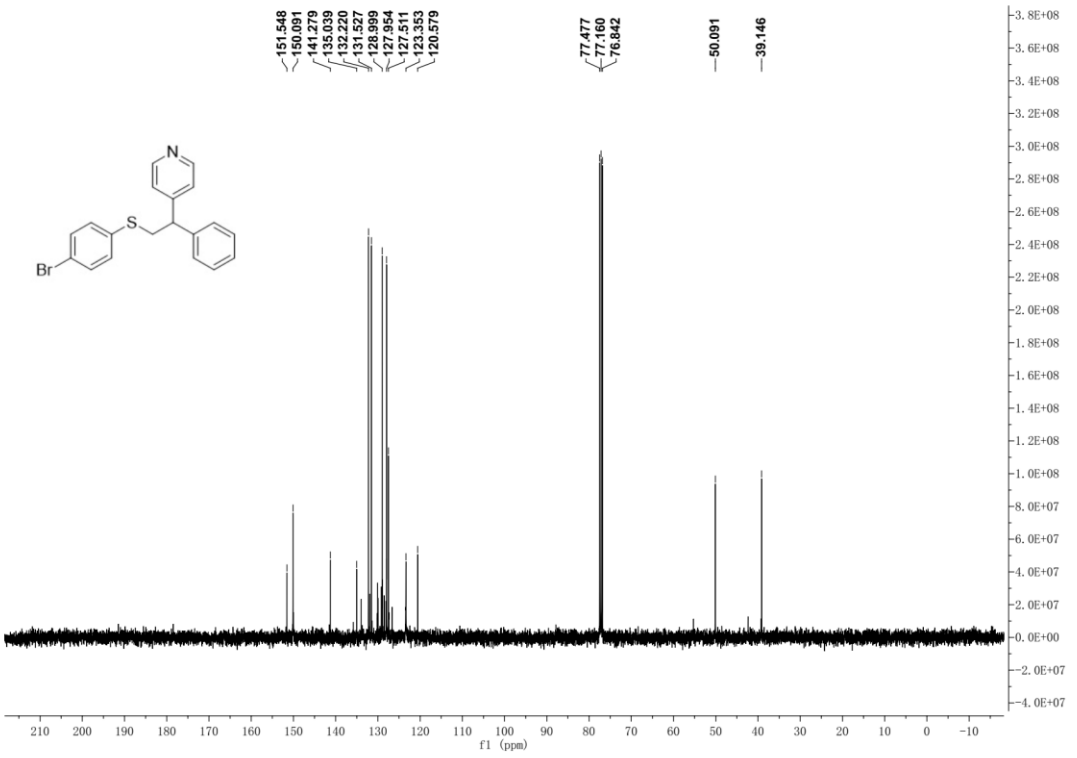


^{1}H NMR of compound 4g



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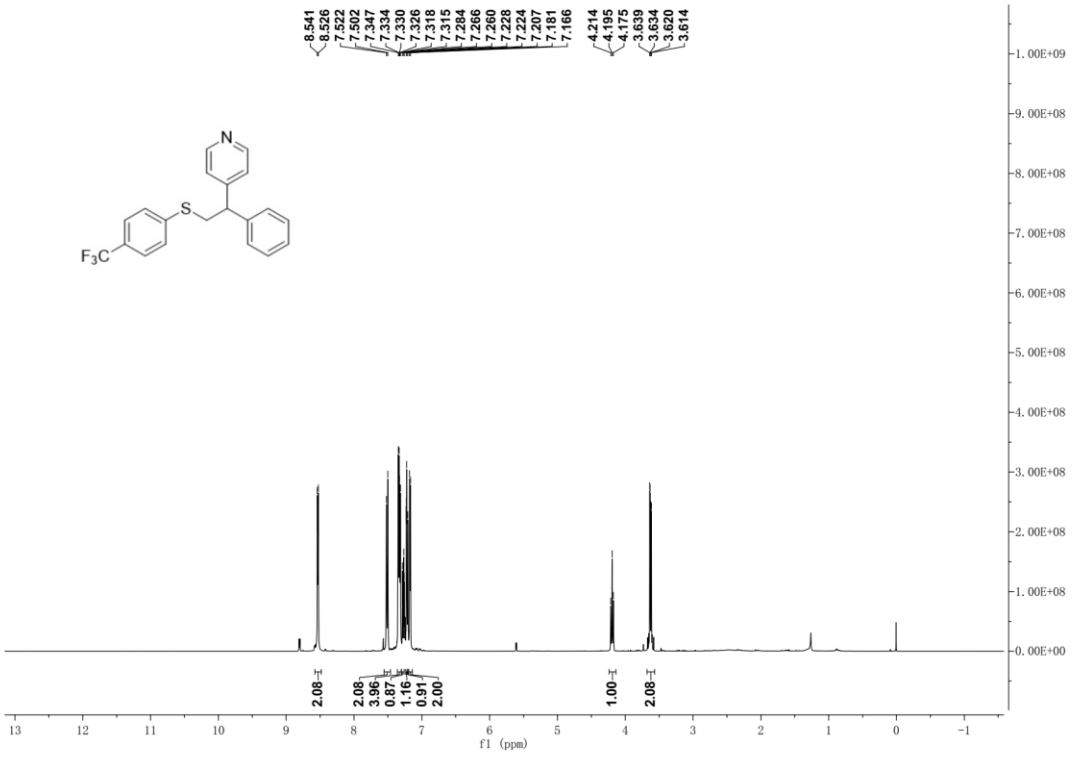
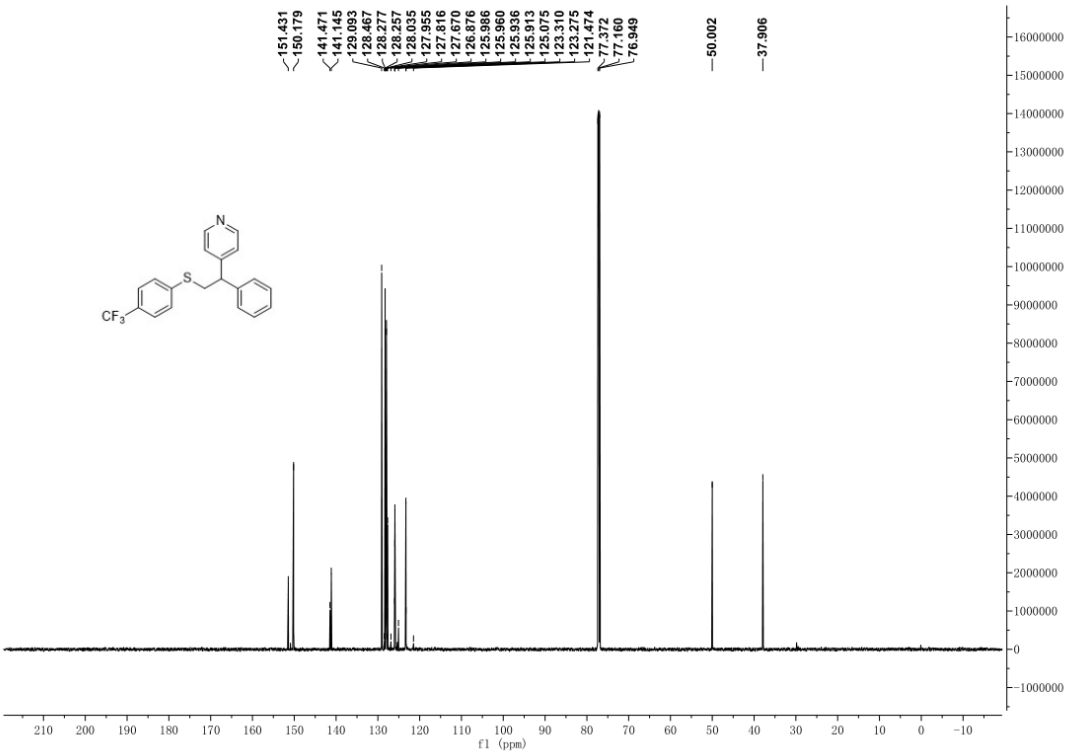
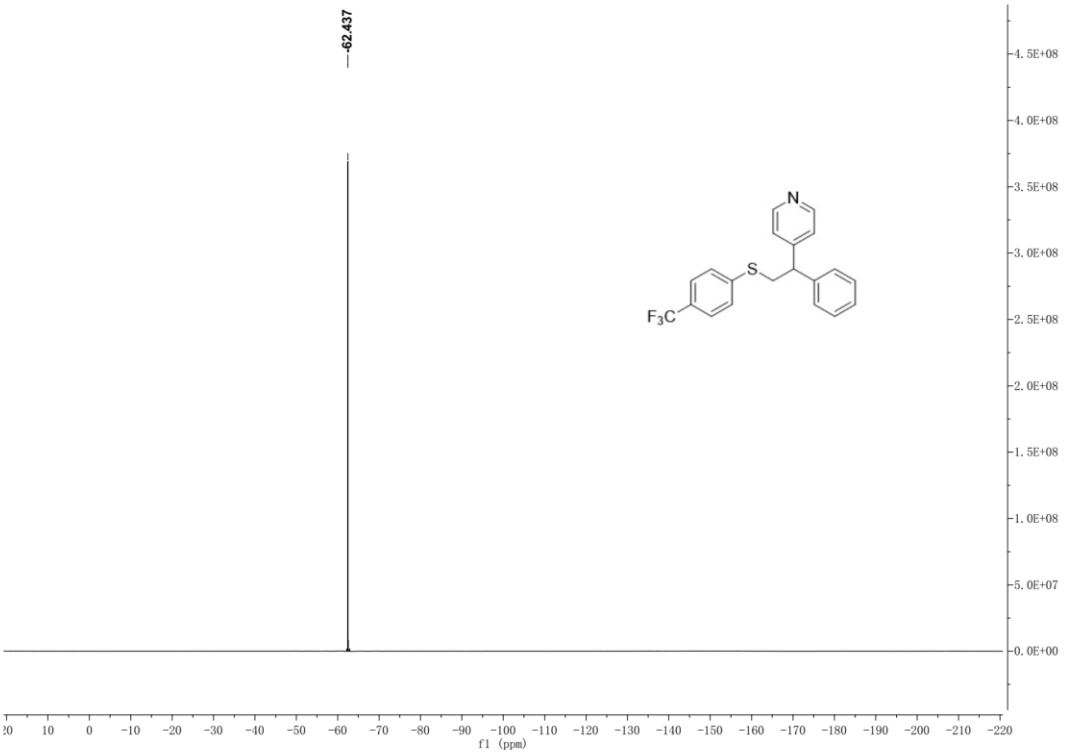


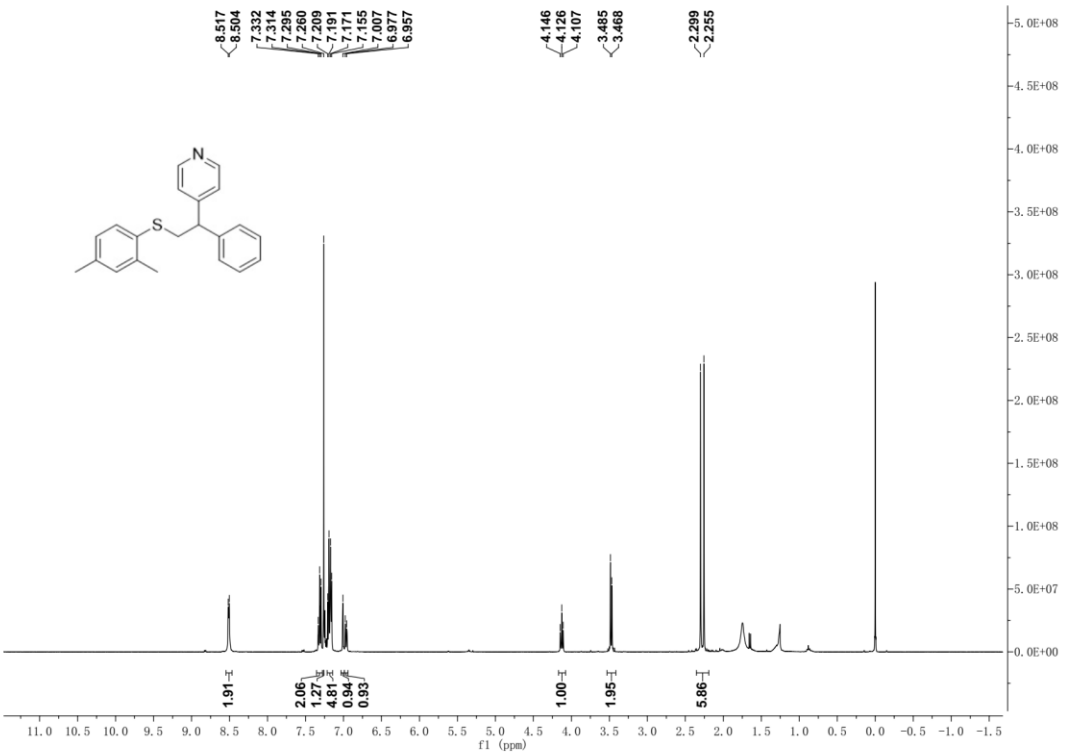
^{1}H NMR of compound 4h



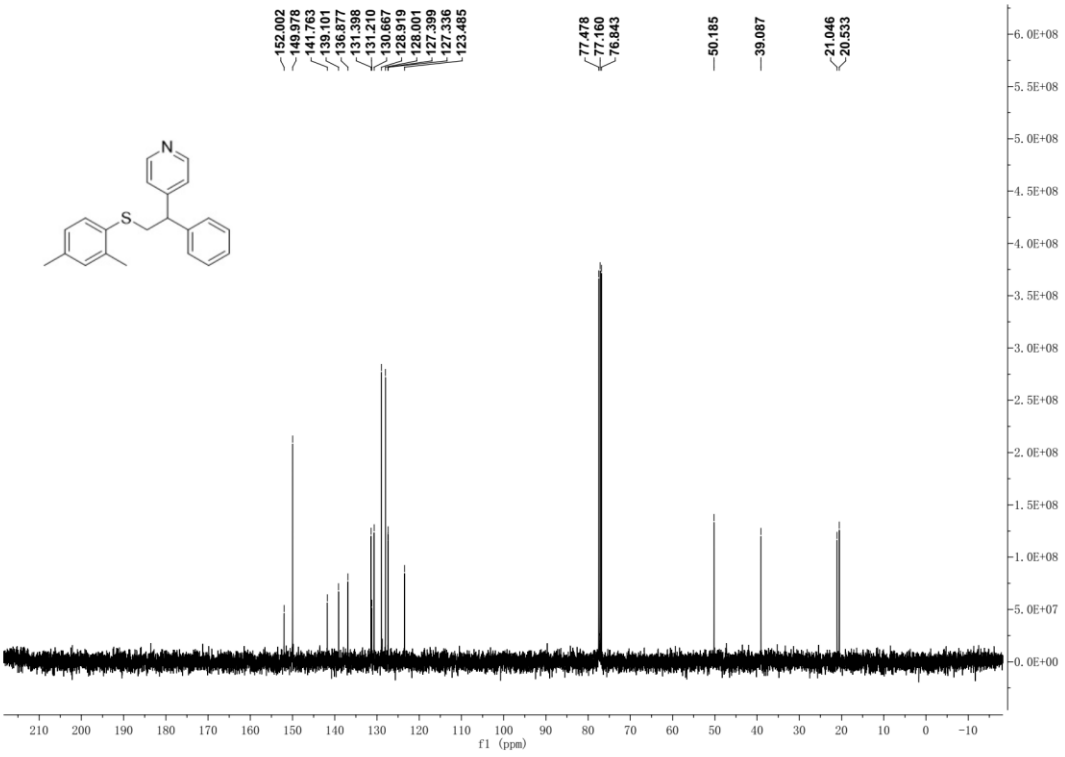
^{13}C NMR of compound 4h



^{19}F NMR of compound 4h



^{1}H NMR of compound 4i



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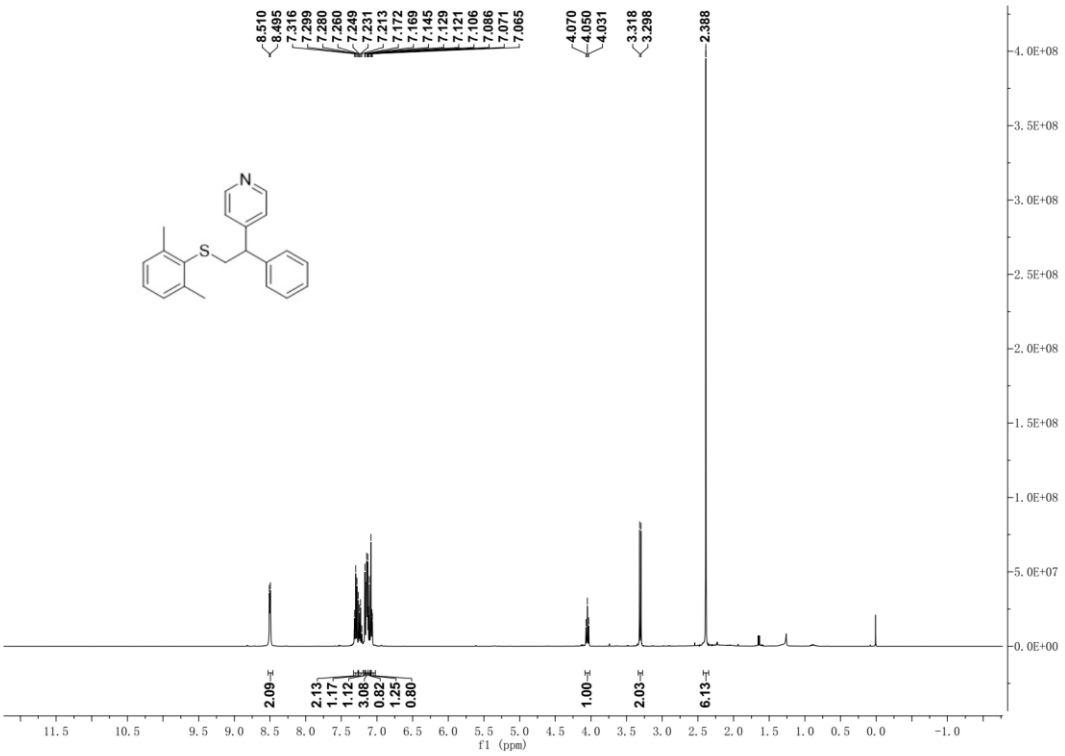

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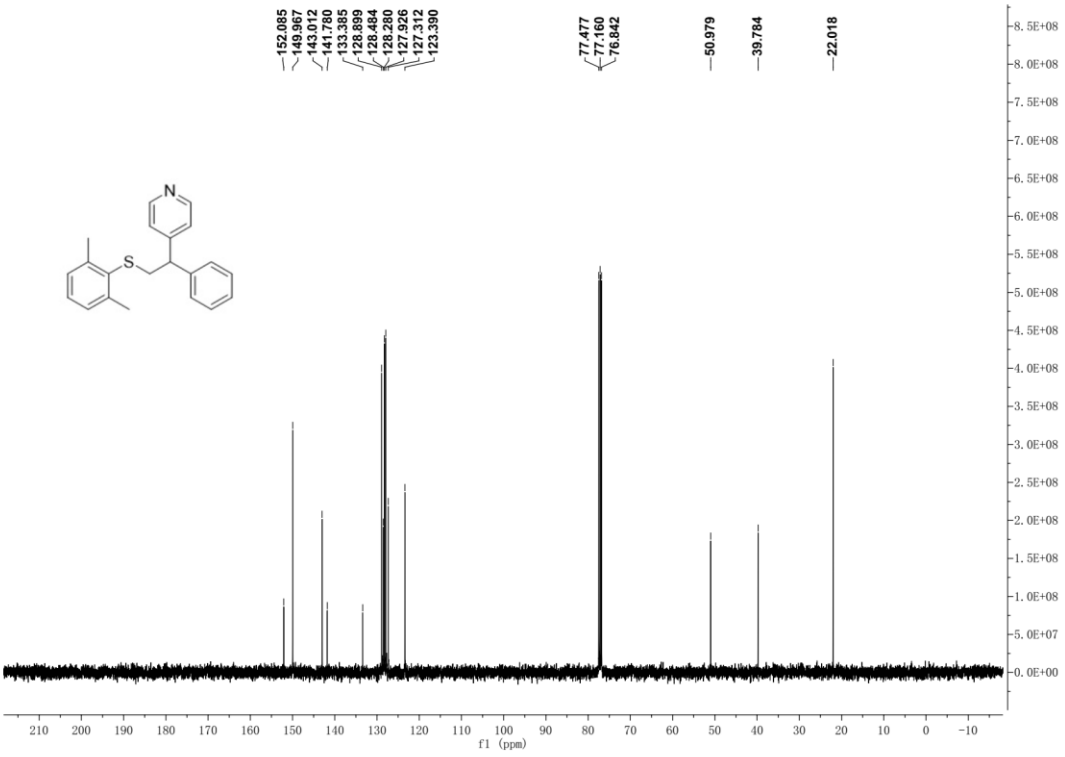

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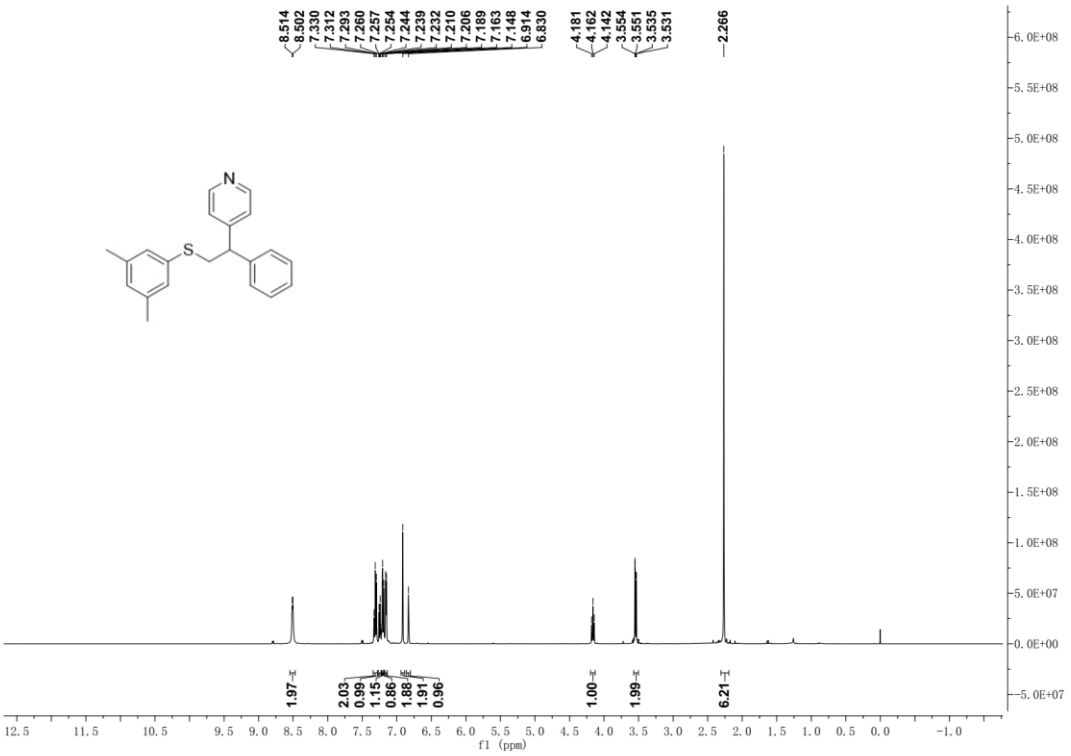

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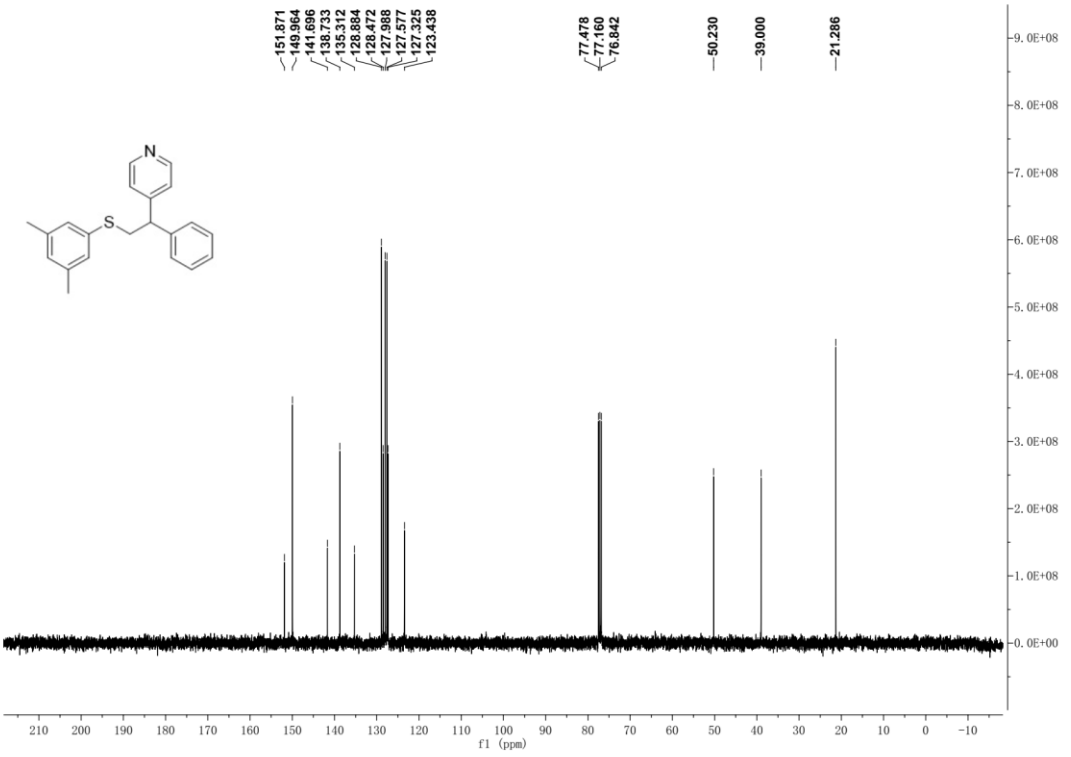
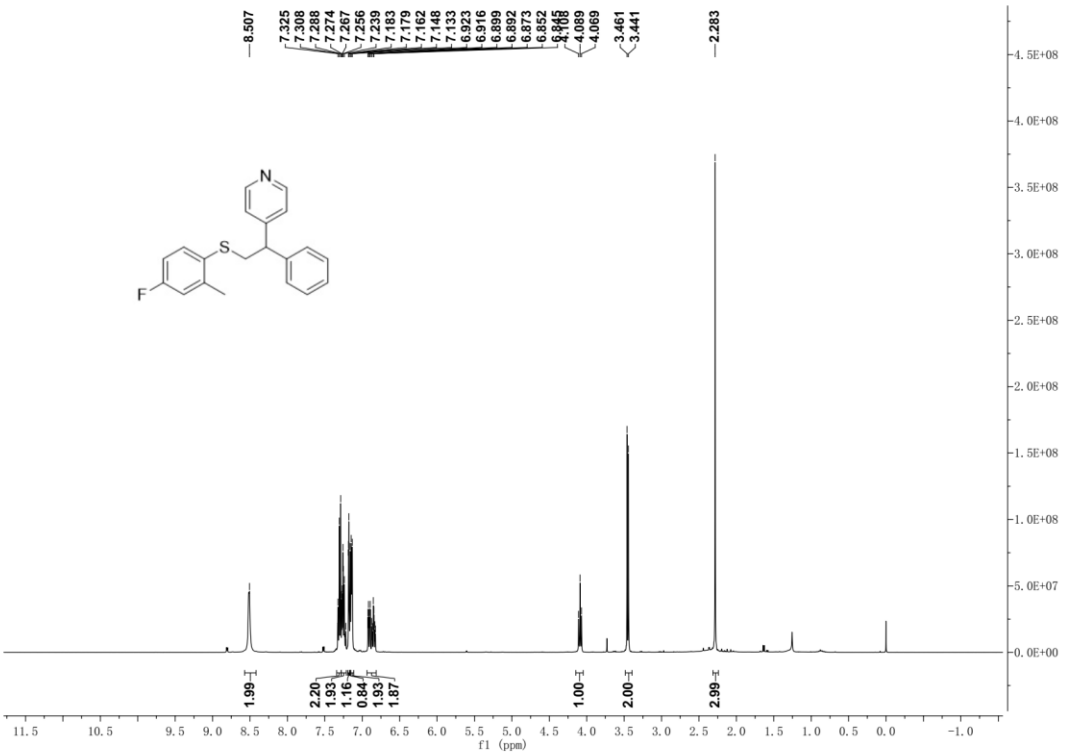
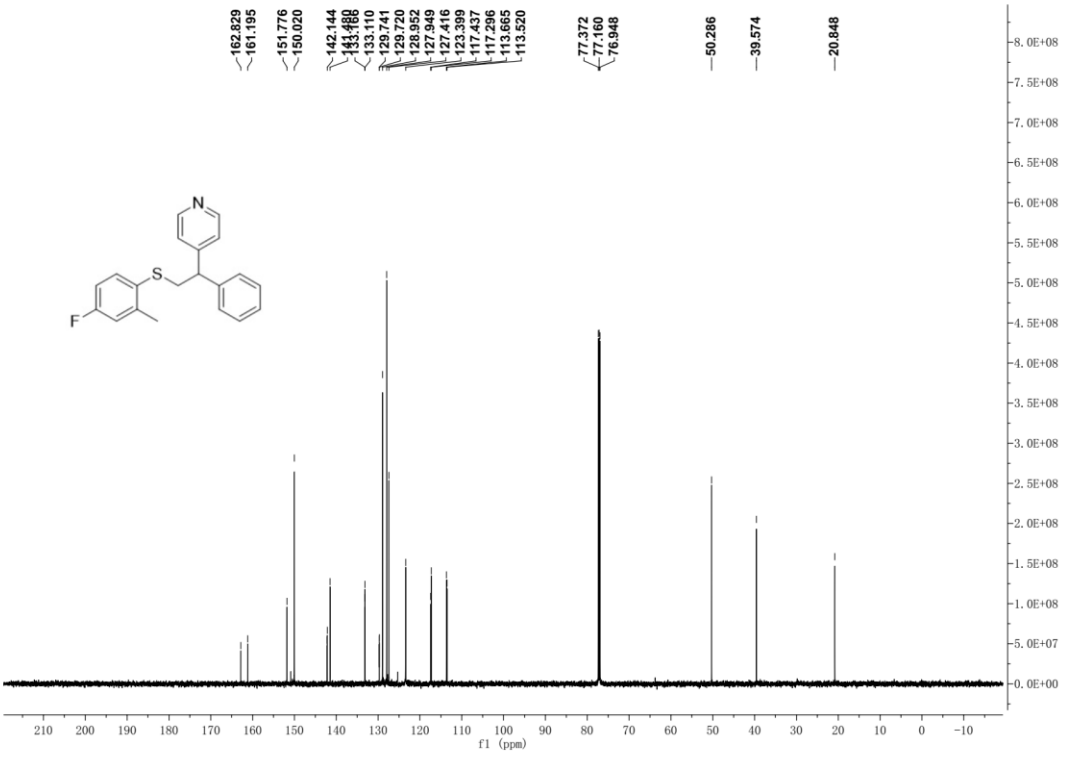


^{13}C NMR of compound 4k

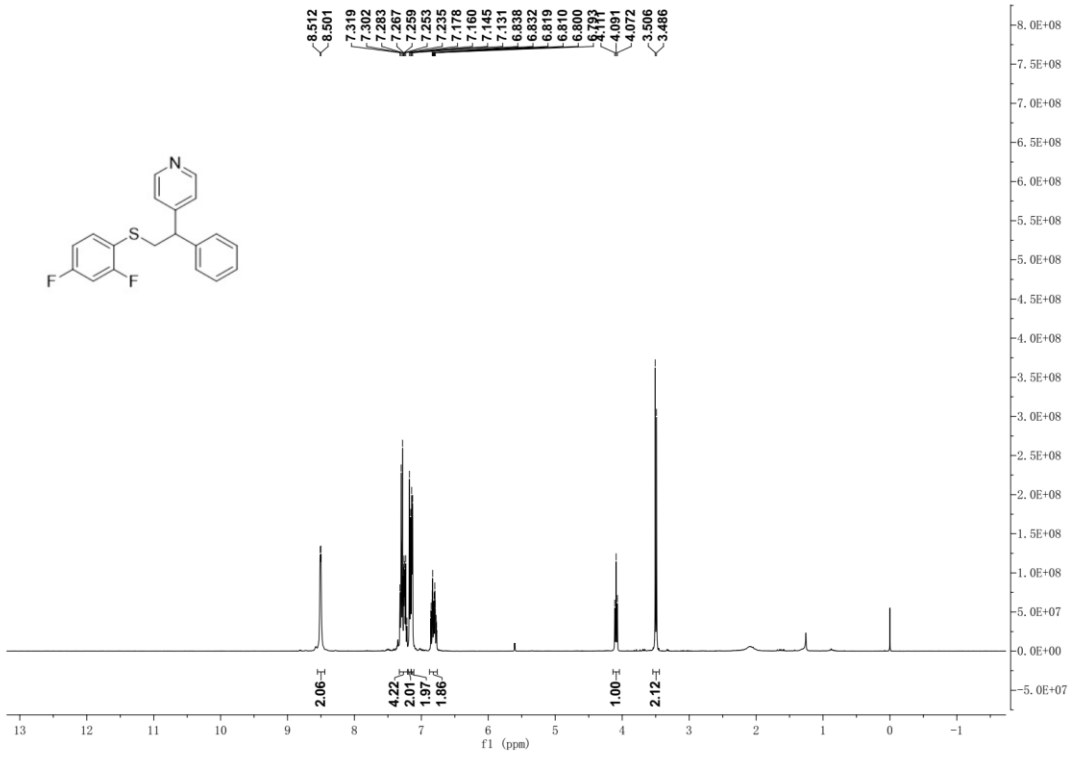


^{1}H NMR of compound 4l

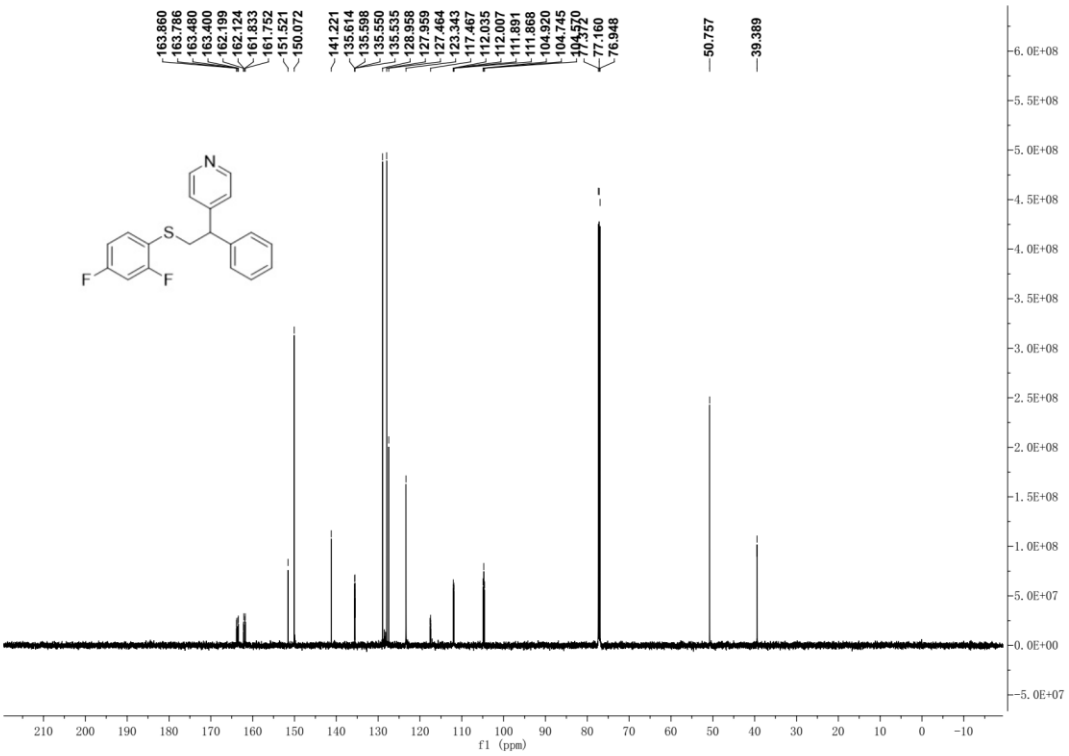


^{13}C NMR of compound 4l

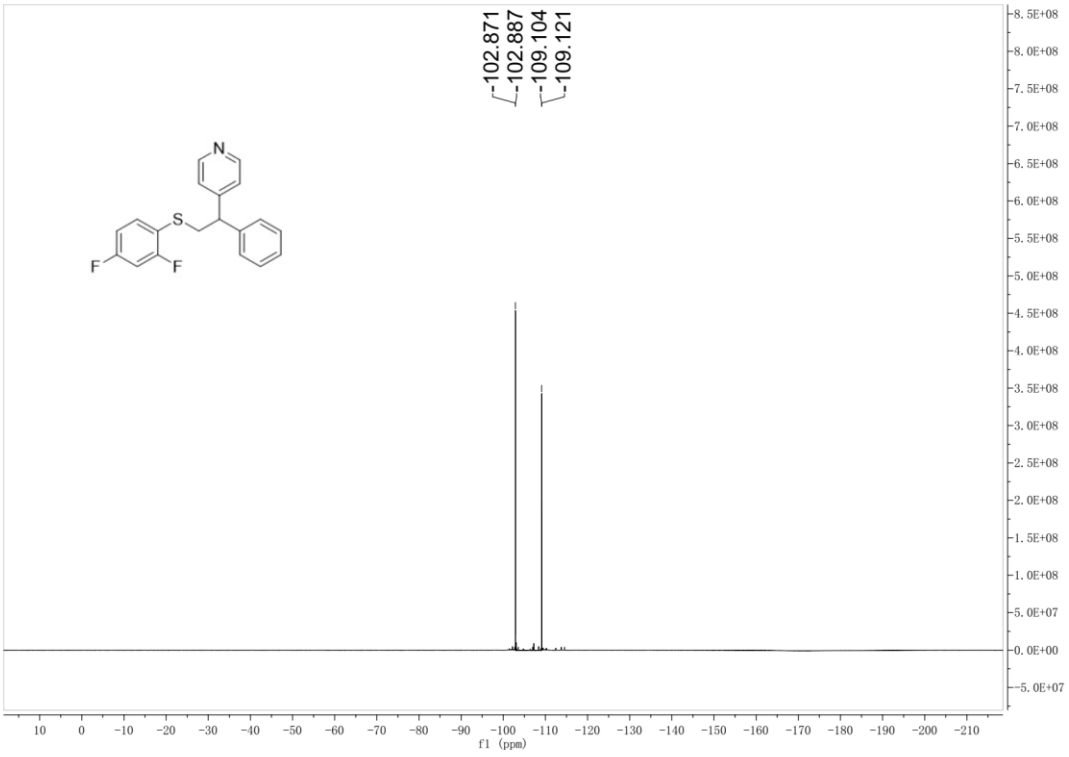
^{19}F NMR of compound 4l



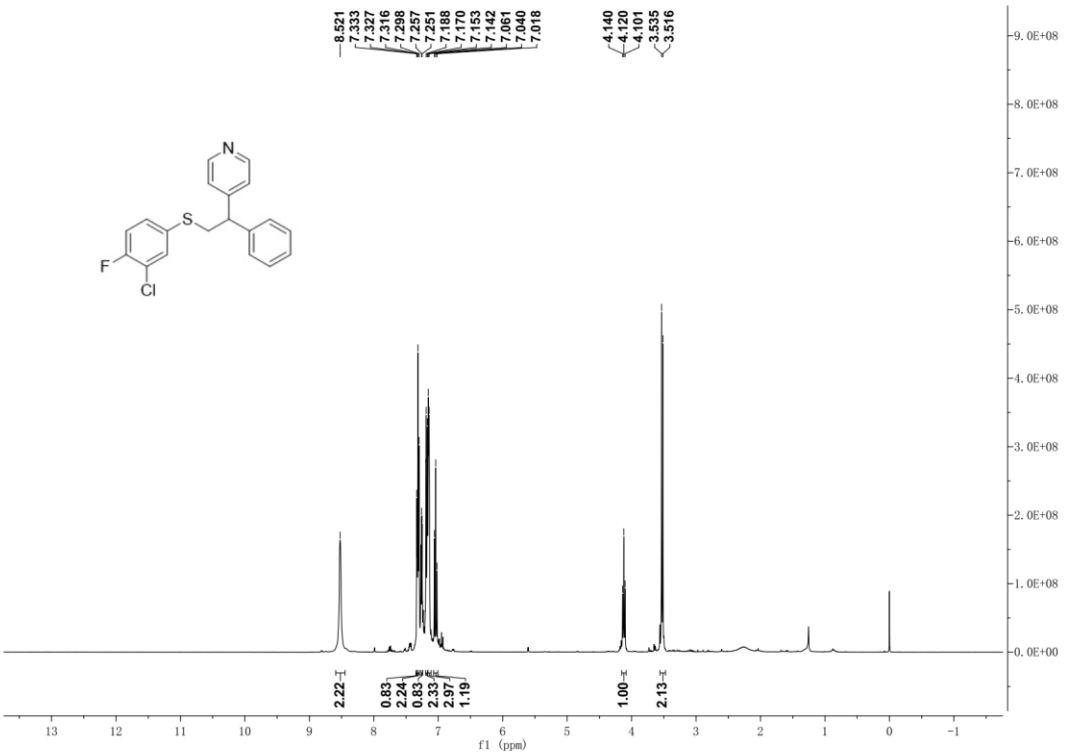
^{1}H NMR of compound 4m



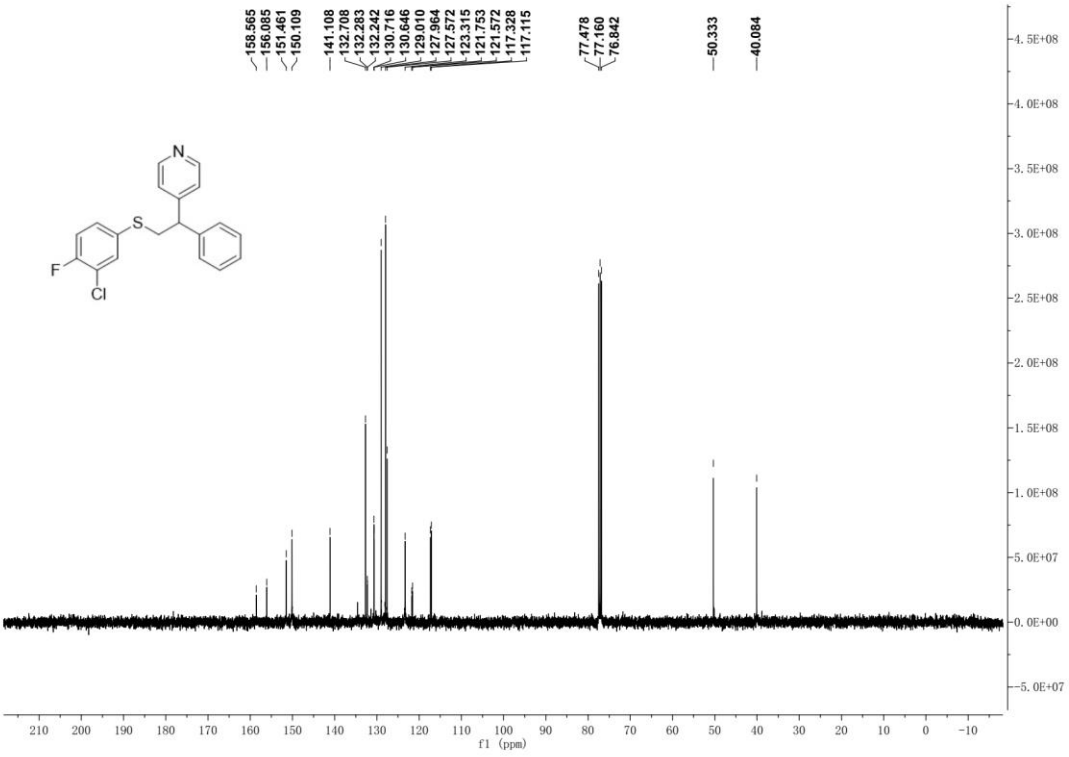
^{13}C NMR of compound 4m



^{19}F NMR of compound 4m

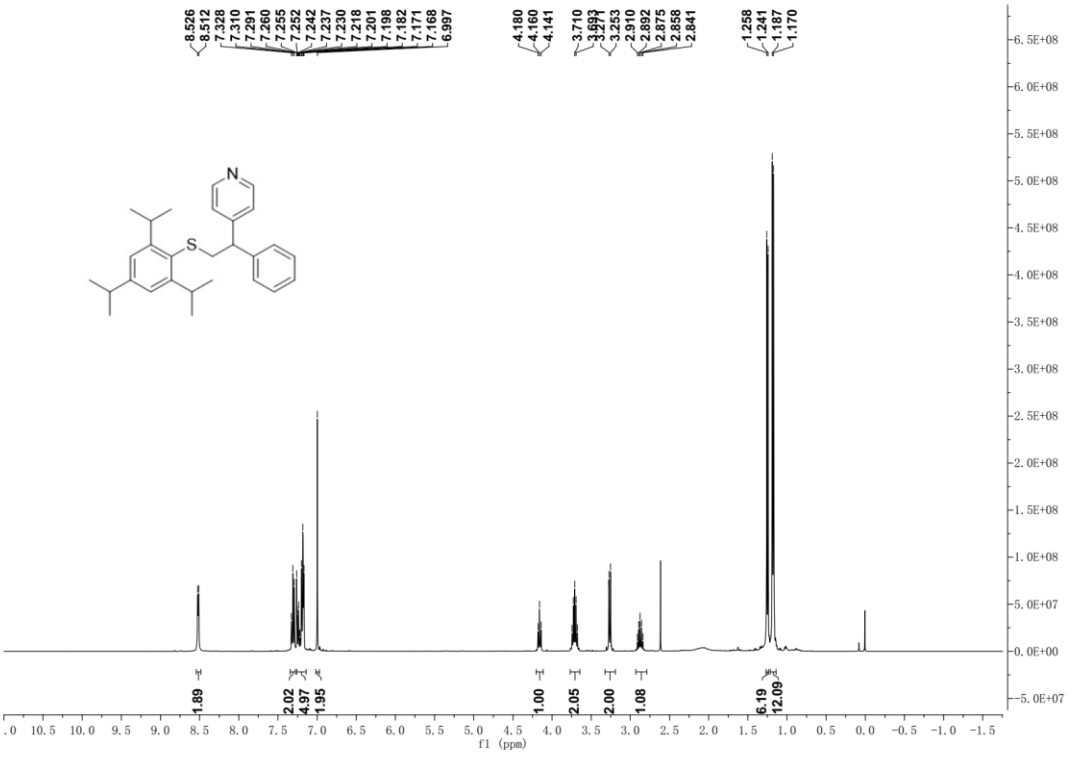


^{1}H NMR of compound 4n

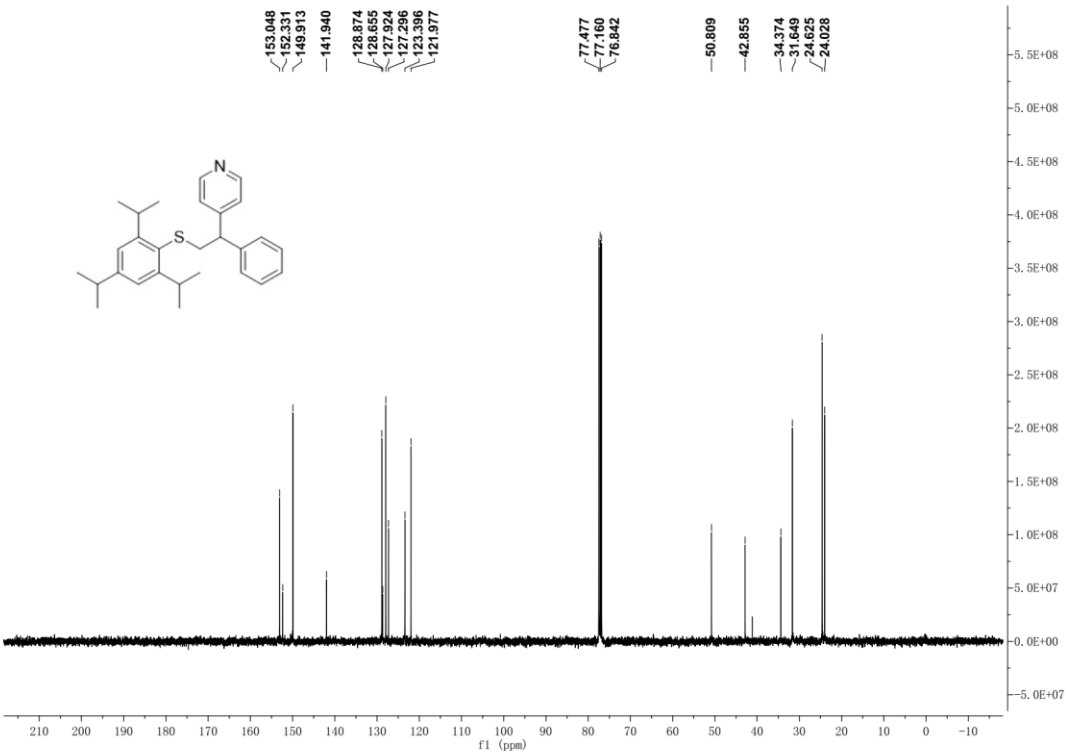


^{13}C NMR of compound 4n

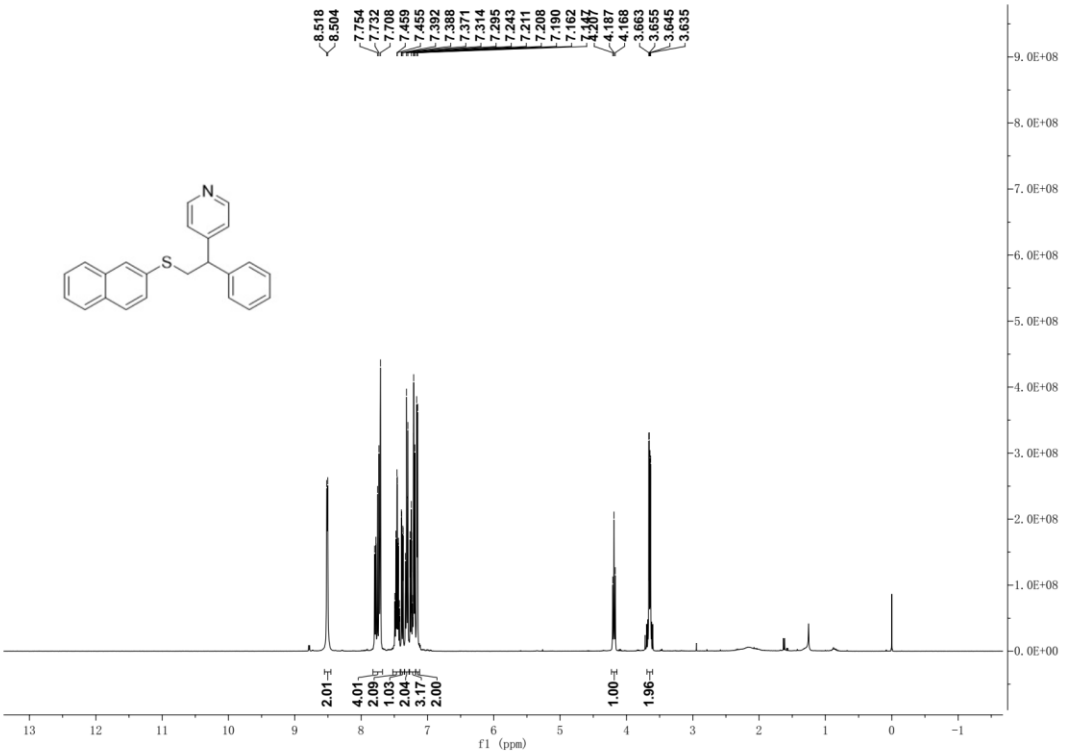
^{19}F NMR of compound 4n



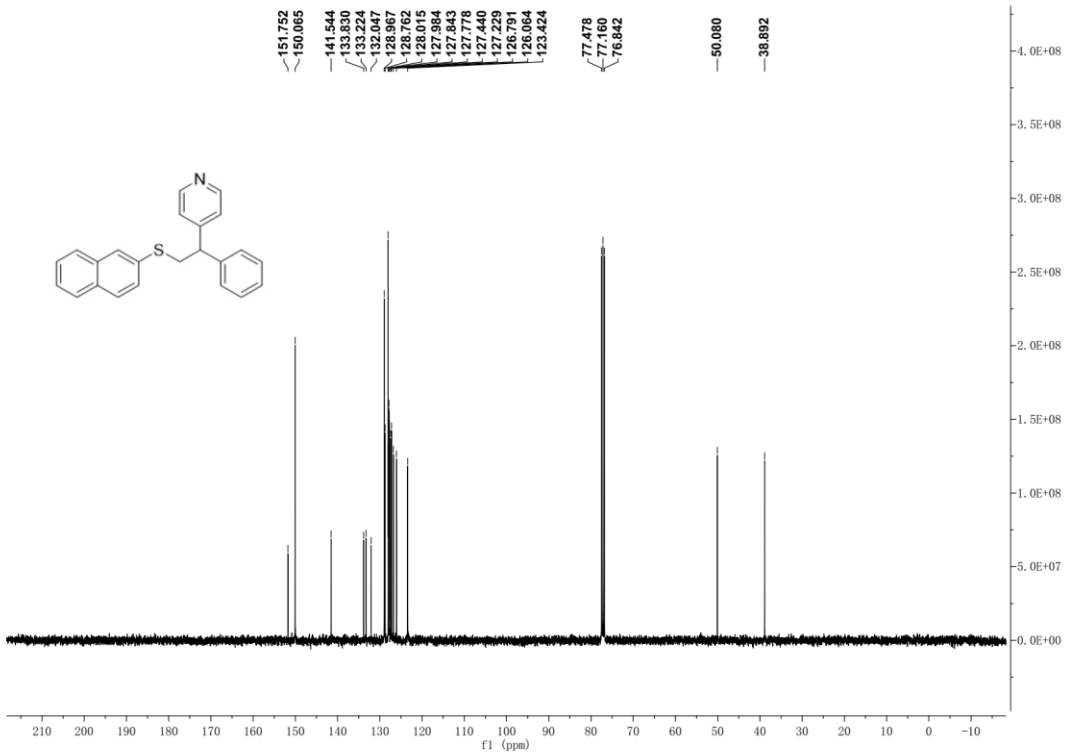
^{1}H NMR of compound 4o



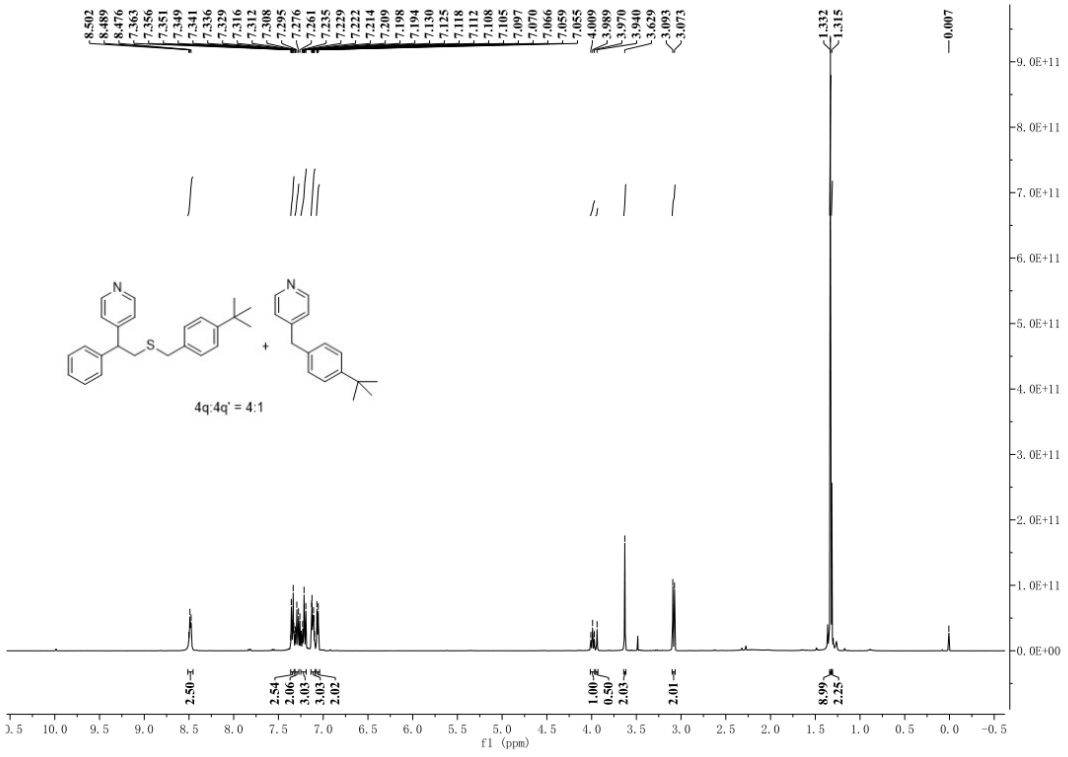
^{13}C NMR of compound 4o



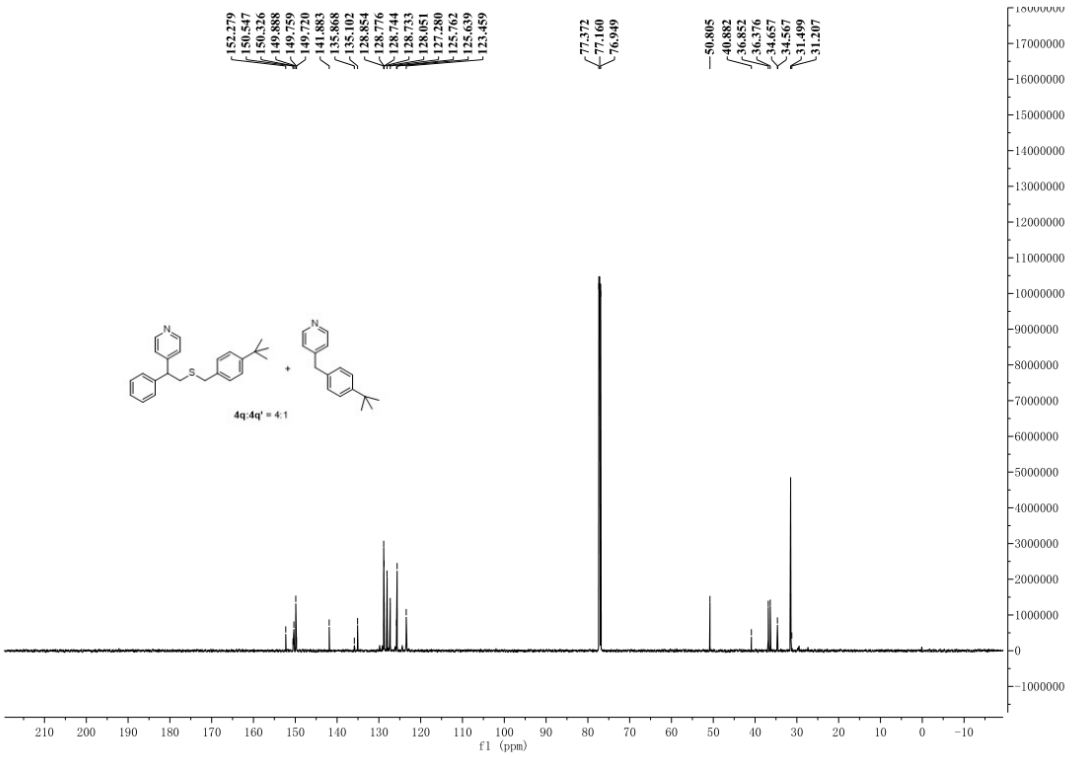
^{1}H NMR of compound 4p



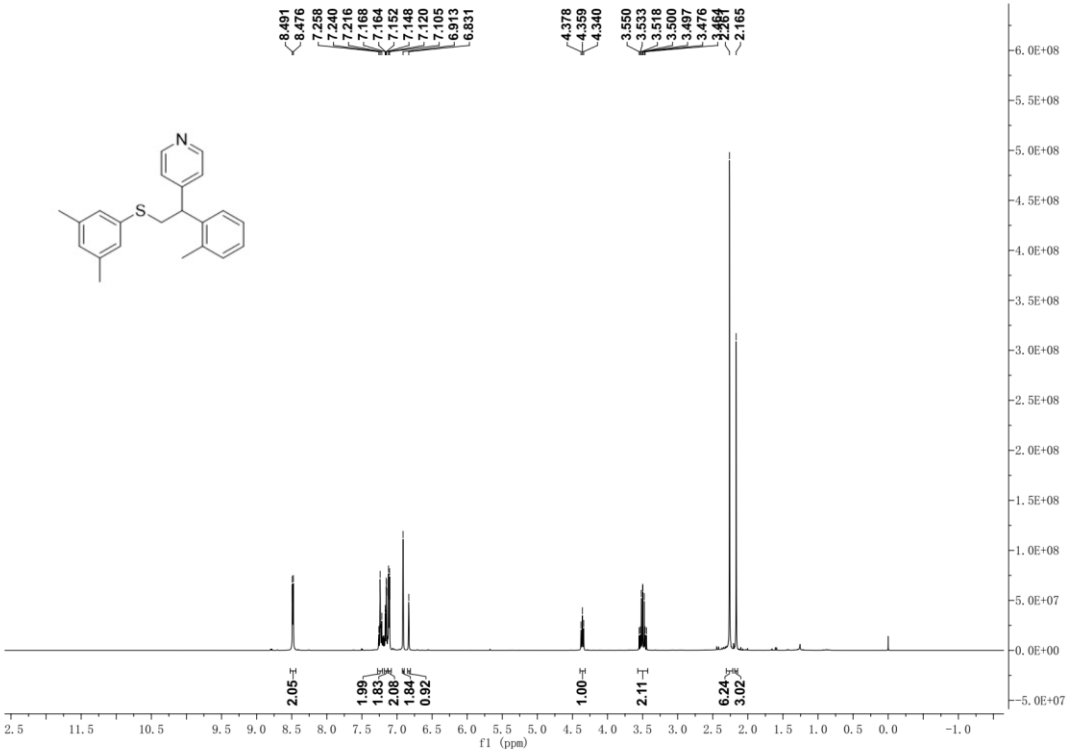
^{13}C NMR of compound 4p



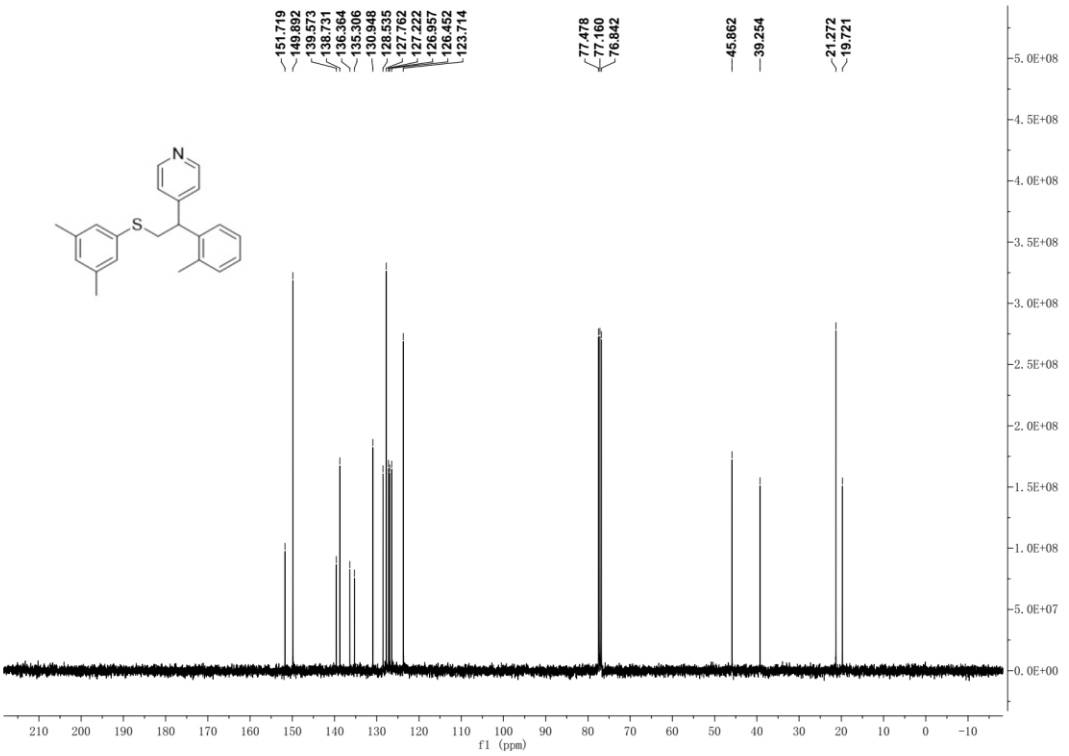
^{1}H NMR of compound 4q+4q'



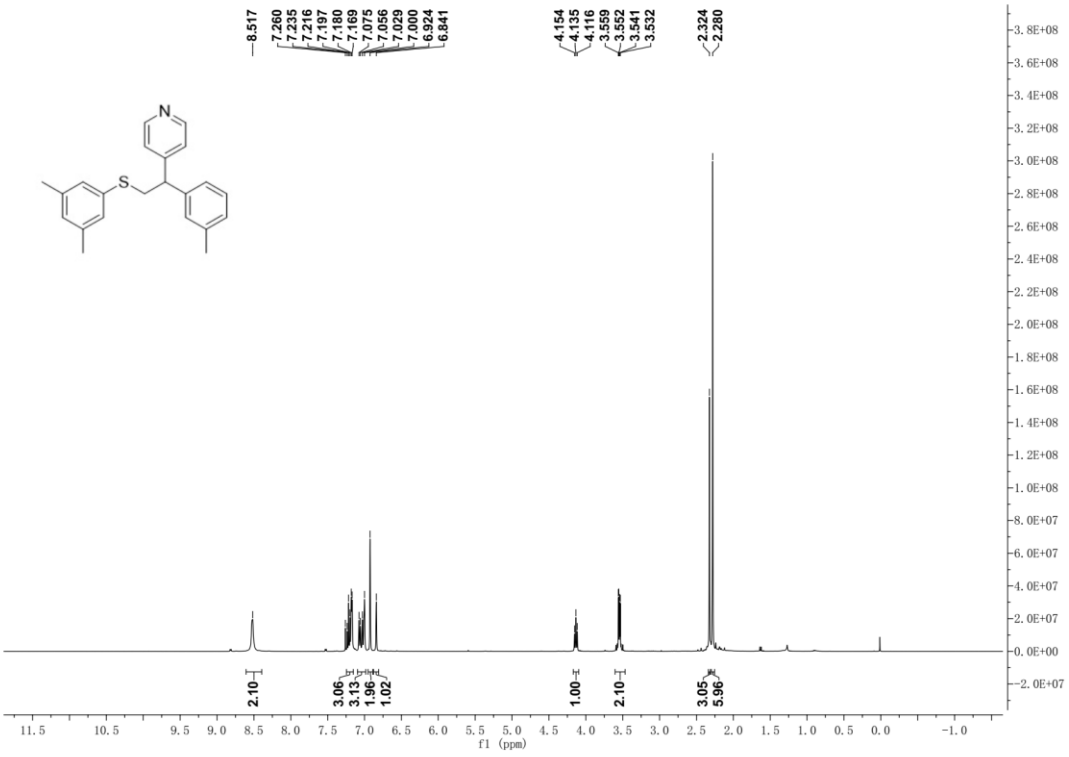
^{13}C NMR of compound 4q+4q'



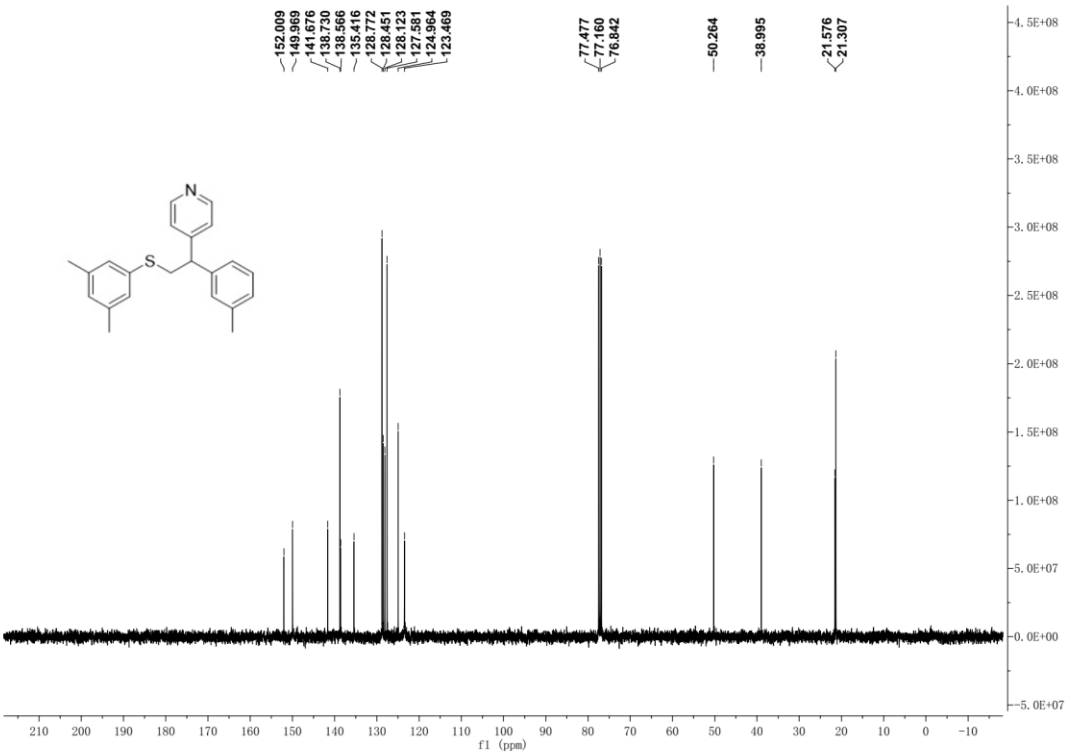
^{1}H NMR of compound 5a



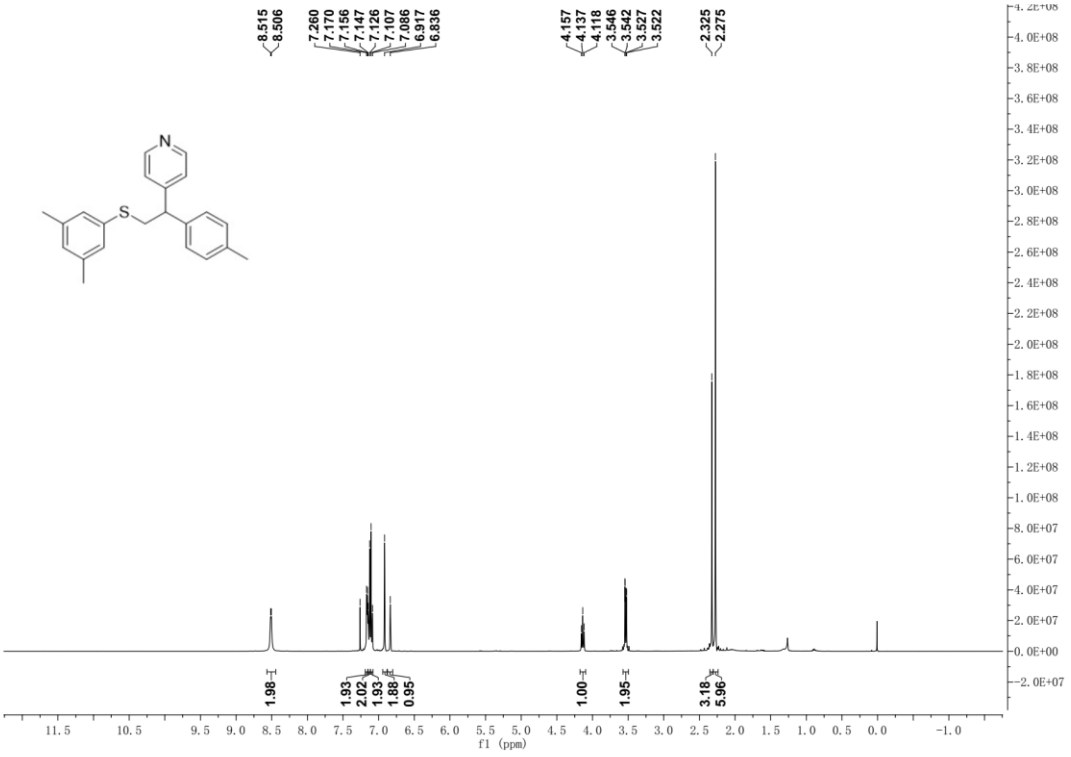
^{13}C NMR of compound 5a



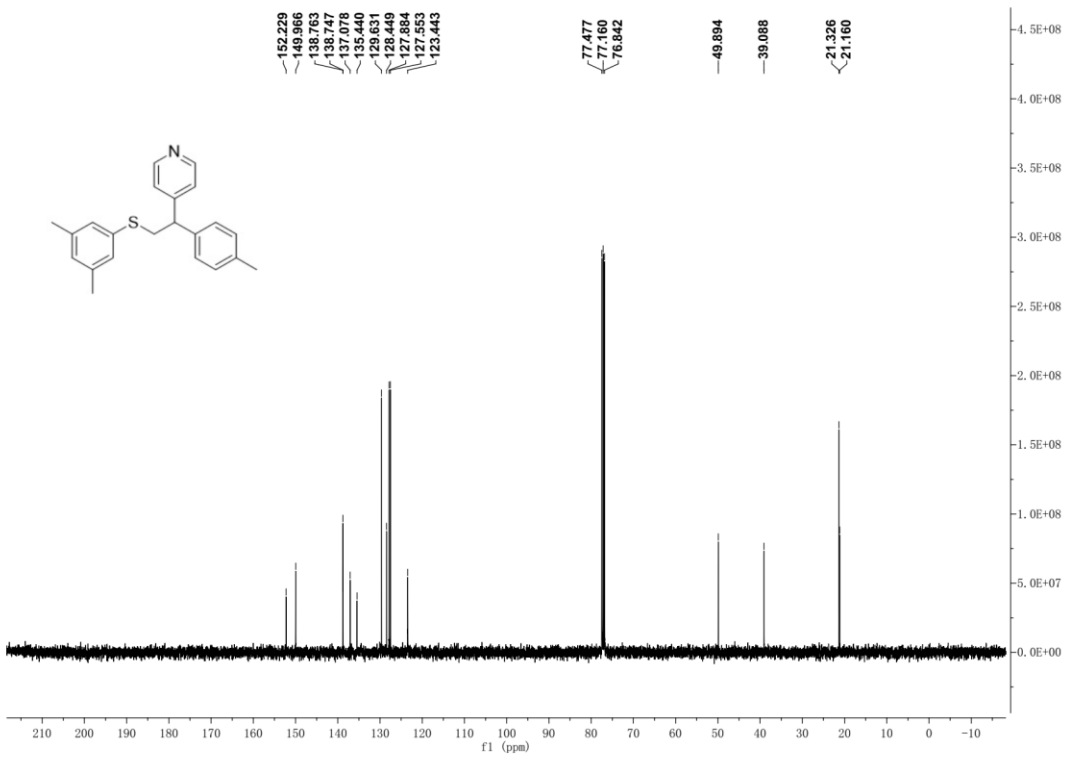
^{1}H NMR of compound 5b



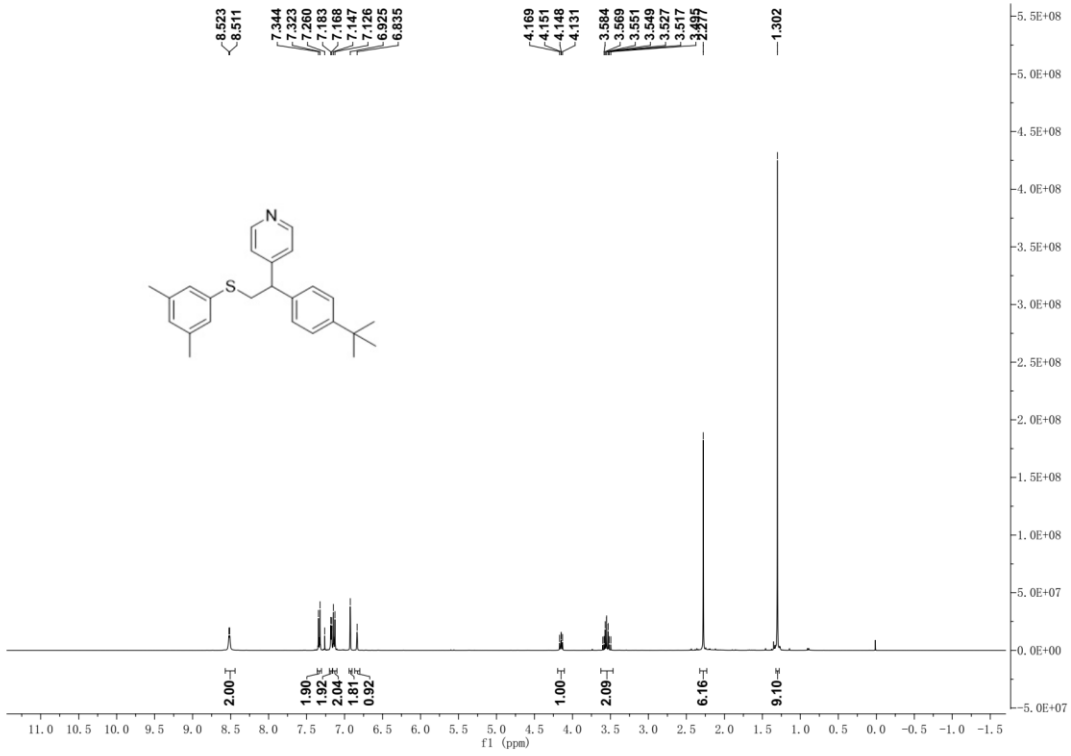
^{13}C NMR of compound 5b



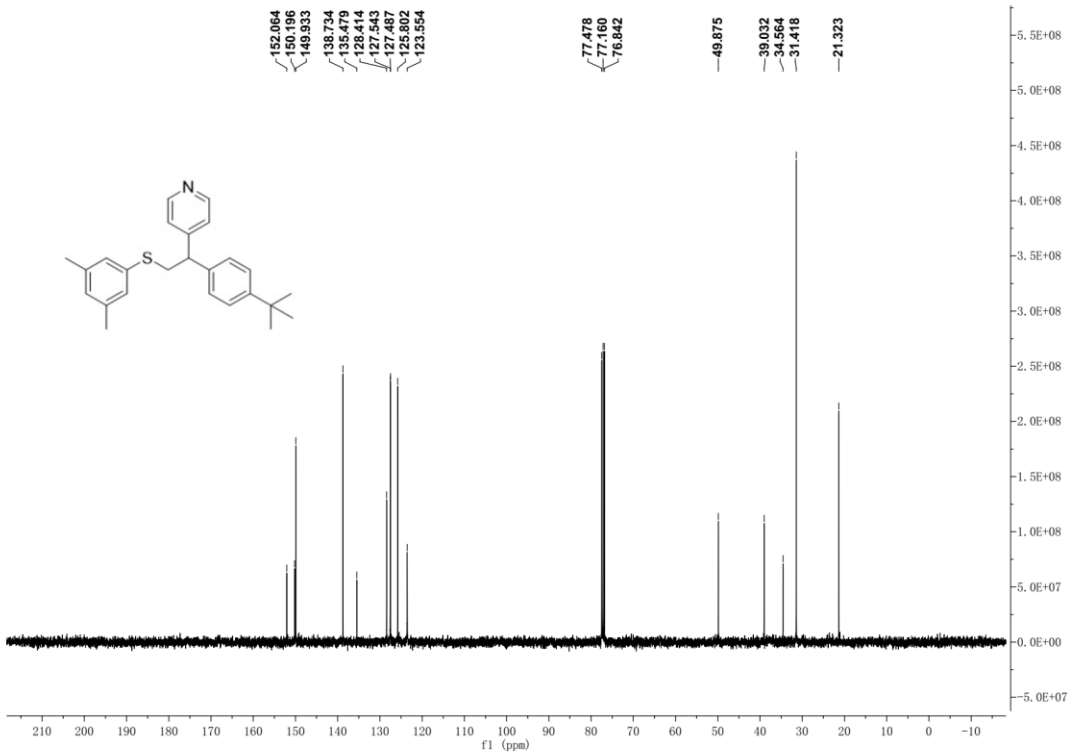
^{1}H NMR of compound 5c



^{13}C NMR of compound 5c



^{1}H NMR of compound 5d



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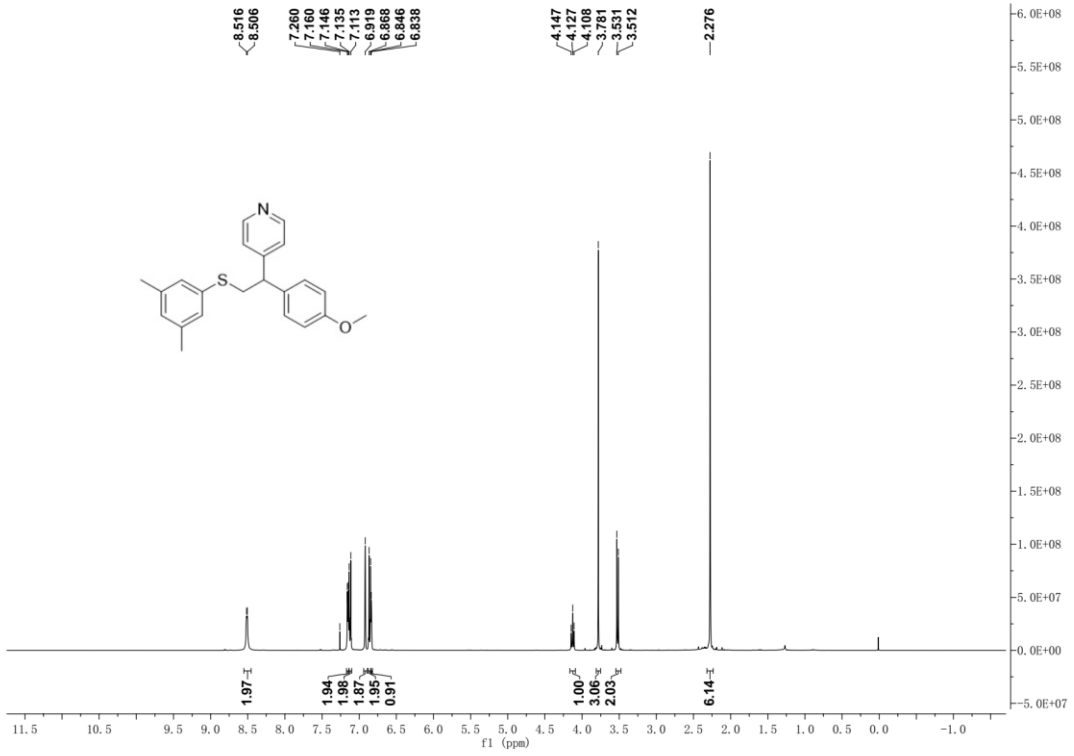
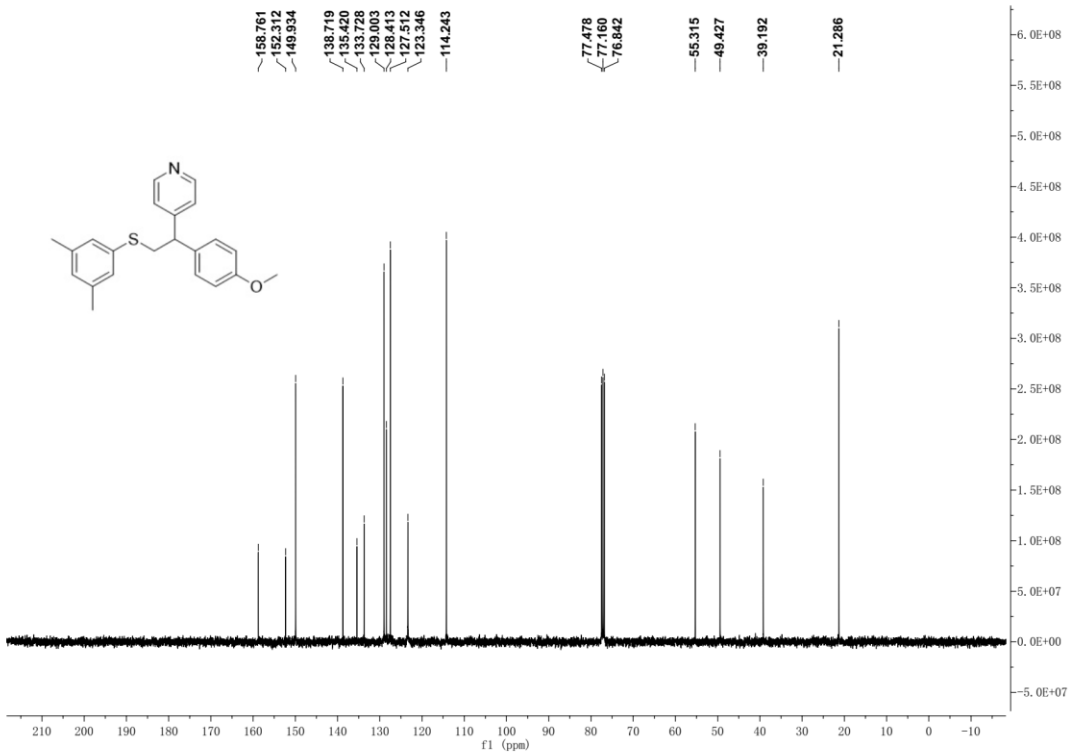
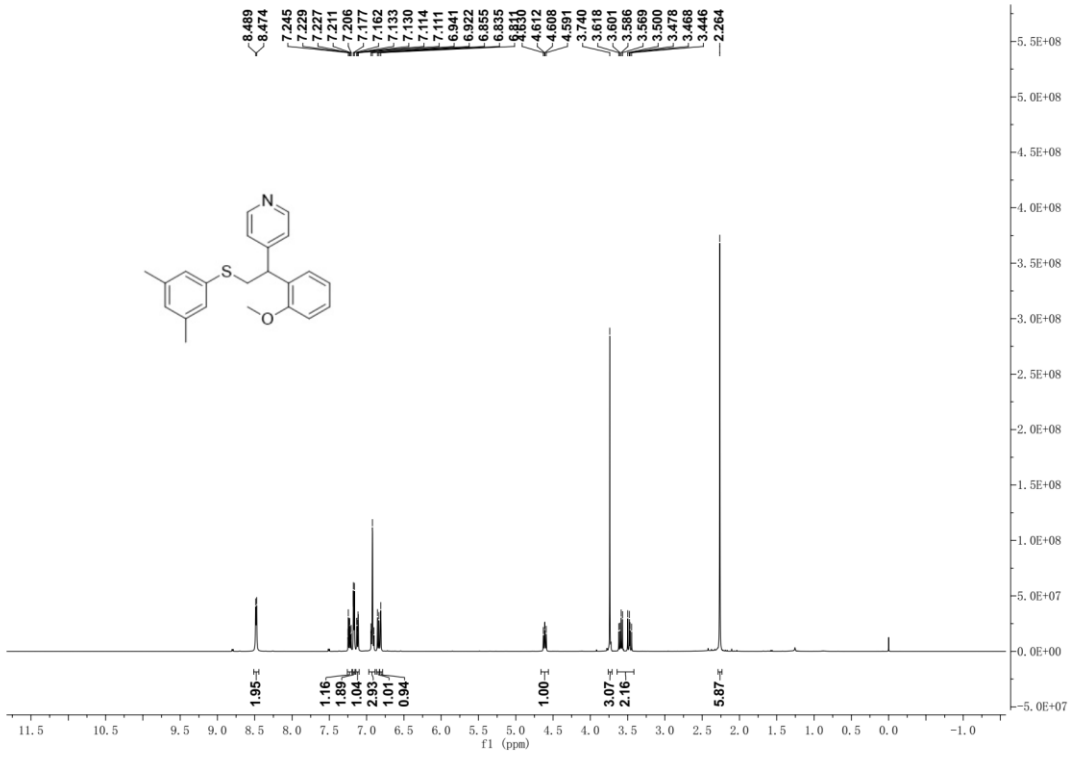


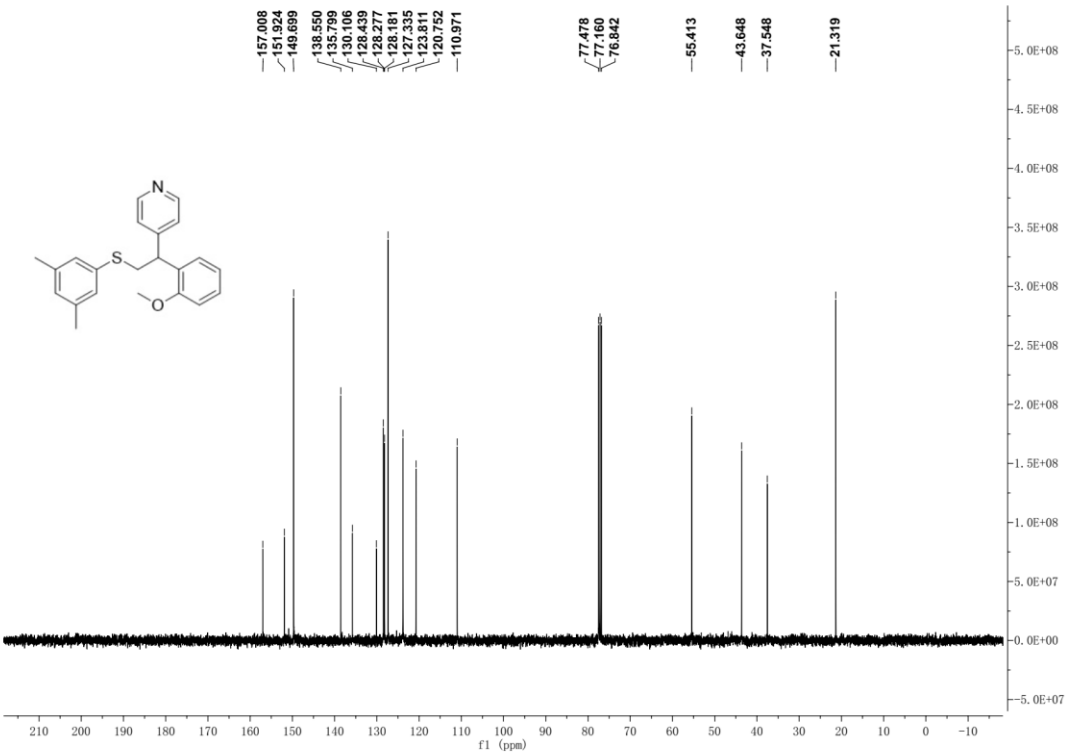
^{1}H NMR of compound 5e



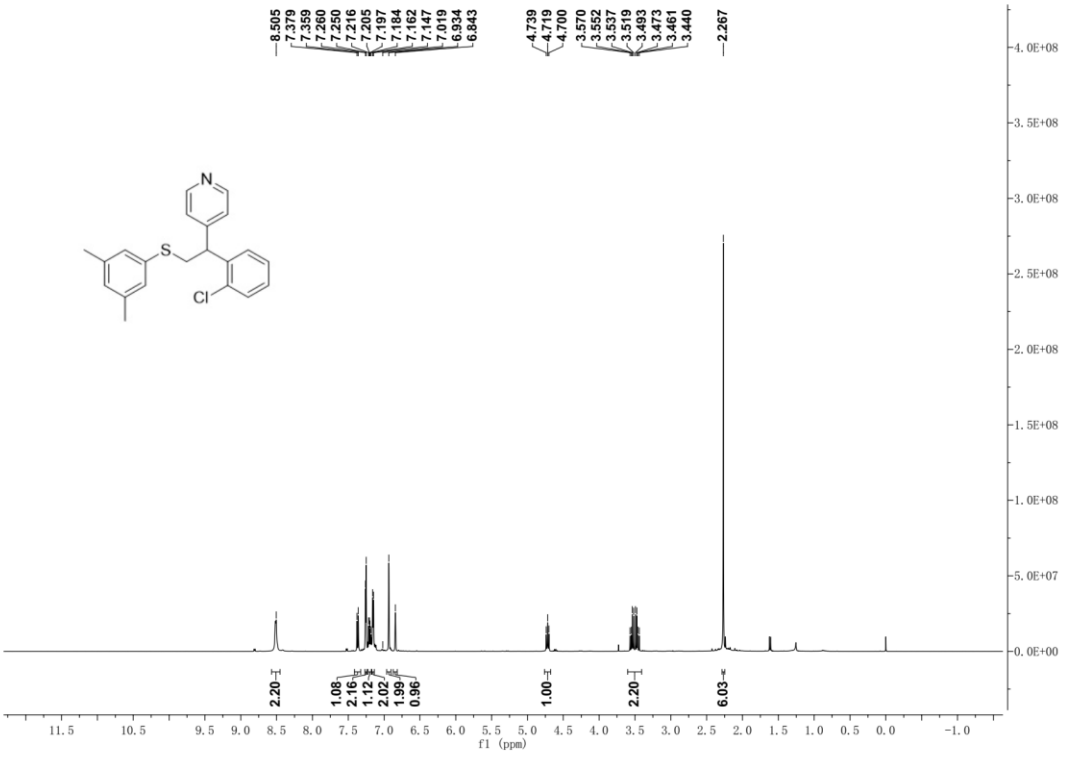
^{13}C NMR of compound 5e



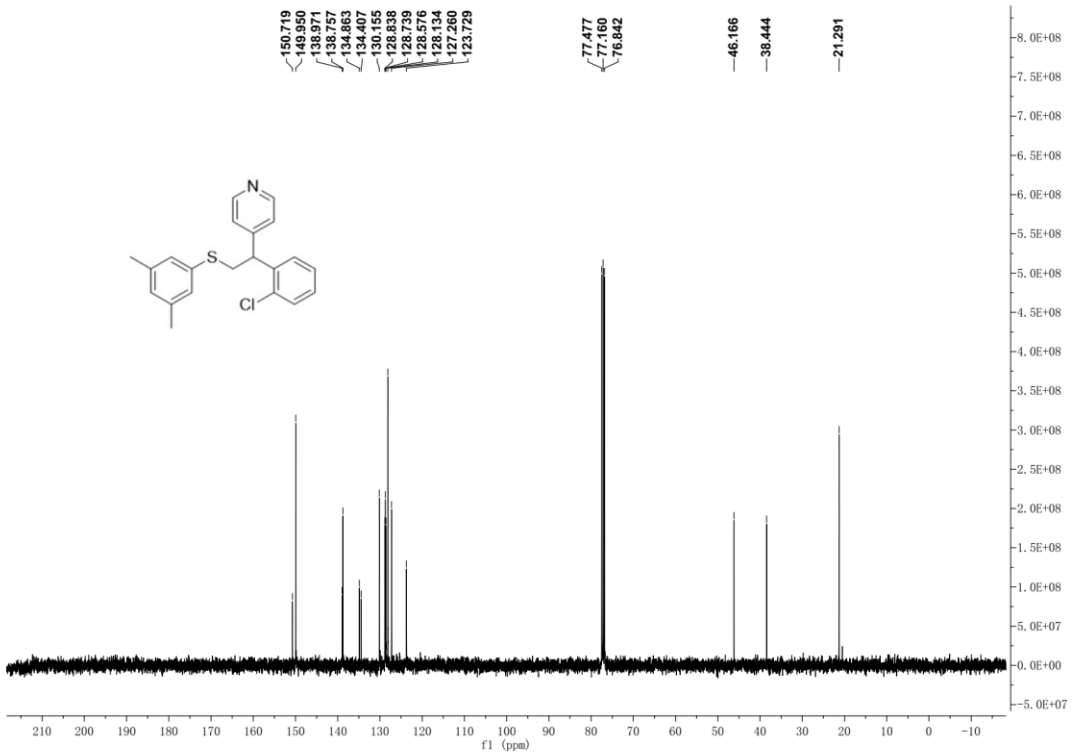
^{1}H NMR of compound 5f



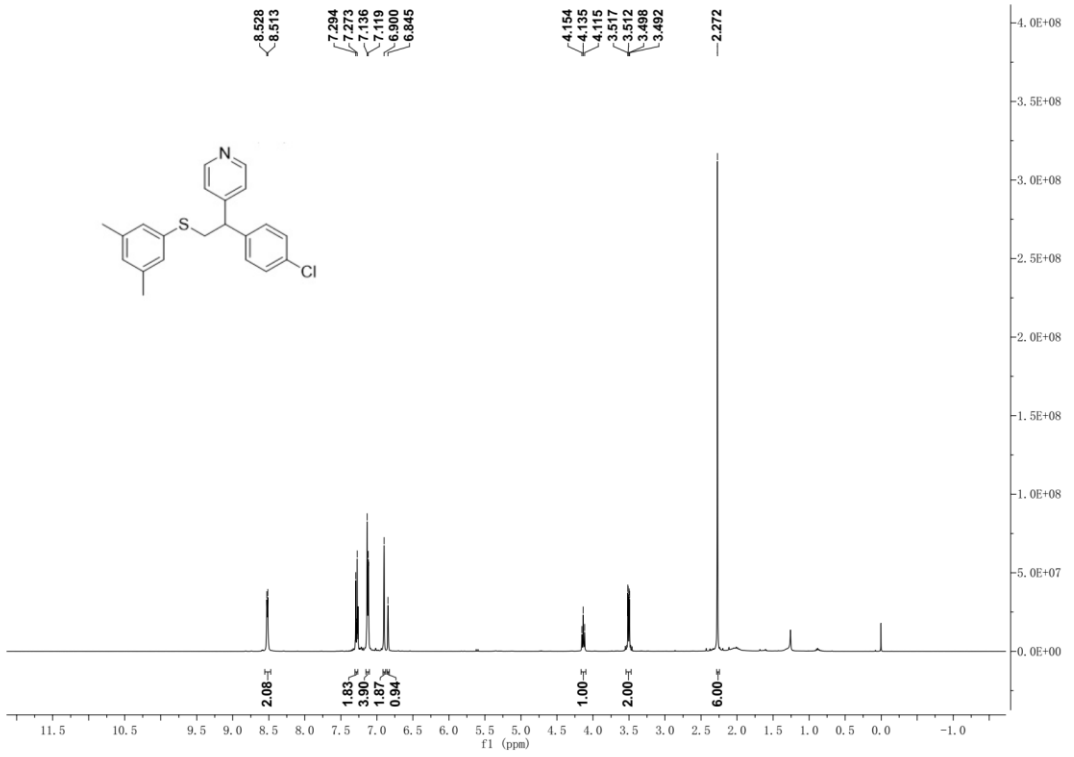
^{13}C NMR of compound 5f



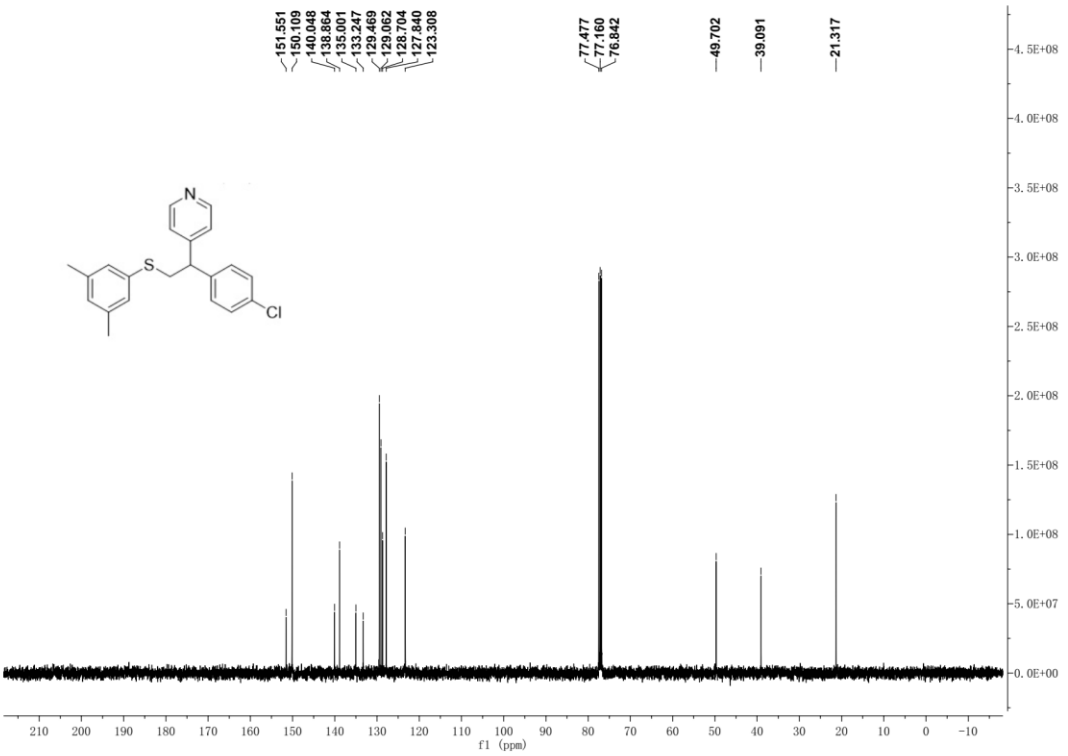
^{1}H NMR of compound 5g



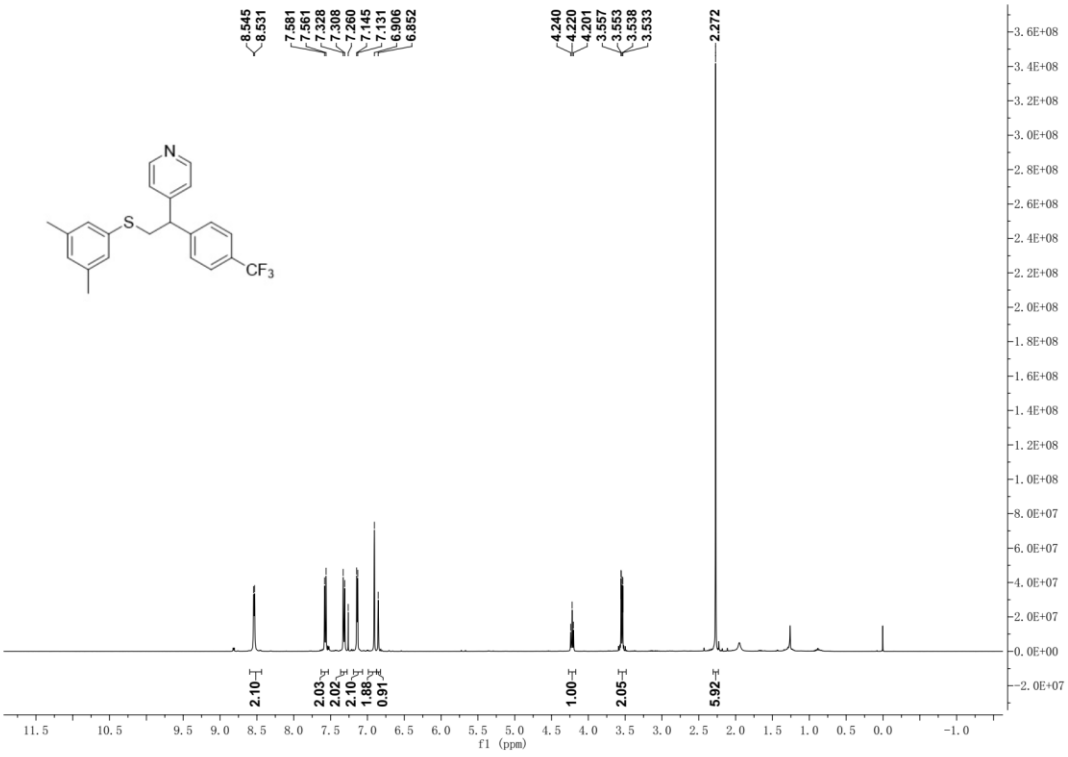
^{13}C NMR of compound 5g



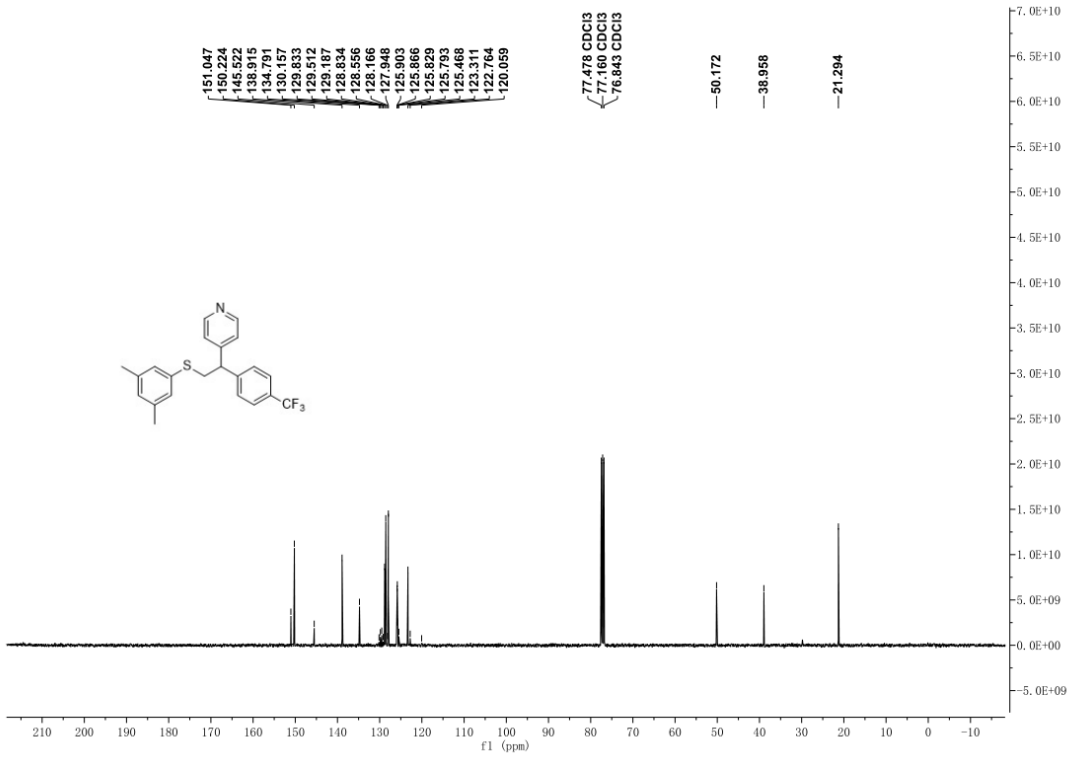
^{1}H NMR of compound 5h



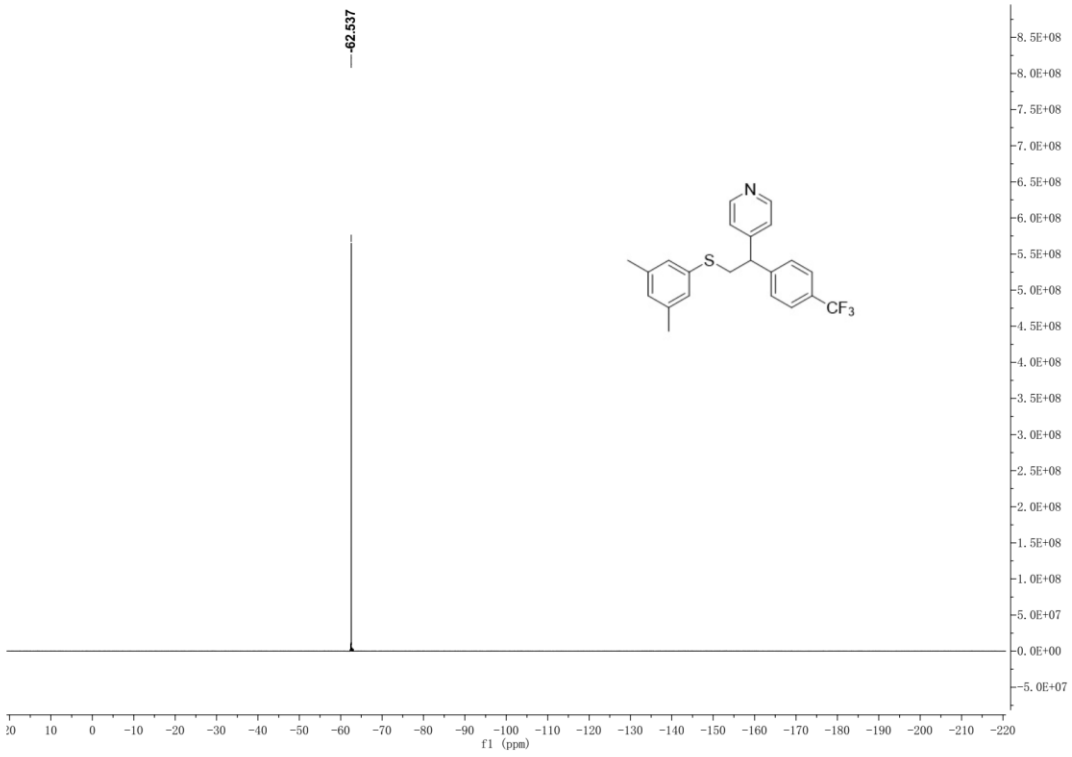
^{13}C NMR of compound 5h



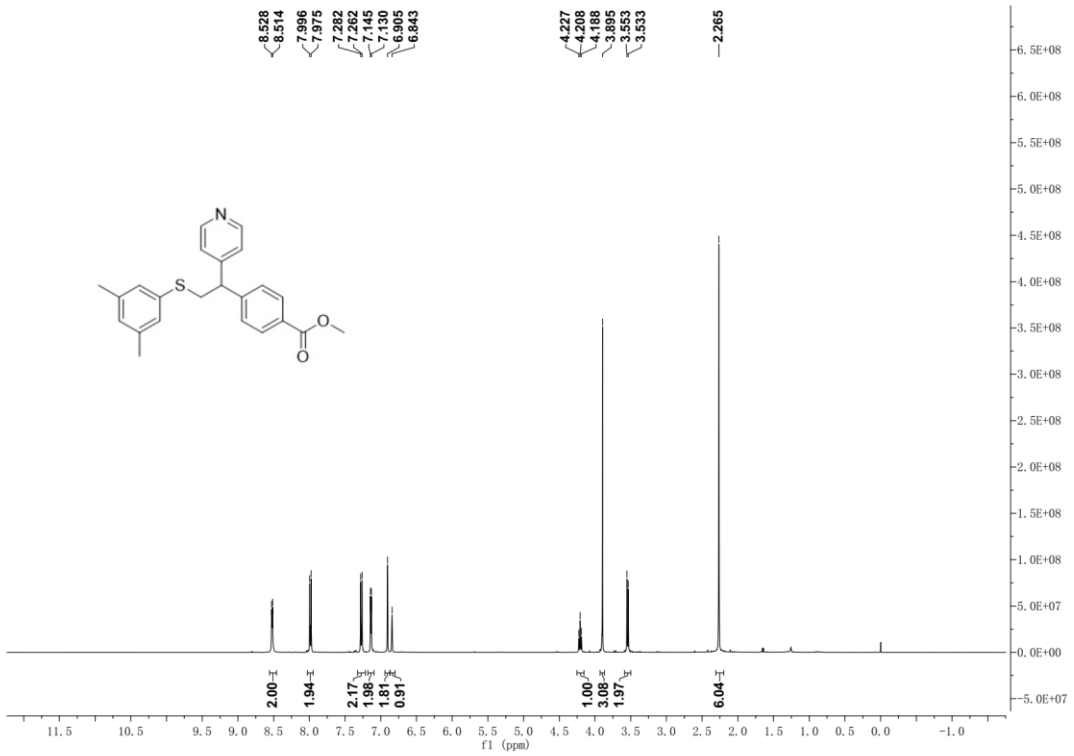
^{1}H NMR of compound 5i



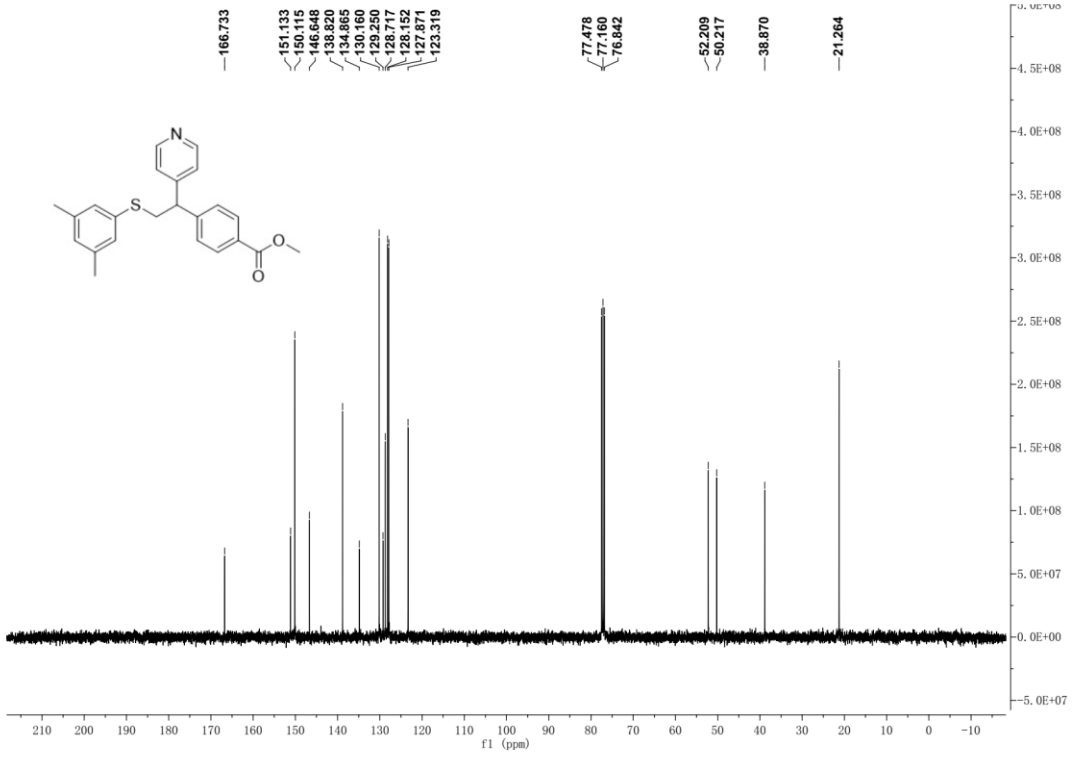
^{13}C NMR of compound 5i



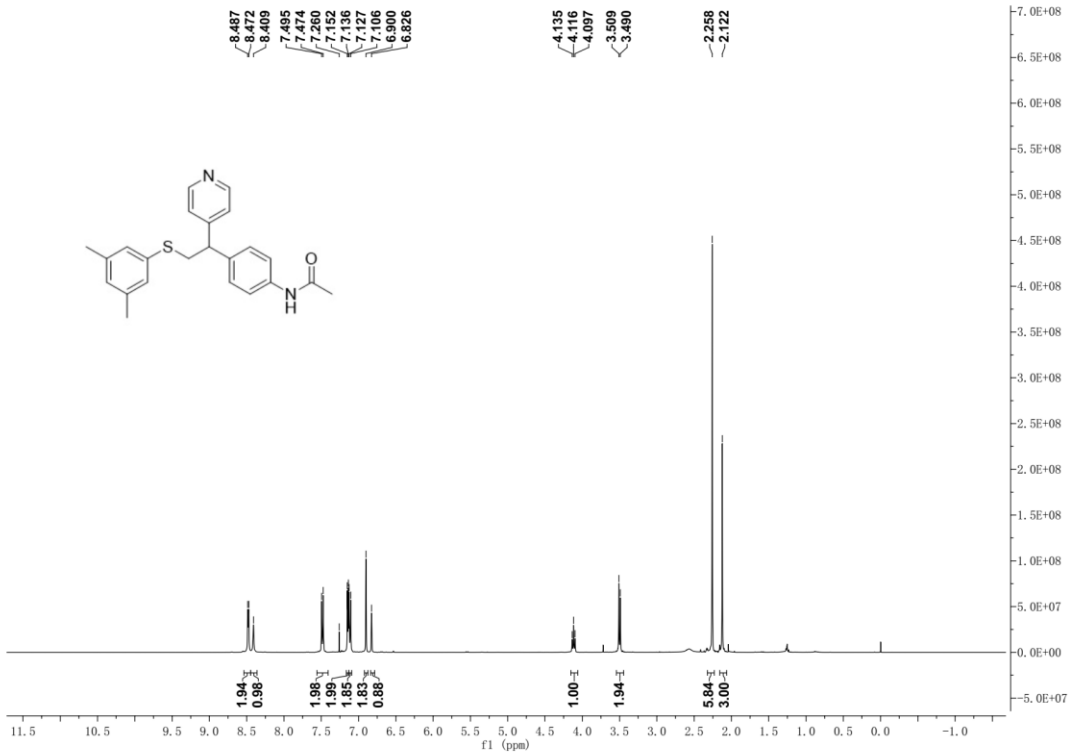
^{19}F NMR of compound 5i



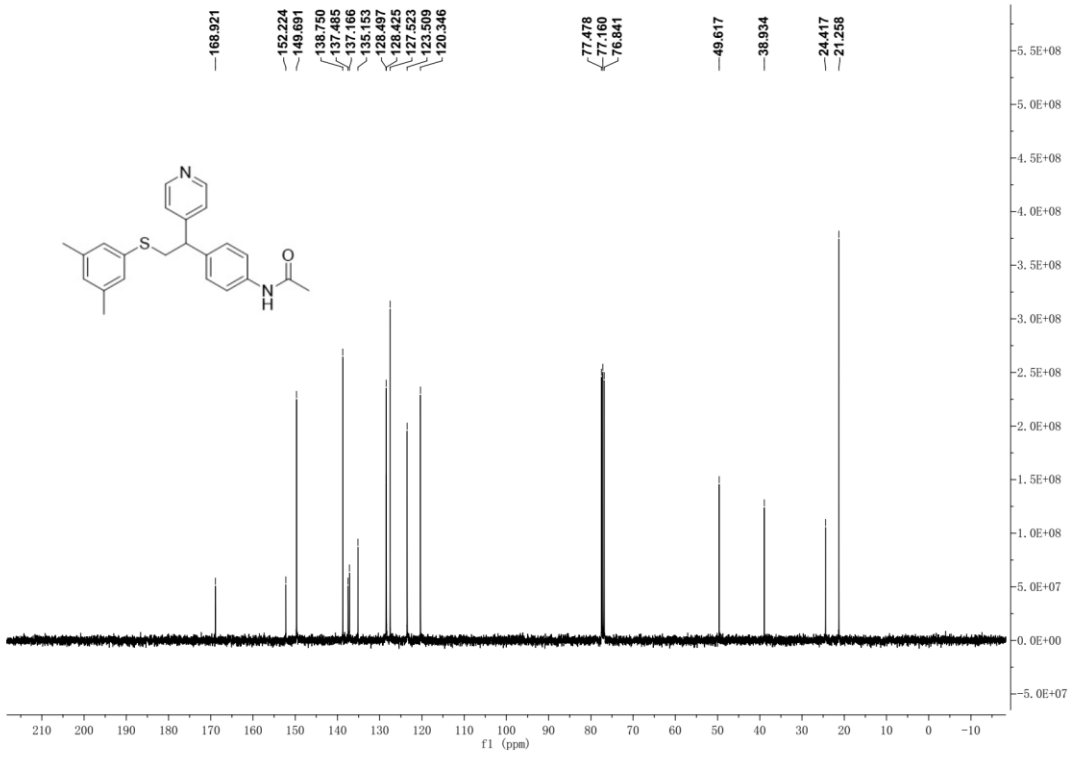
^{1}H NMR of compound 5j



^{13}C NMR of compound 5j



^{1}H NMR of compound 5k



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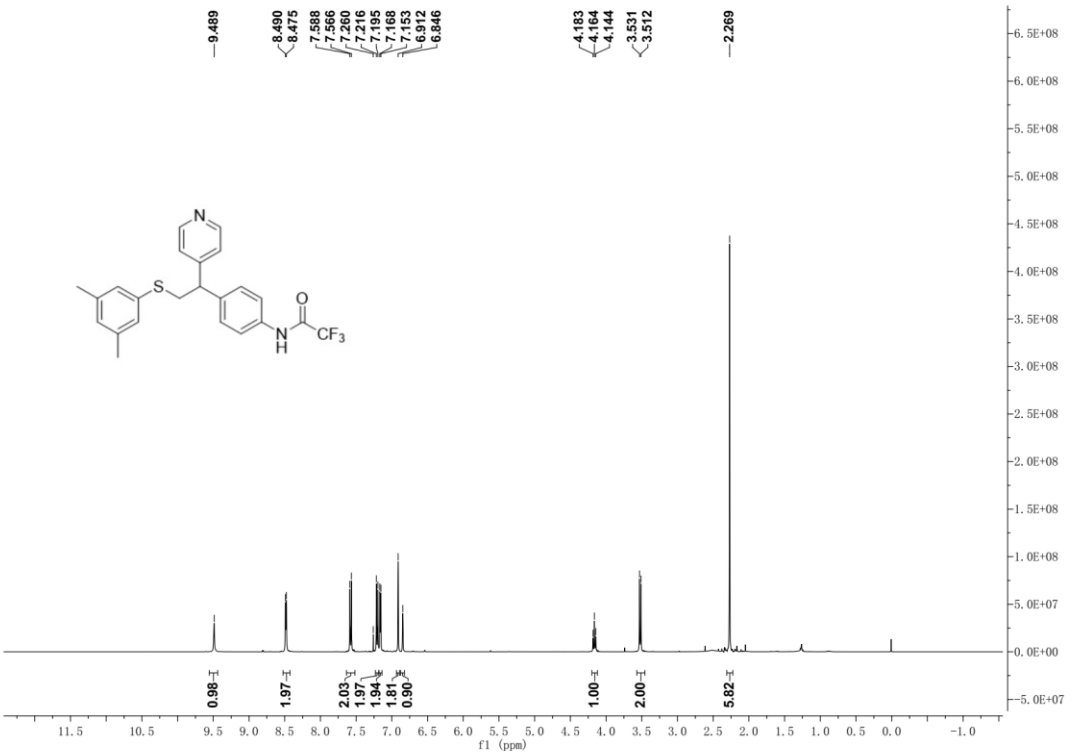
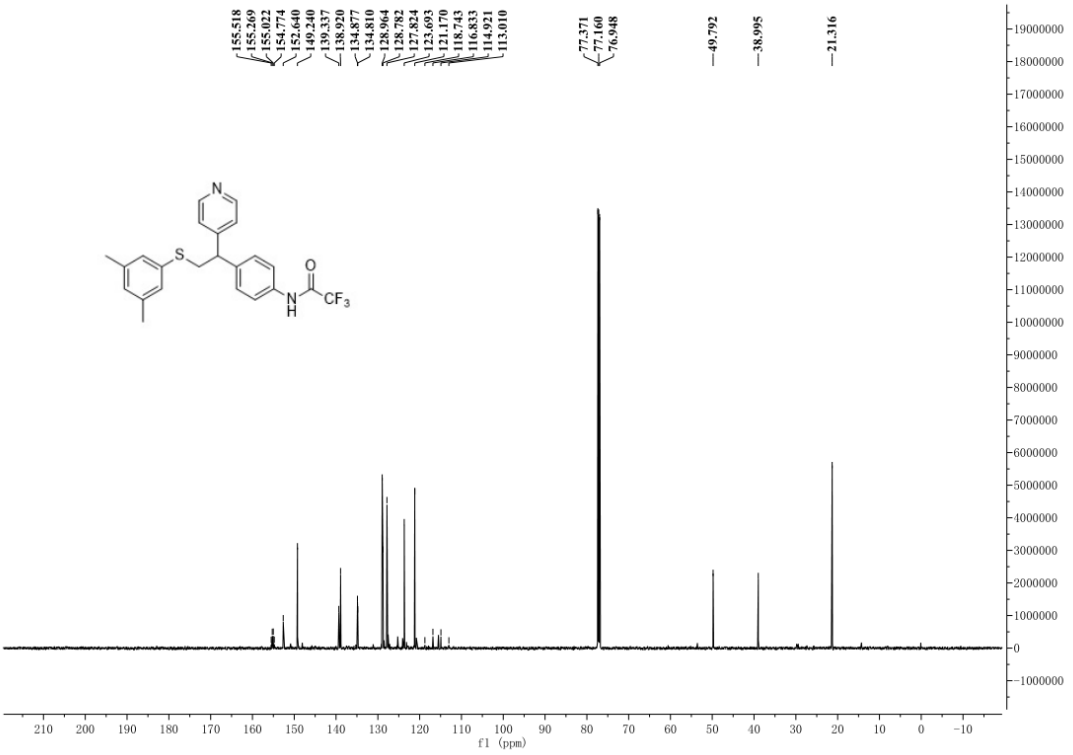
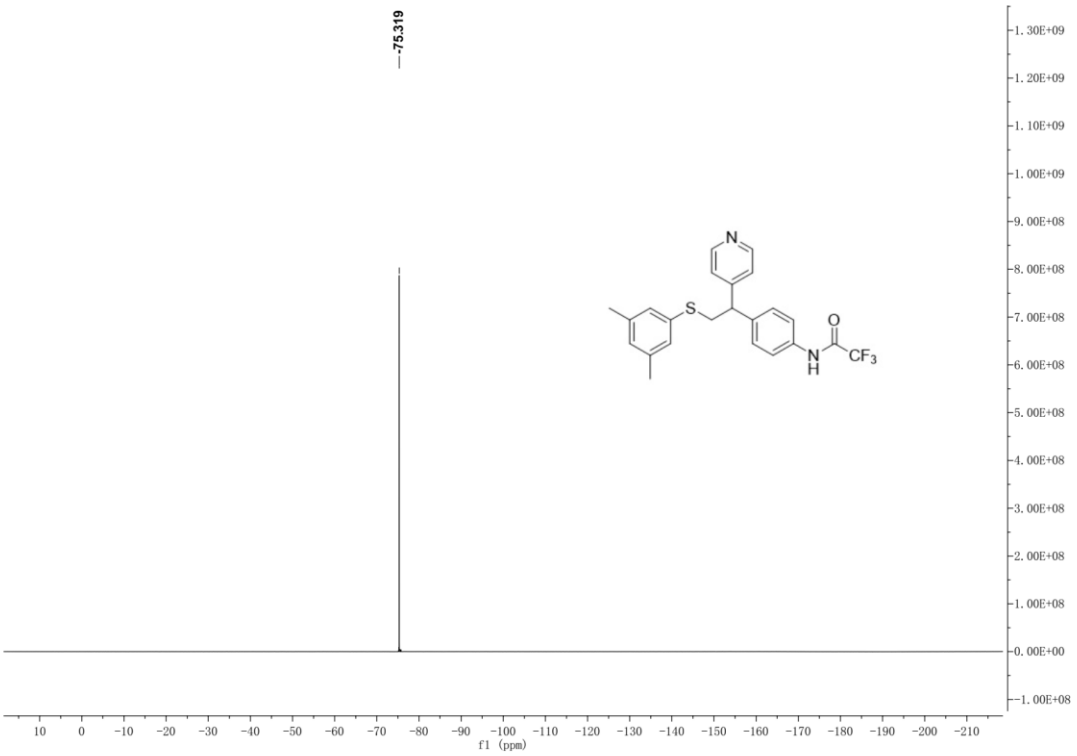


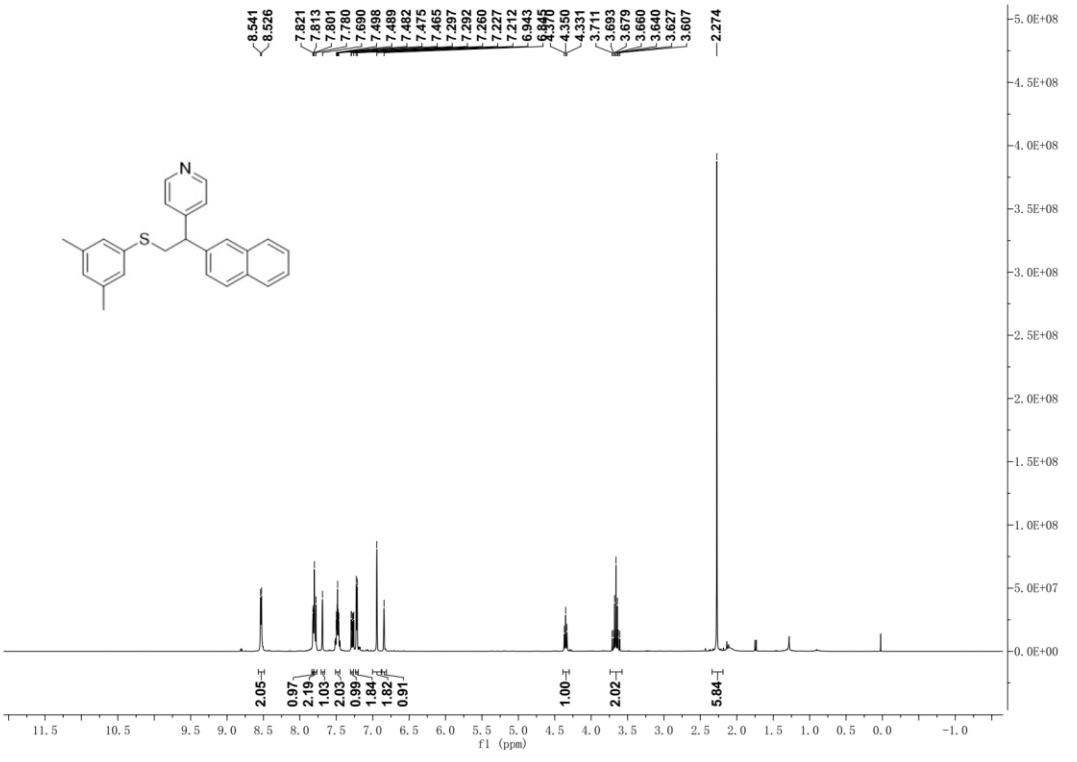
^{1}H NMR of compound 5l



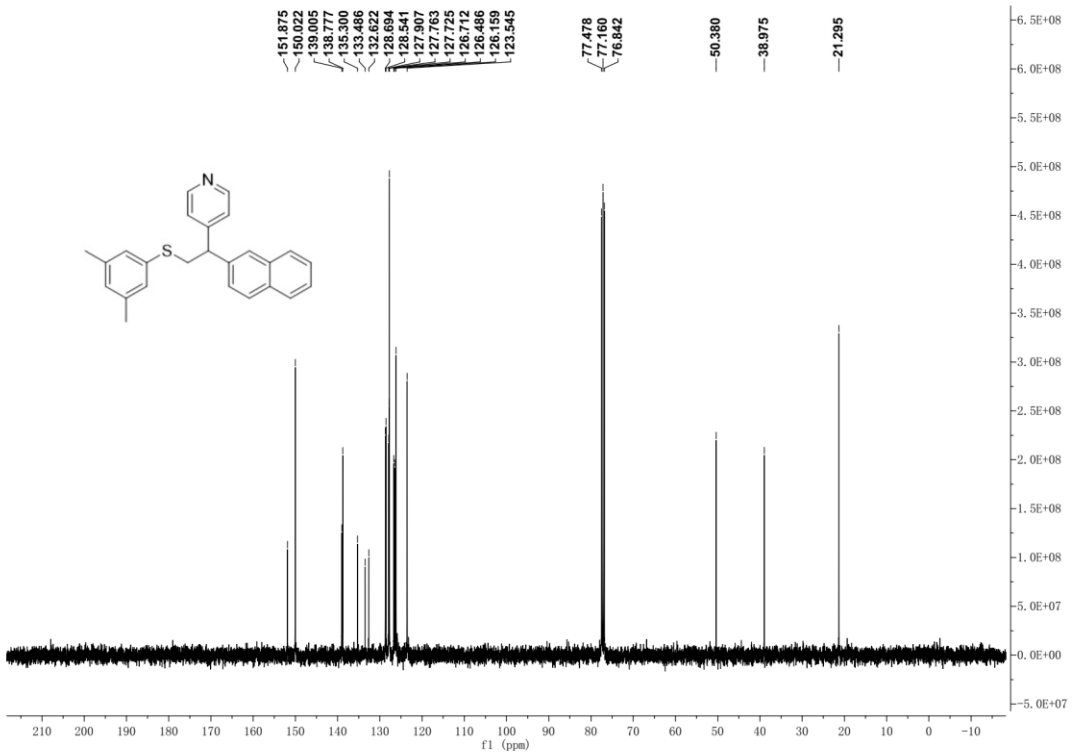
^{13}C NMR of compound 5l



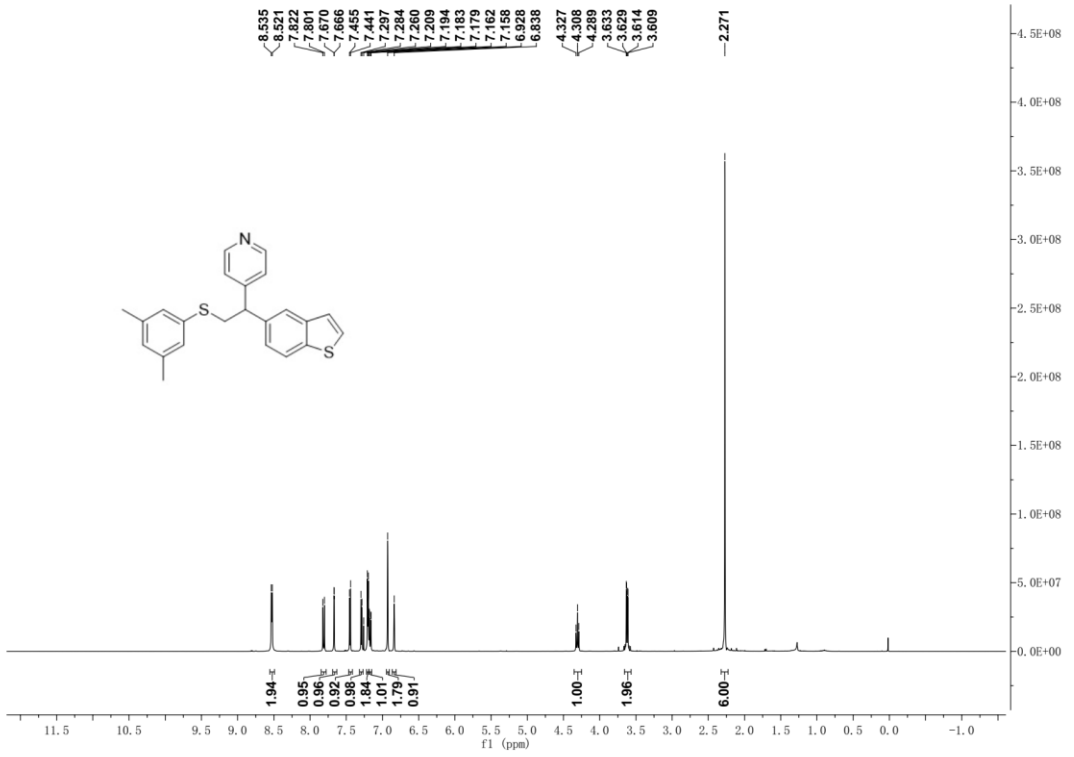
^{19}F NMR of compound 5l



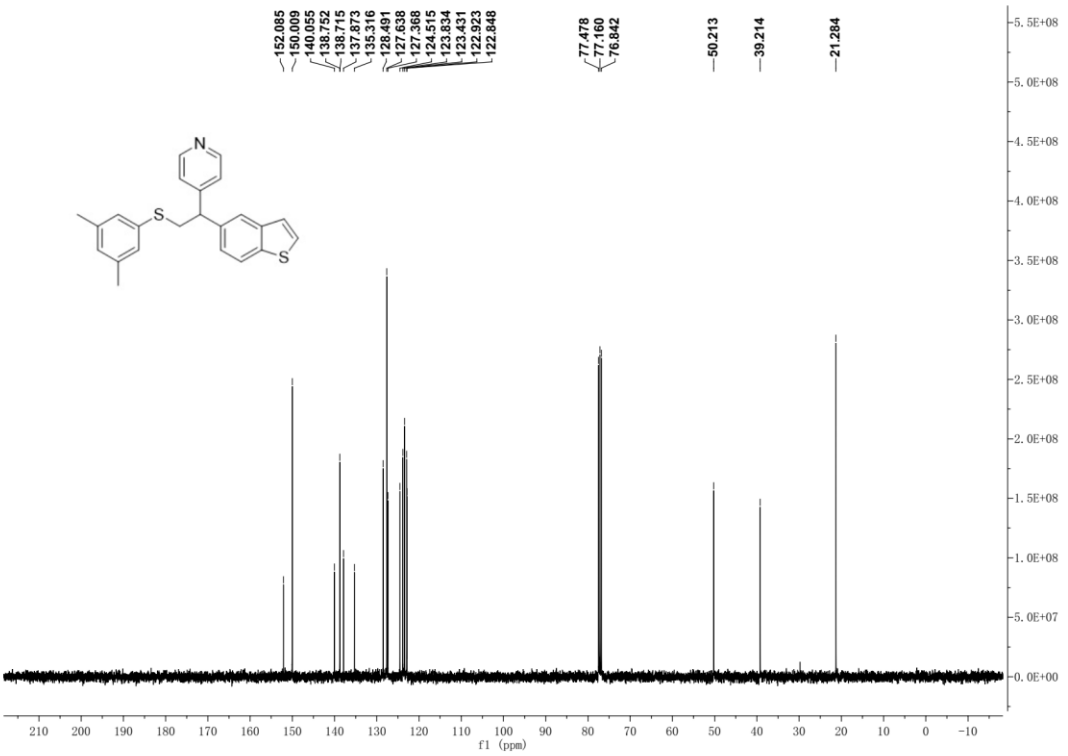
^{1}H NMR of compound 5m



^{13}C NMR of compound 5m



^{1}H NMR of compound 5n



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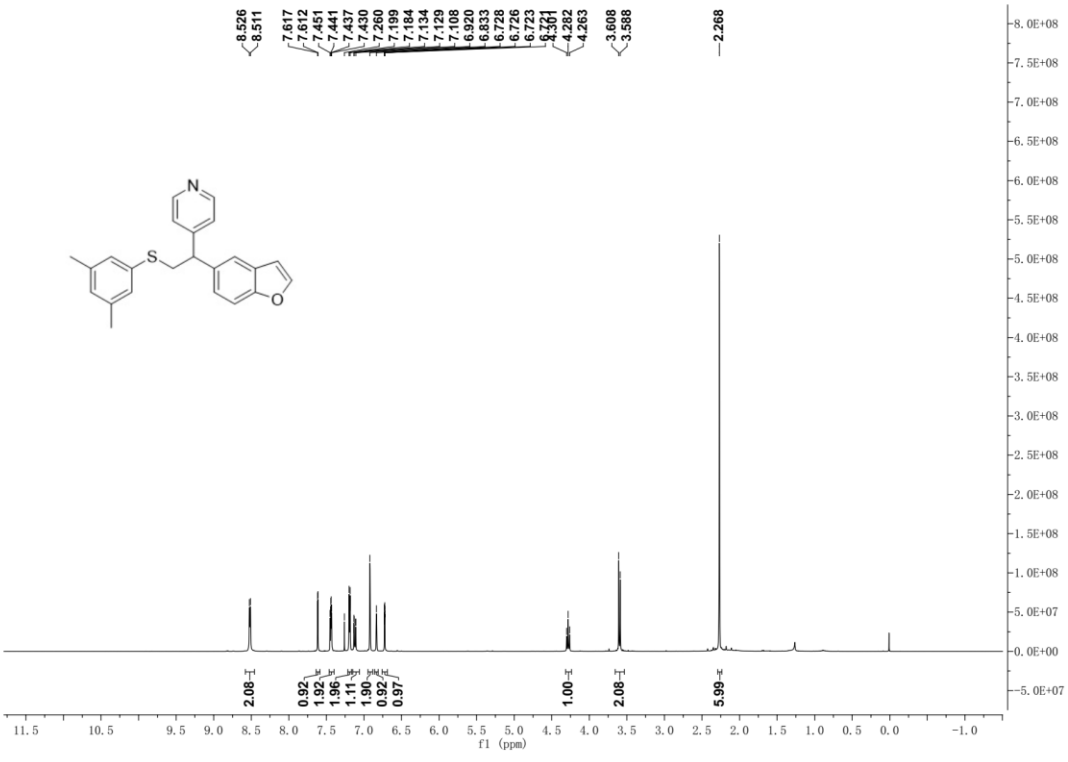
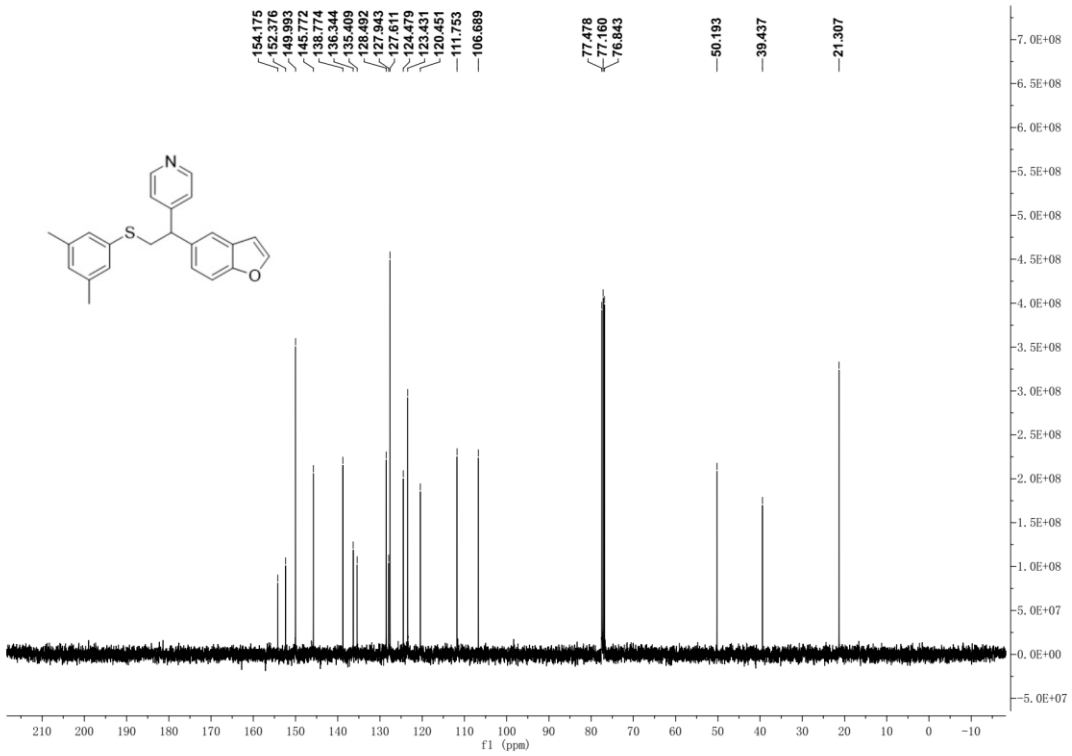


^{1}H NMR of compound 5o



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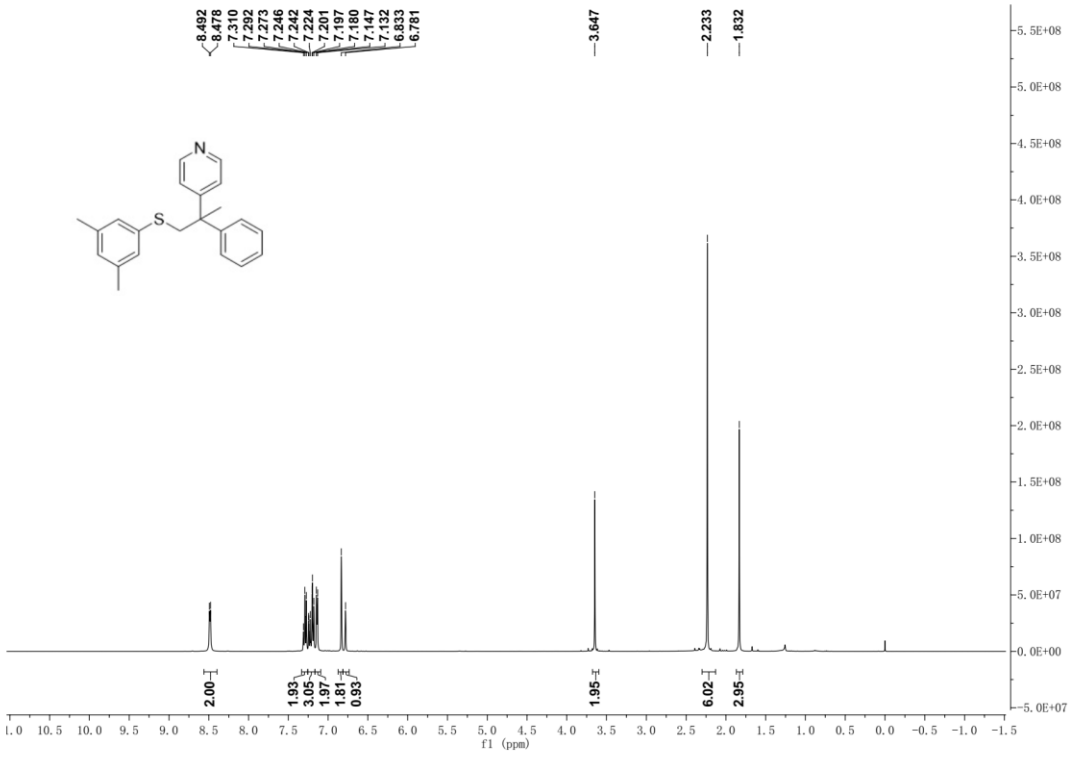

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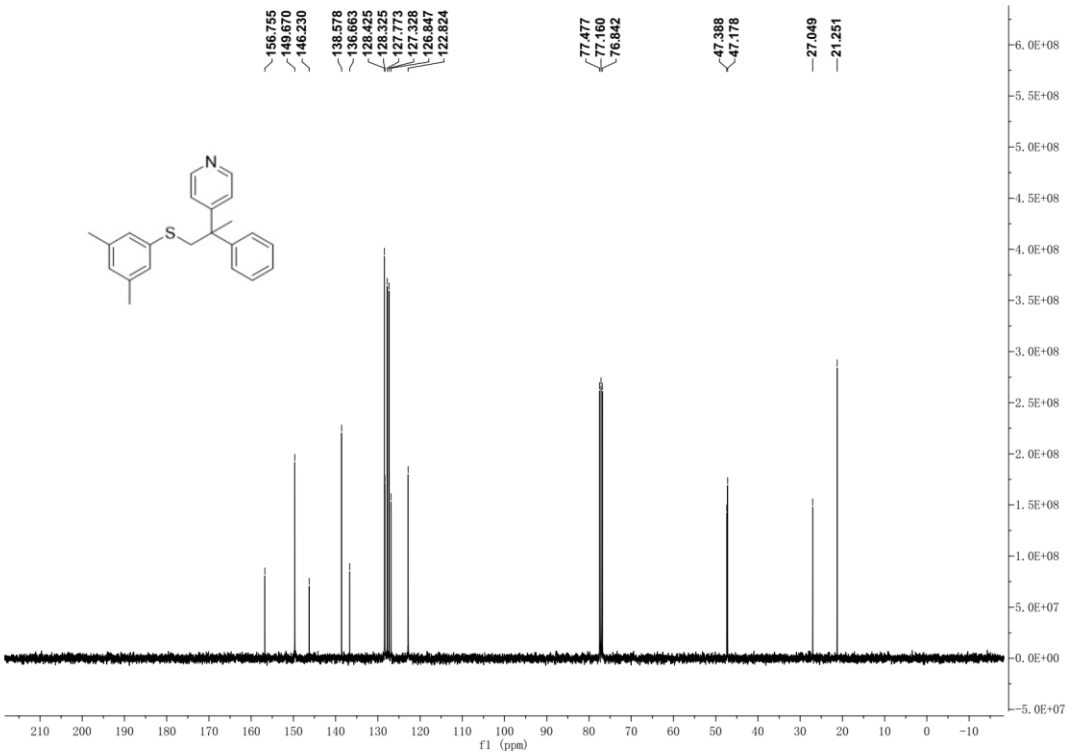
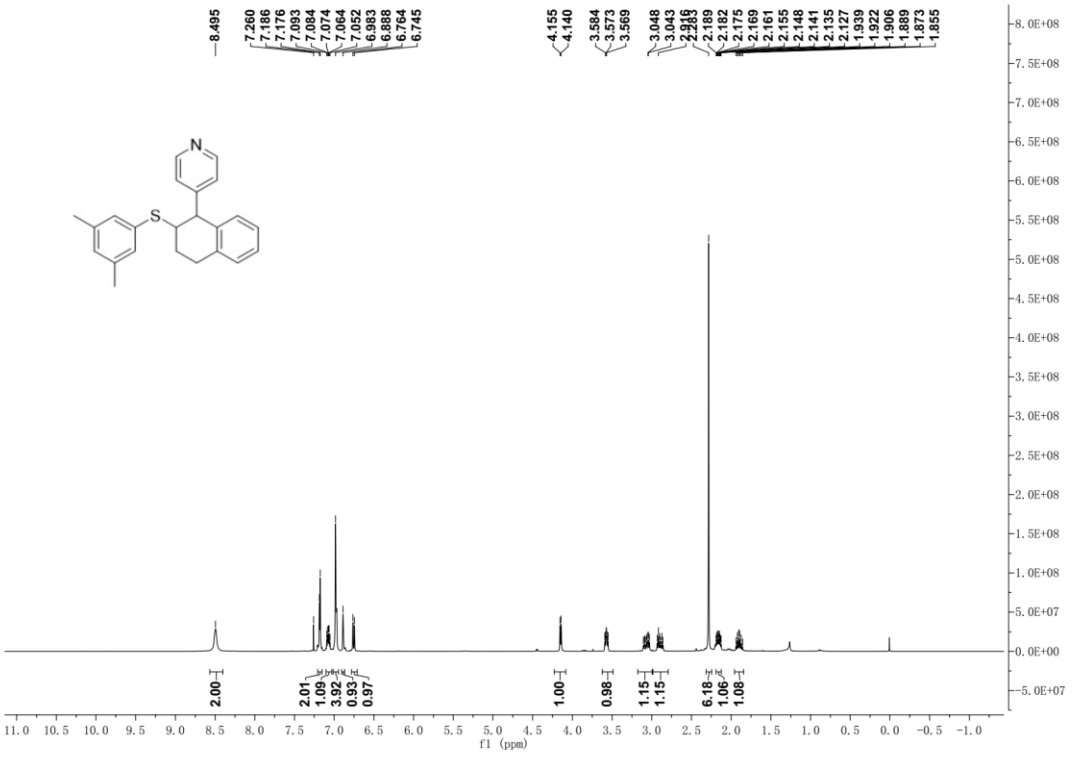
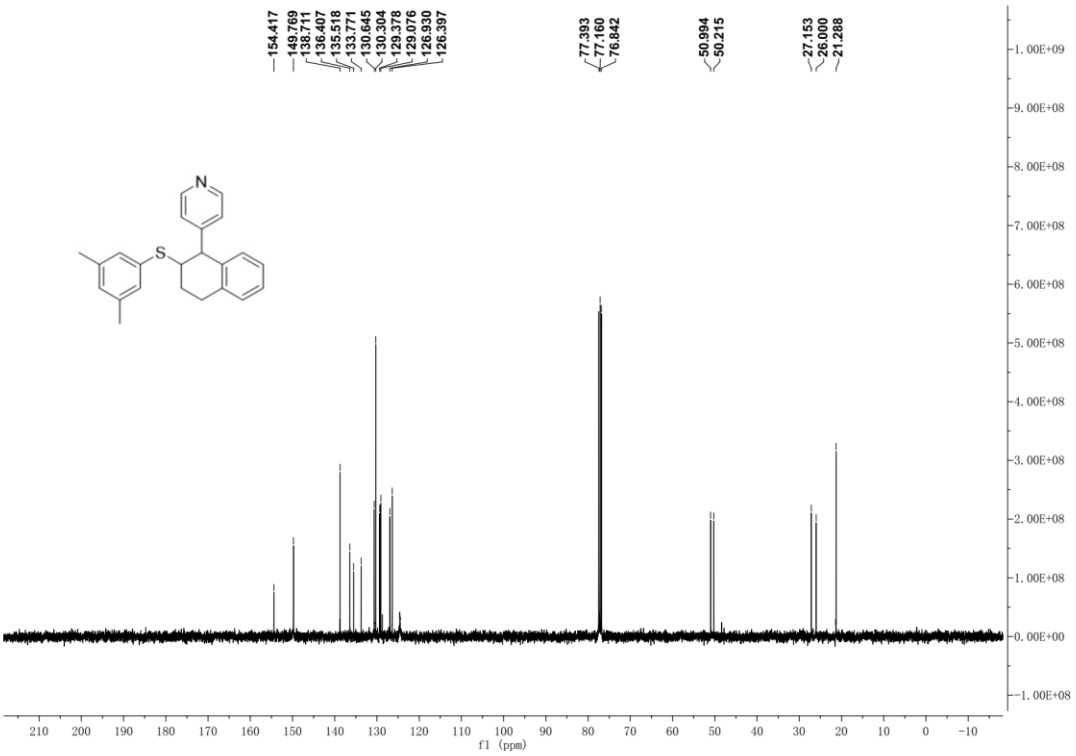


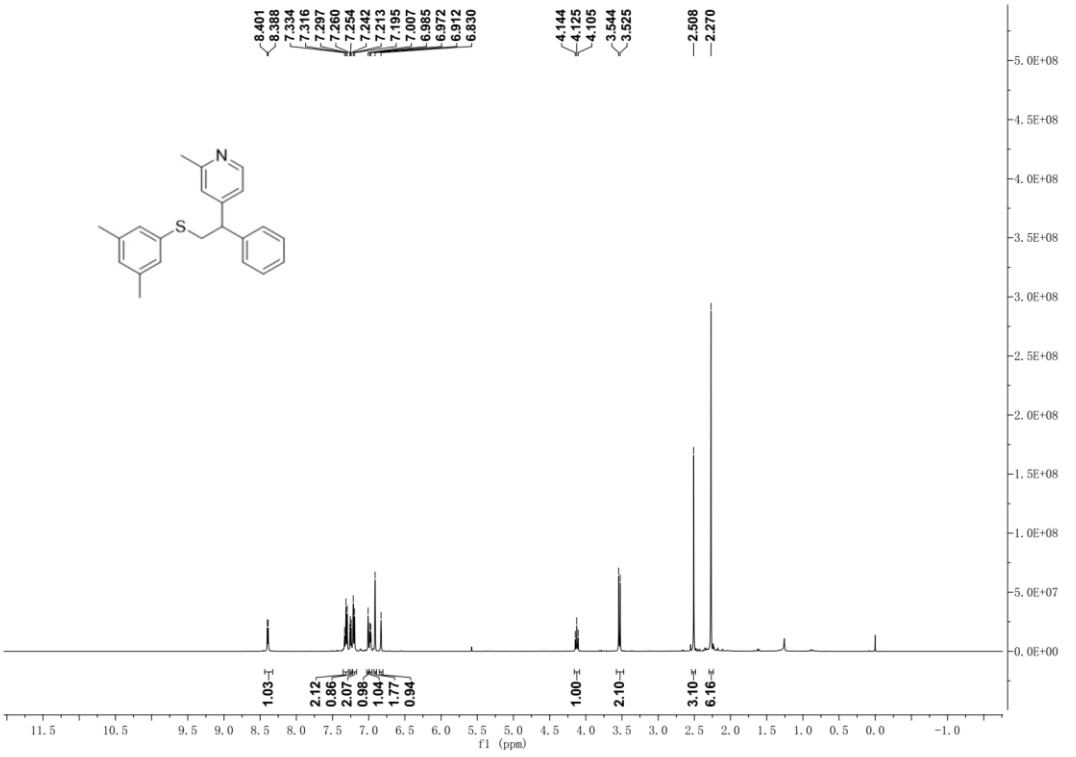
^{13}C NMR of compound 5p



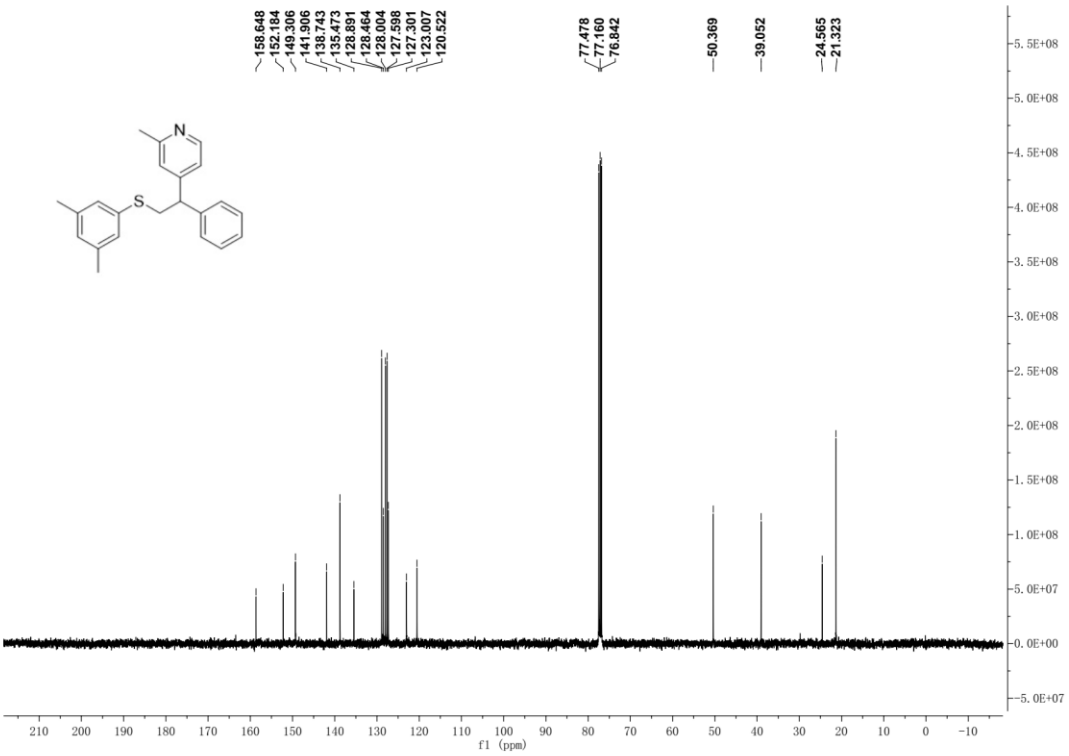
^{1}H NMR of compound 5q



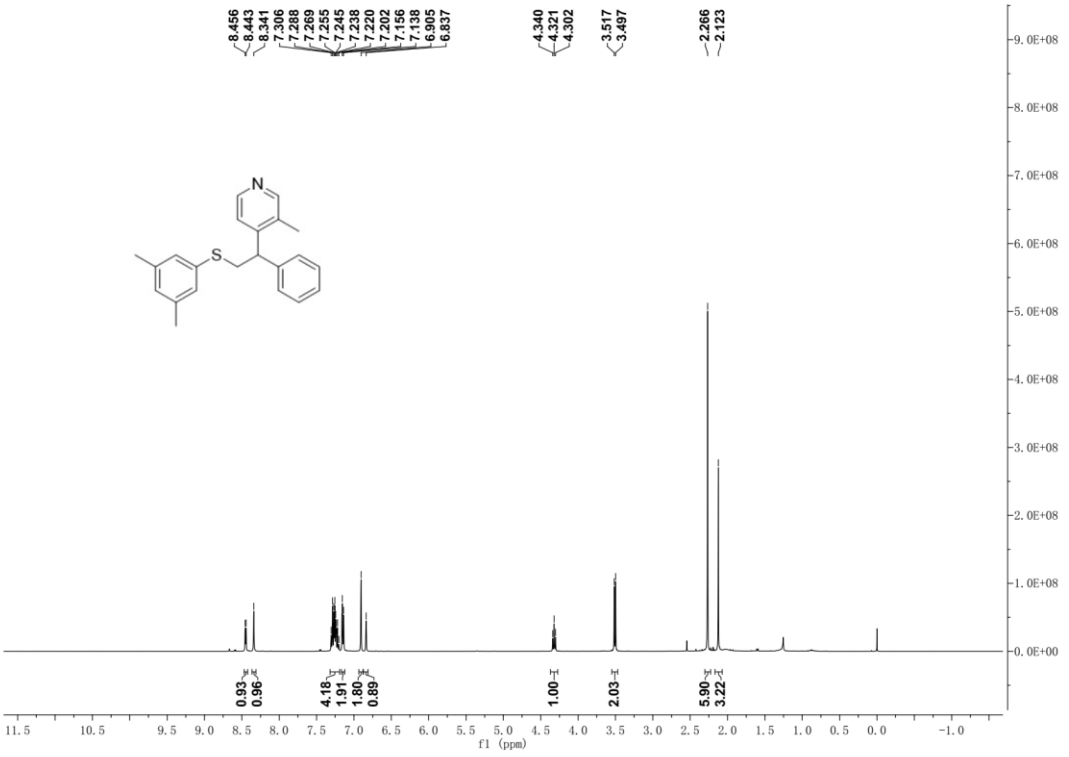
^{13}C NMR of compound 5q



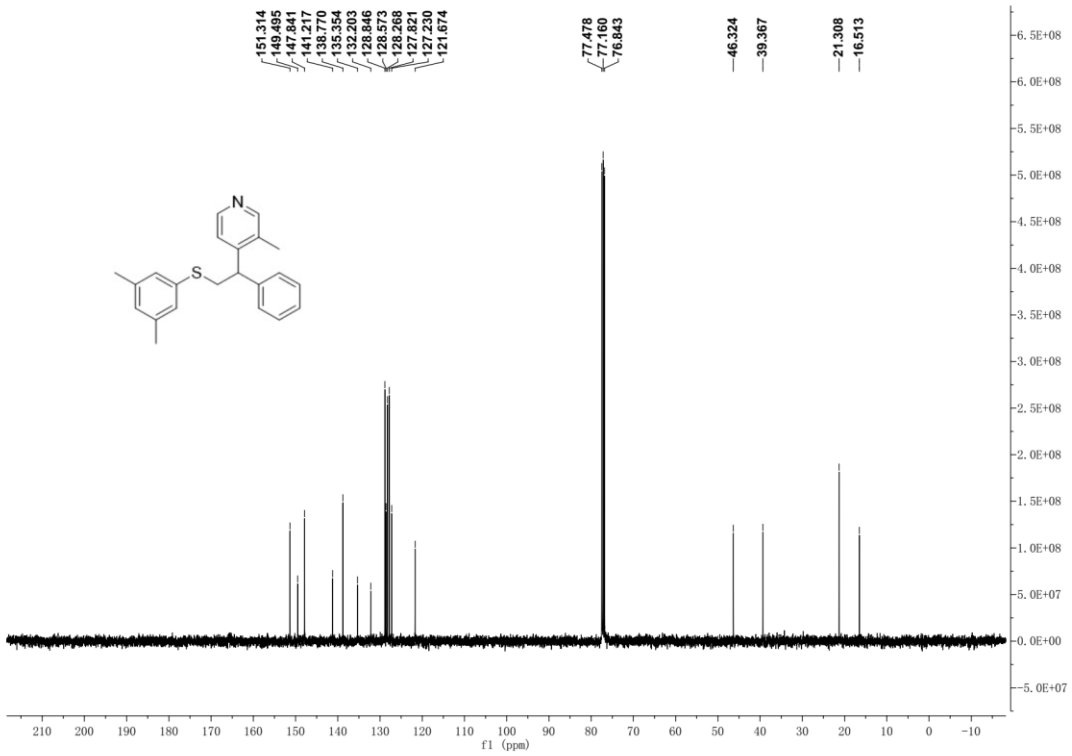
^{1}H NMR of compound 6a



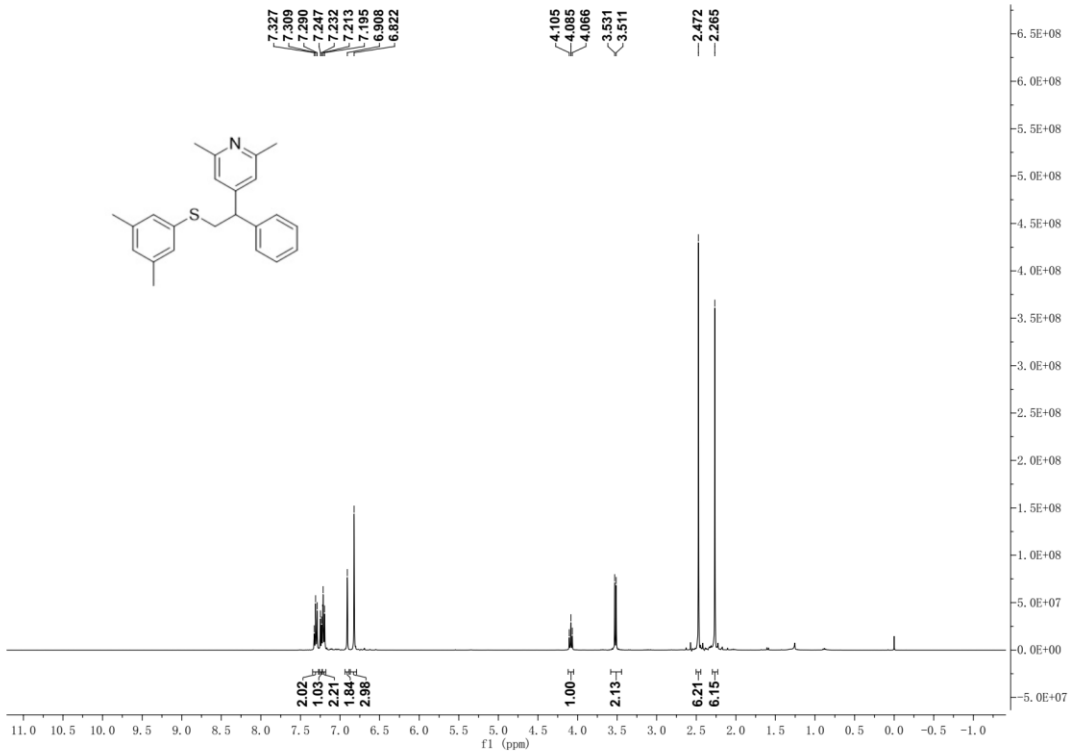
^{13}C NMR of compound 6a



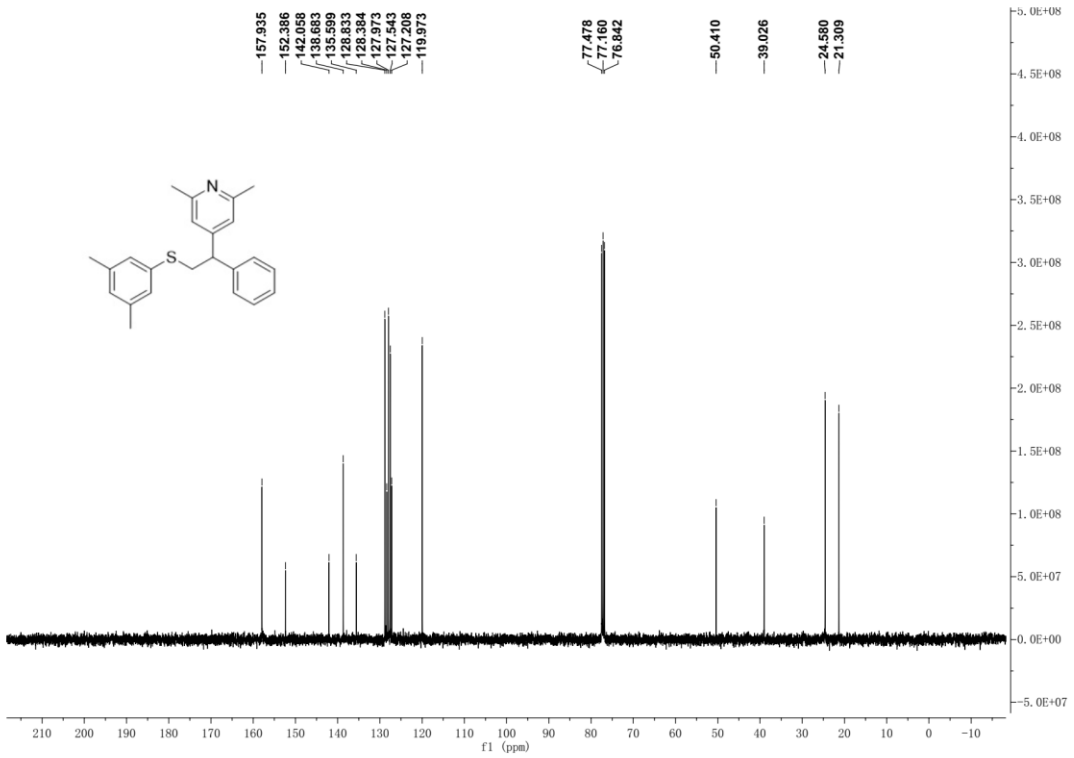
^{1}H NMR of compound 6b



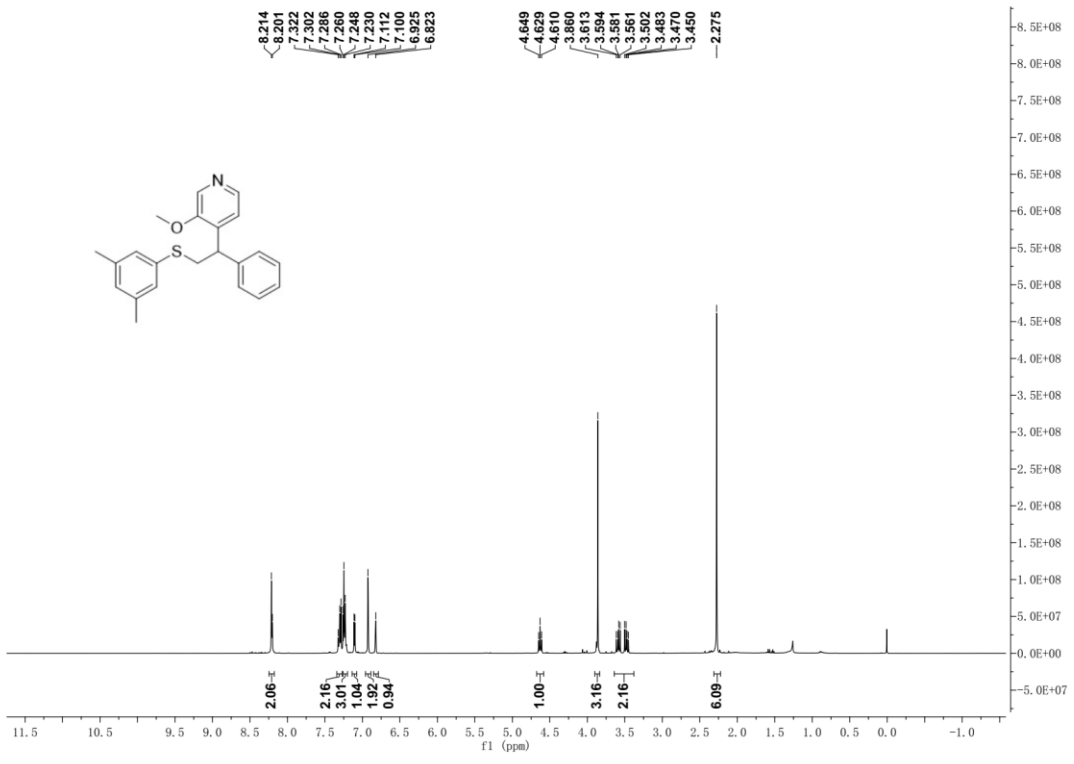
^{13}C NMR of compound 6b



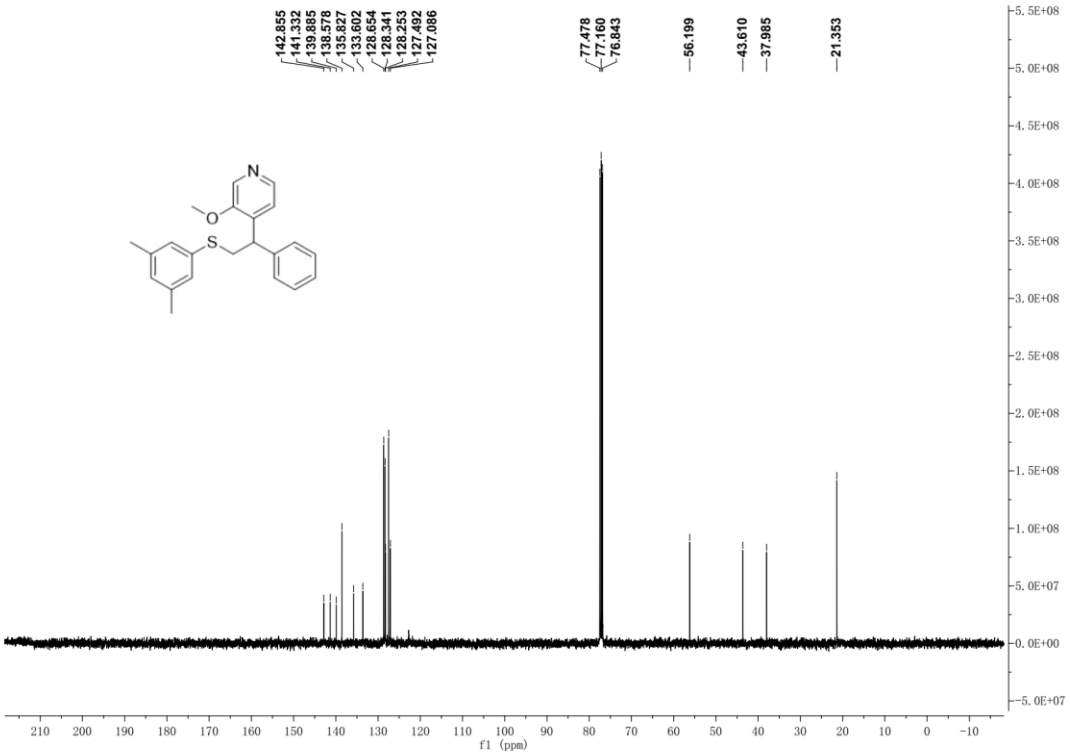
^{1}H NMR of compound 6c



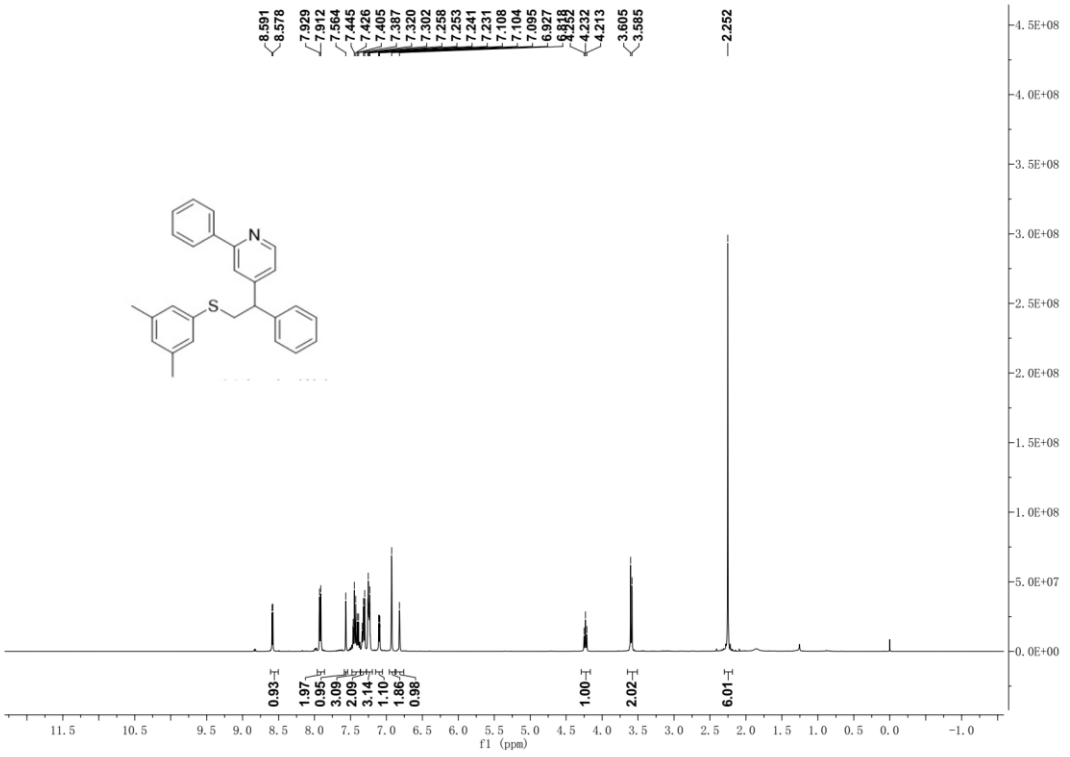
^{13}C NMR of compound 6c



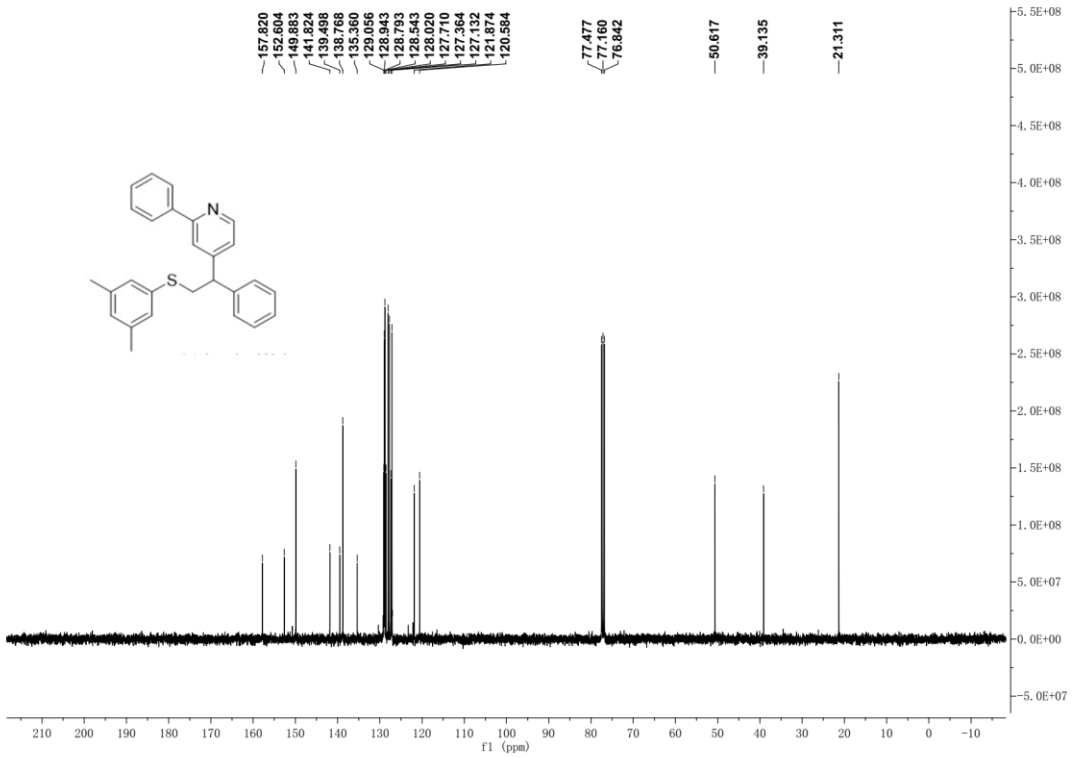
^{1}H NMR of compound 6d



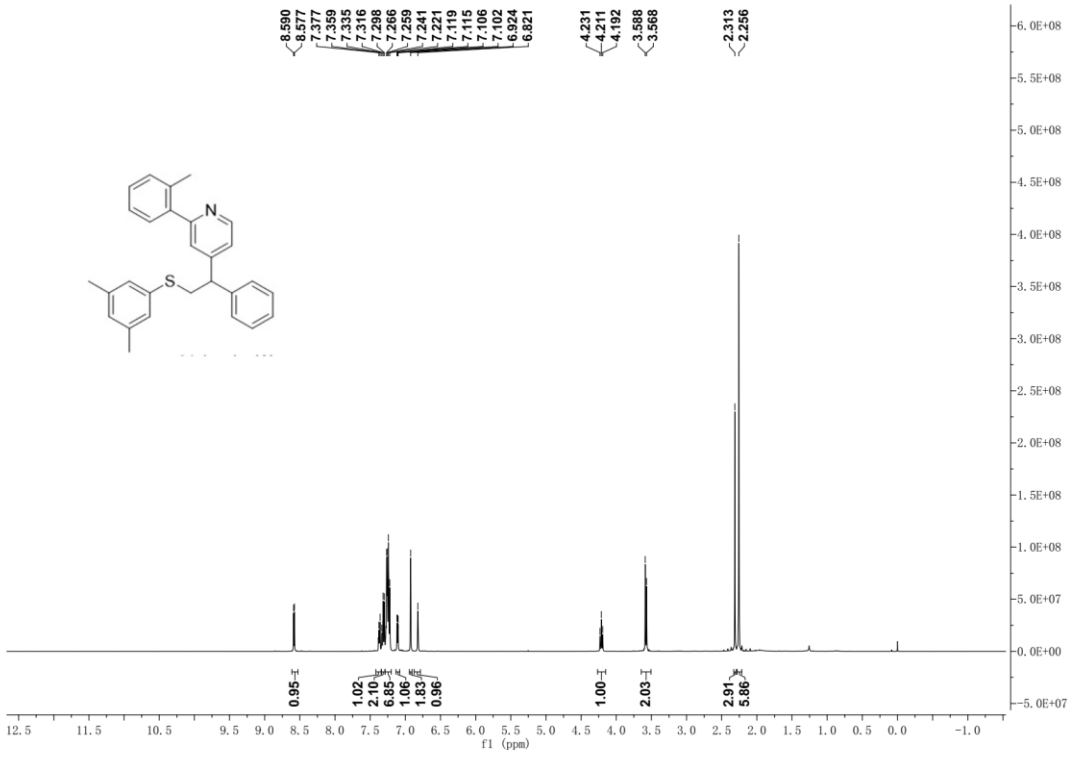
^{13}C NMR of compound 6d



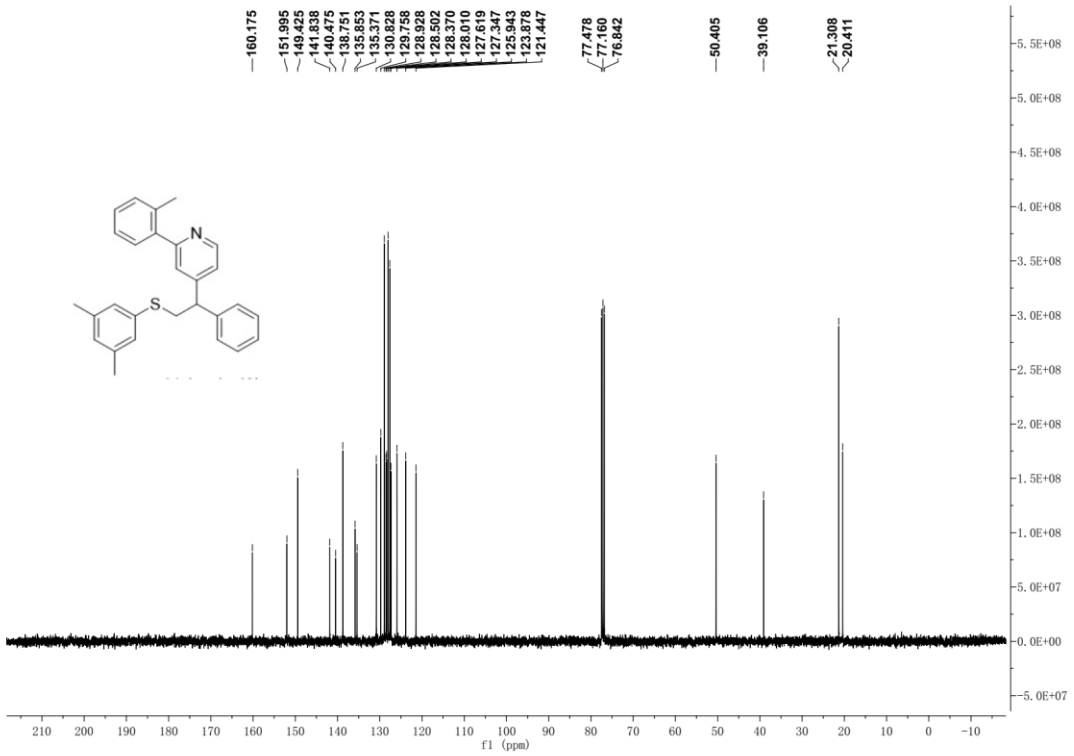
^{1}H NMR of compound 6e



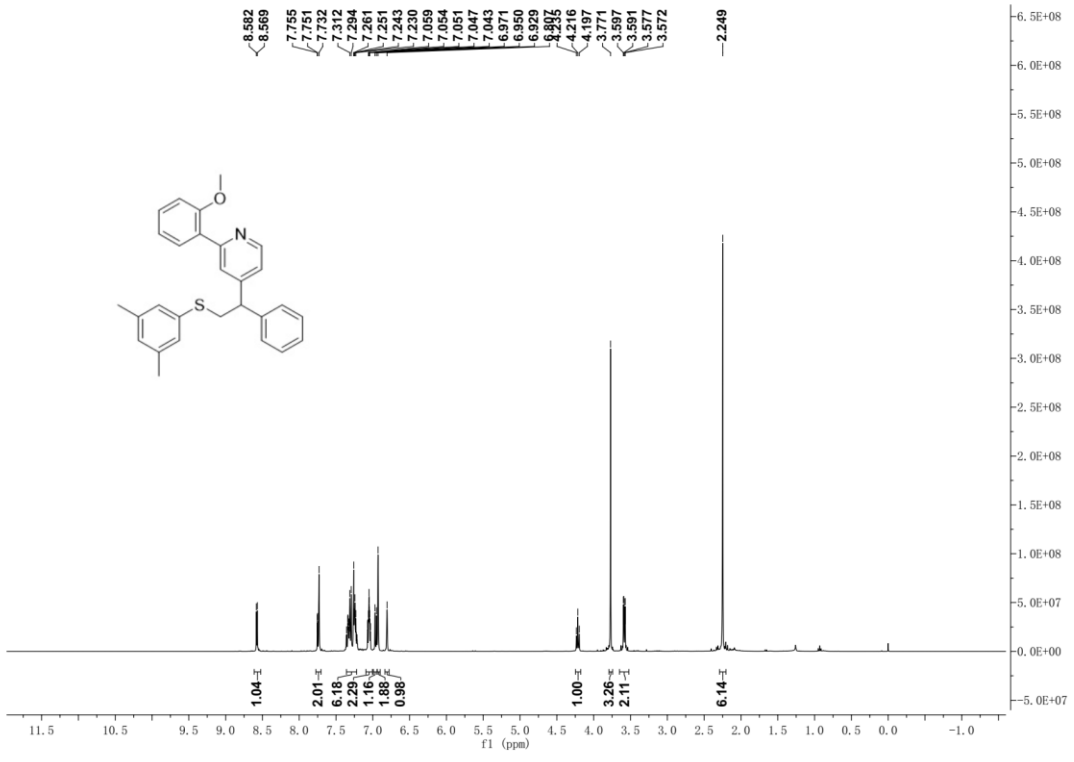
^{13}C NMR of compound 6e



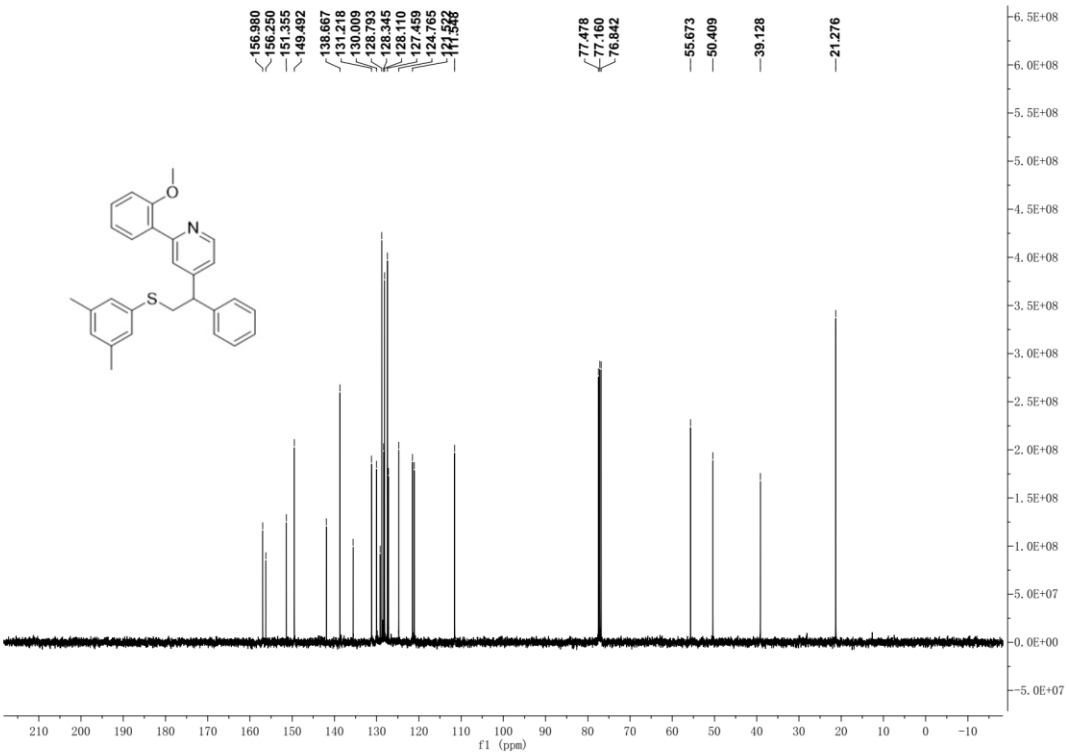
^{1}H NMR of compound 6f



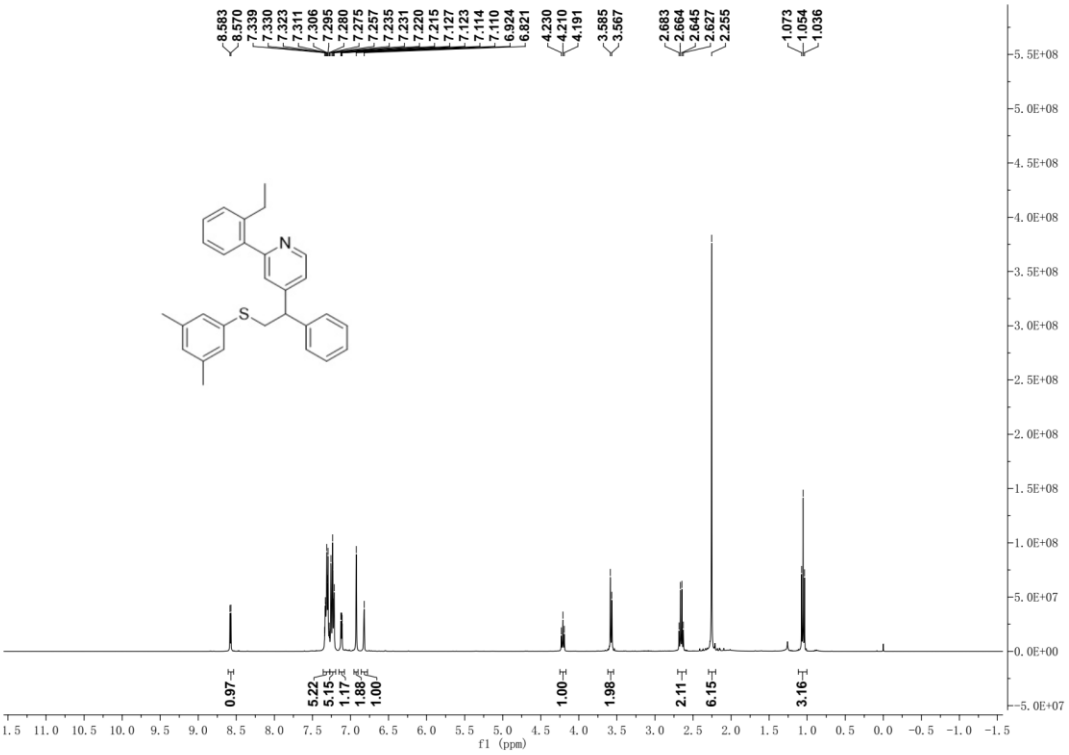
^{13}C NMR of compound 6f



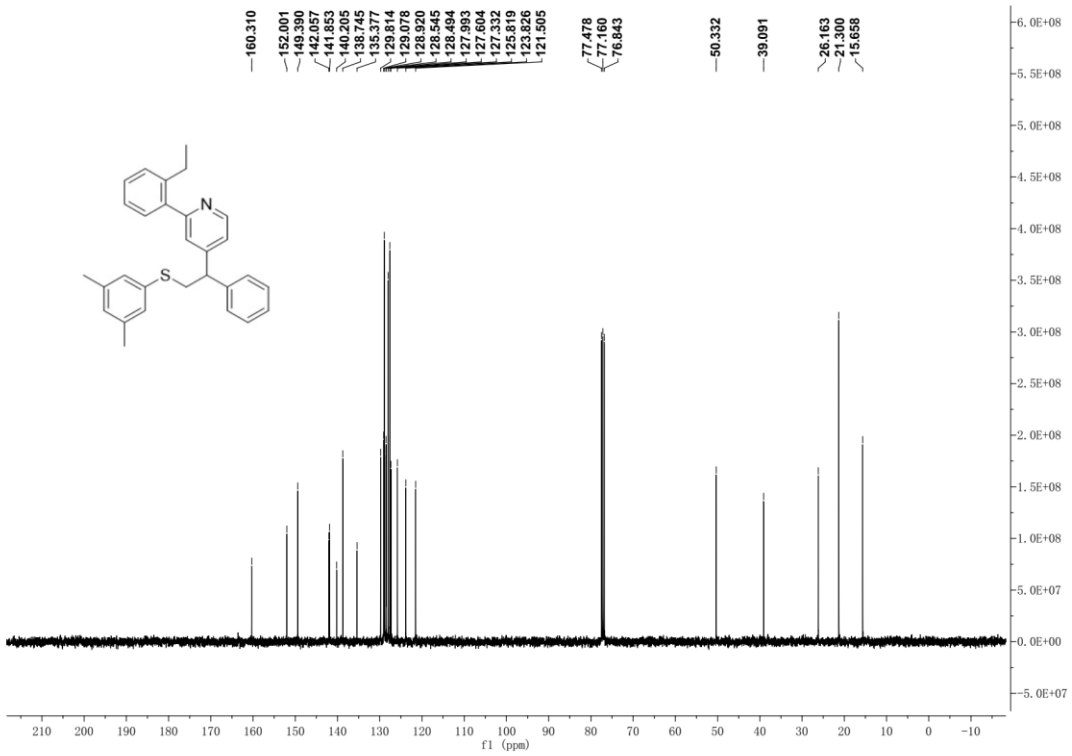
^{1}H NMR of compound 6g



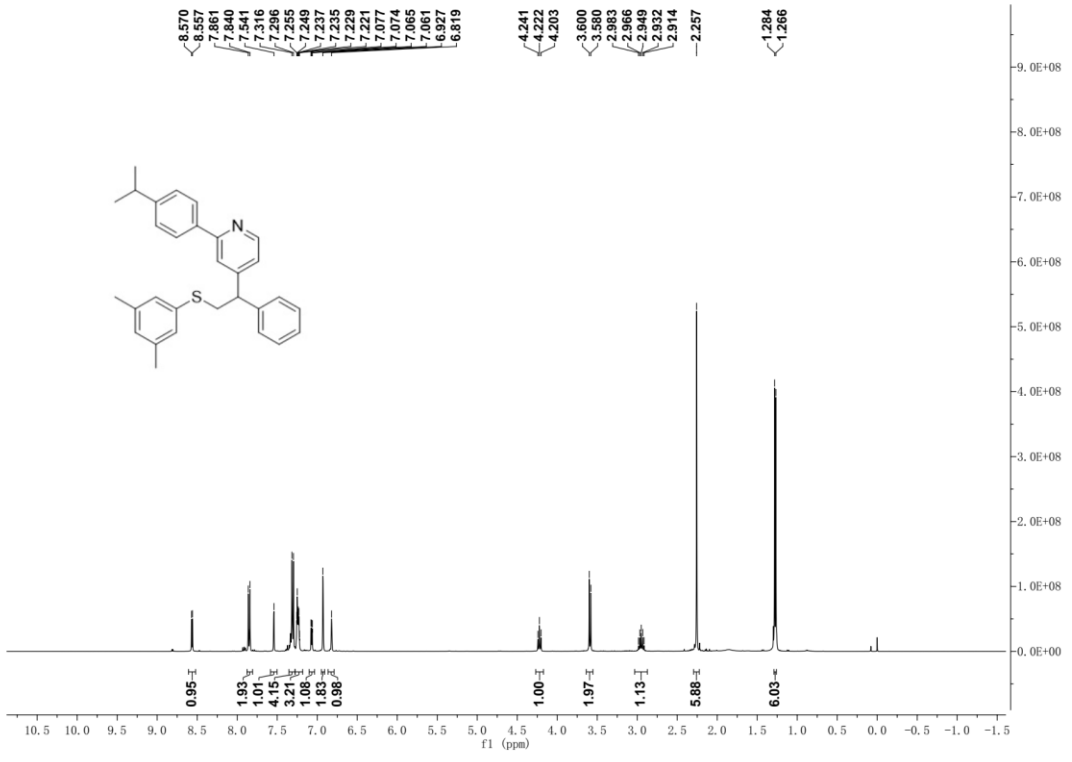
^{13}C NMR of compound 6g



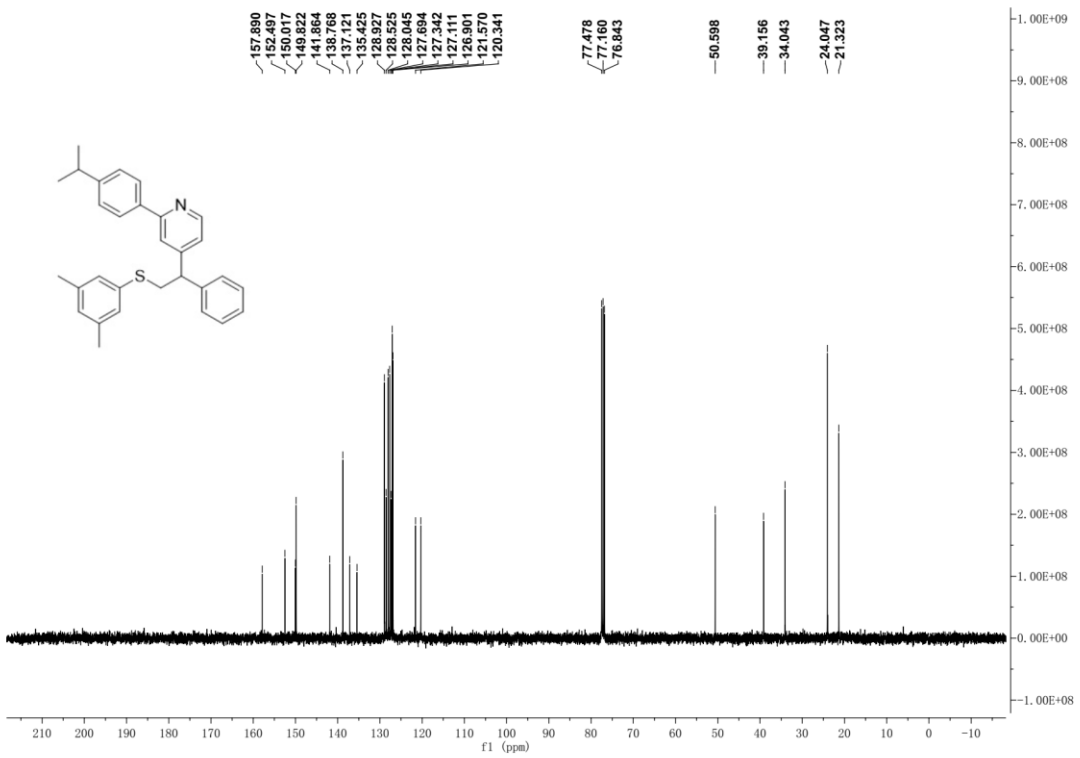
^{1}H NMR of compound 6h



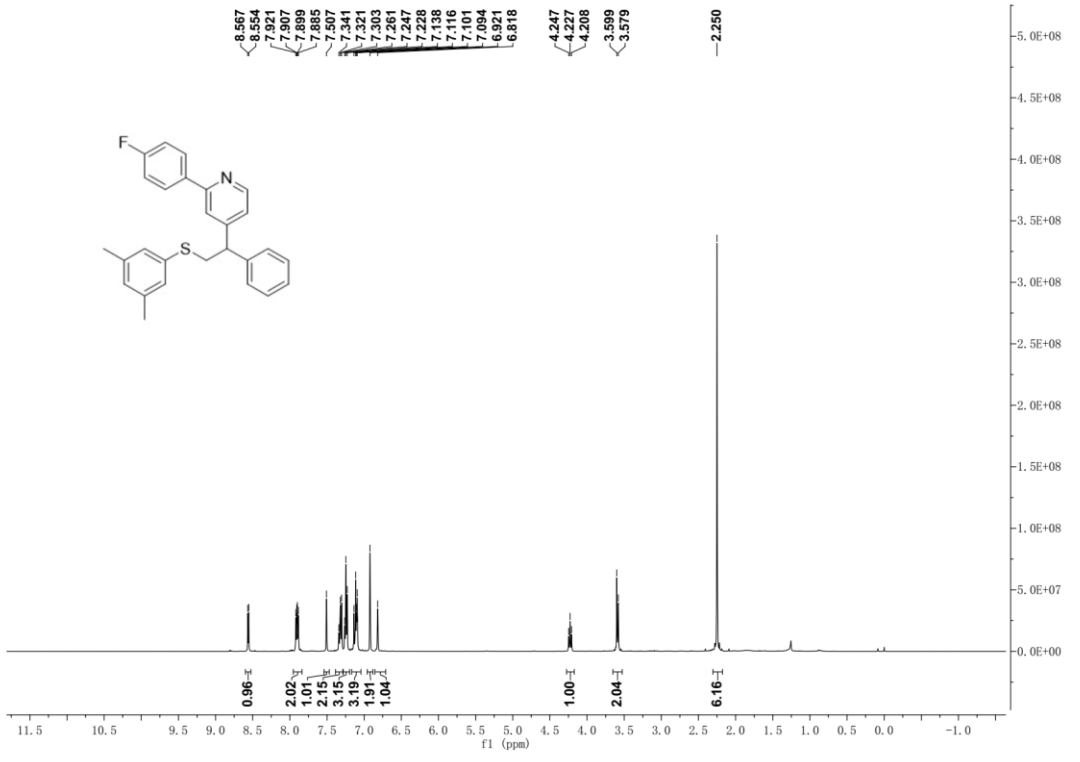
^{13}C NMR of compound 6h



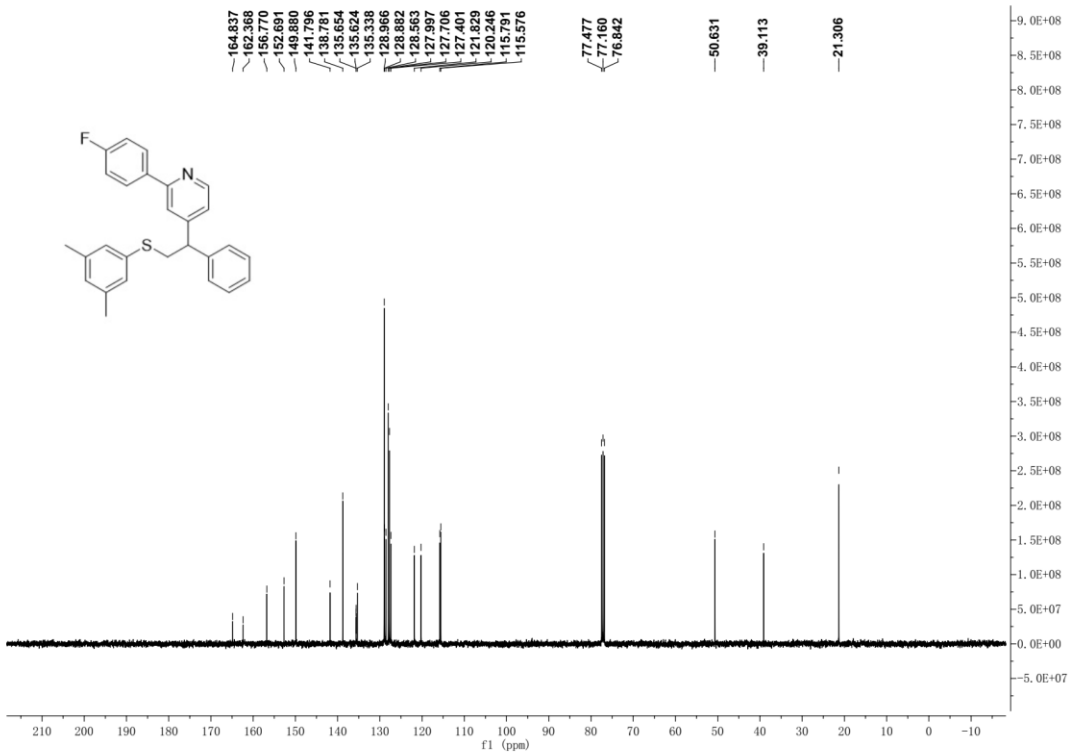
^{1}H NMR of compound 6i



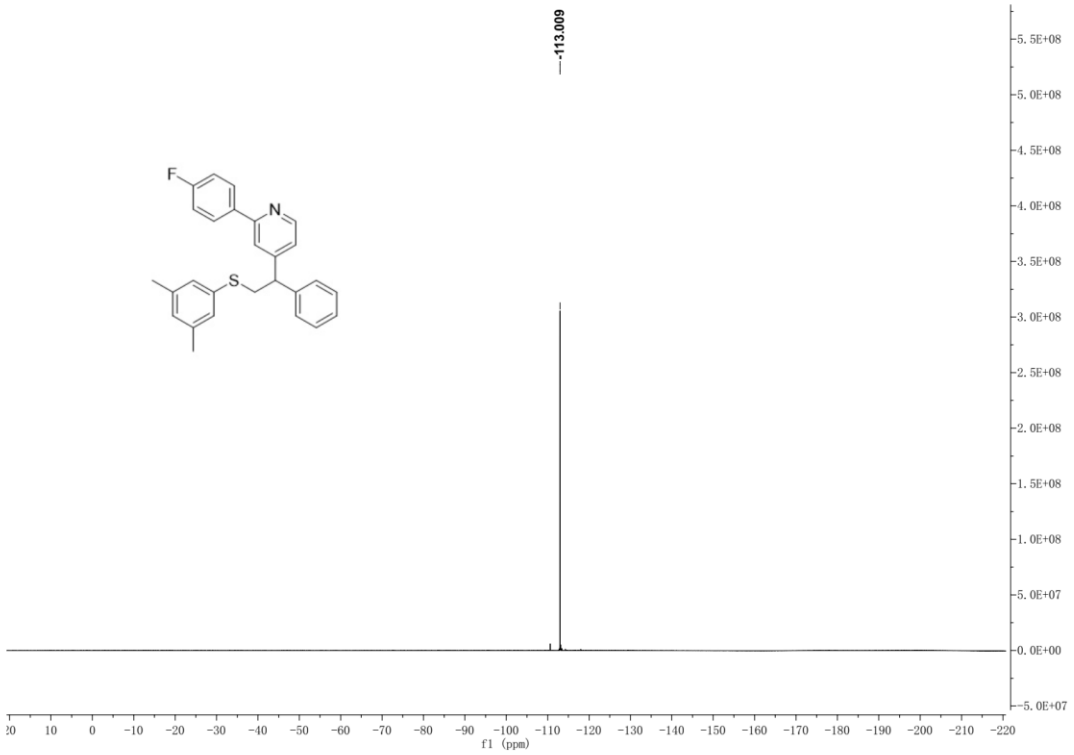
^{13}C NMR of compound 6i



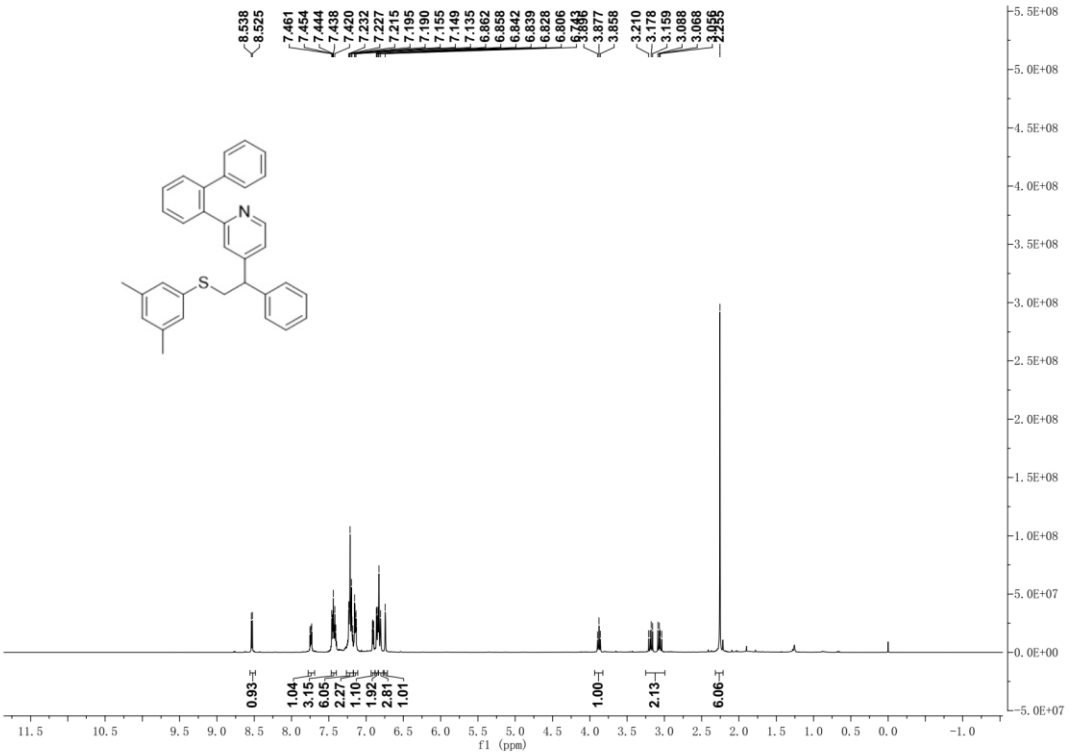
^{1}H NMR of compound 6j



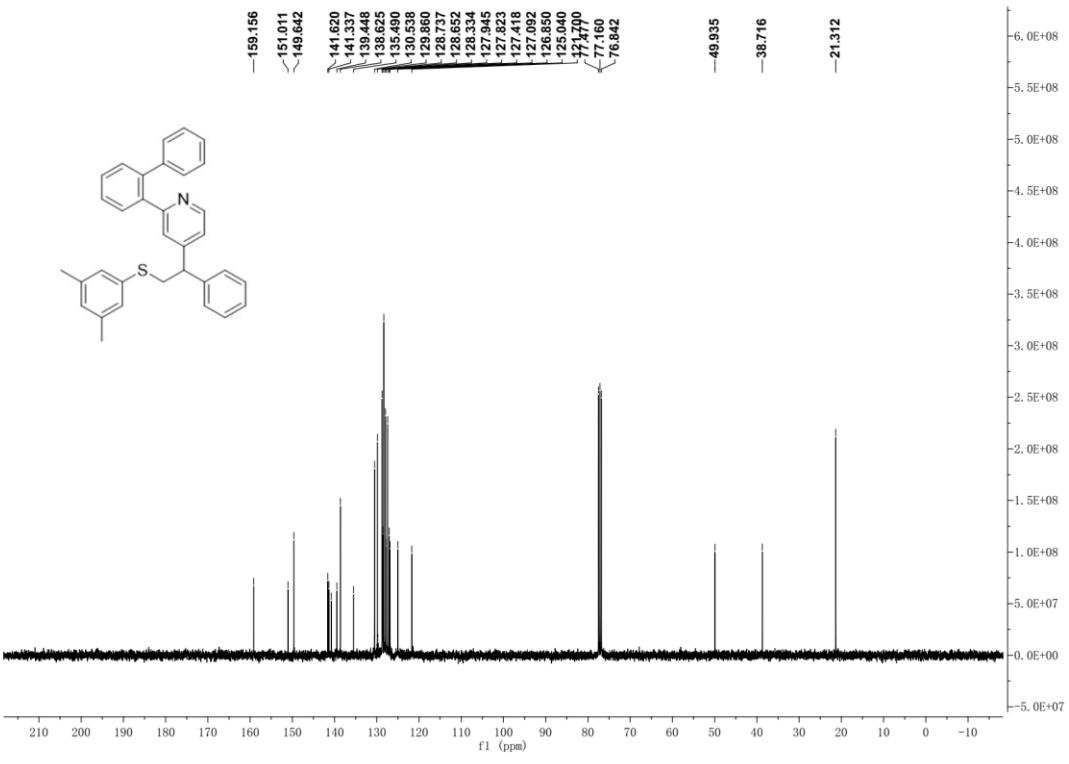
^{13}C NMR of compound 6j



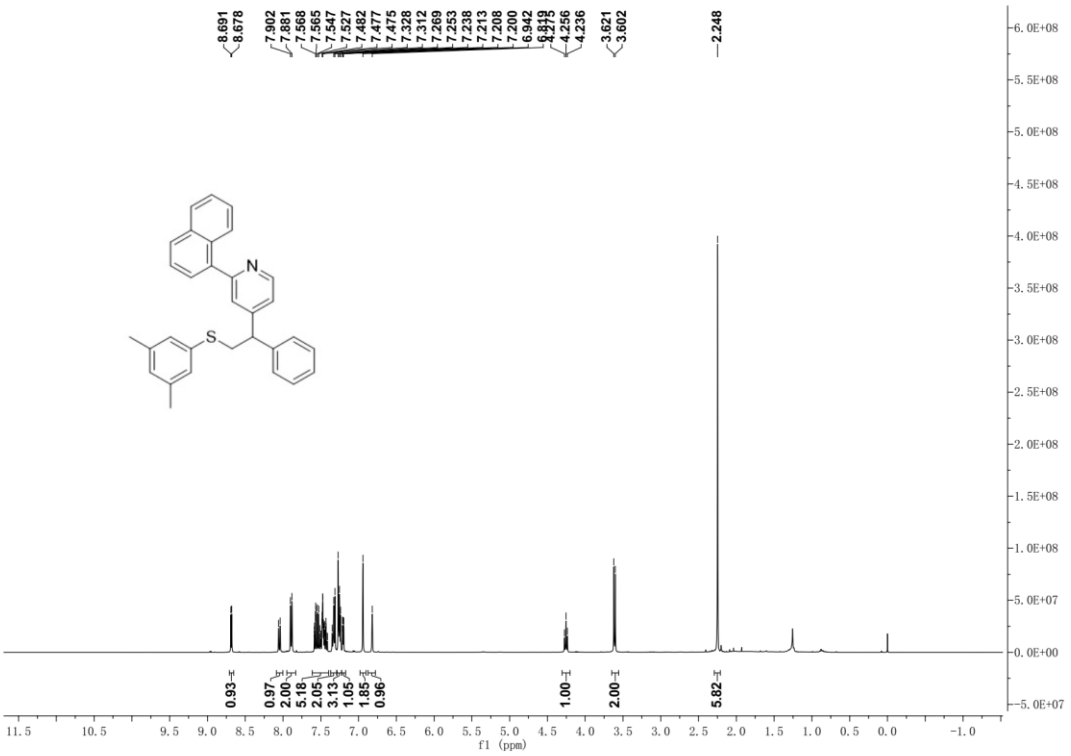
^{19}F NMR of compound 6j



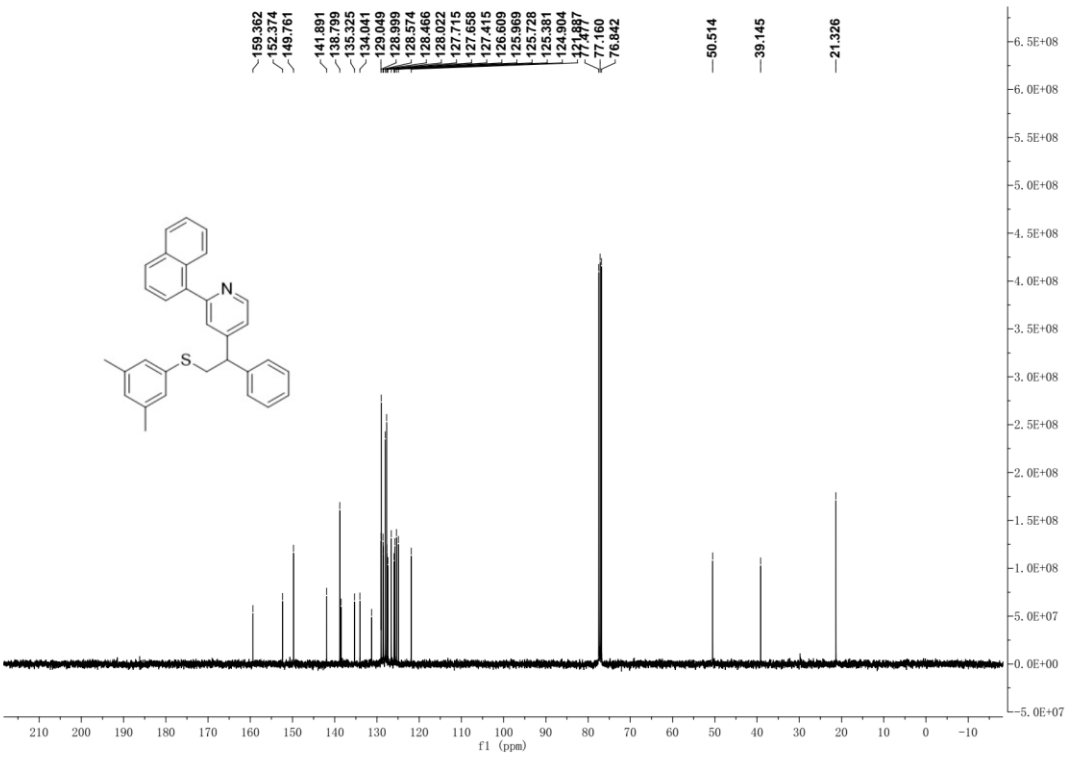
^{1}H NMR of compound 6k



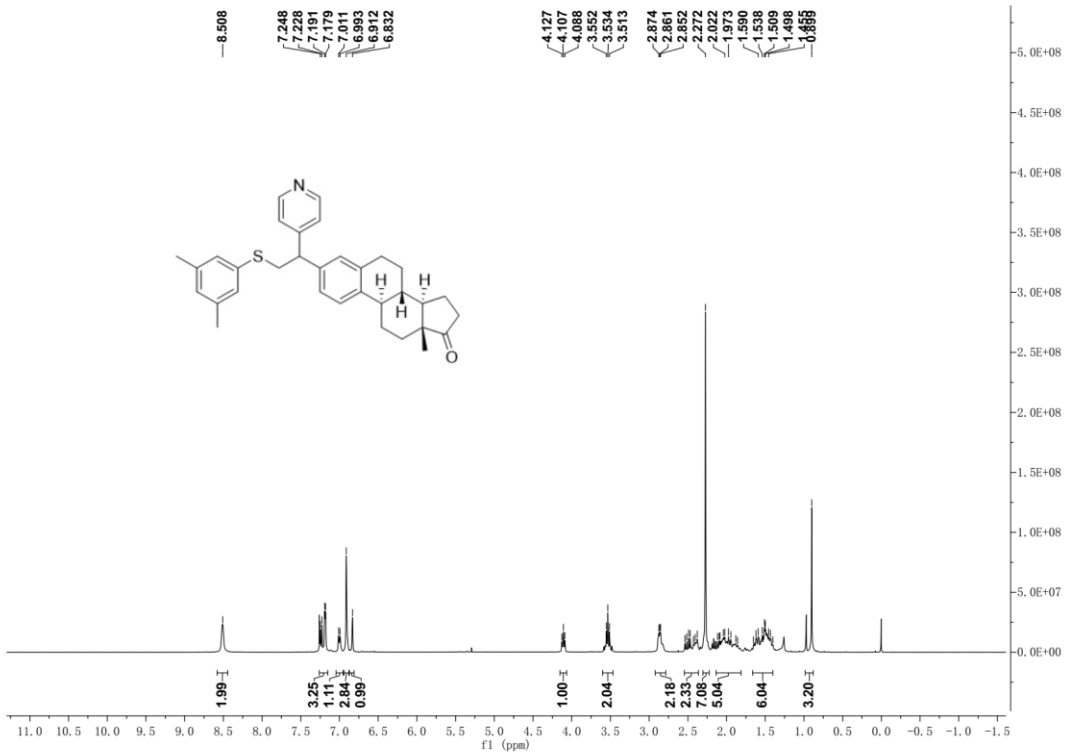
^{13}C NMR of compound 6k



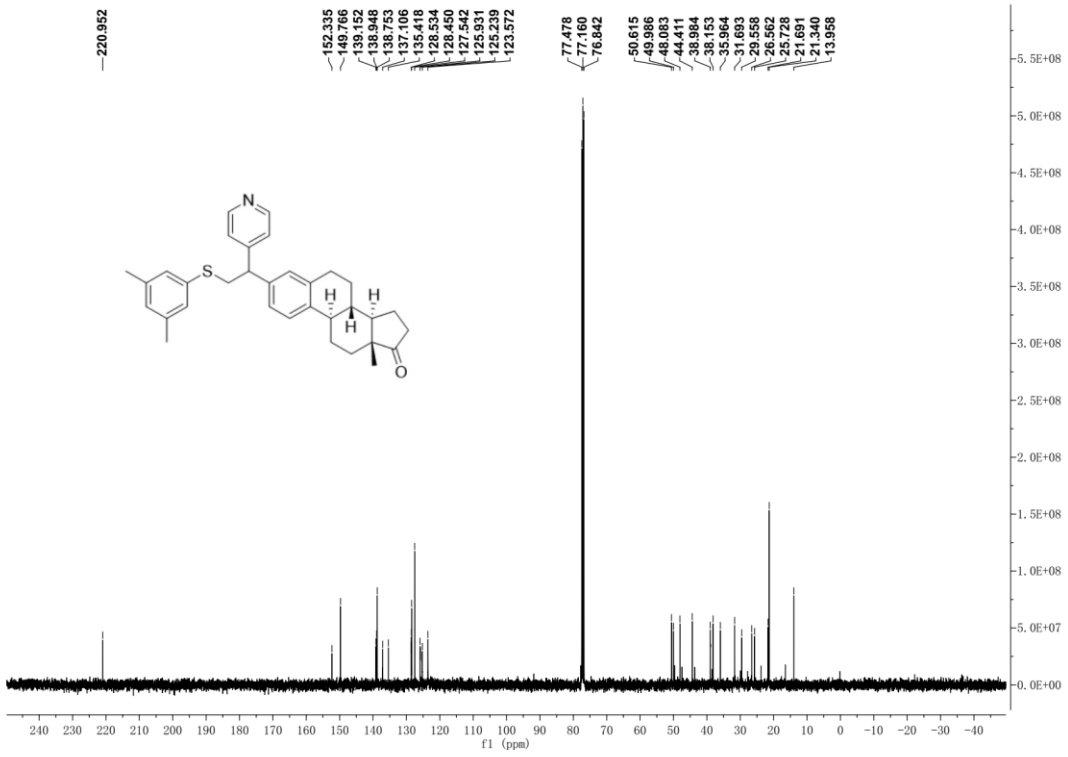
^{1}H NMR of compound 6l



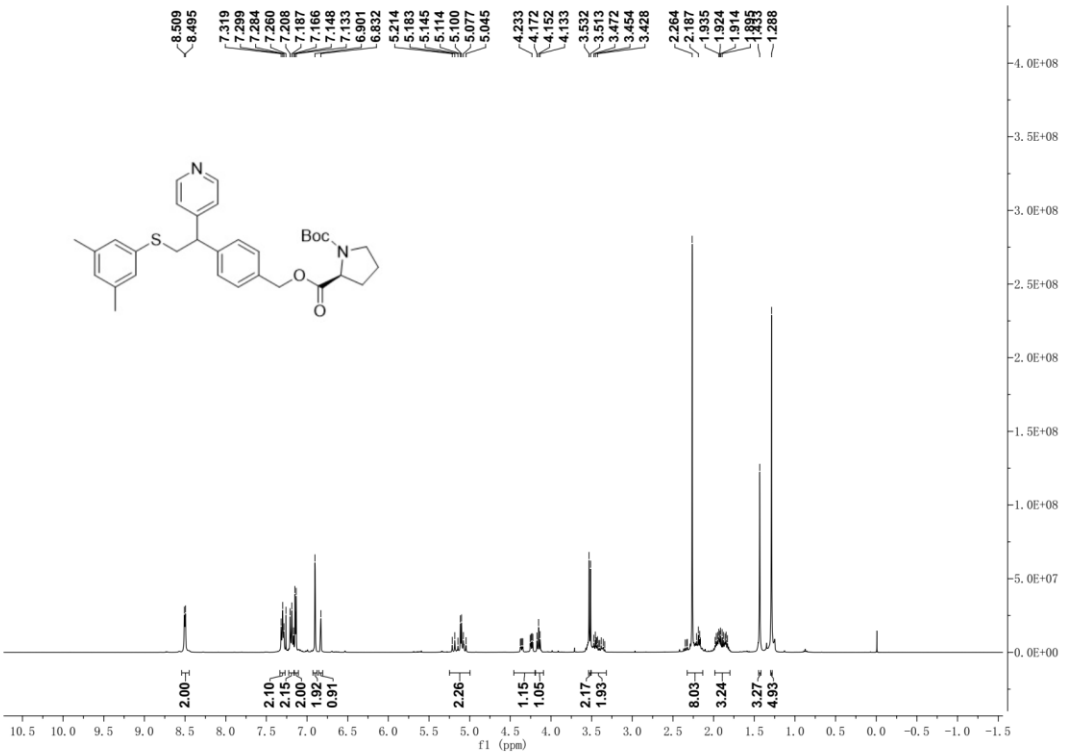
^{13}C NMR of compound 6l



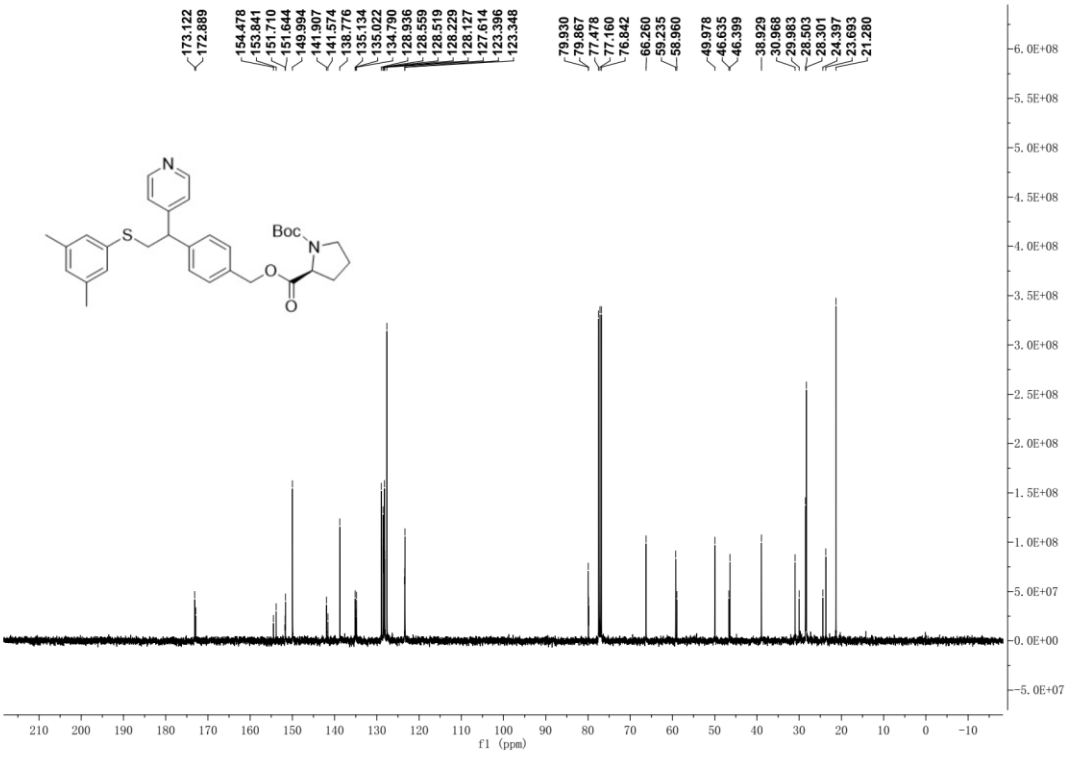
^{1}H NMR of compound 7



^{13}C NMR of compound 7



^{1}H NMR of compound 8



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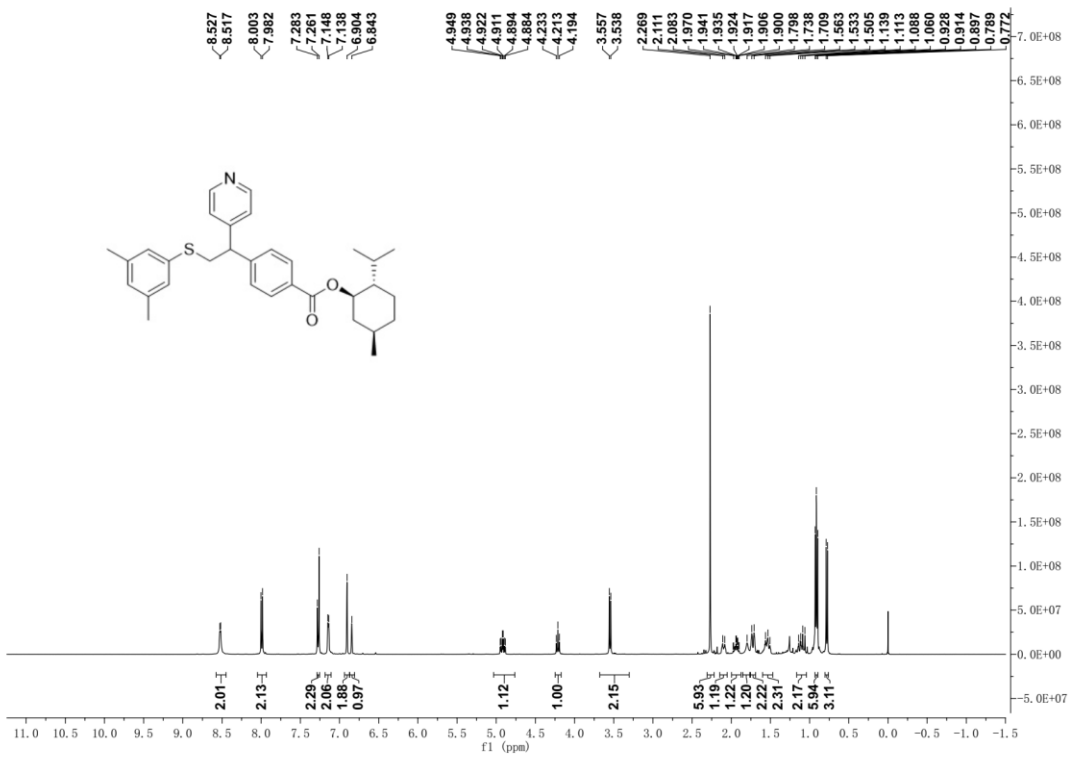
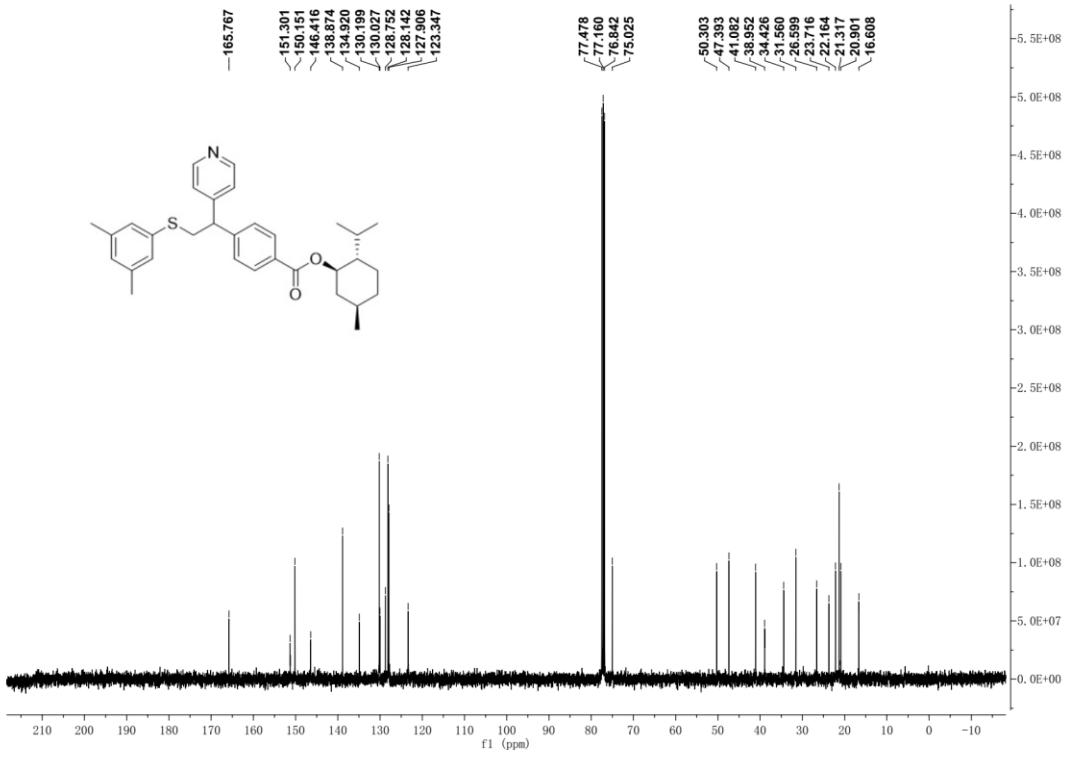
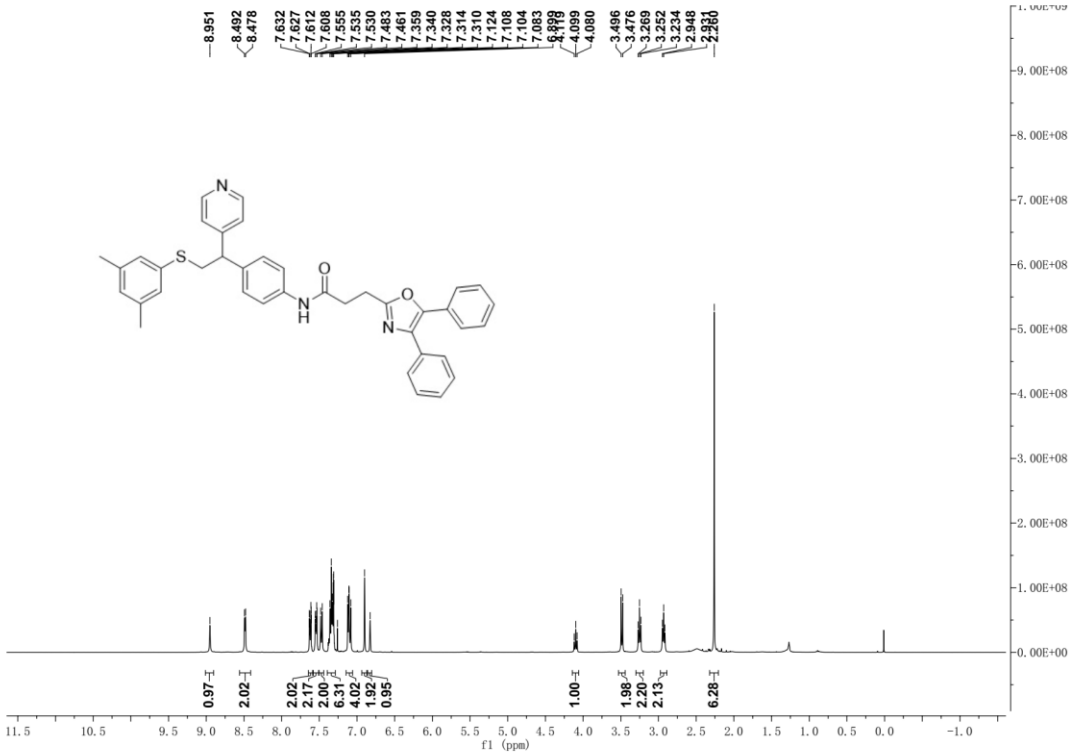


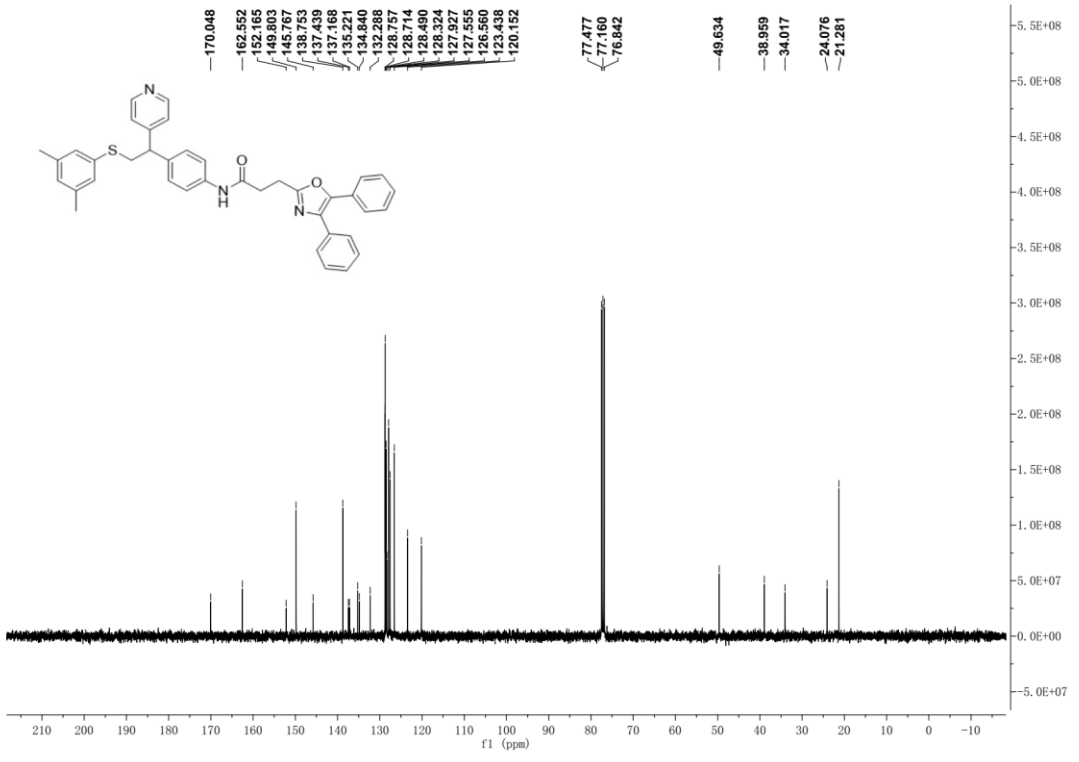
^{1}H NMR of compound 9



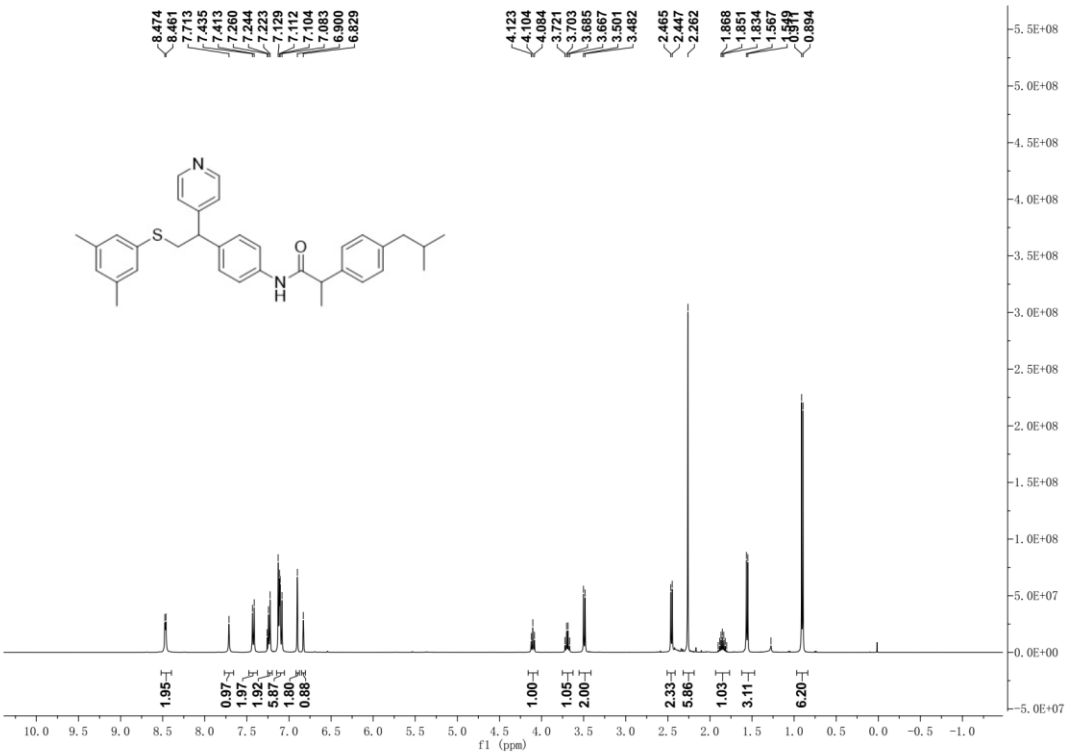
^{13}C NMR of compound 9



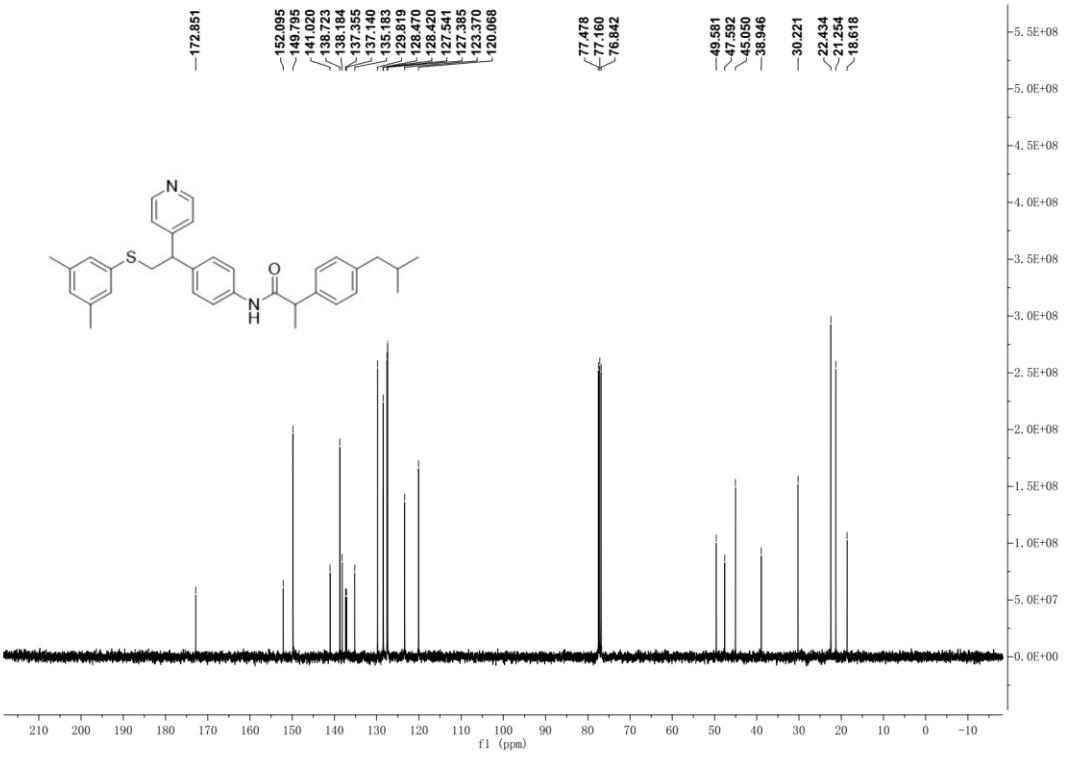
[1]H NMR of compound 10



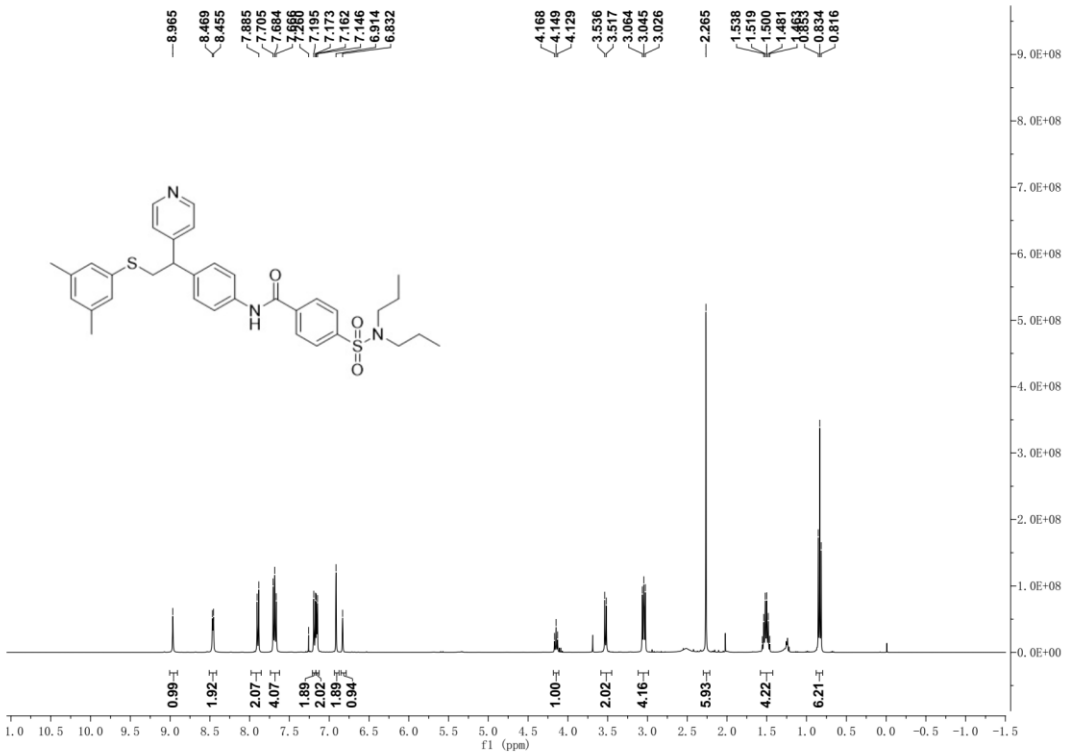
[13]C NMR of compound 10



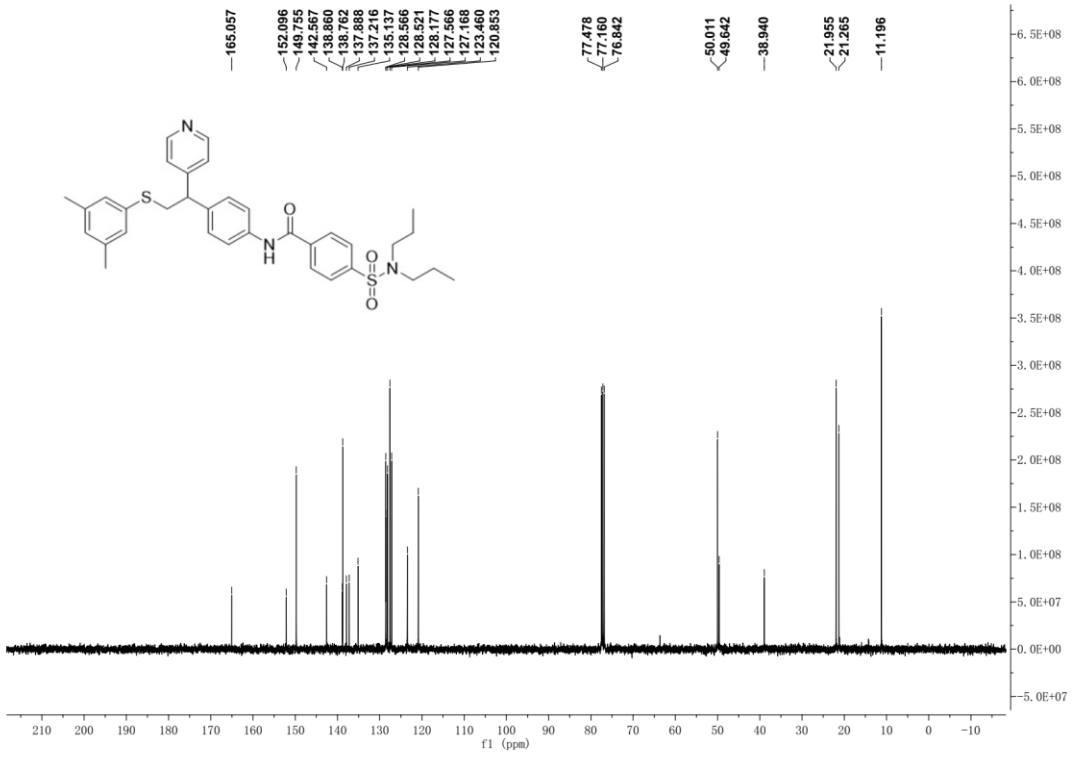
^{1}H NMR of compound 11



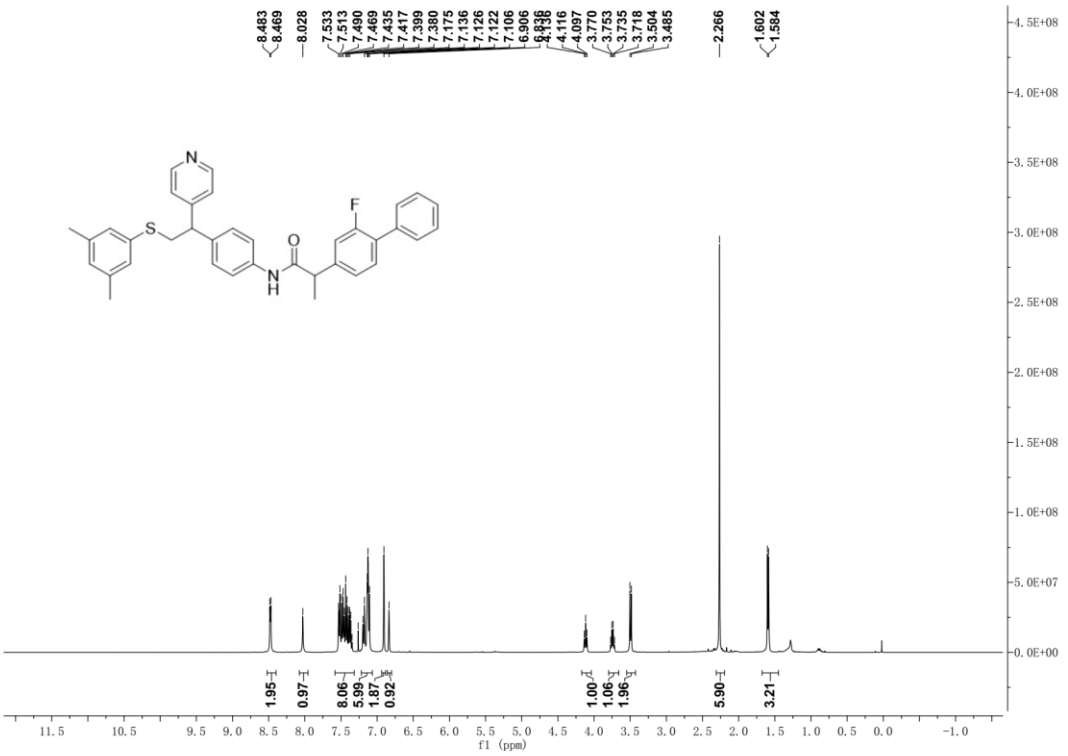
^{13}C NMR of compound 11



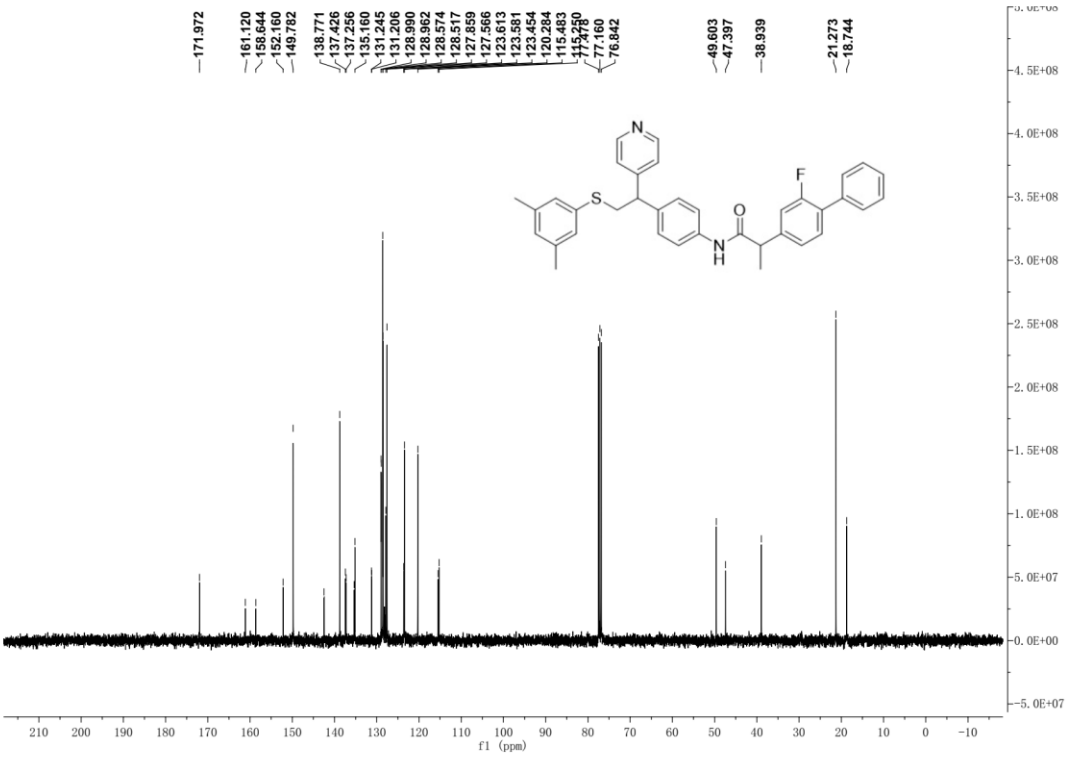
^{1}H NMR of compound 12



^{13}C NMR of compound 12

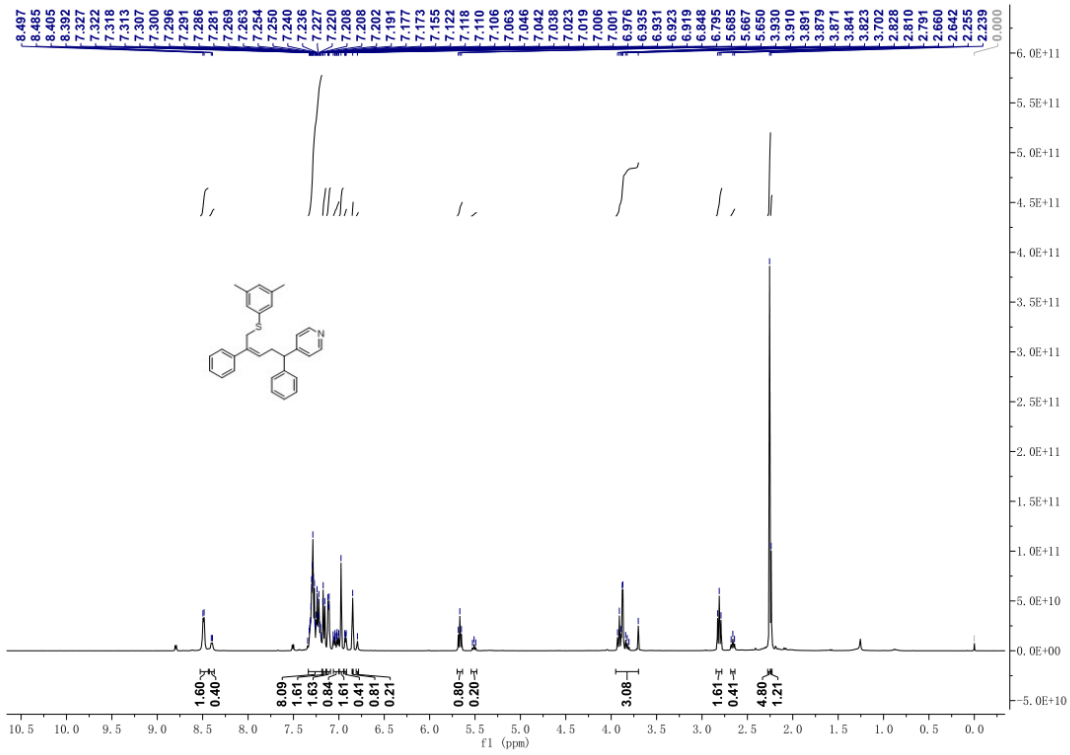


[1]H NMR of compound 13

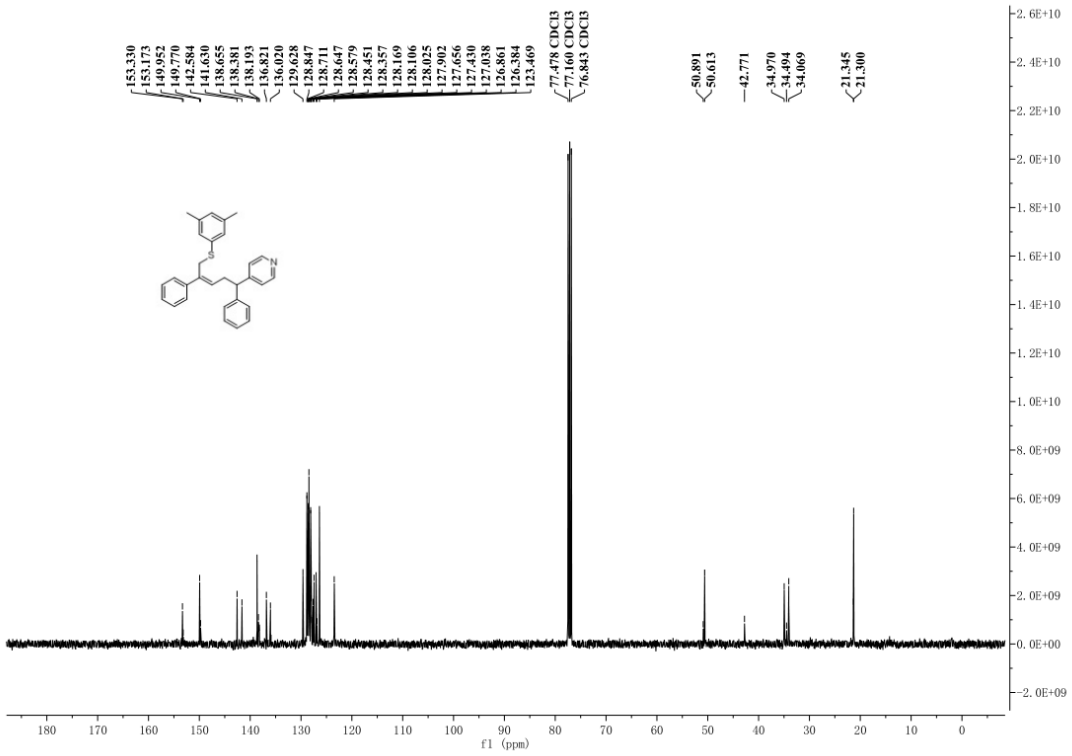


[13]C NMR of compound 13

^{19}F NMR of compound 13



^{1}H NMR of compound 17



^{13}C NMR of compound 17