Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Copper-Catalyzed *ortho*-selective direct sulfenylation of *N*-aryl-7-azaindoles with Disulfides

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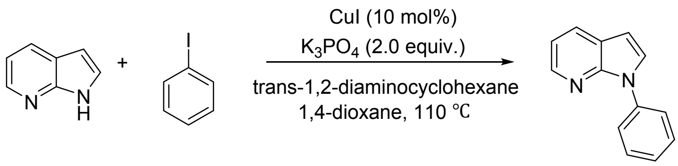
1. General information

Reagents and solvents. All starting materials, which were purchased from commercial sources, were used without further purification. Solvents for column chromatography were technical standard. Column chromatography was performed with silica gel 200-400 mesh. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker Avance 400 Mhz or 500 Mhz spectrometer. Chemical shifts in ^{1}H NMR spectra were reported in parts per million (ppm) downfield from the internal standard Me_4Si (TMS). Chemical shifts in ^{13}C NMR spectra were reported relative to the central line of the chloroform signal (δ = 77.0 ppm). Peaks were labelled as singlet (s), doublet (d), triplet (t), quarter (q), and multiplet (m). High resolution mass spectra were obtained with a Shimadzu LCMS-IT-TOF mass spectrometer. Analytical TLC was performed using EM separations percolated silica gel 0.2 mm layer UV 254 fluorescent sheets.

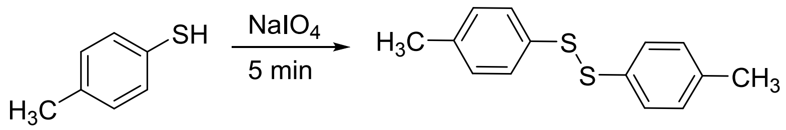
2.1 Synthesis of starting materials

General procedure (A) for the synthesis of *N*-aryl-7-azaindoles (1a-1ai)[1]



To a mixture of 7-azaindole (423 mg, 3.58 mmol), copper iodide (5.7 mg, 0.03 mmol) and potassium phosphate (1.33 g, 6.29 mmol) under a N_2 atmosphere is added racemic *trans*-1,2-diaminocyclohexane (0.035 mL, 0.3 mmol), iodobenzene (0.335 mL, 3 mmol) followed by anhydrous dioxane (5 mL). The resulting suspension is heated in an oil bath at 110 °C. with magnetic stirring for 12 hours. The resulting mixture is filtered through a short pad of silica gel, washing the cake well with ethyl acetate. The filtrate is evaporated to leave a brown oil. and further purified by flash chromatography on a 10-gram silica gel cartridge by elution with heptane:ethyl acetate (20:1). Clean fractions containing the product are combined and evaporated to give 1-phenyl-7-azaindole as a light brown oil.

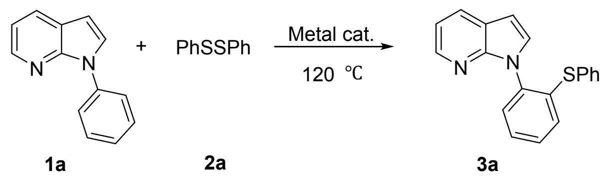
General procedure (B) for the synthesis of disulfides 2[2]



To a mixture of *p*-toluenethiol (620 mg, 5 mol) and $NaIO_4$ (1.06 g, 5 mol), the mixture was grind for 5 minutes, he reaction mixture was then diluted with water and extracted with ethyl acetate. After the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel using petroleum ether to afford the pure product **2.**

2.2 Optimization of Reaction Condition

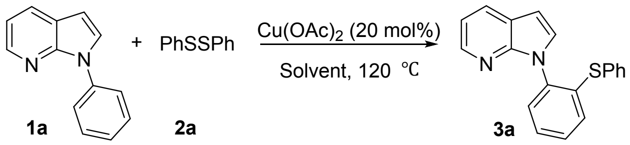
Table S1. Screening of catalyst[a]



Entry	Cat.	Solvent	Temp.(℃)	Yield(%)[b]
1	CuCl	DCE	120	<5
2	CuBr	DCE	120	--
3	CuI	DCE	120	--
4	$CuCl_2$	DCE	120	13
5	$CuBr_2$	DCE	120	34
6	**$Cu(OAc)_2$**	**DCE**	**120**	**50**
7	$Cu(OTf)_2$	DCE	120	--
8	$Pd(OAc)_2$	DCE	120	--
9	$Ni(OAc)_2$	DCE	120	--
10	$Co(OAc)_2$	DCE	120	--

[a] Reactions were carried out by using **1a** (0.1 mmol), **2a** (0.15 mmol), metal catalyst (0.02 mmol) and DCE (1 mL) stirred at 120 ℃ for 12 h.[b] Isolated yields.

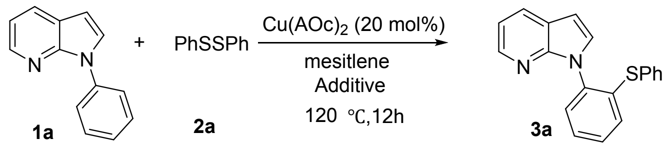
Table S2. Screening of solvent[a]



Entry	Cat.	Solvent	Temp.(℃)	Yield(%)[b]
1	$Cu(OAc)_2$	DCE	120	50
2	$Cu(OAc)_2$	toluene	120	55
3	$Cu(OAc)_2$	DMF	120	--
4	$Cu(OAc)_2$	DMSO	120	37
5	$Cu(OAc)_2$	NMP	120	--
6	$Cu(OAc)_2$	chlorbenzene	120	38
7	$Cu(OAc)_2$	forbenzene	120	24
8	$Cu(OAc)_2$	para-xylene	120	52
9	**$Cu(OAc)_2$**	**mesitylene**	**120**	**57**
10	$Cu(OAc)_2$	1.4-dioxane	120	--

[a] Reactions were carried out by using **1a** (0.1 mmol), **2a** (0.15 mmol), $Cu(OAc)_2$ (0.02 mmol) and solvent (1 mL) stirred at 120℃ for 12 h.[b] Isolated yields.

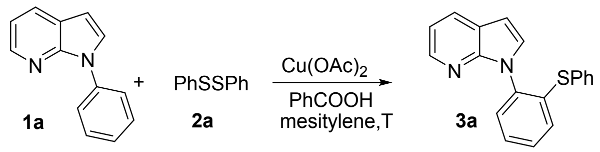
Table S3. Screening of additives[a]



Entry	**Cat.**	**Additive**	**Temp.(℃)**	**Yield(%)**
1	$Cu(OAc)_2$	Li_2CO_3	120	--
2	$Cu(OAc)_2$	Na_2CO_3	120	--
3	$Cu(OAc)_2$	K_2CO_3	120	--
4	$Cu(OAc)_2$	Cs_2CO_3	120	--
5	$Cu(OAc)_2$	$NaHCO_3$	120	23
6	$Cu(OAc)_2$	$KHCO_3$	120	33
7	$Cu(OAc)_2$	K_2HPO_4	120	24
8	**$Cu(OAc)_2$**	**PhCOOH**	**120**	**70**
9	$Cu(OAc)_2$	Piv-OH	120	57
10	$Cu(OAc)_2$	AcOH	120	44

[a] Reactions were carried out by using **1a** (0.1 mmol), **2a** (0.15 mmol), $Cu(OAc)_2$ (0.02 mmol), addtive (0.2 mol) and mesitylene (1 mL) stirred at 120℃ for 12 h.[b] Isolated yields.

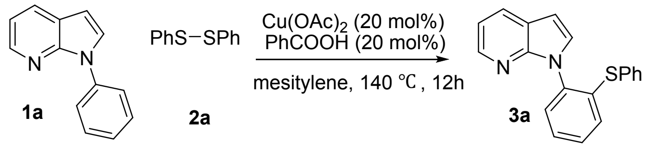
Table S4. Screening of additives equivalent and reaction temperature[a]



Entry	Cat.	Additive	Temp.(℃)	Yield(%)
1	$Cu(OAc)_2$	PhCOOH(1 eq)	120	72
2	$Cu(OAc)_2$	PhCOOH(0.5 eq)	120	70
3	$Cu(OAc)_2$	PhCOOH(0.2 eq)	120	77
4	$Cu(OAc)_2$	PhCOOH(0.1 eq)	120	44
5	$Cu(OAc)_2$	PhCOOH(0.2 eq)	100	55
6	**$Cu(OAc)_2$**	**PhCOOH(0.2 eq)**	**140**	**87**
7	--	PhCOOH(0.2 eq)	140	--

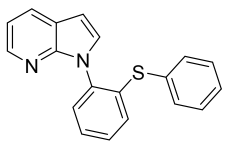
[a] Reactions were carried out by using **1a** (0.1 mmol), **2a** (0.15 mmol), $Cu(OAc)_2$ (0.02 mmol), addtive and mesitylene (1 mL) stirred for 12 h.[b] Isolated yields.

2.3 General Procedures for the Thiolation



To a oven-dried sealed tube was added *N*-aryl-7-azaindoles **1** (0.2 mmol), disulfide **2** (0.3 mmol), $Cu(OAc)_2$ (7.2 mg, 0.04 mmol), PhCOOH (4.9 mg, 0.04 mmol) and mesitylene (2.0 mL). The mixture was stirred at 140℃ for 12 hours until the complete consumption of **1** as monitored by TLC analysis. The reaction mixture was then diluted with water and extracted with ethyl acetate. After the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent (8:1, V/V) to afford the pure product **3**.

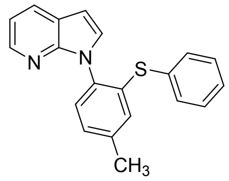
1-(2-(phenylthio)phenyl)-1H-pyrrolo[2,3-*b*]pyridine (*3a*)



^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32 (dd, J = 4.8, 1.5 Hz, 1H), 7.95 (dd, J = 7.8, 1.5 Hz, 1H), 7.50-7.45 (m, 1H), 7.42-7.36 (m, 2H), 7.34 (dd, J = 6.1, 1.5 Hz, 2H), 7.27-

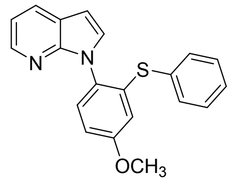
7.25 (m, 1H), 7.24 (dd, J = 2.2, 1.2 Hz, 1H), 7.20-7.13 (m, 3H), 7.10 (dd, J = 7.8, 4.8 Hz, 1H), 6.61 (d, J = 3.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 147.59, 143.01, 137.06, 135.62, 133.89, 133.48, 132.04, 129.60, 129.25, 129.15, 128.99, 127.76, 127.46, 124.76, 120.69, 116.34, 101.03; HRMS (ESI): *m/z* calcd. for $C_{19}H_{15}N_2S$, $[M+H]^+$: 303.0950, found: 303.0942.

1-(4-methyl-2-(phenylthio)phenyl)-1H-pyrrolo[2,3-*b*]pyridine (*3b*)



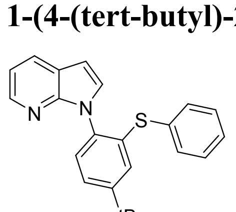
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.33-8.27 (m, 1H), 7.92 (dd, J = 7.8, 1.3 Hz, 1H), 7.41-7.33 (m, 2H), 7.21 (d, J = 5.8 Hz, 4H), 7.19-7.11 (m, 3H), 7.07 (dd, J = 7.8, 4.7 Hz, 1H), 6.57 (d, J = 3.6 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 148.15, 143.34, 139.08, 135.07, 134.75, 134.42, 132.99, 131.58, 129.58, 128.98, 128.88, 128.85, 128.82, 127.15, 120.43, 116.23, 100.68, 21.10; HRMS (ESI): *m/z* calcd. for $C_{20}H_{17}N_2S$, $[M+H]^+$: 317.1107, found: 317.1103.

1-(4-methoxy-2-(phenylthio)phenyl)-1H-pyrrolo[2,3-*b*]pyridine (*3c*)



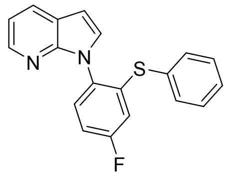
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.33 (dd, J = 4.8, 1.5 Hz, 1H), 7.95 (dd, J = 7.8, 1.5 Hz, 1H), 7.37 (d, J = 8.6 Hz, 1H), 7.33 (d, J = 3.6 Hz, 1H), 7.29 (d, J = 1.8 Hz, 1H), 7.27 (d, J = 1.5 Hz, 1H), 7.21-7.15 (m, 3H), 7.10 (dd, J = 7.8, 4.8 Hz, 1H), 6.90 (dd, J = 8.6, 2.8 Hz, 1H), 6.82 (d, J = 2.8 Hz, 1H), 6.60 (d, J = 3.6 Hz, 1H), 3.74 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.72, 141.81, 136.37, 132.25, 131.50, 129.07, 128.06, 126.73, 119.71, 115.76, 115.20, 111.93, 99.79, 54.52; HRMS (ESI): *m/z* calcd. for $C_{20}H_{17}N_2OS$, $[M+H]^+$: 333.1056, found: 333.1052.

1-(4-(tert-butyl)-2-(phenylthio)phenyl)-1H-pyrrolo[2,3-*b*]pyridine (*3d*)



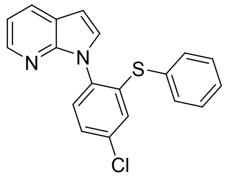
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.31 (dd, J = 4.7, 1.5 Hz, 1H), 7.90 (dd, J = 7.8, 1.4 Hz, 1H), 7.48-7.45 (m, 1H), 7.45-7.41 (m, 2H), 7.35 (s, 1H), 7.21-7.17 (m, 2H), 7.16-7.11 (m, 2H), 7.11-7.07 (m, 1H), 7.08-7.04 (m, 1H), 6.56 (d, J = 3.6 Hz, 1H), 1.29 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 151.79, 148.08, 143.38, 135.19, 134.67, 133.89, 131.15, 130.15, 129.58, 128.74, 128.62, 126.96, 125.33, 120.40, 116.21, 34.78, 31.13; HRMS (ESI): *m/z* calcd. for $C_{23}H_{23}N_2S$, $[M+H]^+$: 359.1576, found: 359.1568.

1-(4-fluoro-2-(phenylthio)phenyl)-1H-pyrrolo[2,3-*b*]pyridine (*3e*)



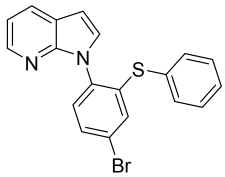
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.34 (dd, *J* = 4.7, 1.5 Hz, 1H), 7.96 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.42-7.38 (m, 1H), 7.38-7.34 (m, 3H), 7.29-7.26 (m, 3H), 7.12 (dd, *J* = 7.8, 4.7 Hz, 1H), 7.03 (dd, *J* = 8.1, 2.8 Hz, 1H), 6.86 (dd, *J* = 9.1, 2.8 Hz, 1H), 6.64 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.56, 161.08, 148.14, 143.60, 139.73, 139.65, 133.65, 131.98, 131.78, 130.52, 130.43, 129.43, 129.31, 129.03, 128.61, 120.45, 116.77, 116.52, 113.97, 113.74, 101.19; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -111.91; HRMS (ESI): *m/z* calcd. for $C_{19}H_{14}FN_2S$, $[M+H]^+$: 321.0856, found: 321.0849.

1-(4-chloro-2-(phenylthio)phenyl)-1H-pyrrolo[2,3-*b*]pyridine (*3f*)



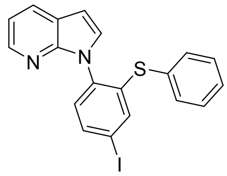
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.33 (dd, *J* = 4.7, 1.3 Hz, 1H), 7.94 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.41-7.35 (m, 2H), 7.33-7.29 (m, 3H), 7.25 (dd, *J* = 5.5, 3.7 Hz, 3H), 7.20 (d, *J* = 2.1 Hz, 1H), 7.11 (dd, *J* = 7.8, 4.7 Hz, 1H), 6.63 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 148.07, 143.62, 138.49, 134.90, 134.59, 134.24, 133.11, 132.13, 130.22, 130.10, 129.35, 129.05, 128.98, 128.36, 127.27, 120.45, 116.59, 101.34; HRMS (ESI): *m/z* calcd. for $C_{19}H_{14}ClN_2S$, $[M+H]^+$: 337.0561, found: 337.0558.

1-(4-bromo-2-(phenylthio)phenyl)-1H-pyrrolo[2,3-*b*]pyridine (*3g*)



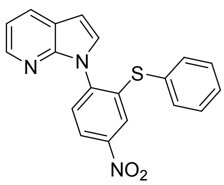
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32 (dd, *J* = 4.7, 1.5 Hz, 1H), 7.95 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.47 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.37-7.35 (m, 2H), 7.34-7.28 (m, 3H), 7.26-7.21 (m, 3H), 7.11 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.63 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 147.89, 143.52, 138.64, 135.49, 133.31, 132.95, 132.25, 130.43, 130.35, 129.35, 129.11, 129.06, 128.32, 122.62, 120.54, 116.62, 101.42; HRMS (ESI): *m/z* calcd. for $C_{19}H_{14}BrN_2S$, $[M+H]^+$: 381.0056, found: 381.0048.

1-(4-iodo-2-(phenylthio)phenyl)-1H-pyrrolo[2,3-*b*]pyridine (*3h*)



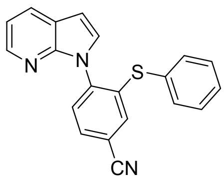
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.33-8.26 (m, 1H), 7.92 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.68 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.59 (d, *J* = 1.8 Hz, 1H), 7.34 (d, *J* = 3.6 Hz, 1H), 7.28-7.23 (m, 2H), 7.19 (m, *J* = 8.1, 4.9 Hz, 4H), 7.09 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.60 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 147.85, 143.49, 139.68, 138.34, 136.54, 132.61, 132.55, 130.67, 129.27, 129.08, 129.03, 128.12, 120.56, 116.61, 101.42, 94.09; HRMS (ESI): *m/z* calcd. for $C_{19}H_{14}IN_2S$, $[M+H]^+$: 482.9917, found: 482.9910.

1-(4-nitro-2-(phenylthio)phenyl)-1H-pyrrolo[2,3-*b*]pyridine (*3i*)



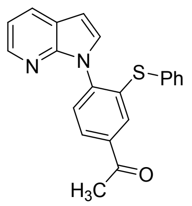
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.34 (d, *J* = 4.6 Hz, 1H), 8.14 (dd, *J* = 8.6, 2.4 Hz, 1H), 8.02 (d, *J* = 2.3 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 8.6 Hz, 1H), 7.47 (d, *J* = 3.6 Hz, 1H), 7.36-7.33 (m, 2H), 7.31-7.26 (m, 3H), 7.15 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.69 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 147.74, 147.17, 143.72, 141.03, 138.87, 134.55, 133.56, 130.91, 129.85, 129.68, 129.49, 129.30, 129.08, 128.36, 125.10, 121.56, 120.75, 117.16, 102.43; HRMS (ESI): *m/z* calcd. for $C_{19}H_{14}N_3O_2S$, $[M+H]^+$: 348.0801, found: 348.0811.

3-(phenylthio)-4-(1H-pyrrolo[2,3-*b*]pyridin-1-yl)benzonitrile (*3j*)



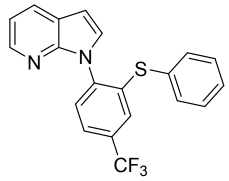
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.36-8.31 (m, 1H), 8.00-7.96 (m, 1H), 7.59 (s, 2H), 7.44 (d, *J* = 3.6 Hz, 1H), 7.43-7.38 (m, 2H), 7.38-7.33 (m, 3H), 7.30 (dd, *J* = 7.3, 3.3 Hz, 3H), 7.17-7.14 (m, 1H), 6.69 (d, *J* = 3.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 147.75, 143.74, 143.17, 139.56, 139.01, 134.79, 133.84, 133.40, 130.86, 130.01, 129.94, 129.79, 129.65, 129.59, 129.37, 129.19, 128.50, 128.07, 120.78, 117.90, 117.13, 112.49, 102.30; HRMS (ESI): *m/z* calcd. for $C_{20}H_{14}N_3S$, $[M+H]^+$: 328.0903, found: 328.0910.

1-(3-(phenylthio)-4-(1H-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)ethan-1-one (*3k*)



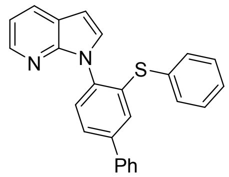
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.36 (dd, *J* = 4.7, 1.4 Hz, 1H), 8.08-8.05 (m, 1H), 8.00-7.92 (m, 3H), 7.62 (d, *J* = 8.3 Hz, 1H), 7.50-7.43 (m, 2H), 7.27-7.25 (m, 1H), 7.19 (dd, *J* = 5.0, 2.2 Hz, 2H), 7.15 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.66 (d, *J* = 3.6 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.66, 170.46, 147.67, 143.38, 140.81, 136.96, 136.43, 133.28, 132.91, 132.23, 131.92, 129.97, 129.19, 128.89, 128.33, 127.96, 127.34, 120.79, 116.80, 101.79, 26.56; HRMS (ESI): *m/z* calcd. for $C_{21}H_{17}N_2OS$, $[M+H]^+$: 345.1056, found: 345.1049.

1-(2-(phenylthio)-4-(trifluoromethyl)phenyl)-1H-pyrrolo[2,3-*b*]pyridine (*3l*)



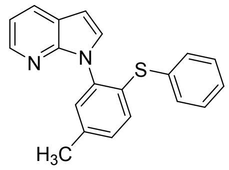
^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.16 (d, *J* = 5.1 Hz, 1H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.40–7.31 (m, 4H), 7.21 (d, *J* = 7.1 Hz, 2H), 7.14 (m, 3H), 7.09 (d, *J* = 5.1 Hz, 1H), 6.69 (d, *J* = 3.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 148.47, 143.67, 139.59, 136.81, 136.05, 135.67, 133.59, 133.39, 132.16, 132.03, 129.96, 129.17, 129.10, 128.95, 127.76, 127.53, 119.73, 116.50, 99.46; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -62.80; HRMS (ESI): *m/z* calcd. for $C_{20}H_{14}F_3N_2S$, $[M+H]^+$: 371.0824, found: 371.0815.

1-(3-(phenylthio)-[1,1'-biphenyl]-4-yl)-1H-pyrrolo[2,3-*b*]pyridine (*3m*)



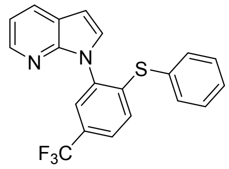
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32 (dd, *J* = 4.7, 1.4 Hz, 1H), 7.92 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.59 (m, 2H), 7.54 (d, *J* = 8.6 Hz, 1H), 7.52-7.48 (m, 2H), 7.44-7.38 (m, 3H), 7.37-7.33 (m, 1H), 7.26 (d, *J* = 1.6 Hz, 1H), 7.25-7.23 (m, 1H), 7.17-7.10 (m, 3H), 7.08 (dd, *J* = 7.8, 4.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 148.16, 143.50, 141.91, 139.79, 136.51, 135.63, 133.97, 131.79, 130.99, 129.42, 128.99, 128.83, 127.74, 127.42, 127.12, 126.70, 120.48, 116.41, 101.01; HRMS (ESI): *m/z* calcd. for $C_{25}H_{19}N_2S$, $[M+H]^+$: 379.1263, found: 379.1251.

1-(5-methyl-2-(phenylthio)phenyl)-1H-pyrrolo[2,3-*b*]pyridine (*3n*)



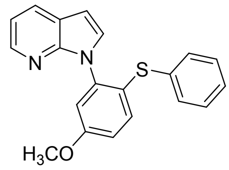
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.30 (dd, *J* = 4.7, 1.5 Hz, 1H), 7.91 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.33 (t, *J* = 2.8 Hz, 2H), 7.20-7.15 (m, 3H), 7.15-7.11 (m, 2H), 7.09 (dd, *J* = 3.7, 2.0 Hz, 1H), 7.08-7.05 (m, 1H), 6.57 (d, *J* = 3.6 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 148.14, 143.41, 138.65, 137.96, 135.21, 133.30, 131.18, 130.95, 129.89, 129.51, 128.78, 128.76, 126.82, 120.39, 116.25, 100.72, 21.01; HRMS (ESI): *m/z* calcd. for $C_{20}H_{17}N_2S$, $[M+H]^+$: 333.1056, found: 333.1048.

1-(2-(phenylthio)-5-(trifluoromethyl)phenyl)-1H-pyrrolo[2,3-*b*]pyridine (*3o*)



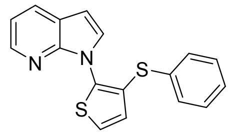
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.37 (dd, *J* = 4.7, 1.5 Hz, 1H), 8.00 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.69 (s, 1H), 7.53-7.49 (m, 1H), 7.40 (m, 3H), 7.33-7.28 (m, 3H), 7.21 (d, *J* = 8.3 Hz, 1H), 7.16 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.69 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 147.79, 143.62, 142.62, 135.69, 134.17, 131.19, 129.74, 129.58, 129.40, 128.95, 128.88, 126.07, 126.03, 125.99, 125.95, 125.52, 125.48, 125.45, 125.41, 124.91, 122.20, 120.69, 116.83, 101.95; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -62.29; HRMS (ESI): *m/z* calcd. for $C_{20}H_{14}F_3N_2S$, $[M+H]^+$: 371.0824, found: 371.0817.

1-(5-methoxy-2-(phenylthio)phenyl)-1H-pyrrolo[2,3-*b*]pyridine (*3p*)



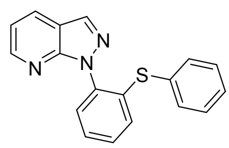
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.28 (dd, *J* = 4.8, 1.5 Hz, 1H), 7.91 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.53 (d, *J* = 8.7 Hz, 1H), 7.32 (d, *J* = 3.6 Hz, 1H), 7.07 (m, 6H), 7.03-6.97 (m, 2H), 6.55 (d, *J* = 3.6 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.27, 143.16, 140.31, 136.73, 136.37, 129.65, 129.27, 128.66, 126.14, 123.84, 120.60, 116.33, 115.48, 114.73, 100.82, 55.60; HRMS (ESI): *m/z* calcd. for $C_{20}H_{17}N_2OS$, $[M+H]^+$: 333.1056, found: 333.1048.

1-(3-(phenylthio)thiophen-2-yl)-1H-pyrrolo[2,3-*b*]pyridine (*3q*)



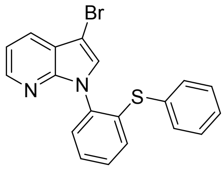
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.31 (dd, *J* = 4.7, 1.5 Hz, 1H), 7.92 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.49-7.45 (m, 1H), 7.39-7.33 (m, 3H), 7.25 (m, 2H), 7.16 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.08 (dd, *J* = 7.8, 4.7 Hz, 1H), 6.59 (d, *J* = 3.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 148.11, 143.48, 137.22, 135.61, 133.94, 132.10, 132.01, 129.37, 129.12, 128.96, 128.81, 127.65, 127.44, 120.40, 116.36, 100.90; HRMS (ESI): *m/z* calcd. for $C_{19}H_{14}FN_2S$, $[M+H]^+$: 321.0856, found: 321.0849.

1-(2-(phenylthio)phenyl)-1H-pyrazolo[3,4-*b*]pyridine (*3r*)



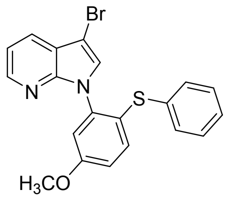
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.58 (d, *J* = 4.5 Hz, 1H), 8.24 (s, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.34 (m, 5H), 7.25-7.17 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 150.46, 148.96, 136.67, 136.23, 133.86, 132.82, 131.43, 130.51, 129.42, 129.07, 128.27, 127.71, 127.11, 117.43, 116.00; HRMS (ESI): *m/z* calcd. for $C_{18}H_{14}N_3S$, $[M+H]^+$: 304.0903, found: 304.0890.

3-bromo-1-(2-(phenylthio)phenyl)-1H-pyrrolo[2,3-*b*]pyridine (*3s*)



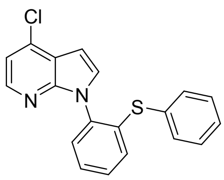
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.33 (dd, *J* = 4.7, 1.4 Hz, 1H), 7.86 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.45-7.35 (m, 5H), 7.23-7.19 (m, 2H), 7.18-7.12 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 146.93, 144.90, 144.57, 136.35, 135.71, 133.52, 132.24, 132.09, 129.22, 129.16, 128.90, 128.16, 127.81, 127.56, 127.54, 119.83, 116.98, 90.06; HRMS (ESI): *m/z* calcd. for $C_{19}H_{14}BrN_2S$, $[M+H]^+$: 381.0056, found: 381.0043.

3-bromo-1-(5-methoxy-2-(phenylthio)phenyl)-1H-pyrrolo[2,3-*b*]pyridine (*3t*)



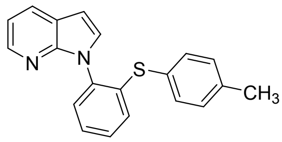
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32-8.26 (m, 1H), 7.83 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.55 (d, *J* = 8.7 Hz, 1H), 7.35 (s, 1H), 7.13 (dd, *J* = 7.9, 4.7 Hz, 1H), 7.07-7.01 (m, 5H), 6.99 (m, 2H), 3.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 160.26, 144.10, 139.13, 136.25, 136.04, 129.58, 128.60, 128.47, 127.94, 126.36, 124.23, 120.06, 116.91, 115.67, 114.90, 90.04, 55.62; HRMS (ESI): *m/z* calcd. for $C_{20}H_{16}BrN_2OS$, $[M+H]^+$: 411.0161, found: 411.0145.

4-chloro-1-(2-(phenylthio)phenyl)-1H-pyrrolo[2,3-*b*]pyridine (*3u*)



^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.18 (d, *J* = 5.2 Hz, 1H), 7.45 (dt, *J* = 7.4, 1.0 Hz, 1H), 7.40 (d, *J* = 3.7 Hz, 2H), 7.39-7.35 (m, 2H), 7.25-7.21 (m, 2H), 7.20-7.14 (m, 3H), 7.11 (d, *J* = 5.2 Hz, 1H), 6.71 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 148.65, 143.83, 136.90, 136.02, 135.74, 133.67, 133.47, 132.21, 132.11, 129.96, 129.20, 129.15, 129.00, 127.81, 127.59, 119.74, 116.55, 99.48; HRMS (ESI): *m/z* calcd. for $C_{19}H_{14}ClN_2S$, $[M+H]^+$: 337.0561, found: 337.0564.

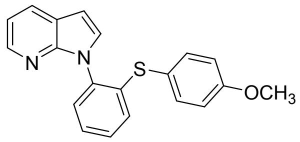
1-(2-(p-tolylthio)phenyl)-1H-pyrrolo[2,3-*b*]pyridine (*3v*)



^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.38-8.30 (m, 1H), 7.96 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.45 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.40 (d, *J* = 3.6 Hz, 1H), 7.33 (m, 2H), 7.24 (dd, *J* = 7.8, 1.5

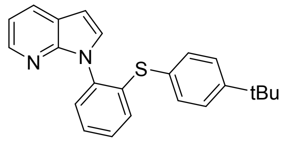
Hz, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.11 (dd, *J* = 7.8, 4.8 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.63 (d, *J* = 3.6 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 143.26, 138.03, 136.85, 136.38, 134.22, 133.15, 130.89, 129.92, 129.57, 129.03, 128.88, 120.64, 116.32, 100.98, 21.08; HRMS (ESI): *m/z* calcd. for $C_{20}H_{17}N_2S$, $[M+H]^+$: 317.1107, found: 317.1103.

1-(2-((4-methoxyphenyl)thio)phenyl)-1H-pyrrolo[2,3-*b*]pyridine (*3w*)



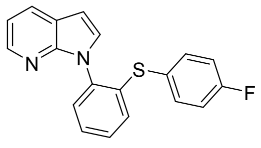
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32 (dd, *J* = 4.7, 1.5 Hz, 1H), 7.95 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.41 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.30-7.28 (m, 2H), 7.27-7.25 (m, 2H), 7.13-7.07 (m, 2H), 6.80-6.74 (m, 2H), 6.64 (d, *J* = 3.6 Hz, 1H), 3.76 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 159.91, 148.12, 143.55, 138.01, 135.80, 135.68, 129.63, 129.45, 128.96, 128.89, 128.79, 126.53, 122.89, 120.49, 116.37, 114.84, 100.94, 99.94, 55.27; HRMS (ESI): *m/z* calcd. for $C_{20}H_{17}N_2OS$, $[M+H]^+$: 333.1056, found: 333.1040.

1-(2-((4-(tert-butyl)phenyl)thio)phenyl)-1H-pyrrolo[2,3-*b*]pyridine (*3x*)



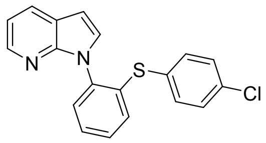
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.30 (dd, *J* = 4.8, 1.5 Hz, 1H), 7.95 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.46 (m, 1H), 7.42 (d, *J* = 3.6 Hz, 1H), 7.40-7.36 (m, 1H), 7.36-7.33 (m, 2H), 7.18 (s, 4H), 7.10 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.62 (d, *J* = 3.6 Hz, 1H), 1.24 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 150.92, 142.82, 136.57, 136.28, 132.27, 131.59, 129.76, 129.74, 129.15, 128.93, 127.45, 126.06, 120.82, 116.30, 101.03, 34.47, 31.17; HRMS (ESI): *m/z* calcd. for $C_{23}H_{23}N_2S$, $[M+H]^+$: 359.1576, found: 359.1562.

1-(2-((4-fluorophenyl)thio)phenyl)-1H-pyrrolo[2,3-*b*]pyridine (*3y*)



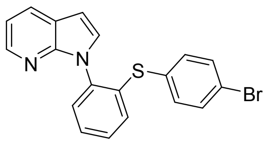
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.33 (d, *J* = 4.5 Hz, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.38 (q, *J* = 11.4, 9.7 Hz, 3H), 7.32 (d, *J* = 5.1 Hz, 1H), 7.26-7.20 (m, 2H), 7.12 (dd, *J* = 7.7, 4.9 Hz, 1H), 6.85 (t, *J* = 8.6 Hz, 2H), 6.63 (d, *J* = 3.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.63, 161.16, 147.38, 143.15, 136.62, 136.16, 134.70, 134.62, 132.73, 131.41, 129.85, 129.52, 129.40, 129.31, 129.26, 129.05, 127.71, 120.71, 116.00; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -113.35; HRMS (ESI): *m/z* calcd. for $C_{19}H_{14}FN_2S$, $[M+H]^+$: 321.0856, found: 321.0850.

1-(2-((4-chlorophenyl)thio)phenyl)-1H-pyrrolo[2,3-*b*]pyridine (*3z*)



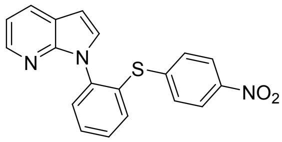
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.34-8.26 (m, 1H), 7.96 (d, J = 7.7 Hz, 1H), 7.49 (d, J = 7.3 Hz, 1H), 7.42 (dq, J = 14.2, 7.2 Hz, 3H), 7.36 (d, J = 3.5 Hz, 1H), 7.09 (q, J = 8.6 Hz, 5H), 6.62 (d, J = 3.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 142.67, 137.37, 134.90, 133.44, 132.71, 132.62, 129.62, 129.47, 129.20, 129.02, 128.45, 120.81, 116.41, 101.29; HRMS (ESI): *m/z* calcd. for $C_{19}H_{14}ClN_2S$, $[M+H]^+$: 337.0561, found: 337.0552.

1-(2-((4-bromophenyl)thio)phenyl)-1H-pyrrolo[2,3-*b*]pyridine (*3aa*)



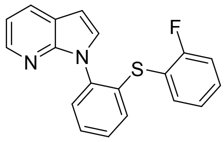
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32-8.27 (m, 1H), 7.95 (d, J = 7.8 Hz, 1H), 7.52–7.47 (m, 1H), 7.47-7.42 (m, 2H), 7.39 (dd, J = 7.0, 1.6 Hz, 1H), 7.36 (d, J = 3.6 Hz, 1H), 7.21 (d, J = 8.5 Hz, 2H), 7.11 (dd, J = 7.8, 4.8 Hz, 1H), 7.03 (d, J = 8.5 Hz, 2H), 6.61 (d, J = 3.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 142.81, 137.54, 134.64, 133.41, 132.97, 132.90, 131.90, 129.55, 129.48, 129.17, 128.53, 124.78, 121.40, 120.60, 116.41, 101.26; HRMS (ESI): *m/z* calcd. for $C_{19}H_{14}BrN_2S$, $[M+H]^+$: 381.0056, found: 381.0040.

1-(2-((4-nitrophenyl)thio)phenyl)-2,3-dihydro-1H-pyrrolo[2,3-*b*]pyridine (*3ab*)



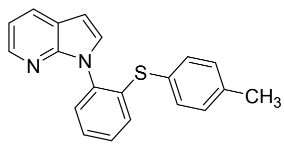
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.21 (d, J = 4.1 Hz, 1H), 8.18 (d, J = 8.8 Hz, 1H), 7.81 (m, 3H), 7.73 (d, J = 7.7 Hz, 1H), 7.63-7.58 (m, 3H), 7.50 (dd, J = 7.9, 4.2 Hz, 1H), 7.32 (d, J = 3.5 Hz, 1H), 7.01 (dd, J = 7.8, 4.8 Hz, 1H), 6.52 (d, J = 3.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 147.82, 146.93, 145.71, 145.50, 144.00, 143.36, 139.87, 135.97, 130.62, 130.57, 130.07, 129.27, 129.05, 128.86, 128.13, 126.35, 124.38, 123.37, 120.20, 116.57, 101.35; HRMS (ESI): *m/z* calcd. for $C_{19}H_{14}N_3O_2S$, $[M+H]^+$: 348.0801, found: 348.0797.

1-(2-((2-fluorophenyl)thio)phenyl)-1H-pyrrolo[2,3-*b*]pyridine (*3ac*)



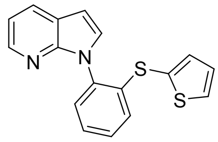
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.35–8.29 (m, 1H), 7.99–7.93 (m, 1H), 7.51–7.46 (m, 1H), 7.46–7.39 (m, 2H), 7.36 (m, 2H), 7.20 (m, 1H), 7.17–7.13 (m, 1H), 7.10 (dd, J = 7.9, 4.8 Hz, 1H), 6.94 (m, 2H), 6.62 (d, J = 3.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 162.68, 160.21, 147.71, 143.10, 137.28, 134.36, 133.94, 132.01, 129.82, 129.75, 129.51, 129.22, 128.99, 128.07, 124.47, 124.43, 121.05, 120.88, 120.67, 116.39, 115.90, 115.68; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -107.79. HRMS (ESI): *m/z* calcd. for $C_{19}H_{14}FN_2S$, $[M+H]^+$: 321.0856, found: 321.0848.

1-(2-(m-tolylthio)phenyl)-1H-pyrrolo[2,3-*b*]pyridine (*3ad*)



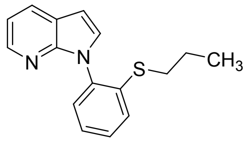
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.33 (dd, *J* = 4.7, 1.5 Hz, 1H), 7.95 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.48 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.42-7.36 (m, 2H), 7.34 (dd, *J* = 6.4, 1.7 Hz, 2H), 7.12-7.09 (m, 1H), 7.08 (d, *J* = 5.2 Hz, 3H), 6.99-6.93 (m, 1H), 6.62 (d, *J* = 3.6 Hz, 1H), 2.22 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 147.84, 143.23, 138.82, 136.98, 135.85, 132.96, 132.79, 132.64, 131.87, 129.53, 129.36, 129.12, 128.93, 128.80, 128.39, 127.54, 120.53, 116.32, 100.89, 21.10; HRMS (ESI): *m/z* calcd. for $C_{20}H_{17}N_2S$, $[M+H]^+$: 317.1107, found: 317.0998.

1-(2-(thiophen-2-ylthio)phenyl)-1H-pyrrolo[2,3-*b*]pyridine (*3ae*)



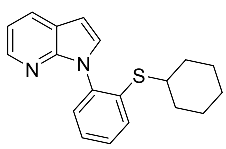
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.41 (dd, *J* = 4.9, 1.4 Hz, 1H), 8.09 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.41 (m, 3H), 7.37-7.33 (m, 2H), 7.19 (m, 3H), 6.99 (dd, *J* = 5.4, 3.6 Hz, 1H), 6.73 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 142.06, 137.83, 136.70, 131.67, 130.59, 130.02, 129.53, 128.81, 128.74, 127.94, 127.07, 121.47, 116.48, 101.70; HRMS (ESI): *m/z* calcd. for $C_{17}H_{13}N_2S_2$, $[M+H]^+$: 309.0515, found: 309.0503.

1-(2-(propylthio)phenyl)-1H-pyrrolo[2,3-*b*]pyridine (*3af*)



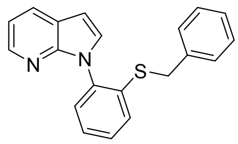
^{1}H NMR (400 MHz, CDCl3) δ: 8.34 (dd, *J* = 4.7, 1.3 Hz, 1H), 7.99 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.53-7.48 (m, 1H), 7.45-7.39 (m, 2H), 7.39 (d, *J* = 3.7 Hz, 1H), 7.33 (m, *J* = 7.5, 1.3 Hz, 1H), 7.12 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.65 (d, *J* = 3.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 147.98, 143.41, 136.78, 136.09, 129.61, 129.23, 129.07, 128.98, 128.77, 126.28, 120.55, 116.33, 100.76, 34.88, 22.04, 13.27; HRMS (ESI): *m/z* calcd. for $C_{16}H_{17}N_2S$, $[M+H]^+$: 269.1107, found: 269.1099.

1-(2-(cyclohexylthio)phenyl)-1H-pyrrolo[2,3-*b*]pyridine (*3ag*)



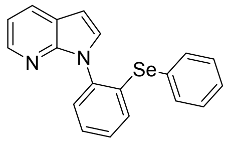
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.36-8.29 (m, 1H), 8.05-7.99 (m, 1H), 7.63-7.57 (m, 1H), 7.49-7.43 (m, 1H), 7.39 (dd, *J* = 6.6, 2.6 Hz, 3H), 7.13 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.65 (d, *J* = 3.6 Hz, 1H), 2.77-2.67 (m, 1H), 1.76 (d, *J* = 11.2 Hz, 2H), 1.63-1.52 (m, 2H), 1.48 (d, *J* = 10.0 Hz, 1H), 1.07 (q, *J* =13.2, 10.9 Hz, 4H), 0.88 (t, *J* = 6.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 142.77, 138.11, 134.41, 132.57, 130.13, 129.46, 129.11, 128.71, 127.38, 120.89, 116.24, 100.70, 46.06, 33.06, 25.85, 25.52; HRMS (ESI): *m/z* calcd. for $C_{19}H_{21}N_2S$, $[M+H]^+$: 309.1420, found: 309.1410.

1-(2-(benzylthio)phenyl)-1H-pyrrolo[2,3-*b*]pyridine (*3ah*)



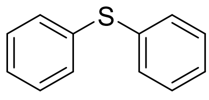
^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.38 (dd, *J* = 4.9, 1.4 Hz, 1H), 8.06 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.53 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.45-7.37 (m, 3H), 7.27 (d, *J* = 3.6 Hz, 2H), 7.21-7.17 (m, 3H), 7.16-7.09 (m, 2H), 6.66 (d, *J* = 3.6 Hz, 1H), 3.90 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 141.84, 136.57, 135.48, 130.85, 130.27, 129.85, 129.26, 128.86, 128.40, 127.38, 127.19, 116.35, 101.26, 38.43; HRMS (ESI): *m/z* calcd. for $C_{20}H_{17}N_2S$, $[M+H]^+$: 317.1107, found: 317.0998.

1-(2-(phenylselanyl)phenyl)-1H-pyrrolo[2,3-*b*]pyridine (*3ai*)



^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.35 (dd, *J* = 4.7, 1.4 Hz, 1H), 7.99 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.46-7.41 (m, 3H), 7.39 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.29 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.26 (d, *J* = 2.6 Hz, 1H), 7.21 (q, *J* = 5.7 Hz, 3H), 7.13 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.65 (d, *J* = 3.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 147.65, 143.12, 137.66, 135.39, 134.54, 133.26, 132.57, 129.38, 129.21, 129.07, 128.75, 127.90, 120.67, 116.40, 101.15; HRMS (ESI): *m/z* calcd. for $C_{19}H_{15}N_2Se$, $[M+H]^+$: 351.0396, found: 351.0385.

Diphenylsulfane 4



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 5.4, 3.4 Hz, 4H), 7.31-7.26 (m, 4H), 7.24 (d, *J* = 1.4 Hz, 1H), 7.22- 7.19 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.75, 131.00, 129.15, 127.00.

Procedure for gram-scale synthesis of compound 3a

To a oven-dried sealed tube was added *N*-aryl-7-azaindoles **1a** (970 mg, 5mol), diphenyl disulfide **2a** (1635 mg, 7.5 mol), $Cu(OAc)_2$ (181.4 mg, 1mol), PhCOOH (122 mg, 1 mmol) and mesitylene (50 mL). The mixture was stirred at 140 ^{o}C for 12 hours until the complete consumption of **1** as monitored by TLC analysis. The reaction mixture was then diluted with water and extracted with ethyl acetate. After the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent (8:1, V/V) to afford the pure product **3a** 1208 mg of 80% yield.

Procedure for removal the directed group 7-azaindoles

To a oven-dried sealed tube was added **1-(2-(phenylthio)phenyl)-1H-pyrrolo[2,3-*b*]pyridine 3a** (60.4 mg, 0.2 mmol), NaOMe (54.0 mg, 1mmol) and DMSO (5 mL). The mixture was stirred at 140 °C for 4 hours until the complete consumption of **3a** as monitored by TLC analysis. The reaction mixture was then diluted with water and extracted with ethyl acetate. After the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent (20:1, V/V) to afford the pure product **4** 29.7 mg of 80% yield.

2.4 Mechanism investigation

Procedures for the radical trapping and control experiment

To a 5 mL tube equipped with a magnetic stirring bar, *N*-aryl-7-azaindole **1a** (19.4 mg, 0.1 mmol), diphenyl disulfide **2a** (32.7 mg, 0.15 mmol), $Cu(OAc)_2$ (3.6 mg, 0.02 mmol), PhCOOH (2.4 mg, 0.02 mmol), 2,2,6,6-tetramethylpiperidineoxy (TEMPO, 46.8 mg, 0.3 mmol) and mesitylene (1 mL) were added. No special precautions were taken to exclude moisture and air. The reaction was stirred at 140 °C for 12 h.

To a 5 mL tube equipped with a magnetic stirring bar, *N*-aryl-7-azaindole **1a** (19.4 mg, 0.1 mmol), diphenyl disulfide **2a** (32.7 mg, 0.15 mmol), $Cu(OAc)_2$ (3.6 mg, 0.02 mmol), PhCOOH (2.4 mg, 0.02 mmol), 2,6-di-tert-butyl-4-methylphenol (BHT, 66 mg, 0.3 mmol) and mesitylene (1 mL) were added. No special precautions were taken to exclude moisture and air. The reaction was stirred at 140 °C for 12 h.

Procedures of 1a reacted with 6

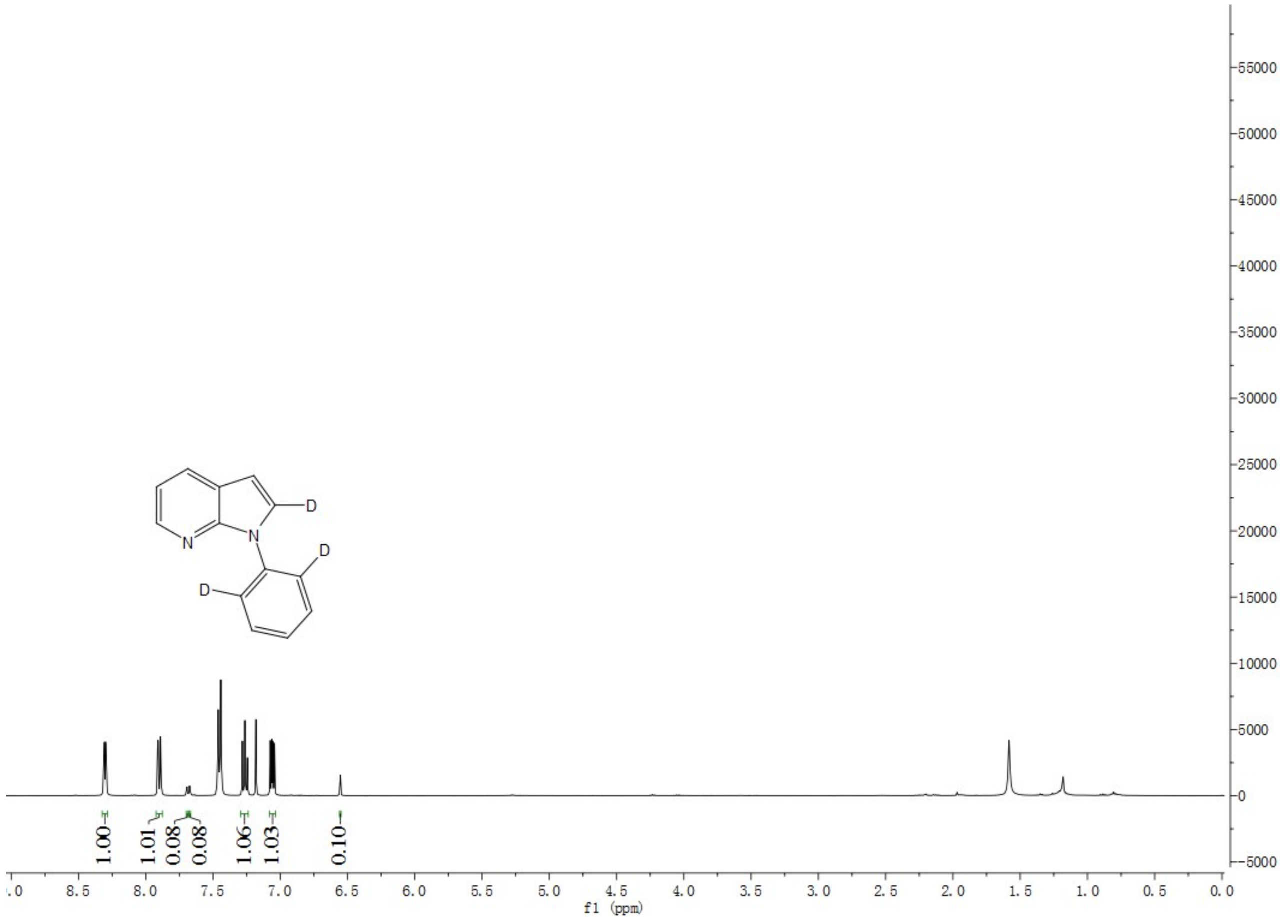
To a solution of 4-methylbenzenethiol **6** (24.8 mg, 0.2 mmol), $Cu(OAc)_2$ (3.6 mg, 0.02 mmol), PhCOOH (2.4 mg, 0.02 mmol) and mesitylene (1 mL) were added. No special precautions were taken to exclude moisture and air. The reaction was stirred at 140 °C for 12 h. The reaction mixture was then diluted with water and extracted with ethyl acetate. After the combined organic layers were washed with brine, dried over

Na_2SO_4, and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel to afford the pure product **2v** (4.9 mg, 20% yield).

***H-D* exchange and *KIE* experiments**

To a oven-dried sealed tube was added *N*-aryl-7-azaindoles **1** (38.8 mg, 0.2 mmol), disulfide **2a** (65.4 mg, 0.3 mmol), $Cu(OAc)_2$ (7.2 mg, 0.04 mmol), PhCOOH (4.9 mg, 0.04 mmol), D_2O (40 mg, 2 mmol) and mesitylene (2.0 mL). The mixture was stirred at 140 ^{o}C for 2 hours. The reaction mixture was then diluted with water and extracted with ethyl acetate. After the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent (20:1, V/V) to recovery **1a**.

Procedure for the synthesis of 1a-d To a oven-dried sealed tube was added *N*-aryl-7-azaindoles **1** (38.8 mg, 0.2 mmol), $[(RhCp_2Cl_2)]Cl_2$ (6.18 mg, 0.01mol), $Cu(OAc)_2 . H_2O$ (40 mg, 0.2 mmol), D_2O (40 mg, 2 mmol) and toluene (2.0 mL). The mixture was stirred at 120 ^{o}C for 4 hours. The reaction mixture was then diluted with water and extracted with ethyl acetate. After the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent (20:1, V/V) to afford the **1a-d (**36 mg of 90% yield and 92% of deuterium).



Procedures of *KIE* experiments

To a 5 mL tube equipped with a magnetic stirring bar, *N*-aryl-7-azaindole **1a** (19.4 mg, 0.1 mmol), diphenyl disulfide **2a** (32.7 mg, 0.15 mmol), $Cu(OAc)_2$ (3.6 mg, 0.02 mmol), PhCOOH (2.4 mg, 0.02 mmol) and mesitylene (1 mL) were added. No special precautions were taken to exclude moisture and air. The reaction was stirred at 140 ^{o}C for 2 h. The reaction mixture was then diluted with water and extracted with ethyl acetate. After the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent (8:1, V/V) to afford the pure product **3a** 4.68 mg of 15.5% yield.

To a 5 mL tube equipped with a magnetic stirring bar, **1a-d** (20.0 mg, 0.1 mmol), diphenyl disulfide **2a** (32.7 mg, 0.15 mmol), $Cu(OAc)_2$ (3.6 mg, 0.02 mmol), PhCOOH (2.4 mg, 0.02 mmol) and mesitylene (1 mL) were added. No special precautions were taken to exclude moisture and air. The reaction was stirred at 140 ^{o}C

for 2 h. The reaction mixture was then diluted with water and extracted with ethyl acetate. After the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent (8:1, V/V) to afford the pure product **3a'** 4.01 mg of 13.2% yield.

Procedures of investigate the role of PhCOOH

To a 25 mL tube equipped with a magnetic stirring bar, CuO (160 mg, 2 mol) and PhCOOH (732 mg, 6 mol) was diulated in 10 mL (V H_2O /MeOH= 1:1), the mixture was reflux for 4h, and extraction gave the pure $Cu(PhCOOH)_2$.

To a oven-dried sealed tube was added *N*-aryl-7-azaindoles **1a** (38.8 mg, 0.2 mmol), diphenyl disulfide **2a** (65.4 mg, 0.3 mmol), $Cu(PhCOO)_2$ (12.1 mg, 0.04 mol), PhCOOH (4.9 mg, 0.04 mmol) and mesitylene 2 mL. The mixture was stirred at 140 ^oC for 12 hours. The reaction mixture was then diluted with water and extracted with ethyl acetate. After the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent (8:1, V/V) to afford the pure product **3a** 7.25 mg of 12% yield.

To a oven-dried sealed tube was added *N*-aryl-7-azaindoles **1a** (38.8 mg, 0.2 mmol), diphenyl disulfide **2a** (65.4 mg, 0.3 mmol), $Cu(PhCOO)_2$ (12.1 mg, 0.04 mol) and mesitylene 2 mL. The mixture was stirred at 140 ^oC for 12 hours. The reaction mixture was then diluted with water and extracted with ethyl acetate. After the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent (8:1, V/V) to afford the pure product **3a** 13.28 mg of 5% yield.

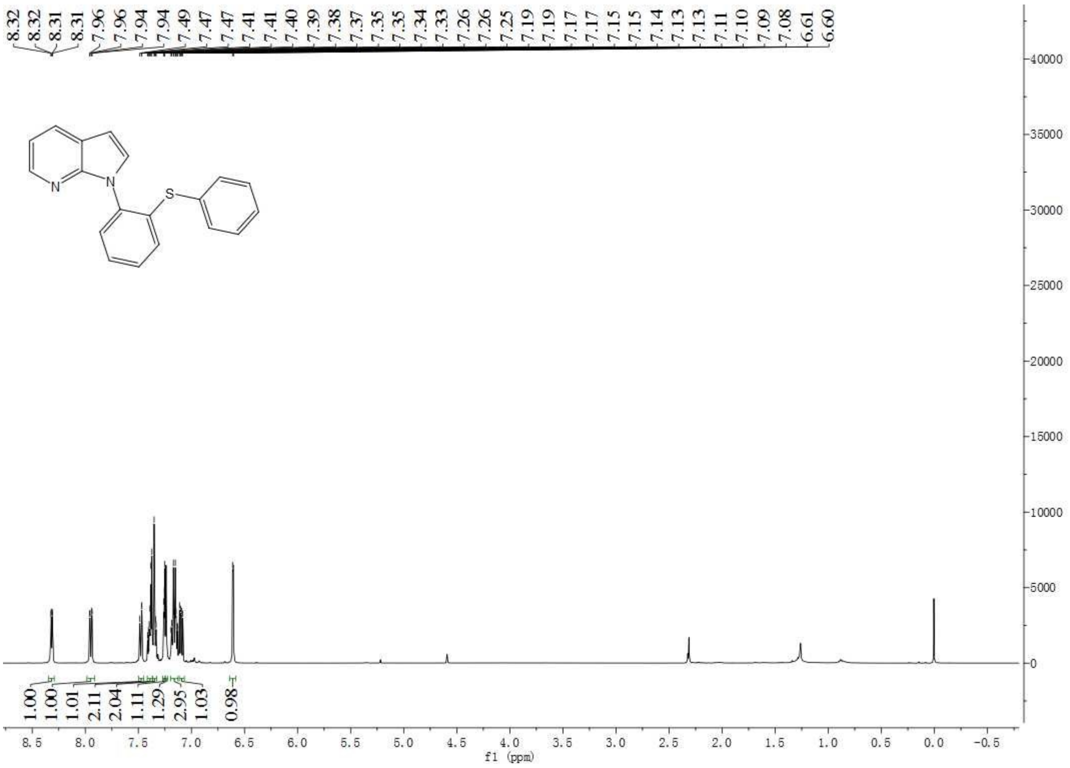
2. Reference

[1] Vats, T. K.; Mishra, A.; Deb, I. *Adv. Synth. Catal.* **2017**, *360*, 2291.

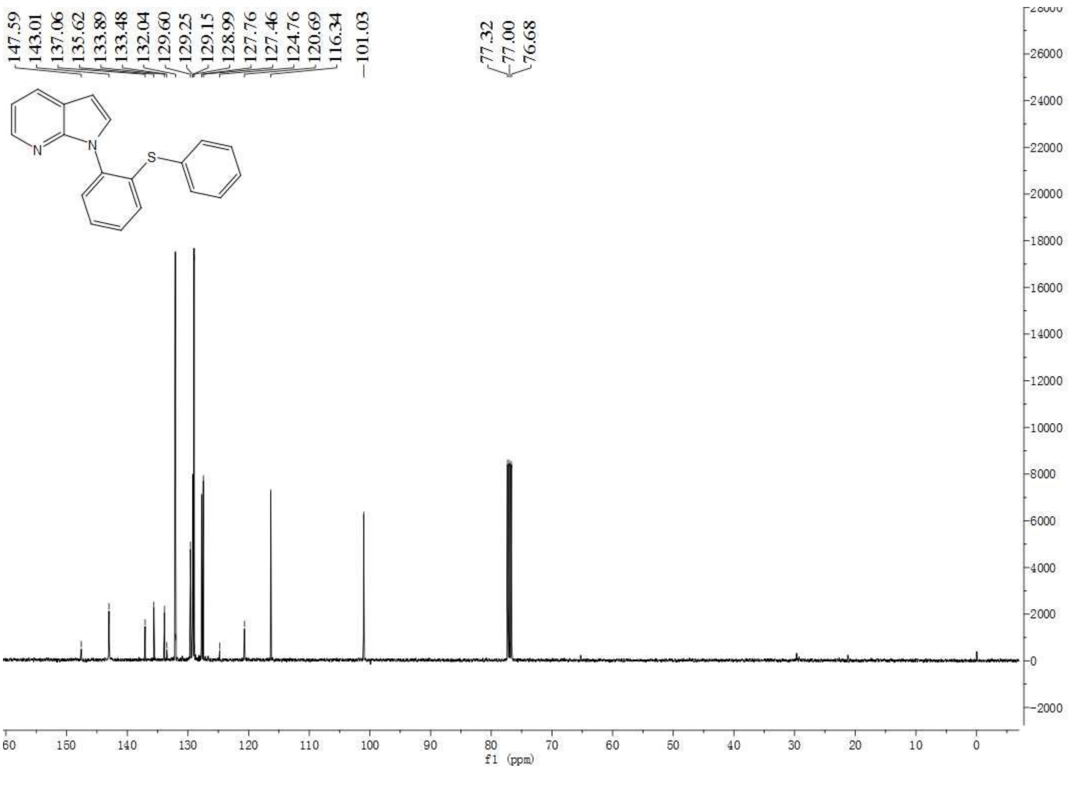
[2] Coelho, F. L.; Campo, L. F. *Tetrahedron. Lett.* **2017**, 14, 2330.

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

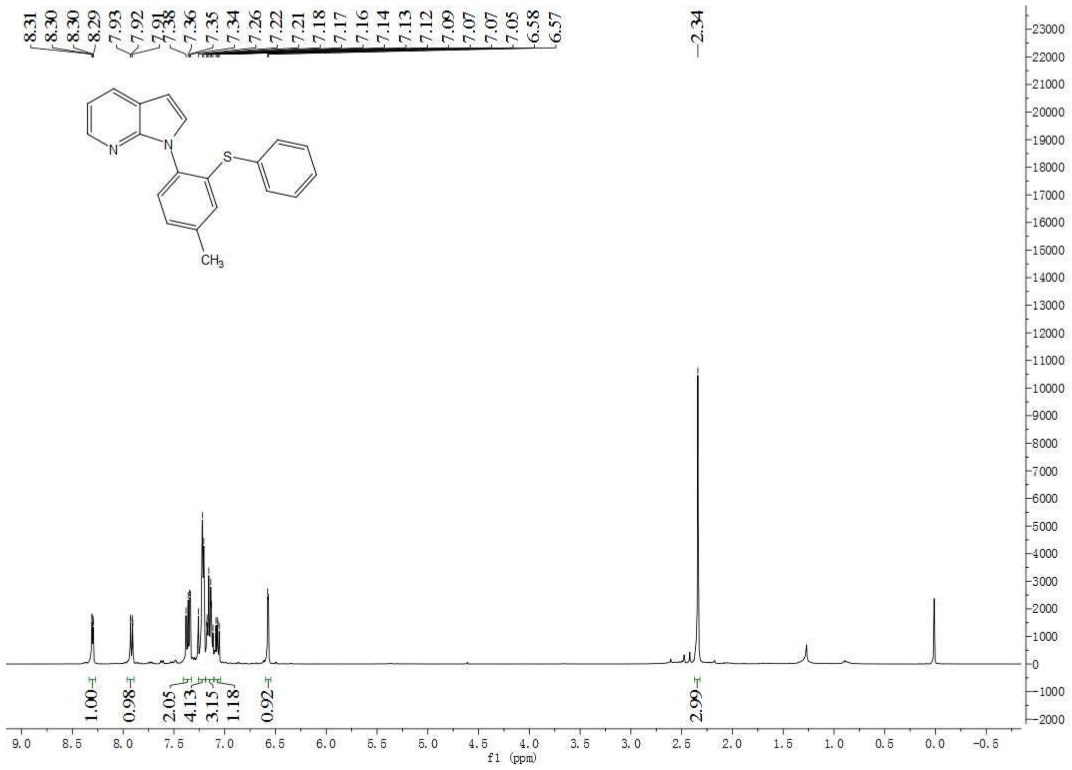
^{1}H NMR spectrum of 3a in $CDCl_3$



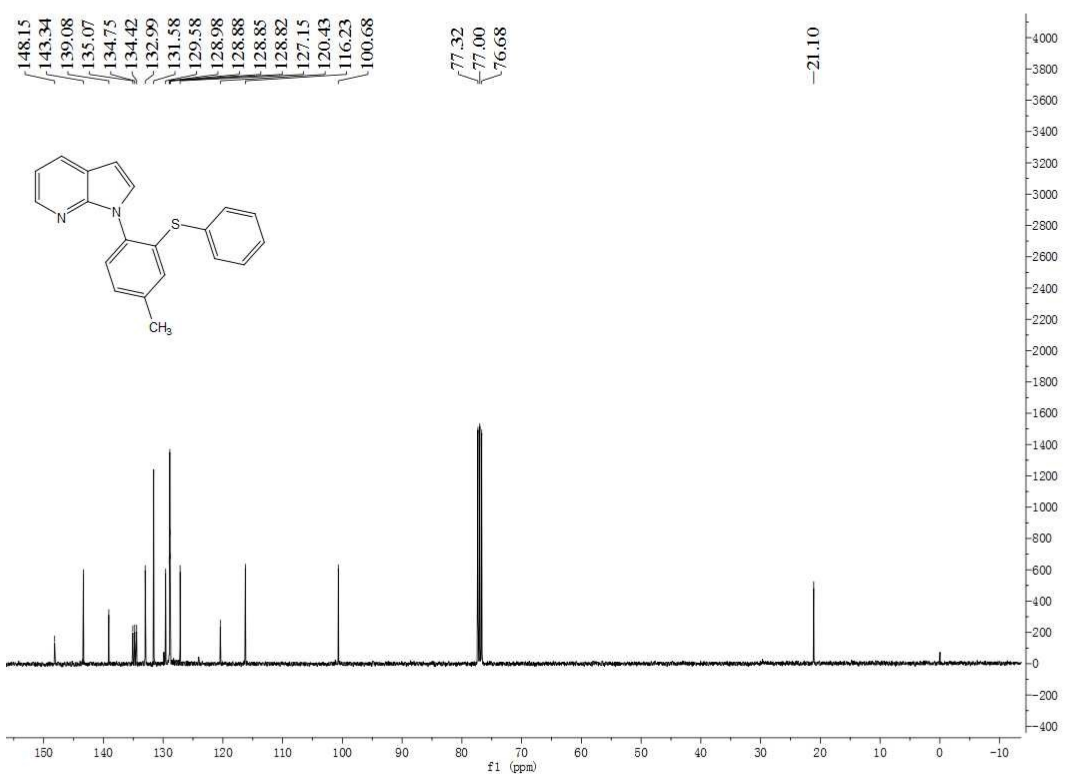
^{13}C NMR spectrum of 3a in $CDCl_3$



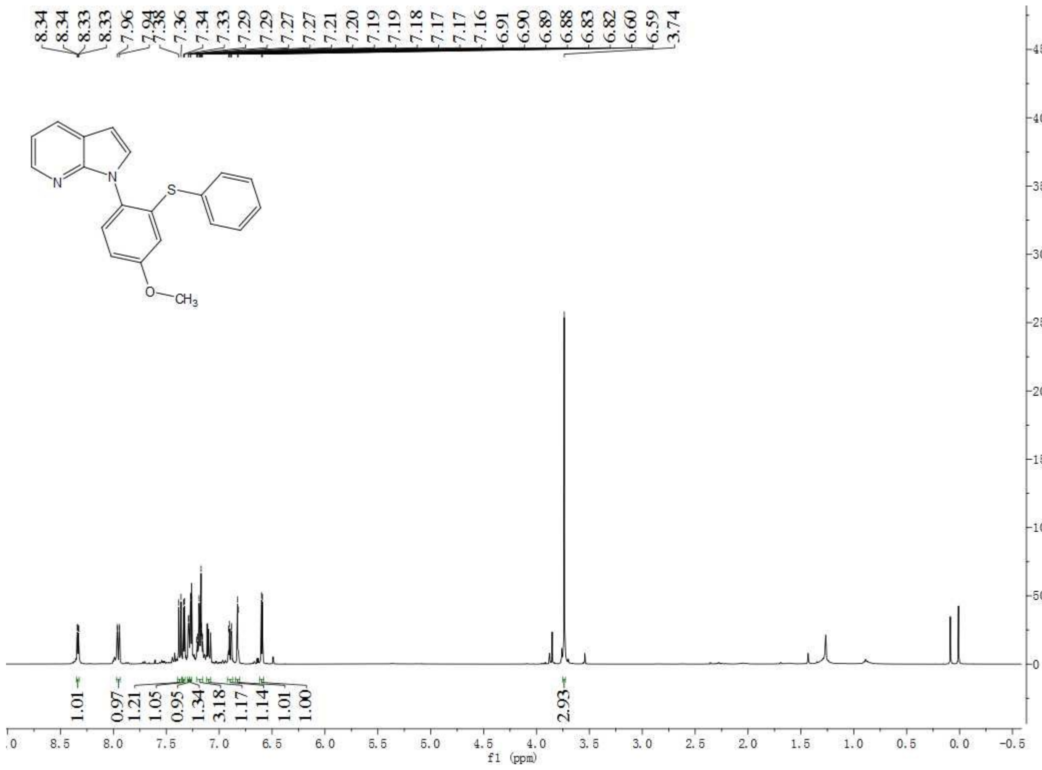
^{1}H NMR spectrum of 3b in $CDCl_3$



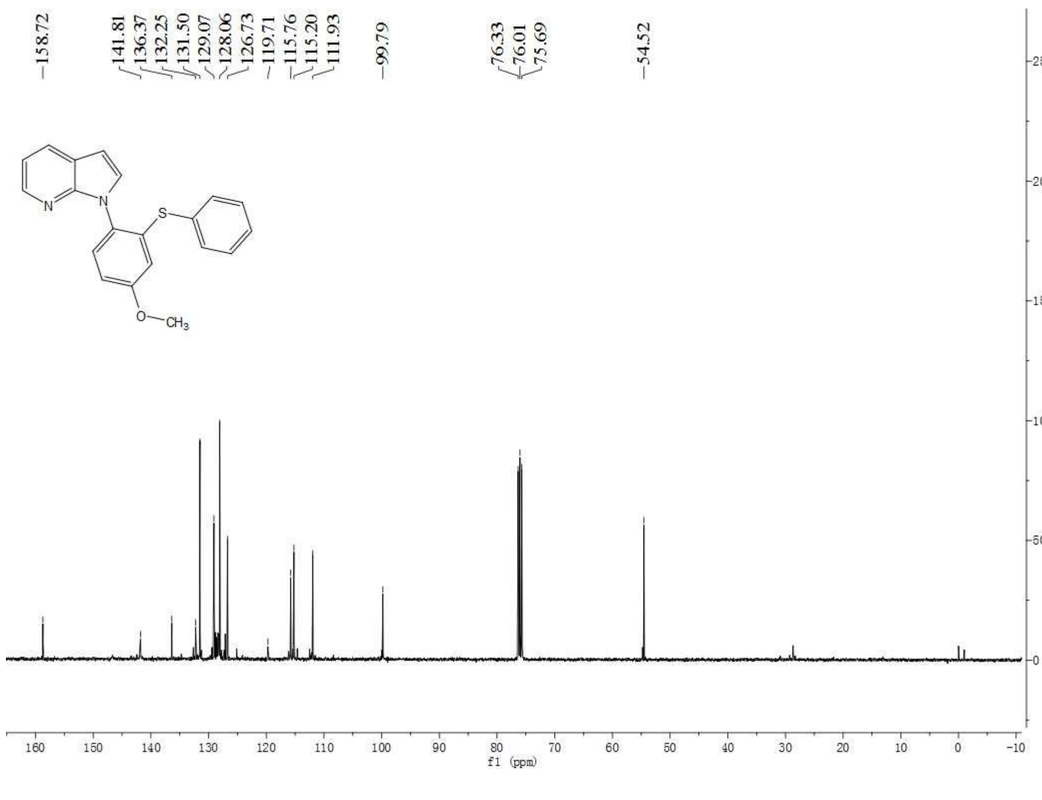
^{13}C NMR spectrum of 3b in $CDCl_3$



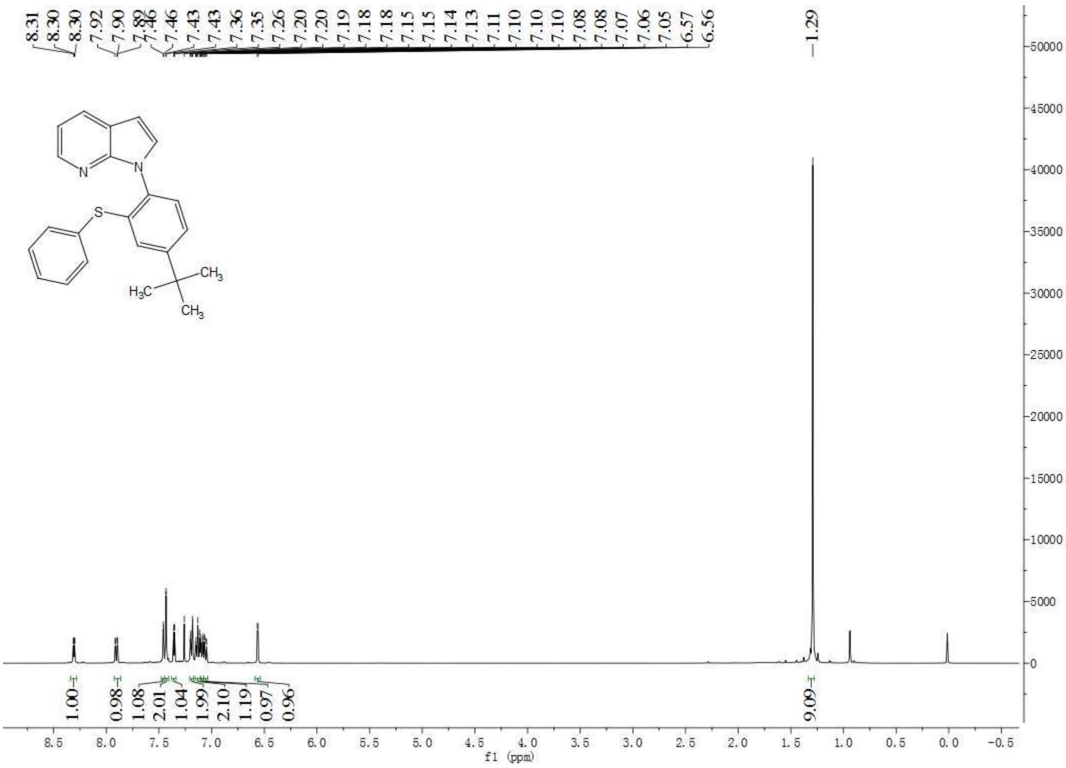
^{1}H NMR spectrum of 3c in $CDCl_3$



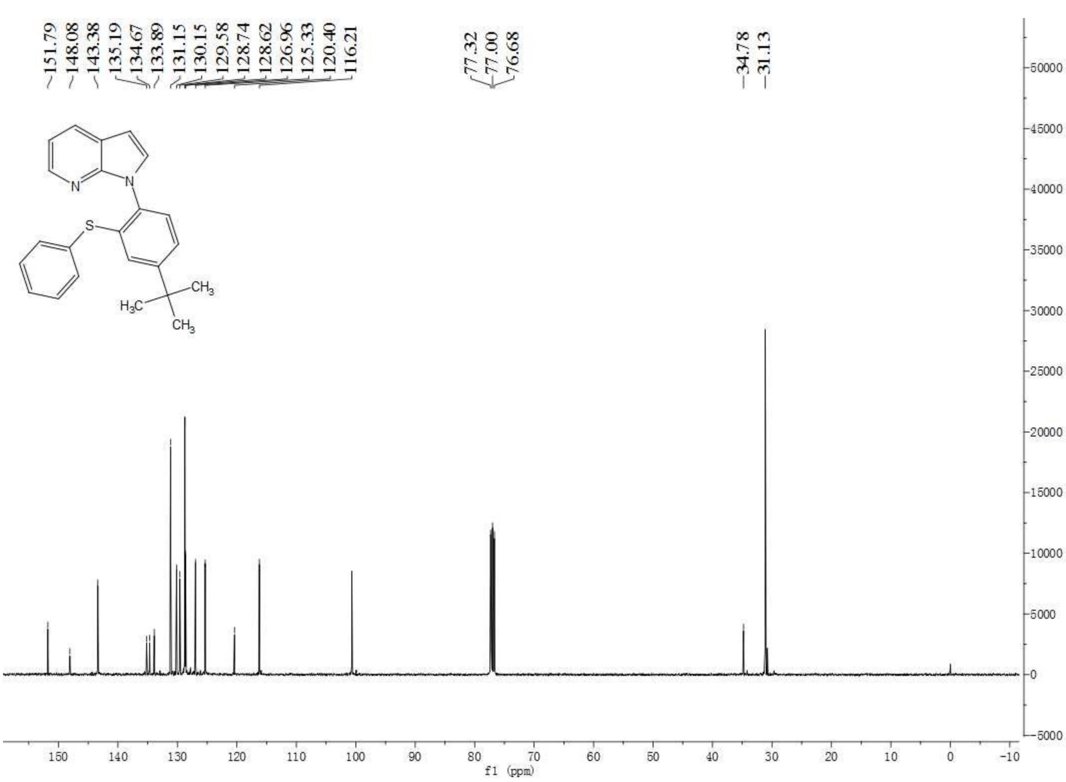
^{13}C NMR spectrum of 3c in $CDCl_3$



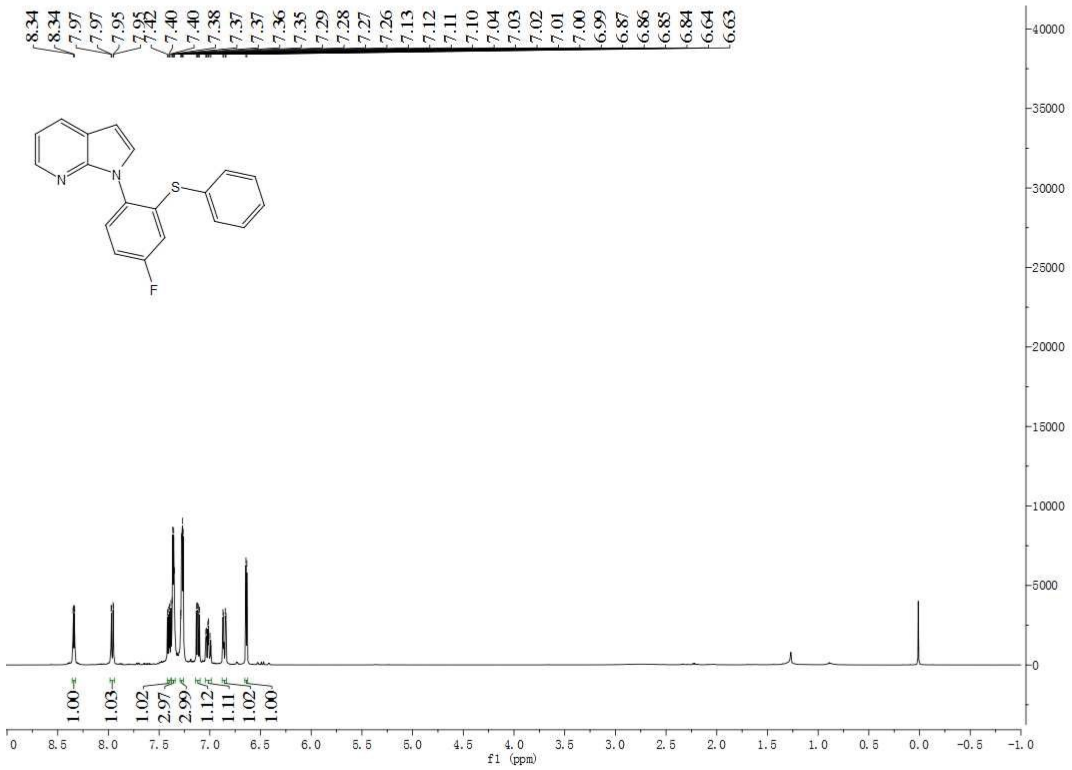
^{1}H NMR spectrum of 3d in $CDCl_3$



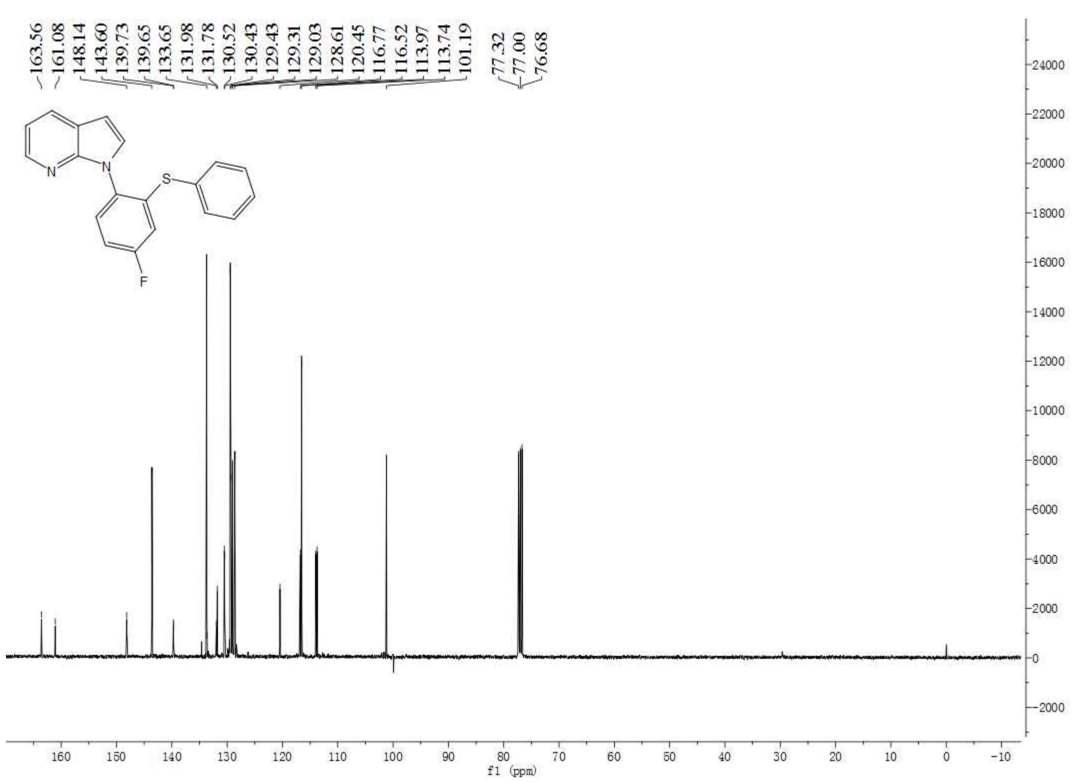
^{13}C NMR spectrum of 3d in $CDCl_3$



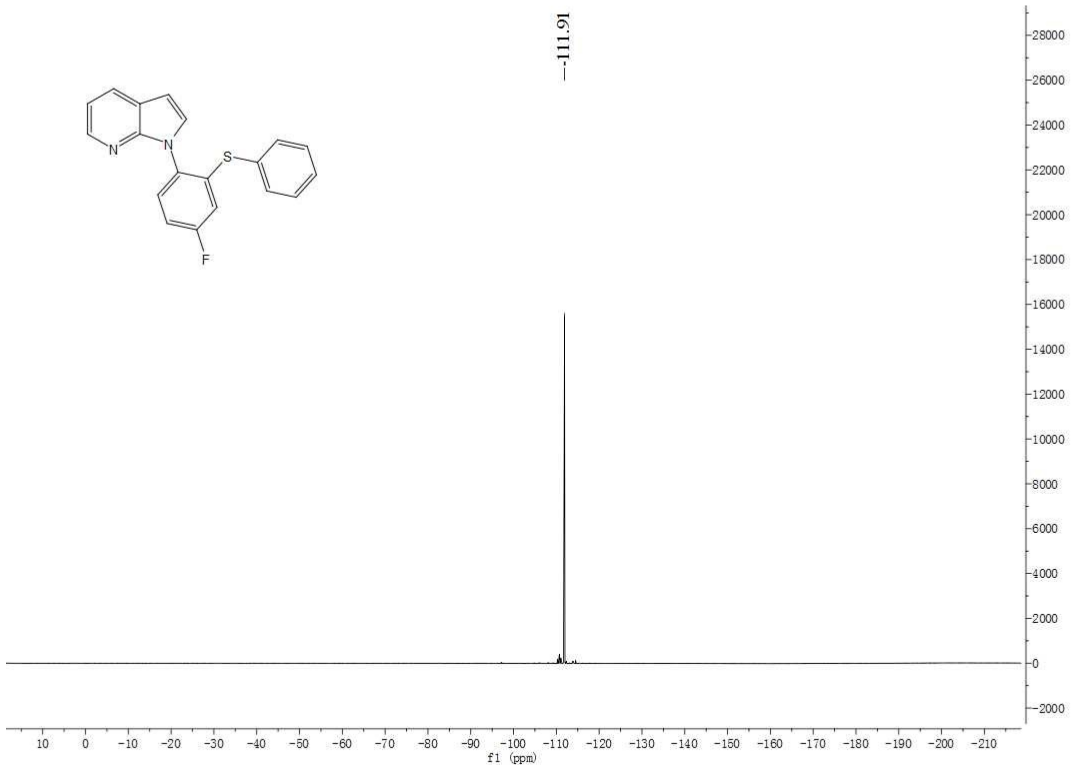
^{1}H NMR spectrum of 3e in $CDCl_3$



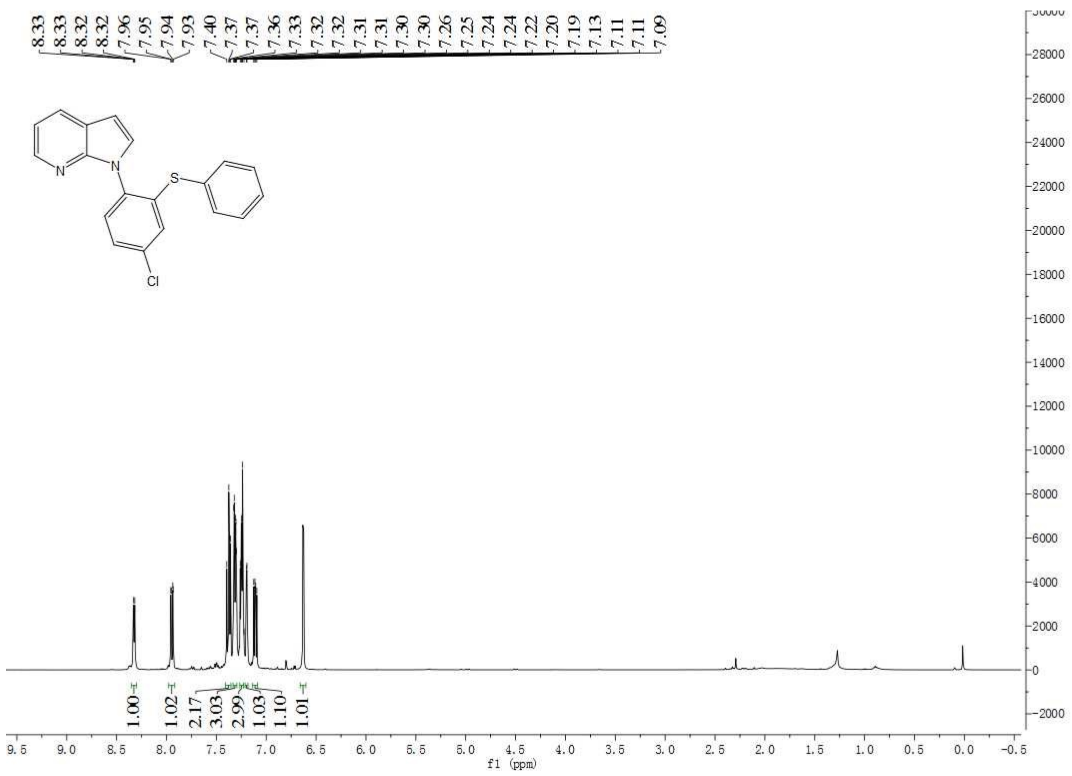
^{13}C NMR spectrum of 3e in $CDCl_3$



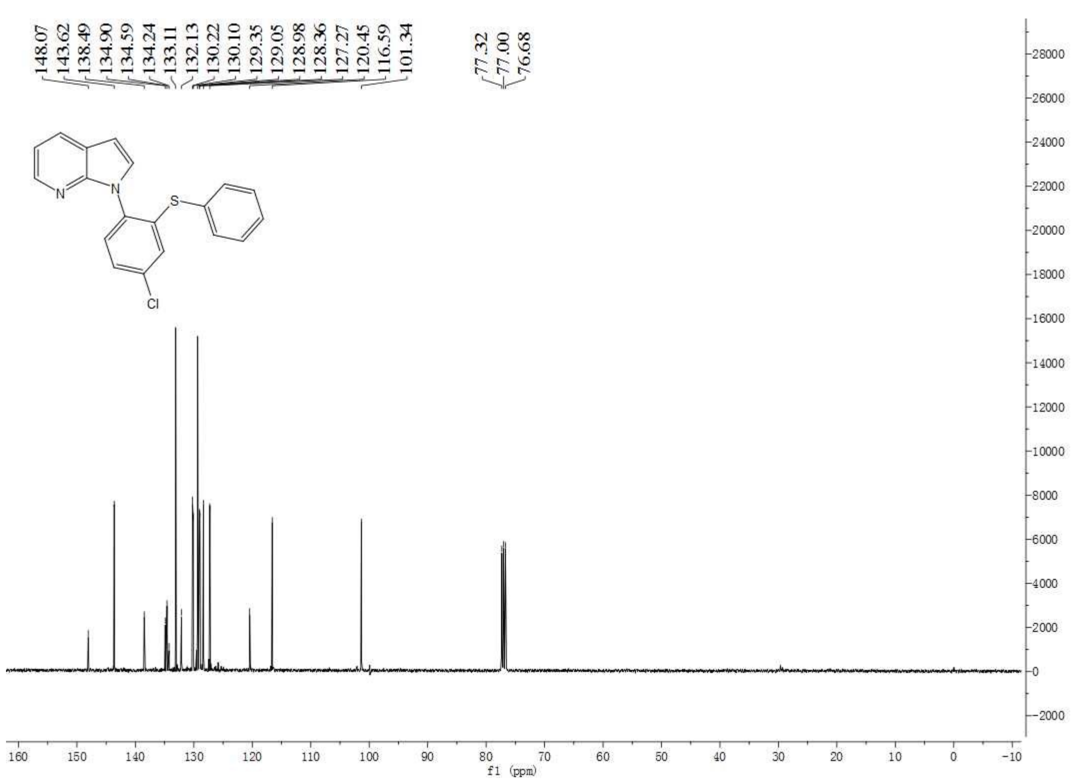
^{19}F NMR spectrum of 3e in $CDCl_3$



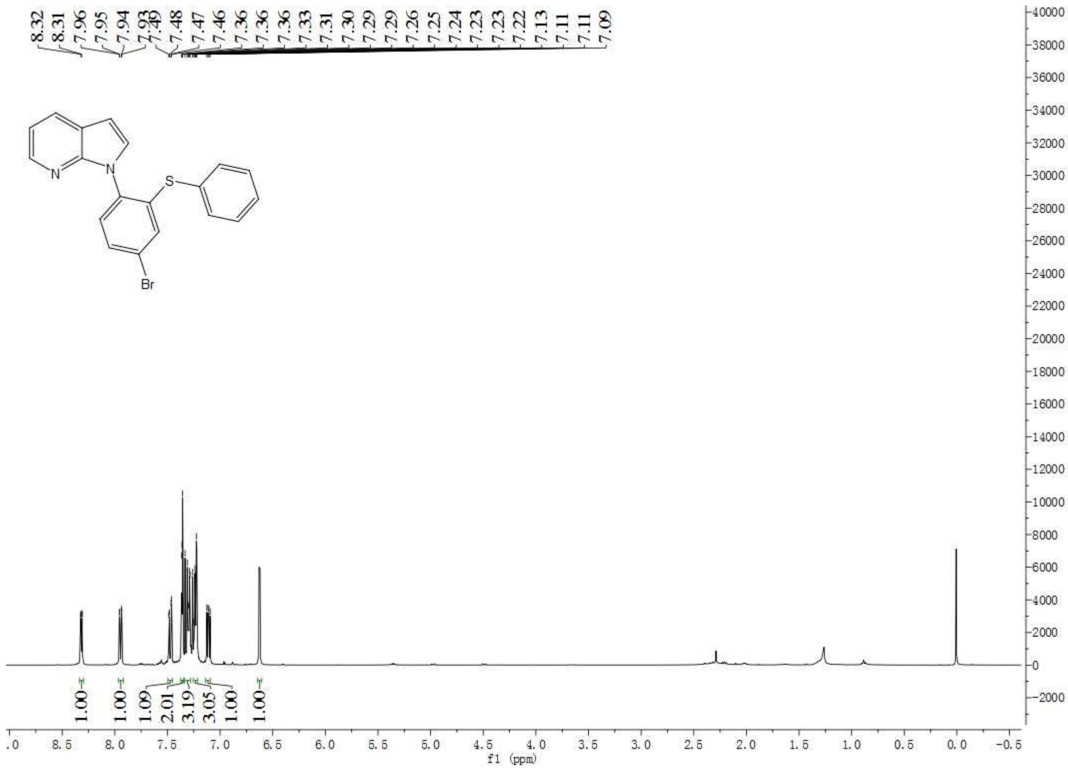
^{1}H NMR spectrum of 3f in CDCl$_3$



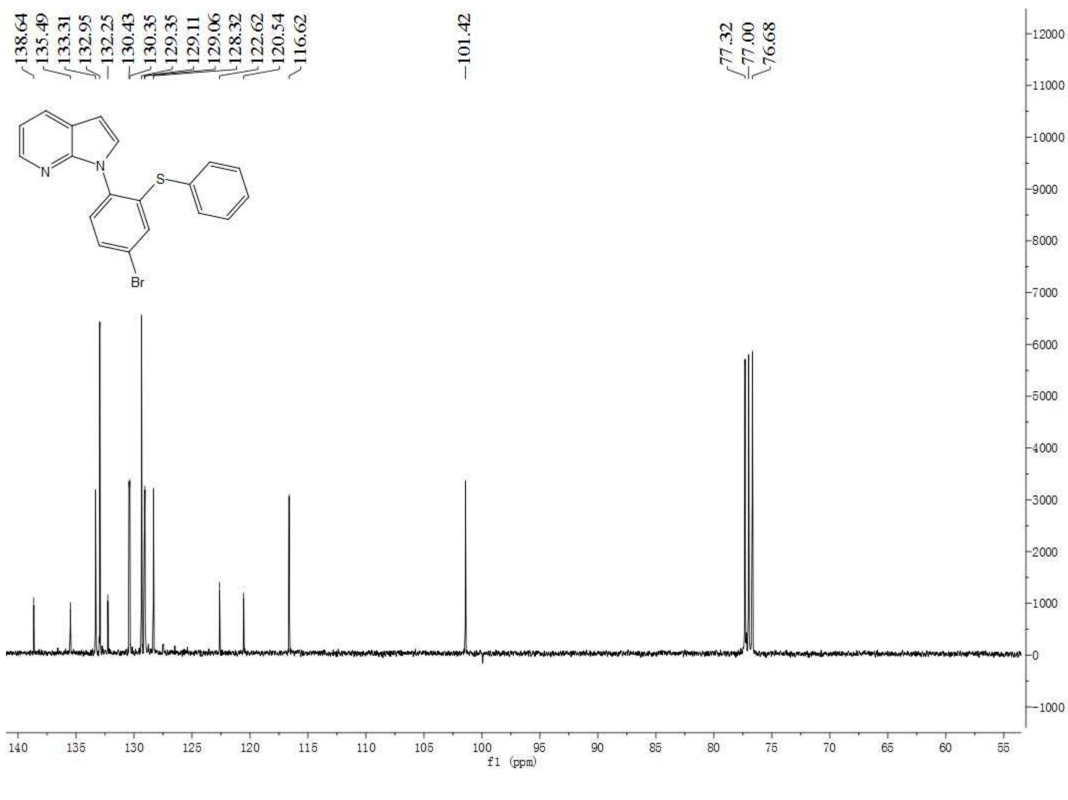
^{13}C NMR spectrum of 3f in CDCl$_3$



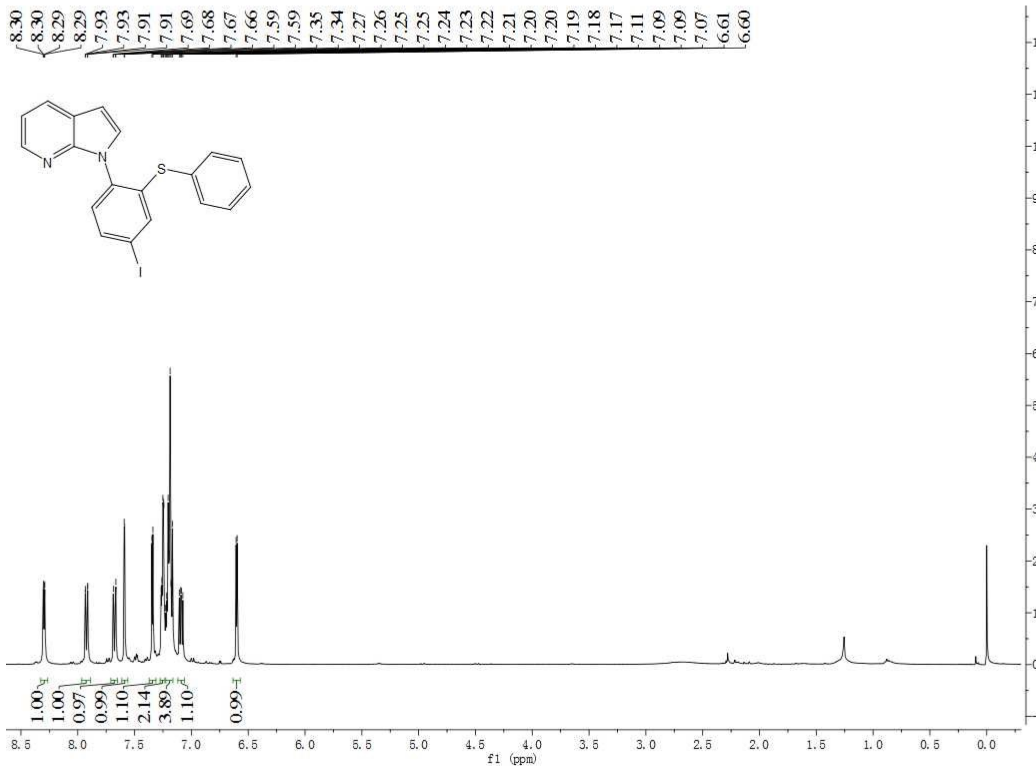
[1]H NMR spectrum of 3g in CDCl$_3$



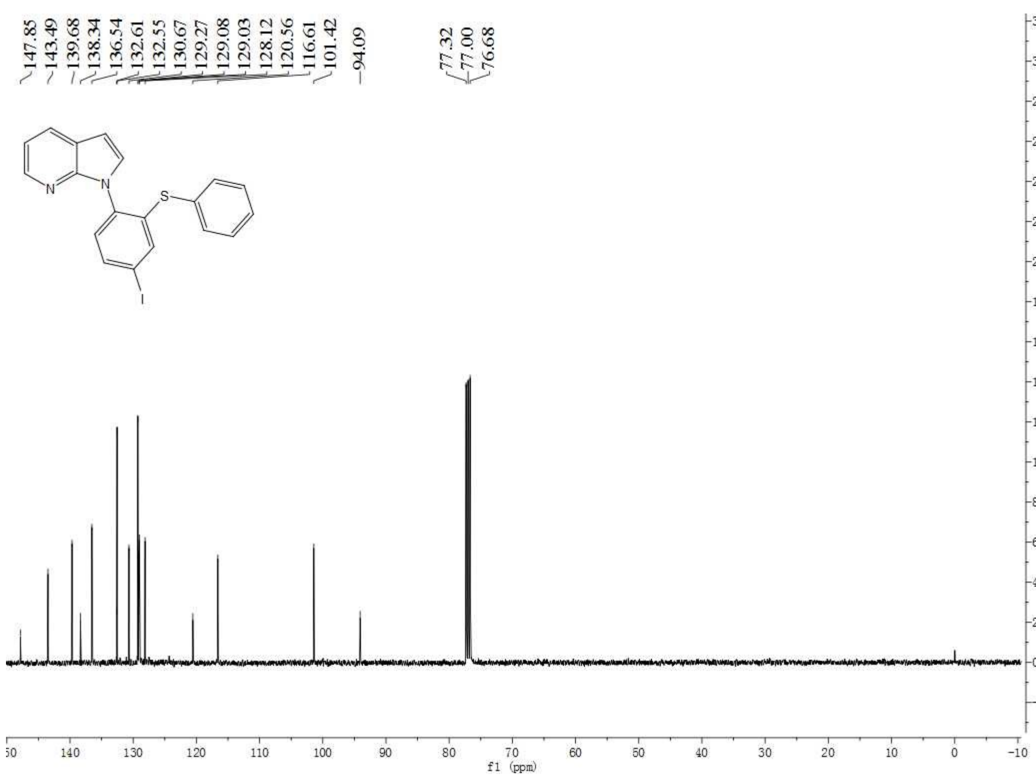
[13]C NMR spectrum of 3g in CDCl$_3$



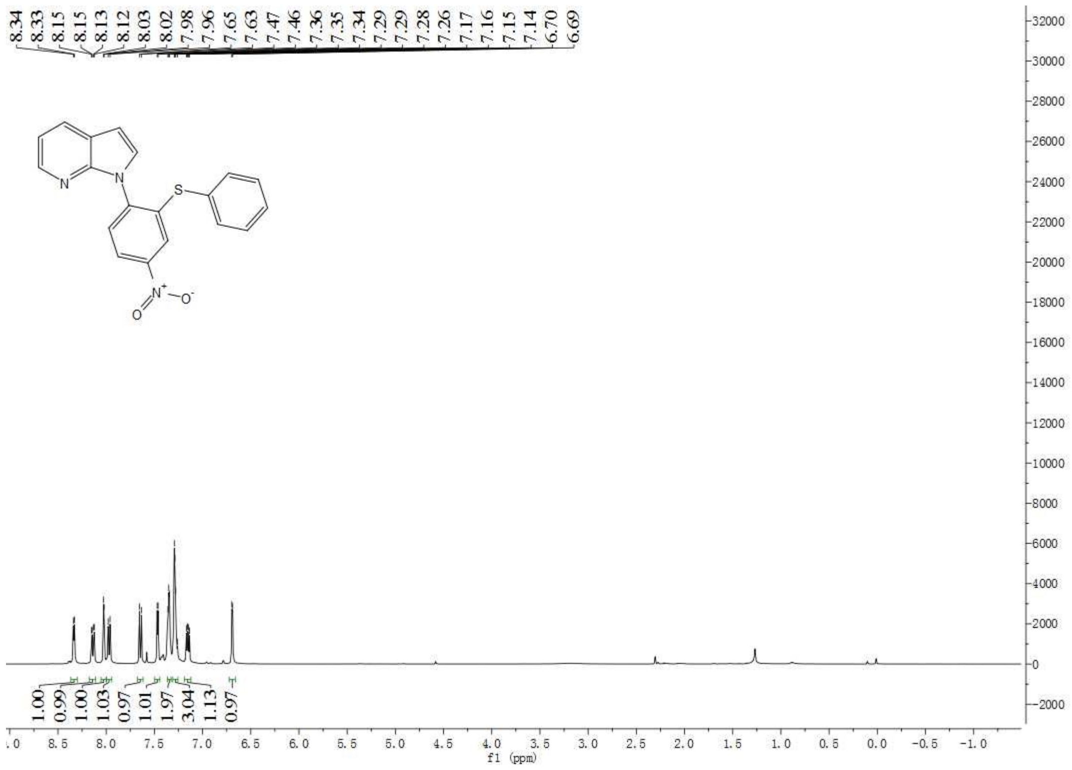
^{1}H NMR spectrum of 3h in $CDCl_3$



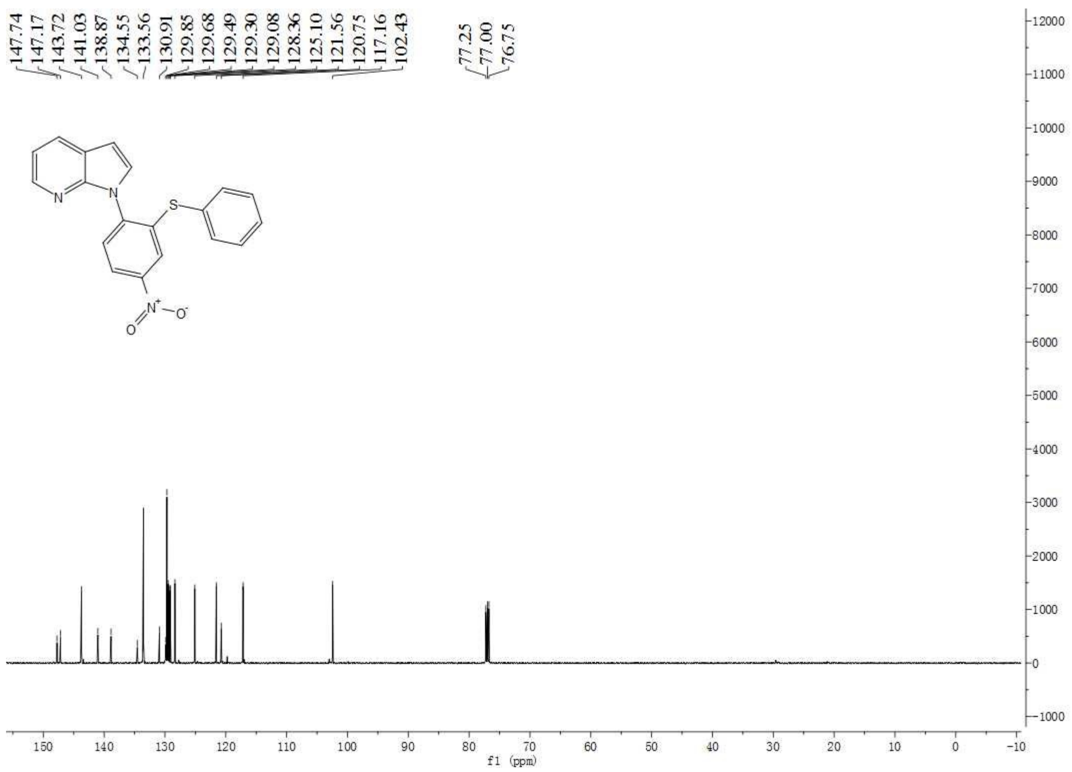
^{13}C NMR spectrum of 3h in $CDCl_3$



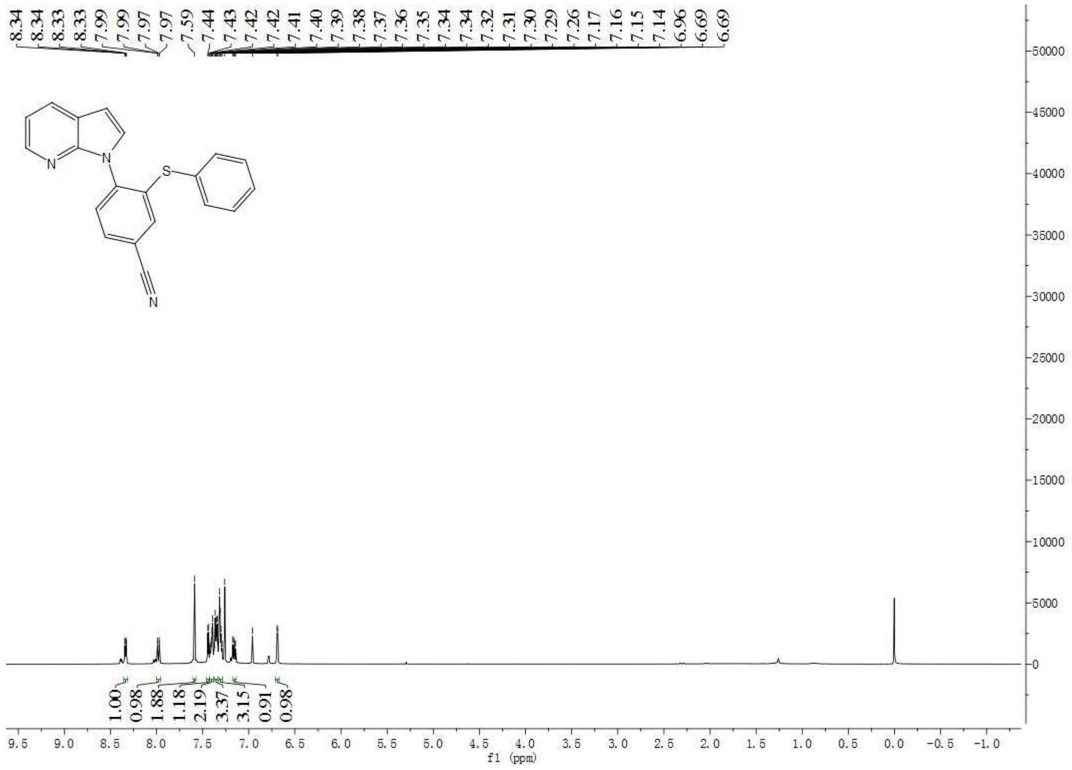
^{1}H NMR spectrum of 3i in $CDCl_3$



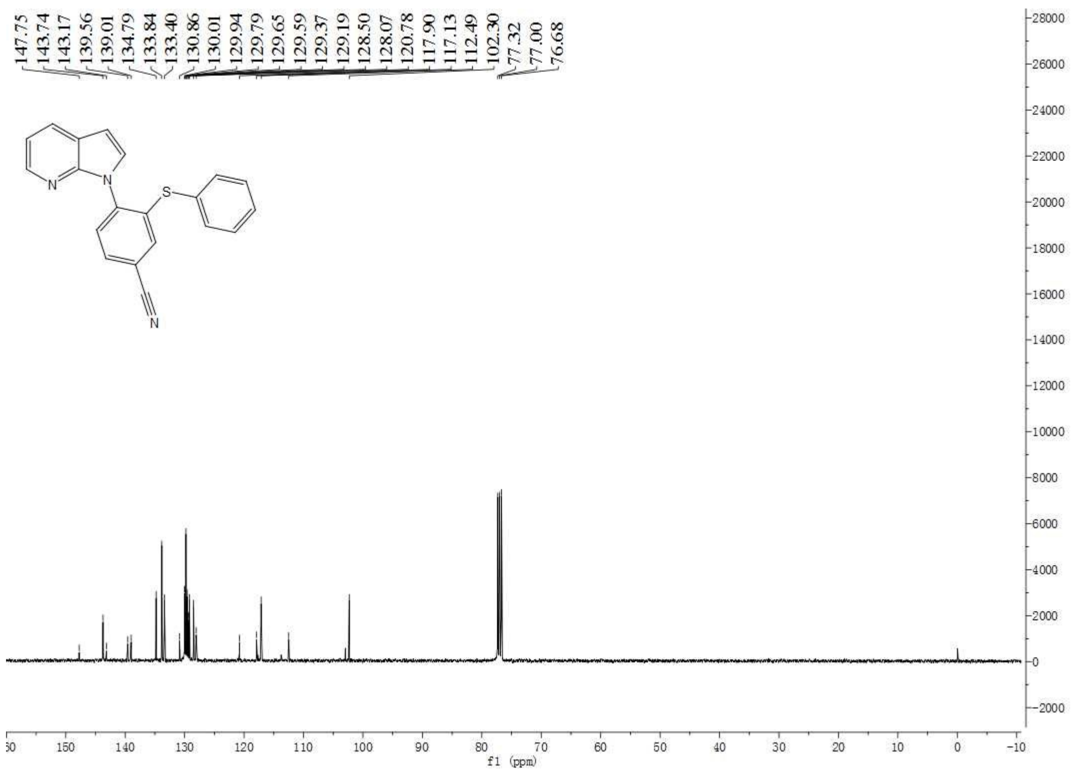
^{13}C NMR spectrum of 3i in $CDCl_3$



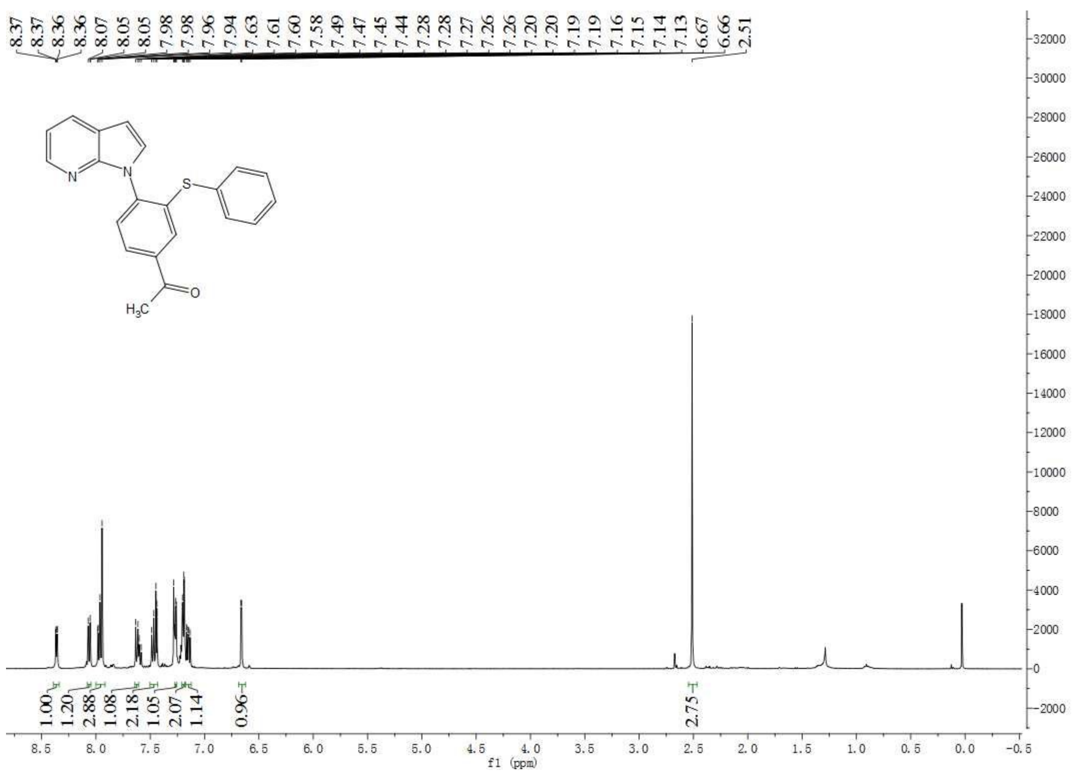
^{1}H NMR spectrum of 3j in CDCl$_3$



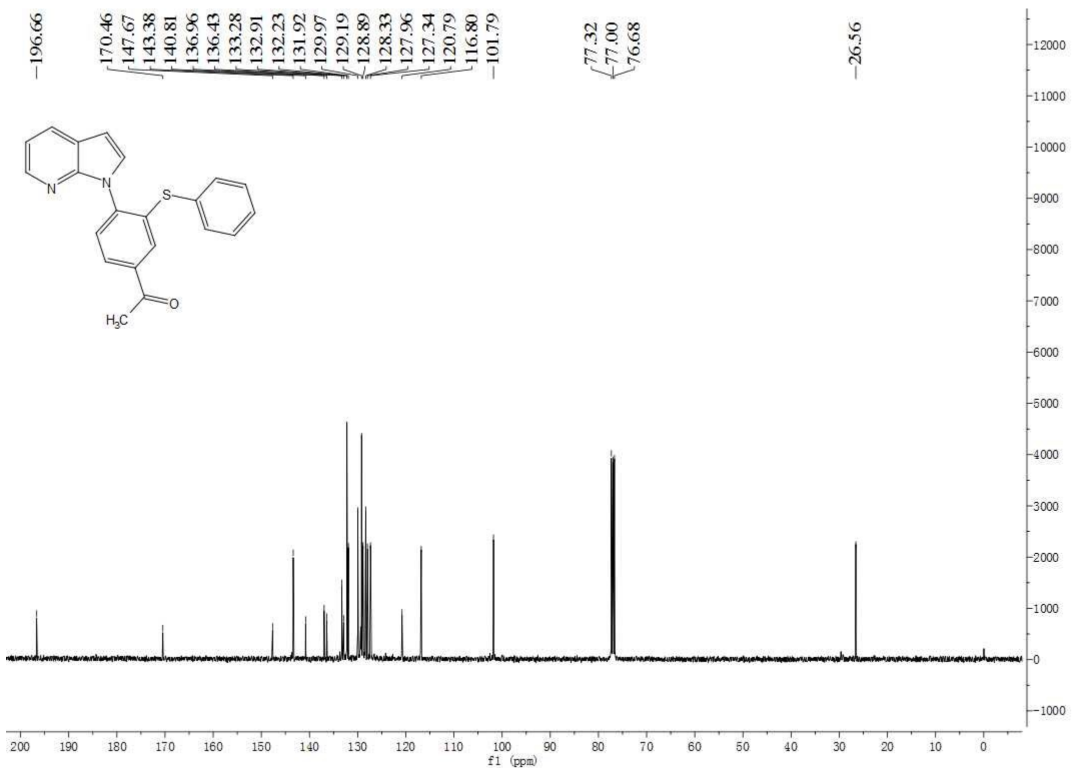
^{13}C NMR spectrum of 3j in CDCl$_3$



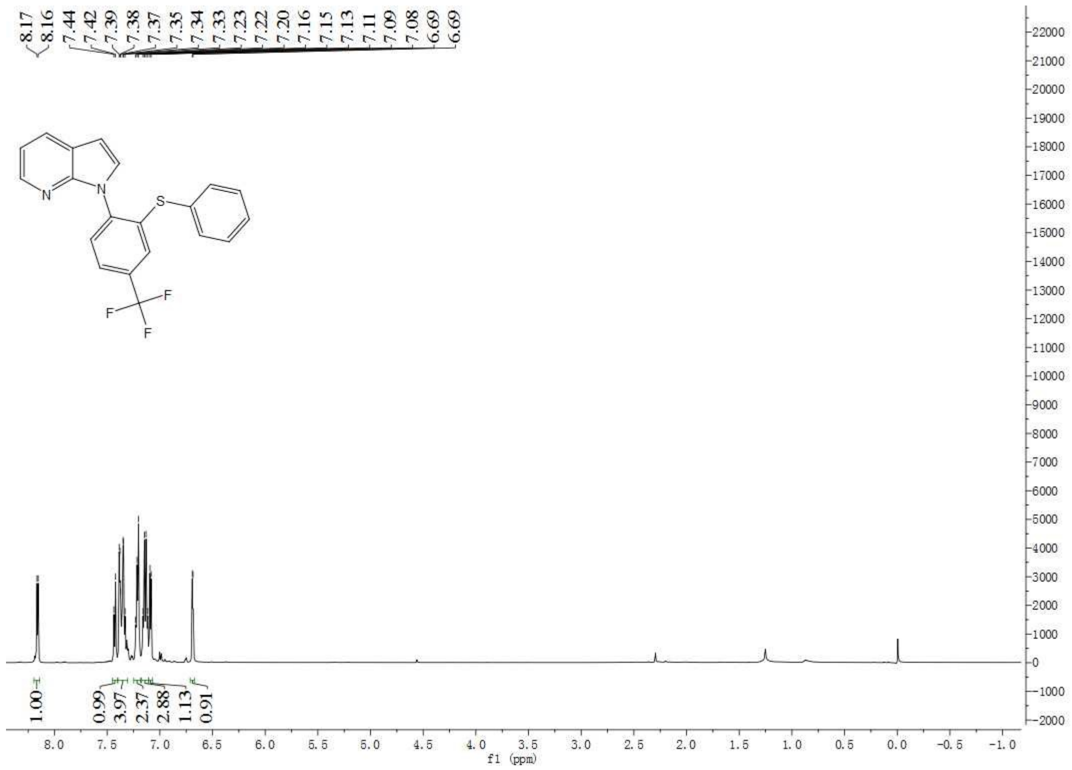
^{1}H NMR spectrum of 3k in $CDCl_3$



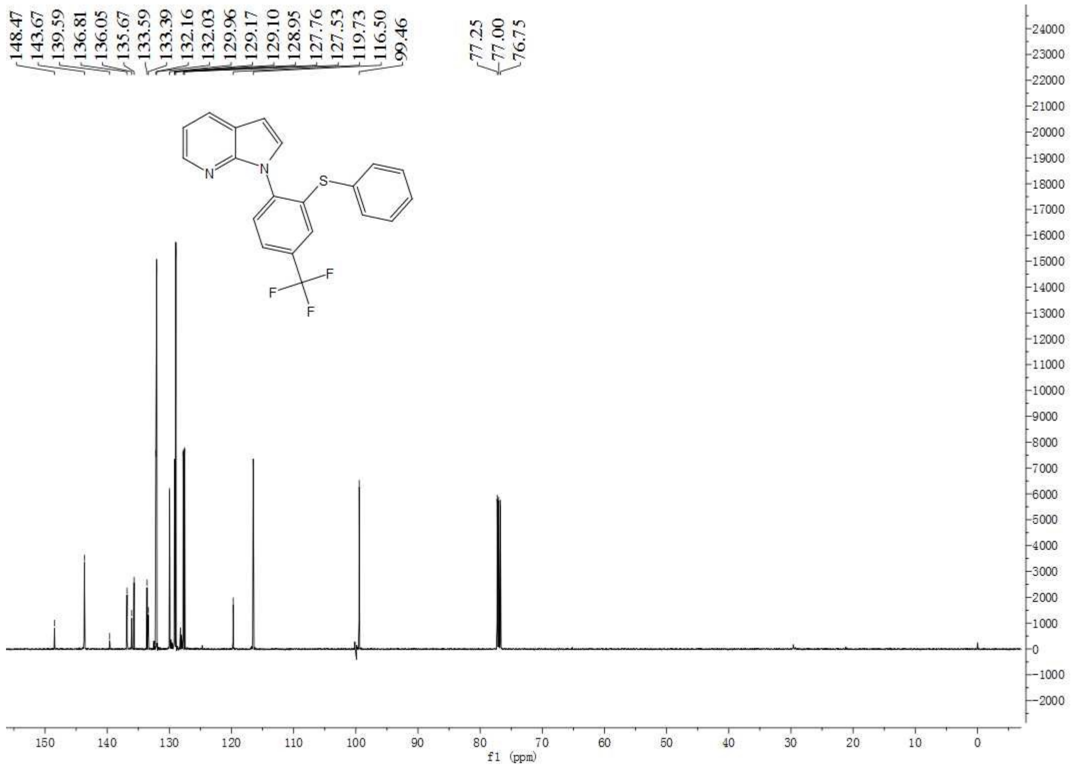
^{13}C NMR spectrum of 3k in $CDCl_3$



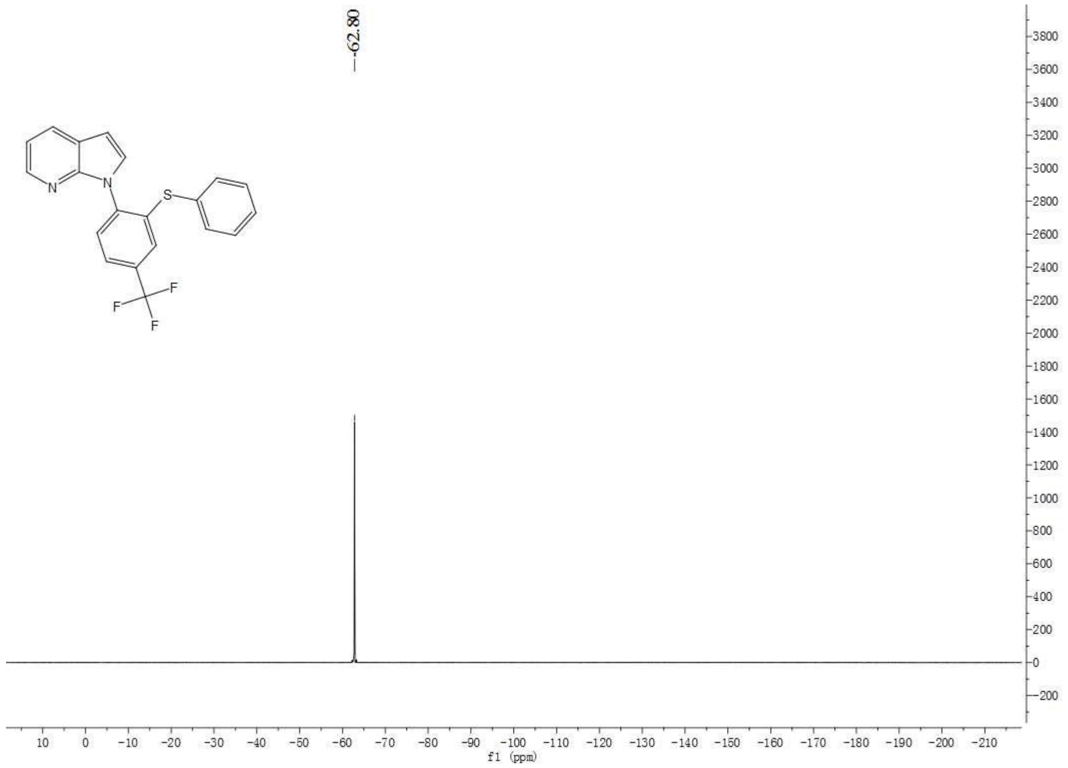
^{1}H NMR spectrum of 3l in $CDCl_3$



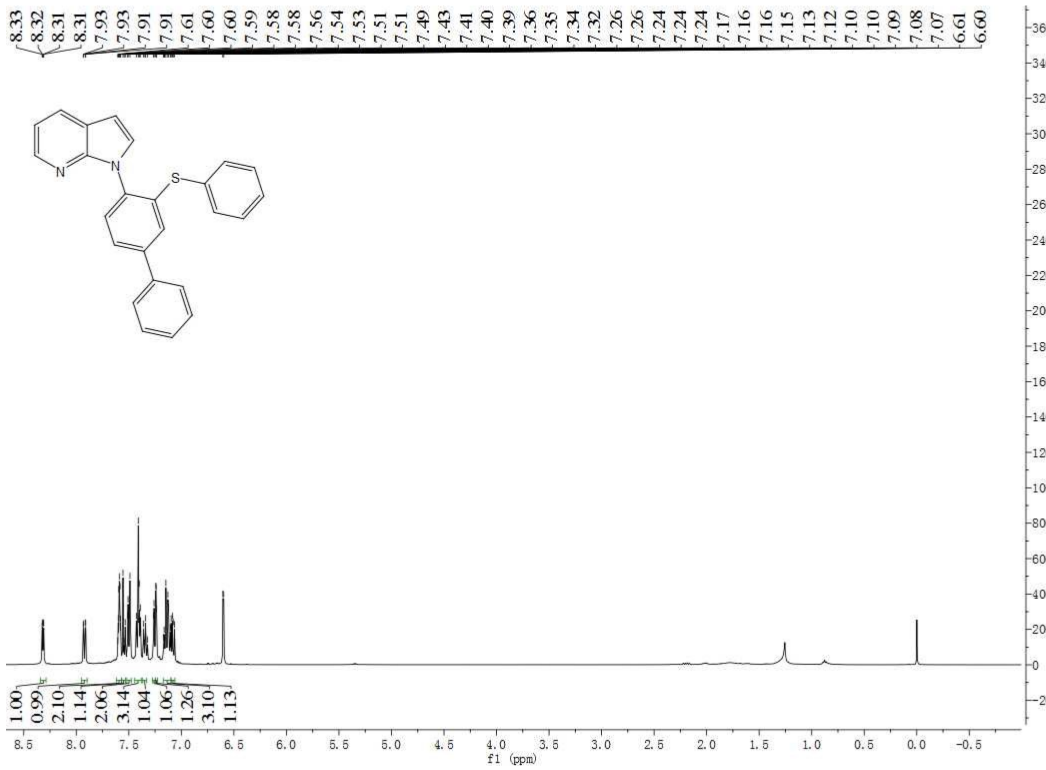
^{13}C NMR spectrum of 3l in $CDCl_3$



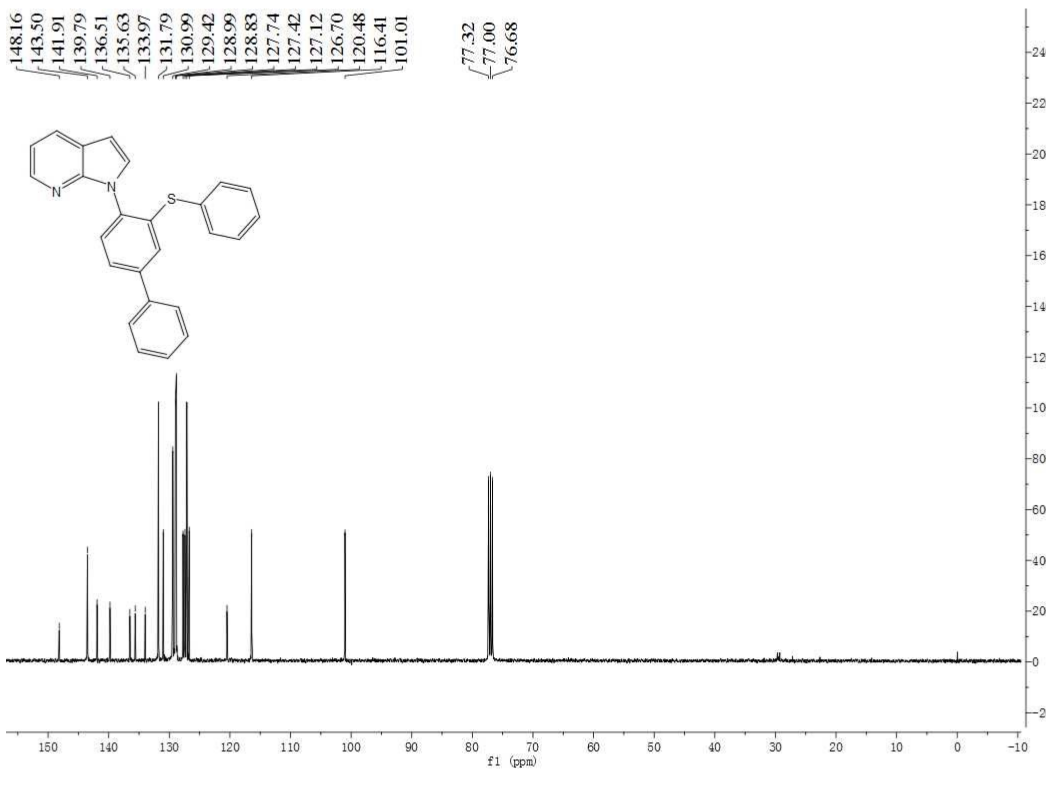
^{19}F NMR spectrum of 3l in $CDCl_3$



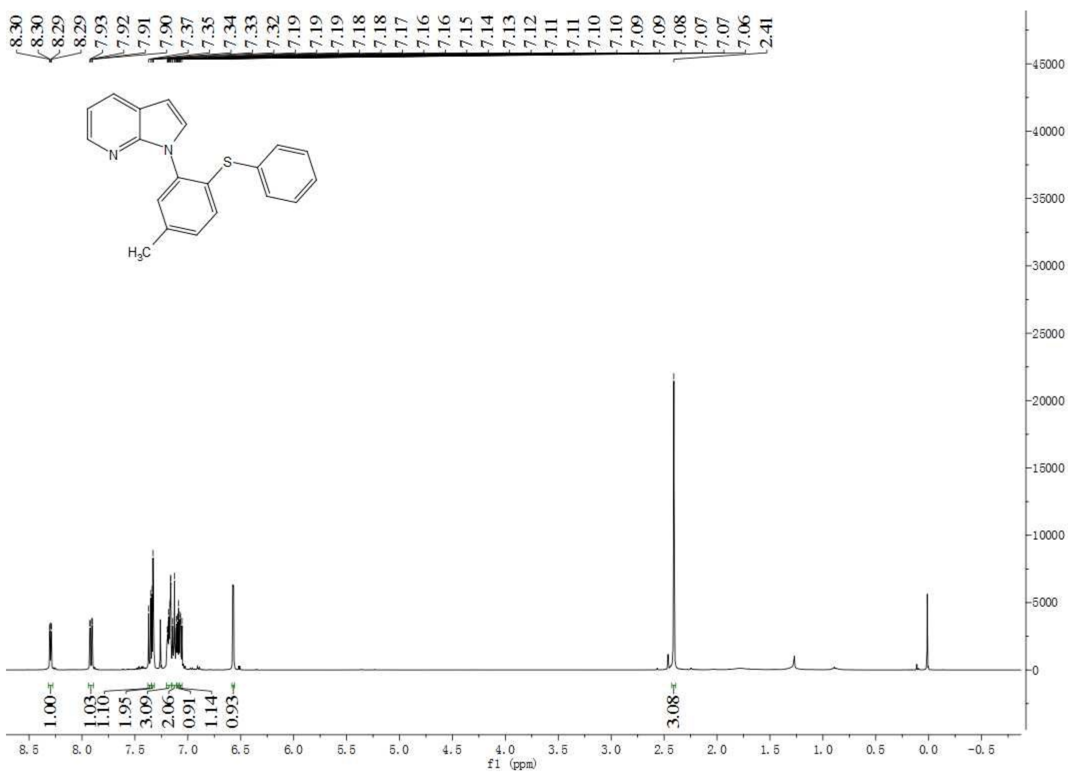
^{1}H NMR spectrum of 3m in $CDCl_3$



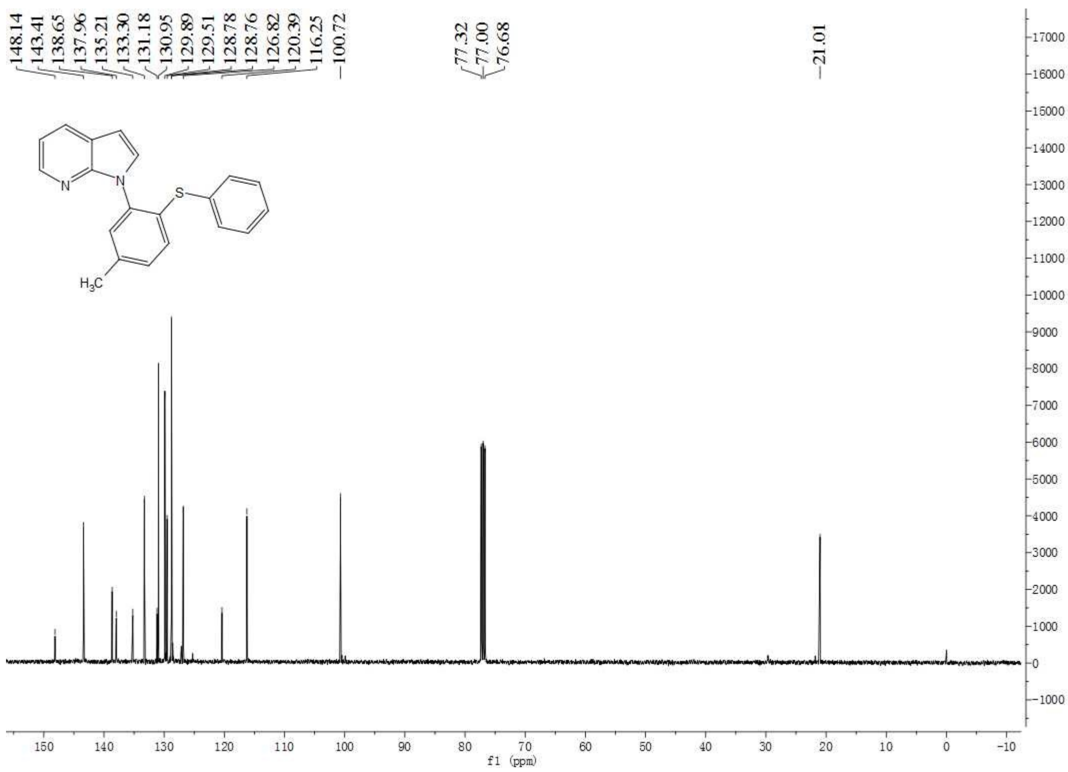
^{13}C NMR spectrum of 3m in $CDCl_3$



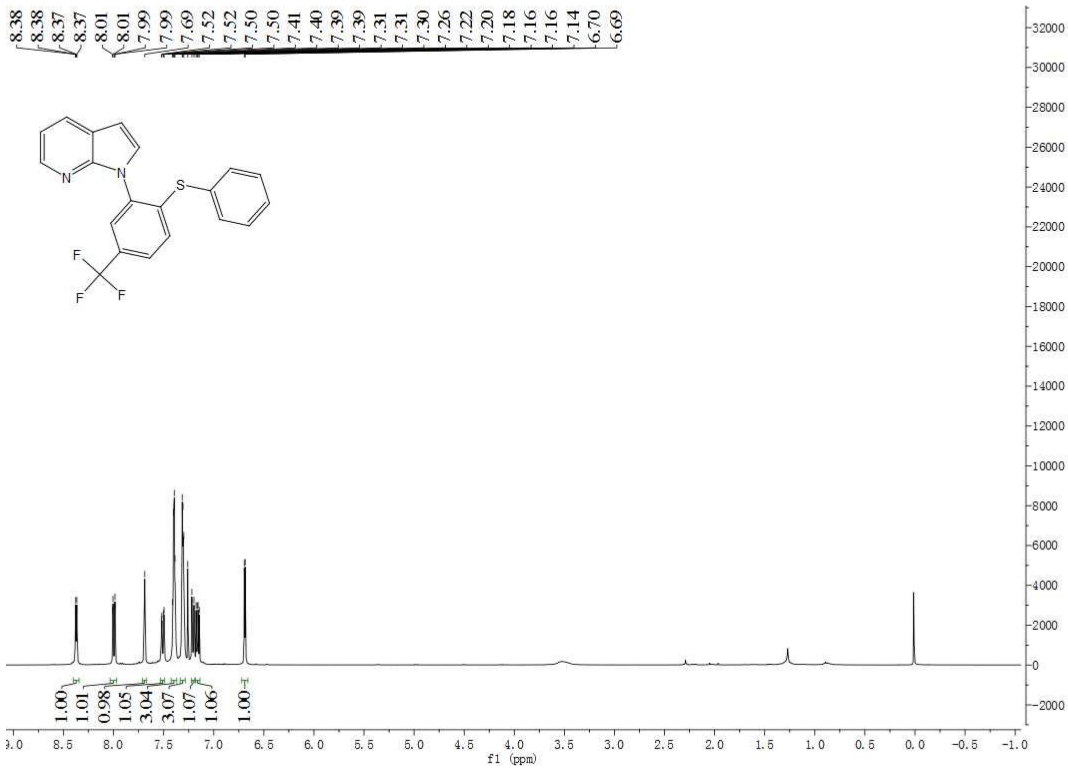
^{1}H NMR spectrum of 3n in CDCl$_3$



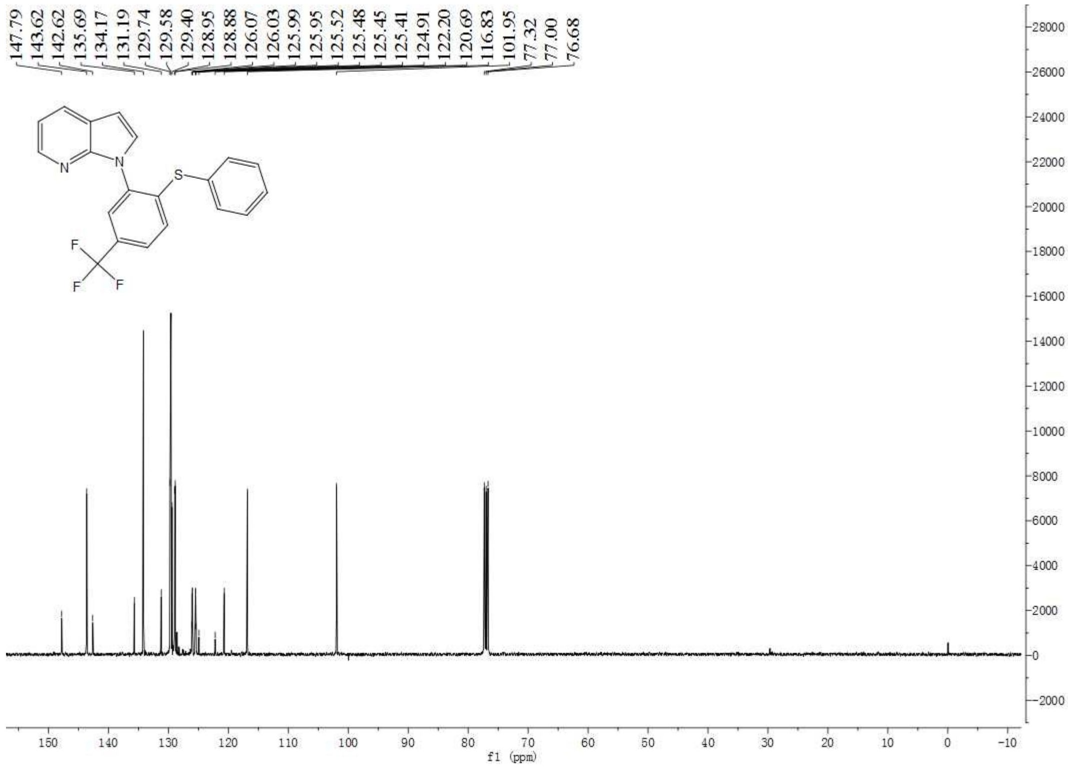
^{13}C NMR spectrum of 3n in CDCl$_3$



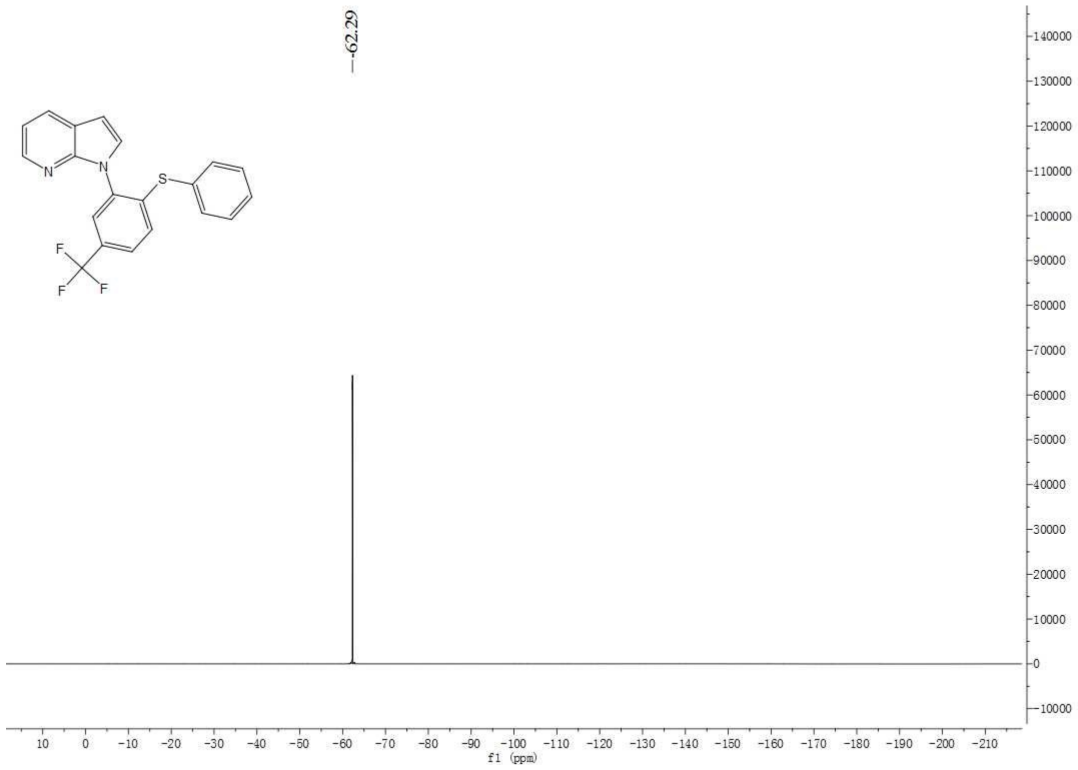
^{1}H NMR spectrum of 3o in $CDCl_3$



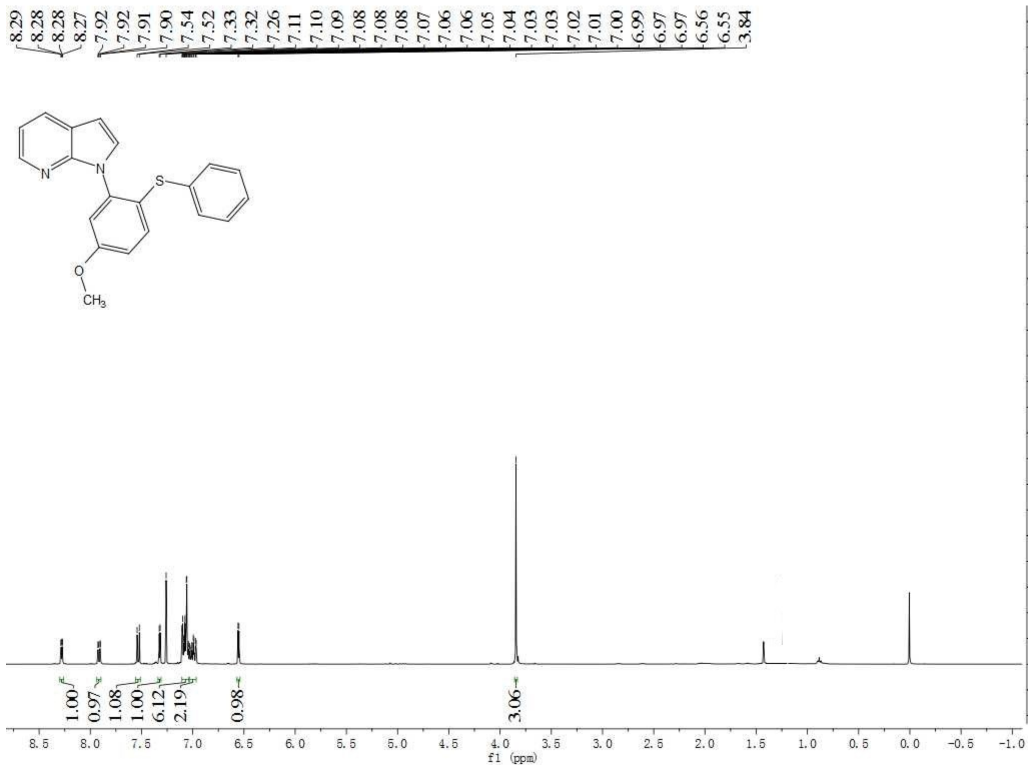
^{13}C NMR spectrum of 3o in $CDCl_3$



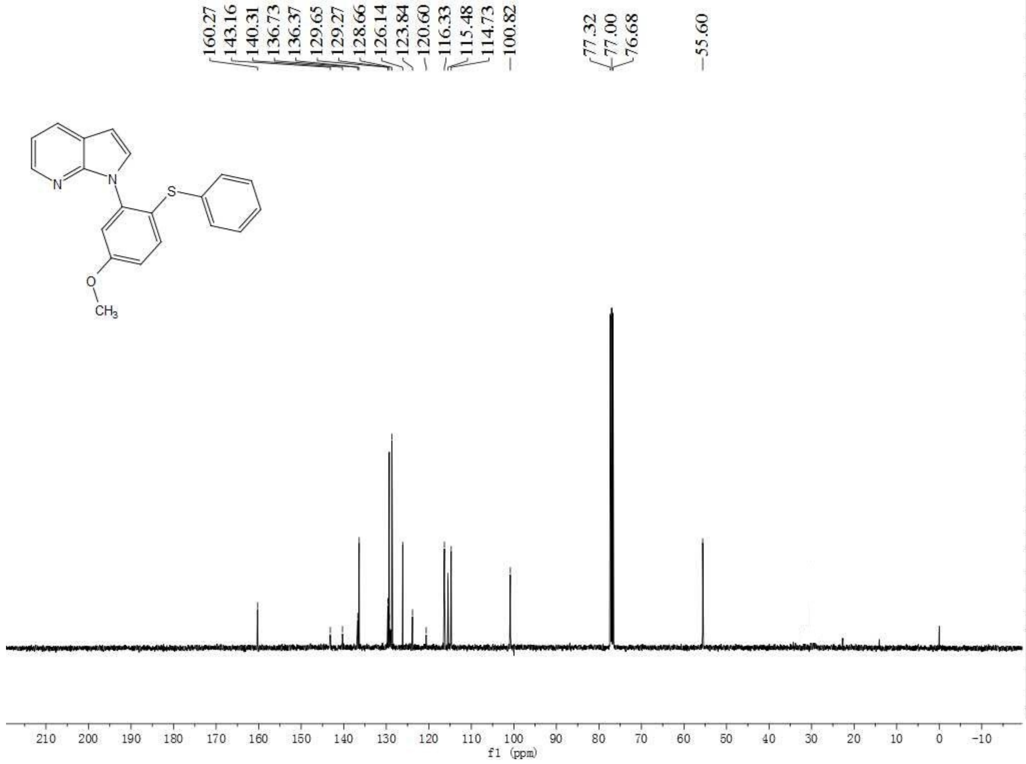
^{19}F NMR spectrum of 3o in CDCl$_3$



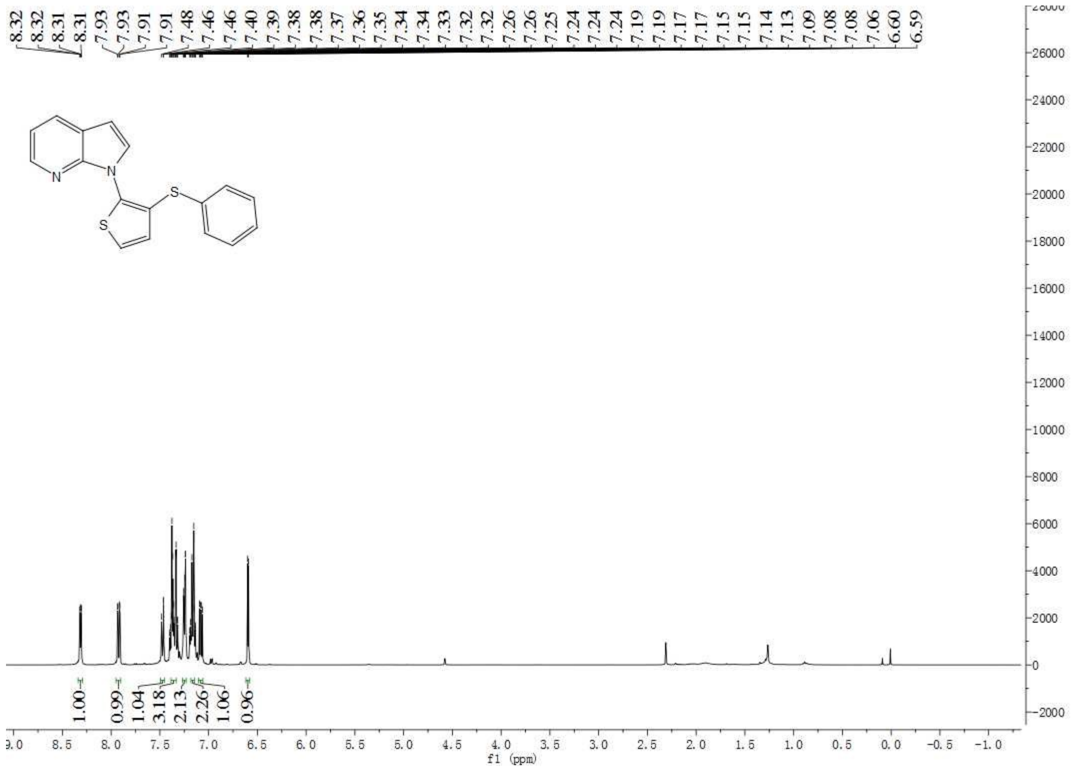
[1]H NMR spectrum of 3p in CDCl$_3$



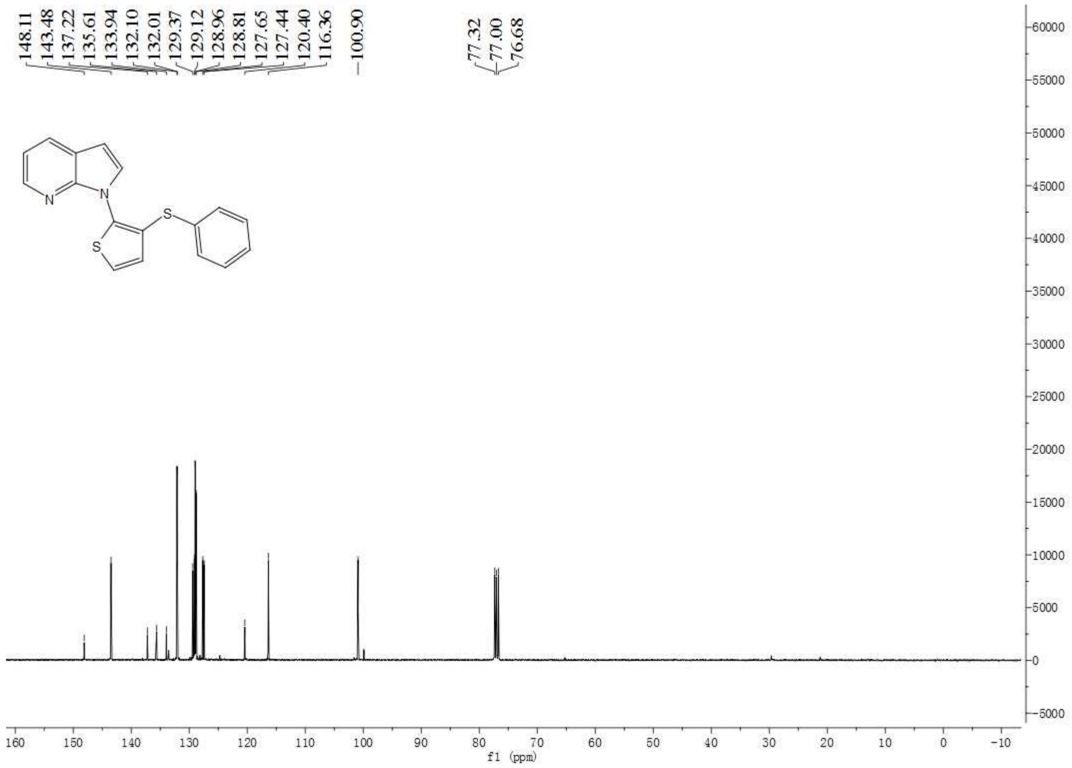
[13]C NMR spectrum of 3p in CDCl$_3$



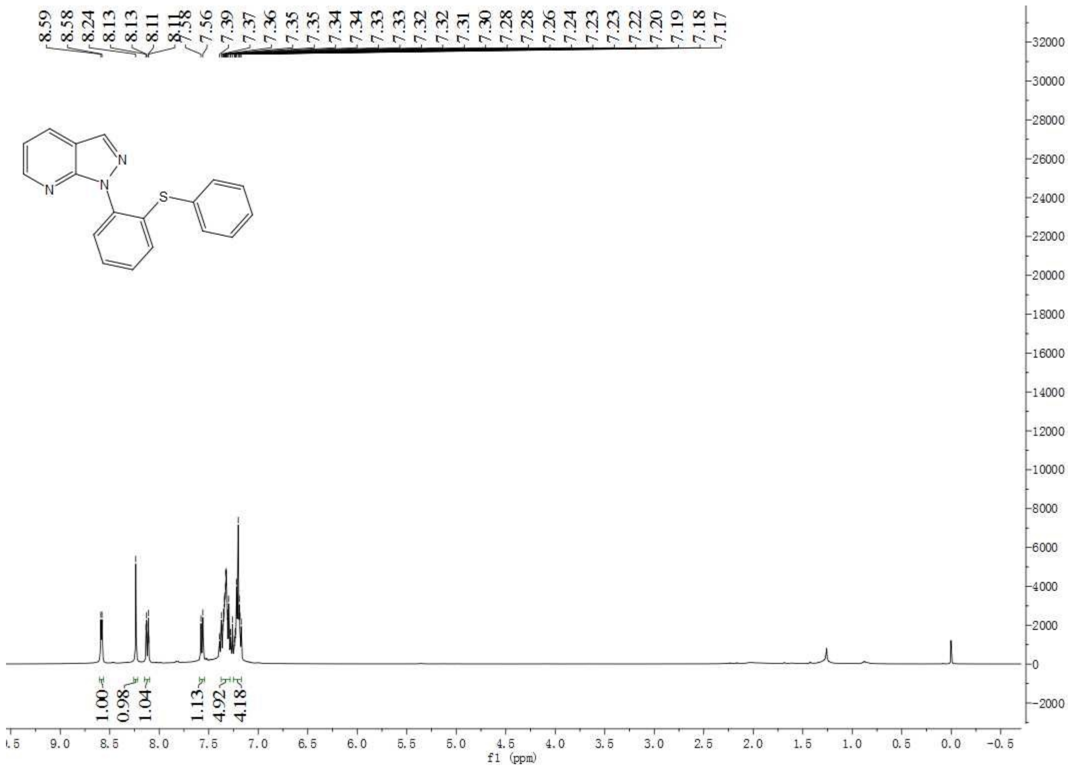
^1H NMR spectrum of 3q in $CDCl_3$



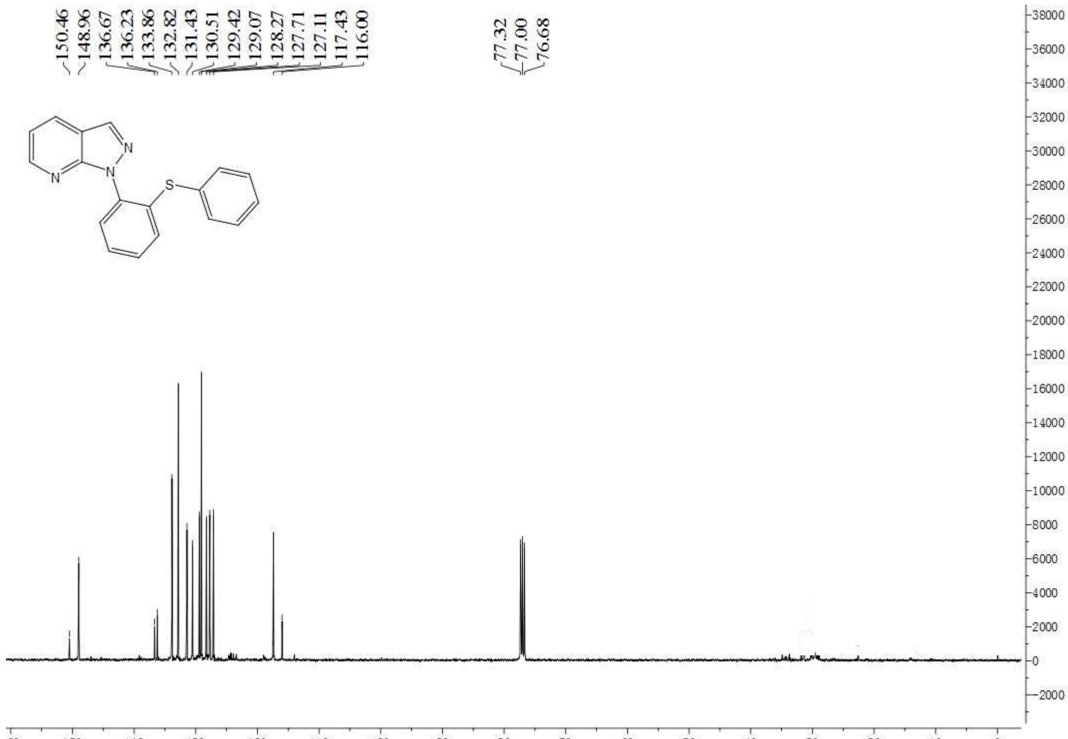
^{13}C NMR spectrum of 3q in $CDCl_3$



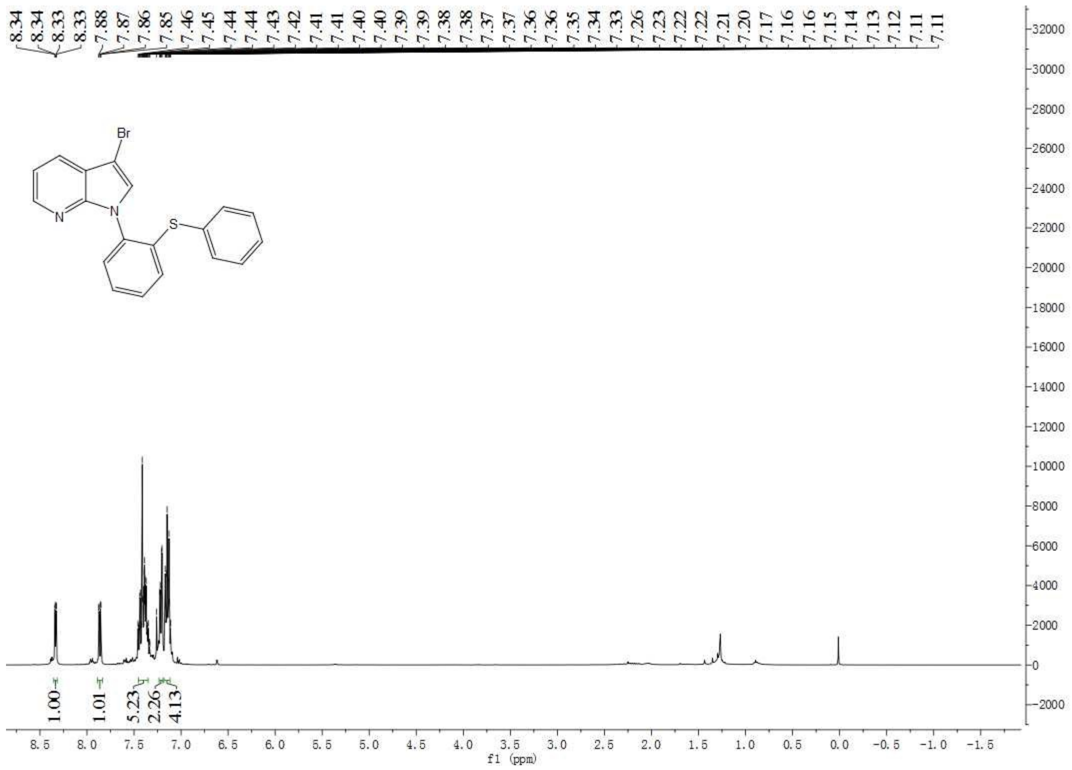
^{1}H NMR spectrum of 3r in $CDCl_3$



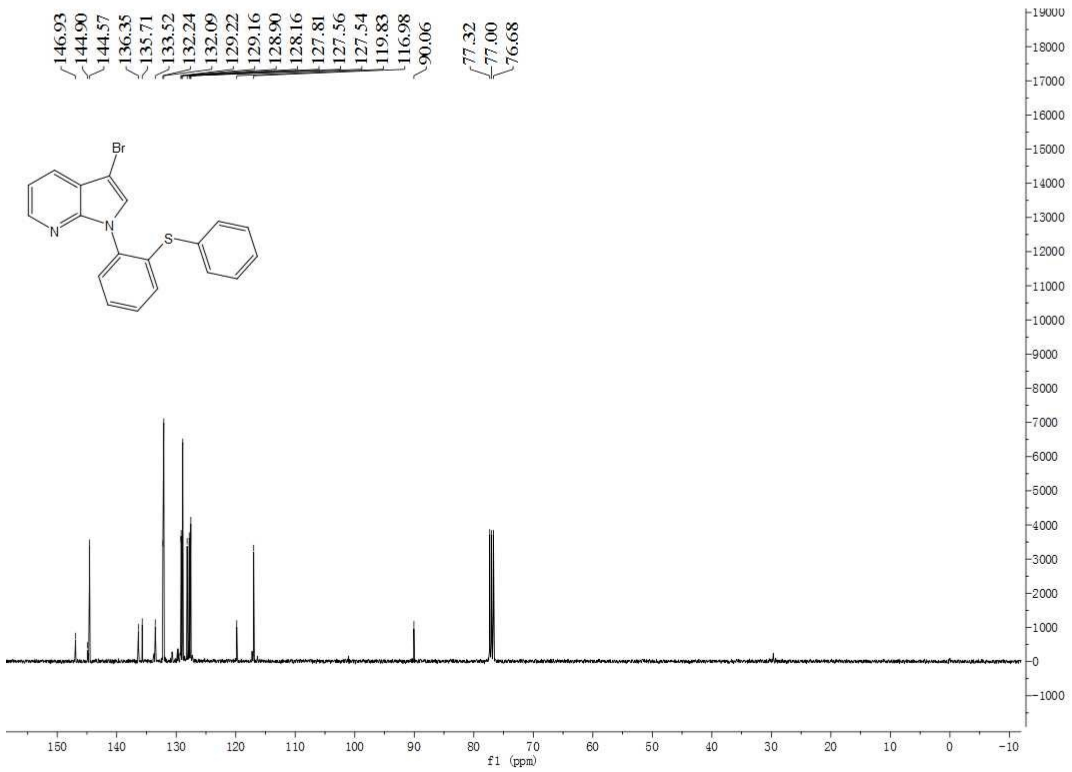
^{13}C NMR spectrum of 3r in $CDCl_3$



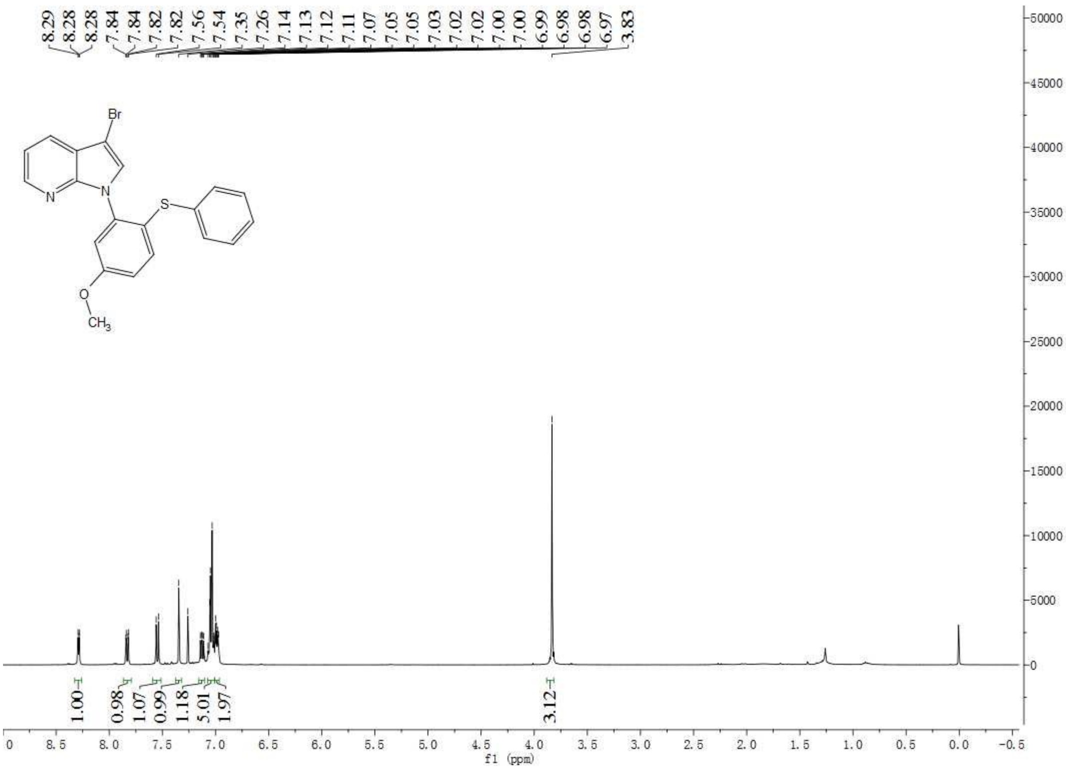
[1]H NMR spectrum of 3s in $CDCl_3$



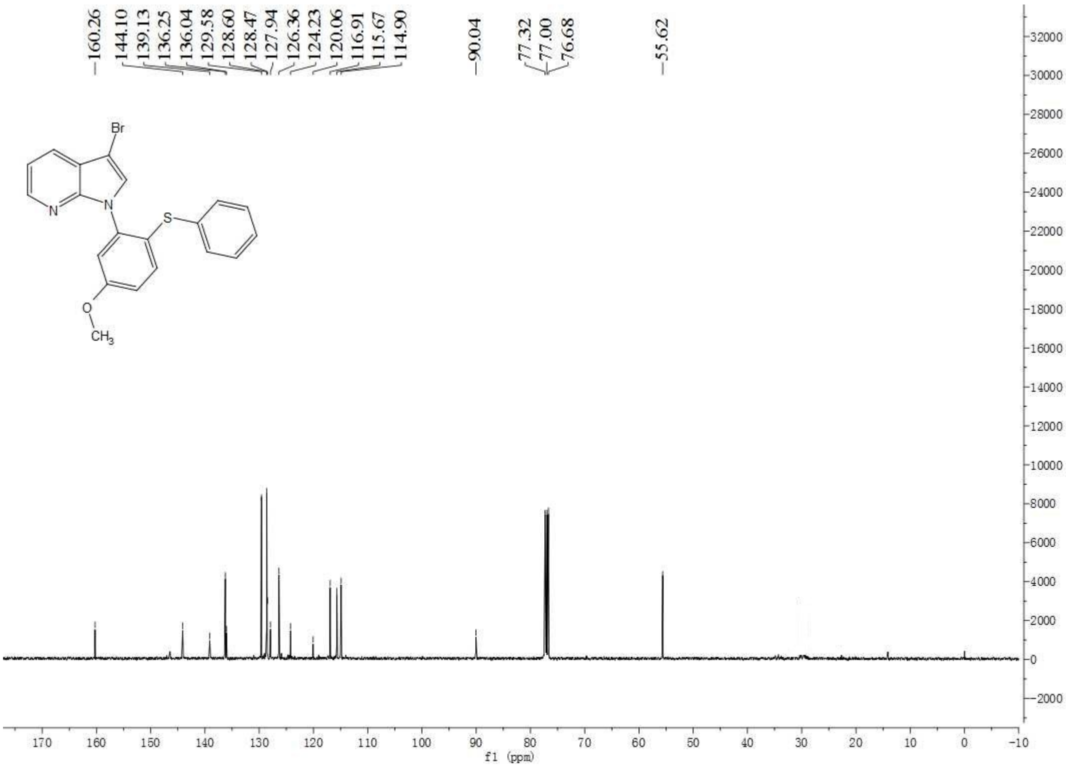
[13]C NMR spectrum of 3s in $CDCl_3$



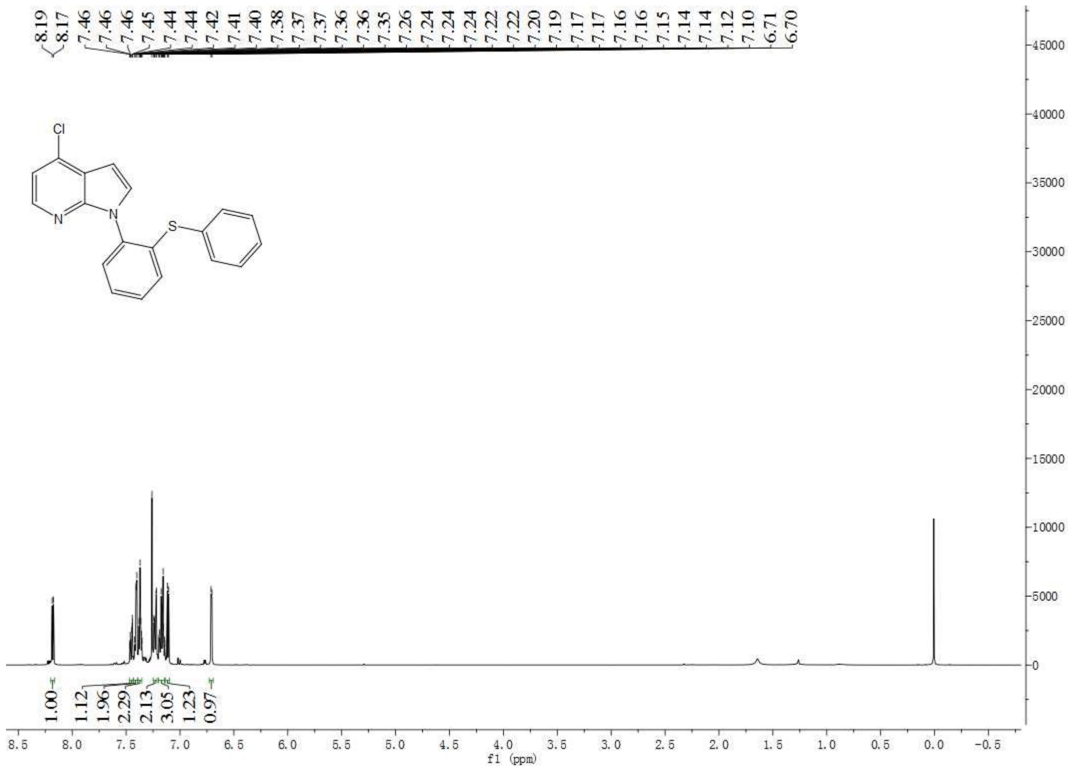
^{1}H NMR spectrum of 3t in $CDCl_3$



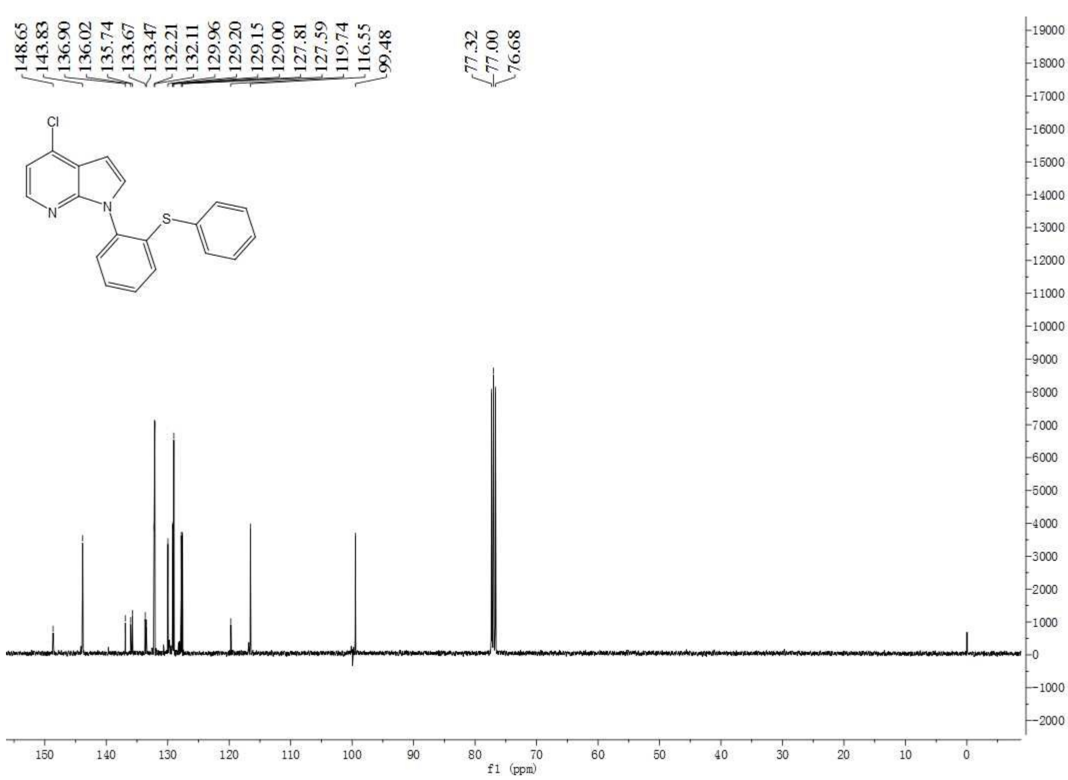
^{13}C NMR spectrum of 3t in $CDCl_3$



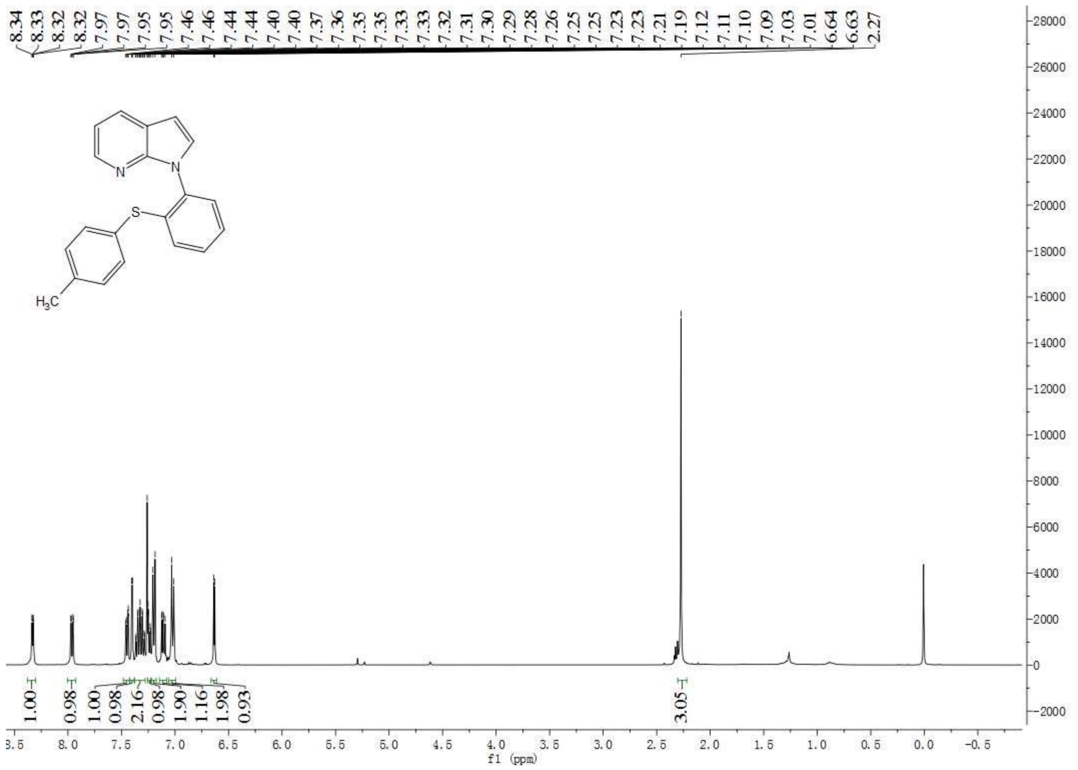
[1]H NMR spectrum of 3u in $CDCl_3$



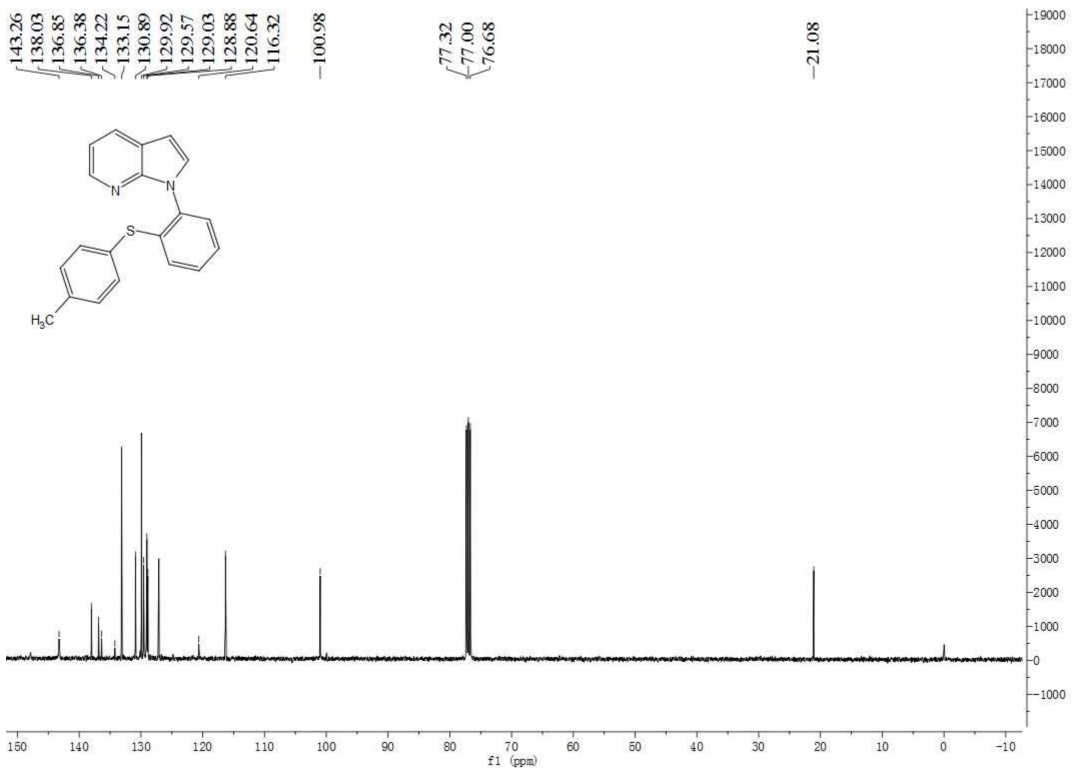
[13]C NMR spectrum of 3u in $CDCl_3$



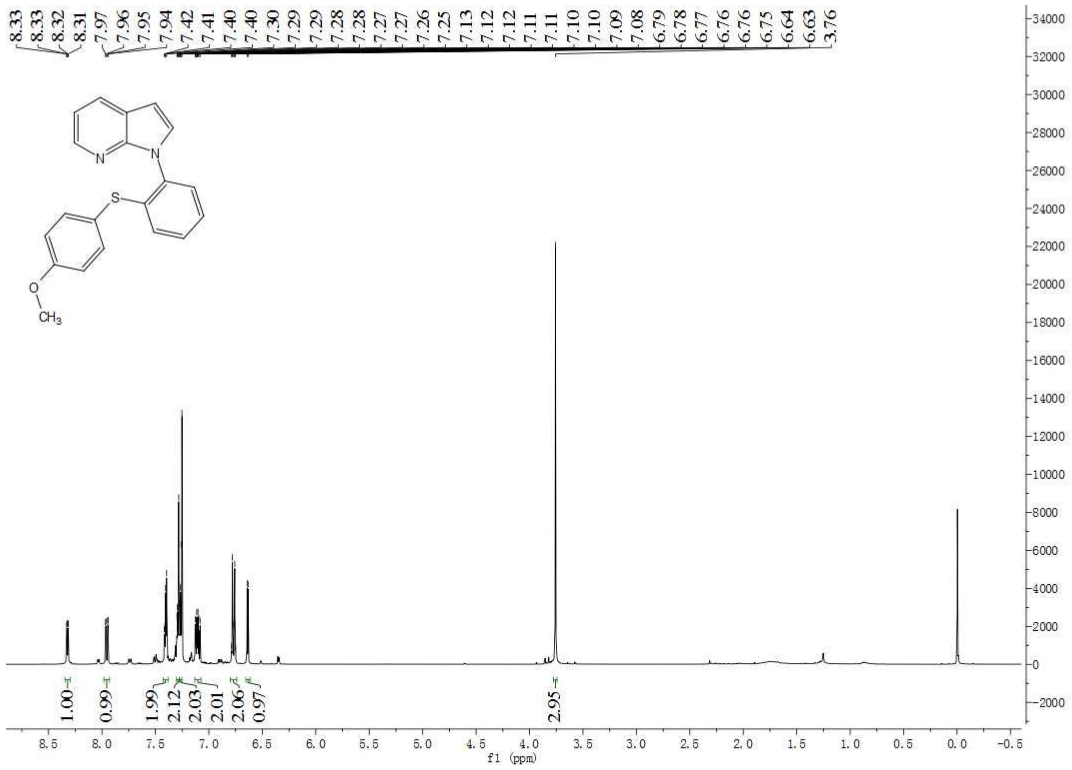
^{1}H NMR spectrum of 3v in $CDCl_3$



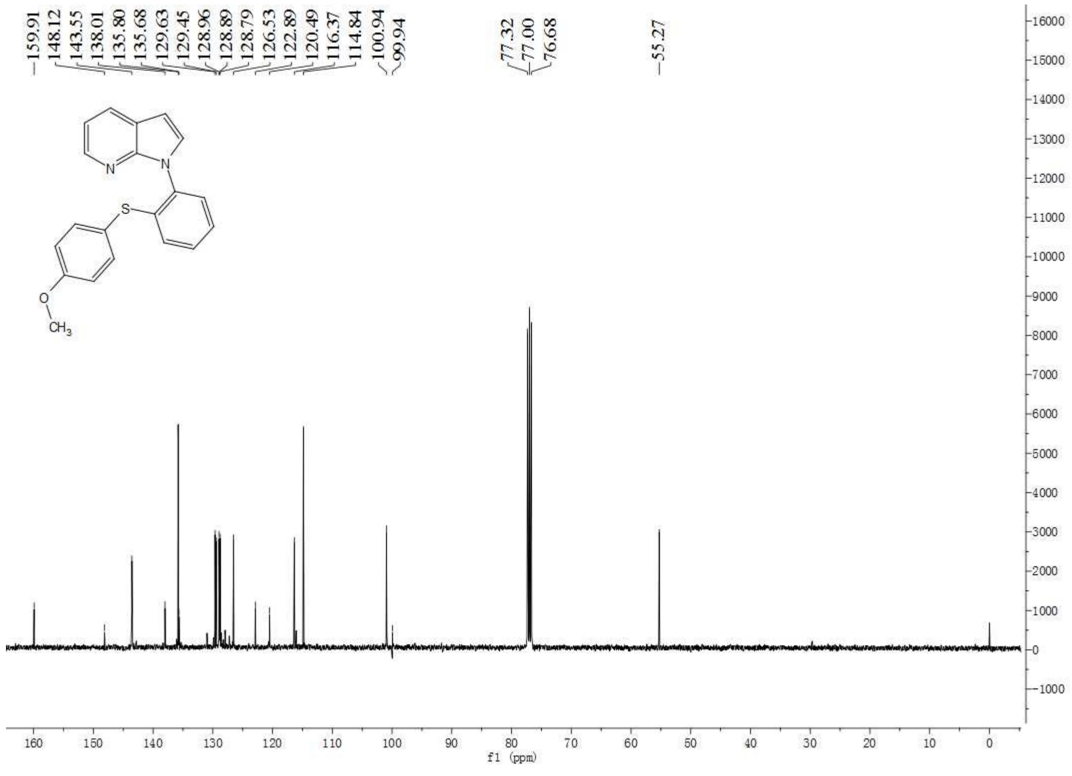
^{13}C NMR spectrum of 3v in $CDCl_3$



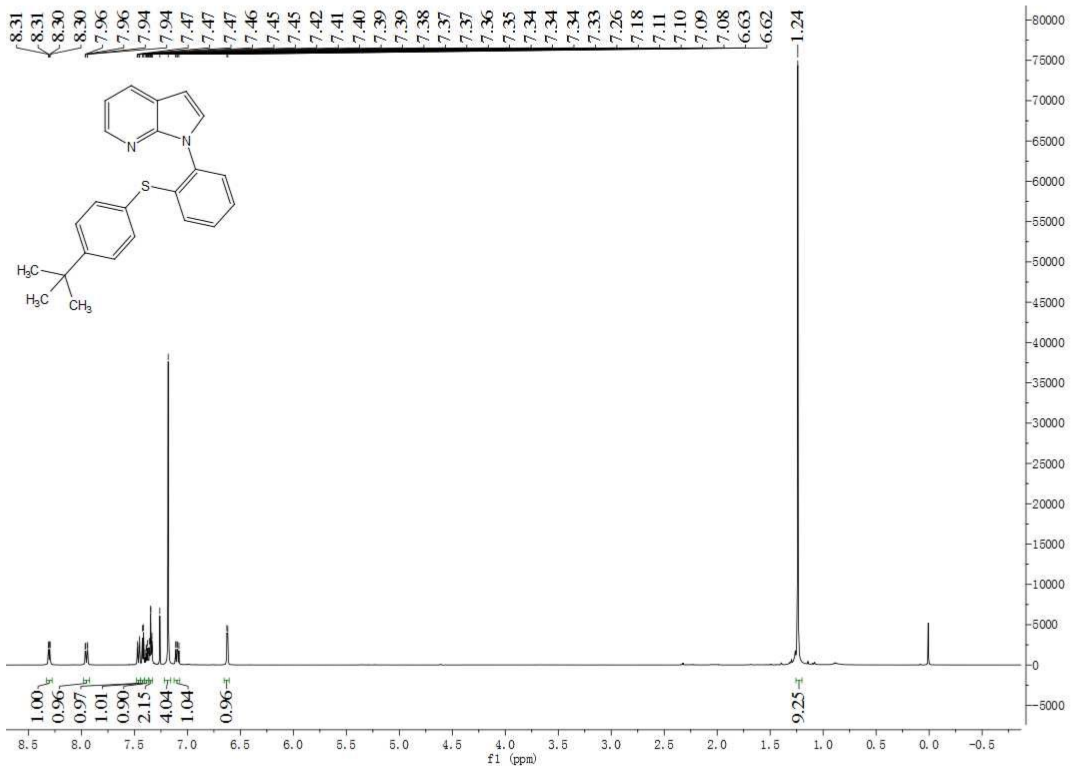
^{1}H NMR spectrum of 3w in $CDCl_3$



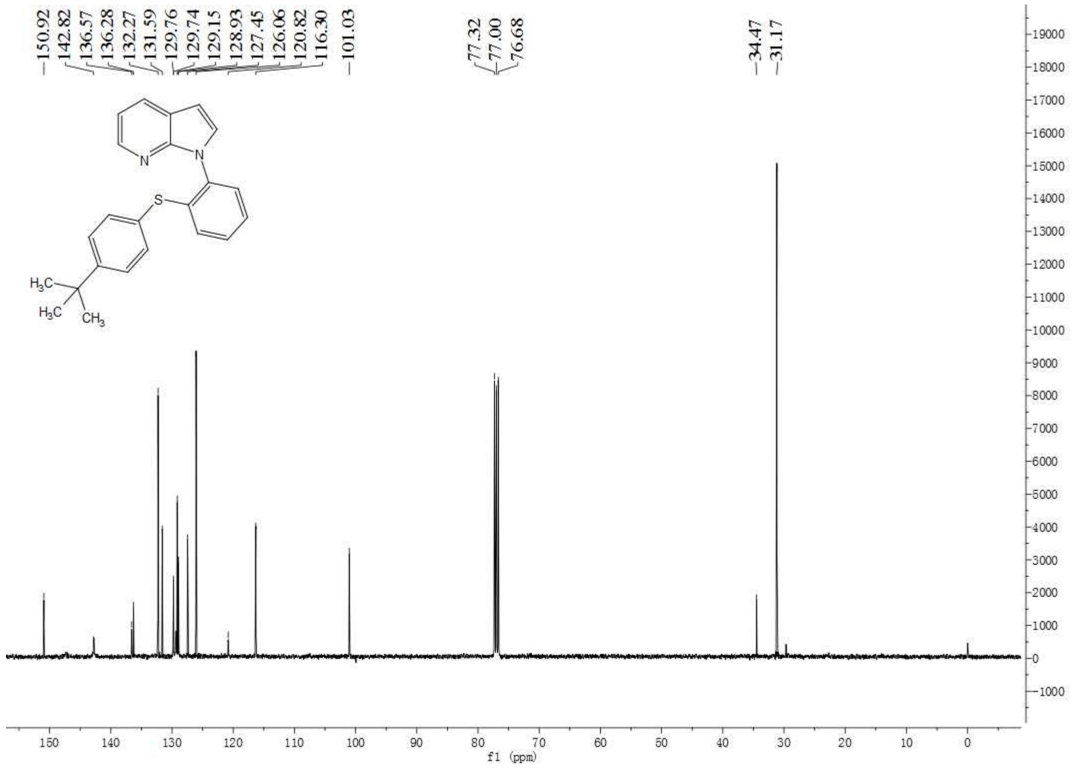
^{13}C NMR spectrum of 3w in $CDCl_3$



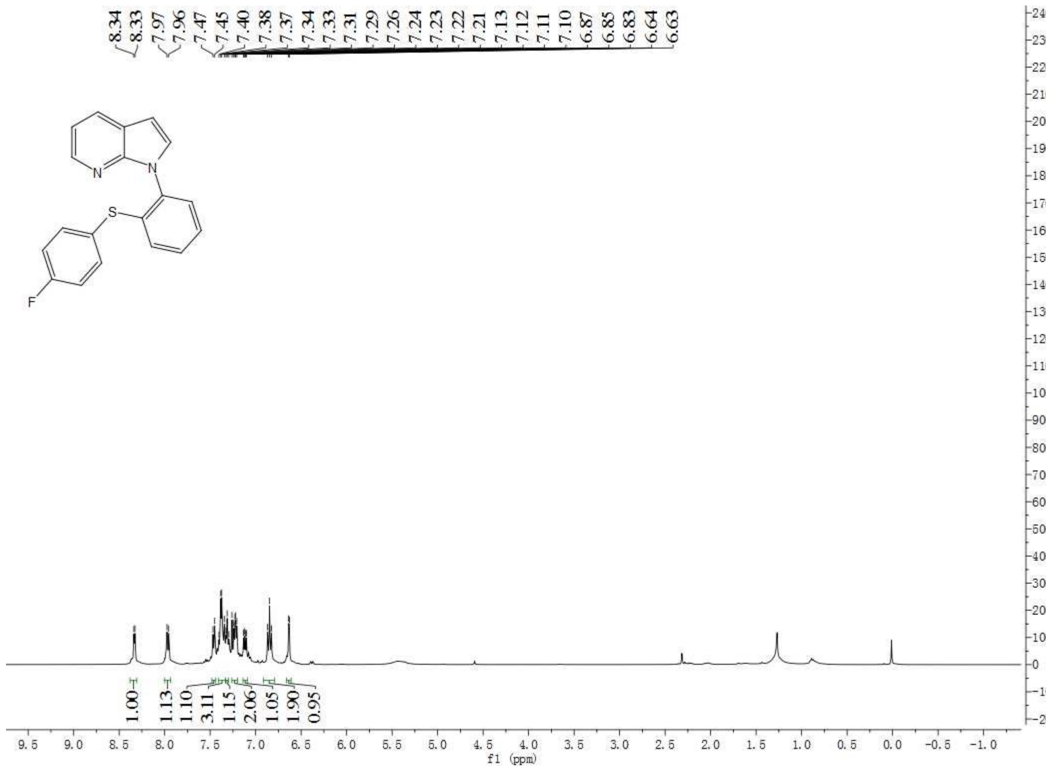
^{1}H NMR spectrum of 3x in $CDCl_3$



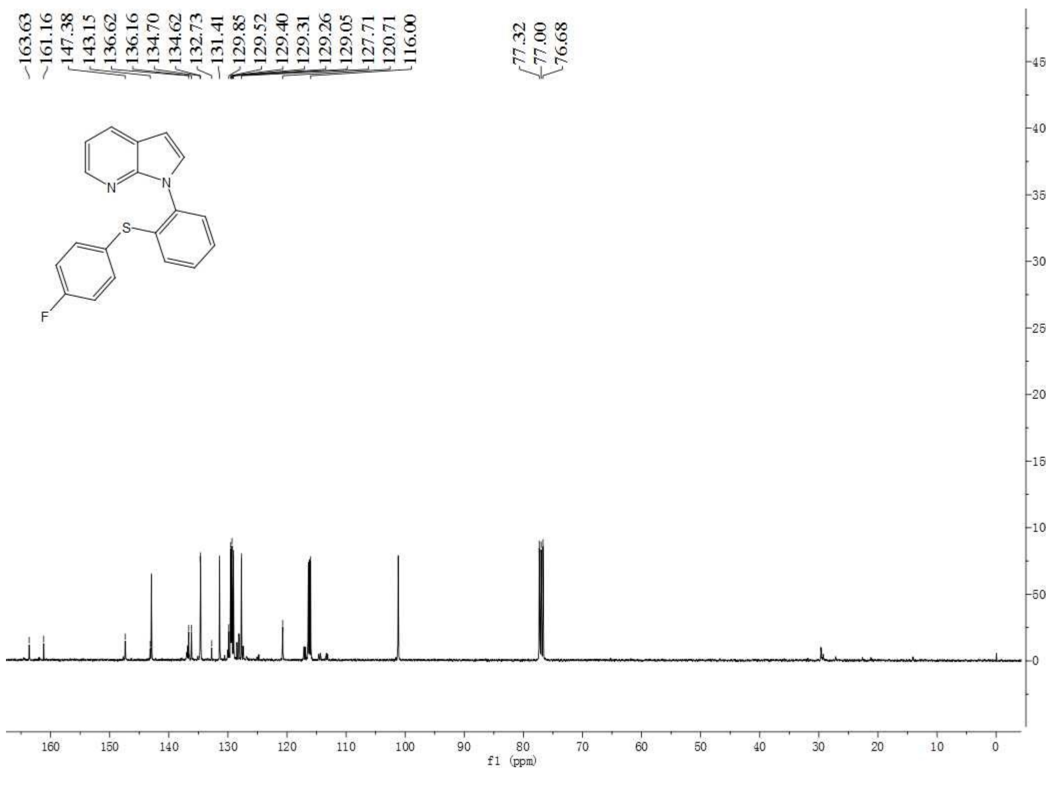
^{13}C NMR spectrum of 3x in $CDCl_3$



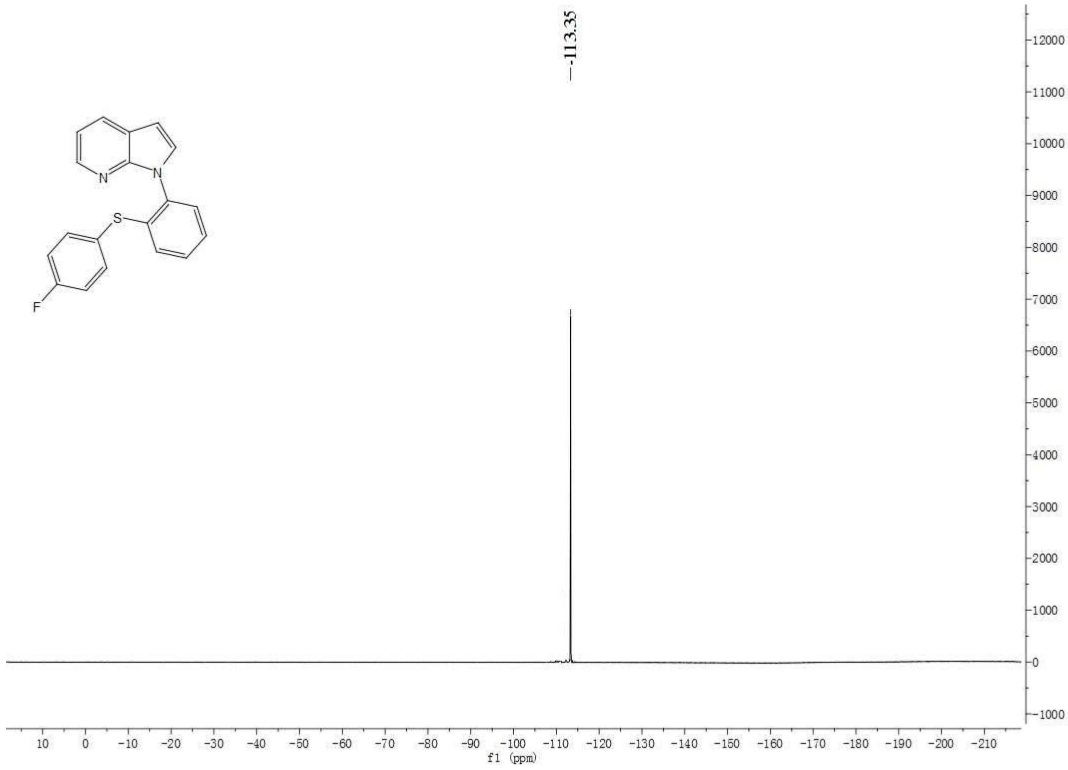
^{1}H NMR spectrum of 3y in $CDCl_3$



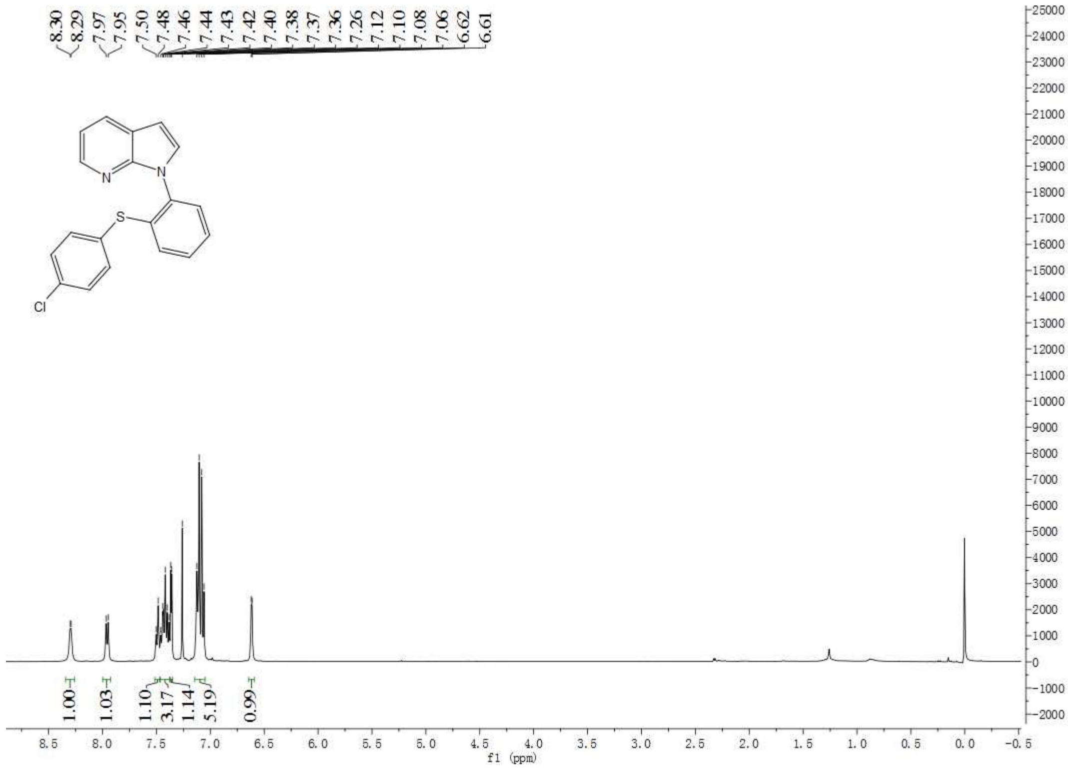
^{13}C NMR spectrum of 3y in $CDCl_3$



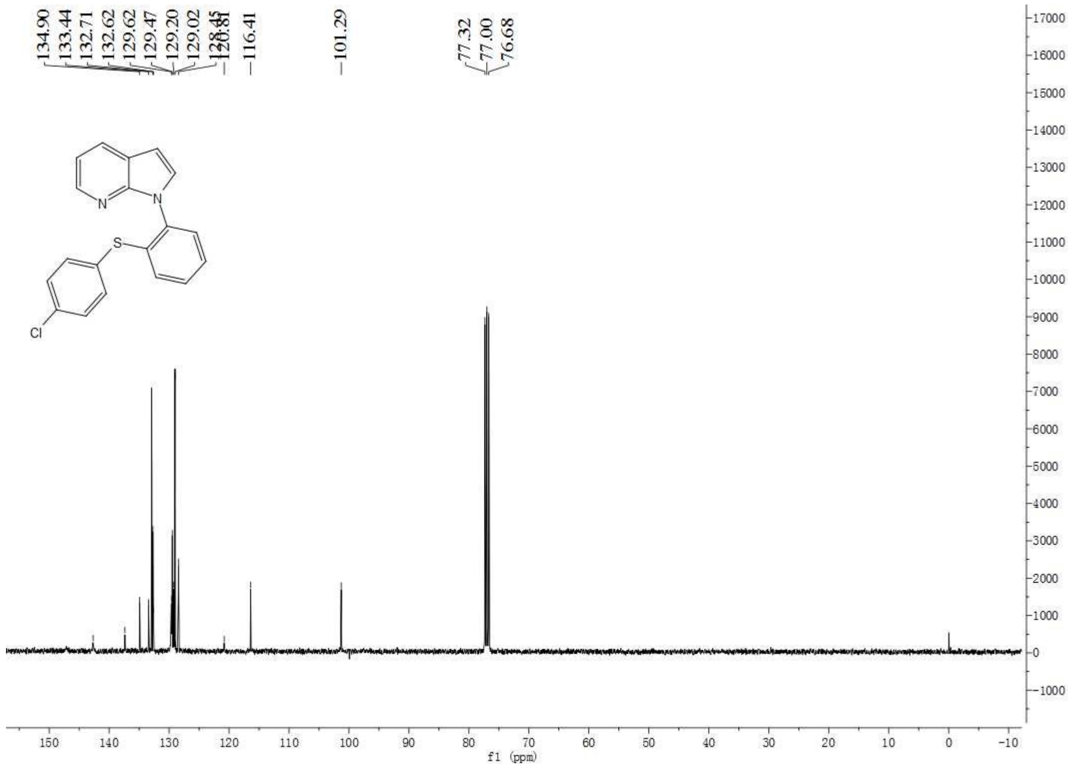
^{19}F NMR spectrum of 3y in $CDCl_3$



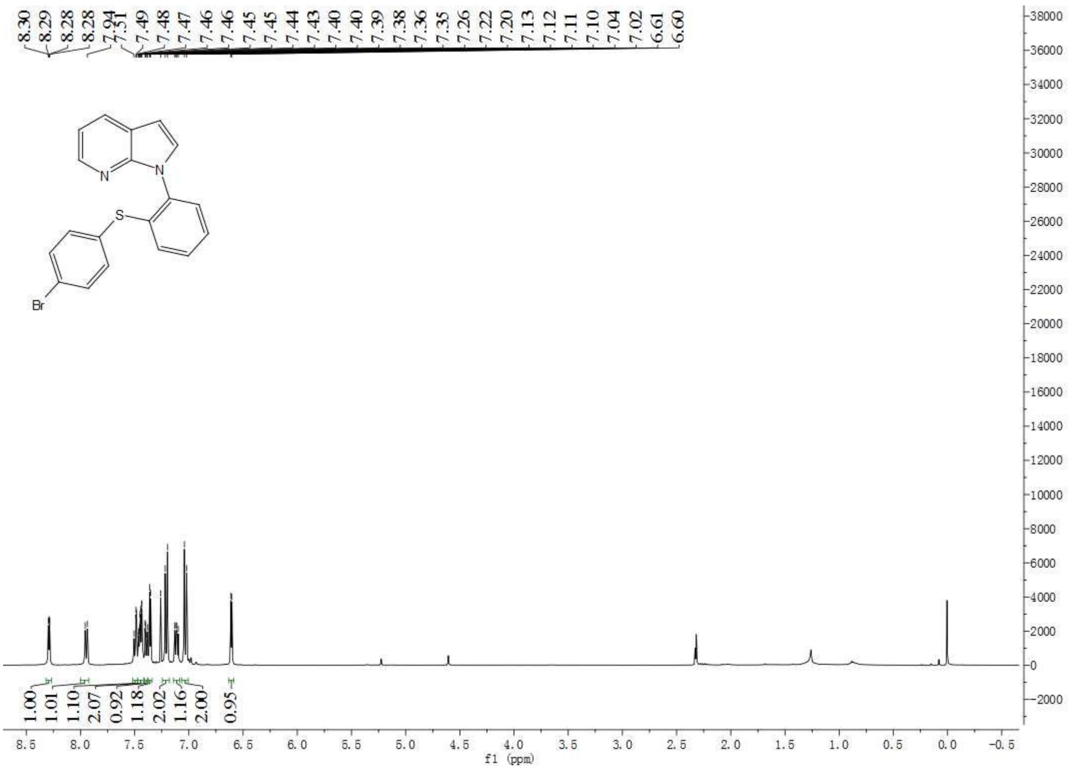
^{1}H NMR spectrum of 3z in CDCl$_3$



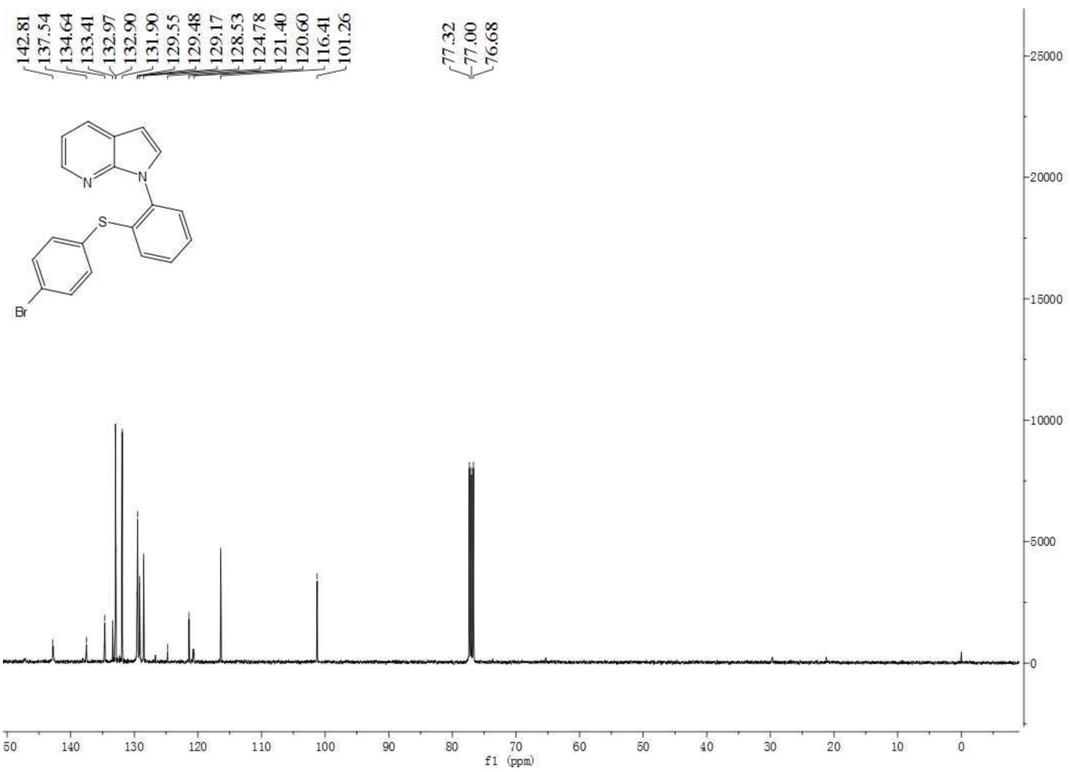
^{13}C NMR spectrum of 3z in CDCl$_3$



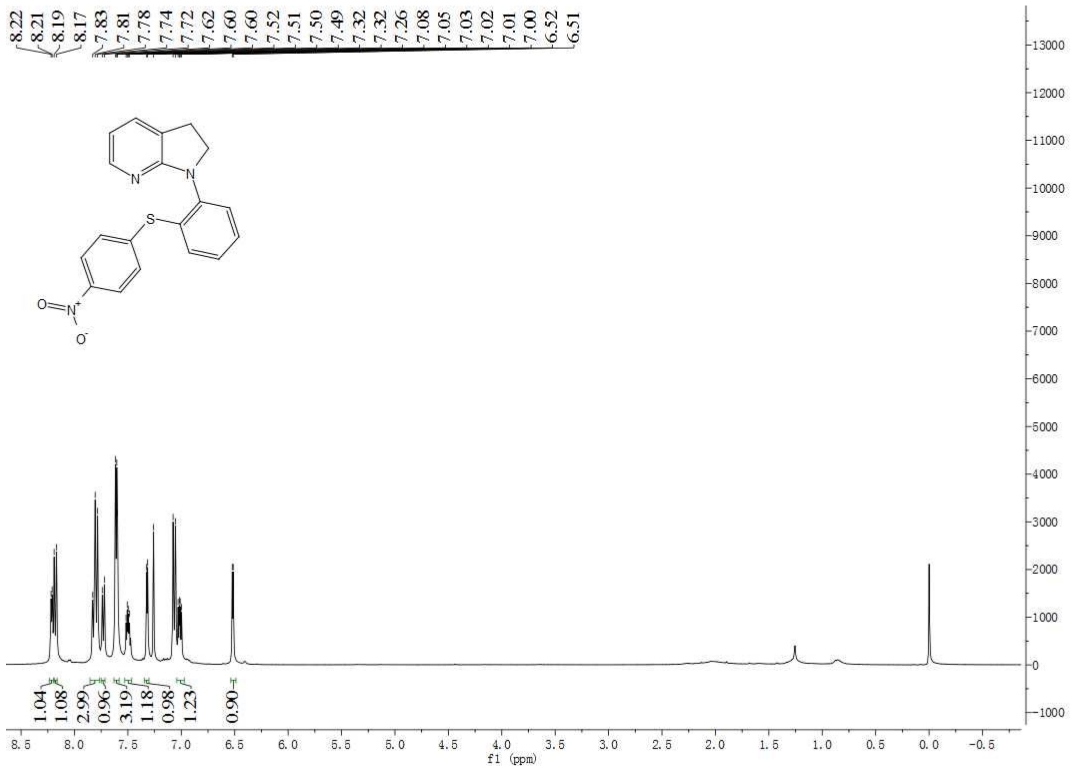
^{1}H NMR spectrum of 3aa in $CDCl_3$



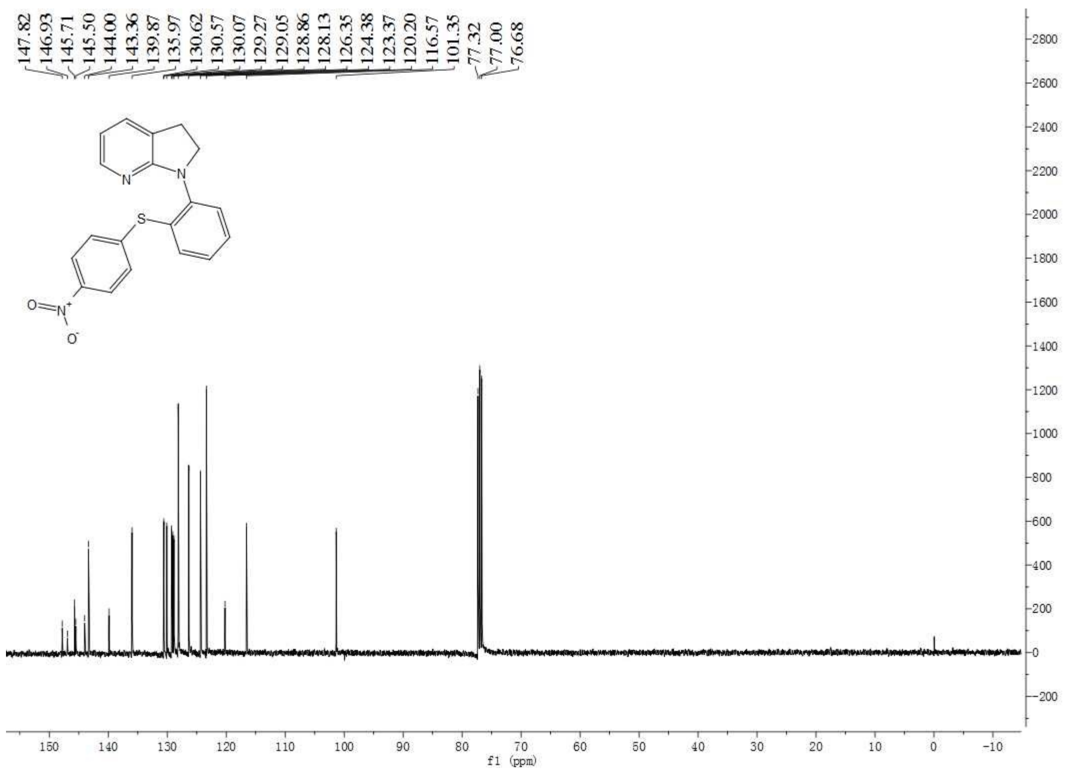
^{13}C NMR spectrum of 3aa in $CDCl_3$



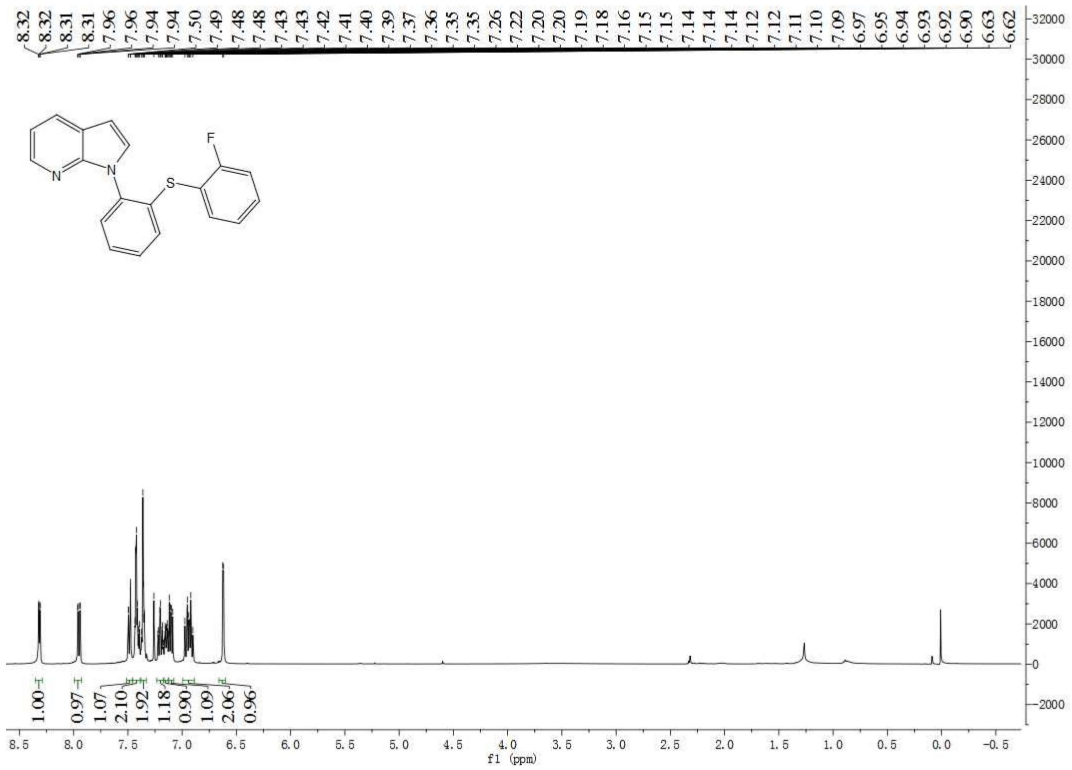
^{1}H NMR spectrum of 3ab in $CDCl_3$



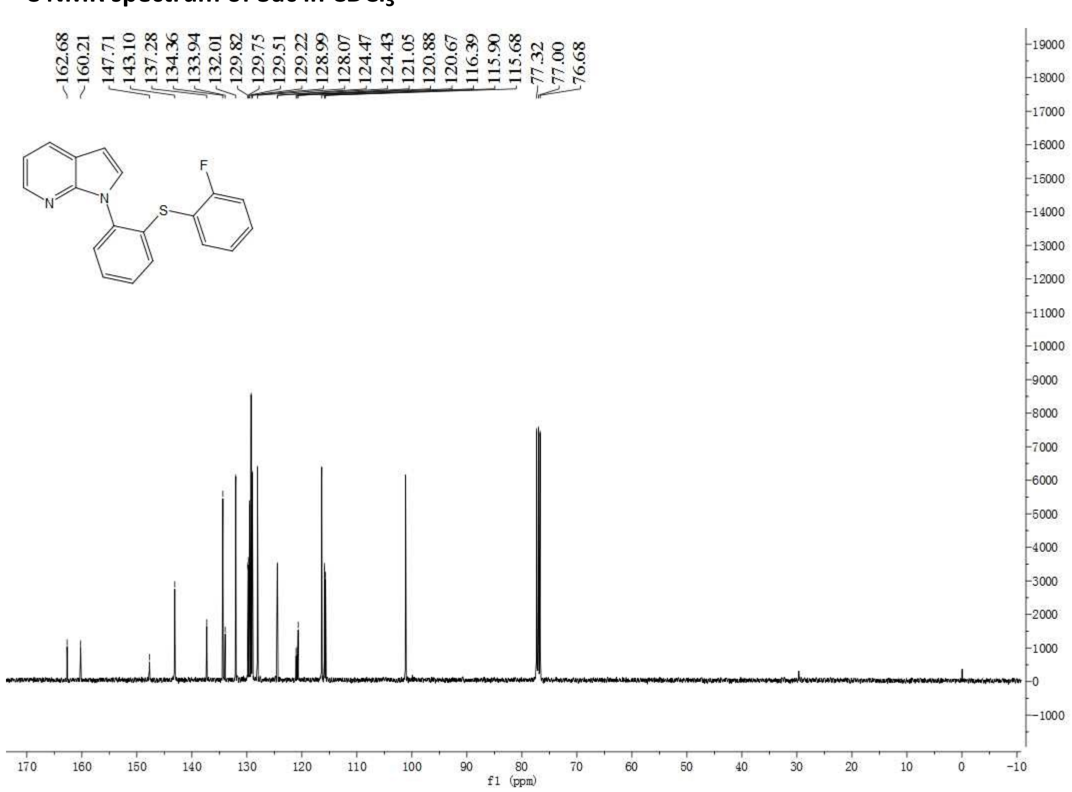
^{13}C NMR spectrum of 3ab in $CDCl_3$



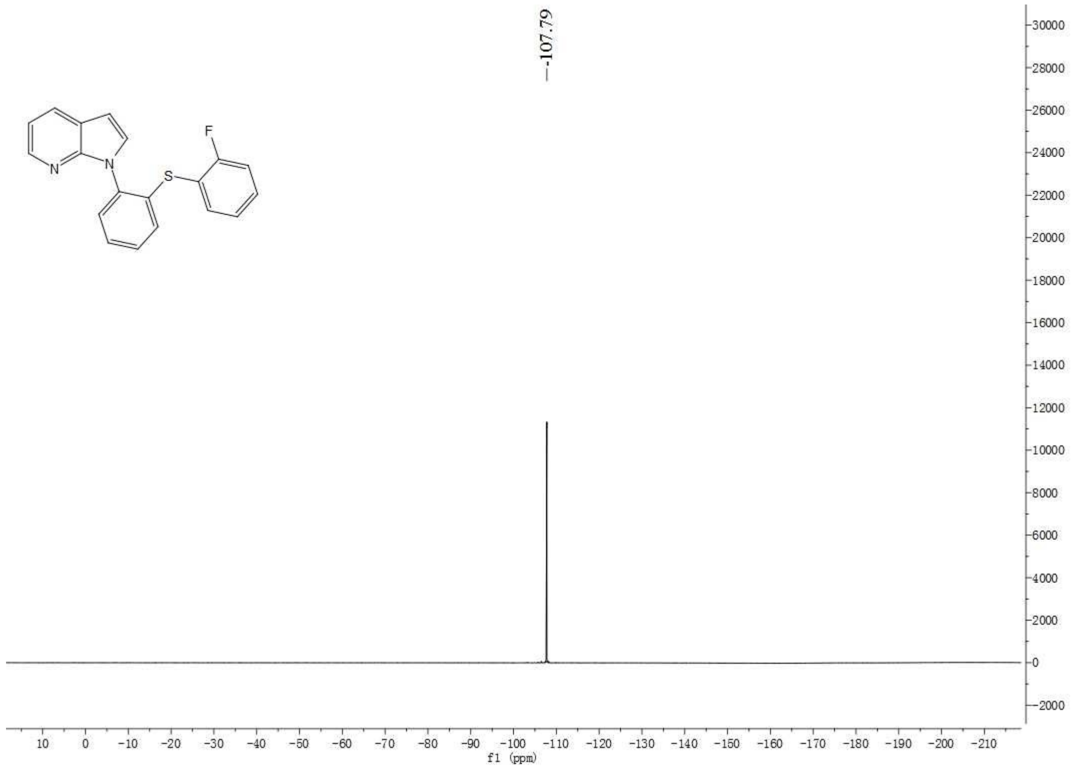
^{1}H NMR spectrum of 3ac in $CDCl_3$



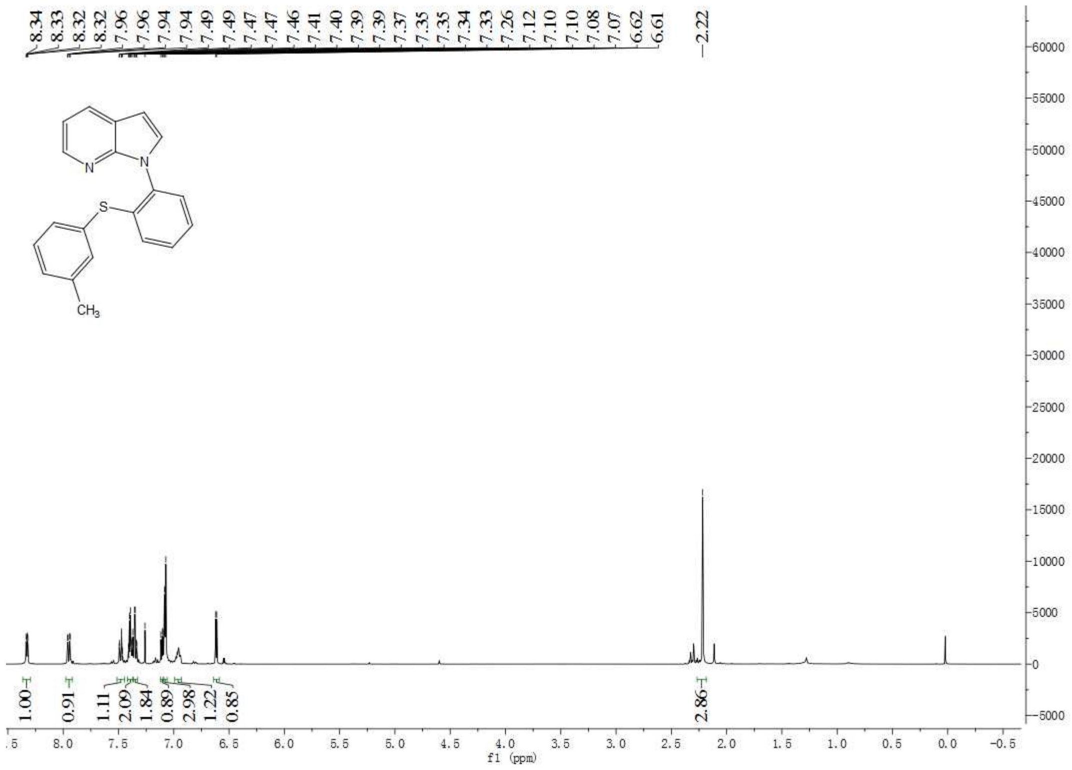
^{13}C NMR spectrum of 3ac in $CDCl_3$



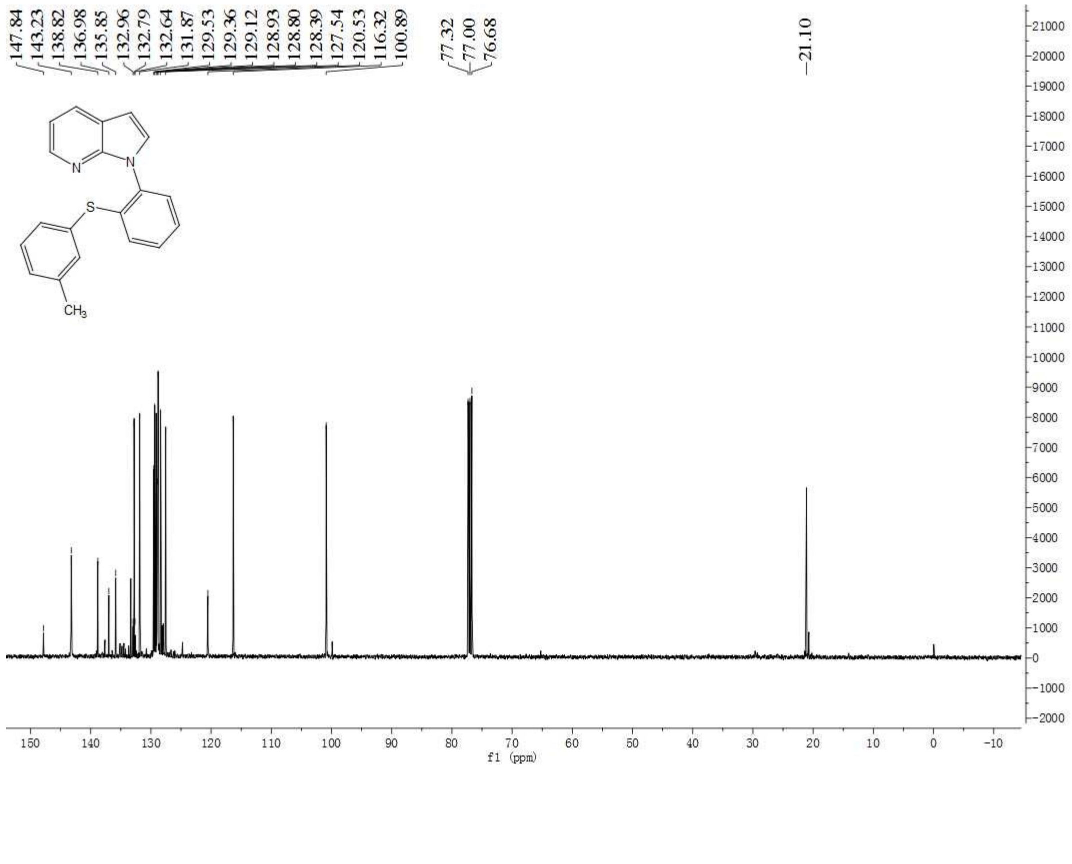
^{19}F NMR spectrum of 3ac in $CDCl_3$



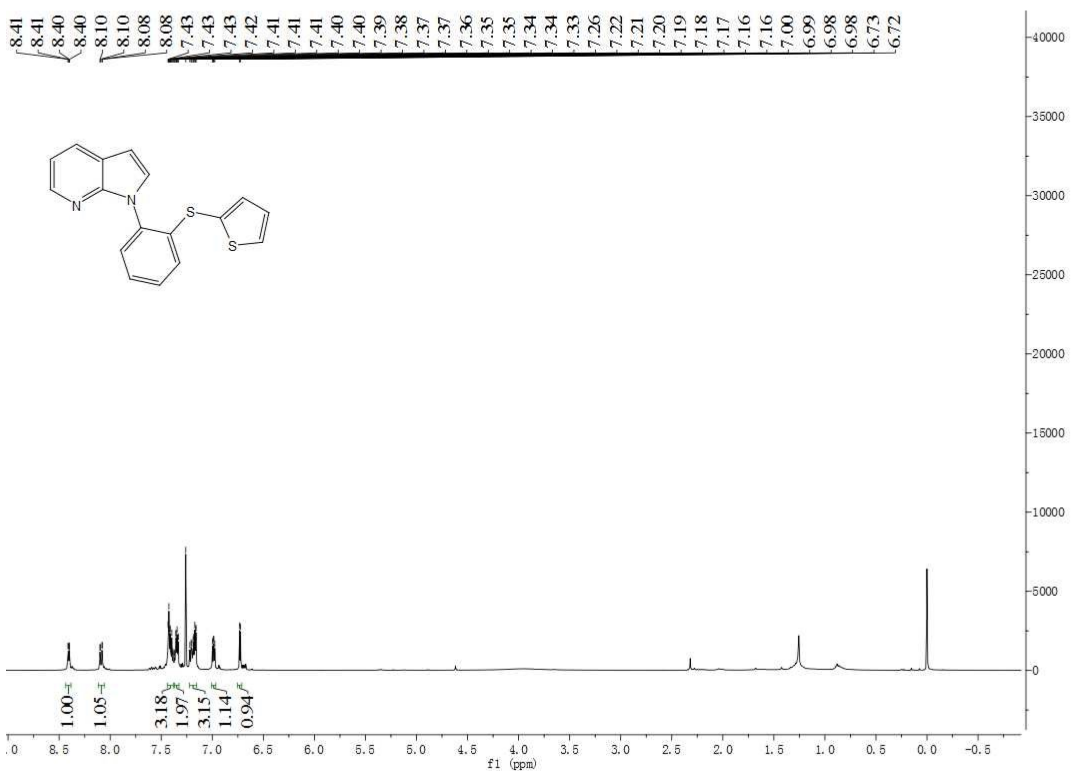
^{1}H NMR spectrum of 3ad in $CDCl_3$



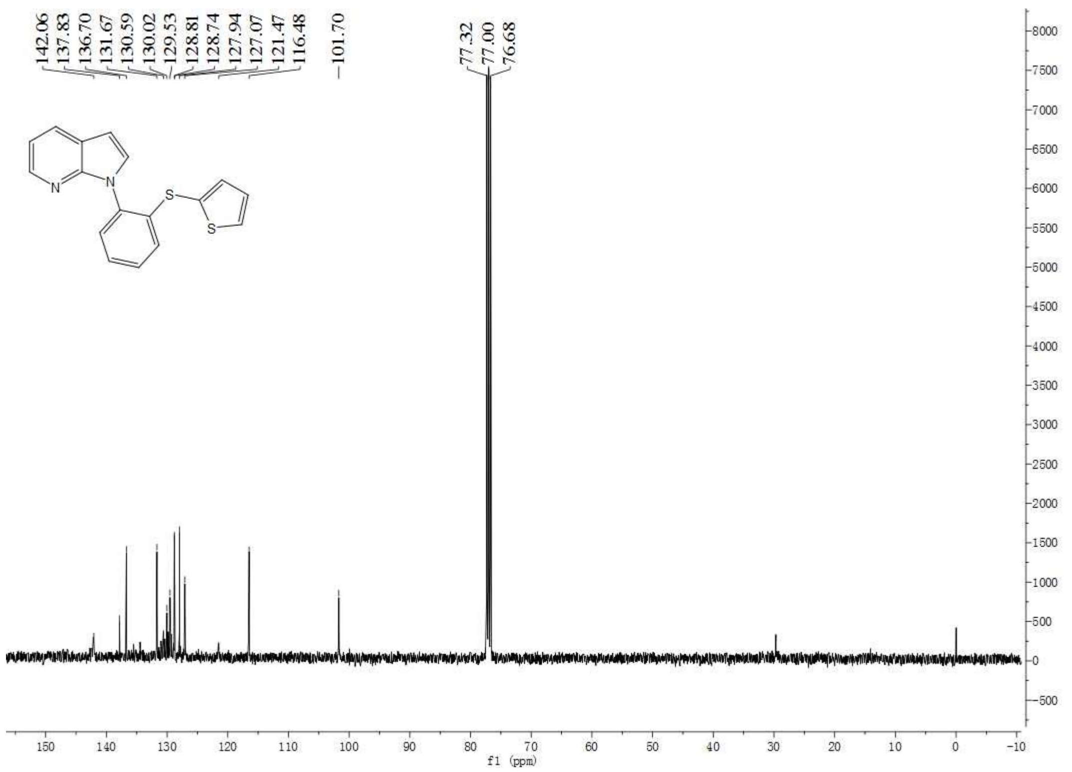
^{13}C NMR spectrum of 3ad in $CDCl_3$



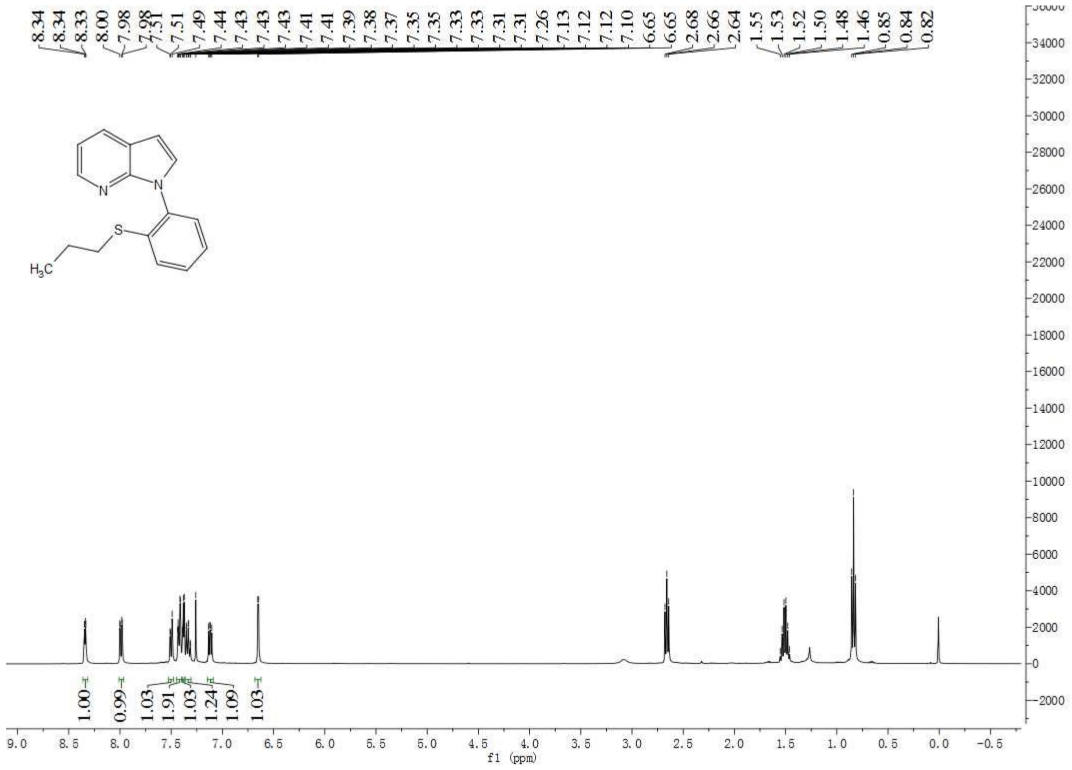
^{1}H NMR spectrum of 3ae in $CDCl_3$



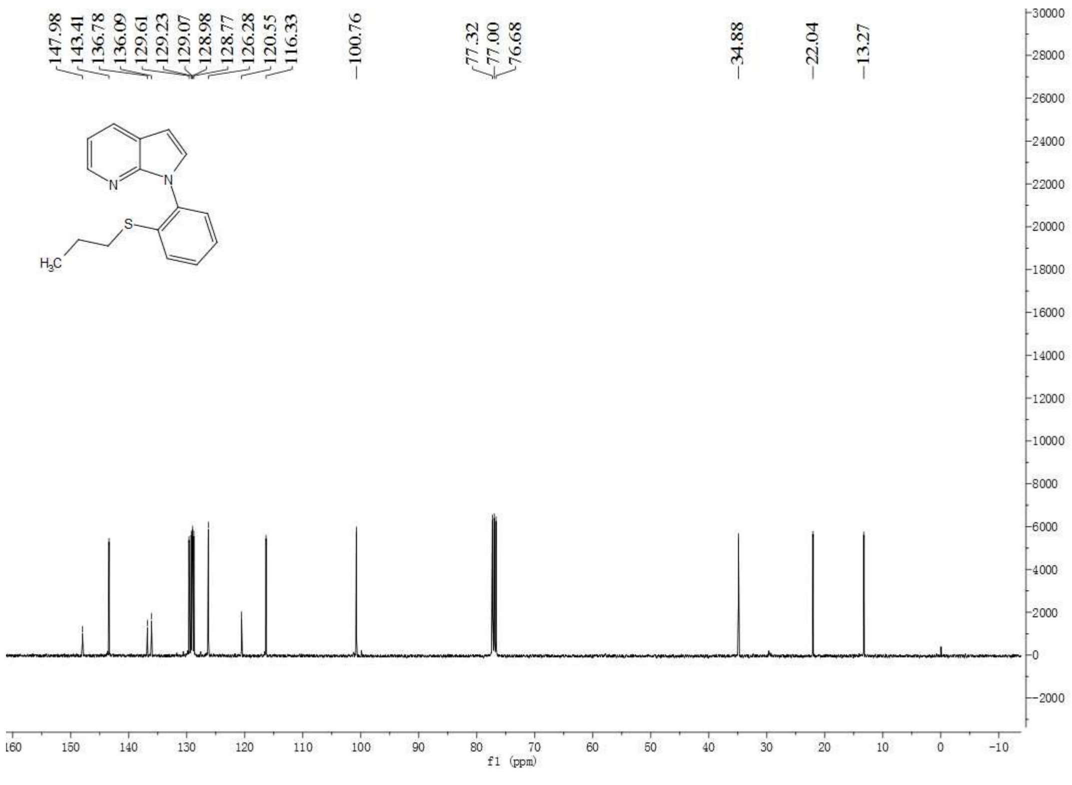
^{13}C NMR spectrum of 3ae in $CDCl_3$



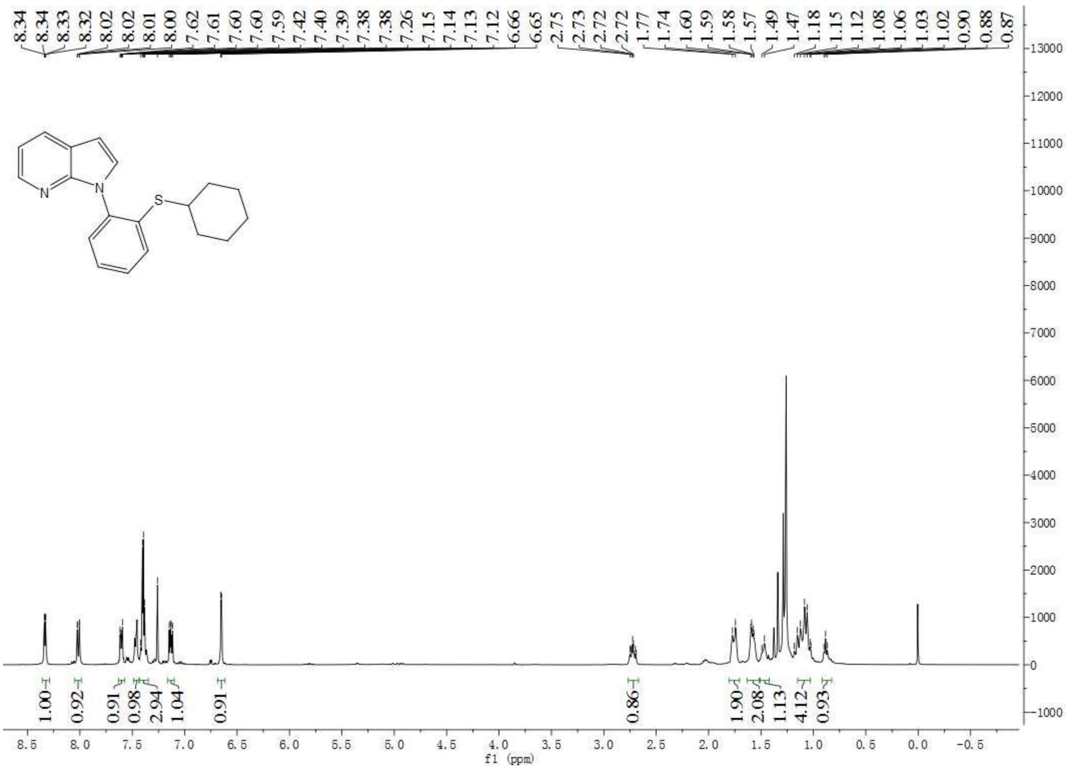
[1]H NMR spectrum of 3af in CDCl$_3$



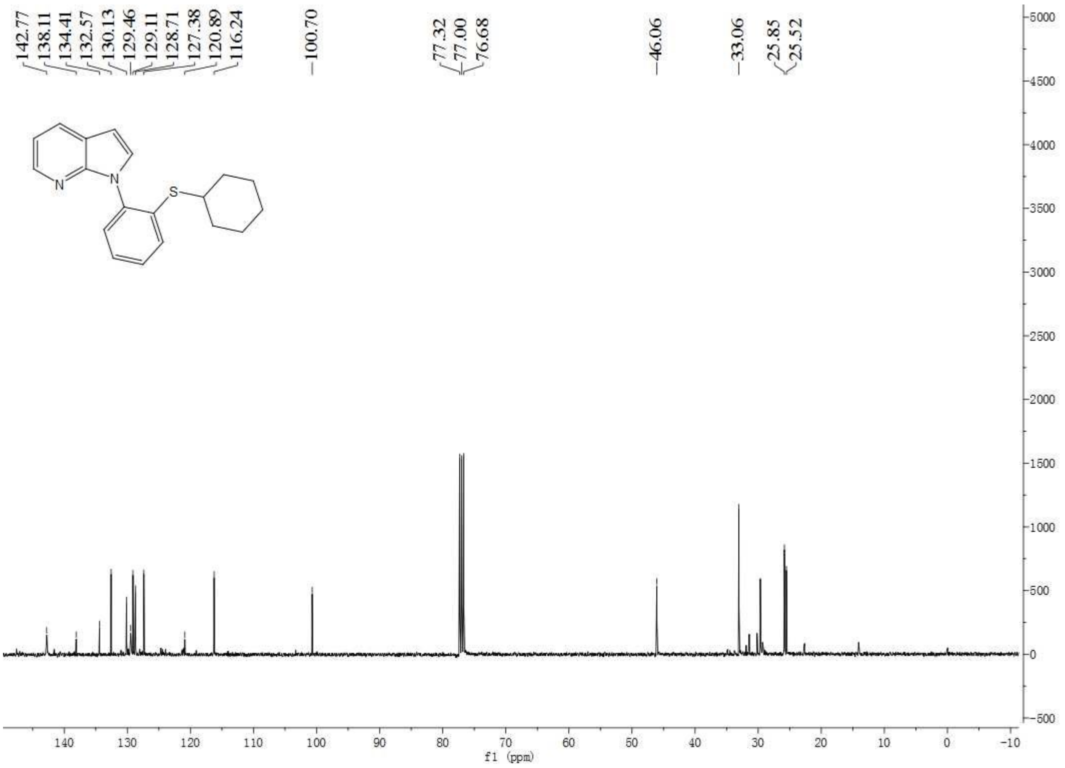
[13]C NMR spectrum of 3af in CDCl$_3$



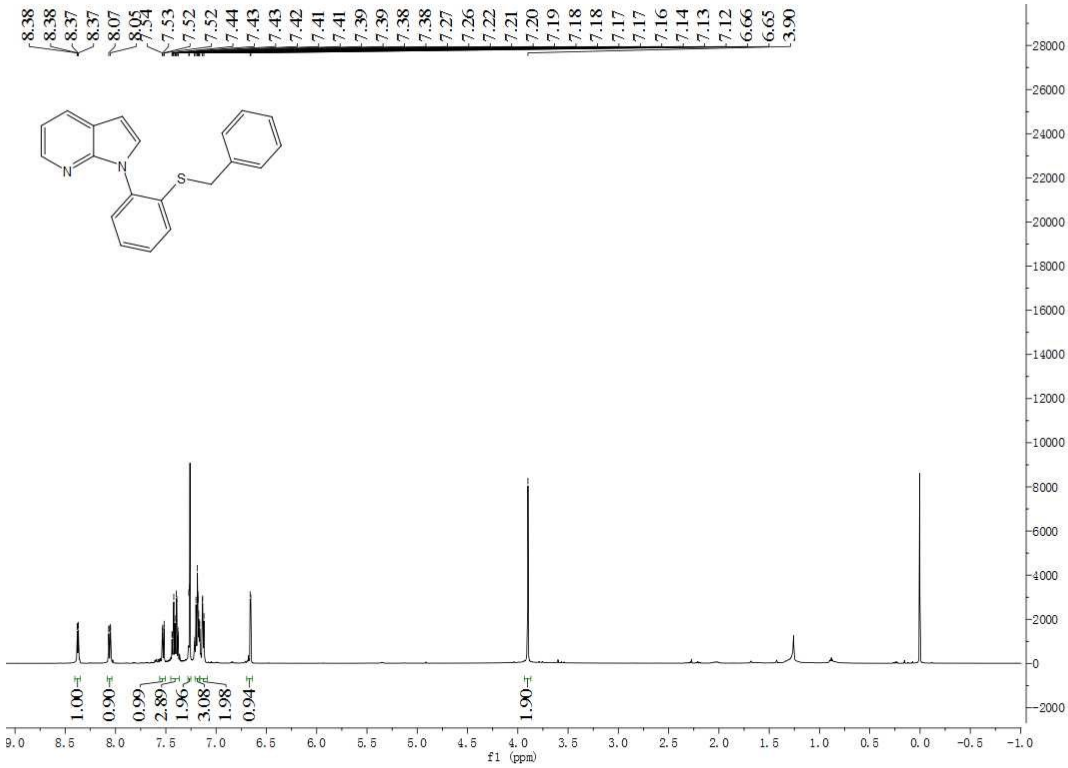
^{1}H NMR spectrum of 3ag in $CDCl_3$



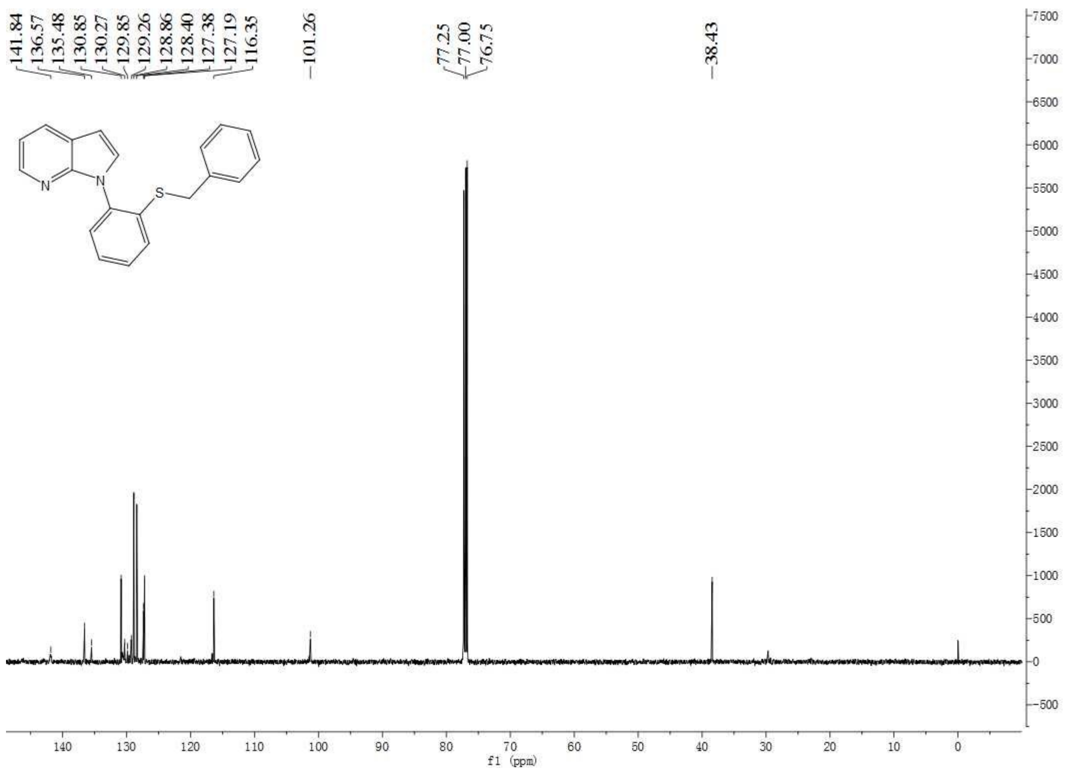
^{13}C NMR spectrum of 3ag in $CDCl_3$



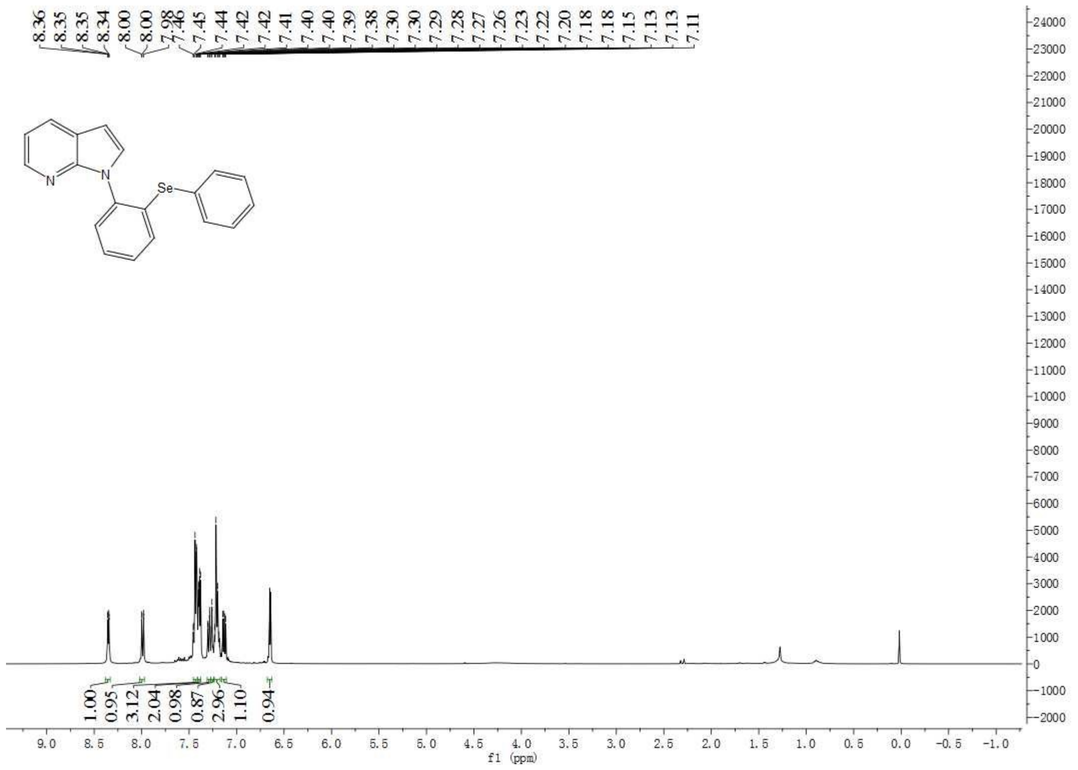
^{1}H NMR spectrum of 3ah in $CDCl_3$



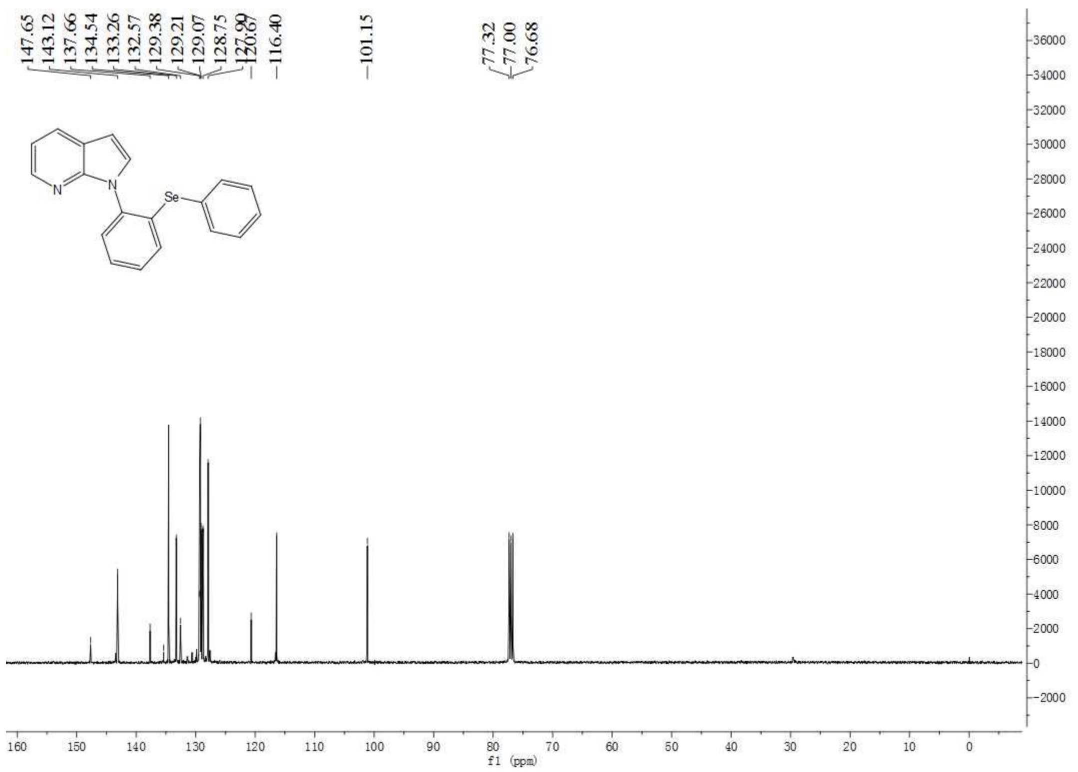
^{13}C NMR spectrum of 3ah in $CDCl_3$



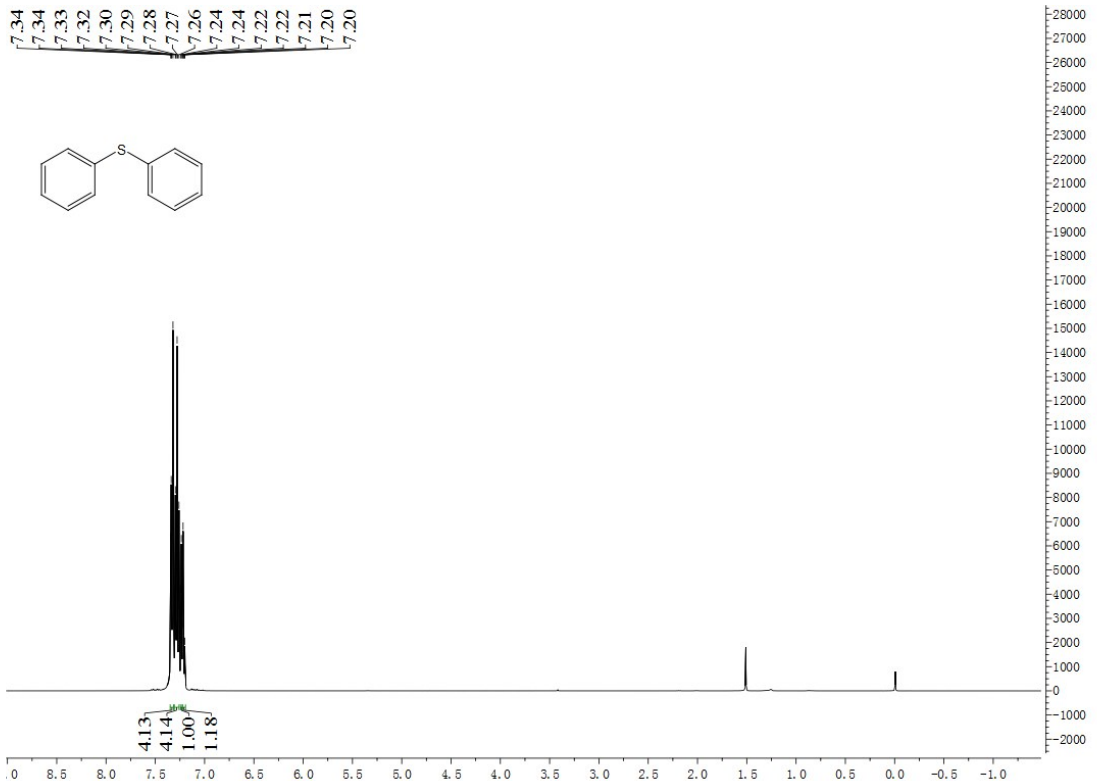
[1]H NMR spectrum of 3ai in $CDCl_3$



[13]C NMR spectrum of 3ai in $CDCl_3$



^1H NMR spectrum of 3ai in $CDCl_3$



^{13}C NMR spectrum of 3ai in $CDCl_3$