Supplementary Information

For

Electrochemically Chalcogenative Annulation Enabled Construction of Functionalized Saturated *N*-Heterocycles

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1. General informations

All the chemical reagents were purchased from commercial suppliers and used without purification. All the relevant solvents were purified according to the procedure from "Purification of Laboratory Chemicals book". Flash column chromatography was performed with silica gel (200–300 mesh). Cyclic voltammograms were recorded on a CHI 760E potentiostat (Shanghai Chenhua, China). NMR spectra were recorded on Bruker AV-400 instruments in $CDCl_3$ with TMS as internal standard. Data were reported as chemical shifts in ppm relative to TMS (0.00 ppm) for ^1H and $CDCl_3$ (77.2 ppm) for ^{13}C. The abbreviations used for explaining the multiplicities were as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet. High resolution mass spectra (HRMS) were recorded on a Bruker Esquire LC 6000 ion trap mass spectrometer using electrospray ionization.

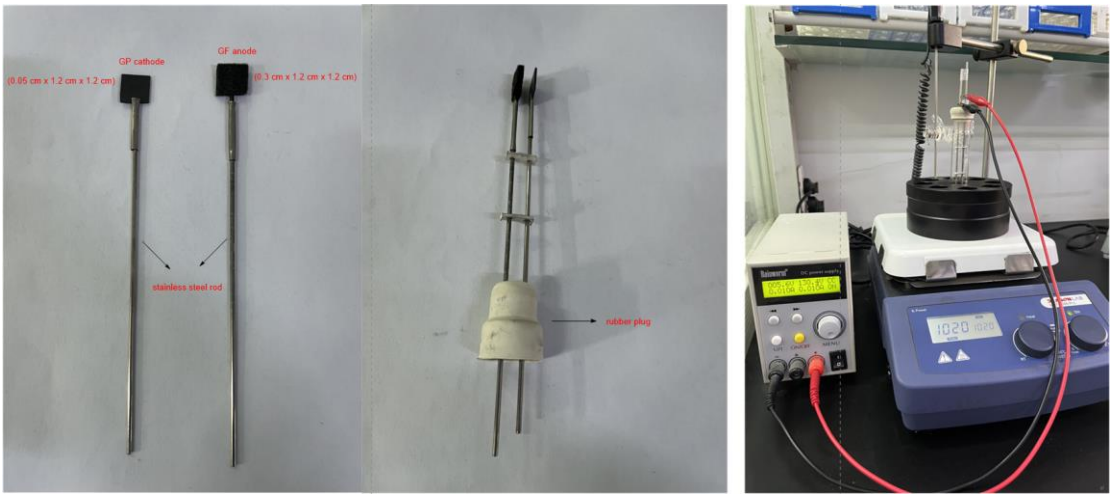
2. Procedures for electrolysis

General procedure A for the chalcogenataive annulation. To a 10 mL dry Schlenk tube was added alkenes (0.2 mmol), dichalcogenides (0.2 mmol, 1.0 equiv), $TBABF_4$ (0.1 mmol) and HFIP (5 mL). The tube was equipped with a graphite felt (GF) anode (0.3 cm x 1.2 cm x 1.2 cm) and a graphite plate (GP) cathode (0.05 cm x 1.2 cm x 1.2 cm). The solution was bubbled with N_2 for 2-3 minutes and then electrolyzed using a constant current (10 mA) at room temperature, the progress was monitored by TLC until completion. The reaction mixture was concentrated under reduced pressure and then chromatographed through silica gel eluting with petroleum ether/ethyl acetate to afford the desired products.

General procedure B for the alkene oxychalcogenation. To a 10 mL dry Schlenk tube was added alkenes (0.2 mmol), diphenyl dichalcogenides (0.2 mmol, 1.0 equiv), $TBABF_4$ (0.1 mmol), and TFE (5 mL). The tube was equipped with a graphite felt (GF) anode (0.3 cm x 1.2 cm x 1.2 cm) and a graphite plate (GP) cathode (0.05 cm x 1.2 cm x 1.2 cm). The solution was bubbled with N_2 for 2-3 minutes and then electrolyzed using a constant current (10 mA) at room temperature, the progress was monitored by TLC until completion. The reaction mixture was concentrated under reduced pressure and then chromatographed through silica gel eluting with petroleum ether/ethyl acetate to afford the desired products.

General procedure C for the alkene hydrooxysulfenylation. To a 10 mL dry Schlenk tube was added alkenes (0.2 mmol), diphenyl disulfides (0.2 mmol, 1.0 equiv), H_2O (10 μL, 3.0 equiv), $TBABF_4$ (0.5 mmol). The tube was equipped with a graphite felt (GF) anode (0.3 cm x 1.2 cm x 1.2 cm) and a graphite plate (GP) cathode (0.05 cm x 1.2 cm x 1.2 cm). The solution was bubbled with N_2 for 2-3 minutes and then electrolyzed using a constant current (10 mA) at

room temperature, the progress was monitored by TLC until completion. The reaction mixture was concentrated under reduced pressure and then chromatographed through silica gel eluting with petroleum ether/ethyl acetate to afford the desired products.

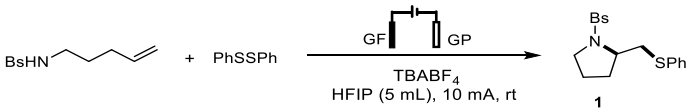


a **b**

Figure S1. a) Electrodes; b) Assembled reaction setup.

3. Condition screening

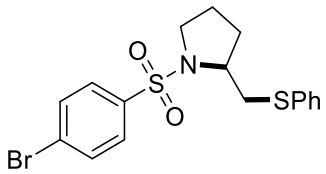
Table S1. Optimization of the electrochemical annulation conditions[a]



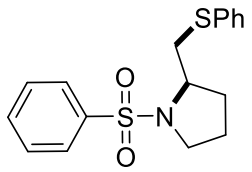
Entry	Deviation from standard conditions	Yield(%)[b]
1	None	92
2	No electricity	NR
3	Under air atmosphere	90
4	TFE as solvent	88
5	MeOH, MeCN, DCM as solvent	Trace
6[c]	TFE, MeCN, DCM as solvent	30-90
7	0.7 equiv of diphenyl disulfide	80
8	TBAI as electrolyte	Trace
9	$^{n}Bu_4NPF_6$, $^{n}Bu_4NClO_4$, $LiClO_4$ as electrolyte	85-91
10	5 mA for 5.0 h	90
11	15 mA for 1.6 h	72
12	GP(+)|GP (-)	83
13	Pt (+)|GP (-)	30
14	GF(+)|GF (-)	32
15	GF(+)|Pt (-)	92

[a]Reaction conditions: **1** (0.2 mmol), **2** (0.2 mmol), $TBABF_4$ (0.1 mmol), HFIP (5 mL), GF anode, GP cathode, N_2 atomsphere, constant current (10 mA), 2.5 h (4.7 F mol^{-1}), undivided cell. [b]Isolated yield. [c]HFIP (1.0 mmol) was added to these systems. Bs: 4-bromobenzenesulfonyl; HFIP: 1,1,1,3,3,3-hexafluoro-2-propanol; TFE: 2,2,2-trifluoroethan-1-ol

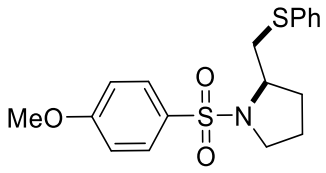
4. Characterization data for products



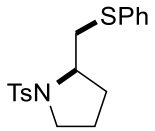
1-((4-bromophenyl)sulfonyl)-2-((phenylthio)methyl)pyrrolidine (1). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). White solid. Y = 92% (75.6 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.52 – 7.43 (m, 4H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 7.4 Hz, 1H), 3.66 (dd, *J* = 13.7, 2.7 Hz, 1H), 3.58 (ddt, *J* = 11.0, 7.1, 3.1 Hz, 1H), 3.51 (ddd, *J* = 10.5, 6.7, 4.1 Hz, 1H), 3.07 (q, *J* = 7.9 Hz, 1H), 2.77 (dd, *J* = 13.6, 10.7 Hz, 1H), 1.97 – 1.88 (m, 1H), 1.82 (dtd, *J* = 15.3, 8.5, 7.8, 5.2 Hz, 1H), 1.66 (td, *J* = 12.1, 9.6, 5.7 Hz, 1H), 1.57 (pd, *J* = 6.6, 2.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.91, 135.21, 132.46, 129.41, 129.22, 129.05, 127.87, 126.37, 59.17, 49.94, 38.52, 30.40, 23.86. ESI HRMS *m/z* $(M+Na)^+$ calcd 433.9855, obsd 433.9861.



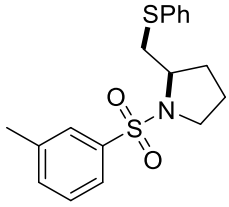
1-(phenylsulfonyl)-2-((phenylthio)methyl)pyrrolidine (2). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). Colorless oil. Y = 68% (45.3 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.50 – 7.41 (m, 4H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 3.75 – 3.58 (m, 2H), 3.50 (ddt, *J* = 9.4, 6.9, 3.3 Hz, 1H), 3.11 (dt, *J* = 9.9, 7.2 Hz, 1H), 2.78 (dd, *J* = 13.2, 10.4 Hz, 1H), 1.89 (ddd, *J* = 14.3, 6.5, 3.2 Hz, 1H), 1.84 – 1.75 (m, 1H), 1.68 – 1.58 (m, 1H), 1.52 (qd, *J* = 6.9, 2.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.82, 135.38, 132.85, 129.20, 129.10, 127.56, 126.20, 59.08, 49.89, 38.44, 30.38, 23.87. ESI HRMS *m/z* $(M+Na)^+$ calcd 356.0749, obsd 356.0753.



1-((4-methoxyphenyl)sulfonyl)-2-((phenylthio)methyl)pyrrolidine (3). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). Colorless oil. Y = 89% (63.8 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.9 Hz, 2H), 7.46 (d, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 8.9 Hz, 2H), 3.84 (s, 3H), 3.68 (dd, *J* = 13.6, 3.0 Hz, 1H), 3.61 (tt, *J* = 7.8, 3.4 Hz, 1H), 3.48 (ddd, *J* = 10.5, 6.8, 4.3 Hz, 1H), 3.09 (ddd, *J* = 9.9, 8.1, 6.7 Hz, 1H), 2.77 (dd, *J* = 13.5, 10.6 Hz, 1H), 1.93 – 1.84 (m, 1H), 1.83 – 1.75 (m, 1H), 1.71 – 1.61 (m, 1H), 1.58 – 1.49 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.03, 135.53, 129.67, 129.17, 129.11, 128.68, 126.15, 114.32, 59.05, 55.70, 49.88, 38.54, 30.43, 23.91. ESI HRMS *m/z* $(M+Na)^+$ calcd 386.0855, obsd 386.0856.

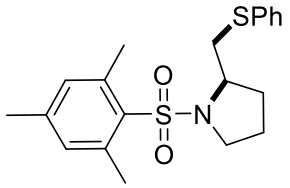


2-((phenylthio)methyl)-1-tosylpyrrolidine (4)[1]. The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). Colorless oil. Y = 93% (64.4 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.20 – 7.10 (m, 3H), 3.62 (dd, *J* = 13.5, 3.1 Hz, 1H), 3.54 (ddt, *J* = 11.1, 7.3, 3.2 Hz, 1H), 3.41 (ddd, *J* = 10.5, 6.8, 4.2 Hz, 1H), 3.01 (dt, *J* = 9.6, 6.8 Hz, 1H), 2.69 (dd, *J* = 13.6, 10.7 Hz, 1H), 2.31 (s, 3H), 1.94 – 1.66 (m, 2H), 1.62 – 1.49 (m, 1H), 1.44 (ddt, *J* = 14.4, 6.9, 3.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.61, 135.43, 133.84, 129.79, 129.17, 129.03, 127.60, 126.13, 58.99, 49.87, 38.43, 30.37, 23.86, 21.62. ESI HRMS *m/z* $(M+Na)^+$ calcd 370.0906, obsd 370.0910.

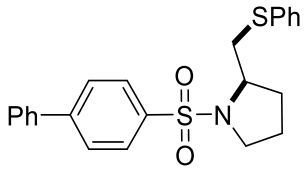


2-((phenylthio)methyl)-1-(m-tolylsulfonyl)pyrrolidine (5). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). Colorless oil. Y = 98% (68.8 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.36 (m, 4H), 7.27 (q, *J* = 7.3 Hz, 4H), 7.15 (t, *J* = 7.4 Hz, 1H), 3.63 (dd, *J* = 13.7, 3.1 Hz, 1H), 3.54 (ddt, *J* = 11.1, 7.9, 3.2 Hz, 1H), 3.43 (ddd, *J* = 10.4, 6.7, 4.1 Hz, 1H), 3.03 (ddd, *J* = 9.9, 8.1, 6.5 Hz, 1H), 2.68 (dd, *J* = 13.7, 10.8 Hz, 1H), 2.27 (s,

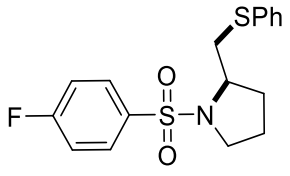
3H), 1.87 – 1.77 (m, 1H), 1.77 – 1.67 (m, 1H), 1.59 – 1.51 (m, 1H), 1.46 (dtd, *J* = 11.3, 7.8, 6.8, 4.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.32, 136.58, 135.32, 133.65, 129.15, 129.04, 129.00, 127.92, 126.14, 124.66, 58.92, 49.91, 38.34, 30.37, 23.85, 21.51. ESI HRMS *m/z* $(M+Na)^+$ calcd 370.0906, obsd 370.0911.



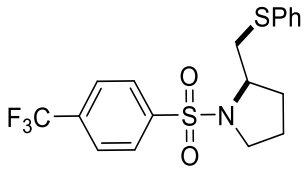
1-(mesitylsulfonyl)-2-((phenylthio)methyl)pyrrolidine (6). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). Colorless oil. Y = 85% (63.7 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 7.06 (m, 5H), 6.85 (s, 2H), 3.91 (dtd, *J* = 10.7, 5.4, 3.4 Hz, 1H), 3.33 (dt, *J* = 9.8, 7.7 Hz, 1H), 3.13 (ddd, *J* = 9.7, 6.6, 4.8 Hz, 1H), 2.96 (dd, *J* = 13.5, 3.4 Hz, 1H), 2.59 – 2.50 (m, 1H), 2.50 (s, 6H), 2.22 (s, 3H), 1.96 (dt, *J* = 8.0, 6.2 Hz, 1H), 1.87 – 1.75 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.84, 140.39, 135.30, 132.89, 132.13, 129.24, 129.13, 126.30, 58.22, 48.06, 37.43, 30.50, 24.11, 23.03, 21.14. ESI HRMS *m/z* $(M+Na)^+$ calcd 398.1219, obsd 398.1220.



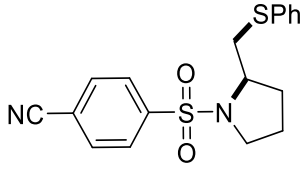
1-([1,1'-biphenyl]-4-ylsulfonyl)-2-((phenylthio)methyl)pyrrolidine (7). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). Colorless oil. Y = 80% (65.0 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 7.5 Hz, 2H), 7.52 – 7.44 (m, 4H), 7.43 – 7.32 (m, 3H), 7.24 (t, *J* = 7.3 Hz, 1H), 3.80 – 3.62 (m, 2H), 3.54 (ddd, *J* = 10.5, 6.8, 4.2 Hz, 1H), 3.15 (dt, *J* = 9.7, 7.0 Hz, 1H), 2.88 – 2.71 (m, 1H), 1.91 (ddd, *J* = 14.9, 6.8, 3.4 Hz, 1H), 1.82 (ddt, *J* = 12.9, 8.5, 6.8 Hz, 1H), 1.67 (p, *J* = 8.4 Hz, 1H), 1.57 (dtt, *J* = 11.0, 6.7, 3.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.64, 139.26, 135.46, 135.42, 129.20, 129.17, 129.13, 128.63, 128.11, 127.75, 127.39, 126.21, 59.11, 49.93, 38.48, 30.42, 23.89. ESI HRMS *m/z* $(M+Na)^+$ calcd 432.1062, obsd 432.1061.



1-((4-fluorophenyl)sulfonyl)-2-((phenylthio)methyl)pyrrolidine (8). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). Colorless oil. Y = 95% (66.7 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (dd, *J* = 8.7, 5.2 Hz, 2H), 7.43 – 7.37 (m, 2H), 7.28 (t, *J* = 7.8 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.04 (t, *J* = 8.5 Hz, 2H), 3.60 (dd, *J* = 13.7, 3.1 Hz, 1H), 3.51 (ddt, *J* = 11.0, 7.8, 3.2 Hz, 1H), 3.43 (ddd, *J* = 10.4, 6.7, 4.0 Hz, 1H), 2.99 (ddd, *J* = 9.6, 8.1, 6.6 Hz, 1H), 2.70 (dd, *J* = 13.6, 10.7 Hz, 1H), 1.84 (ddd, *J* = 15.1, 7.0, 3.6 Hz, 1H), 1.79 – 1.69 (m, 1H), 1.64 – 1.53 (m, 1H), 1.48 (tdd, *J* = 11.0, 6.8, 4.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ165.21 (d, J_{C-F} = 255.1 Hz), 135.26, 132.98 (d, J_{C-F} = 3.5 Hz), 130.19 (d, J_{C-F} = 8.9 Hz), 129.33, 129.21, 126.32, 116.42 (d, J_{C-F} = 22.4 Hz), 59.12, 49.93, 38.48, 30.38, 23.85; ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.12. ESI HRMS *m/z* $(M+Na)^+$ calcd 374.0650, obsd 374.0659.

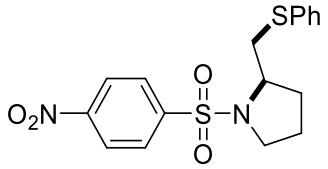


2-((phenylthio)methyl)-1-((4-(trifluoromethyl)phenyl)sulfonyl)pyrrolidine (9). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). Colorless oil. Y = 97% (77.8 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.40 (dd, *J* = 7.5, 1.6 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.17 (d, *J* = 7.7 Hz, 1H), 3.60 (dd, *J* = 13.6, 3.0 Hz, 1H), 3.57 – 3.43 (m, 2H), 3.02 (ddd, *J* = 9.8, 8.2, 6.6 Hz, 1H), 2.71 (dd, *J* = 13.6, 10.6 Hz, 1H), 1.86 (ddt, *J* = 14.8, 6.2, 3.3 Hz, 1H), 1.82 – 1.73 (m, 1H), 1.64 – 1.55 (m, 1H), 1.51 (ddd, *J* = 14.5, 6.8, 3.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.49, 135.13, 134.47 (q, J_{C-F} = 33.1 Hz), 129.45, 129.27, 128.05, 126.46, 126.36 (q, J_{C-F} = 3.7 Hz), 123.34 (q, J_{C-F} = 273.1 Hz), 59.26, 49.97, 38.47, 30.41, 23.86; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.07. ESI HRMS *m/z* $(M+Na)^+$ calcd 424.0623, obsd 424.0626.

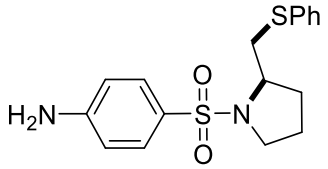


4-((2-((phenylthio)methyl)pyrrolidin-1-yl)sulfonyl)benzonitrile (10). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1). White solid. Y = 76% (54.5 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (s, 4H), 7.43 – 7.36 (m, 2H), 7.34 – 7.25 (m, 2H), 7.24 – 7.15 (m, 1H), 3.58 (dd, *J* = 13.6, 3.0 Hz, 1H), 3.49 (dddd, *J* = 13.9, 10.6, 7.4, 3.6 Hz, 2H), 3.01 (ddd, *J* = 9.9, 8.2, 6.7 Hz, 1H), 2.71 (dd, *J* = 13.6, 10.6 Hz, 1H), 1.92 – 1.84 (m, 1H), 1.83 – 1.73 (m, 1H), 1.65 – 1.48 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.15, 135.02, 133.00,

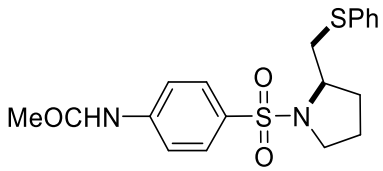
129.59, 129.27, 128.09, 126.54, 117.38, 116.52, 59.32, 49.98, 38.48, 30.40, 23.85. ESI HRMS *m/z* $(M+Na)^+$ calcd 381.0702, obsd 381.0709.



1-((4-nitrophenyl)sulfonyl)-2-((phenylthio)methyl)pyrrolidine (11). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1). White solid. Y = 70% (53.0 mg). Electricity = 4.6 F mol^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 8.8 Hz, 2H), 7.73 (d, *J* = 8.8 Hz, 2H), 7.45 – 7.35 (m, 2H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.27 – 7.11 (m, 1H), 3.73 – 3.36 (m, 3H), 3.10 – 2.97 (m, 1H), 2.71 (dd, *J* = 13.6, 10.5 Hz, 1H), 1.93 – 1.84 (m, 1H), 1.84 – 1.75 (m, 1H), 1.64 – 1.48 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.13, 142.69, 134.95, 129.62, 129.27, 128.67, 126.59, 124.41, 59.36, 50.02, 38.50, 30.41, 23.86. ESI HRMS *m/z* $(M+Na)^+$ calcd 401.0600, obsd 401.0598.

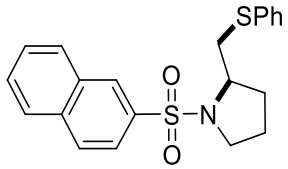


4-((2-((phenylthio)methyl)pyrrolidin-1-yl)sulfonyl)aniline (12). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2/1). Brown oil. Y = 70% (48.7 mg). Electricity = 4.6 F mol^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.35 (dd, *J* = 13.8, 8.2 Hz, 4H), 7.25 (t, *J* = 7.6 Hz, 2H), 7.13 (t, *J* = 7.3 Hz, 1H), 6.51 (d, *J* = 8.5 Hz, 2H), 3.89 (s, 2H), 3.58 (dd, *J* = 13.6, 2.7 Hz, 1H), 3.52 (ddt, *J* = 10.8, 6.9, 3.2 Hz, 1H), 3.36 (ddd, *J* = 10.3, 6.3, 4.5 Hz, 1H), 3.07 – 2.90 (m, 1H), 2.68 (dd, *J* = 13.3, 10.7 Hz, 1H), 1.82 – 1.74 (m, 1H), 1.73 – 1.64 (m, 1H), 1.56 (dq, *J* = 11.5, 7.7 Hz, 1H), 1.44 (tdd, *J* = 11.2, 6.1, 3.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.79, 135.51, 129.56, 129.11, 128.91, 126.03, 124.67, 114.14, 58.88, 49.84, 38.50, 30.36, 23.86. ESI HRMS *m/z* $(M+Na)^+$ calcd 371.0858, obsd 371.0861.

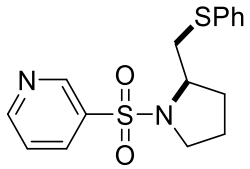


***N*-(4-((2-((phenylthio)methyl)pyrrolidin-1-yl)sulfonyl)phenyl)acetamide (13).** The product was prepared according to procedure A and purified by column chromatography on silica gel

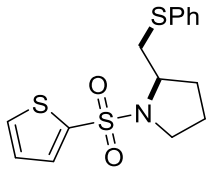
(petroleum ether/ethyl acetate = 2/1). Brown oil. Y = 75% (58.5 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (s, 1H), 7.69 – 7.51 (m, 4H), 7.47 – 7.39 (m, 2H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 3.62 (tt, *J* = 12.8, 3.2 Hz, 2H), 3.48 (ddd, *J* = 10.5, 6.8, 4.3 Hz, 1H), 3.09 (dt, *J* = 9.7, 6.9 Hz, 1H), 2.89 – 2.67 (m, 1H), 2.18 (s, 3H), 1.91 – 1.75 (m, 2H), 1.69 – 1.58 (m, 1H), 1.53 (dtt, *J* = 11.3, 6.8, 3.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.24, 142.46, 135.32, 131.26, 129.30, 129.22, 128.74, 126.36, 119.49, 59.19, 49.96, 38.68, 30.40, 24.77, 23.90. ESI HRMS *m/z* $(M+Na)^+$ calcd 413.0964, obsd 413.0967.



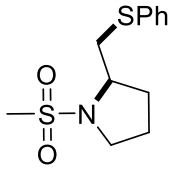
1-(naphthalen-2-ylsulfonyl)-2-((phenylthio)methyl)pyrrolidine (14). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). Colorless oil. Y = 93% (71.5 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 (s, 1H), 7.88 (dd, *J* = 8.1, 4.6 Hz, 3H), 7.67 (d, *J* = 8.7 Hz, 1H), 7.60 (p, *J* = 6.9 Hz, 2H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 15.5 Hz, 1H), 3.74 (td, *J* = 13.4, 5.4 Hz, 2H), 3.55 (ddd, *J* = 10.3, 6.6, 4.5 Hz, 1H), 3.19 (q, *J* = 7.9 Hz, 1H), 2.94 – 2.68 (m, 1H), 1.96 – 1.74 (m, 2H), 1.66 – 1.55 (m, 1H), 1.51 (ddt, *J* = 11.6, 8.7, 4.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.38, 134.90, 133.93, 132.20, 129.45, 129.38, 129.20, 129.12, 128.92, 128.87, 127.97, 127.62, 126.21, 122.87, 59.11, 49.96, 38.44, 30.39, 23.89. ESI HRMS *m/z* $(M+Na)^+$ calcd 406.0906, obsd 406.0910.



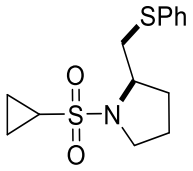
3-((2-((phenylthio)methyl)pyrrolidin-1-yl)sulfonyl)pyridine (15). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 4/1). Colorless oil. Y = 60% (40.0 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.84 (s, 1H), 8.71 (d, *J* = 4.7 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.33 (dd, *J* = 8.0, 4.7 Hz, 1H), 7.28 (t, *J* = 7.7 Hz, 2H), 7.18 (t, *J* = 9.0 Hz, 1H), 3.57 (ddt, *J* = 13.3, 7.7, 3.0 Hz, 2H), 3.47 (dq, *J* = 6.9, 3.8, 3.3 Hz, 1H), 3.03 (dt, *J* = 9.8, 7.3 Hz, 1H), 2.84 – 2.55 (m, 1H), 1.95 – 1.84 (m, 1H), 1.81 – 1.72 (m, 1H), 1.66 – 1.40 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.37, 148.12, 135.25, 135.02, 133.69, 129.24, 126.43, 123.91, 59.26, 49.89, 38.38, 30.37, 23.87. ESI HRMS *m/z* $(M+Na)^+$ calcd 357.0702, obsd 357.0710.



2-((phenylthio)methyl)-1-(thiophen-2-ylsulfonyl)pyrrolidine (16). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1). White solid. Y = 95% (64.4 mg). Electricity = 4.6 F mol^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.47 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.40 – 7.34 (m, 3H), 7.26 (t, *J* = 7.7 Hz, 2H), 7.13 (t, *J* = 7.3 Hz, 1H), 6.99 (dd, *J* = 5.0, 3.7 Hz, 1H), 3.62 (tq, *J* = 9.1, 3.1 Hz, 2H), 3.46 (ddd, *J* = 10.7, 6.8, 4.3 Hz, 1H), 3.19 – 3.01 (m, 1H), 2.73 (dd, *J* = 14.3, 11.4 Hz, 1H), 1.84 (dt, *J* = 10.3, 6.2 Hz, 1H), 1.80 – 1.72 (m, 1H), 1.67 – 1.57 (m, 1H), 1.54 – 1.43 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.79, 135.34, 132.37, 131.98, 129.19, 128.73, 127.60, 126.08, 59.45, 50.08, 38.15, 30.38, 23.95. ESI HRMS *m/z* $(M+Na)^+$ calcd 362.0314, obsd 362.0322.

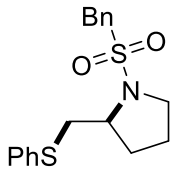


1-(methylsulfonyl)-2-((phenylthio)methyl)pyrrolidine (17). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7/1). Colorless oil. Y = 50% (27.1 mg). Electricity = 4.6 F mol^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 7.5 Hz, 2H), 7.09 (t, *J* = 7.3 Hz, 1H), 3.77 (dq, *J* = 9.7, 5.5 Hz, 1H), 3.45 (dd, *J* = 13.7, 3.4 Hz, 1H), 3.38 (dt, *J* = 10.6, 5.7 Hz, 1H), 3.26 – 3.15 (m, 1H), 2.77 (dd, *J* = 13.6, 10.2 Hz, 1H), 2.70 (s, 3H), 2.00 – 1.92 (m, 2H), 1.88 (dd, *J* = 14.5, 7.1 Hz, 1H), 1.80 (dq, *J* = 12.2, 5.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.60, 129.16, 128.43, 125.99, 59.29, 49.49, 38.14, 35.22, 30.71, 24.44. ESI HRMS *m/z* $(M+Na)^+$ calcd 294.0593, obsd 294.0599.

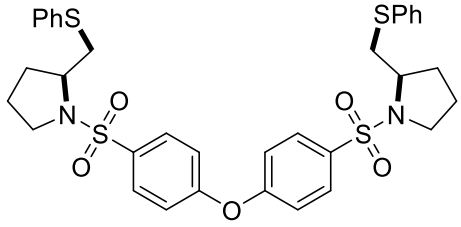


1-(cyclopropylsulfonyl)-2-((phenylthio)methyl)pyrrolidine (18). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). Brown oil. Y = 90% (53.8 mg). Electricity = 4.6 F mol^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 3.97 (ddt, *J* = 11.0, 7.4, 3.7 Hz, 1H), 3.54 (dd, *J* = 13.7, 3.3 Hz, 1H), 3.50 – 3.36 (m,

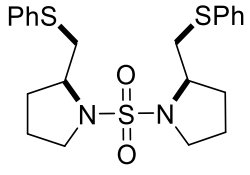
2H), 2.79 (dd, *J* = 13.7, 10.3 Hz, 1H), 2.26 (tt, *J* = 8.3, 4.8 Hz, 1H), 2.06 (dq, *J* = 11.0, 5.0 Hz, 2H), 1.91 (tq, *J* = 12.3, 6.3 Hz, 2H), 1.16 (dqd, *J* = 6.7, 5.0, 4.3, 2.0 Hz, 1H), 1.12 – 1.04 (m, 1H), 0.91 (hd, *J* = 8.8, 4.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.63, 129.15, 128.69, 126.03, 59.00, 49.57, 38.26, 30.73, 26.70, 24.53, 4.82, 4.45. ESI HRMS *m/z* $(M+Na)^+$ calcd 320.0749, obsd 320.0745.



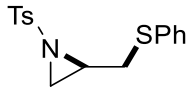
1-(benzylsulfonyl)-2-((phenylthio)methyl)pyrrolidine (19). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). Colorless oil. Y = 93% (64.5 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.17 (m, 9H), 7.13 – 7.05 (m, 1H), 4.15 (d, *J* = 2.2 Hz, 2H), 3.57 (ddt, *J* = 10.2, 6.7, 3.5 Hz, 1H), 3.21 (ddt, *J* = 10.9, 7.5, 3.7 Hz, 2H), 3.15 – 3.01 (m, 1H), 2.49 (dd, *J* = 13.6, 10.4 Hz, 1H), 1.87 – 1.65 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.53, 130.74, 129.13, 129.07, 128.83, 128.81, 128.37, 125.87, 59.35, 56.74, 49.47, 37.56, 30.35, 24.29. ESI HRMS *m/z* $(M+Na)^+$ calcd 370.0906, obsd 370.0904.



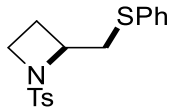
1,1'-(oxybis(4,1-phenylenesulfonyl))bis(2-((phenylthio)methyl)pyrrolidine) (20). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/2). White solid. Y = 95% (129.2 mg), d.r. = 1:1. Electricity = 7.4 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.7 Hz, 4H), 7.37 (d, *J* = 7.9 Hz, 4H), 7.24 (td, *J* = 7.7, 1.8 Hz, 4H), 7.15 – 7.06 (m, 2H), 6.95 (dd, *J* = 9.3, 2.5 Hz, 4H), 3.64 – 3.50 (m, 4H), 3.43 (ddd, *J* = 10.4, 6.7, 4.0 Hz, 2H), 3.02 (ddd, *J* = 9.6, 8.1, 6.6 Hz, 2H), 2.81 – 2.62 (m, 2H), 1.89 – 1.80 (m, 2H), 1.76 (ddd, *J* = 11.8, 9.4, 4.4 Hz, 2H), 1.65 – 1.55 (m, 2H), 1.50 (ddq, *J* = 11.1, 6.9, 4.3, 2.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.31, 135.25, 135.24, 132.42, 132.40, 129.90, 129.08, 128.93, 128.90, 126.10, 119.26, 59.01, 49.84, 38.26, 38.24, 30.34, 23.82. ESI HRMS *m/z* $(M+Na)^+$ calcd 703.1399, obsd 703.1402.



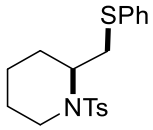
1,1'-sulfonylbis(2-((phenylthio)methyl)pyrrolidine) (21). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/2). Colorless oil; Y = 75% (65.1 mg), d.r. = 1.9:1. Electricity = 7.4 F mol^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 7.3 Hz, 4H), 7.21 – 7.13 (m, 4H), 7.05 (td, *J* = 7.3, 4.8 Hz, 2H), 3.88 (ddq, *J* = 10.7, 7.4, 4.1 Hz, 2H), 3.37 (dd, *J* = 13.4, 3.3 Hz, 2H), 3.28 – 3.10 (m, 4H), 2.63 (ddd, *J* = 13.5, 10.3, 5.5 Hz, 2H), 1.97 – 1.85 (m, 4H), 1.83 – 1.72 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.72, 135.70, 129.07, 128.61, 128.54, 125.99, 125.95, 59.67, 59.16, 49.48, 49.10, 37.69, 37.62, 30.42, 30.21, 24.33, 24.30. ESI HRMS *m/z* $(M+Na)^+$ calcd 471.1205, obsd 471.1209.



2-((phenylthio)methyl)-1-tosylaziridine (22). The product was prepared according to procedure A with TFE (5.0 mL) as solvent and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). Colorless oil. Y = 36% (23.0 mg). Electricity = 4.6 F mol^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.40 – 7.08 (m, 7H), 3.01 – 2.87 (m, 2H), 2.82 (dd, *J* = 13.3, 5.8 Hz, 1H), 2.56 (d, *J* = 6.6 Hz, 1H), 2.35 (s, 3H), 2.01 (d, *J* = 4.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.81, 134.83, 134.78, 130.34, 129.81, 129.19, 128.14, 127.00, 39.13, 35.53, 33.78, 21.79. ESI HRMS *m/z* $(M+Na)^+$ calcd 342.0593, obsd 342.0592.

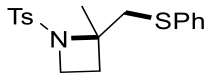


2-((phenylthio)methyl)-1-tosylazetidine (23). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). Colorless oil. Y = 71% (47.1 mg). Electricity = 4.6 F mol^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.28 – 7.14 (m, 7H), 3.60 (dd, *J* = 10.3, 6.6 Hz, 1H), 3.54 (p, *J* = 6.3 Hz, 1H), 3.36 – 3.22 (m, 2H), 3.05 (dd, *J* = 10.3, 5.5 Hz, 1H), 2.37 (s, 3H), 2.11 (dq, *J* = 13.5, 6.9 Hz, 1H), 1.70 (dq, *J* = 13.1, 6.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.76, 134.07, 133.69, 131.76, 129.87, 129.26, 127.74, 127.58, 53.86, 47.03, 44.80, 31.92, 21.72. ESI HRMS *m/z* $(M+Na)^+$ calcd 356.0749, obsd 356.0752.

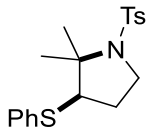


2-((phenylthio)methyl)-1-tosylpiperidine (24)[2]. The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl

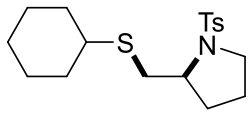
acetate = 6/1). Colorless oil. Y = 50% (37.5 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.41 – 7.22 (m, 7H), 4.16 (qd, *J* = 6.7, 6.2, 3.9 Hz, 1H), 3.90 – 3.78 (m, 1H), 3.10 (d, *J* = 7.7 Hz, 2H), 3.00 (td, *J* = 13.3, 2.7 Hz, 1H), 2.43 (s, 3H), 2.00 (d, *J* = 10.5 Hz, 1H), 1.62 – 1.52 (m, 2H), 1.50 – 1.39 (m, 2H), 1.32 (tdd, *J* = 11.5, 7.9, 4.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.22, 138.27, 135.41, 129.81, 129.64, 129.16, 127.14, 126.49, 51.77, 41.11, 33.09, 25.38, 24.66, 21.67, 18.21. ESI HRMS *m/z* $(M+Na)^+$ calcd 384.1062, obsd 384.1071.



2-methyl-2-((phenylthio)methyl)-1-tosylazetidine (25). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). White solid. Y = 76% (52.7 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.9 Hz, 2H), 7.43 – 7.23 (m, 7H), 3.56 – 3.39 (m, 2H), 3.34 (d, *J* = 10.4 Hz, 1H), 3.18 (d, *J* = 10.5 Hz, 1H), 2.43 (s, 3H), 1.92 (ddd, *J* = 12.8, 7.4, 5.2 Hz, 1H), 1.77 (dt, *J* = 13.0, 7.5 Hz, 1H), 1.24 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.62, 137.17, 134.25, 131.12, 129.79, 129.41, 129.03, 127.64, 59.04, 53.32, 46.93, 38.33, 26.21, 21.69. ESI HRMS *m/z* $(M+Na)^+$ calcd 370.0906, obsd 370.0914.

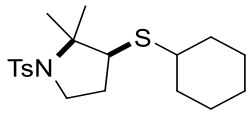


2,2-dimethyl-3-(phenylthio)-1-tosylpyrrolidine (26). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). Colorless oil. Y = 90% (65.2 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.32 (dd, *J* = 8.0, 1.7 Hz, 2H), 7.25 – 7.12 (m, 5H), 3.50 (td, *J* = 9.0, 2.6 Hz, 1H), 3.24 – 3.08 (m, 2H), 2.32 (s, 3H), 2.14 (dtd, *J* = 13.1, 6.7, 2.6 Hz, 1H), 1.88 (ddt, *J* = 12.8, 11.4, 9.0 Hz, 1H), 1.45 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.98, 138.58, 134.82, 132.30, 129.59, 129.25, 127.59, 127.22, 67.20, 59.55, 46.51, 30.26, 26.92, 23.69, 21.61. ESI HRMS *m/z* $(M+Na)^+$ calcd 384.1062, obsd 384.1061.

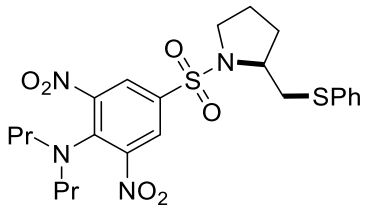


2-((cyclohexylthio)methyl)-1-tosylpyrrolidine (27). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). Colorless oil. Y = 73% (51.5 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 3.61 (ddt, *J* = 10.8, 7.0, 3.2 Hz, 1H), 3.38 (ddd, *J* = 10.9, 6.8, 4.4 Hz, 1H), 3.14 – 2.93 (m, 2H), 2.67 (ddt, *J* = 10.8, 7.1, 3.7

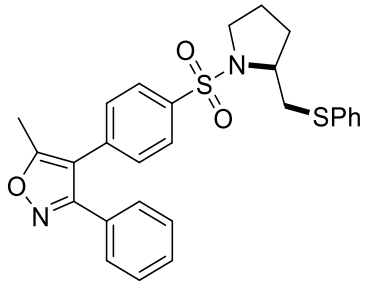
Hz, 1H), 2.52 (dd, *J* = 13.1, 10.5 Hz, 1H), 2.36 (s, 3H), 2.07 – 1.87 (m, 2H), 1.83 – 1.67 (m, 4H), 1.57 (dq, *J* = 10.9, 3.4 Hz, 2H), 1.46 (qt, *J* = 7.0, 3.3 Hz, 1H), 1.36 – 1.10 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.64, 134.47, 129.86, 127.65, 60.52, 49.65, 44.32, 36.07, 34.04, 33.83, 30.48, 26.31, 26.25, 25.94, 23.98, 21.69. ESI HRMS *m/z* $(M+Na)^+$ calcd 376.1375, obsd 376.1382.



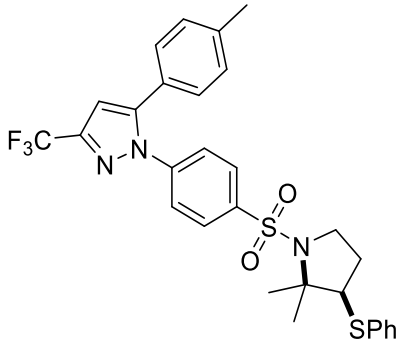
3-(cyclohexylthio)-2,2-dimethyl-1-tosylpyrrolidine (28). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). Colorless oil. Y = 96% (70.4 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 3.46 (td, *J* = 9.0, 1.9 Hz, 1H), 3.13 (td, *J* = 9.7, 6.9 Hz, 1H), 2.70 (dd, *J* = 12.0, 6.5 Hz, 1H), 2.52 (td, *J* = 8.5, 6.5, 3.9 Hz, 1H), 2.34 (s, 3H), 2.11 (dtd, *J* = 13.3, 6.8, 1.9 Hz, 1H), 1.90 – 1.75 (m, 3H), 1.70 – 1.60 (m, 2H), 1.51 (dd, *J* = 9.9, 4.1 Hz, 1H), 1.46 (s, 3H), 1.28 – 1.11 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.87, 138.61, 129.55, 127.24, 67.04, 54.34, 46.47, 44.48, 34.43, 34.04, 31.51, 26.32, 26.16, 26.09, 25.73, 23.28, 21.59. ESI HRMS *m/z* $(M+Na)^+$ calcd 390.1532, obsd 390.1538.



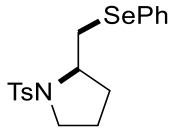
2,6-dinitro-4-((2-((phenylthio)methyl)pyrrolidin-1-yl)sulfonyl)-N,N-dipropylaniline (29). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1/1). Yellow solid. Y = 28% (29 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (s, 2H), 7.44 (d, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.21 (m, 1H), 3.76 – 3.49 (m, 3H), 3.15 (dt, *J* = 9.9, 7.5 Hz, 1H), 3.04 – 2.86 (m, 4H), 2.84 – 2.72 (m, 1H), 2.09 – 1.99 (m, 1H), 1.97 – 1.89 (m, 1H), 1.86 – 1.70 (m, 2H), 1.66 – 1.57 (m, 4H), 0.87 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.77, 141.62, 134.60, 129.53, 129.31, 128.70, 128.14, 126.87, 59.27, 54.05, 50.25, 38.43, 30.57, 23.99, 20.83, 11.30. ESI HRMS *m/z* $(M+Na)^+$ calcd 545.1499, obsd 545.1505.



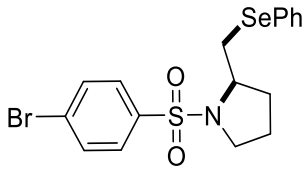
5-methyl-3-phenyl-4-(4-((2-((phenylthio)methyl)pyrrolidin-1-yl)sulfonyl)phenyl)isoxazole (30). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 4/1). Colorless oil. Y = 88% (92.0 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 7.4 Hz, 2H), 7.40 (td, *J* = 5.9, 3.0 Hz, 1H), 7.36 – 7.21 (m, 8H), 7.18 (t, *J* = 7.3 Hz, 1H), 3.67 (dq, *J* = 10.9, 3.7 Hz, 2H), 3.52 (ddd, *J* = 10.6, 6.7, 4.4 Hz, 1H), 3.15 (dt, *J* = 9.9, 7.4 Hz, 1H), 2.80 (dd, *J* = 14.2, 11.2 Hz, 1H), 2.46 (s, 3H), 1.94 (ddd, *J* = 15.3, 7.0, 3.7 Hz, 1H), 1.89 – 1.77 (m, 1H), 1.67 (dq, *J* = 11.8, 7.6 Hz, 1H), 1.56 (tdd, *J* = 11.4, 6.3, 4.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.24, 161.15, 136.11, 135.30, 135.26, 130.34, 129.81, 129.17, 129.15, 128.74, 128.52, 128.49, 127.89, 126.23, 114.47, 59.16, 49.86, 38.44, 30.39, 23.87, 11.83. ESI HRMS *m/z* $(M+Na)^+$ calcd 513.1277, obsd 513.1281.



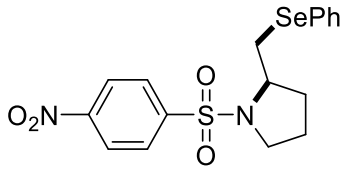
1-(4-((2,2-dimethyl-3-(phenylthio)pyrrolidin-1-yl)sulfonyl)phenyl)-5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazole (31). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1). White solid. Y = 99% (113.2 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.33 – 7.29 (m, 2H), 7.24 – 7.12 (m, 3H), 7.06 (d, *J* = 7.9 Hz, 2H), 7.00 (d, *J* = 7.9 Hz, 2H), 6.65 (s, 1H), 3.51 (td, *J* = 8.9, 2.8 Hz, 1H), 3.16 (ddd, *J* = 16.5, 9.8, 6.6 Hz, 2H), 2.27 (s, 3H), 2.15 (dtd, *J* = 13.2, 6.8, 2.7 Hz, 1H), 1.86 (dq, *J* = 12.5, 9.0 Hz, 1H), 1.40 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.37, 144.12 (q, *J* = 38.7 Hz), 142.19, 141.08, 139.88, 134.59, 132.32, 129.84, 129.32, 128.82, 128.15, 127.70, 125.78, 125.60, 121.22 (q, *J* = 269.2 Hz), 106.25 (d, *J* = 2.3 Hz), 67.62, 59.52, 46.74, 30.08, 26.98, 23.78, 21.43; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.35. ESI HRMS *m/z* $(M+Na)^+$ calcd 594.1467, obsd 594.1473.



2-((phenylselanyl)methyl)-1-tosylpyrrolidine (32)[3]. The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). Colorless oil. Y = 98% (77.5 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.47 (m, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.17 (m, 3H), 7.13 (d, *J* = 7.9 Hz, 2H), 3.63 – 3.49 (m, 2H), 3.40 (ddd, *J* = 10.7, 6.5, 4.6 Hz, 1H), 3.03 (dt, *J* = 9.6, 7.0 Hz, 1H), 2.74 (dd, *J* = 13.0, 11.3 Hz, 1H), 2.30 (s, 3H), 1.82 – 1.64 (m, 2H), 1.63 – 1.53 (m, 1H), 1.46 – 1.33 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.49, 133.82, 132.44, 129.70, 129.34, 129.27, 127.50, 126.97, 59.85, 49.96, 32.94, 31.06, 23.86, 21.56; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 269.92. ESI HRMS *m/z* $(M+Na)^+$ calcd 418.0350, obsd 418.0347.

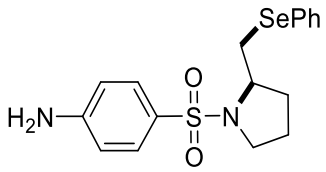


1-((4-bromophenyl)sulfonyl)-2-((phenylselanyl)methyl)pyrrolidine (33). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). Colorless oil. Y = 99% (90.8 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.42 (m, 4H), 7.39 – 7.32 (m, 2H), 7.29 – 7.20 (m, 3H), 3.54 – 3.46 (m, 2H), 3.42 (ddd, *J* = 10.2, 6.7, 4.5 Hz, 1H), 3.01 (dt, *J* = 9.9, 7.3 Hz, 1H), 2.84 – 2.69 (m, 1H), 1.75 (tdd, *J* = 14.7, 6.7, 5.1 Hz, 2H), 1.67 – 1.54 (m, 1H), 1.44 (tdt, *J* = 11.3, 6.9, 4.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.85, 132.76, 132.36, 129.33, 129.12, 128.98, 127.74, 127.17, 60.00, 50.06, 32.84, 31.08, 23.86. ESI HRMS *m/z* $(M+Na)^+$ calcd 481.9299, obsd 481.9291. ^{77}Se NMR (76 MHz, $CDCl_3$) δ 272.68.

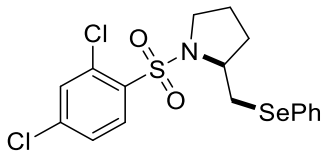


1-((4-nitrophenyl)sulfonyl)-2-((phenylselanyl)methyl)pyrrolidine (34). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 4/1). Brown solid. Y = 75% (63.9 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 (d, *J* = 8.6 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.56 – 7.48 (m, 2H), 7.36 – 7.21 (m, 3H), 3.50 (dtd, *J* = 12.9, 7.0, 6.6, 3.8 Hz, 3H), 3.06 (dt, *J* = 9.7, 7.3 Hz, 1H), 2.86 – 2.68 (m, 1H), 1.89 – 1.74 (m, 2H), 1.64 (dt, *J* = 11.3, 7.7 Hz, 1H), 1.49 (dtt,

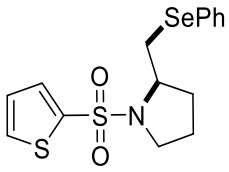
J = 11.6, 7.3, 3.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.12, 142.78, 133.08, 129.47, 128.96, 128.68, 127.46, 124.40, 60.29, 50.20, 32.76, 31.18, 23.94; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 274.89. ESI HRMS *m/z* $(M+Na)^+$ calcd 449.0045, obsd 449.0040.



4-((2-((phenylselanyl)methyl)pyrrolidin-1-yl)sulfonyl)aniline (35). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1). Brown oil; Y = 93% (73.6 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 7.26 – 7.15 (m, 3H), 6.51 (d, *J* = 8.6 Hz, 2H), 3.84 (s, 2H), 3.52 (ddd, *J* = 12.6, 9.5, 5.3 Hz, 2H), 3.37 (dt, *J* = 10.0, 5.6 Hz, 1H), 3.02 (dt, *J* = 9.7, 7.1 Hz, 1H), 2.83 – 2.71 (m, 1H), 1.77 – 1.65 (m, 2H), 1.65 – 1.56 (m, 1H), 1.47 – 1.34 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.66, 132.41, 129.57, 129.50, 129.30, 126.95, 124.93, 114.18, 59.82, 50.01, 33.16, 31.15, 23.96; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 268.79. ESI HRMS *m/z* $(M+Na)^+$ calcd 419.0303, obsd 419.0302.

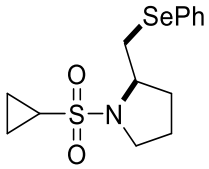


1-((2,4-dichlorophenyl)sulfonyl)-2-((phenylselanyl)methyl)pyrrolidine (36). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). Colorless oil. Y = 97% (86.1 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.5 Hz, 1H), 7.49 (q, *J* = 3.4, 2.7 Hz, 3H), 7.34 – 7.10 (m, 4H), 4.05 (ddt, *J* = 10.5, 7.1, 3.5 Hz, 1H), 3.55 – 3.46 (m, 1H), 3.46 – 3.35 (m, 2H), 2.81 (dd, *J* = 12.6, 10.7 Hz, 1H), 2.08 – 1.86 (m, 3H), 1.84 – 1.71 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.42, 135.64, 133.26, 133.18, 132.60, 131.97, 129.38, 129.34, 127.38, 127.19, 60.37, 49.31, 32.45, 31.32, 24.16; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 270.65. ESI HRMS *m/z* $(M+Na)^+$ calcd 471.9414, obsd 471.9408.

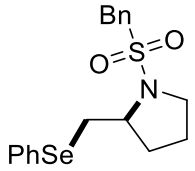


2-((phenylselanyl)methyl)-1-(thiophen-2-ylsulfonyl)pyrrolidine (37). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). Brown oil. Y = 93% (71.9 mg). Electricity = 4.6 F mol^{-1}.

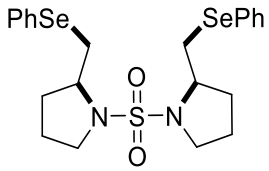
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (ddd, *J* = 10.1, 6.6, 1.6 Hz, 3H), 7.33 – 7.28 (m, 1H), 7.26 – 7.12 (m, 3H), 6.98 (dd, *J* = 5.0, 3.8 Hz, 1H), 3.63 (ddt, *J* = 10.9, 7.4, 3.3 Hz, 1H), 3.52 (dd, *J* = 12.6, 3.0 Hz, 1H), 3.45 (dt, *J* = 11.0, 6.0 Hz, 1H), 3.12 (dt, *J* = 10.0, 7.0 Hz, 1H), 2.80 (dd, *J* = 12.4, 11.0 Hz, 1H), 1.76 (ddt, *J* = 13.9, 11.4, 6.7 Hz, 2H), 1.64 (ddt, *J* = 14.8, 7.4, 3.2 Hz, 1H), 1.51 – 1.38 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.86, 132.31, 132.18, 131.92, 129.38, 129.34, 127.55, 126.97, 60.40, 50.17, 32.70, 31.09, 23.99; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 268.69. ESI HRMS *m/z* $(M+Na)^+$ calcd 409.9758, obsd 409.9755.



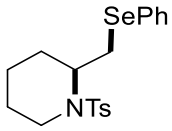
1-(cyclopropylsulfonyl)-2-((phenylselanyl)methyl)pyrrolidine (38). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). Brown oil. Y = 95% (65.5 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.37 (m, 2H), 7.28 – 6.99 (m, 3H), 3.92 (ddt, *J* = 10.9, 7.4, 3.4 Hz, 1H), 3.37 (dt, *J* = 12.8, 4.7 Hz, 3H), 2.80 (dd, *J* = 12.5, 10.3 Hz, 1H), 2.17 (tt, *J* = 8.0, 4.8 Hz, 1H), 2.01 (qd, *J* = 9.7, 8.5, 5.9 Hz, 1H), 1.93 – 1.72 (m, 3H), 1.14 – 1.02 (m, 1H), 1.01 – 0.92 (m, 1H), 0.82 (tq, *J* = 8.2, 4.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.02, 129.62, 129.27, 126.88, 59.79, 49.63, 32.88, 31.44, 26.75, 24.58, 4.80, 4.40; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 264.21. ESI HRMS *m/z* $(M+Na)^+$ calcd 368.0194, obsd 368.0189.



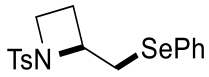
1-(benzylsulfonyl)-2-((phenylselanyl)methyl)pyrrolidine (39). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). Colorless oil. Y = 97% (76.6 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.33 (m, 2H), 7.30 – 7.21 (m, 5H), 7.21 – 7.10 (m, 3H), 4.12 (d, *J* = 2.0 Hz, 2H), 3.63 (ddt, *J* = 10.5, 7.0, 3.3 Hz, 1H), 3.15 (qdd, *J* = 16.4, 9.0, 5.2 Hz, 3H), 2.57 (dd, *J* = 12.5, 10.5 Hz, 1H), 1.98 – 1.52 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.77, 130.74, 129.66, 129.24, 129.12, 128.78, 126.78, 60.21, 56.82, 49.56, 32.23, 31.11, 24.37; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 264.28. ESI HRMS *m/z* $(M+Na)^+$ calcd 418.0350, obsd 418.0351.



1,1'-sulfonylbis(2-((phenylselanyl)methyl)pyrrolidine) (40). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1). Colorless oil; Y = 99% (104.9 mg), d.r. = 1:1; Electricity = 7.4 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 7.2 Hz, 4H), 7.15 (qd, *J* = 8.3, 6.9, 3.2 Hz, 6H), 3.91 (ddq, *J* = 11.0, 7.3, 3.5 Hz, 2H), 3.38 – 3.09 (m, 6H), 2.73 (dt, *J* = 12.4, 10.0 Hz, 2H), 1.95 (dp, *J* = 12.6, 8.5 Hz, 2H), 1.87 – 1.68 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.03, 131.95, 129.86, 129.84, 129.26, 129.25, 126.90, 126.86, 60.47, 59.96, 49.63, 49.31, 32.59, 32.42, 31.28, 31.05, 24.45, 24.43; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 262.84, 261.19. ESI HRMS *m/z* $(M+Na)^+$ calcd 567.0094, obsd 567.0092.

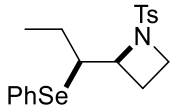


2-((phenylselanyl)methyl)-1-tosylpiperidine (41). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). Colorless oil. Y = 98% (80.0 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.43 – 7.36 (m, 2H), 7.17 (dd, *J* = 5.0, 2.0 Hz, 3H), 7.12 (d, *J* = 8.1 Hz, 2H), 4.14 – 4.01 (m, 1H), 3.78 – 3.53 (m, 1H), 2.99 (dd, *J* = 12.3, 10.4 Hz, 1H), 2.92 – 2.79 (m, 2H), 2.29 (s, 3H), 1.88 – 1.78 (m, 1H), 1.46 – 1.25 (m, 4H), 1.25 – 1.12 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.00, 138.09, 132.87, 129.64, 129.44, 129.13, 127.18, 126.89, 52.59, 40.75, 27.22, 26.04, 24.51, 21.50, 17.96; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 274.40. ESI HRMS *m/z* $(M+Na)^+$ calcd 432.0507, obsd 432.0510.

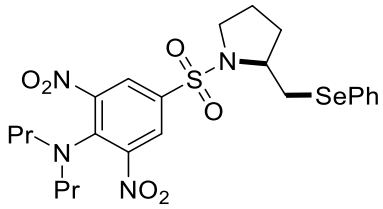


2-((phenylselanyl)methyl)-1-tosylazetidine (42). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). Colorless oil. Y = 98% (74.6 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.1 Hz, 2H), 7.39 – 7.28 (m, 2H), 7.26 – 7.09 (m, 5H), 3.60 (dd, *J* = 10.7, 6.7 Hz, 1H), 3.45 (p, *J* = 6.6 Hz, 1H), 3.31 – 3.19 (m, 2H), 3.10 (dd, *J* = 10.8, 6.3 Hz, 1H), 2.32 (s, 3H), 2.08 (dq, *J* = 13.2, 6.7 Hz, 1H), 1.68 (dq, *J* = 13.8, 7.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.57, 134.59, 133.48, 129.72, 129.20, 128.02, 127.48, 54.24, 47.21, 38.11, 32.41, 21.55; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 366.59. ESI HRMS *m/z* $(M+Na)^+$ calcd 404.0194, obsd 404.0192.

2-methyl-2-((phenylselanyl)methyl)-1-tosylazetidine (43). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). White solid. Y = 73% (58 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 6.8 Hz, 2H), 7.42 – 7.20 (m, 5H), 3.54 – 3.34 (m, 3H), 3.22 (d, *J* = 10.8 Hz, 1H), 2.43 (s, 3H), 1.94 (ddd, *J* = 12.6, 7.0, 5.2 Hz, 1H), 1.76 (dt, *J* = 13.2, 7.5 Hz, 1H), 1.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.59, 138.02, 134.20, 129.78, 129.22, 129.13, 127.62, 126.94, 59.91, 48.70, 47.15, 39.14, 27.19, 21.69. ESI HRMS *m/z* $(M+Na)^+$ calcd 418.0350, obsd 418.0359.

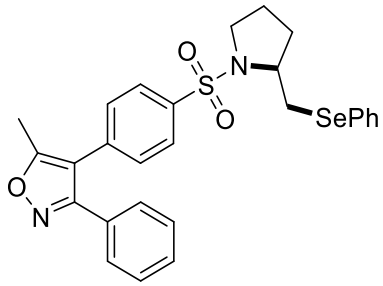


2-(1-(phenylselanyl)propyl)-1-tosylazetidine (44). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). Brown oil. Y = 57% (46.6 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.3 Hz, 2H), 7.29 (dt, *J* = 6.2, 1.8 Hz, 2H), 7.24 – 7.13 (m, 5H), 3.69 (ddd, *J* = 8.2, 6.7, 5.2 Hz, 1H), 3.43 (ddd, *J* = 11.0, 8.2, 4.0 Hz, 1H), 3.23 (dt, *J* = 11.0, 8.0 Hz, 1H), 2.94 (dt, *J* = 10.5, 6.8 Hz, 1H), 2.35 (s, 3H), 1.99 – 1.83 (m, 2H), 1.81 – 1.69 (m, 1H), 1.53 (dt, *J* = 13.8, 7.5 Hz, 1H), 0.98 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.68, 135.12, 133.73, 129.91, 129.33, 129.26, 127.77, 127.54, 64.52, 47.18, 44.32, 31.44, 25.18, 21.69, 11.06; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 307.88. ESI HRMS *m/z* $(M+Na)^+$ calcd 432.0507, obsd 432.0509.

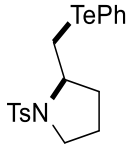


2,6-dinitro-4-((2-((phenylselanyl)methyl)pyrrolidin-1-yl)sulfonyl)-N,N-dipropylaniline (45). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/2). Yellow solid. Y = 36% (40.7 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (s, 2H), 7.68 – 7.50 (m, 2H), 7.38 – 7.28 (m, 3H), 3.63 (ddt, *J* = 10.7, 6.7, 3.1 Hz, 1H), 3.56 (ddd, *J* = 12.7, 7.3, 3.6 Hz, 2H), 3.16 (dt, *J* = 9.8, 6.9 Hz, 1H), 3.04 – 2.86 (m, 4H), 2.83 (dd, *J* = 12.6, 10.6 Hz, 1H), 2.03 – 1.79 (m, 3H), 1.76 – 1.68 (m, 1H), 1.67 – 1.54 (m, 4H), 0.87 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.81, 141.55, 132.74, 129.44, 128.67, 128.56, 128.35, 127.65, 60.22, 54.03, 50.28, 32.63, 31.25, 24.05, 20.83, 11.29; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 272.10.

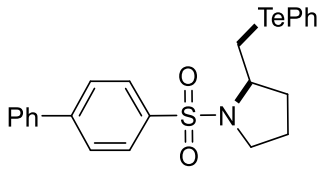
ESI HRMS *m/z* $(M+Na)^+$ calcd 593.0943, obsd 593.0947.



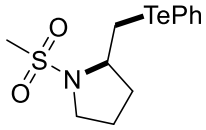
5-methyl-3-phenyl-4-(4-((2-((phenylselanyl)methyl)pyrrolidin-1-yl)sulfonyl)phenyl)isoxazole (46). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1). Colorless oil. Y = 93% (116.0 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (t, *J* = 8.3 Hz, 4H), 7.40 (ddd, *J* = 8.8, 6.2, 3.2 Hz, 1H), 7.35 – 7.30 (m, 4H), 7.29 – 7.18 (m, 5H), 3.65 (ddt, *J* = 11.0, 7.5, 3.5 Hz, 1H), 3.58 (dd, *J* = 12.5, 3.0 Hz, 1H), 3.51 (dt, *J* = 10.9, 5.7 Hz, 1H), 3.17 (dt, *J* = 9.9, 7.0 Hz, 1H), 2.85 (t, *J* = 11.6 Hz, 1H), 2.46 (s, 3H), 1.94 – 1.77 (m, 2H), 1.71 (dq, *J* = 14.8, 10.7, 9.3 Hz, 1H), 1.58 – 1.44 (m, *J* = 5.9, 4.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.17, 161.07, 136.04, 135.13, 132.59, 130.23, 129.74, 129.24, 129.15, 128.67, 128.49, 128.43, 127.77, 127.03, 114.41, 59.98, 49.96, 32.84, 31.06, 23.87, 11.77; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 271.41. ESI HRMS *m/z* $(M+Na)^+$ calcd 561.0722, obsd 561.0727.



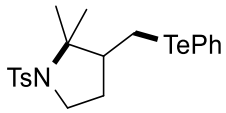
2-((phenyltellanyl)methyl)-1-tosylpyrrolidine (47). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). Colorless oil. Y = 71% (63.2 mg). Electricity = 11.2 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 6.8 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.24 (td, *J* = 7.9, 6.4 Hz, 4H), 3.72 (dtd, *J* = 11.0, 5.8, 2.9 Hz, 1H), 3.55 (dd, *J* = 12.0, 3.0 Hz, 1H), 3.49 (dt, *J* = 10.3, 6.0 Hz, 1H), 3.23 – 3.12 (m, 1H), 2.97 (dd, *J* = 12.0, 10.5 Hz, 1H), 2.40 (s, 3H), 1.76 (tt, *J* = 11.8, 4.2 Hz, 3H), 1.50 – 1.37 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.49, 138.42, 134.14, 129.75, 129.45, 127.84, 127.57, 111.17, 61.50, 50.25, 32.59, 24.06, 21.63, 16.14. ESI HRMS *m/z* $(M+Na)^+$ calcd 468.0247, obsd 468.0255.



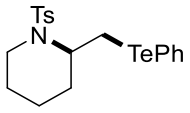
1-([1,1'-biphenyl]-4-ylsulfonyl)-2-((phenyltellanyl)methyl)pyrrolidine (48). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). Colorless oil. Y = 61% (61.9 mg). Electricity = 11.2 F mol^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.0 Hz, 2H), 7.73 – 7.61 (m, 4H), 7.61 – 7.54 (m, 2H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.43 – 7.38 (m, 1H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.30 – 7.22 (m, 2H), 3.78 (dtd, *J* = 11.4, 5.6, 2.8 Hz, 1H), 3.68 – 3.46 (m, 2H), 3.31 – 3.14 (m, 1H), 2.99 (dd, *J* = 12.0, 10.5 Hz, 1H), 1.90 – 1.73 (m, 3H), 1.50 (dt, *J* = 12.0, 5.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.51, 139.29, 138.48, 135.71, 129.48, 129.17, 128.61, 128.06, 127.88, 127.70, 127.38, 111.15, 61.60, 50.31, 32.62, 24.09, 16.07. ESI HRMS *m/z* $(M+Na)^+$ calcd 530.0404, obsd 530.0406.



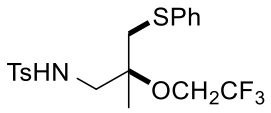
1-(methylsulfonyl)-2-((phenyltellanyl)methyl)pyrrolidine (49). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). Colorless oil. Y = 50% (37.0 mg). Electricity = 11.2 F mol^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.69 (m, 2H), 7.32 – 7.16 (m, 3H), 4.09 – 3.86 (m, 1H), 3.46 (dt, *J* = 11.1, 6.3 Hz, 1H), 3.40 – 3.30 (m, 2H), 3.10 (dd, *J* = 12.1, 9.8 Hz, 1H), 2.77 (s, 3H), 2.20 – 2.05 (m, 1H), 2.01 – 1.91 (m, 1H), 1.90 – 1.78 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.01, 129.49, 127.83, 111.47, 61.62, 49.84, 35.73, 33.08, 24.72, 16.19. ESI HRMS *m/z* $(M+Na)^+$ calcd 391.9934, obsd 391.9939.



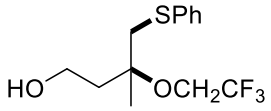
2,2-dimethyl-3-((phenyltellanyl)methyl)-1-tosylpyrrolidine (50). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). Colorless oil. Y = 44% (41.6 mg). Electricity = 11.2 F mol^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.2 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.28 – 7.16 (m, 4H), 3.57 (td, *J* = 8.6, 2.2 Hz, 1H), 3.27 (dd, *J* = 12.1, 6.5 Hz, 1H), 3.20 – 3.09 (m, 1H), 2.40 (s, 3H), 2.28 (dtd, *J* = 14.1, 7.6, 7.2, 2.6 Hz, 1H), 2.22 – 2.12 (m, 1H), 1.56 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.95, 140.34, 138.58, 129.60, 129.53, 128.63, 127.27, 111.07, 68.31, 48.95, 39.86, 32.75, 27.50, 26.32, 21.64. ESI HRMS *m/z* $(M+Na)^+$ calcd 496.0560, obsd 496.0566.



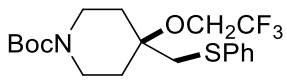
2-((phenyltellanyl)methyl)-1-tosylpiperidine (51). The product was prepared according to procedure A and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). White solid. Y = 30% (27.5 mg). Electricity = 11.2 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 7.3 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 4H), 4.30 (ddt, *J* = 10.9, 5.5, 3.0 Hz, 1H), 3.84 – 3.65 (m, 1H), 3.10 (dd, *J* = 11.9, 10.5 Hz, 1H), 3.04 – 2.91 (m, 2H), 2.40 (s, 3H), 2.02 – 1.82 (m, 1H), 1.55 – 1.40 (m, 3H), 1.40 – 1.23 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.13, 139.01, 138.30, 129.81, 129.44, 128.13, 127.13, 111.46, 54.46, 40.58, 27.63, 24.76, 21.68, 18.06, 9.10. ESI HRMS *m/z* $(M+Na)^+$ calcd 482.0404, obsd 482.0408.



4-methyl-*N*-(2-methyl-3-(phenylthio)-2-(2,2,2-trifluoroethoxy)propyl)benzenesulfonamide (52). The product was prepared according to procedure B and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/2). Colorless oil. Y = 66% (57.2 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 7.7 Hz, 4H), 7.19 (t, *J* = 7.2 Hz, 1H), 4.93 (t, *J* = 6.4 Hz, 1H), 3.71 (q, *J* = 8.3 Hz, 2H), 3.22 – 2.90 (m, 4H), 2.40 (s, 3H), 1.28 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.72, 136.64, 136.00, 130.07, 129.89, 129.21, 127.07, 126.80, 123.76 (q, *J* = 277.8 Hz), 78.80, 60.84 (q, *J* = 35.0 Hz), 49.39, 40.92, 21.56, 20.14; ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.17. ESI HRMS *m/z* $(M+Na)^+$ calcd 456.0885, obsd 456.0889.

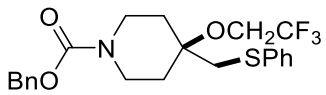


3-methyl-4-(phenylthio)-3-(2,2,2-trifluoroethoxy)butan-1-ol (53). The product was prepared according to procedure B and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1/1). Colorless oil. Y = 60% (35.3 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 3.84 – 3.62 (m, 4H), 3.15 – 3.00 (m, 2H), 1.98 (dt, *J* = 12.2, 6.5 Hz, 2H), 1.81 (dt, *J* = 14.8, 6.0 Hz, 1H), 1.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.53, 130.05, 129.24, 126.73, 124.02 (q, *J* = 277.4 Hz), 79.88, 60.72 (q, *J* = 34.8 Hz), 58.83, 43.27, 40.08, 22.60; ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.28. ESI HRMS *m/z* $(M+Na)^+$ calcd 317.0794, obsd 317.0803.

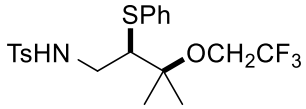


Tert-butyl 4-((phenylthio)methyl)-4-(2,2,2-trifluoroethoxy)piperidine-1-carboxylate (54).

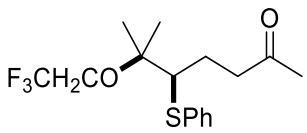
The product was prepared according to procedure B and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/2). Colorless oil. Y = 43% (35.0 mg). Electricity = 4.6 F mol^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 7.4 Hz, 2H), 7.22 (t, *J* = 7.7 Hz, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 3.83 – 3.72 (m, 2H), 3.68 (q, *J* = 8.4 Hz, 2H), 3.01 (t, *J* = *J* = 12.0 Hz, 4H), 1.81 (d, *J* = 12.0 Hz, 2H), 1.54 (ddd, *J* = 13.9, 11.9, 4.8 Hz, 2H), 1.38 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.87, 136.38, 130.03, 129.27, 126.74, 124.07 (d, q = 277.5 Hz), 79.80, 75.77, 60.23 (q, *J* = 34.8 Hz), 42.67, 39.25, 33.21, 28.56; ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.84. ESI HRMS *m/z* $(M+Na)^+$ calcd 428.1478, obsd 428.1486.



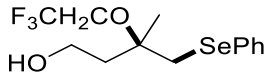
Benzyl 4-((phenylthio)methyl)-4-(2,2,2-trifluoroethoxy)piperidine-1-carboxylate (55). The product was prepared according to procedure B and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1). Colorless oil. Y = 64% (56.2 mg). Electricity = 4.6 F mol^{-1}.^1H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.18 (m, 9H), 7.13 (q, *J* = 7.8, 7.2 Hz, 1H), 5.04 (s, 2H), 4.00 – 3.77 (m, 2H), 3.66 (q, *J* = 8.4 Hz, 2H), 3.14 – 3.04 (m, 2H), 2.99 (s, 2H), 1.81 (d, *J* = 13.9 Hz, 2H), 1.63 – 1.42 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.31, 136.84, 136.25, 130.04, 129.27, 128.64, 128.17, 128.03, 126.78, 124.03 (d, *J* = 278.0 Hz), 75.68, 67.27, 60.22 (q, *J* = 34.8 Hz), 42.64, 39.48, 33.40, 32.82; ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.82. ESI HRMS *m/z* $(M+Na)^+$ calcd 462.1321, obsd 462.1328.



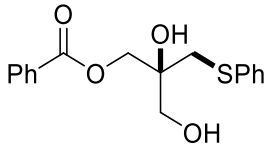
4-methyl-*N*-(3-methyl-2-(phenylthio)-3-(2,2,2-trifluoroethoxy)butyl)benzenesulfonamide (56). The product was prepared according to procedure B and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1). Colorless oil. Y = 50% (44.7 mg). Electricity = 4.6 F mol^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.26 (dd, *J* = 7.6, 2.1 Hz, 2H), 7.19 (td, *J* = 6.2, 5.2, 3.8 Hz, 5H), 5.39 – 5.11 (m, 1H), 3.66 (qq, *J* = 11.1, 8.4 Hz, 2H), 3.42 (ddd, *J* = 13.4, 7.0, 4.8 Hz, 1H), 3.05 (dd, *J* = 7.9, 4.8 Hz, 1H), 2.98 (ddd, *J* = 13.4, 7.9, 5.3 Hz, 1H), 2.34 (s, 3H), 1.22 (s, 3H), 1.15 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.54, 137.02, 135.01, 131.71, 129.83, 129.43, 127.65, 127.24, 124.05 (q, *J* = 277.7 Hz), 80.44, 60.62 (q, *J* = 34.7 Hz), 59.27, 43.64, 24.34, 21.65, 21.47; ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.21. ESI HRMS *m/z* $(M+Na)^+$ calcd 470.1042, obsd 470.1050.



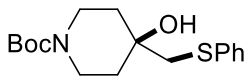
6-methyl-5-(phenylthio)-6-(2,2,2-trifluoroethoxy)heptan-2-one (57). The product was prepared according to procedure B and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 4/1). Colorless oil. Y = 42% (28.0 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.27 (m, 2H), 7.20 (dt, *J* = 7.9, 2.9 Hz, 2H), 7.16 – 7.10 (m, 1H), 3.80 (dq, *J* = 11.1, 8.6 Hz, 1H), 3.66 (dq, *J* = 11.1, 8.6 Hz, 1H), 3.07 (dd, *J* = 11.6, 2.8 Hz, 1H), 2.73 (dd, *J* = 7.7, 6.0 Hz, 2H), 2.26 (dtd, *J* = 14.5, 7.8, 2.8 Hz, 1H), 1.97 (s, 3H), 1.66 – 1.44 (m, 1H), 1.24 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.07, 137.62, 130.71, 129.27, 126.75, 124.33 (q, *J* = 277.4 Hz), 80.64, 60.71 (q, *J* = 34.3 Hz), 58.29, 41.39, 30.09, 24.67, 24.08, 22.18; ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.31. ESI HRMS *m/z* $(M+Na)^+$ calcd 357.1107, obsd 357.1112.



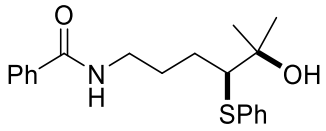
3-methyl-4-(phenylselanyl)-3-(2,2,2-trifluoroethoxy)butan-1-ol (58). The product was prepared according to procedure B and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2/1). Colorless oil. Y = 57 % (39.0 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.35 – 7.20 (m, 3H), 3.93 – 3.59 (m, 4H), 3.31 – 3.04 (m, 2H), 2.07 (s, 1H), 2.06 (dt, *J* = 14.8, 6.3 Hz, 1H), 1.90 (dt, *J* = 14.8, 6.0 Hz, 1H), 1.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.28, 130.48, 129.41, 127.53, 124.03 (q, *J* = 277.8 Hz), 80.03, 60.68 (q, *J* = 34.7 Hz), 58.95, 40.53, 37.57, 22.98; ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.25; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 253.74. ESI HRMS *m/z* $(M+Na)^+$ calcd 365.0238, obsd 365.0245.



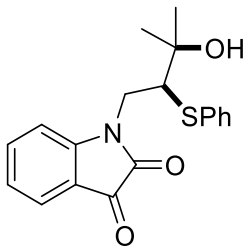
2,3-dihydroxy-2-((phenylthio)methyl)propyl benzoate (59). The product was prepared according to procedure C and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2/3). Colorless oil. Y = 90% (57.2 mg). Electricity = 4.6 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 7.7 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.40 – 7.30 (m, 4H), 7.15 (t, *J* = 7.4 Hz, 2H), 7.08 (t, *J* = 7.3 Hz, 1H), 4.30 (q, *J* = 11.5 Hz, 2H), 3.61 – 3.55 (m, 2H), 3.20 (s, 2H), 3.15 (s, 1H), 2.66 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.83, 136.16, 133.57, 130.15, 129.87, 129.45, 129.26, 128.61, 126.88, 74.33, 66.10, 65.17, 39.63. ESI HRMS *m/z* $(M+Na)^+$ calcd 341.0818, obsd 341.0827.



tert-butyl 4-hydroxy-4-((phenylthio)methyl)piperidine-1-carboxylate (60). The product was prepared according to procedure C and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1/1). Colorless oil. Y = 55% (35.5 mg). Electricity = 4.6 F mol^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.29 (m, 2H), 7.24 – 7.17 (m, 2H), 7.12 (t, *J* = 7.3 Hz, 1H), 4.02 – 3.60 (m, 2H), 3.14 – 2.92 (m, 4H), 2.30 (s, 1H), 1.60 – 1.51 (m, 2H), 1.47 – 1.41 (m, 2H), 1.37 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.86, 136.63, 129.86, 129.24, 126.66, 79.61, 69.83, 48.12, 40.12, 39.36, 36.37, 28.56. ESI HRMS *m/z* $(M+Na)^+$ calcd 346.1447 obsd 346.1456.

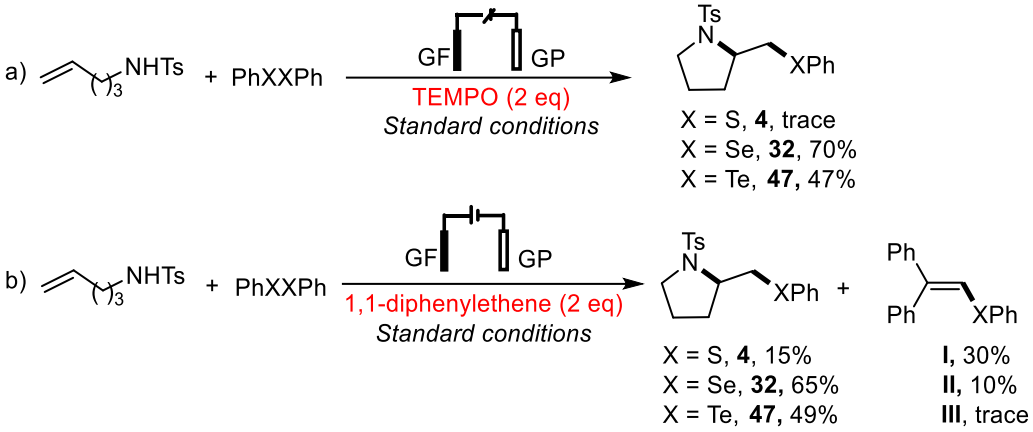


***N*-(5-hydroxy-5-methyl-4-(phenylthio)hexyl)benzamide (61).** The product was prepared according to procedure C and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1). Colorless oil. Y = 52% (35.7 mg). Electricity = 4.6 F mol^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 7.3 Hz, 2H), 7.48 – 7.30 (m, 5H), 7.19 (t, *J* = 7.4 Hz, 2H), 7.11 (t, *J* = 7.3 Hz, 1H), 6.19 (s, 1H), 3.55 – 3.27 (m, 2H), 3.04 (dd, *J* = 11.5, 2.3 Hz, 1H), 2.62 (s, 1H), 2.05 – 1.82 (m, 2H), 1.70 (ddt, *J* = 11.9, 8.6, 5.9 Hz, 1H), 1.57 – 1.38 (m, 1H), 1.24 (s, 3H), 1.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.86, 137.46, 134.73, 131.60, 130.72, 129.25, 128.73, 127.00, 126.76, 73.43, 64.03, 39.59, 29.57, 28.55, 26.82, 26.80. ESI HRMS *m/z* $(M+Na)^+$ calcd 366.1498, obsd 366.1507.



1-(3-hydroxy-3-methyl-2-(phenylthio)butyl)indoline-2,3-dione (62). The product was prepared according to procedure C and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2/1). Brown oil. Y = 63 % (50.0 mg). Electricity = 4.6 F mol^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.38 (m, 1H), 7.33 (d, *J* = 7.4 Hz, 1H), 7.06 – 6.91 (m, 6H), 6.83 (d, *J* = 7.9 Hz, 1H), 4.15 (dd, *J* = 14.4, 4.1 Hz, 1H), 3.96 (dd, *J* = 14.4, 10.7 Hz, 1H), 3.66 (dd, *J* = 10.7, 4.1 Hz, 1H), 2.74 (s, 1H), 1.43 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.91, 158.58, 151.09, 138.03, 134.93, 131.07, 129.17, 127.22, 125.13, 123.64, 117.43, 110.83, 72.50, 59.41, 42.93, 28.32, 26.65. ESI HRMS *m/z* $(M+Na)^+$ calcd 364.0978, obsd 364.0985.

5. Radical trapping experiments



(2,2-diphenylvinyl)(phenyl)sulfane (I)[4]. Compound **I** was isolated from the electrochemical reaction system for product **4** preparation by adding 2.0 equiv of ethene-1,1-diyldibenzenes. Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (dd, *J* = 9.7, 7.0 Hz, 4H), 7.38 – 7.27 (m, 6H), 7.27 – 7.20 (m, 5H), 6.86 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.63, 141.25, 139.35, 136.66, 129.94, 129.69, 129.30, 128.57, 128.49, 128.00, 127.48, 127.37, 126.96, 124.27.

(2,2-diphenylvinyl)(phenyl)selane (II)[4]. Compound **I** was isolated from the electrochemical reaction system for product **32** preparation by adding 2.0 equiv of ethene-1,1-diyldibenzenes. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (dd, *J* = 7.3, 2.3 Hz, 2H), 7.42 (dd, *J* = 7.9, 6.4 Hz, 2H), 7.39 – 7.32 (m, 3H), 7.31 – 7.22 (m, 8H), 7.12 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.22, 141.73, 140.50, 132.68, 131.75, 129.50, 129.48, 128.70, 128.46, 128.10, 127.59, 127.41, 127.33, 122.74; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 376.80.

6. Cyclic Voltammetry Studies

The cyclic voltammograms were recorded on a CHI 760E electrochemical workstation (Shanghai Chenhua, China) at room temperature in HFIP (5 mL) with $TBABF_4$ (0.1 M) as electrolyte. Note the CV of 1,2-diphenylditellane was measured in TFE due to the poor solubility in HFIP. A glassy carbon disk (diameter, 1 mm) was used as working electrode, a Pt wire as auxiliary electrode and a SCE as reference electrode. The glass carbon electrode was polished by Al_2O_3 powder (0.05 μm) before cyclic voltammetry. The scan rate was 100 mV/s. The IUPAC convention was used for plotting the CV data.

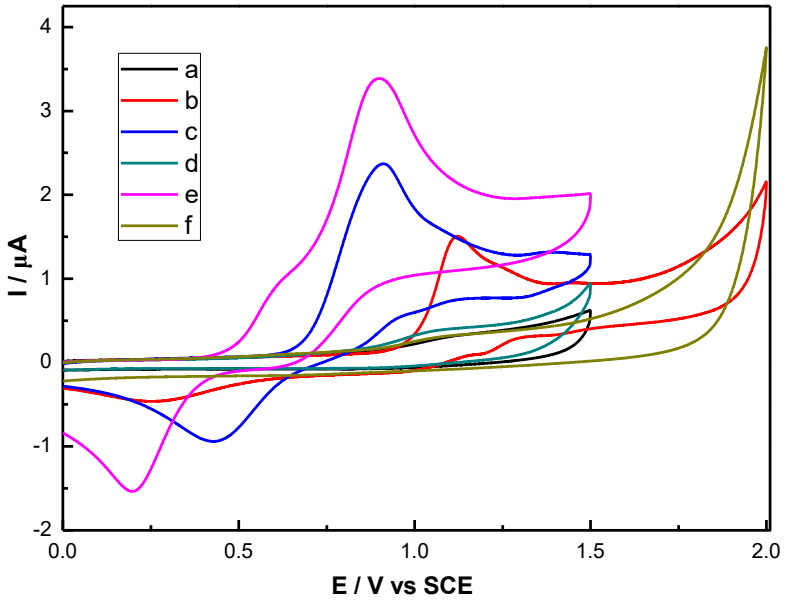


Figure S2. Cyclic voltammograms. a. $TBABF_4$ (0.1 M), HFIP (5 mL). b. Diphenyl disulfide (3.0 mM), $TBABF_4$ (0.1 M), HFIP (5 mL). c. Diphenyl diselenide (3 mM), $TBABF_4$ (0.1 M), HFIP (5 mL). d. $TBABF_4$ (0.1 M), TFE (5 mL). e. Diphenyl ditelluride (3 mM), $TBABF_4$ (0.1 M), TFE (5 mL). f. 4-methyl-N-(pent-4-en-1-yl)benzene-sulfonamide, $TBABF_4$ (0.1 M), HFIP (5 mL).

7. Reference

1. Mizar, P.; Niebuhr, R.; Hutchings, M.; Farooq, U.; Wirth, T., Thioamination of Alkenes with Hypervalent Iodine Reagents. *Chem. Eur. J.* **2016,** *22* (5), 1614-1617.

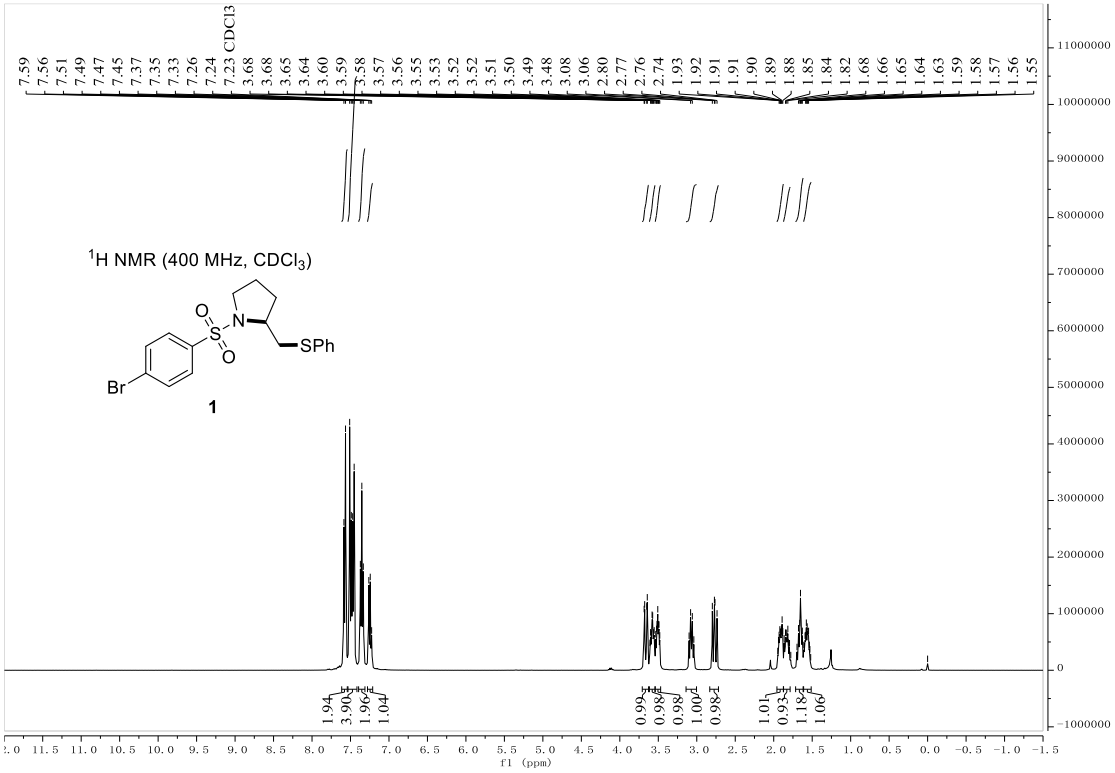
2. Ni, Y.; Zuo, H.; Li, Y.; Wu, Y.; Zhong, F., Copper-Catalyzed Regioselective Intramolecular Electrophilic Sulfenoamination via Lewis Acid Activation of Disulfides under Aerobic Conditions. *Org. Lett.* **2018,** *20* (14), 4350-4353.

3. Ashikari, Y.; Shimizu, A.; Nokami, T.; Yoshida, J.-i., Halogen and Chalcogen Cation Pools Stabilized by DMSO. Versatile Reagents for Alkene Difunctionalization. *J. Am. Chem. Soc.* **2013,** *135* (43), 16070-16073.

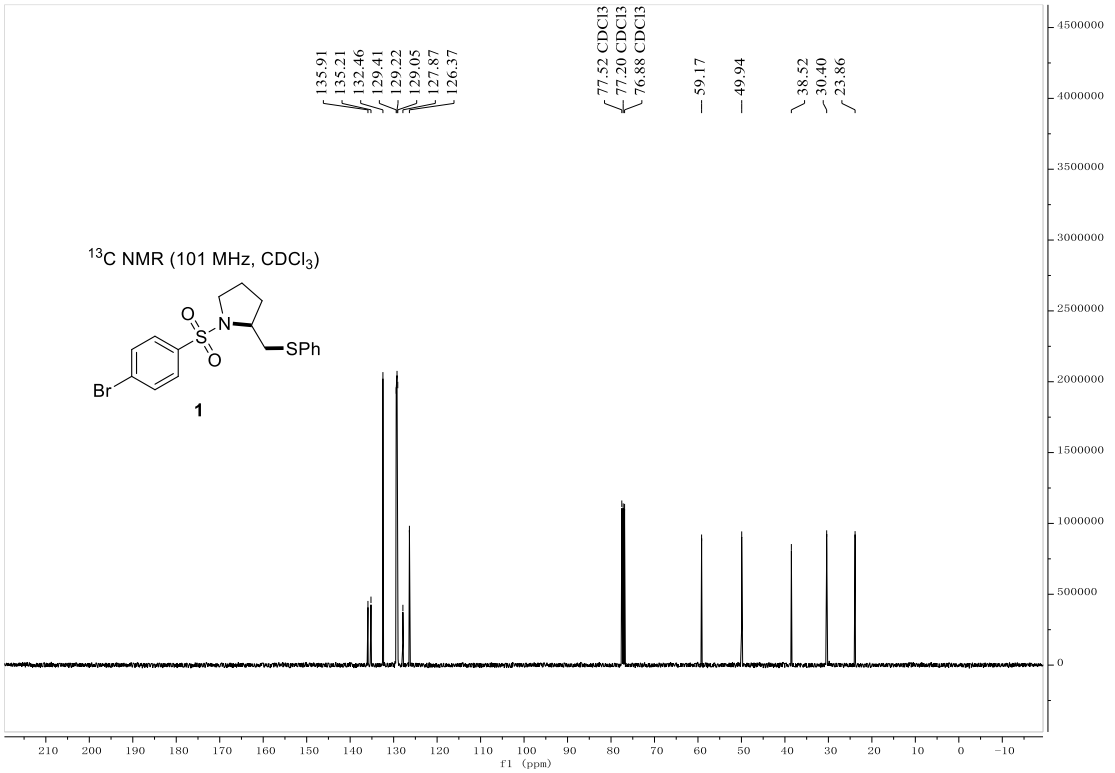
4. Mukherjee, N.; Chatterjee, T., Recyclable iodine-catalyzed oxidative C–H chalcogenation of 1,1-diarylethenes in water: green synthesis of trisubstituted vinyl sulfides and selenides. *Green Chem.* **2023,** *25* (21), 8798-8807.

8. **NMR spectra**

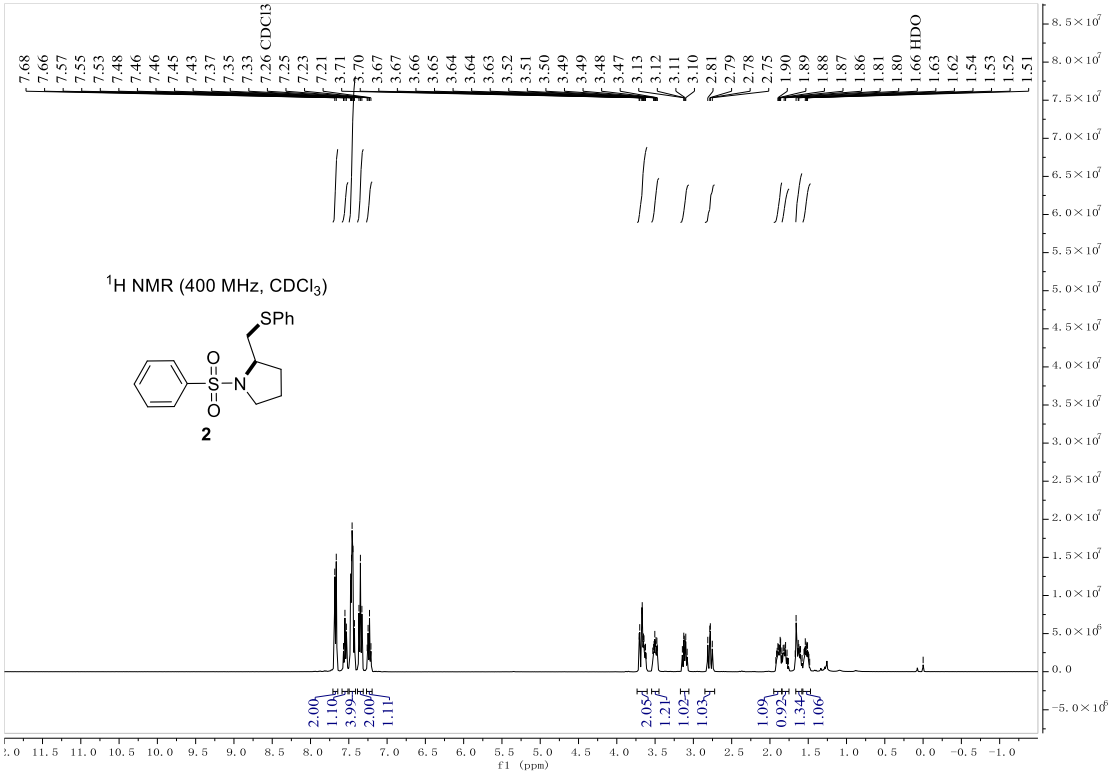
^{1}H NMR of compound **1**



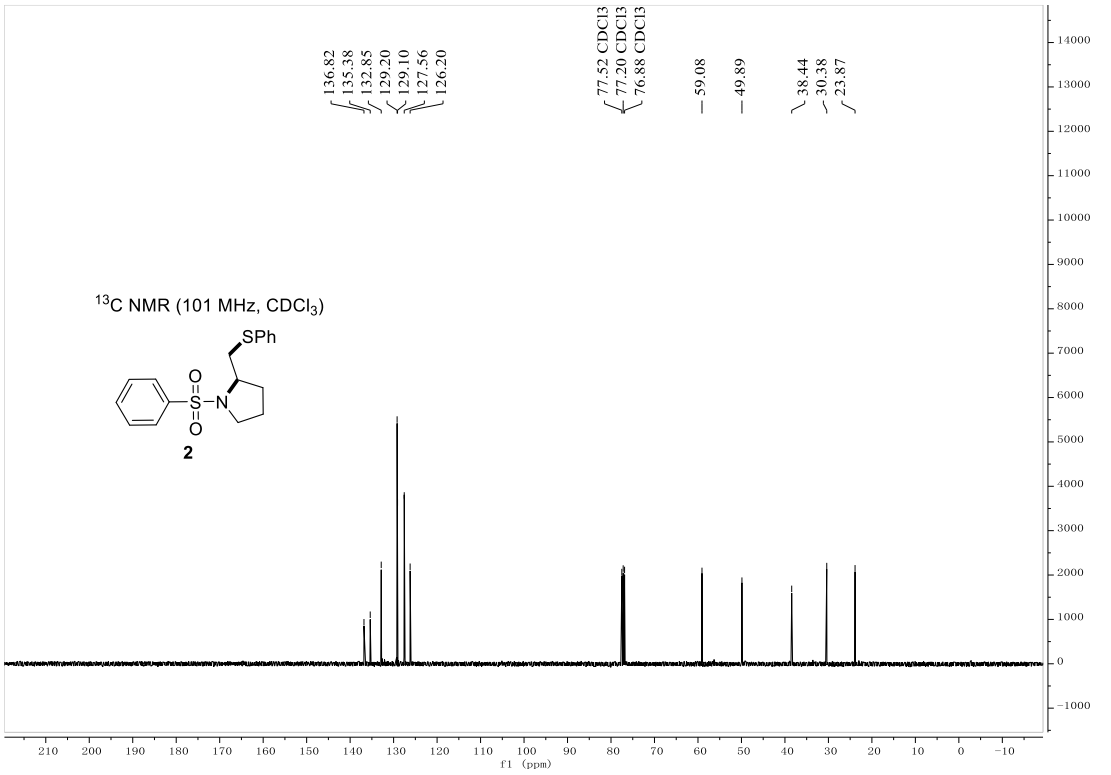
^{13}C NMR of compound **1**



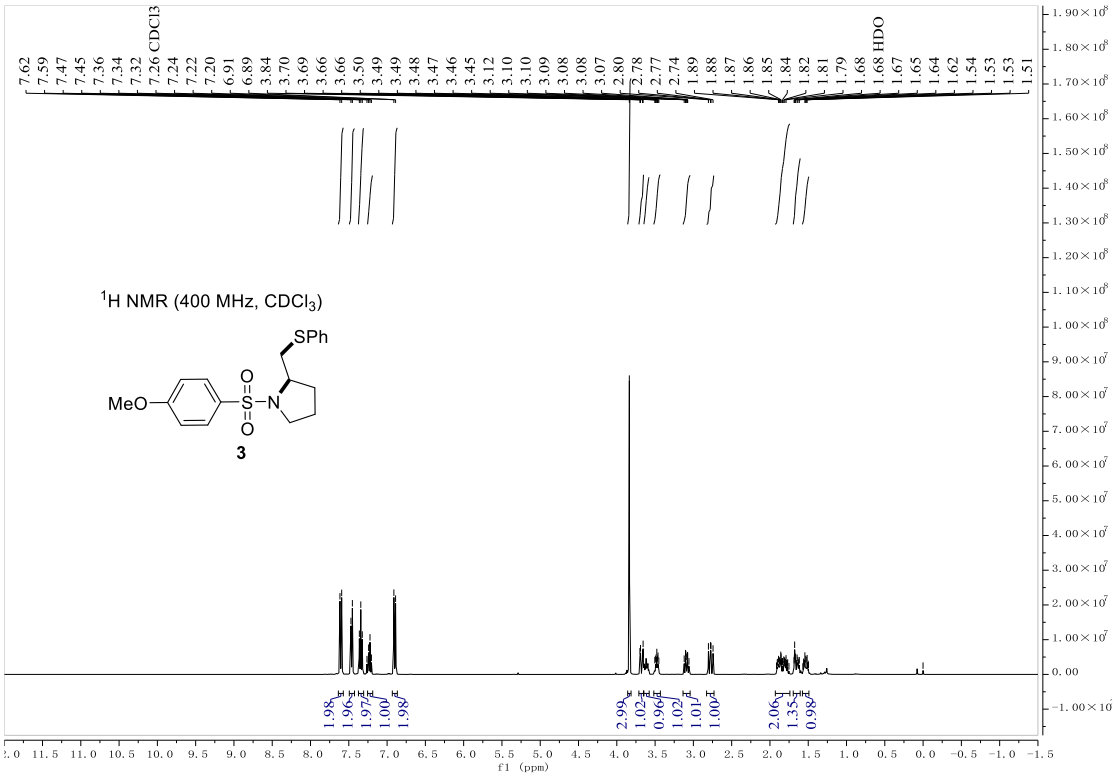
^{1}H NMR of compound **2**



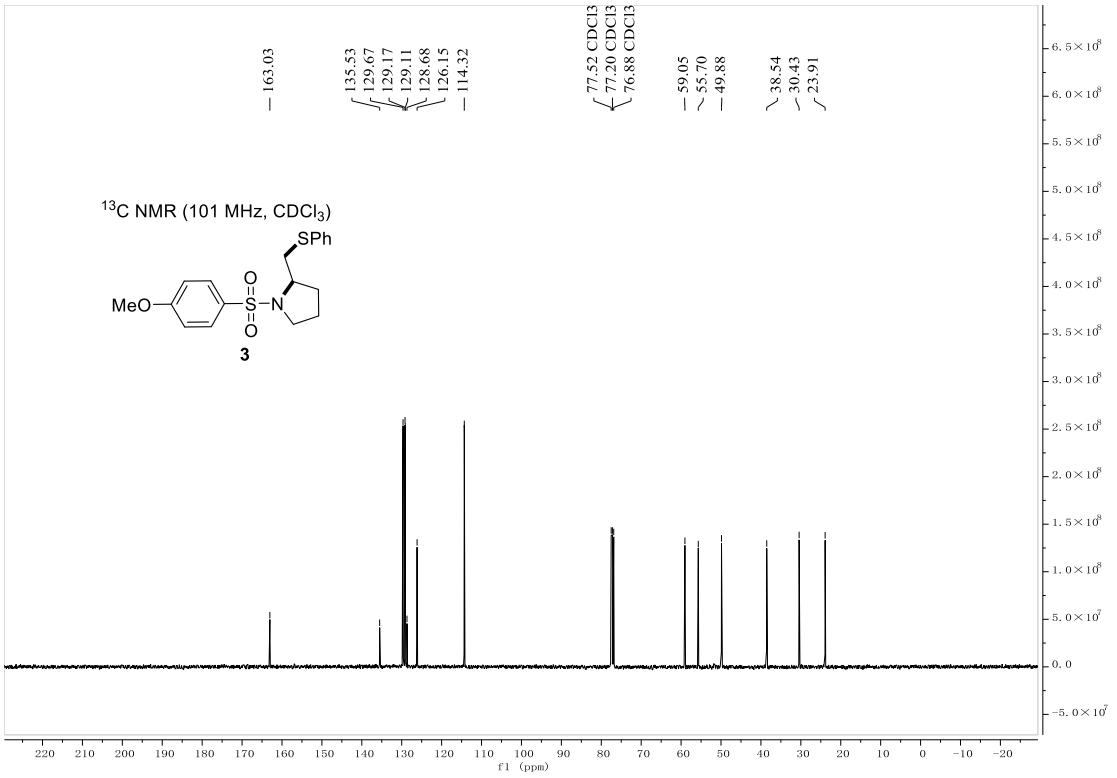
^{13}C NMR of compound **2**



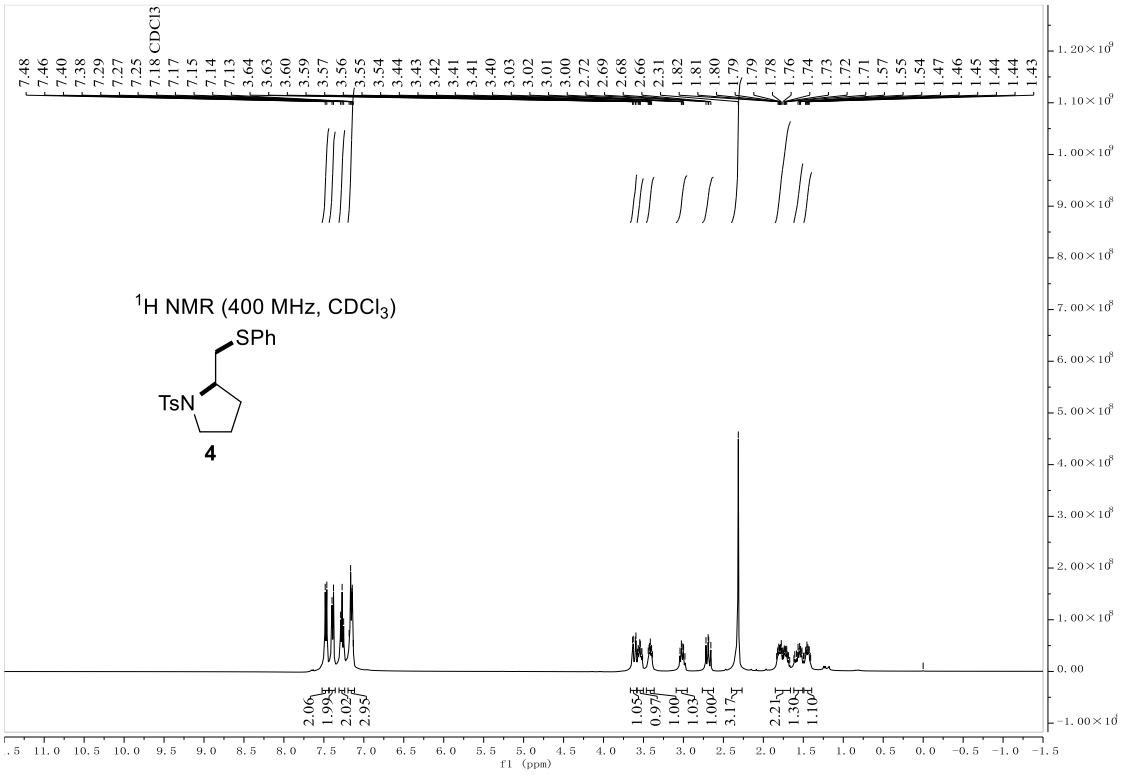
^{1}H NMR of compound **3**



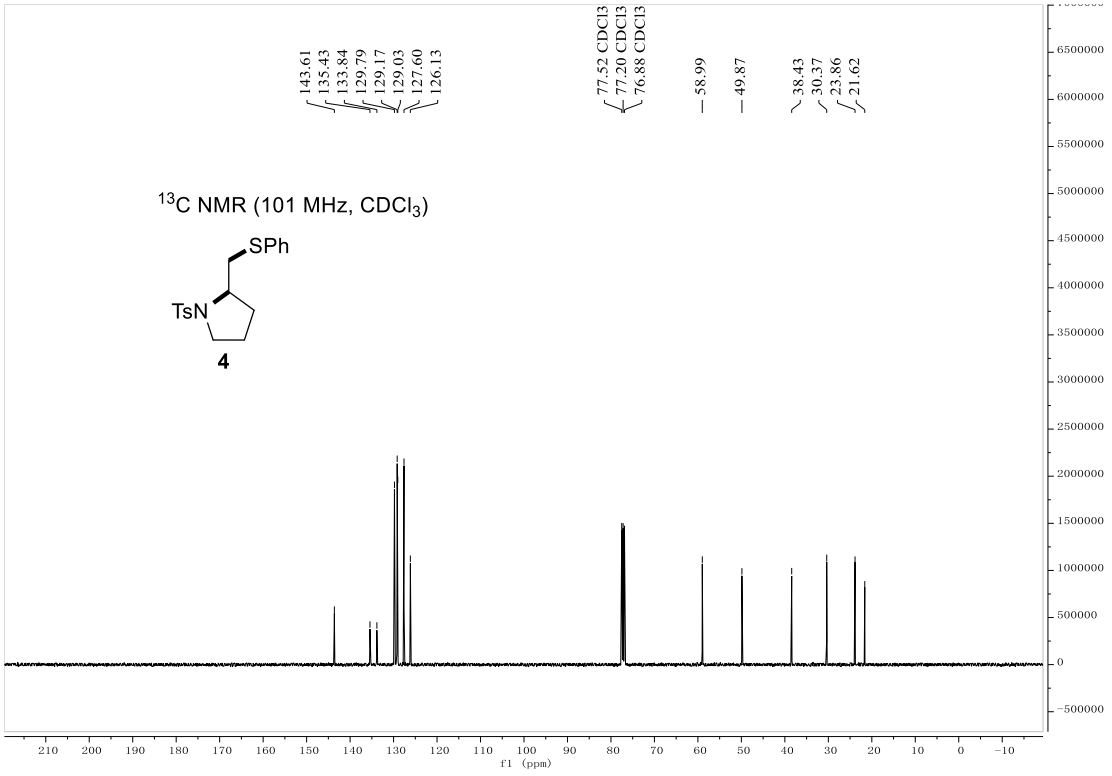
^{13}C NMR of compound **3**



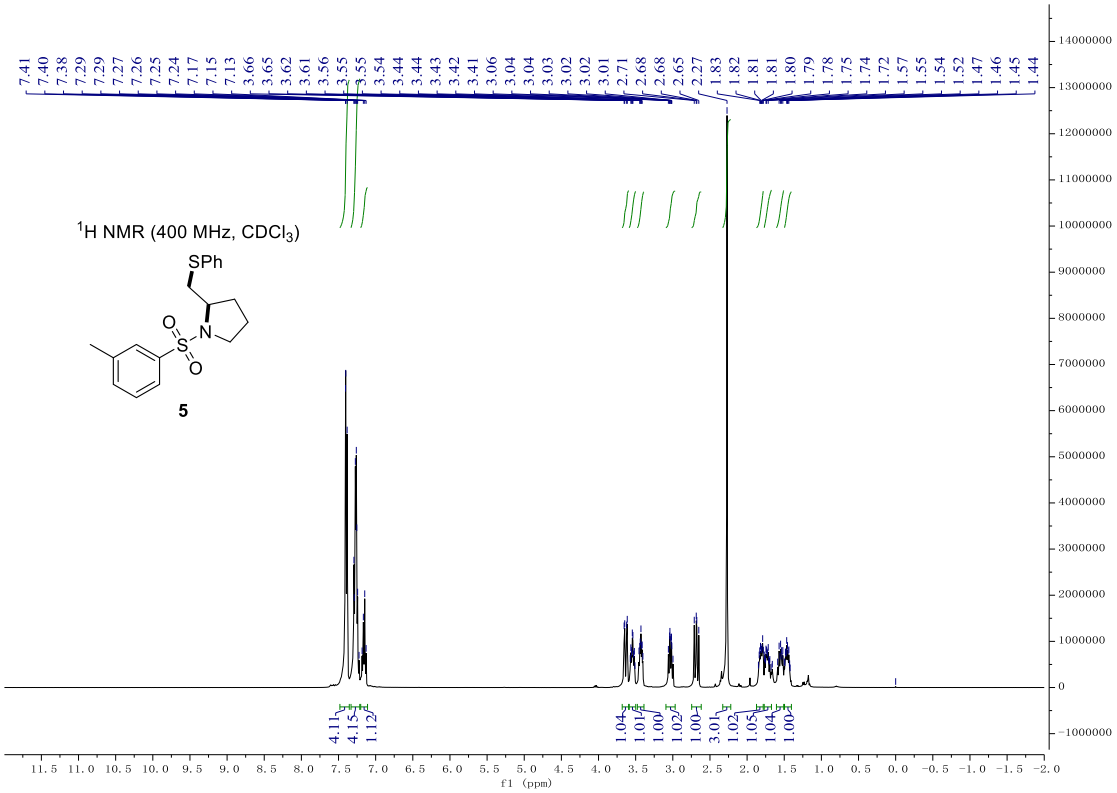
^{1}H NMR of compound **4**



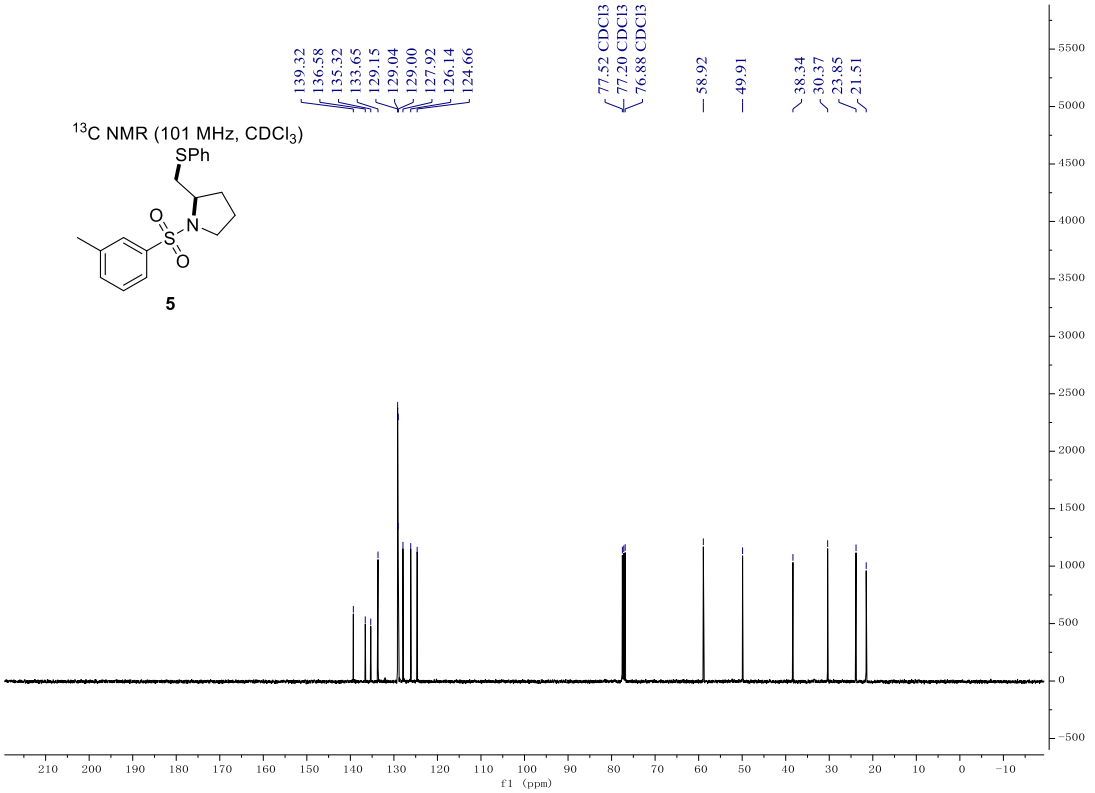
^{13}C NMR of compound **4**



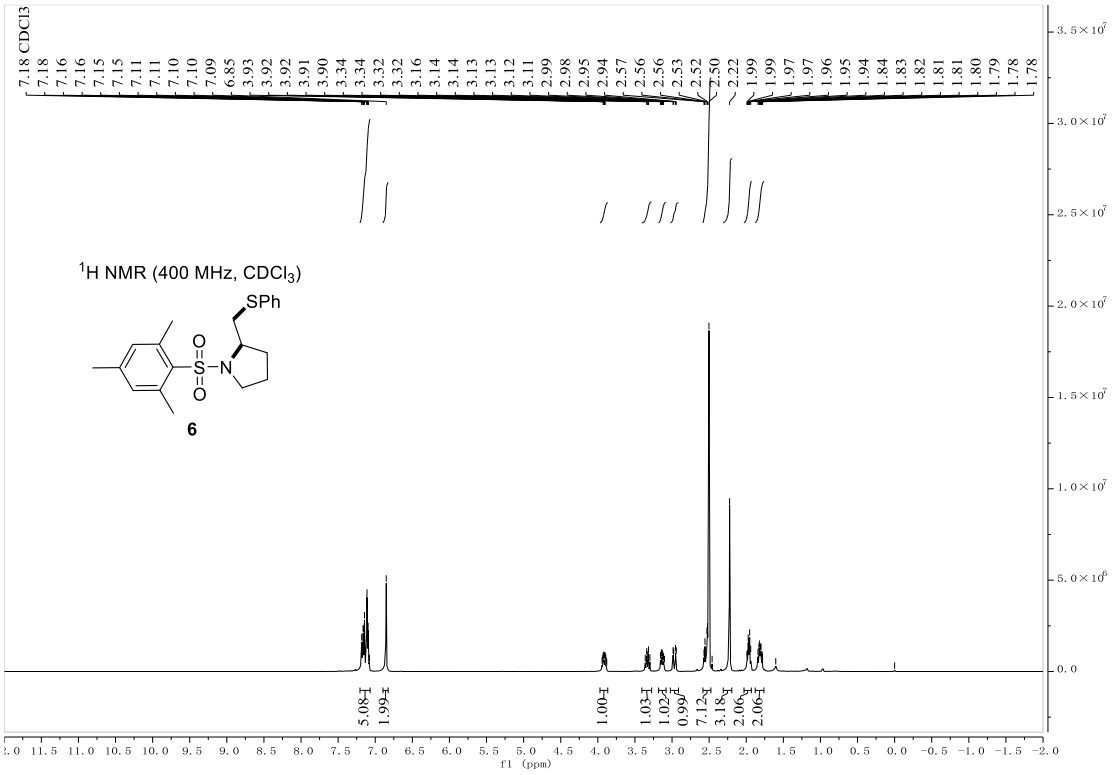
^{1}H NMR of compound **5**



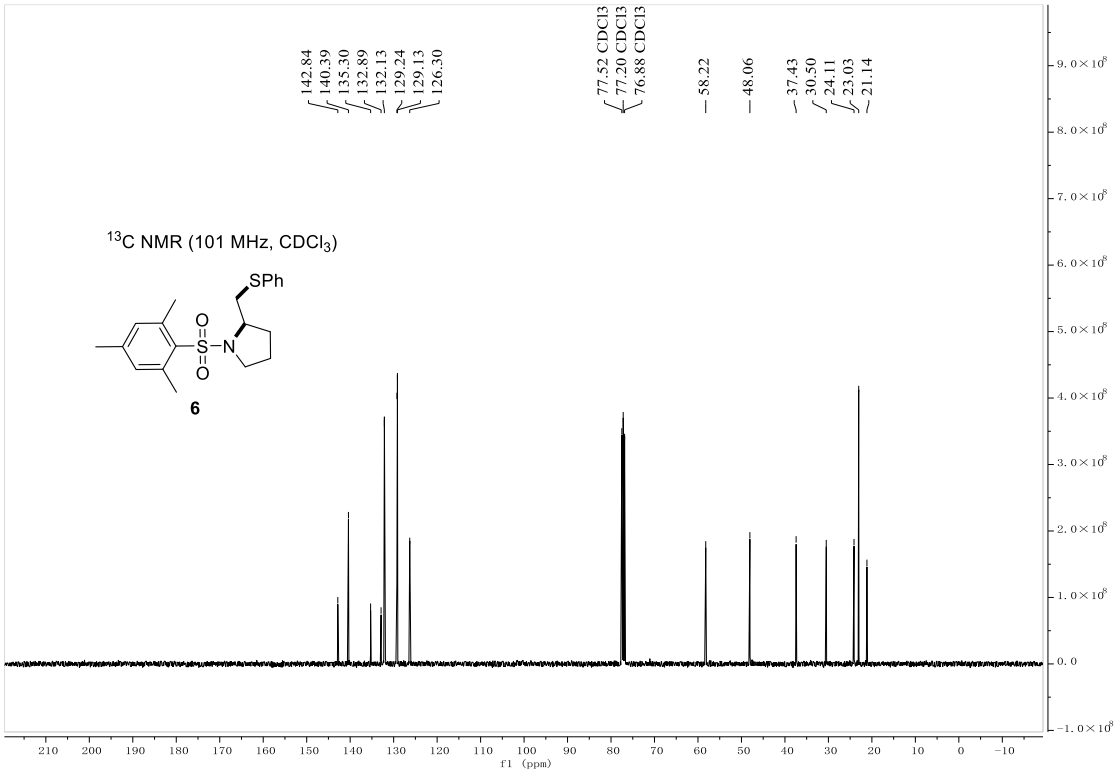
^{13}C NMR of compound **5**



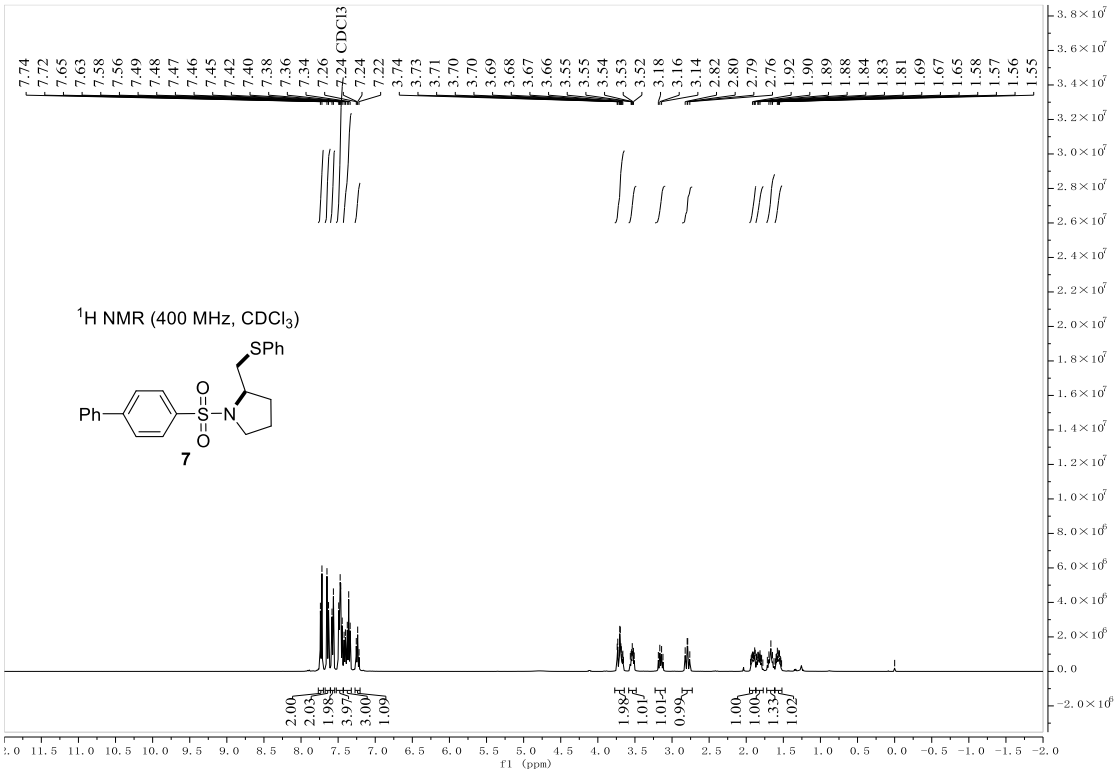
^{1}H NMR of compound **6**



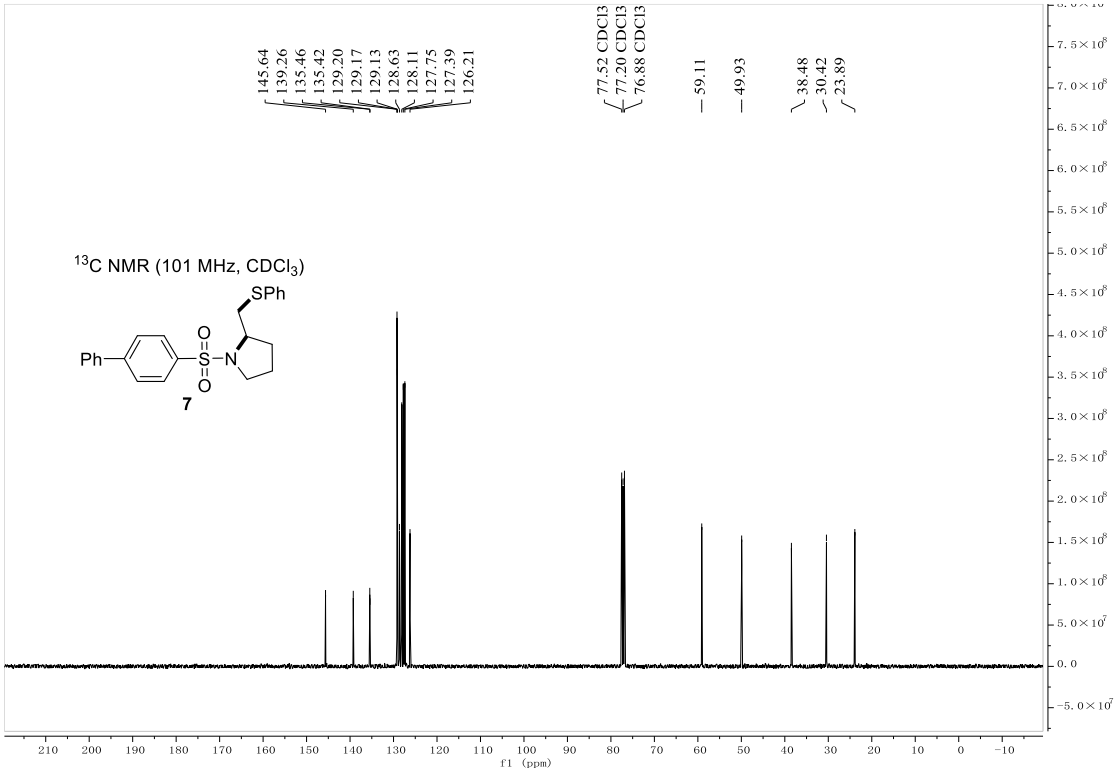
^{13}C NMR of compound **6**



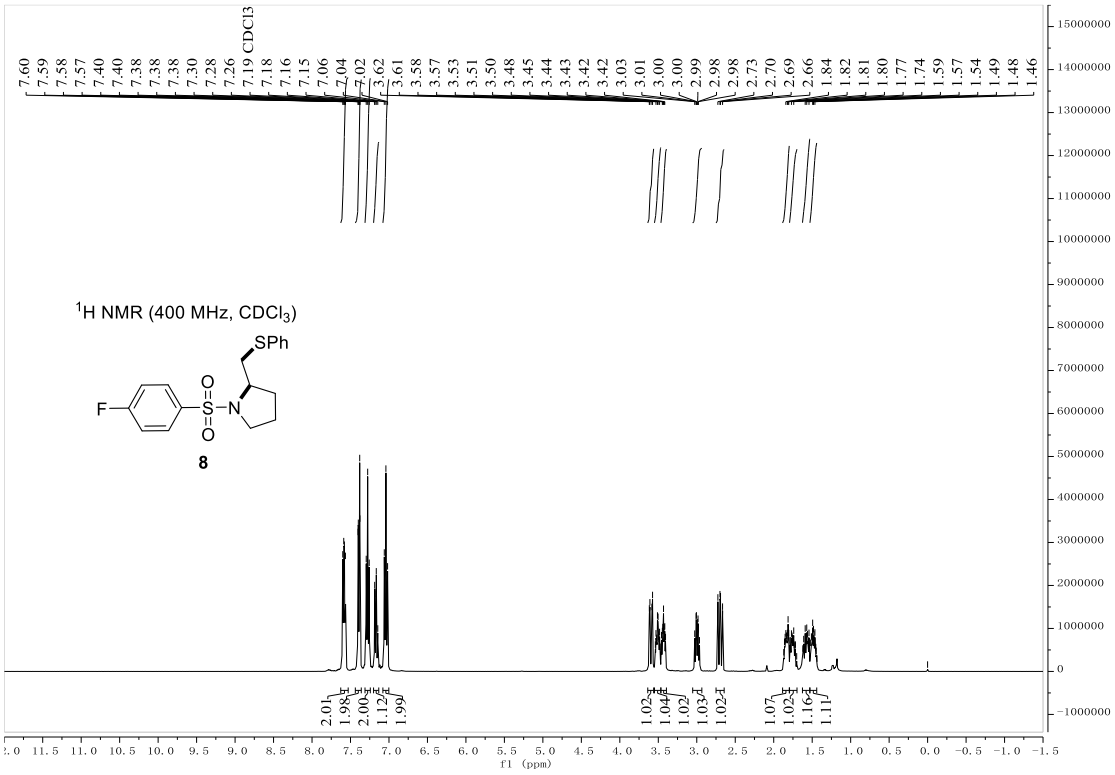
^{1}H NMR of compound **7**



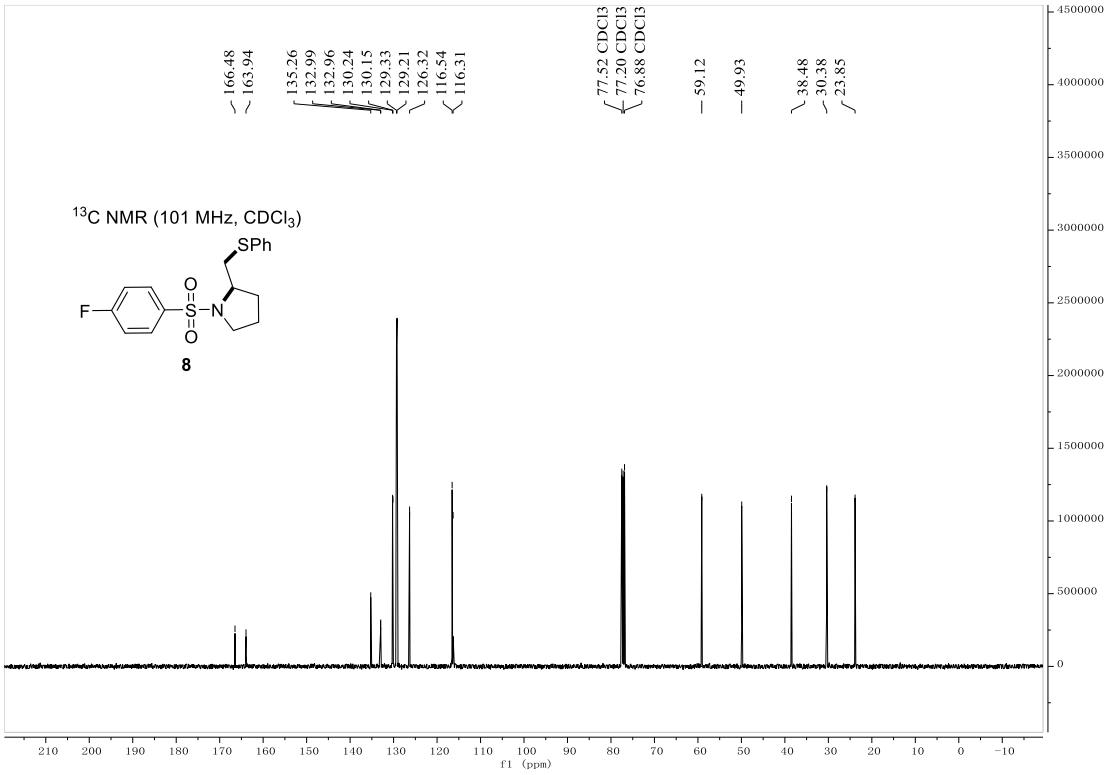
^{13}C NMR of compound **7**



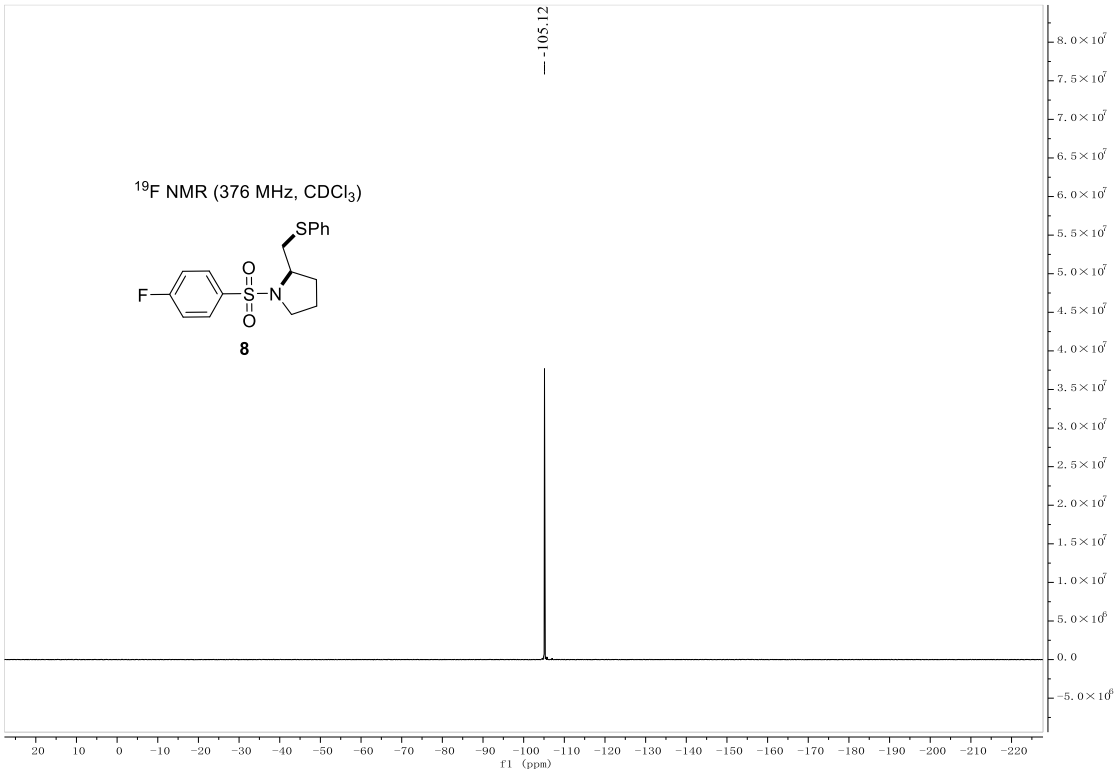
^{1}H NMR of compound **8**



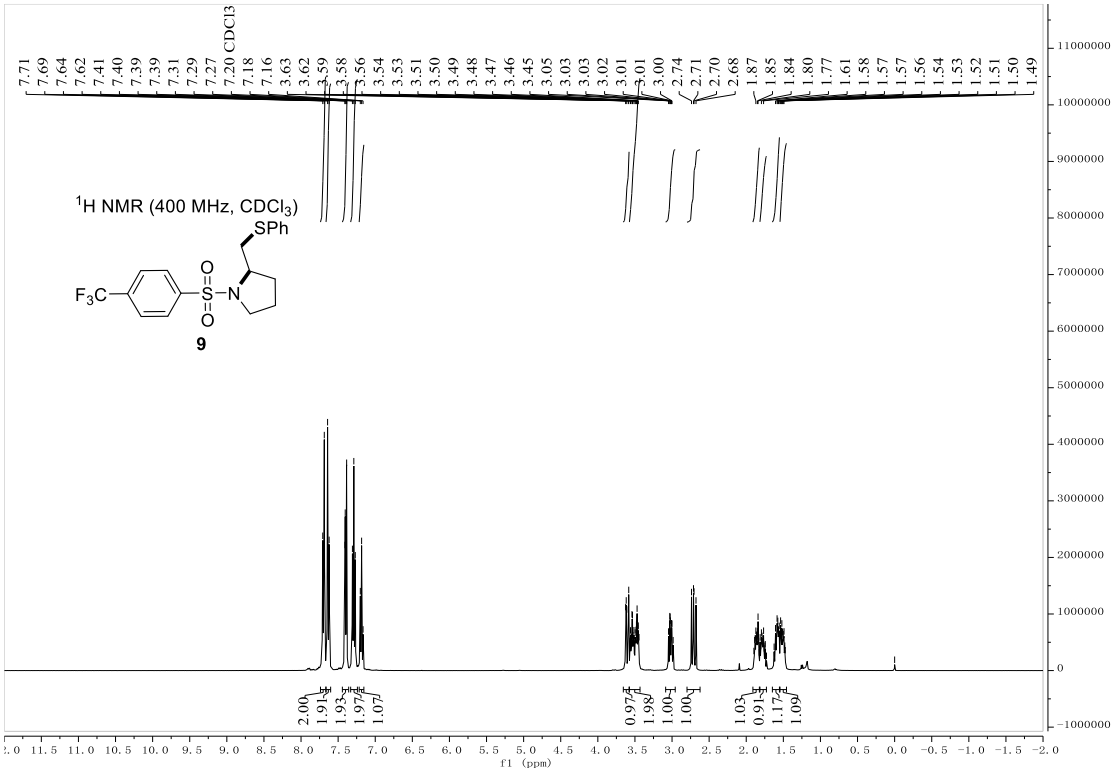
^{13}C NMR of compound **8**



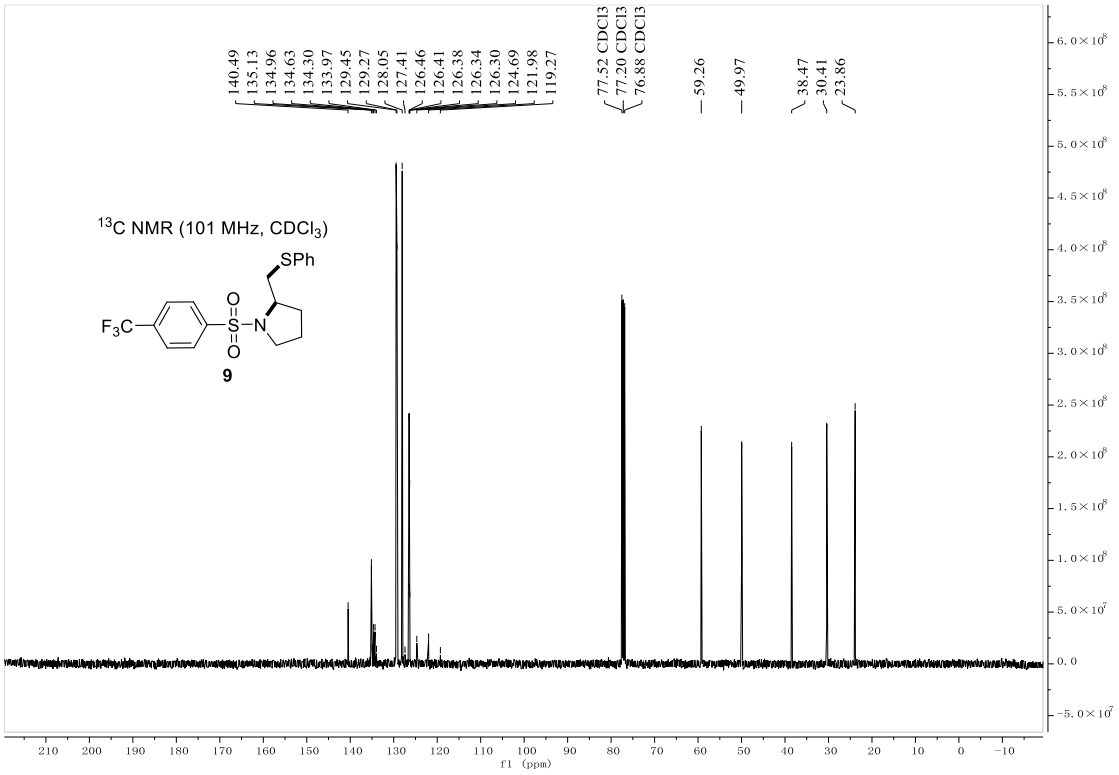
^{19}F NMR of compound **8**



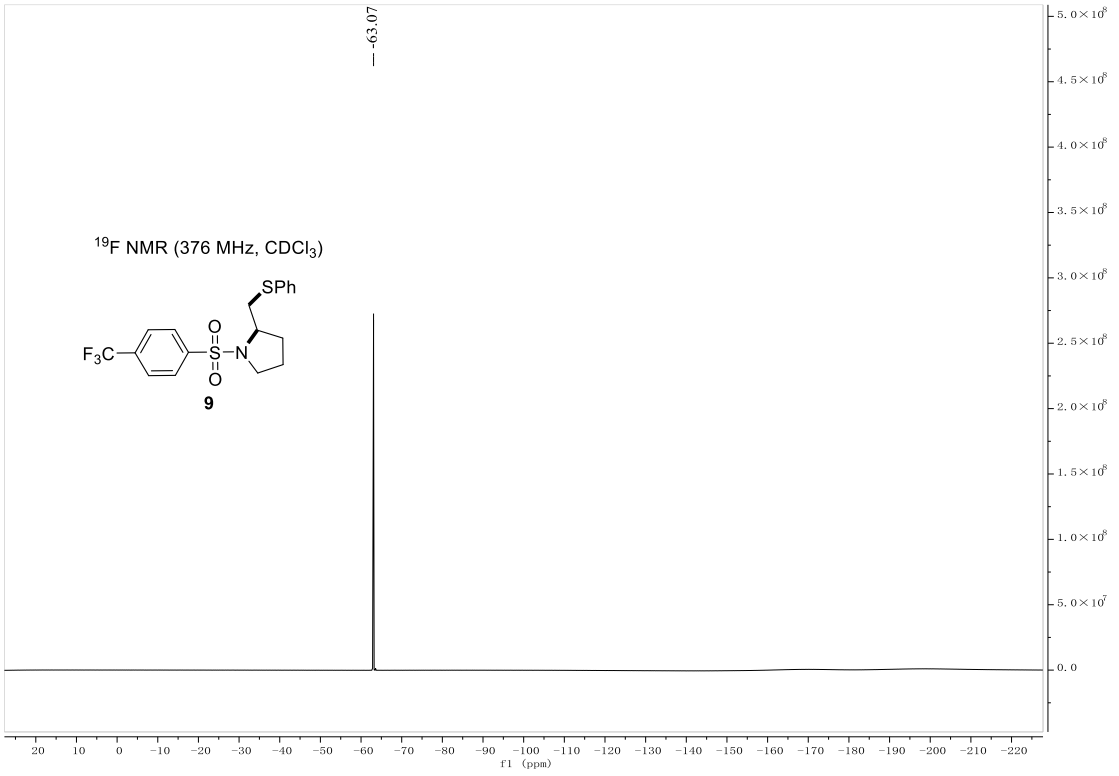
^{1}H NMR of compound **9**



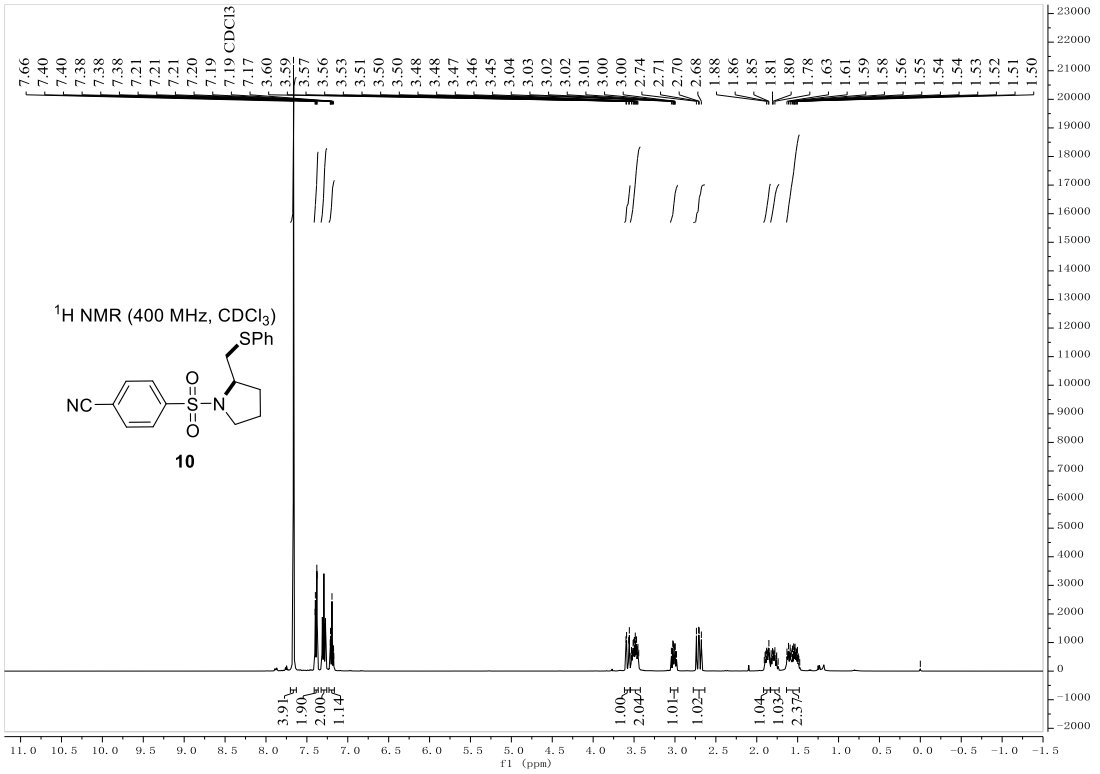
^{13}C NMR of compound **9**



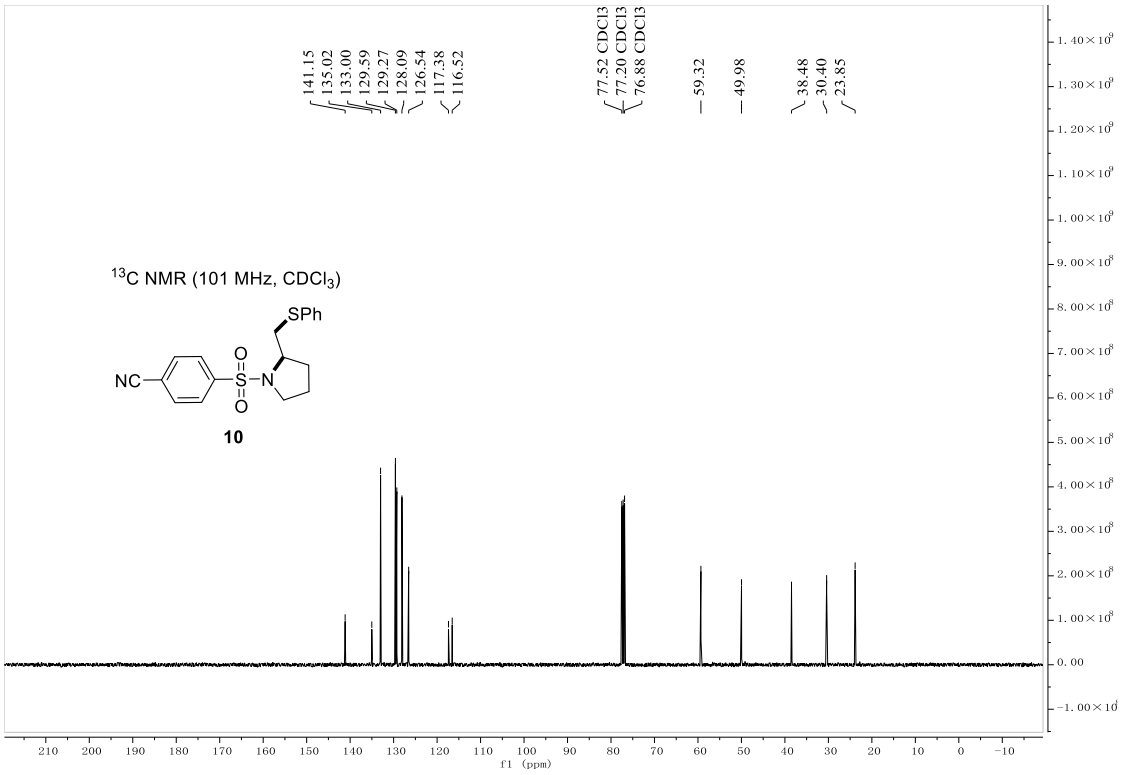
^{19}F NMR of compound **9**



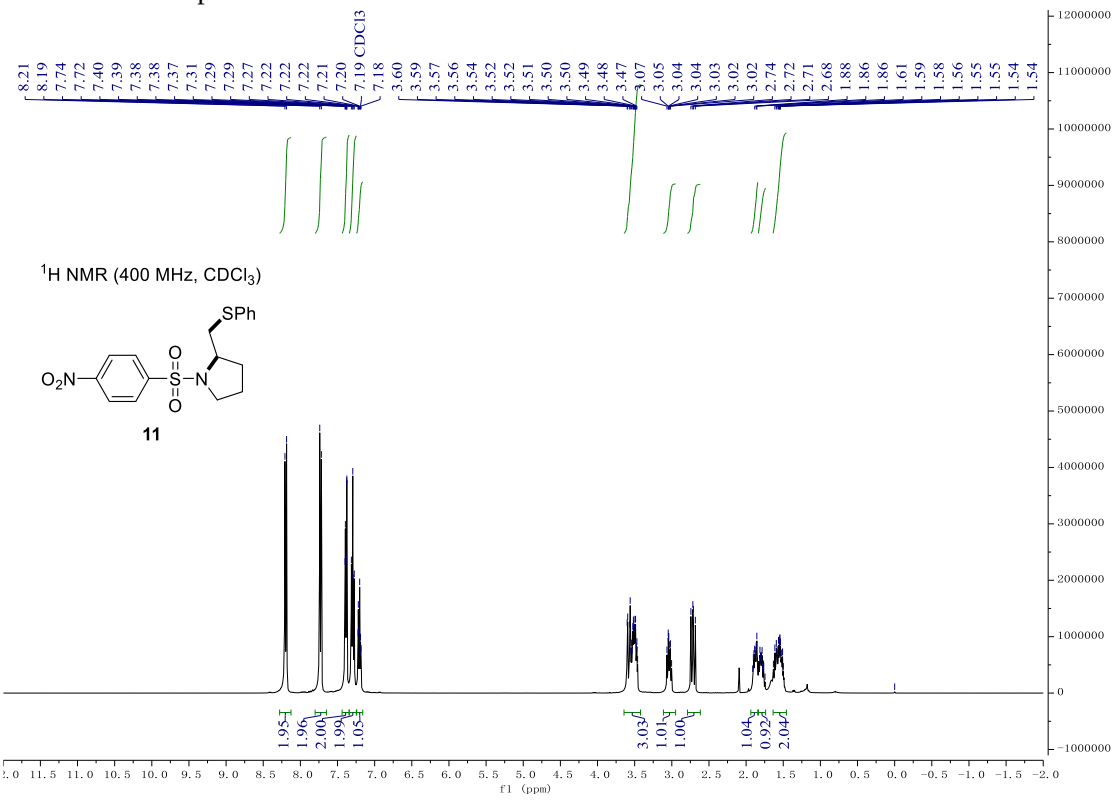
^{1}H NMR of compound **10**



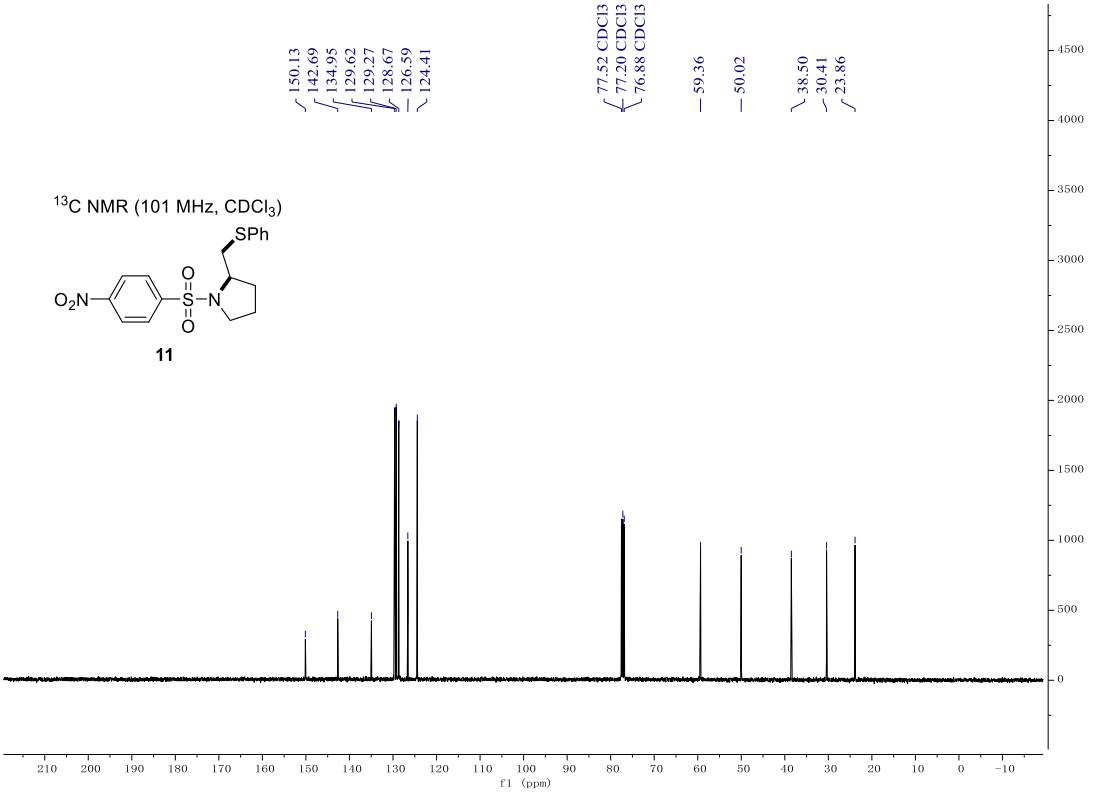
^{13}C NMR of compound **10**



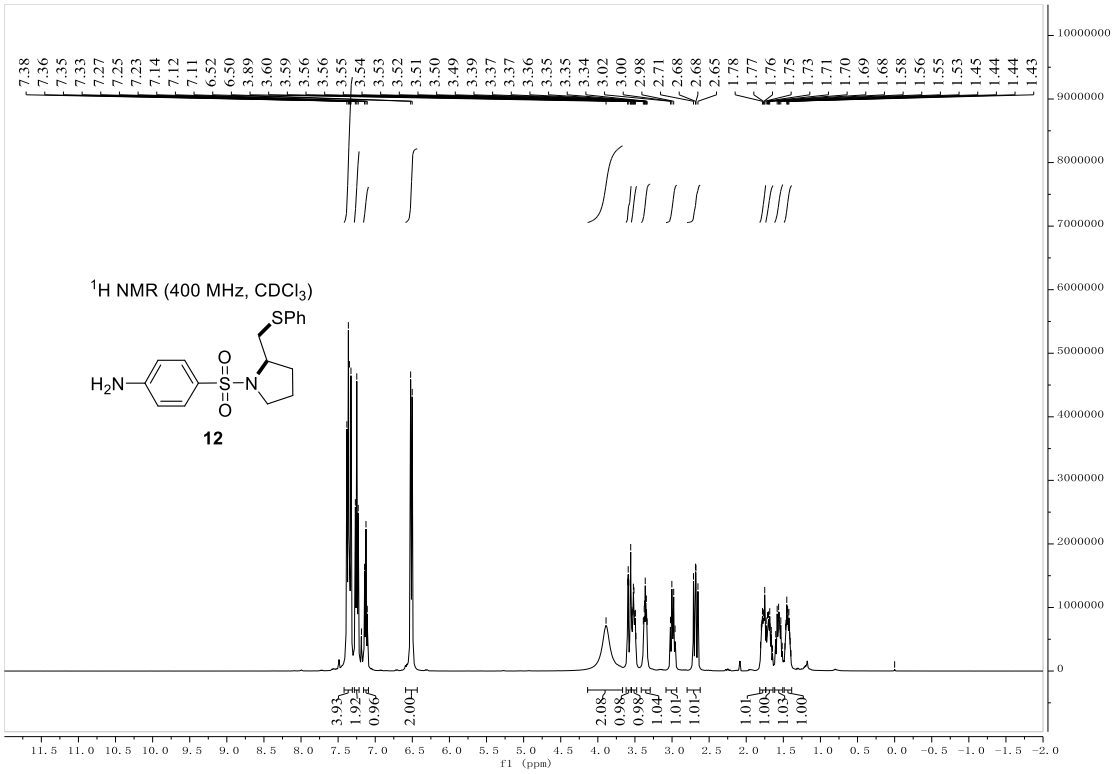
^{1}H NMR of compound **11**



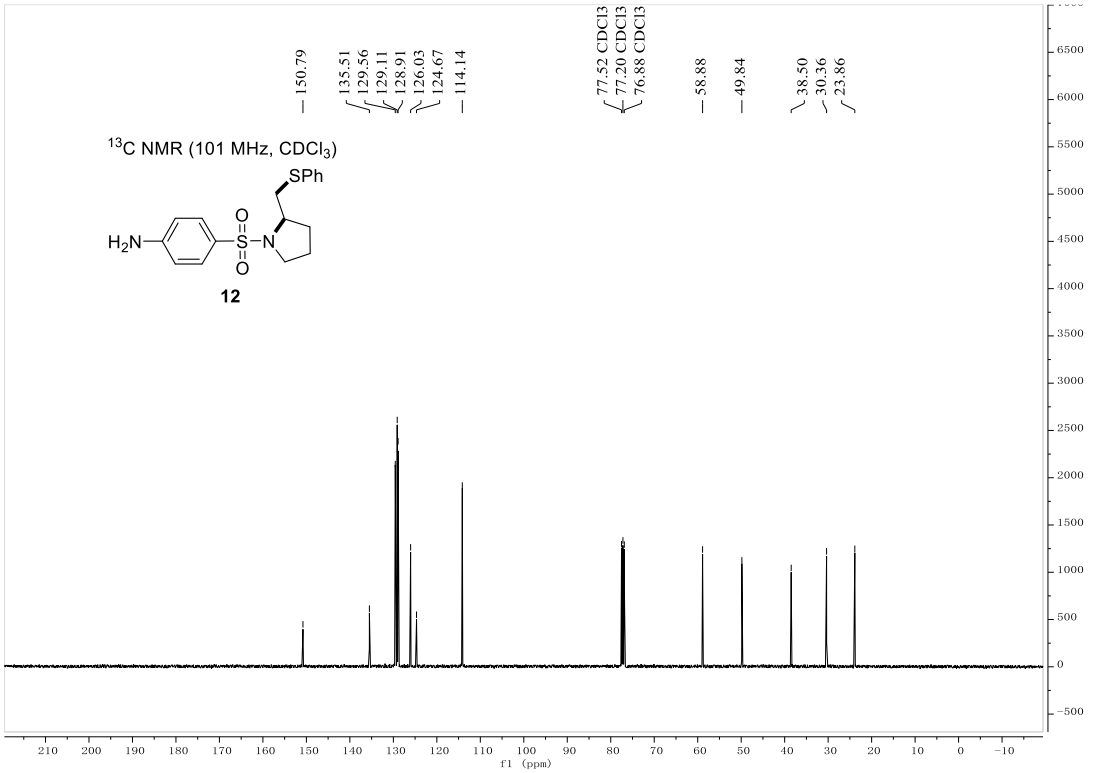
^{13}C NMR of compound **11**



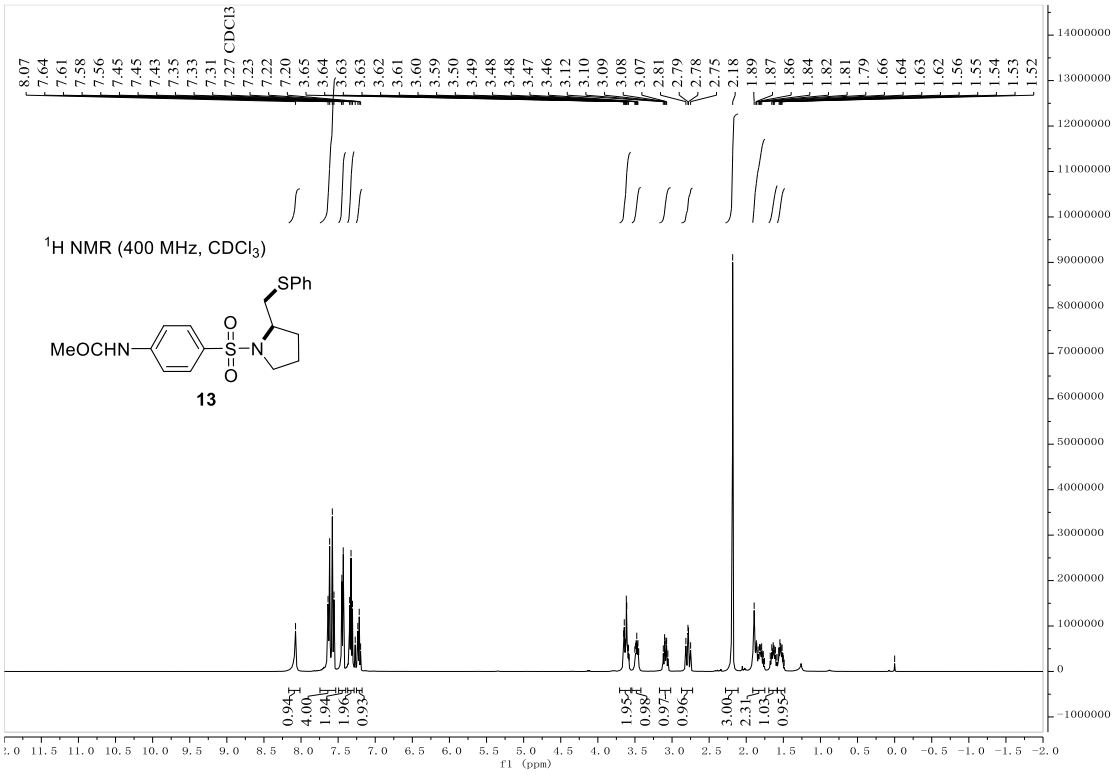
^{1}H NMR of compound **12**



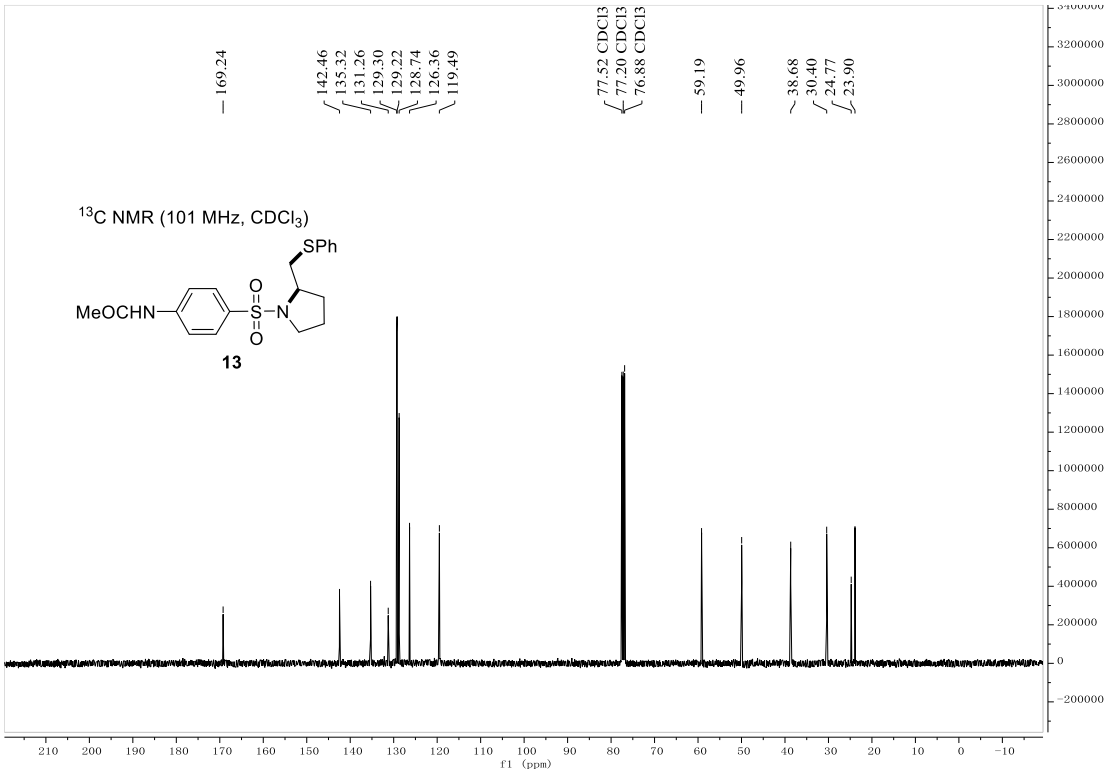
^{13}C NMR of compound **12**



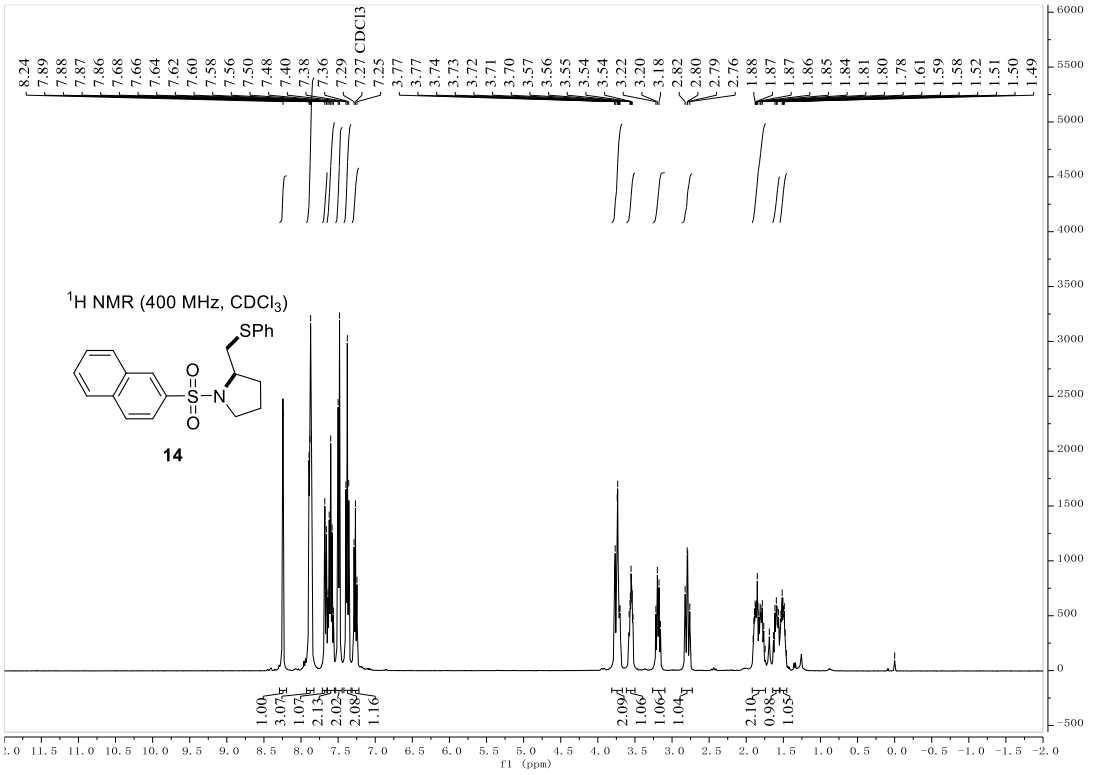
^{1}H NMR of compound **13**



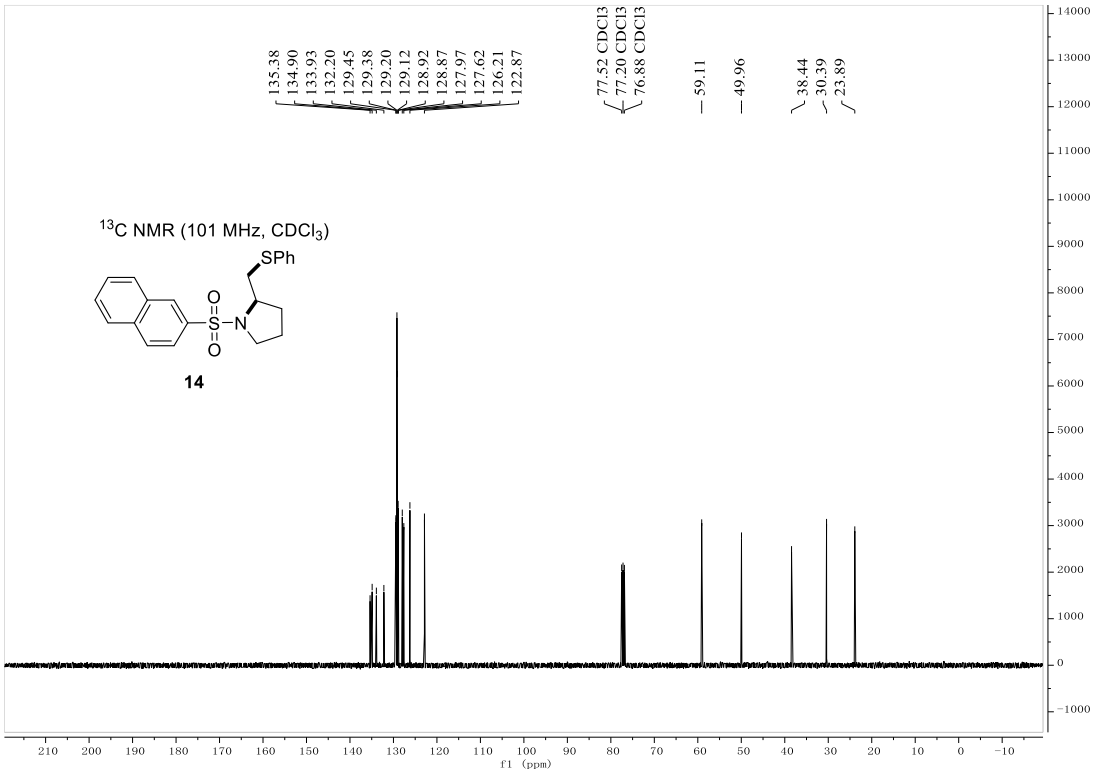
^{13}C NMR of compound **13**



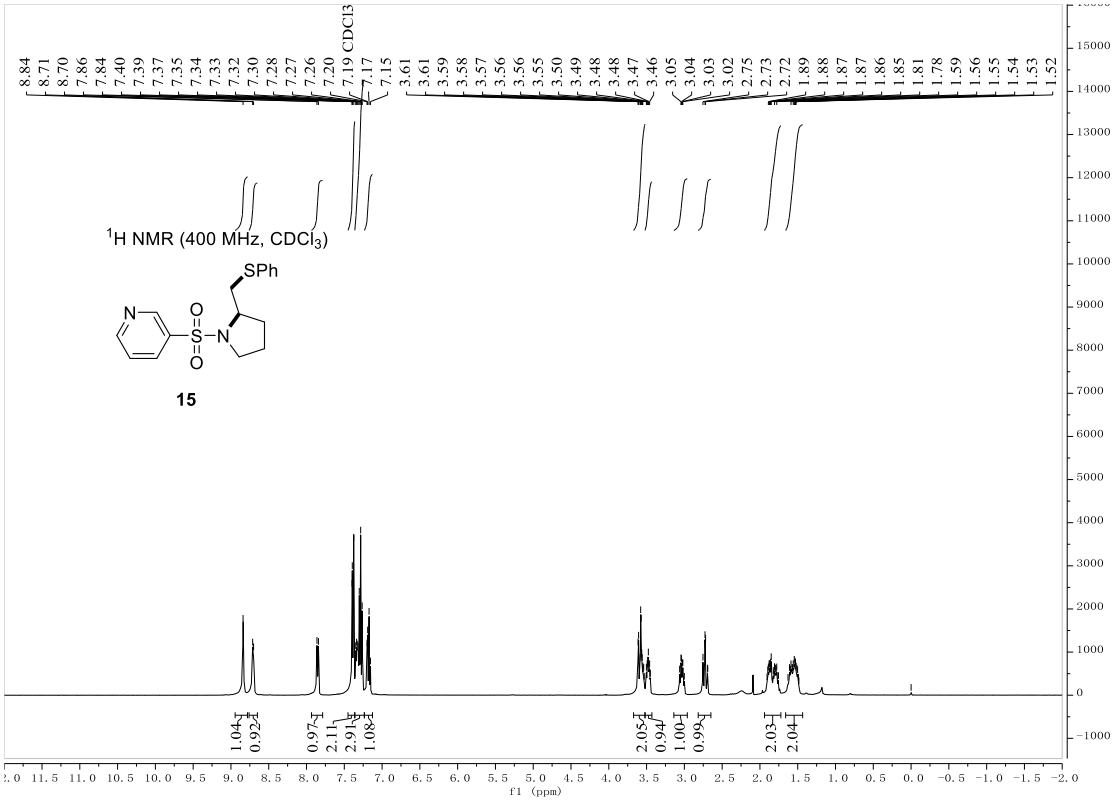
^{1}H NMR of compound **14**



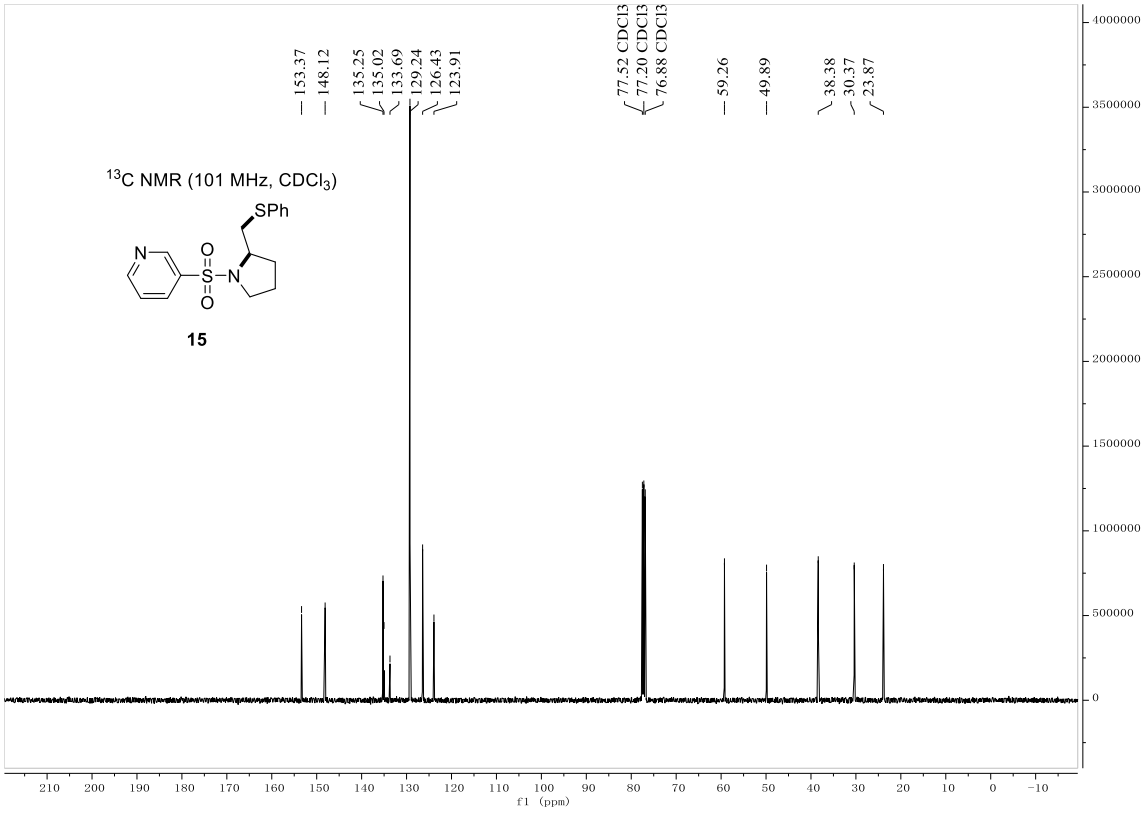
^{13}C NMR of compound **14**



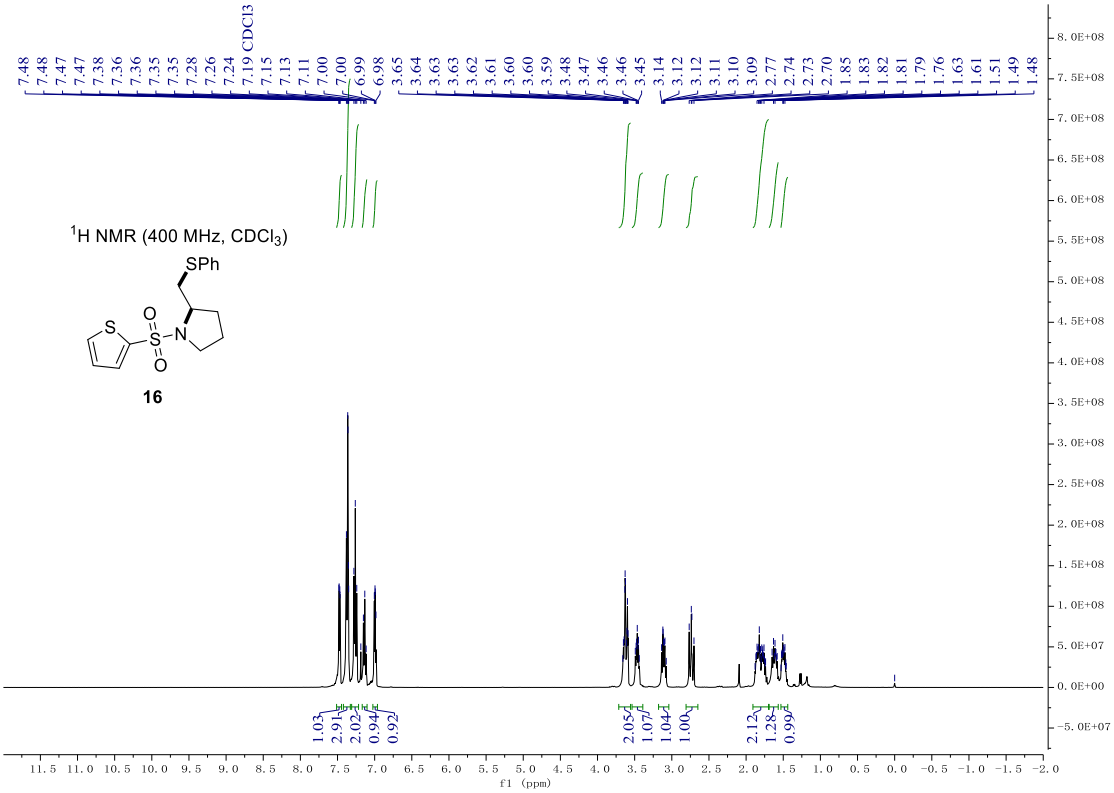
^{1}H NMR of compound **15**



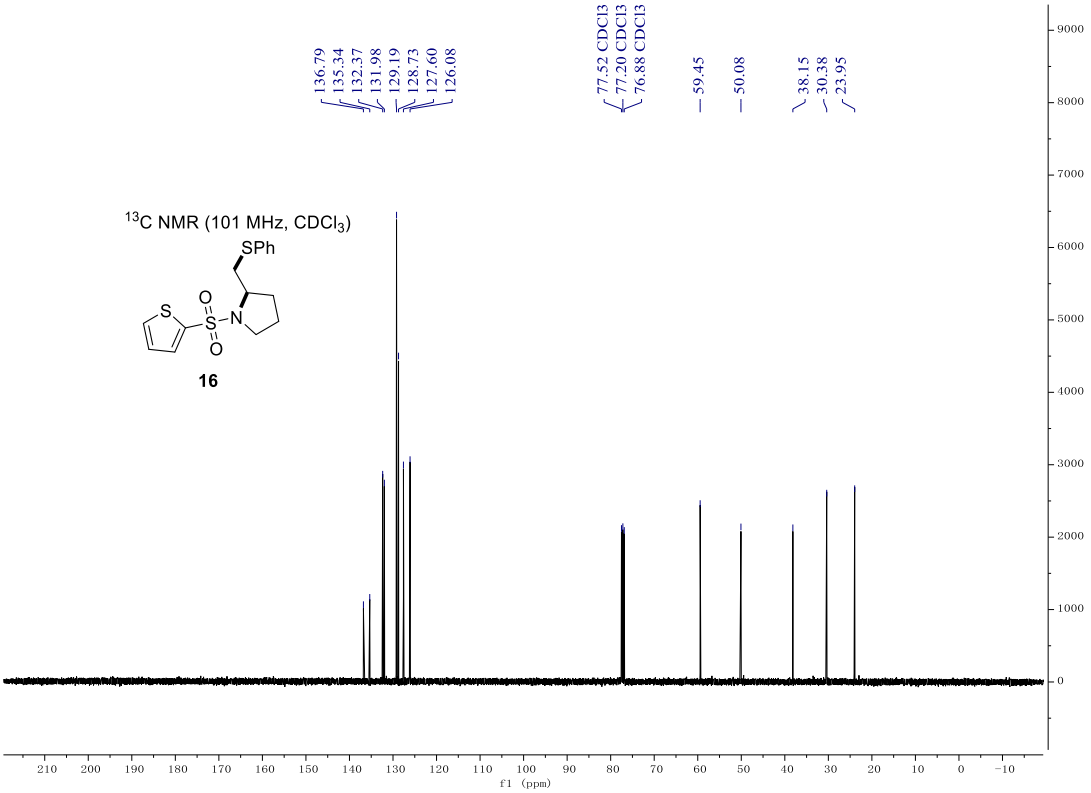
^{13}C NMR of compound **15**



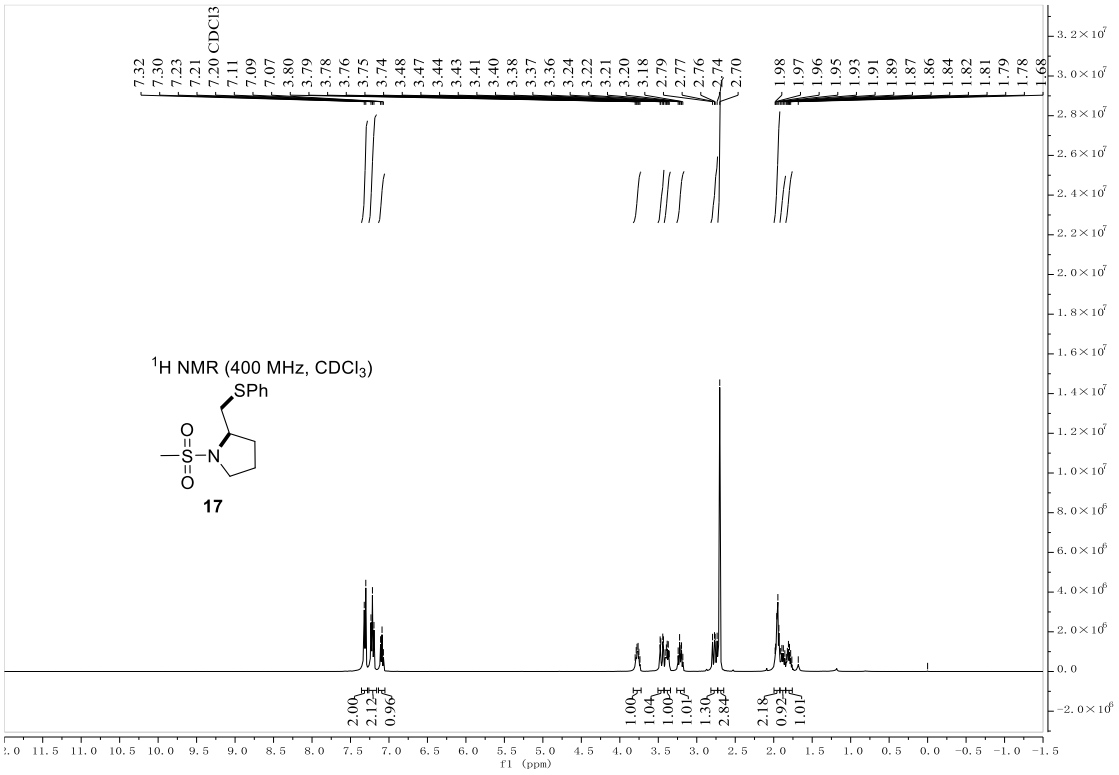
^{1}H NMR of compound **16**



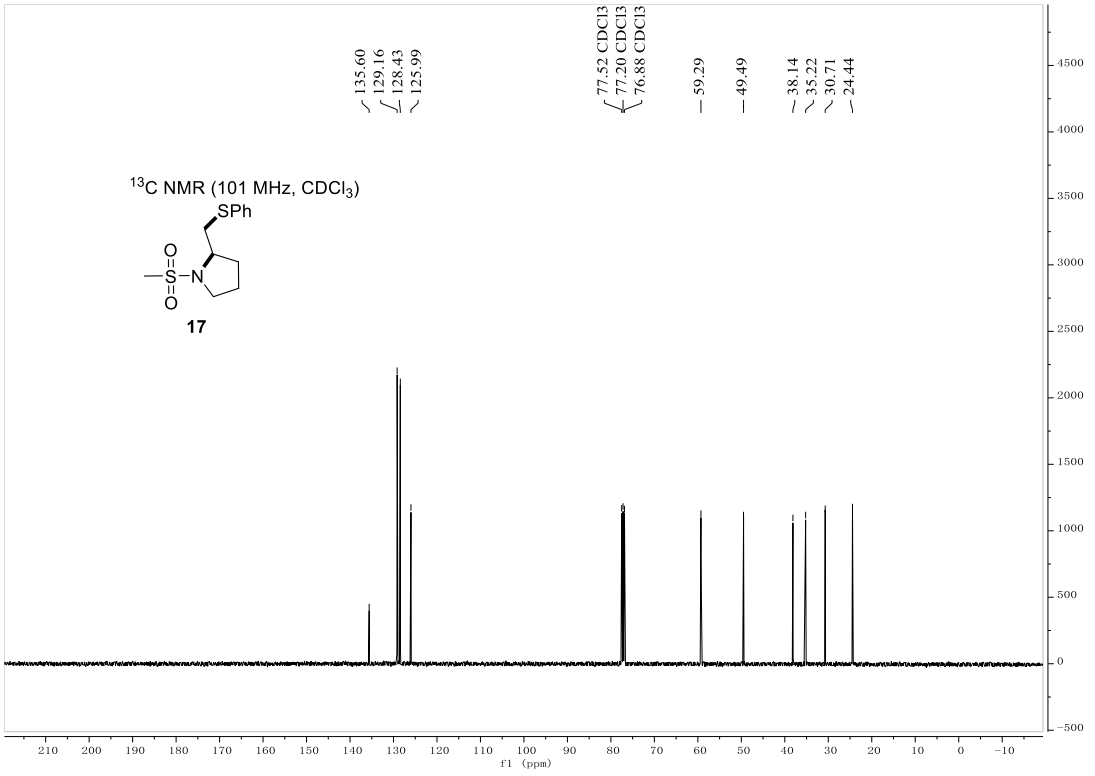
^{13}C NMR of compound **16**



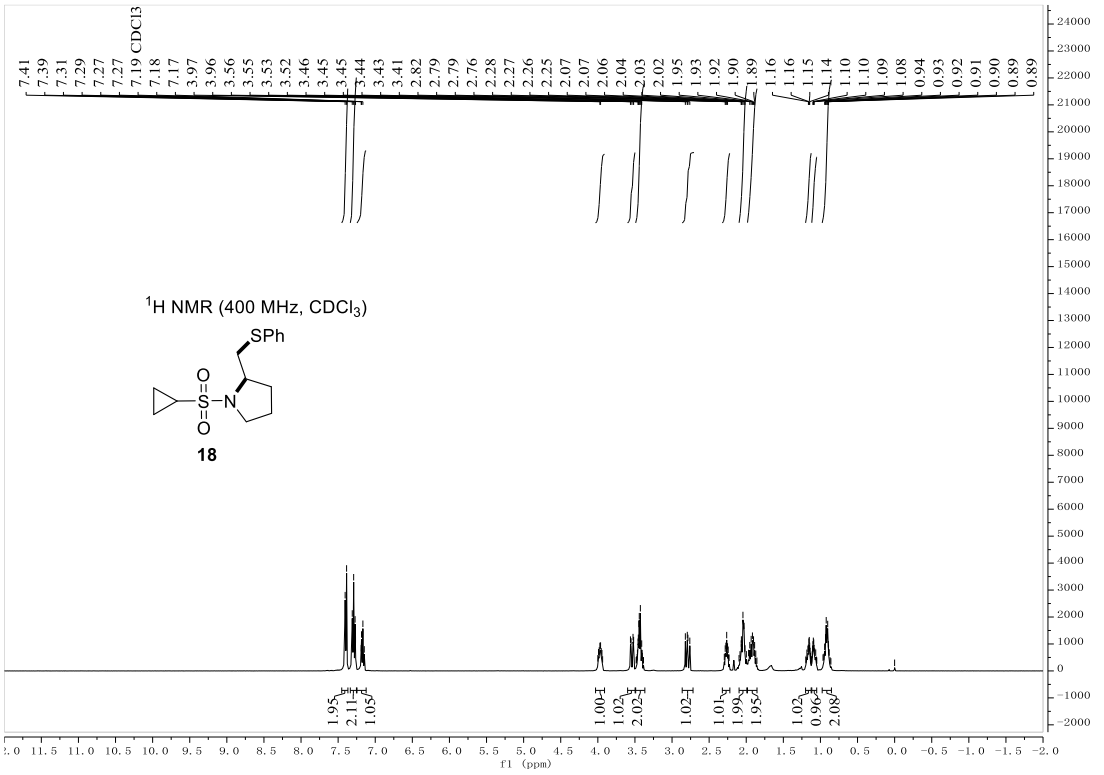
^{1}H NMR of compound **17**



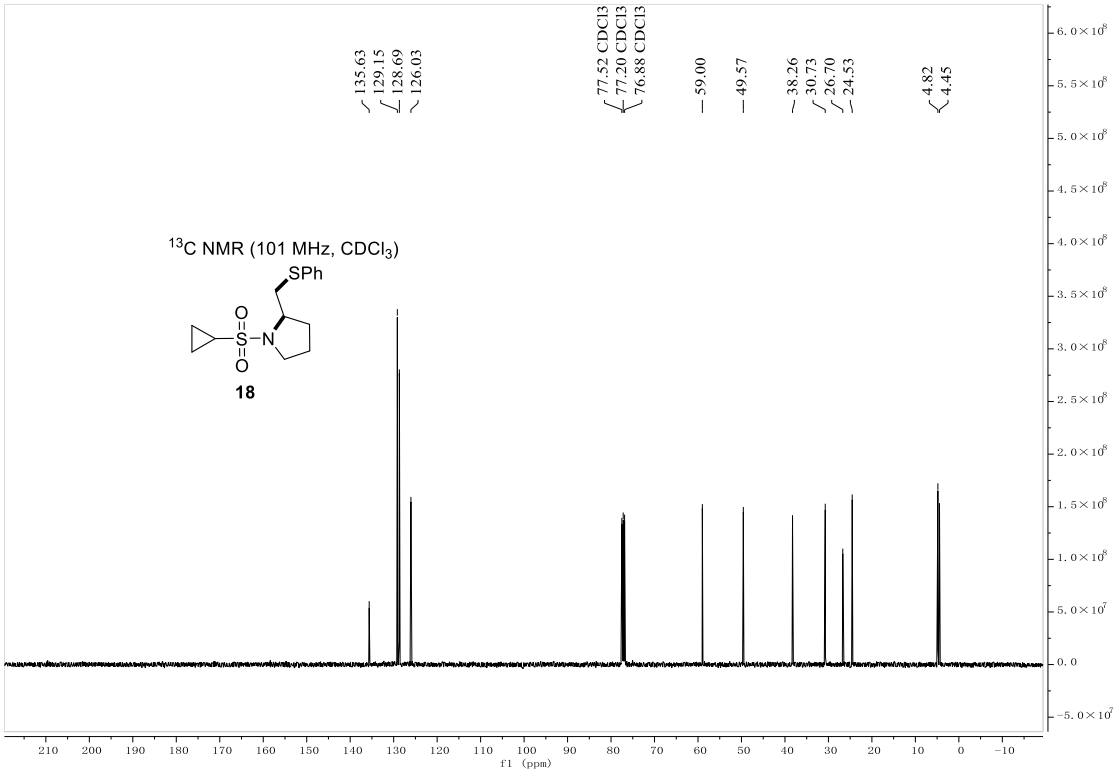
^{13}C NMR of compound **17**



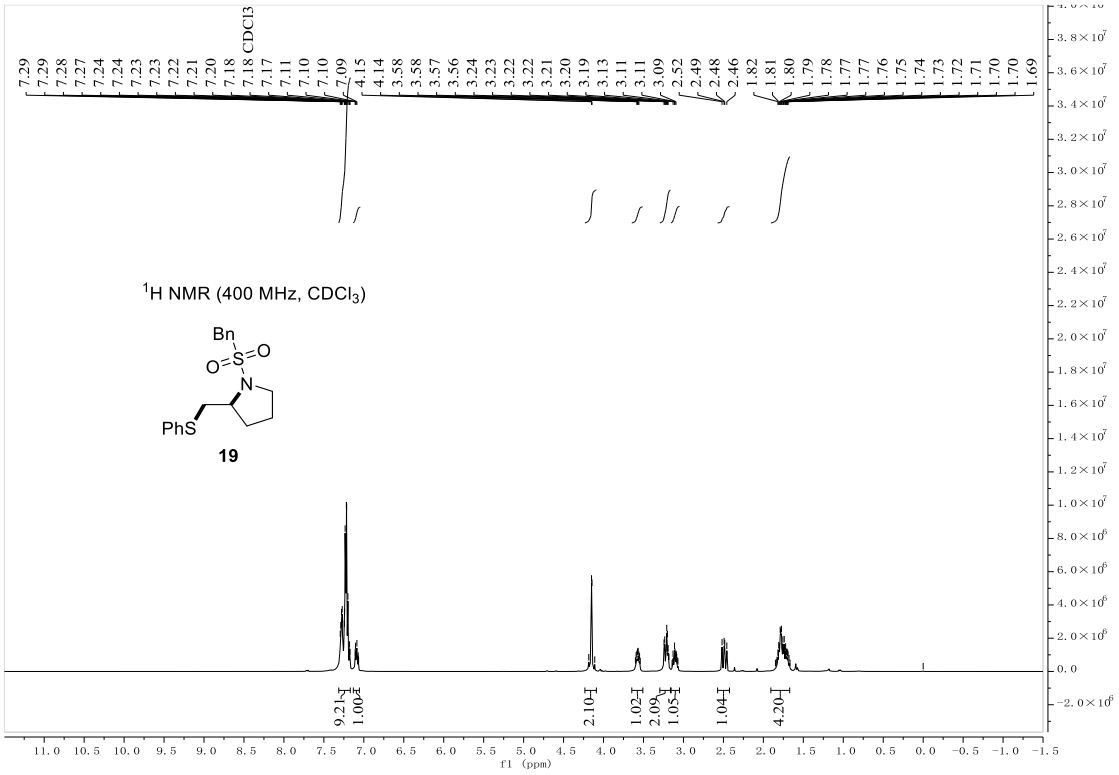
^{1}H NMR of compound **18**



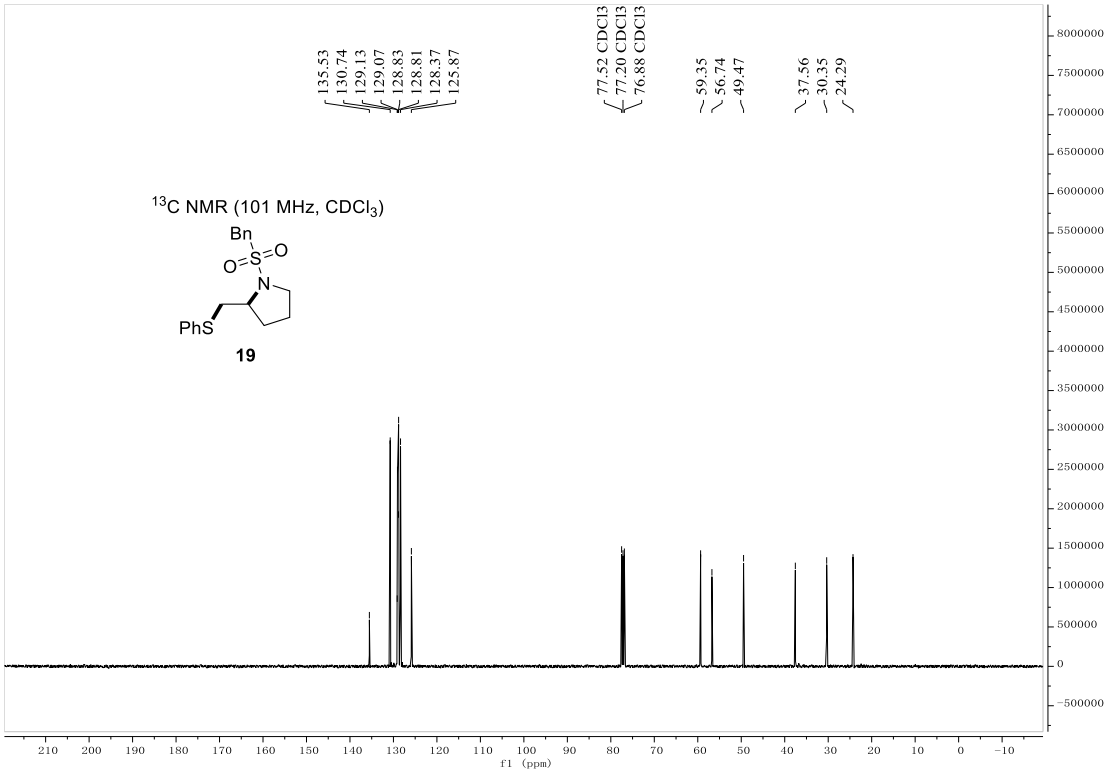
^{13}C NMR of compound **18**



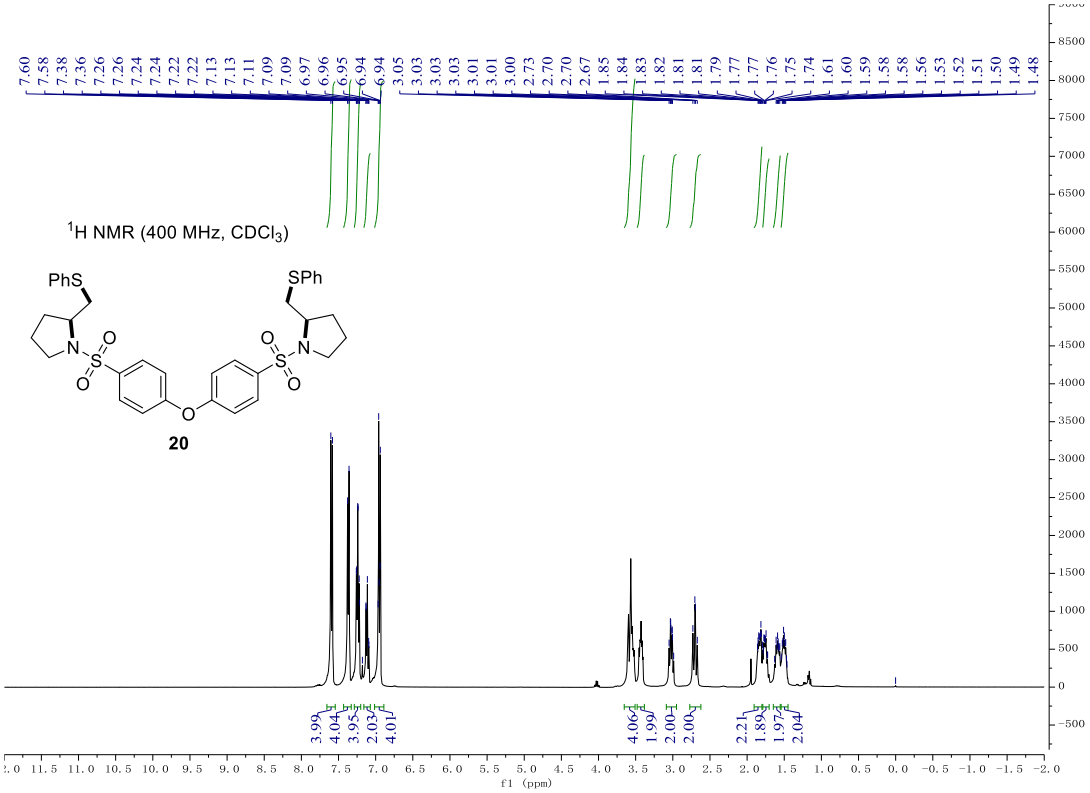
^{1}H NMR of compound **19**



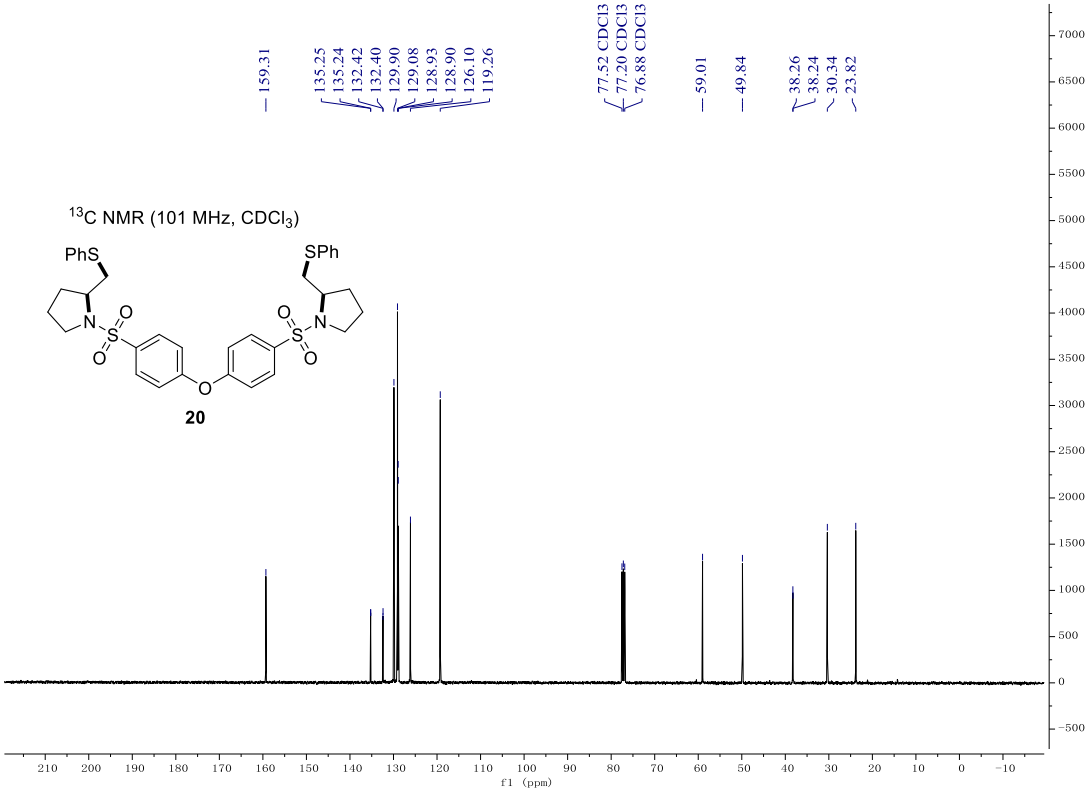
^{13}C NMR of compound **19**



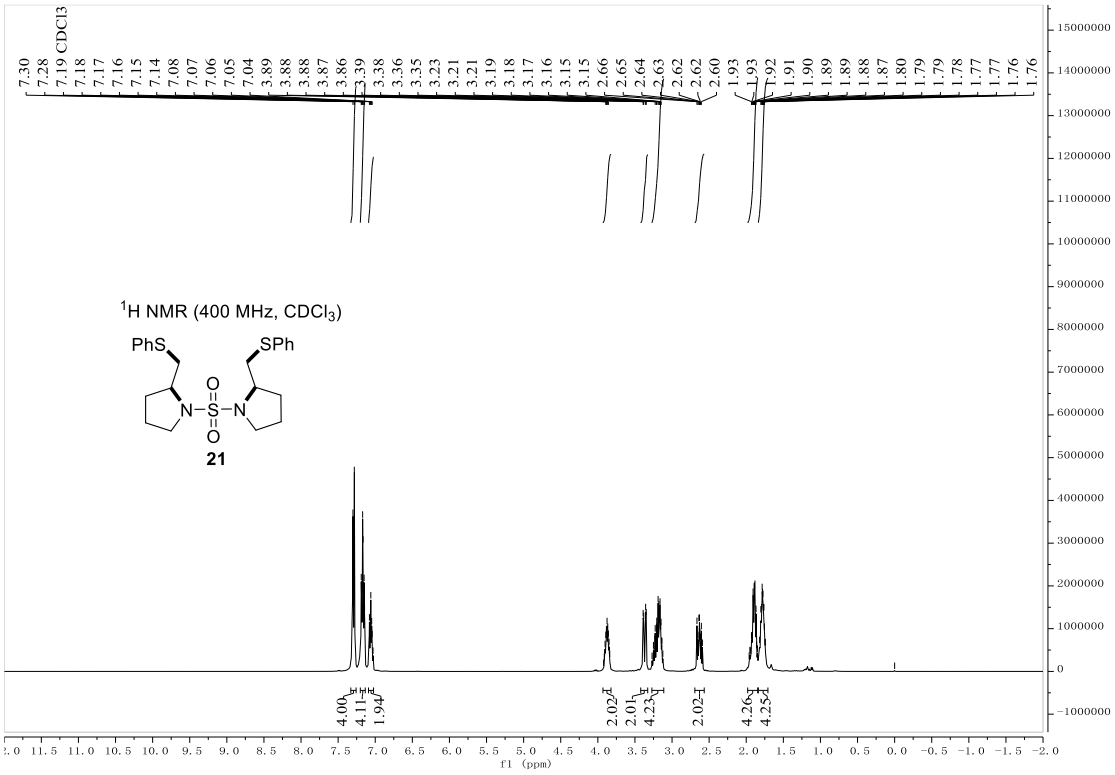
^{1}H NMR of compound **20**



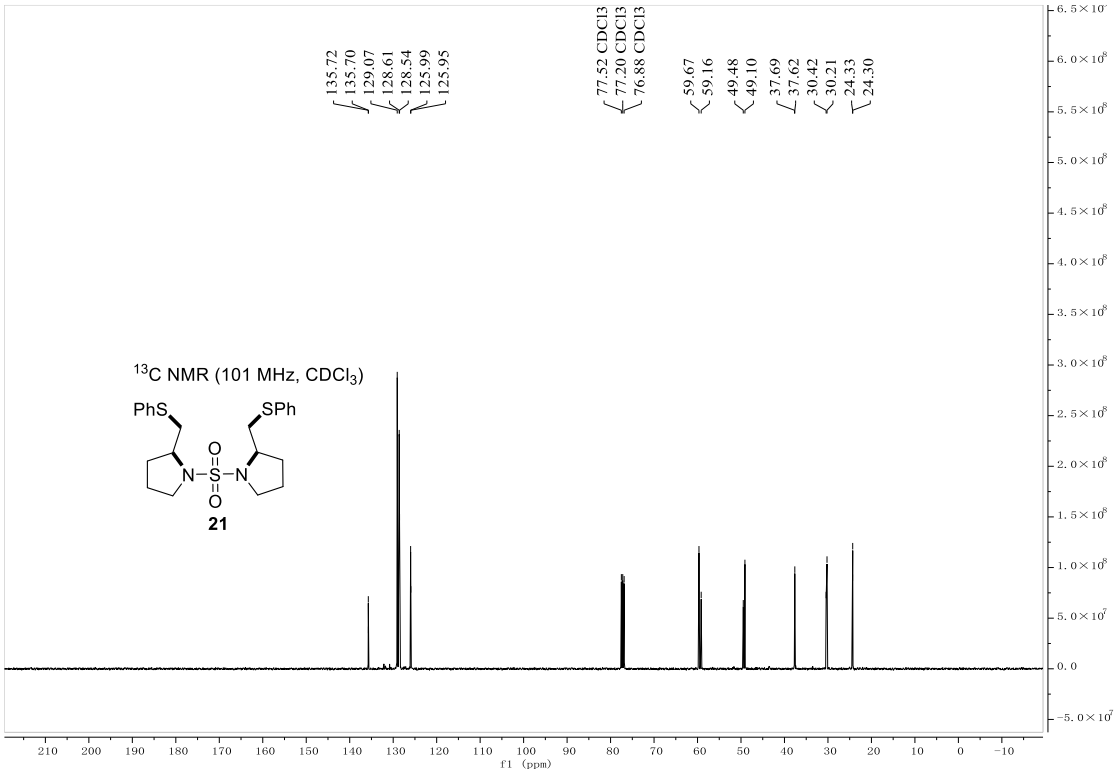
^{13}C NMR of compound **20**



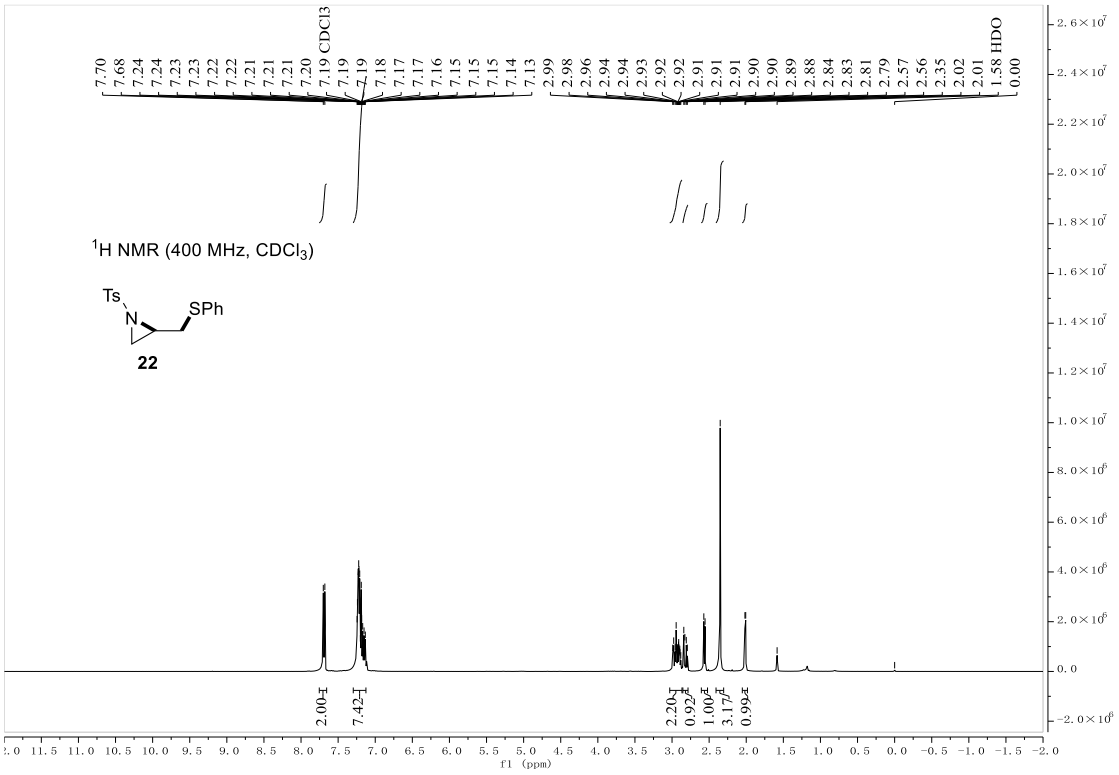
^{1}H NMR of compound **21**



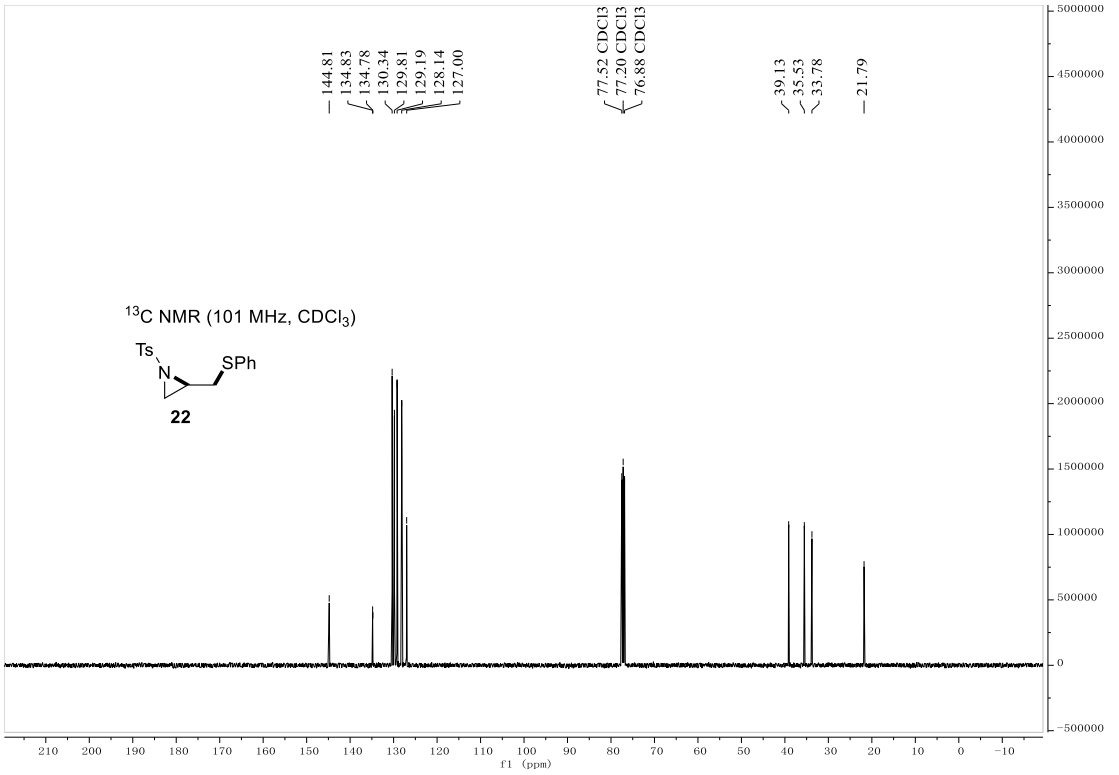
^{13}C NMR of compound **21**



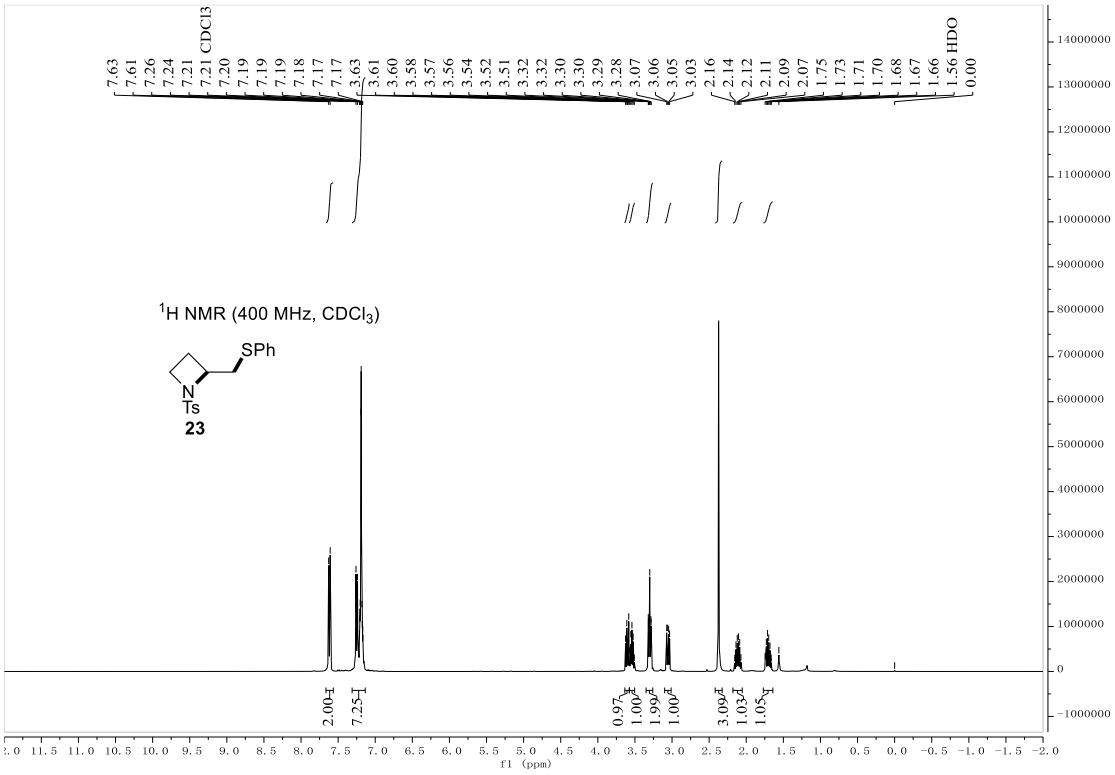
^{1}H NMR of compound **22**



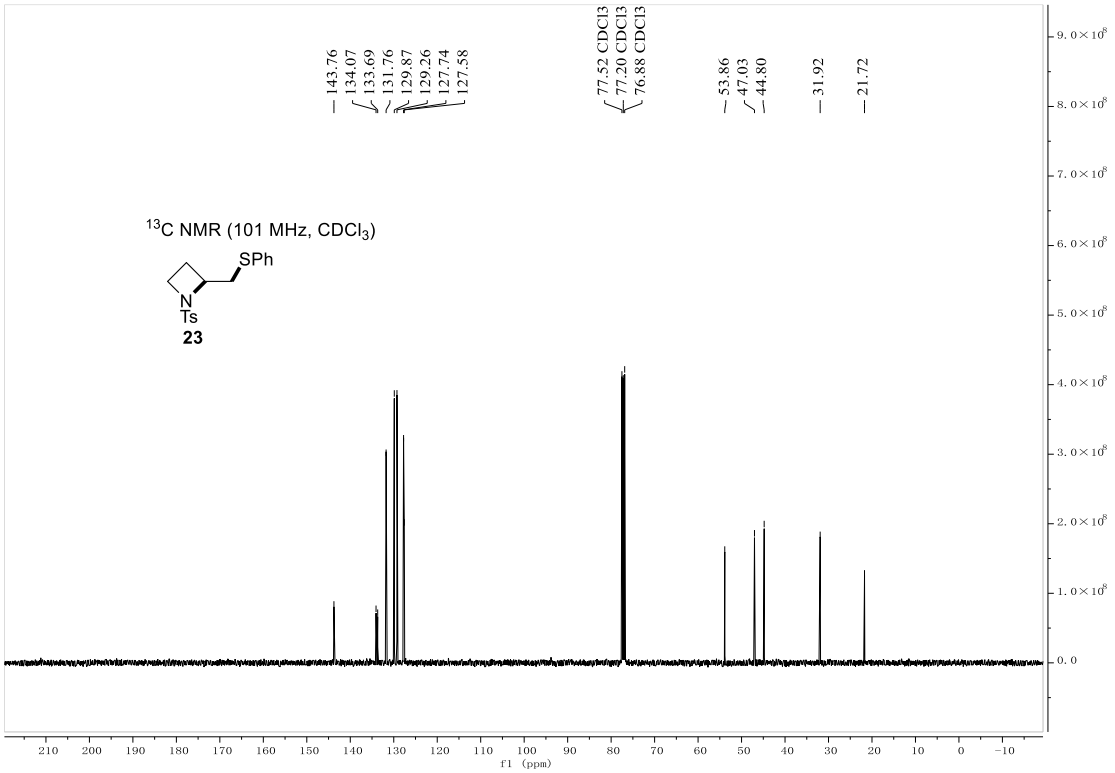
^{13}C NMR of compound **22**



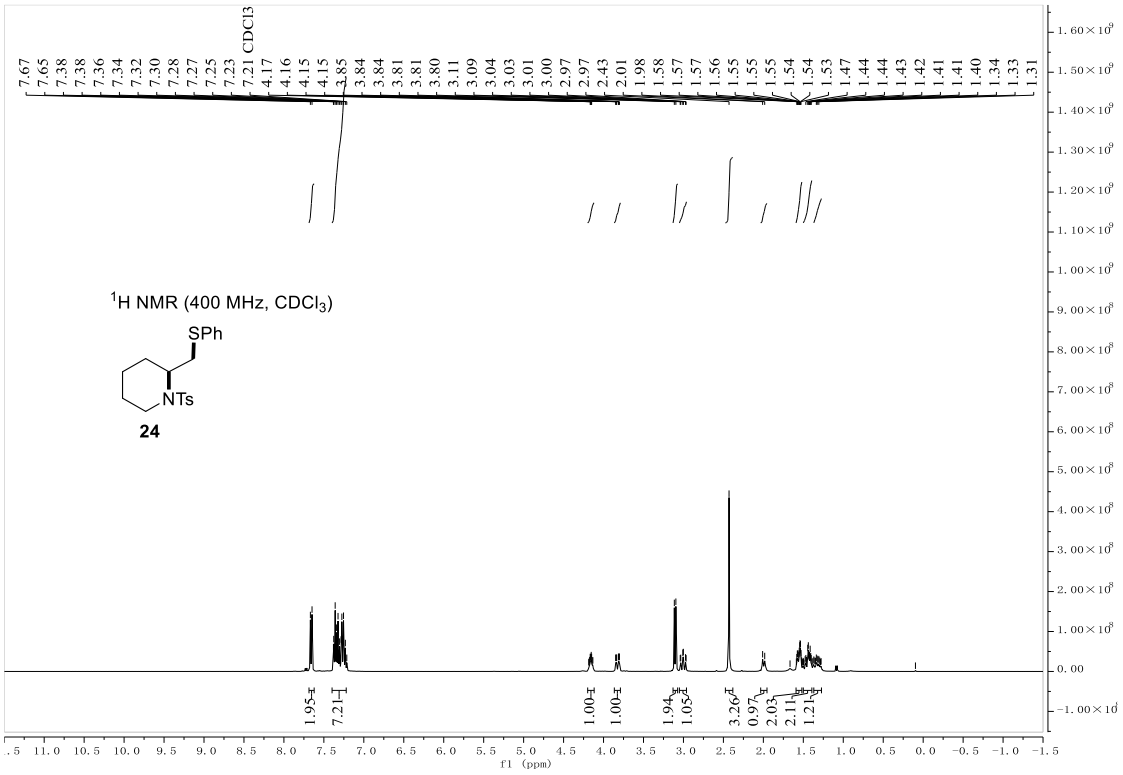
^{1}H NMR of compound **23**



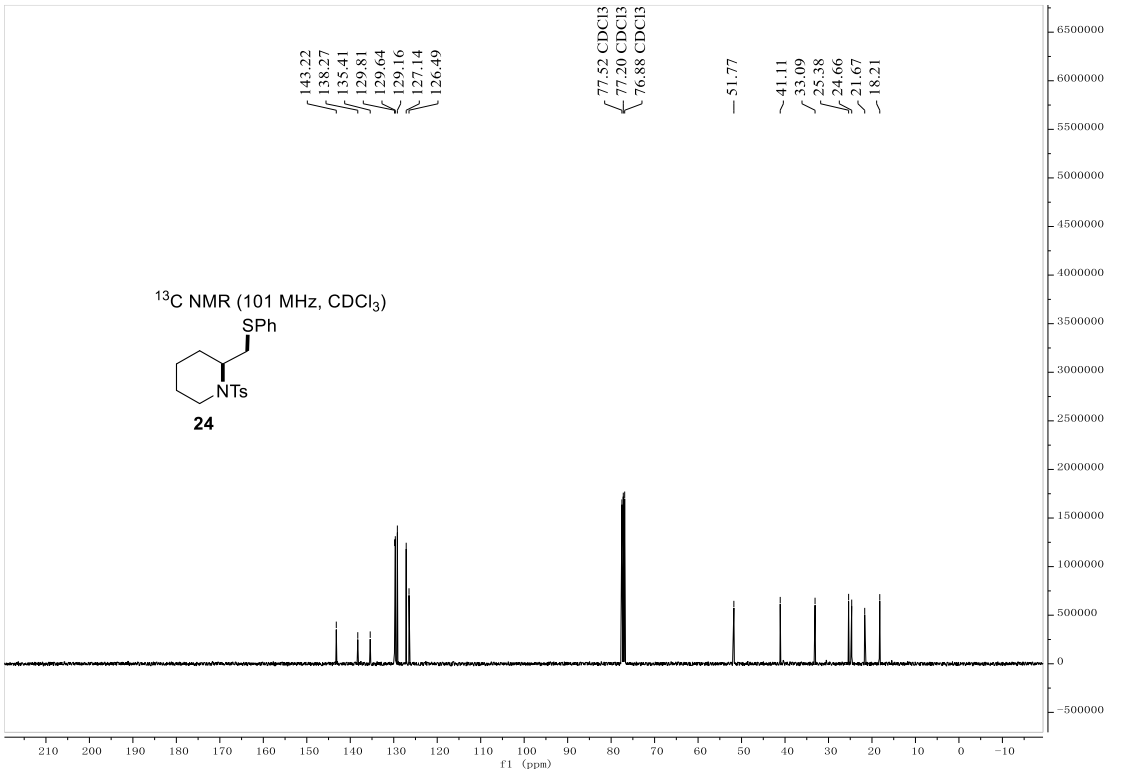
^{13}C NMR of compound **23**



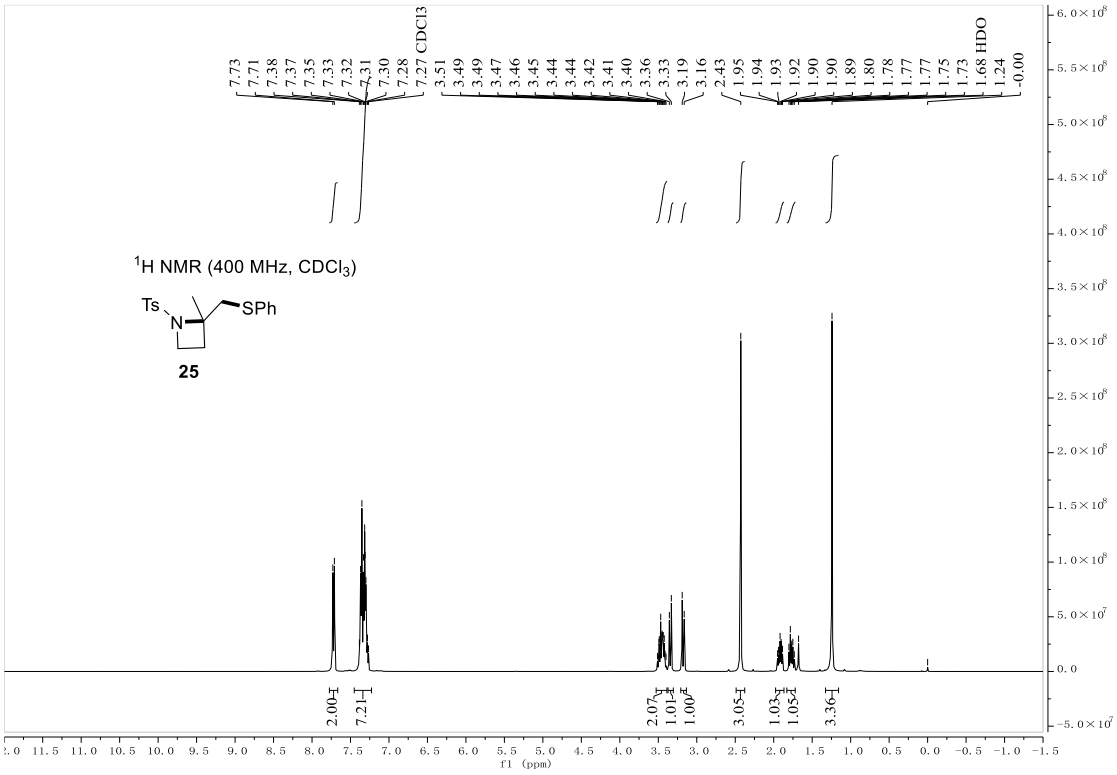
^{1}H NMR of compound **24**



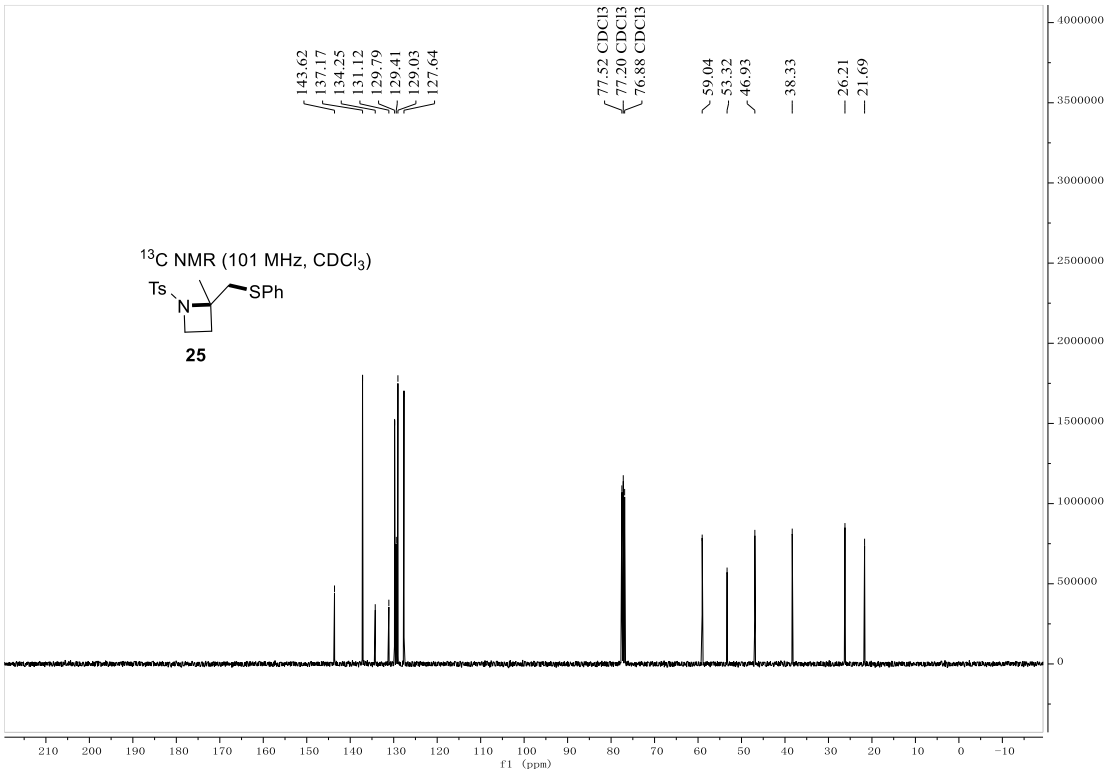
^{13}C NMR of compound **24**



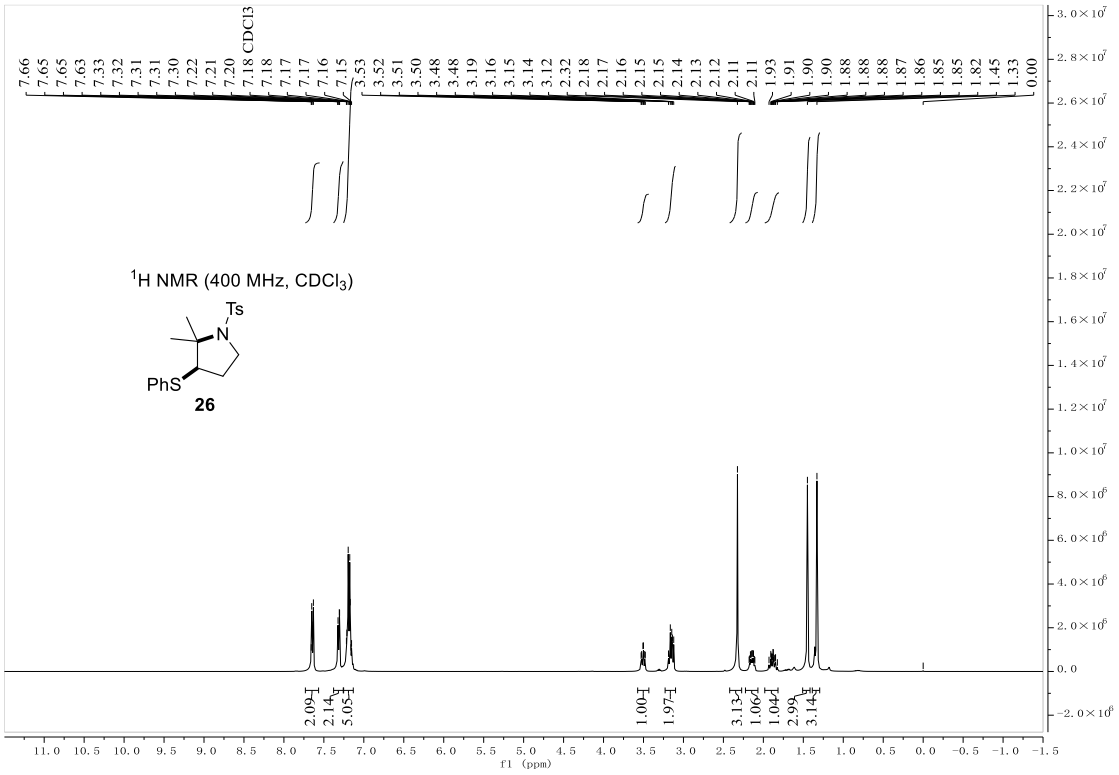
^{1}H NMR of compound **25**



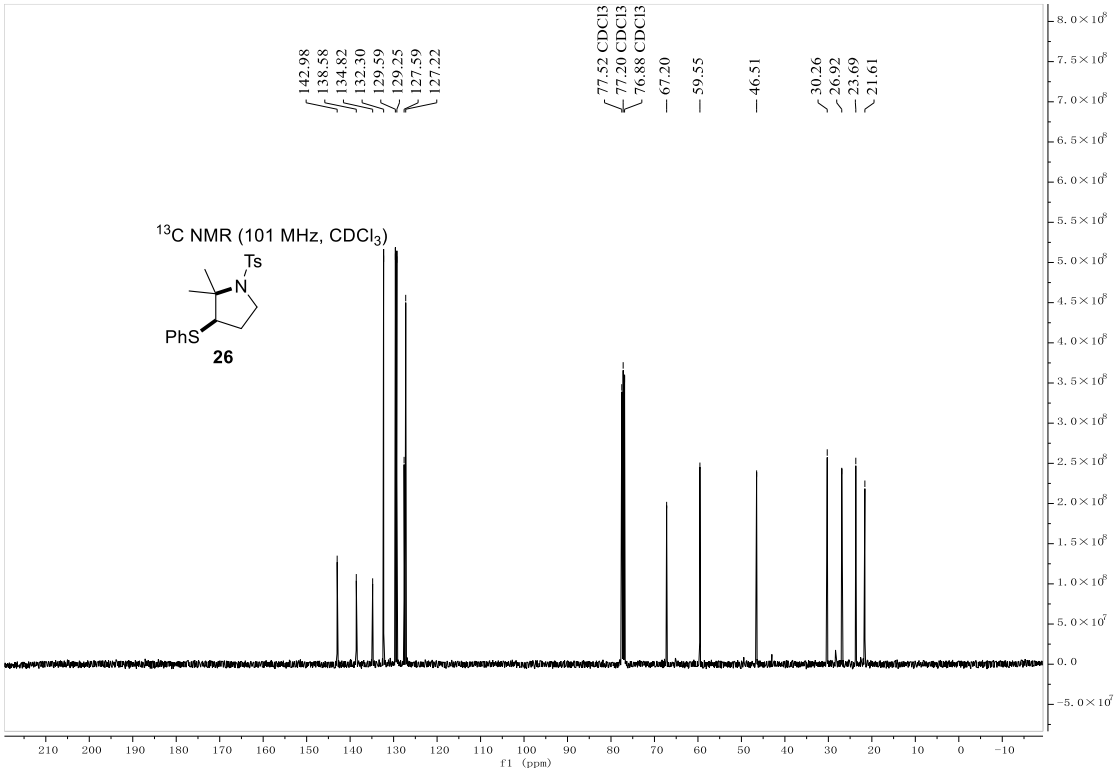
^{13}C NMR of compound **25**



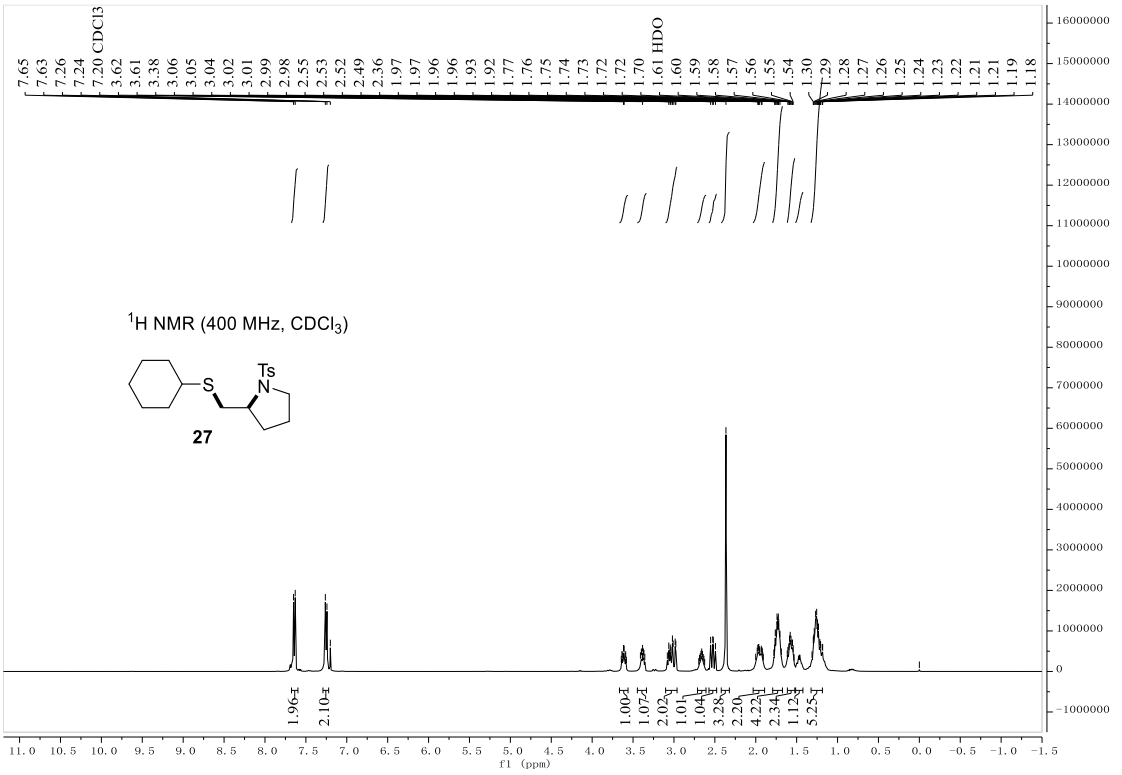
^{1}H NMR of compound **26**



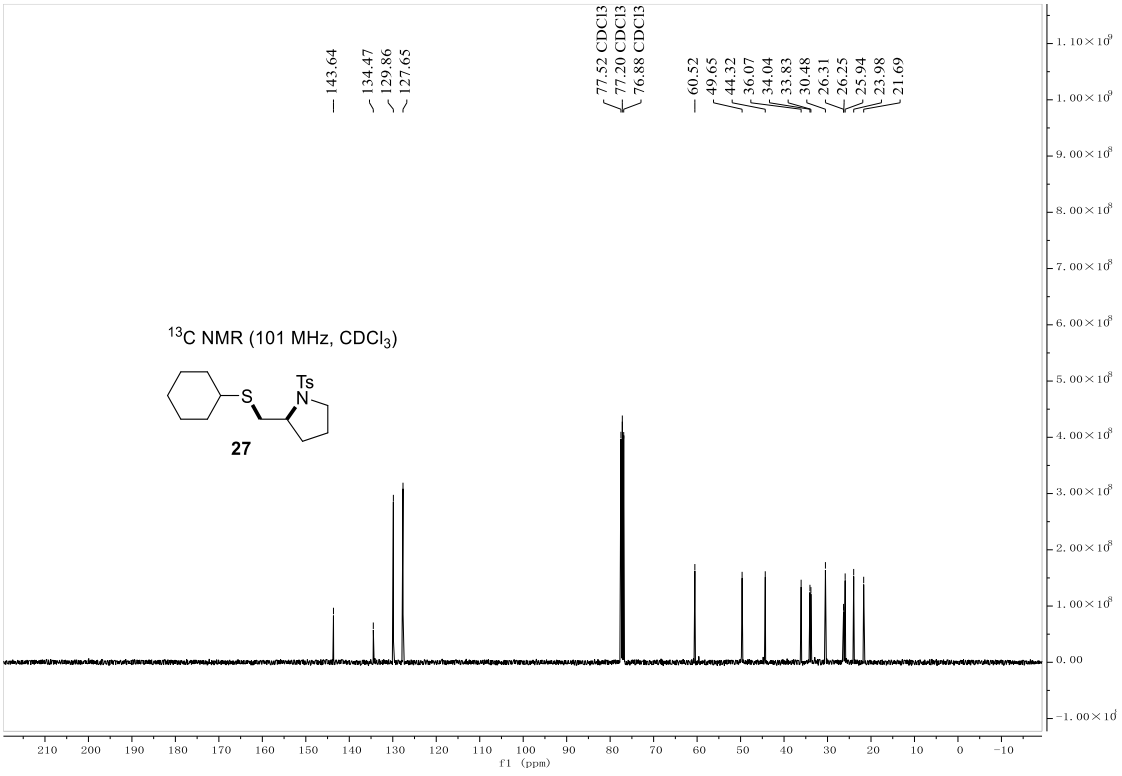
^{13}C NMR of compound **26**



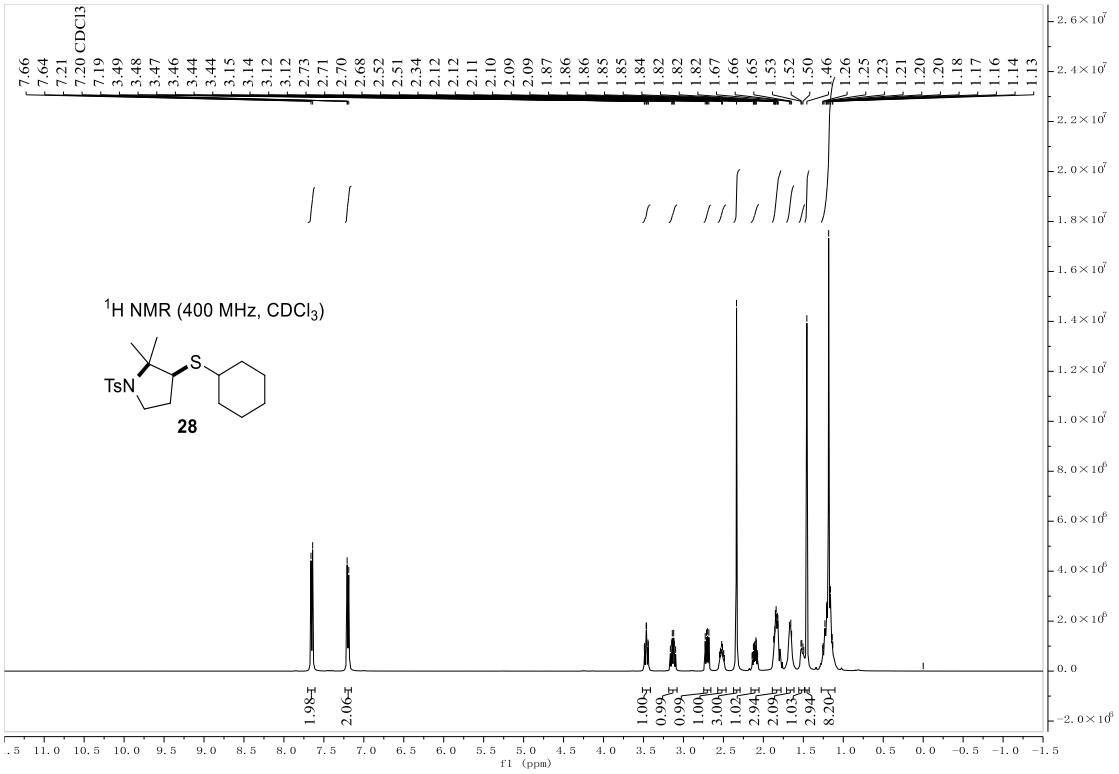
^{1}H NMR of compound **27**



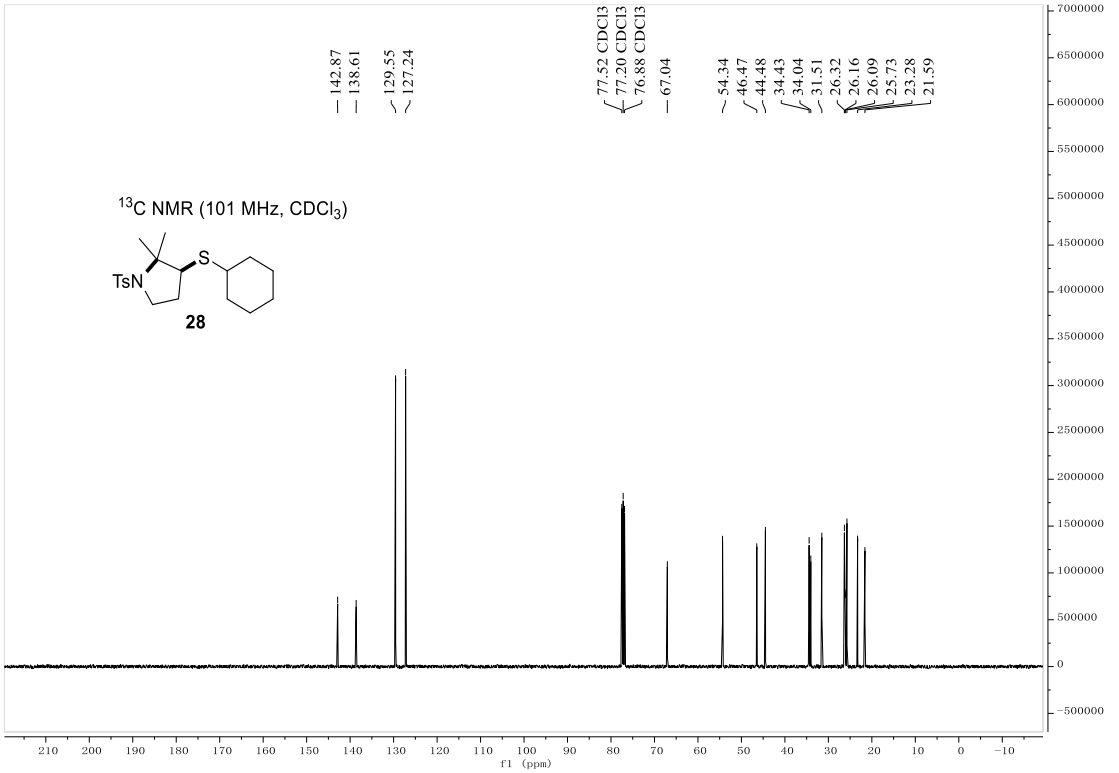
^{13}C NMR of compound **27**



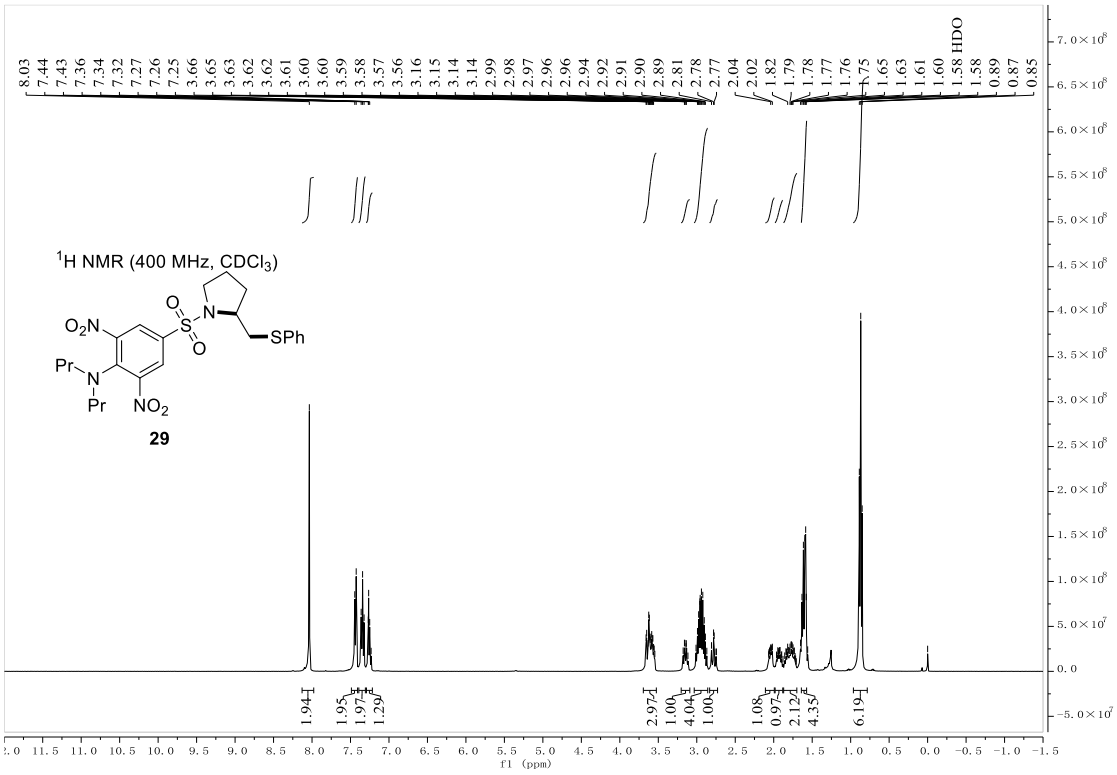
^{1}H NMR of compound **28**



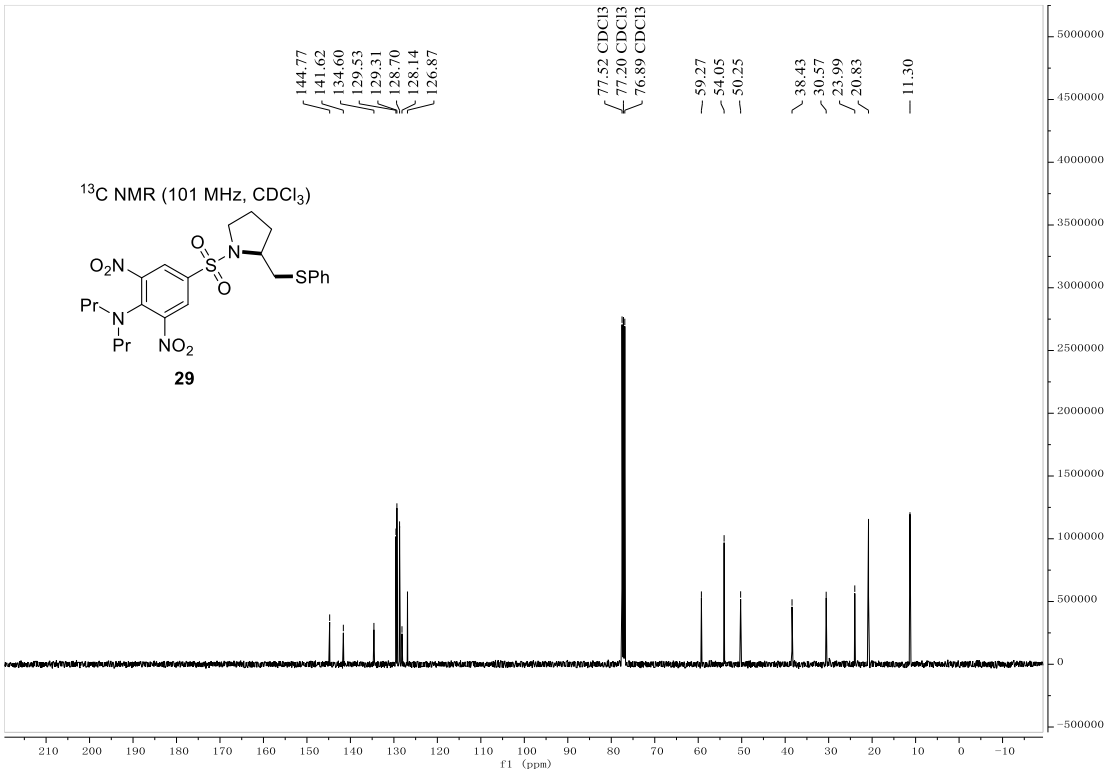
^{13}C NMR of compound **28**



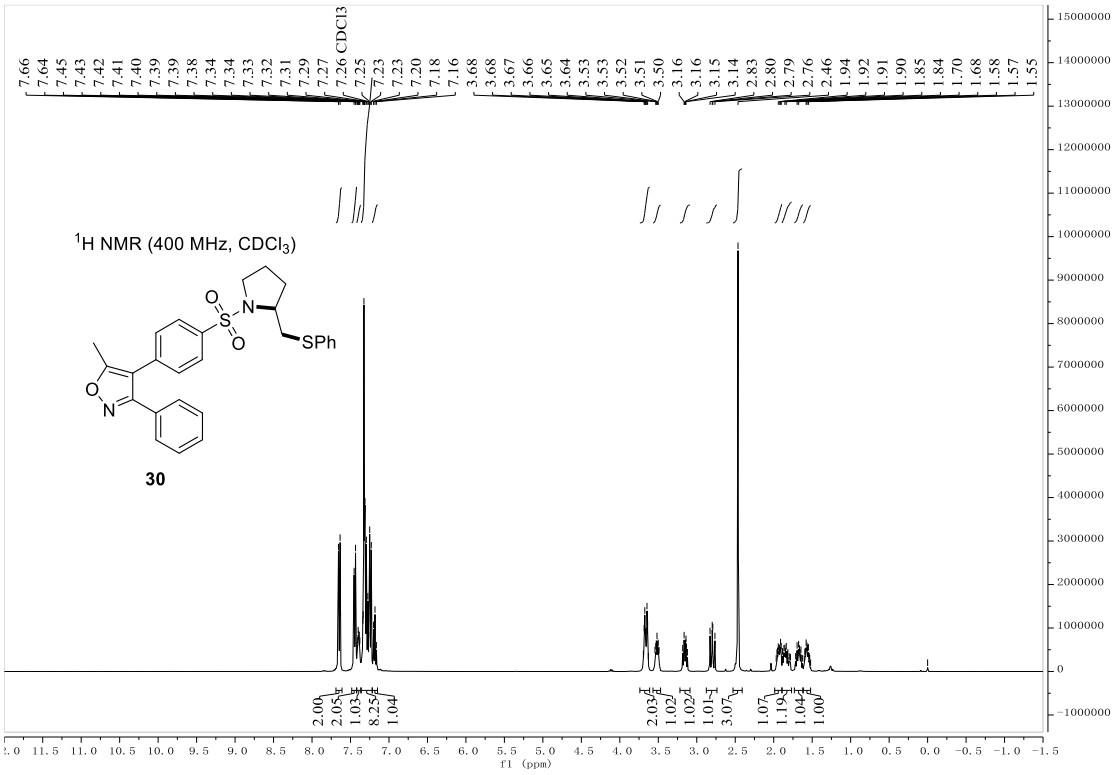
^{1}H NMR of compound **29**



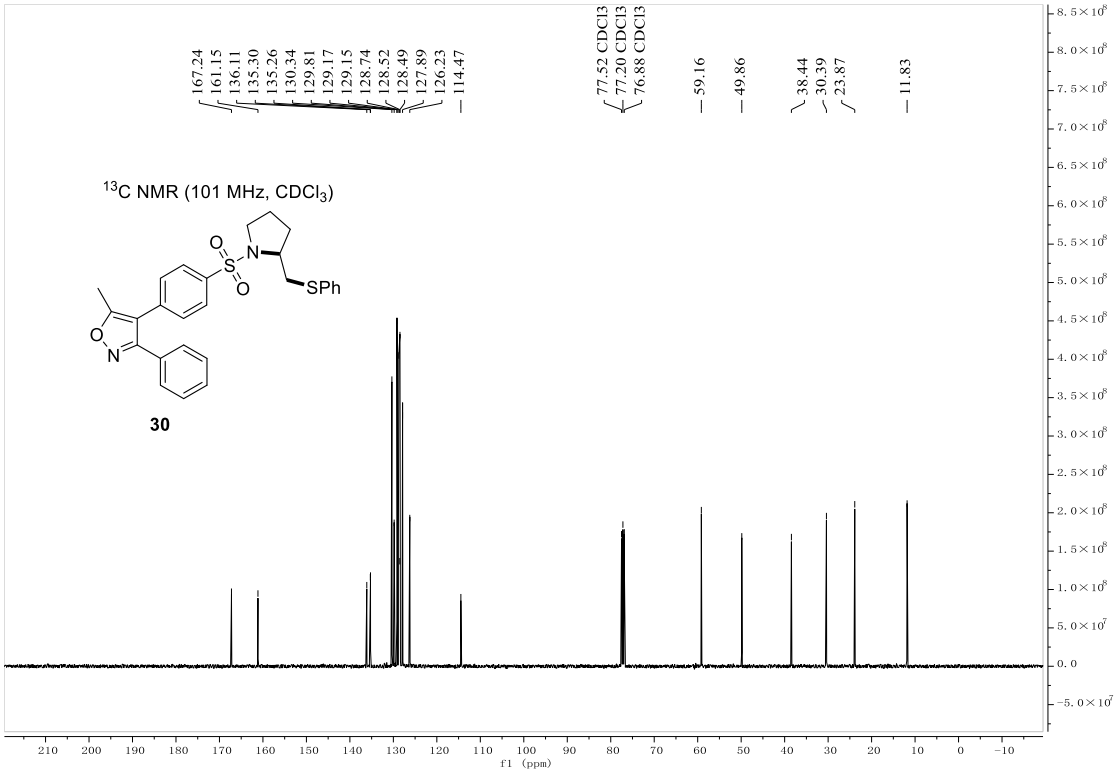
^{13}C NMR of compound **29**



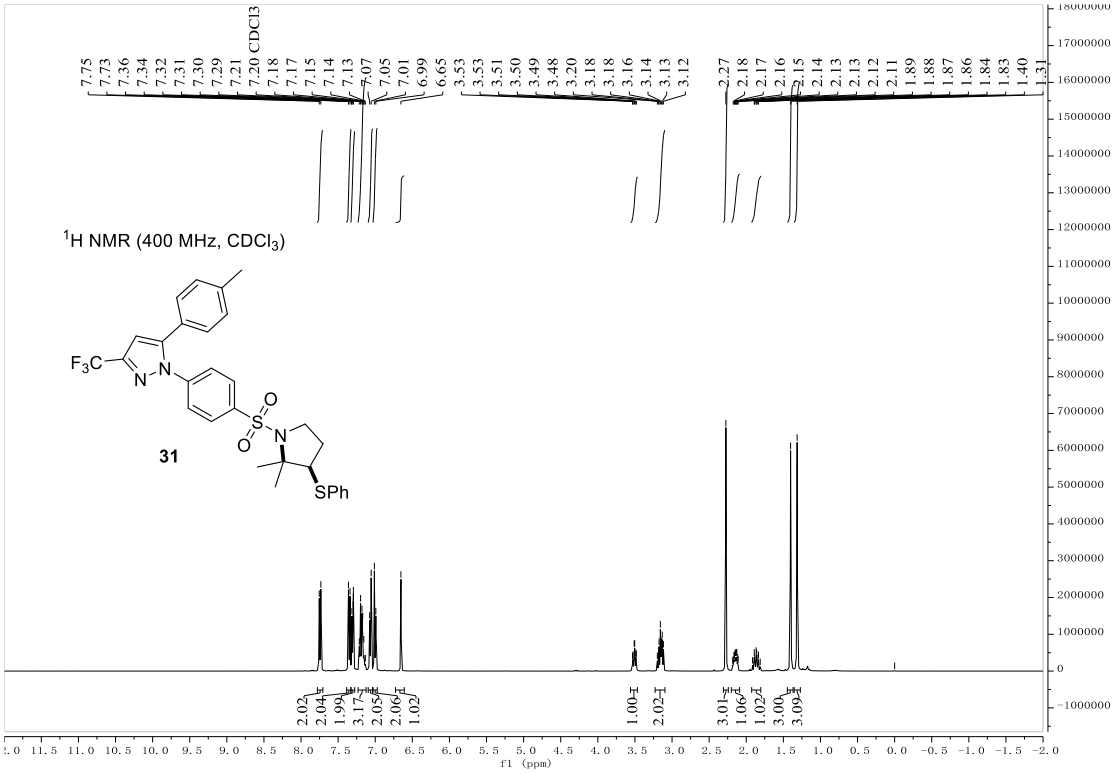
^{1}H NMR of compound **30**



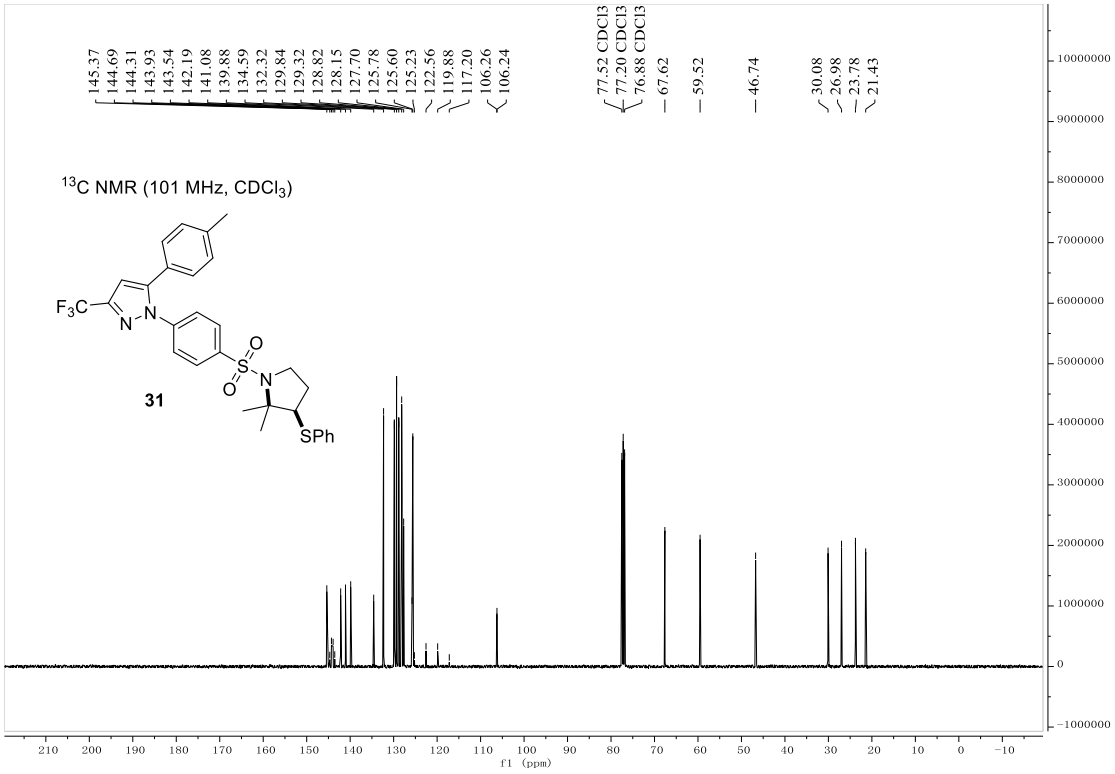
^{13}C NMR of compound **30**



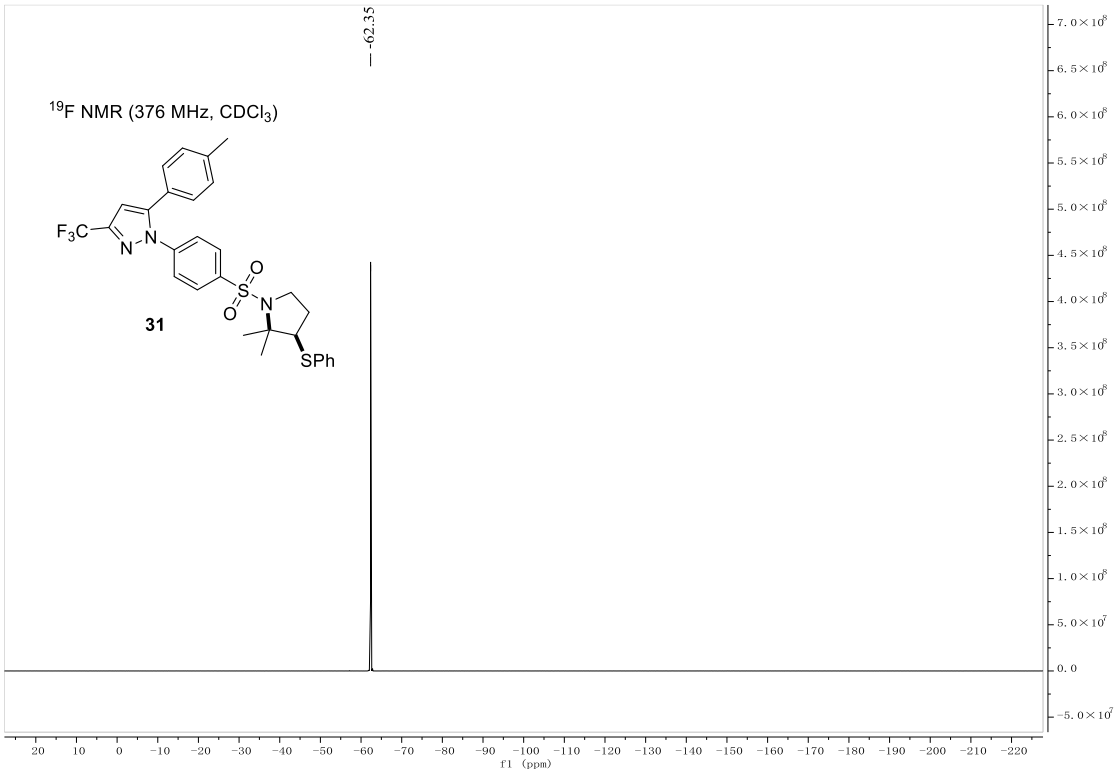
^{1}H NMR of compound **31**



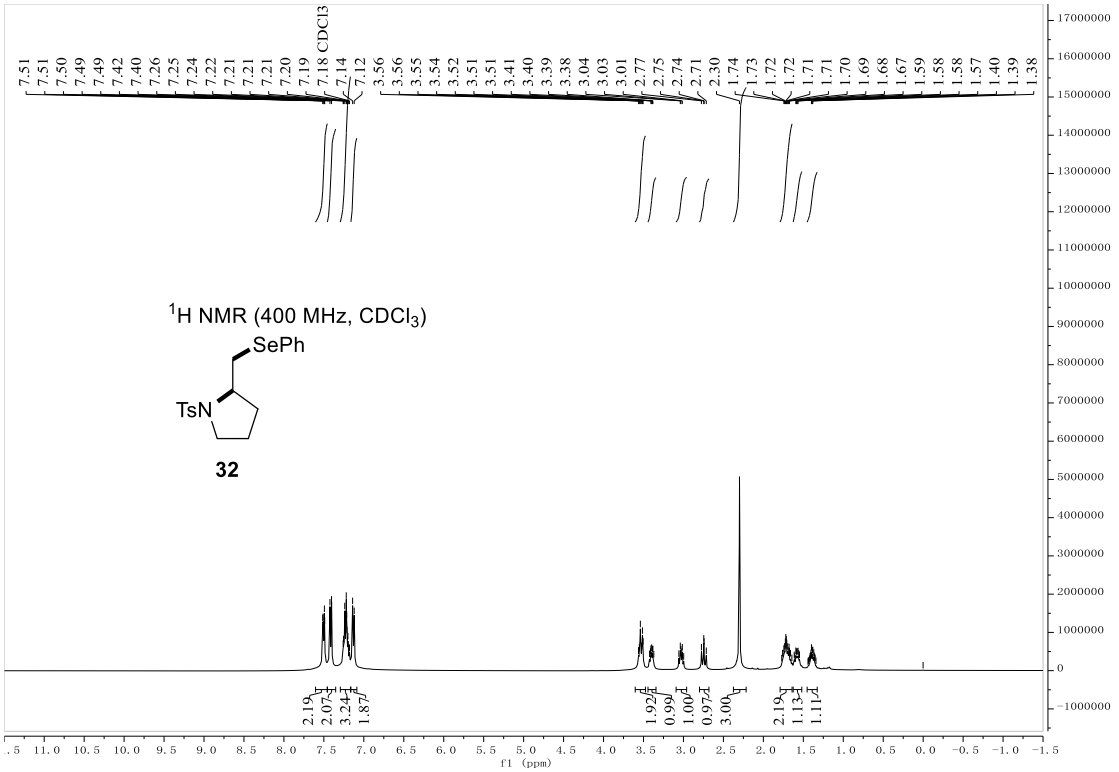
^{13}C NMR of compound **31**



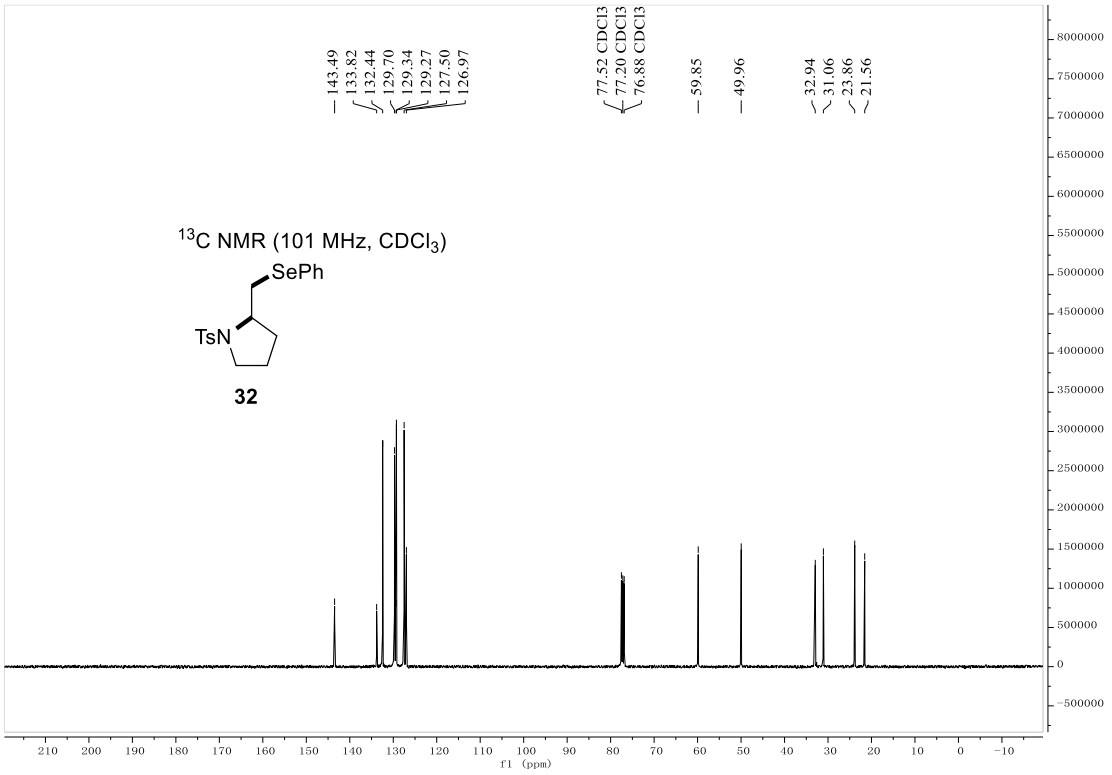
^{19}F NMR of compound **31**



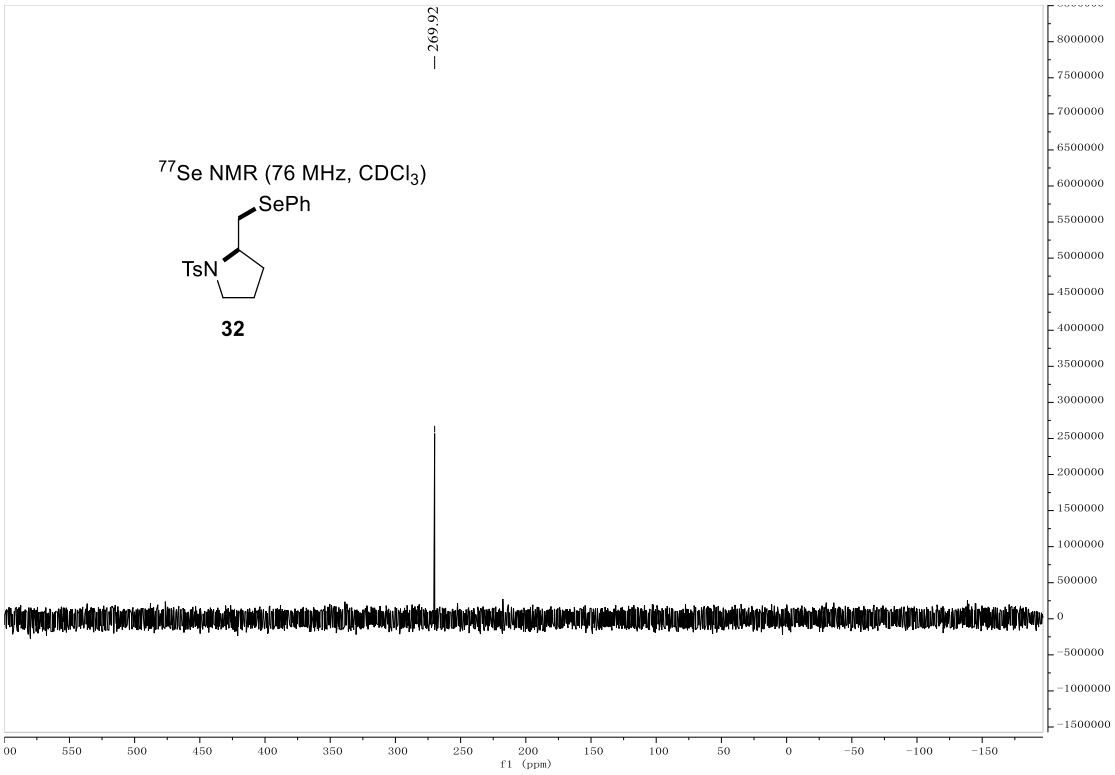
^{1}H NMR of compound **32**



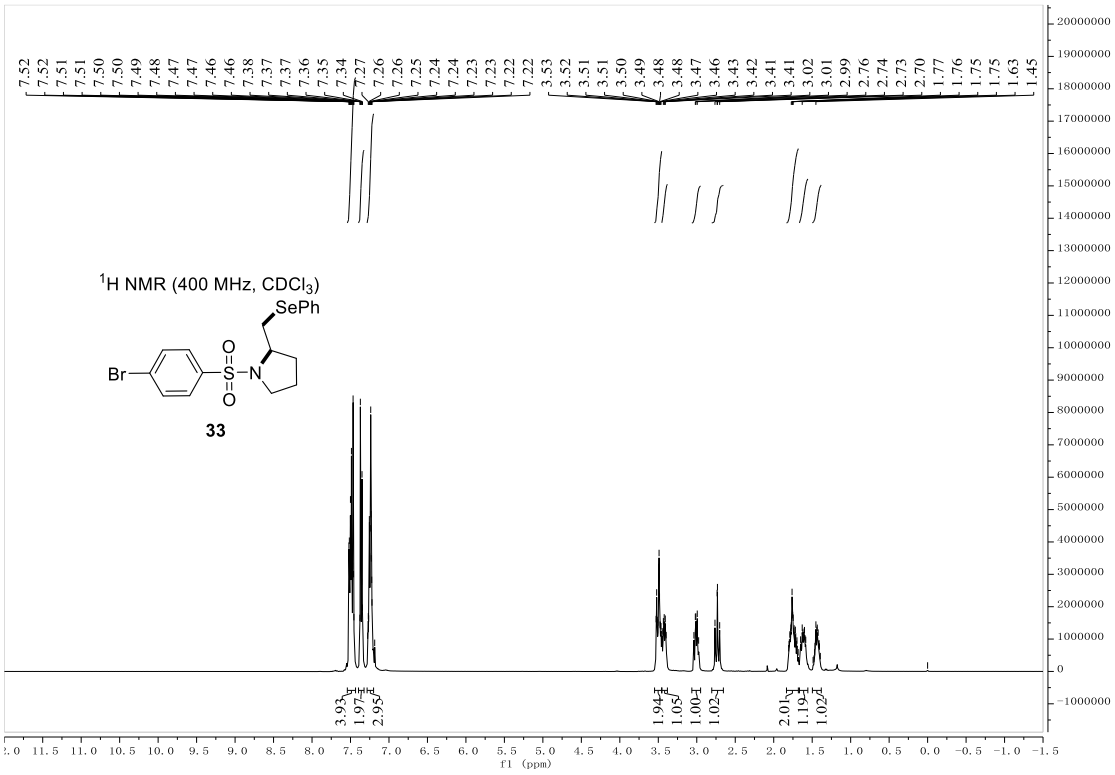
^{13}C NMR of compound **32**



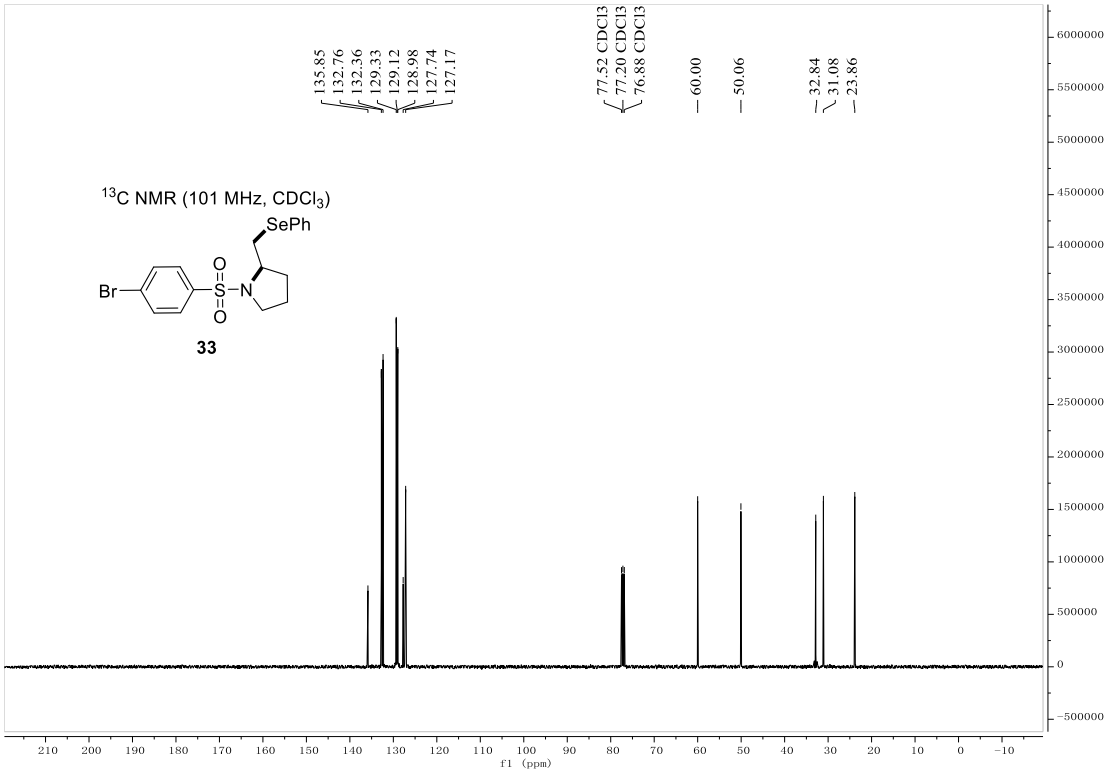
^{77}Se NMR of compound **32**



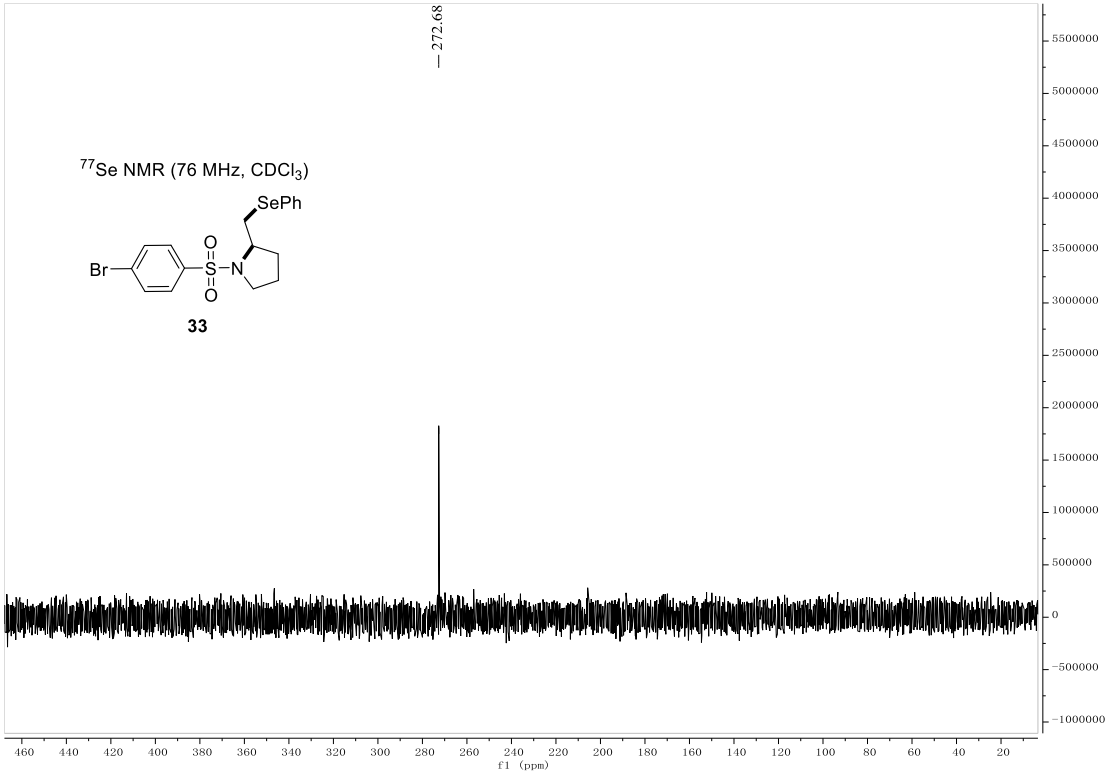
^{1}H NMR of compound **33**



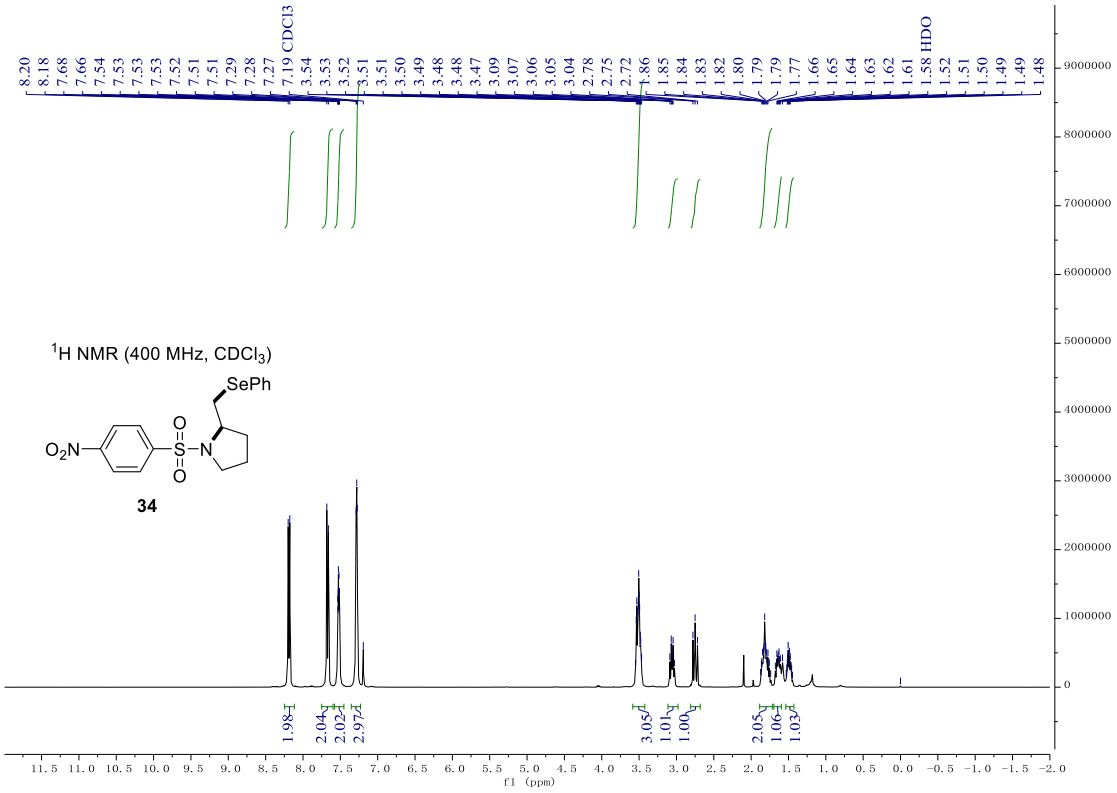
^{13}C NMR of compound **33**



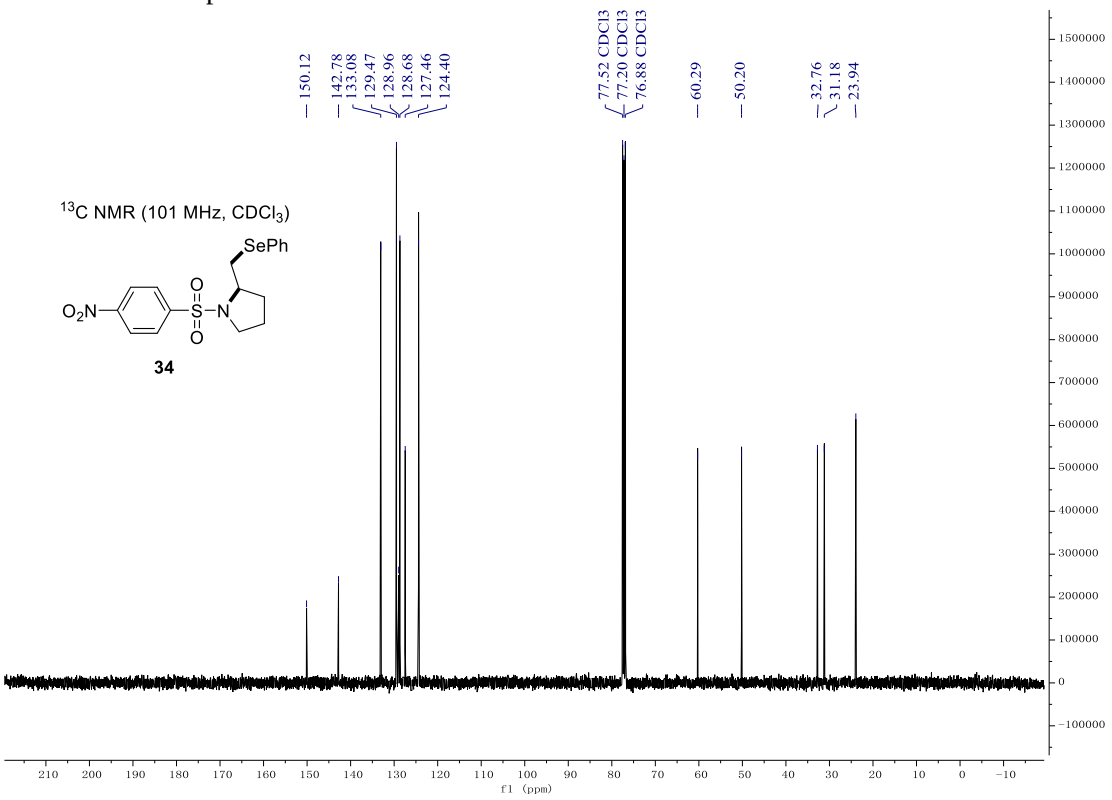
^{77}Se NMR of compound **33**



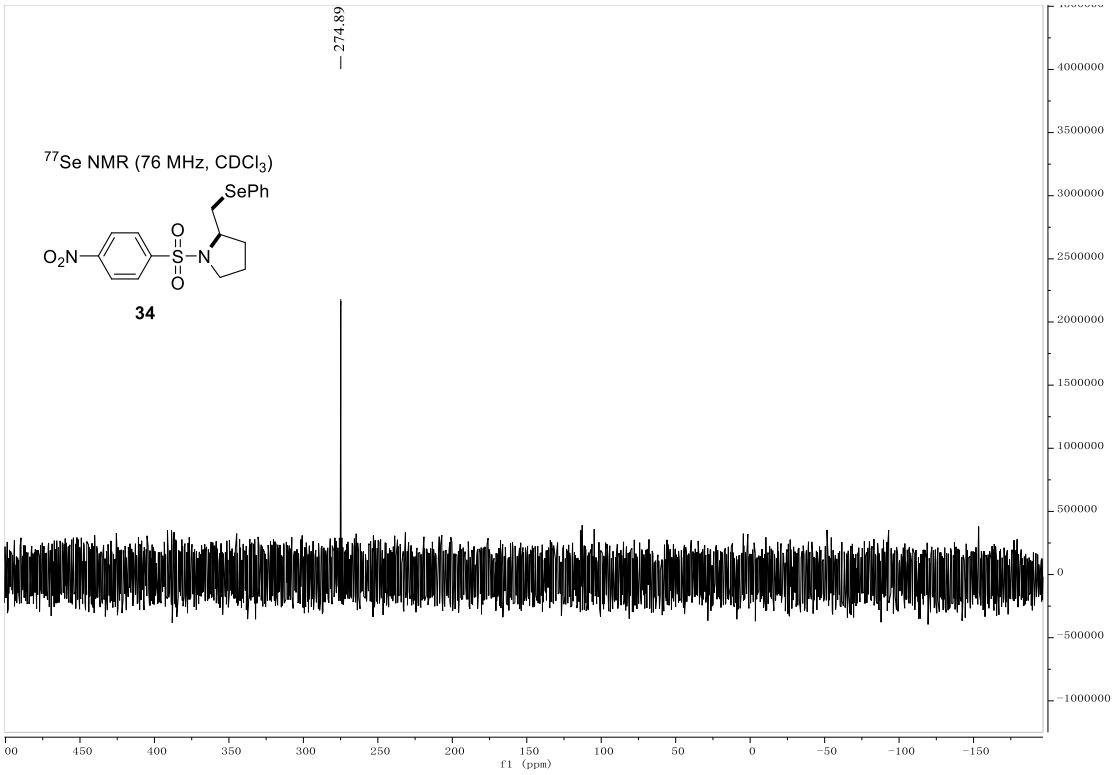
^{1}H NMR of compound **34**



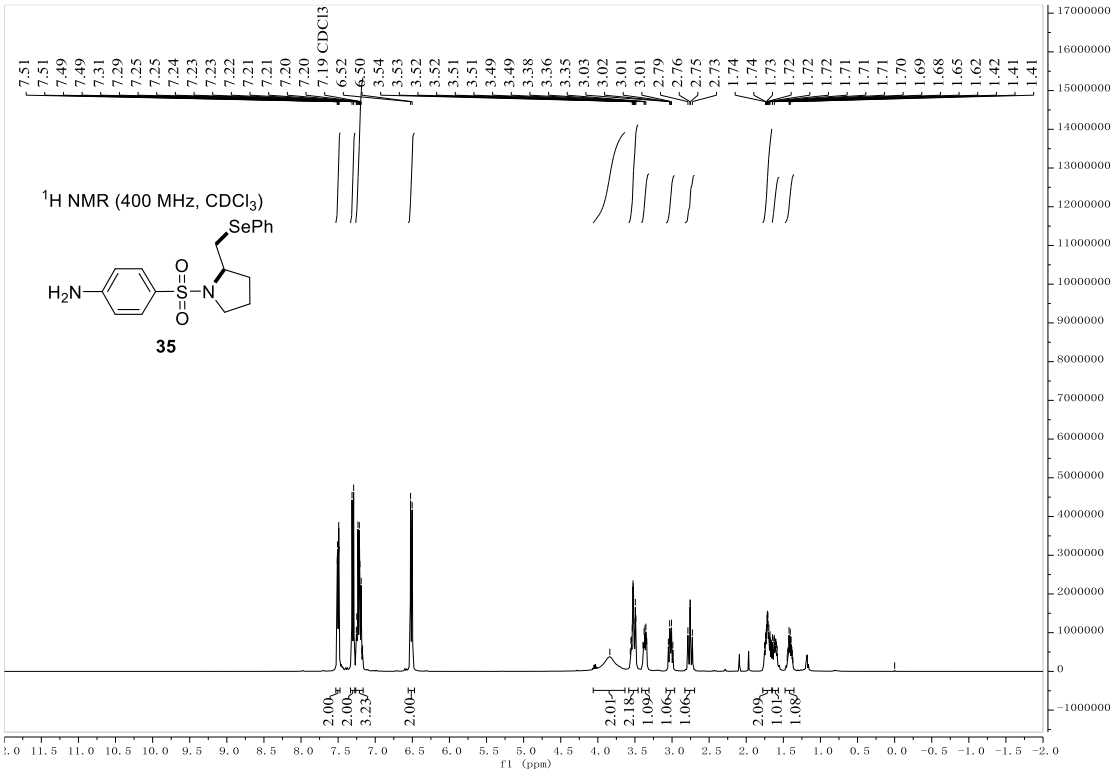
^{13}C NMR of compound **34**



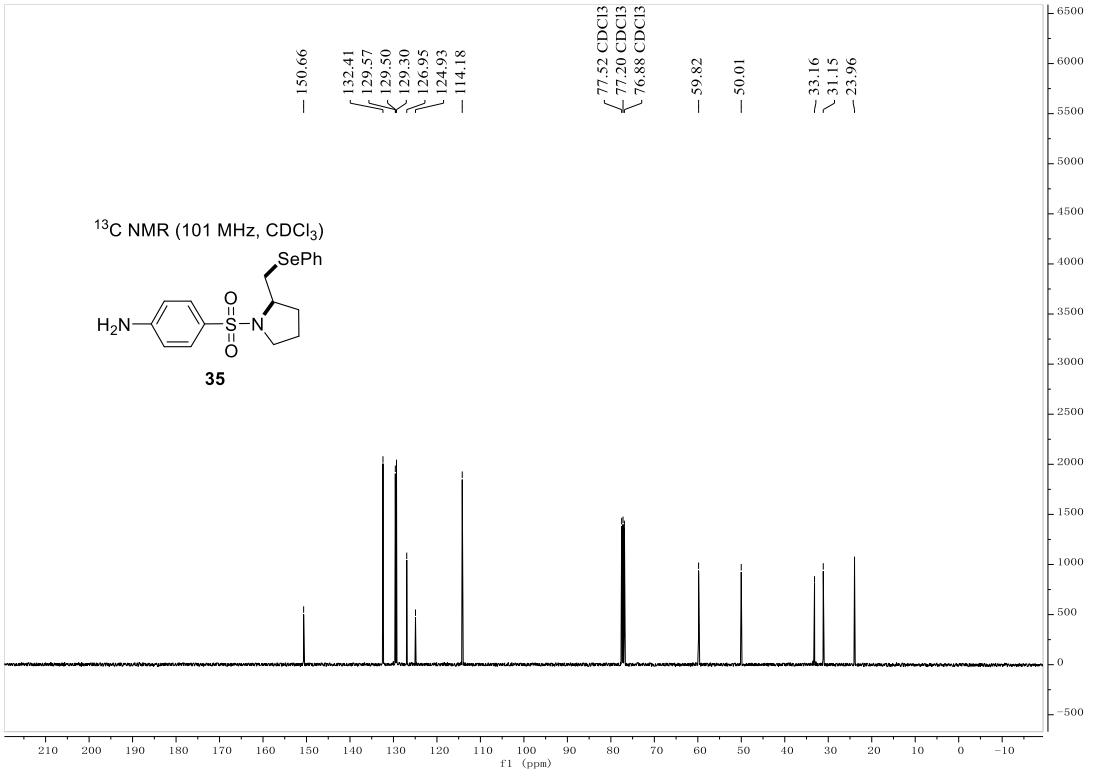
^{77}Se NMR of compound **34**



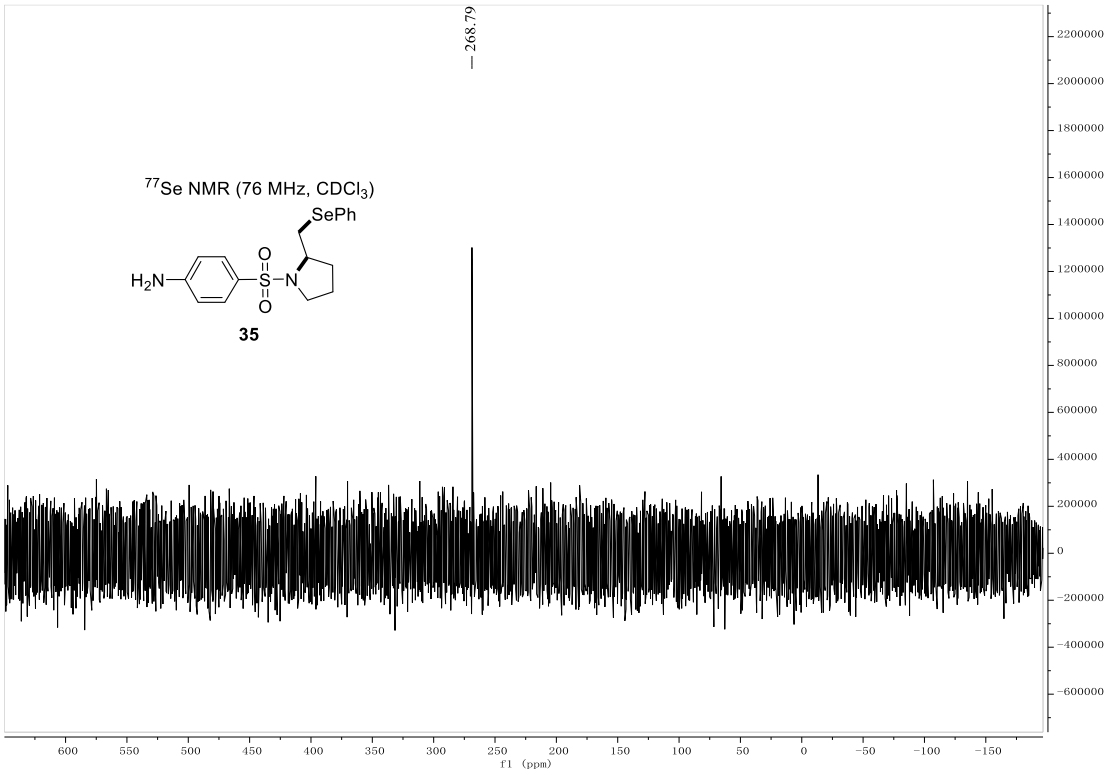
^{1}H NMR of compound **35**



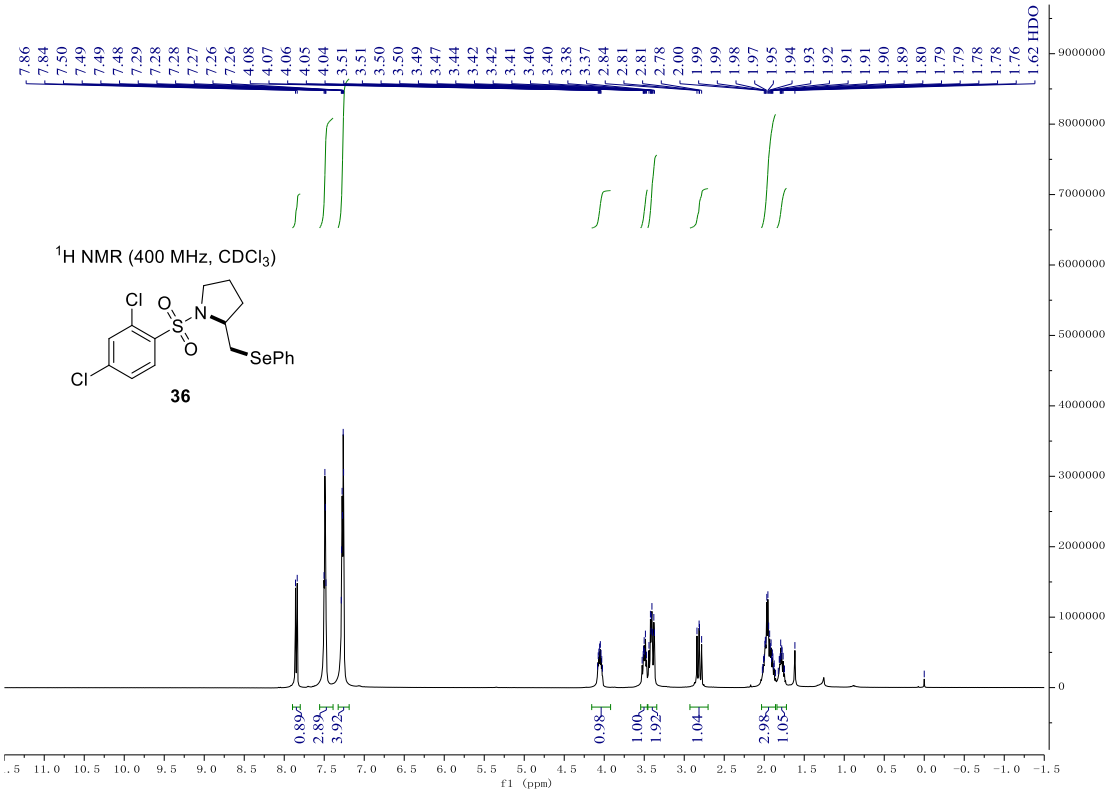
^{13}C NMR of compound **35**



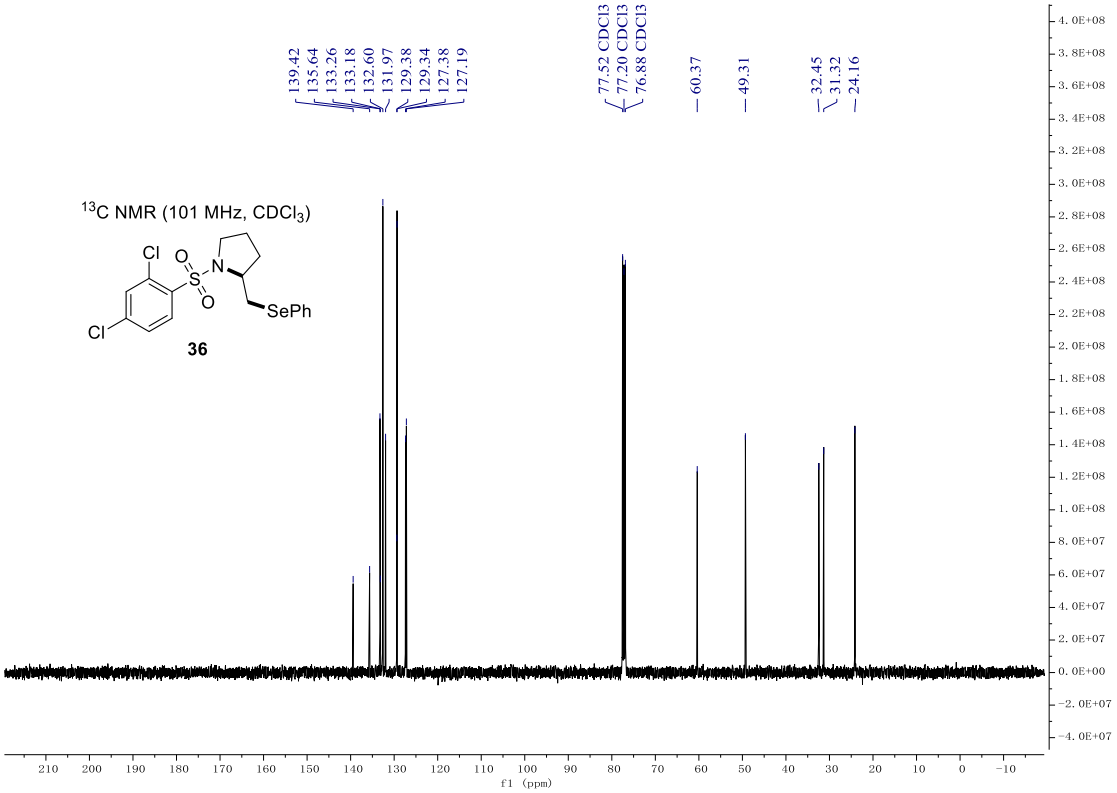
^{77}Se NMR of compound **35**



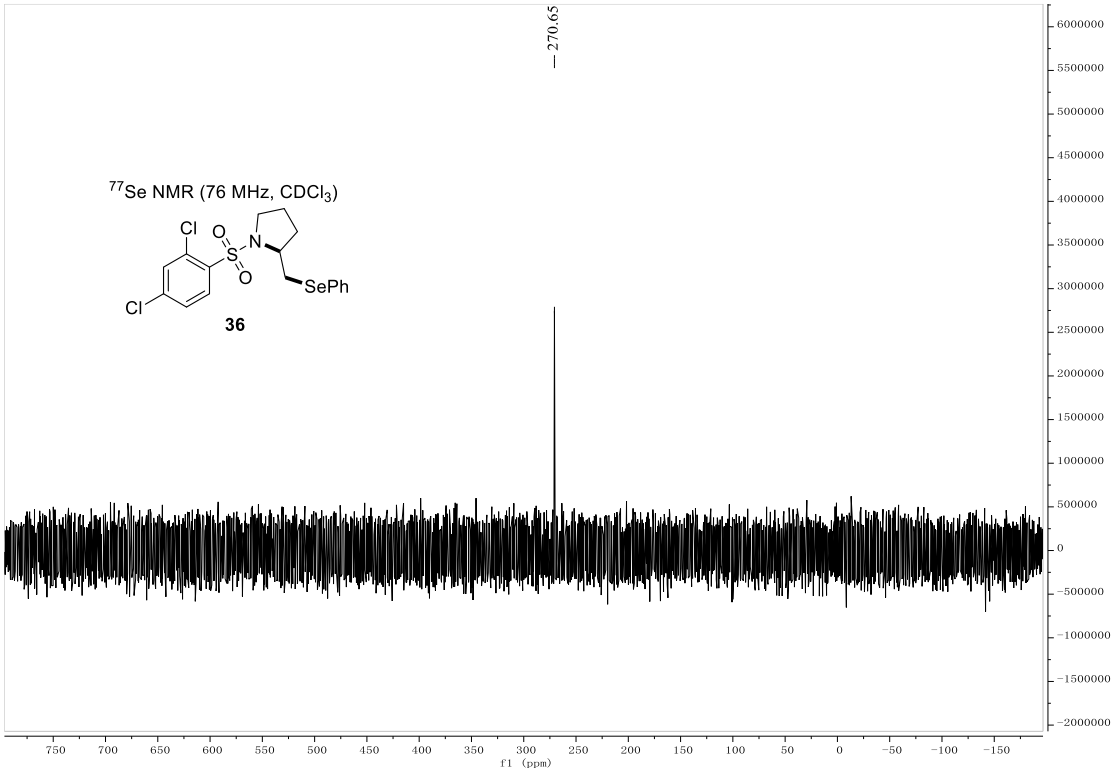
^{1}H NMR of compound **36**



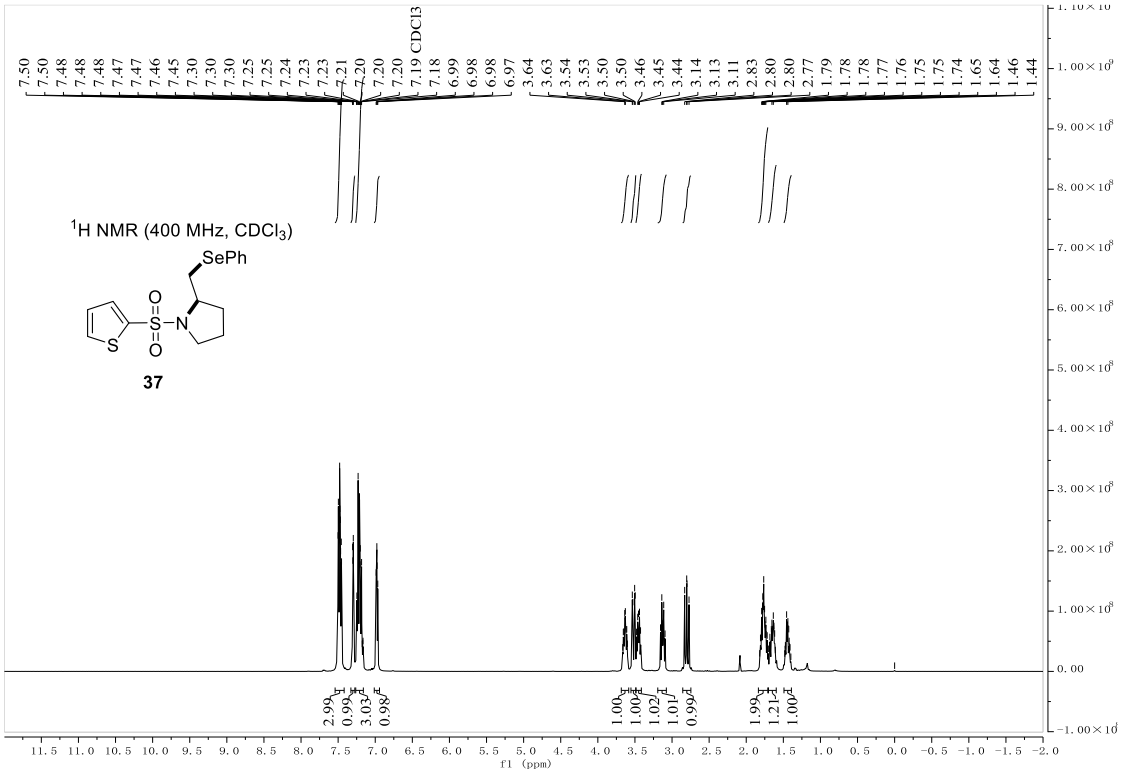
^{13}C NMR of compound **36**



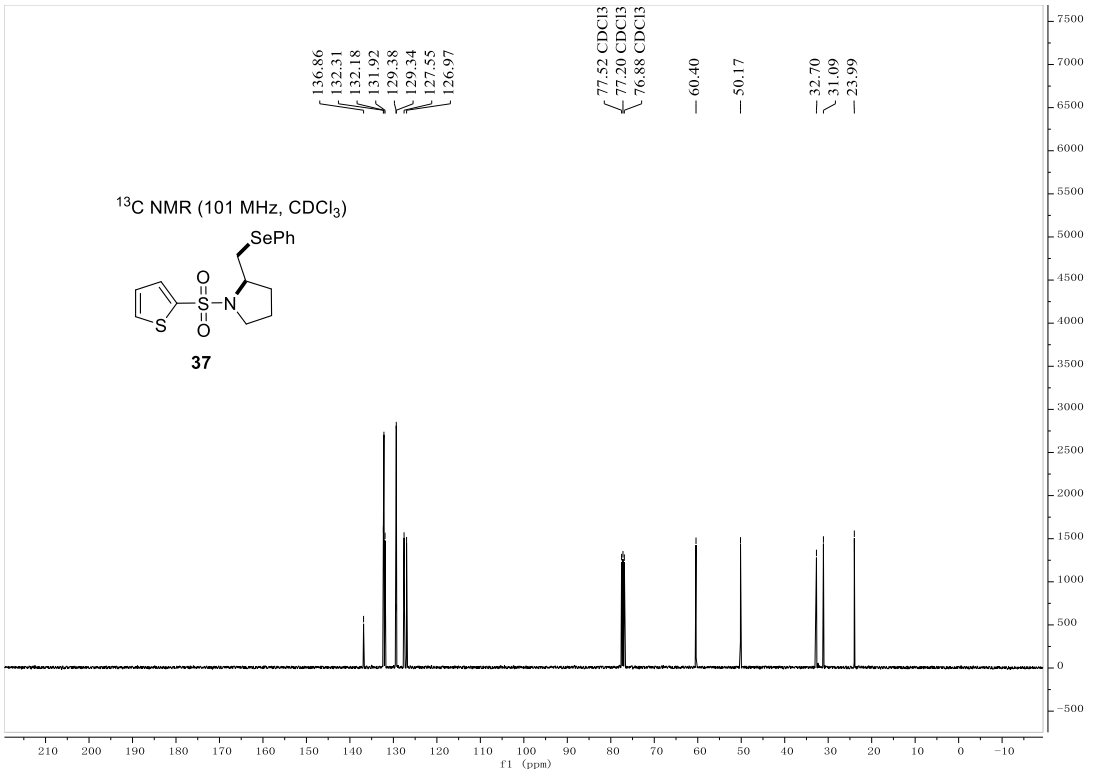
^{77}Se NMR of compound **36**



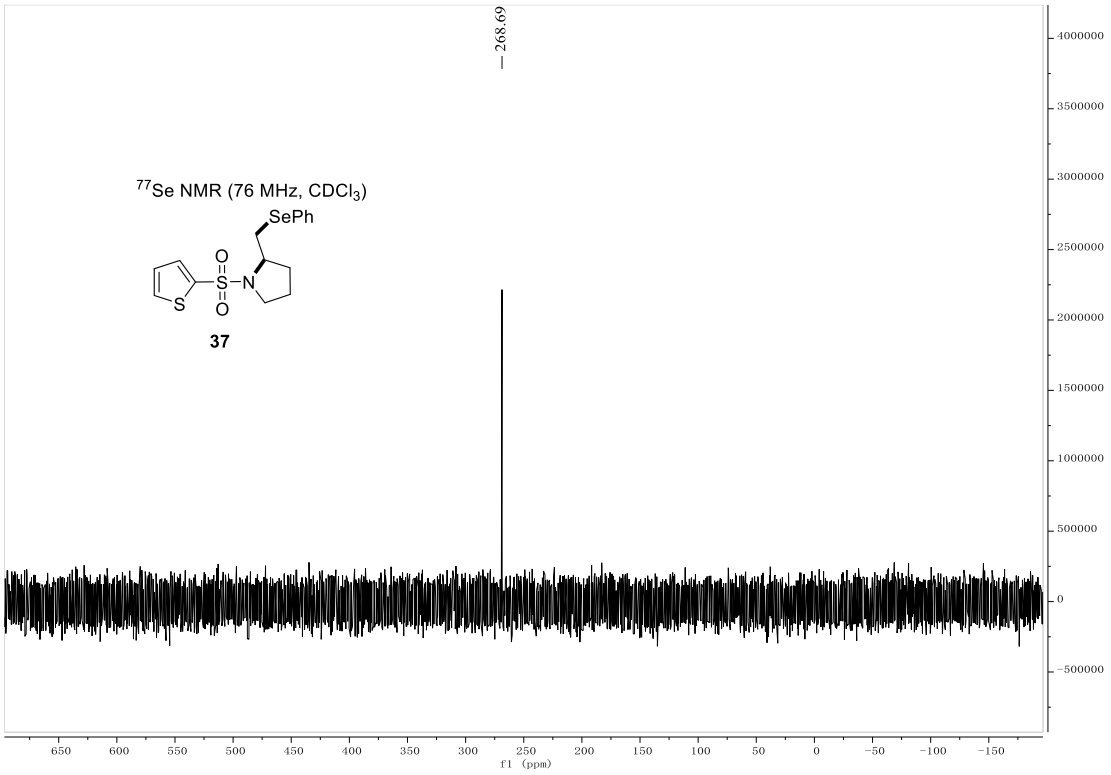
^{1}H NMR of compound **37**



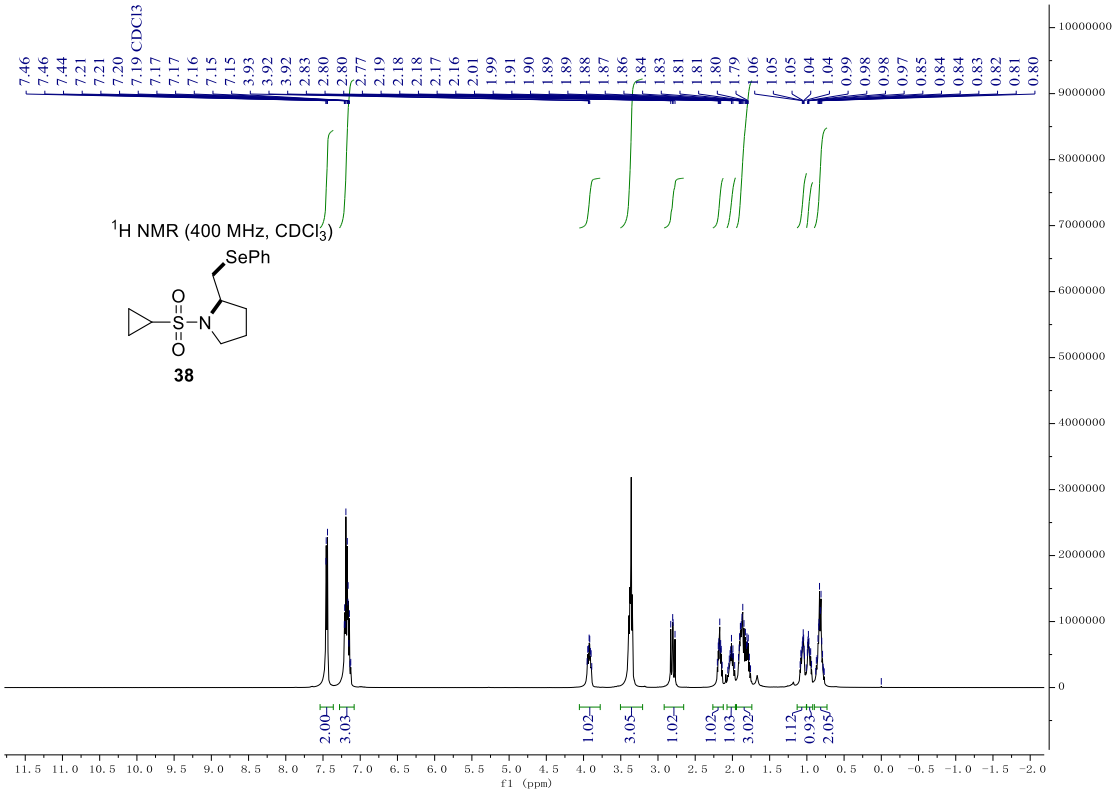
^{13}C NMR of compound **37**



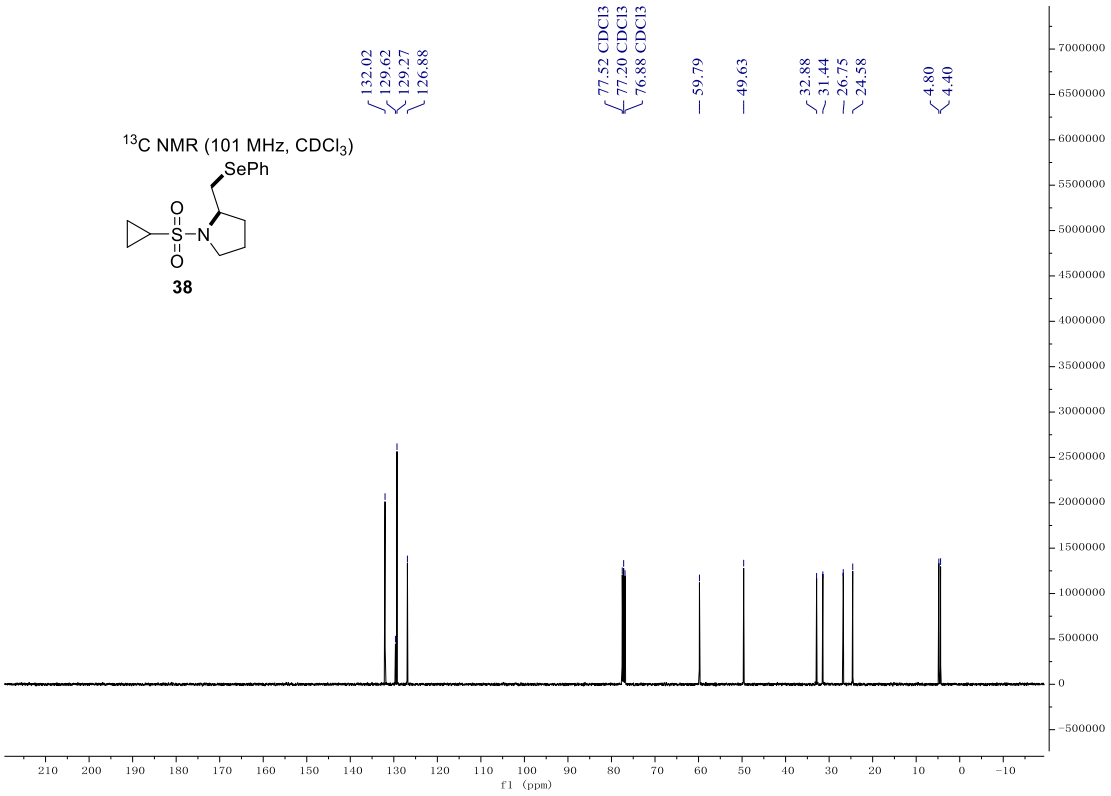
^{77}Se NMR of compound **37**



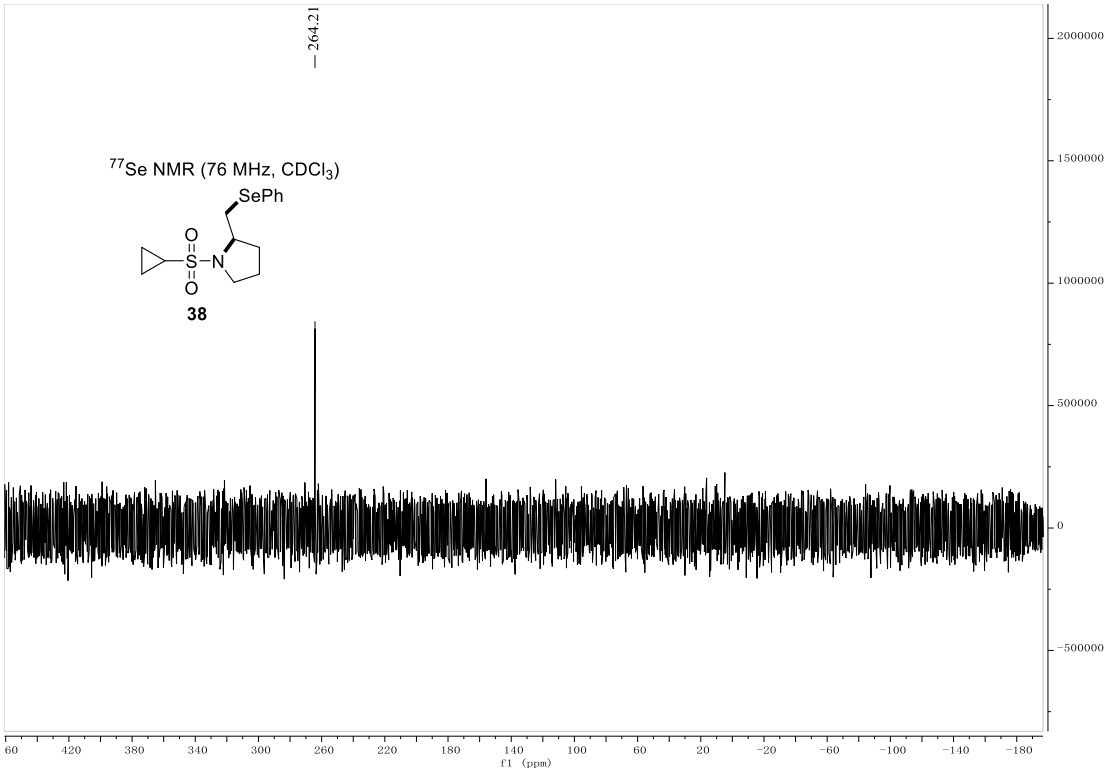
^{1}H NMR of compound **38**



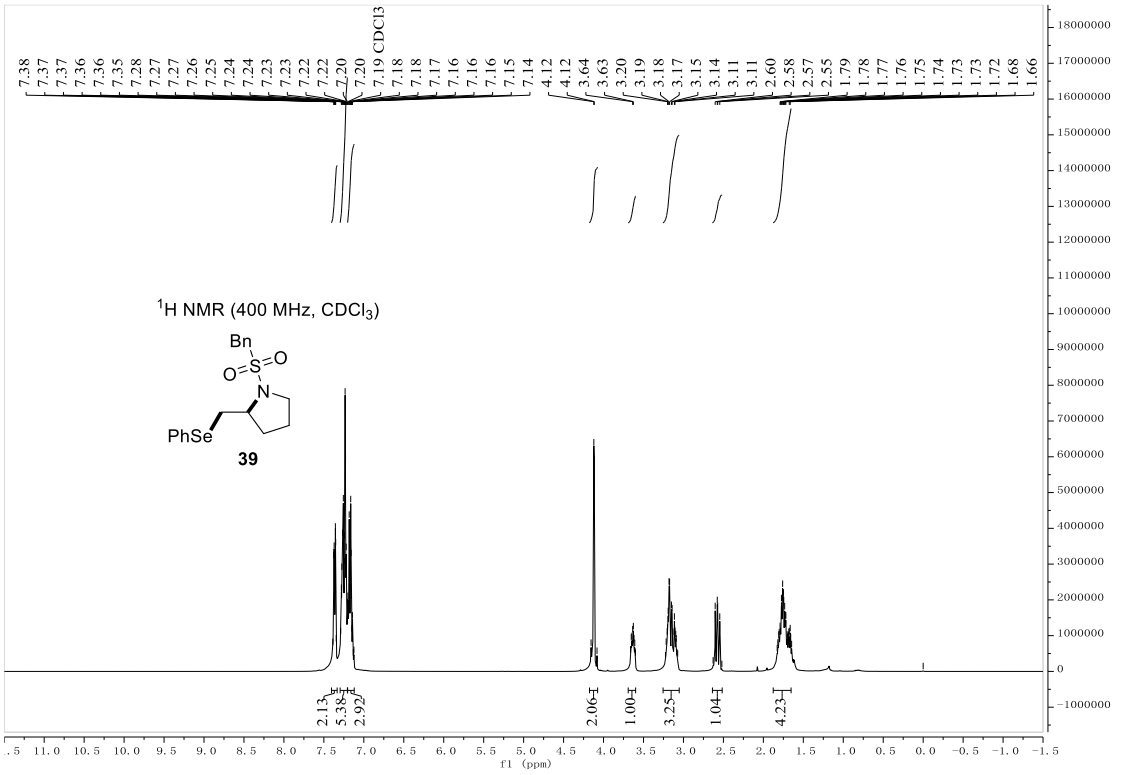
^{13}C NMR of compound **38**



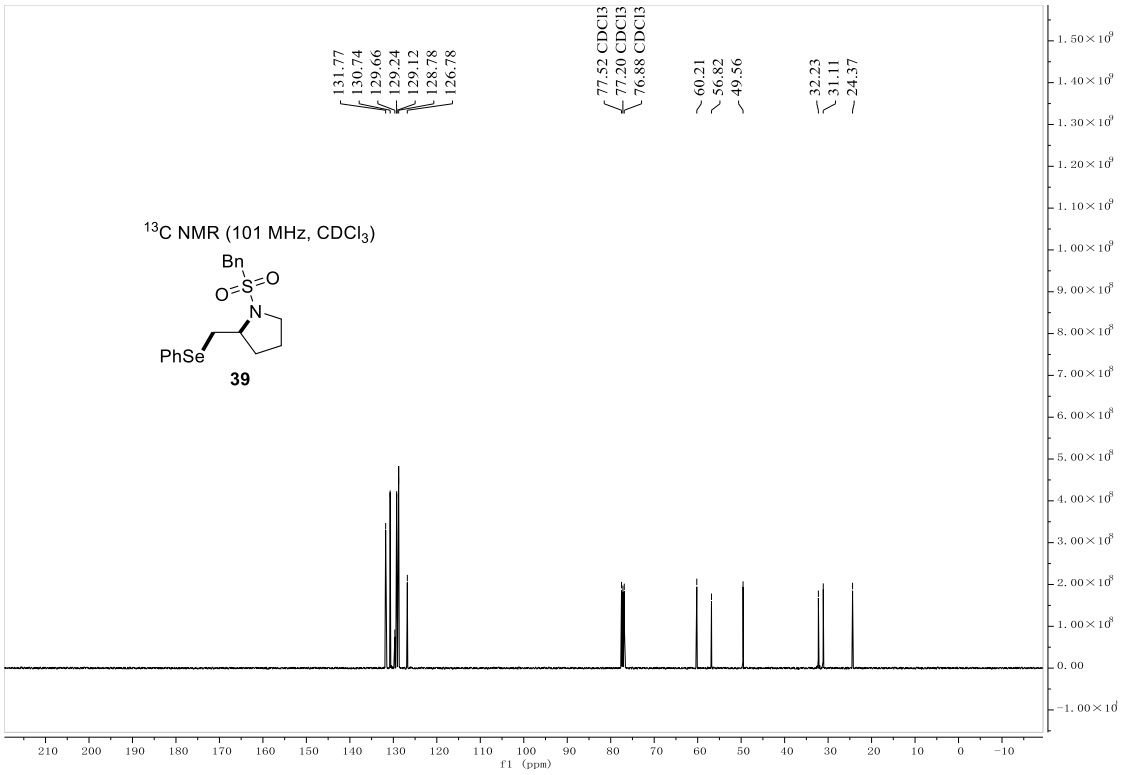
^{77}Se NMR of compound **38**



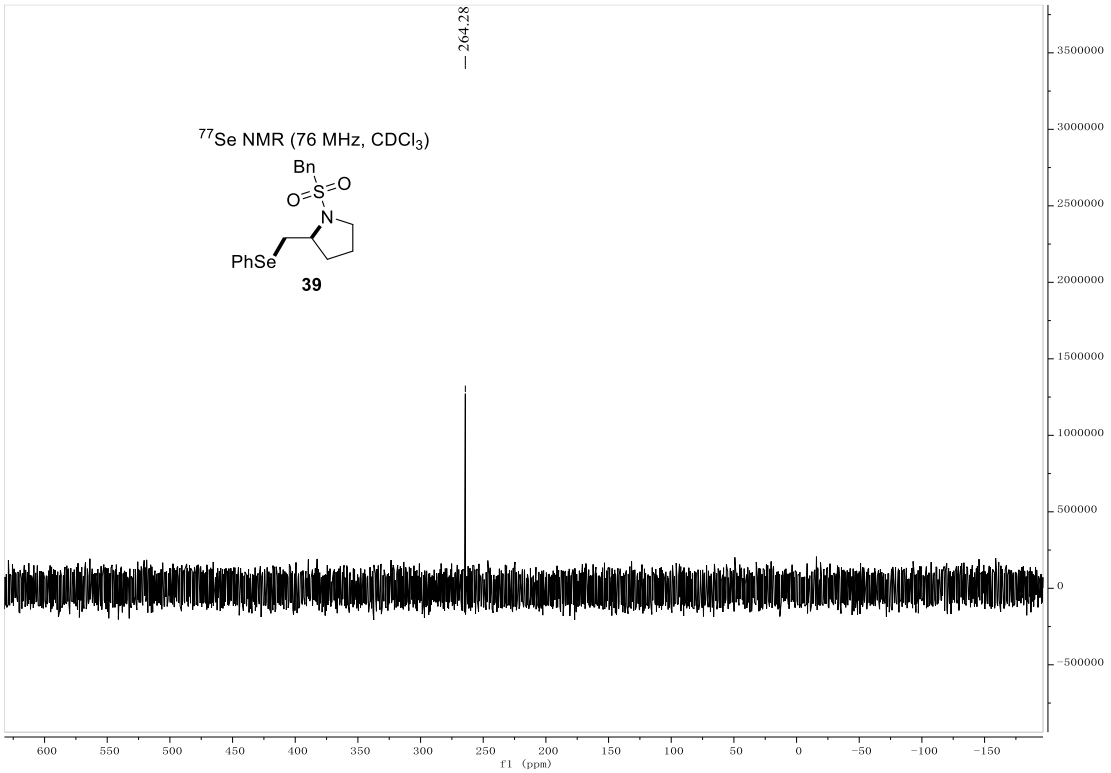
^{1}H NMR of compound **39**



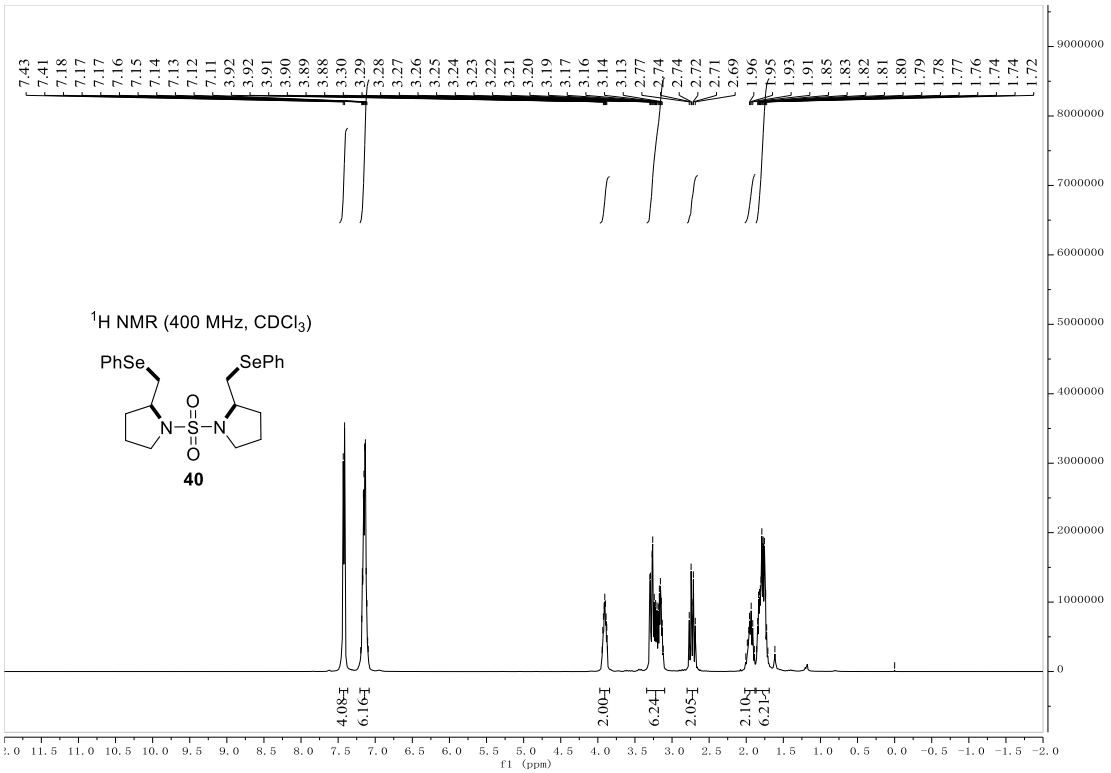
^{13}C NMR of compound **39**



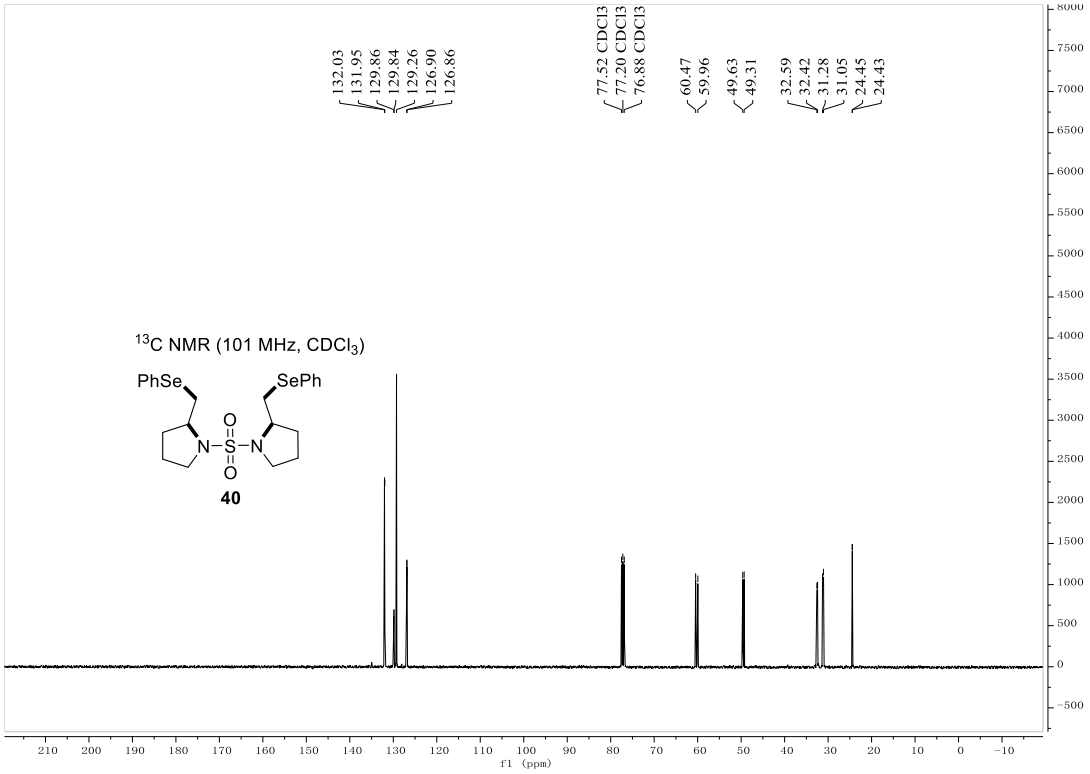
^{77}Se NMR of compound **39**



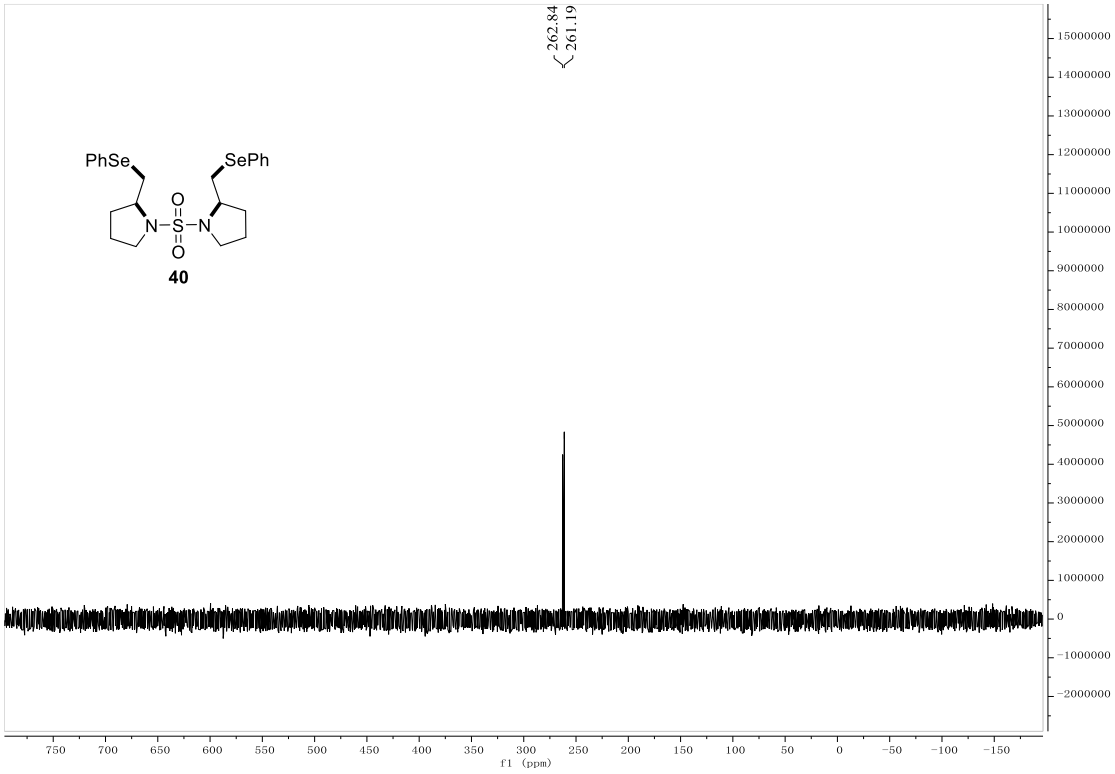
^{1}H NMR of compound **40**



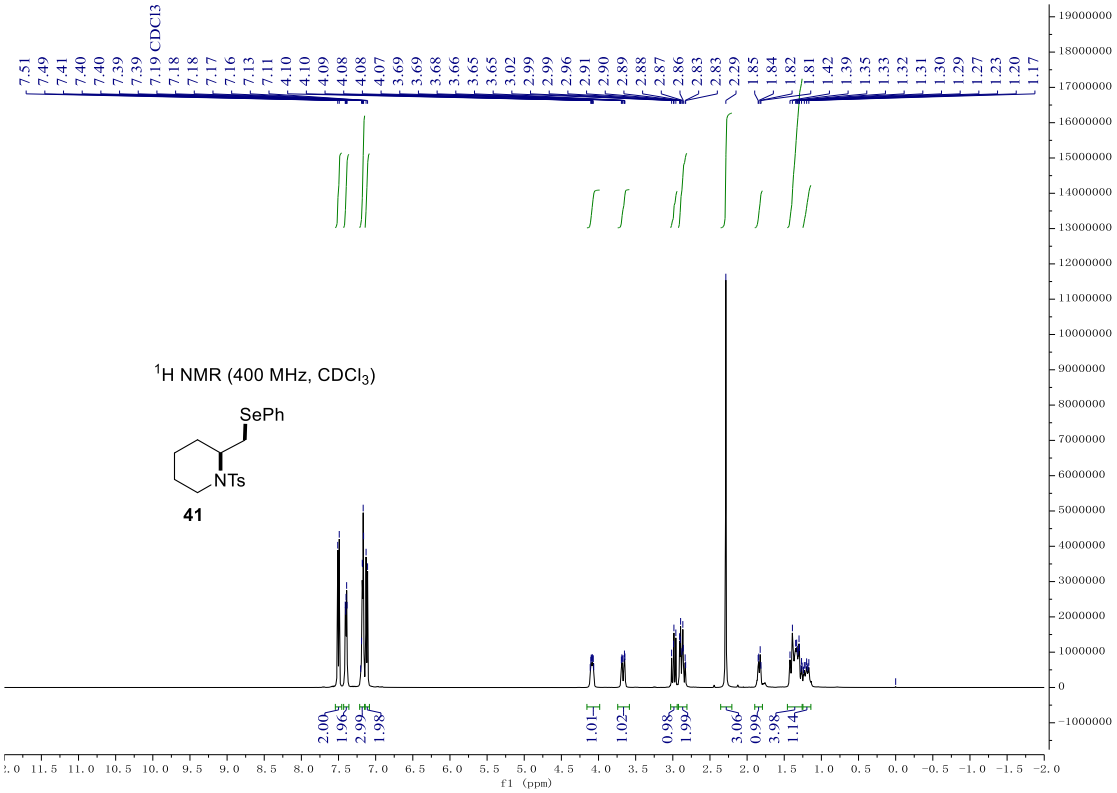
^{13}C NMR of compound **40**



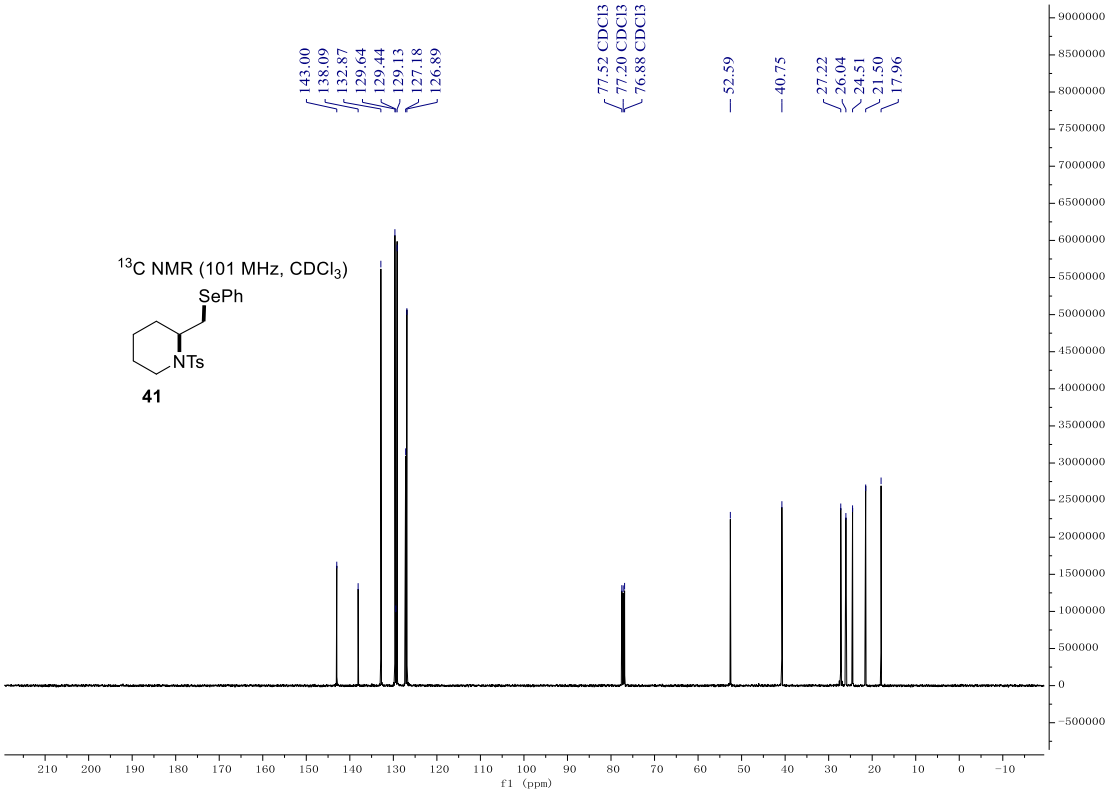
^{77}Se NMR of compound **40**



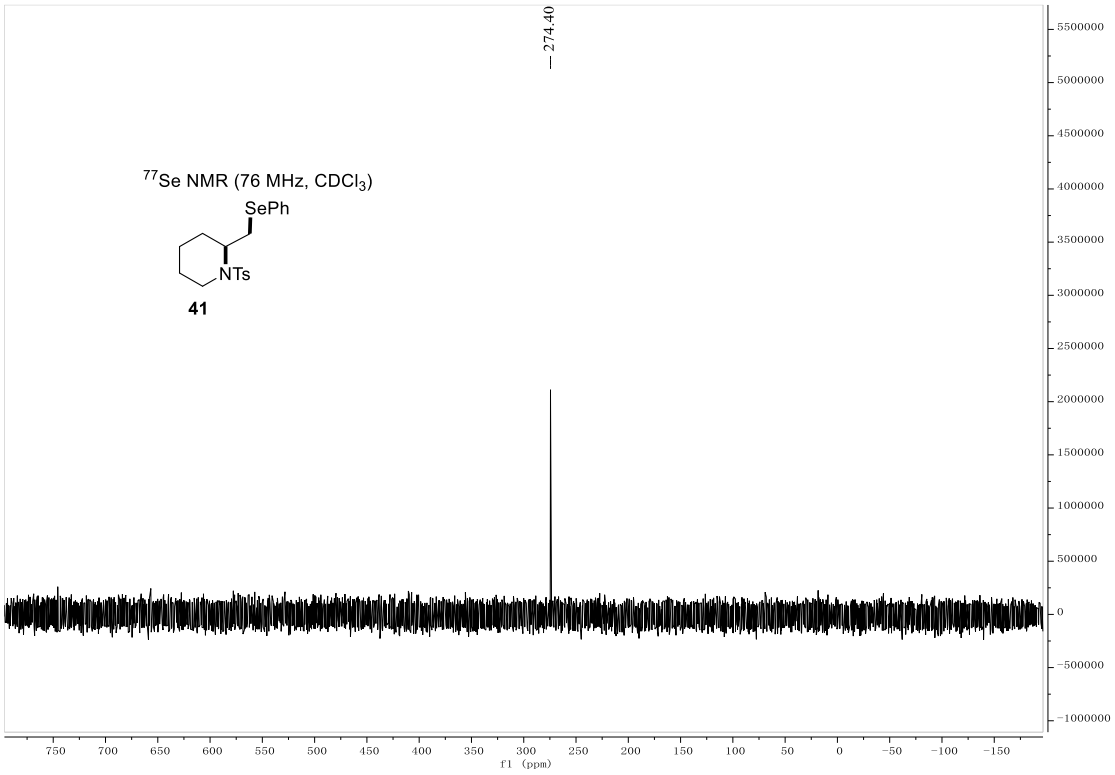
^{1}H NMR of compound **41**



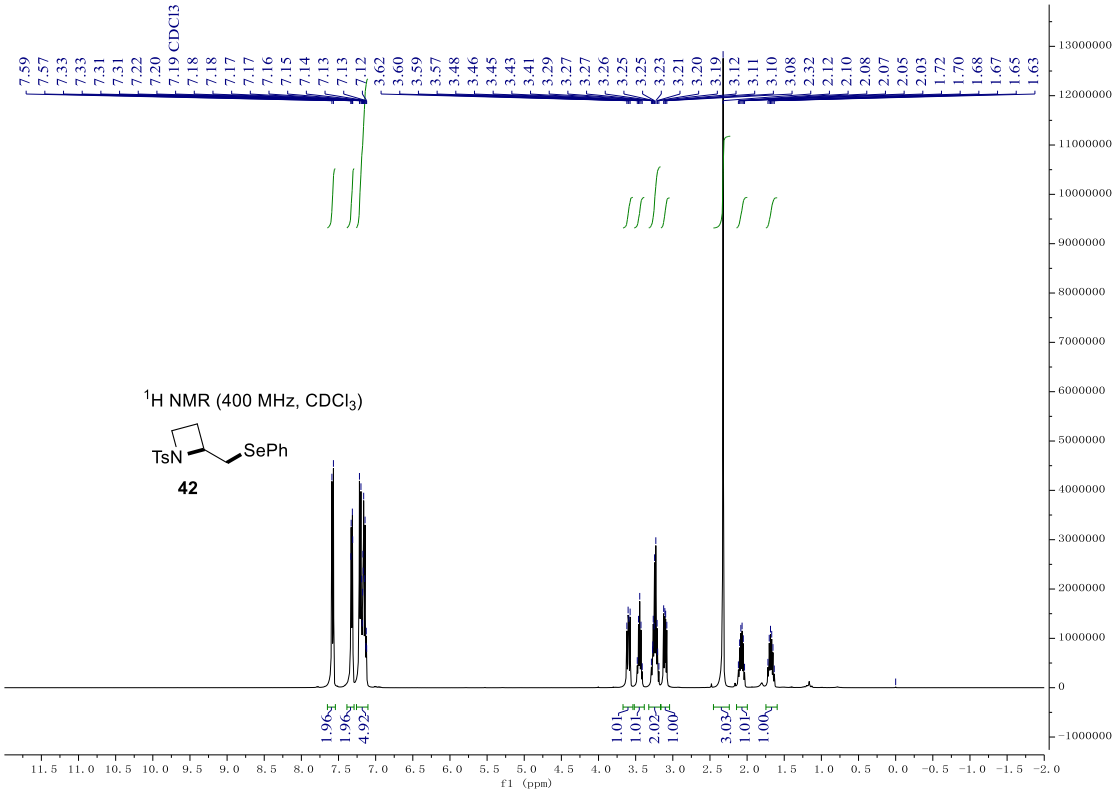
^{13}C NMR of compound **41**



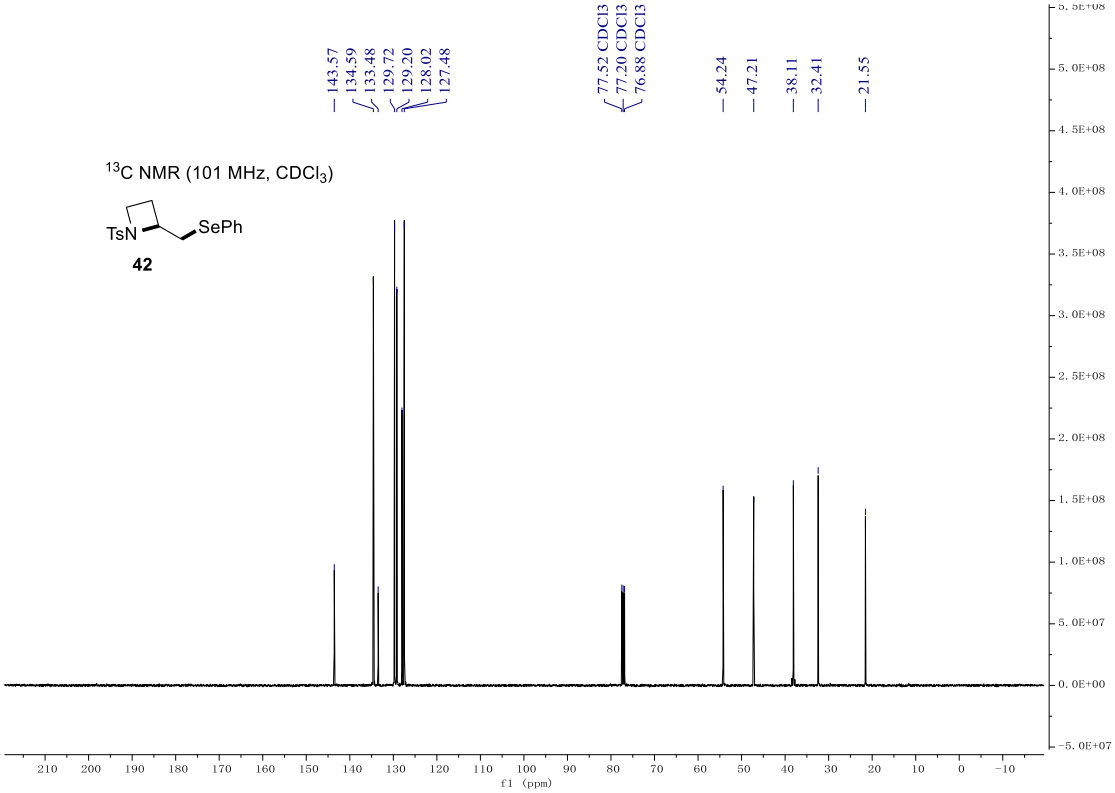
^{77}Se NMR of compound **41**



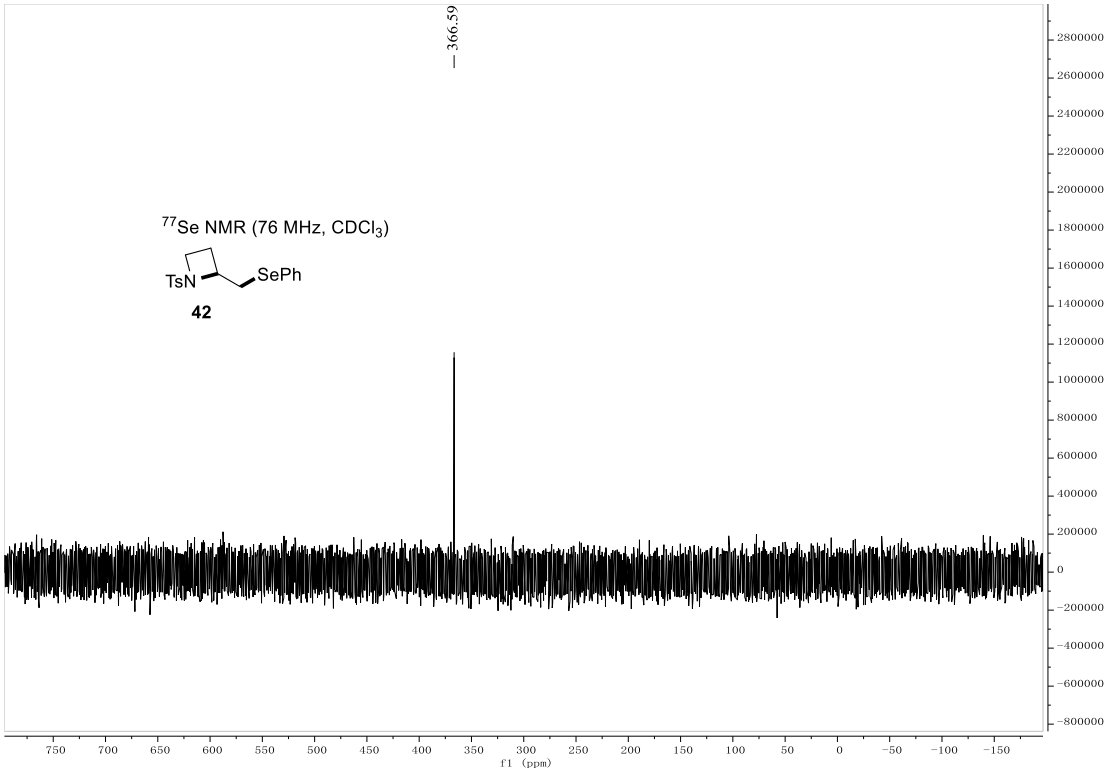
^{1}H NMR of compound **42**



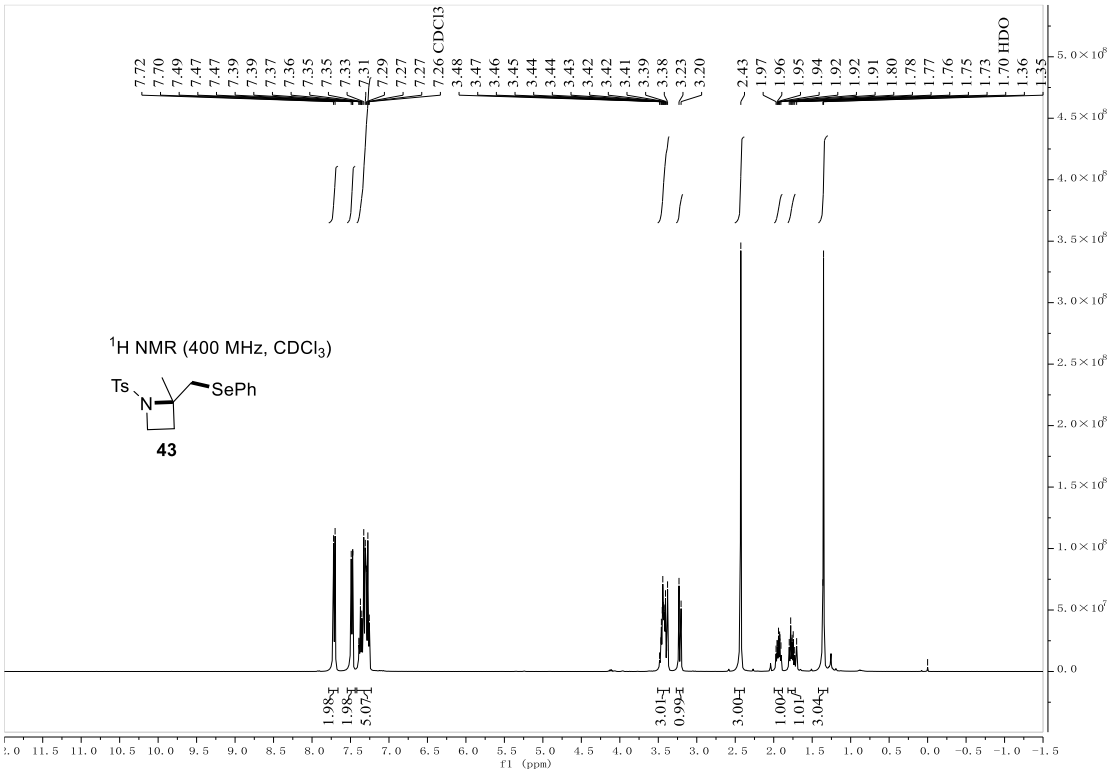
^{13}C NMR of compound **42**



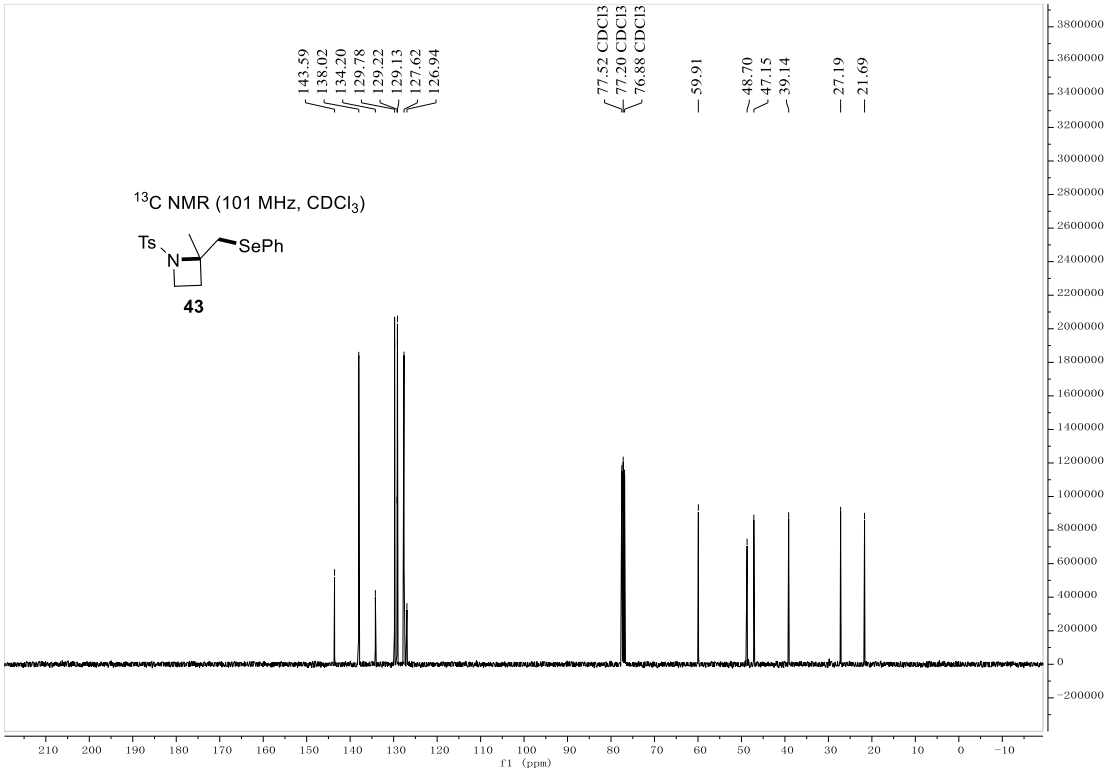
^{77}Se NMR of compound **42**



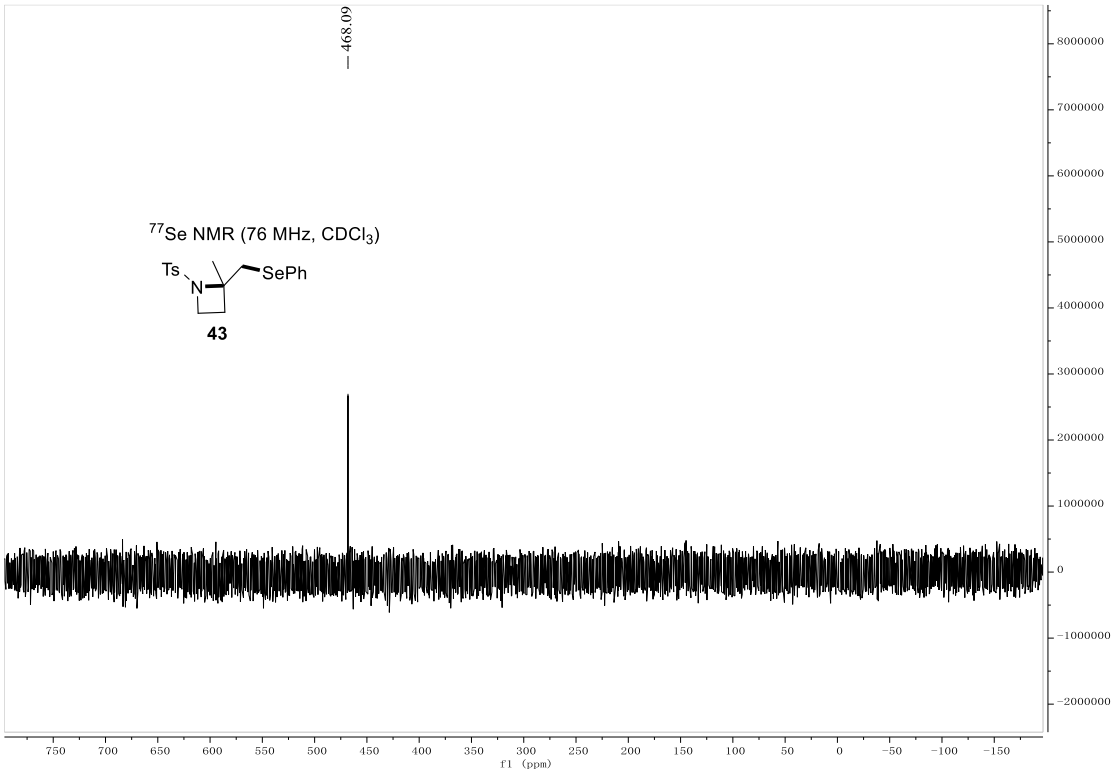
^{1}H NMR of compound **43**



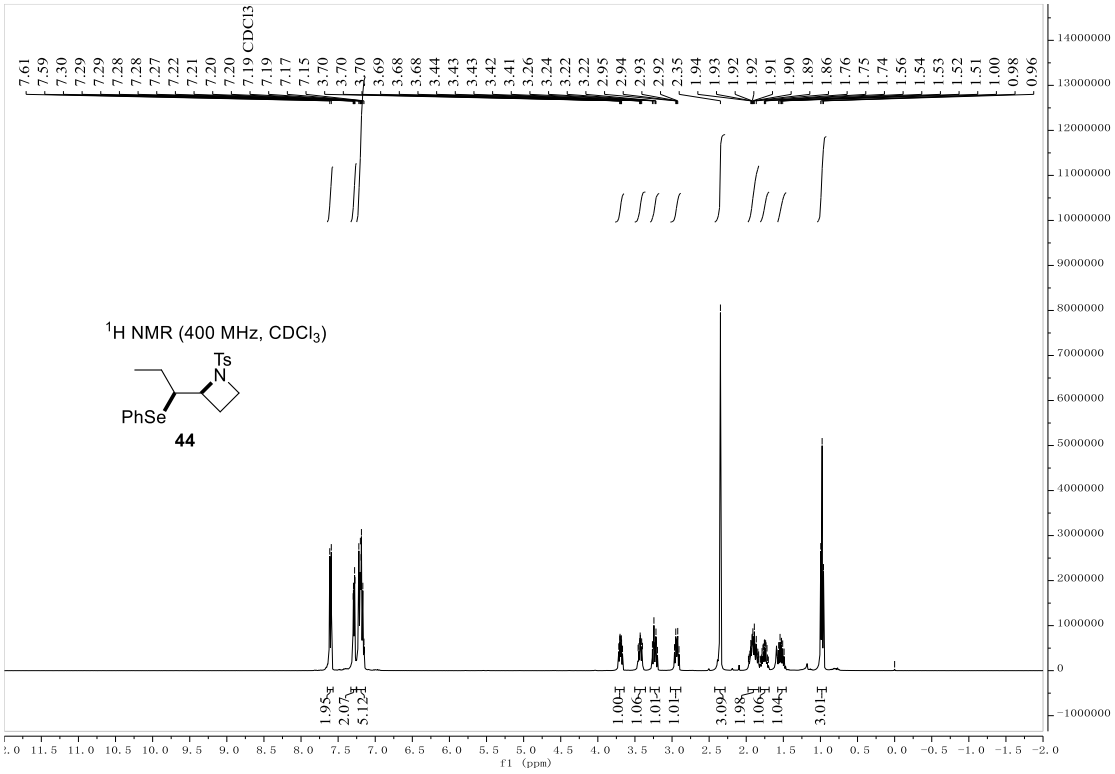
^{13}C NMR of compound **43**



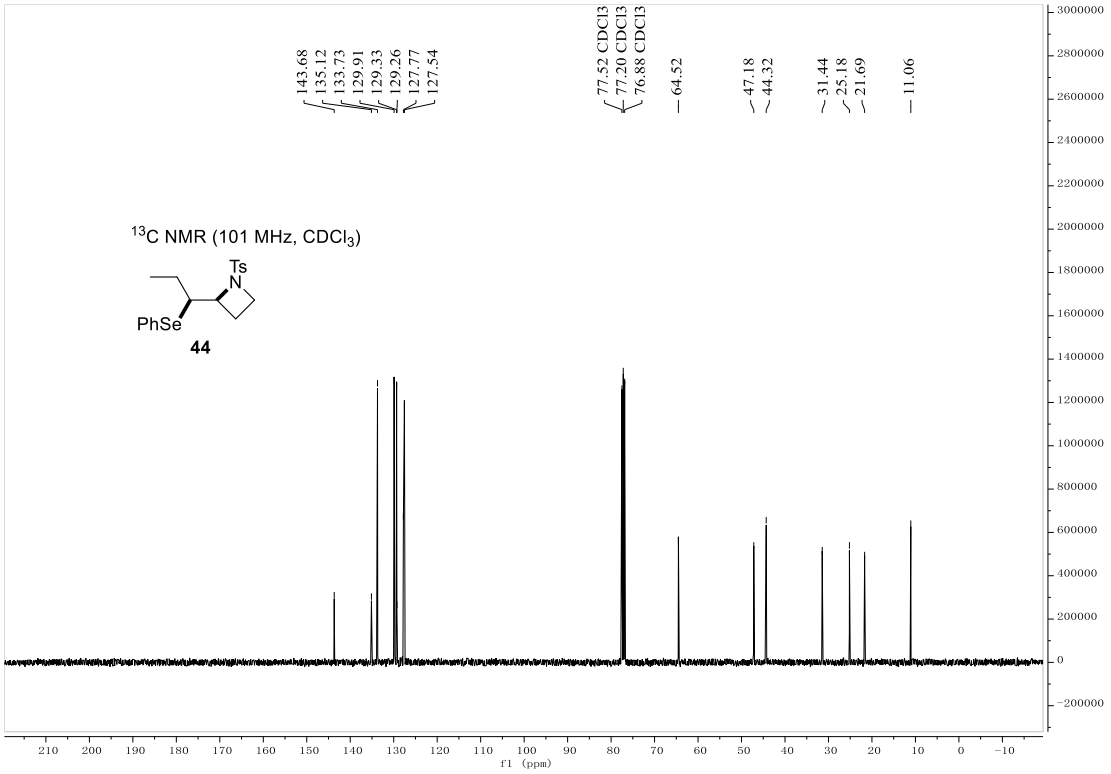
^{77}Se NMR of compound **43**



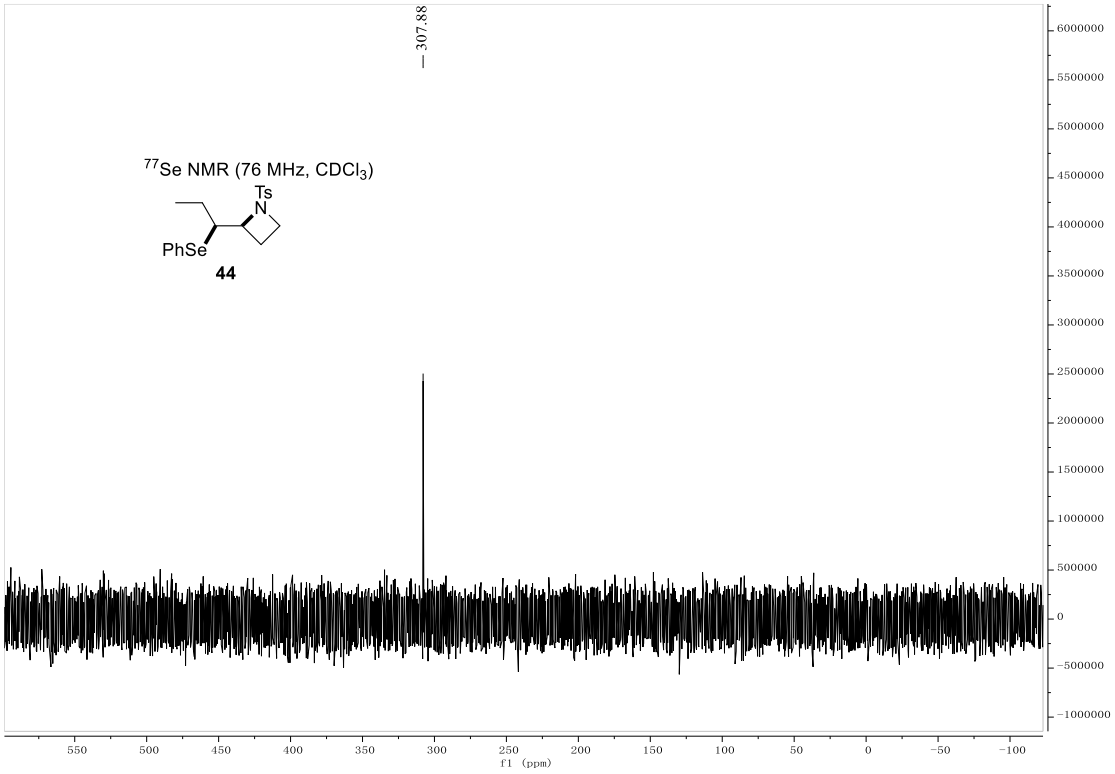
^{1}H NMR of compound **44**



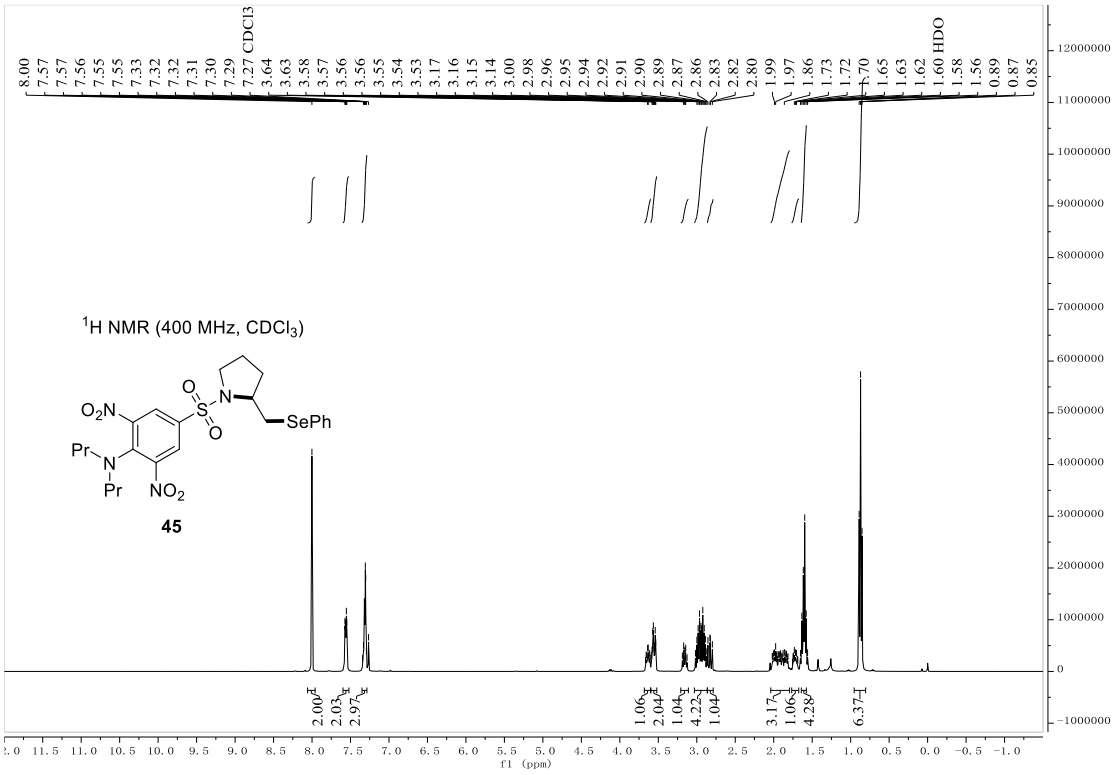
^{13}C NMR of compound **44**



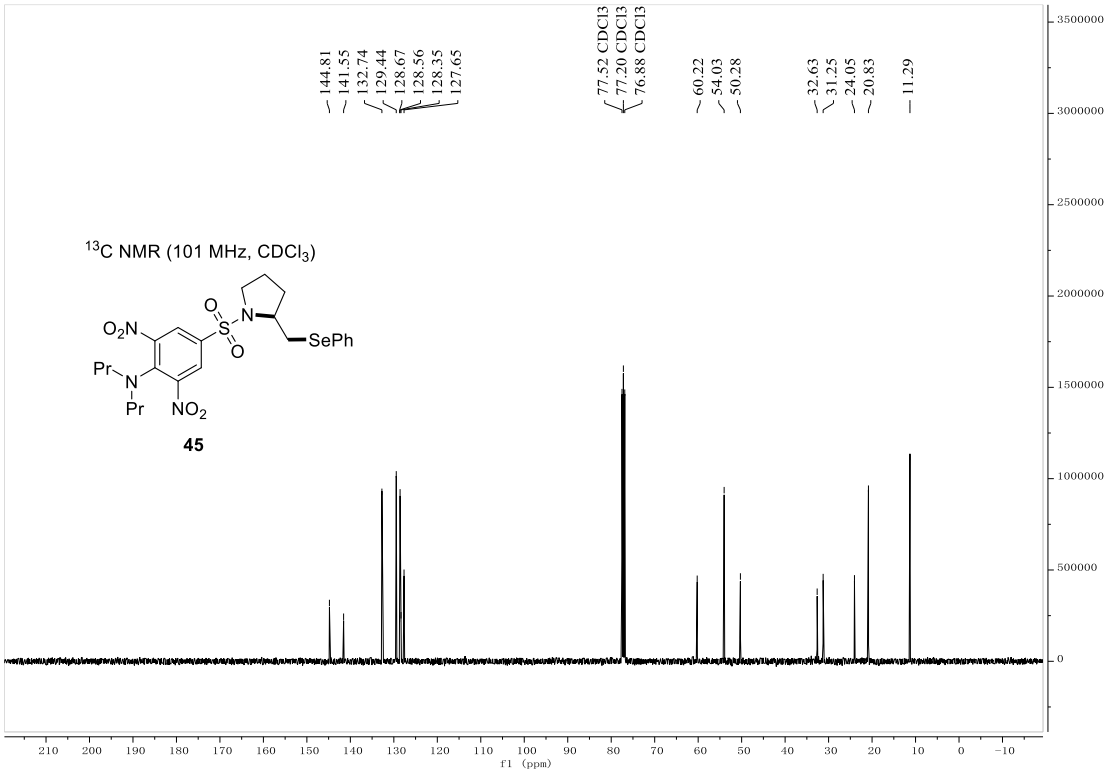
^{77}Se NMR of compound **44**



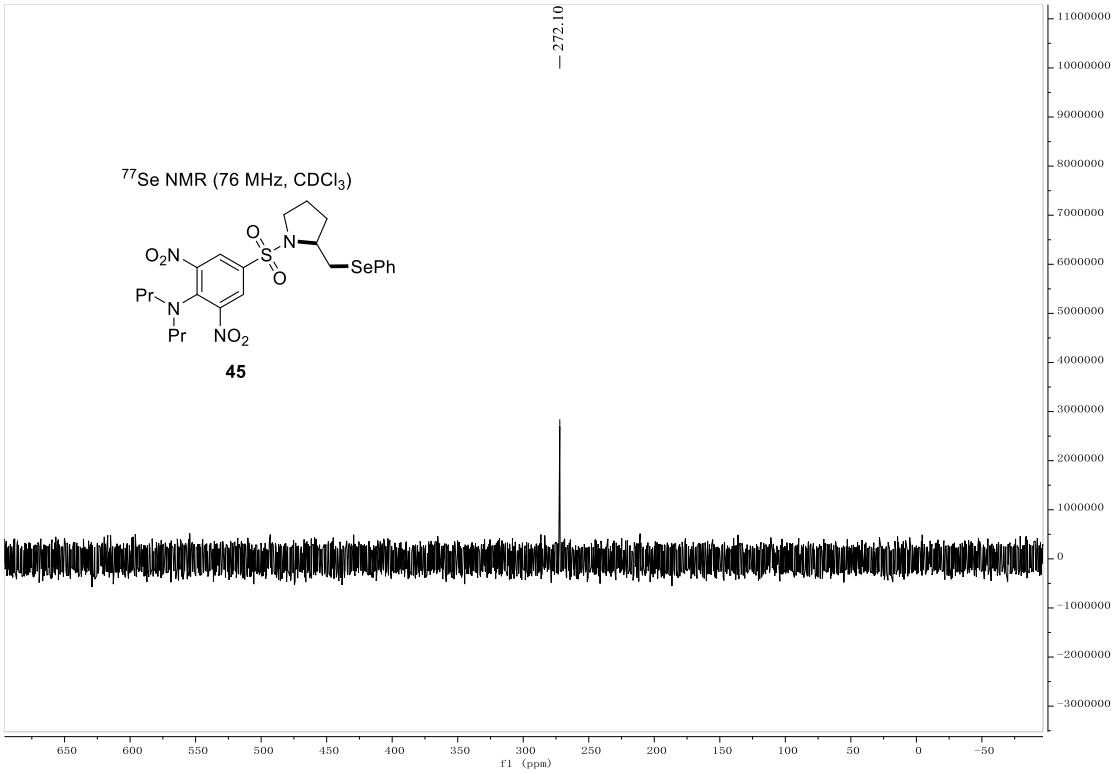
^{1}H NMR of compound **45**



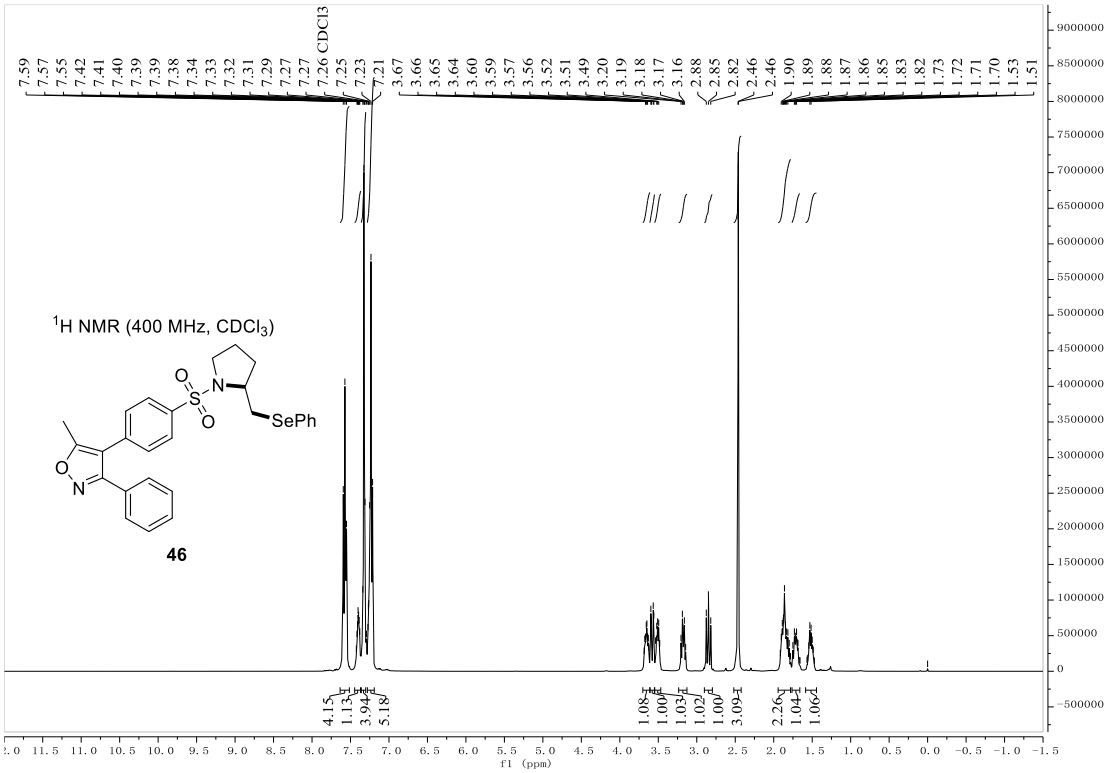
^{13}C NMR of compound **45**



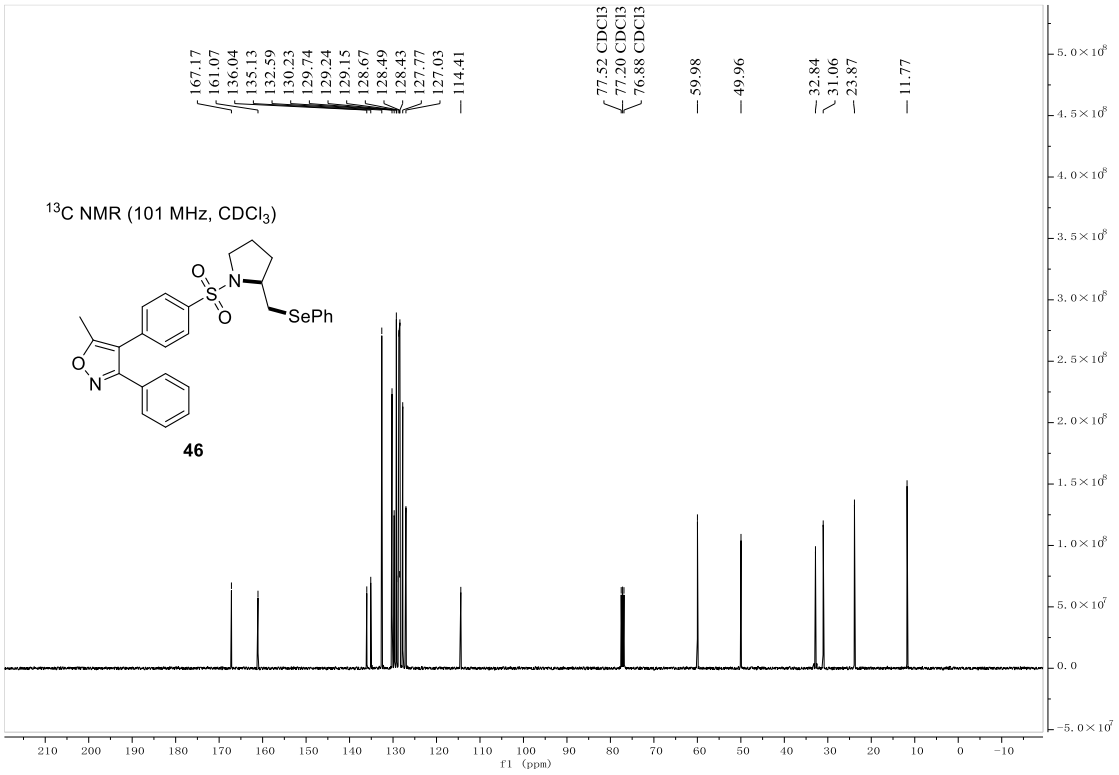
^{77}Se NMR of compound **45**



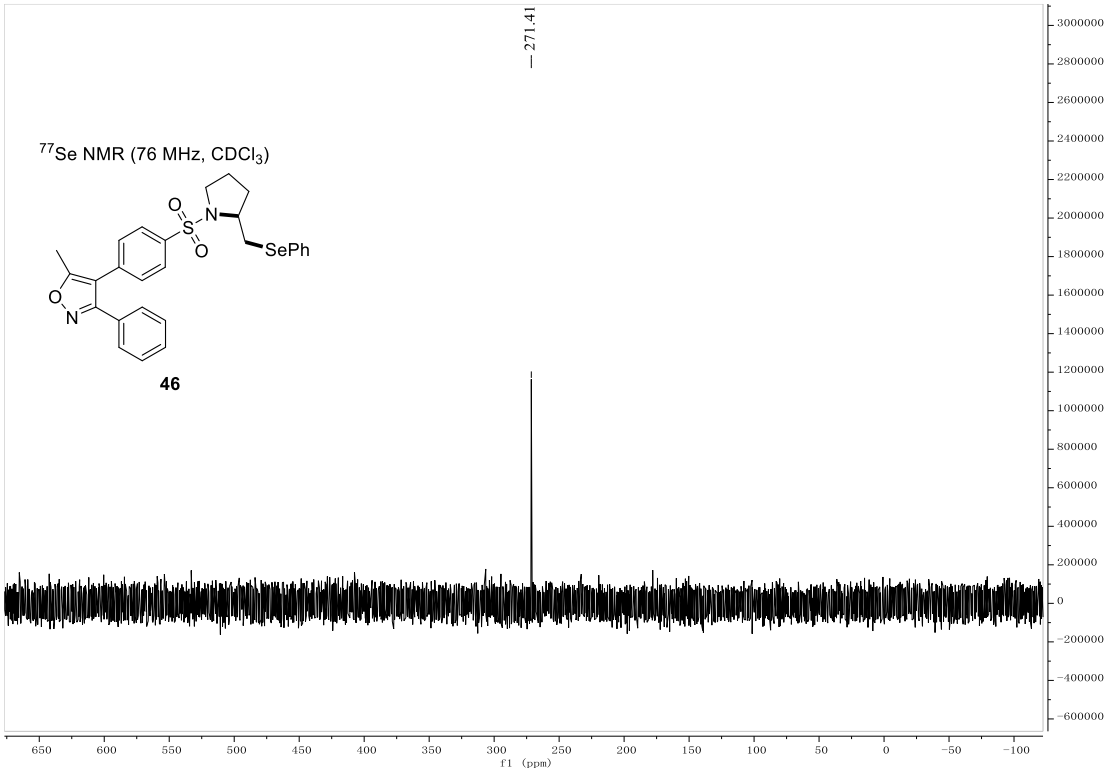
^{1}H NMR of compound **46**



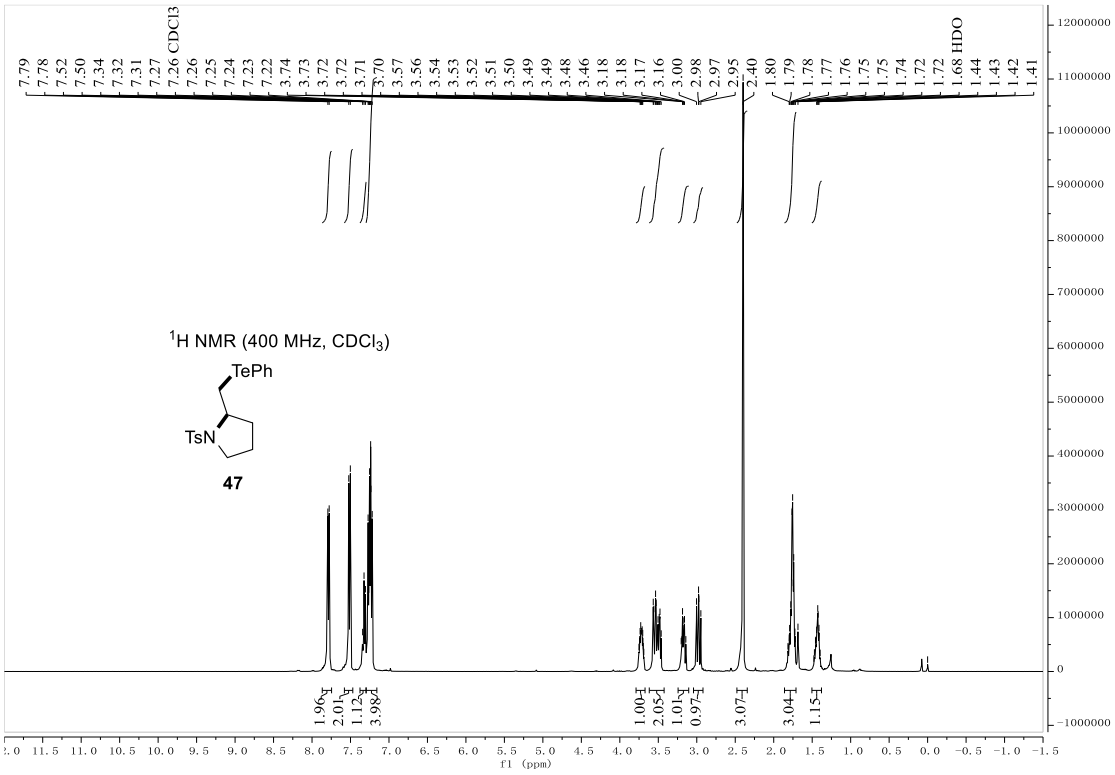
^{13}C NMR of compound **46**



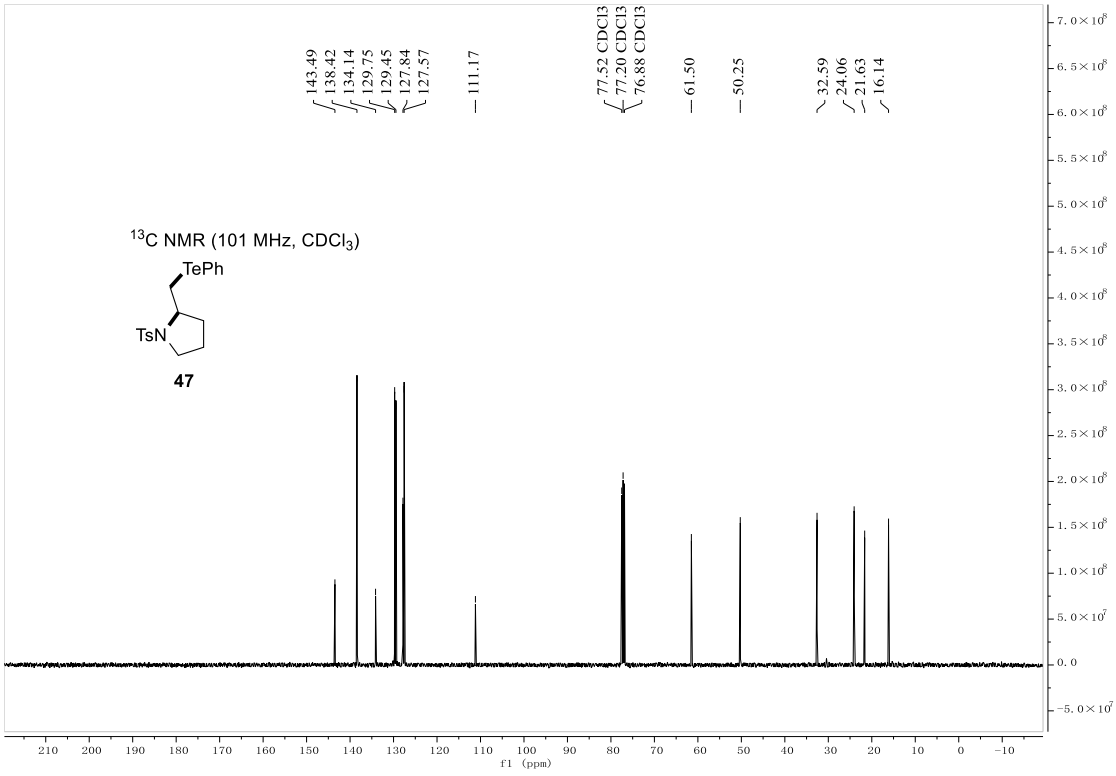
^{77}Se NMR of compound **46**



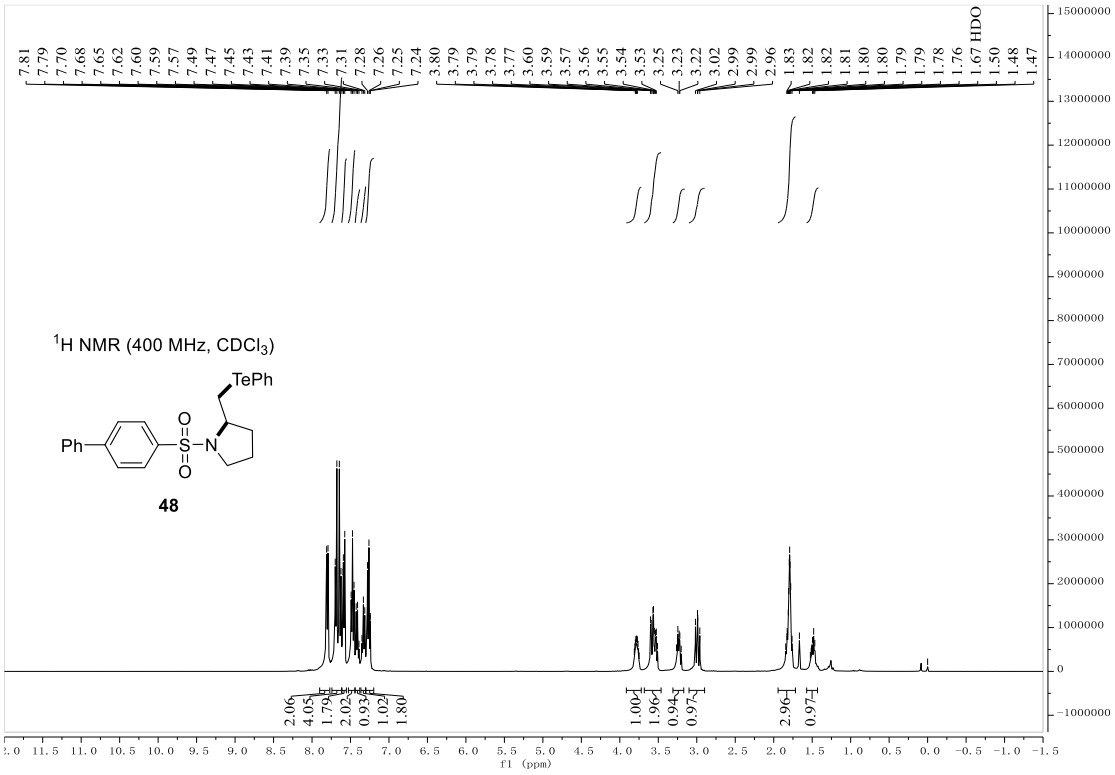
^{1}H NMR of compound **47**



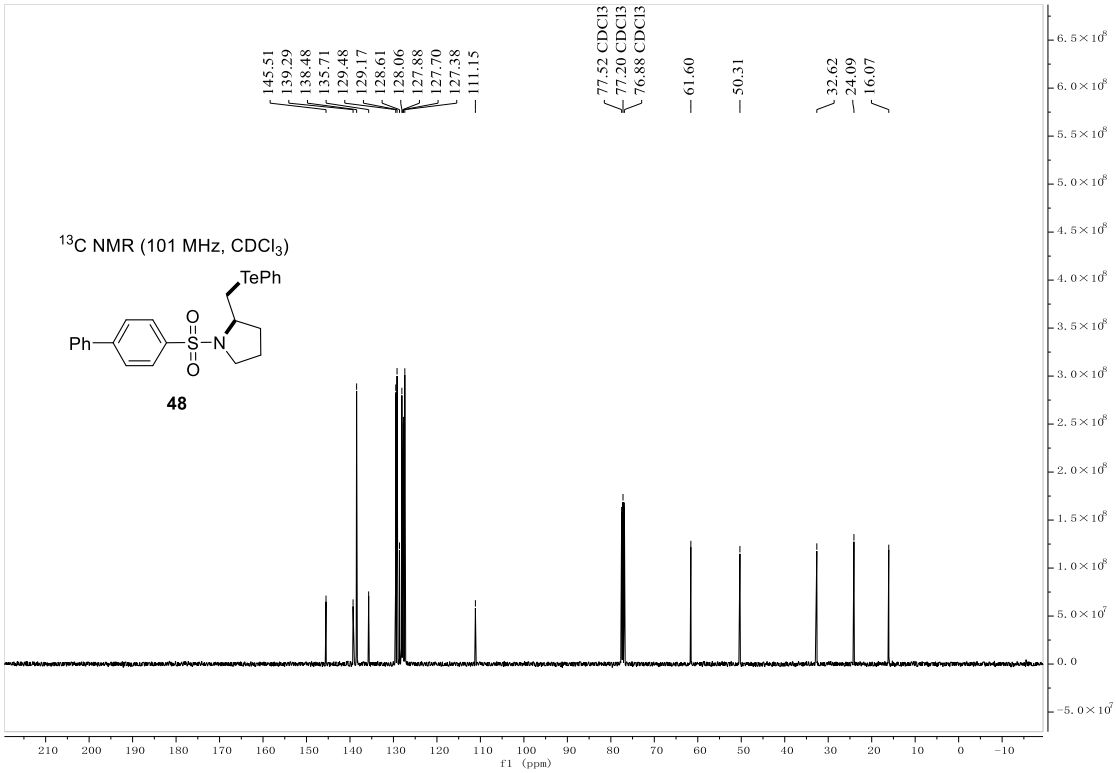
^{13}C NMR of compound **47**



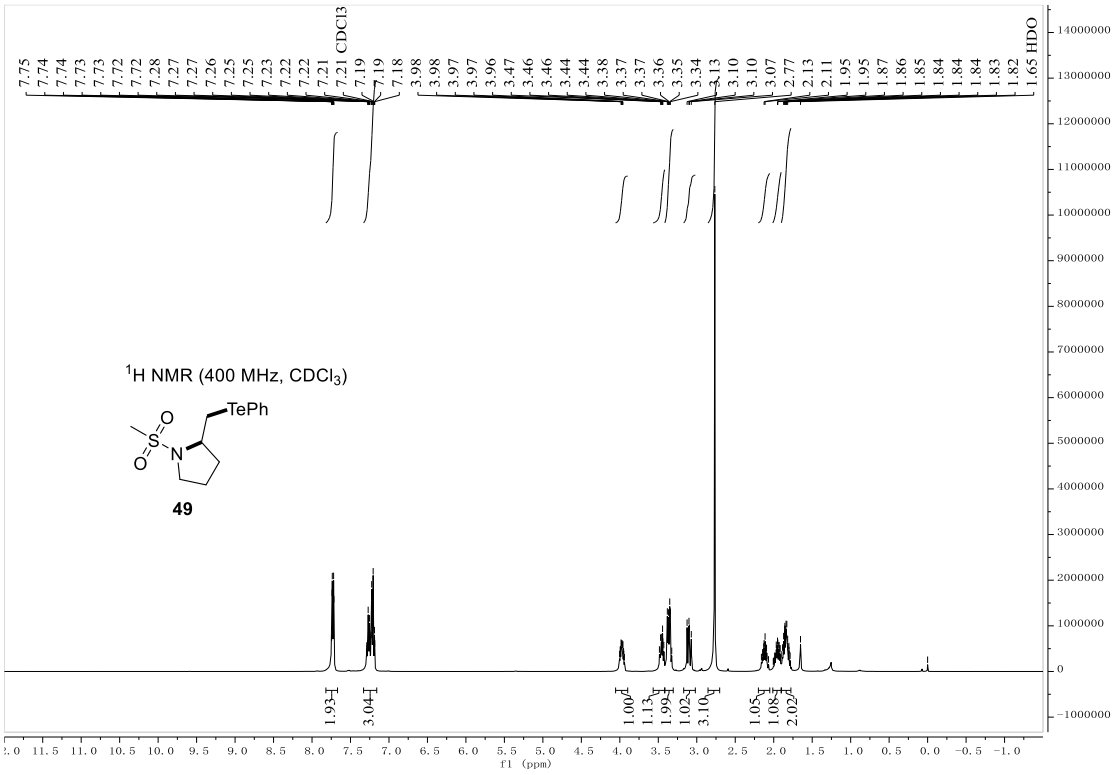
^{1}H NMR of compound **48**



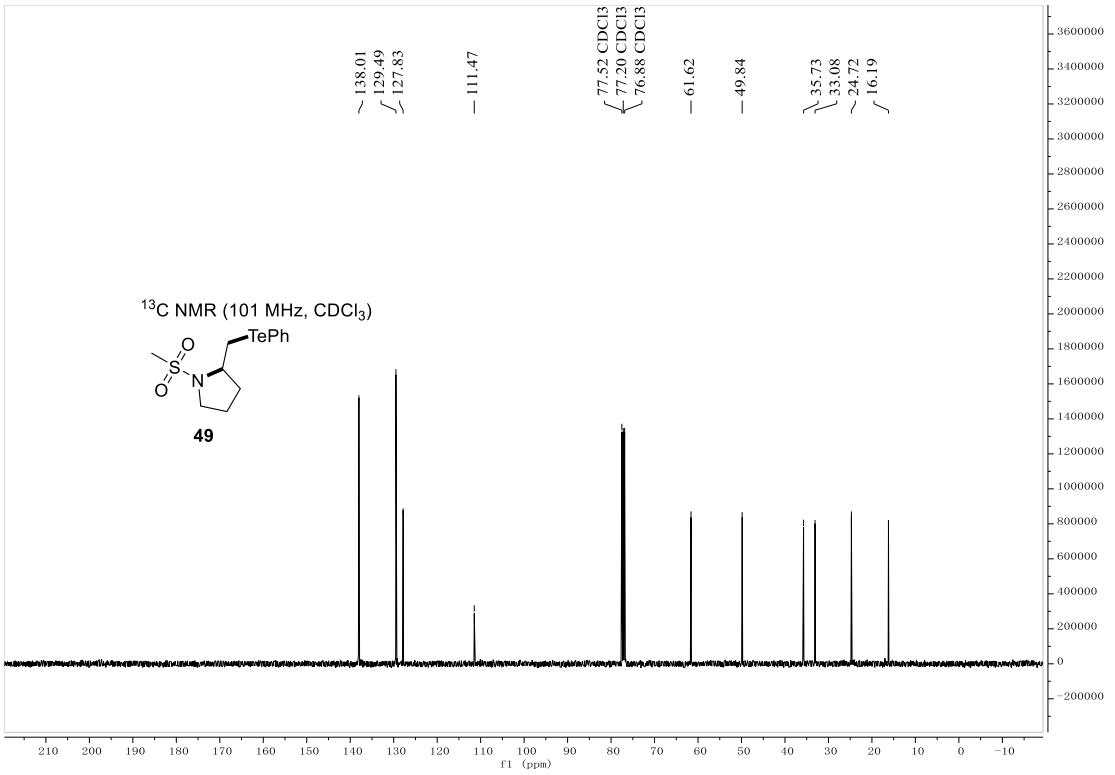
^{13}C NMR of compound **48**



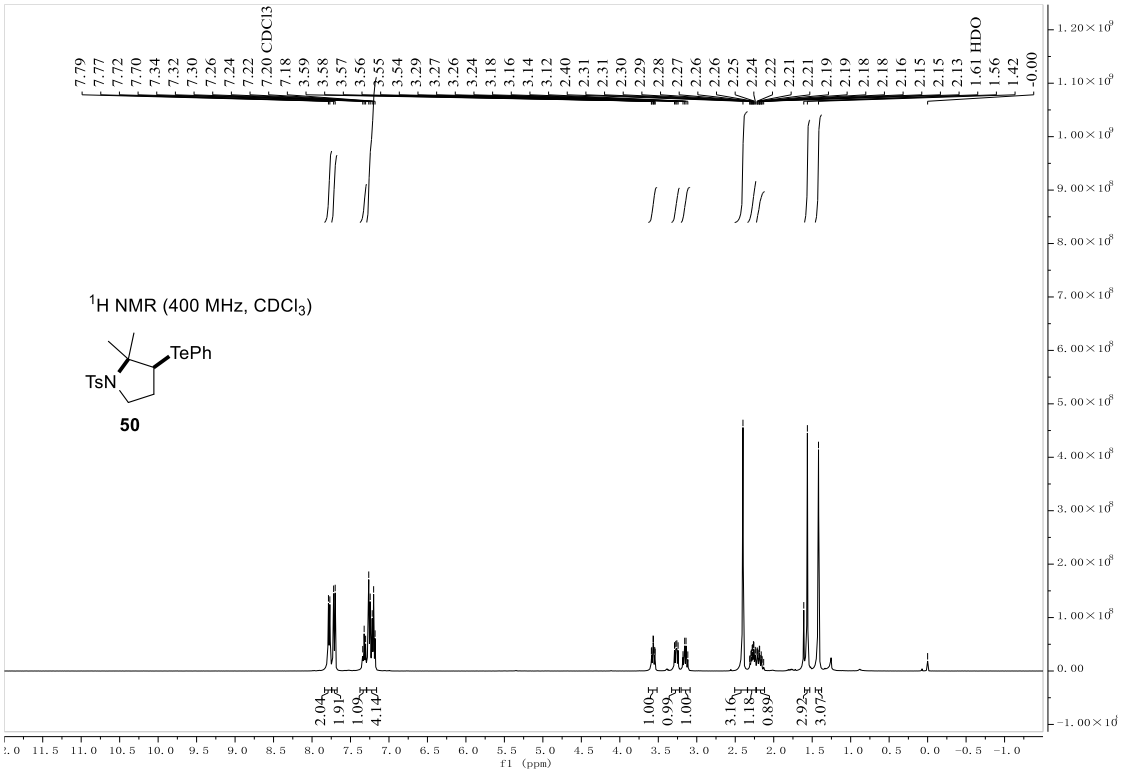
^{1}H NMR of compound **49**



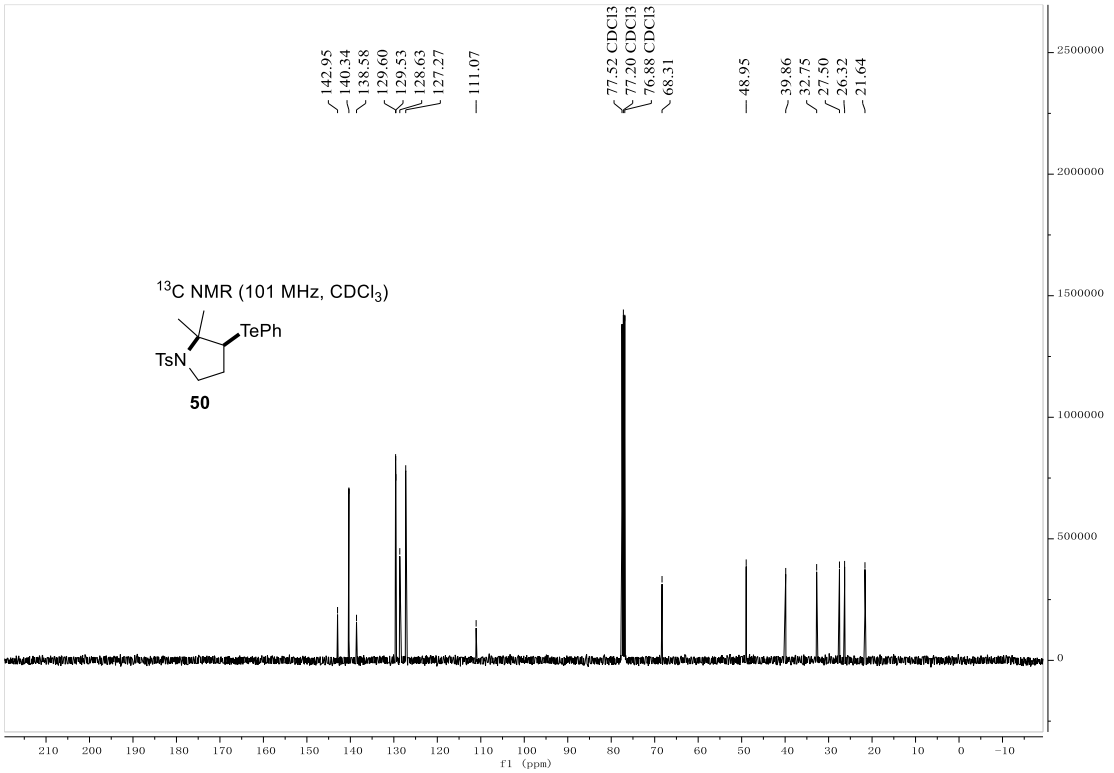
^{13}C NMR of compound **49**



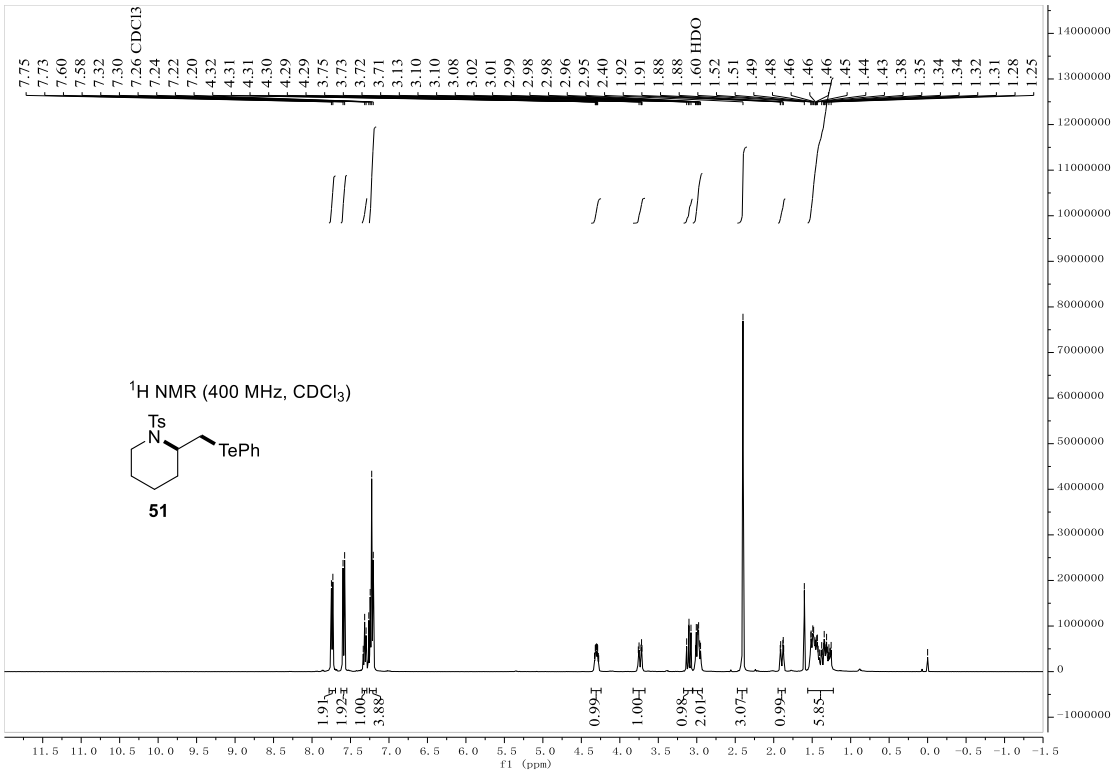
^{1}H NMR of compound **50**



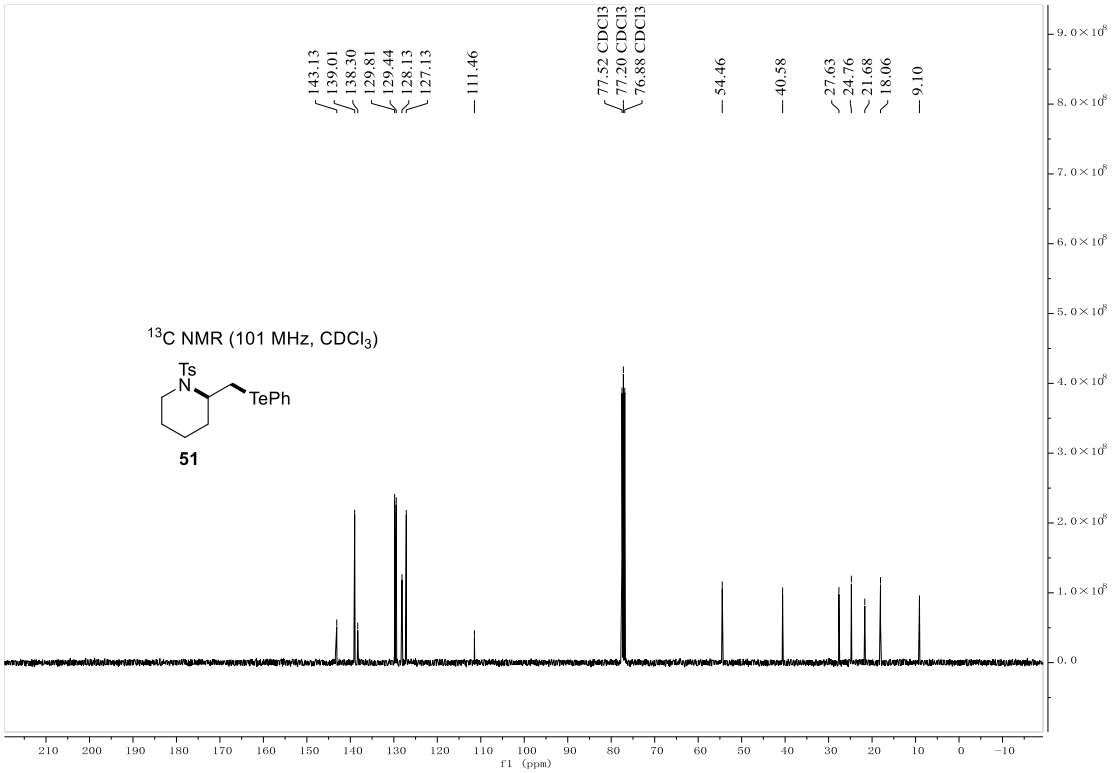
^{13}C NMR of compound **50**



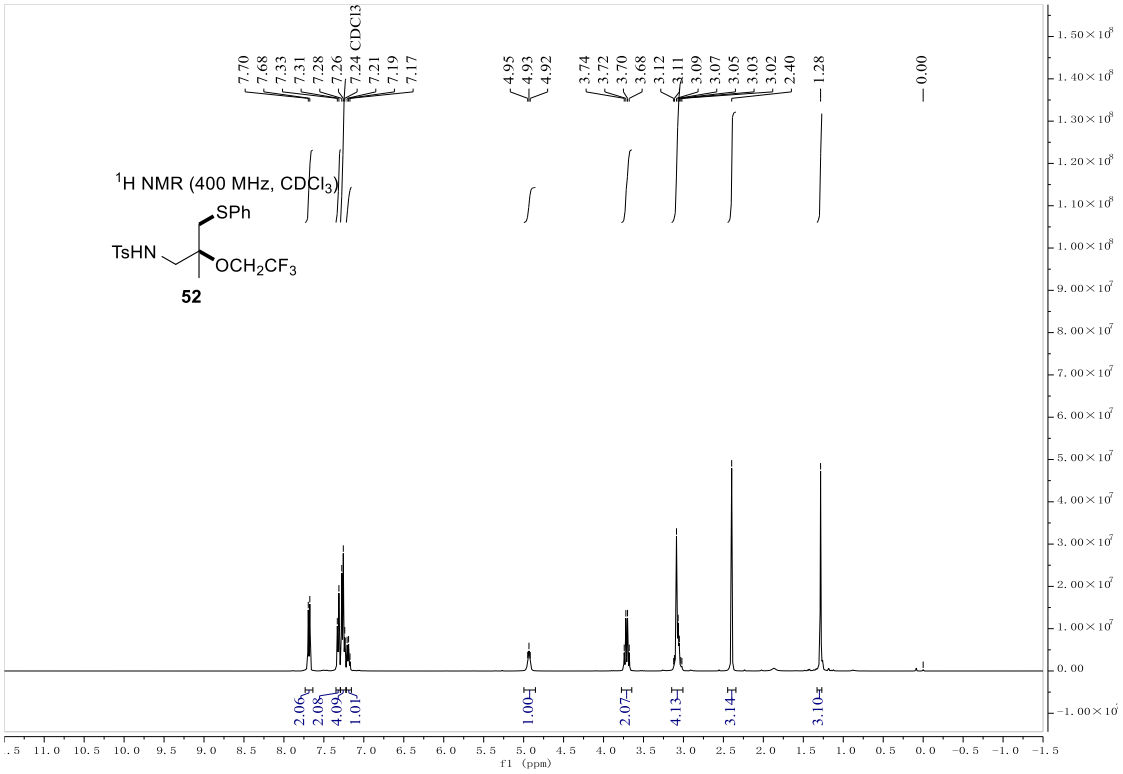
^{1}H NMR of compound **51**



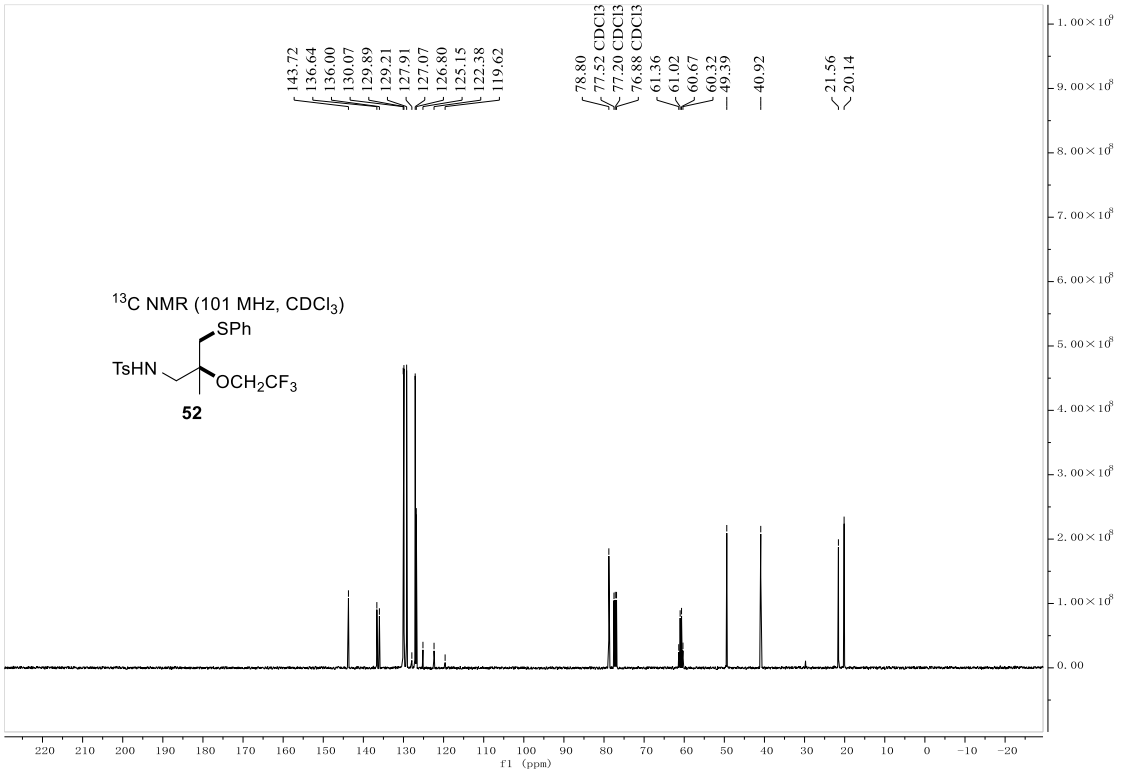
^{13}C NMR of compound **51**



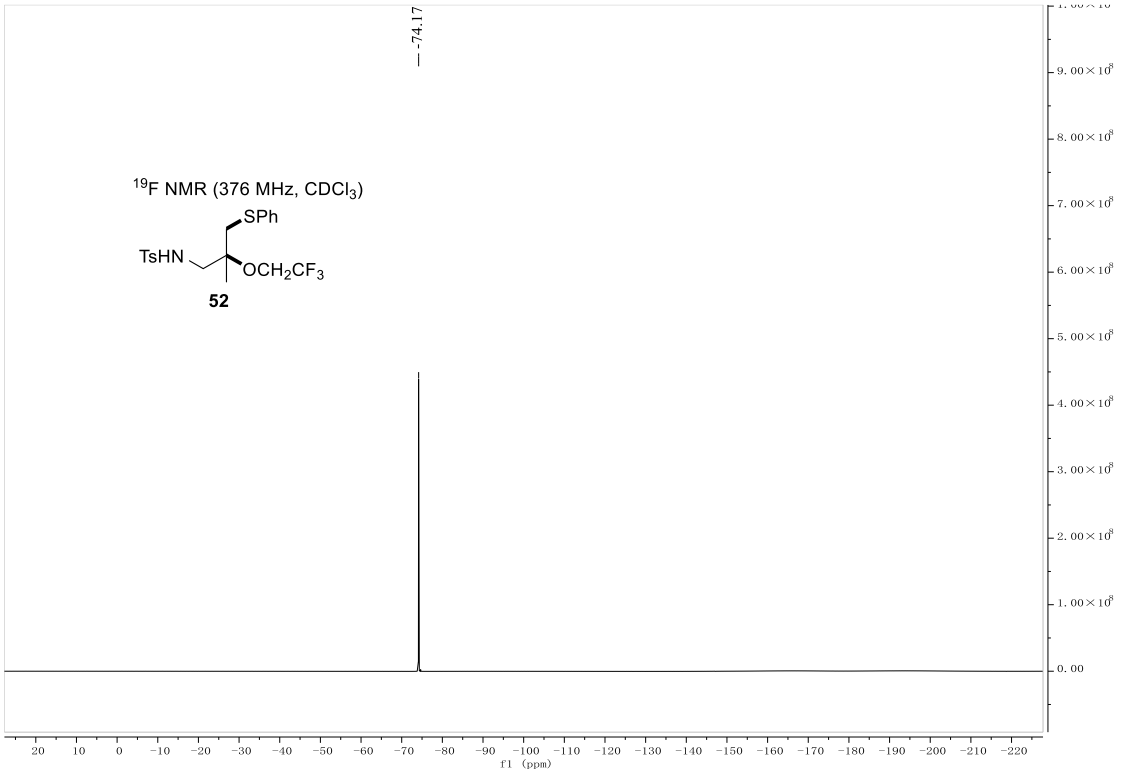
^{1}H NMR of compound **52**



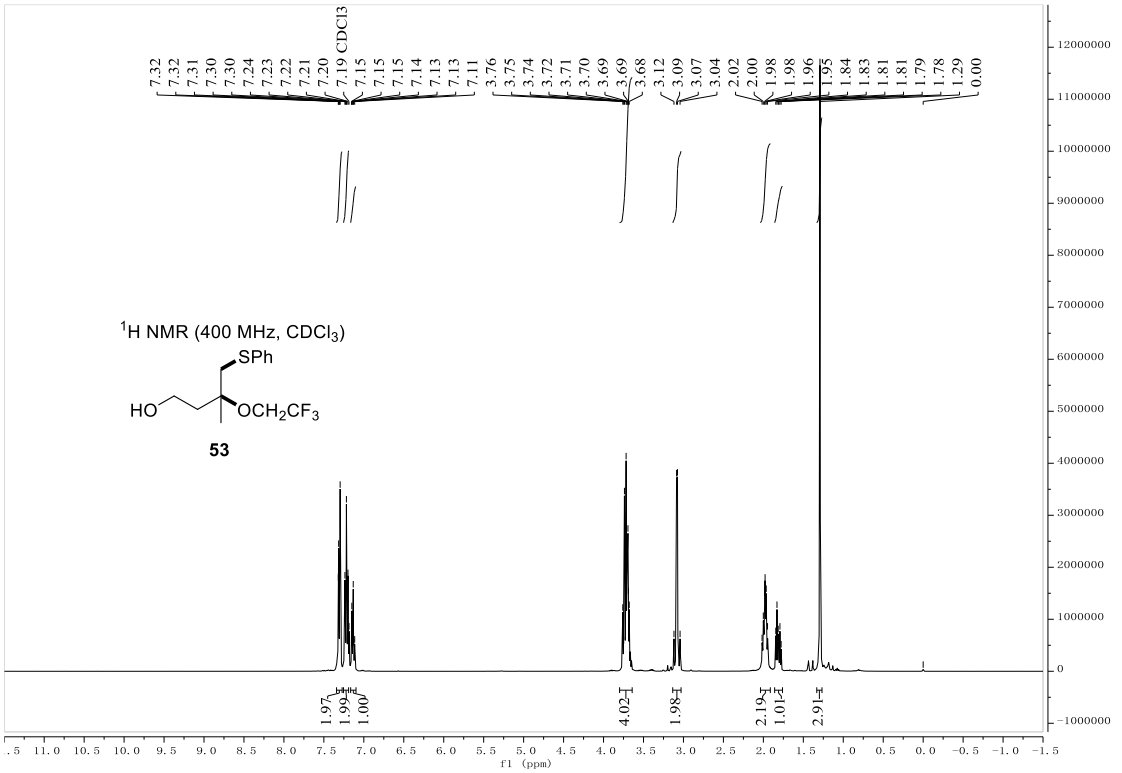
^{13}C NMR of compound **52**



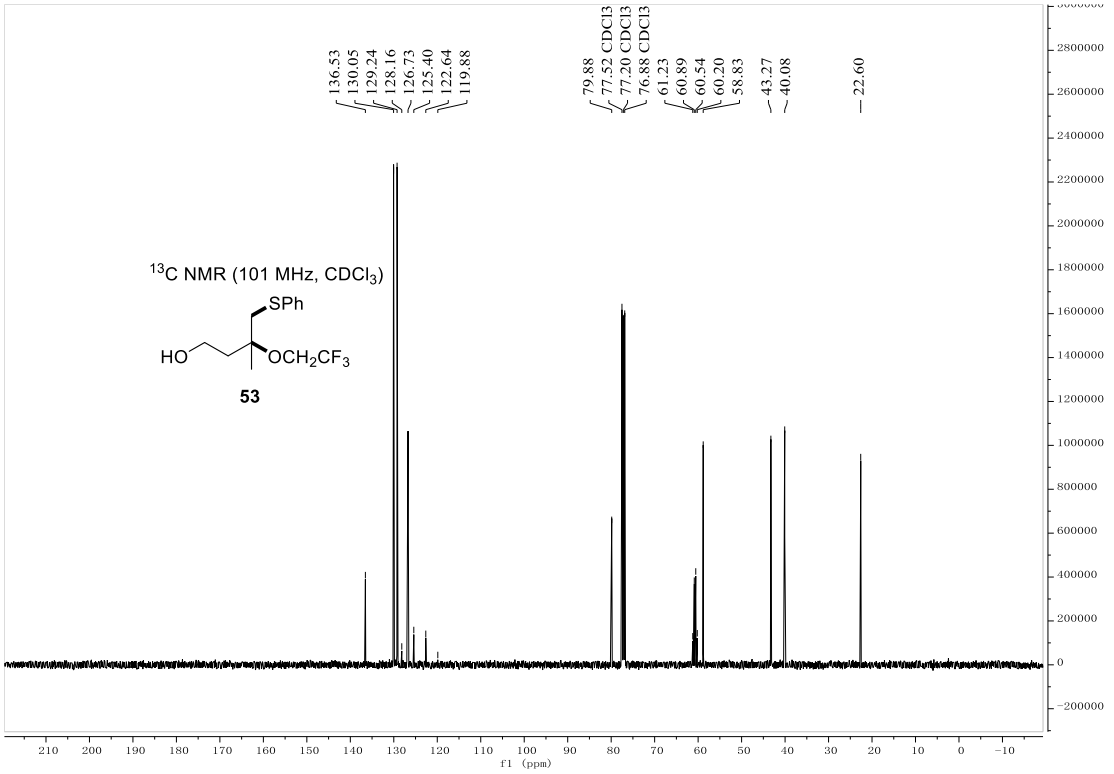
^{19}F NMR of compound **52**



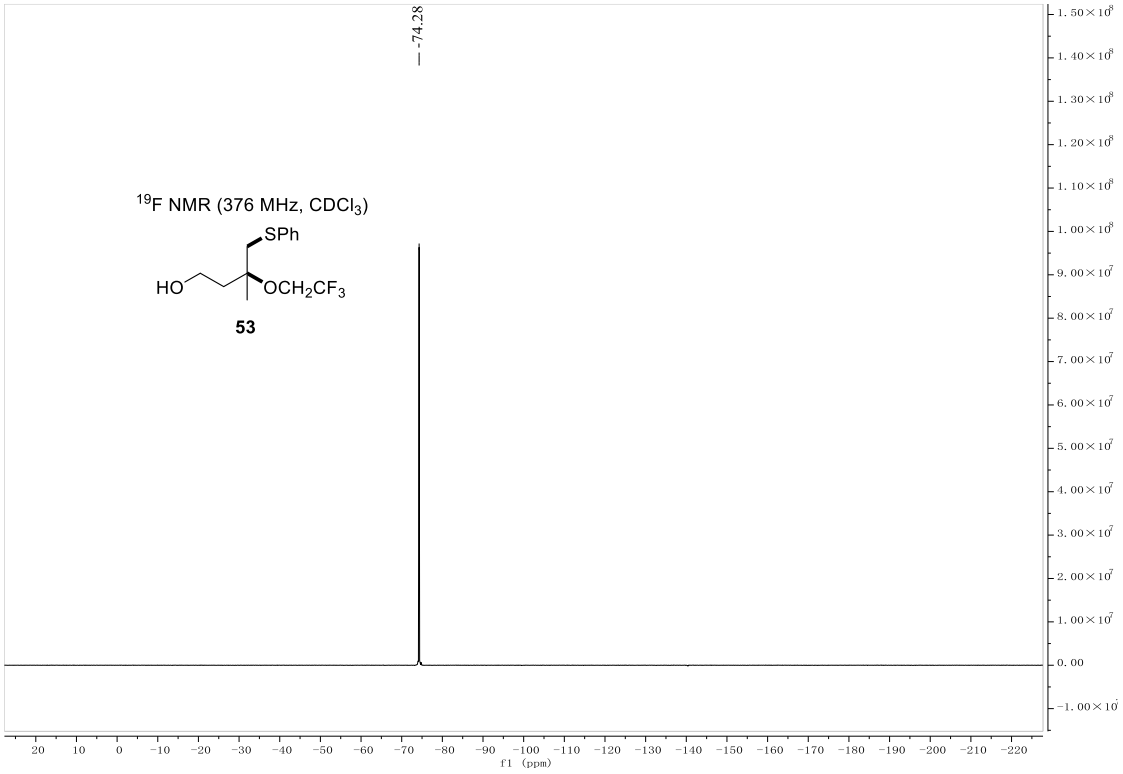
^{1}H NMR of compound **52**



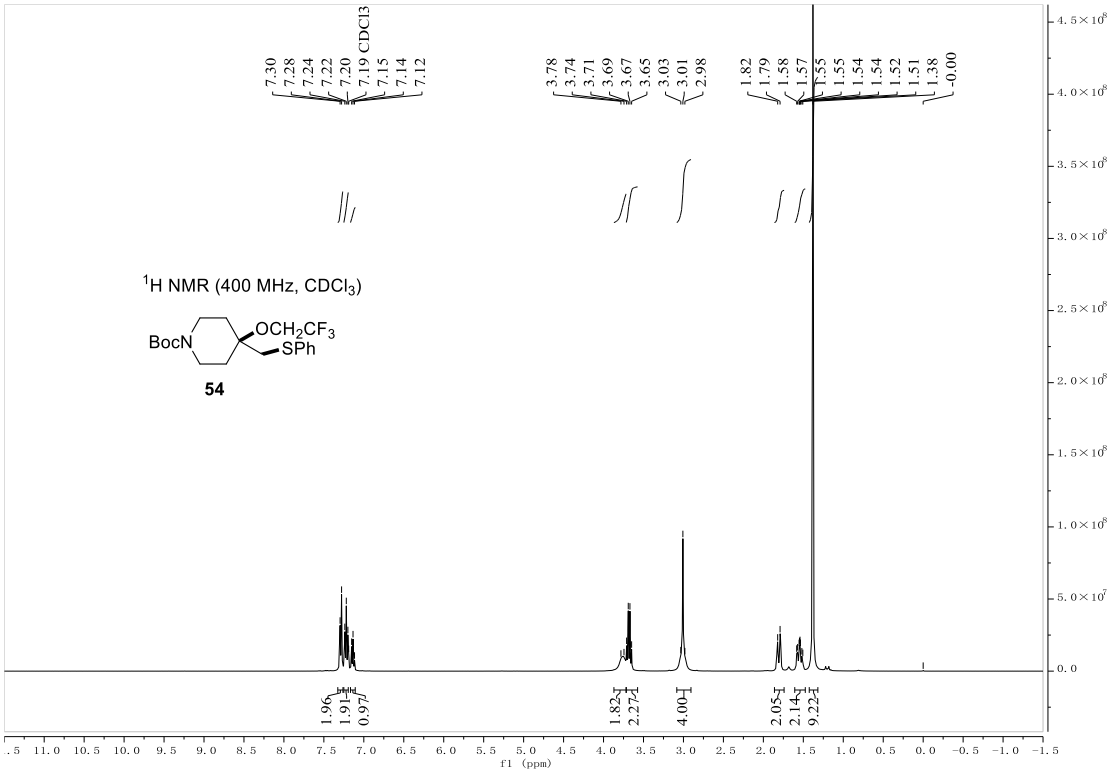
^{13}C NMR of compound **53**



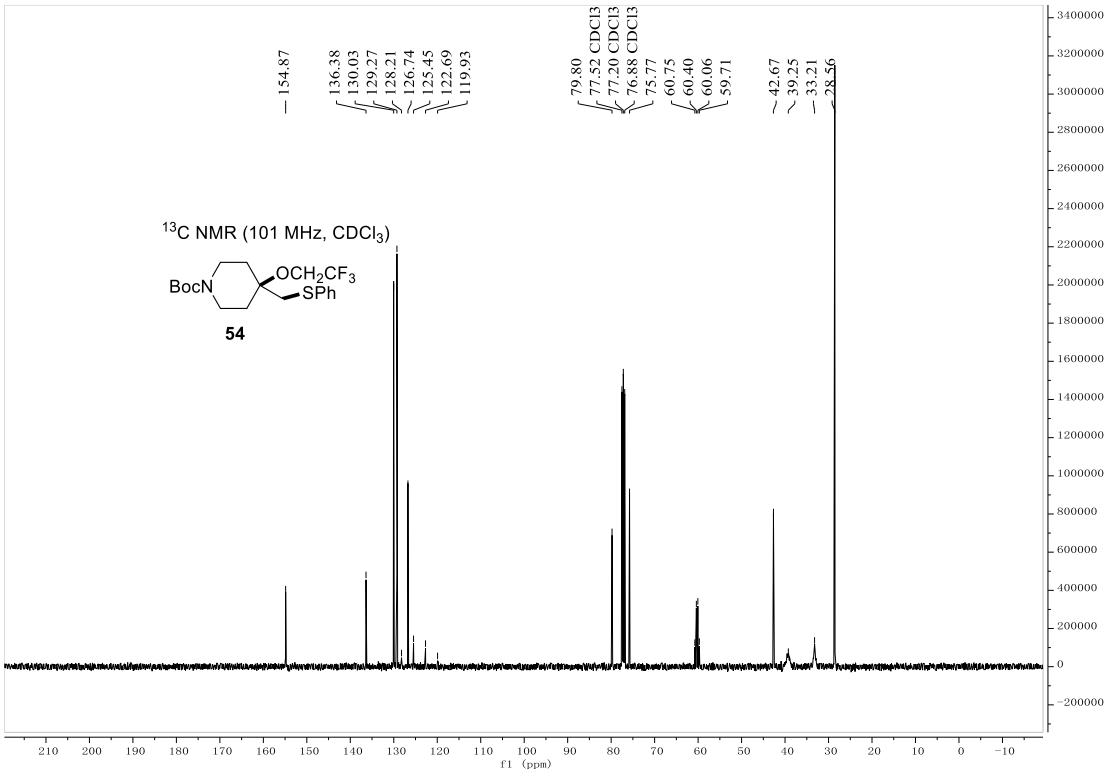
^{19}F NMR of compound **53**



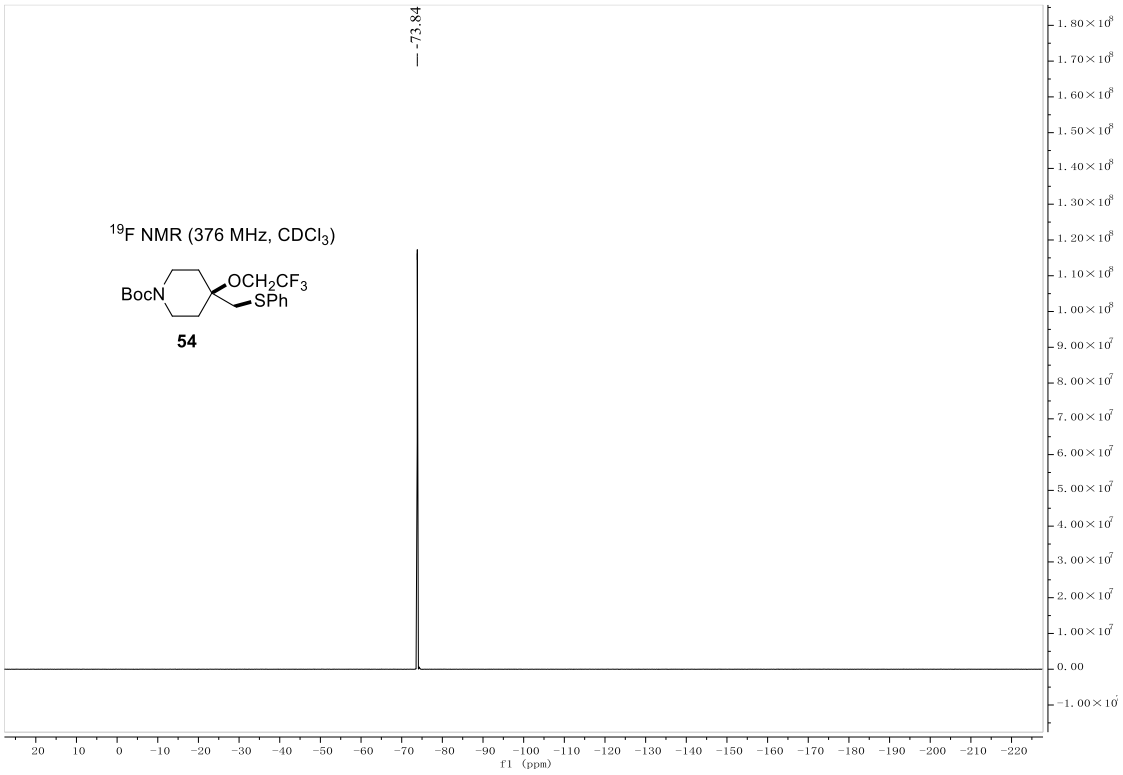
^{1}H NMR of compound **54**



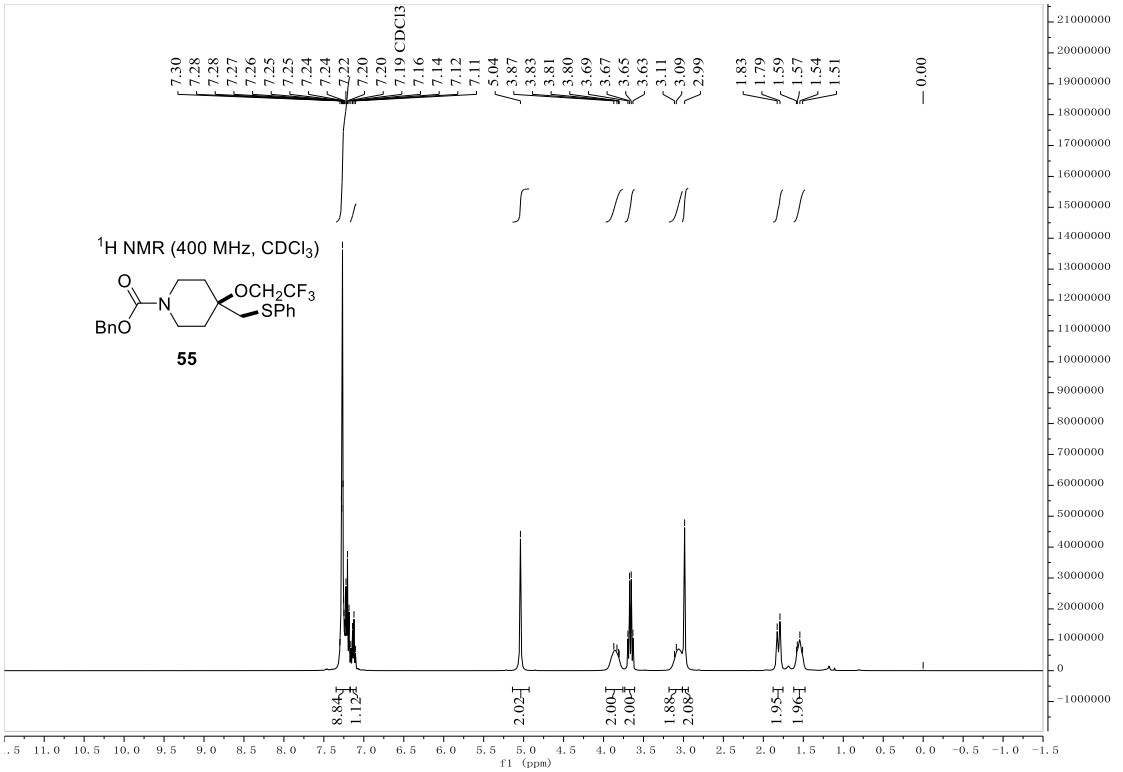
^{13}C NMR of compound **54**



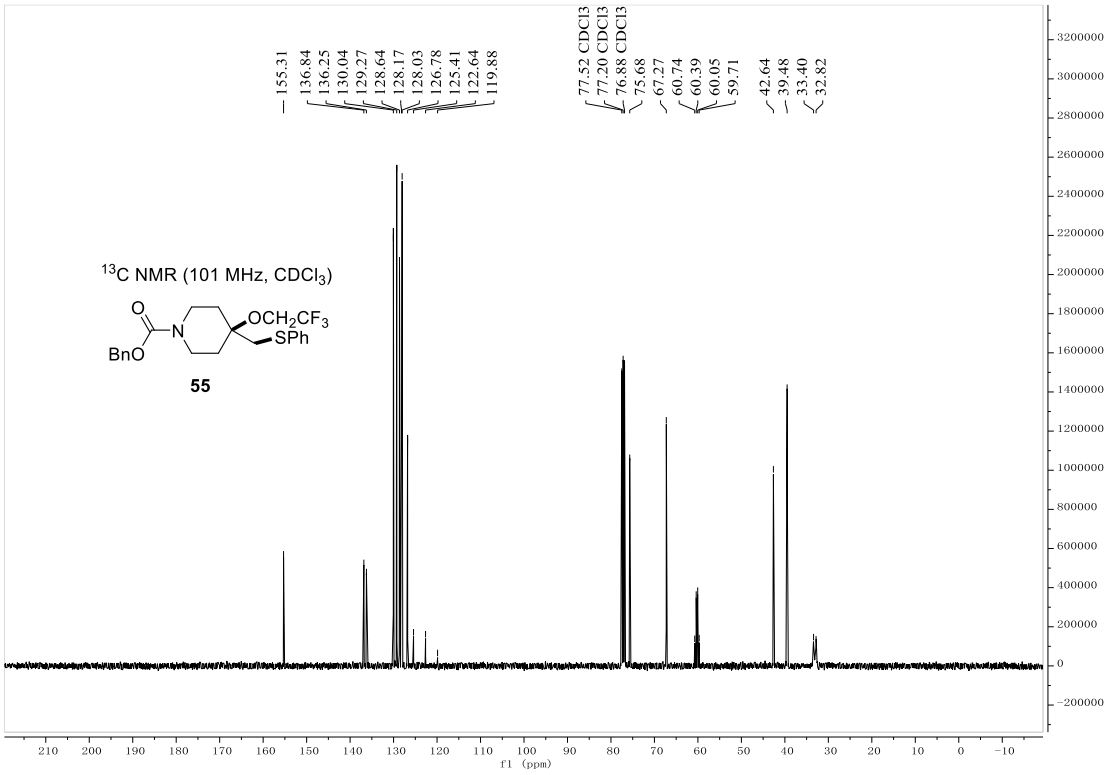
^{19}F NMR of compound **54**



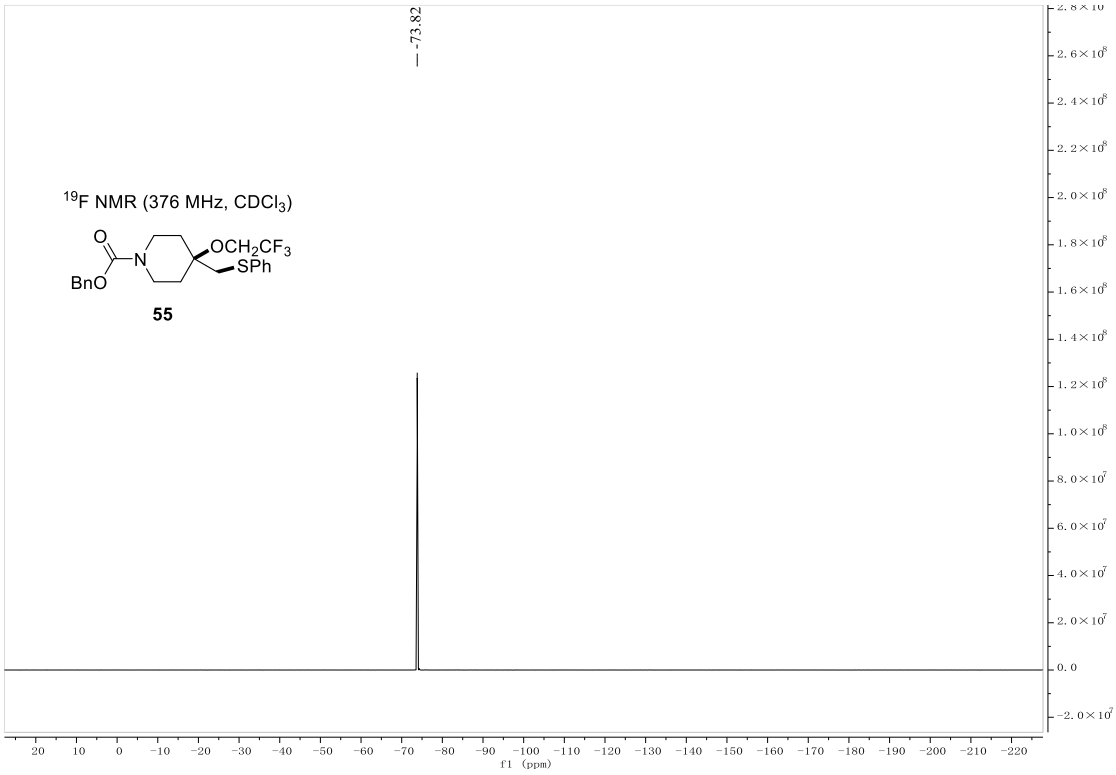
^{1}H NMR of compound **55**



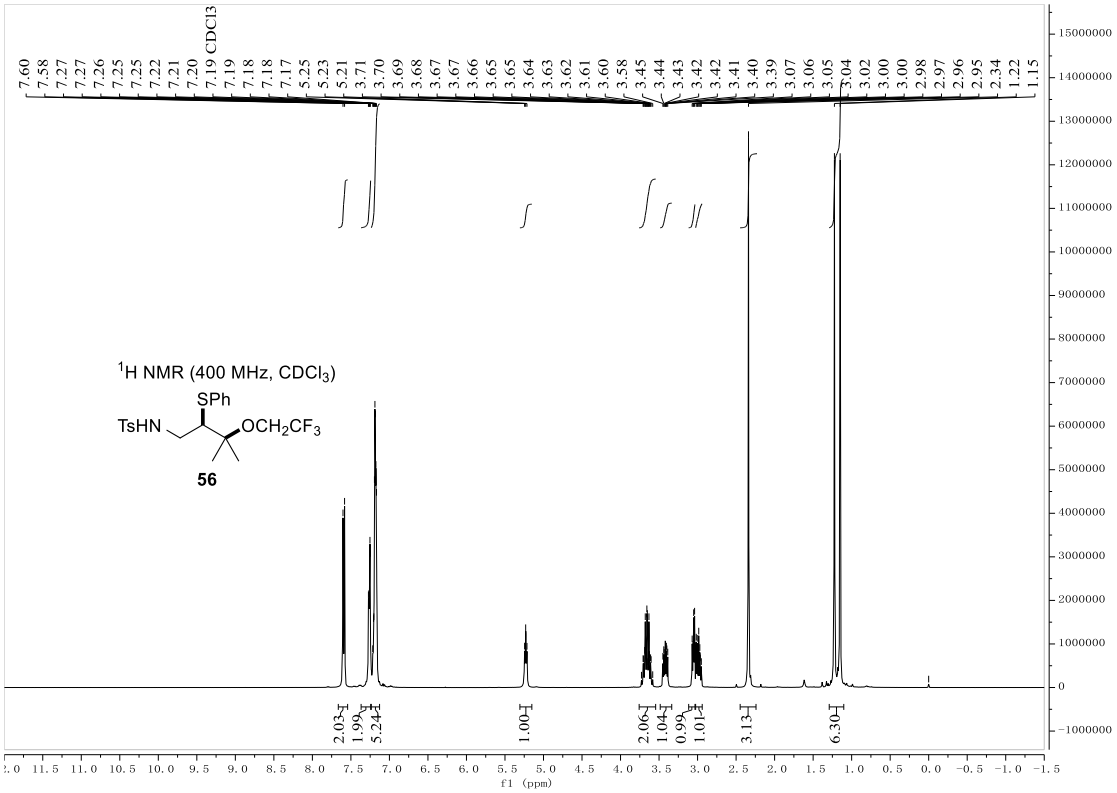
^{13}C NMR of compound **55**



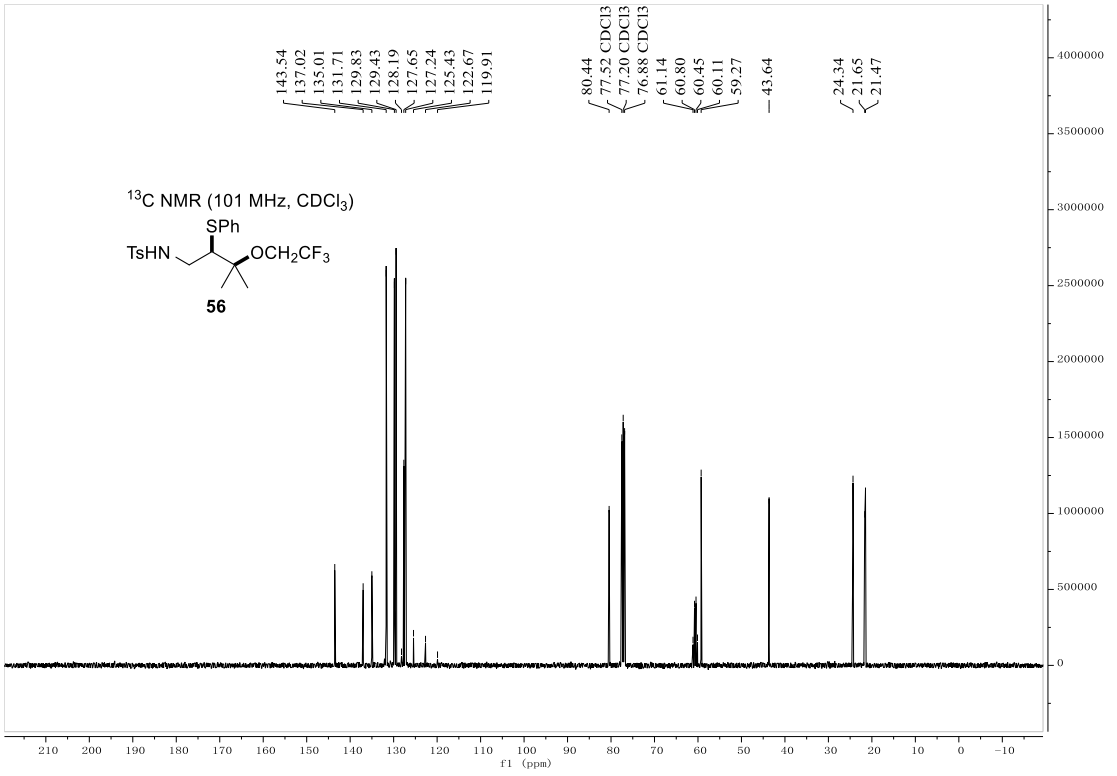
^{19}F NMR of compound **55**



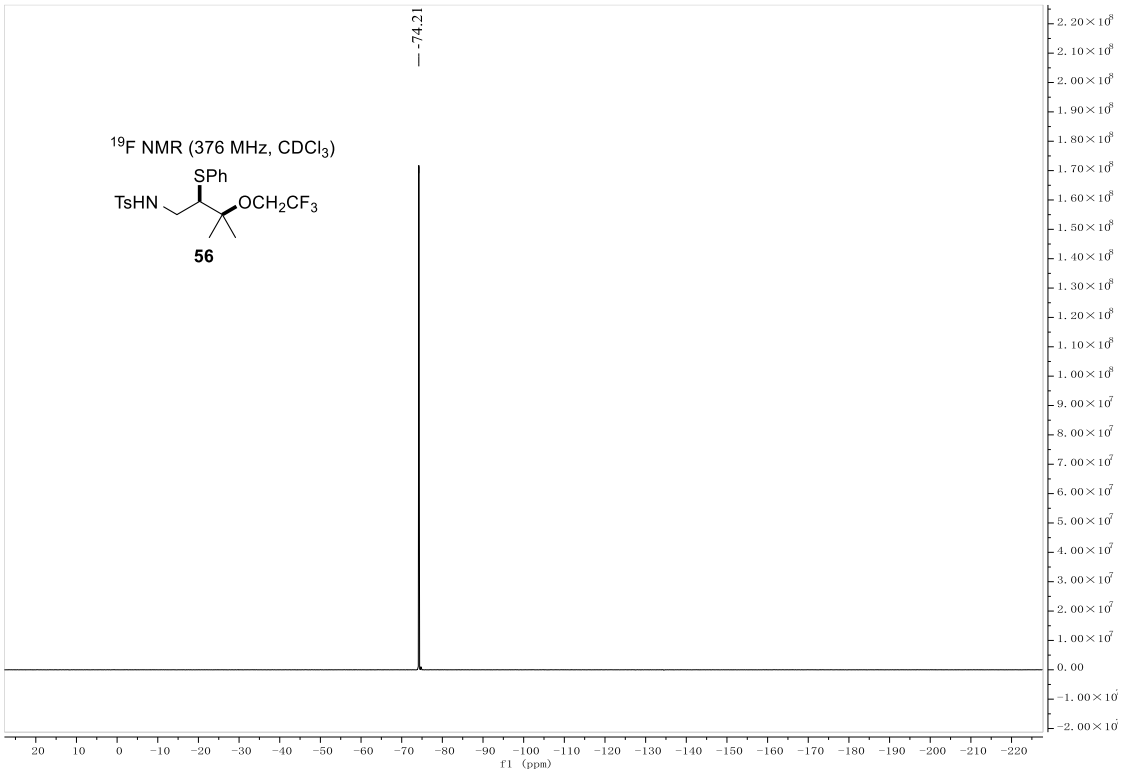
^{1}H NMR of compound **56**



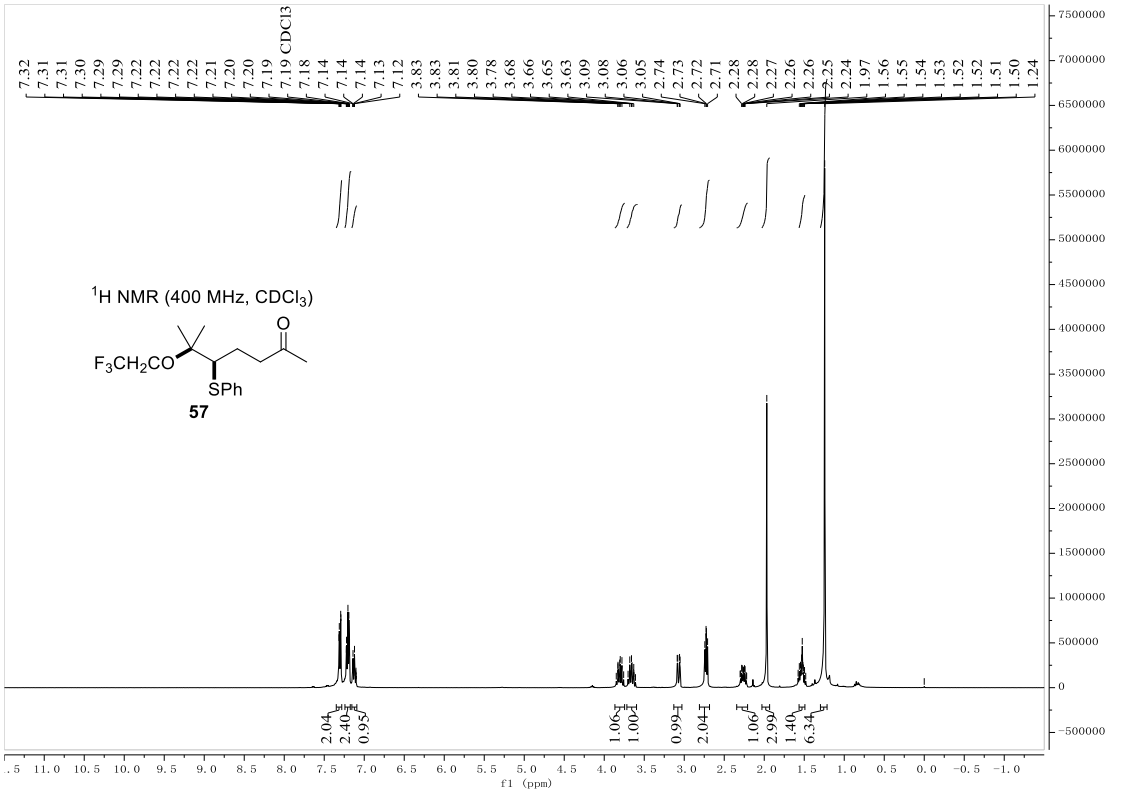
^{13}C NMR of compound **56**



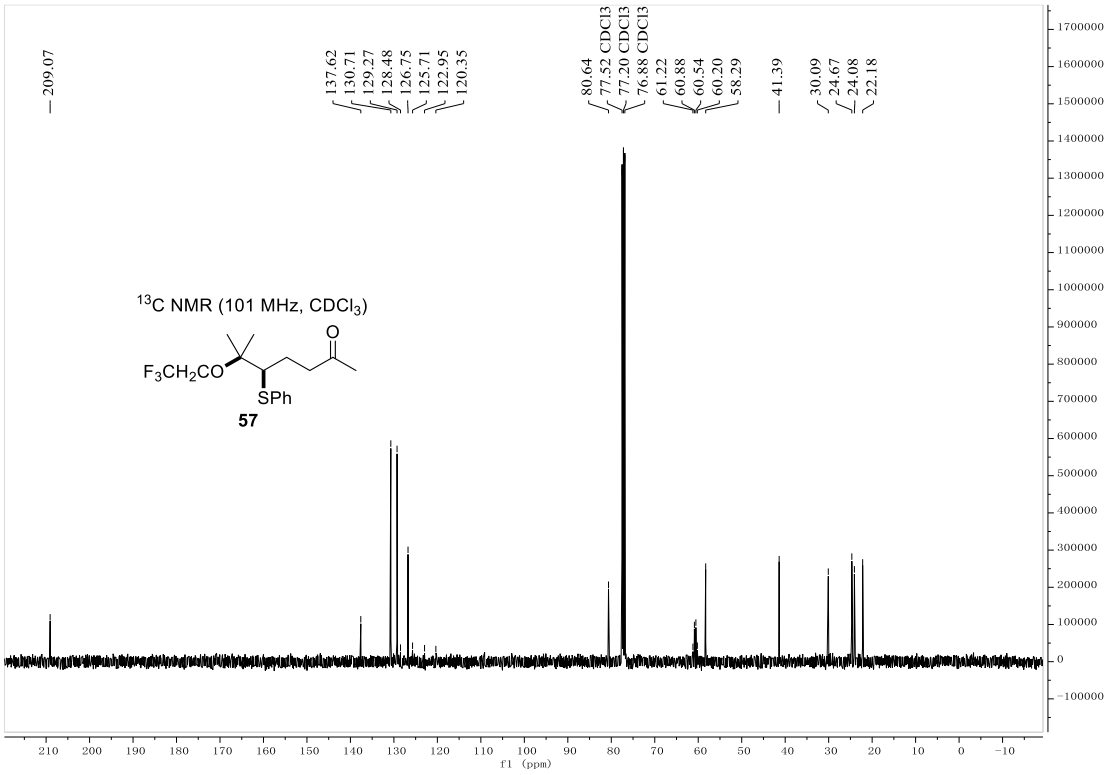
^{19}F NMR of compound **56**



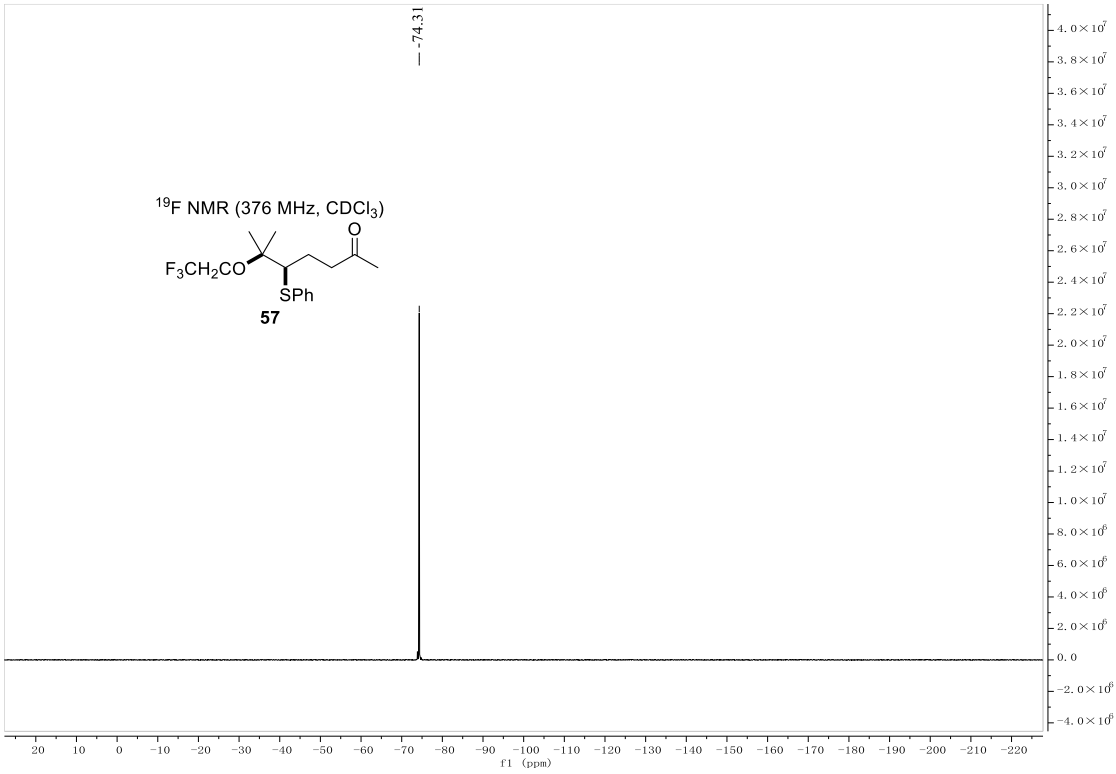
^{1}H NMR of compound **57**



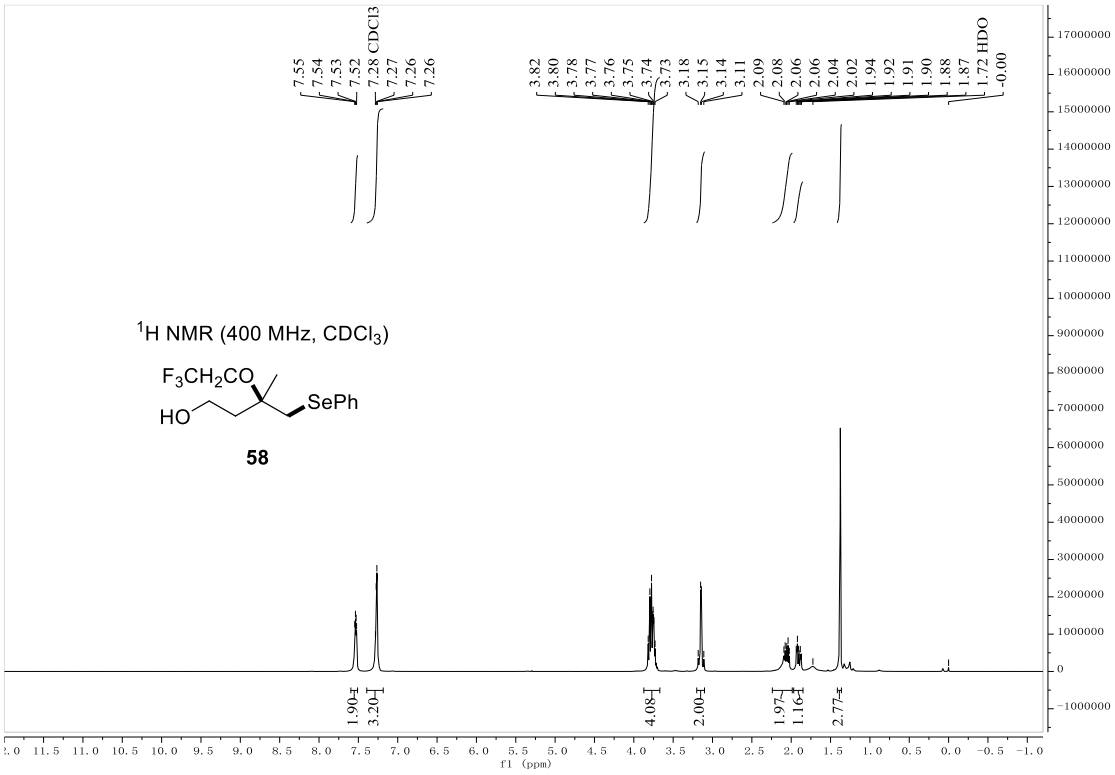
^{13}C NMR of compound **57**



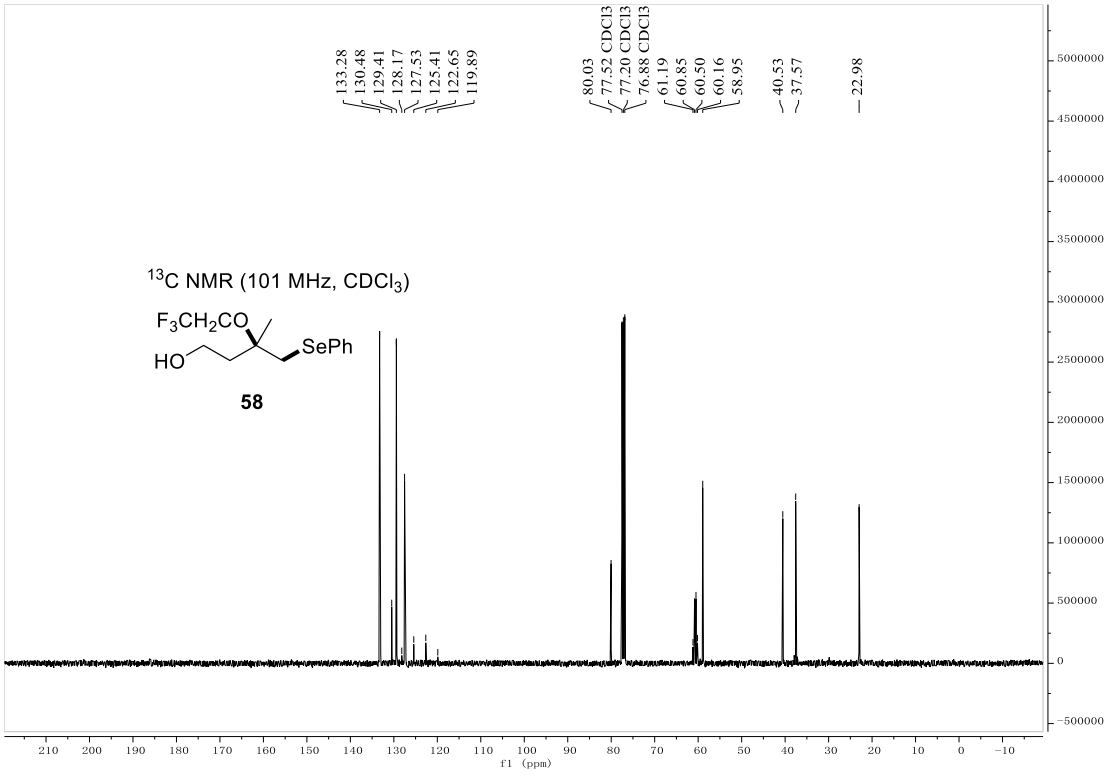
^{19}F NMR of compound **57**



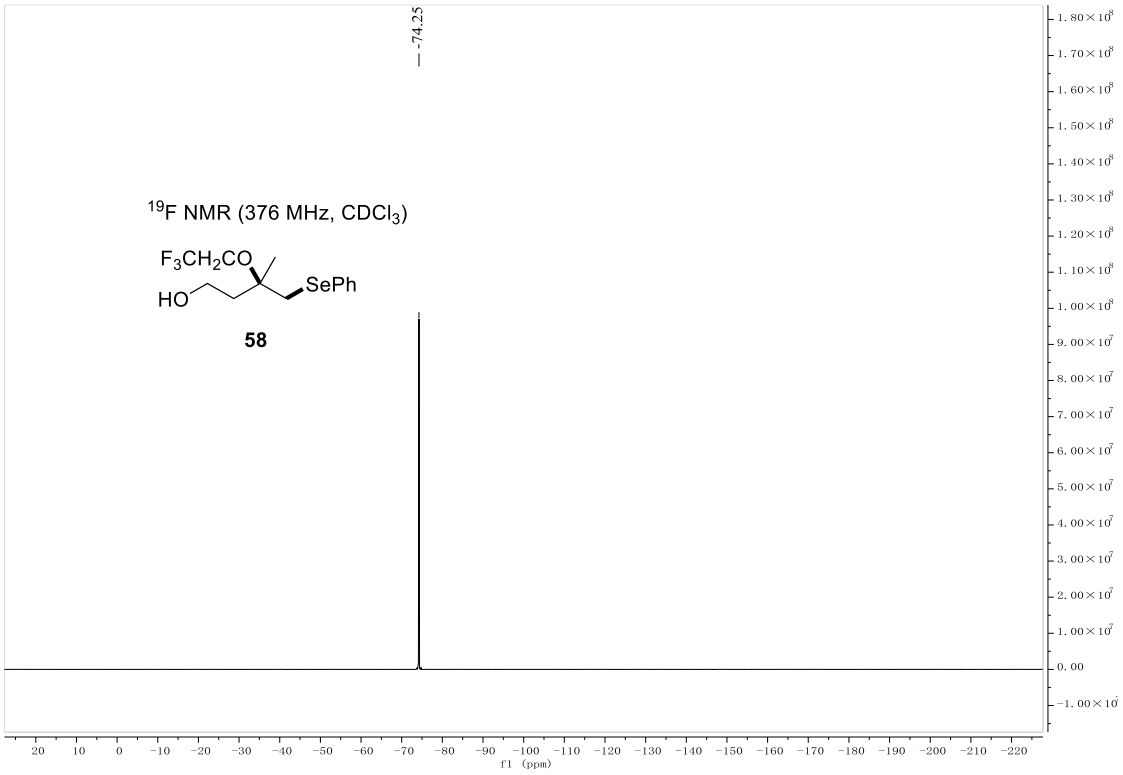
^{1}H NMR of compound **58**



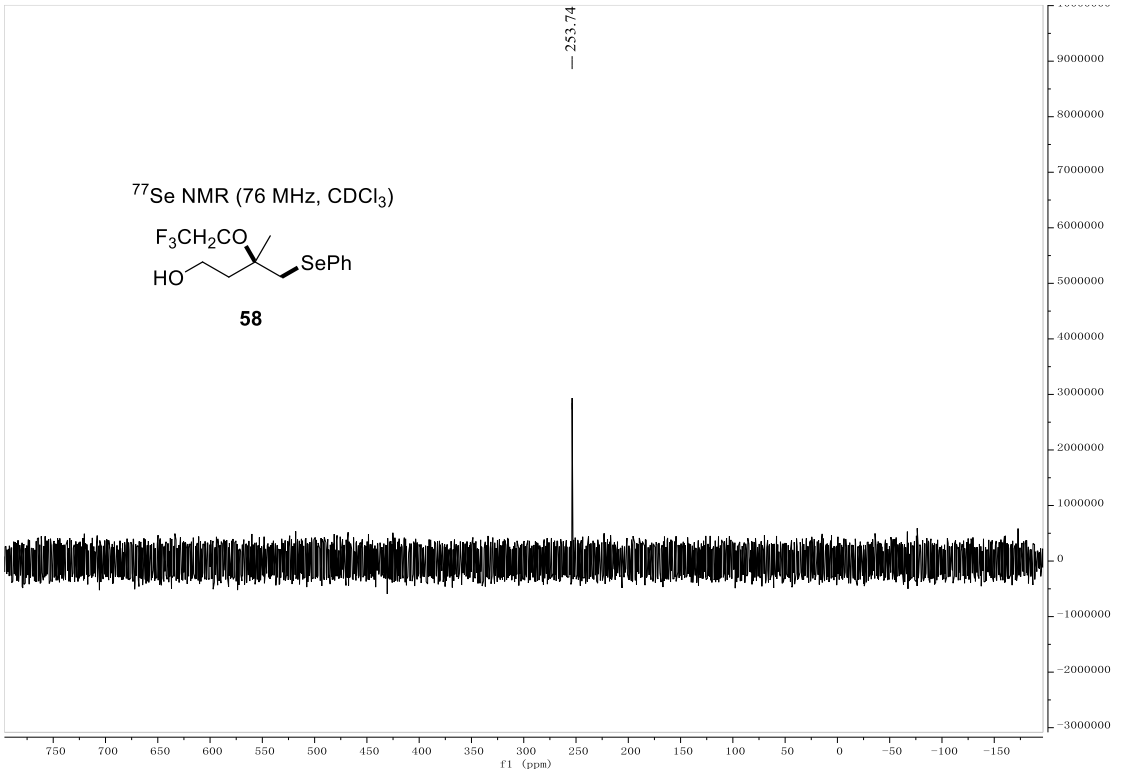
^{13}C NMR of compound **58**



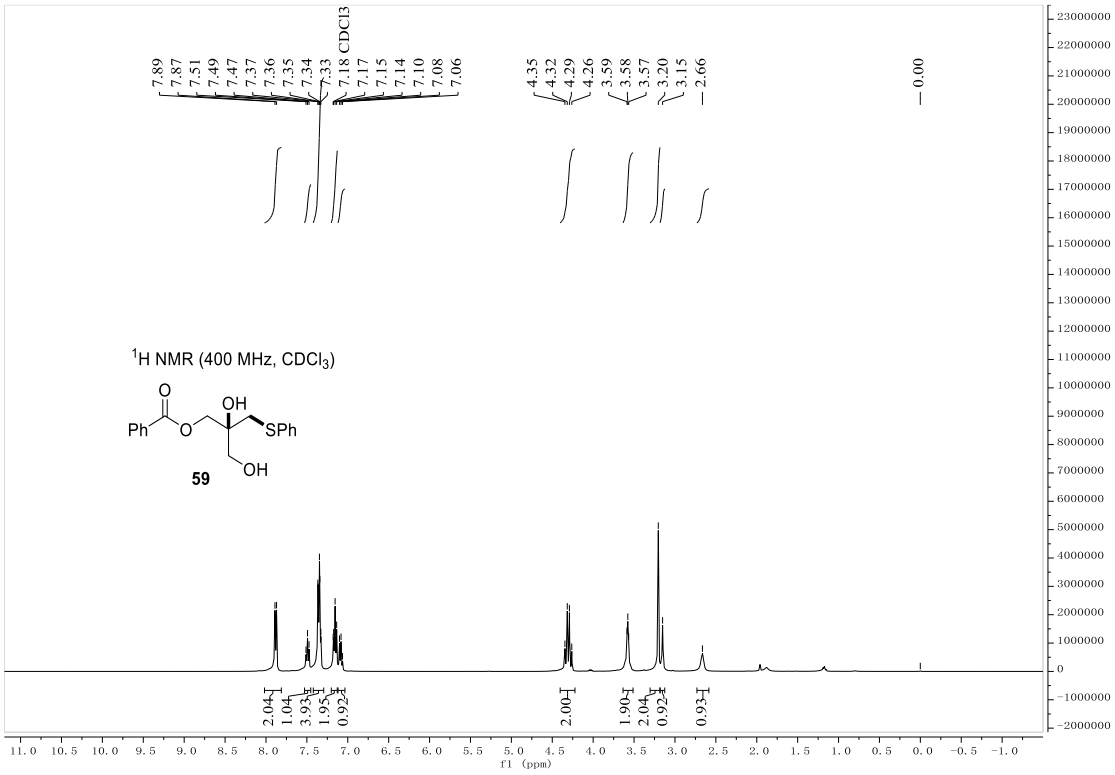
^{19}F NMR of compound **58**



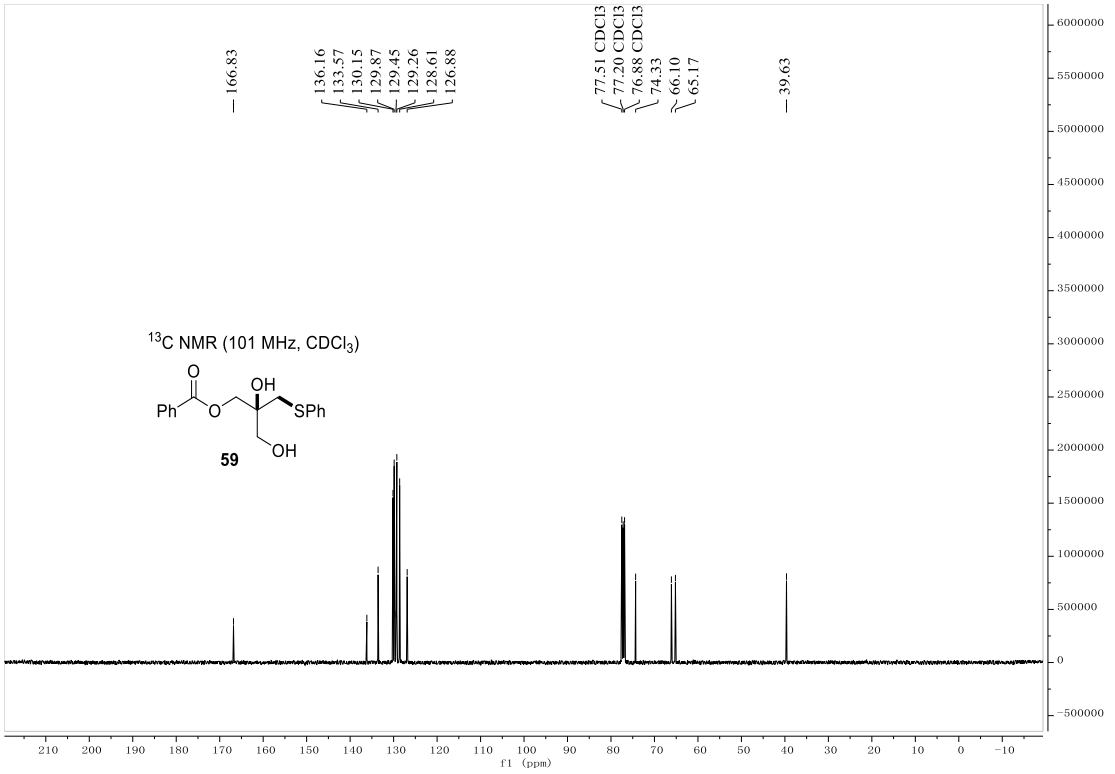
^{77}Se NMR of compound **58**



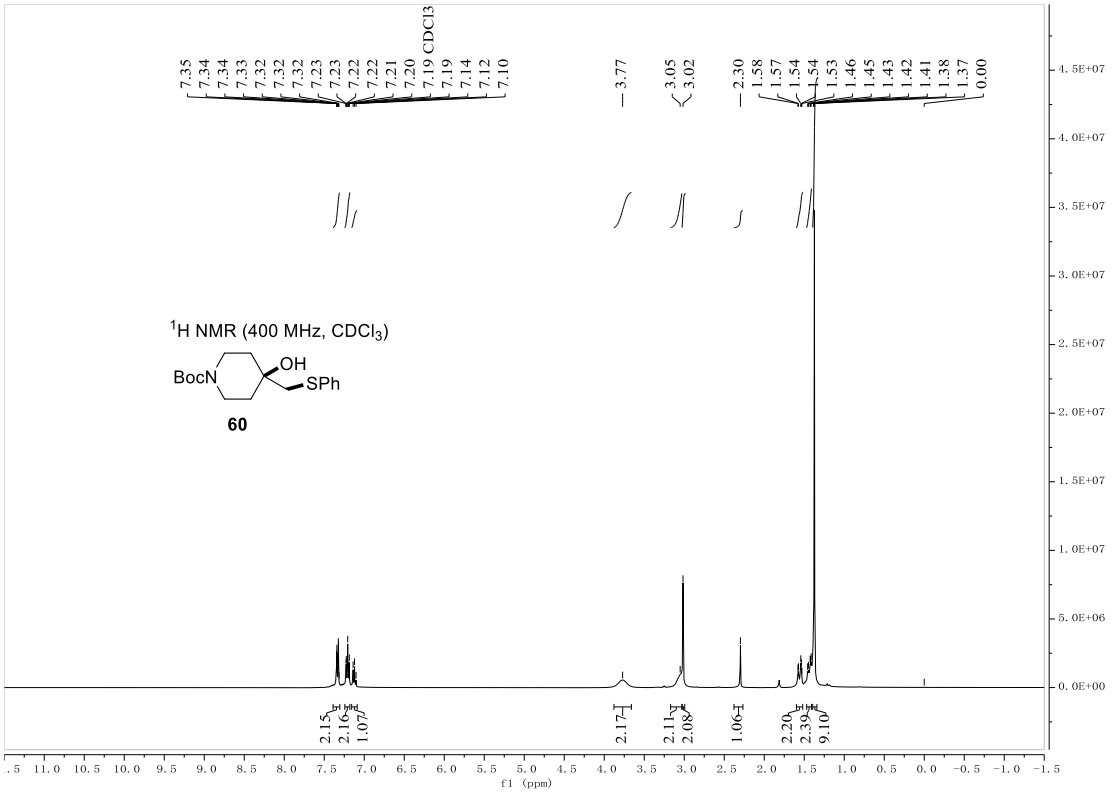
^{1}H NMR of compound **59**



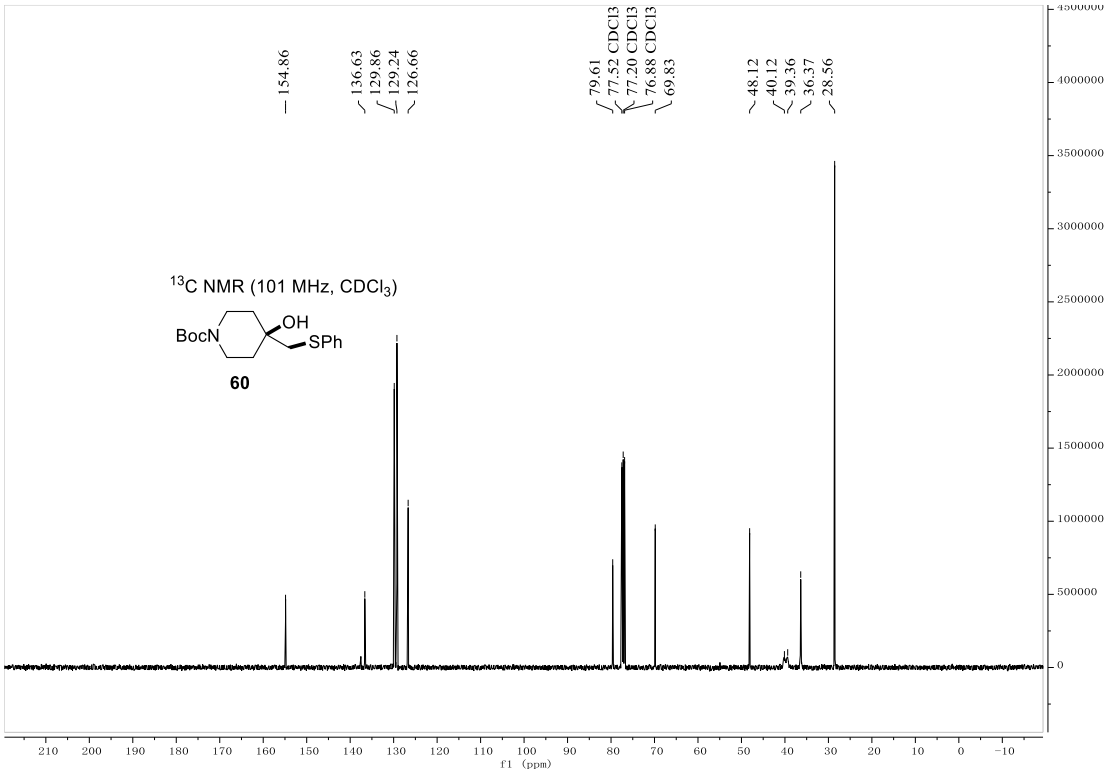
^{13}C NMR of compound **59**



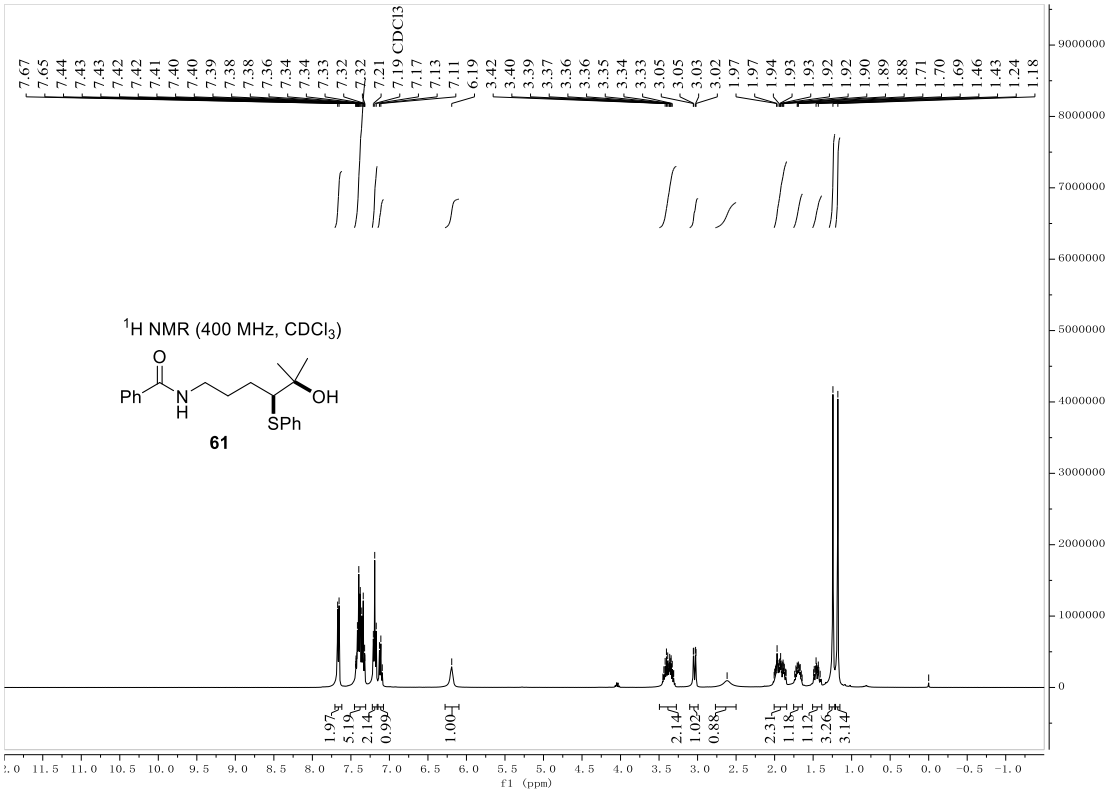
^{1}H NMR of compound **60**



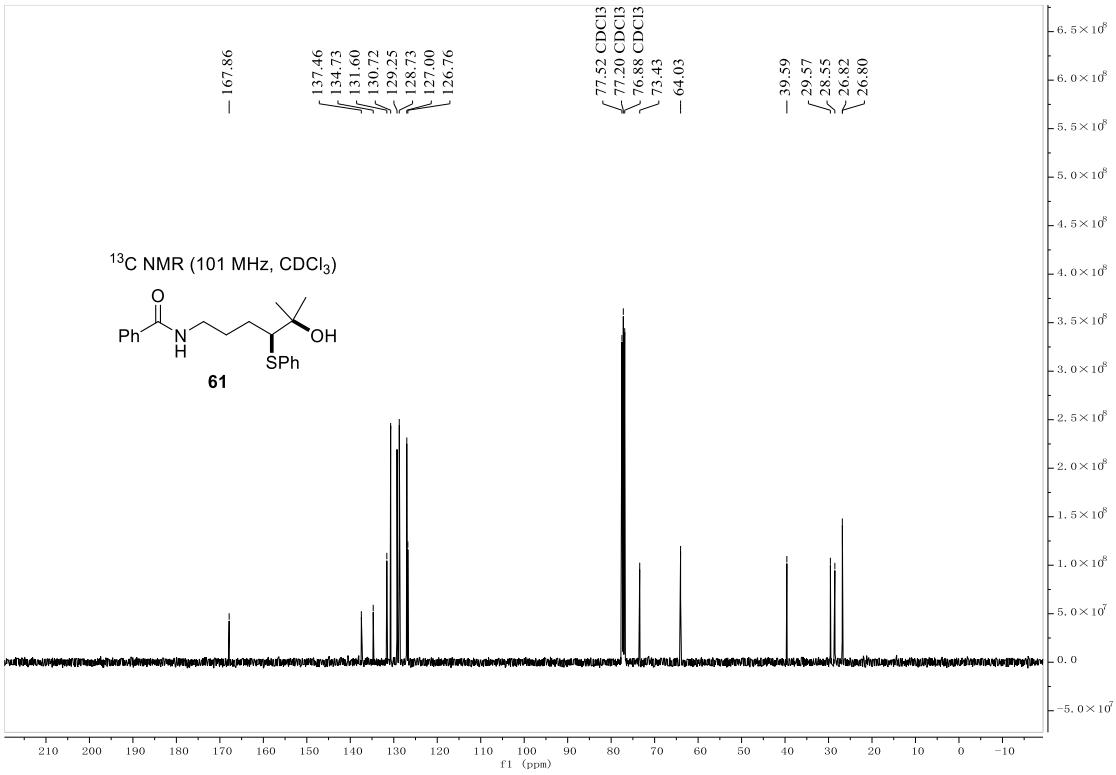
^{13}C NMR of compound **60**



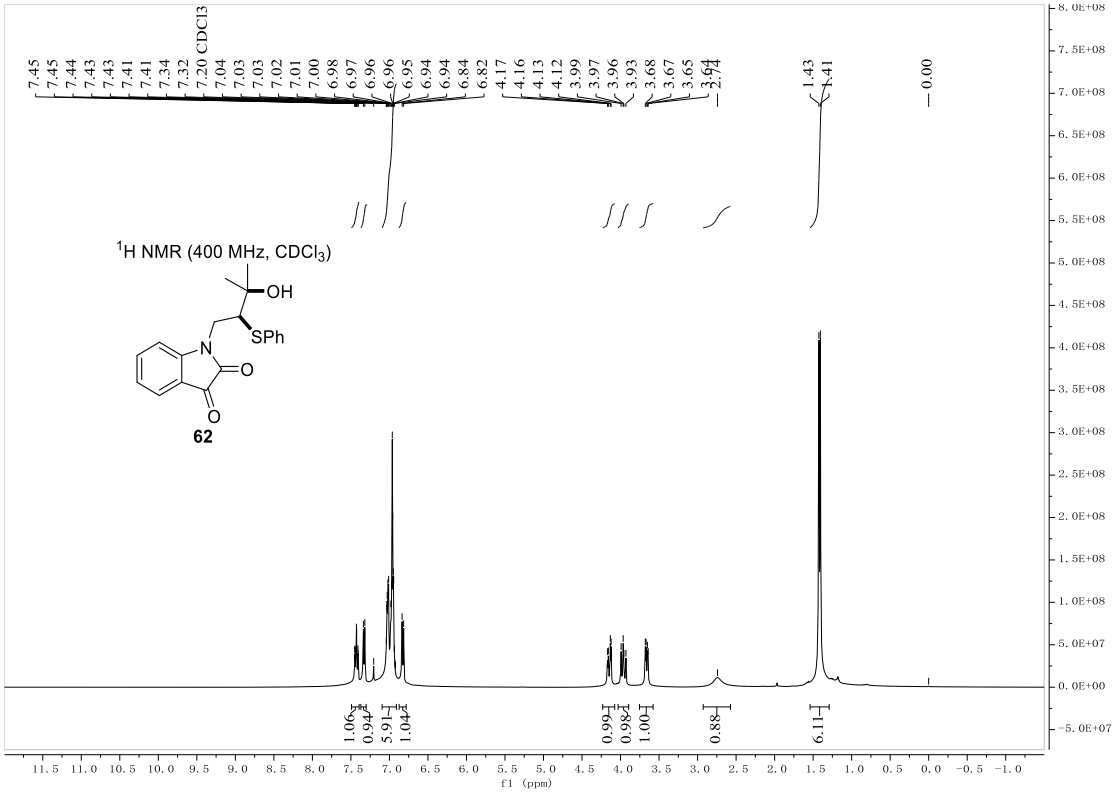
^{1}H NMR of compound **61**



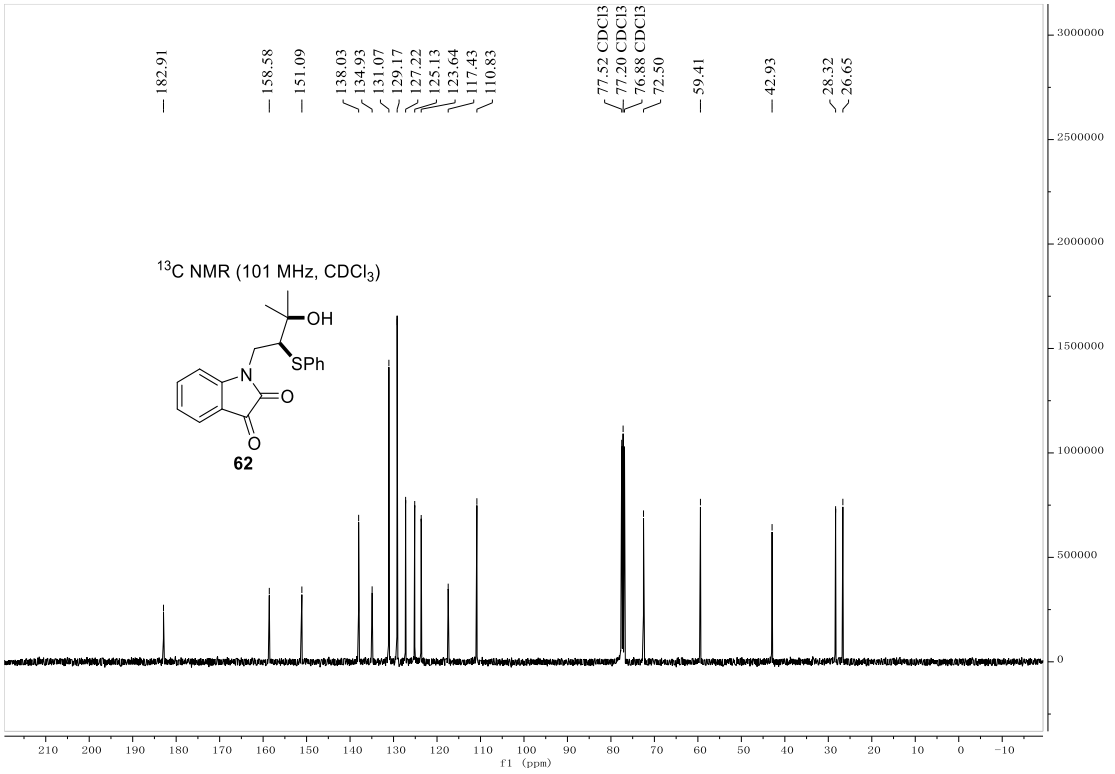
^{13}C NMR of compound **61**



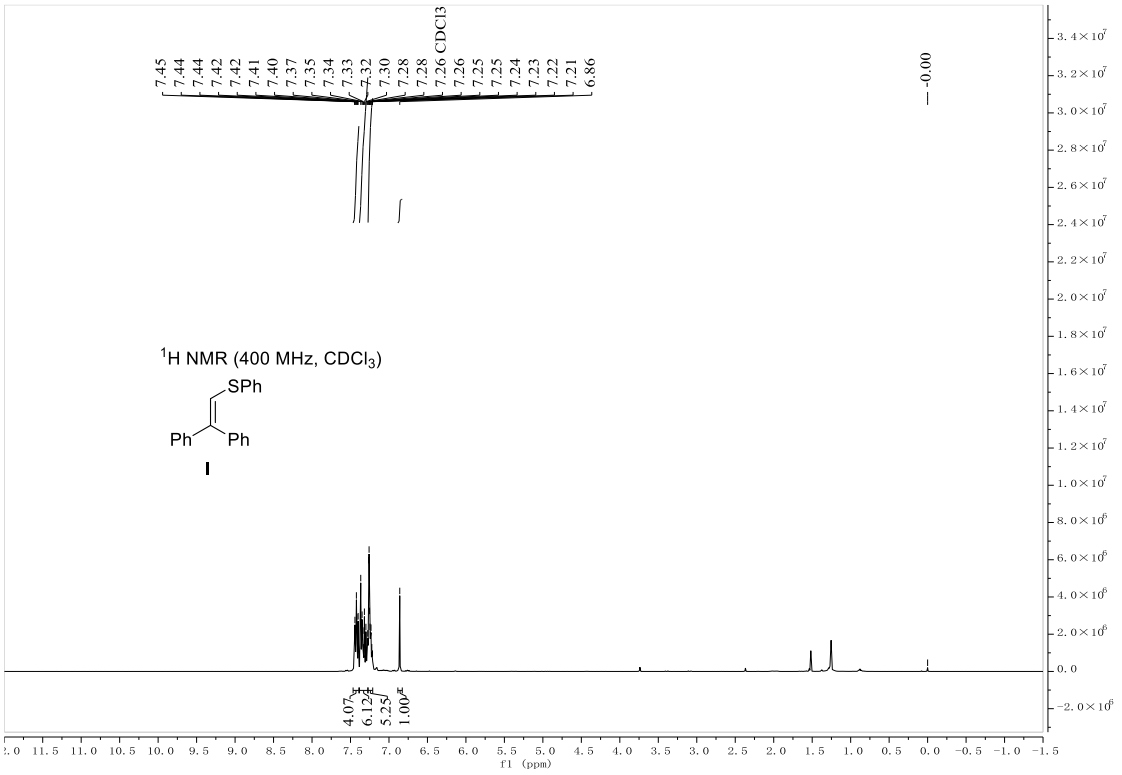
^{1}H NMR of compound **62**



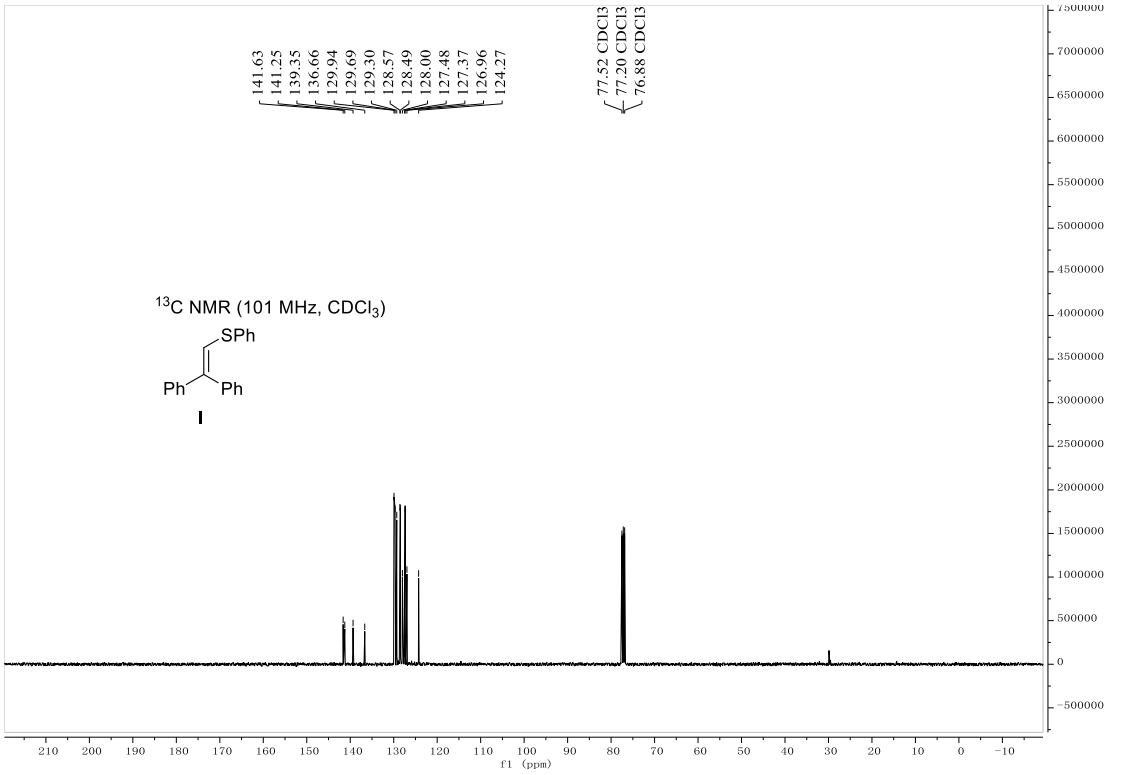
^{13}C NMR of compound **62**



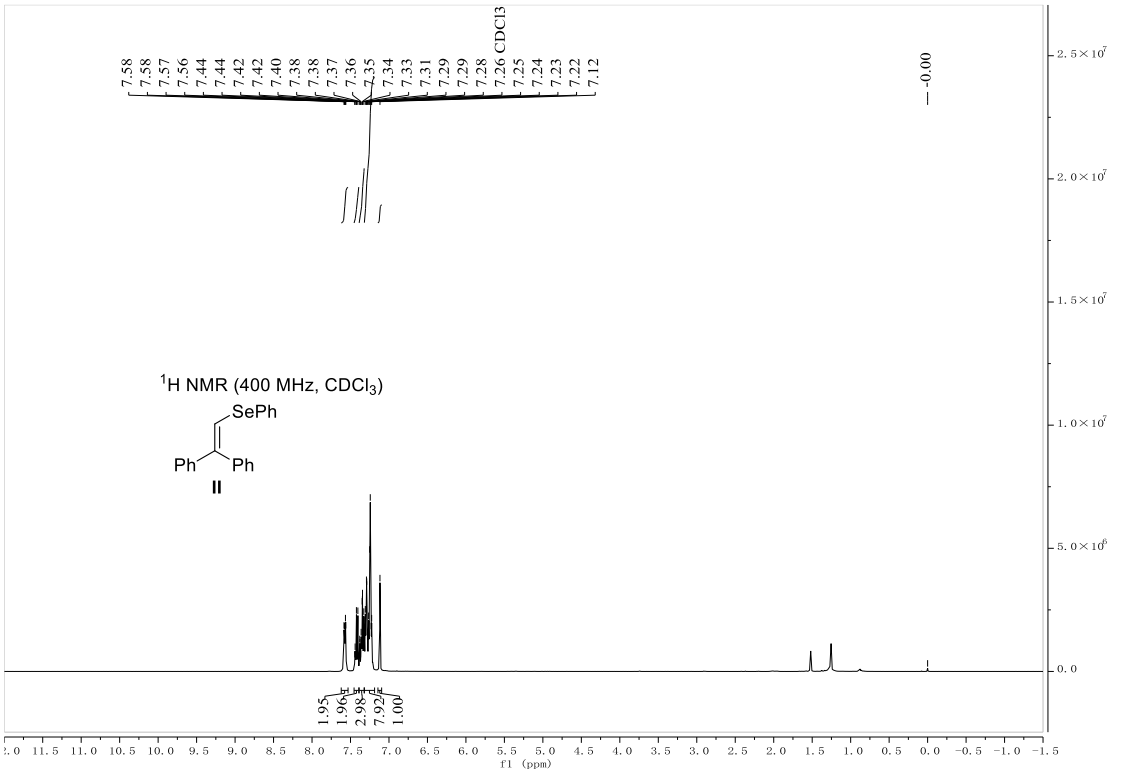
^{1}H NMR of compound **I**



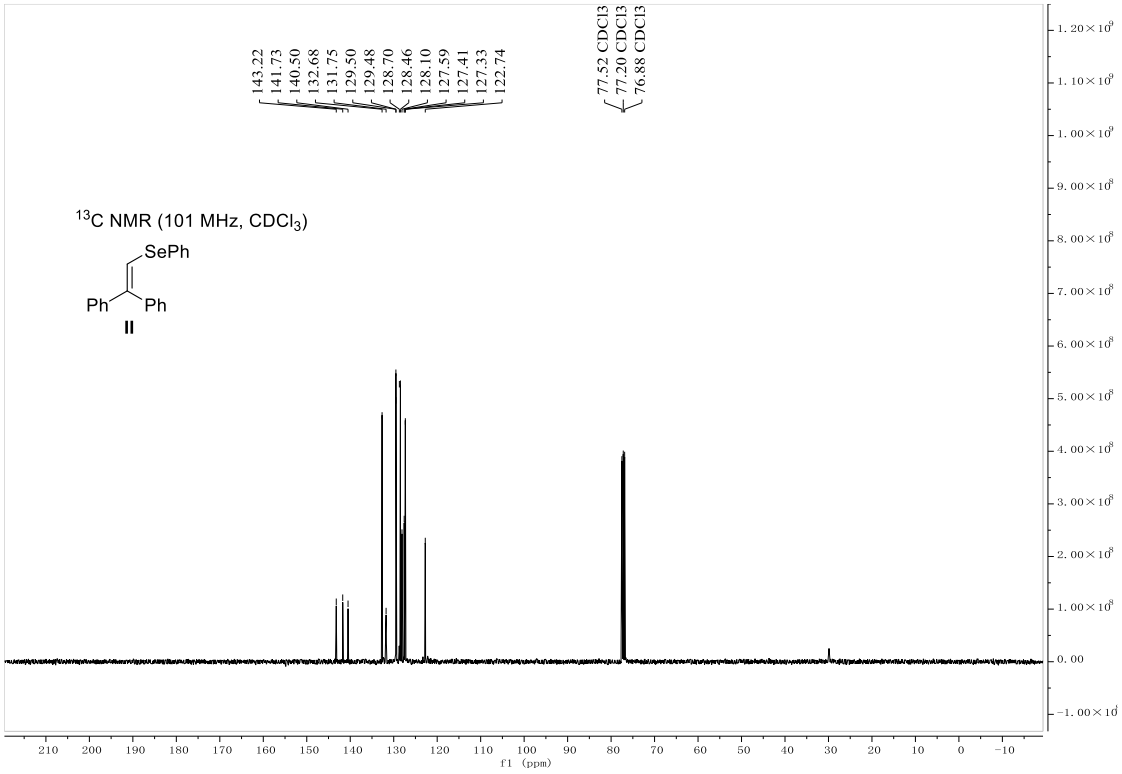
^{13}C NMR of compound **I**



^{1}H NMR of compound **II**



^{13}C NMR of compound **II**



^{77}Se NMR of compound **II**