Supporting Information

Catalytic base-controlled regiodivergent heteronucleophilic hydrofunctionalization of *β,γ*-unsaturated amides

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I. General

^{1}H NMR spectra were acquired on Jeol 400 MHz spectrometers and chemical shifts were recorded relative to tetramethylsilane (δ 0.00) or residual protiated solvent ($CDCl_3$: δ 7.26). Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). The number of protons (n) for a given resonance was indicated by nH. Coupling constants were reported as a *J* value in Hz. ^{13}C NMR spectra were obtained at 100 MHz on 400 MHz instruments and chemical shifts were recorded relative to solvent resonance ($CDCl_3$: δ 77.16). ^{31}P NMR spectra were obtained at 162 MHz on 400 MHz instrument. Proof of purity of new compounds was demonstrated with copies of ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR spectra.

Glassware was dried in an oven at 120 ^{o}C for at least 2 hours before use. Unless noted otherwise, commercially available chemicals were used without further purification. The GC standard, *n*-dodecane was degassed with argon bubbling and dried over activated 4 Å molecular sieve beads for a few days in the glove box before use.

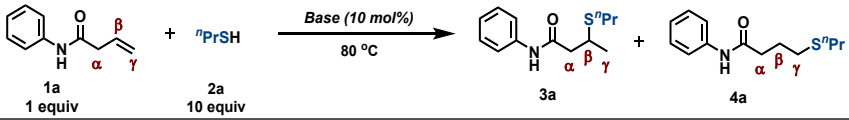
Thin-layer chromatography (TLC) was conducted with Merck 60 F254 coated silica gel plate (0.2 mm thickness). Flash chromatography was performed using Merck silica gel 60 (0.040-0.063 mm) or SiliCycle silica gel F60 (0.040-0.063 mm). The dilute solvents usually used Ethyl Acetate/Petroleum Ether, which was abbreviated as EA:PE.

GCMS analysis was conducted on a Thermo Scientific DSQ II single quadrupole GC/MS instrument with Agilent J & W GC column DB-5MS-UI. ESI/MS analysis was conducted on a ThermoFinnigan LCQ Fleet MS spectrometer. Gas chromatographic (GC) analysis was performed on a SHIMADZU GC-2010 plus instrument equipped with an FID detector and a Agilent J & W GC column DB-5MS-UI.

II. Condition optimization for the Model Reaction

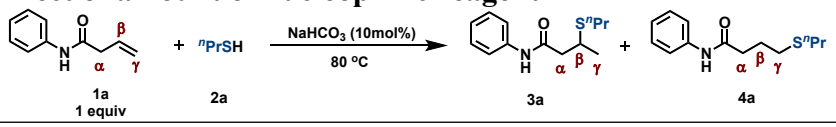
Typical procedure for condition optimization: To a dry 10-mL Schlenk tube containing a magnetic stir bar was added alkenes **1a** (1 equiv, 0.1 mmol, 16.1 mg), catalytic base, nucleophilic reagent **2a** (10 equiv, 1 mmol, 76 mg) were added sequentially. The tube was capped tightly and the mixture was vigorously stirred in a *pre*-warmed 80 °C oil bath. After 24 hours, 10 uL dodecane was added in the tube. After filtering, the filtrate was subjected to GC analysis to determine the conversion of alkenes **1a**, calibrated GC yield of the coupling product. The major byproducts from alkene are the mixture of isomerized cis/trans alkenes and removed aniline group.

Table S1 Effect of base catalysts



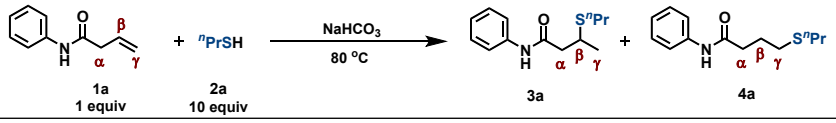
Entry	Base	Alkene (**1a**) /Conversion (%)	Yield of **3a** (%)	Yield of **4a** (%)
1	**$NaHCO_3$**	**100**	**1**	**90**
2	**Cs_2CO_3**	**100**	**88**	**2**
3	Li_2CO_3	97	1	66
4	Na_2CO_3	100	2	83
5	K_2CO_3	100	29	50
6	NaOAc	60	3	23
7	KOAc	94	2	81
8	LiOAc	100	2	85
9	CsOAc	83	2	75
10	$KHCO_3$	100	6	78
11	EtONa	97	2	71
12	CsF	100	71	24
13	LiF	97	1	88
14	KF	94	2	65
15	NaF	98	1	86
16	NaI	96	2	87
17	KI	97	1	71
18	K_3PO_4	100	61	12
19	K_2HPO_4	100	2	83
20	KH_2PO_4	78	2	67
21	CF_3COONa	100	1	77
22	$CsOH·H_2O$	78	23	20
23	NaOH	100	87	2
24	KOH	100	77	14
25	^{t}BuOK	100	88	6
26	^{t}BuONa	100	89	3
27	^{t}BuOLi	100	62	31
28	CH_3ONa	100	2	89
29	CH_3OK	100	1	85
30	CH_3OLi	100	25	64
31	/	86	1	71

Table S2 Effect of amount of nucleophilic reagent



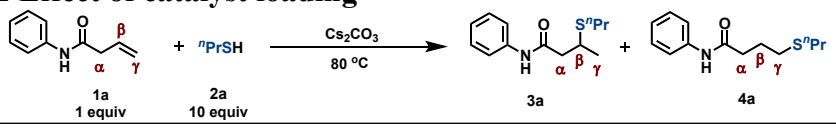
Entry	RSH/ equiv	Alkene (**1a**) /Conversion (%)	Yield of **3a** (%)	Yield of **4a** (%)
1	1	19	1	8
2	2	60	3	41
3	3	75	2	53
4	4	95	1	59
5	5	98	2	76
6	**10**	**100**	**1**	**90**
7	20	100	3	85

Table S3-1 Effect of catalyst loading



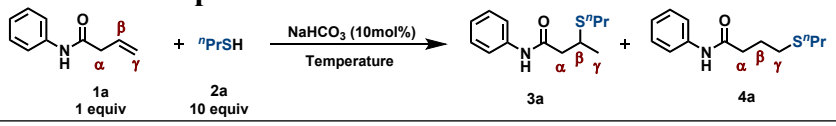
Entry	Catalyst loading	Alkene (**1a**) /Conversion (%)	Yield of **3a** (%)	Yield of **4a** (%)
1	2%	100	1	78
2	4%	100	2	87
3	6%	100	2	88
4	8%	100	2	88
5	**10%**	**100**	**1**	**90**

Table S3-2 Effect of catalyst loading



Entry	Catalyst loading	Alkene (**1a**) /Conversion (%)	Yield of **3a** (%)	Yield of **4a** (%)
1	2%	100	67	23
2	4%	100	80	11
3	6%	100	84	7
4	8%	100	89	4
5	**10%**	**100**	**88**	**2**
6	20%	100	88	2

Table S4-1 Effect of temperature



Entry	Temperature	Alkene (**1a**) /Conversion (%)	Yield of **3a** (%)	Yield of **4a** (%)
1	R.T.	50	0	45
2	40	91	1	75
3	60	100	1	87
4	**80**	**100**	**1**	**90**
5	100	100	1	83

Table S4-2 Effect of temperature

1a
1 equiv

2a
10 equiv

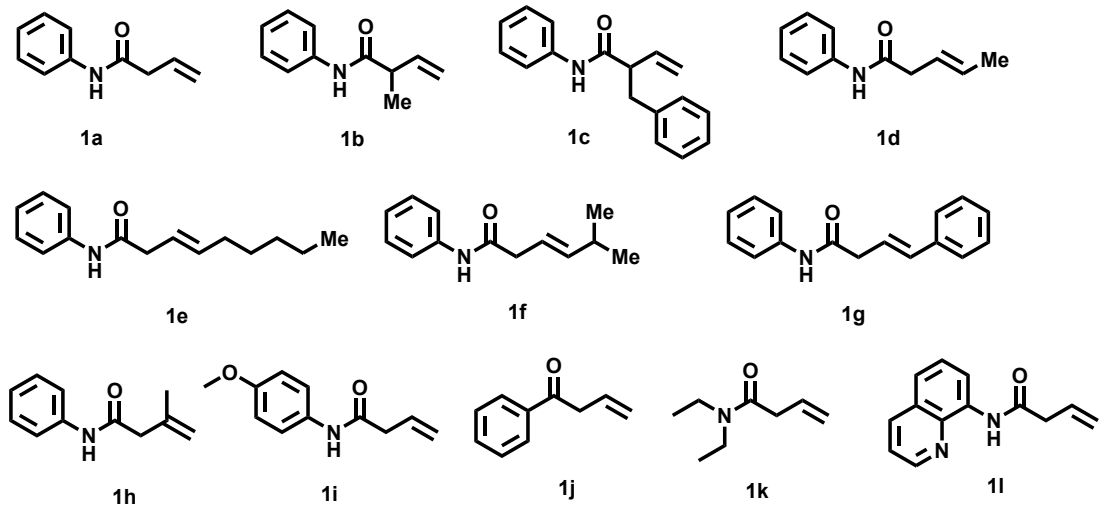
3a

4a

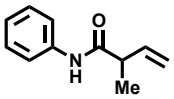
Entry	Temperature	Alkene (**1a**) /Conversion (%)	Yield of **3a** (%)	Yield of **4a** (%)
1	R.T.	7	1	1
2	40	29	8	8
3	60	100	74	16
4	70	100	84	8
5	**80**	**100**	**88**	**2**
6	90	100	89	2
7	100	100	88	2

III. Synthesis of alkene substrates

Table S5. Alkene substrates 1a-1l

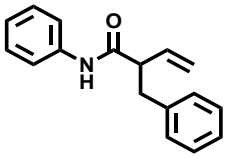


Note: alkene substrates 1a[1], 1d[2], 1f[3], 1g[4], 1h[5], 1i[6], 1j[1], 1k[7], 1l[8], were prepared according to the corresponding literature methods.



2-methyl-*N*-phenylbut-3-enamide (1b): 2-methylbut-3-enoic acid was prepared according to the literature[9]. 2-methylbut-3-enoic acid (500 mg, 5 mmol) was charged into a 50 mL RB flask containing 20 mL DCM at 0 °C. Aniline (418 mg, 4.5 mmol), EDCl (958 mg, 5 mmol), HOBt (765 mg, 5 mmol), and DMAP (56 mg, 0.45 mmol) were added sequentially, and the reaction was stirred at 0 °C for 16 h. The solution was diluted with DCM (100 mL), washed with sat. $NaHCO_3$ (100 mL, ×2) and brine (100 mL, ×1), and purified by column chromatography (EA: PE=1: 5) to afford 700 mg (89%) yield of product as a white solid.

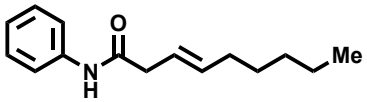
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.50 (m, 2H), 7.34-7.29 (m, 3H), 7.12-7.08 (m, 1H), 6.04-5.95 (m, 1H), 5.35-5.27 (m, 2H), 3.18-3.14 (m, 1H), 1.37 (d, J = 7.0 Hz, 3H).



2-benzyl-*N*-phenylbut-3-enamide (1c): 2-benzylbut-3-enoic acid was prepared according to the literature[10]. 2-benzylbut-3-enoic acid (880 mg, 5 mmol) was charged

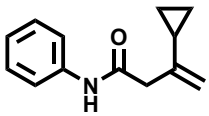
into a 50 mL RB flask containing 20 mL DCM at 0 °C. Aniline (418 mg, 4.5 mmol), EDCl (958 mg, 5 mmol), HOBt (765 mg, 5 mmol), and DMAP (56 mg, 0.45 mmol) were added sequentially, and the reaction was stirred at 0 °C for 16 h. The solution was diluted with DCM (100 mL), washed with sat. $NaHCO_3$ (100 mL, ×2) and brine (100 mL, ×1), and purified by column chromatography (EA: PE=1: 5) to afford 926 mg (82%) yield of product as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.40 (m, 2H), 7.31-7.28 (m, 4H), 7.22-7.19 (m, 3H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.02-5.93 (m, 1H), 5.25-5.19 (m, 2H), 3.32-3.20 (m, 2H), 2.93-2.88 (m, 1H).



(*E*)-*N*-phenylnon-3-enamide (1e): (E)-non-3-enoic acid was prepared according to the literature[3]. (E)-non-3-enoic acid (780 mg, 5 mmol) was charged into a 50 mL RB flask containing 20 mL DCM at 0 °C. Aniline (418 mg, 4.5 mmol), EDCl (958 mg, 5 mmol), HOBt (765 mg, 5 mmol), and DMAP (56 mg, 0.45 mmol) were added sequentially, and the reaction was stirred at 0 °C for 16 h. The solution was diluted with DCM (100 mL), washed with sat. $NaHCO_3$ (100 mL, ×2) and brine (100 mL, ×1), and purified by column chromatography (EA: PE=1: 5) to afford 883 mg (85%) yield of product as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.49 (m, 2H), 7.35 (s, 1H), 7.34-7.30 (m, 2H), 7.13-7.08 (m, 1H), 5.78-5.71 (m, 1H), 5.66-5.58 (m, 1H), 3.11 (dd, *J* = 7.0, 1.1 Hz, 2H), 2.11 (q, *J* = 6.9 Hz, 2H), 1.46-1.39 (m, 2H), 1.36-1.29 (m, 4H), 0.89 (t, *J* = 6.9 Hz, 3H).



3-cyclopropyl-N-phenylbut-3-enamide (11a): 3-cyclopropylbut-3-enoic acid was prepared according to the literature[11]. 3-cyclopropylbut-3-enoic acid (25.2 mg, 0.20 mmol) was charged into a 5 mL RB flask containing 2 mL DCM at 0 °C. Aniline (17 mg, 0.18 mmol), EDCl (38 mg, 0.2 mmol), HOBt (31 mg, 0.2 mmol), and DMAP (2.3 mg, 0.02 mmol) were added sequentially, and the reaction was stirred at 0 °C for 16 h. The solution was diluted with DCM (5 mL), washed with sat. $NaHCO_3$ (5 mL, ×2)

and brine (5 mL, ×1), and purified by column chromatography (EA: PE=1: 5) to afford 28.1 mg (70%) yield of product as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (s, 1H), 7.52-7.49 (m, 2H), 7.35-7.30 (m, 2H), 7.13-7.09 (m, 1H), 5.04-4.98 (m, 2H), 3.13 (d, J = 0.9 Hz, 2H), 1.49-1.42 (m, 1H), 0.77-0.72 (m, 2H), 0.57-0.53 (m, 3H).

IV. Base-catalyzed reactions of various nucleophiles and alkenes

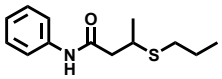
General Procedure A: To a dry 10-mL Schlenk tube containing a magnetic stir bar was charged with alkenes (1 equiv, 0.1 mmol, 16.1 mg), Cs_2CO_3 (10 mol%, 0.01 mmol, 3.3 mg), nucleophilic reagent (10 equiv, 1 mmol) sequentially. The tube was capped tightly and the mixture was vigorously stirred in a pre-warmed 80 ^oC oil bath. After alkenes was almost fully consumed (monitored by GC), the reaction mixture was concentrated on a rotary evaporator, then the resulting residue was directly subjected to preparative TLC. The structure of the desired product was confirmed by ^1H and ^{13}C NMR spectroscopy of the purified sample. The typical procedure using 0.1 mmol of alkenes was applied for all the isolation, unless stated otherwise.

General Procedure B: To a dry 10-mL Schlenk tube containing a magnetic stir bar was charged with alkenes (1 equiv, 0.1 mmol, 16.1 mg), $NaHCO_3$ (10 mol%, 0.01 mmol, 0.8 mg), nucleophilic reagent (10 equiv, 1mmol) sequentially. The tube was capped tightly and the mixture was vigorously stirred in a pre-warmed 80 ^oC oil bath. After alkenes was almost fully consumed (monitored by GC), the reaction mixture was concentrated on a rotary evaporator, then the resulting residue was directly subjected to preparative TLC. The structure of the desired product was confirmed by ^1H and ^{13}C NMR spectroscopy of the purified sample. The typical procedure using 0.1 mmol of alkenes was applied for all the isolation, unless stated otherwise.

General Procedure C: To a dry 10-mL Schlenk tube containing a magnetic stir bar was charged with alkenes (1 equiv, 0.1 mmol, 16.1 mg), CH_3OLi (20 mol%, 0.02 mmol, 0.8 mg), nucleophilic reagent (2 equiv, 0.2 mmol) and THF (0.1 mL) sequentially. The tube was capped tightly and the mixture was vigorously stirred in a pre-warmed 100 ^oC oil bath. After alkenes was almost fully consumed (monitored by GC), the reaction mixture was concentrated on a rotary evaporator, then the resulting residue was directly subjected to preparative TLC. The structure of the desired product was confirmed by ^1H and ^{13}C NMR spectroscopy of the purified sample. The typical procedure using 0.1 mmol of alkenes was applied for all the isolation, unless stated otherwise.

General Procedure D: To a dry 10-mL Schlenk tube containing a magnetic stir bar was charged with alkenes (1 equiv, 0.1 mmol, 16.1 mg), Na_3PO_4 (10 mol%, 0.01 mmol, 1.6 mg), nucleophilic reagent (2 equiv, 0.2 mmol) and THF (0.1 mL) sequentially. The tube was capped tightly and the mixture was vigorously stirred in a pre-warmed 100 ^oC oil bath. After alkenes was almost fully consumed (monitored by GC), the reaction mixture

was concentrated on a rotary evaporator, then the resulting residue was directly subjected to preparative TLC. The structure of the desired product was confirmed by ^{1}H and ^{13}C NMR spectroscopy of the purified sample. The typical procedure using 0.1 mmol of alkenes was applied for all the isolation, unless stated otherwise.

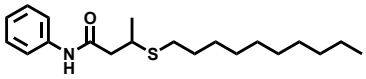


***N*-phenyl-3-(propylthio)butanamide (3a).** The reaction was conducted according to general procedure A, the reaction mixture was stirred at 80 °C for 6 hours. The product was purified by preparative TLC (1:10 EA:PE) as colorless oil (21 mg, 88%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (s, 1H), 7.52 (d, *J* = 7.9 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.10 (t, *J* = 7.3 Hz, 1H), 3.33-3.24 (m, 1H), 2.64-2.49 (m, 4H), 1.66-1.57 (m, 2H), 1.36 (d, *J* = 6.8 Hz, 3H), 0.97 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.42, 137.88, 129.07, 124.45, 120.10, 45.31, 37.00, 33.19, 23.15, 21.92, 13.67.

HRMS (ESI): Calcd for $C_{13}H_{19}NOS$ $[M+H]^+$: 238.1266, Found: 238.1268.

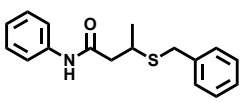


3-(decylthio)-*N*-phenylbutanamide (3b). The reaction was conducted according to general procedure A, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:10 EA:PE) as white solid (26 mg, 77%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (s, 1H), 7.52 (d, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.9 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 3.31-3.25 (m, 1H), 2.64-2.50 (m, 4H), 1.63-1.56 (m, 2H), 1.38 (d, *J* = 6.8 Hz, 3H), 1.34-1.25 (m, 14H), 0.87 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.16, 137.84, 129.11, 124.45, 119.95, 45.37, 37.12, 31.99, 31.28, 29.82, 29.65, 29.63, 29.42, 29.32, 29.09, 22.79, 21.97, 14.25.

HRMS (ESI): Calcd for $C_{20}H_{33}NOS$ $[M+H]^+$: 336.2361, Found: 336.2366.

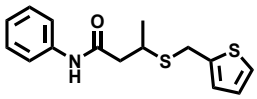


3-(benzylthio)-*N*-phenylbutanamide (3c). The reaction was conducted according to general procedure A, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:10 EA:PE) as yellow oil (26 mg, 91%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (s, 1H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.35-7.29 (m, 6H), 7.26-7.22 (m, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 3.84-3.76 (m, 2H), 3.27-2.18 (m, 1H), 2.58-2.44 (m, 2H), 1.35 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.12, 138.34, 137.80, 129.07, 128.93, 128.76, 127.29, 124.47, 120.06, 45.15, 36.85, 35.72, 21.62.

HRMS (ESI): Calcd for $C_{17}H_{19}NOS$ $[M+H]^+$: 286.1266, Found: 286.1267.

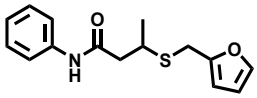


***N*-phenyl-3-((thiophen-2-ylmethyl)thio)butanamide (3d).** The reaction was conducted according to general procedure A, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:10 EA:PE) as yellow soild (29 mg, 98%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.49 (m, 3H), 7.35-7.30 (m, 2H), 7.21 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.13-7.09 (m, 1H), 6.98-6.96 (m, 1H), 6.93-6.91 (m, 1H), 4.08-3.98 (m, 2H), 3.33-3.24 (m, 1H), 2.61-2.47 (m, 2H), 1.38 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.03, 141.83, 137.79, 129.08, 126.94, 126.33, 125.20, 124.50, 120.09, 45.12, 37.00, 30.13, 21.50.

HRMS (ESI): Calcd for $C_{15}H_{17}NOS_2$ $[M+H]^+$: 292.0830, Found: 292.0830.

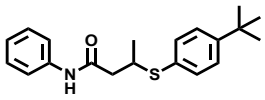


3-((furan-2-ylmethyl)thio)-*N*-phenylbutanamide (3e). The reaction was conducted according to general procedure A, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:10 EA:PE) as yellow oil (25 mg, 92%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (s, 1H), 7.50 (d, *J* = 7.7 Hz, 2H), 7.34-7.29 (m, 3H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.31-6.21 (m, 2H), 3.86-3.77 (m, 2H), 3.32-3.24 (m, 1H), 2.59-2.45 (m, 2H), 1.36 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.07, 151.49, 142.29, 137.83, 129.08, 124.46, 120.04, 110.75, 107.83, 45.02, 37.15, 27.73, 21.54.

HRMS (ESI): Calcd for $C_{15}H_{17}NO_2S$ $[M+H]^+$: 276.1058, Found: 276.1059.

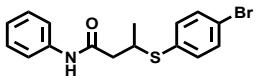


3-((4-(tert-butyl)phenyl)thio)-*N*-phenylbutanamide (3f). The reaction was conducted according to general procedure A, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:10 EA:PE) as yellow solid (25 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (s, 1H), 7.50-7.48 (m, 2H), 7.39-7.37 (m, 2H), 7.33-7.29 (m, 4H), 7.10 (t, *J* = 7.4 Hz, 1H), 3.74-3.66 (m, 1H), 2.68-2.63 (m, 1H), 2.48-2.42 (m, 1H), 1.39 (d, *J* = 6.8 Hz, 3H), 1.29 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.09, 151.05, 137.78, 132.82, 130.01, 129.13, 126.28, 124.52, 120.01, 44.73, 40.36, 34.69, 31.35, 21.15.

HRMS (ESI): Calcd for $C_{20}H_{25}NOS$ $[M+H]^+$: 328.1735, Found: 328.1734.

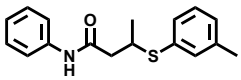


3-((4-bromophenyl)thio)-*N*-phenylbutanamide (3g). The reaction was conducted according to general procedure A, 4-bromobenzenethiol (2 equiv, 0.2 mmol, 38 mg), THF (0.1 mL) was added, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:10 EA:PE) as yellow oil (27 mg, 77%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (s, 1H), 7.49-7.47 (m, 2H), 7.41-7.38 (m, 2H), 7.32-7.26 (m, 4H), 7.13-7.09 (m, 1H), 3.79-3.70 (m, 1H), 2.64 (dd, *J* = 14.8, 6.3 Hz, 1H), 2.46 (dd, *J* = 14.8, 7.6 Hz, 1H), 1.36 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.90, 137.65, 133.85, 133.29, 132.22, 129.11, 124.69, 121.62, 120.20, 44.68, 40.20, 21.11.

HRMS (ESI): Calcd for $C_{16}H_{16}BrNOS$ $[M+H]^+$: 350.0214, Found: 350.0212.

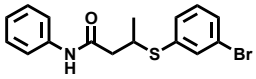


***N*-phenyl-3-(m-tolylthio)butanamide (3h).** The reaction was conducted according to general procedure A, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:10 EA:PE) as yellow solid (21 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.51 (d, *J* = 7.7 Hz, 2H), 7.32-7.23 (m, 4H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.13-7.05 (m, 2H), 3.81-3.72 (m, 1H), 2.70-2.64 (m, 1H), 2.50-2.44 (m, 1H), 2.31 (s, 3H), 1.38 (d, *J* = 6.7Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.19, 138.96, 137.76, 133.59, 133.05, 129.42, 129.06, 128.98, 128.39, 124.51, 120.12, 44.59, 40.05, 21.39, 21.08.

HRMS (ESI): Calcd for $C_{17}H_{19}NOS$ $[M+H]^+$: 286.1266, Found: 286.1268.

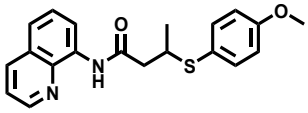


3-((3-bromophenyl)thio)-*N*-phenylbutanamide (3i). The reaction was conducted according to general procedure A, 3-bromobenzenethiol (2 equiv, 0.2 mmol, 38 mg), THF (0.1 mL) was added, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:10 EA:PE) as yellow solid (30 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (s, 1H), 7.57 (t, *J* = 1.8 Hz, 1H), 7.51-7.48 (m, 2H), 7.37-7.29 (m, 4H), 7.17-7.09 (m, 2H), 3.84-3.76 (m, 1H), 2.69-2.63 (m, 1H), 2.51-2.45 (m, 1H), 1.39 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.73, 137.59, 136.57, 134.40, 130.50, 130.42, 129.14, 124.69, 122.85, 120.11, 44.66, 40.06, 21.11.

HRMS (ESI): Calcd for $C_{16}H_{16}BrNOS$ $[M+H]^+$: 350.0214, Found: 350.0210.

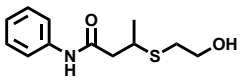


3-((4-methoxyphenyl)thio)-*N*-(quinolin-8-yl)butanamide (3j). The reaction was conducted according to general procedure A, alkene 2l (1 equiv, 0.1 mmol, 21.2 mg) was added, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:20 EA:PE) as yellow oil (28 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.87 (s, 1H), 8.81 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.75 (dd, *J* = 6.7, 2.3 Hz, 1H), 8.16 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.55-7.44 (m, 5H), 6.85-6.82 (m, 2H), 3.78 (s, 3H), 3.74-3.65 (m, 1H), 2.83 (dd, *J* = 14.8, 6.2 Hz, 1H), 2.62 (dd, *J* = 14.8, 7.8 Hz, 1H), 1.40 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.46, 159.80, 148.28, 138.39, 136.49, 136.28, 134.40, 128.01, 127.49, 123.90, 121.76, 121.72, 116.66, 114.60, 55.40, 45.39, 41.12, 21.13.

HRMS (ESI): Calcd for $C_{20}H_{20}N_2O_2S$ $[M+H]^+$: 353.1324, Found: 353.1327.

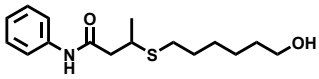


3-((2-hydroxyethyl)thio)-*N*-phenylbutanamide (3k). The reaction was conducted according to general procedure A, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:10 MeOH:DCM) as yellow oil (17 mg, 71%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (s, 1H), 7.52 (d, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 3.81-3.76 (m, 2H), 3.43-3.35 (m, 1H), 3.04 (s, 1H), 2.76 (t, *J* = 5.7 Hz, 2H), 2.57 (d, *J* = 7.0 Hz, 2H), 1.37 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.54, 137.75, 129.13, 124.62, 120.15, 61.53, 45.35, 36.90, 34.10, 22.32.

HRMS (ESI): Calcd for $C_{12}H_{17}NO_2S[M+H]^+$: 240.1058, Found: 240.1061.

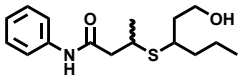


3-((6-hydroxyhexyl)thio)-*N*-phenylbutanamide (3l). The reaction was conducted according to general procedure A, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:10 MeOH:DCM) as yellow oil (27 mg, 91%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (s, 1H), 7.52 (d, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.10 (t, *J* = 7.7 Hz, 1H), 3.62 (t, *J* = 6.8 Hz, 2H), 3.31-3.26 (m, 1H), 2.63-2.49 (m, 4H), 1.64-1.52 (m, 5H), 1.42-1.33 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.33, 137.90, 129.12, 124.49, 120.05, 62.89, 45.48, 37.13, 32.63, 31.08, 29.67, 28.67, 25.36, 21.99.

HRMS (ESI): Calcd for $C_{16}H_{25}NO_2S$ $[M+H]^+$: 296.1684, Found: 296.1691.

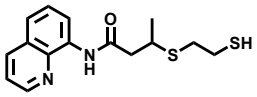


3-((1-hydroxyhexan-3-yl)thio)-*N*-phenylbutanamide (3m). The reaction was conducted according to general procedure A, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:10 MeOH:DCM) as colorless oil (21 mg, 72%). The dr value is 1.1:1 analysis by GCMS.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 47.1 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 3.88-3.82 (m, 1H), 3.79-3.65 (m, 1H), 3.42-3.29 (m, 1H), 2.96-2.88 (m, 1H), 2.86-2.48 (m, 3H), 1.94-1.84 (m, 2H), 1.61-1.42 (m, 4H), 1.40-1.37 (m, 3H), 0.93-0.85 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.65, 169.62, 137.93, 137.82, 129.12, 129.09, 124.55, 124.46, 120.05, 119.98, 60.52, 60.14, 45.90, 45.88, 43.55, 41.65, 39.11, 38.46, 38.04, 37.62, 37.51, 36.54, 22.86, 22.51, 20.13, 20.07, 14.18, 14.10.

HRMS (ESI): Calcd for $C_{16}H_{25}NO_2S$ $[M+H]^+$: 296.1684, Found: 296.1687.

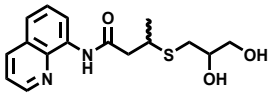


3-((2-mercaptoethyl)thio)-*N*-(quinolin-8-yl)butanamide (3n). The reaction was conducted according to general procedure A, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:8 EA/PE) as yellow oil (21 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.90 (s, 1H), 8.81 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.78 (dd, *J* = 6.8, 2.2 Hz, 1H), 8.16 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.56-7.44 (m, 3H), 3.50-3.42 (m, 1H), 2.88-2.82 (m, 3H), 2.79-2.69 (m, 3H), 1.74 (t, *J* = 8.0 Hz, 1H), 1.44 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.28, 148.38, 138.46, 136.54, 134.39, 128.08, 127.53, 121.88, 121.81, 116.74, 46.34, 37.08, 35.36, 25.07, 22.12.

HRMS (ESI): Calcd for $C_{15}H_{18}N_2OS_2$ $[M+H]^+$: 307.0939, Found: 307.0937.

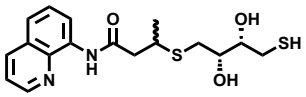


3-((2,3-dihydroxypropyl)thio)-*N*-(quinolin-8-yl)butanamide (3o). The reaction was conducted according to general procedure A, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:10 MeOH:DCM) as yellow oil (19 mg, 60%). The dr value is 1:1 analysis by GCMS.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.98 (s, 1H), 8.81-8.76 (m, 2H), 8.18-8.15 (m, 1H), 7.54-7.44 (m, 3H), 3.95-3.88 (m, 1H), 3.75-3.71 (m, 1H), 3.62-3.57 (m, 1H), 3.56-3.44 (m, 1H), 2.86-2.78 (m, 3H), 2.75-2.63 (m, 1H), 1.45 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.80, 169.73, 148.46, 148.44, 138.44, 136.75, 136.72, 134.24, 134.22, 128.16, 128.16, 127.55, 122.10, 122.08, 121.80, 117.18, 117.12, 71.87, 70.31, 65.59, 65.52, 45.73, 45.64, 37.69, 36.91, 34.83, 34.30, 22.49, 22.20.

HRMS (ESI): Calcd for $C_{16}H_{20}N_2O_3S$ $[M+H]^+$: 321.1273, Found: 321.1271.

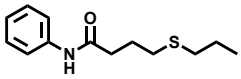


3-(((2*S*,3*S*)-2,3-Dihydroxy-4-mercaptobutyl)thio)-*N*-(quinolin-8-yl)butanamide (3p). The reaction was conducted according to general procedure A, (2*R*,3*S*)-3,4-dimercaptobutane-1,2-diol (2 equiv, 0.2 mmol, 30 mg) was added, neat condition, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:10 MeOH:DCM) as yellow oil (22 mg, 61%). The dr value is 1:1 analysis by GCMS.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.94 (d, *J* = 4.5 Hz, 1H), 8.79-8.73 (m, 2H), 8.14-8.11 (m, 1H), 7.54-7.41 (m, 3H), 3.93-3.83 (m, 2H), 3.53-3.44 (m, 1H), 3.02-2.95 (m, 1H), 2.93-2.90 (m, 1H), 2.88-2.81 (m, 2H), 2.79-2.70 (m, 2H), 1.44-1.41 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.80, 169.73, 148.44, 138.36, 136.68, 136.64, 134.12, 128.09, 127.48, 122.08, 121.76, 117.12, 117.08, 74.08, 72.05, 70.73, 45.65, 37.69, 36.96, 35.23, 34.79, 28.59, 22.40, 22.16.

HRMS (ESI): Calcd for $C_{17}H_{22}N_2O_3S_2$ $[M+H]^+$: 367.1150, Found: 367.1150.

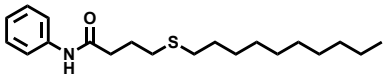


***N*-phenyl-4-(propylthio)butanamide (4a).** The reaction was conducted according to general procedure B, the reaction mixture was stirred at 80 °C for 6 hours. The product was purified by preparative TLC (1:10 EA:PE) as yellow solid (21 mg, 90%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (s, 1H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.28 (t, *J* = 8.0 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 2.56 (t, *J* = 7.0 Hz, 2H), 2.49-2.44 (m, 4H), 2.02-1.95 (m, 2H), 1.62-1.53 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.10, 137.97, 128.98, 124.29, 120.00, 36.02, 33.90, 31.27, 25.01, 22.93, 13.57.

HRMS (ESI): Calcd for $C_{13}H_{19}NOS$ $[M+H]^+$: 238.1266, Found: 238.1273.

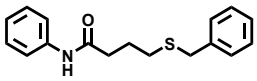


4-(decylthio)-*N*-phenylbutanamide (4b). The reaction was conducted according to general procedure B, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:10 EA:PE) as yellow solid (21 mg, 64%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 7.7 Hz, 3H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 2.60 (t, *J* = 6.9 Hz, 2H), 2.52-2.47 (m, 4H), 2.05-1.98 (m, 2H), 1.58-1.53 (m, 2H), 1.49-1.31 (m, 2H), 1.29-1.25 (m, 12H), 0.87 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.73, 137.93, 129.16, 124.39, 119.82, 36.11, 32.03, 32.00, 31.40, 29.75, 29.71, 29.68, 29.46, 29.39, 29.08, 24.88, 22.83, 14.28.

HRMS (ESI): Calcd for $C_{20}H_{33}NOS$ $[M+H]^+$: 336.2361, Found: 336.2364.

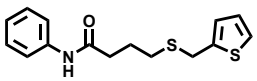


4-(benzylthio)-*N*-phenylbutanamide (4c). The reaction was conducted according to general procedure B, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:10 EA:PE) as white solid (24 mg, 83%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.3 Hz, 2H), 7.39 (s, 1H), 7.33-7.29 (m, 6H), 7.24-7.21 (m, 1H), 7.12-7.08 (m, 1H), 3.71 (s, 2H), 2.51 (t, *J* = 6.9 Hz, 2H), 2.43 (t, *J* = 7.2 Hz, 2H), 2.01-1.94 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.76, 138.39, 137.89, 129.09, 128.95, 128.63, 127.13, 124.38, 119.92, 36.06, 30.70, 24.53.

HRMS (ESI): Calcd for $C_{17}H_{19}NOS$ $[M+H]^+$: 286.1266, Found: 286.1270.

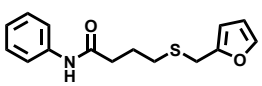


***N*-phenyl-4-((thiophen-2-ylmethyl)thio)butanamide (4d).** The reaction was conducted according to general procedure B, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:10 EA:PE) as yellow solid (26 mg, 89%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.7 Hz, 2H), 7.33-7.25 (m, 3H), 7.17 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.91-6.87 (m, 2H), 3.92 (s, 2H), 2.58 (t, *J* = 6.9 Hz, 2H), 2.44 (t, *J* = 7.2 Hz, 2H), 2.02-1.95 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.66, 141.97, 137.88, 129.11, 126.82, 126.31, 125.07, 124.40, 119.92, 36.05, 30.93, 30.41, 24.44.

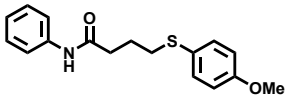
HRMS (ESI): Calcd for $C_{15}H_{17}NOS_2$ $[M+H]^+$: 292.0830, Found: 292.0829.



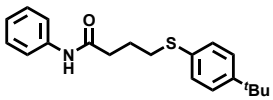
4-((furan-2-ylmethyl)thio)-*N*-phenylbutanamide (4e). The reaction was conducted according to general procedure B, the reaction mixture was stirred at 80 °C for 24 hours.

The product was purified by preparative TLC (1:10 EA:PE) as yellow oil (18 mg, 64%).

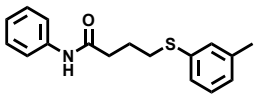
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 7.7 Hz, 2H), 7.33-7.29 (m, 4H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.29-6.28 (m, 1H), 6.18 (d, *J* = 3.2 Hz, 1H), 3.72 (s, 2H), 2.60 (t, *J* = 6.9 Hz, 2H), 2.46 (t, *J* = 7.2 Hz, 2H), 2.03-1.96 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 170.66, 151.50, 142.29, 137.89, 129.12, 124.41, 119.88, 110.56, 107.74, 36.01, 31.10, 28.14, 24.50.
HRMS (ESI): Calcd for $C_{15}H_{17}NO_2S$ $[M+H]^+$: 276.1058, Found: 276.1059.



4-((4-methoxyphenyl)thio)-*N*-phenylbutanamide (4f). The reaction was conducted according to general procedure B, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:10 EA:PE) as yellow solid (16 mg, 54%).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.38-7.35 (m, 2H), 7.33-7.29 (m, 2H), 7.14 (s, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.86-6.82 (m, 2H), 3.78 (s, 3H), 2.92 (t, *J* = 6.8 Hz, 2H), 2.51 (t, *J* = 7.2 Hz, 2H), 2.04-1.97 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 133.54, 129.15, 124.43, 119.82, 114.79, 55.47, 35.81, 35.22, 24.88.
HRMS (ESI): Calcd for $C_{17}H_{19}NO_2S$ $[M+H]^+$: 302.1215, Found: 302.1213.



4-((4-(tert-butyl)phenyl)thio)-*N*-phenylbutanamide (4g). The reaction was conducted according to general procedure B, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:10 EA:PE) as yellow oil (30 mg, 93%).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.48 (m, 2H), 7.35 (s, 1H), 7.33-7.28 (m, 6H), 7.10 (t, *J* = 7.4 Hz, 1H), 2.99 (t, *J* = 6.9 Hz, 2H), 2.52 (t, *J* = 7.2 Hz, 2H), 2.09-2.02 (m, 2H), 1.30 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 170.63, 149.64, 137.85, 132.17, 129.75, 129.11, 126.20, 124.41, 119.91, 35.85, 34.58, 33.46, 31.38, 24.78.
HRMS (ESI): Calcd for $C_{20}H_{25}NOS$ $[M+H]^+$: 328.1735, Found: 328.1739.

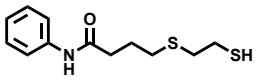


3-(benzyl(methyl)amino)-*N*-(quinolin-8-yl)butanamide (4h). The reaction was conducted according to general procedure B, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:10 EA:PE) as yellow solid (21 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.8 Hz, 2H), 7.34 (s, 1H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.19-7.14 (m, 3H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.99 (d, *J* = 6.8 Hz, 1H), 3.01 (t, *J* = 6.8 Hz, 2H), 2.51 (t, *J* = 7.1 Hz, 2H), 2.31 (s, 3H), 2.10-2.03 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.57, 138.94, 137.85, 135.65, 130.06, 129.10, 128.95, 127.16, 126.39, 124.41, 119.89, 35.83, 32.99, 24.73, 21.47.

HRMS (ESI): Calcd for $C_{17}H_{19}NOS$ $[M+H]^+$: 286.1266, Found: 286.1266.

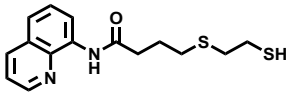


4-((2-mercaptoethyl)thio)-*N*-phenylbutanamide (4i). The reaction was conducted according to general procedure B, NaOAc (10 mol%, 0.01 mmol, 0.8 mg) was added, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:5 EA:PE) as white solid (23 mg, 92%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 7.8 Hz, 2H), 7.34-7.30 (m, 3H), 7.11 (t, *J* = 7.4 Hz, 1H), 2.88-2.69 (m, 4H), 2.64 (t, *J* = 6.9 Hz, 2H), 2.50 (t, *J* = 7.1 Hz, 2H), 2.06-1.99 (m, 2H), 1.73 (t, *J* = 7.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.52, 137.85, 129.17, 124.48, 119.87, 35.92, 31.25, 24.93, 24.79.

HRMS (ESI): Calcd for $C_{12}H_{17}NOS_2$ $[M+H]^+$: 256.0830, Found: 256.0830.

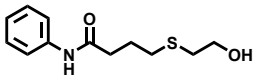


4-((2-mercaptoethyl)thio)-*N*-(quinolin-8-yl)butanamide (4j). The reaction was conducted according to general procedure A, NaOAc (10 mol%, 0.01 mmol, 0.8 mg) was added, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:8 EA/PE) as yellow oil (29 mg, 95%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.82 (s, 1H), 8.79 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.75 (dd, *J* = 7.2, 1.9 Hz, 1H), 8.15 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.54-7.43 (m, 3H), 2.80-2.73 (m, 3H), 2.72-2.66 (m, 5H), 2.13-2.06 (m, 2H), 1.72 (t, *J* = 7.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.87, 148.26, 138.35, 136.48, 134.46, 128.01, 127.48, 121.73, 121.61, 116.51, 36.53, 36.04, 31.40, 25.24, 24.81.

HRMS (ESI): Calcd for $C_{15}H_{18}N_2OS_2$ $[M+H]^+$: 307.0939, Found: 307.0941.

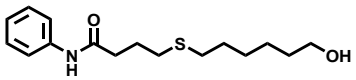


4-((2-hydroxyethyl)thio)-*N*-phenylbutanamide (4k). The reaction was conducted according to general procedure B, NaOAc (10 mol%, 0.8 mg, 0.01 mmol) was added, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:1 EA:PE) as yellow solid (20 mg, 84%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (s, 1H), 7.50 (d, *J* = 1.1 Hz, 2H), 7.30 (t, *J* = 7.9 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 3.74-3.71 (m, 2H), 2.71 (t, *J* = 5.9 Hz, 2H), 2.61 (t, *J* = 6.9 Hz, 2H), 2.49 (t, *J* = 7.1 Hz, 2H), 2.04-1.97 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.94, 137.90, 129.11, 124.45, 119.98, 60.54, 35.87, 35.03, 31.04, 25.04.

HRMS (ESI): Calcd for $C_{12}H_{17}NO_2S$ $[M+H]^+$: 240.1058, Found: 240.1062.

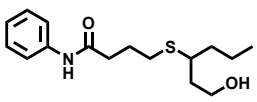


4-((6-hydroxyhexyl)thio)-*N*-phenylbutanamide (4l). The reaction was conducted according to general procedure B, NaOAc (10 mol%, 0.8 mg, 0.01 mmol) was added, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:2 EA:PE) as white solid (27 mg, 90%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (s, 1H), 7.51 (d, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.9 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 3.63 (t, *J* = 6.5 Hz, 2H), 2.59 (t, *J* = 6.9 Hz, 2H), 2.52-2.46 (m, 4H), 2.04-1.96 (m, 2H), 1.76 (s, 1H), 1.62-1.52 (m, 4H), 1.42-1.33 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.96, 138.01, 129.09, 124.34, 119.89, 62.87, 36.03, 32.60, 31.77, 31.37, 29.48, 28.57, 25.35, 24.93.

HRMS (ESI): Calcd for $C_{16}H_{25}NO_2S$ $[M+H]^+$: 296.1684, Found: 296.1685.

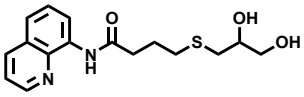


4-((1-hydroxyhexan-3-yl)thio)-*N*-phenylbutanamide (4m). The reaction was conducted according to general procedure B, NaOAc (10 mol%, 0.8 mg, 0.01 mmol) was added, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:10 EA:PE) as yellow oil (24 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.53-7.51 (m, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 3.90-3.89 (m, 1H), 3.79-3.74 (m, 1H), 2.82-2.76 (m, 2H), 2.60 (t, *J* = 7.0 Hz, 2H), 2.57-2.51 (m, 1H), 2.48-2.40 (m, 1H), 2.07-1.97(m, 2H), 1.90-1.82 (m, 1H), 1.70-1.62 (m, 1H), 1.57-1.48 (m, 2H), 1.47-1.37 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.25, 138.05, 129.08, 124.35, 119.91, 119.88, 60.91, 42.87, 38.19, 37.04, 36.03, 29.74, 25.32, 20.12, 14.11.

HRMS (ESI): Calcd for $C_{16}H_{25}NO_2S$ $[M+H]^+$: 296.1684, Found: 296.1688.

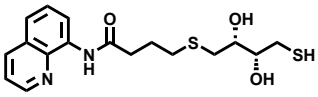


4-((2,3-dihydroxypropyl)thio)-*N*-(quinolin-8-yl)butanamide (4n). The reaction was conducted according to general procedure B, NaOAc (10 mol%, 0.8 mg, 0.01 mmol) was added, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:10 MeOH:DCM) as yellow oil (26 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.83 (s, 1H), 8.79 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.73 (dd, *J* = 7.1, 1.9 Hz, 1H), 8.15 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.55-7.43 (m, 3H), 3.86-3.81 (m, 1H), 3.76-3.72 (m, 1H), 3.59-3.55 (m, 1H), 2.77-2.61 (m, 6H), 2.16-2.05 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.22, 148.36, 138.39, 136.58, 134.37, 128.08, 127.51, 121.80, 121.77, 116.73, 70.36, 65.45, 36.52, 35.61, 31.87, 25.21.

HRMS (ESI): Calcd for $C_{16}H_{20}N_2O_3S$ $[M+H]^+$: 321.1273, Found: 321.1275.



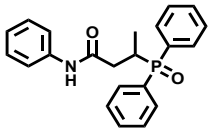
4-(((2*R*,3*R*)-2,3-dihydroxy-4-mercaptobutyl)thio)-*N*-(quinolin-8-yl)butanamide (4o). The reaction was conducted according to general procedure B, (2*R*,3*S*)-3,4-dimercaptobutane-1,2-diol (2 equiv, 0.2 mmol, 30 mg) and NaOAc (10 mol%, 0.01 mmol, 0.8 mg) was added, neat condition, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:20 MeOH:DCM) as yellow oil (30 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.83 (s, 1H), 8.78 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.71 (dd, *J* = 7.3, 1.8 Hz, 1H), 8.12 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.53-7.41 (m, 3H), 3.96-3.92 (m,

1H), 3.81-3.77 (m, 1H), 3.54 (s, 1H), 3.42 (s, 1H), 3.02-2.88 (m, 2H), 2.85-2.71 (m, 2H), 2.68 (t, J = 7.2 Hz, 4H), 2.15-2.03 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.38, 148.39, 138.38, 136.57, 134.33, 128.07, 127.50, 121.86, 121.78, 116.81, 71.20, 71.15, 71.02, 43.08, 42.90, 36.59, 36.57, 35.93, 35.91, 31.86, 25.25, 25.23.

HRMS (ESI): Calcd for $C_{17}H_{22}N_2O_3S_2$ $[M+H]^+$: 367.1150, Found: 367.1154.



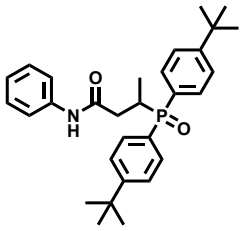
3-(diphenylphosphoryl)-*N*-phenylbutanamide (6a). The reaction was conducted according to general procedure C, the reaction mixture was stirred at 100 °C for 24 hours. The product was purified by preparative TLC (1:20 MeOH:DCM) as white solid (29 mg, 79%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.82 (s, 1H), 7.85-7.78 (m, 6H), 7.53-7.43 (m, 6H), 7.31-7.26 (m, 2H), 7.08-7.05 (m, 1H), 3.29-3.23 (m, 1H), 2.94-2.86 (m, 1H), 2.72-2.65 (m, 1H), 1.22 (dd, J = 16.4, 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.71 (d, $J_{c\text{-}p}$ = 16 Hz), 139.45, 132.10 (d, $J_{c\text{-}p}$ = 2.9 Hz), 132.06 (d, $J_{c\text{-}p}$ = 21.6 Hz), 132.01 (d, $J_{c\text{-}p}$ = 2.8 Hz), 131.10 (d, $J_{c\text{-}p}$ = 20.2 Hz), 130.91, 130.88, 130.82, 130.79, 129.16 (d, $J_{c\text{-}p}$ = 11.3 Hz), 128.99 (d, $J_{c\text{-}p}$ = 11.5 Hz), 128.88, 123.66, 119.81, 36.79, 29.04 (d, $J_{c\text{-}p}$ = 74.0 Hz), 12.58 (d, $J_{c\text{-}p}$ = 2.9 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 39.25.

HRMS (ESI): Calcd for $C_{22}H_{22}NO_2P$ $[M+H]^+$: 364.1466, Found: 364.1468.



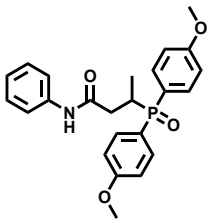
3-(bis(4-(tert-butyl)phenyl)phosphoryl)-*N*-phenylbutanamide (6b). The reaction was conducted according to general procedure C, the reaction mixture was stirred at 100 °C for 24 hours. The product was purified by preparative TLC (1:20 MeOH:DCM) as yellow solid (42 mg, 88%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.99 (s, 1H), 7.82-7.75 (m, 6H), 7.50-7.44 (m, 4H), 7.28 (t, J = 7.9 Hz, 2H), 7.05 (t, J = 7.4 Hz, 1H), 3.26-3.20 (m, 1H), 2.96-2.88 (m, 1H), 2.74-2.67 (m, 1H), 1.31 (s, 9H), 1.26 (s, 9H), 1.23-1.19 (m , 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.07 (d, $J_{c\text{-}p}$ = 16.1 Hz), 155.35 (t, $J_{c\text{-}p}$ = 3.0 Hz), 139.60, 130.76 (d, $J_{c\text{-}p}$ = 2.2 Hz), 130.67 (d, $J_{c\text{-}p}$ = 2.2 Hz), 128.96, 128.82, 127.90 (d, $J_{c\text{-}p}$ = 13.5 Hz), 126.11 (d, $J_{c\text{-}p}$ = 11.6 Hz), 125.94 (d, $J_{c\text{-}p}$ = 11.6 Hz), 123.49, 119.76, 36.82, 35.08 (d, $J_{c\text{-}p}$ = 0.6 Hz), 35.03 (d, $J_{c\text{-}p}$ = 0.6 Hz), 31.20, 31.13, 29.37 (d, $J_{c\text{-}p}$ = 74.3 Hz), 12.63 (d, $J_{c\text{-}p}$ = 2.7 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 39.32.

HRMS (ESI): Calcd for $C_{30}H_{38}NO_2P$ $[M+H]^+$: 476.2718, Found: 476.2719.



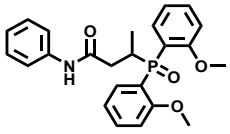
3-(bis(4-methoxyphenyl)phosphoryl)-*N*-phenylbutanamide (6c). The reaction was conducted according to general procedure C, the reaction mixture was stirred at 100 °C for 24 hours. The product was purified by preparative TLC (1:20 MeOH:DCM) as yellow solid (40 mg, 95%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.88 (s, 1H), 7.77 (d, J = 8.3 Hz, 2H), 7.75-7.69 (m, 4H), 7.28 (t, J = 7.4 Hz, 2H), 7.05 (t, J = 7.4 Hz, 1H), 6.98 (dd, J = 8.6, 1.7 Hz, 2H), 6.91 (dd, J = 8.6, 1.7 Hz, 2H), 3.83 (s, 3H), 3.77 (s, 3H), 3.17-3.12 (m, 1H), 2.89-2.81 (m, 1H), 2.72-2.65 (m, 1H), 1.20 (dd, J = 16.2, 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.96 (d, $J_{c\text{-}p}$ = 15.6 Hz), 162.43 (d, $J_{c\text{-}p}$ = 2.6 Hz), 139.52, 132.68 (d, $J_{c\text{-}p}$ = 3.7 Hz), 132.58 (d, $J_{c\text{-}p}$ = 3.7 Hz), 128.83, 123.54, 119.77, 114.58 (d, $J_{c\text{-}p}$ = 2.5 Hz), 114.58 (d, $J_{c\text{-}p}$ = 27.1 Hz), 55.46, 55.40, 36.95, 29.37 (d, $J_{c\text{-}p}$ = 75.2 Hz), 12.72 (d, $J_{c\text{-}p}$ = 2.5 Hz)

^{31}P NMR (162 MHz, $CDCl_3$): δ 39.44.

HRMS (ESI): Calcd for $C_{24}H_{26}NO_4P$ $[M+H]^+$: 424.1678, Found: 424.1684.



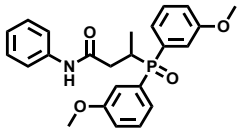
3-(bis(2-methoxyphenyl)phosphoryl)-*N*-phenylbutanamide (6d). The reaction was conducted according to general procedure C, the reaction mixture was stirred at 100 °C for 24 hours. The product was purified by preparative TLC (1:20 MeOH:DCM) as yellow solid (38 mg, 91%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.84 (s, 1H), 7.94-7.88 (m, 1H), 7.85 (d, J = 7.7 Hz, 2H), 7.82-7.76 (m, 1H), 7.45 (t, J = 7.8 Hz, 1H), 7.38 (t, J = 7.8 Hz, 1H), 7.29 (t, J = 7.9 Hz, 2H), 7.07-7.01 (m, 2H), 6.98-6.94 (m, 1H), 6.84-6.79 (m, 2H), 3.65 (s, 3H), 3.64 (s, 3H), 3.62-3.57 (m, 1H), 2.83-2.79 (m, 2H), 1.18 (dd, J = 17.7, 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.63 (d, $J_{c\text{-}p}$ = 15.4 Hz), 160.74 (d, $J_{c\text{-}p}$ = 3.3 Hz), 160.28 (d, $J_{c\text{-}p}$ = 4.0 Hz), 139.71, 134.23 (d, $J_{c\text{-}p}$ = 5.9 Hz), 133.80 (d, $J_{c\text{-}p}$ = 6.7 Hz), 133.53 (d, $J_{c\text{-}p}$ = 2.0 Hz), 133.46 (d, $J_{c\text{-}p}$ = 2.0 Hz), 128.70, 123.37, 121.03 (d, $J_{c\text{-}p}$ = 5.2 Hz), 120.80 (d, $J_{c\text{-}p}$ = 5.4 Hz), 120.69 (d, $J_{c\text{-}p}$ = 5.3 Hz), 120.03, 111.24 (d, $J_{c\text{-}p}$ = 6.5 Hz), 110.95 (d, $J_{c\text{-}p}$ = 6.7 Hz), 55.49, 55.43, 38.00, 28.64 (d, $J_{c\text{-}p}$ = 77.1 Hz), 13.47 (d, $J_{c\text{-}p}$ = 2.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 39.61.

HRMS (ESI): Calcd for $C_{24}H_{26}NO_4P$ $[M+H]^+$:424.1678, Found: 424.1679.



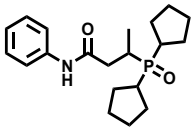
3-(bis(3-methoxyphenyl)phosphanyl)-*N*-phenylbutanamide (6e). The reaction was conducted according to general procedure C, the reaction mixture was stirred at 100 °C for 24 hours. The product was purified by preparative TLC (1:20 MeOH:DCM) as yellow solid (36 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.66 (s, 1H), 7.77 (d, J = 8.3 Hz, 2H), 7.41-7.34 (m, 5H), 7.32-7.25 (m, 3H), 7.05 (t, J = 7.1 Hz, 2H), 6.97 (d, J = 7.3 Hz, 1H), 3.76 (s, 3H), 3.63 (s, 3H), 3.26-3.17 (m, 1H), 2.90-2.82 (m, 1H), 2.72-2.65 (m, 1H), 1.25-1.20 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.67 (d, $J_{c\text{-}p}$ = 16.5 Hz), 160.01 (d, $J_{c\text{-}p}$ = 3.4 Hz), 159.87 (d, $J_{c\text{-}p}$ = 3.4 Hz), 139.46, 133.33 (d, $J_{c\text{-}p}$ = 25.0 Hz), 132.37 (d, $J_{c\text{-}p}$ = 23.7 Hz), 130.42 (d, $J_{c\text{-}p}$ = 13.5 Hz), 130.26 (d, $J_{c\text{-}p}$ = 13.6 Hz), 128.88, 123.66, 130.26 (d, $J_{c\text{-}p}$ = 13.6 Hz), 119.72, 118.39 (d, $J_{c\text{-}p}$ = 2.5 Hz), 118.34 (d, $J_{c\text{-}p}$ = 2.8 Hz), 115.51 (d, $J_{c\text{-}p}$ = 4.4 Hz), 115.42 (d, $J_{c\text{-}p}$ = 4.6 Hz), 55.43, 55.25, 36.78, 28.96 (d, $J_{c\text{-}p}$ = 74.5 Hz), 12.57 (d, $J_{c\text{-}p}$ = 2.9 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 39.68.

HRMS (ESI): Calcd for $C_{24}H_{26}NO_4P$ $[M+H]^+$:424.1678, Found: 424.1677.



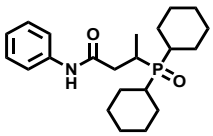
3-(dicyclopentylphosphoryl)-*N*-phenylbutanamide (6f). The reaction was conducted according to general procedure C, the reaction mixture was stirred at 100 °C for 24 hours. The product was purified by preparative TLC (1:20 MeOH:DCM) as white solid (22 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.35 (s, 1H), 7.64-7.62 (m, 2H), 7.28-7.25 (m, 2H), 7.06-7.02 (m, 1H), 3.13-3.05 (m, 1H), 2.60-2.53 (m, 1H), 2.46-2.39 (m, 1H), 2.17-2.06 (m, 2H), 1.94-1.84 (m, 6H), 1.80-1.67 (m, 6H), 1.64-1.56 (m, 4H), 1.26 (dd, J = 15.5, 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.11 (d, $J_{c\text{-}p}$ = 9.7 Hz), 139.15, 128.78, 123.59, 119.75, 38.67 (d, $J_{c\text{-}p}$ = 2.0 Hz), 36.76, 36.10, 35.46, 29.41 (d, $J_{c\text{-}p}$ = 62.0 Hz), 27.50 (d, $J_{c\text{-}p}$ = 1.0 Hz), 27.30 (d, $J_{c\text{-}p}$ = 1.1 Hz), 27.17 (d, $J_{c\text{-}p}$ = 2.2 Hz), 26.87 (d, $J_{c\text{-}p}$ = 1.9 Hz), 26.57 (d, $J_{c\text{-}p}$ = 9.6 Hz), 26.29 (d, $J_{c\text{-}p}$ = 9.7 Hz), 26.13 (d, $J_{c\text{-}p}$ = 9.8 Hz), 15.36.

^{31}P NMR (162 MHz, $CDCl_3$): δ 59.64.

HRMS (ESI): Calcd for $C_{20}H_{30}NO_2P$ $[M+H]^+$: 348.2092, Found: 348.2094.



3-(dicyclohexylphosphoryl)-*N*-phenylbutanamide (6g). The reaction was conducted according to general procedure B, CH_3OLi (20 mol%, 0.02 mmol, 0.8 mg) was added, the reaction mixture was stirred at 100 °C for 24 hours. The product was purified by preparative TLC (1:20 MeOH:DCM) as white solid (34 mg, 91%).

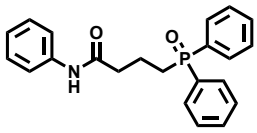
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.59 (s, 1H), 7.66 (d, J = 8.1 Hz, 2H), 7.27 (t, J = 7.8 Hz, 2H), 7.04 (t, J = 7.4 Hz, 1H), 3.00-2.92 (m, 1H), 2.69-2.62 (m, 1H), 2.60-2.52 (m, 1H), 2.04-1.95 (m, 3H), 1.93-1.81 (m, 7H), 1.76-1.71 (m, 2H), 1.55-1.35 (m, 4H), 1.30-1.18 (m, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.91 (d, $J_{c\text{-}p}$ = 10.2 Hz), 139.29, 128.77, 123.54, 119.79, 38.62, 36.14 (d, $J_{c\text{-}p}$ = 44.7 Hz), 35.54 (d, $J_{c\text{-}p}$ = 44.4 Hz), 26.94 (d, $J_{c\text{-}p}$ = 12.4

Hz), 26.67 (d, $J_{c\text{-}p}$ = 14.7 Hz), 26.39, 26.22 (d, $J_{c\text{-}p}$ = 2.5 Hz), 26.12, 25.78, 14.93 (d, $J_{c\text{-}p}$ = 4.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 56.52.

HRMS (ESI): Calcd for $C_{22}H_{34}NO_2P$ $[M+H]^+$:376.2405, Found: 376.2404.



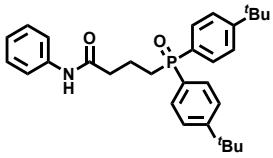
4-(diphenylphosphoryl)-*N*-phenylbutanamide (7a). The reaction was conducted according to general procedure D, the reaction mixture was stirred at 100 °C for 24 hours. The product was purified by preparative TLC (1:20 MeOH:DCM) as colorless oil (34 mg, 93%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.28 (s, 1H), 7.77-7.72 (m, 4H), 7.65-7.63 (m, 2H), 7.57-7.47 (m, 6H), 7.30 (t, *J* = 7.8 Hz, 3H), 7.07 (t, *J* = 7.4 Hz, 1H), 2.60 (t, *J* = 6.8 Hz, 2H), 2.45-2.38 (m, 2H), 2.12-2.01 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.11, 138.70, 132.24 (d, $J_{c\text{-}p}$ = 98.9 Hz), 132.18 (d, $J_{c\text{-}p}$ = 6.1 Hz), 130.85, 130.76, 129.06, 128.95, 123.87, 119.77, 37.21 (d, $J_{c\text{-}p}$ = 7.1 Hz), 27.75 (d, $J_{c\text{-}p}$ = 71.3 Hz), 19.21 (d, *J* = 4.6 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 35.52.

HRMS (ESI): Calcd for $C_{22}H_{22}NO_2P$ $[M+H]^+$: 364.1466, Found: 364.1465.



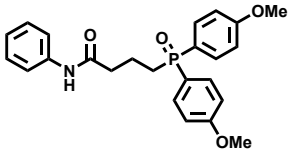
4-(bis(4-(tert-butyl)phenyl)phosphoryl)-*N*-phenylbutanamide (7b). The reaction was conducted according to general procedure D, the reaction mixture was stirred at 100 °C for 24 hours. The product was purified by preparative TLC (1:20 MeOH:DCM) as yellow oil (40 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.69 (s, 1H), 7.67-7.62 (m, 6H), 7.48-7.45 (m, 4H), 7.29-7.25 (m, 2H), 7.06-7.02 (m, 1H), 2.59 (t, *J* = 6.9 Hz, 2H), 2.39-2.33 (m, 2H), 2.09-1.98 (m, 2H), 1.30 (s, 18H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.36, 155.58 (d, $J_{c\text{-}p}$ = 2.4 Hz), 138.81, 130.67 (d, $J_{c\text{-}p}$ = 9.6 Hz), 128.95, 125.99 (d, $J_{c\text{-}p}$ = 11.9 Hz), 123.77, 119.71, 37.28 (d, $J_{c\text{-}p}$ = 5.7 Hz), 31.20, 27.78 (d, $J_{c\text{-}p}$ = 71.2 Hz), 19.52 (d, $J_{c\text{-}p}$ = 4.3 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 35.59.

HRMS (ESI): Calcd for $C_{30}H_{38}NO_2P$ $[M+H]^+$: 476.2718, Found: 476.2728.



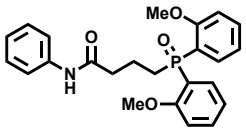
4-(bis(4-methoxyphenyl)phosphoryl)-*N*-phenylbutanamide (7c). The reaction was conducted according to general procedure D, the reaction mixture was stirred at 100 °C for 24 hours. The product was purified by preparative TLC (1:20 MeOH:DCM) as yellow solid (36 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.71 (s, 1H), 7.64-7.57 (m, 6H), 7.27-7.23 (m, 2H), 7.05-7.01 (m, 1H), 6.96-6.92 (m, 4H), 3.80 (s, 6H), 2.56 (t, J = 7.0 Hz, 2H), 2.34-2.28 (m, 2H), 2.05-1.94 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.32, 162.48 (d, $J_{c\text{-}p}$ = 2.8 Hz), 138.84, 132.58 (d, $J_{c\text{-}p}$ = 10.6 Hz), 128.87, 124.04, 123.68, 123.00, 119.68, 114.45 (d, $J_{c\text{-}p}$ = 12.7 Hz), 37.22 (d, $J_{c\text{-}p}$ = 8.0 Hz), 28.13 (d, $J_{c\text{-}p}$ = 72.1 Hz), 19.29 (d, $J_{c\text{-}p}$ = 4.3 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 35.38.

HRMS (ESI): Calcd for $C_{24}H_{26}NO_4P$ $[M+H]^+$: 424.1678 Found: 424.1674.



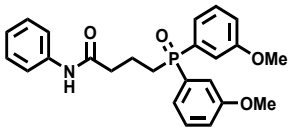
4-(bis(2-methoxyphenyl)phosphoryl)-*N*-phenylbutanamide (7d). The reaction was conducted according to general procedure D, the reaction mixture was stirred at 100 °C for 24 hours. The product was purified by preparative TLC (1:20 MeOH:DCM) as yellow solid (35 mg, 82%). The NMR spectra of product contained corresponding branched product.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.43 (s, 1H), 7.77-7.75 (m, 2H), 7.60-7.50 (m, 5H), 7.30-7.26 (m, 2H), 7.06-7.01 (m, 3H), 6.95-6.92 (m, 2H), 3.61 (s, 6H), 2.75-2.68 (m, 2H), 2.52-2.49 (m, 2H), 1.97-1.84 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.91, 160.78 (d, $J_{c\text{-}p}$ = 3.5 Hz), 139.16, 134.00, 133.90 (d, $J_{c\text{-}p}$ = 7.1 Hz), 128.64, 123.30, 120.91 (d, $J_{c\text{-}p}$ = 11.5 Hz), 119.63, 119.24 (d, $J_{c\text{-}p}$ = 100.9 Hz), 110.92 (d, $J_{c\text{-}p}$ = 6.6 Hz), 55.38, 37.25 (d, $J_{c\text{-}p}$ = 6.0 Hz), 26.93 (d, $J_{c\text{-}p}$ = 72.9 Hz), 20.31 (d, $J_{c\text{-}p}$ = 4.9 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 38.62.

HRMS (ESI): Calcd for $C_{24}H_{26}NO_4P$ $[M+H]^+$: 424.1678 Found: 424.1677.



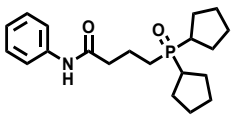
4-(bis(3-methoxyphenyl)phosphoryl)-*N*-phenylbutanamide (7e). The reaction was conducted according to general procedure D, the reaction mixture was stirred at 100 °C for 24 hours. The product was purified by preparative TLC (1:20 MeOH:DCM) as yellow oil (33 mg, 79%). The NMR spectra of product contained corresponding branched product.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 1H), 7.58-7.56 (m, 2H), 7.42-7.37 (m, 2H), 7.31-7.21 (m, 6H), 7.10-7.06 (m, 3H), 3.80 (s, 1H), 2.58 (t, J = 6.8 Hz, 2H), 2.46-2.39 (m, 2H), 2.11-2.04 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.03 (d, $J_{c\text{-}p}$ = 15.0 Hz), 138.18, 132.08 (d, $J_{c\text{-}p}$ = 99.8 Hz), 130.42 (d, $J_{c\text{-}p}$ = 14.3 Hz), 129.03, 124.29, 122.74 (d, $J_{c\text{-}p}$ = 10.2 Hz), 119.93, 118.62 (d, $J_{c\text{-}p}$ = 3.0 Hz), 115.85 (d, $J_{c\text{-}p}$ = 10.7 Hz), 55.57, 37.06 (d, $J_{c\text{-}p}$ = 9.4 Hz), 27.75 (d, $J_{c\text{-}p}$ = 71.5 Hz), 18.59 (d, $J_{c\text{-}p}$ = 4.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 39.15.

HRMS (ESI): Calcd for $C_{24}H_{26}NO_4P$ $[M+H]^+$: 424.1678 Found: 424.1678.



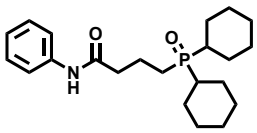
4-(dicyclopentylphosphoryl)-*N*-phenylbutanamide (7f). The reaction was conducted according to general procedure D, NaOH (20 mol%, 0.02 mmol, 0.8 mg) was added, the reaction mixture was stirred at 100 °C for 24 hours. The product was purified by preparative TLC (1:20 MeOH:DCM) as green solid (27 mg, 79%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.63 (s, 1H), 7.63 (d, J = 7.9 Hz, 2H), 7.29 (d, J = 7.7 Hz, 2H), 7.05 (t, J = 7.4 Hz, 1H), 2.63 (t, J = 6.9 Hz, 2H), 2.16-2.03 (m, 5H), 1.94-1.85 (m, 4H), 1.82-1.75 (m, 4H), 1.73-1.58 (m, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.33, 138.86, 128.89, 123.73, 119.62, 37.75 (d, $J_{c\text{-}p}$ = 6.1 Hz), 37.68, 37.01, 26.97 (d, $J_{c\text{-}p}$ = 1.3 Hz), 26.78 (d, $J_{c\text{-}p}$ = 1.7 Hz), 26.54 (d, $J_{c\text{-}p}$ = 4.8 Hz), 26.44 (d, $J_{c\text{-}p}$ = 4.8 Hz), 23.89 (d, $J_{c\text{-}p}$ = 61.9 Hz), 19.80 (d, $J_{c\text{-}p}$ = 4.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 56.65.

HRMS (ESI): Calcd for $C_{20}H_{30}NO_2P$ $[M+H]^+$: 348.2092, Found: 348.2097.



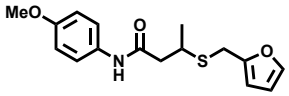
4-(dicyclohexylphosphoryl)-*N*-phenylbutanamide (7g). The reaction was conducted according to general procedure D, NaOH (20 mol%, 0.02 mmol, 0.8 mg) was added, the reaction mixture was stirred at 100 °C for 24 hours. The product was purified by preparative TLC (1:20 MeOH:DCM) as white solid (33 mg, 88%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.67 (s, 1H), 7.65-7.62 (m, 2H), 7.30-7.26 (m, 2H), 7.07-7.03 (m, 1H), 2.61 (t, J = 6.8 Hz, 2H), 2.17-2.06 (m, 2H), 1.99-1.93 (m, 2H), 1.85-1.73 (m, 11H), 1.39-1.18 (m, 11H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.38, 138.85, 128.86, 123.66, 119.62, 37.75 (d, $J_{c\text{-}p}$ = 5.6 Hz), 36.58, 35.95, 26.69 (d, $J_{c\text{-}p}$ = 2.2 Hz), 26.57 (d, $J_{c\text{-}p}$ = 2.3 Hz), 25.98, 25.67 (d, $J_{c\text{-}p}$ = 2.7 Hz), 21.54 (d, $J_{c\text{-}p}$ = 59.5 Hz), 19.85 (d, $J_{c\text{-}p}$ = 4.9 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 54.25.

HRMS (ESI): Calcd for $C_{22}H_{34}NO_2P$ $[M+H]^+$: 376.2405, Found: 376.2407.

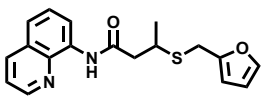


3-((furan-2-ylmethyl)thio)-*N*-(4-methoxyphenyl)butanamide (8a). The reaction was conducted according to general procedure A, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:10 EA:PE) as yellow solid (29 mg, 96%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (s, 1H), 7.40-7.26 (m, 3H), 6.84 (d, J = 8.5 Hz, 2H), 6.26 (d, J = 35.0 Hz, 2H), 3.85-3.78 (m, 5H), 3.31-3.23 (m, 1H), 2.57-2.42 (m, 2H), 1.35 (d, J = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.91, 156.47, 151.53, 142.26, 130.92, 121.97, 114.15, 110.72, 55.56, 44.85, 37.18, 27.70, 21.54.

HRMS (ESI): Calcd for $C_{16}H_{19}NO_3S$ $[M+H]^+$: 306.1164 Found: 306.1168.

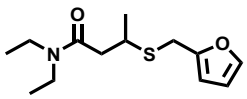


3-((furan-2-ylmethyl)thio)-*N*-(quinolin-8-yl)butanamide (8b). The reaction was conducted according to general procedure A, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:20 EA/PE) as yellow oil (32 mg, 99%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.88 (s, 1H), 8.81-8.77 (m, 2H), 8.17-8.15 (m, 1H), 7.55-7.44 (m, 3H), 7.37-7.36 (m, 1H), 6.31-6.25 (m, 2H), 3.90-3.80 (m, 2H), 3.47-3.38 (m, 1H), 2.85 (dd, *J* = 14.6, 6.2 Hz, 1H), 2.65 (dd, *J* = 14.8, 7.9 Hz, 1H), 1.41 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.31, 151.68, 148.29, 142.22, 138.40, 136.47, 134.41, 128.01, 127.48, 121.76, 116.63, 110.64, 107.67, 45.95, 37.03, 27.89, 21.40.

HRMS (ESI): Calcd for $C_{18}H_{18}N_2O_2S$ $[M+H]^+$: 327.1167, Found: 327.1164.

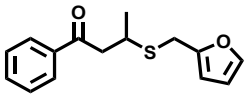


***N*,*N*-diethyl-3-((furan-2-ylmethyl)thio)butanamide (8c).** The reaction was conducted according to general procedure A, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:10 EA/PE) as yellow oil (24 mg, 96%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.33 (m, 1H), 6.29-6.20 (m, 2H), 3.84-3.75 (m, 2H), 3.38-3.33 (m, 3H), 3.30-3.24 (m, 2H), 2.61-2.56 (m, 1H), 2.42-2.36 (m, 1H), 1.29 (d, *J* = 6.7 Hz, 3H), 1.16-1.08 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.82, 151.86, 142.10, 110.61, 107.50, 42.14, 40.71, 40.46, 37.08, 27.96, 21.56, 14.56, 13.21.

HRMS (ESI): Calcd for $C_{13}H_{21}NO_2S$ $[M+H]^+$: 256.1371, Found: 256.1376.

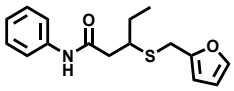


3-((furan-2-ylmethyl)thio)-1-phenylbutan-1-one (8d). The reaction was conducted according to general procedure A, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:10 EA/PE) as yellow oil (19 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93-7.91 (m, 2H), 7.59-7.55 (m, 1H), 7.48-7.44 (m, 2H), 7.35-7.34 (m, 1H), 6.30-6.29 (m, 1H), 6.20-6.19 (m, 1H), 3.86-3.77 (m, 2H), 3.50-3.42 (m, 1H), 3.30-3.24 (m, 1H), 3.11-3.05 (m, 1H), 1.34 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 198.09, 151.76, 142.19, 136.92, 133.39, 128.77, 128.21, 110.64, 107.59, 46.07, 35.71, 27.83, 21.52.

HRMS (ESI): Calcd for $C_{15}H_{16}O_2S$ $[M+H]^+$: 261.0949, Found: 261.0948c.

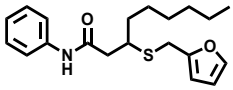


3-((furan-2-ylmethyl)thio)-*N*-phenylpentanamide (8e). The reaction was conducted according to general procedure A, the reaction mixture was stirred at 80 °C for 48 hours. The product was purified by preparative TLC (1:10 EA/PE) as brown solid (29 mg, 99%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (s, 1H), 7.52-7.50 (m, 2H), 7.33-7.29 (m, 3H), 7.12-7.08 (m, 1H), 6.30-6.21 (m, 2H), 3.84-3.73 (m, 2H), 3.10-3.03 (m, 1H), 2.61-2.56 (m, 1H), 2.51-2.45 (m, 1H), 1.72-1.56 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.41, 151.58, 142.27, 137.92, 129.07, 124.40, 120.03, 110.72, 107.95, 44.28, 43.48, 28.18, 27.99, 11.33.

HRMS (ESI): Calcd for $C_{16}H_{19}NO_2S$ $[M+H]^+$: 290.1215, Found: 290.1219.

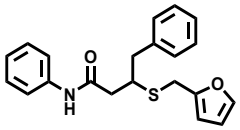


3-((furan-2-ylmethyl)thio)-*N*-phenylnonanamide (8f). The reaction was conducted according to general procedure A, the reaction mixture was stirred at 80 °C for 48 hours. The product was purified by preparative TLC (1:10 EA:PE) as yellow oil (31 mg, 90%). The NMR spectra of product contained corresponding starting material.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (s, 1H), 7.52-7.48 (m, 2H), 7.34-7.30 (m, 3H), 7.10 (t, J = 7.4 Hz, 1H), 6.31-6.30 (m, 1H), 6.22 (d, J = 3.2 Hz, 1H), 3.85-3.73 (m, 2H), 3.13-3.07 (m, 1H), 2.61-2.56 (m, 1H), 2.51-2.45 (m, 1H), 1.63-1.55 (m, 2H), 1.44-1.36 (m, 2H), 1.34-1.22 (m, 6H), 0.86 (t, J = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.35, 151.60, 142.28, 137.93, 129.10, 124.41, 120.00, 110.75, 107.99, 43.94, 42.75, 35.24, 31.82, 29.10, 28.01, 26.82, 22.72, 14.23.

HRMS (ESI): Calcd for $C_{20}H_{27}NO_2S$ $[M+H]^+$: 346.1841 Found: 346.1840.

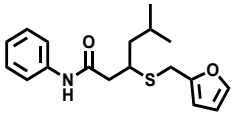


3-((furan-2-ylmethyl)thio)-*N*,4-diphenylbutanamide (8g). The reaction was conducted according to general procedure A, the reaction mixture was stirred at 80 °C for 48 hours. The product was purified by preparative TLC (1:10 EA:PE) as yellow oil (33 mg, 95%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (s, 1H), 7.50-7.48 (m, 2H), 7.32-7.28 (m, 5H), 7.25-7.19 (m, 3H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.30-6.28 (m, 1H), 6.17 (d, *J* = 3.2 Hz, 1H), 3.77-3.59 (m, 2H), 3.41-3.34 (m, 1H), 2.92 (d, *J* = 7.2 Hz, 2H), 2.62-2.57 (m, 1H), 2.46-2.40 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.04, 151.24, 142.37, 138.40, 137.84, 129.56, 129.04, 128.57, 126.84, 124.41, 120.02, 110.66, 108.19, 43.43, 42.70, 42.15, 28.49.

HRMS (ESI): Calcd for $C_{21}H_{21}NO_2S$ $[M+H]^+$: 352.1371, Found: 352.1367.

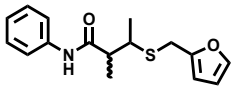


3-((furan-2-ylmethyl)thio)-5-methyl-*N*-phenylhexanamide (8h). The reaction was conducted according to general procedure A, the reaction mixture was stirred at 80 °C for 48 hours. The product was purified by preparative TLC (1:10 EA:PE) as yellow oil (25 mg, 79%). The NMR spectra of product contained corresponding starting material.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (s, 1H), 7.53-7.50 (m, 2H), 7.34-7.30 (m, 3H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.32-6.31 (m, 1H), 6.23 (d, *J* = 3.2 Hz, 1H), 3.86-3.73 (m, 2H), 3.19-3.12 (m, 1H), 2.61-2.56 (m, 1H), 2.50-2.44 (m, 1H), 1.85-1.76 (m, 1H), 1.51-1.37 (m, 2H), 0.88 (d, *J* = 6.6 Hz, 3H), 0.82 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.31, 151.62, 142.29, 137.94, 129.11, 124.41, 119.99, 110.80, 108.07, 44.29, 44.19, 40.61, 27.68, 25.47, 22.88, 22.46, 21.93.

HRMS (ESI): Calcd for $C_{18}H_{23}NO_2S$ $[M+H]^+$: 318.1528, Found: 318.1530.

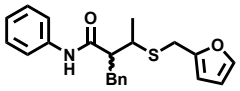


3-((furan-2-ylmethyl)thio)-2-methyl-*N*-phenylbutanamide (8i). The reaction was conducted according to general procedure A, the reaction mixture was stirred at 80 °C for 48 hours. The product was purified by preparative TLC (1:10 EA:PE) as brown oil (27 mg, 95%). The dr value is 5:1 analysis by GCMS.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.54-7.50 (m, 2H), 7.37-7.33 (m, 3H), 7.12-7.08 (m, 1H), 6.35-6.30 (m, 1H), 6.23-6.20 (m, 1H), 3.88-3.72 (m, 2H), 3.10-2.97 (m, 1H), 2.54-2.39 (m, 1H), 1.31-1.24 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.24, 172.22, 152.04, 151.28, 142.42, 142.20, 137.96, 129.10, 129.06, 124.40, 124.31, 120.00, 119.97, 110.77, 110.75, 107.97, 107.76, 47.91, 46.64, 43.93, 42.73, 28.15, 18.53, 18.18, 15.53, 14.24.

HRMS (ESI): Calcd for $C_{16}H_{19}NO_2S$ [M+H]$^+$: 290.1215, Found: 290.1218.

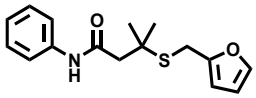


2-benzyl-3-((furan-2-ylmethyl)thio)-*N*-phenylbutanamide (8j). The reaction was conducted according to general procedure A, the reaction mixture was stirred at 80 °C for 48 hours. The product was purified by preparative TLC (1:10 EA:PE) as white solid (32 mg, 88%). The dr value is 4:1 analysis by GCMS.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (s, 0.63H), 7.38-7.35 (m, 2H), 7.30-7.26 (m, 3H), 7.23-7.16 (m, 5H), 7.10-7.06 (m, 1H), 6.81 (s, 0.26H), 6.35-6.24 (m, 1.3H), 6.02-6.02 (m, 0.6H), 3.89-3.70 (m, 2H), 3.18-2.95 (m, 3H), 2.57-2.42 (m, 1H), 1.44-1.35 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.18, 170.75, 152.10, 151.38, 142.37, 142.25, 139.77, 139.60, 137.57, 137.51, 129.16, 129.02, 128.98, 128.71, 126.60, 126.55, 124.47, 124.44, 120.24, 120.21, 110.82, 107.89, 107.85, 56.63, 55.06, 42.45, 42.23, 36.71, 34.89, 28.32, 28.21, 18.61, 18.00.

HRMS (ESI): Calcd for $C_{22}H_{23}NO_2S$ [M+H]$^+$: 366.1528, Found: 366.1529.

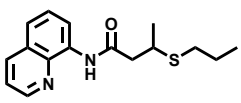


3-((furan-2-ylmethyl)thio)-3-methyl-*N*-phenylbutanamide (8k). The reaction was conducted according to general procedure A, the reaction mixture was stirred at 80 °C for 48 hours. The product was purified by preparative TLC (1:10 EA:PE) as yellow oil (22 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1H), 7.54-7.51 (m, 2H), 7.37-7.36 (m, 1H), 7.24-7.29 (m, 2H), 7.12-7.07 (m, 1H), 6.34-6.33 (m, 1H), 6.23-6.22 (m, 1H), 3.87 (s, 2H), 2.46 (s, 2H), 1.47 (s, 6H).

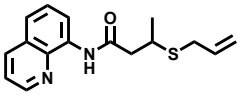
^{13}C NMR (100 MHz, $CDCl_3$): δ 168.51, 151.38, 142.25, 138.08, 129.05, 124.22, 119.91, 111.07, 107.95, 49.54, 44.83, 29.20, 25.90.

HRMS (ESI): Calcd for $C_{16}H_{19}NO_2S$ [M+H]$^+$: 290.1215, Found: 290.1215.



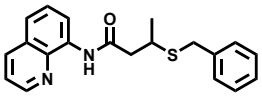
3-(propylthio)-*N*-(quinolin-8-yl)butanamide (8l). The reaction was conducted according to general procedure A, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:20 EA/PE) as yellow oil (29 mg, 99%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.92 (s, 1H), 8.81-8.77 (m, 2H), 8.16 (m, 1H), 7.56-7.44 (m, 3H), 3.46-3.38 (m, 1H), 2.89-2.84 (m, 1H), 2.71-2.65 (m, 1H), 2.60 (t, *J* = 7.4 Hz, 2H), 1.69-1.59 (m, 2H), 1.42 (d, *J* = 6.8 Hz, 3H), 0.98 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 169.60, 148.32, 138.43, 136.48, 134.45, 128.02, 127.50, 121.77, 121.75, 116.64, 46.29, 36.82, 33.17, 23.22, 21.86, 13.75.
HRMS (ESI): Calcd for $C_{16}H_{20}N_2OS$ $[M+H]^+$: 289.1375, Found: 289.1374.



3-(allylthio)-*N*-(quinolin-8-yl)butanamide (3m). The reaction was conducted according to general procedure A, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:20 EA/PE) as yellow oil (27 mg, 85%).

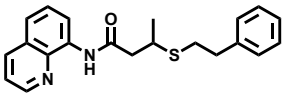
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.91 (s, 1H), 8.82-8.77 (m, 2H), 8.16 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.56-7.44 (m, 3H), 5.91-5.81 (m, 1H), 5.22-5.11 (m, 2H), 3.44-3.35 (m, 1H), 3.31-3.21 (m, 2H), 2.88 (dd, *J* = 14.6, 6.5 Hz, 1H), 2.68 (dd, *J* = 14.6, 7.9 Hz, 1H), 1.42 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 169.42, 148.31, 138.41, 136.49, 134.60, 134.43, 128.02, 127.50, 121.76, 117.36, 116.63, 46.00, 35.92, 34.40, 21.57.
HRMS (ESI): Calcd for $C_{16}H_{18}N_2OS$ $[M+H]^+$: 287.1218, Found: 287.1215.



3-(benzylthio)-*N*-(quinolin-8-yl)butanamide (3n). The reaction was conducted according to general procedure A, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:20 EA/PE) as yellow oil (33 mg, 99%).

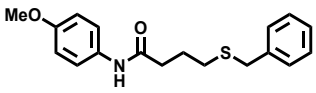
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.88 (s, 1H), 8.82-8.77 (m, 2H), 8.16 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.56-7.44 (m, 3H), 7.38-7.35 (m, 2H), 7.31-7.26 (m, 2H), 7.23-7.20 (m, 1H), 3.88-3.80 (m, 2H), 3.41-3.32 (m, 1H), 2.85 (dd, *J* = 14.6, 6.4 Hz, 1H), 2.66 (dd, *J* = 14.6, 7.8 Hz, 1H), 1.40 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.39, 148.29, 138.42, 138.39, 136.46, 134.43, 128.98, 128.65, 128.02, 127.48, 127.10, 121.75, 116.66, 46.09, 36.87, 35.86, 21.60.
HRMS (ESI): Calcd for $C_{20}H_{20}N_2OS$ [M+H]$^+$: 337.1375, Found: 337.1375.

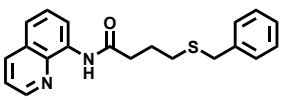


3-(phenethylthio)-*N*-(quinolin-8-yl)butanamide (3o). The reaction was conducted according to general procedure A, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:20 EA/PE) as yellow oil (32 mg, 90%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.92 (s, 1H), 8.81-8.79 (m, 2H), 8.16 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.57-7.44 (m, 3H), 7.28-7.25 (m, 2H), 7.20-7.18 (m, 3H), 3.53-3.44 (m, 1H), 2.94-2.83 (m, 5H), 2.73-2.67 (m, 1H), 1.44 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 169.46, 148.32, 140.62, 138.39, 136.47, 134.40, 128.60, 128.53, 128.01, 127.48, 126.43, 121.77, 116.64, 46.24, 37.04, 36.36, 32.67, 21.85.
HRMS (ESI): Calcd for $C_{21}H_{22}N_2OS$ [M+H]$^+$: 351.1531, Found: 351.1533.

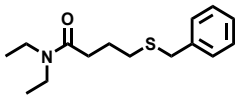


4-(benzylthio)-*N*-(4-methoxyphenyl)butanamide (9a). The reaction was conducted according to general procedure B, the reaction mixture was stirred at 80 °C for 48 hours. The product was purified by preparative TLC (1:10 EA:PE) as white solid (20 mg, 64%).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.35 (m, 2H), 7.32 (s, 1H), 7.30-7.27(m, 4H), 7.25-7.20 (m, 1H), 6.88-6.82 (m, 2H), 3.78 (s, 3H), 3.70 (s, 2H), 2.50 (t, *J* = 6.9 Hz, 2H), 2.40 (t, *J* = 7.3 Hz, 2H), 2.00-1.93 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 170.61, 156.44, 138.42, 130.98, 128.95, 128.62, 127.11, 121.91, 114.16, 55.57, 36.06, 35.88, 30.74, 24.64.
HRMS (ESI): Calcd for $C_{18}H_{21}NO_2S$ [M+H]$^+$: 316.1371, Found: 316.1371.

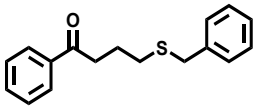


4-(benzylthio)-*N*-(quinolin-8-yl)butanamide (9b). The reaction was conducted according to general procedure B, the reaction mixture was stirred at 80 °C for 48 hours. The product was purified by preparative TLC (1:5 EA:PE) as yellow oil (25 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.81 (s, 1H), 8.81 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.77 (dd, *J* = 7.2, 1.8 Hz, 1H), 8.16 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.56-7.49 (m, 2H), 7.46 (dd, *J* = 8.3, 4.3 Hz, 1H), 7.33-7.25 (m, 4H), 7.22-7.18 (m, 1H), 3.74 (s, 2H), 2.67 (t, *J* = 7.3 Hz, 2H), 2.57 (t, *J* = 7.1 Hz, 2H), 2.12-2.05 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 171.09, 148.26, 138.42, 138.38, 136.49, 134.53, 128.98, 128.59, 128.03, 127.52, 127.06, 121.75, 121.58, 116.51, 36.70, 36.08, 30.73, 24.77.
HRMS (ESI): Calcd for $C_{20}H_{20}N_2OS$ $[M+H]^+$: 337.1375, Found: 337.1375.



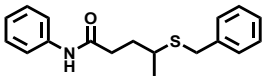
4-(benzylthio)-*N*,*N*-diethylbutanamide (9c). The reaction was conducted according to general procedure B, the reaction mixture was stirred at 80 °C for 48 hours. The product was purified by preparative TLC (1:10 EA:PE) as colorless oil (15 mg, 56%).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.28 (m, 4H), 7.25-7.20 (m, 1H), 3.70 (s, 2H), 3.35 (q, *J* = 7.1 Hz, 2H), 3.27 (q, *J* = 7.2 Hz, 2H), 2.48 (t, *J* = 6.9 Hz, 2H), 2.38 (t, *J* = 7.3Hz, 2H), 1.96-1.89 (m, 2H), 1.15 (t, *J* = 7.2 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 171.44, 138.56, 128.97, 128.58, 127.02, 42.00, 40.22, 36.03, 31.61, 31.01, 24.55, 14.46, 13.23.
HRMS (ESI): Calcd for $C_{15}H_{23}NOS$ $[M+H]^+$: 266.1579, Found: 266.1580.



4-(benzylthio)-1-phenylbutan-1-one (9d). The reaction was conducted according to general procedure B, the reaction mixture was stirred at 80 °C for 48 hours. The product was purified by preparative TLC (1:10 EA:PE) as yellow oil (15 mg, 54%).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.1 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.31-7.28 (m, 4H), 7.25-7.23 (m, 1H), 3.71 (s, 2H), 3.07 (t, *J* = 7.2 Hz, 2H), 2.53 (t, *J* = 6.9 Hz, 2H), 2.05-1.98 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 199.74, 138.49, 136.96, 133.21, 129.00, 128.72, 128.64, 128.17, 127.10, 37.25, 36.10, 30.89, 23.36.

HRMS (ESI): Calcd for $C_{17}H_{18}OS$ $[M+H]^+$: 271.1157, Found: 271.1156.

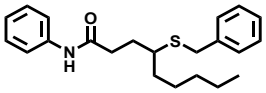


4-(benzylthio)-*N*-phenylpentanamide (9e). The reaction was conducted according to general procedure B, the reaction mixture was stirred at 80 °C for 48 hours. The product was purified by preparative TLC (1:10 EA:PE) as yellow oil (12 mg, 40%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.45 (m, 2H), 7.33-7.28 (m, 5H), 7.25-7.17 (m, 2H), 7.14-7.09 (m, 2H), 3.79-3.70 (m, 2H), 2.78-2.71 (m, 1H), 2.45-2.41 (m, 2H), 2.06-1.97 (m, 1H), 1.89-1.80 (m, 1H), 1.32 (d, J = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.91, 138.73, 137.92, 129.11, 128.93, 128.65, 127.11, 124.37, 119.89, 39.40, 34.88, 34.77, 31.90, 21.74.

HRMS (ESI): Calcd for $C_{18}H_{21}NOS$ $[M+H]^+$: 300.1422, Found: 300.1422.

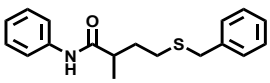


4-(benzylthio)-*N*-phenylnonanamide (9f). The reaction was conducted according to general procedure B, the reaction mixture was stirred at 80 °C for 48 hours. The product was purified by preparative TLC (1:10 EA:PE) as yellow oil (10 mg, 28%). The NMR spectra of product contained corresponding starting material.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.46 (m, 2H), 7.33-7.29 (m, 5H), 7.26-7.25 (m, 1H), 7.22-1.78 (m, 1H), 7.15-7.08 (m, 2H), 3.74-3.66 (m, 2H), 2.61-2.55 (m, 1H), 2.42 (t, J = 7.4 Hz, 2H), 2.10-2.02 (m, 1H), 1.83-1.71 (m, 2H), 1.59-1.50 (m, 1H), 1.44-1.35 (m, 2H), 1.33-1.21 (m, 4H), 0.87 (t, J = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.13, 138.93, 137.98, 129.09, 129.03, 128.61, 127.09, 124.32, 119.89, 45.19, 35.22, 34.80, 34.76, 31.83, 29.87, 26.61, 22.70, 14.20.

HRMS (ESI): Calcd for $C_{22}H_{29}NOS$ $[M+H]^+$: 356.2048, Found: 356.2046.



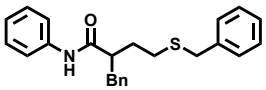
4-(benzylthio)-2-methyl-*N*-phenylbutanamide (9g). The reaction was conducted according to general procedure B, the reaction mixture was stirred at 80 °C for 48 hours.

The product was purified by preparative TLC (1:10 EA:PE) as white solid (21 mg, 69%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.48 (m, 2H), 7.42 (s, 1H), 7.33-7.25 (m, 6H), 7.23-7.19 (m, 1H), 7.13-7.08 (m, 1H), 3.70 (s, 2H), 2.56-2.42 (m, 3H), 2.06-1.97 (m, 1H), 1.71-1.63 (m, 1H), 1.19 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 174.19, 138.35, 137.92, 129.07, 128.91, 128.64, 127.15, 124.36, 119.94, 40.78, 36.23, 33.23, 29.44, 17.84.

HRMS (ESI): Calcd for $C_{18}H_{21}NOS$ $[M+H]^+$: 300.1422, Found: 300.1426.

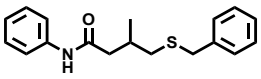


2-benzyl-4-(benzylthio)-*N*-phenylbutanamide (9h). The reaction was conducted according to general procedure B, the reaction mixture was stirred at 80 °C for 48 hours. The product was purified by preparative TLC (1:10 EA:PE) as white solid (30 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.30 (m, 2H), 7.29-7.28 (m, 2H), 7.27-7.26 (m, 2H), 7.25-7.18 (m, 8H), 7.11-7.07 (m, 2H), 3.69-3.61 (m, 2H), 3.04-2.99 (m, 1H), 2.76-2.71 (m, 1H), 2.70-2.63 (m, 1H), 2.61-2.54 (m, 1H), 2.46-2.39 (m, 1H), 2.15-2.06 (m, 1H), 1.79-1.71 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.69, 139.49, 138.23, 137.49, 129.05, 128.98, 128.91, 128.71, 128.64, 127.16, 126.64, 124.51, 120.25, 49.19, 39.14, 36.00, 31.30, 29.34.

HRMS (ESI): Calcd for $C_{24}H_{25}NOS$ $[M+H]^+$: 376.1735, Found: 376.1734.

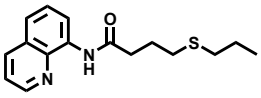


4-(benzylthio)-3-methyl-*N*-phenylbutanamide (9i). The reaction was conducted according to general procedure B, the reaction mixture was stirred at 80 °C for 48 hours. The product was purified by preparative TLC (1:10 EA:PE) as yellow oil (15 mg, 49%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.7 Hz, 2H), 7.41 (s, 1H), 7.33-7.28 (m, 6H), 7.24-7.20 (m, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 3.74-3.67 (m, 2H), 2.53-2.44 (m, 3H), 2.35-2.27 (m, 1H), 2.20-2.14 (m, 1H), 1.06 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.41, 138.43, 137.92, 129.08, 129.00, 128.62, 127.12, 124.38, 119.96, 43.67, 38.27, 36.66, 30.72, 19.87.

HRMS (ESI): Calcd for $C_{18}H_{21}NOS$ $[M+H]^+$: 300.1422, Found: 300.1423.

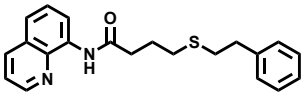


4-(propylthio)-*N*-(quinolin-8-yl)butanamide (9j). The reaction was conducted according to general procedure B, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:10 EA:PE) as yellow oil (27 mg, 95%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.83 (s, 1H), 8.79 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.76 (dd, *J* = 7.3, 1.8 Hz, 1H), 8.15 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.55-7.43 (m, 3H), 2.71 (t, *J* = 7.3 Hz, 2H), 2.66 (t, *J* = 7.1 Hz, 2H), 2.52 (t, *J* = 7.2 Hz, 2H), 2.14-2.07 (m, 2H), 1.66-1.57 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.14, 148.23, 138.38, 136.46, 134.54, 128.01, 127.49, 121.69, 121.54, 116.51, 36.73, 34.08, 31.51, 25.26, 23.04, 13.61.

HRMS (ESI): Calcd for $C_{16}H_{20}N_2OS$ $[M+H]^+$: 289.1375, Found: 289.1374.

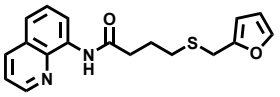


4-(phenethylthio)-*N*-(quinolin-8-yl)butanamide (9k). The reaction was conducted according to general procedure B, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:10 EA:PE) as yellow oil (30 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.84 (s, 1H), 8.80-8.77 (m, 2H), 8.16 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.56-7.43 (m, 3H), 7.30-7.26 (m, 2H), 7.22-7.18 (m, 3H), 2.92-2.87 (m, 2H), 2.84-2.79 (m, 2H), 2.72-2.67 (m, 4H), 2.15-2.08 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.07, 148.25, 140.63, 138.38, 136.48, 134.53, 128.60, 128.55, 128.03, 127.51, 126.42, 121.72, 121.59, 116.54, 36.65, 36.38, 33.53, 31.69, 25.17.

HRMS (ESI): Calcd for $C_{21}H_{22}N_2OS$ $[M+H]^+$: 351.1531, Found: 351.1533.



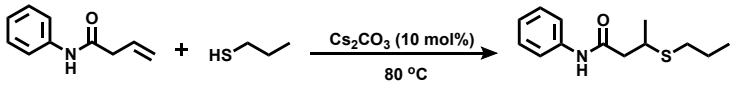
4-((furan-2-ylmethyl)thio)-*N*-(quinolin-8-yl)butanamide (9l). The reaction was conducted according to general procedure B, the reaction mixture was stirred at 80 °C for 24 hours. The product was purified by preparative TLC (1:10 EA:PE) as yellow oil (22 mg, 69%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.82 (s, 1H), 8.81 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.76 (dd, *J* = 7.1, 1.8 Hz, 1H), 8.16 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.56-7.44 (m, 3H), 7.33 (dd, *J* = 1.9, 0.9 Hz, 1H), 6.27-6.26 (m, 1H), 6.19-6.18 (m, 1H), 3.75 (s, 2H), 2.70-2.64 (m, 4H), 2.12-2.05 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.06, 151.67, 148.29, 142.27, 138.44, 136.53, 134.58, 128.08, 127.55, 121.76, 121.61, 116.58, 110.53, 107.68, 36.67, 31.23, 28.22, 24.82

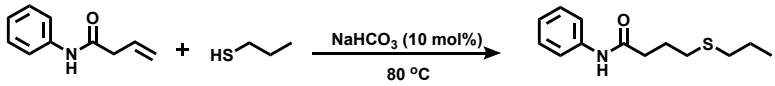
HRMS (ESI): Calcd for $C_{18}H_{18}N_2O_2S$ $[M+H]^+$: 327.1167, Found: 327.1165.

V. Gram-scale reaction



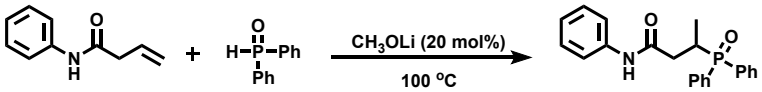
3a, 1.12g, 95%

General procedure for gram-scale reaction: In a dry 100-mL Schlenk tube containing a magnetic stirbar was charged with Cs_2CO_3 (10 mol%, 165 mg, 0.5 mmol), alkene 1a (1 equiv, 805 mg, 5 mmol) and 1-popanethiol (10 equiv, 3.80 g, 50 mmol). The mixture was stirred at 80 ºC for 24 h. The reaction mixture was concentrated on a rotary evaporator, then the resulting residue was directly subjected to silica gel flash chromatography (1:10 EA:PE), product was obtained as yellow oil (1.12 g, 95%).



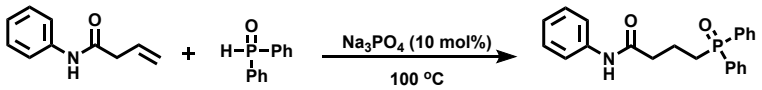
4a, 1.09g, 92%

General procedure for gram-scale reaction: In a dry 100-mL Schlenk tube containing a magnetic stirbar was charged with $NaHCO_3$ (10 mol%, 42 mg, 0.5 mmol), alkene 1a (1 equiv, 805 mg, 5 mmol) and 1-popanethiol (10 equiv, 3.80 g, 50 mmol). The mixture was stirred at 80 ºC for 24 h. The reaction mixture was concentrated on a rotary evaporator, then the resulting residue was directly subjected to silica gel flash chromatography (1:10 EA:PE), product was obtained as yellow oil (1.09 g, 92%).



6a, 1.42g, 78%

General procedure for gram-scale reaction: In a dry 100-mL Schlenk tube containing a magnetic stirbar was charged with CH_3OLi (20 mol%, 38 mg, 1.0 mmol), alkene 1a (1 equiv, 805 mg, 5 mmol) and diphenylphosphine oxide (2 equiv, 2.02 g, 10 mmol). The mixture was stirred at 80 ºC for 24 h. The reaction mixture was concentrated on a rotary evaporator, then the resulting residue was directly subjected to silica gel flash chromatography (1:50 MeOH:DCM), product was obtained as white solid (1.42 g, 78%).

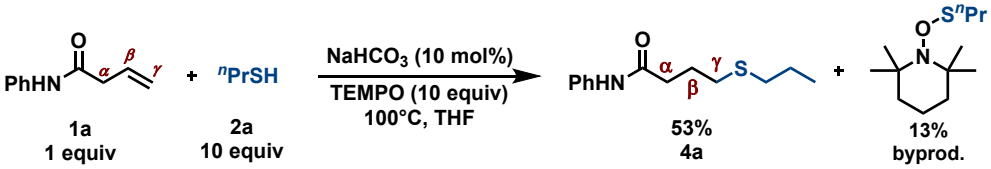


7a, 1.47g, 81%

General procedure for gram-scale reaction: In a dry 100-mL Schlenk tube containing a magnetic stirbar was charged with Na_3PO_4 (10 mol%, 82 mg, 0.5 mmol), alkene 1a (1 equiv, 805 mg, 5 mmol) and diphenylphosphine oxide (2 equiv, 2.02 g, 10 mmol). The mixture was stirred at 80 ºC for 24 h. The reaction mixture was concentrated on a rotary evaporator, then the resulting residue was directly subjected to silica gel flash chromatography (1:50 MeOH:DCM), product was obtained as colorless oil (1.47 g, 81%).

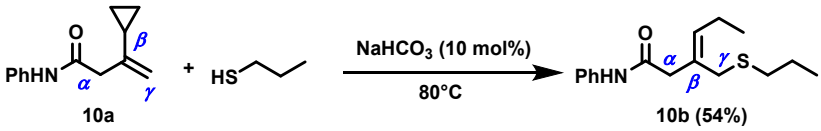
VI. Study on reaction progress

Table S6. Conditions for radical trapping experiment.



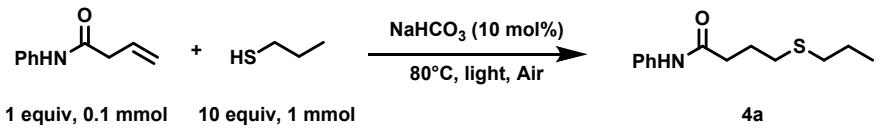
Entry	Alkene (**1a**) /Conversion (%)	Yield of **4a** (%)	Yield of **byprod.** (%)
1	100	53	13

General Procedure for radical trapping experiment: To a dry 10-mL Schlenk tube containing a magnetic stir bar was charged with alkenes 1a (1 equiv, 0.3 mmol, 48.3 mg), $NaHCO_3$ (10 mol%, 0.03 mmol, 2.7 mg), 1-propanethiol (10 equiv, 3.0 mmol, 228 mg), TEMPO (10 equiv, 3.0 mmol, 469 mg), THF (1.0 mL), 30 uL dodecane sequentially. The tube was capped tightly and the mixture was vigorously stirred in a pre-warmed 80 °C oil bath. The reaction result was analyzed by GC.



General Procedure for radical clock experiment: To a dry 10-mL Schlenk tube containing a magnetic stir bar was charged with alkenes 10a (1 equiv, 0.1 mmol, 20.1 mg), $NaHCO_3$ (10 mol%, 0.01 mmol, 0.9 mg), 1-propanethiol (10 equiv, 1.0 mmol, 76 mg), 10 uL dodecane sequentially. The tube was capped tightly and the mixture was vigorously stirred in a pre-warmed 80 °C oil bath. The product was purified by preparative TLC (1:10 EA:PE) as yellow oil (15 mg, 54%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (s, 1H), 7.52-7.49 (m, 2H), 7.33-7.30 (m, 2H), 7.11-7.08 (m, 1H), 5.62 (t, J = 7.8 Hz, 1H), 3.28 (s, 2H), 3.22 (s, 2H), 2.42 (t, J = 7.4 Hz), 2.18-2.10 (m, 2H), 1.64-1.59 (m, 2H), 1.03 (t, J = 7.5 Hz, 3H), 0.97 (t, J = 7.3 Hz, 3H).

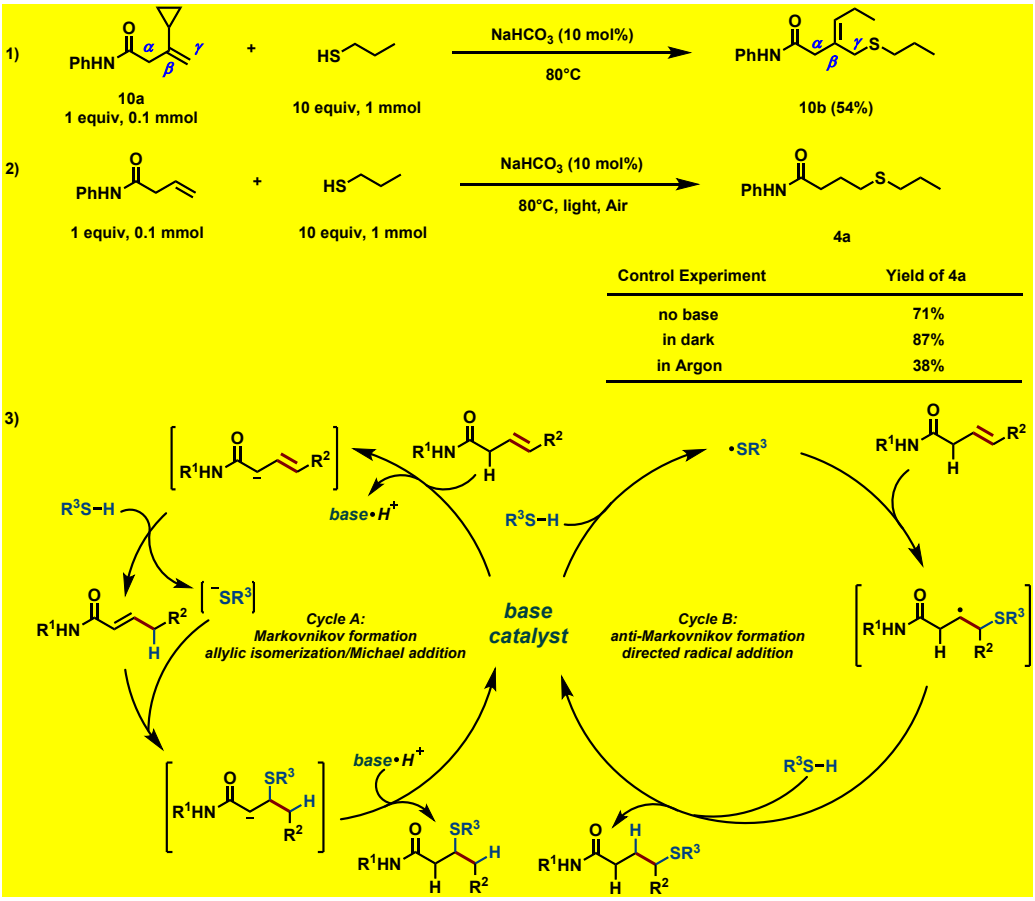


1 equiv, 0.1 mmol 10 equiv, 1 mmol 4a

Control Experiment	Yield of 4a
no base	71%
in dark	87%
in Argon	38%

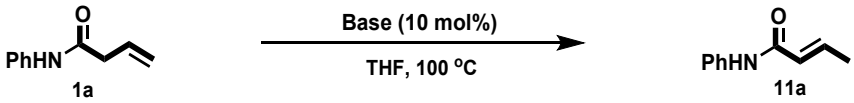
General Procedure for control experiment: To a dry 10-mL Schlenk tube containing a magnetic stir bar was charged with alkenes 1a (1 equiv, 0.1 mmol, 20.1 mg), $NaHCO_3$ (10 mol%, 0.01 mmol, 0.9 mg), 1-propanethiol (10 equiv, 1.0 mmol, 76 mg), 10 uL dodecane sequentially. The tube was capped tightly and the mixture was vigorously stirred in a pre-warmed 80 °C oil bath. The reaction was monitored by GC.

Collectively, based on the mechanisum studies in the **Scheme S1, eq 1 and 2,** two possible catalytic cycles for the regiodivergent hydrofunctionalization of *β,γ*-unsaturated amides have been proposed in **Scheme S1, eq 3.**

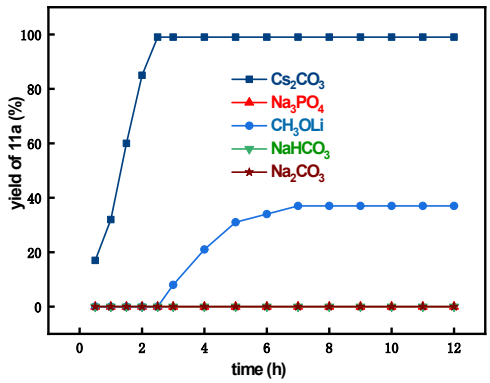


Scheme S1. Mechanism study and proposed catalytic cycles for the regiodivergent hydrofunctionalization of β,γ-unsaturated amides.

Table S7. Monitoring of the base-catalyzed conjugative isomerization of β,γ-unsaturated amide (**1a**).

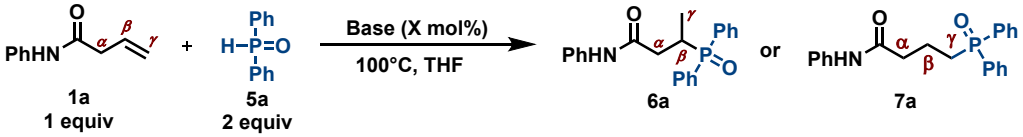


Entry	1	2	3	4	5
Base	Cs_2CO_3	Na_3PO_4	CH_3OLi	$NaHCO_3$	Na_2CO_3



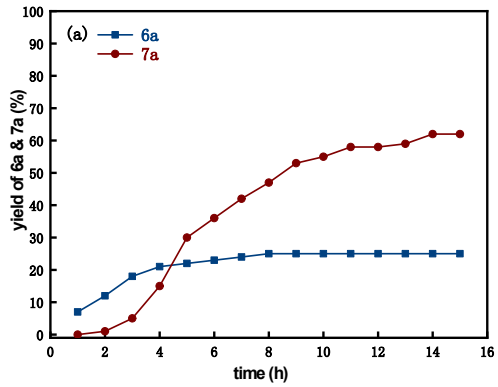
General Procedure for conjugative isomerization of allyl amide: To a dry 10-mL Schlenk tube containing a magnetic stir bar was charged with alkenes **1a** (1 equiv, 0.5 mmol, 81 mg), base (10 mol%), THF (5 mL), 50 uL dodecane sequentially. The tube was capped tightly and the mixture was vigorously stirred in a pre-warmed 100 °C oil bath. The reaction process was monitored by GC hourly.

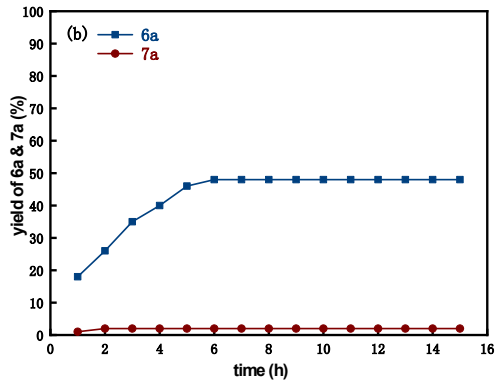
Table S8. Conditions for monitoring of reaction process.

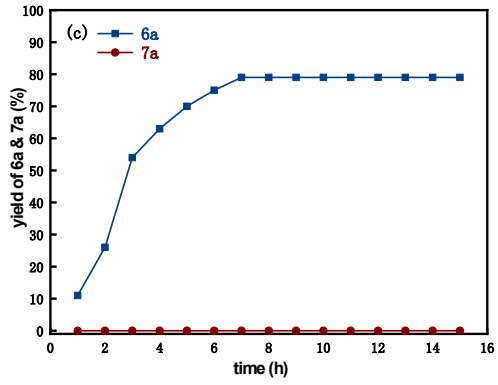


Entry	Base	Amount of Base
1	Cs_2CO_3	10 mol%
2	Cs_2CO_3	50 mol%
3	CH_3OLi	20 mol%
4	Na_3PO_4	20 mol%

General Procedure for reaction progress: To a dry 10-mL Schlenk tube containing a magnetic stir bar was charged with alkenes 1a (1 equiv, 0.5 mmol, 81 mg), base (10-50 mol%), diphenylphosphine oxide (2 equiv, 1.0 mmol, 202 mg), THF (1 mL), 50 uL dodecane sequentially. The tube was capped tightly and the mixture was vigorously stirred in a pre-warmed 100 °C oil bath. The reaction process was monitored by GC hourly.







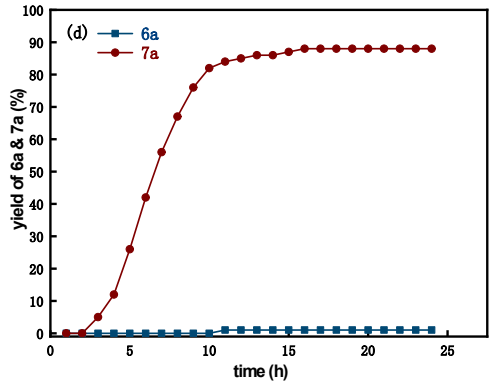


Figure S1. Monitoring of reaction progress. (a) Comparison of reaction rates for the formation of 6a and 6h in 10 mol% Cs_2CO_3. (b) Comparison of reaction rates for the formation of 6a and 6h in 50 mol% Cs_2CO_3. (c) Comparison of reaction rates for the formation of 6a and 6h in 20 mol% CH_3OLi. (d) Comparison of reaction rates for the formation of 6a and 6h in 20 mol% Na_3PO_4.

VII. Reference

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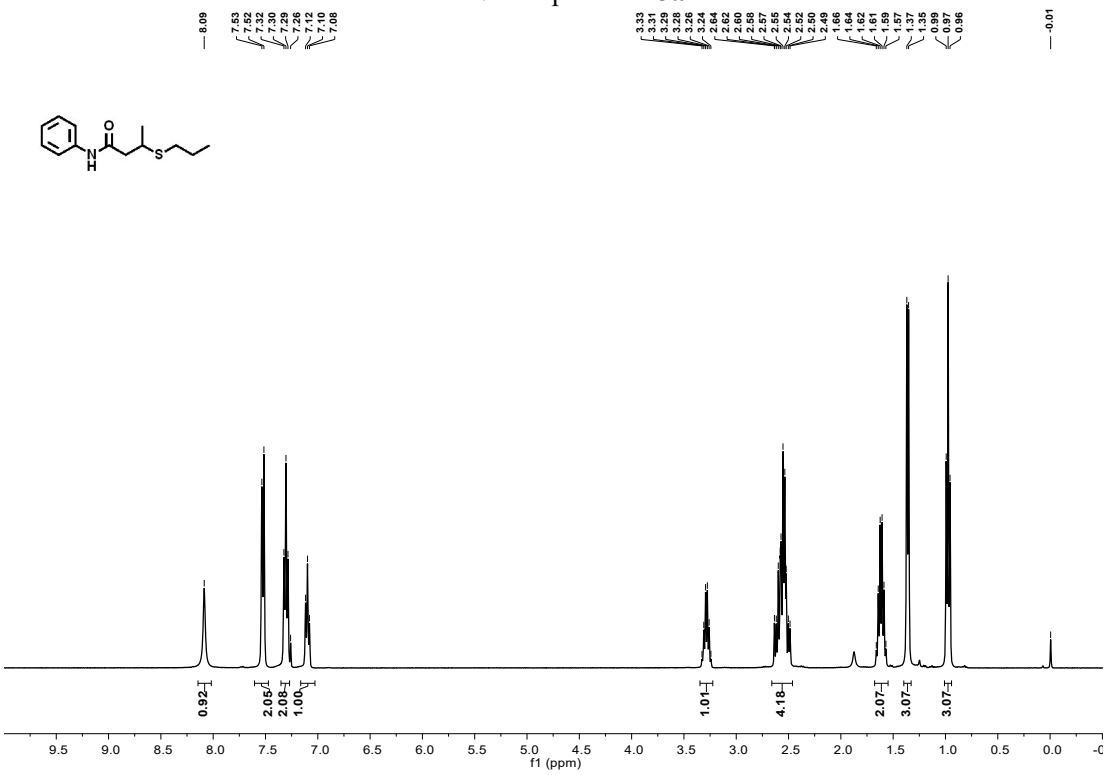
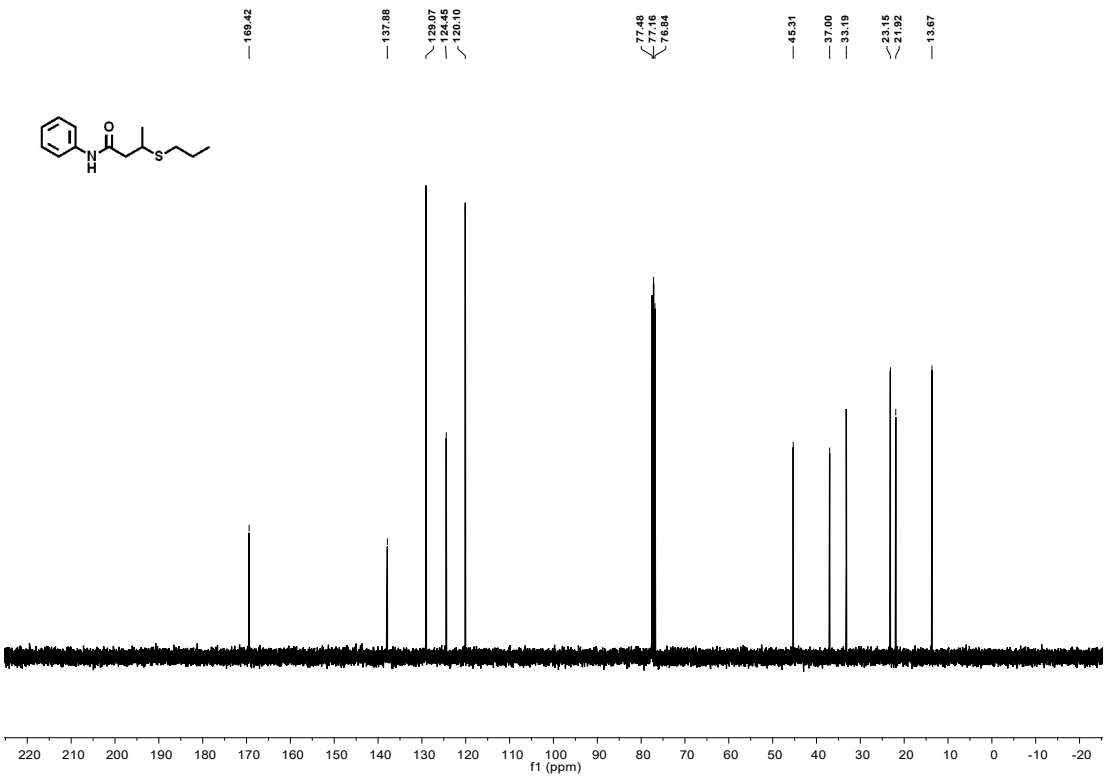
VIII. **NMR** spectra

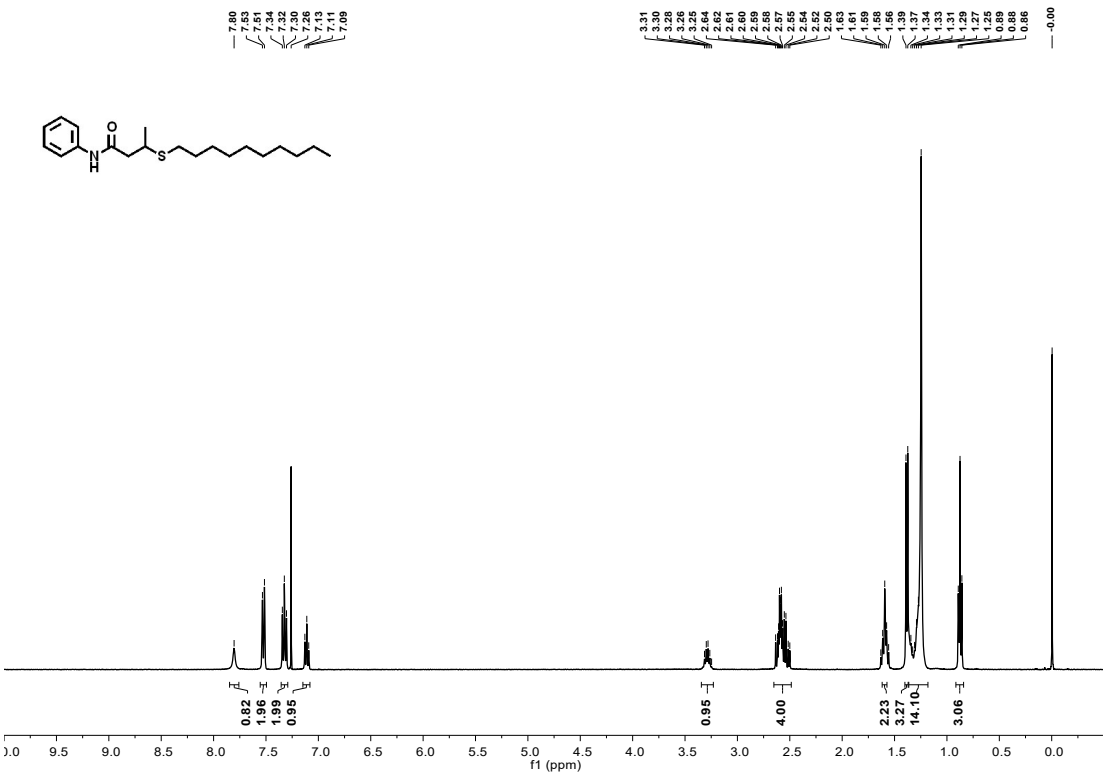
^{1}H NMR spectra of **3a**



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



^{1}H NMR spectra of **3b**



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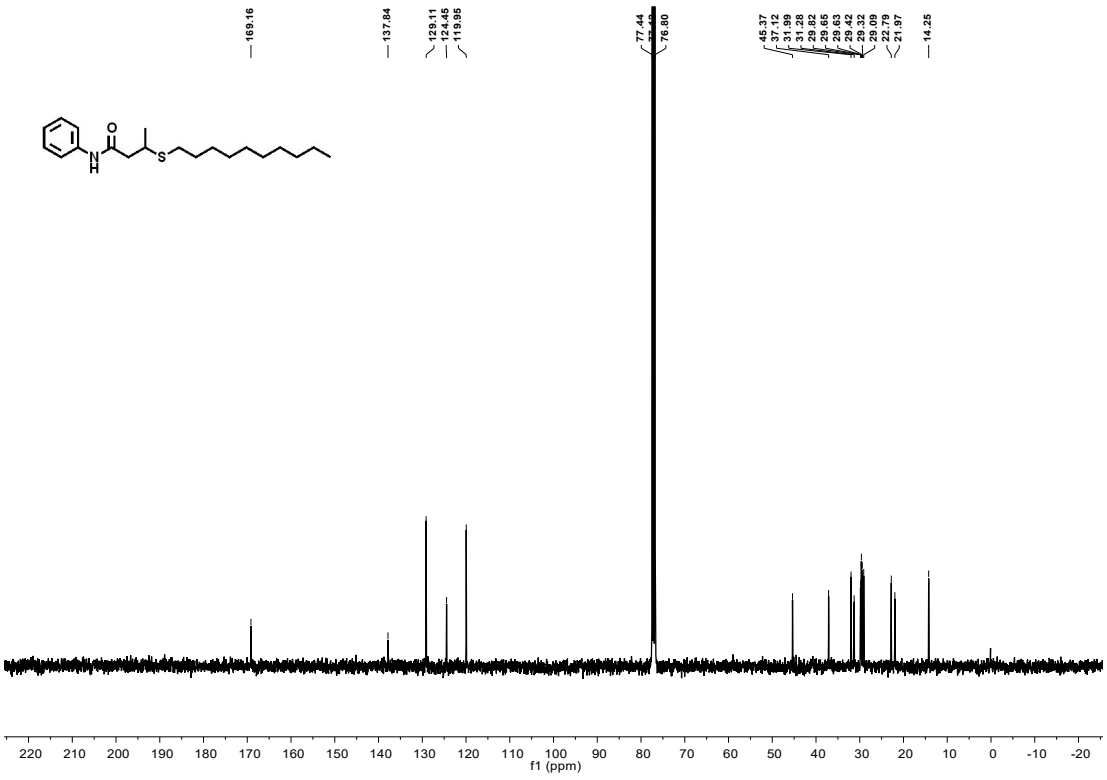
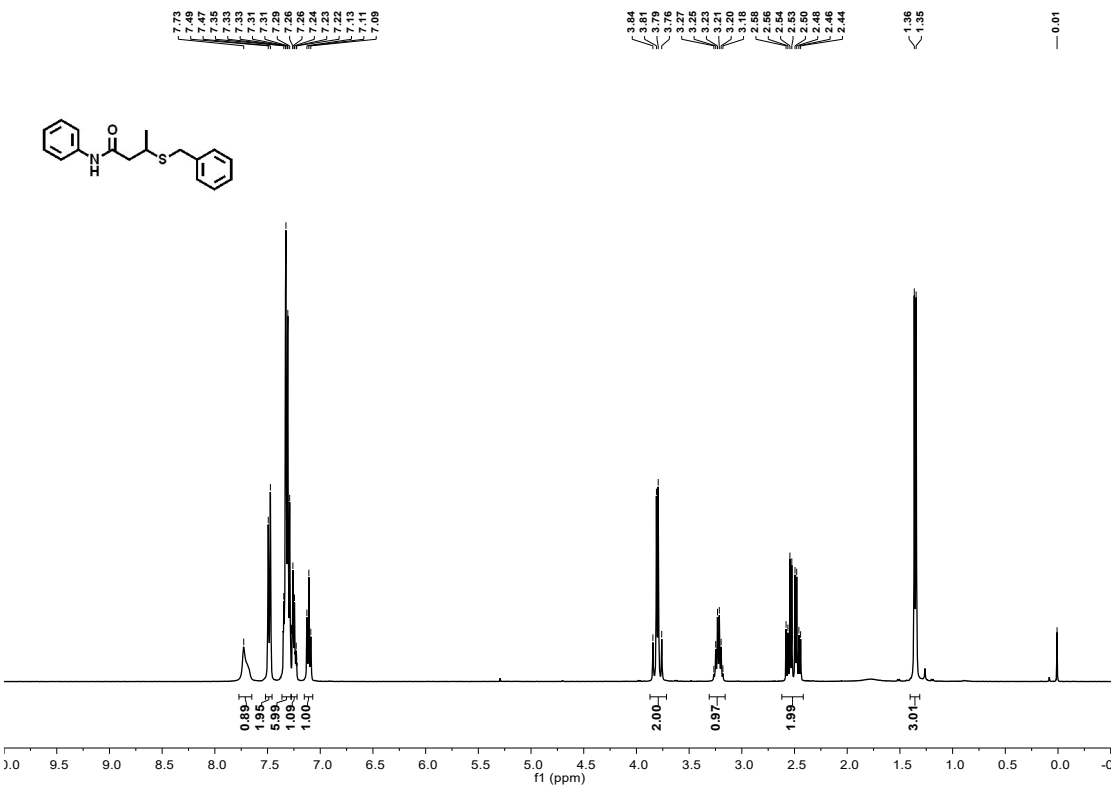


^{1}H NMR spectra of **3c**



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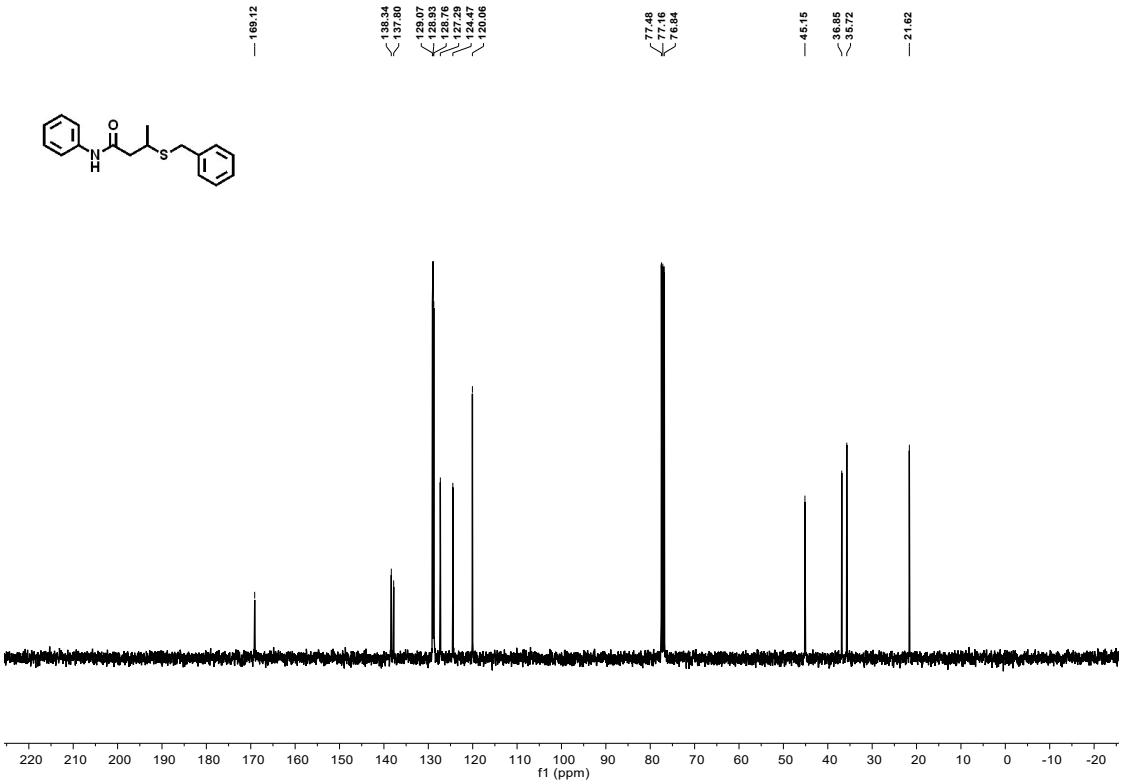
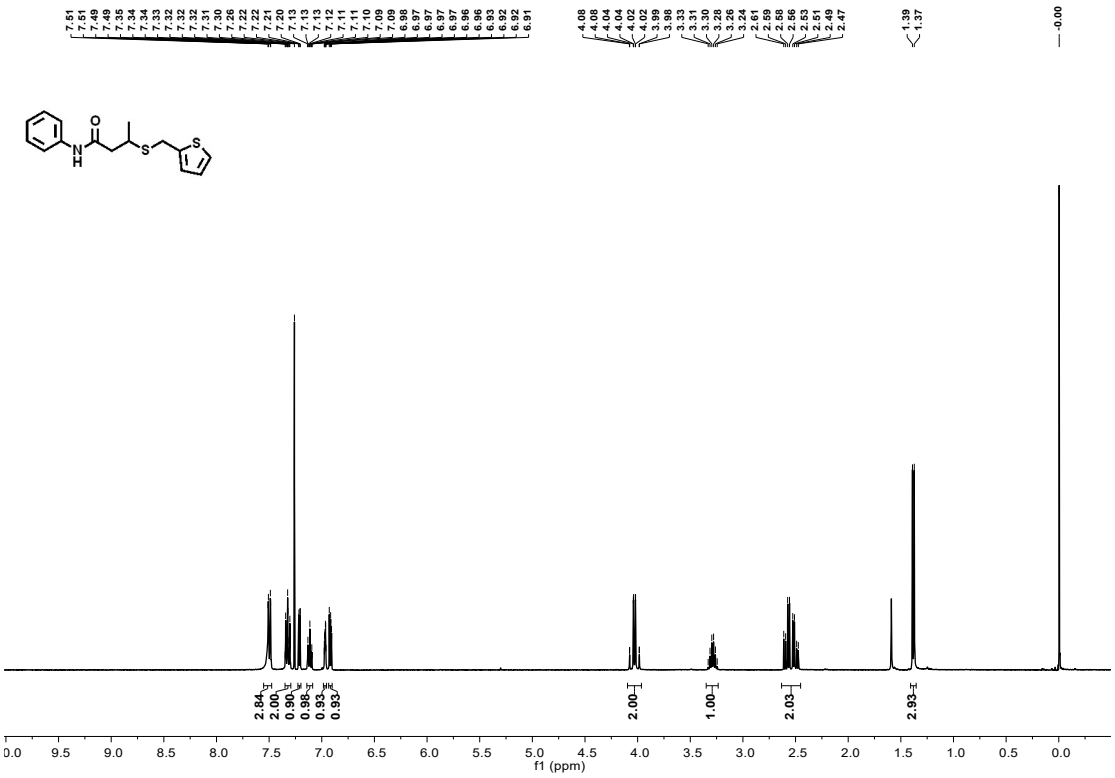


^{1}H NMR spectra of **3d**



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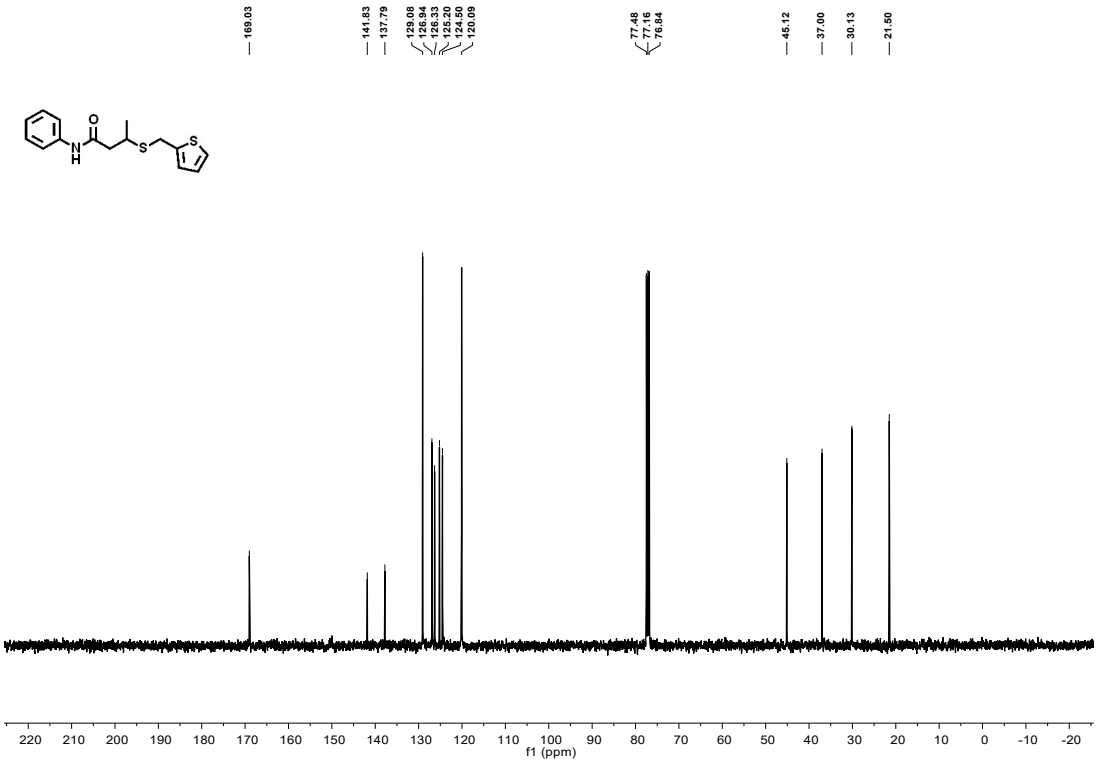

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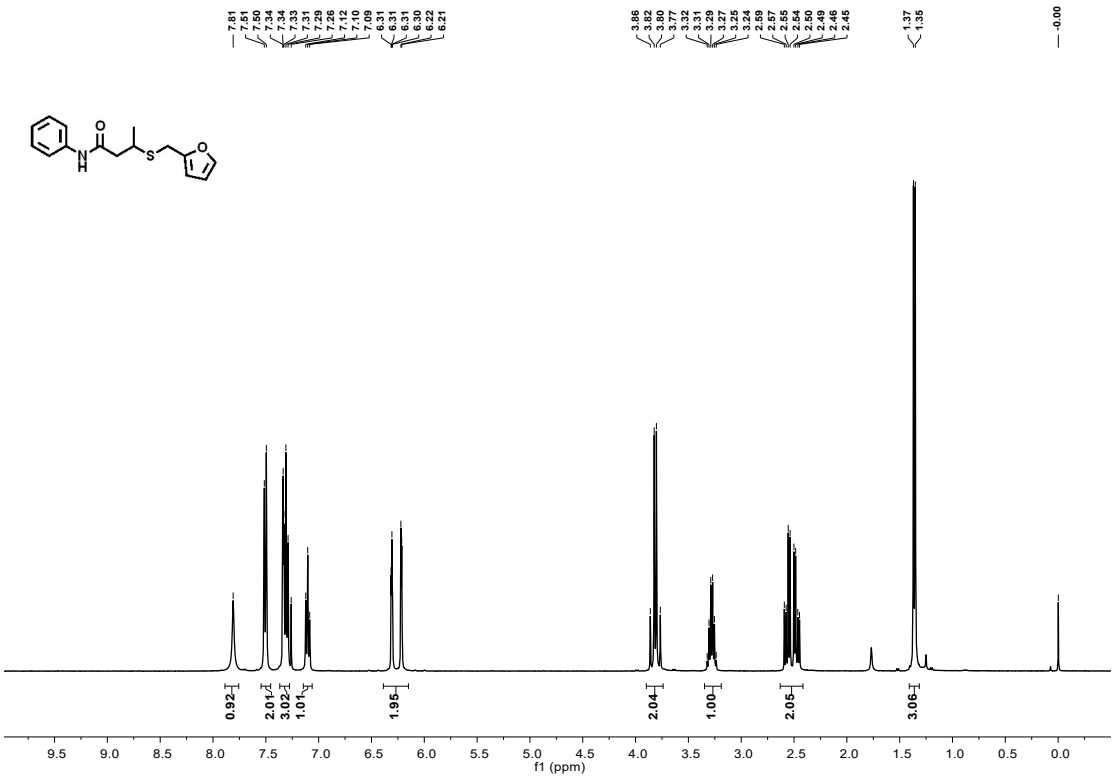

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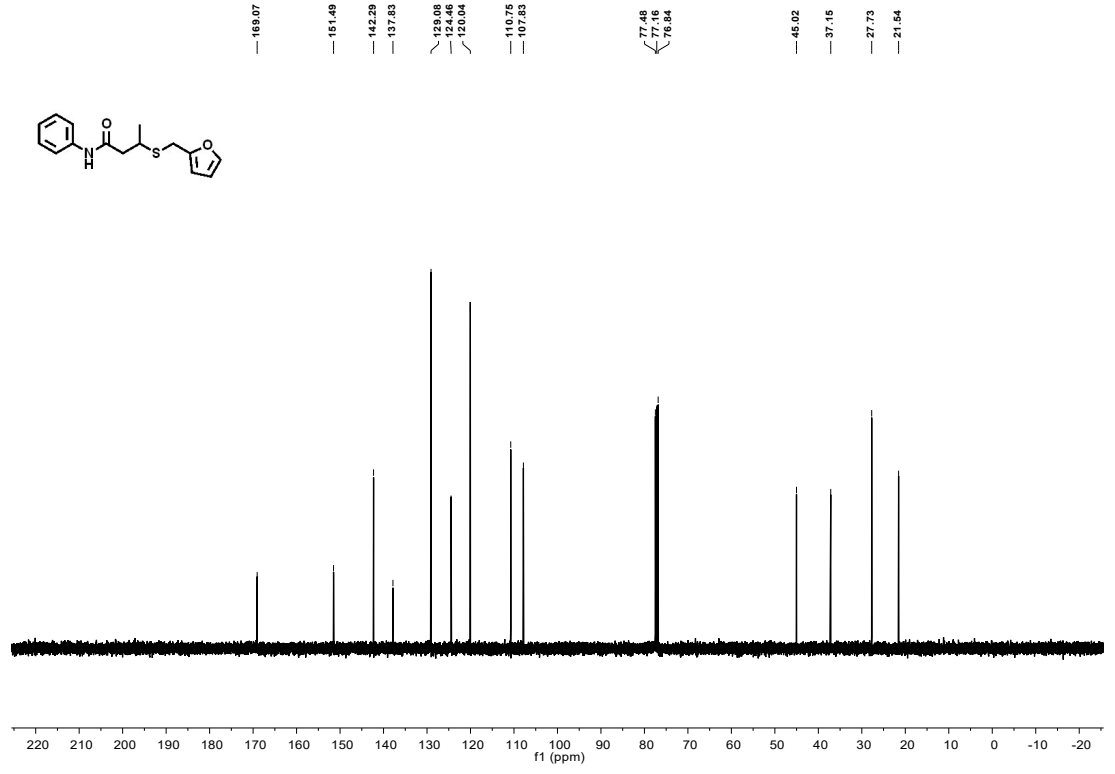
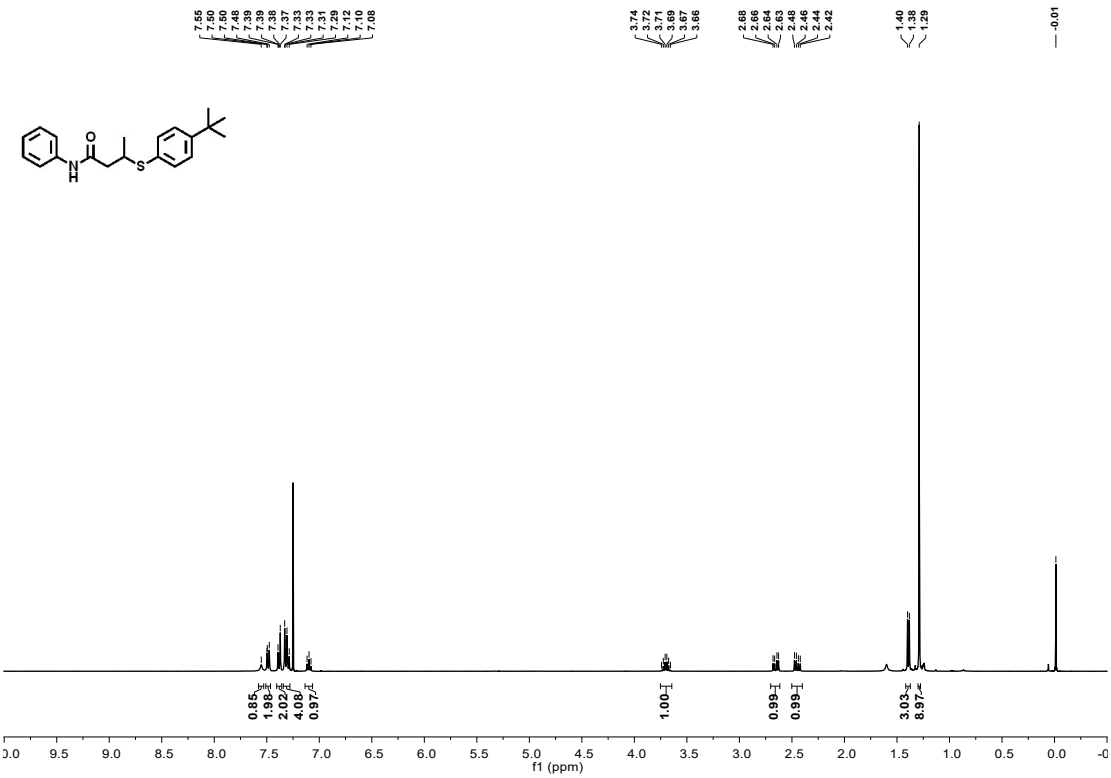


^{1}H NMR spectra of **3f**



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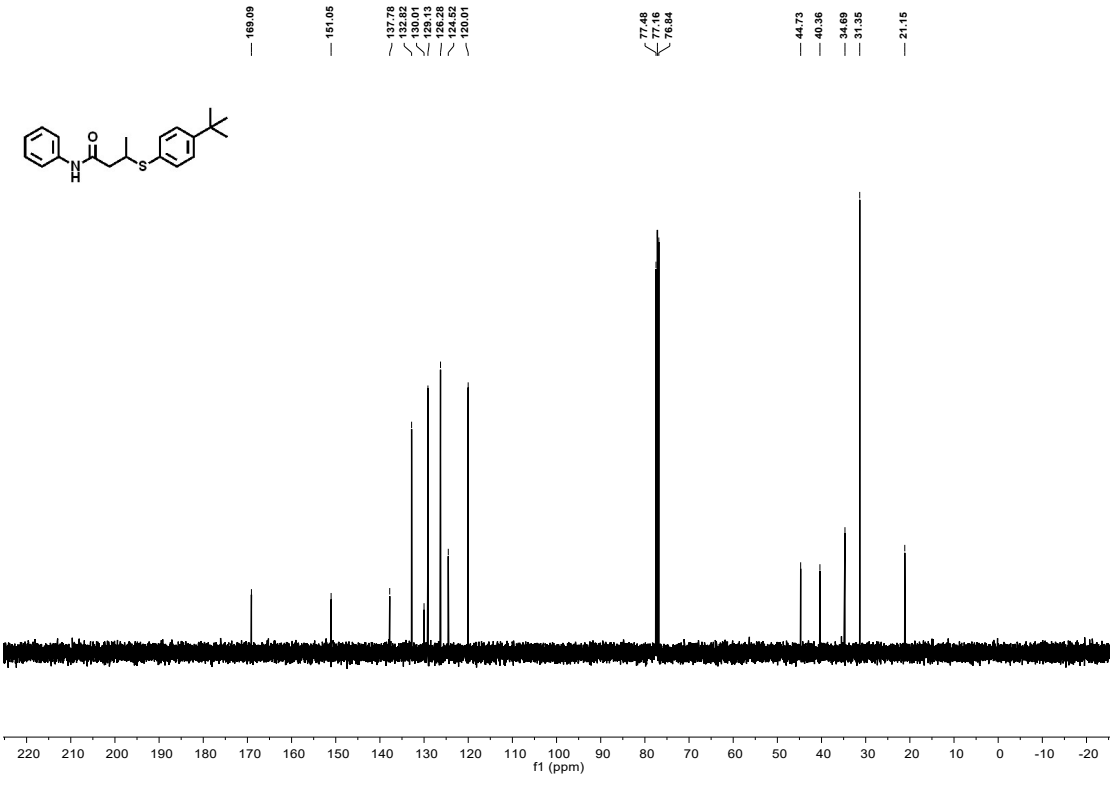
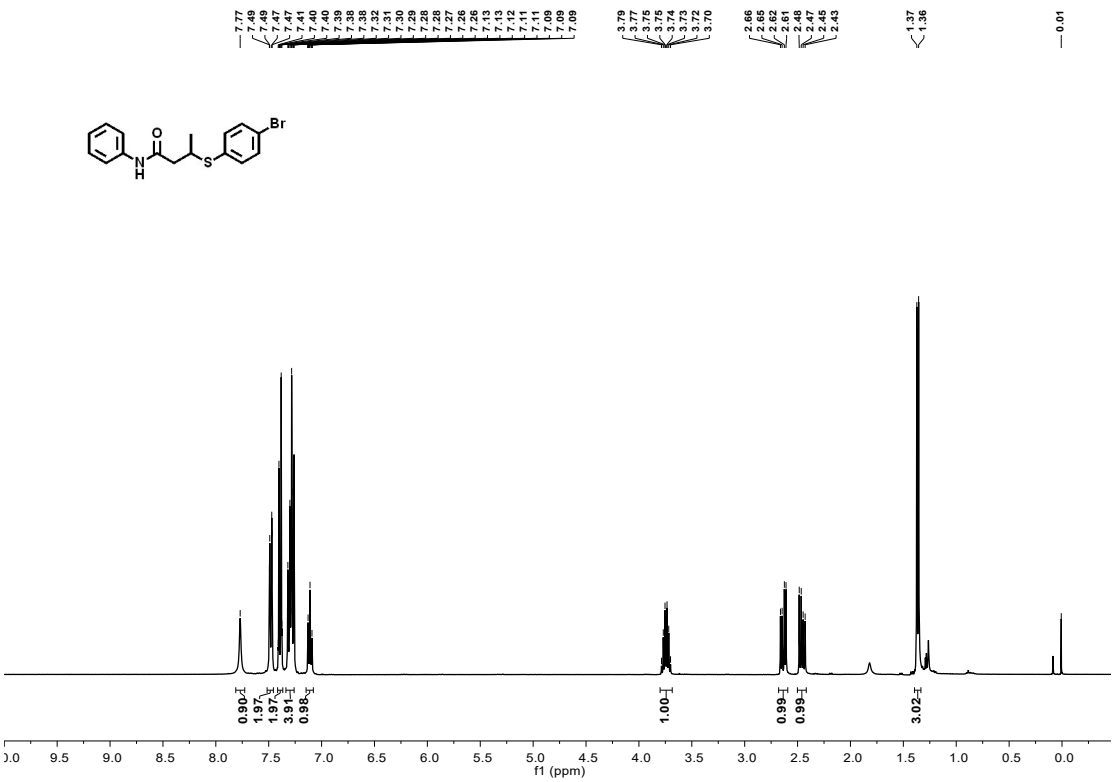
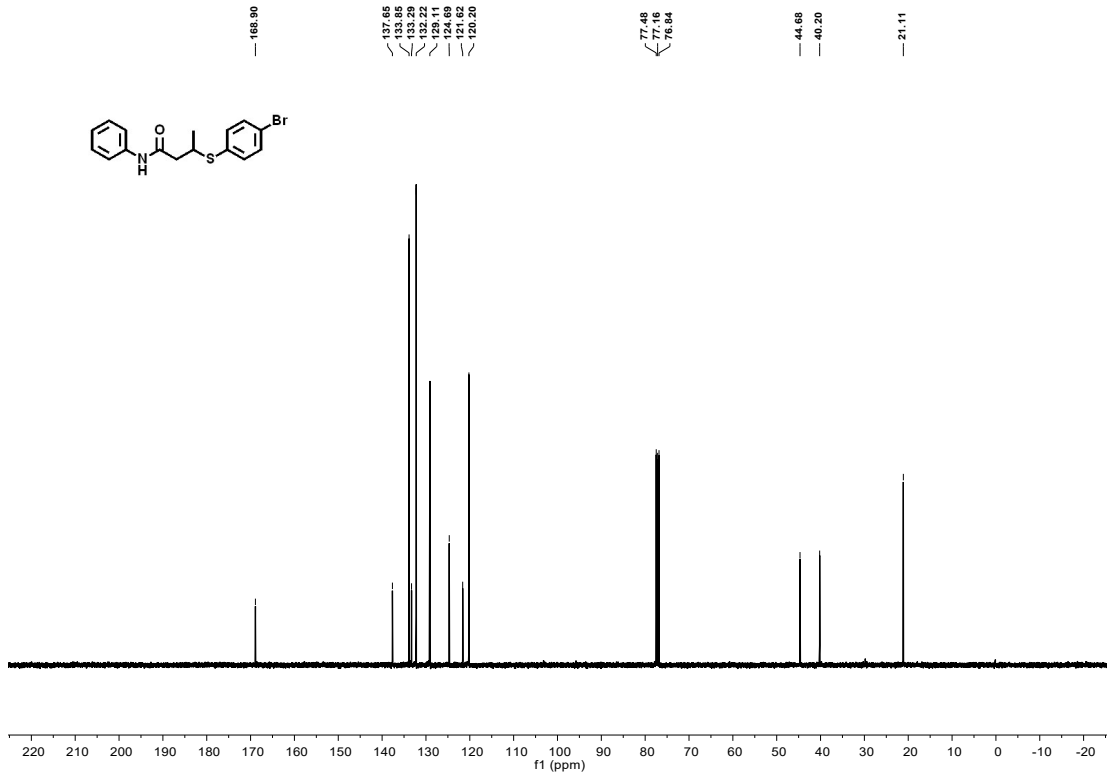


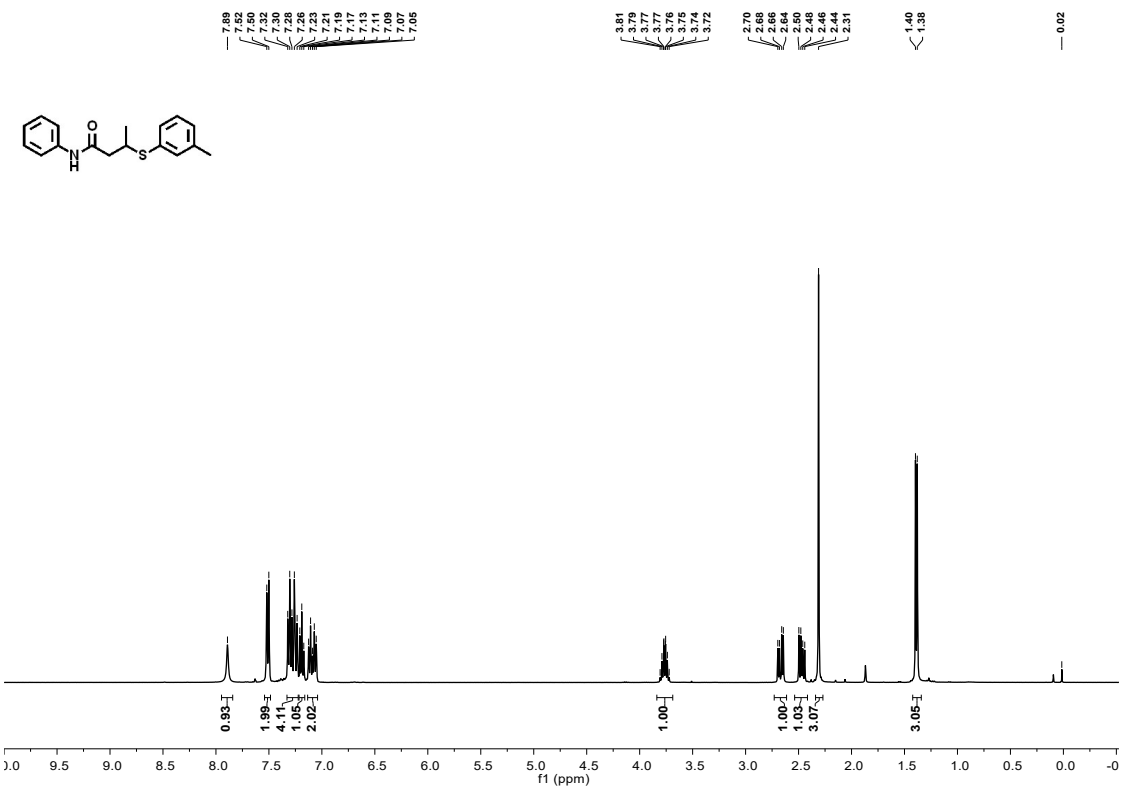
^{1}H NMR spectra of **3g**



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



^{1}H NMR spectra of **3h**



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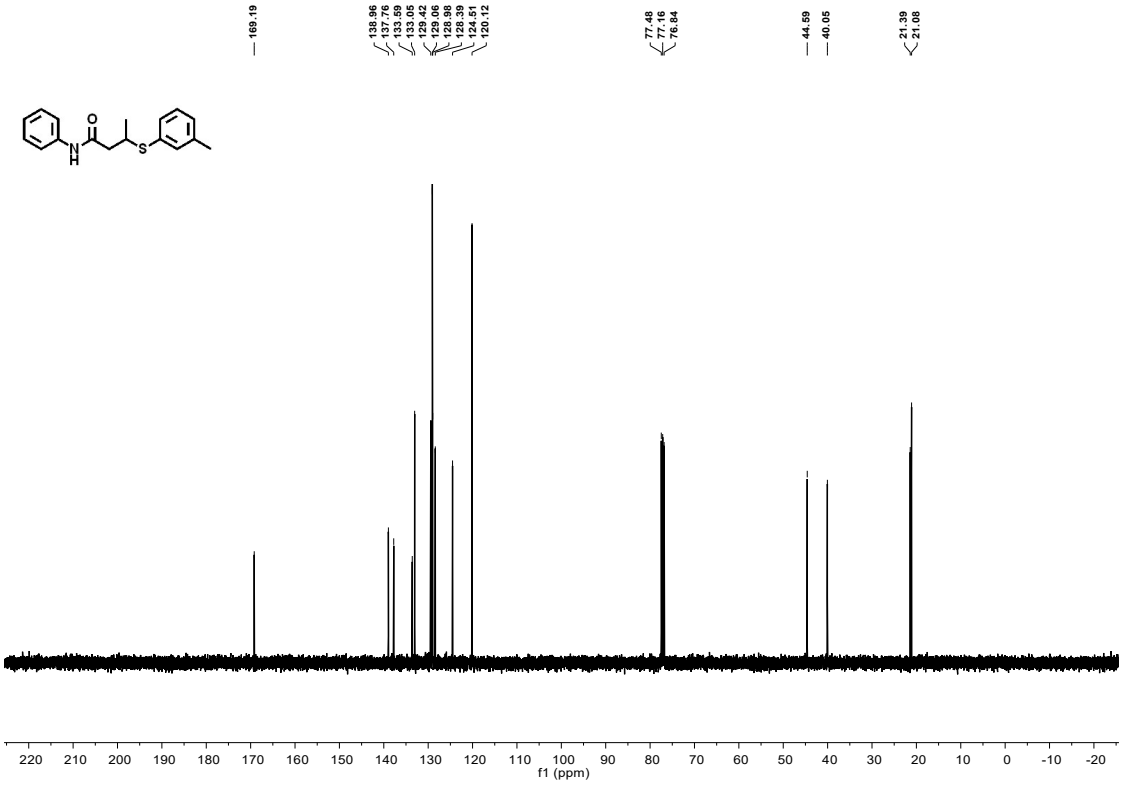
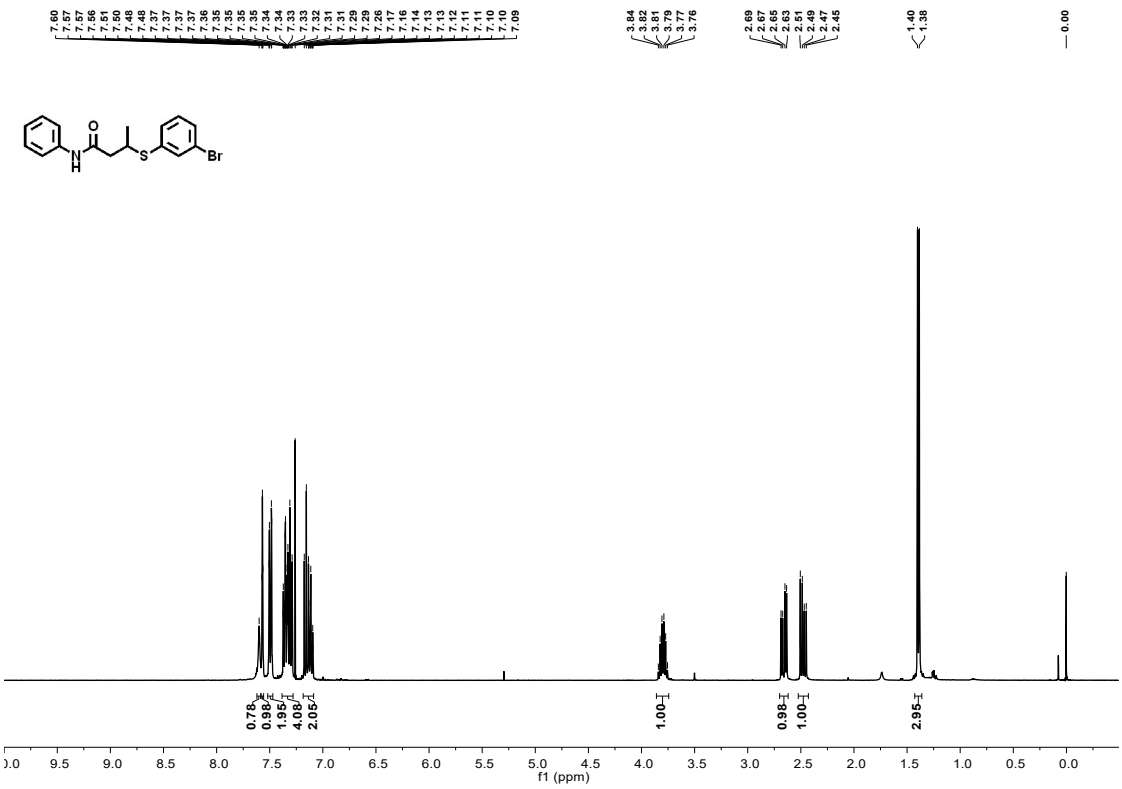
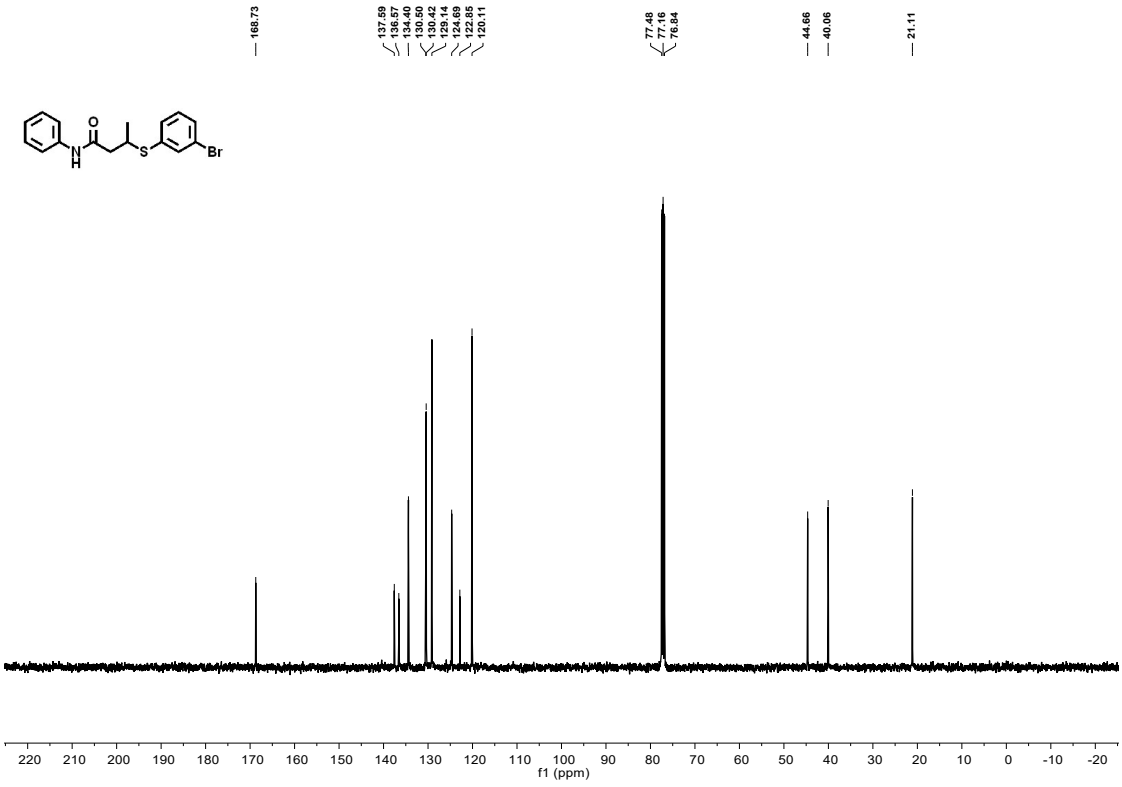


^{1}H NMR spectra of **3i**



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



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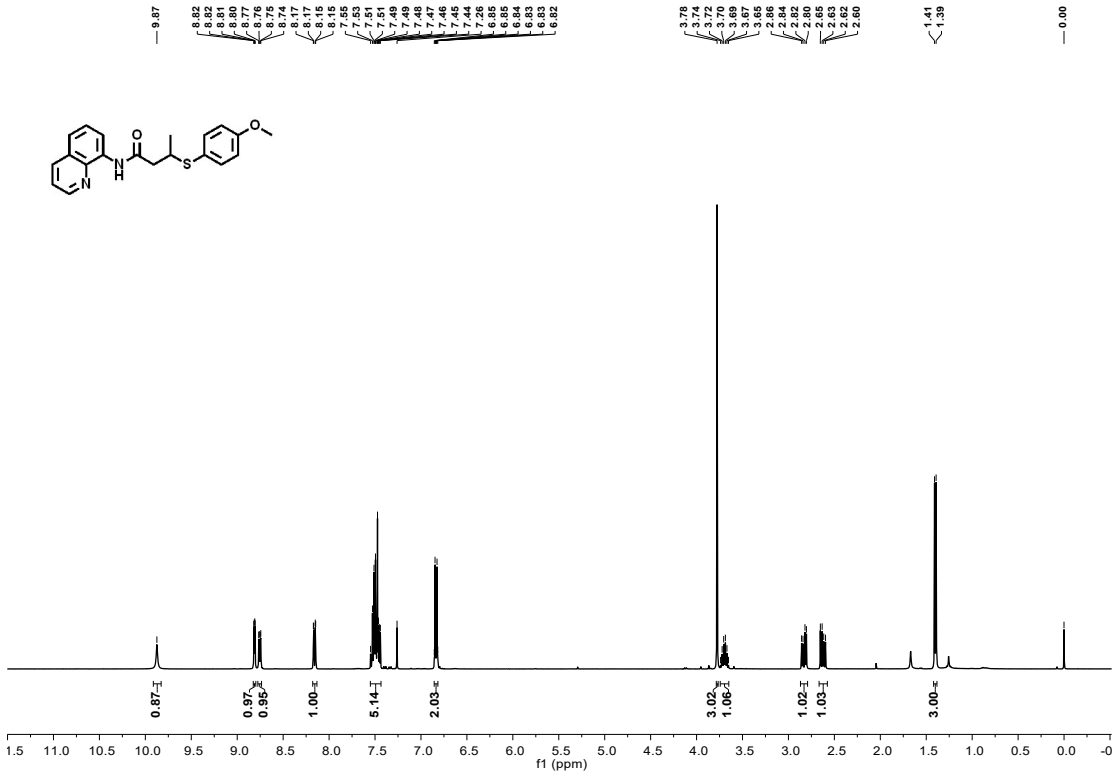

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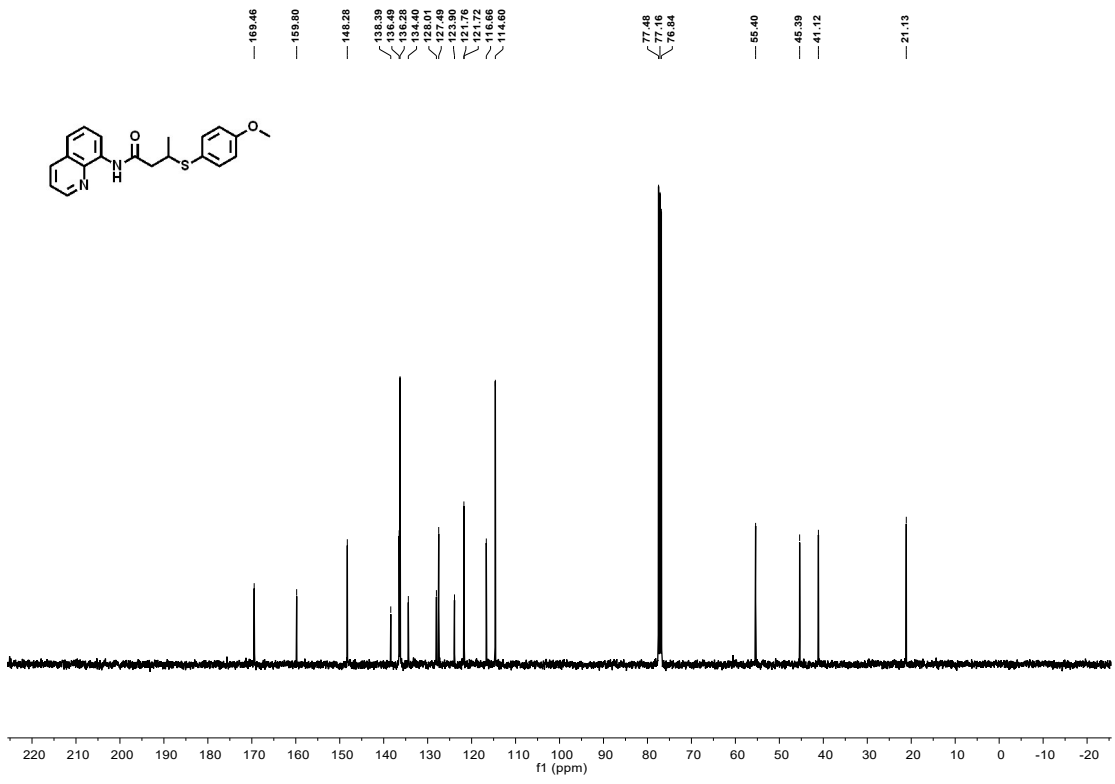

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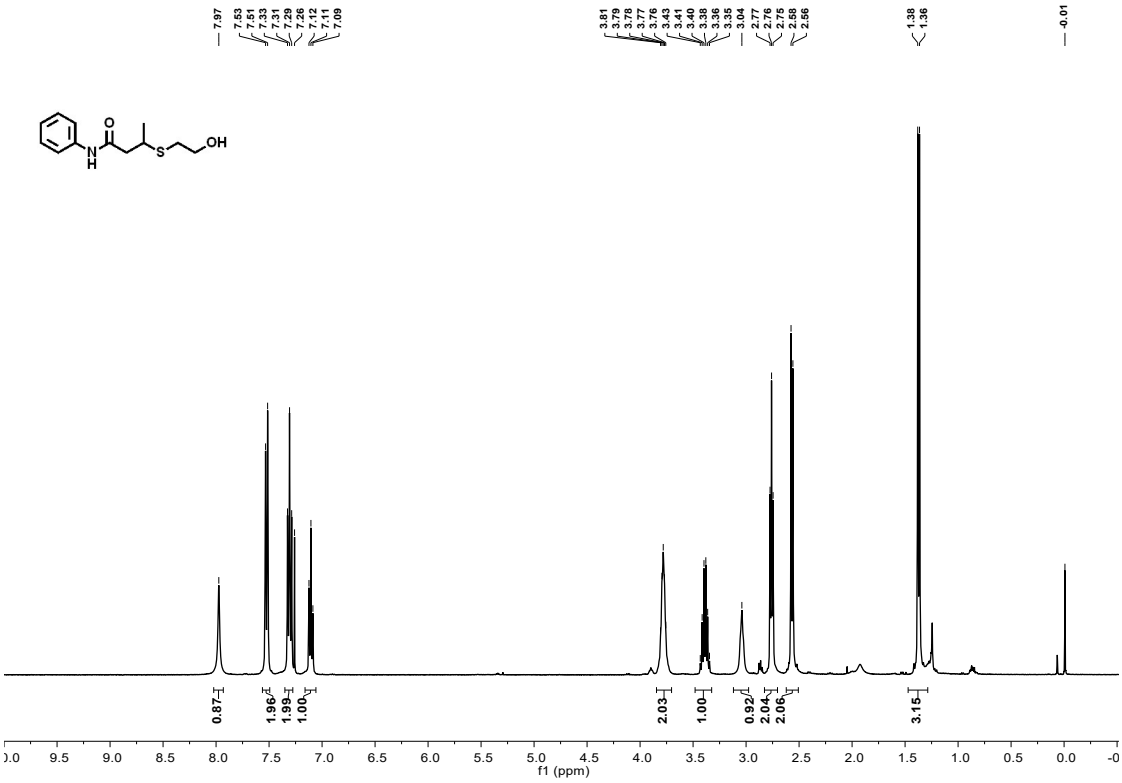

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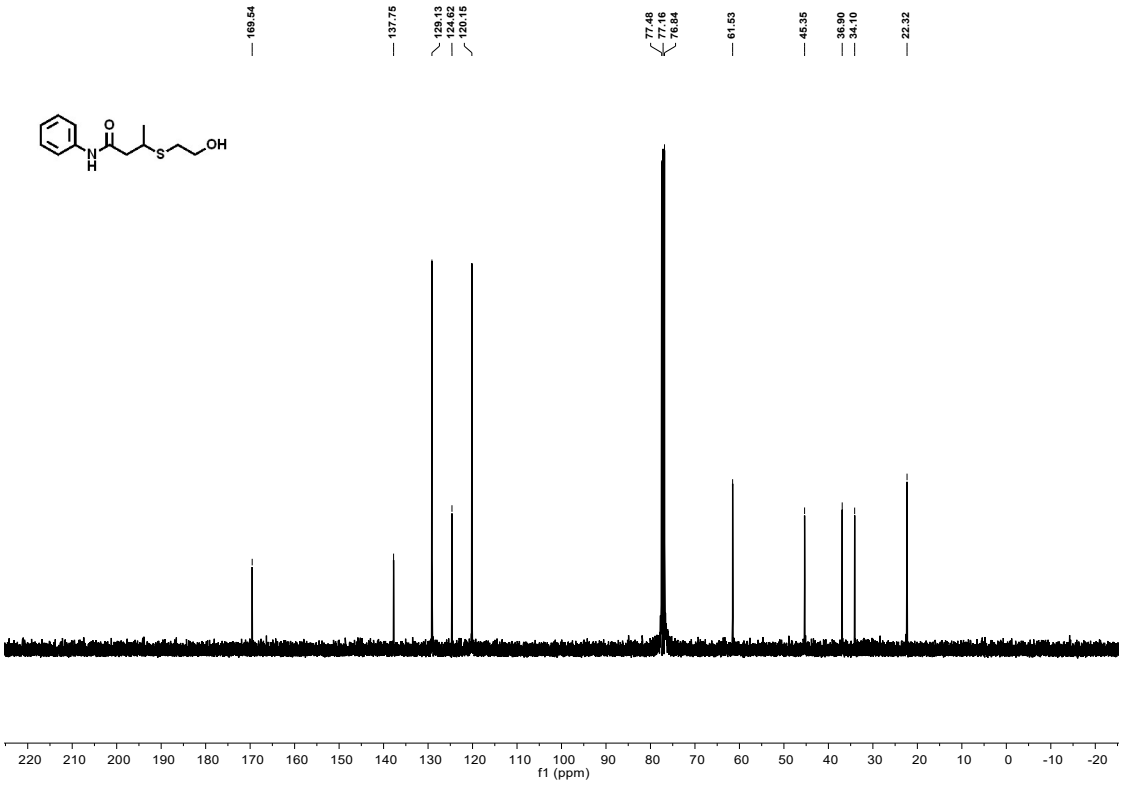

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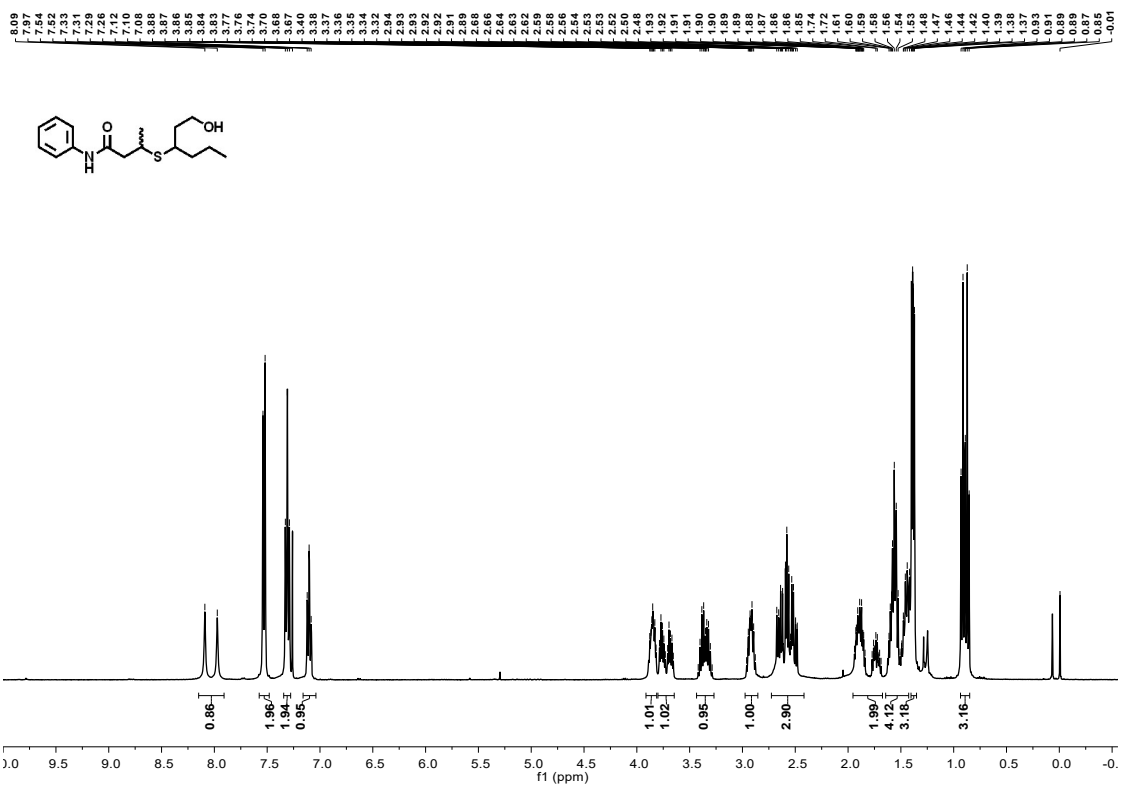

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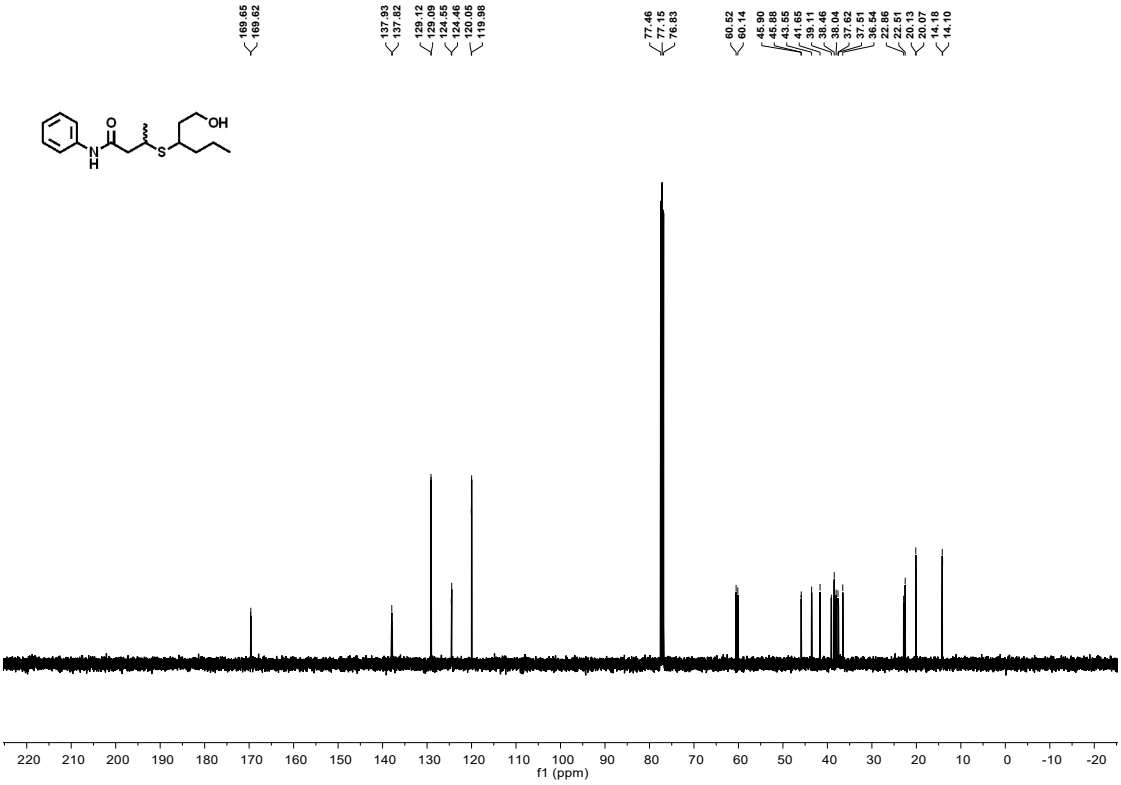
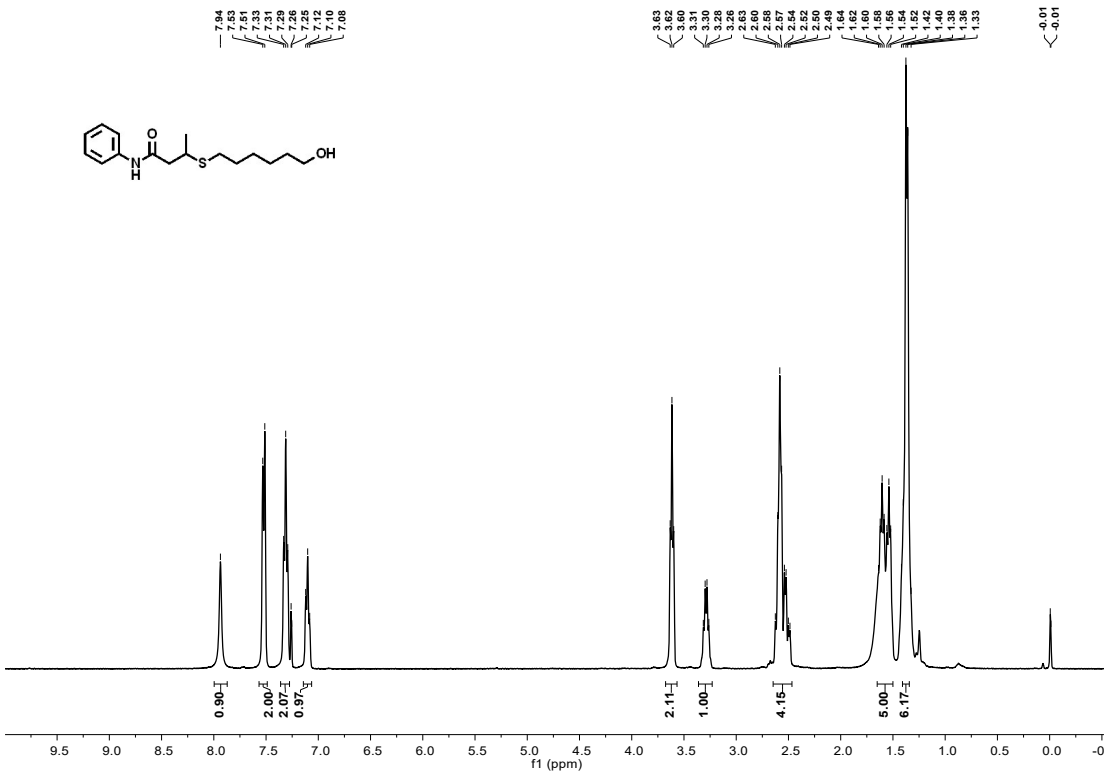


^{1}H NMR spectra of **3m**



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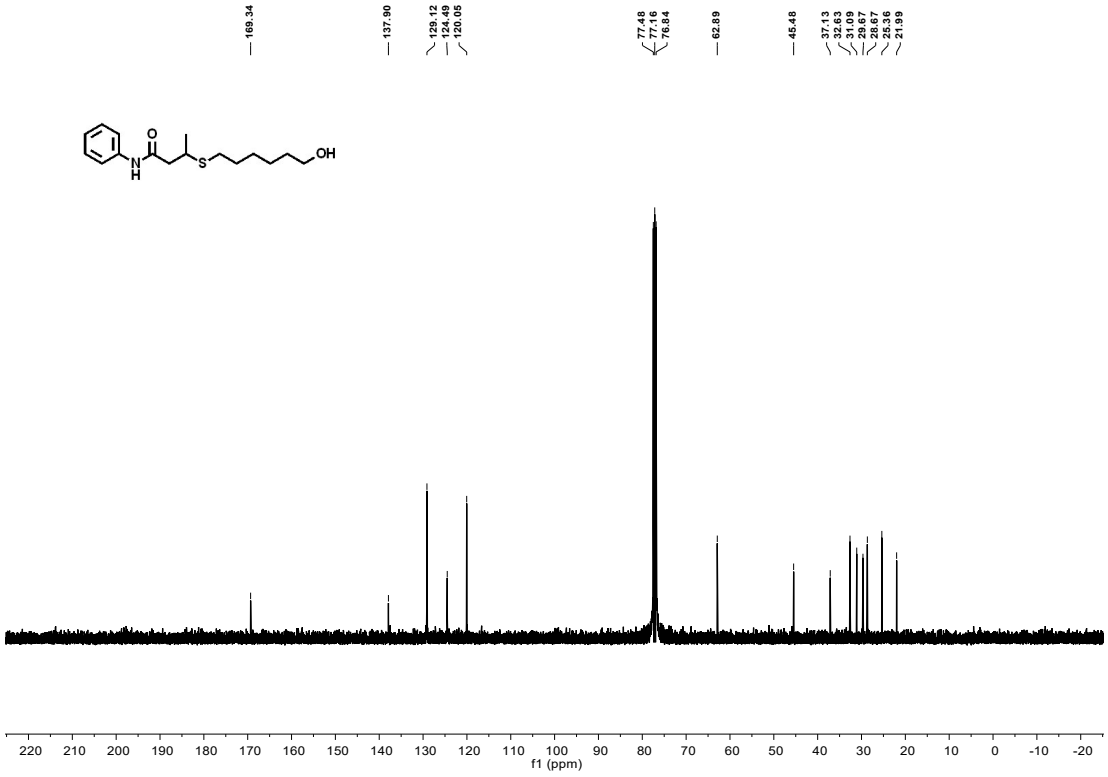

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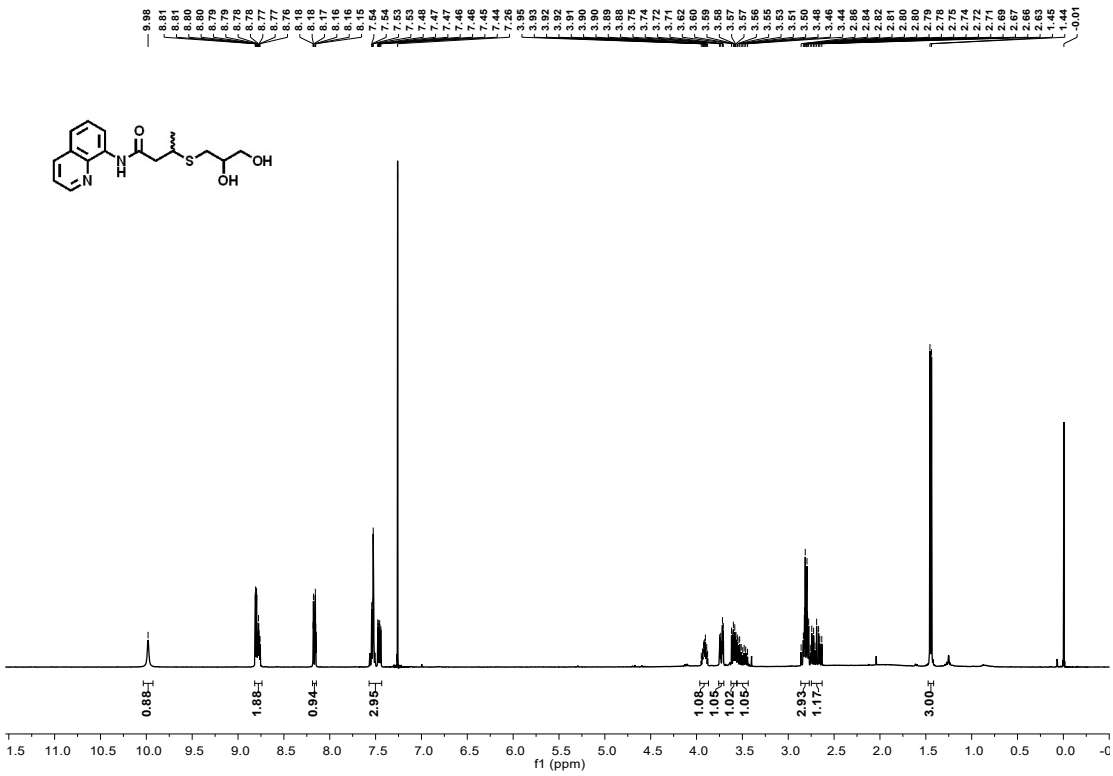

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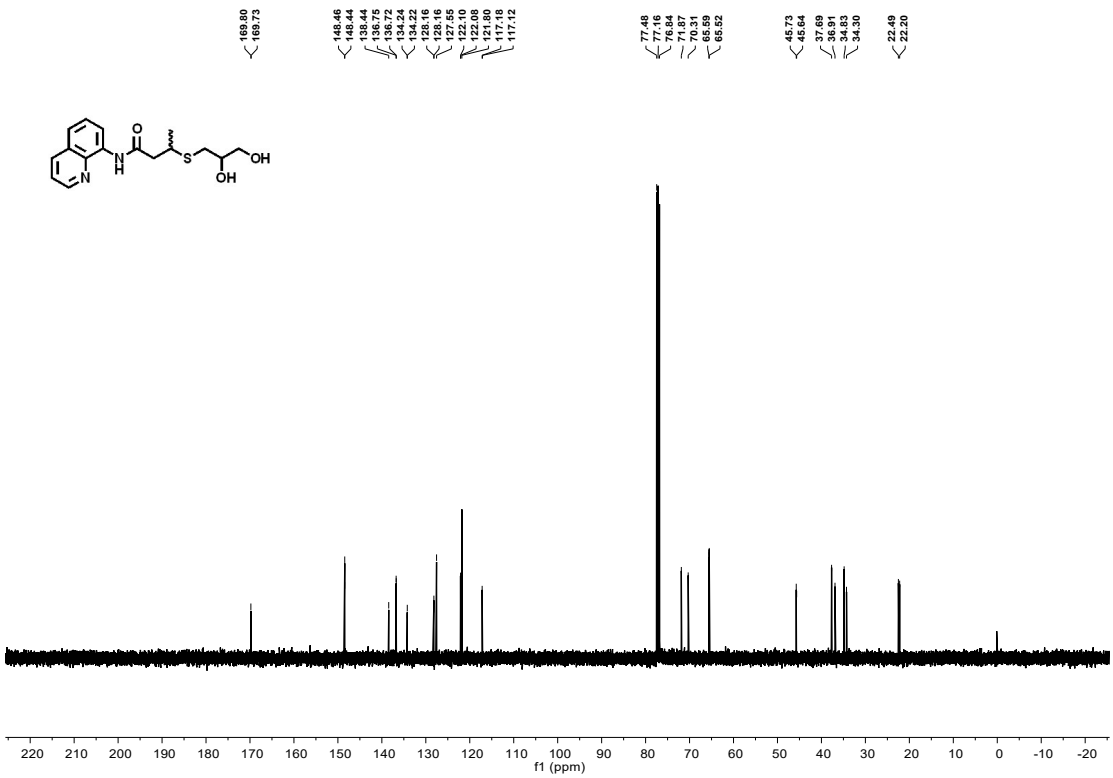

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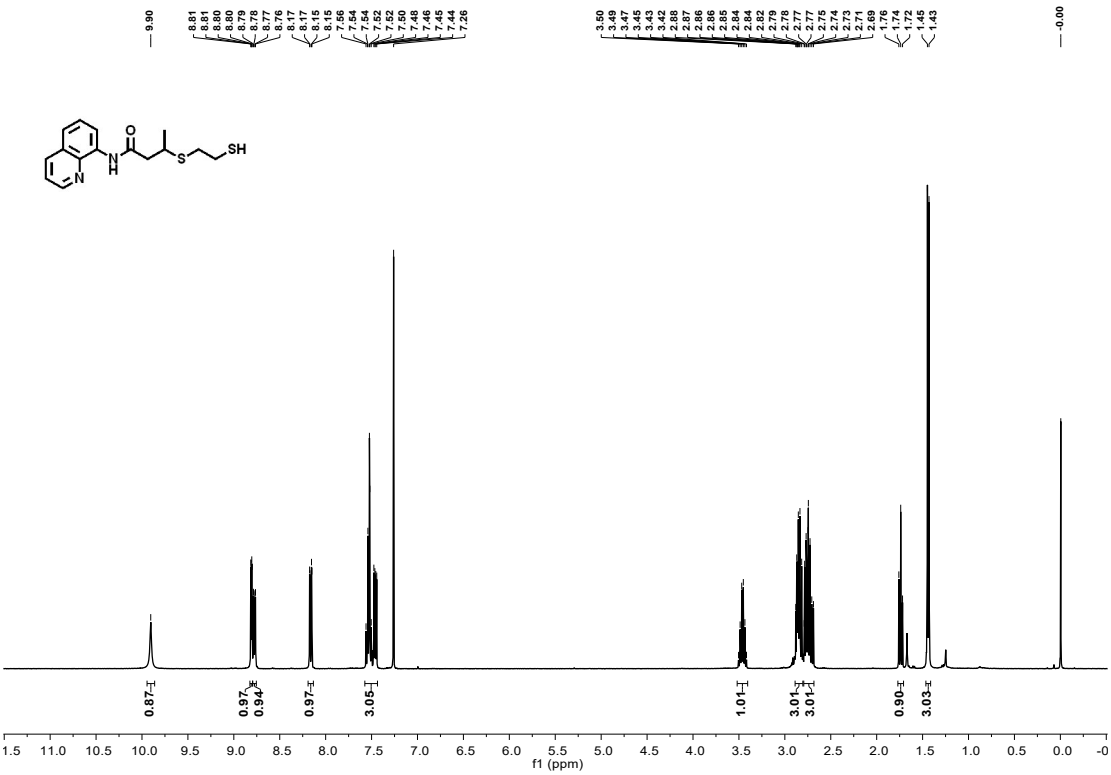

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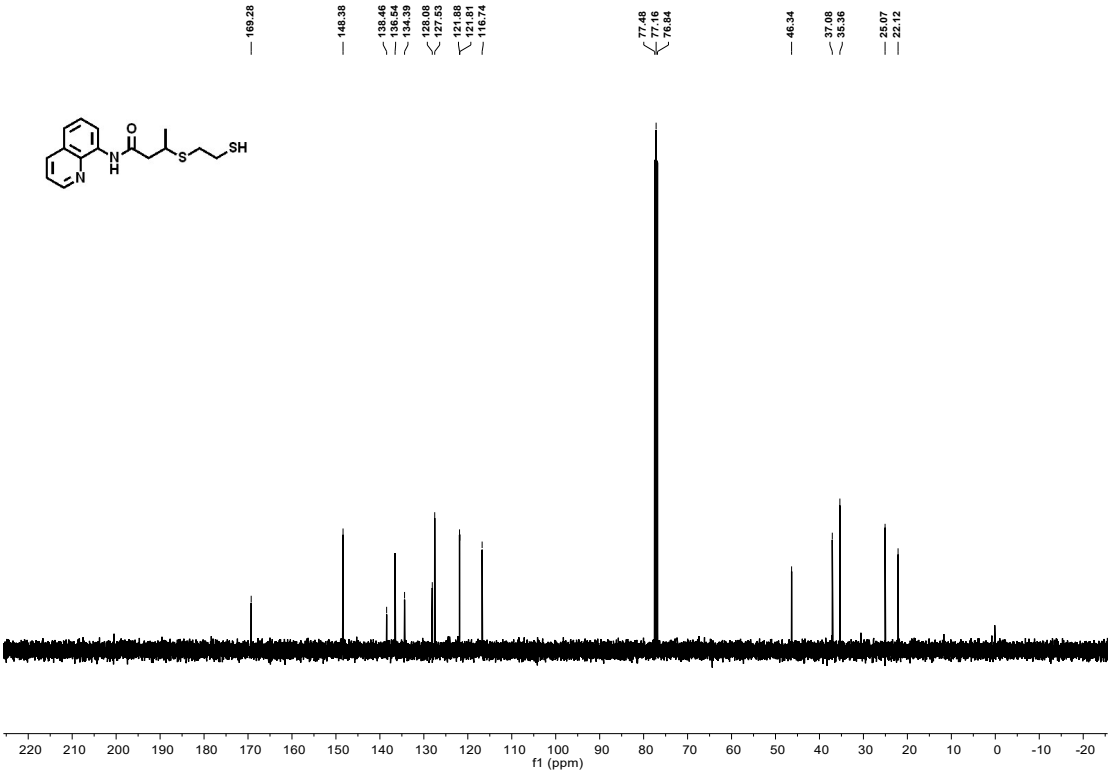
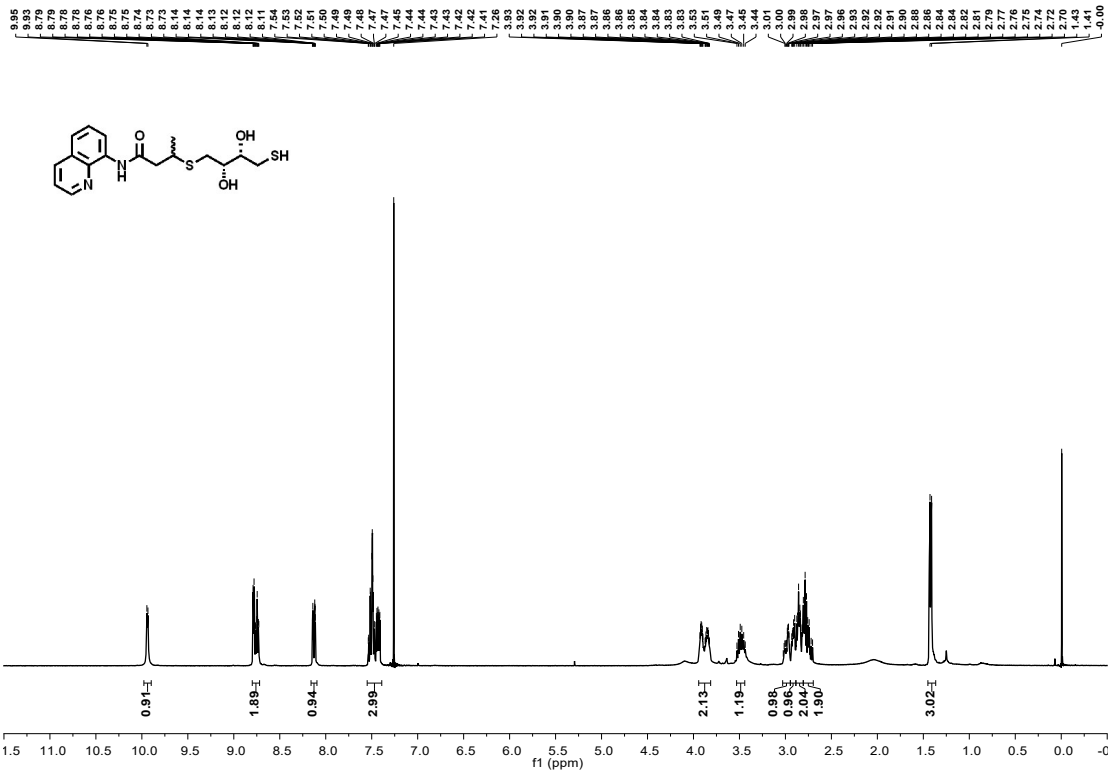
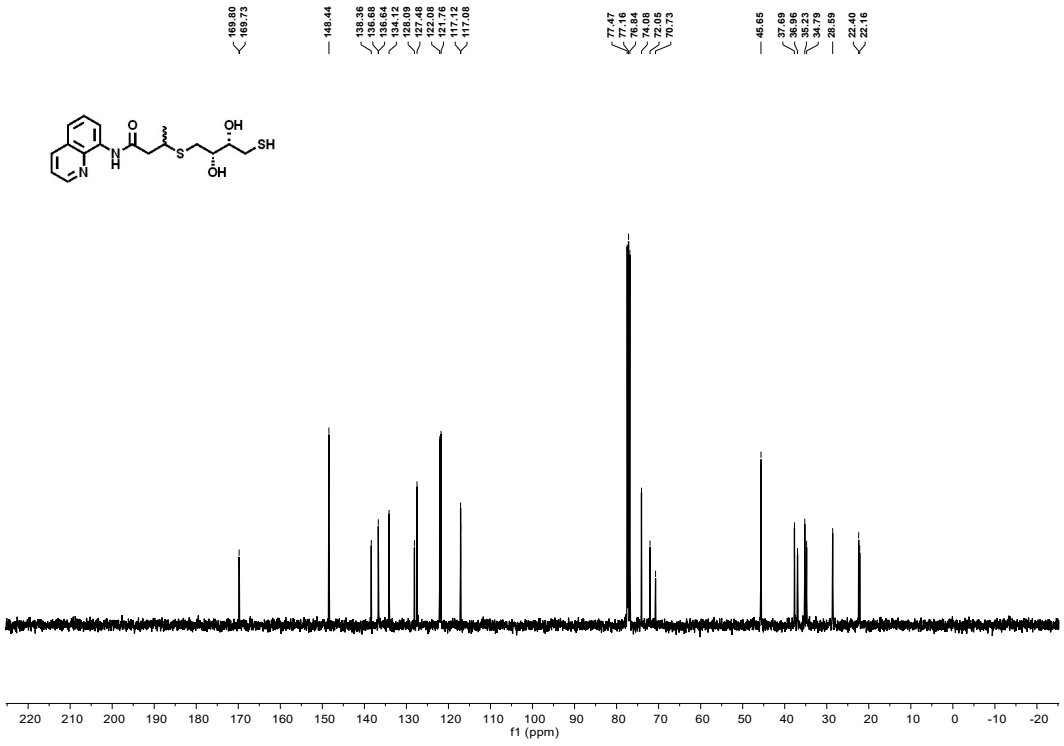


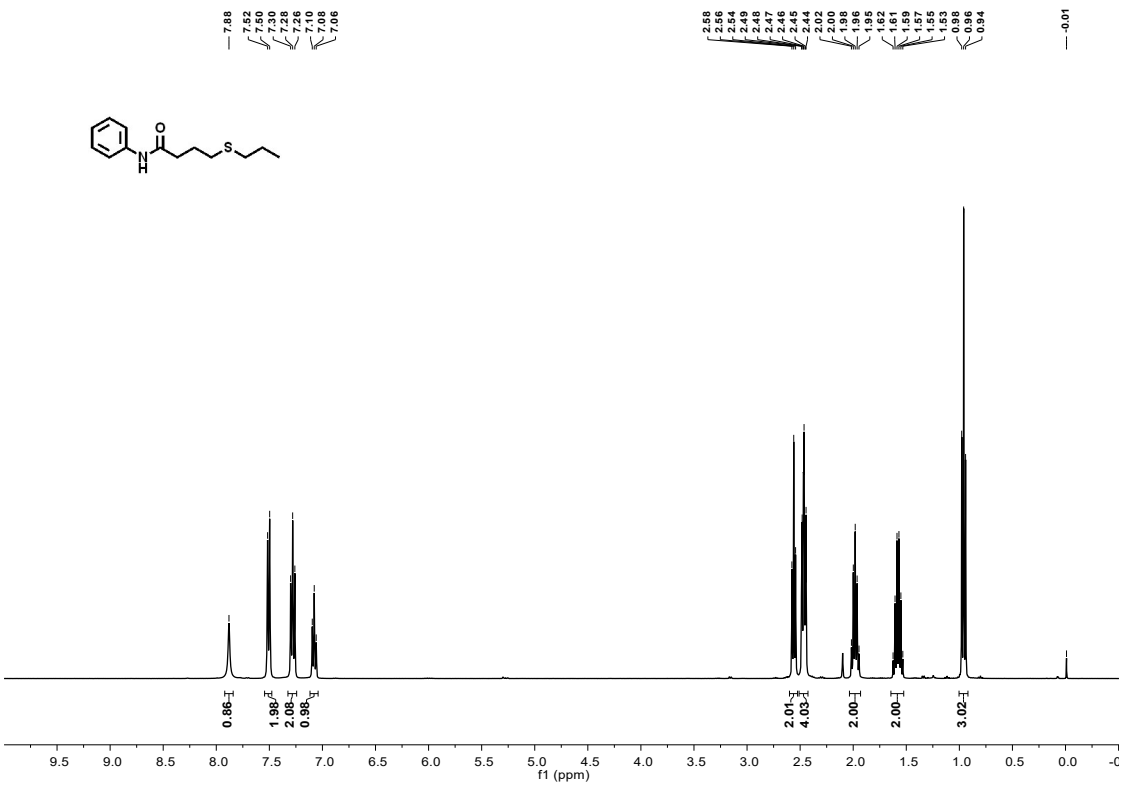
^{1}H NMR spectra of **3p**



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



^{1}H NMR spectra of **4a**



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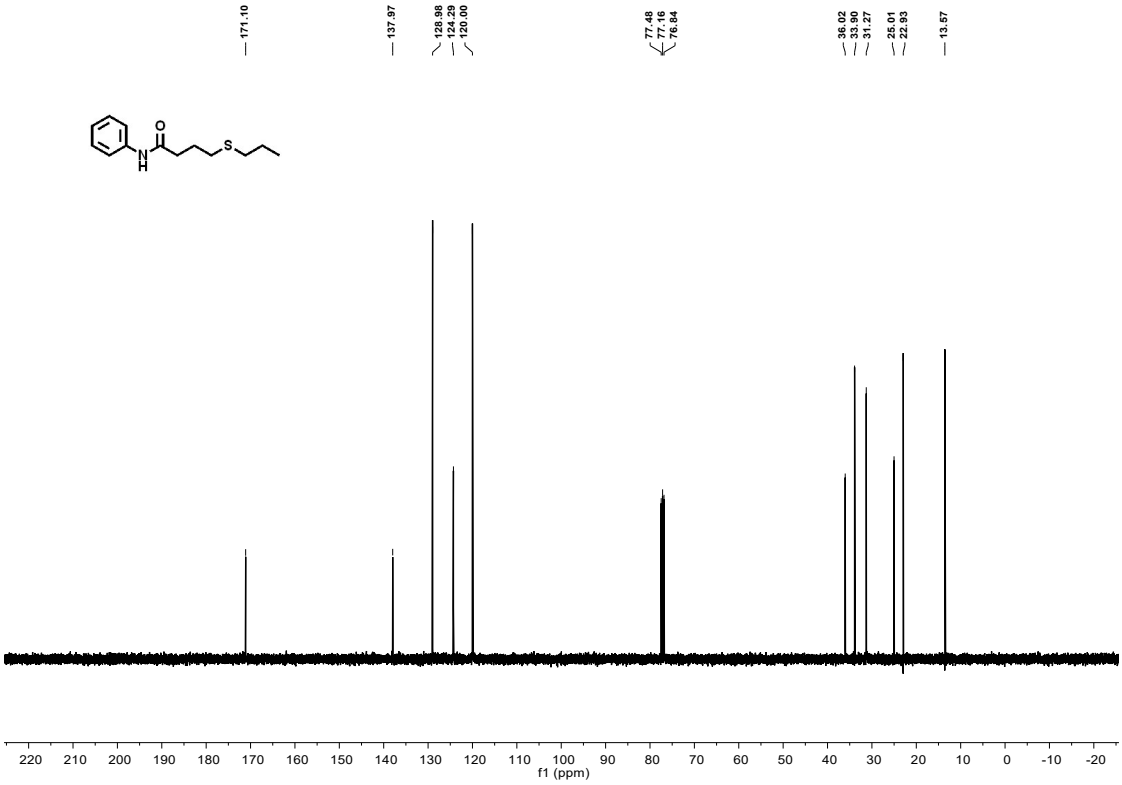

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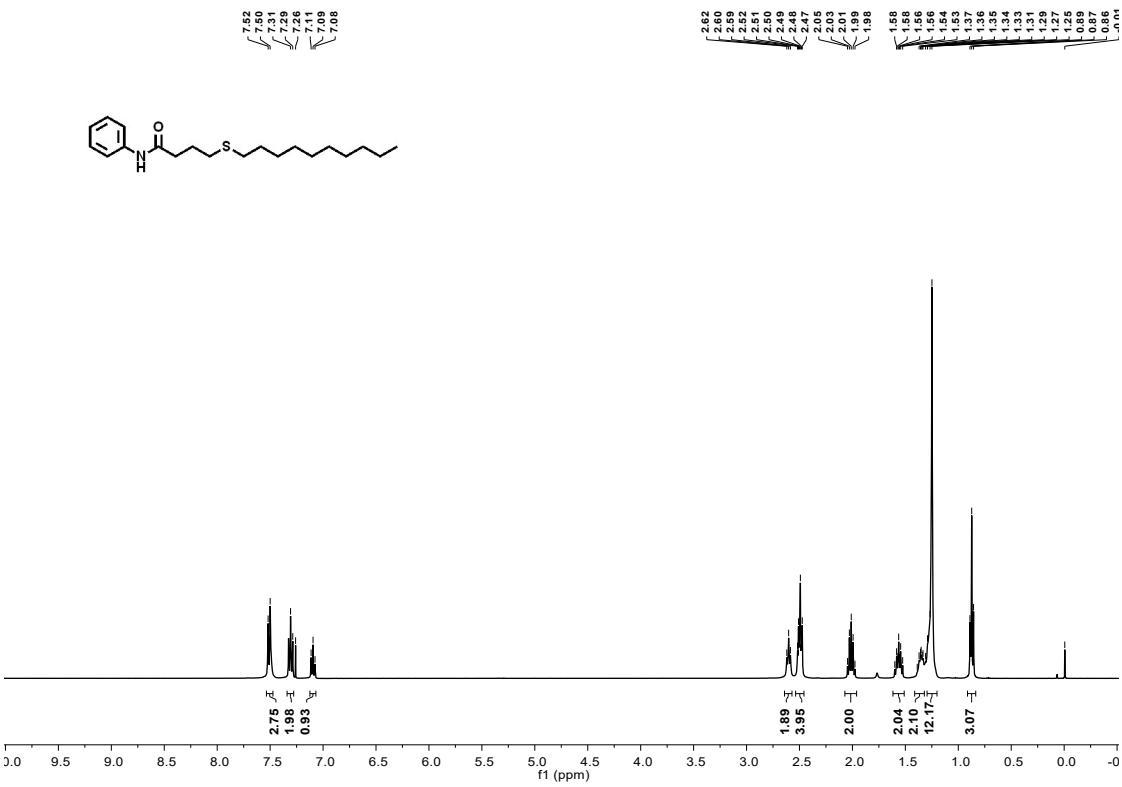

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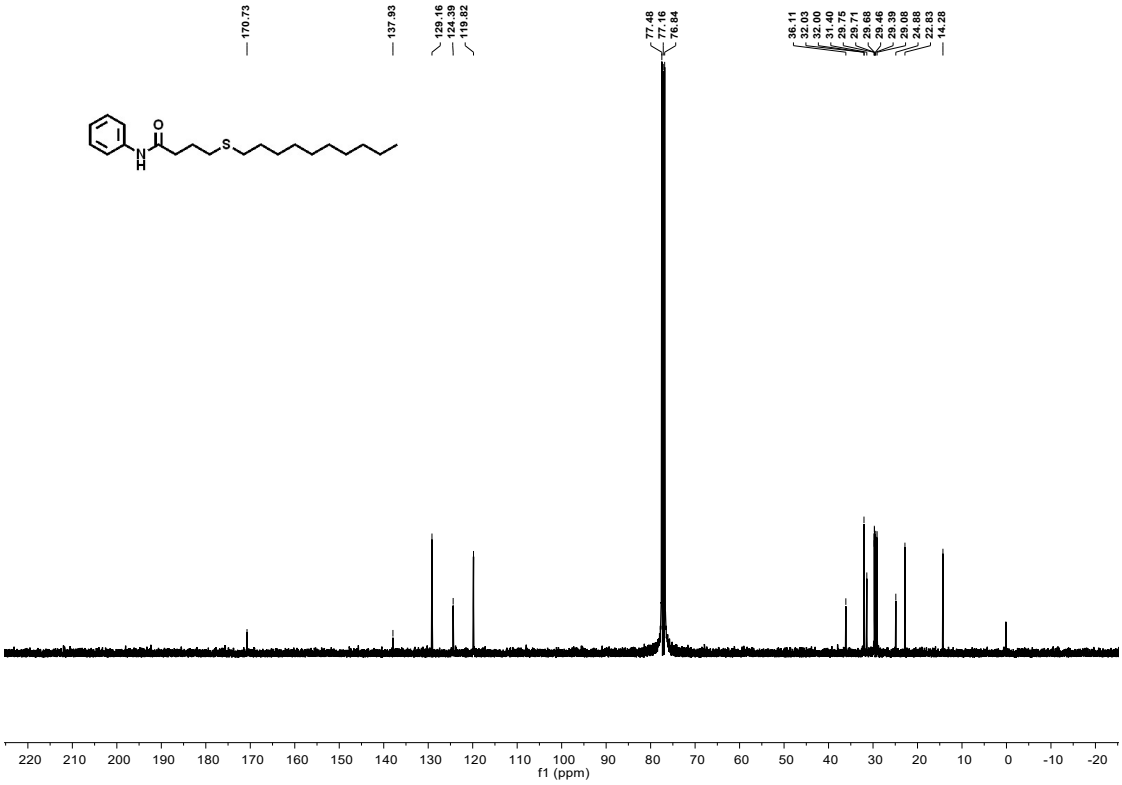
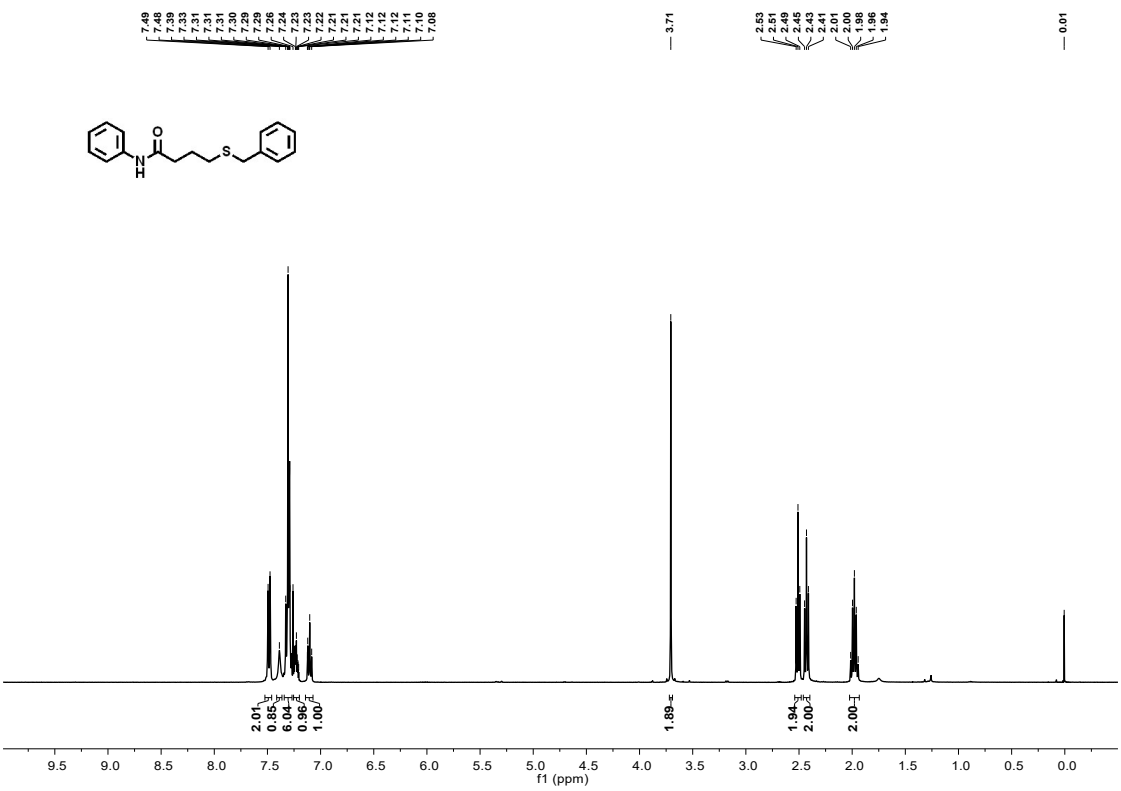


^{1}H NMR spectra of **4c**



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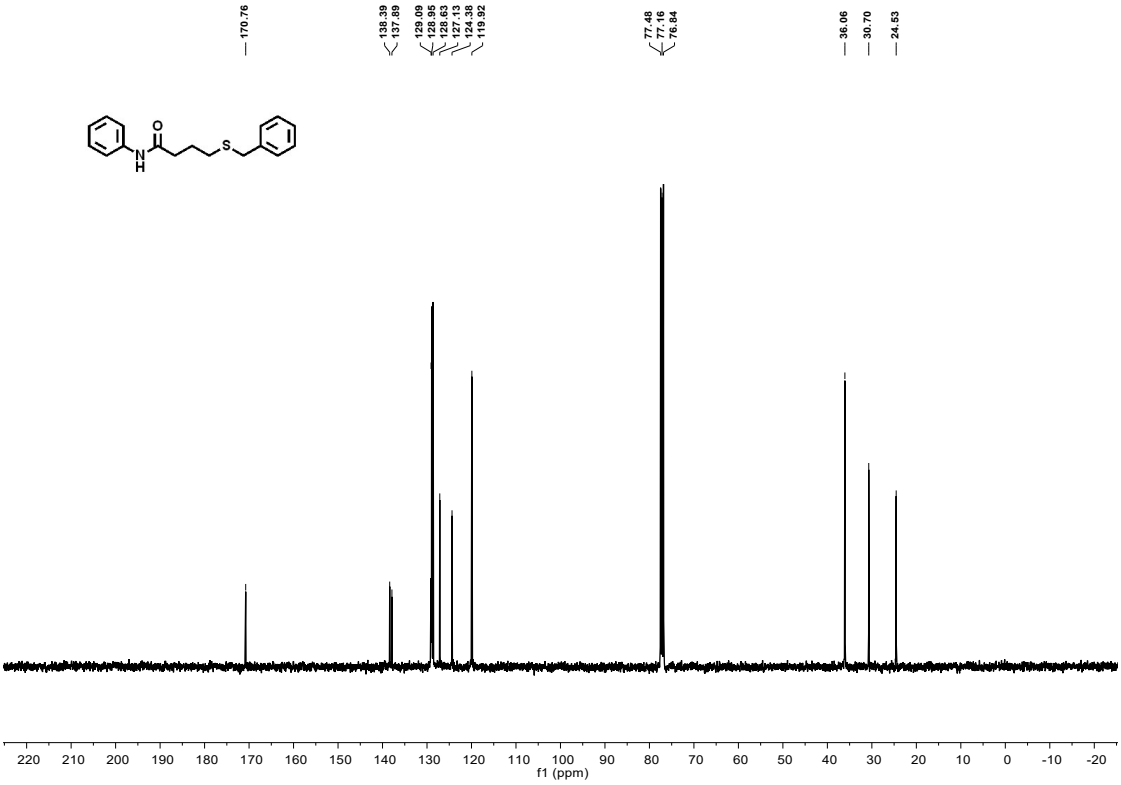
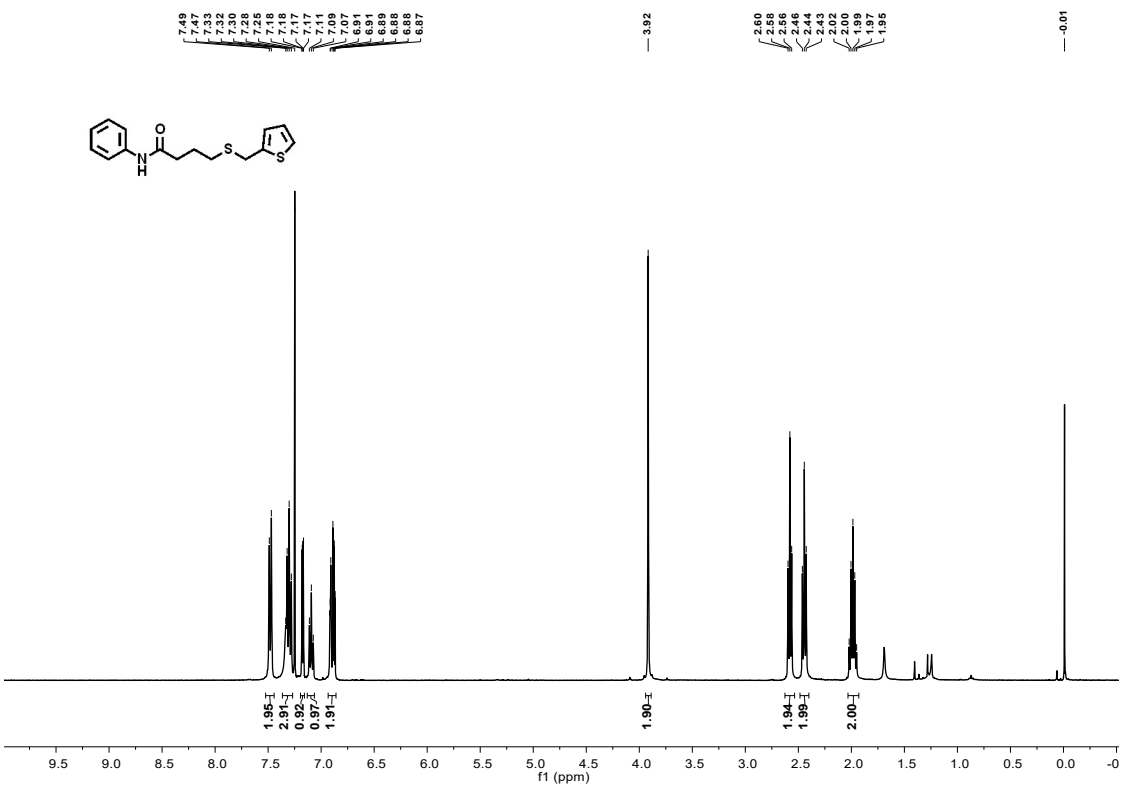


^{1}H NMR spectra of **4d**



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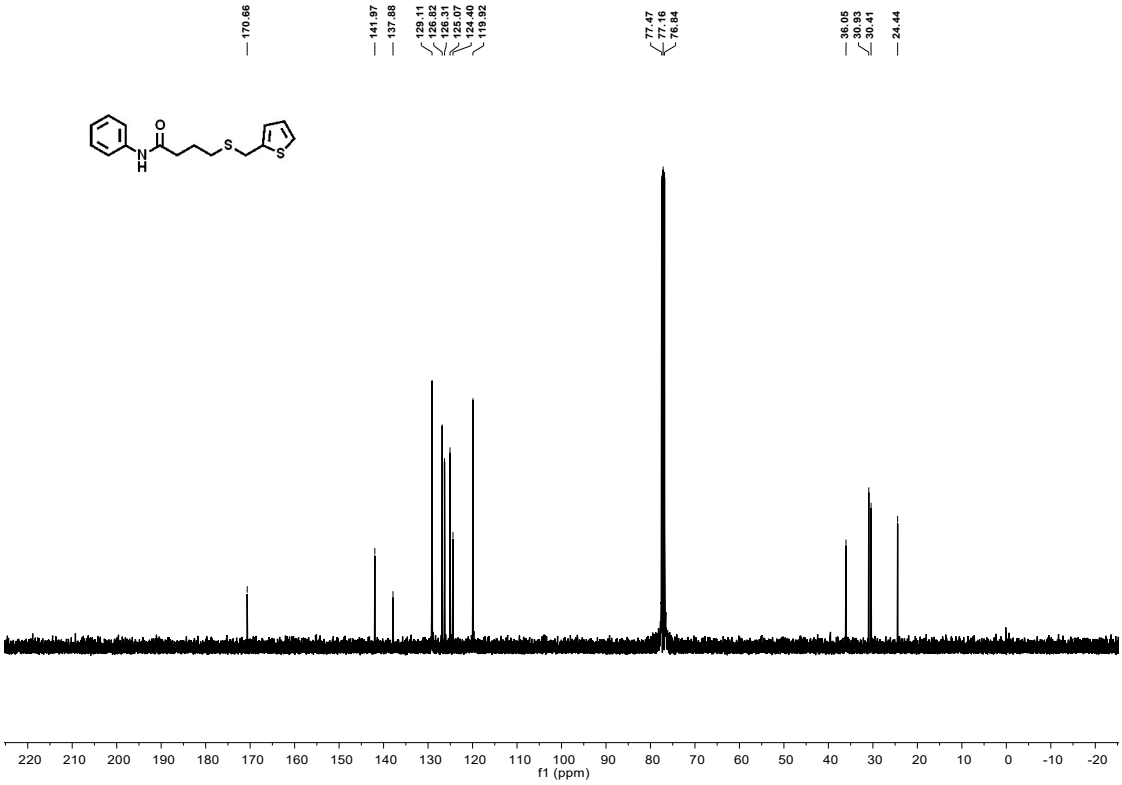

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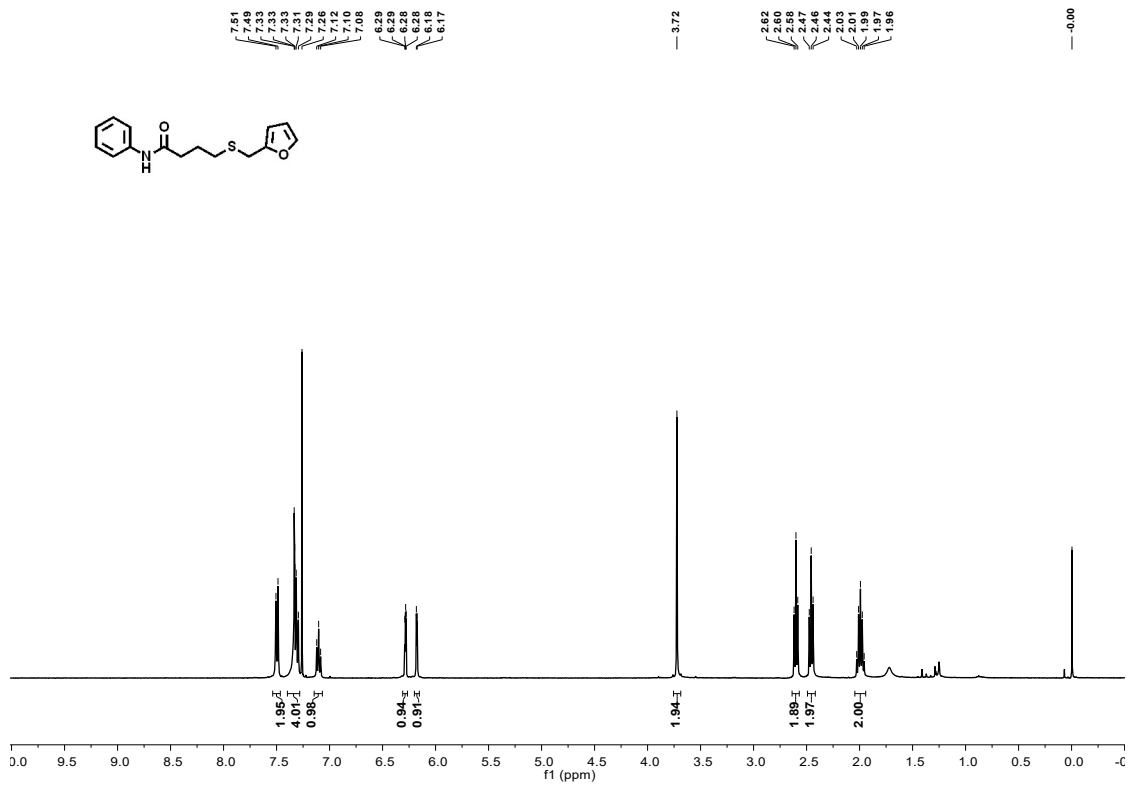

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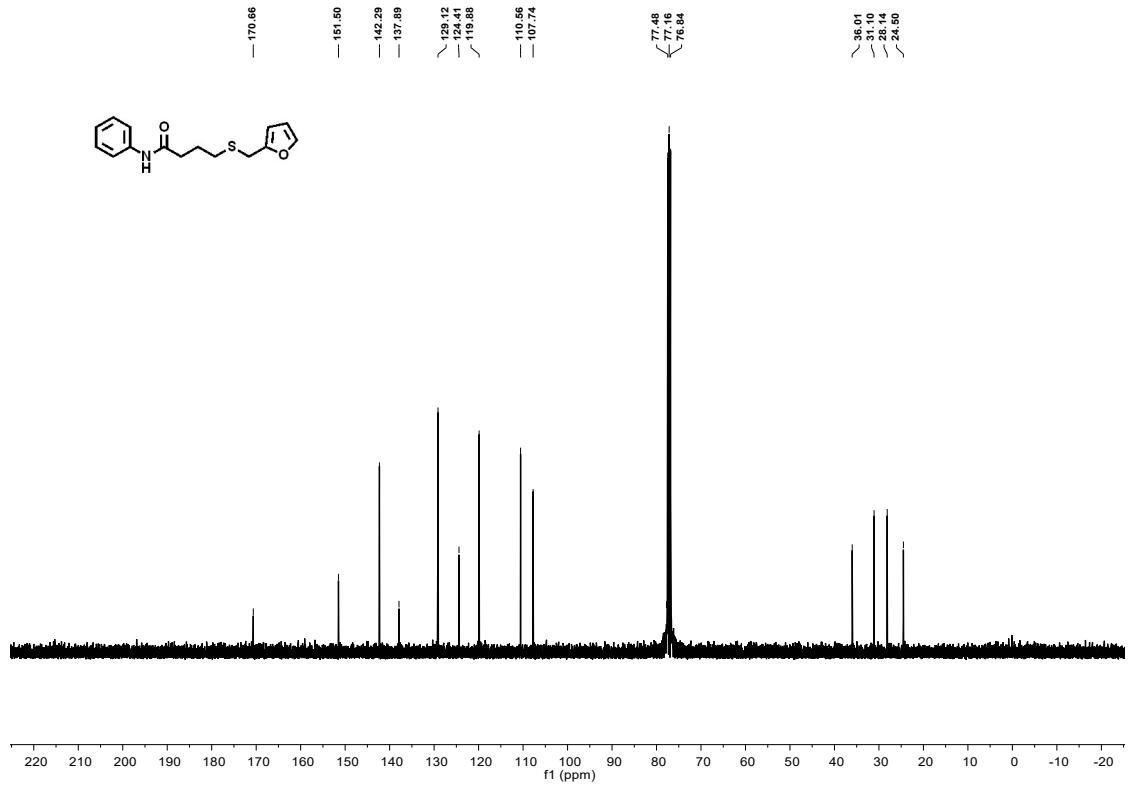
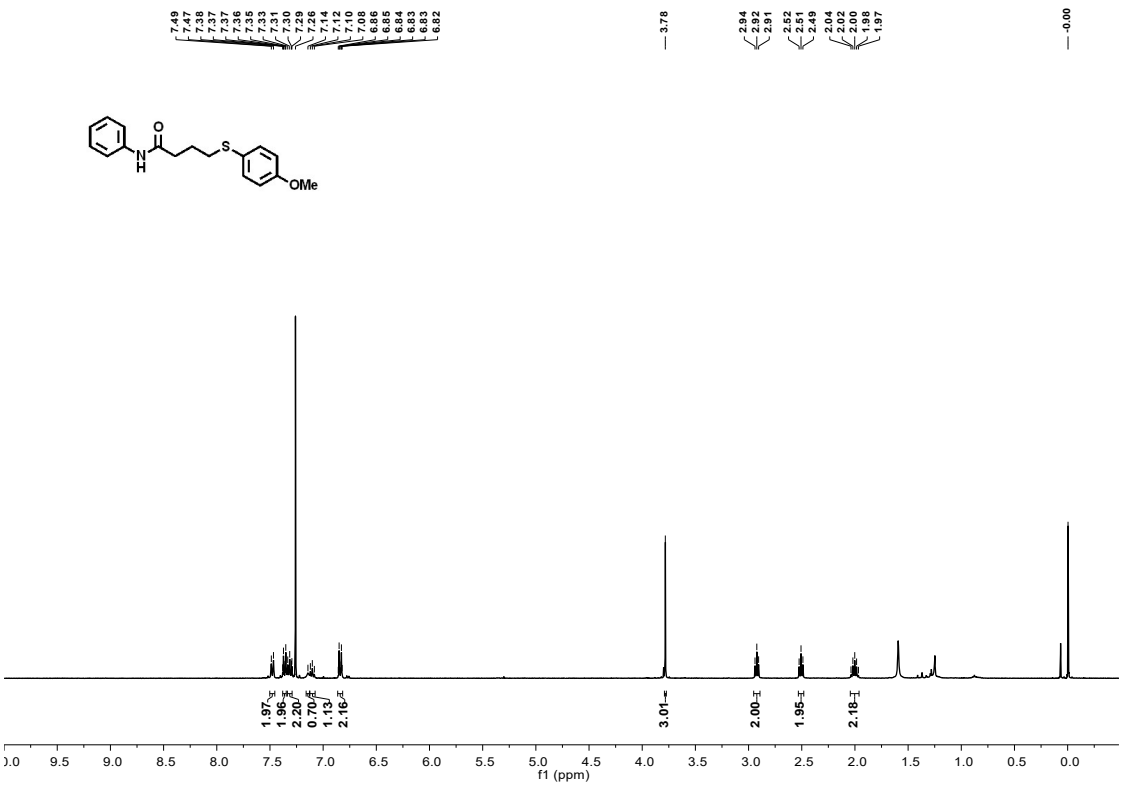
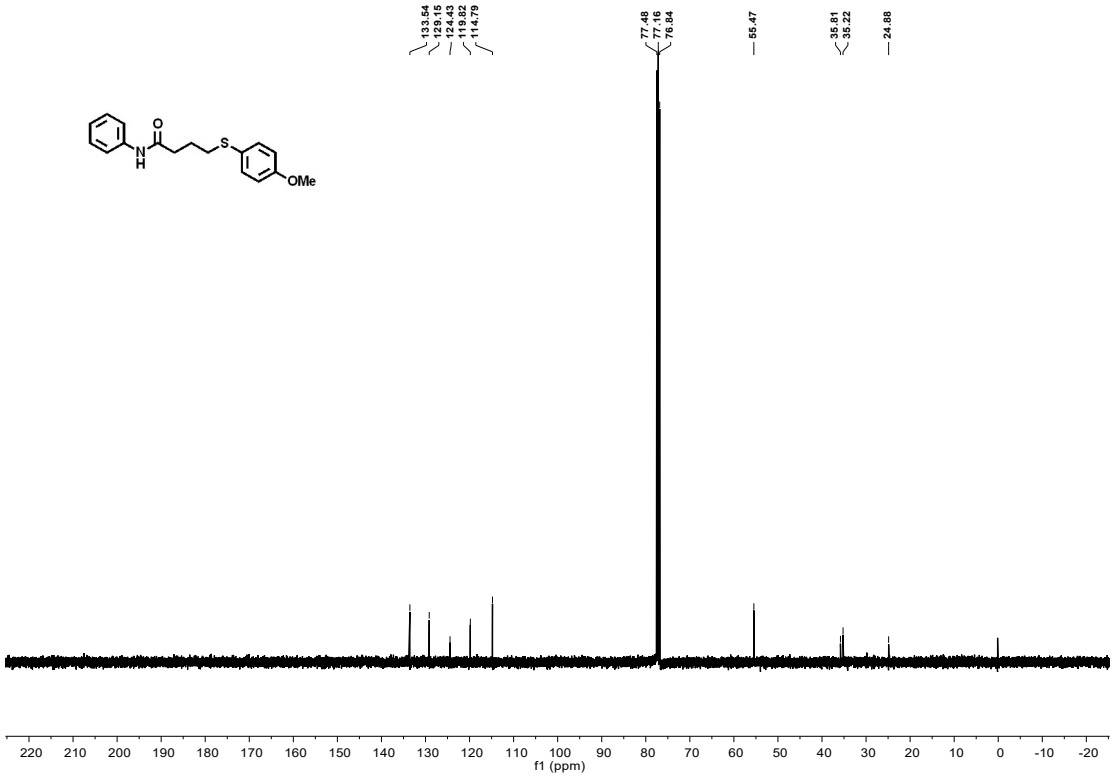


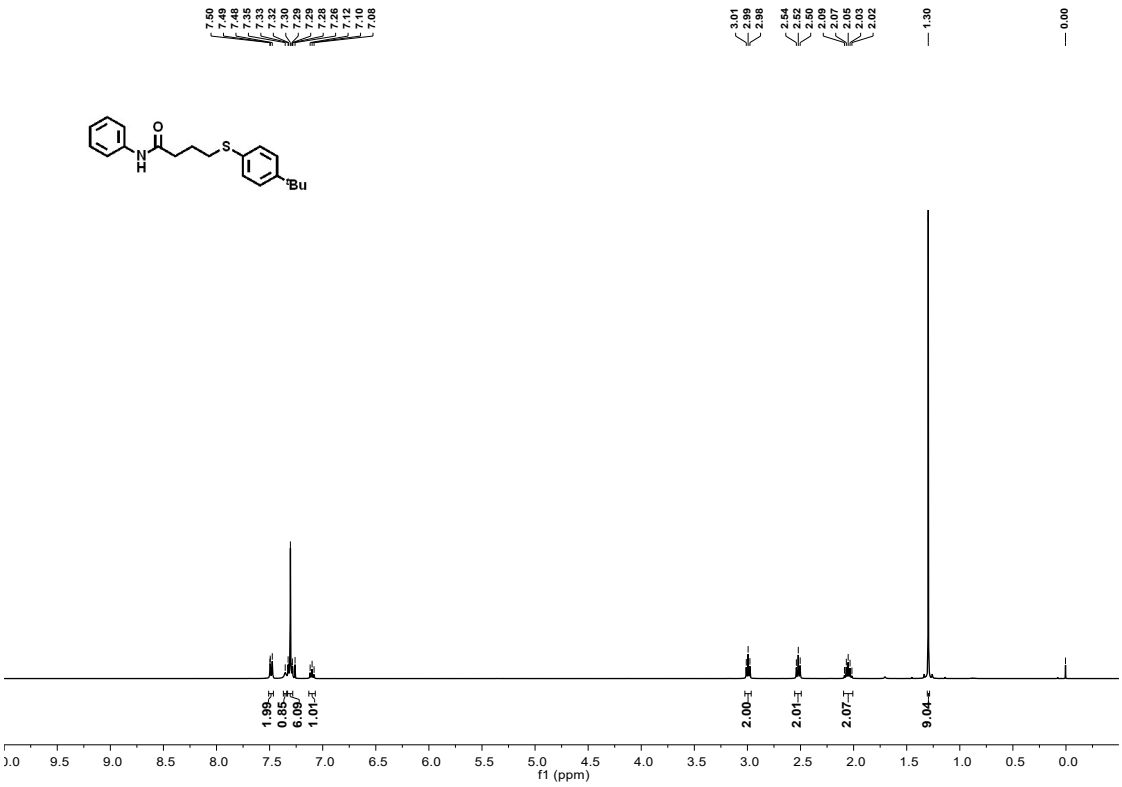
^{1}H NMR spectra of **4f**



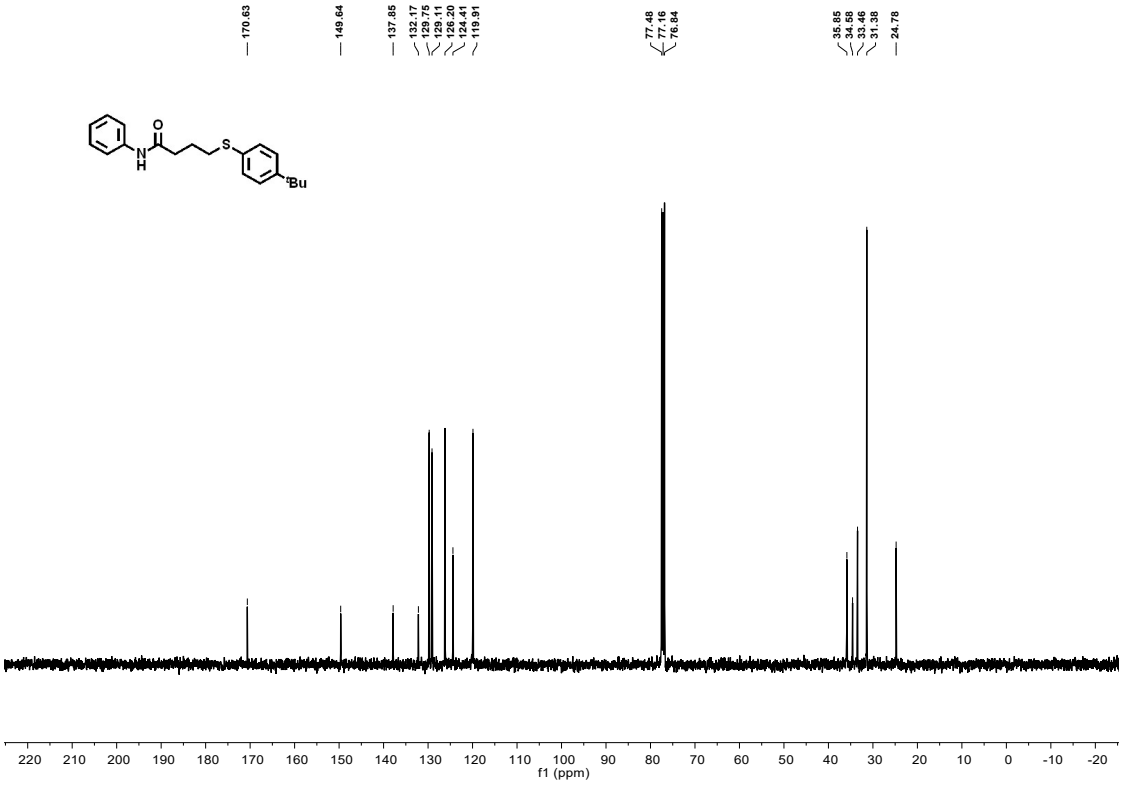
^{13}C NMR spectra of **4f**



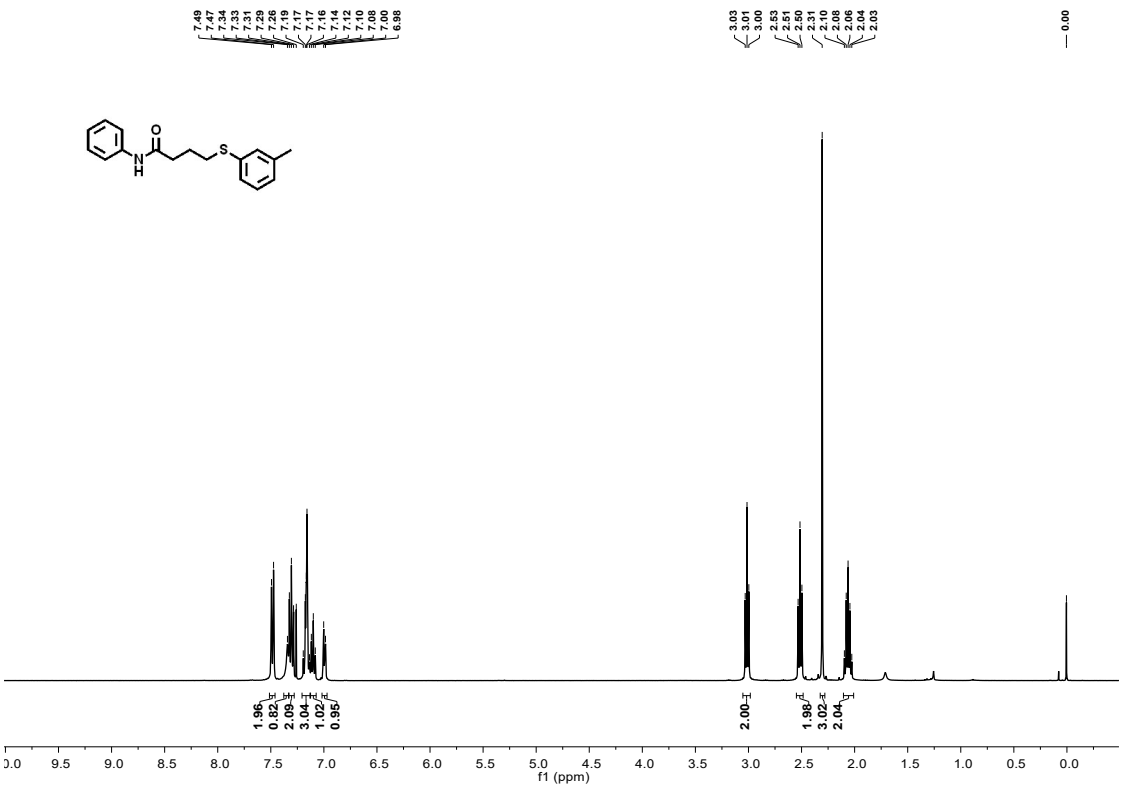
^{1}H NMR spectra of **4g**



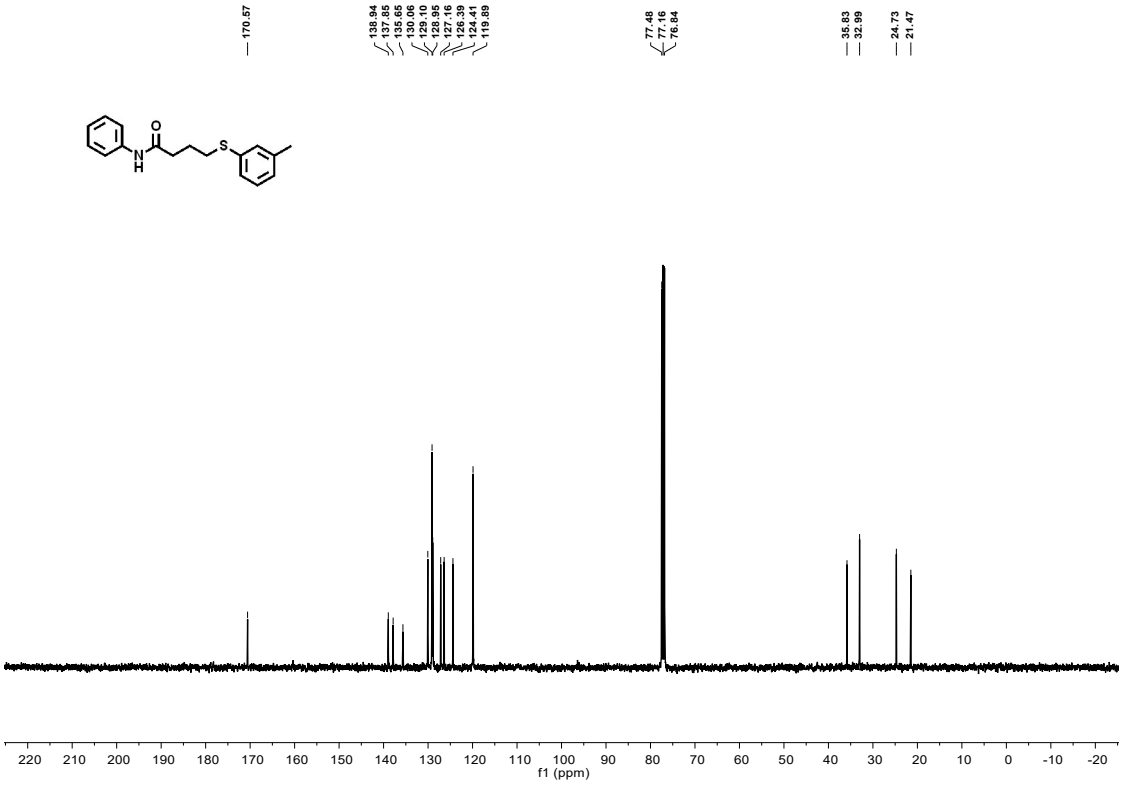
^{13}C NMR spectra of **4g**



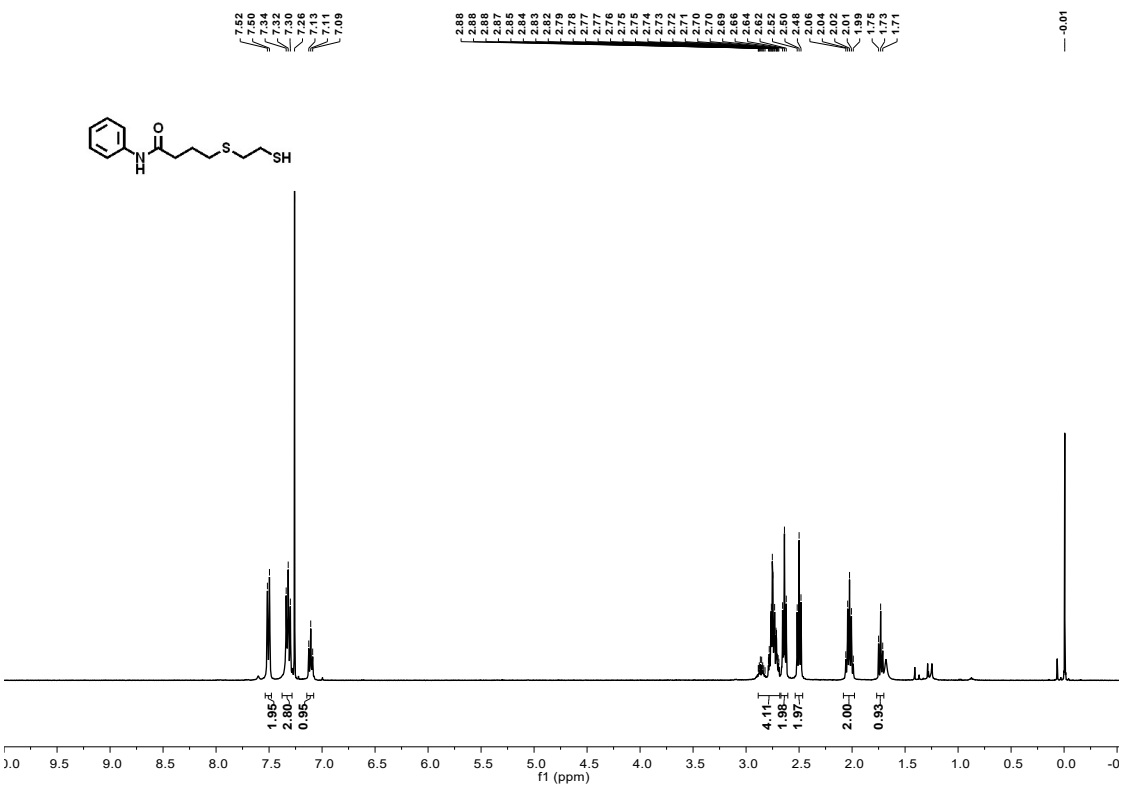
^{1}H NMR spectra of **4h**



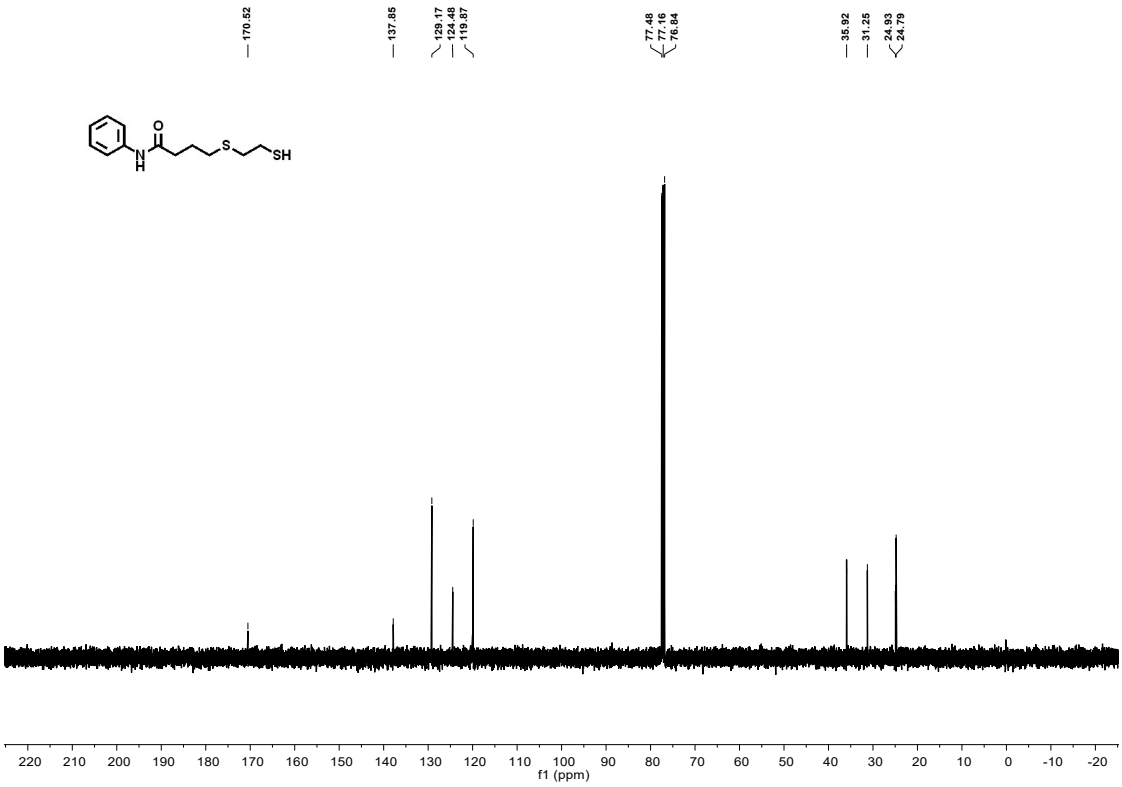
^{13}C NMR spectra of **4h**



^{1}H NMR spectra of **4i**



^{13}C NMR spectra of **4i**



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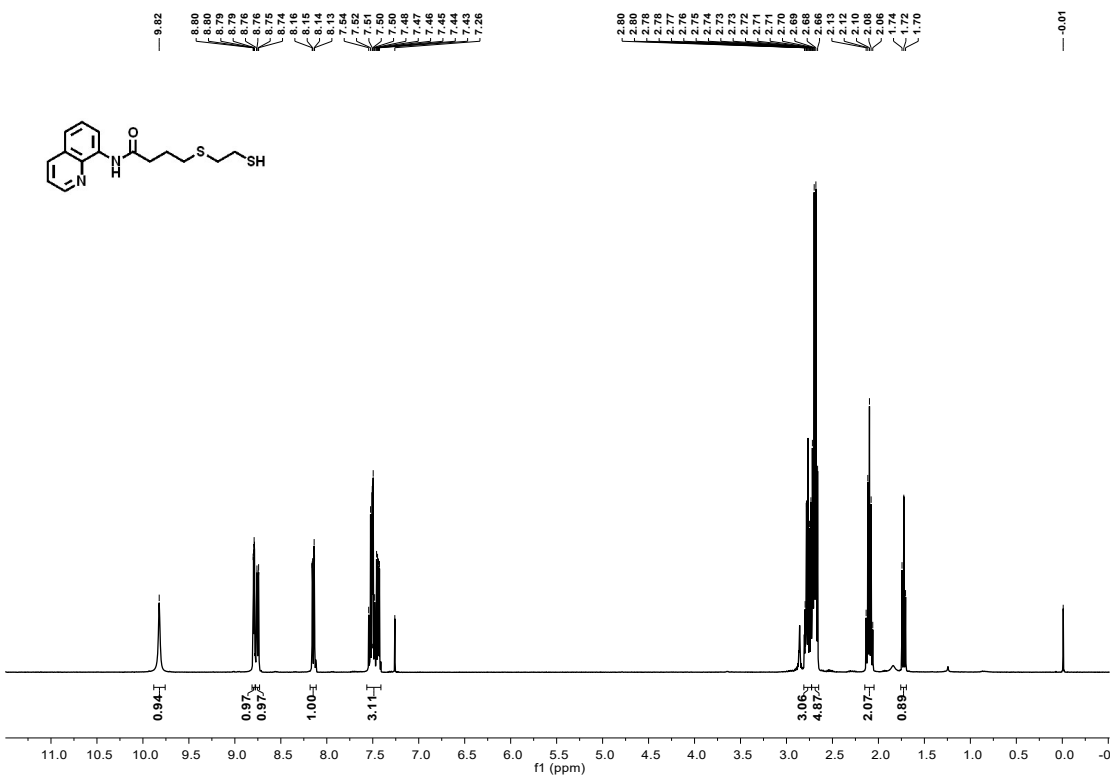

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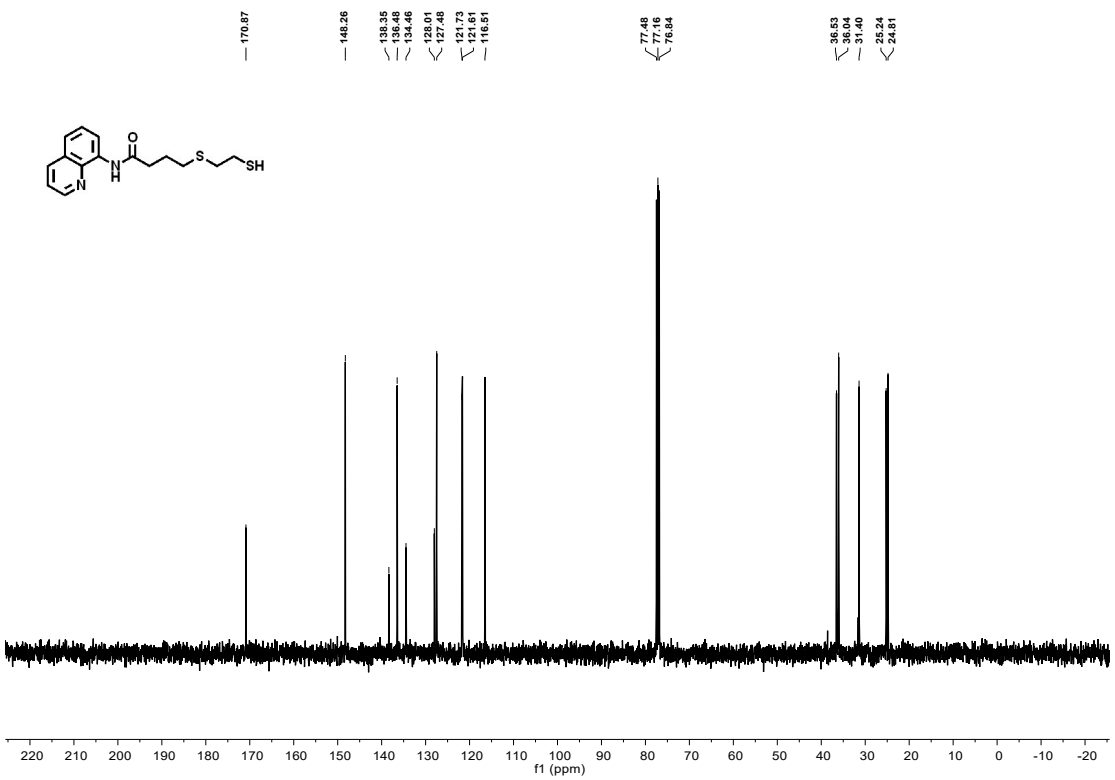
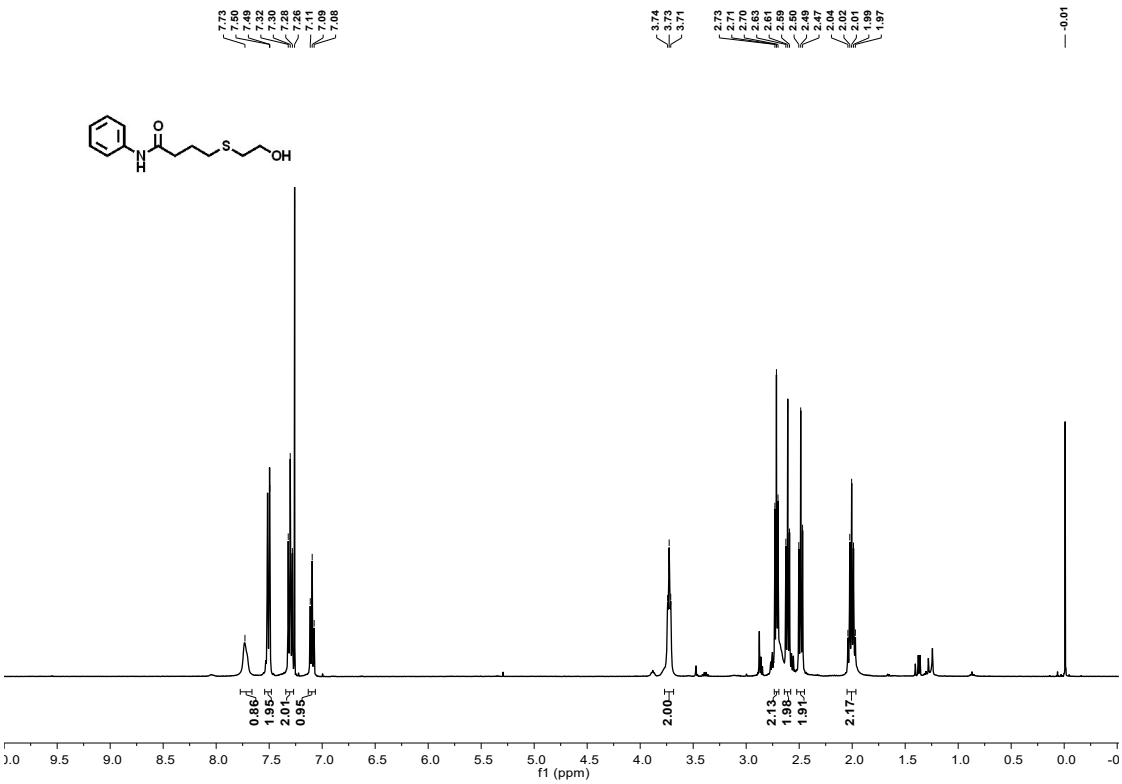


^{1}H NMR spectra of **4k**



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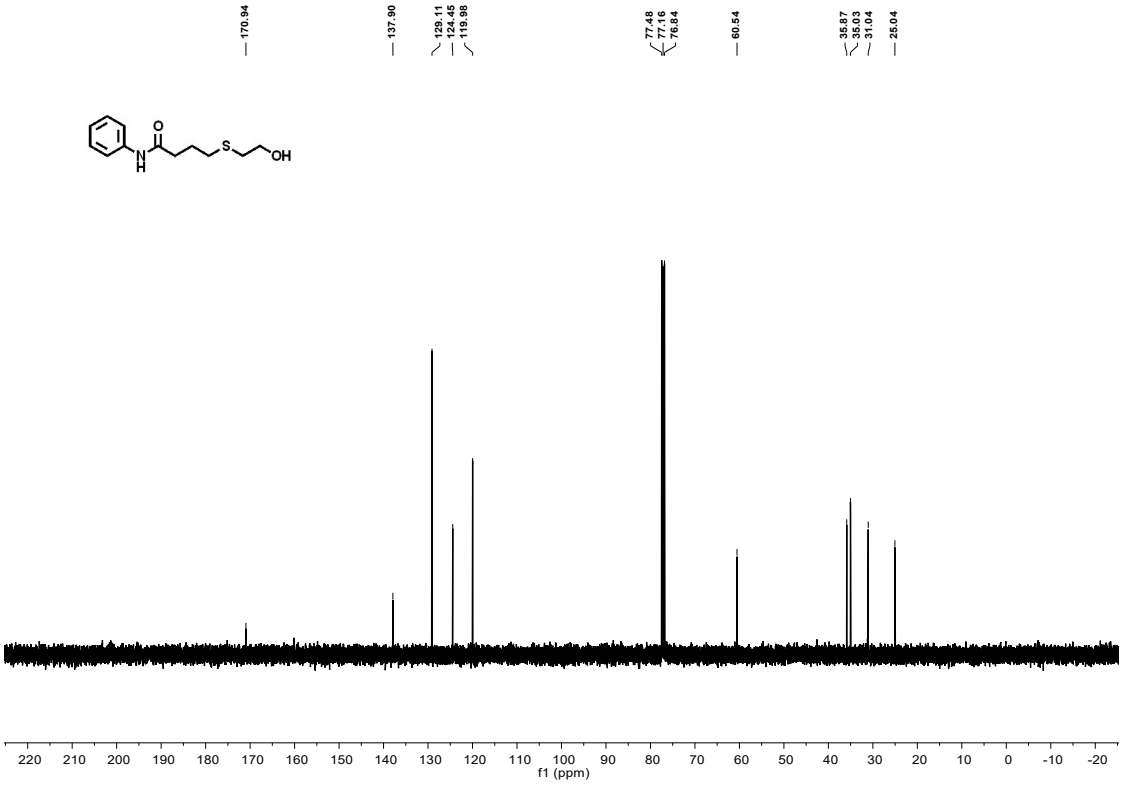
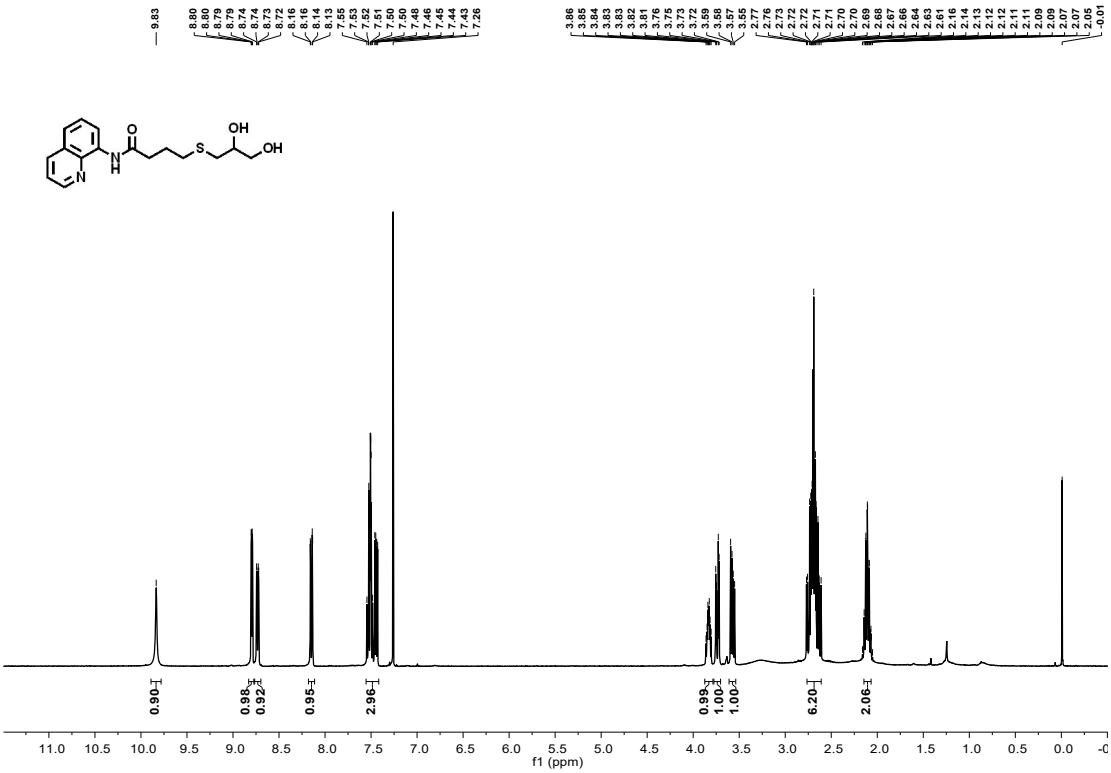


^{1}H NMR spectra of **4l**



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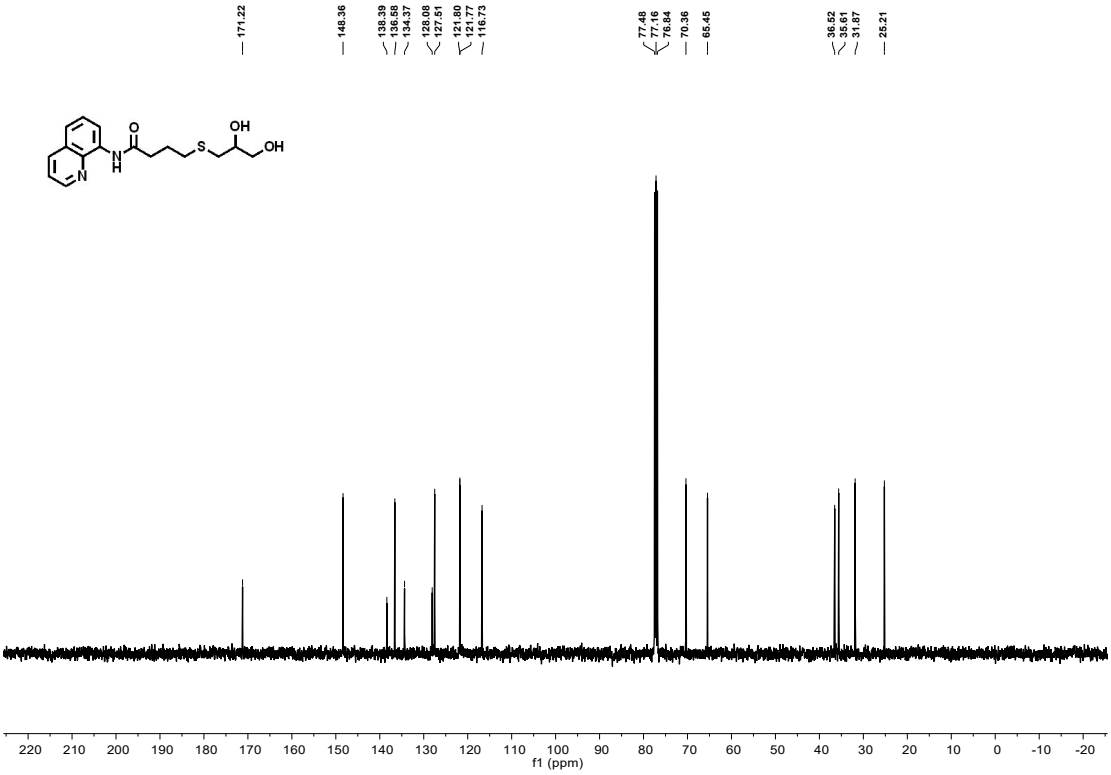
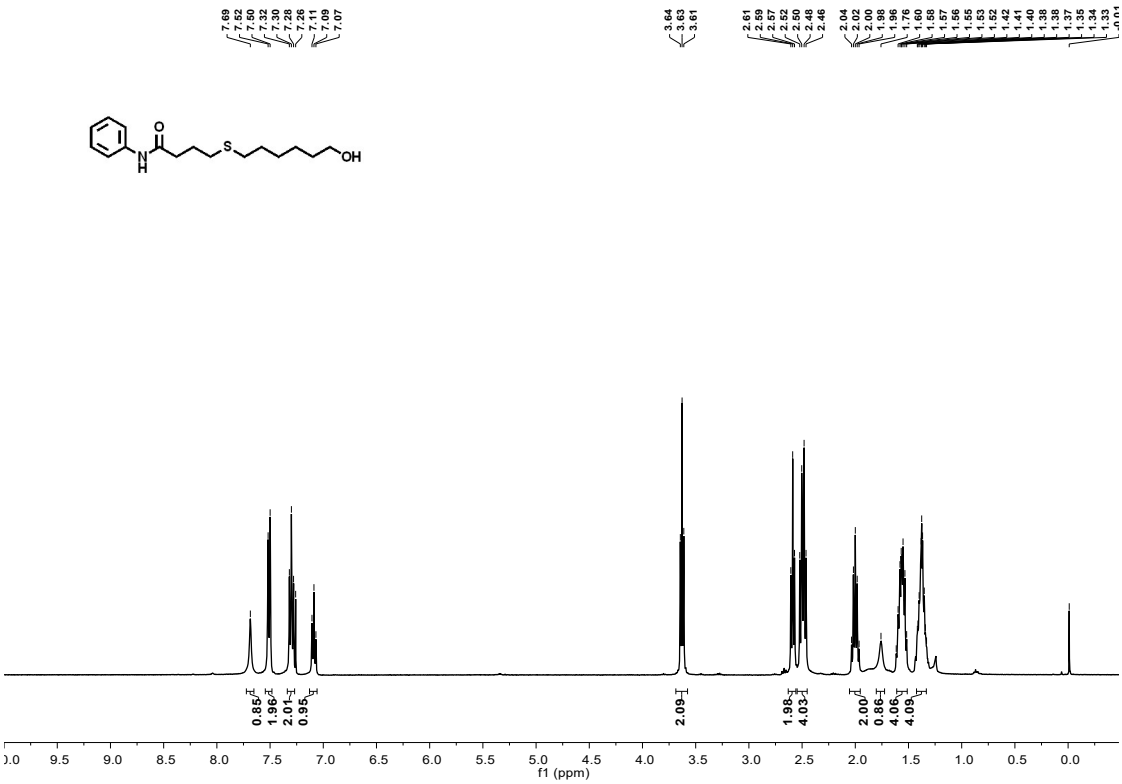
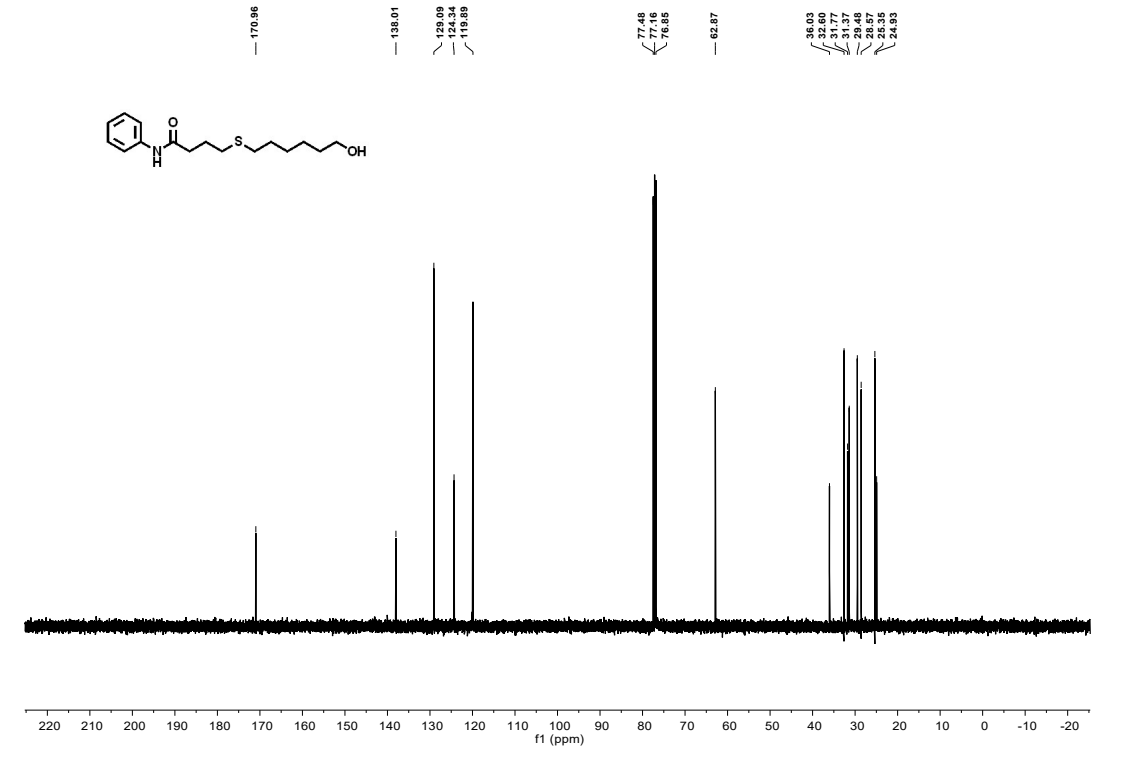


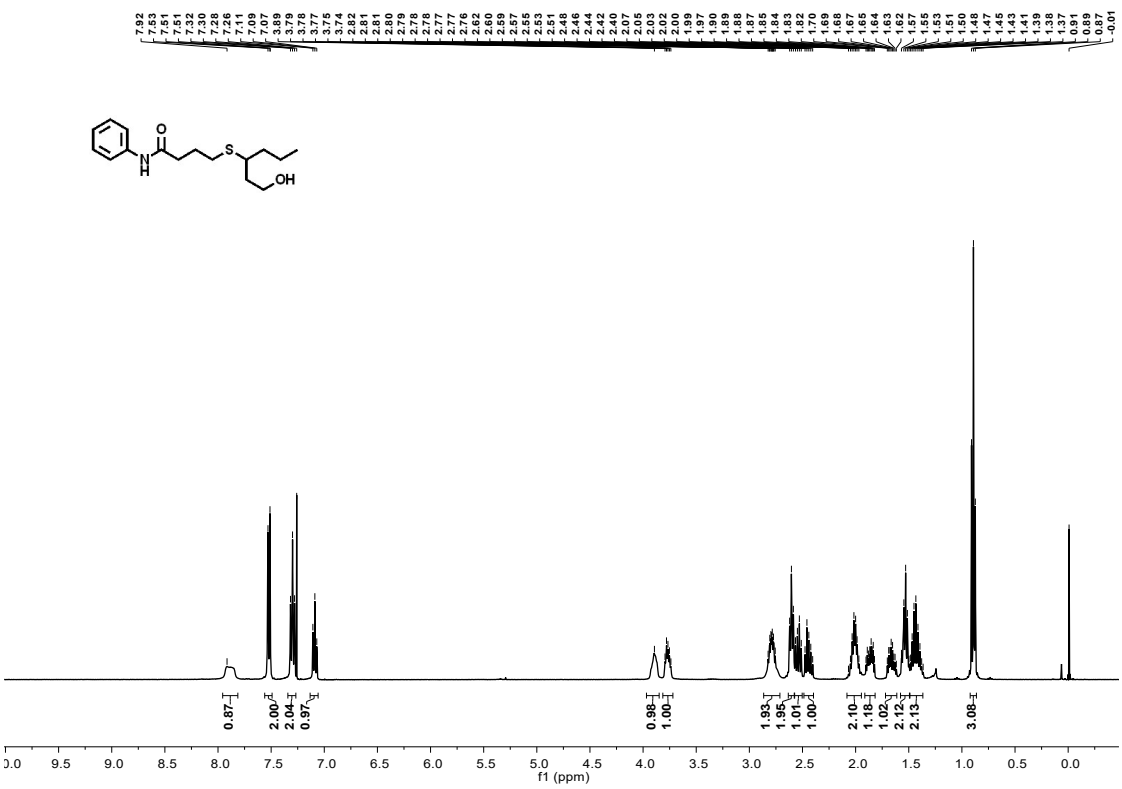
^{1}H NMR spectra of **4m**



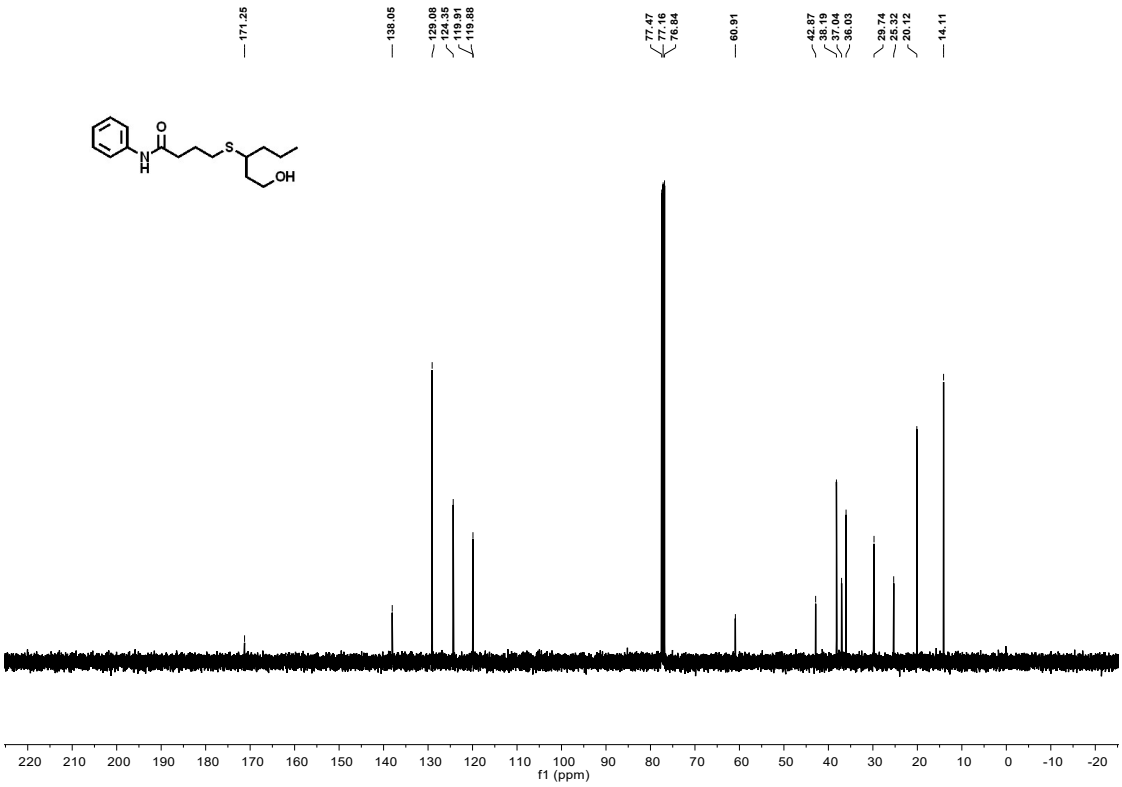
^{13}C NMR spectra of **4m**



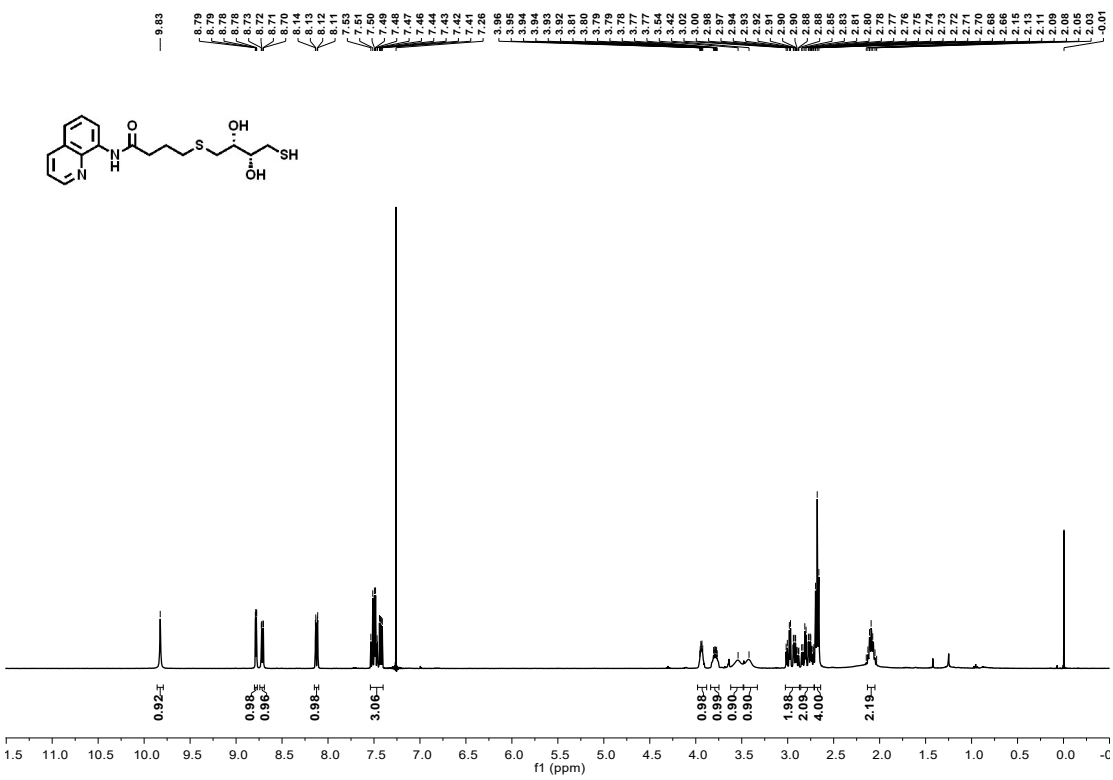
^{1}H NMR spectra of **4n**



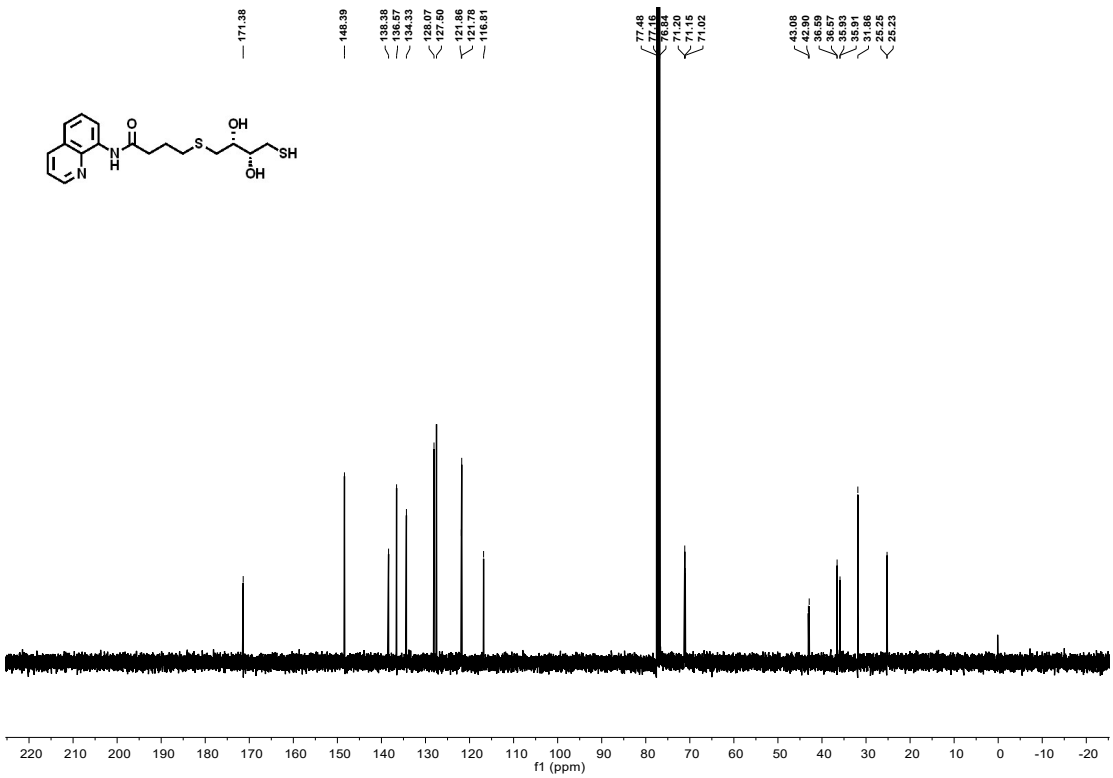
^{13}C NMR spectra of **4n**



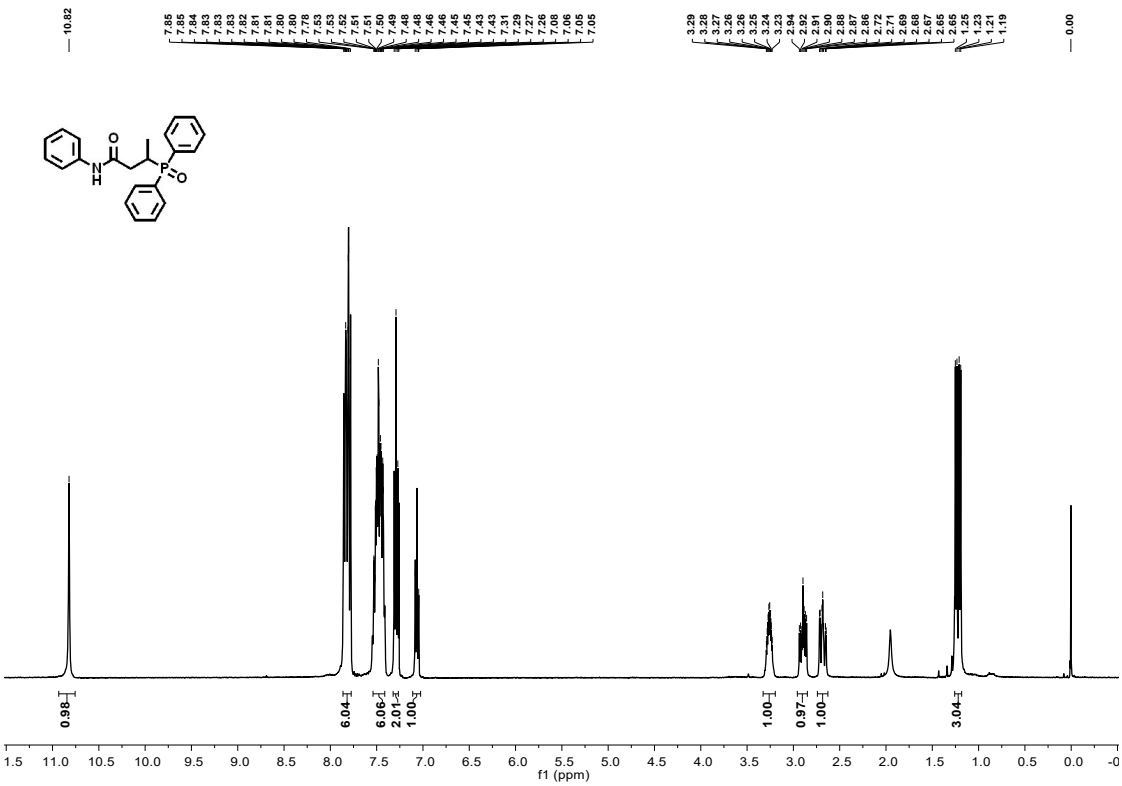
^{1}H NMR spectra of **4o**



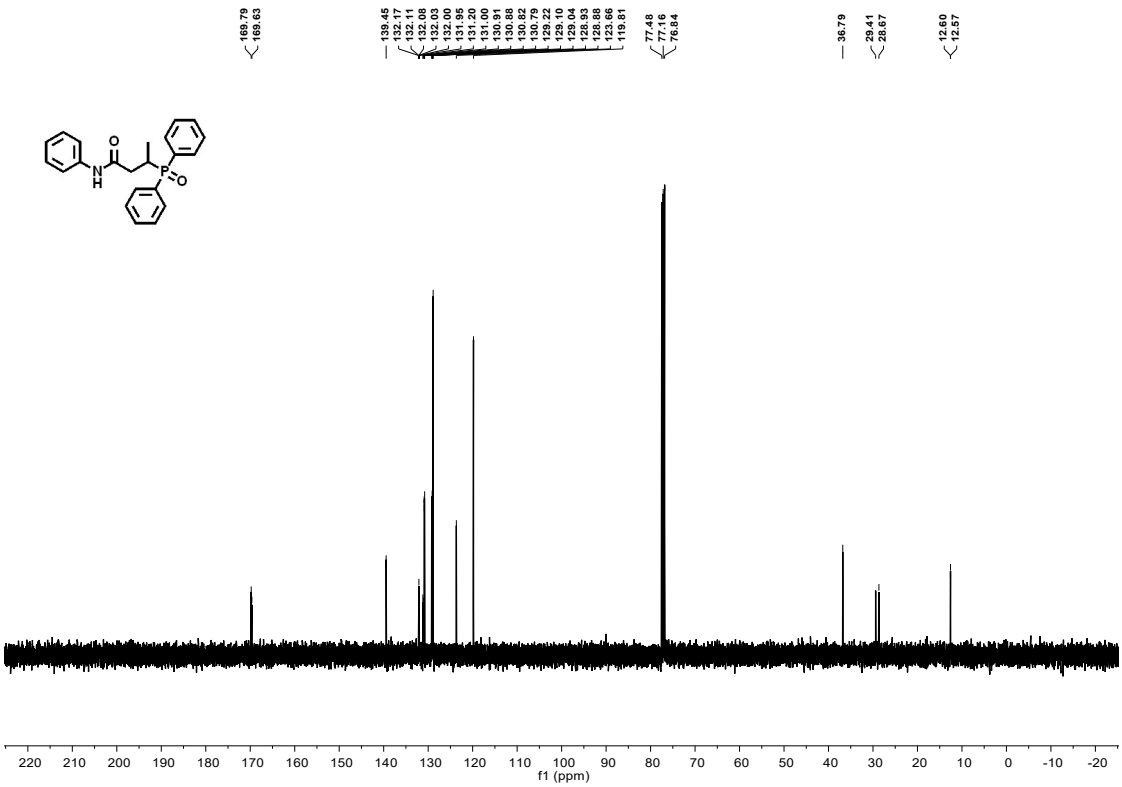
^{13}C NMR spectra of **4o**



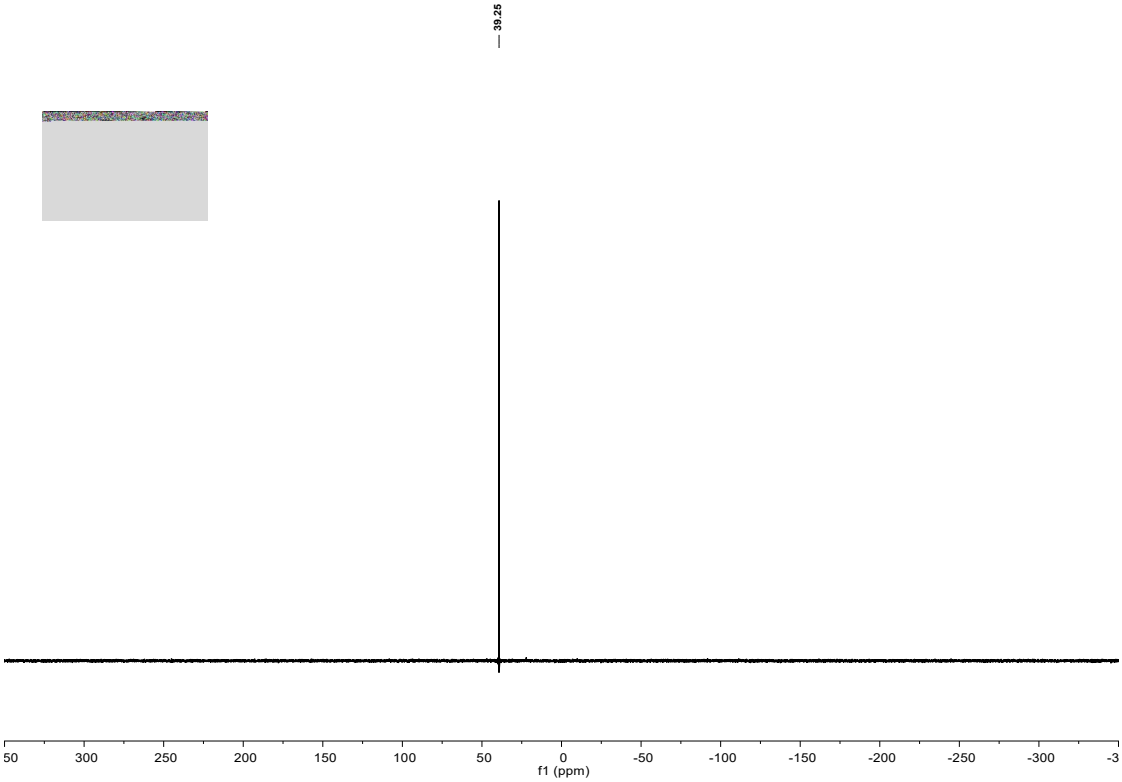
^{1}H NMR spectra of **6a**



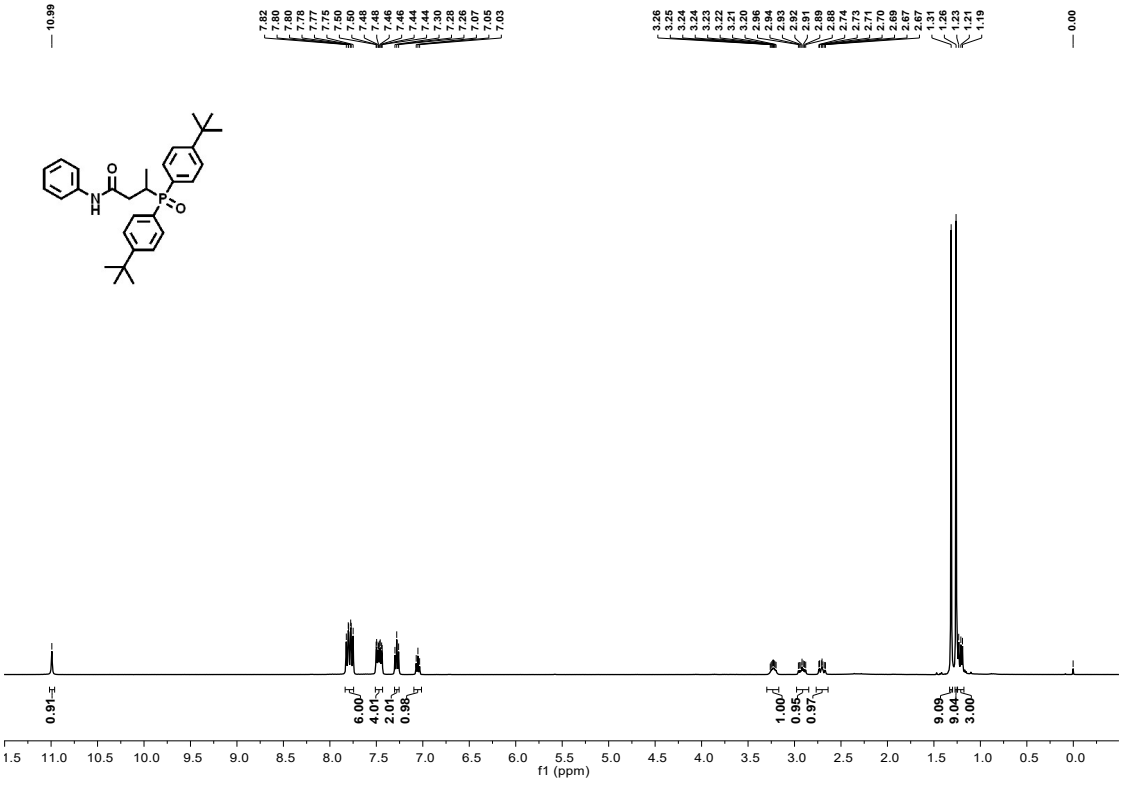
^{13}C NMR spectra of **6a**



^{31}P NMR spectra of **6a**



^{1}H NMR spectra of **6b**



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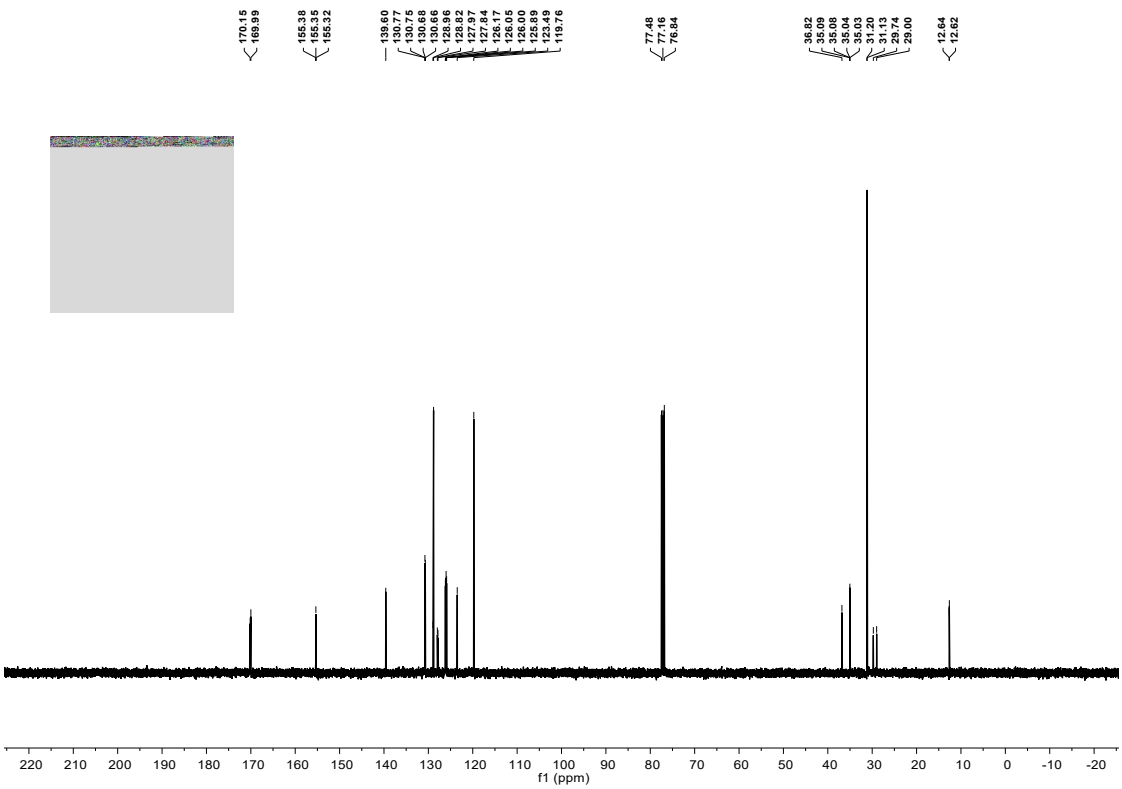

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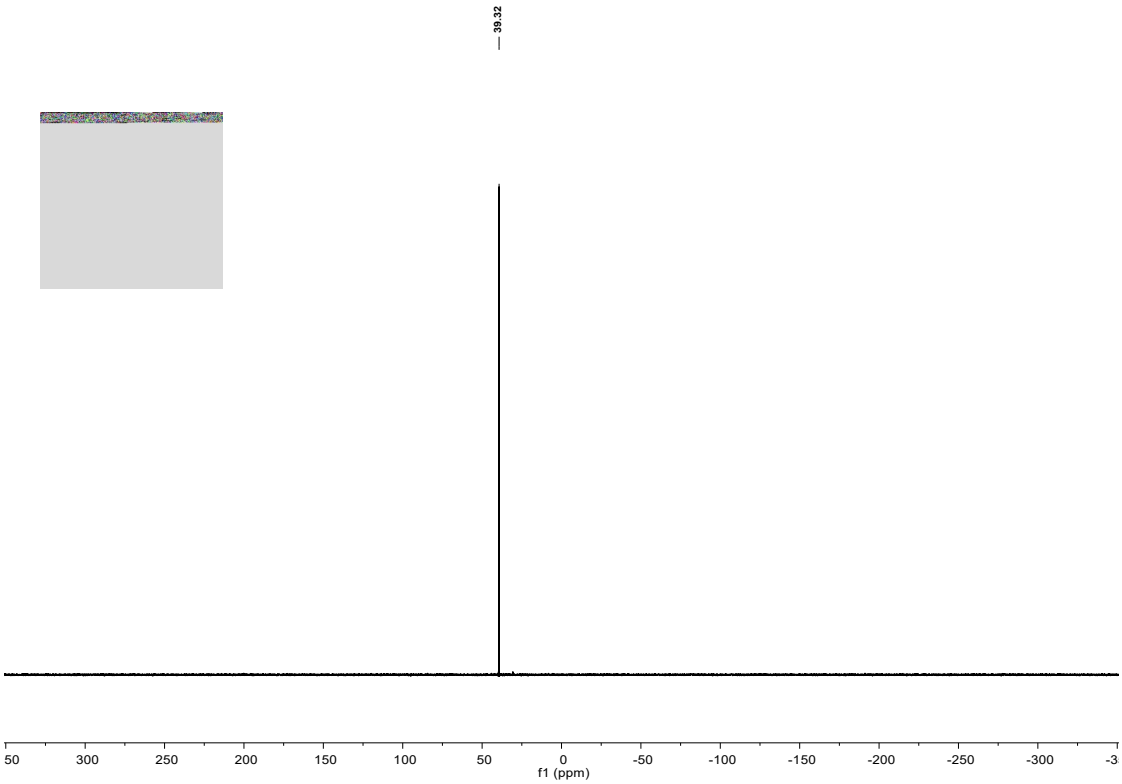
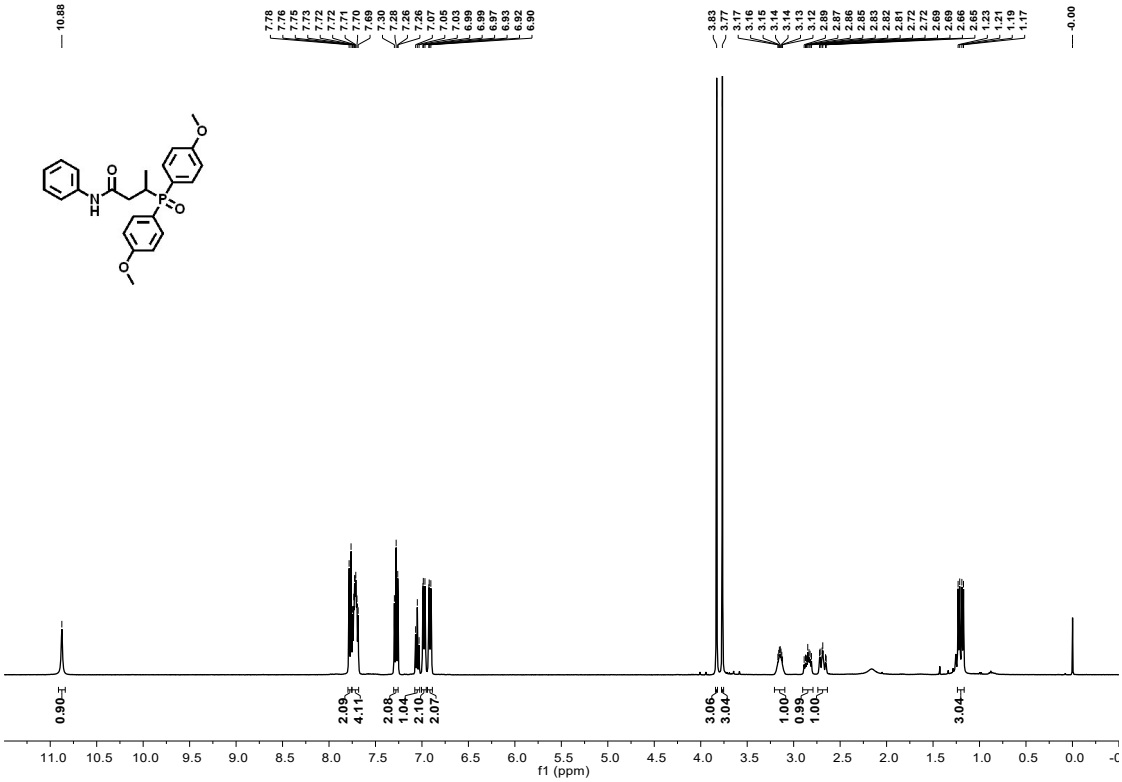
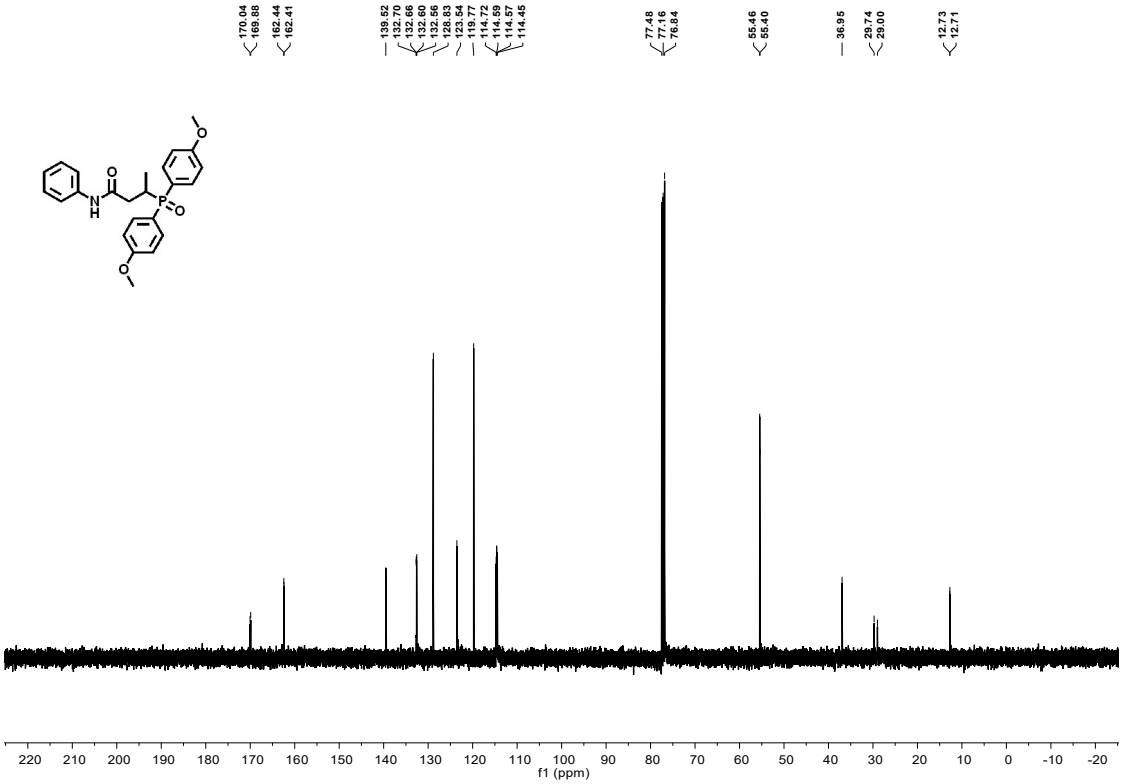


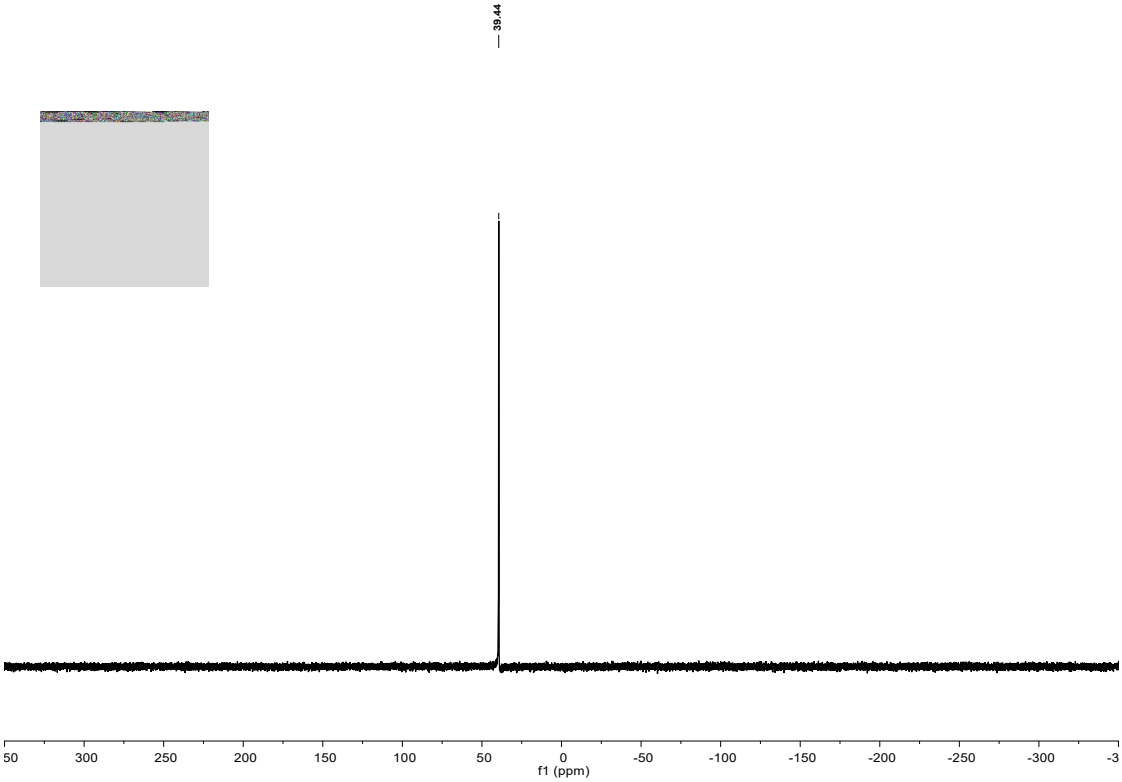
^{1}H NMR spectra of **6c**



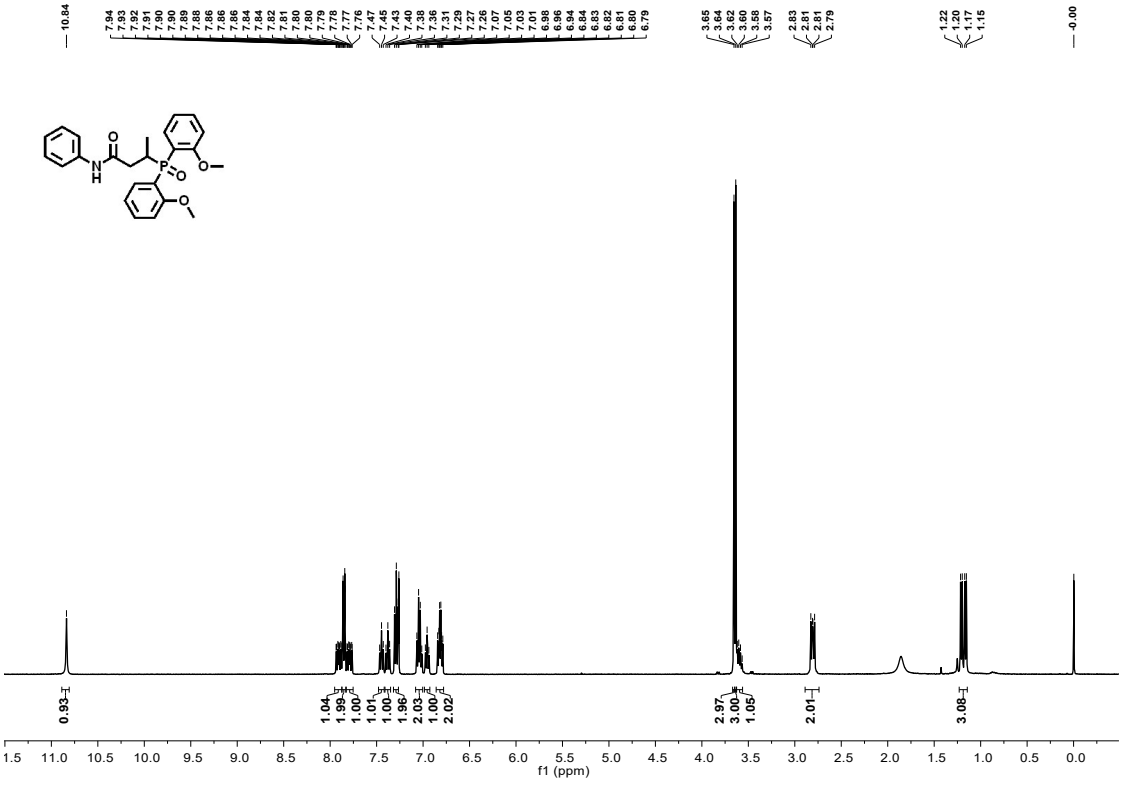
^{13}C NMR spectra of **6c**



^{31}P NMR spectra of **6c**



^{1}H NMR spectra of **6d**



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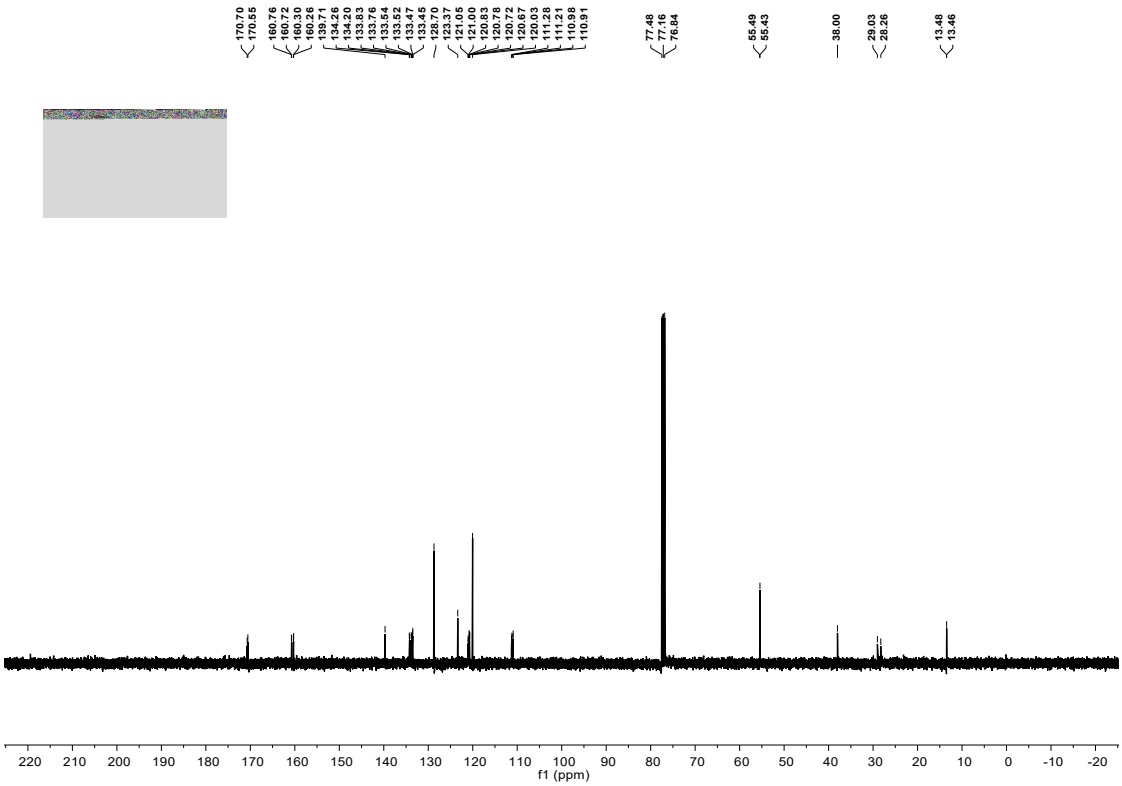

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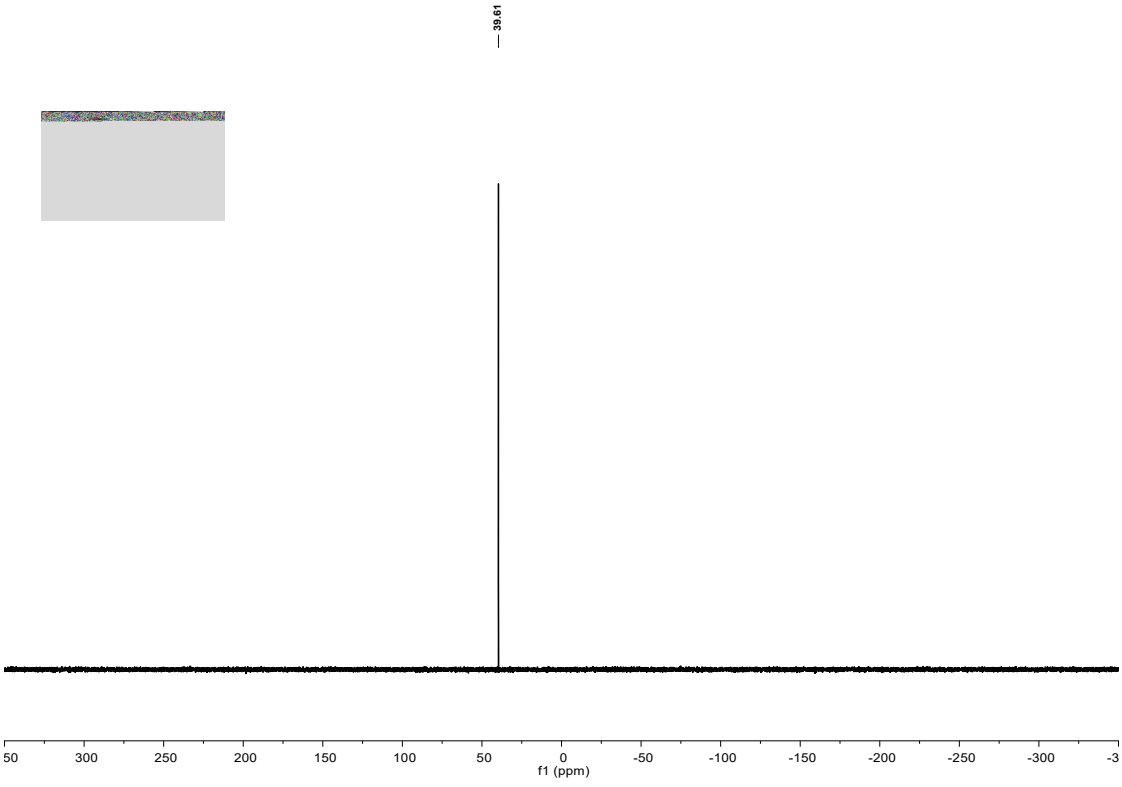
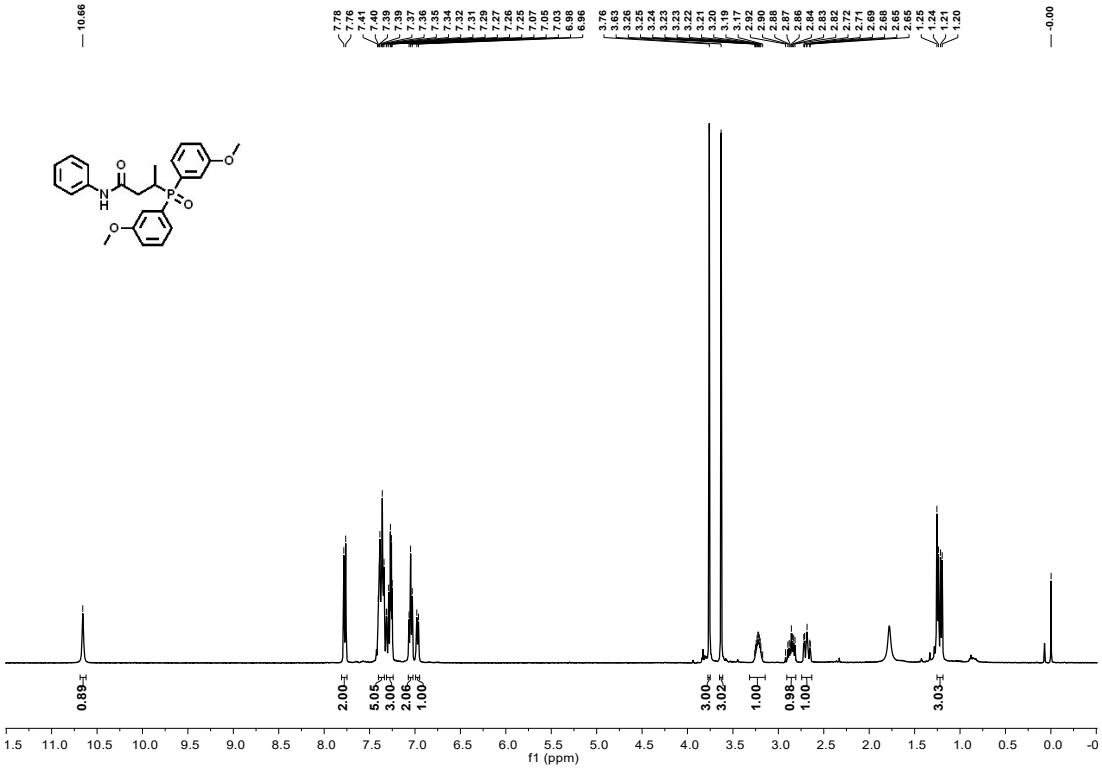
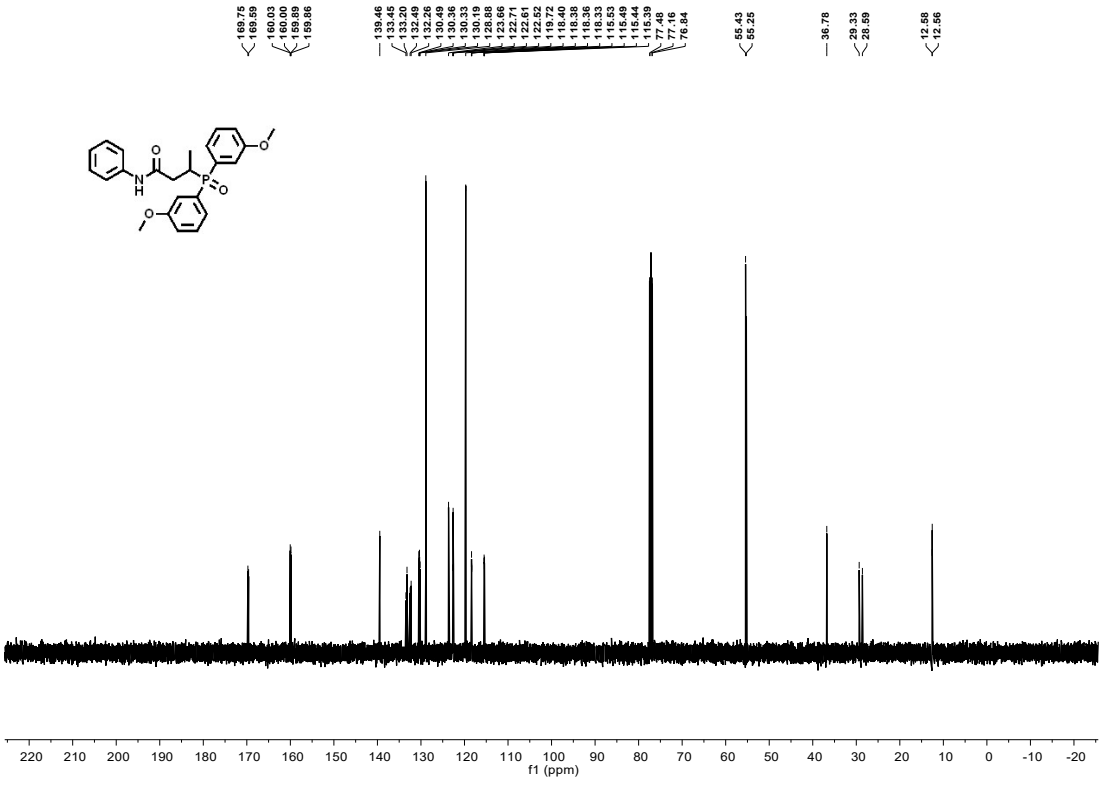


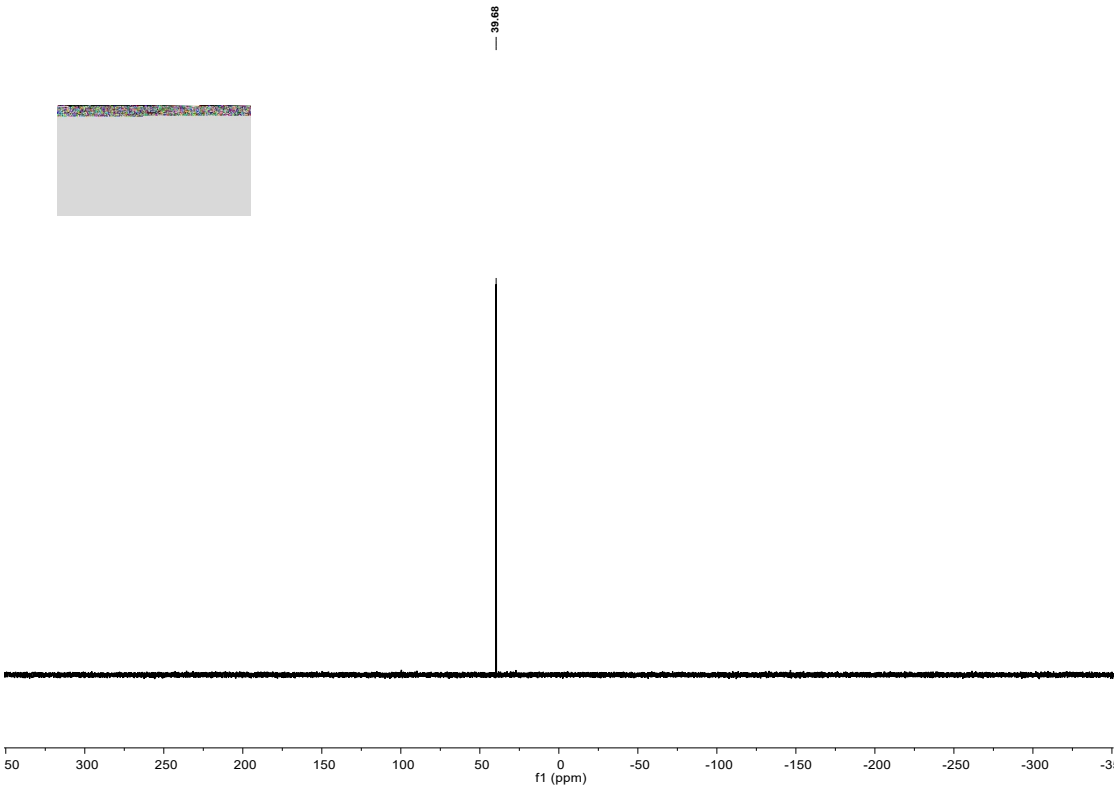
^{1}H NMR spectra of **6e**



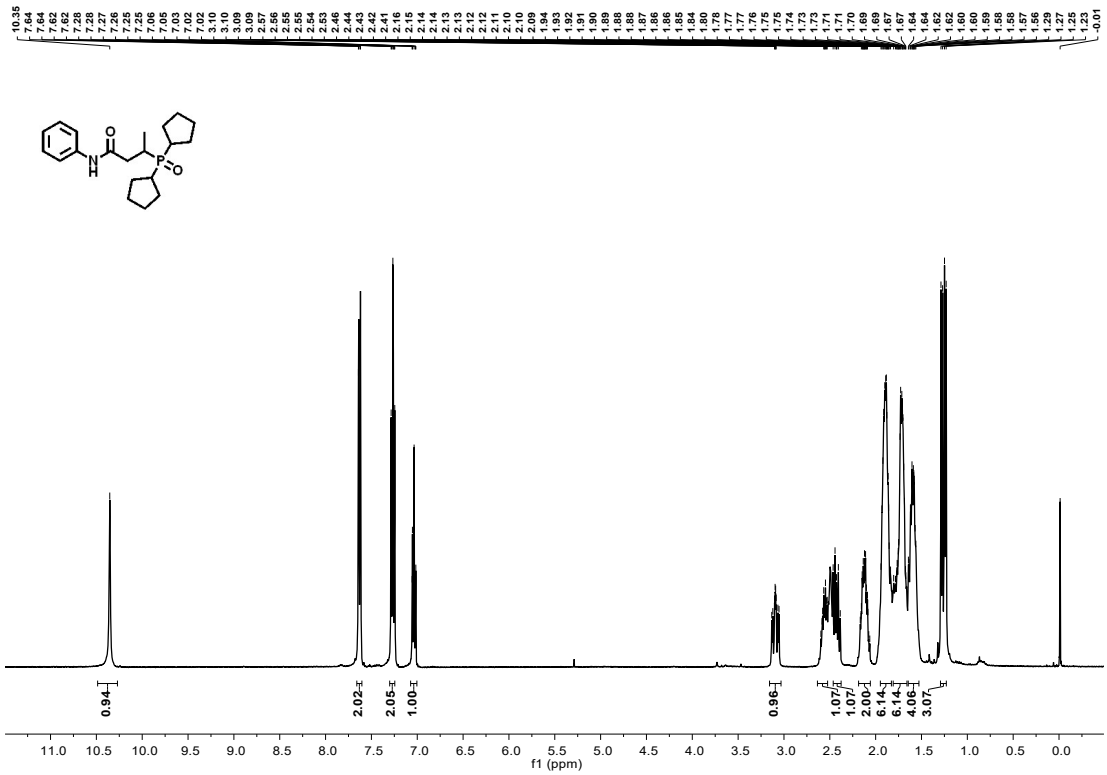
^{13}C NMR spectra of **6e**



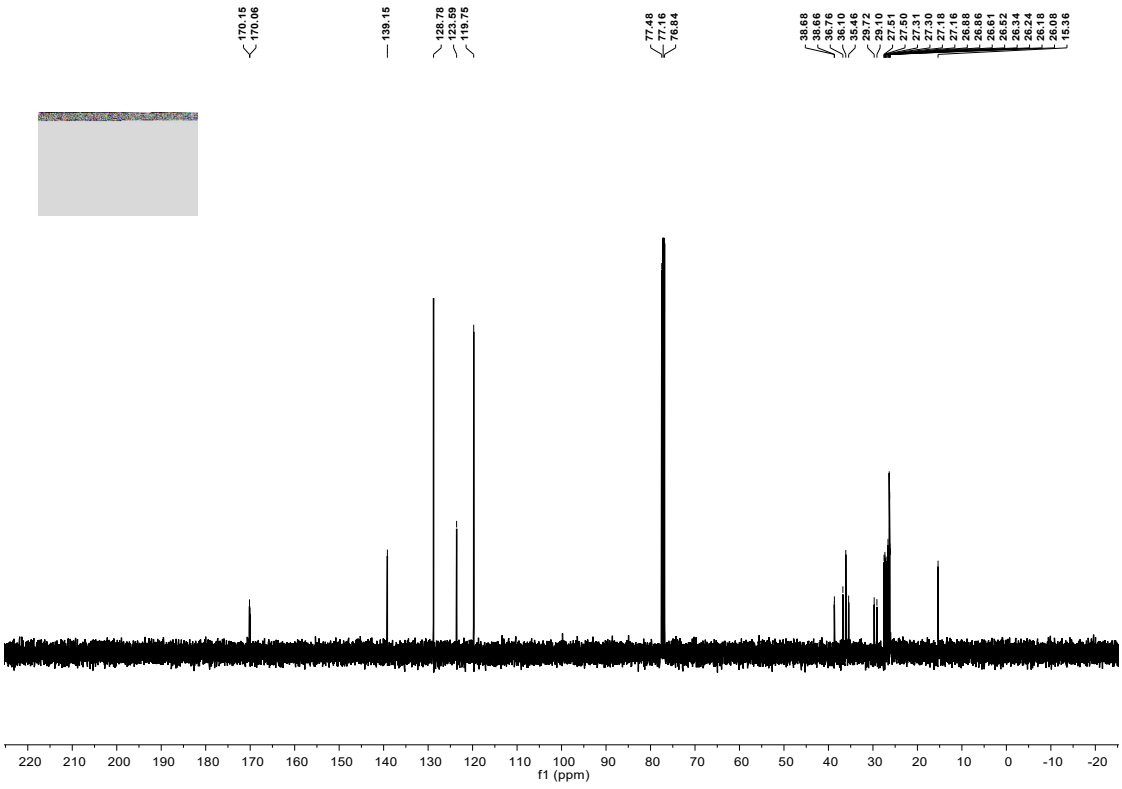
^{31}P NMR spectra of **6e**



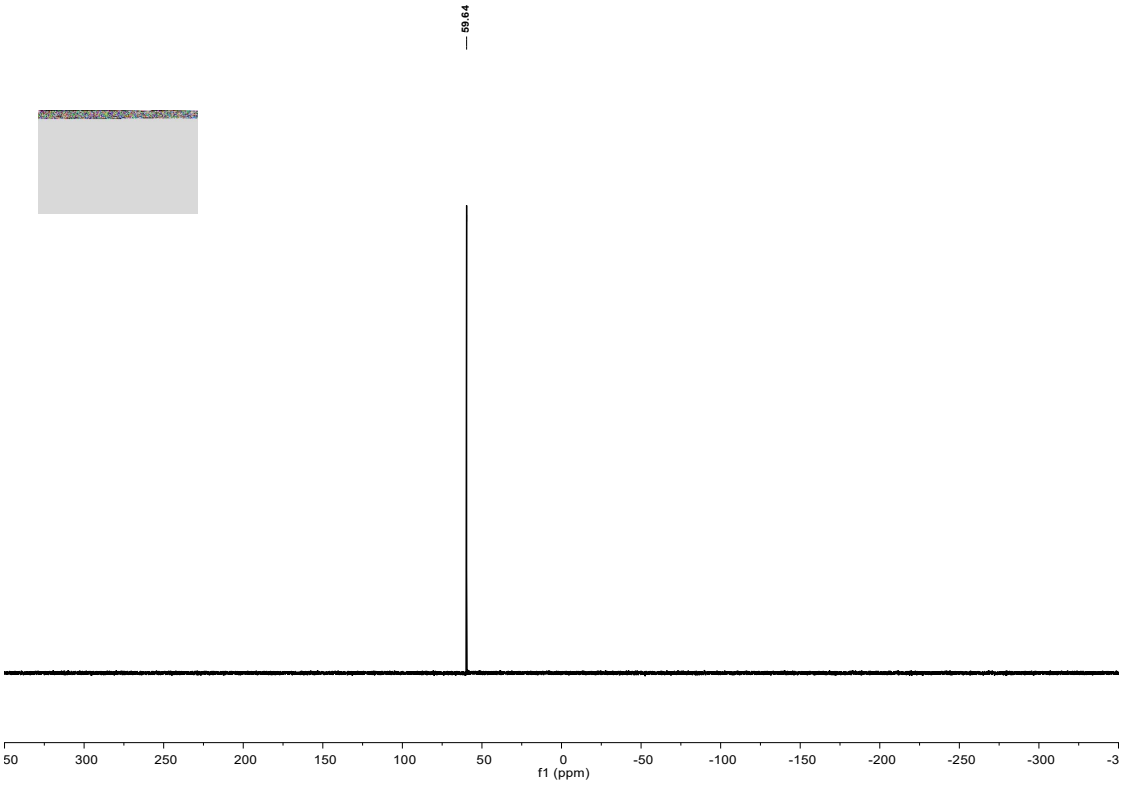
^{1}H NMR spectra of **6f**



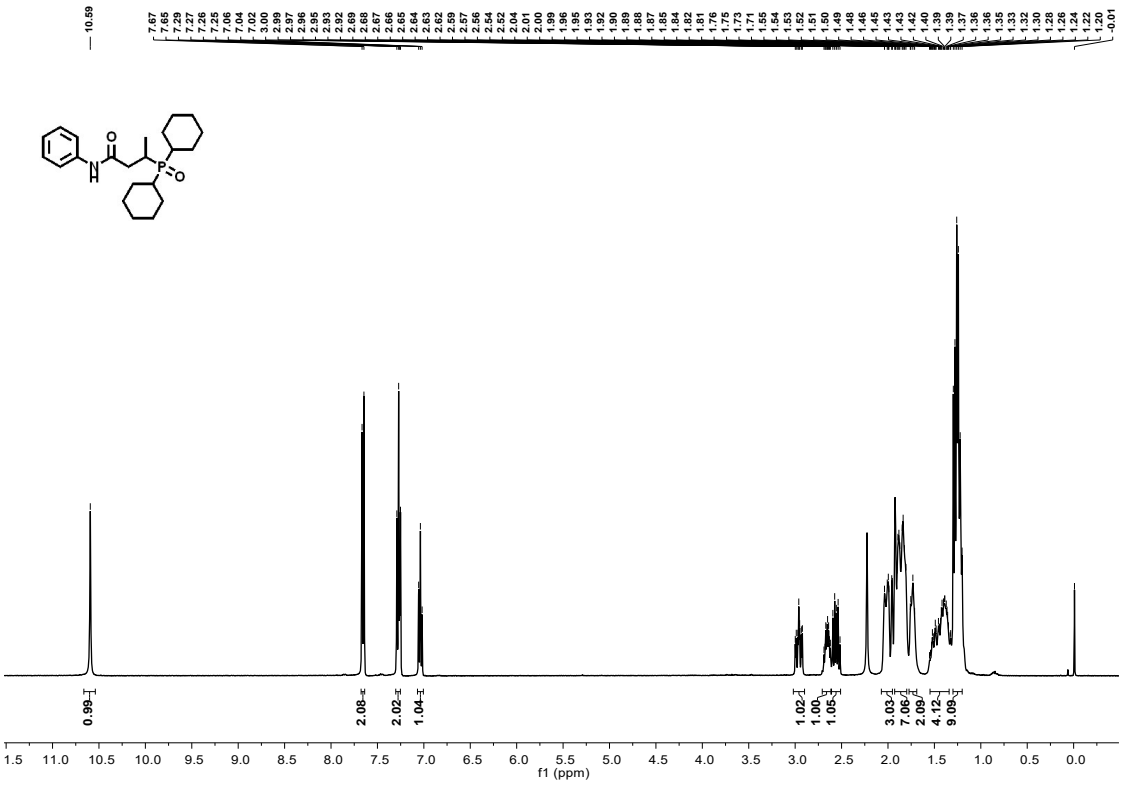
^{13}C NMR spectra of **6f**



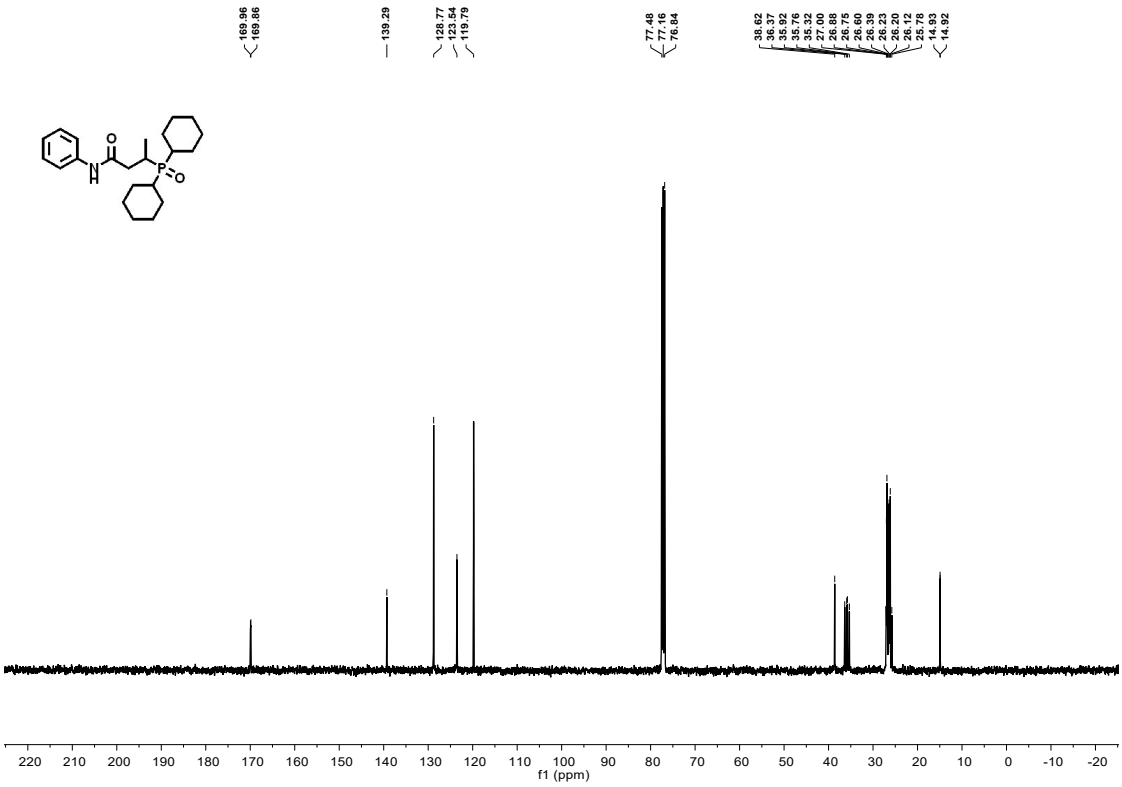
^{31}P NMR spectra of **6f**



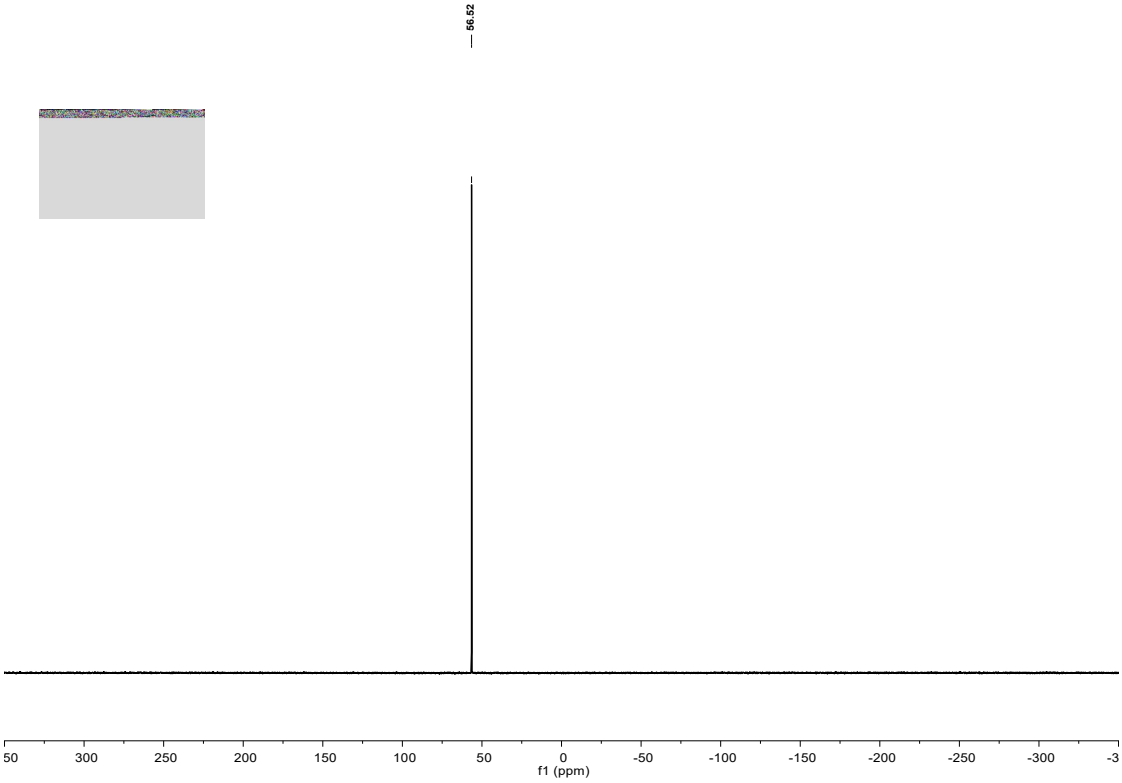
^{1}H NMR spectra of **6g**



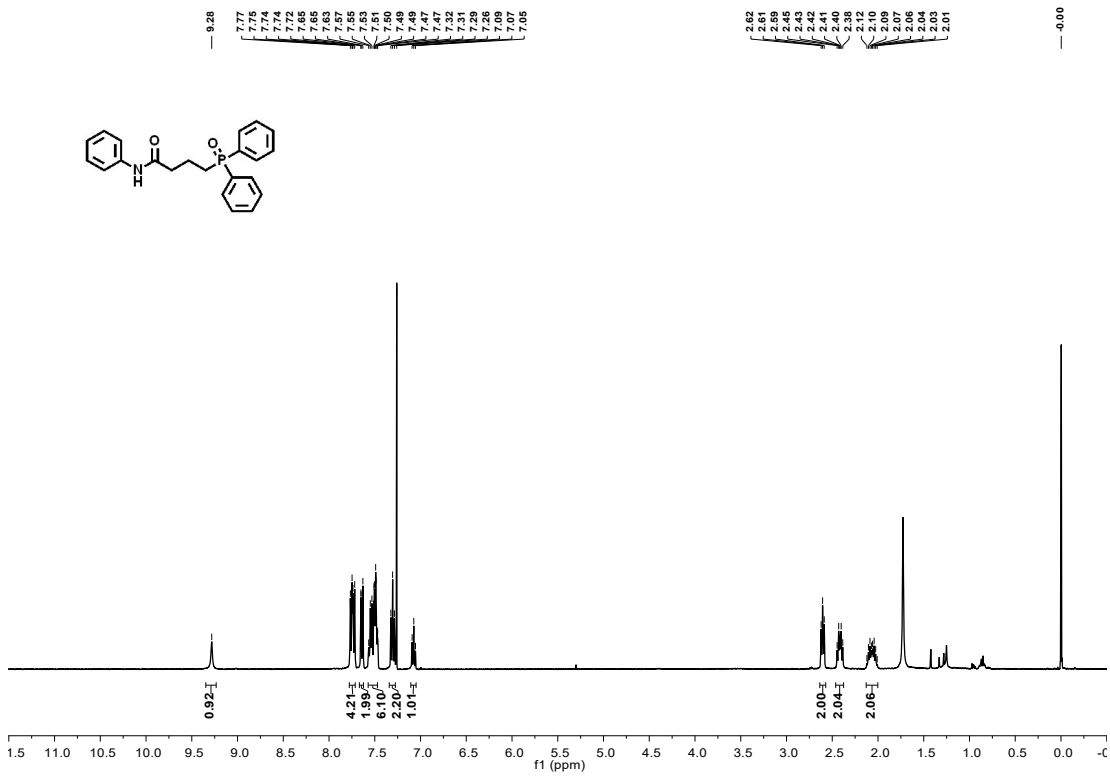
^{13}C NMR spectra of **6g**



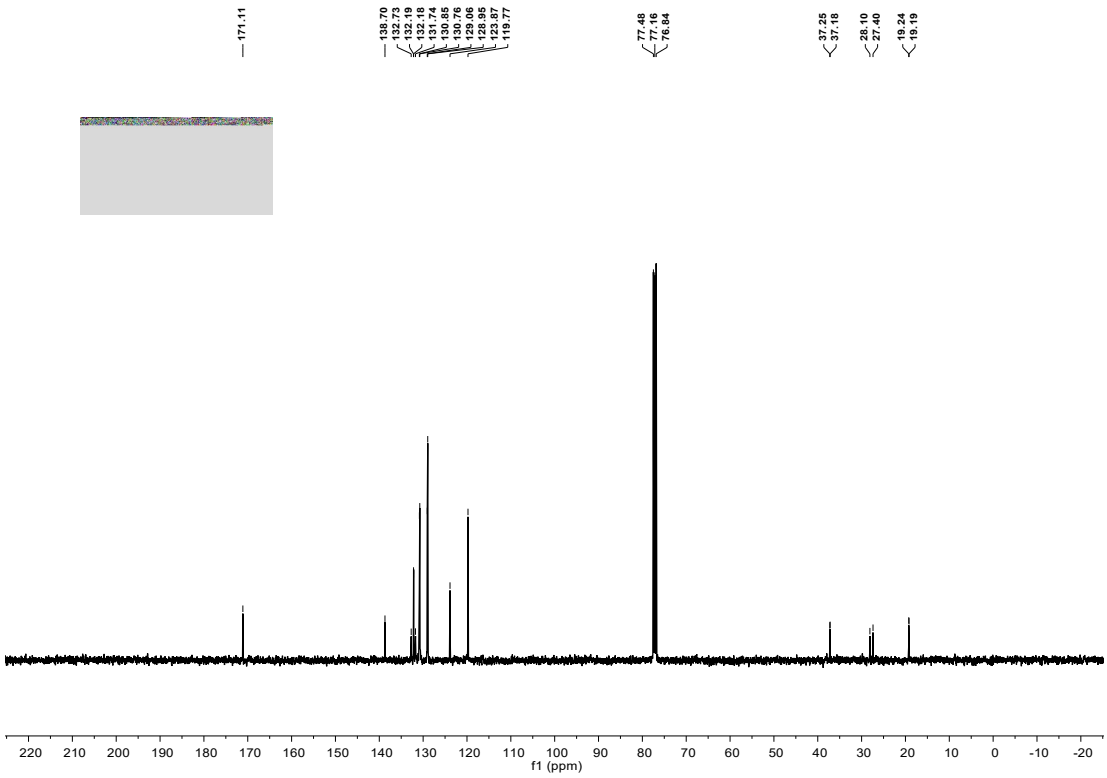
^{31}P NMR spectra of **6g**



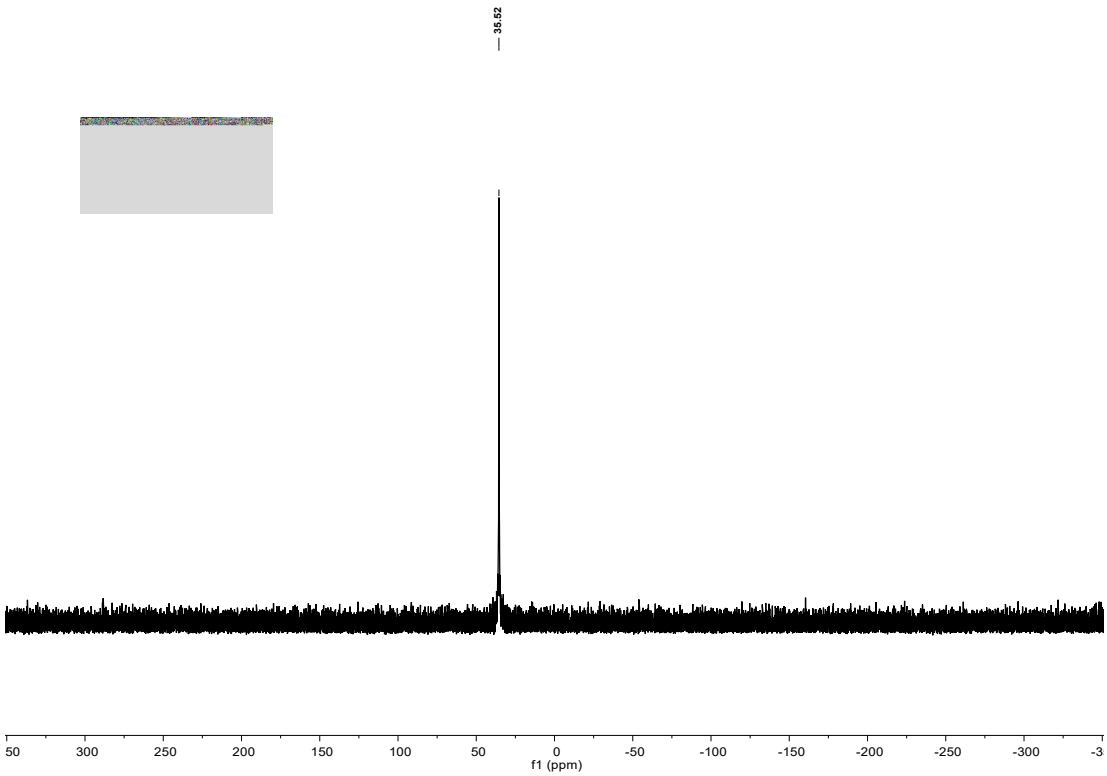
^{1}H NMR spectra of **7a**



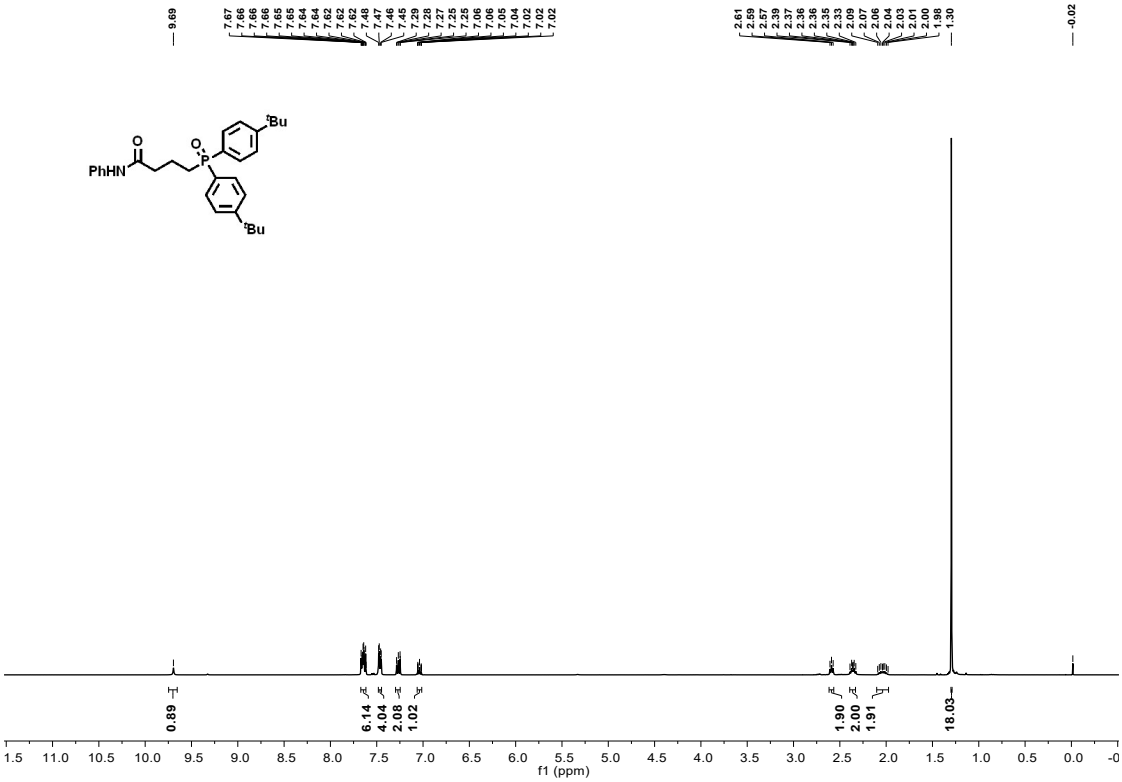
^{13}C NMR spectra of **7a**



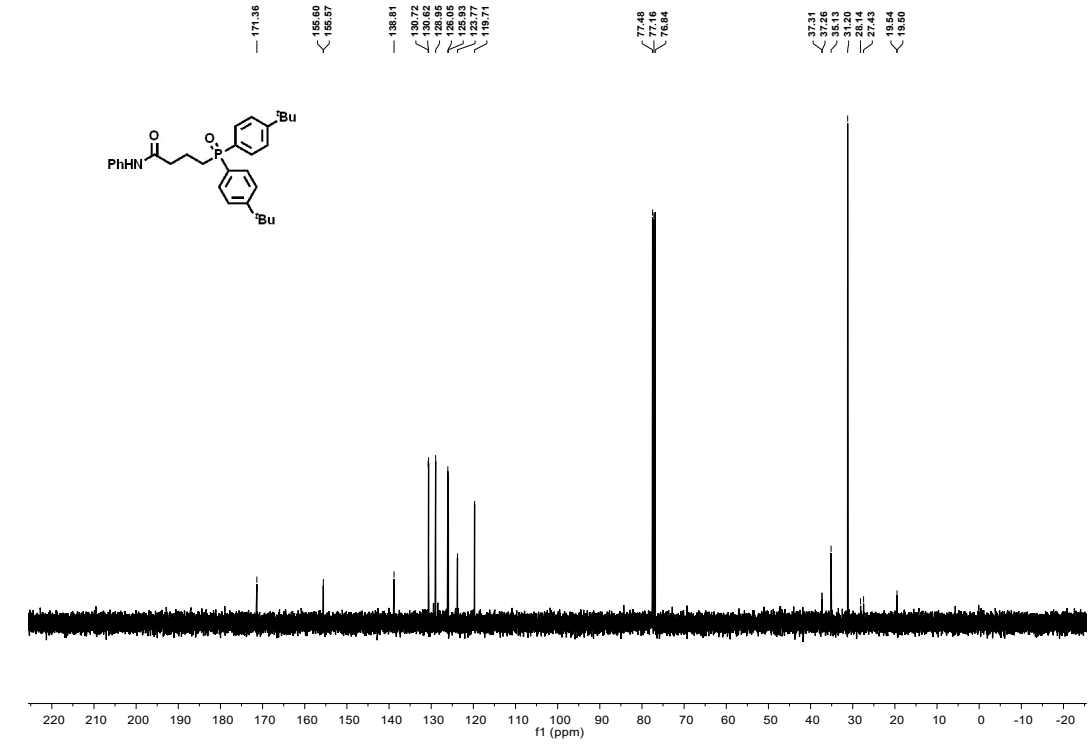
^{31}P NMR spectra of **7a**



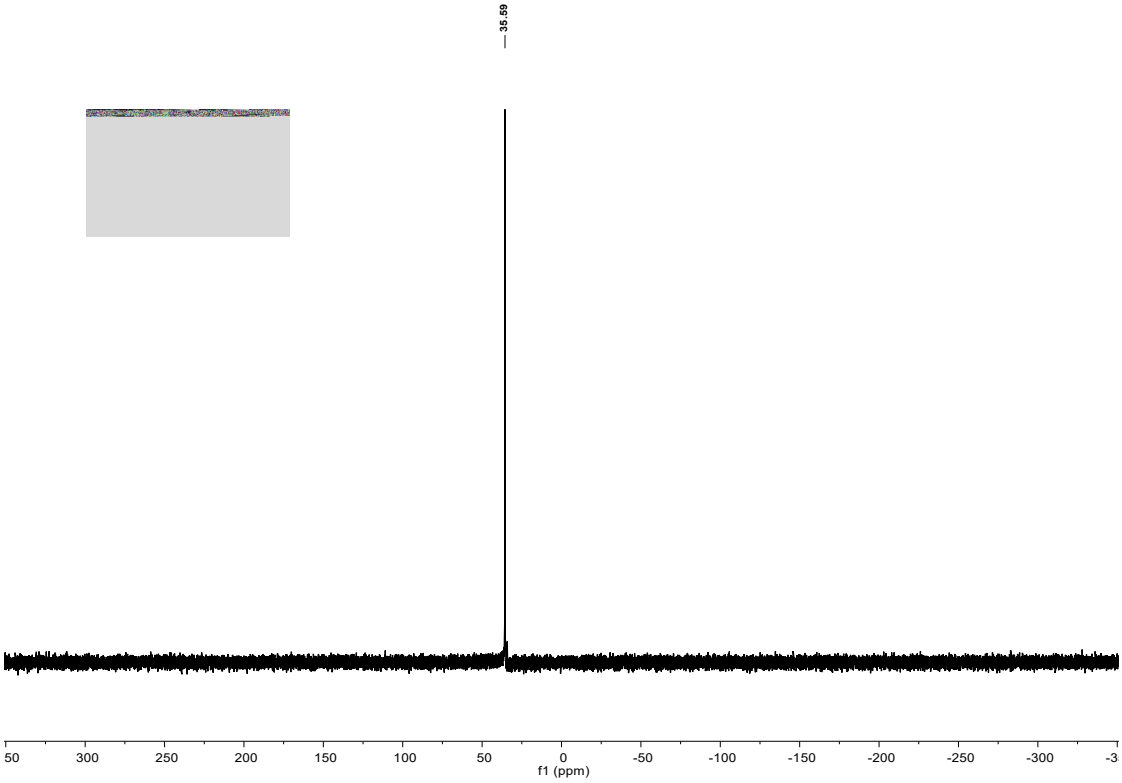
^{1}H NMR spectra of **7b**



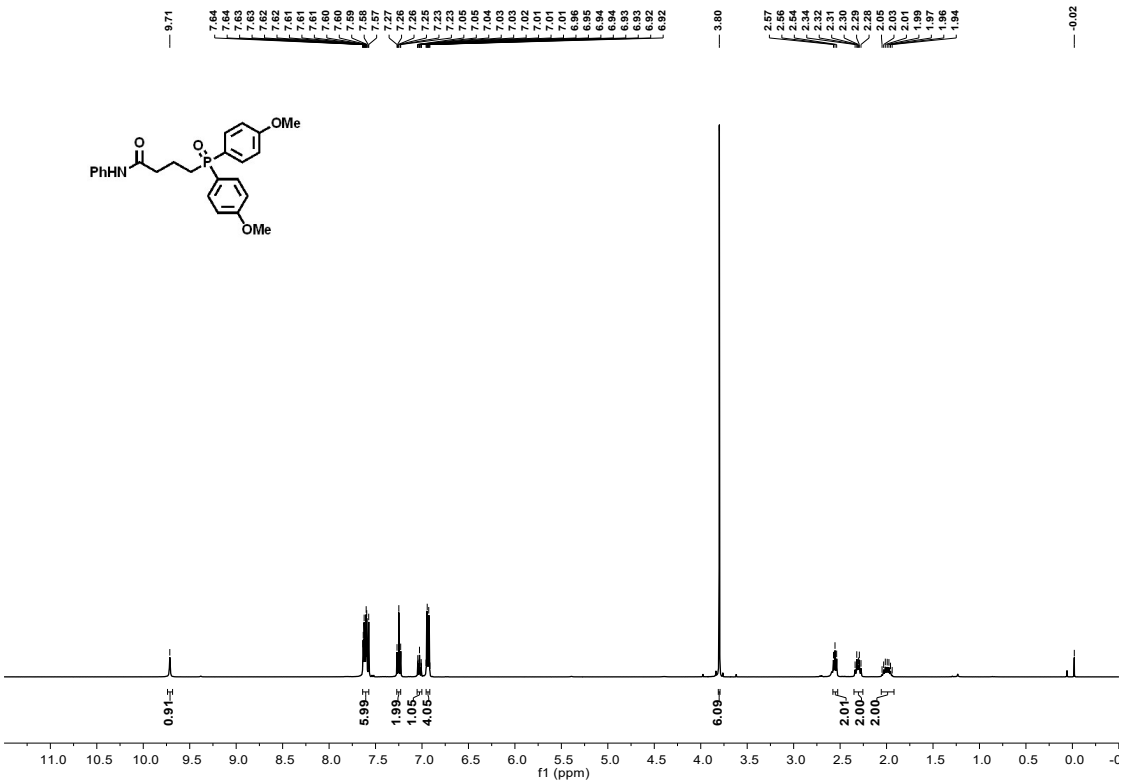
^{13}C NMR spectra of **7b**



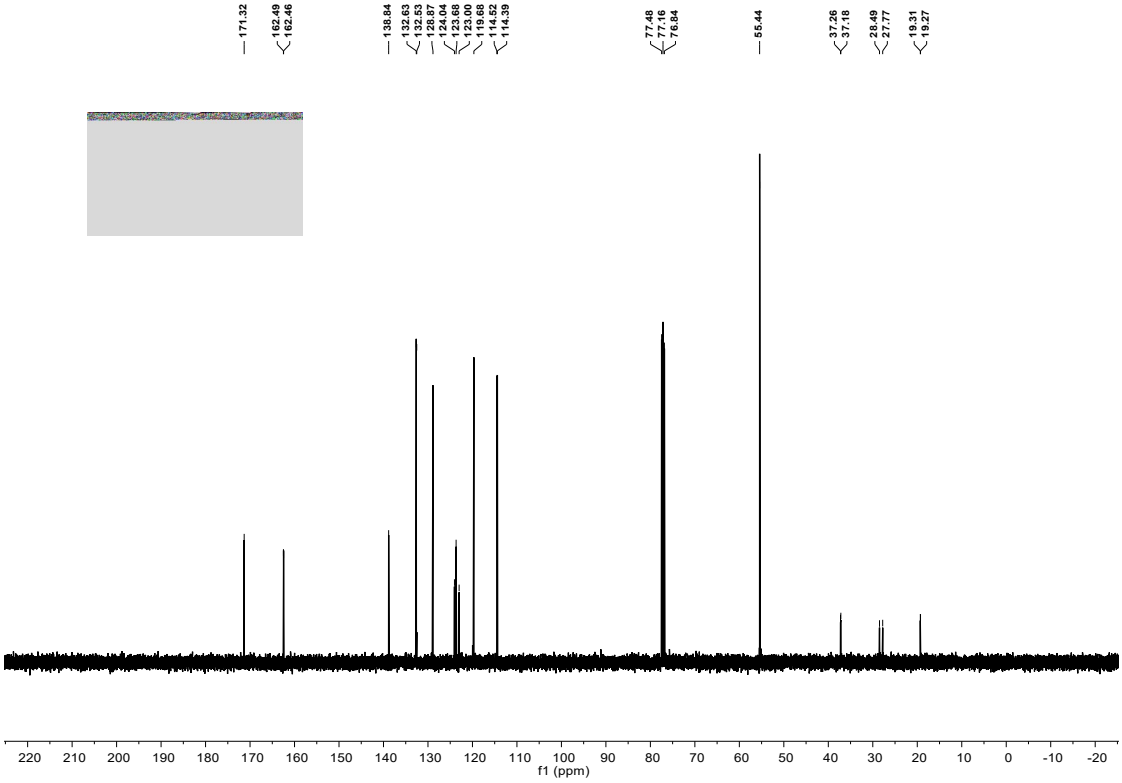
^{31}P NMR spectra of **7b**



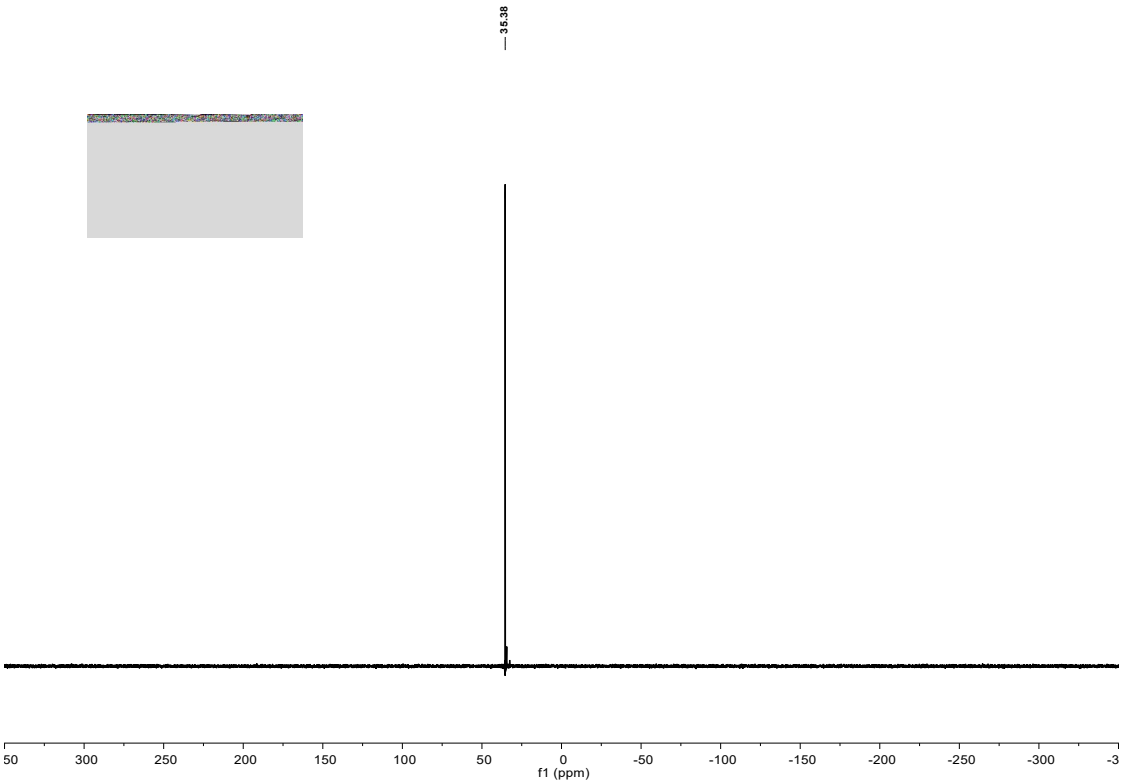
^{1}H NMR spectra of **7c**



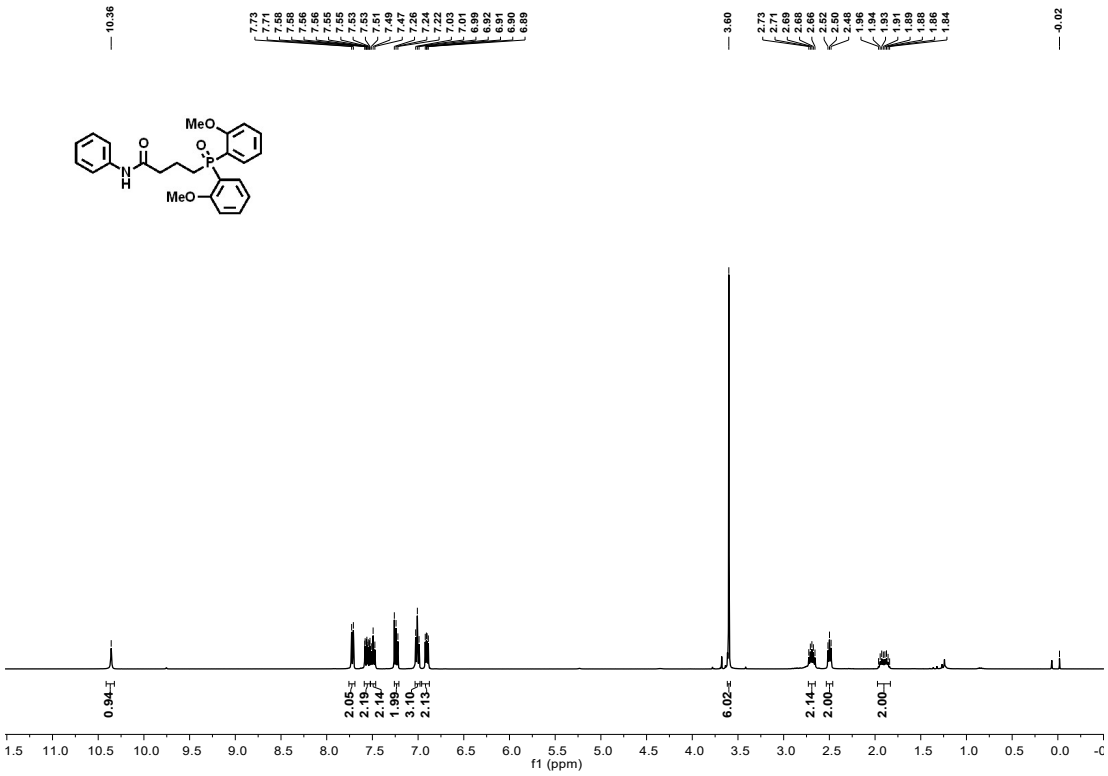
^{13}C NMR spectra of **7c**



^{31}P NMR spectra of **7c**



^{1}H NMR spectra of **7d**



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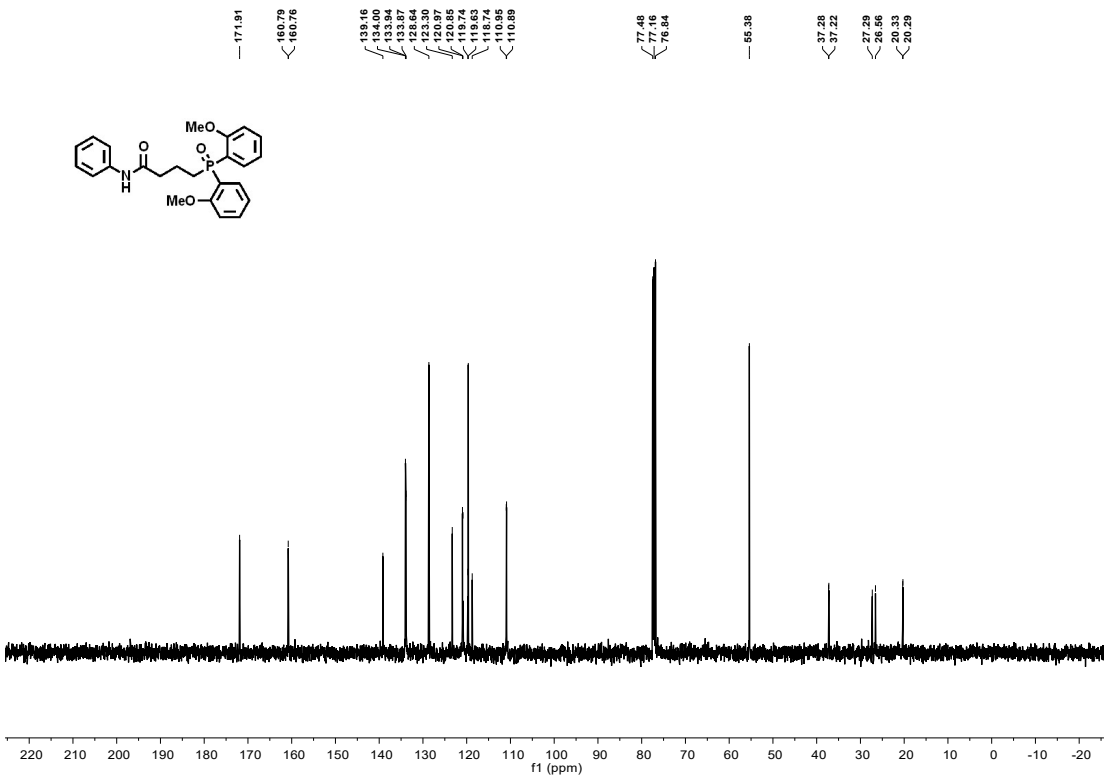

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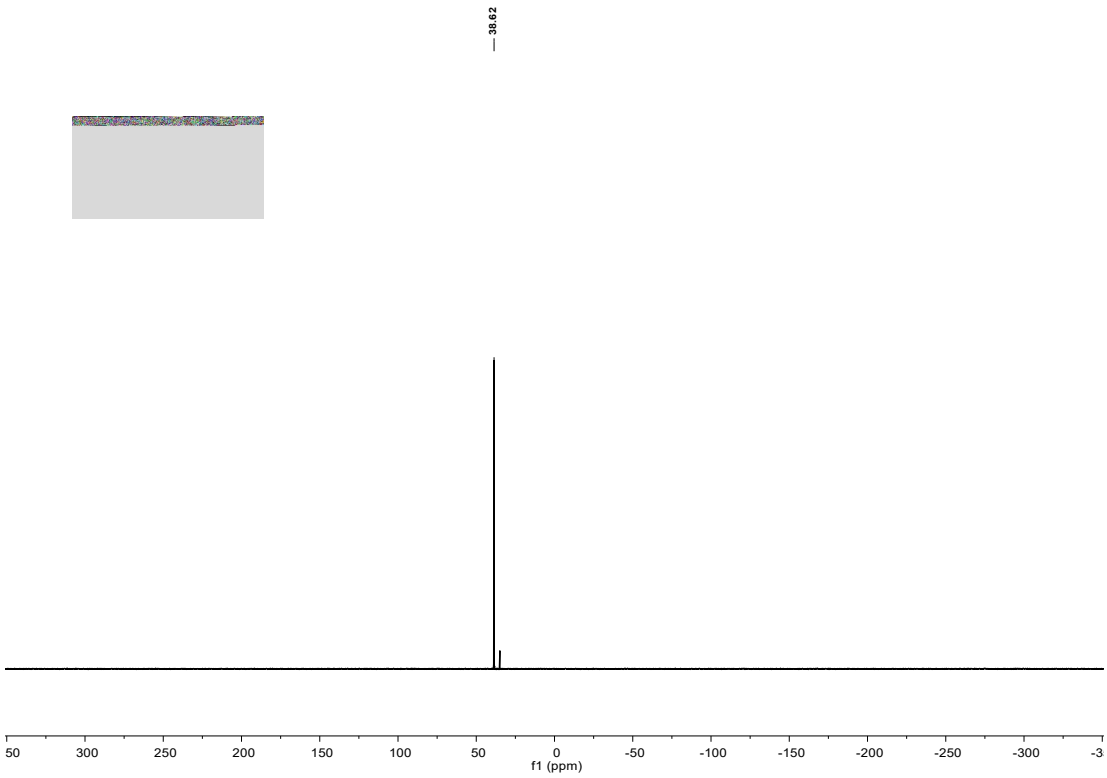

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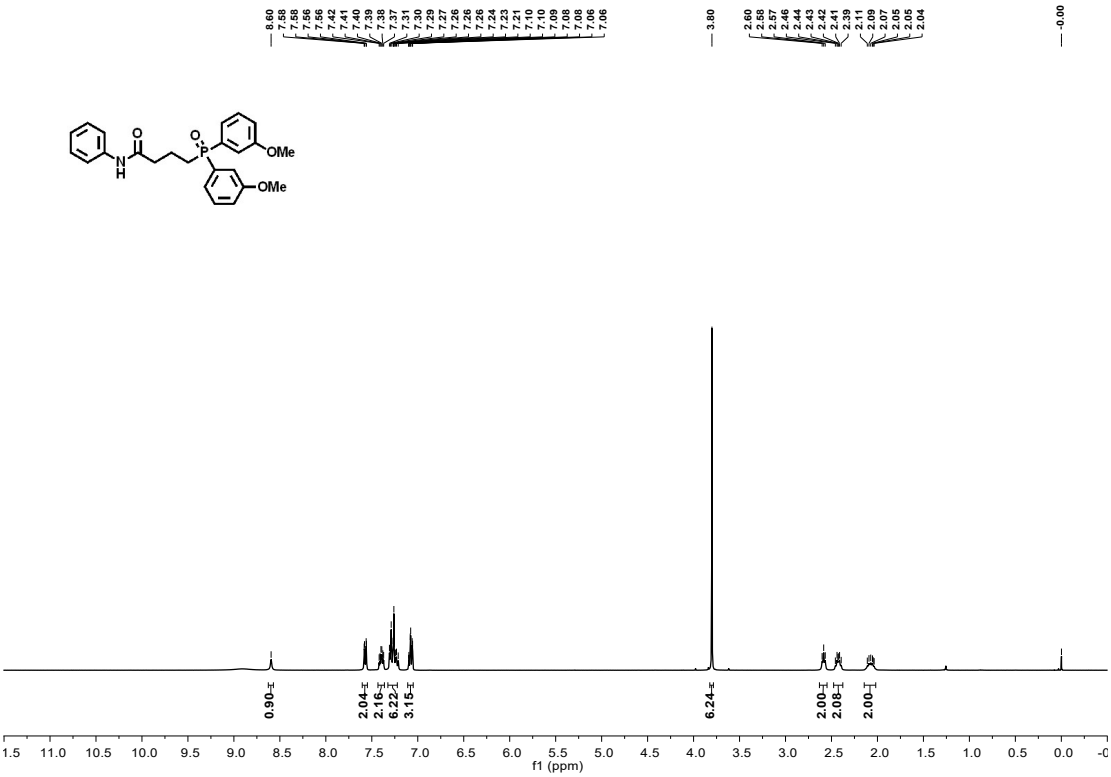
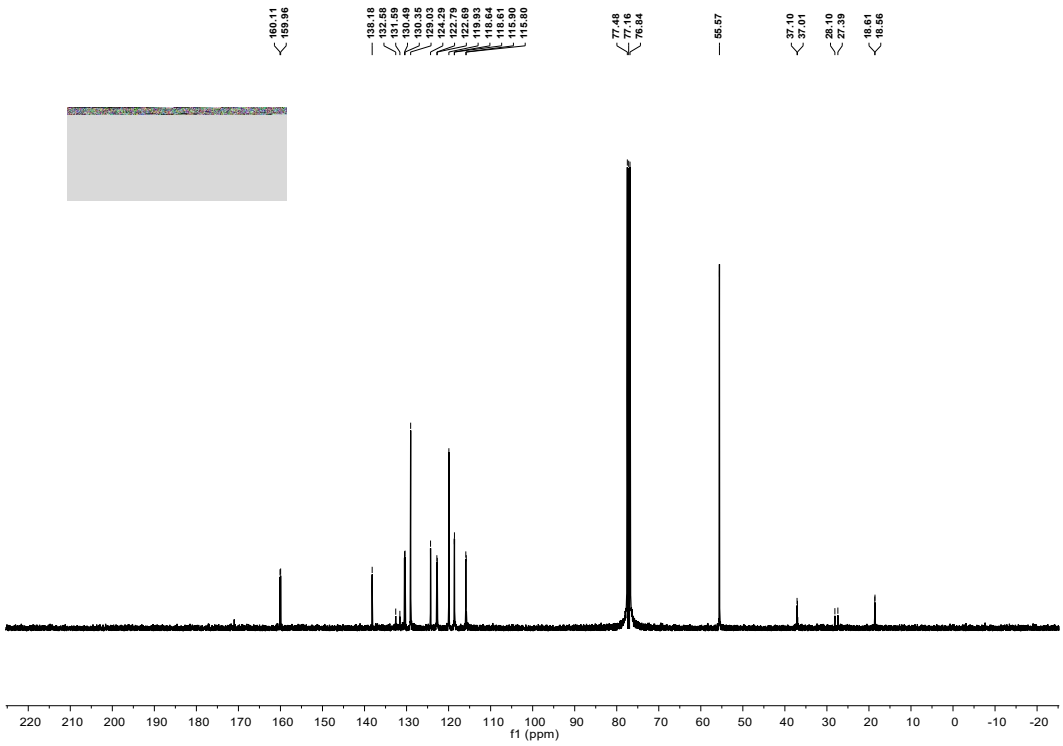
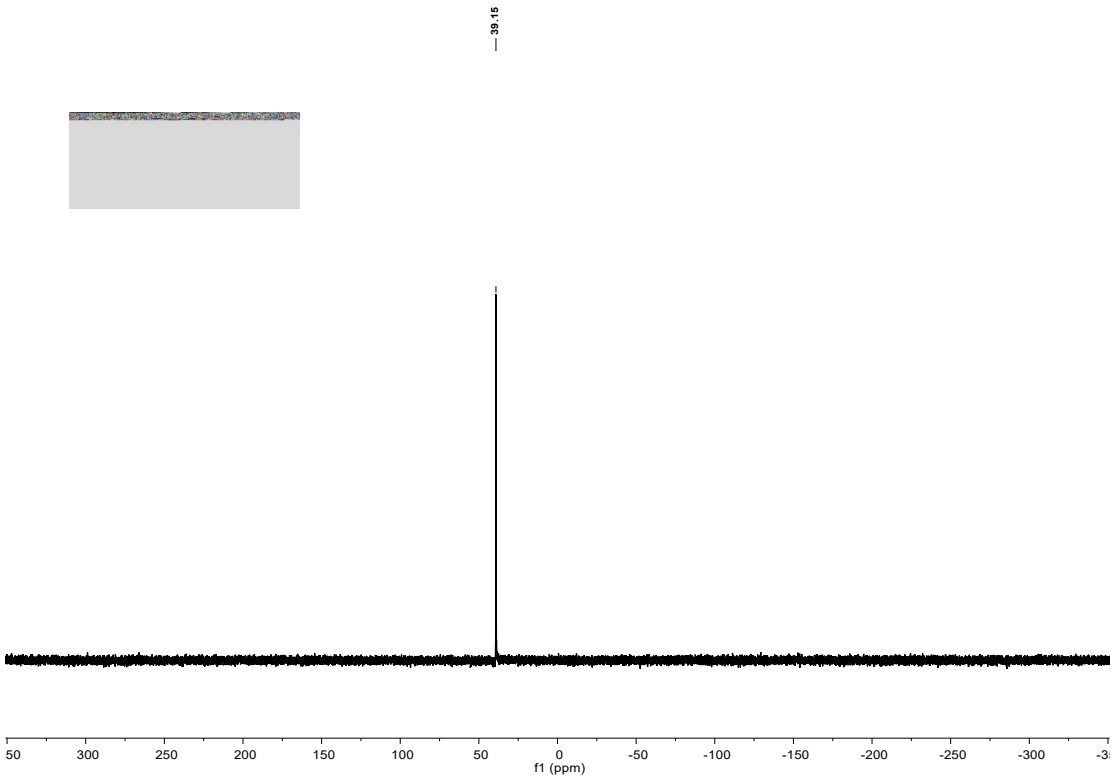


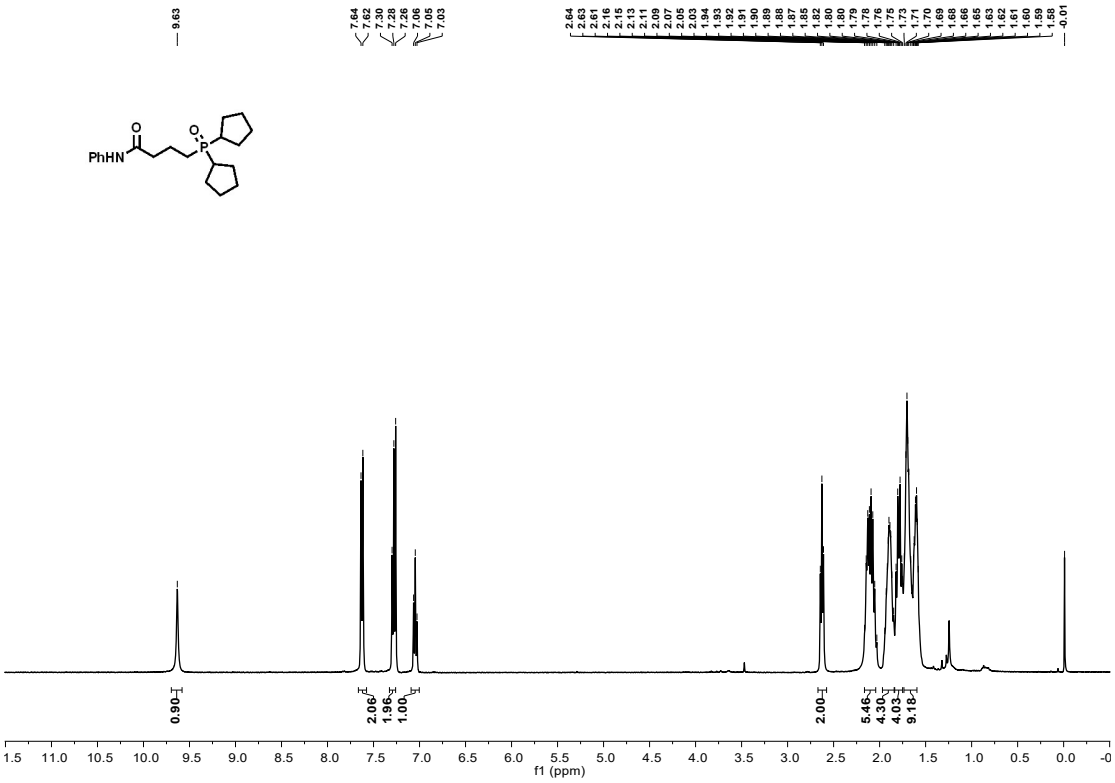
^{13}C NMR spectra of **7e**



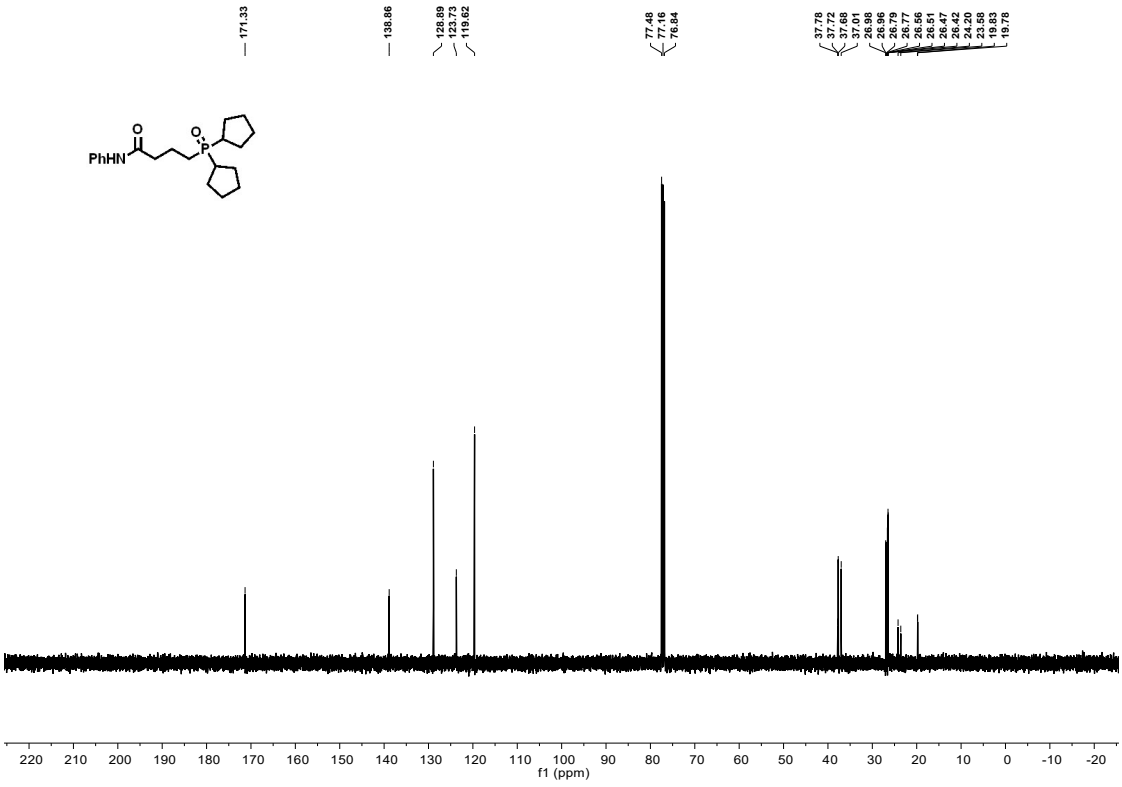
^{31}P NMR spectra of **7e**



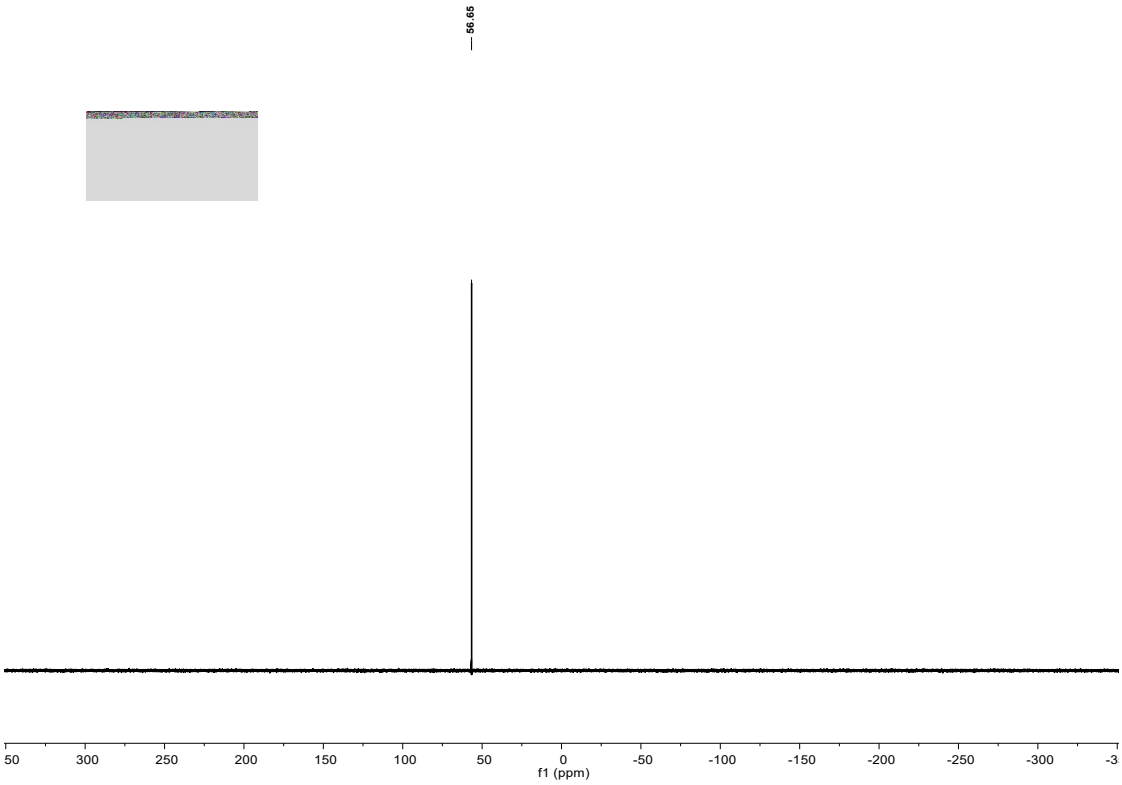
^{1}H NMR spectra of **7f**



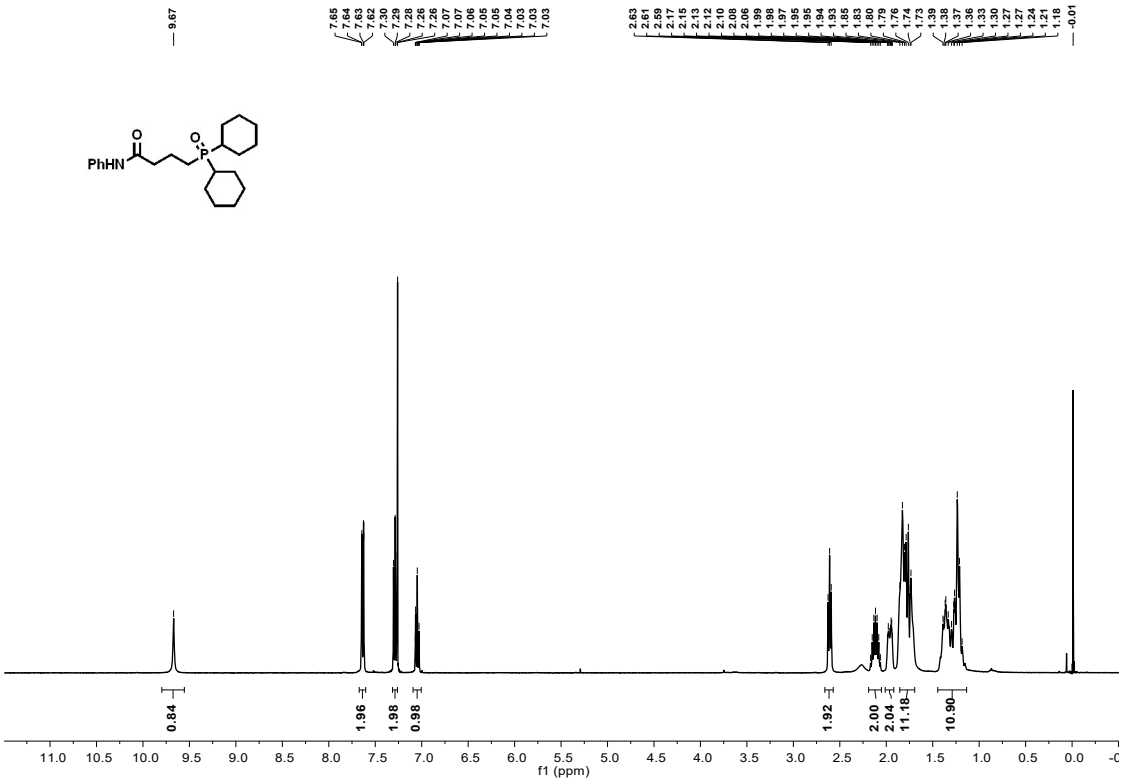
^{13}C NMR spectra of **7f**



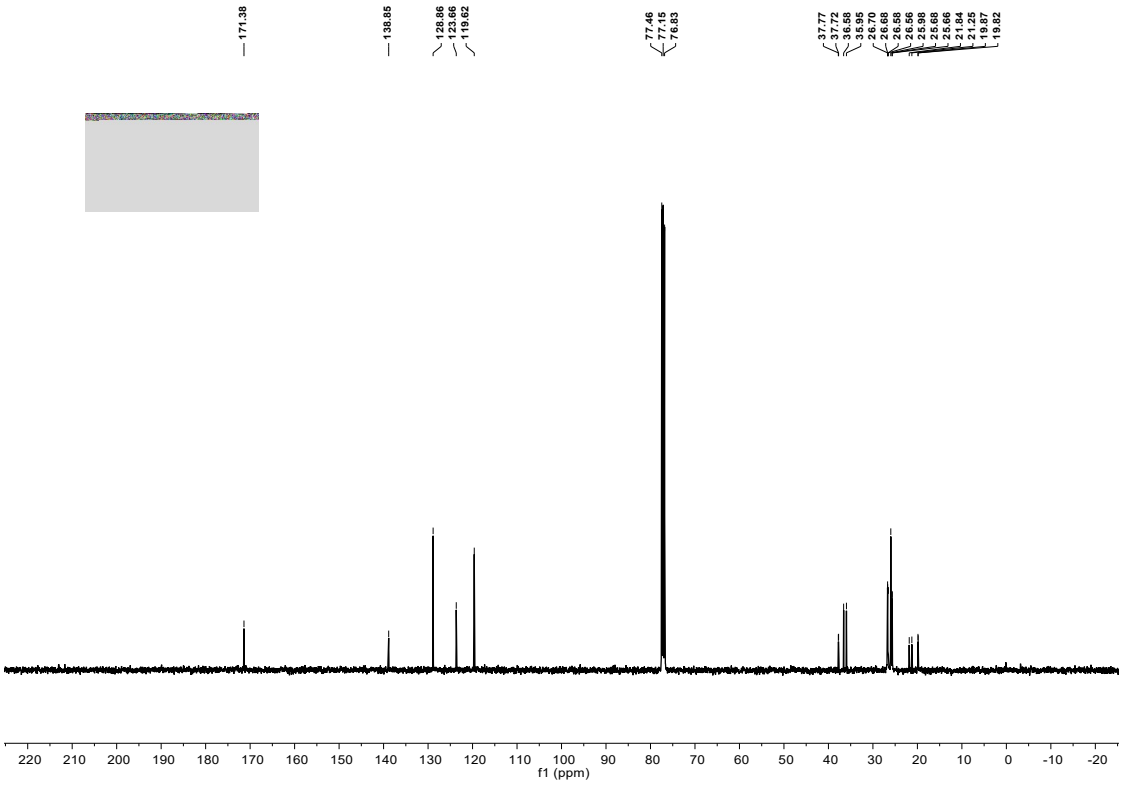
^{31}P NMR spectra of **7f**



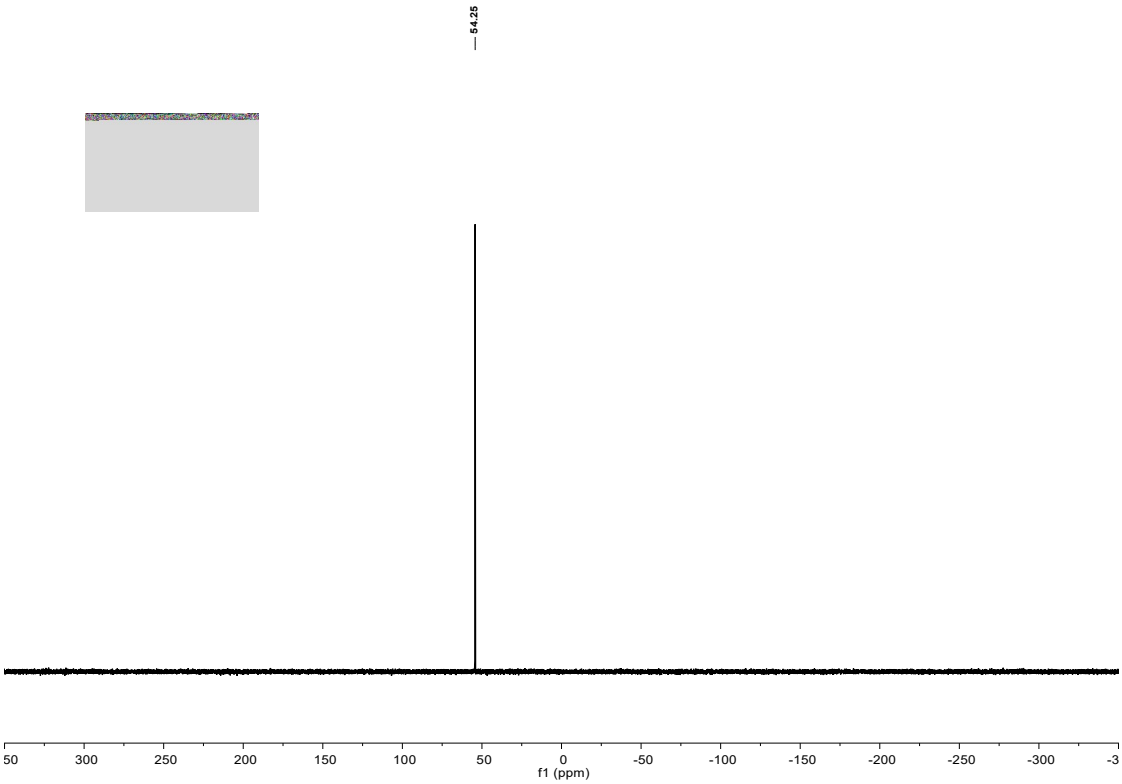
^{1}H NMR spectra of **7g**



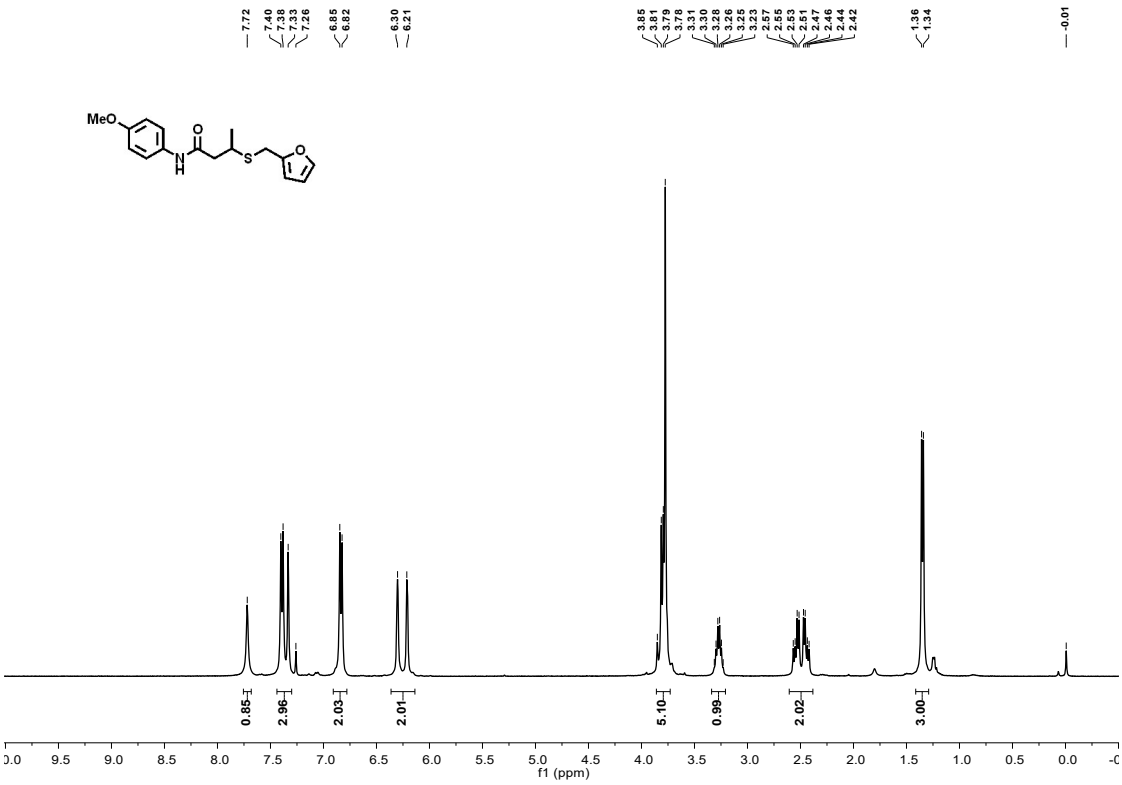
^{13}C NMR spectra of **7g**



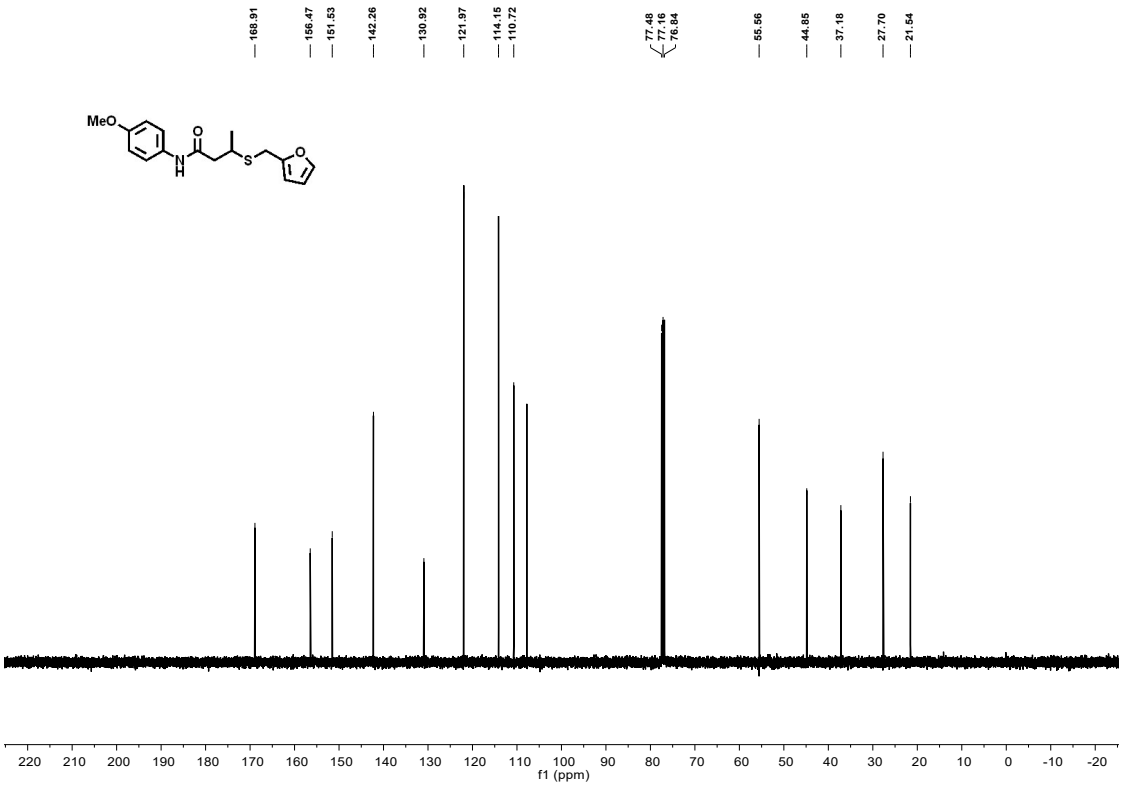
^{31}P NMR spectra of **7g**



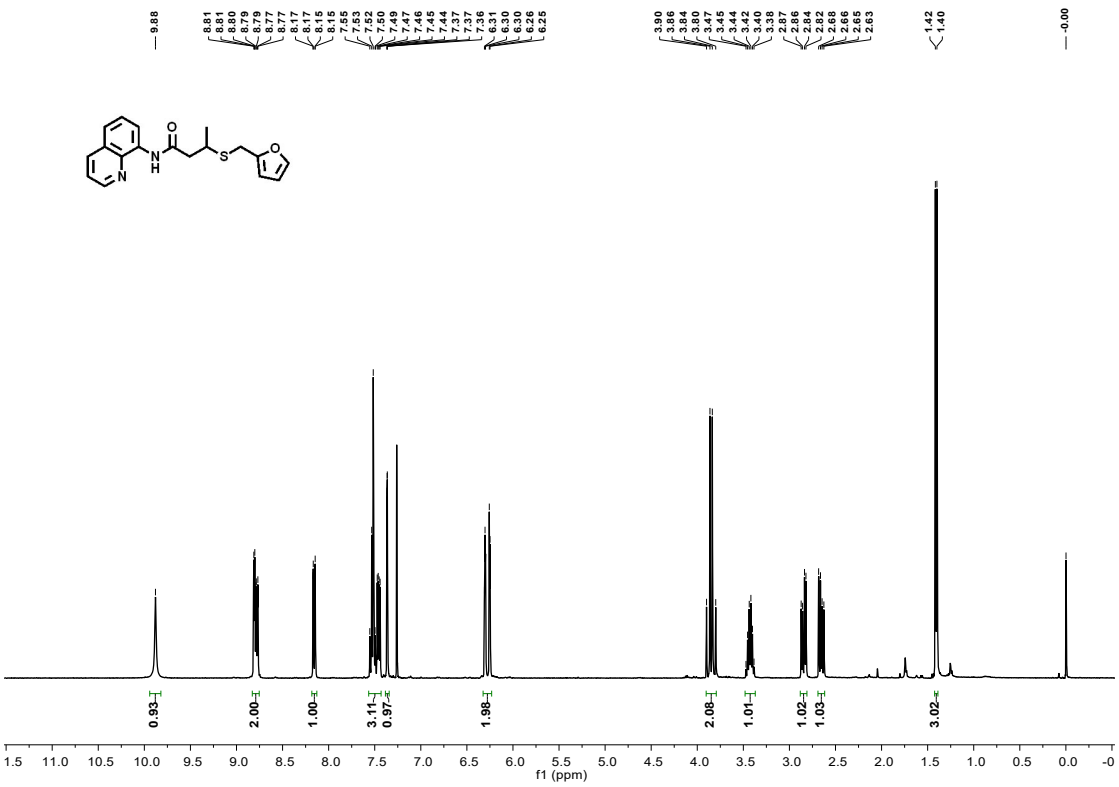
^{1}H NMR spectra of **8a**



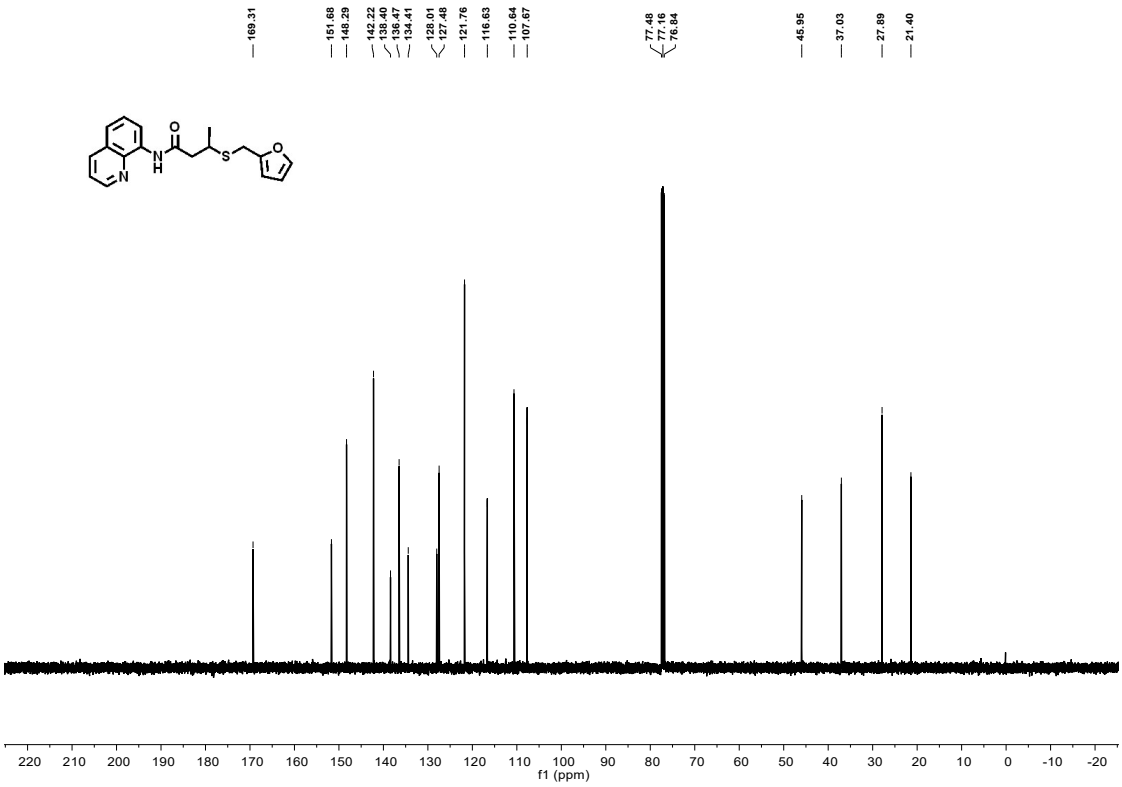
^{13}C NMR spectra of **8a**



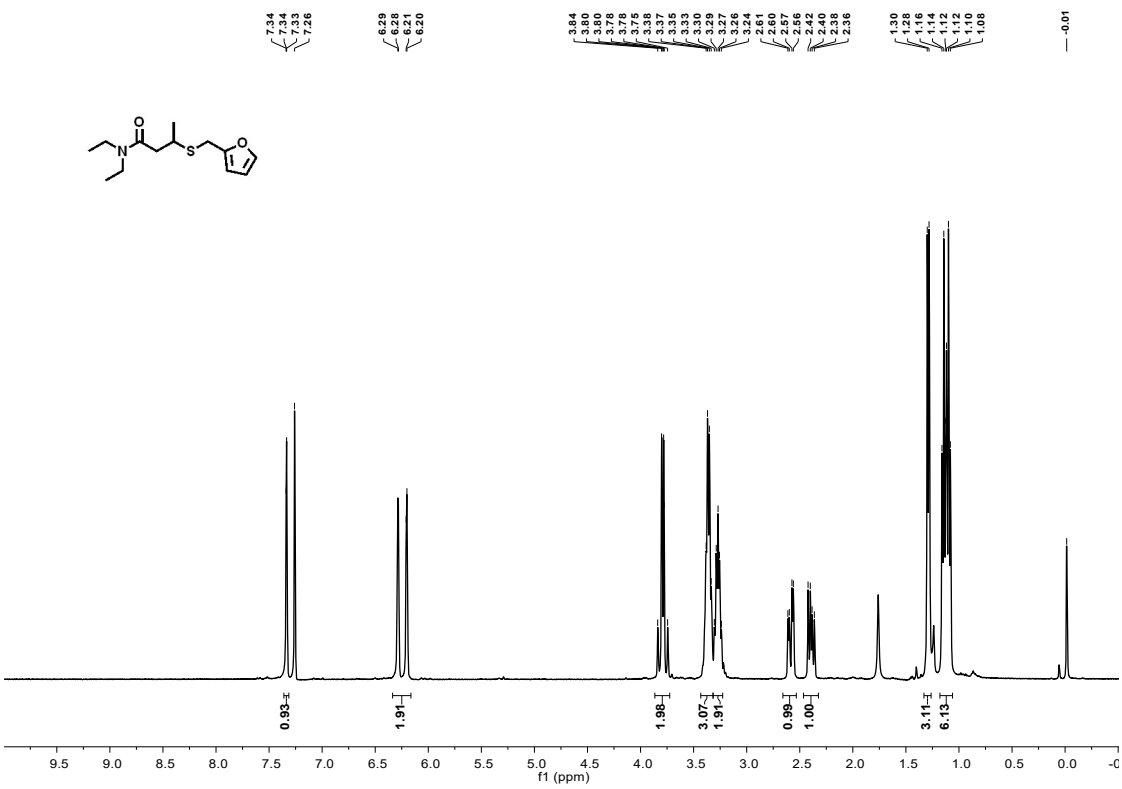
^{1}H NMR spectra of **8b**



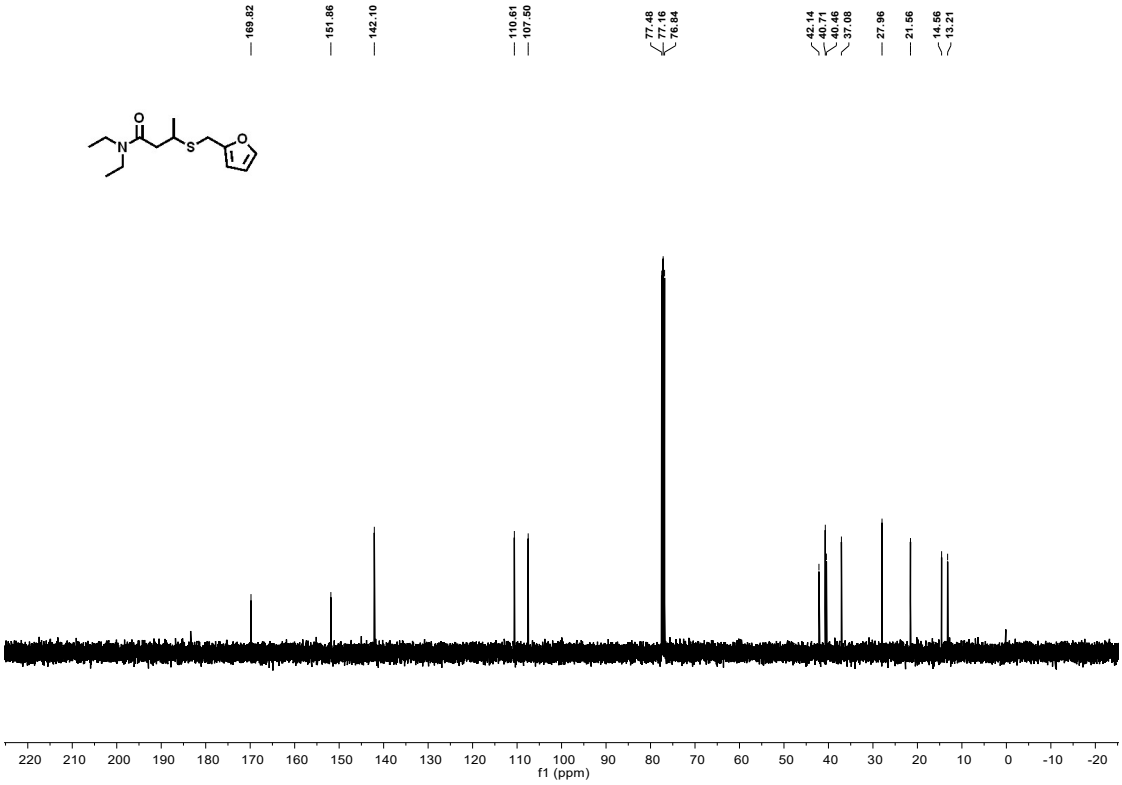
^{13}C NMR spectra of **8b**



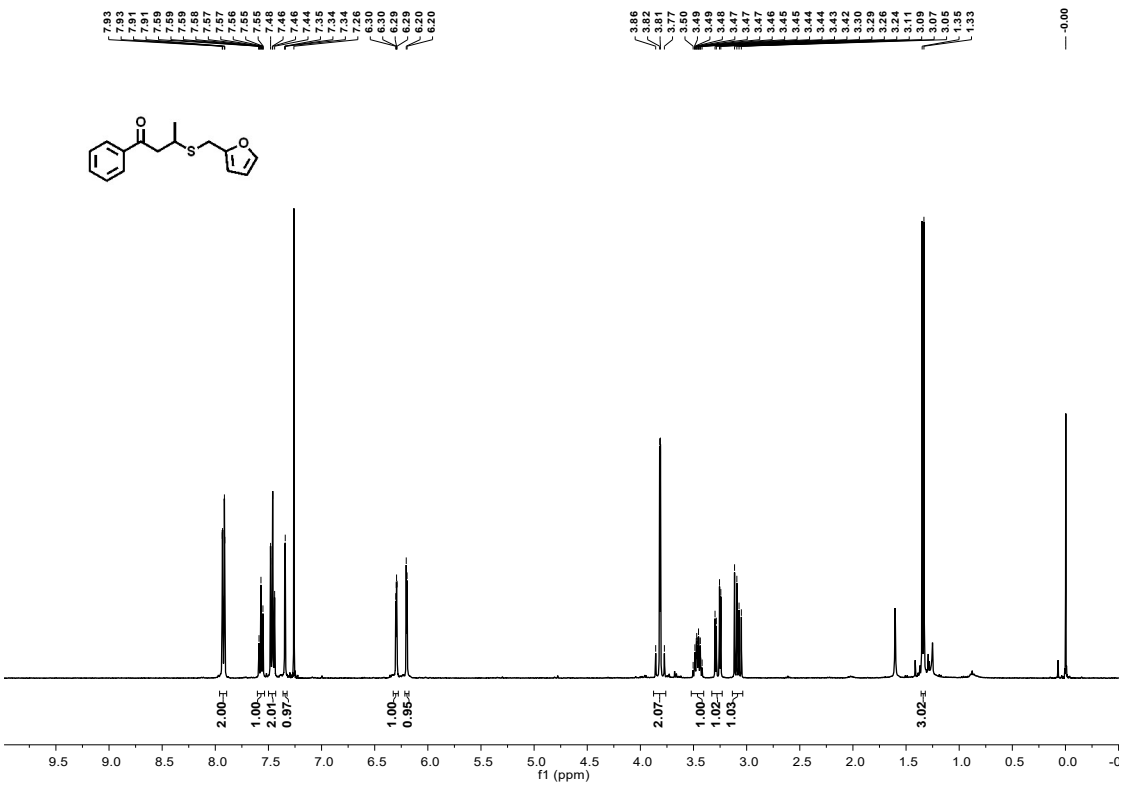
^{1}H NMR spectra of **8c**



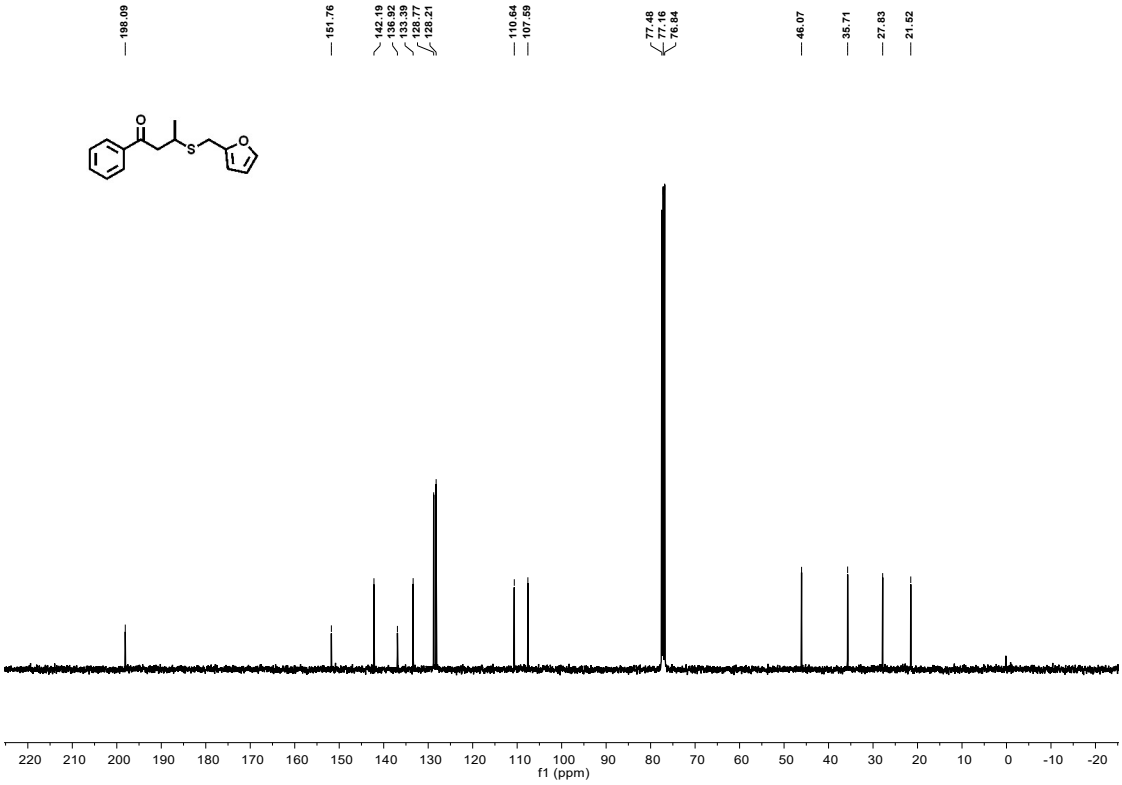
^{13}C NMR spectra of **8c**



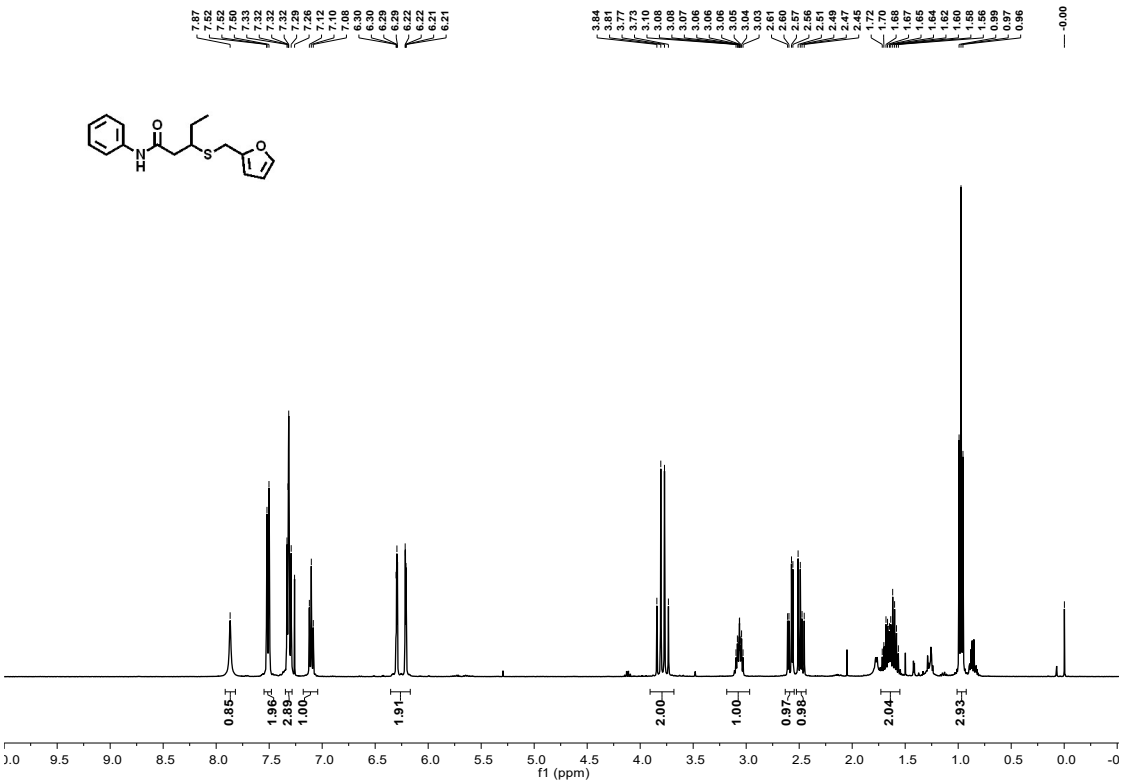
^{1}H NMR spectra of **8d**



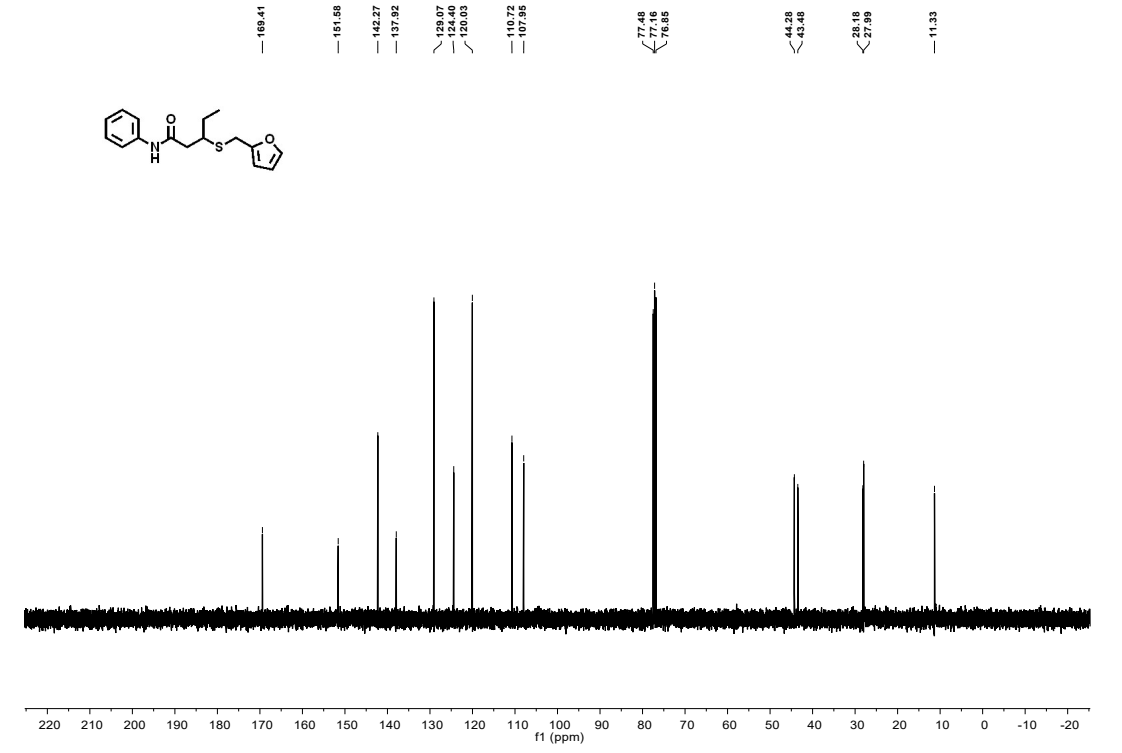
^{13}C NMR spectra of **8d**



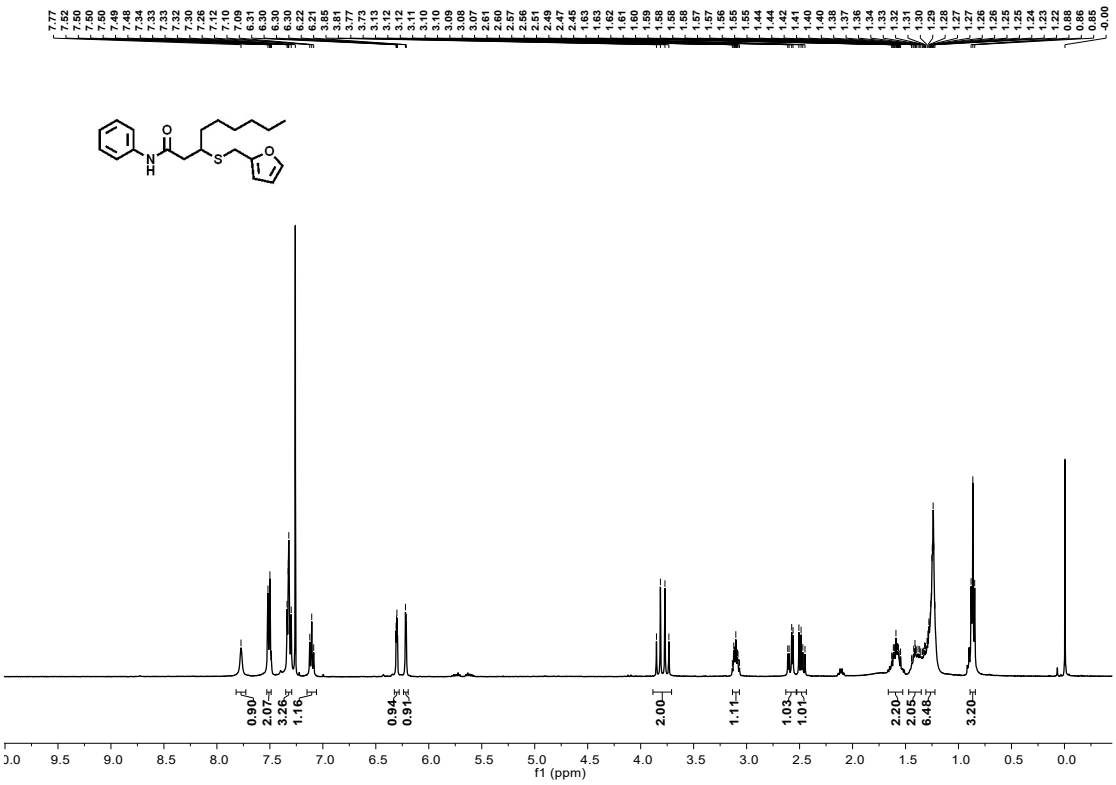
^{1}H NMR spectra of **8e**



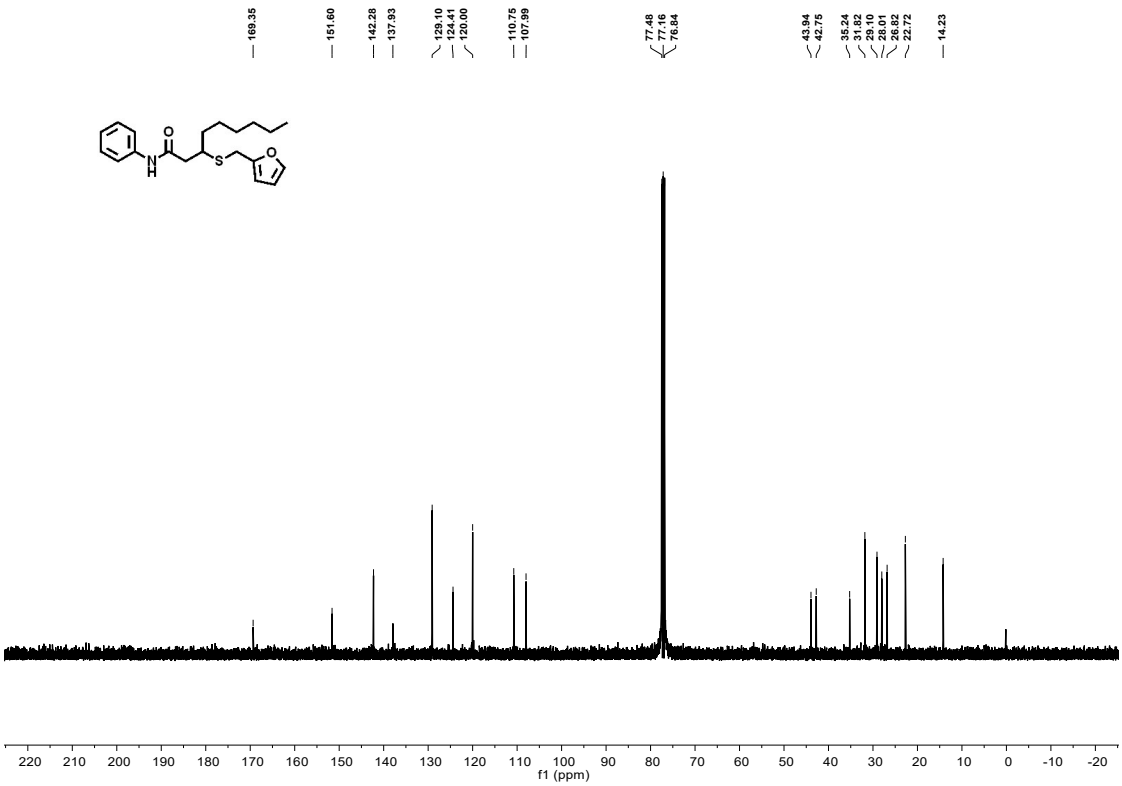
^{13}C NMR spectra of **8e**



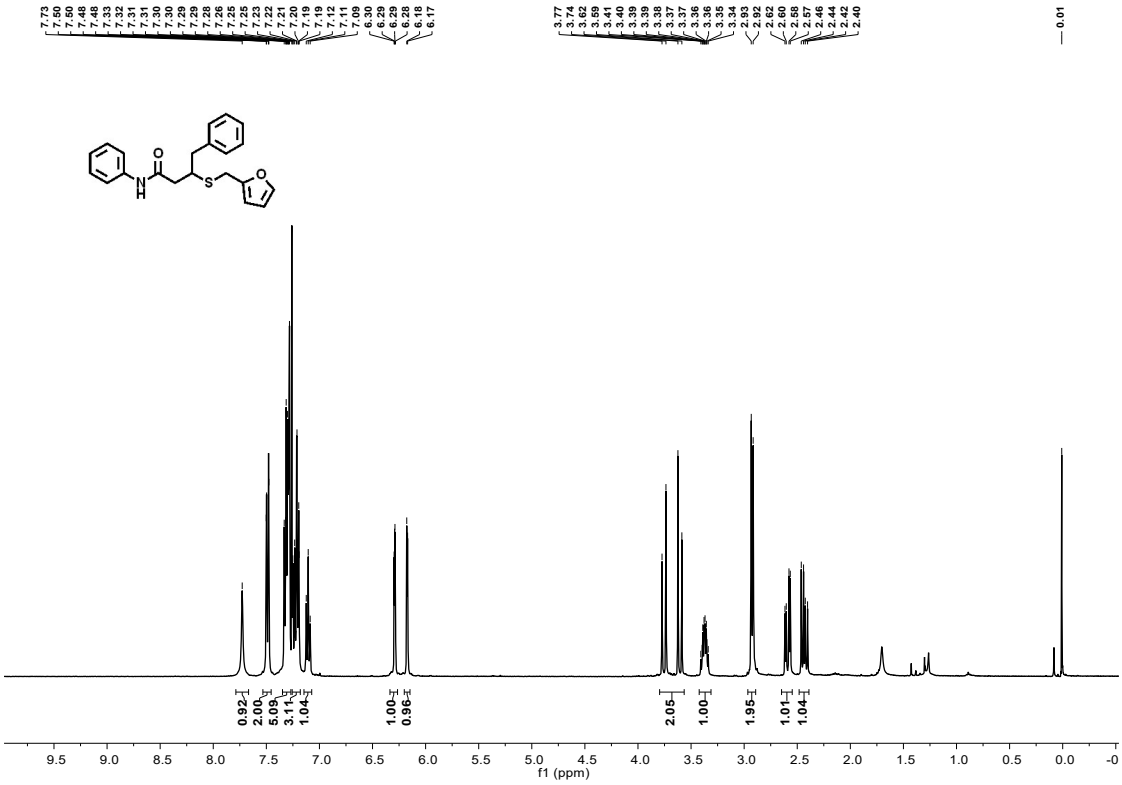
^{1}H NMR spectra of **8f**



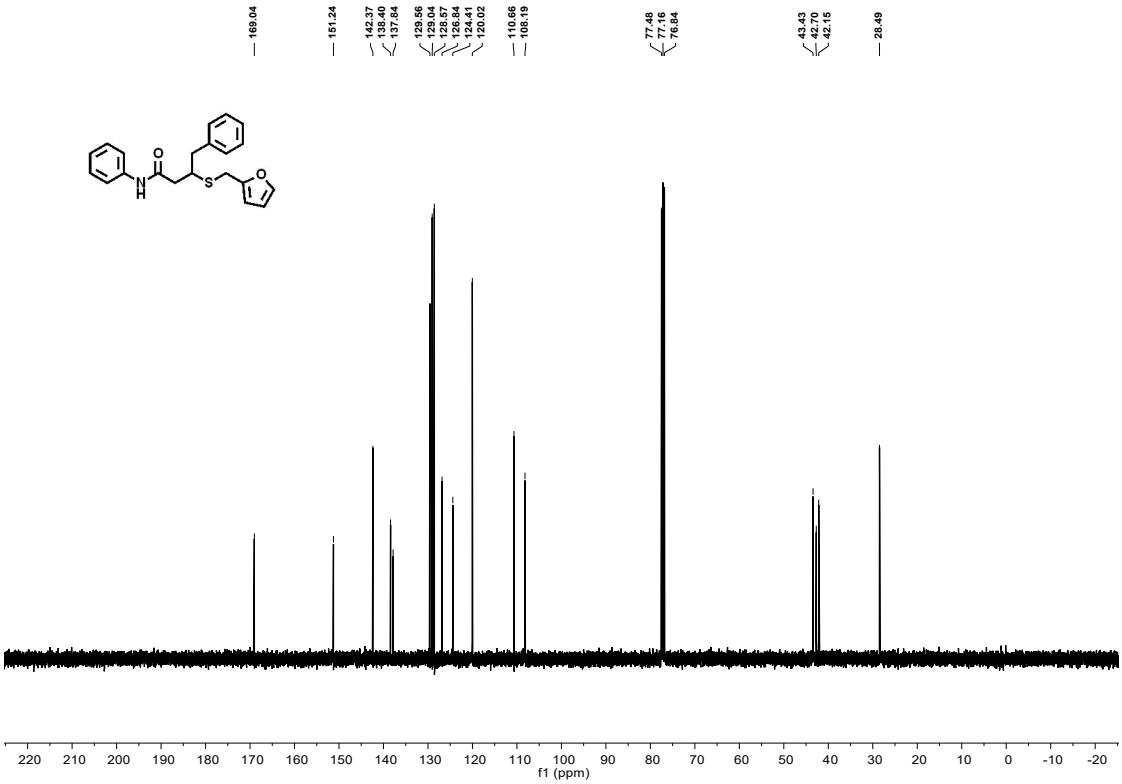
^{13}C NMR spectra of **8f**



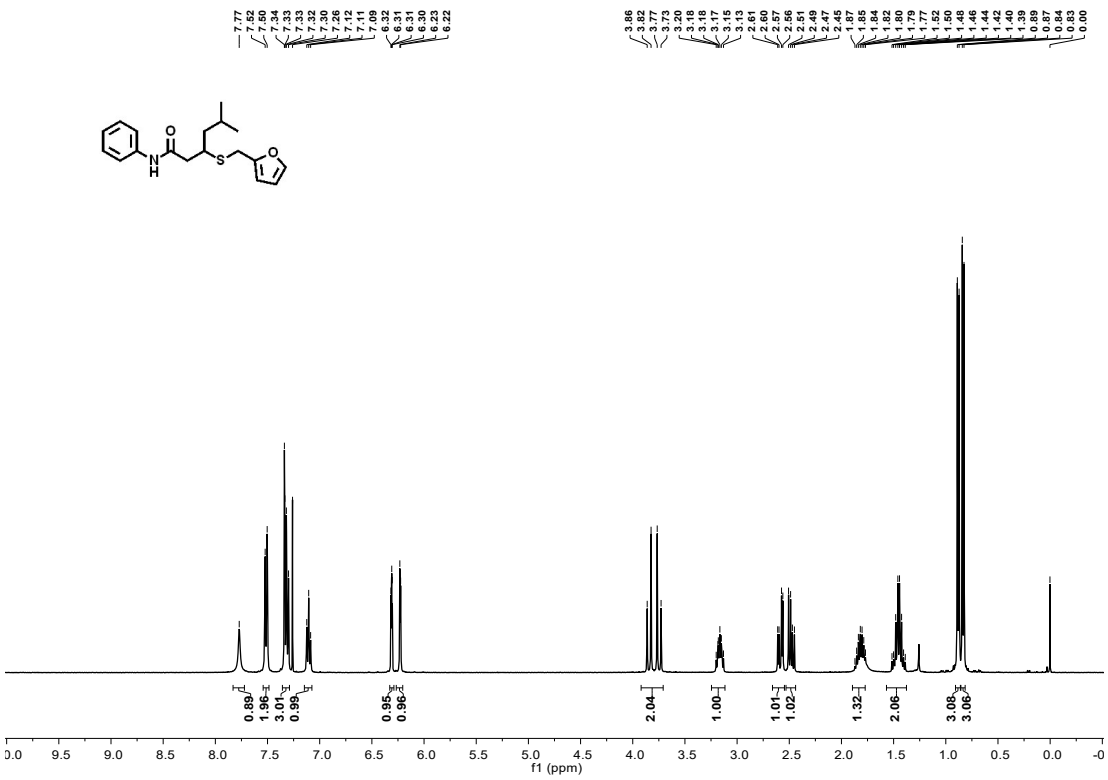
^{1}H NMR spectra of **8g**



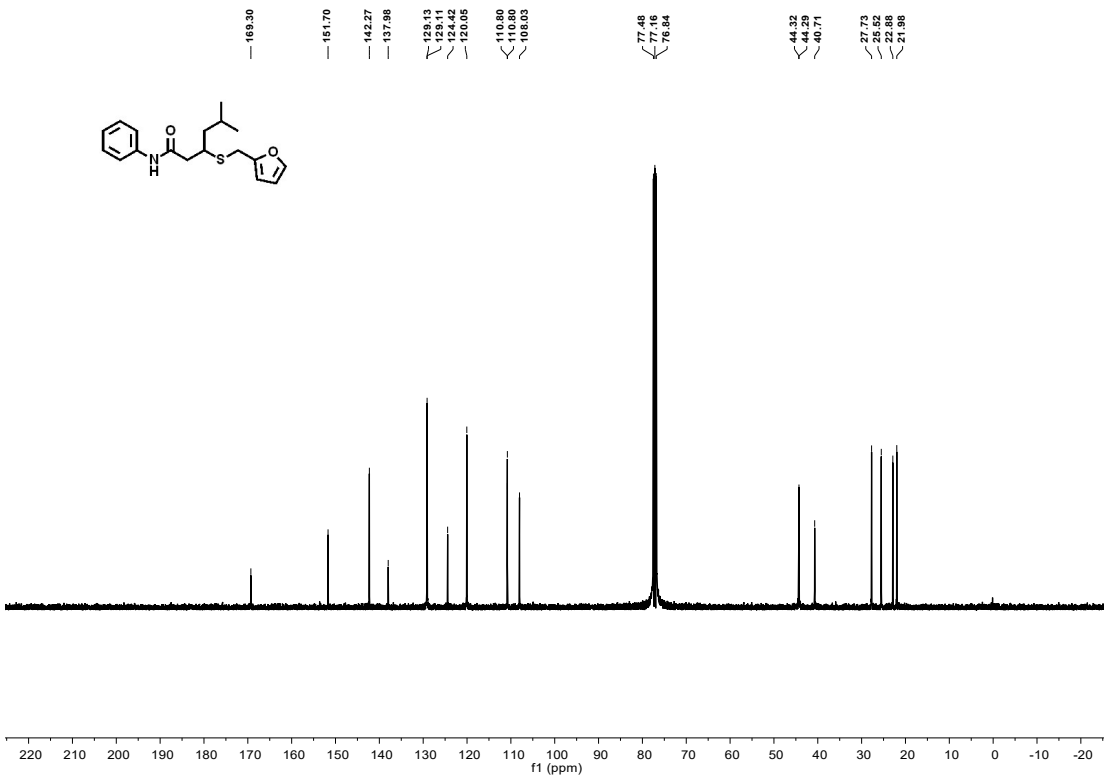
^{13}C NMR spectra of **8g**



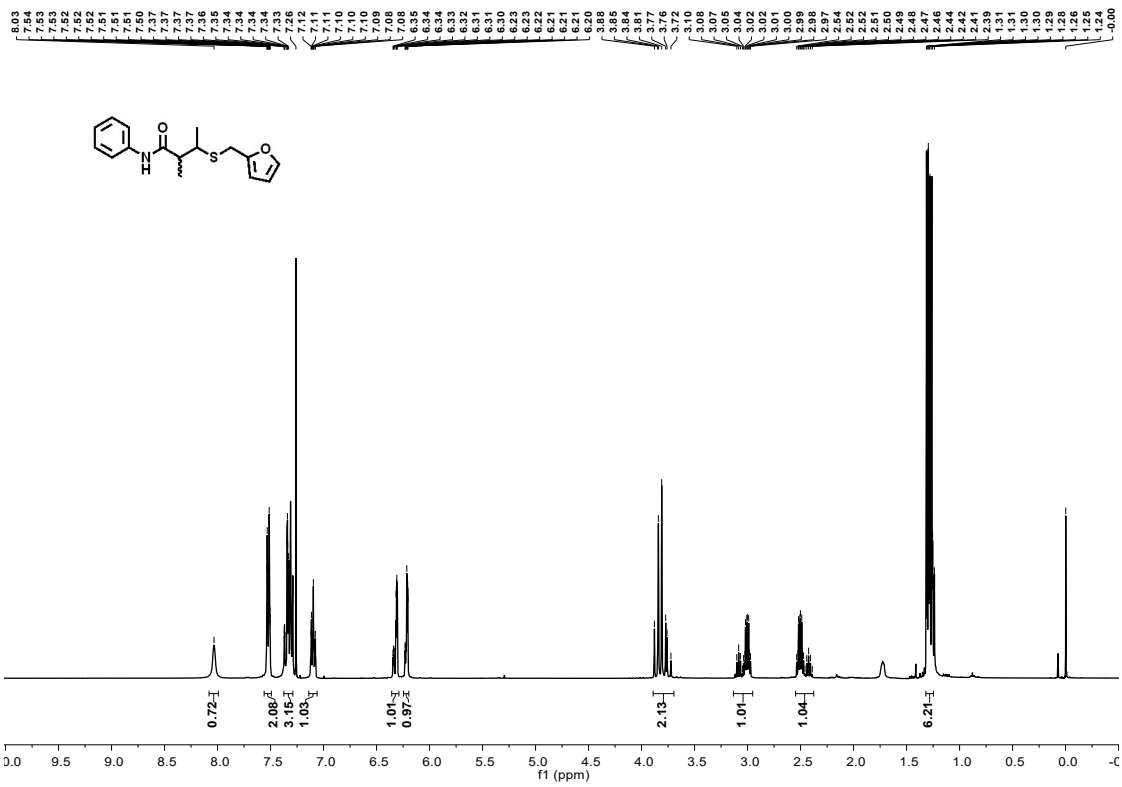
^{1}H NMR spectra of **8h**



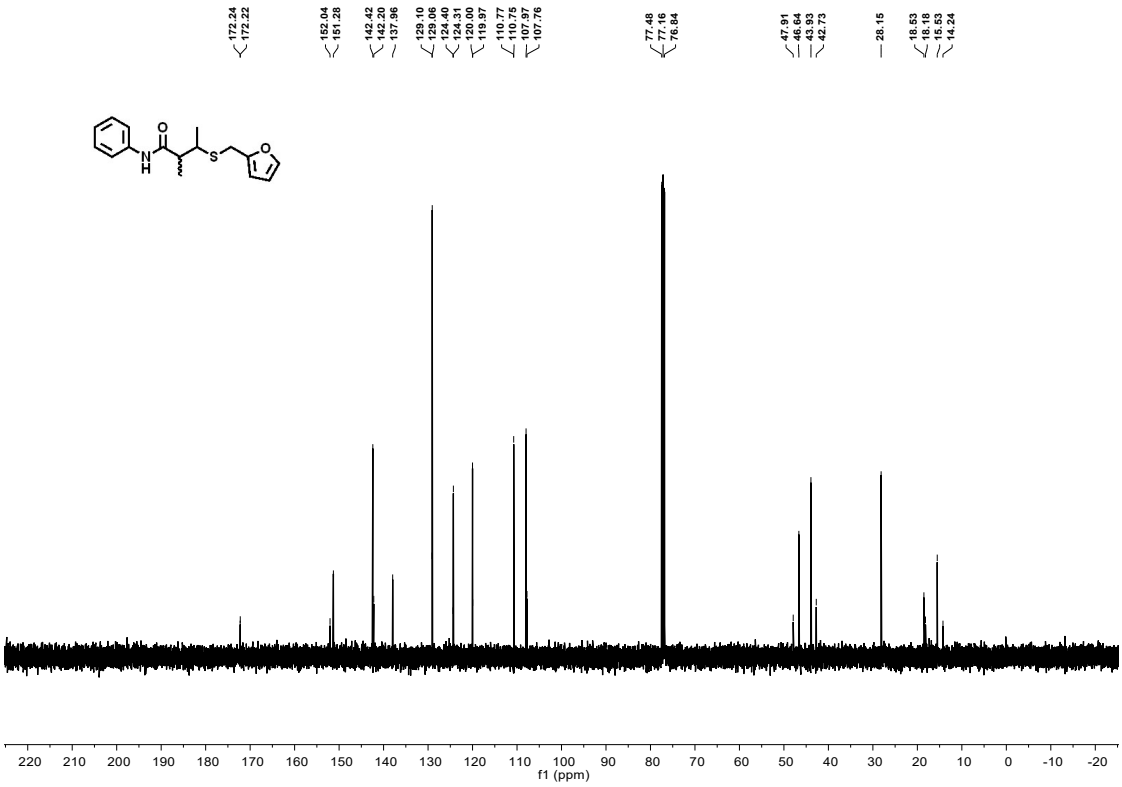
^{13}C NMR spectra of **8h**



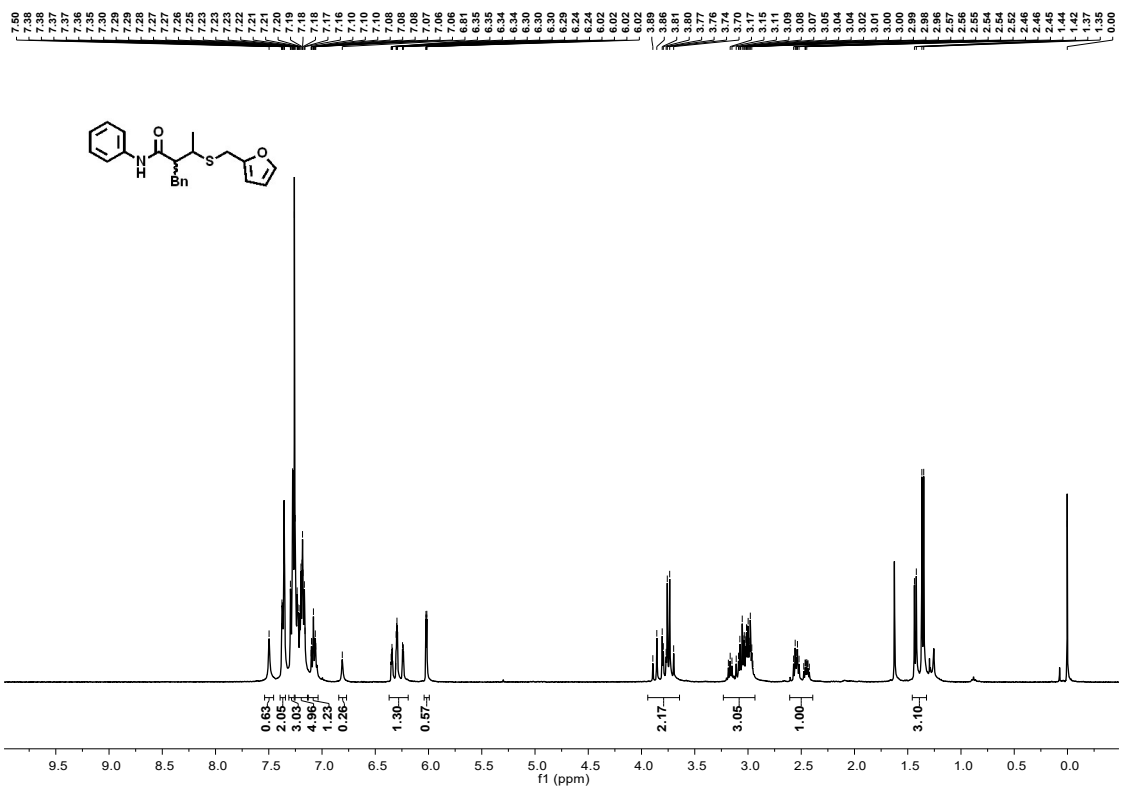
^{1}H NMR spectra of **8i**



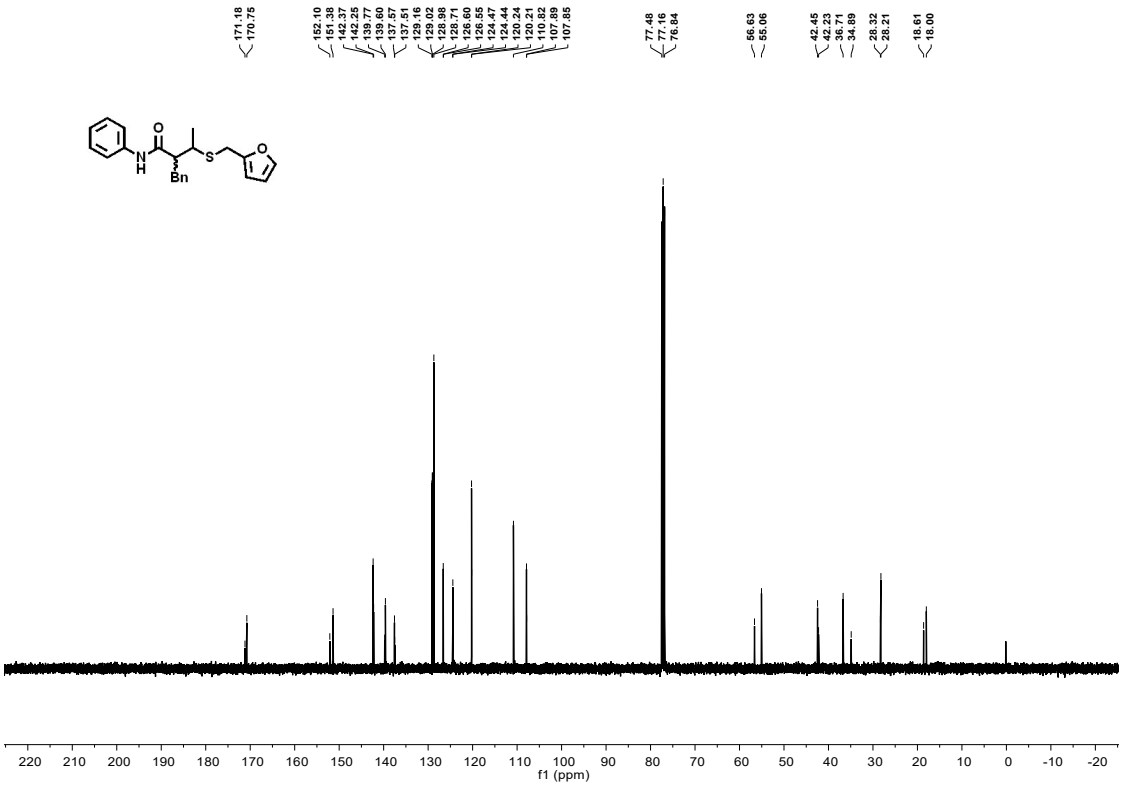
^{13}C NMR spectra of **8i**



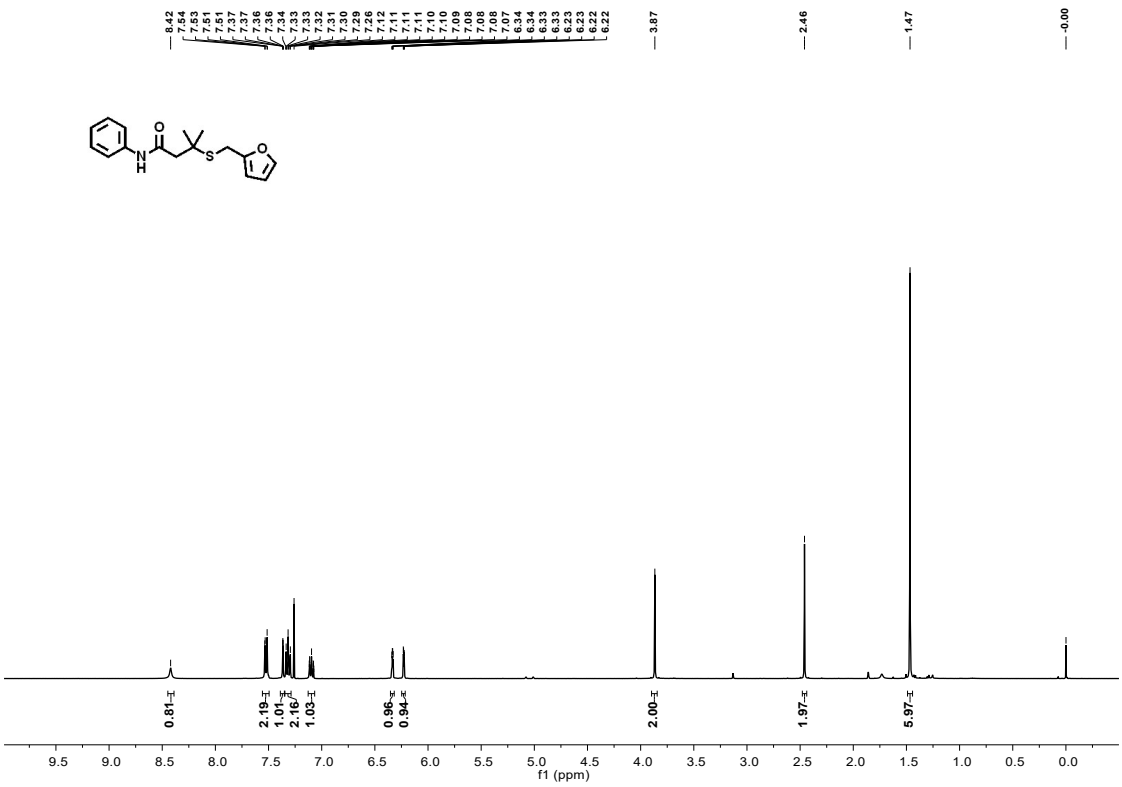
^{1}H NMR spectra of **8j**



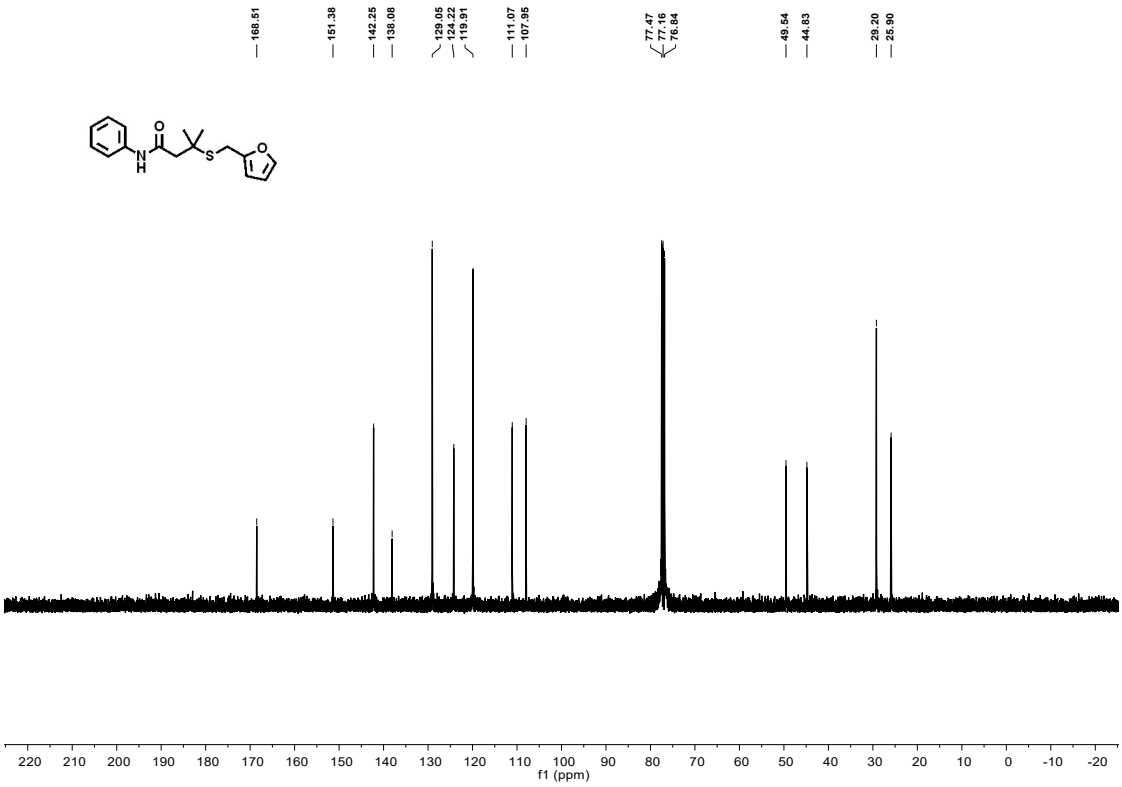
^{13}C NMR spectra of **8j**



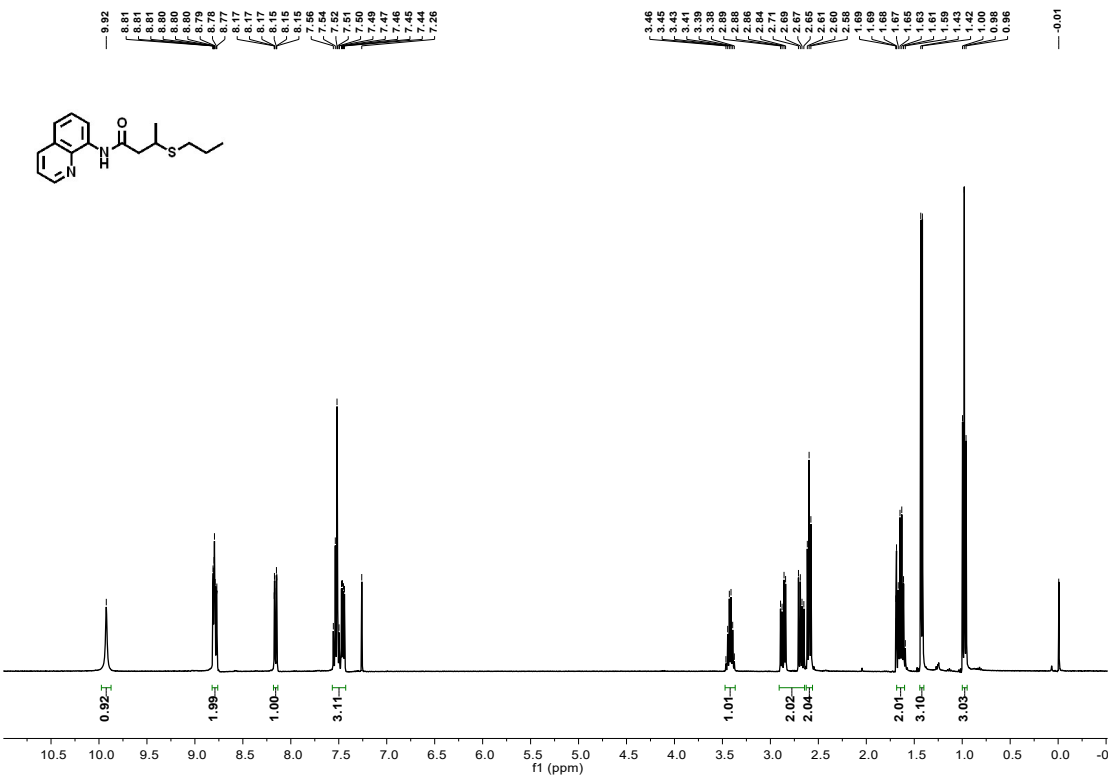
^{1}H NMR spectra of **8k**



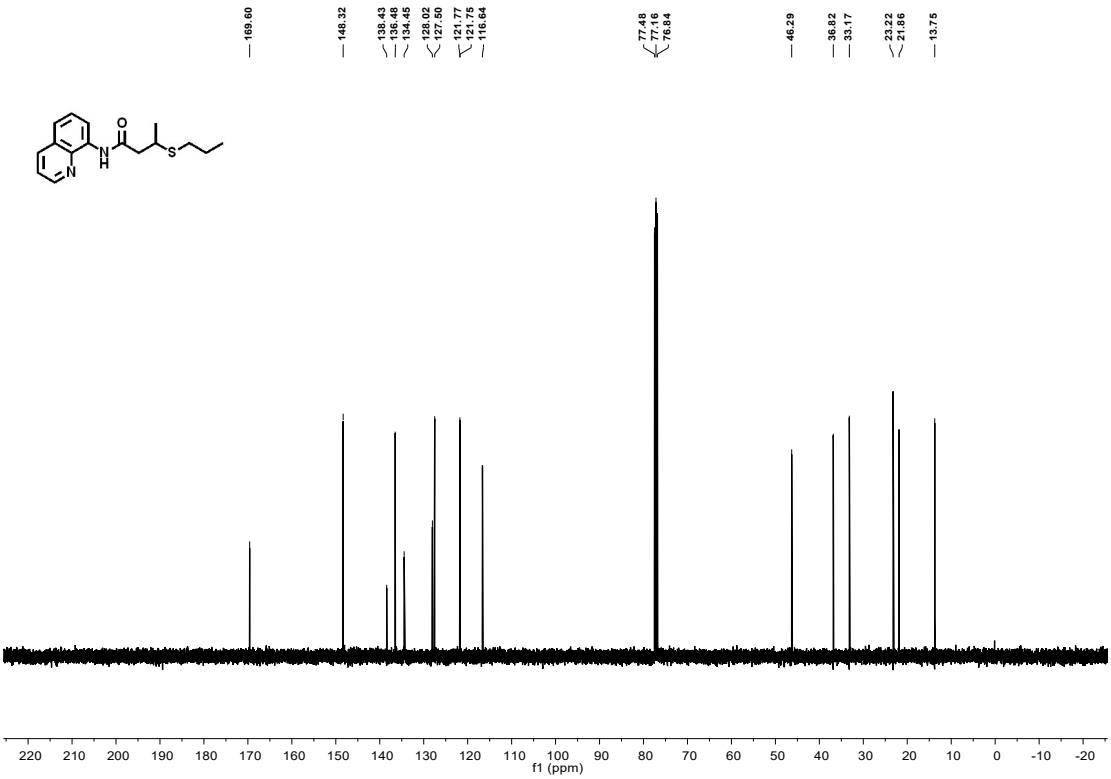
^{13}C NMR spectra of **8k**



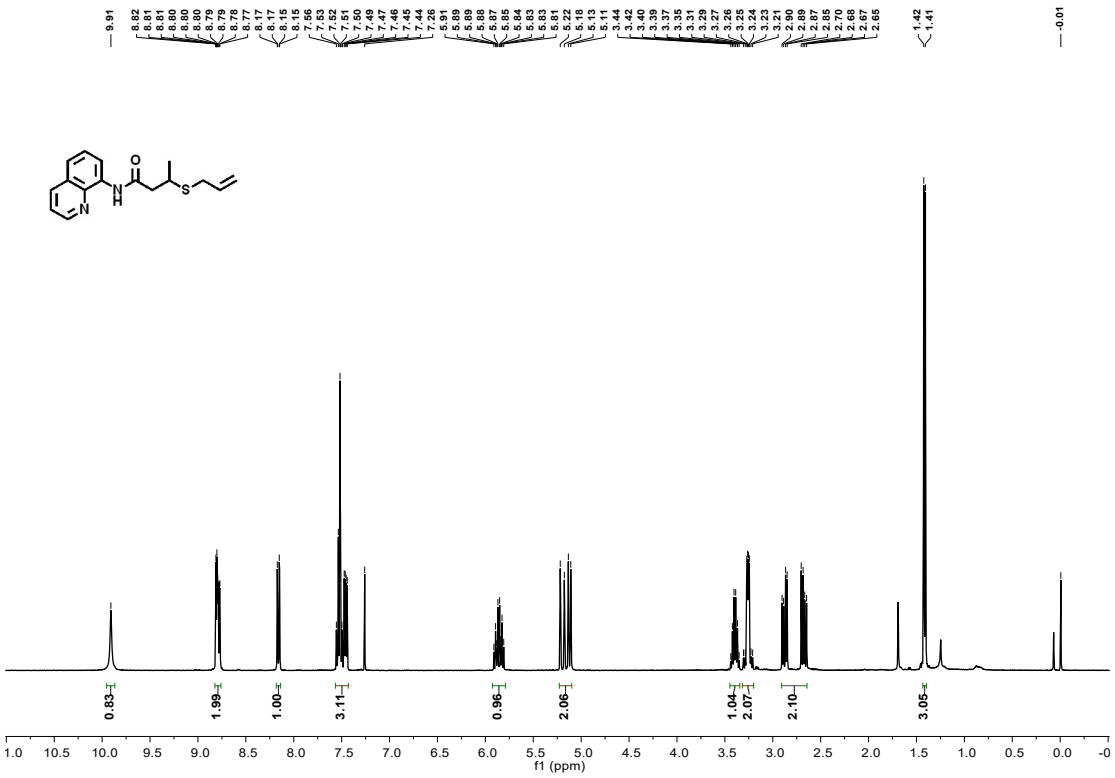
^{1}H NMR spectra of **8l**



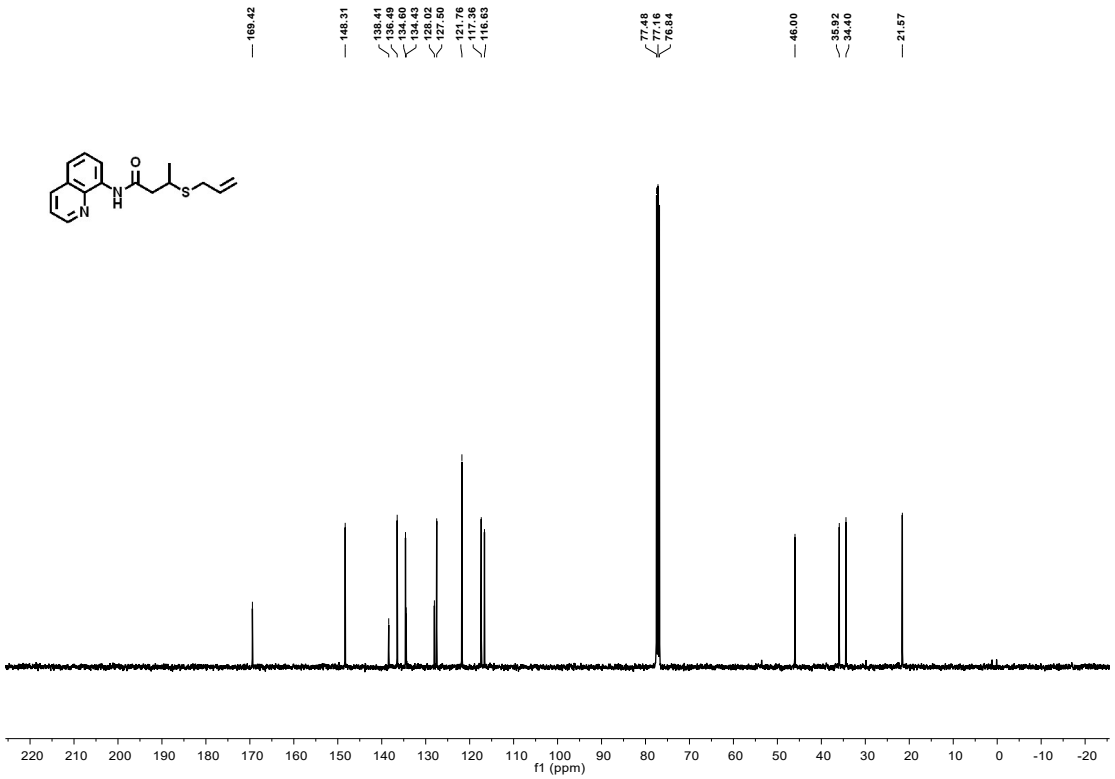
^{13}C NMR spectra of **8l**



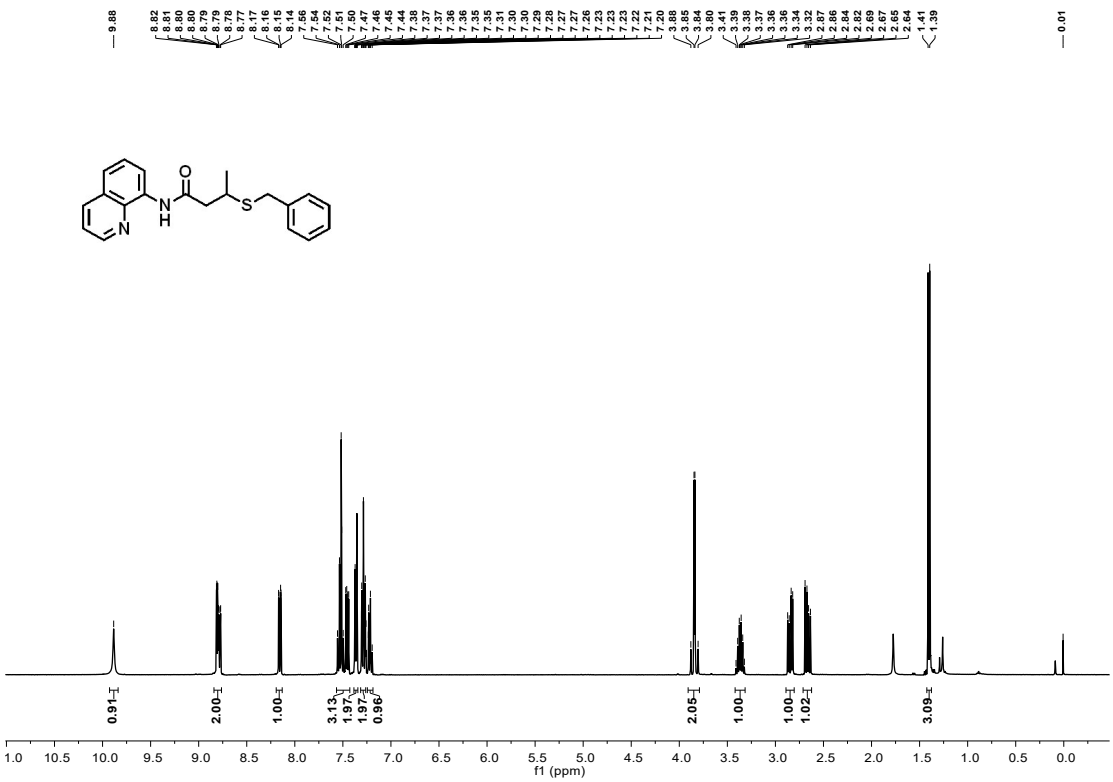
^{1}H NMR spectra of **8m**



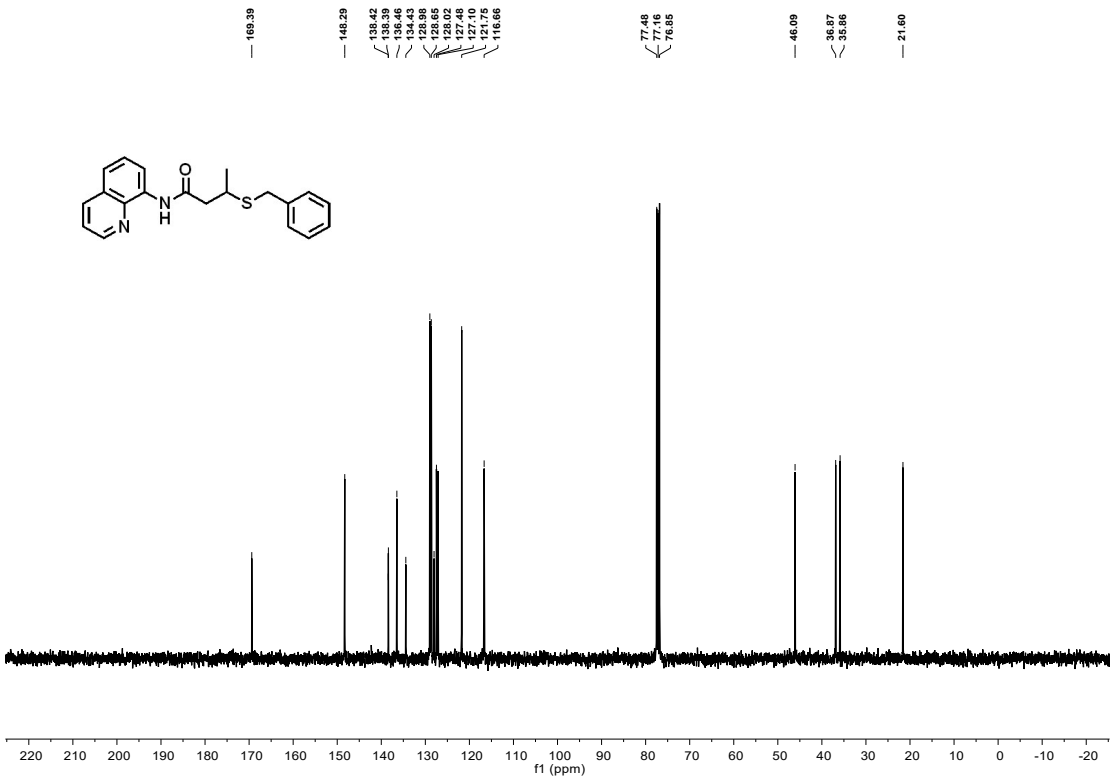
^{13}C NMR spectra of **8m**



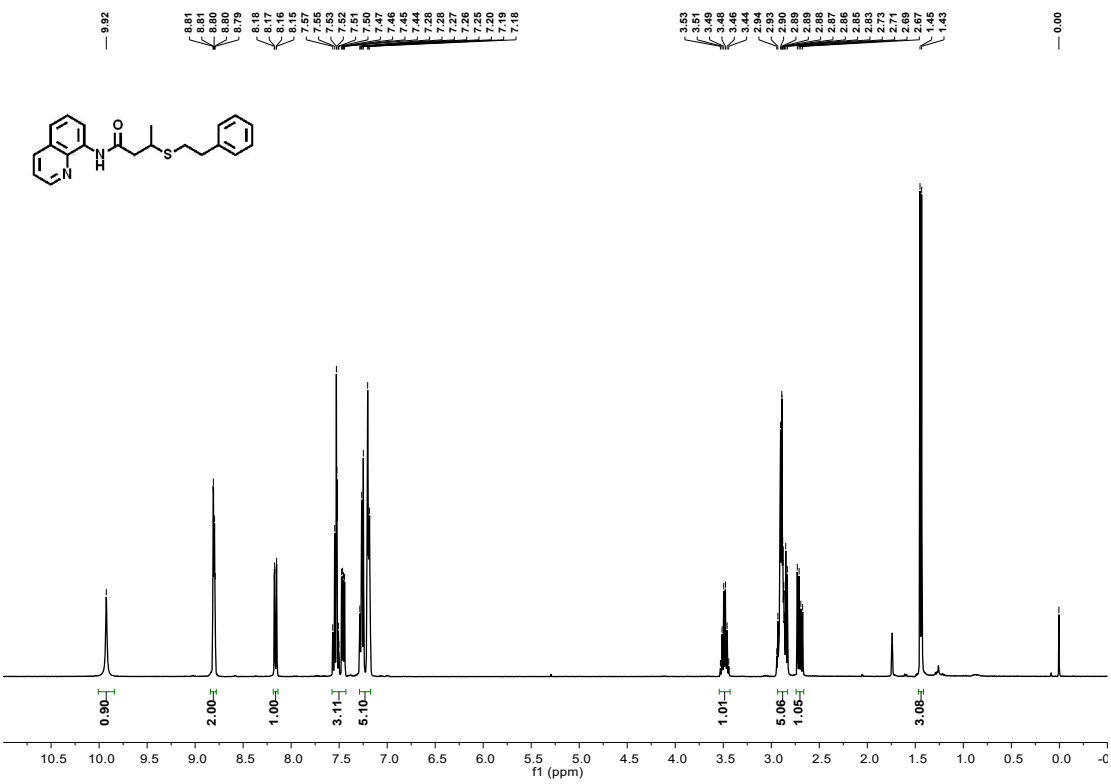
^{1}H NMR spectra of **8n**



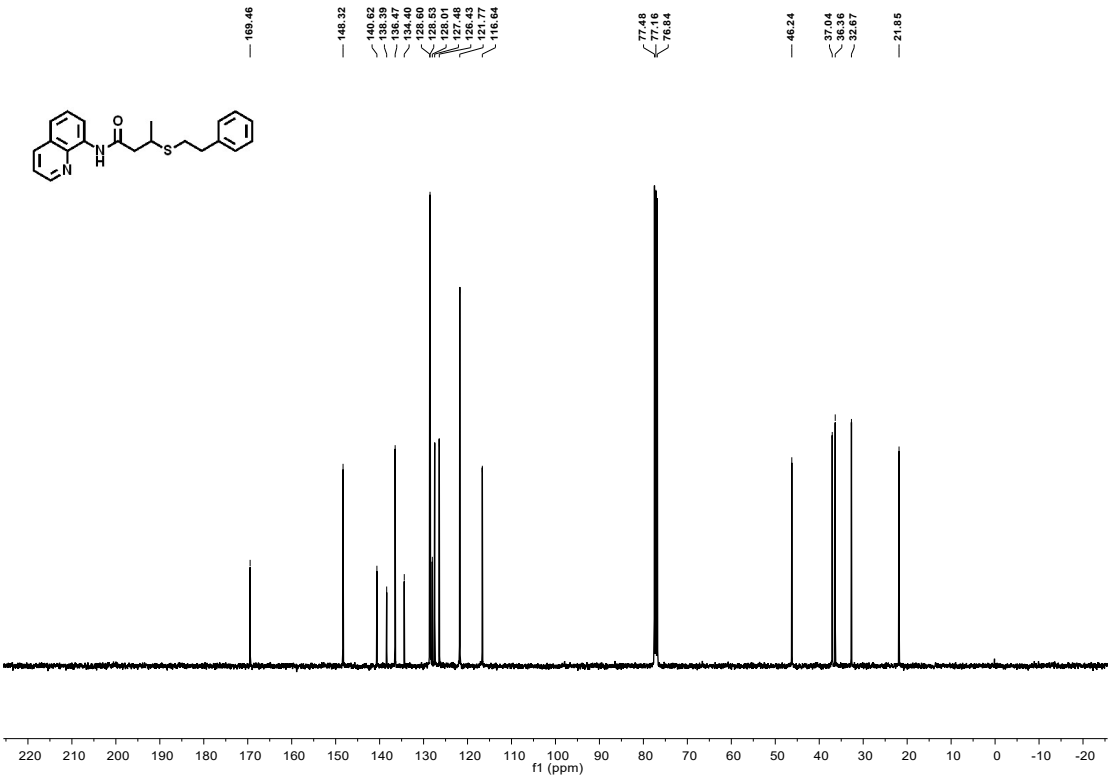
^{13}C NMR spectra of **8n**



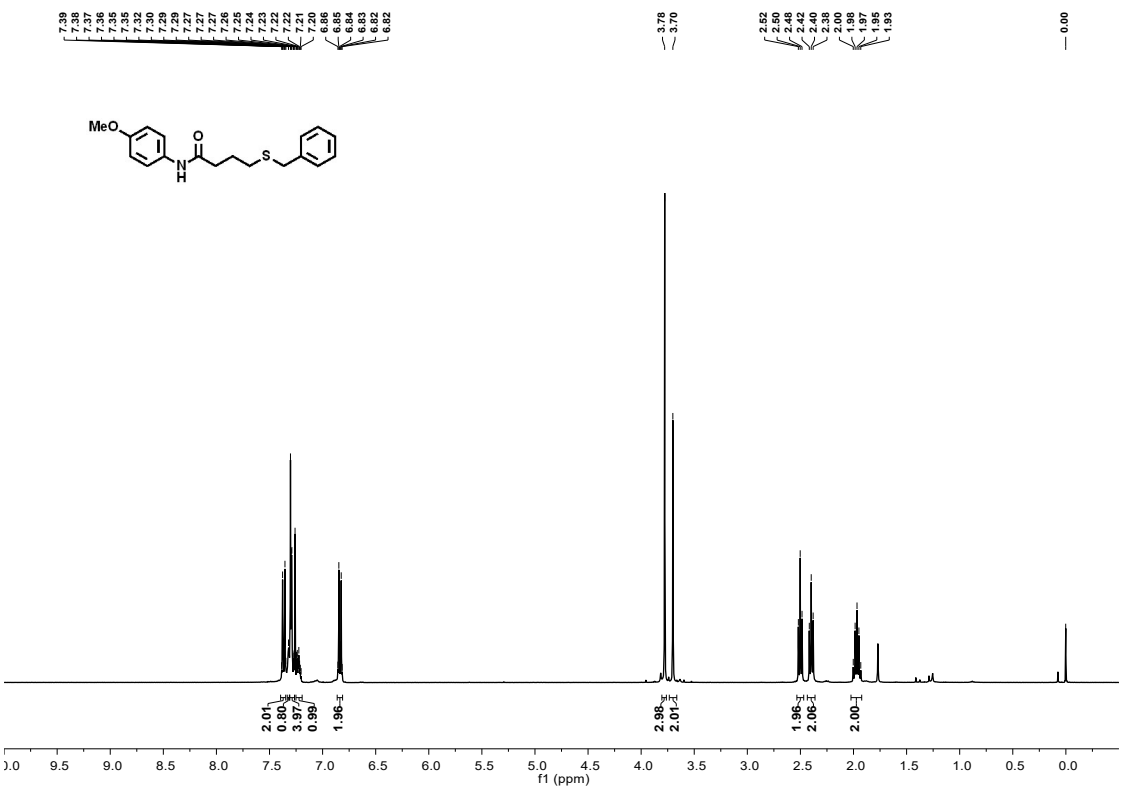
^{1}H NMR spectra of **8o**



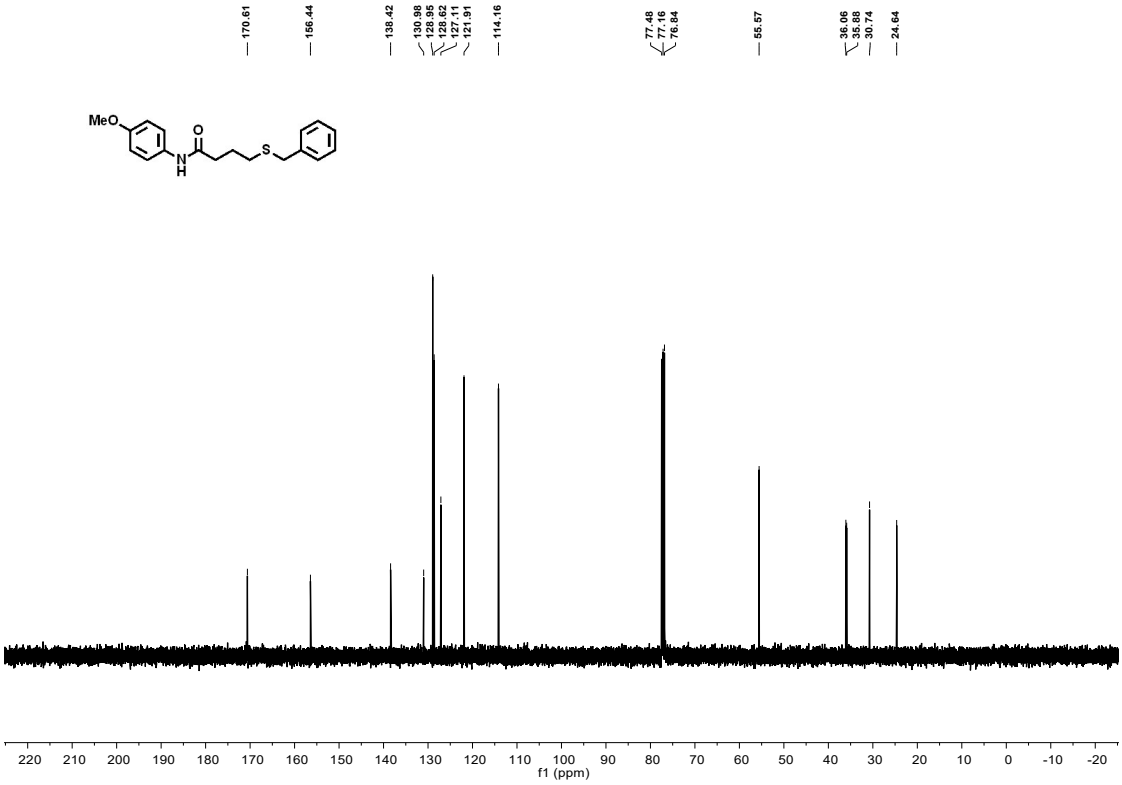
^{13}C NMR spectra of **8o**



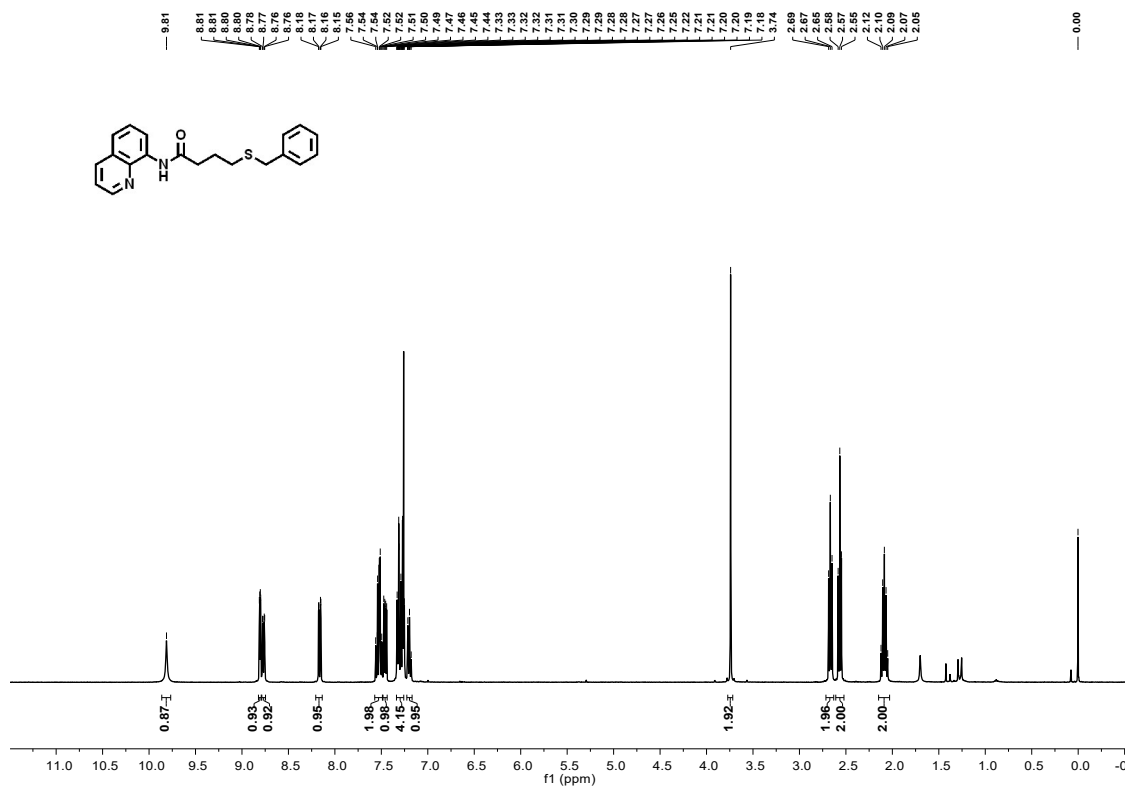
^{1}H NMR spectra of **9a**



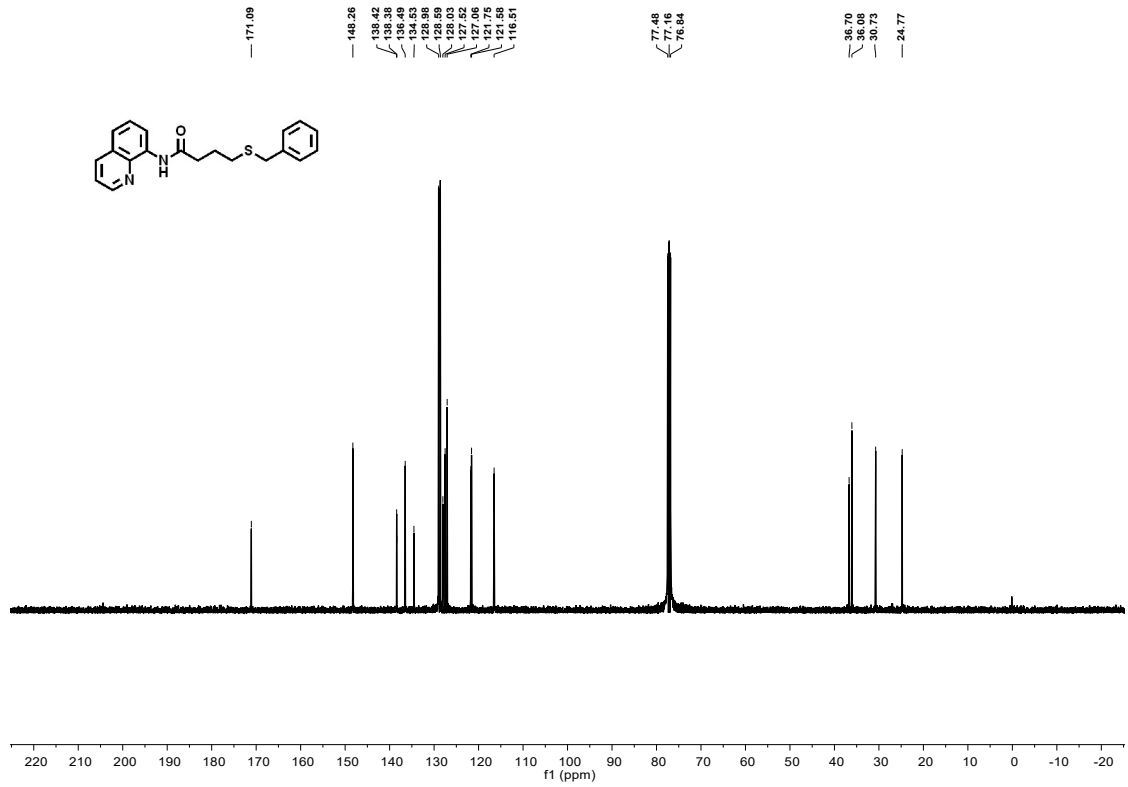
^{13}C NMR spectra of **9a**



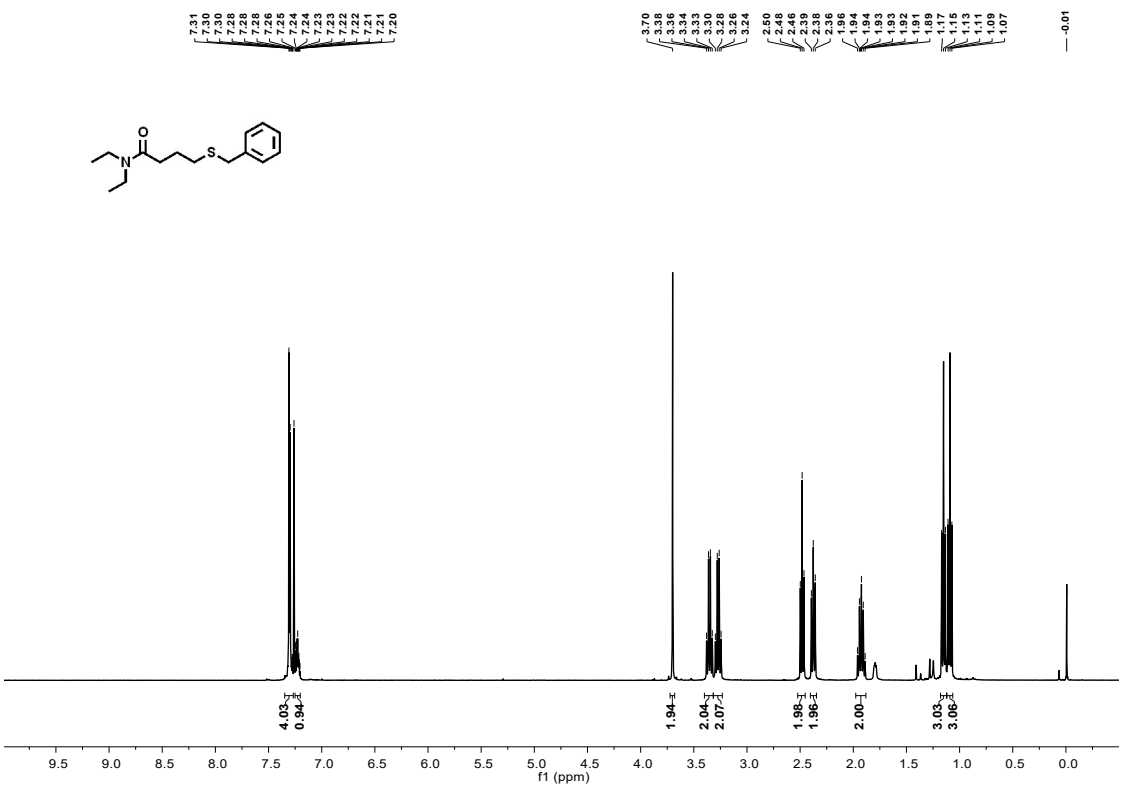
^{1}H NMR spectra of **9b**



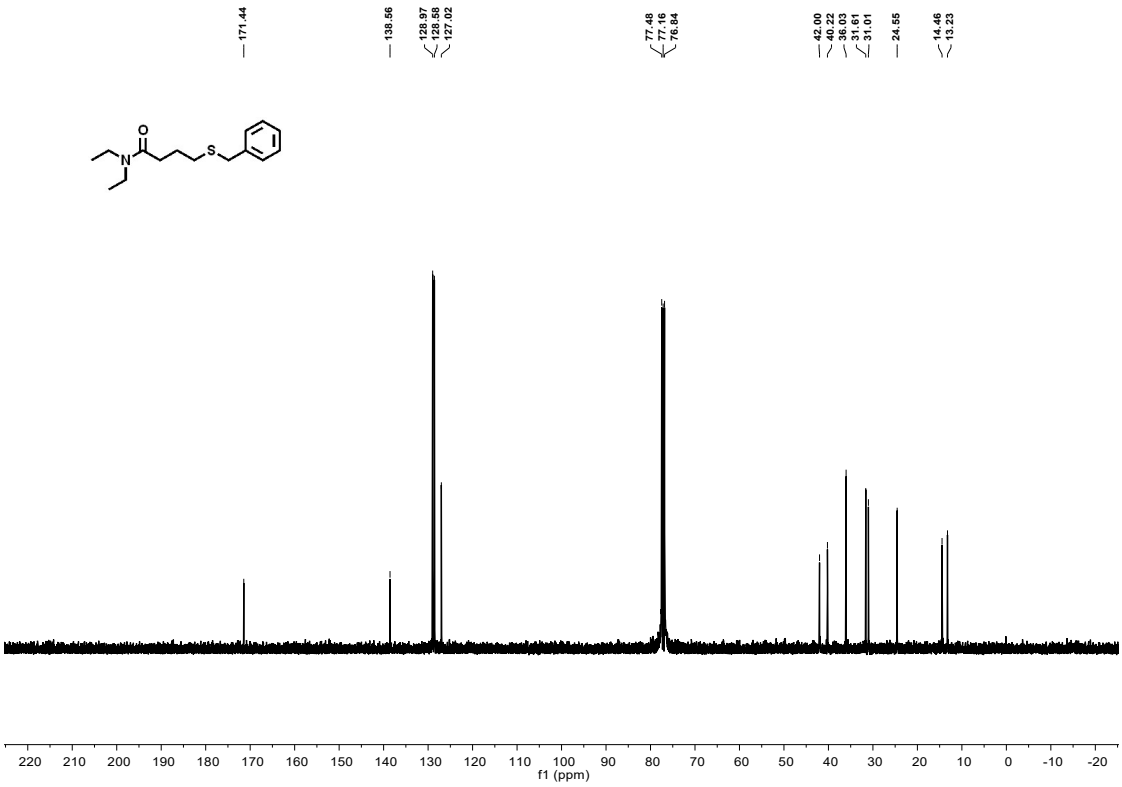
^{13}C NMR spectra of **9b**



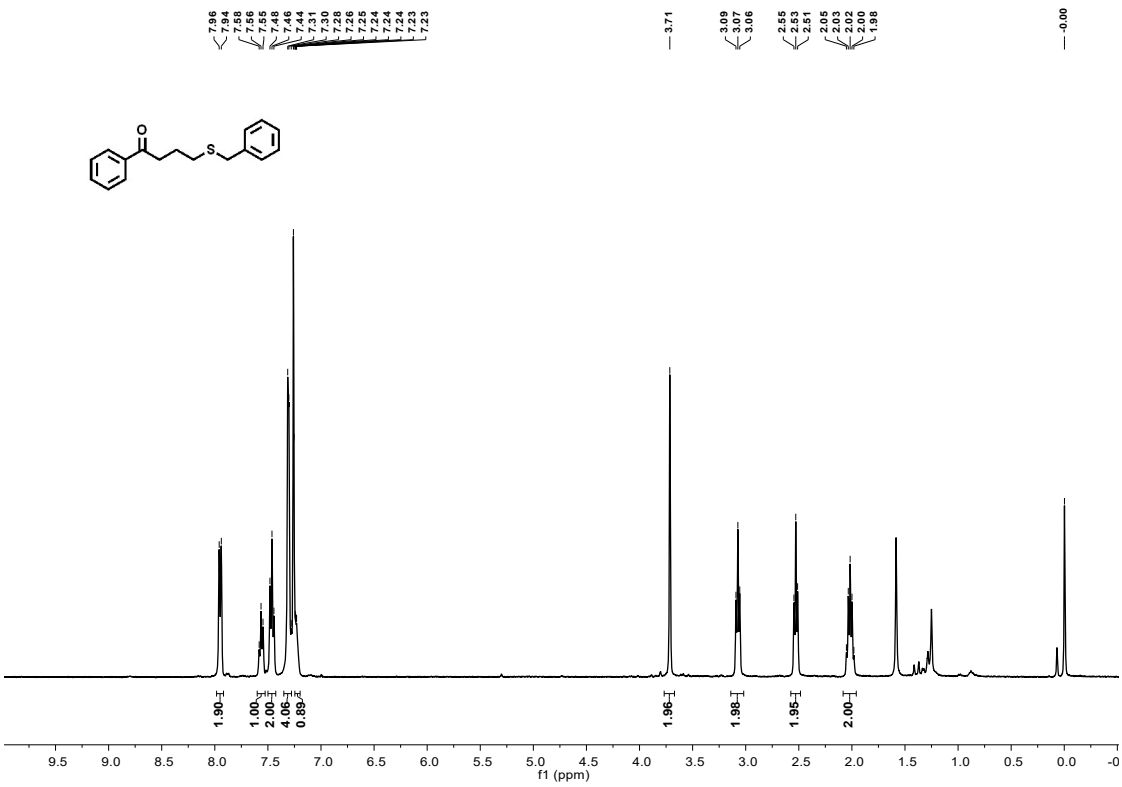
^{1}H NMR spectra of **9c**



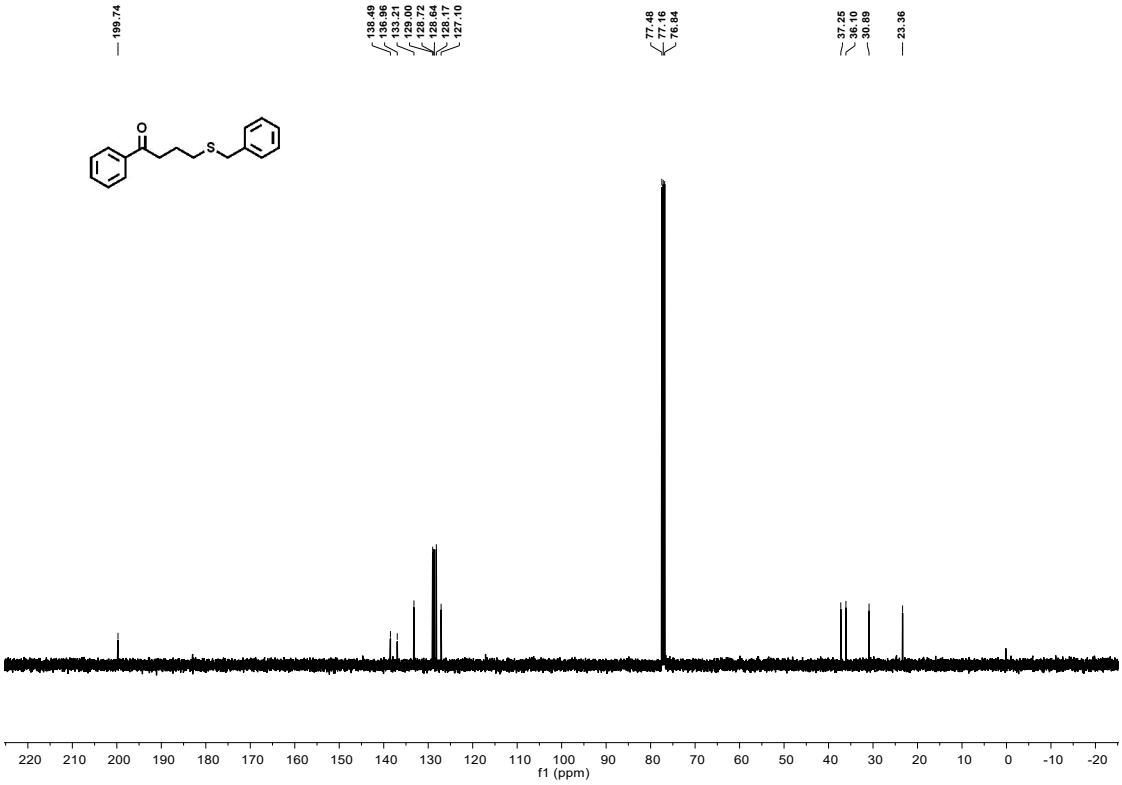
^{13}C NMR spectra of **9c**



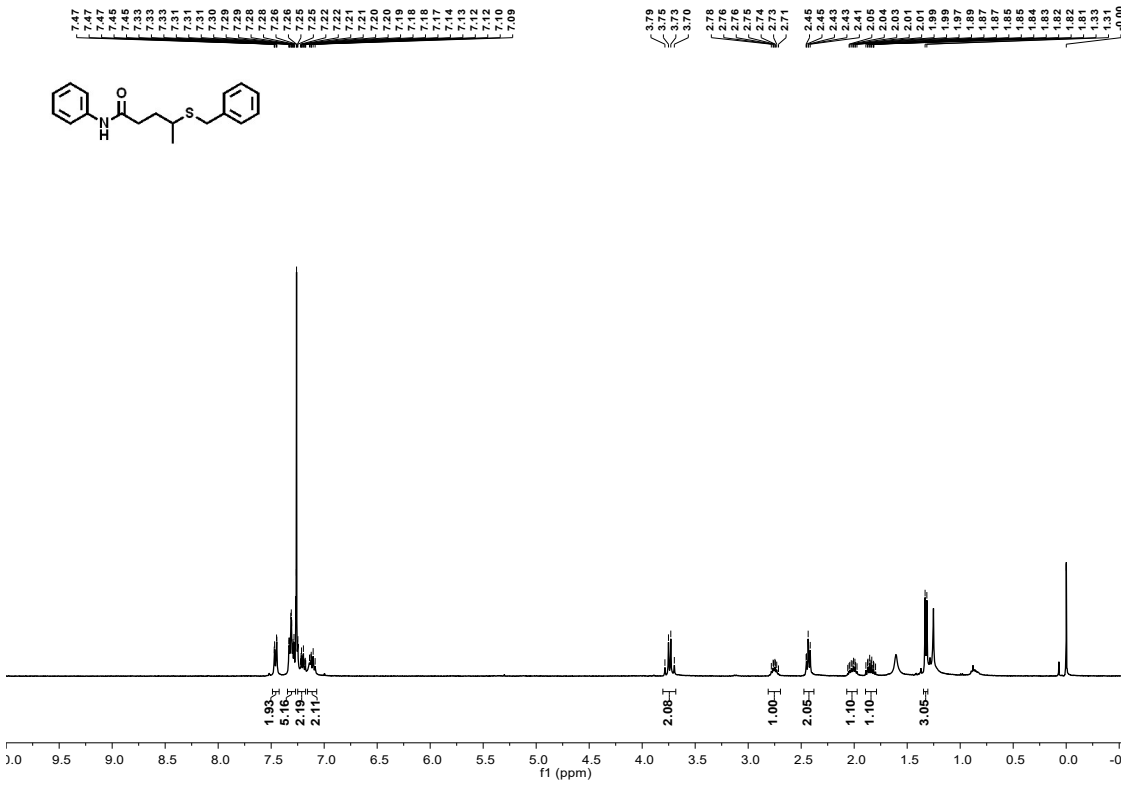
^{1}H NMR spectra of **9d**



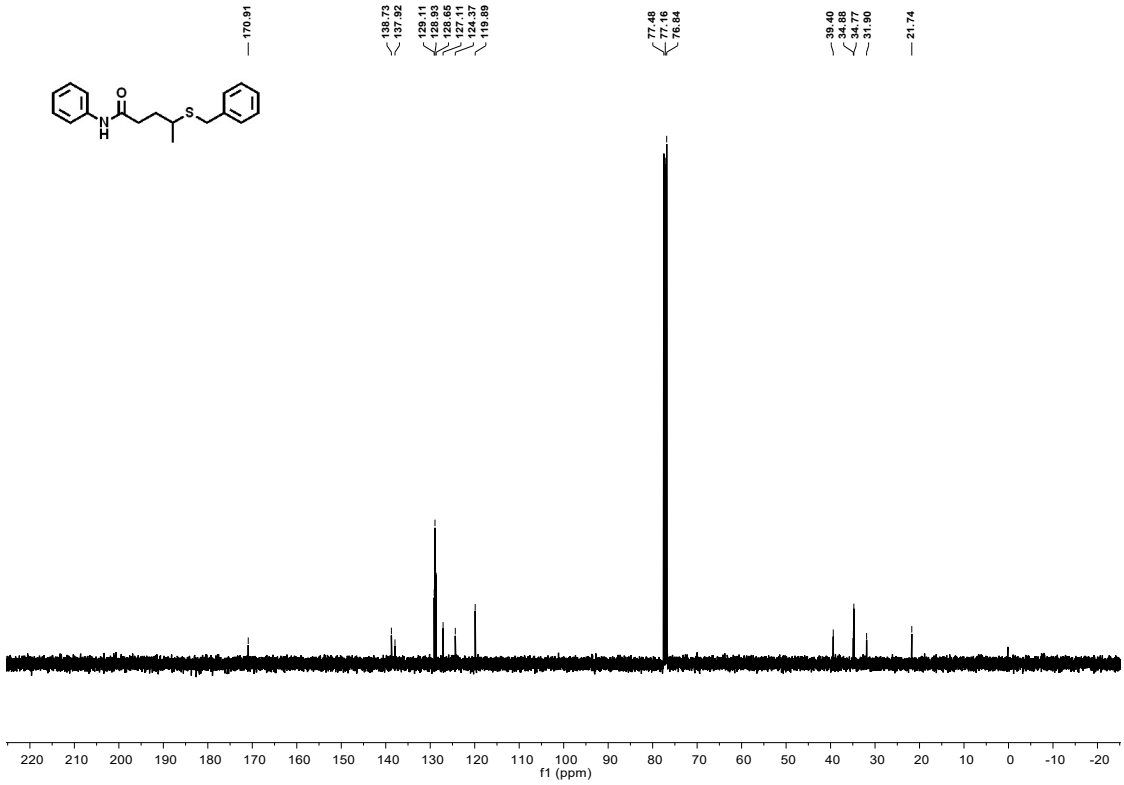
^{13}C NMR spectra of **9d**



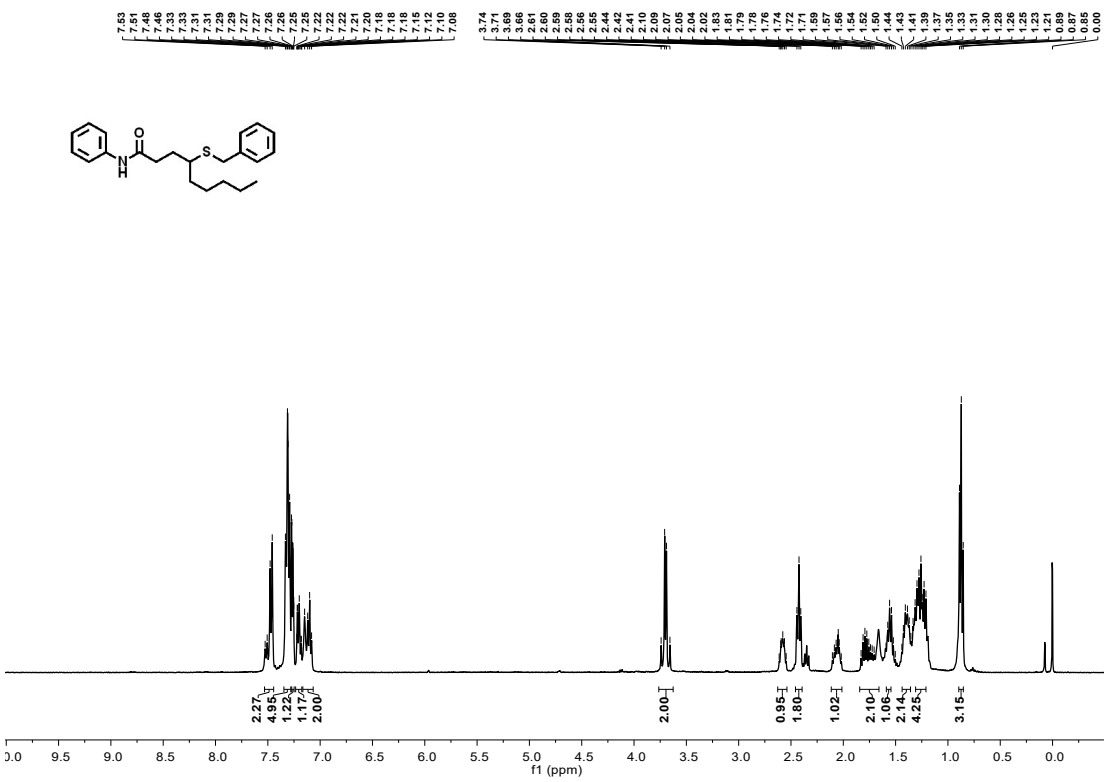
^{1}H NMR spectra of **9e**



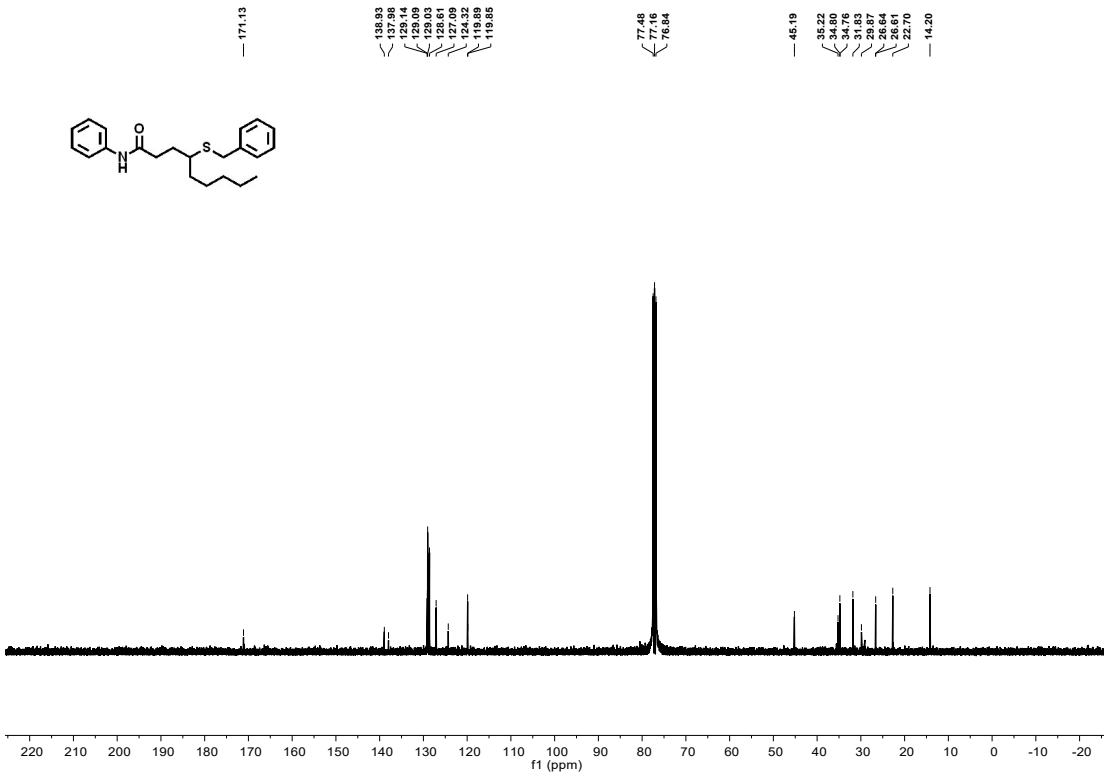
^{13}C NMR spectra of **9e**



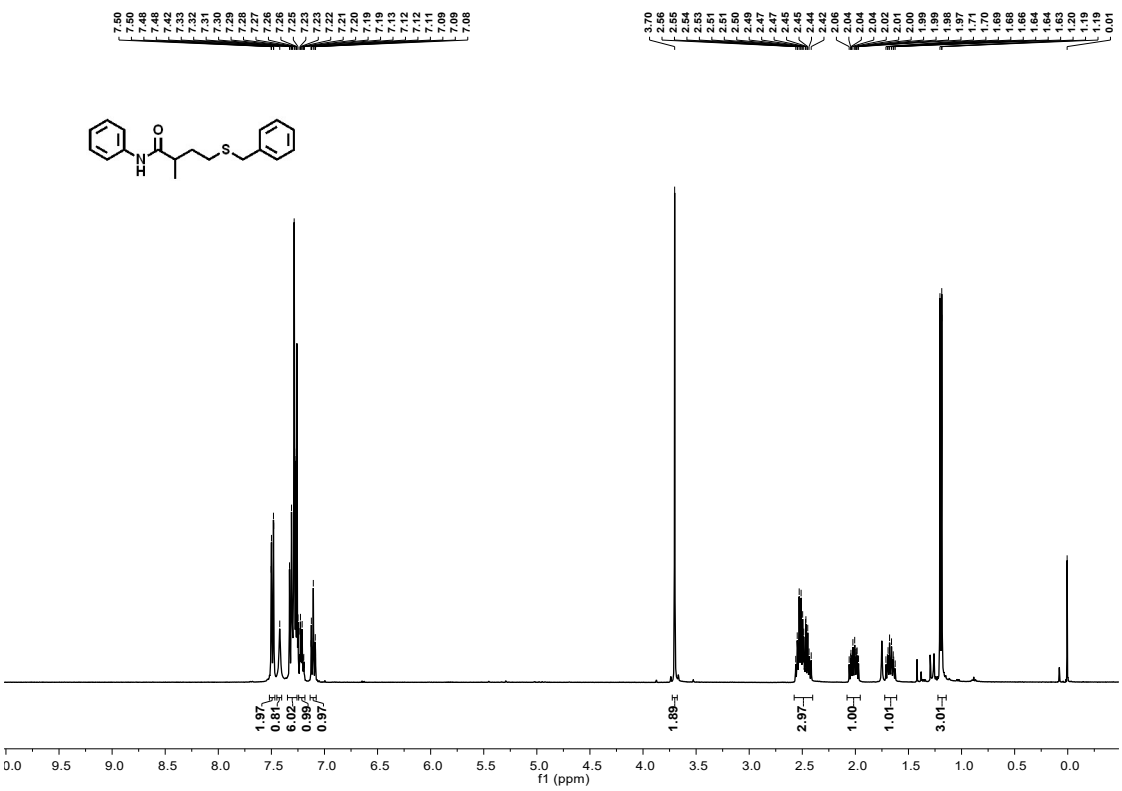
^{1}H NMR spectra of **9f**



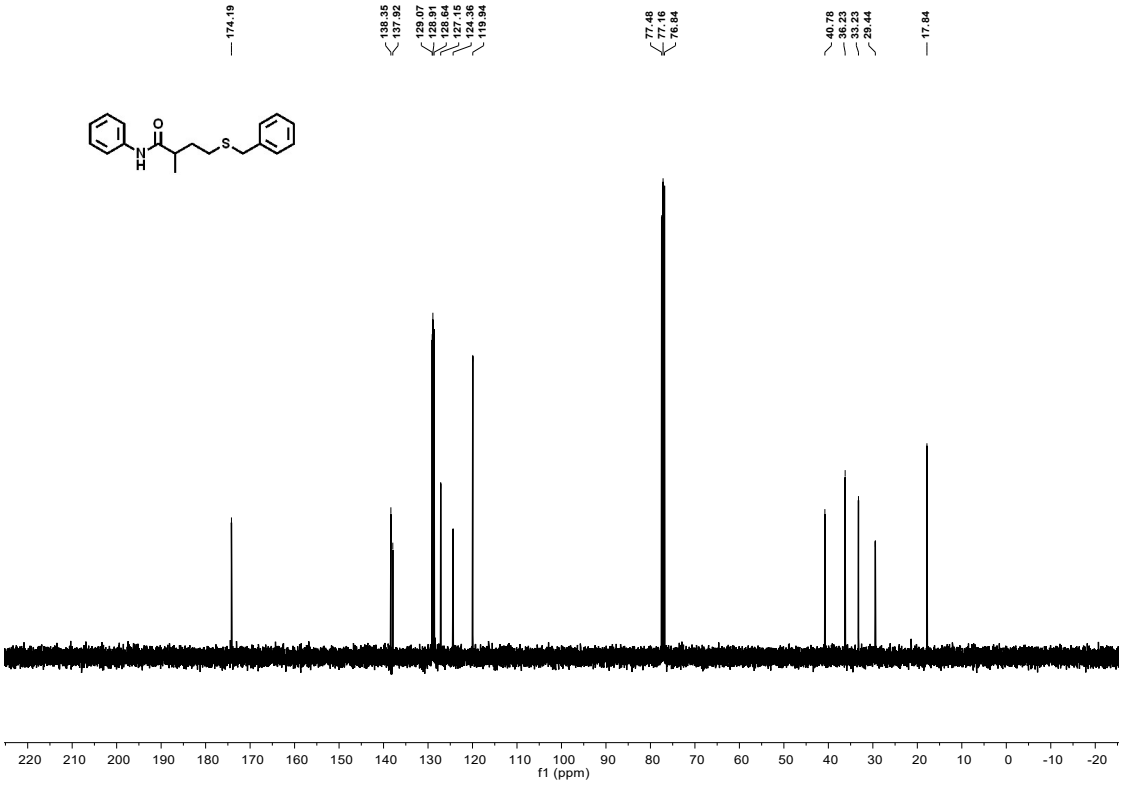
^{13}C NMR spectra of **9f**



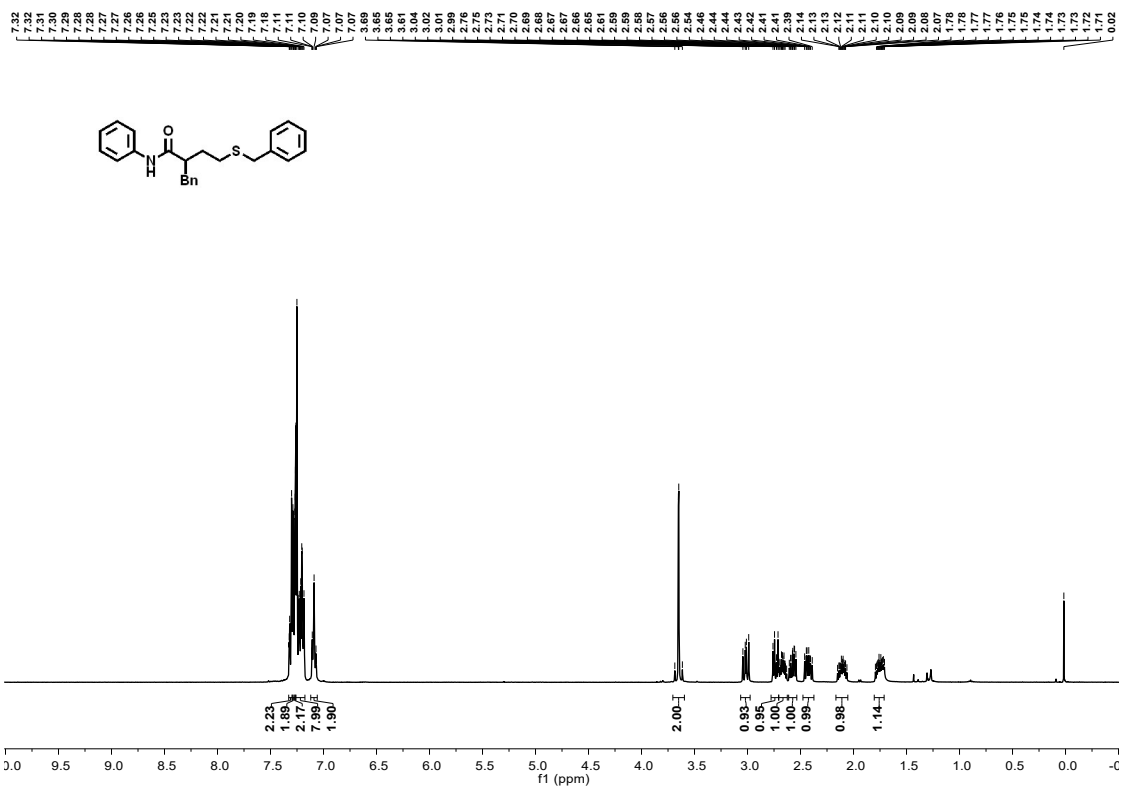
^{1}H NMR spectra of **9g**



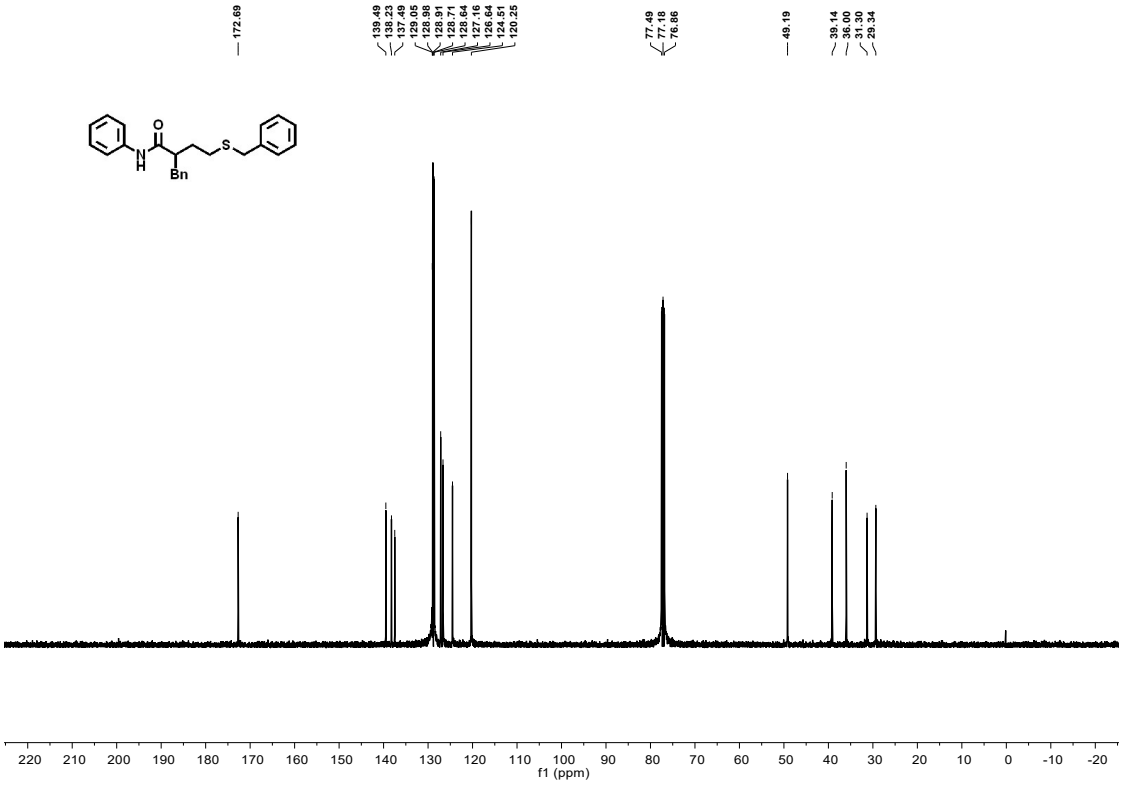
^{13}C NMR spectra of **9g**



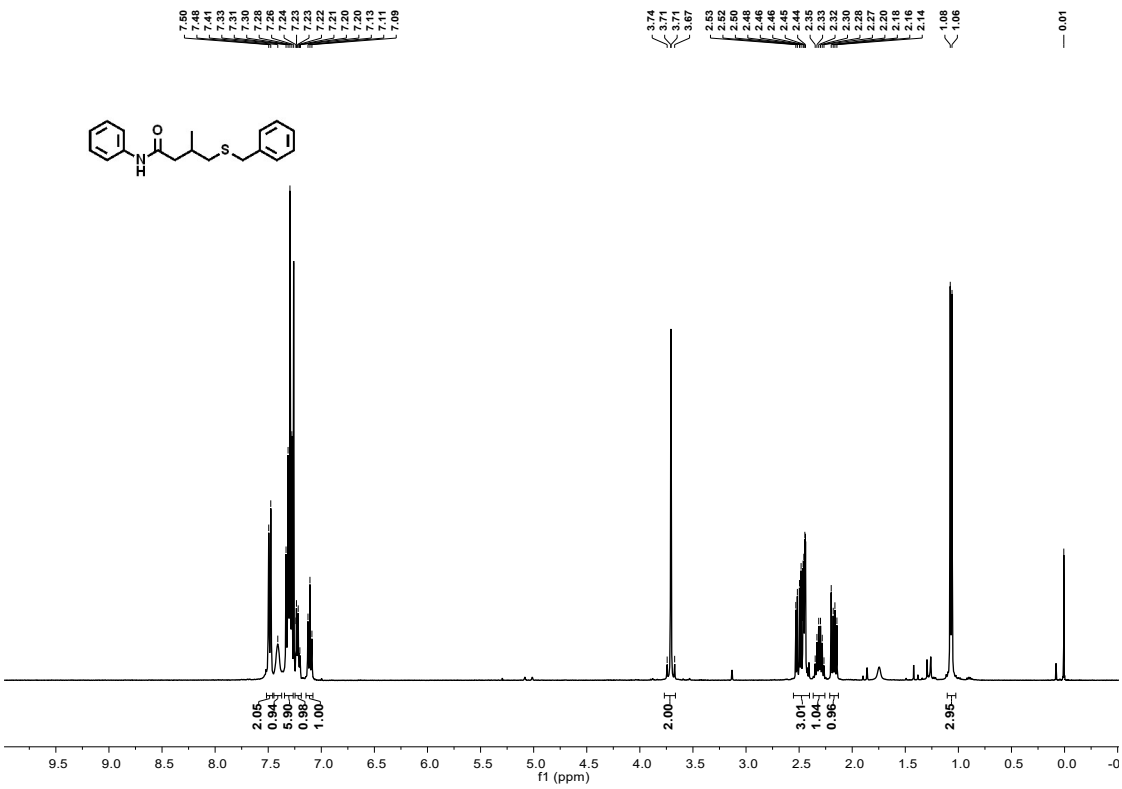
^{1}H NMR spectra of **9h**



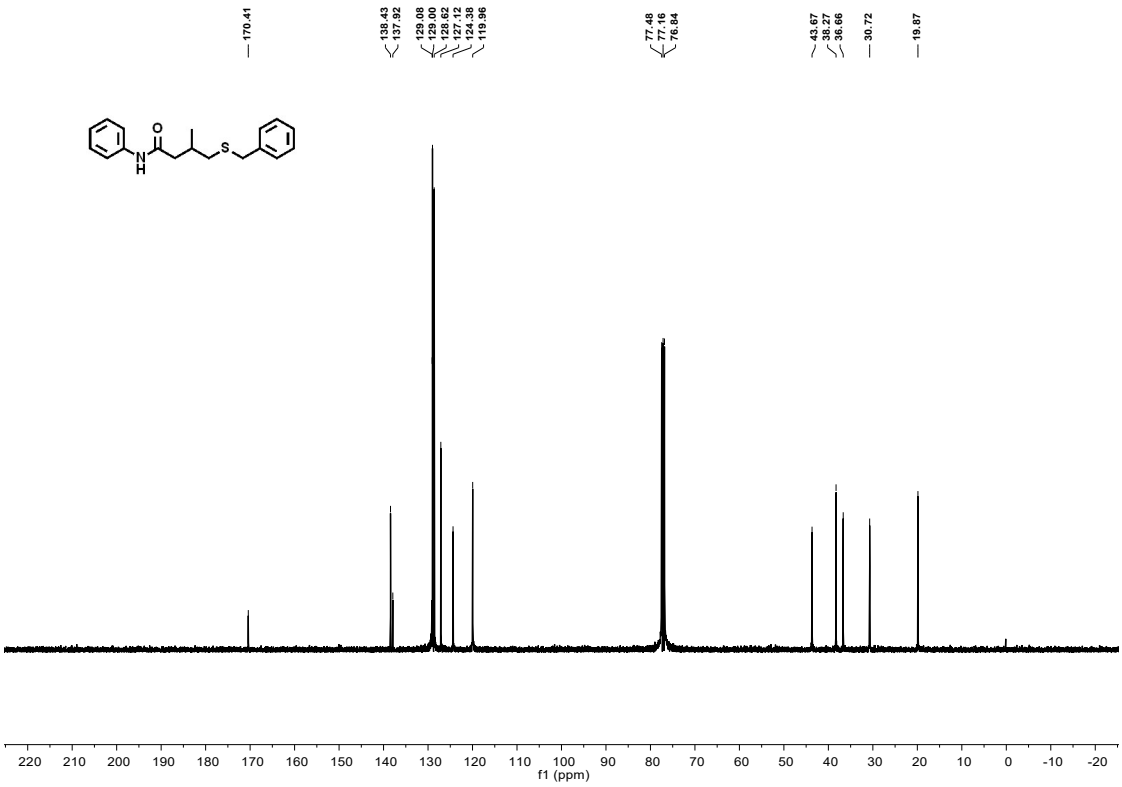
^{13}C NMR spectra of **9h**



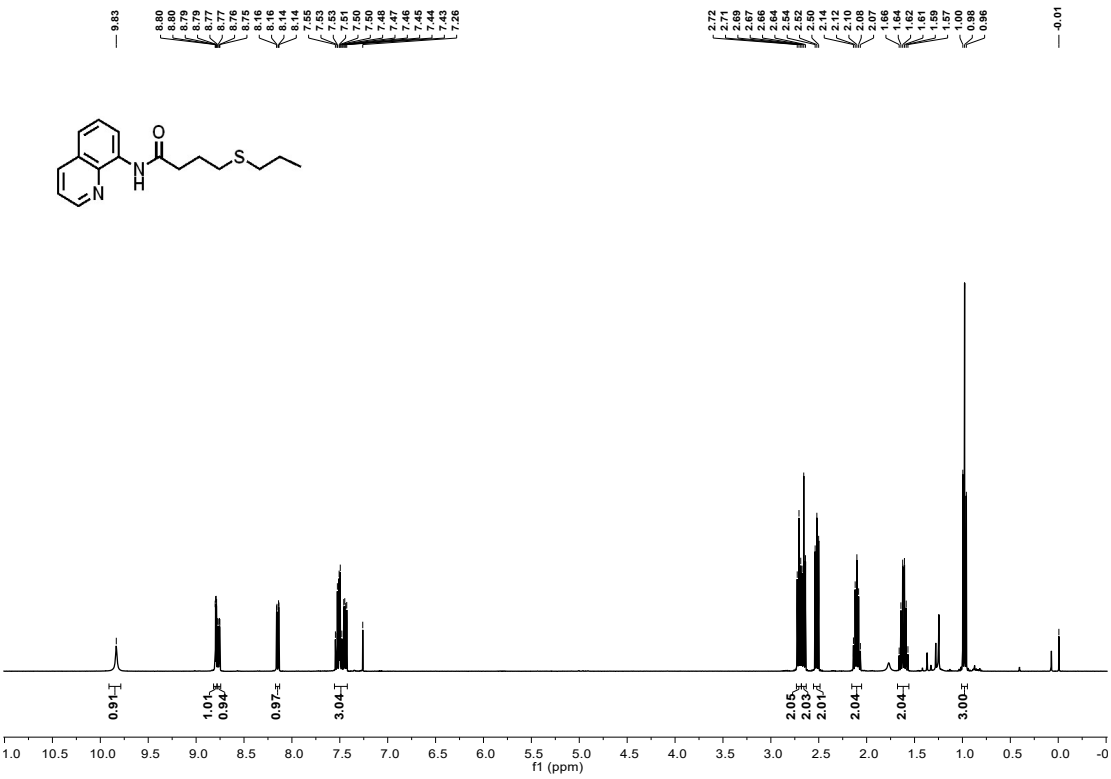
^{1}H NMR spectra of **9i**



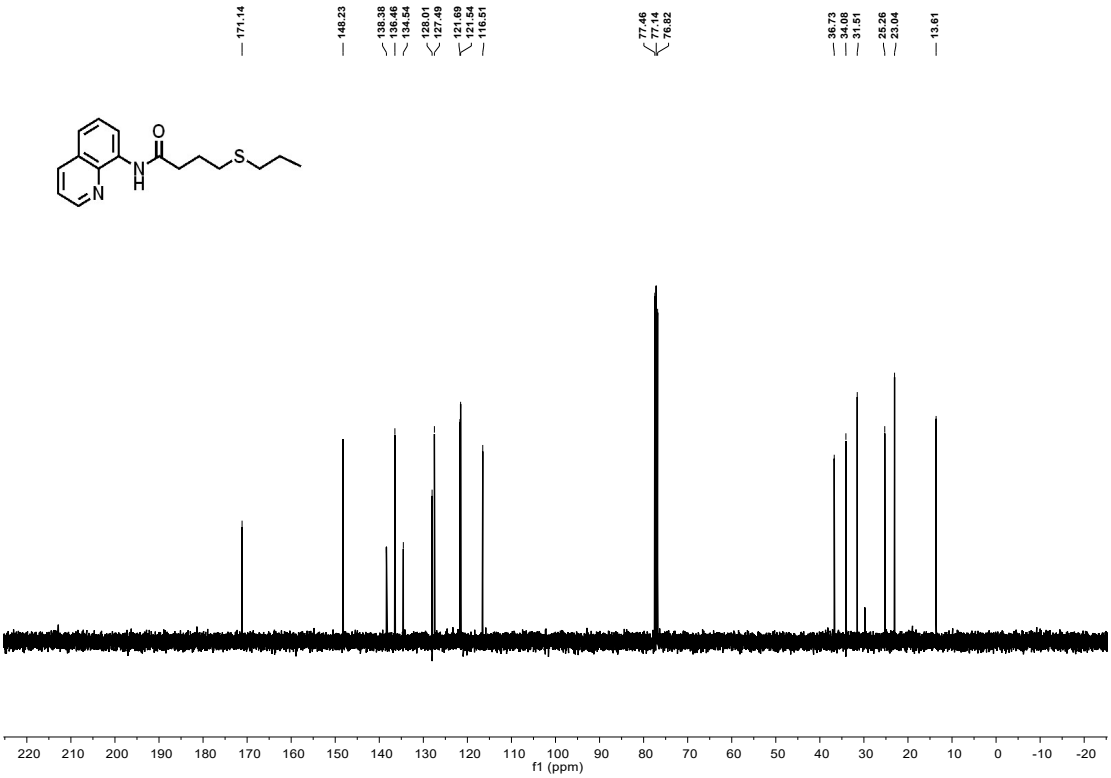
^{13}C NMR spectra of **9i**



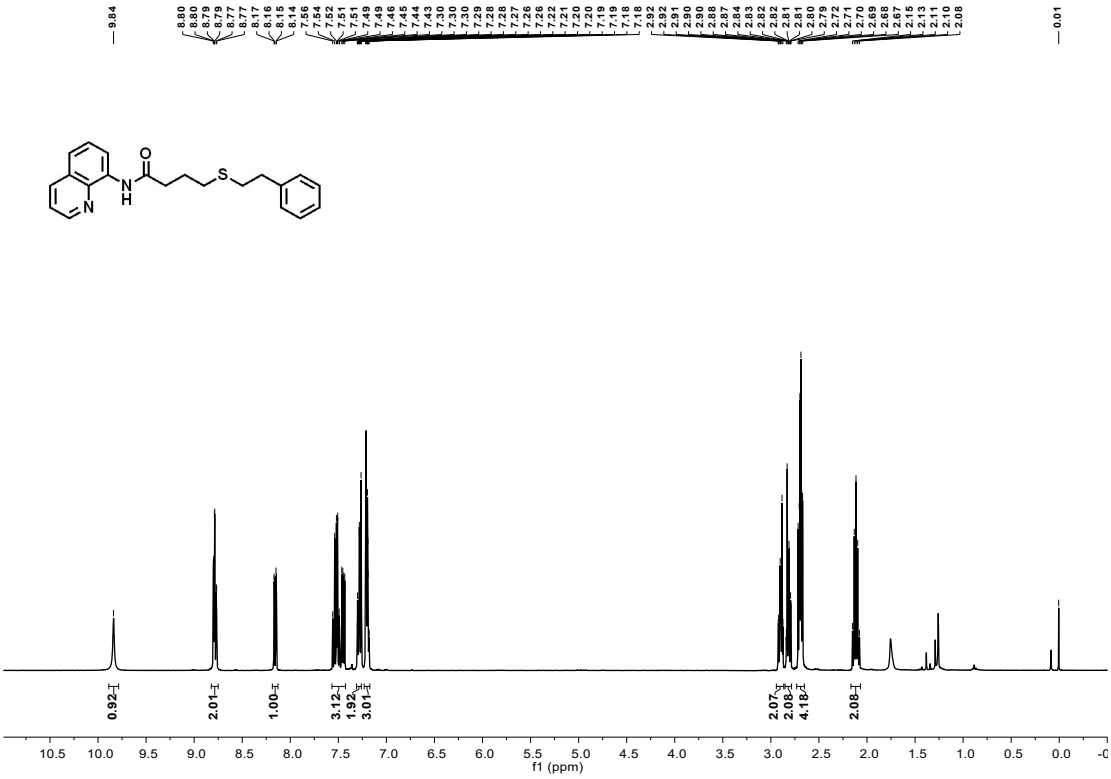
^{1}H NMR spectra of **9j**



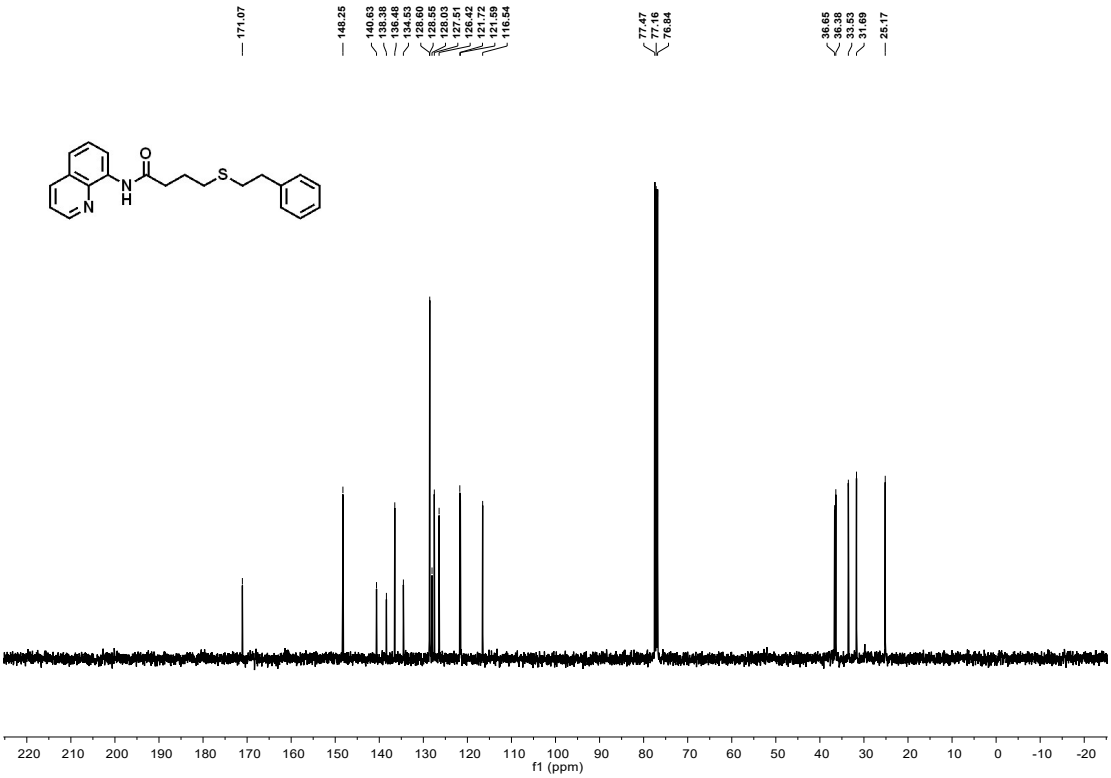
^{13}C NMR spectra of **9j**



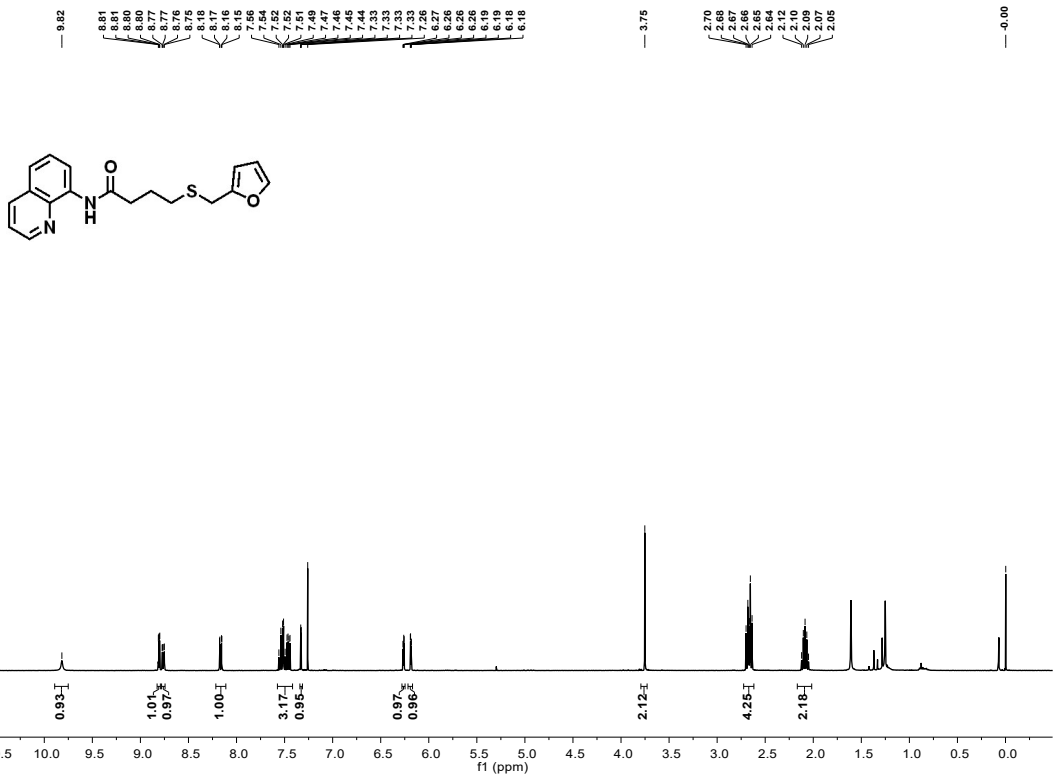
^{1}H NMR spectra of **9k**



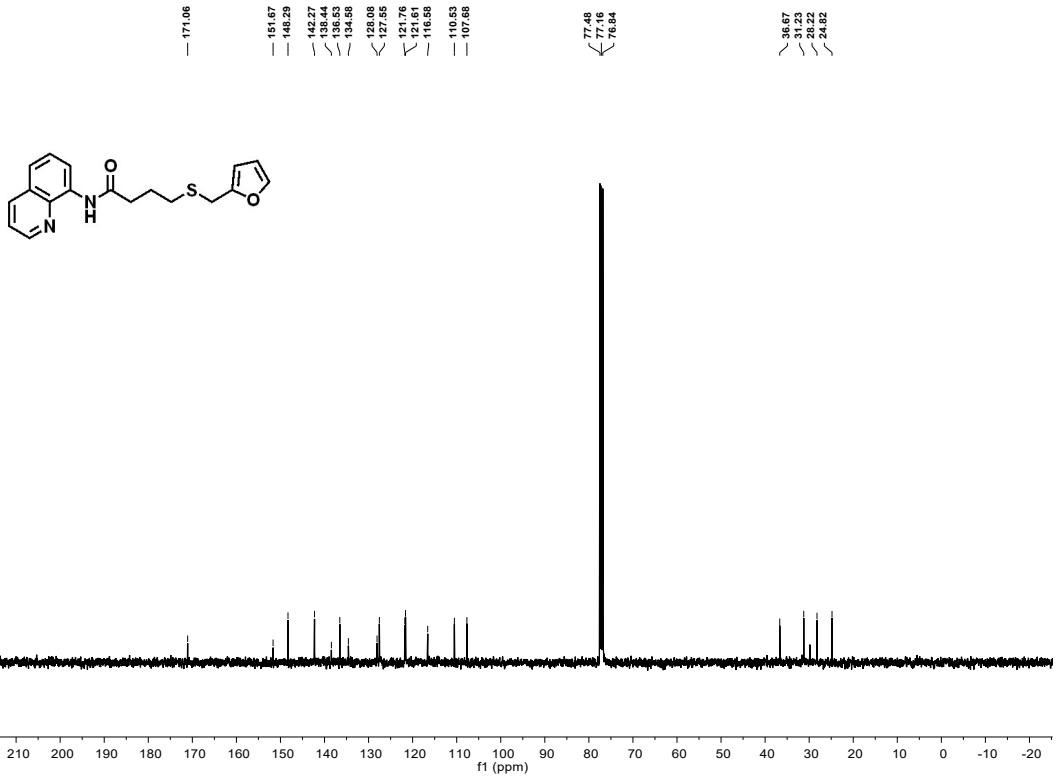
^{13}C NMR spectra of **9k**



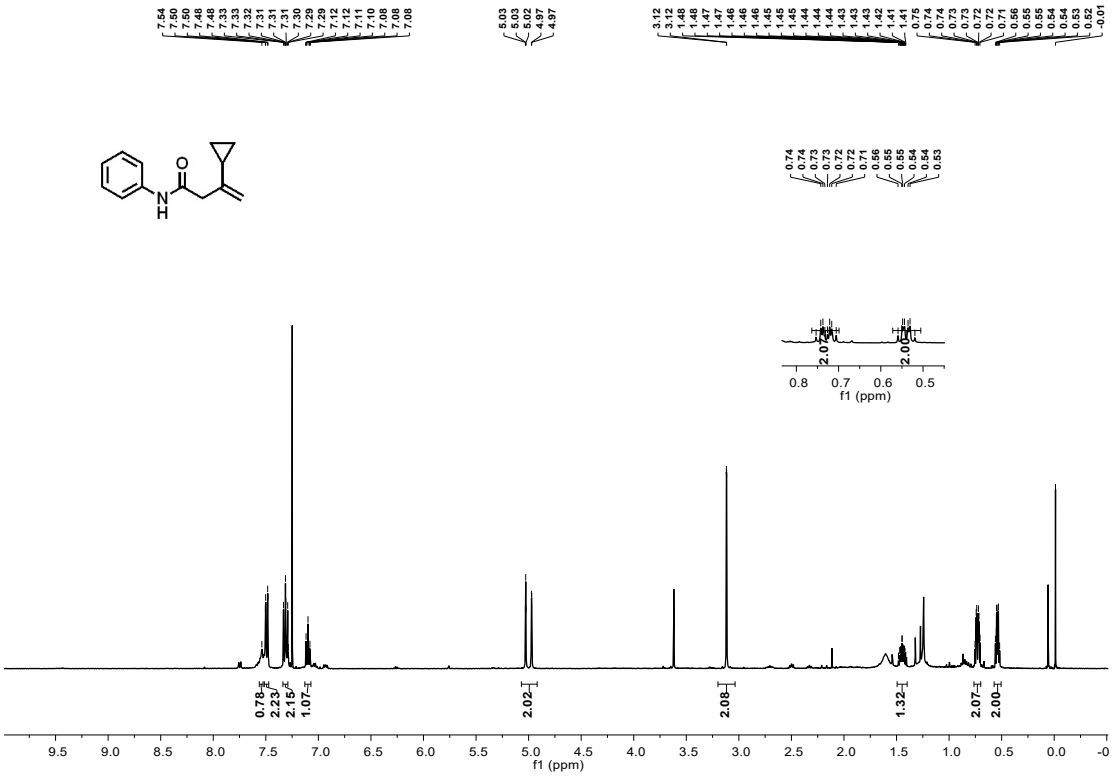
^{1}H NMR spectra of **9l**



^{13}C NMR spectra of **9l**



^{1}H NMR spectra of **10a**



^{1}H NMR spectra of **10b**