Supporting Information

Iron-Catalyzed Benzylic C-H Thiolation via Photoinduced Ligand-to-Metal Charge-Transfer

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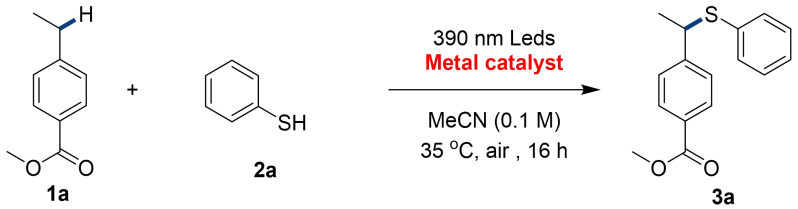
1. The Optimization of Benzylic C-H Thiolation

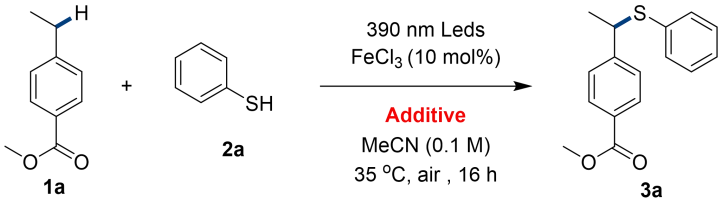
Table S1. The optimization of metal catalysts [a]



Entry	Metal catalyst	yield(3a) [b]
1	$FeCl_3$ (10 mol%)	16%
2	$FeCl_2$ (10mol%)	n.d.[c]
3	$FeBr_3$ (10 mol%)	n.d.[c]
4	$Fe(acac)_3$ (10 mol%)	n.d.[c]
5	$CuCl_2$ (10 mol%)	n.d.[c]
6	$NiCl_2$ (10 mol%)	n.d.[c]
7	$FeCl_3$ (5 mol%)	9%
8	$FeCl_3$ (20 mol%)	14%
9	$FeCl_3$ (50 mol%)	13%

[a] Conditions employed 390 nm Leds, **1a** (1.0 mmol), **2a** (0.2 mmol), Metal catalyst (5-50 mol%), CH_3CN (2 mL), the reaction mixture was degassed via freeze pump thaw (× 3 times) and refilled with dry air (dried with anhydrous $CaCl_2$), 35 °C, 16 h, unless otherwise noted; [b] Isolated yields were reported; [c] Not detected.

Table S2. The optimization of the additive [a]

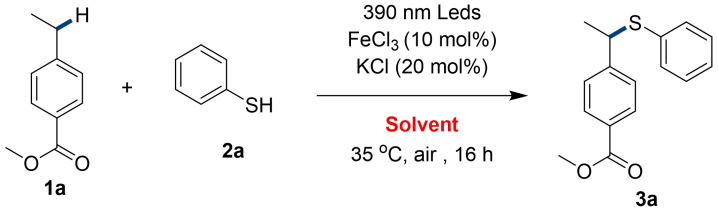


Entry	Additive	yield(3a) [b]
1	TBAB (10 mol%)	24%
2	$CuBr_2$ (10 mol%)	trace
3	$FeBr_3$ (10mol%)	42%
4	LiBr (10 mol%)	33%
5	NaBr (10 mol%)	45%
6	KBr (10 mol%)	56%
7	$NiBr_2$ (10 mol%)	trace
8	$NiBr_2$ • dme (10 mol%)	trace
9	NBS (10 mol%)	31%
10	CBr_4 10 mol%)	trace
11	TMSBr 10 mol%)	n.d.[c]
12	LiCl (10 mol%)	55%
13	NH_4Cl (10 mol%)	20%
14	NaCl (10 mol%)	51%
15	$NiCl_2$ • dme (10 mol%)	54%
16	KCl (10 mol%)	59%
17	TBAC (10 mol%)	25%
18	KCl (5 mol%)	46%

19	KCl (20 mol%)	61%
20	KCl (50 mol%)	47%
21	KCl (100 mol%)	42%

[a] Conditions employed 390 nm Leds, **1a** (1.0 mmol), **2a** (0.2 mmol), $FeCl_3$ (10 mol%), additive (5-100 mol%), CH_3CN (2 mL), the reaction mixture was degassed via freeze pump thaw (× 3 times) and refilled with dry air (dried with anhydrous $CaCl_2$), 35 °C, 16 h, unless otherwise noted; [b] Isolated yields were reported; [c] Not detected.

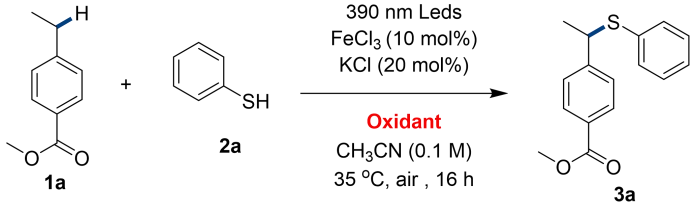
Table S3. The optimization of the solvent [a]



Entry	Solvent	yield(3a) [b]
1	CH_3CN (0.1 M)	61%
2	anhydrous CH_3CN (0.1 M)	61%
3	DCE (0.1 M)	trace
4	DCM (0.1 M)	n.d.[c]
5	EtOAc (0.1 M)	trace
6	CH_3OH (0.1 M)	n.d.[c]
7	CH_3COOH (0.1 M)	trace
8	THF (0.1 M)	trace
9	DMSO (0.1 M)	n.d.[c]
10	HFIP (0.1 M）	trace
11	Acetone (0.1 M）	26%
12	DCE：HFIP=1：1 (0.1 M)	trace
13	DMSO：MeCN=1：10 (0.1 M)	n.d.[c]
14	anhydrous CH_3CN+2 equiv H_2O (0.1 M)	56%
15	anhydrous CH_3CN+10 equiv H_2O (0.1 M)	45%
16	anhydrous CH_3CN+20 equiv H_2O (0.1 M)	27%
17	anhydrous CH_3CN+50 equiv H_2O (0.1 M)	trace

[a] Conditions employed 390 nm Leds, **1a** (1 mmol), **2a** (0.2 mmol), $FeCl_3$ (10 mol%), KCl (20 mol%), solvent (2 mL), the reaction mixture was degassed via freeze pump thaw (× 3 times) and refilled with dry air (dried with anhydrous $CaCl_2$), 35 °C, 16 h, unless otherwise noted; [b] Isolated yields were reported; [c] Not detected.

Table S4. The optimization of the oxidant [a]

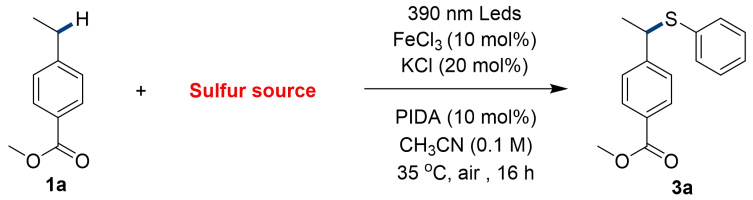


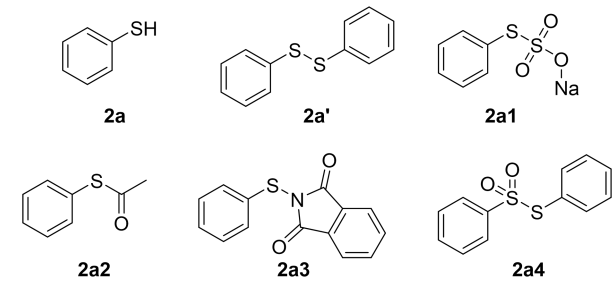
Entry	Oxidant	yield(3a) [b]
1	TPPO (10 mol%)	53%
2	UHP (10 mol%)	66%
3	APS (10 mol%)	40%
4	PIDA (10 mol%)	67%

5	PIFA (10 mol%)	43%
6	NFSI (10 mol%)	53%
7	SelectFluor (10 mol%)	33%
8	NIS (10 mol%)	n.d.[c]
9	NCS (10 mol%)	27%
10	NBS (10 mol%)	63%
11	DMSO (10 mol%)	52%
12	ACS (10 mol%)	47%
13	Oxone (10 mol%)	57%
14	PIDA (5 mol%)	64%
15	PIDA (20 mol%)	55%
16	PIDA (50 mol%)	55%

[a] Conditions employed 390 nm Leds, **1a** (1.0 mmol), **2a** (0.2 mmol), $FeCl_3$ (10 mol%), KCl (20 mol%), oxidant (5-50 mol%), anhydrous CH_3CN (2 mL), the reaction mixture was degassed via freeze pump thaw (× 3 times) and refilled with dry air (dried with anhydrous $CaCl_2$), 35 °C, 16 h, unless otherwise noted; [b] Isolated yields were reported. [c] Not detected.

Table S5. The optimization of the sulfur source [a]

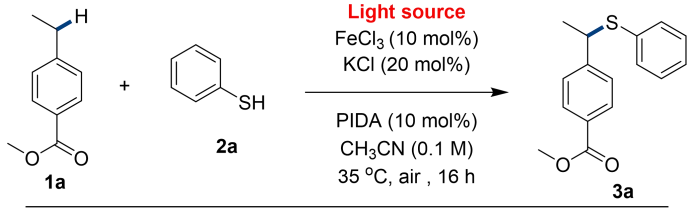




Entry	Sulfur source	yield(3a) [b]
1	**2a**	67%
2	**2a'**	35%
3	**2a1**	trace
4	**2a2**	trace
5	**2a3**	10%
6	**2a4**	38%

[a] Conditions employed Leds, **1a** (1.0 mmol), sulfur source (0.2 mmol), $FeCl_3$ (10 mol%), KCl (20 mol%), PIDA (10 mol%), anhydrous CH_3CN (2 mL), the reaction mixture was degassed via freeze pump thaw (× 3 times) and refilled with dry air (dried with anhydrous $CaCl_2$), 35 °C, 16 h, unless otherwise noted; [b] Isolated yields were reported.

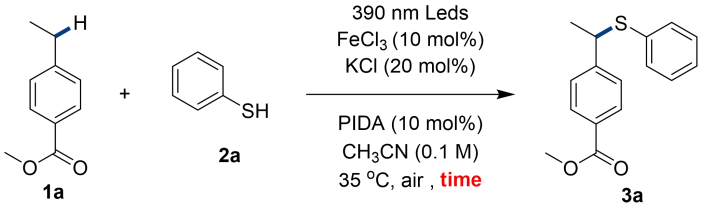
Table S6. The optimization of the light source [a]



Entry	Light source	yield(3a) [b]
1	390 nm Leds	67%
2	12 W Blue Leds	trace
3	360 nm Blue Leds	38%

[a] Conditions employed Leds, **1a** (1.0 mmol), **2a** (0.2 mmol), $FeCl_3$ (10 mol%), KCl (20 mol%), PIDA (10 mol%), anhydrous CH_3CN (2 mL), the reaction mixture was degassed via freeze pump thaw (× 3 times) and refilled with dry air (dried with anhydrous $CaCl_2$), 35 °C, 16 h, unless otherwise noted; [b] Isolated yields were reported.

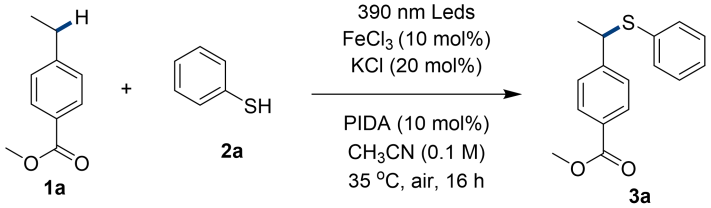
Table S7. The optimization of the reaction time [a]



Entry	Reaction time	yield(3a) [b]
1	4 h	trace
2	8 h	32%
3	12 h	45%
4	16 h	67%
5	24 h	61%
6	48 h	49%

[a] Conditions employed 390 nm Leds, **1a** (1.0 mmol), **2a** (0.2 mmol), $FeCl_3$ (10 mol%), KCl (20 mol%), PIDA (10 mol%), anhydrous CH_3CN (2 mL), the reaction mixture was degassed via freeze pump thaw (× 3 times) and refilled with dry air (dried with anhydrous $CaCl_2$), 35 °C, reaction time (4 - 48 h), unless otherwise noted; [b] Isolated yields were reported.

Table S8. Control Experiments [a]



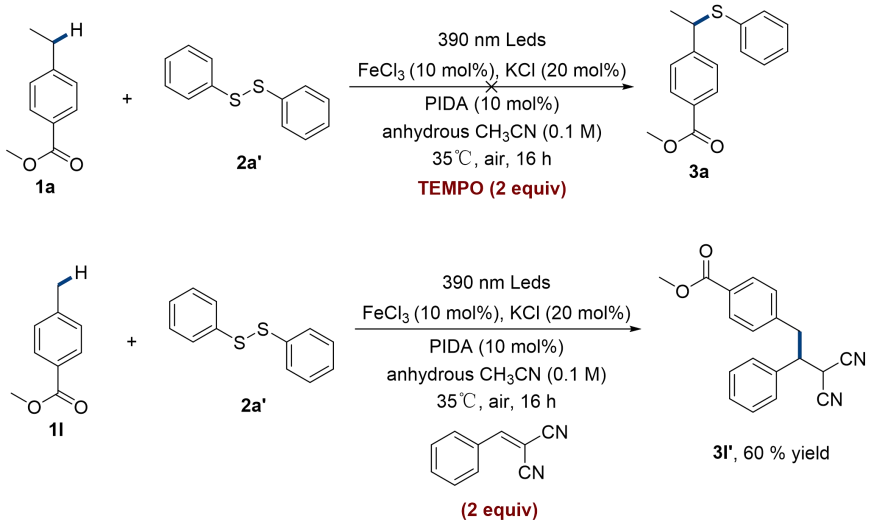
Entry	Conditions	yield(3a) [b]
1	Standard	67%
2	No $FeCl_3$	n.d.[c]
3	In darkness	n.d.[c]
4	No KCl	16%
5	No PIDA	61%
6	Under N_2	7%

[a] Conditions employed 390 nm Leds, **1a** (1.0 mmol), **2a** (0.2 mmol), $FeCl_3$ (10 mol%), KCl (20 mol%), PIDA (10 mol%), anhydrous CH_3CN (2 mL), the reaction mixture was degassed via freeze

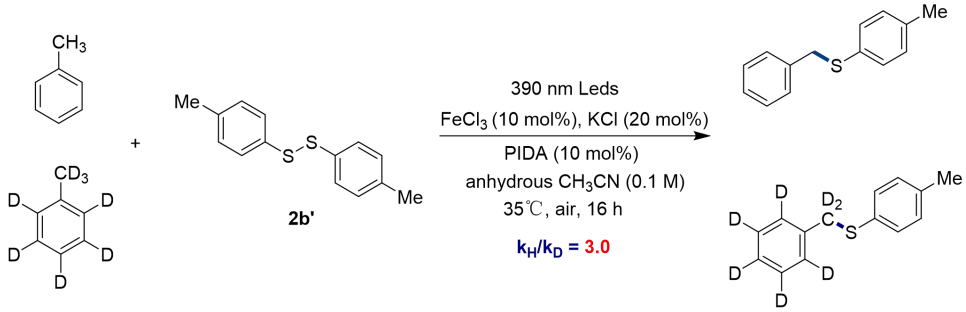
pump thaw (× 3 times) and refilled with dry air (dried with anhydrous $CaCl_2$), 35 ºC, 16 h, unless otherwise noted; [b] Isolated yields were reported; [c] Not detected.

2. The Study of the Mechanism of Benzylic C-H Thiolation

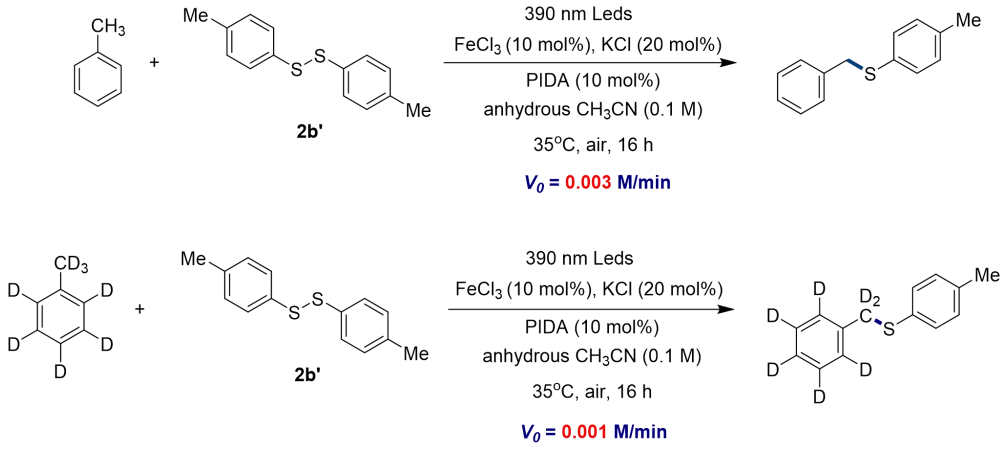
Scheme S1. The radical quenching and trappinmg experiments



Scheme S2. The kinetic isotopic effect determination from intermolecular competition reactions employing toluene and d^8-toluene as coupling partner



Scheme S3. The kinetic isotopic effect determination from two parallel reactions employing toluene and d^8-toluene as coupling partner



Entry	Time(min)	NMR Yield (%) [b]	[Product](M)	V_0
toluene	10	1	0.002	0.0003M/min
	20	2	0.004	
	30	3.5	0.007	

	40	5	0.01	
	50	6.5	0.013	
	60	7.5	0.015	

Entry	Time(min)	NMR Yield (%)	[Product](M)	V_0
d^8-toluene	10	0.5	0.001	0.0001M/min
	20	1	0.002	
	30	2	0.004	
	40	2.5	0.005	
	50	3	0.005	
	60	3.5	0.007	

[a] Conditions employed 390 nm Leds, toluene (or d^8-toluene) (1 mmol), **2b'** (0.2 mmol), $FeCl_3$ (10 mol%), KCl (20 mol%), PIDA (10 mol%), anhydrous CH_3CN (2 mL) the reaction mixture was degassed via freeze pump thaw (× 3 times) and refilled with dry air (dried with anhydrous $CaCl_2$), 35 °C; [b] Analyzed by NMR spectroscopy for the formation of product with 1,3,5-trimethoxybenzene as an internal standard.

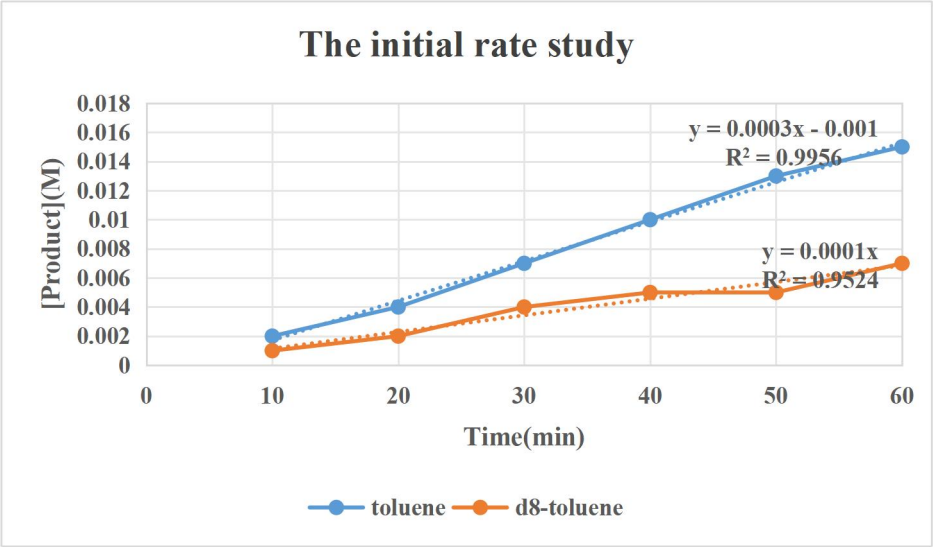
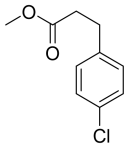


Fig. S1 The initial rate study of toluene and d^8-toluene based coupling reaction with **2b'**

3. Synthesis of Starting Compounds



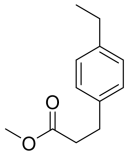
methyl 3-(4-chlorophenyl)propanoate (**1o**):

1o was prepared according to literature procedures.[1] 3-(4-Chlorophenyl)propanoic acid (10.0 mmol) was dissolved in 30 mL methanol contained in a 100 mL round bottom flask equipped with a magnetic stirring bar. Into this solution was added dropwise 107 uL of conc. sulfuric acid (2.0 mmol) over 5 min at room temperature. The resulting solution was stirred at reflux for 3 h. The reaction mixture was then cooled down to room temperature, and into the flask were added 1.0 M aqueous NaOH solution (15 mL) and water (15 mL). The product was extracted three times with ethyl acetate (3 × 30 mL). The combined organic layers were washed twice with water (30 mL), dried with anhydrous Na_2SO_4 and concentrated in vacuo. Purification of the crude product by flash chromatography (2 % ethyl acetate/petroleum ether) to provide **1o** as a colorless oil (1.82 g, 92% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, J = 8.3 Hz, 2H), 7.15 (d, J = 8.2 Hz, 2H), 3.69 (s, 3H), 2.94 (t, J = 7.7 Hz, 2H), 2.63 (t, J = 7.7 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.26, 138.82, 131.99, 129.61, 128.54, 51.71, 35.45, 30.16.

Spectral data is in agreement with the literature.[2]



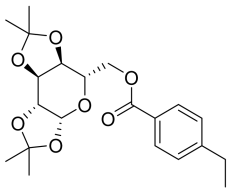
methyl 3-(4-ethylphenyl)propanoate (**1p**):

1p was prepared according to literature procedures.[1] 3-(4-ethylphenyl)propanoic acid (10.0 mmol) was dissolved in 30 mL methanol contained in a 100 mL round bottom flask equipped with a magnetic stirring bar. Into this solution was added dropwise 107 uL of conc. sulfuric acid (2.0 mmol) over 5 min at room temperature. The resulting solution was stirred at reflux for 3 h. The reaction mixture was then cooled down to room temperature, and into the flask were added 1.0 M aqueous NaOH solution (15 mL) and water (15 mL). The product was extracted three times with ethyl acetate (3 × 30 mL). The combined organic layers were washed twice with water (30 mL), dried with anhydrous Na_2SO_4 and concentrated in vacuo. Purification of the crude product by flash chromatography (2 % ethyl acetate/petroleum ether) to provide **1p** as a colorless oil (1.73 g, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 - 7.08 (m, 4H), 3.68 (s, 3H), 2.96 - 2.88 (m, 2H), 2.68 - 2.57 (m, 4H), 1.23 (t, J = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.48, 142.2, 137.70, 128.22, 128.01, 51.62, 35.83, 30.56, 28.45, 15.63.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{12}H_{17}O_2$ 193.1223, found 193.1232.



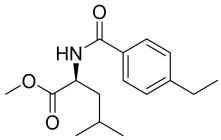
((3a*R*,5*S*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 4-ethylbenzoate (**1z**):

1z was prepared according to literature procedures.[3] 1,2;3,4-di-O-isopropylidene-*α*-D-galactopyranose (2.0 g, 7.7 mmol) was dissolved in dry CH_2Cl_2 (25 mL). To the mixture was added DMAP (0.1 g, 0.77 mmol), Et_3N (1.6 mL, 12 mmol) and finally 4-ethylbenzoyl chloride (4.6 mL, 31 mmol). The solution was stirred at room temperature for 2 hours and then quenched by addition of 3-(dimethylamino)-1-propylamine (3.9 mL, 31 mmol). The mixture was stirred for an additional 30 min. before diluted with CH_2Cl_2 and washed thrice with hydrochloric acid (1 M.), aqueous saturated bicarbonate solution and then brine. The organic layer was dried with anhydrous Na_2SO_4 and concentrated in vacuo. Purification of the crude product by flash chromatography (20 % ethyl acetate/petroleum ether) to provide **1z** as a white solid (2.72 g, 90% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.26 (t, *J* = 5.8 Hz, 2H), 5.57 (d, *J* = 4.9 Hz, 1H), 4.65 (dd, *J* = 7.9, 2.4 Hz, 1H), 4.52 (dd, *J* = 11.5, 4.9 Hz, 1H), 4.41 (dd, *J* = 11.5, 7.5 Hz, 1H), 4.37 - 4.31 (m, 2H), 4.21 - 4.16 (m, 1H), 2.70 (q, *J* = 7.6 Hz, 2H), 1.50 (d, *J* = 22.0 Hz, 6H), 1.35 (d, *J* = 13.9 Hz, 6H), 1.25 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 166.45, 149.79, 129.81, 127.83, 127.49, 109.61, 108.76, 96.29, 66.12, 63.62, 28.92, 25.99, 25.94, 24.95, 24.45, 15.20.

Spectral data is in agreement with the literature.[3]

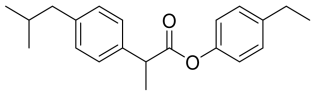


methyl (4-ethylbenzoyl)-*L*-leucinate (**1aa**):

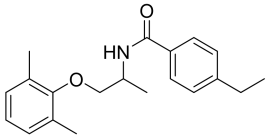
1aa was prepared according to literature procedures.[4] A 100 mL oven dried round bottom flask containing a stirring bar was charged with methyl *L*-leucinate hydrochloride (10 mmol). Dichloromethane (30 mL) and 4-ethylbenzoyl chloride (10 mmol) were added respectively followed by slow addition of triethyl amine (22 mmol). The resulting mixture was stirred over night at r.t. After complete disappearance of the substrate on TLC board, the reaction mixture was washed with hydrochloric acid (1 M, 50 mL). The organic layer was dried with anhydrous Na_2SO_4 and concentrated in vacuo. Purification of the crude product by flash chromatography (2 % ethyl acetate/petroleum ether) to provide **1aa** as a white solid (2.35 g, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 6.59 (d, *J* = 8.1 Hz, 1H), 4.90 - 4.83 (m, 1H), 3.76 (s, 3H), 2.69 (q, *J* = 7.6 Hz, 2H), 1.79 - 1.61 (m, 3H), 1.24 (t, *J* = 7.6 Hz, 3H), 0.98 (dd, *J* = 7.3, 6.3 Hz, 6H).

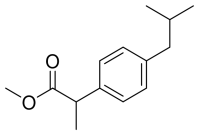
^{13}C NMR (100 MHz, $CDCl_3$) δ 173.77, 166.99, 148.37, 131.24, 128.00, 127.12, 52.30, 51.00, 41.83, 28.74, 24.93, 22.80, 22.01, 15.29.
Spectral data is in agreement with the literature.[4]



4-ethylphenyl 2-(4-isobutylphenyl)propanoate (**1ab**):
1ab was prepared according to literature procedures.[5] To a solution of 2-(4-isobutylphenyl)propanoic acid (2.06 g, 10.0 mmol) and 4-ethylphenol (1.22 g, 10.0 mmol) in CH_2Cl_2 (20 mL) were added 1-(3-dimethylaminopropyl) -3-ehtylcarbodiimide hydrochloride (2.11 g, 11.0 mmol) and 4-dimethylaminopyridine (305 mg, 2.50 mmol). The reaction mixture was stirred at room temperature for 12 h, then concentrated under reduced pressure. Purification of the crude product by flash chromatography (5 % ethyl acetate/petroleum ether) to provide **1ab** as a colorless oil (2.54 g, 82% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.1 Hz, 2H), 7.16 (dd, *J* = 8.4, 2.7 Hz, 4H), 6.96 - 6.88 (m, 2H), 3.95 (q, *J* = 7.1 Hz, 1H), 2.64 (q, *J* = 7.6 Hz, 2H), 2.49 (d, *J* = 7.2 Hz, 2H), 2.00 - 1.77 (m, 1H), 1.62 (d, *J* = 7.2 Hz, 3H), 1.23 (t, *J* = 7.6 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 173.37, 148.73, 141.59, 140.70, 137.32, 129.44, 128.59, 127.19, 121.05, 45.22, 45.02, 30.16, 28.23, 22.36, 18.53, 15.56.
Spectral data is in agreement with the literature.[5]



N-(1-(2,6-dimethylphenoxy)propan-2-yl)-4-ethylbenzamide (**1ac**):
1ac was prepared according to literature procedures.[4] A 100 mL oven dried round bottom flask containing a stirring bar was charged with Mexiletine hydrochloride (10 mmol). Dichloromethane (30 mL) and 4-ethylbenzoyl chloride (10 mmol) were added respectively followed by slow addition of triethyl amine (22 mmol). The resulting mixture was stirred over night at r.t. After complete disappearance of the substrate on TLC board, the reaction mixture was washed with hydrochloric acid (1 M, 50 mL). The organic layer was dried with anhydrous Na_2SO_4 and concentrated in vacuo. Purification of the crude product by flash chromatography (5 % ethyl acetate/petroleum ether) to provide **1ac** as a white solid (2.65 g, 85% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 6.93 (d, *J* = 7.4 Hz, 2H), 6.85 (dd, *J* = 8.2, 6.6 Hz, 1H), 6.55 (d, *J* = 8.0 Hz, 1H), 4.54 - 4.39 (m, 1H), 3.79 (ddd, *J* = 12.0, 9.1, 3.4 Hz, 2H), 2.62 (q, *J* = 7.6 Hz, 2H), 2.20 (s, 6H), 1.44 (d, *J* = 6.8 Hz, 3H), 1.18 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.75, 154.80, 148.08, 131.96, 130.73, 128.99, 128.06, 126.91, 124.11, 73.92, 45.73, 28.73, 17.86, 16.19, 15.29.
HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{26}NO_2$ 312.1958, found 312.1969.



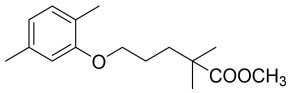
methyl 2-(4-isobutylphenyl)propanoate (**1ad**):

1ad was prepared according to literature procedures.[1] 2-(4-isobutylphenyl)propanoic acid (10.0 mmol) was dissolved in 30 mL methanol contained in a 100 mL round bottom flask equipped with a magnetic stirring bar. Into this solution was added dropwise 107 uL of conc. sulfuric acid (2.0 mmol) over 5 min at room temperature. The resulting solution was stirred at reflux for 3 h. The reaction mixture was then cooled down to room temperature, and into the flask were added 1.0 M aqueous NaOH solution (15 mL) and water (15 mL). The product was extracted three times with ethyl acetate (3 × 30 mL). The combined organic layers were washed twice with water (30 mL), dried with anhydrous Na_2SO_4 and concentrated in vacuo. Purification of the crude product by flash chromatography (5 % ethyl acetate/petroleum ether) to provide **1ad** as a colorless oil (2.05 g, 93% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 3.71 (q, *J* = 7.2 Hz, 1H), 3.66 (s, 3H), 2.45 (d, *J* = 7.2 Hz, 2H), 1.91 - 1.80 (m, 1H), 1.49 (d, *J* = 7.2 Hz, 3H), 0.91 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 140.51 137.71, 129.31, 127.09, 51.94, 45.00, 44.98, 30.14, 22.36, 18.58.

Spectral data is in agreement with the literature.[6]



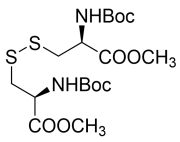
methyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (**1ae**):

1ae was prepared according to literature procedures.[1] 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoic acid (10.0 mmol) was dissolved in 30 mL methanol contained in a 100 mL round bottom flask equipped with a magnetic stirring bar. Into this solution was added dropwise 107 uL of conc. sulfuric acid (2.0 mmol) over 5 min at room temperature. The resulting solution was stirred at reflux for 3 h. The reaction mixture was then cooled down to room temperature, and into the flask were added 1.0 M aqueous NaOH solution (15 mL) and water (15 mL). The product was extracted three times with ethyl acetate (3 × 30 mL). The combined organic layers were washed twice with water (30 mL), dried with anhydrous Na_2SO_4 and concentrated in vacuo. Purification of the crude product by flash chromatography (5 % ethyl acetate/petroleum ether) to provide **1ae** as a colorless oil (2.48 g, 94% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 7.5 Hz, 1H), 6.67 (d, *J* = 7.5 Hz, 1H), 6.62 (s, 1H), 3.93 (t, *J* = 5.2 Hz, 2H), 3.68 (s, 3H), 2.32 (s, 3H), 2.19 (s, 3H), 1.73 (d, *J* = 2.9 Hz, 4H), 1.24 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 178.27, 156.89, 136.39, 130.24, 123.52, 120.62, 111.87, 67.81, 51.68, 42.05, 37.07, 25.14, 21.36, 15.70.

Spectral data is in agreement with the literature.[7]



dimethyl 3,3'-disulfanediyl(2*S*,2'*S*)-bis(2-((*tert*-butoxycarbonyl)amino)propanoate) (**2k**):

2k was prepared according to literature procedures.[8] A 250 mL round bottom flask charged with a stir bar was added dimethyl 3,3'-disulfanediyl(2*R*,2'*R*)-bis (2-aminopropanoate) dihydrogen chloride (5.12 g, 15 mmol), water (75 mL), tetrahydrofuran (75 mL), 10 mL of triethylamine (7.6 g, 75 mmol), and *di*-*tert*-butyl dicarbonate (6.9 g, 31.5 mmol) in an ice bath. The reaction mixture was allowed to stir at room temperature for 12 h. After completion, THF was removed under reduced pressure and the resulting aqueous solution was extracted with ethyl acetate (3 × 150 mL). The combined organic layers were washed three times with brine and dried with anhydrous Na_2SO_4 and concentrated in vacuo. Purification of the crude product by flash chromatography (20 % ethyl acetate/petroleum ether) to provide **2k** as a white solid (5.1 g, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.39 (d, *J* = 7.2 Hz, 2H), 4.59 (d, *J* = 7.3 Hz, 2H), 3.76 (s, 6H), 3.15 (d, *J* = 4.9 Hz, 4H), 1.44 (s, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.15, 155.02, 80.28, 52.74, 52.62, 41.25, 28.27.

Spectral data is in agreement with the literature.[8]

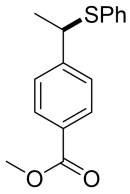
4. Experiment Procedures and Product Characterization

Commercial reagents and solvents were used as received, unless otherwise stated. Organic solution was concentrated under reduced pressure on a IKA rotary evaporator using an alcohol bath. Analytical thin layer chromatography (TLC) was performed on 0.25 mm silica gel plates (Qingdao Haiyang Chemical China), and the compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with $KMnO_4$. Flash chromatography was performed on silica gel 200-300 mesh (purchased from Qingdao Haiyang Chemical China) with commercial solvents (purchased from Energy Chemical® and Adamas-beta®). The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 400/600 Spectrometer (400/600 and 100/150 MHz for ^{1}H and ^{13}C NMR, respectively) and are internally referenced to residual solvent signals (note: $CDCl_3$ referenced at 7.26 and 77.00 ppm in ^{1}H and ^{13}C NMR, respectively). Multiplicities were given as s (singlet), d (doublet), t (triplet), dd (double of doublet) and m (multiplets). Coupling constants were reported in Hertz (Hz). Data for ^{13}C NMR are reported in terms of chemical shift. High-resolution mass spectrometry (HRMS) was recorded on Waters Xevo G2 TOF MS.

General Procedure A:
To a 10 mL vial equipped with a Teflon septum and magnetic stir bar were added the corresponding alkylarene substrate (if solid, 2.5 mmol, 5.0 equiv.), the corresponding thiol substrate (if solid, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (0.05 mmol, 10 mol%), KCl (0.1 mmol, 20 mol%), and PIDA (0.05 mmol, 10 mol%). The vial was sealed and placed under dry air atmosphere, then anhydrous CH_3CN (5.0 mL, 0.1 M), alkylarene substrate (if liquid, 2.5 mmol, 5.0 equiv.), thiol substrate (if liquid, 0.5 mmol, 1.0 equiv.) were added into the vial via injection through the cap, the reaction mixture was degassed via freeze pump thaw (× 3 times) and refilled with dry air (dried with anhydrous $CaCl_2$). The sealed vial was placed in 390 nm Led (Kessil Photoredox LED Lights PR160 Series) and irradiated for 16 hours. When the reaction finished, the reaction mixture was diluted with saturated $NaHCO_3$ aqueous solution, extracted with ethyl acetate (3 × 20 mL), the combined organic extracts were washed with brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.

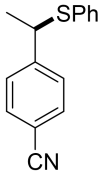
General Procedure B:
To a 10 mL vial equipped with a Teflon septum and magnetic stir bar were added the corresponding alkylarene substrate (if solid, 2.5 mmol, 5.0 equiv.), the corresponding disulfide substrate (if solid, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (0.05 mmol, 10 mol%), KCl (0.1 mmol, 20 mol%), and PIDA (0.05 mmol, 10 mol%). The vial was sealed and placed under dry air atmosphere, then anhydrous CH_3CN (5.0 mL, 0.1 M), alkylarene substrate (if liquid, 2.5 mmol, 5.0 equiv.), disulfide substrate (if liquid, 0.5 mmol, 1.0 equiv.) were added into the vial via injection through the cap, the reaction mixture was degassed via freeze pump thaw (× 3 times) and refilled with dry air (dried with anhydrous $CaCl_2$). The sealed vial was placed in 390 nm Led (Kessil Photoredox LED Lights PR160 Series) and irradiated for 16 hours. When the reaction finished, the reaction mixture was diluted with saturated $NaHCO_3$ aqueous solution, extracted with ethyl acetate (3 × 20 mL), the combined organic extracts were washed with brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification of the

crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.



methyl 4-(1-(phenylthio)ethyl)benzoate (**3a**):

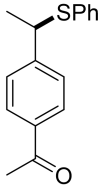
According to the general procedure A, methyl 4-ethylbenzoate (411 mg, 2.5 mmol, 5.0 equiv.), thiophenol (55 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (2 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (91 mg, 67 % yield).
According to the general procedure B, methyl 4-ethylbenzoate (411 mg, 2.5 mmol, 5.0 equiv.), 1,2-diphenyldisulfane (109 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%), and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (2 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (95 mg, 35 % yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.2 Hz, 2H), 7.32 (d, *J* = 7.3 Hz, 2H), 7.22 - 7.27 (m, 2H), 7.22 -7.17 (m, 3H), 4.34 (q, *J* =7.6 Hz, 1H), 3.89 (s, 3H), 1.63 (d, *J* = 5.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.83, 148.63, 134.22, 132.83, 129.66, 128.83, 127.46, 127.25, 52.02, 47.86, 21.92.
Spectral data is in agreement with the literature.[9]



4-(1-(phenylthio)ethyl)benzonitrile (**3b**):

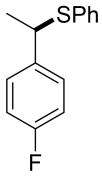
According to the general procedure A, 4-ethylbenzonitrile (328 mg, 2.5 mmol, 5.0 equiv.), thiophenol (55 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (2 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (56 mg, 47 % yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H),

7.28-7.18 (m, 5H), 4.31 (q, *J* = 6.8 Hz, 1H), 1.63 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 139.00, 129.84, 129.44, 128.81, 126.33, 121.13, 114.14, 112.90, 55.16, 39.07.
Spectral data is in agreement with the literature.[10]



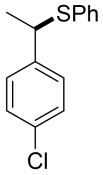
1-(4-(1-(phenylthio)ethyl)phenyl)ethan-1-one (**3c**):

According to the general procedure A, 1-(4-ethylphenyl)ethan-1-one (371 mg, 2.5 mmol, 5.0 equiv.), thiophenol (55 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (10 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (71 mg, 55 % yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 6.9 Hz, 2H), 7.35 (d, *J* = 7.0 Hz, 2H), 7.28 - 7.23 (m, 2H), 7.23 - 7.16 (m, 3H), 4.35 (q, *J* = 7.8 Hz, 1H), 2.56 (s, 3H), 1.64 (d, *J* = 5.8 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 197.61, 148.85, 135.90, 134.22, 132.72, 128.73, 128.47, 127.44, 127.40, 47.77, 26.56, 21.92 .
HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{16}H_{16}NaOS$ 279.0814, found 279.0819.



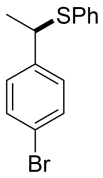
(1-(4-fluorophenyl)ethyl)(phenyl)sulfane(**3d**):

According to the general procedure A, 1-ethyl-4-fluorobenzene (310 mg, 2.5 mmol, 5.0 equiv.), thiophenol (55 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (1 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (36 mg, 31% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 - 7.25 (m, 3H), 7.25 - 7.19 (m, 4H), 6.95 (t, *J* = 8.6 Hz, 2H), 4.31 (q, *J* = 7.0 Hz, 1H), 1.60 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.99, 138.96, 134.70, 132.75, 128.80, 128.70, 127.31, 115.24 (115.02), 47.35, 22.34.
Spectral data is in agreement with the literature.[11]



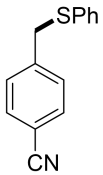
(1-(4-chlorophenyl)ethyl)(phenyl)sulfane (**3e**):

According to the general procedure A, 1-chloro-4-ethylbenzene (352 mg, 2.5 mmol, 5.0 equiv.), thiophenol (55 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (1 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (88 mg, 71 % yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 - 7.24 (m, 3H), 7.24 - 7.17 (m, 6H), 4.29 (q, *J* = 7.0 Hz, 1H), 1.60 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.84, 132.71, 128.73, 128.58, 128.45, 127.37, 47.41, 22.18.
Spectral data is in agreement with the literature.[11]



(1-(4-bromophenyl)ethyl)(phenyl)sulfane (**3f**):

According to the general procedure A, 1-bromo-4-ethylbenzene (463 mg, 2.5 mmol, 5.0 equiv.), thiophenol (55 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (2 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (95 mg, 65 % yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.0 Hz, 2H), 7.29 - 7.18 (m, 5H), 7.14 (d, *J* = 7.2 Hz, 2H), 4.28 (q, *J* = 8.0 Hz, 1H), 1.60 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.39, 134.50, 132.70, 131.42, 128.95, 128.75, 127.38, 120.77, 47.47, 22.15.
Spectral data is in agreement with the literature.[11]



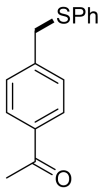
4-((phenylthio)methyl)benzonitrile (**3g**):

According to the general procedure A, 4-methylbenzonitrile (293 mg, 2.5 mmol, 5.0 equiv.), thiophenol (55 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (2 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (34 mg, 30 % yield).

^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.29 - 7.18 (m, 5H), 4.09 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.36, 134.63, 132.19, 130.82, 129.44, 128.99, 127.14, 118.71, 110.90, 39.14.

Spectral data is in agreement with the literature.[12]



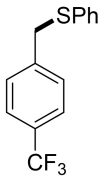
1-(4-((phenylthio)methyl)phenyl)ethan-1-one (**3h**):

According to the general procedure A, 1-(*p*-tolyl)ethan-1-one (335 mg, 2.5 mmol, 5.0 equiv.), thiophenol (55 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (4 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (42 mg, 35 % yield).

^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 6.8 Hz, 2H), 7.35 (d, *J* = 7.3 Hz, 2H), 7.31 - 7.15 (m, 5H), 4.12 (s, 2H), 2.57 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.67, 143.26, 135.99, 135.33, 130.44, 128.95, 128.92, 128.55, 126.81, 39.01, 26.59.

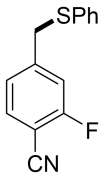
Spectral data is in agreement with the literature.[13]



phenyl(4-(trifluoromethyl)benzyl)sulfane (**3i**):

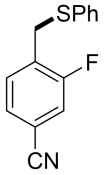
According to the general procedure A, 1-methyl-4-(trifluoromethyl)benzene (400 mg, 2.5 mmol, 5.0 equiv.), thiophenol (55 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (2 % ethyl acetate/petroleum ether) to provide the

title compound as a colourless oil (51 mg, 38 % yield).
^{1}H NMR (400 MHz,$CDCl_3$) δ 7.52 (d, *J* = 7.6 Hz, 2H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.33 - 7.15 (m, 5H), 4.12 (s, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.81, 134.80, 130.34, 129.35 (129.16), 129.03 (128.95), 127.15 (126.95), 126.83 (126.61), 125.35, 38.76.
Spectral data is in agreement with the literature.[14]



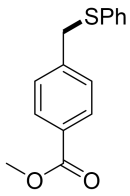
2-fluoro-4-((phenylthio)methyl)benzonitrile (**3j**):

According to the general procedure A, 2-fluoro-4-methylbenzonitrile (338 mg, 2.5 mmol, 5.0 equiv.), thiophenol (55 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (2 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (40 mg, 33 % yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 - 7.47 (m, 1H), 7.31 - 7.20 (m, 5H), 7.14 - 7.05 (m, 2H), 4.07 (s, 2H).
^{13}C NMR (100 MHz,$CDCl_3$) δ 164.31 (161.73), 146.78, 134.08, 133.31, 131.09, 129.13, 127.49, 125.13 (125.10), 116.71 (116.51), 113.85, 39.08 .
HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{14}H_{10}FNNaS$ 266.0410, found 266.0421.



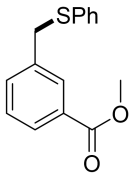
3-fluoro-4-((phenylthio)methyl)benzonitrile (**3k**):

According to the general procedure A, 3-fluoro-4-methylbenzonitrile (338 mg, 2.5 mmol, 5.0 equiv.), thiophenol (55 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (2 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (41 mg, 34% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 - 7.32 (m, 2H), 7.32 - 7.30 (m, 2H), 7.30 - 7.26 (m, 5H), 4.10 (s, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.29 (158.79), 131.70 (131.68), 131.45, 129.07, 128.00 (127.98), 127.54, 119.17 (118.92), 117.48, 112.27, 32.38 .
HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{14}H_{10}FNNaS$ 266.0410, found 266.0417.



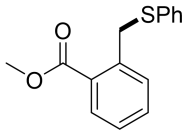
methyl 4-((phenylthio)methyl)benzoate (**3l**):

According to the general procedure A, methyl 4-methylbenzoate (375 mg, 2.5 mmol, 5.0 equiv.), thiophenol (55 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (2 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (66 mg, 51 % yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.40 - 7.12 (m, 7H), 4.11 (s, 2H), 3.89 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.78, 142.96, 135.31, 130.43, 129.71, 128.91, 128.87, 128.74, 126.76, 52.03, 39.02.
Spectral data is in agreement with the literature.[15]



methyl 3-((phenylthio)methyl)benzoate (**3m**):

According to the general procedure A, methyl 3-methylbenzoate (375 mg, 2.5 mmol, 5.0 equiv.), thiophenol (55 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (2 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (59 mg, 46 % yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 7.3 Hz, 1H), 7.37 - 7.14 (m, 6H), 4.12 (s, 2H), 3.89 (s, 3H).
^{13}C NMR (100 MHz,$CDCl_3$) δ 166.77, 137.96, 135.58, 133.21, 130.31, 130.17, 129.90, 128.85, 128.48, 128.34, 126.60, 52.08, 38.79.
Spectral data is in agreement with the literature.[16]



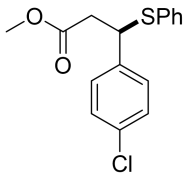
methyl 2-((phenylthio)methyl)benzoate (**3n**):

According to the general procedure A, methyl 2-methylbenzoate (375 mg, 2.5 mmol, 5.0 equiv.), thiophenol (55 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (2 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (43 mg, 33 % yield).

^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.5 Hz, 1H), 7.39 - 7.32 (m, 1H), 7.32 - 7.26 (m, 3H), 7.25 - 7.15 (m, 4H), 4.51 (s, 2H), 3.88 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.66, 139.63, 135.94, 131.88, 131.09, 131.02, 130.94, 129.28, 128.73, 127.15, 126.70, 104.98, 52.13, 38.00.

Spectral data is in agreement with the literature.[17]



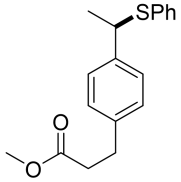
methyl 3-(4-chlorophenyl)-3-(phenylthio)propanoate (**3o**):

According to the general procedure A, methyl 3-(4-chlorophenyl)propanoate (497 mg, 2.5 mmol, 5.0 equiv.), thiophenol (55 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (4 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (77 mg, 50 % yield).

^1H NMR (400 MHz, $CDCl_3$) δ 7.33 - 7.27 (m, 2H), 7.26 - 7.22 (m, 4H), 7.22 - 7.20 (m, 1H), 7.16 (d, *J* = 8.4 Hz, 2H), 4.60 (t, *J* = 7.7 Hz, 1H), 3.60 (s, 3H), 2.91 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.92, 139.11, 133.54, 133.54, 133.23, 133.09, 128.96, 128.94, 128.61, 128.06, 51.87, 48.49, 40.59 .

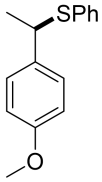
HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{16}H_{15}ClNaO_2S$ 329.0373, found 329.0382.



methyl 3-(4-(1-(phenylthio)ethyl)phenyl)propanoate (**3p**):

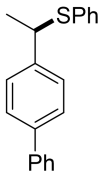
According to the general procedure A, methyl 3-(4-ethylphenyl)propanoate (481 mg, 2.5 mmol, 5.0 equiv.), thiophenol (55 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (4 % ethyl acetate/petroleum ether) to provide the

title compound as a colourless oil (135 mg, 90 % yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 - 7.26 (m, 2H), 7.25 - 7.15 (m, 5H), 7.10 (d, *J* = 7.6 Hz, 2H), 4.32(q, *J* = 6.6 Hz, 1H), 3.66 (s, 3H), 2.90 (t, *J* = 7.7 Hz, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 1.60 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 173.26, 141.05, 139.32, 135.14, 132.33, 128.62, 128.24, 127.35, 127.01, 51.56, 47.56, 35.58, 30.50, 22.25 .
HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{18}H_{20}NaO_2S$ 323.1076, found 323.1087.



(1-(4-methoxyphenyl)ethyl)(phenyl)sulfane (**3q**):

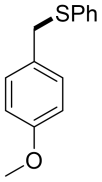
According to the general procedure A, 1-ethyl-4-methoxybenzene (340 mg, 2.5 mmol, 5.0 equiv.), thiophenol (55 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (2 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (106 mg, 87 % yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.25 (m, 2H), 7.24 - 7.12 (m, 5H), 6.80 (d, *J* = 7.2 Hz, 2H), 4.32 (q, *J* = 6.6Hz, 1H), 3.76 (s, 3H), 1.59 (d, *J* = 6.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.54, 135.14, 132.38, 128.61, 128.26, 126.97, 113.67, 55.18, 47.30, 22.38.
Spectral data is in agreement with the literature.[11]



(1-([1,1'-biphenyl]-4-yl)ethyl)(phenyl)sulfane (**3r**):

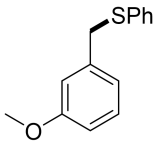
According to the general procedure A, 4-ethyl-1,1'-biphenyl (456 mg, 2.5 mmol, 5.0 equiv.), thiophenol (55 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (2 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (67 mg, 46 % yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.6 Hz, 2H), 7.51 (d, *J* = 7.2 Hz, 2H), 7.46 - 7.39 (m, 2H), 7.38 - 7.29 (m, 5H), 7.22 (d, *J* = 5.9 Hz, 3H), 4.38 (q, *J* = 6.6 Hz, 1H), 1.66 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.24, 140.73, 139.95, 135.03, 132.49, 128.71, 128.70, 127.65, 127.20, 127.14, 127.07, 126.98, 47.68, 22.26 .
HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{20}H_{18}NaS$ 313.1021, found 313.1028.



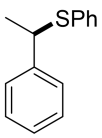
(4-methoxybenzyl)(phenyl)sulfane (**3s**):

According to the general procedure A, 1-methoxy-4-methylbenzene (305 mg, 2.5 mmol, 5.0 equiv.), thiophenol (55 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (2 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (70 mg, 61 % yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 - 7.22 (m, 4H), 7.22 - 7.14 (m, 3H), 6.81 (d, *J* = 8.4 Hz, 2H), 4.07 (s, 2H), 3.78 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.72, 136.51, 129.89, 129.74, 129.35, 128.78, 126.22, 113.87, 55.23, 38.43.
Spectral data is in agreement with the literature.[18]



(3-methoxybenzyl)(phenyl)sulfane (**3t**):

According to the general procedure A, 1-methoxy-3-methylbenzene (305 mg, 2.5 mmol, 5.0 equiv.), thiophenol (55 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (2 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (46 mg, 40 % yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.3 Hz, 2H), 7.28 – 7.22 (m, 2H), 7.22 - 7.15 (m, 2H), 6.88 (d, *J* = 7.5 Hz, 1H), 6.83 (s, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 4.09 (s, 2H), 3.76 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.62, 138.99, 129.82, 129.43, 128.81, 126.33, 121.12, 114.13, 112.90, 55.16, 39.06.
Spectral data is in agreement with the literature.[19]



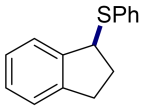
phenyl(1-phenylethyl)sulfane (**3u**):

According to the general procedure A, ethylbenzene (265 mg, 2.5 mmol, 5.0 equiv.), thiophenol (55 mg, 0.5 mmol, 1.0 equiv.), FeCl3 (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (1 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (59 mg, 55 % yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 - 7.28 (m, 5H), 7.28 - 7.15 (m, 5H), 4.33 (q, *J* = 6.6 Hz, 1H), 1.62 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.19, 132.46, 128.64, 128.36, 127.24, 127.09, 47.74, 21.70.

Spectral data is in agreement with the literature.[20]



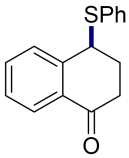
(2,3-dihydro-1*H*-inden-1-yl)(phenyl)sulfane (**3v**):

According to the general procedure A, 2,3-dihydro-1*H*-indene (295 mg, 2.5 mmol, 5.0 equiv.), thiophenol (55 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (1 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (92 mg, 81 % yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 - 7.36 (m, 2H), 7.35 - 7.27 (m, 3H), 7.26 - 7.19(m, 3H), 7.17 (d, *J* = 7.3 Hz, 1H), 4.76 (dd, *J* = 6.7, 3.8 Hz, 1H), 3.10 - 2.95 (m, 1H), 2.90 - 2.80 (m, 1H), 2.60 - 2.47 (m, 1H), 2.27 - 2.13 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.72, 142.70, 135.94, 134.73, 131.17, 128.97, 127.70, 126.62, 126.43, 124.86, 124.64, 51.74, 33.54, 30.72.

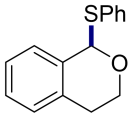
Spectral data is in agreement with the literature.[21]



4-(phenylthio)-3,4-dihydronaphthalen-1(2*H*)-one (**3w**):

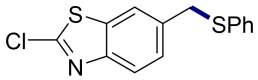
According to the general procedure A, 3,4-dihydronaphthalen-1(2*H*)-one (365 mg, 2.5 mmol, 5.0 equiv.), thiophenol (55 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (4 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (86 mg, 68 % yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.5 Hz, 1H), 7.55 - 7.44 (m, 3H), 7.42 - 7.25 (m, 5H), 4.68 - 4.62 (m, 1H), 3.30 - 3.20 (m, 1H), 2.60 (d, *J* = 17.5 Hz, 1H), 2.44 (t, *J* = 13.5 Hz, 1H), 2.31 - 2.21 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 197.23, 142.34, 134.25, 133.55, 133.10, 131.96, 129.45, 129.18, 128.12, 127.98, 127.36, 47.43, 34.07, 27.27.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{16}H_{14}NaOS$ 277.0658, found 277.0669.



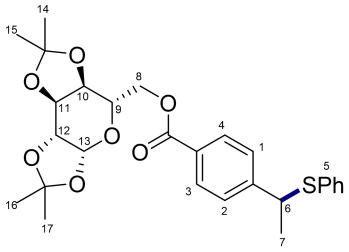
1-(phenylthio)isochromane (**3x**):

According to the general procedure A, isochromane (335 mg, 2.5 mmol, 5.0 equiv.), thiophenol (55 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (4 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (84 mg, 69 % yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.1 Hz, 2H), 7.39 - 7.30 (m, 3H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.23 - 7.18 (m, 2H), 7.15 - 7.00 (m, 1H), 6.49 (s, 1H), 4.54 (t, *J* = 10.5 Hz, 1H), 4.00 (dd, *J* = 10.4, 6.3 Hz, 1H), 3.19 - 3.03 (m, 1H), 2.69 (d, *J* = 15.2 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 135.96, 133.80, 133.70, 131.11, 128.86, 128.74, 127.68, 127.10, 127.04, 126.00, 85.81, 58.17, 27.69.
Spectral data is in agreement with the literature.[22]



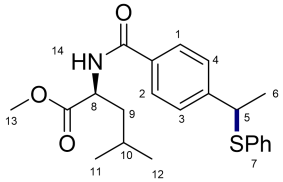
2-chloro-6-((phenylthio)methyl)benzo[*d*]thiazole (**3y**):

According to the general procedure A, 2-chloro-6-methylbenzo[*d*]thiazole (459 mg, 2.5 mmol, 5.0 equiv.), thiophenol (55 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (4 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (51 mg, 35 % yield).
^{1}H NMR (400 MHz, $CDCl_3$ δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.63 (s, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.29 - 7.17 (m, 5H), 4.18 (s, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 153.22, 150.13, 136.26, 135.80, 130.44, 128.95, 127.77, 126.84, 122.72, 120.97, 39.24.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{14}H_{10}ClNNaS_2$ 313.9835, found 313.9837.



((3a*R*,5*S*,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5*H*-*bis*([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 4-(1-(phenylthio)ethyl)benzoate (**3z**):

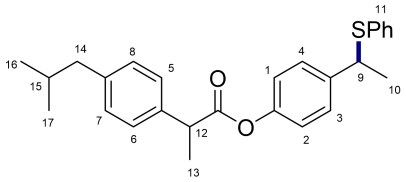
According to the general procedure A, ((3a*R*,5*S*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyl tetrahydro-5*H*-*bis*([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 4-ethylbenzoate (981 mg, 2.5 mmol, 5.0 equiv.), thiophenol (55 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (10 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (68 mg, 27 % yield).
^{1}H NMR (600 MHz, $CDCl_3$), mixture of diastereoisomers (d.r. = 1: 1): δ 8.10 - 7.85 (m, 2H, H-3, H-4), 7.40 - 7.28 (m, 2H, H-1, H-2), 7.28 - 7.17 (m, 5H, H-5), 5.65 - 5.50 m, 1H, H-13), 4.70 - 4.60 (m, 1H, H-11), 4.58 - 4.47 (m, 1H, H-12), 4.47 - 4.39 (m, 1H, H-8b), 4.39 - 4.32 (m, 2H, H-10, H-6), 4.32 - 4.27 (m, 1H, H-9), 4.25 - 4.10 (m, 1H, H-8a), 1.63 (d, *J* =6.7 Hz, 3H, H-7), 1.53 - 1.46 (m, 6H, H-14, H-15), 1.39 - 1.31 (m, 6H, H-16, H-17).
^{13}C NMR (150 MHz, $CDCl_3$), mixture of diastereoisomers (d.r. = 1: 1): δ 166.17, 132.80, 129.85, 128.76, 127.46, 127.26, 109.68 (108.79), 96.31, 71.12, 70.71 (70.51), 66.12, 63.82, 47.88, 26.01 (25.96), 24.97 (24.48), 21.99.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{27}H_{32}NaO_7S$ 523.1761, found 523.1770.



methyl (4-(1-(phenylthio)ethyl)benzoyl)-*L*-leucinate (**3aa**):

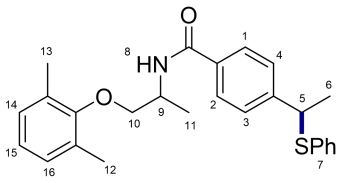
According to the general procedure A, methyl (4-ethylbenzoyl)-*L*-leucinate (693 mg, 2.5 mmol, 5.0 equiv.), thiophenol (55 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (20 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (102 mg, 53 % yield).
^{1}H NMR (400 MHz, $CDCl_3$), mixture of diastereoisomers (d.r. = 1: 1): δ 7.68 (d, *J* = 7.5 Hz, 2H, H-1 and 2), 7.30 (d, *J* = 7.7 Hz, 2H, H-3 and 4), 7.27 - 7.14 (m, 5H, H-7),

6.60 (d, *J* = 7.3 Hz, 1H, H-14), 4.90 - 4.75 (m, 1H, H-8), 4.33 (q, *J* = 6.7 Hz, 1H, H-5), 3.74 (s, 3H, H-13), 1.60 (d, *J* = 6.7 Hz, 3H, H-6), 1.35 - 1.17 (m, 2H, H-9), 1.15 - 1.04 (m, 1H, H-10), 0.99 - 0.91 (m, 6H, H-11, H-12).
^{13}C NMR (100 MHz, $CDCl_3$), mixture of diastereoisomers (d.r. = 1: 1): δ 173.69, 166.67, 147.37, 132.55, 132.51, 128.72, 127.38, 127.16, 52.33, 51.02, 47.62, 41.75, 24.91, 22.79, 22.02 (21.98).
HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{22}H_{27}NNaO_3S$ 408.1604, found 408.1607.



4-(1-(phenylthio)ethyl)phenyl 2-(4-isobutylphenyl)propanoate (**3ab**):

According to the general procedure A, 4-ethylphenyl 2-(4-isobutylphenyl)propanoate (776 mg, 2.5 mmol, 5.0 equiv.), thiophenol (55 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (4 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (86 mg, 41 % yield).
^{1}H NMR (600 MHz, $CDCl_3$) mixture of diastereoisomers (d.r. = 2.7: 1): δ 7.28 (d, *J* = 7.4 Hz, 2H, H-3, H-4), 7.26 - 7.21 (m, 4H, H-1, H-2, H-5, H-6), 7.19 (d, *J* = 6.4 Hz, 2H, H-7, H-8), 7.15 - 7.10 (m, 3H, H-11), 6.89 (d, *J* = 7.4 Hz, 1.54H, H-11), 6.84 (d, *J* = 7.4 Hz, 0.57H, H-11), 4.30 (q, *J* = 6.5 Hz, 0.74H, H-9), 3.96 (q, *J* = 6.5 Hz, 0.28H, H-9), 3.91 (q, *J* = 6.8 Hz, 1H, H-12), 2.61 (d, *J* = 6.6 Hz, 0.62H, H-14), 2.46 (d, *J* = 6.6 Hz, 1.63H, H-14), 2.21 - 2.15 (m, 0.29H, H-15), 1.88 - 1.84 (m, 0.83H, H-15), 1.61 - 1.56 (m, 6H, H-10, H-13), 0.90 (d, *J* = 5.8 Hz, 6H, H-16, H-17).
^{13}C NMR (150 MHz, $CDCl_3$) mixture of diastereoisomers (d.r. = 2.7: 1): δ 173.12, 149.72 (148.68), 140.75 (141.64), 137.18 (138.44), 132.57 (131.85), 129.46, 128.67 (128.59), 128.11, 127.16 (127.19), 121.19 (121.00), 47.39, 45.21, 45.00, 30.14 (28.22), 22.36 (22.28), 18.48, 15.56.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{27}H_{30}NaO_2S$ 441.1859, found 441.1867.



N-(1-(2,6-dimethylphenoxy)propan-2-yl)-4-(1-(phenylthio)ethyl)benzamide (**3ac**):

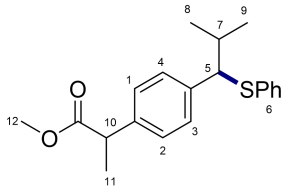
According to the general procedure A, *N*-(1-(2,6-dimethylphenoxy)propan-2-yl) -4-ethylbenzamide (779 mg, 2.5 mmol, 5.0 equiv.), thiophenol (55 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used.

After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (2 % methanol/dichloromethane) to provide the title compound as a colourless oil (78 mg, 37 % yield).

^{1}H NMR (600 MHz, $CDCl_3$) mixture of diastereoisomers (d.r. = 1: 1): δ 7.75 - 7.65 (m, 2H, H-1, H-2), 7.35 -7.25 (m, 2H, H-3, H-4), 7.23 - 7.05 (m, 5H, H-7), 7.10 - 6.85 (m, 2H, H-14, H-16), 6.78 - 6.62 (m, 1H, H-15), 4.55 (br, 1H, H-8), 4.40 - 4.27 (m, 0.49H, H-5), 4.26 - 4.13 (m, 0.48H, H-5), 4.12 - 4.03 (m, 0.49H, H-9), 4.03 - 3.97 (m, 0.47H, H-9), 3.95 - 3.85 (m, 1H, H-10), 3.85 - 3.75 (m, 1H, H-10), 2.65 (s, 1H, H-12, H-13), 2.25 (s, 5H, H-12, H-13), 1.62 (s, 1.5H, H-6), 1.54 - 1.42 (m, 3H, H-6, H-11), 1.22 (s, 1.5H, H-11).

^{13}C NMR (150 MHz, $CDCl_3$) mixture of diastereoisomers (d.r. = 1: 1): δ 166.77 (166.40), 154.74 (154.65), 147.87 (146.97), 136.58, 134.31, 132.63, 130.80 (130.61), 129.54, 128.92, 128.74 (128.66), 127.88, 127.39, 126.93, 126.18, 124.27 (124.05), 75.18 (73.79), 47.61, 45.76 (45.60), 33.61 (28.62), 21.96 (17.73), 16.20 (15.18).

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{29}NNaO_2S$ 442.1811, found 442.1820.



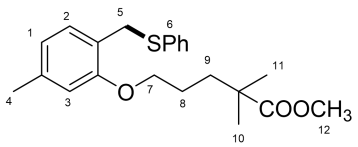
methyl 2-(4-(-2-methyl-1-(phenylthio)propyl)phenyl)propanoate (**3ad**):

According to the general procedure A, methyl 2-(4-isobutylphenyl)propanoate (551 mg, 2.5 mmol, 5.0 equiv.), thiophenol (55 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (4 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (48 mg, 29 % yield).

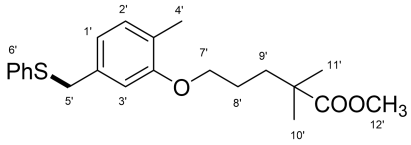
^{1}H NMR (600 MHz, $CDCl_3$) mixture of diastereoisomers (d.r. = 3: 1): δ 7.24 - 7.20 (m, 2H, H-6), 7.20 - 7.17 (m, 3H, H-6), 7.16 - 7.14 (m, 2H, H-3, H-4), 7.13 - 7.08 (m, 2H, H-1, H-2), 3.97 - 3.93 (m, 1H, H-5), 3.74 - 3.69 (m, 1H, H-10), 3.67 (s, 0.76H, H-12), 3.65 (s, 2.39H, H-12), 2.12 - 2.02 (m, 0.81H, H-7), 2.02 - 1.97 (m, 0.27H, H-7), 1.49 (d, J = 7.1 Hz, 0.81H, H-11), 1.46 (d, J = 7.1 Hz, 2.65H, H-11), 1.21 (d, J = 6.6 Hz, 0.84H, H-8, H-9), 1.10 (d, J = 6.6 Hz, 2.5H, H-8, H-9), 1.02 (d, J = 6.6 Hz, 0.8H, H-8, H-9), 0.91 (d, J = 6.6 Hz, 2.47H, H-8, H-9).

^{13}C NMR (150 MHz, $CDCl_3$) mixture of diastereoisomers (d.r. = 3: 1): δ 175.06 (175.03), 140.32, 138.87 (138.85), 135.87, 131.54, 129.47, 128.79 (128.73), 128.67 (128.52), 127.30 (127.02), 126.44, 61.01, 51.96, 44.97, 33.91, 20.96 (20.51), 18.50.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{20}H_{24}NaO_2S$ 351.1389, found 351.1396.



methyl 2,2-dimethyl-5-(5-methyl-2-((phenylthio)methyl)phenoxy)pentanoate (**3ae**)



and

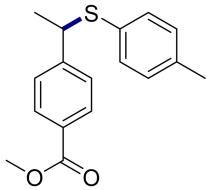
methyl 2,2-dimethyl-5-(2-methyl-5-((phenylthio)methyl)phenoxy)pentanoate (**3ae'**):

According to the general procedure A, methyl 5-(2,5-dimethylphenoxy)-2,2 -dimethylpentanoate (661 mg, 2.5 mmol, 5.0 equiv.), thiophenol (55 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (4 % ethyl acetate/petroleum ether) to provide the title compounds as a colourless oil (50 mg, 27 % yield).

^{1}H NMR (600 MHz, $CDCl_3$) mixture of **3ae** and **3ae'** (1.2: 1): δ 7.45 (d, *J* = 8.1 Hz, 0.43H, H-6'), 7.32 (d, *J* = 8.1 Hz, 0.56H, H-6), 7.31 - 7.29 (m, 1H, H-6, H-6'), 7.26 - 7.21 (m, 2H, H-6, H-6'), 7.20 - 7.12 (m, 1H, H-6, H-6'), 7.08 (d, *J* = 7.6 Hz, 0.58H, H-1), 7.02 (d, *J* = 7.6 Hz, 0.45H, H-2'), 6.76 (d, *J* = 7.5 Hz, 0.42H, H-1'), 6.71 (s, 0.43H, H-3'), 6.65 (d, *J* = 7.5 Hz, 0.56H, H-2), 6.63 (s, 0.57H, H-3), 4.12 (s, 1.12H, H-5), 4.07 (s, 0.85H, H-5'), 3.94 - 3.91 (m, 1.08H, H-7), 3.87 - 3.84 (m, 0.84H, H-7'), 3.65 (s, 1.33H, H-12'), 3.64 (s, 1.66H, H-12), 2.30 (s, 1.82H, H-4), 2.18 (s, 1.39H, H-4'), 1.73 - 1.71 (m, 2.16H, H-8, H-9), 1.71 - 1.69 (m, 1.75H, H-8', H-9'), 1.21 (s, 2.64H, H-10', H-11'), 1.19 (s, 3.3H, H-10, H-11).

^{13}C NMR (150 MHz, $CDCl_3$) mixture of **3ae** and **3ae'** (1.2: 1): δ 178.20, 157.00 (156.42), 138.40 (137.31), 135.91, 132.58, 130.39 (129.90), 129.63 (129.56), 128.75 (128.61), 127.64, 126.15 (125.85), 122.80, 120.91 (120.45), 112.29 (111.25), 68.04 (67.81), 51.66, 42.01, 39.03 (37.03), 33.01, 25.13, 21.51, 15.86.

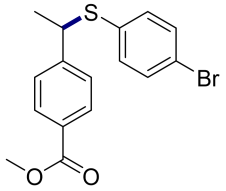
HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{22}H_{28}NaO_3S$ 395.1651, found 395.1662.



methyl 4-(1-(*p*-tolylthio)ethyl)benzoate (**4b**):

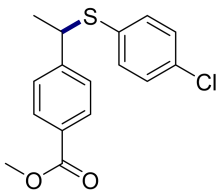
According to the general procedure A, methyl 4-ethylbenzoate (411 mg, 2.5 mmol, 5.0 equiv.), 4-methylbenzenethiol (62 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction

mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (4 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (102 mg, 71 % yield).
According to the general procedure B, methyl 4-ethylbenzoate (411 mg, 2.5 mmol, 5.0 equiv.), 1,2-*di*-*p*-tolyldisulfane (123 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (4 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (112 mg, 39 % yield).
^1H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 3.1 Hz, 2H), 7.30 (d, *J* = 3.4 Hz, 2H), 7.13 (d, *J* = 1.8 Hz, 2H), 7.01 (d, *J* = 7.2 Hz, 2H), 4.27 (q, *J* = 7.6 Hz,1H), 3.89 (s, 3H), 2.28 (s, 3H), 1.61 (d, *J* = 6.6 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 166.85, 148.79, 137.73, 133.48, 130.37, 129.60, 129.49, 128.73, 127.27, 51.99, 48.17, 21.74, 21.06.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{17}H_{18}NaO_2S$ 309.0920, found 309.0931.



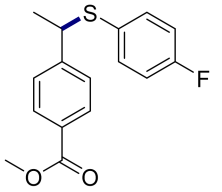
methyl 4-(1-((4-bromophenyl)thio)ethyl)benzoate (**4c**):

According to the general procedure A, methyl 4-ethylbenzoate (411 mg, 2.5 mmol, 5.0 equiv.), 4-bromobenzenethiol (95 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (4 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (104 mg, 59 % yield).
According to the general procedure B, methyl 4-ethylbenzoate (411 mg, 2.5 mmol, 5.0 equiv.), 1,2-*bis*(4-bromophenyl)disulfane (188 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (4 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (123 mg, 35 % yield).
^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.4 Hz, 2H), 7.36 - 7.24 (m, 4H), 7.08 (d, *J* = 6.6 Hz, 2H), 4.31 (q, *J* = 6.4Hz, 1H), 3.90 (s, 3H), 1.63 (d, *J* = 5.9 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.79, 148.21, 134.37, 133.31, 131.84, 129.77, 129.02, 127.26, 121.80, 52.12, 47.95, 21.86.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{16}H_{15}BrNaO_2S$ 372.9868, found 372.9877.



methyl 4-(1-((4-chlorophenyl)thio)ethyl)benzoate (**4d**):

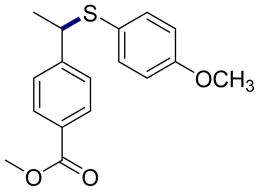
According to the general procedure A, methyl 4-ethylbenzoate (411 mg, 2.5 mmol, 5.0 equiv.), 4-chlorobenzenethiol (72 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (2 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (94 mg, 61 % yield).
According to the general procedure B, methyl 4-ethylbenzoate (411 mg, 2.5 mmol, 5.0 equiv.), 1,2-*bis*(4-chlorophenyl)disulfane (144 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (2 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (109 mg, 36 % yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.23 - 7.11 (m, 4H), 4.30 (q, J = 7.1 Hz, 1H), 3.90 (s, 3H), 1.63 (d, J = 7.0 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.78, 149.27, 135.29, 133.66, 130.75, 130.06, 129.91, 128.26, 53.07, 49.14, 22.82.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{16}H_{15}ClNaO_2S$ 329.0373, found 329.0378.



methyl 4-(1-((4-fluorophenyl)thio)ethyl)benzoate (**4e**):

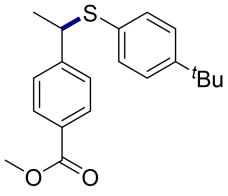
According to the general procedure A, methyl 4-ethylbenzoate (411mg, 2.5 mmol, 5.0 equiv.), 4-fluorobenzenethiol (64 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (4 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (54 mg, 37 % yield).
According to the general procedure B, methyl 4-ethylbenzoate (411 mg, 2.5 mmol, 5.0 equiv.), 1,2-*bis*(4-fluorophenyl)disulfane (127 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the

reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (4 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (67 mg, 23 % yield).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.7 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 7.22 - 7.15 (m, 2H), 6.89 (t, *J* = 8.2 Hz, 2H), 4.24 (q, *J* = 6.4 Hz, 1H), 3.90 (s, 3H), 1.62 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 166.81, 163.48 (161.83), 148.40, 135.98, 135.93, 129.65, 128.92, 127.28, 115.90 (115.75), 52.05, 48.65, 21.52.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{16}H_{15}FNaO_2S$ 313.0669, found 313.0672.



methyl 4-(1-((4-methoxyphenyl)thio)ethyl)benzoate (**4f**):

According to the general procedure A, methyl 4-ethylbenzoate (411 mg, 2.5 mmol, 5.0 equiv.), 4-methoxybenzenethiol (70 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (4 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (101 mg, 67 % yield).
According to the general procedure B, methyl 4-ethylbenzoate (411 mg, 2.5 mmol, 5.0 equiv.), 1,2-*bis*(4-methoxyphenyl)disulfane (139 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (4 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (88 mg, 29 % yield).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 8.8 Hz, 2H), 4.18 (q, *J* = 7.0 Hz, 1H), 3.89 (s, 3H), 3.75 (s, 3H), 1.60 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 166.82, 159.68, 148.76, 136.13, 129.49, 128.61, 127.27, 124.13, 114.16, 55.14, 51.95, 48.76, 21.29.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{17}H_{18}NaO_3S$ 325.0869, found 325.0876.



methyl 4-(1-((4-(*tert*-butyl)phenyl)thio)ethyl)benzoate (**4g**):

According to the general procedure A, methyl 4-ethylbenzoate (411 mg, 2.5 mmol,

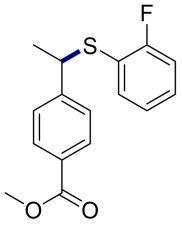
5.0 equiv.), 4-(*tert*-butyl)benzenethiol (83 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (4 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (76 mg, 46 % yield).

According to the general procedure B, methyl 4-ethylbenzoate (411 mg, 2.5 mmol, 5.0 equiv.), 1,2-*bis*(4-(*tert*-butyl)phenyl)disulfane (165 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (4 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (87 mg, 27 % yield).

^1H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 4.30 (q, *J* = 6.7 Hz, 1H), 3.90 (s, 3H), 1.62 (d, *J* = 6.7 Hz, 3H), 1.27 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 166.92, 150.84, 148.88, 132.81, 130.72, 129.68, 128.80, 127.30, 125.80, 52.04, 48.01, 34.51, 31.20, 22.01.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{20}H_{24}NaO_2S$ 351.1389, found 351.1395.



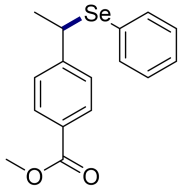
methyl 4-(1-((2-fluorophenyl)thio)ethyl)benzoate (**4h**):

According to the general procedure A, methyl 4-ethylbenzoate (411 mg, 2.5 mmol, 5.0 equiv.), 2-fluorobenzenethiol (64 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (4 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (48 mg, 33 % yield).

According to the general procedure B, methyl 4-ethylbenzoate (411 mg, 2.5 mmol, 5.0 equiv.), 1,2-bis(2-fluorophenyl)disulfane (127 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (4 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (51 mg, 18 % yield).

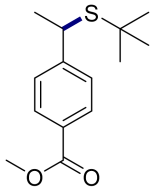
^1H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.23 - 7.11 (m, 2H), 7.01 (t, *J* = 8.7 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 4.46 (q, *J* = 6.9 Hz, 1H), 3.89 (s, 3H), 1.64 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 166.86, 163.41 (161.78), 148.24, 135.66, 130.08 (130.03), 129.70, 129.00, 127.25, 124.31 (124.29), 121.15 (121.03), 115.79 (115.64), 52.07, 46.83, 21.73.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{16}H_{15}FNaO_2S$ 313.0669, found 313.0677.



methyl 4-(1-(phenylselanyl)ethyl)benzoate (**4i**):

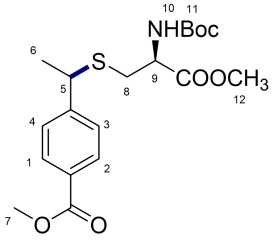
According to the general procedure A, methyl 4-ethylbenzoate (411 mg, 2.5 mmol, 5.0 equiv.), benzeneselenol (79 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (4 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (61 mg, 38 % yield).
According to the general procedure B, methyl 4-ethylbenzoate (411 mg, 2.5 mmol, 5.0 equiv.), diphenyl diselenide (156 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (4 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (67 mg, 21 % yield).
^{1}H NMR (400 MHz,$CDCl_3$) δ 7.90 (d, J = 7.9 Hz, 2H), 7.38 (d, J = 7.2 Hz, 2H), 7.31 - 7.15 (m, 5H), 4.45 (q, J = 6.7 Hz, 1H), 3.90 (s, 3H), 1.76 (d, J = 6.9 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.87, 149.08, 135.75, 129.58, 128.86, 128.12, 127.16, 52.03, 41.91, 21.64.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{16}H_{16}NaO_2Se$ 343.0208, found 343.0213.



methyl 4-(1-(*tert*-butylthio)ethyl)benzoate (**4j**):

According to the general procedure A, methyl 4-ethylbenzoate (411 mg, 2.5 mmol, 5.0 equiv.), 4-(*tert*-butyl)benzenethiol (45 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (4 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (73 mg, 58 % yield).

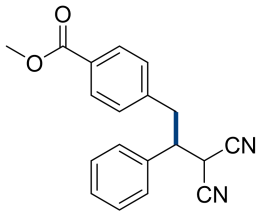
According to the general procedure B, methyl 4-ethylbenzoate (411 mg, 2.5 mmol, 5.0 equiv.), 1,2-*di-tert*-butyldisulfane (89 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (4 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (64 mg, 26 % yield).
^1H NMR (400 MHz, $CDCl_3$) δ 8.07 - 7.94 (m, 2H), 7.51 - 7.35 (m, 2H), 4.03 (q, J = 6.5 Hz, 1H), 3.91 (s, 3H), 1.67 (d, J = 6.1 Hz, 3H), 1.29 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.83, 147.8, 129.98, 129.70, 129.18, 127.66, 126.53 52.07, 50.87, 48.00, 30.05, 21.05.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{14}H_{20}NaO_2S$ 275.1076, found 275.1079.



methyl 4-(1-(((*R*)-2-((*tert*-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)thio)ethyl) benzoate (**4k**):

According to the general procedure A, methyl 4-ethylbenzoate (411 mg, 2.5 mmol, 5.0 equiv), methyl (*tert*-butoxycarbonyl)-*L*-cysteinate (118 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (2 % methanol/dichloromethane) to provide the title compound as a colourless oil (113 mg, 57 % yield).
According to the general procedure B, methyl 4-ethylbenzoate (411 mg, 2.5 mmol, 5.0 equiv.), dimethyl 3,3'-disulfanediyl(2*R*,2'*R*)-*bis*(2-((*tert*-butoxycarbonyl)amino) propanoate) (234 mg, 0.5 mmol, 1.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (2 % methanol/dichloromethane) to provide the title compound as a colourless oil (155 mg, 39 % yield).
^1H NMR (400 MHz, $CDCl_3$) mixture of diastereoisomers (d.r. = 2: 1): δ 8.04 - 7.95 (m, 2H, H-1, H-2), 7.45 - 7.37 (m, 2H, H-3, H-4), 5.42 - 5.32 (m, 0.37H, H-9), 5.30 - 5.18 (m, 0.74H, H-9), 4.56 (br, 0.38H, H-10), 4.47 (br, 0.79H, H-10), 4.16 - 4.06 (m, 0.7H, H-5), 4.06 - 3.98 (m, 0.42H, H-5), 3.97 - 3.88 (m, 3H, H-7), 3.77 - 3.74 (m, 0.97H, H-12), 3.74 - 3.66 (m, 1.95H, H-12), 3.03 - 2.90 (m, 0.68H, H-8), 2.76 - 2.65 (m, 1.35H, H-8), 1.67 (d, J = 6.6 Hz, 1.05H, H-6), 1.55 (d, J = 6.6 Hz, 1.97H, H-6), 1.47 (s, 3H, H-11), 1.44 (s, 6H, H-11).

^{13}C NMR (100 MHz, $CDCl_3$) mixture of diastereoisomers (d.r. = 2: 1): δ 171.47 (171.25), 166.72, 154.97, 148.63, 147.35 (147.06), 129.94 (129.78), 127.70 (127.68), 127.37 (127.31), 80.17, 52.97 (52.12), 49.76 (49.56), 44.12 (43.96), 33.55, 28.27, 22.29 (20.16).
HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{19}H_{27}NNaO_6S$ 420.1451, found 420.1462.



methyl 4-(3,3-dicyano-2-phenylpropyl)benzoate (**3l'**):

According to the modified general procedure A, methyl 4-methylbenzoate (375 mg, 2.5 mmol, 5.0 equiv.), 1,2-diphenyldisulfane (109 mg, 0.5 mmol, 1.0 equiv.), benzalmalononitrile (154 mg, 1.0 mmol, 2.0 equiv.), $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol%), KCl (7.5 mg, 0.1 mmol, 20 mol%), PIDA (16.1 mg, 0.05 mmol, 10 mol%). and 5.0 mL anhydrous CH_3CN were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (10 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (183 mg, 60% yield).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, J = 7.3 Hz, 2H), 7.37 (d, J = 7.5 Hz, 3H), 7.33 (d, J = 6.5 Hz, 2H), 7.20 (d, J = 7.4 Hz, 2H), 3.94 (d, J = 4.4 Hz, 1H), 3.88 (s, 3H), 3.51 (d, J = 6.8 Hz, 1H), 3.37 (dd, J = 13.6, 7.4 Hz, 1H), 3.28 (dd, J = 13.1, 8.5 Hz, 1H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 166.49 141.75, 135.79, 130.04, 129.19, 129.13, 129.02, 128.92, 127.81, 111.80, 111.43, 52.03, 47.74, 38.33, 28.84.
HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{17}N_2O_2$ 305.1285, found 305.1293.

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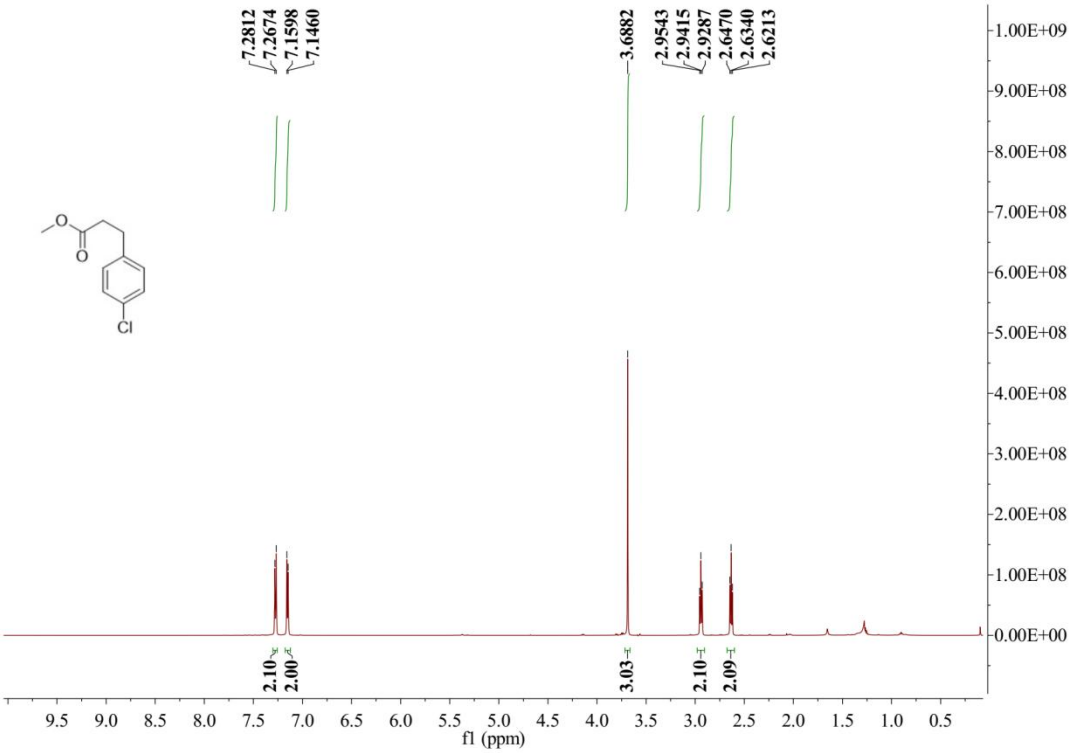
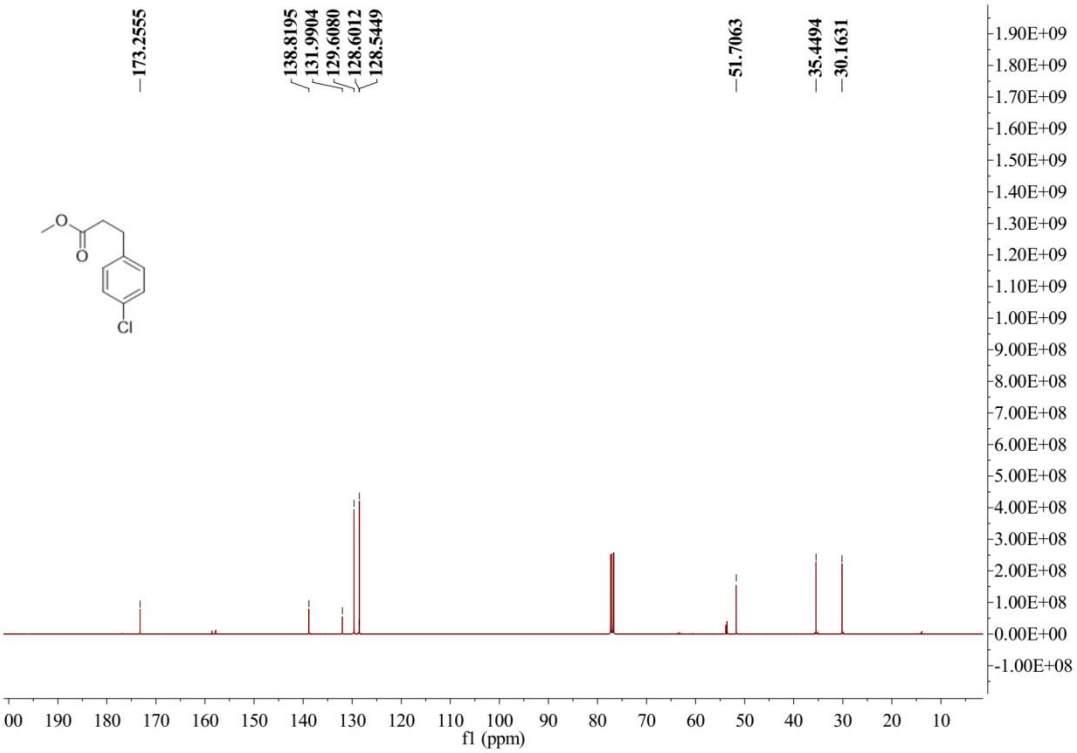
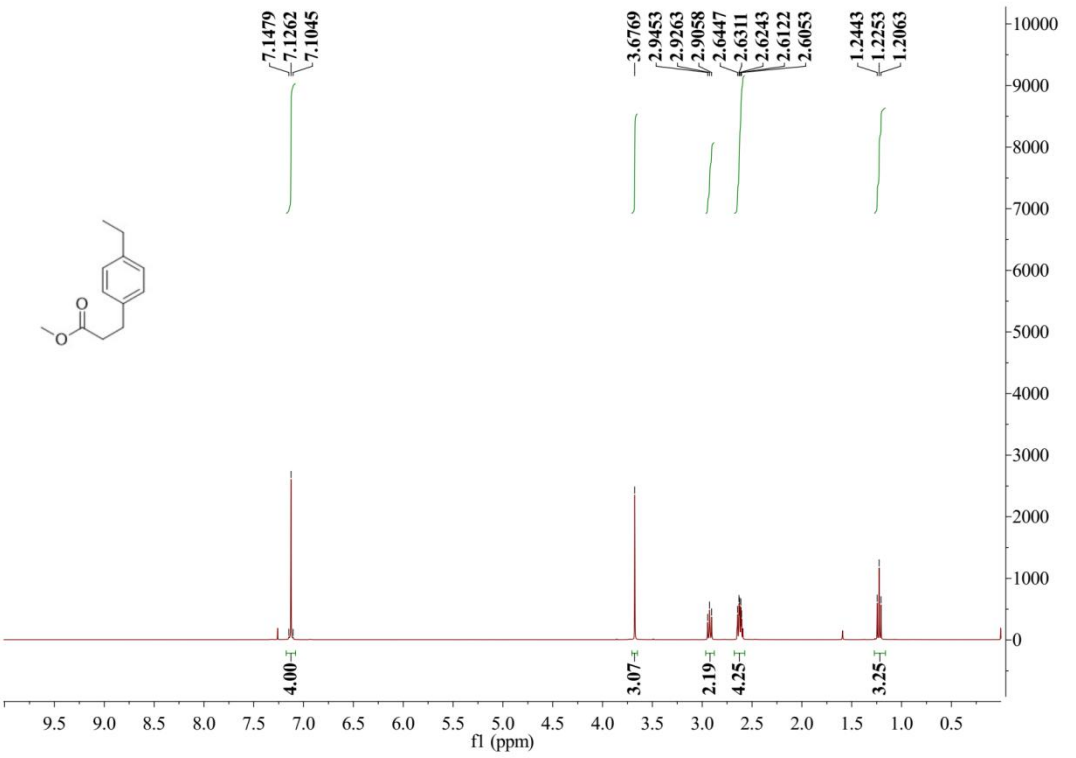
5. Spectral Data for Products



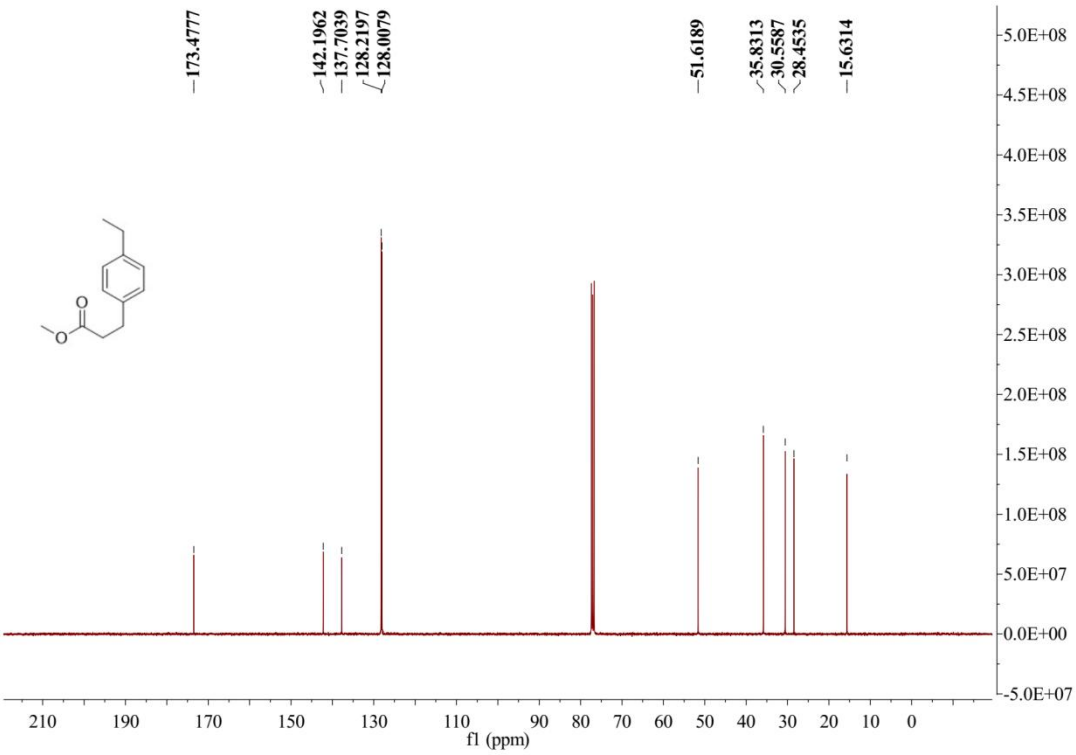
^{1}H NMR (600 MHz, $CDCl_3$) of **1o**



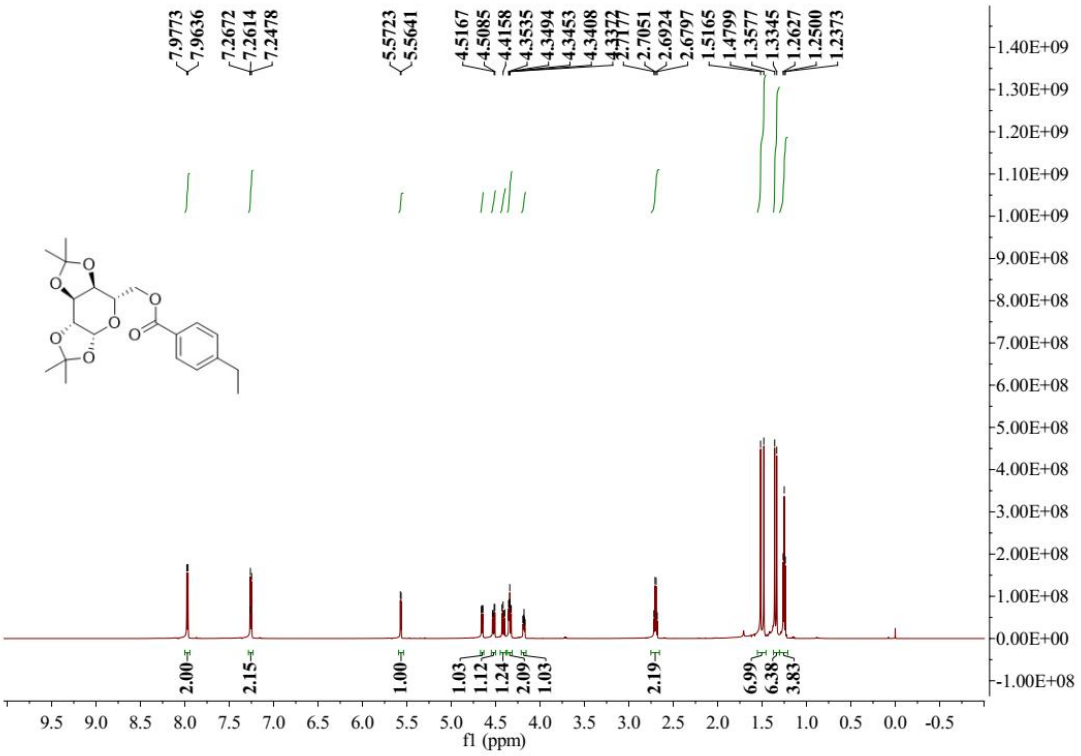
^{13}C NMR (100 MHz, $CDCl_3$) of **1o**



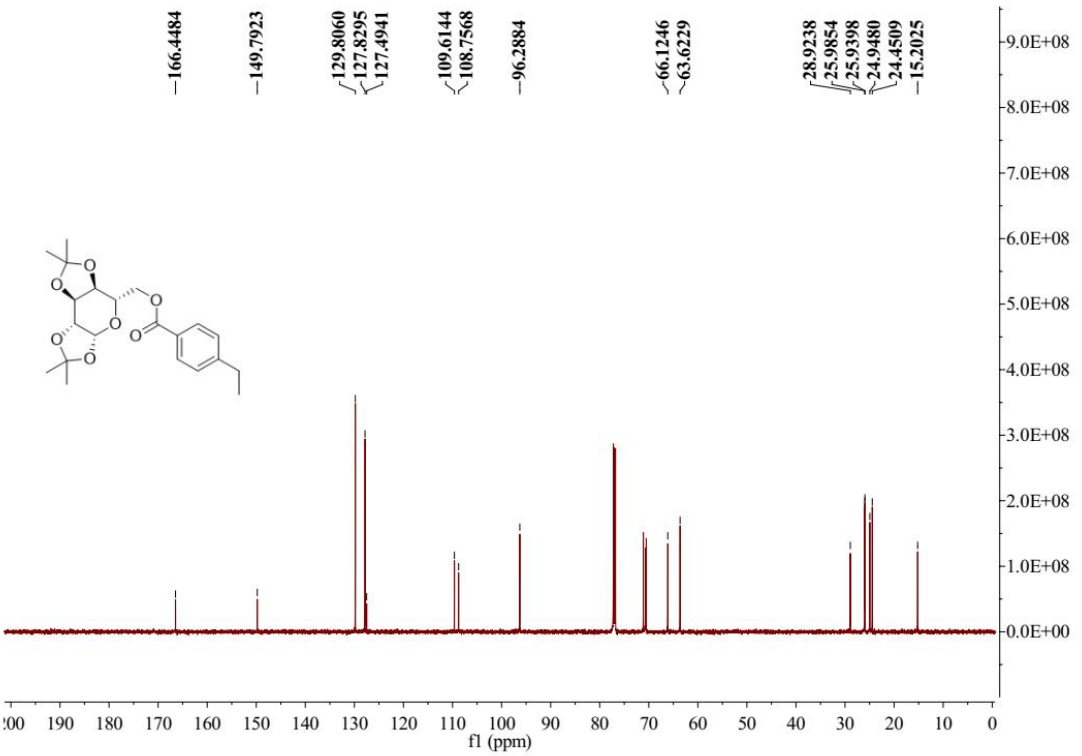
^{1}H NMR (400 MHz, $CDCl_3$) of **1p**



^{13}C NMR (100 MHz, $CDCl_3$) of **1p**



^{1}H NMR (600 MHz, $CDCl_3$) of **1z**



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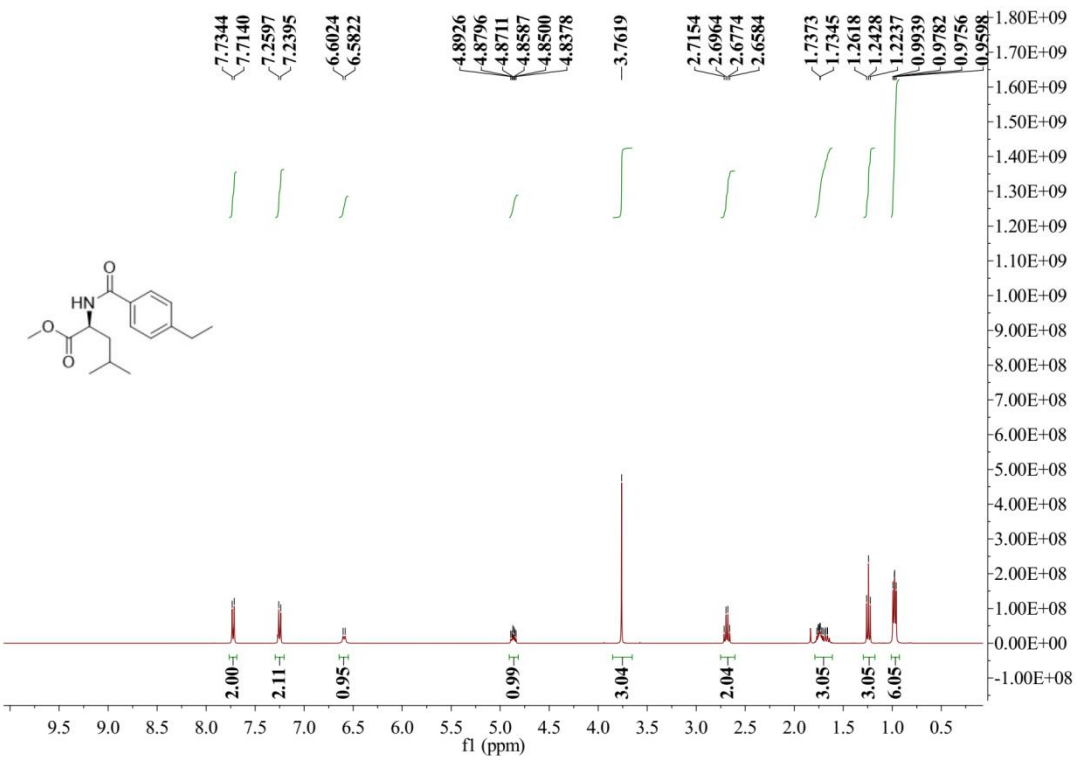
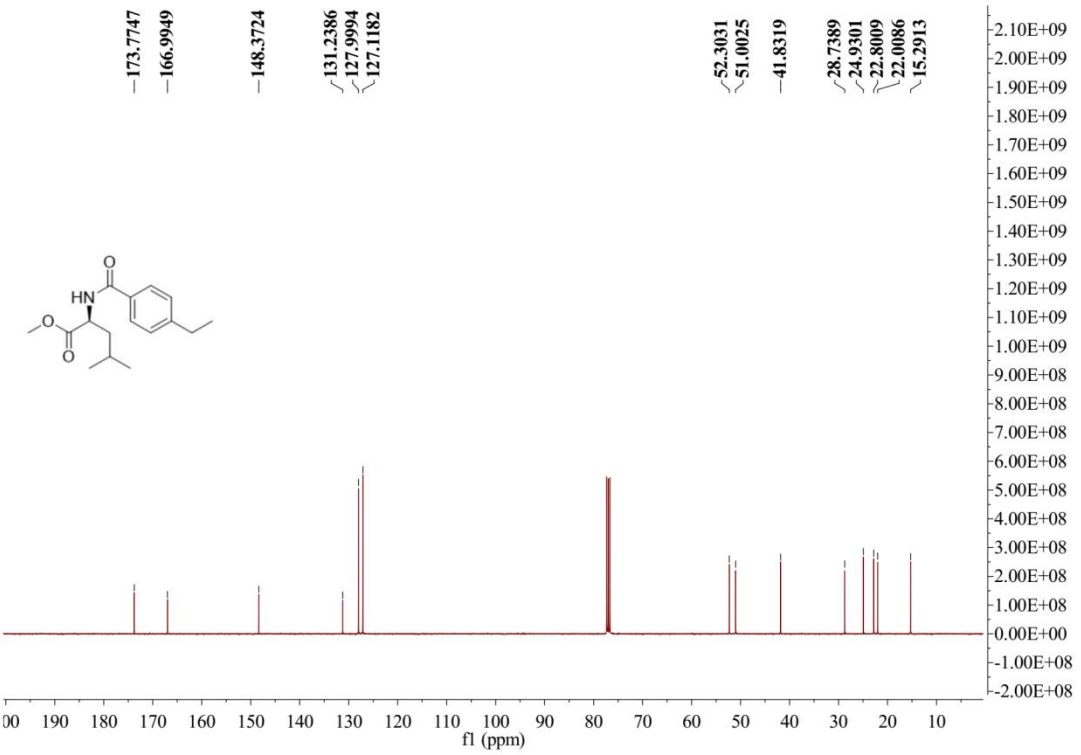
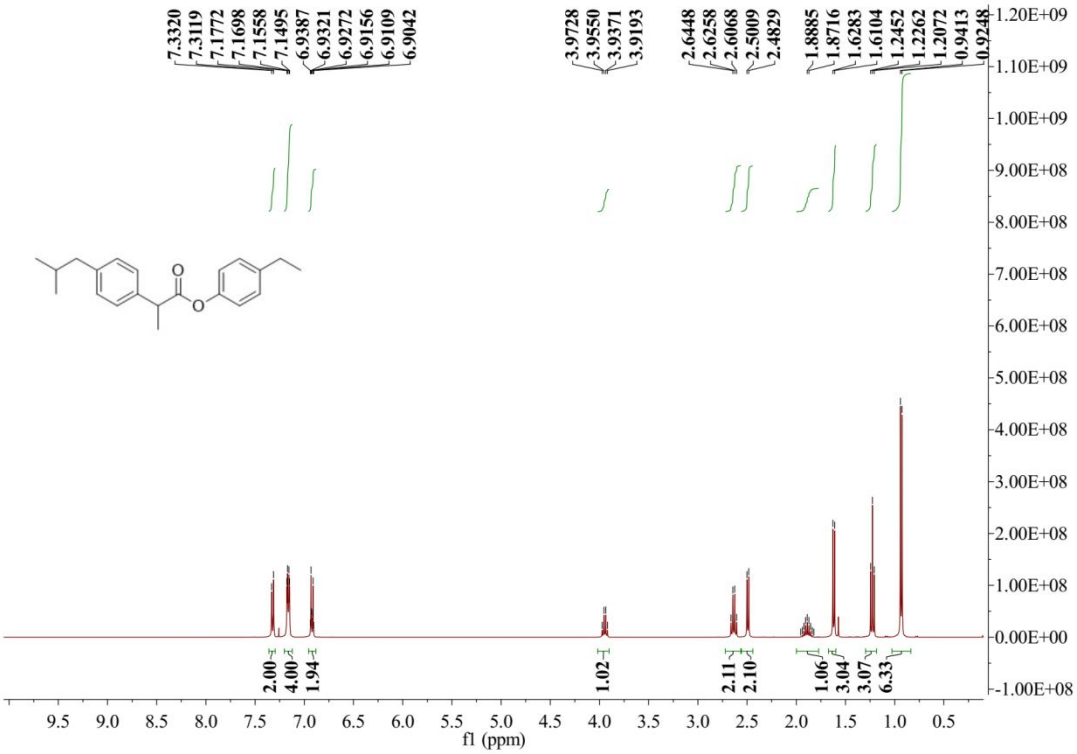


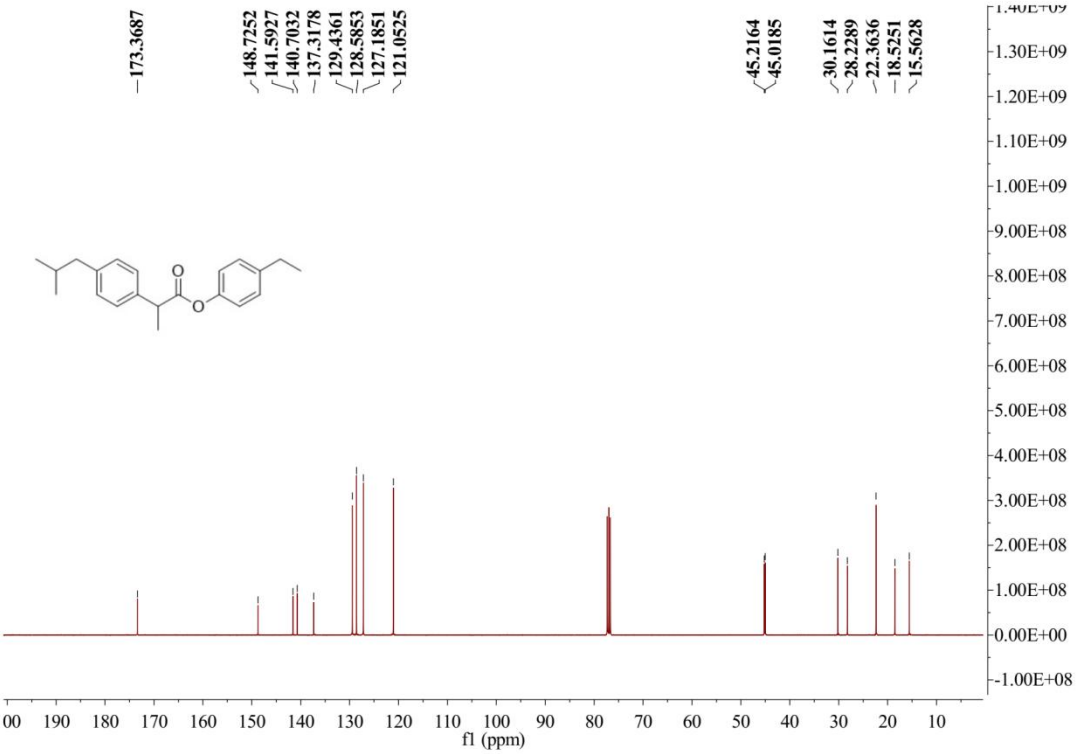
^{1}H NMR (400 MHz, $CDCl_3$) of **1aa**



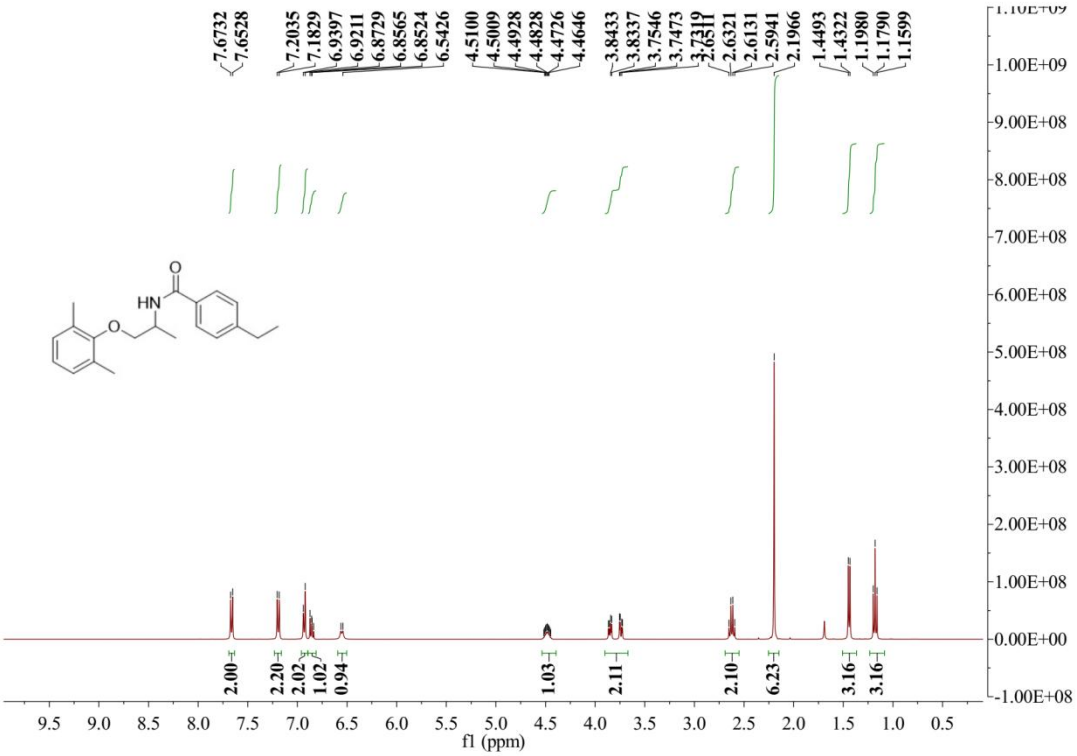
^{13}C NMR (100 MHz, $CDCl_3$) of **1aa**



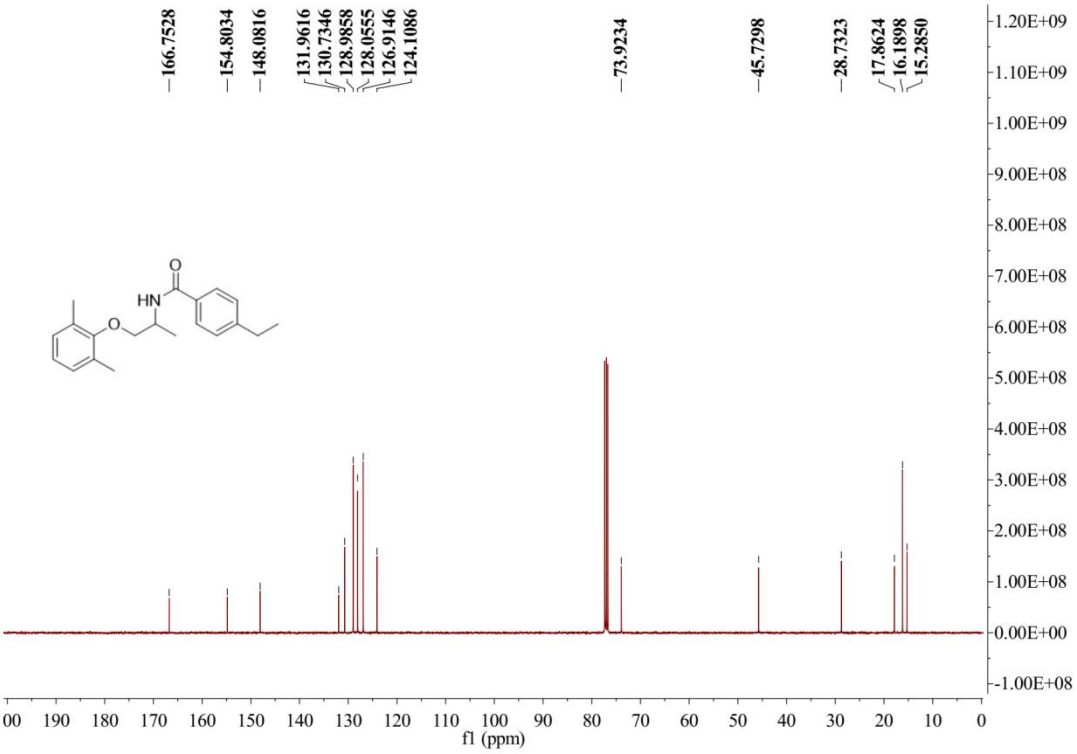
^{1}H NMR (400 MHz, $CDCl_3$) of **1ab**



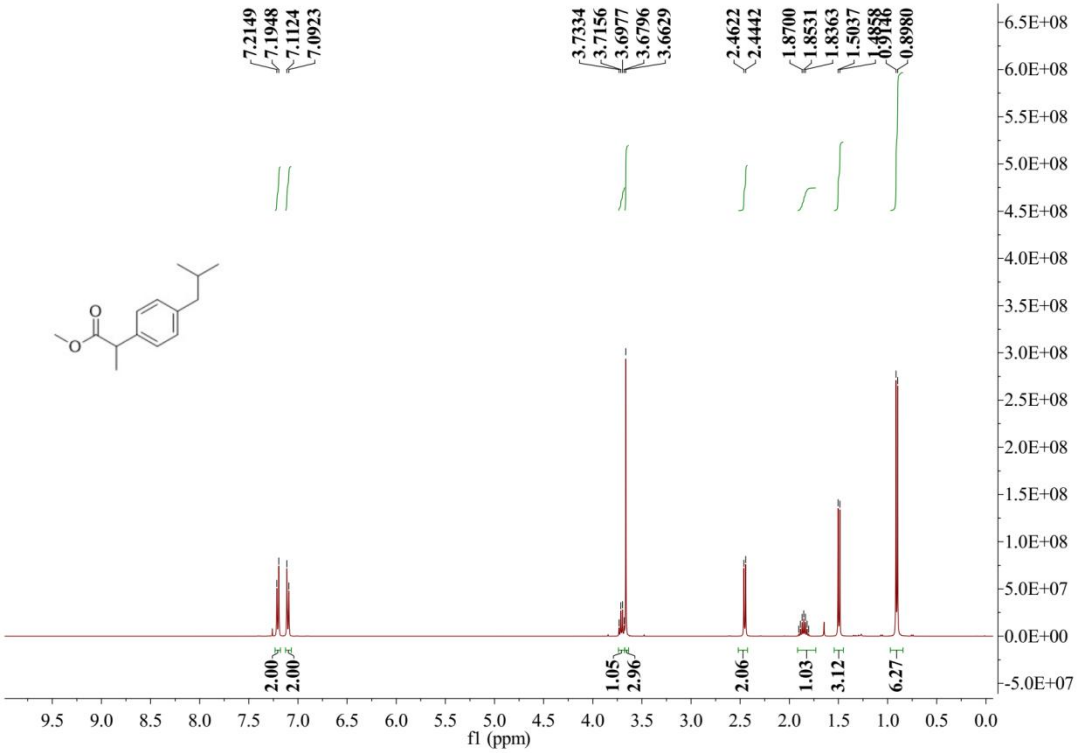
^{13}C NMR (100 MHz, $CDCl_3$) of **1ab**



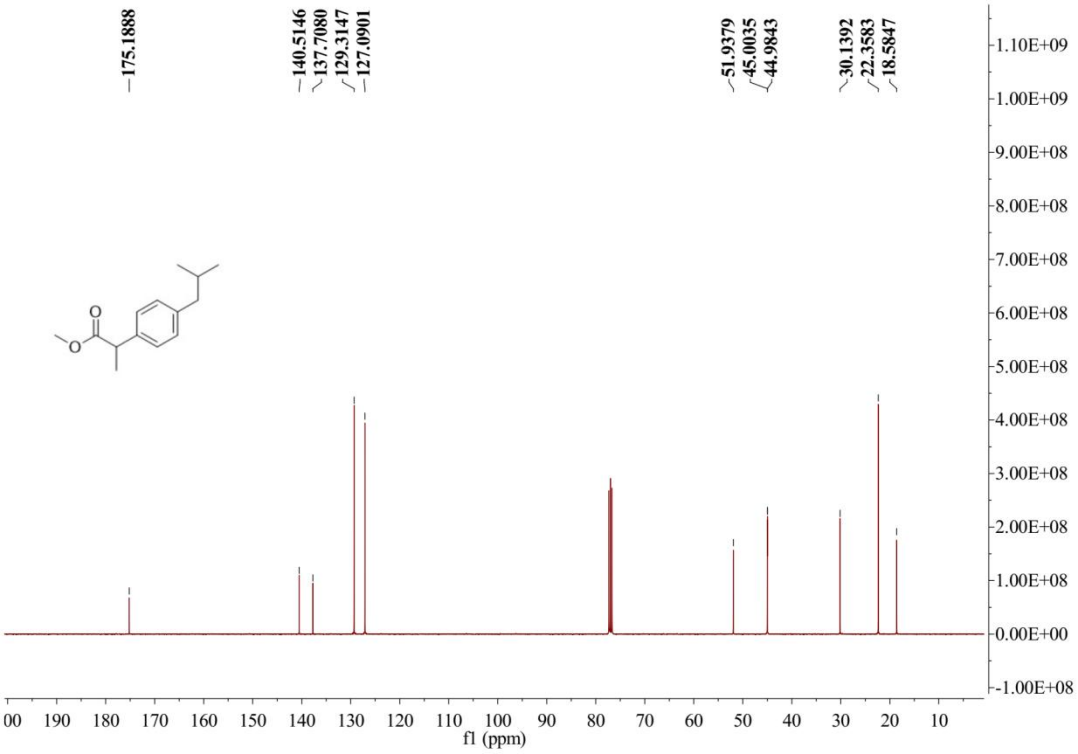
^{1}H NMR (400 MHz, $CDCl_3$) of **1ac**



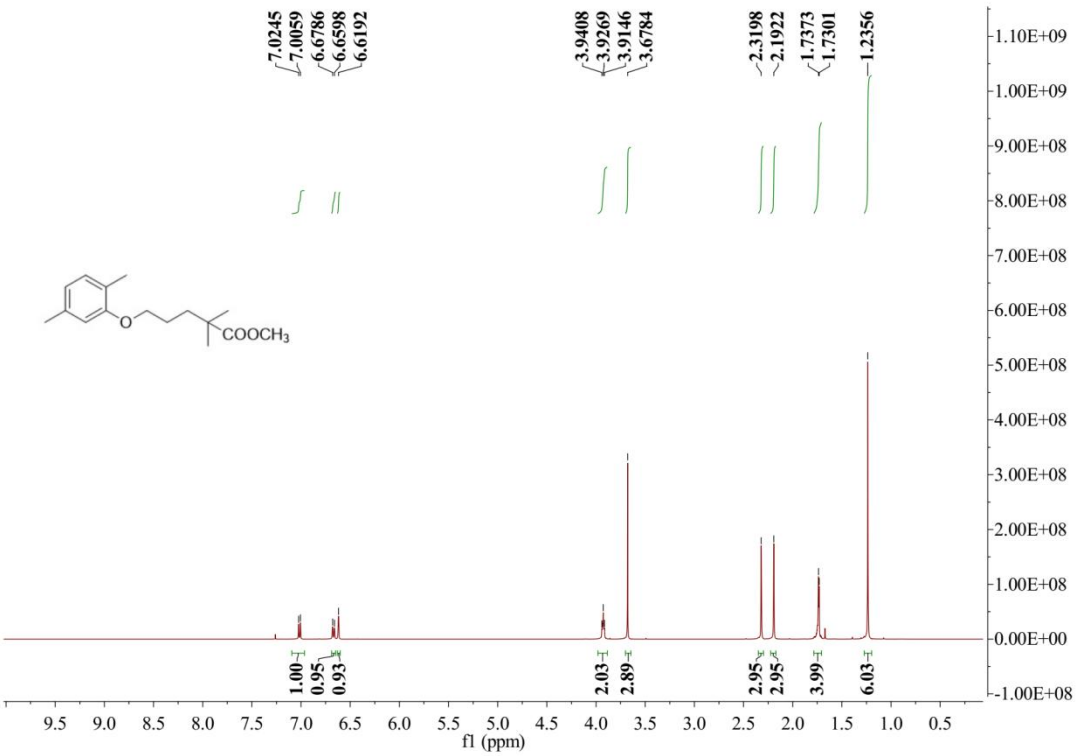
^{13}C NMR (100 MHz, $CDCl_3$) of **1ac**



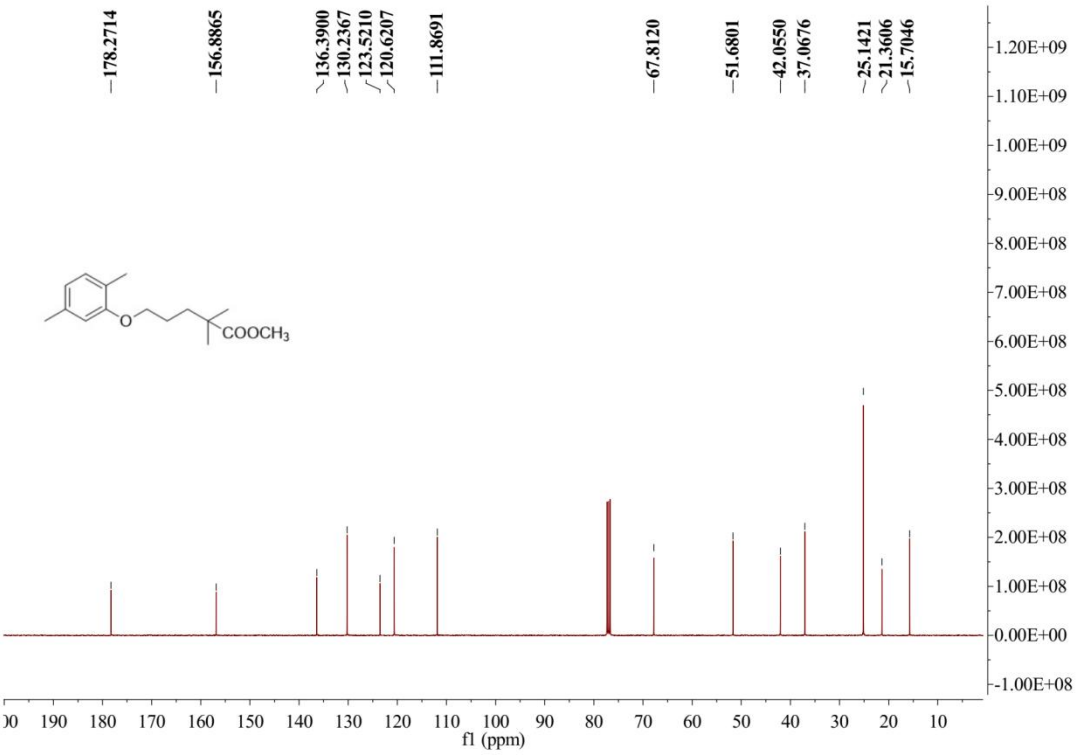
^{1}H NMR (400 MHz, $CDCl_3$) of **1ad**



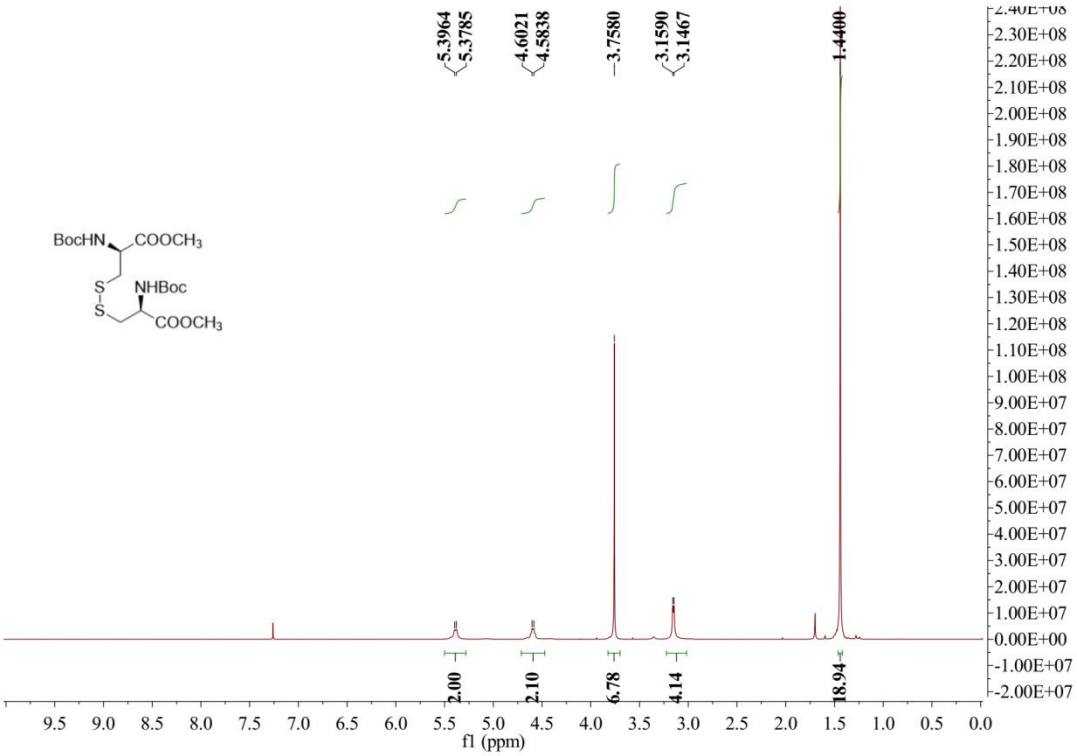
^{13}C NMR (100 MHz, $CDCl_3$) of **1ad**



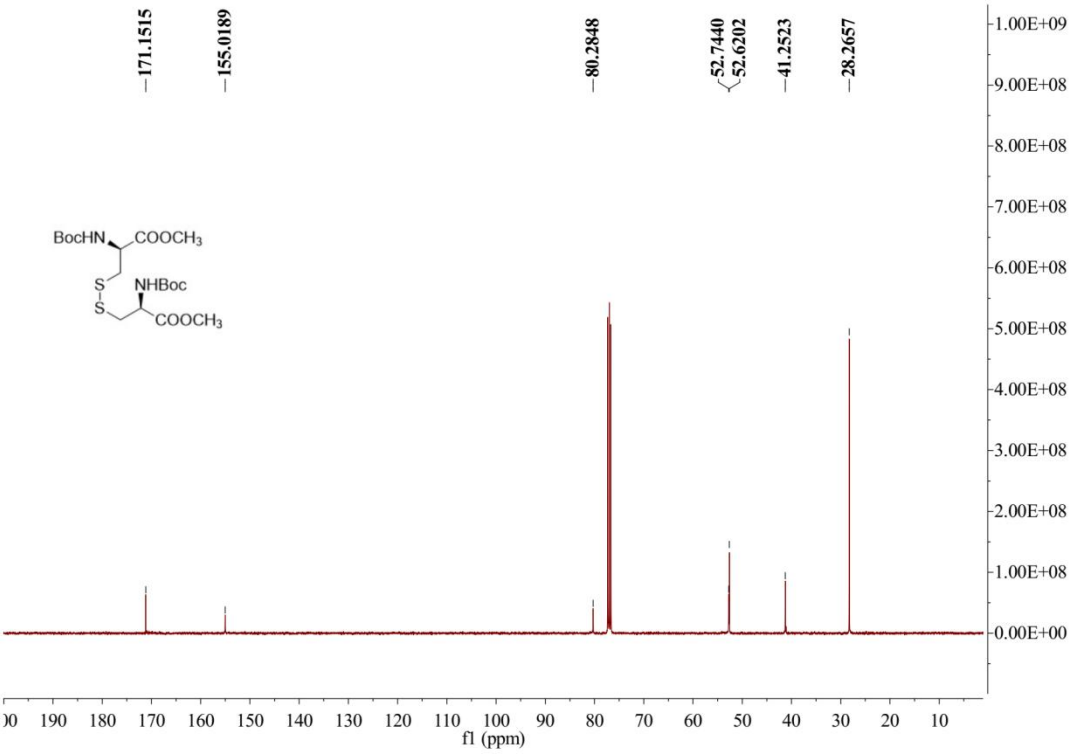
^{1}H NMR (400 MHz, $CDCl_3$) of **1ae**



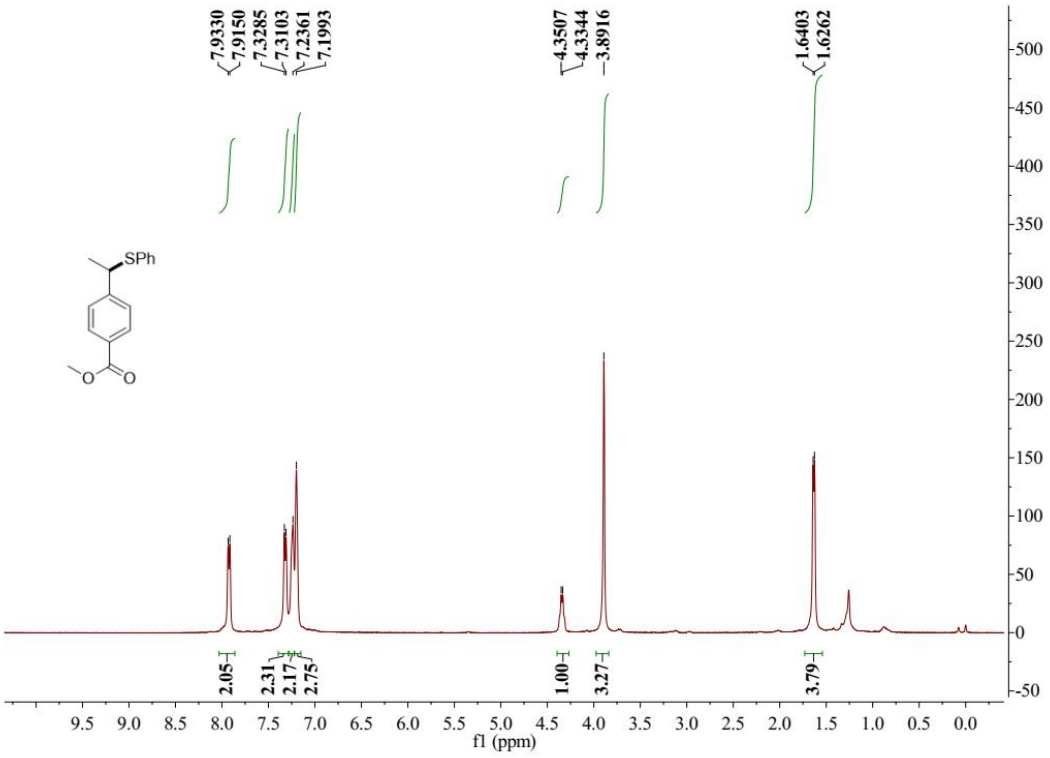
^{13}C NMR (100 MHz, $CDCl_3$) of **1ae**



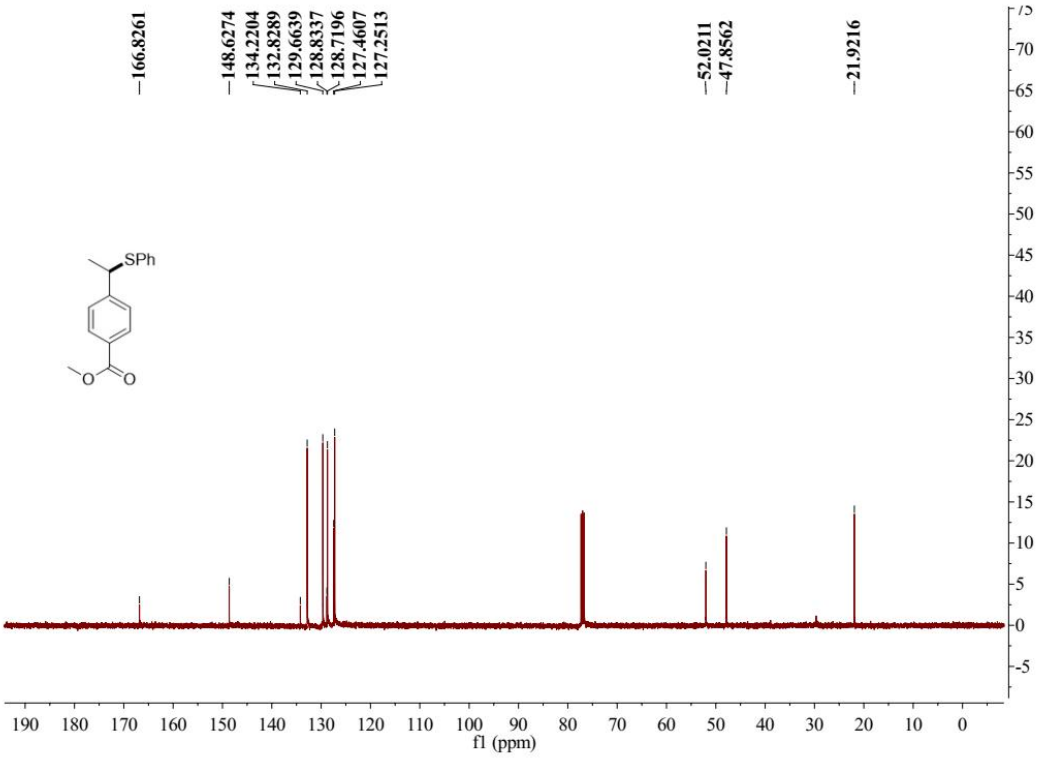
^{1}H NMR (400 MHz, $CDCl_3$) of **2k**



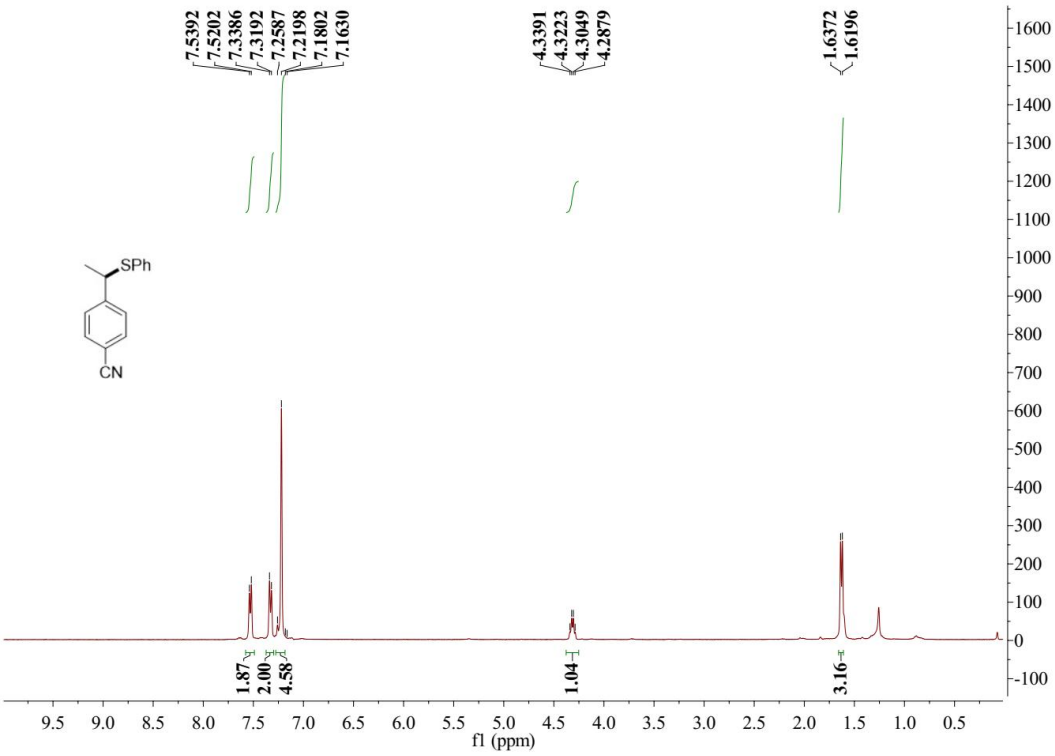
^{13}C NMR (100 MHz, $CDCl_3$) of **2k**



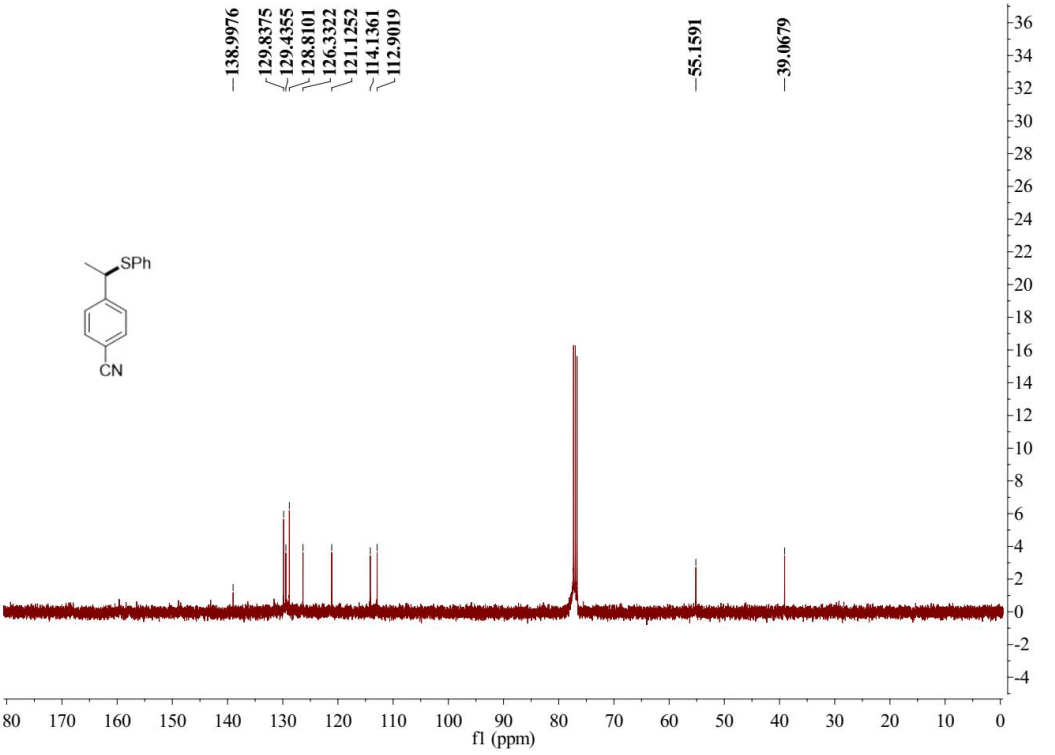
^{1}H NMR (400 MHz, $CDCl_3$) of **3a**



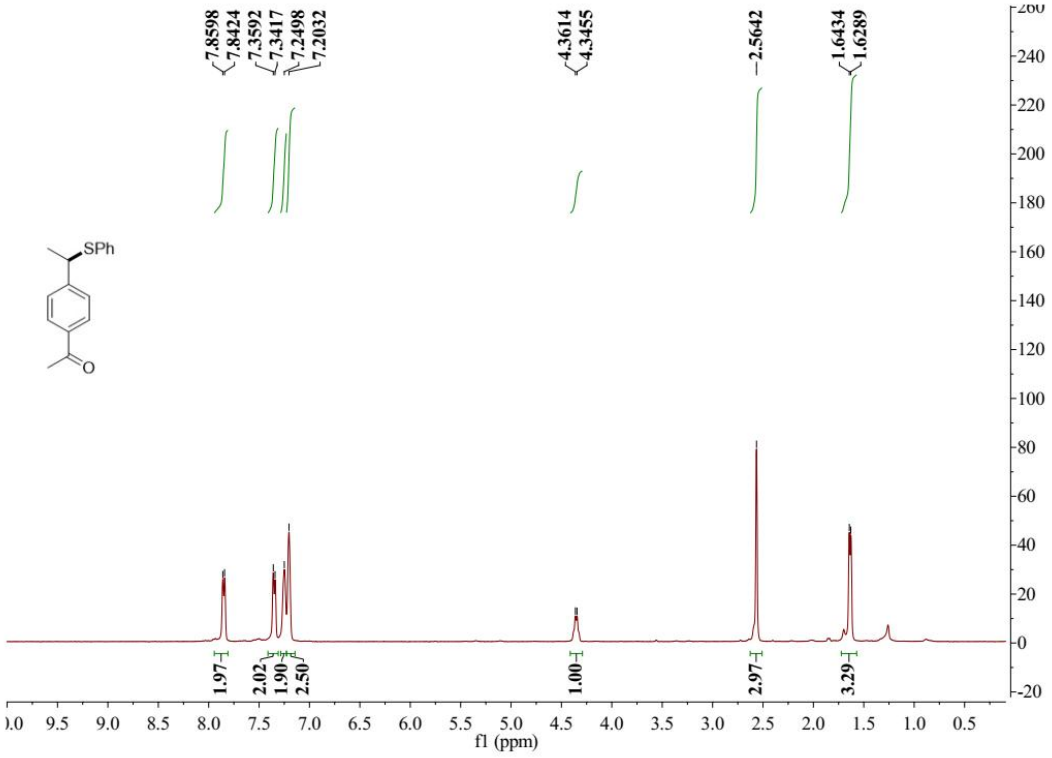
^{13}C NMR (100 MHz, $CDCl_3$) of **3a**



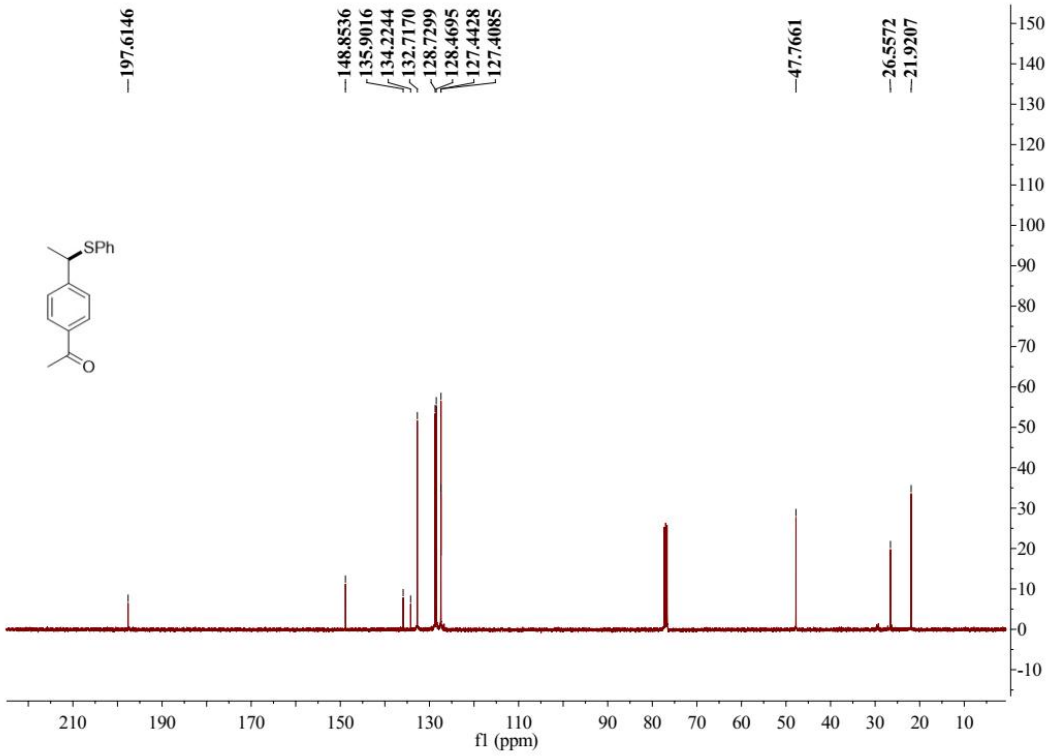
^{1}H NMR (400 MHz, $CDCl_3$) of **3b**



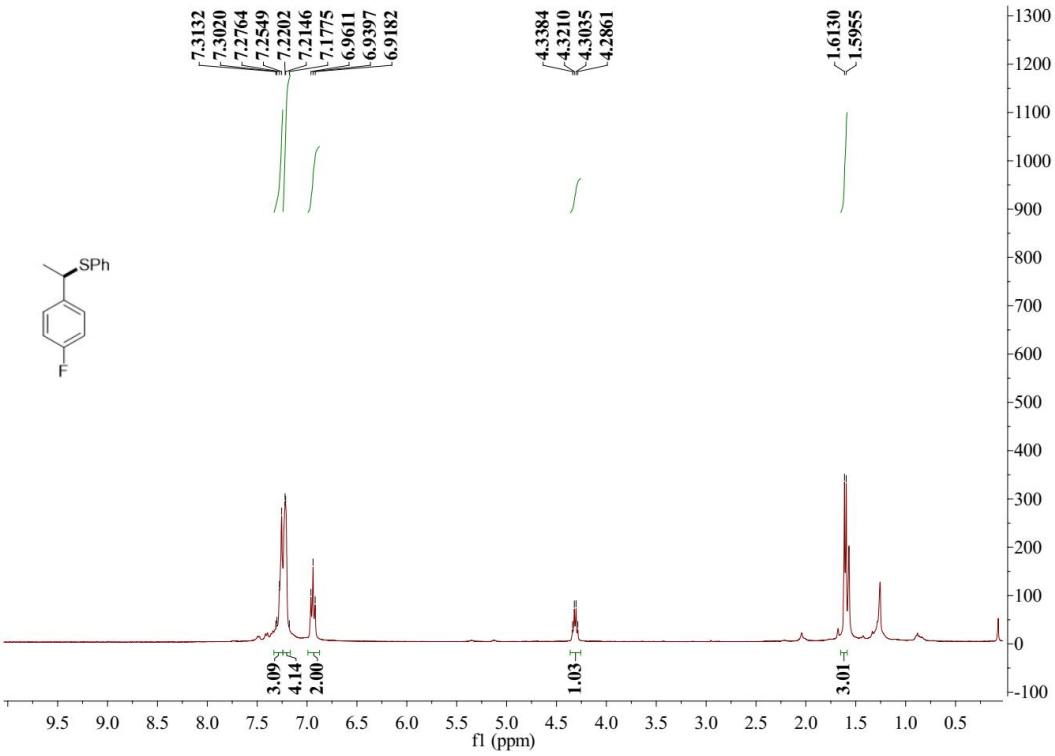
^{13}C NMR (100 MHz, $CDCl_3$) of **3b**



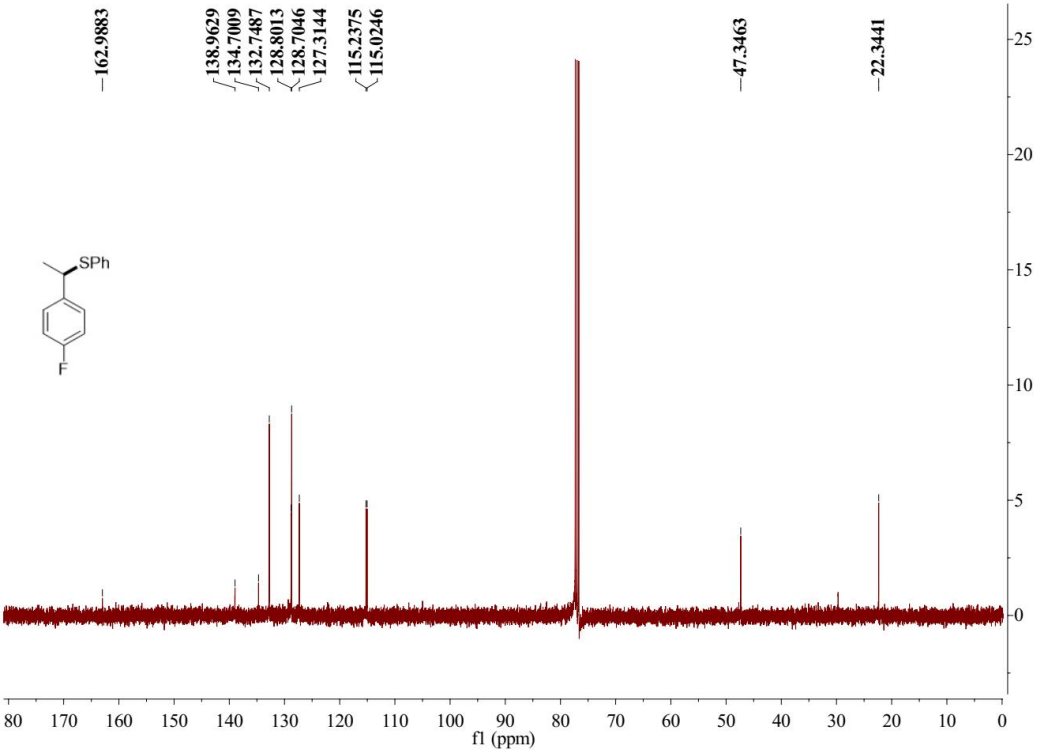
^{1}H NMR (400 MHz, $CDCl_3$) of **3c**



^{13}C NMR (100 MHz, $CDCl_3$) of **3c**



^{1}H NMR (400 MHz, $CDCl_3$) of **3d**



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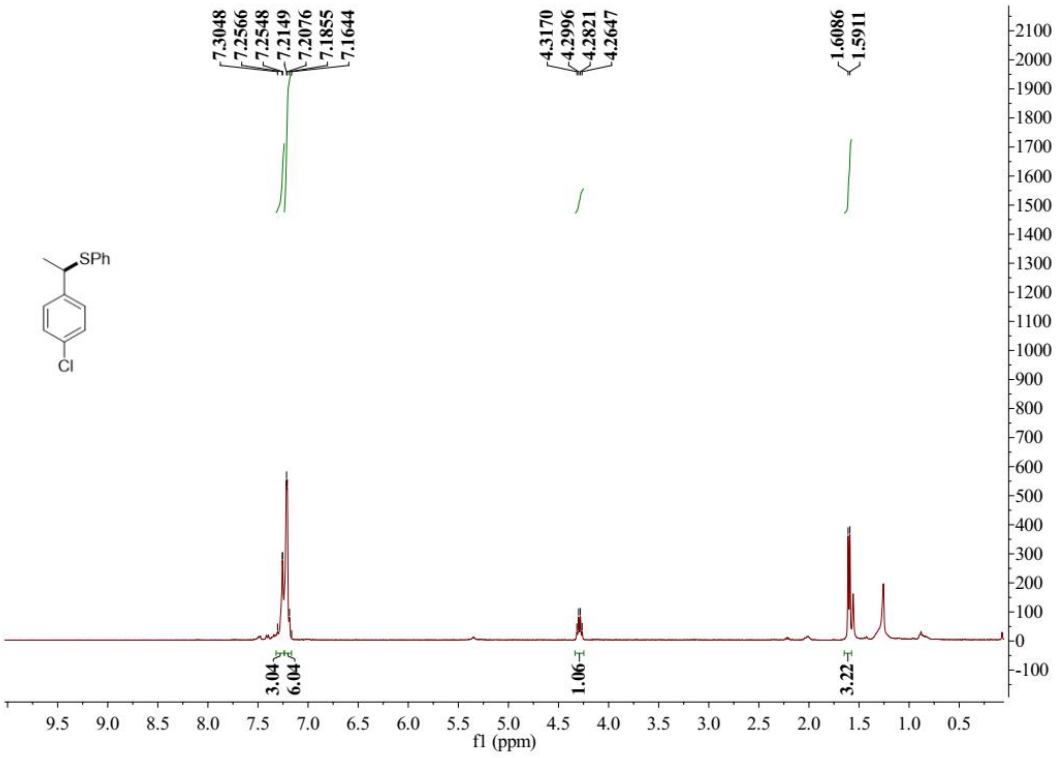

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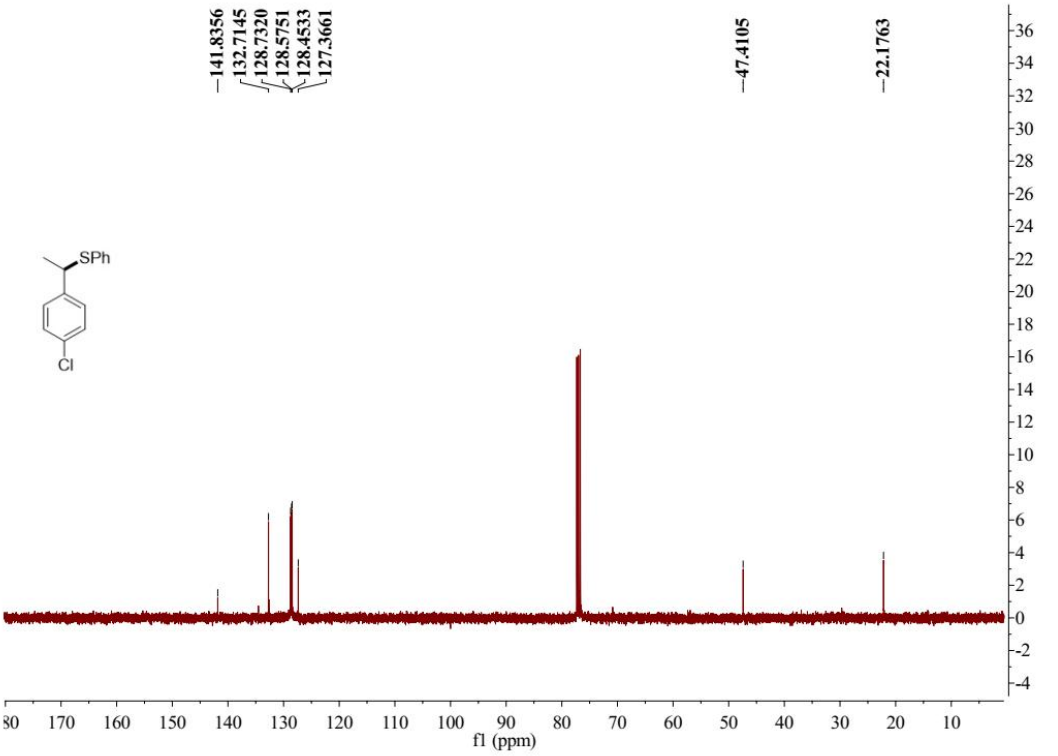

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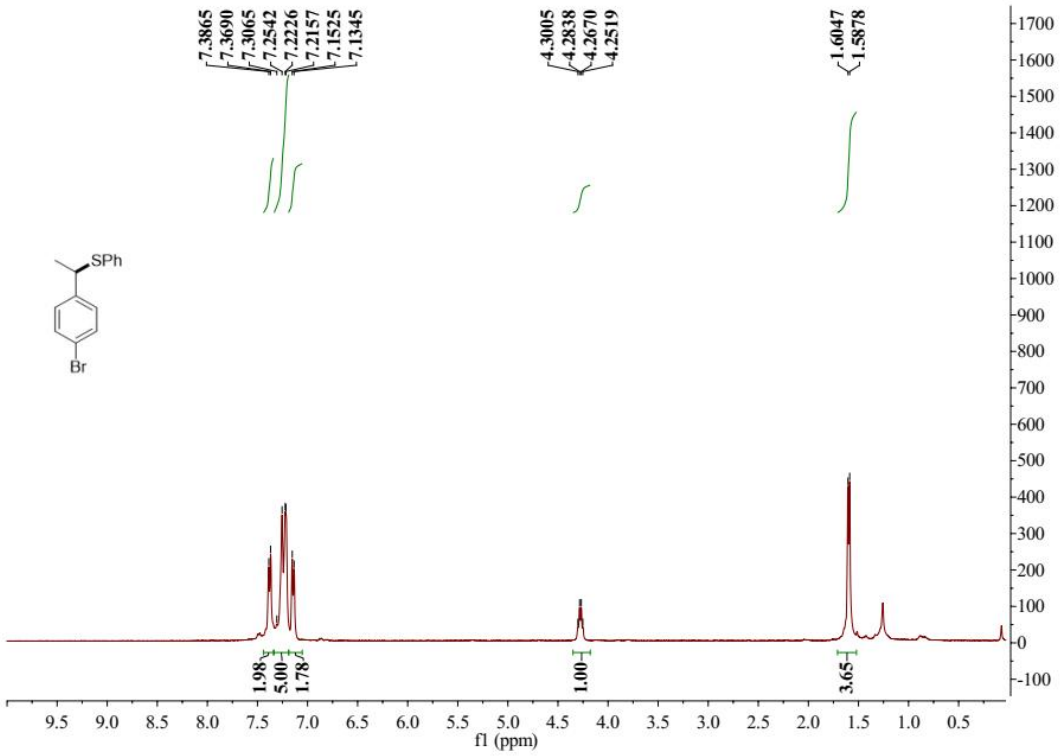

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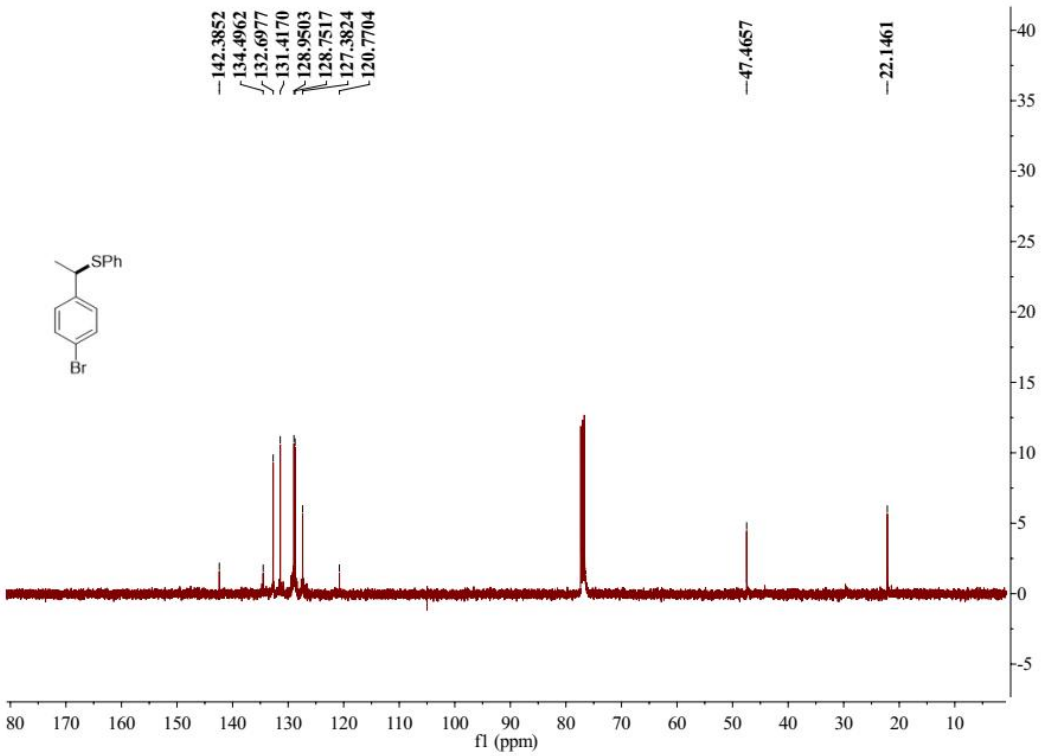

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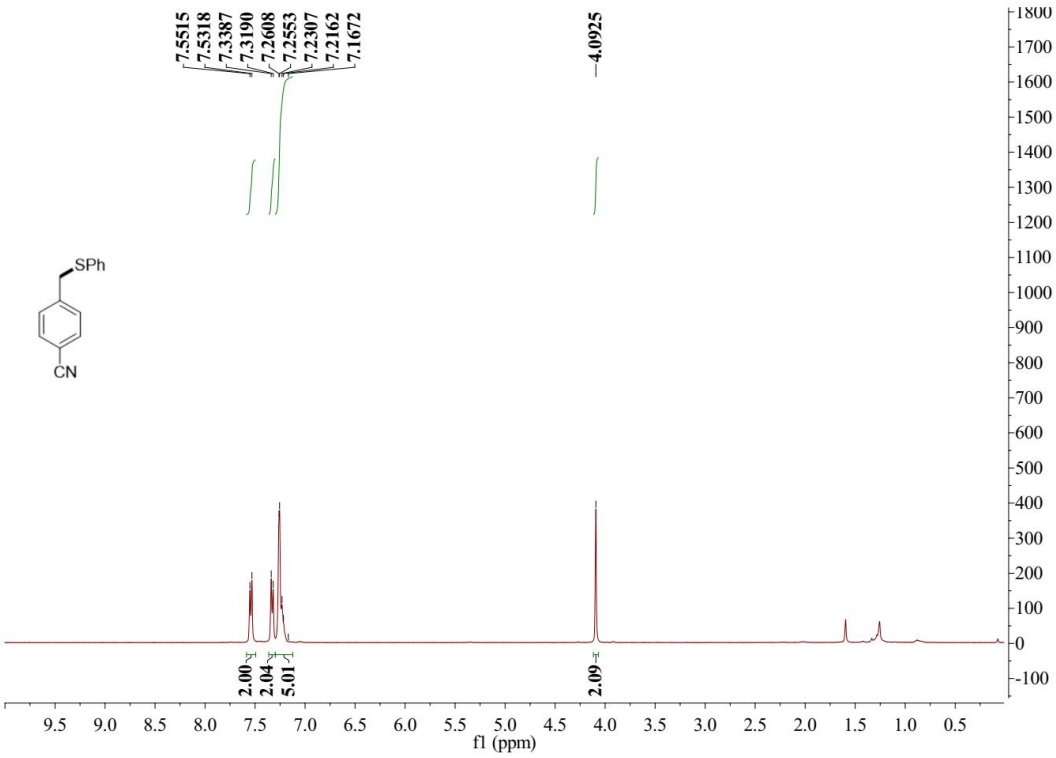
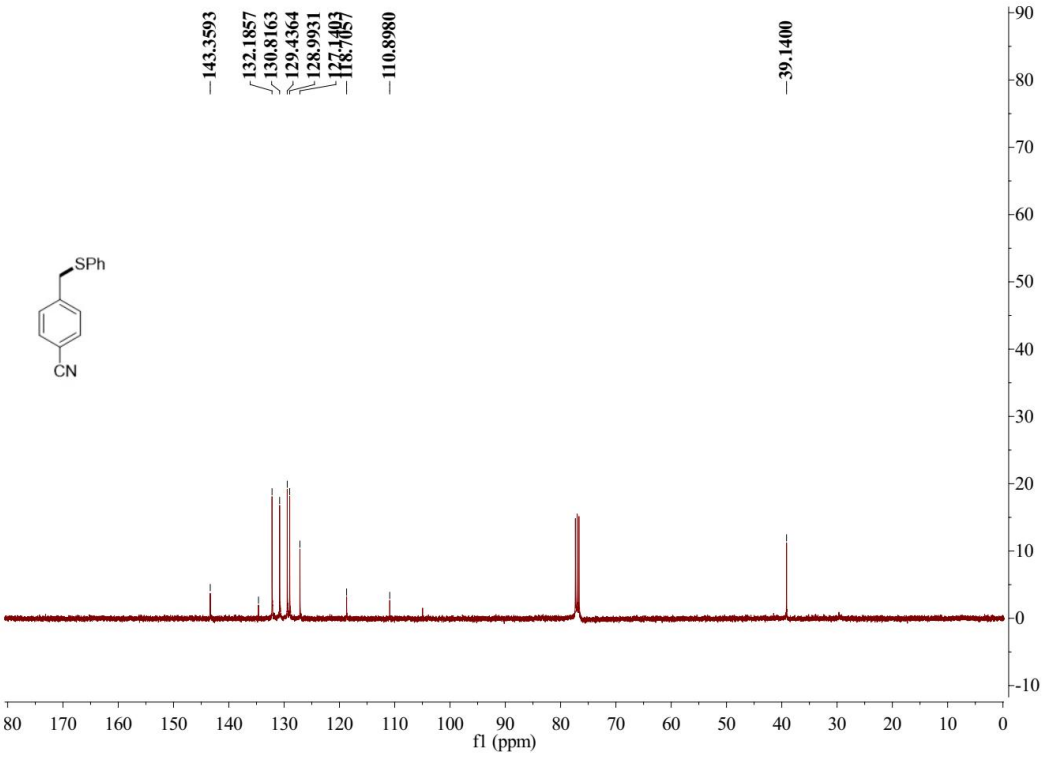


^{1}H NMR (400 MHz, $CDCl_3$) of **3g**



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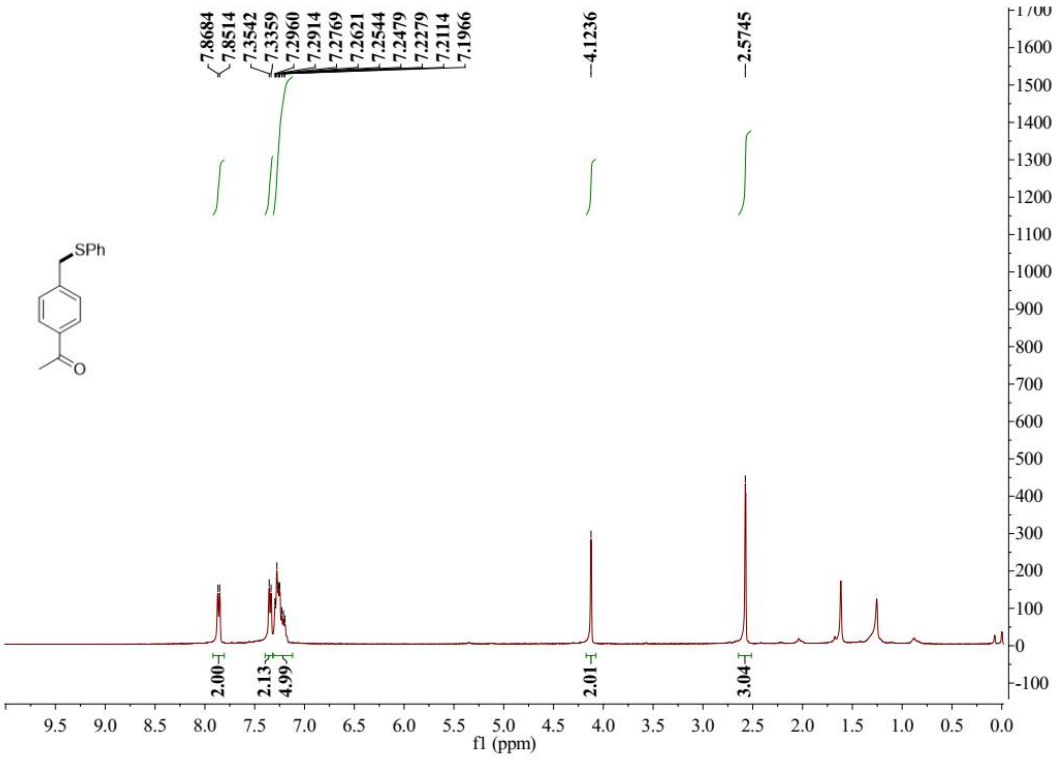
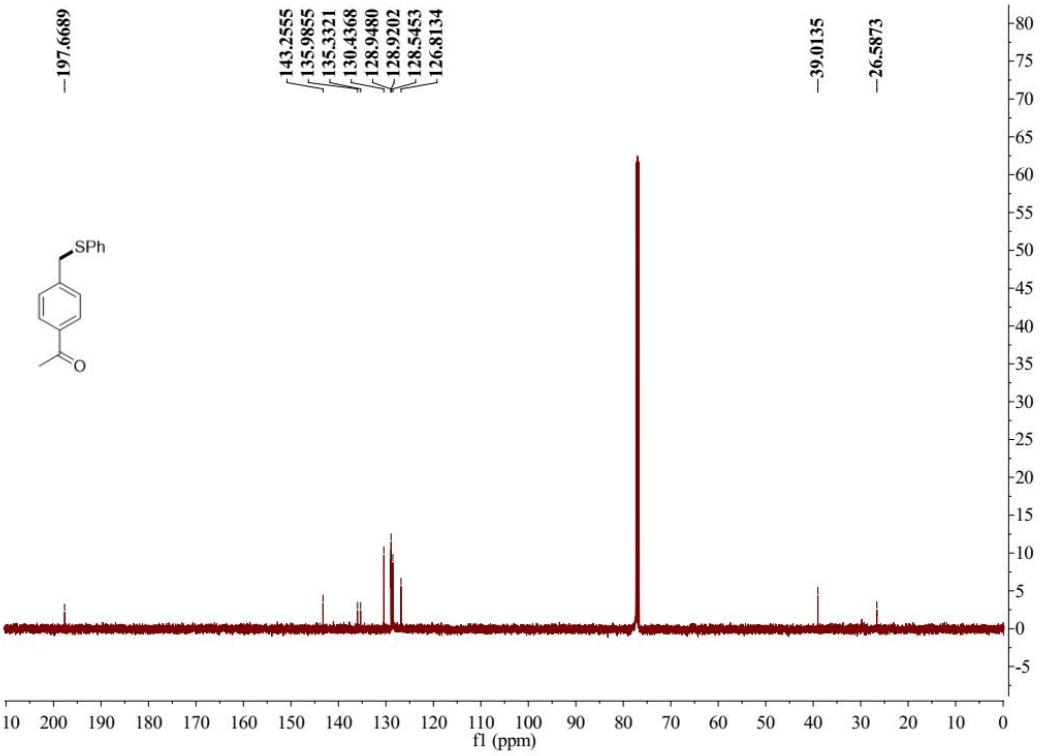


^{1}H NMR (400 MHz, $CDCl_3$) of **3h**



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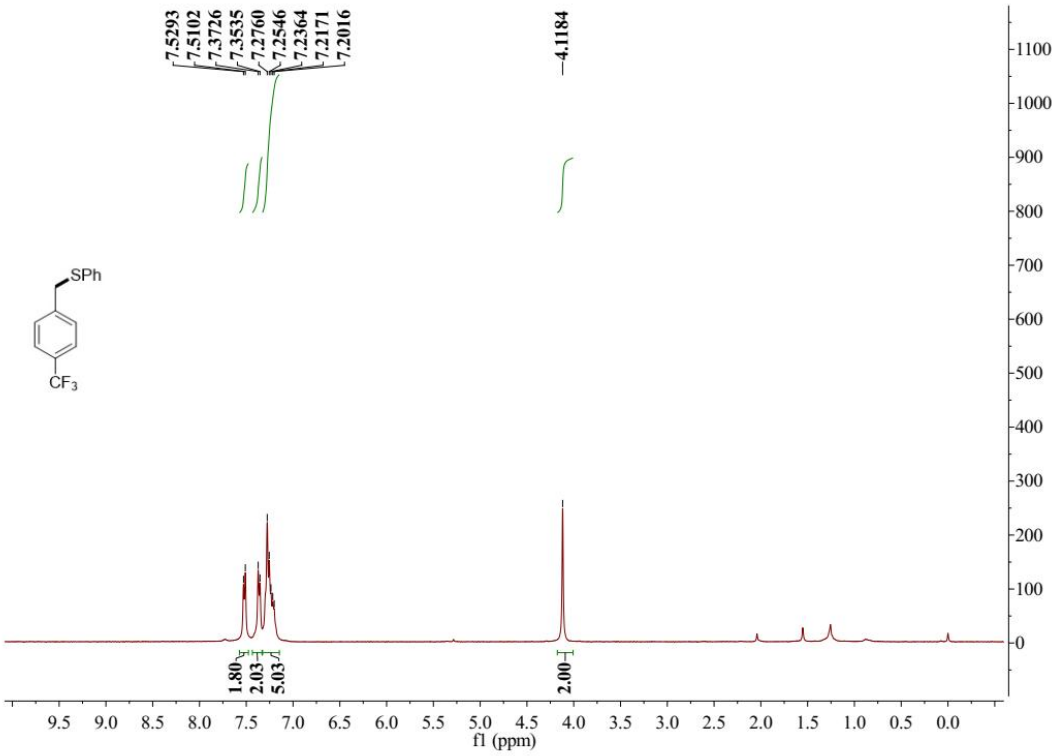

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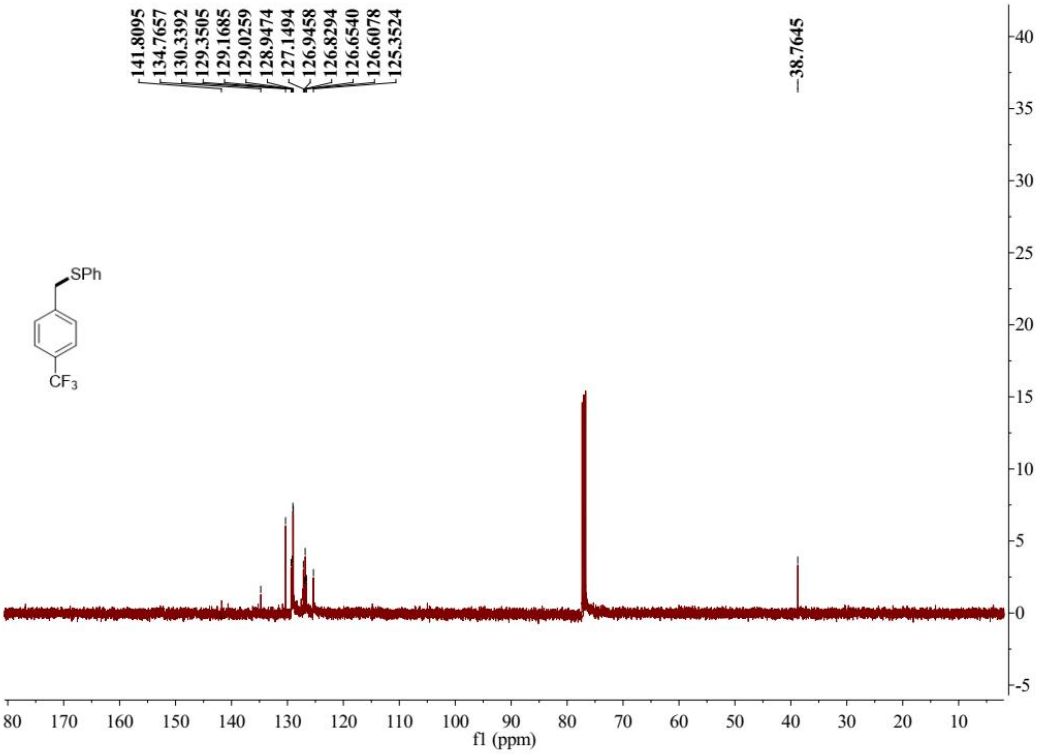

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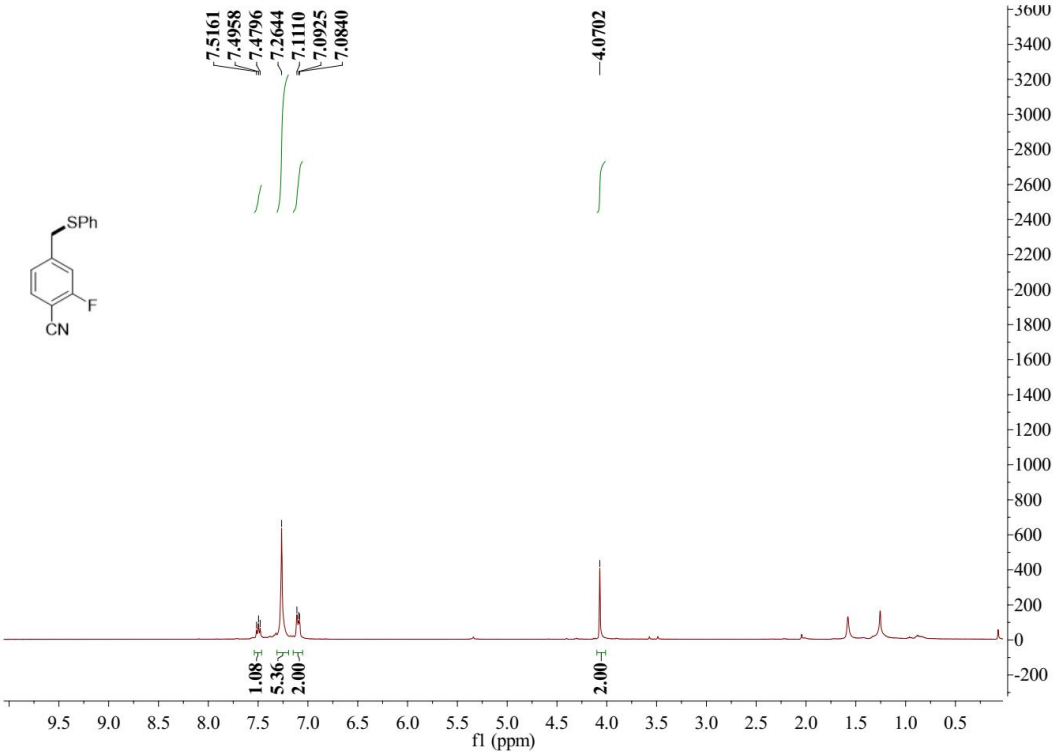

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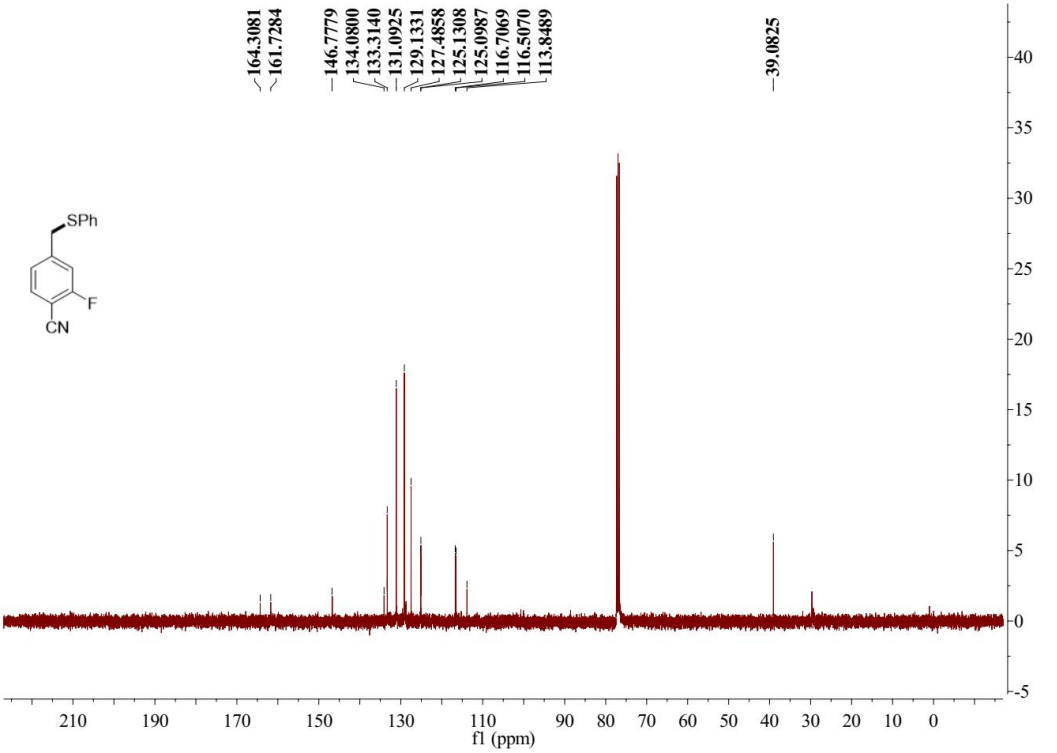

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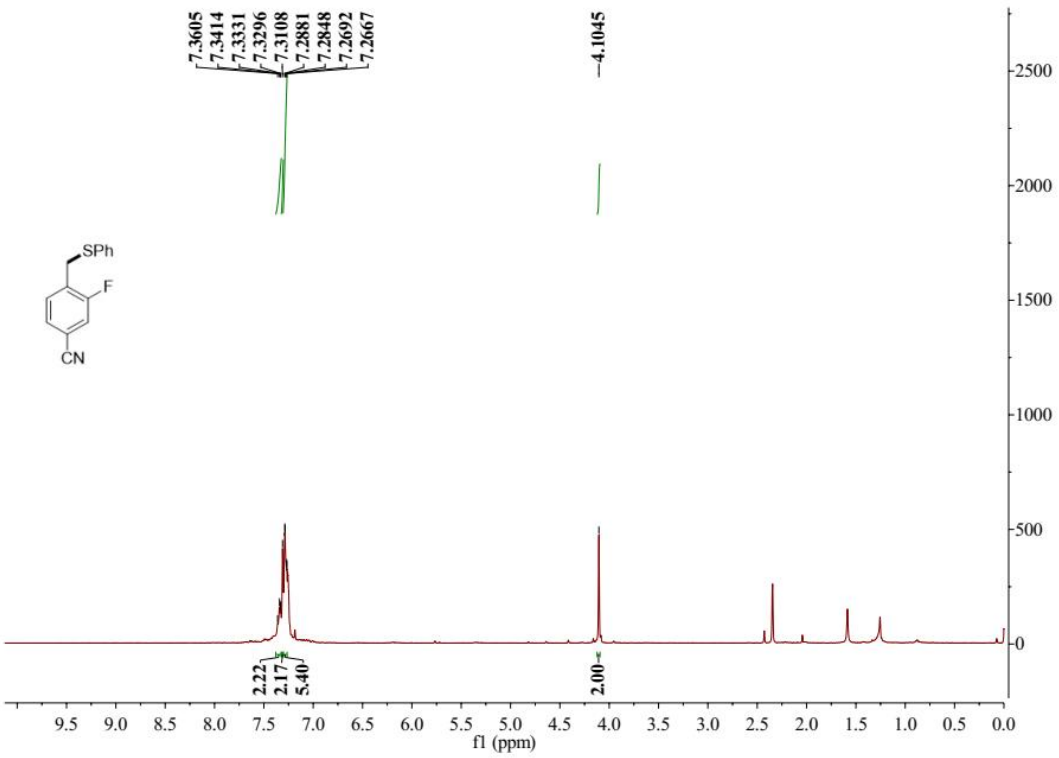

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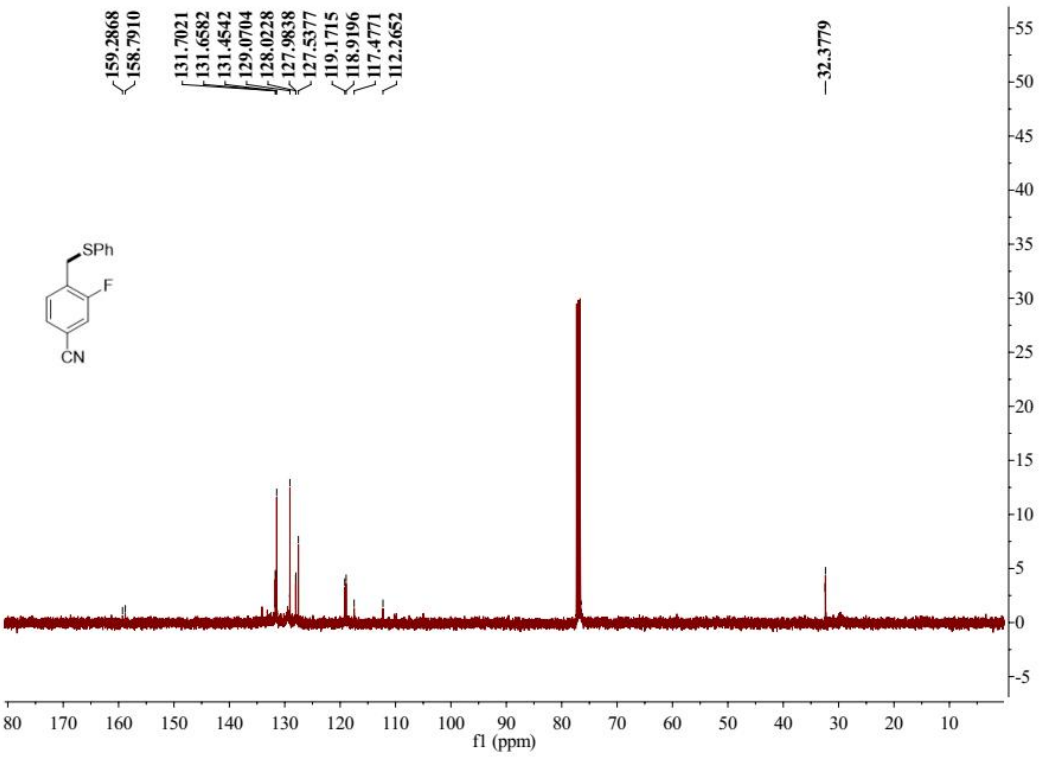

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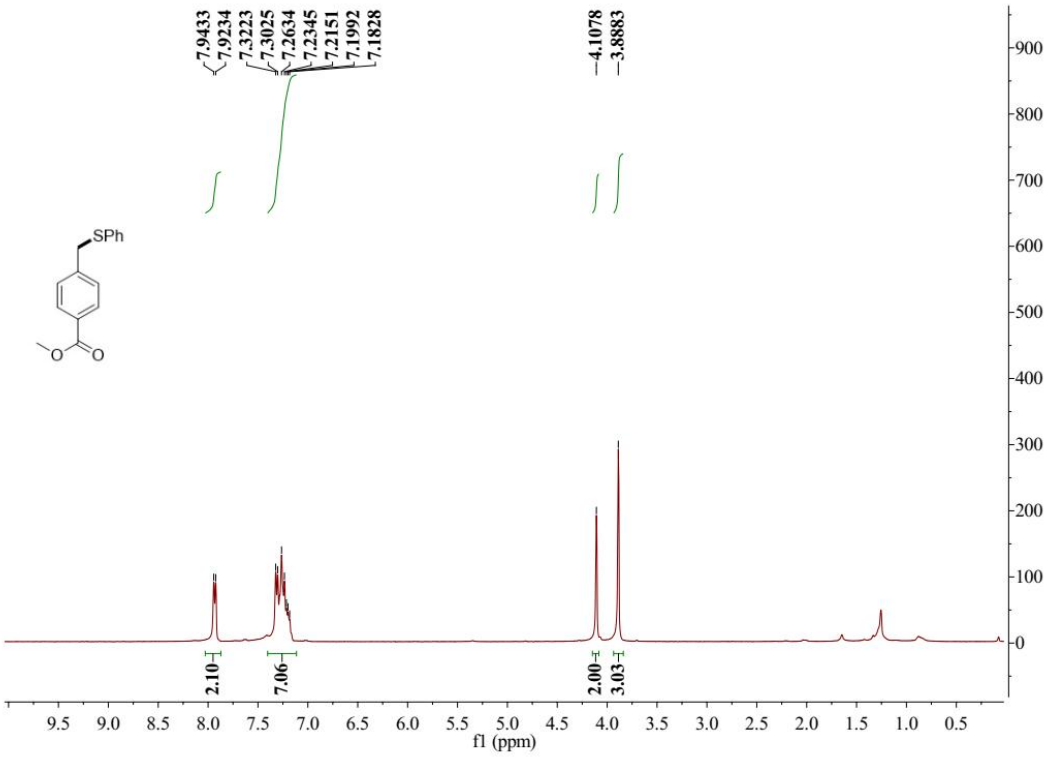

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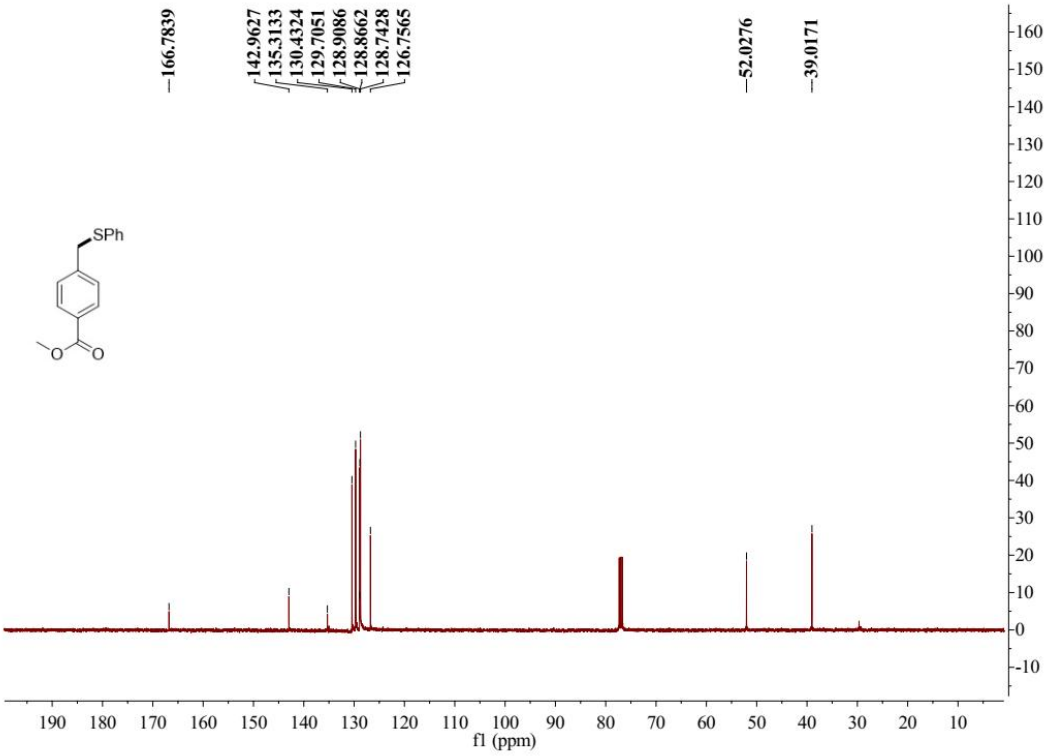

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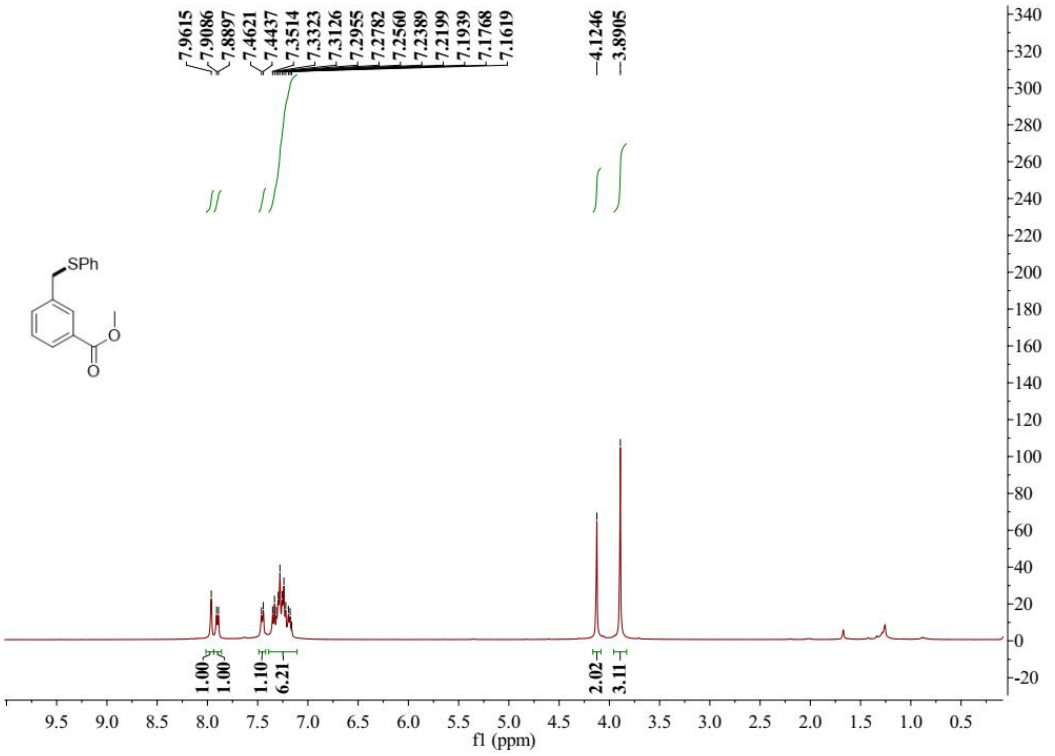
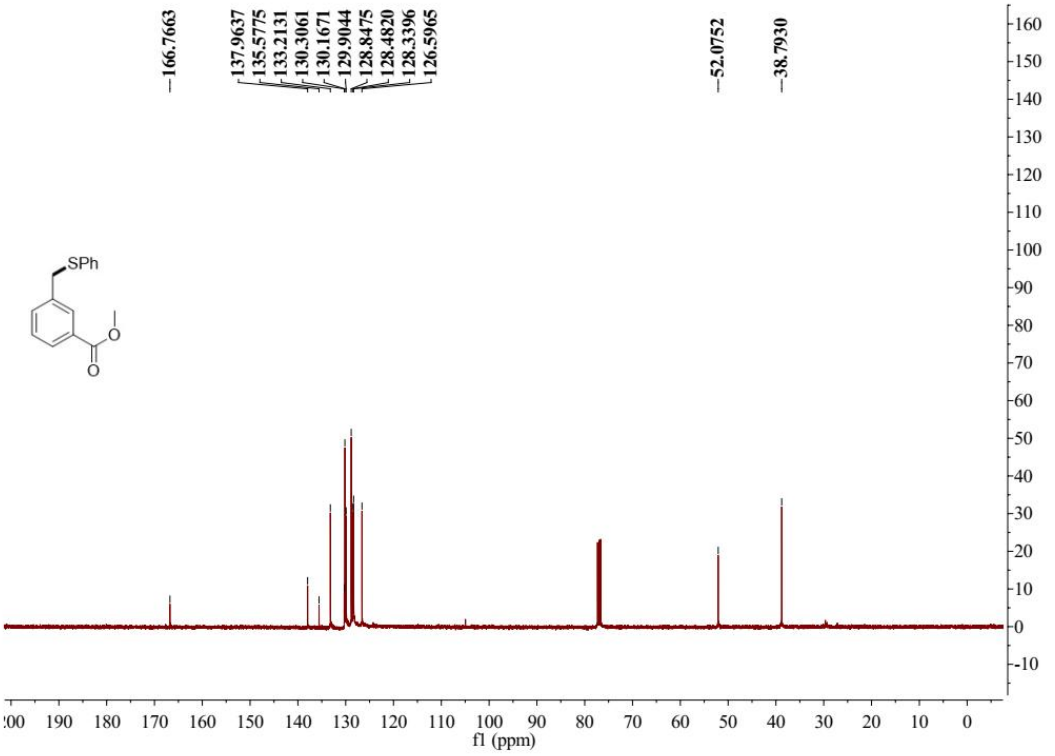


^{1}H NMR (100 MHz, $CDCl_3$) of **3m**



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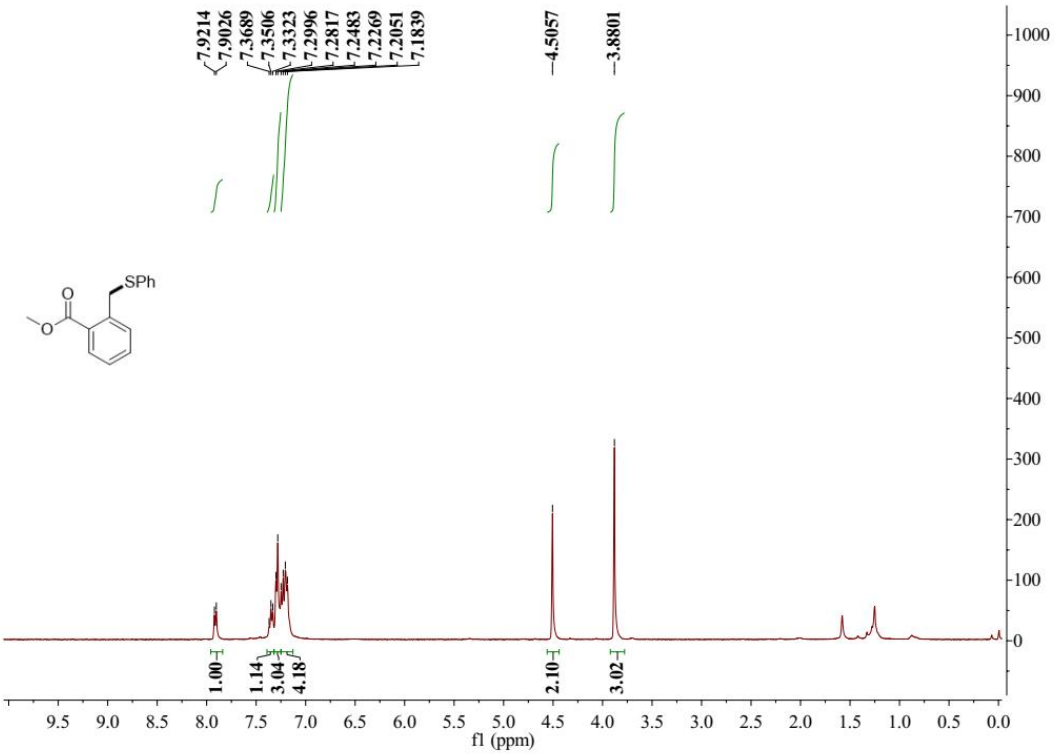
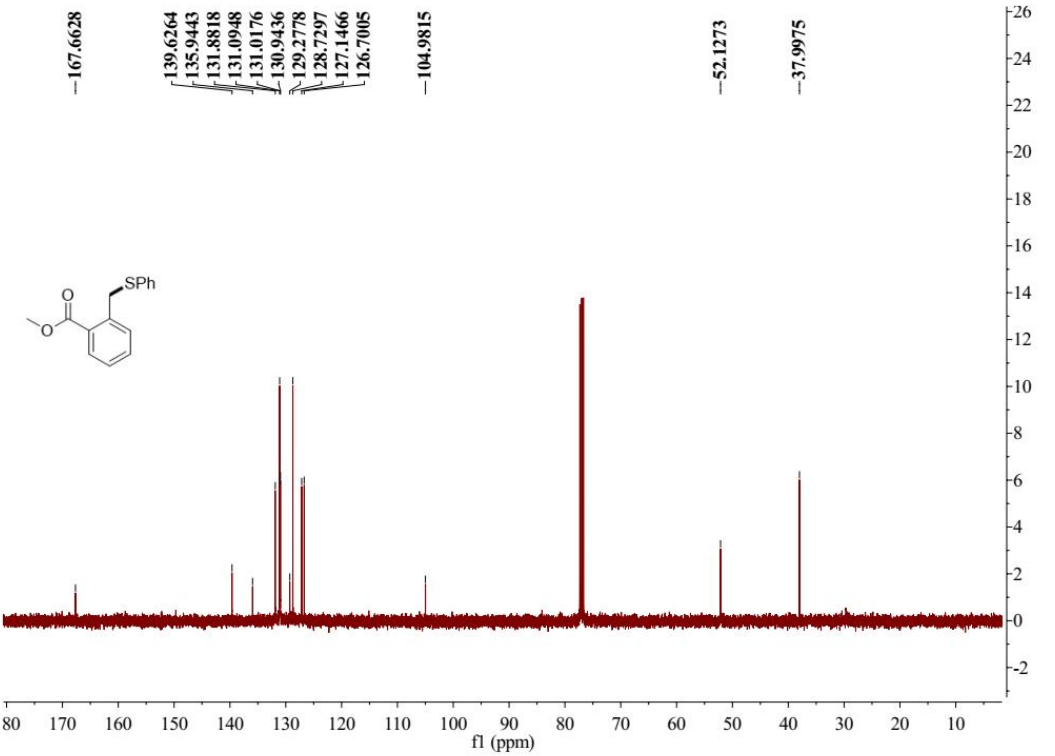


^{1}H NMR (400 MHz, $CDCl_3$) of **3n**



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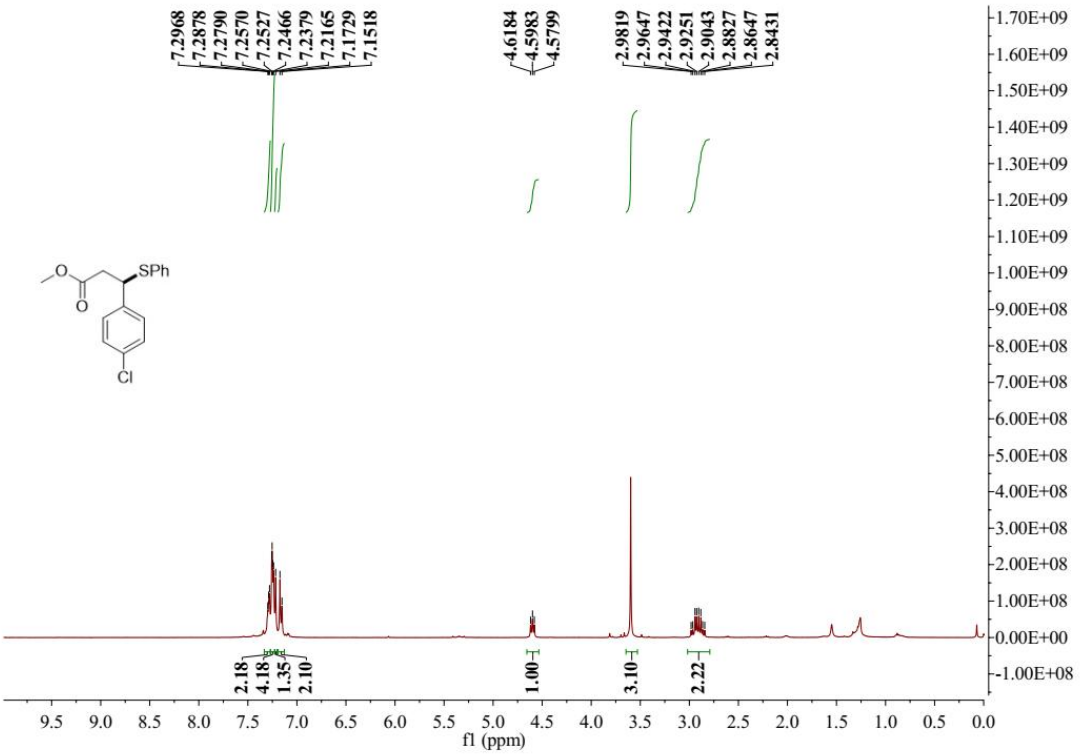

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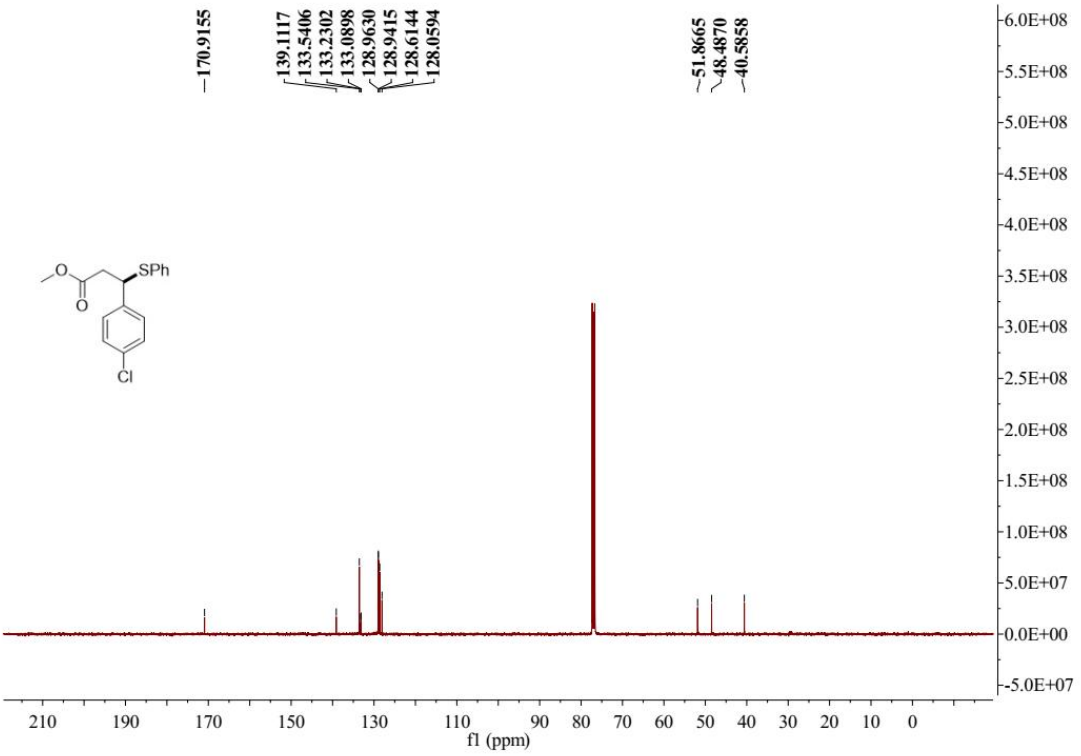

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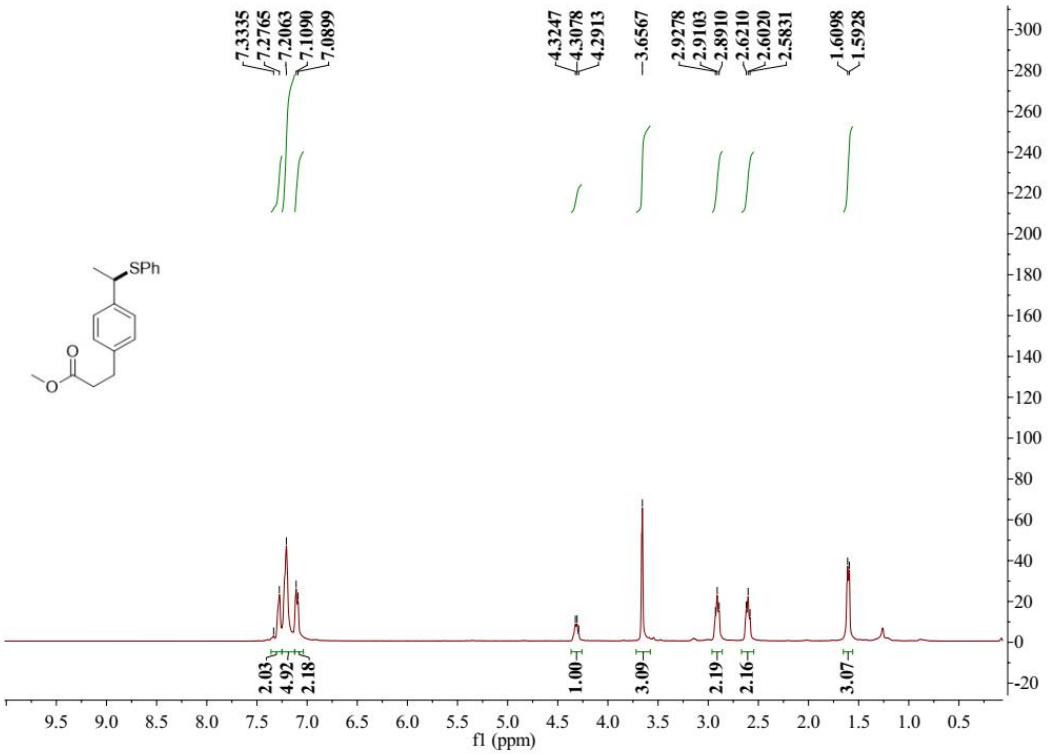
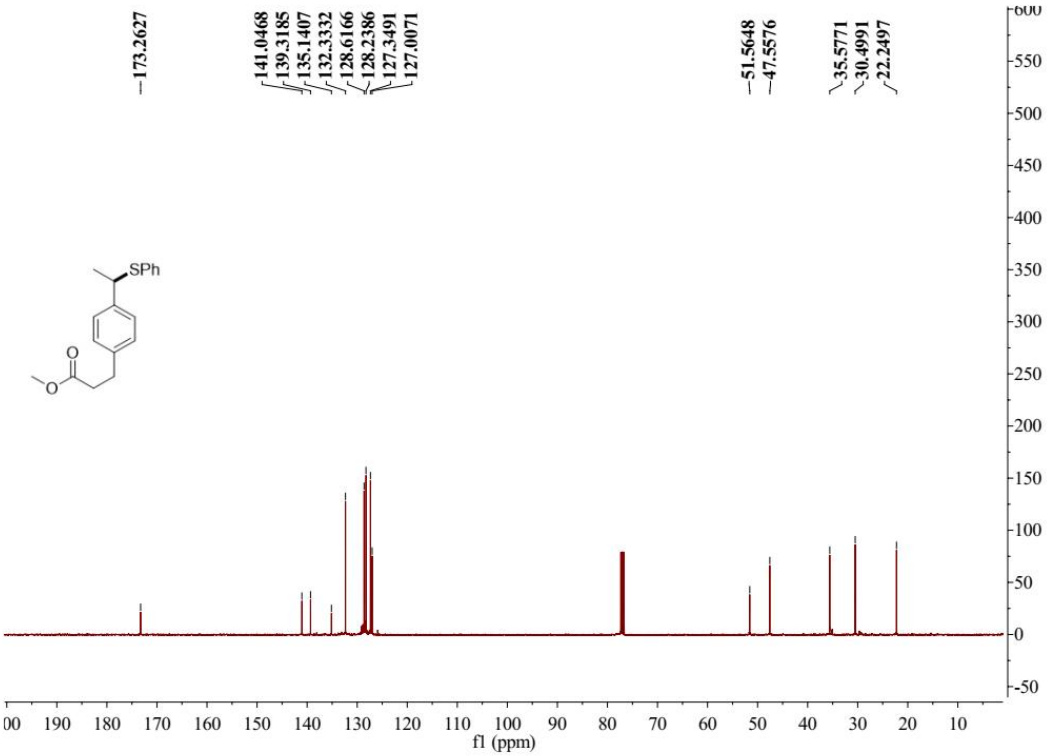
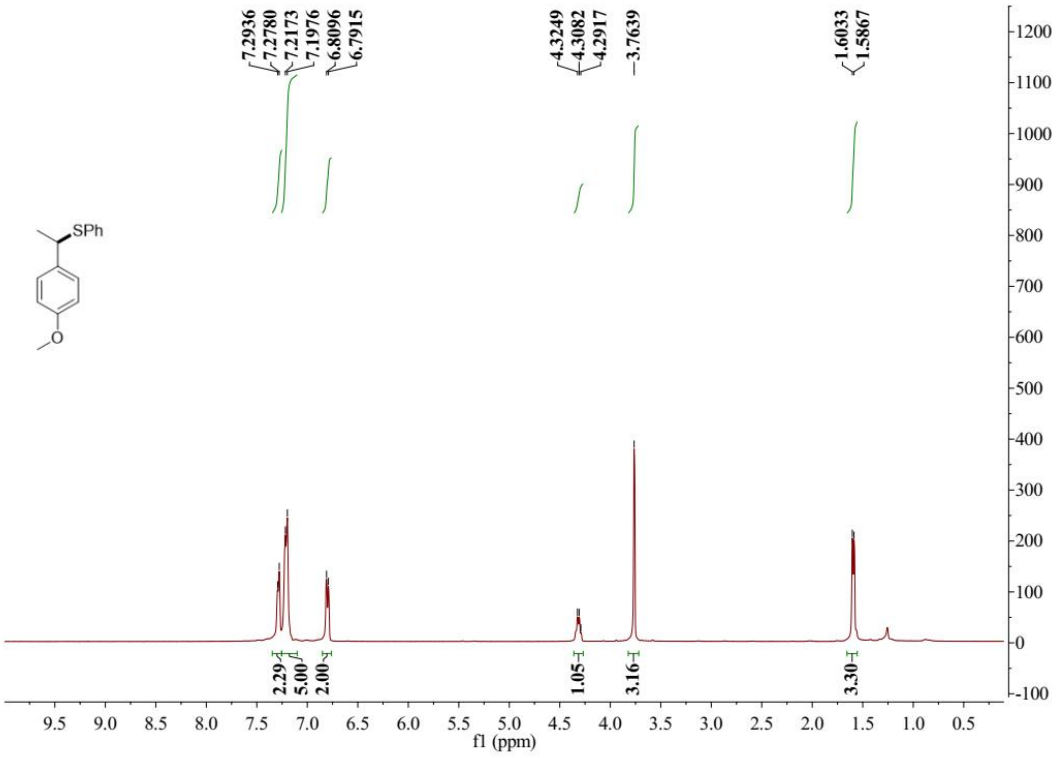


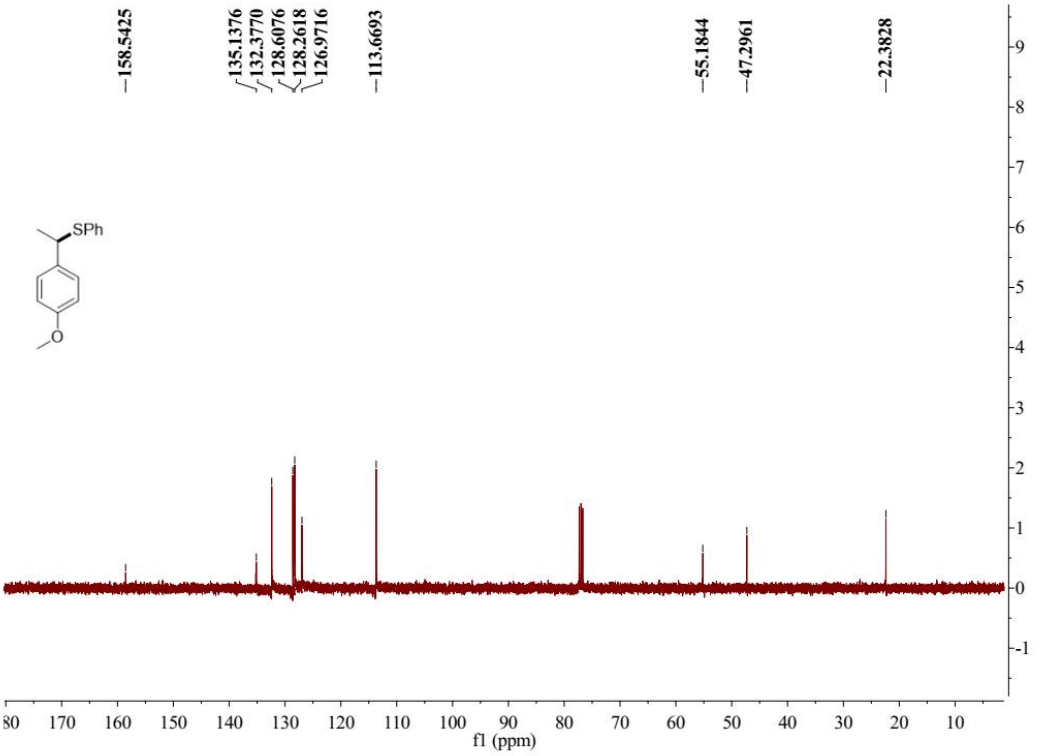
^{1}H NMR (400 MHz, $CDCl_3$) of **3p**



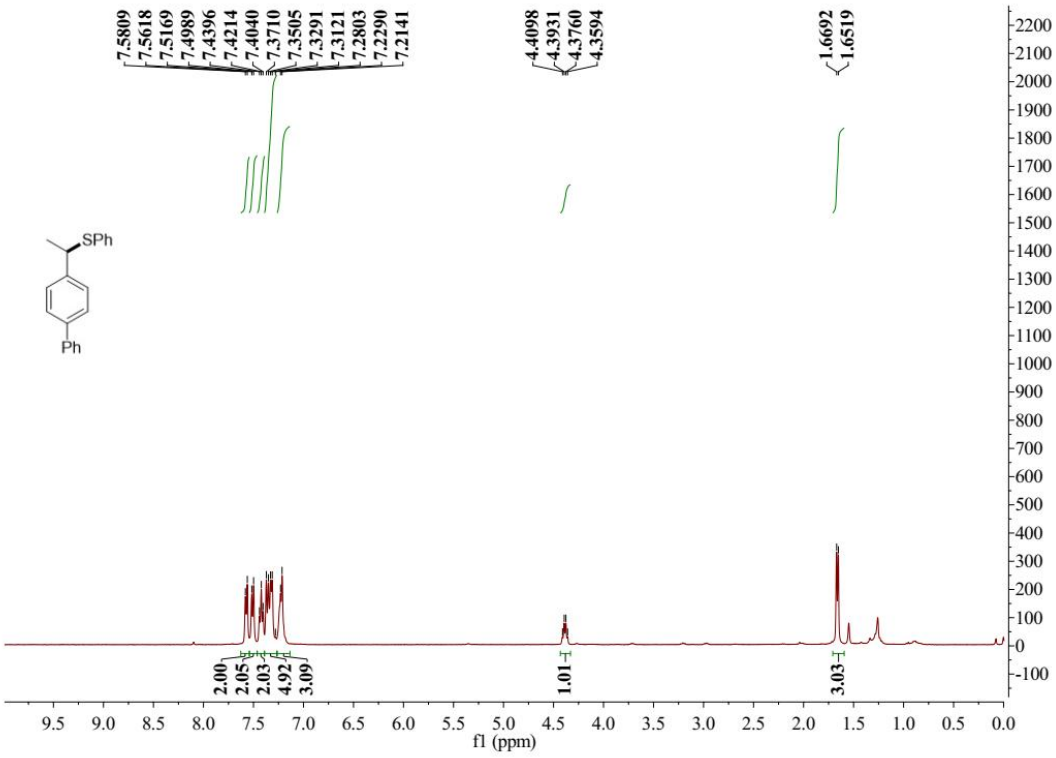
^{13}C NMR (100 MHz, $CDCl_3$) of **3p**



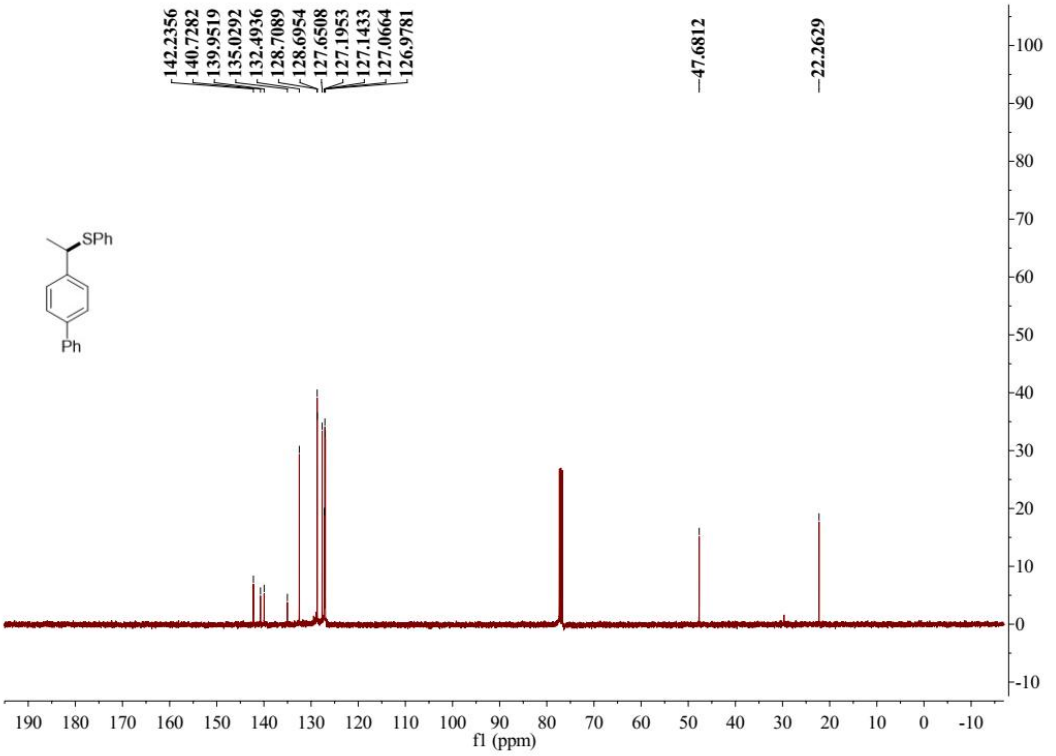
^{1}H NMR (400 MHz, $CDCl_3$) of **3q**



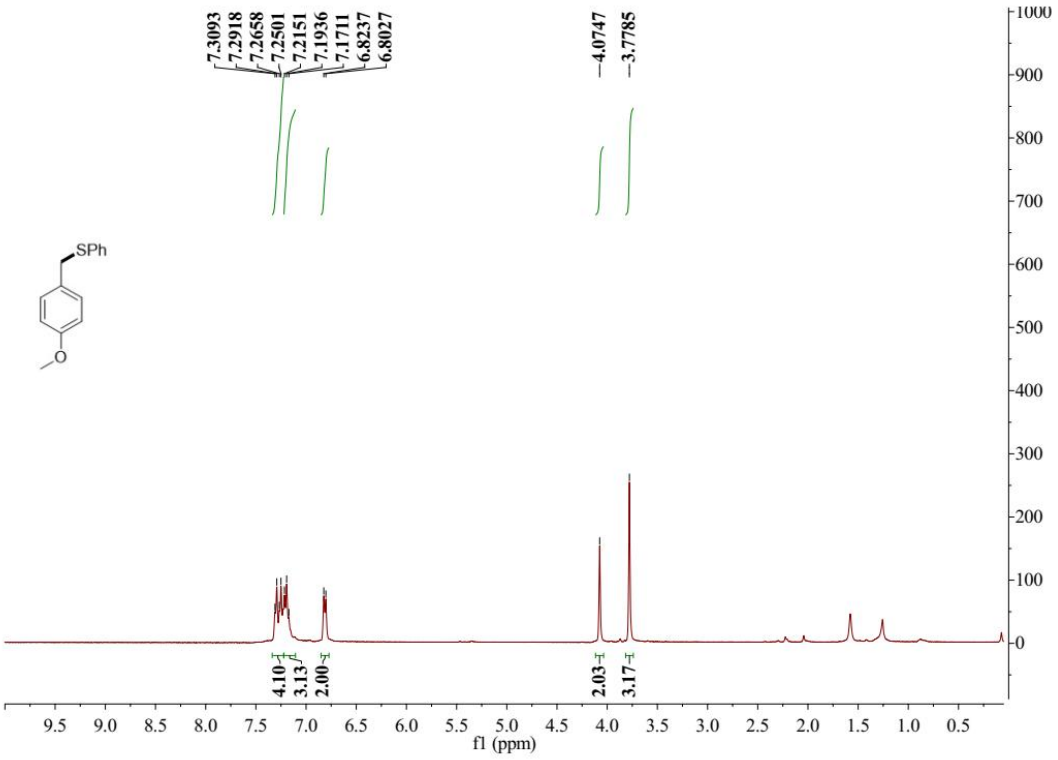
^{13}C NMR (100 MHz, $CDCl_3$) of **3q**



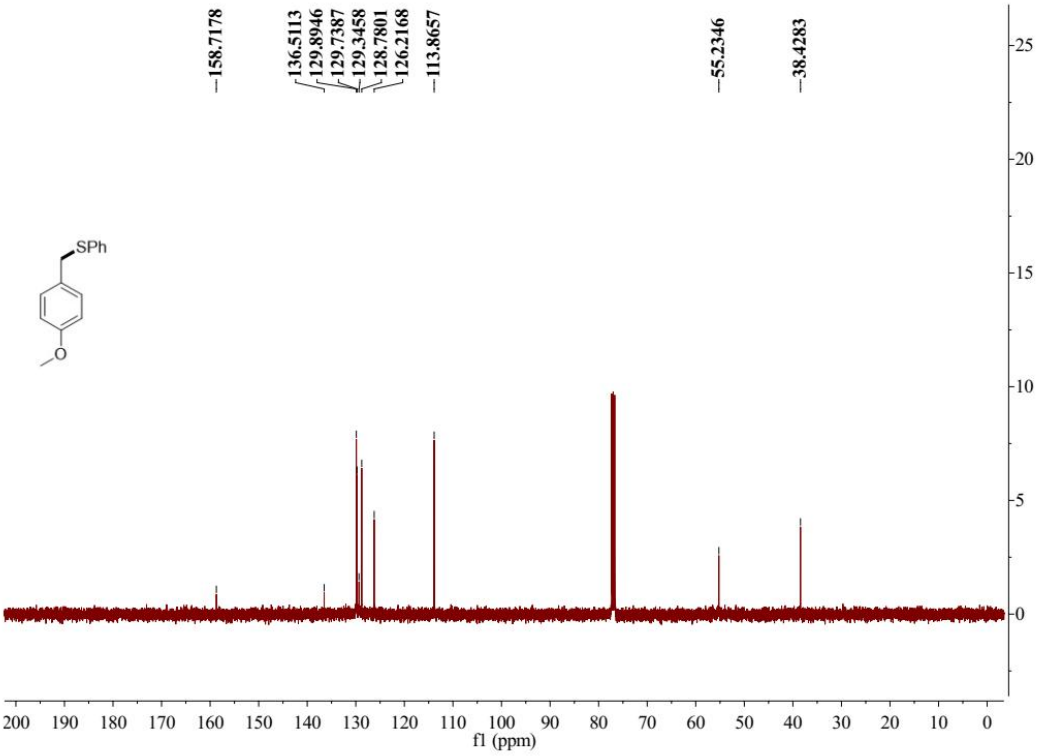
^{1}H NMR (400 MHz, $CDCl_3$) of **3r**



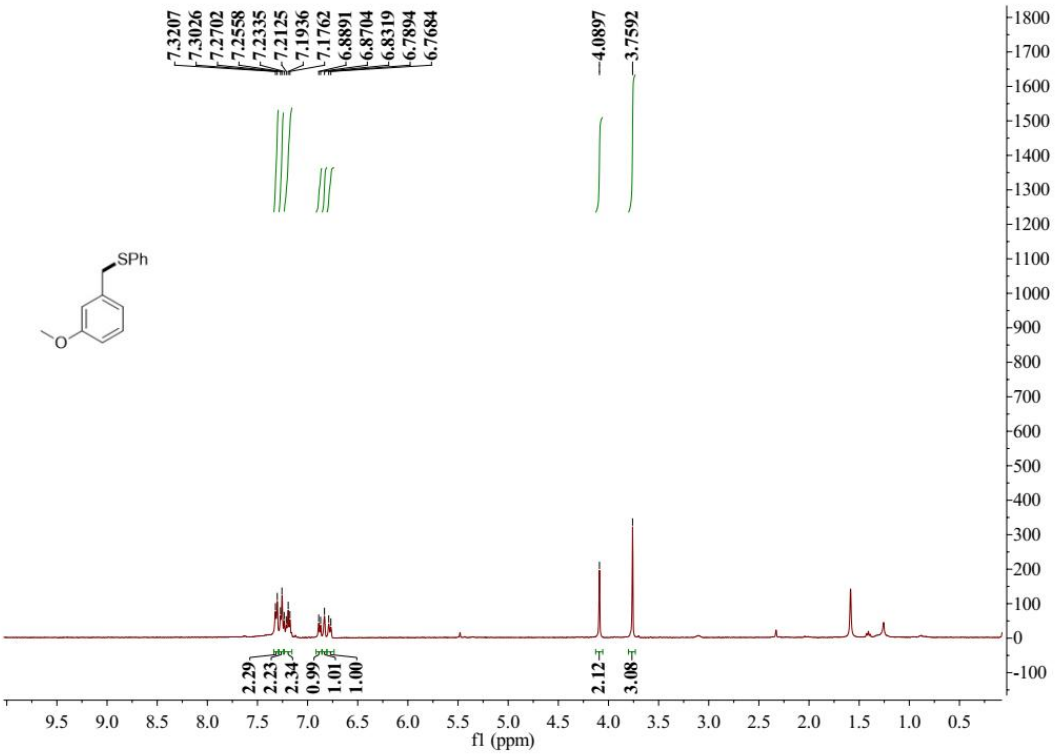
^{13}C NMR (100 MHz, $CDCl_3$) of **3r**



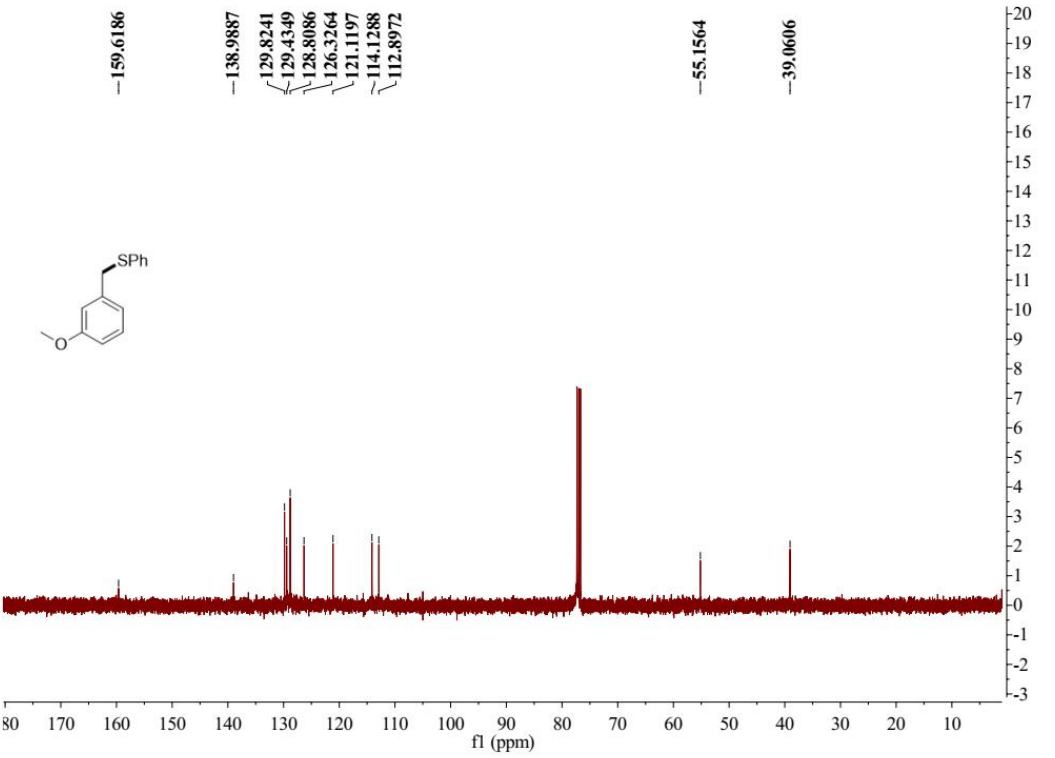
^{1}H NMR (400 MHz, $CDCl_3$) of **3s**



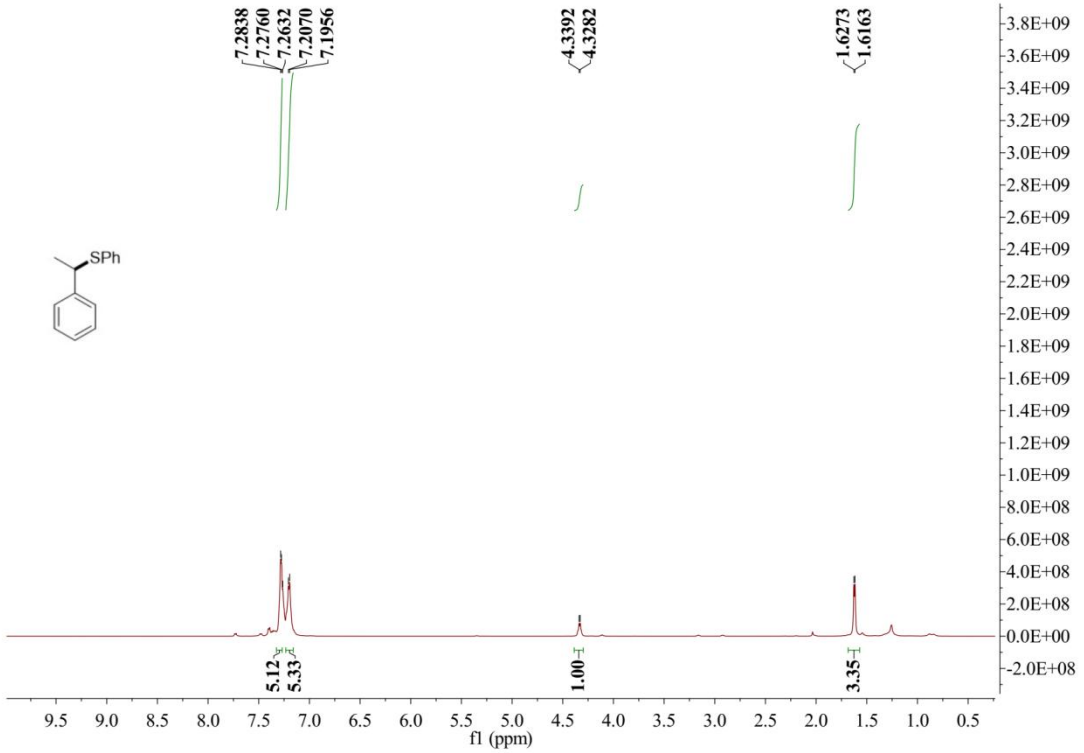
^{13}C NMR (100 MHz, $CDCl_3$) of **3s**



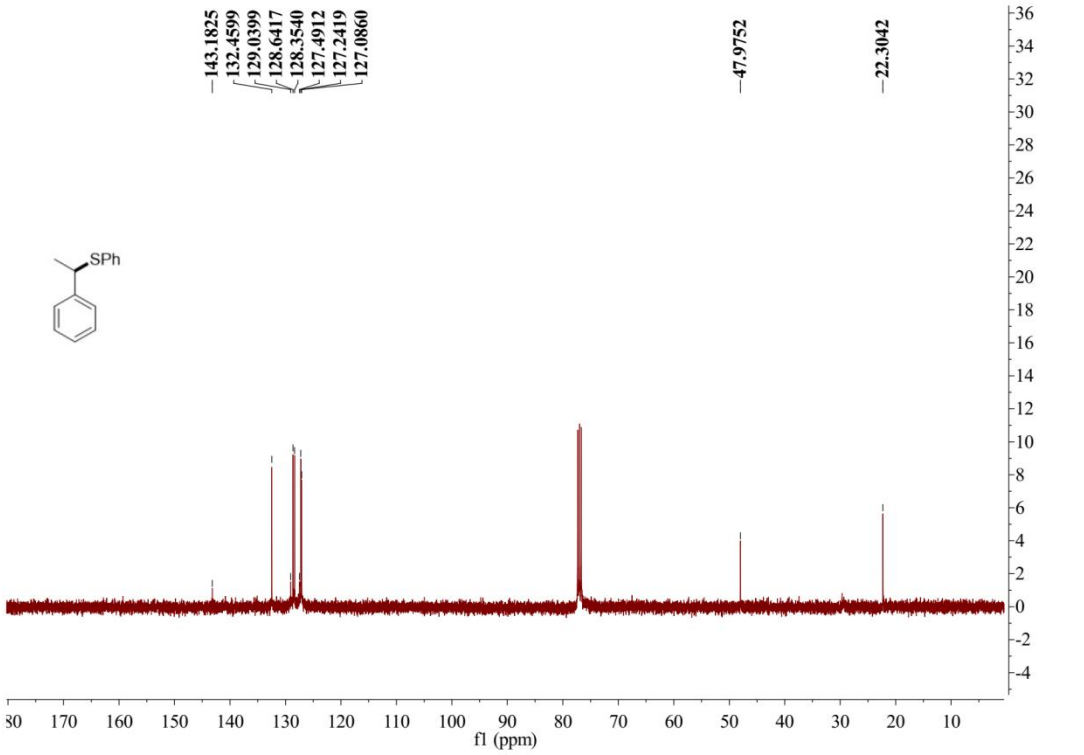
^{1}H NMR (400 MHz, $CDCl_3$) of **3t**



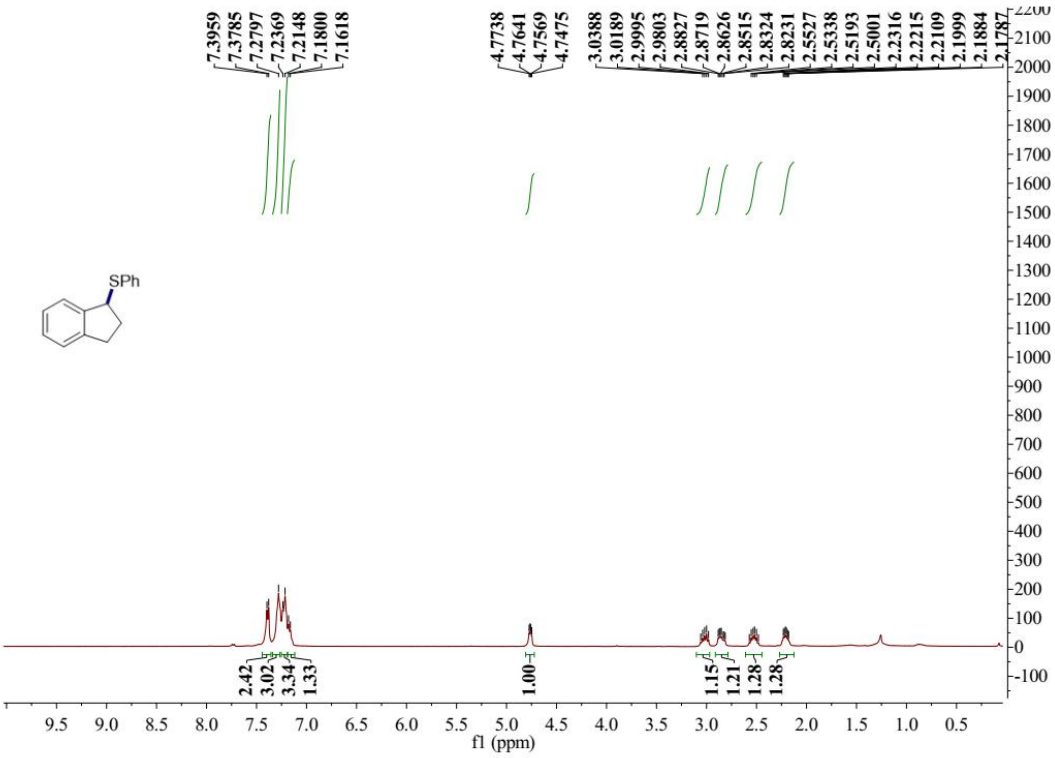
^{13}C NMR (100 MHz, $CDCl_3$) of **3t**



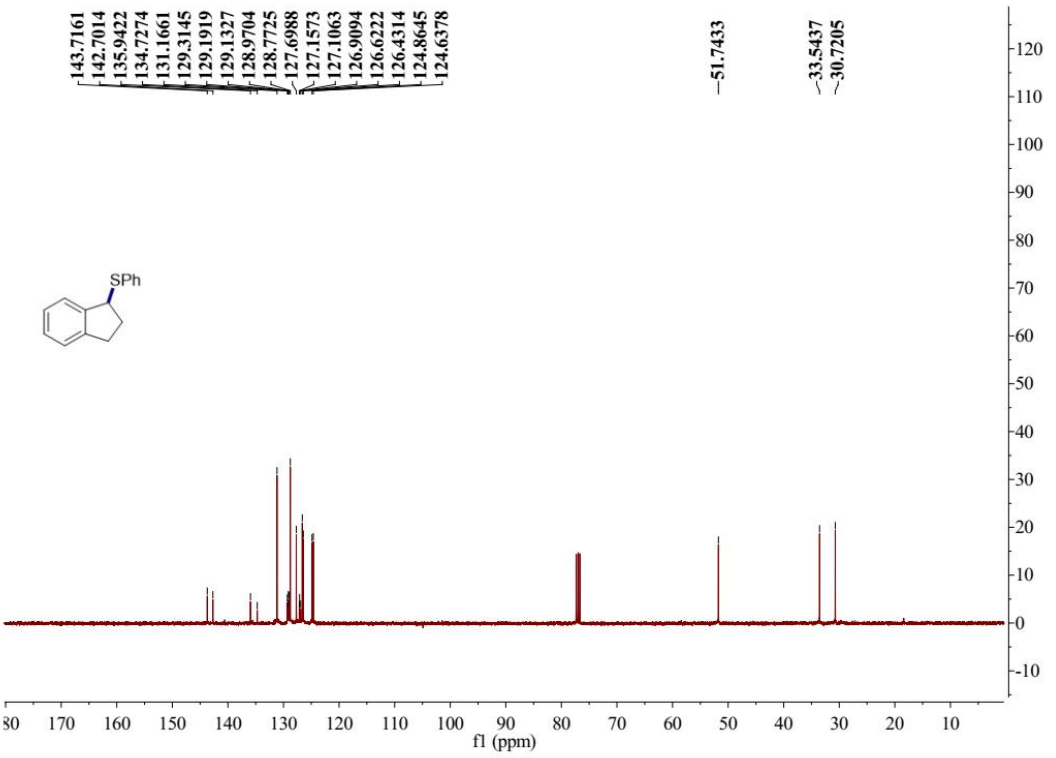
^{1}H NMR (600 MHz, $CDCl_3$) of **3u**



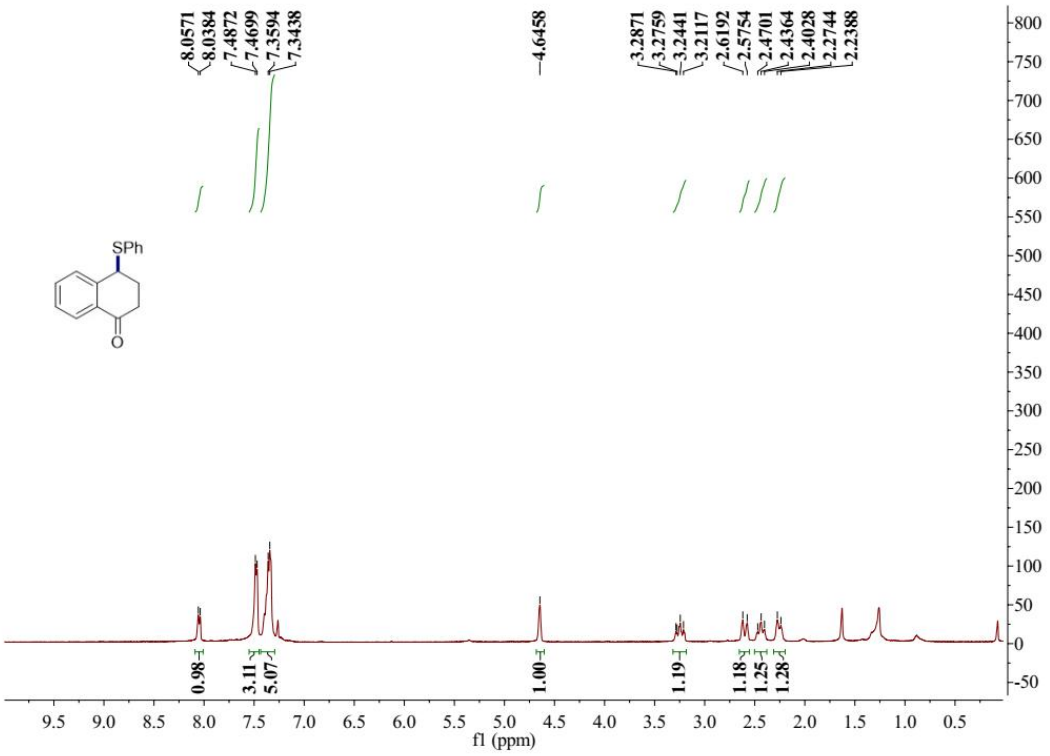
^{13}C NMR (100 MHz, $CDCl_3$) of **3u**



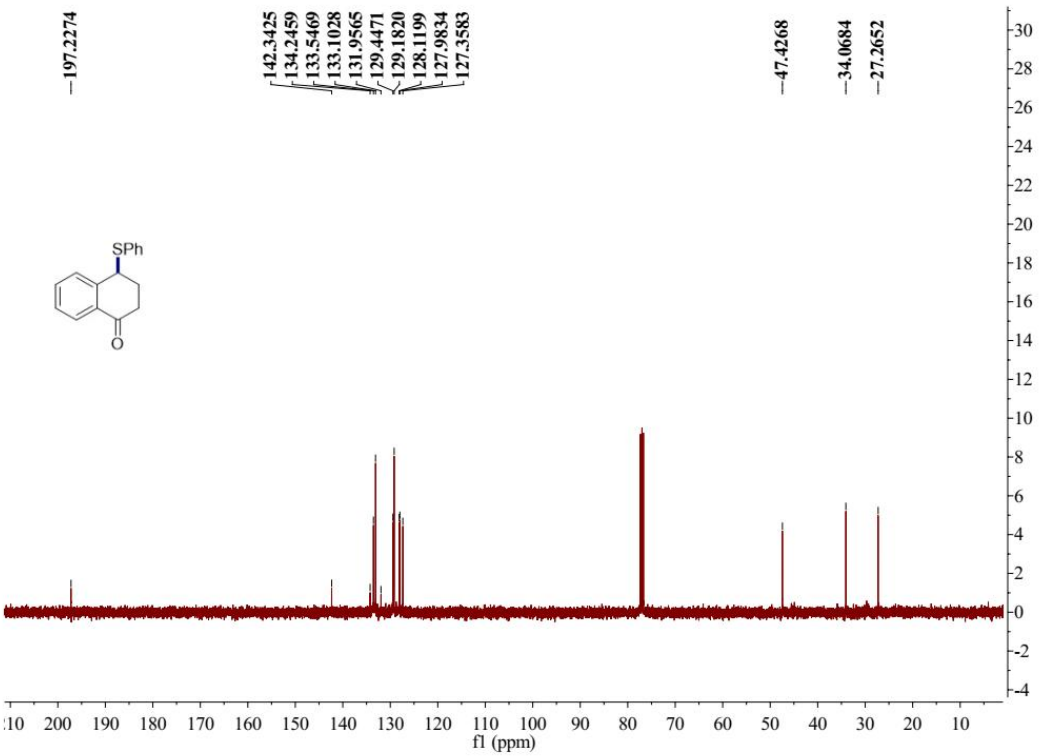
^{1}H NMR (400 MHz, $CDCl_3$) of **3v**



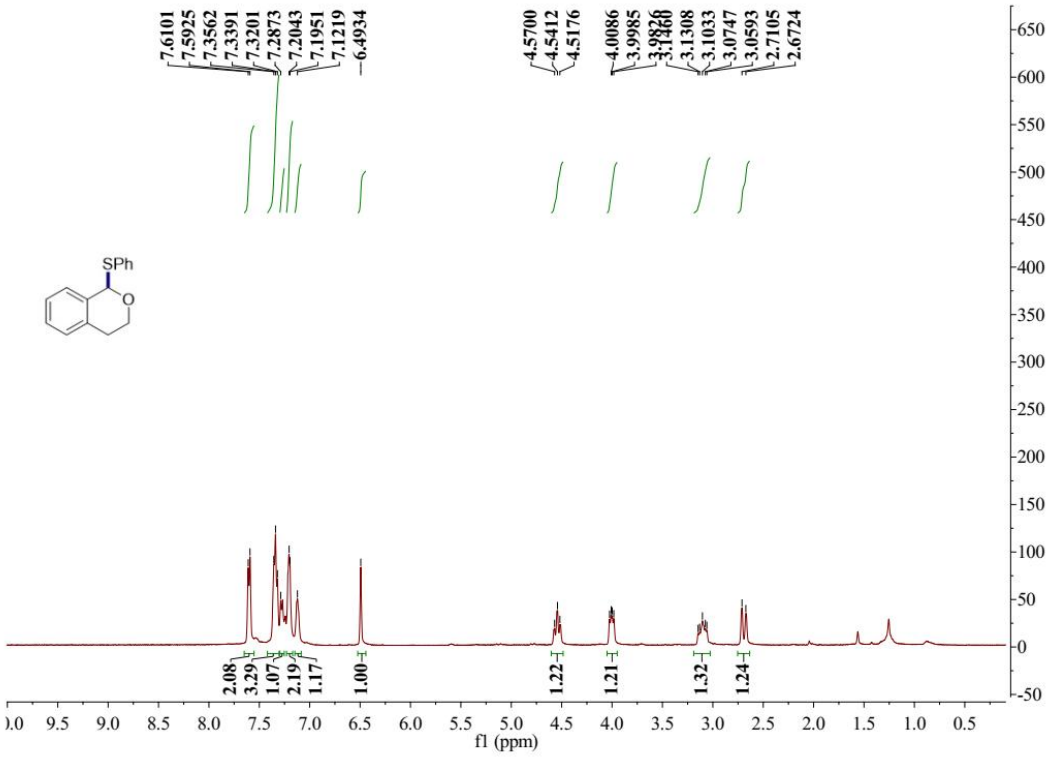
^{13}C NMR (100 MHz, $CDCl_3$) of **3v**



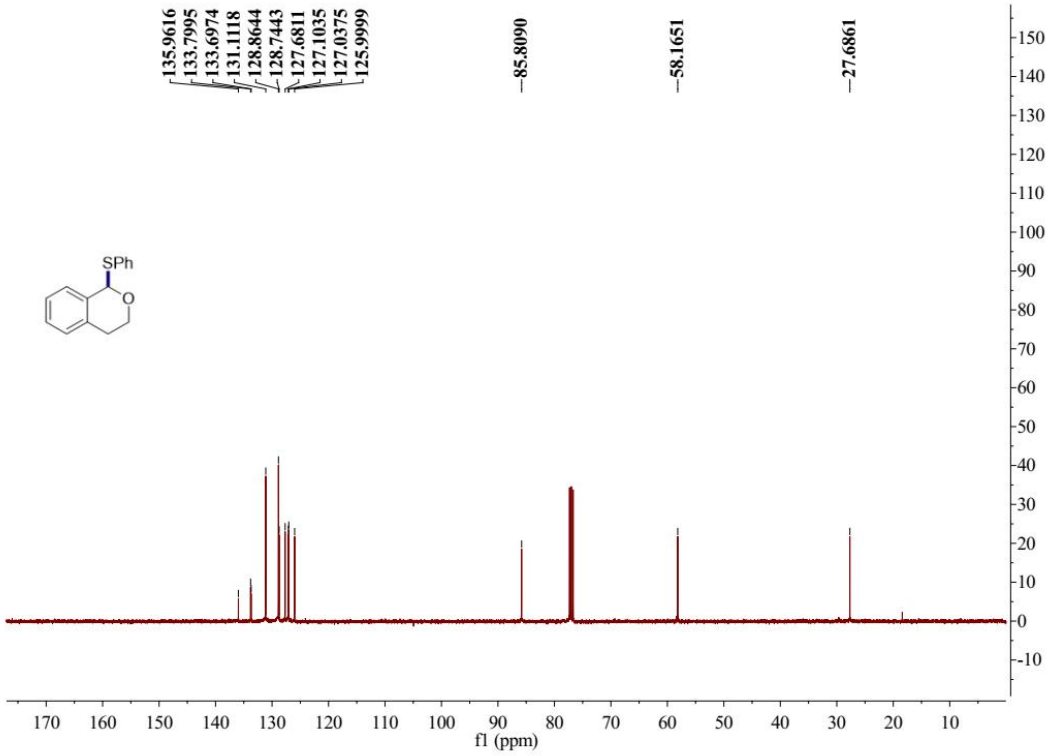
^{1}H NMR (400 MHz, $CDCl_3$) of **3w**



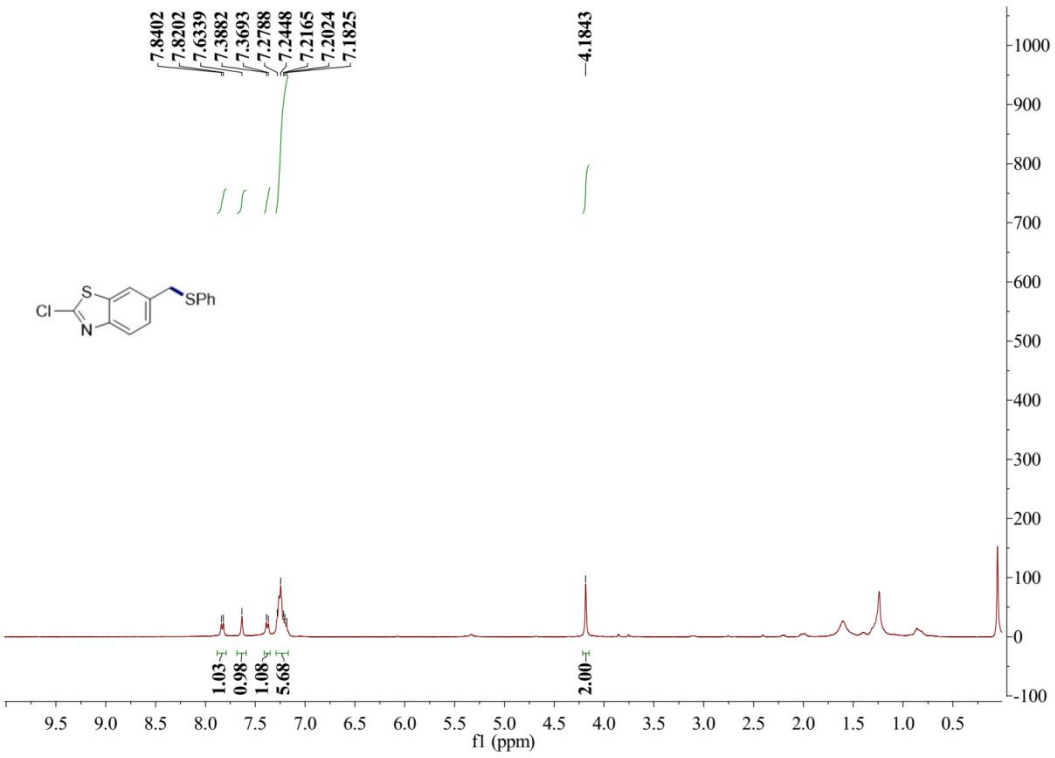
^{13}C NMR (100 MHz, $CDCl_3$) of **3w**



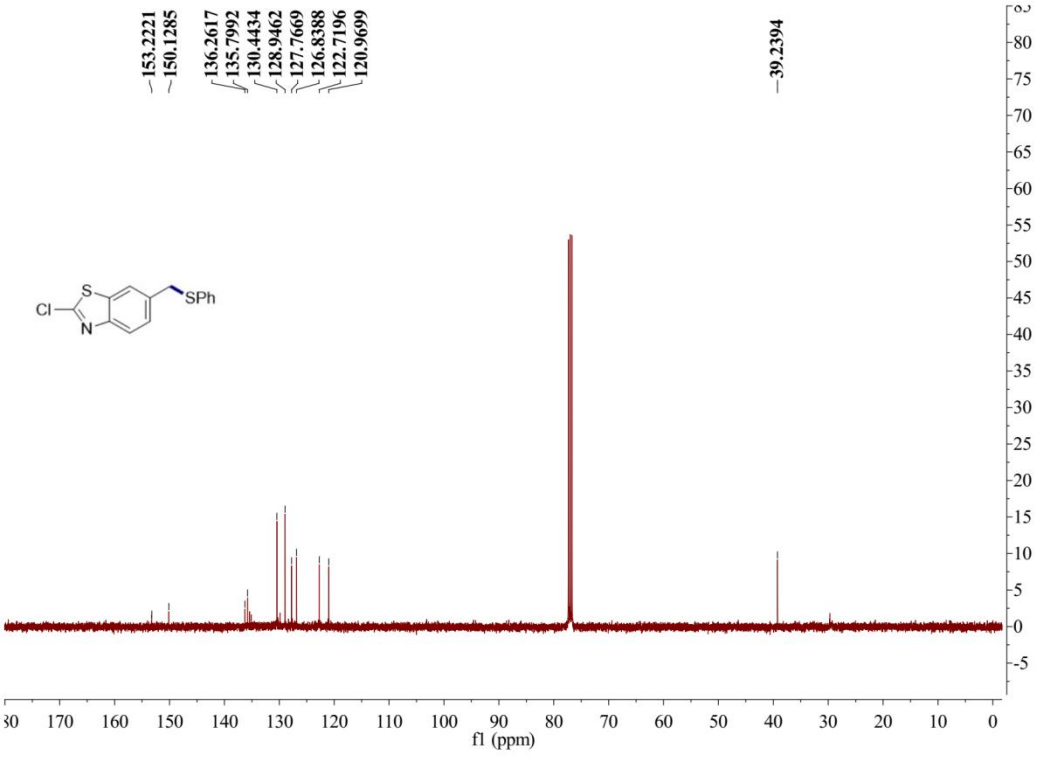
^{1}H NMR (400 MHz, $CDCl_3$) of **3x**



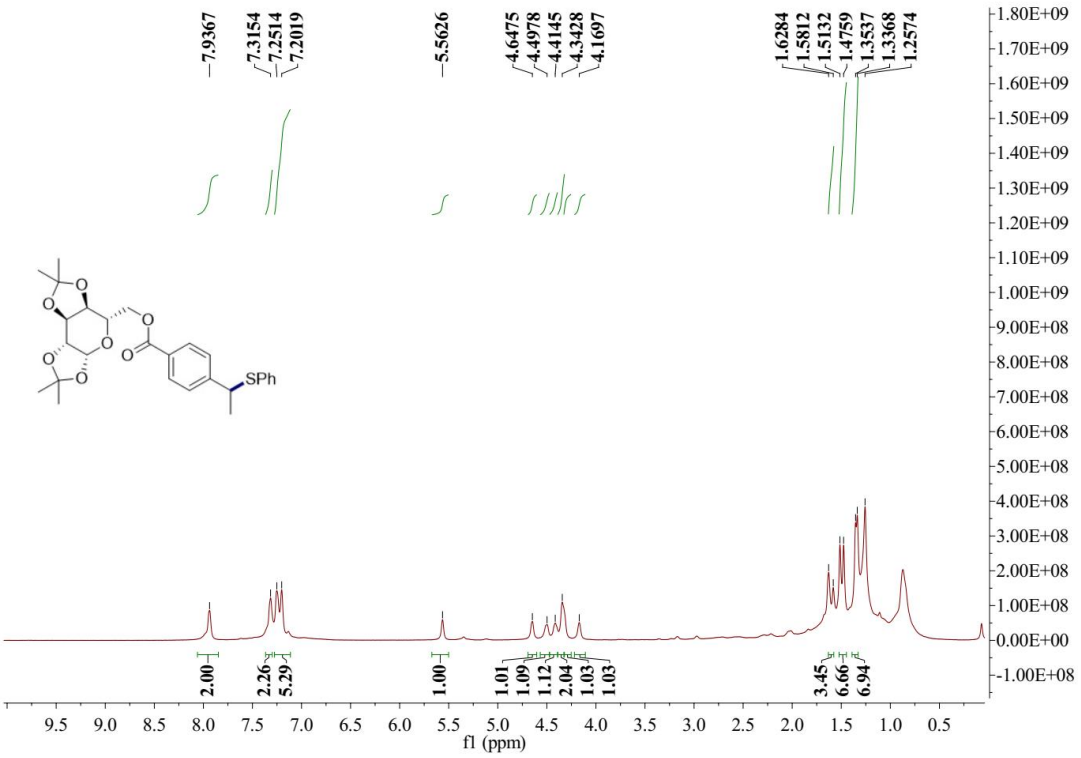
^{13}C NMR (100 MHz, $CDCl_3$) of **3x**



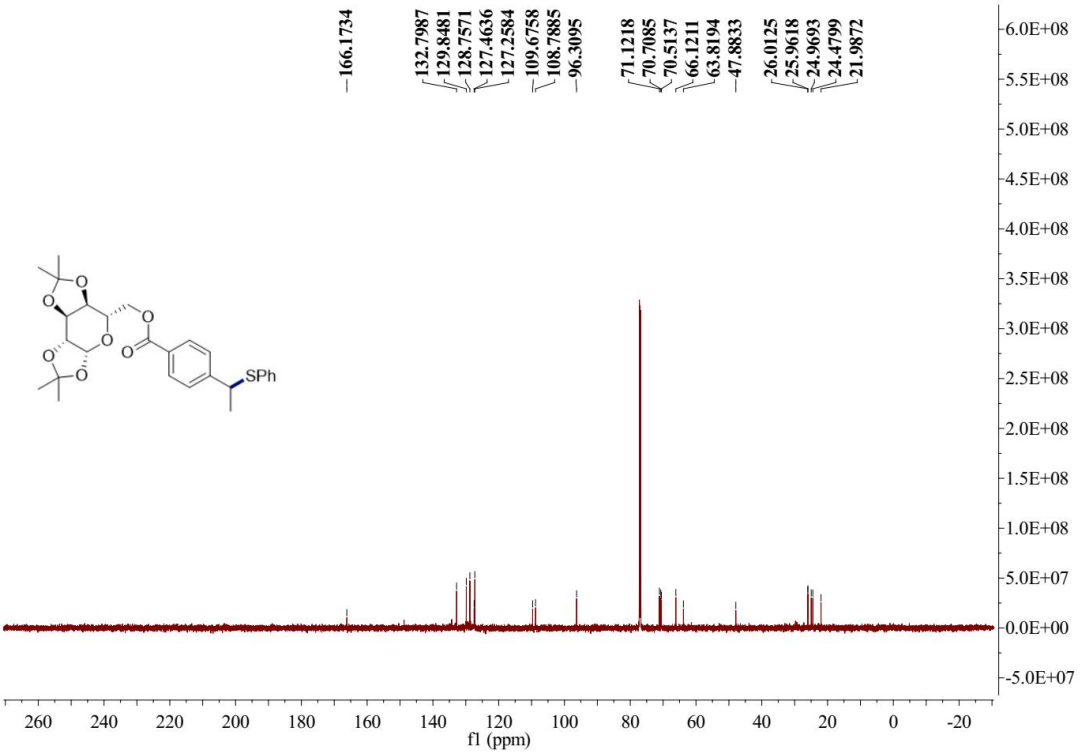
^{1}H NMR (400 MHz, $CDCl_3$) of **3y**



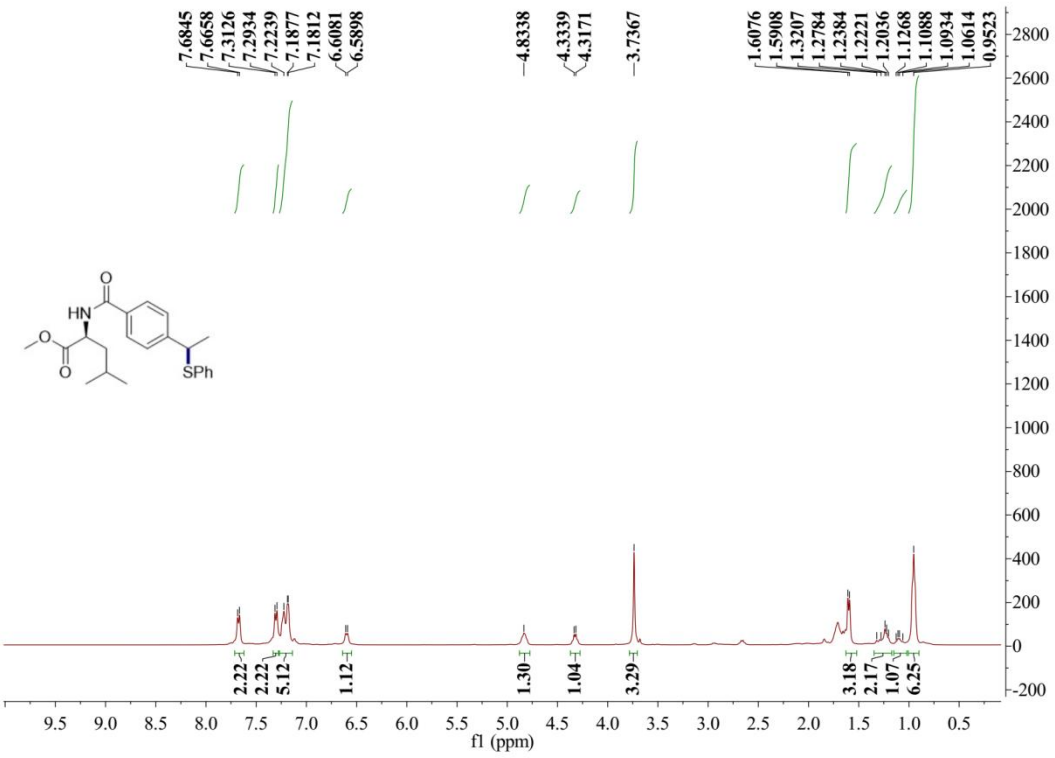
^{13}C NMR (100 MHz, $CDCl_3$) of **3y**



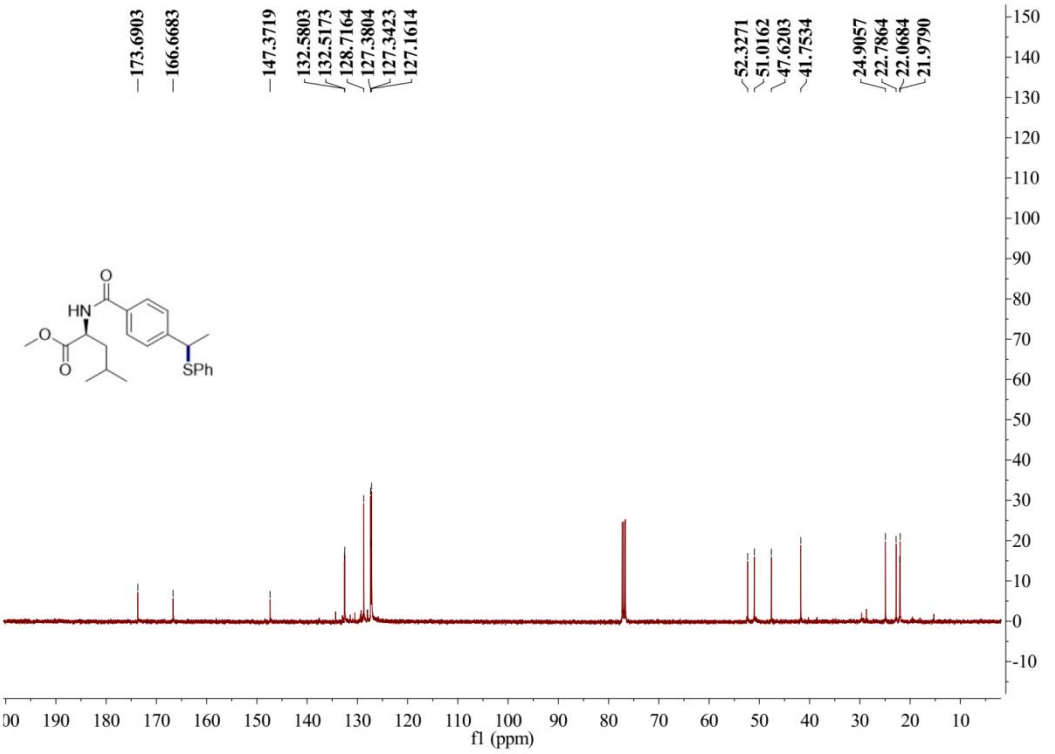
^{1}H NMR (600 MHz, $CDCl_3$) of **3z**



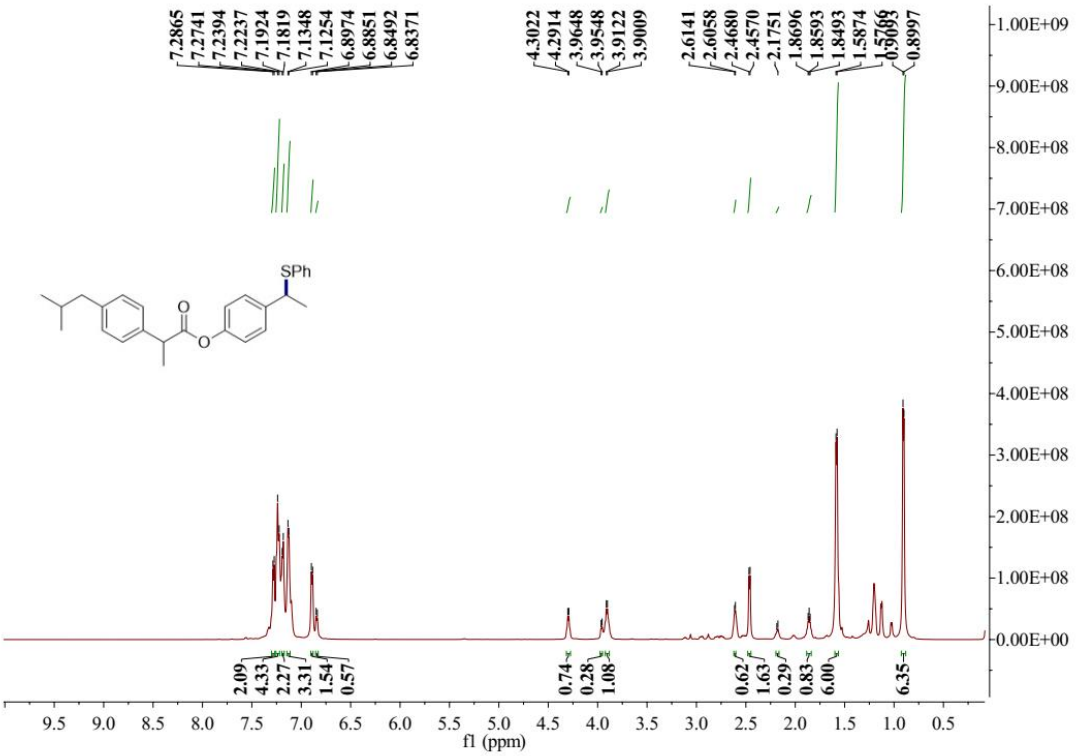
^{13}C NMR (150 MHz, $CDCl_3$) of **3z**



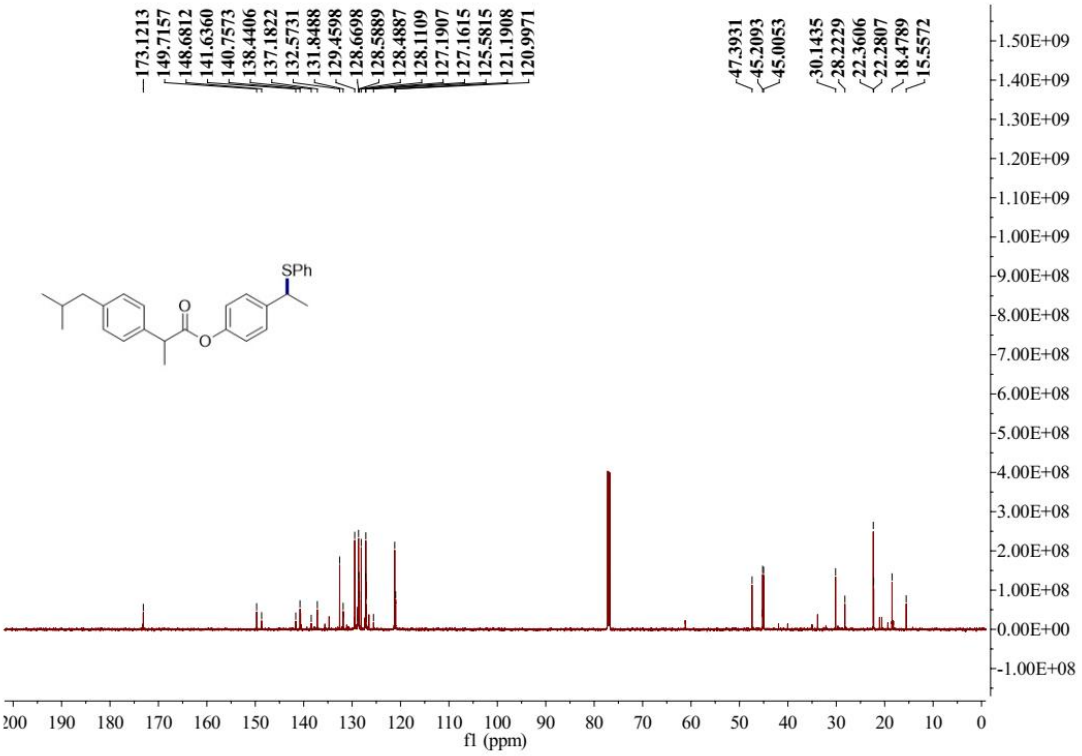
^{1}H NMR (400 MHz, $CDCl_3$) of **3aa**



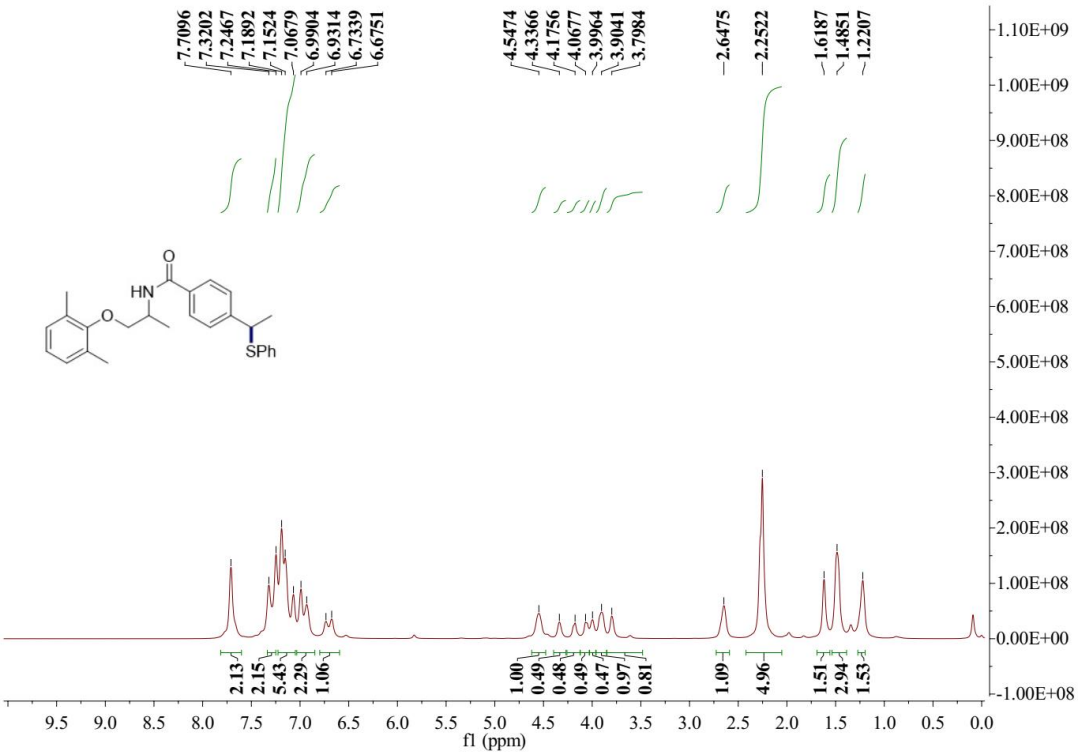
^{13}C NMR (100 MHz, $CDCl_3$) of **3aa**



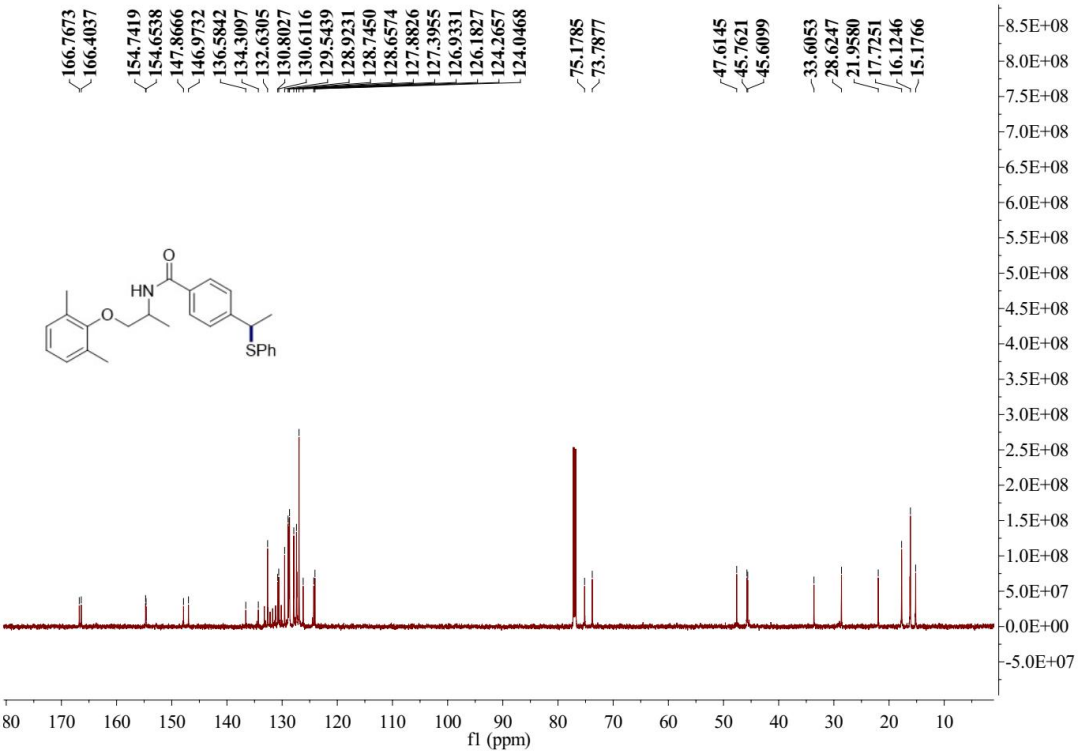
^{1}H NMR (600 MHz, $CDCl_3$) of **3ab**



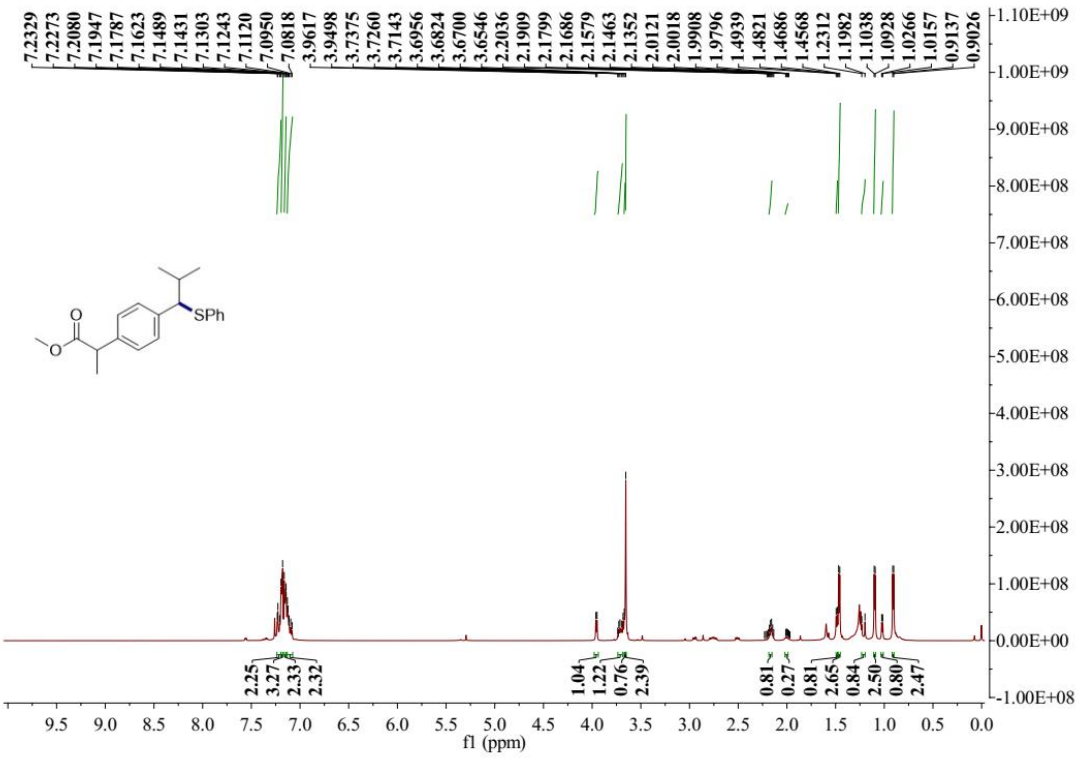
^{13}C NMR (150 MHz, $CDCl_3$) of **3ab**



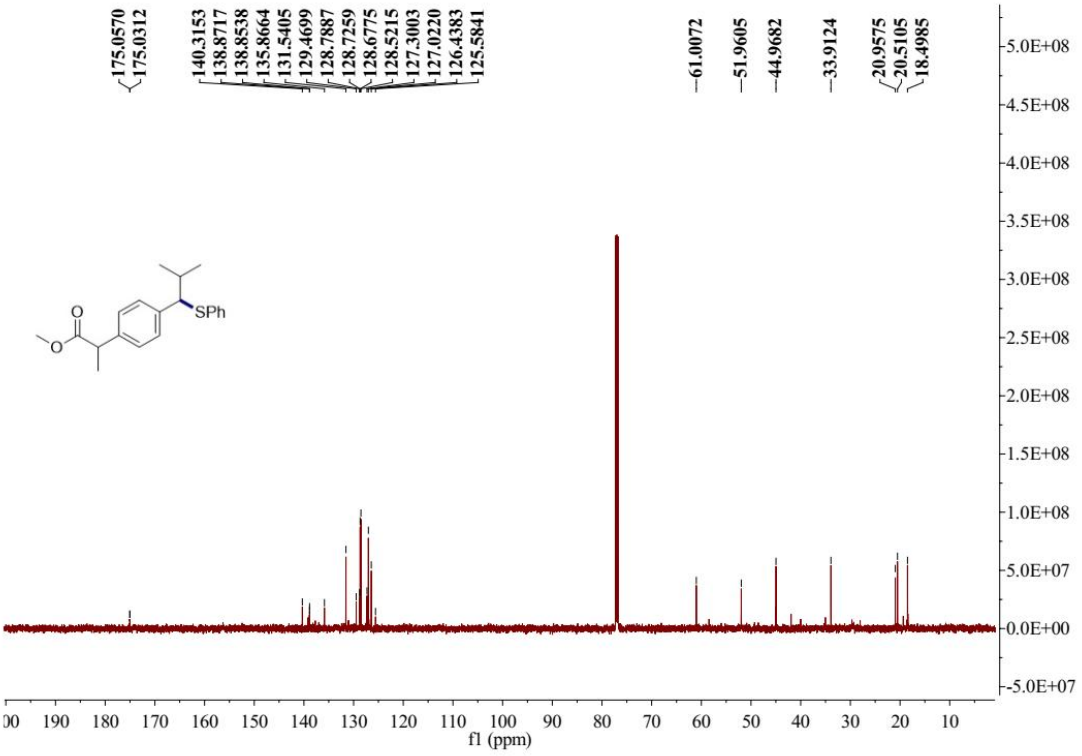
^{1}H NMR (600 MHz, $CDCl_3$) of **3ac**



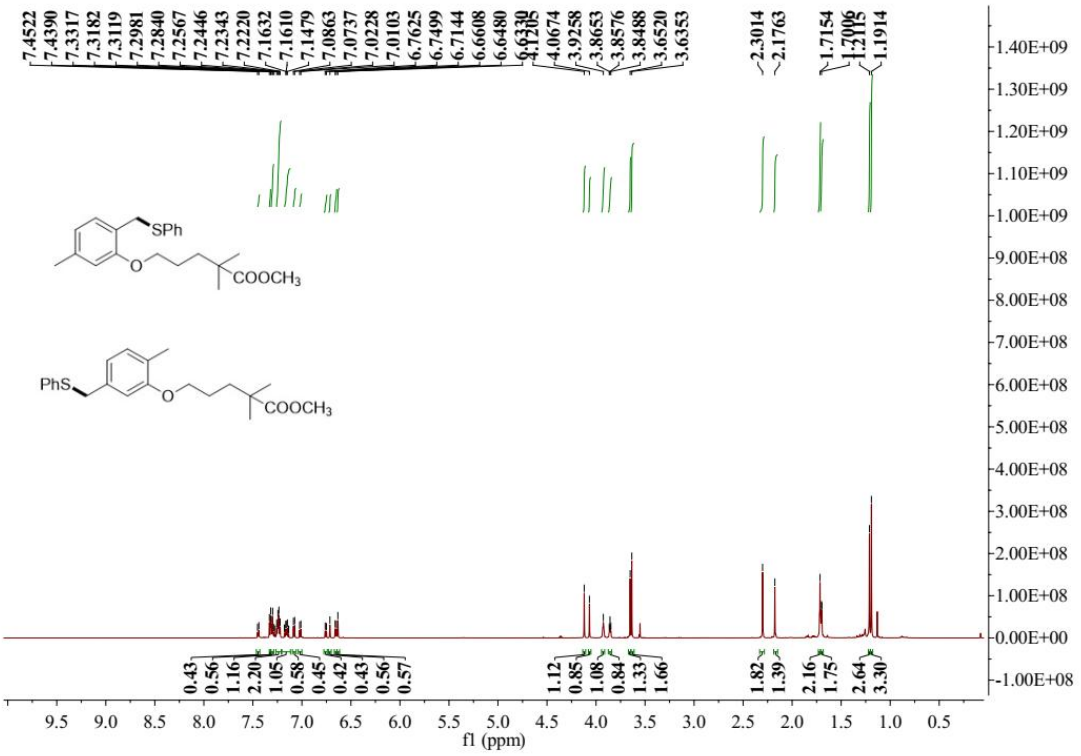
^{13}C NMR (150 MHz, $CDCl_3$) of **3ac**



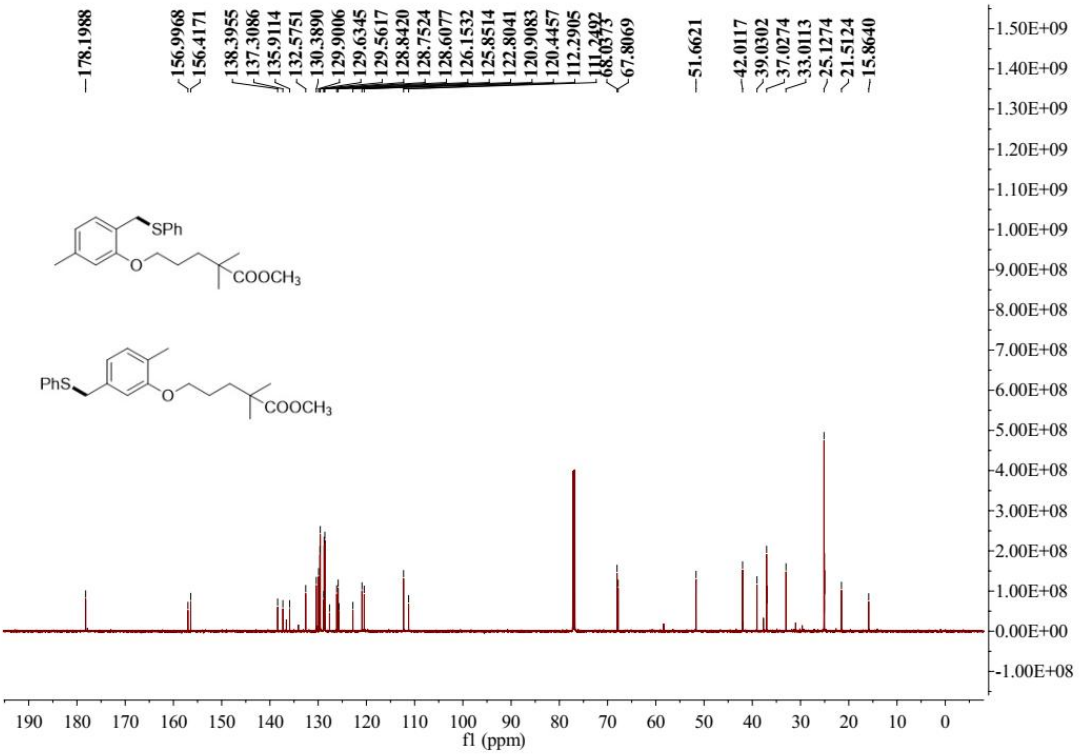
^{1}H NMR (600 MHz, $CDCl_3$) of **3ad**



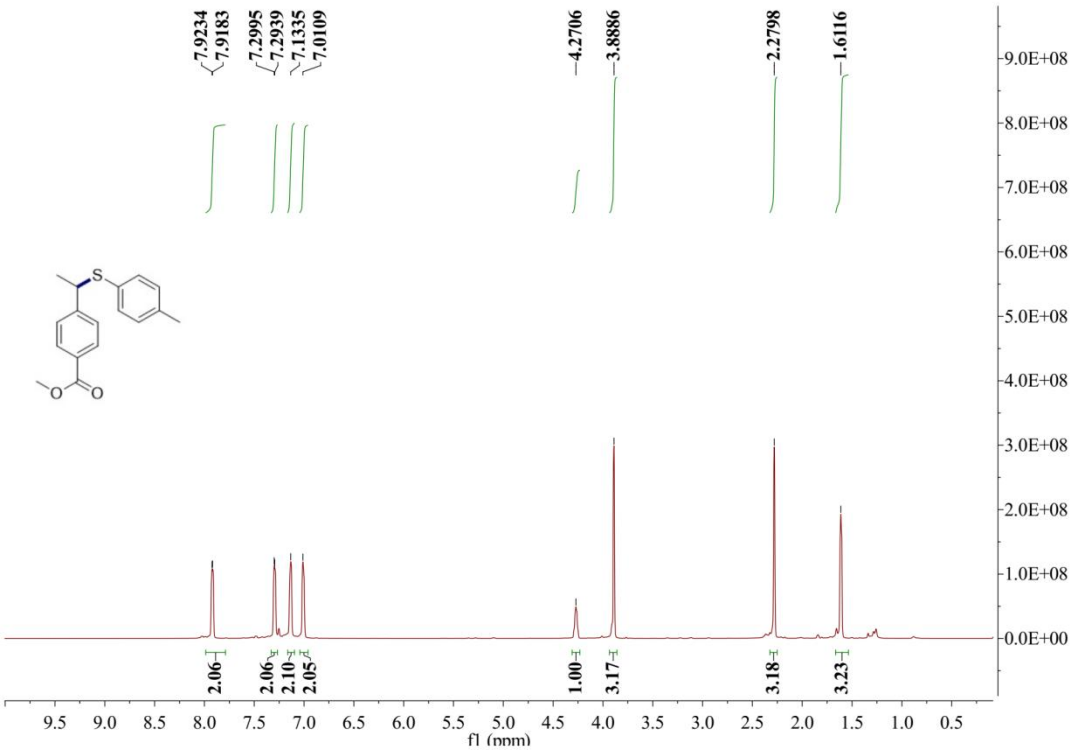
^{13}C NMR (150 MHz, $CDCl_3$) of **3ad**



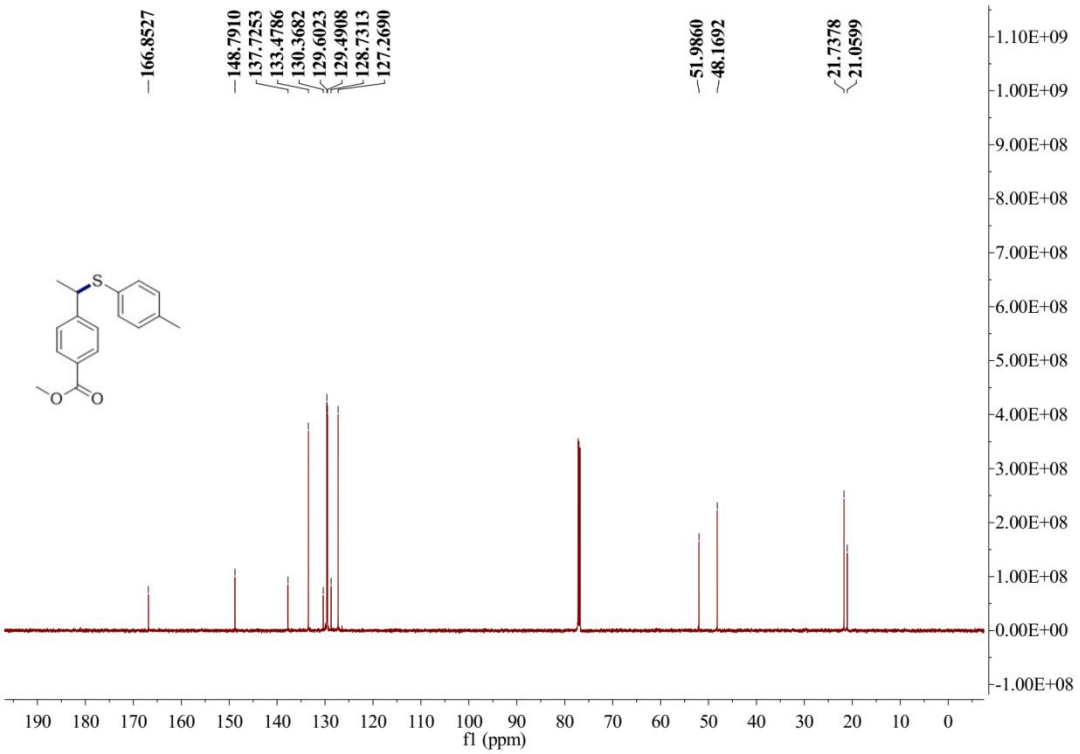
^{1}H NMR (600 MHz, $CDCl_3$) of **3ae**



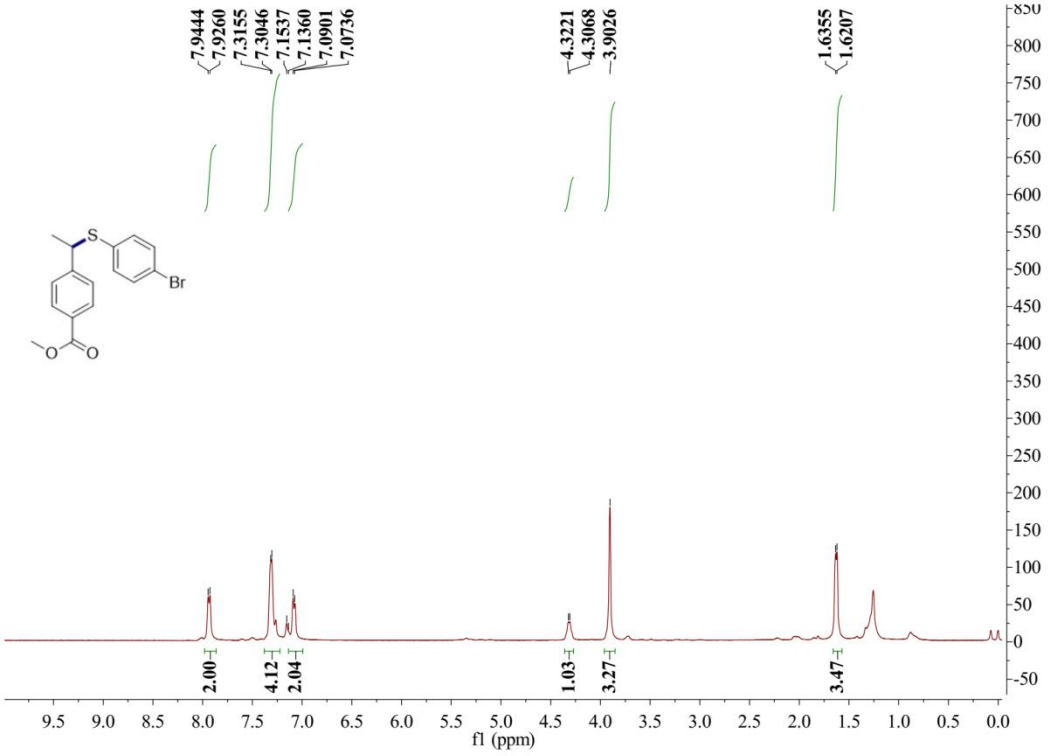
^{13}C NMR (150 MHz, $CDCl_3$) of **3ae**



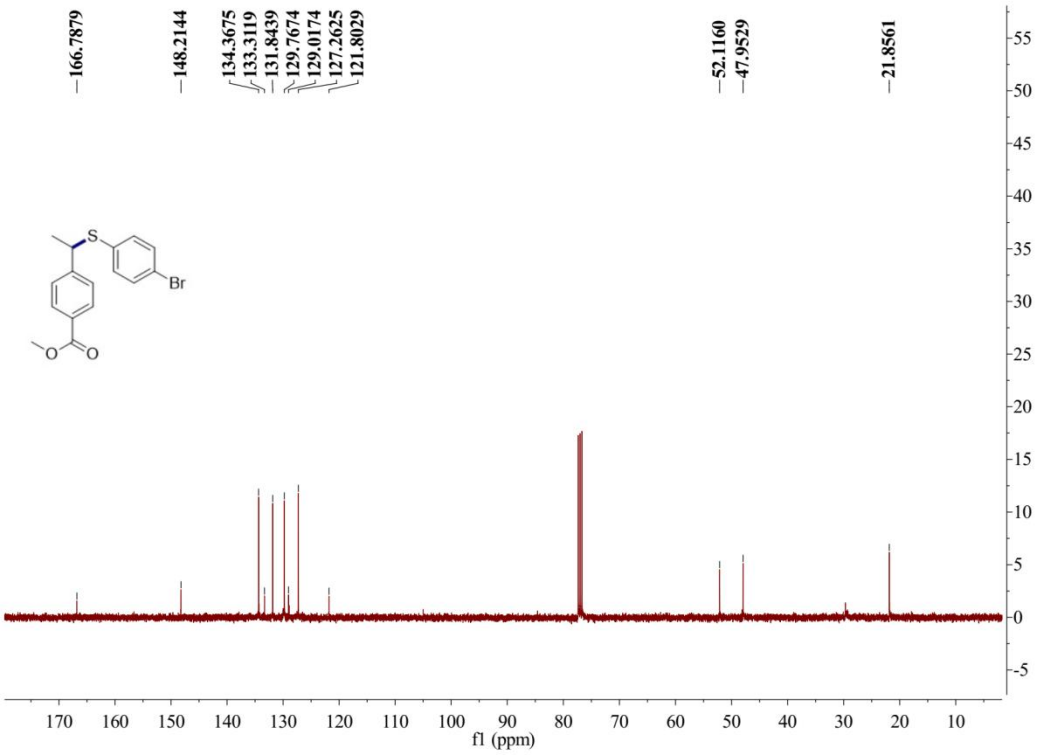
^{1}H NMR (600 MHz, $CDCl_3$) of **4b**



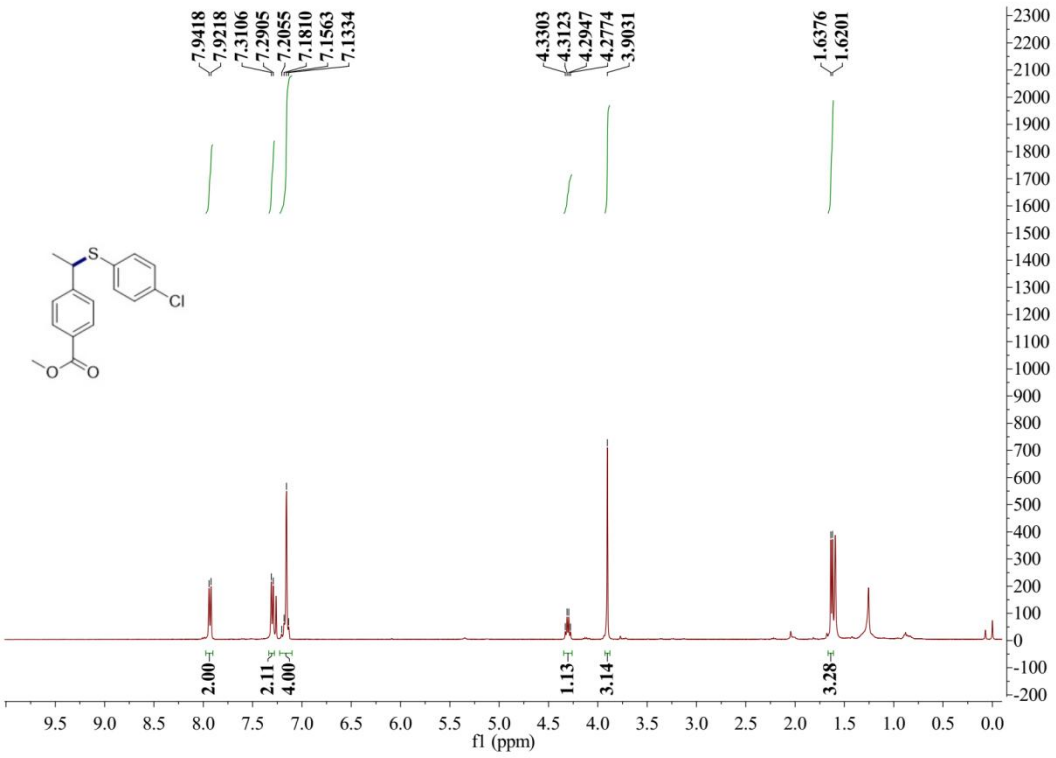
^{13}C NMR (150 MHz, $CDCl_3$) of **4b**



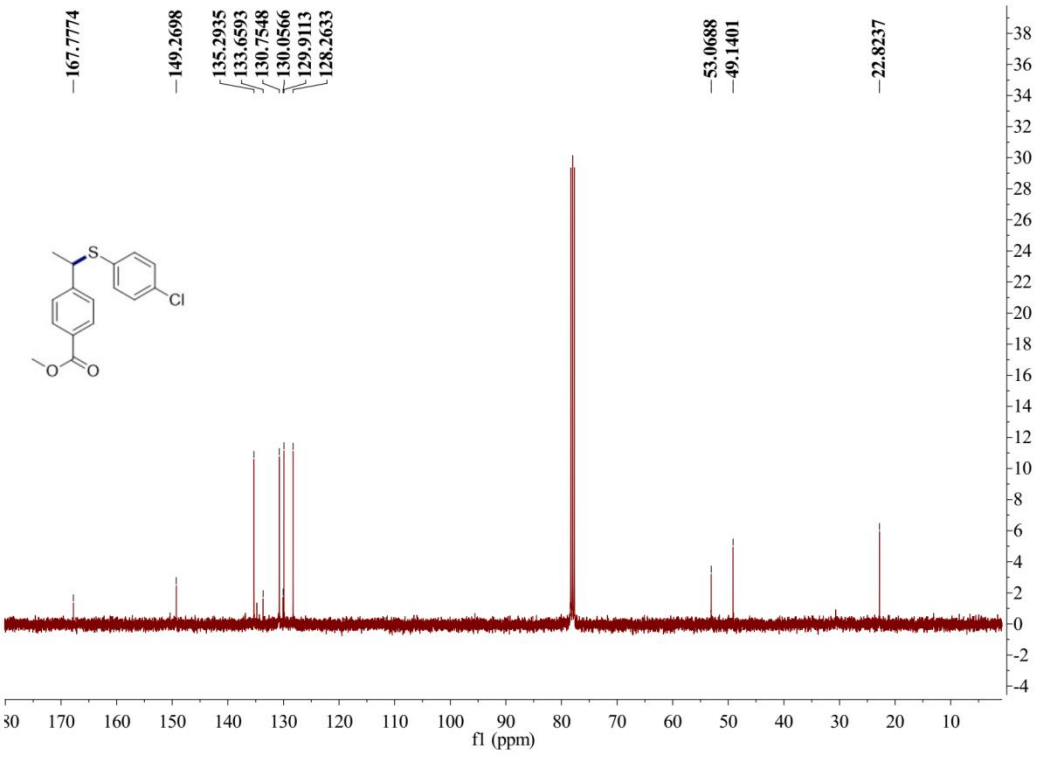
^{1}H NMR (400 MHz, $CDCl_3$) of **4c**



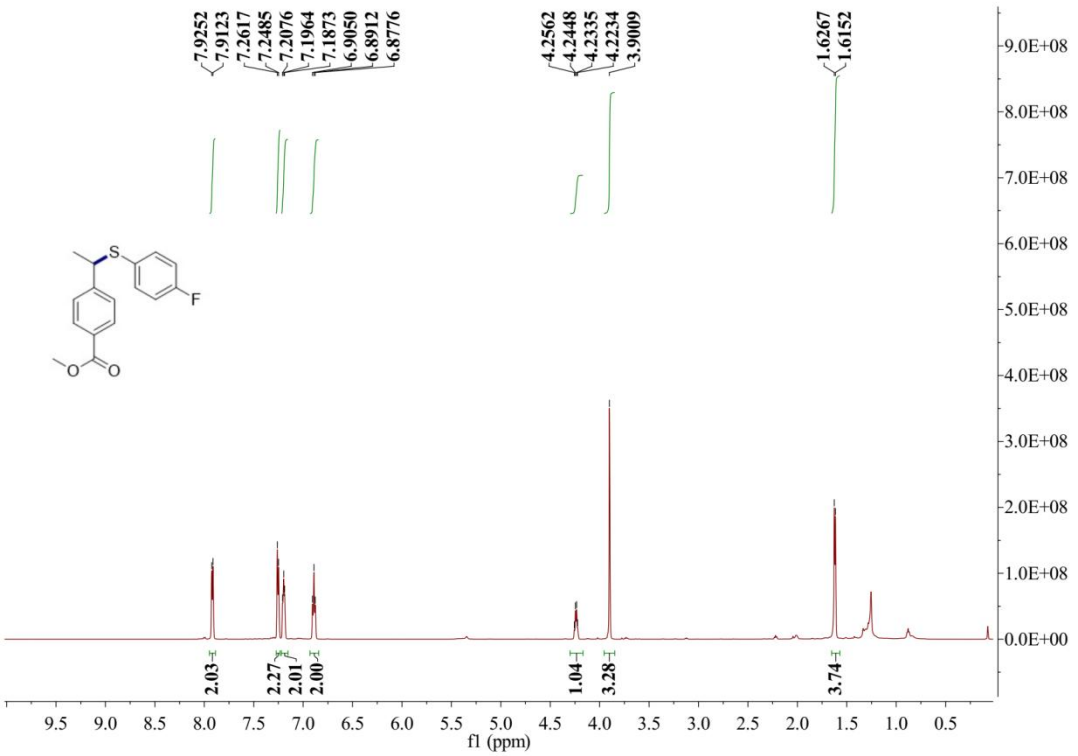
^{13}C NMR (100 MHz, $CDCl_3$) of **4c**



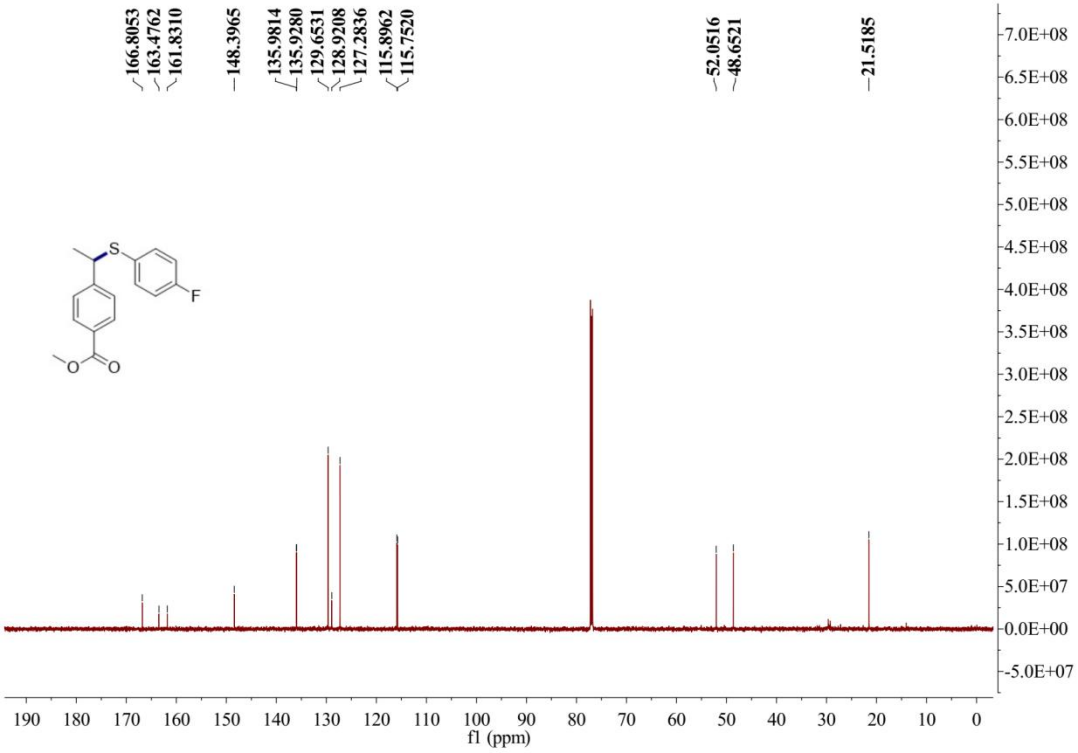
^{1}H NMR (400 MHz, $CDCl_3$) of **4d**



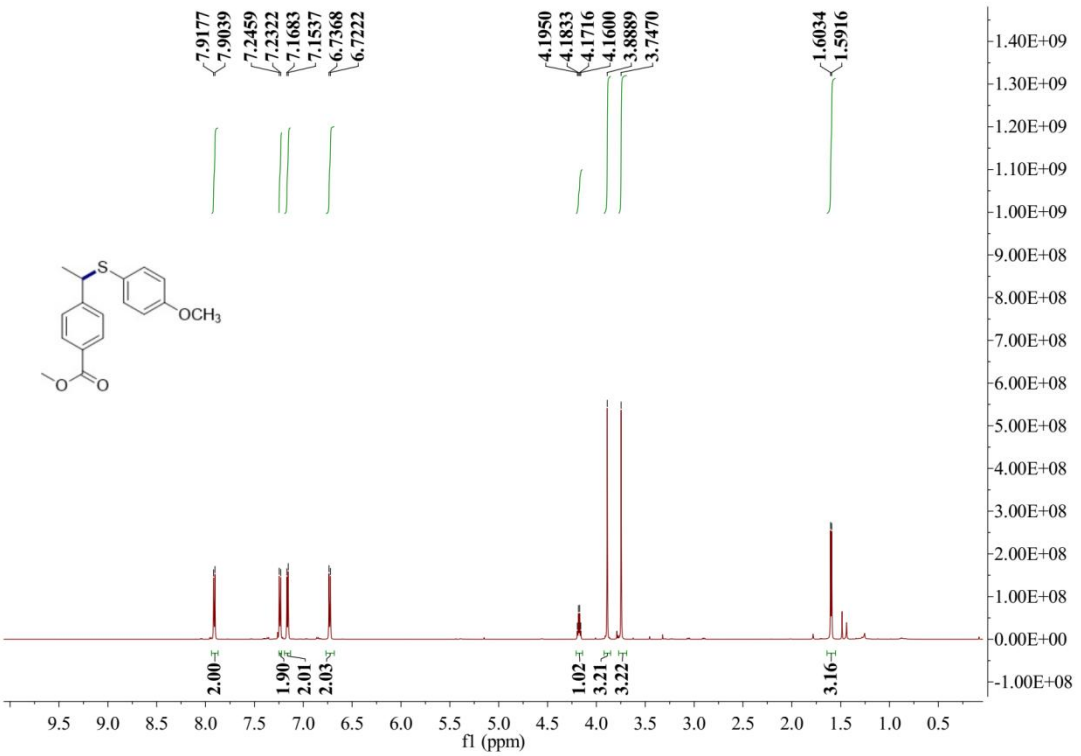
^{13}C NMR (100 MHz, $CDCl_3$) of **4d**



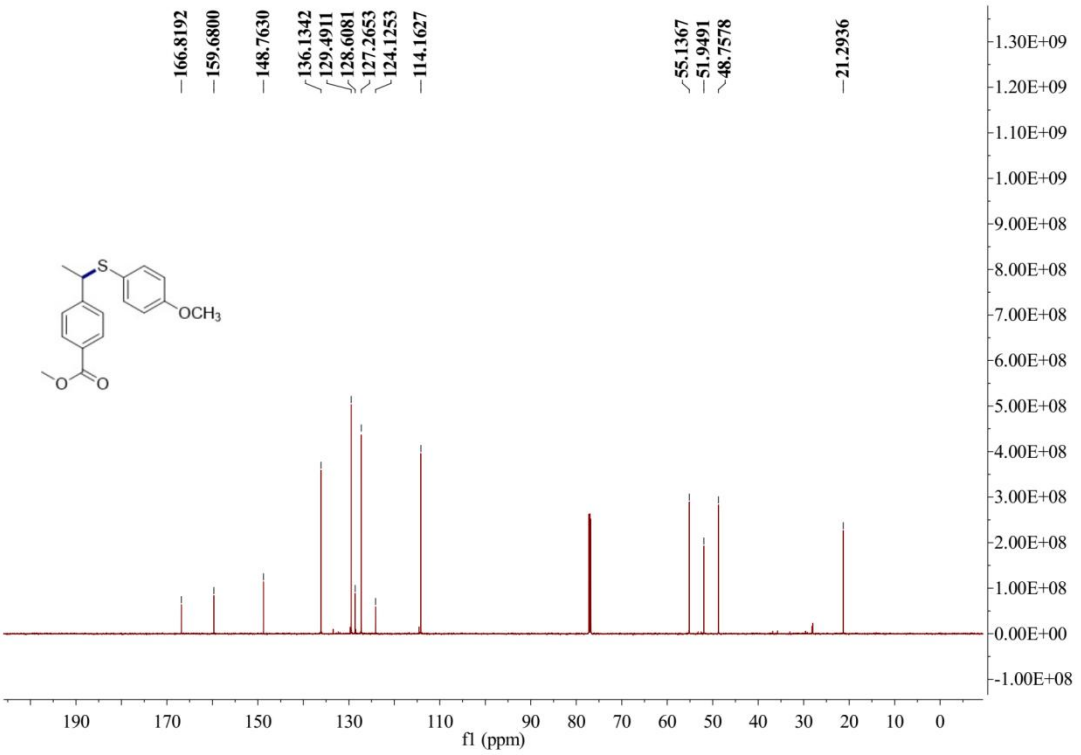
^{1}H NMR (600 MHz, $CDCl_3$) of **4e**



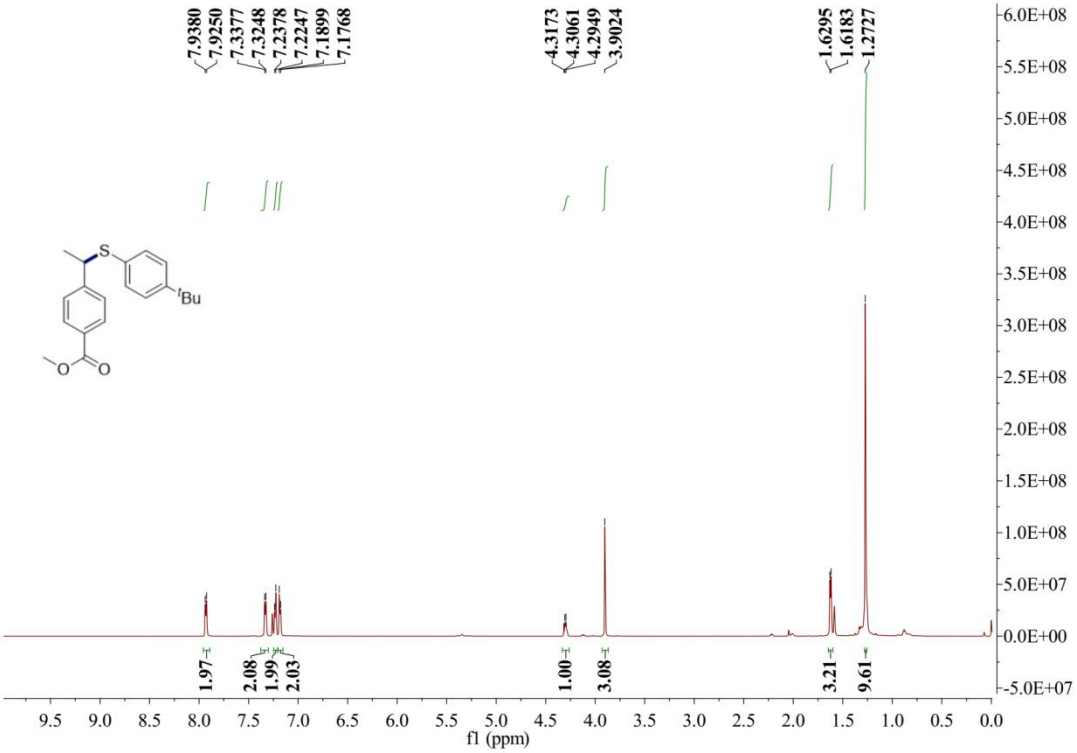
^{13}C NMR (150 MHz, $CDCl_3$) of **4e**



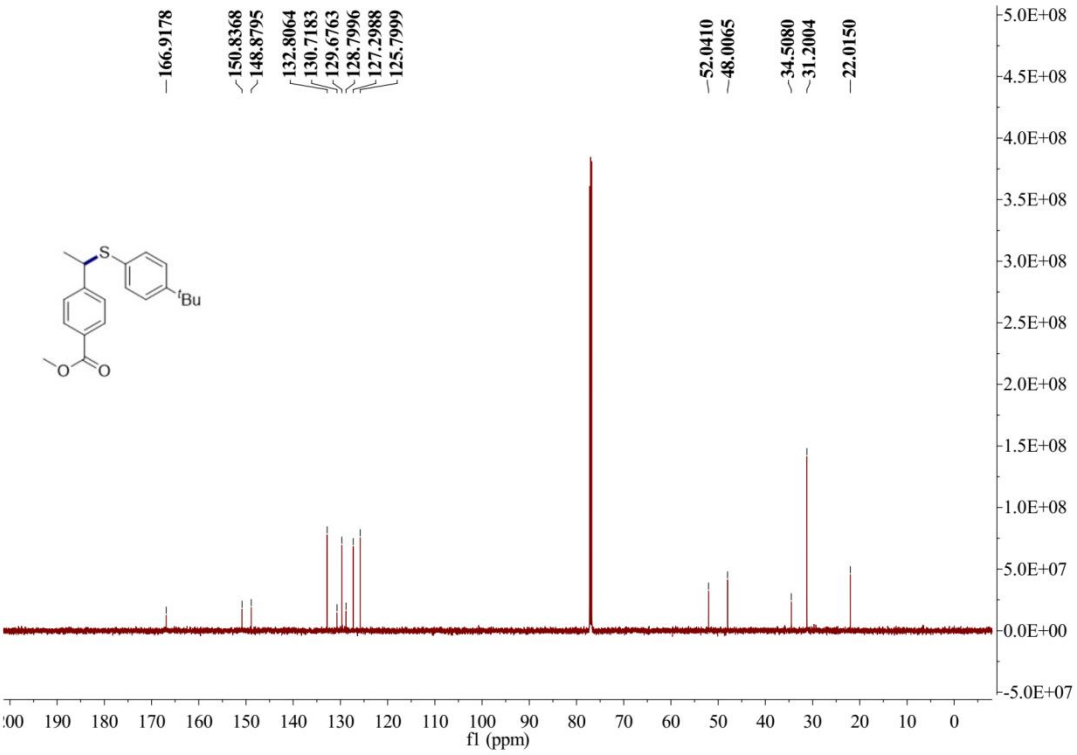
^{1}H NMR (600 MHz, $CDCl_3$) of **4f**



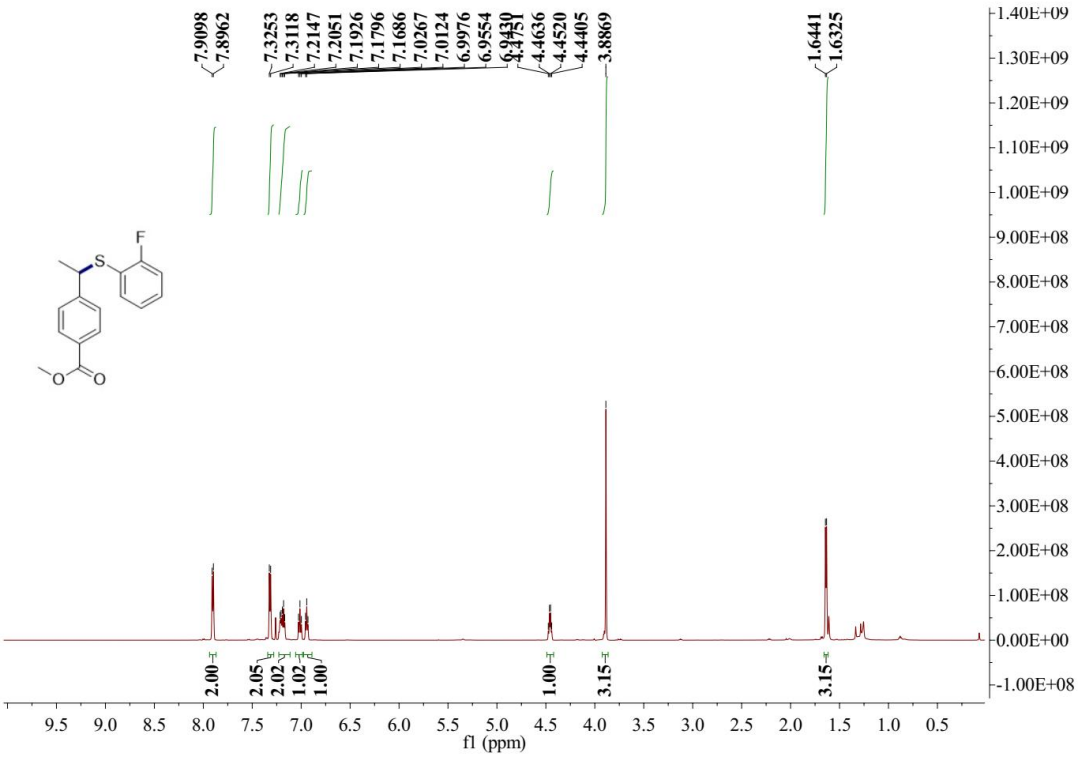
^{13}C NMR (150 MHz, $CDCl_3$) of **4f**



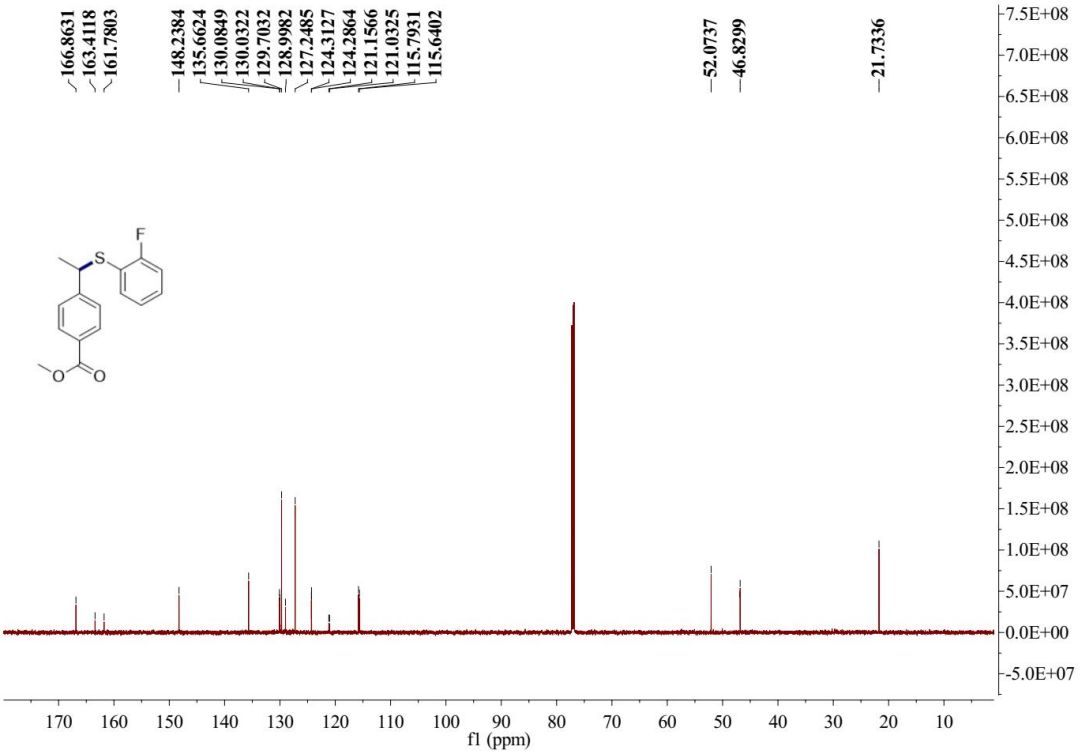
^{1}H NMR (600 MHz, $CDCl_3$) of **4g**



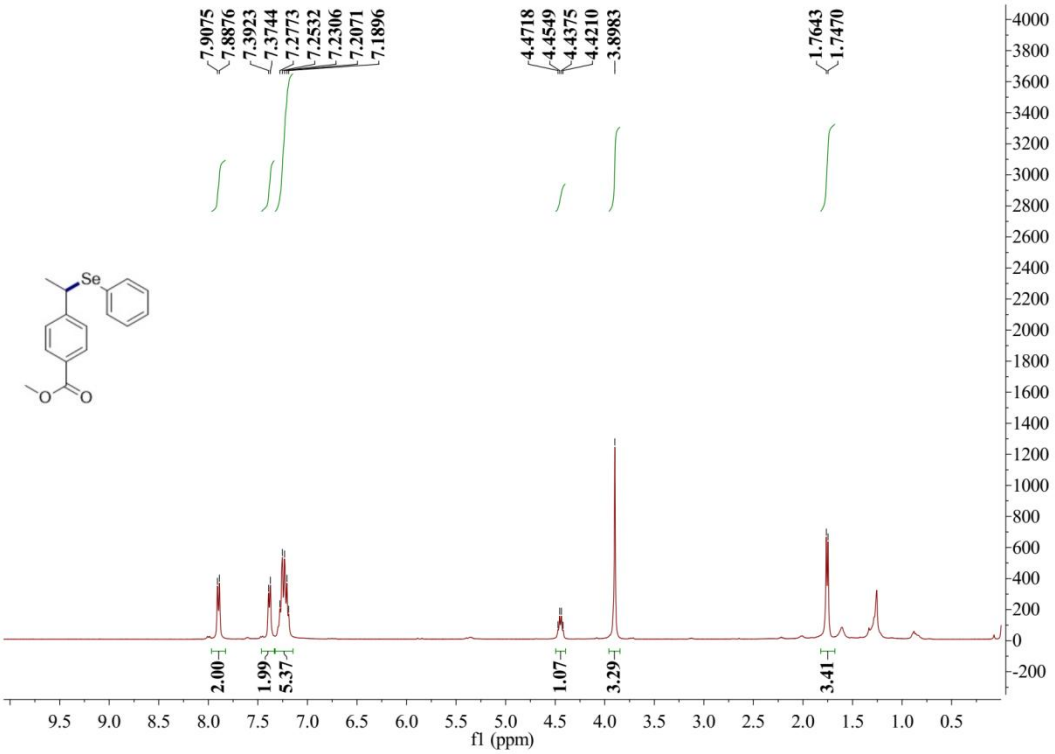
^{13}C NMR (150 MHz, $CDCl_3$) of **4g**



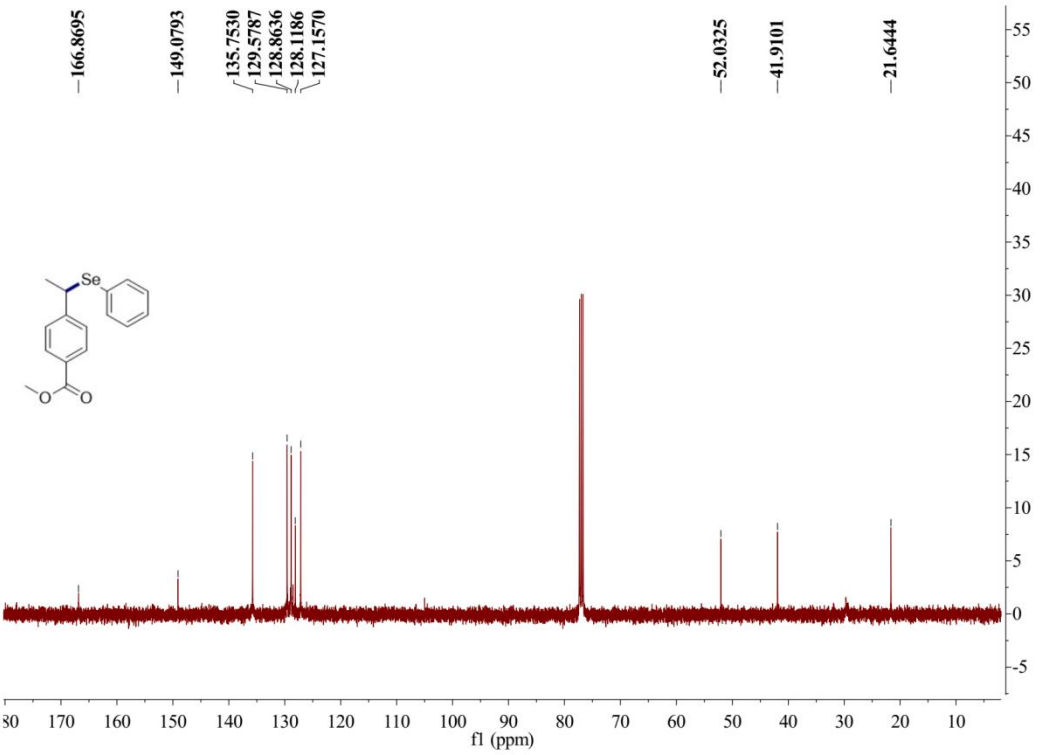
^{1}H NMR (600 MHz, $CDCl_3$) of **4h**



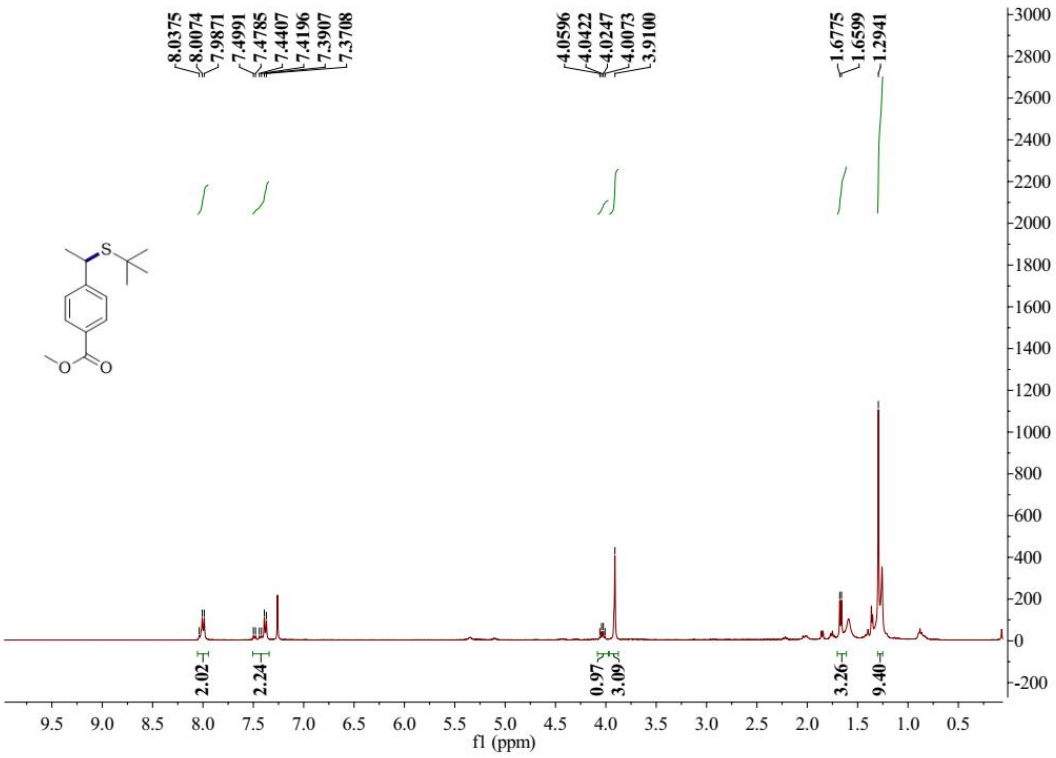
^{13}C NMR (150 MHz, $CDCl_3$) of **4h**



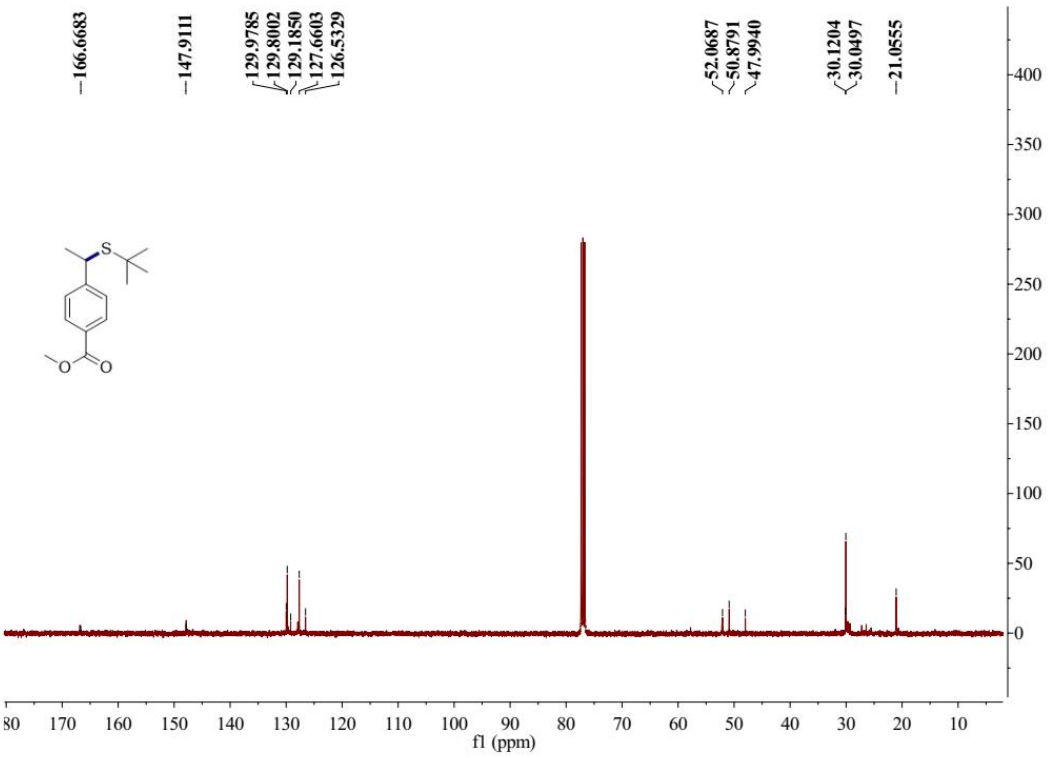
^{1}H NMR (400 MHz, $CDCl_3$) of **4i**



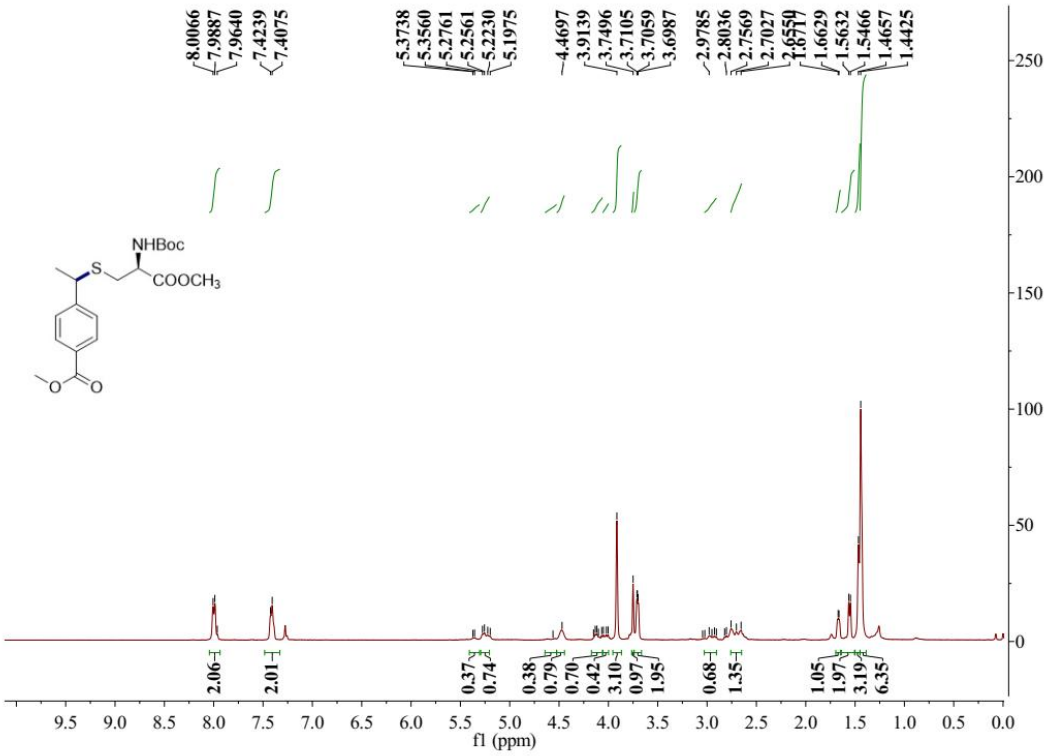
^{13}C NMR (100 MHz, $CDCl_3$) of **4i**



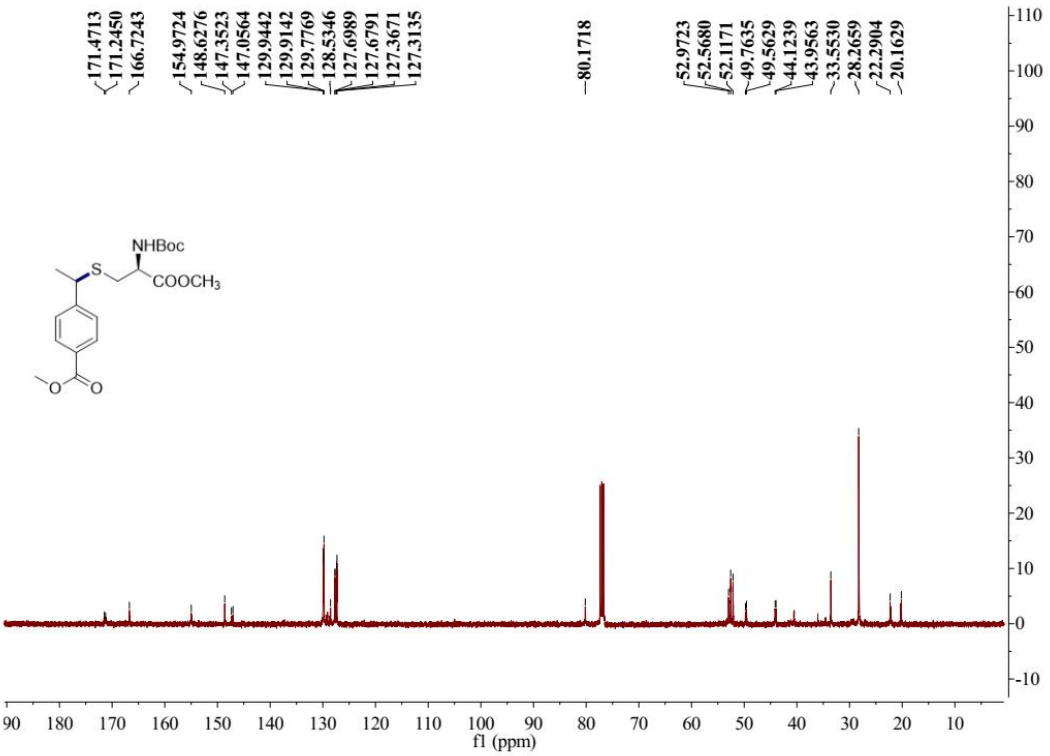
^{1}H NMR (400 MHz, $CDCl_3$) of **4j**



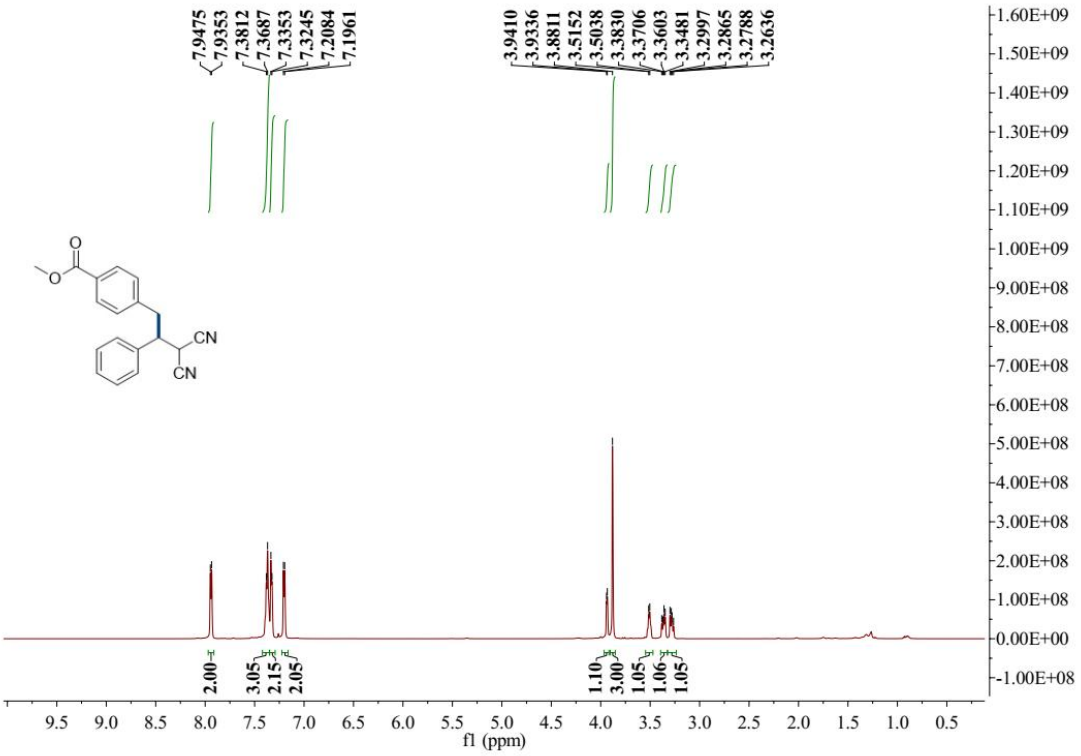
^{13}C NMR (100 MHz, $CDCl_3$) of **4j**



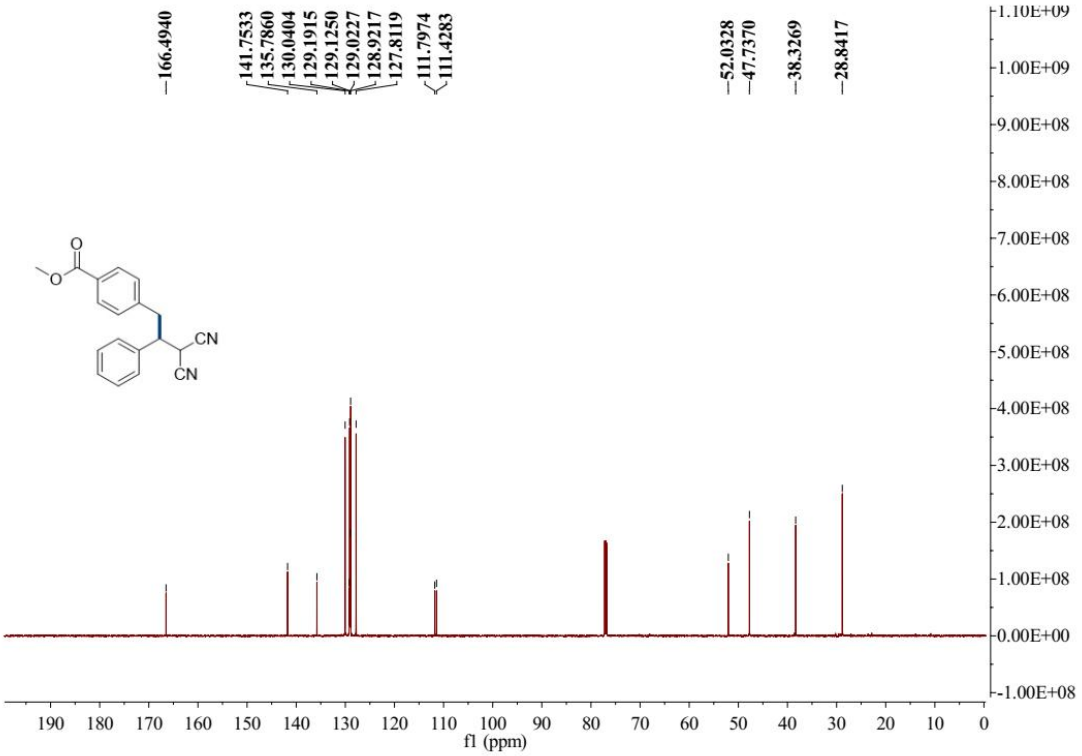
^{1}H NMR (400 MHz, $CDCl_3$) of **4k**



^{13}C NMR (100 MHz, $CDCl_3$) of **4k**



^{1}H NMR (600 MHz, $CDCl_3$) of **3l'**



^{13}C NMR (150 MHz, $CDCl_3$) of **3l'**