Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Scandium-Catalyzed Electrophilic Alkene Difunctionalization: Regioselective Synthesis of Thiosulfone Derivatives

Shuai Huang,[a] Haoyu Li,[a] Tian Xie,[a] Fang Wei,*[a] Chen-Ho Tung[a] and Zhenghu Xu*[ab]

[a]Key Lab for Colloid and Interface Chemistry of Education Ministry, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, PR China

[b]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

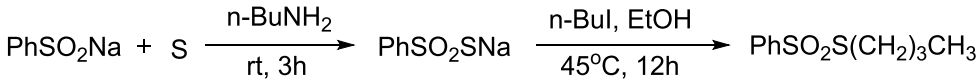
xuzh@sdu.edu.cn; weifang511@126.com.

content

1. General information

Unless otherwise noted, all the reagents were obtained commercially and used without further purification and reactions were monitored by TLC. Reaction solvents were dried with CaH_2. All NMR spectra were recorded on Bruker-500 MHz spectrometer. HRMS were measured on the Q-TOF6510 instruments.

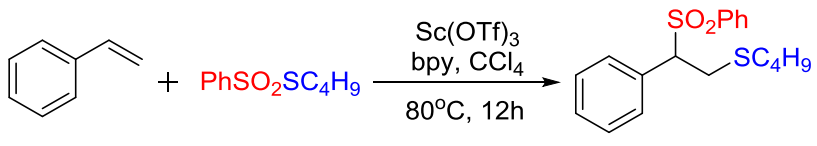
2. Synthesis of the starting materials



2a

Benzenesulfonothioate (**2a-2z**) were prepared by reported procedure[1]: To a solution of $PhSO_2Na$ (40 mmol) in n-$BuNH_2$ (40 mL) was added S (42 mmol) at room temperature and the solution was stirred for 3 h. The reaction mixture was evaporated under reduced pressure to removal of solvent. The residue was washed by Et_2O to obtain white powder. To a solution of $PhSO_2SNa$ in EtOH (50 mL) was added n-C_4H_9I (60 mmol). Then the solution was stirred at 45℃ for 12 h. Upon completion, water (40 mL) was added to the reaction mixture and the solution was extracted with CH_2Cl_2 (30 mL × 3). The combined organic layer was dried with anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified through column chromatography afforded the product (**2a**).

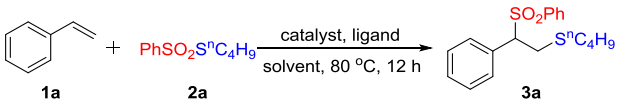
3. Typical procedure for the Thiosulfonylation of Alkenes



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

To a mixture of $Sc(OTf)_3$ (20 mol%), 2,2'-Bipyridine (20 mol%) in CCl_4 (1 mL) under N_2 atmosphere, alkene (0.2 mmol), thiosulfonylation reagent **2a** (0.4 mmol) were added. The reaction system was stirred at 80 ^oC for 12 h. Then, the resulting mixture was evaporated under reduced pressure and purified by silica gel flash chromatography to afford the desired product (**3a**).

4. Optimization of Reaction Conditions[a]



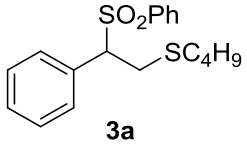
1a **2a** **3a**

entry	cat.	ligand	solvent	yield/%[b]
1	$Pd(OAc)_2$	1,10-phen	CH_3CN	0
2	AgOTf	1,10-phen	CH_3CN	0
3	$Zn(OTf)_2$	1,10-phen	CH_3CN	0
4	$Cu(OTf)_2$	1,10-phen	CH_3CN	0
6	$Bi(OTf)_3$	1,10-phen	CH_3CN	0
7	$In(OTf)_3$	1,10-phen	CH_3CN	0
8	$Ga(OTf)_3$	1,10-phen	CH_3CN	0
9	$La(OTf)_3$	1,10-phen	CH_3CN	0
10	$Eu(OTf)_3$	1,10-phen	CH_3CN	0
11	$Er(OTf)_3$	1,10-phen	CH_3CN	0
12	$Yb(OTf)_3$	1,10-phen	CH_3CN	0
13	$Y(OTf)_3$	1,10-phen	CH_3CN	0
14	$Sc(OTf)_3$	1,10-phen	CH_3CN	45
15	$ScCl_3$	1,10-phen	CH_3CN	0
16	$Sc(OTf)_3$	--	CH_3CN	0
17	--	1,10-phen	CH_3CN	0
18	$Sc(OTf)_3$	1,10-phen	DMSO	0
19	$Sc(OTf)_3$	1,10-phen	DMF	0
20	$Sc(OTf)_3$	1,10-phen	THF	0
21	$Sc(OTf)_3$	1,10-phen	dioxane	0
22	$Sc(OTf)_3$	1,10-phen	toluene	trace
23	$Sc(OTf)_3$	1,10-phen	DCE	51
24	$Sc(OTf)_3$	1,10-phen	CCl_4	78

25	**$Sc(OTf)_3$**	**bpy**	**CCl_4**	**88**

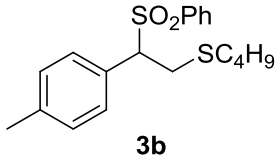
[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), catalyst (20 mol %), ligand (20 mol %), solvent (1 mL) was stirred at 80 °C under N_2 atmosphere for 12 h. [b]Isolated yield. bpy = 2,2'-Bipyridine, 1,10-phen = 1,10-Phenanthroline.

5. Characterization Data



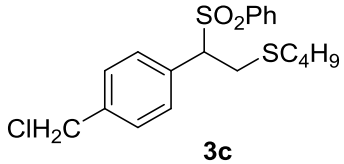
3a

Yield: 84%, 56.1 mg, white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (m, 3H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.12 (d, *J* = 7.4 Hz, 2H), 4.23 (dd, *J* = 11.8, 3.3 Hz, 1H), 3.51 (dd, *J* = 13.3, 3.3 Hz, 1H), 3.28 (dd, *J* = 13.1, 12.0 Hz, 1H), 2.41-2.31 (m, 2H), 1.46 (m, 2H), 1.29 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.0, 133.7, 131.4, 129.9, 129.1, 128.8, 128.5, 71.8, 32.5, 31.4, 29.8, 21.8, 13.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{18}H_{22}NaO_2S_2$ 357.0953; found 357.0950.



3b

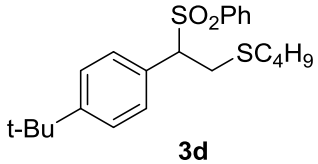
Yield: 60%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 3H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.06 (d, *J* = 7.5 Hz, 2H), 7.01 (d, *J* = 7.6 Hz, 2H), 4.19 (d, *J* = 11.8 Hz, 1H), 3.47 (d, *J* = 13.2 Hz, 1H), 3.24 (t, *J* = 12.6 Hz, 1H), 2.37 (t, *J* = 7.3 Hz, 2H), 2.31 (s, 3H), 1.50 – 1.40 (m, 2H), 1.29 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.1, 137.1, 133.7, 129.8, 129.3, 129.1, 128.7, 128.2, 71.4, 32.5, 31.4, 29.8, 21.8, 21.3, 13.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{19}H_{24}NaO_2S_2$ 371.1110; found 371.1120.



3c

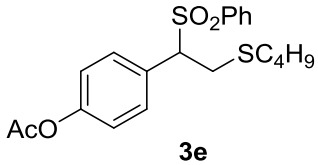
Yield: 54%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.51 (m, 3H), 7.40 (m, 2H), 7.30 – 7.25 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 4.54 (s, 2H), 4.24 (dd, *J* = 11.9, 3.2 Hz, 1H), 3.48 (dd, *J* = 13.3, 3.3 Hz, 1H), 3.26 (t, *J* = 12.6 Hz, 1H), 2.38 (t, *J* = 7.4 Hz, 2H), 1.46 (m, 2H), 1.29 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H). ^{13}C

NMR (126 MHz, $CDCl_3$) δ 138.5, 136.9, 133.9, 131.6, 130.3, 129.0, 128.9, 128.7, 71.3, 45.6, 32.49, 31.4, 29.7, 21.8, 13.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{19}H_{23}ClNaO_2S_2$ 405.0720; found 405.0710.



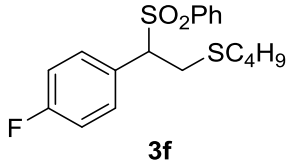
3d

Yield: 61%. ^1H NMR (500 MHz, $CDCl_3$) δ 7.56-7.49 (m, 3H), 7.39-7.34 (m, 2H), 7.27-7.23 (m, 2H), 7.07-7.03 (m, 2H), 4.21 (dd, *J* = 11.7, 3.3 Hz, 1H), 3.45 (dd, *J* = 13.4, 3.3 Hz, 1H), 3.27 (dd, *J* = 13.3, 11.8 Hz, 1H), 2.38-2.32 (m, 2H), 1.44 (M, 2H), 1.32-1.23 (m, 12H), 0.83 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.4, 137.2, 133.6, 129.6, 129.1, 128.6, 128.1, 125.4, 71.6, 34.6, 32.5, 31.4, 31.3, 29.7, 21.8, 13.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{22}H_{30}NaO_2S_2$ 413.1579; found 413.1590.



3e

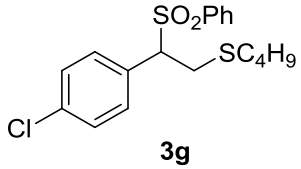
Yield: 54%. ^1H NMR (500 MHz, $CDCl_3$) δ 7.56 (t, *J* = 7.4 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 8.6 Hz, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 4.23 (dd, *J* = 11.7, 3.3 Hz, 1H), 3.51 (dd, *J* = 13.4, 3.3 Hz, 1H), 3.27-3.19 (m, 1H), 2.38 (t, *J* = 7.4 Hz, 2H), 2.28 (s, 3H), 1.47 (m, 2H), 1.31 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9, 151.3, 136.8, 133.8, 130.9, 129.0, 128.9, 128.9, 121.7, 71.2, 32.5, 31.4, 29.7, 21.8, 21.2, 13.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{20}H_{24}NaO_4S_2$ 415.1008; found 415.1010.



3f

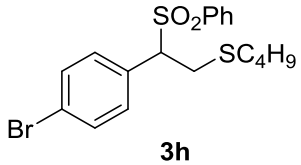
Yield: 74%. ^1H NMR (500 MHz, $CDCl_3$) δ 7.62-7.51 (m, 3H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.11 (m, 2H), 6.95 (t, *J* = 8.5 Hz, 2H), 4.22 (dd, *J* = 12.0, 3.2 Hz, 1H), 3.49 (dd, *J* = 13.3, 3.3 Hz, 1H), 3.22 (t, *J* = 12.7 Hz, 1H), 2.38 (t, *J* = 7.4 Hz, 2H), 1.45 (m, 2H), 1.30 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz,

$CDCl_3$) δ 164.1, 162.1, 136.8, 133.9, 131.7 (d, *J* = 8.4 Hz), 129.0 (d, *J* = 11.2 Hz), 127.2 (d, *J* = 3.2 Hz), 115.7, 115.6, 70.8, 32.5, 31.4, 29.8, 21.8, 13.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{18}H_{21}FNaO_2S_2$ 375.0859; found 375.0869.



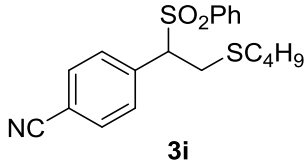
3g

Yield: 77%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61-7.53 (m, 3H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 8.5 Hz, 2H), 4.21 (dd, *J* = 12.0, 3.3 Hz, 1H), 3.48 (dd, *J* = 13.3, 3.4 Hz, 1H), 3.25-3.17 (m, 1H), 2.38 (t, *J* = 7.4 Hz, 2H), 1.50-1.42 (m, 2H), 1.30 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.8, 135.3, 134.0, 131.2, 130.0, 129.0, 129.0, 128.8, 70.9, 32.5, 31.4, 29.8, 21.8, 13.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{18}H_{21}ClNaO_2S_2$ 391.0564; found 391.0546.



3h

Yield: 54%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (t, *J* = 7.4 Hz, 1H), 7.57-7.53 (m, 2H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 4.19 (dd, *J* = 12.0, 3.3 Hz, 1H), 3.47 (dd, *J* = 13.3, 3.4 Hz, 1H), 3.20 (dd, *J* = 13.2, 12.1 Hz, 1H), 2.38 (t, *J* = 7.3 Hz, 2H), 1.46 (p, *J* = 7.1 Hz, 2H), 1.30 (dq, *J* = 14.6, 7.3 Hz, 2H), 0.85 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.8, 134.0, 131.7, 131.5, 130.5, 129.0, 129.0, 123.5, 71.0, 32.5, 31.4, 29.7, 21.8, 13.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{18}H_{21}BrNaO_2S_2$ 435.0059; found 435.0046.



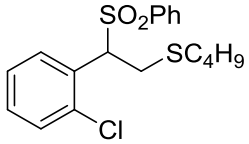
3i

Yield: 59%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (t, *J* = 7.4 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 4H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.29-7.24 (m, 2H), 4.28 (dd, *J* = 12.0, 3.3 Hz, 1H), 3.49 (dd, *J* = 13.4, 3.4 Hz, 1H), 3.28-3.19 (m, 1H), 2.39 (t, *J* = 7.4 Hz, 2H), 1.46 (m, 2H), 1.30 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126

MHz, $CDCl_3$) δ 136.9, 136.6, 134.3, 132.2, 130.7, 129.1, 129.0, 118.2, 113.1, 77.3, 77.1, 76.8, 71.1, 32.6, 31.3, 29.6, 21.8, 13.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{19}H_{21}NNaO_2S_2$ 382.0906; found 382.0901.

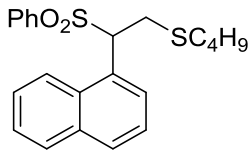
3j

Yield: 58%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (m, 3H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.16-7.09 (m, 2H), 6.91 (d, *J* = 6.4 Hz, 2H), 4.19 (dd, *J* = 11.8, 3.2 Hz, 1H), 3.47 (dd, *J* = 13.3, 3.3 Hz, 1H), 3.26 (t, *J* = 12.6 Hz, 1H), 2.37 (t, *J* = 7.4 Hz, 2H), 2.25 (s, 3H), 1.50-1.42 (m, 2H), 1.30 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.2, 137.1, 133.7, 131.2, 130.7, 129.9, 129.1, 128.7, 128.3, 127.0, 71.8, 32.4, 31.4, 29.7, 21.8, 21.3, 13.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{19}H_{24}NaO_2S_2$ 371.1110; found 371.1111.



3k

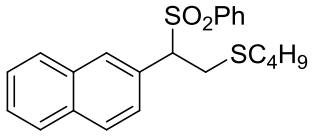
Yield: 87%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.56 (m, 3H), 7.38 (t, *J* = 7.9 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.24 (m, 1H), 7.18 (m, 1H), 5.08 (dd, *J* = 11.8, 3.4 Hz, 1H), 3.58 (dd, *J* = 13.6, 3.5 Hz, 1H), 3.26 (dd, *J* = 13.4, 12.0 Hz, 1H), 2.42 (m, 2H), 1.47 (m, 2H), 1.31 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.4, 136.5, 133.9, 130.2, 129.9, 129.7, 129.4, 129.0, 128.8, 127.2, 65.5, 32.1, 31.3, 30.0, 21.8, 13.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{22}ClO_2S_2$ 369.0744; found 369.0750.



3l

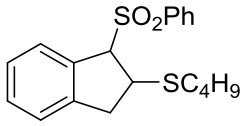
Yield: 53%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.67 (t, *J* = 7.2 Hz, 2H), 7.52-7.43 (m, 3H), 7.39-7.29 (m, 3H), 7.18 (t, *J* = 7.8 Hz, 2H), 5.30 (dd, *J* = 11.5, 3.5 Hz, 1H), 3.74-3.65 (m, 1H), 3.47 (dd, *J* = 13.2, 11.5 Hz, 1H), 2.35 (t, *J* = 7.4 Hz, 2H), 1.46-1.38 (m, 2H), 1.24 (m, 2H), 0.79 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.0, 133.6, 133.5,

132.8, 129.8, 129.0, 128.9, 128.5, 127.7, 126.8, 126.6, 125.6, 125.0, 121.8, 77.1, 64.9, 32.6, 31.4, 30.9, 21.8, 13.5. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{22}H_{24}NaO_2S_2$ 407.1110; found 407.1118.



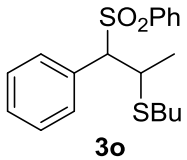
3m

Yield: 66%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.7 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.56-7.43 (m, 6H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.27 (dd, *J* = 8.5, 1.7 Hz, 1H), 4.40 (dd, *J* = 11.9, 3.3 Hz, 1H), 3.58 (dd, *J* = 13.4, 3.4 Hz, 1H), 3.39 (dd, *J* = 13.2, 12.0 Hz, 1H), 2.42-2.33 (m, 2H), 1.49-1.41 (m, 2H), 1.31-1.23 (m, 2H), 0.82 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.0, 133.8, 133.4, 132.9, 130.2, 129.1, 128.8, 128.8, 128.3, 128.1, 127.7, 126.8, 126.5, 126.4, 71.9, 32.5, 31.4, 29.9, 21.8, 13.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{22}H_{24}NaO_2S_2$ 407.1110; found 407.1106.



3n

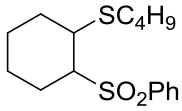
Yield: 61%.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66-7.60 (m, 3H), 7.45 (dd, *J* = 8.7, 7.1 Hz, 2H), 7.34-7.27 (m, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 4.65 (s, 1H), 3.99 (d, *J* = 7.9 Hz, 1H), 3.11 (dd, *J* = 17.2, 7.9 Hz, 1H), 2.70 (d, *J* = 17.1 Hz, 1H), 2.58-2.47 (m, 2H), 1.57-1.49 (m, 2H), 1.39-1.32 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.0, 135.8, 132.9, 131.6, 128.7, 128.2, 127.9, 126.5, 126.0, 123.9, 77.1, 42.7, 38.1, 30.3, 30.3, 21.0, 12.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{19}H_{22}NaO_2S_2$ 369.0953; found 369.0935.



3o

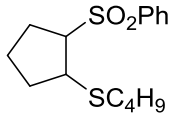
Yield: 65%, d.r.=1.3:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.9 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.44 (m, 6H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.28-7.22 (m, 6H), 7.20 (m, 2H), 7.14 (m, 5H), 4.56 (d, *J* = 4.6 Hz, 1H), 4.11 (d, *J* = 9.2 Hz, 1H),

3.86-3.78 (m, 1H), 3.50-3.42 (m, 1H), 2.36 (m, 3H), 2.26 (m, 2H), 1.80 (d, *J* = 6.8 Hz, 4H), 1.44 (m, 9H), 1.35-1.22 (m, 8H), 0.83 (m, 8H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.9, 138.6, 133.4, 133.2, 133.1, 130.2, 128.9, 128.9, 128.6, 128.6, 128.6, 128.4, 128.2, 127.6, 66.1, 48.8, 40.5, 31.4, 31.4, 31.0, 30.9, 22.1, 21.9, 21.9, 13.6, 10.5. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{19}H_{24}NaO_2S_2$ 371.1110; found 371.1111.



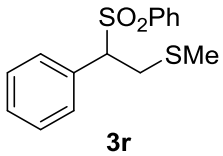
3p

Yield: 82%, d.r.>20:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95-7.88 (m, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 2H), 3.32 (q, *J* = 3.9 Hz, 1H), 3.19 (dd, *J* = 8.5, 4.1 Hz, 1H), 2.42-2.28 (m, 3H), 2.12-1.86 (m, 3H), 1.76-1.67 (m, 1H), 1.66-1.43 (m, 3H), 1.39-1.23 (m, 4H), 0.84 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.8, 133.6, 129.2, 128.6, 64.6, 40.1, 31.6, 31.4, 29.1, 22.0, 21.6, 21.6, 13.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{16}H_{24}NaO_2S_2$ 335.1110; found 335.1100.



3q

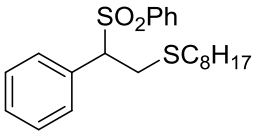
Yield: 44%, d.r.>20:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.66 (t, *J* = 7.3 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 2H), 3.60-3.44 (m, 2H), 2.38 (t, *J* = 7.4 Hz, 2H), 2.17 (m, 2H), 2.05 (m, 1H), 1.83 (m, 2H), 1.69 (m, 1H), 1.43 (m, 2H), 1.35-1.27 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.5, 133.7, 129.2, 128.6, 71.4, 44.2, 34.6, 31.6, 31.4, 27.2, 25.1, 21.9, 13.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{22}NaO_2S_2$ 321.0953; found 321.0964.



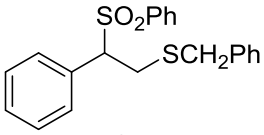
3r

Yield: 86%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58-7.50 (m, 3H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.27-7.22 (m, 2H), 7.13 (d, *J* = 7.6 Hz, 2H), 4.25 (dd, *J* = 11.8, 3.3 Hz, 1H), 3.51 (dd, *J* = 13.5, 3.4 Hz, 1H), 3.31-3.21 (m, 1H), 1.97 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.0, 133.8, 131.4, 129.9, 129.2, 129.0, 128.8, 128.5, 71.4, 32.0, 16.2. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for

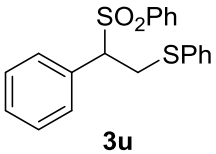
$C_{15}H_{16}NaO_2S_2$ 315.0484; found 315.0483.



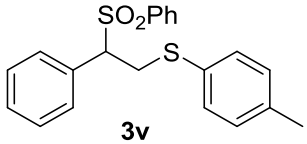
3s Yield: 71%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (m, 3H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.24 (t, *J* = 7.4 Hz, 2H), 7.12 (d, *J* = 7.4 Hz, 2H), 4.23 (dd, *J* = 11.8, 3.3 Hz, 1H), 3.51 (dd, *J* = 13.4, 3.3 Hz, 1H), 3.28 (dd, *J* = 13.2, 12.0 Hz, 1H), 2.39-2.32 (m, 2H), 1.51-1.42 (m, 2H), 1.27 (m, 11H), 0.87 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.0, 133.7, 131.4, 129.9, 129.2, 129.0, 128.8, 128.5, 77.4, 77.1, 76.9, 71.8, 32.8, 31.8, 29.7, 29.4, 29.2, 29.1, 28.7, 22.7, 14.1. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{22}H_{30}NaO_2S_2$ 413.1579; found 413.1580.



3t Yield: 59%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (t, *J* = 7.4 Hz, 1H), 7.48-7.43 (m, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.28 (m, 4H), 7.25-7.17 (m, 4H), 6.99 (d, *J* = 7.3 Hz, 2H), 3.98 (dd, *J* = 11.9, 3.4 Hz, 1H), 3.62-3.52 (m, 2H), 3.42 (dd, *J* = 13.6, 3.4 Hz, 1H), 3.21 (dd, *J* = 13.6, 11.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.8, 137.1, 133.7, 131.3, 130.0, 129.1, 129.0, 128.9, 128.7, 128.7, 128.5, 127.3, 71.2, 37.3, 29.7. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{21}H_{20}NaO_2S_2$ 391.0797; found 391.0786.

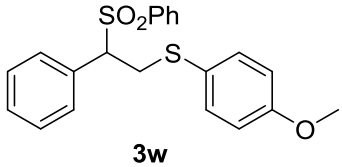


3u Yield: 87%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (t, *J* = 7.4 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.22 (m, 7H), 7.06 (d, *J* = 7.6 Hz, 2H), 4.18 (dd, *J* = 11.9, 3.1 Hz, 1H), 3.99 (dd, *J* = 13.7, 3.2 Hz, 1H), 3.55 – 3.48 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.0, 134.2, 133.8, 130.9, 130.4, 130.0, 129.2, 129.2, 129.0, 128.8, 128.5, 127.1, 70.5, 32.2. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{20}H_{18}NaO_2S_2$ 377.0640; found 377.0644.



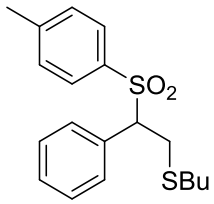
3v

Yield: 74%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (t, *J* = 7.4 Hz, 1H), 7.48 (d, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 7.06 (dd, *J* = 7.9, 1.3 Hz, 4H), 4.15 (dd, *J* = 12.0, 3.2 Hz, 1H), 3.93 (dd, *J* = 13.7, 3.2 Hz, 1H), 3.47 (dd, *J* = 13.5, 12.1 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.4, 137.0, 133.7, 131.2, 130.9, 130.2, 130.1, 130.0, 129.1, 129.0, 128.8, 128.5, 70.5, 32.7, 21.1. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{21}H_{20}NaO_2S_2$ 391.0797; found 391.0794.



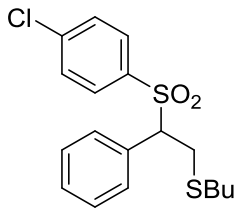
3w

Yield: 87%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (t, *J* = 7.4 Hz, 1H), 7.46 (d, *J* = 7.9 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 8.6 Hz, 2H), 7.04 (d, *J* = 7.6 Hz, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 4.11 (dd, *J* = 12.0, 3.2 Hz, 1H), 3.84 (dd, *J* = 13.6, 3.2 Hz, 1H), 3.79 (s, 3H), 3.47-3.37 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.6, 137.0, 134.3, 133.7, 130.9, 130.1, 129.1, 129.0, 128.8, 128.5, 124.0, 114.8, 70.6, 55.4, 33.9. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{21}H_{20}NaO_3S_2$ 407.0746; found 407.0732.



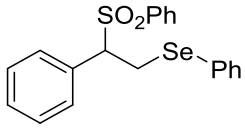
3x

Yield: 70%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.3 Hz, 2H), 7.33-7.28 (m, 1H), 7.25 (t, *J* = 7.2 Hz, 2H), 7.20-7.12 (m, 4H), 4.21 (dd, *J* = 11.9, 3.3 Hz, 1H), 3.49 (dd, *J* = 13.3, 3.3 Hz, 1H), 3.30-3.22 (m, 1H), 2.38 (s, 3H), 2.37-2.33 (m, 2H), 1.49-1.41 (m, 2H), 1.29 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.8, 134.0, 131.5, 130.0, 129.4, 129.1, 129.1, 128.5, 71.7, 32.4, 31.4, 29.8, 21.8, 21.7, 13.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{19}H_{24}NaO_2S_2$ 371.1110; found 371.1101.



3y

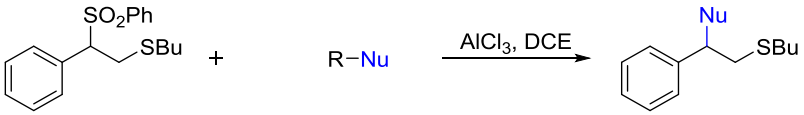
Yield: 67%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.40 (m, 2H), 7.33 (m, 3H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.13 (d, *J* = 7.3 Hz, 2H), 4.22 (dd, *J* = 11.8, 3.4 Hz, 1H), 3.52 (dd, *J* = 13.3, 3.4 Hz, 1H), 3.27 (dd, *J* = 13.2, 11.9 Hz, 1H), 2.42-2.33 (m, 2H), 1.51-1.43 (m, 2H), 1.30 (m, 3H), 0.85 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.6, 135.5, 131.2, 130.5, 129.9, 129.4, 129.1, 128.7, 71.9, 32.5, 31.4, 29.6, 21.8, 13.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{18}H_{21}ClNaO_2S_2$ 391.0564; found 391.0569.



3z

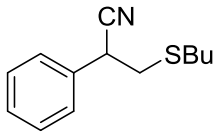
Yield: 98%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56-7.51 (m, 1H), 7.48 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.38-7.31 (m, 4H), 7.31-7.27 (m, 1H), 7.26-7.23 (m, 1H), 7.20 (t, *J* = 7.4 Hz, 4H), 7.04 (d, *J* = 7.3 Hz, 2H), 4.22 (dd, *J* = 12.3, 3.3 Hz, 1H), 3.85 (dd, *J* = 12.5, 3.3 Hz, 1H), 3.48 (t, *J* = 12.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.0, 133.7, 133.3, 131.3, 129.9, 129.3, 129.2, 129.0, 128.8, 128.7, 128.5, 127.7, 71.6, 24.5. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{20}H_{18}NaO_2SSe$ 425.0085; found 425.0076.

6. Synthetic Applications of 3



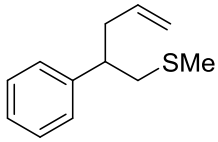
To a mixture of $AlCl_3$ (0.15 mmol), 3 (0.1 mmol) in DCE (1 mL) under N_2 atmosphere, nucleophile [trimethylsilyl cyanide (0.15 mmol), allyltrimethylsilane (0.2 mmol), 1,3,5-trimethoxybenzene (0.5 mmol)] were added. The reaction system was stirred at 40-85 ^{o}C for 24 h. Then, the resulting mixture was evaporated under reduced

pressure and purified by silica gel flash chromatography to afford the desired product (**5, 7, 9**).



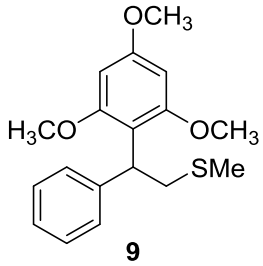
5

Yield: 88%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.32 (m, 5H), 3.98 (dd, *J* = 8.3, 6.3 Hz, 1H), 2.98 (ddd, *J* = 20.0, 13.7, 7.3 Hz, 2H), 2.59-2.49 (m, 2H), 1.55 (dt, *J* = 15.0, 7.4 Hz, 2H), 1.37 (dt, *J* = 14.6, 7.4 Hz, 2H), 0.90 (t, *J* = 7.3 Hz, 3H).



7

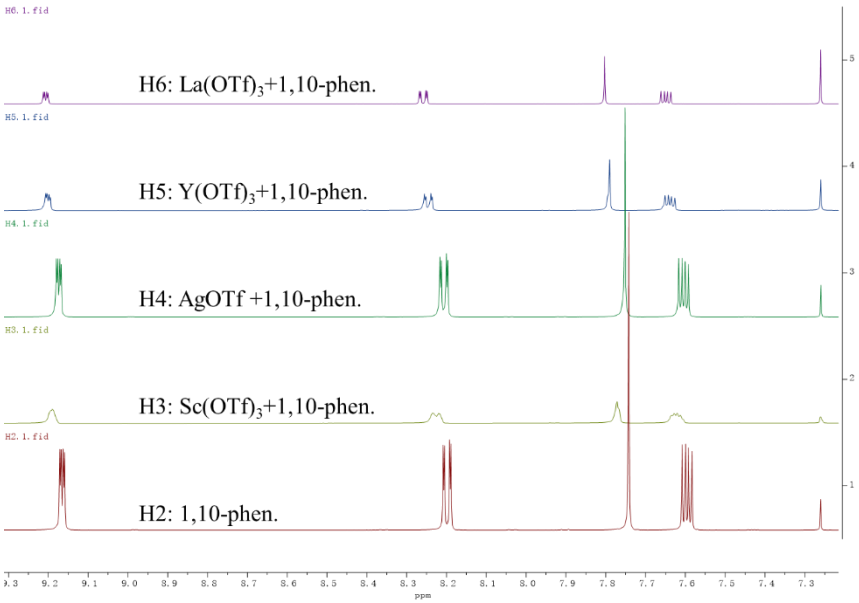
Yield: 54%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.5 Hz, 2H), 7.24-7.17 (m, 3H), 5.70-5.60 (m, 1H), 5.04-4.92 (m, 2H), 2.88 (dt, *J* = 14.2, 7.1 Hz, 1H), 2.77 (ddd, *J* = 20.6, 12.8, 7.2 Hz, 2H), 2.58 (dt, *J* = 13.6, 6.7 Hz, 1H), 2.45-2.38 (m, 1H), 2.00 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.6, 136.3, 128.4, 127.7, 126.6, 116.6, 45.5, 40.8, 39.7, 16.2. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{12}H_{17}S$ 193.1045; found 193.1044.



9

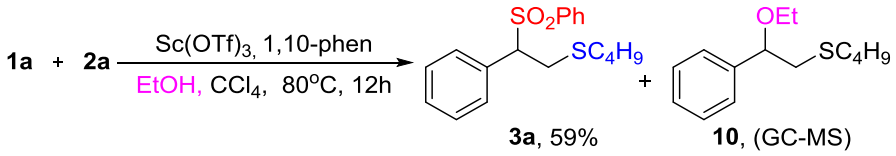
Yield: 85%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.3 Hz, 2H), 7.22 (t, *J* = 7.7 Hz, 2H), 7.12 (t, *J* = 7.3 Hz, 1H), 6.12 (s, 2H), 4.86 (dd, *J* = 9.2, 7.0 Hz, 1H), 3.78 (s, 3H), 3.75 (s, 6H), 3.37 (ddd, *J* = 19.7, 12.8, 8.1 Hz, 2H), 2.07 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.9, 159.3, 144.2, 128.0, 127.8, 125.6, 112.4, 91.3, 55.8, 55.2, 39.4, 37.3, 15.8. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{18}H_{23}O_3S$ 319.1362; found 319.1360.

7. NMR Experiments

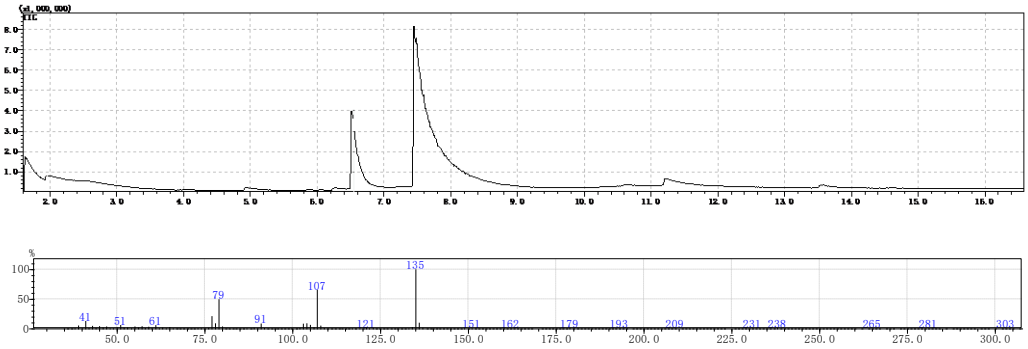


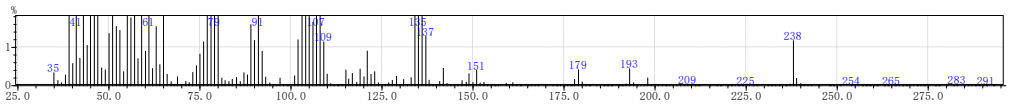
^{1}H NMR experiment. H2: 1,10-phen in $CDCl_3$, H3: $Sc(OTf)_3$+1,10-phen (1:1) in $CDCl_3$, H4: AgOTf +1,10-phen (1:1) in $CDCl_3$, H5: $Y(OTf)_3$+1,10-phen (1:1) in $CDCl_3$, H6: $La(OTf)_3$+1,10-phen (1:1) in $CDCl_3$.

8. Control Experiments



To a mixture of $Sc(OTf)_3$ (20 mol%), 2,2'-Bipyridine (20 mol%) in CCl_4 (1 mL) under N_2 atmosphere, alkene (0.2 mmol), thiosulfonylation reagent 2a (0.4 mmol), EtOH were added. The reaction system was stirred at 80 ^oC for 12 h. The desired product **3a** and product **10** was found in GC-MS (6.6 min).

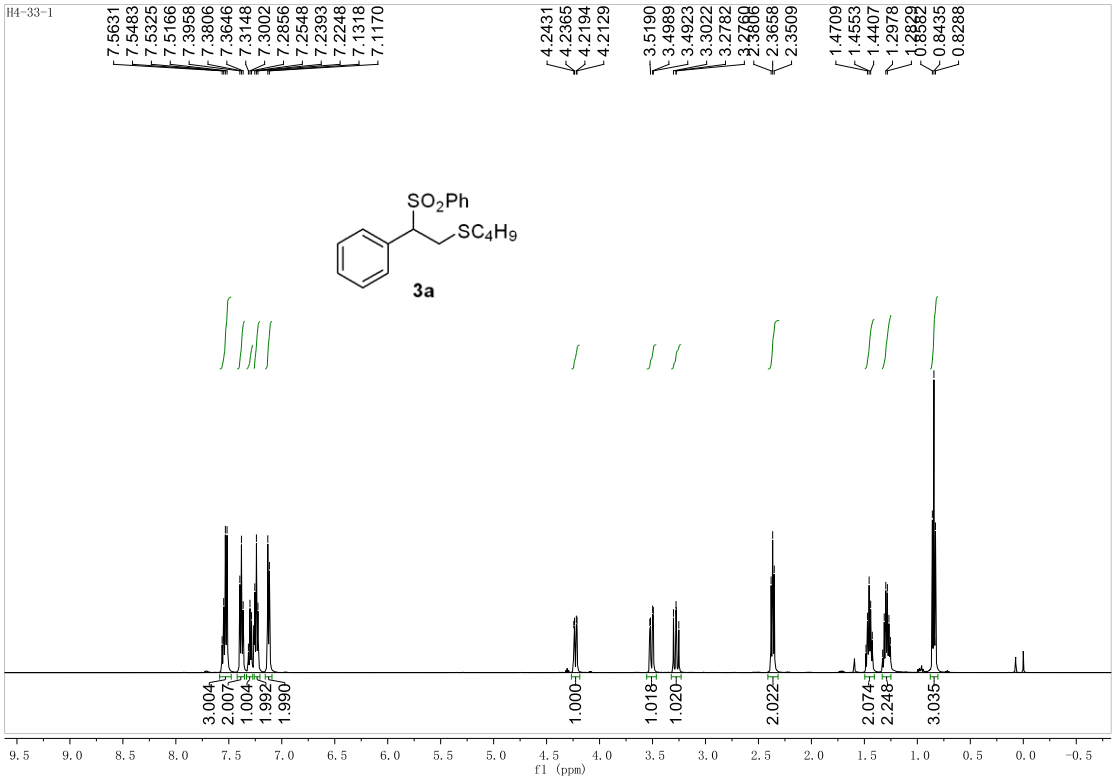


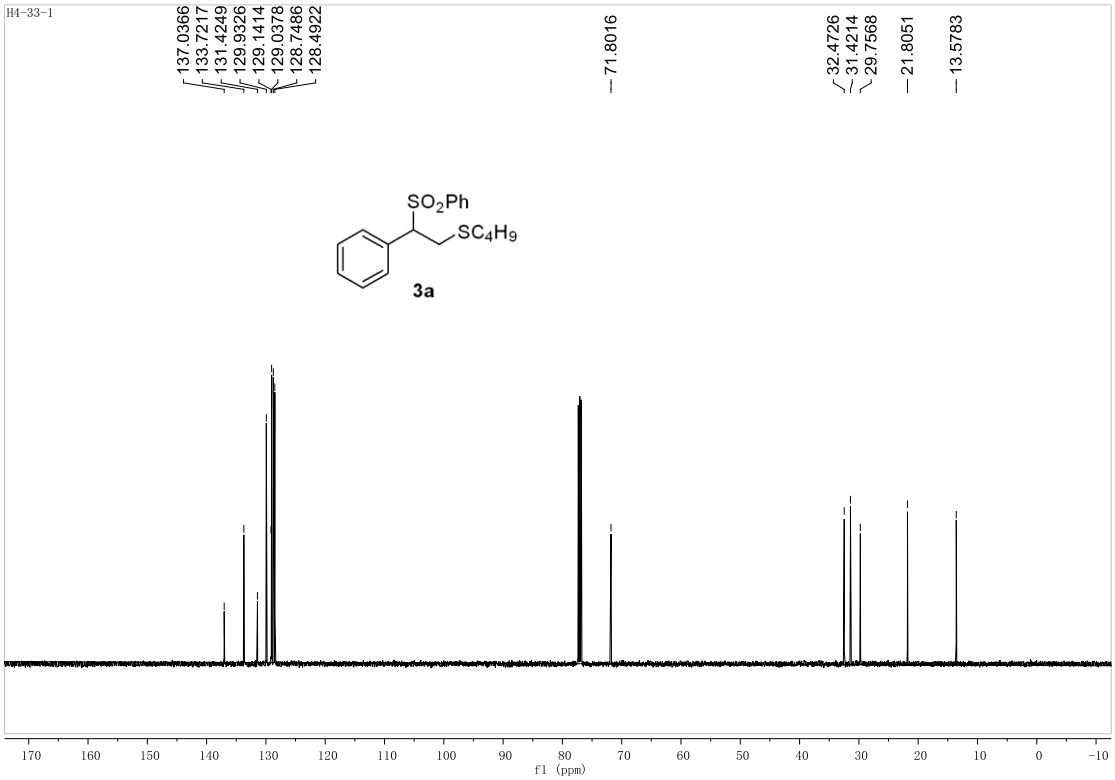


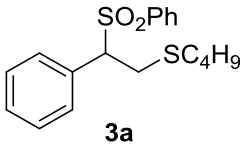
9. References

[1] Wang, W.; Peng, X.; Wei, F.; Tung, C.-H.; Xu, Z. *Angew. Chem. Int. Ed.* **2016**, *55*, 649-653.

10. NMR and HRMS spectra of the products

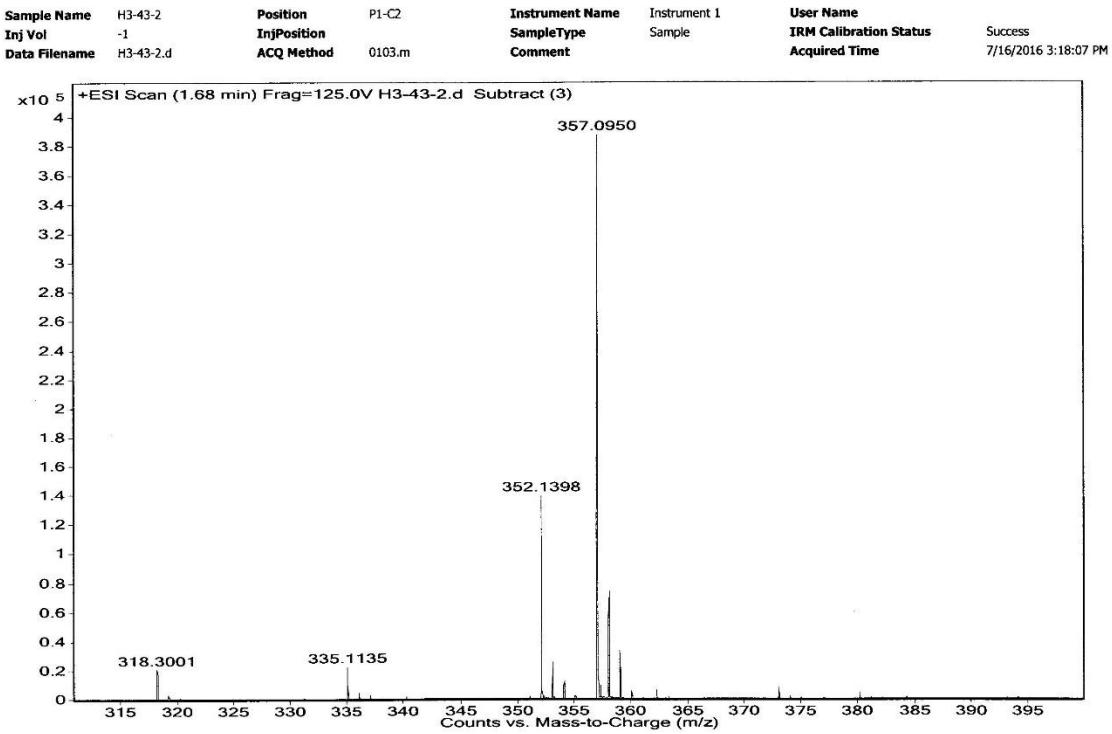




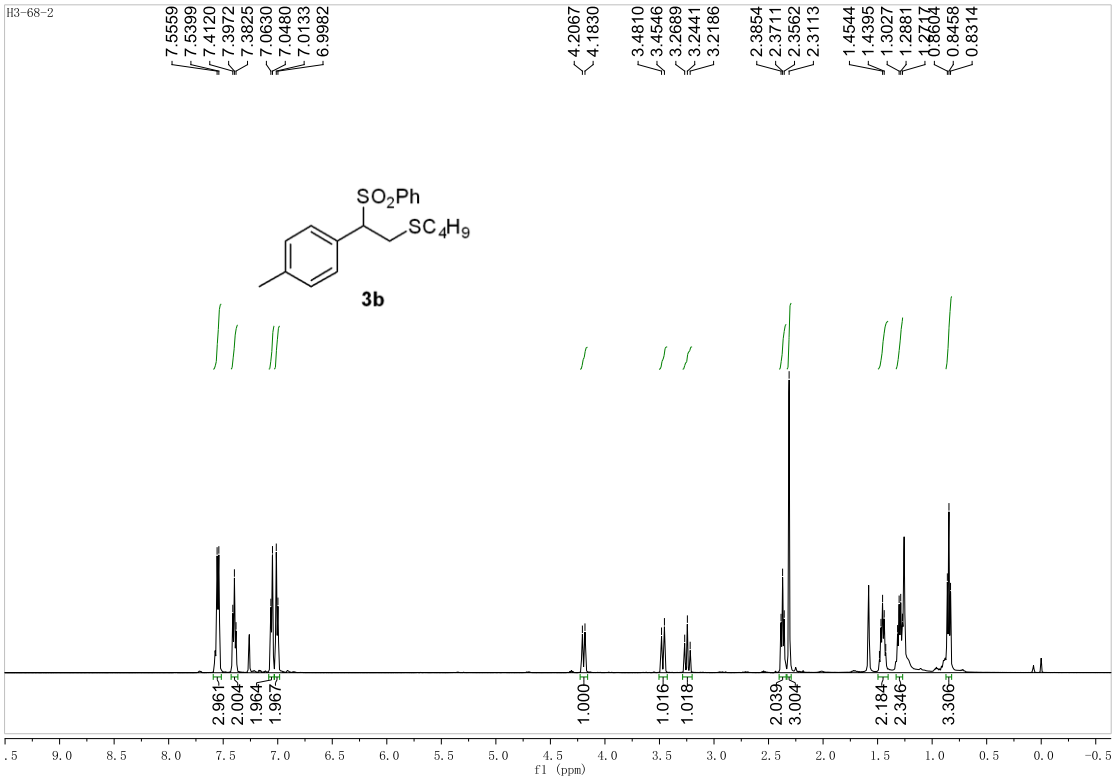


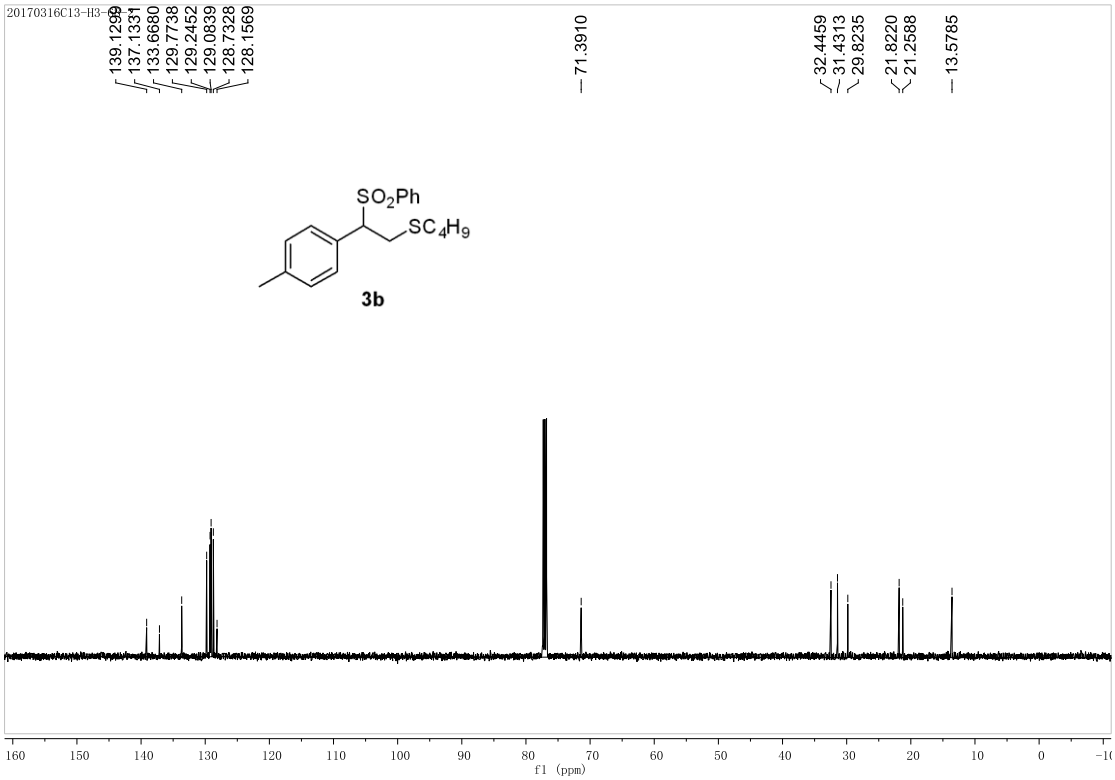
3a

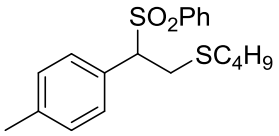
Chemical Formula: $C_{18}H_{22}O_2S_2$
Exact Mass: 334.1061
Molecular Weight: 334.4920
m/z: 334.1061 (100.0%), 335.1095 (19.5%), 336.1019 (9.0%), 336.1128 (1.8%), 337.1053 (1.8%), 335.1055 (1.6%)
Elemental Analysis: C, 64.63; H, 6.63; O, 9.57; S, 19.17



HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{18}H_{22}NaO_2S_2$ 357.0953; found 357.0950.

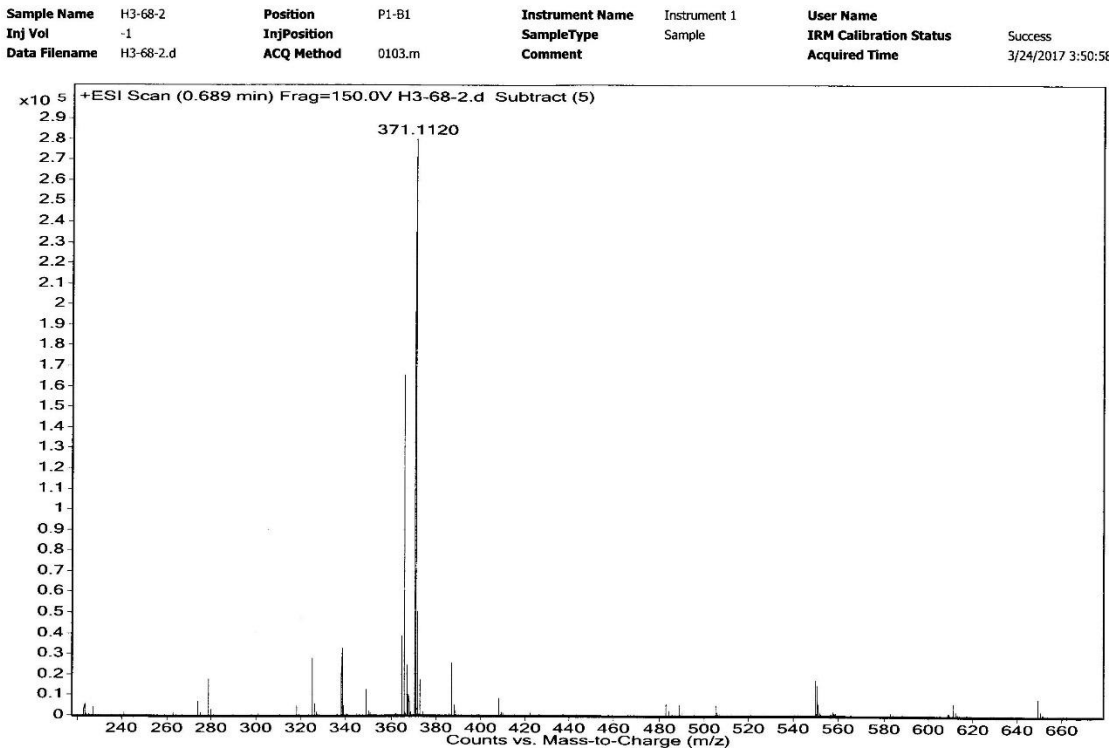




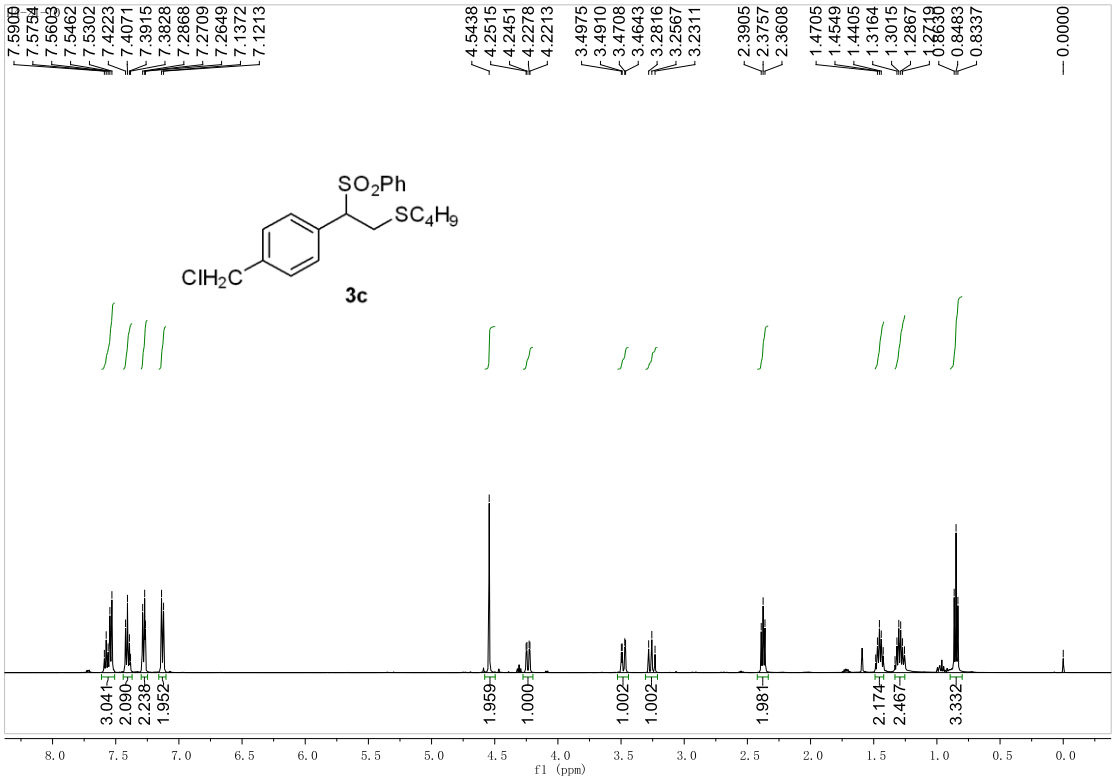


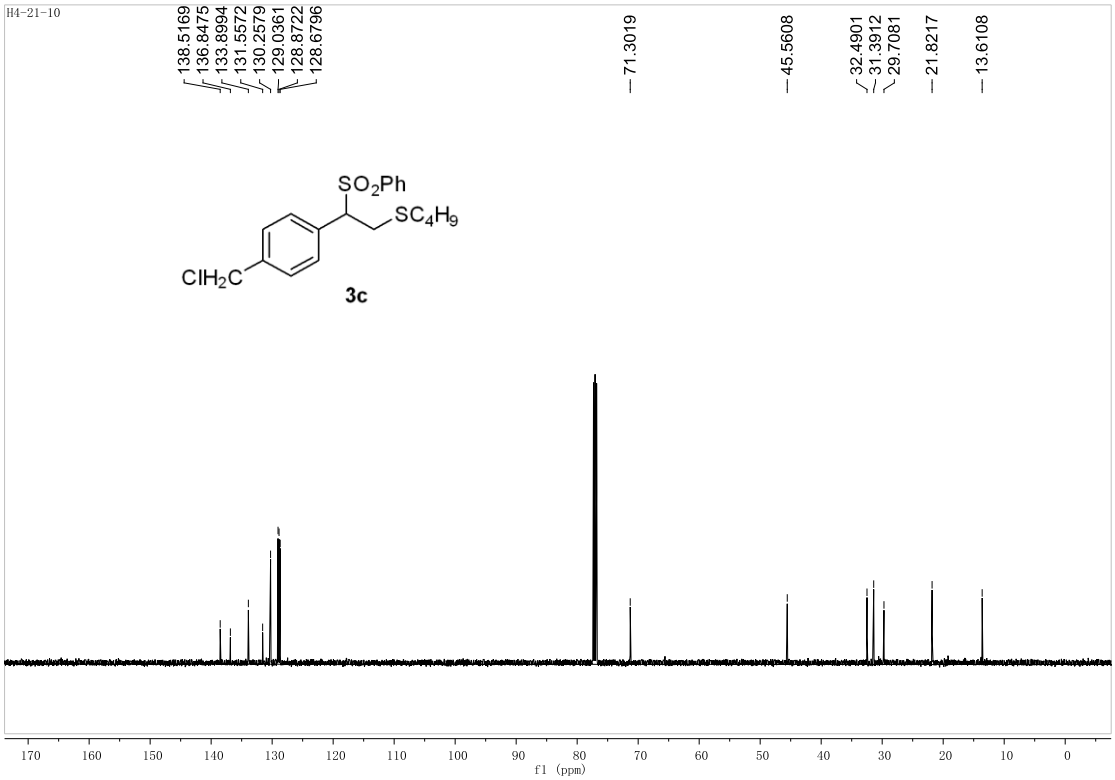
3b

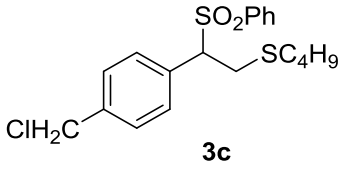
Chemical Formula: $C_{19}H_{24}O_2S_2$
Exact Mass: 348.1218
Molecular Weight: 348.5190
m/z: 348.1218 (100.0%), 349.1251 (20.5%), 350.1176 (9.0%), 350.1285 (2.0%), 351.1209 (1.9%), 349.1212 (1.6%)
Elemental Analysis: C, 65.48; H, 6.94; O, 9.18; S, 18.40



HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{19}H_{24}NaO_2S_2$ 371.1110; found 371.1120.

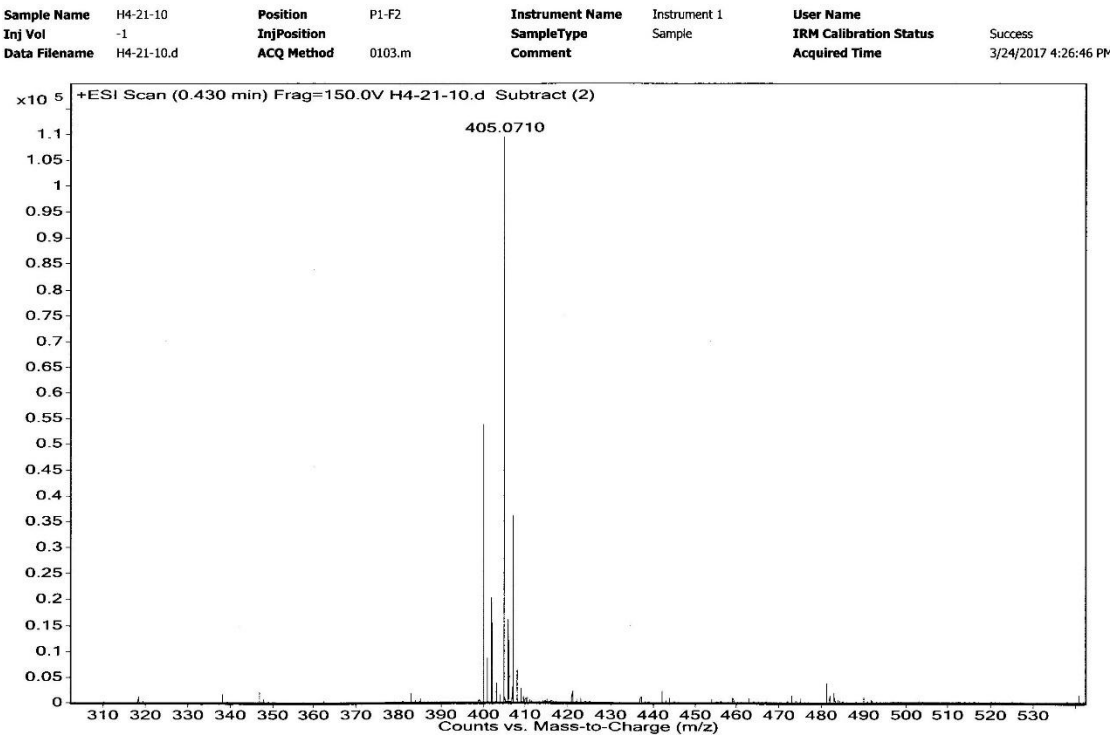




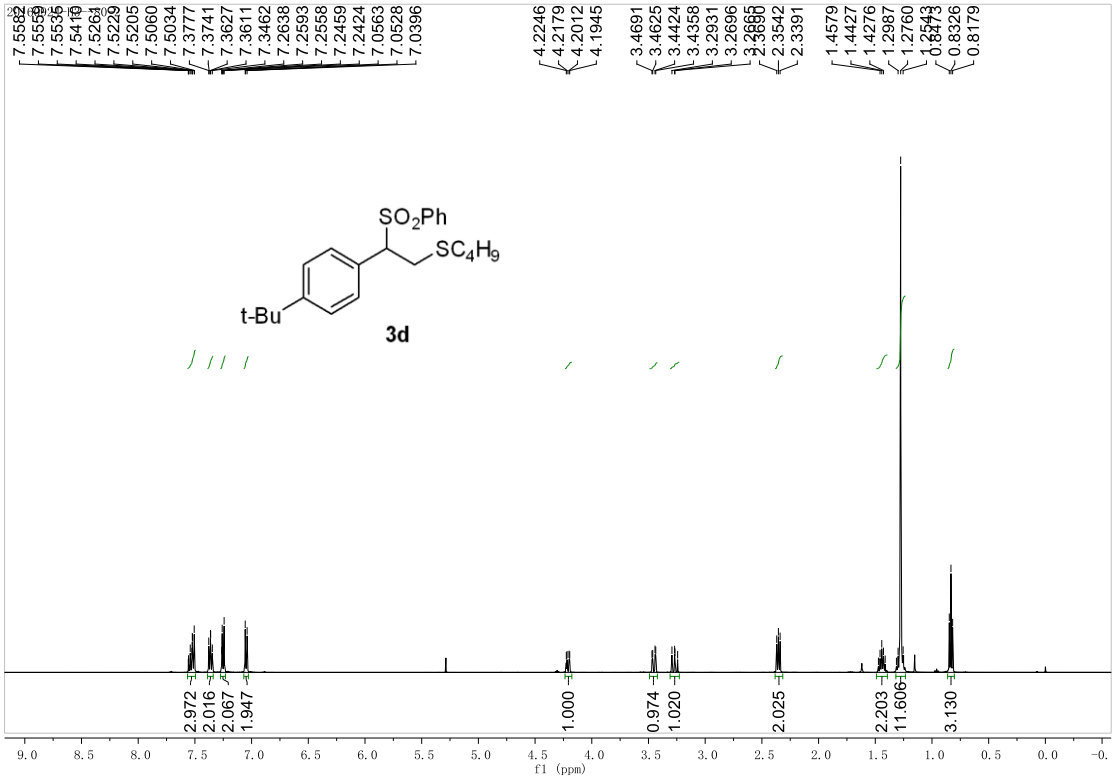


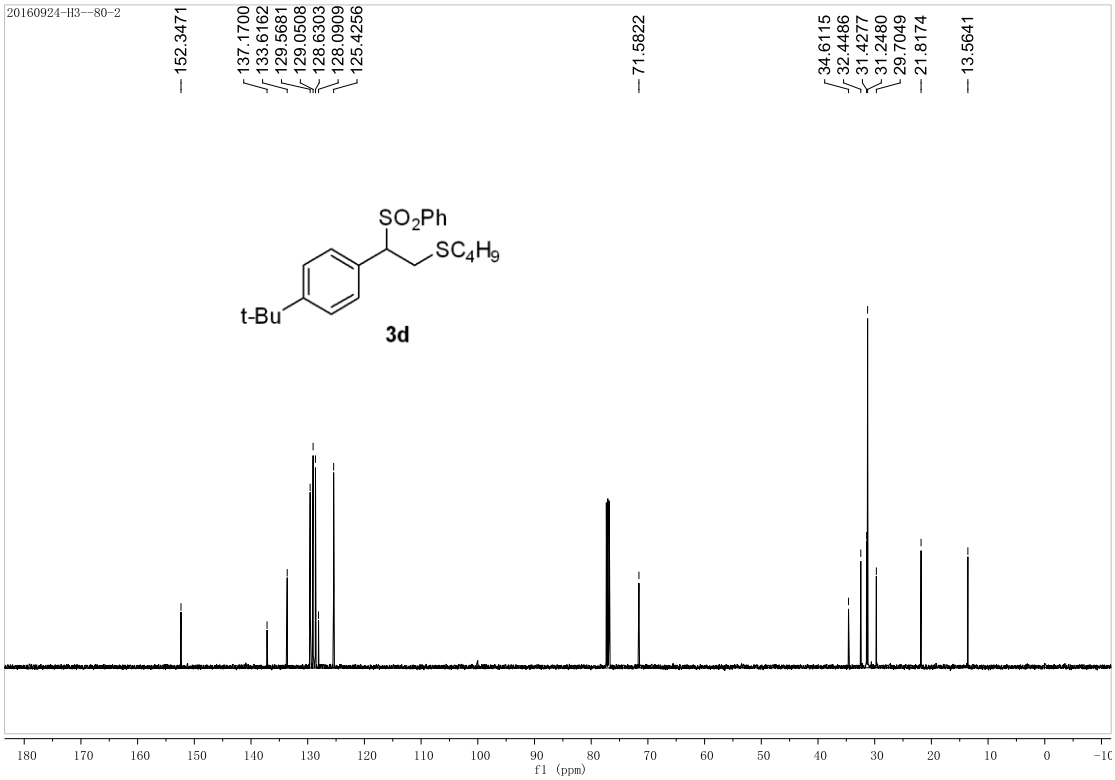
3c

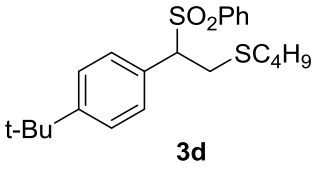
Chemical Formula: $C_{19}H_{23}ClO_2S_2$
Exact Mass: 382.0828
Molecular Weight: 382.9610
m/z: 382.0828 (100.0%), 384.0798 (32.0%), 383.0862 (20.5%), 384.0786 (9.0%), 385.0832 (6.6%), 386.0756 (2.9%), 384.0895 (2.0%), 385.0820 (1.9%), 383.0822 (1.6%)
Elemental Analysis: C, 59.59; H, 6.05; Cl, 9.26; O, 8.36; S, 16.74



HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{19}H_{23}ClNaO_2S_2$ 405.0720; found 405.0710.

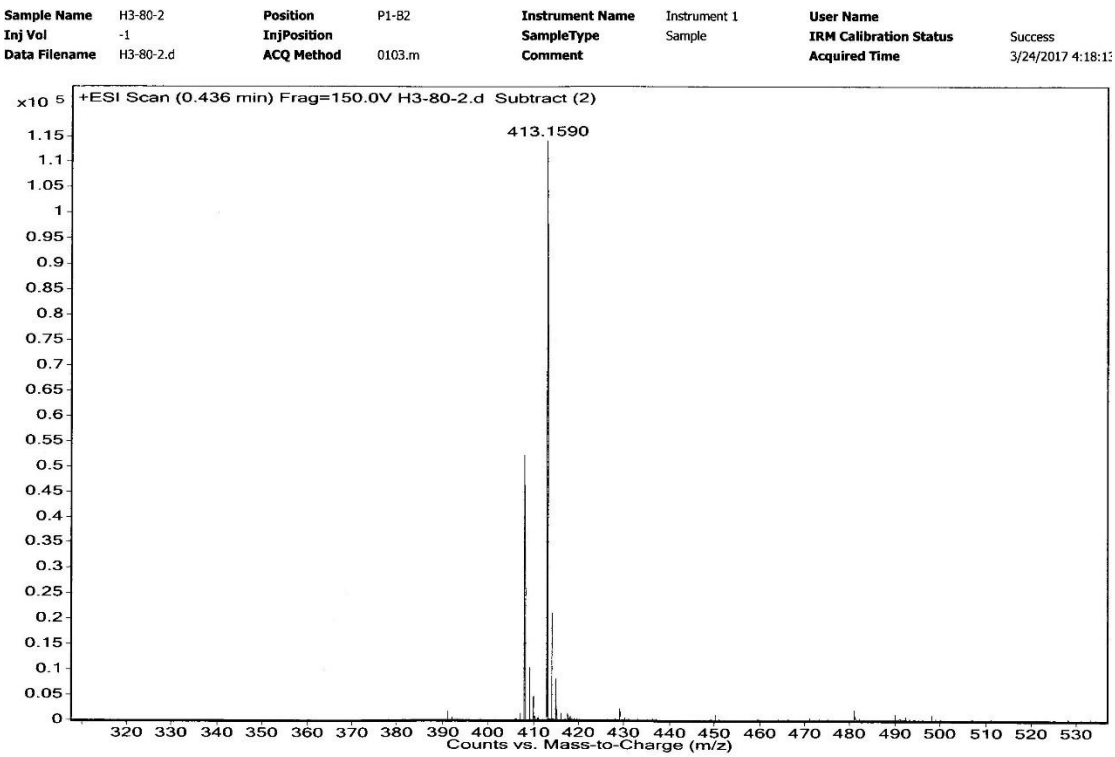




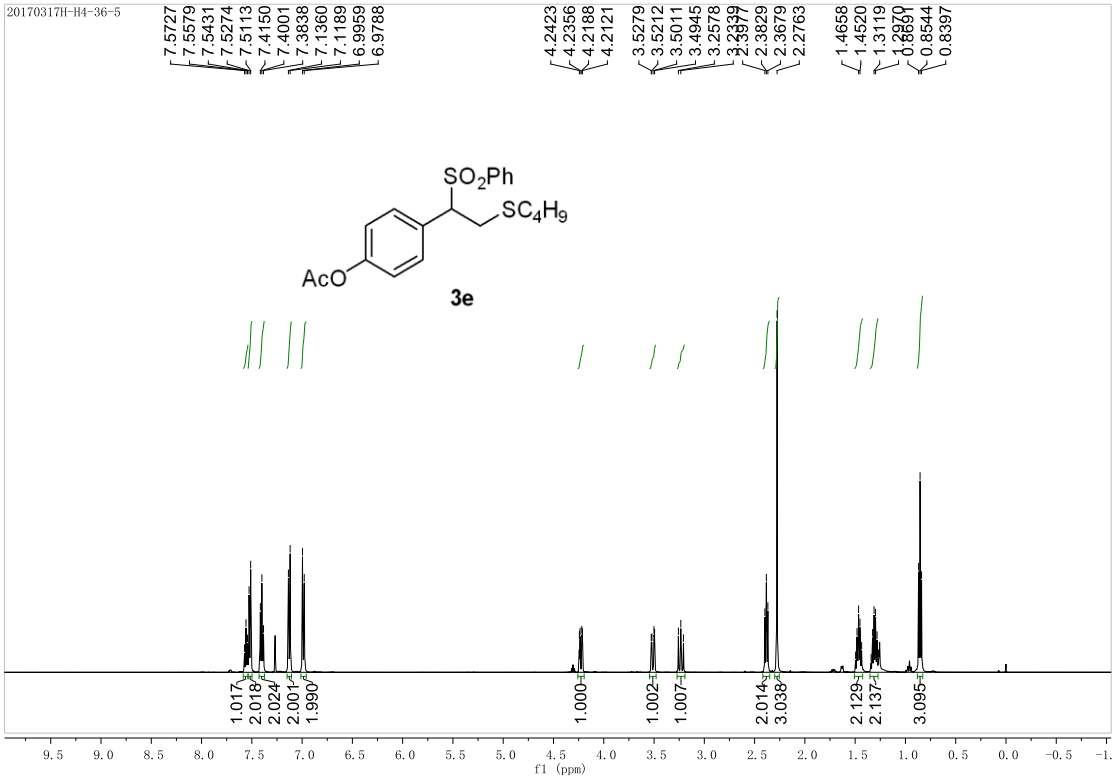


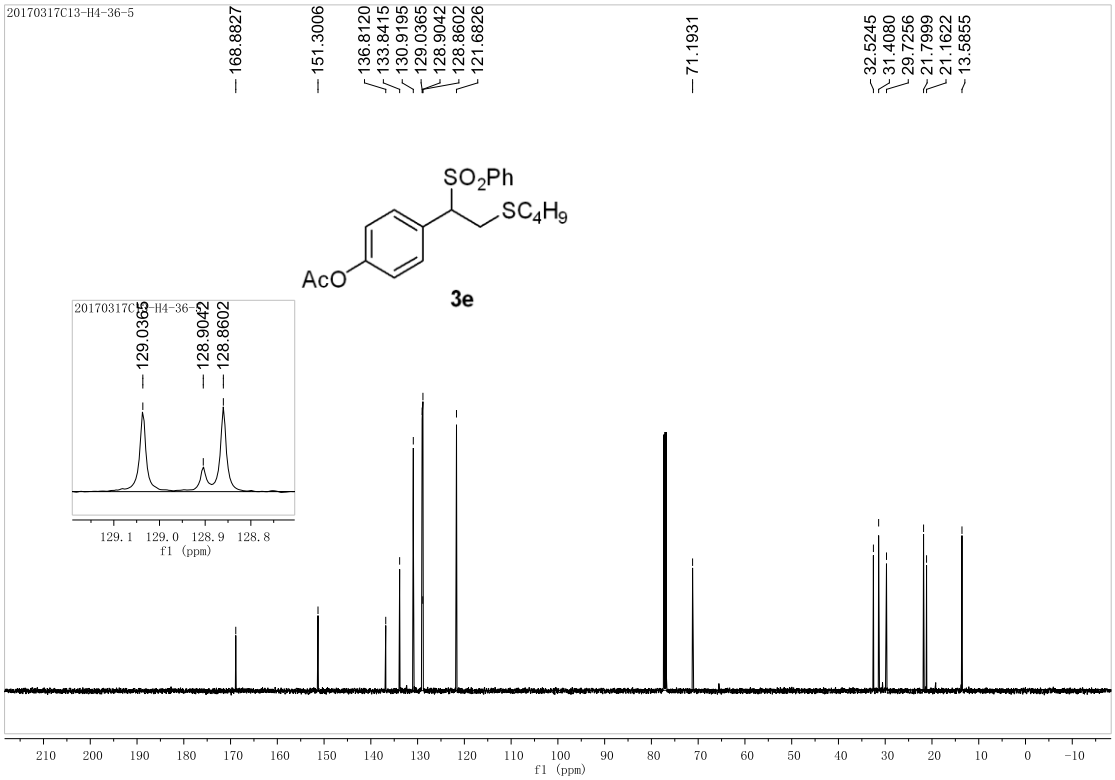
3d

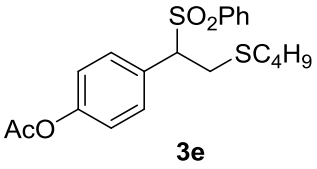
Chemical Formula: $C_{22}H_{30}O_2S_2$
Exact Mass: 390.1687
Molecular Weight: 390.6000
m/z: 390.1687 (100.0%), 391.1721 (23.8%), 392.1645 (9.0%), 392.1754 (2.7%), 393.1679 (2.2%), 391.1681 (1.6%)
Elemental Analysis: C, 67.65; H, 7.74; O, 8.19; S, 16.42



HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{22}H_{30}NaO_2S_2$ 413.1579; found 413.1590.







3e

Chemical Formula: $C_{20}H_{24}O_4S_2$
Exact Mass: 392.1116
Molecular Weight: 392.5280
m/z: 392.1116 (100.0%), 393.1150 (21.6%), 394.1074 (9.0%), 394.1183 (2.2%), 395.1108 (2.0%), 393.1110 (1.6%)
Elemental Analysis: C, 61.20; H, 6.16; O, 16.30; S, 16.34

Sample Name	Unavailable	**Position**	Unavailable	**Instrument Name**	Unavailable	**User Name**	Unavailable
Inj Vol	Unavailable	**InjPosition**	Unavailable	**SampleType**	Unavailable	**IRM Calibration Status**	Success
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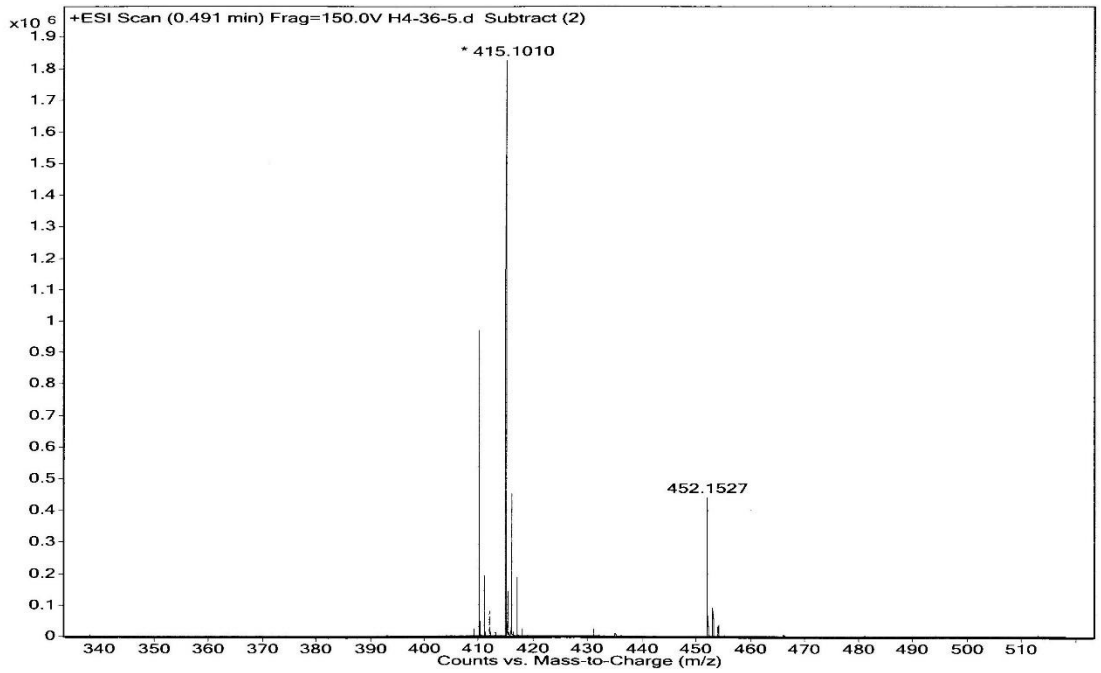
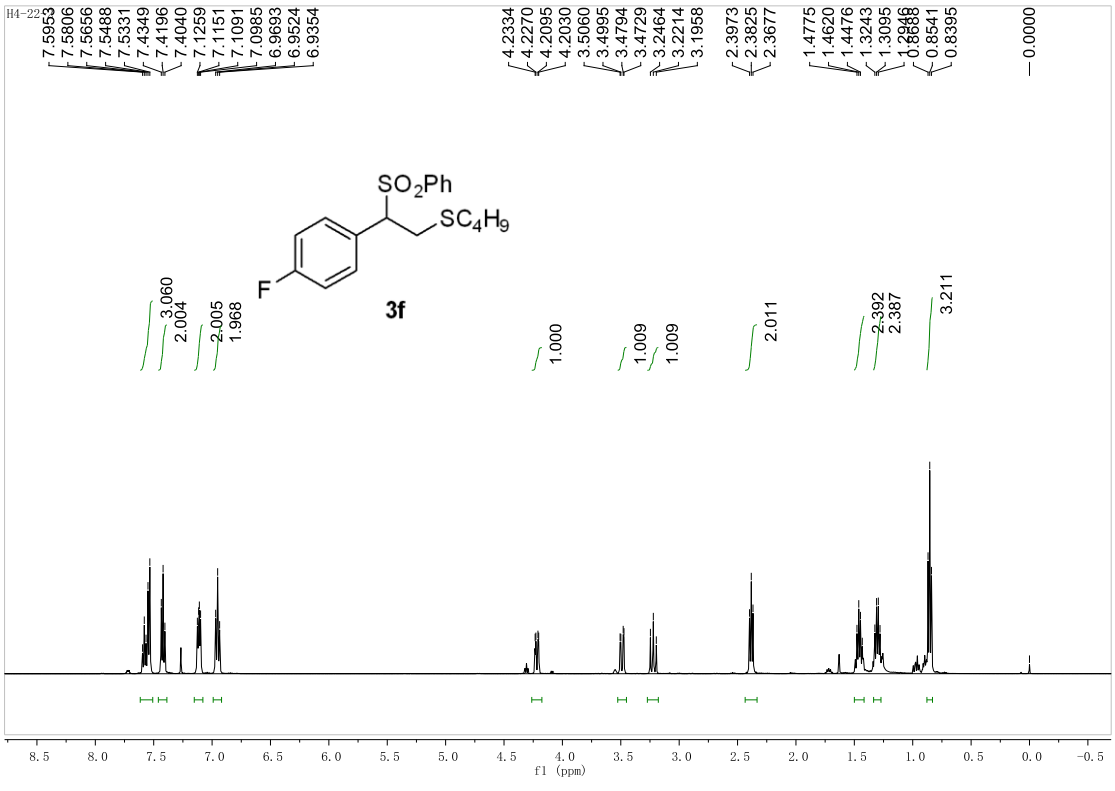
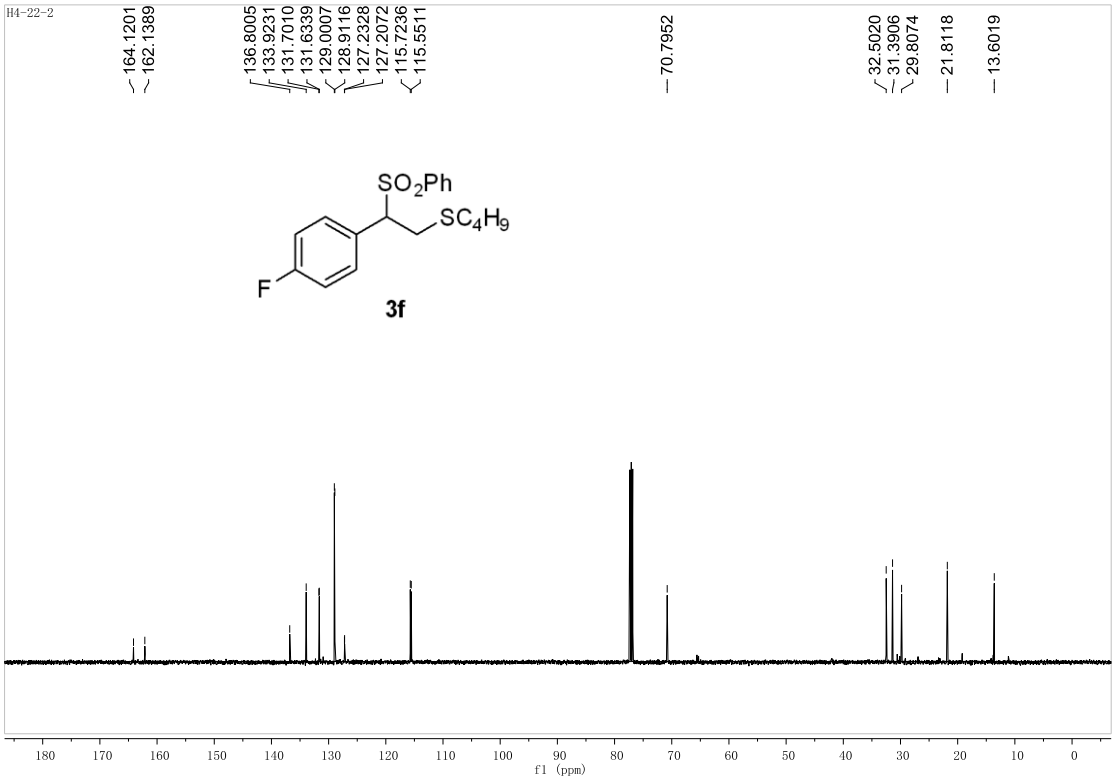
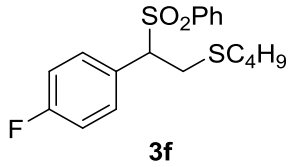


HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{20}H_{24}NaO_4S_2$ 415.1008; found 415.1010.







3f

Chemical Formula: $C_{18}H_{21}FO_2S_2$
Exact Mass: 352.0967
Molecular Weight: 352.4824
m/z: 352.0967 (100.0%), 353.1001 (19.5%), 354.0925 (9.0%), 354.1034 (1.8%), 355.0959 (1.8%), 353.0961 (1.6%)
Elemental Analysis: C, 61.34; H, 6.01; F, 5.39; O, 9.08; S, 18.19

Sample Name	Unavailable	**Position**	Unavailable	**Instrument Name**	Unavailable	**User Name**	Unavailable
Inj Vol	Unavailable	**InjPosition**	Unavailable	**SampleType**	Unavailable	**IRM Calibration Status**	Success
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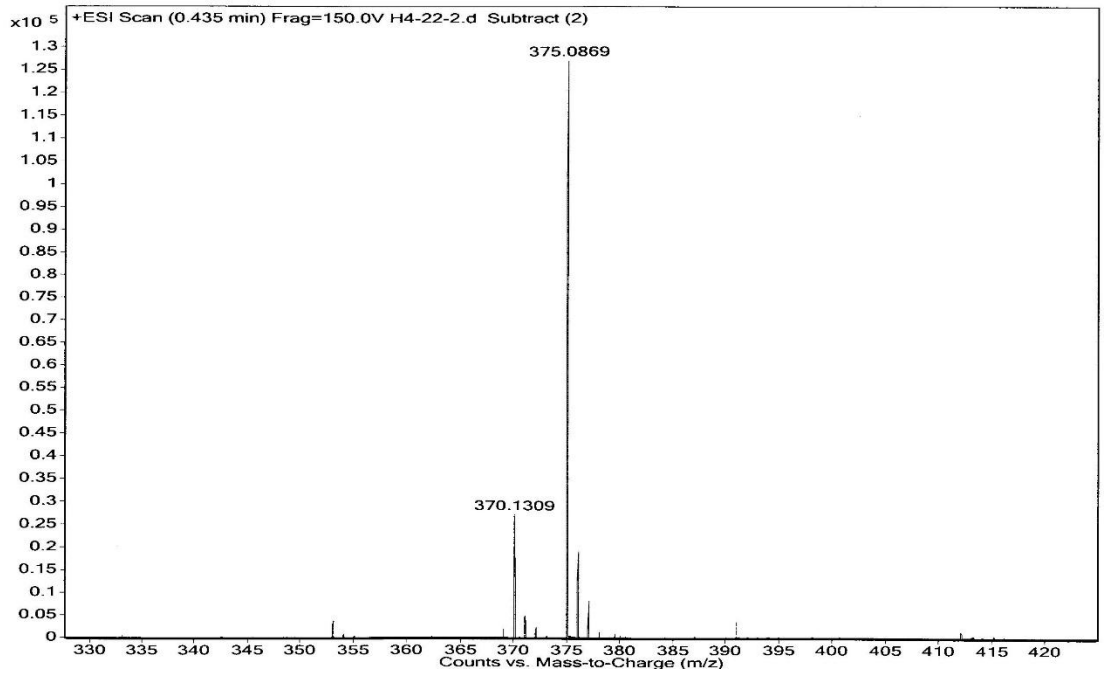
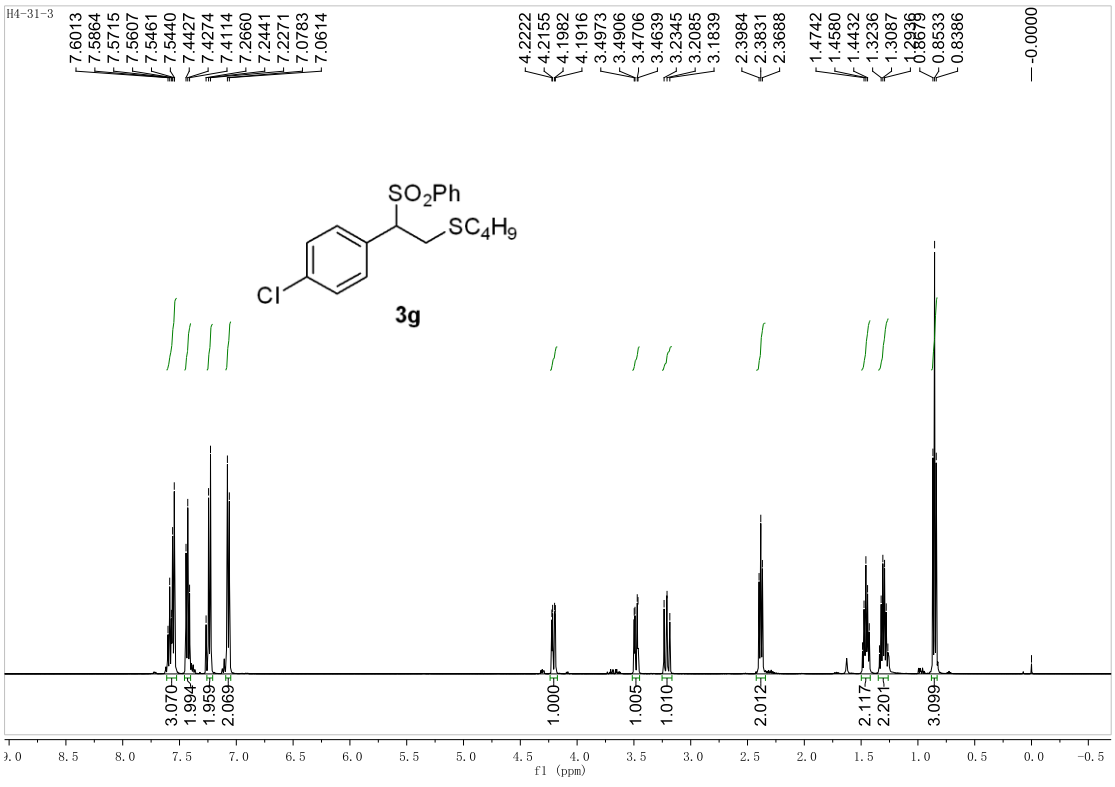
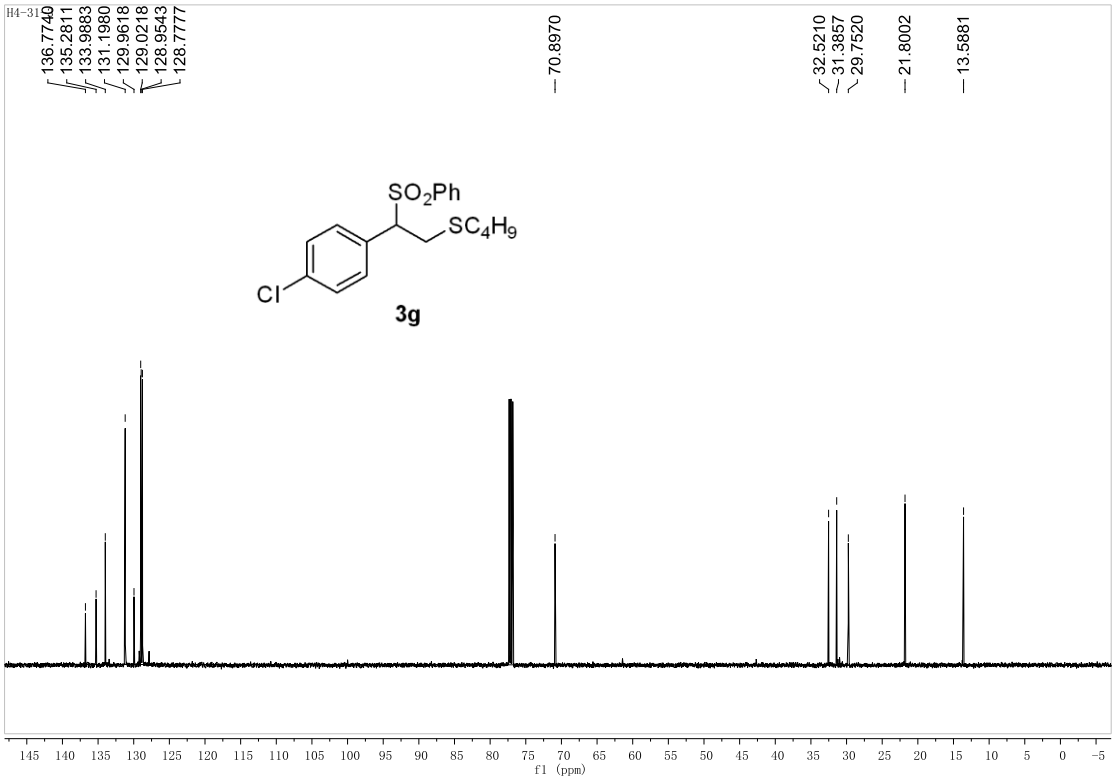
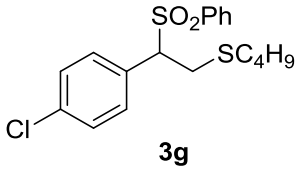


HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{18}H_{21}FNaO_2S_2$ 375.0859; found 375.0869.



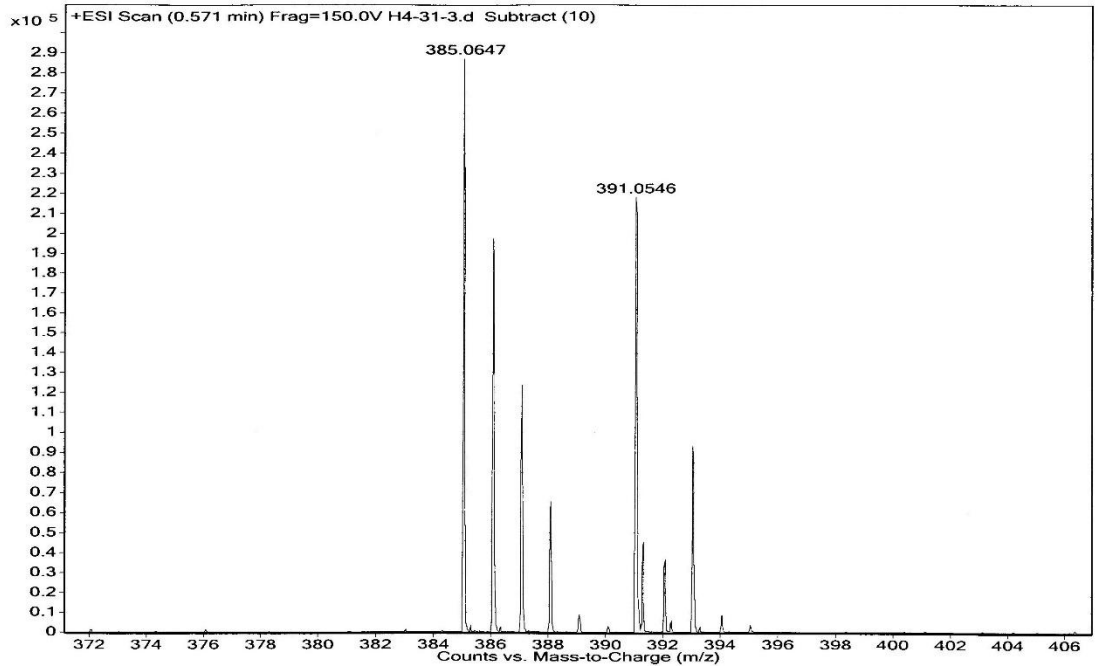




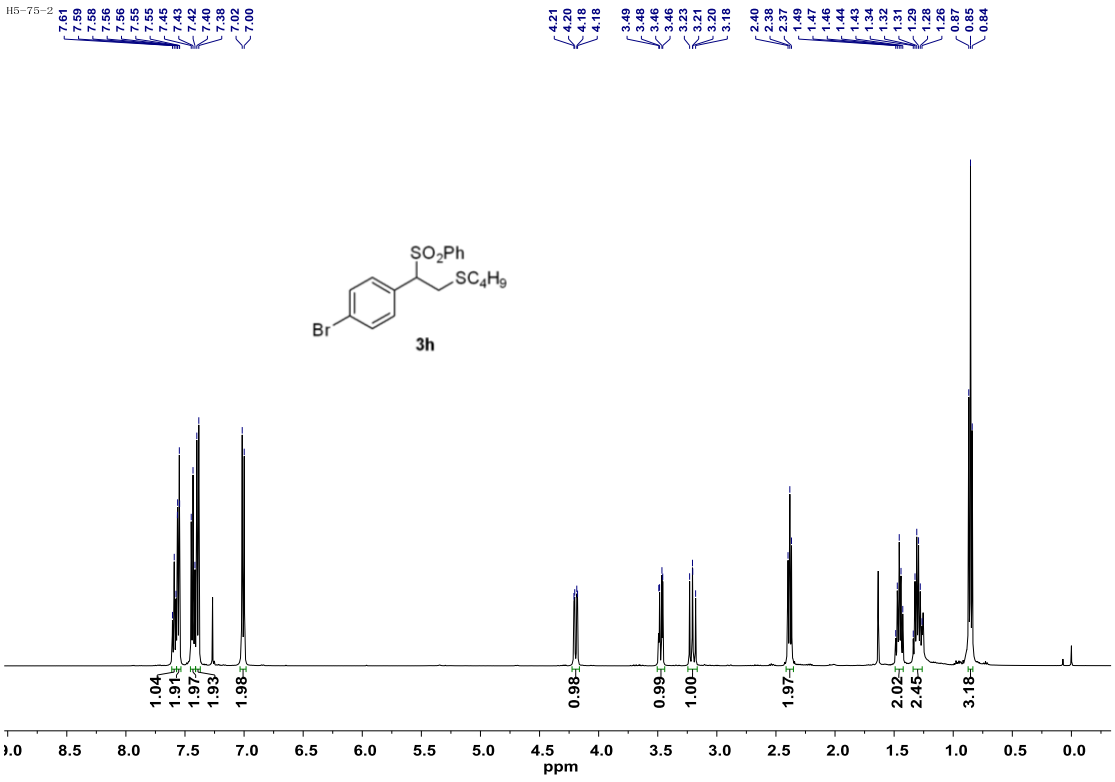
3g

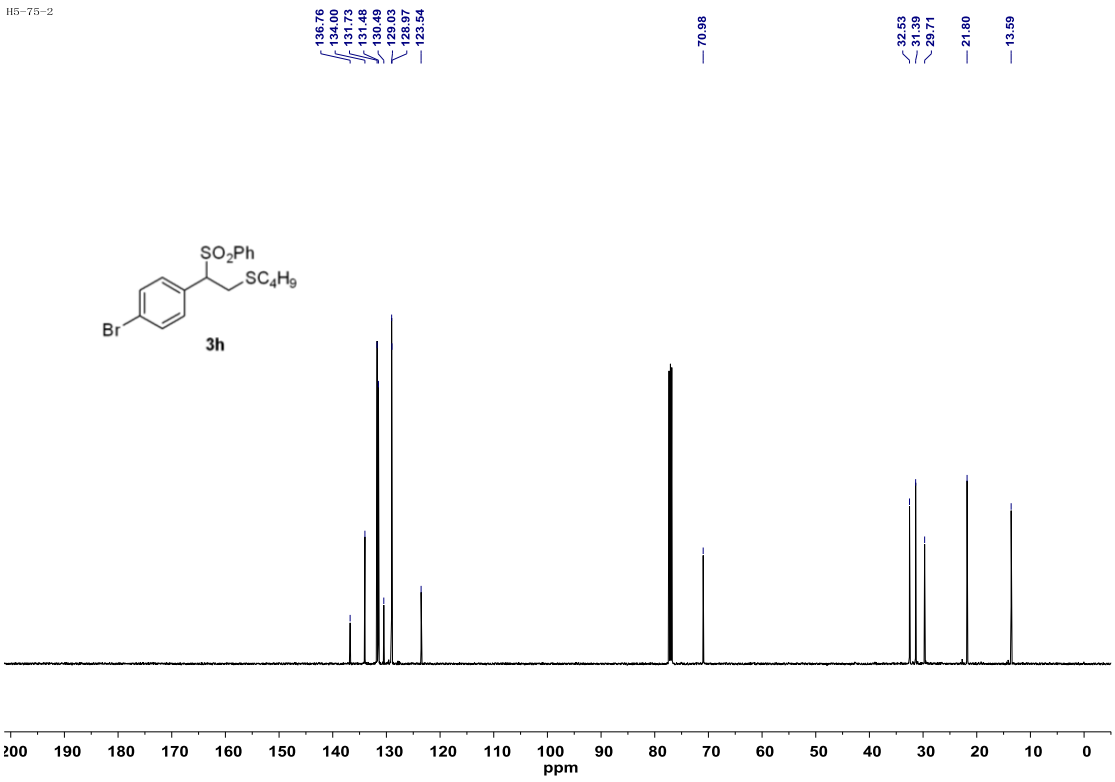
Chemical Formula: $C_{18}H_{21}ClO_2S_2$
Exact Mass: 368.0671
Molecular Weight: 368.9340
m/z: 368.0671 (100.0%), 370.0642 (32.0%), 369.0705 (19.5%), 370.0629 (9.0%), 371.0676 (6.2%), 372.0600 (2.9%), 370.0739 (1.8%), 371.0663 (1.8%), 369.0665 (1.6%)
Elemental Analysis: C, 58.60; H, 5.74; Cl, 9.61; O, 8.67; S, 17.38

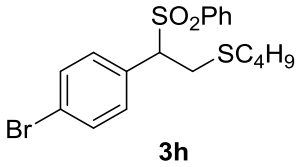
Sample Name	Unavailable	**Position**	Unavailable	**Instrument Name**	Unavailable	**User Name**	Unavailable
Inj Vol	Unavailable	**InjPosition**	Unavailable	**SampleType**	Unavailable	**IRM Calibration Status**	Success
Data Filename	H4-31-3.d	**ACQ Method**		**Comment**	Sample information is unavailable	**Acquired Time**	Unavailable



HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{18}H_{21}ClNaO_2S_2$ 391.0564; found 391.0546.







3h

Chemical Formula: $C_{18}H_{21}BrO_2S_2$
Exact Mass: 412.0166
Molecular Weight: 413.3880
m/z: 412.0166 (100.0%), 414.0146 (97.3%), 415.0179 (18.9%), 413.0200 (16.2%), 414.0124 (9.0%), 416.0104 (8.8%), 413.0200 (3.2%), 416.0213 (1.7%), 417.0137 (1.7%), 413.0160 (1.6%), 415.0140 (1.6%), 415.0158 (1.5%), 414.0233 (1.1%)
Elemental Analysis: C, 52.30; H, 5.12; Br, 19.33; O, 7.74; S, 15.51

Sample Name	Unavailable	**Position**	Unavailable	**Instrument Name**	Unavailable	**User Name**	Unavailable
Inj Vol	Unavailable	**InjPosition**	Unavailable	**SampleType**	Unavailable	**IRM Calibration Status**	Success
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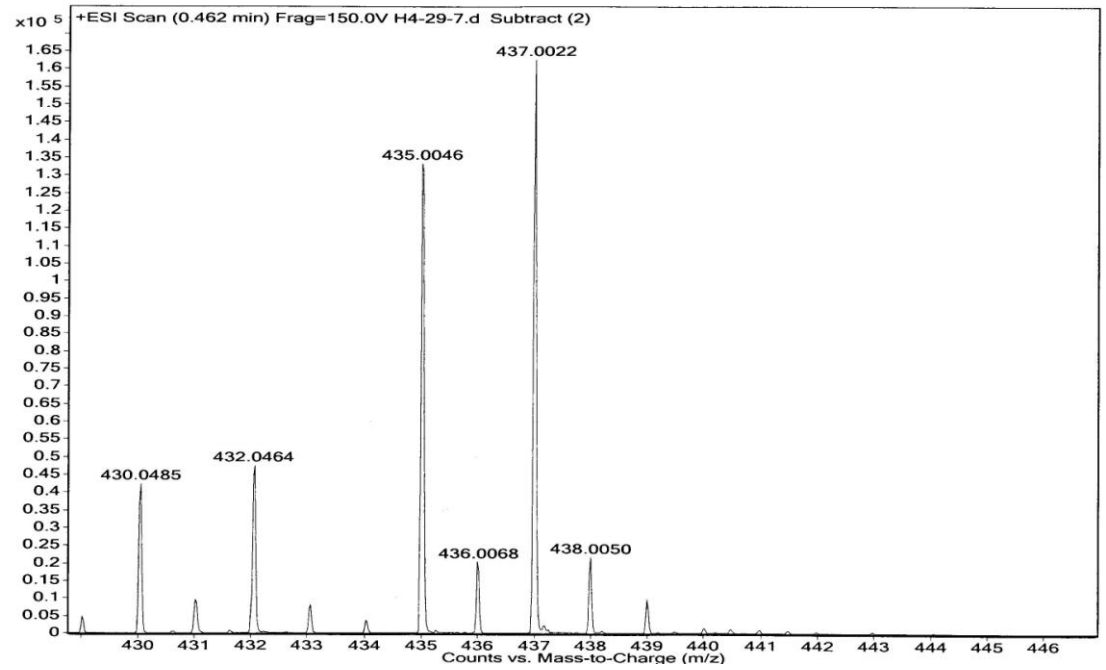
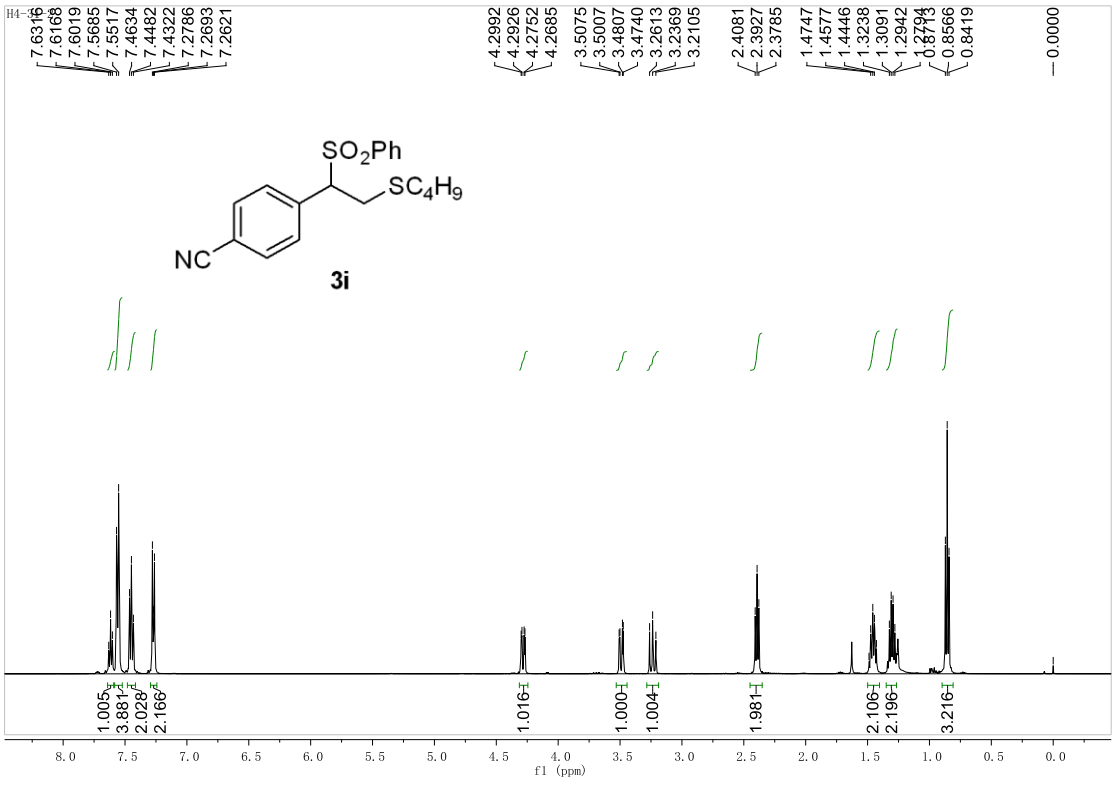
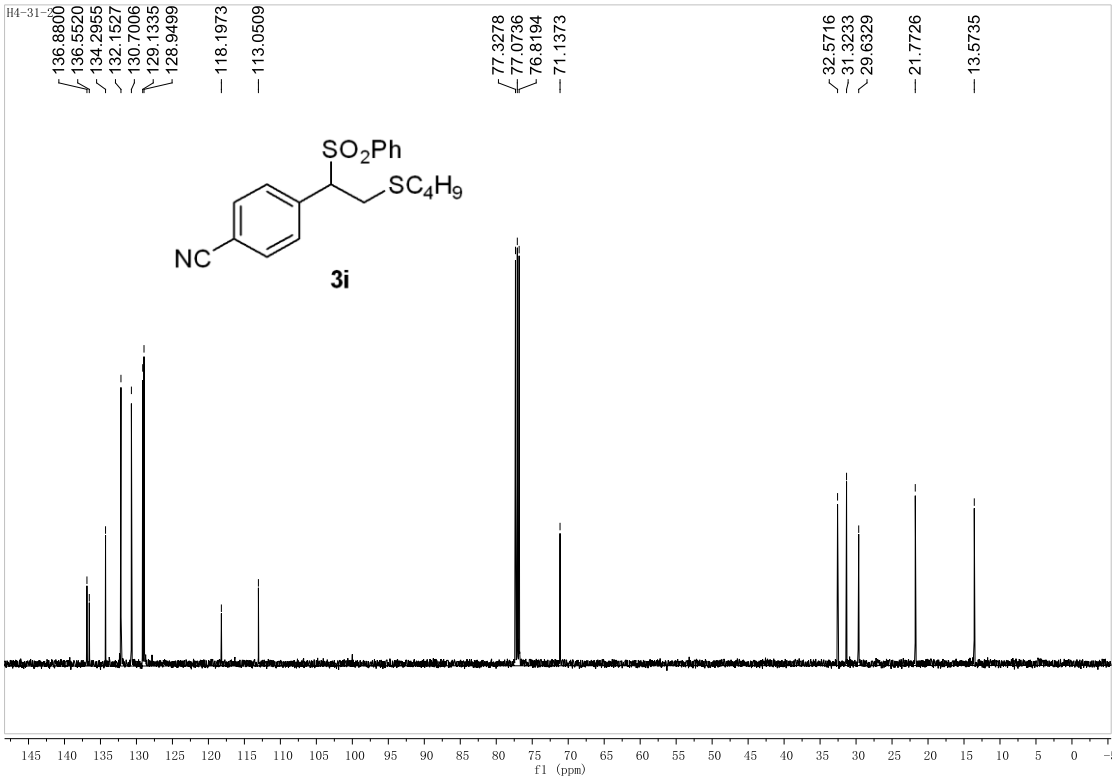
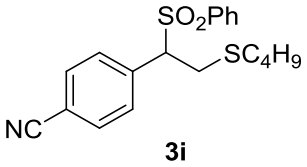


HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{18}H_{21}BrNaO_2S_2$ 435.0059; found 435.0046.

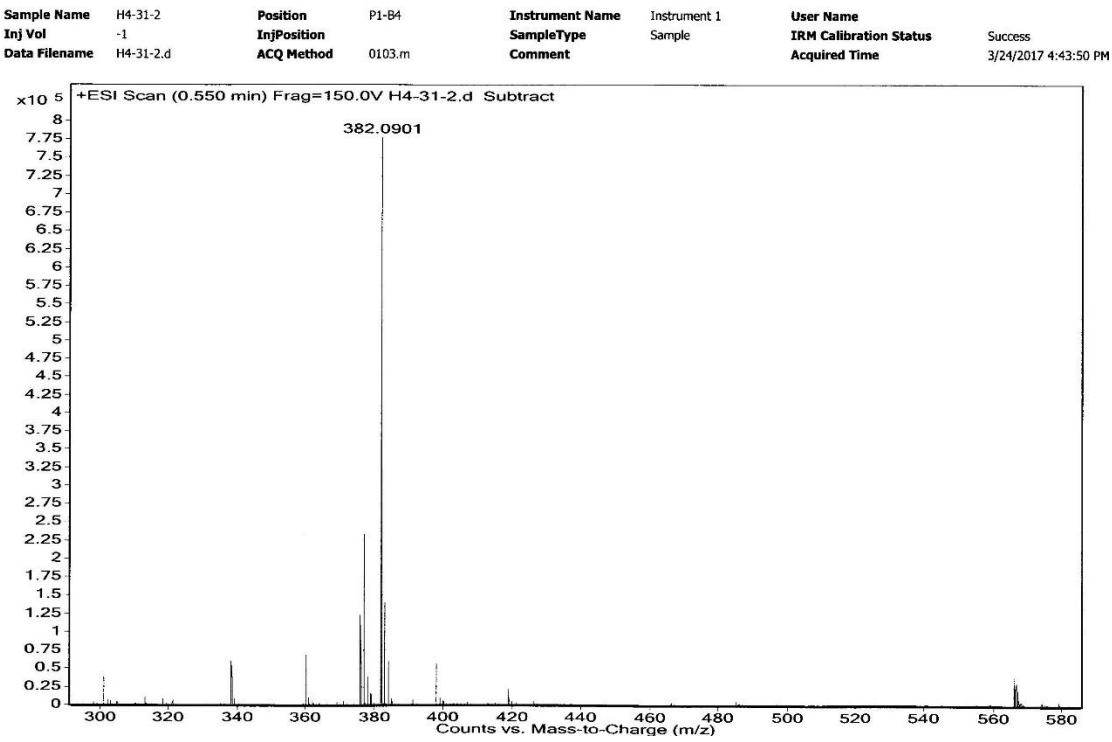




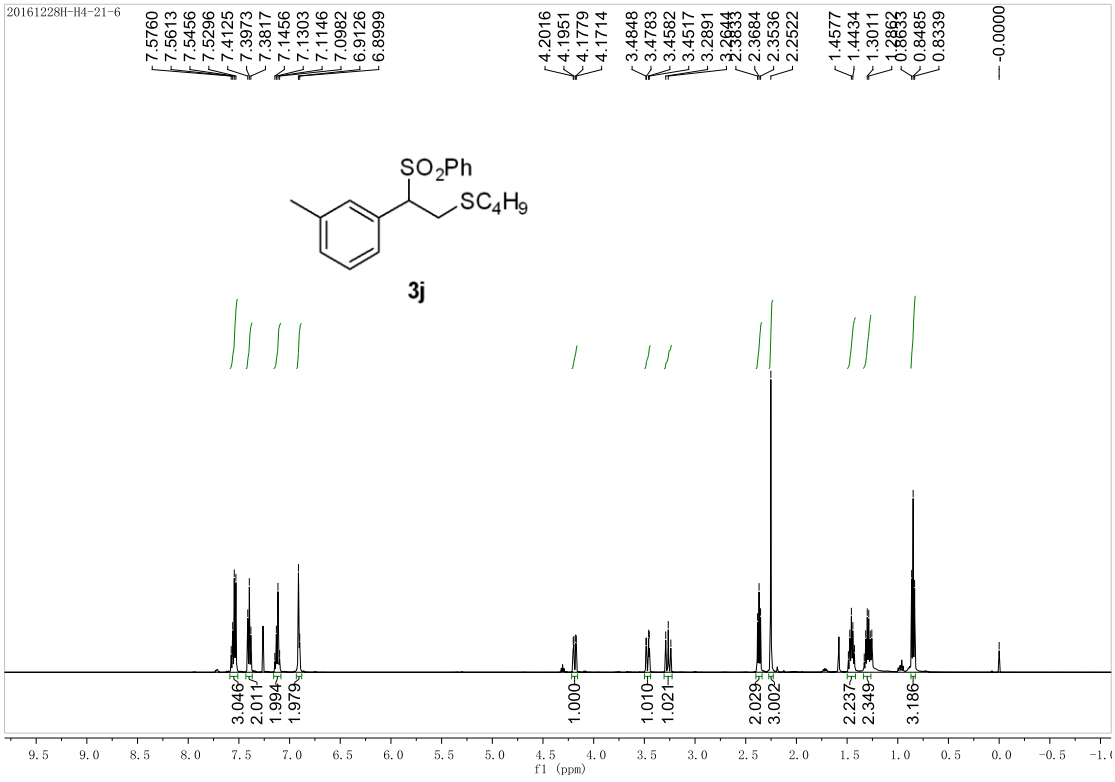


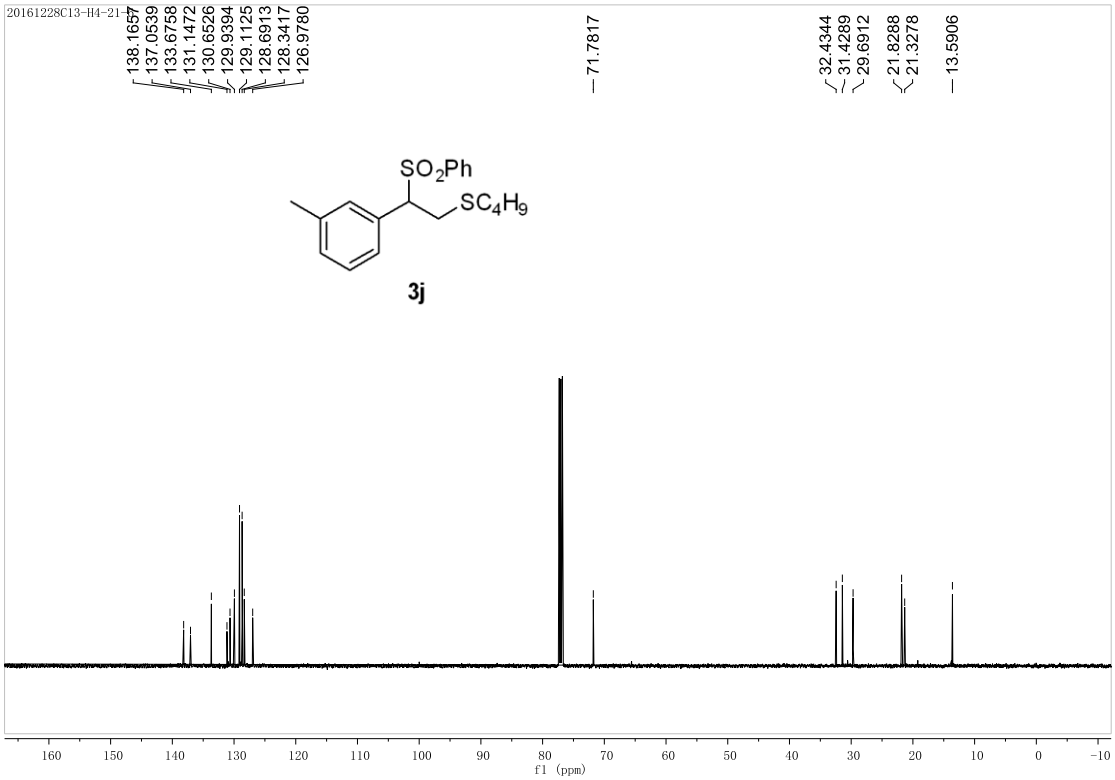
3i

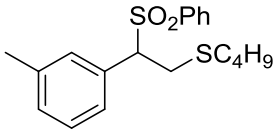
Chemical Formula: $C_{19}H_{21}NO_2S_2$
Exact Mass: 359.1014
Molecular Weight: 359.5020
m/z: 359.1014 (100.0%), 360.1047 (20.5%), 361.0972 (9.0%), 361.1081 (2.0%), 362.1005 (1.9%), 360.1008 (1.6%)
Elemental Analysis: C, 63.48; H, 5.89; N, 3.90; O, 8.90; S, 17.84



HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{19}H_{21}NNaO_2S_2$ 382.0906; found 382.0901.

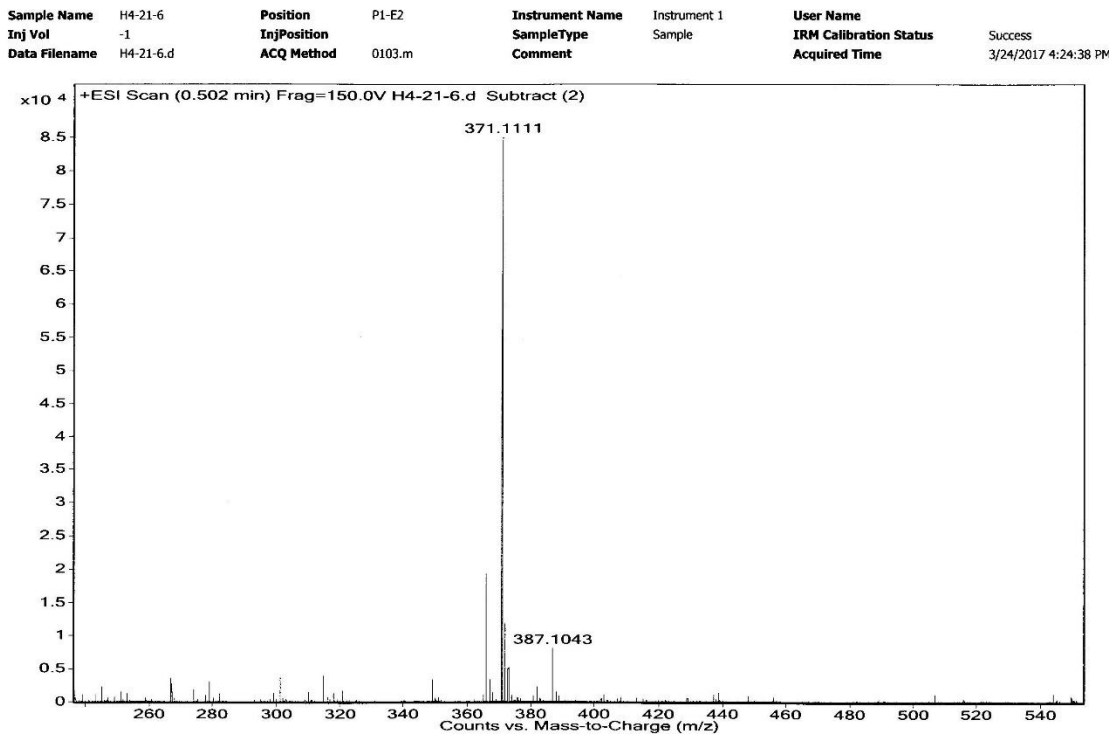




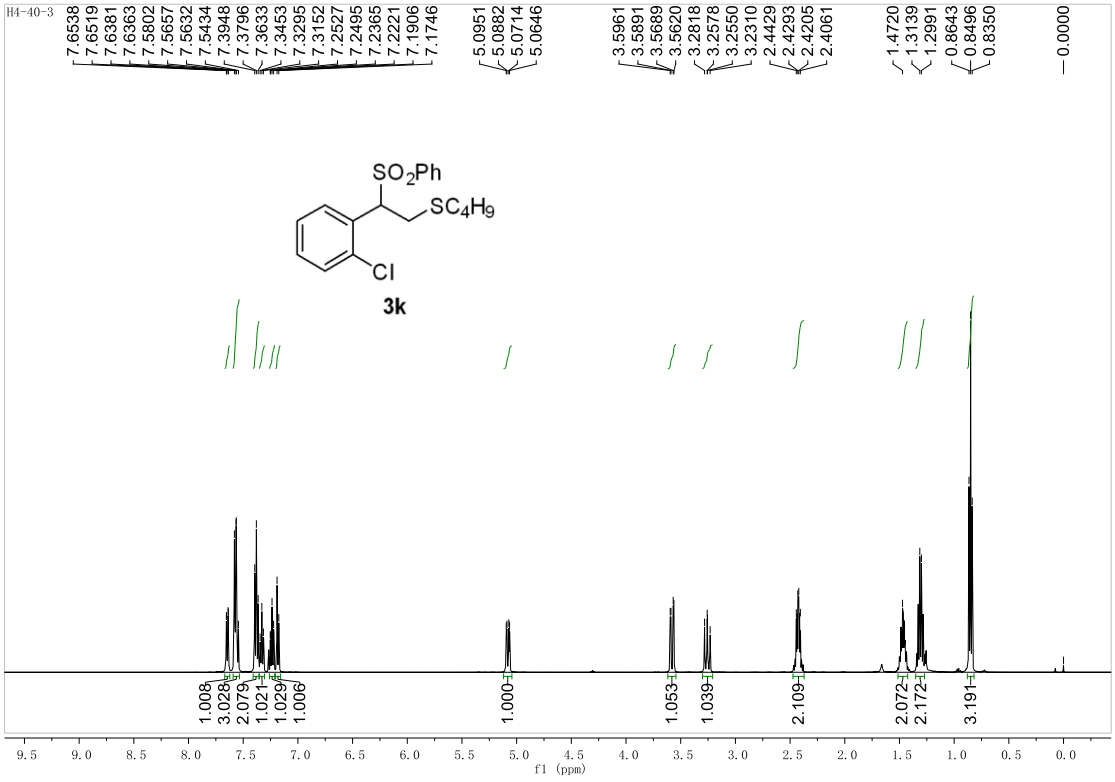


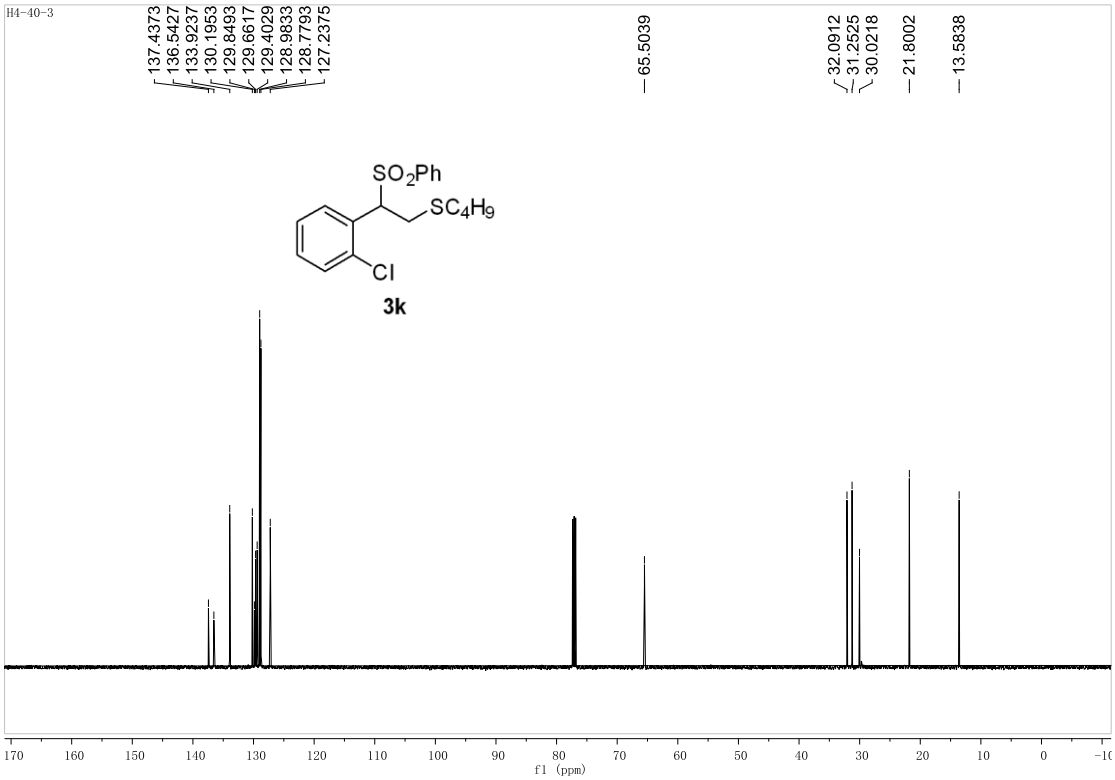
3j

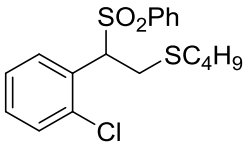
Chemical Formula: $C_{19}H_{24}O_2S_2$
Exact Mass: 348.1218
Molecular Weight: 348.5190
m/z: 348.1218 (100.0%), 349.1251 (20.5%), 350.1176 (9.0%), 350.1285 (2.0%), 351.1209 (1.9%), 349.1212 (1.6%)
Elemental Analysis: C, 65.48; H, 6.94; O, 9.18; S, 18.40



HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{19}H_{24}NaO_2S_2$ 371.1110; found 371.1111.



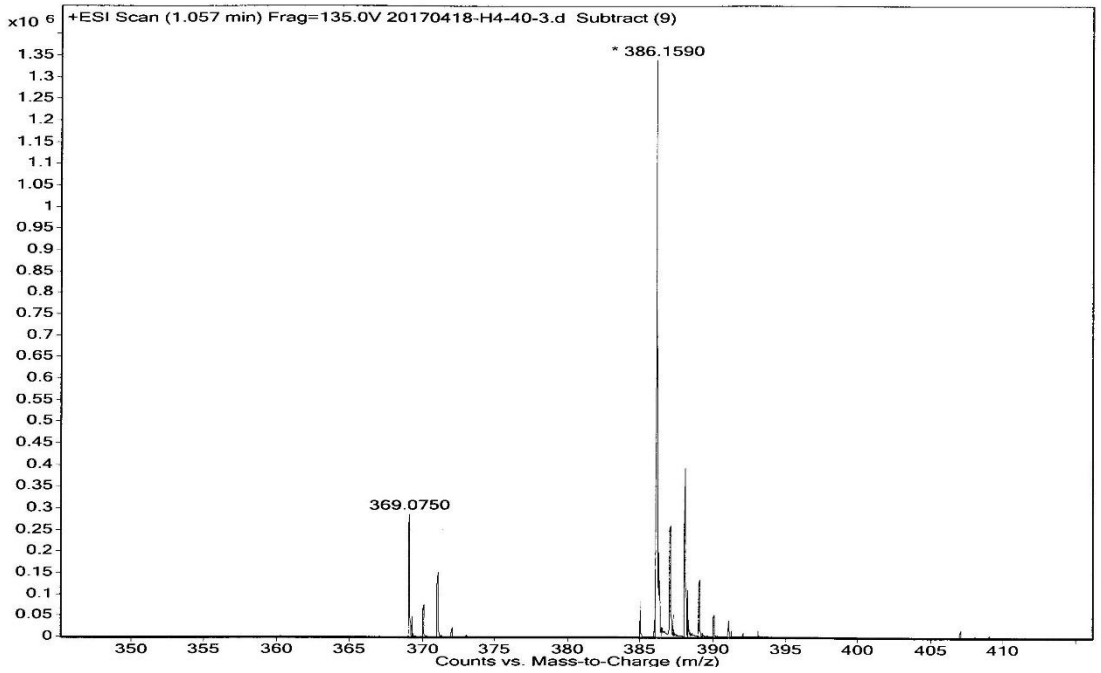




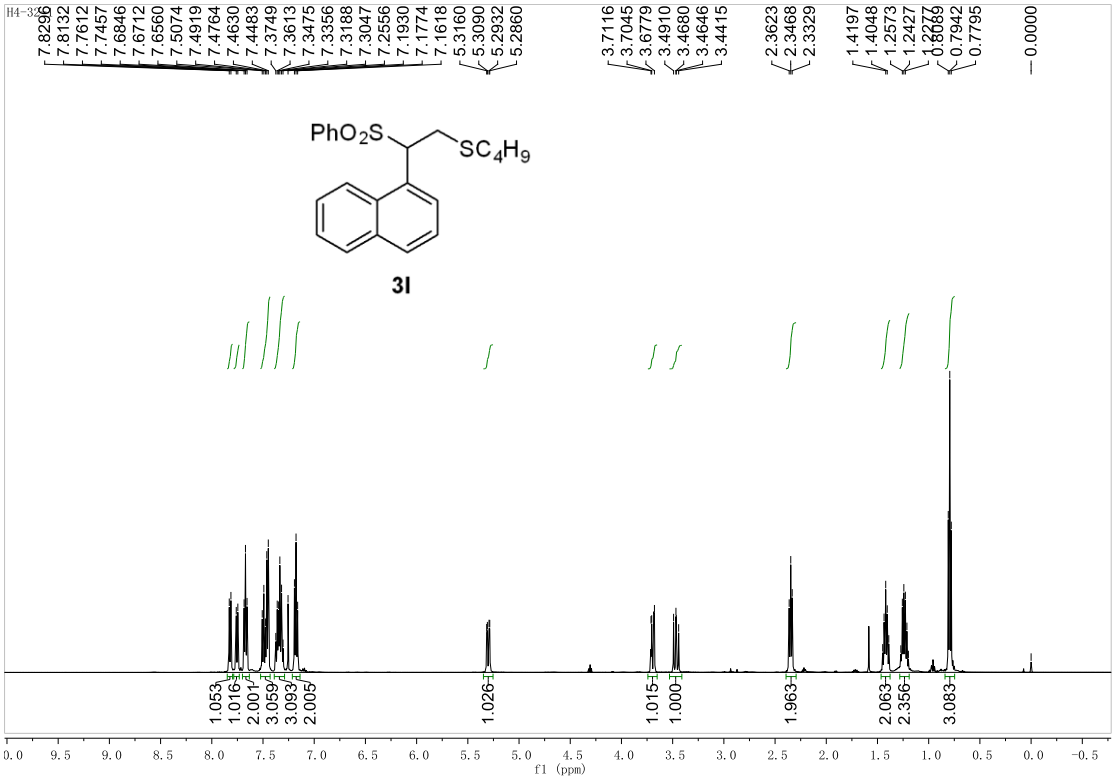
3k

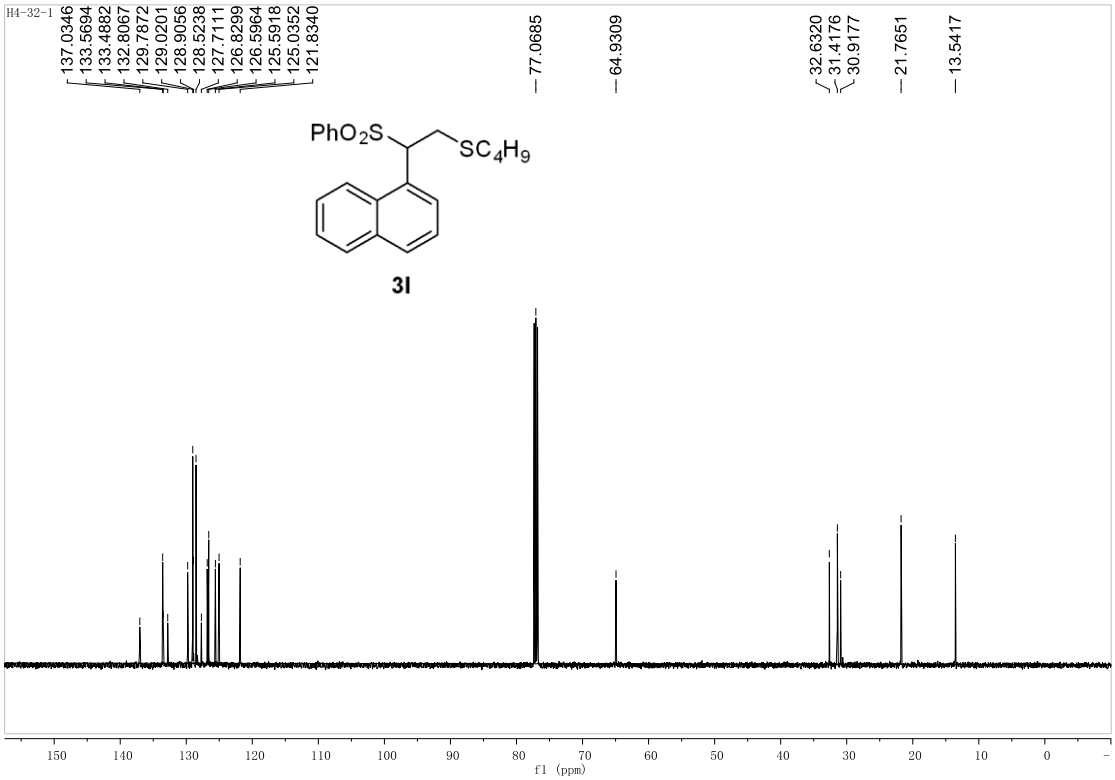
Chemical Formula: $C_{18}H_{21}ClO_2S_2$
Exact Mass: 368.0671
Molecular Weight: 368.9340
m/z: 368.0671 (100.0%), 370.0642 (32.0%), 369.0705 (19.5%), 370.0629 (9.0%), 371.0676 (6.2%), 372.0600 (2.9%), 370.0739 (1.8%), 371.0663 (1.8%), 369.0665 (1.6%)
Elemental Analysis: C, 58.60; H, 5.74; Cl, 9.61; O, 8.67; S, 17.38

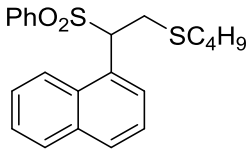
Sample Name	20170418-H4-40-3	**Position**	P1-E7	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	20170418-H4-40-3.d	**ACQ Method**	0103.m	**Comment**		**Acquired Time**	4/18/2017 6:21:50



HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{22}ClO_2S_2$ 369.0744; found 369.0750.



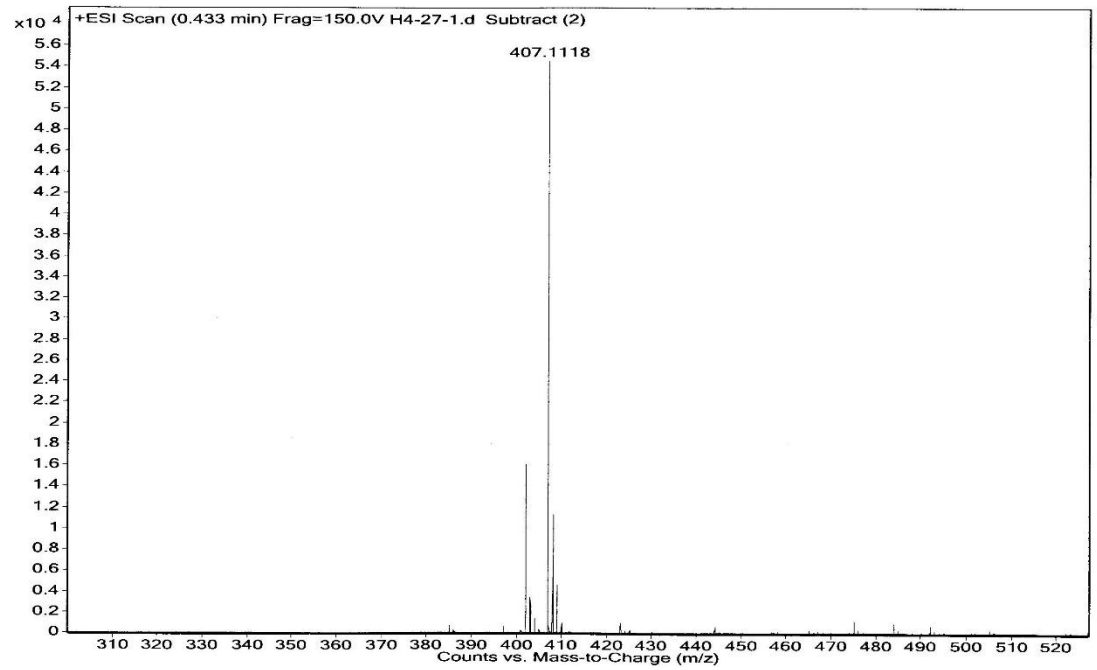




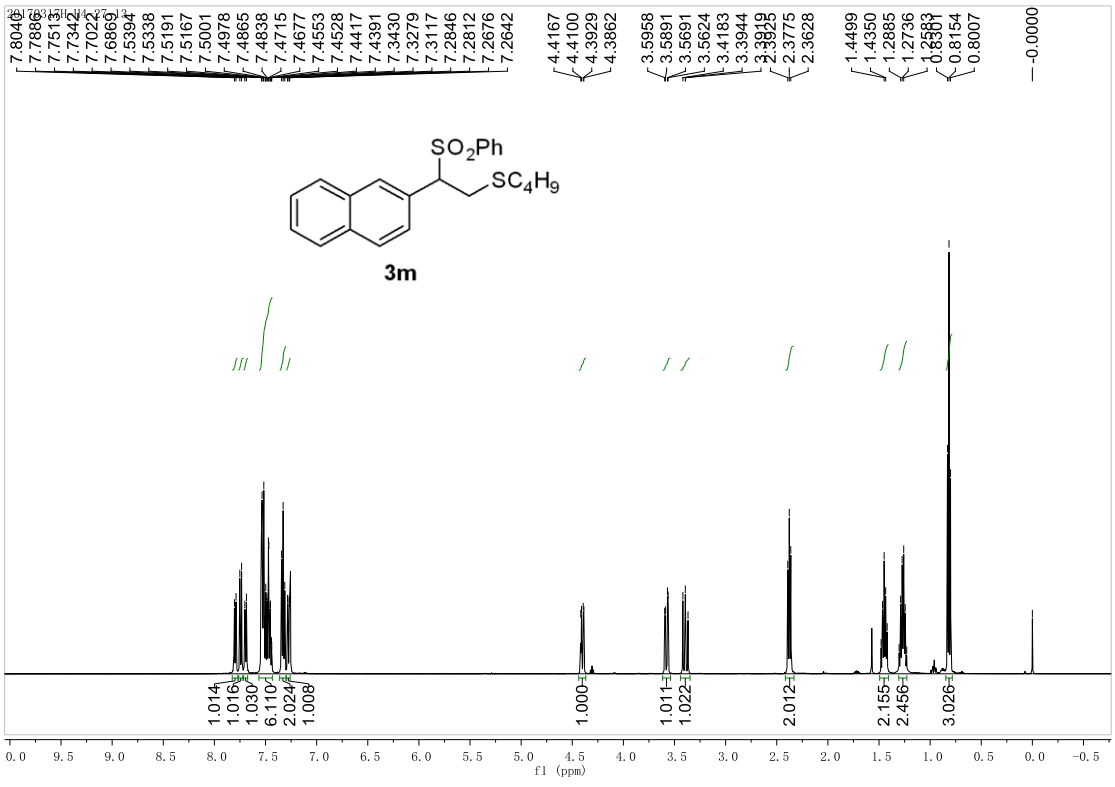
3l

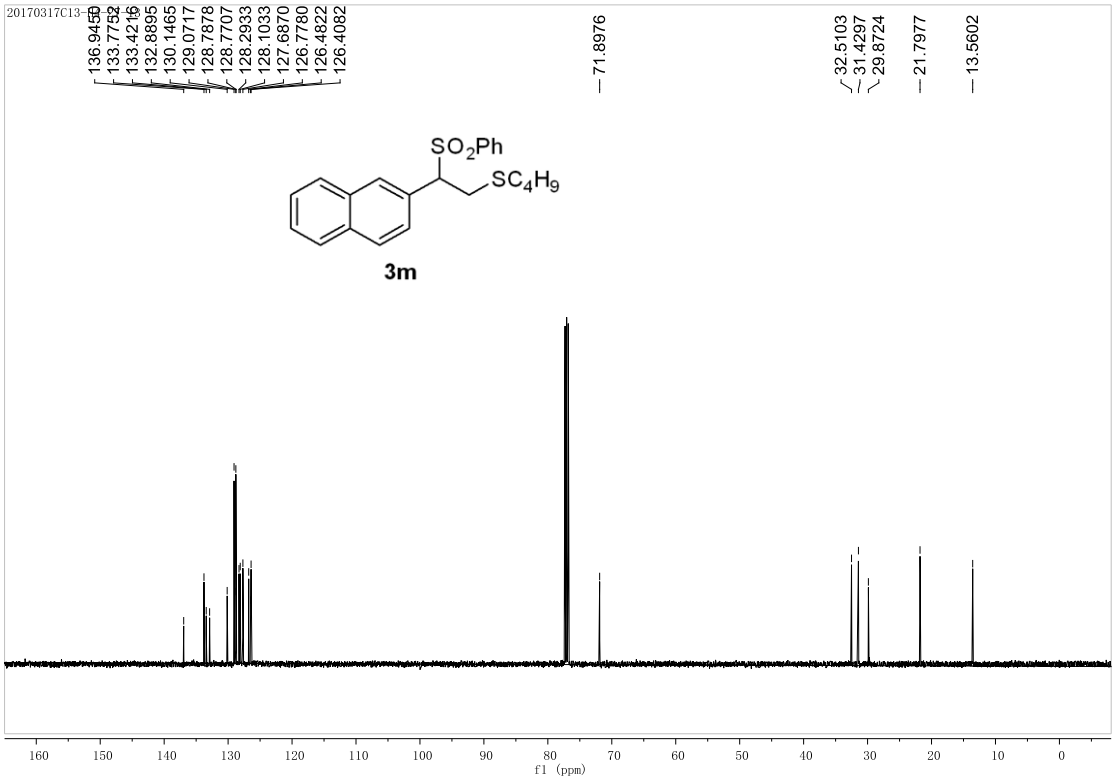
Chemical Formula: $C_{22}H_{24}O_2S_2$
Exact Mass: 384.1218
Molecular Weight: 384.5520
m/z: 384.1218 (100.0%), 385.1251 (23.8%), 386.1176 (9.0%), 386.1285 (2.7%), 387.1209 (2.2%), 385.1212 (1.6%)
Elemental Analysis: C, 68.71; H, 6.29; O, 8.32; S, 16.67

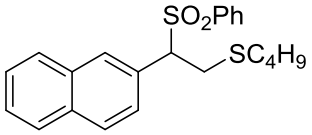
Sample Name	Unavailable	**Position**	Unavailable	**Instrument Name**	Unavailable	**User Name**	Unavailable
Inj Vol	Unavailable	**InjPosition**	Unavailable	**SampleType**	Unavailable	**IRM Calibration Status**	Success
Data Filename	H4-27-1.d	**ACQ Method**		**Comment**	Sample information is unavailable	**Acquired Time**	Unavailable



HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{18}H_{15}NaO_2S$ 407.1110; found 407.1118.

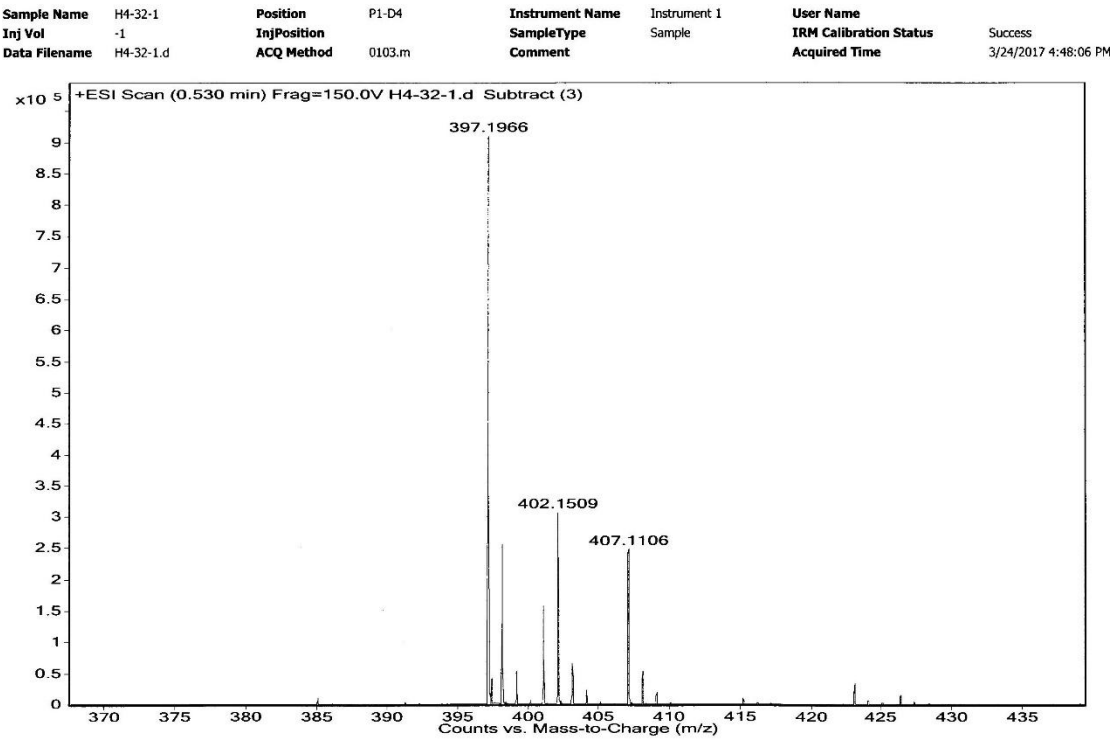




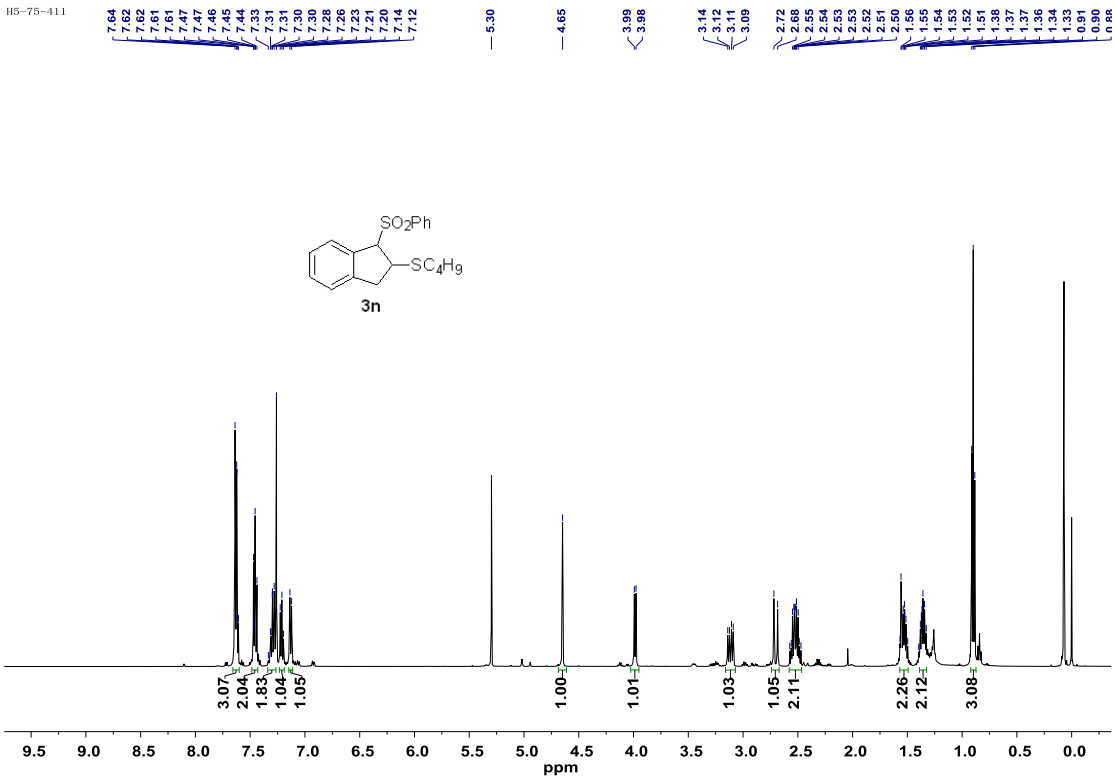


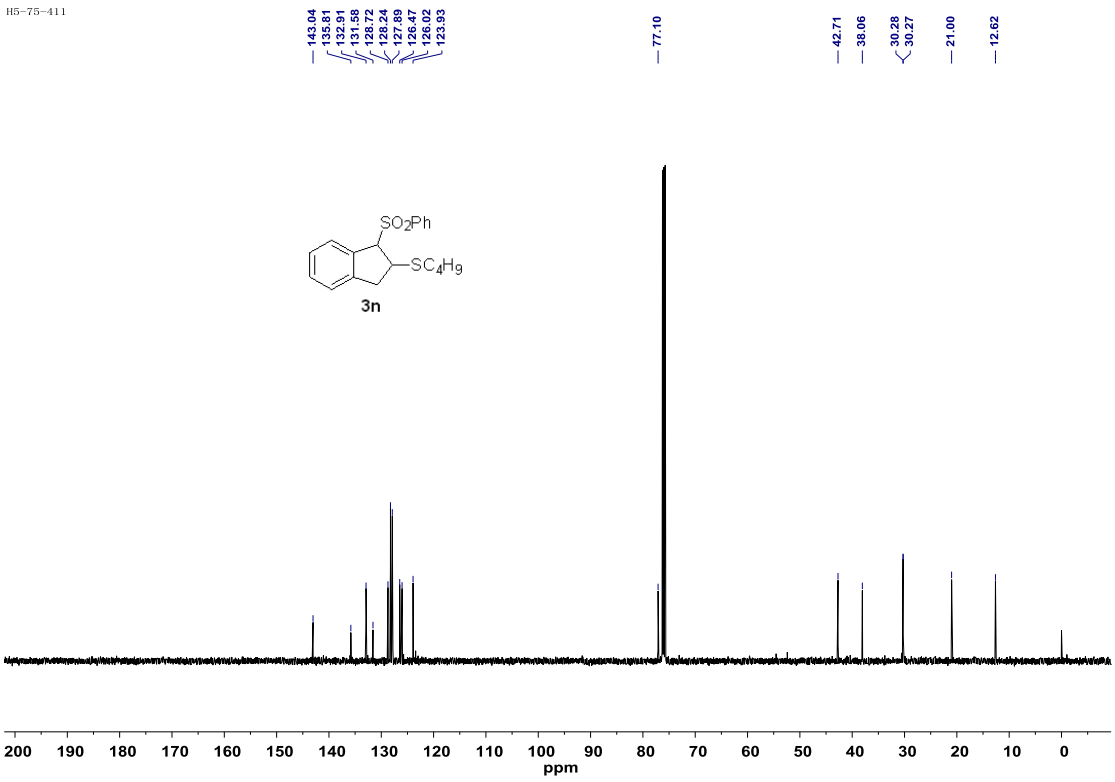
3m

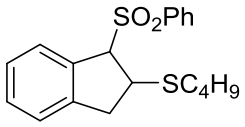
Chemical Formula: $C_{22}H_{24}O_2S_2$
Exact Mass: 384.1218
Molecular Weight: 384.5520
m/z: 384.1218 (100.0%), 385.1251 (23.8%), 386.1176 (9.0%), 386.1285 (2.7%), 387.1209 (2.2%), 385.1212 (1.6%)
Elemental Analysis: C, 68.71; H, 6.29; O, 8.32; S, 16.67



HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{22}H_{24}NaO_2S_2$ 407.1110; found 407.1106.

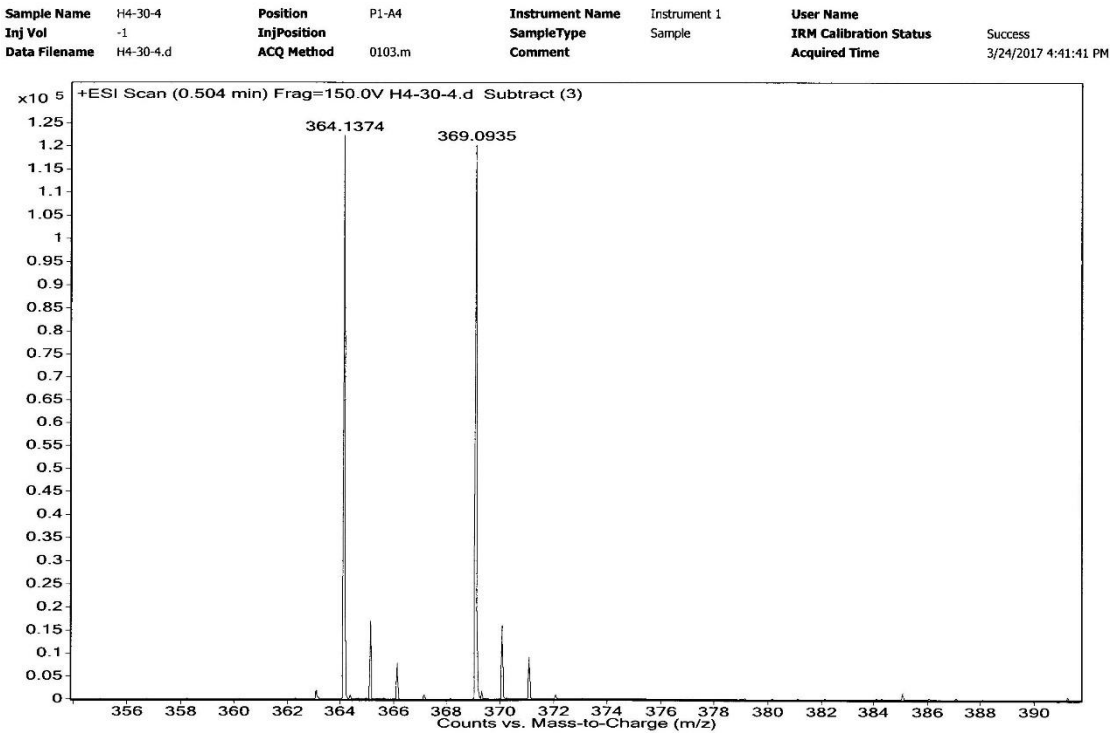




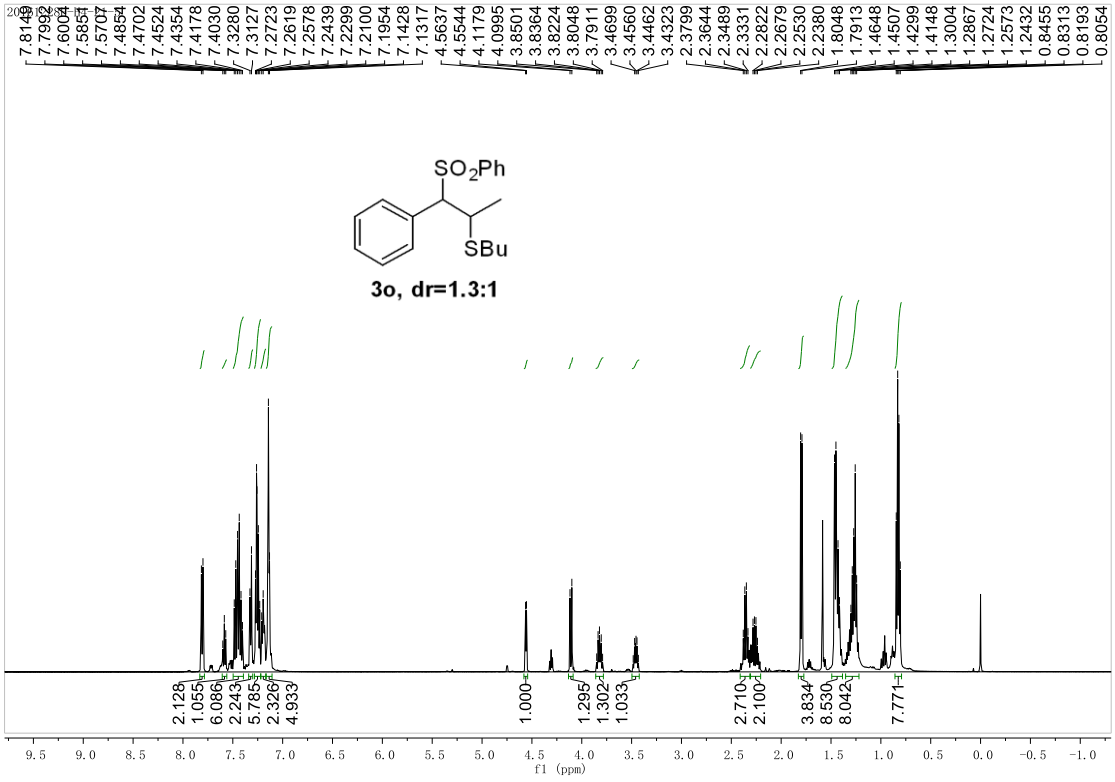


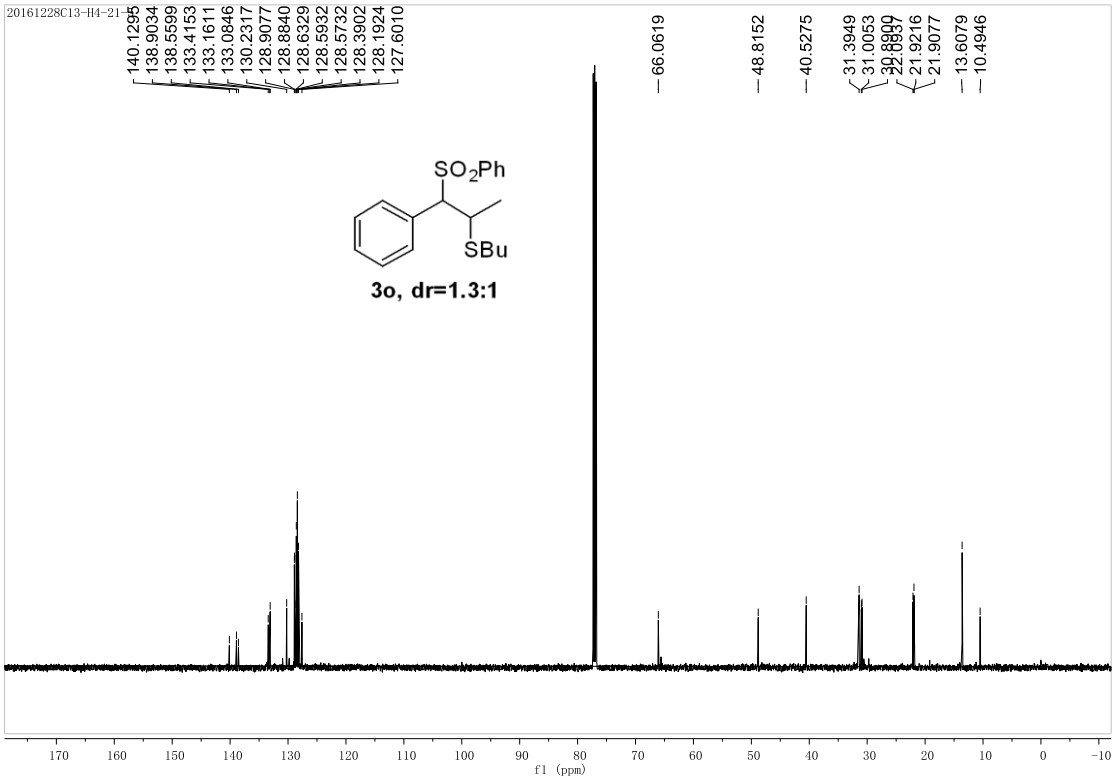
3n

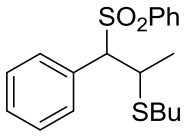
Chemical Formula: $C_{19}H_{22}O_2S_2$
Exact Mass: 346.1061
Molecular Weight: 346.5030
m/z: 346.1061 (100.0%), 347.1095 (20.5%), 348.1019 (9.0%), 348.1128 (2.0%), 349.1053 (1.9%), 347.1055 (1.6%)
Elemental Analysis: C, 65.86; H, 6.40; O, 9.23; S, 18.50



HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{19}H_{22}NaO_2S_2$ 369.0953; found 369.0935.

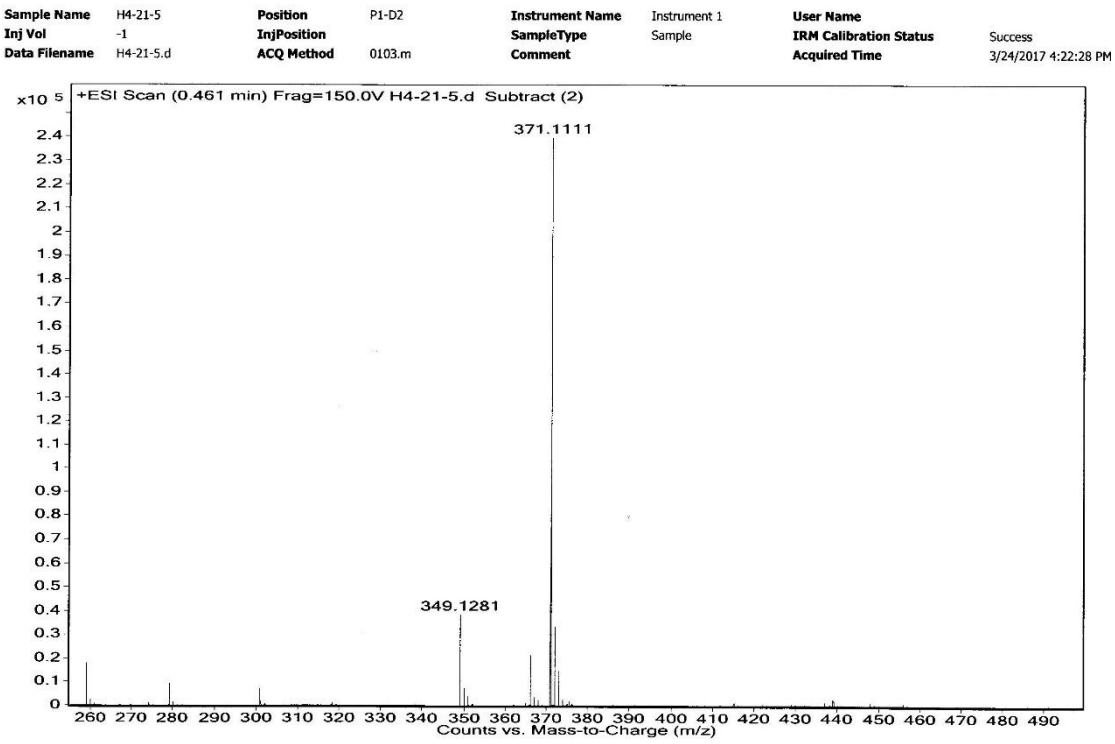




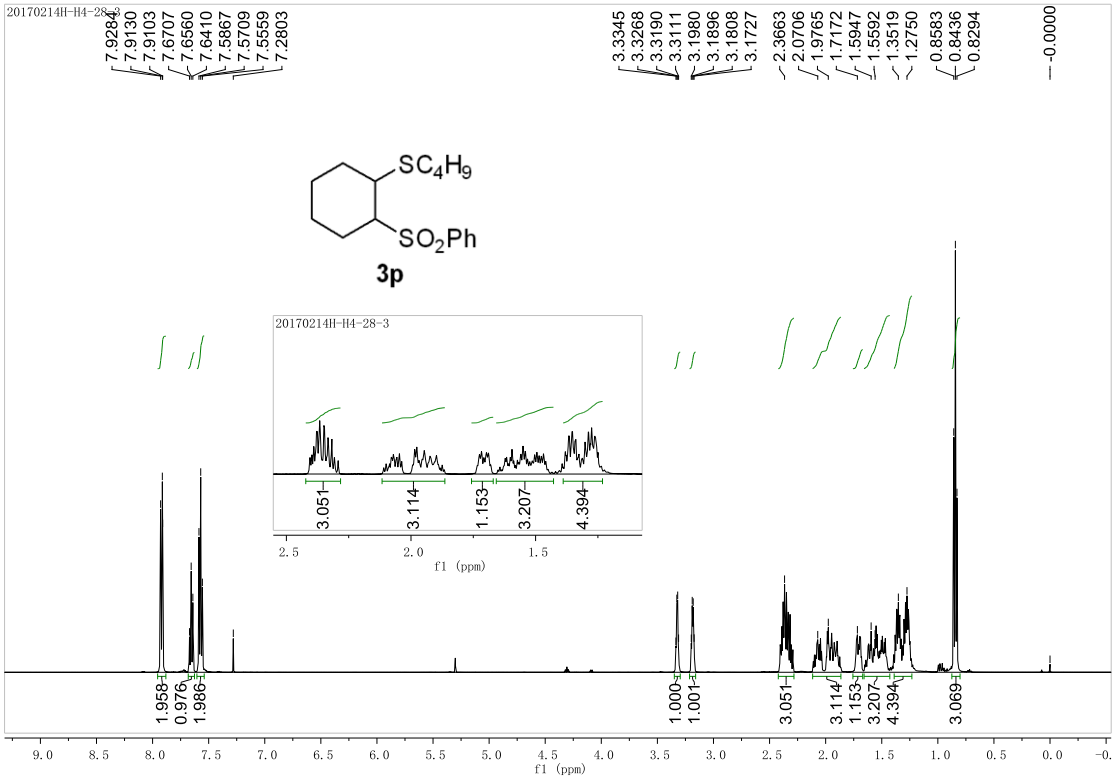


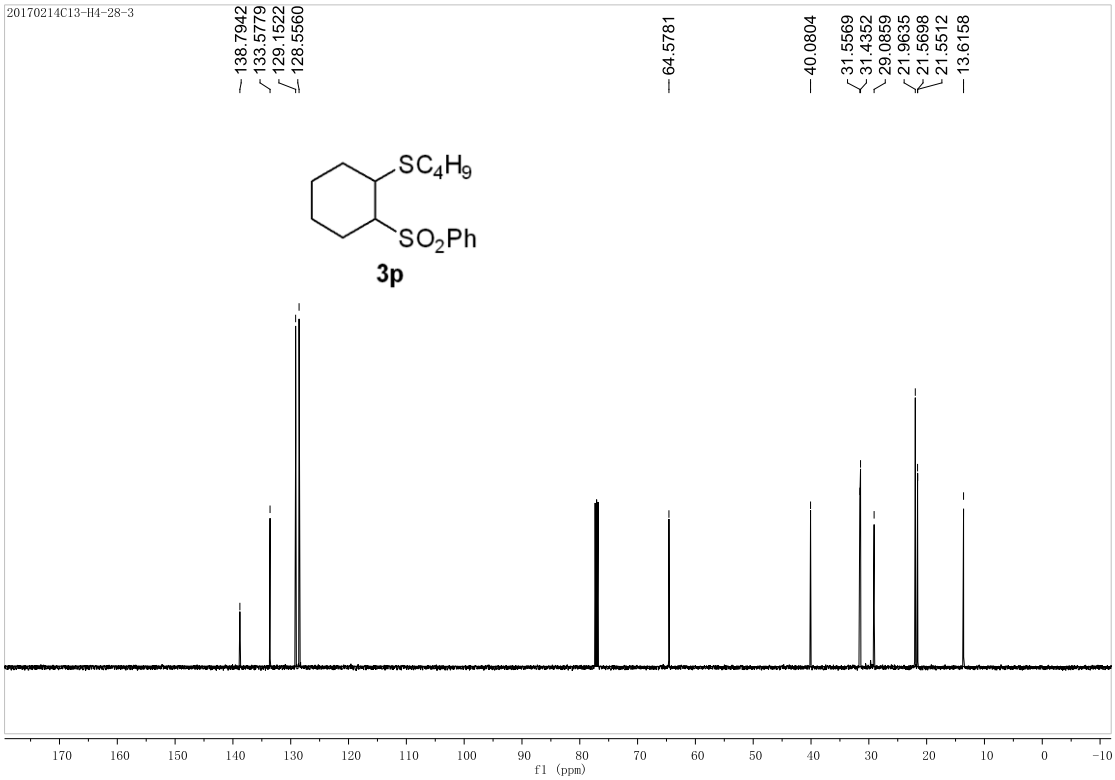
3o

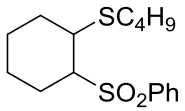
Chemical Formula: $C_{19}H_{24}O_2S_2$
Exact Mass: 348.1218
Molecular Weight: 348.5190
m/z: 348.1218 (100.0%), 349.1251 (20.5%), 350.1176 (9.0%), 350.1285 (2.0%), 351.1209 (1.9%), 349.1212 (1.6%)
Elemental Analysis: C, 65.48; H, 6.94; O, 9.18; S, 18.40



HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{19}H_{24}NaO_2S_2$ 371.1110; found 371.1111.



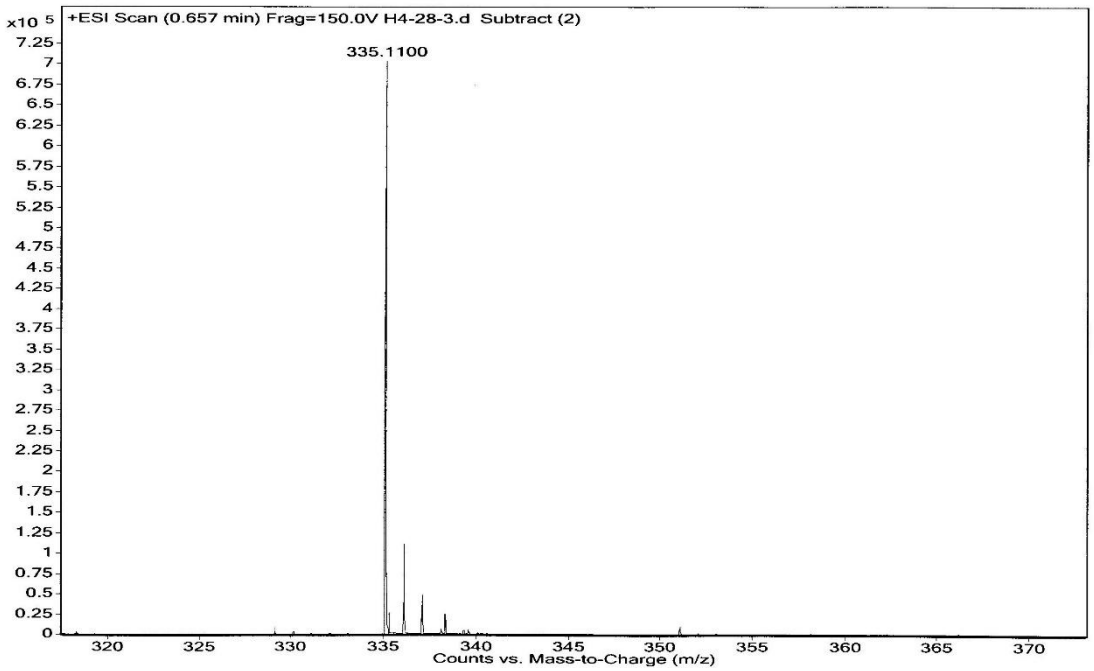




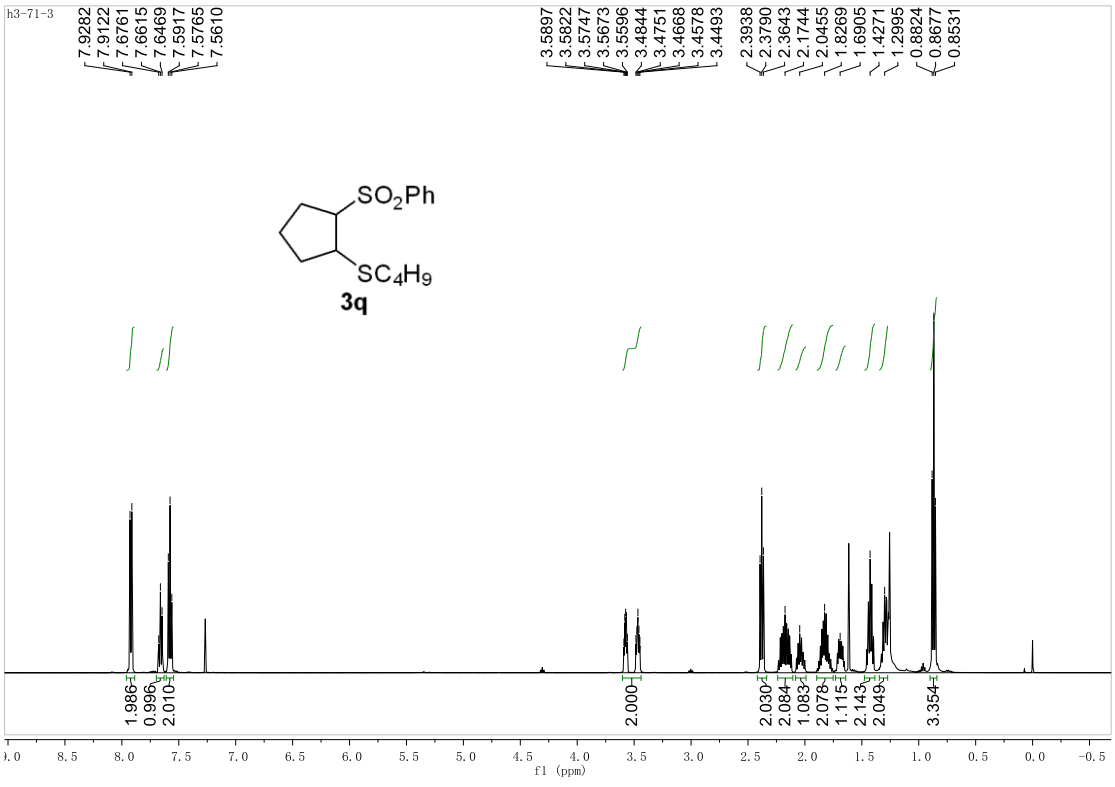
3p

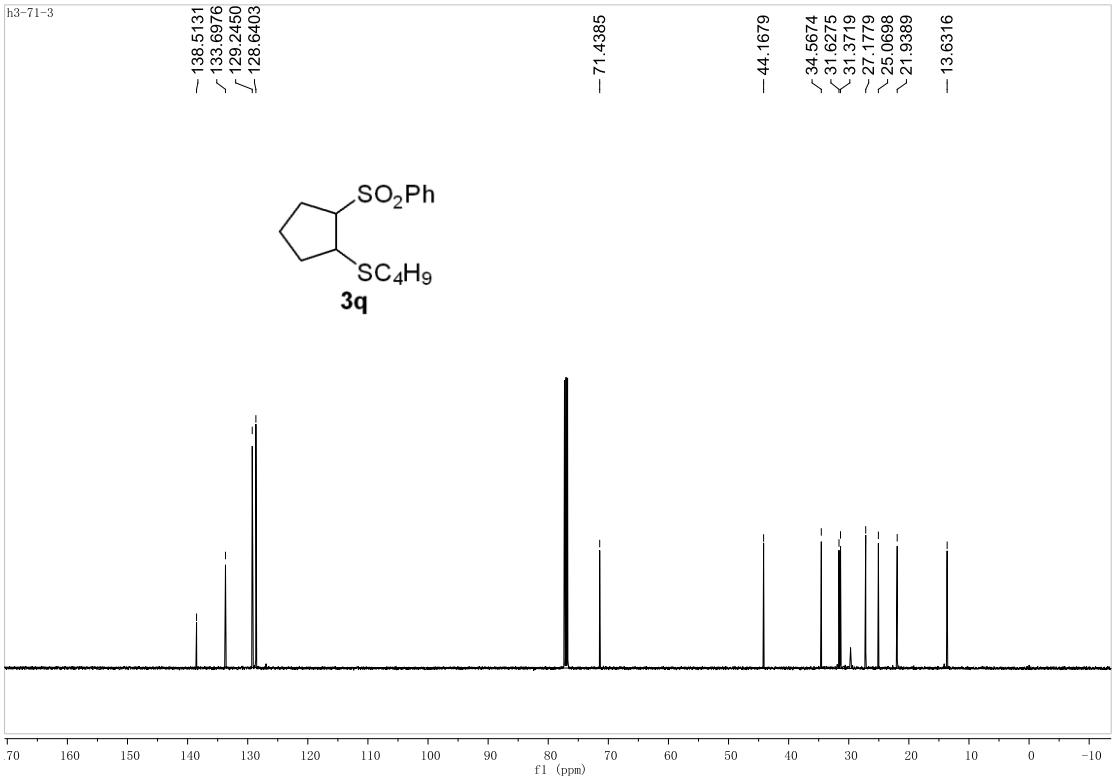
Chemical Formula: $C_{16}H_{24}O_2S_2$
Exact Mass: 312.1218
Molecular Weight: 312.4860
m/z: 312.1218 (100.0%), 313.1251 (17.3%), 314.1176 (9.0%), 313.1212 (1.6%), 314.1285 (1.4%)
Elemental Analysis: C, 61.50; H, 7.74; O, 10.24; S, 20.52

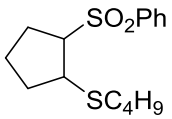
Sample Name	Unavailable	**Position**	Unavailable	**Instrument Name**	Unavailable	**User Name**	Unavailable
Inj Vol	Unavailable	**InjPosition**	Unavailable	**SampleType**	Unavailable	**IRM Calibration Status**	Success
Data Filename	H4-28-3.d	**ACQ Method**		**Comment**	Sample information is unavailable	**Acquired Time**	Unavailable



HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{16}H_{24}NaO_2S_2$ 335.1110; found 335.1100.

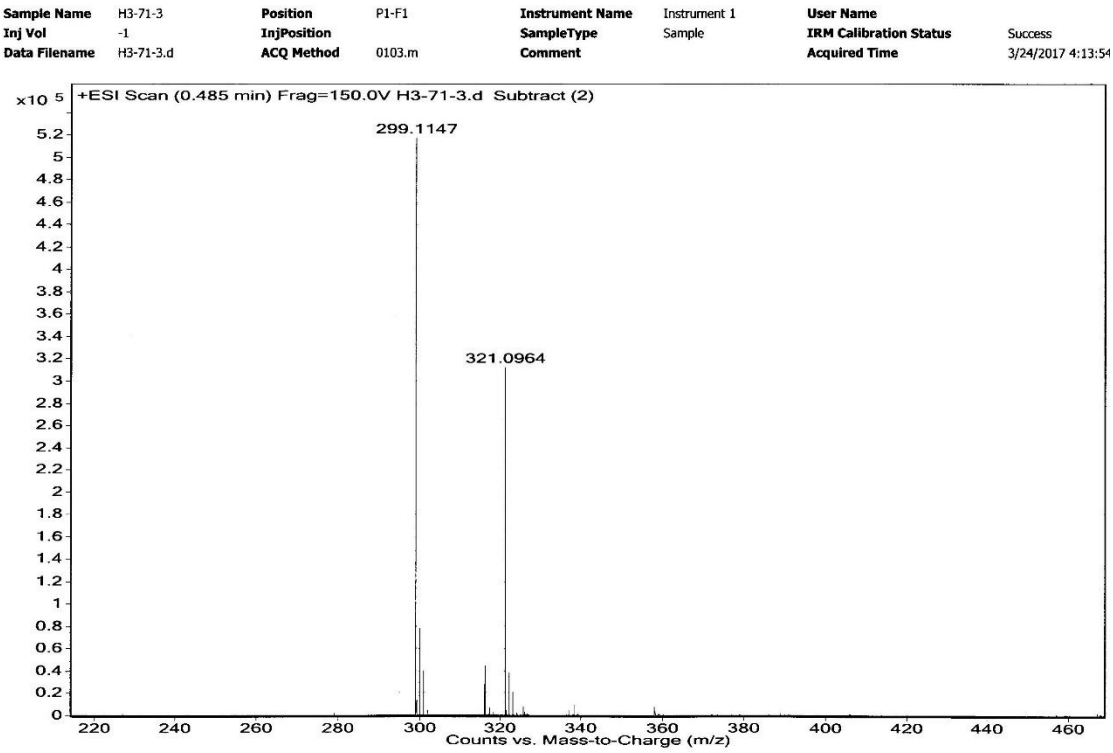




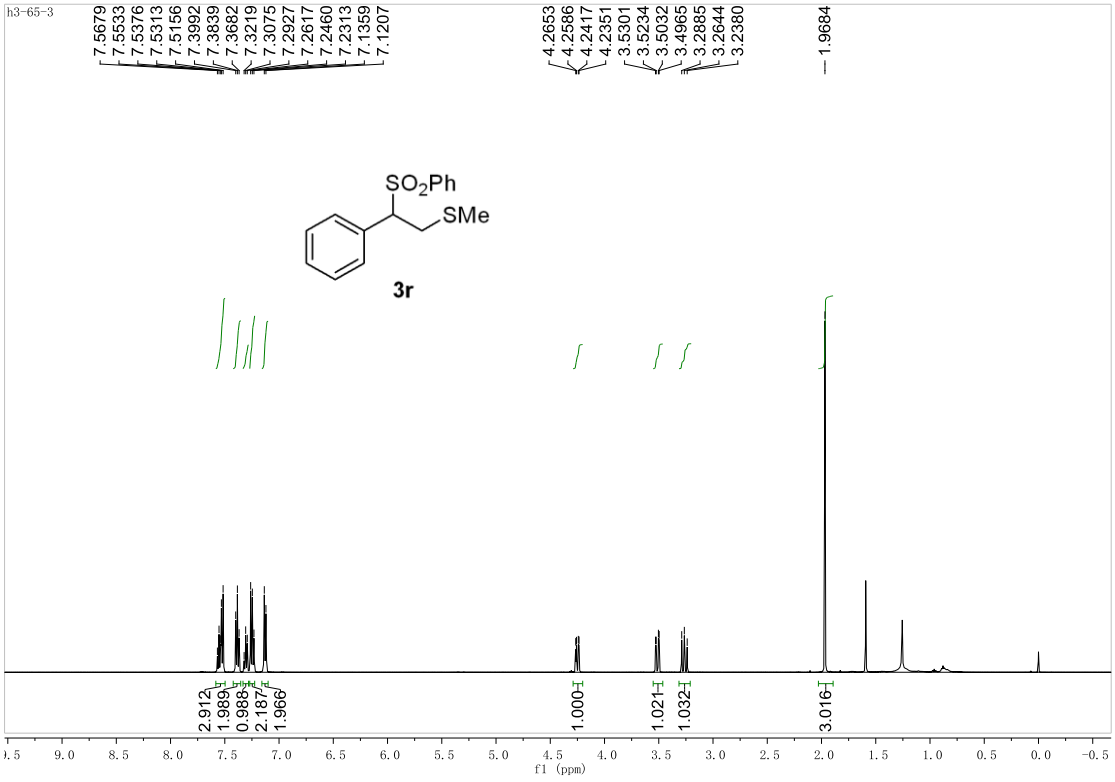


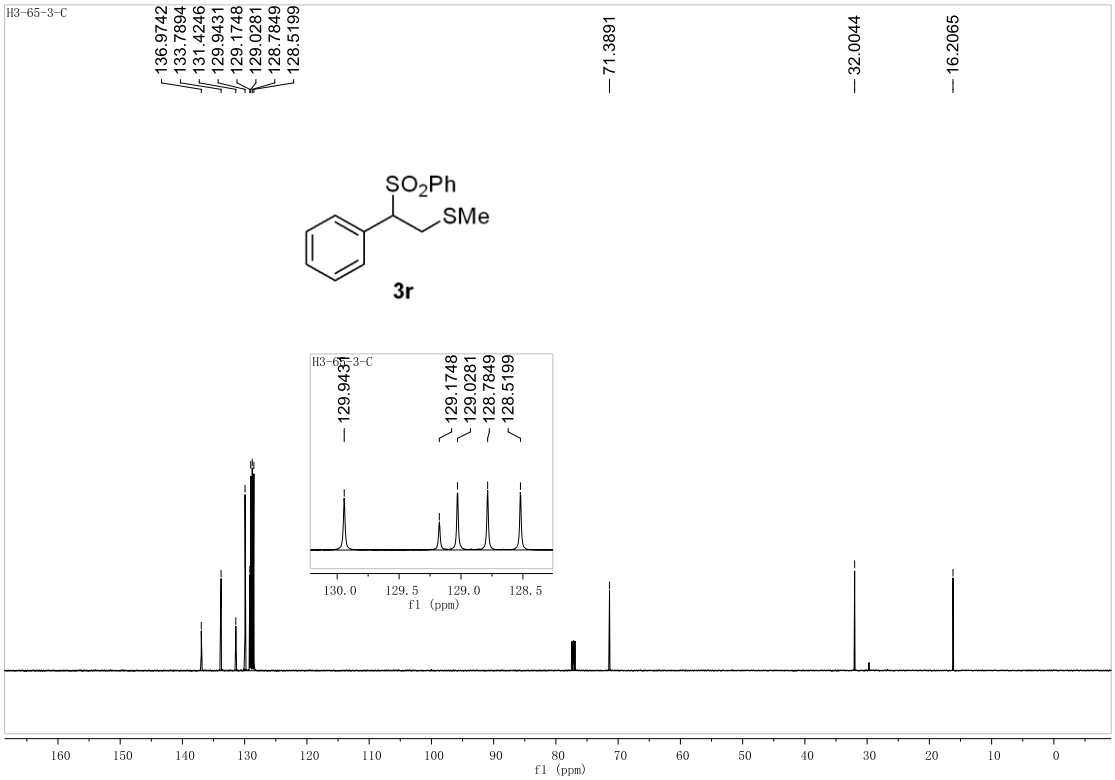
3q

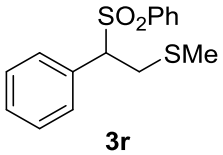
Chemical Formula: $C_{15}H_{22}O_2S_2$
Exact Mass: 298.1061
Molecular Weight: 298.4590
m/z: 298.1061 (100.0%), 299.1095 (16.2%), 300.1019 (9.0%), 299.1055 (1.6%), 300.1128 (1.2%)
Elemental Analysis: C, 60.37; H, 7.43; O, 10.72; S, 21.48



HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{22}NaO_2S_2$ 321.0953; found 321.0964.

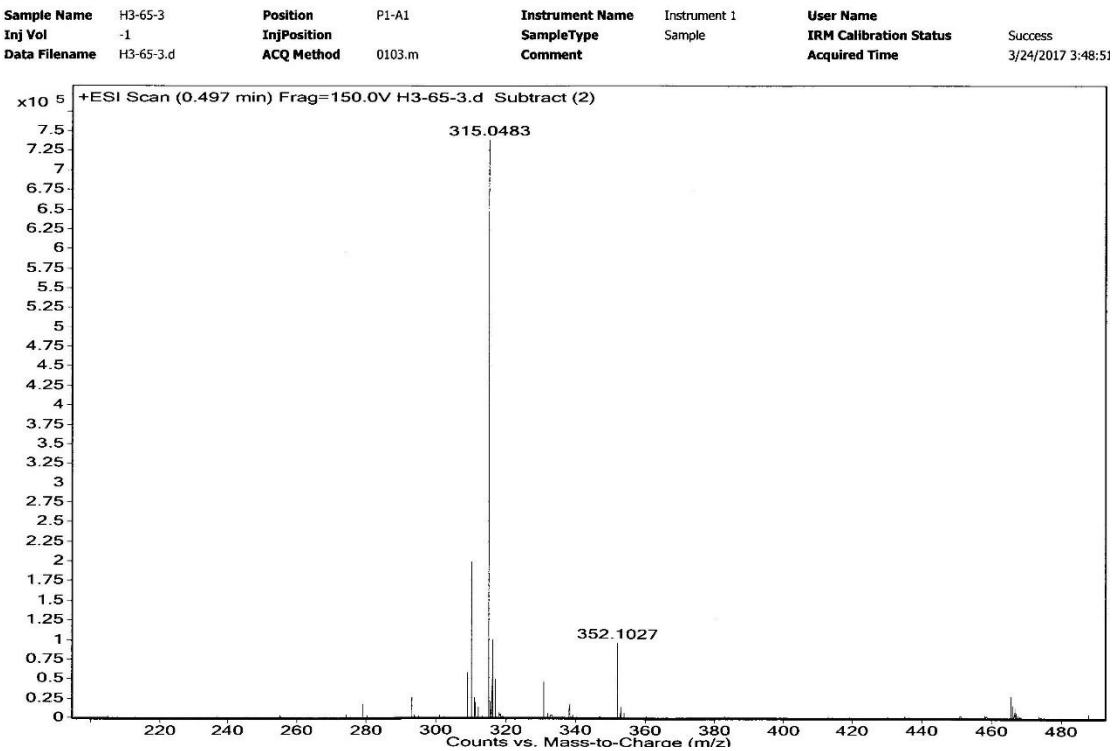




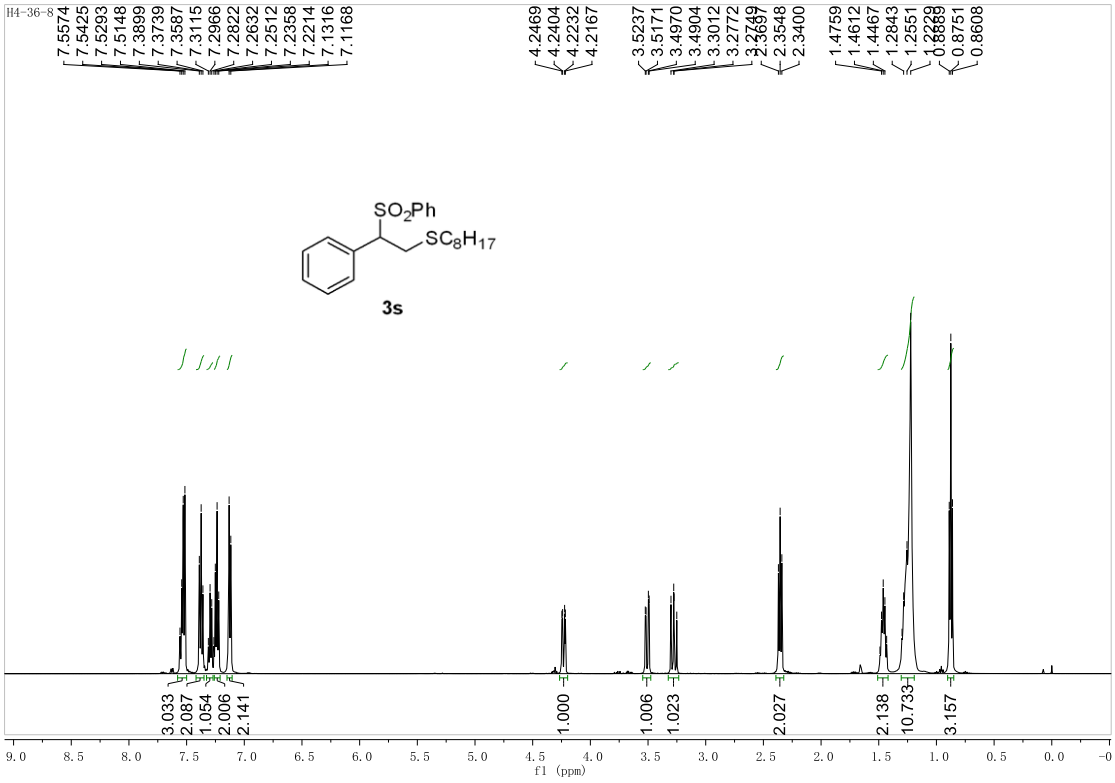


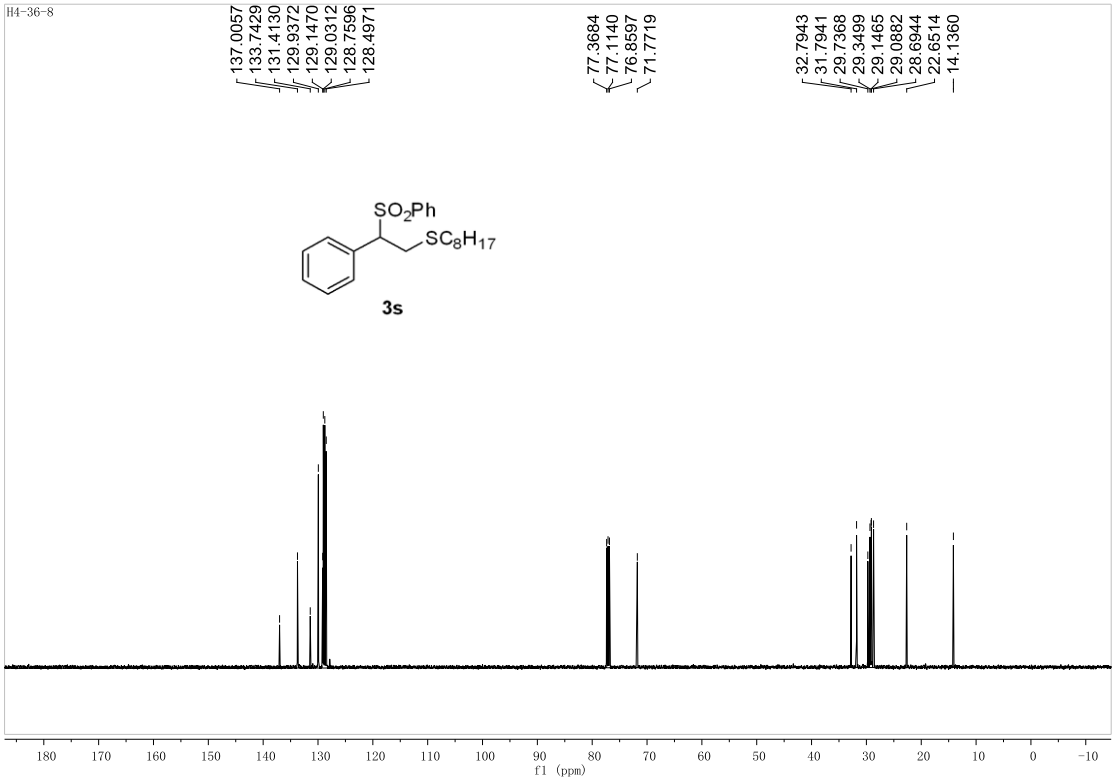
3r

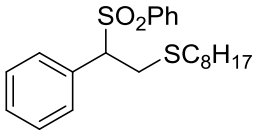
Chemical Formula: $C_{15}H_{16}O_2S_2$
Exact Mass: 292.0592
Molecular Weight: 292.4110
m/z: 292.0592 (100.0%), 293.0625 (16.2%), 294.0550 (9.0%), 293.0586 (1.6%), 294.0659 (1.2%)
Elemental Analysis: C, 61.61; H, 5.52; O, 10.94; S, 21.93



HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{16}NaO_2S_2$ 315.0484; found 315.0483.



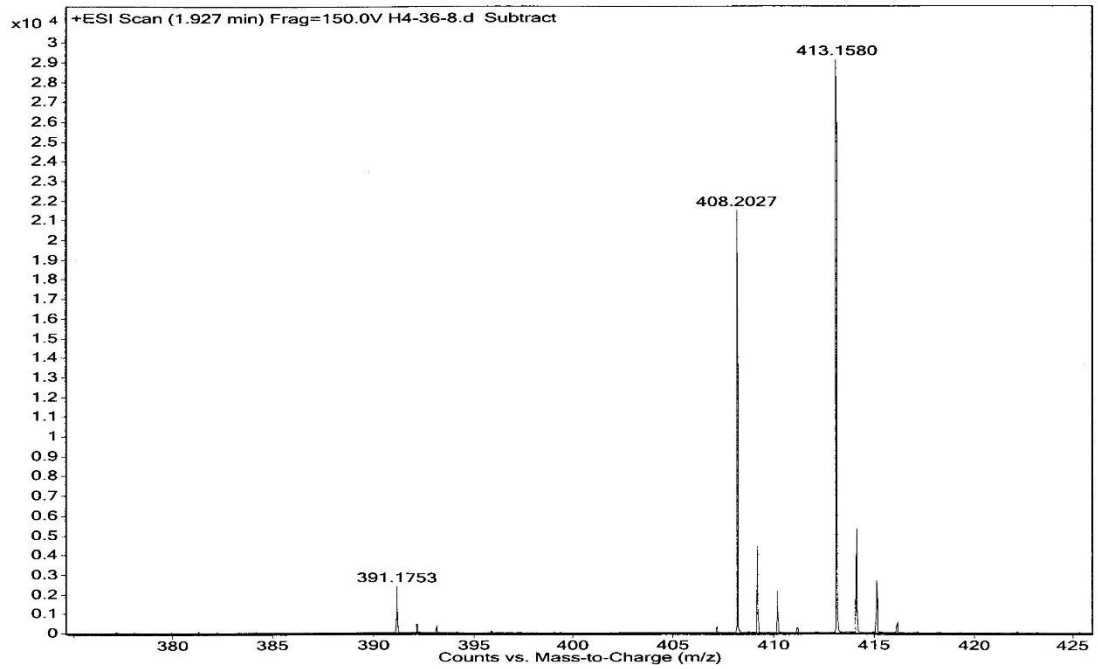




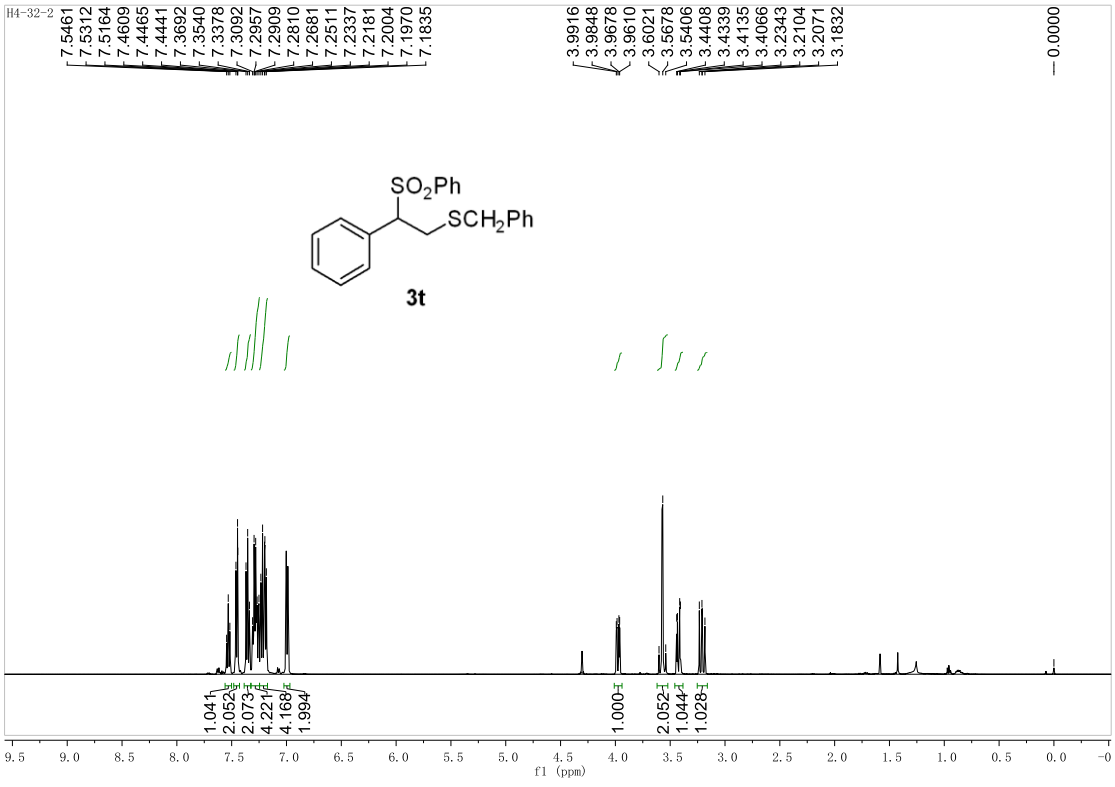
3s

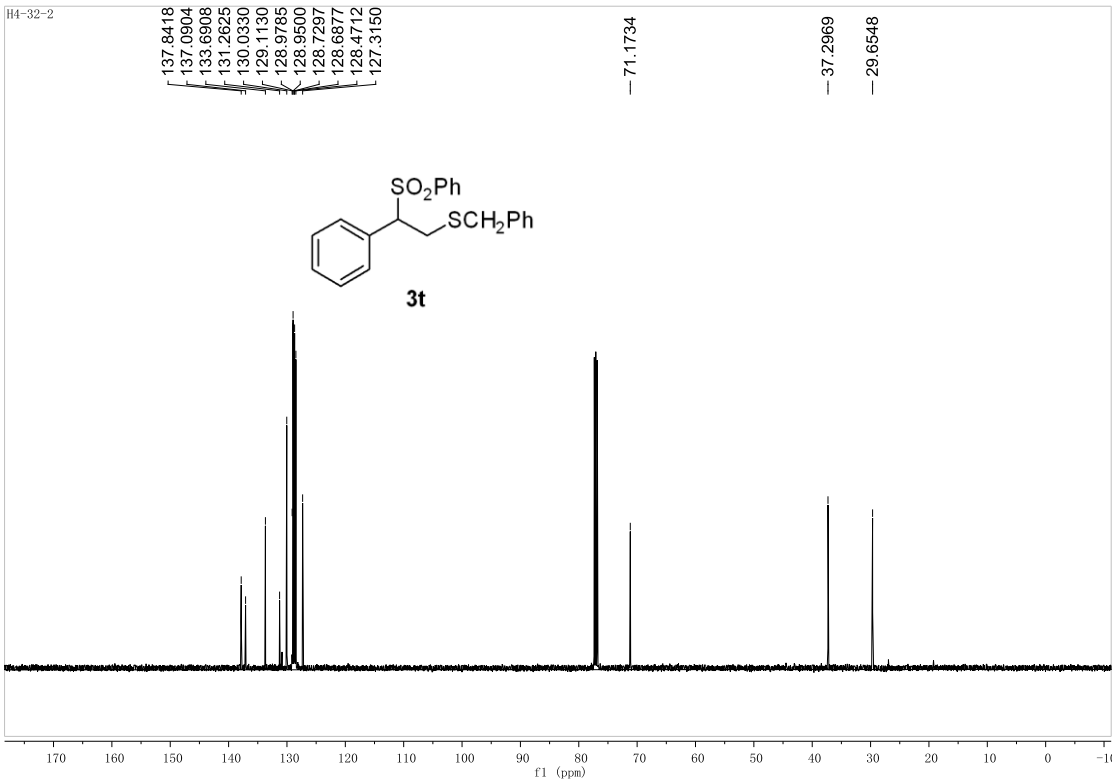
Chemical Formula: $C_{22}H_{30}O_2S_2$
Exact Mass: 390.1687
Molecular Weight: 390.6000
m/z: 390.1687 (100.0%), 391.1721 (23.8%), 392.1645 (9.0%), 392.1754 (2.7%), 393.1679 (2.2%), 391.1681 (1.6%)
Elemental Analysis: C, 67.65; H, 7.74; O, 8.19; S, 16.42

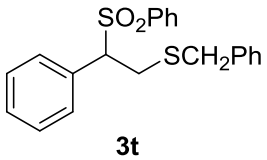
Sample Name	H4-36-8	**Position**	P1-B9	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	H4-36-8.d	**ACQ Method**	0103.m	**Comment**		**Acquired Time**	7/26/2017 12:50:18



HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{22}H_{30}NaO_2S_2$ 413.1579; found 413.1580.

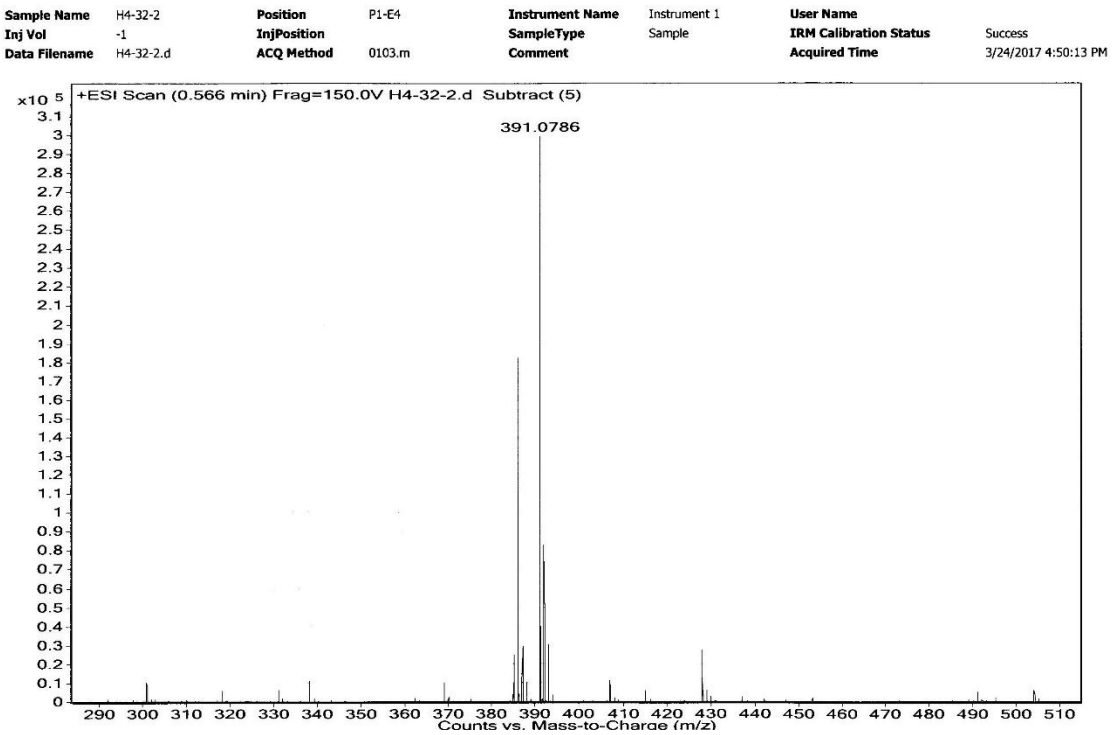




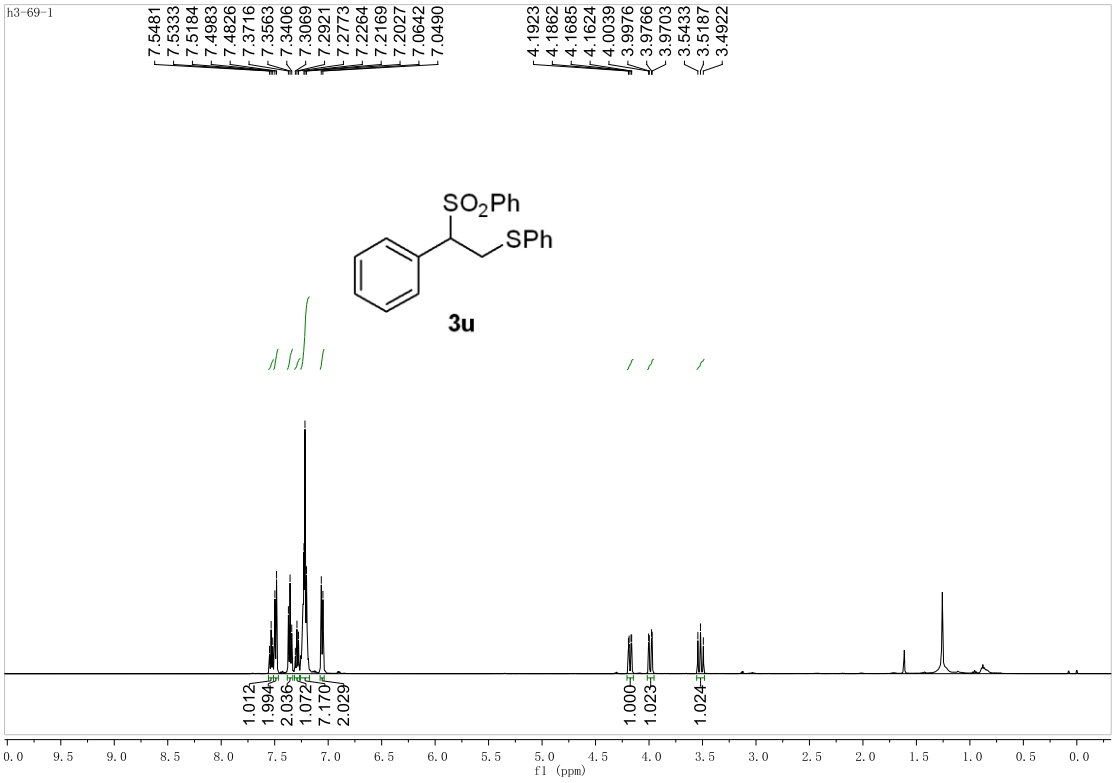


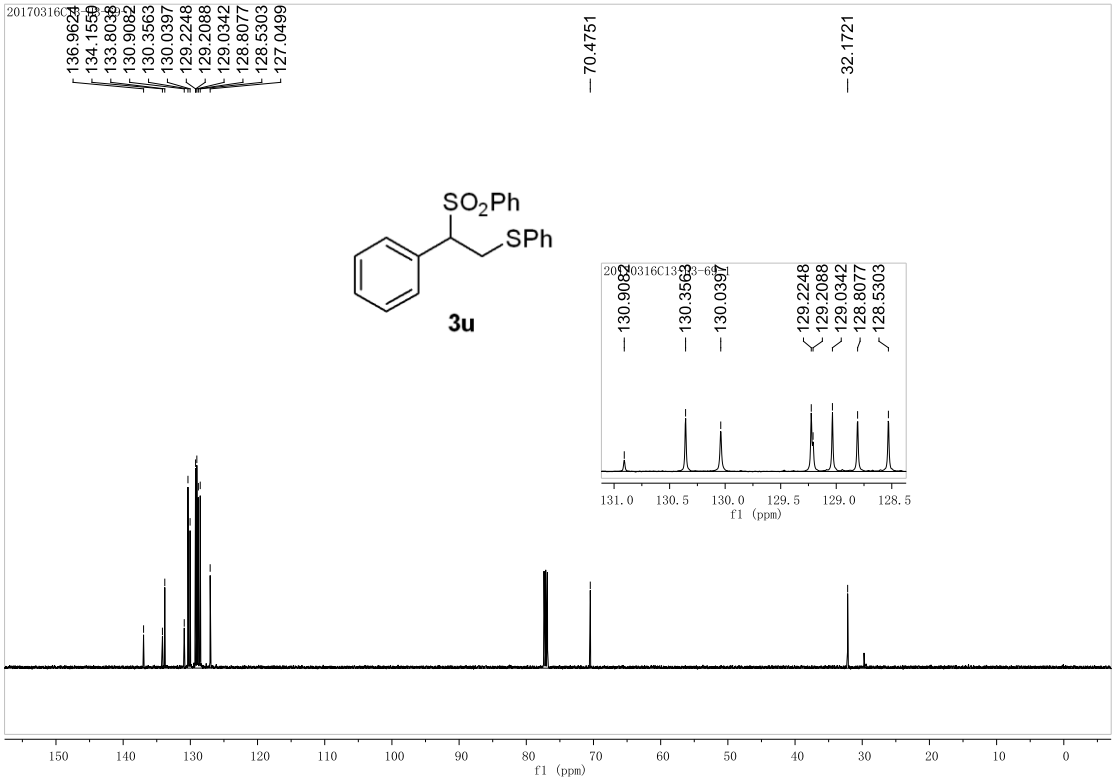
3t

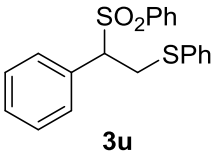
Chemical Formula: $C_{21}H_{20}O_2S_2$
Exact Mass: 368.0905
Molecular Weight: 368.5090
m/z: 368.0905 (100.0%), 369.0938 (22.7%), 370.0863 (9.0%), 370.0972 (2.5%), 371.0896 (2.1%), 369.0899 (1.6%)
Elemental Analysis: C, 68.45; H, 5.47; O, 8.68; S, 17.40



HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{21}H_{20}NaO_2S_2$ 391.0797; found 391.0786.

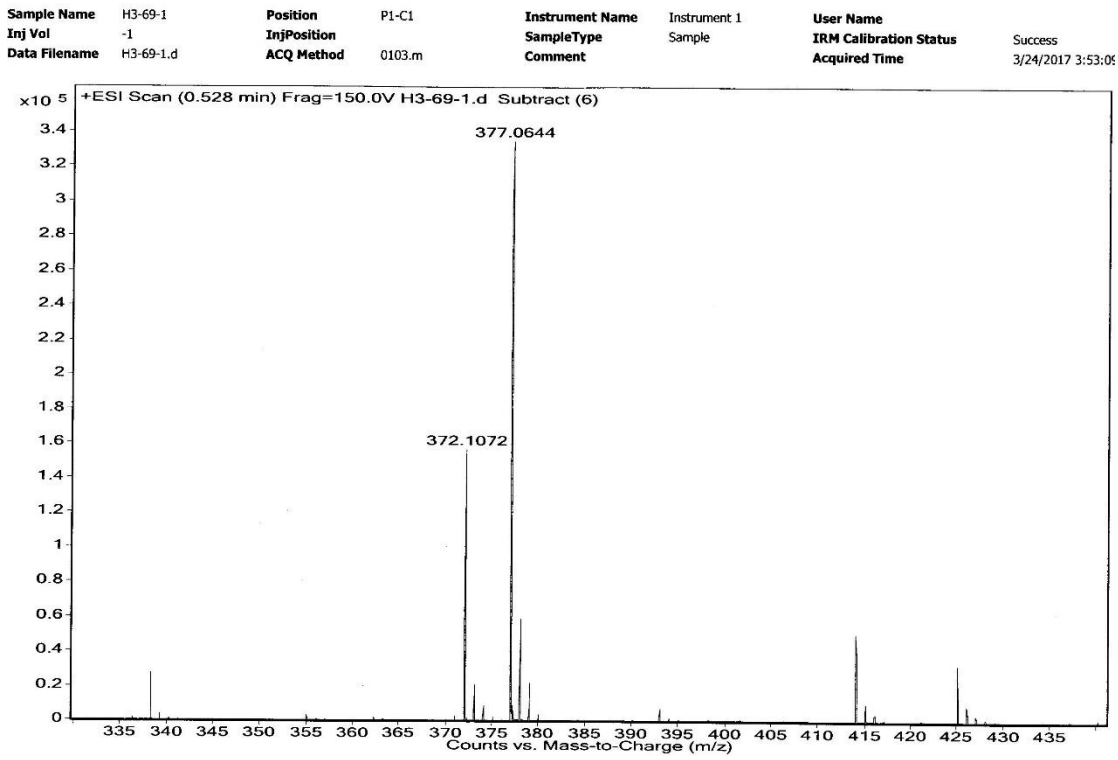




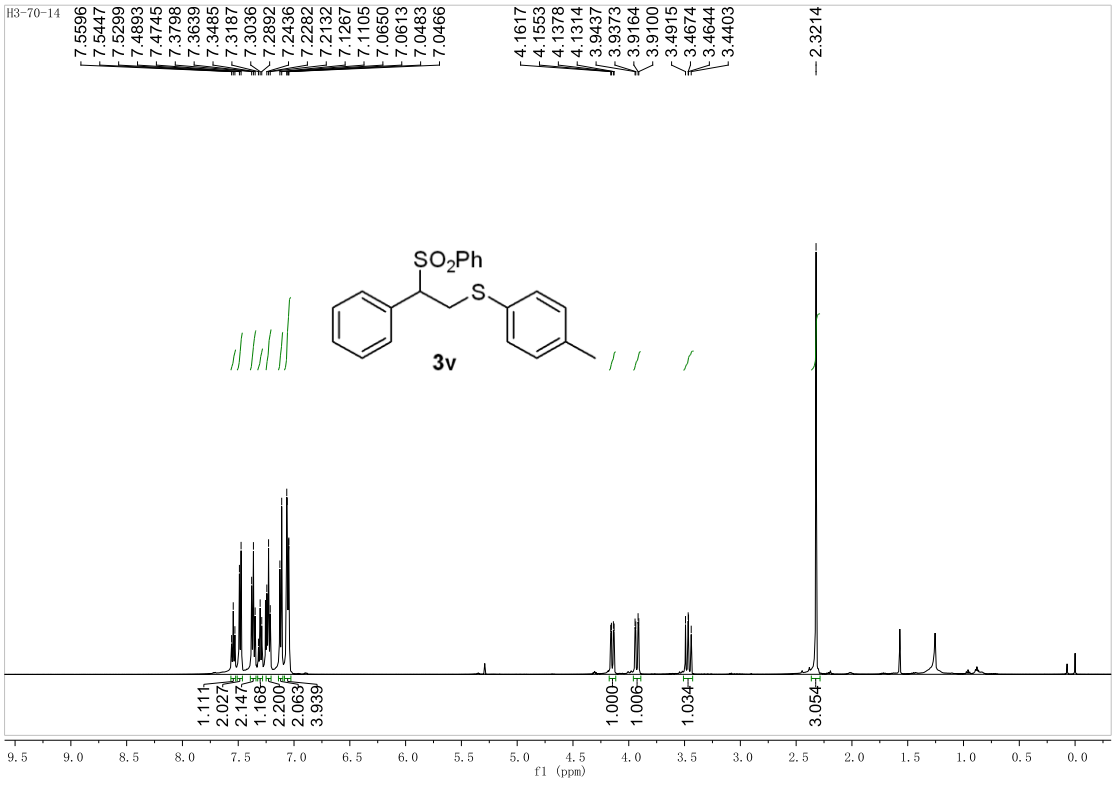


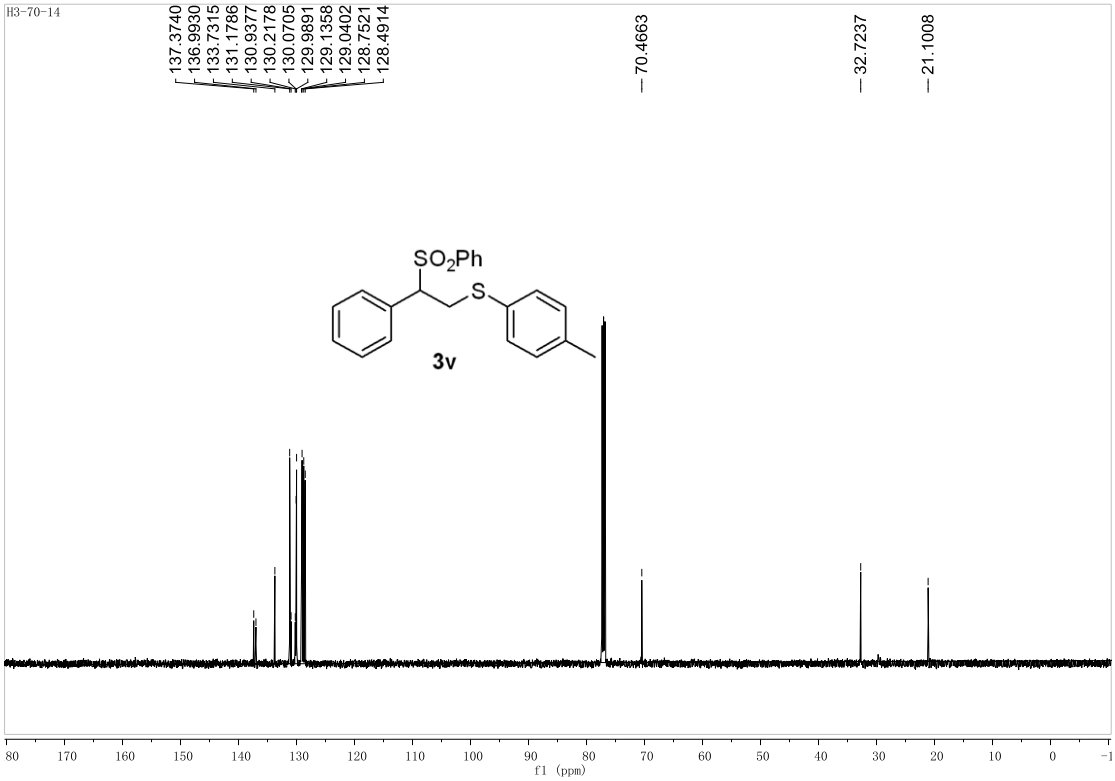
3u

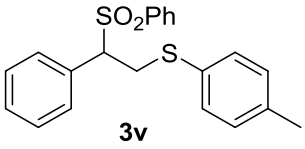
Chemical Formula: $C_{20}H_{18}O_2S_2$
Exact Mass: 354.0748
Molecular Weight: 354.4820
m/z: 354.0748 (100.0%), 355.0782 (21.6%), 356.0706 (9.0%), 356.0815 (2.2%), 357.0740 (2.0%), 355.0742 (1.6%)
Elemental Analysis: C, 67.77; H, 5.12; O, 9.03; S, 18.09



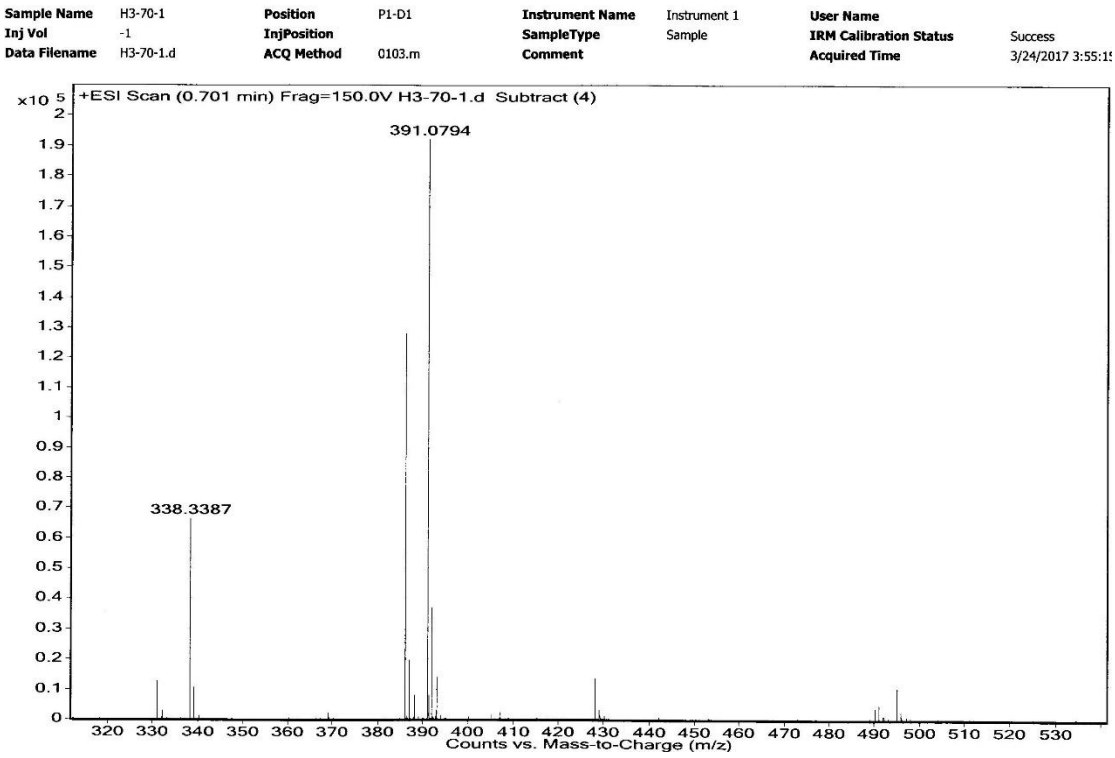
HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{20}H_{18}NaO_2S_2$ 377.0640; found 377.0644.



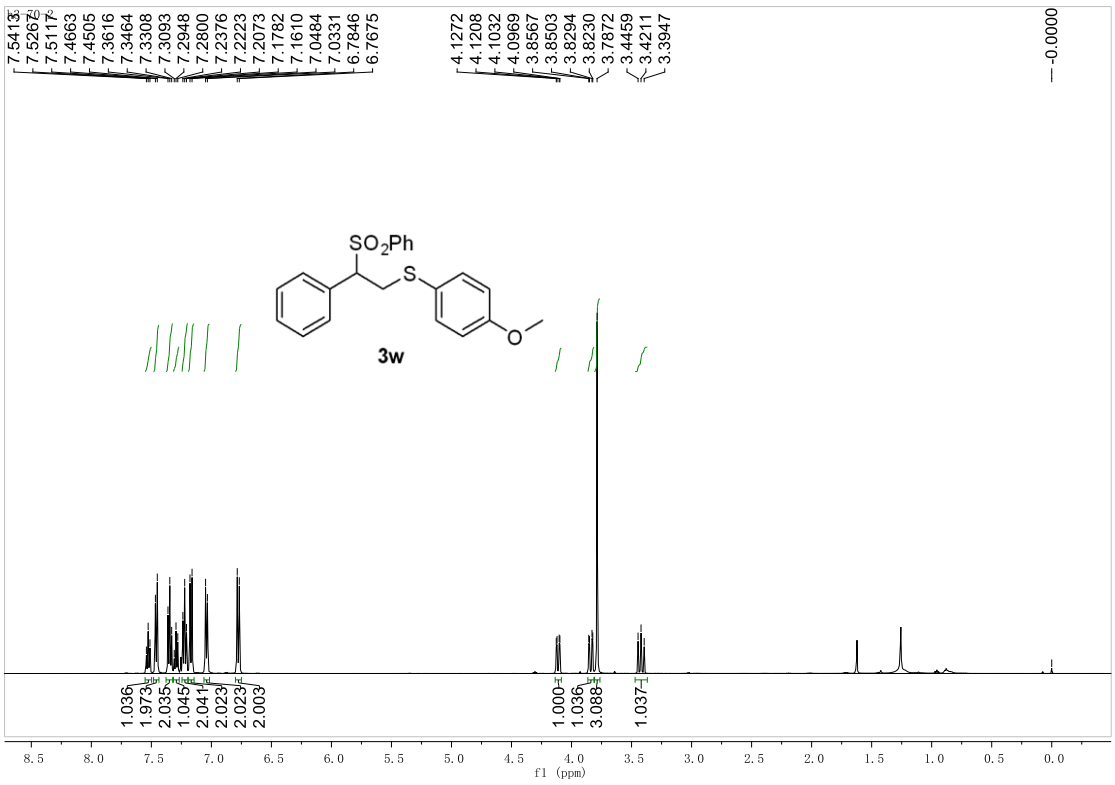


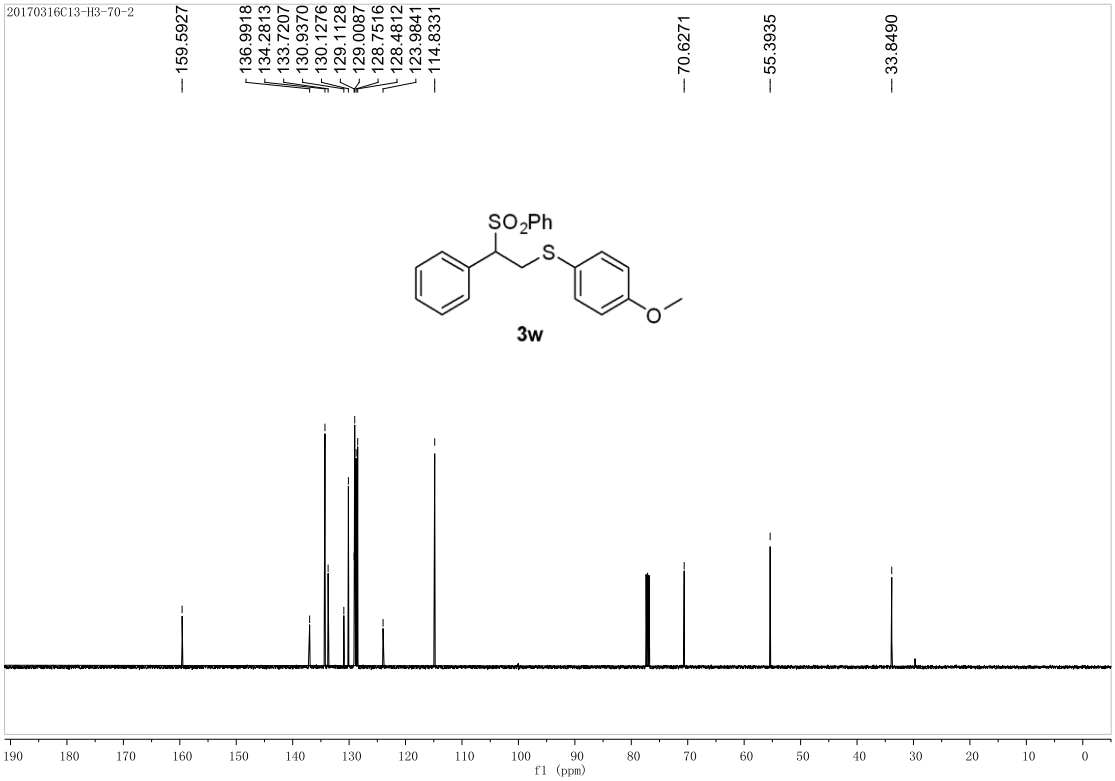


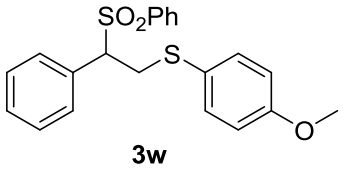
Chemical Formula: $C_{21}H_{20}O_2S_2$
Exact Mass: 368.0905
Molecular Weight: 368.5090
m/z: 368.0905 (100.0%), 369.0938 (22.7%), 370.0863 (9.0%), 370.0972 (2.5%), 371.0896 (2.1%), 369.0899 (1.6%)
Elemental Analysis: C, 68.45; H, 5.47; O, 8.68; S, 17.40



HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{21}H_{20}NaO_2S_2$ 391.0797; found 391.0794.



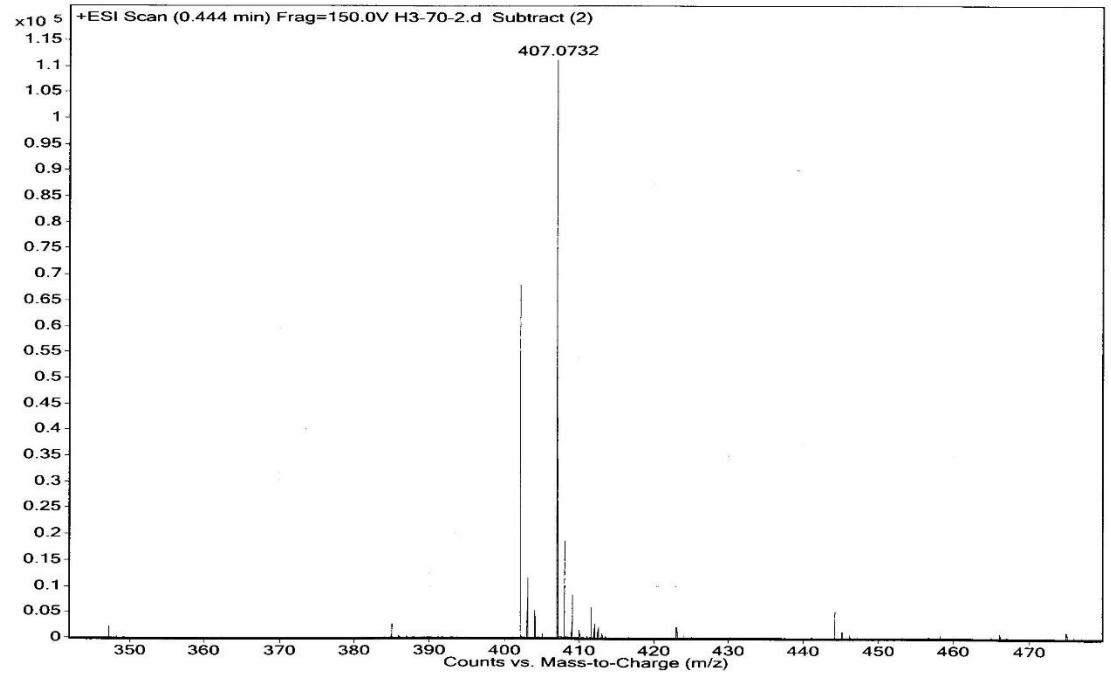




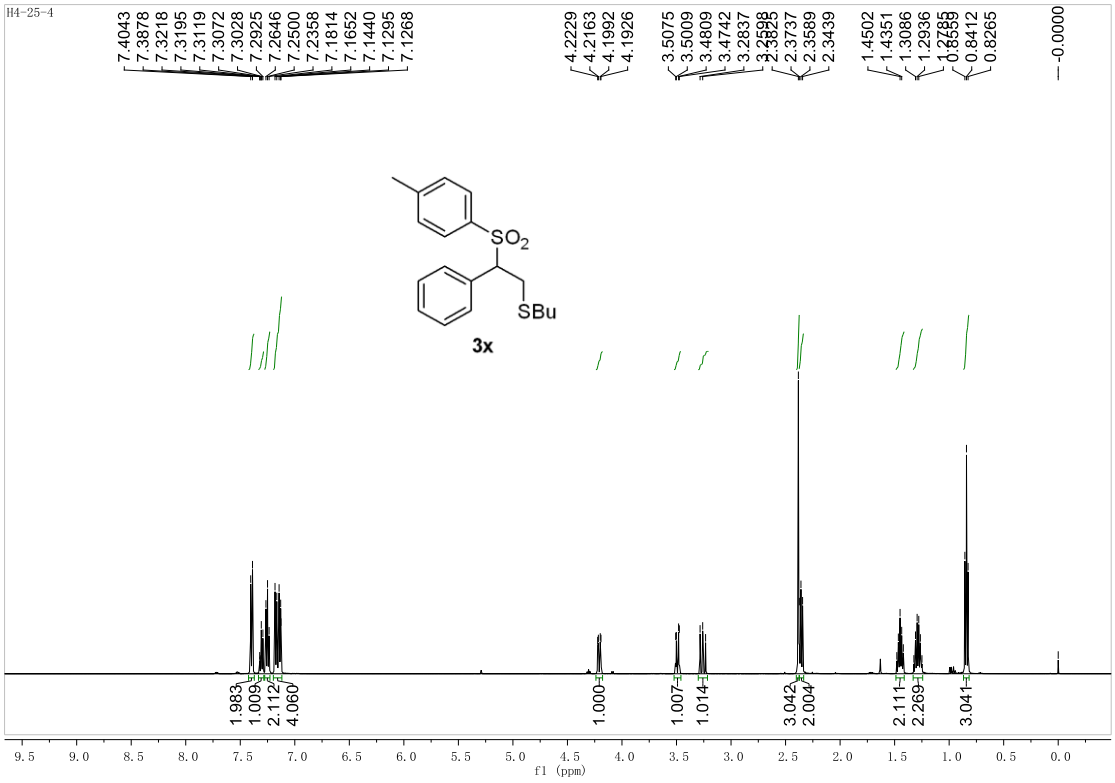
3w

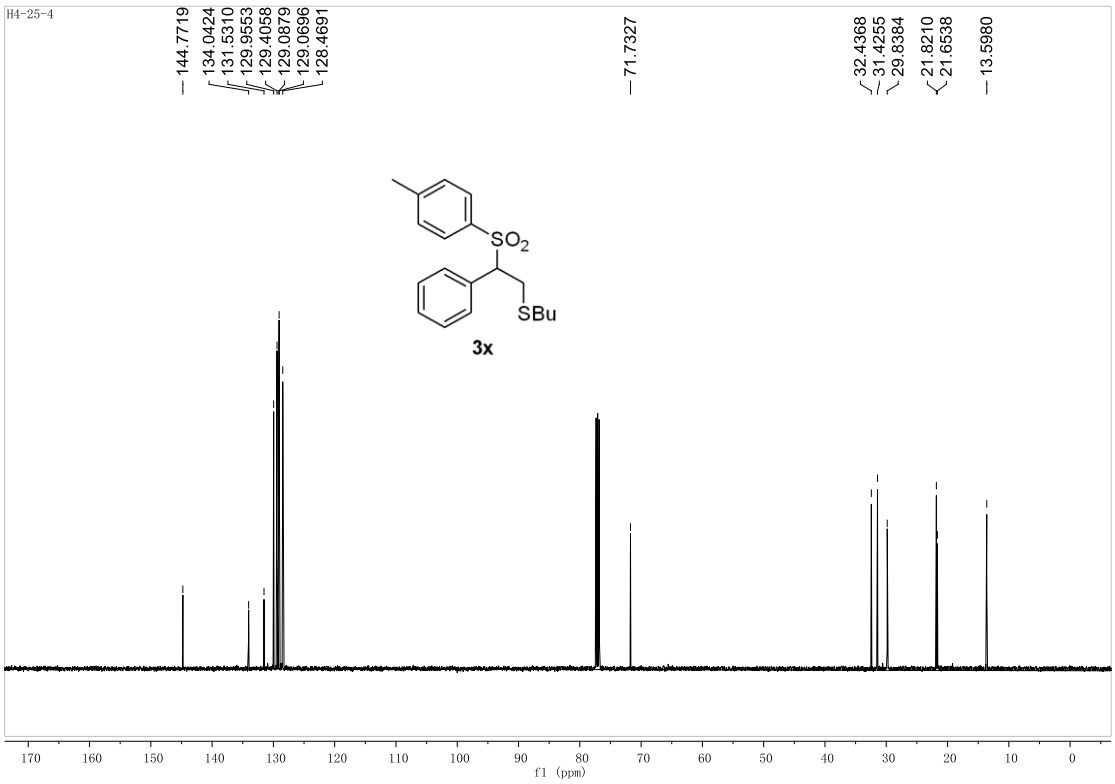
Chemical Formula: $C_{21}H_{20}O_3S_2$
Exact Mass: 384.0854
Molecular Weight: 384.5080
m/z: 384.0854 (100.0%), 385.0887 (22.7%), 386.0812 (9.0%), 386.0921 (2.5%), 387.0845 (2.1%), 385.0848 (1.6%)
Elemental Analysis: C, 65.60; H, 5.24; O, 12.48; S, 16.68

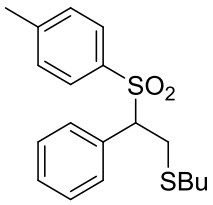
Sample Name	H3-70-2	**Position**	P1-E1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	H3-70-2.d	**ACQ Method**	0103.m	**Comment**		**Acquired Time**	3/24/2017 4:11:47



HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{21}H_{20}NaO_3S_2$ 407.0746; found 407.0732.

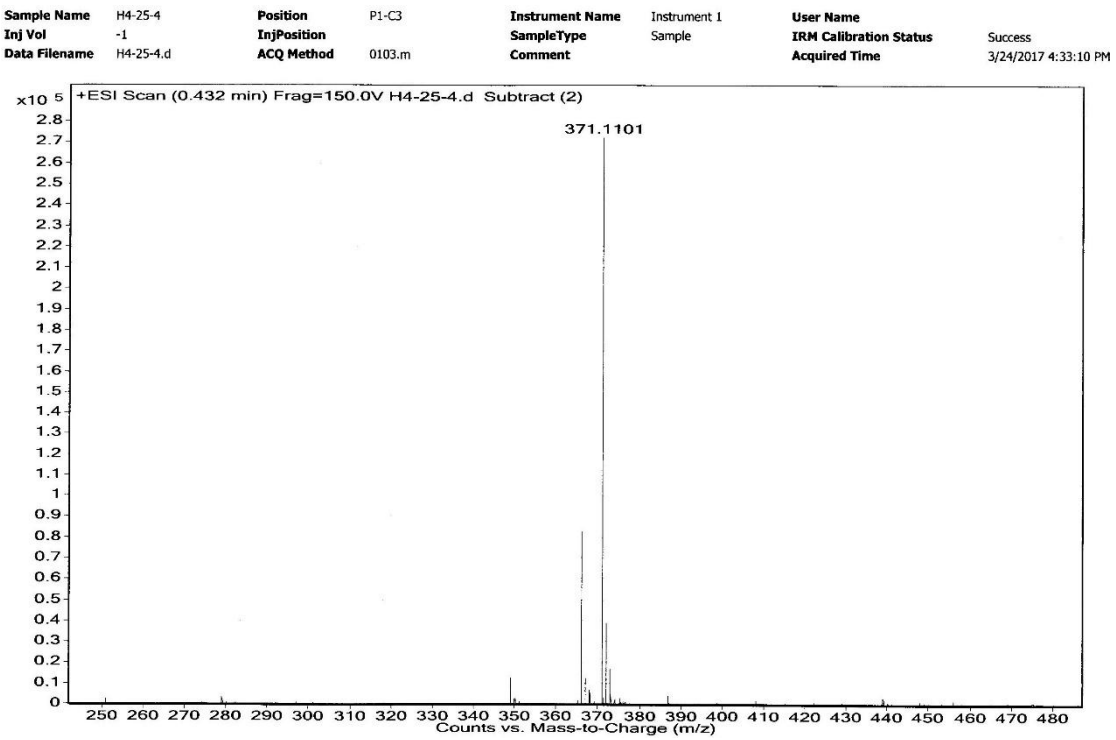




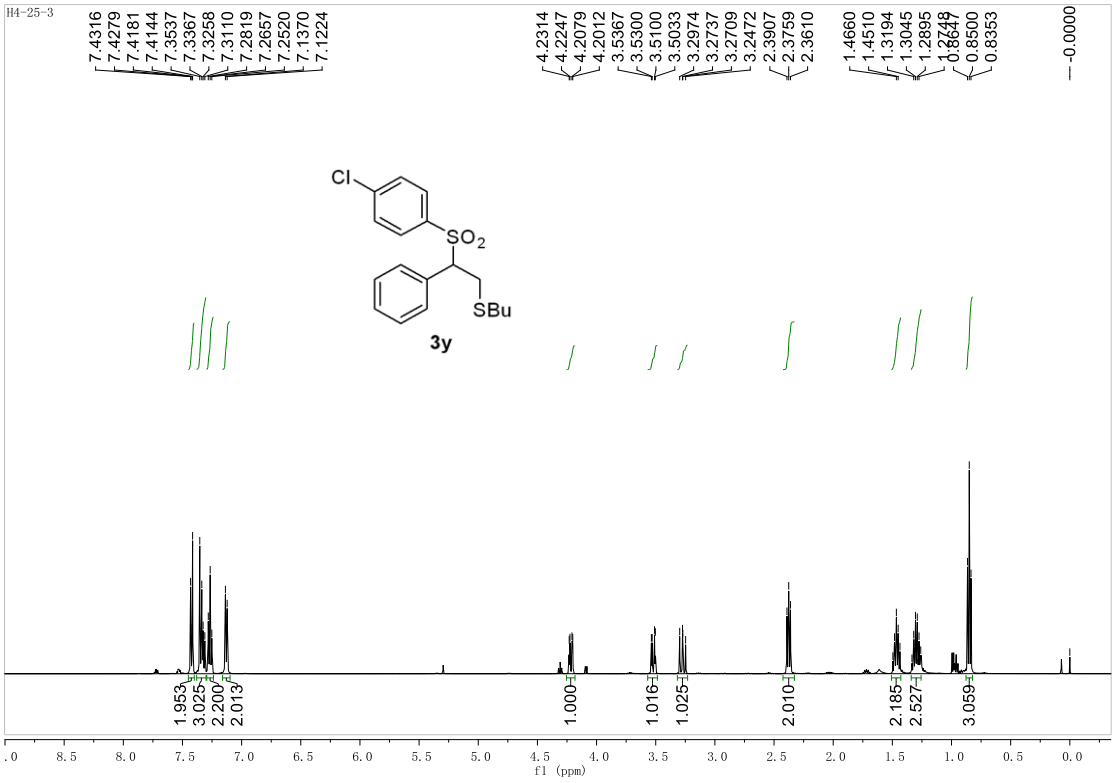


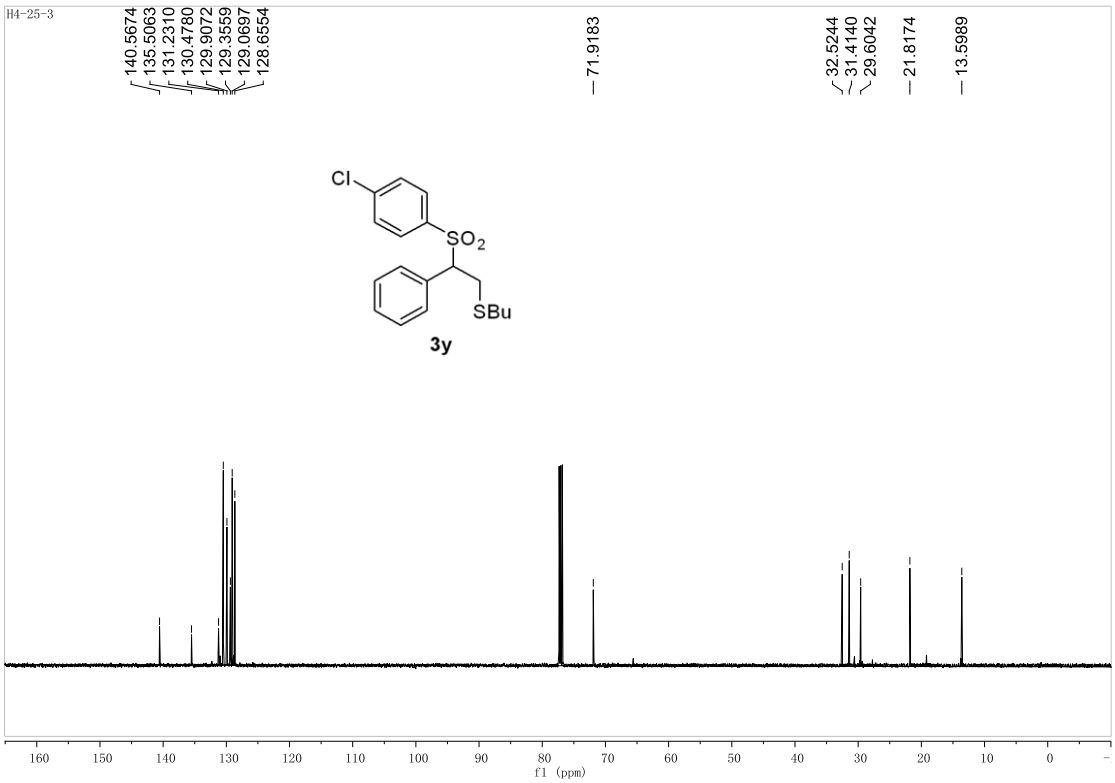
3x

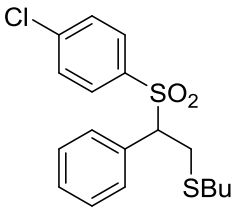
Chemical Formula: $C_{19}H_{24}O_2S_2$
Exact Mass: 348.1218
Molecular Weight: 348.5190
m/z: 348.1218 (100.0%), 349.1251 (20.5%), 350.1176 (9.0%), 350.1285 (2.0%), 351.1209 (1.9%), 349.1212 (1.6%)
Elemental Analysis: C, 65.48; H, 6.94; O, 9.18; S, 18.40



HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{19}H_{24}NaO_2S_2$ 371.1110; found 371.1101.



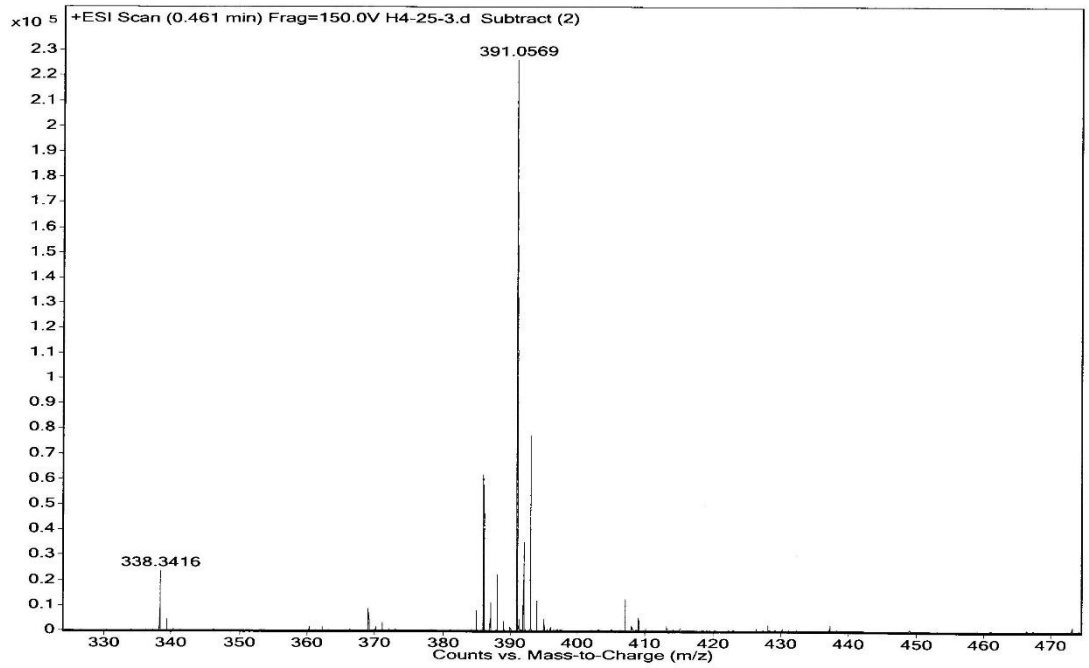




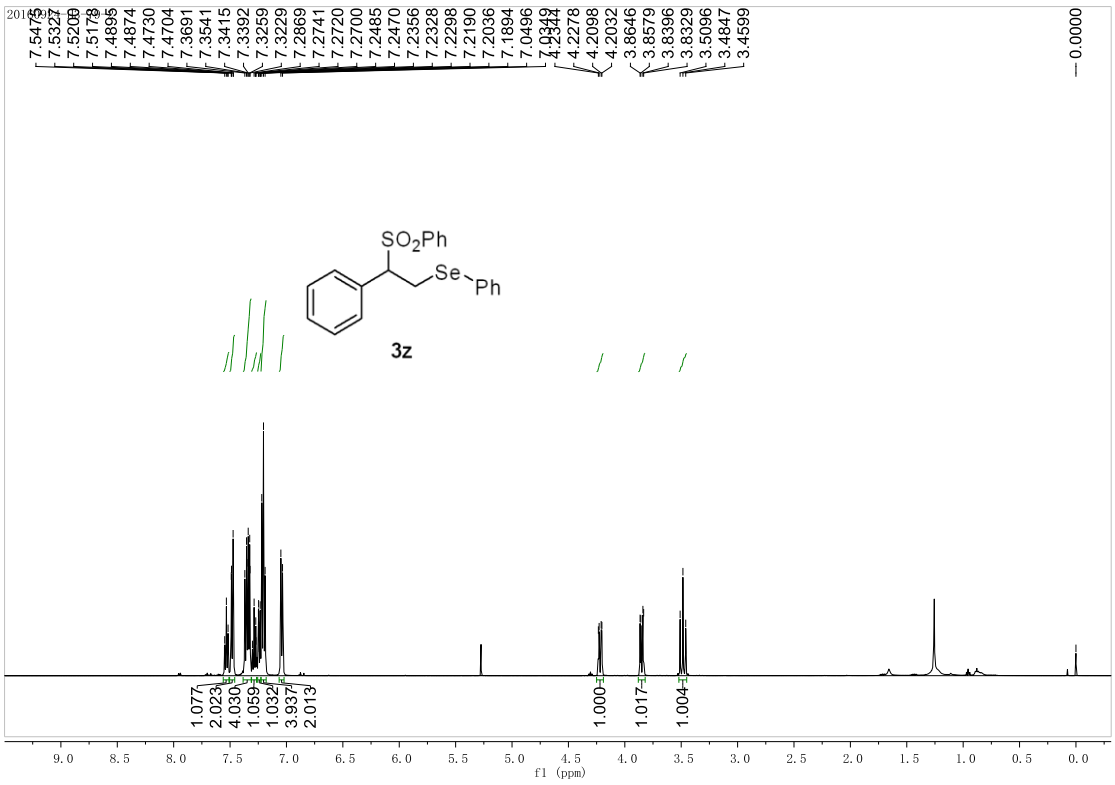
3y

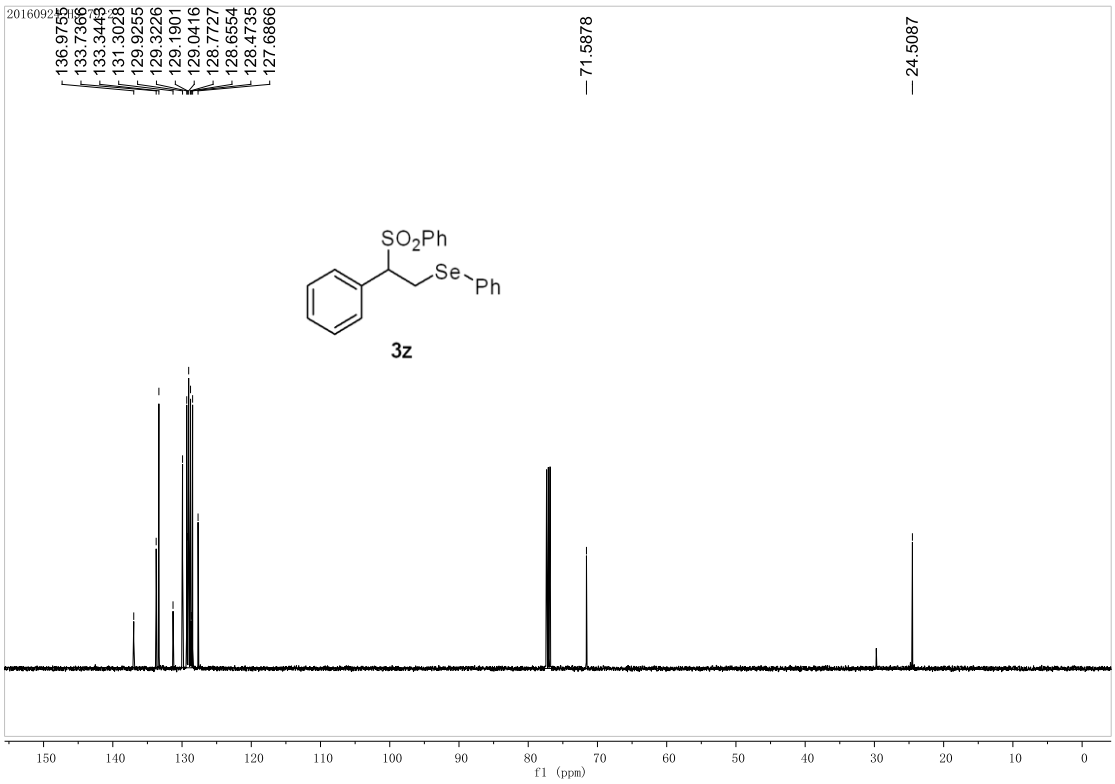
Chemical Formula: $C_{18}H_{21}ClO_2S_2$
Exact Mass: 368.0671
Molecular Weight: 368.9340
m/z: 368.0671 (100.0%), 370.0642 (32.0%), 369.0705 (19.5%), 370.0629 (9.0%), 371.0676 (6.2%), 372.0600 (2.9%), 370.0739 (1.8%), 371.0663 (1.8%), 369.0665 (1.6%)
Elemental Analysis: C, 58.60; H, 5.74; Cl, 9.61; O, 8.67; S, 17.38

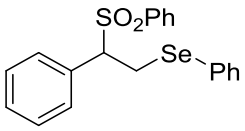
Sample Name	H4-25-3	**Position**	P1-B3	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	H4-25-3.d	**ACQ Method**	0103.m	**Comment**		**Acquired Time**	3/24/2017 4:31:02 PM



HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{18}H_{21}ClNaO_2S_2$ 391.0564; found 391.0569.

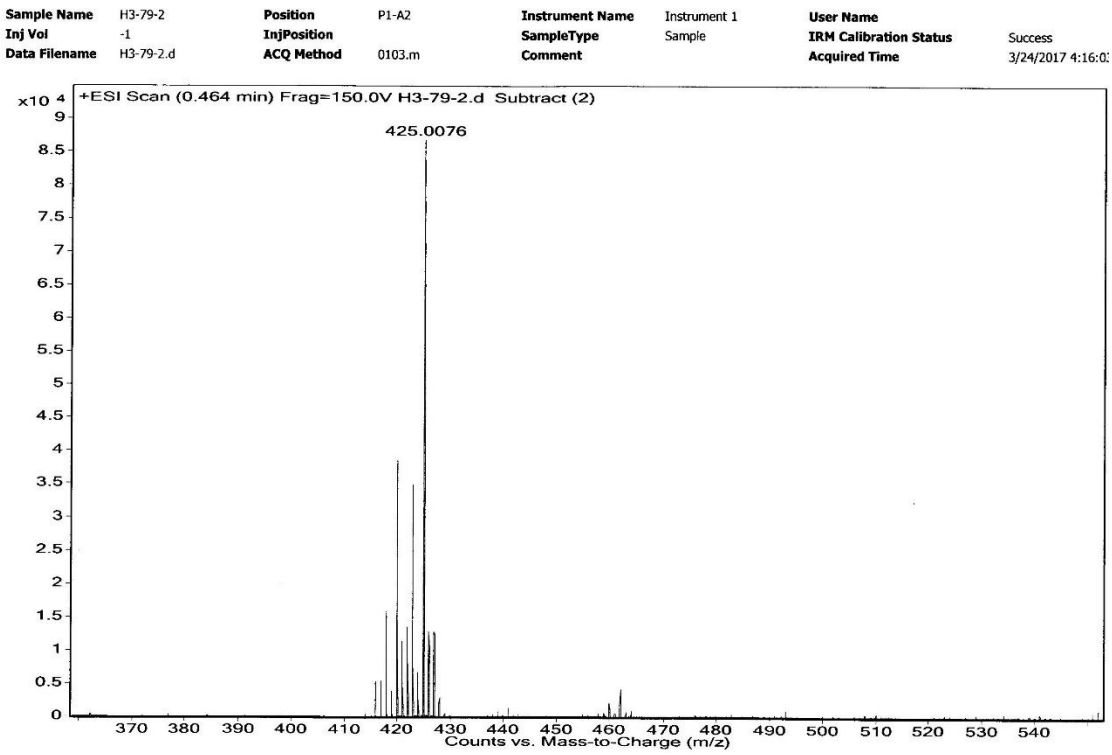




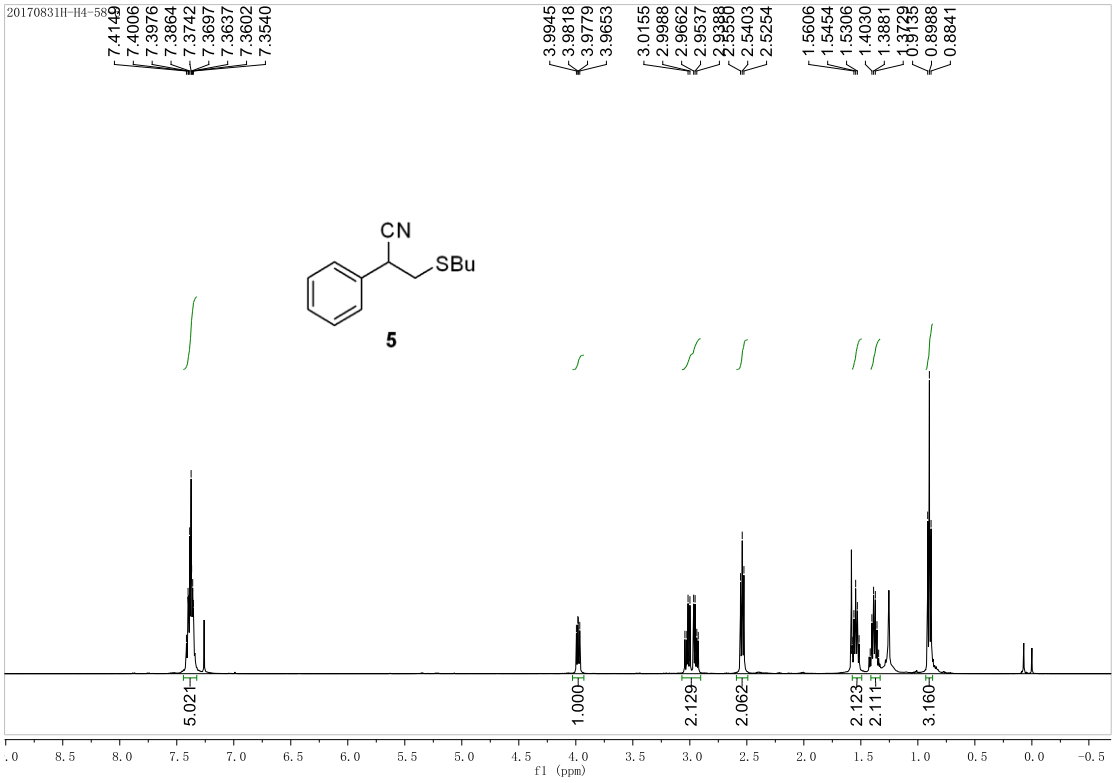


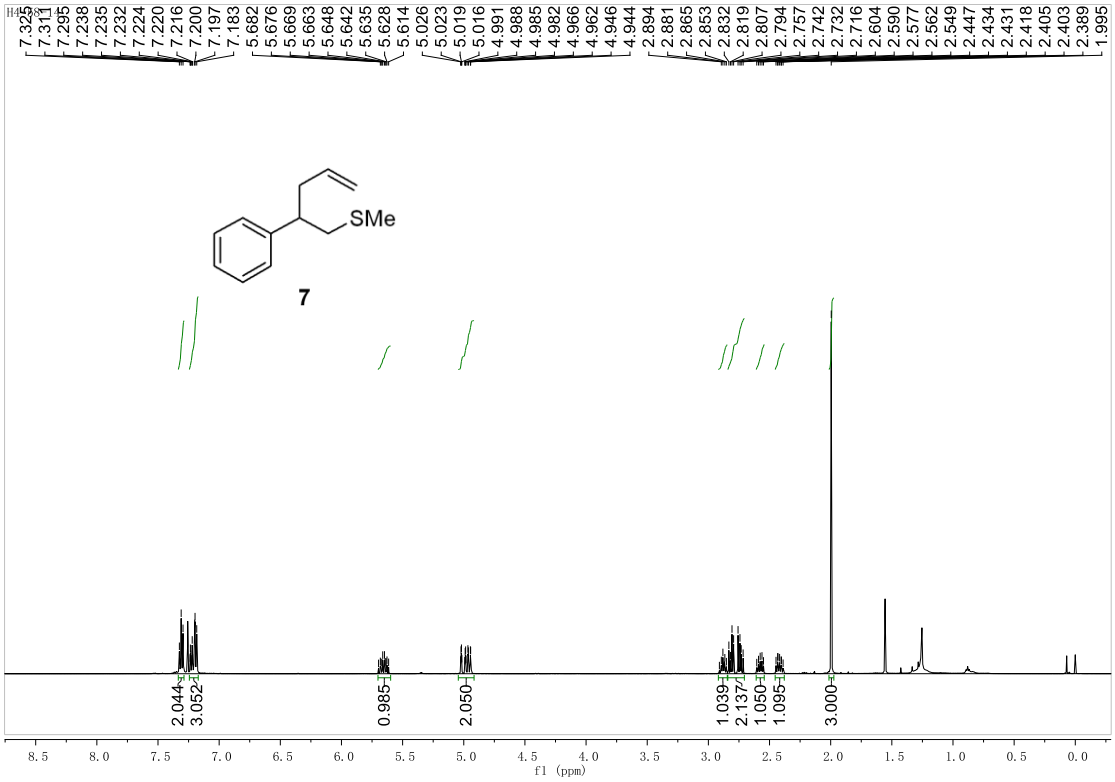
3z

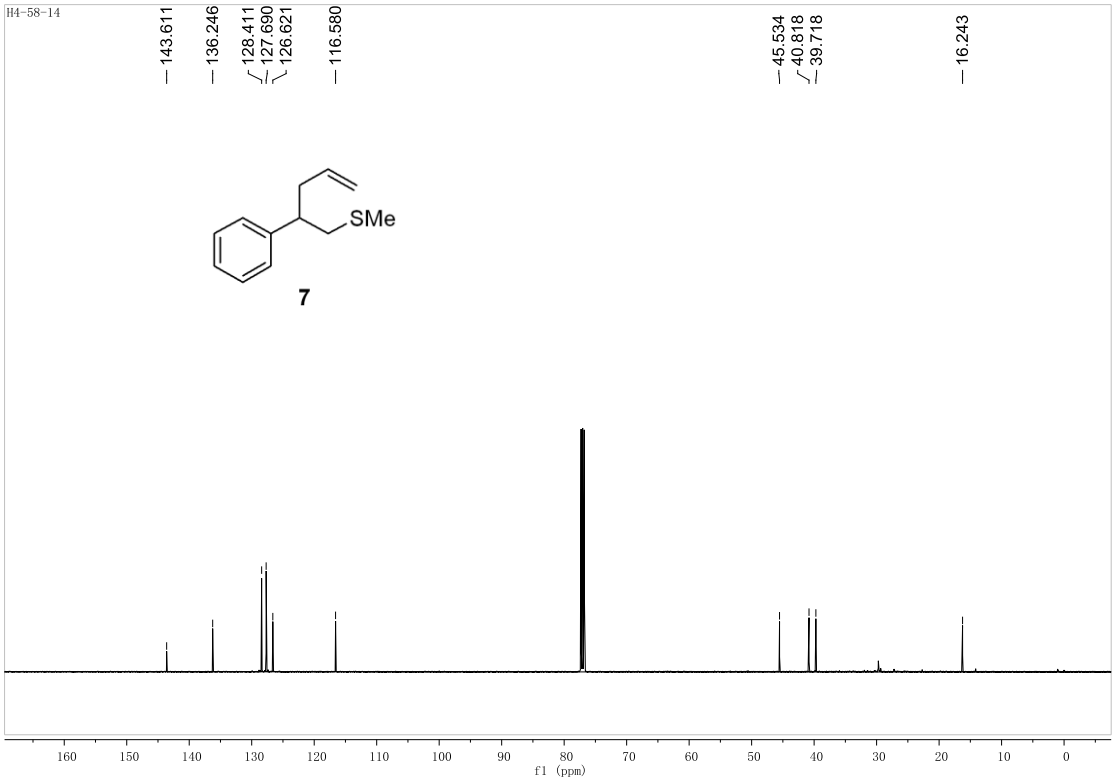
Chemical Formula: $C_{20}H_{18}O_2SSe$
Exact Mass: 402.0193
Molecular Weight: 401.3820
m/z: 402.0193 (100.0%), 400.0201 (47.9%), 403.0226 (21.6%), 398.0220 (18.9%), 404.0195 (17.6%), 399.0227 (15.4%), 401.0234 (10.4%), 404.0151 (4.5%), 399.0253 (4.1%), 405.0228 (3.8%), 400.0260 (3.3%), 404.0260 (2.2%), 402.0159 (2.2%), 396.0252 (1.8%), 402.0268 (1.1%)
Elemental Analysis: C, 59.85; H, 4.52; O, 7.97; S, 7.99; Se, 19.67

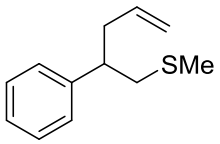


HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{20}H_{18}NaO_2SSe$ 425.0085; found 425.0076.




7.325
7.311
7.295
7.238
7.235
7.232
7.224
7.220
7.216
7.200
7.197
7.183
5.682
5.676
5.669
5.663
5.648
5.642
5.635
5.628
5.614
5.026
5.023
5.019
5.016
4.991
4.988
4.985
4.982
4.966
4.962
4.946
4.944
2.894
2.881
2.865
2.853
2.832
2.819
2.807
2.794
2.757
2.742
2.732
2.716
2.604
2.590
2.577
2.562
2.549
2.447
2.434
2.431
2.418
2.405
2.403
2.389
1.995
SMe
7
2.044
3.052
0.985
2.050
1.039
2.137
1.050
1.095
3.000
f1 (ppm)

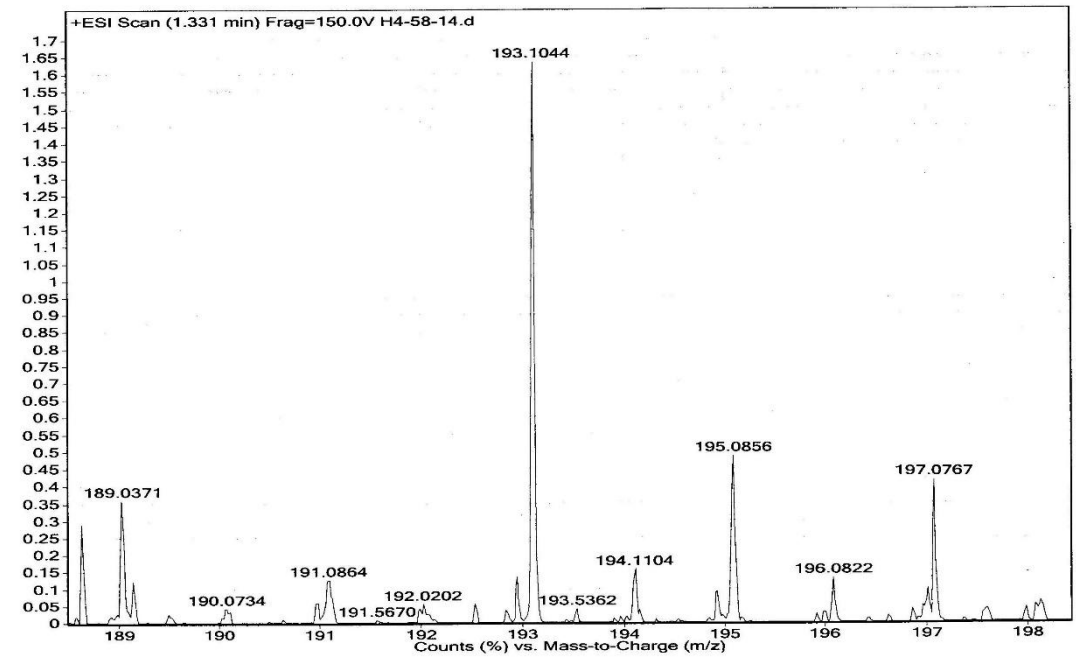

H4-58-14
143.611
136.246
128.411
127.690
126.621
116.580
45.534
40.818
39.718
16.243
SMe
7
f1 (ppm)



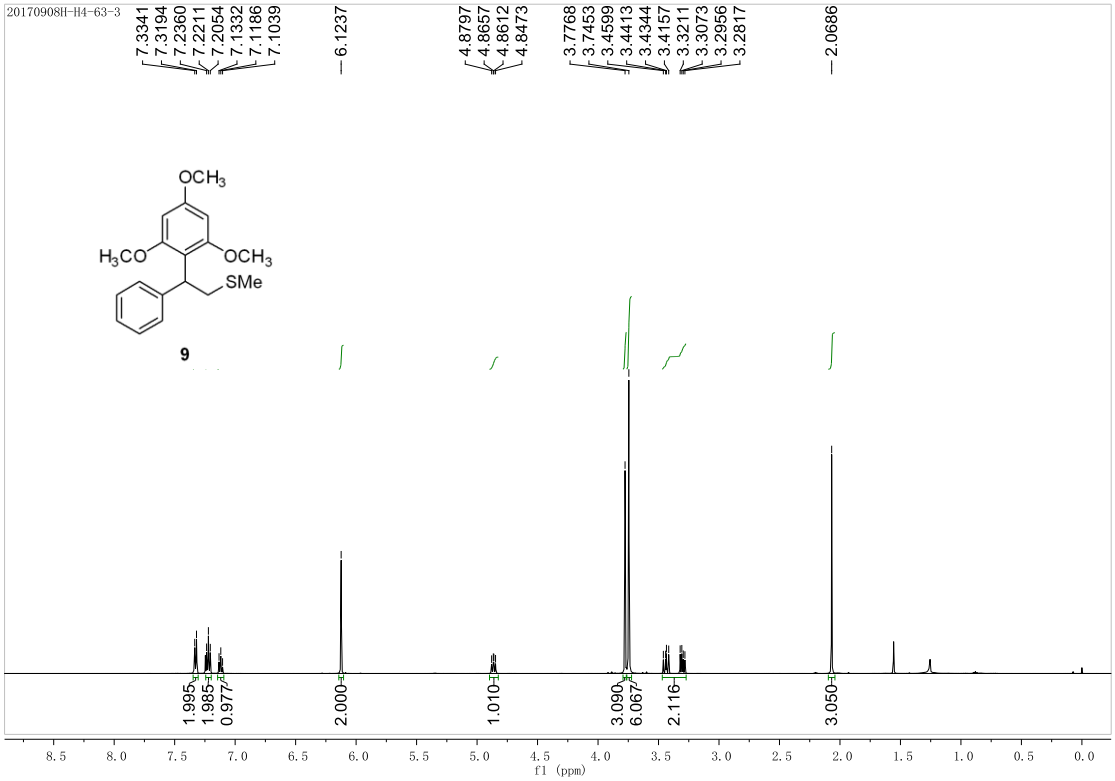
7

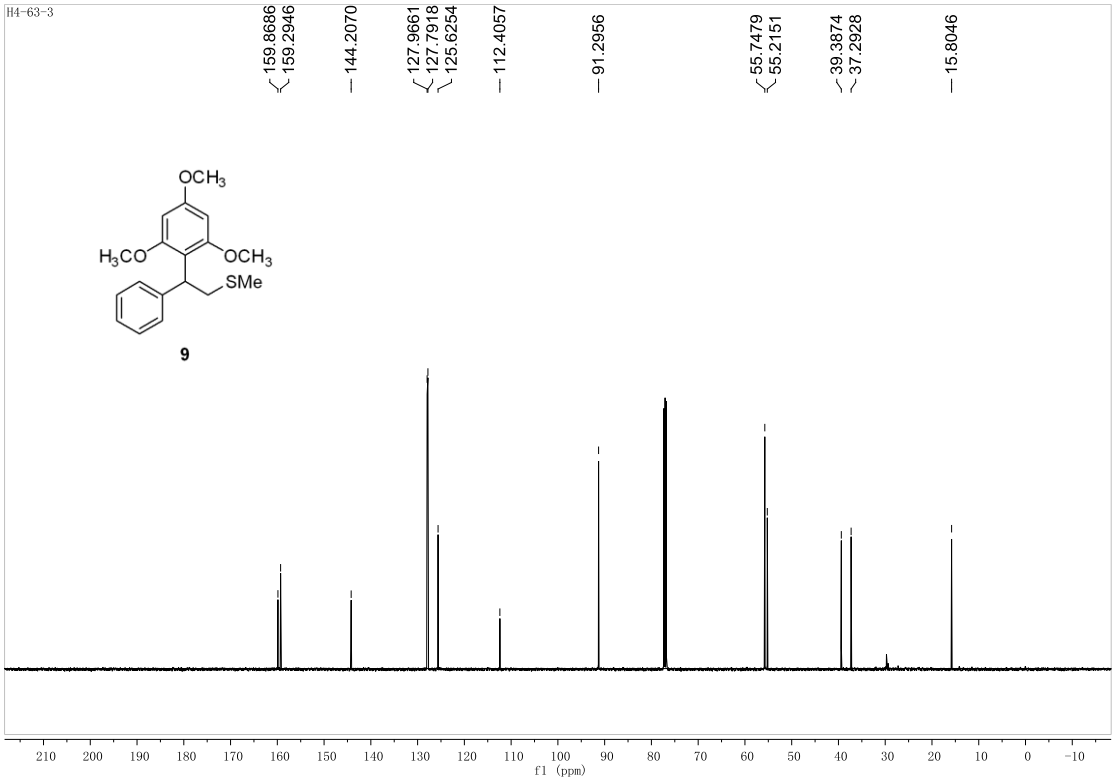
Chemical Formula: $C_{12}H_{16}S$
Exact Mass: 192.0973
Molecular Weight: 192.3200
m/z: 192.0973 (100.0%), 193.1006 (13.0%), 194.0931 (4.5%)
Elemental Analysis: C, 74.94; H, 8.39; S, 16.67

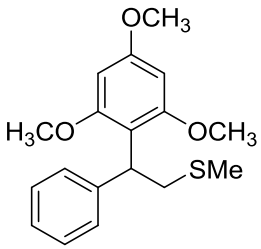
Sample Name	Unavailable	**Position**	Unavailable	**Instrument Name**	Unavailable	**User Name**	Unavailable
Inj Vol	Unavailable	**InjPosition**	Unavailable	**SampleType**	Unavailable	**IRM Calibration Status**	Success
Data Filename	H4-58-14.d	**ACQ Method**		**Comment**	Sample information is unavailable	**Acquired Time**	Unavailable



HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{12}H_{17}S$ 193.1045; found 193.1044.


20170908H-H4-63-3
7.3341
7.3194
7.2360
7.2211
7.2054
7.1332
7.1186
7.1039
6.1237
4.8797
4.8657
4.8612
4.8473
3.7768
3.7453
3.4599
3.4413
3.4344
3.4157
3.3211
3.3073
3.2956
3.2817
2.0686
OCH3
H3CO
OCH3
SMe
9
1.995
1.985
0.977
2.000
1.010
3.090
6.067
2.116
3.050
f1 (ppm)

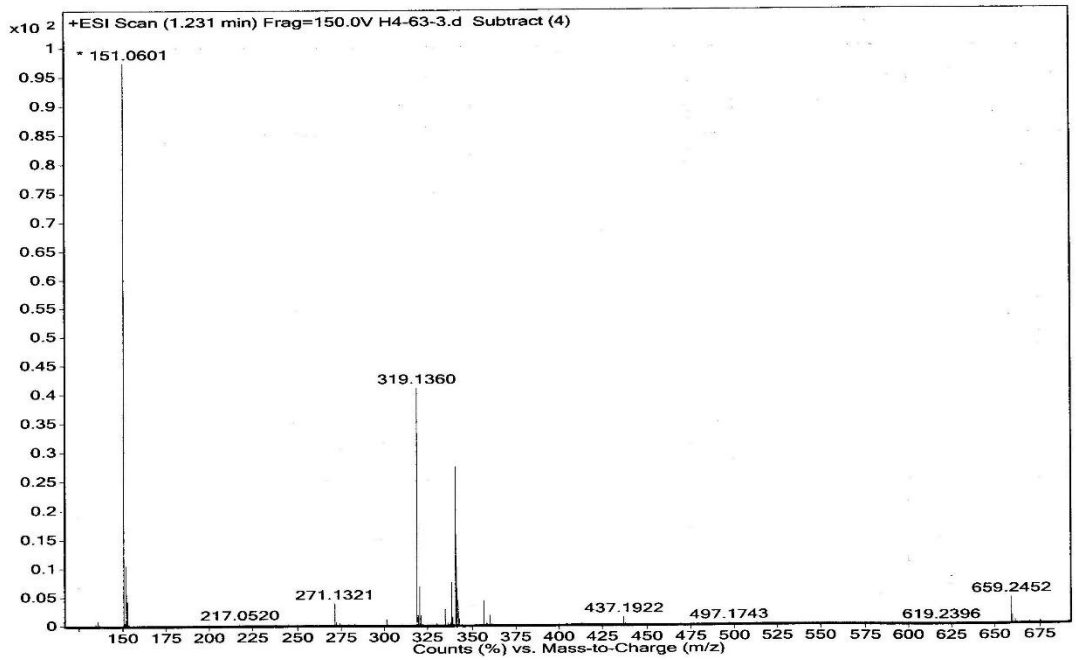

H4-63-3
159.8686
159.2946
144.2070
127.9661
127.7918
125.6254
112.4057
91.2956
55.7479
55.2151
39.3874
37.2928
15.8046
OCH3
H3CO
OCH3
SMe
9
f1 (ppm)



9

Chemical Formula: $C_{18}H_{22}O_3S$
Exact Mass: 318.1290
Molecular Weight: 318.4310
m/z: 318.1290 (100.0%), 319.1323 (19.5%), 320.1248 (4.5%), 320.1357 (1.8%)
Elemental Analysis: C, 67.89; H, 6.96; O, 15.07; S, 10.07

Sample Name	Unavailable	**Position**	Unavailable	**Instrument Name**	Unavailable	**User Name**	Unavailable
Inj Vol	Unavailable	**InjPosition**	Unavailable	**SampleType**	Unavailable	**IRM Calibration Status**	Success
Data Filename	H4-63-3.d	**ACQ Method**		**Comment**	Sample information is unavailable	**Acquired Time**	Unavailable



HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{18}H_{23}O_3S$ 319.1362; found 319.1360.