Electronic Supplementary Information for

Air Oxidative Radical Oxysulfurization of Alkynes Leading to α-Thioaldehydes

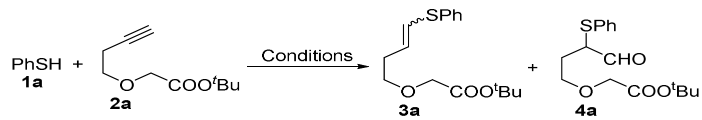
Shao-Fang Zhou,[a] Xiang-Qiang Pan,*[a] Zhi-Hao Zhou,[a] Adedamola Shoberu,[a] Pei-Zhi Zhang,[a] Jian-Ping Zou*[a,b]

[a] *Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry and Chemical Engineering, Soochow University, 199 Renai Street, Suzhou, Jiangsu 215123, China.* jpzou@suda.edu.cn; panxq@suda.edu.cn

[b] *Key Laboratory of Synthetic Chemistry of Natural Substances, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China.*

Table of contents

SI-1. Optimization of the reaction conditions in detail

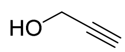


Entry	Solvent	Ratio (**1a**:**2a**)	Temp (℃)	Time (h)	Yield(%) (**3a**)/(***Z*** and ***E***)[a]	Yield(%) (**4a**)[a]
1	DMF	2:1	25	24	37	0
2	Toluene	2:1	25	24	2.2	0
3	CH_2Cl_2	2:1	25	24	29	0
4	CH_3CN	2:1	25	24	0	0
5	^{t}BuOH	2:1	25	24	11	25
6	1,4-Dioxane	2:1	25	24	17	28
7	THF	2:1	25	24	15	29
8	1,2-dimethoxyethane	2:1	25	24	14	21
9[b]	DMF	2:1	25	24	30	0
10[b]	THF	2:1	25	24	20	38
11[c]	THF	2:1	25	24	0	0
12[b]	THF	0.5:1	25	24	14	0
13[b]	THF	1:1	25	24	34	5
14[b]	THF	1.5:1	25	24	16	31
15[b]	THF	2.5:1	25	24	20	40
16[b]	THF	3:1	25	24	32	31
17[b,d]	THF	2:1	25	1	0	0
18[b,d]	THF	2:1	25	4	29	0
19[b,d]	THF	2:1	25	8	42	0
20[b,d]	THF	2:1	25	12	35	22
21[b,d]	THF	2:1	25	24	20	45
22[e]	DMF	2:1	25	24	68	0
23[b,d,e]	THF	2:1	25	24	25	75
24[b,d,e]	THF	2:1	25	48	2	98
25[b,d,e]	THF	2:1	25	72	9	90
26[b,e]	THF	2:1	0	48	0	0
27[b,e]	THF	2:1	13	48	27	0
28[b,e]	THF	2:1	25	48	0	77
29[b,e]	THF	2:1	40	48	70	25
30[b,e]	THF	2:1	60	48	86	1.4
31[d,e,f]	THF	2:1	25	48	12	70
32[b,d,g]	THF	2:1	25	48	34	0

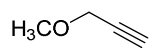
[a]Isolated yield. [b]Addition of 5% mol H_2O (1 μL). [c]Anhydrous THF. [d]Gas chromatography yield. [e]Addition of 0.5% mol TBHP (1 μL). [f]Addition of 4 μL H_2O. [g]Addition of 5% mol TBHP (10 μL).

The discussion of the reactions of 3-hydroxypropyne, *α*-methoxypropyne and *α-tert*-butoxy-propyne with thiophenol

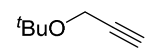
The reaction of 3-hydroxypropyne with thiophenol was complicated**.** It may be attributed to the α-hydroxyl group can activate the C≡C triple bond thus leading to complicated mixtures. To support this, reactions of substrates such as α-methoxypropyne and α-*tert*-butoxypropyne were carried out and unsurprisingly, similar results were obtained. In the case of 5-hydroxypentyne (**2o**), the hydroxy group is farther and could not activate the C≡C triple bond, instead directing the reaction to form selectively alkenylsulfide.



3-hydroxypropyne

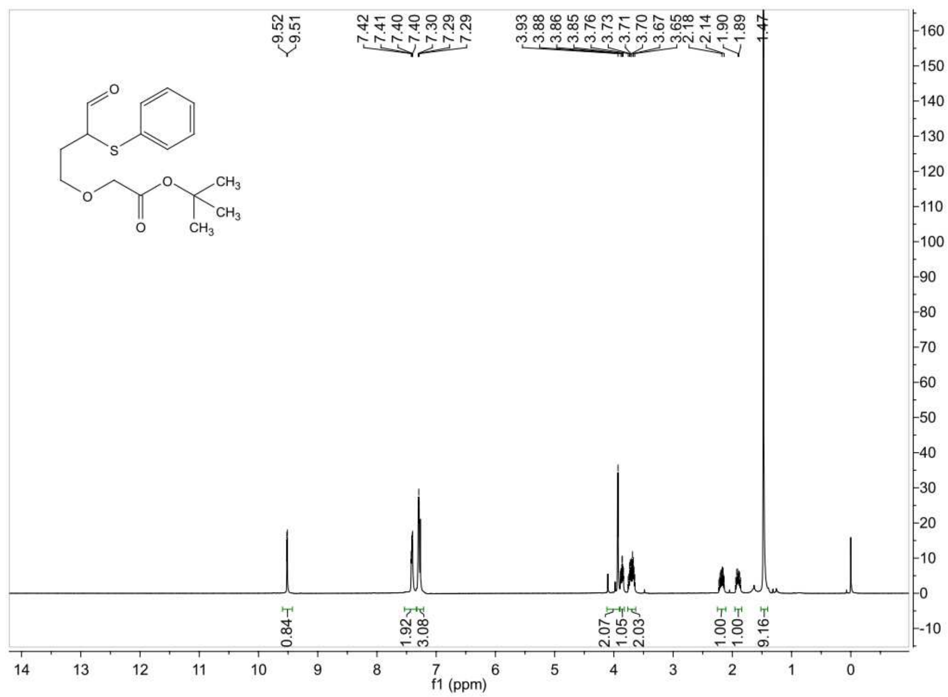


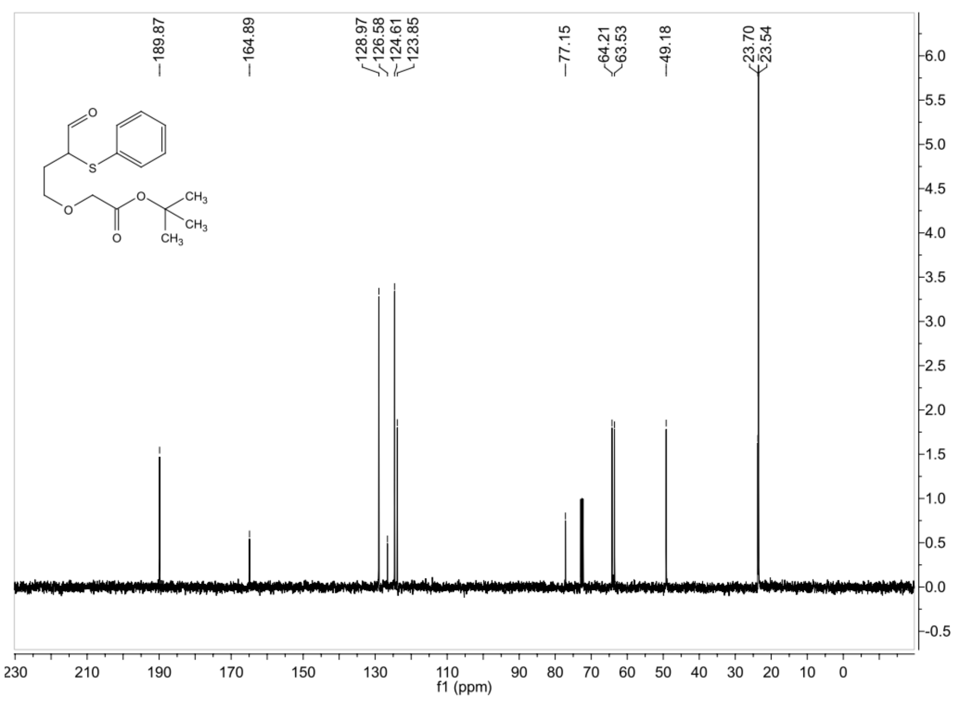
α-methoxypropyne



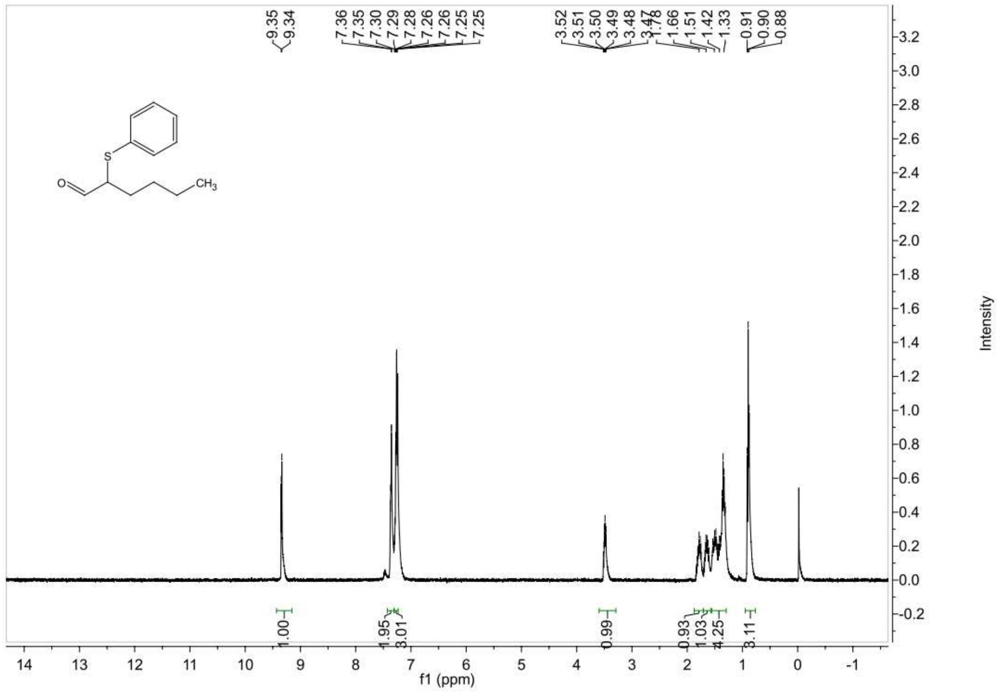
α-tert-butoxypropyne

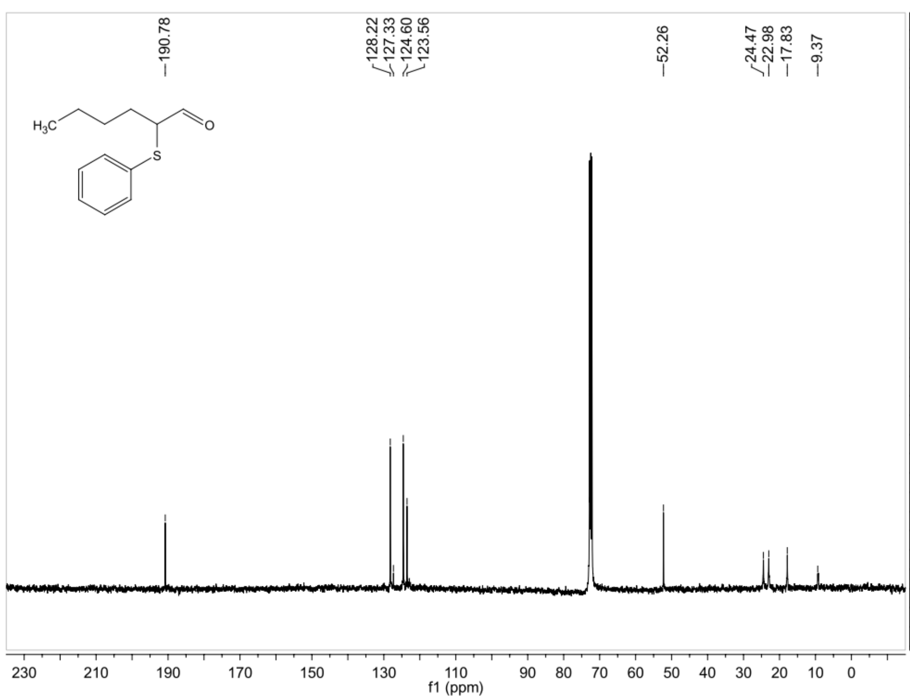
Compound 4a


9.52
9.51
7.42
7.41
7.40
7.40
7.30
7.29
7.29
3.93
3.88
3.86
3.85
3.76
3.73
3.71
3.70
3.67
3.65
2.18
2.14
1.90
1.89
1.47
0.84
1.92
3.08
2.07
1.05
2.03
1.00
1.00
9.16
f1 (ppm)

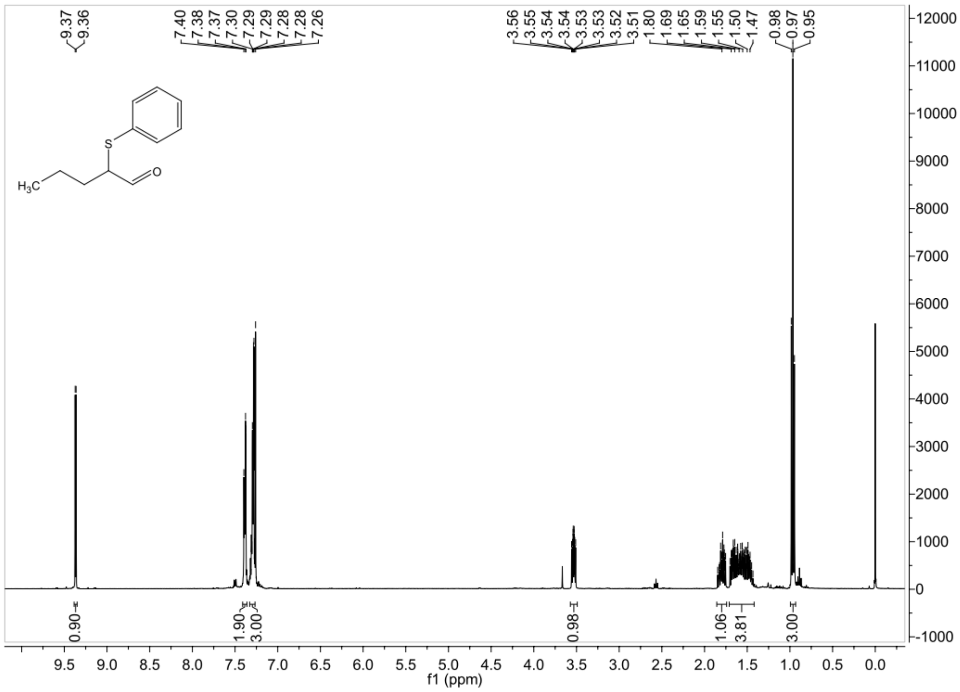

189.87
164.89
128.97
126.58
124.61
123.85
77.15
64.21
63.53
49.18
23.70
23.54
f1 (ppm)

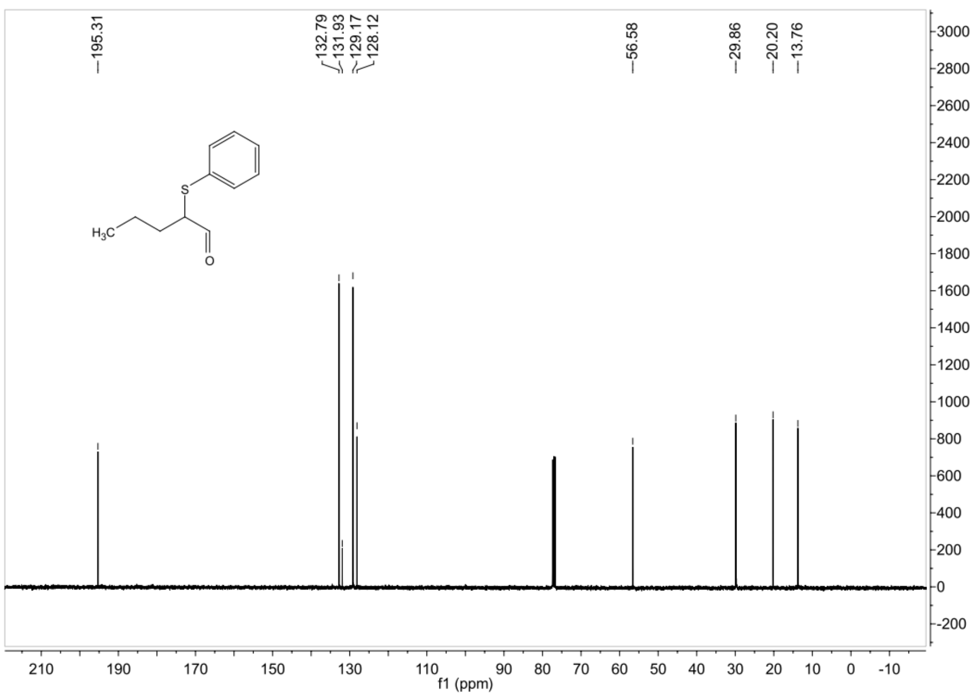
Compound 4b



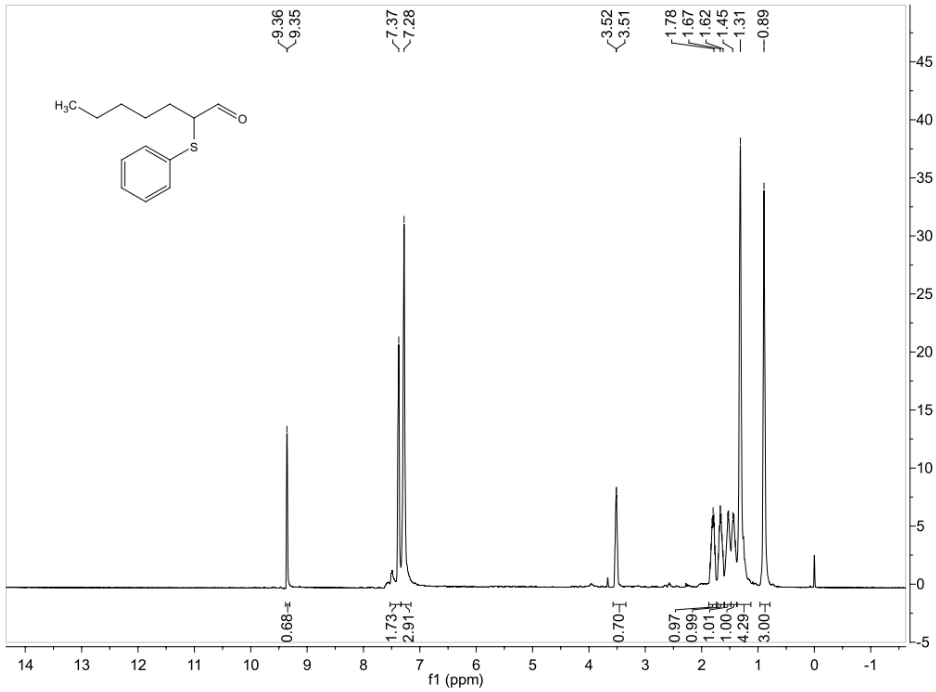


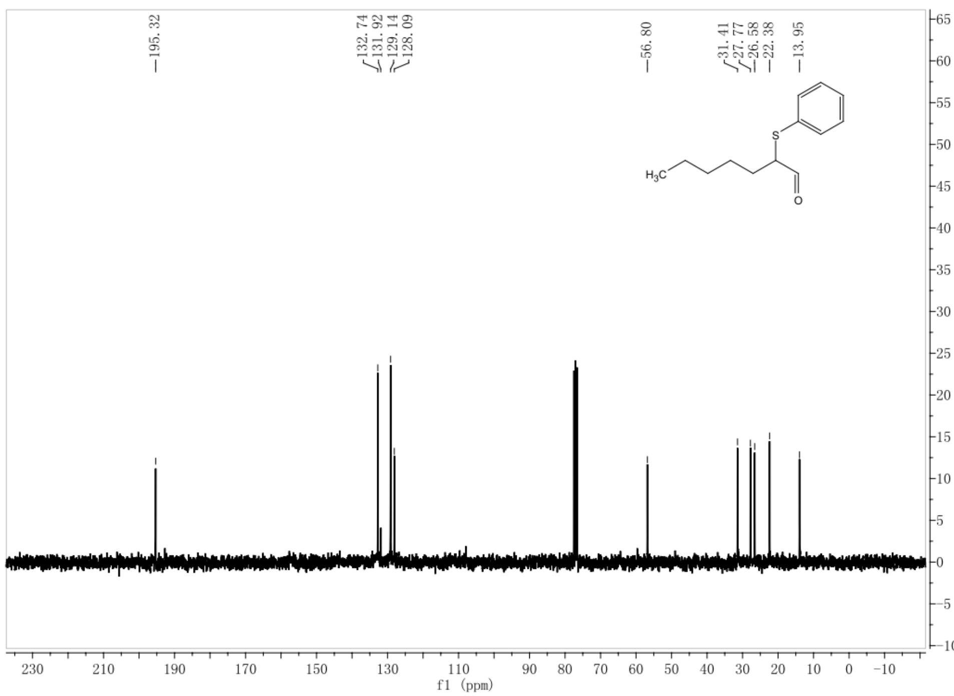
Compound 4c



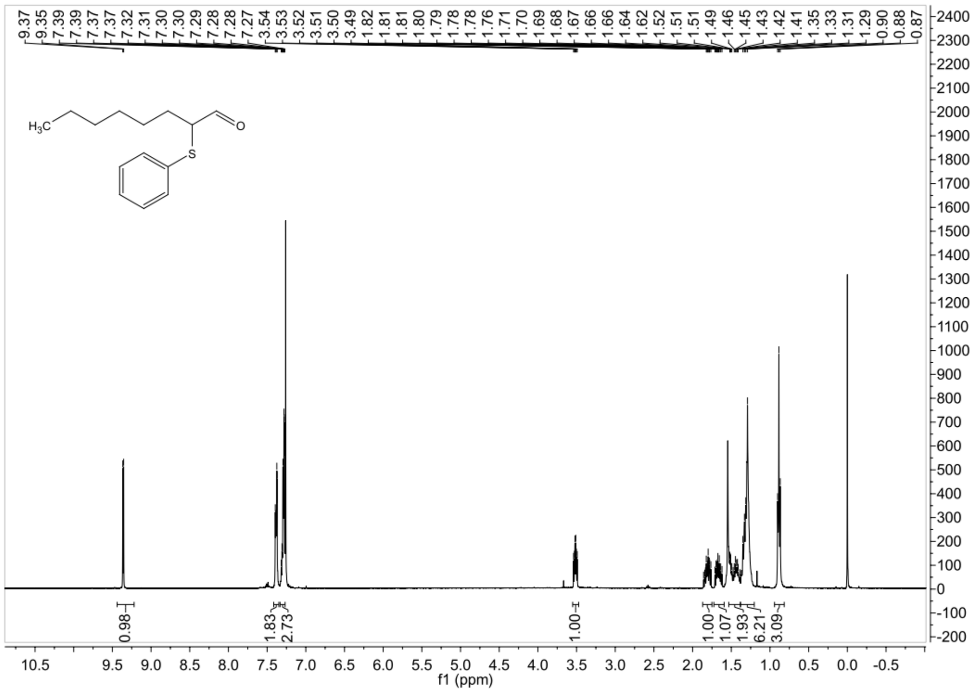


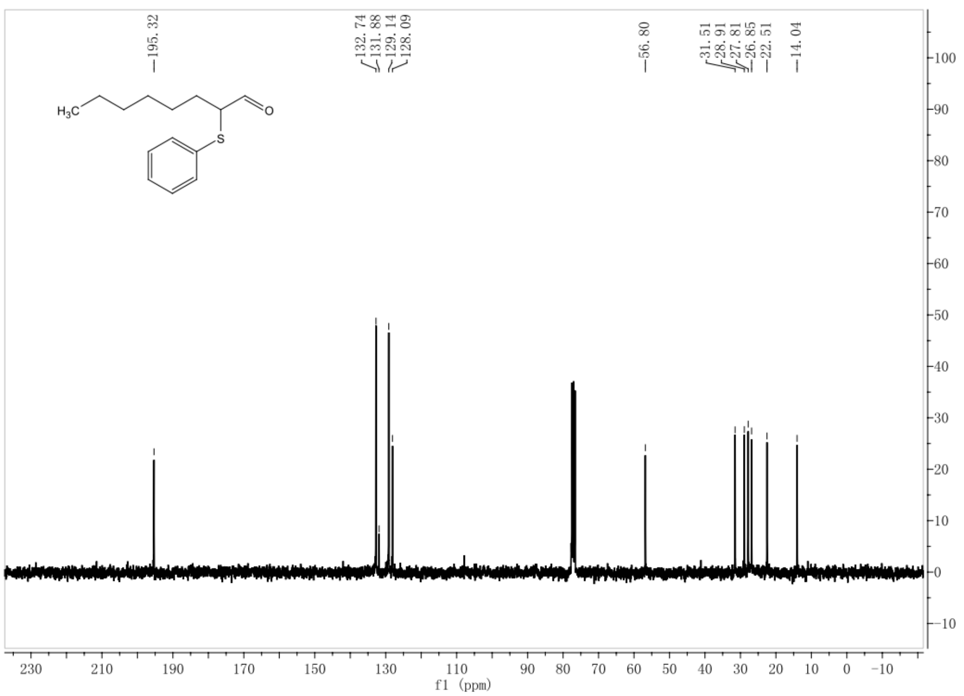
Compound 4d



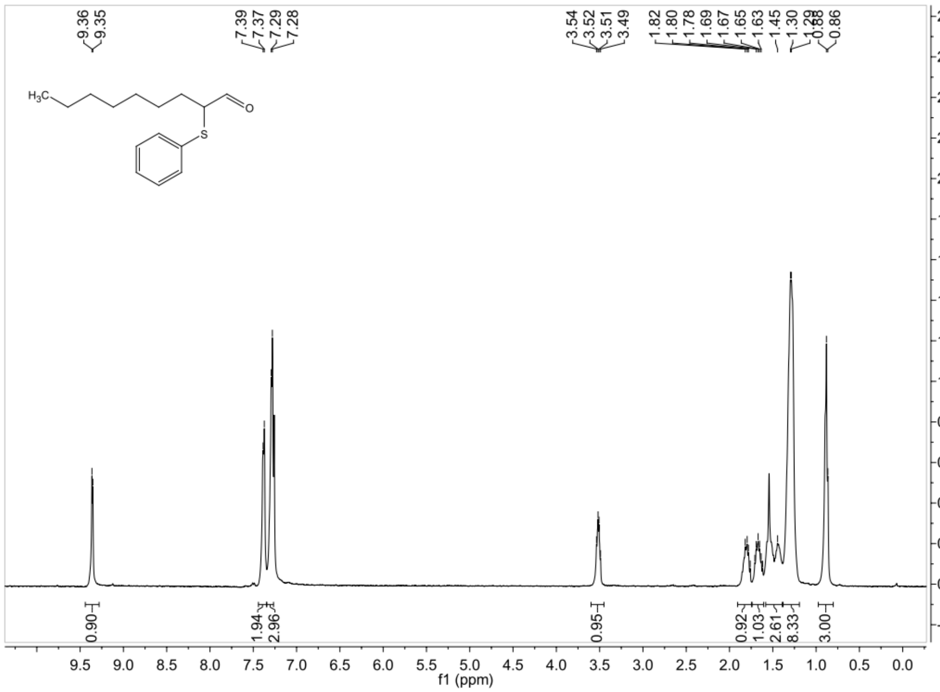


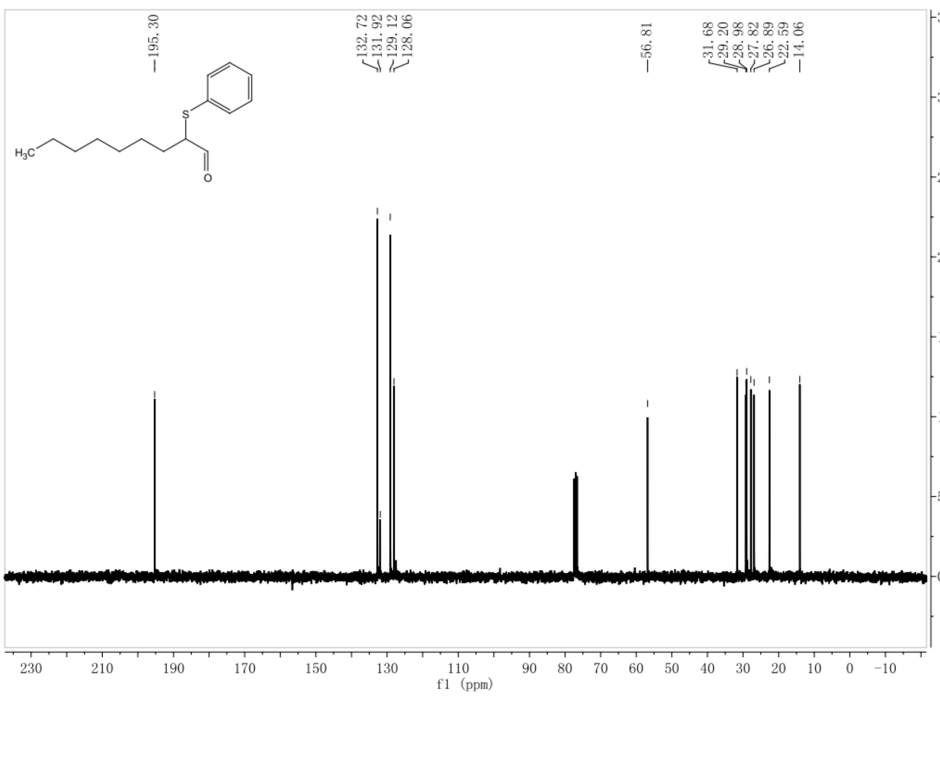
Compound 4e



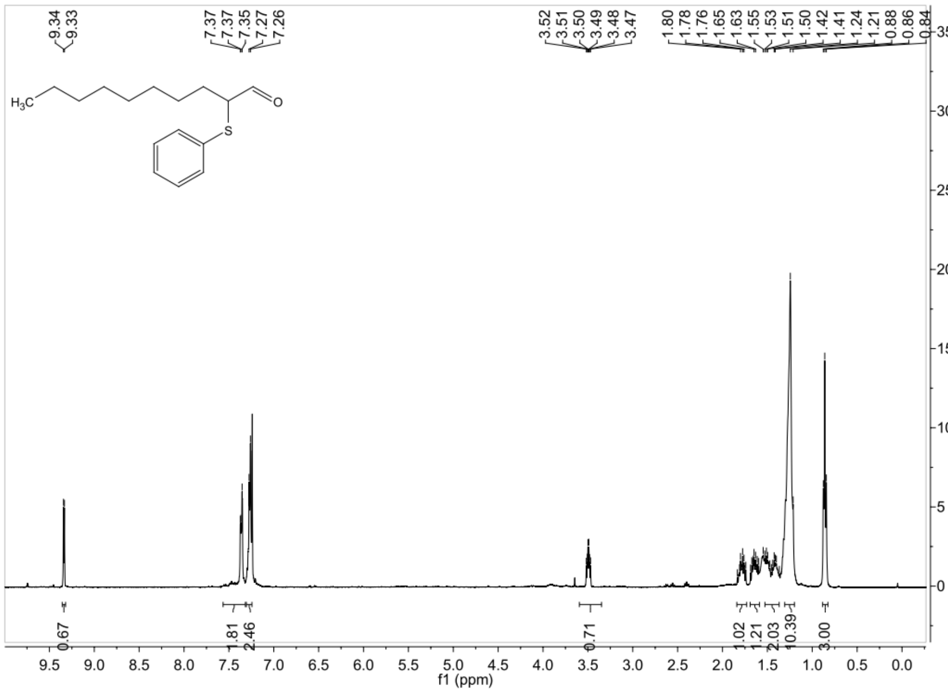


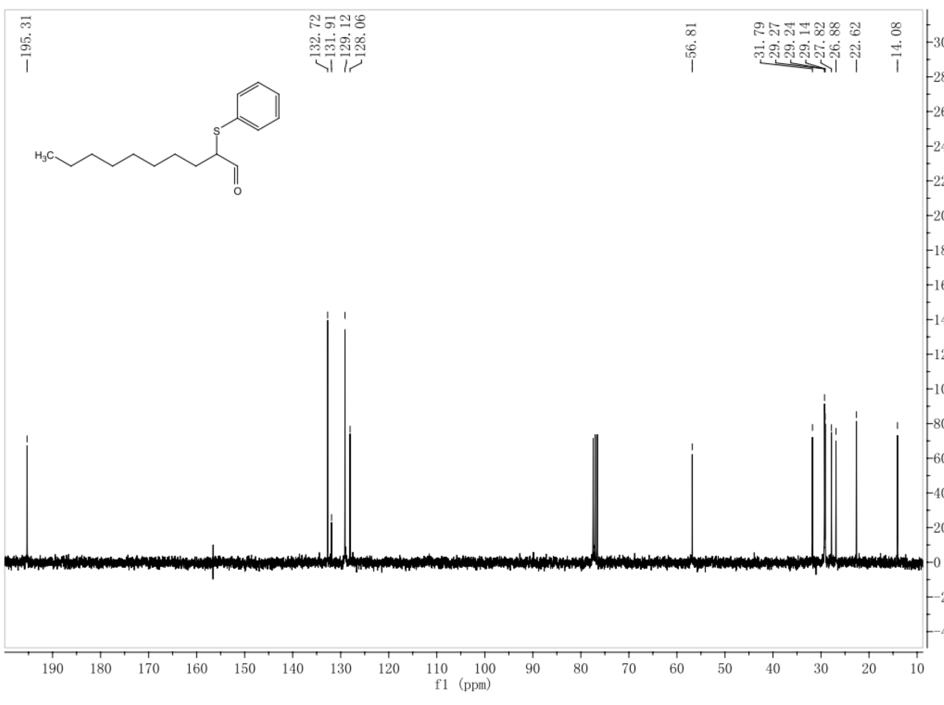
Compound 4f


9.36
9.35
7.39
7.37
7.29
7.28
3.54
3.52
3.51
3.49
1.82
1.80
1.78
1.69
1.67
1.65
1.63
1.45
1.30
0.88
0.86
H_3C
O
S
0.90
1.94
2.96
0.95
0.92
1.03
2.61
8.33
3.00
f1 (ppm)

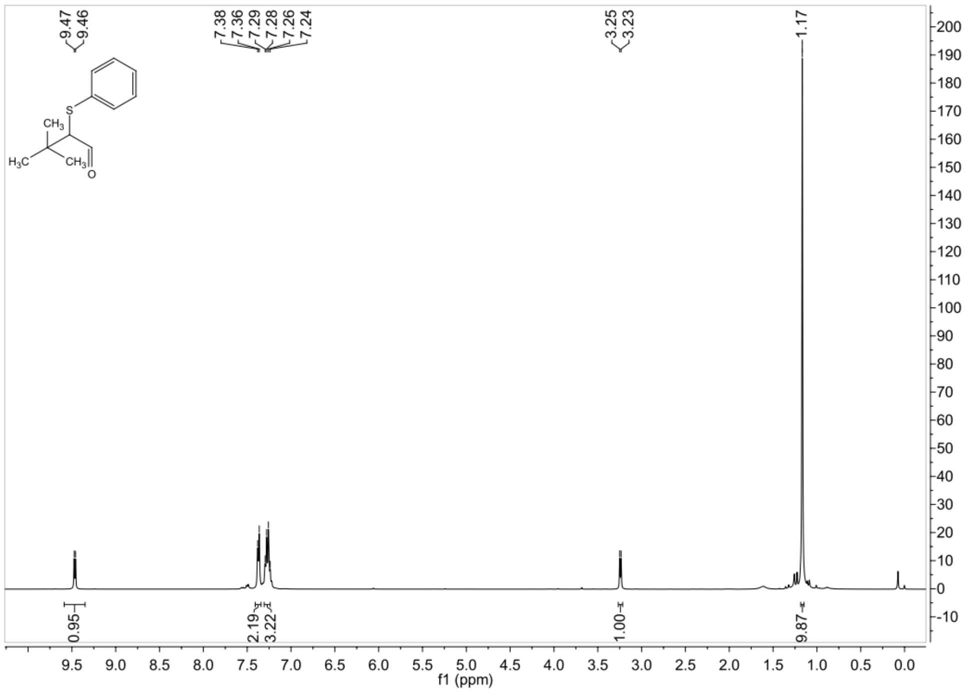

195.30
132.72
131.92
129.12
128.06
56.81
31.68
29.20
28.98
27.82
26.89
22.59
14.06
H_3C
S
O
f1 (ppm)

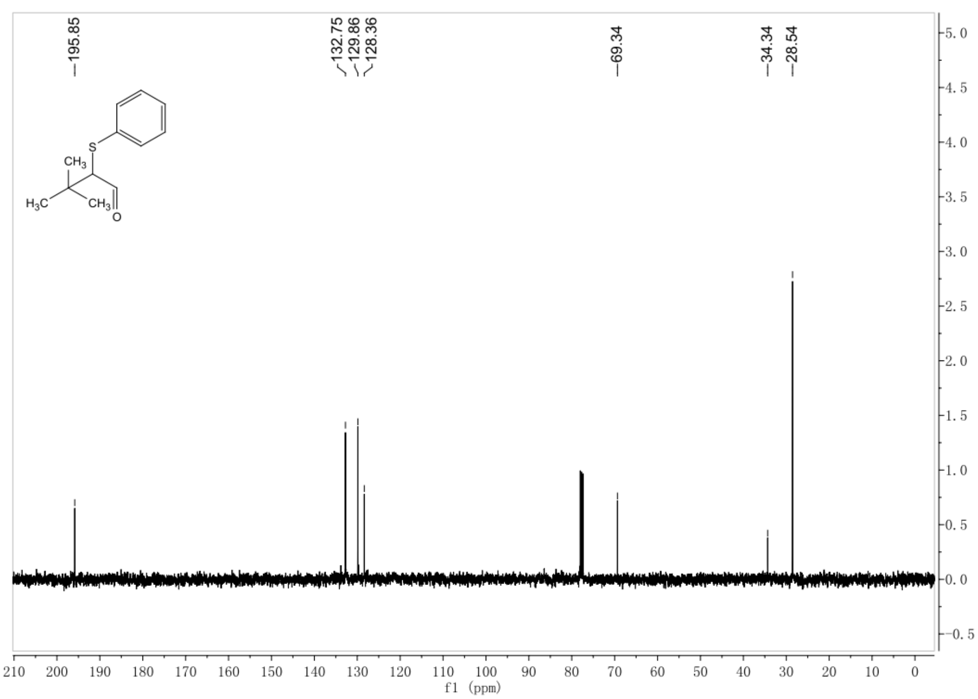
Compound 4g



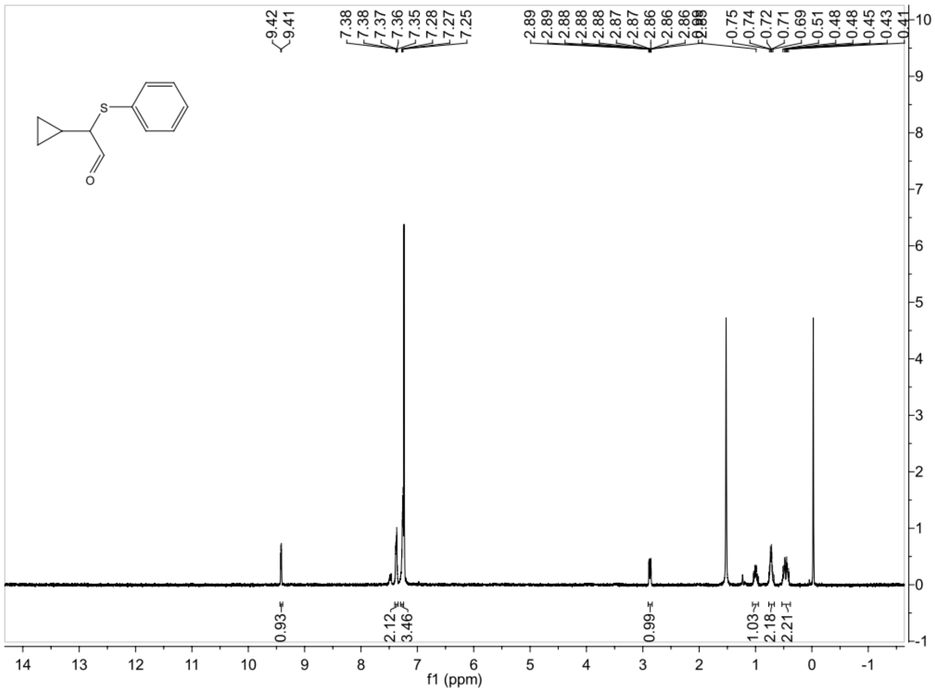


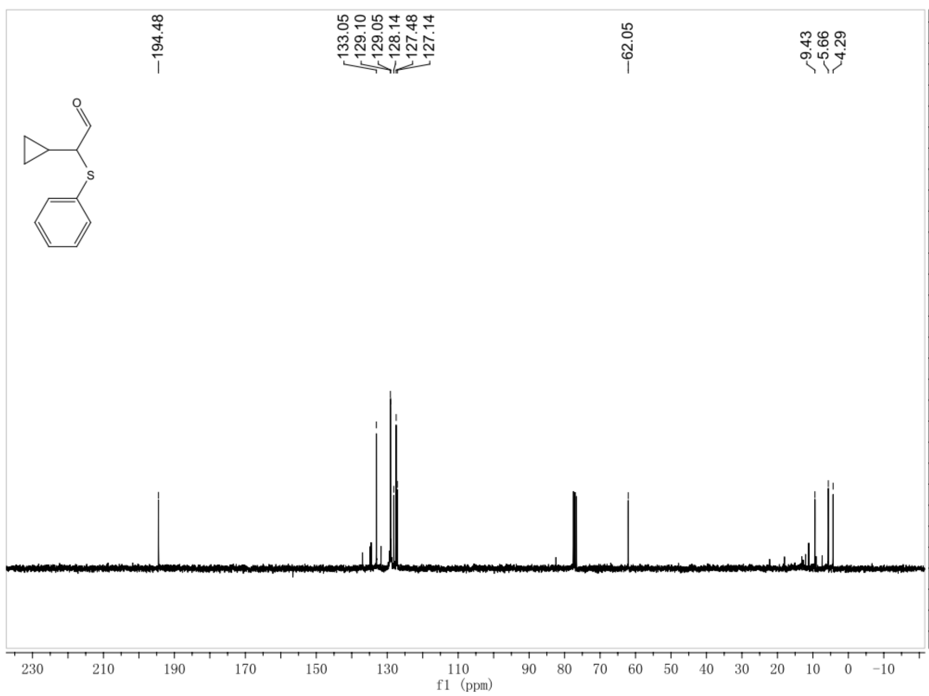
Compounds 4h



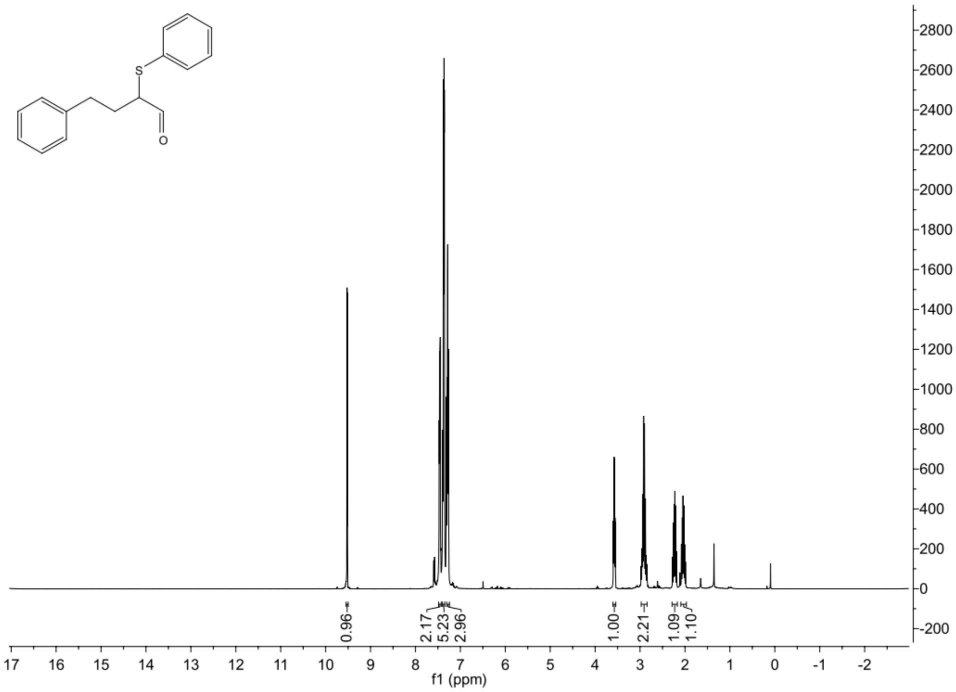


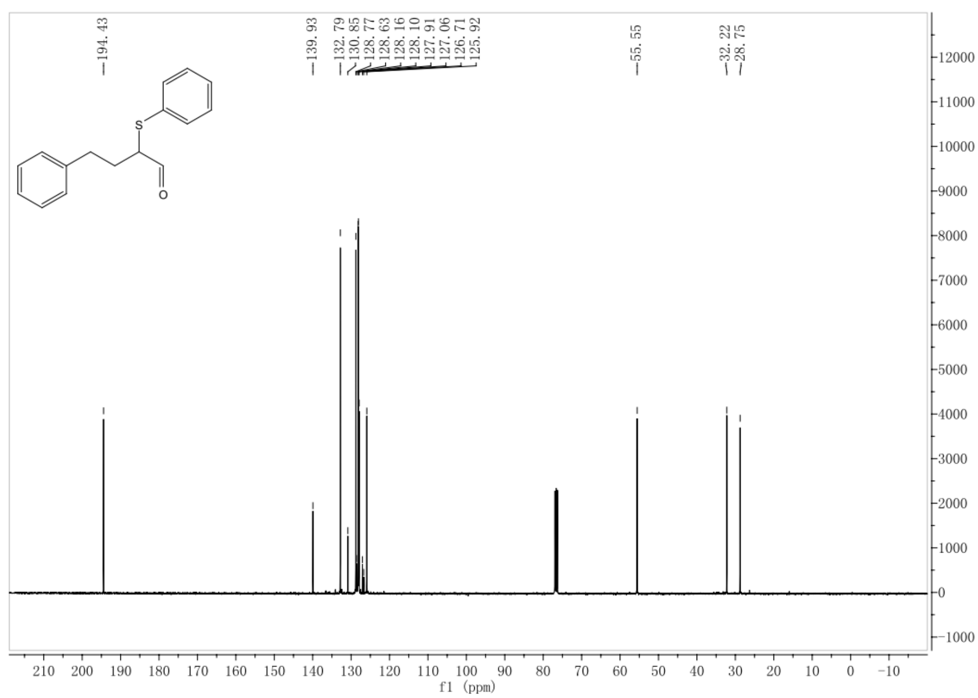
Compound 4i



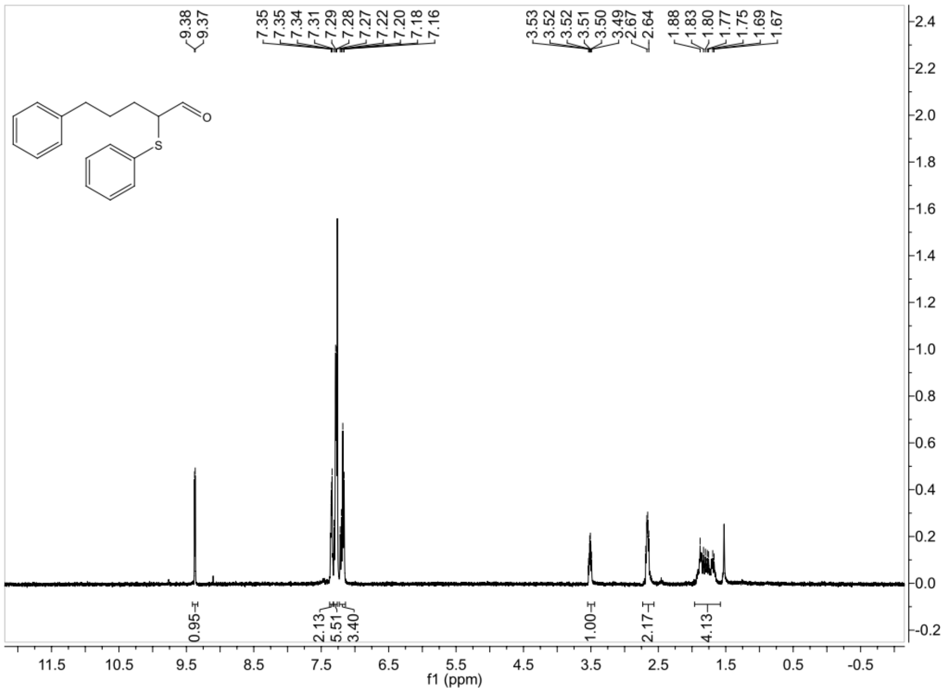


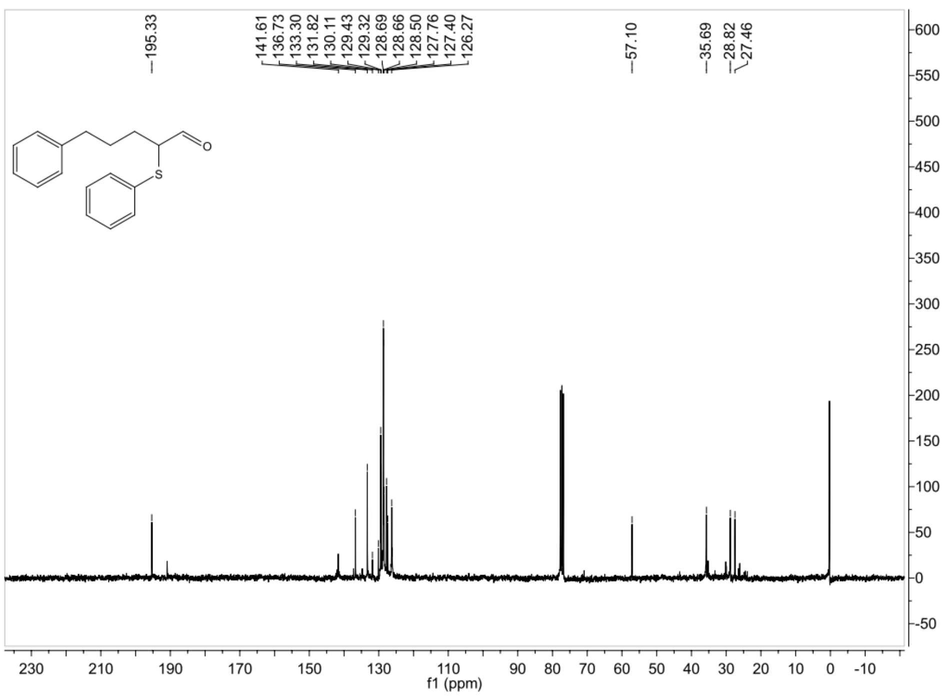
Compound 4k



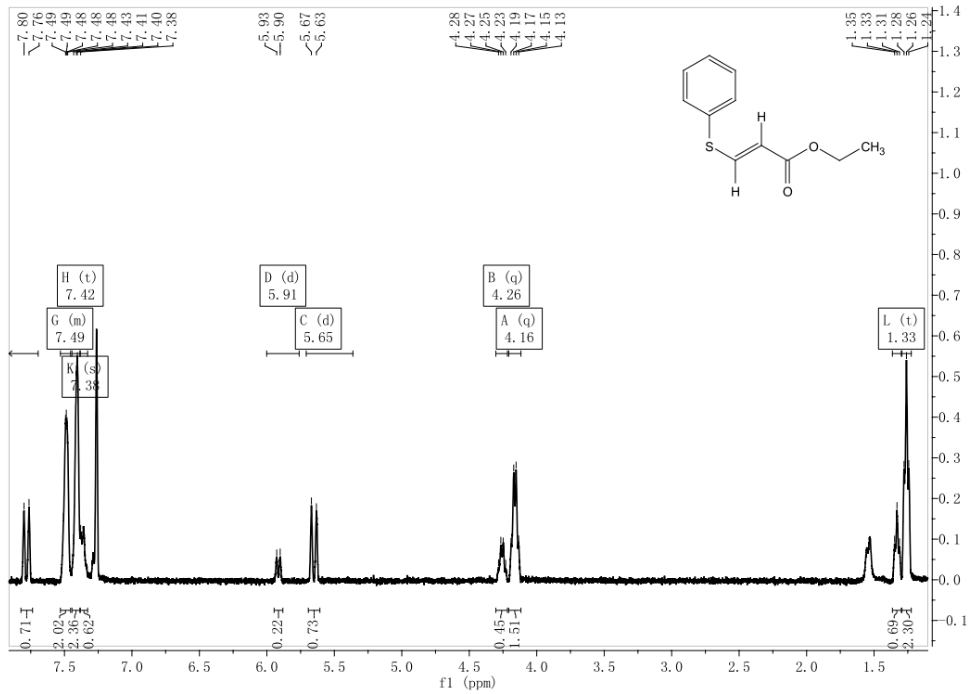


Compound 4l

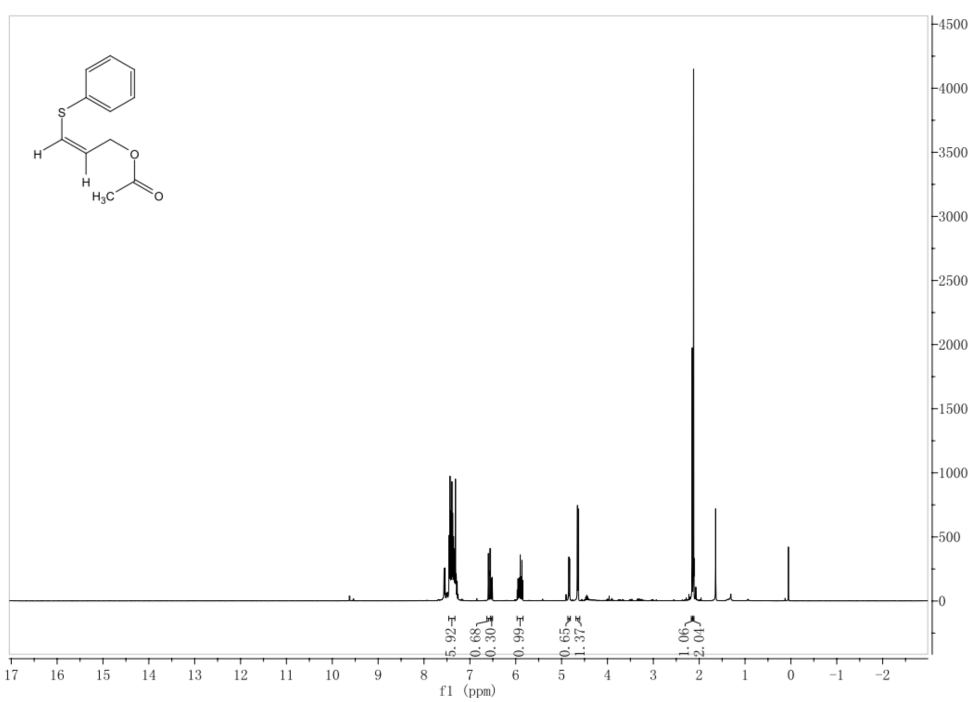

9.38
9.37
7.35
7.35
7.34
7.31
7.29
7.28
7.27
7.22
7.20
7.18
7.16
3.53
3.52
3.52
3.51
3.50
3.49
2.67
2.64
1.88
1.83
1.80
1.77
1.75
1.69
1.67
S
O
0.95
2.13
5.51
3.40
1.00
2.17
4.13
f1 (ppm)


195.33
141.61
136.73
133.30
131.82
130.11
129.43
129.32
128.69
128.66
128.50
127.76
127.40
126.27
57.10
35.69
28.82
27.46
S
O
f1 (ppm)

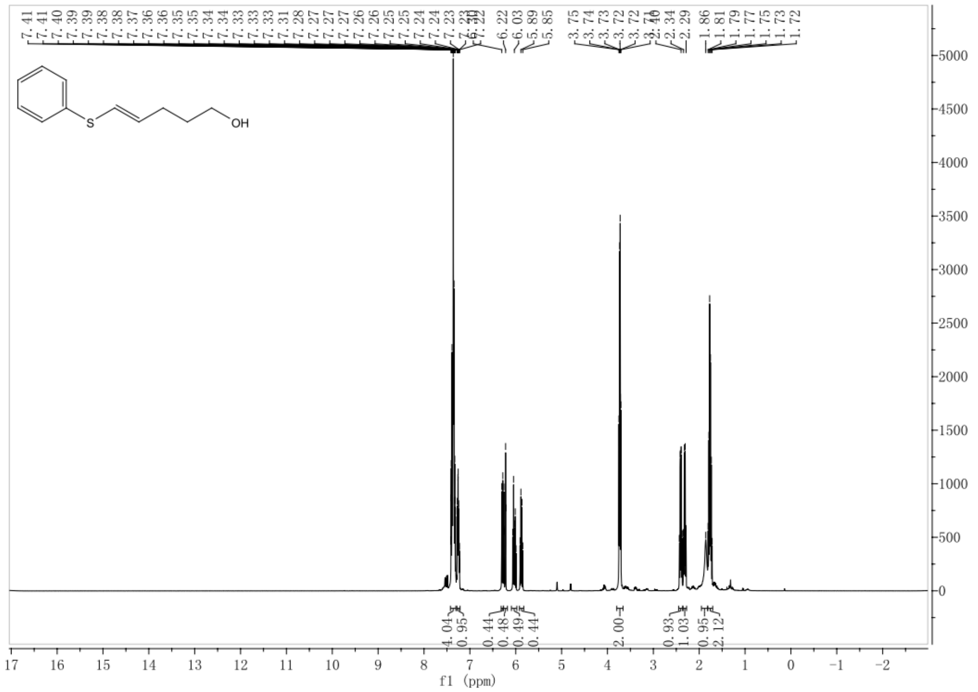
Compound 3m

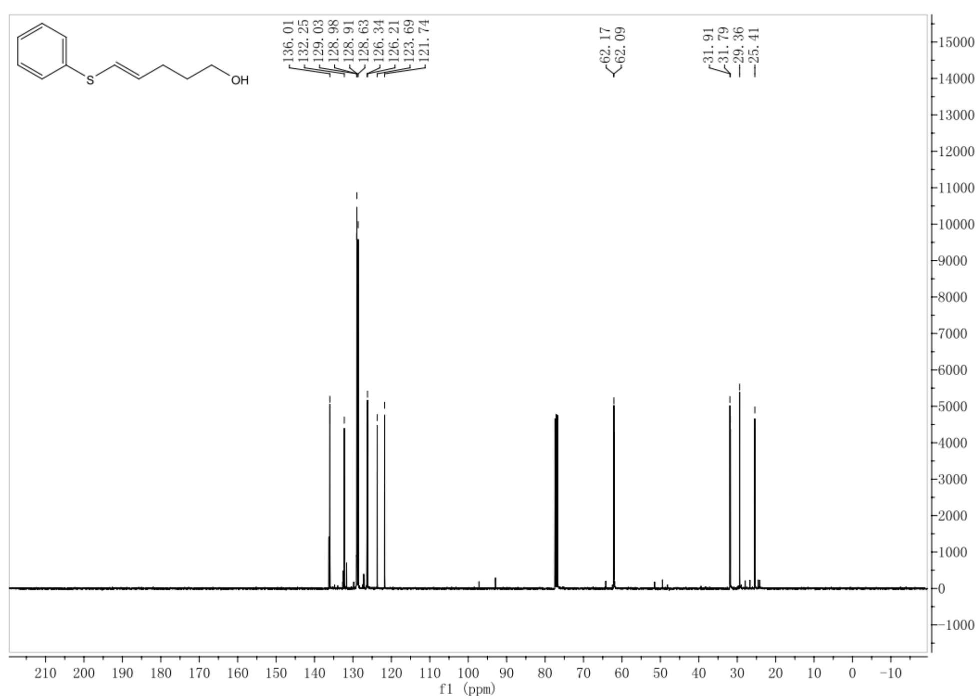


Compound 3n

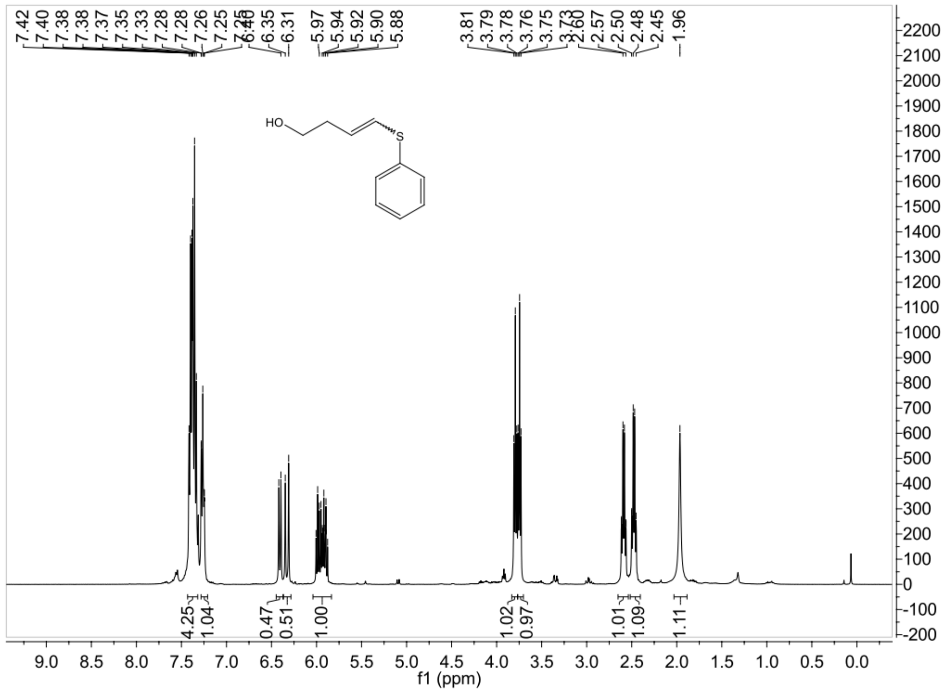


Compound 3o

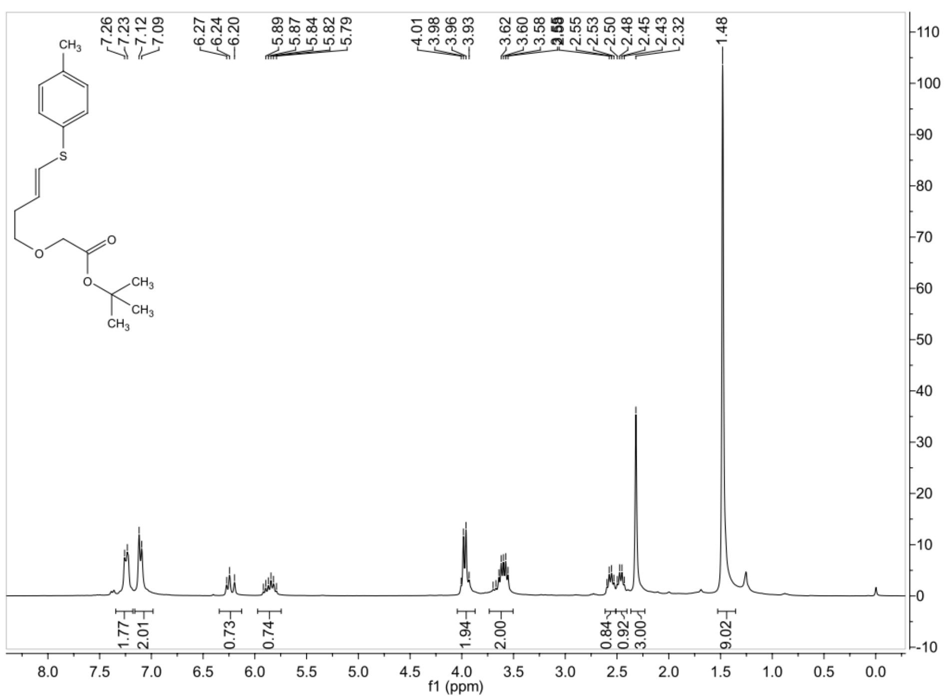


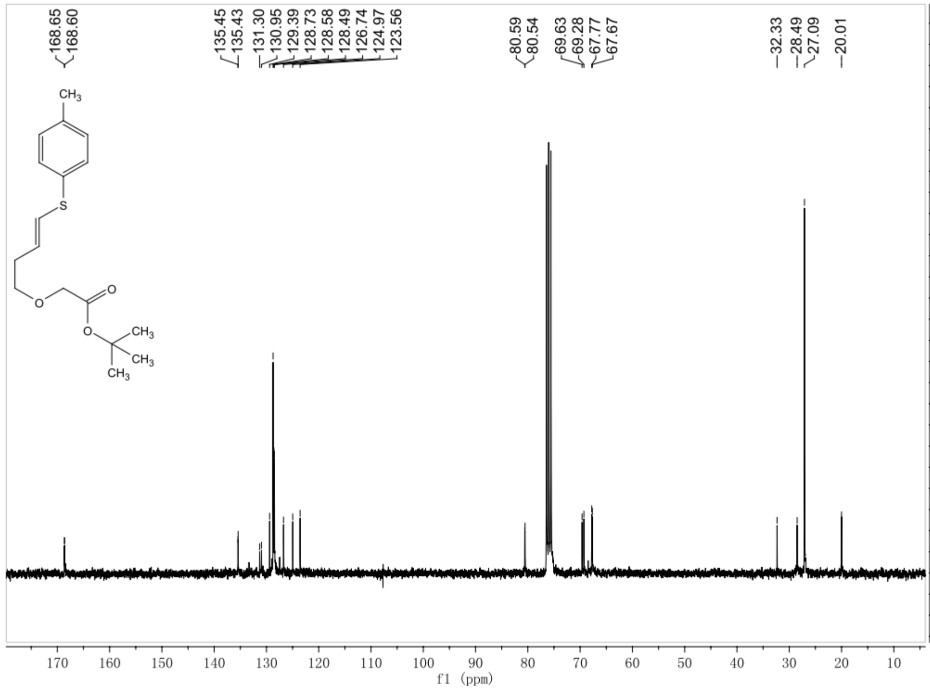


Compound 3p

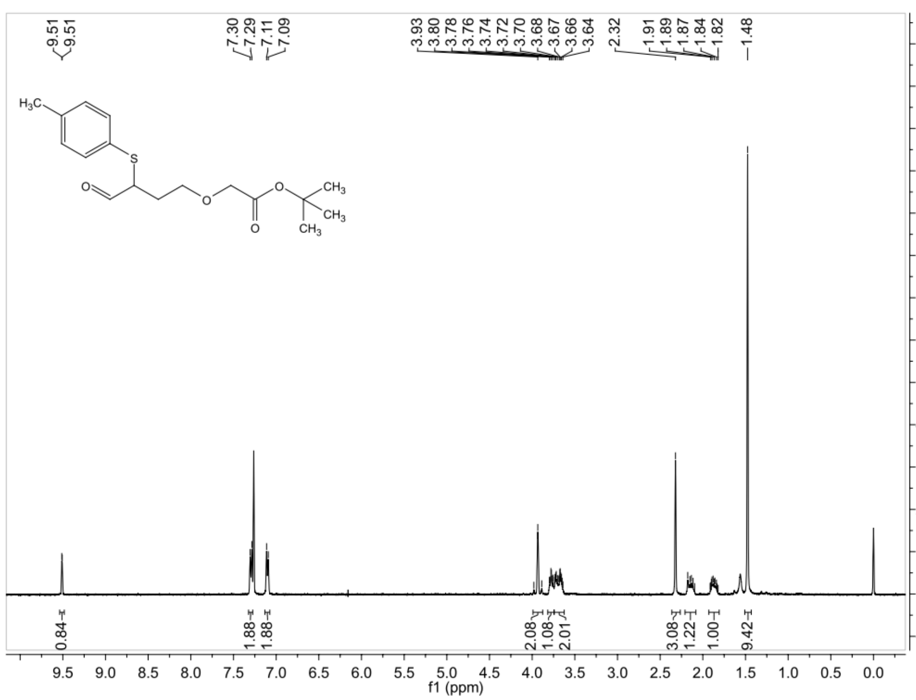


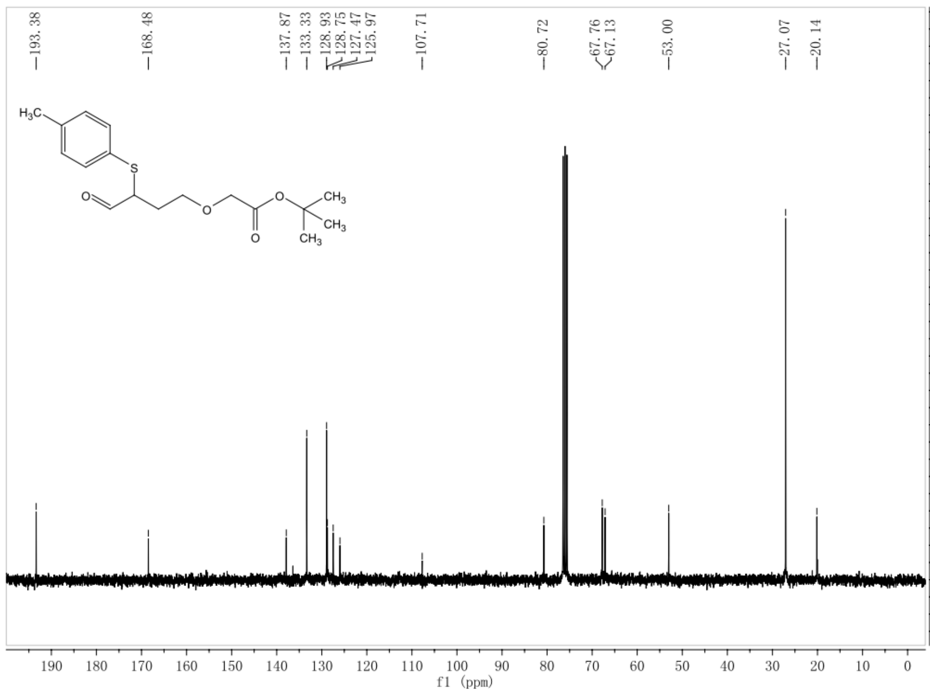
Compound 3ba



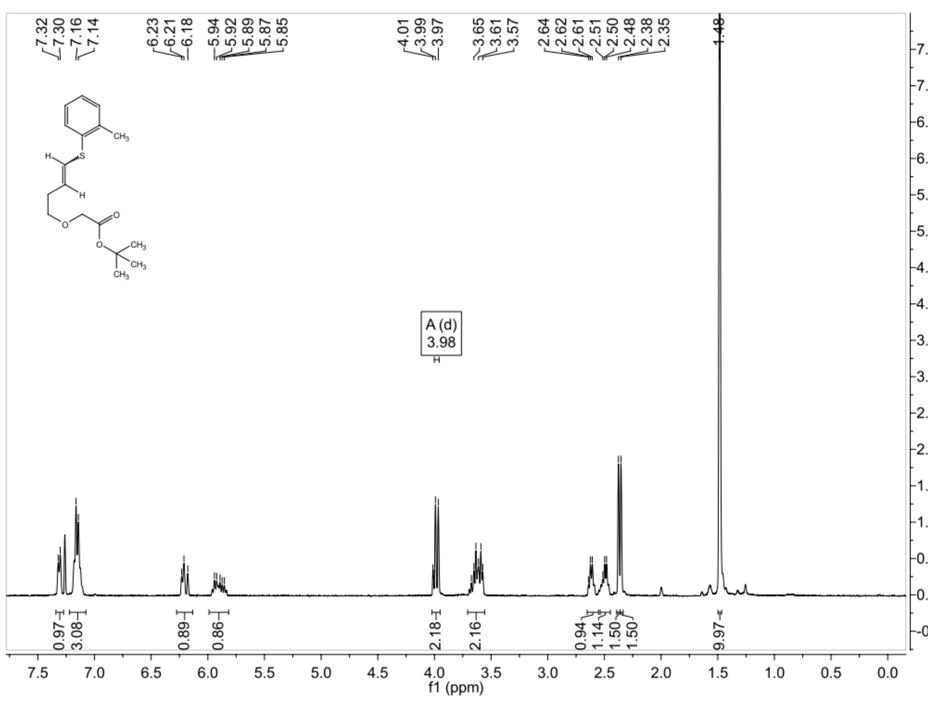


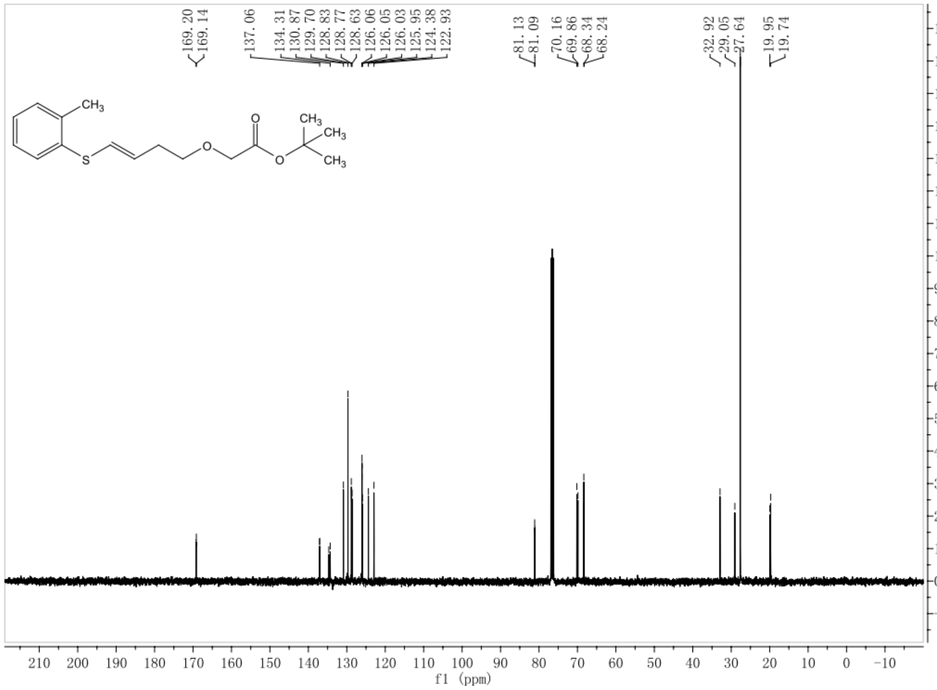
Compound 4ba



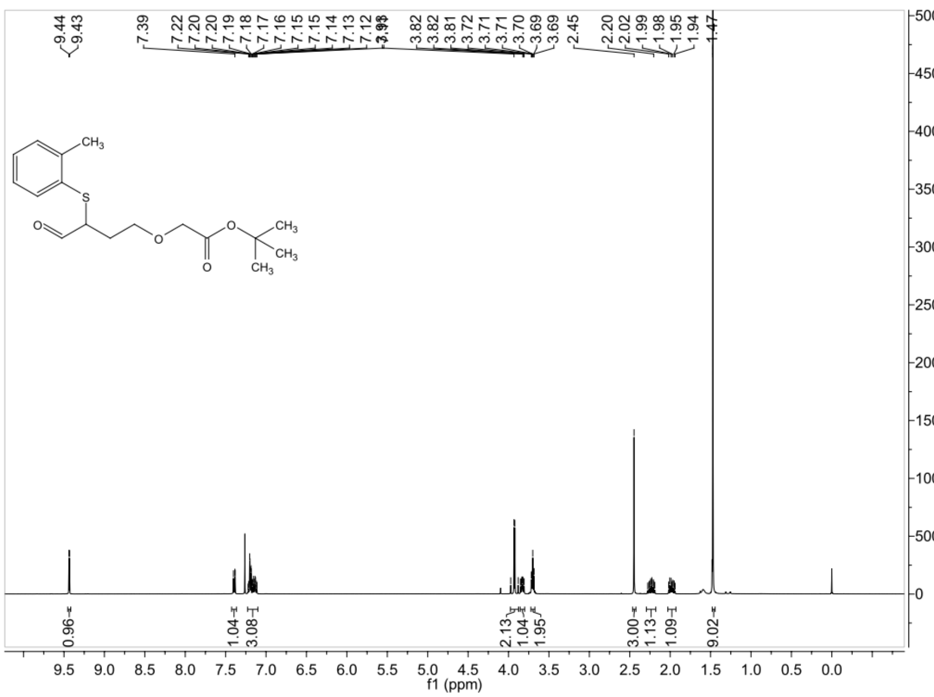


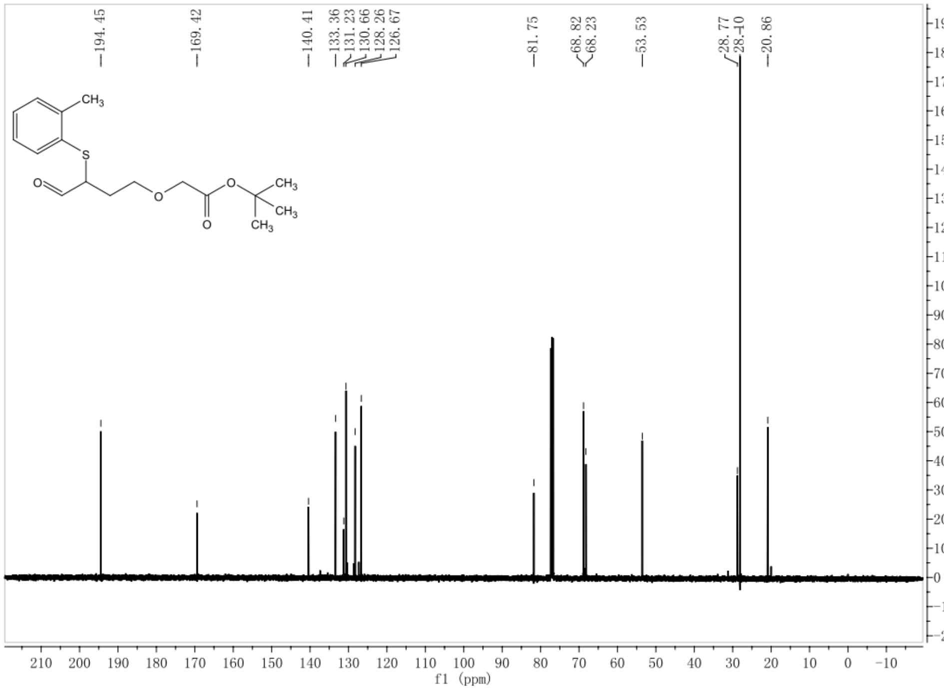
Compound 3ca



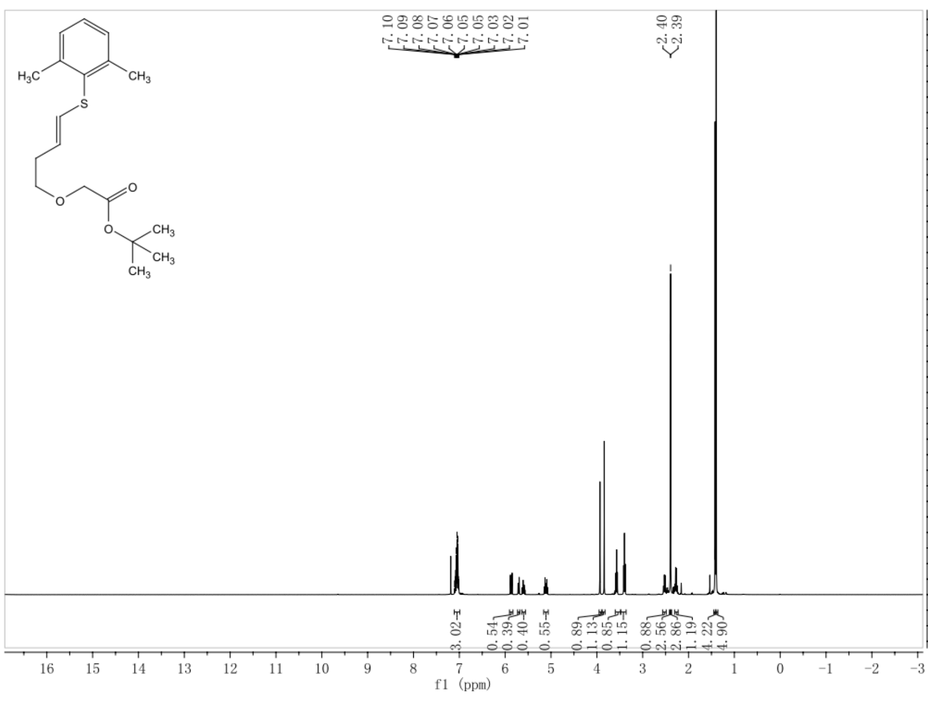


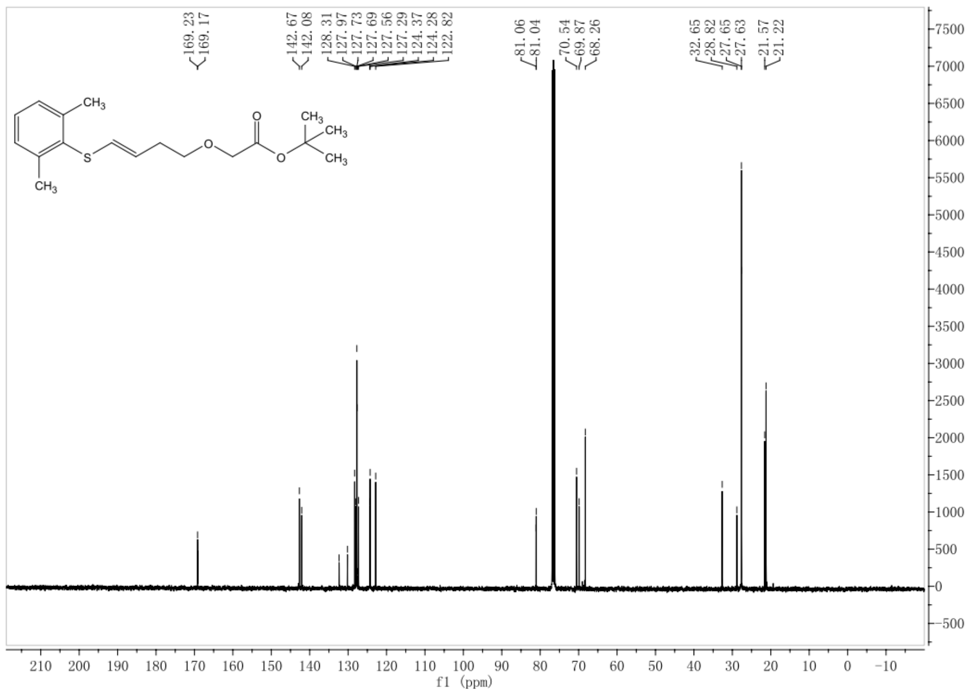
Compounds 4ca



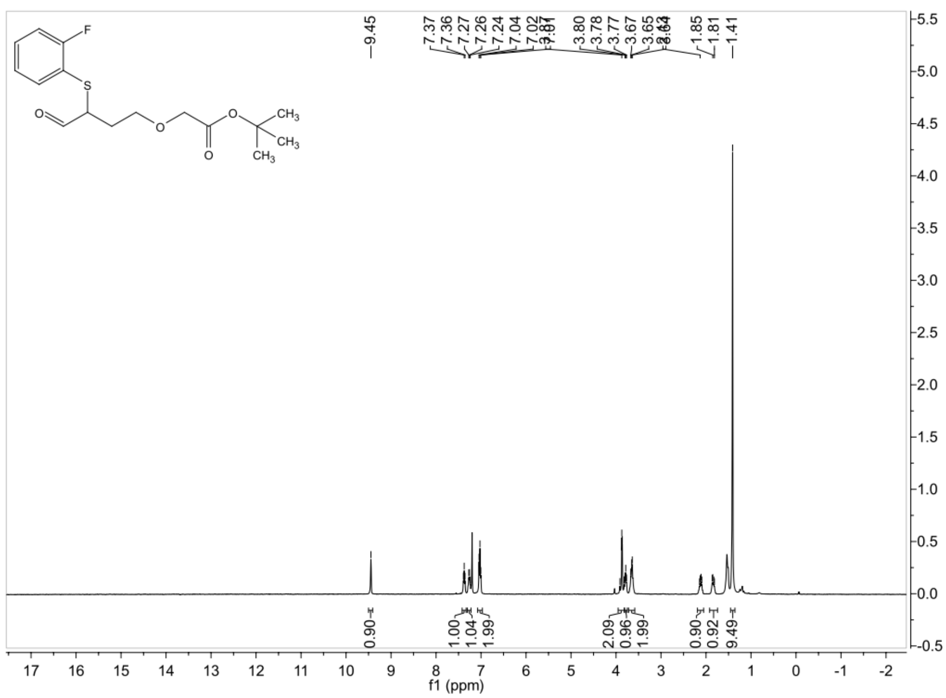


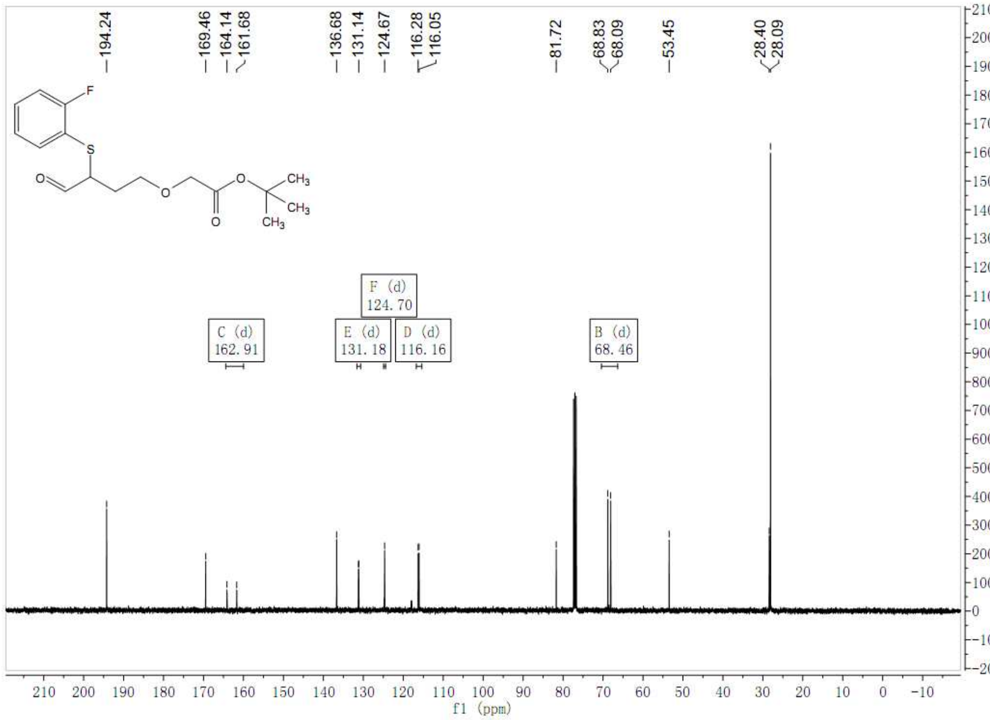
Compound 3da



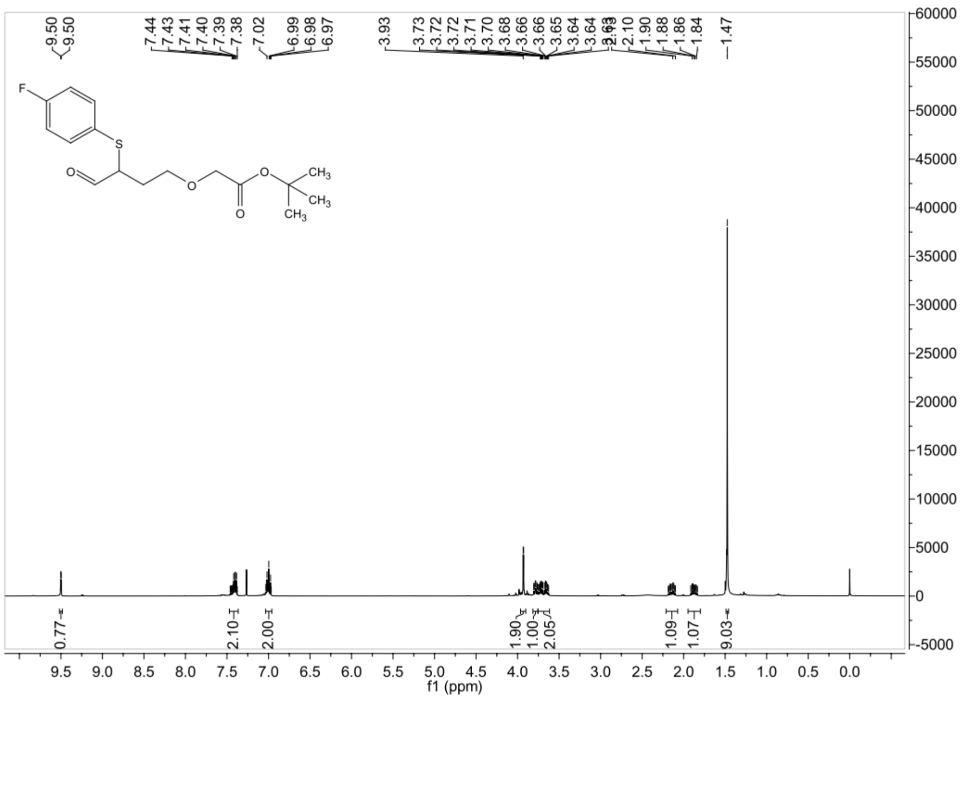


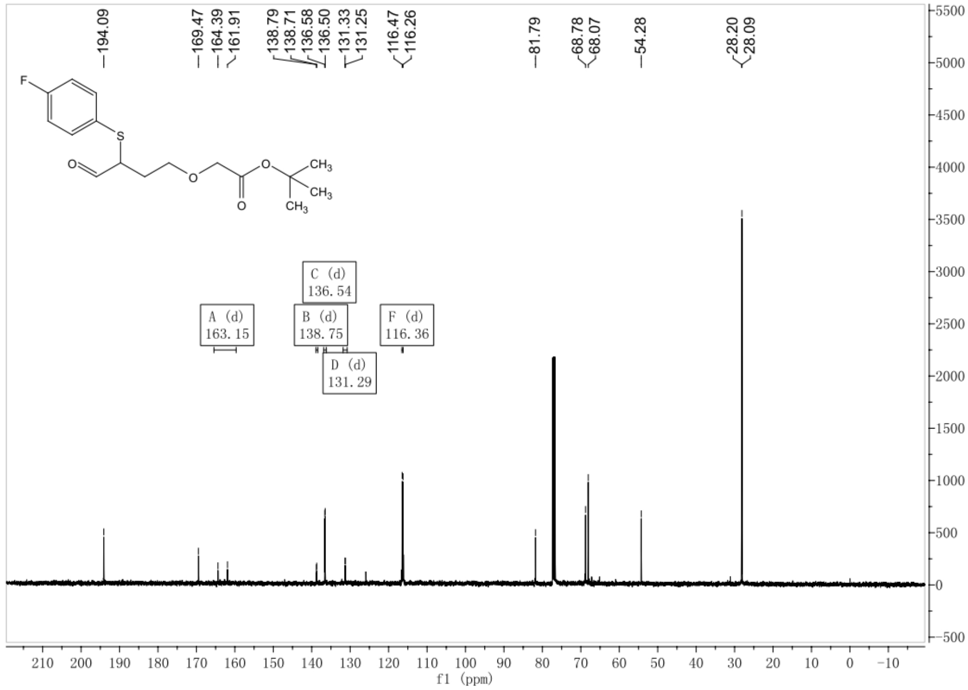
Compound 4ga



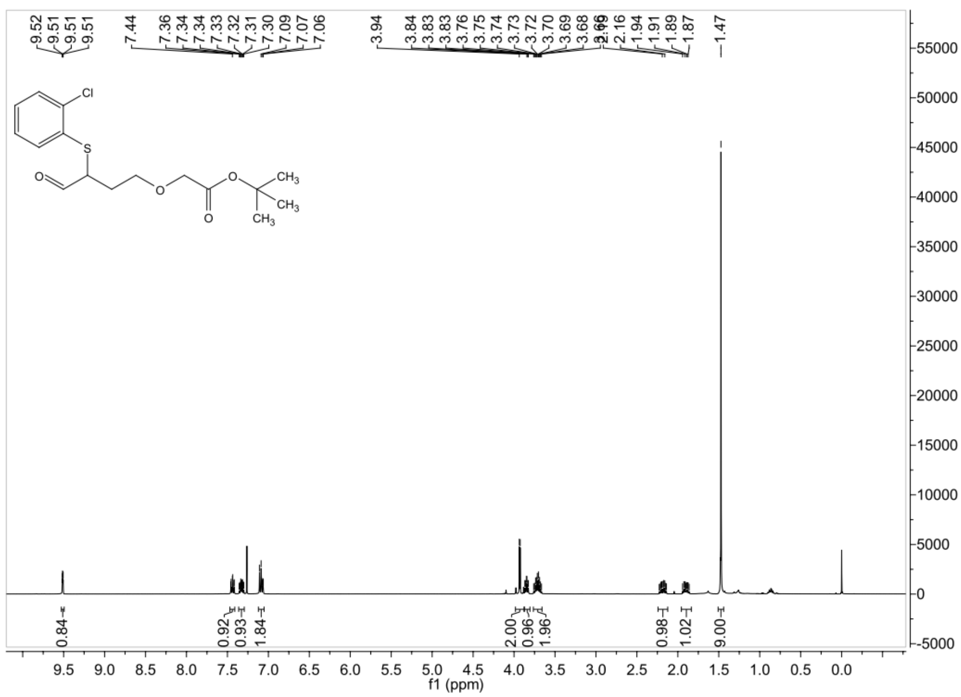


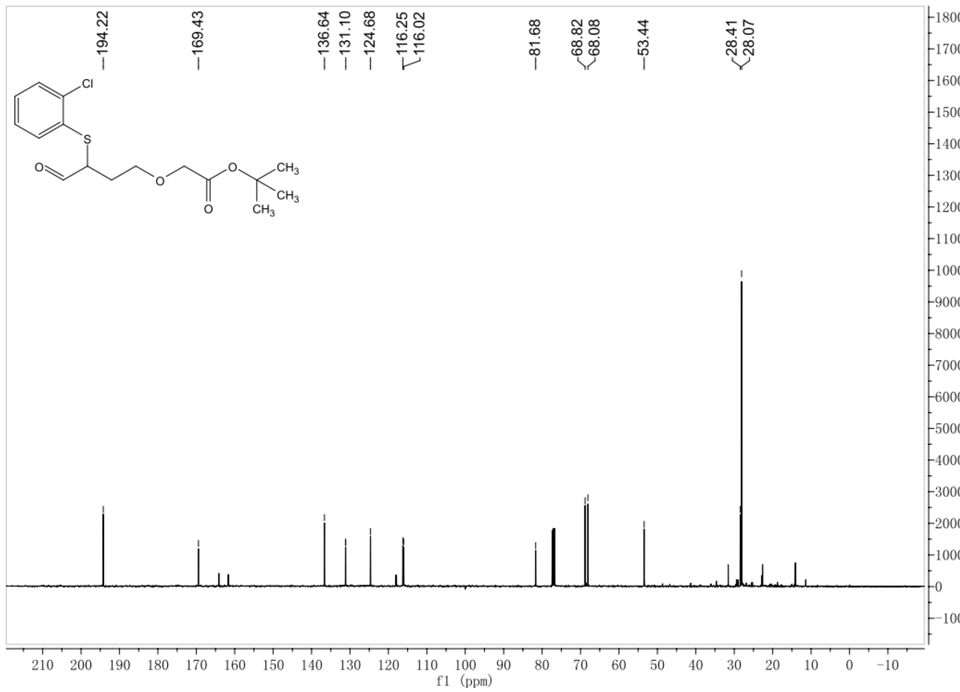
Compound 4ha



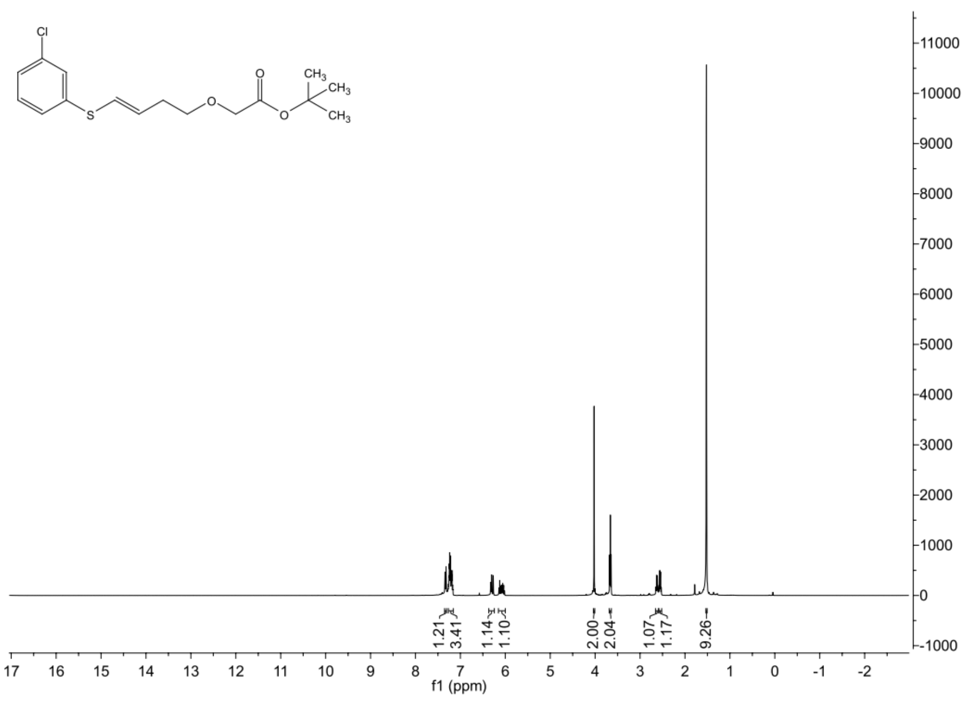


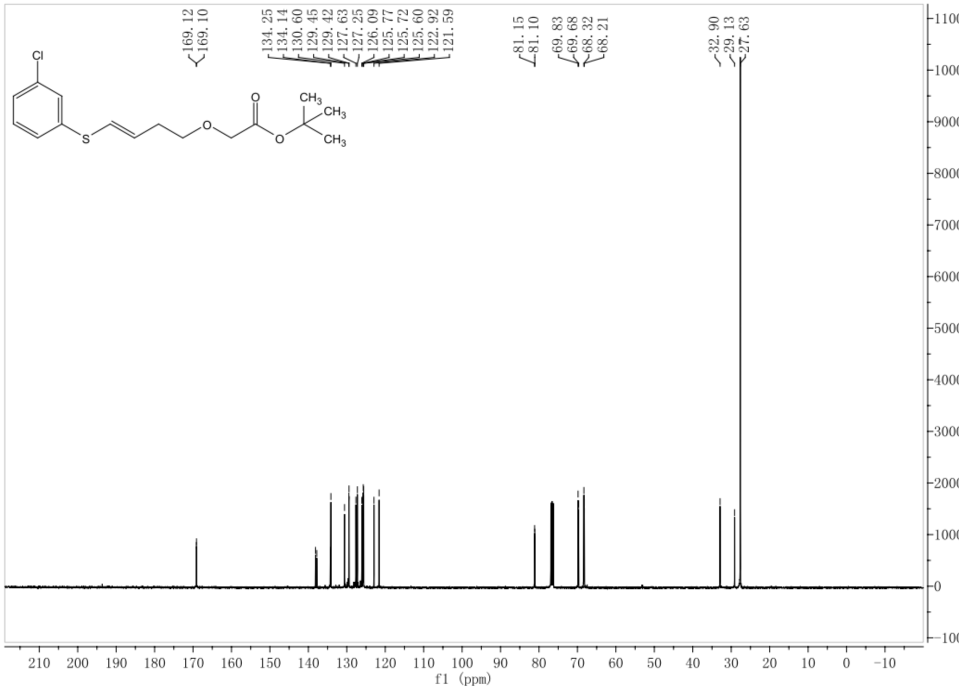
Compound 4ia



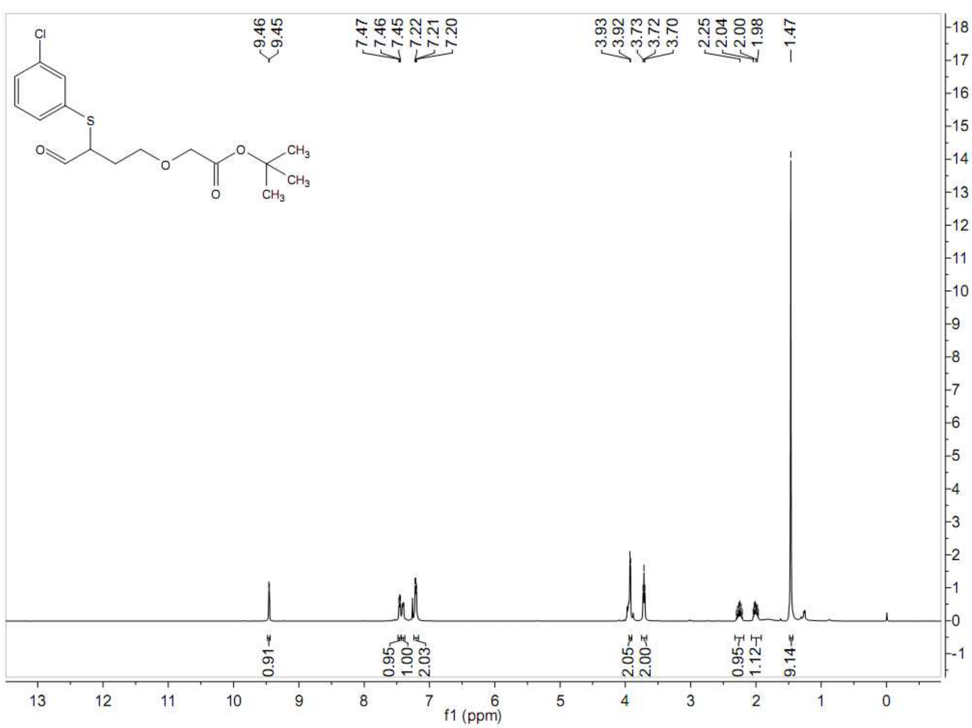


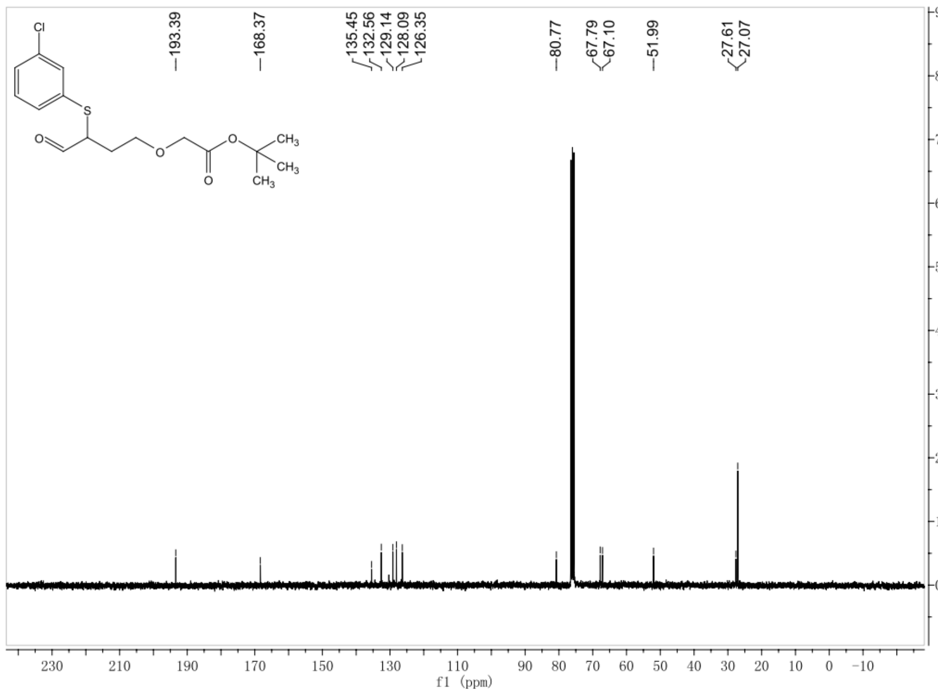
Compound 3ja



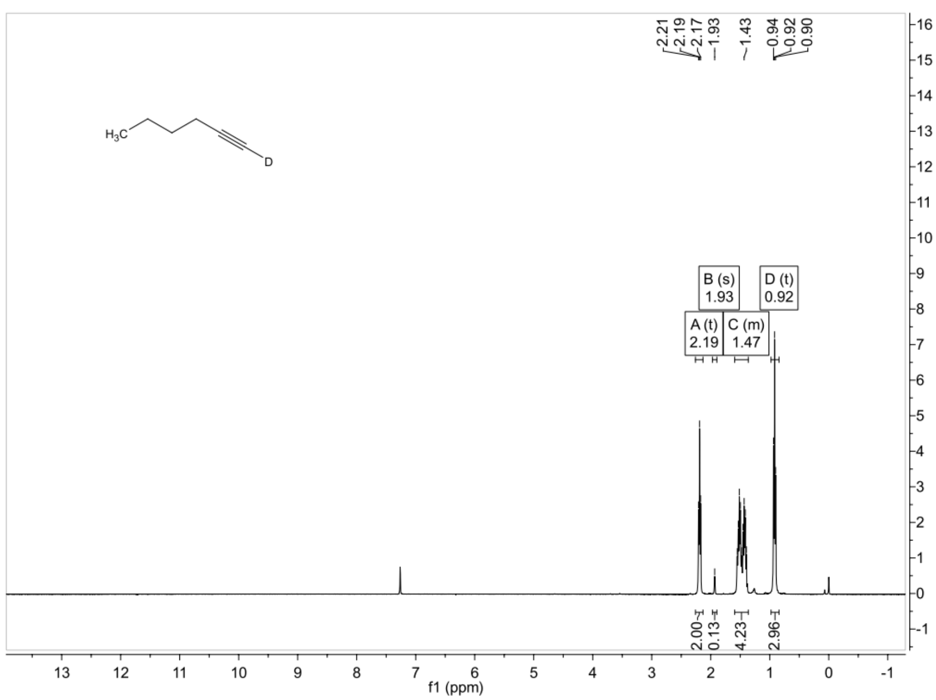


Compound 4ja

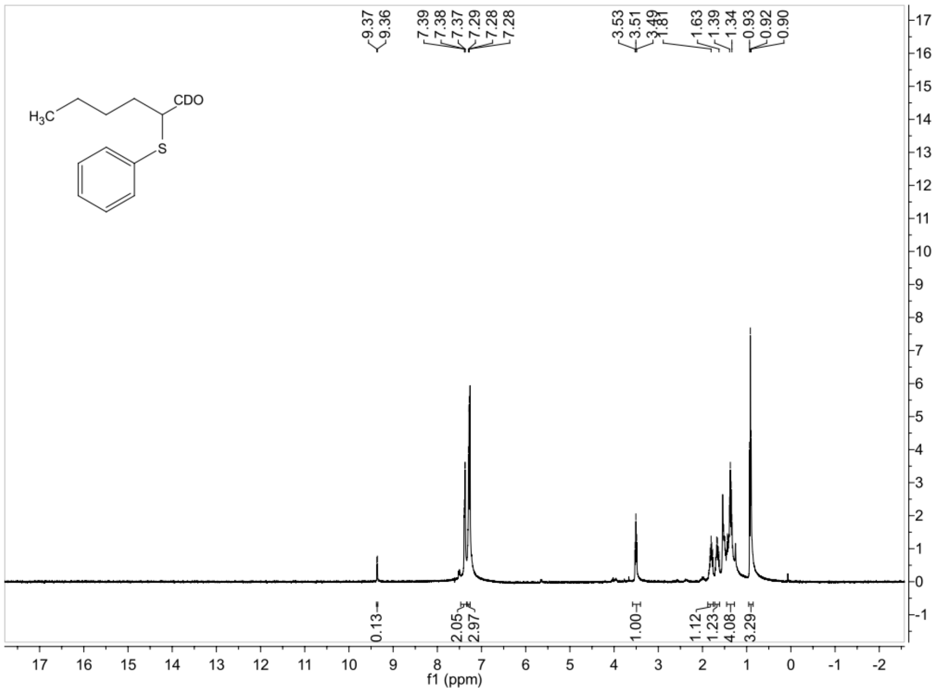



Cl
S
O
O
O
O
CH3
CH3
CH3
193.39
168.37
135.45
132.56
129.14
128.09
126.35
80.77
67.79
67.10
51.99
27.61
27.07
f1 (ppm)

Compound 2b'


H3C
D
2.21
2.19
2.17
1.93
1.43
0.94
0.92
0.90
B (s)
1.93
D (t)
0.92
A (t)
2.19
C (m)
1.47
2.00
0.13
4.23
2.96
f1 (ppm)

Compound 4b'



Compound 6