Supporting Information

Decarboxylative Sulfenylation of Carboxylic Acids via Metallaphotoredox Catalysis

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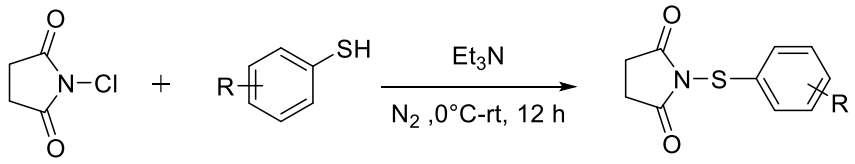
General information

Unless otherwise noted, all the reagents were obtained commercially and used without further purification. Solvents used directly. Chromatographic purification of products was accomplished by column chromatography on silica gel (Qingdao Haiyang, 200-300 mesh). Thin layer chromatography (TLC) was performed on Jianqiang Weiye 0.2 mm silica gel plates. All NMR spectra were recorded on Bruker-400 MHz spectrometer and Bruker-500 MHz spectrometer. HRMS were measured on the Q-TOF6510 instruments. The light source for the reaction is 8W 450nm blue LED. Thermo Scientific Lumina Fluorescence Instrument was used for Emission Quenching Experiments.

Synthesis of the starting materials.[1]



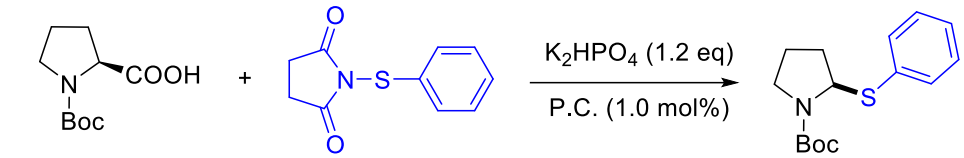
14~85% yield

To a solution of N-chlorosuccinimide (NCS; 1.0 equiv) in CH_2Cl_2 (5.0 mL for 2.0 mmol) was added thiophenol 1(1.0 equiv) and Et_3N (1.0 equiv) dropwise at 0 ℃ under argon. The resulting mixture was stirred at room temperature for 12 h. Upon completion, the reaction was quenched by the addition of a saturated aqueous NH_4Cl solution. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL, for 1.0 mmol). The combined organic extracts were washed with brine and dried with Na_2SO_4. After filtration, the mixture was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (hexane/ethyl acetate, 4:1).

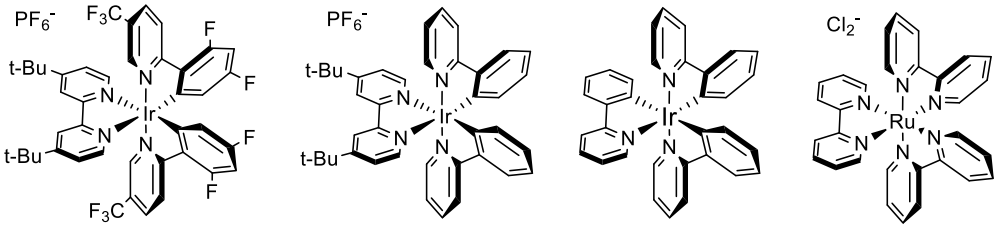
General Procedure for the Sulfur arylation of Carboxylic Acids

A mixture of Boc-Pro-OH **1a** (0.4 mmol), N-(Arylthio)succinimides **4a** (0.2 mmol), **PC-1** (1 mol%), $Ni(acac)_2$ (10 mol%), dtbpy (15 mol%), K_2HPO_4 (1.2 equiv), 1,4-dioxane (1 mL) was stirred at room temperature under irradiation with 8 w blue LED at N_2 atmosphere for 24 h. The organic layer was filtered on celite and evaporated under reduced pressure. The crude reaction mixture was purified by silica gel flash chromatography to afford the desired product.

Optimization of the Photocatalyst and Solvent



1a **4a** **3a**

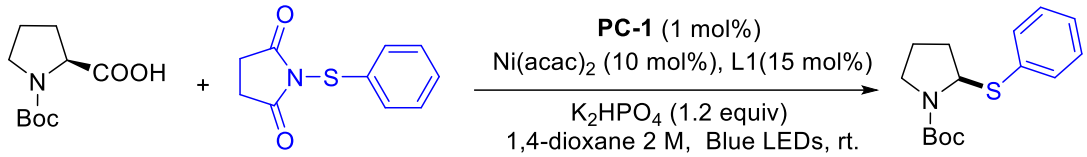


PC-1 **PC-2** **PC-3** **PC-4**

Entry	PC	Solvent	T/°C	Time/h	Yield(%)
1	PC-1	DMF	r.t.	24	57
2	PC-2	DMF	r.t.	24	7
3	PC-3	DMF	r.t.	24	6
4	PC-4	DMF	r.t.	24	<5
5	No PC or no hv	DMF	70	24	<5
6	PC-1	CH_3CN	r.t.	24	<5
7	PC-1	1,4-dioxane	r.t.	24	65
8	PC-1	DMSO	r.t.	24	<5
9	PC-1	CH_2Cl_2	r.t.	24	<5
10	PC-1	DMA	r.t.	24	23
11	PC-1	THF	r.t.	24	50
12	PC-1	toluene	r.t.	24	50
13	PC-1	1,4-dioxane/DMF 1:1	r.t.	24	40

Table S1. Reaction conditions: a mixture of 1a (0.2 mmol), 4a (0.4 mmol), K_2HPO_4 (0.24 mmol), photocatalyst (0.002 mmol), in 1,4-dioxane (1 mL) was stirred at room temperature under irridiation of LED at N_2 atmosphere.

Optimization of Metal and Ligand

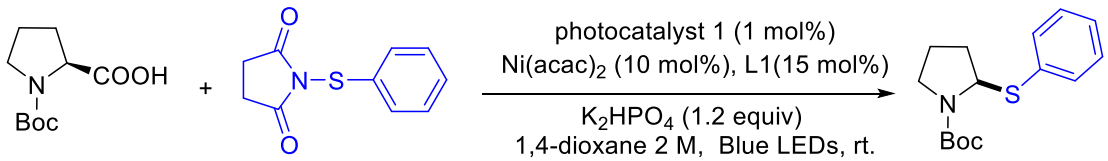


1a **4a** **3a**

entry	[M]	Ligand	T/°C	Time/h	Yield(%)
1	CuCl	dtbpy	r.t.	24	<5
2	$Cu(CH_3CN)_4BF_4$	dtbpy	r.t.	24	10
3	$NiBr_2$	dtbpy	r.t.	24	81
4	$NiCl_2$	dtbpy	r.t.	24	65
5	NiI_2	dtbpy	r.t.	24	<5
6	$Ni(acac)_2$	dtbpy	r.t.	24	84
7	$Ni(OTf)_2$	dtbpy	r.t.	24	27
8	$Ni(PPh_3)Cl_2$	dtbpy	r.t.	24	20
9	$Ni(PCy_3)_2Cl_2$	dtbpy	r.t.	24	43
10	$NiCl_2$·DPPP	dtbpy	r.t.	24	59
11	$NiCl_2$·DME	dtbpy	r.t.	24	71
12	$NiCl_2$·DPPE	dtbpy	r.t.	24	61
13	$Ni(acac)_2$	bpy	r.t.	24	65
14	$Ni(acac)_2$	1,10-phen	r.t.	24	79

Table S2. Reaction conditions: a mixture of 1a (0.2 mmol), 4a (0.4 mmol), K_2HPO_4 (0.24 mmol), **PC-1** (0.002 mmol), in 1,4-dioxane (1 mL) was stirred at room temperature under irridiation of LED at N_2 atmosphere.

Control Experiment



1a **4a** **3a**

Entry	Variation from the "standard" condition	Yiield (%)
1	None	84
2	No P.C.	11
3	No hv	0
4	No metal	43
5	No ligand	40
6	No base	54
7	Na_2HPO_4 instead of K_2HPO_4	77
8	Cs_2CO_3 instead of K_2HPO_4	67
9	DIPEA instead of K_2HPO_4	0
10	CH_3CN instead of 1,4-dioxane	trace
11	CH_3OH instead of 1,4-dioxane	0
12	DCE instead of 1,4-dioxane	76
13	THF instead of 1,4-dioxane	75

Table S3. Reaction conditions: a mixture of 1a (0.2 mmol), 4a (0.4 mmol), K_2HPO_4 (0.24 mmol), **PC-1** (0.002 mmol), in 1,4-dioxane (1 mL) was stirred at room temperature under irridiation of LED at N_2 atmosphere.

Emission Quenching Experiments for PC-1

Emission intensities were recorded using a HITACHI F-4500 Fluorescence Spectrometer. All $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ solutions were excited at 380 nm and the emission intensity at 477 nm was observed. 1,4-dioxane was degassed with a stream of N_2 for 30 min and then moved to glove box. All the solutions were prepared in the glove box. In a typical experiment, the emission spectrum of a 5×10^{-5} M solution of $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ in 1, 4-dioxane was collected. Then, appropriate amount of quencher was added to the measured solution and the emission spectrum of the sample was collected.

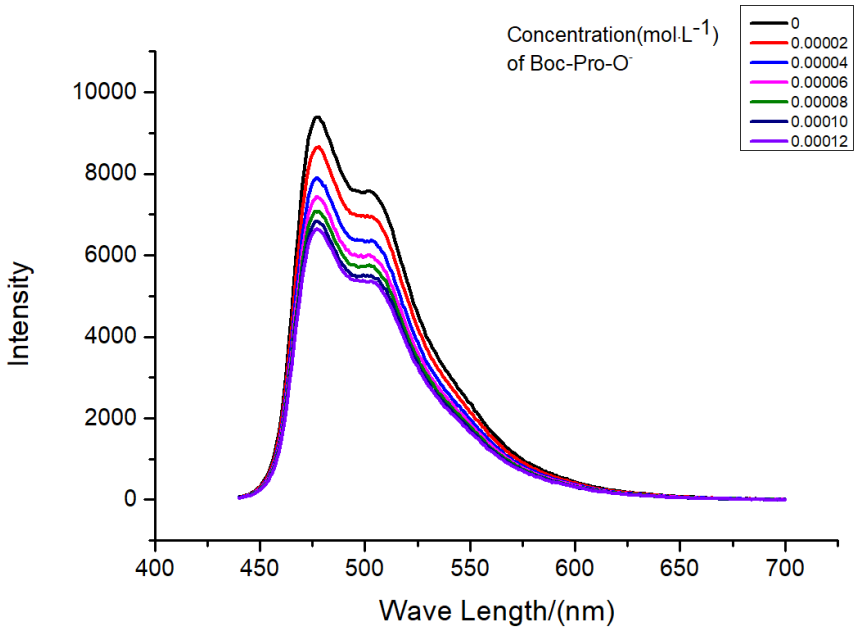


Figure S1. $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ Emission Quenching by Boc-Pro-O^-.

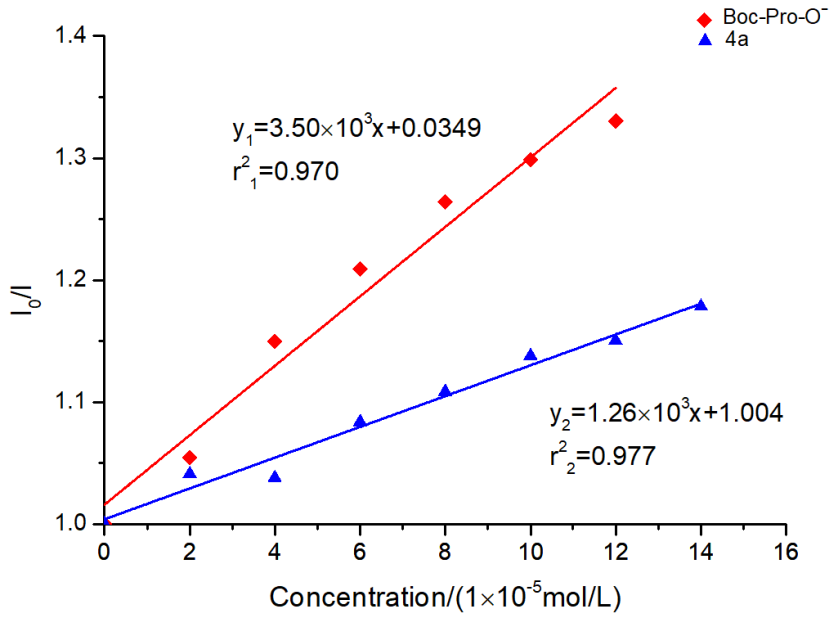
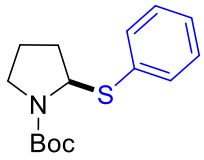


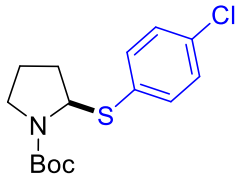
Figure S1. $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ Ru(bpy) 3 (SbF 6) 2 emission quenching with Boc-Pro-O^- and 4a; I_0 and I represent the intensities of the emission in the absence and presence of the quencher. Emission Quenching by Boc-Pro-O^- , kq= 3.50×10^3 mol -1 •L

Characterization Data



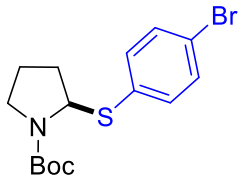
3a

Yield: 83%.[2] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 20.2 Hz, 2H), 7.29 (s, 3H), 5.43 – 5.22 (m, 1H), 3.52 – 3.21 (m, 2H), 2.24 – 1.95 (m, 3H), 1.88 (d, *J* = 3.4 Hz, 1H), 1.39 (d, *J* = 46.4 Hz, 9H).



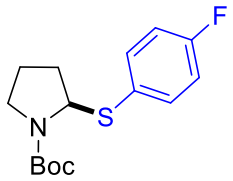
3b

Yield: 99%.[2] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.34 (m, 2H), 7.27 (s, 2H), 5.30 (d, *J* = 57.4 Hz, 1H), 3.36 (d, *J* = 58.6 Hz, 2H), 2.24 – 1.95 (m, 3H), 1.90 (dd, *J* = 7.4, 2.8 Hz, 1H), 1.38 (d, *J* = 38.2 Hz, 9H).



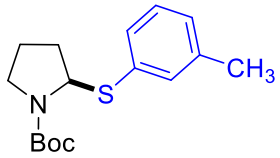
3c

Yield: 97%.[2] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.29 (m, 4H), 5.31 (d, *J* = 58.3 Hz, 1H), 3.51 – 3.23 (m, 2H), 2.24 – 1.96 (m, 3H), 1.95 – 1.84 (m, 1H), 1.38 (d, *J* = 39.6 Hz, 9H).



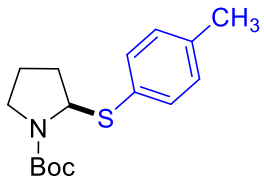
3d

Yield: 68%.[2] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 26.9 Hz, 2H), 6.98 (d, *J* = 6.8 Hz, 2H), 5.26 (d, *J* = 51.1 Hz, 1H), 3.49 – 3.20 (m, 2H), 2.04 (dd, *J* = 49.1, 17.5 Hz, 3H), 1.87 (d, *J* = 6.6 Hz, 1H), 1.37 (d, *J* = 35.8 Hz, 9H).



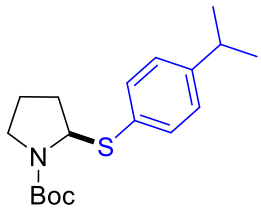
3e

Yield: 82%.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 14.9 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 7.7 Hz, 1H), 5.46 – 5.21 (m, 1H), 3.52 – 3.21 (m, 2H), 2.32 (s, 3H), 2.05 (t, *J* = 9.6 Hz, 3H), 1.88 (d, *J* = 4.0 Hz, 1H), 1.39 (d, *J* = 41.4 Hz, 9H).



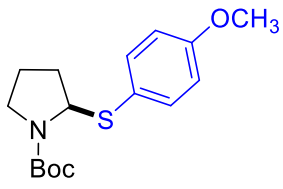
3f

Yield: 97%.[2] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.31 (m, 2H), 7.10 (d, *J* = 6.1 Hz, 2H), 5.40 – 5.13 (m, 1H), 3.50 – 3.17 (m, 2H), 2.32 (s, 3H), 2.02 (d, *J* = 7.8 Hz, 3H), 1.84 (d, *J* = 14.1 Hz, 1H), 1.39 (d, *J* = 41.9 Hz, 9H).



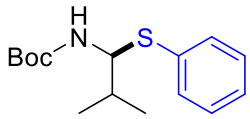
3g

Yield: 87%.[2] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.36 (m, 2H), 7.16 (d, *J* = 7.0 Hz, 2H), 5.39 – 5.22 (m, 1H), 3.53 – 3.22 (m, 2H), 2.88 (dt, *J* = 13.2, 6.5 Hz, 1H), 2.07 (ddd, *J* = 23.8, 17.1, 9.7 Hz, 3H), 1.89 (d, *J* = 6.6 Hz, 1H), 1.37 (d, *J* = 56.0 Hz, 9H), 1.23 (d, *J* = 6.9 Hz, 6H).



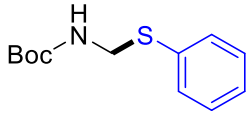
3h

Yield: 71%.[2] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.33 (m, 2H), 6.83 (d, *J* = 7.4 Hz, 2H), 5.19 (dd, *J* = 47.7, 4.8 Hz, 1H), 3.78 (s, 3H), 3.48 – 3.17 (m, 2H), 2.16 – 1.90 (m, 3H), 1.90 – 1.77 (m, 1H), 1.38 (d, *J* = 35.6 Hz, 9H).



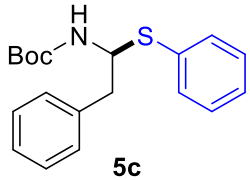
5a

Yield: 53%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, J = 7.3 Hz, 2H), 7.28 (d, J = 6.9 Hz, 2H), 7.25 – 7.19 (m, 1H), 5.08 (dd, J = 10.4, 5.1 Hz, 1H), 4.71 (d, J = 10.1 Hz, 1H), 2.03 (dq, J = 13.3, 6.7 Hz, 1H), 1.32 (s, 9H), 1.05 (dd, J = 6.7, 4.8 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.89, 133.44, 132.74, 128.86, 127.28, 79.72, 64.88, 33.86, 28.23, 19.49, 18.24. HRMS (ESI, m/z) calcd for $C_{15}H_{23}NO_2S$ $[M+Na]^+$ 304.1347, found 304.1353.



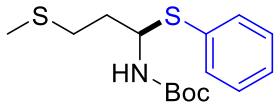
5b

Yield: 42%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 7.3 Hz, 3H), 7.32 (dt, J = 15.7, 4.8 Hz, 3H), 4.91 (s, 1H), 4.59 (d, J = 6.3 Hz, 2H), 1.40 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.94, 133.85, 131.66, 129.14, 127.35, 80.19, 45.82, 28.28. HRMS (ESI, m/z) calcd for $C_{15}H_{17}NO_2S$ $[M+Na]^+$ 262.0878, found 262.0878.



5c

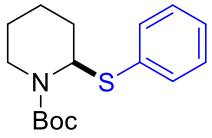
Yield: 53%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, J = 6.8 Hz, 2H), 7.35 – 7.27 (m, 6H), 7.25 (s, 2H), 5.43 (d, J = 8.8 Hz, 1H), 4.72 (d, J = 9.2 Hz, 1H), 3.08 (ddd, J = 20.4, 14.1, 6.8 Hz, 2H), 1.30 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.47, 133.71, 132.24, 128.98, 127.95, 80.07, 58.25, 35.64, 30.74, 28.25, 15.59. HRMS (ESI, m/z) calcd for $C_{19}H_{23}NO_2S$ $[M+Na]^+$ 352.1347, found 352.1348.



5d

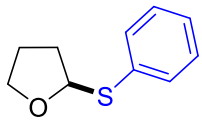
Yield: 74%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, J = 6.2 Hz, 2H), 7.30 (d, J = 7.0

Hz, 3H), 5.23 (d, J = 8.3 Hz, 1H), 4.75 (d, J = 9.6 Hz, 1H), 2.63 (t, J = 7.5 Hz, 2H), 2.10 (s, 3H), 2.07 – 1.87 (m, 2H), 1.34 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.47, 133.71, 132.24, 128.98, 127.95, 80.07, 58.25, 35.64, 30.74, 28.25, 15.59. HRMS (ESI, m/z) calcd for $C_{15}H_{23}NO_2S_2$ $[M+Na]^+$ 330.1068, found 330.1064.



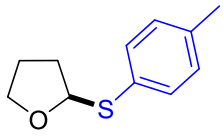
5e

Yield: 90%.[3] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (s, 2H), 7.28 (s, 3H), 5.91 (d, J = 133.1 Hz, 1H), 4.19 – 3.69 (m, 1H), 3.30 (td, J = 13.1, 2.8 Hz, 1H), 2.06 – 1.79 (m, 3H), 1.78 – 1.58 (m, 2H), 1.53 – 1.37 (m, 1H), 1.22 (d, J = 74.8 Hz, 9H).



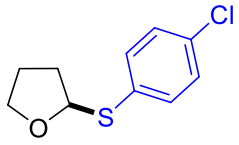
5f

Yield: 72%.[4] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 2H), 7.32 – 7.26 (m, 2H), 7.26 – 7.19 (m, 1H), 5.65 (dd, J = 7.2, 4.0 Hz, 1H), 4.06 – 3.99 (m, 1H), 3.98 – 3.92 (m, 1H), 2.43 – 2.31 (m, 1H), 2.07 – 1.93 (m, 2H), 1.93 – 1.81 (m, 1H).



5g

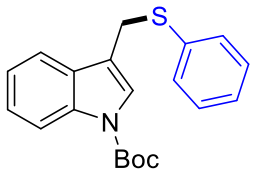
Yield: 67%.[4] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 7.9 Hz, 2H), 5.58 (dd, J = 7.2, 3.9 Hz, 1H), 4.03 (dd, J = 15.4, 7.9 Hz, 1H), 3.95 (td, J = 8.1, 4.1 Hz, 1H), 2.39 – 2.31 (m, 4H), 2.07 – 1.92 (m, 2H), 1.87 (qdd, J = 8.0, 6.7, 5.0 Hz, 1H).



5h

Yield: 61%.[4] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.28 – 7.24 (m, 2H), 5.60 (dd, J = 7.2, 3.9 Hz, 1H), 4.05 – 3.99 (m, 1H), 3.96 (td, J = 8.1, 4.1 Hz, 1H), 2.37

(dddd, J = 14.8, 12.8, 12.2, 7.6 Hz, 1H), 2.07 – 1.92 (m, 2H), 1.92 – 1.83 (m, 1H).



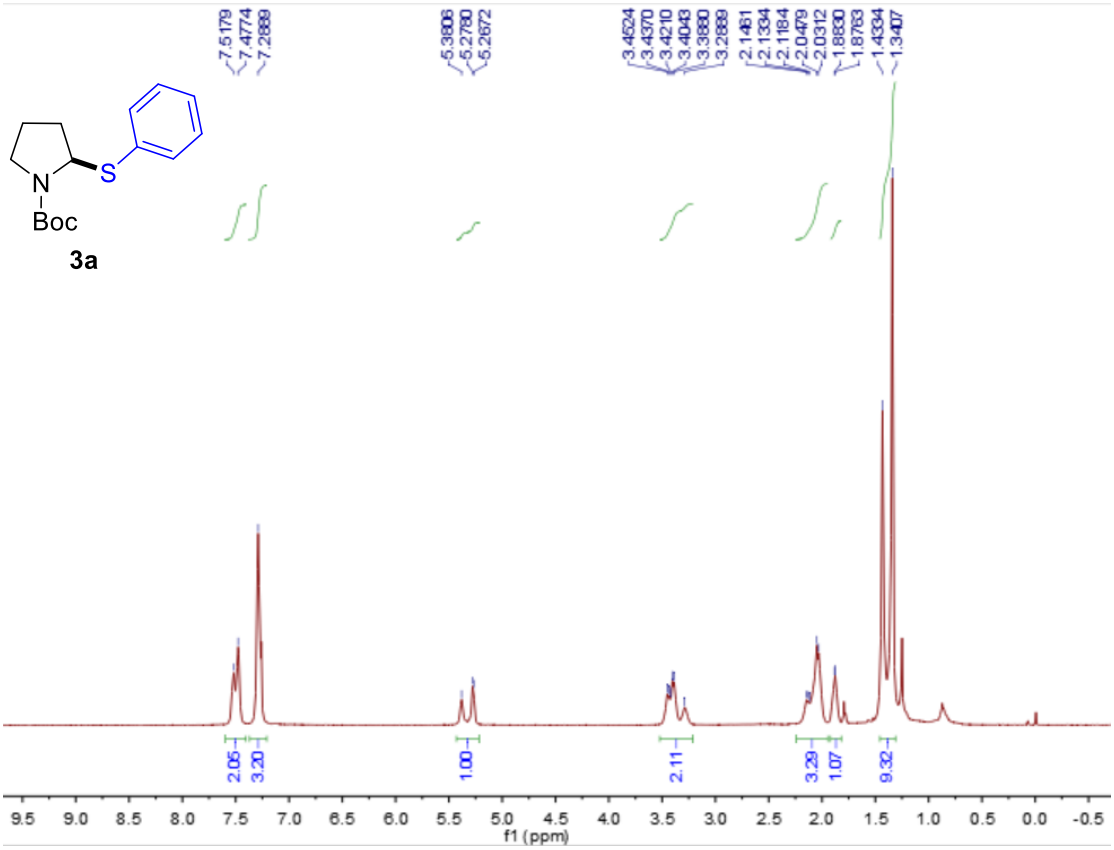
5i

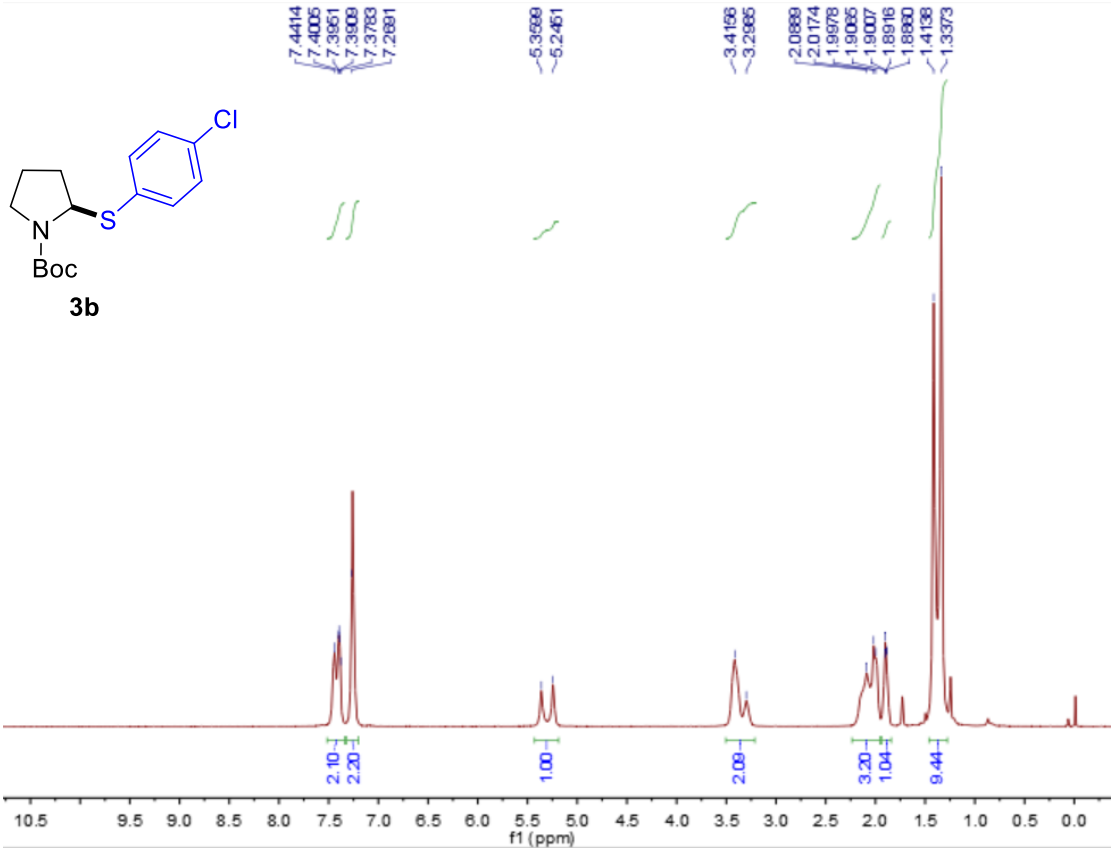
Yield: 26%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.63 (d, J = 7.7 Hz, 1H), 7.44 (s, 1H), 7.35 (ddd, J = 17.0, 5.7, 1.2 Hz, 3H), 7.30 – 7.24 (m, 4H), 7.23 – 7.18 (m, 1H), 4.24 (s, 2H), 1.65 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.69, 136.61, 130.20, 129.03, 126.60, 124.74, 124.47, 122.72, 119.43, 116.55, 115.45, 83.81, 29.76, 28.33. HRMS (ESI, m/z) calcd for $C_{20}H_{21}NO_2S$ $[M+Na]^+$ 362.1185, found 362.1191.

References

1. E. Ramesh, T. Guntreddi and A. K. Sahoo, *Eur. J. Org. Chem.*, **2017**, 4405-4413.
2. Y. Jin, H. Yang and H. Fu, *Chem. Commun.*, 2016, **52**, 12909-12912.
3. P. Beak and W. K. Lee, *Tetrahedron Lett.*, 1989, **30**, 197-200.
4. Y. Hu and R. Tang, *Synthetic Communication,* 2014, **44**, 2015-2050.

Supplementary spectra

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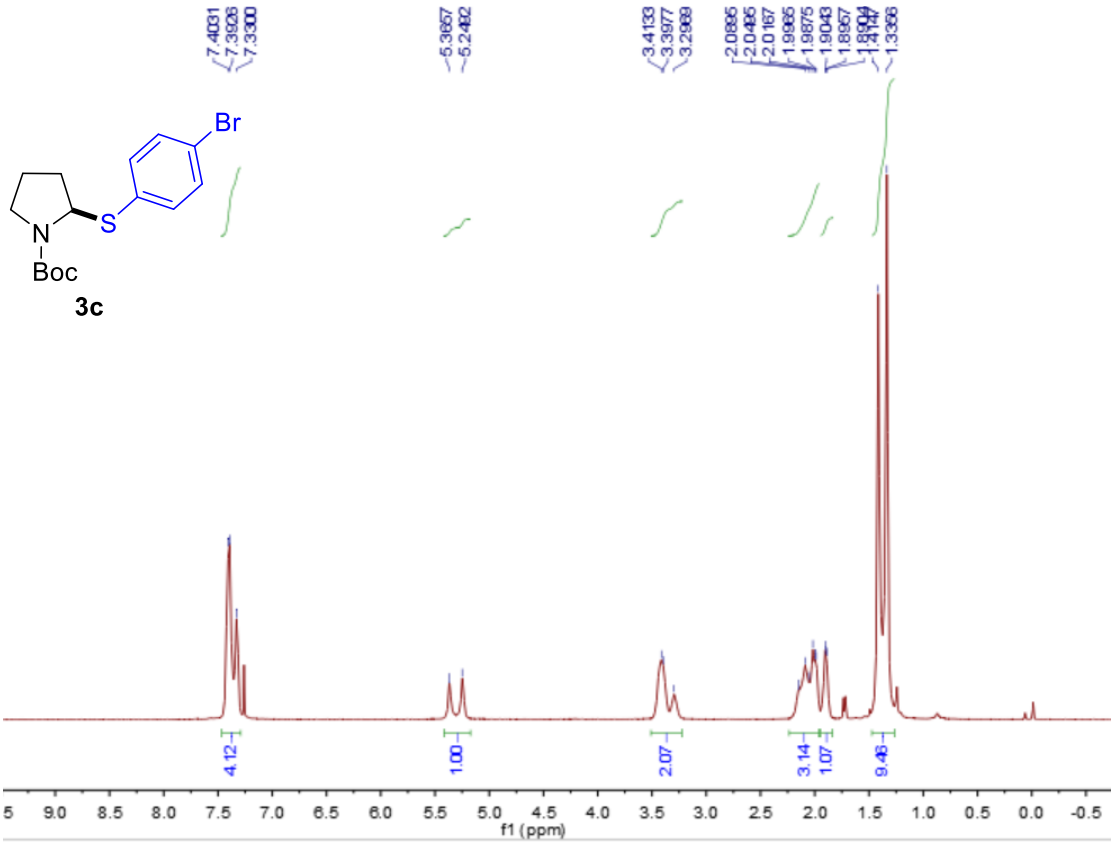
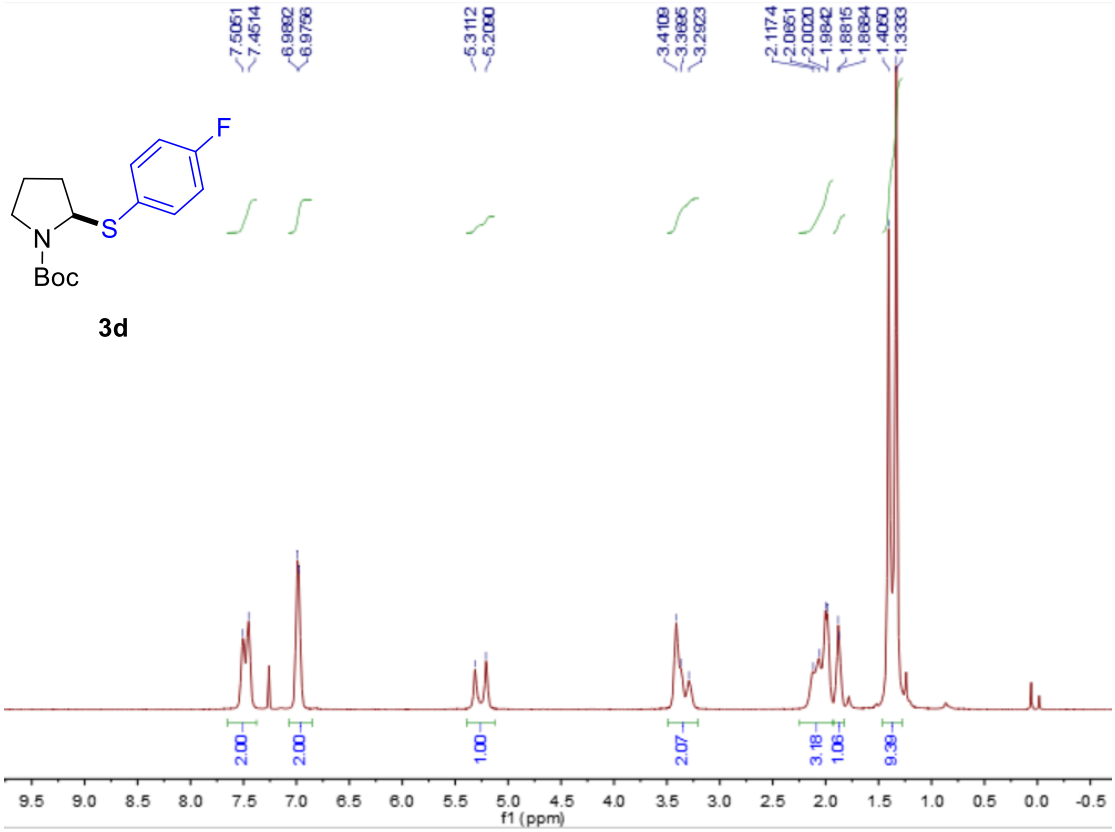
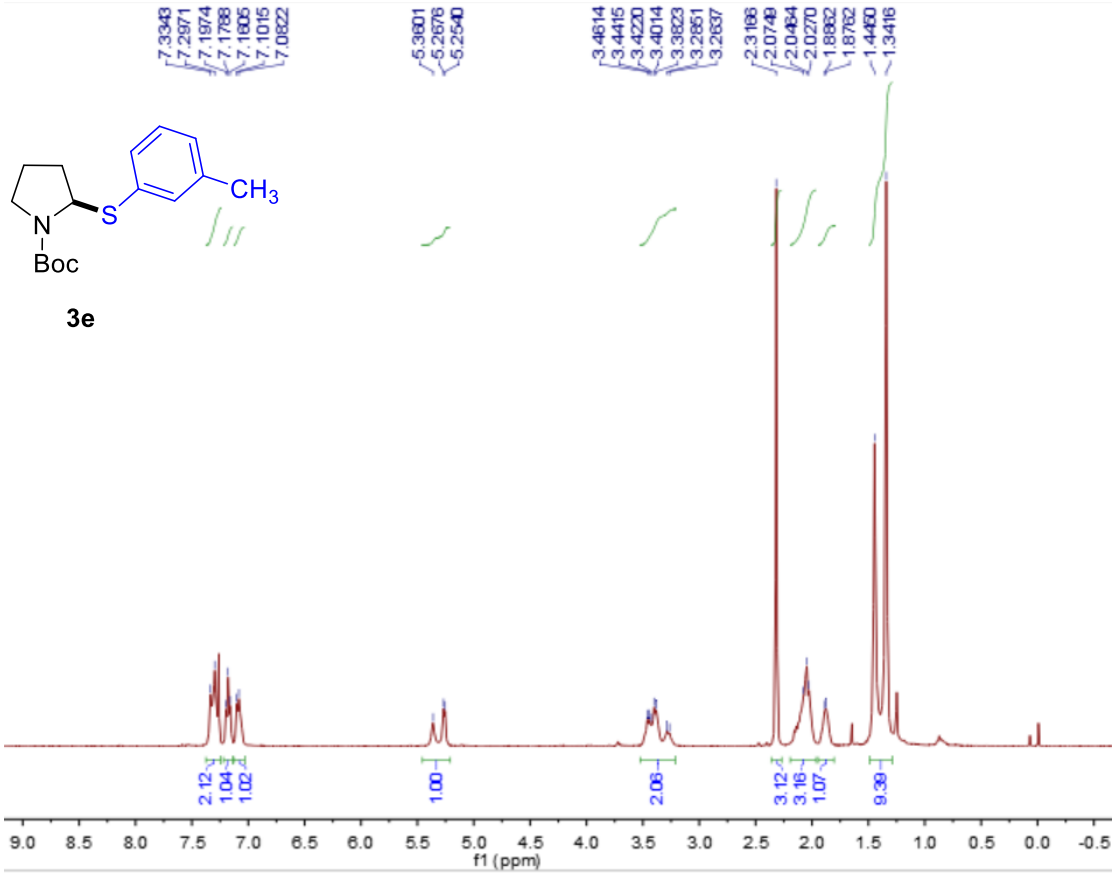
S
N
Boc
3b
7.4414
7.4005
7.3951
7.3909
7.3783
7.2691
5.3599
5.2451
3.4166
3.3985
2.0889
2.0174
1.9978
1.9065
1.9007
1.8916
1.8880
1.4138
1.3373
2.10
2.20
1.00
2.09
3.20
1.04
9.44
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Br
S
N
Boc
3c
7.4031
7.3926
7.3300
5.3657
5.2482
3.4133
3.3977
3.2988
2.0895
2.0485
2.0167
1.9965
1.9875
1.9043
1.8957
1.4147
1.3396
4.12
1.00
2.07
3.14
1.07
9.43
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


F
S
N
Boc
7.5051
7.4514
6.9892
6.9756
5.3112
5.2060
3.4109
3.3695
3.2923
2.1174
2.0851
2.0020
1.9842
1.8815
1.8694
1.4050
1.3333
2.00
2.00
1.00
2.07
3.18
1.06
9.39
f1 (ppm)

3d


CH3
S
N
Boc
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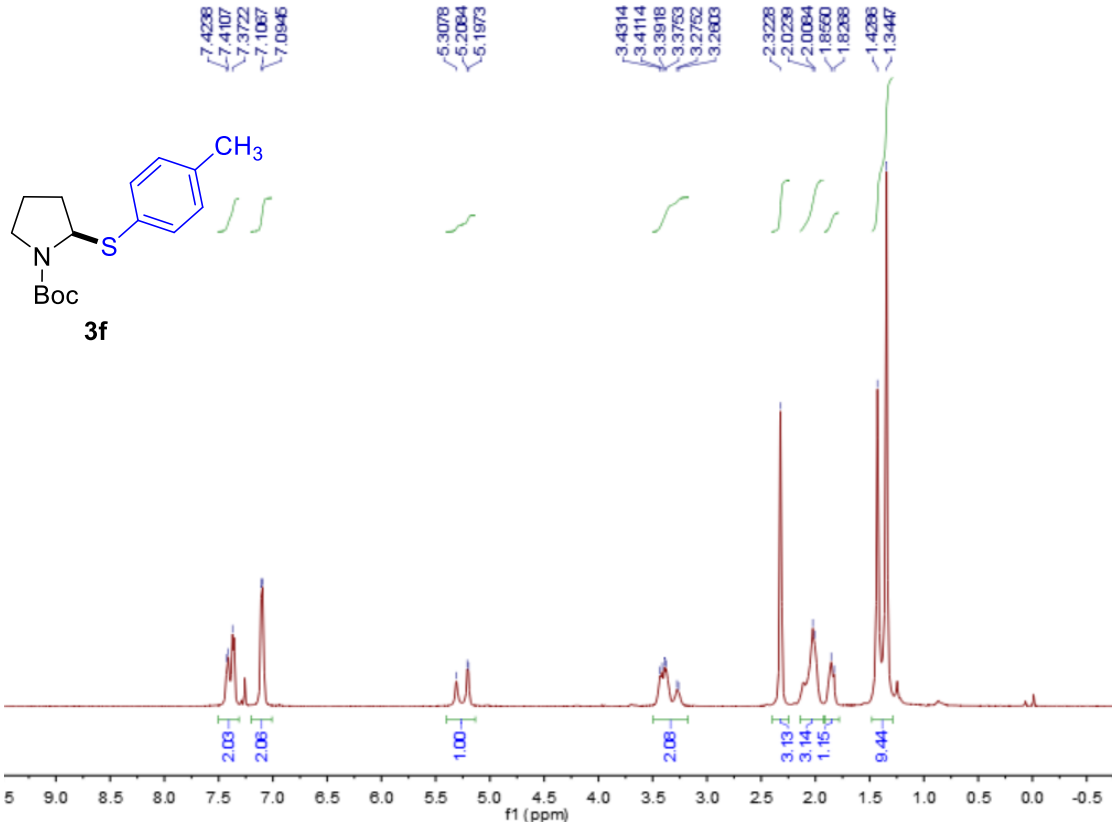
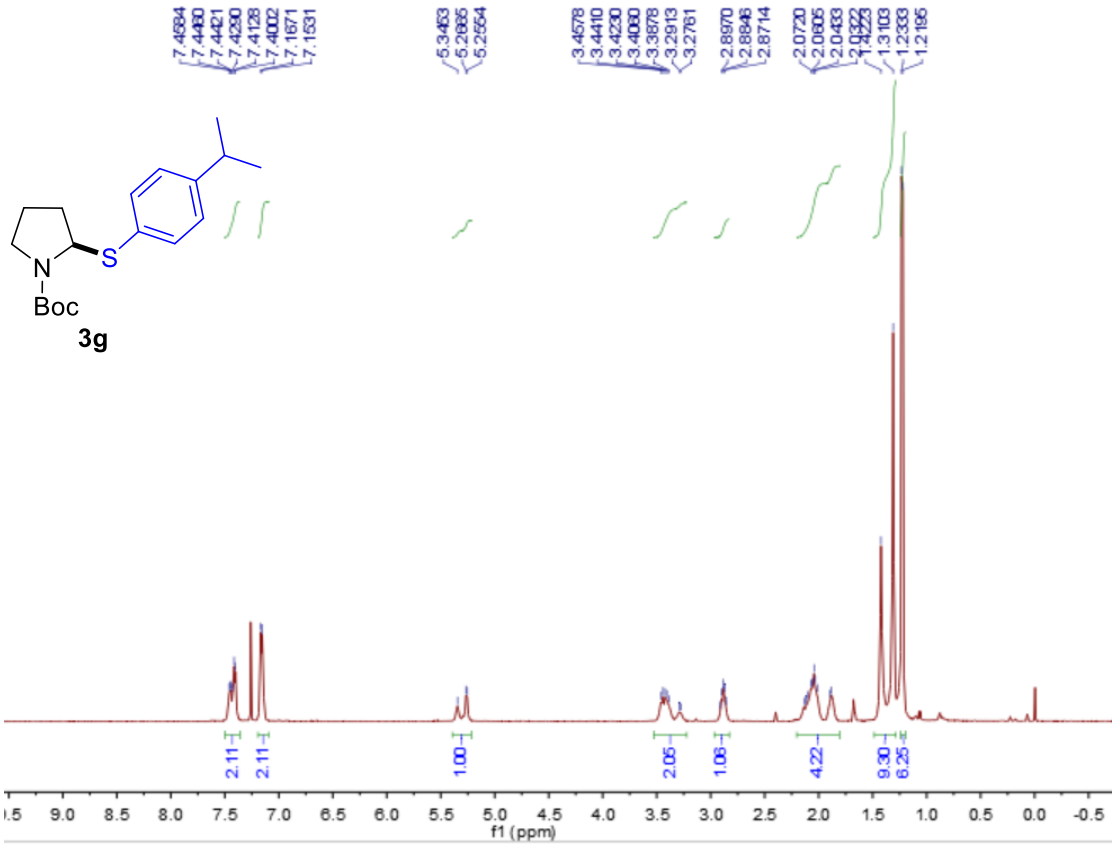
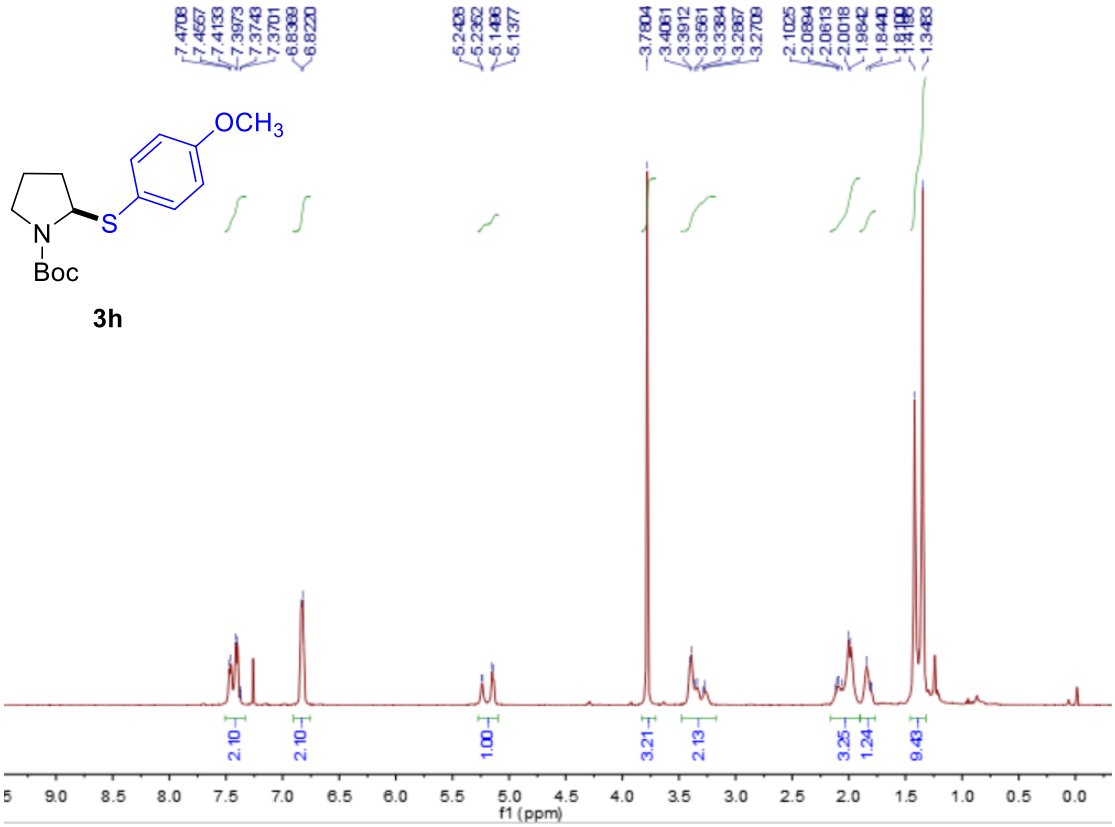
7.2971
7.1974
7.1788
7.1605
7.1015
7.0822
5.3601
5.2676
5.2540
3.4614
3.4415
3.4220
3.4014
3.3823
3.2851
3.2637
2.3166
2.0749
2.0464
2.0270
1.8862
1.8762
1.4460
1.3416
2.12
1.04
1.02
1.00
2.06
3.12
3.16
1.07
9.39
f1 (ppm)

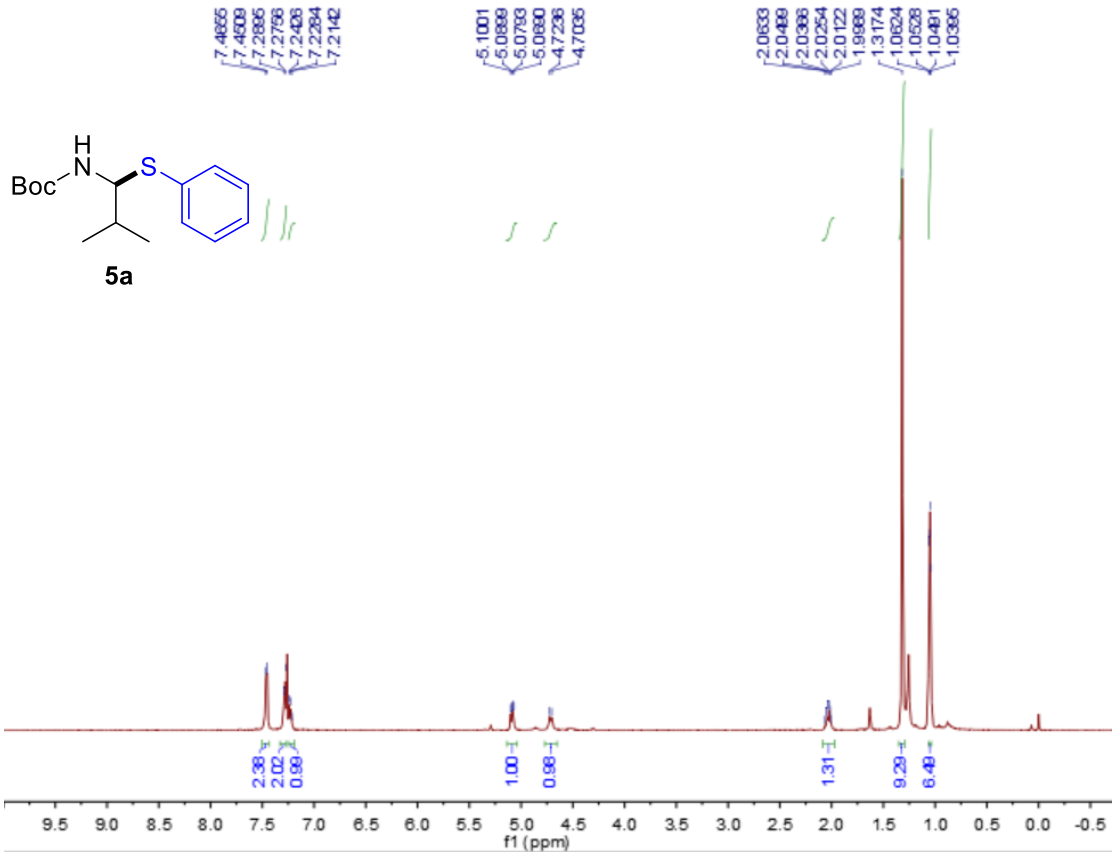
3e


CH3
S
N
Boc
3f
f1 (ppm)

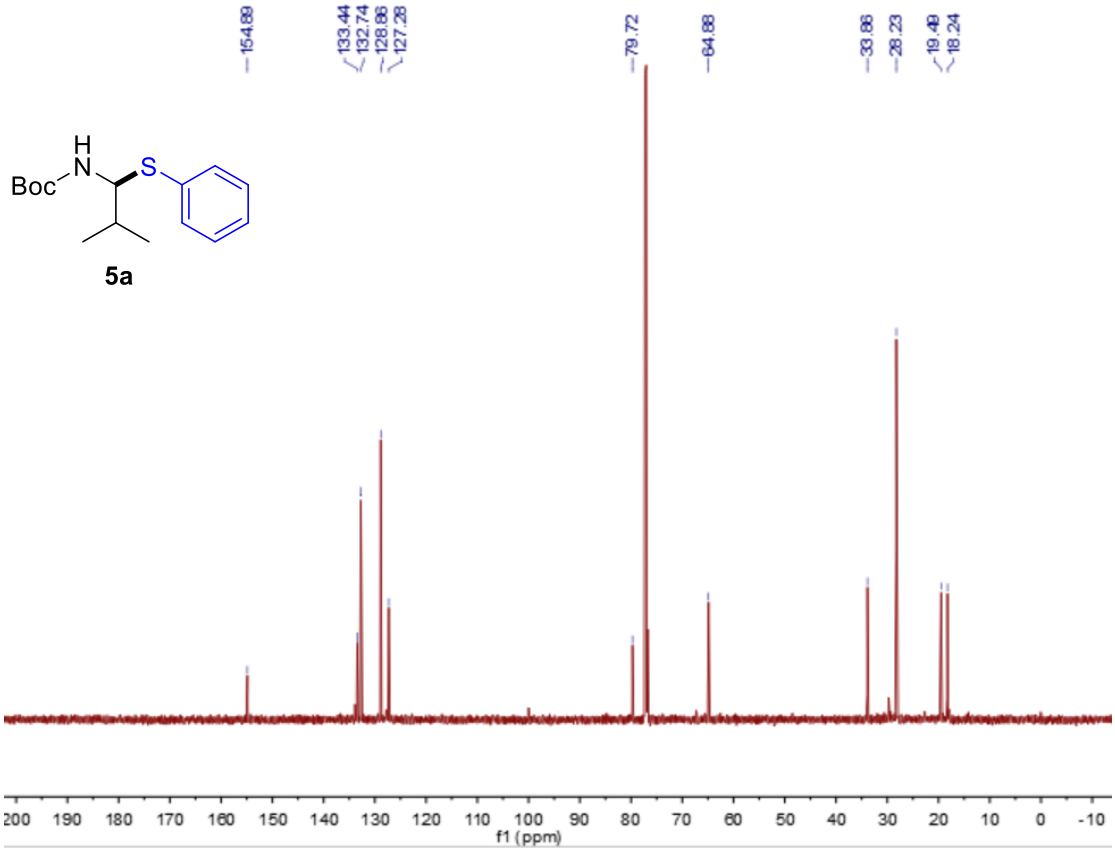

S
N
Boc
3g
f1 (ppm)



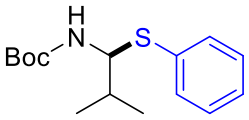
3h



5a

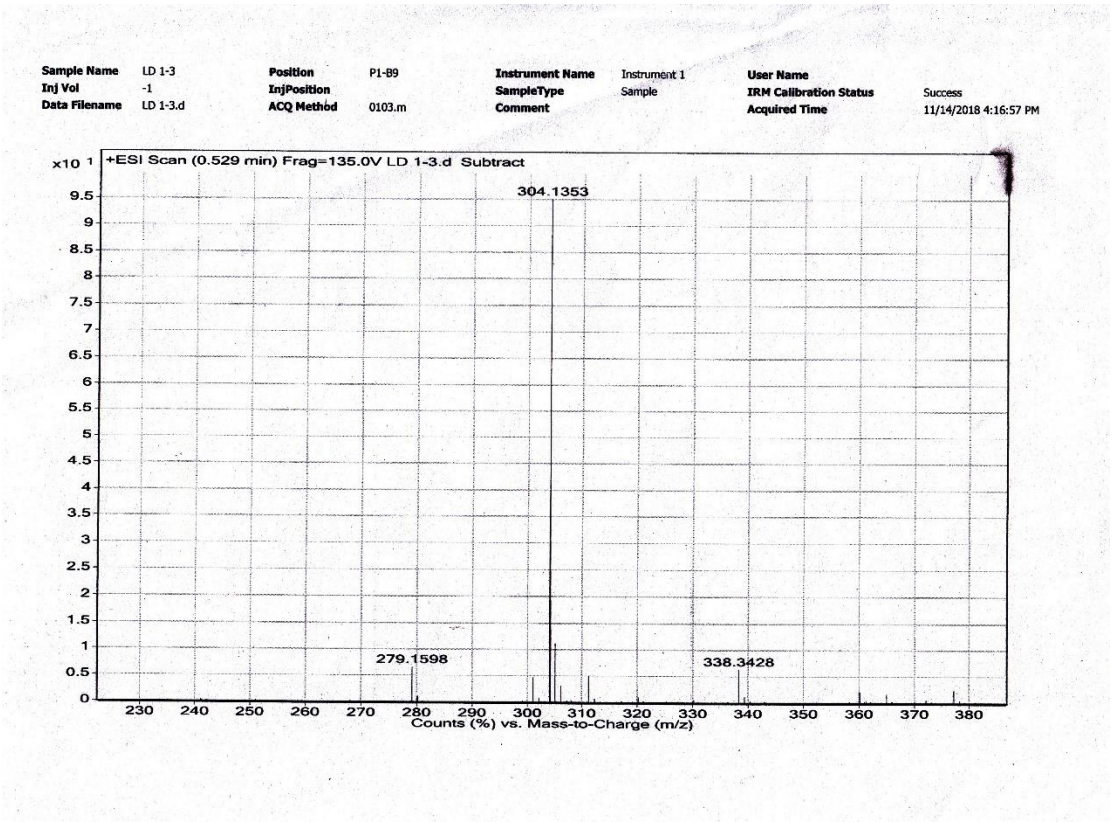


5a

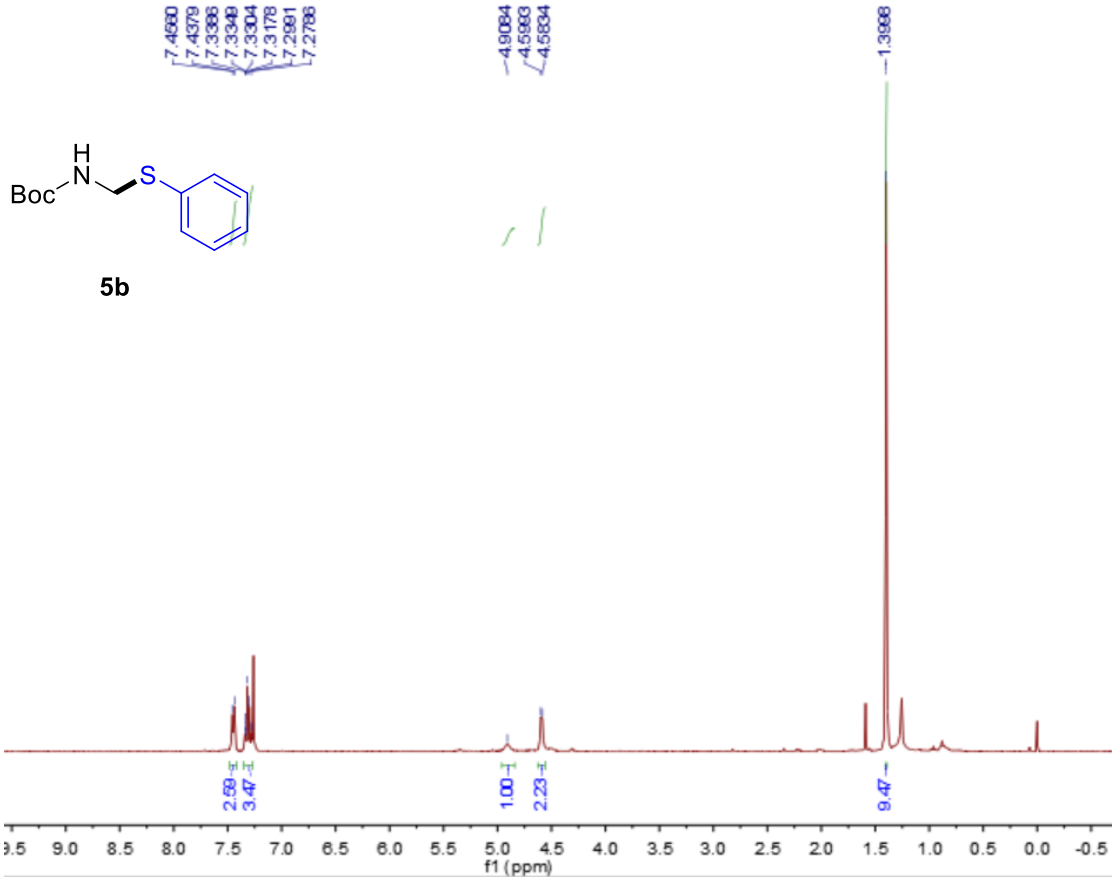


5a

Chemical Formula: $C_{15}H_{23}NO_2S$
Exact Mass: 281.14495
Molecular Weight: 281.41400
m/z: 281.14495 (100.0%), 282.14830 (16.2%), 283.14075 (4.5%), 283.15166 (1.2%)
Elemental Analysis: C, 64.02; H, 8.24; N, 4.98; O, 11.37; S, 11.39



HRMS (ESI, m/z) calcd for $C_{15}H_{23}NO_2S$ $[M+Na]^+$ 304.1347, found 304.1353.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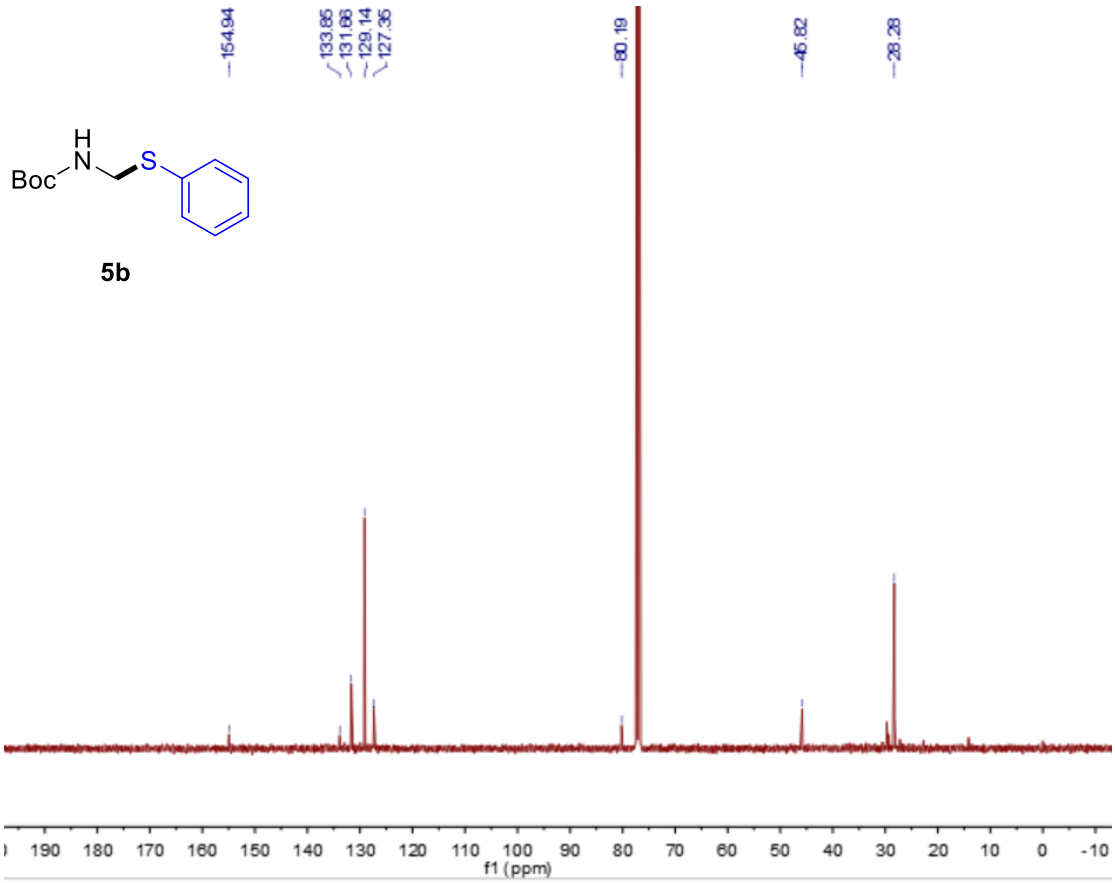
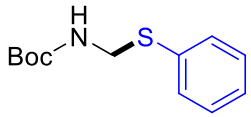
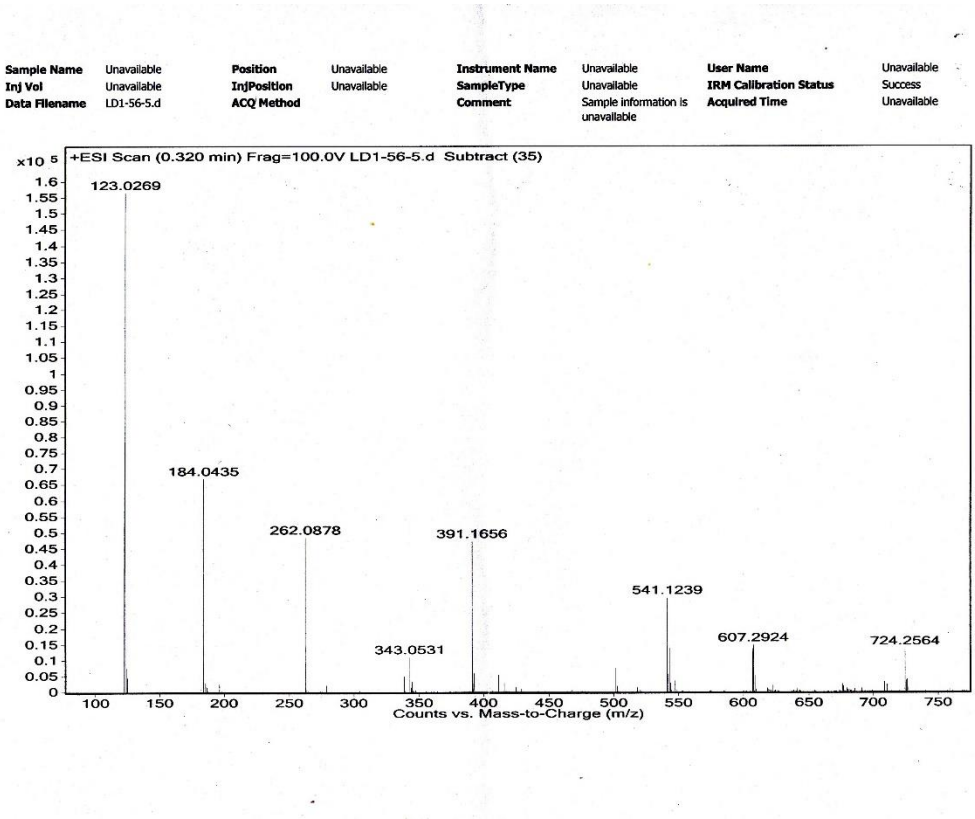
7.4379
7.3366
7.3349
7.3304
7.3178
7.2991
7.2788
4.9084
4.5993
4.5834
1.3998
Boc
H
N
S
5b
2.59
3.47
1.00
2.23
9.47
f1 (ppm)


154.94
133.85
131.66
129.14
127.35
80.19
45.82
29.28
Boc
H
N
S
5b
f1 (ppm)

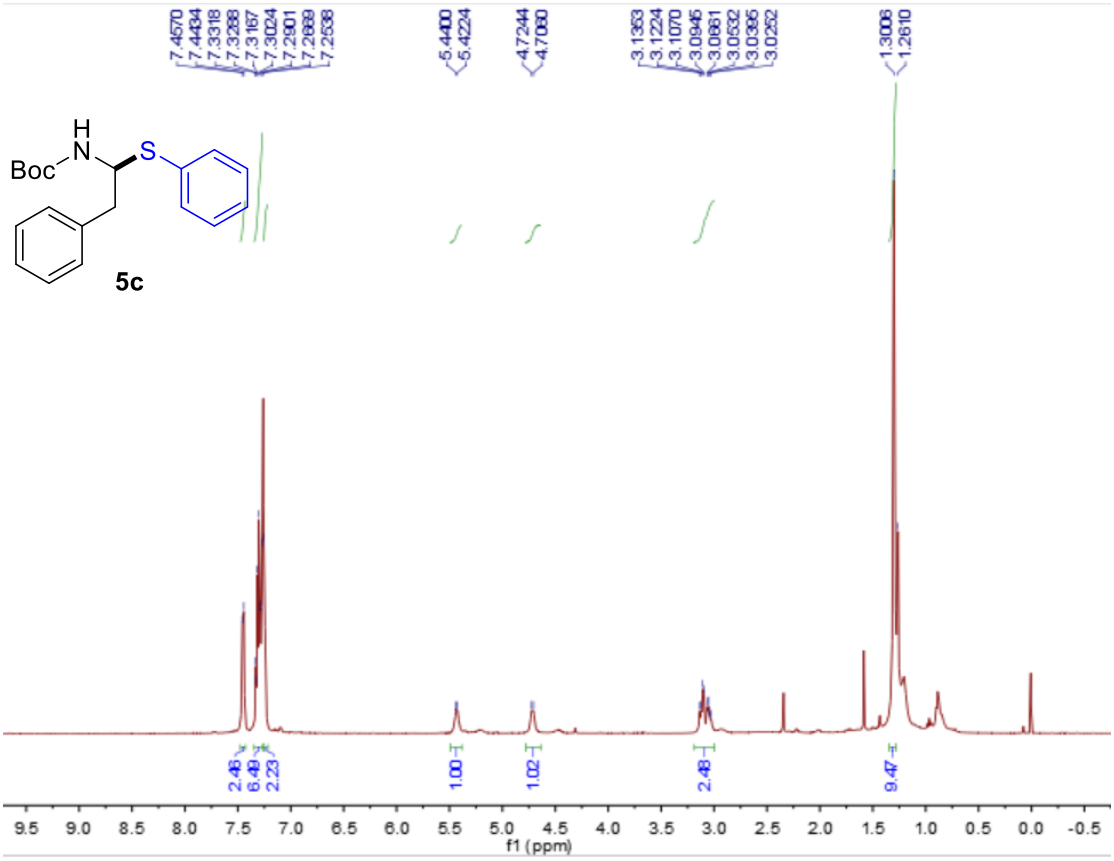


5b

Chemical Formula: $C_{12}H_{17}NO_2S$
Exact Mass: 239.09800
Molecular Weight: 239.33300
m/z: 239.09800 (100.0%), 240.10135 (13.0%), 241.09380 (4.5%)
Elemental Analysis: C, 60.22; H, 7.16; N, 5.85; O, 13.37; S, 13.40



HRMS (ESI, m/z) calcd for $C_{15}H_{17}NO_2S$ $[M+Na]^+$ 262.0878, found 262.0878.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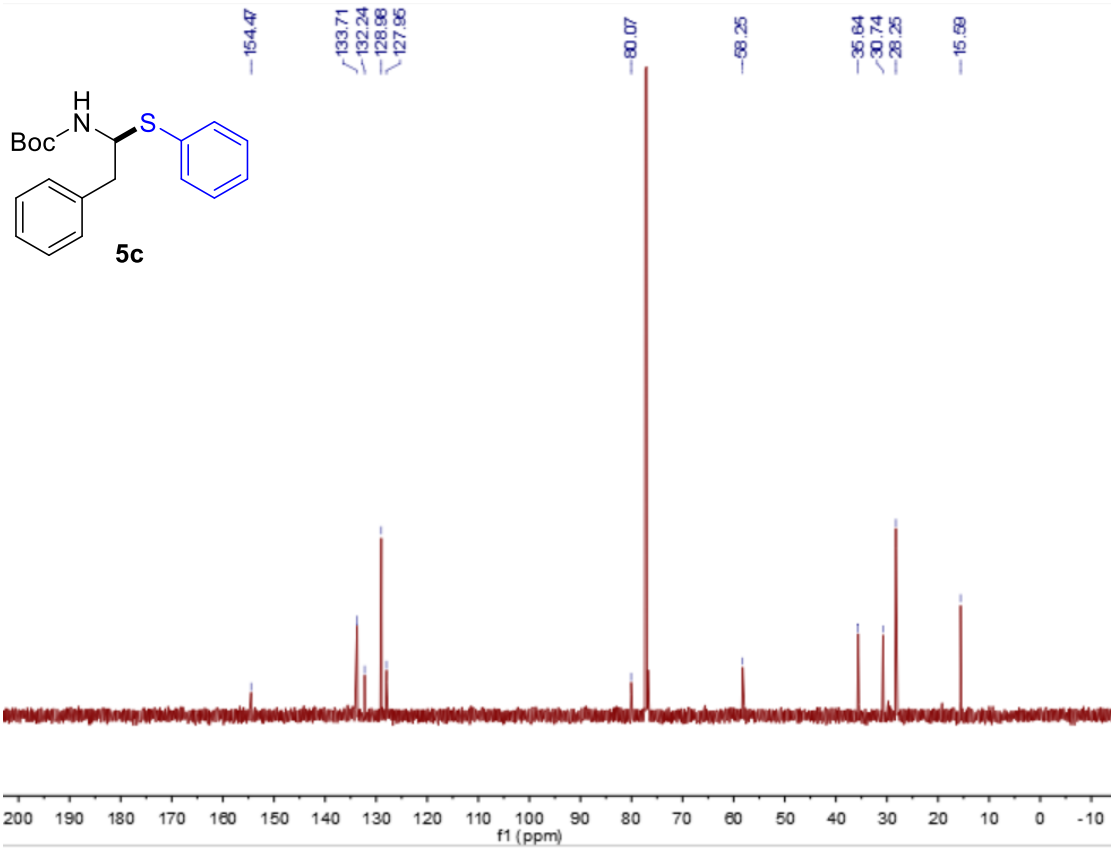
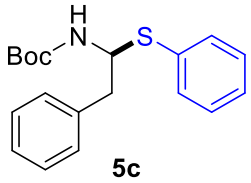
7.3288
7.3167
7.3024
7.2901
7.2689
7.2538
5.4400
5.4224
4.7244
4.7060
3.1363
3.1224
3.1070
3.0945
3.0861
3.0532
3.0385
3.0252
1.3006
1.2610
Boc
N
H
S
5c
2.46
6.48
2.23
1.00
1.02
2.48
9.47
f1 (ppm)


154.47
133.71
132.24
128.98
127.95
80.07
58.25
35.64
30.74
28.25
15.59
Boc
N
H
S
5c
f1 (ppm)



5c

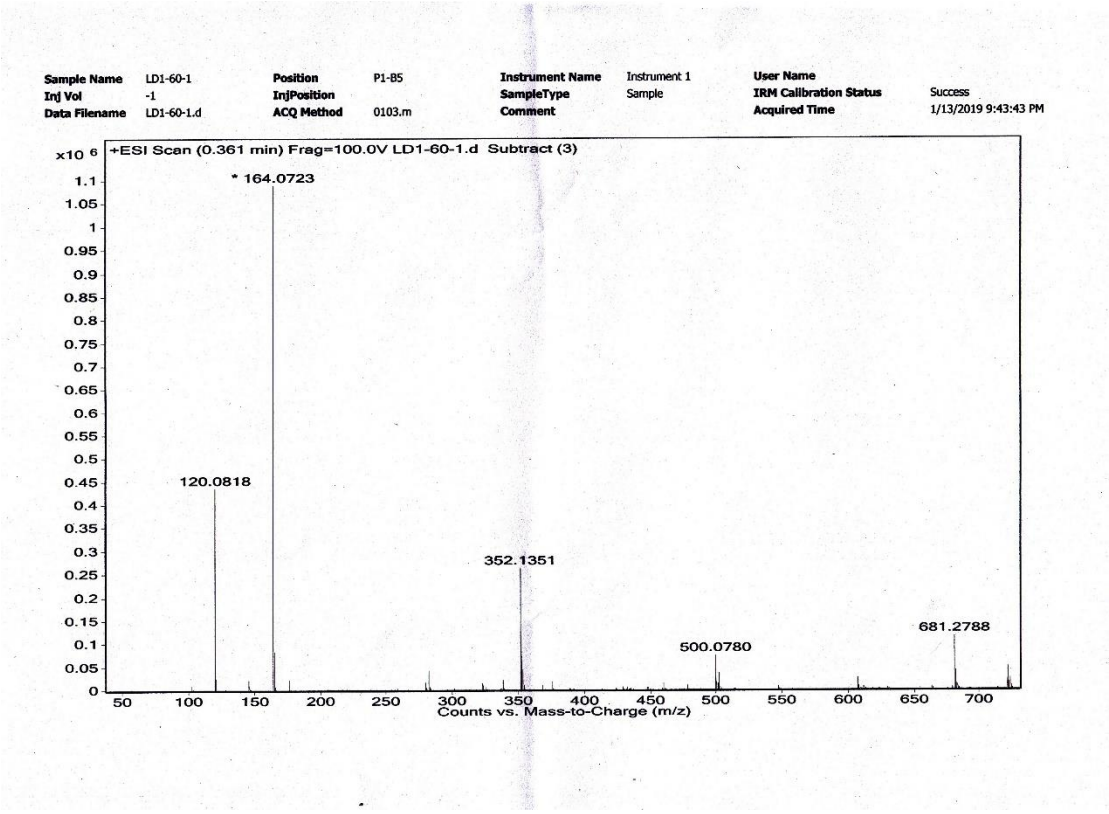
Chemical Formula: $C_{19}H_{23}NO_2S$

Exact Mass: 329.14495

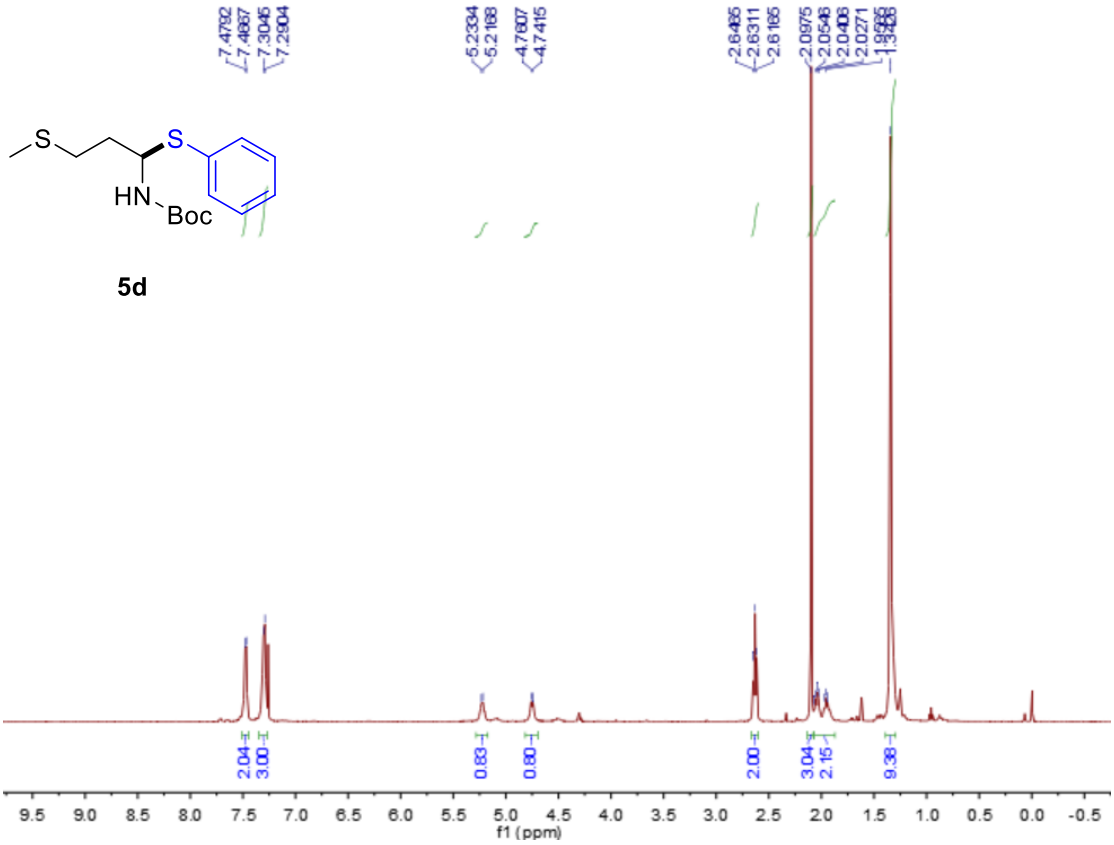
Molecular Weight: 329.45800

m/z: 329.14495 (100.0%), 330.14830 (20.5%), 331.14075 (4.5%), 331.15166 (2.0%)

Elemental Analysis: C, 69.27; H, 7.04; N, 4.25; O, 9.71; S, 9.73



HRMS (ESI, m/z) calcd for $C_{19}H_{23}NO_2S$ $[M+Na]^+$ 352.1347, found 352.1348.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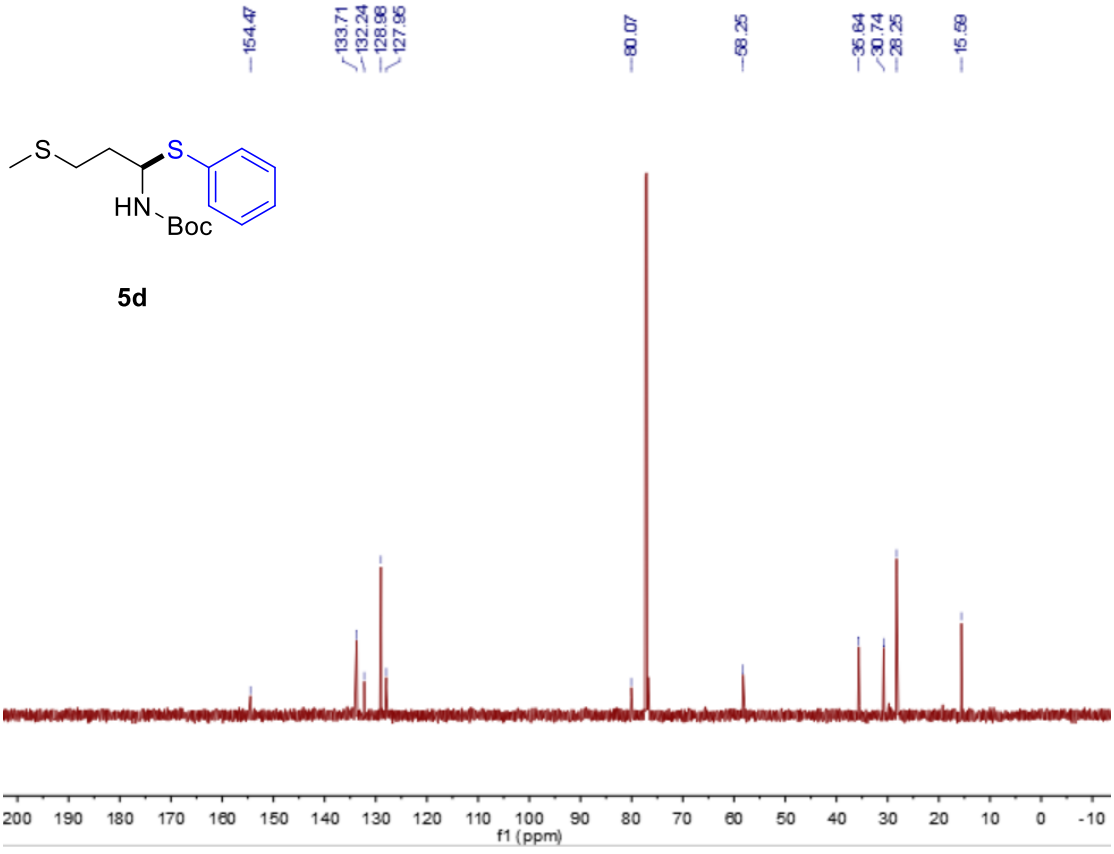
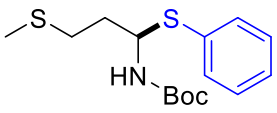
7.2904
5.2334
5.2168
4.7607
4.7415
2.6435
2.6311
2.6185
2.0975
2.0548
2.0406
2.0271
1.9555
1.3328
S
S
HN
Boc
2.04
3.00
0.83
0.80
2.00
3.04
2.15
9.38
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

5d

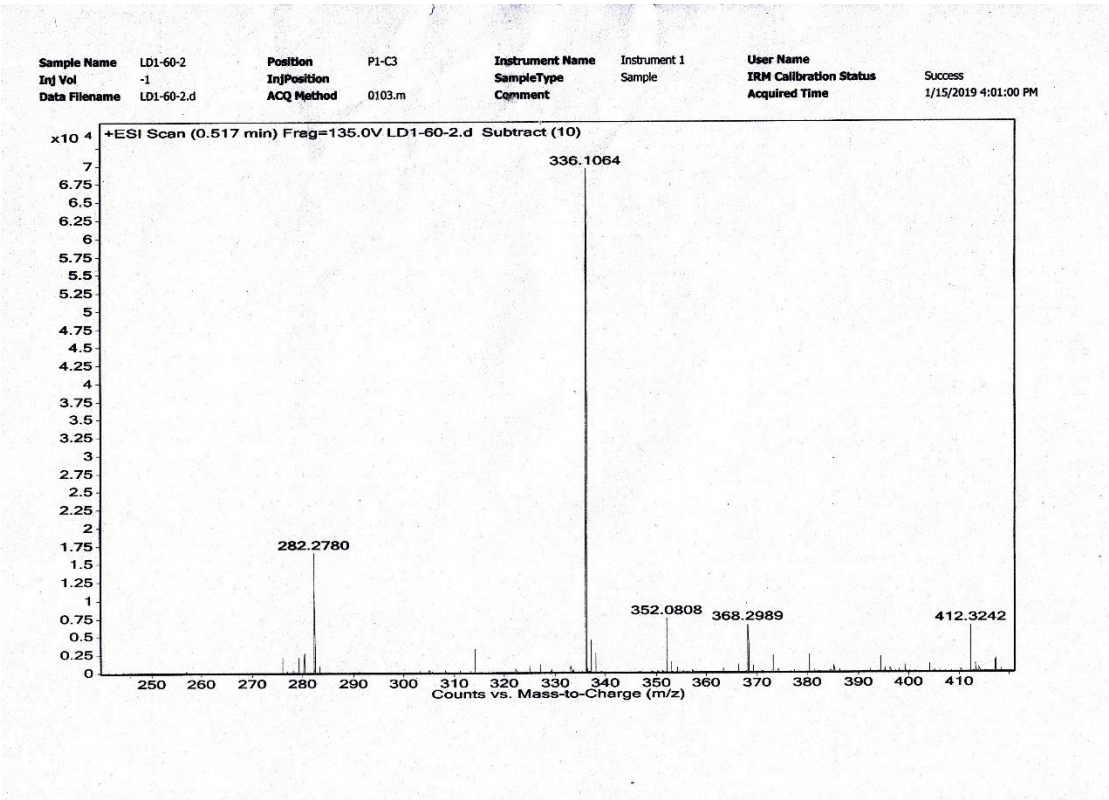

154.47
133.71
132.24
128.98
127.95
80.07
68.25
35.64
30.74
28.25
15.59
S
S
HN
Boc
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

5d

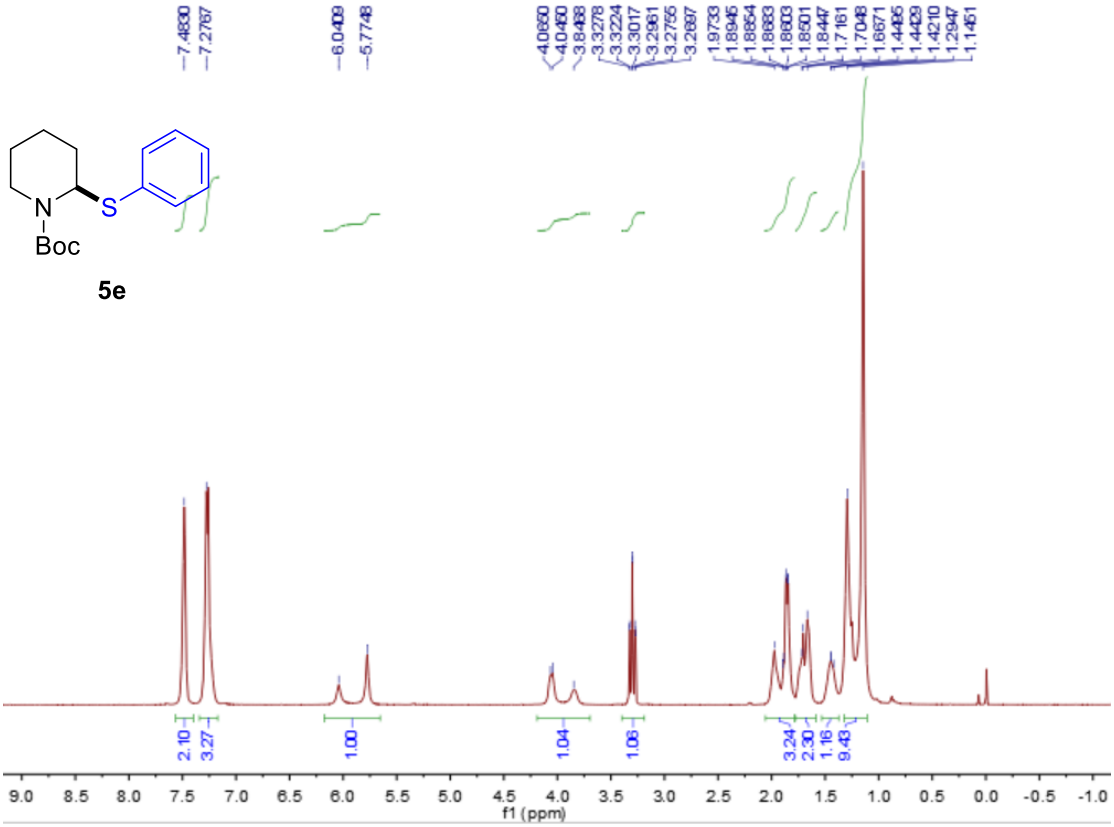


5d

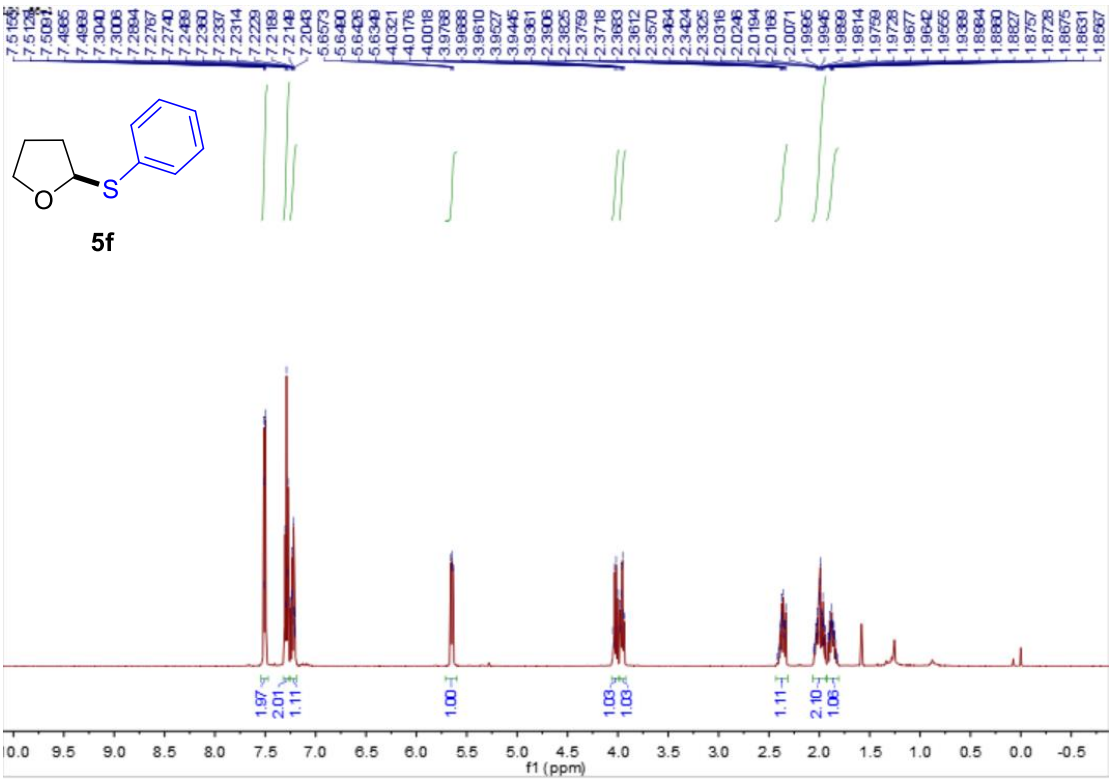
Chemical Formula: $C_{15}H_{23}NO_2S_2$
Exact Mass: 313.11702
Molecular Weight: 313.47400
m/z: 313.11702 (100.0%), 314.12038 (16.2%), 315.11282 (4.5%), 315.11282 (4.5%), 316.11617 (1.5%), 315.12373 (1.2%)
Elemental Analysis: C, 57.47; H, 7.40; N, 4.47; O, 10.21; S, 20.45



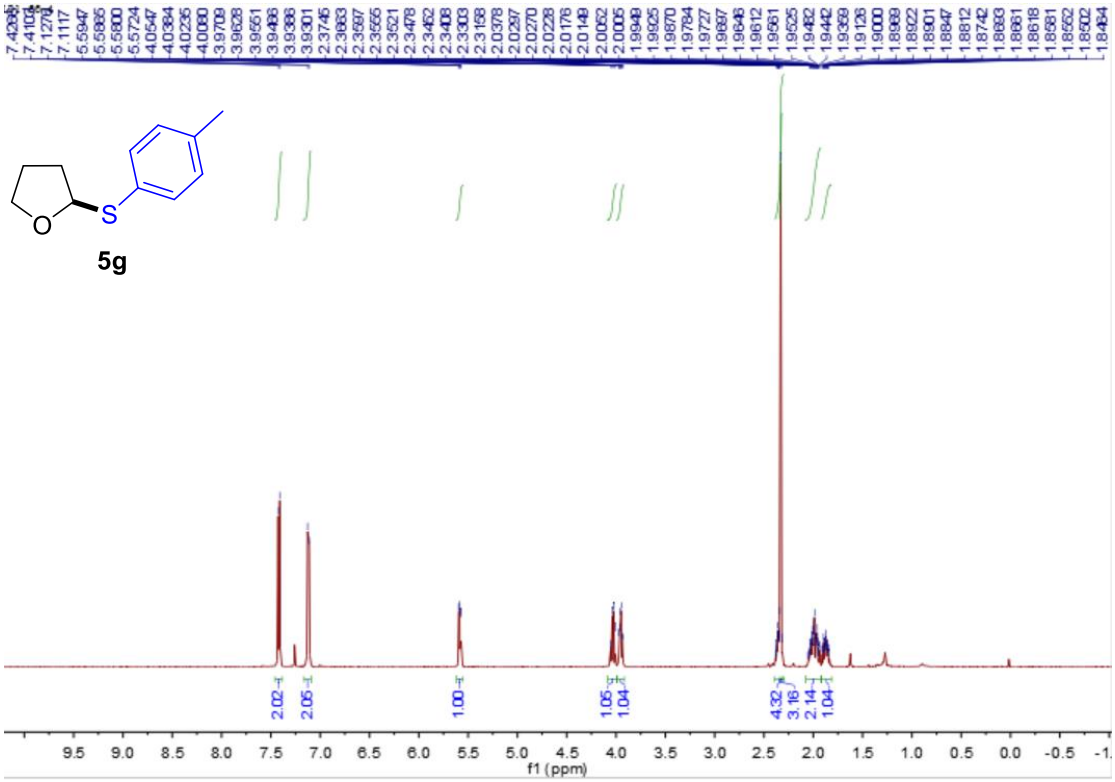
HRMS (ESI, m/z) calcd for $C_{15}H_{23}NO_2S_2$ $[M+Na]^+$ 330.1068, found 330.1064.



5e



5f


O
S
5g
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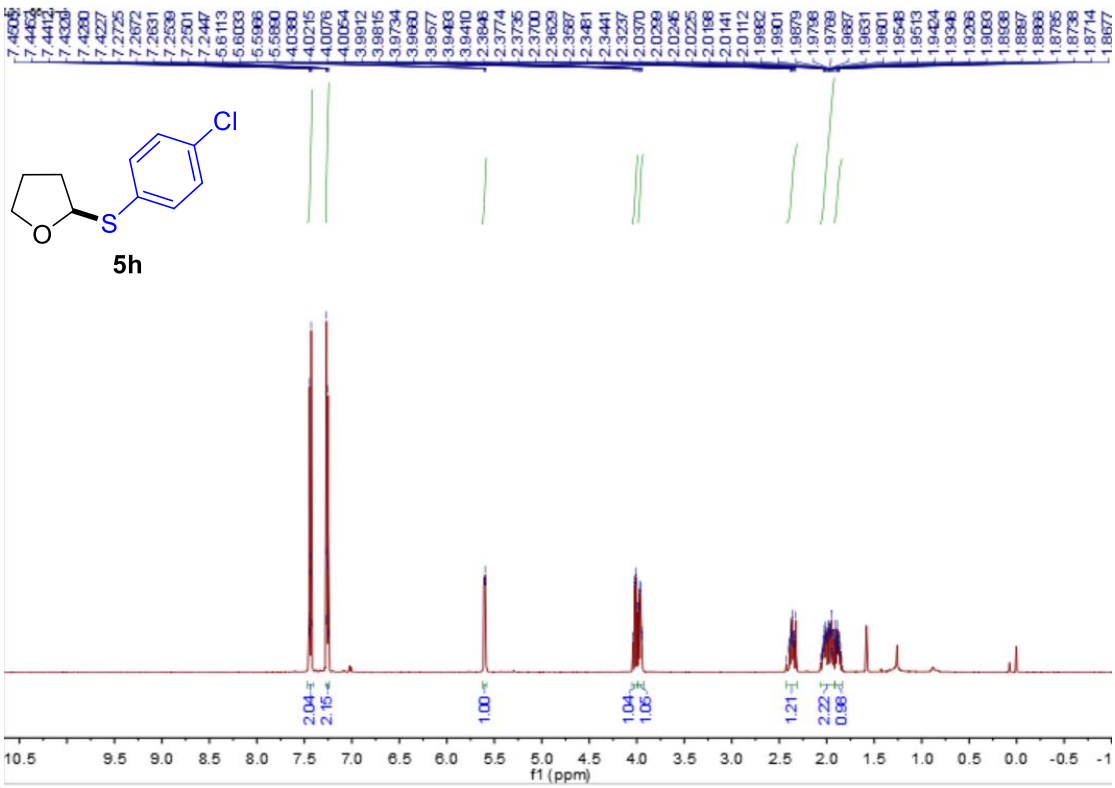
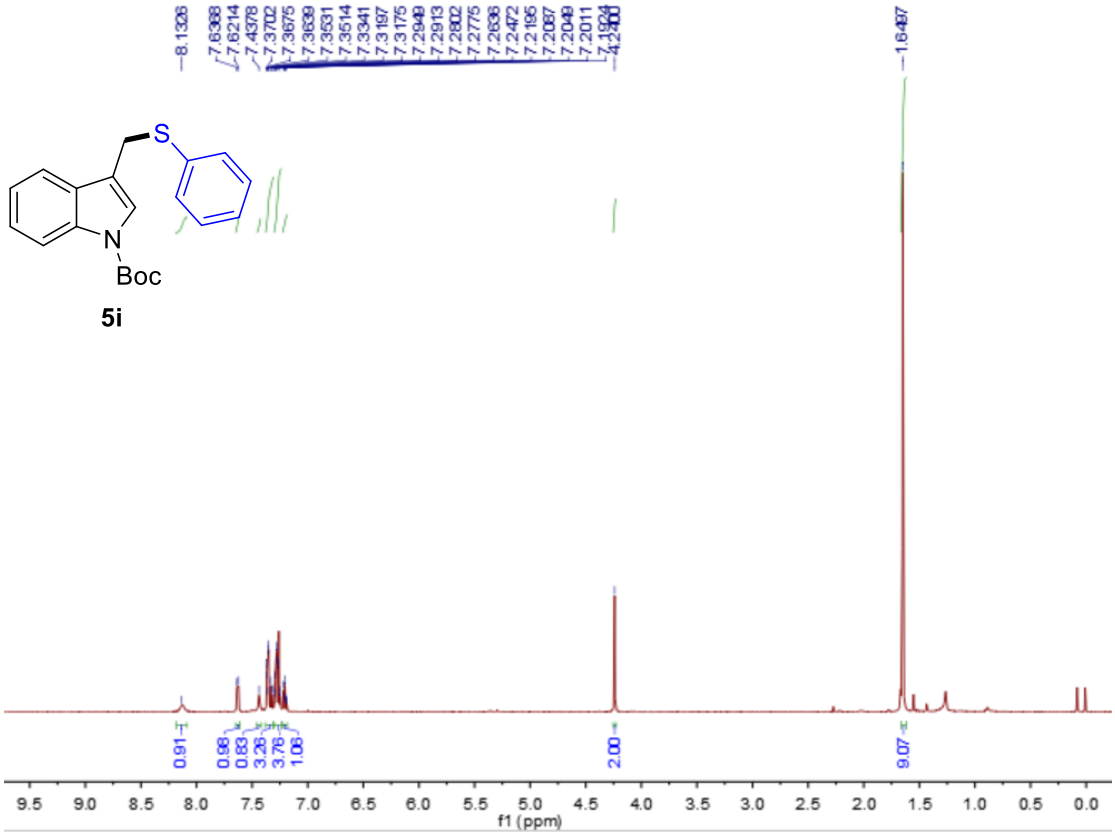
2.05
1.00
1.05
1.04
4.32
3.16
2.14
1.04
f1 (ppm)


Cl
O
S
5h
2.04
2.15
1.00
1.04
1.05
1.21
2.22
0.98
f1 (ppm)


S
N
Boc
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7.6388
7.6214
7.4378
7.3702
7.3675
7.3639
7.3531
7.3514
7.3341
7.3197
7.3175
7.2949
7.2913
7.2802
7.2775
7.2638
7.2472
7.2195
7.2057
7.2049
7.2011
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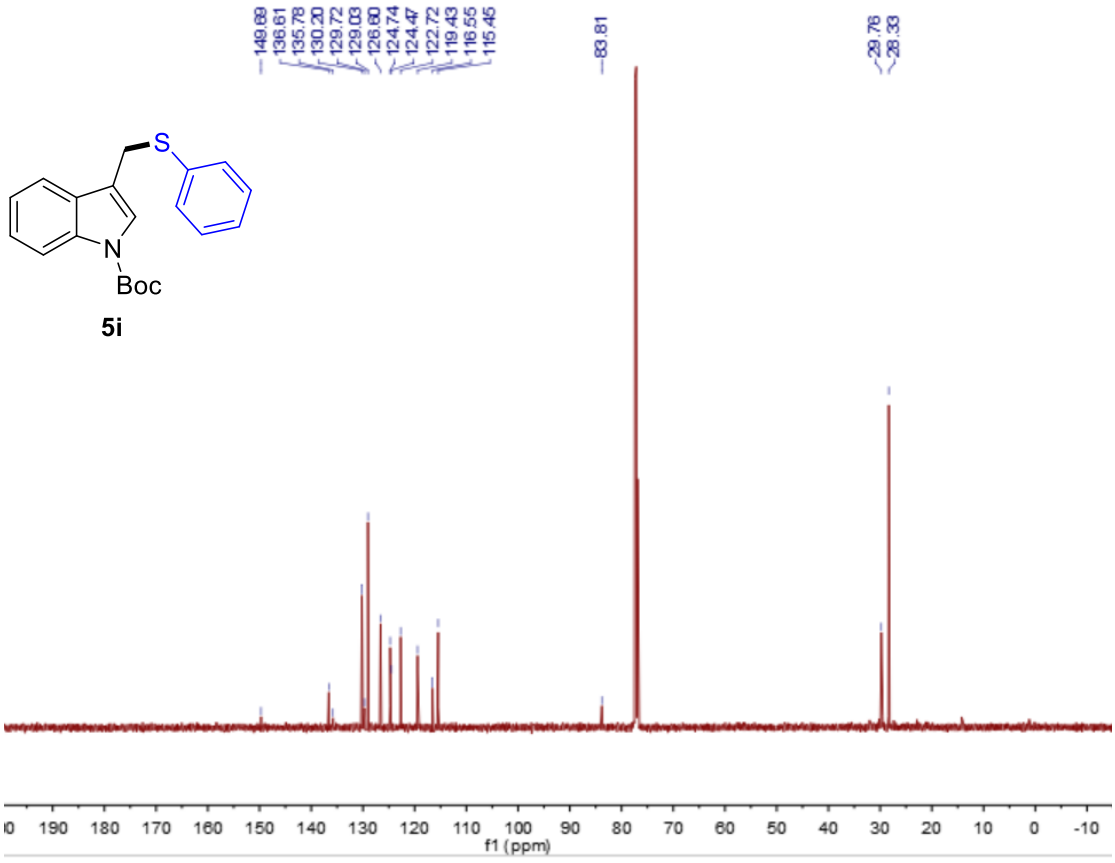
0.98
0.83
3.26
3.76
1.08
2.00
9.07
f1 (ppm)

5i


S
N
Boc
149.69
136.61
135.78
130.20
129.72
129.03
126.60
124.74
124.47
122.72
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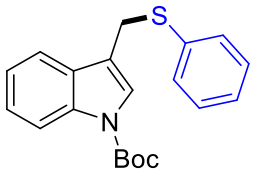
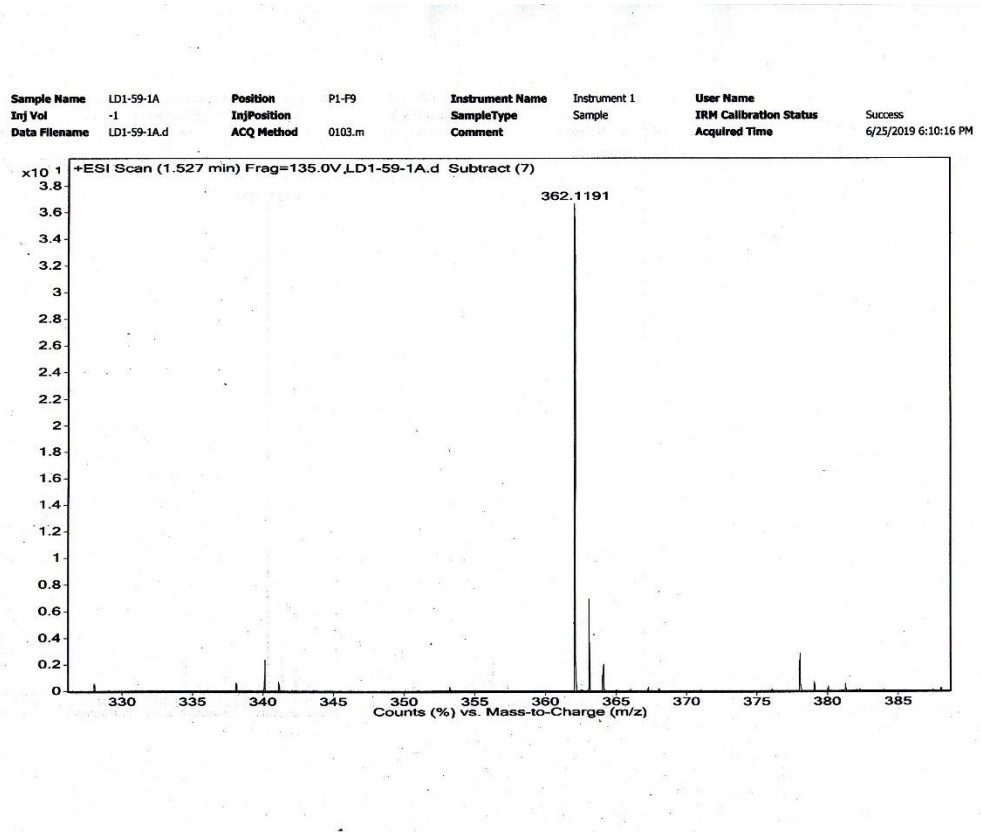
116.55
115.45
83.81
29.76
28.33
f1 (ppm)

5i



5i

Chemical Formula: $C_{20}H_{21}NO_2S$
Exact Mass: 339.12930
Molecular Weight: 339.45300
m/z: 339.12930 (100.0%), 340.13265 (21.6%), 341.12510 (4.5%), 341.13601 (2.2%)
Elemental Analysis: C, 70.77; H, 6.24; N, 4.13; O, 9.43; S, 9.44



HRMS (ESI, m/z) calcd for $C_{20}H_{21}NO_2S$ $[M+Na]^+$ 362.1185, found 362.1191.