ORGANOCATALYZED REARRANGEMENT OF S-(2-OXOALKYL) THIOENOATES

David M. Leace, Matthew R. Straub, Benjamin A. Matz, and Vladimir B. Birman*

Department of Chemistry, Washington University, Campus Box 1134, One Brookings Drive, Saint Louis, Missouri 63130

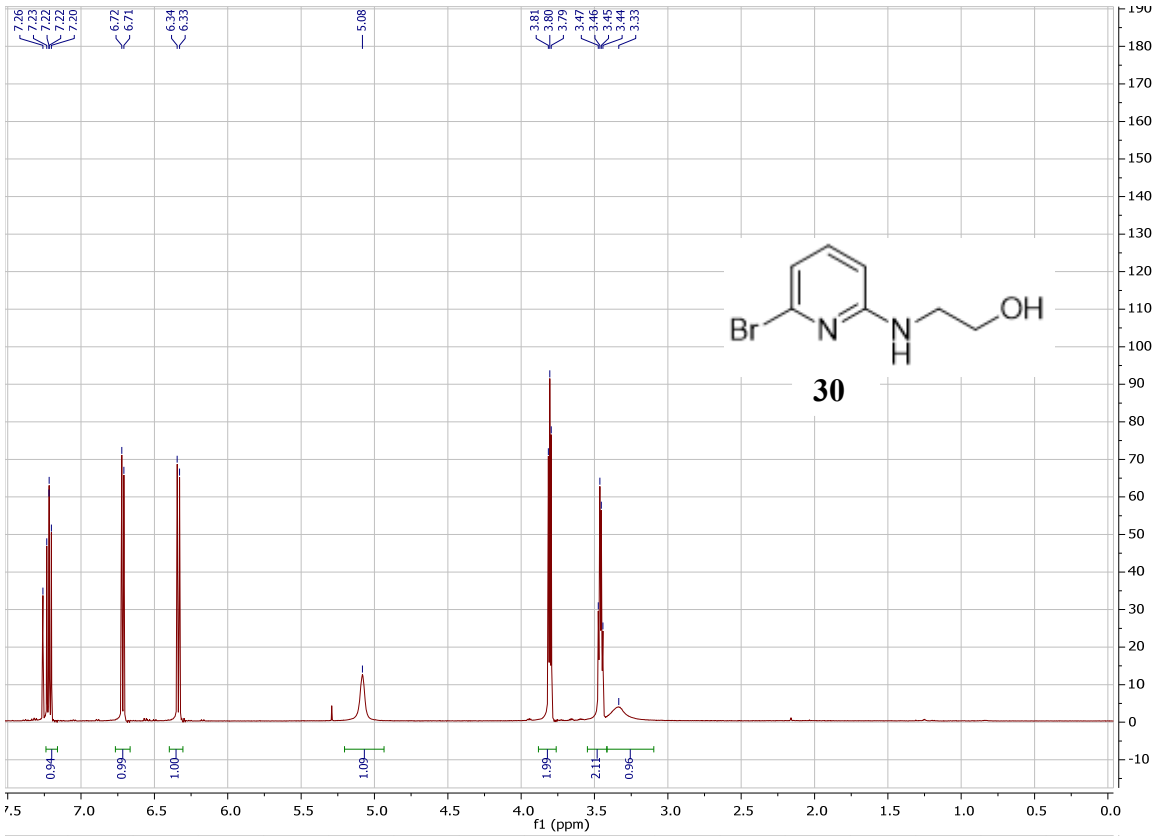
* birman@wustl.edu

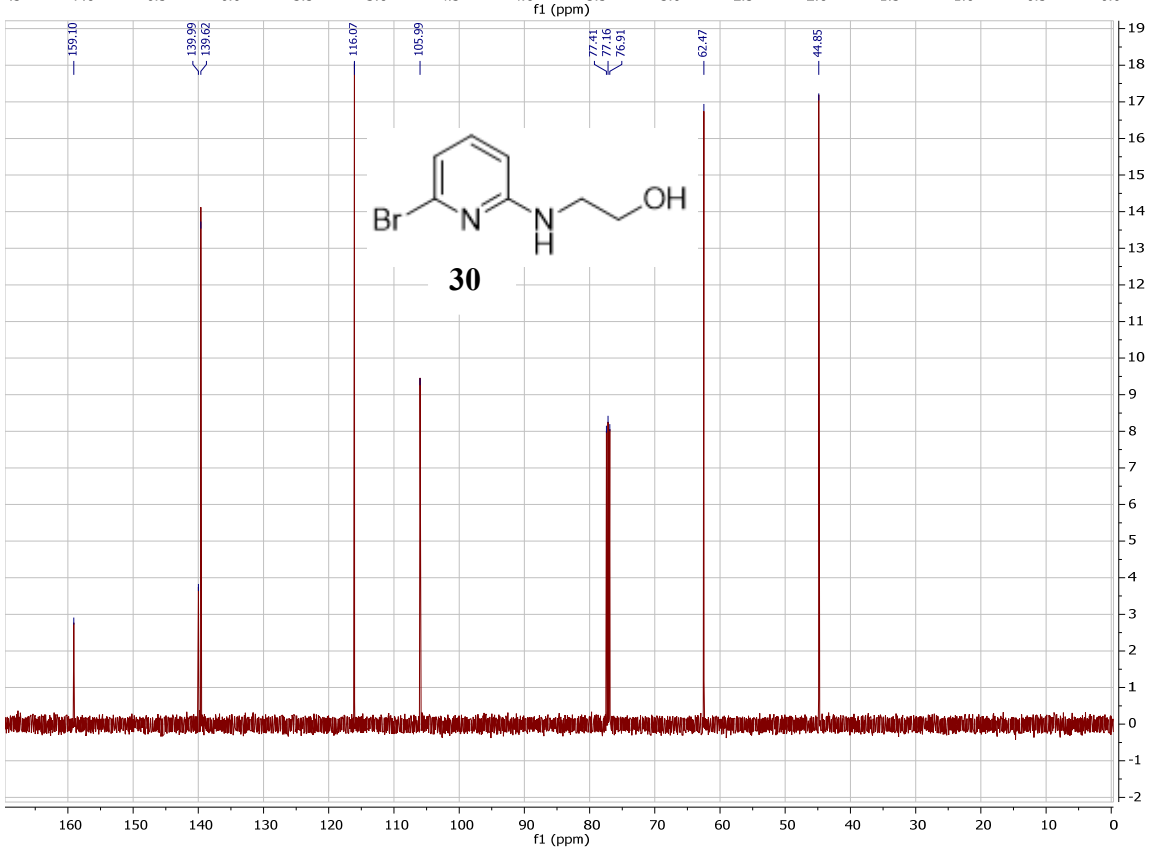
SUPPORTING INFORMATION

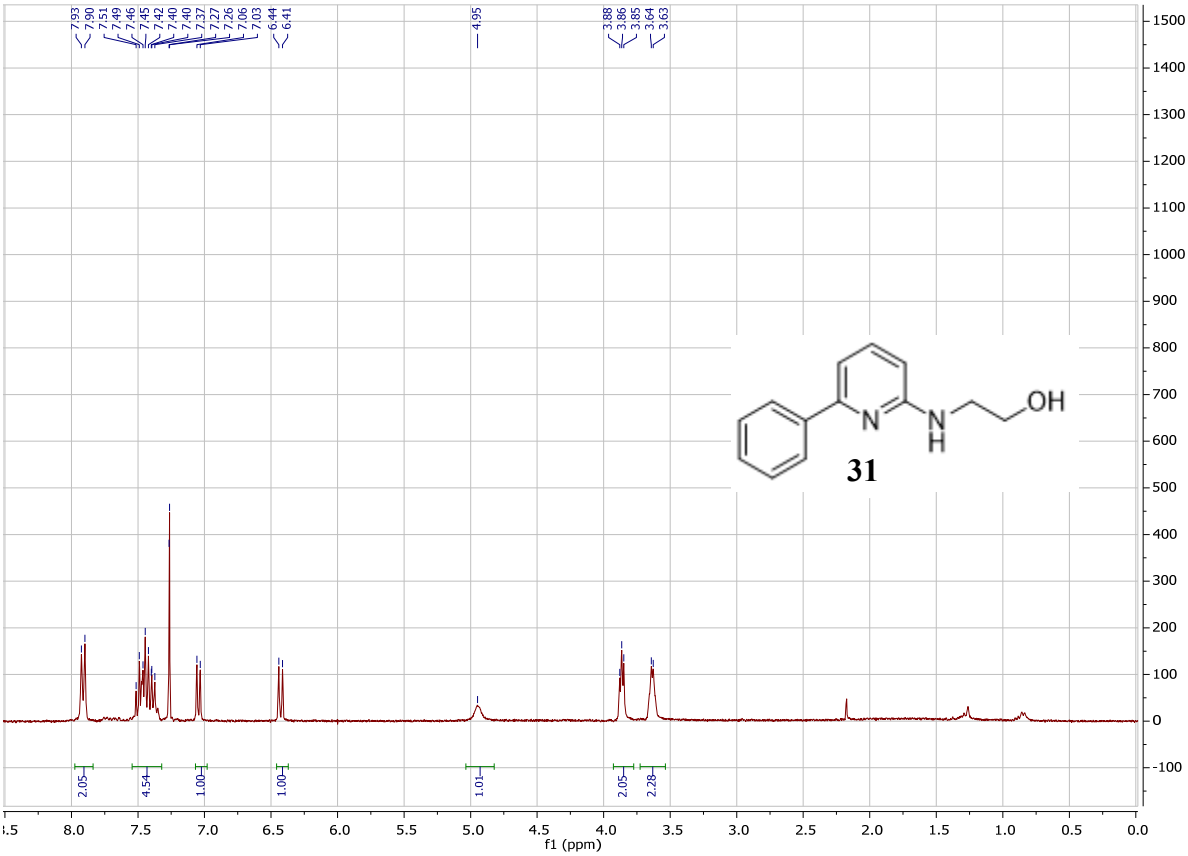
TABLE OF CONTENTS

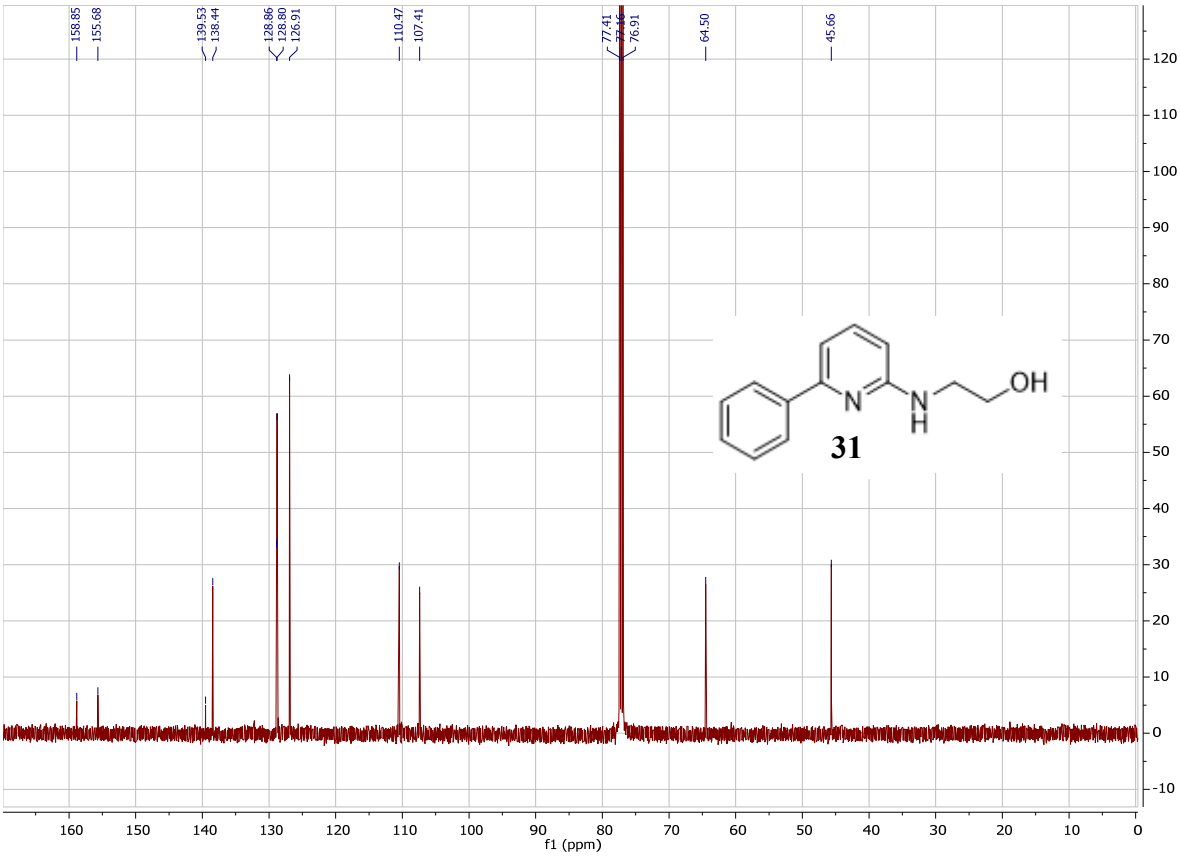
		Pages
1.	^{1}H and ^{13}C NMR spectra	S-2
2	HPLC data	S-44

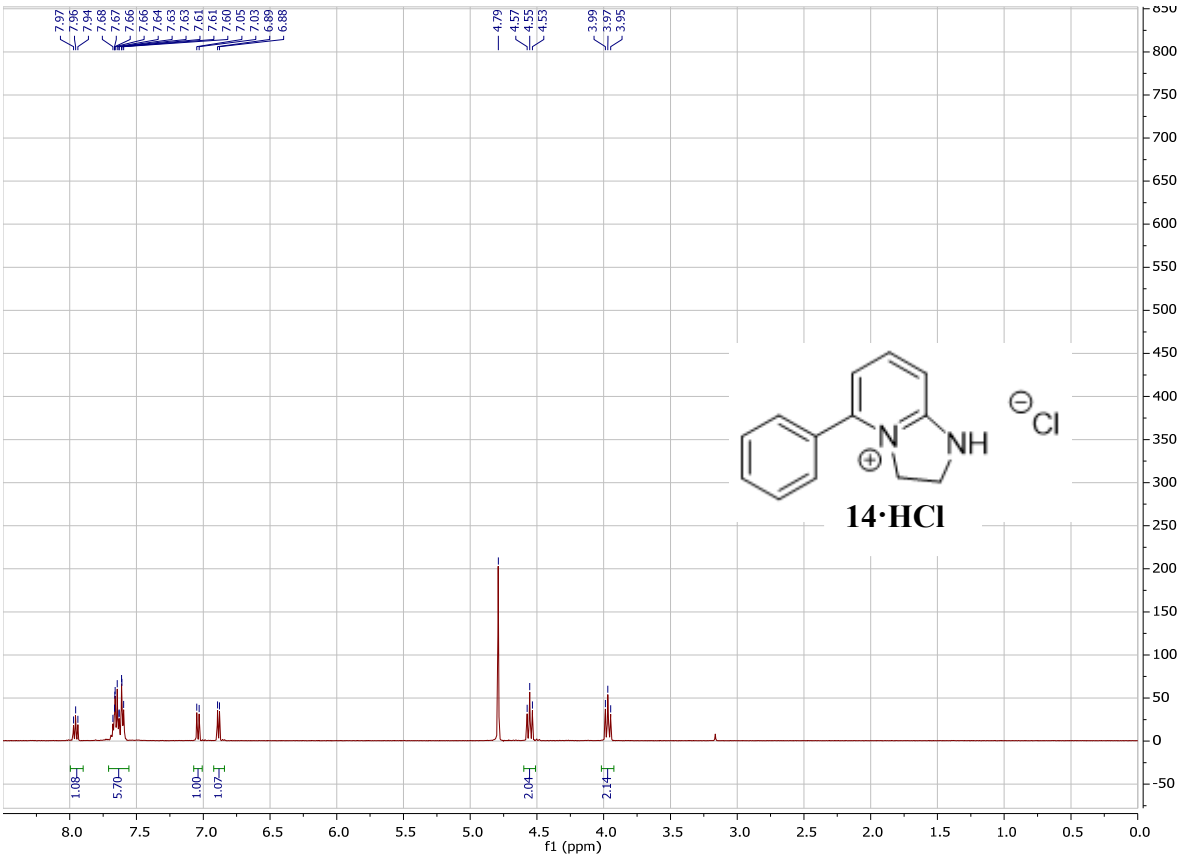
1. ^{1}H and ^{13}C NMR spectra

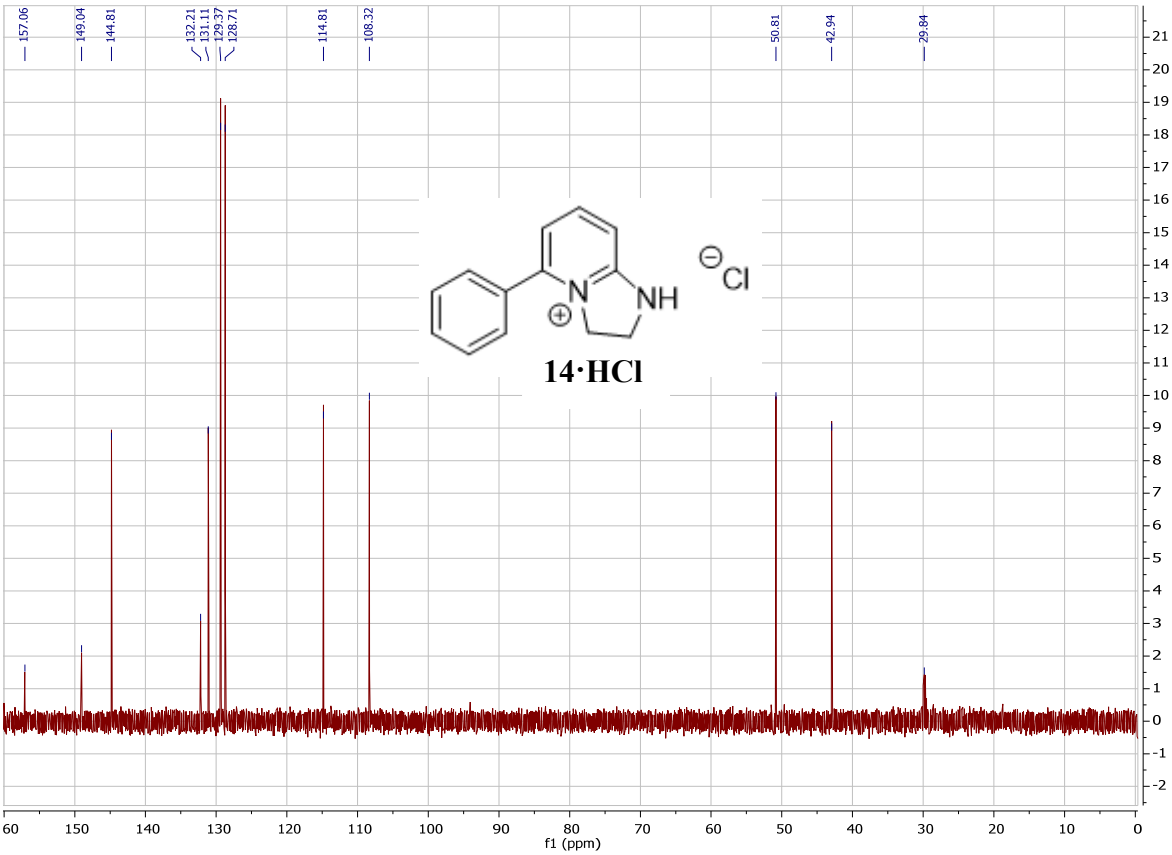


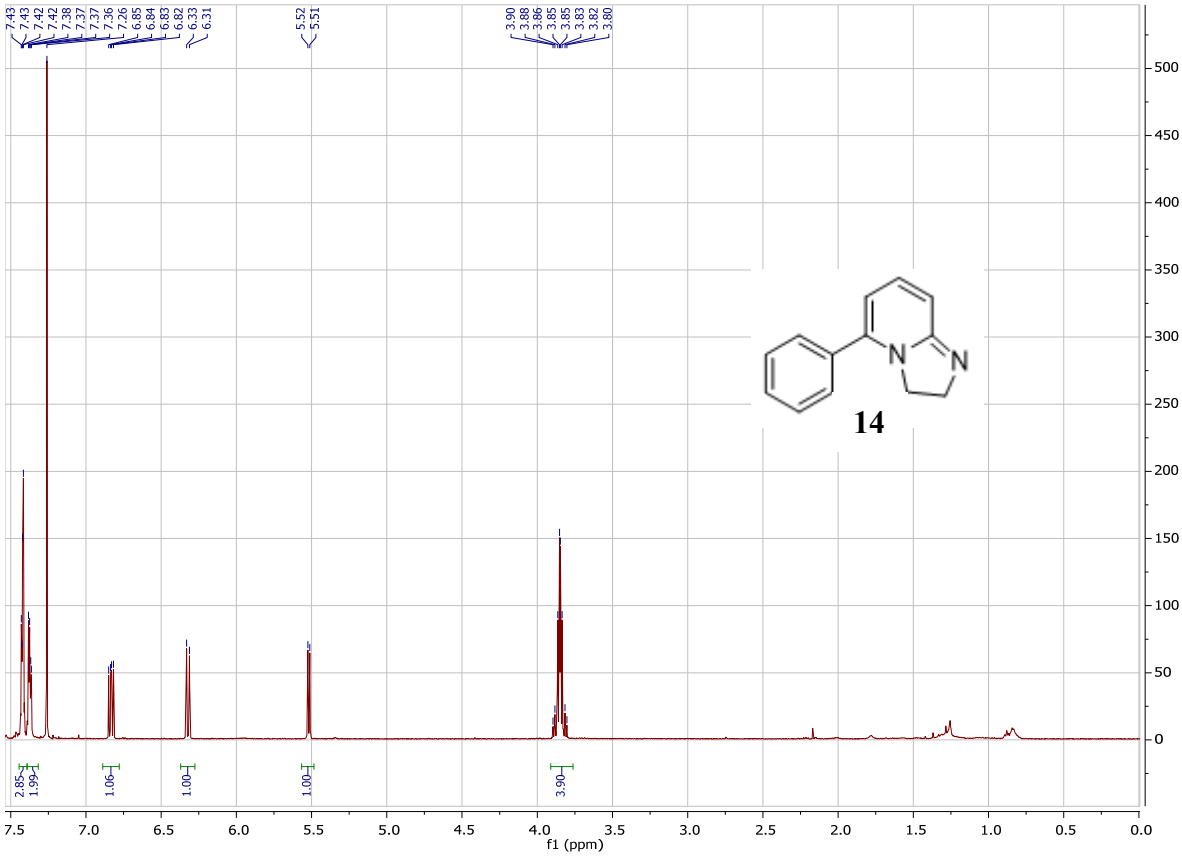


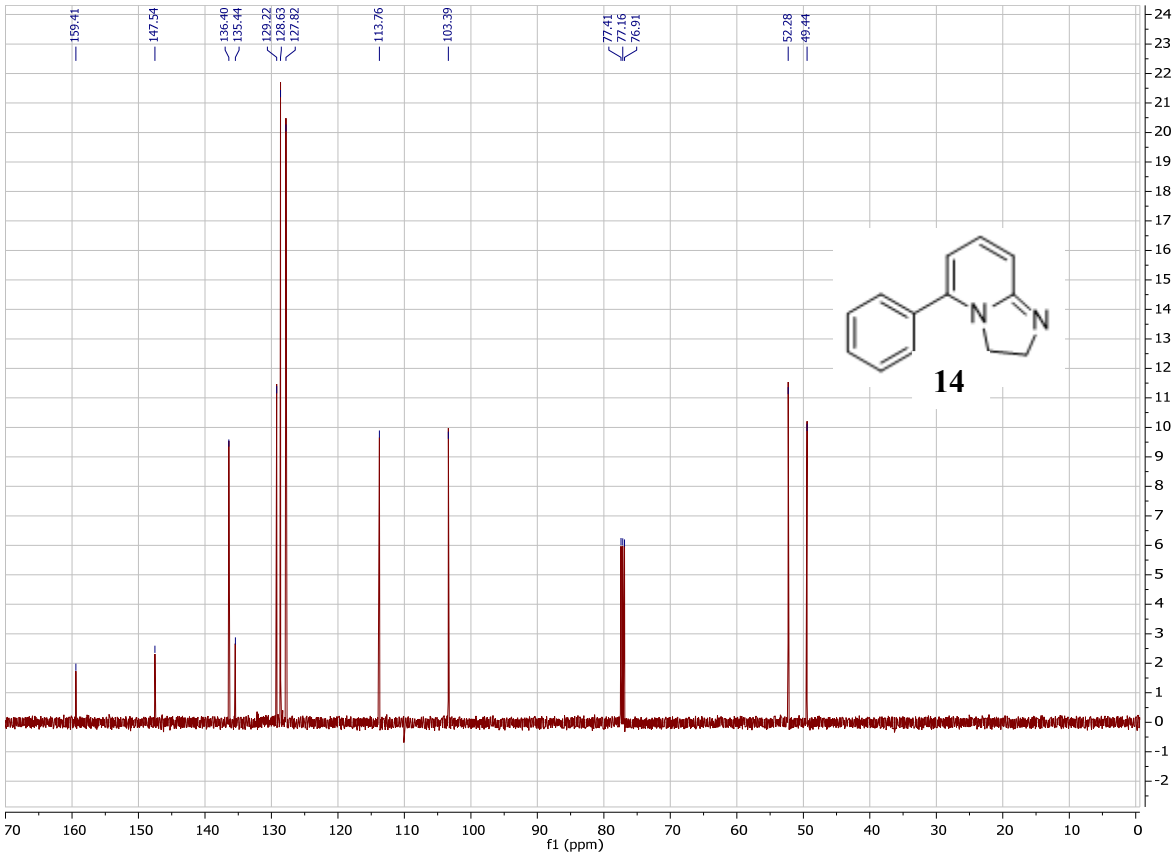

7.93
7.90
7.51
7.49
7.46
7.45
7.42
7.40
7.40
7.37
7.27
7.26
7.06
7.03
6.44
6.41
4.95
3.88
3.86
3.85
3.64
3.63
2.05
4.54
1.00
1.00
1.01
2.05
2.28
N
N
H
OH
31
f1 (ppm)

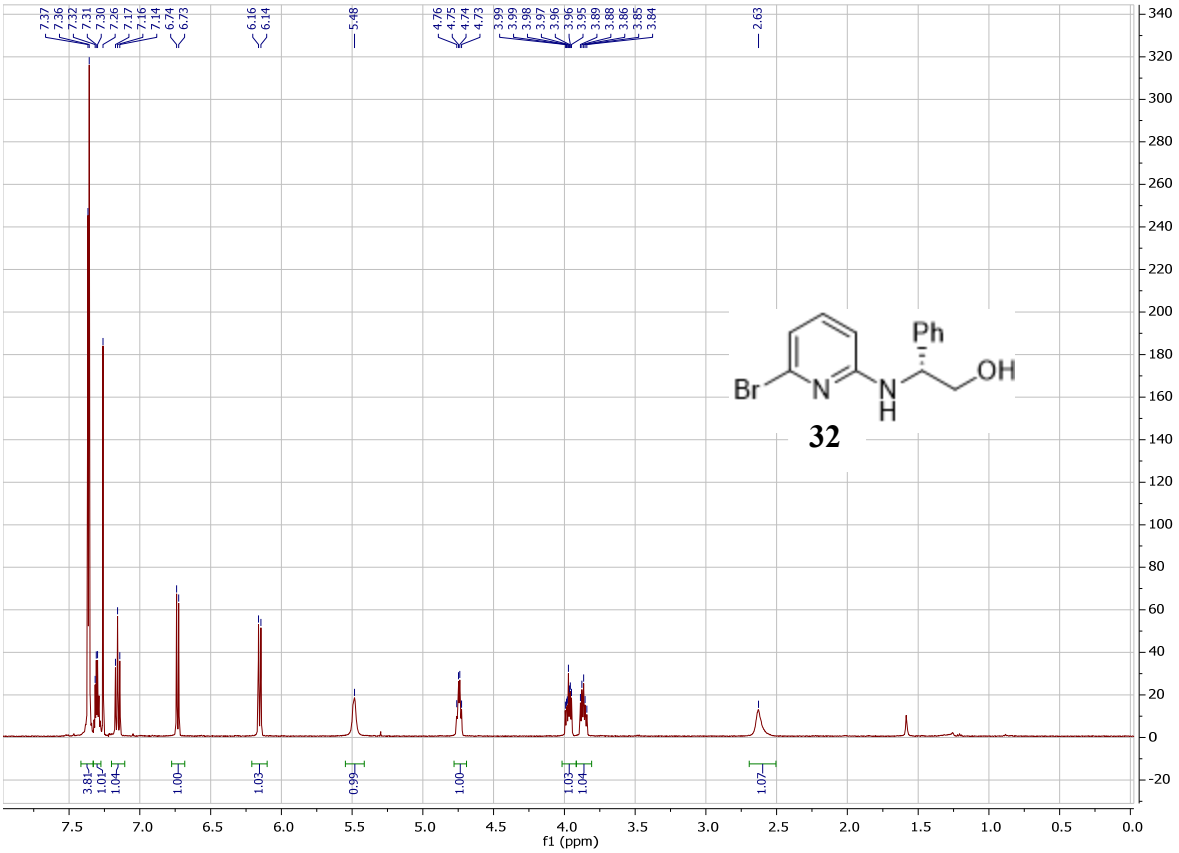

158.85
155.68
139.53
138.44
128.86
128.80
126.91
110.47
107.41
77.41
77.16
76.91
64.50
45.66
N
N
H
OH
31
f1 (ppm)

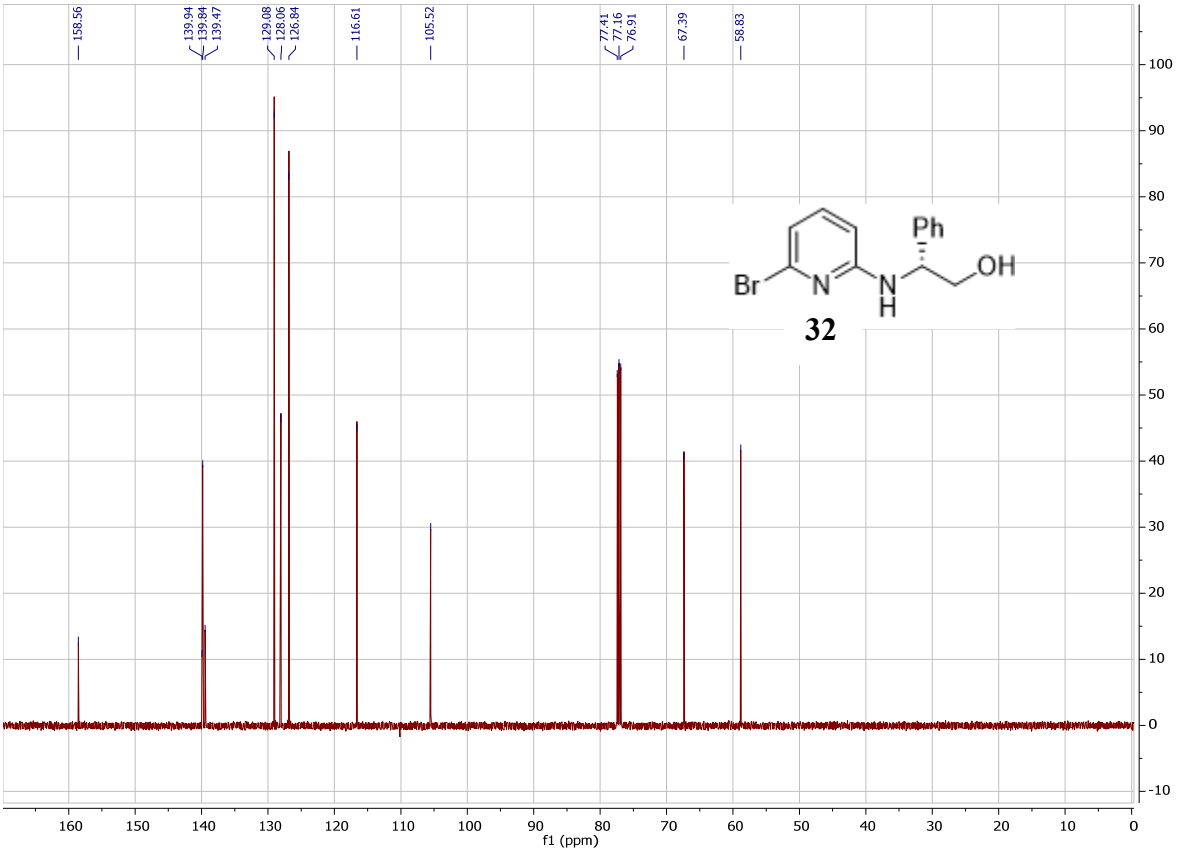

7.97
7.96
7.94
7.68
7.67
7.66
7.66
7.66
7.64
7.63
7.63
7.61
7.61
7.60
7.05
7.03
6.89
6.88
4.79
4.57
4.55
4.53
3.99
3.97
3.95
1.08
5.70
1.00
1.07
2.04
2.14
f1 (ppm)
N
NH
Cl
14·HCl

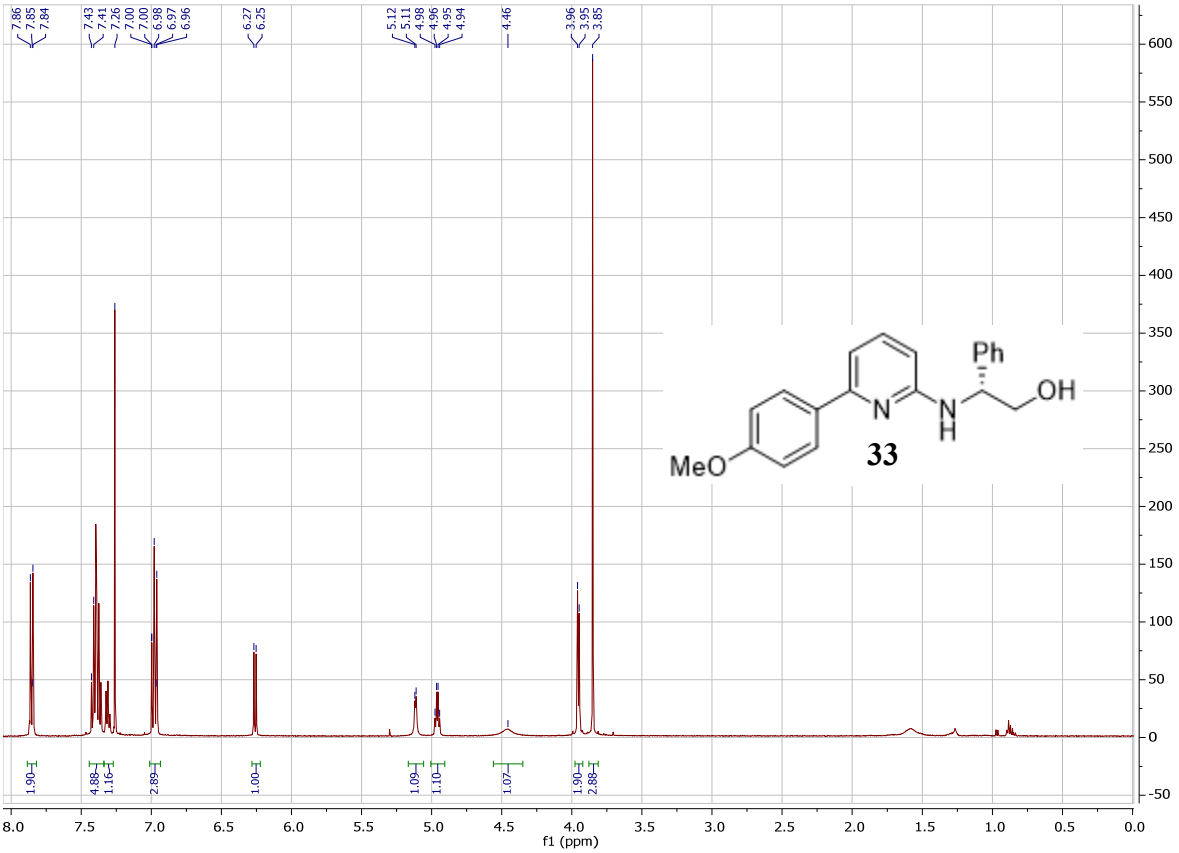

157.06
149.04
144.81
132.21
131.11
129.37
128.71
114.81
108.32
50.81
42.94
29.84
f1 (ppm)
N
NH
Cl
14·HCl

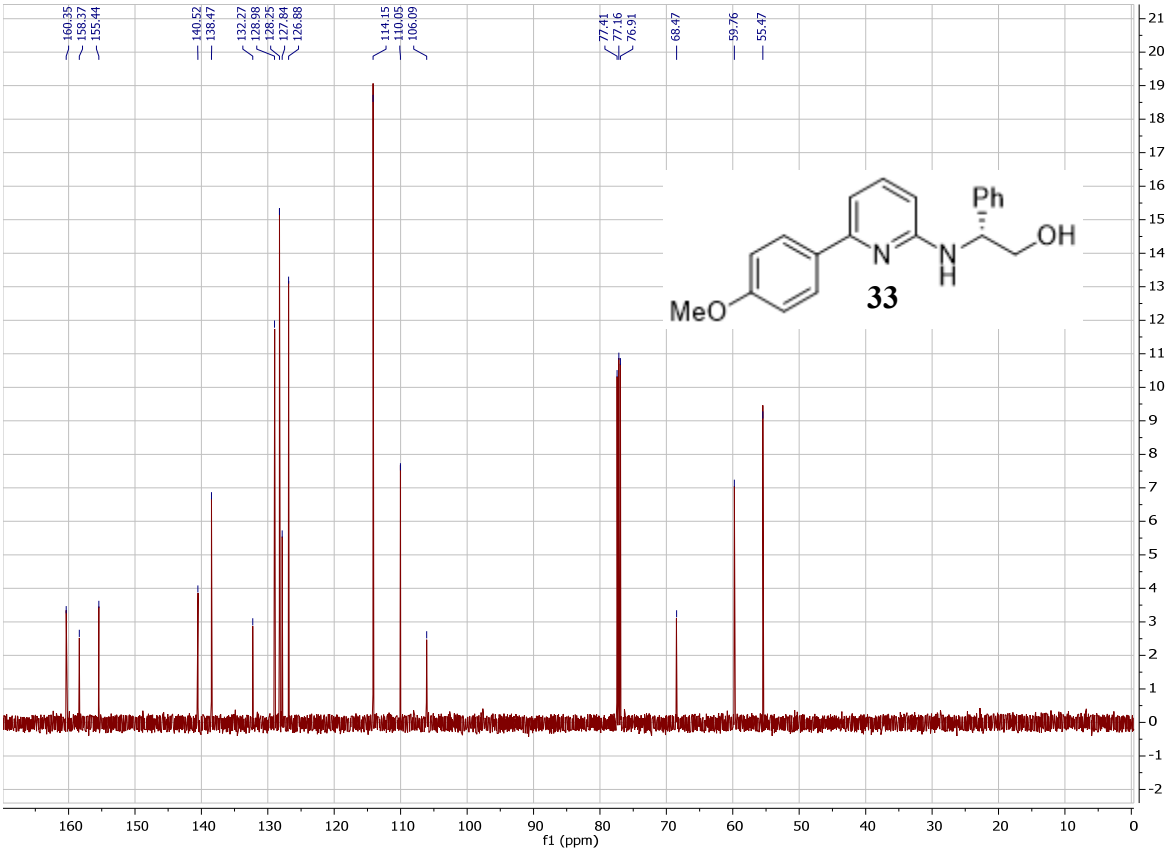

7.43
7.43
7.42
7.42
7.38
7.37
7.37
7.36
7.26
6.85
6.84
6.83
6.82
6.33
6.31
5.52
5.51
3.90
3.88
3.86
3.85
3.85
3.83
3.82
3.80
2.85
1.99
1.06
1.00
1.00
3.90
f1 (ppm)
N
N
14

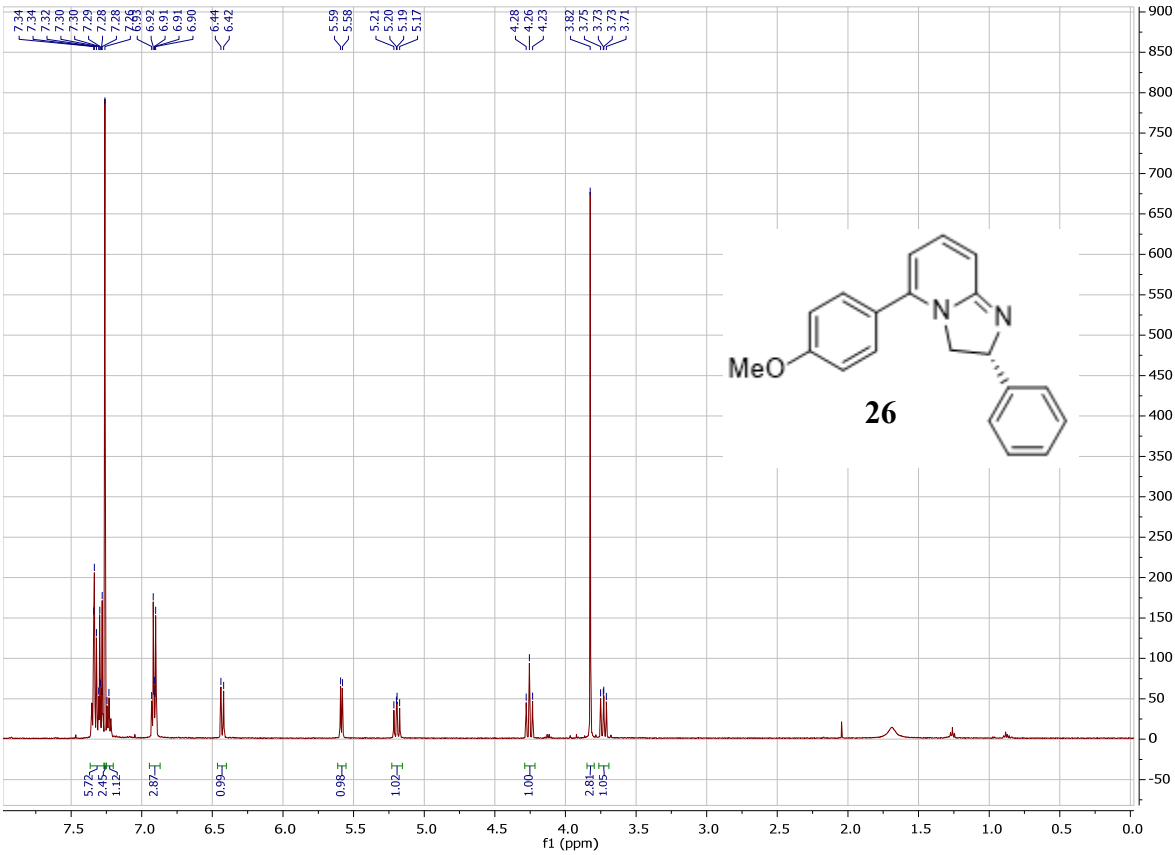

159.41
147.54
136.40
135.44
129.22
128.63
127.82
113.76
103.39
77.41
77.16
76.91
52.28
49.44
f1 (ppm)
N
N
14

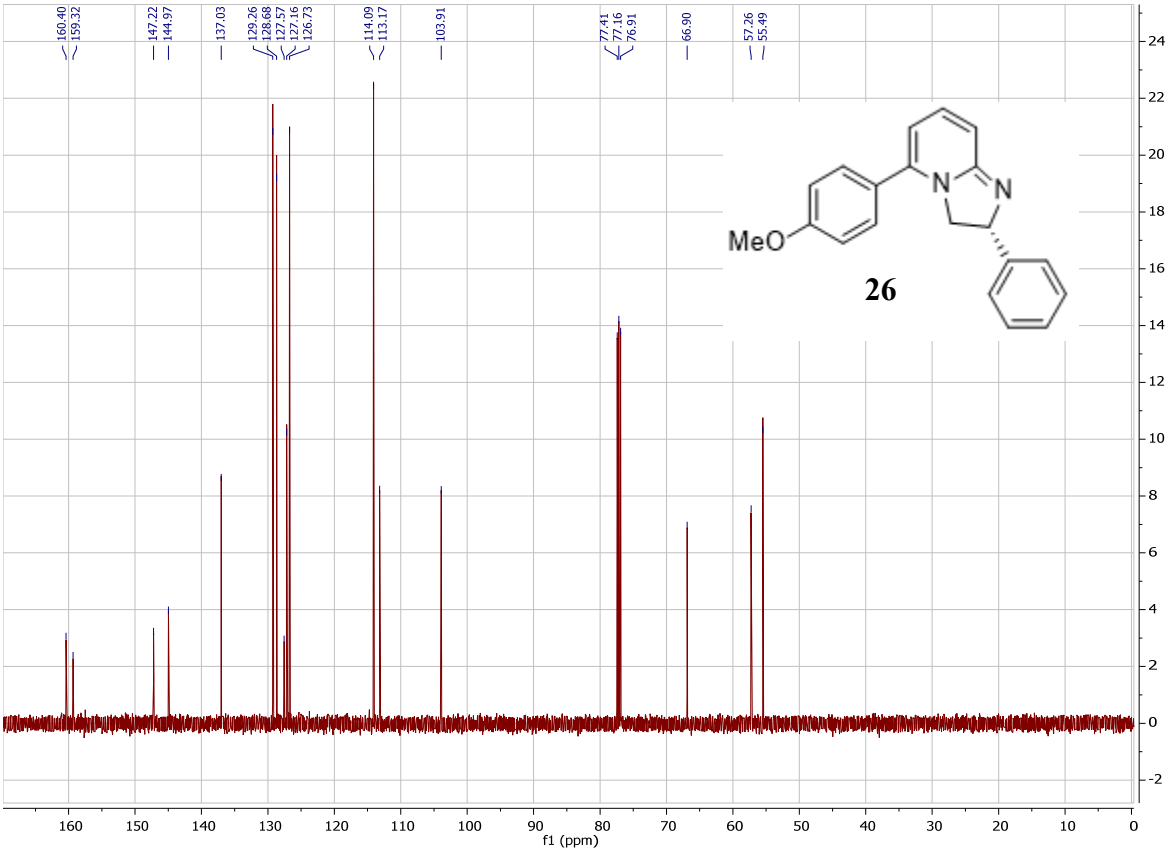

7.37
7.36
7.32
7.31
7.30
7.26
7.17
7.16
7.14
6.74
6.73
6.16
6.14
5.48
4.76
4.75
4.74
4.73
3.99
3.99
3.98
3.97
3.96
3.96
3.95
3.89
3.88
3.86
3.85
3.84
2.63
3.81
1.01
1.04
1.00
1.03
0.99
1.00
1.03
1.04
1.07
f1 (ppm)
Br
N
N
H
Ph
OH
32

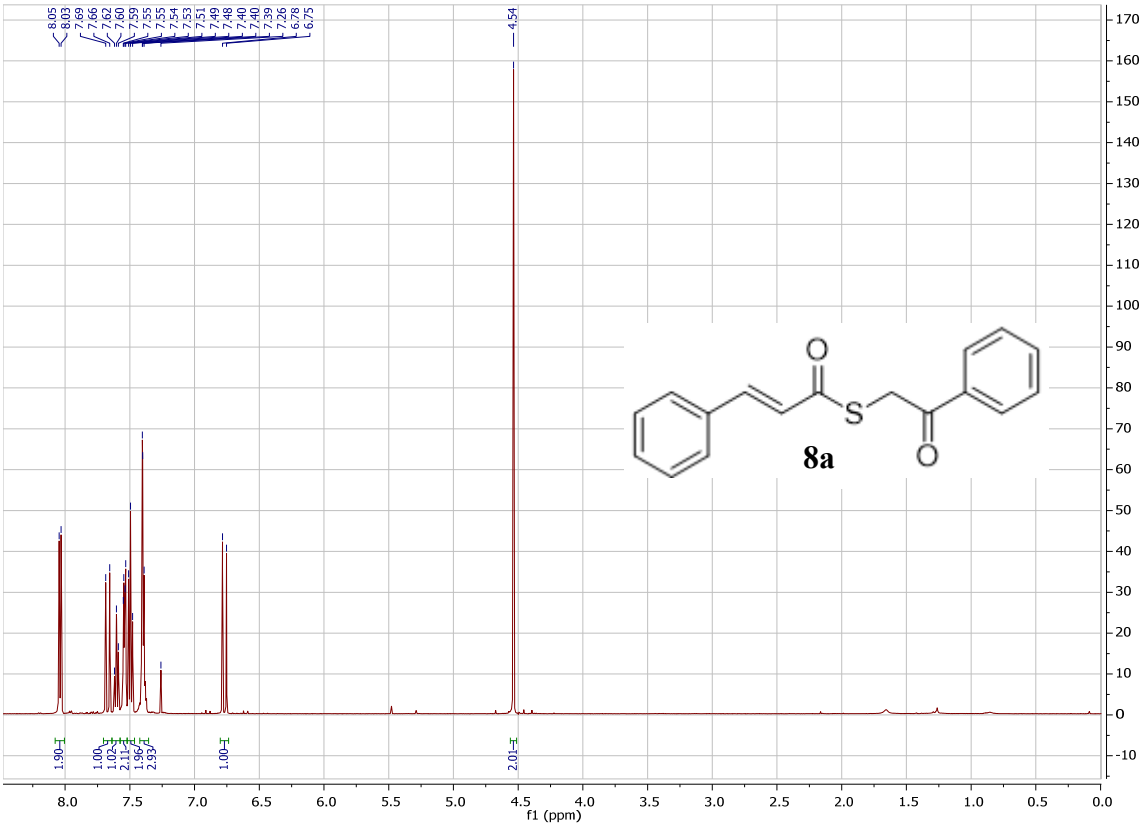

158.56
139.94
139.84
139.47
129.08
128.06
126.84
116.61
105.52
77.41
77.16
76.91
67.39
58.83
f1 (ppm)
Br
N
N
H
Ph
OH
32

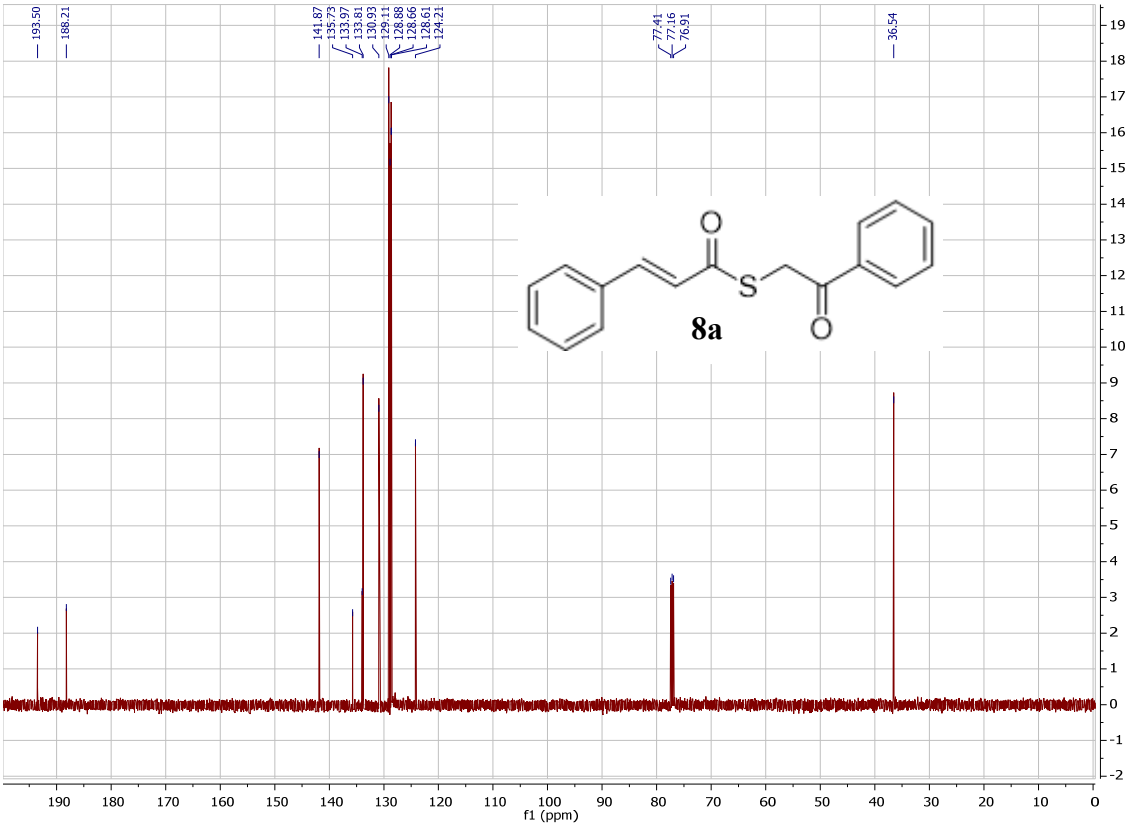

7.86
7.85
7.84
7.43
7.41
7.26
7.00
7.00
6.98
6.97
6.96
6.27
6.25
5.12
5.11
4.98
4.96
4.95
4.94
4.46
3.96
3.95
3.85
1.90
4.88
1.16
2.89
1.00
1.09
1.10
1.07
1.90
2.88
f1 (ppm)
Ph
OH
N
N
H
MeO
33

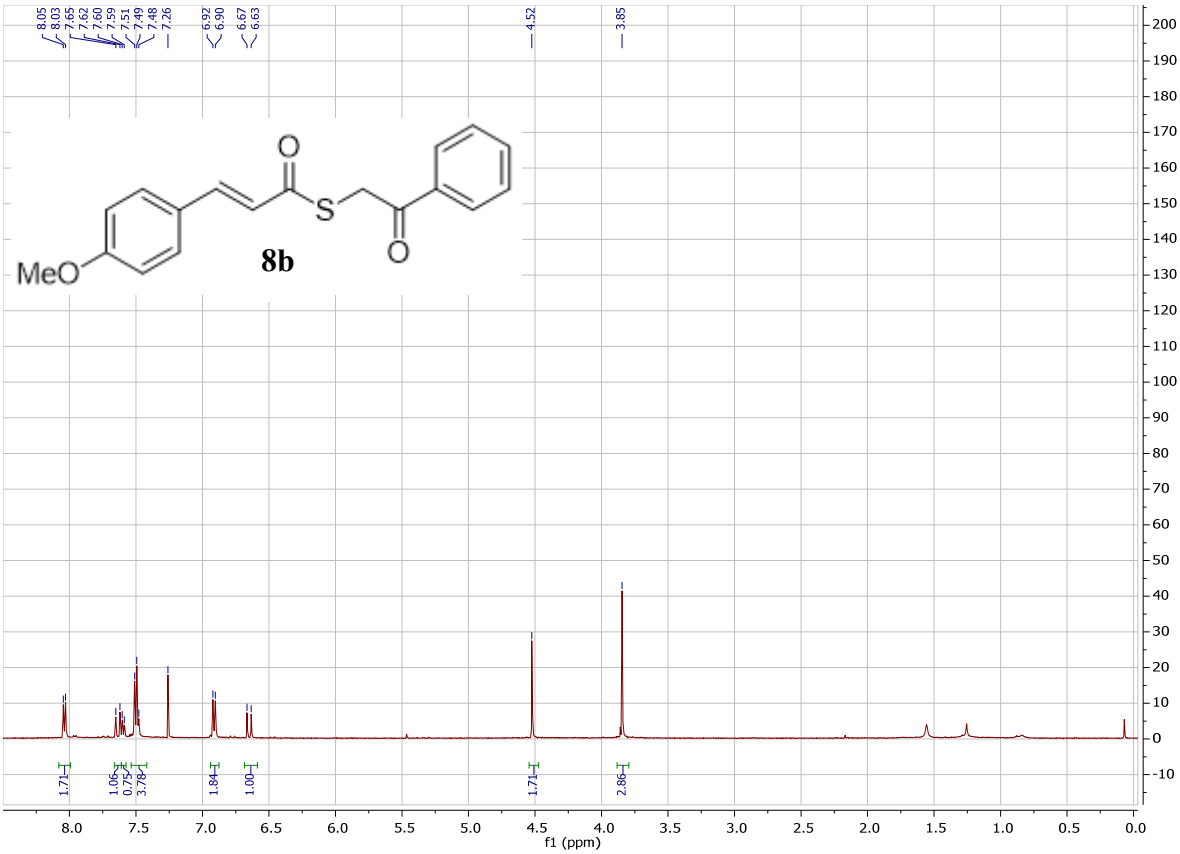

160.35
158.37
155.44
140.52
138.47
132.27
128.98
128.25
127.84
126.88
114.15
110.05
106.09
77.41
77.16
76.91
68.47
59.76
55.47
f1 (ppm)
Ph
OH
N
N
H
MeO
33

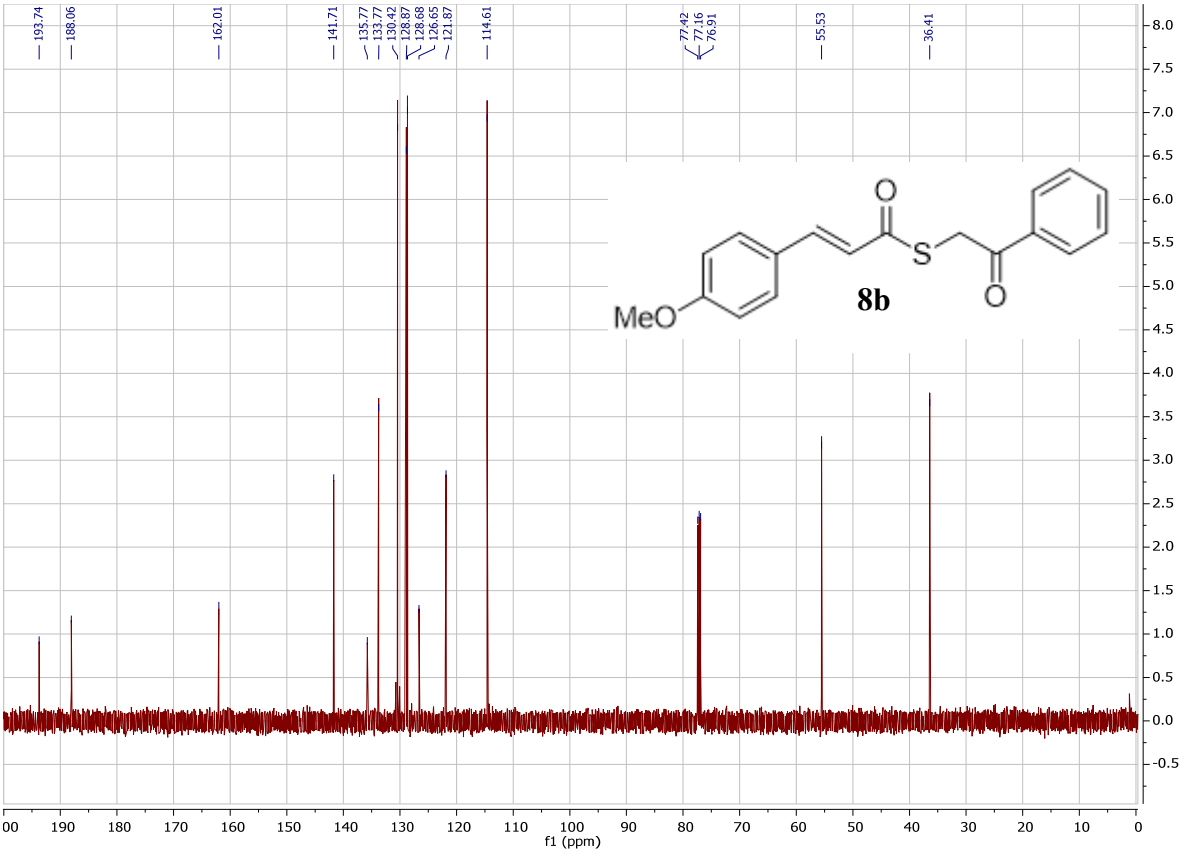

7.34
7.34
7.32
7.30
7.30
7.29
7.28
7.28
7.26
6.93
6.92
6.91
6.91
6.90
6.44
6.42
5.59
5.58
5.21
5.20
5.19
5.17
4.28
4.26
4.23
3.82
3.75
3.73
3.73
3.71
5.72
2.45
1.12
2.87
0.99
0.98
1.02
1.00
2.81
1.05
f1 (ppm)
MeO
N
N
26

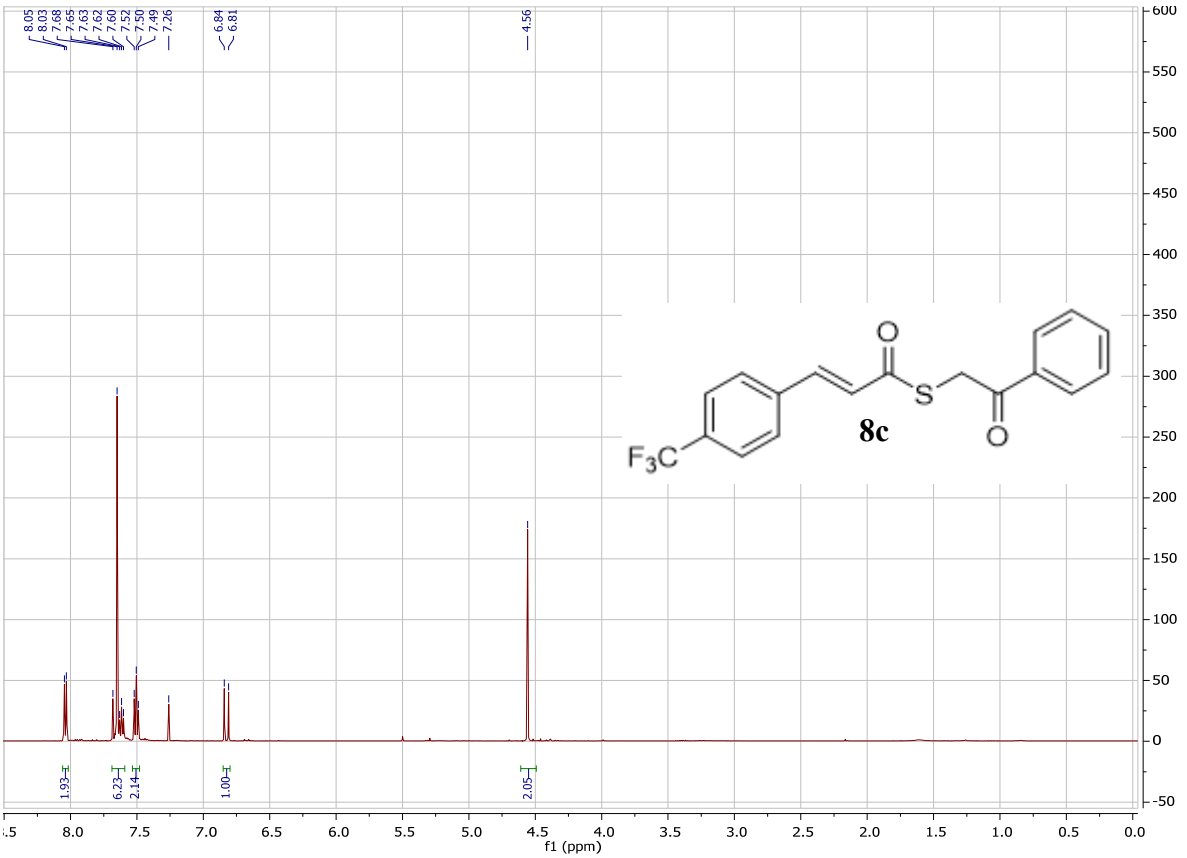

160.40
159.32
147.22
144.97
137.03
129.26
128.68
127.57
127.16
126.73
114.09
113.17
103.91
77.41
77.16
76.91
66.90
57.26
55.49
f1 (ppm)
MeO
N
N
26

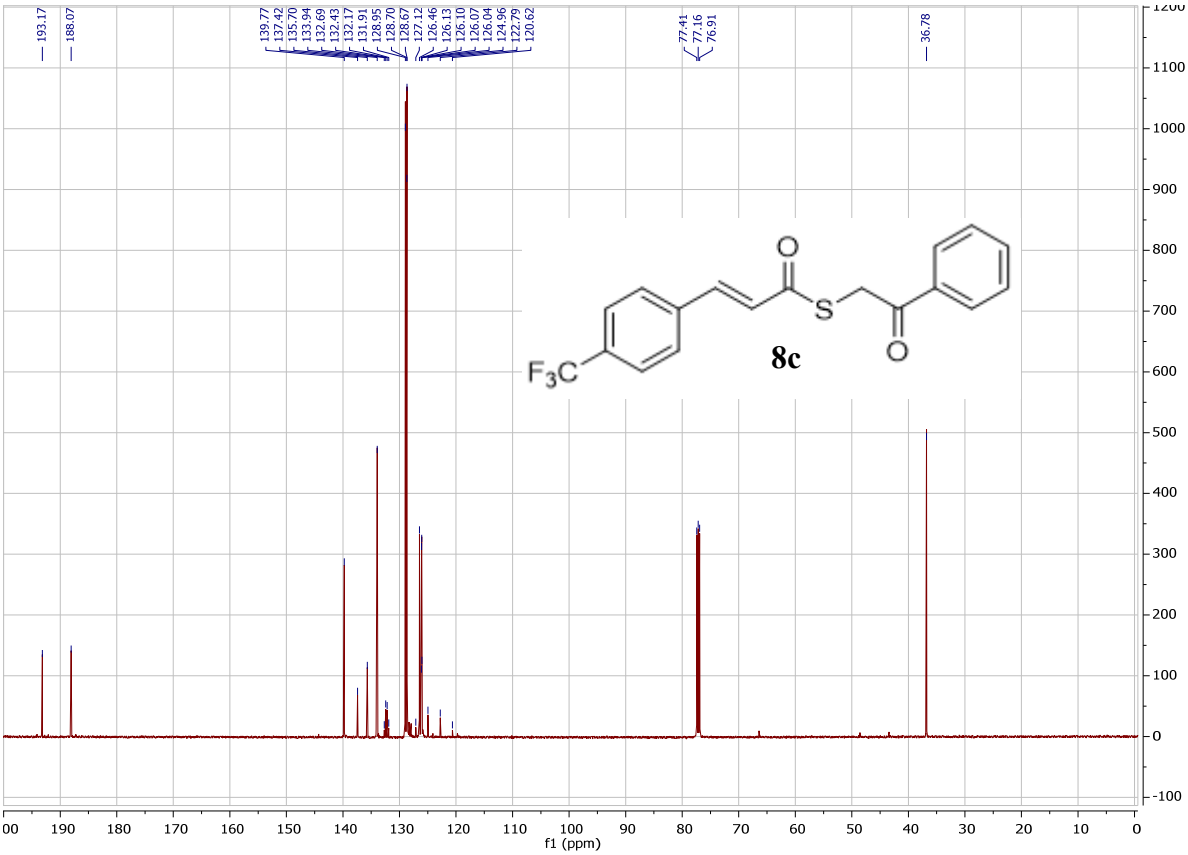

8.05
8.03
7.69
7.66
7.62
7.60
7.59
7.55
7.55
7.54
7.53
7.51
7.49
7.48
7.40
7.40
7.39
7.26
6.78
6.75
4.54
1.90
1.00
1.02
2.11
1.96
2.93
1.00
2.01
f1 (ppm)
8a

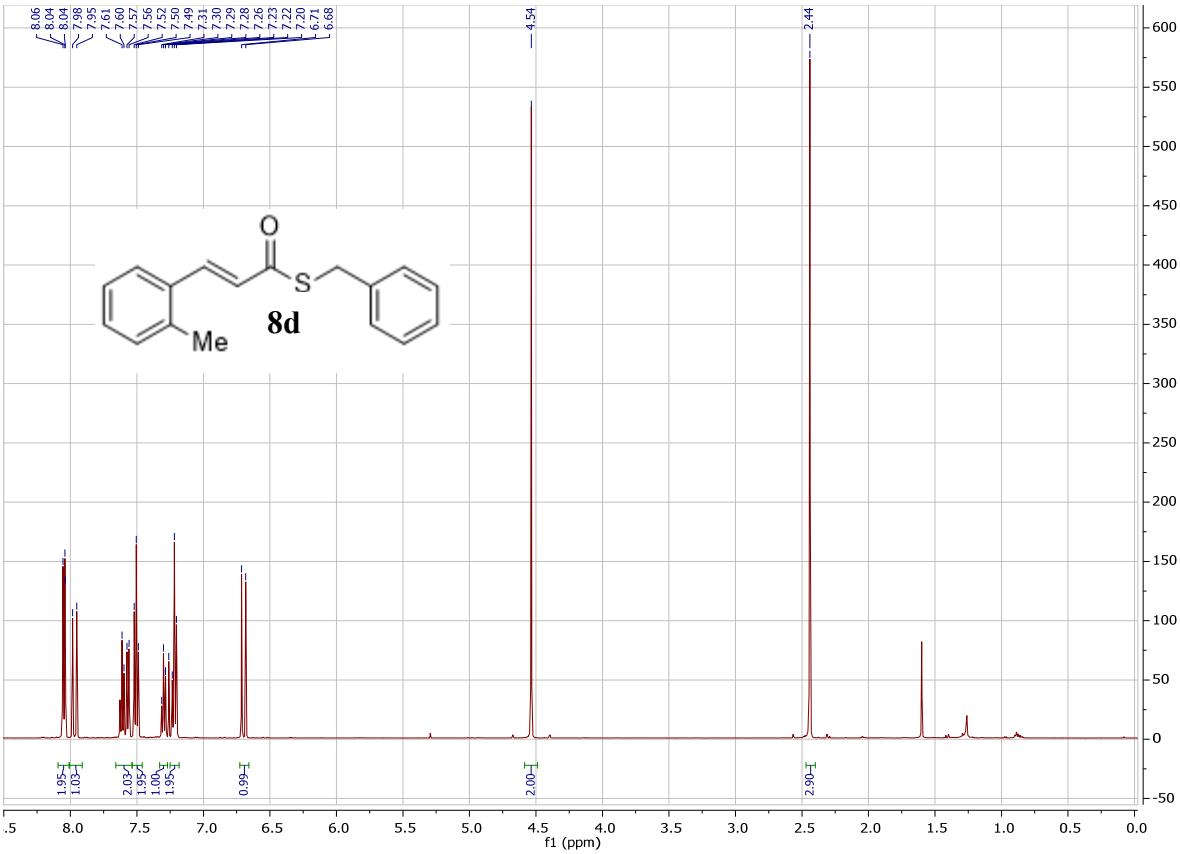

193.50
188.21
141.87
135.73
133.97
133.81
130.93
129.11
128.88
128.66
128.61
124.21
77.41
77.16
76.91
36.54
f1 (ppm)
8a

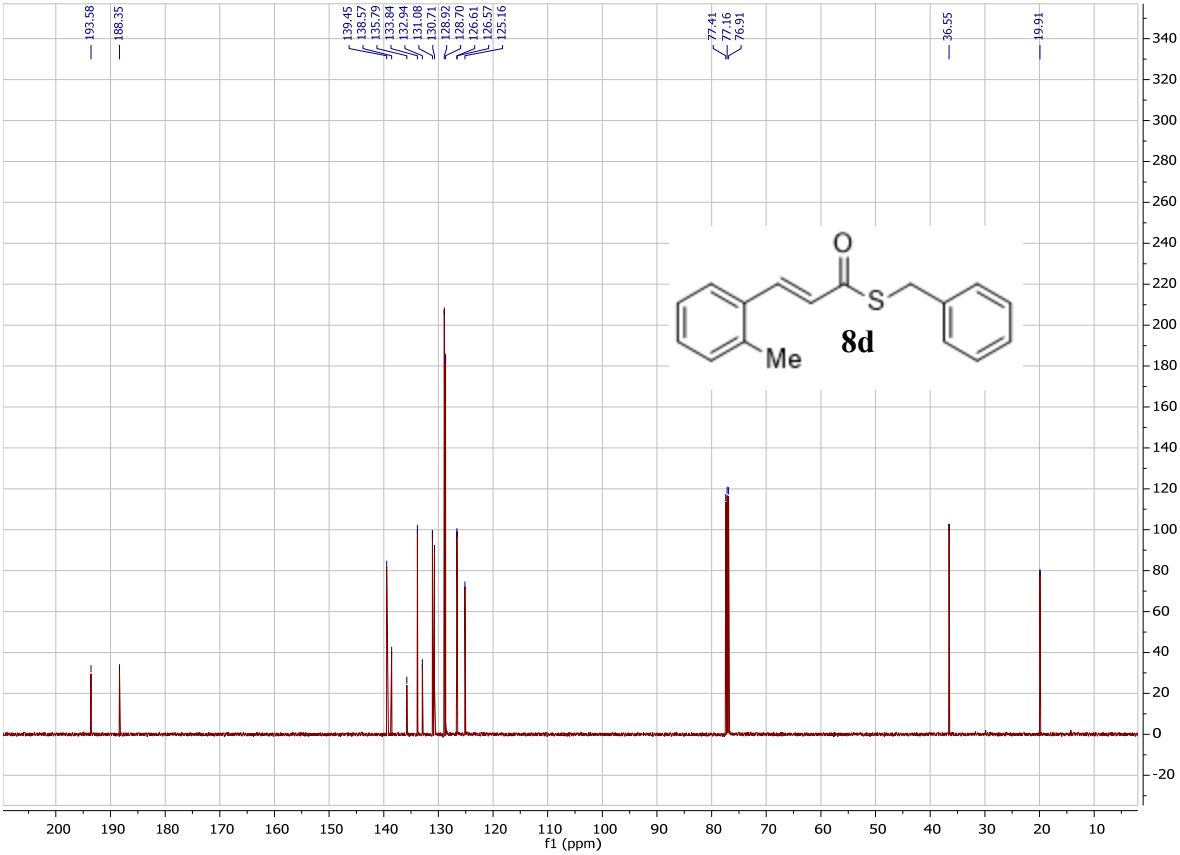

8.05
8.03
7.65
7.62
7.60
7.59
7.51
7.49
7.48
7.26
6.92
6.90
6.67
6.63
4.52
3.85
MeO
8b
1.71
1.06
0.75
3.78
1.84
1.00
1.71
2.86
f1 (ppm)

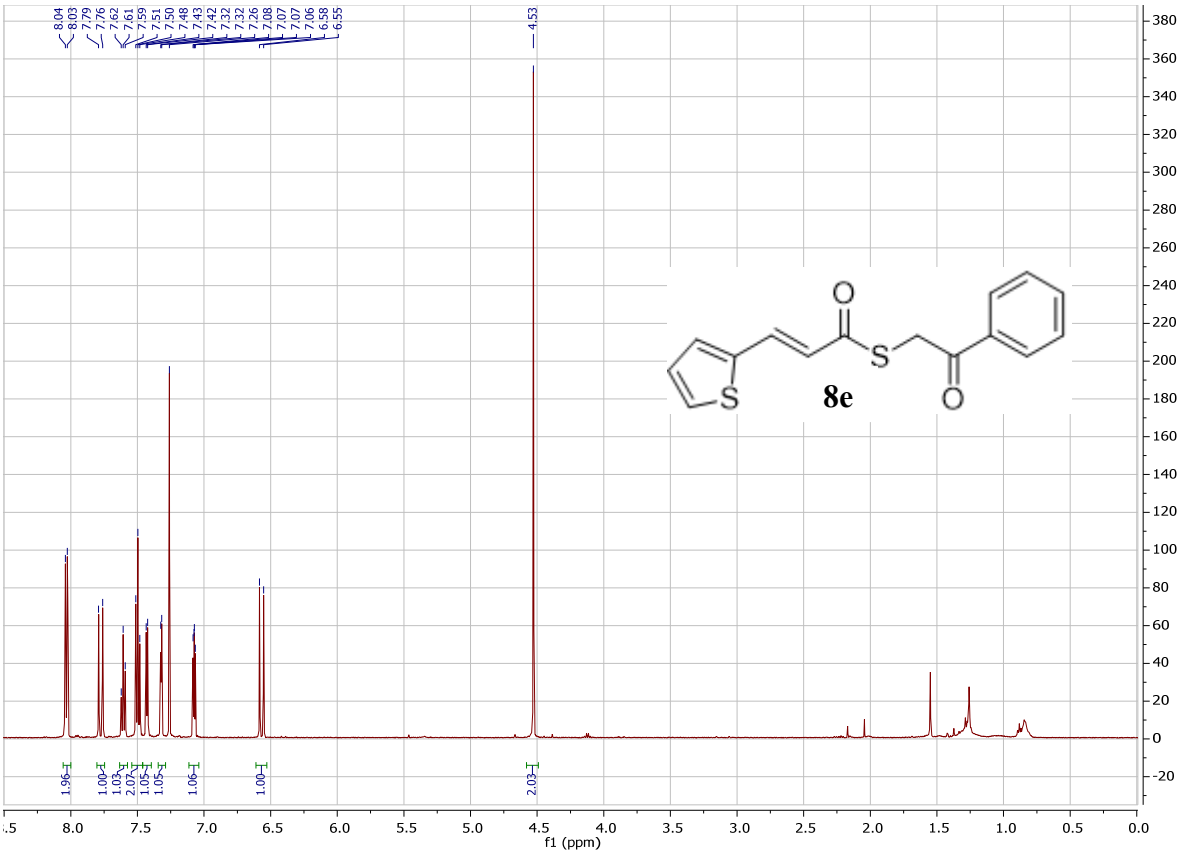

193.74
188.06
162.01
141.71
135.77
133.77
130.42
128.87
128.68
126.65
121.87
114.61
77.42
77.16
76.91
55.53
36.41
MeO
8b
f1 (ppm)

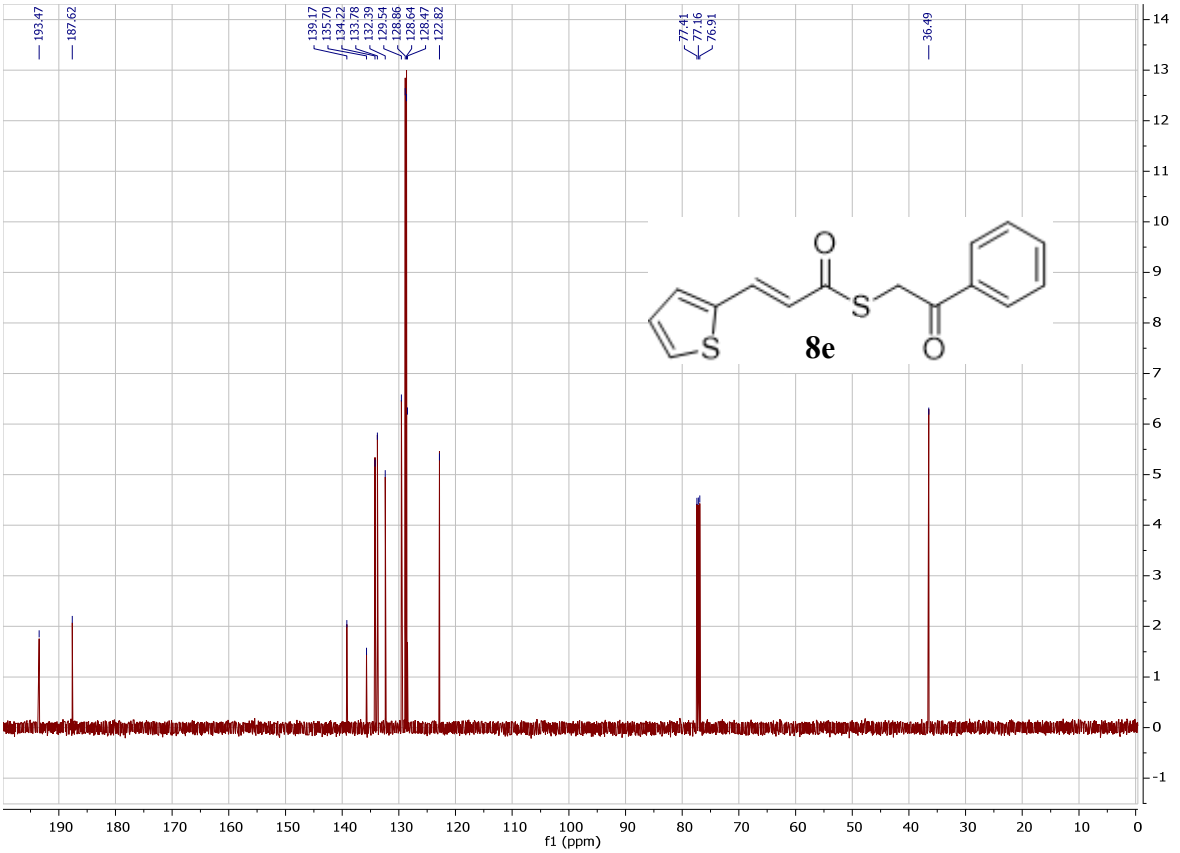

8.05
8.03
7.68
7.65
7.63
7.62
7.60
7.52
7.50
7.49
7.26
6.84
6.81
4.56
1.93
6.23
2.14
1.00
2.05
f1 (ppm)
8c

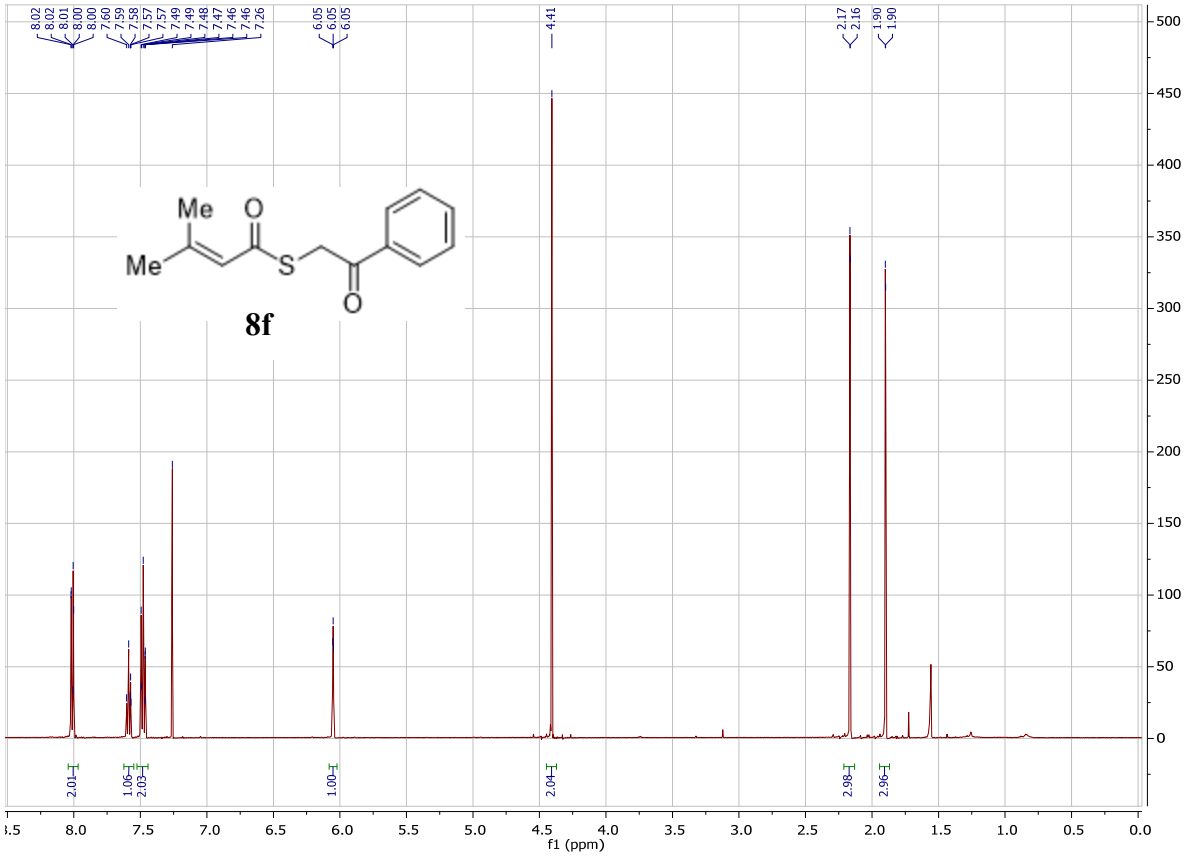

193.17
188.07
139.77
137.42
135.70
133.94
132.69
132.43
132.17
131.91
128.95
128.70
128.67
127.12
126.46
126.13
126.10
126.07
126.04
124.96
122.79
120.62
77.41
77.16
76.91
36.78
f1 (ppm)
8c

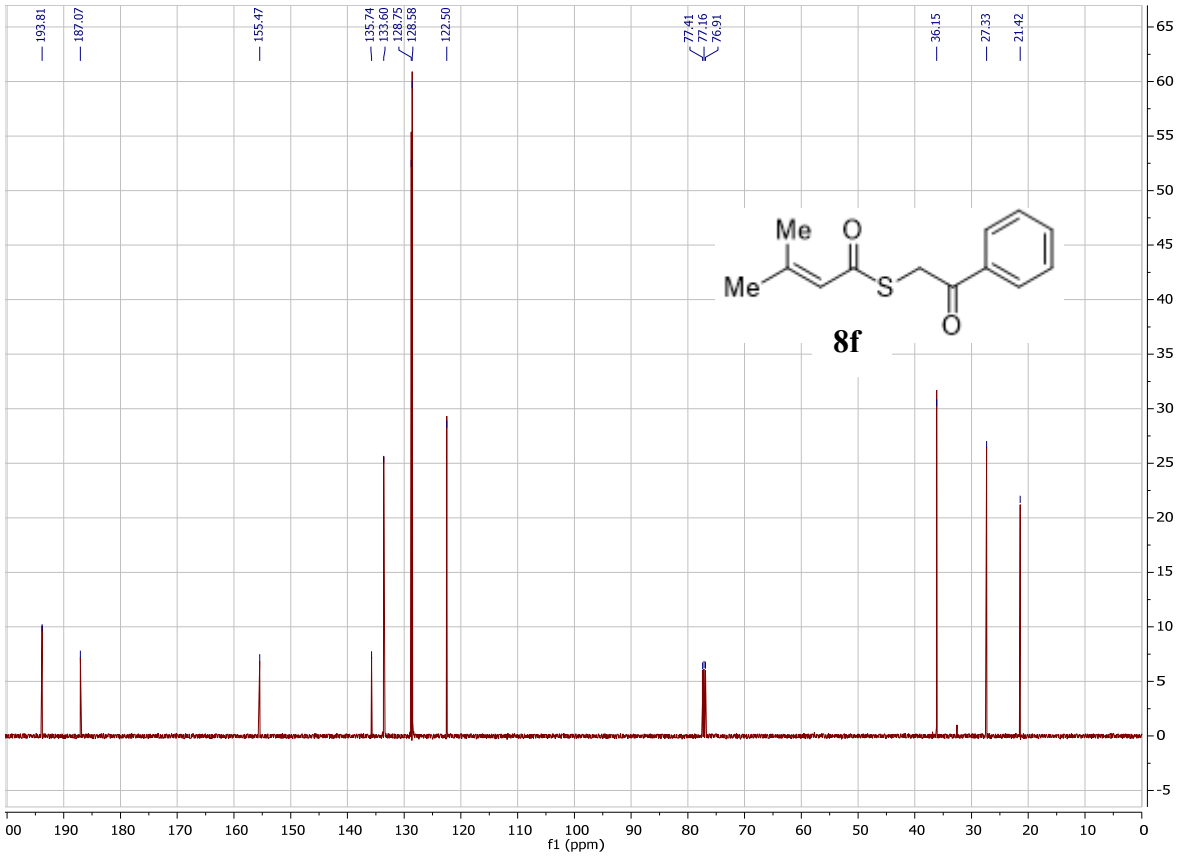

8.06
8.04
8.04
7.98
7.95
7.61
7.60
7.57
7.56
7.52
7.50
7.49
7.31
7.30
7.29
7.28
7.26
7.23
7.22
7.20
6.71
6.68
4.54
2.44
O
S
Me
8d
1.95
1.03
2.03
1.95
1.00
1.95
0.99
2.00
2.90
f1 (ppm)

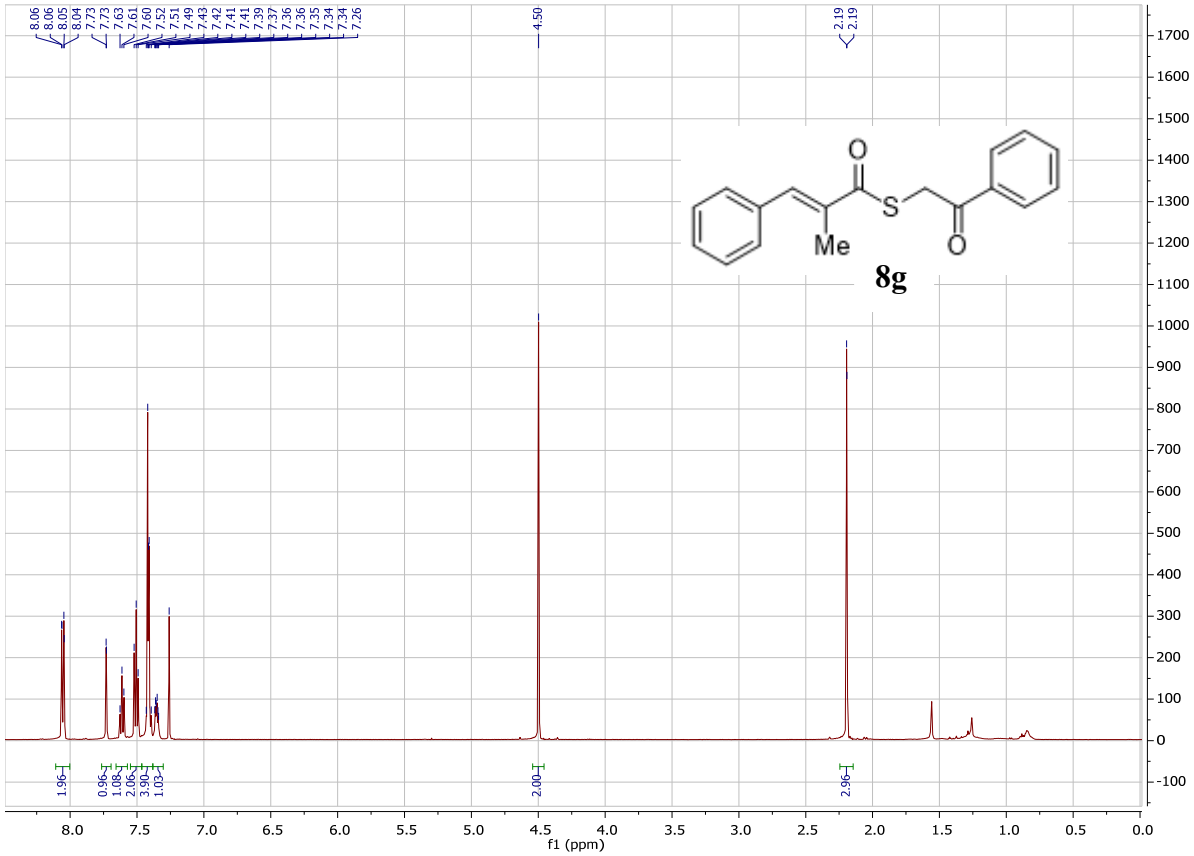

193.58
188.35
139.45
138.57
135.79
133.84
132.94
131.08
130.71
128.92
128.70
126.61
126.57
125.16
77.41
77.16
76.91
36.55
19.91
O
S
Me
8d
f1 (ppm)

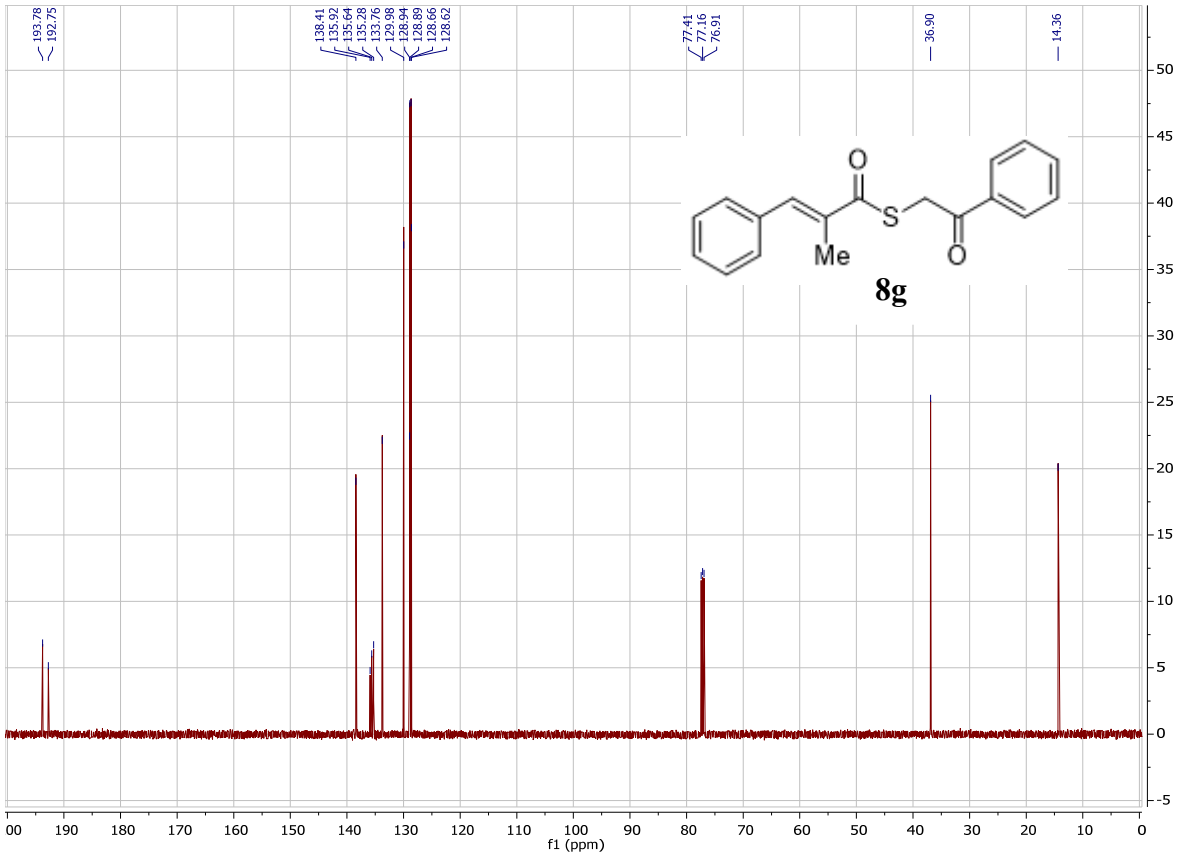

8.04
8.03
7.79
7.76
7.62
7.61
7.59
7.51
7.50
7.48
7.43
7.42
7.32
7.32
7.26
7.08
7.07
7.07
7.06
6.58
6.55
4.53
1.96
1.00
1.03
2.07
1.05
1.05
1.06
1.00
2.03
f1 (ppm)
8e

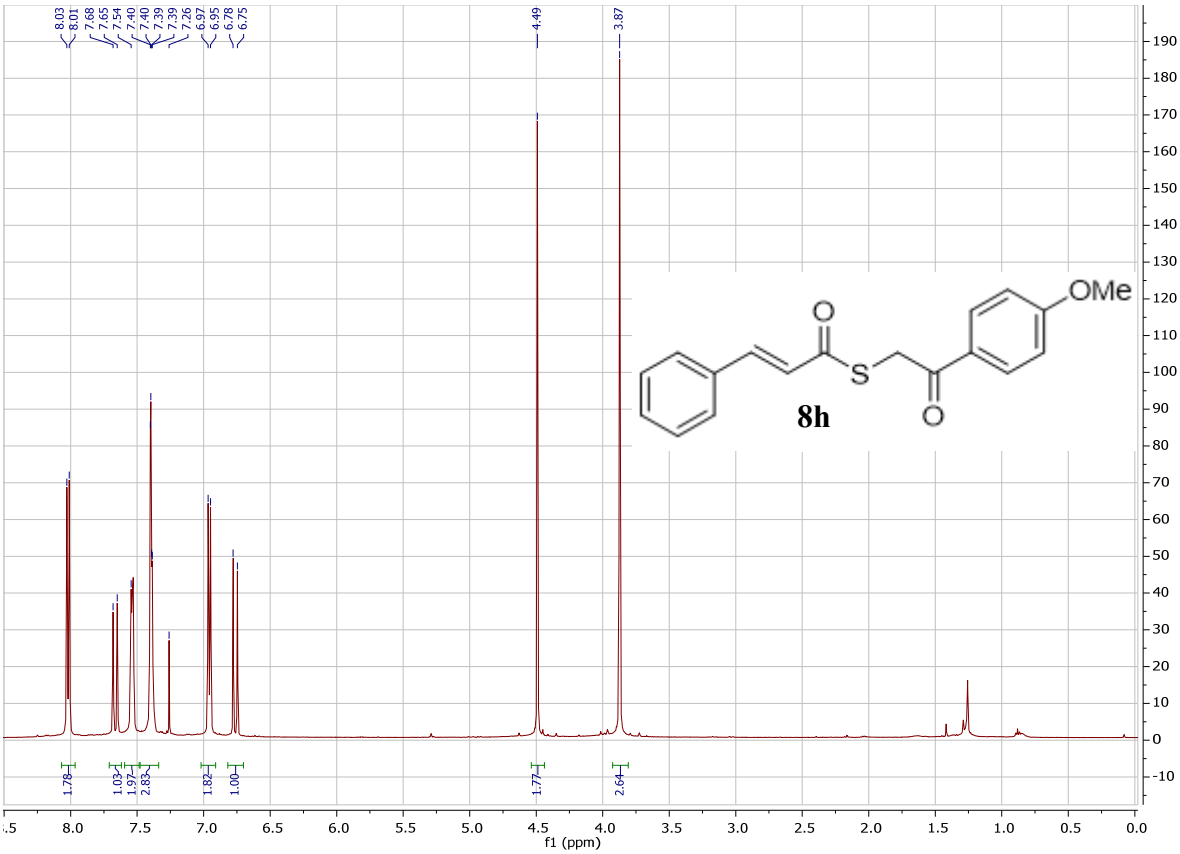

193.47
187.62
139.17
135.70
134.22
133.78
132.39
129.54
128.86
128.64
128.47
122.82
77.41
77.16
76.91
36.49
f1 (ppm)
8e

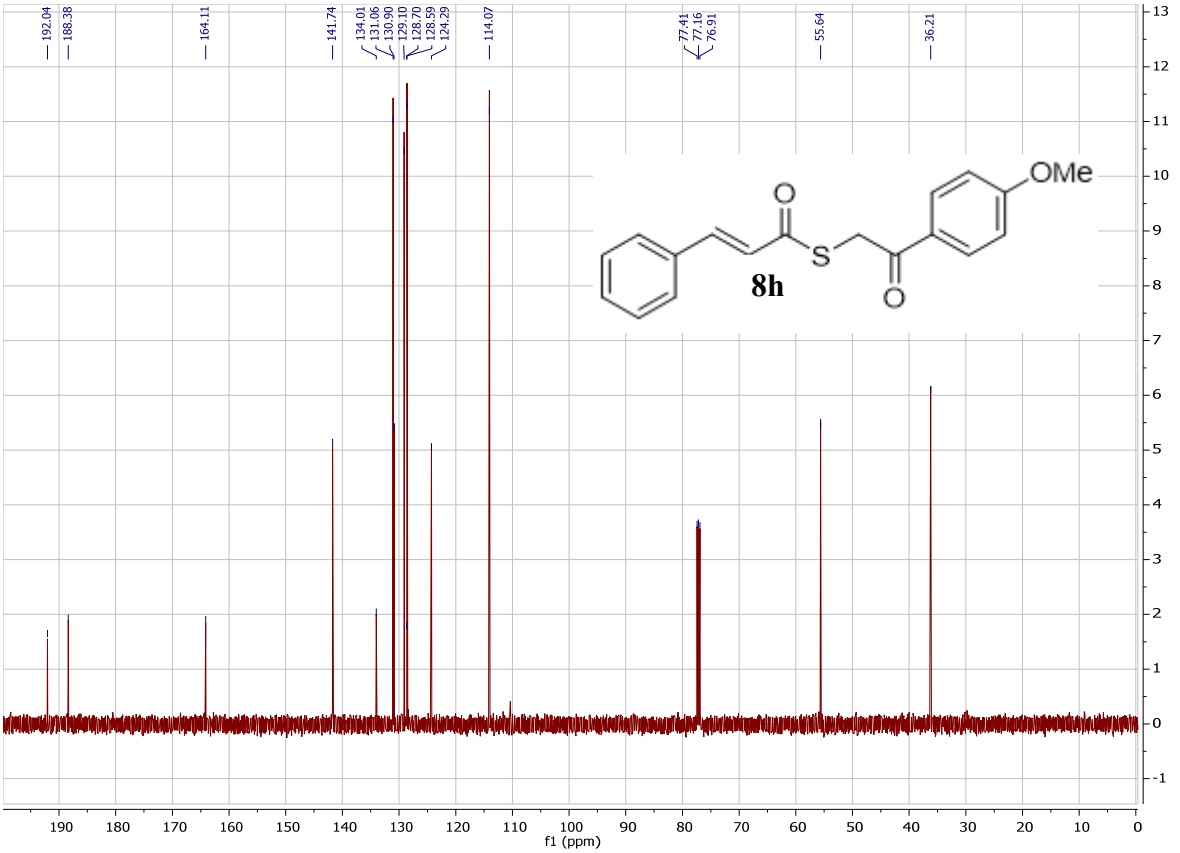

8f
f1 (ppm)

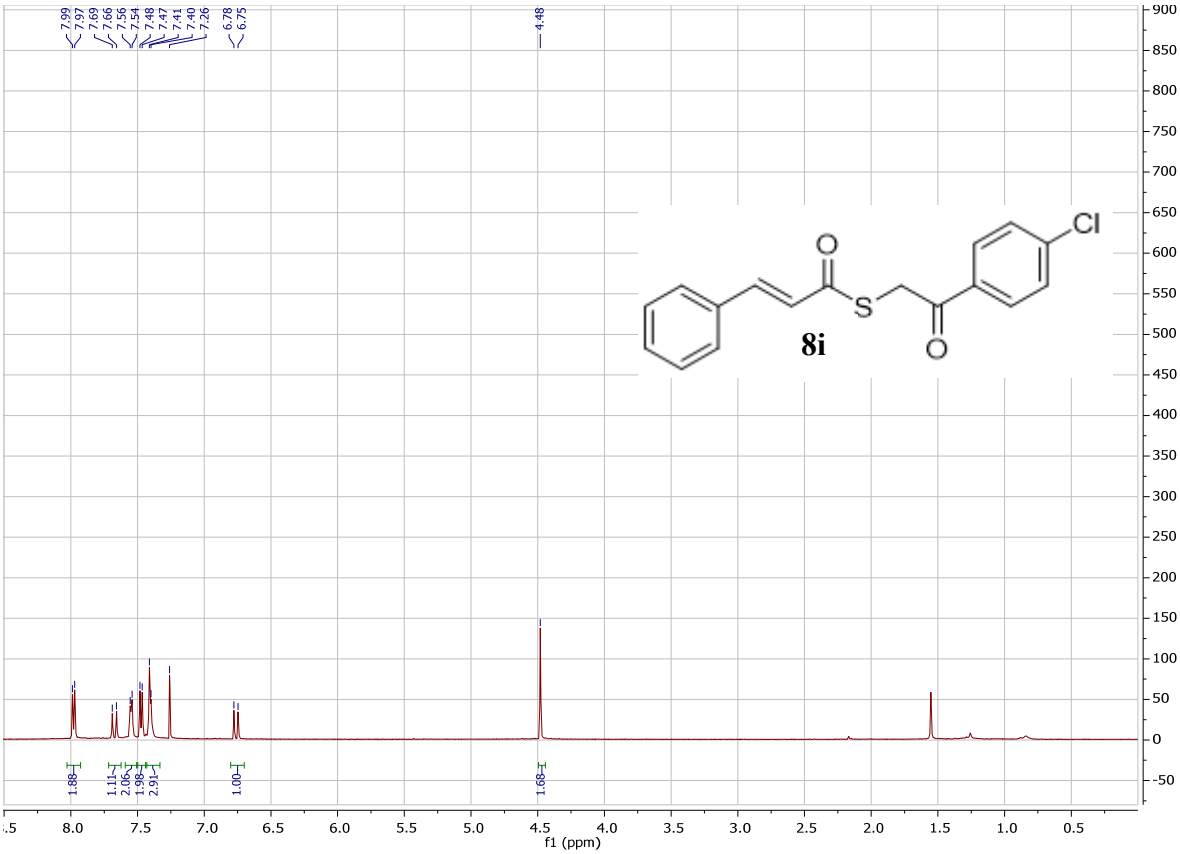

8f
f1 (ppm)

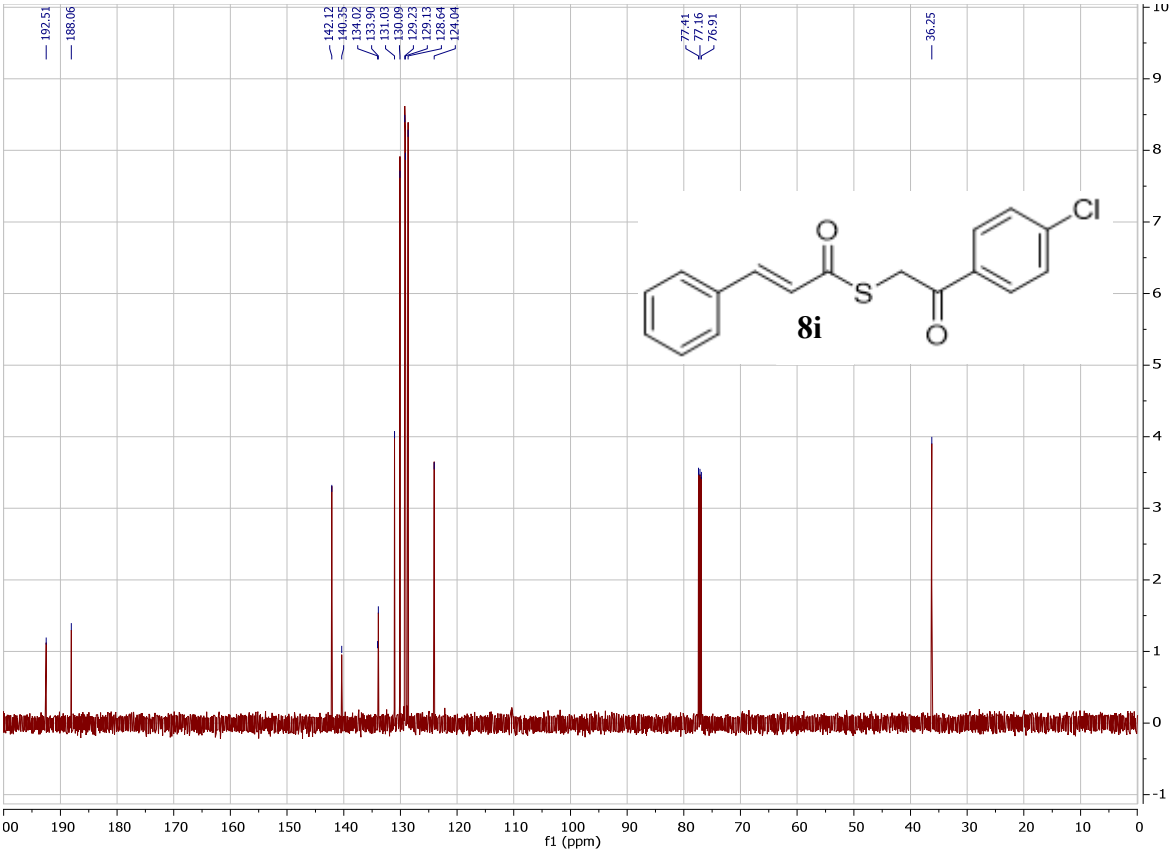

8g
f1 (ppm)

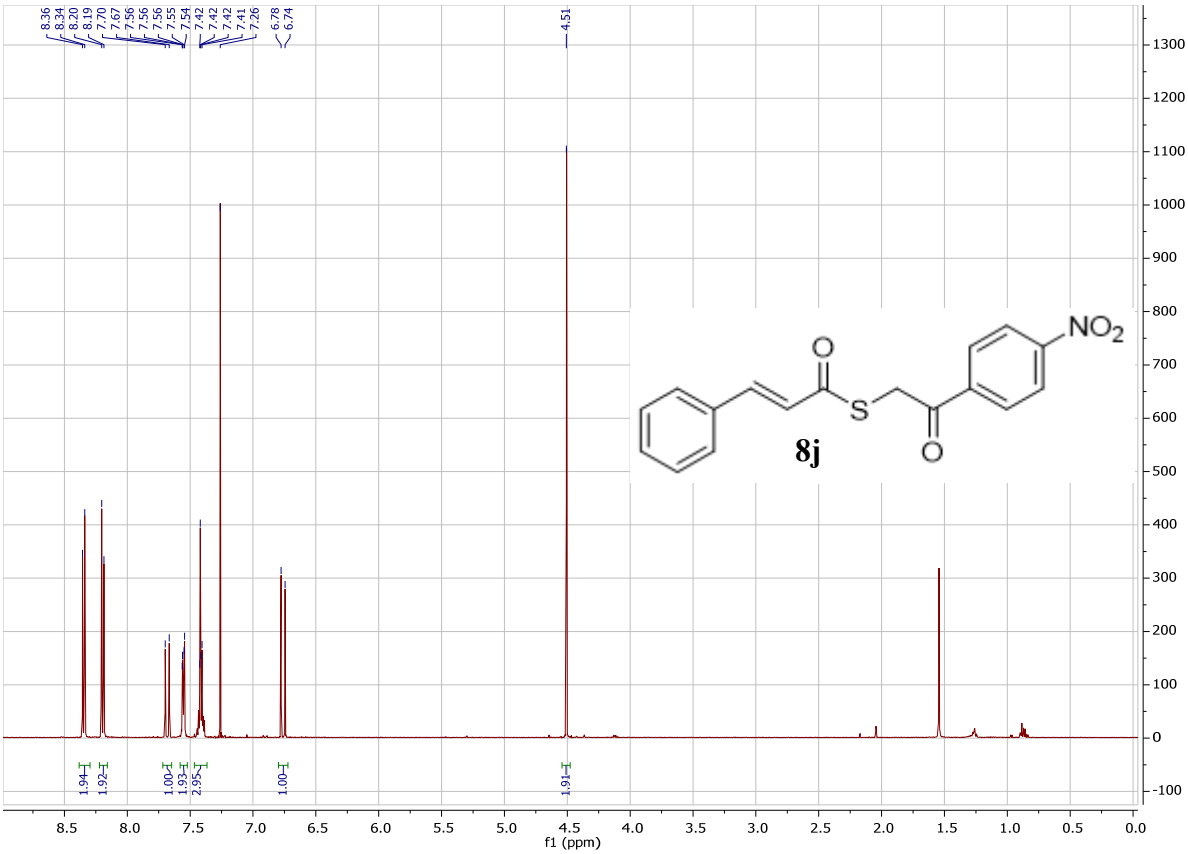

8g
f1 (ppm)

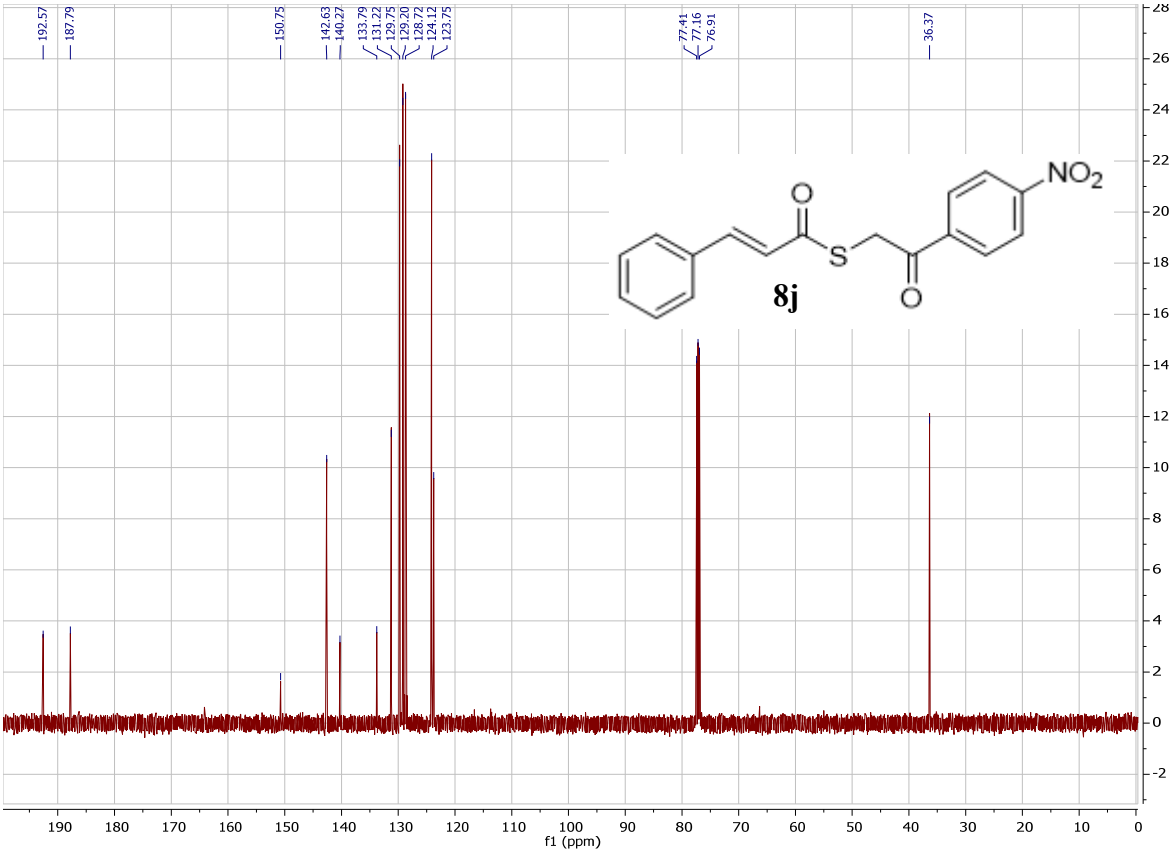

8.03
8.01
7.68
7.65
7.54
7.40
7.40
7.39
7.39
7.26
6.97
6.95
6.78
6.75
4.49
3.87
1.78
1.03
1.97
2.85
1.82
1.00
1.77
2.64
OMe
O
S
O
8h
f1 (ppm)

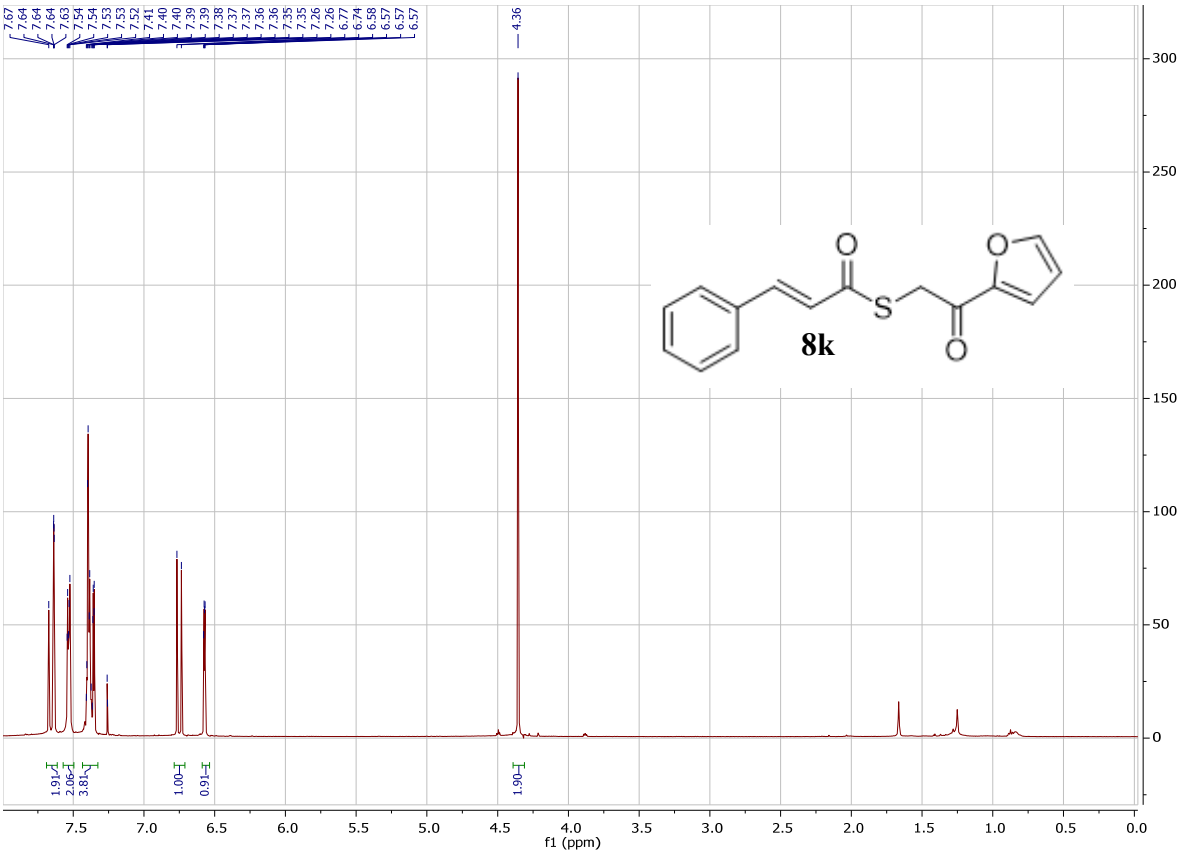

192.04
188.38
164.11
141.74
134.01
131.06
130.90
129.10
128.70
128.59
124.29
114.07
77.41
77.16
76.91
55.64
36.21
OMe
O
S
O
8h
f1 (ppm)

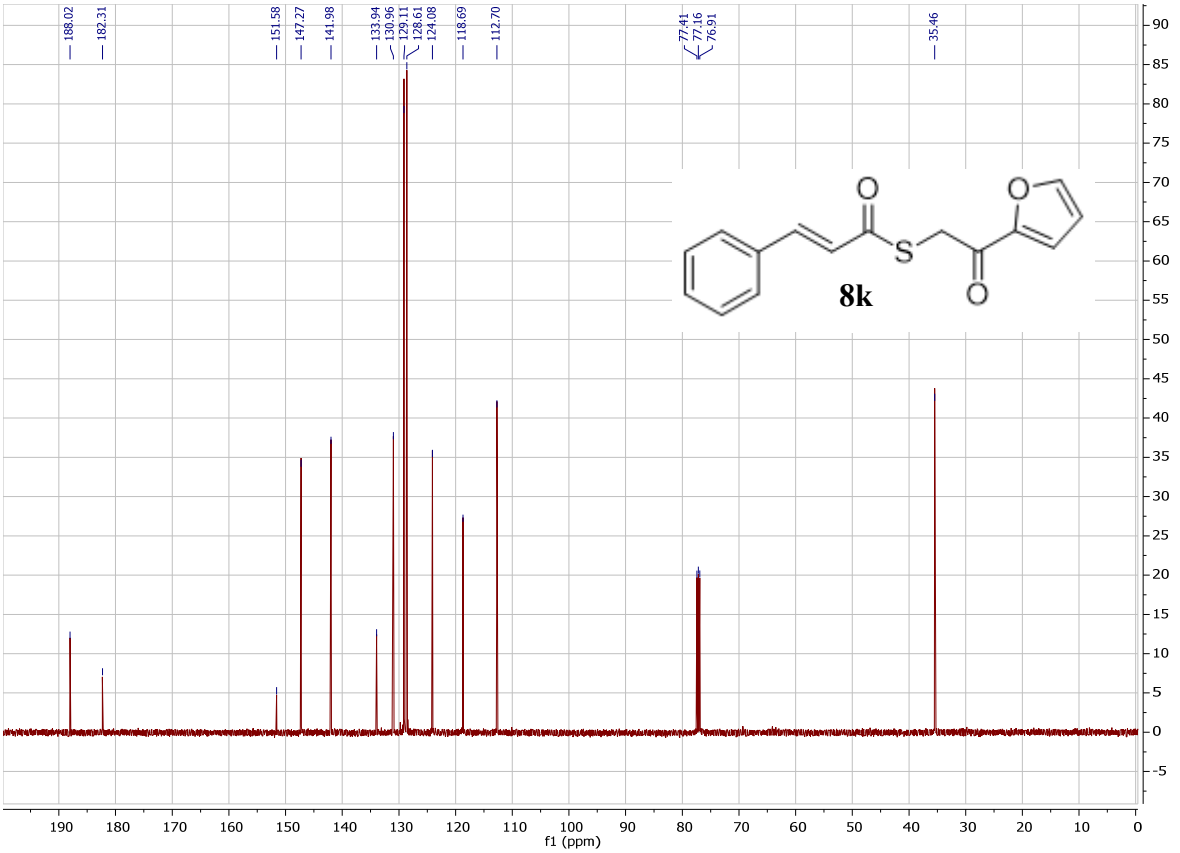

8i
Cl
f1 (ppm)

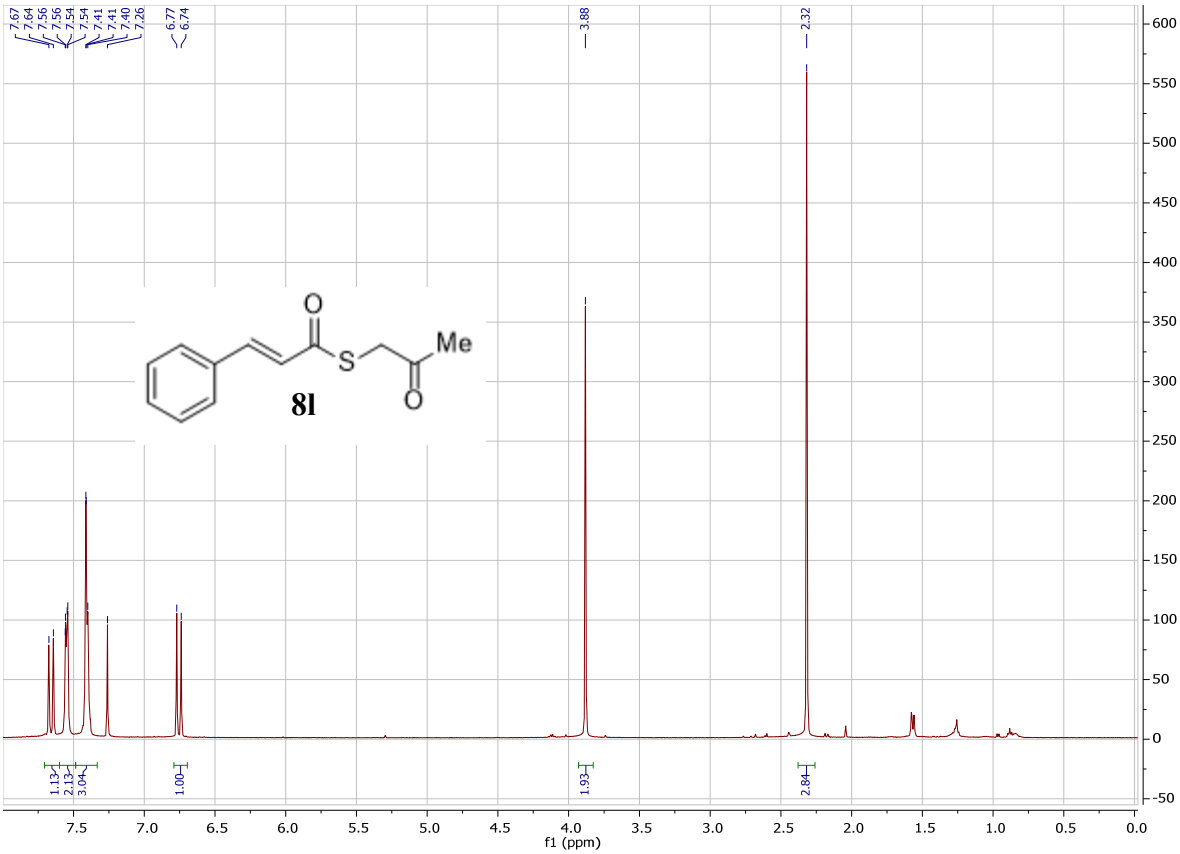

8i
Cl
f1 (ppm)

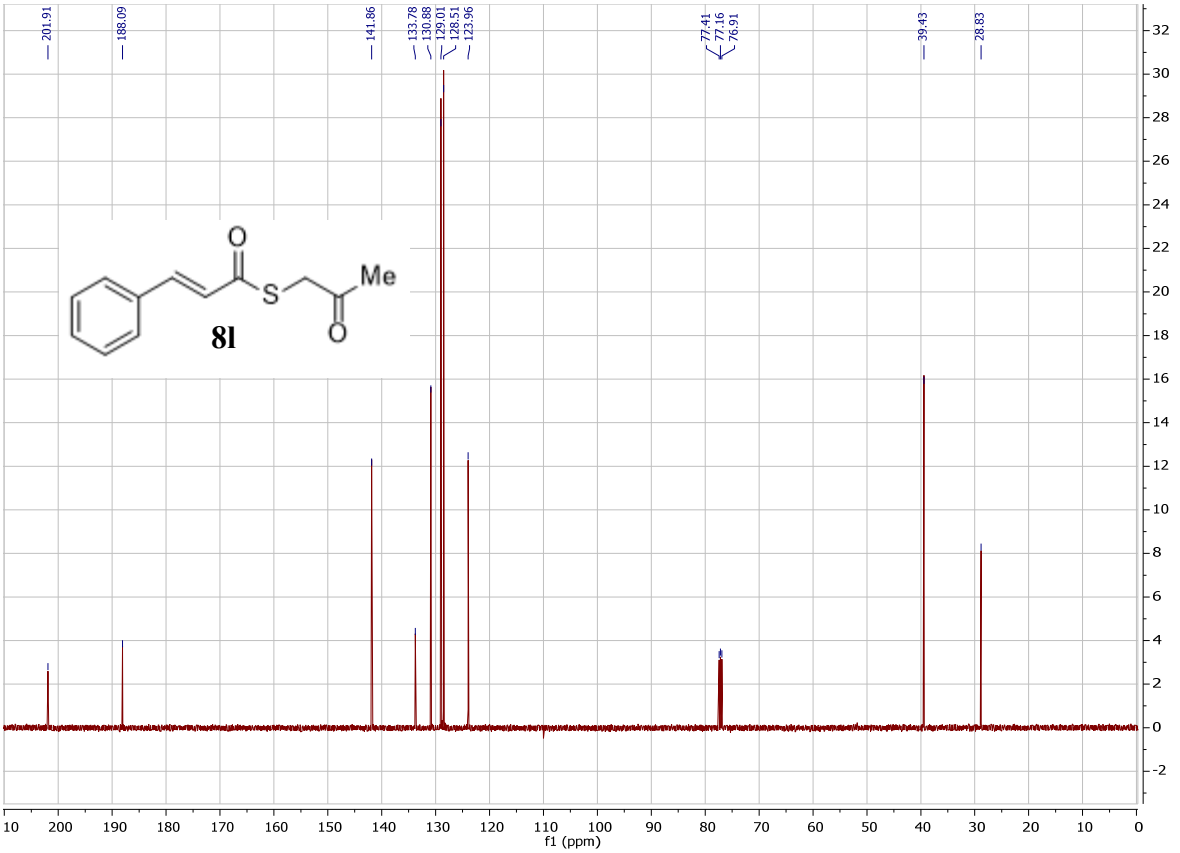

8.36
8.34
8.20
8.19
7.70
7.67
7.56
7.56
7.56
7.55
7.54
7.42
7.42
7.42
7.41
7.26
6.78
6.74
4.51
1.94
1.92
1.00
1.93
2.95
1.00
1.91
f1 (ppm)
NO2
O
S
O
8j

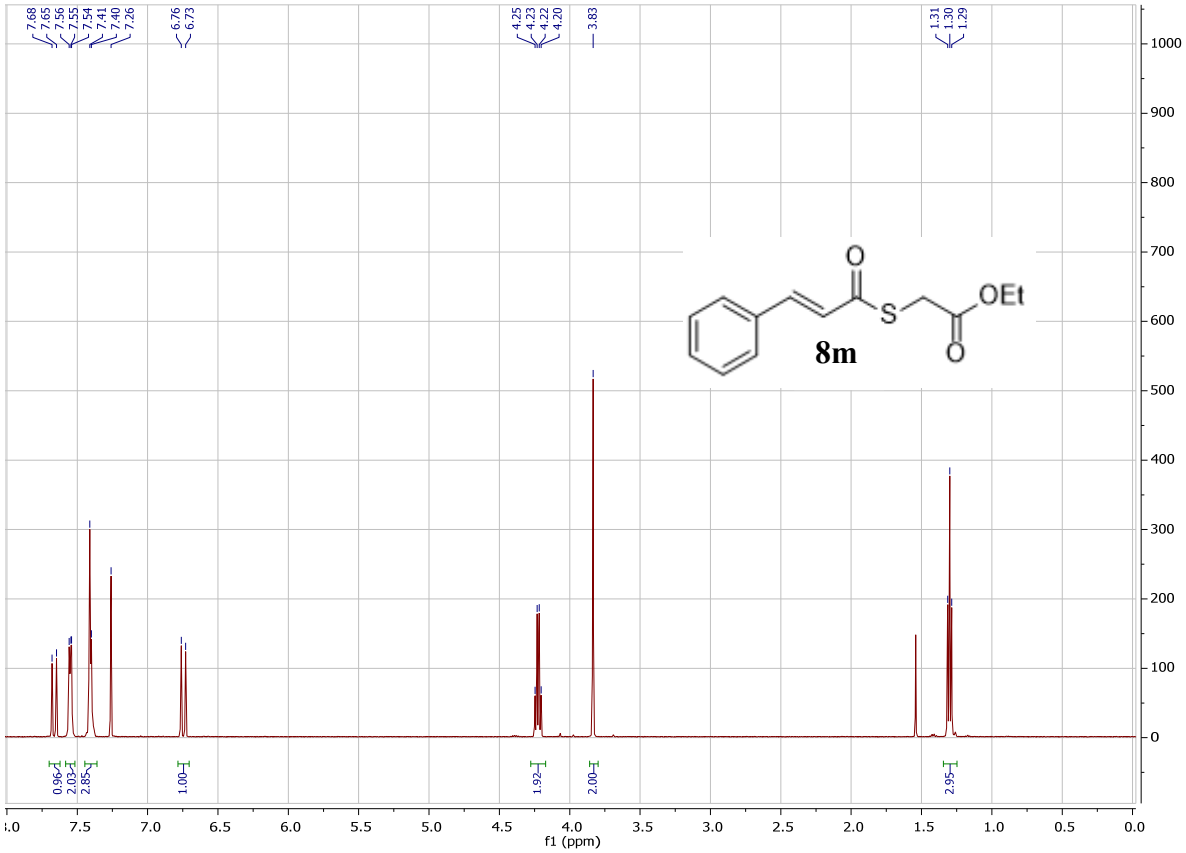

192.57
187.79
150.75
142.63
140.27
133.79
131.22
129.75
129.20
128.72
124.12
123.75
77.41
77.16
76.91
36.37
f1 (ppm)
NO2
O
S
O
8j

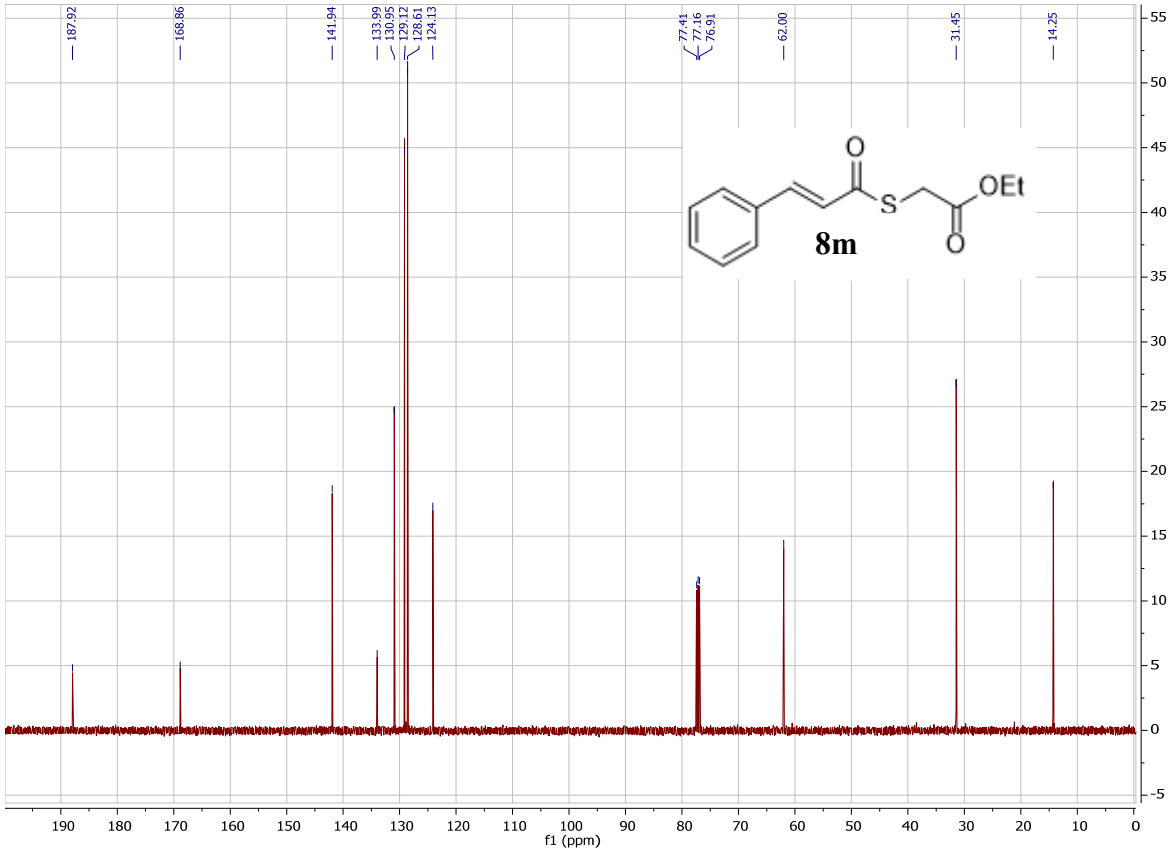

8k
f1 (ppm)

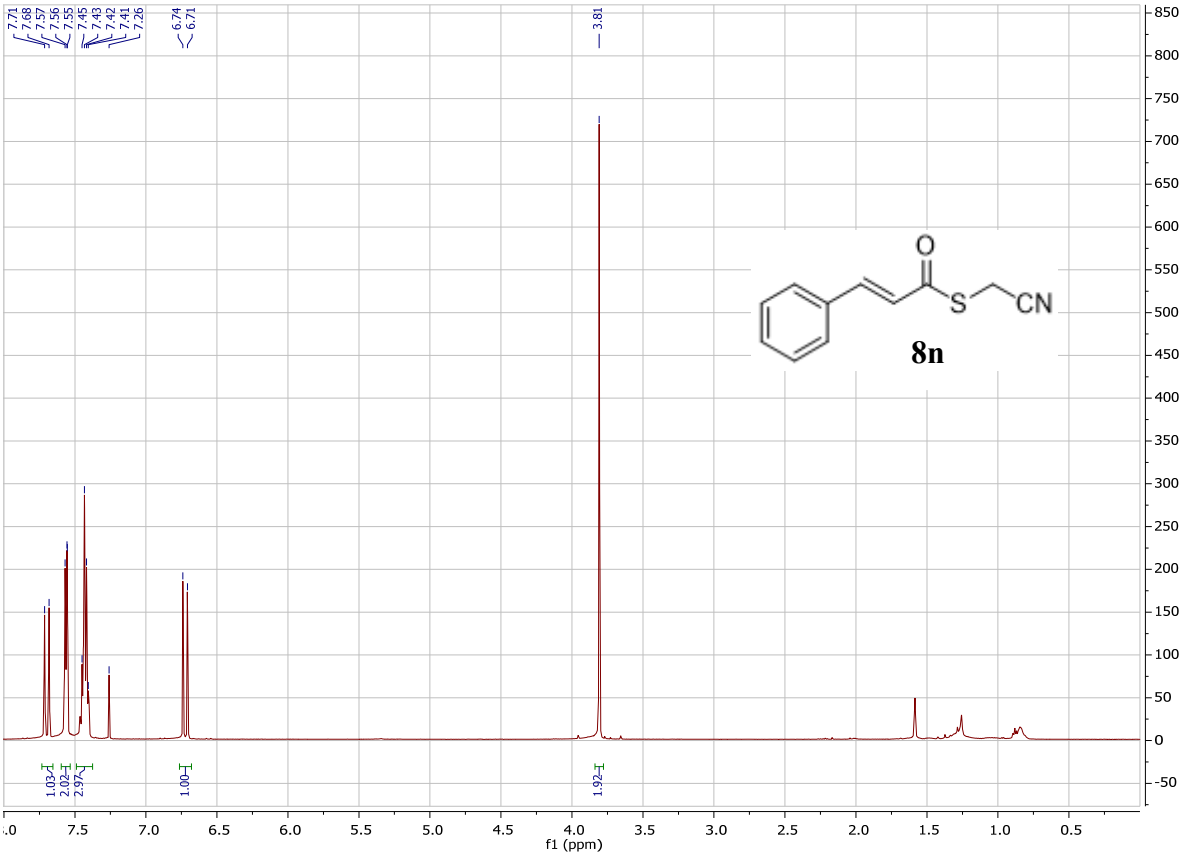

8k
f1 (ppm)

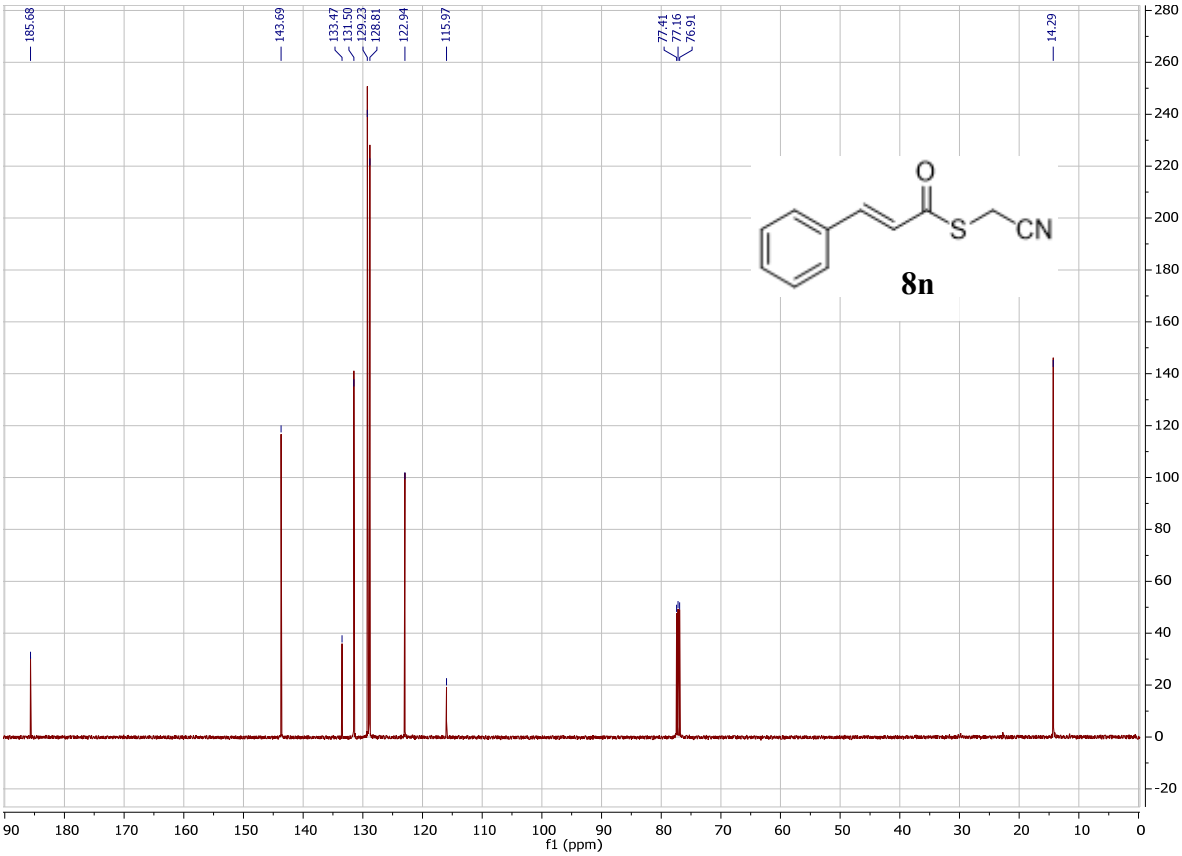

7.67
7.64
7.56
7.56
7.54
7.54
7.41
7.41
7.40
7.26
6.77
6.74
3.88
2.32
1.13
2.13
3.04
1.00
1.93
2.84
f1 (ppm)
O
S
Me
O
8l

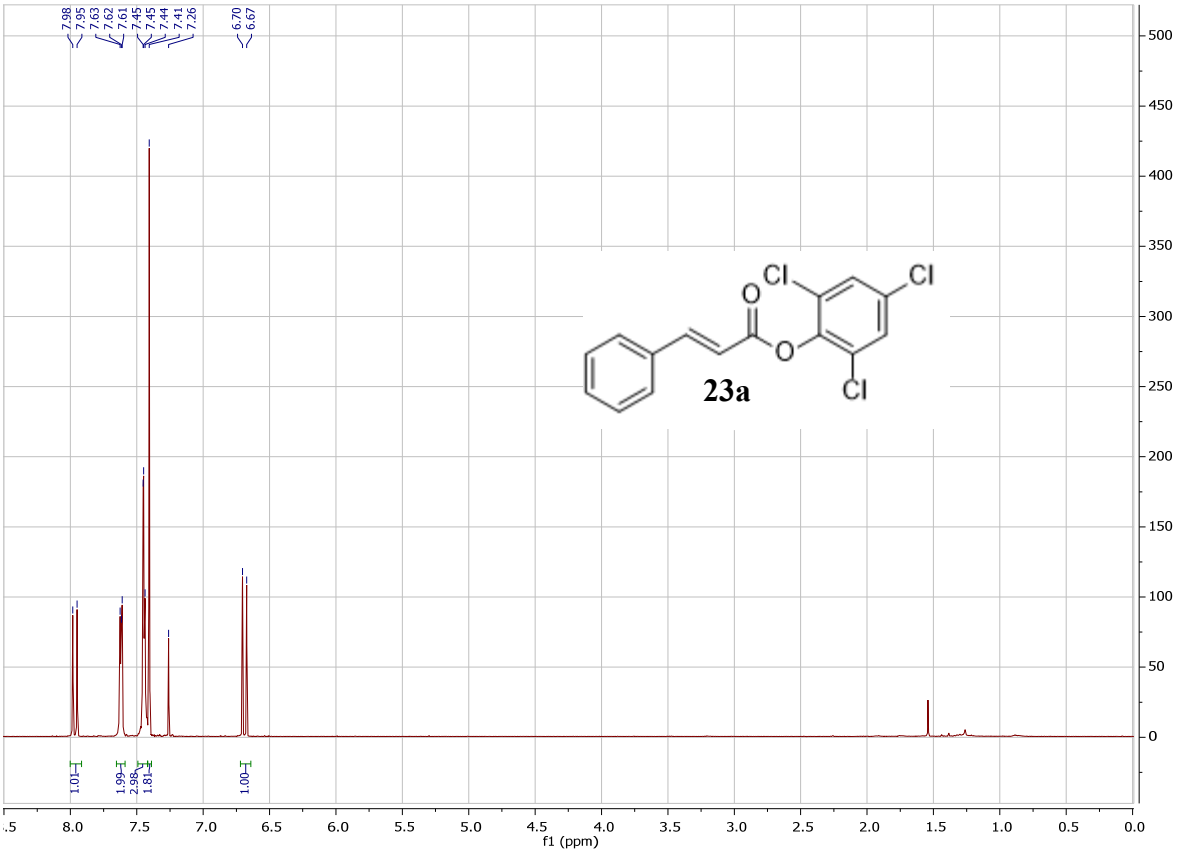

201.91
188.09
141.86
133.78
130.68
129.01
128.51
123.96
77.41
77.16
76.91
39.43
28.83
f1 (ppm)
O
S
Me
O
8l

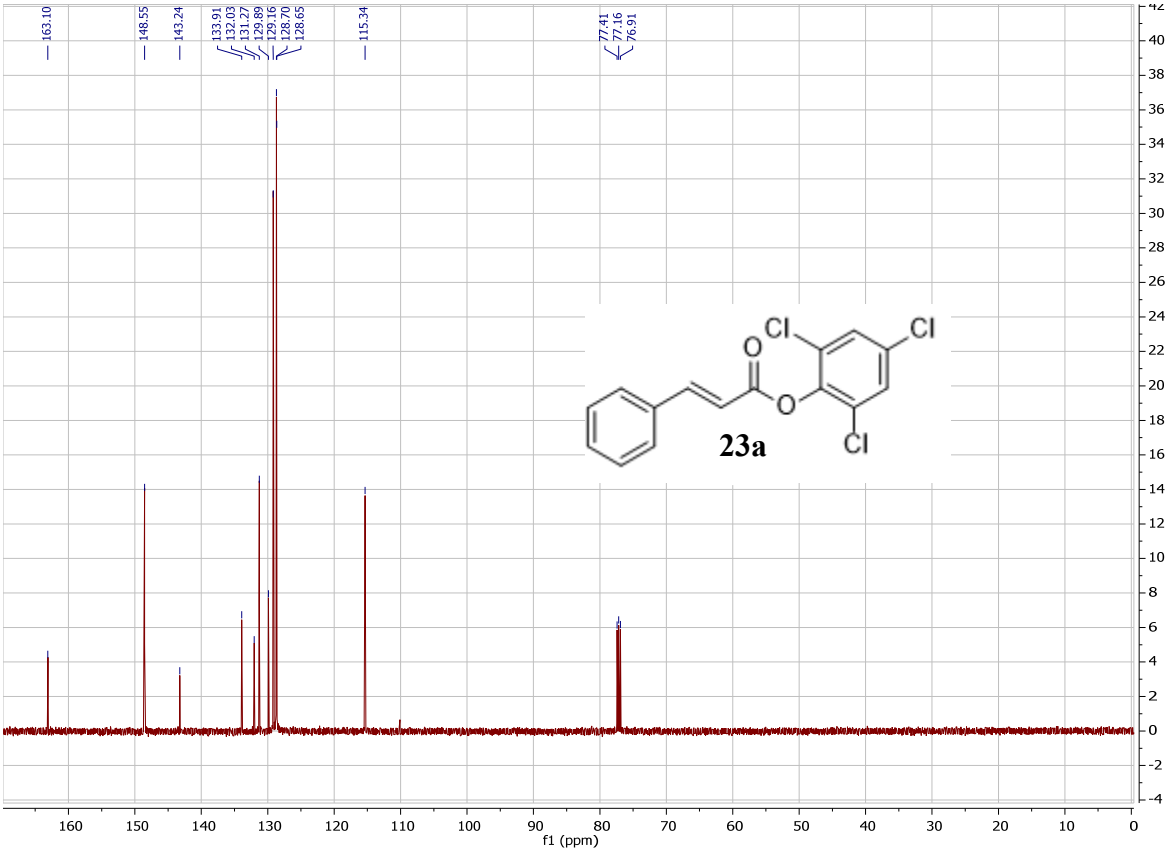

7.68
7.65
7.56
7.55
7.54
7.41
7.40
7.26
6.76
6.73
4.25
4.23
4.22
4.20
3.83
1.31
1.30
1.29
0.96
2.03
2.85
1.00
1.92
2.00
2.95
8m
f1 (ppm)

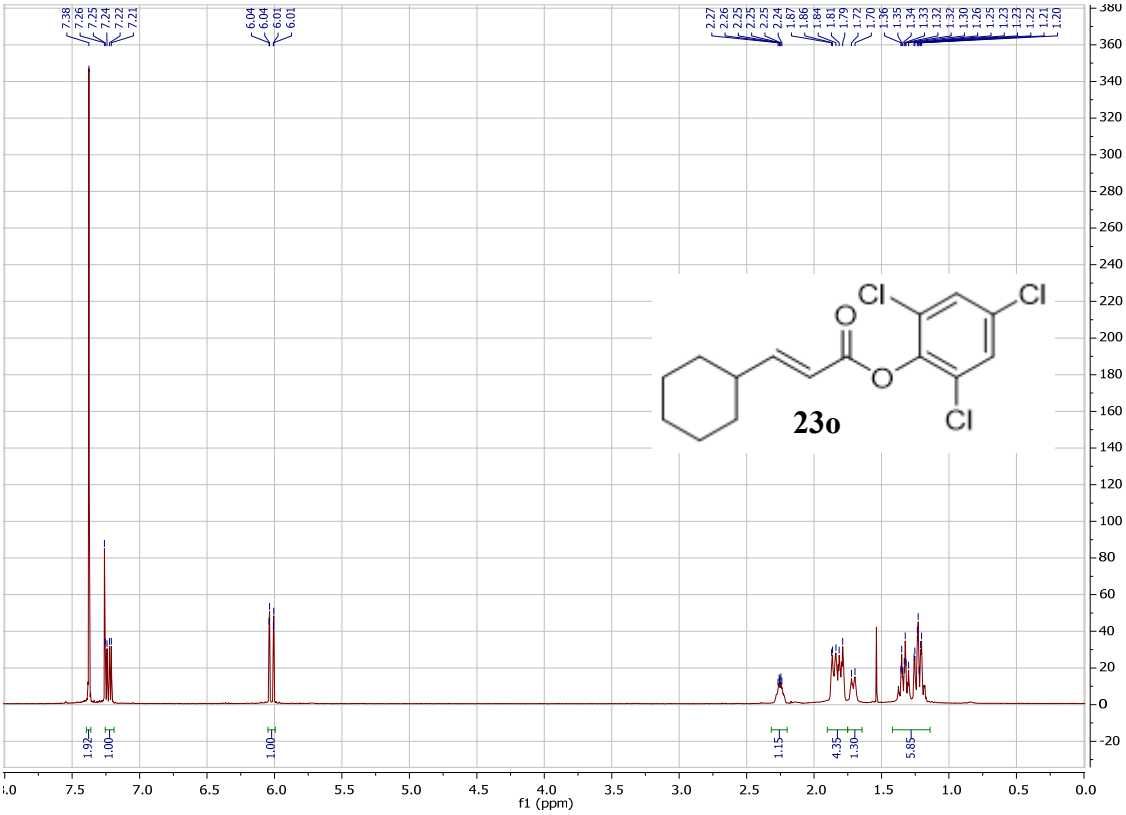

187.92
168.86
141.94
133.99
130.95
129.12
128.61
124.13
77.41
77.16
76.91
62.00
31.45
14.25
8m
f1 (ppm)

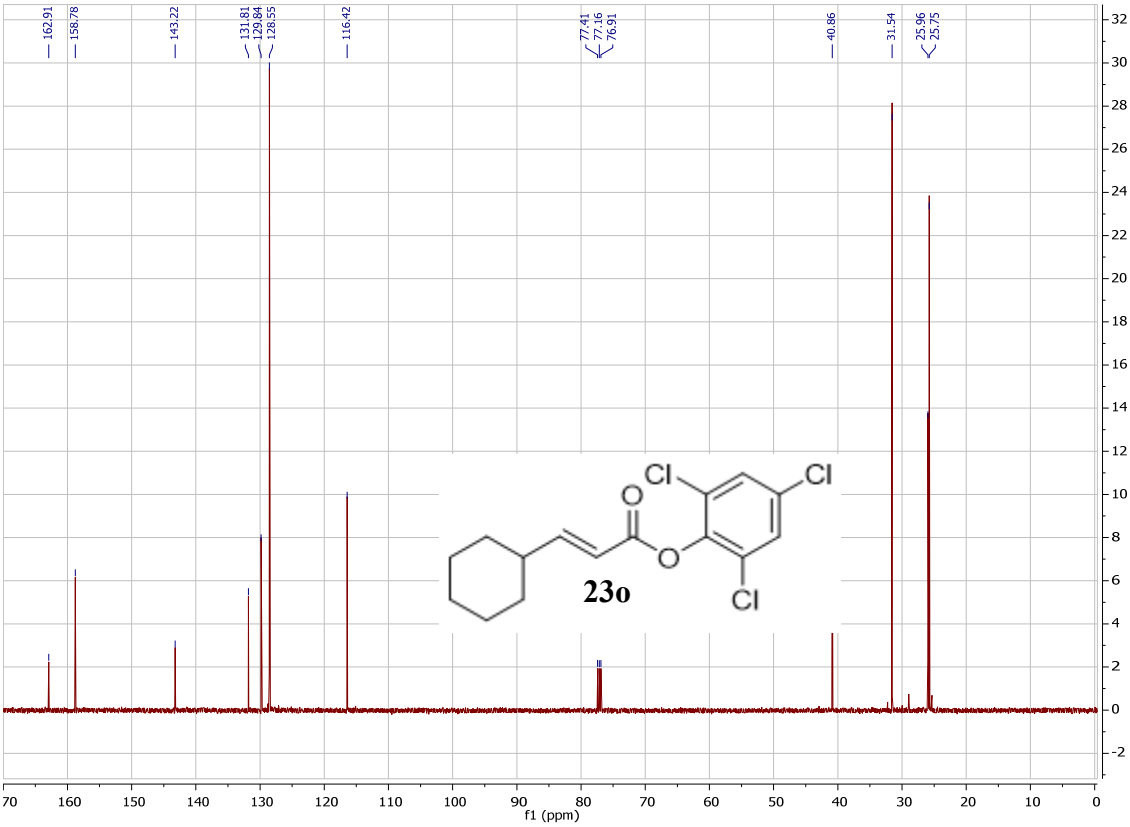

7.71
7.68
7.57
7.56
7.55
7.45
7.43
7.42
7.41
7.26
6.74
6.71
3.81
1.03
2.02
2.97
1.00
1.92
O
S
CN
8n
f1 (ppm)

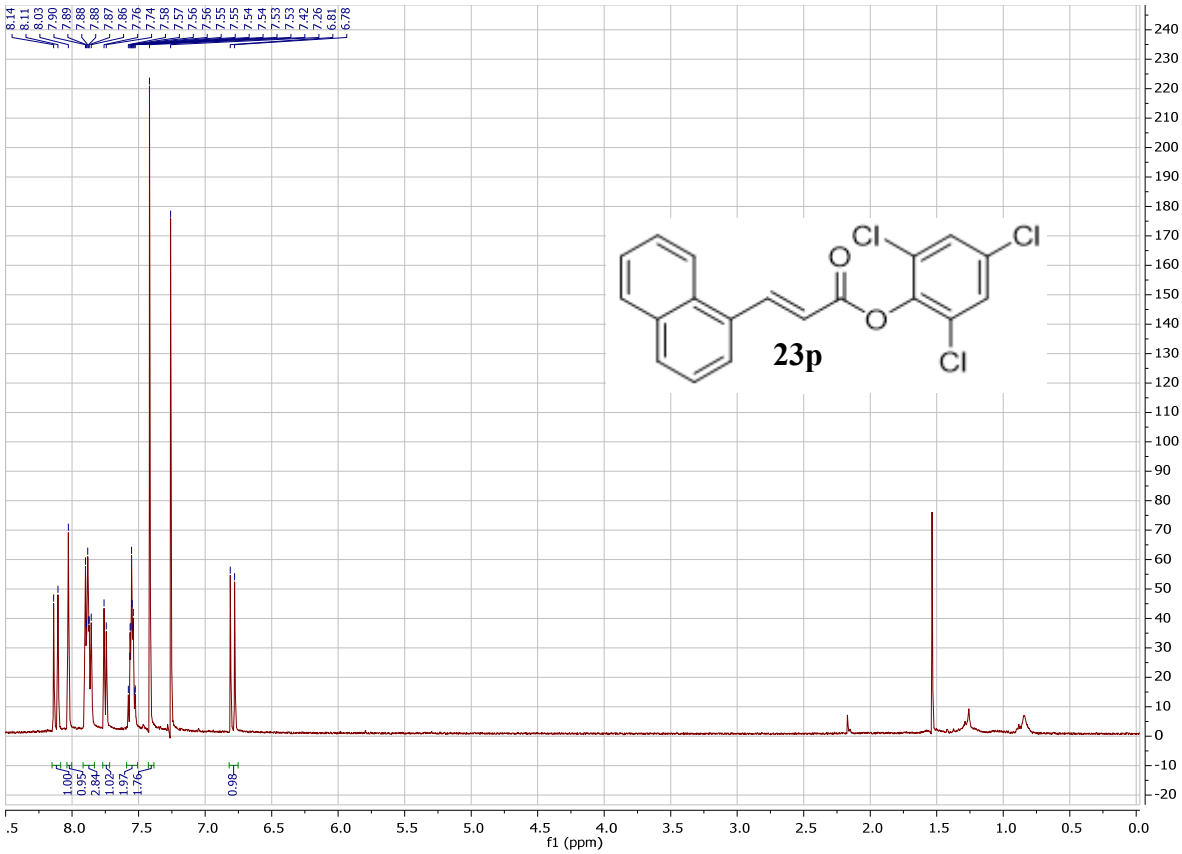

185.68
143.69
133.47
131.50
129.23
128.81
122.94
115.97
77.41
77.16
76.91
14.29
O
S
CN
8n
f1 (ppm)

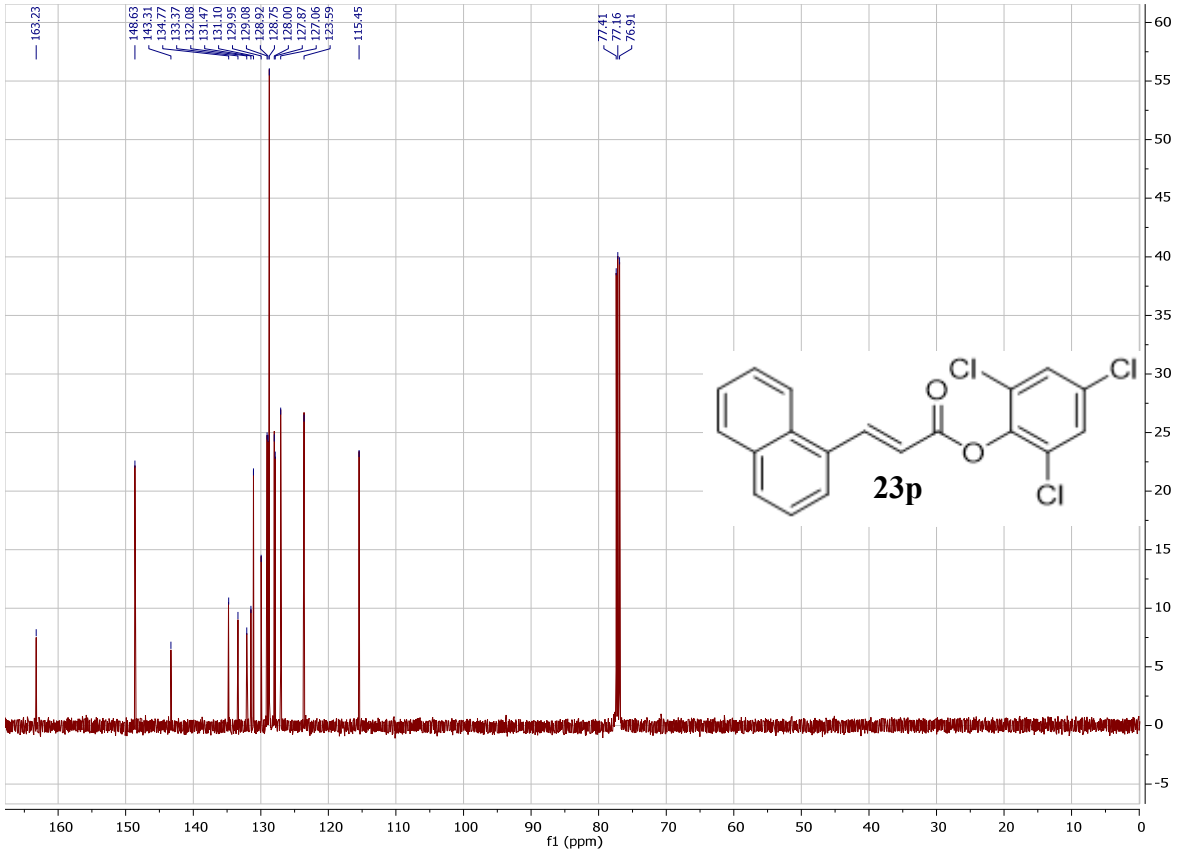

7.98
7.95
7.63
7.62
7.61
7.45
7.45
7.44
7.41
7.26
6.70
6.67
1.01
1.99
2.98
1.81
1.00
f1 (ppm)
23a

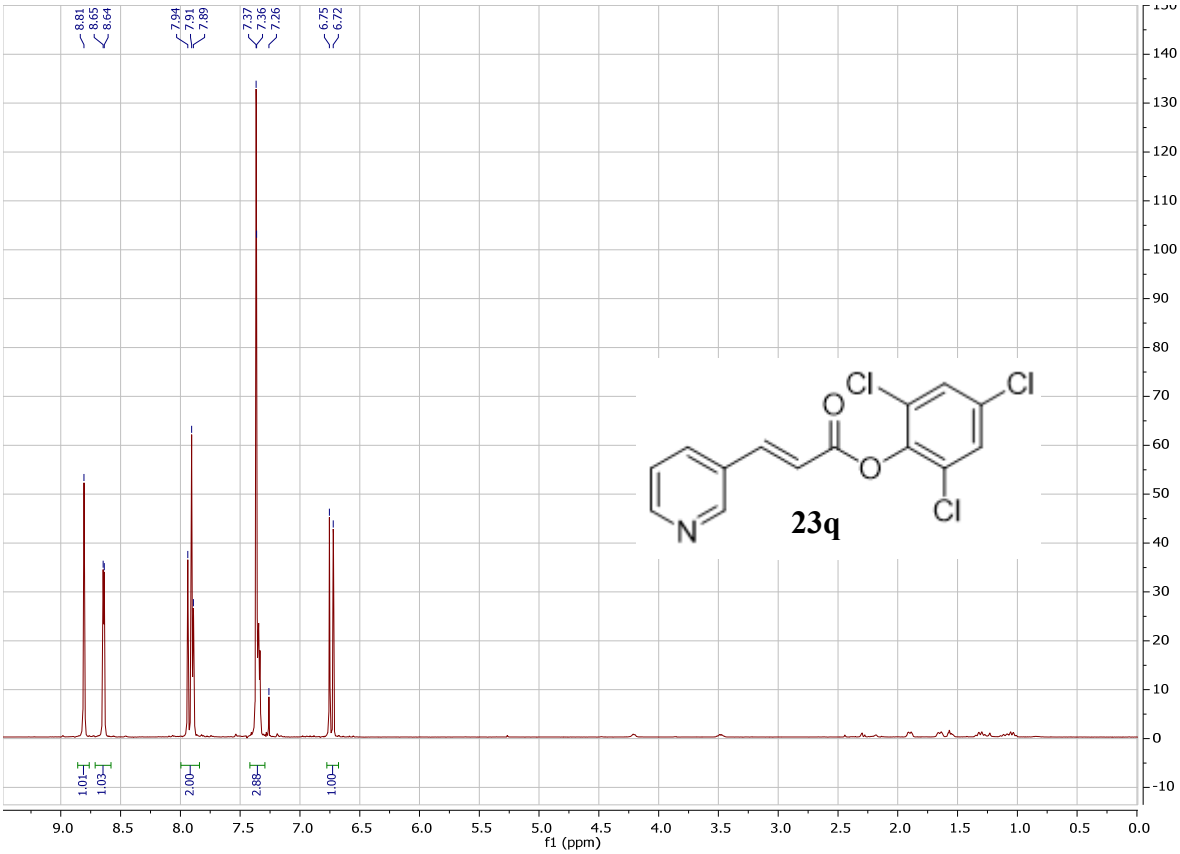

163.10
148.55
143.24
133.91
132.03
131.27
129.89
129.16
128.70
128.65
115.34
77.41
77.16
76.91
f1 (ppm)
23a

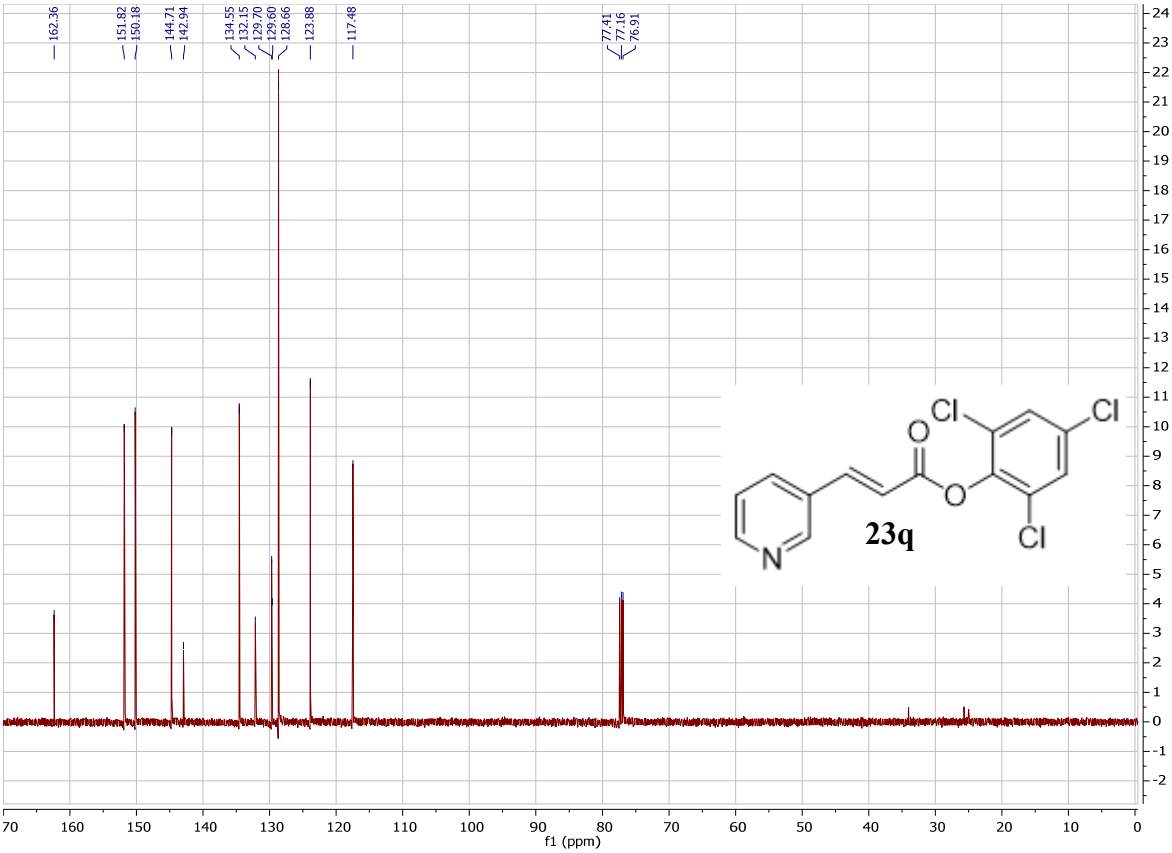

7.38
7.26
7.25
7.24
7.22
7.21
6.04
6.04
6.01
6.01
2.27
2.26
2.25
2.25
2.25
2.24
1.87
1.86
1.84
1.81
1.79
1.72
1.70
1.36
1.35
1.34
1.33
1.32
1.32
1.30
1.26
1.25
1.23
1.23
1.22
1.21
1.20
1.92
1.00
1.00
1.15
4.35
1.30
5.85
f1 (ppm)
Cl
Cl
O
O
Cl
23o

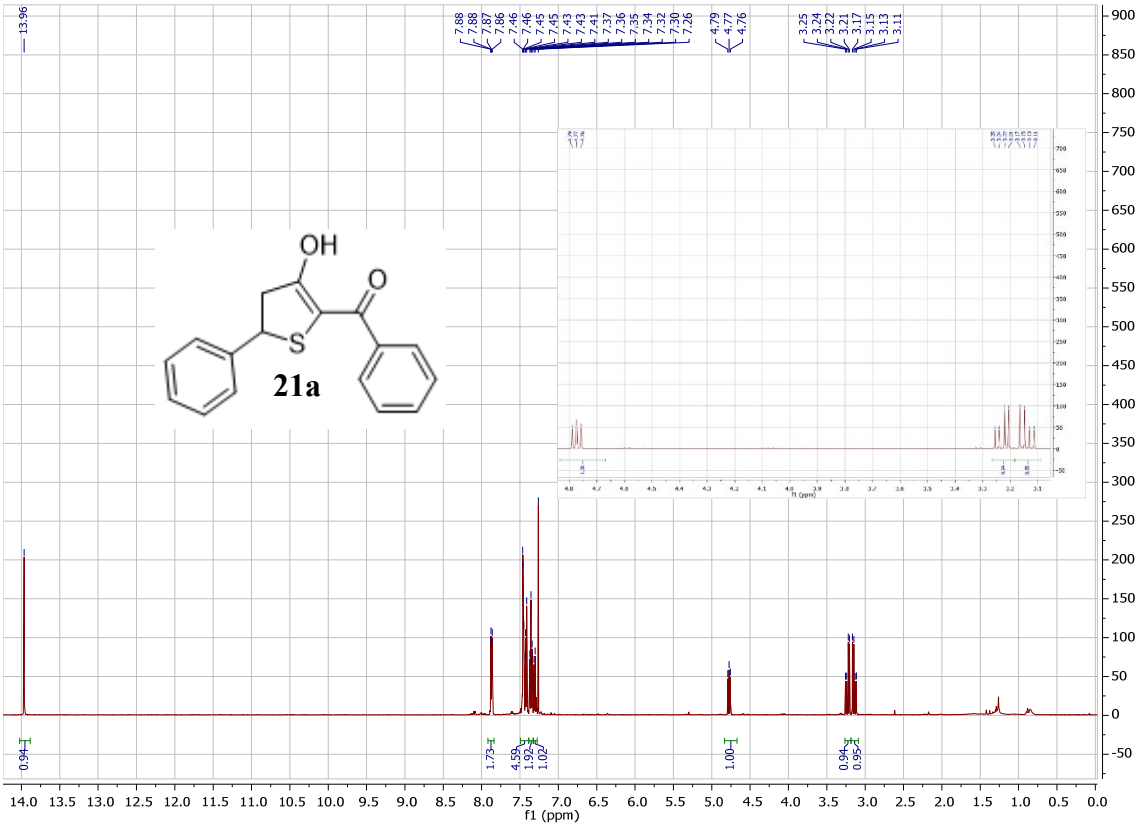

162.91
158.78
143.22
131.81
129.84
128.55
116.42
77.41
77.16
76.91
40.86
31.54
25.96
25.75
f1 (ppm)
Cl
Cl
O
O
Cl
23o

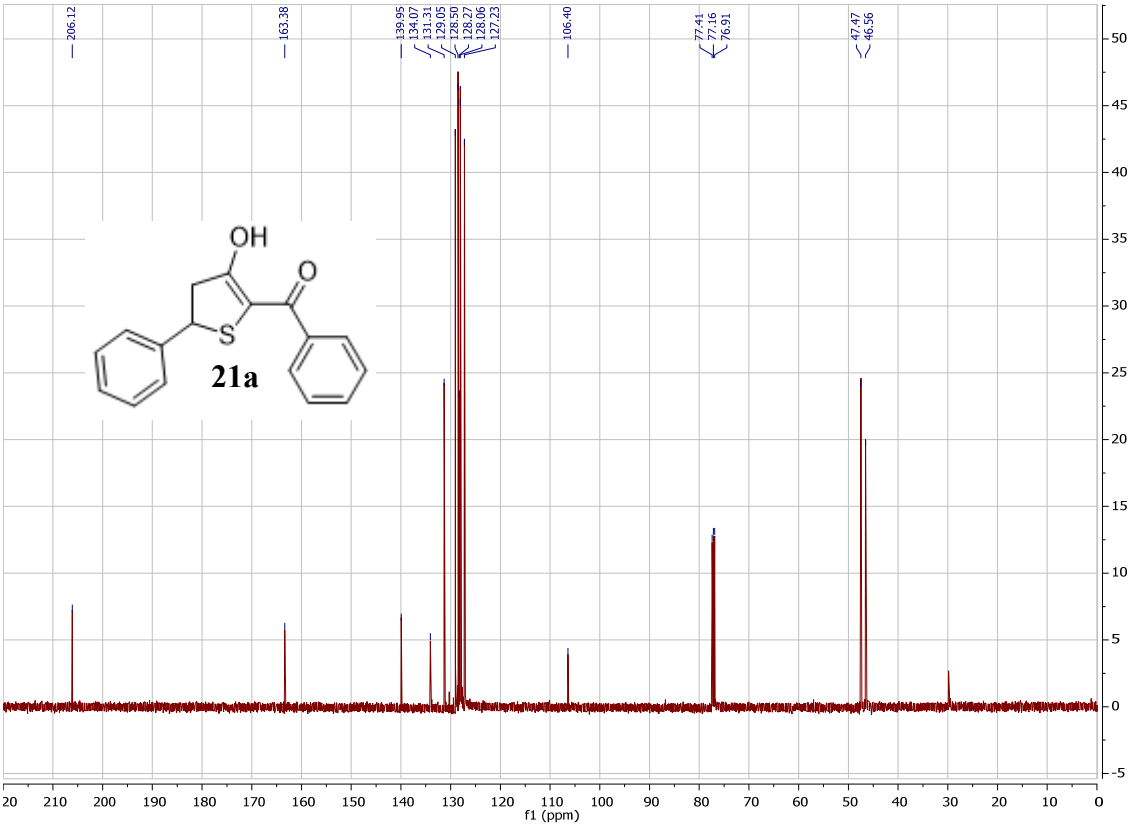

8.14
8.11
8.03
7.90
7.89
7.88
7.88
7.87
7.86
7.76
7.74
7.58
7.57
7.56
7.56
7.55
7.55
7.54
7.54
7.53
7.53
7.42
7.26
6.81
6.78
1.00
0.95
2.84
1.02
1.97
1.76
0.98
f1 (ppm)
23p

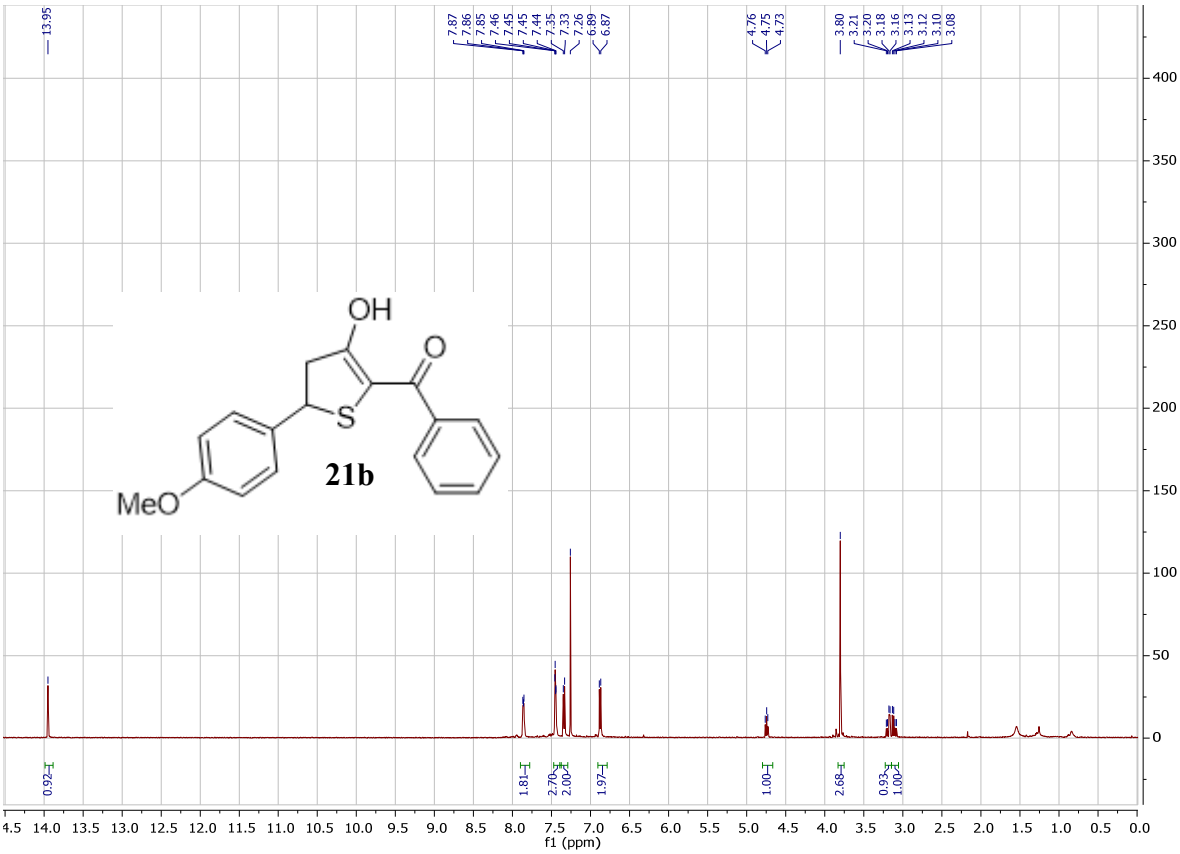

163.23
148.63
143.31
134.77
133.37
132.08
131.47
131.10
129.95
129.08
128.92
128.75
128.00
127.87
127.06
123.59
115.45
77.41
77.16
76.91
f1 (ppm)
23p

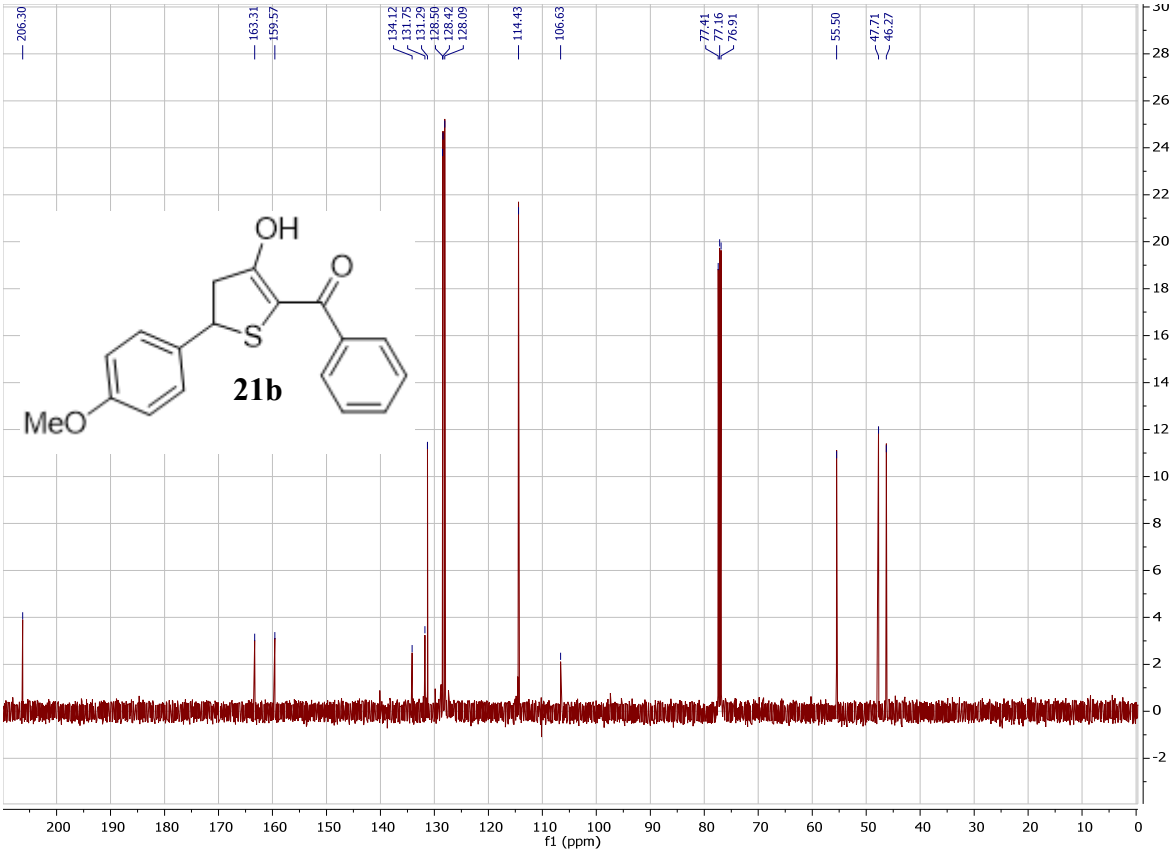

8.81
8.65
8.64
7.94
7.91
7.89
7.37
7.36
7.26
6.75
6.72
1.01
1.03
2.00
2.88
1.00
f1 (ppm)
23q

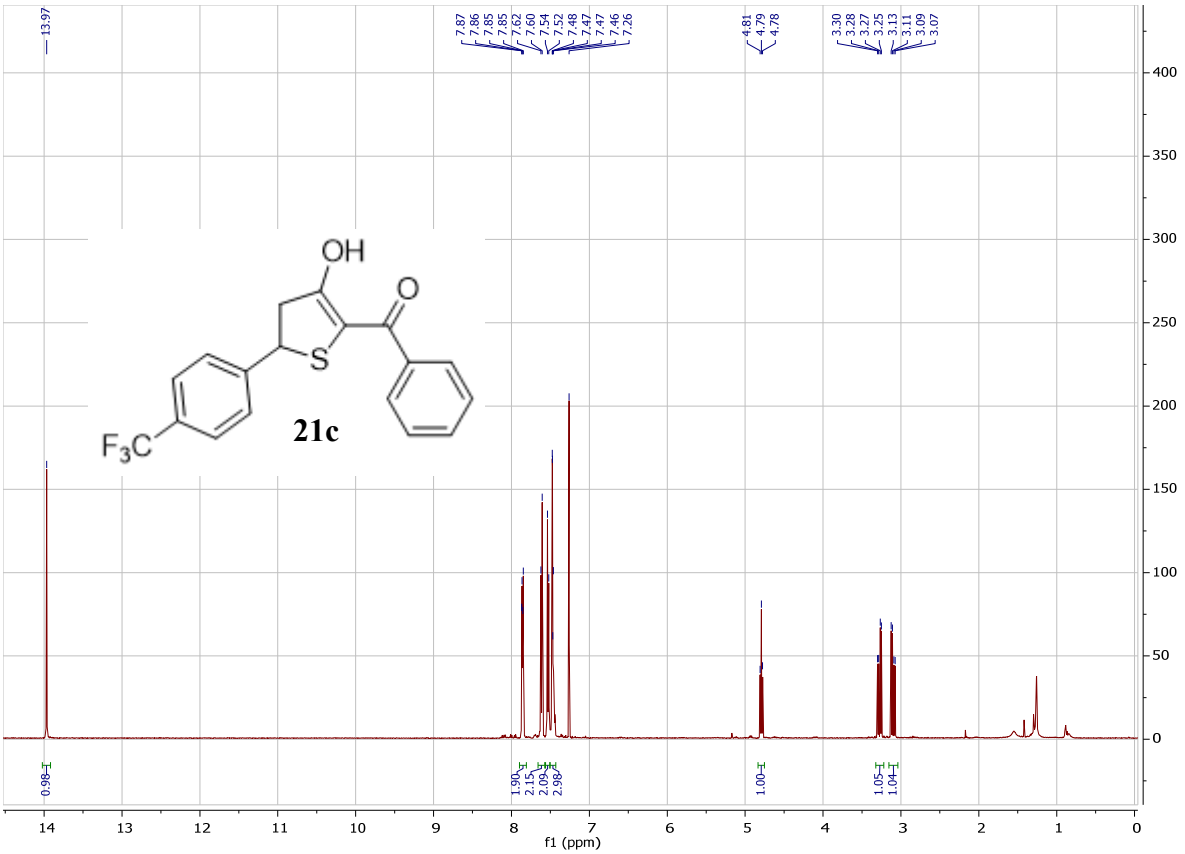

162.36
151.82
150.18
144.71
142.94
134.55
132.15
129.70
129.60
128.66
123.88
117.48
77.41
77.16
76.91
f1 (ppm)
23q

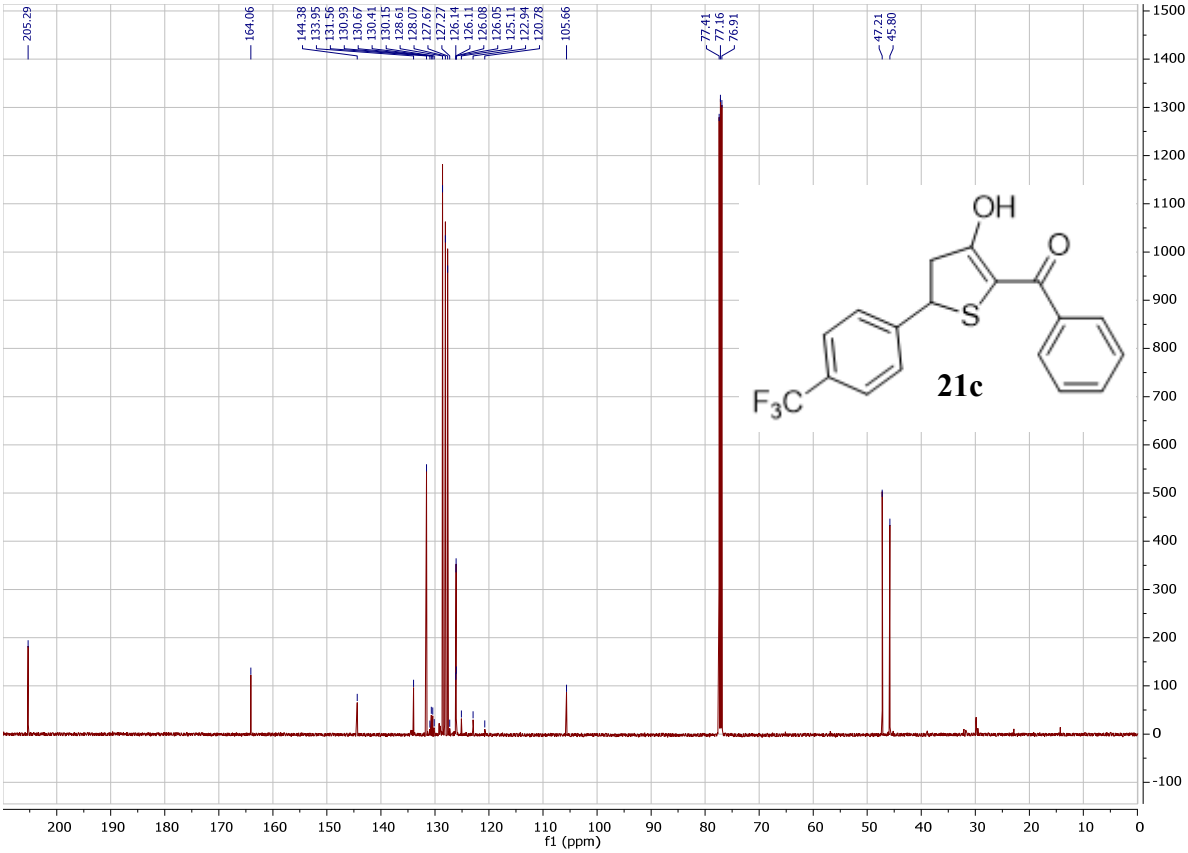

OH
O
S
21a
f1 (ppm)

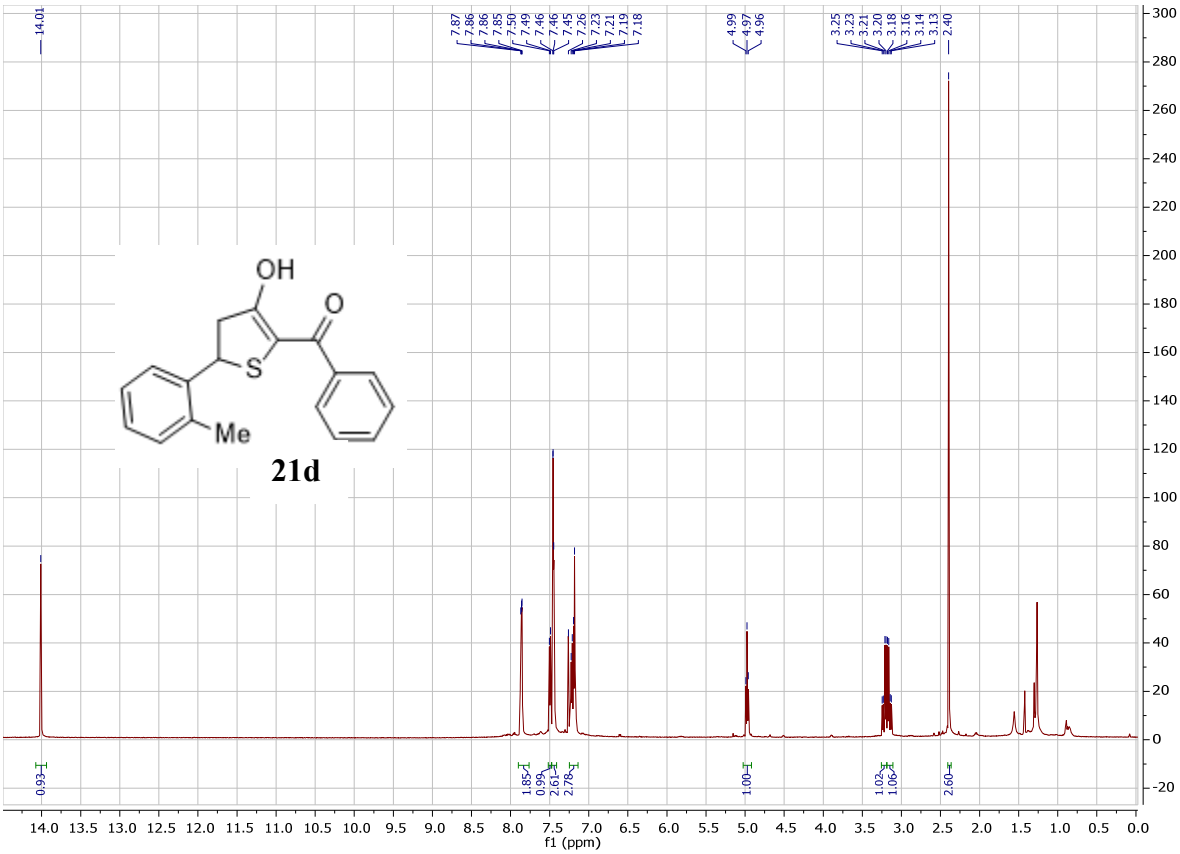

OH
O
S
21a
f1 (ppm)

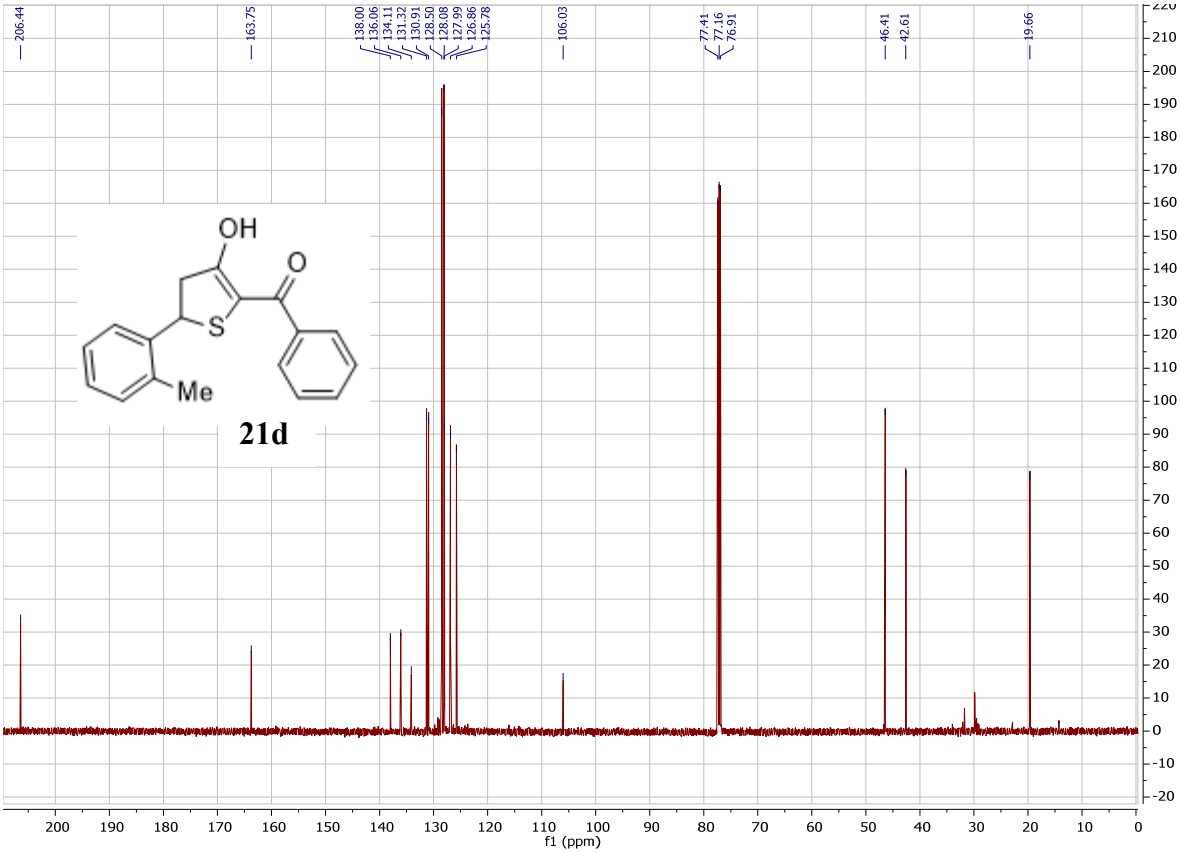

13.95
7.87
7.86
7.85
7.46
7.45
7.45
7.44
7.35
7.33
7.26
6.89
6.87
4.76
4.75
4.73
3.80
3.21
3.20
3.18
3.16
3.13
3.12
3.10
3.08
OH
O
S
MeO
21b
0.92
1.81
2.70
2.00
1.97
1.00
2.68
0.93
1.00
f1 (ppm)

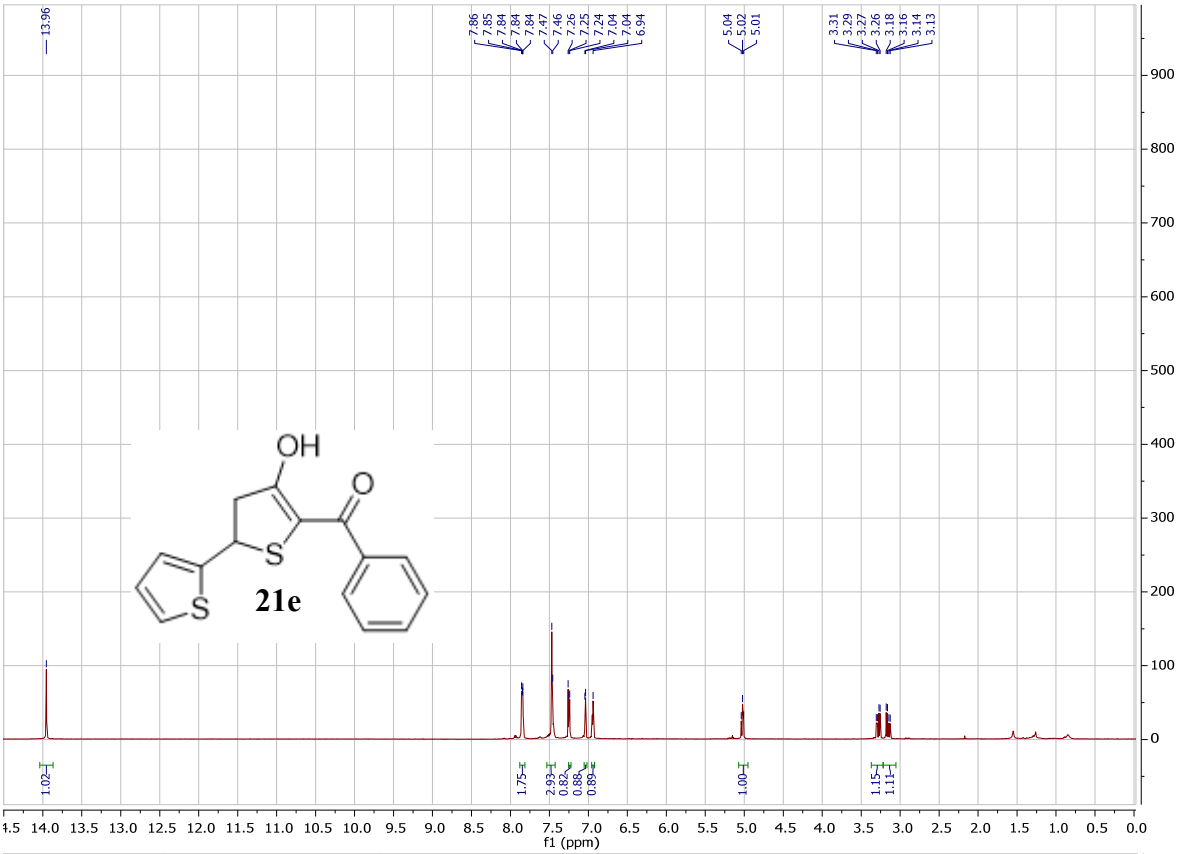

206.30
163.31
159.57
134.12
131.75
131.29
128.50
128.42
128.09
114.43
106.63
77.41
77.16
76.91
55.50
47.71
46.27
OH
O
S
MeO
21b
f1 (ppm)

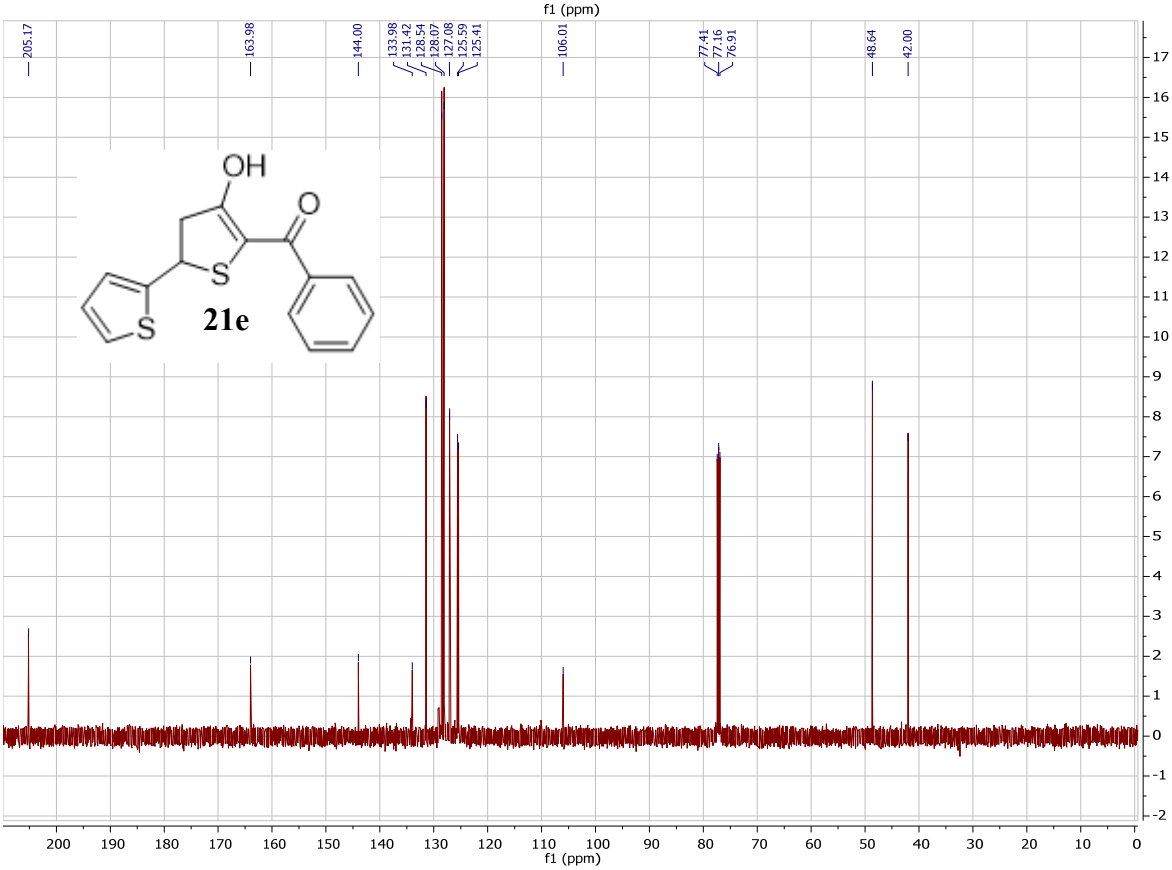

13.97
7.87
7.86
7.85
7.85
7.62
7.60
7.54
7.52
7.48
7.47
7.47
7.46
7.26
4.81
4.79
4.78
3.30
3.28
3.27
3.25
3.13
3.11
3.09
3.07
OH
O
S
F3C
21c
0.98
1.90
2.15
2.09
2.98
1.00
1.05
1.04
f1 (ppm)

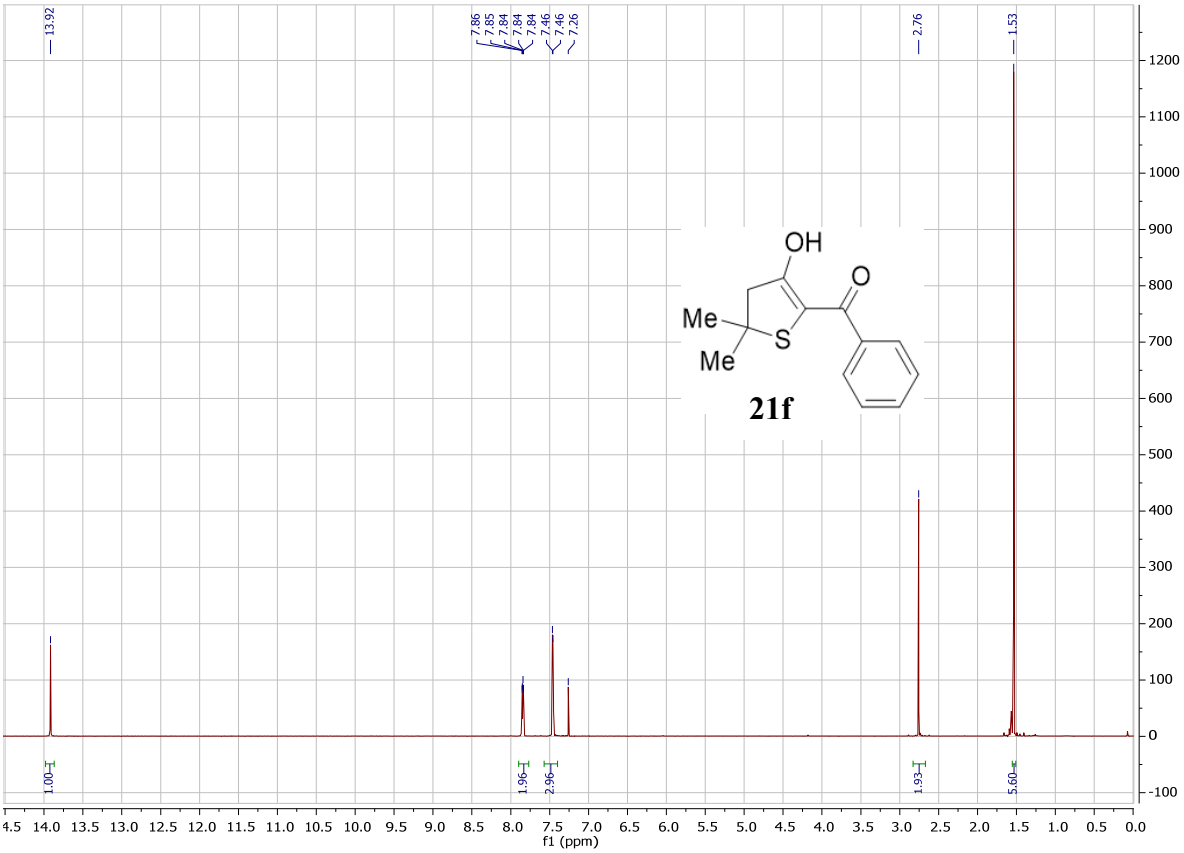

205.29
164.06
144.38
133.95
131.56
130.93
130.67
130.41
130.15
128.64
128.07
127.67
127.27
126.14
126.11
126.08
126.05
125.11
122.94
120.78
105.66
77.41
77.16
76.91
47.21
45.80
OH
O
S
F3C
21c
f1 (ppm)

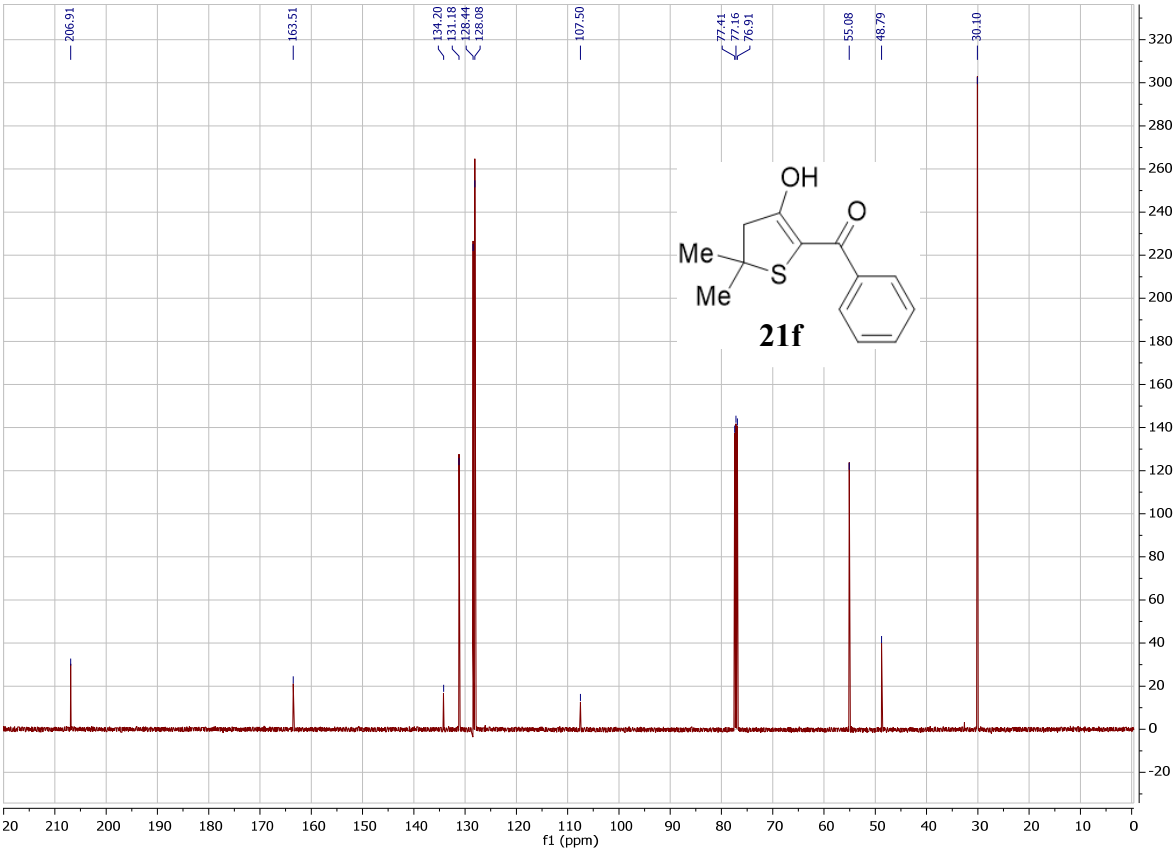

OH
O
S
Me
21d
f1 (ppm)

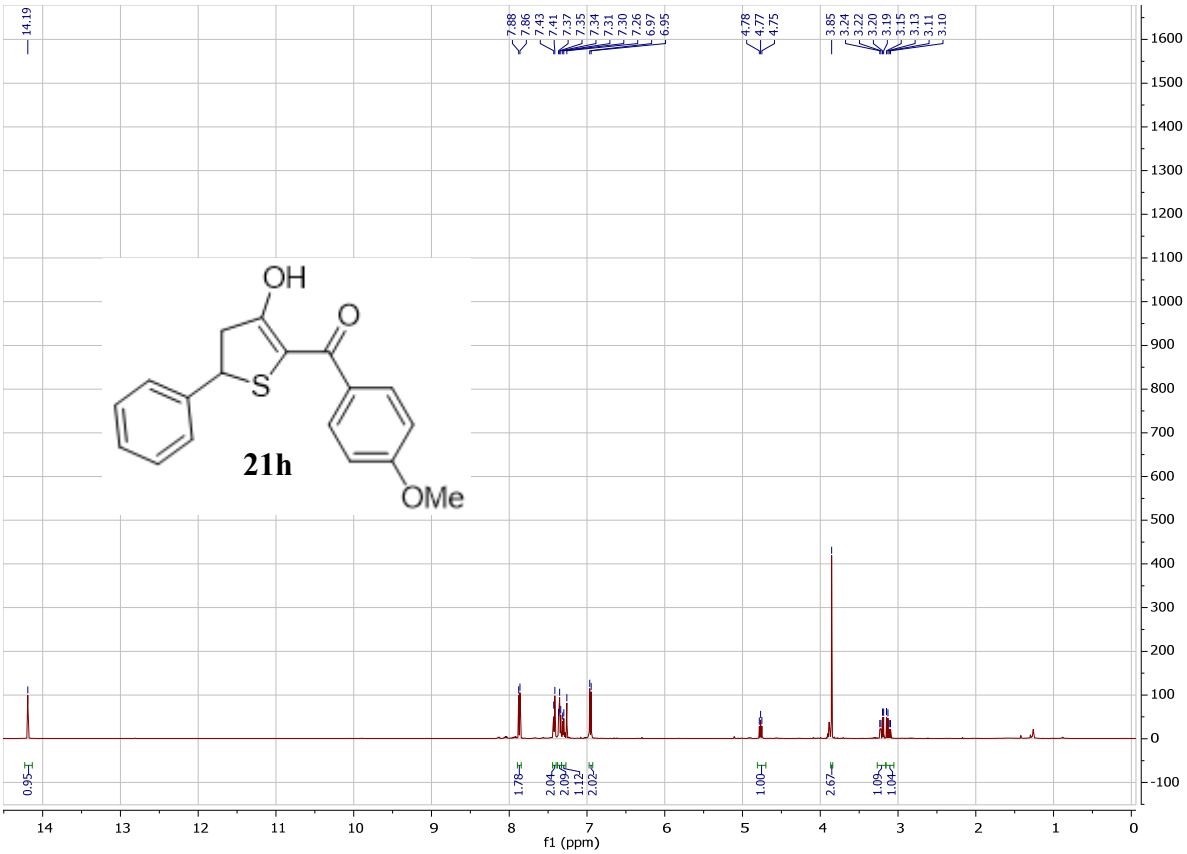

OH
O
S
Me
21d
f1 (ppm)

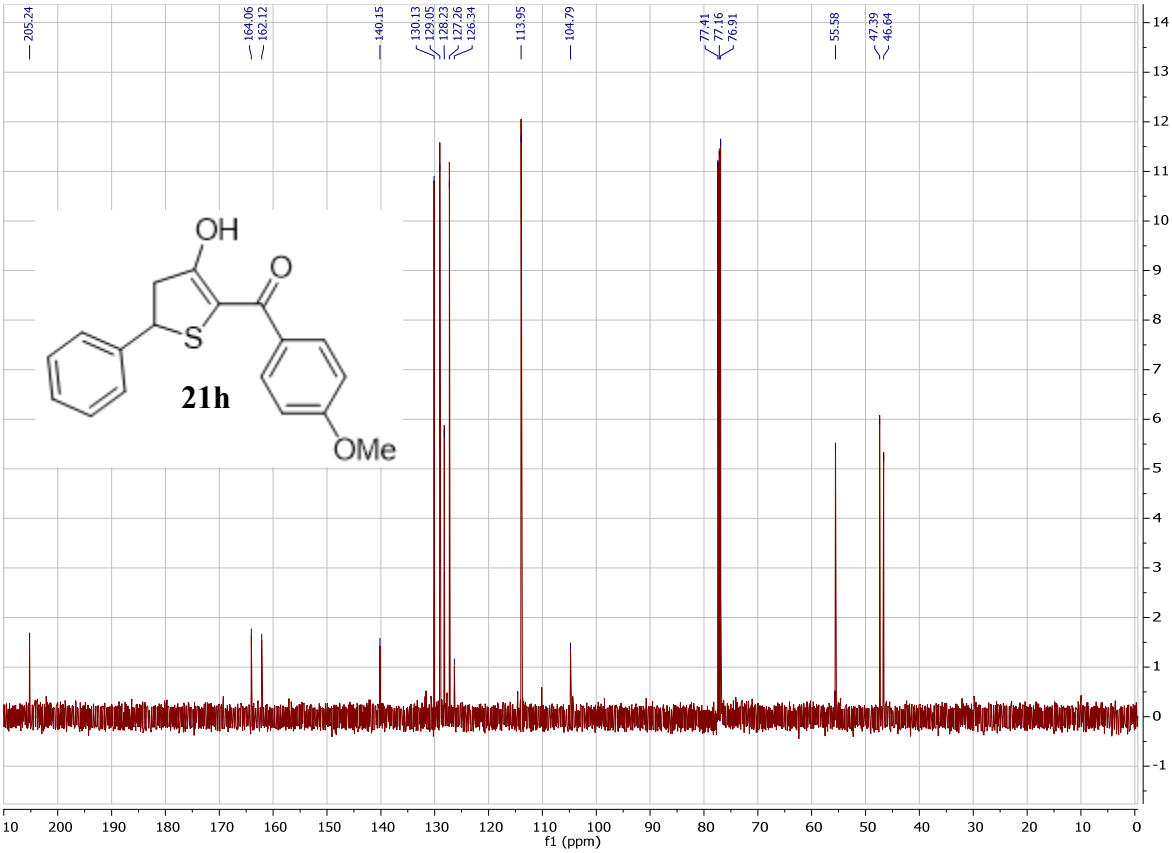

13.96
7.86
7.85
7.84
7.84
7.84
7.47
7.46
7.26
7.25
7.24
7.04
7.04
6.94
5.04
5.02
5.01
3.31
3.29
3.27
3.26
3.18
3.16
3.14
3.13
OH
O
S
S
21e
1.02
1.75
2.93
0.82
0.88
0.89
1.00
1.15
1.11
f1 (ppm)

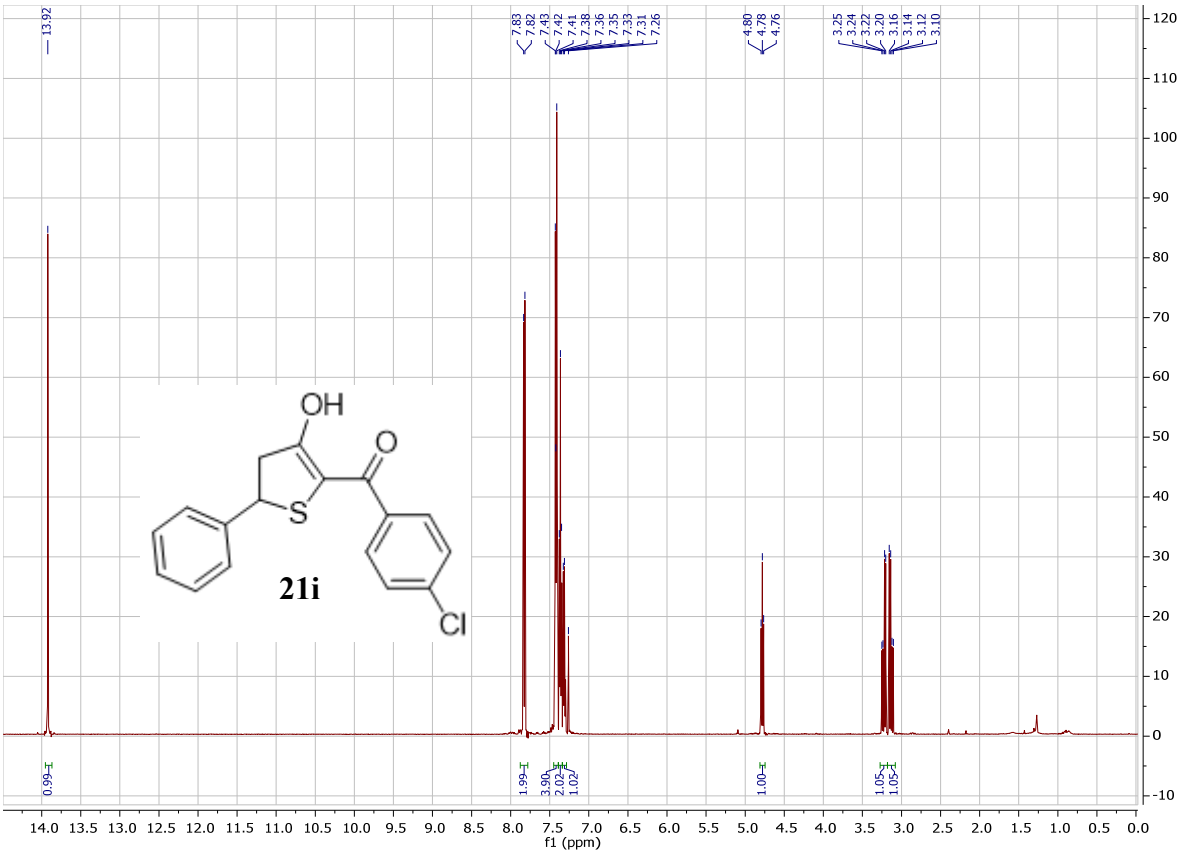

205.17
163.98
144.00
133.98
131.42
128.54
128.07
127.08
125.59
125.41
106.01
77.41
77.16
76.91
48.64
42.00
OH
O
S
S
21e
f1 (ppm)

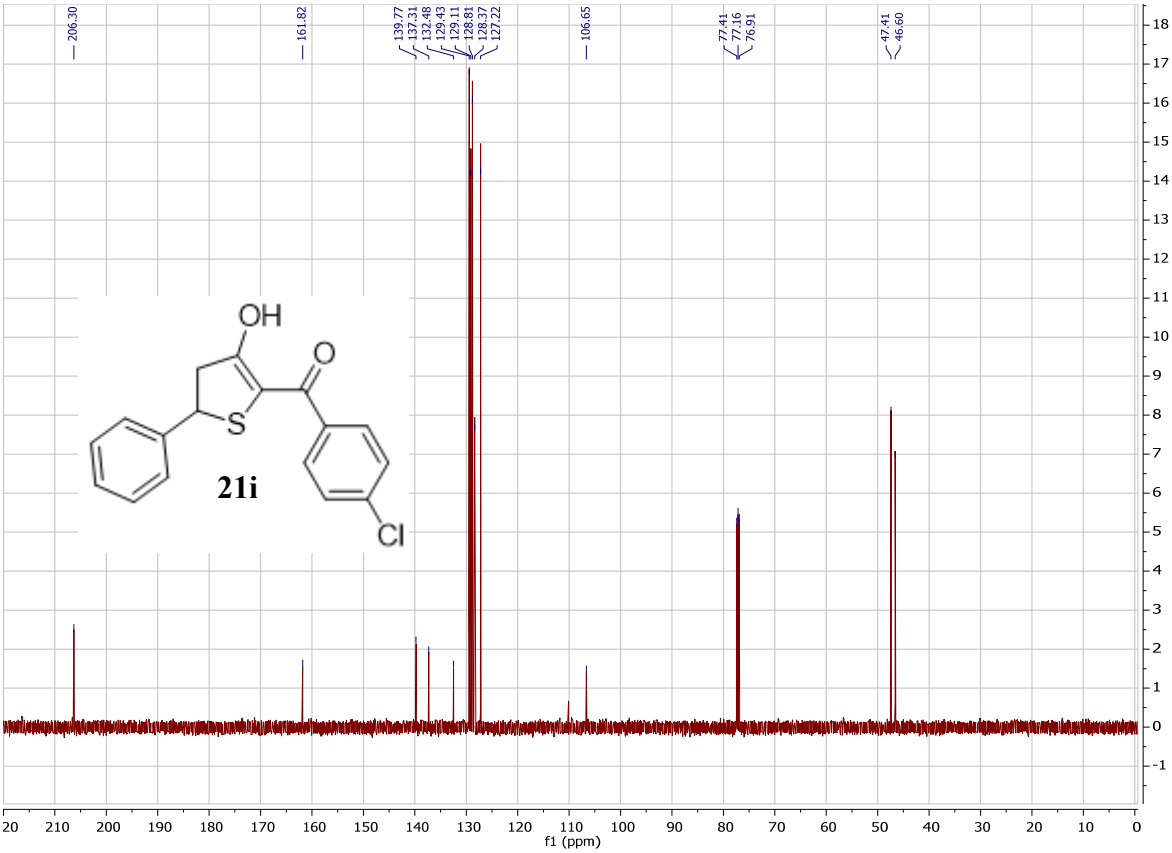

13.92
7.86
7.85
7.84
7.84
7.84
7.46
7.46
7.26
2.76
1.53
OH
O
Me
S
Me
21f
1.00
1.96
2.96
1.93
5.60
f1 (ppm)

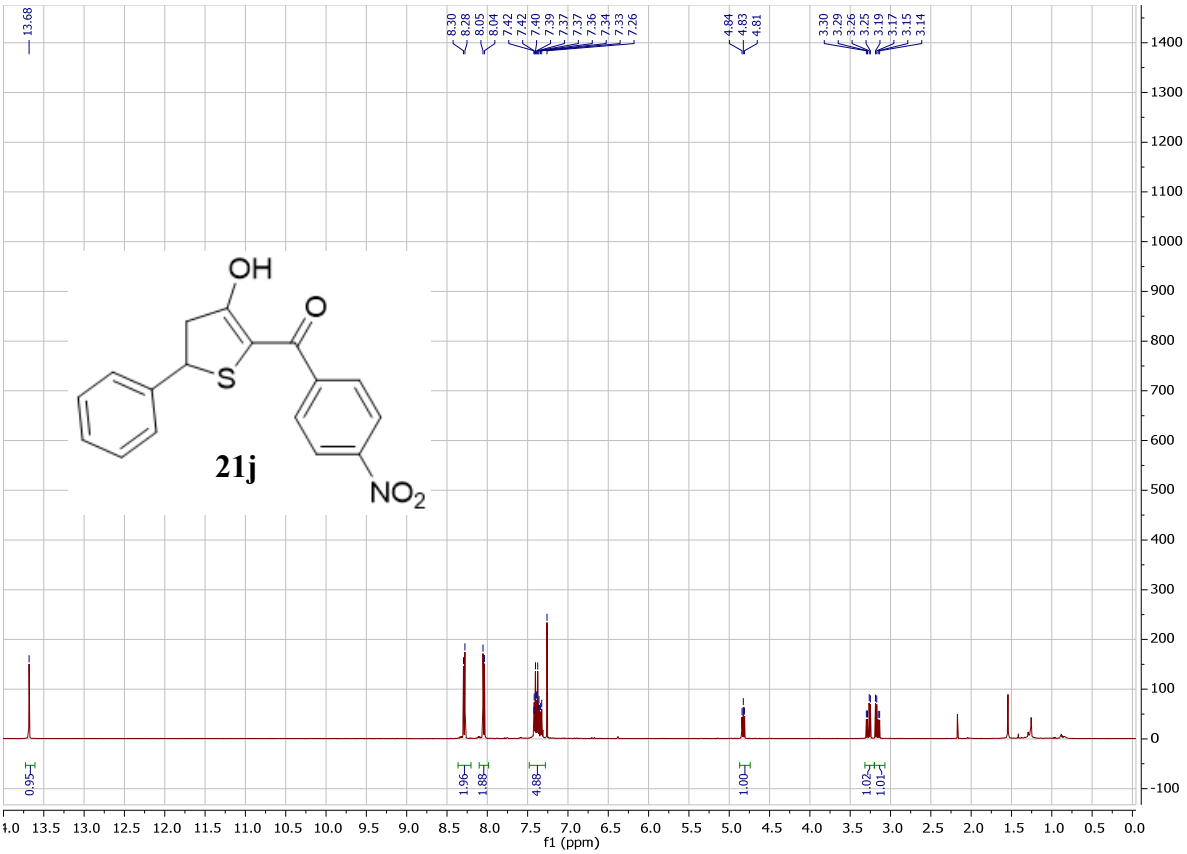

206.91
163.51
134.20
131.18
128.44
128.08
107.50
77.41
77.16
76.91
55.08
48.79
30.10
OH
O
Me
S
Me
21f
f1 (ppm)

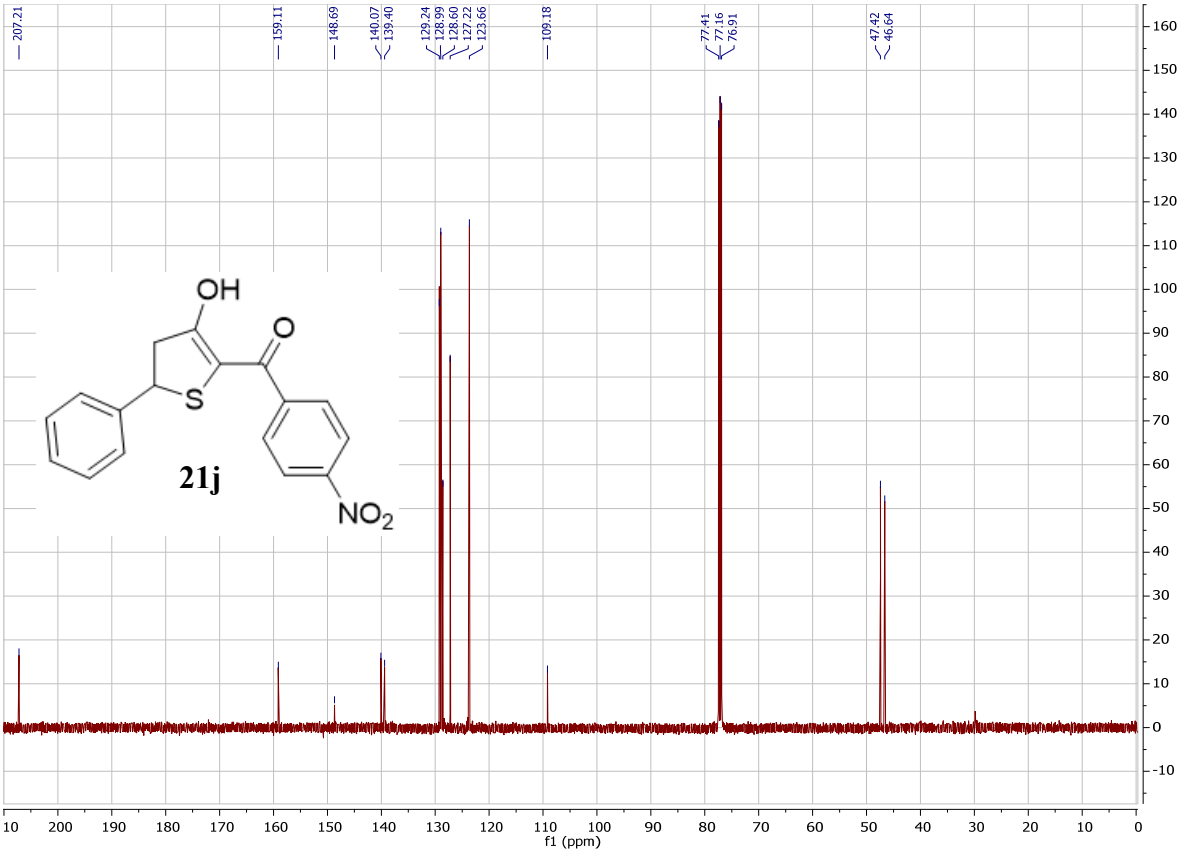

OH
O
S
21h
OMe
f1 (ppm)

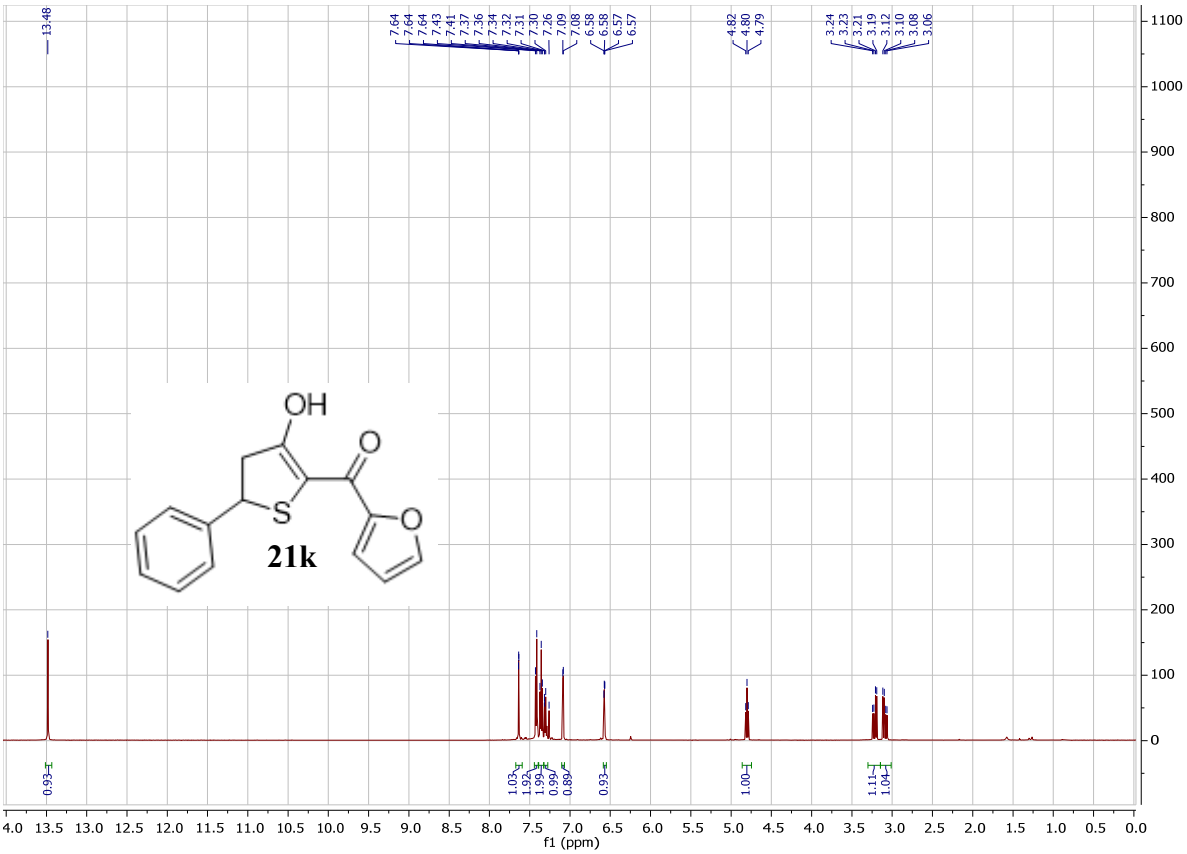

OH
O
S
21h
OMe
f1 (ppm)

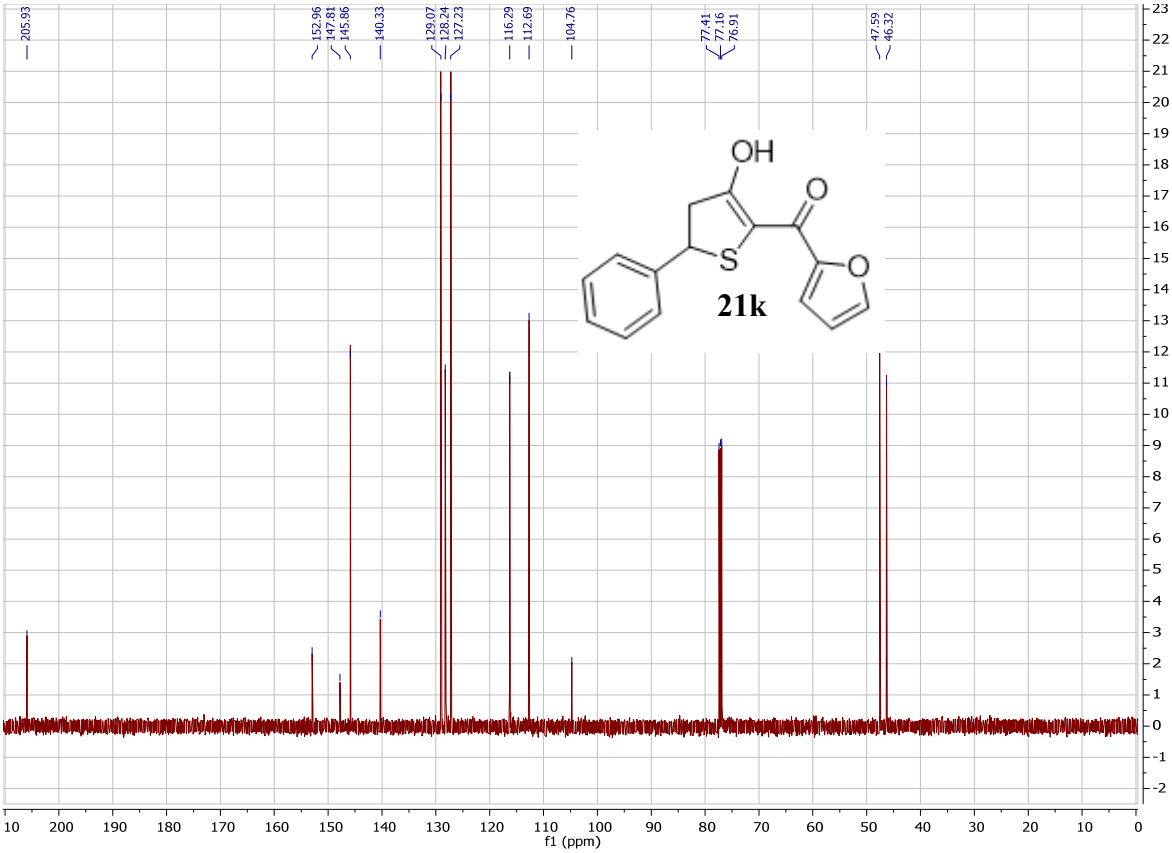

13.92
7.83
7.82
7.43
7.42
7.41
7.38
7.36
7.35
7.33
7.31
7.26
4.80
4.78
4.76
3.25
3.24
3.22
3.20
3.16
3.14
3.12
3.10
OH
O
S
Cl
21i
0.99
1.99
3.90
2.02
1.02
1.00
1.05
1.05
f1 (ppm)

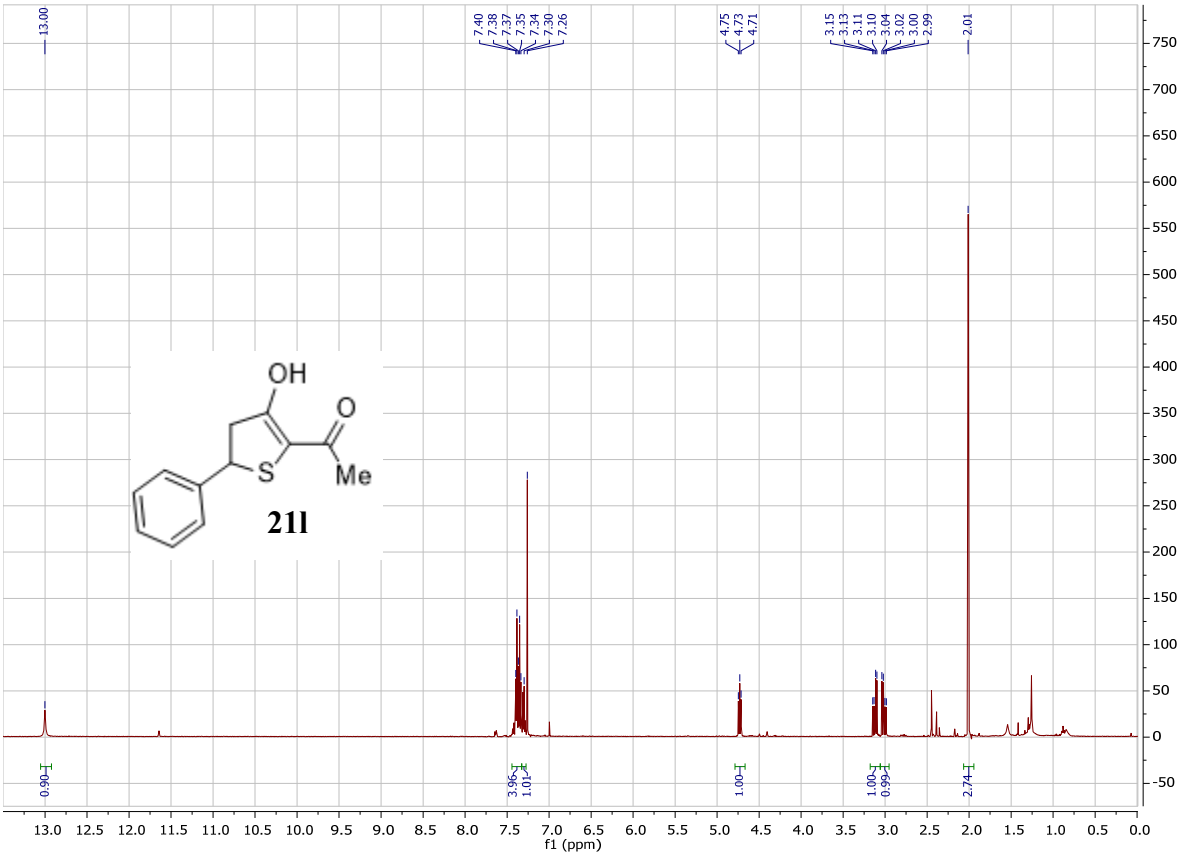

206.30
161.82
139.77
137.31
132.48
129.43
129.11
128.81
128.37
127.22
106.65
77.41
77.16
76.91
47.41
46.60
OH
O
S
Cl
21i
f1 (ppm)

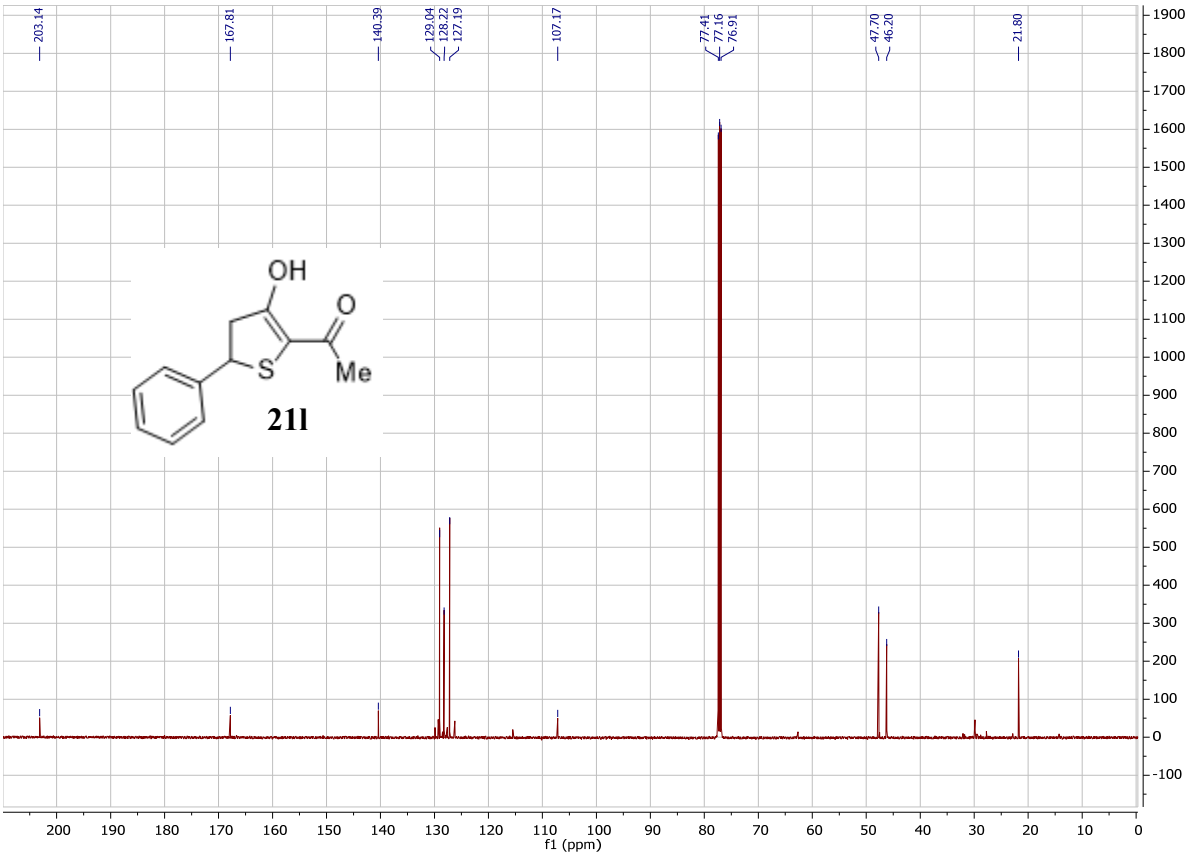

13.68
8.30
8.28
8.05
8.04
7.42
7.42
7.40
7.39
7.37
7.37
7.36
7.34
7.33
7.26
4.84
4.83
4.81
3.30
3.29
3.26
3.25
3.19
3.17
3.15
3.14
OH
O
S
21j
NO2
0.95
1.96
1.88
4.88
1.00
1.02
1.01
f1 (ppm)

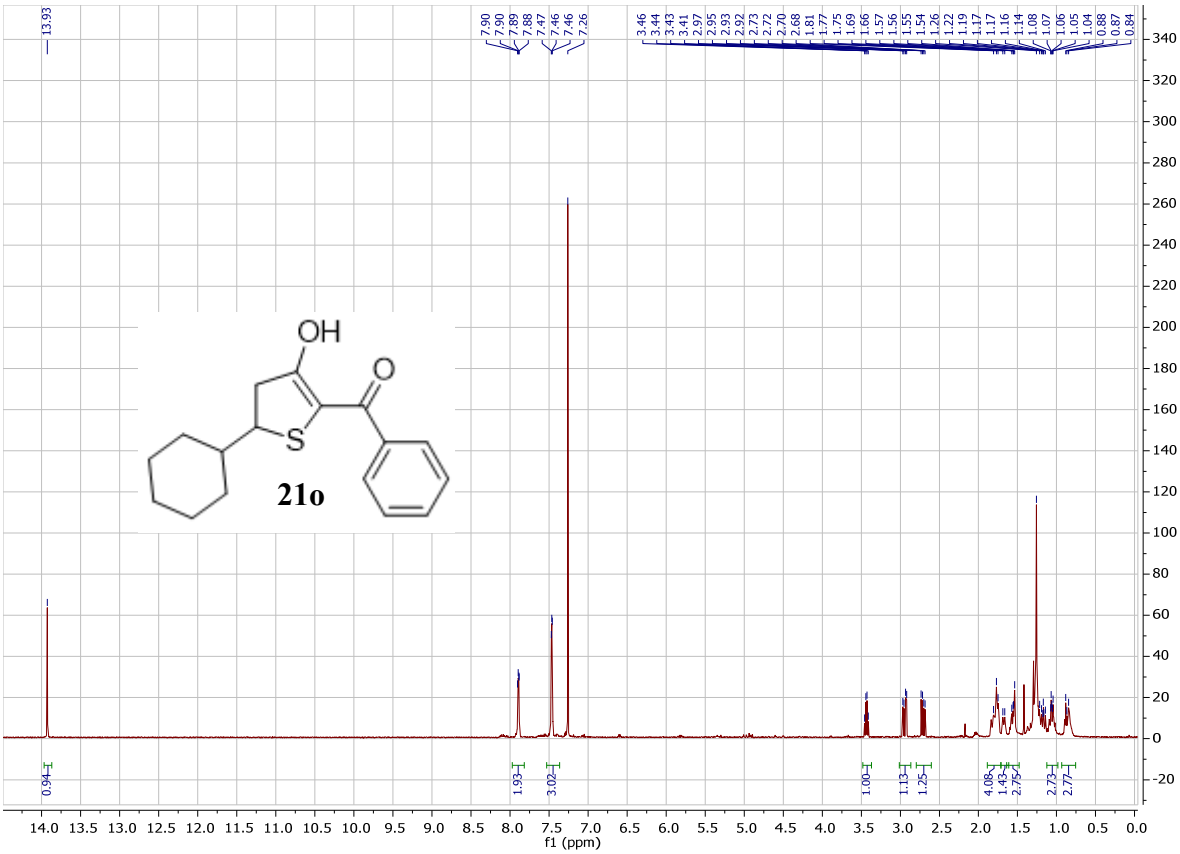

207.21
159.11
148.69
140.07
139.40
129.24
128.99
128.60
127.22
123.66
109.18
77.41
77.16
76.91
47.42
46.64
OH
O
S
21j
NO2
f1 (ppm)

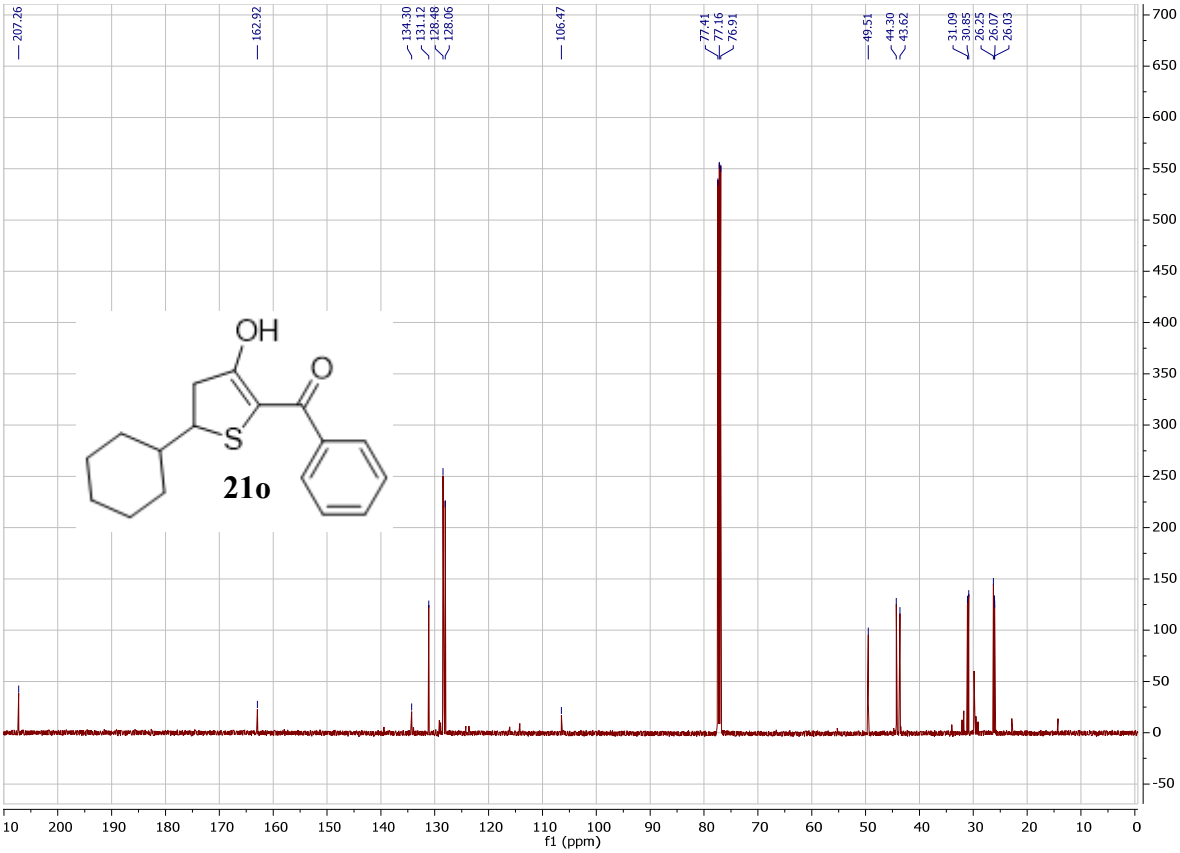

13.48
7.64
7.64
7.64
7.43
7.41
7.37
7.36
7.34
7.32
7.31
7.30
7.26
7.09
7.08
6.58
6.58
6.57
6.57
6.57
4.82
4.80
4.79
3.24
3.23
3.21
3.19
3.12
3.10
3.08
3.06
OH
O
S
O
21k
0.93
1.03
1.92
1.99
0.99
0.89
0.93
1.00
1.11
1.04
f1 (ppm)

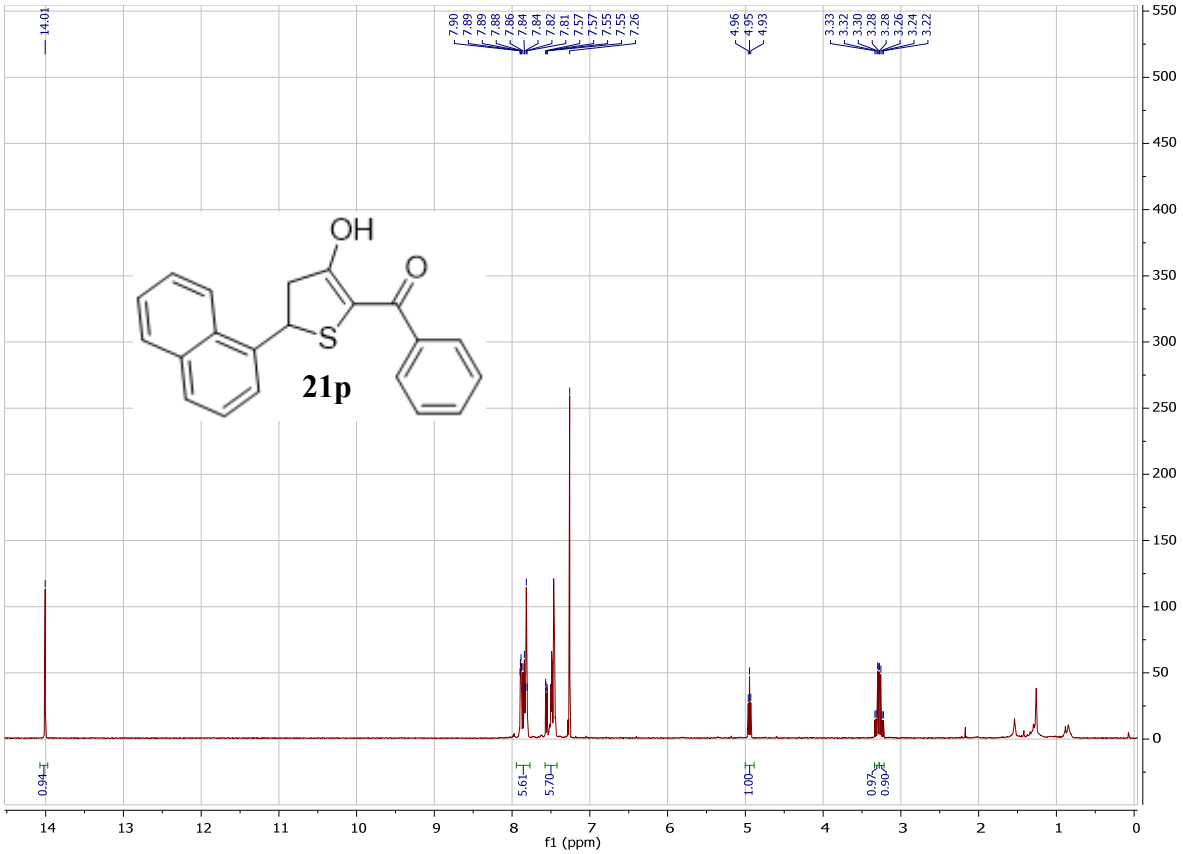

205.93
152.96
147.81
145.86
140.33
129.07
128.24
127.23
116.29
112.69
104.76
77.41
77.16
76.91
47.59
46.32
OH
O
S
O
21k
f1 (ppm)

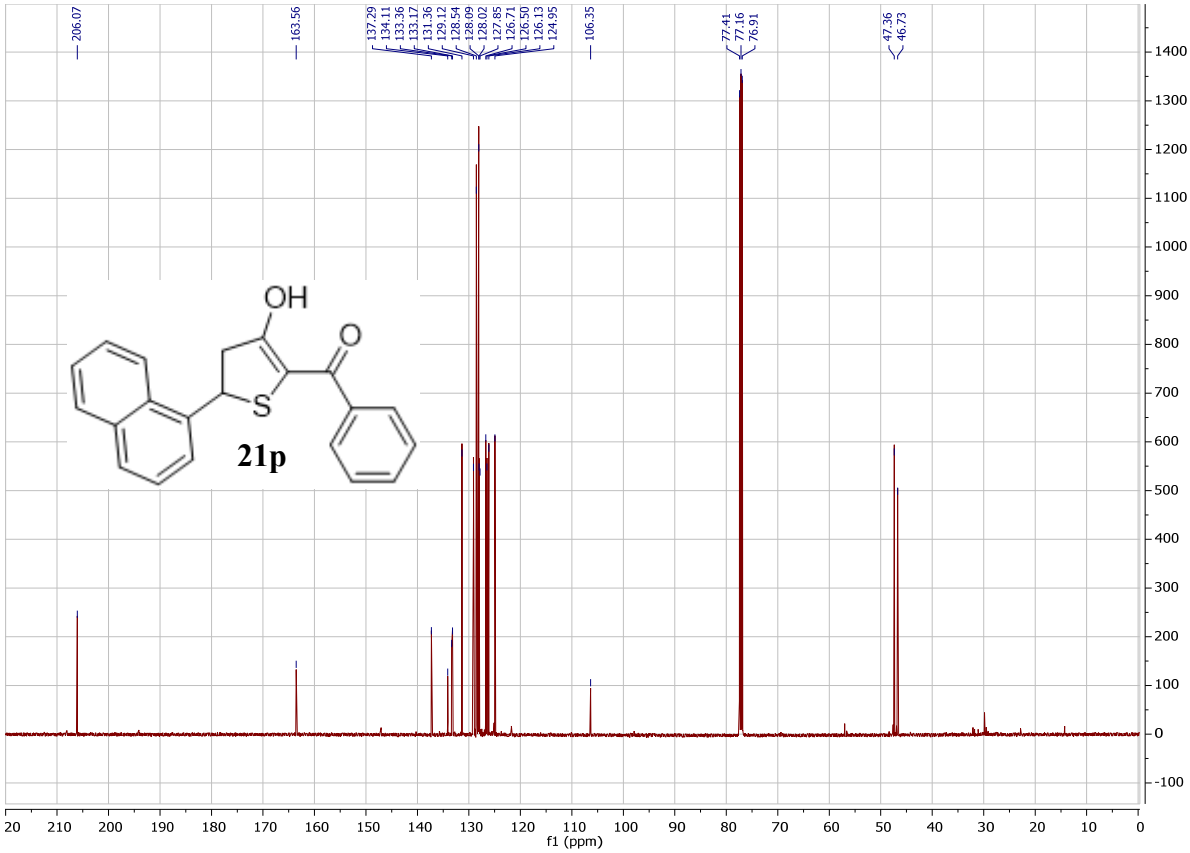

13.00
7.40
7.38
7.37
7.35
7.34
7.30
7.26
4.75
4.73
4.71
3.15
3.13
3.11
3.10
3.04
3.02
3.00
2.99
2.01
OH
O
S
Me
21l
0.90
3.96
1.01
1.00
1.00
0.99
2.74
f1 (ppm)

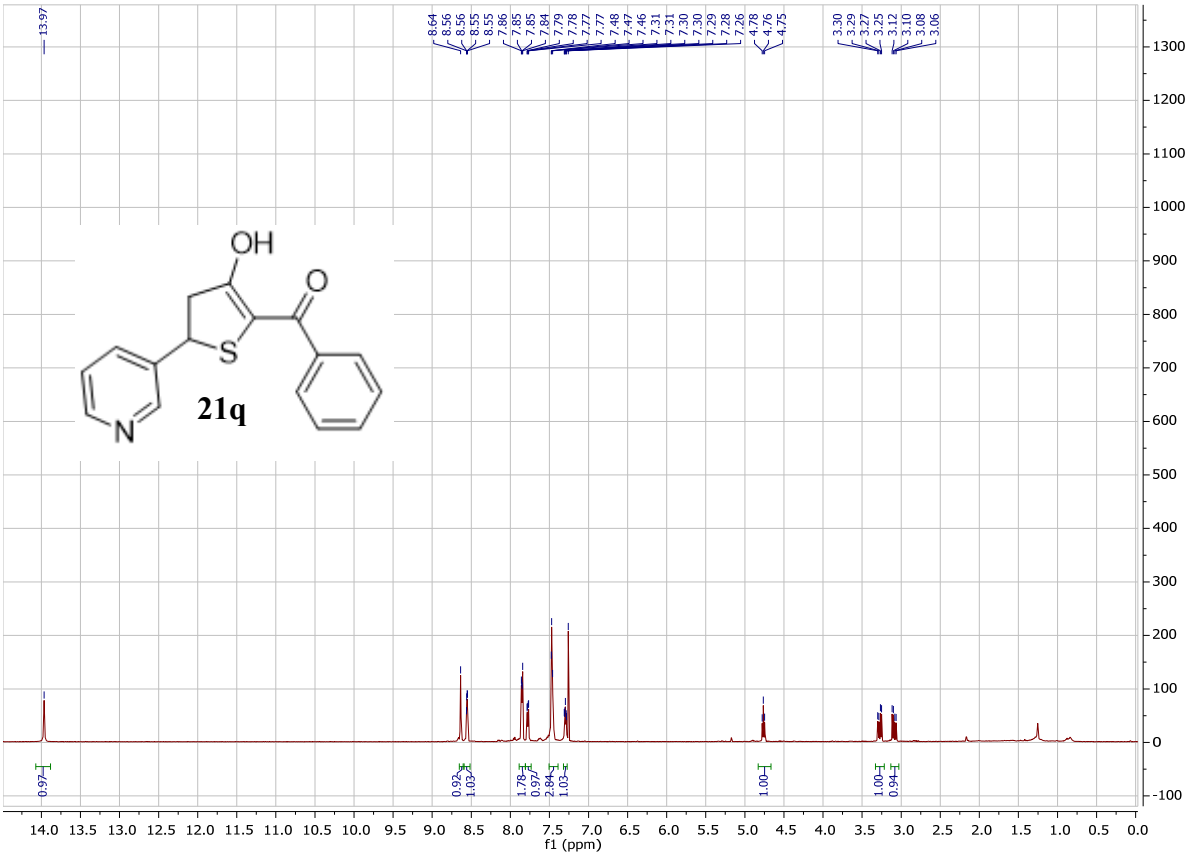

203.14
167.81
140.39
129.04
128.22
127.19
107.17
77.41
77.16
76.91
47.70
46.20
21.80
OH
O
S
Me
21l
f1 (ppm)

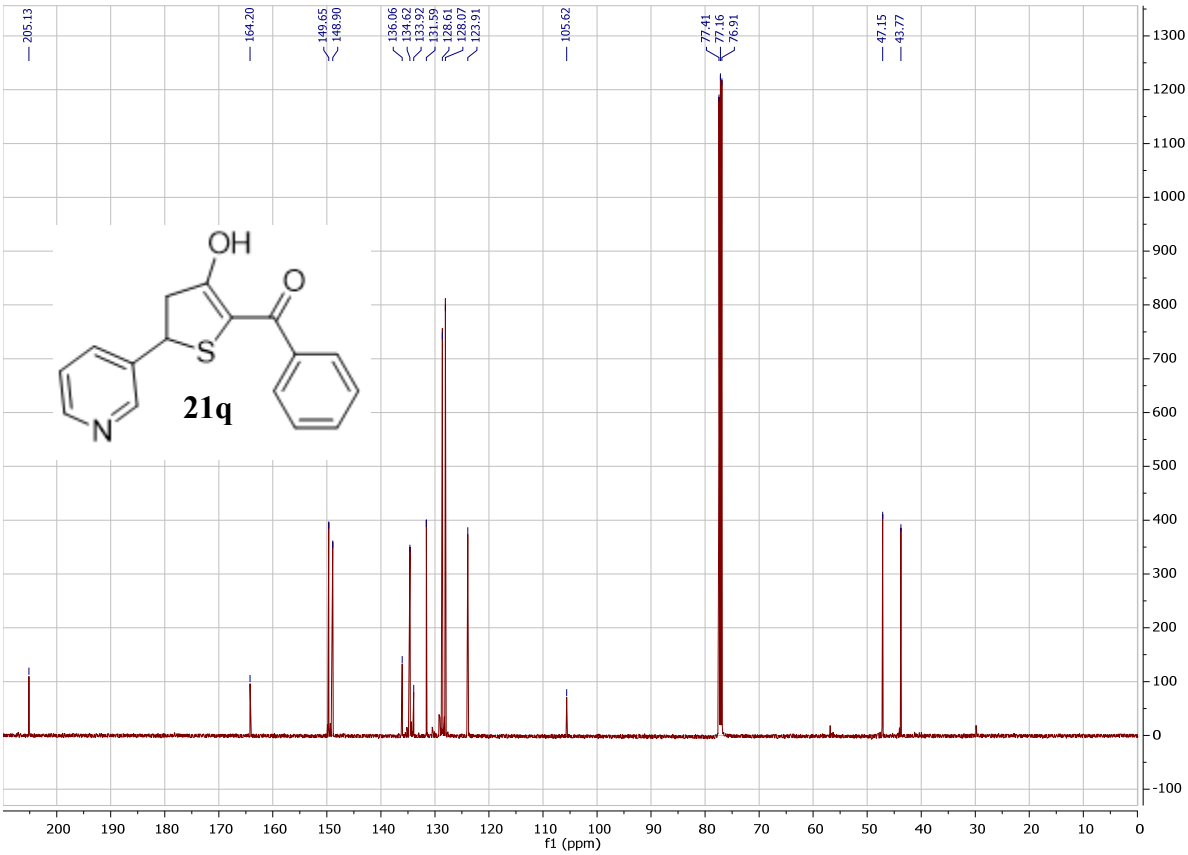

OH
O
S
21o
f1 (ppm)


OH
O
S
21o
f1 (ppm)

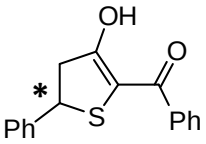

14.01
7.90
7.89
7.89
7.88
7.86
7.84
7.84
7.82
7.81
7.57
7.57
7.55
7.55
7.55
7.26
4.96
4.95
4.93
3.33
3.32
3.30
3.28
3.26
3.24
3.22
OH
O
S
21p
0.94
5.61
5.70
1.00
0.97
0.90
f1 (ppm)


206.07
163.56
137.29
134.11
133.36
133.17
131.36
129.12
128.54
128.09
128.02
127.85
126.71
126.50
126.13
124.95
106.35
77.41
77.16
76.91
47.36
46.73
OH
O
S
21p
f1 (ppm)

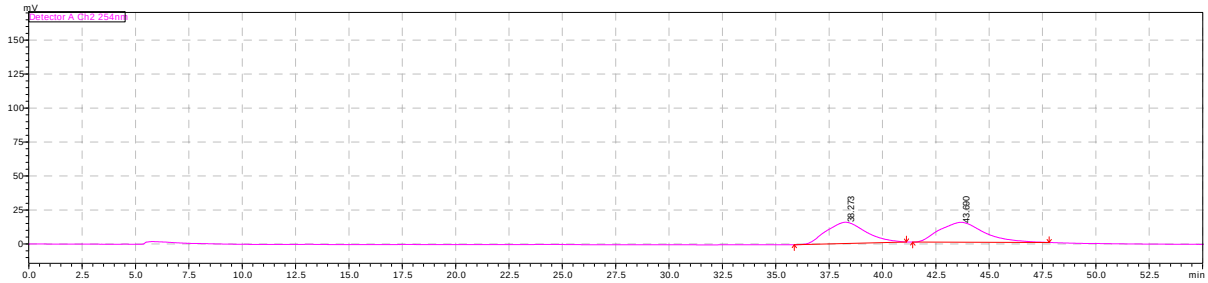

OH
O
S
N
21q
f1 (ppm)


OH
O
S
N
21q
f1 (ppm)

2. HPLC data

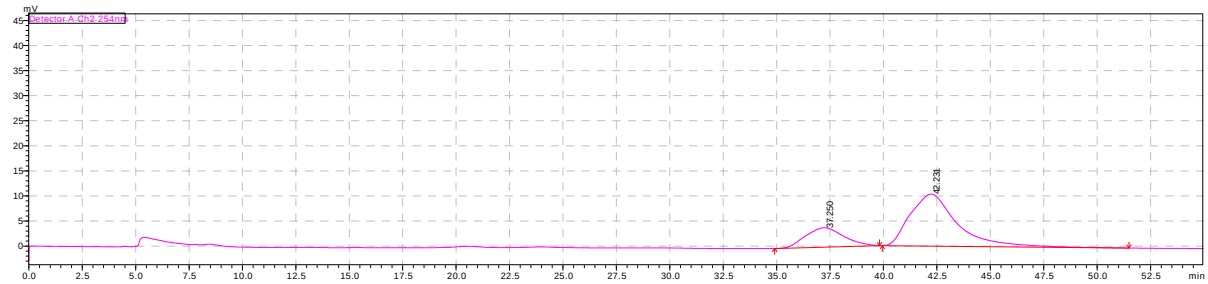
21a 

With catalyst **13**



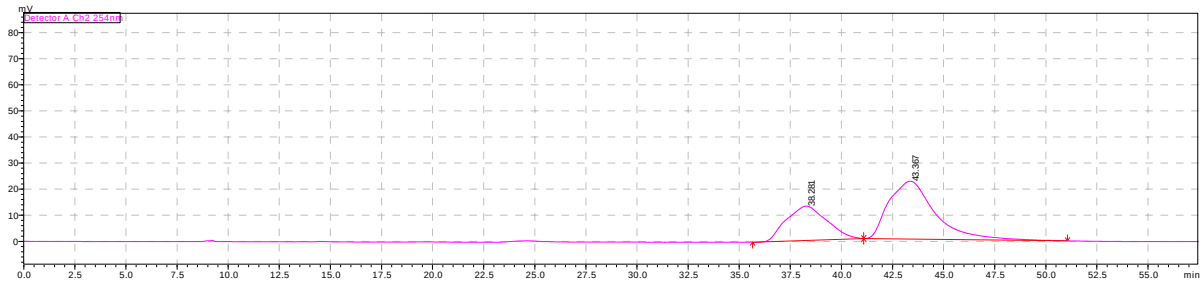
Peak#	Ret. Time	Area	Height	Area%
1	38.273	2004875	15564	48.334
2	43.69	2143115	14653	51.666
Total		4147989	30218	100

With catalyst **25**



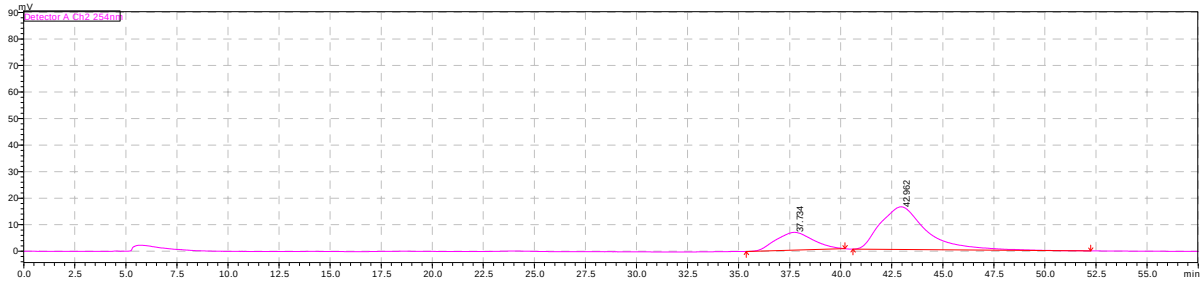
Peak#	Ret. Time	Area	Height	Area%
1	37.25	478894	3866	23.15
2	42.231	1589788	10369	76.85
Total		2068682	14235	100

With catalyst **26**



Peak#	Ret. Time	Area	Height	Area%
1	38.281	1806748	13149	34.104
2	43.367	3490995	22180	65.896
Total		5297743	35328	100

With catalyst **27**



Peak#	Ret. Time	Area	Height	Area%
1	37.734	845452	6684	25.044
2	42.962	2530477	16068	74.956
Total		3375929	22752	100