From Tetrahydrofurans to Tetrahydrobenzo*[d]*oxepines via a Regioselective Control of Alkyne Insertion in Rhodium-Catalyzed Arylative Cyclization

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Supporting Information

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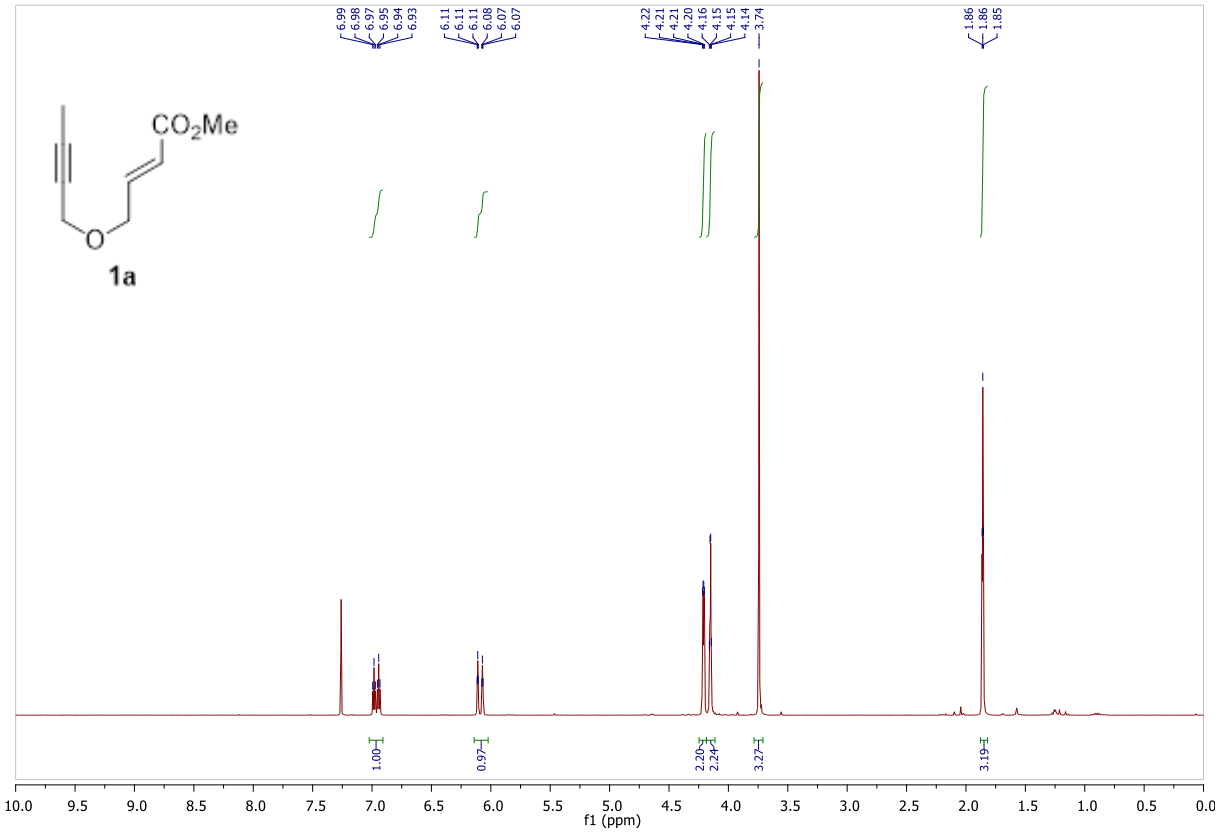
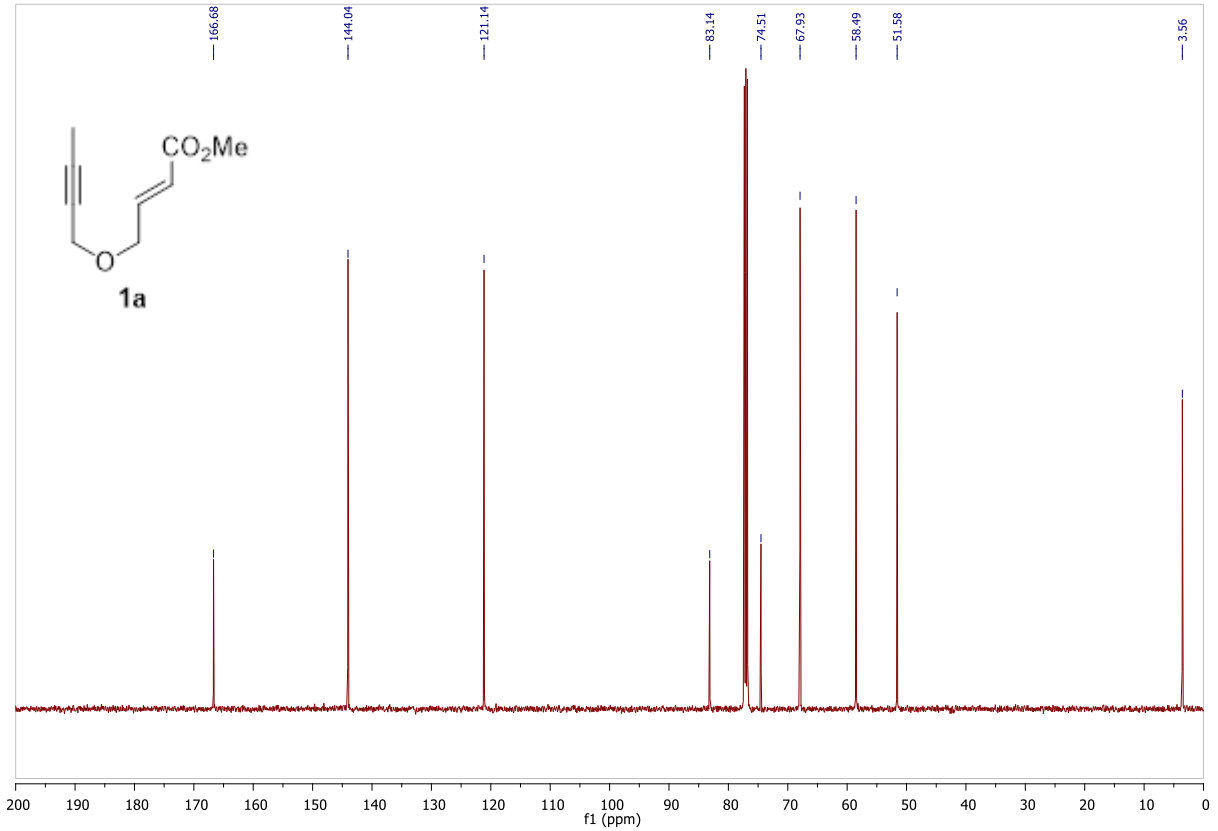
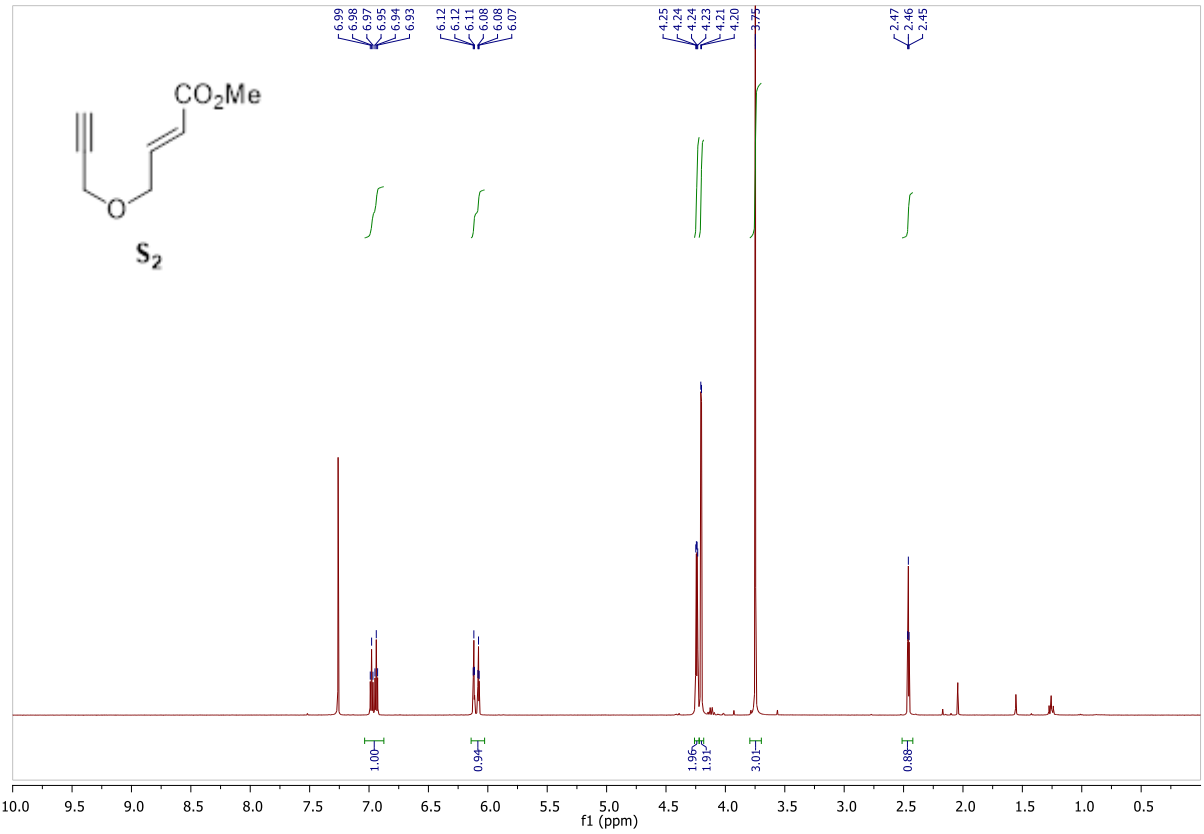
I. NMR and HPLC spectra



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2.45
CO2Me
O
S2
1.00
0.94
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1.91
3.01
0.88
10.0
9.5
9.0
8.5
8.0
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6.0
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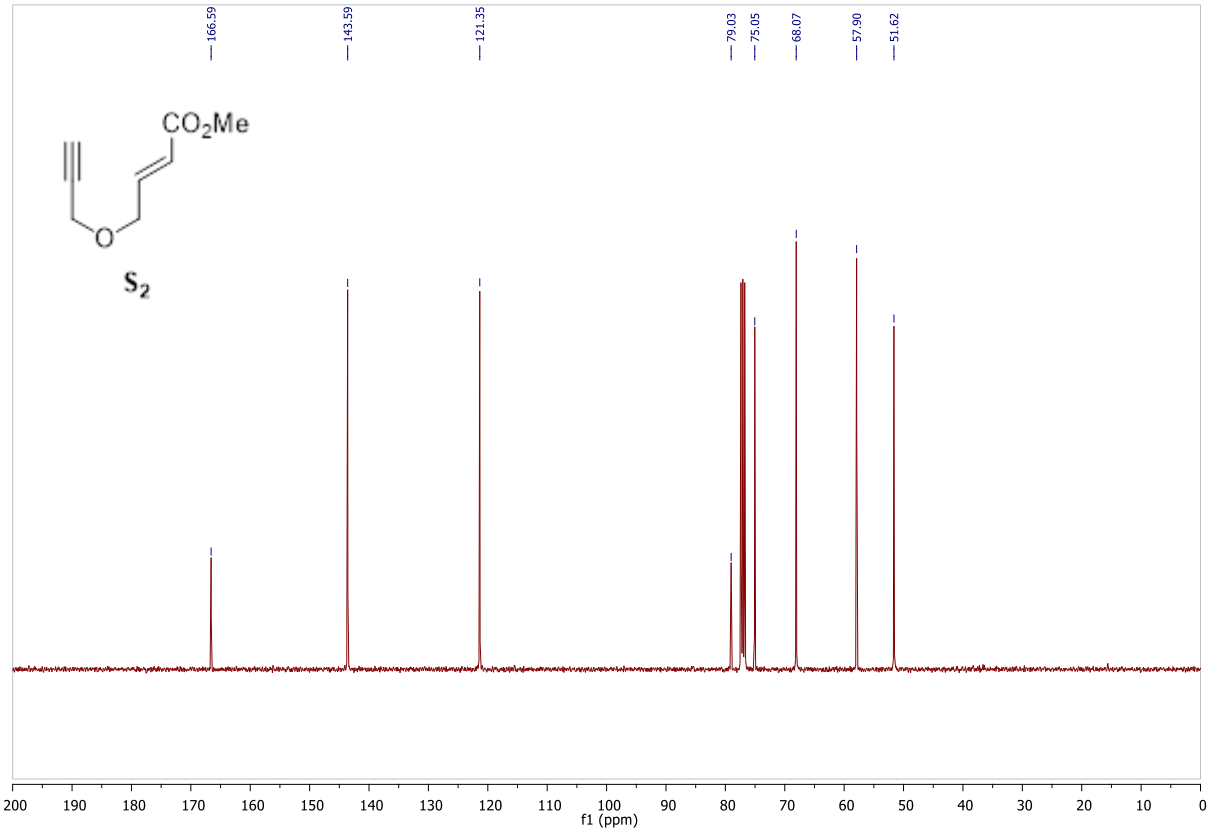
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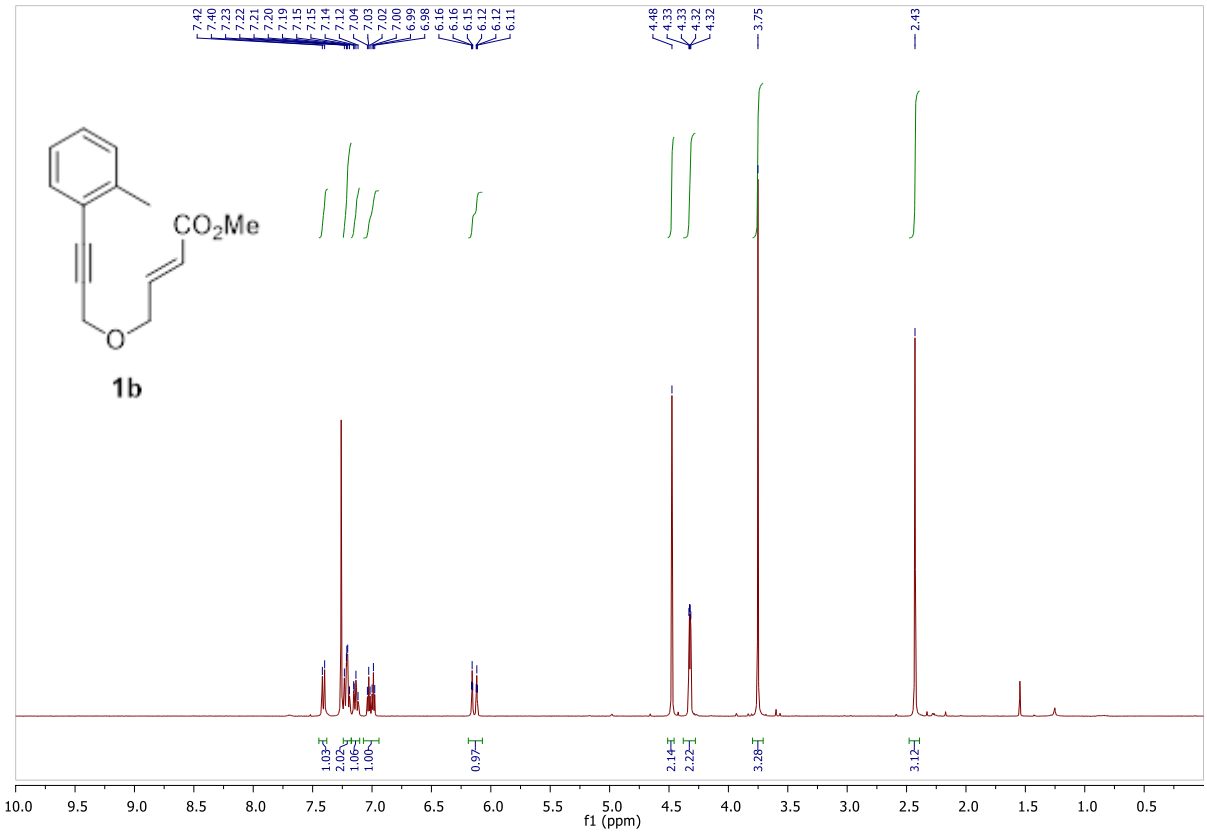
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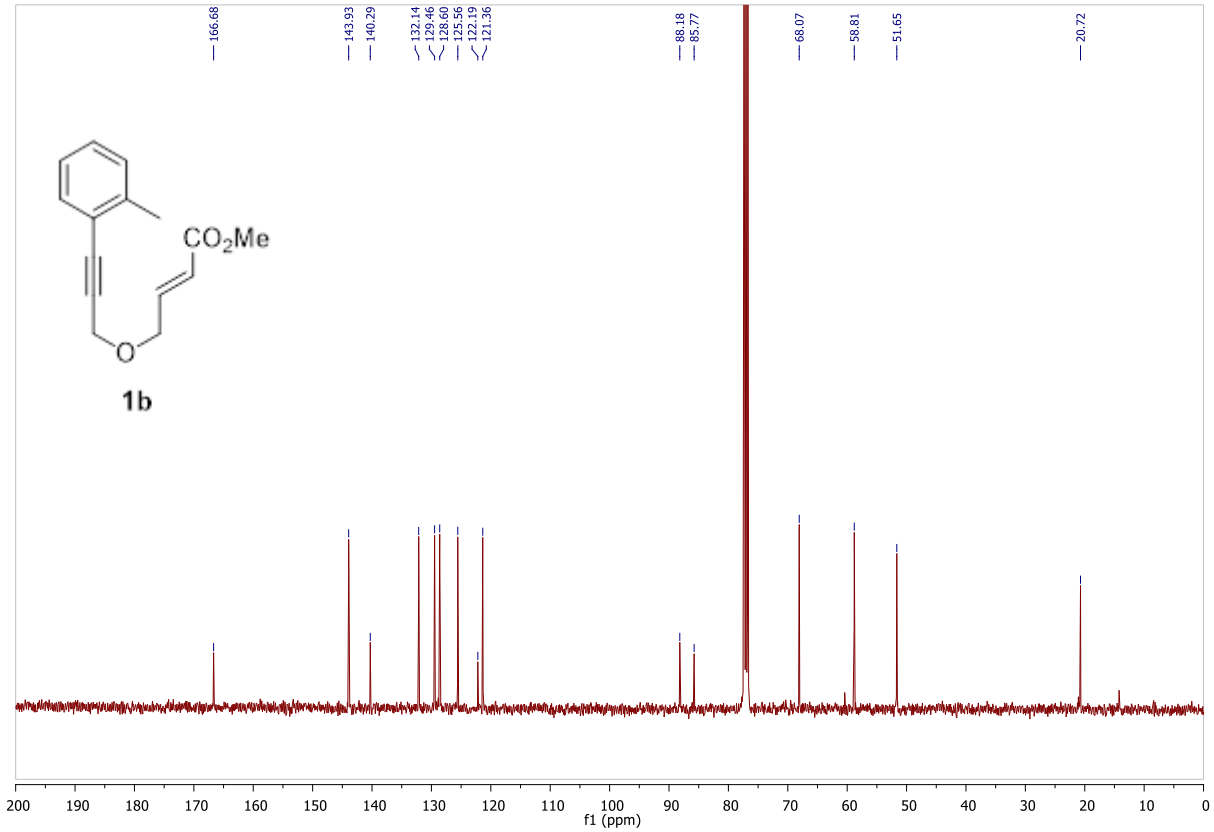
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O
1b
200
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180
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50
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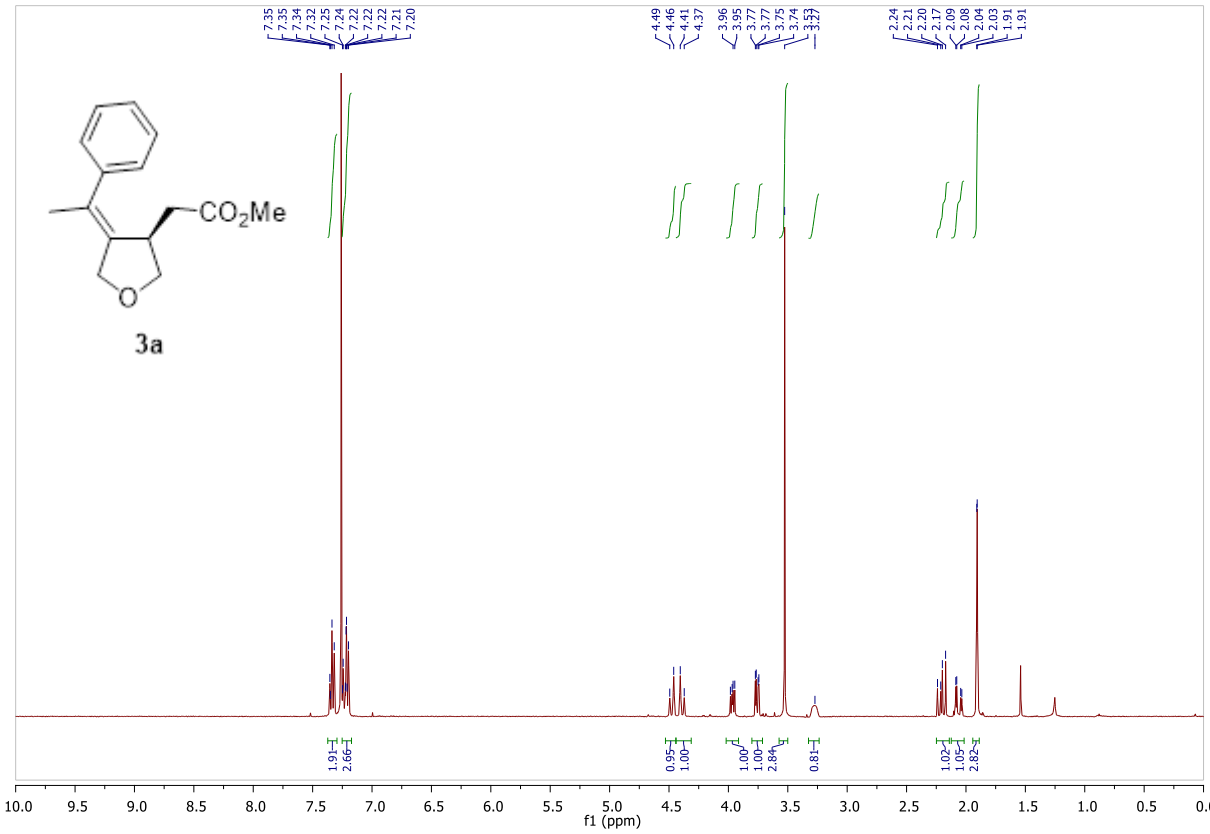
f1 (ppm)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1.05
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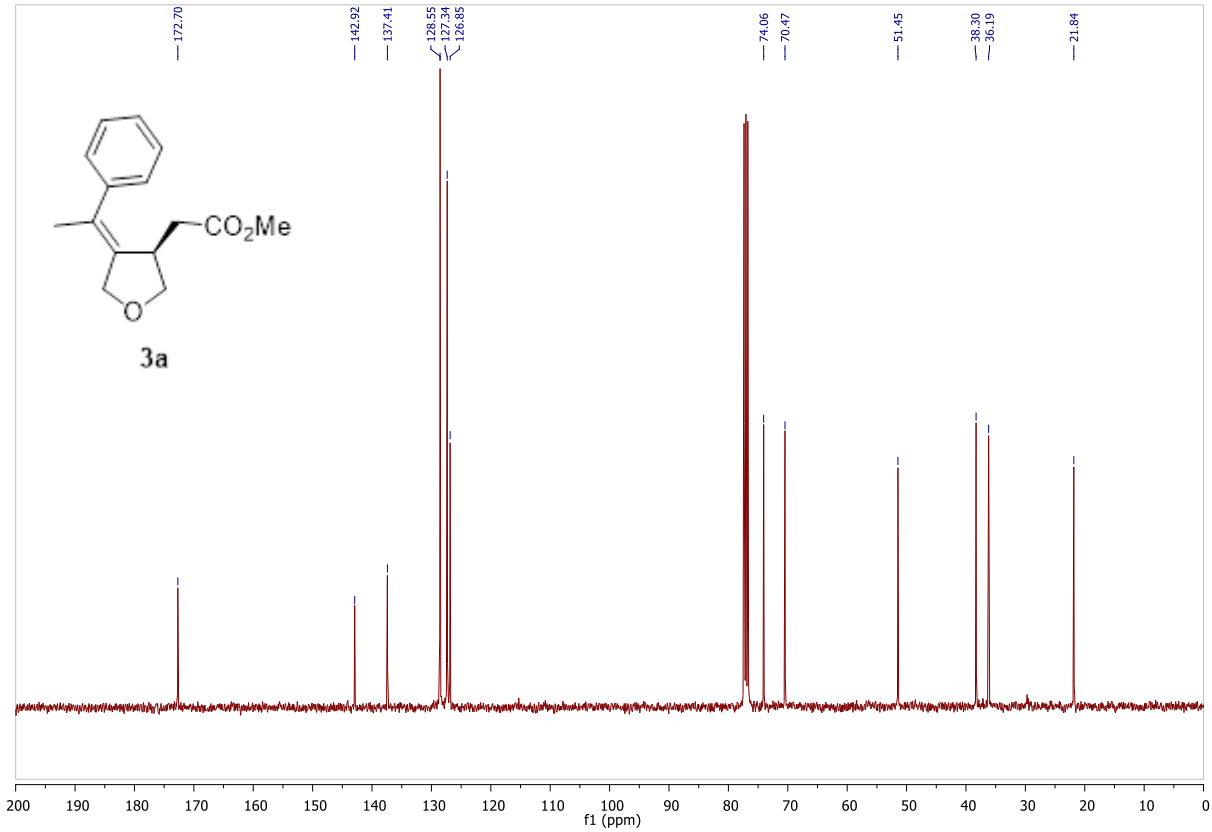
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O
3a
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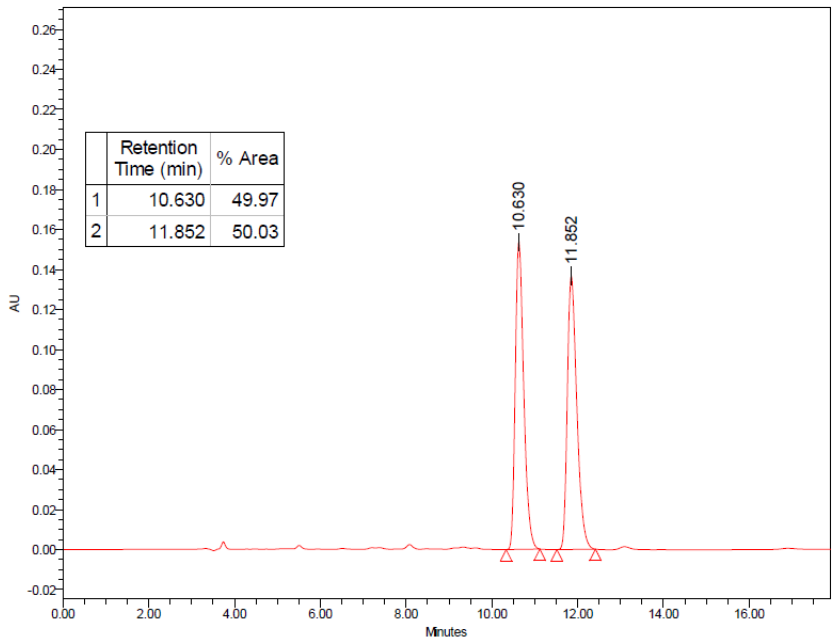
f1 (ppm)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10.630
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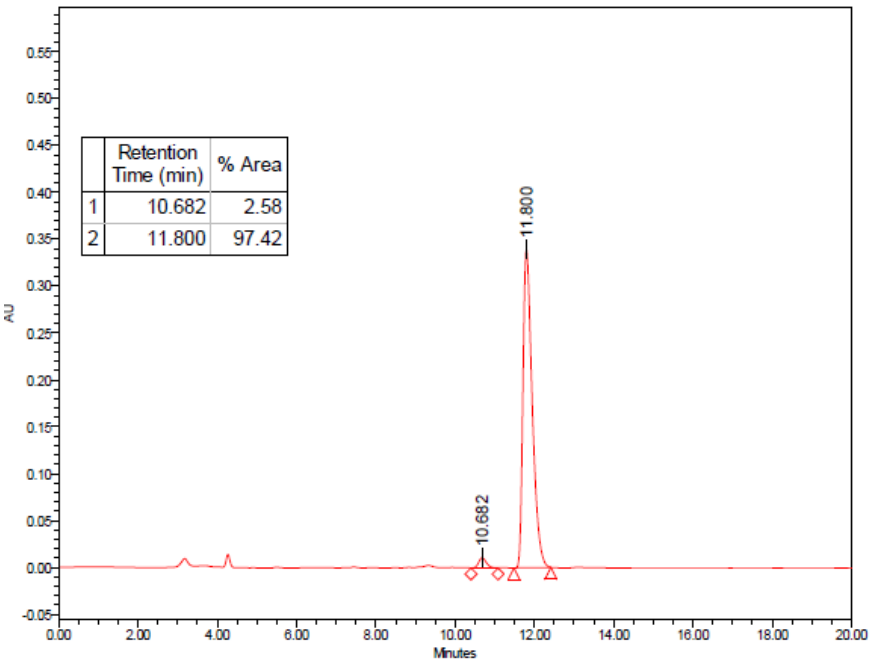
Minutes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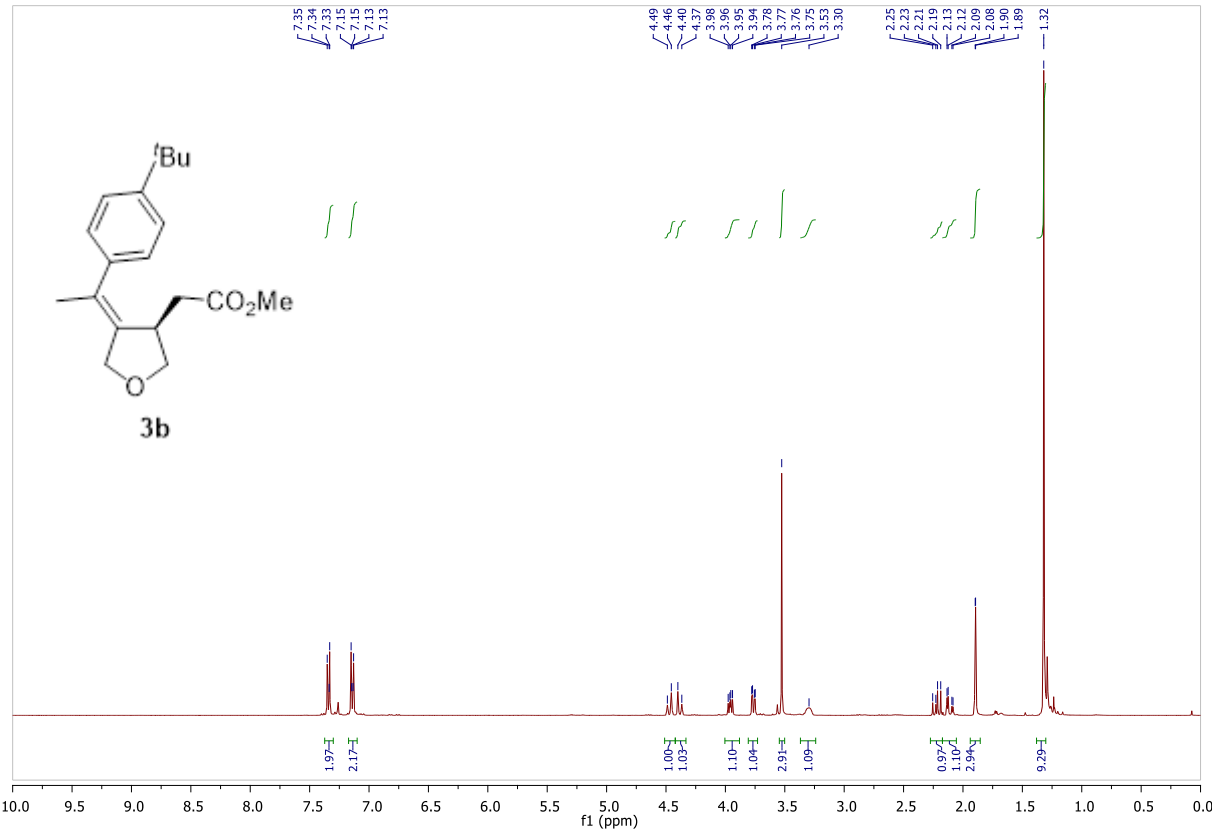
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3.94
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2.19
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2.08
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CO2Me
O
3b
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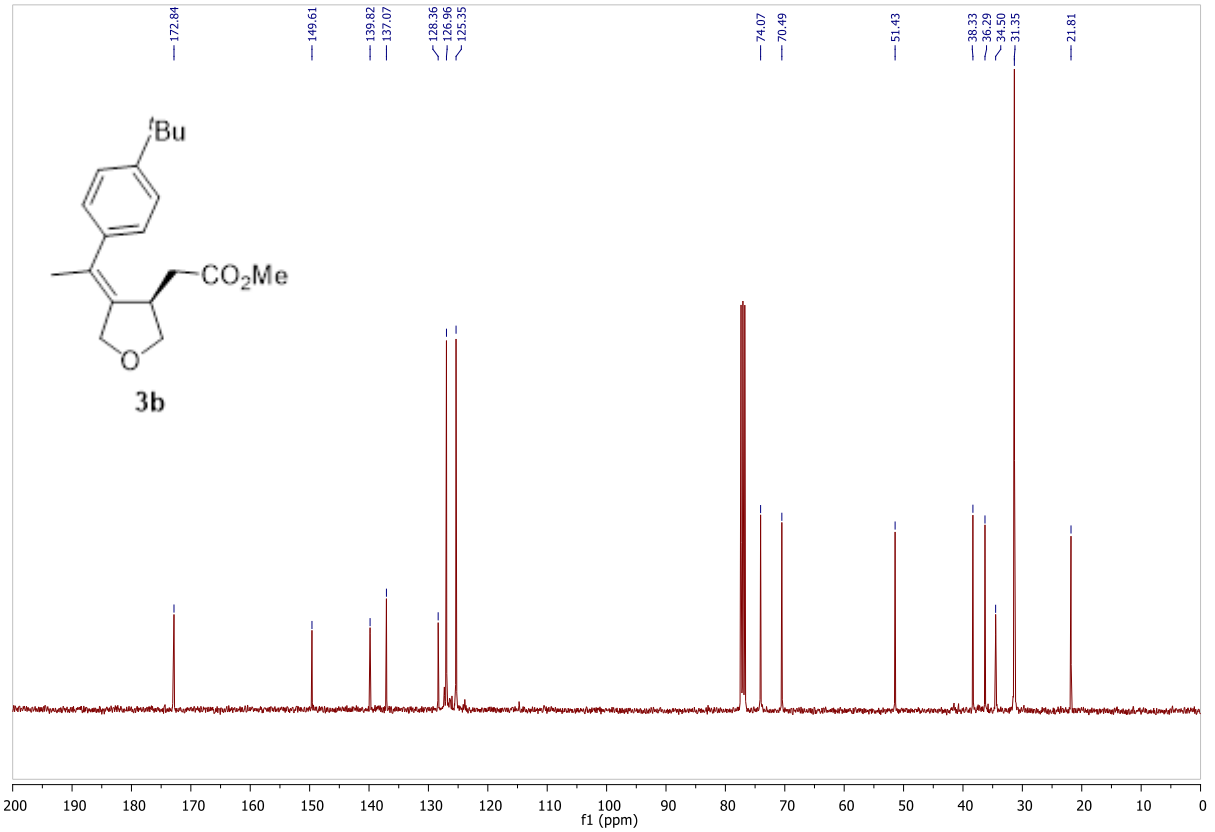
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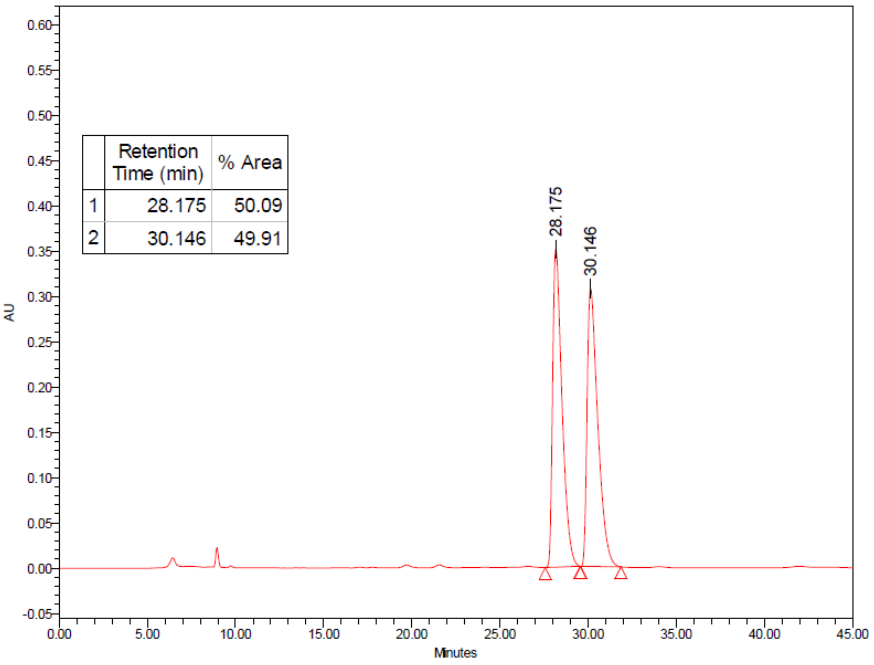
21.81
tBu
CO2Me
O
3b
f1 (ppm)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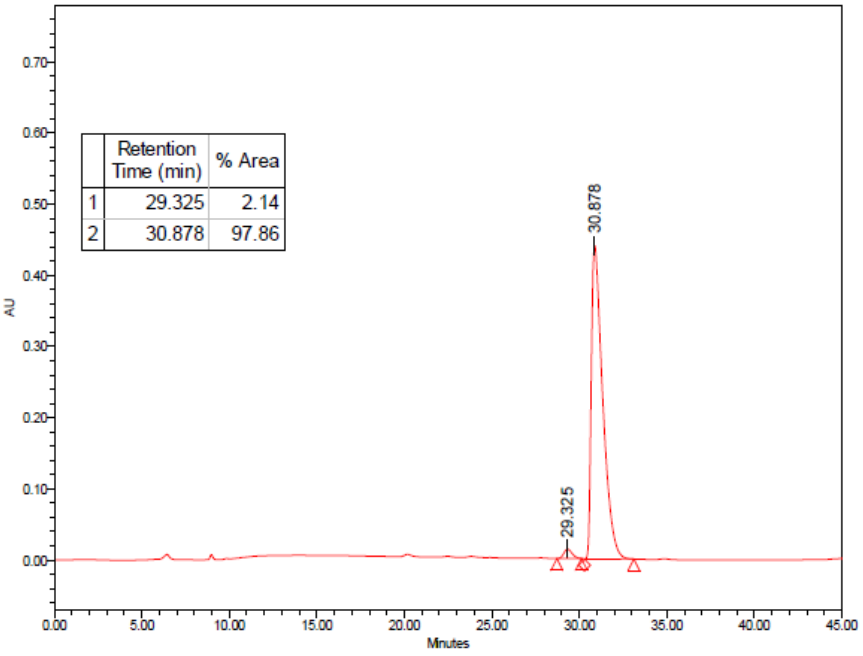
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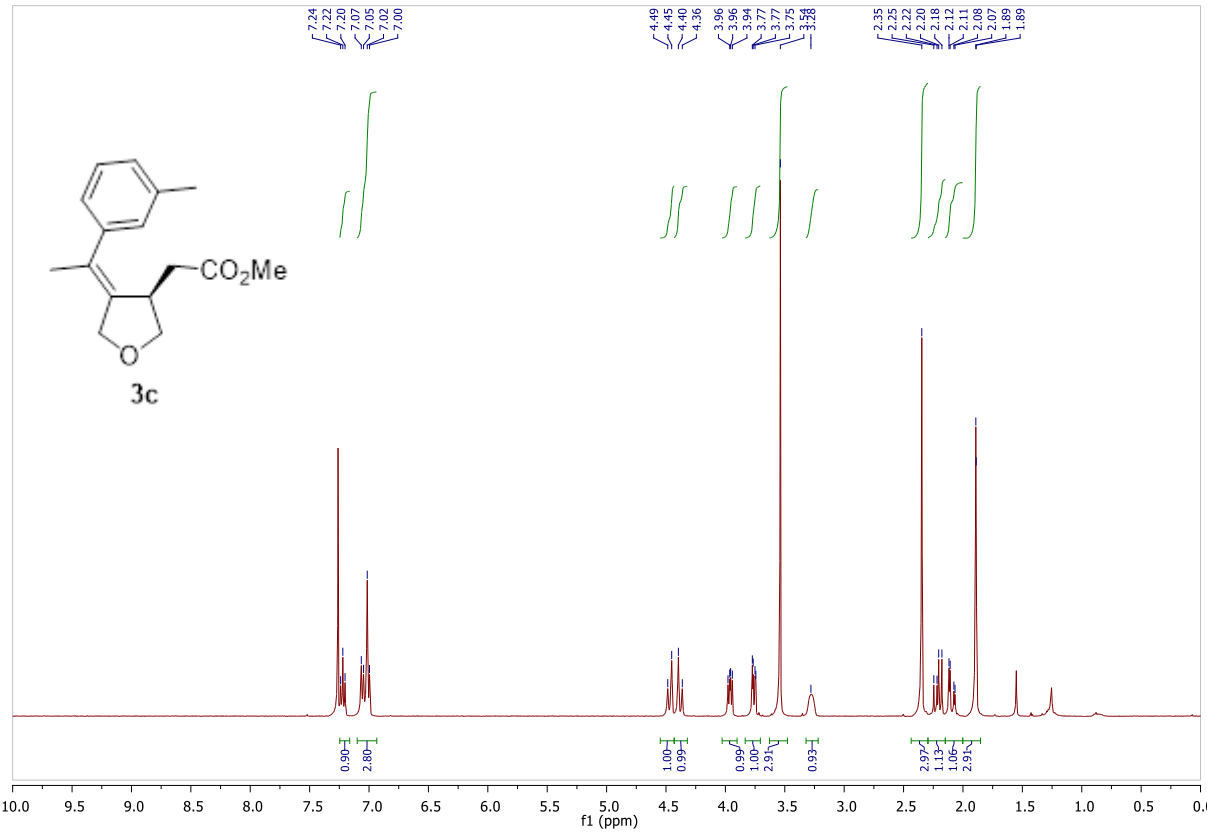
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2.25
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2.07
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1.89
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O
3c
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2.80
1.00
0.99
0.99
1.00
2.91
0.93
2.97
1.13
1.06
2.91
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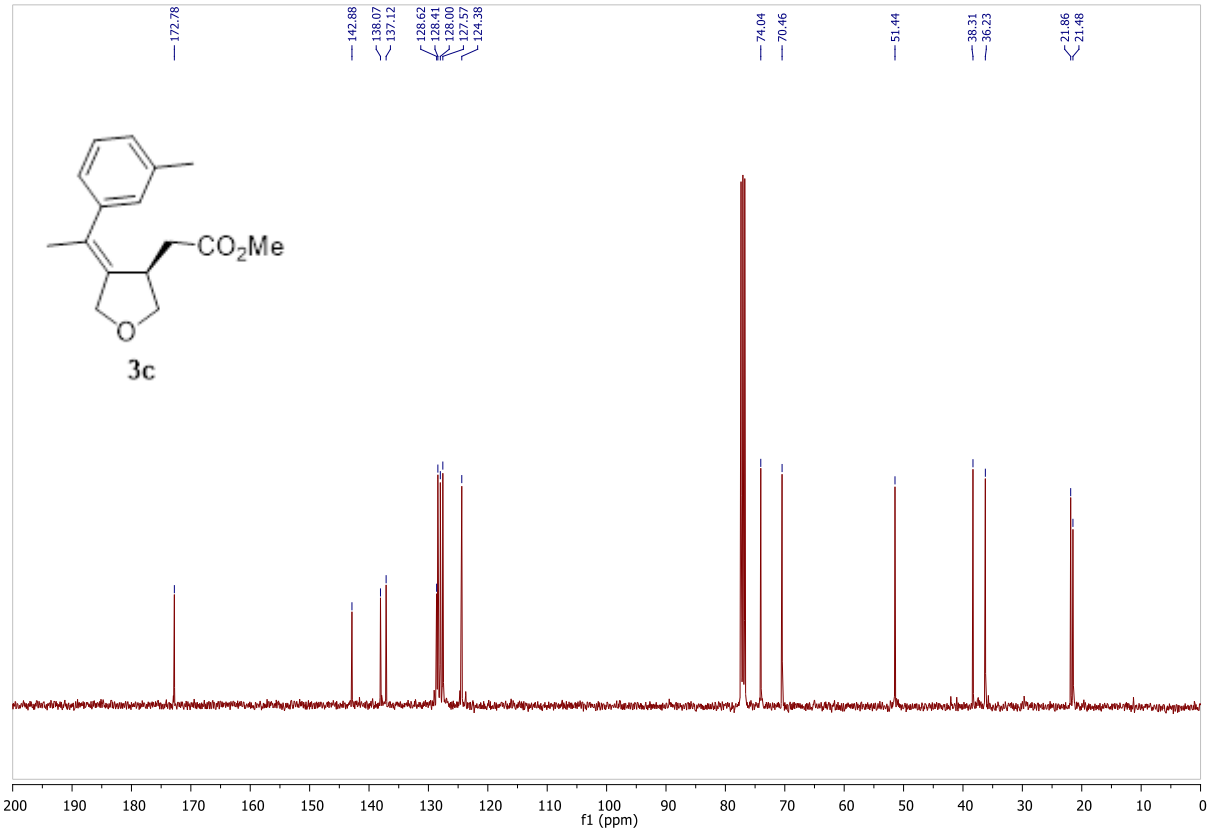
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CO2Me
O
3c
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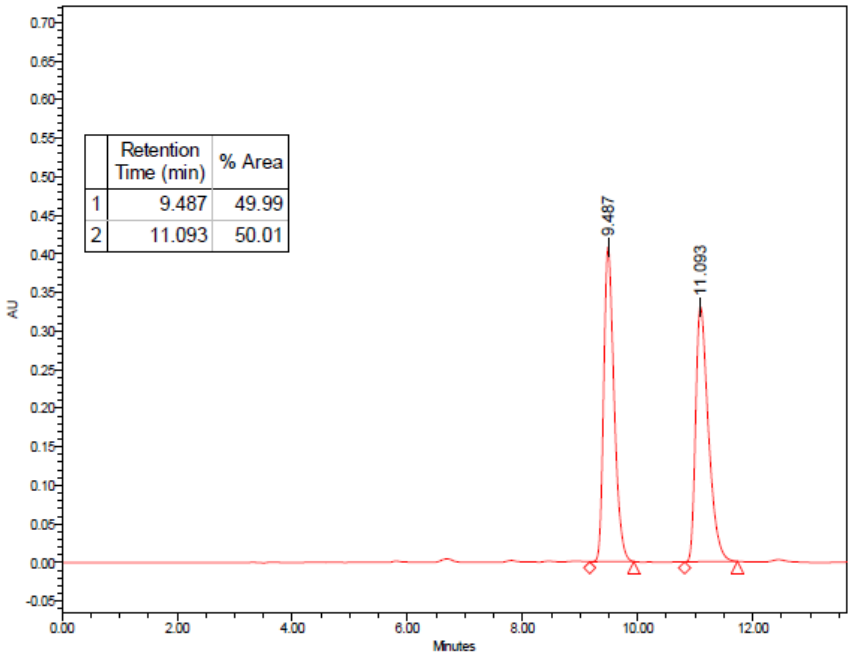
f1 (ppm)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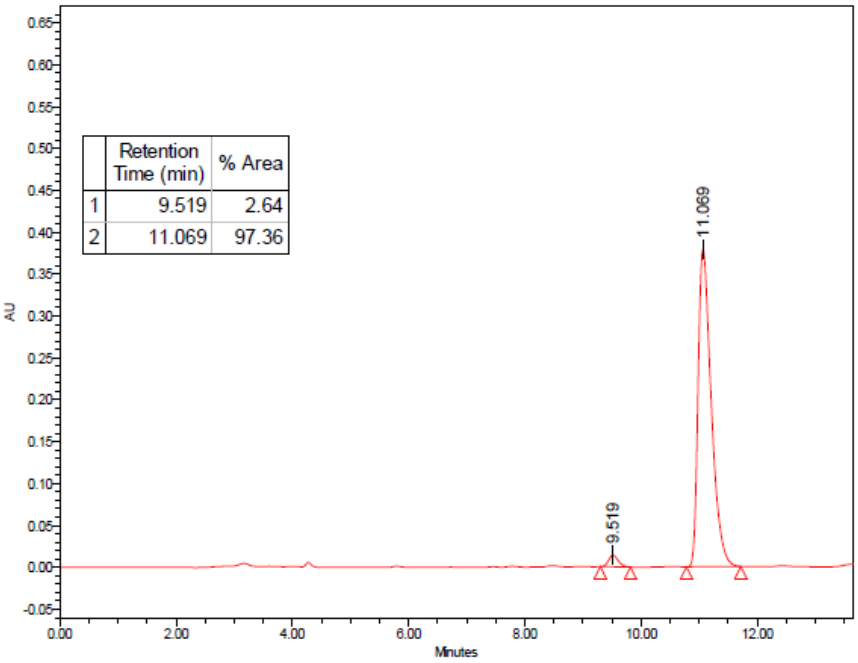
Minutes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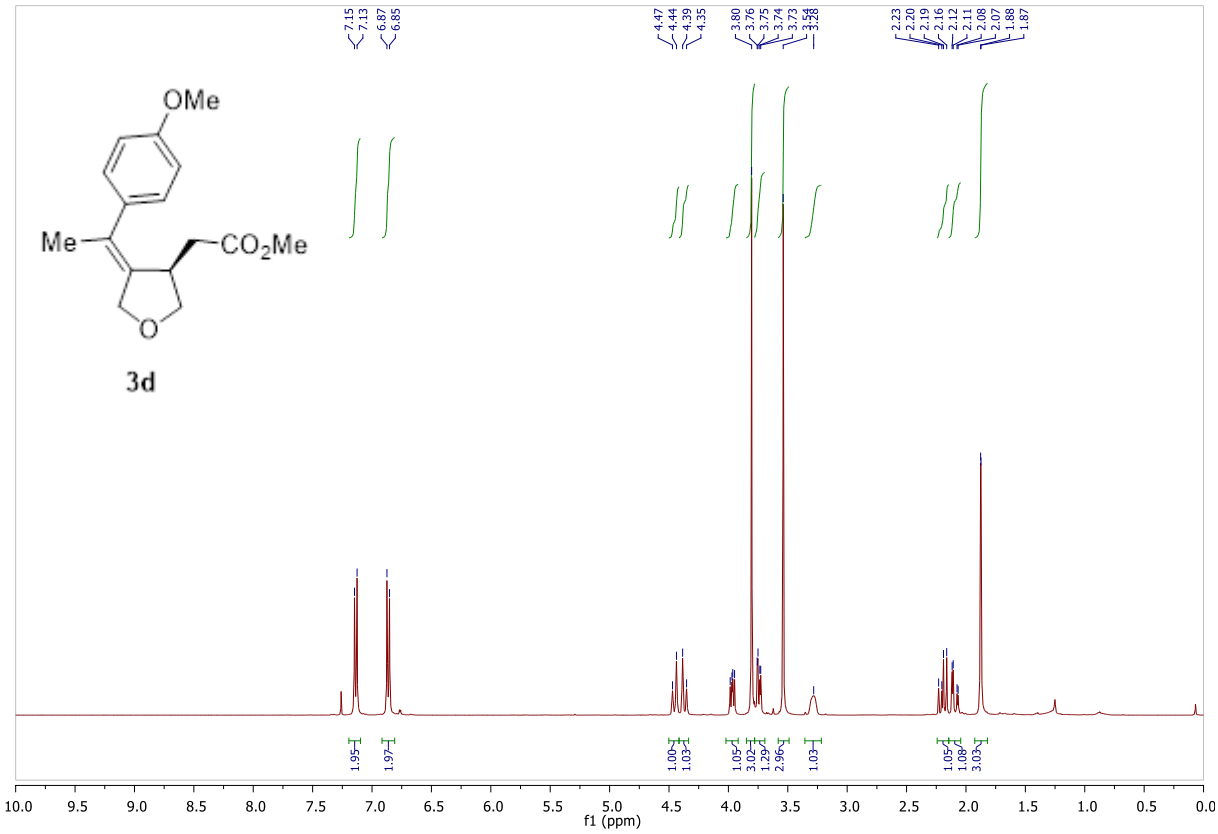
Minutes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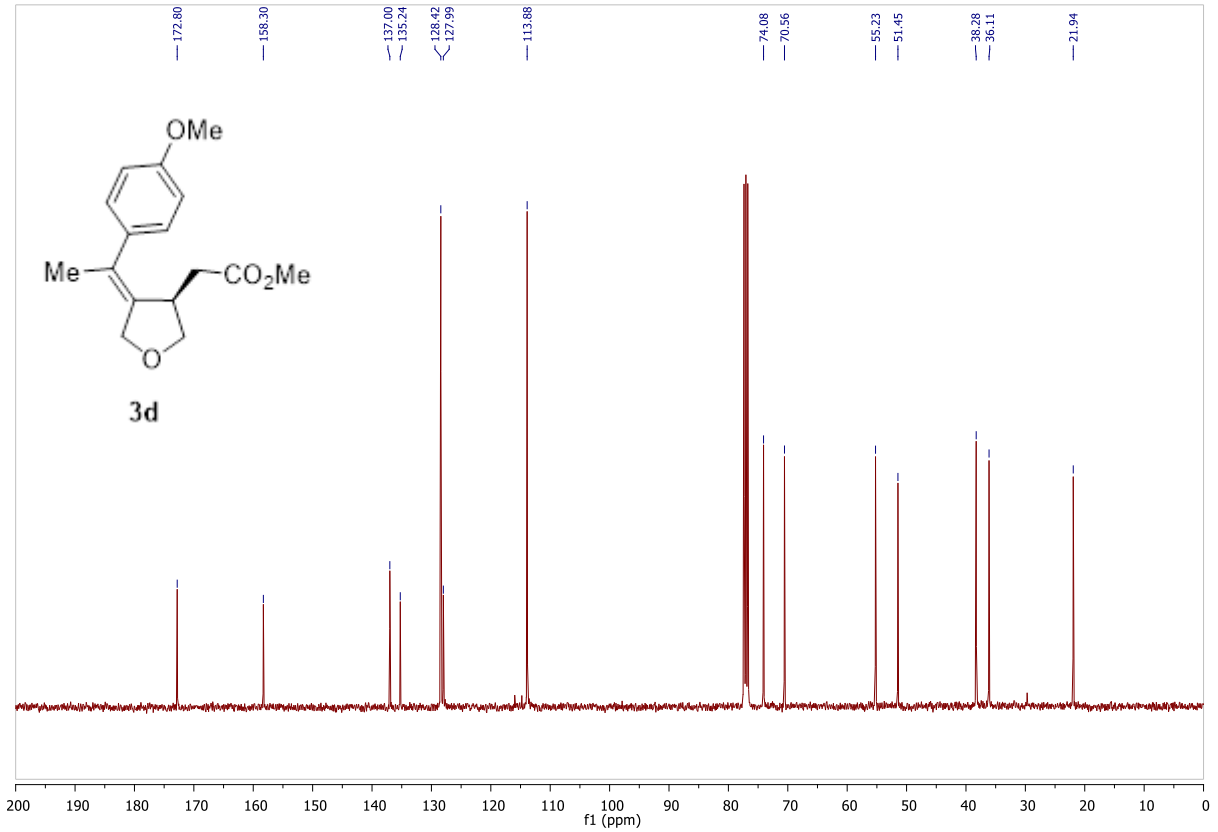
Me
CO2Me
O
3d
f1 (ppm)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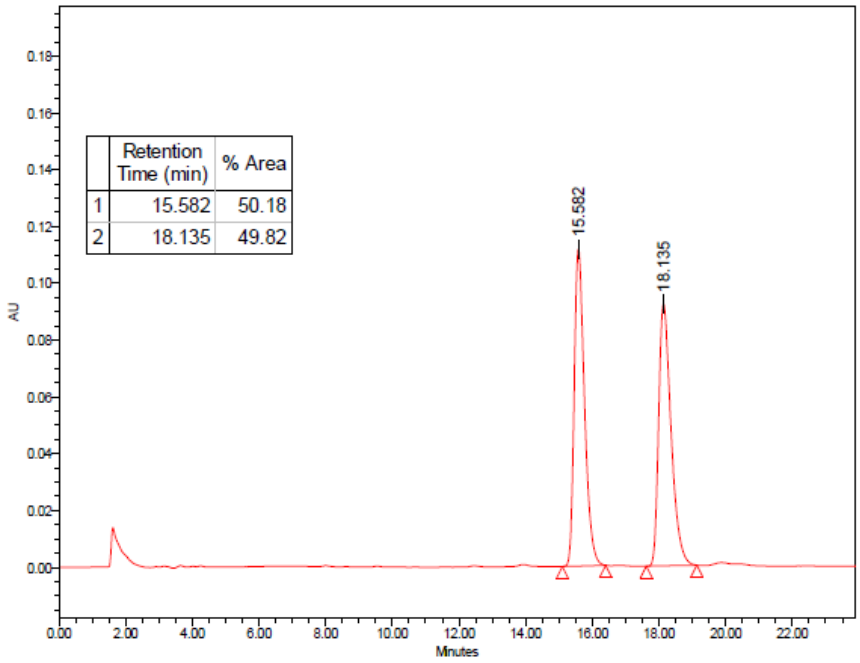
Me
CO2Me
O
3d
f1 (ppm)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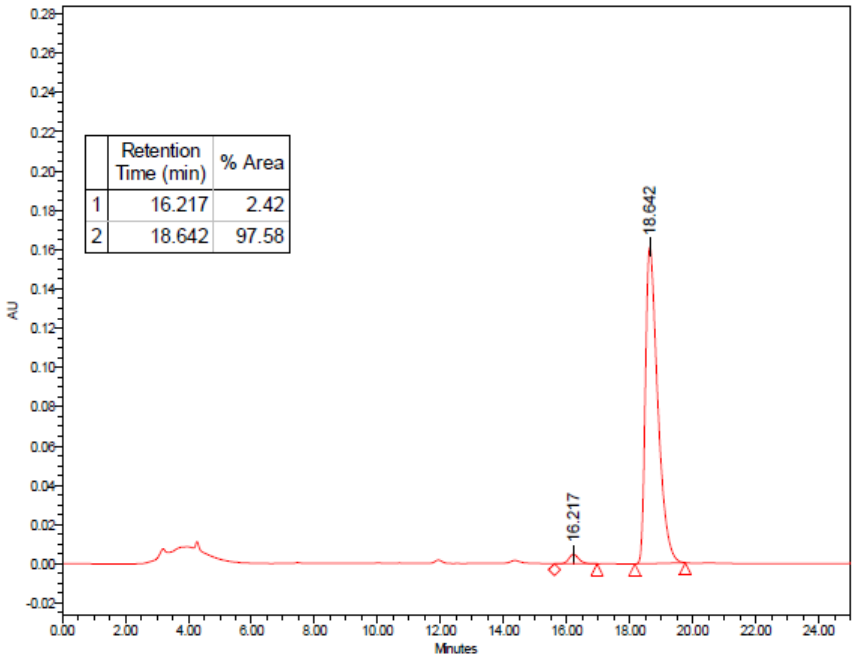
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16.217
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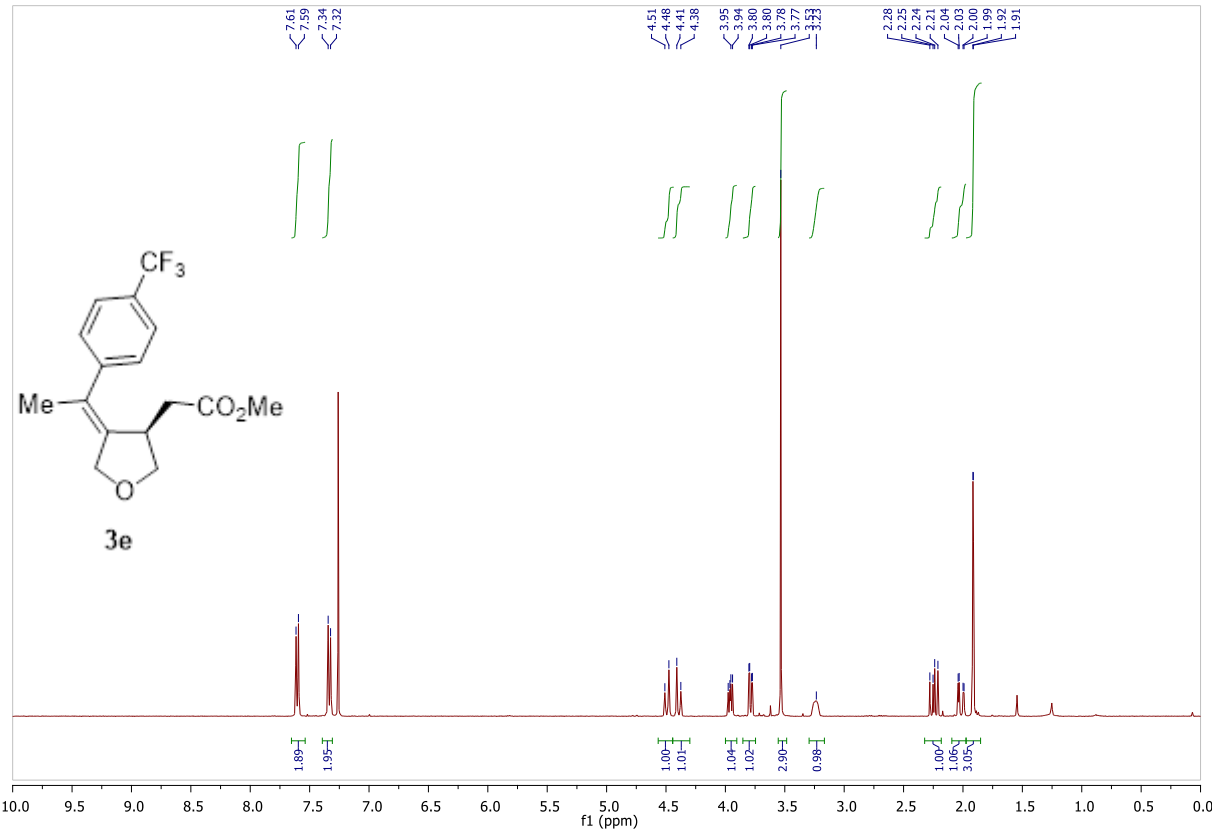
Minutes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3.77
3.53
3.23
2.28
2.25
2.24
2.21
2.04
2.03
2.00
1.99
1.92
1.91
CF3
Me
CO2Me
O
3e
1.89
1.95
1.00
1.01
1.04
1.02
2.90
0.98
1.00
1.06
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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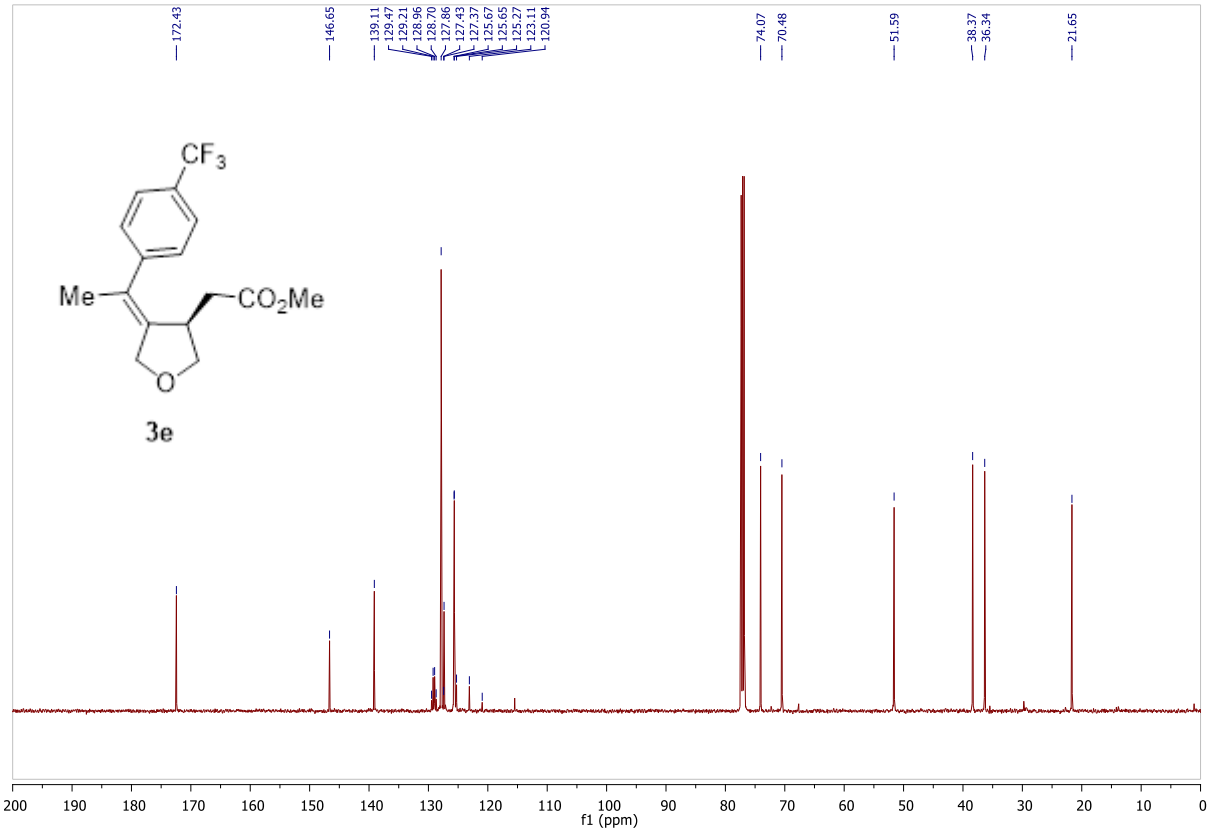
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123.11
120.94
74.07
70.48
51.59
38.37
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CF3
Me
CO2Me
O
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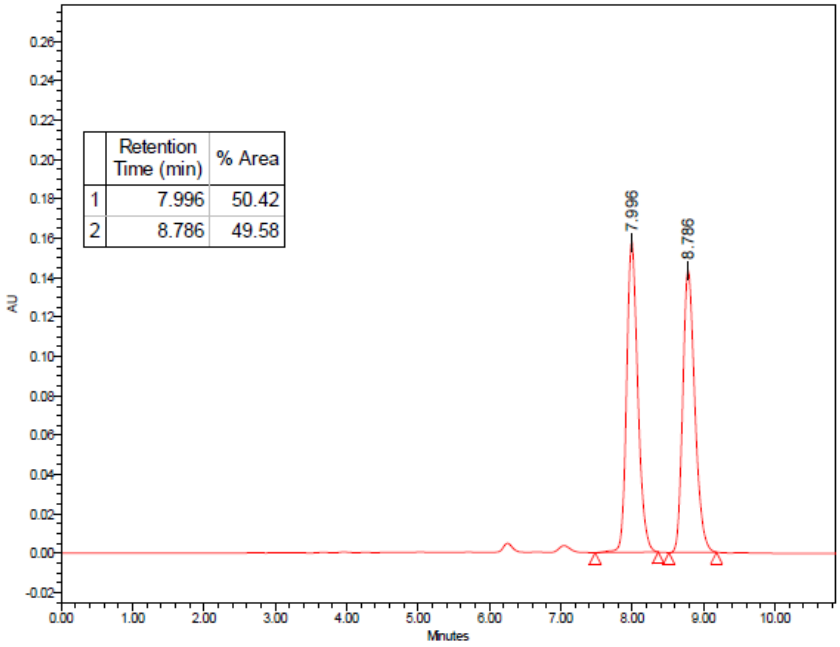
f1 (ppm)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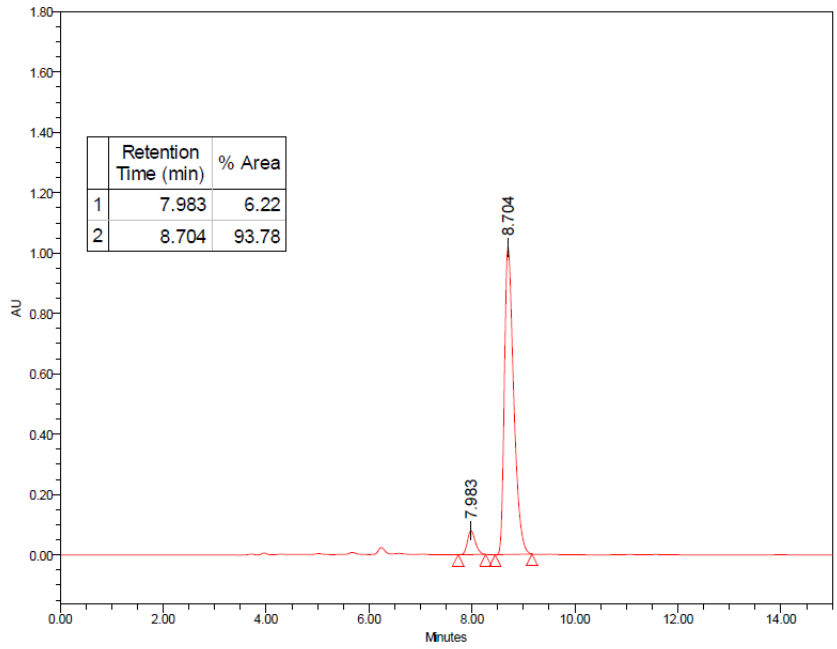
8.786
AU
Minutes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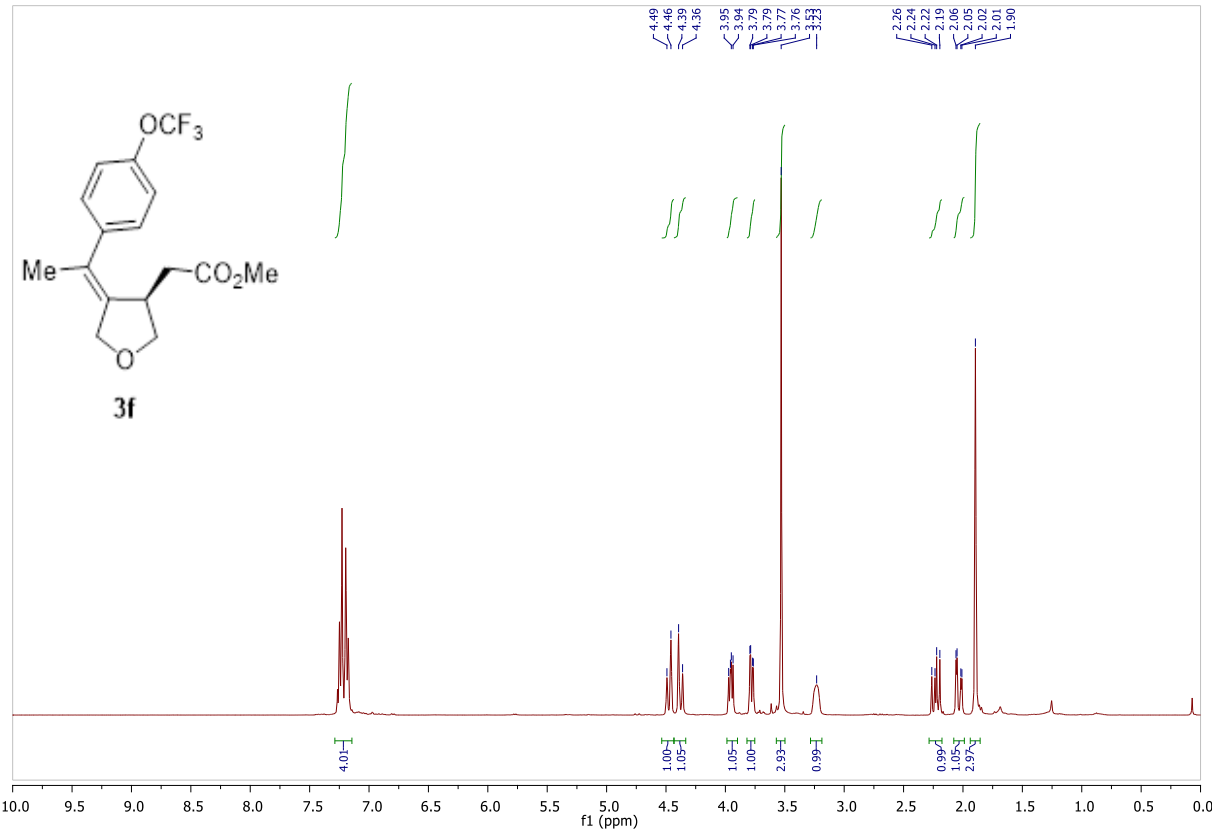
7.983
AU
Minutes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3.76
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3.53
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2.02
2.01
1.90
OCF3
Me
CO2Me
O
3f
4.01
1.00
1.05
1.05
1.00
2.93
0.99
0.99
1.05
2.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 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
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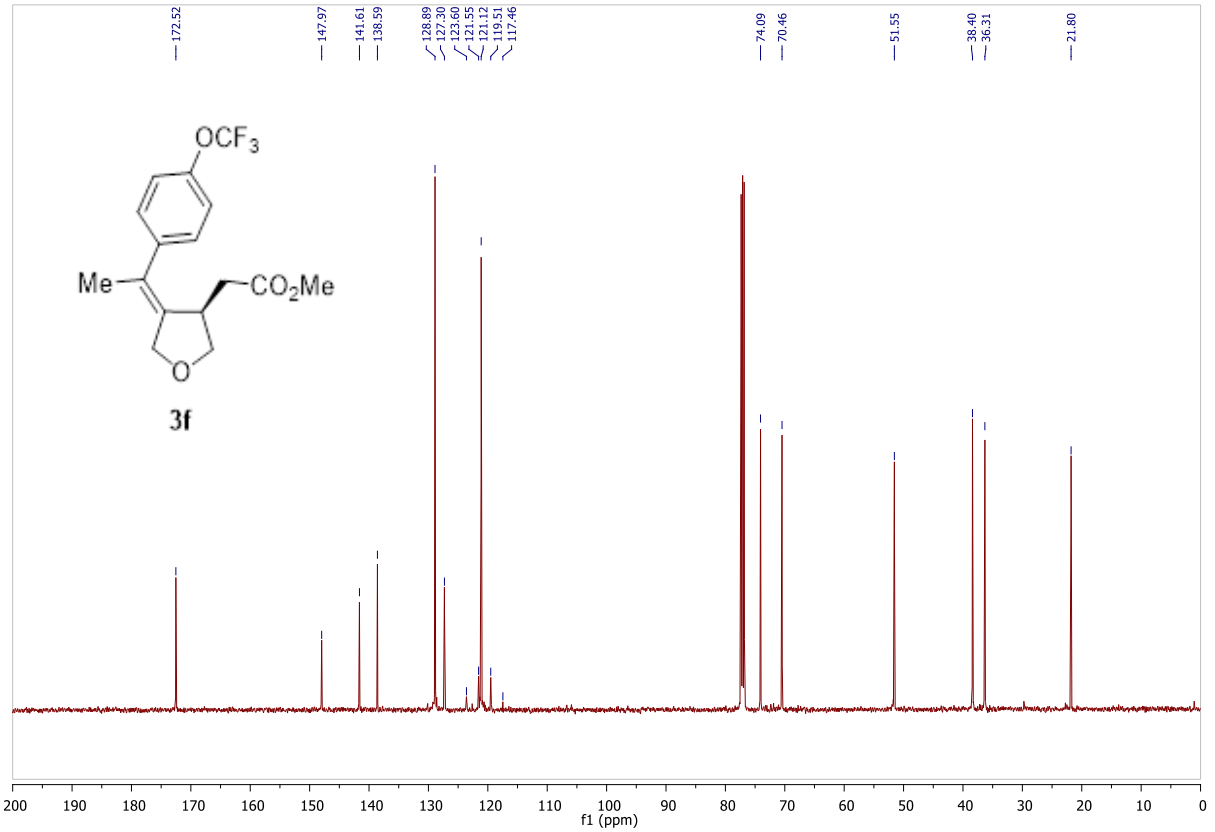
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74.09
70.46
51.55
38.40
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Me
CO2Me
O
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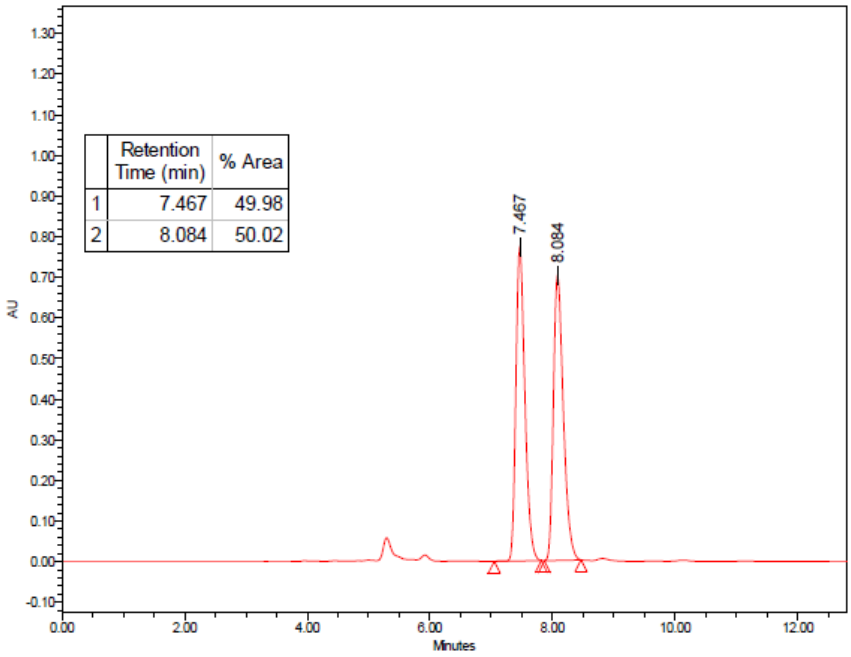
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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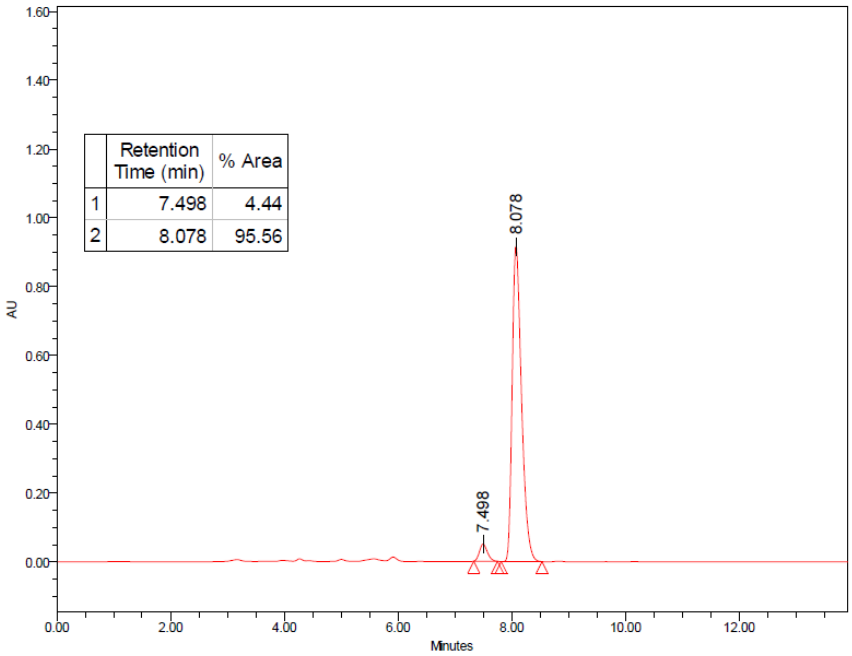
8.084
AU
Minutes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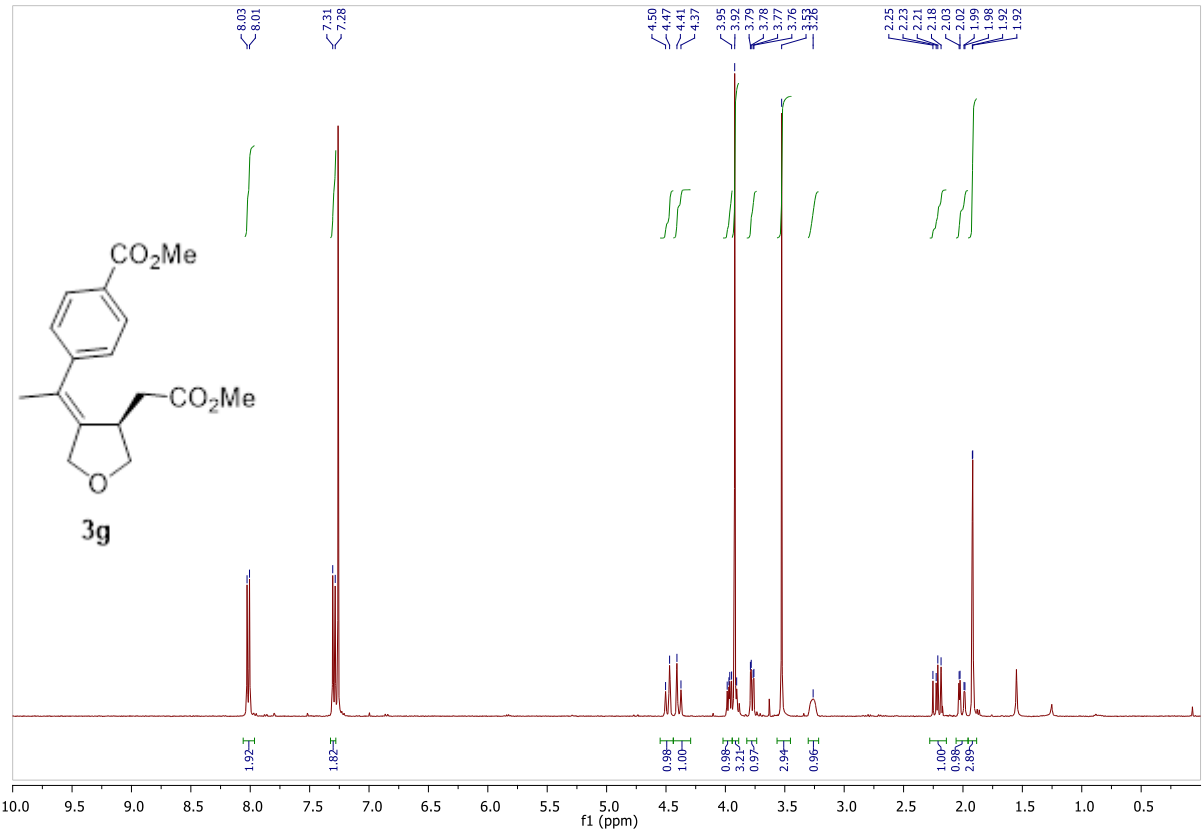
Minutes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3.76
2.25
2.23
2.21
2.18
2.03
2.02
1.99
1.98
1.92
1.92
CO2Me
CO2Me
O
3g
1.92
1.82
0.98
1.00
0.98
3.21
0.97
2.94
0.96
1.00
0.98
2.89
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
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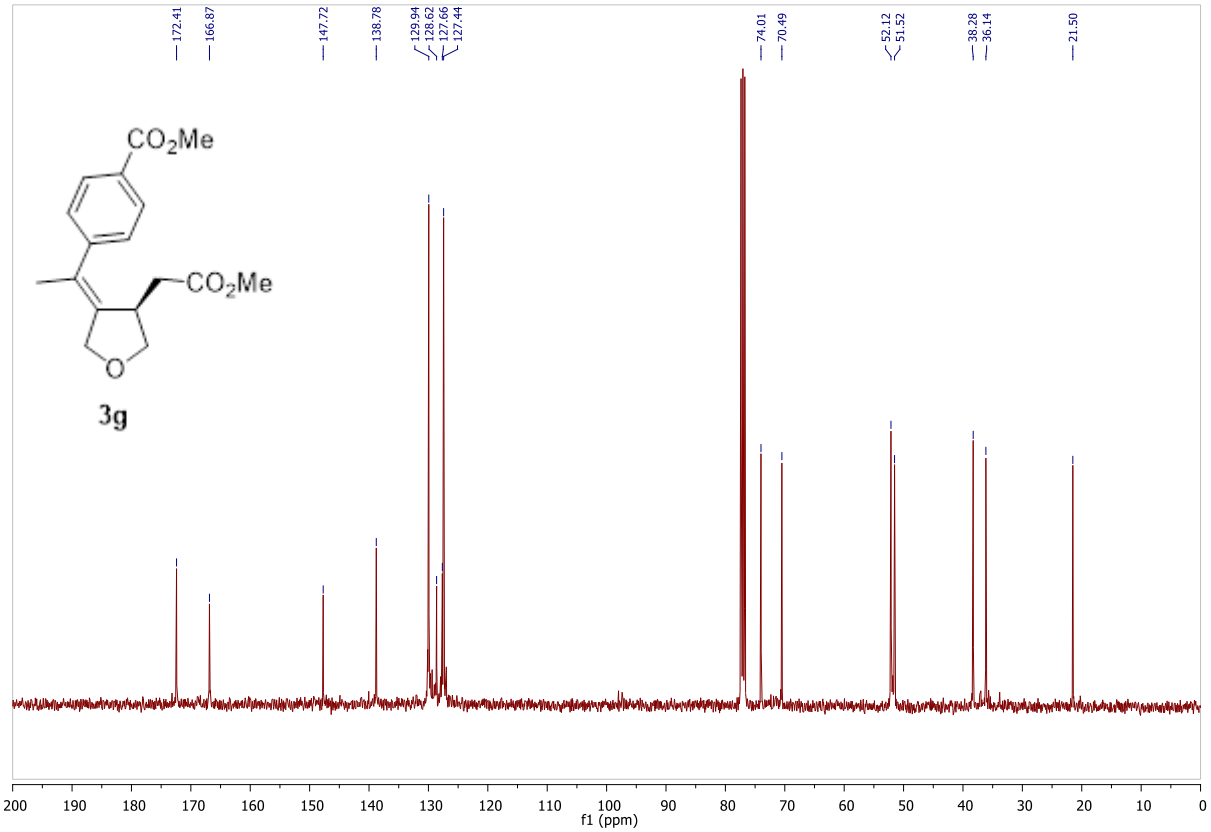
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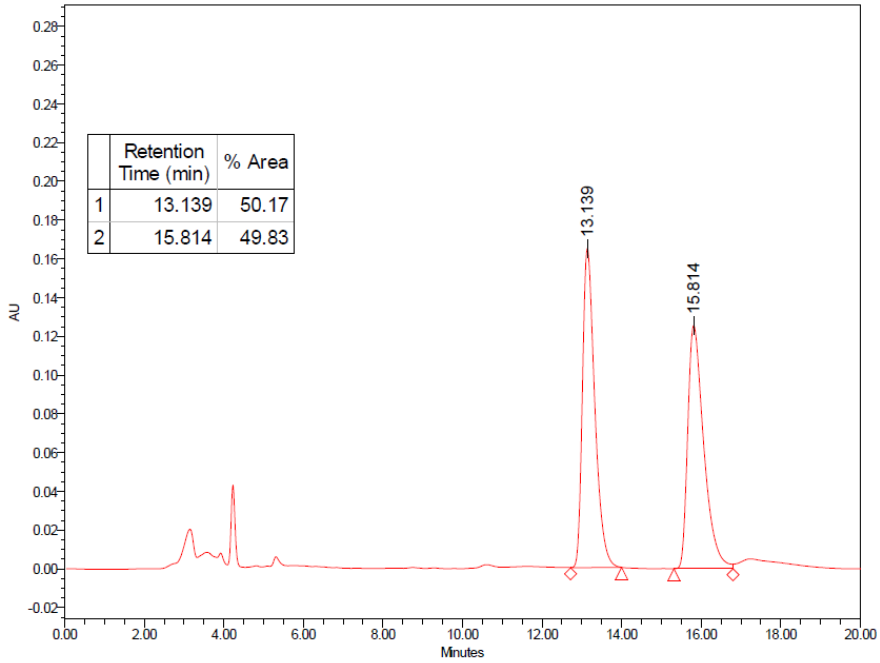
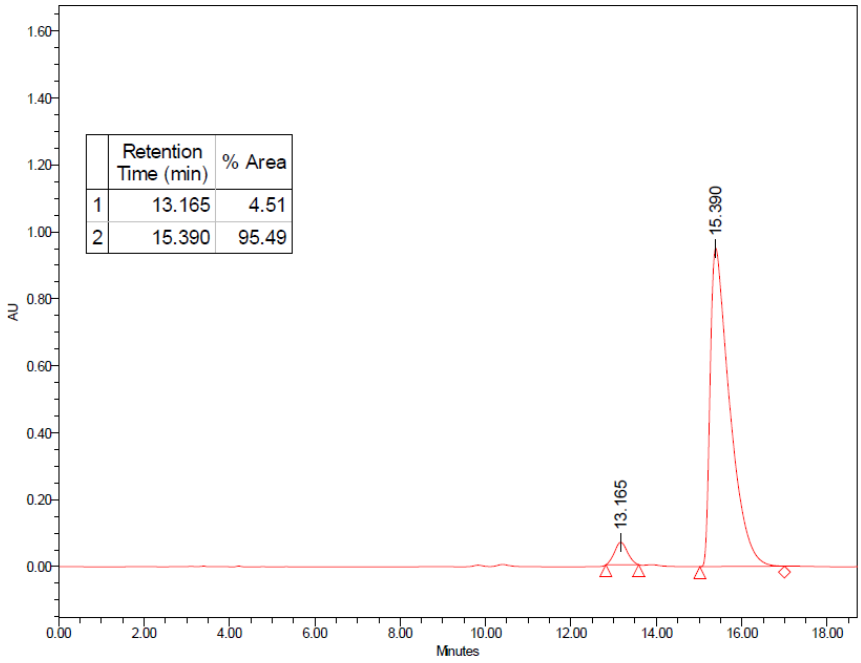
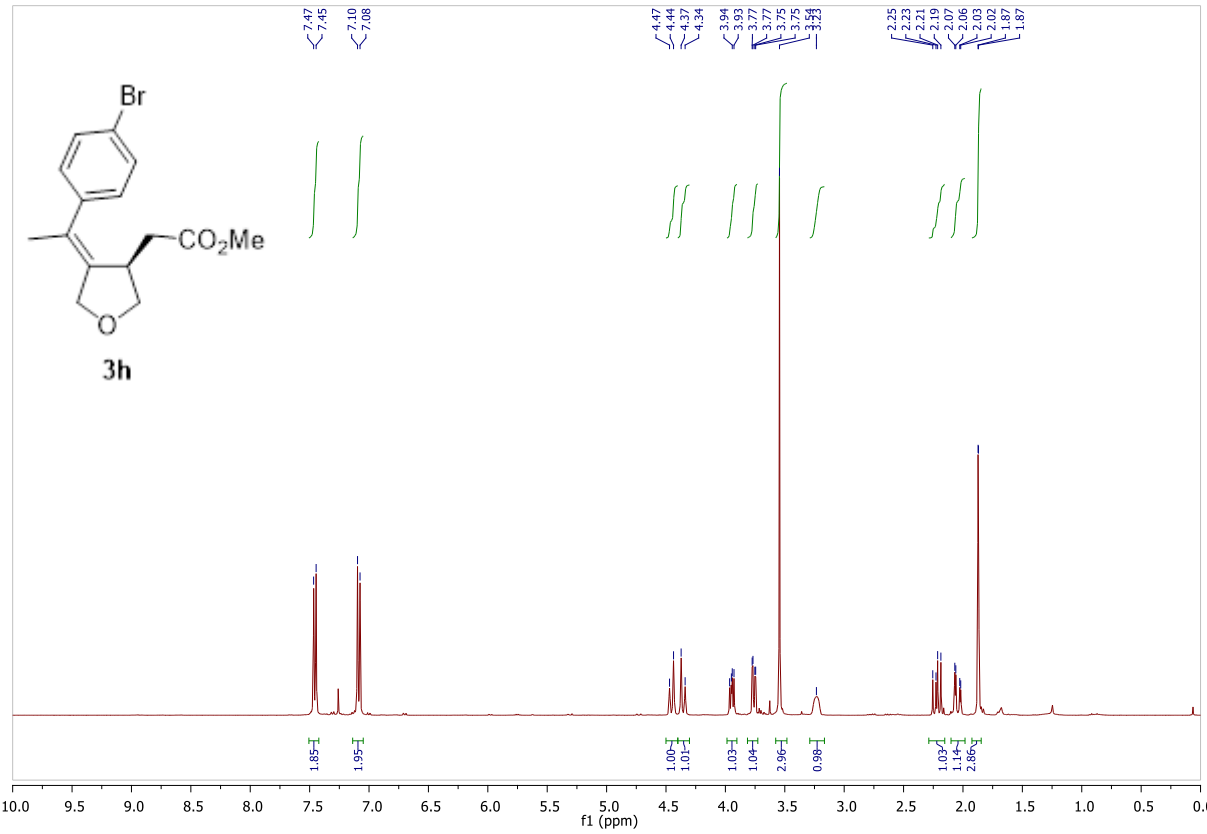
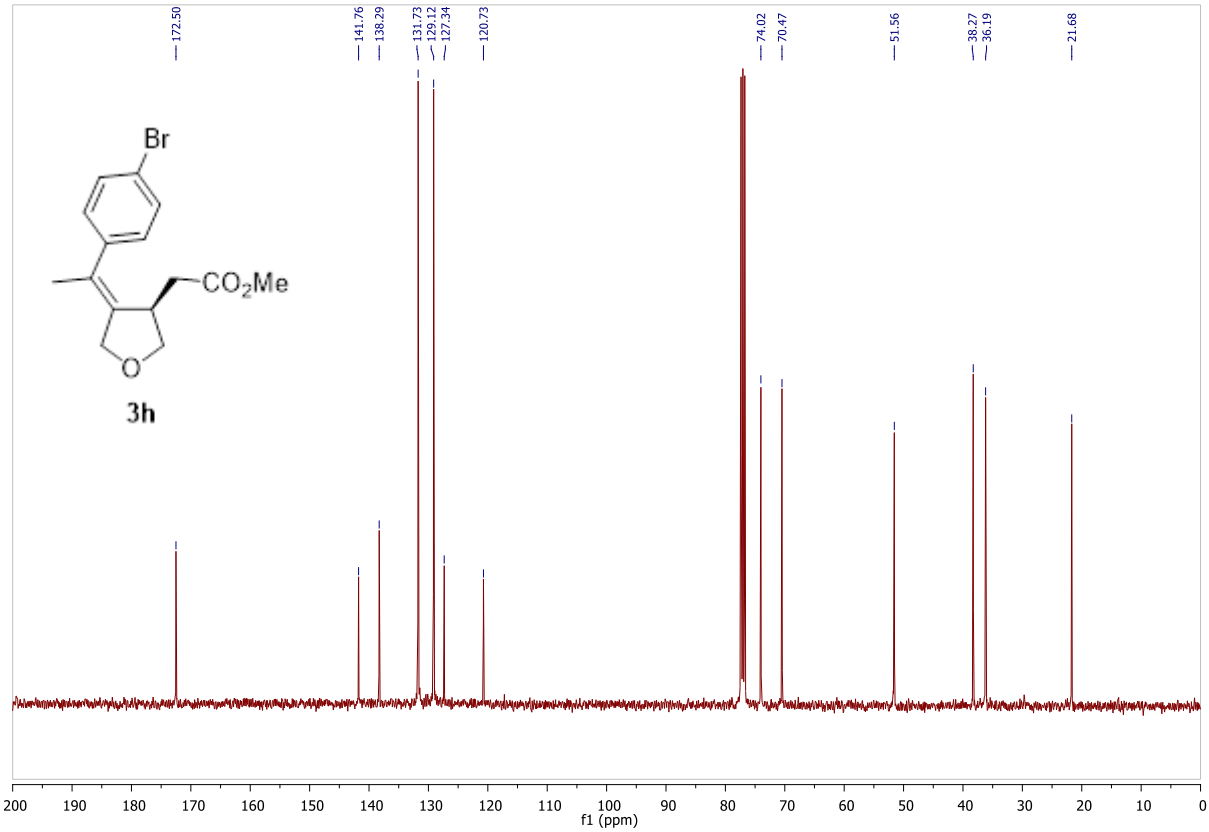
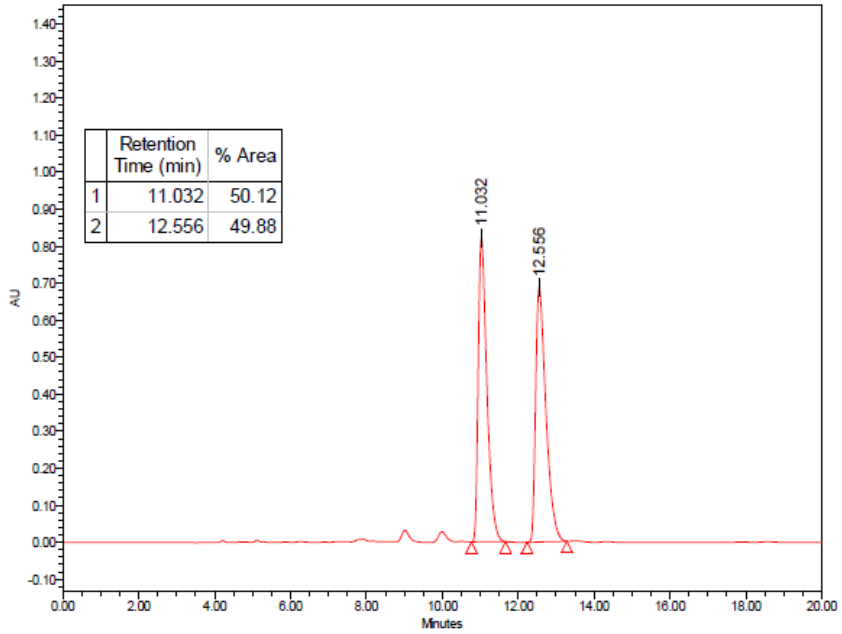
127.44
74.01
70.49
52.12
51.52
38.28
36.14
21.50
CO2Me
CO2Me
O
3g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

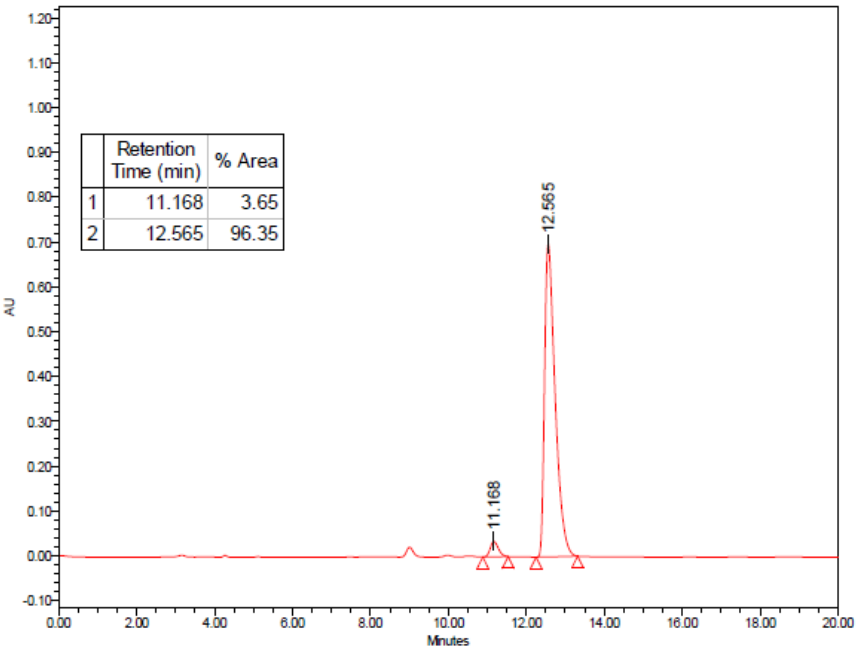

Retention Time (min) | % Area
1 | 13.139 | 50.17
2 | 15.814 | 49.83
13.139
15.814
AU
Minutes

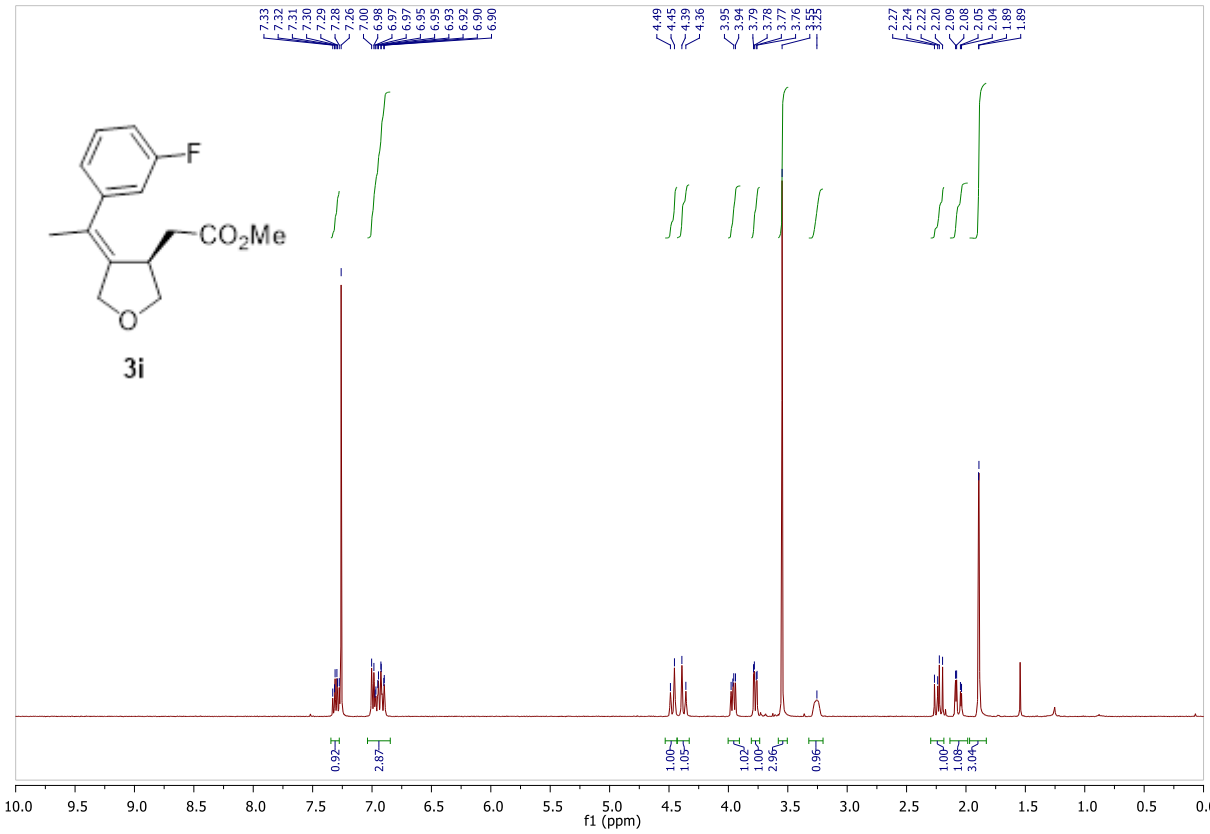

Retention Time (min) | % Area
1 | 13.165 | 4.51
2 | 15.390 | 95.49
13.165
15.390
AU
Minutes

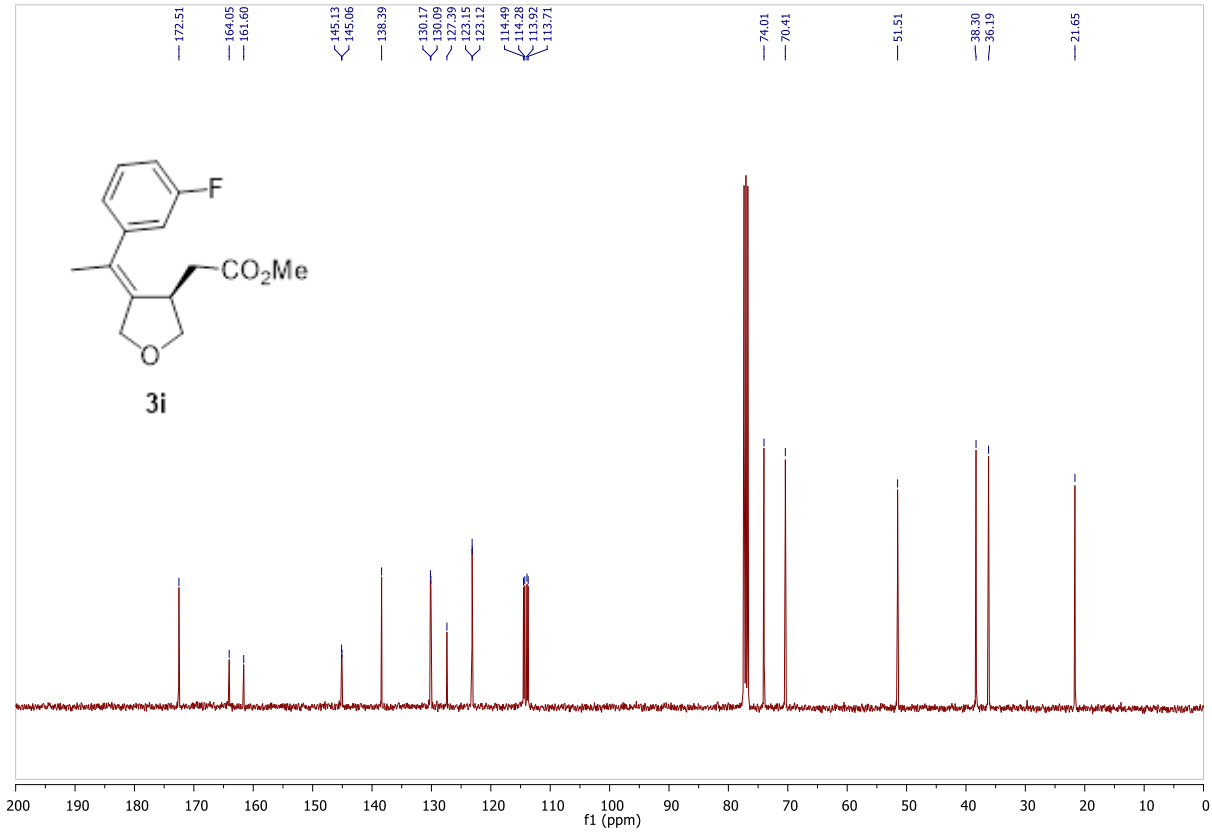

Br
CO2Me
O
3h
7.47
7.45
7.10
7.08
4.47
4.44
4.37
4.34
3.94
3.93
3.77
3.77
3.75
3.75
3.54
3.53
2.25
2.23
2.21
2.19
2.07
2.06
2.03
2.02
1.87
1.87
1.85
1.95
1.00
1.01
1.03
1.04
2.96
0.98
1.03
1.14
2.86
f1 (ppm)

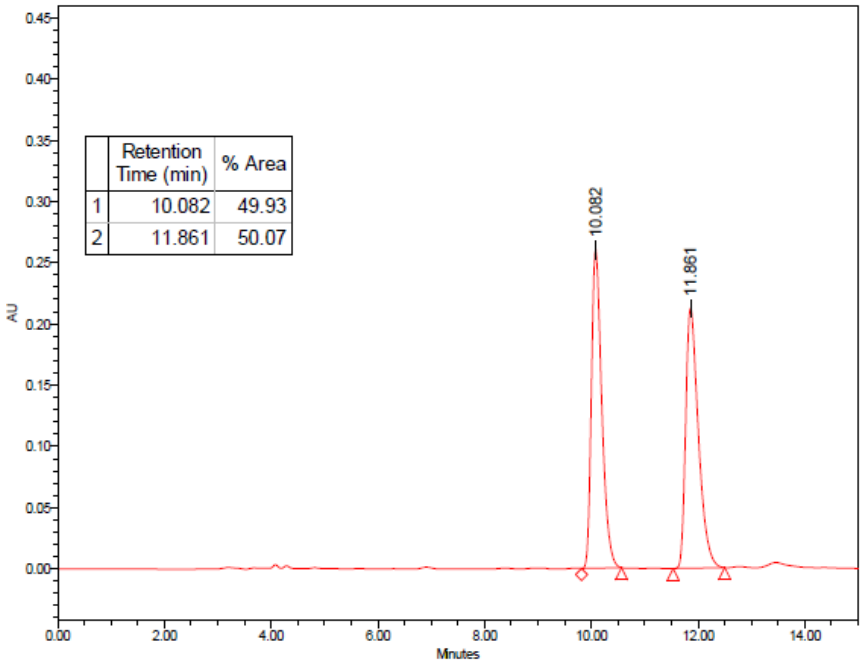

Br
CO2Me
O
3h
172.50
141.76
138.29
131.73
129.12
127.34
120.73
74.02
70.47
51.56
38.27
36.19
21.68
f1 (ppm)

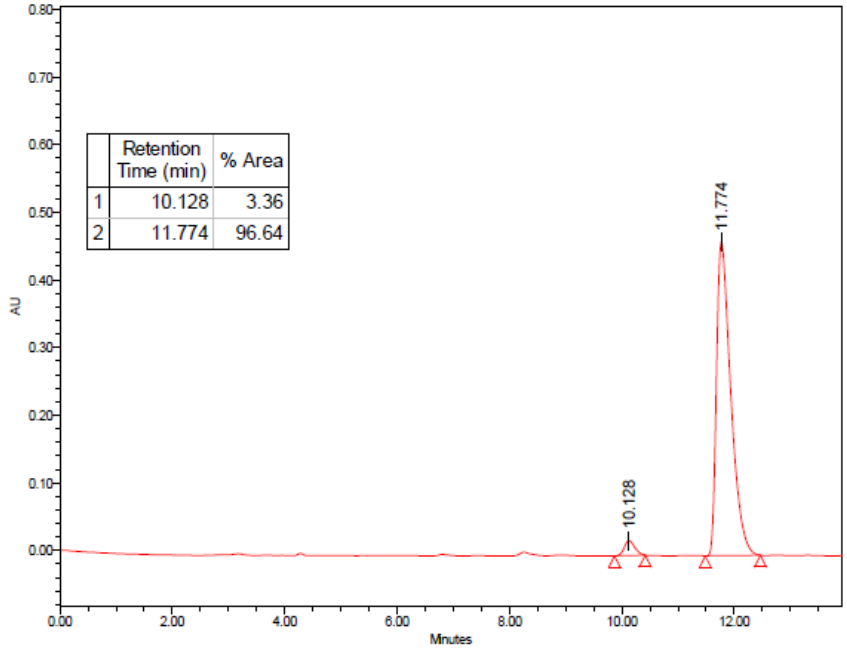

Retention Time (min)
% Area
1 11.032 50.12
2 12.556 49.88
11.032
12.556
AU
Minutes

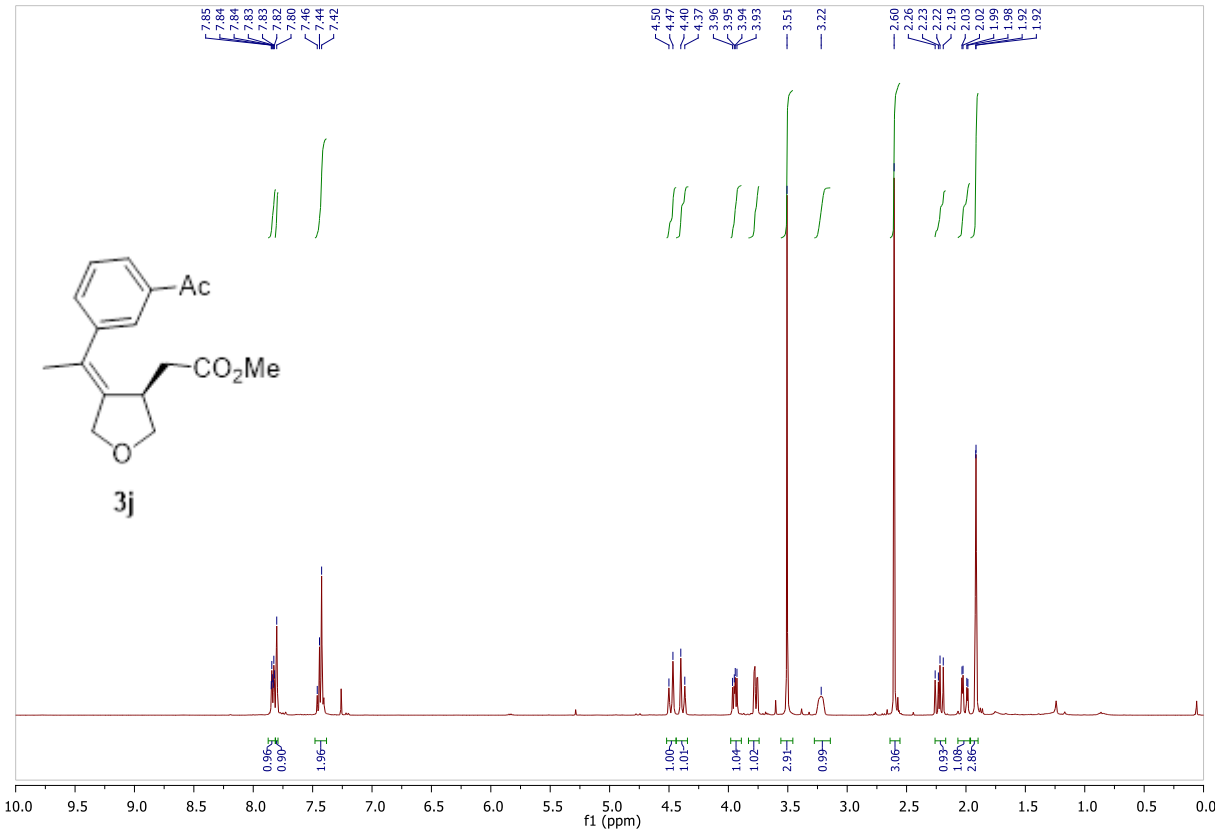

Retention Time (min)
% Area
1 11.168 3.65
2 12.565 96.35
11.168
12.565
AU
Minutes

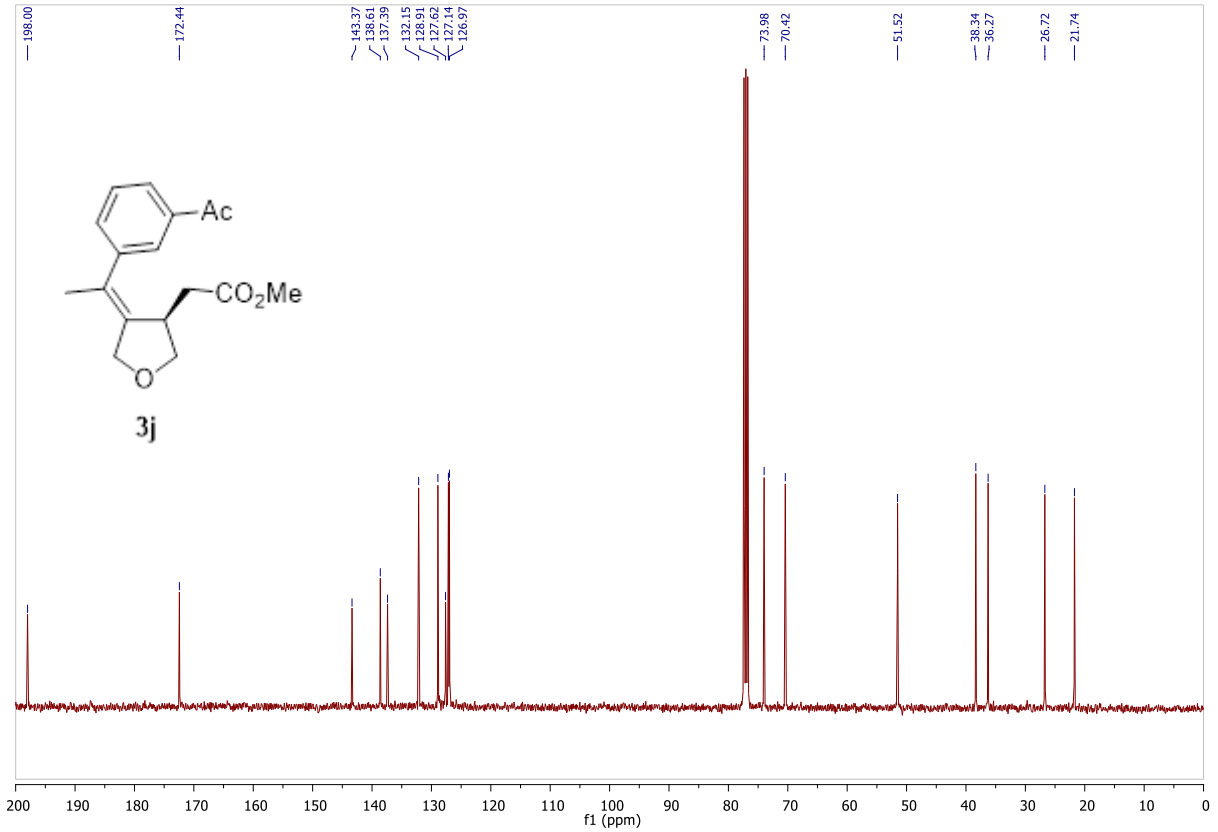

F
CO2Me
O
3i
f1 (ppm)

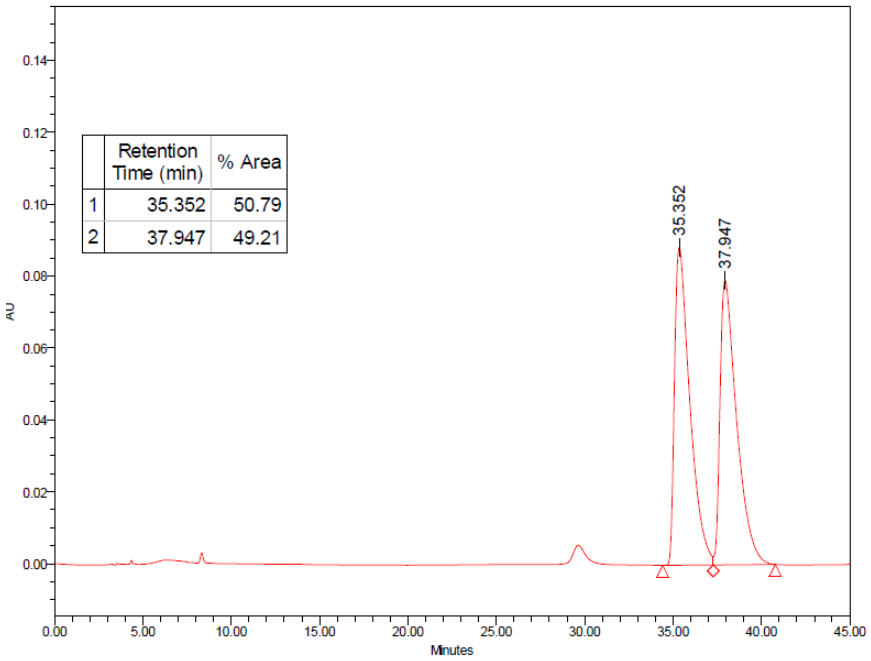

F
CO2Me
O
3i
f1 (ppm)

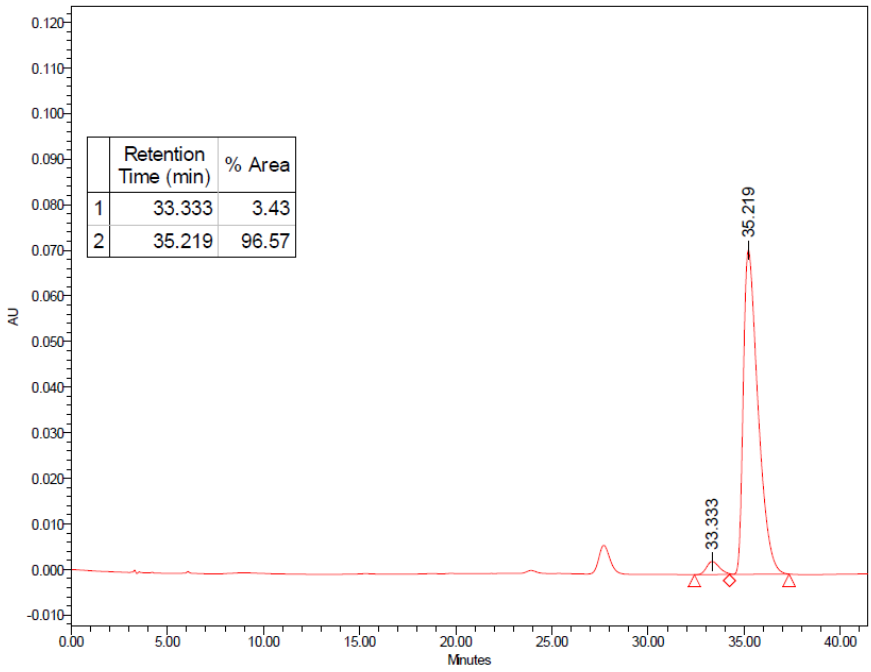

Retention Time (min) | % Area
1 | 10.082 | 49.93
2 | 11.861 | 50.07
10.082
11.861
AU
Mnutes

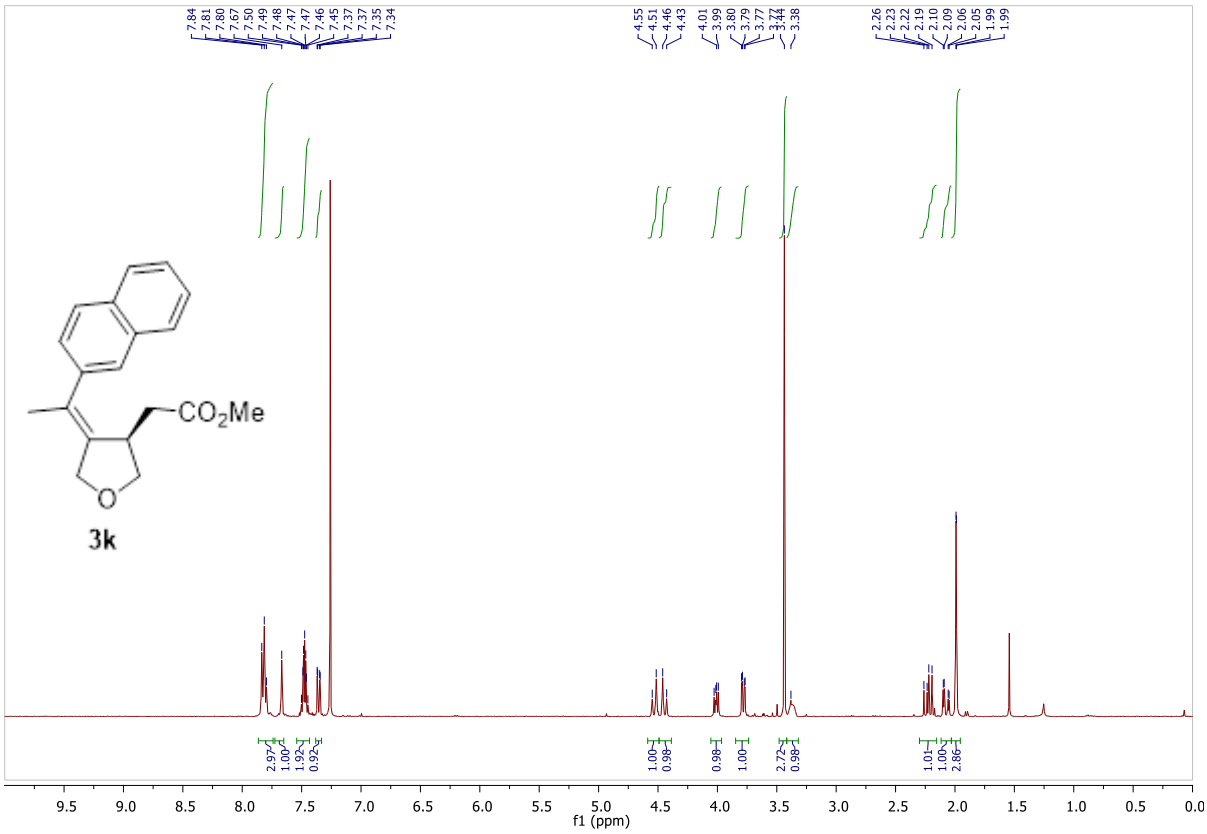

Retention Time (min) | % Area
1 | 10.128 | 3.36
2 | 11.774 | 96.64
11.774
10.128
AU
Mnutes

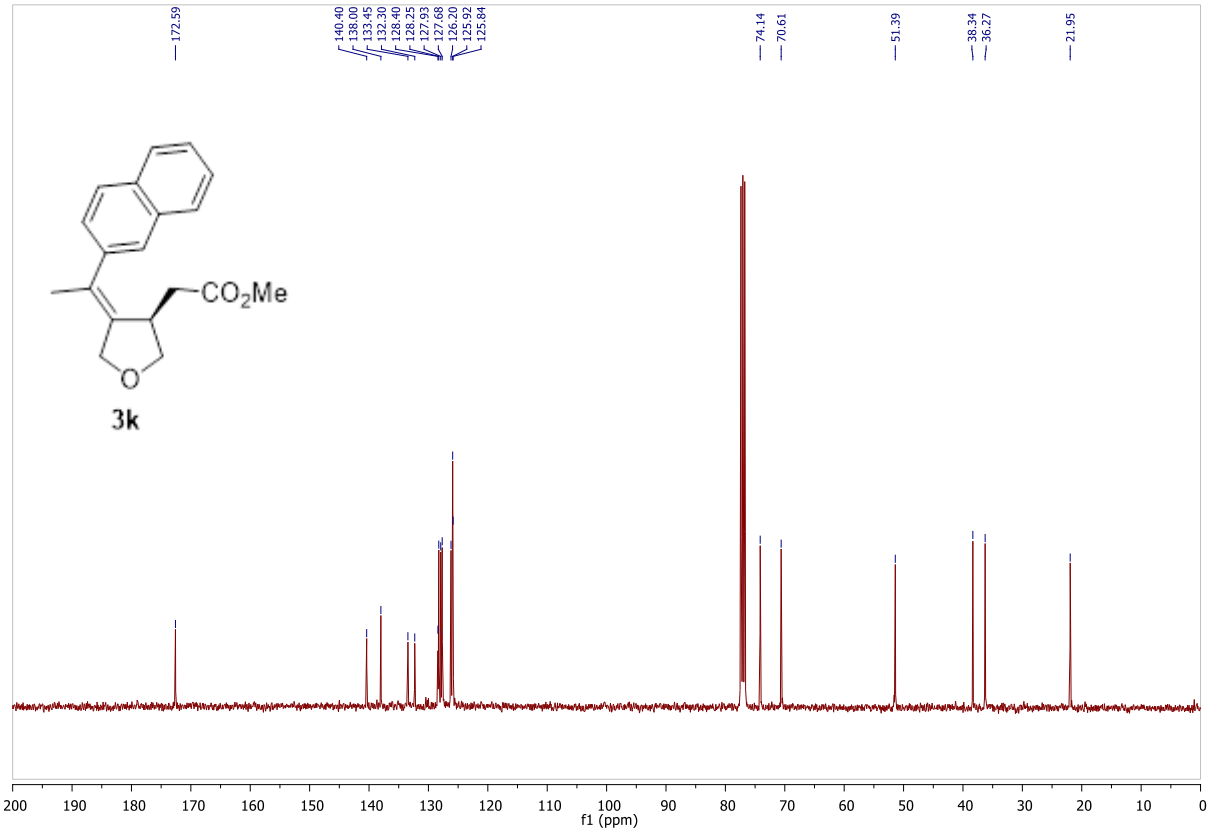

7.85
7.84
7.84
7.83
7.83
7.82
7.80
7.46
7.44
7.42
4.50
4.47
4.40
4.37
3.96
3.95
3.94
3.93
3.51
3.22
2.60
2.26
2.23
2.22
2.19
2.03
2.02
1.99
1.98
1.92
1.92
Ac
CO2Me
O
3j
0.96
0.90
1.96
1.00
1.01
1.04
1.02
2.91
0.99
3.06
0.93
1.08
2.86
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

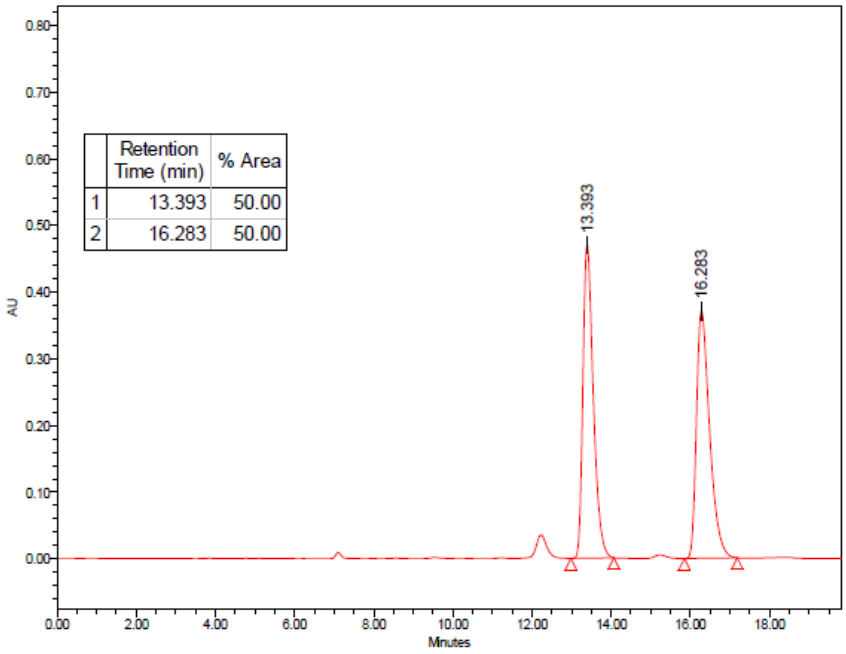

198.00
172.44
143.37
138.61
137.39
132.15
128.91
127.62
127.14
126.97
73.98
70.42
51.52
38.34
36.27
26.72
21.74
Ac
CO2Me
O
3j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

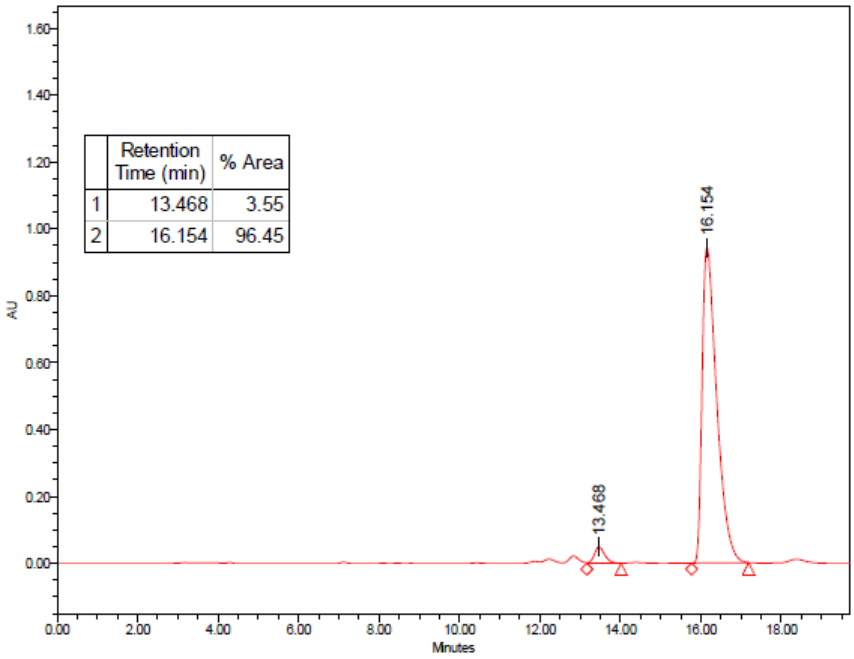

Retention Time (min) | % Area
1 | 35.352 | 50.79
2 | 37.947 | 49.21
35.352
37.947
AU
Minutes

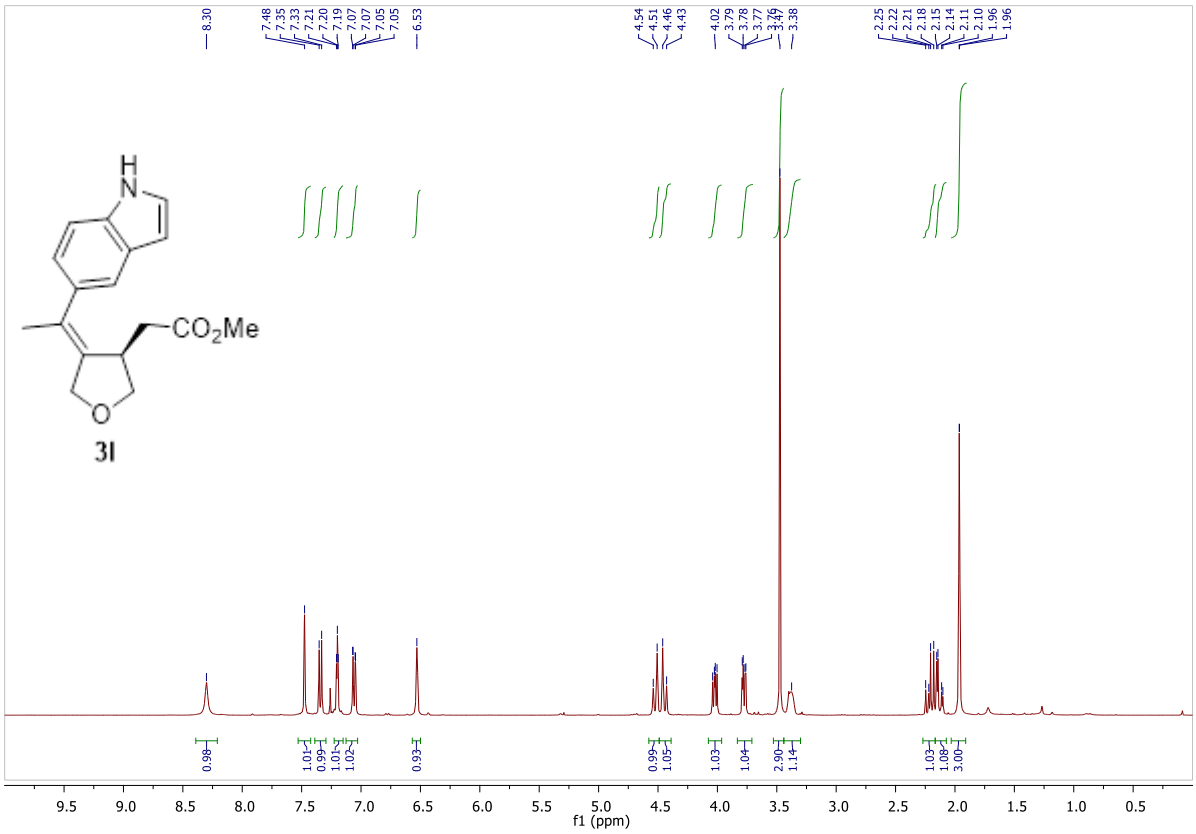

Retention Time (min) | % Area
1 | 33.333 | 3.43
2 | 35.219 | 96.57
35.219
33.333
AU
Minutes

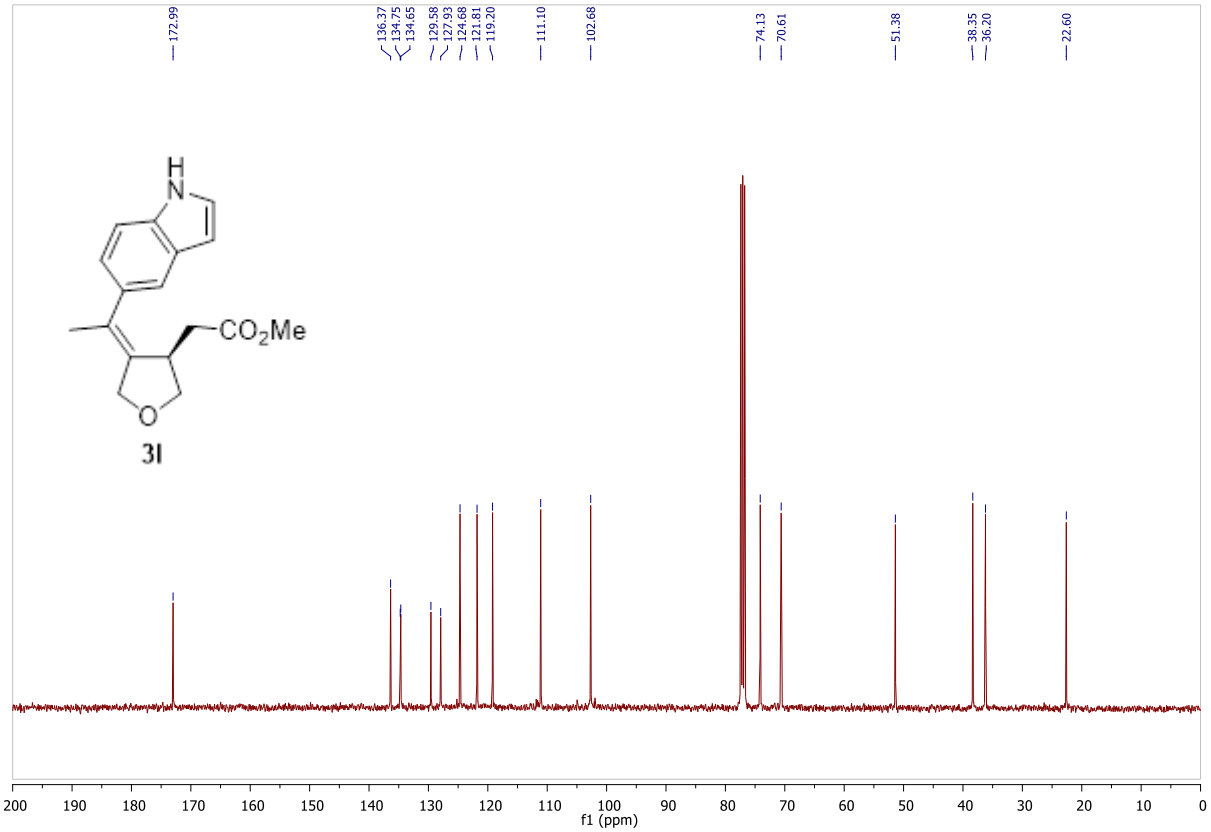

7.84
7.81
7.80
7.67
7.50
7.49
7.48
7.47
7.47
7.46
7.45
7.37
7.37
7.35
7.34
4.55
4.51
4.46
4.43
4.01
3.99
3.80
3.79
3.77
3.38
2.26
2.23
2.22
2.19
2.10
2.09
2.06
2.05
1.99
1.99
CO2Me
O
3k
2.97
1.00
1.92
0.92
1.00
0.98
0.98
1.00
2.72
0.98
1.01
1.00
2.86
f1 (ppm)

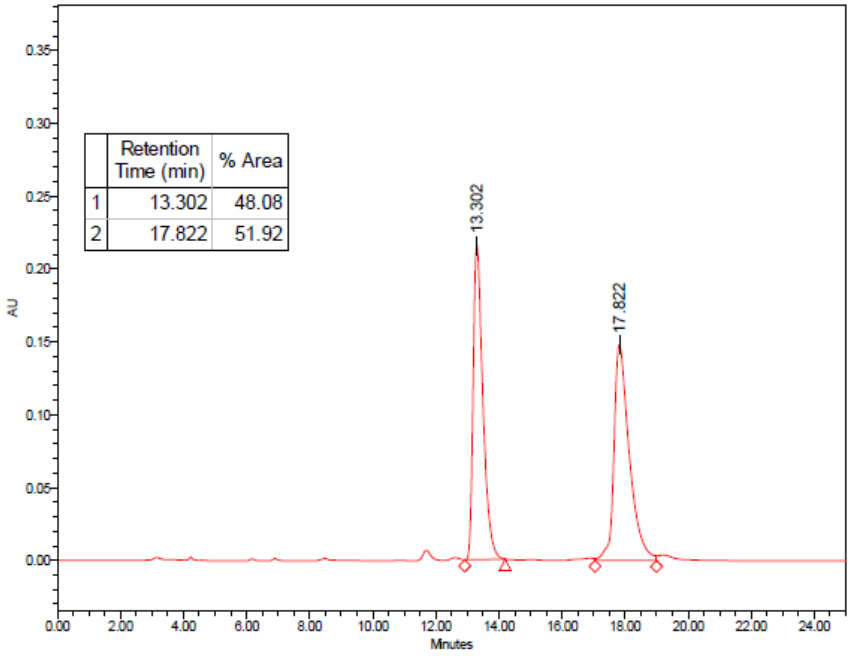

172.59
140.40
138.00
133.45
132.30
128.40
128.25
127.93
127.68
126.20
125.92
125.84
74.14
70.61
51.39
38.34
36.27
21.95
CO2Me
O
3k
f1 (ppm)

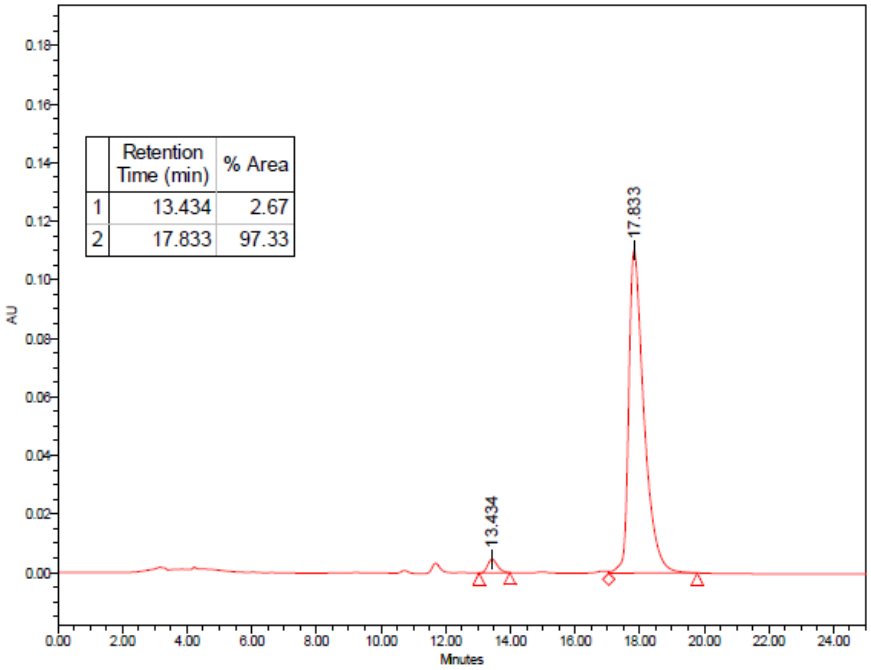

Retention Time (min) | % Area
1 | 13.393 | 50.00
2 | 16.283 | 50.00
13.393
16.283
AU
Minutes

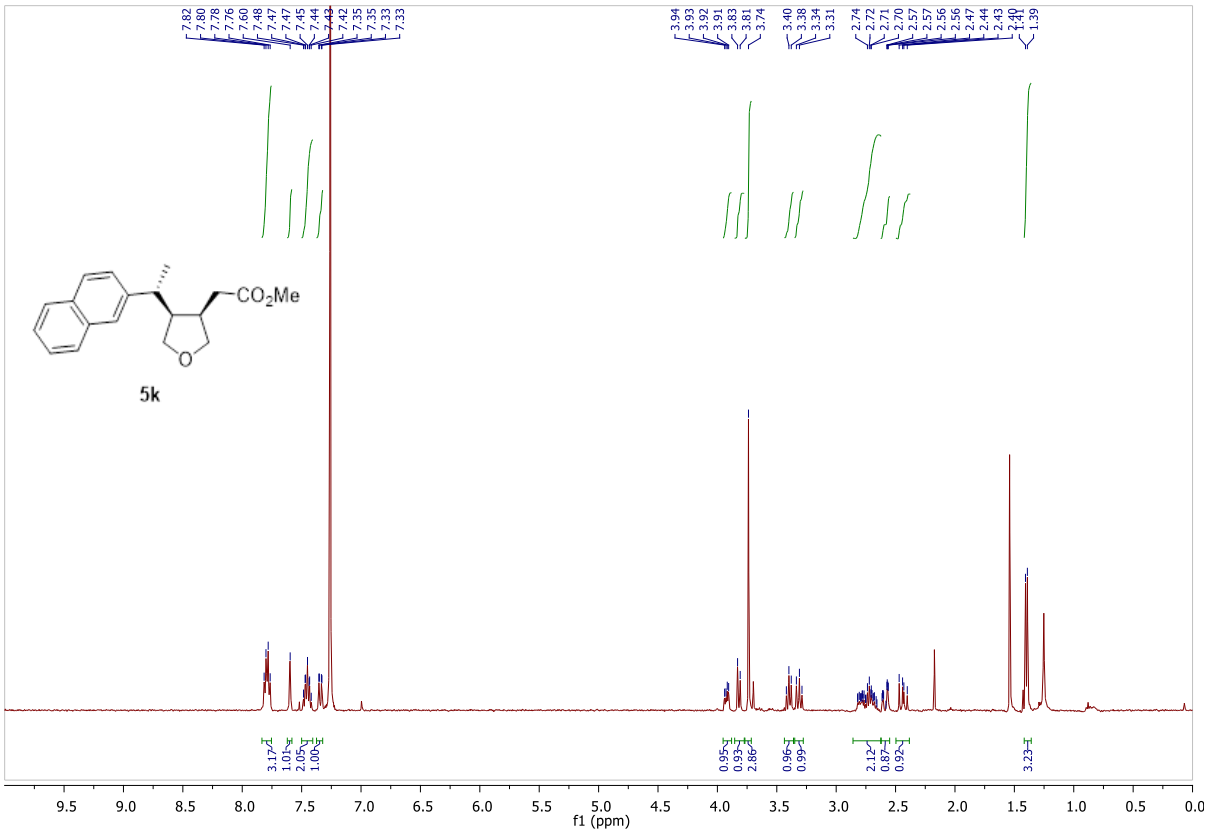

Retention Time (min) | % Area
1 | 13.468 | 3.55
2 | 16.154 | 96.45
13.468
16.154
AU
Minutes

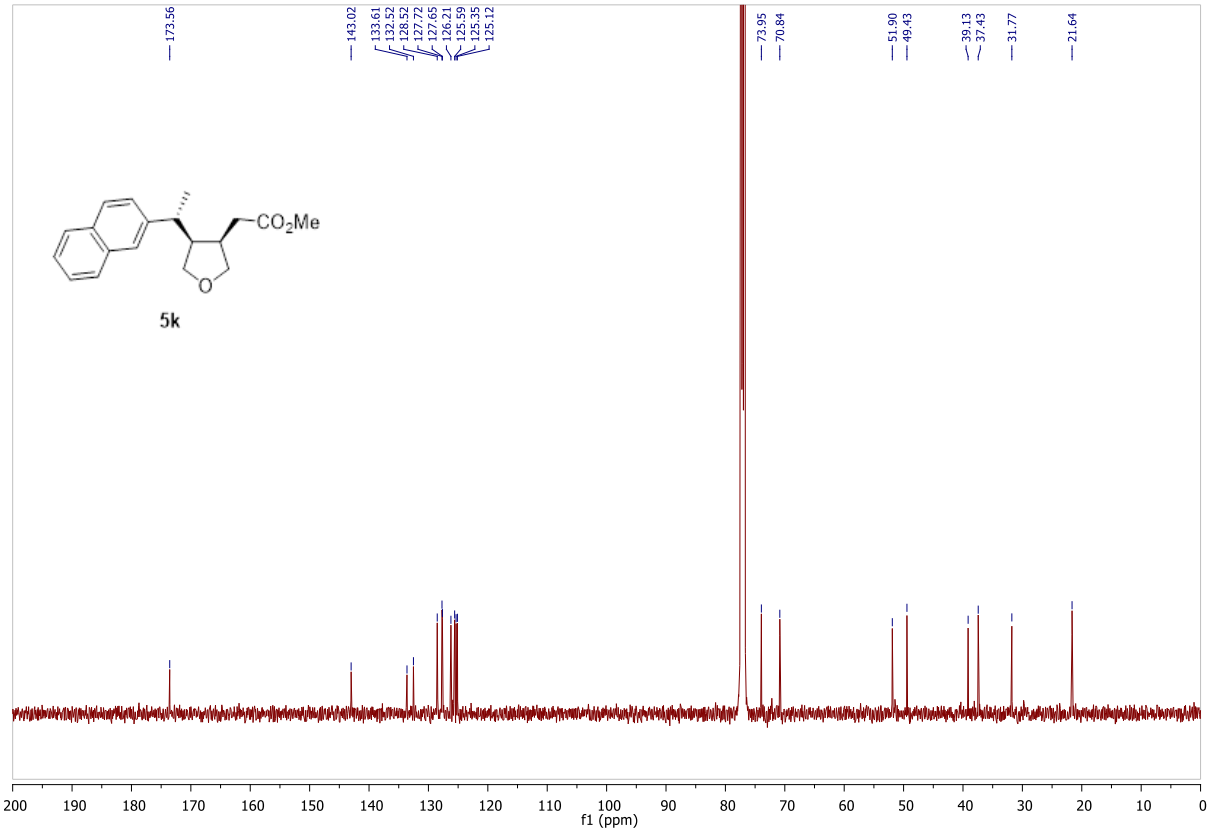

8.30
7.48
7.35
7.33
7.21
7.20
7.19
7.07
7.07
7.05
7.05
6.53
4.54
4.51
4.46
4.43
4.02
3.79
3.78
3.77
3.49
3.38
2.25
2.22
2.21
2.18
2.15
2.14
2.11
2.10
1.96
1.96
0.98
1.01
0.99
1.01
1.02
0.93
0.99
1.05
1.03
1.04
2.90
1.14
1.03
1.08
3.00
CO2Me
3l
f1 (ppm)

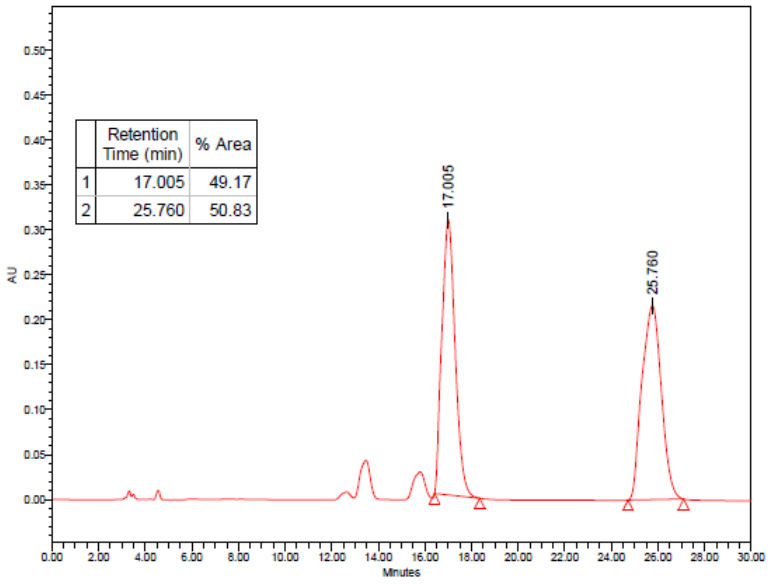

172.99
136.37
134.75
134.65
129.58
127.93
124.68
121.81
119.20
111.10
102.68
74.13
70.61
51.38
38.35
36.20
22.60
CO2Me
3l
f1 (ppm)

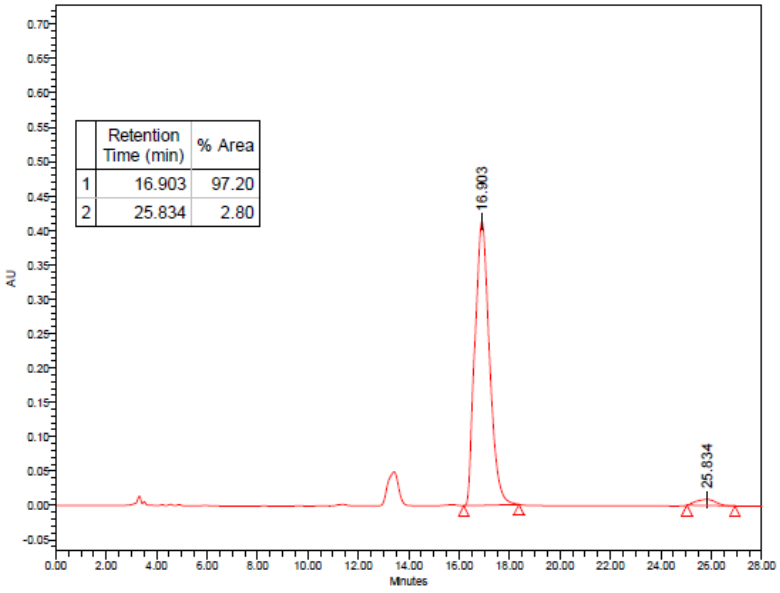

Retention Time (min) | % Area
1 | 13.302 | 48.08
2 | 17.822 | 51.92
13.302
17.822
AU
Minutes

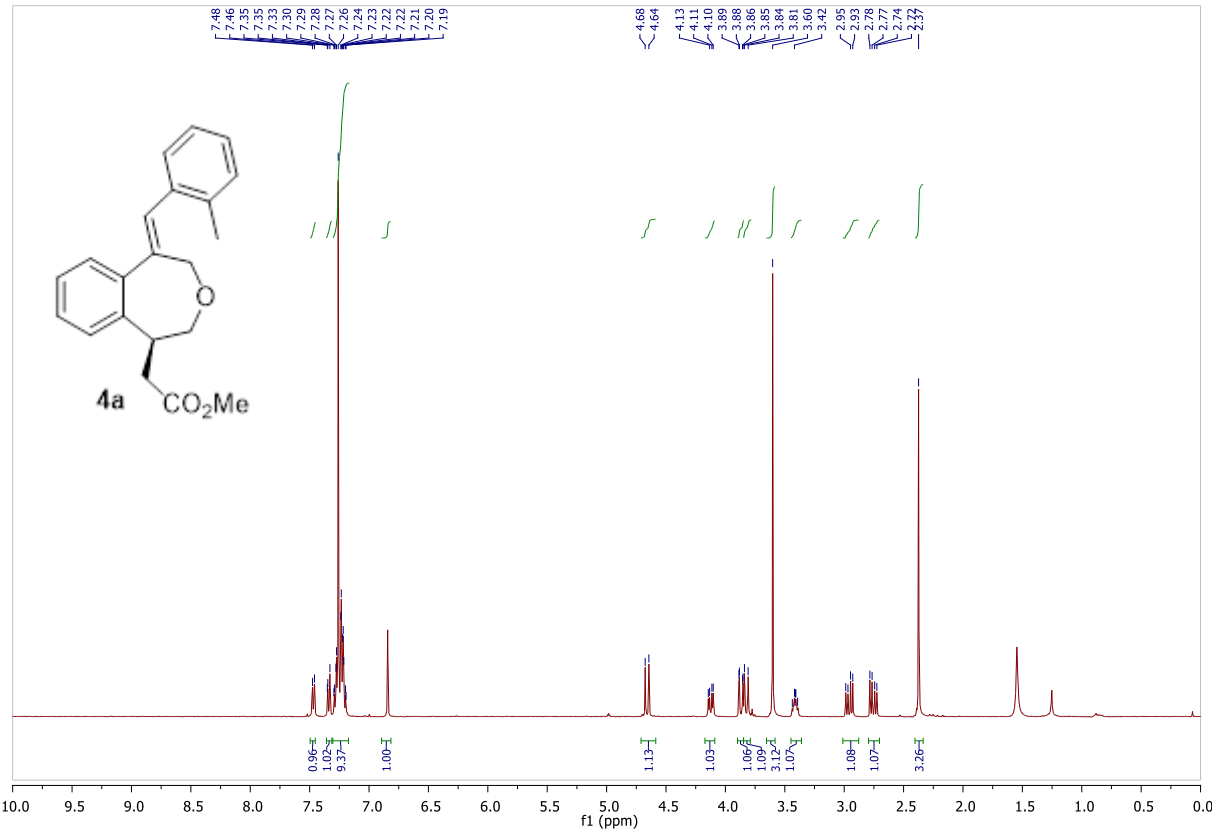

Retention Time (min) | % Area
1 | 13.434 | 2.67
2 | 17.833 | 97.33
13.434
17.833
AU
Minutes

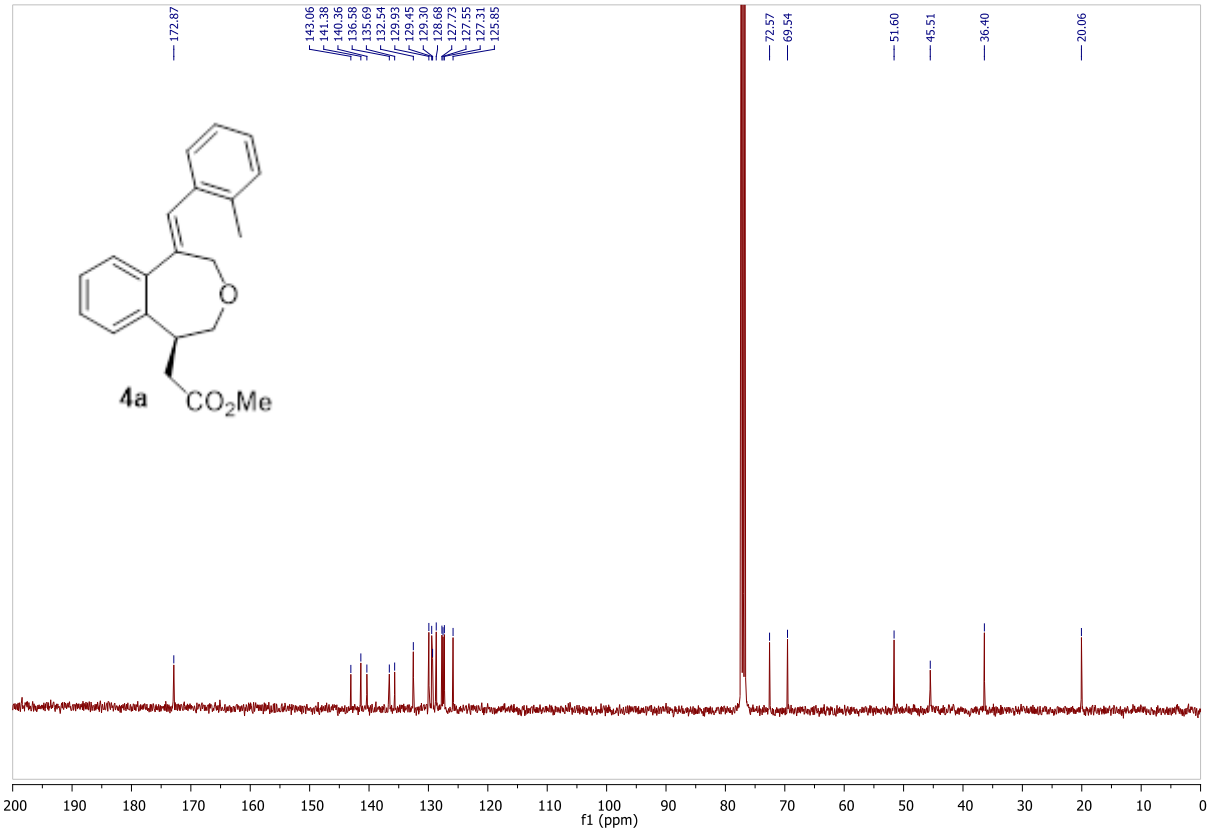

7.82
7.80
7.78
7.76
7.60
7.48
7.47
7.45
7.44
7.43
7.42
7.35
7.35
7.33
7.33
3.94
3.93
3.92
3.91
3.83
3.81
3.74
3.40
3.38
3.34
3.31
2.74
2.72
2.71
2.70
2.57
2.57
2.56
2.47
2.44
2.43
2.40
2.41
1.39
CO2Me
O
5k
3.17
1.01
2.05
1.00
0.95
0.93
2.86
0.96
0.99
2.12
0.87
0.92
3.23
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 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)

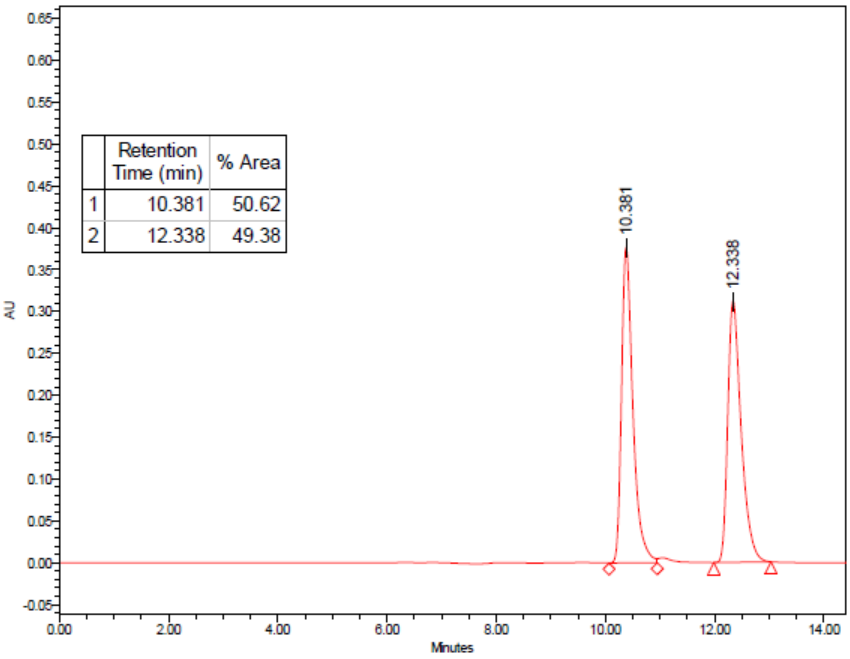

173.56
143.02
133.61
132.52
128.52
127.72
127.65
126.21
125.59
125.35
125.12
73.95
70.84
51.90
49.43
39.13
37.43
31.77
21.64
CO2Me
O
5k
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

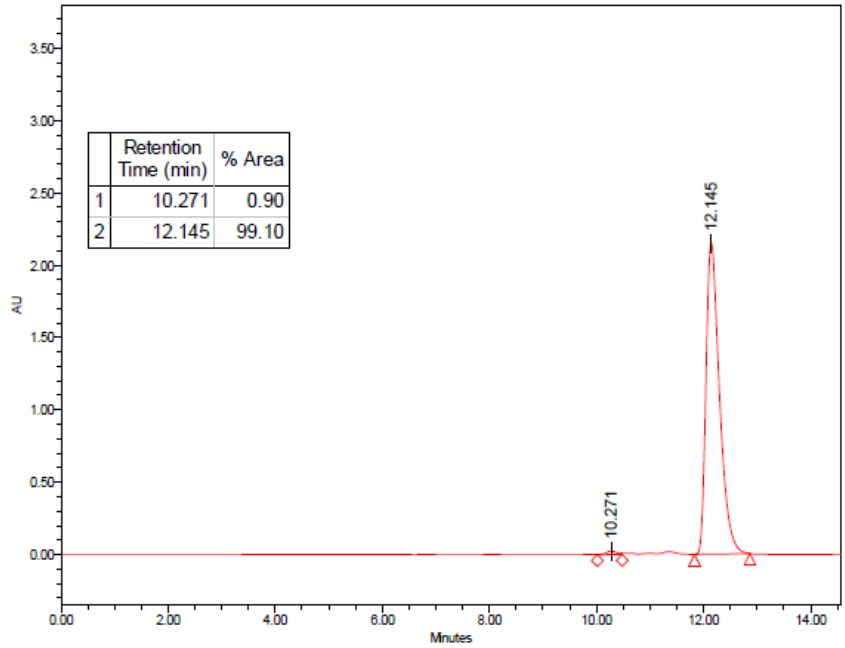

Retention Time (min)
% Area
1
17.005
49.17
2
25.760
50.83
17.005
25.760
AU
Minutes

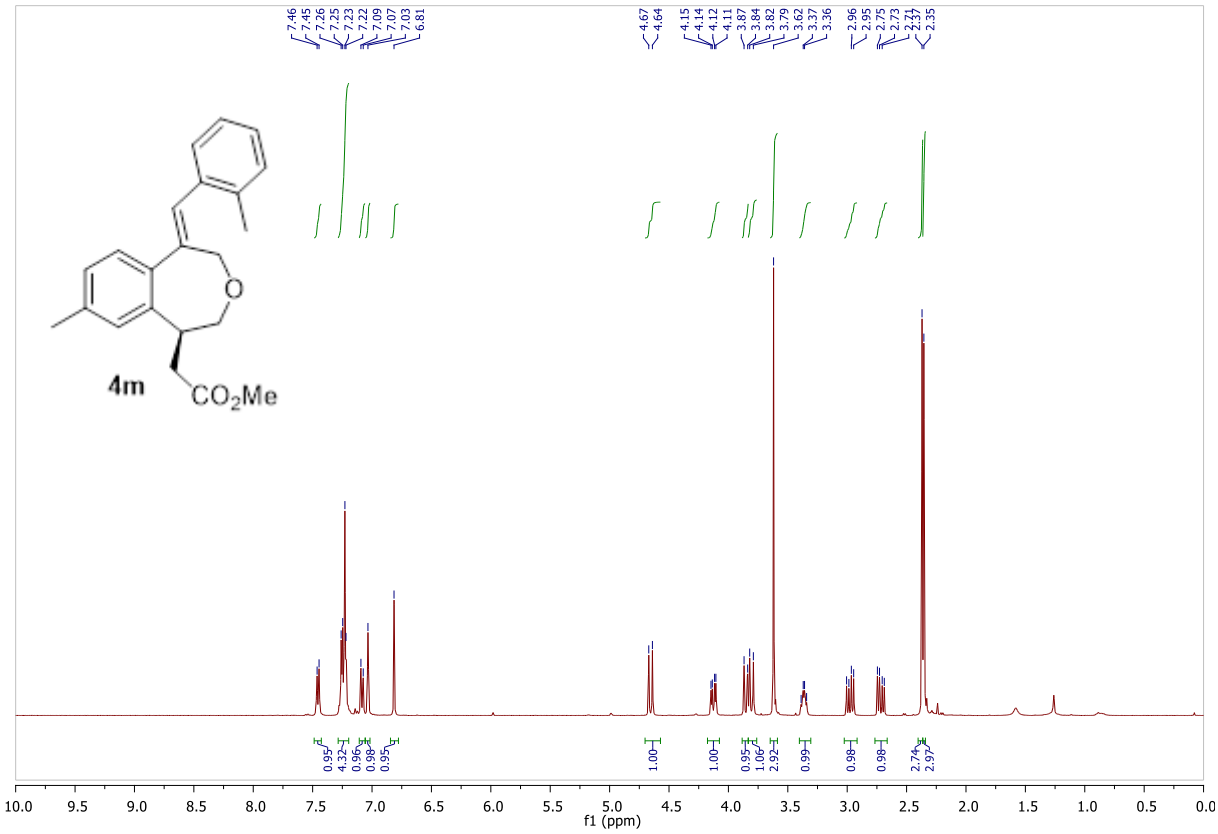

Retention Time (min)
% Area
1
16.903
97.20
2
25.834
2.80
16.903
25.834
AU
Minutes

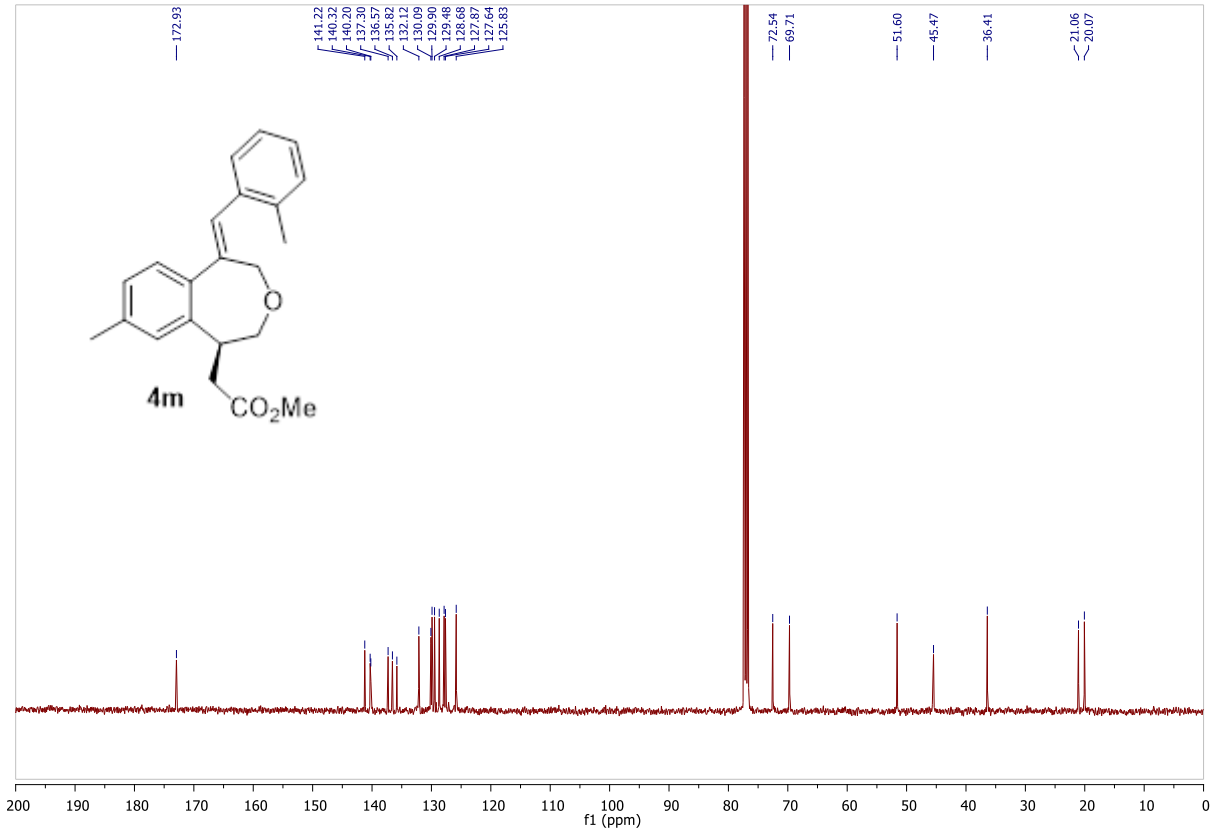

7.48
7.46
7.35
7.35
7.33
7.30
7.29
7.28
7.27
7.26
7.24
7.23
7.22
7.22
7.21
7.20
7.19
4.68
4.64
4.13
4.11
4.10
3.89
3.88
3.86
3.85
3.84
3.81
3.60
3.42
2.95
2.93
2.78
2.77
2.74
2.72
2.37
0.96
1.02
9.37
1.00
1.13
1.03
1.06
1.09
3.12
1.07
1.08
1.07
3.26
4a
CO2Me
f1 (ppm)

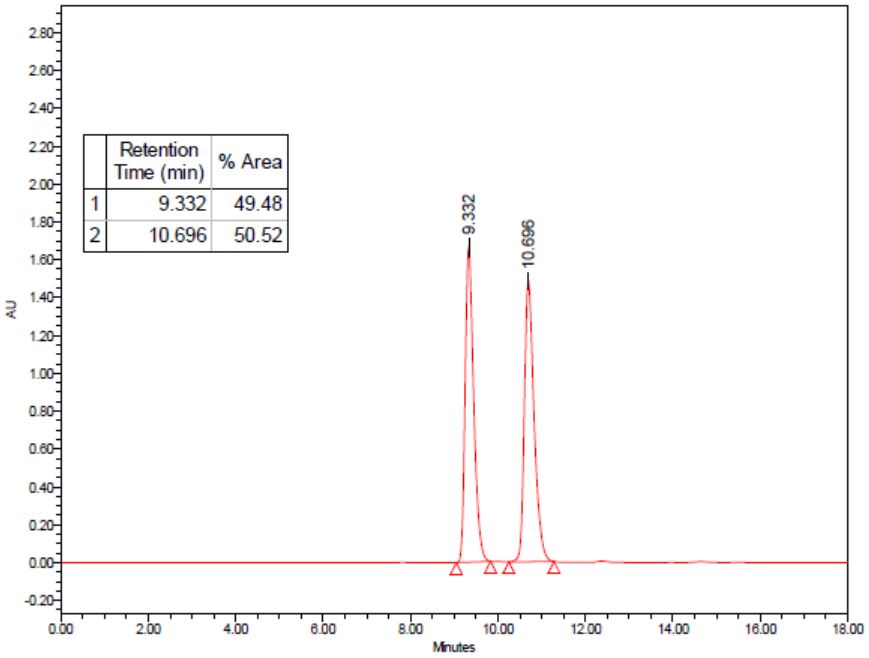

172.87
143.06
141.38
140.36
136.58
135.69
132.54
129.93
129.45
129.30
128.68
127.73
127.55
127.31
125.85
72.57
69.54
51.60
45.51
36.40
20.06
4a
CO2Me
f1 (ppm)

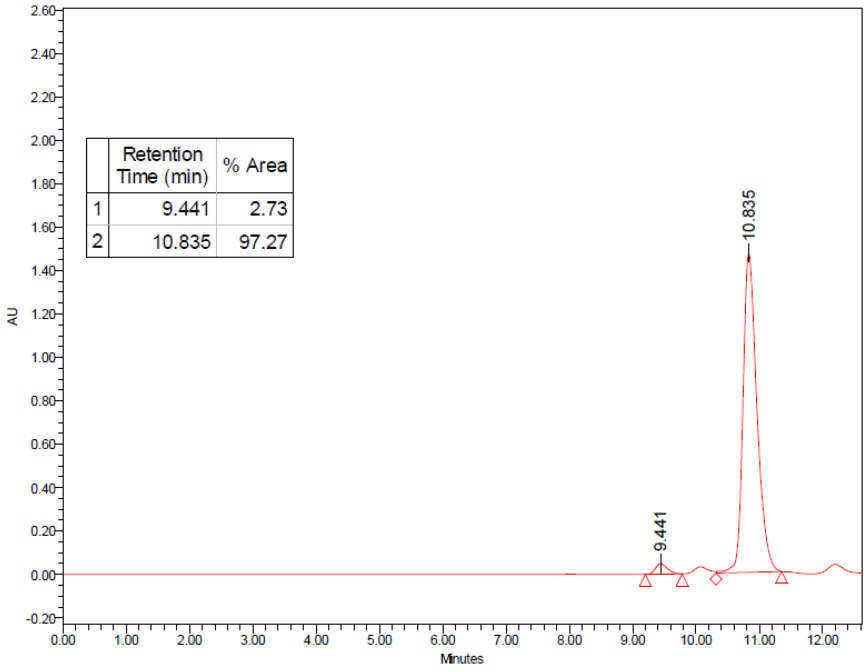

Retention Time (min) | % Area
1 | 10.381 | 50.62
2 | 12.338 | 49.38
10.381
12.338
AU
Minutes

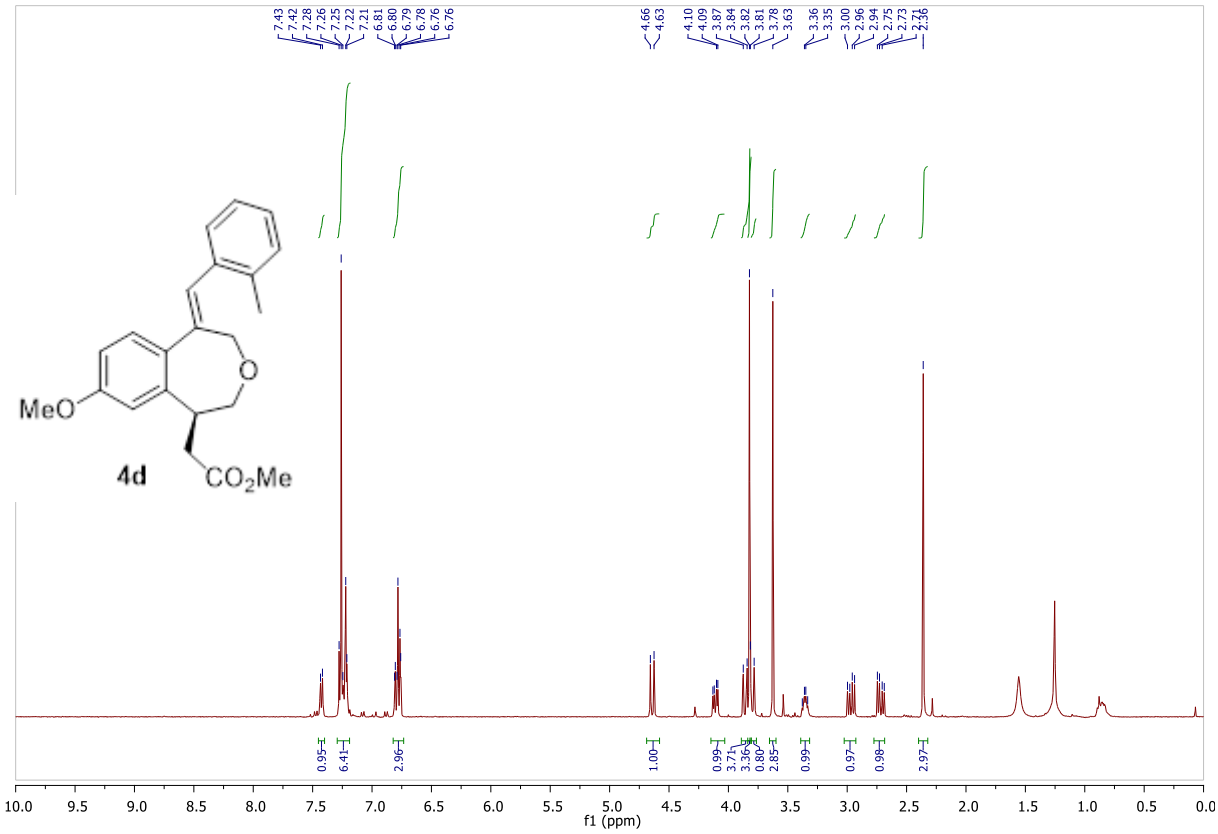

Retention Time (min) | % Area
1 | 10.271 | 0.90
2 | 12.145 | 99.10
10.271
12.145
AU
Minutes

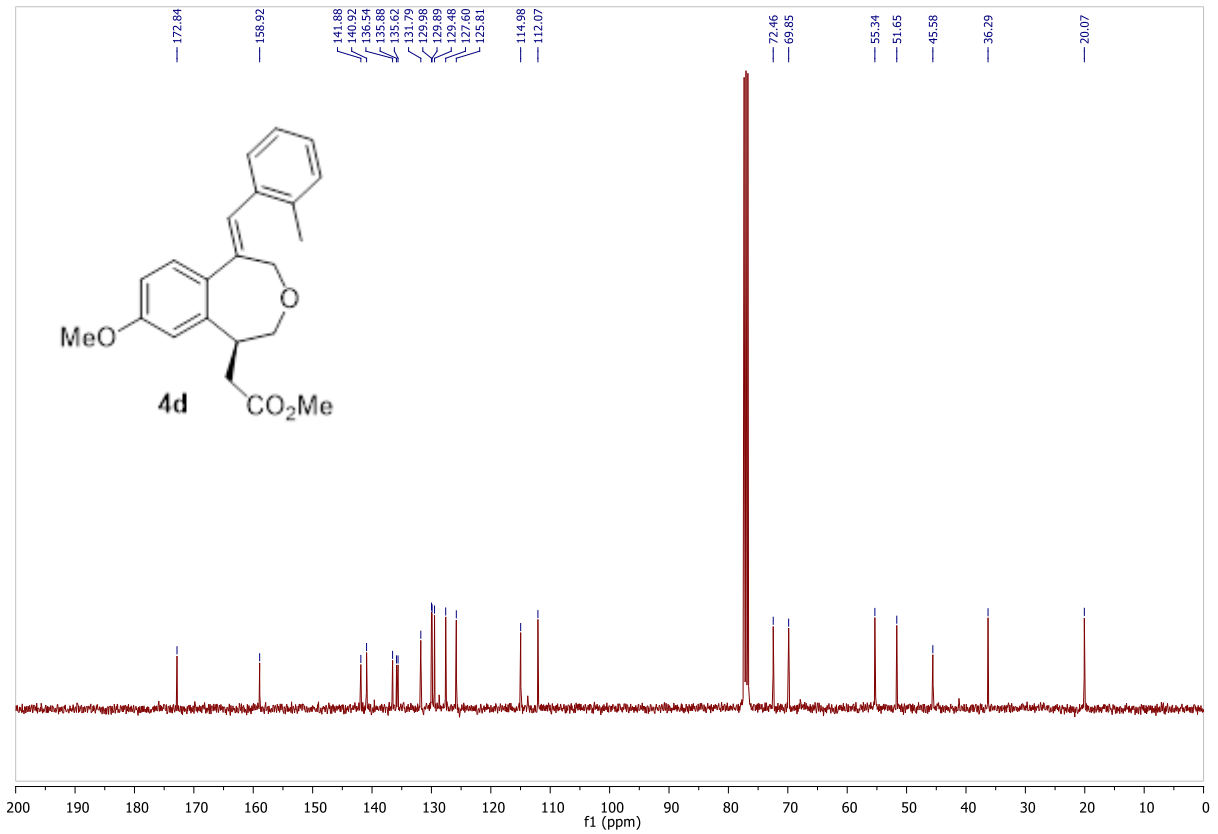

7.46
7.45
7.26
7.25
7.23
7.22
7.09
7.07
7.03
6.81
4.67
4.64
4.15
4.14
4.12
4.11
3.87
3.84
3.82
3.79
3.62
3.37
3.36
2.96
2.95
2.75
2.73
2.37
2.35
O
4m
CO2Me
0.95
4.32
0.96
0.98
0.95
1.00
1.00
0.95
1.06
2.92
0.99
0.98
0.98
2.74
2.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

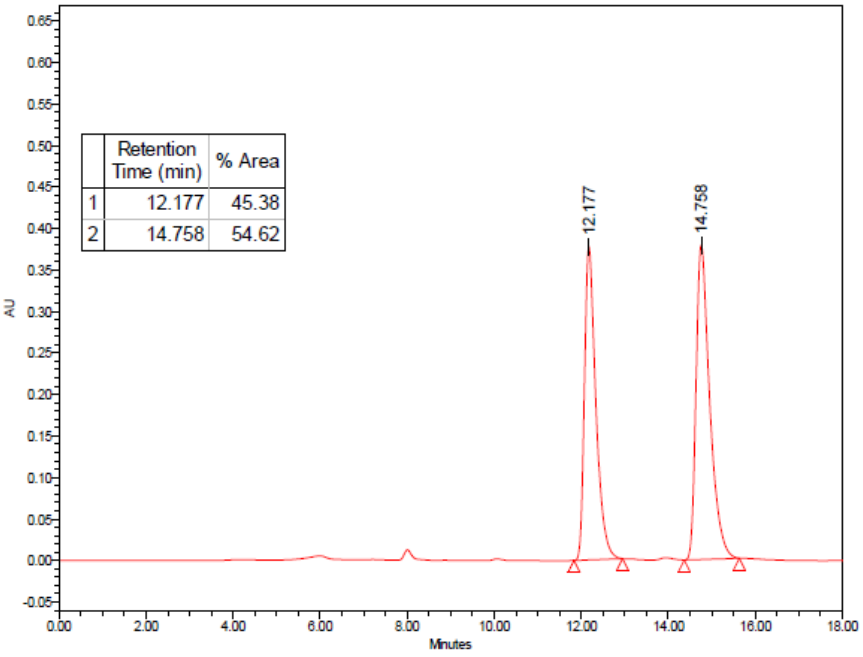

172.93
141.22
140.32
140.20
137.30
136.57
135.82
132.12
130.09
129.90
129.48
128.68
127.87
127.64
125.83
72.54
69.71
51.60
45.47
36.41
21.06
20.07
O
4m
CO2Me
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

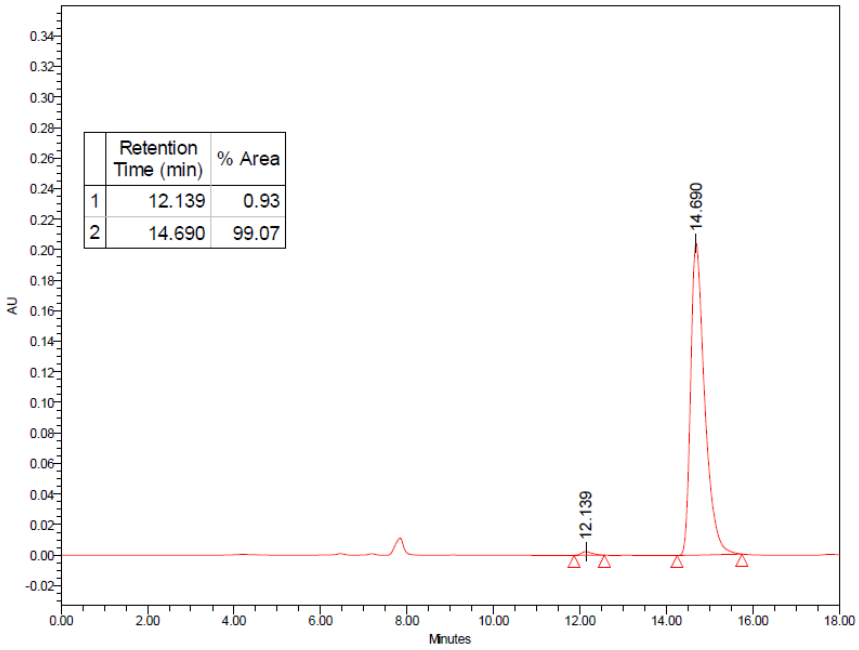

Retention Time (min) | % Area
1 | 9.332 | 49.48
2 | 10.696 | 50.52
9.332
10.696
AU
Minutes

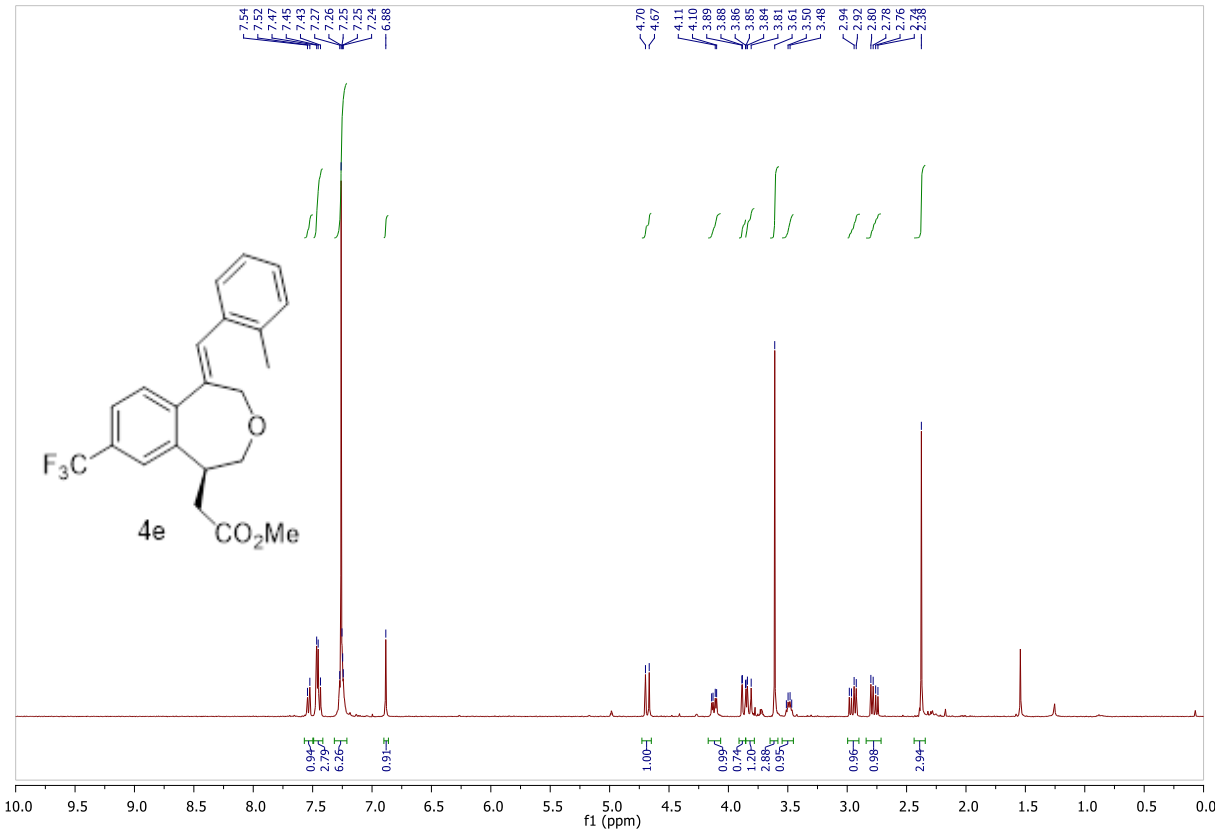

Retention Time (min) | % Area
1 | 9.441 | 2.73
2 | 10.835 | 97.27
10.835
9.441
AU
Minutes

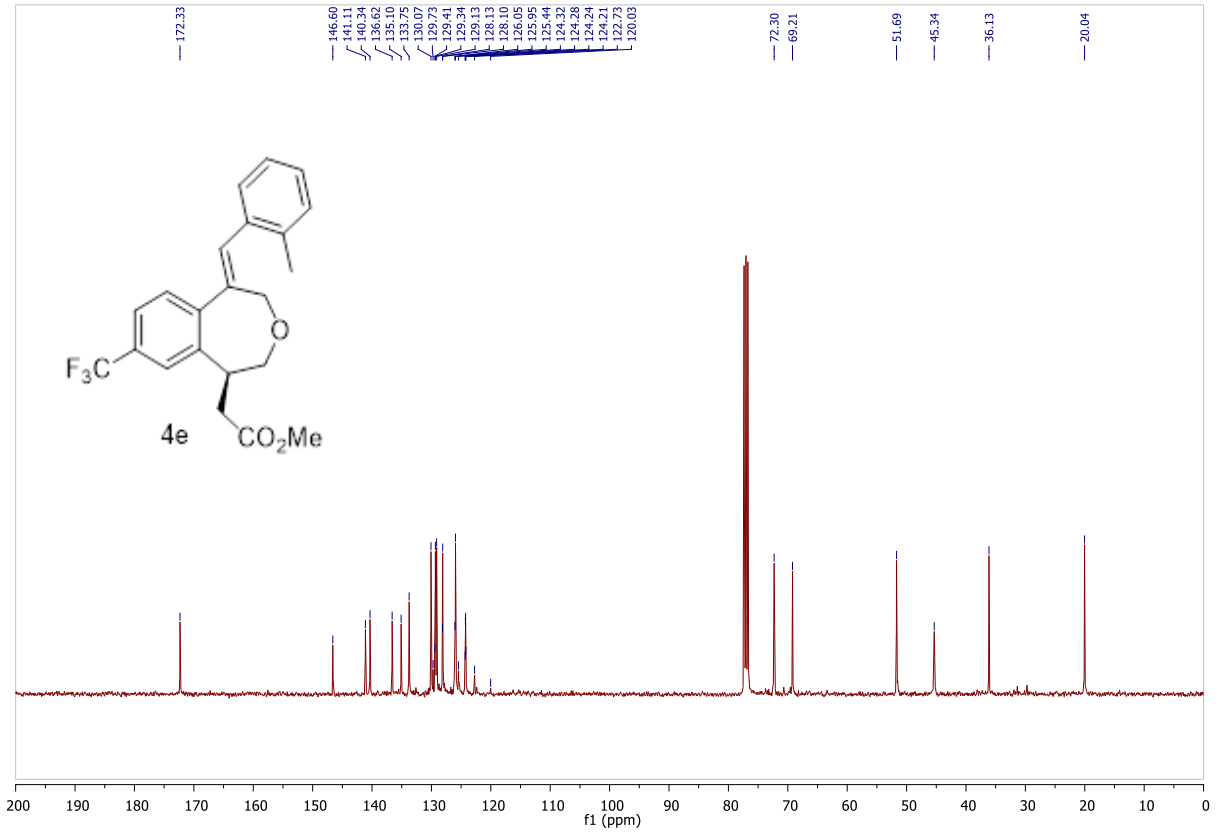

7.43
7.42
7.28
7.26
7.25
7.22
7.21
6.81
6.80
6.79
6.78
6.76
6.76
4.66
4.63
4.10
4.09
3.87
3.84
3.82
3.81
3.78
3.63
3.36
3.35
3.00
2.96
2.94
2.75
2.73
2.71
MeO
O
4d
CO2Me
0.95
6.41
2.96
1.00
0.99
3.71
3.36
0.80
2.85
0.99
0.97
0.98
2.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

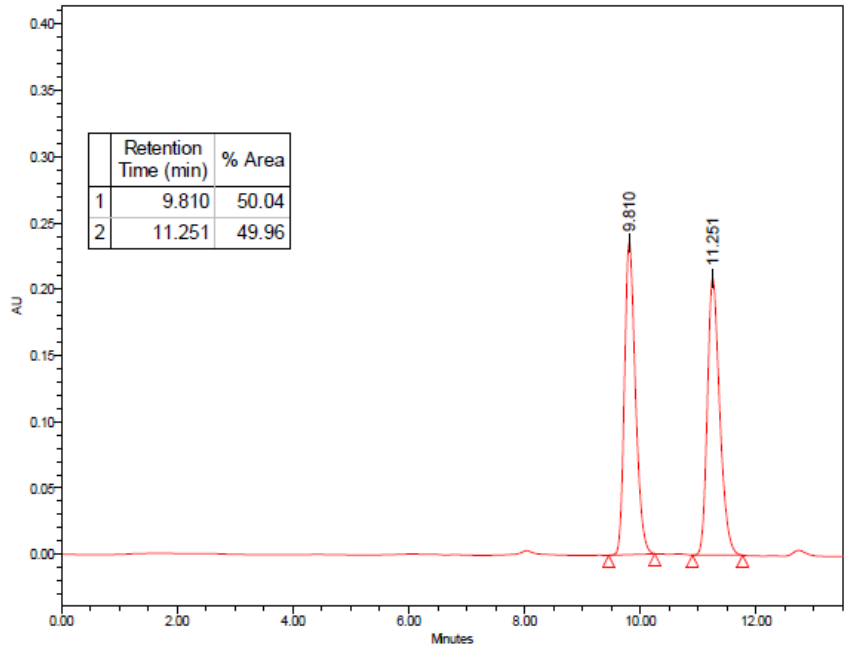

172.84
158.92
141.88
140.92
136.54
135.88
135.62
131.79
129.98
129.89
129.48
127.60
125.81
114.98
112.07
72.46
69.85
55.34
51.65
45.58
36.29
20.07
MeO
O
4d
CO2Me
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

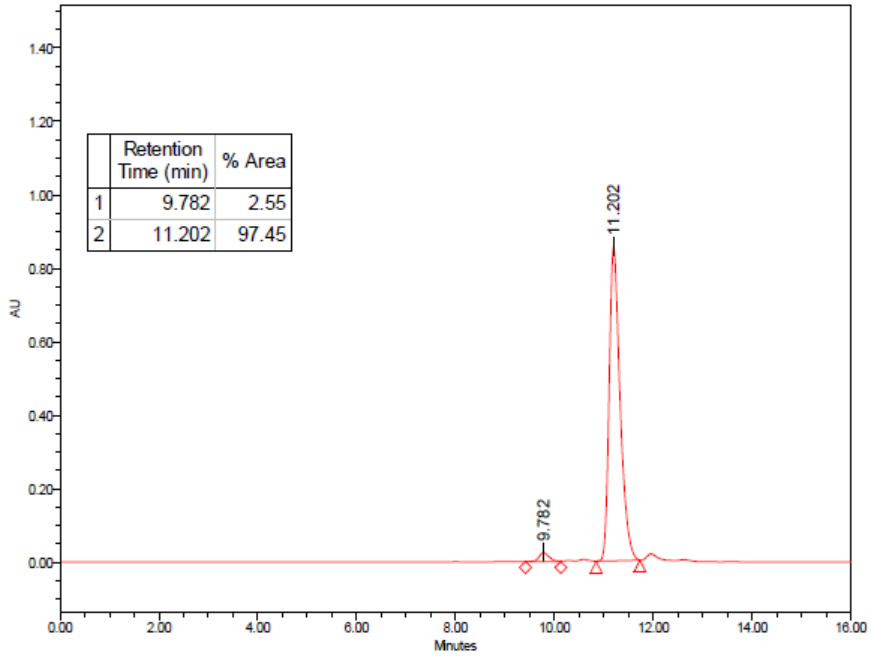

Retention Time (min) | % Area
1 | 12.177 | 45.38
2 | 14.758 | 54.62
12.177
14.758
AU
Minutes

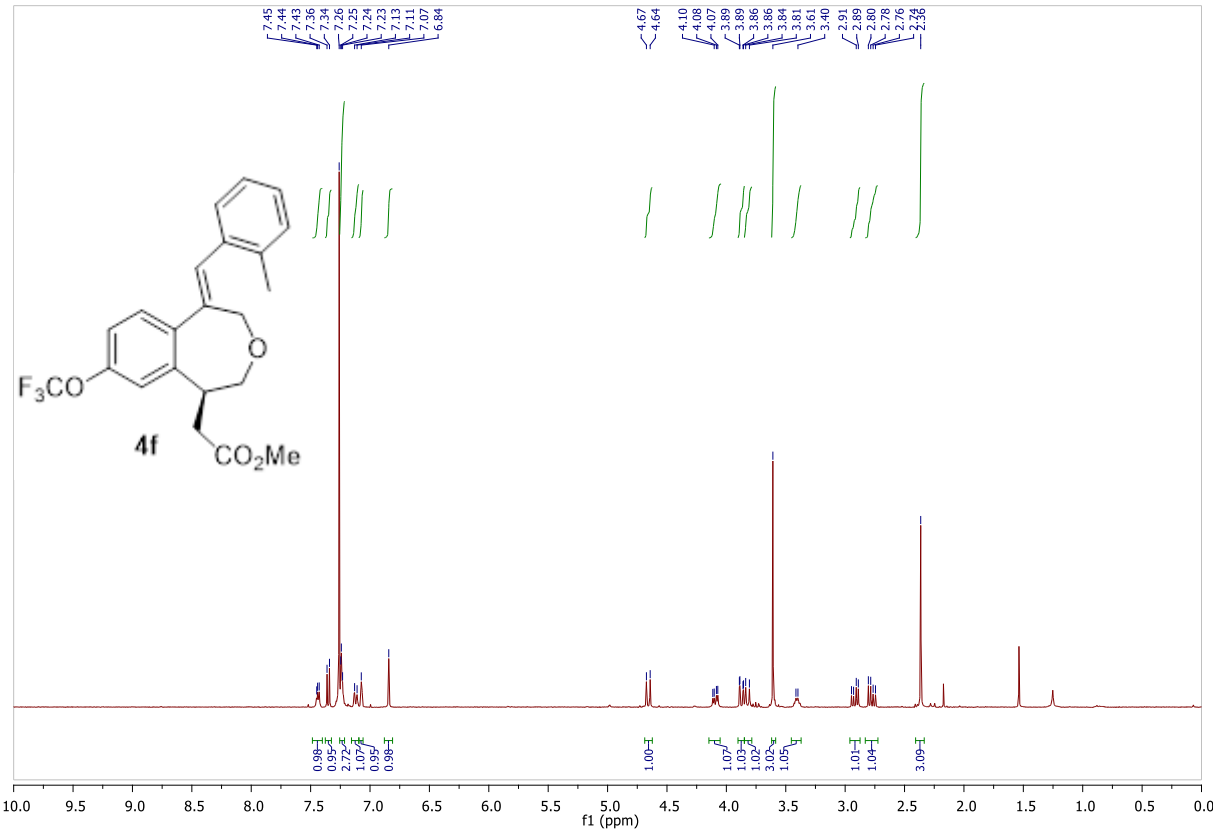

Retention Time (min) | % Area
1 | 12.139 | 0.93
2 | 14.690 | 99.07
12.139
14.690
AU
Minutes

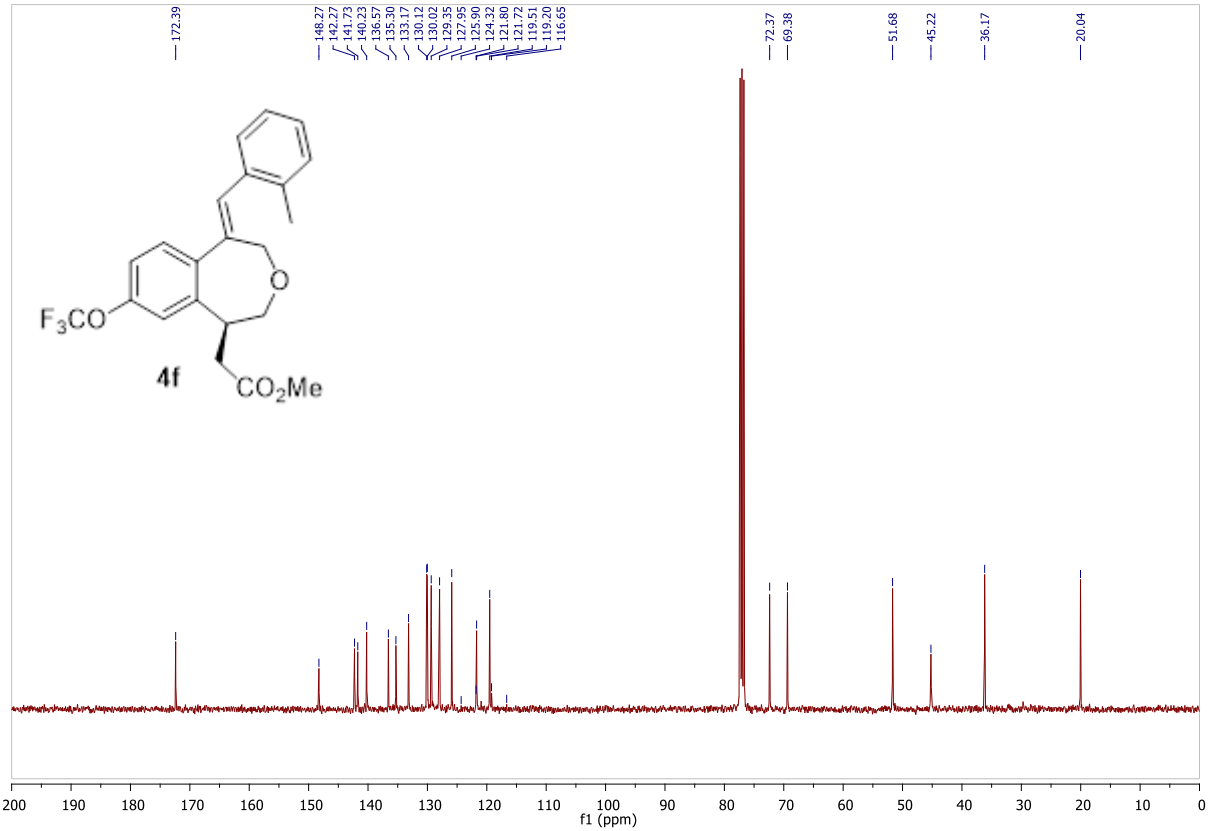

7.54
7.52
7.47
7.45
7.43
7.27
7.26
7.25
7.25
7.24
6.88
4.70
4.67
4.11
4.10
3.89
3.88
3.86
3.85
3.84
3.81
3.61
3.50
3.48
2.94
2.92
2.80
2.78
2.76
2.74
2.38
F3C
O
4e
CO2Me
0.94
2.79
6.26
0.91
1.00
0.99
0.74
1.20
2.86
0.95
0.96
0.98
2.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

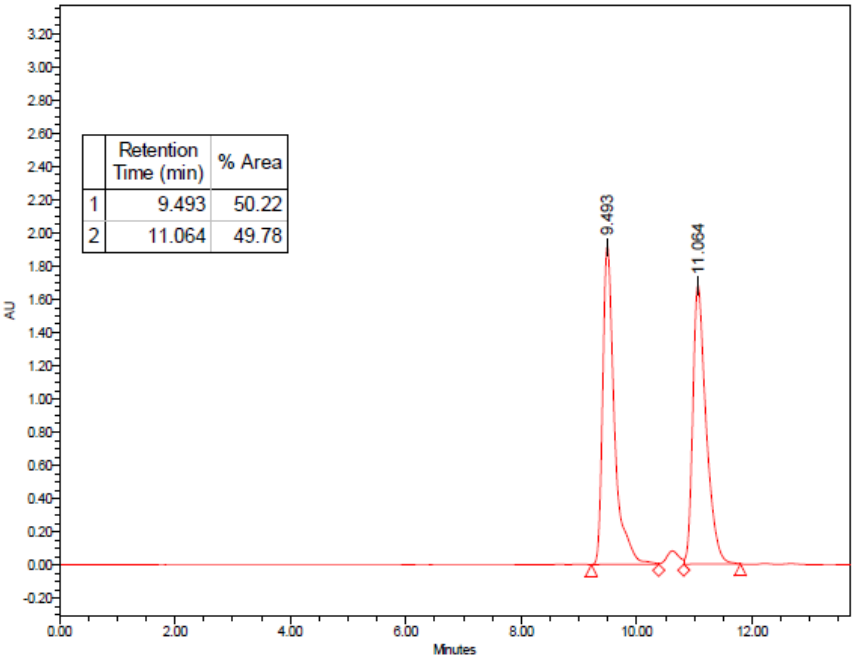

172.33
146.60
141.11
140.34
136.62
135.10
133.75
130.07
129.73
129.41
129.34
129.13
128.13
128.10
126.05
125.95
125.44
124.32
124.28
124.24
124.21
122.73
120.03
72.30
69.21
51.69
45.34
36.13
20.04
F3C
O
4e
CO2Me
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

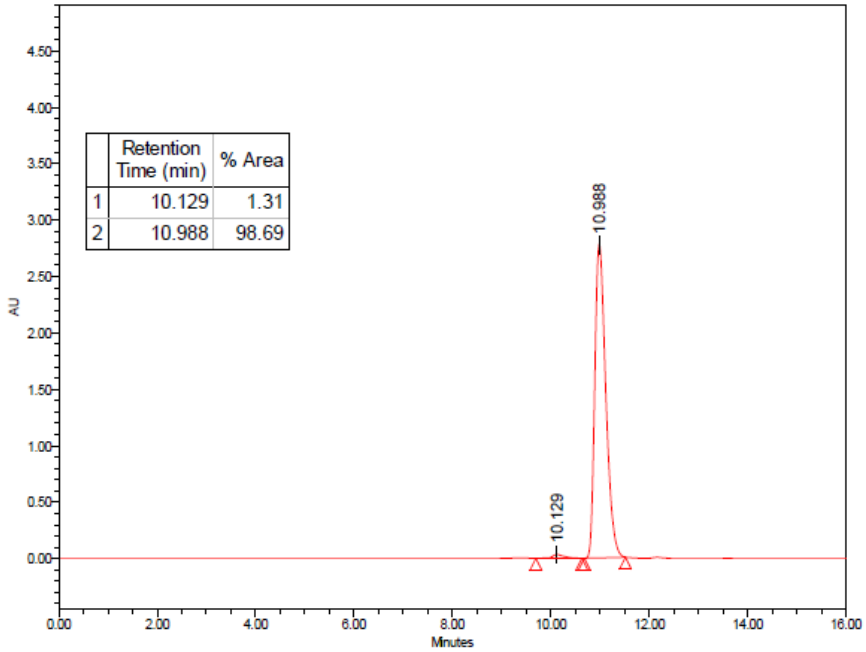

Retention Time (min) | % Area
1 | 9.810 | 50.04
2 | 11.251 | 49.96
9.810
11.251
AU
Minutes

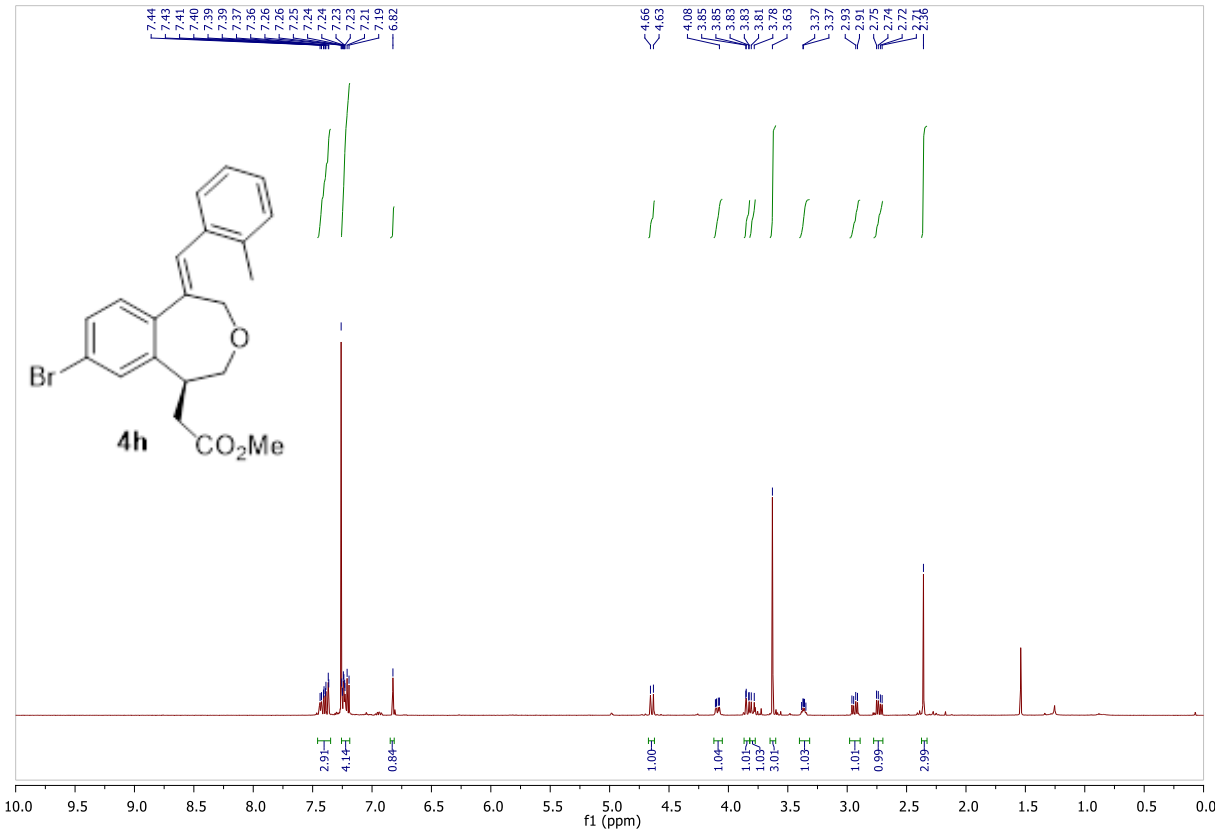

Retention Time (min) | % Area
1 | 9.782 | 2.55
2 | 11.202 | 97.45
11.202
9.782
AU
Minutes

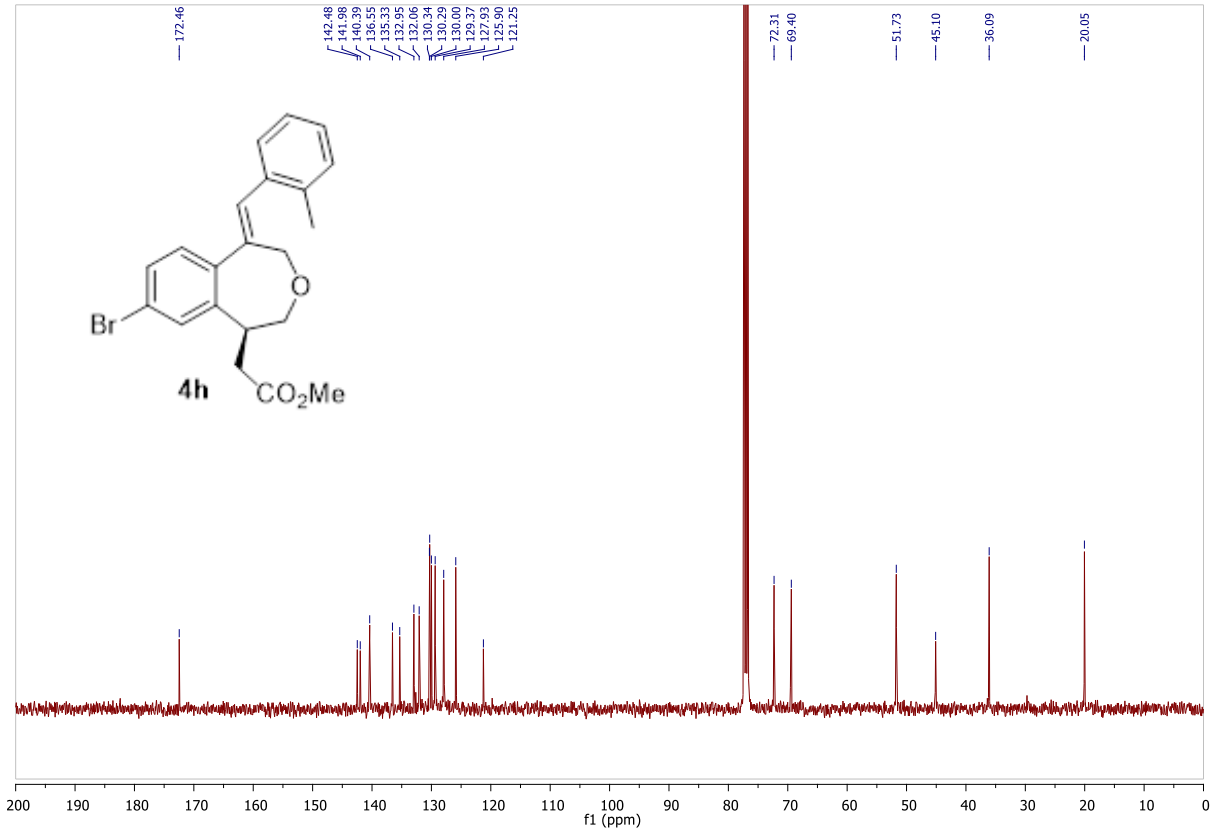

7.45
7.44
7.43
7.36
7.34
7.26
7.25
7.24
7.23
7.13
7.11
7.07
6.84
4.67
4.64
4.10
4.08
4.07
3.89
3.89
3.86
3.86
3.84
3.81
3.61
3.40
2.91
2.89
2.80
2.78
2.76
2.74
2.36
O
F3CO
4f
CO2Me
0.98
0.95
2.72
1.07
0.99
0.98
1.00
1.07
1.03
1.02
3.02
1.05
1.01
1.04
3.09
f1 (ppm)

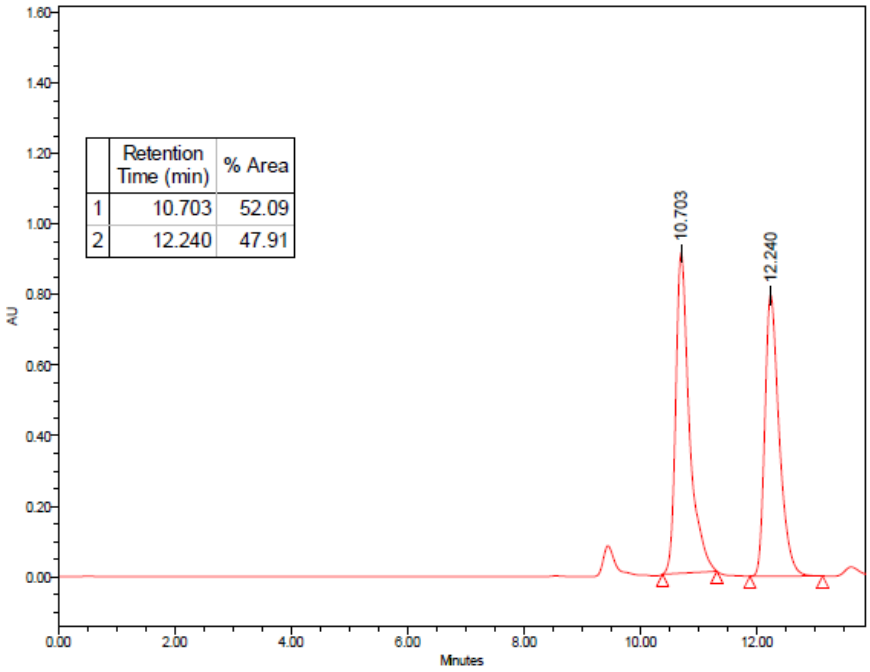

172.39
148.27
142.27
141.73
140.23
136.57
135.30
133.17
130.12
130.02
129.35
127.95
125.90
124.32
121.80
121.72
119.51
119.20
116.65
72.37
69.38
51.68
45.22
36.17
20.04
O
F3CO
4f
CO2Me
f1 (ppm)

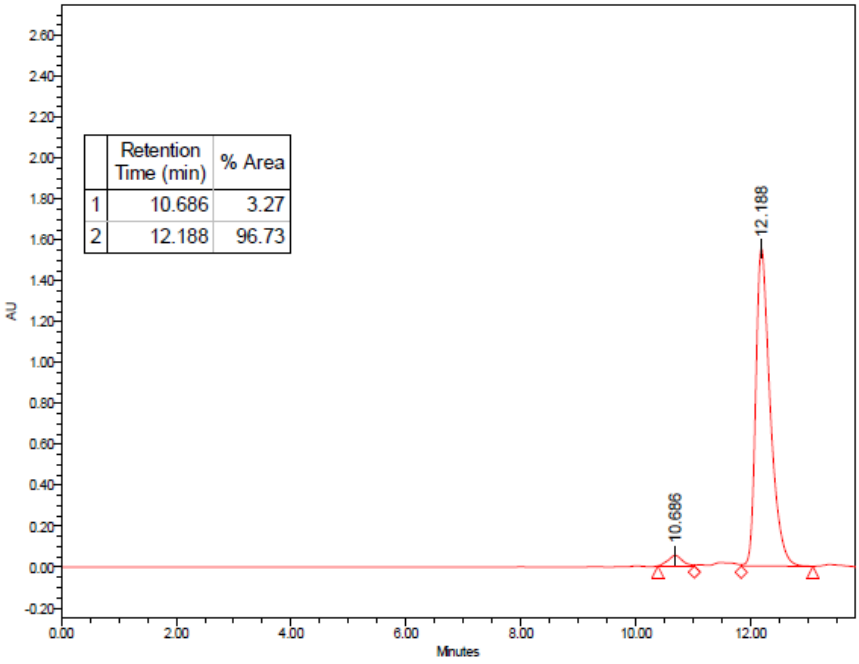

Retention Time (min) | % Area
1 | 9.493 | 50.22
2 | 11.064 | 49.78
9.493
11.064
AU
Minutes

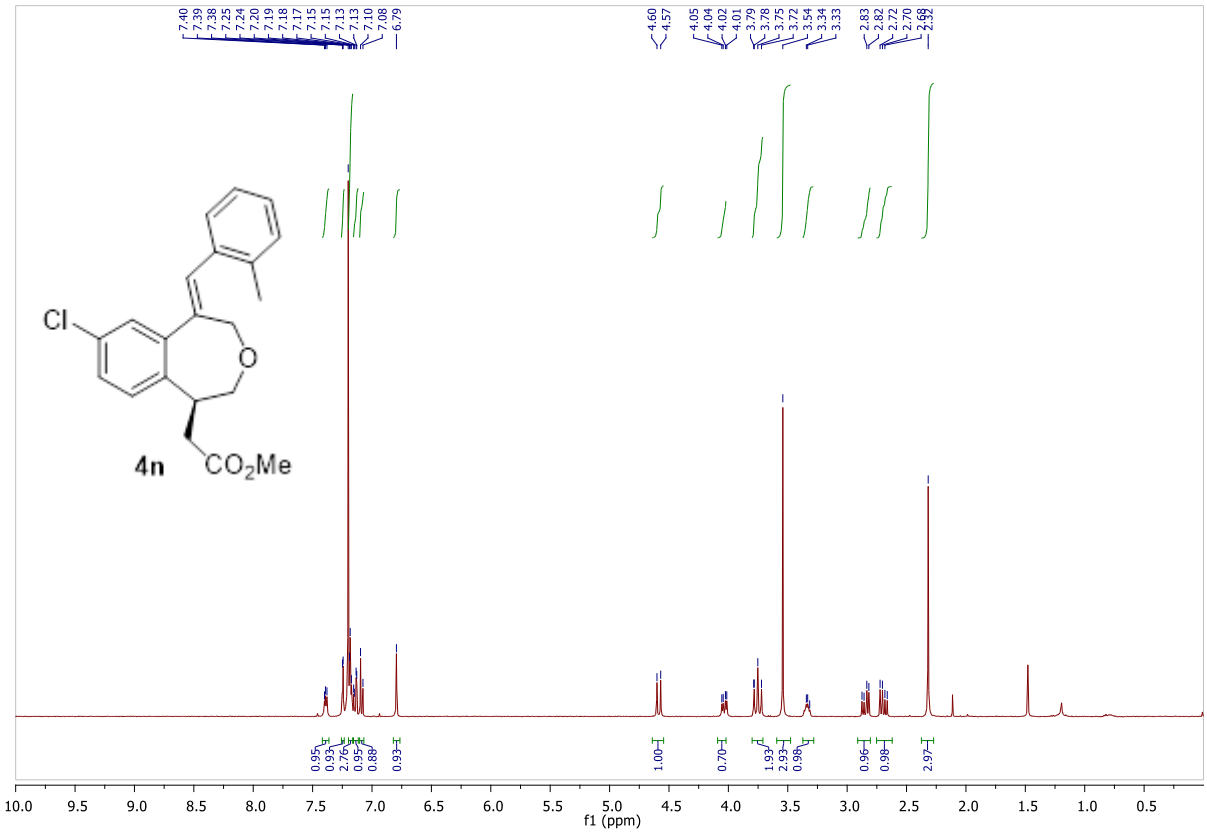

Retention Time (min) | % Area
1 | 10.129 | 1.31
2 | 10.988 | 98.69
10.988
10.129
AU
Minutes

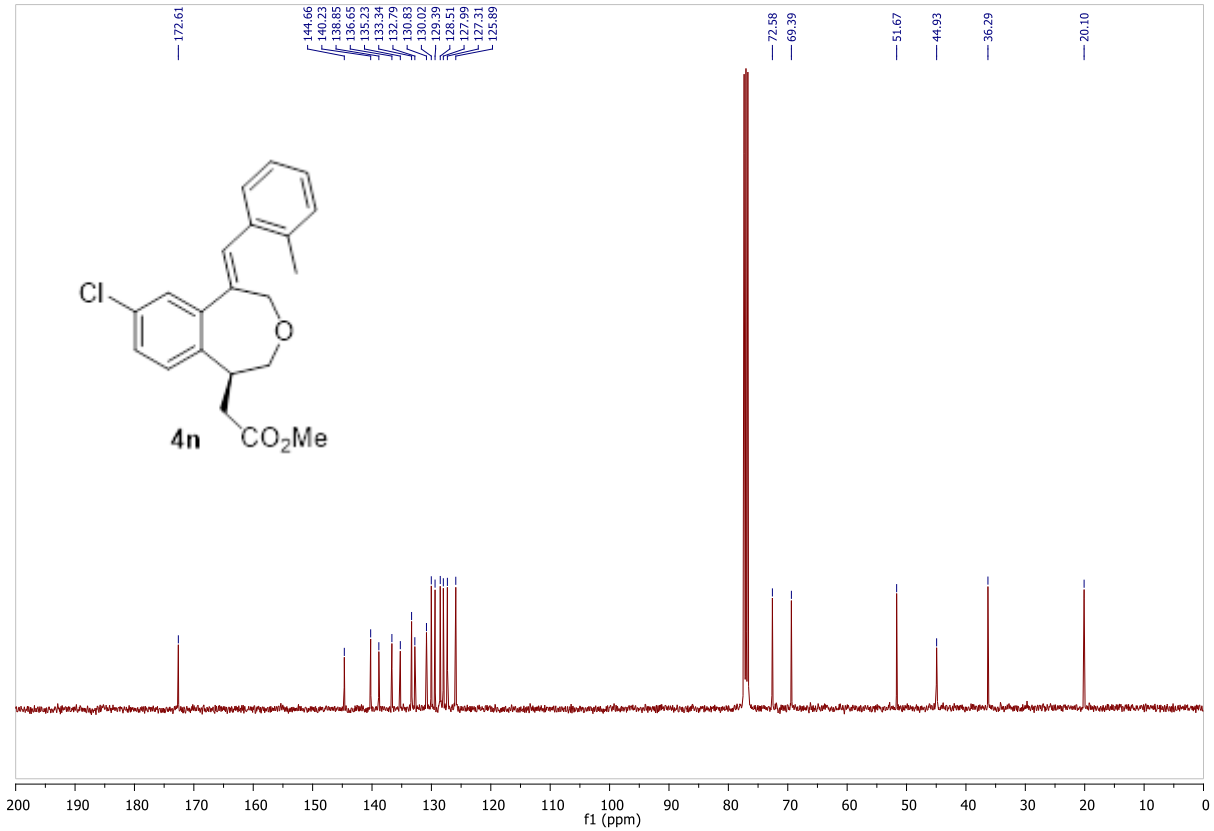

7.44
7.43
7.41
7.40
7.39
7.39
7.37
7.36
7.26
7.26
7.25
7.24
7.24
7.23
7.23
7.21
7.19
6.82
4.66
4.63
4.08
3.85
3.85
3.83
3.83
3.81
3.78
3.63
3.37
3.37
2.93
2.91
2.75
2.74
2.72
2.71
2.36
Br
O
4h
CO2Me
2.91
4.14
0.84
1.00
1.04
1.01
1.03
3.01
1.03
1.01
0.99
2.99
f1 (ppm)

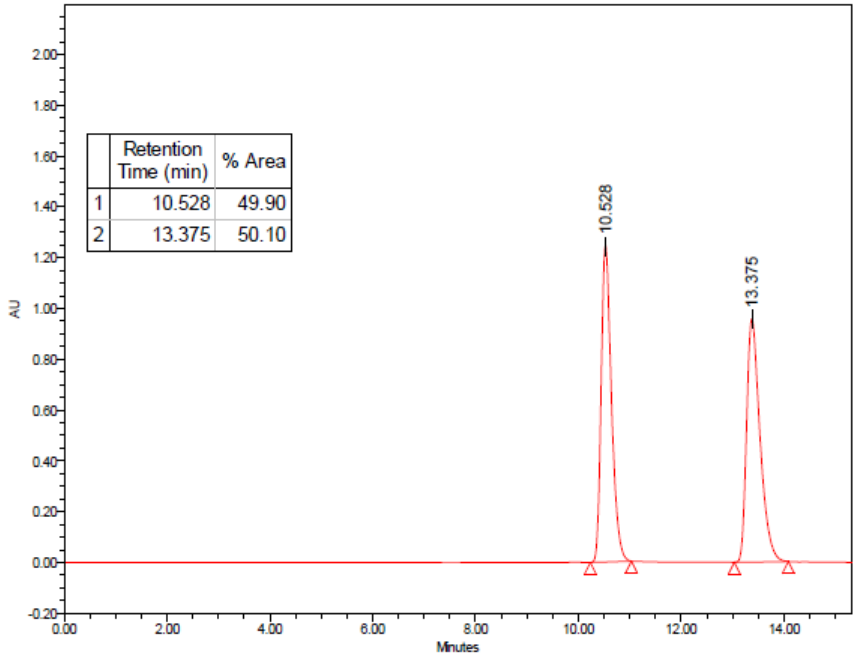

172.46
142.48
141.98
140.39
136.55
135.33
132.95
132.06
130.34
130.29
130.00
129.37
127.93
125.90
121.25
72.31
69.40
51.73
45.10
36.09
20.05
Br
O
4h
CO2Me
f1 (ppm)

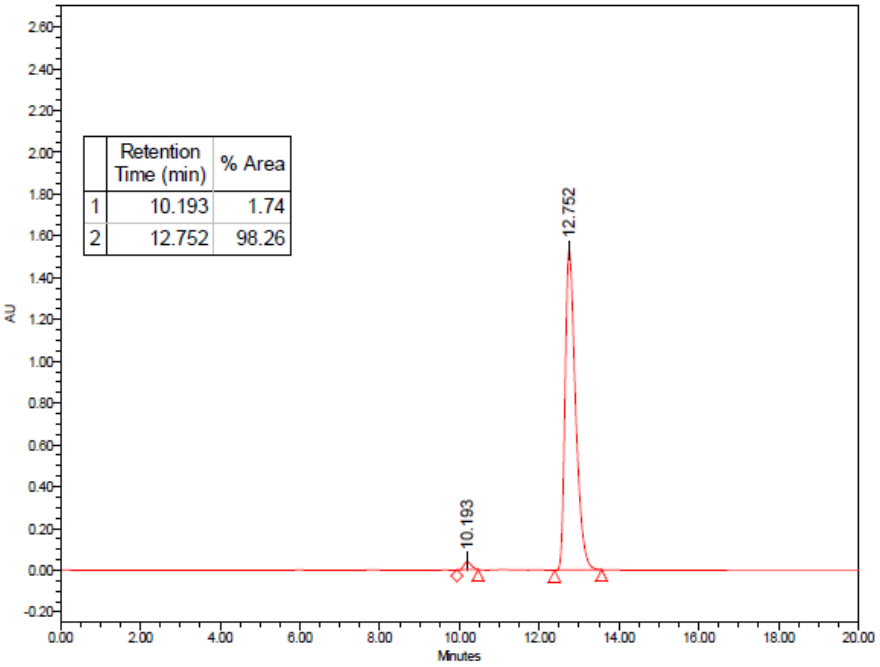

Retention Time (min) | % Area
1 | 10.703 | 52.09
2 | 12.240 | 47.91
10.703
12.240
AU
Minutes

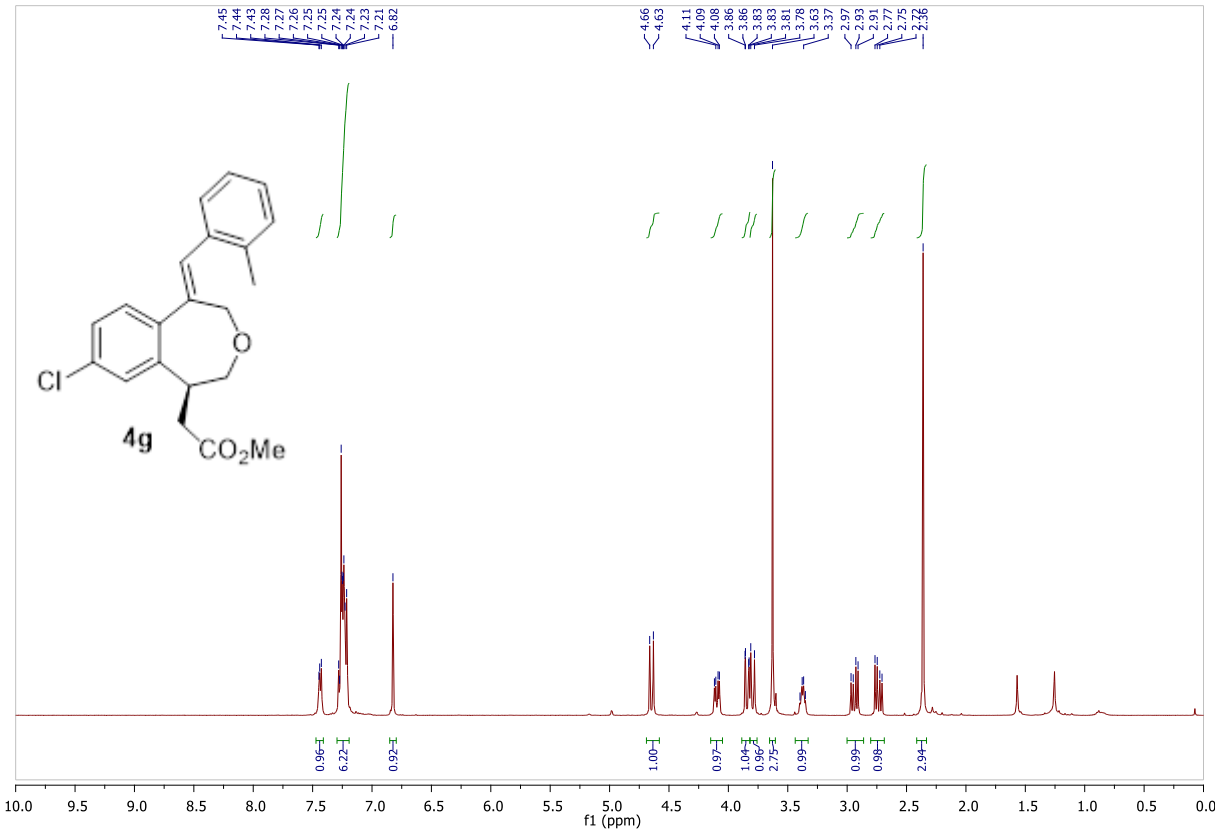

Retention Time (min) | % Area
1 | 10.686 | 3.27
2 | 12.188 | 96.73
12.188
10.686
AU
Minutes

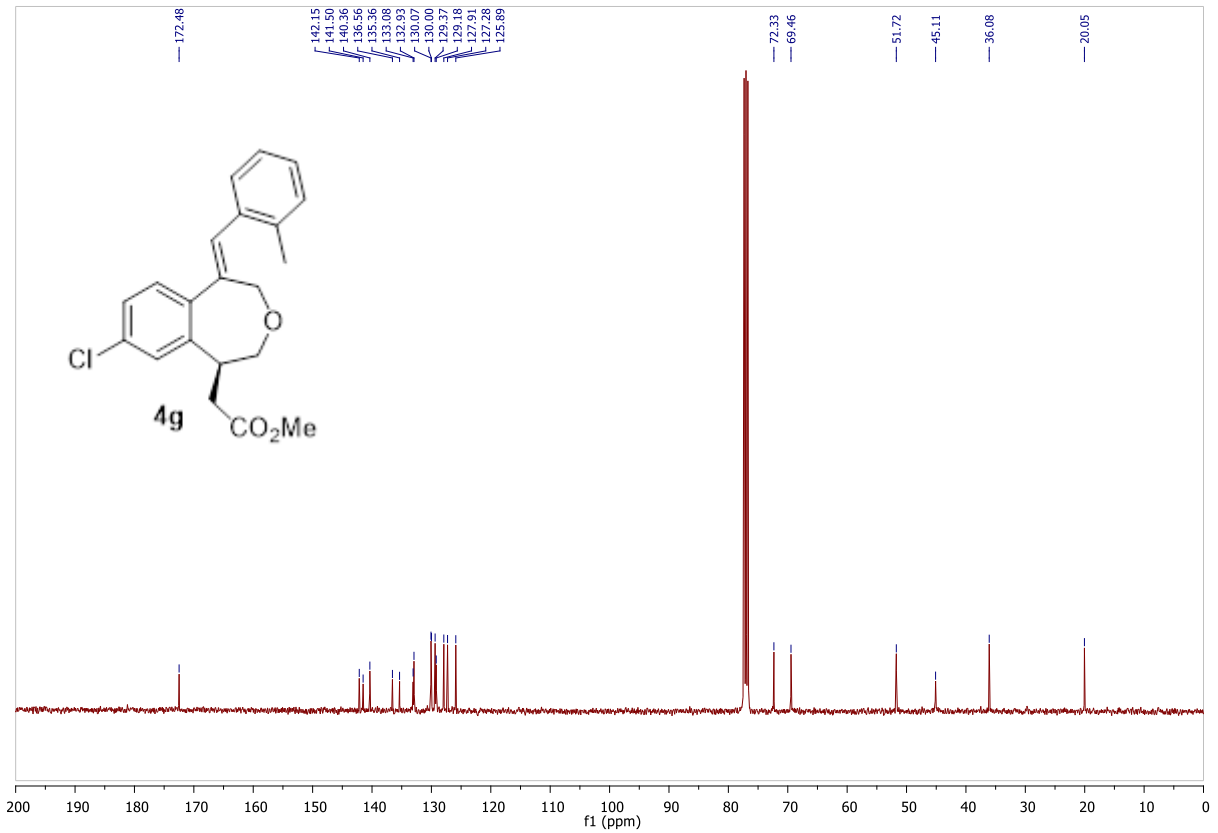

7.40
7.39
7.38
7.25
7.24
7.20
7.19
7.18
7.17
7.15
7.15
7.13
7.13
7.10
7.08
6.79
4.60
4.57
4.05
4.04
4.02
4.01
3.79
3.78
3.75
3.72
3.54
3.34
3.33
2.83
2.82
2.72
2.70
2.68
2.68
Cl
O
4n
CO2Me
0.95
0.93
2.76
0.95
0.88
0.93
1.00
0.70
1.93
2.93
0.98
0.96
0.98
2.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

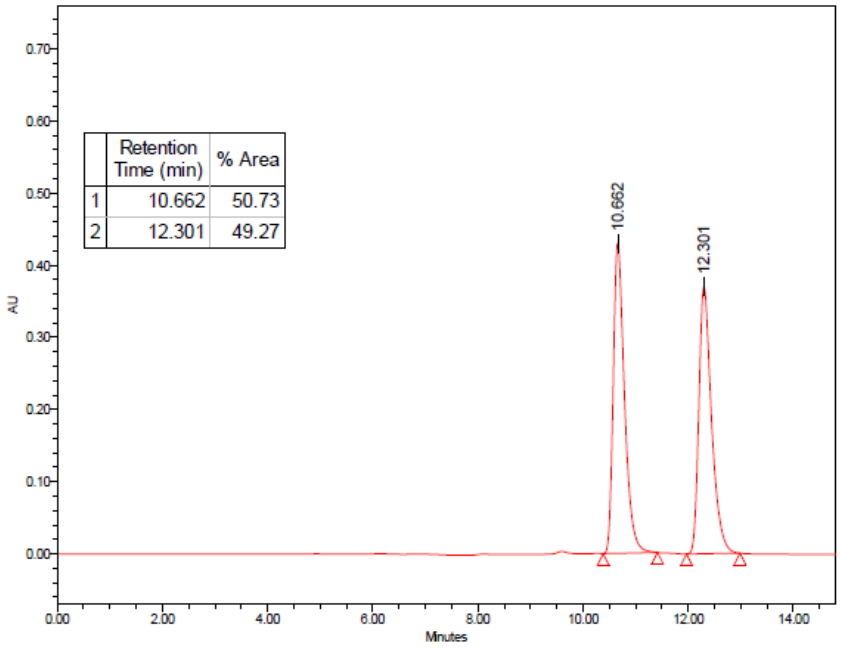

172.61
144.66
140.23
138.85
136.65
135.23
133.34
132.79
130.83
130.02
129.39
128.51
127.99
127.31
125.89
72.58
69.39
51.67
44.93
36.29
20.10
Cl
O
4n
CO2Me
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

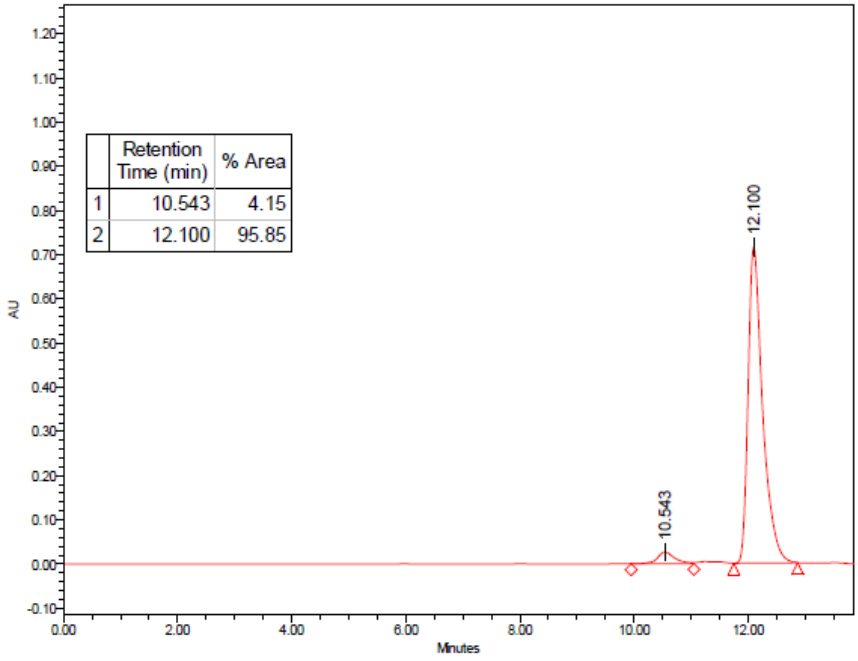

Retention Time (min) | % Area
1 | 10.528 | 49.90
2 | 13.375 | 50.10
10.528
13.375
AU
Minutes

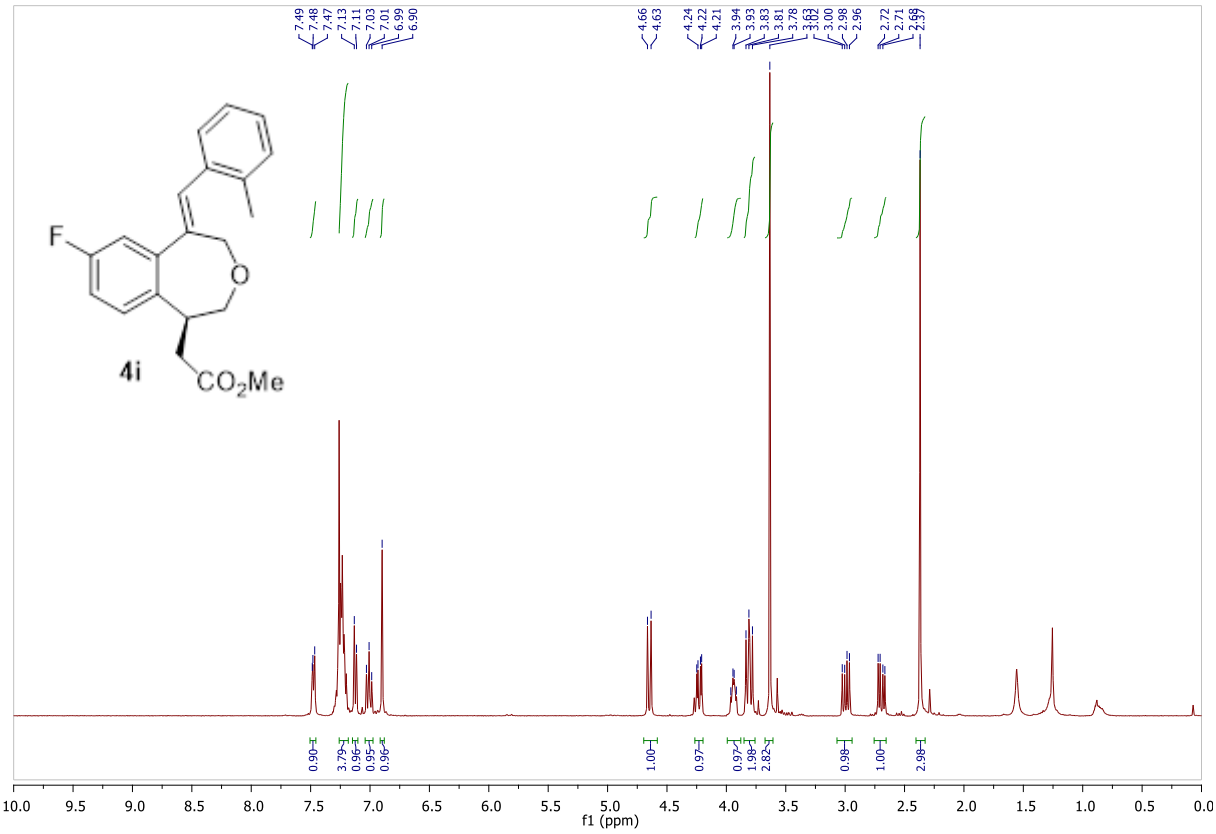

Retention Time (min) | % Area
1 | 10.193 | 1.74
2 | 12.752 | 98.26
12.752
10.193
AU
Minutes

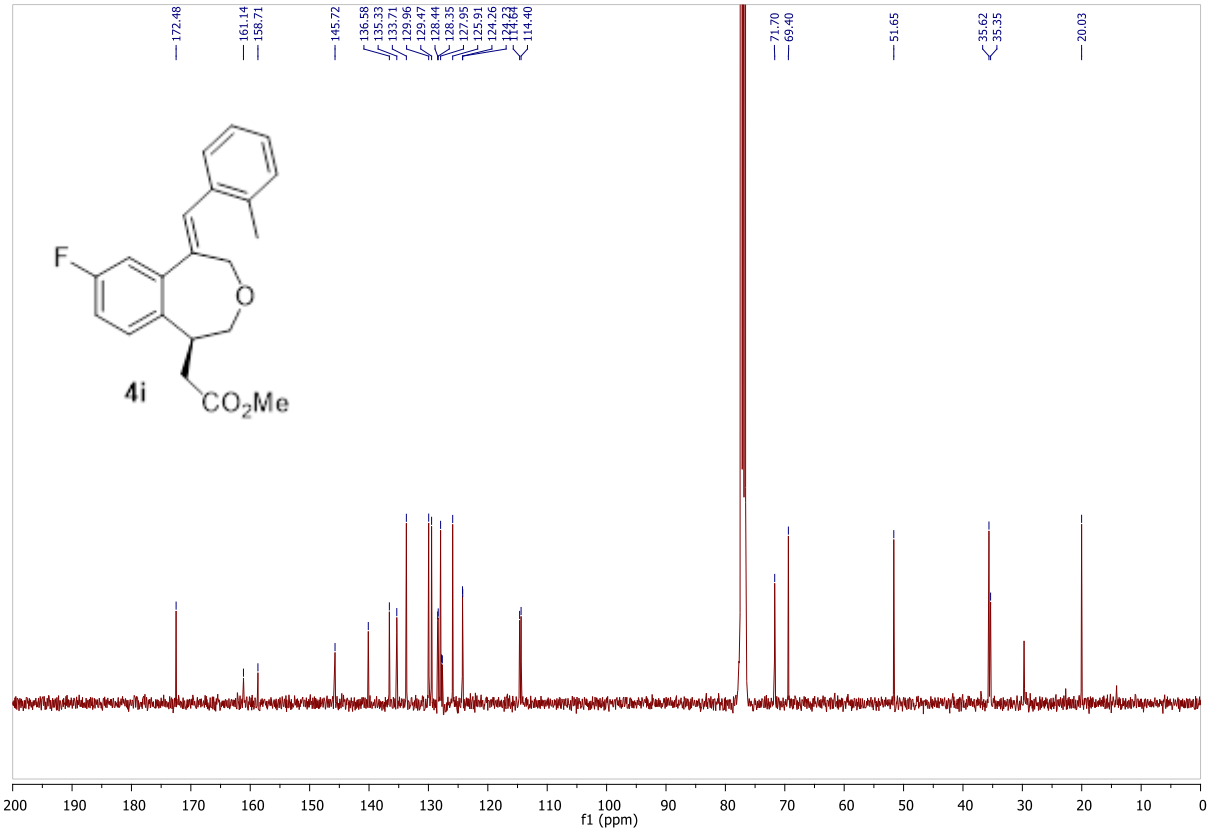

7.45
7.44
7.43
7.28
7.27
7.26
7.25
7.25
7.24
7.24
7.23
7.21
6.82
4.66
4.63
4.11
4.09
4.08
3.86
3.86
3.83
3.83
3.81
3.78
3.63
3.37
2.97
2.93
2.91
2.77
2.75
2.36
0.96
6.22
0.92
1.00
0.97
1.04
0.96
2.75
0.99
0.99
0.98
2.94
Cl
O
4g
CO2Me
f1 (ppm)


172.48
142.15
141.50
140.36
136.56
135.36
133.08
132.93
130.07
130.00
129.37
129.18
127.91
127.28
125.89
72.33
69.46
51.72
45.11
36.08
20.05
Cl
O
4g
CO2Me
f1 (ppm)


Retention Time (min) | % Area
1 | 10.662 | 50.73
2 | 12.301 | 49.27
10.662
12.301
AU
Minutes


Retention Time (min) | % Area
1 | 10.543 | 4.15
2 | 12.100 | 95.85
10.543
12.100
AU
Minutes


7.49
7.48
7.47
7.13
7.11
7.03
7.01
6.99
6.90
4.66
4.63
4.24
4.22
4.21
3.94
3.93
3.83
3.81
3.78
3.00
2.98
2.96
2.72
2.71
2.68
2.37
F
O
4i
CO2Me
0.90
3.79
0.96
0.95
0.96
1.00
0.97
0.97
1.98
2.82
0.98
1.00
2.98
f1 (ppm)


172.48
161.14
158.71
145.72
136.58
135.33
133.71
129.96
129.47
128.44
128.35
127.95
125.91
124.26
114.64
114.40
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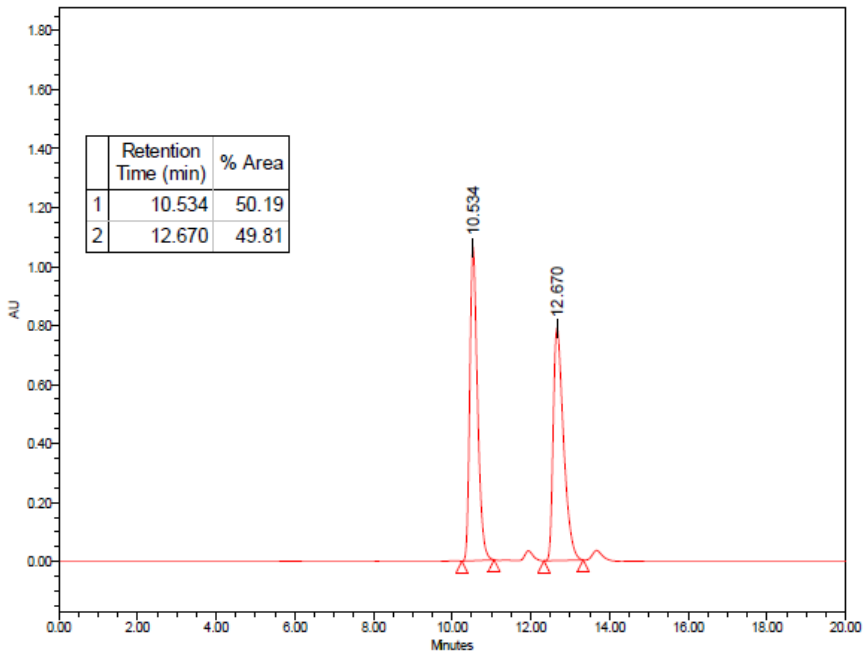
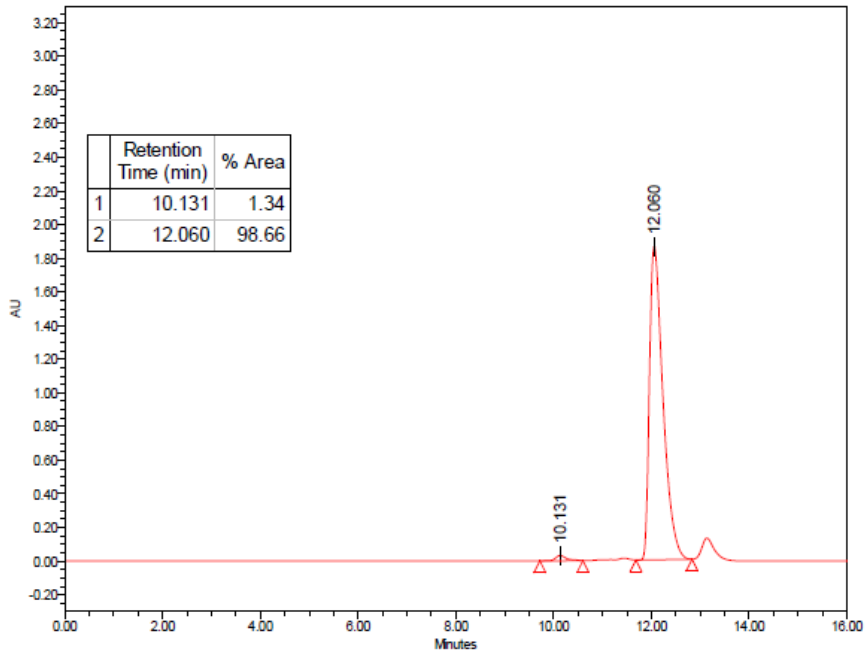
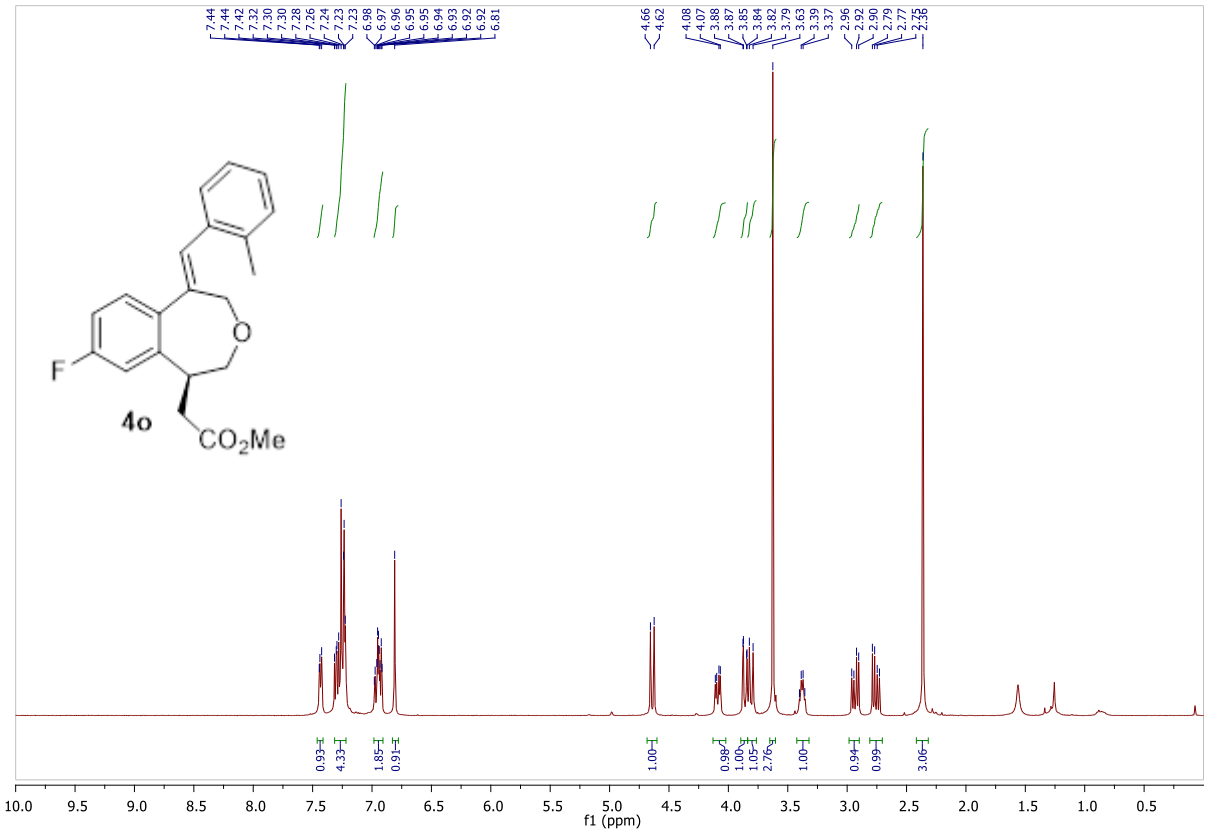
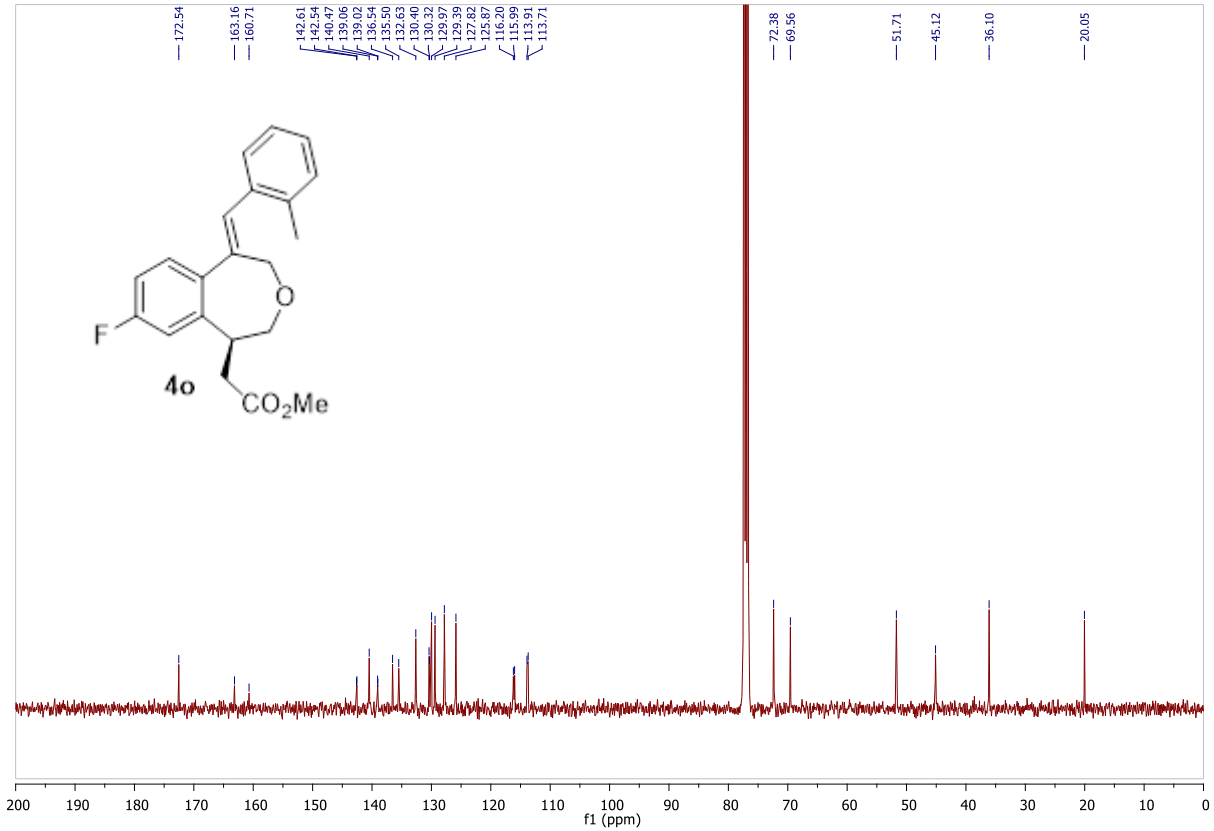
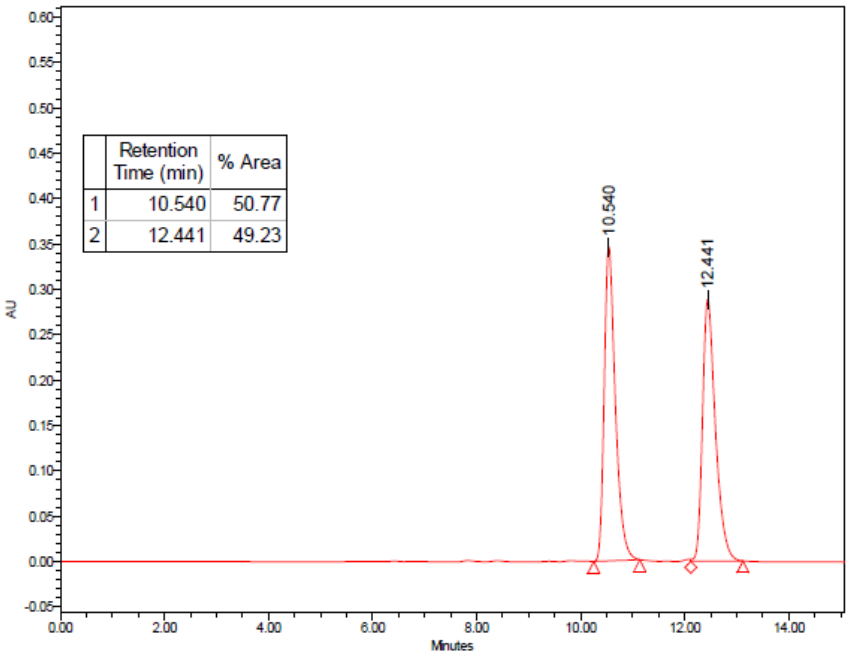
69.40
51.65
35.62
35.35
20.03
F
O
4i
CO2Me
f1 (ppm)

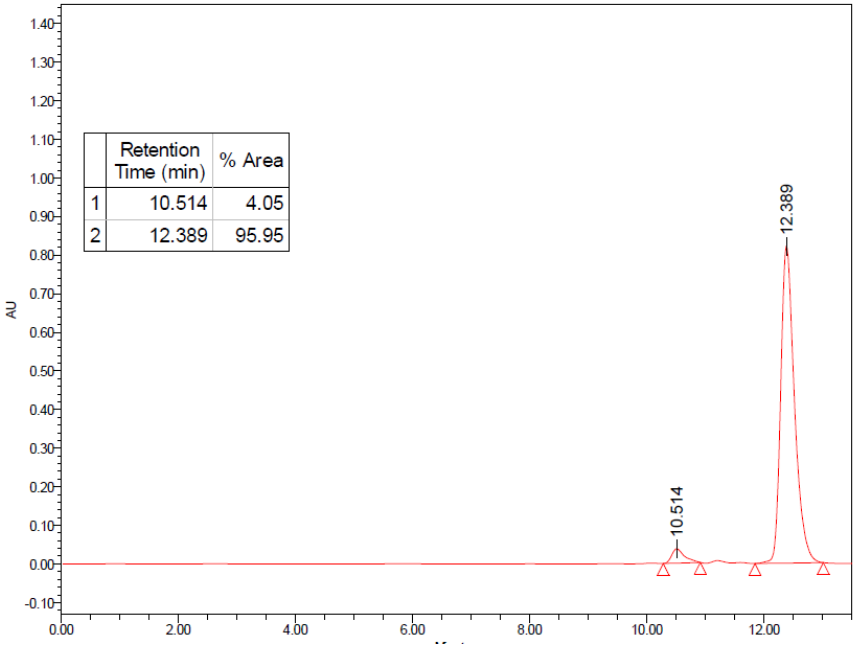

Retention Time (min) | % Area
1 | 10.534 | 50.19
2 | 12.670 | 49.81
10.534
12.670
AU
Minutes

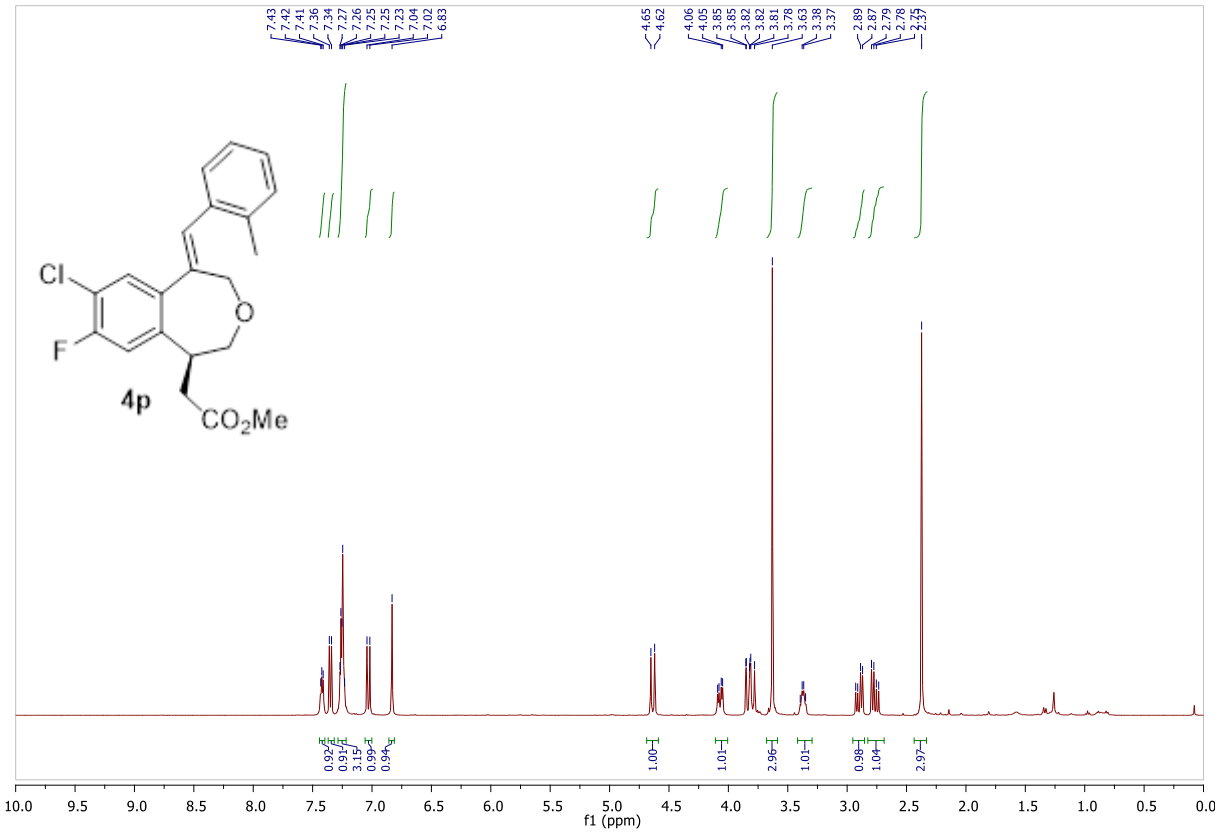

Retention Time (min) | % Area
1 | 10.131 | 1.34
2 | 12.060 | 98.66
12.060
10.131
AU
Minutes

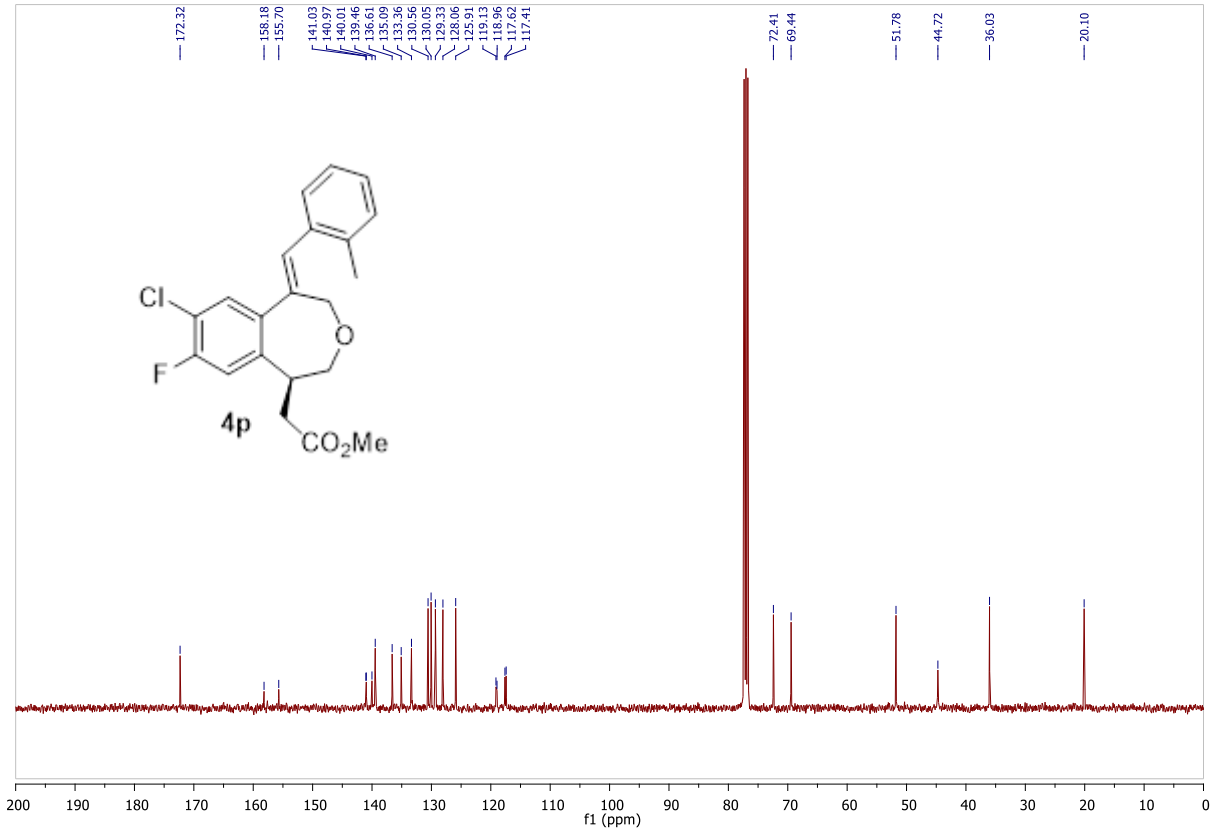

7.44
7.44
7.42
7.32
7.30
7.30
7.28
7.26
7.24
7.23
7.23
6.98
6.97
6.96
6.95
6.95
6.94
6.93
6.92
6.92
6.81
4.66
4.62
4.08
4.07
3.88
3.87
3.85
3.84
3.82
3.79
3.63
3.39
3.37
2.96
2.92
2.90
2.79
2.77
2.75
2.36
O
F
4o
CO2Me
0.93
4.33
1.85
0.91
1.00
0.98
1.00
1.05
2.76
1.00
0.94
0.99
3.06
10.0
9.5
9.0
8.5
8.0
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
f1 (ppm)

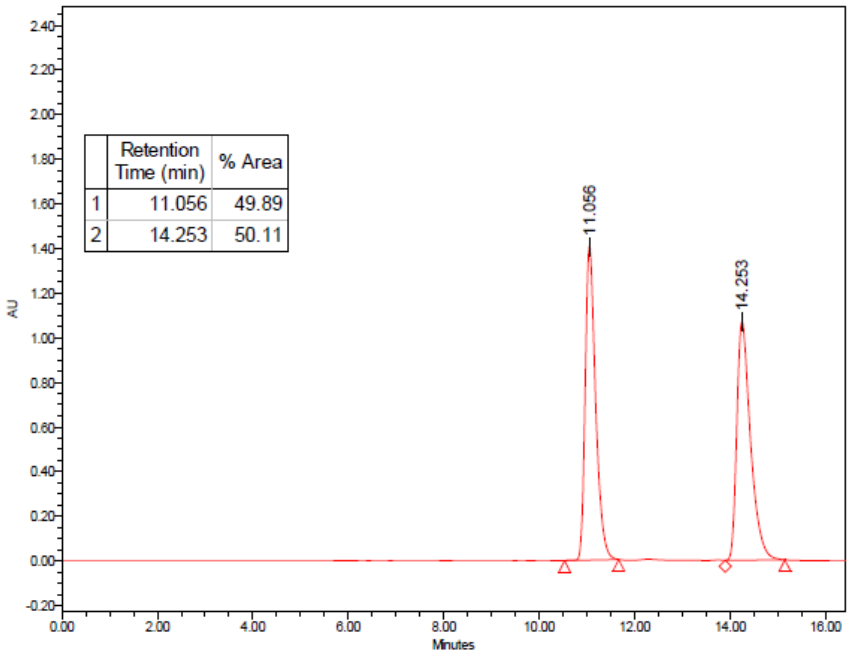

172.54
163.16
160.71
142.61
142.54
140.47
139.06
139.02
136.54
135.50
132.63
130.40
130.32
129.97
129.39
127.82
125.87
116.20
115.99
113.91
113.71
72.38
69.56
51.71
45.12
36.10
20.05
O
F
4o
CO2Me
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

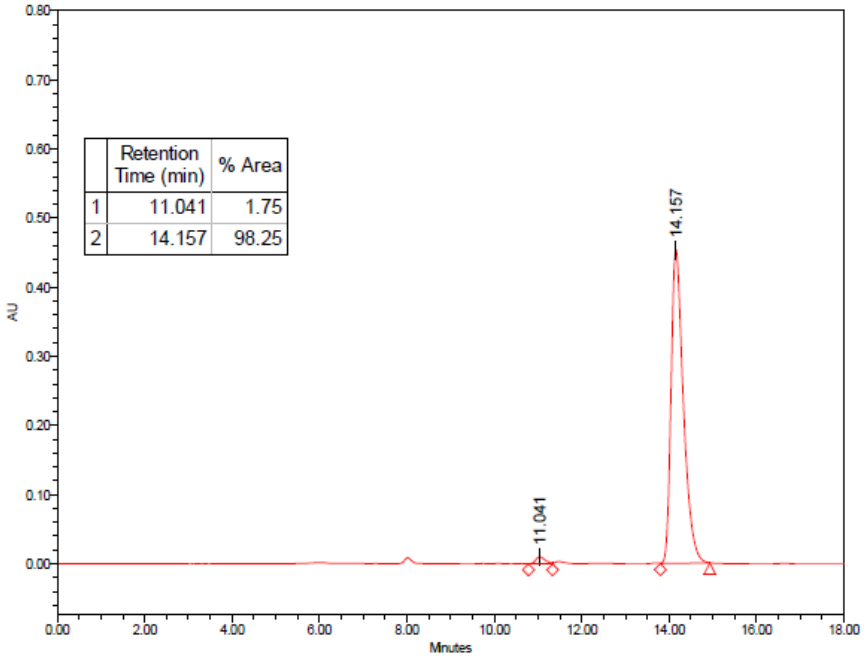

Retention Time (min) | % Area
1 | 10.540 | 50.77
2 | 12.441 | 49.23
10.540
12.441
AU
Minutes

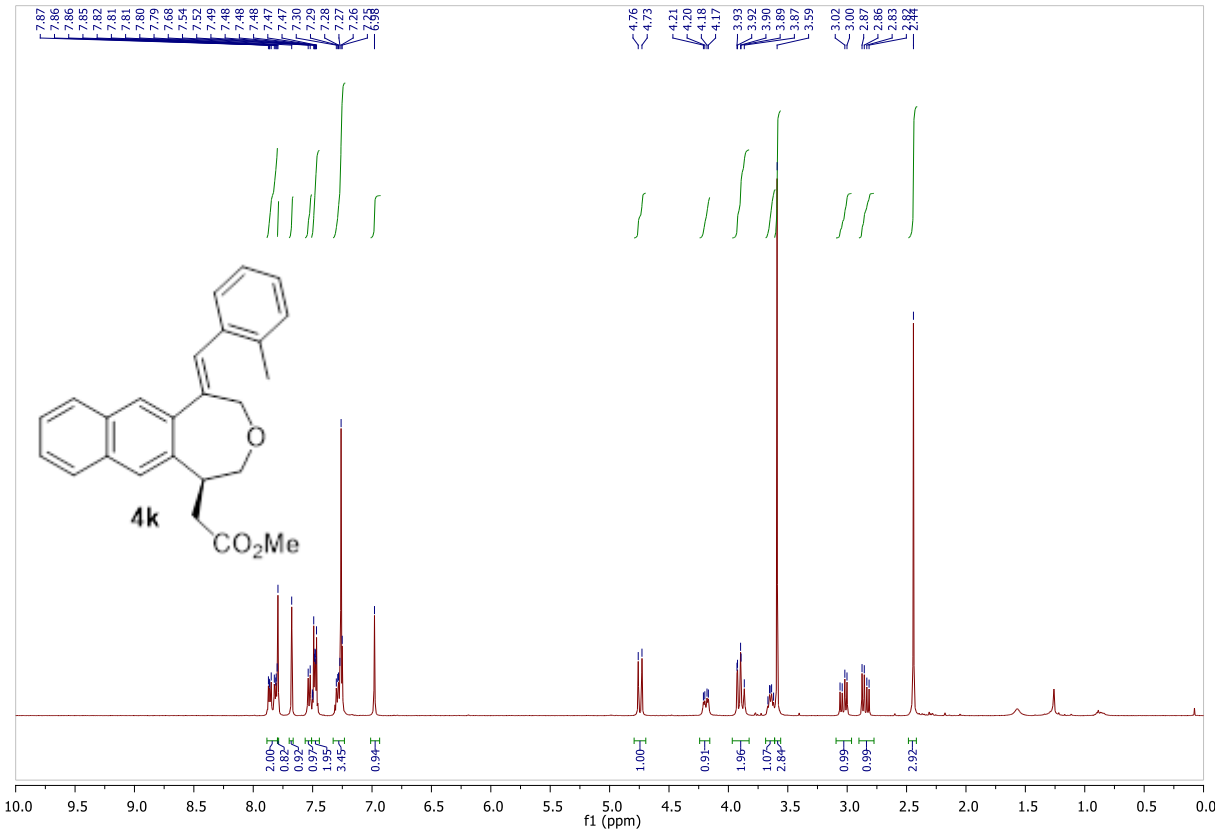

Retention Time (min) | % Area
1 | 10.514 | 4.05
2 | 12.389 | 95.95
12.389
10.514
AU

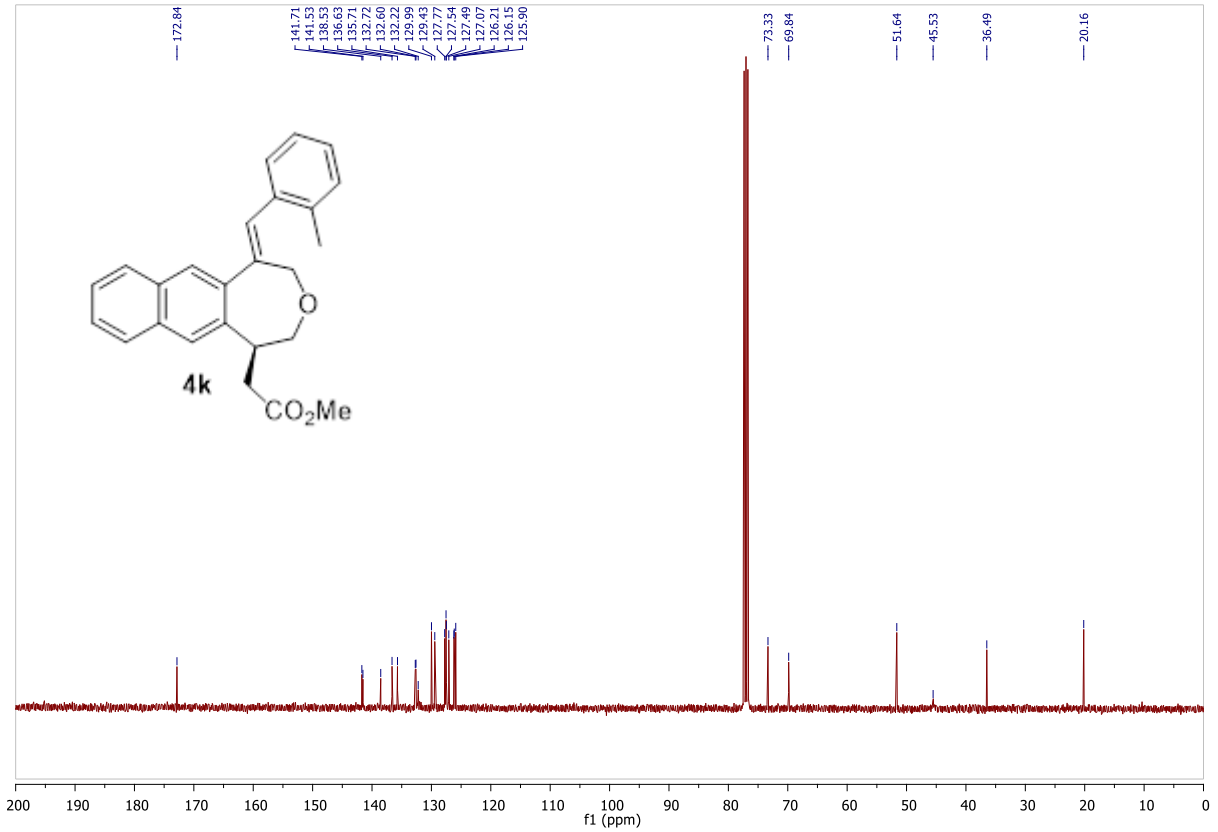

7.43
7.42
7.41
7.36
7.34
7.27
7.26
7.25
7.25
7.23
7.04
7.02
6.83
4.65
4.62
4.06
4.05
3.85
3.85
3.82
3.82
3.81
3.78
3.63
3.38
3.37
2.89
2.87
2.79
2.78
2.75
2.37
Cl
F
O
4p
CO2Me
0.92
0.91
3.15
0.99
0.94
1.00
1.01
2.96
1.01
0.98
1.04
2.97
f1 (ppm)

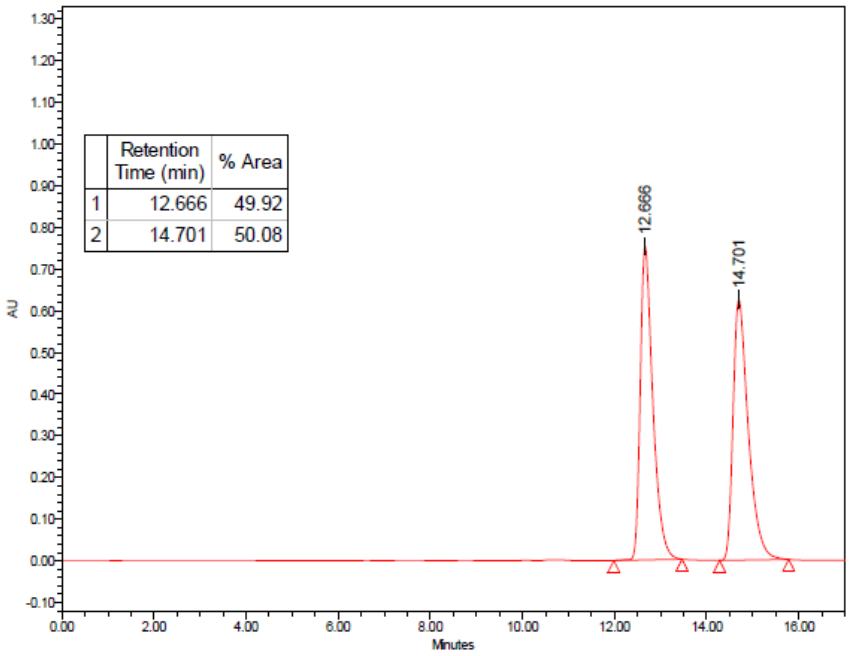

172.32
158.18
155.70
141.03
140.97
140.01
139.46
136.61
135.09
133.36
130.56
130.05
129.33
128.06
125.91
119.13
118.96
117.62
117.41
72.41
69.44
51.78
44.72
36.03
20.10
Cl
F
O
4p
CO2Me
f1 (ppm)

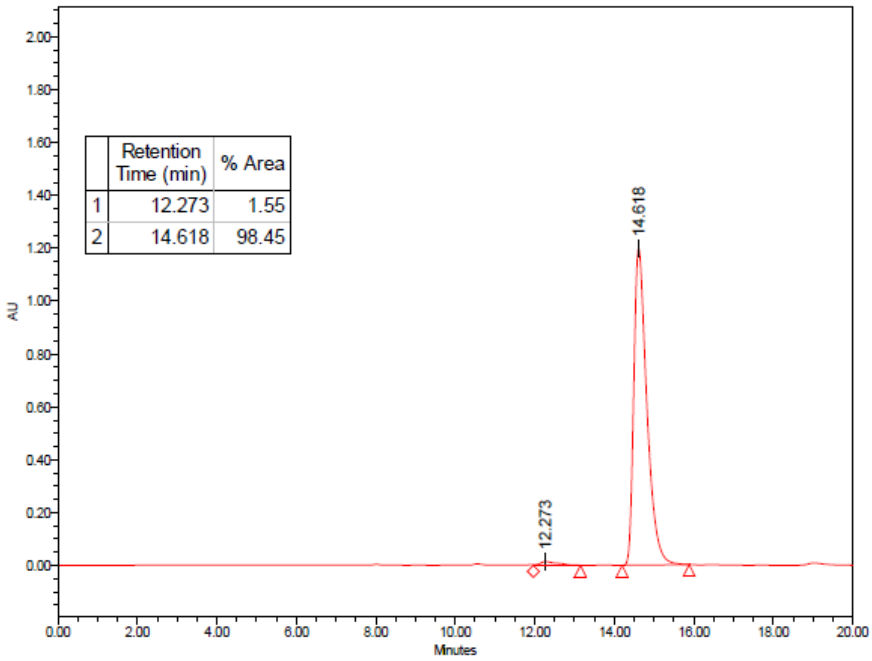

Retention Time (min) | % Area
1 | 11.056 | 49.89
2 | 14.253 | 50.11
11.056
14.253
AU
Minutes

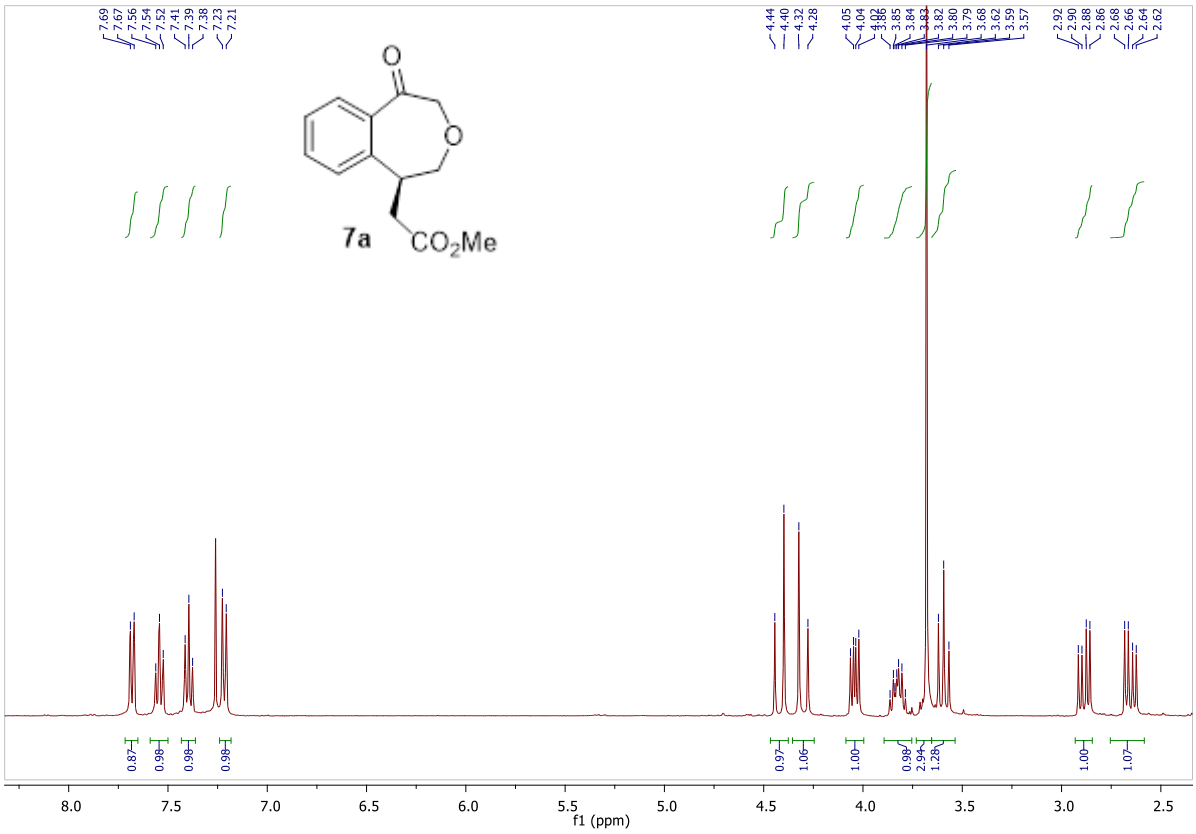

Retention Time (min) | % Area
1 | 11.041 | 1.75
2 | 14.157 | 98.25
14.157
11.041
AU
Minutes

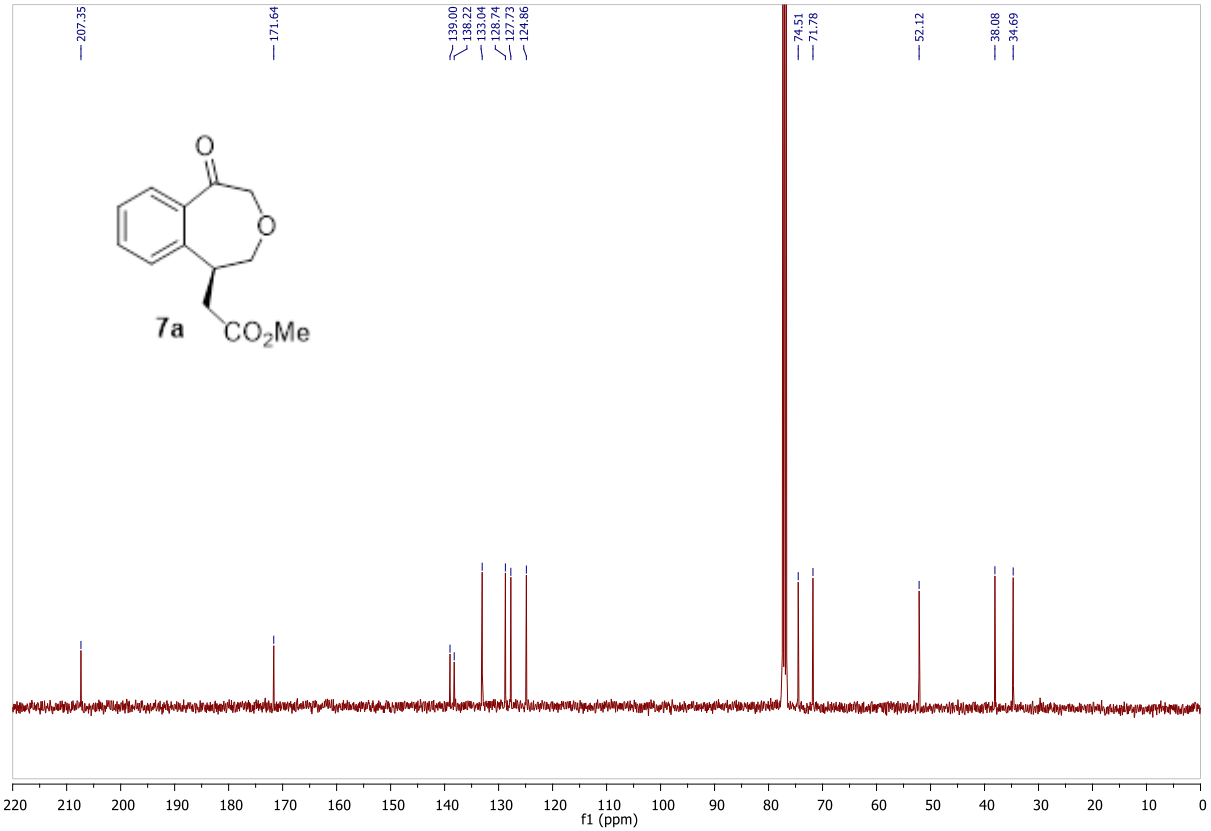

7.87
7.86
7.86
7.85
7.82
7.81
7.81
7.80
7.79
7.68
7.54
7.52
7.49
7.48
7.48
7.48
7.47
7.47
7.30
7.29
7.28
7.27
7.26
7.25
6.98
4.76
4.73
4.21
4.20
4.18
4.17
3.93
3.92
3.90
3.89
3.87
3.59
3.02
3.00
2.87
2.86
2.83
2.82
2.44
2.00
0.82
0.92
0.97
1.95
3.45
0.94
1.00
0.91
1.96
1.07
2.84
0.99
0.99
2.92
O
4k
CO2Me
f1 (ppm)

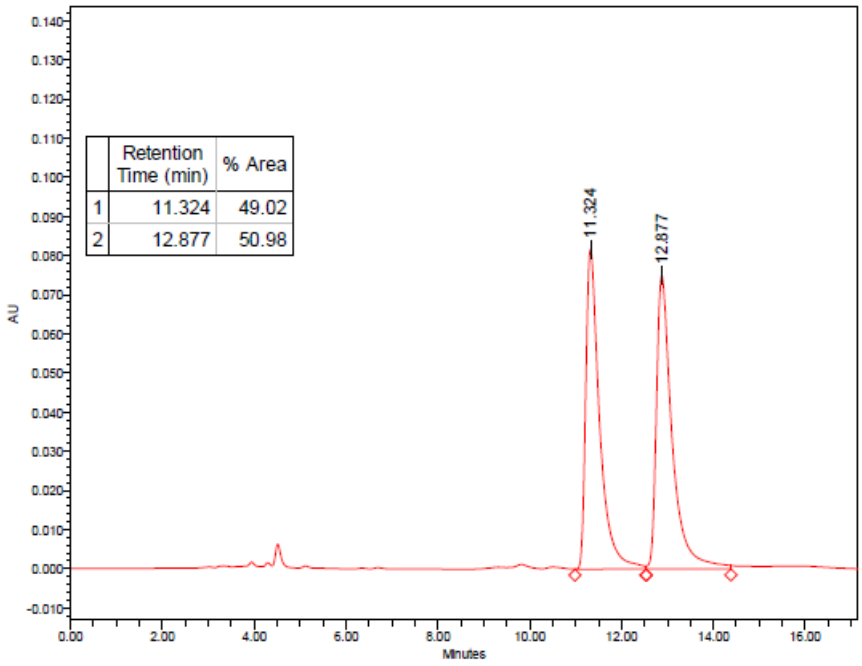

172.84
141.71
141.53
138.53
136.63
135.71
132.72
132.60
132.22
129.99
129.43
127.77
127.54
127.49
127.07
126.21
126.15
125.90
73.33
69.84
51.64
45.53
36.49
20.16
O
4k
CO2Me
f1 (ppm)

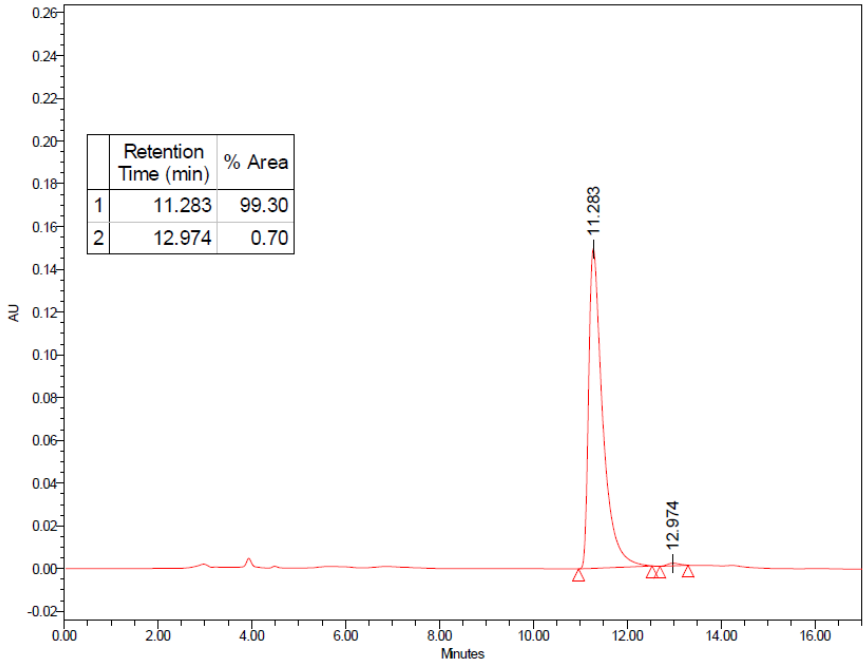

Retention Time (min)
% Area
1
12.666
49.92
2
14.701
50.08
12.666
14.701
AU
Minutes

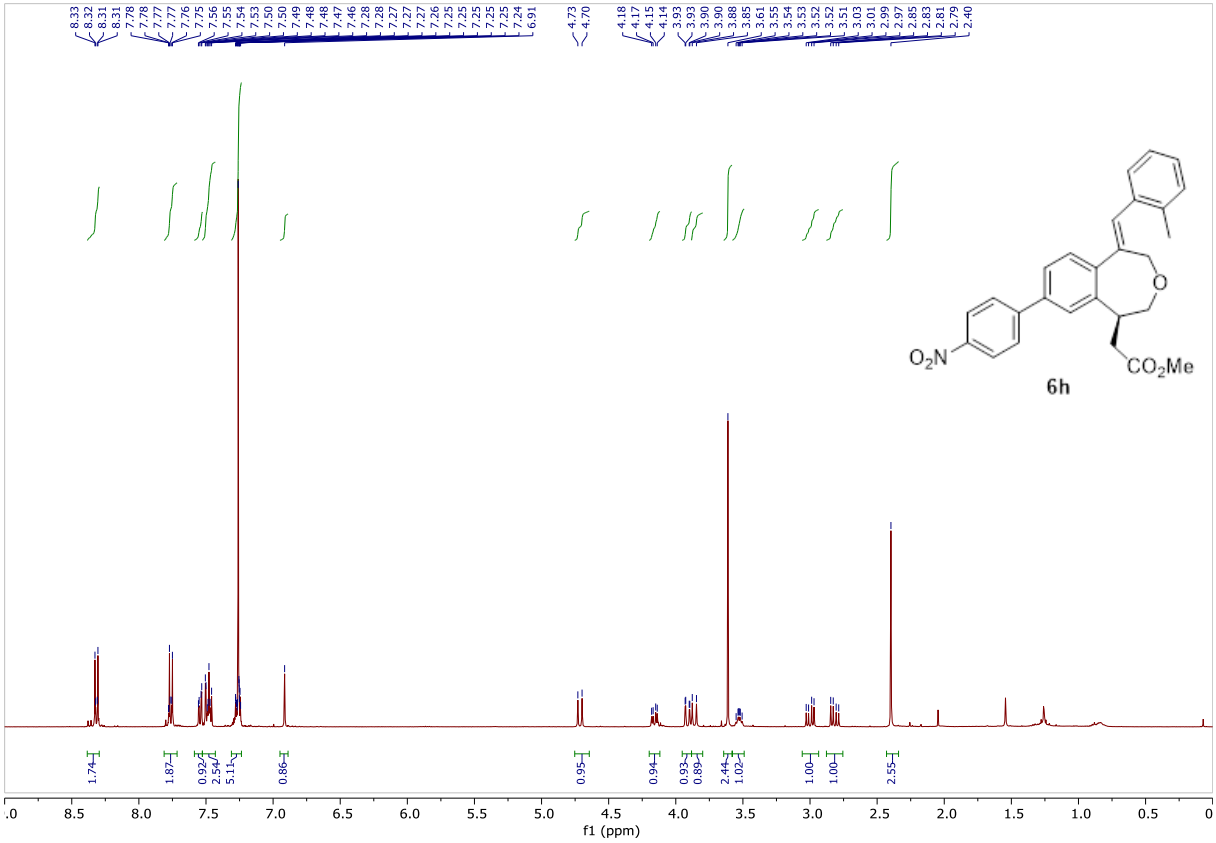

Retention Time (min)
% Area
1
12.273
1.55
2
14.618
98.45
14.618
12.273
AU
Minutes

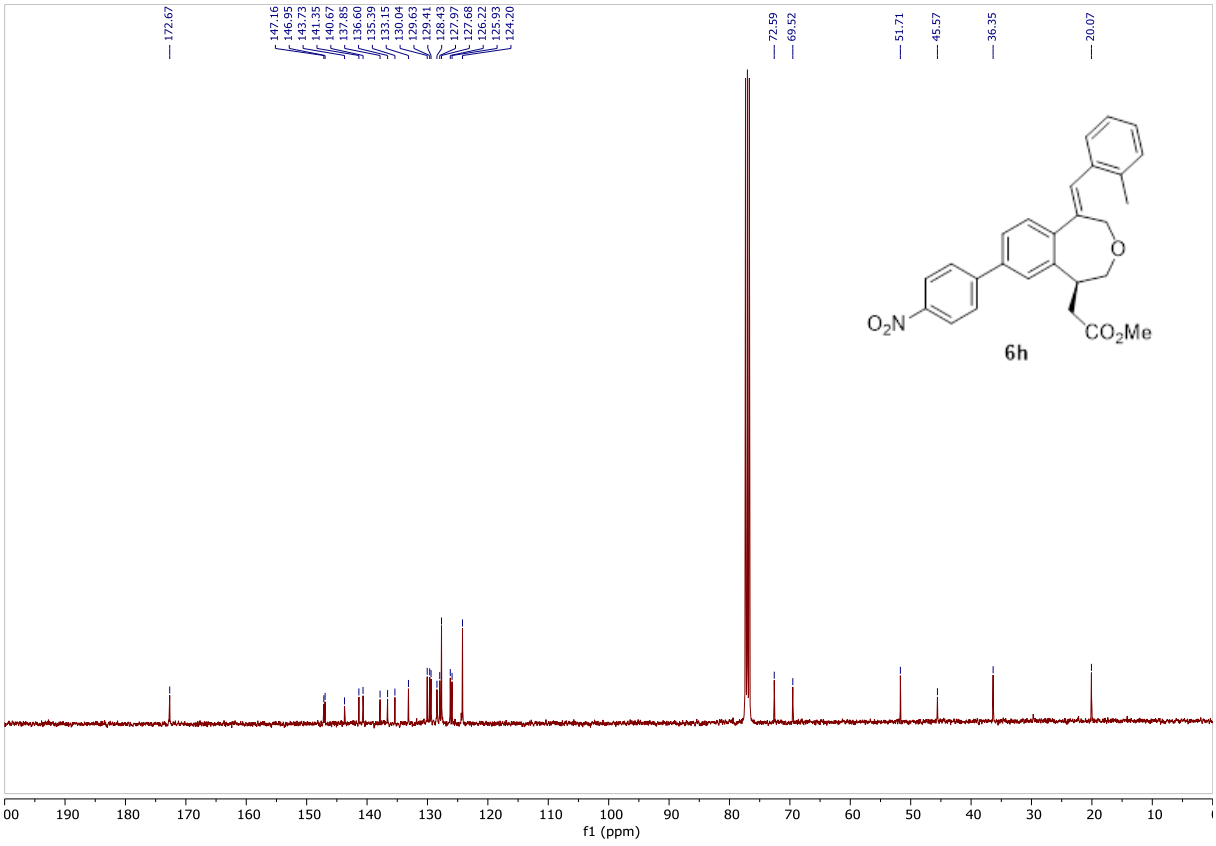

7.69
7.67
7.56
7.54
7.52
7.41
7.39
7.38
7.23
7.21
4.44
4.40
4.32
4.28
4.05
4.04
3.86
3.85
3.84
3.82
3.80
3.79
3.68
3.62
3.59
3.57
2.92
2.90
2.88
2.86
2.68
2.66
2.64
2.62
O
O
7a
CO2Me
0.87
0.98
0.98
0.98
0.97
1.06
1.00
0.98
2.94
1.28
1.00
1.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)


207.35
171.64
139.00
138.22
133.04
128.74
127.73
124.86
74.51
71.78
52.12
38.08
34.69
O
O
7a
CO2Me
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Retention Time (min) | % Area
1 | 11.324 | 49.02
2 | 12.877 | 50.98
11.324
12.877
AU
Minutes


Retention Time (min) | % Area
1 | 11.283 | 99.30
2 | 12.974 | 0.70
11.283
12.974
AU
Minutes


8.33 8.32 8.31 8.31 7.78 7.78 7.77 7.77 7.76 7.75 7.56 7.55 7.54 7.53 7.50 7.50 7.49 7.48 7.48 7.47 7.46 7.28 7.28 7.27 7.27 7.27 7.26 7.25 7.25 7.25 7.25 7.24 6.91
4.73 4.70
4.18 4.17 4.15 4.14 3.93 3.93 3.90 3.90 3.88 3.85 3.61 3.55 3.54 3.53 3.52 3.52 3.51 3.03 3.01 2.99 2.97 2.85 2.83 2.81 2.79 2.40
1.74 1.87 0.92 2.54 5.11 0.86 0.95 0.94 0.93 0.89 2.44 1.02 1.00 1.00 2.55
f1 (ppm)
O2N
CO2Me
6h

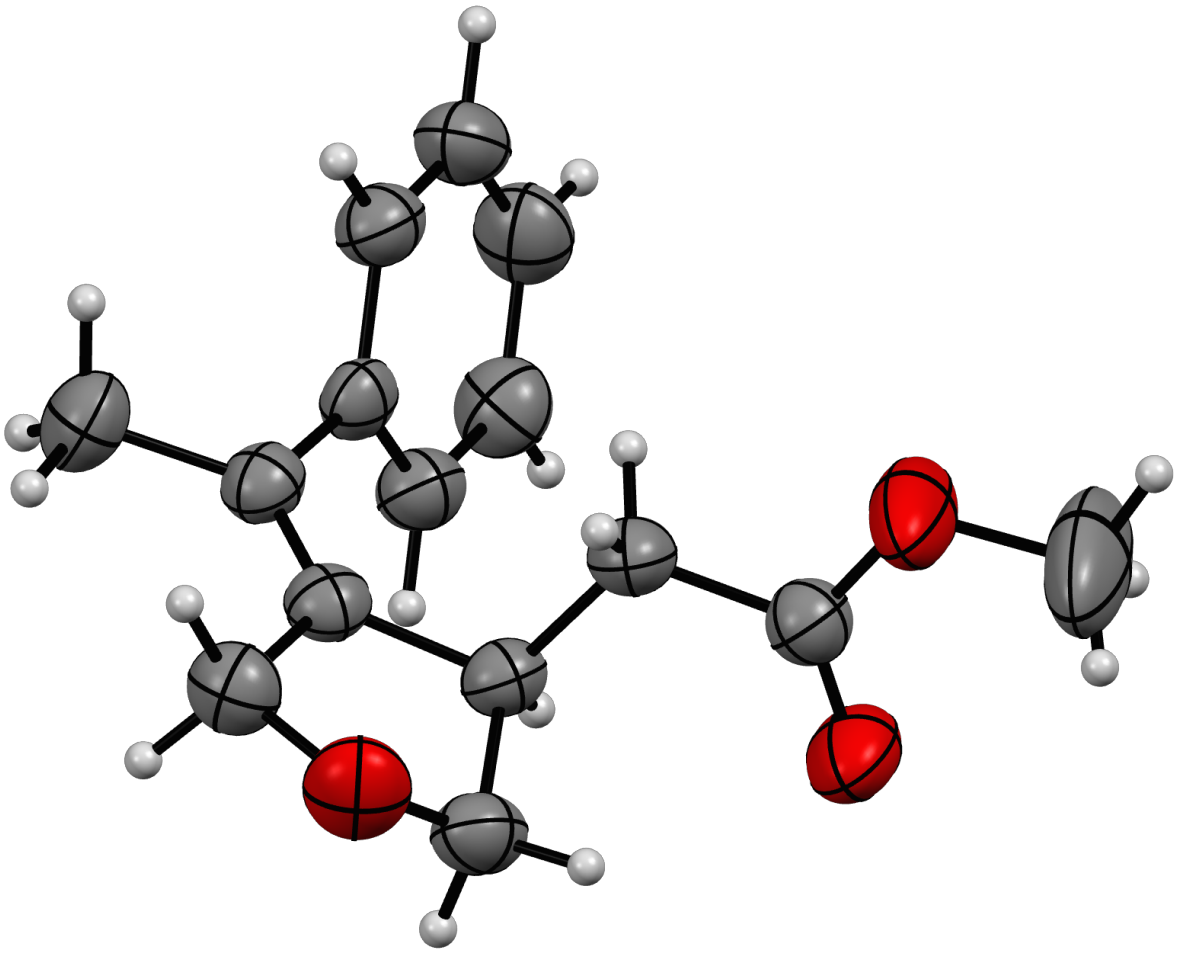

172.67
147.16 146.95 143.73 141.35 140.67 137.85 136.60 135.39 133.15 130.04 129.63 129.41 128.43 127.97 127.68 126.22 125.93 124.20
72.59 69.52 51.71 45.57 36.35 20.07
f1 (ppm)
O2N
CO2Me
6h

II. X-ray diffraction

Single crystals were selected, mounted and transferred into a cold nitrogen gas stream. Intensity data was collected with a Bruker Kappa-APEX2 system using micro-source Cu-Kα radiation. Unit-cell parameters determination, data collection strategy, integration and absorption correction were carried out with the Bruker APEX2 suite of programs. The structures were solved with SHELXT-2014[1] and refined anisotropically by full-matrix least-squares methods with SHELXL-2014[1] using the WinGX suite.[2] Absolute structures were determined by anomalous scattering effects analysis and chemical absolute configurations were then deduced.[3]

A. X-ray diffraction of 3a

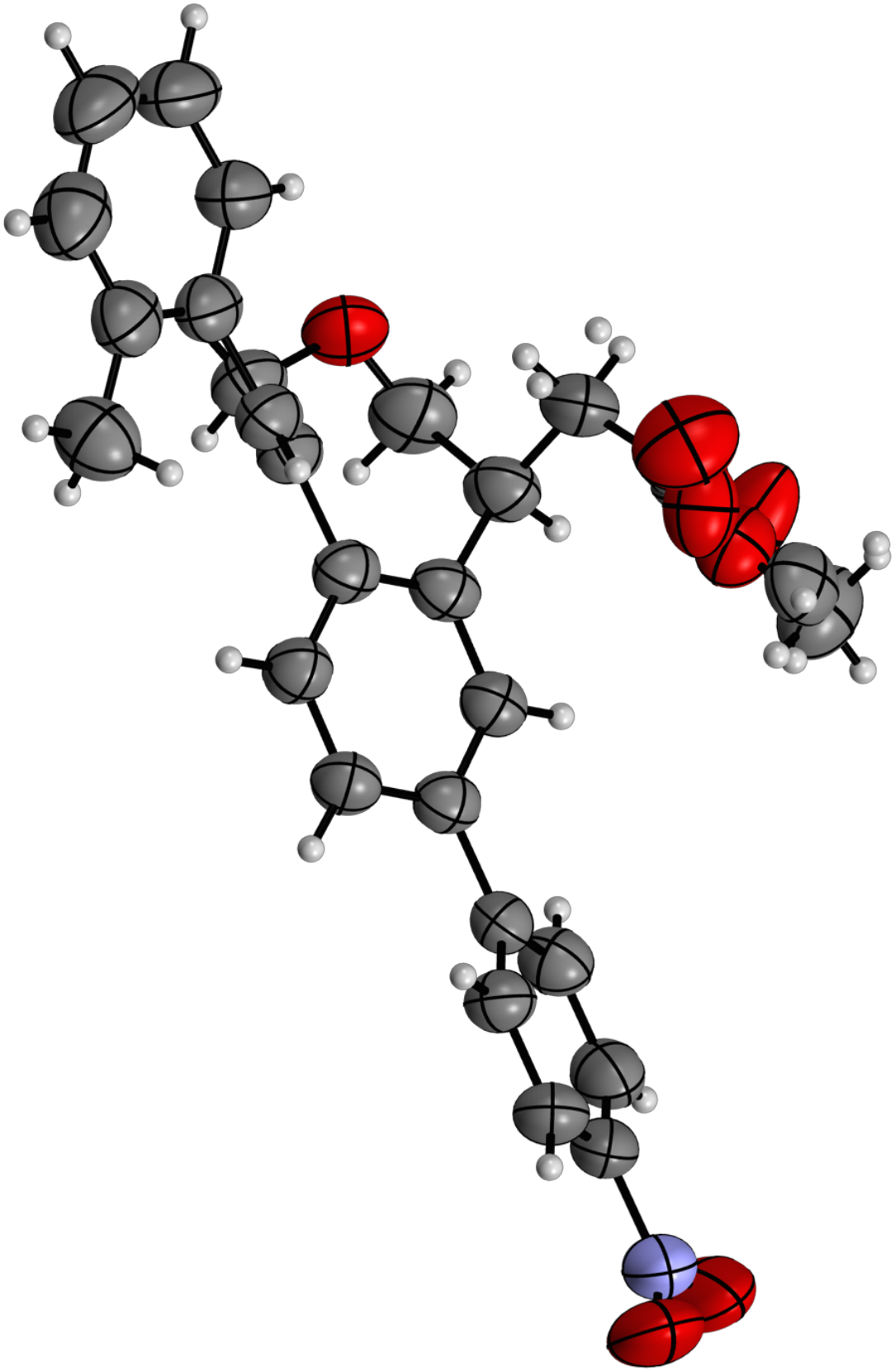
Crystal data for 3a. $C_{15}H_{18}O_2$, orthorhombic P 2_1 2_1 2_1, a = 8.0793(1) Å, b = 8.1611(1) Å, c = 20.7538(3) Å, α = β = γ = 90°, V = 1368.42(3) Å^3, Z = 4, colorless prism 0.35 x 0.3 x 0.25 mm, μ = 0.664 mm^{-1}, min / max transmission = 0.78 / 0.97, T= 200(1) K, λ = 1.54178 Å, θ range = 5.83° to 66.53°, 8571 reflections measured, 2414 independent, R_{int} = 0.0217, completeness = 0.997, 165 parameters, 0 restraints, Flack x = -0.11(10), final R indices R1 [I>2σ(I)] = 0.0311 and wR2 (all data) = 0.0948, GOF on F^2 = 1.102, largest difference peak / hole = 0.15 / -0.15 e.Å^{-3}.



Thermal ellipsoid plot/ORTEP of **3a** (contour at 70% probability level).

B. X-ray diffraction of 6h

Crystal data for 6h. $C_{27}H_{25}NO_5$, orthorhombic P 2_1 2_1 2_1, a = 7.4815(2) Å, b = 12.4851(2) Å, c = 24.3339(5) Å, α = β = γ = 90°, V = 2272.96(8) Å^3, Z = 4, colorless prism 0.3 x 0.1 x 0.05 mm, μ = 0.728 mm^{-1}, min / max transmission = 0.88 / 1.00, T= 200(1) K, λ = 1.54178 Å, θ range = 6.19° to 66.64°, 11200 reflections measured, 4003 independent, R_{int} = 0.0197, completeness = 0.997, 335 parameters, 32 restraints, Flack x = --0.06(9), final R indices R1 [I>2σ(I)] = 0.0306 and wR2 (all data) = 0.0840, GOF on F^2 = 1.059, largest difference peak / hole = 0.12 / -0.17 e.Å^{-3}.



Thermal ellipsoid plot/ORTEP of **6h** (contour at 70% probability level).

Références

[1] Sheldrick, G. M., *Acta Crystallogr C Struct Chem* **2015**, *71*, 3.
[2] Farrugia, L. J., *J Appl Crystallogr* **1999**, *32*, 837.
[3] Flack, H. D.; Bernardinelli, G., *J Appl Crystallogr* **2000**, *33*, 1143.