Supporting Information

Thio-Claisen Rearrangement Used in Preparing Anti-β-Functionalized γ,δ-Unsaturated Amino Acids: Scope and Limitations

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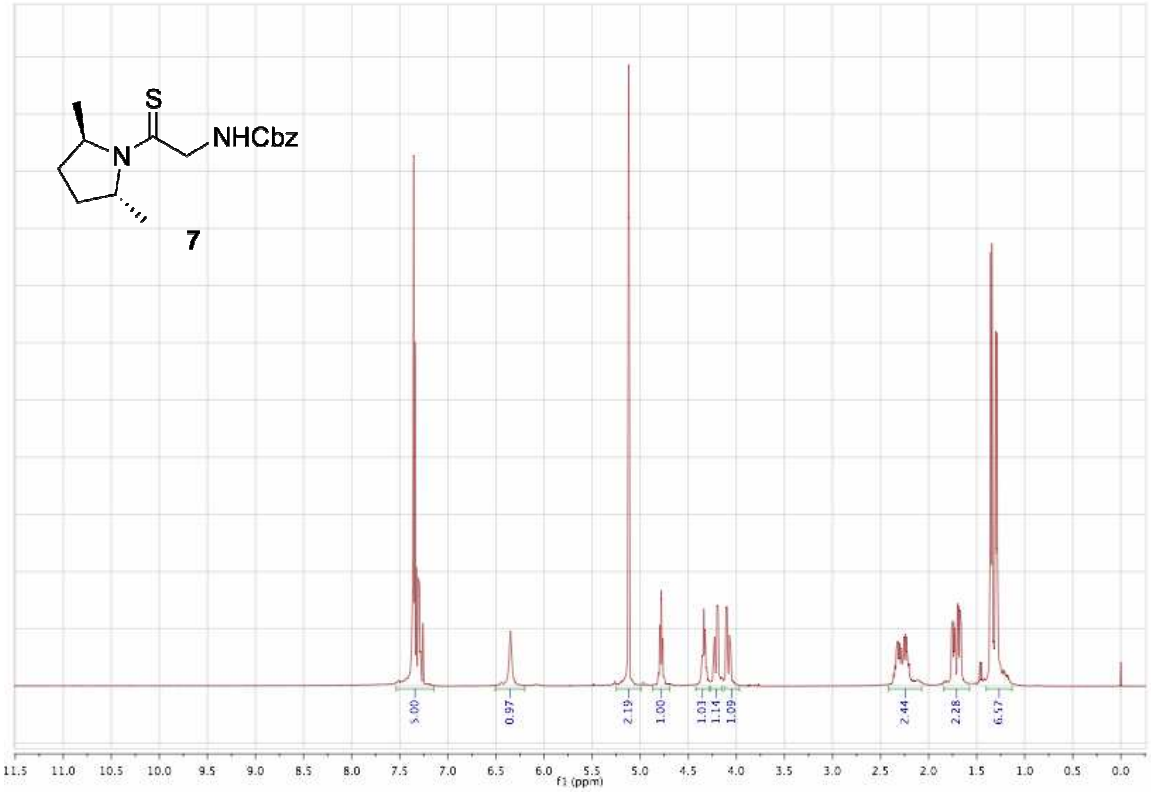
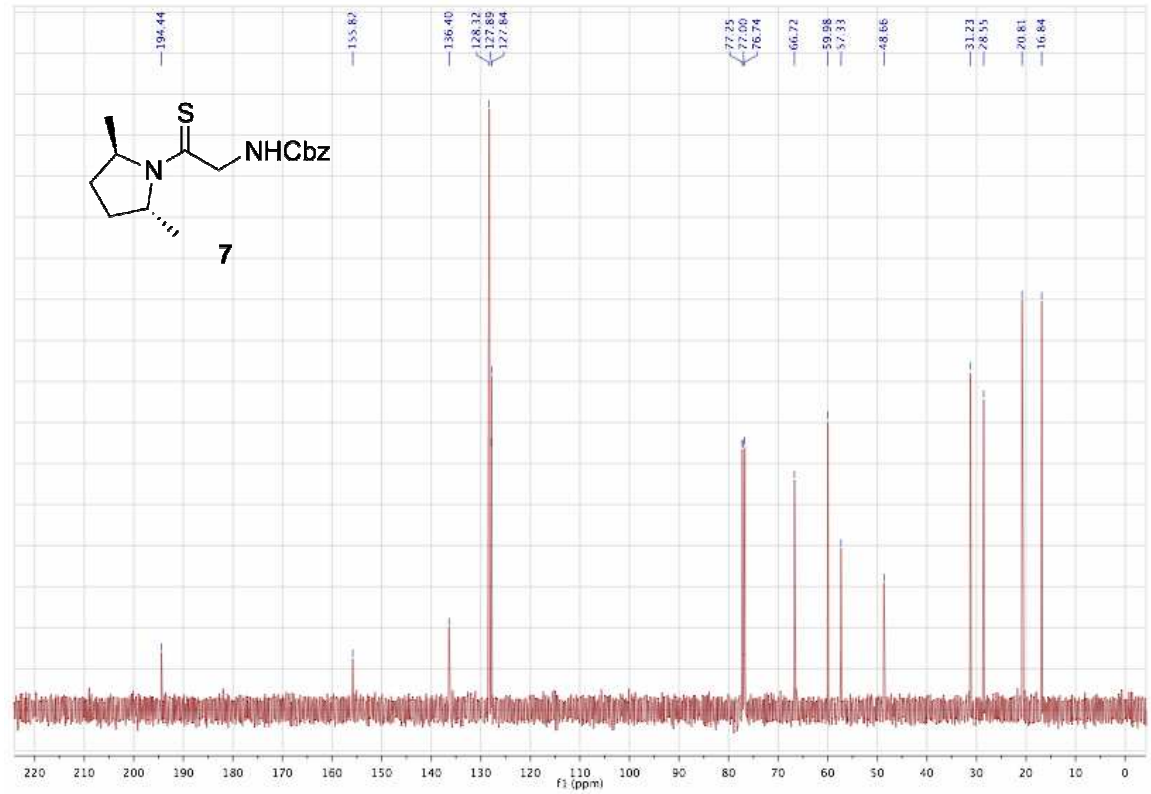
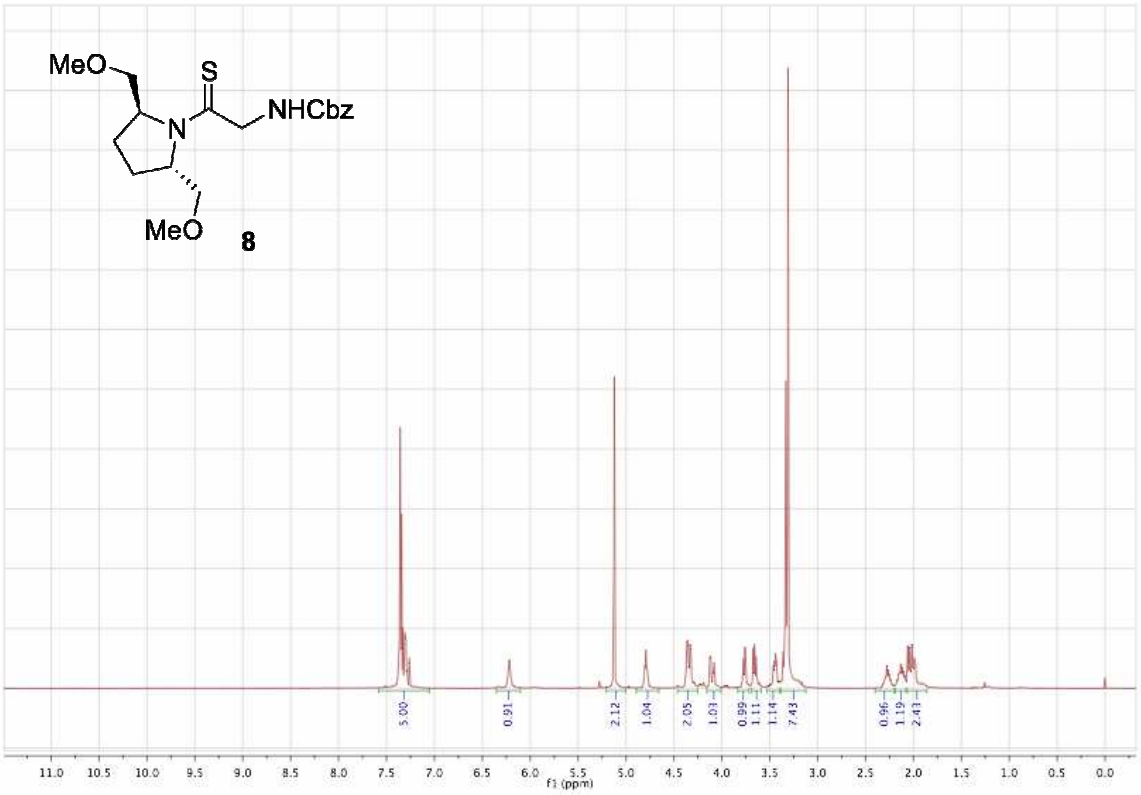
General Information: All starting materials and reagents were used as received without further purification unless otherwise noted. Dried THF was obtained from distillation over sodium and benzophenone. Dried DCM was obtained from distillation over Calcium hydride. Dried MeCN was used as received. NMR spectra were acquired on 500 MHz or 600 MHz spectrometers; $CDCl_3$ or TMS is used as internal standard for reporting chemical shift values. Data are presented as follows: chemical shift (ppm), multiplicity (*s* = singlet, *d* = doublet, *t* = triplet, *m* = multiplet, *br* = broad), coupling constant *J* (Hz) and integration. IR spectra were recorded using NaCl plates. Flash column chromatography was performed using silica gel 60 as the packing material, and pressurized by common compressed air. Analytical thin-layer chromatography (TLC) was performed on glass gel plates (0.25 mm) precoated with a fluorescent indicator. Plates were visualized by UV or $KMnO_4$ stain. High-performance liquid chromatography (HPLC) analyses were performed a chiral column. Optical rotations were recorded on a digital polarimeter and reported as follows: $[\alpha]^{20}_{D}$ (concentration in g/100 mL solvent).

The ^{1}H and ^{13}C NMR spectra for new compounds.



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1.19
2.41
11.0 10.5 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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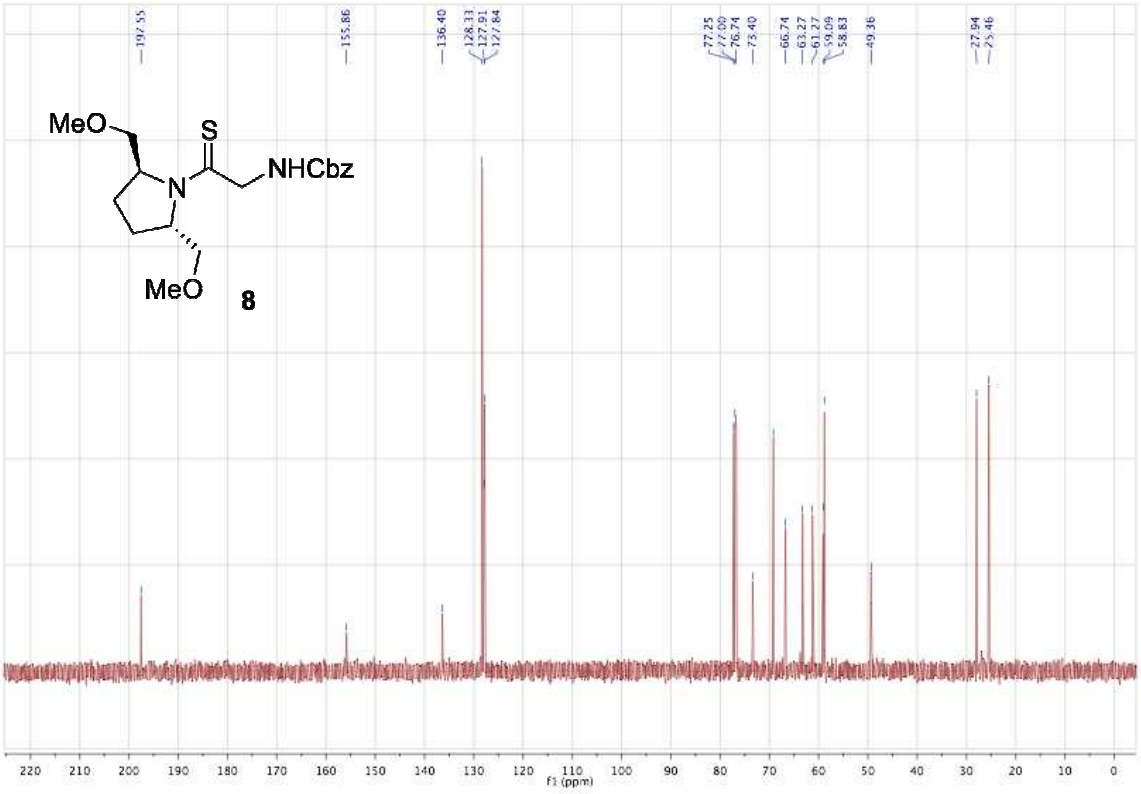
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59.09
58.83
49.36
27.94
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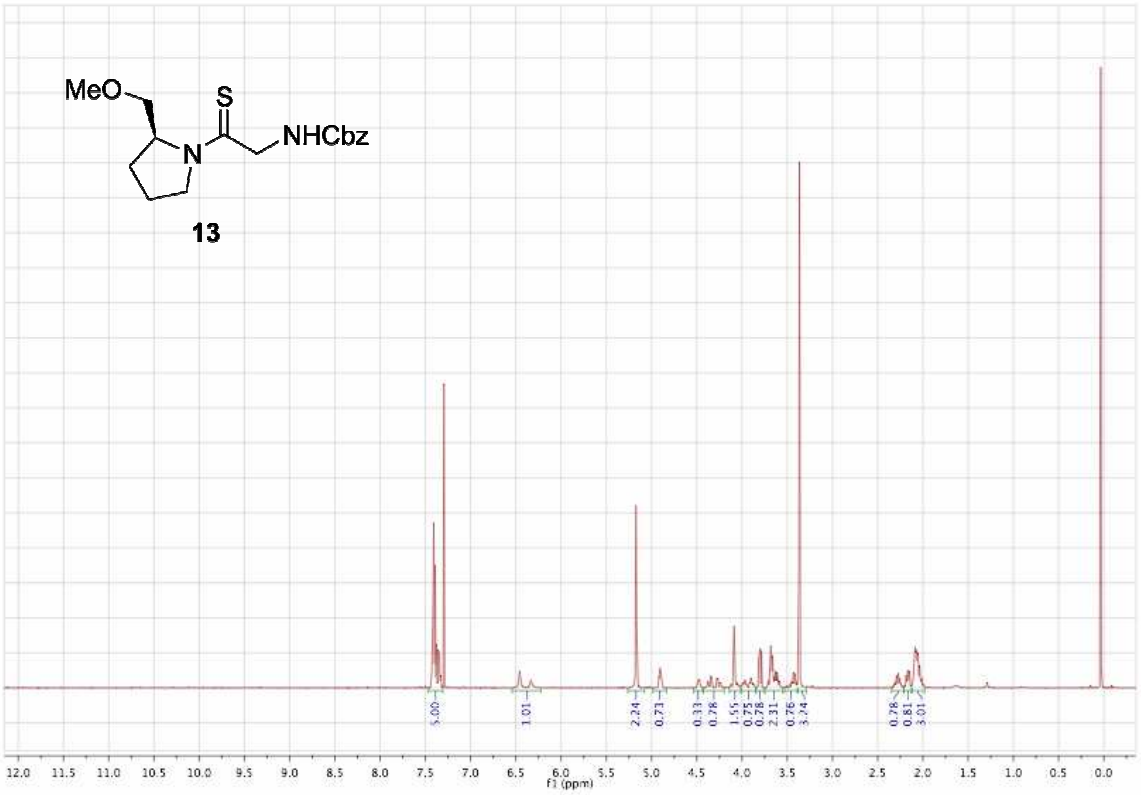
f1 (ppm)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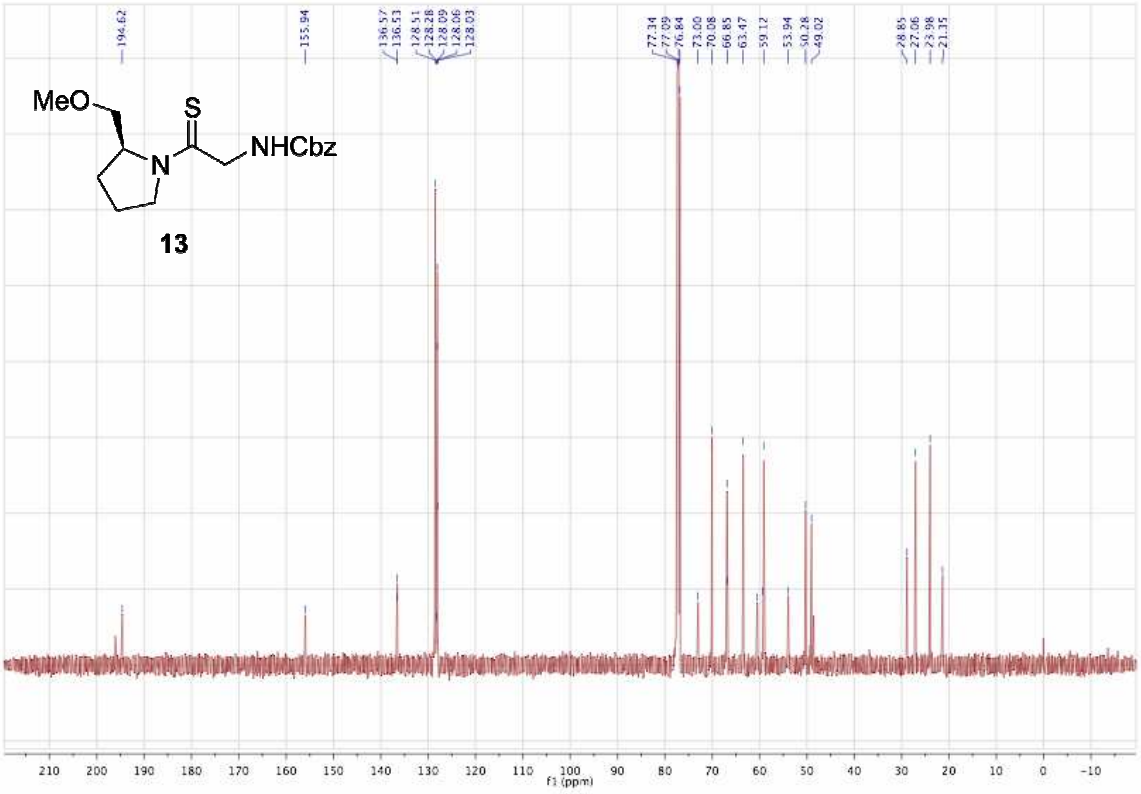
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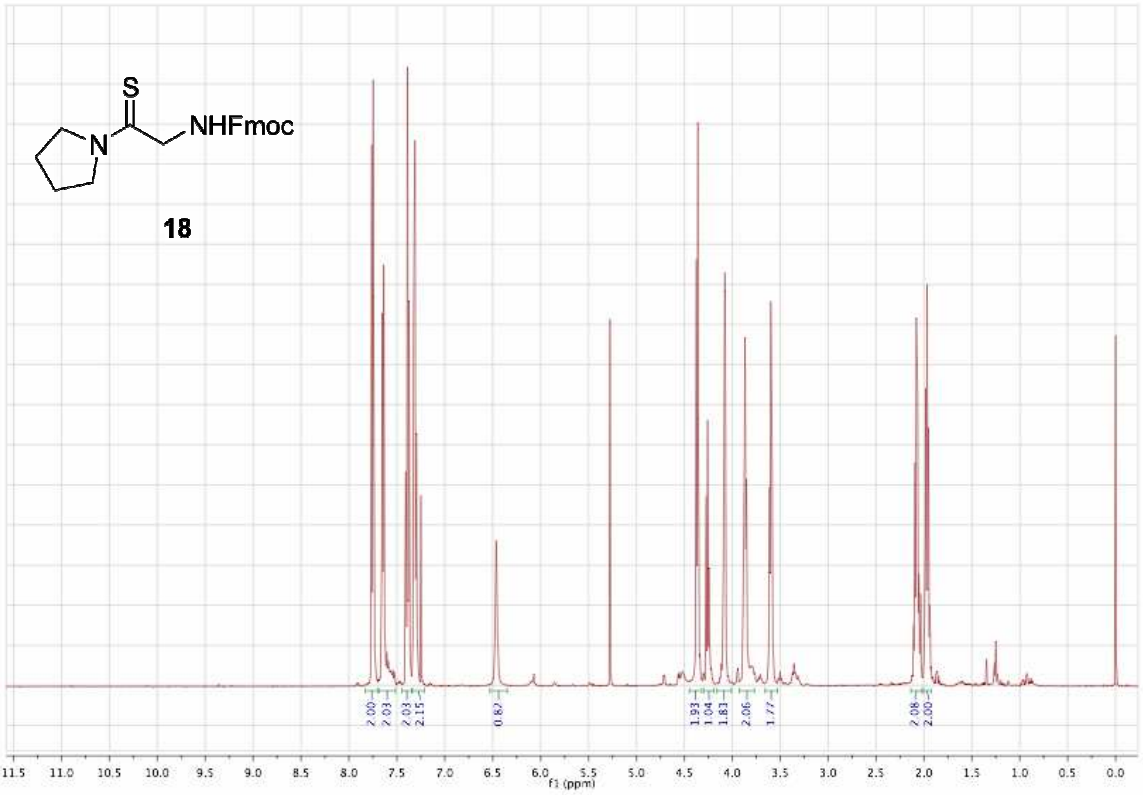
f1 (ppm)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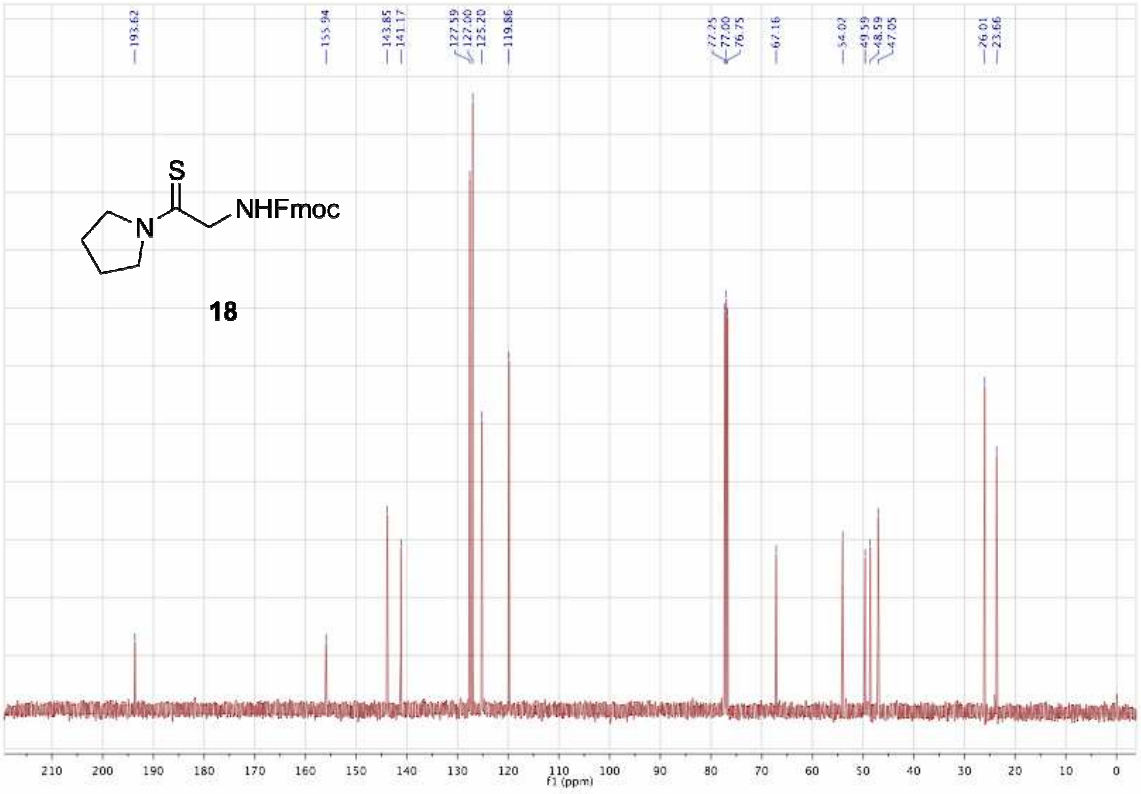
F1 (ppm)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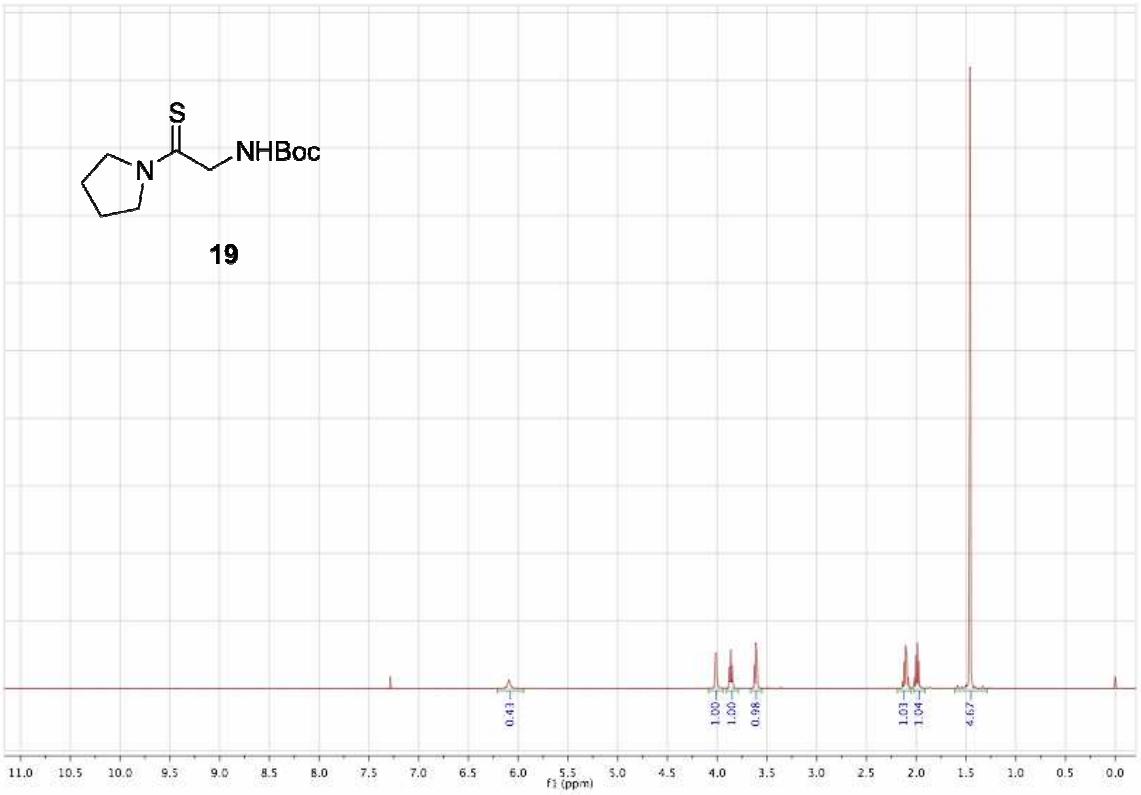
F1 (ppm)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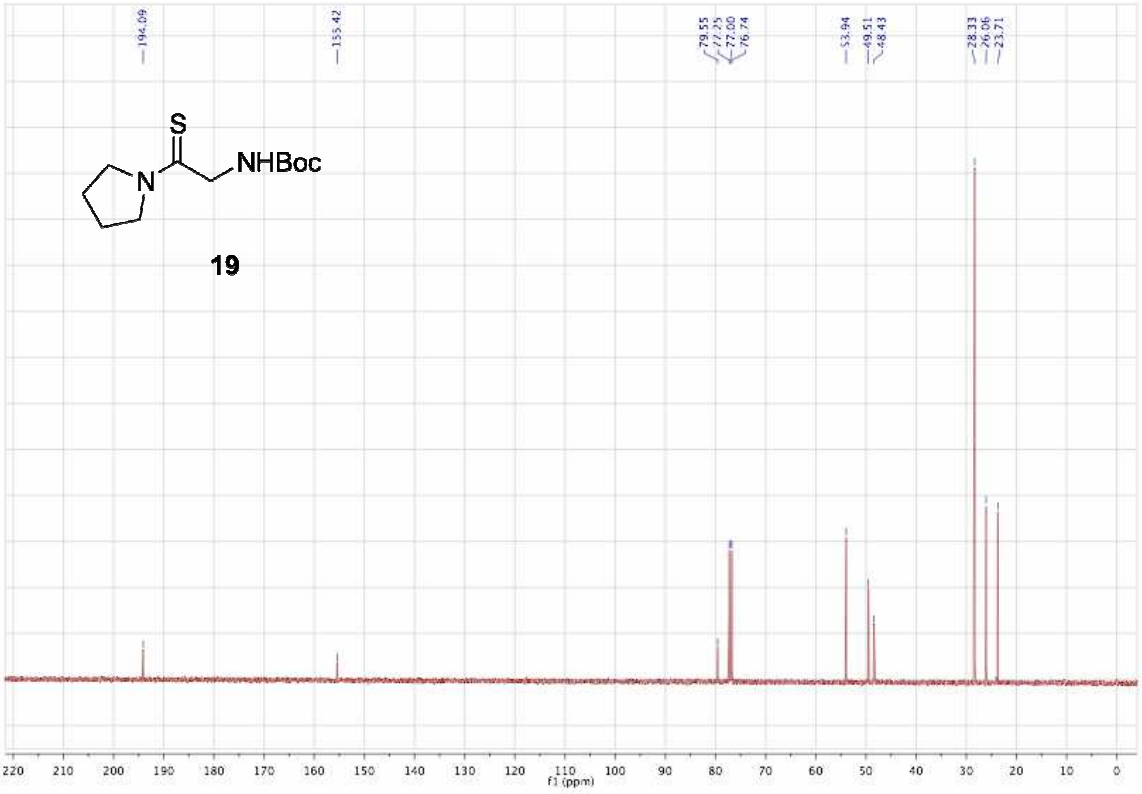
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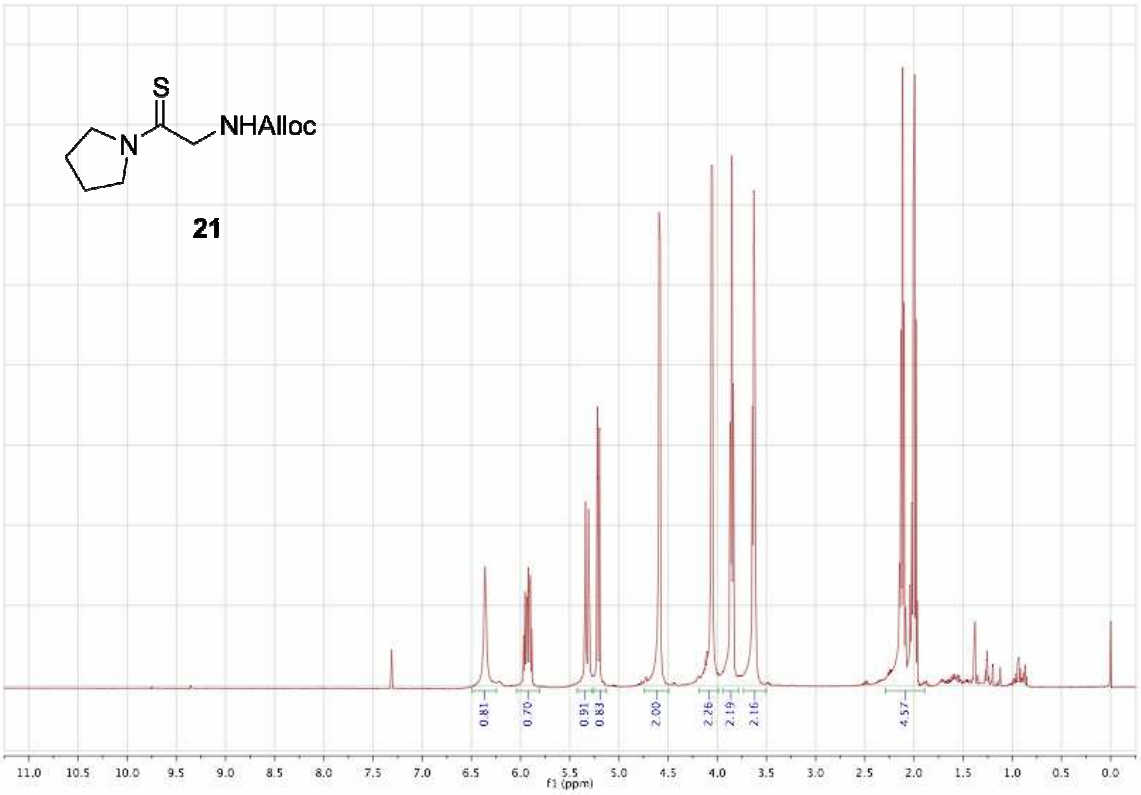
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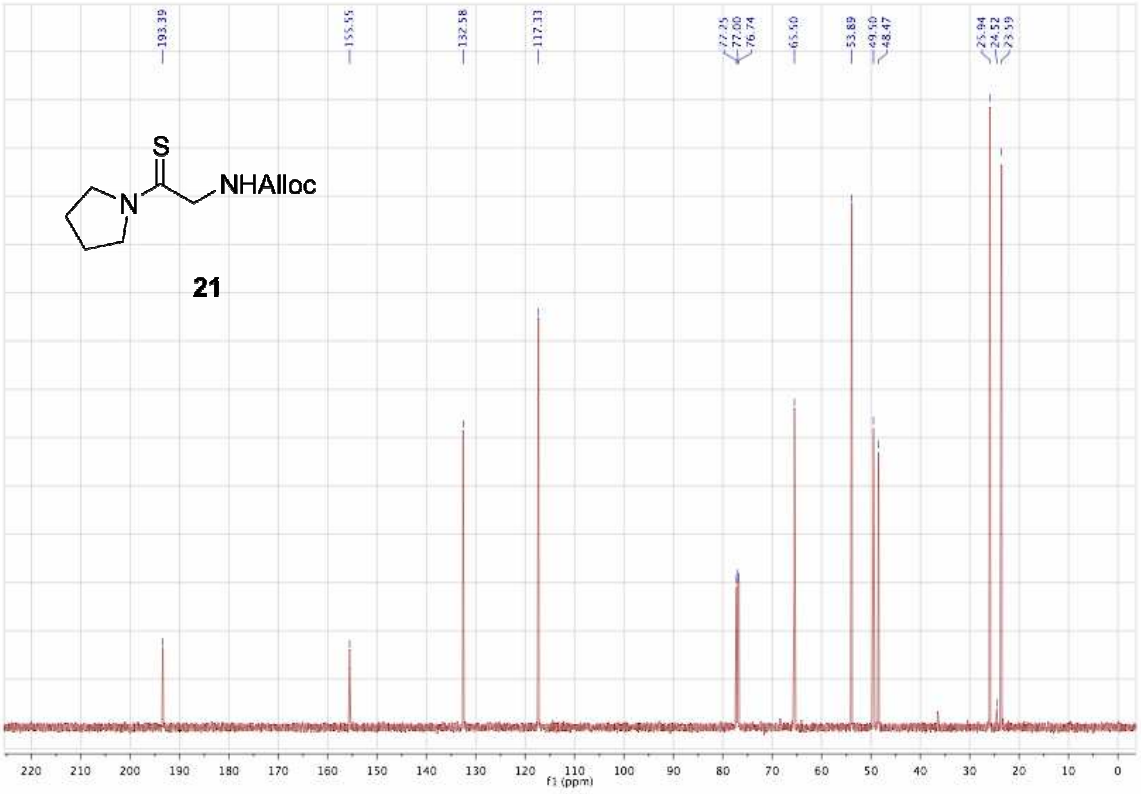
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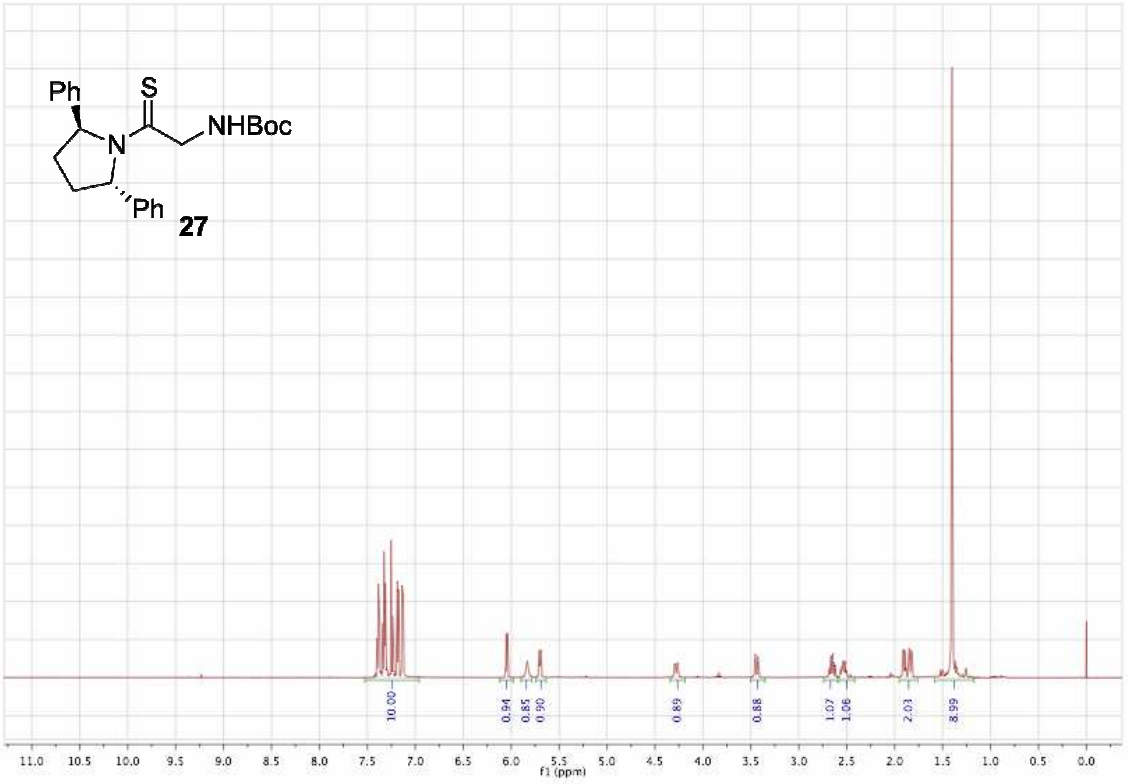
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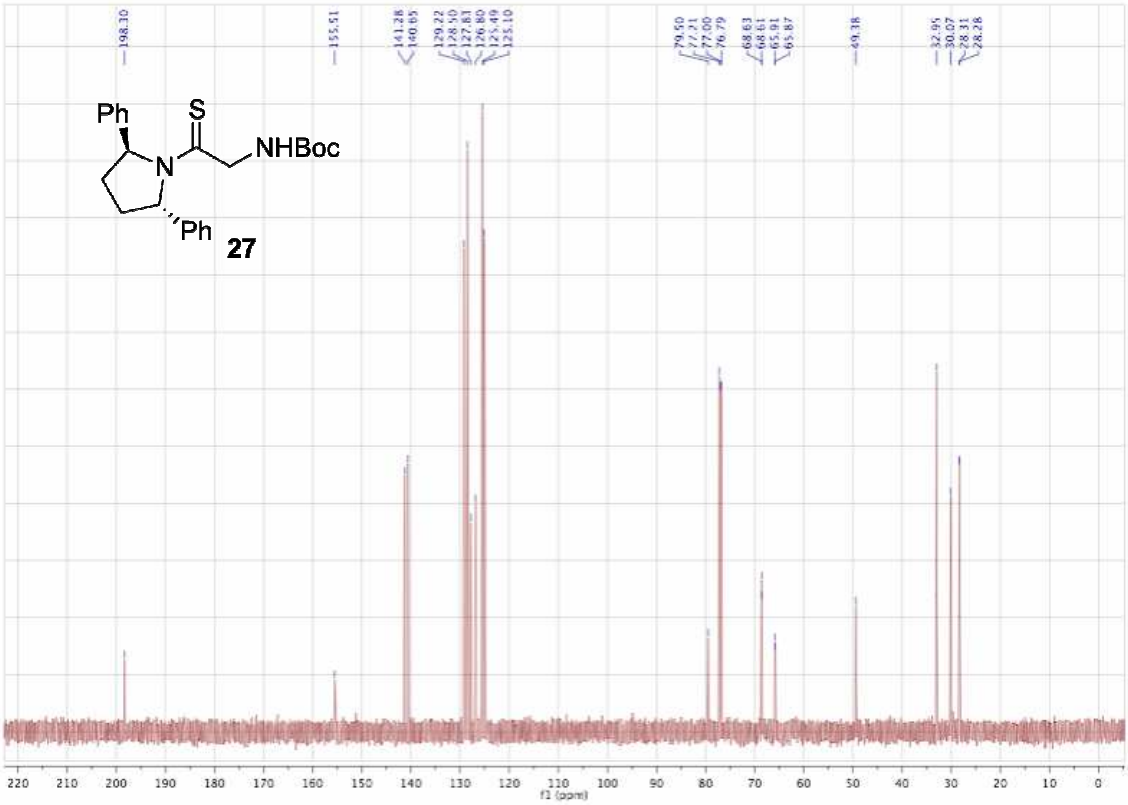
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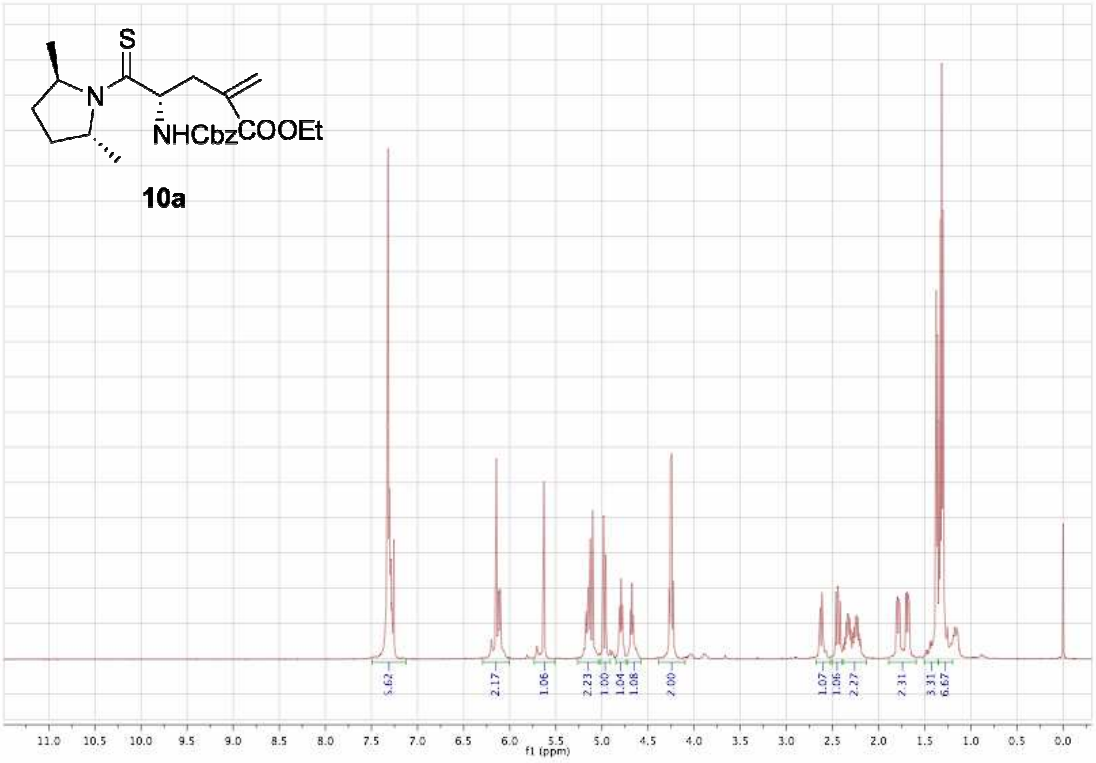
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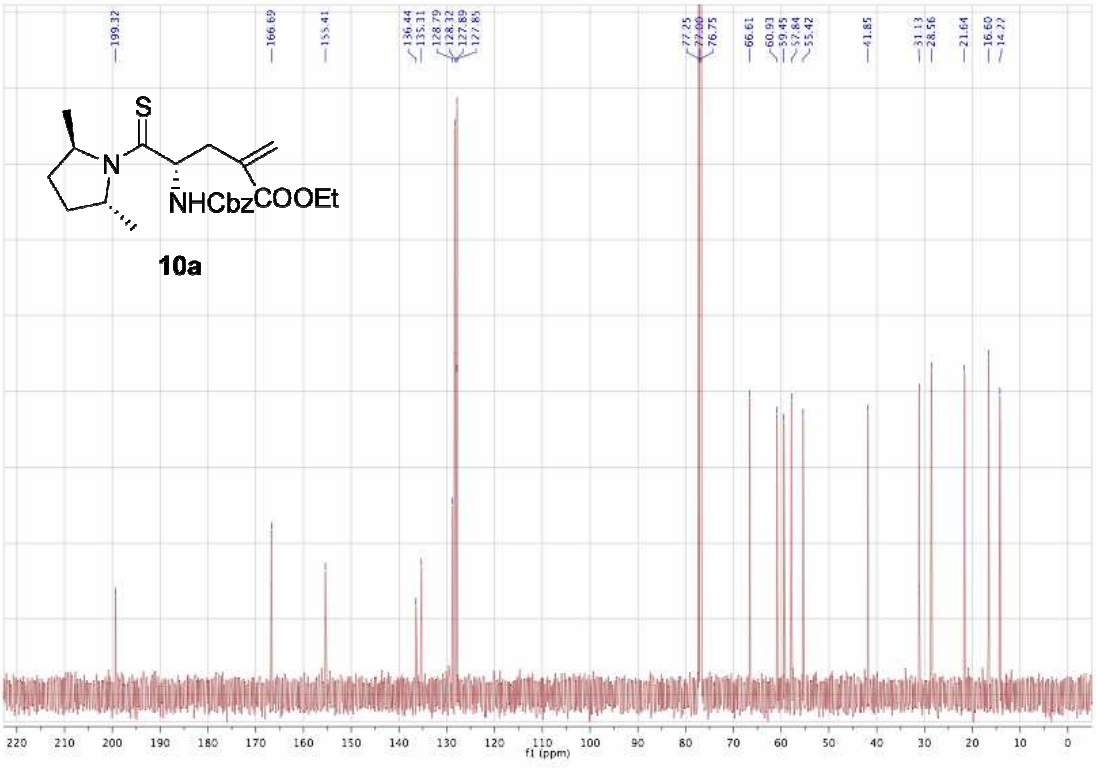
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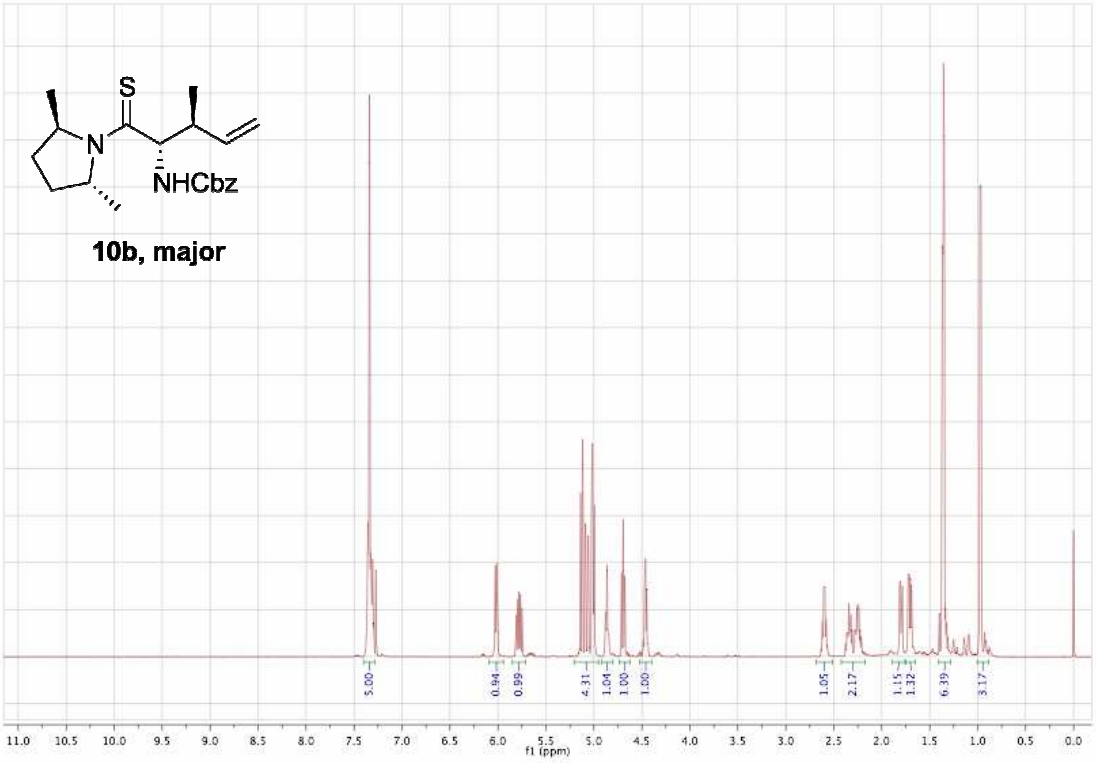
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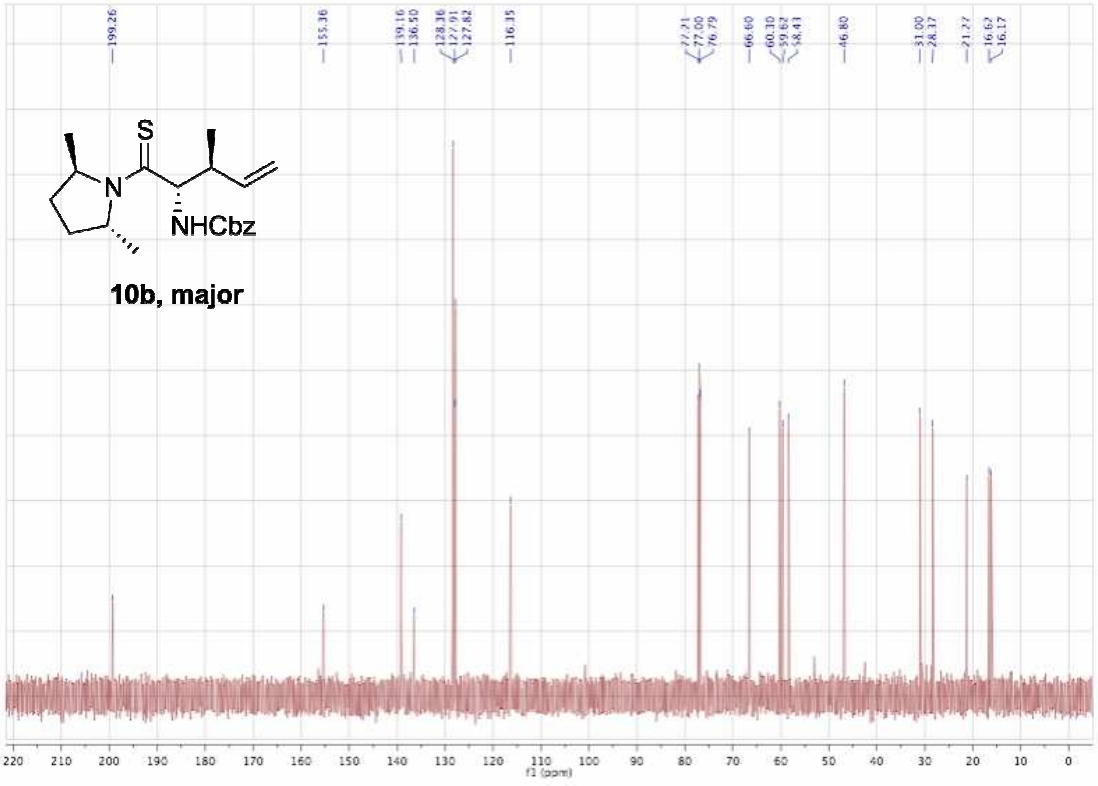
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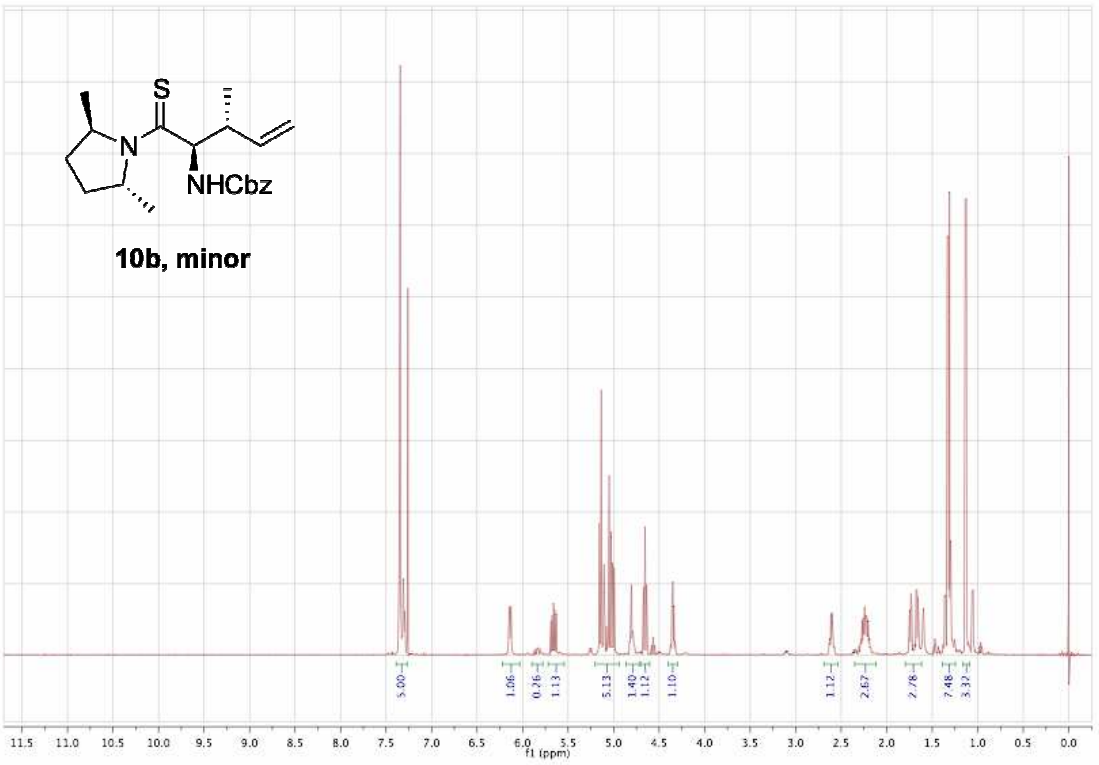
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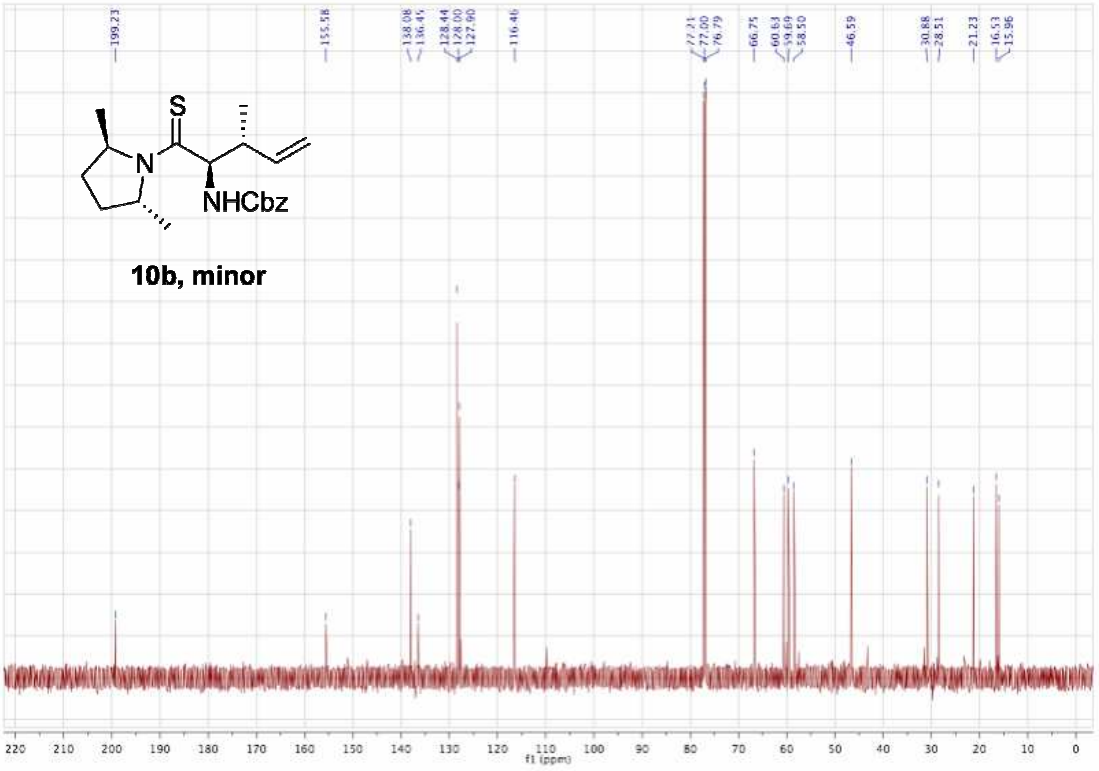
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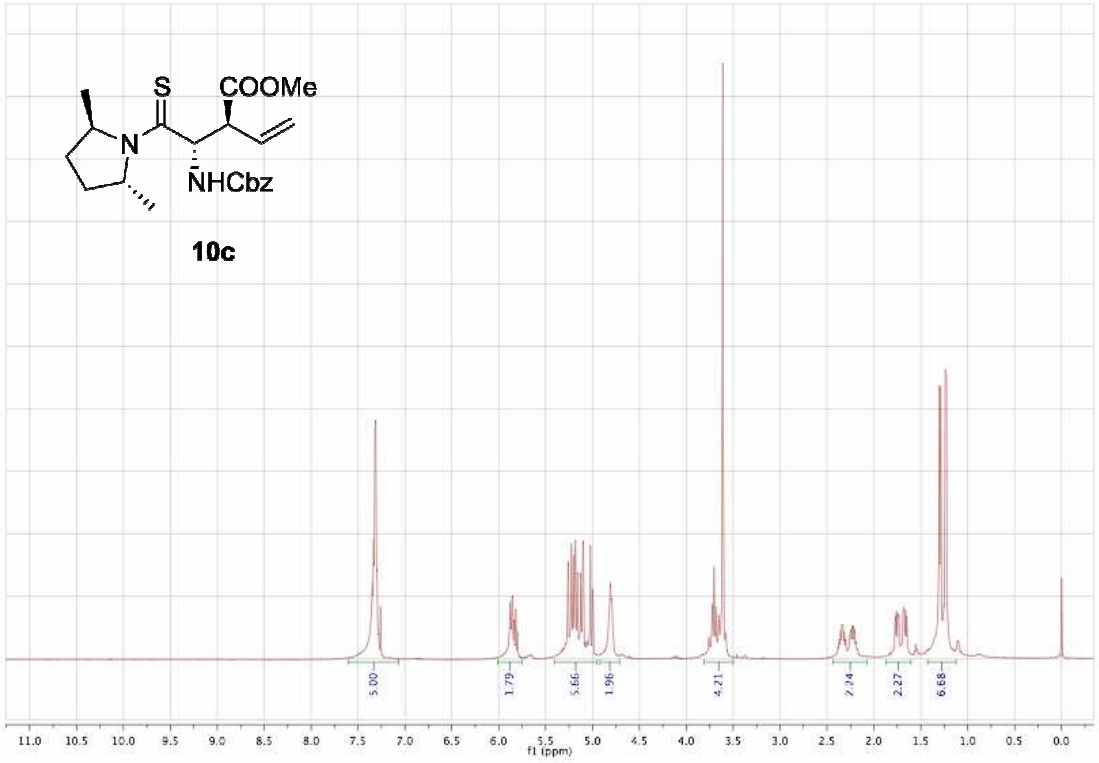
f1 (ppm)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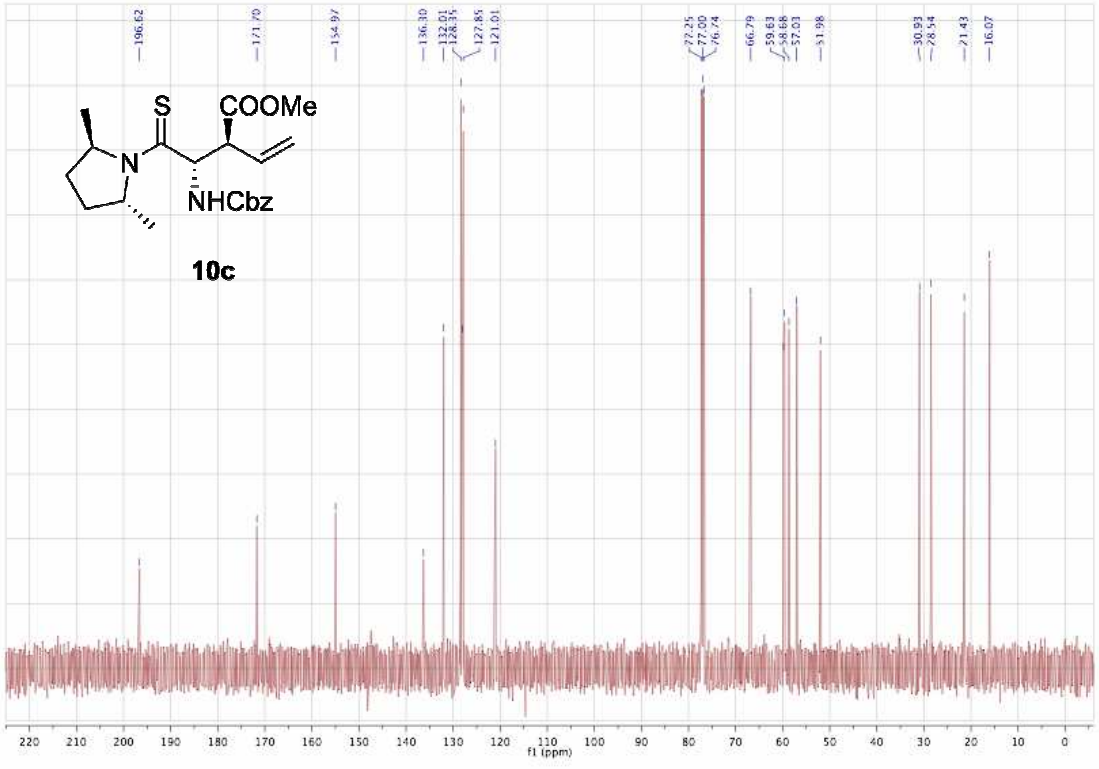
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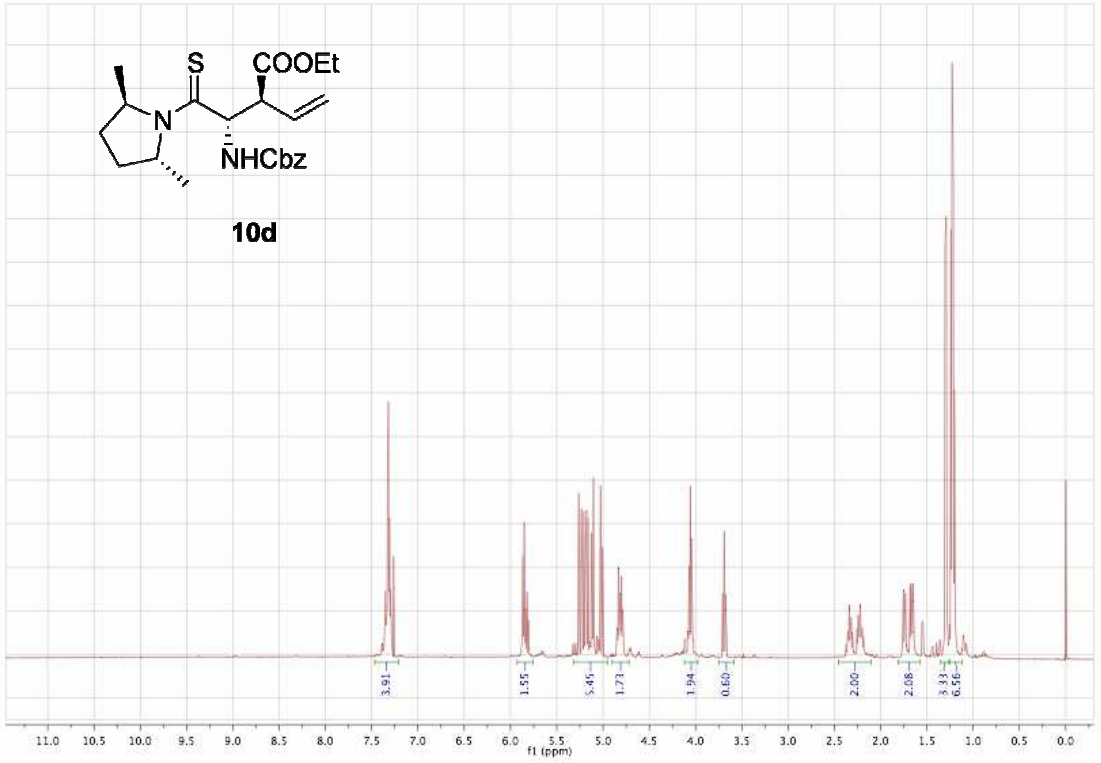
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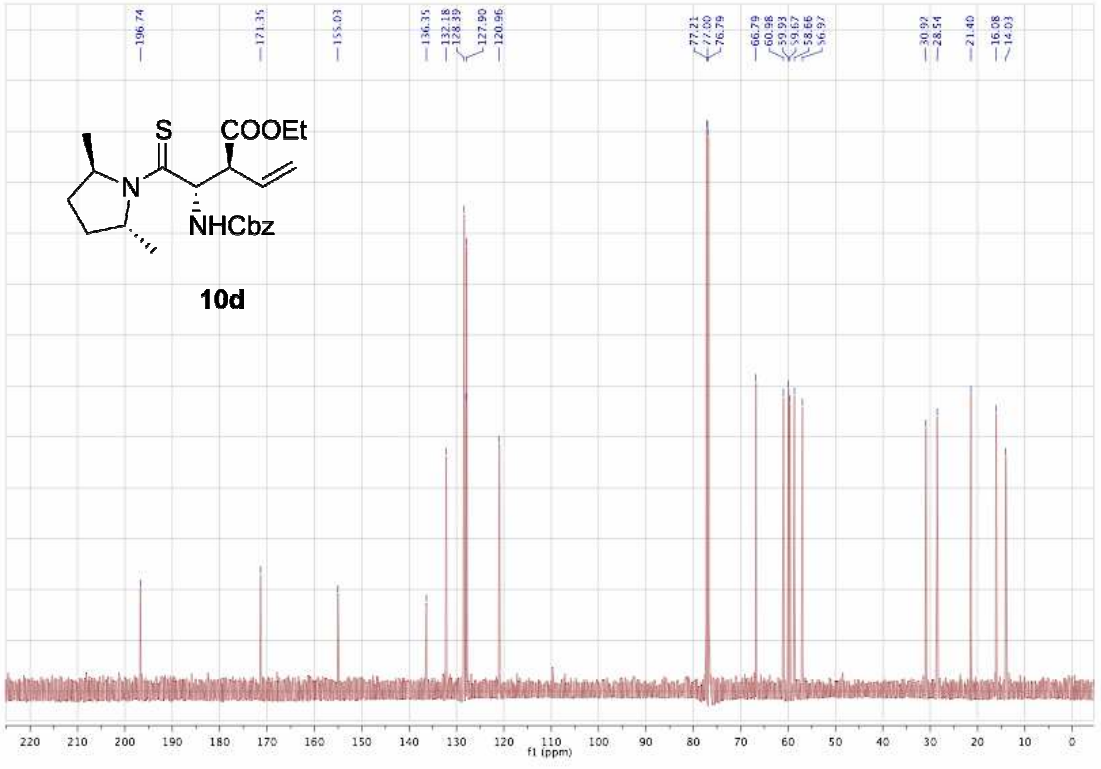
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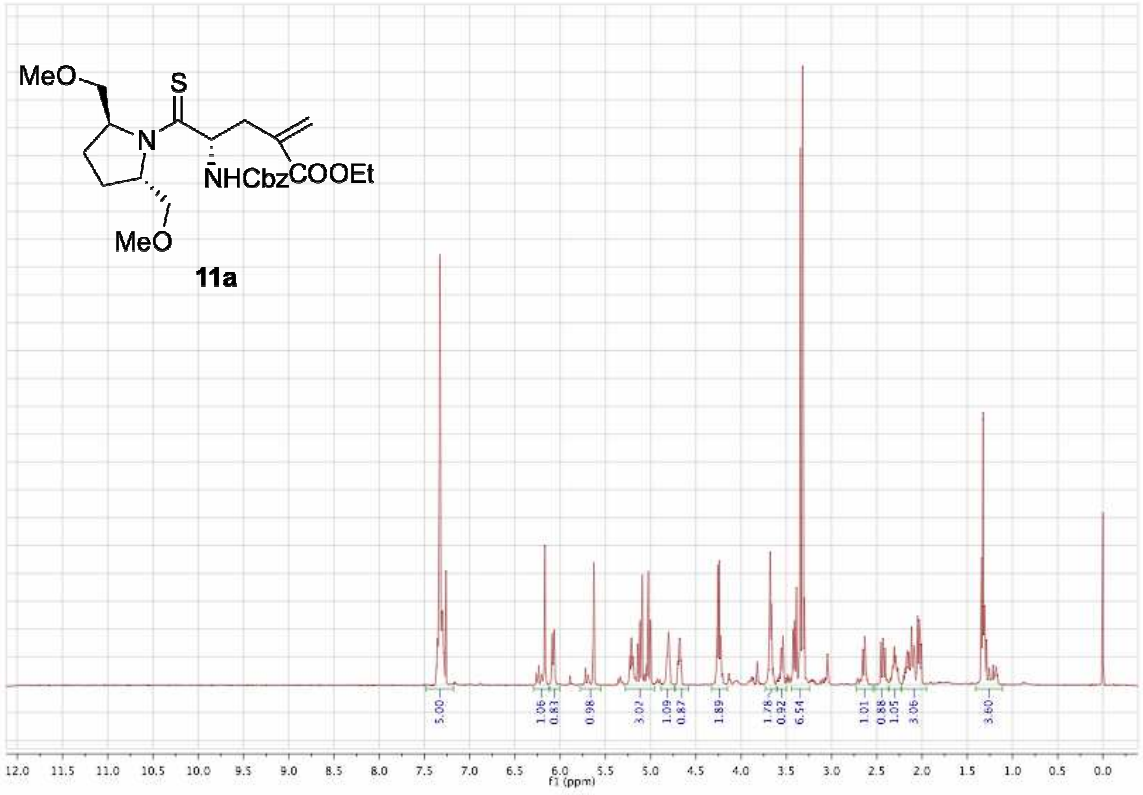
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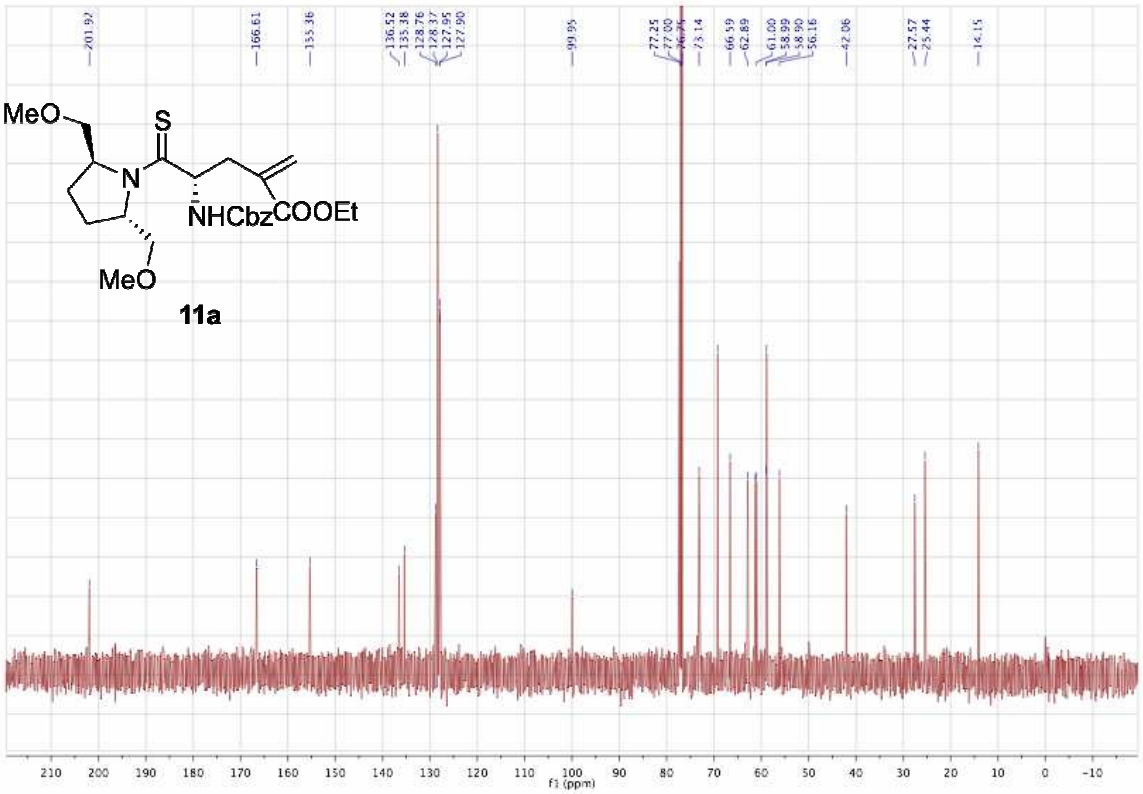
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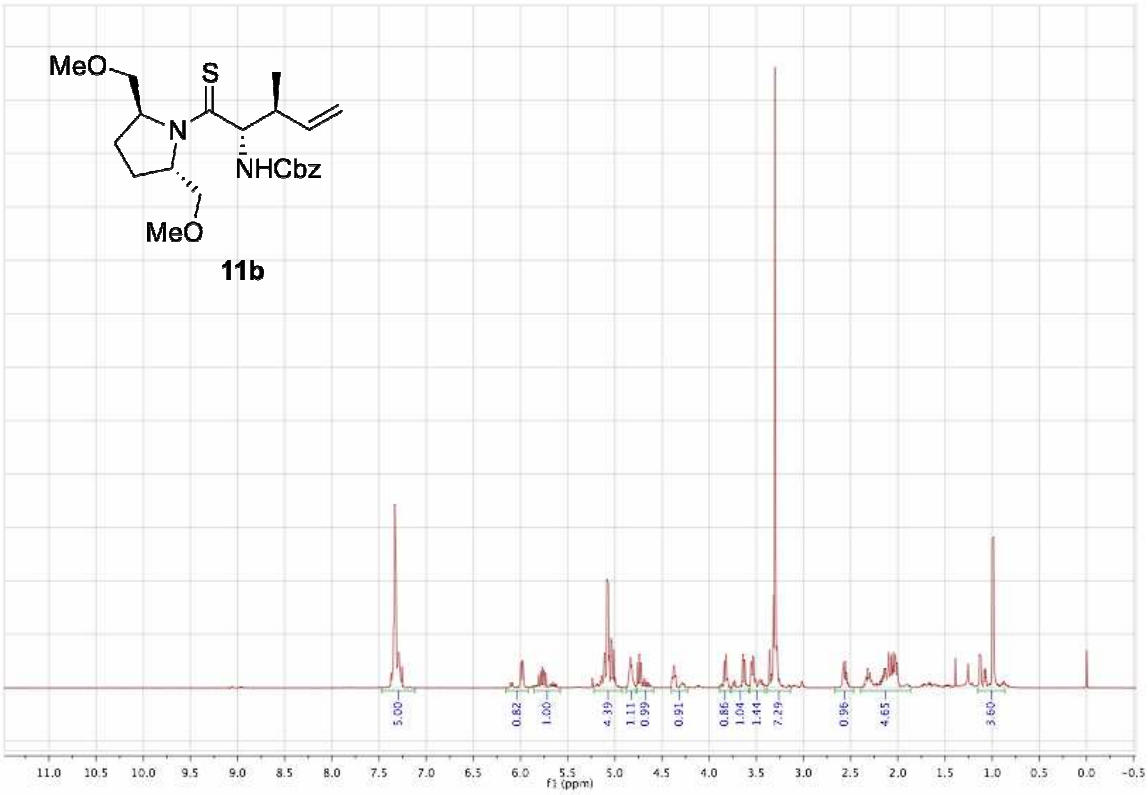
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3.60
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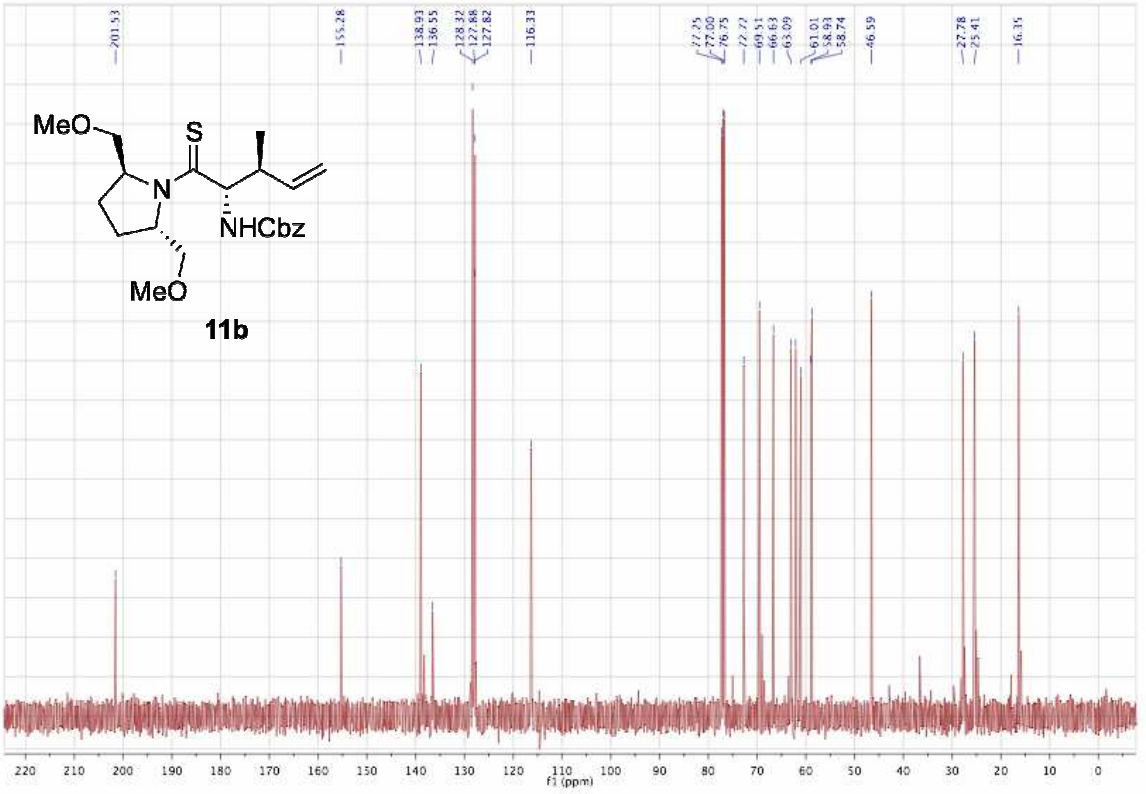
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46.59
27.78
25.41
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11b
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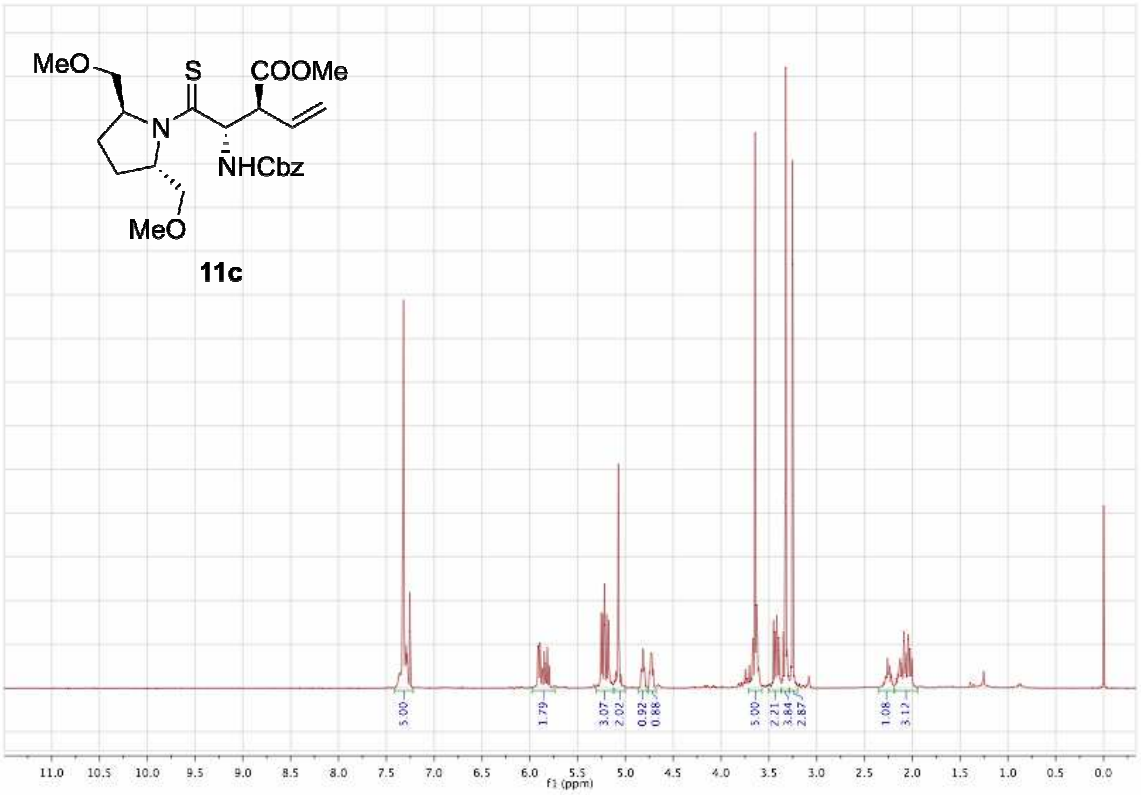
f1 (ppm)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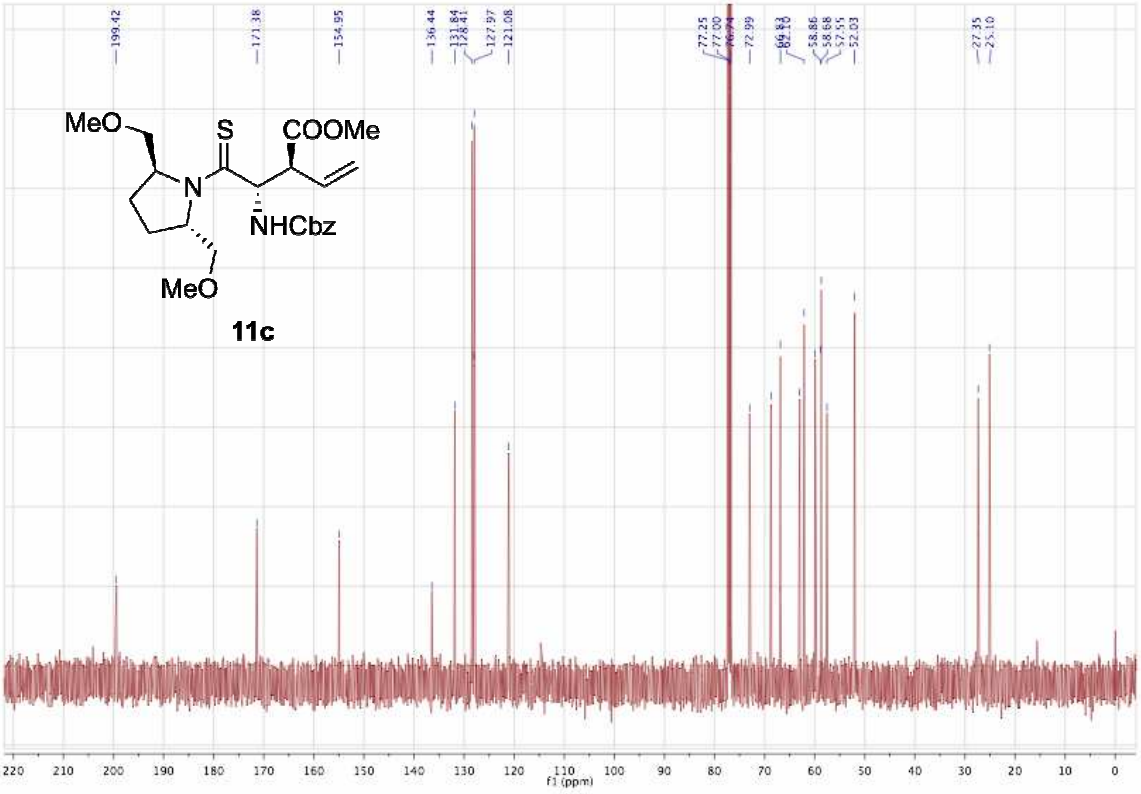
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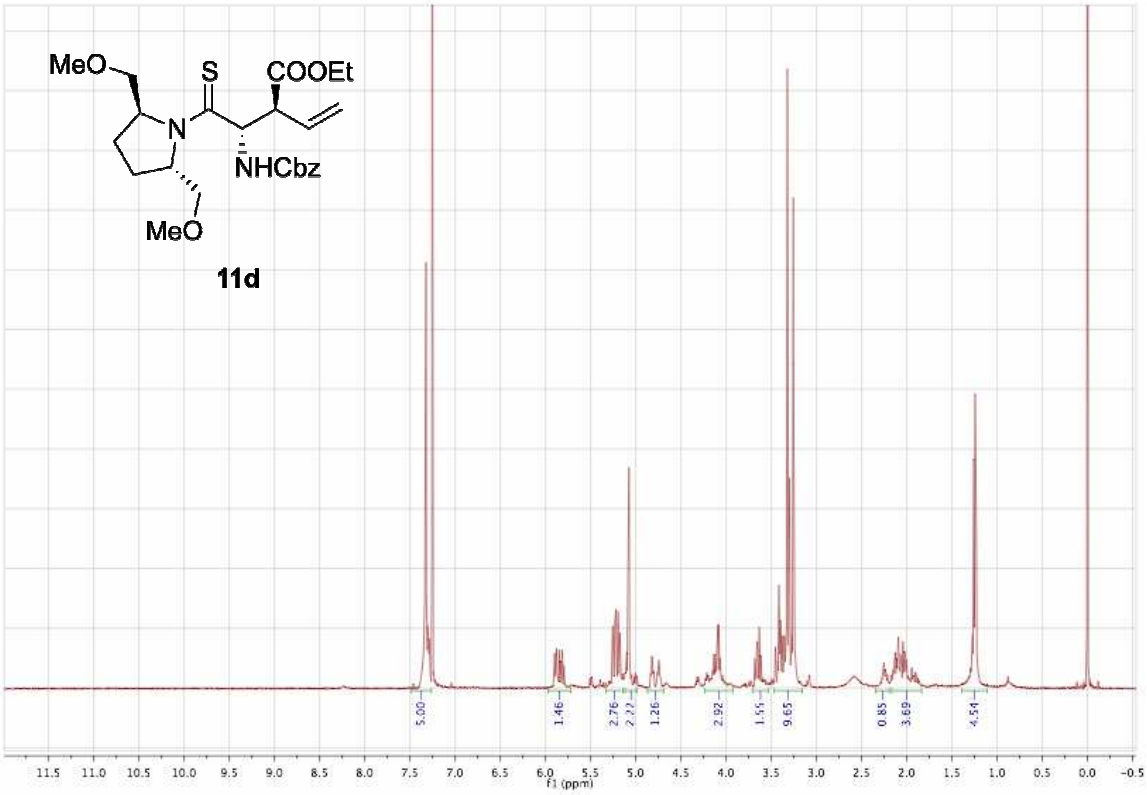
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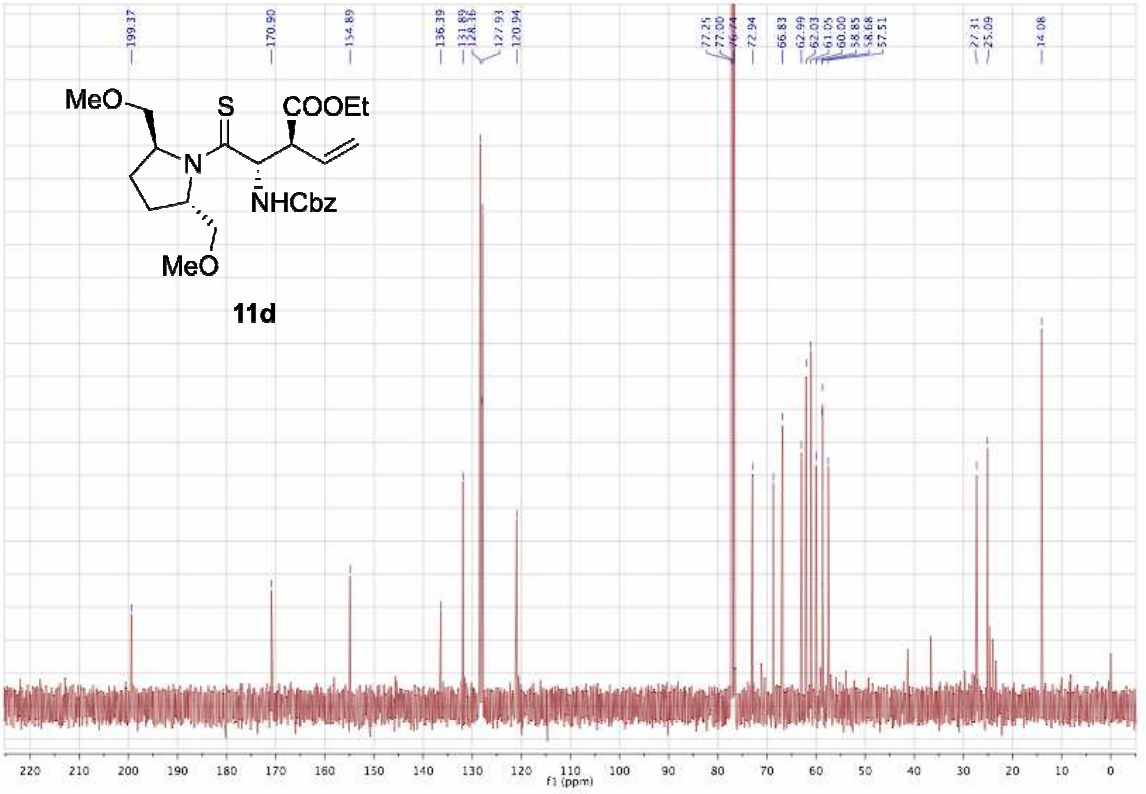
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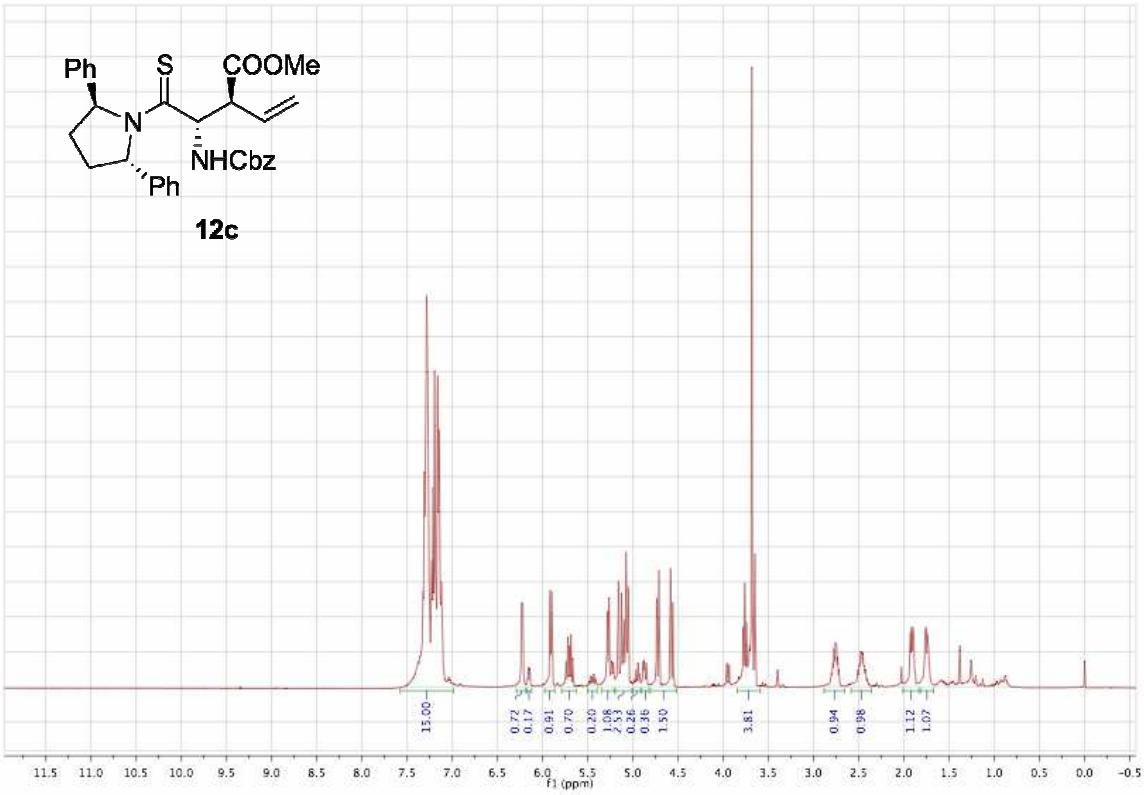
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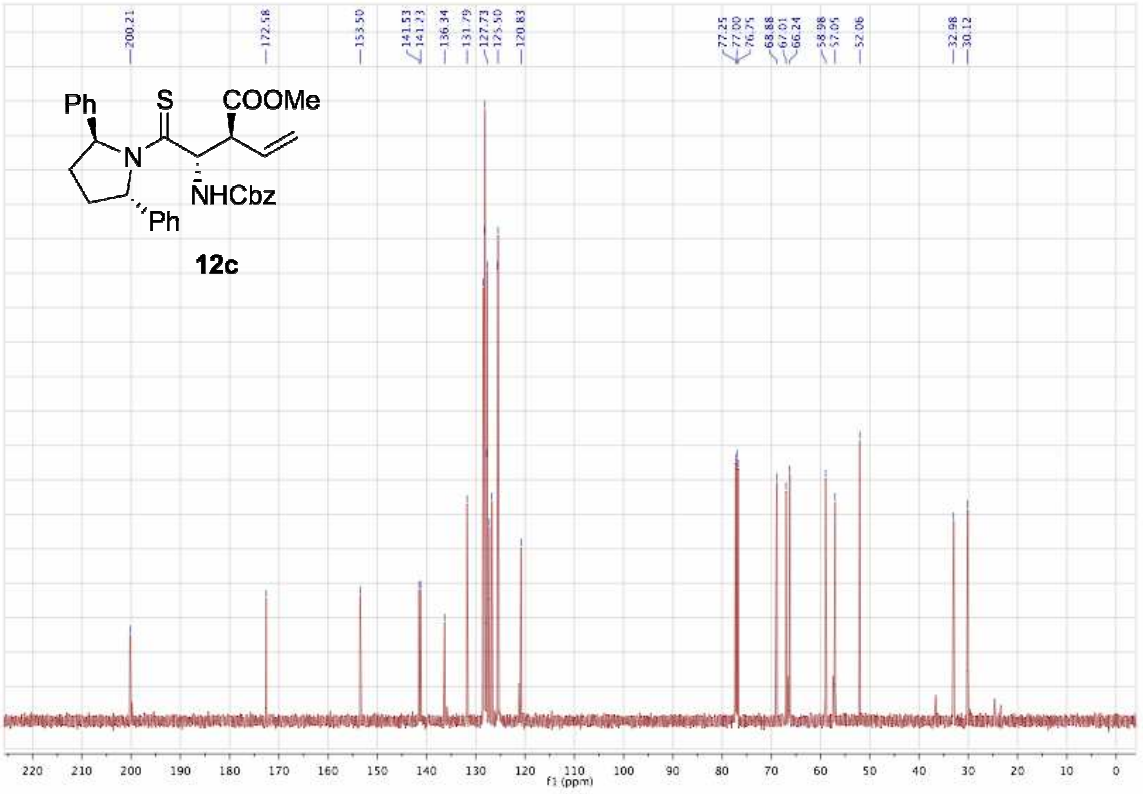
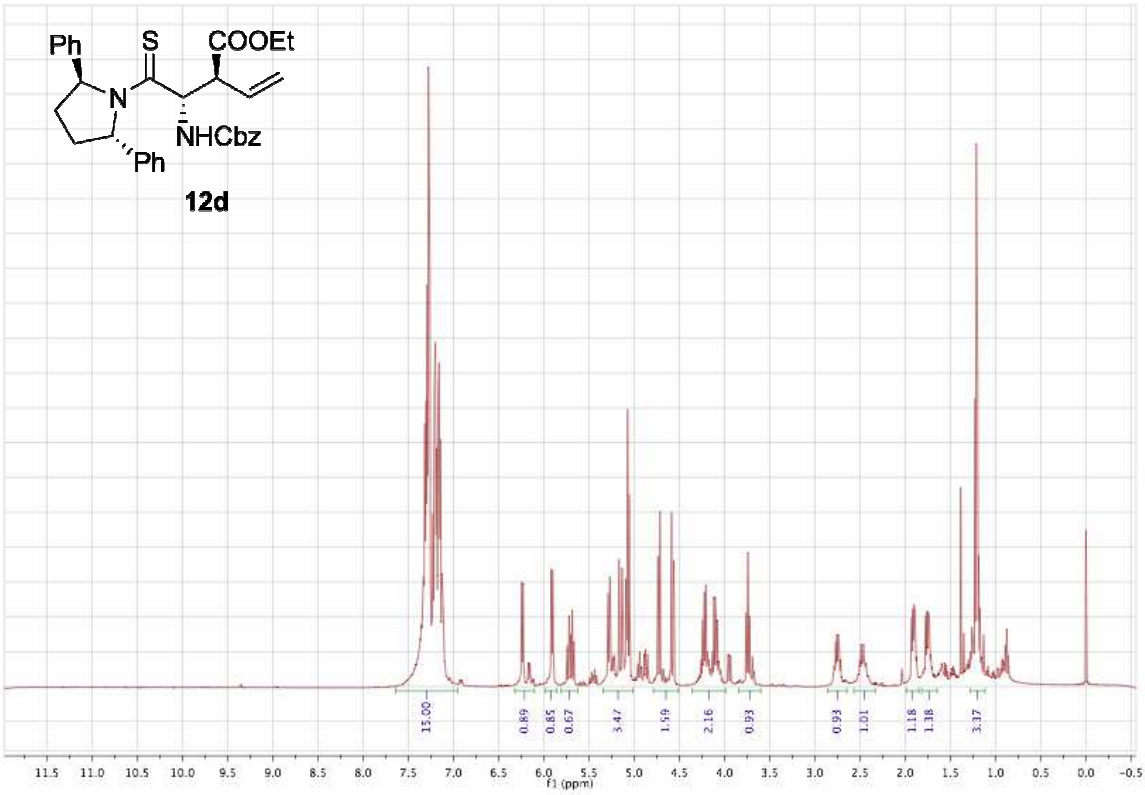
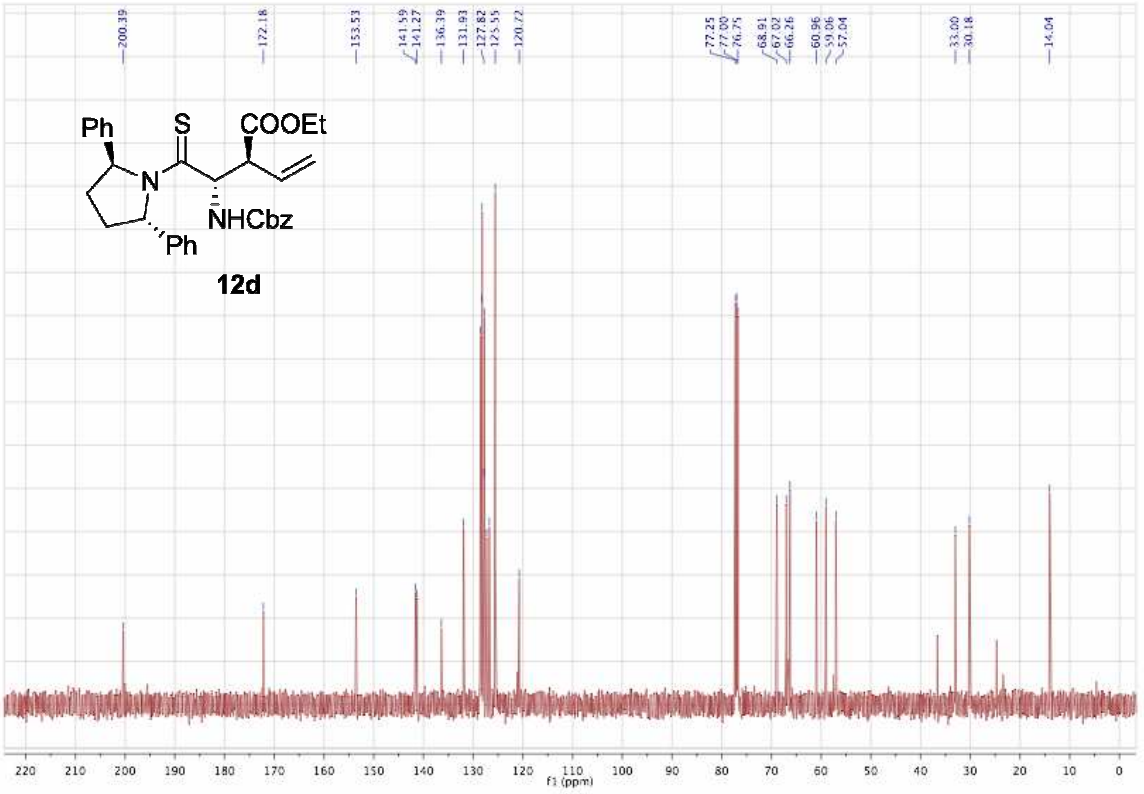
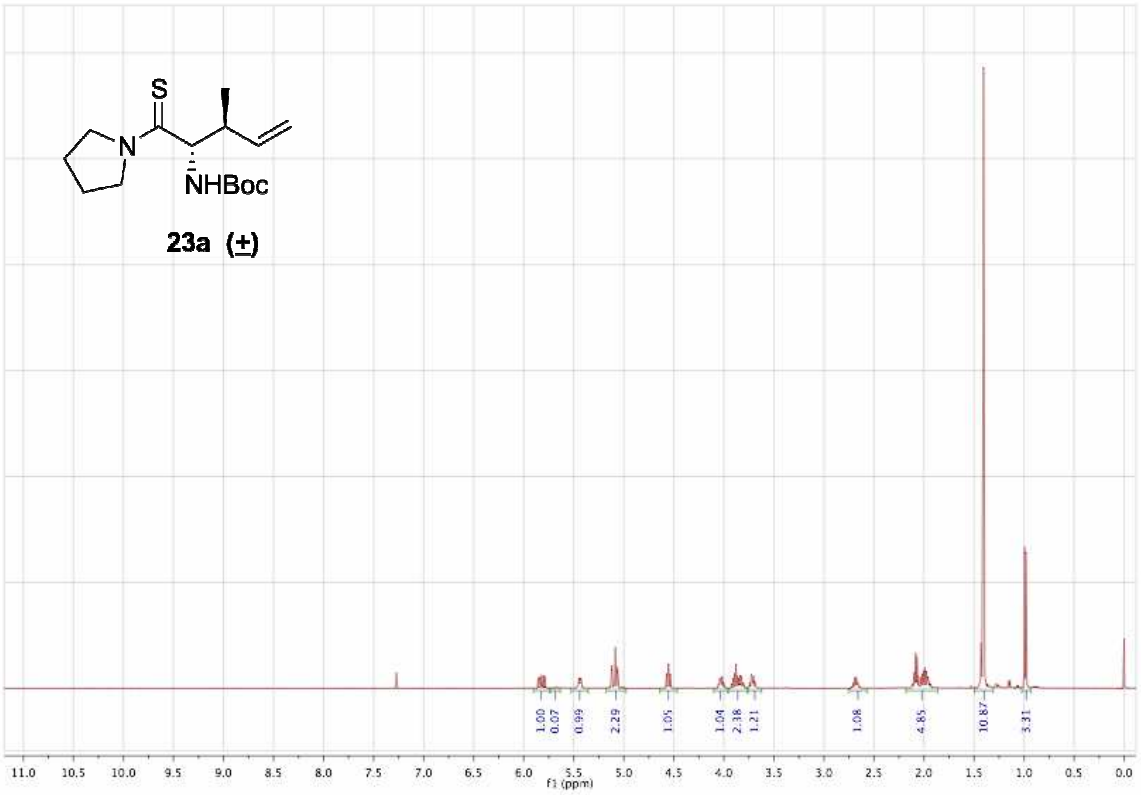
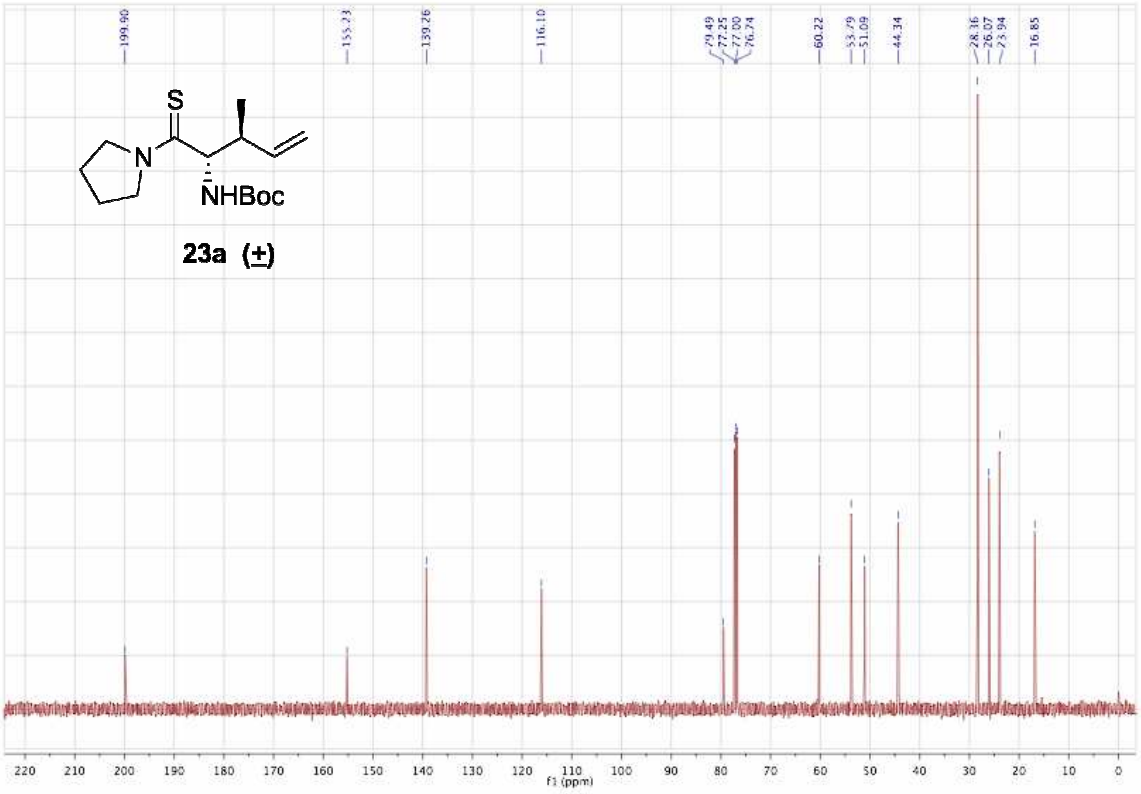
1.07
f1 (ppm)

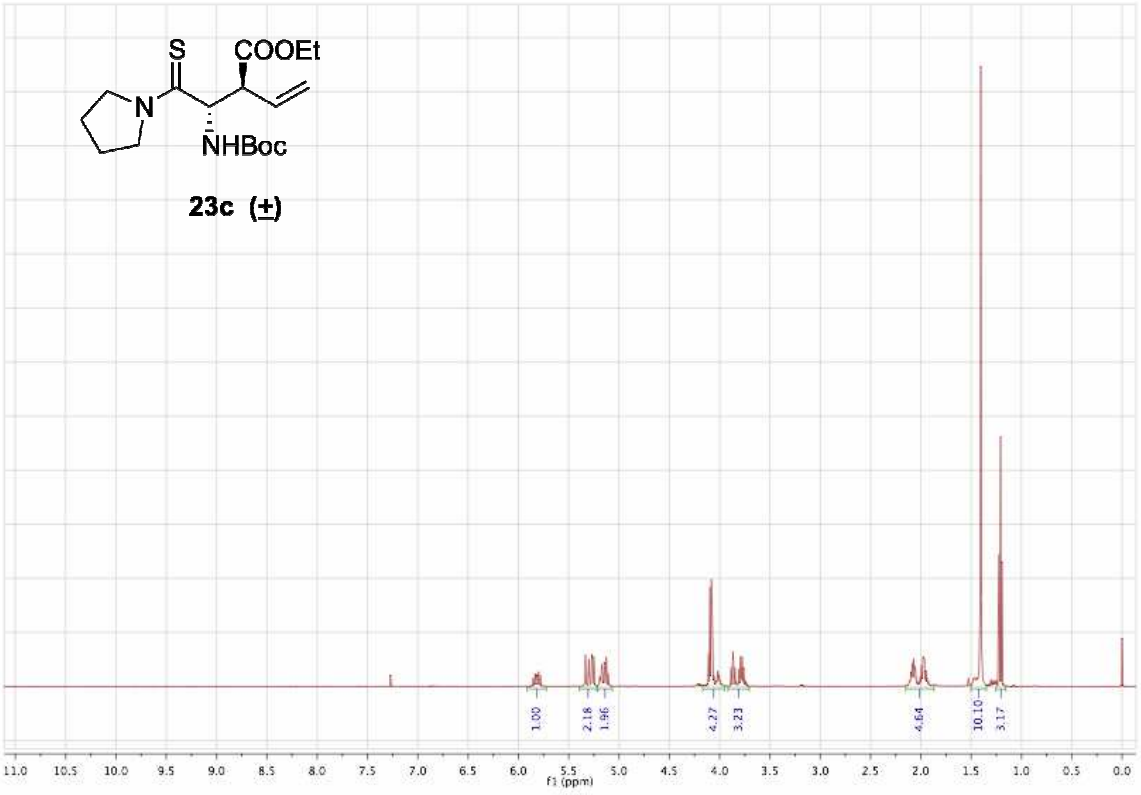

200.21
172.58
153.50
141.53
141.73
136.34
131.79
127.73
125.50
120.83
77.25
77.00
76.75
68.88
67.01
66.24
58.98
57.05
52.06
32.98
30.12
Ph
S
COOMe
N
NHCbz
Ph
12c
f1 (ppm)

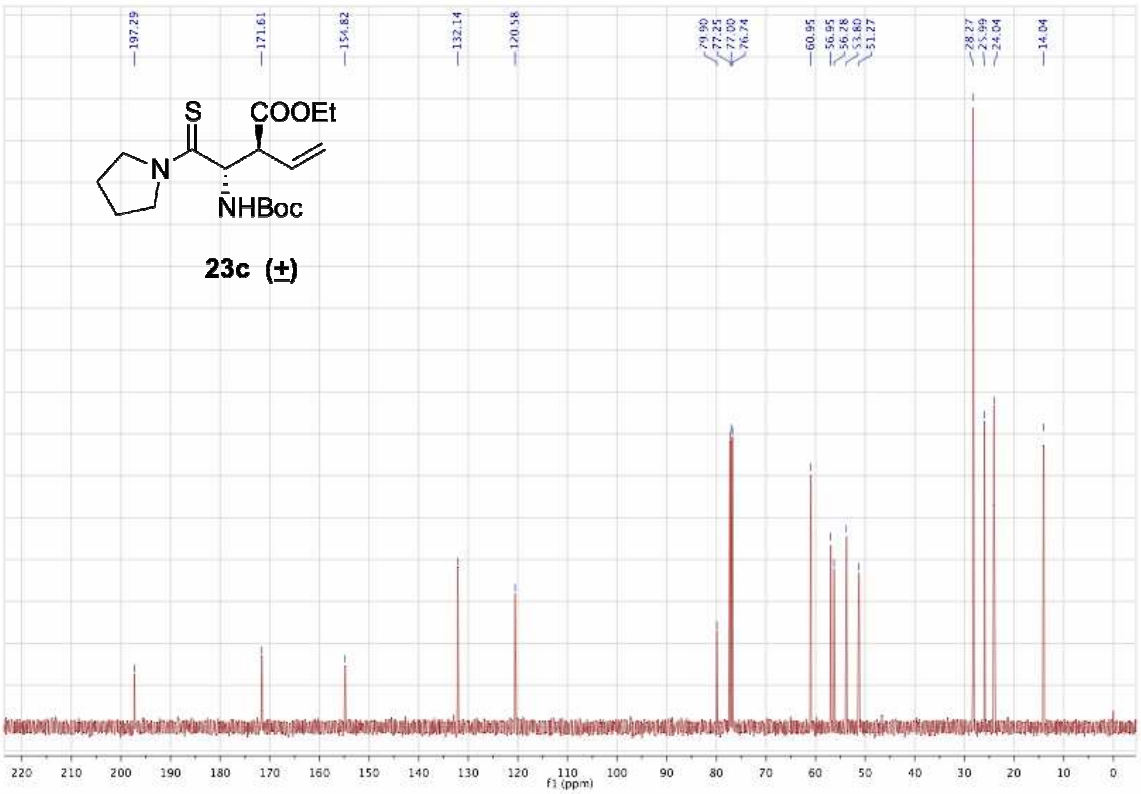

Ph
S
COOEt
N
NHCbz
Ph
12d
15.00
0.89
0.85
0.67
3.47
1.59
2.16
0.93
0.93
1.01
1.18
1.38
3.37
F1 (ppm)

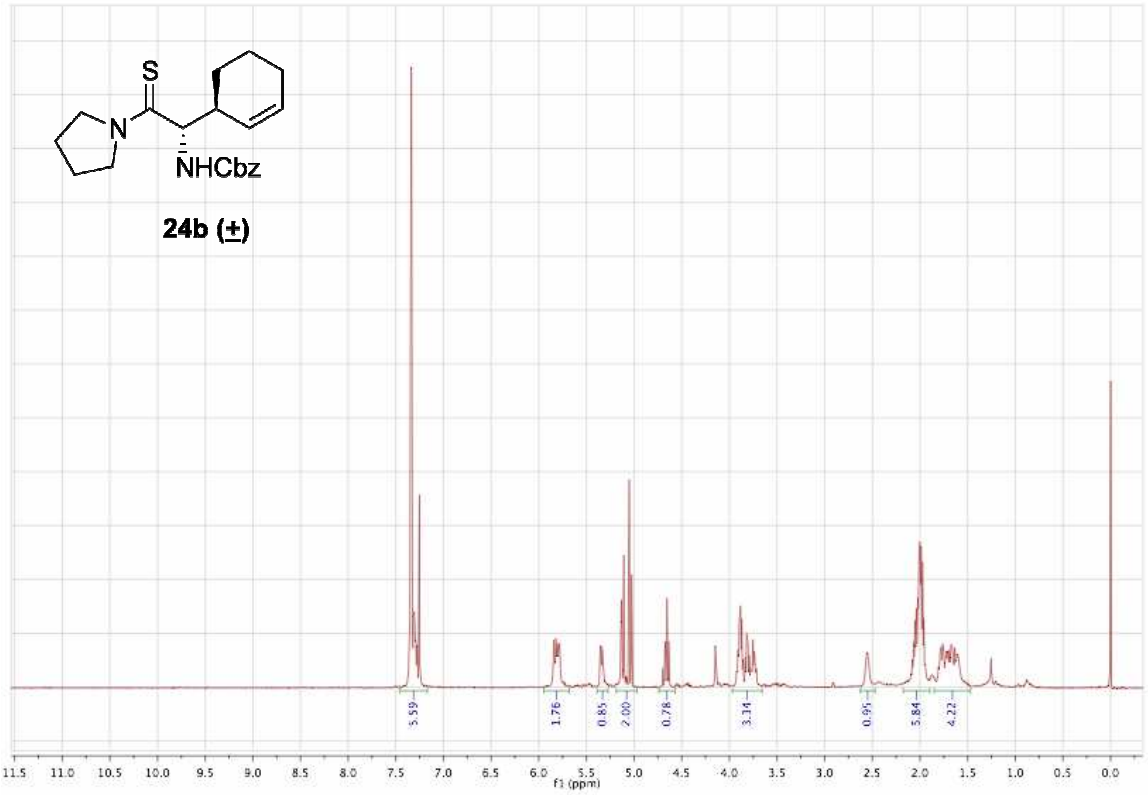

200.39
172.18
153.53
141.59
141.27
136.39
131.93
127.82
125.55
120.72
77.25
77.00
76.75
68.91
67.02
66.26
60.96
59.06
57.04
33.00
30.18
14.04
Ph
S
COOEt
N
NHCbz
Ph
12d
F1 (ppm)

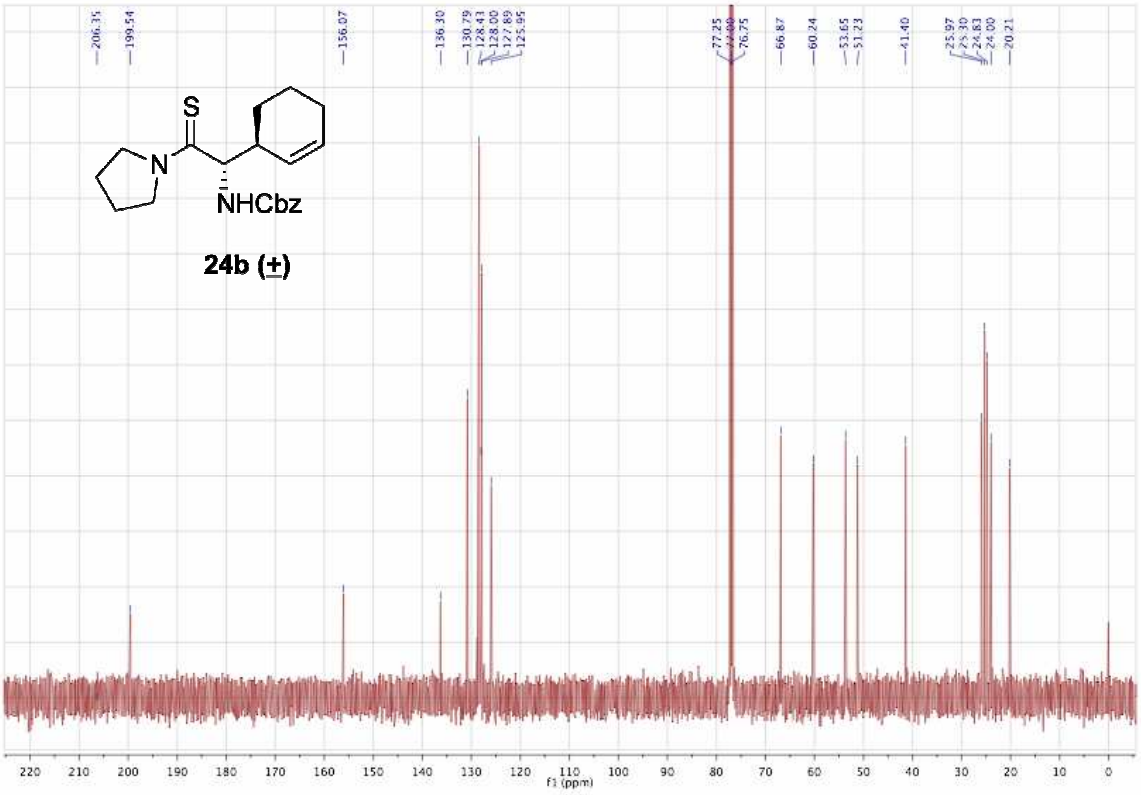

S
N
NHBoc
23a (±)
1.00
0.07
0.99
2.29
1.05
1.04
2.38
1.21
1.08
4.85
10.87
3.31
f1 (ppm)

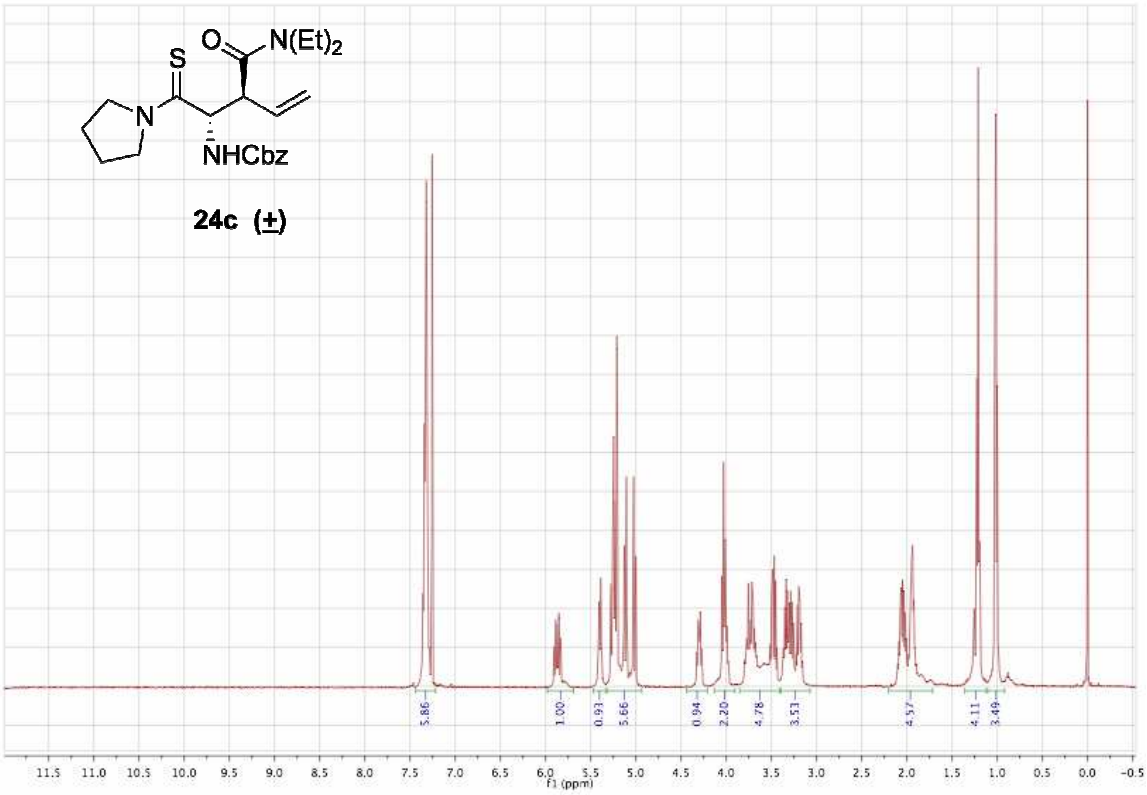

199.90
155.33
139.26
116.10
79.49
77.25
77.00
76.74
60.22
53.79
51.09
44.34
28.36
26.07
23.94
16.85
S
N
NHBoc
23a (±)
f1 (ppm)

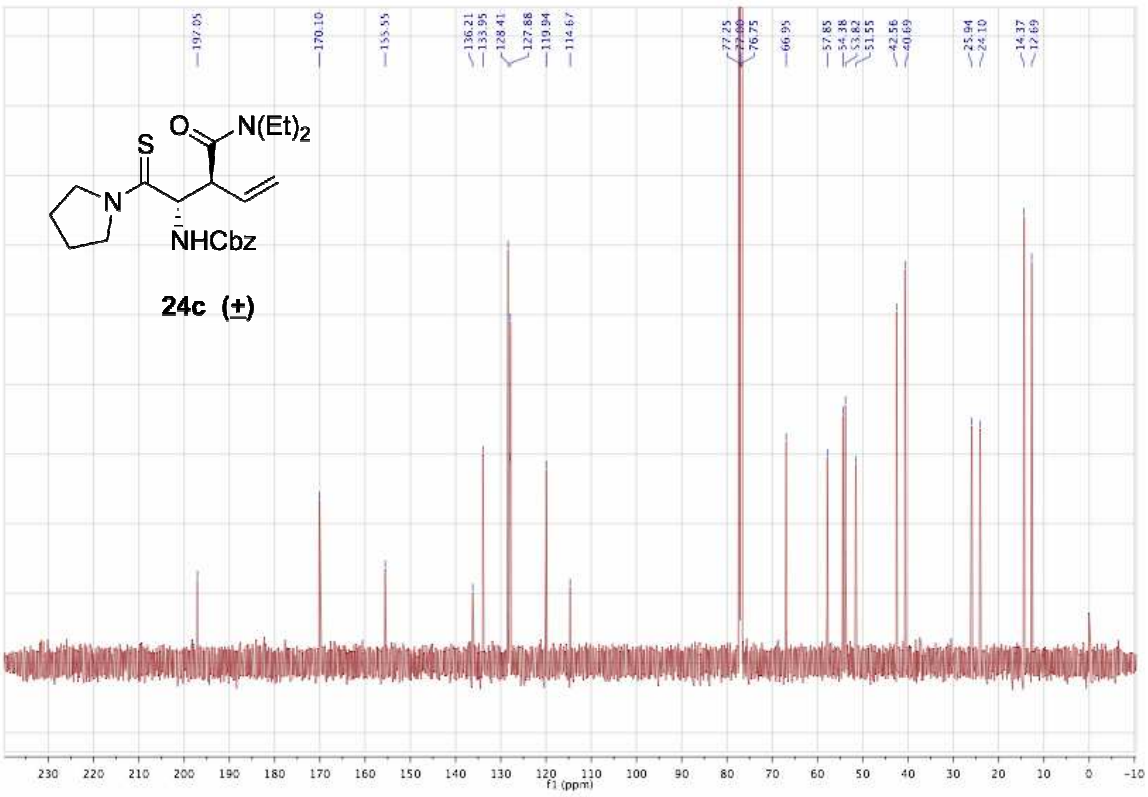

S
COOEt
N
NHBoc
23c (±)
1.00
2.18
1.96
4.27
3.23
4.64
10.10
3.17
f1 (ppm)

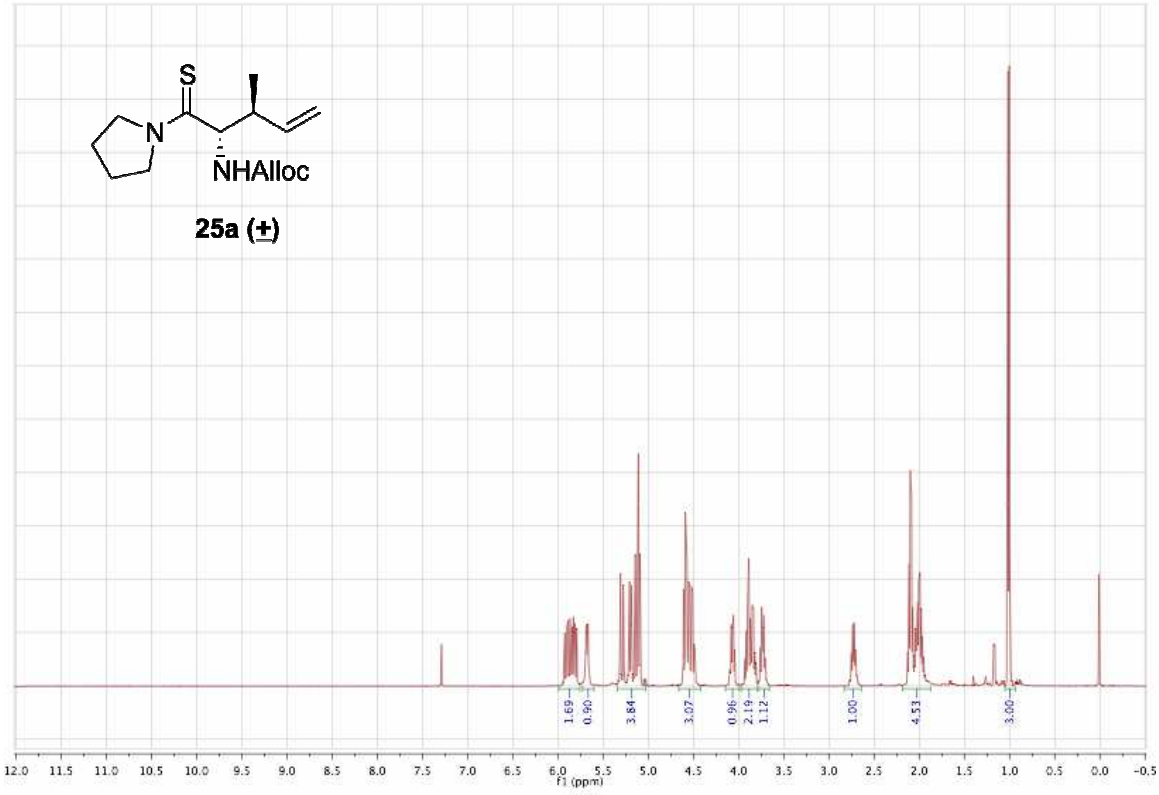

197.29
171.61
154.82
132.14
120.58
79.90
77.25
77.00
76.74
60.95
56.95
56.78
53.80
51.27
28.27
25.99
24.04
14.04
S
COOEt
N
NHBoc
23c (±)
f1 (ppm)

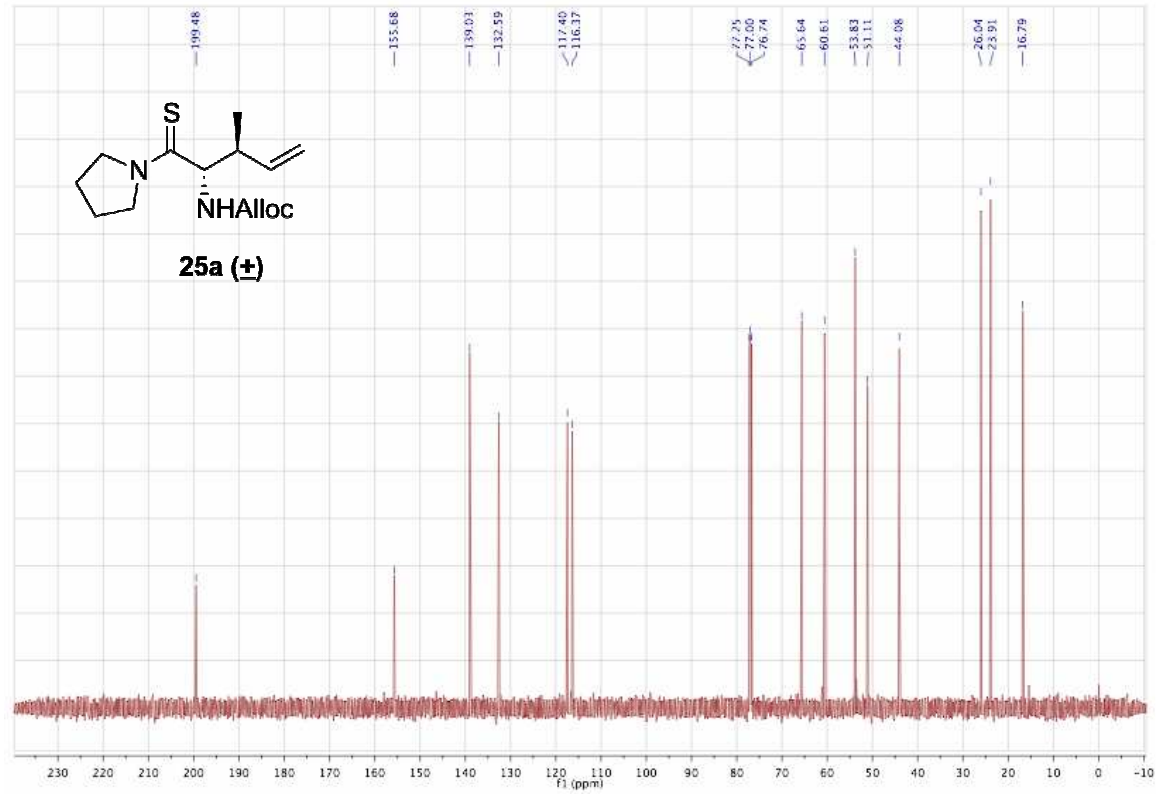

S
N
NHCbz
24b (±)
5.59
1.76
0.85
2.00
0.78
3.14
0.91
5.84
4.22
f1 (ppm)

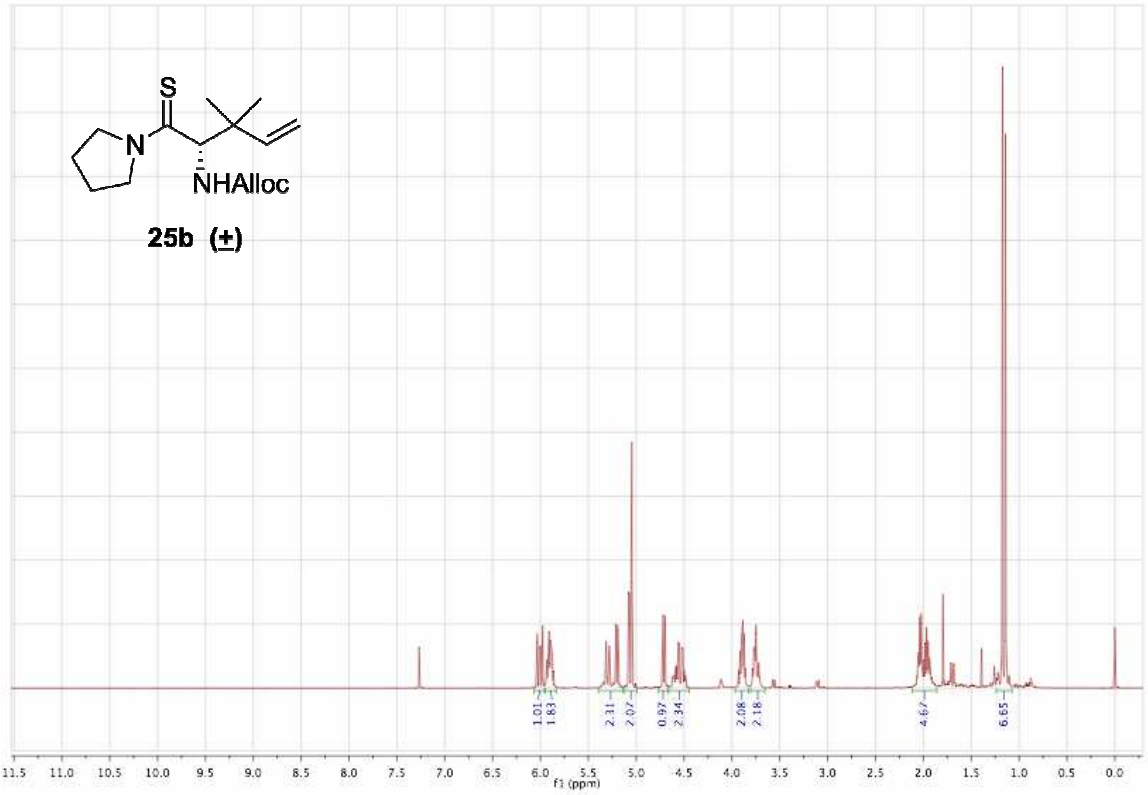

206.35
199.54
156.07
136.30
130.79
128.41
128.00
127.69
125.95
77.25
76.75
66.87
60.24
53.65
51.23
41.40
25.97
25.30
24.83
24.00
20.21
S
N
NHCbz
24b (±)
f1 (ppm)

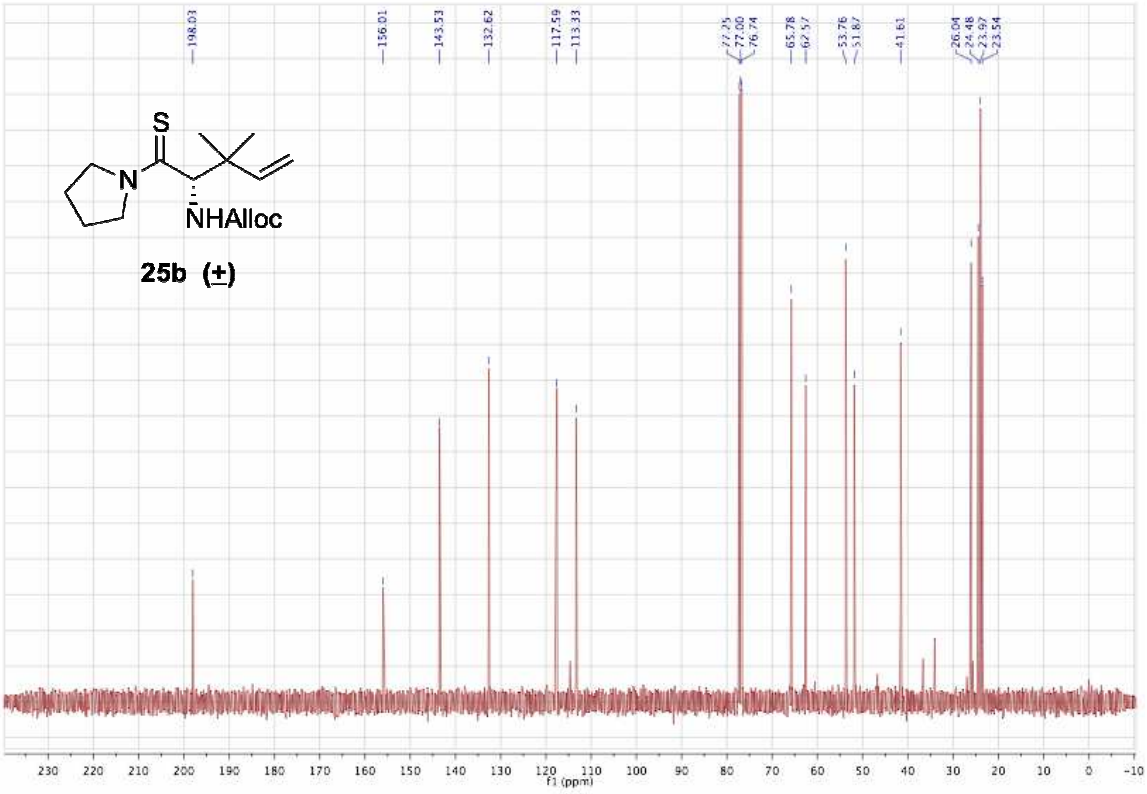

O
N(Et)2
S
N
NHCbz
24c (±)
5.86
1.00
0.93
5.66
0.94
2.20
4.78
3.53
4.57
4.11
3.49
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

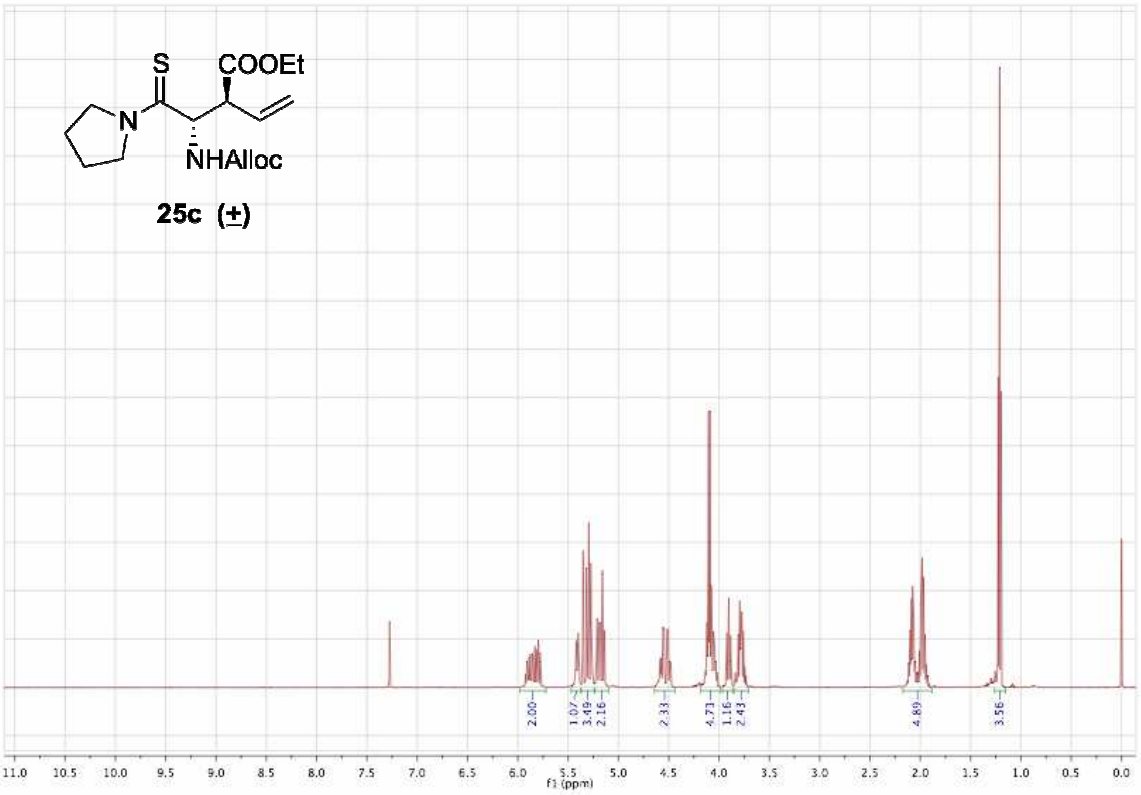

197.05
170.10
155.55
136.21
133.95
128.41
127.88
119.94
114.67
77.25
77.00
76.75
66.95
57.85
54.38
53.82
51.55
42.56
40.69
25.94
24.10
14.37
12.69
O
N(Et)2
S
N
NHCbz
24c (±)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

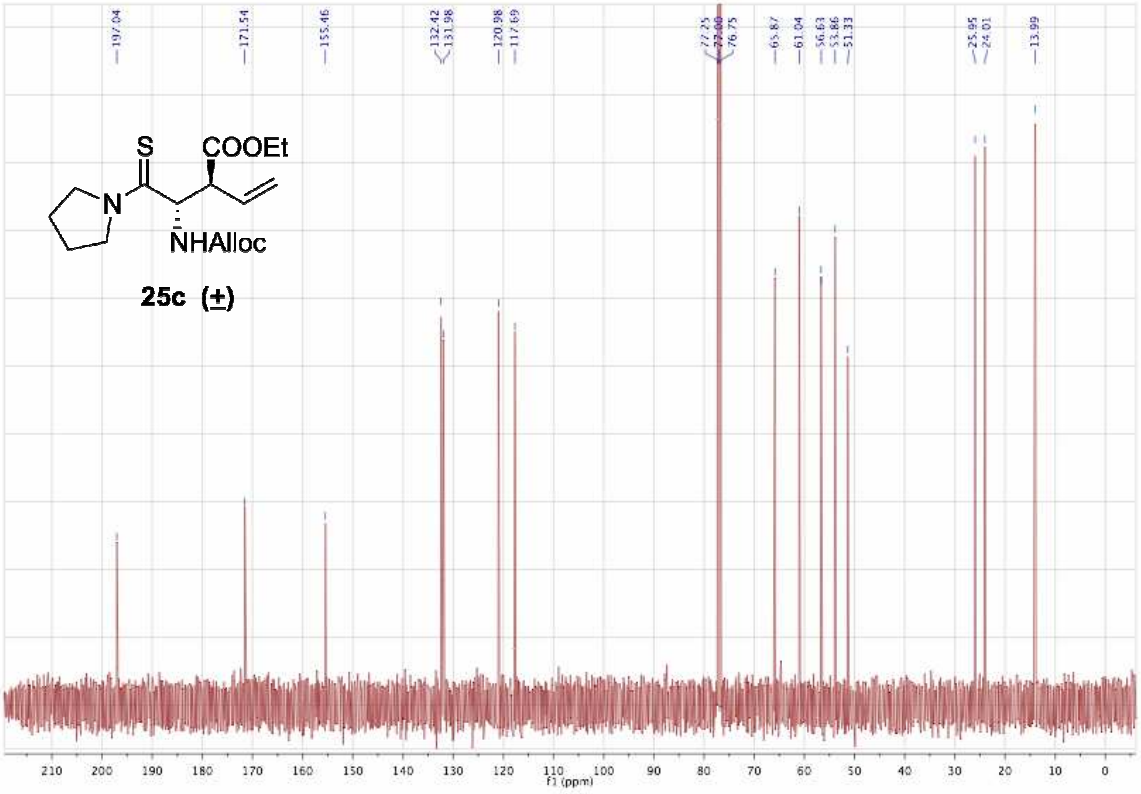

S
N
NHAlloc
25a (±)
1.69
0.90
3.84
3.07
0.96
2.19
1.12
1.00
4.53
3.06
f1 (ppm)

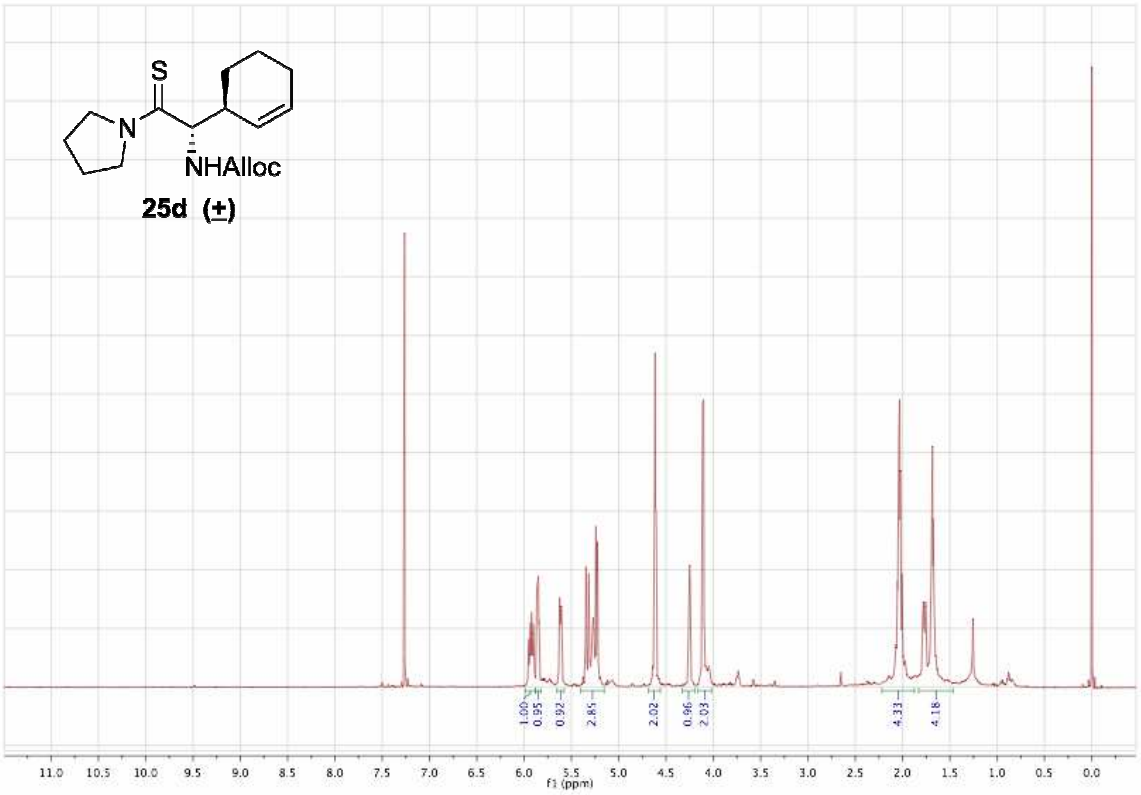

199.48
155.68
139.03
132.59
117.40
116.37
77.25
77.00
76.74
65.64
60.61
53.83
51.11
46.08
26.04
23.91
16.79
S
N
NHAlloc
25a (±)
f1 (ppm)

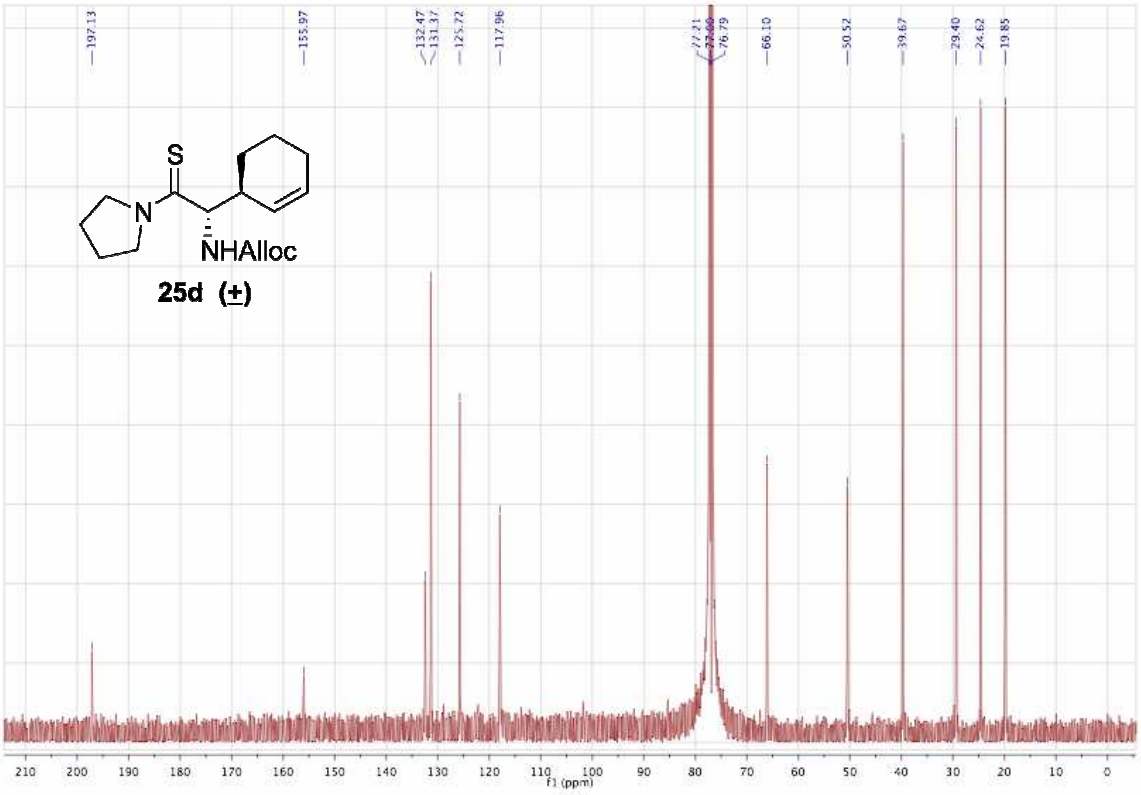

S
N
NHAlloc
25b (±)
1.01
1.83
2.31
2.07
0.97
2.34
2.08
2.18
4.67
6.65
f1 (ppm)

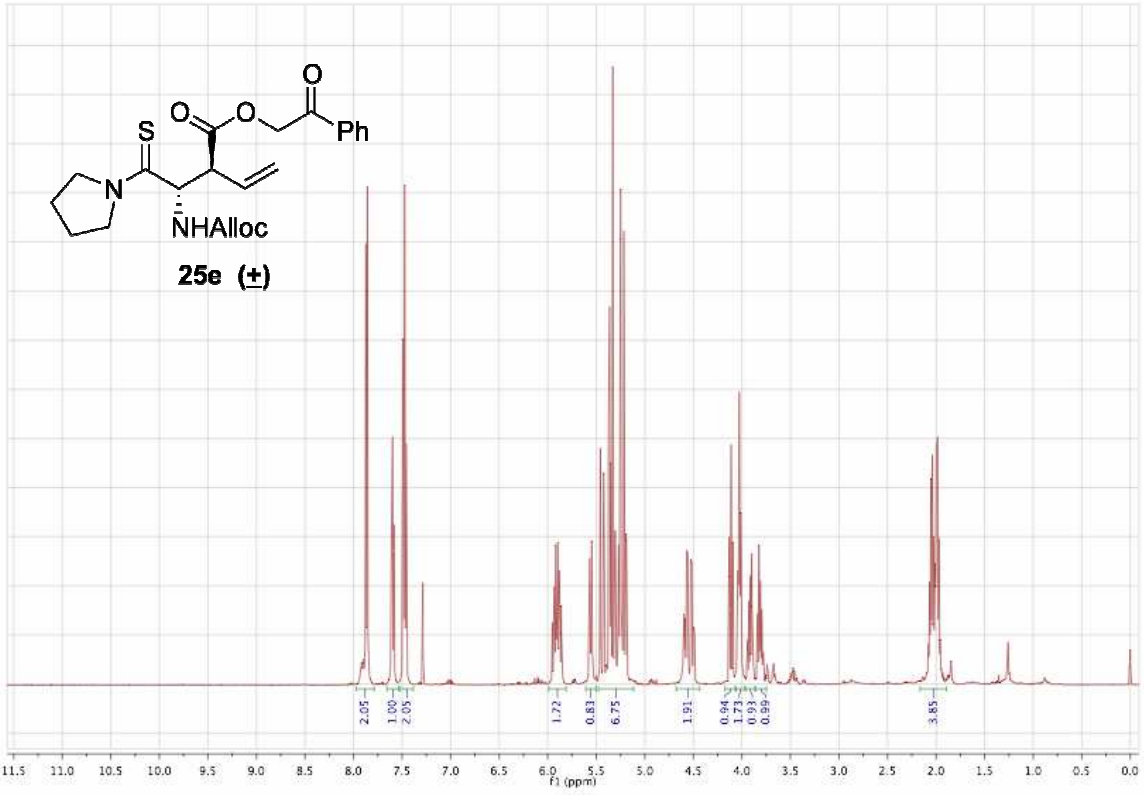

198.03
156.01
143.53
132.62
117.59
113.33
77.25
77.00
76.74
65.78
62.57
53.76
51.87
41.61
26.04
24.48
23.97
23.54
S
N
NHAlloc
25b (±)
f1 (ppm)

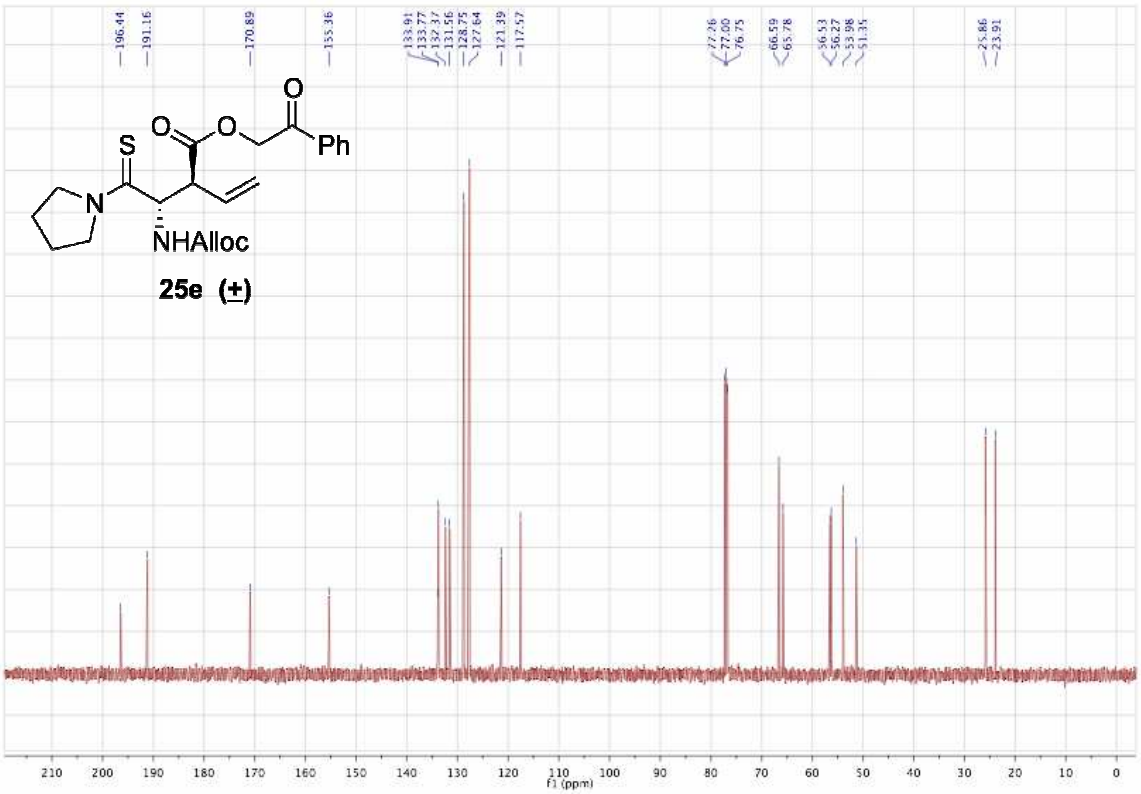

S
COOEt
N
NHAlloc
25c (±)
2.00
1.07
3.49
2.16
2.33
4.73
1.16
2.43
4.89
3.56
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

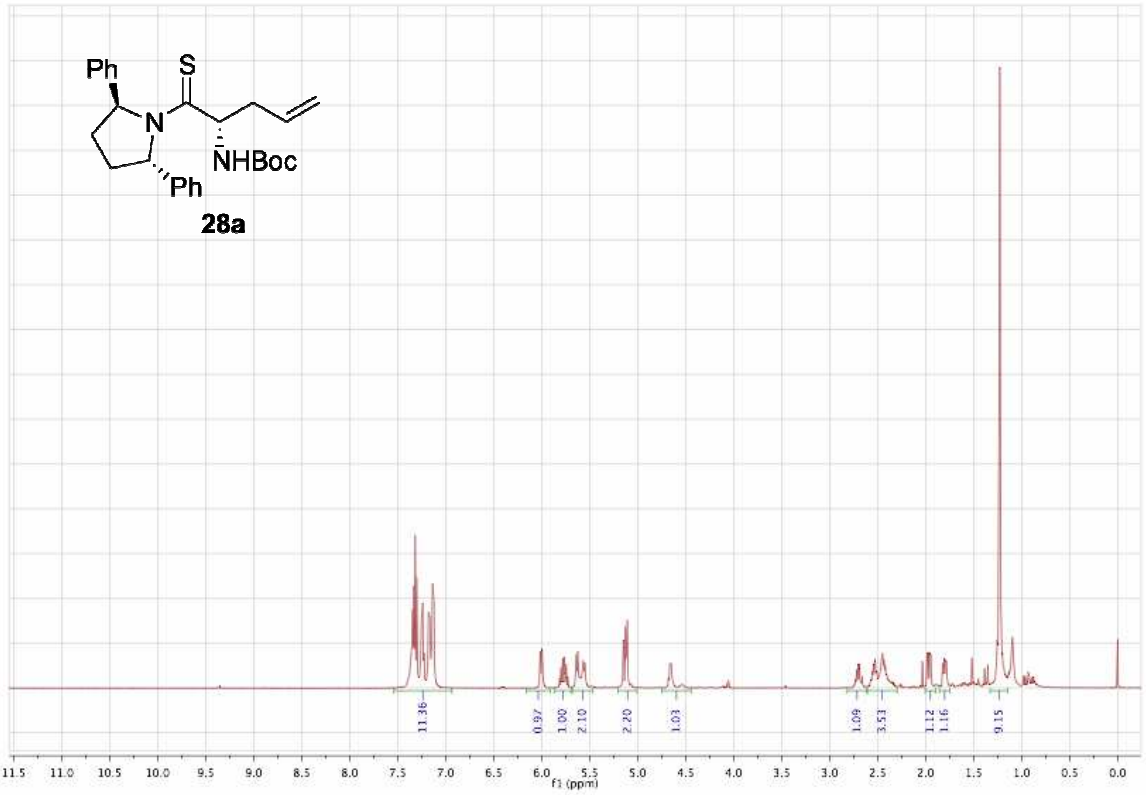

197.04
171.54
155.46
132.42
131.98
120.98
117.69
77.25
77.00
76.75
65.87
61.04
56.63
53.86
51.33
25.95
24.01
13.99
S
COOEt
N
NHAlloc
25c (±)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

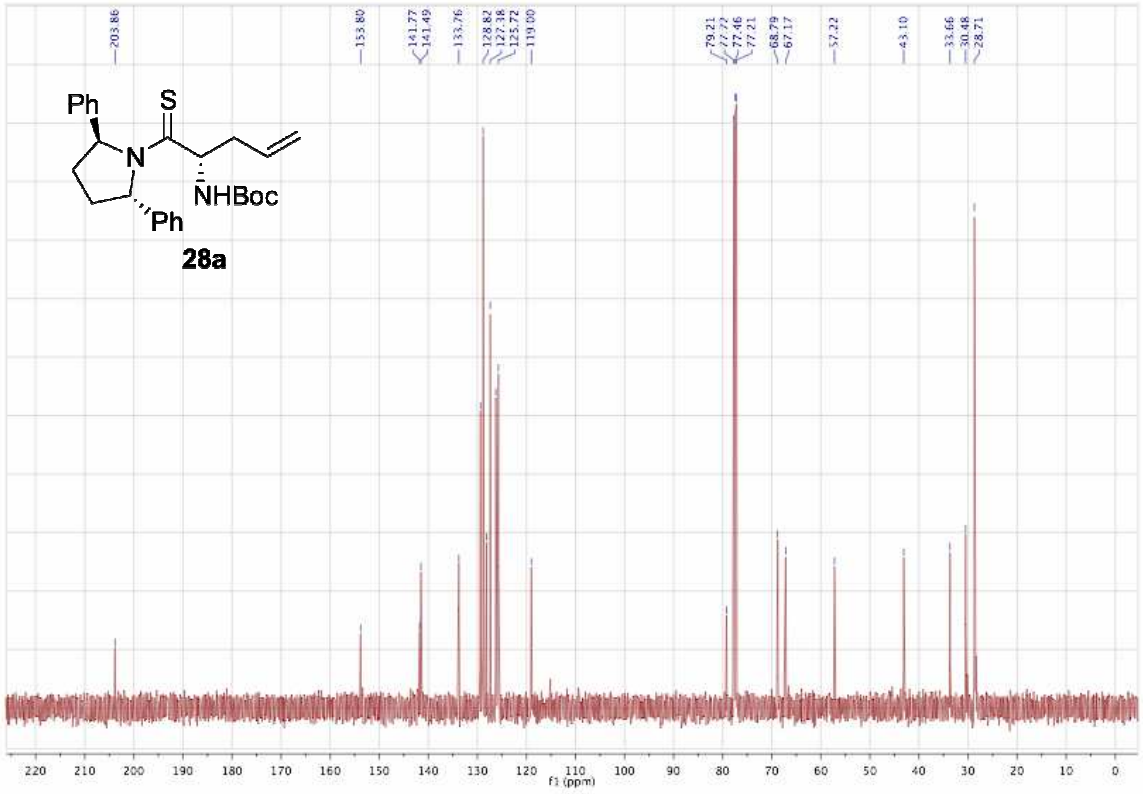

S
N
NHAlloc
25d (±)
1.00
0.95
0.92
2.85
2.02
0.96
2.03
4.33
4.18
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

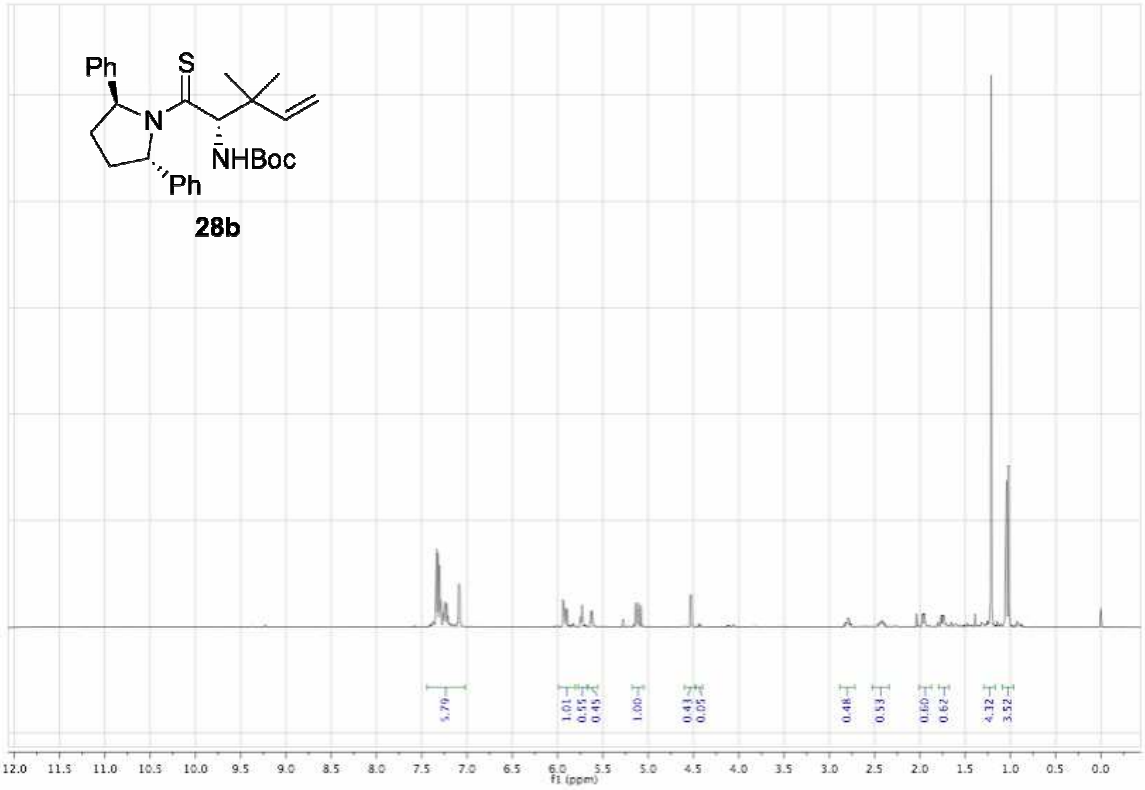

197.13
155.97
132.47
131.37
125.72
117.96
77.21
77.00
76.79
66.10
50.52
39.67
29.40
24.62
19.85
S
N
NHAlloc
25d (±)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

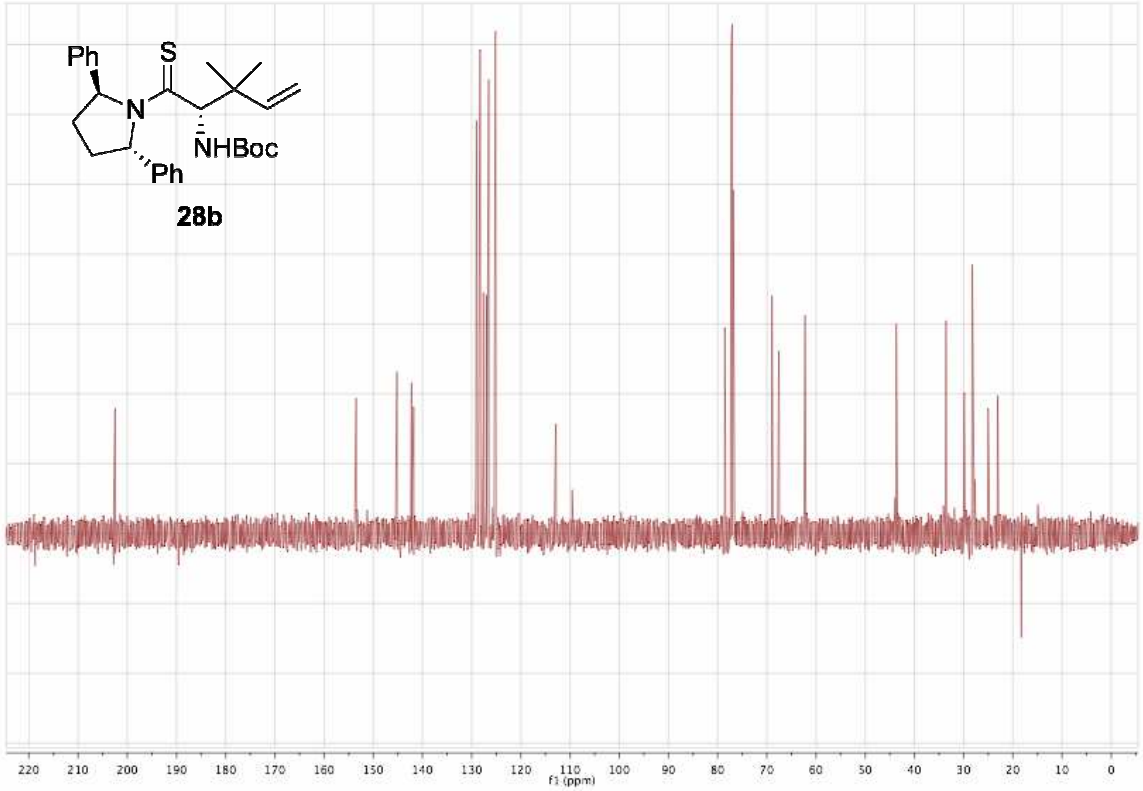

25e (±)
NHAlloc
Ph
f1 (ppm)

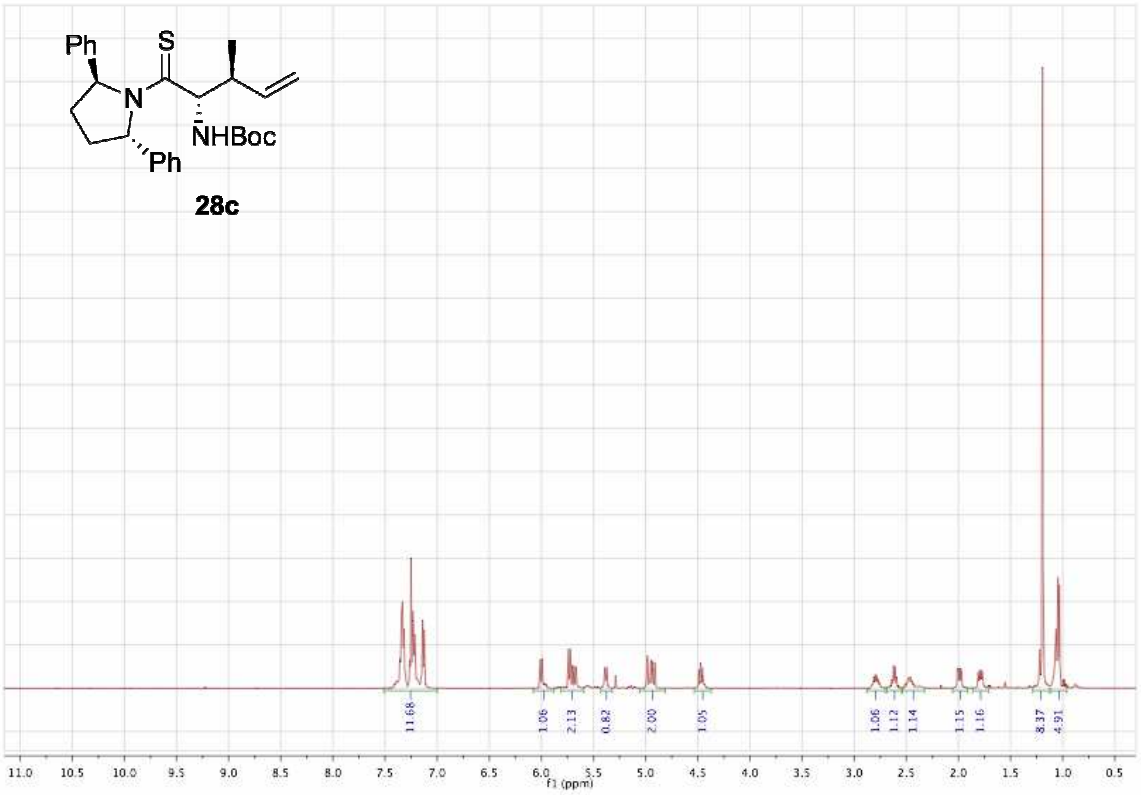

25e (±)
NHAlloc
Ph
f1 (ppm)

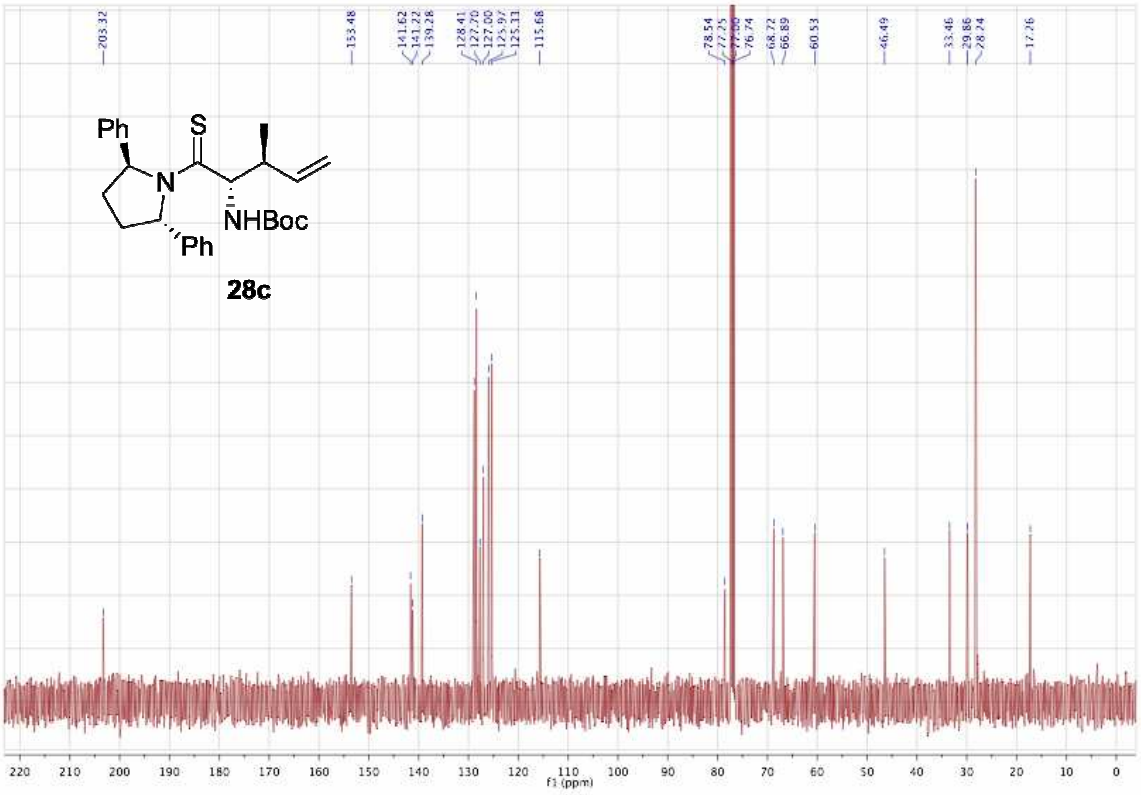

Ph
S
N
NHBoc
Ph
28a
11.36
0.97
1.00
2.10
2.20
1.03
1.09
3.53
1.12
1.16
9.15
F1 (ppm)

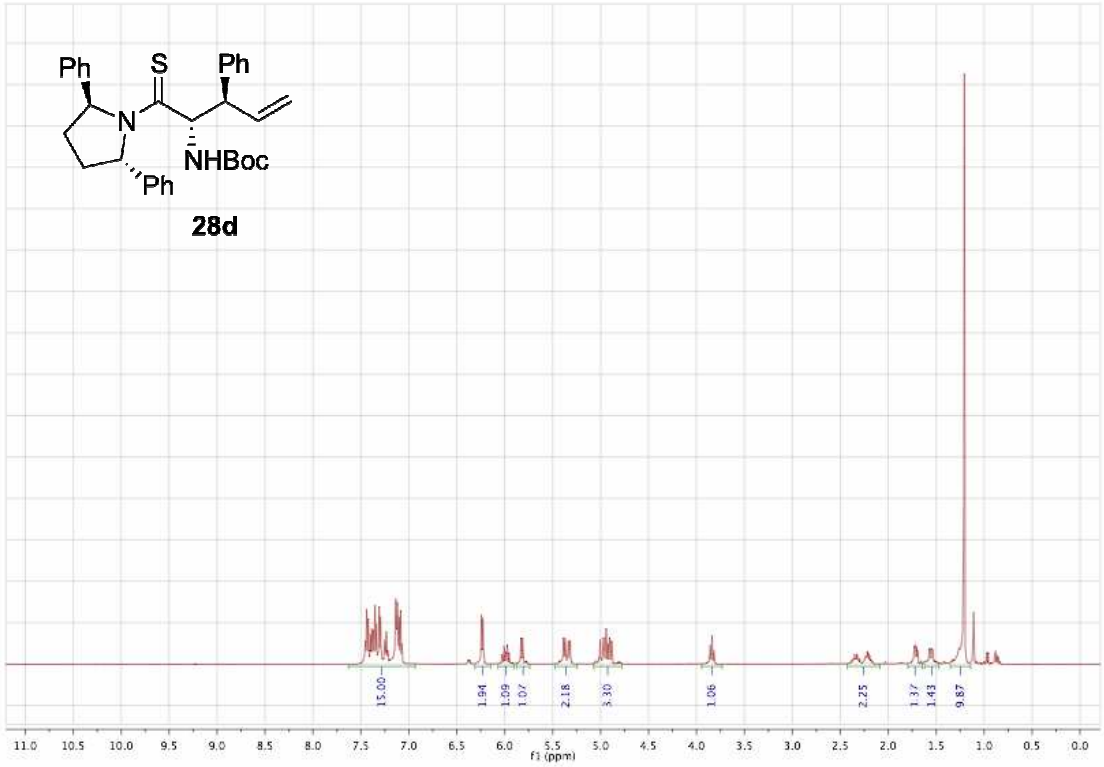

203.86
153.80
141.77
141.49
133.76
128.82
127.38
125.72
119.00
79.21
77.72
77.46
77.21
68.79
67.17
57.22
43.10
33.66
30.48
28.71
Ph
S
N
NHBoc
Ph
28a
F1 (ppm)

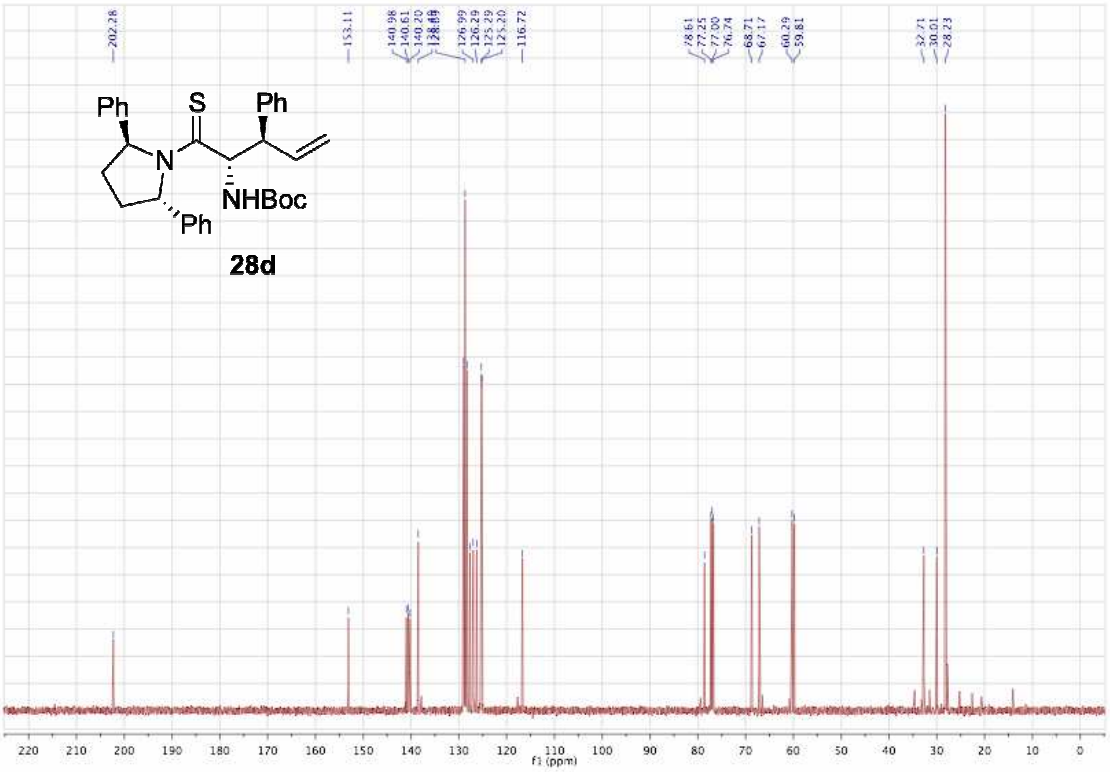

Ph
S
N
NHBoc
Ph
28b
5.79
1.01
0.55
0.49
1.00
0.43
0.05
0.48
0.53
0.60
0.62
4.32
3.52
f1 (ppm)

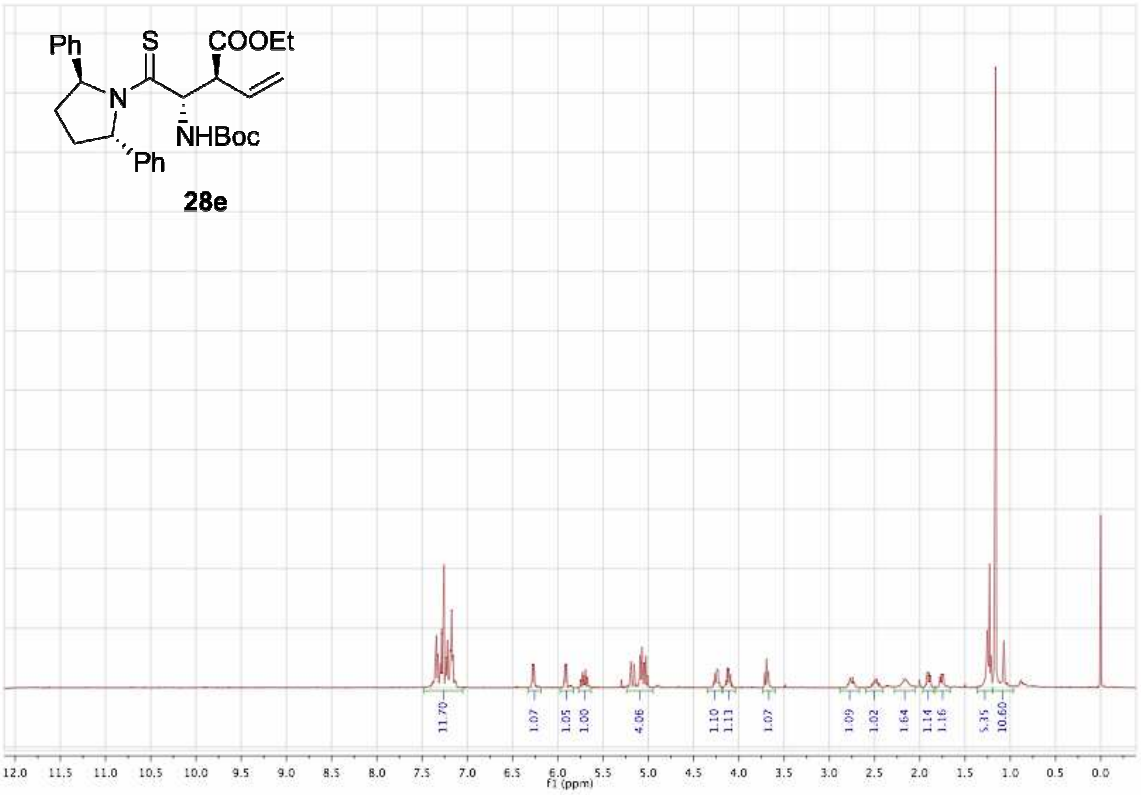

Ph
S
N
NHBoc
Ph
28b
f1 (ppm)

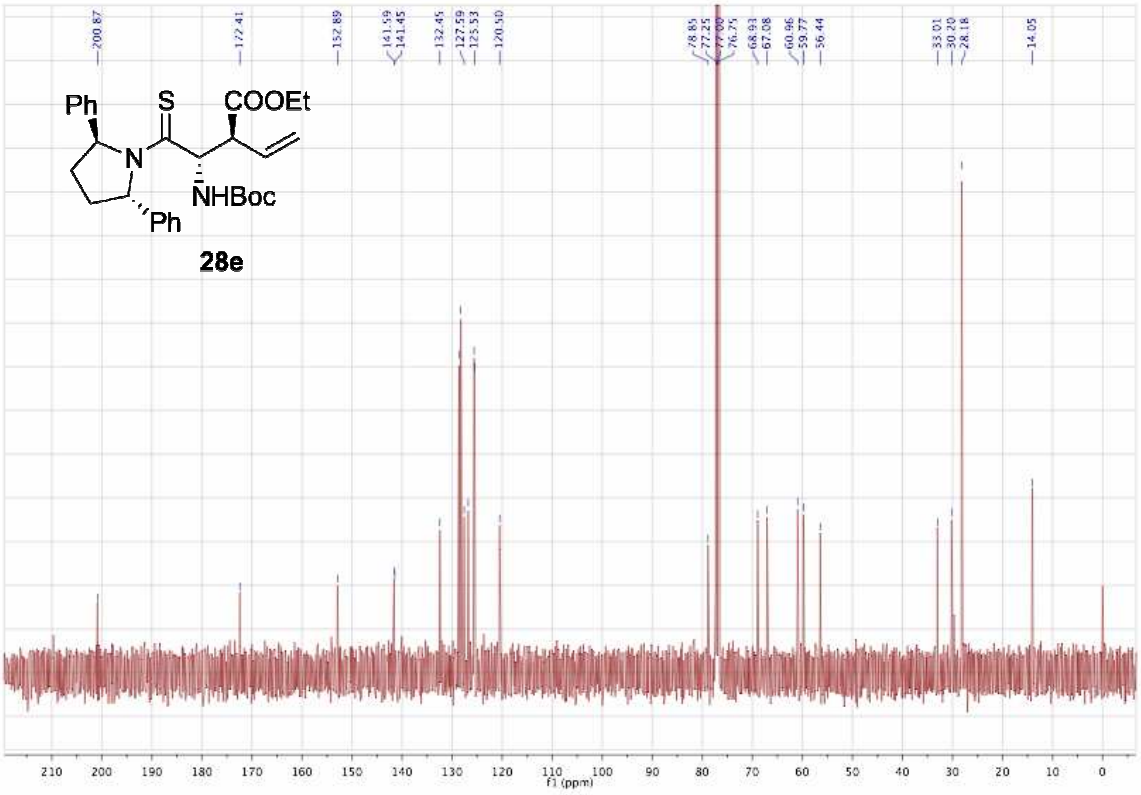

Ph
S
N
NHBoc
Ph
28c
11.68
1.06
2.13
0.82
2.00
1.05
1.06
1.12
1.14
1.15
1.16
8.37
4.91
f1 (ppm)

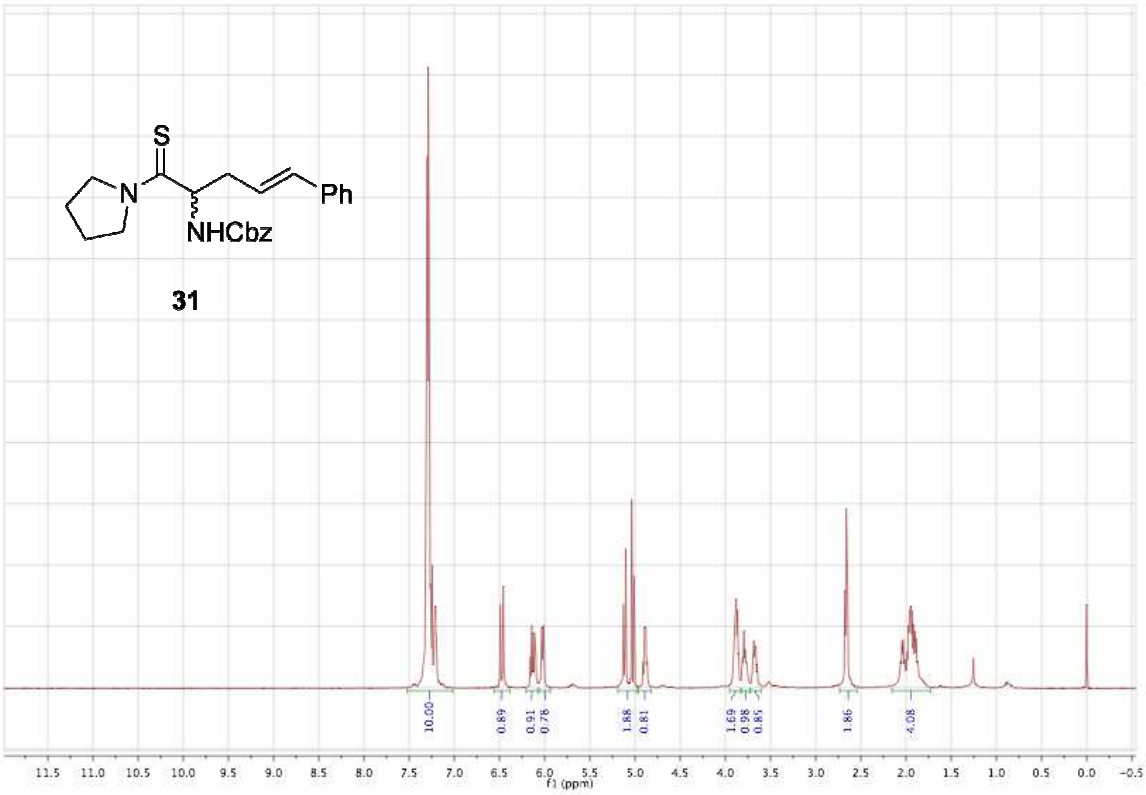

203.32
153.48
141.62
141.22
139.26
128.41
127.70
127.00
125.97
125.33
115.68
78.54
77.25
76.74
68.72
66.89
60.53
46.49
33.46
29.86
28.24
17.26
Ph
S
N
NHBoc
Ph
28c
f1 (ppm)

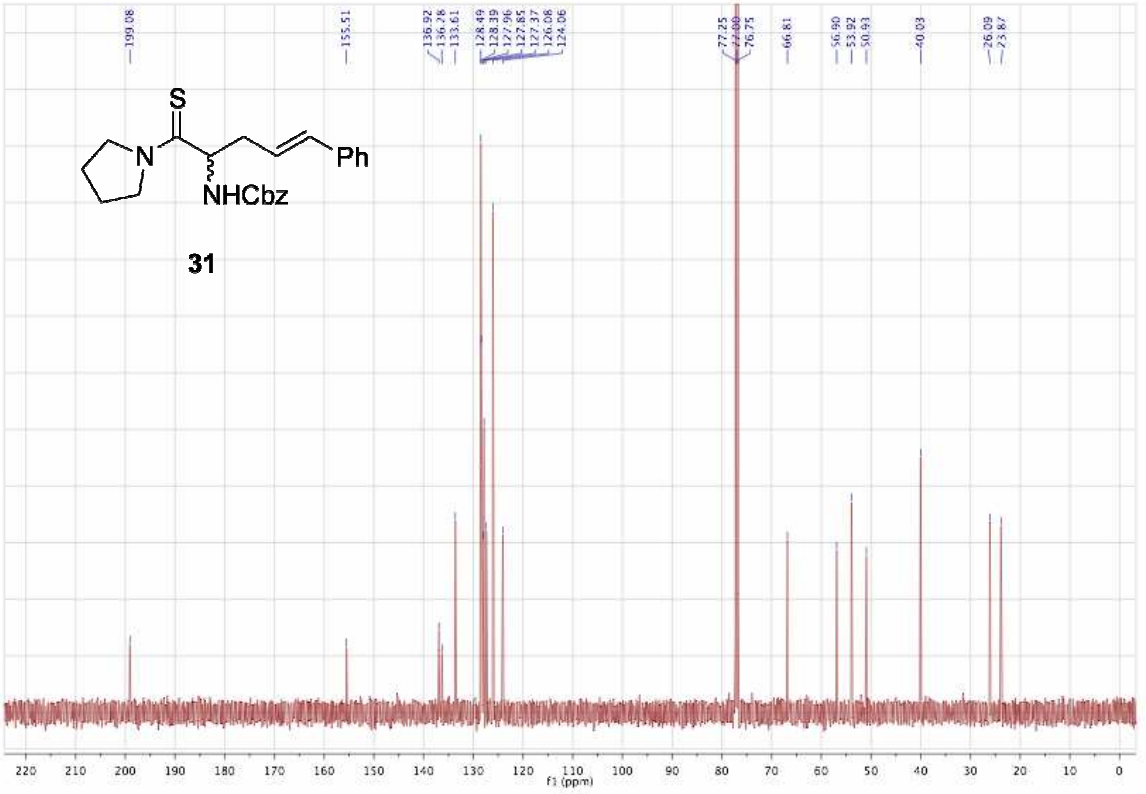

Ph
S
Ph
N
NHBoc
Ph
28d
15.00
1.94
1.09
1.07
2.18
3.30
1.06
2.25
1.37
1.43
9.87
f1 (ppm)

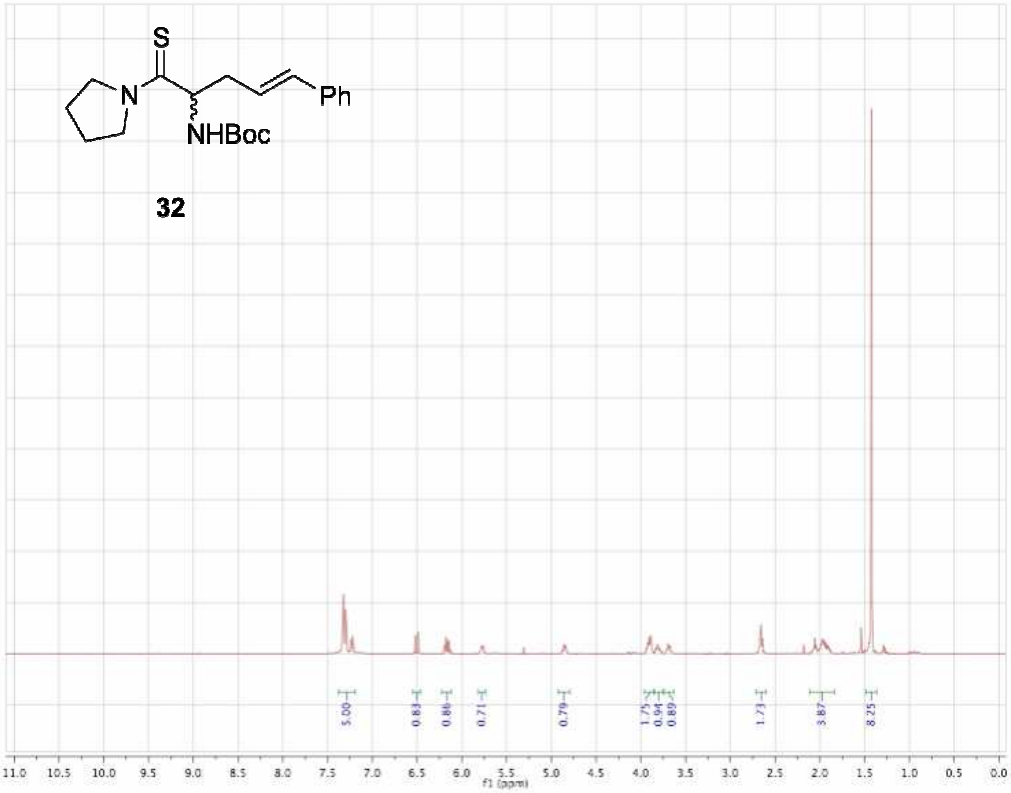

202.28
153.11
140.98
140.61
140.20
126.99
126.29
125.29
125.20
116.72
78.61
77.25
77.00
76.74
68.71
67.17
60.29
59.81
32.71
30.01
28.23
Ph
S
Ph
N
NHBoc
Ph
28d
f1 (ppm)

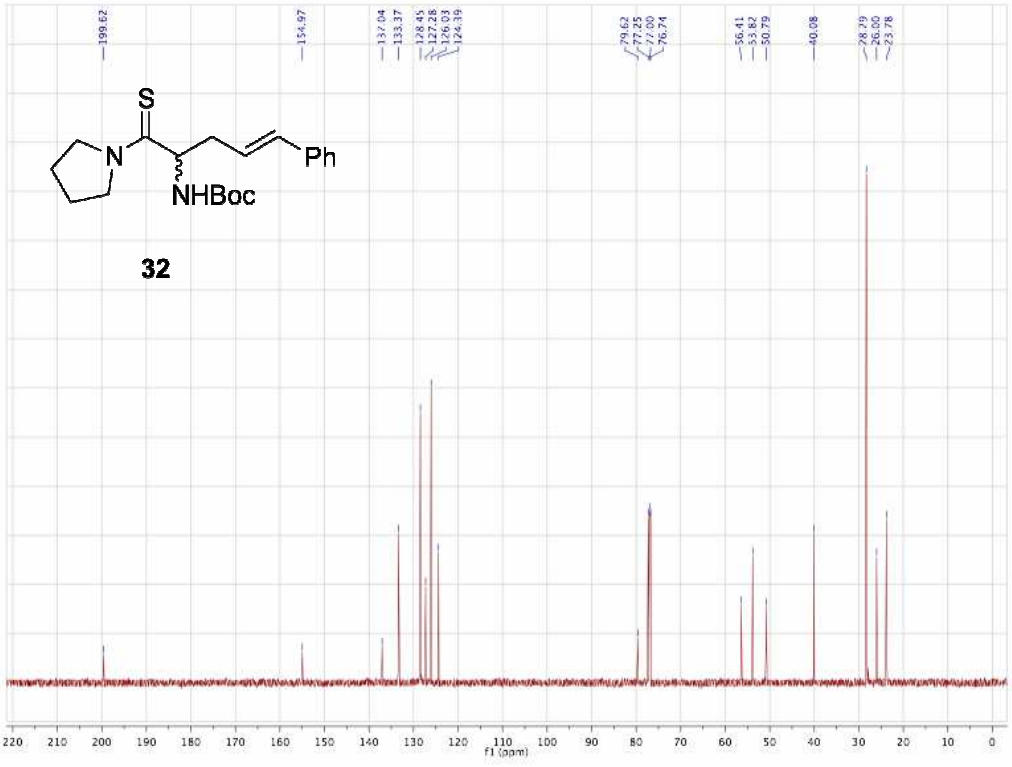

Ph
S
COOEt
N
NHBoc
Ph
28e
11.70
1.07
1.05
1.00
4.06
1.10
1.11
1.07
1.09
1.02
1.64
1.14
1.16
5.35
10.60
f1 (ppm)

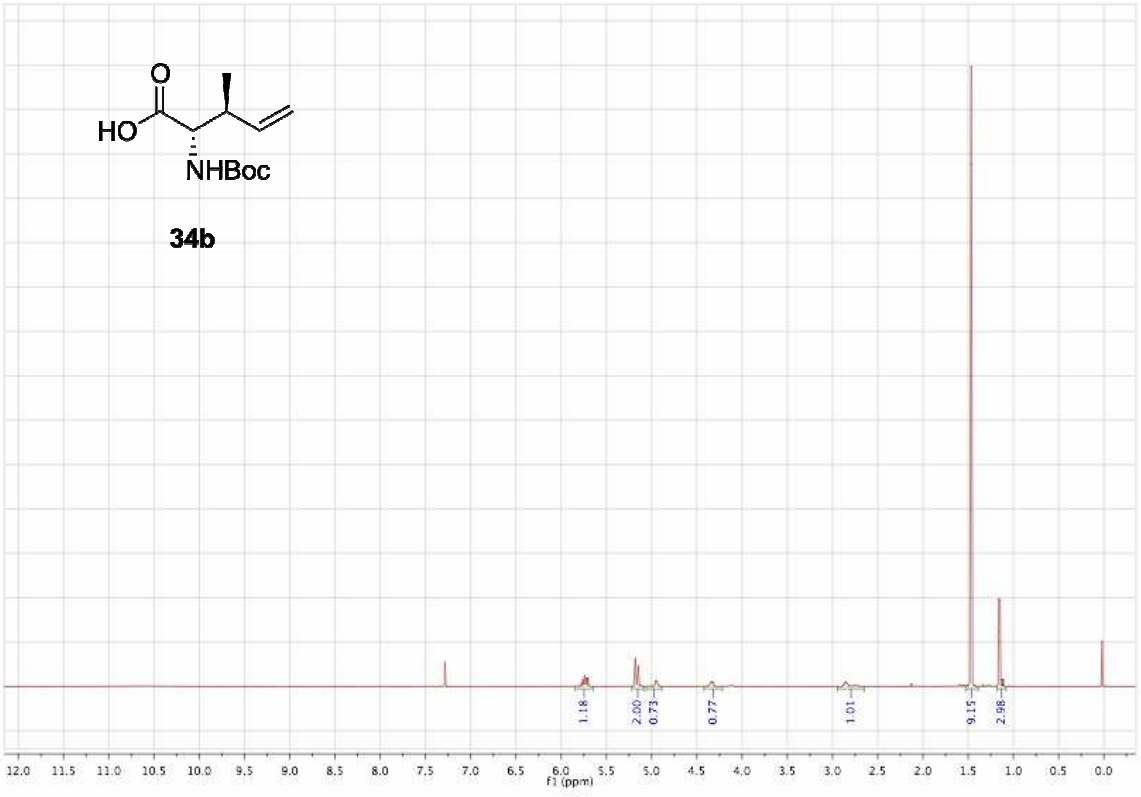

200.87
172.41
152.89
141.59
141.45
132.45
127.59
125.53
120.50
78.85
77.25
77.00
76.71
68.93
67.08
60.96
59.77
56.44
33.01
30.20
28.18
14.05
Ph
S
COOEt
N
NHBoc
Ph
28e
f1 (ppm)

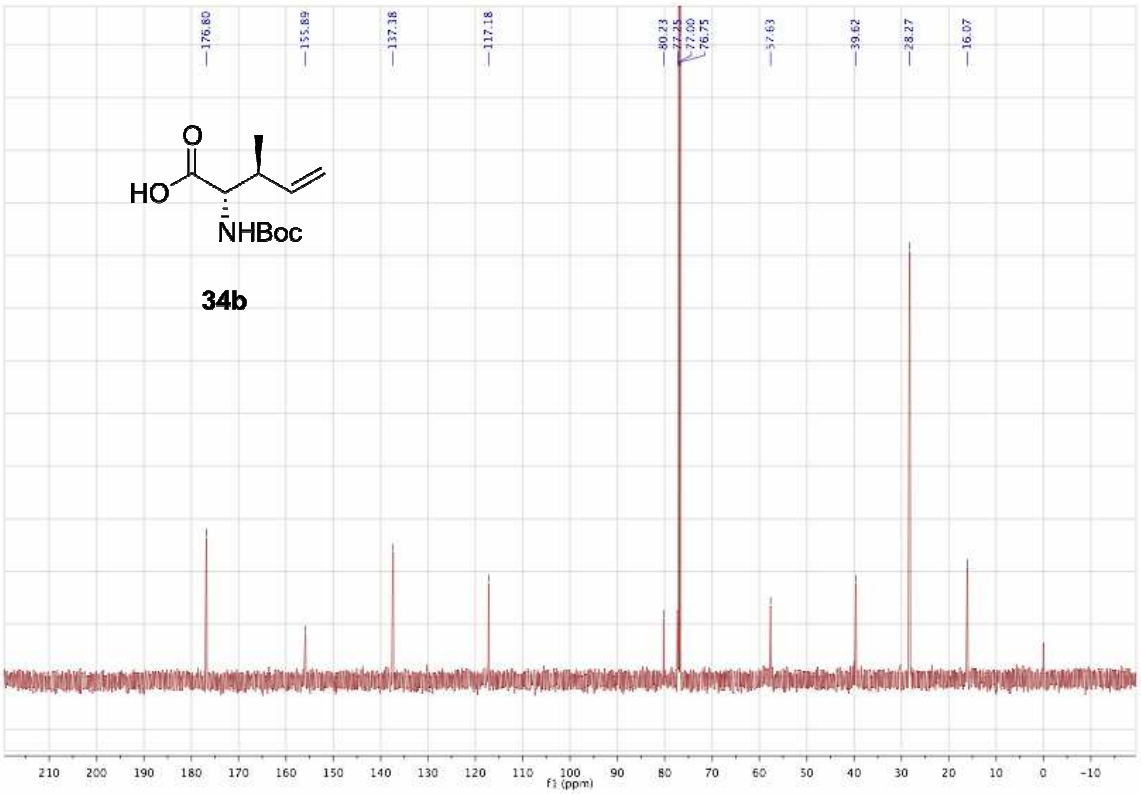

S
N
Ph
NHCbz
31
10.00
0.89
0.91
0.78
1.88
0.81
1.69
0.98
0.85
1.86
4.08
f1 (ppm)

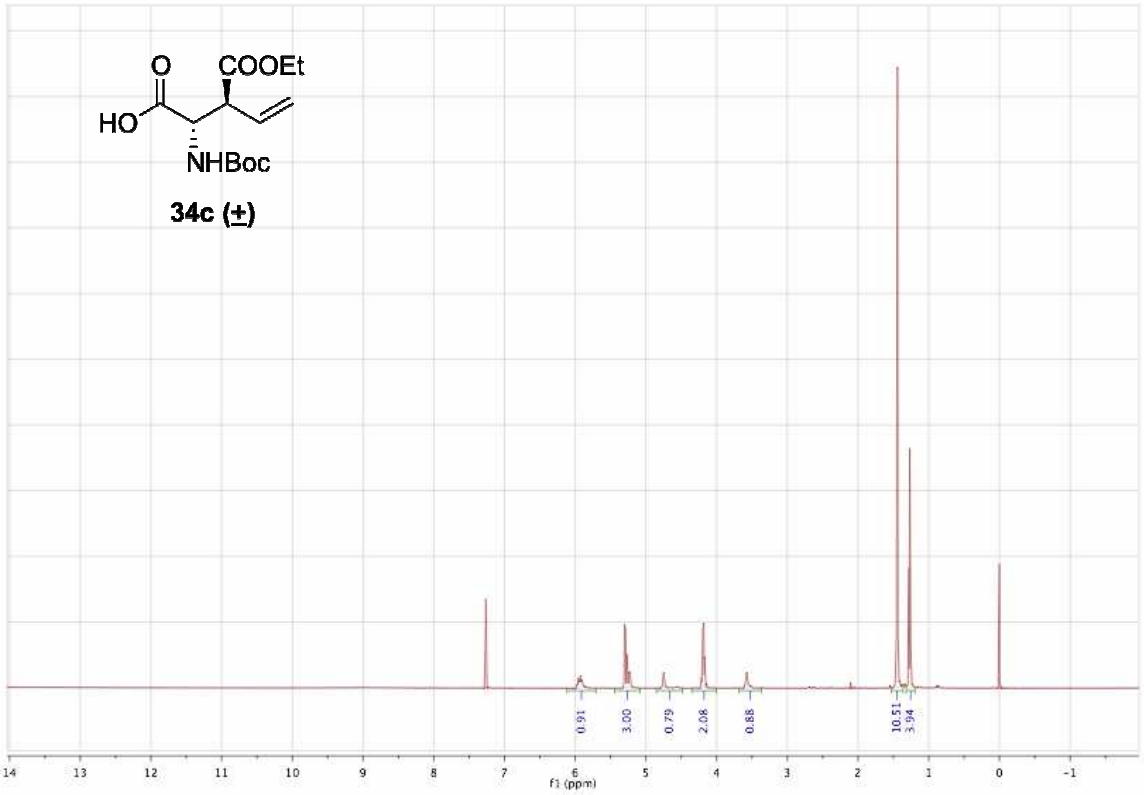

199.08
155.51
136.92
136.28
133.61
128.49
128.39
127.96
127.65
127.37
126.08
124.06
77.25
77.00
76.75
66.81
56.90
53.92
50.93
40.03
26.09
23.87
S
N
Ph
NHCbz
31
f1 (ppm)

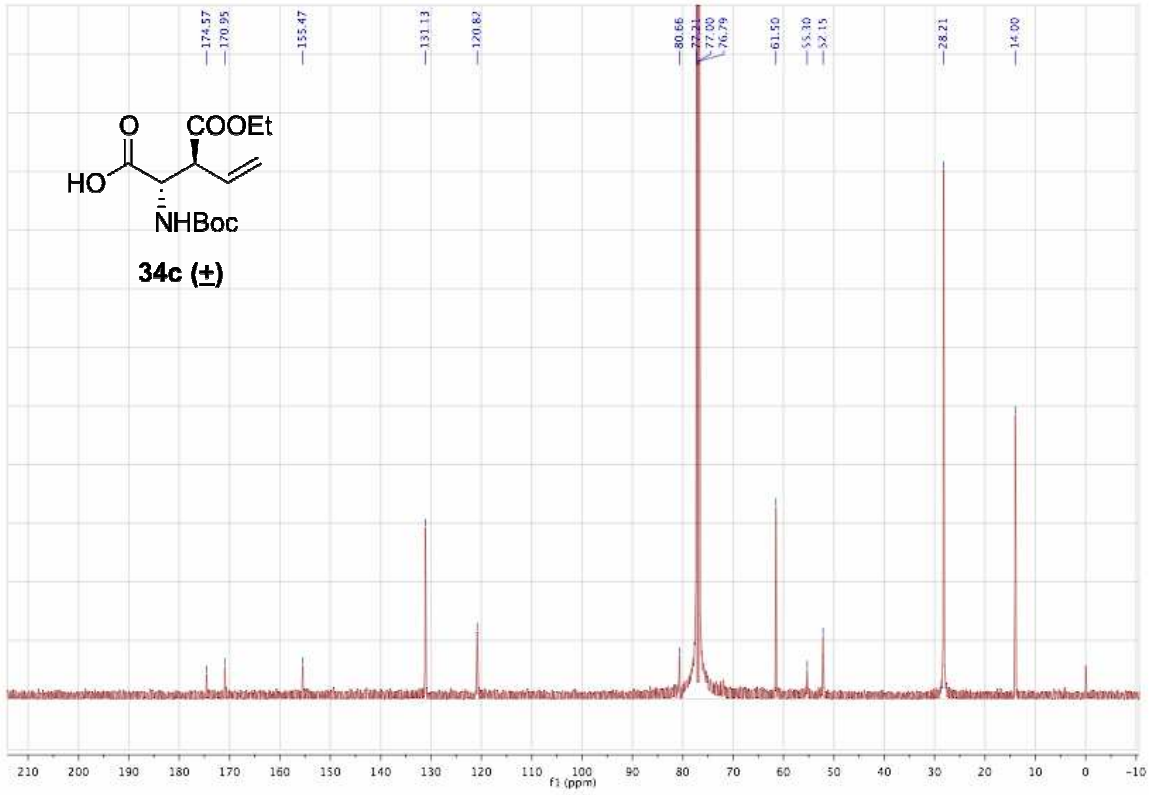

S
N
Ph
NHBoc
32
5.00
0.83
0.86
0.71
0.79
1.75
0.94
0.89
1.73
3.87
8.25
f1 (ppm)

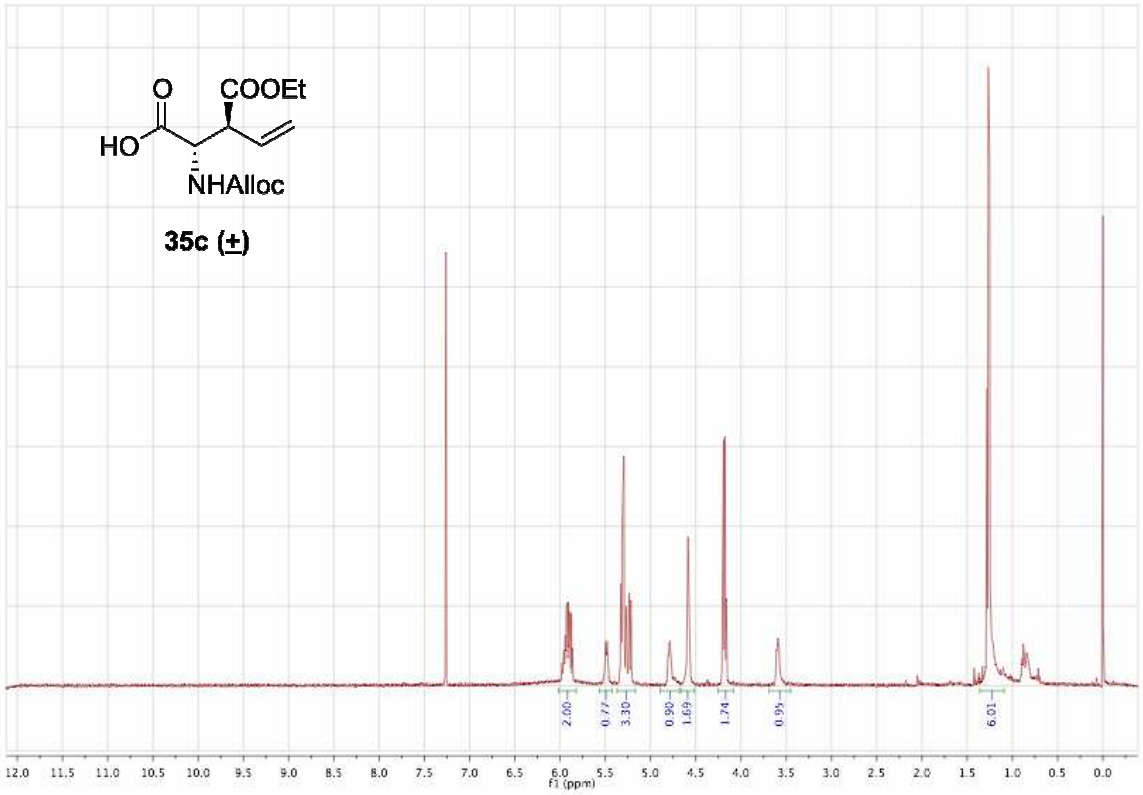

199.62
154.97
137.04
133.37
128.45
127.28
126.03
124.39
79.62
77.25
77.00
76.74
56.41
53.82
50.79
40.08
28.29
26.00
23.78
S
N
Ph
NHBoc
32
f1 (ppm)

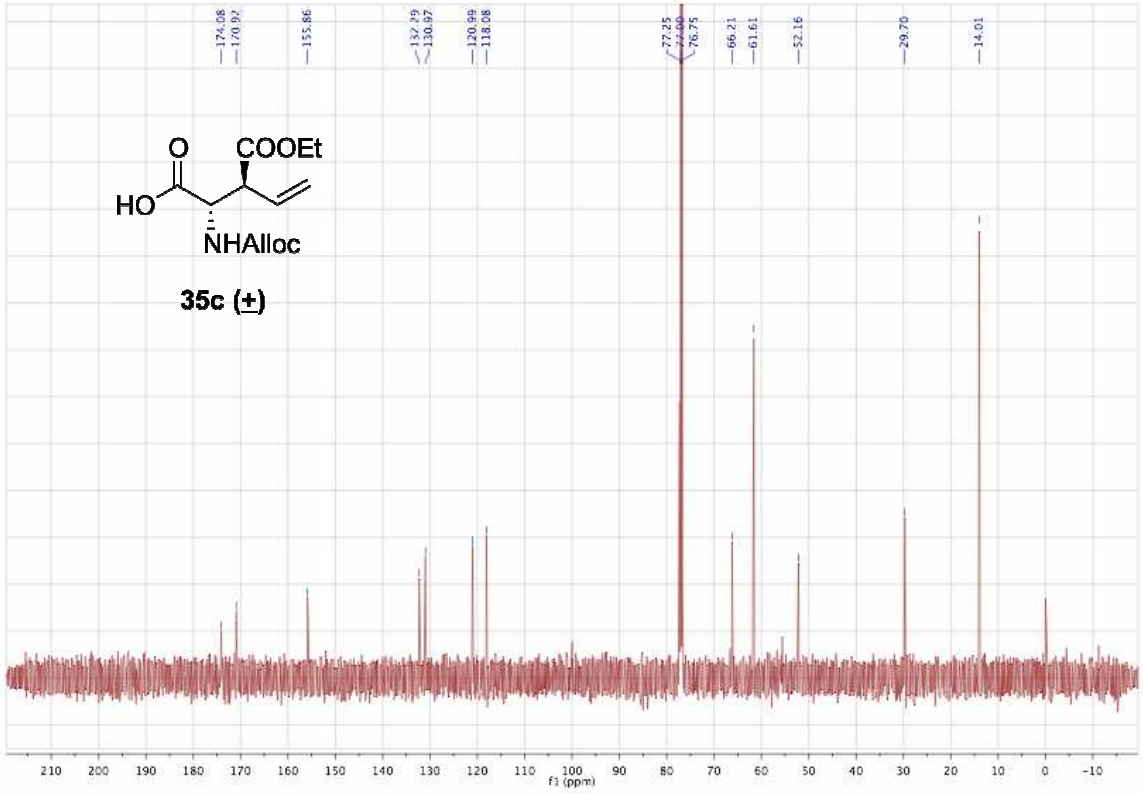

HO
O
NHBoc
34b
1.18
2.00
0.73
0.77
1.01
9.15
2.98
f1 (ppm)

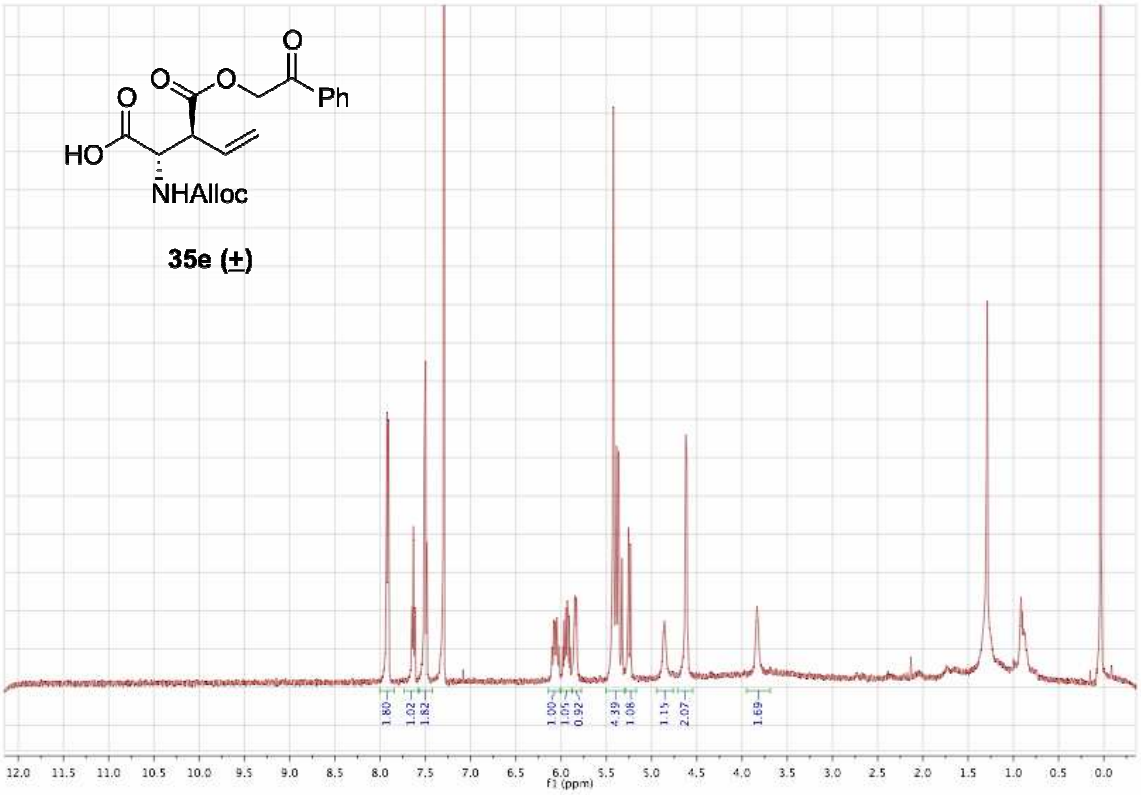

176.80
155.89
137.38
117.18
80.23
77.25
77.00
76.75
57.63
39.62
28.27
16.07
HO
O
NHBoc
34b
f1 (ppm)

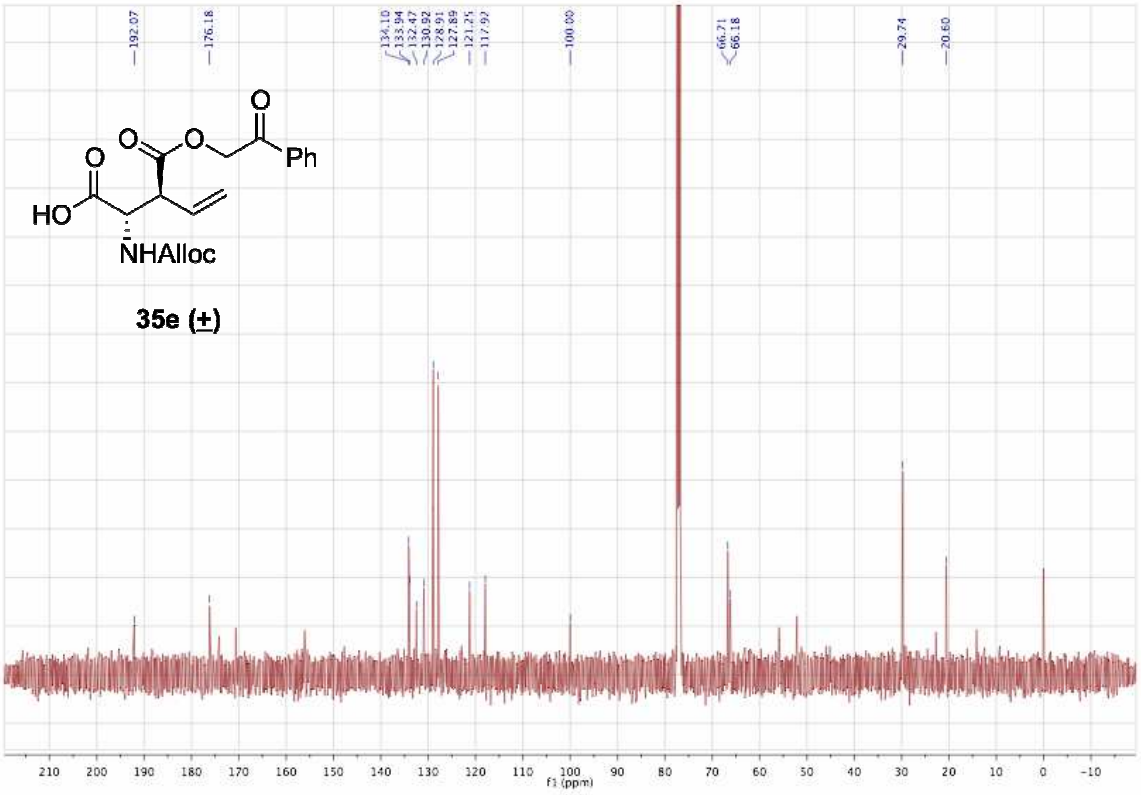

O
COOEt
HO
NHBoc
34c (±)
0.91
3.00
0.79
2.08
0.88
10.51
3.94
f1 (ppm)

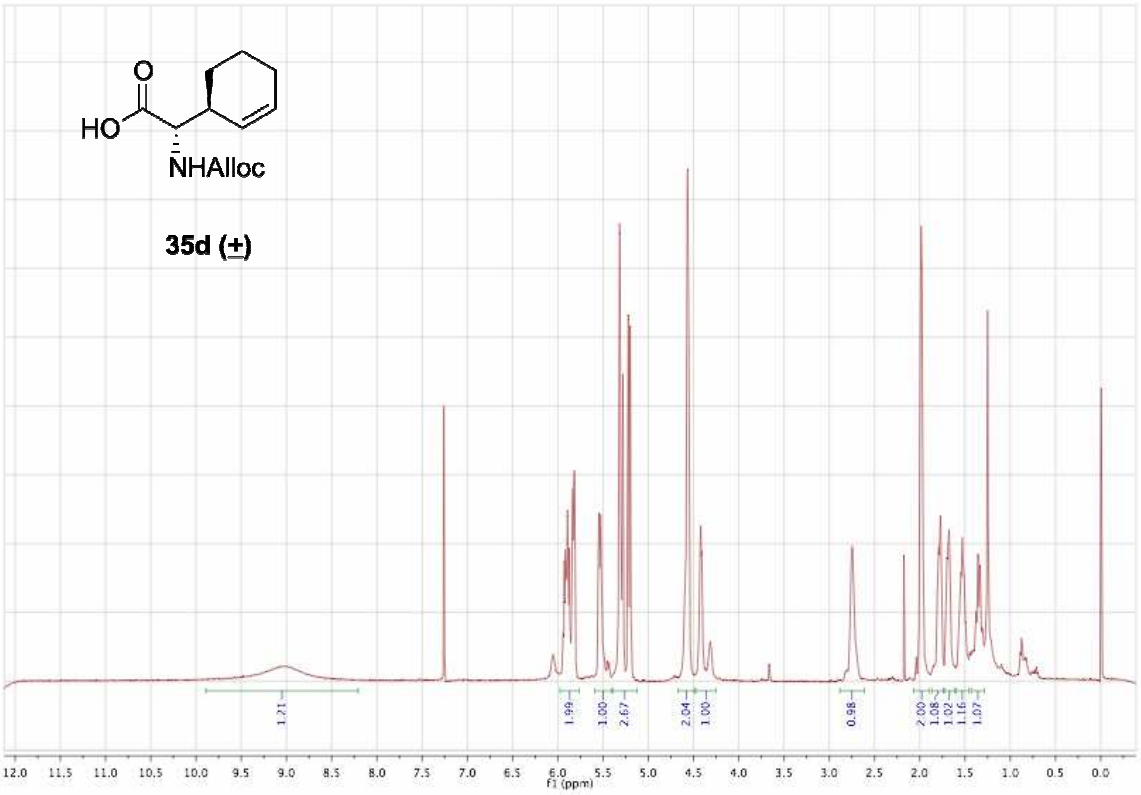

174.57
170.95
155.47
131.13
120.82
80.66
77.21
77.00
76.79
61.50
55.30
52.15
28.21
14.00
O
COOEt
HO
NHBoc
34c (±)
f1 (ppm)

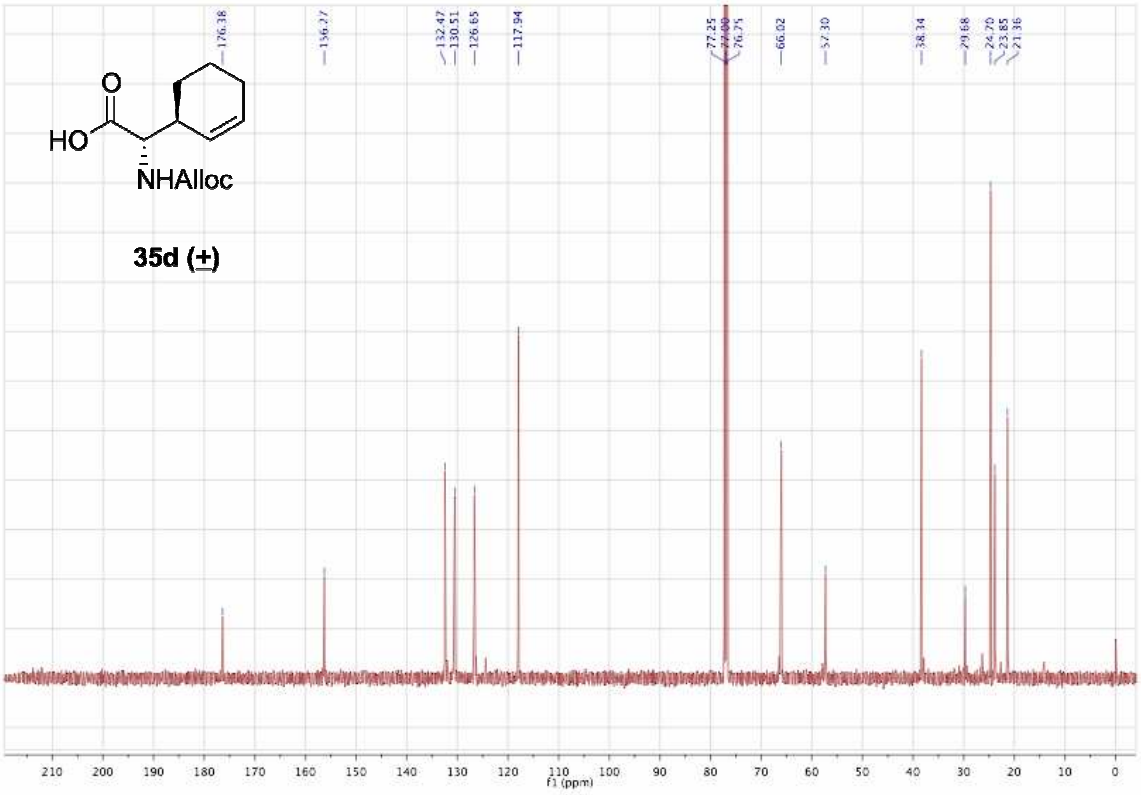

O
COOEt
HO
NHAlloc
35c (±)
2.00
0.77
3.30
0.90
1.69
1.74
0.95
6.01
f1 (ppm)


174.08
170.92
155.86
132.79
130.87
120.99
118.08
77.25
76.75
66.21
61.61
52.16
29.70
14.01
O
COOEt
HO
NHAlloc
35c (±)
f1 (ppm)


HO
NHAlloc
Ph
35e (±)


HO
NHAlloc
Ph
35e (±)


HO
O
NHAlloc
35d (±)
1.21
1.99
1.00
2.67
2.04
1.00
0.98
2.00
1.08
1.02
1.16
1.07
f1 (ppm)


HO
O
NHAlloc
35d (±)
176.38
136.27
132.47
130.51
126.65
117.94
77.25
77.00
76.75
66.02
57.30
38.34
29.68
24.70
23.85
21.36
f1 (ppm)