Supporting information

Peptide cyclization via Ring-Closing Metathesis: the *N*-alkenoxy peptides approach

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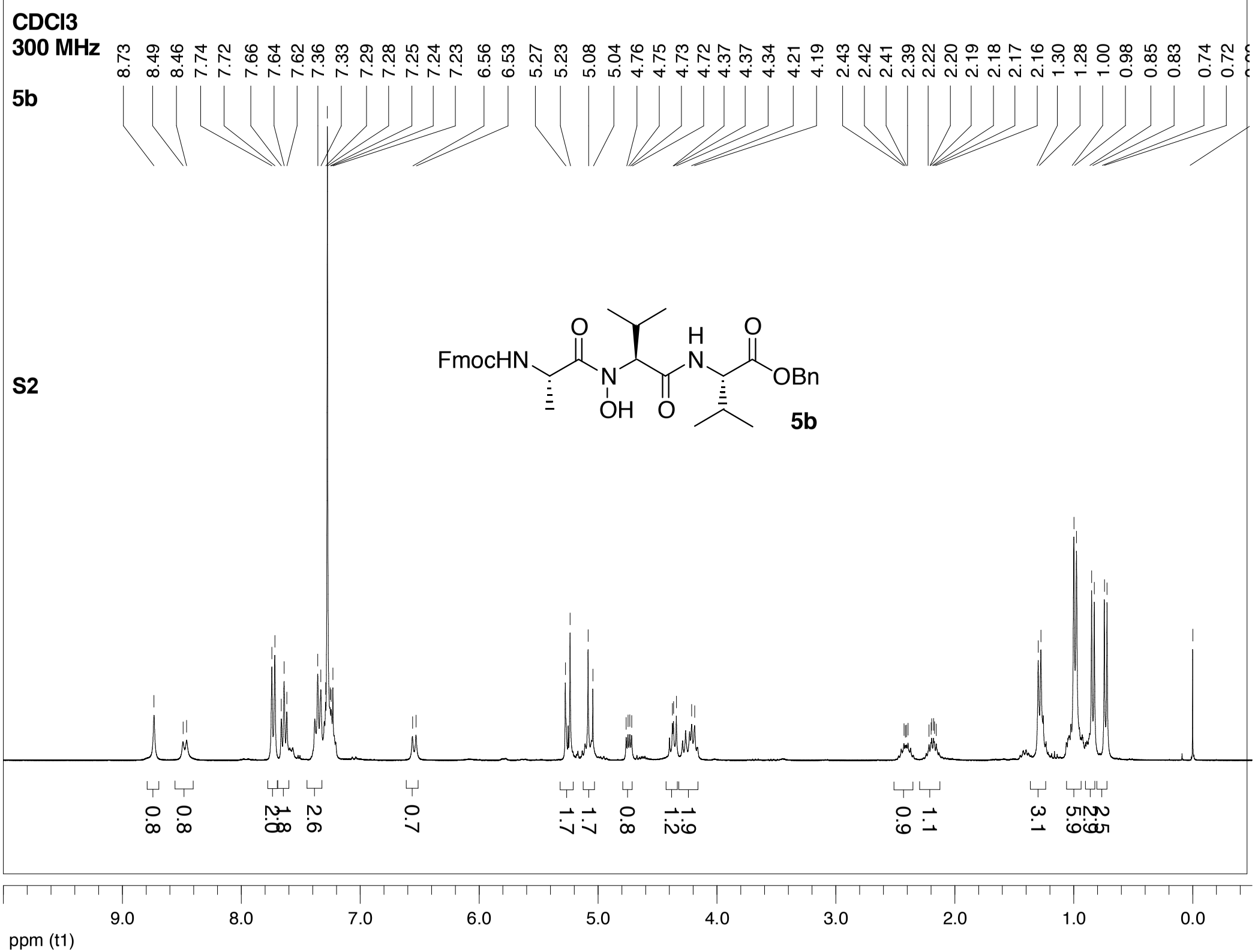
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7.33
7.29
7.28
7.25
7.24
7.23
6.56
6.53
5.27
5.23
5.08
5.04
4.76
4.75
4.73
4.72
4.37
4.37
4.34
4.21
4.19
2.43
2.42
2.41
2.39
2.22
2.20
2.19
2.18
2.17
2.16
1.30
1.28
1.00
0.98
0.85
0.83
0.74
0.72
FmocHN
O
N
OH
O
H
N
O
OBn
5b
0.8
0.8
2.0
1.8
2.6
0.7
1.7
1.7
0.8
1.2
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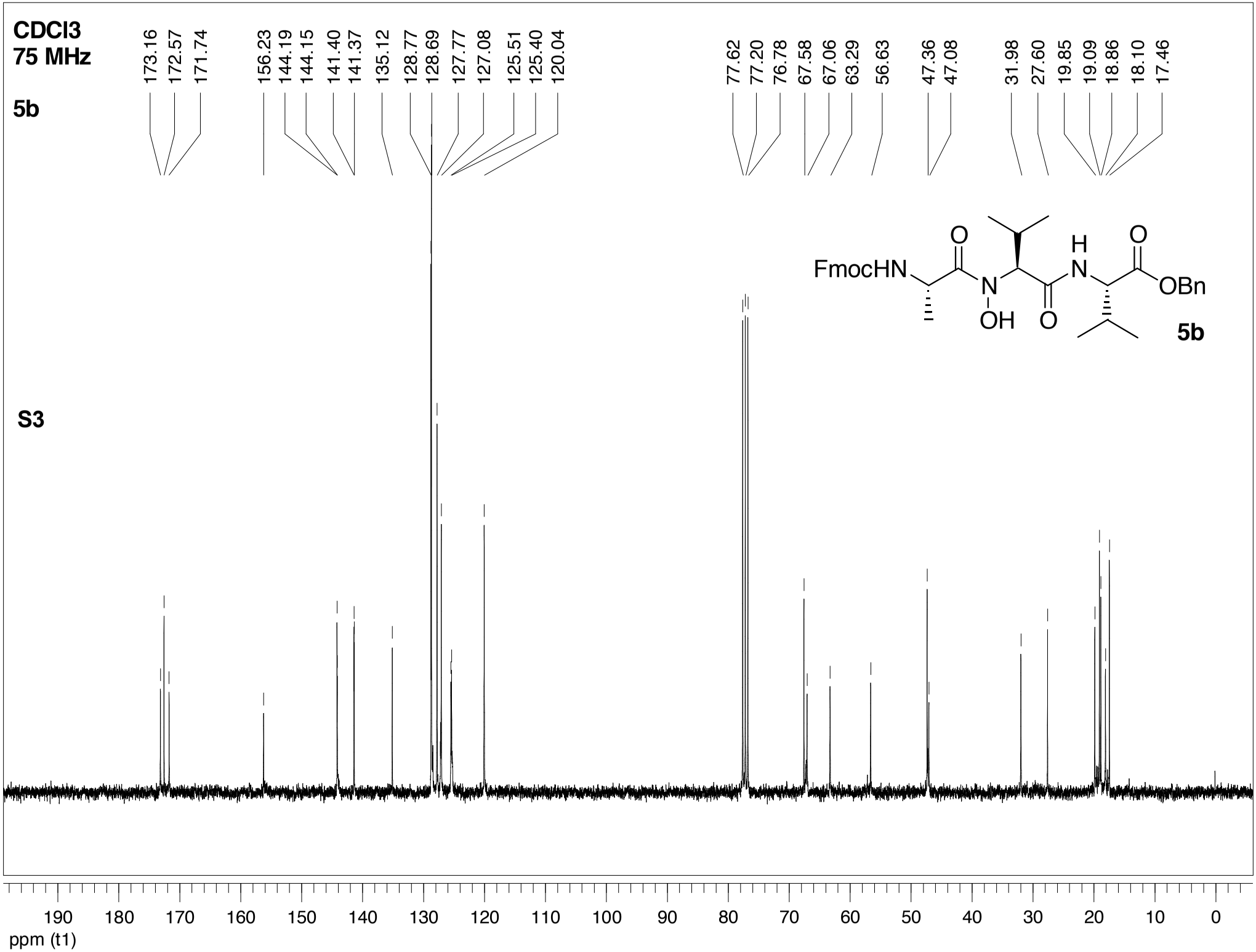
ppm (t1)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141.37
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128.69
127.77
127.08
125.51
125.40
120.04
77.62
77.20
76.78
67.58
67.06
63.29
56.63
47.36
47.08
31.98
27.60
19.85
19.09
18.86
18.10
17.46
FmocHN
O
N
OH
H
N
O
O
OBn
O
5b
190
180
170
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110
100
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50
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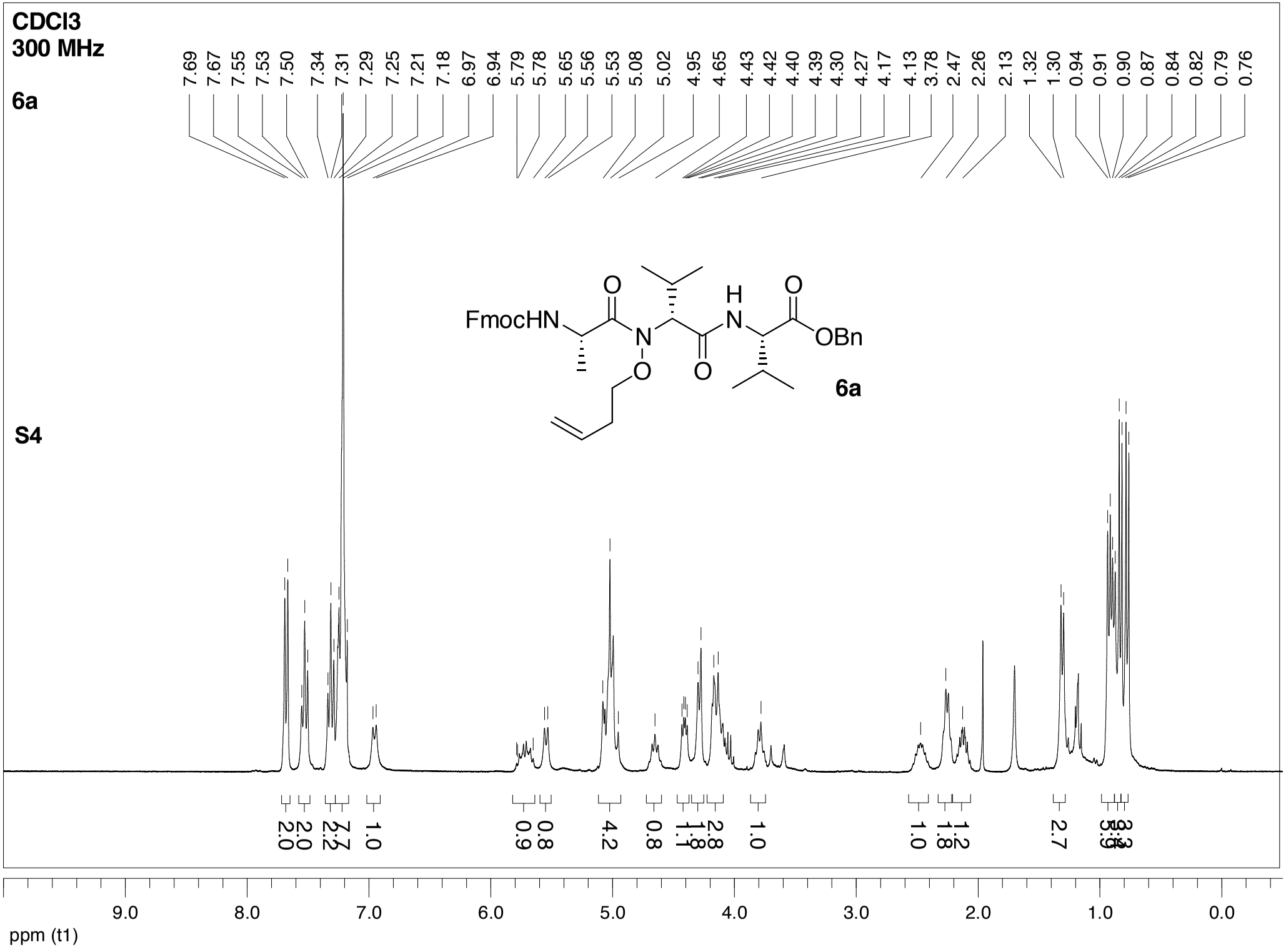
30
20
10
0
ppm (t1)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7.25
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7.18
6.97
6.94
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5.78
5.65
5.56
5.53
5.08
5.02
4.95
4.65
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4.42
4.40
4.39
4.30
4.27
4.17
4.13
3.78
2.47
2.26
2.13
1.32
1.30
0.94
0.91
0.90
0.87
0.84
0.82
0.79
0.76
FmocHN
O
N
O
H
N
O
OBn
O
6a
2.0
2.0
2.2
2.7
1.0
0.9
0.8
4.2
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1.1
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2.8
1.0
1.0
1.2
1.8
2.7
3.3
3.8
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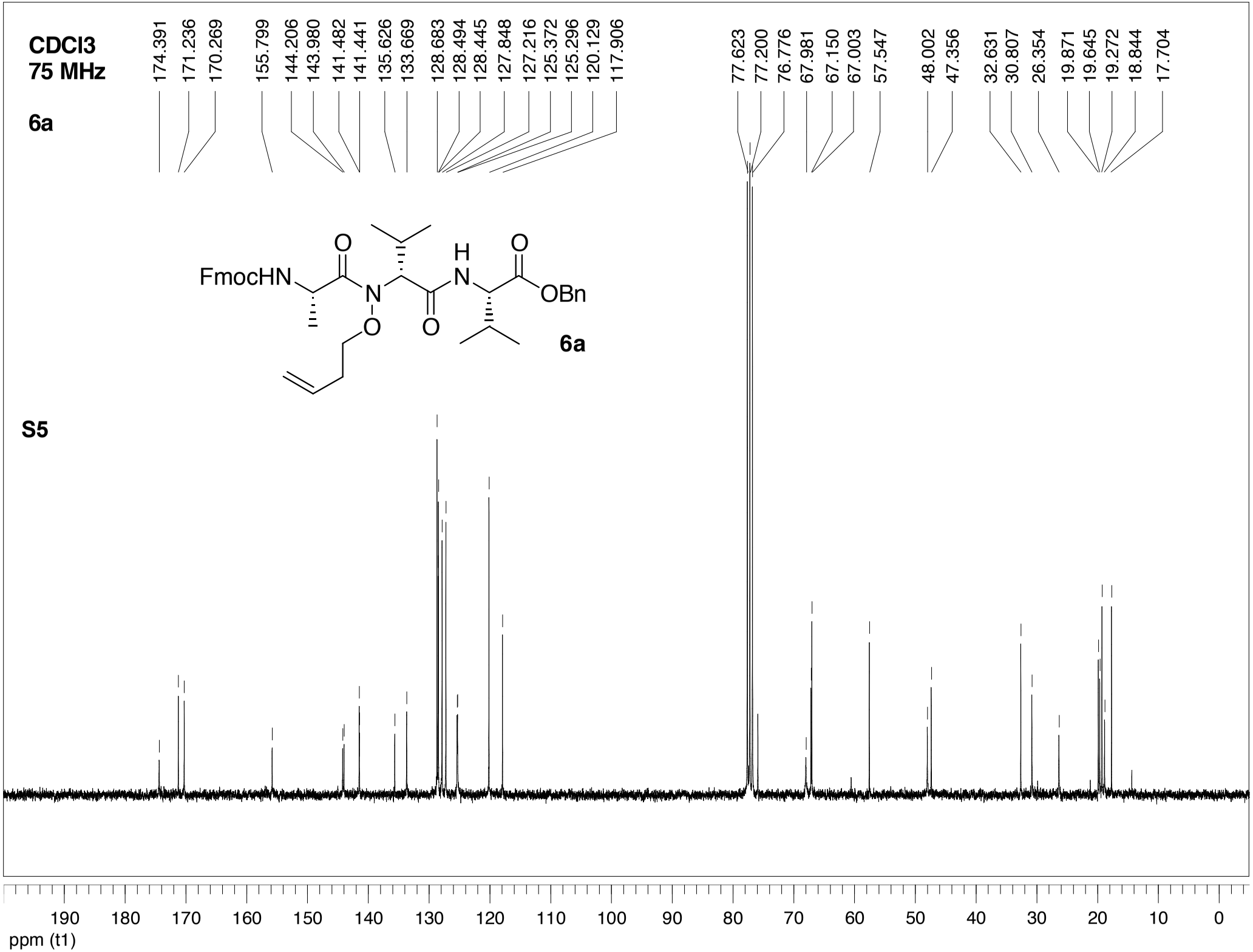
0.0
ppm (t1)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133.669
128.683
128.494
128.445
127.848
127.216
125.372
125.296
120.129
117.906
77.623
77.200
76.776
67.981
67.150
67.003
57.547
48.002
47.356
32.631
30.807
26.354
19.871
19.645
19.272
18.844
17.704
FmocHN
O
N
O
H
N
O
O
OBn
6a
S5
190
180
170
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130
120
110
100
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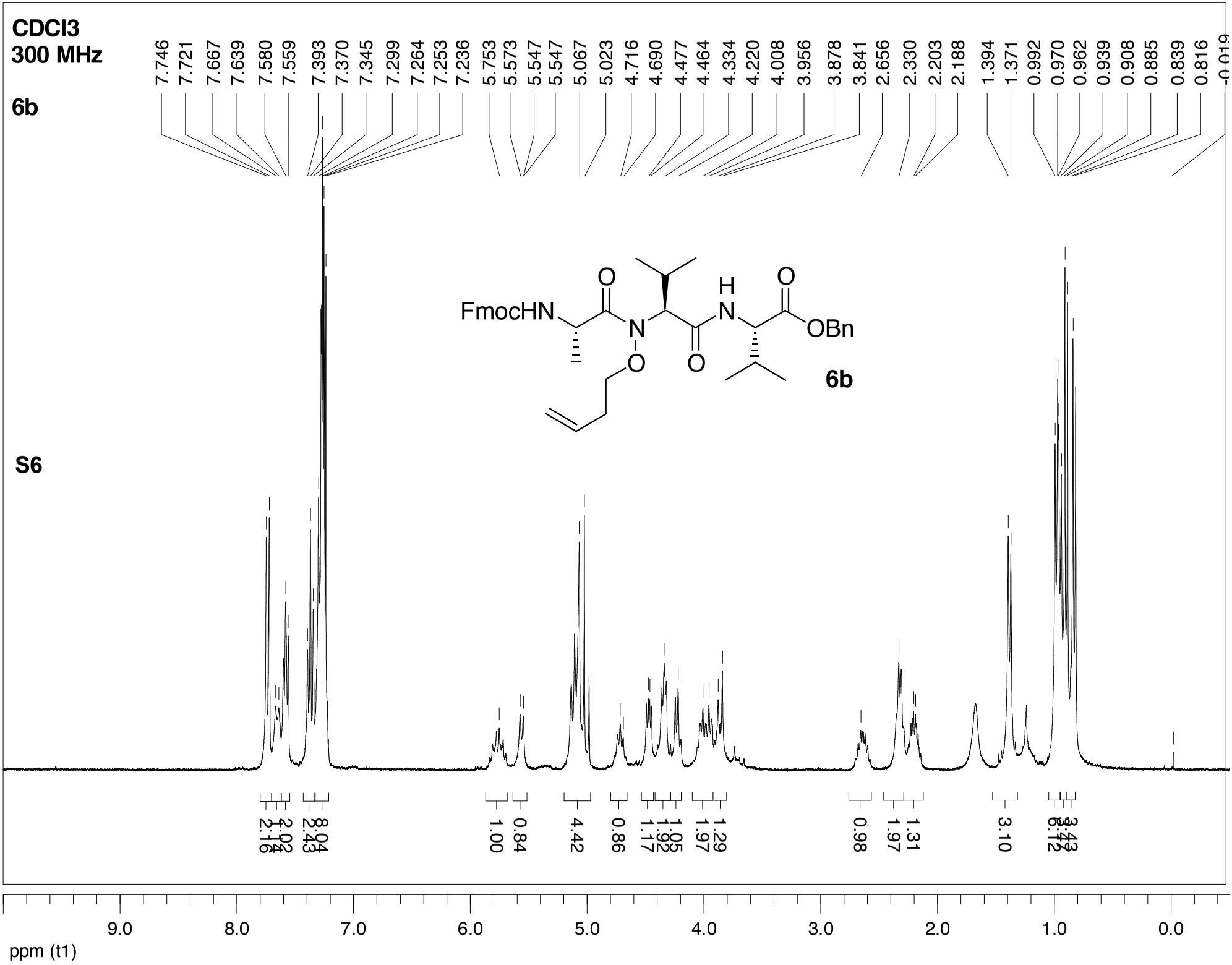
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7.559
7.393
7.370
7.345
7.299
7.264
7.253
7.236
5.753
5.573
5.547
5.547
5.067
5.023
4.716
4.690
4.477
4.464
4.334
4.220
4.008
3.956
3.878
3.841
2.656
2.330
2.203
2.188
1.394
1.371
0.992
0.970
0.962
0.939
0.908
0.885
0.839
0.816
FmocHN
O
N
O
H
N
O
OBn
O
6b
2.16
2.02
2.04
8.04
2.43
1.00
0.84
4.42
0.86
1.17
1.92
1.05
1.97
1.29
0.98
1.97
1.31
3.10
6.12
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2.0
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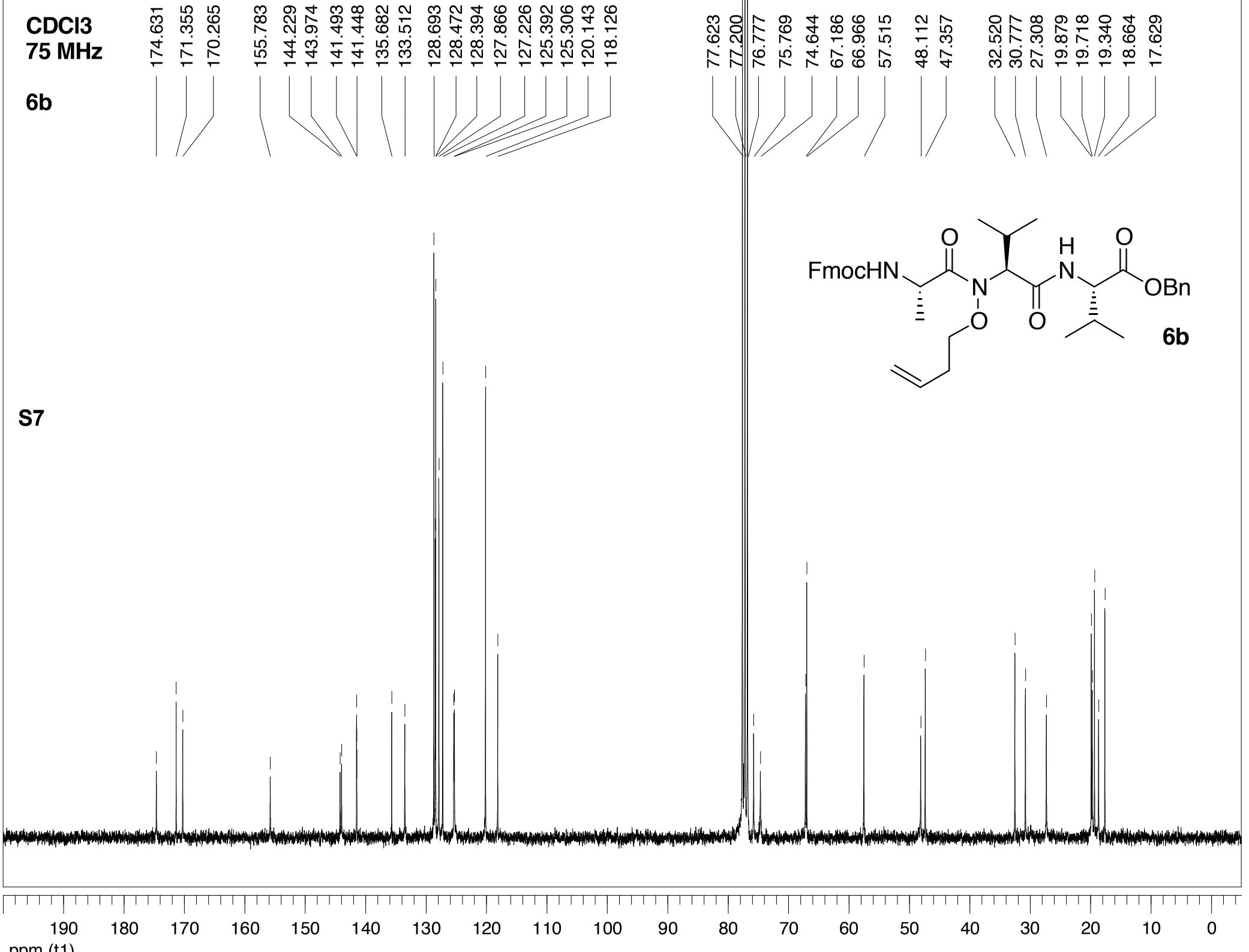
ppm (t1)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127.226
125.392
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120.143
118.126
77.623
77.200
76.777
75.769
74.644
67.186
66.966
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48.112
47.357
32.520
30.777
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19.879
19.718
19.340
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17.629
FmocHN
O
N
O
H
N
O
O
OBn
6b
S7
190
180
170
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130
120
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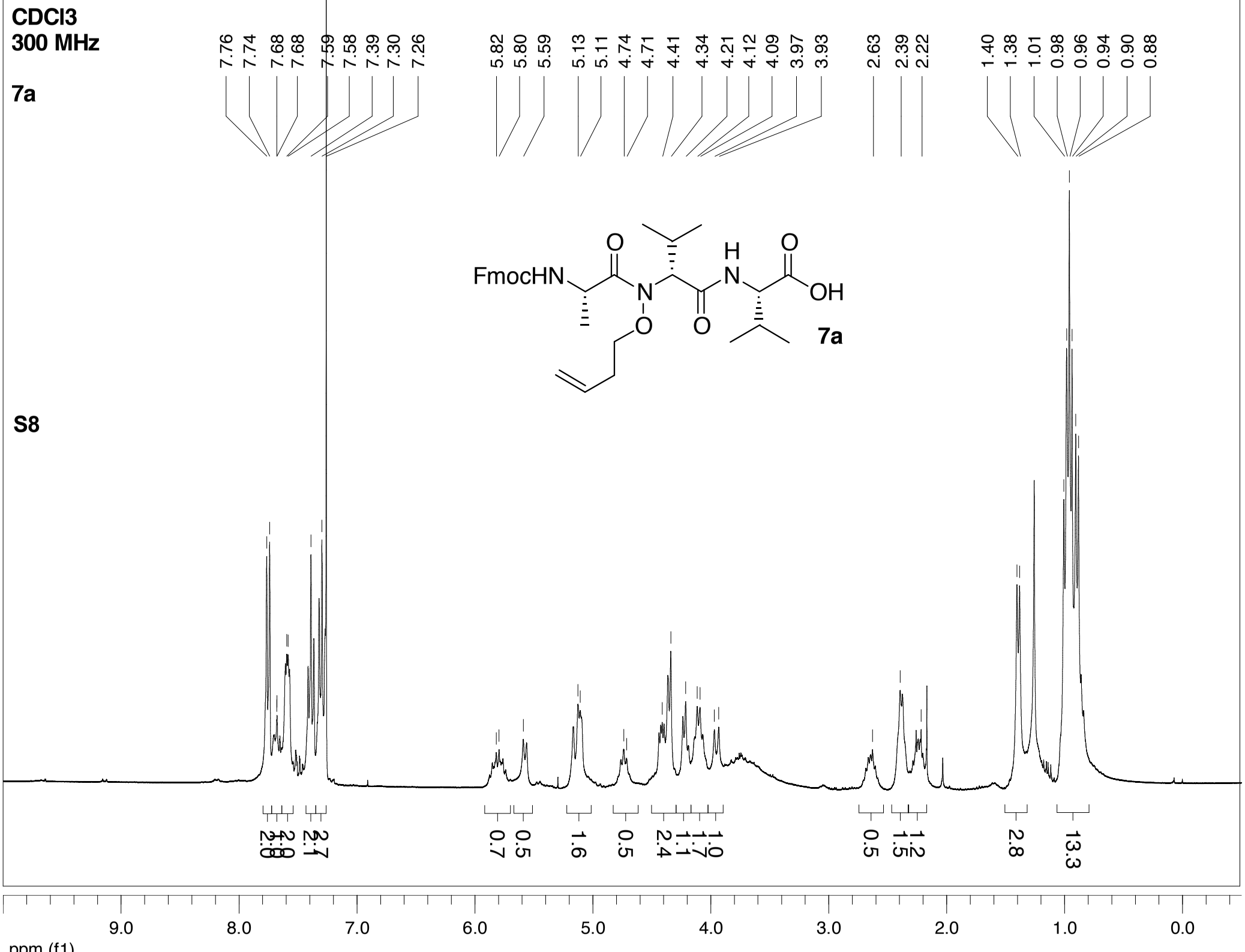
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)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7.58
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7.26
5.82
5.80
5.59
5.13
5.11
4.74
4.71
4.41
4.34
4.21
4.12
4.09
3.97
3.93
2.63
2.39
2.22
1.40
1.38
1.01
0.98
0.96
0.94
0.90
0.88
FmocHN
O
N
O
H
N
O
OH
O
O
7a
S8
2.0
2.0
2.0
2.0
2.1
2.7
0.7
0.5
1.6
0.5
2.4
1.1
1.7
1.0
0.5
1.5
1.2
2.8
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7.0
6.0
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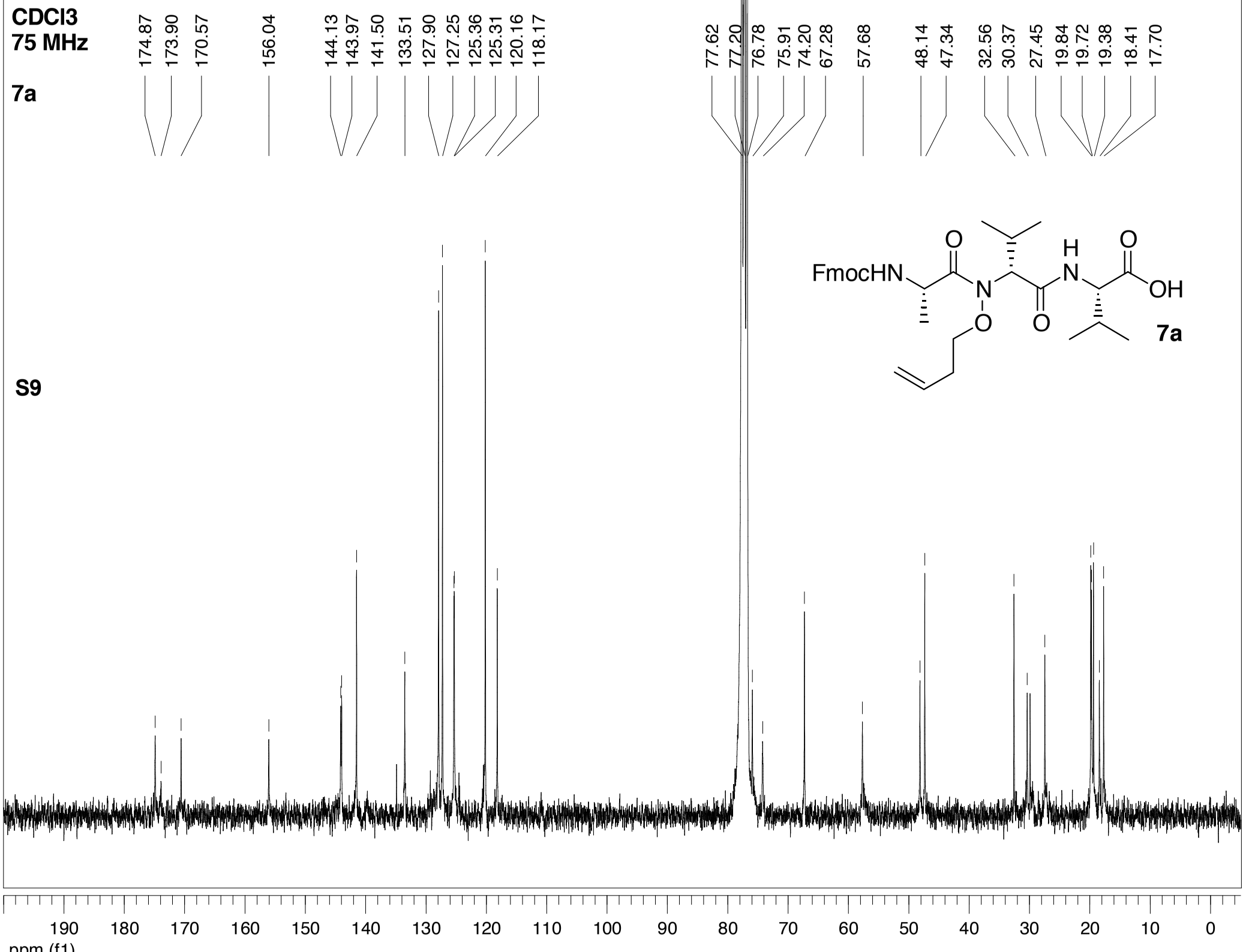
2.0
1.0
0.0
ppm (f1)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127.25
125.36
125.31
120.16
118.17
77.62
77.20
76.78
75.91
74.20
67.28
57.68
48.14
47.34
32.56
30.37
27.45
19.84
19.72
19.38
18.41
17.70
FmocHN
O
N
O
H
N
O
O
OH
O
7a
S9
190
180
170
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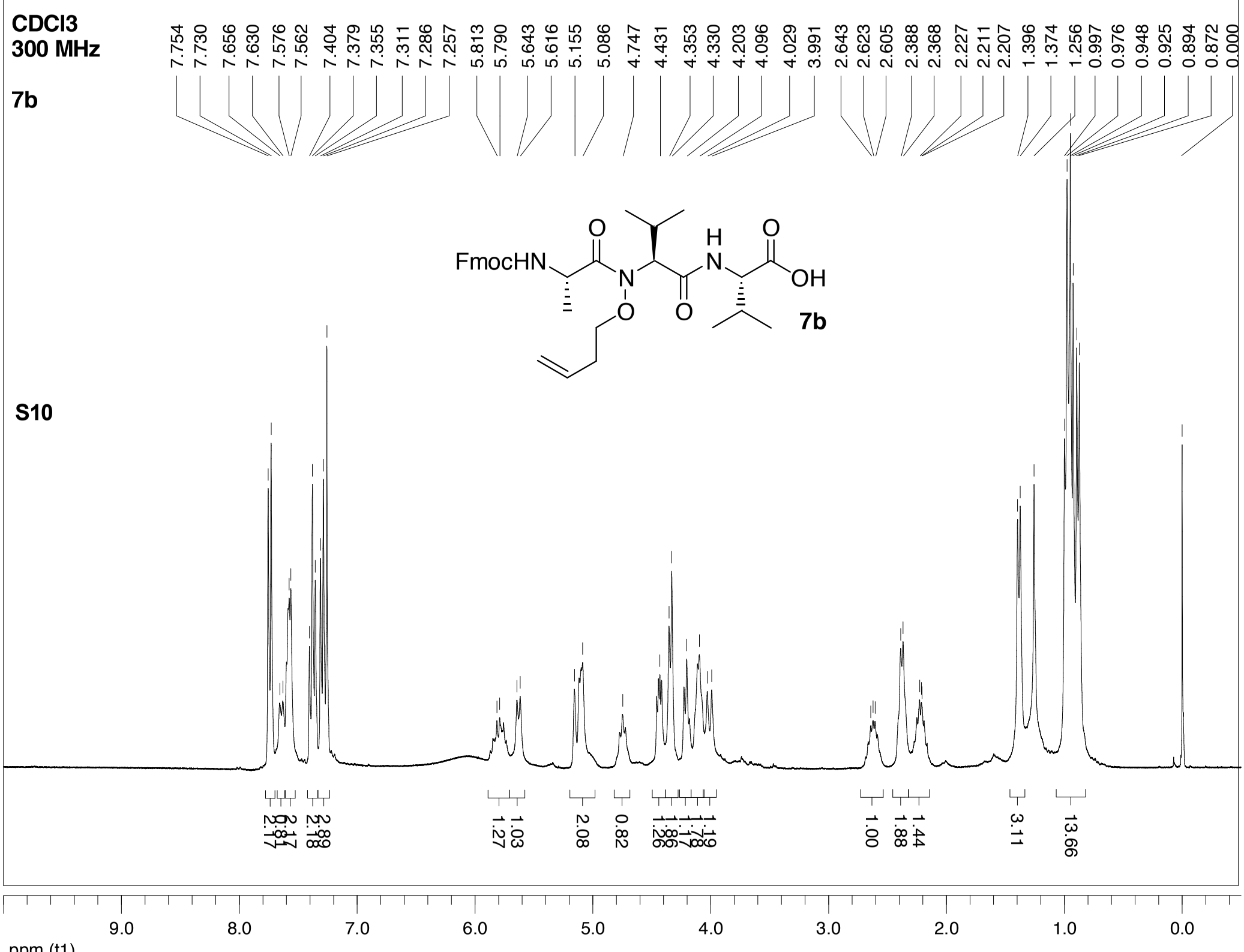
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (f1)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7.355
7.311
7.286
7.257
5.813
5.790
5.643
5.616
5.155
5.086
4.747
4.431
4.353
4.330
4.203
4.096
4.029
3.991
2.643
2.623
2.605
2.388
2.368
2.227
2.211
2.207
1.396
1.374
1.256
0.997
0.976
0.948
0.925
0.894
0.872
0.000
FmocHN
O
N
O
O
H
N
O
OH
7b
S10
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0.81
2.18
2.89
1.27
1.03
2.08
0.82
1.26
1.86
1.17
1.78
1.19
1.00
1.88
1.44
3.11
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5.0
4.0
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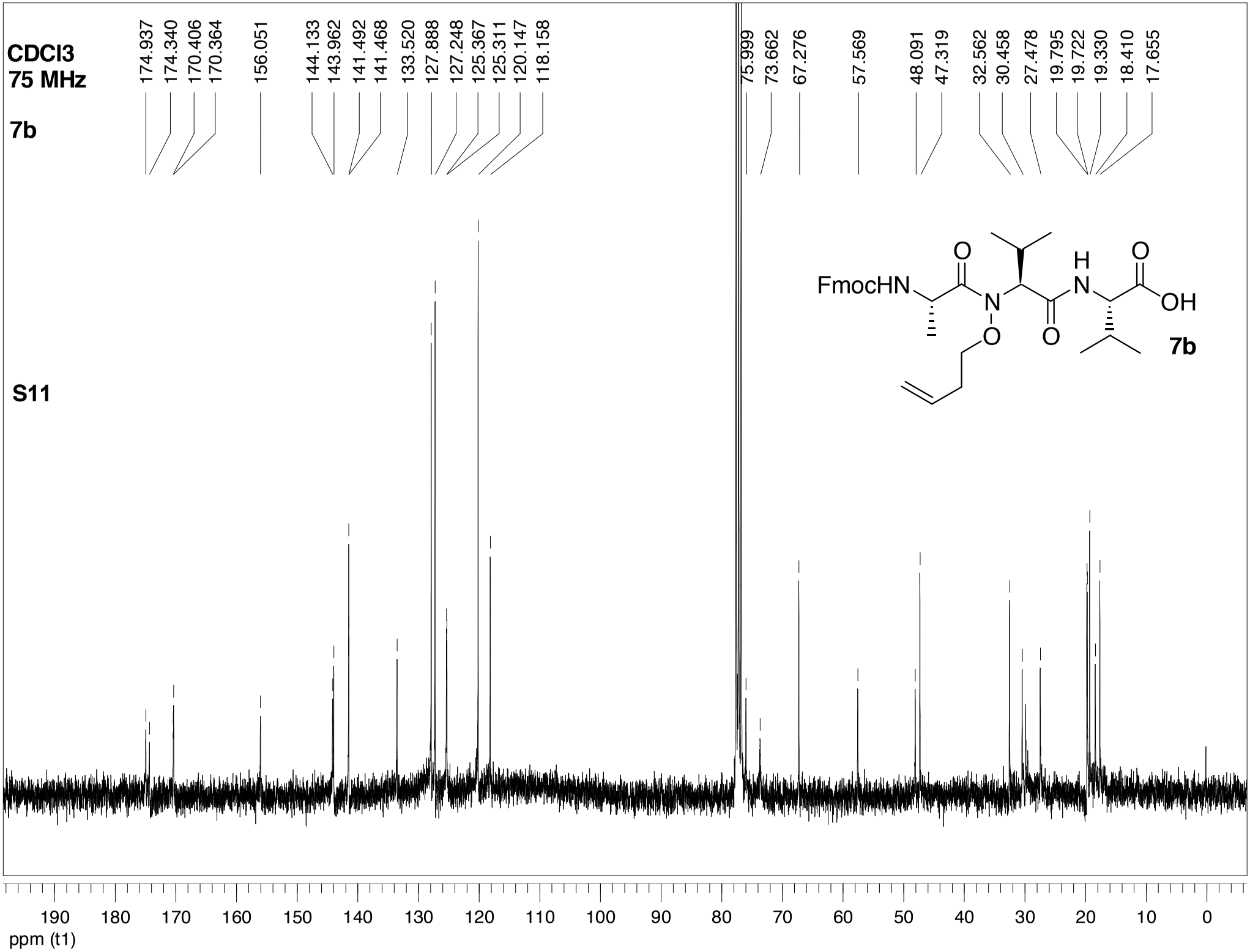
2.0
1.0
0.0
ppm (t1)


CDCl3
75 MHz
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141.492
141.468
133.520
127.888
127.248
125.367
125.311
120.147
118.158
75.999
73.662
67.276
57.569
48.091
47.319
32.562
30.458
27.478
19.795
19.722
19.330
18.410
17.655
FmocHN
O
N
O
H
N
O
O
OH
7b
S11
190
180
170
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130
120
110
100
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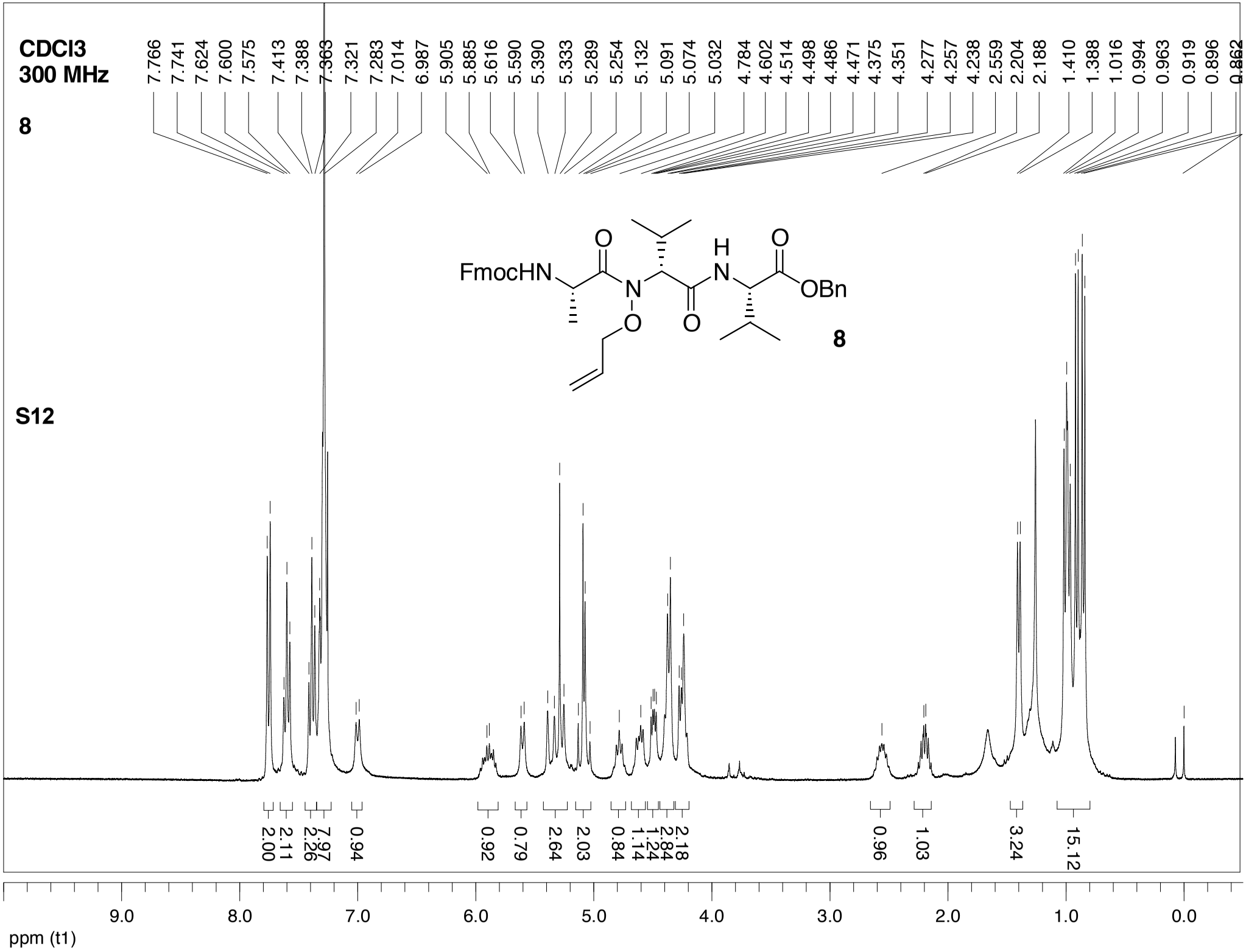
80
70
60
50
40
30
20
10
0
ppm (t1)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7.600
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7.363
7.321
7.283
7.014
6.987
5.905
5.885
5.616
5.590
5.390
5.333
5.289
5.254
5.132
5.091
5.074
5.032
4.784
4.602
4.514
4.498
4.486
4.471
4.375
4.351
4.277
4.257
4.238
2.559
2.204
2.188
1.410
1.388
1.016
0.994
0.963
0.919
0.896
FmocHN
O
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O
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N
O
OBn
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8
2.00
2.11
2.26
7.97
0.94
0.92
0.79
2.64
2.03
0.84
1.14
1.24
2.84
2.18
0.96
1.03
3.24
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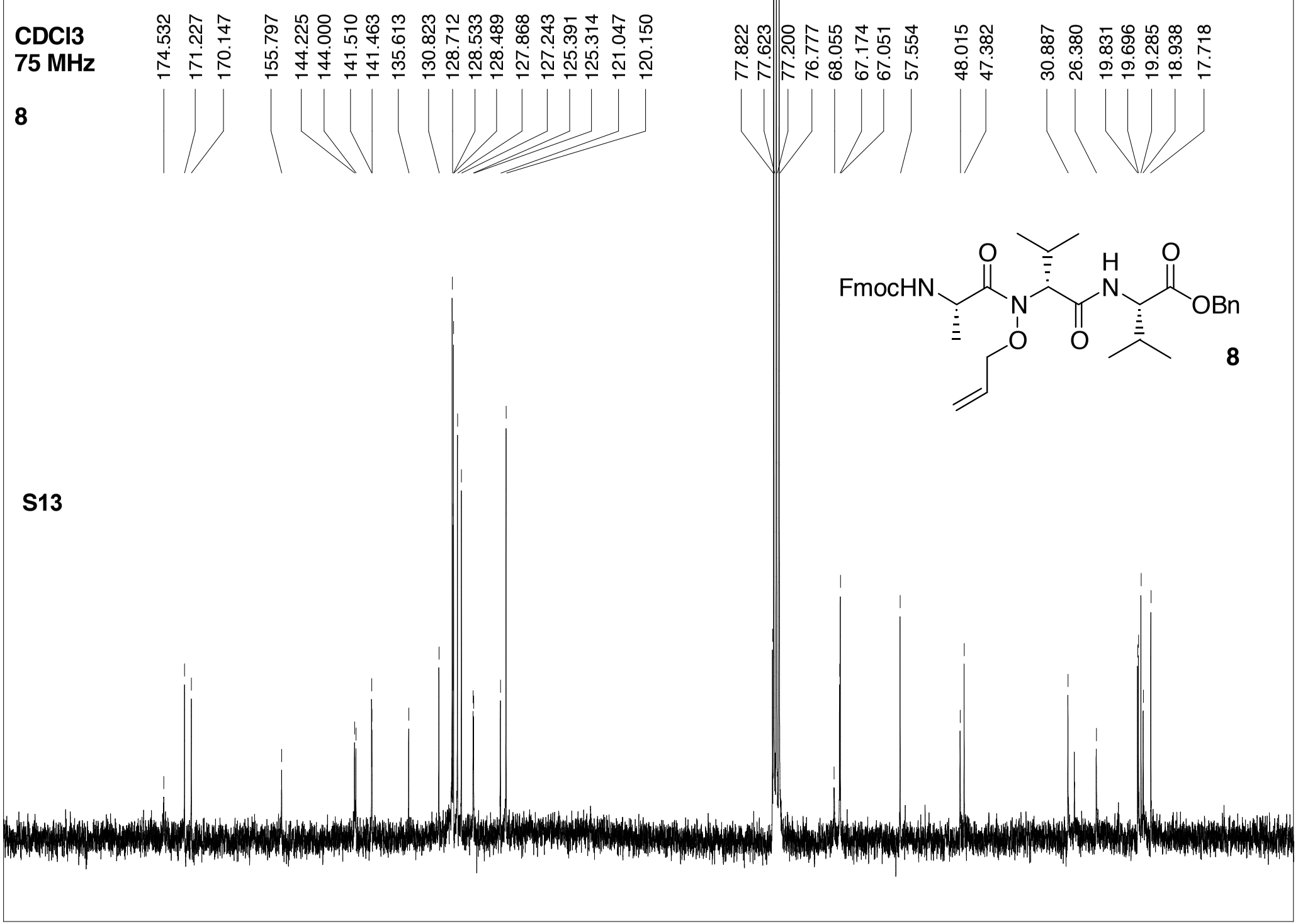
0.0
ppm (t1)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75 MHz
8
174.532
171.227
170.147
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128.712
128.533
128.489
127.868
127.243
125.391
125.314
121.047
120.150
77.822
77.623
77.200
76.777
68.055
67.174
67.051
57.554
48.015
47.382
30.887
26.380
19.831
19.696
19.285
18.938
17.718
FmocHN
O
N
O
H
N
O
O
OBn
O
8
S13
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
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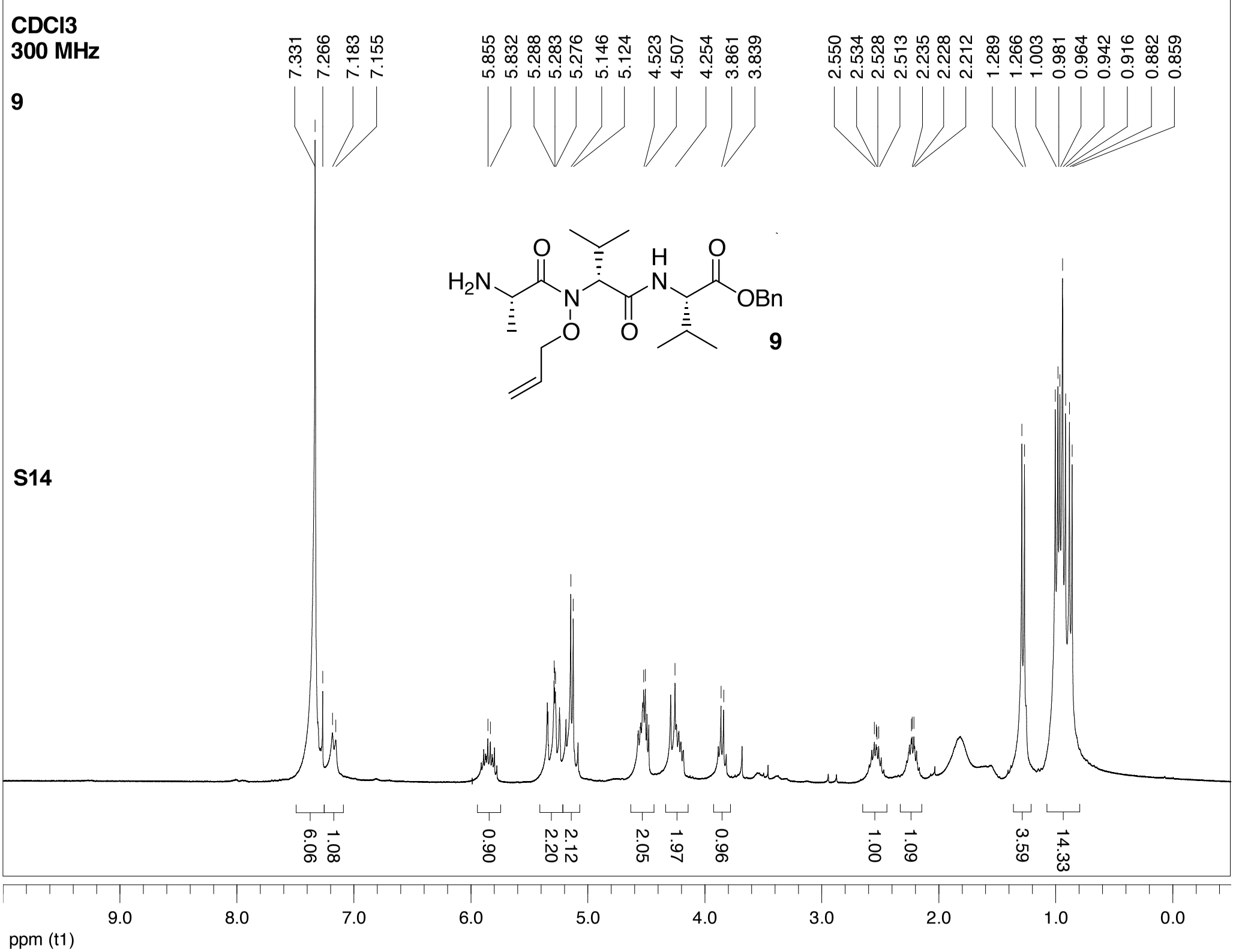
ppm (t1)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5.146
5.124
4.523
4.507
4.254
3.861
3.839
2.550
2.534
2.528
2.513
2.235
2.228
2.212
1.289
1.266
1.003
0.981
0.964
0.942
0.916
0.882
0.859
H2N
O
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O
H
N
O
OBn
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O
9
6.06
1.08
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2.12
2.05
1.97
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1.00
1.09
3.59
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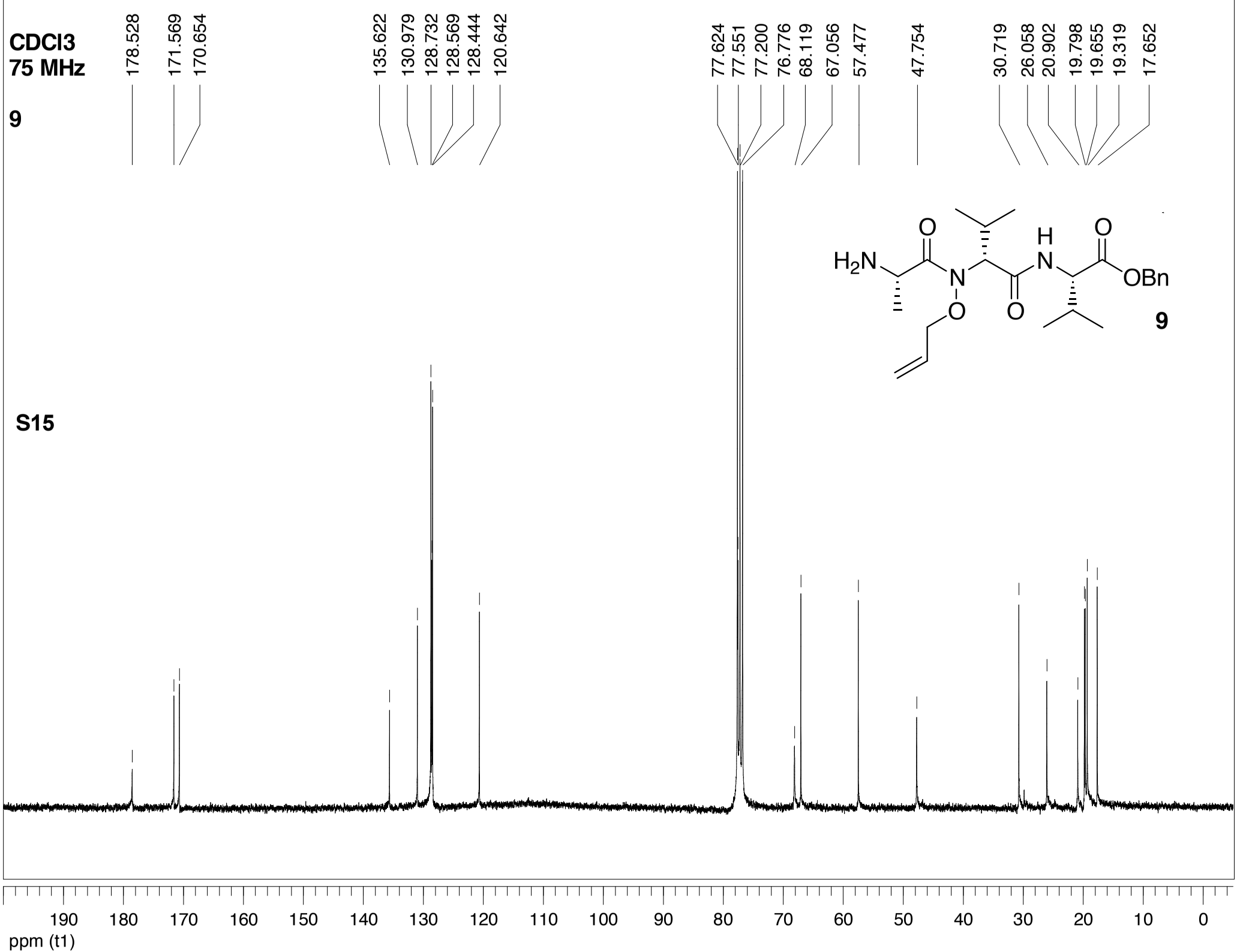
ppm (t1)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128.444
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77.624
77.551
77.200
76.776
68.119
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26.058
20.902
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19.655
19.319
17.652
S15
9
190
180
170
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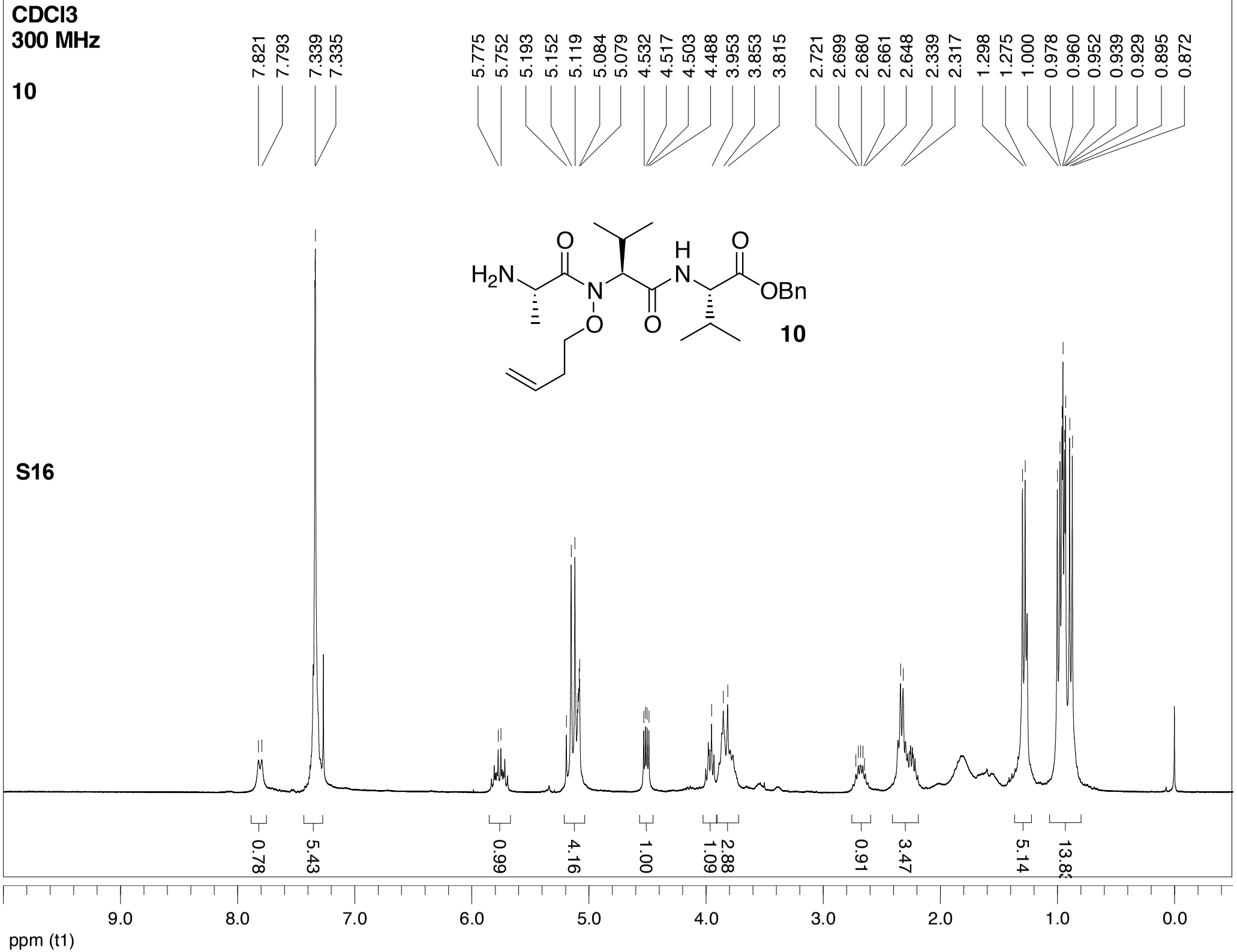
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)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300 MHz
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7.793
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5.775
5.752
5.193
5.152
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5.084
5.079
4.532
4.517
4.503
4.488
3.953
3.853
3.815
2.721
2.699
2.680
2.661
2.648
2.339
2.317
1.298
1.275
1.000
0.978
0.960
0.952
0.939
0.929
0.895
0.872
H2N
O
N
O
H
N
O
OBn
O
10
S16
0.78
5.43
0.99
4.16
1.00
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2.88
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3.47
5.14
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7.0
6.0
5.0
4.0
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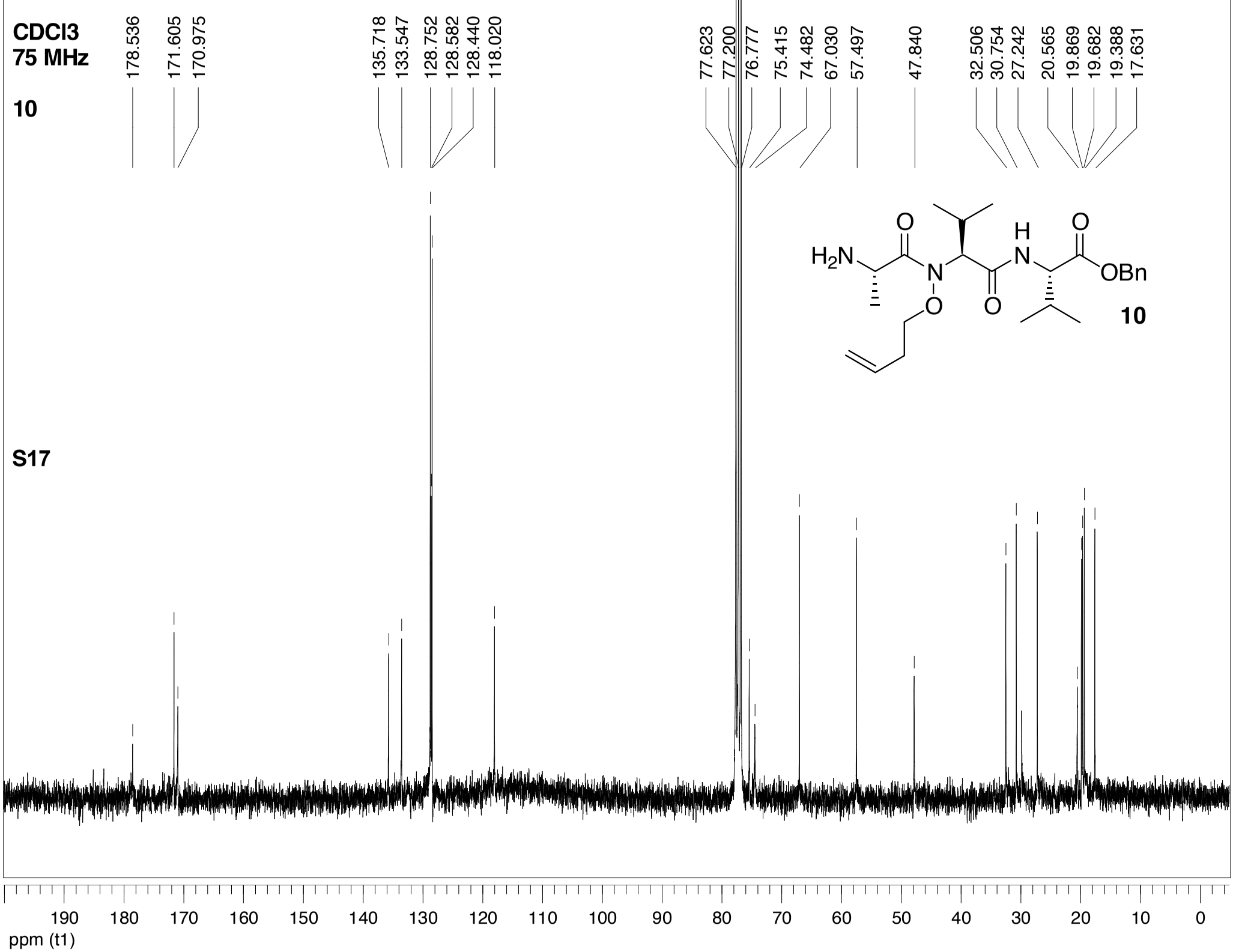
2.0
1.0
0.0
ppm (t1)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75 MHz
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171.605
170.975
135.718
133.547
128.752
128.582
128.440
118.020
77.623
77.200
76.777
75.415
74.482
67.030
57.497
47.840
32.506
30.754
27.242
20.565
19.869
19.682
19.388
17.631
H2N
O
N
O
H
N
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OBn
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10
S17
190
180
170
160
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130
120
110
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90
80
70
60
50
40
30
20
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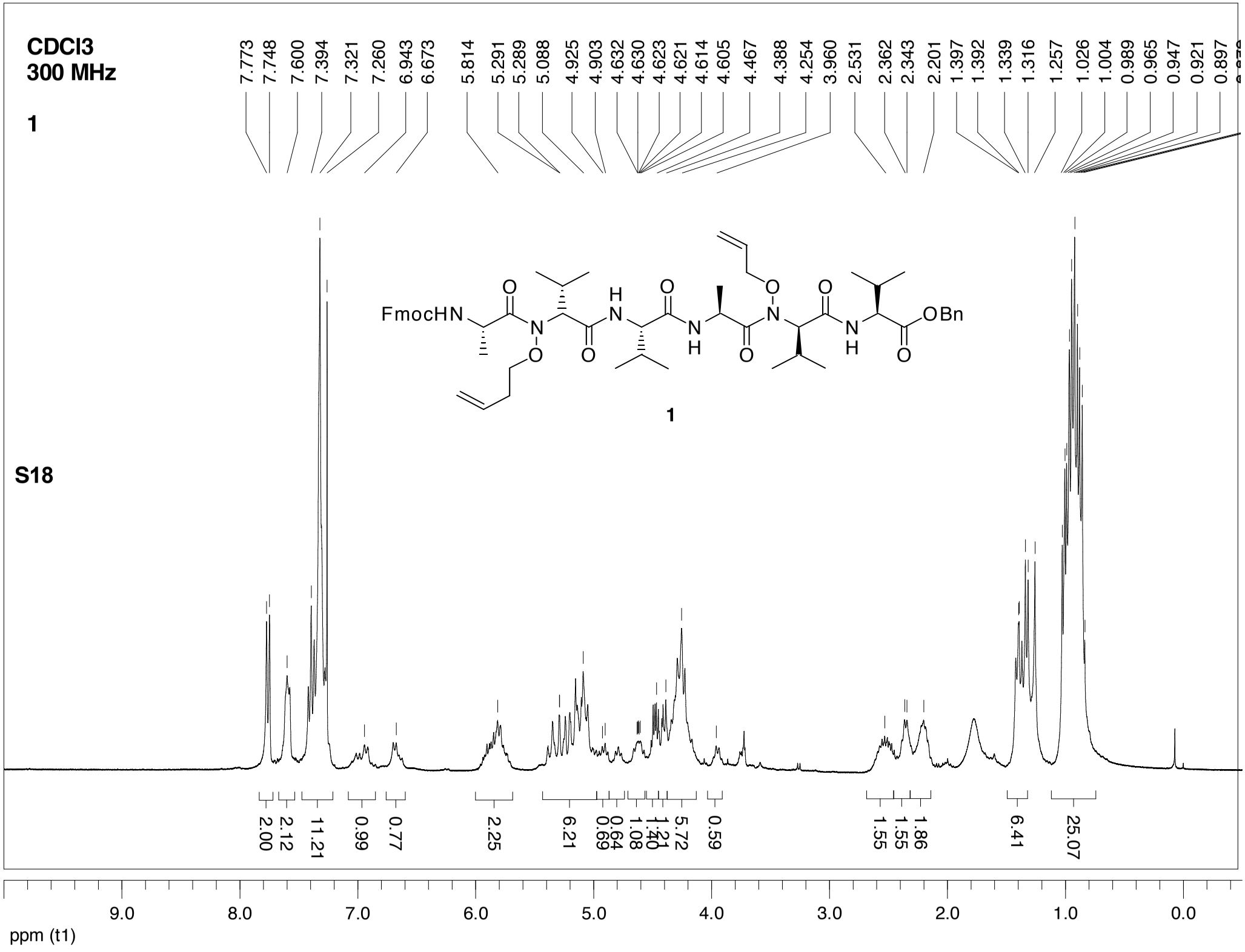
0
ppm (t1)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6.673
5.814
5.291
5.289
5.088
4.925
4.903
4.632
4.630
4.623
4.621
4.614
4.605
4.467
4.388
4.254
3.960
2.531
2.362
2.343
2.201
1.397
1.392
1.339
1.316
1.257
1.026
1.004
0.989
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0.947
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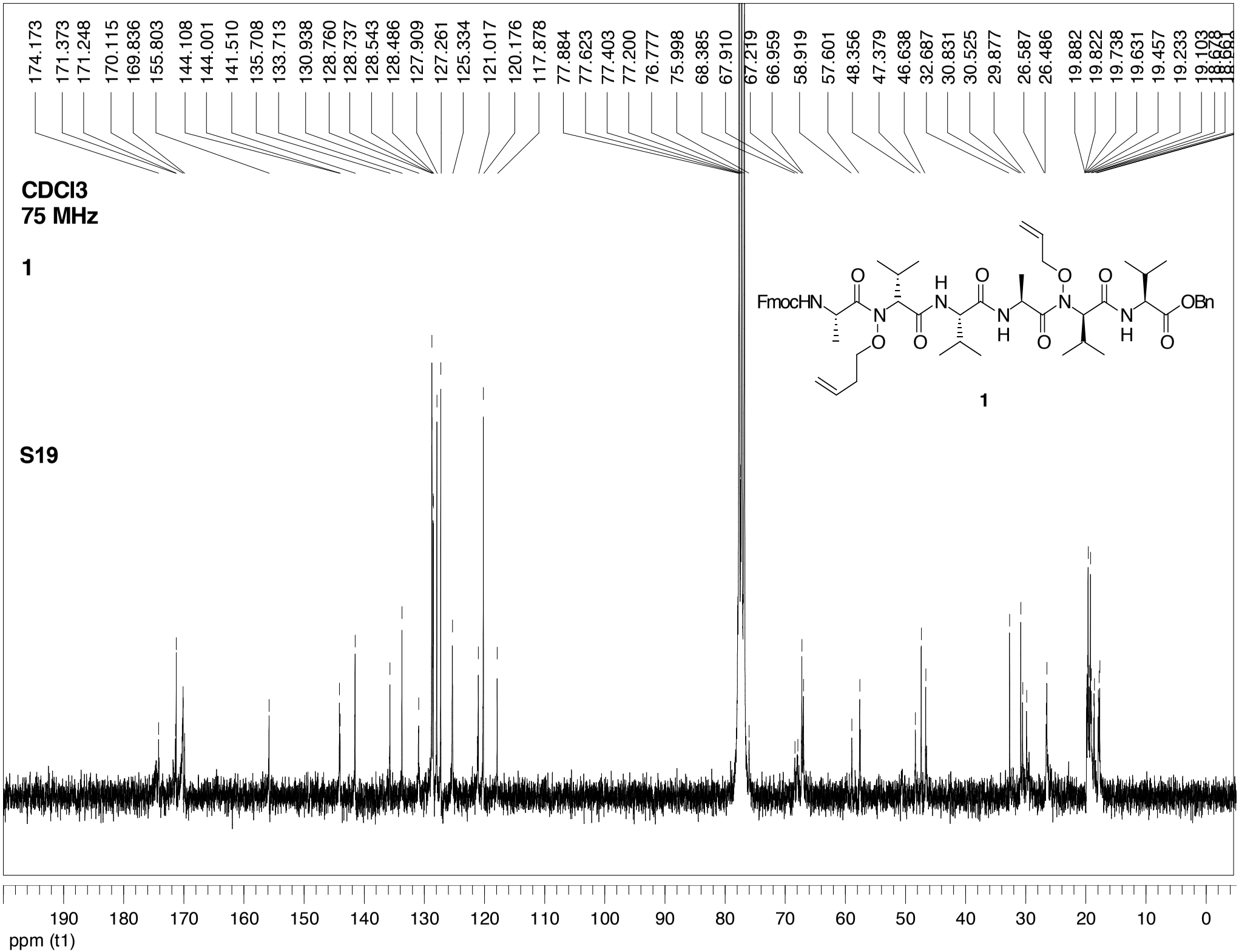
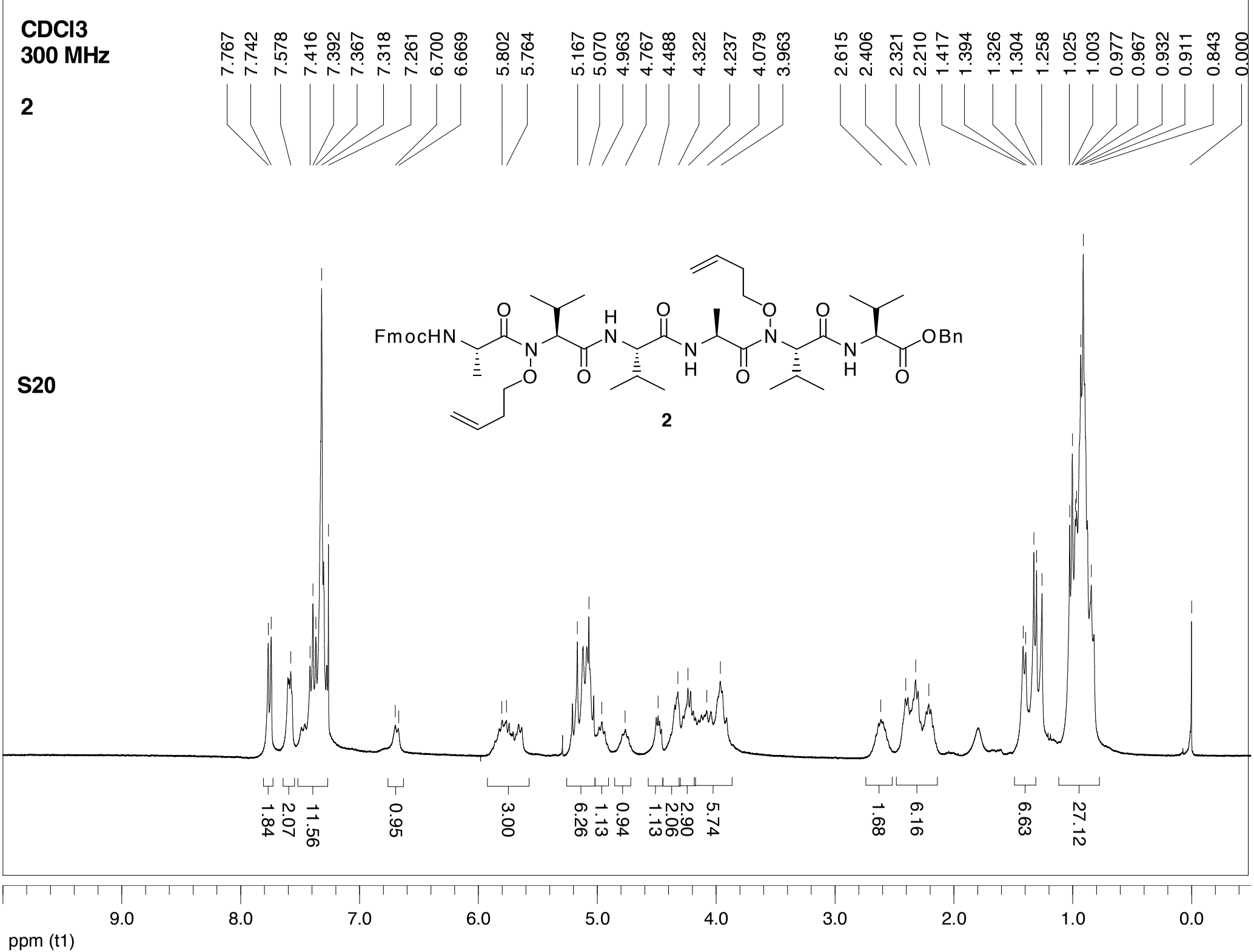
0.897
FmocHN
OBn
1
2.00
2.12
11.21
0.99
0.77
2.25
6.21
0.64
0.69
1.08
1.40
1.21
5.72
0.59
1.55
1.55
1.86
6.41
25.07
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


174.173
171.373
171.248
170.115
169.836
155.803
144.108
144.001
141.510
135.708
133.713
130.938
128.760
128.737
128.543
128.486
127.909
127.261
125.334
121.017
120.176
117.878
77.884
77.623
77.403
77.200
76.777
75.998
68.385
67.910
67.219
66.959
58.919
57.601
48.356
47.379
46.638
32.687
30.831
30.525
29.877
26.587
26.486
19.882
19.822
19.738
19.631
19.457
19.233
19.103
CDCl3
75 MHz
1
S19
FmocHN
OBn
1
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

CDCl3
300 MHz

2

S20

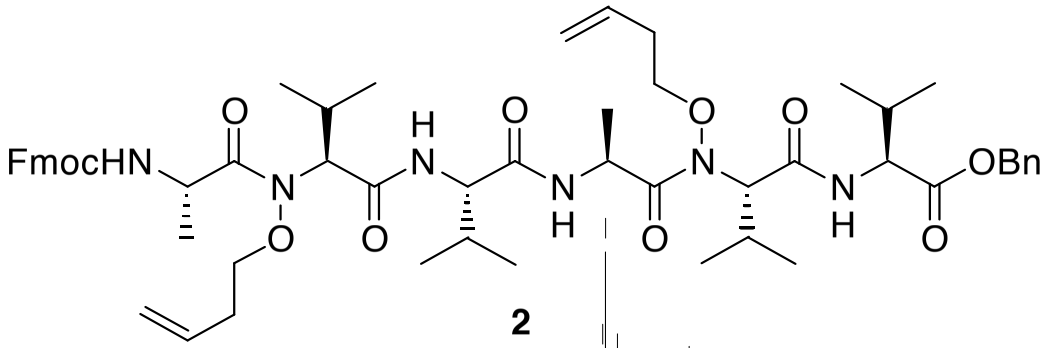


CDCl3
75 MHz

2

174.824 174.243 171.399 170.108 170.016 169.809 155.833 144.094 143.958 141.463 135.728 133.571 133.468 128.715 128.490 128.446 127.881 127.244 125.287 120.142 118.112 118.030

77.200 76.020 75.884 73.527 72.838 67.236 66.981 58.815 57.438 48.015 47.287 46.127 32.620 32.509 30.655 27.318 27.279 19.874 19.788 19.702 19.510 19.321 18.528

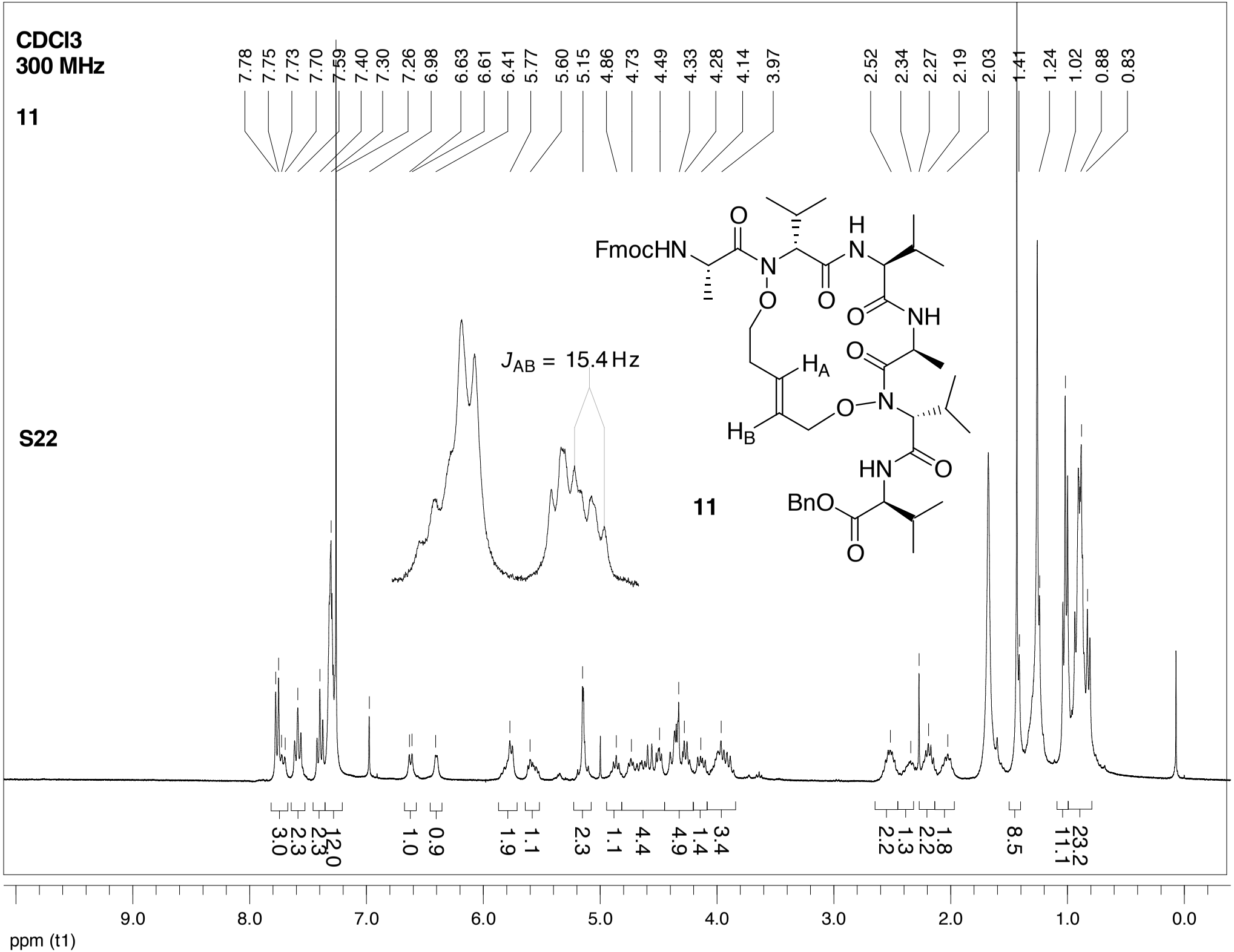


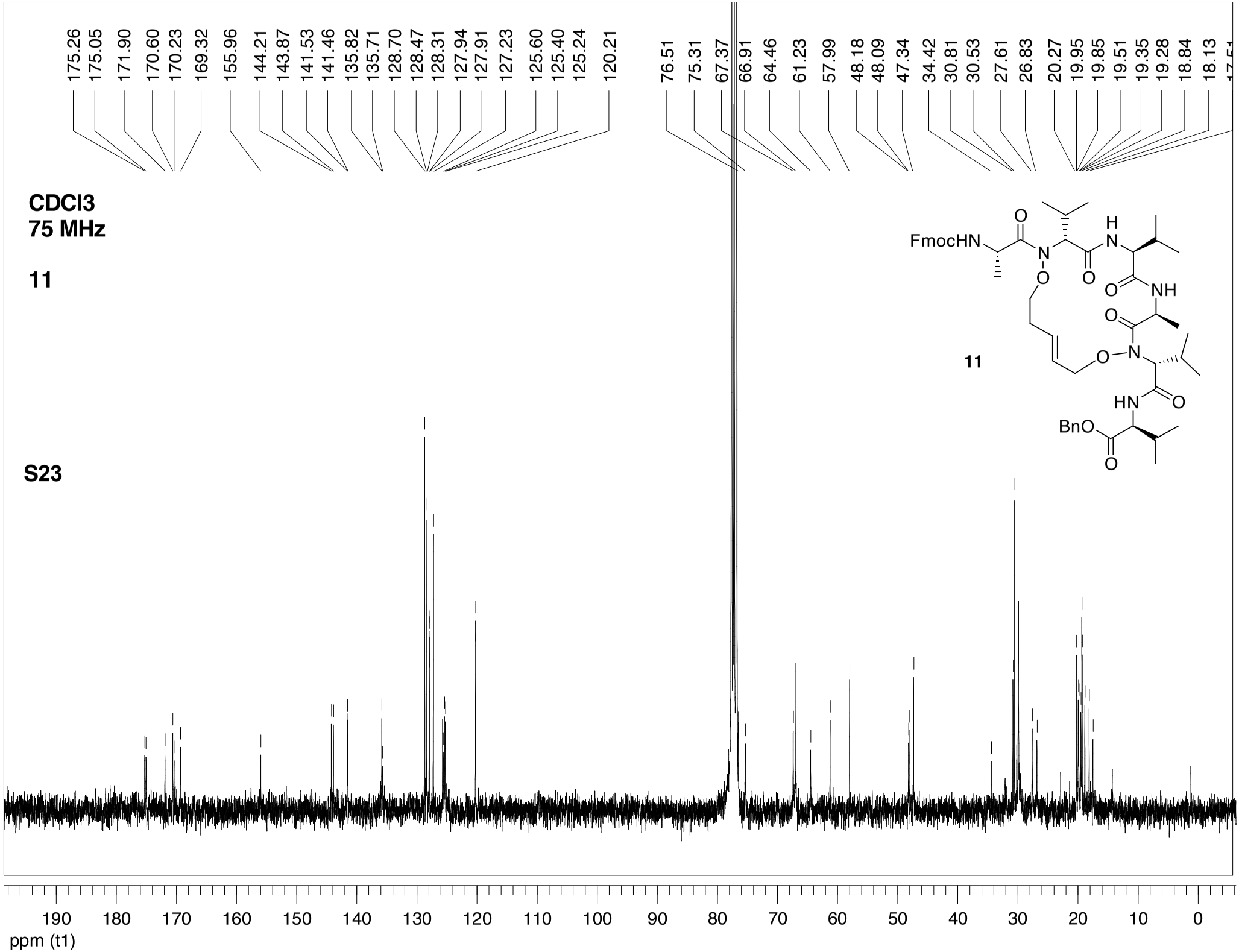
2

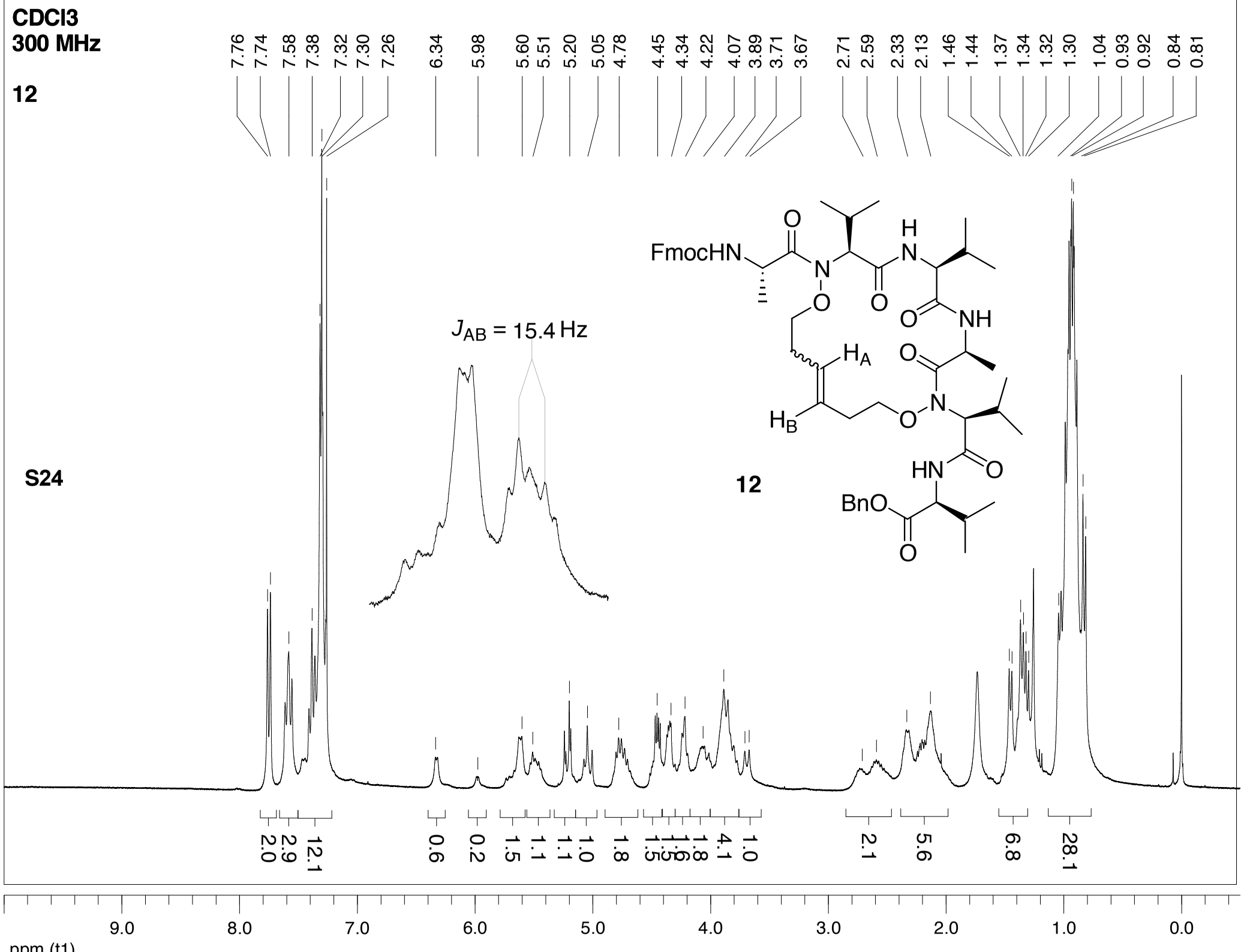
S21

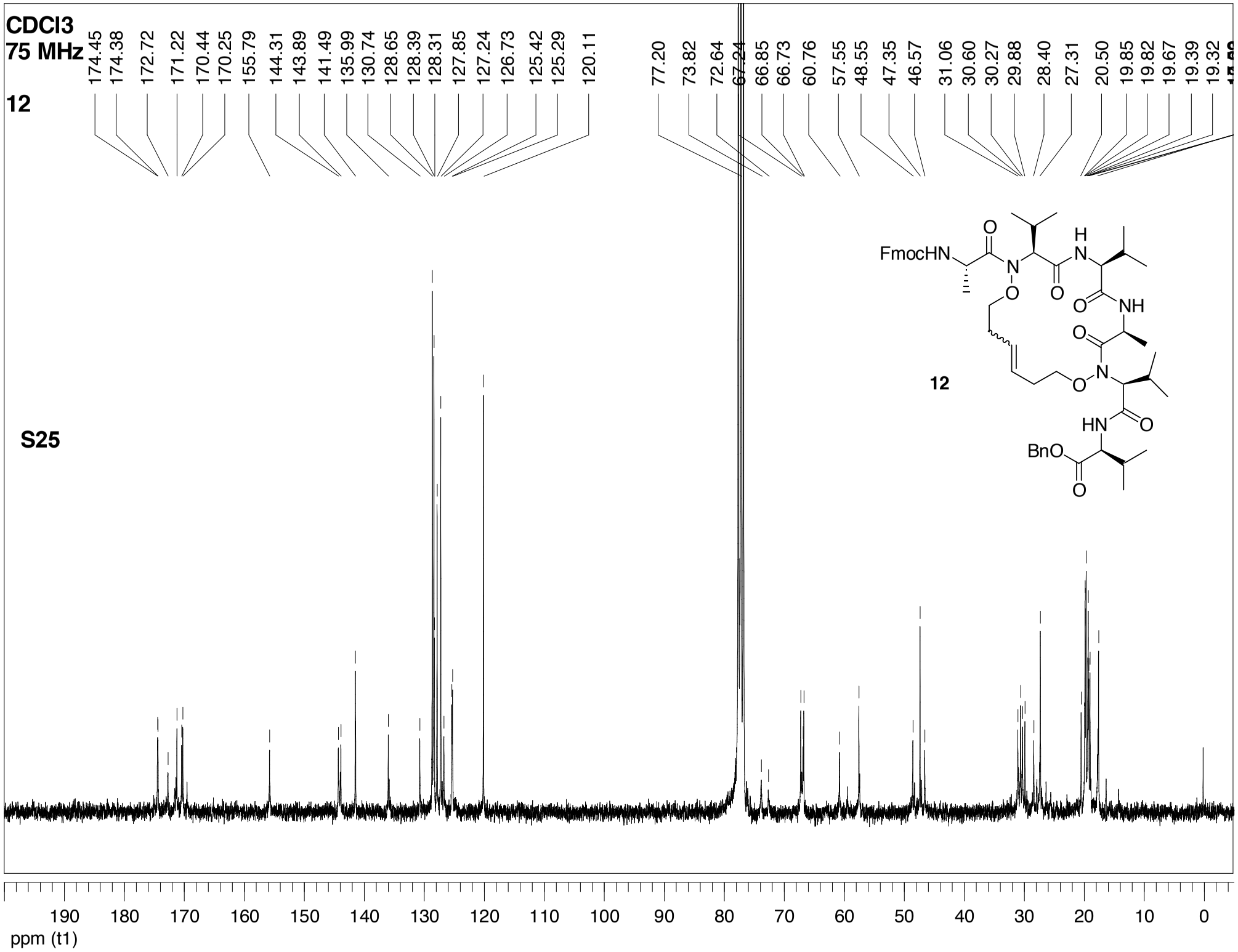
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

ppm (t1)

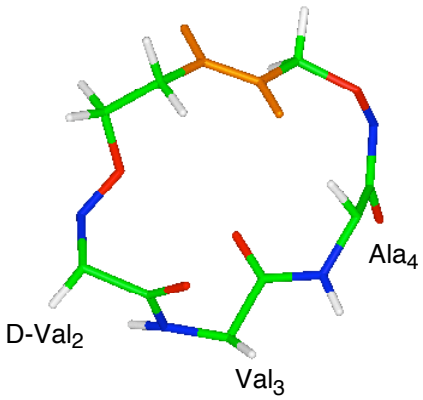

CDCl3
300 MHz
11
S22
7.78
7.75
7.73
7.70
7.59
7.40
7.30
7.26
6.98
6.63
6.61
6.41
5.77
5.60
5.15
4.86
4.73
4.49
4.33
4.28
4.14
3.97
2.52
2.34
2.27
2.19
2.03
1.41
1.24
1.02
0.88
0.83
J_{AB} = 15.4 Hz
FmocHN
H_A
H_B
BnO
11
3.0
2.3
2.3
12.0
1.0
0.9
1.9
1.1
2.3
1.1
4.4
4.9
1.4
3.4
2.2
1.3
2.2
1.8
8.5
11.1
23.2
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


175.26
175.05
171.90
170.60
170.23
169.32
155.96
144.21
143.87
141.53
141.46
135.82
135.71
128.70
128.47
128.31
127.94
127.91
127.23
125.60
125.40
125.24
120.21
76.51
75.31
67.37
66.91
64.46
61.23
57.99
48.18
48.09
47.34
34.42
30.81
30.53
27.61
26.83
20.27
19.95
19.85
19.51
19.35
19.28
18.84
18.13
CDCl3
75 MHz
11
S23
FmocHN
BnO
11
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

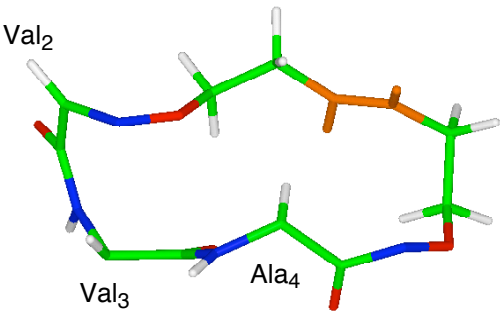

CDCl3
300 MHz
12
7.76
7.74
7.58
7.38
7.32
7.30
7.26
6.34
5.98
5.60
5.51
5.20
5.05
4.78
4.45
4.34
4.22
4.07
3.89
3.71
3.67
2.71
2.59
2.33
2.13
1.46
1.44
1.37
1.34
1.32
1.30
1.04
0.93
0.92
0.84
0.81
J_{AB} = 15.4 Hz
FmocHN
O
N
O
O
H
N
O
NH
H_A
H_B
O
N
O
HN
O
BnO
O
12
S24
2.0
2.9
12.1
0.6
0.2
1.5
1.1
1.1
1.0
1.8
1.5
1.5
1.6
1.8
4.1
1.0
2.1
5.6
6.8
28.1
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


CDCl3
75 MHz
12
174.45
174.38
172.72
171.22
170.44
170.25
155.79
144.31
143.89
141.49
135.99
130.74
128.65
128.39
128.31
127.85
127.24
126.73
125.42
125.29
120.11
77.20
73.82
72.64
67.24
66.85
66.73
60.76
57.55
48.55
47.35
46.57
31.06
30.60
30.27
29.88
28.40
27.31
20.50
19.85
19.82
19.67
19.39
19.32
FmocHN
O
N
O
H
N
O
O
NH
O
N
O
HN
O
BnO
O
12
S25
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

Representative structures of **11** and **12** from conformational analysis data: only the backbone of the ring is shown (in orange the ethylene bond and ethylenic protons).



11



12