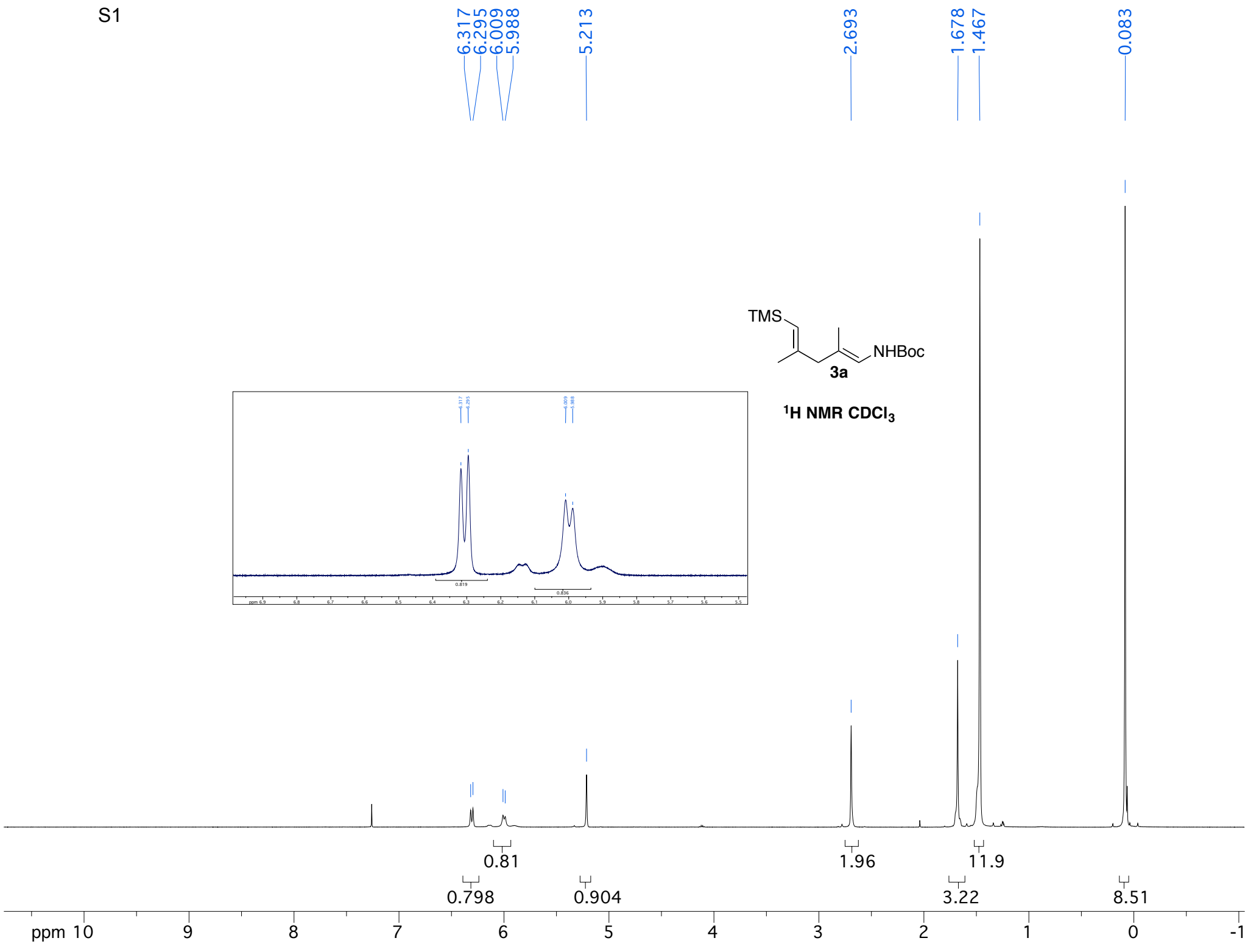
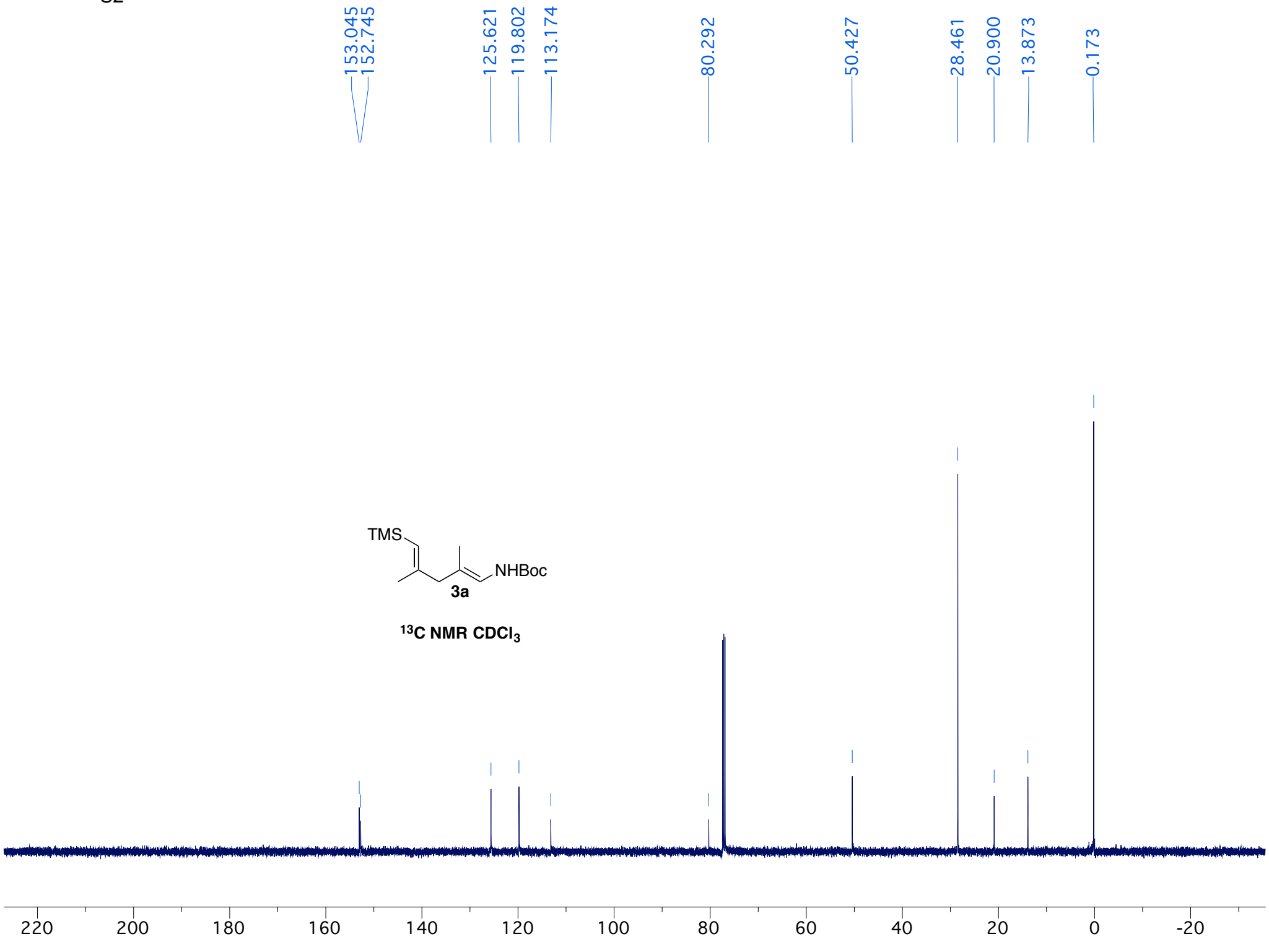
Ruthenium Catalyzed Alkene-Alkyne Coupling of Disubstituted Olefins: Application to the Stereoselective Synthesis of Trisubstituted Enecarbamates.

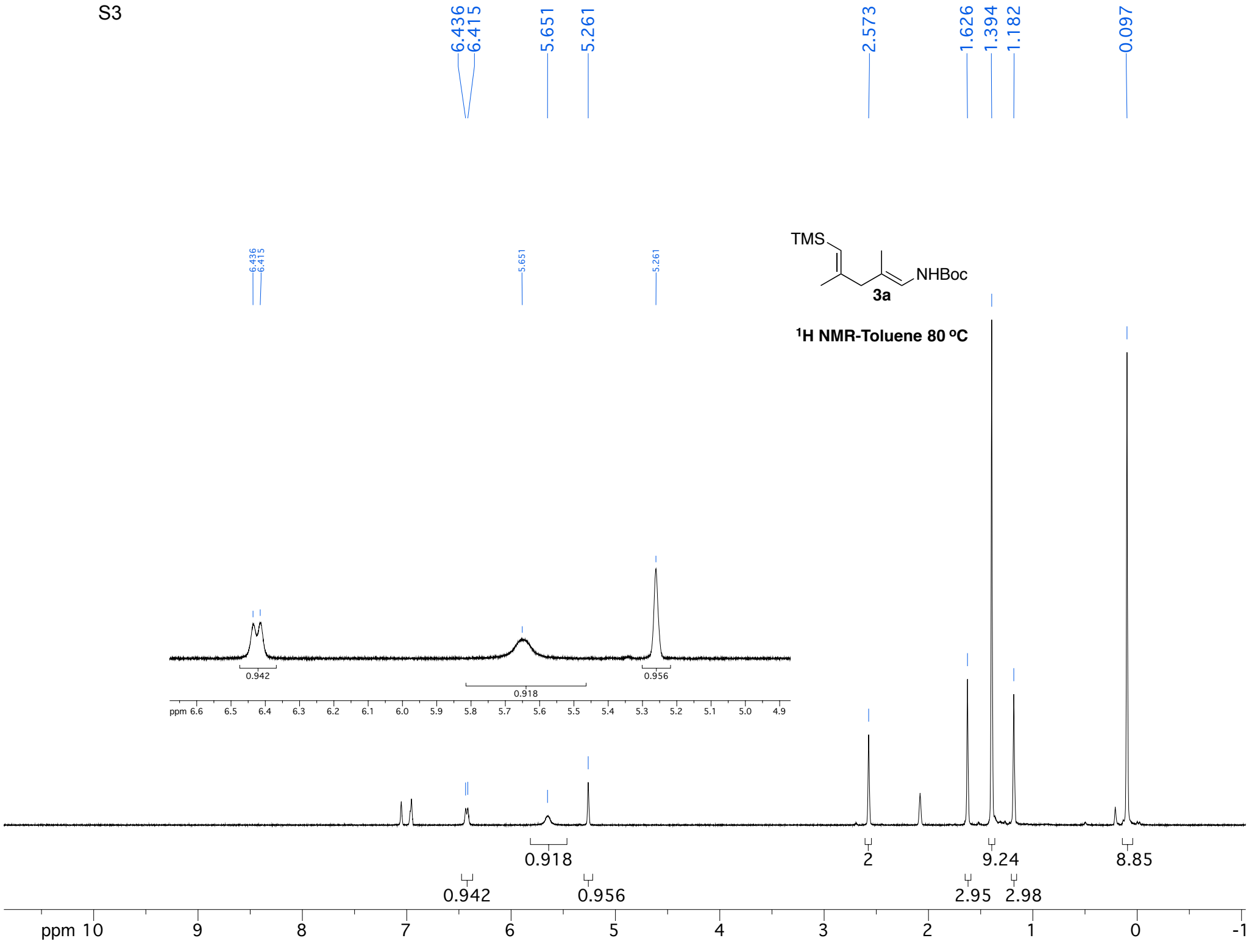
Barry M. Trost, James J. Cregg

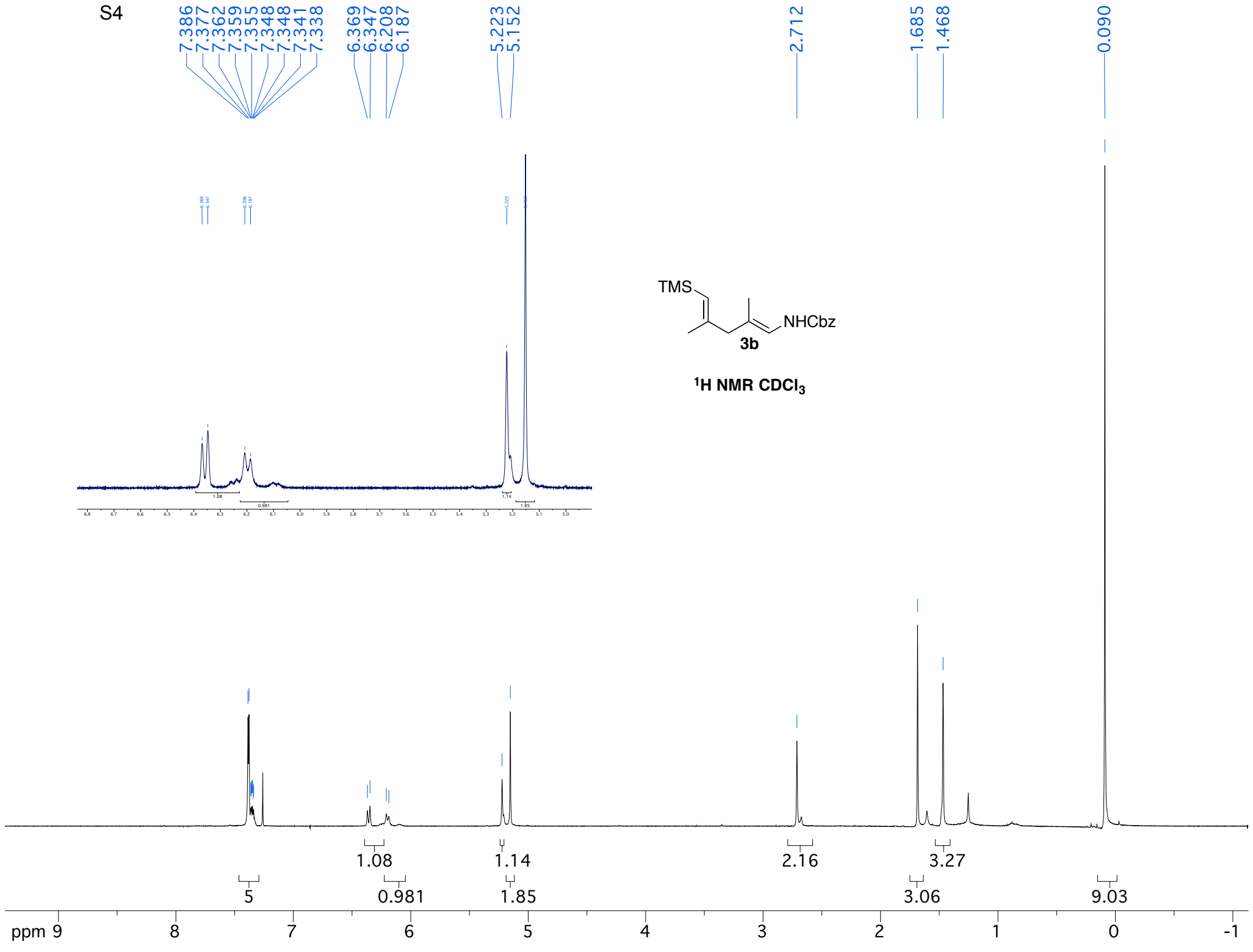
Department of Chemistry, Stanford University, Stanford, California, 94305-5080, United States

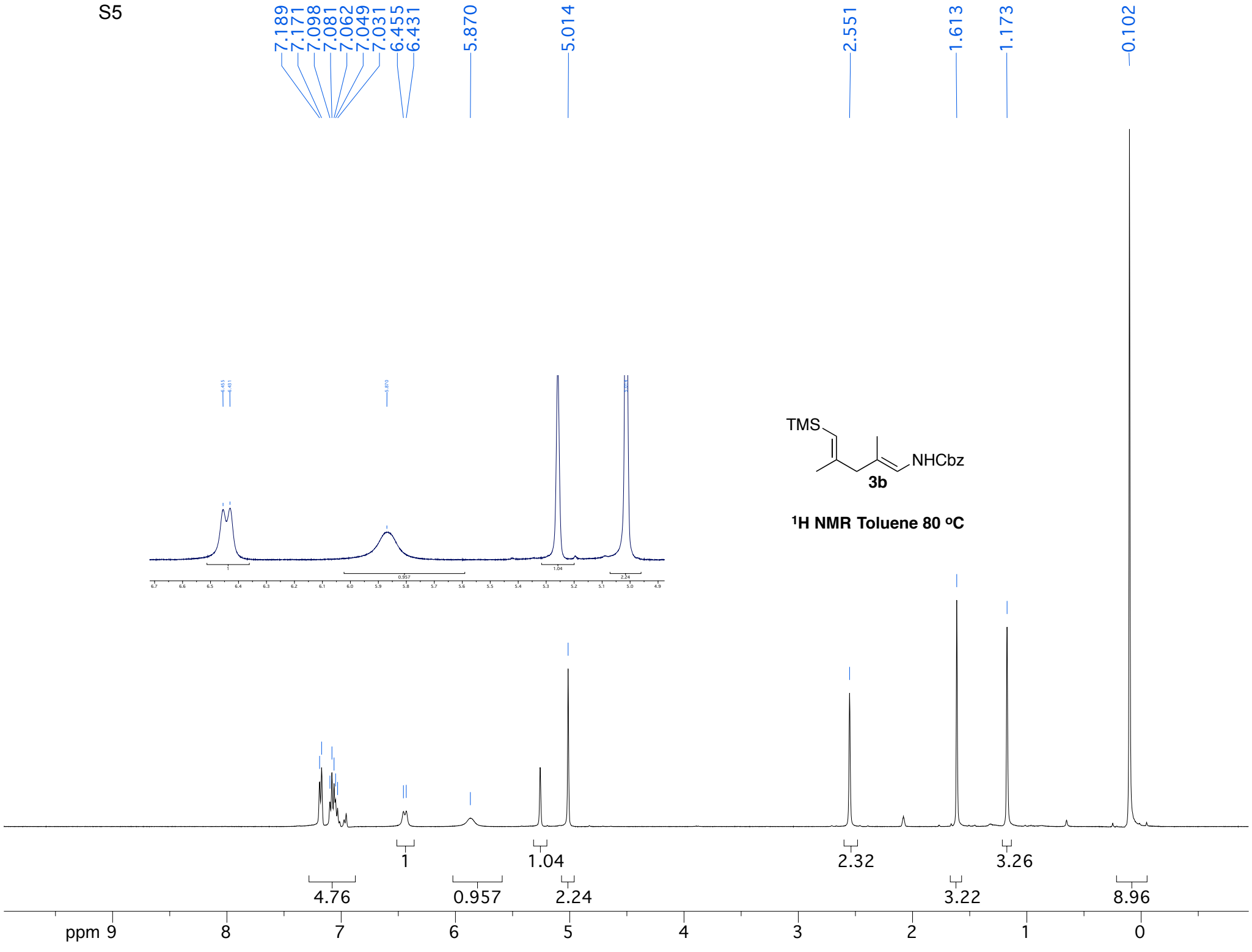
SUPPLEMENTAL INFORMATION: SPECTRAL DATA

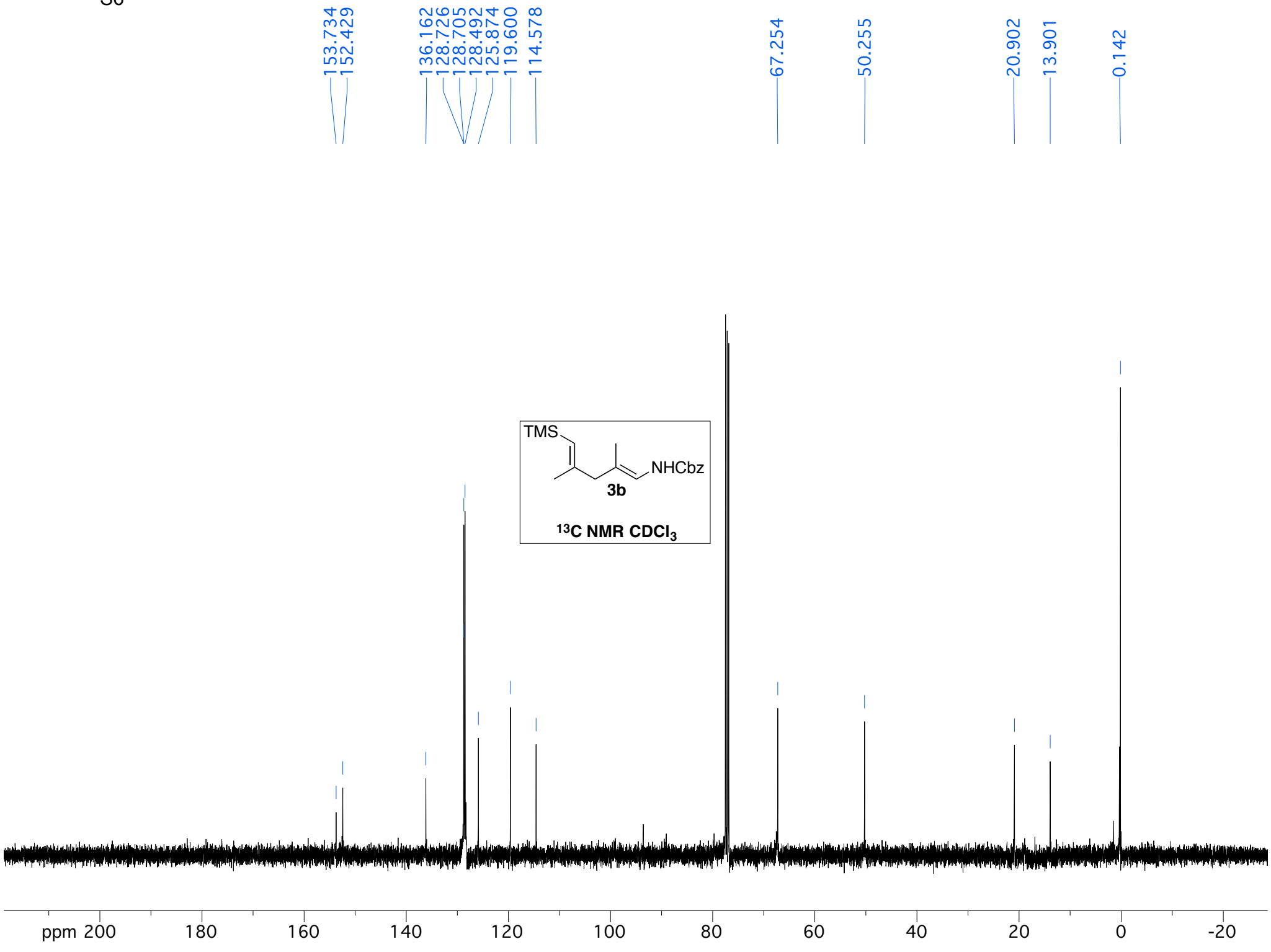

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6.009
5.988
5.213
2.693
1.678
1.467
0.083
TMS
NHBoc
3a
^{1}H NMR CDCl$_3$
0.81
1.96
11.9
0.798
0.904
3.22
8.51
ppm 10
9
8
7
6
5
4
3
2
1
0
-1

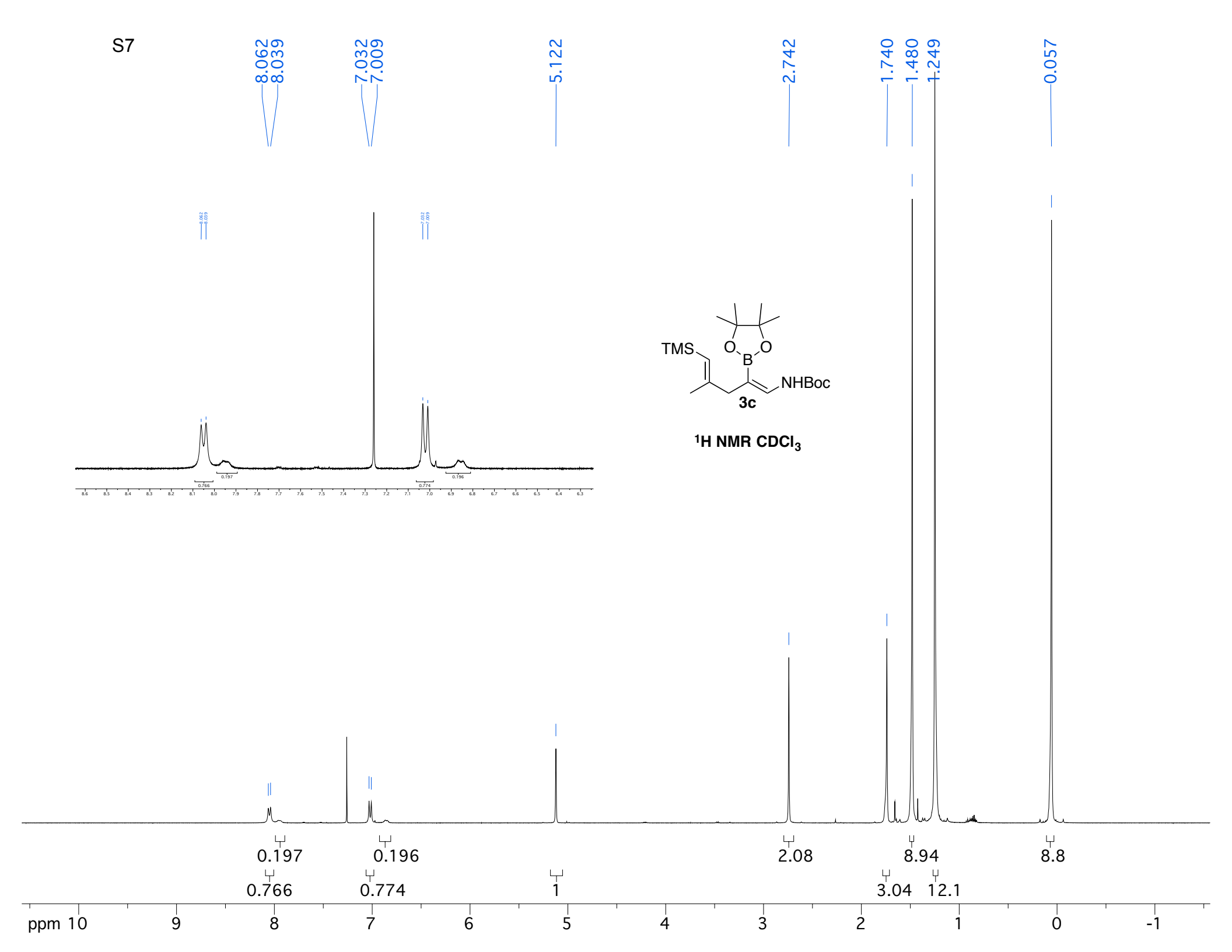

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152.745
125.621
119.802
113.174
80.292
50.427
28.461
20.900
13.873
0.173
TMS
NHBoc
3a
13C NMR CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
-20


6.436
6.415
5.651
5.261
2.573
1.626
1.394
1.182
0.097
TMS
NHBoc
3a
¹H NMR-Toluene 80 °C
0.942
0.918
0.956
2
9.24
8.85
2.95
2.98
ppm 10
9
8
7
6
5
4
3
2
1
0
-1

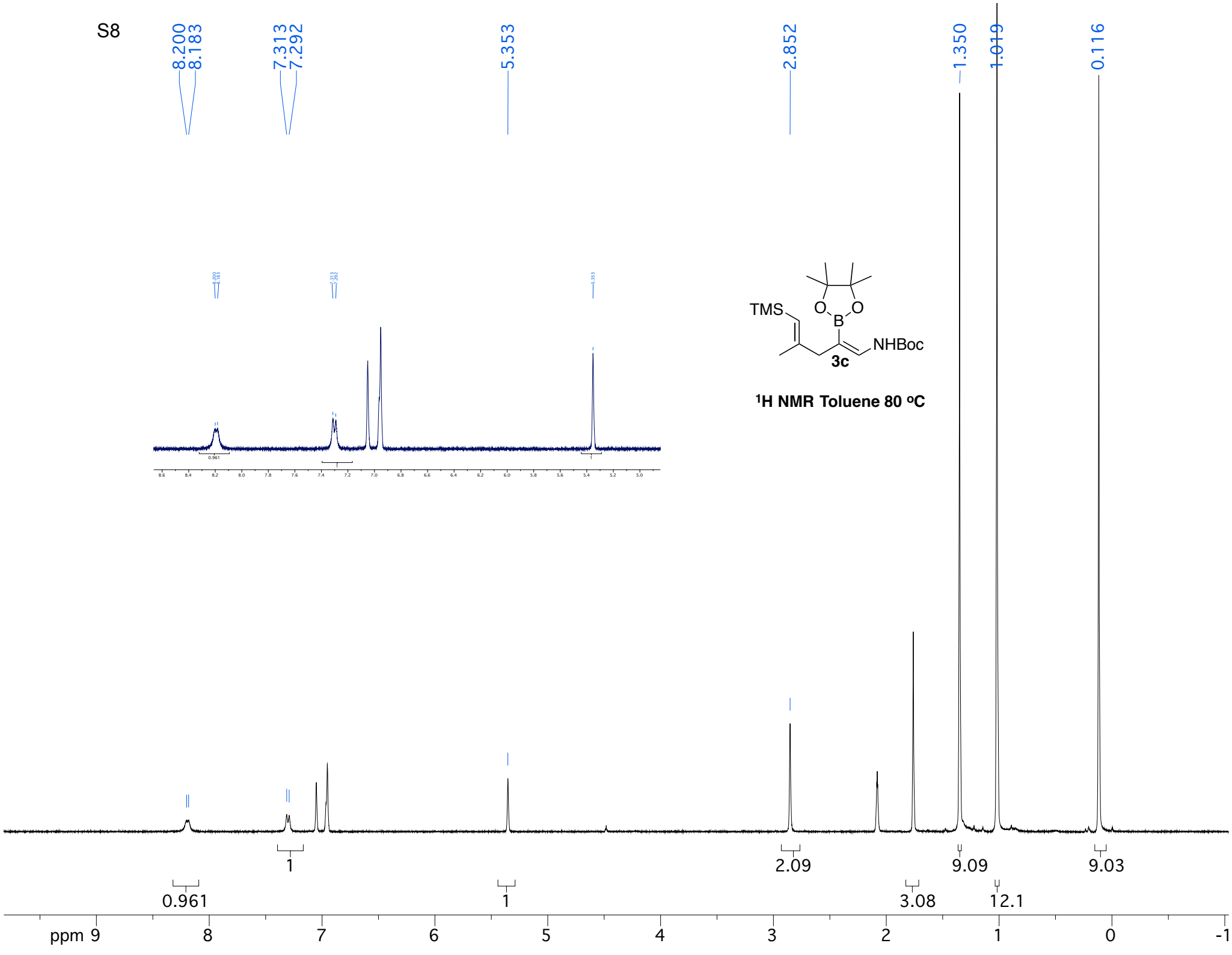

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7.362
7.359
7.355
7.348
7.348
7.341
7.338
6.369
6.347
6.208
6.187
5.223
5.152
2.712
1.685
1.468
0.090
TMS
NHCbz
3b
1H NMR CDCl3
1.08
1.14
2.16
3.27
5
0.981
1.85
3.06
9.03
ppm 9
8
7
6
5
4
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2
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0
-1

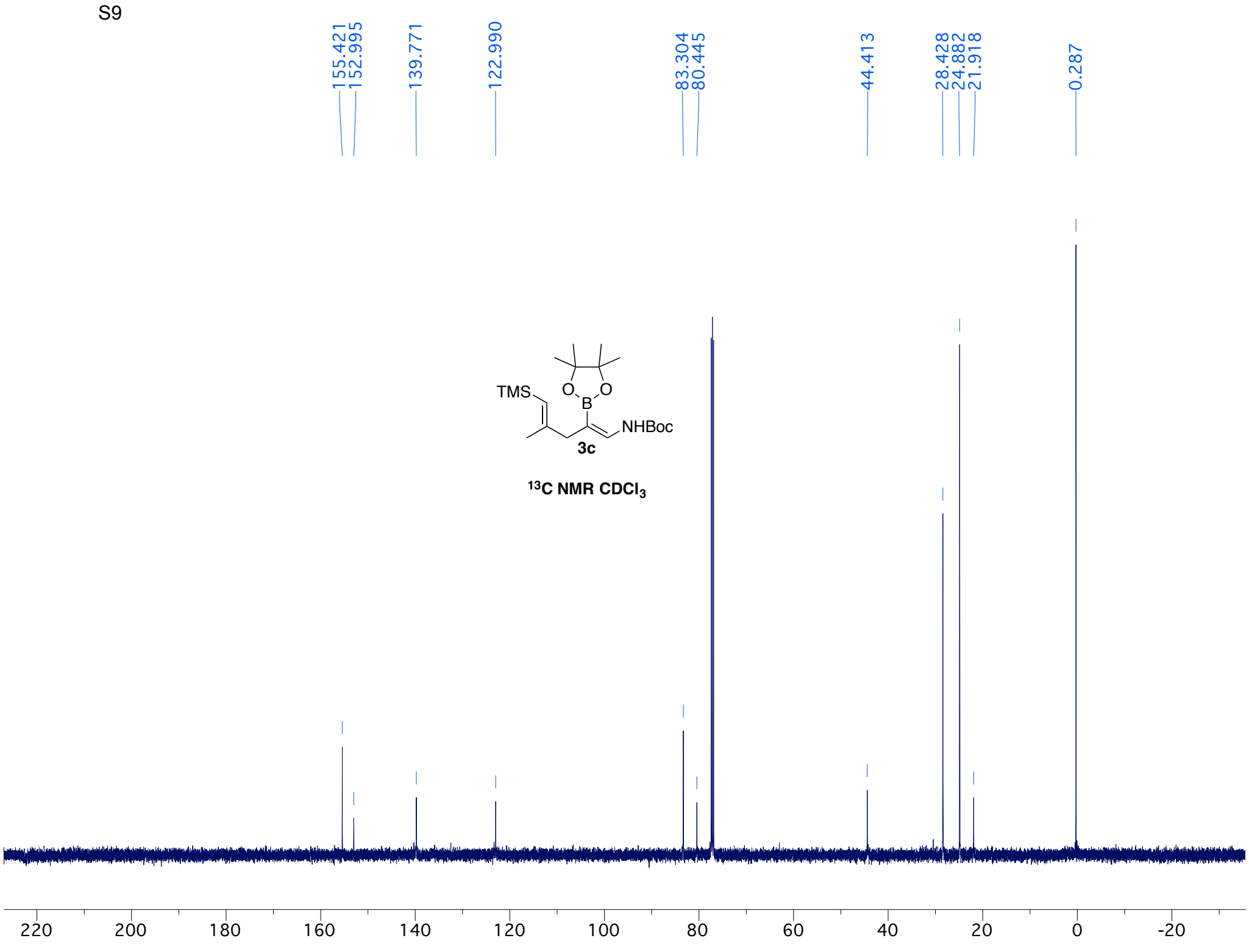

7.189
7.171
7.098
7.081
7.062
7.049
7.031
6.455
6.431
5.870
5.014
2.551
1.613
1.173
0.102
TMS
NHCbz
3b
1H NMR Toluene 80 oC
1
1.04
2.32
3.26
4.76
0.957
2.24
3.22
8.96
ppm 9
8
7
6
5
4
3
2
1
0

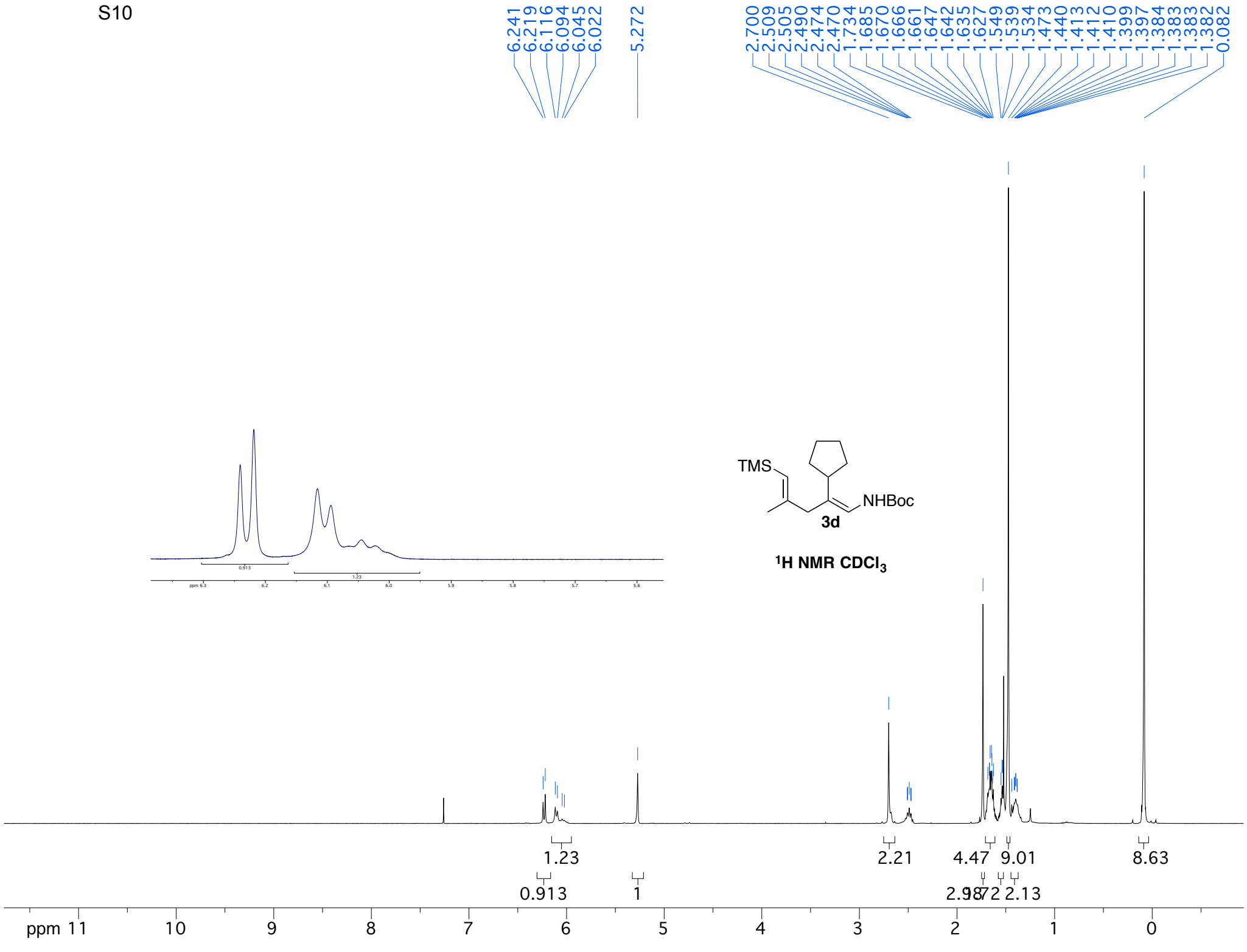

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128.726
128.705
128.492
125.874
119.600
114.578
67.254
50.255
20.902
13.901
0.142
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NHCbz
3b
13C NMR CDCl3
ppm 200
180
160
140
120
100
80
60
40
20
0
-20

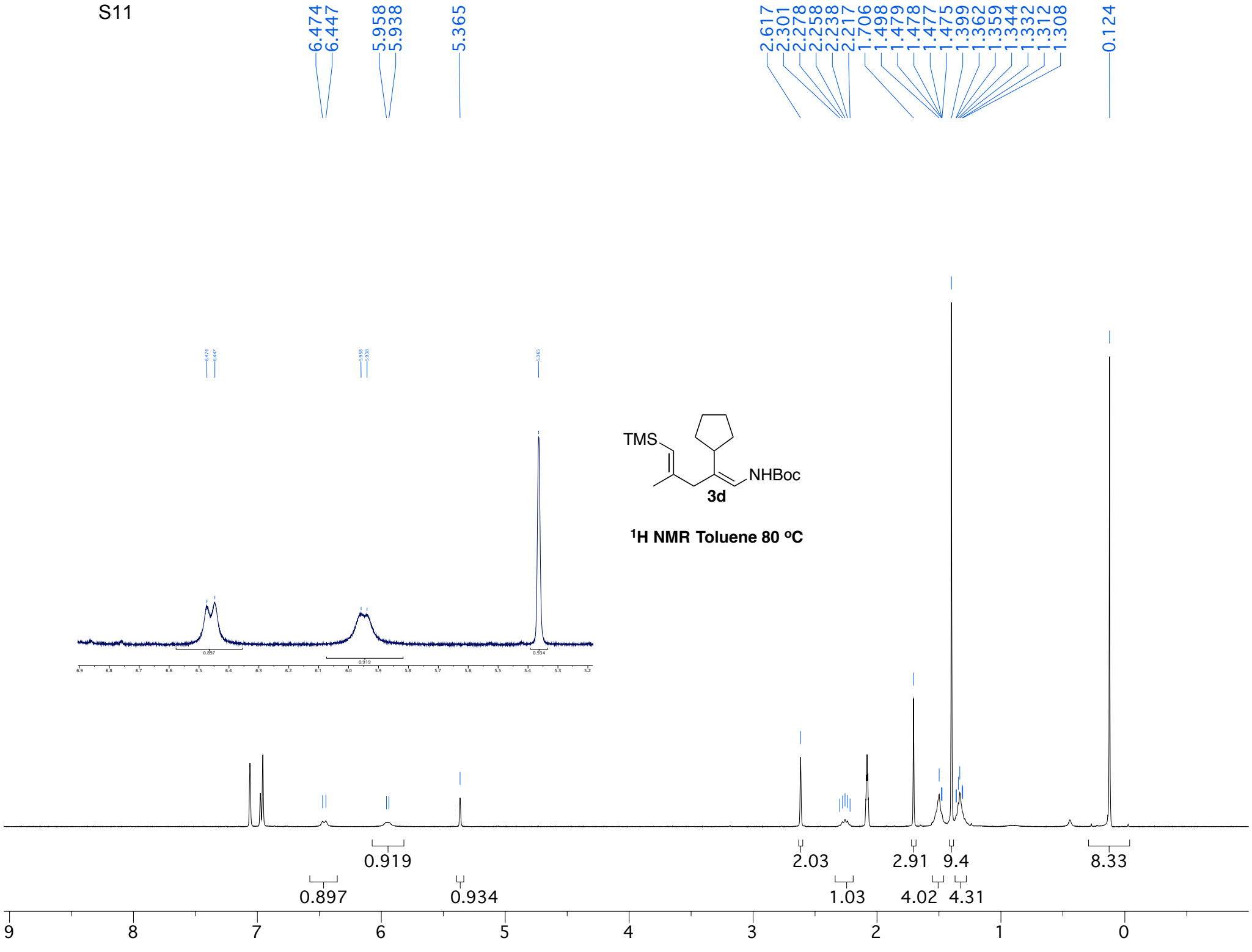

8.062
8.039
7.032
7.009
5.122
2.742
1.740
1.480
1.249
0.057
TMS
O
B
O
NHBoc
3c
0.197
0.196
2.08
8.94
8.8
0.766
0.774
1
3.04
12.1
ppm 10
9
8
7
6
5
4
3
2
1
0
-1

^{1}H NMR $CDCl_3$

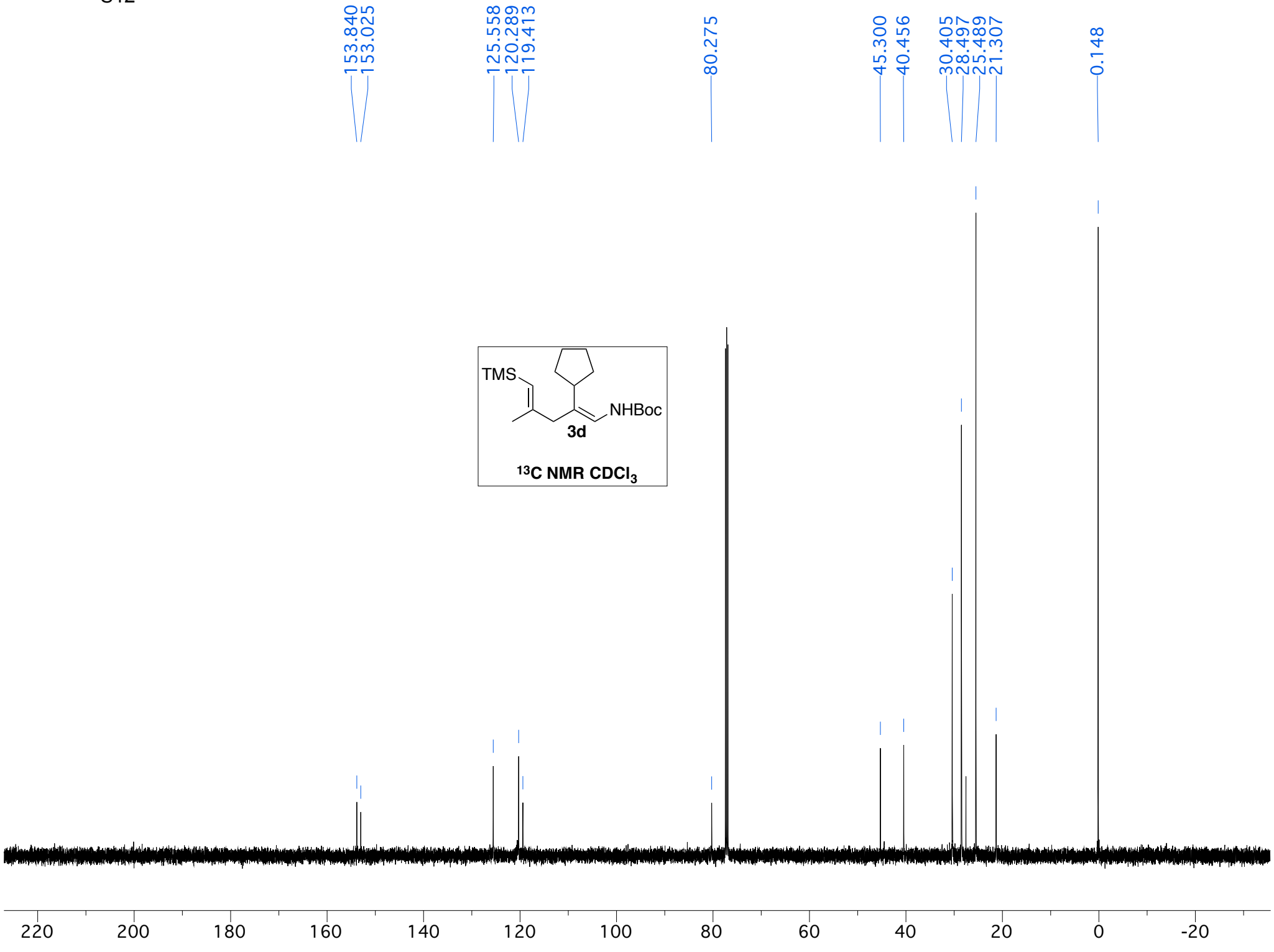

8.200
8.183
7.313
7.292
5.353
2.852
1.350
1.019
0.116
TMS
O
B
O
NHBoc
3c
1H NMR Toluene 80 oC
0.961
1
1
2.09
9.09
9.03
0.961
1
3.08
12.1
ppm 9
8
7
6
5
4
3
2
1
0
-1

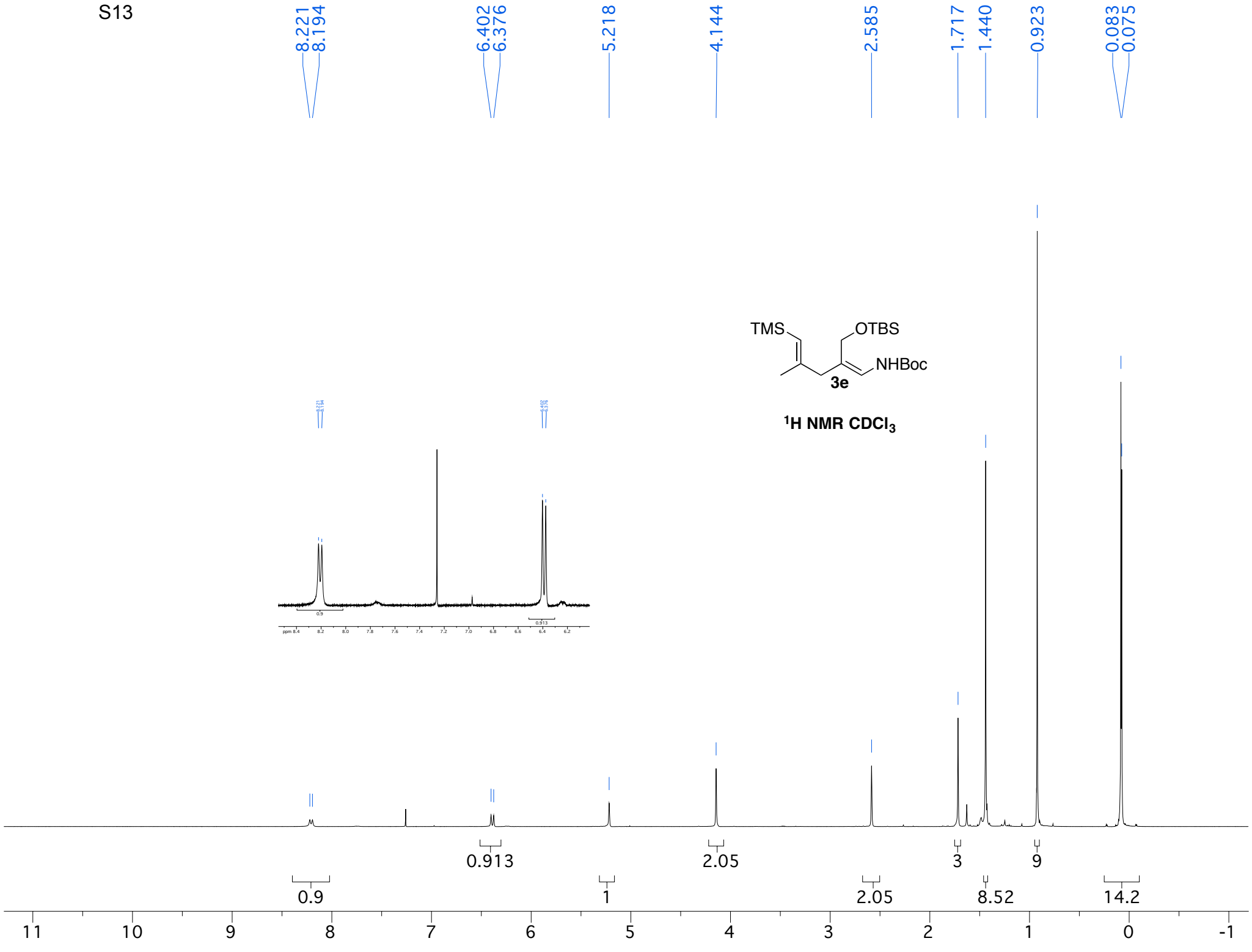

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152.995
139.771
122.990
83.304
80.445
44.413
28.428
24.882
21.918
0.287
TMS
O
B
O
NHBoc
3c
13C NMR CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
-20

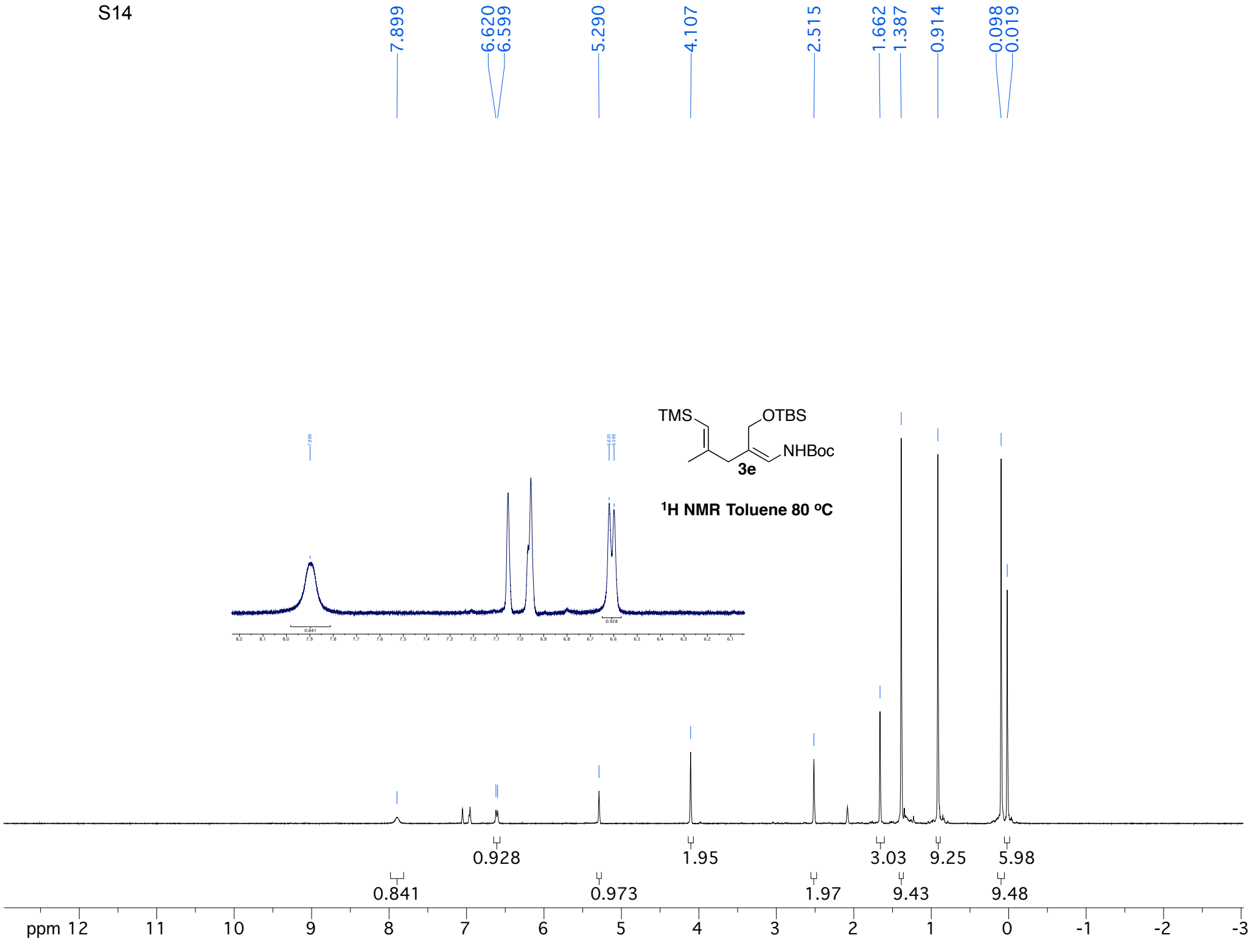

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6.094
6.045
6.022
5.272
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2.505
2.490
2.474
2.470
1.734
1.685
1.670
1.666
1.661
1.647
1.642
1.635
1.627
1.549
1.539
1.534
1.473
1.440
1.413
1.412
1.410
1.399
1.397
1.384
1.383
1.383
1.382
0.082
TMS
NHBoc
3d
1H NMR CDCl3
1.23
2.21
4.47
9.01
8.63
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1
2.13
ppm 11
10
9
8
7
6
5
4
3
2
1
0

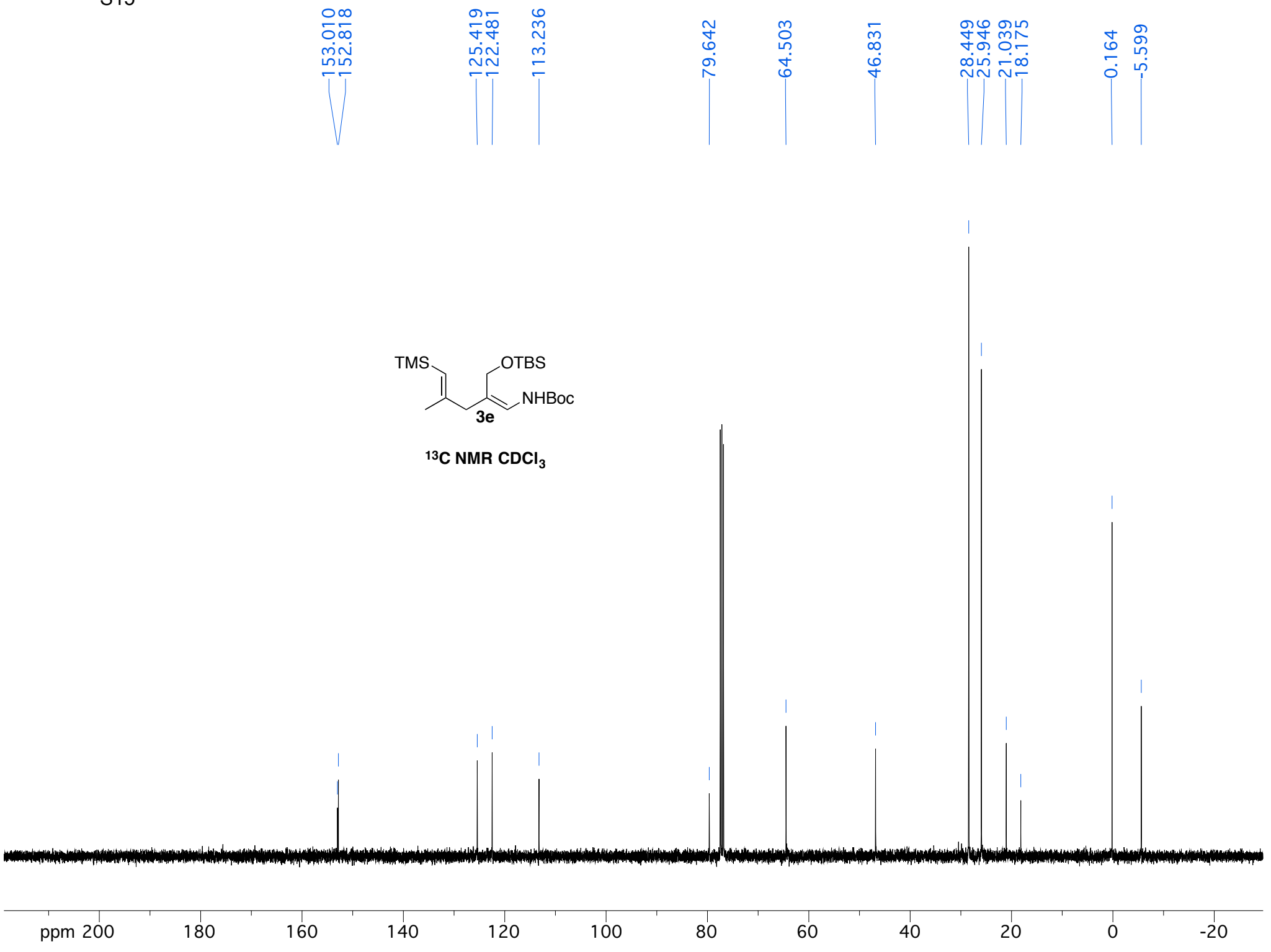


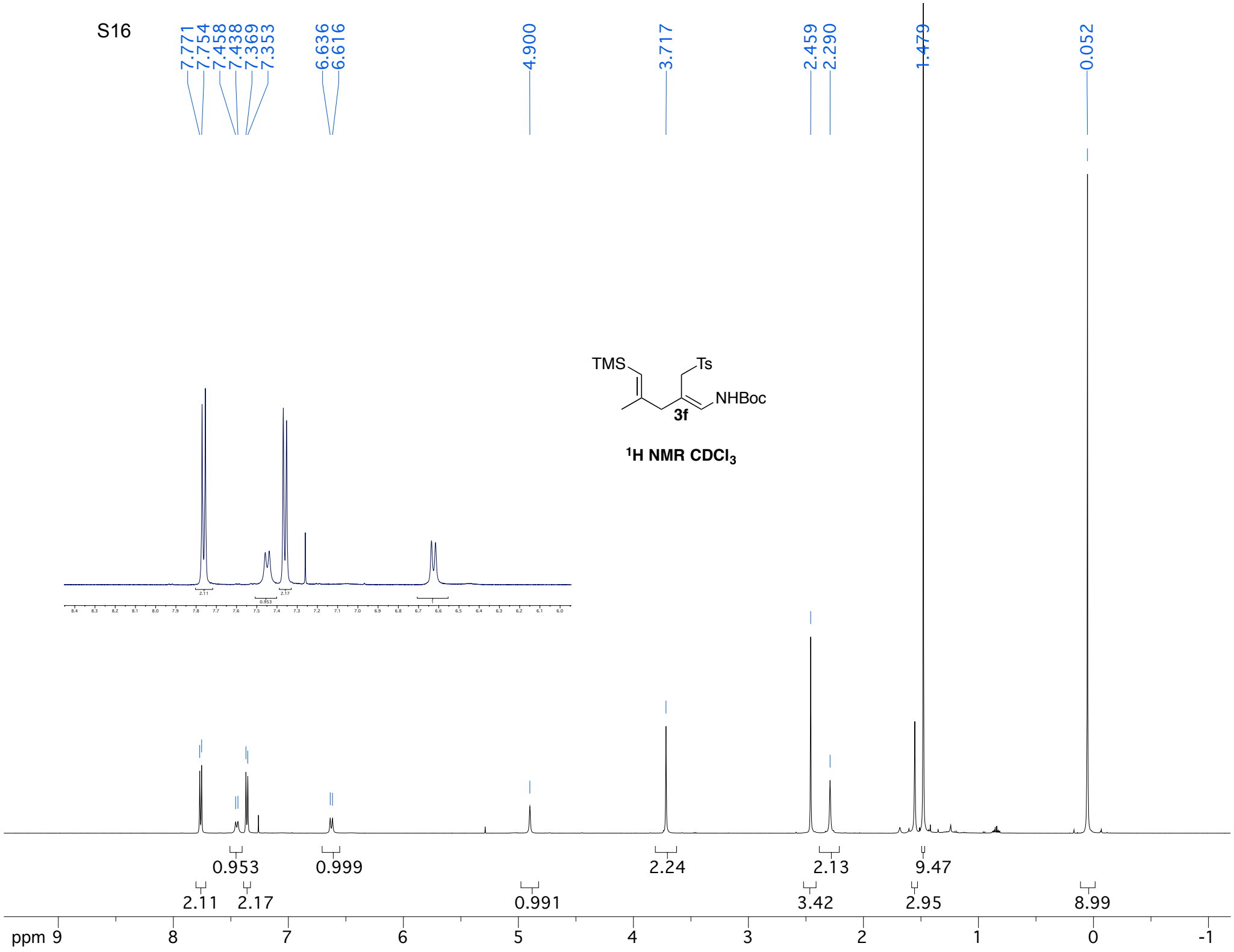
^{1}H NMR Toluene 80 ºC


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119.413
80.275
45.300
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30.405
28.497
25.489
21.307
0.148
TMS
NHBoc
3d
^{13}C NMR CDCl$_3$
220
200
180
160
140
120
100
80
60
40
20
0
-20

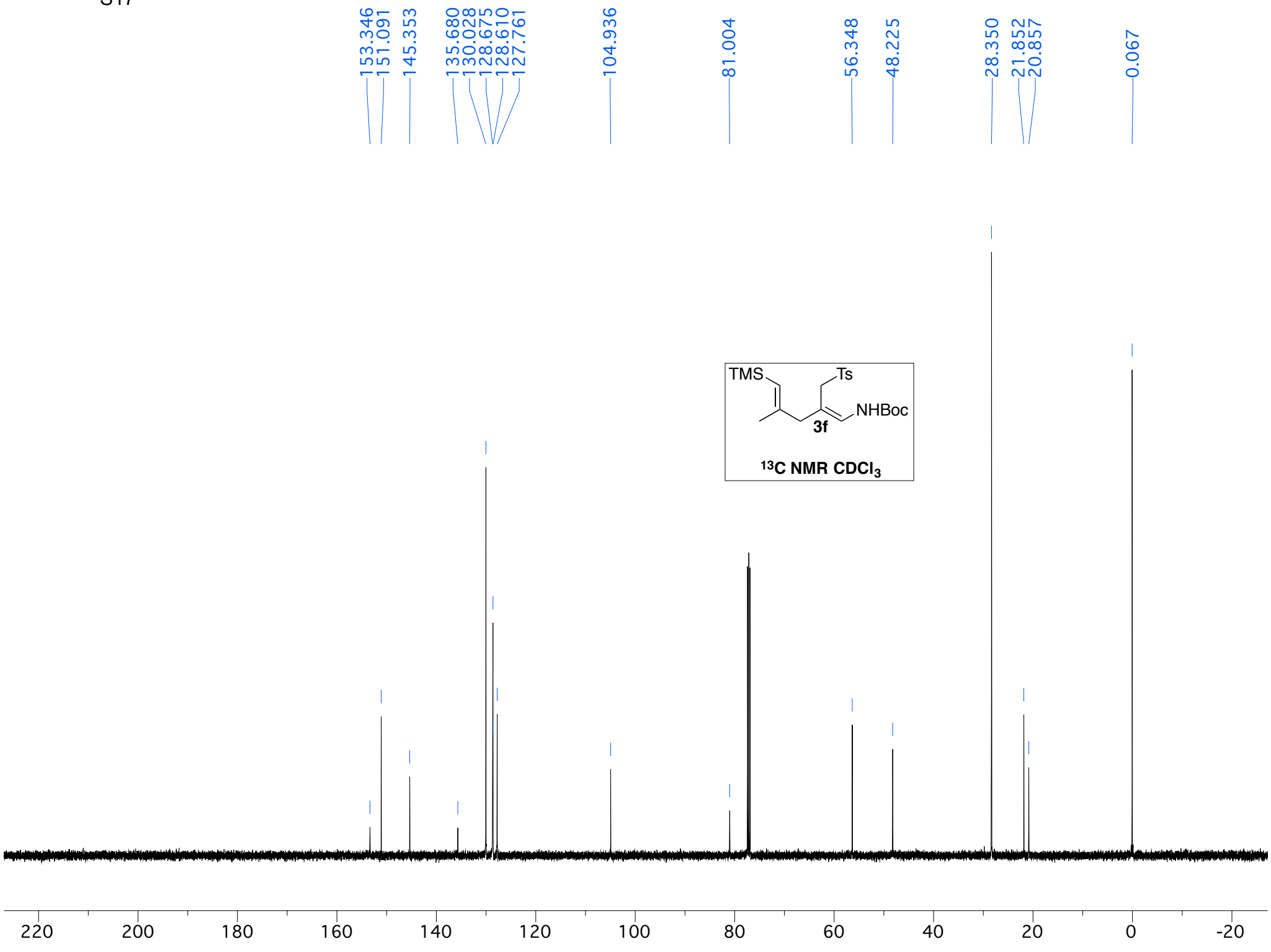

8.221
8.194
6.402
6.376
5.218
4.144
2.585
1.717
1.440
0.923
0.083
0.075
TMS
OTBS
NHBoc
3e
^{1}H NMR CDCl$_3$
0.913
2.05
3
9
0.9
1
2.05
8.52
14.2
11
10
9
8
7
6
5
4
3
2
1
0
-1

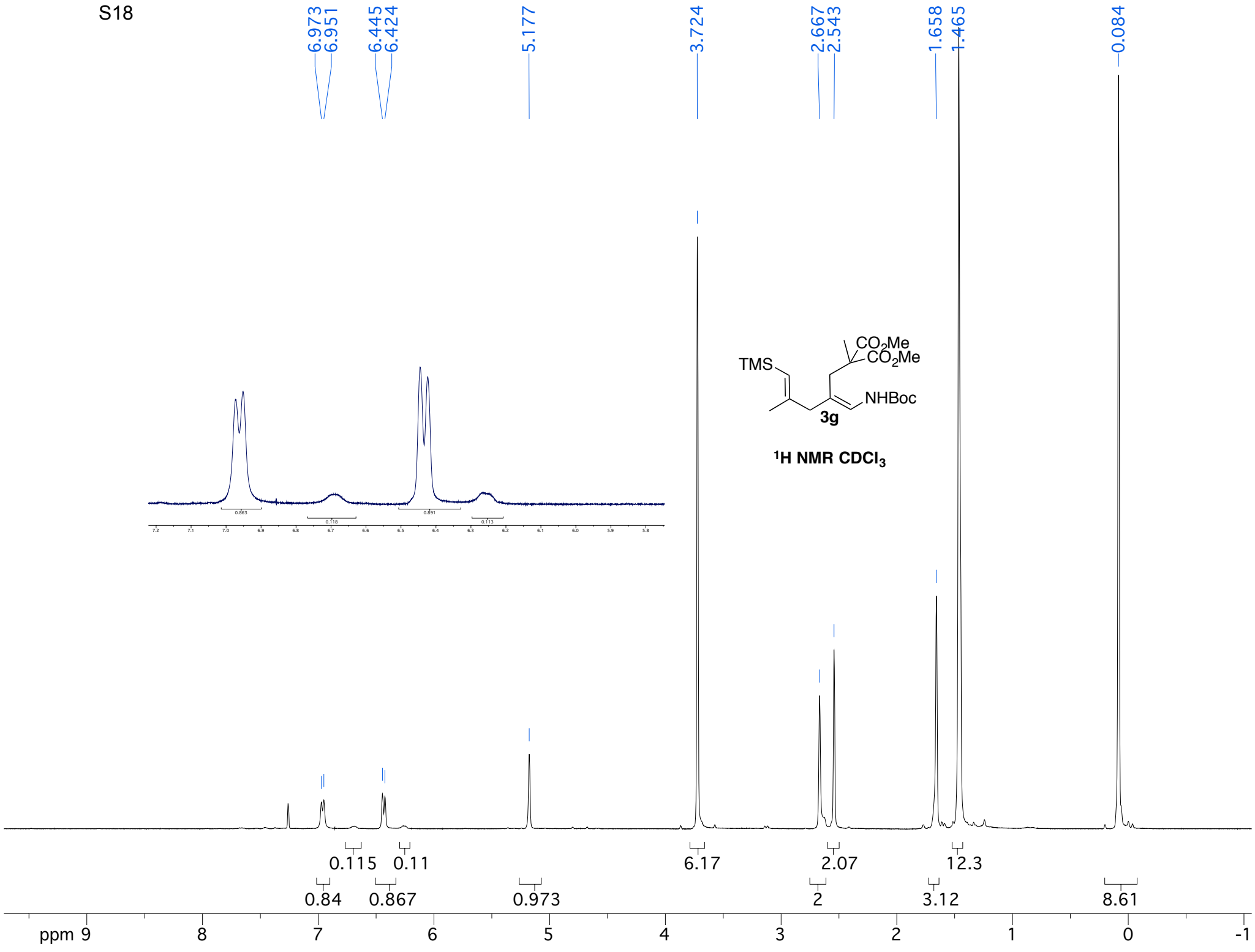

7.899
6.620
6.599
5.290
4.107
2.515
1.662
1.387
0.914
0.098
0.019
TMS
OTBS
NHBoc
3e
¹H NMR Toluene 80 ºC
0.928
1.95
3.03
9.25
5.98
0.841
0.973
1.97
9.43
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11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3

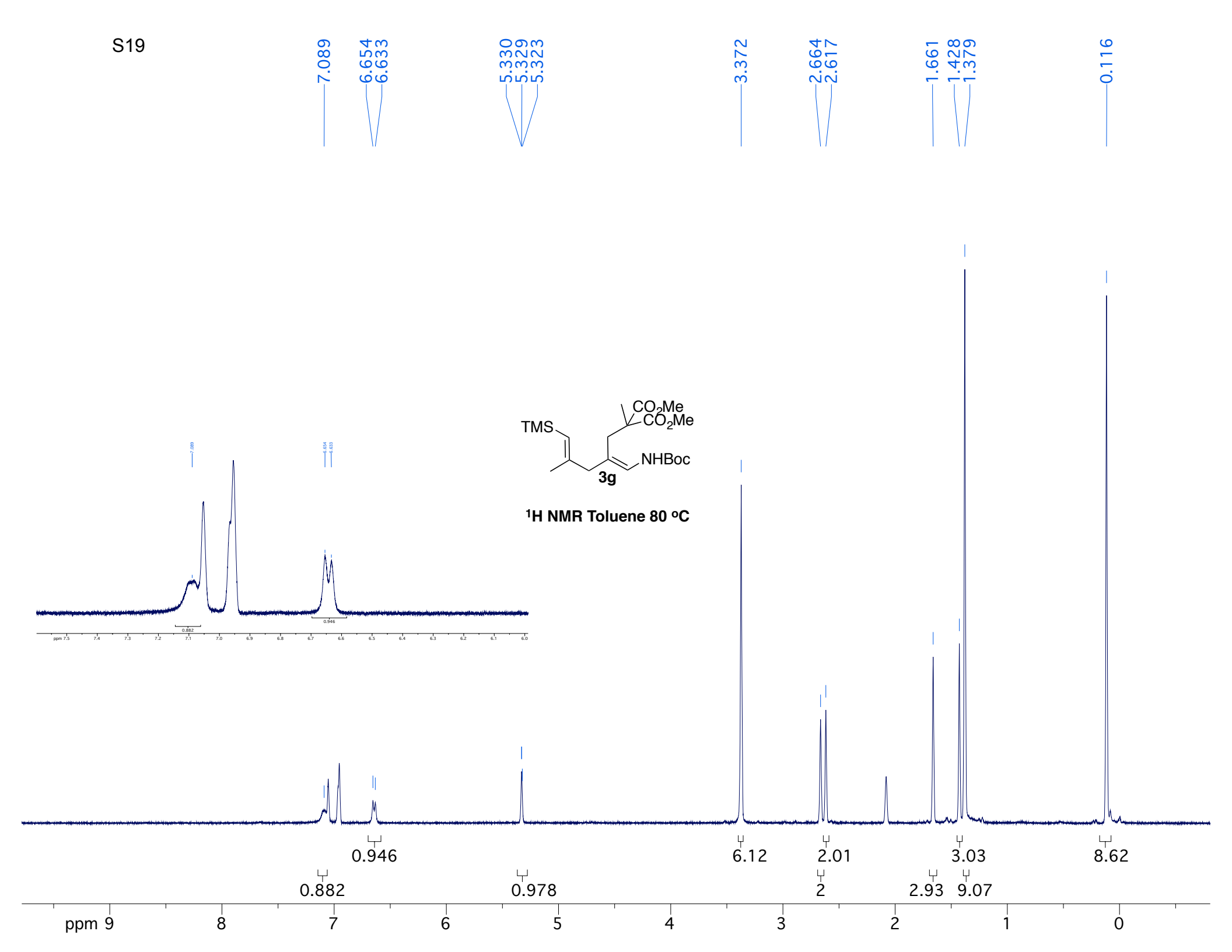

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46.831
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25.946
21.039
18.175
0.164
-5.599
TMS
OTBS
NHBoc
3e
13C NMR CDCl3
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180
160
140
120
100
80
60
40
20
0
-20

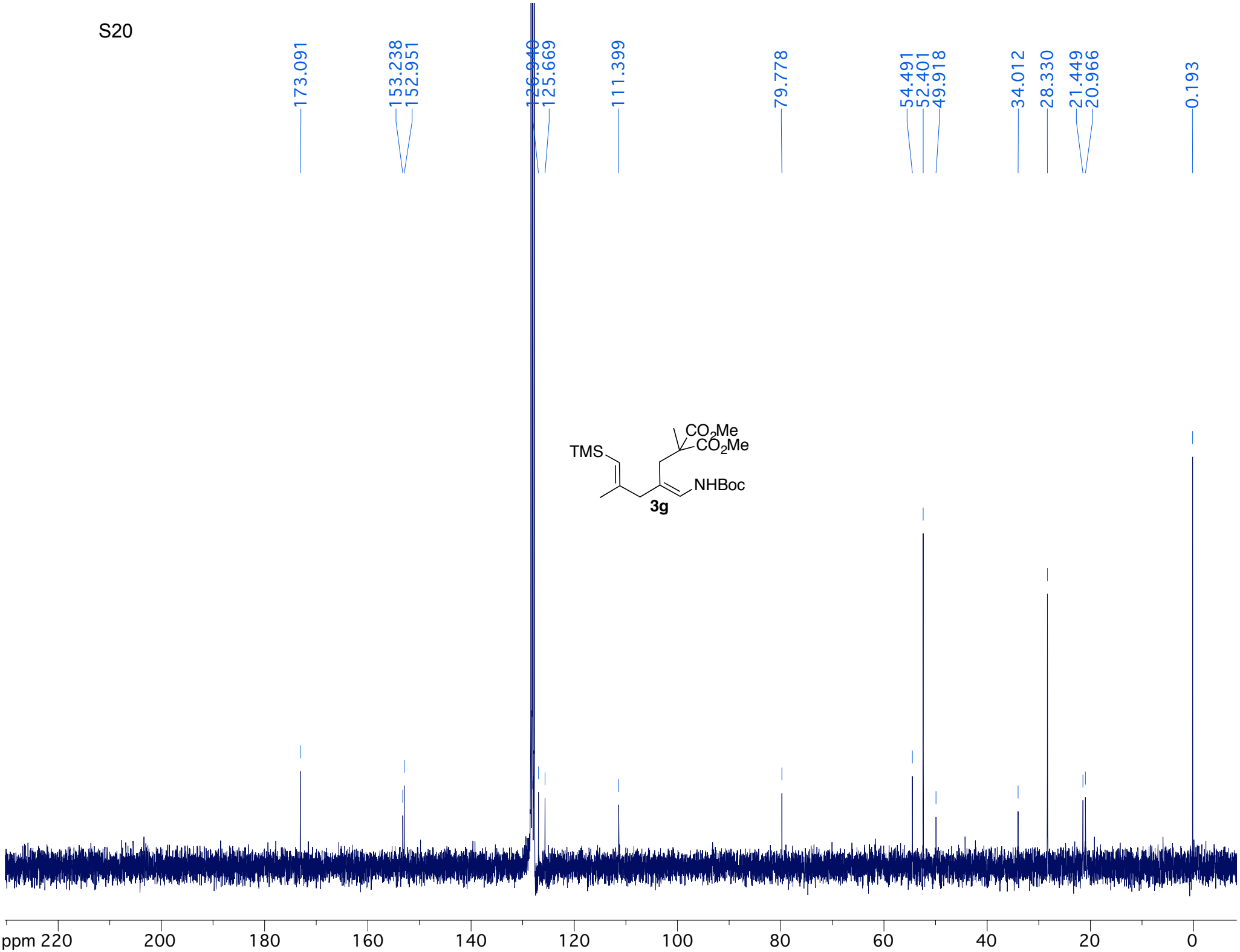

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7.754
7.458
7.438
7.369
7.353
6.636
6.616
4.900
3.717
2.459
2.290
1.479
0.052
TMS
Ts
NHBoc
3f
0.953
0.999
2.24
2.13
9.47
2.11
2.17
0.991
3.42
2.95
8.99
ppm 9
8
7
6
5
4
3
2
1
0
-1

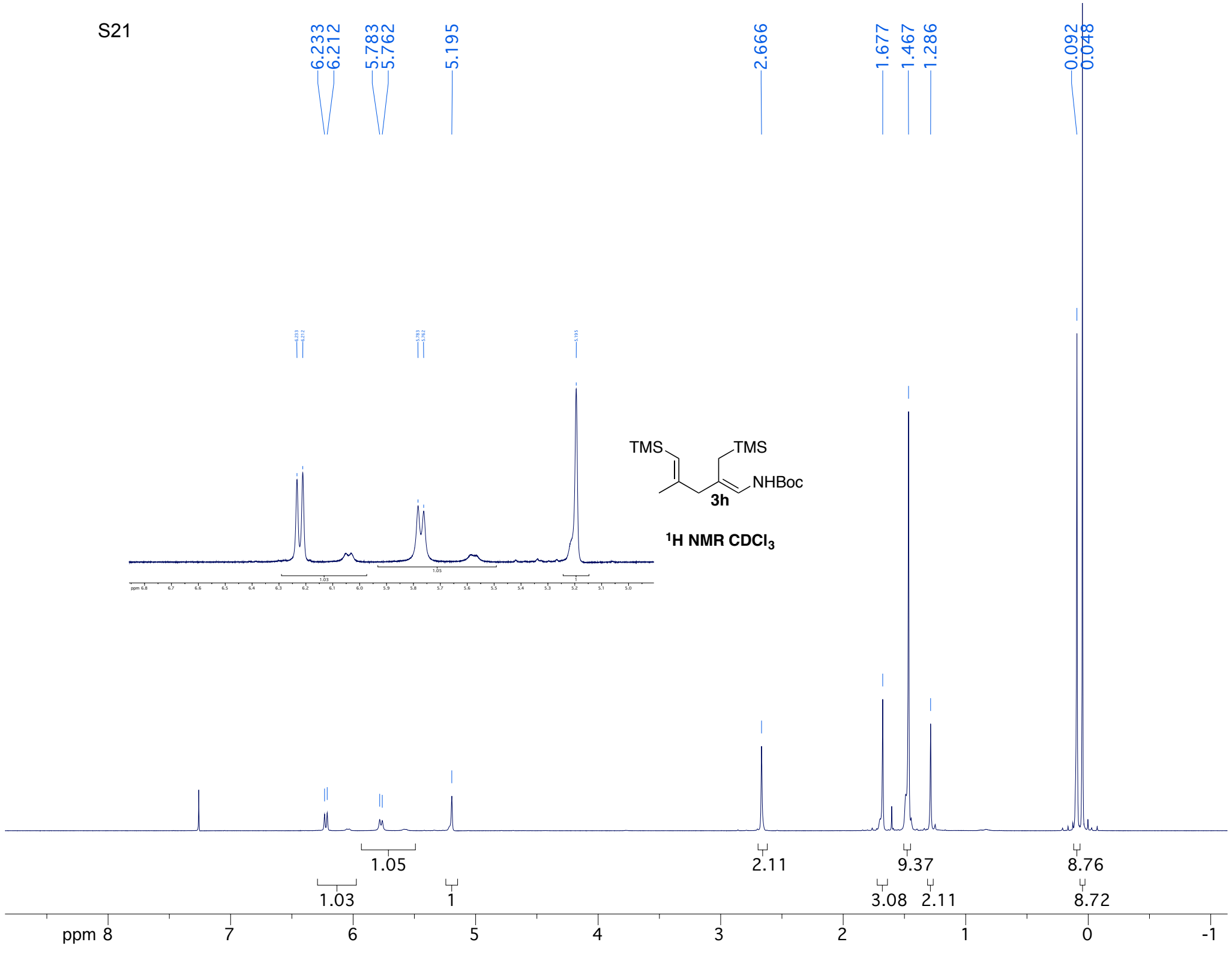
^{1}H NMR $CDCl_3$

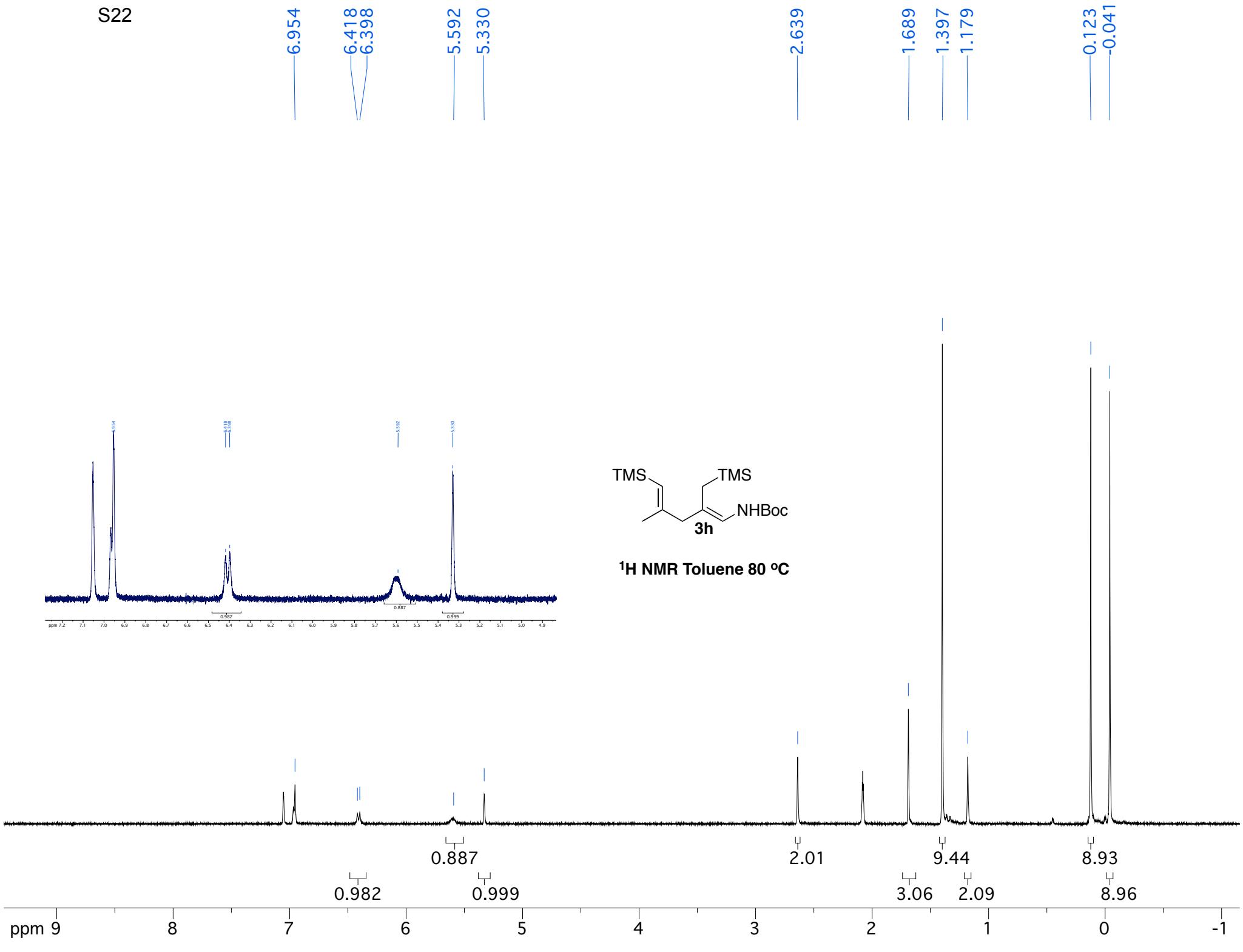

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128.675
128.610
127.761
104.936
81.004
56.348
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28.350
21.852
20.857
0.067
TMS
Ts
NHBoc
3f
13C NMR CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
-20


6.973
6.951
6.445
6.424
5.177
3.724
2.667
2.543
1.658
1.465
0.084
TMS
CO2Me
CO2Me
NHBoc
3g
1H NMR CDCl3
0.115
0.11
6.17
2.07
12.3
0.84
0.867
0.973
2
3.12
8.61
ppm 9
8
7
6
5
4
3
2
1
0
-1

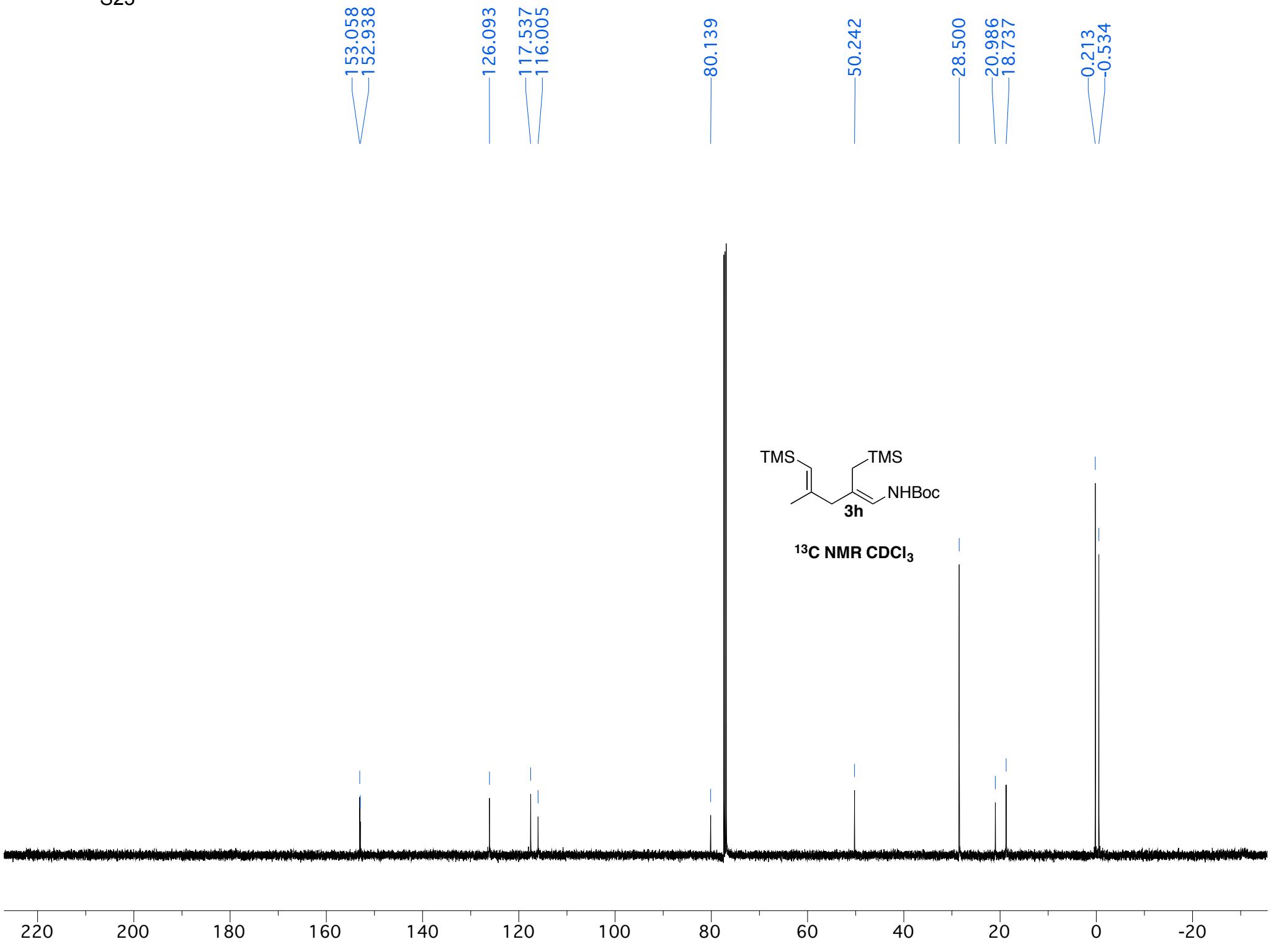

7.089
6.654
6.633
5.330
5.329
5.323
3.372
2.664
2.617
1.661
1.428
1.379
0.116
CO2Me
CO2Me
TMS
NHBoc
3g
1H NMR Toluene 80 oC
0.946
6.12
2.01
3.03
8.62
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0.978
2
2.93
9.07
ppm 9
8
7
6
5
4
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2
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0

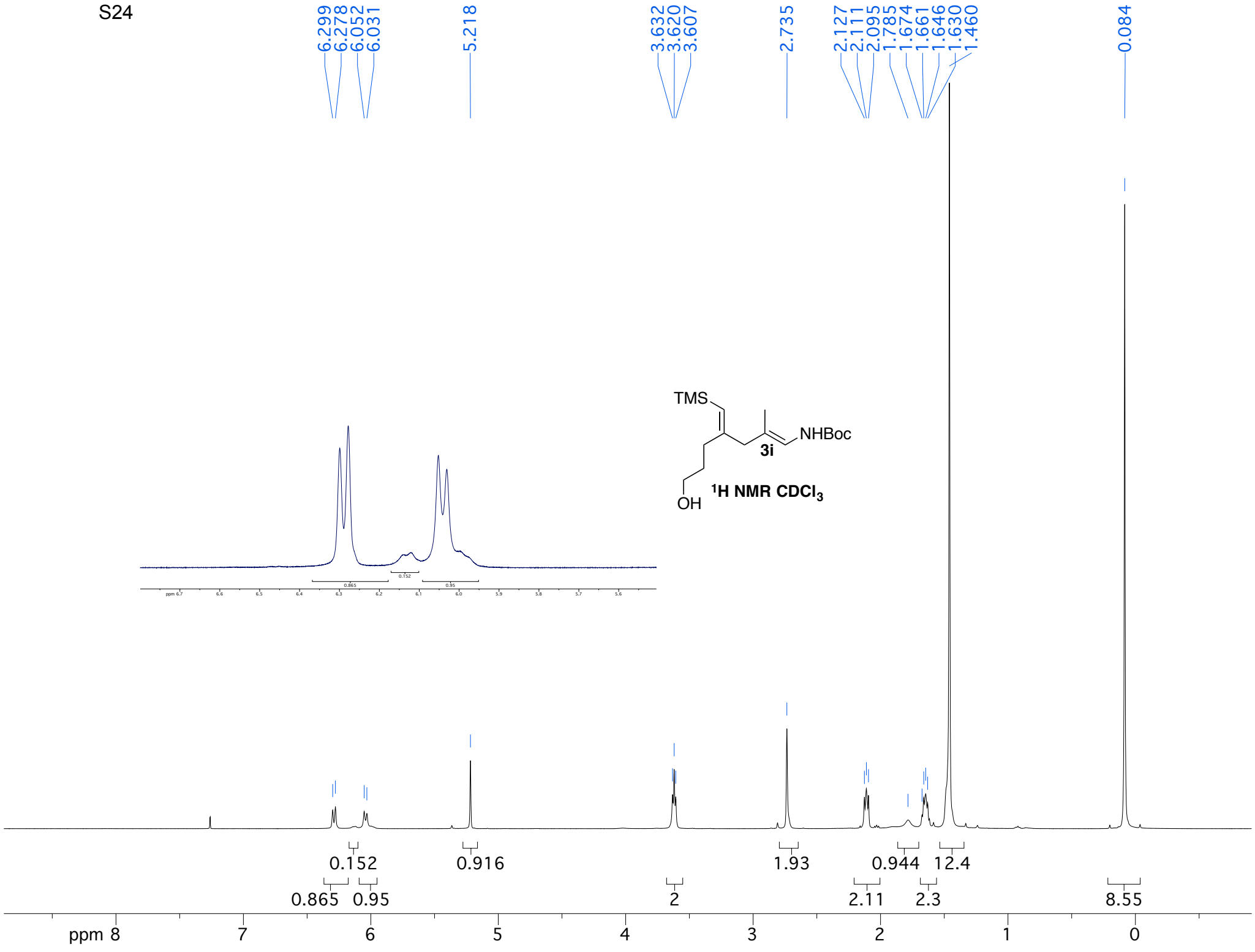

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126.940
125.669
111.399
79.778
54.491
52.401
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34.012
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21.449
20.966
0.193
TMS
CO2Me
CO2Me
NHBoc
3g
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200
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140
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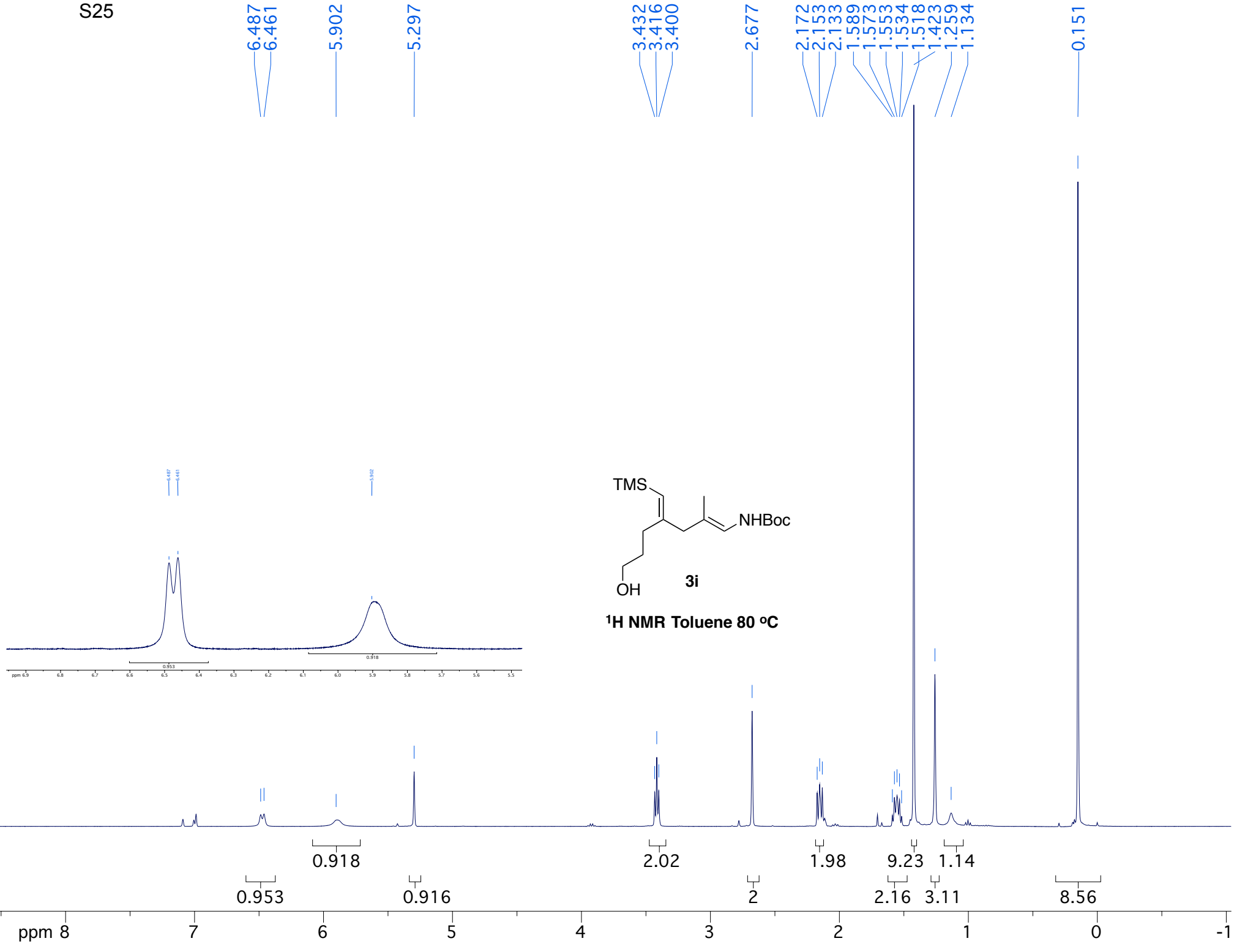

6.233
6.212
5.783
5.762
5.195
2.666
1.677
1.467
1.286
0.092
0.048
TMS
TMS
NHBoc
3h
1H NMR CDCl3
1.05
2.11
9.37
8.76
1.03
1
3.08
2.11
8.72
ppm 8
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6
5
4
3
2
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0
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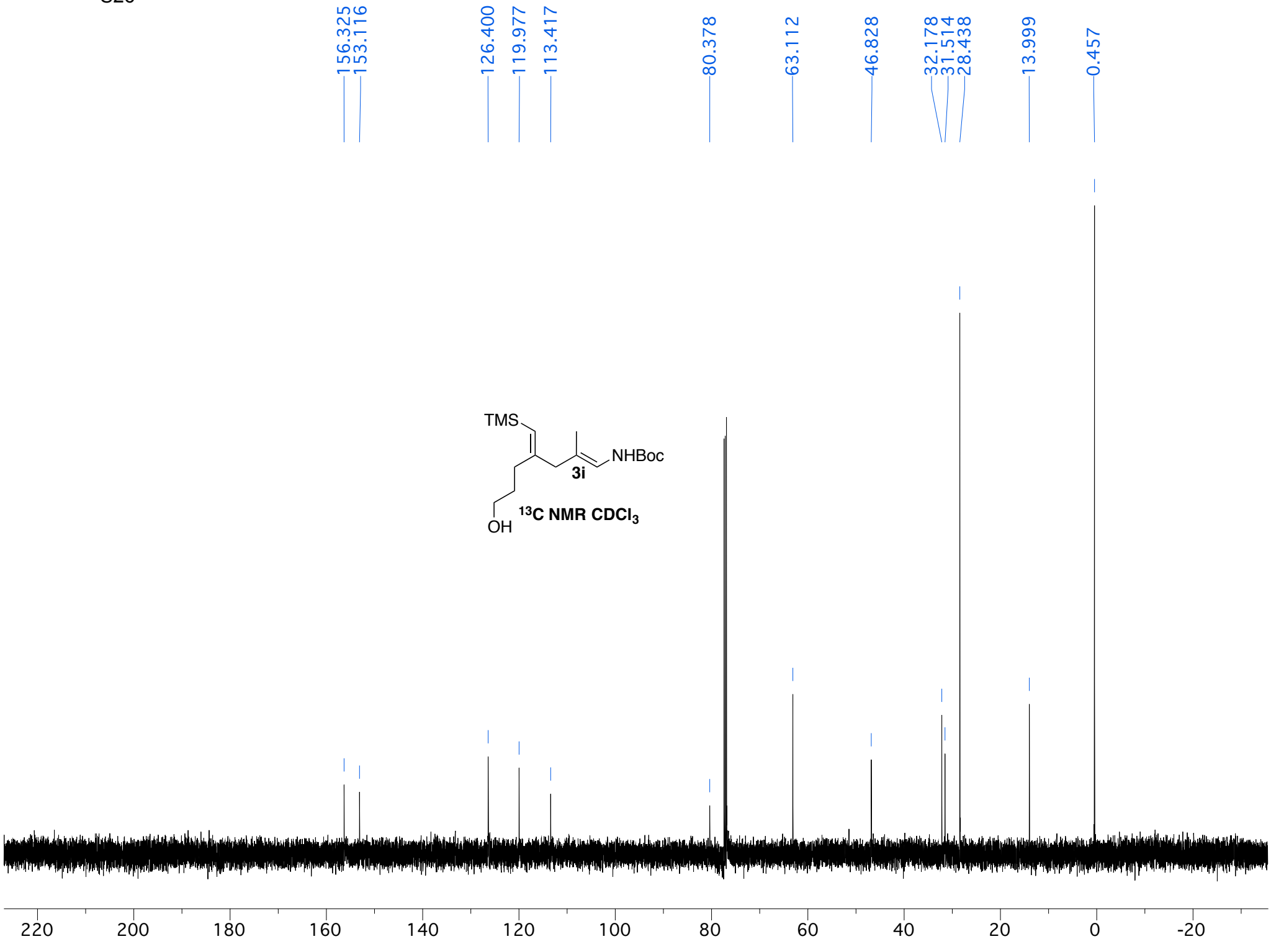
^{1}H NMR Toluene 80 ^{o}C

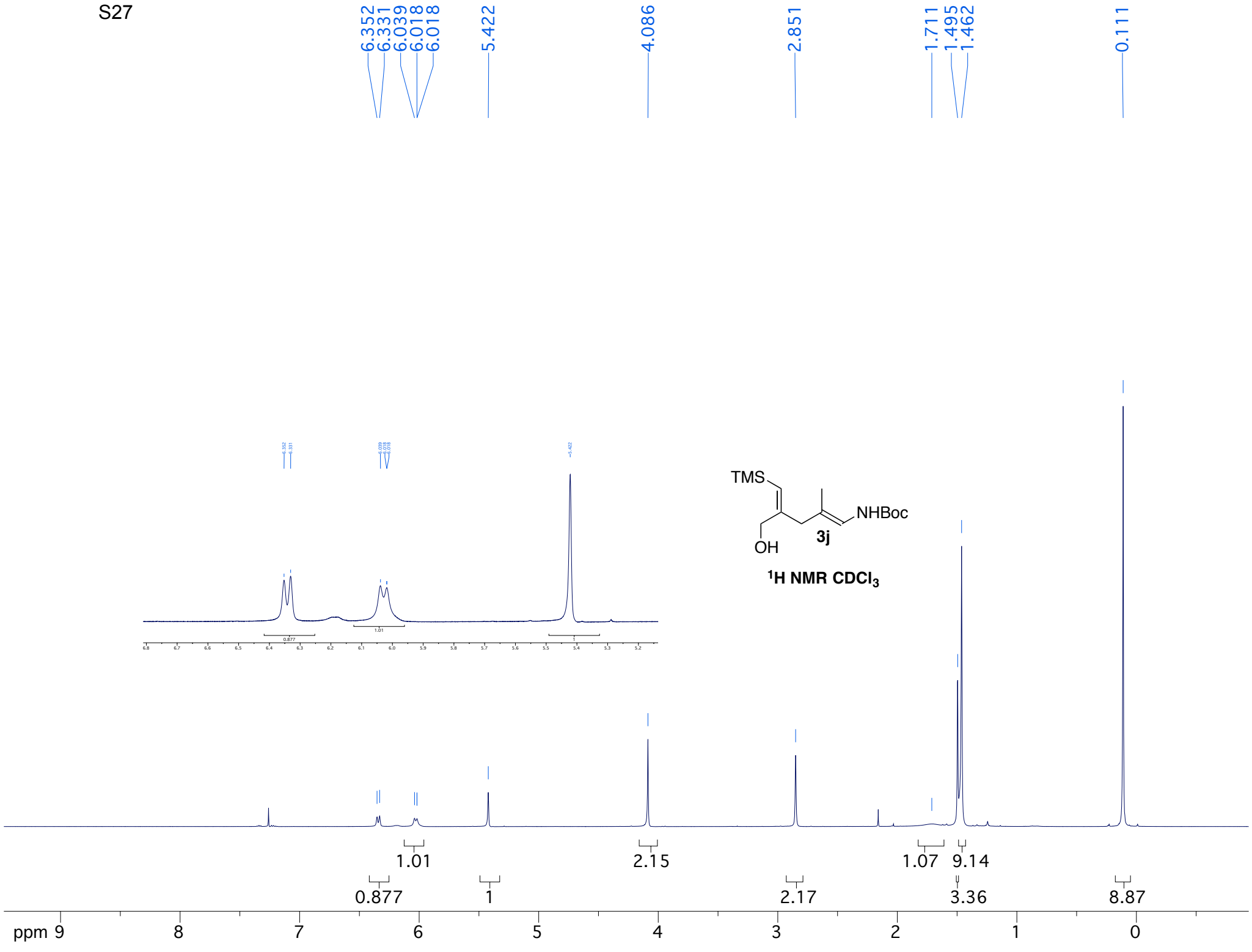

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126.093
117.537
116.005
80.139
50.242
28.500
20.986
18.737
0.213
-0.534
TMS
TMS
NHBoc
3h
13C NMR CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
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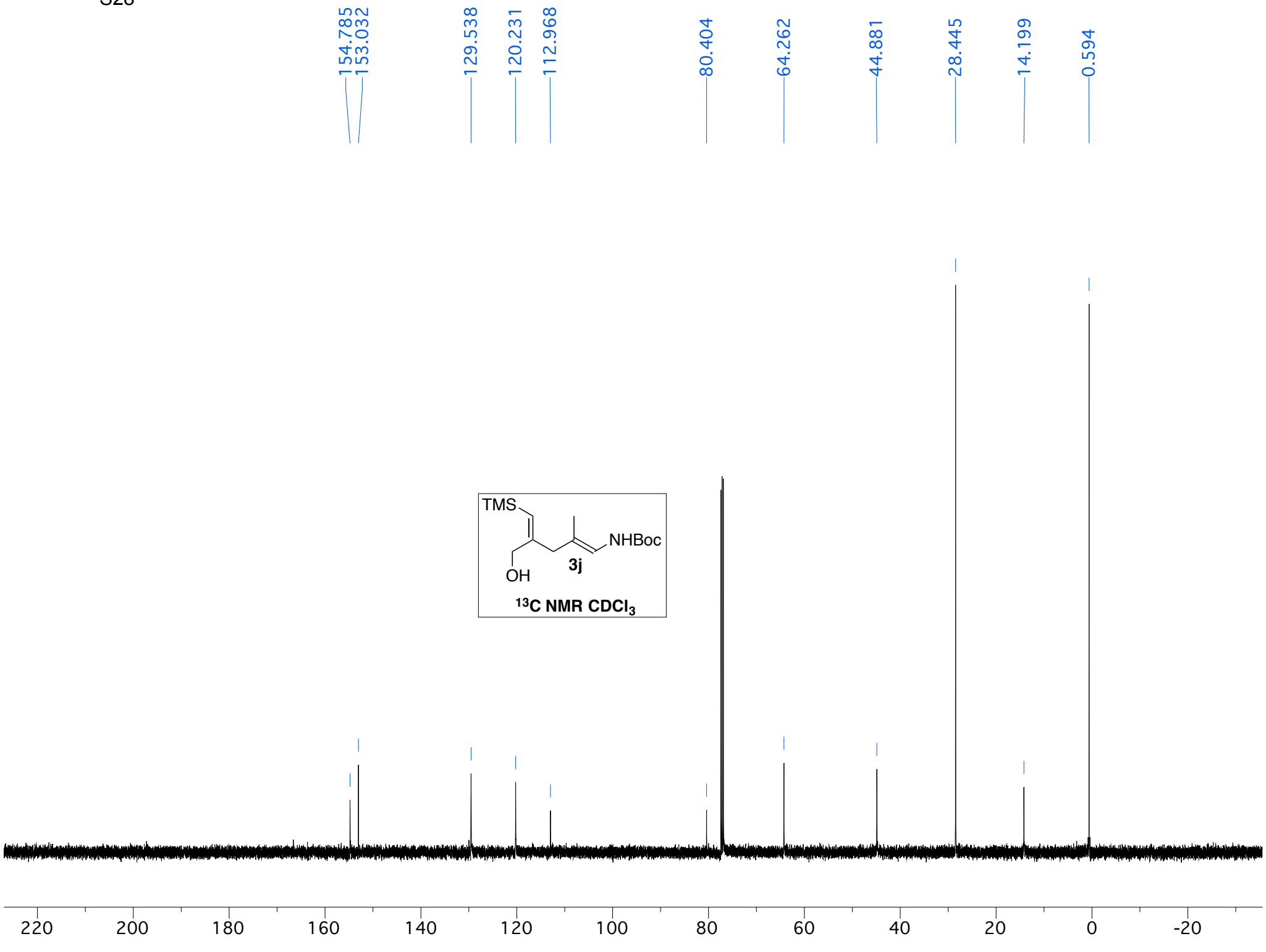

6.299
6.278
6.052
6.031
5.218
3.632
3.620
3.607
2.735
2.127
2.111
2.095
1.785
1.674
1.661
1.646
1.630
1.460
0.084
TMS
NHBoc
3i
OH
¹H NMR CDCl₃
0.152
0.916
1.93
0.944
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2.3
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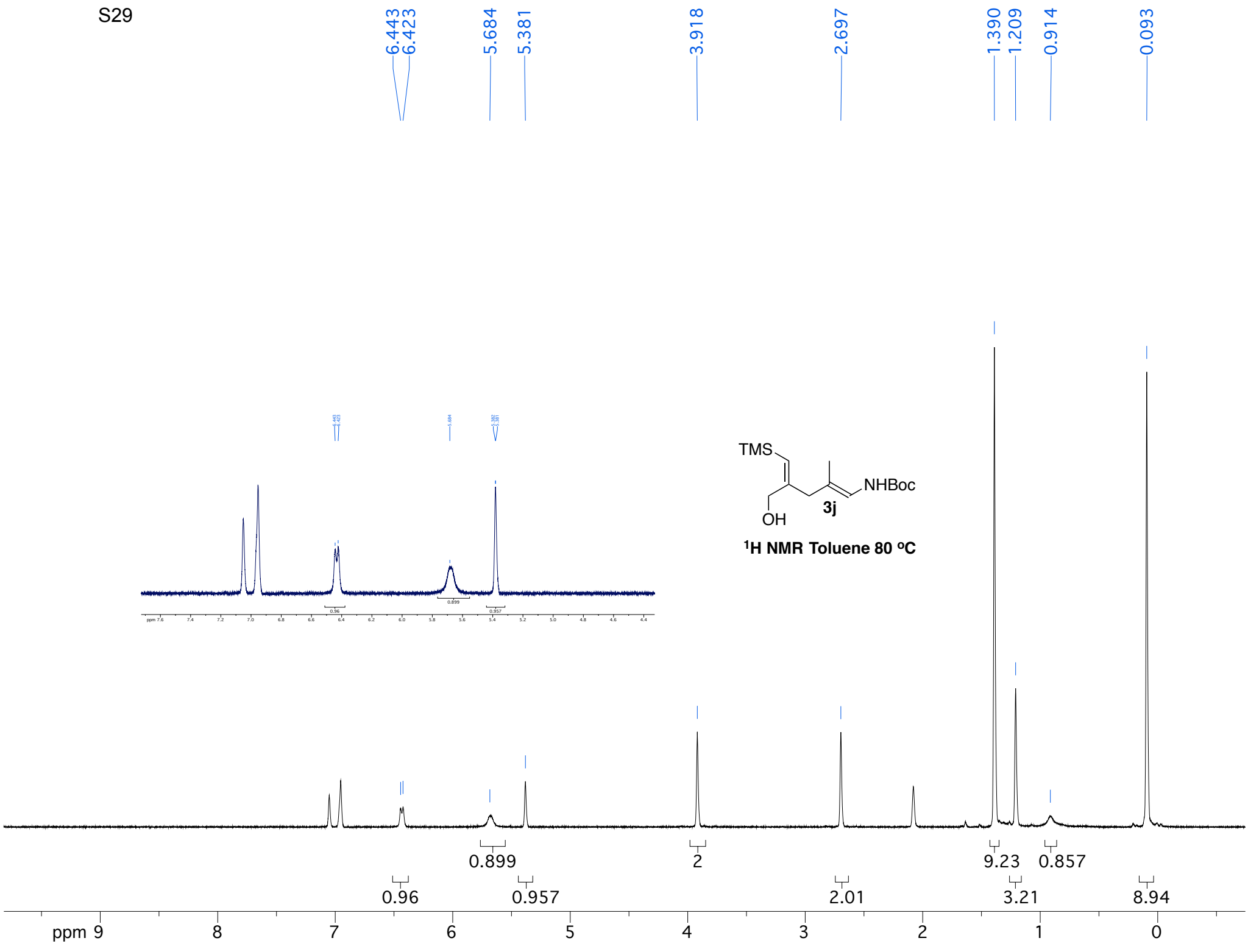


^{1}H NMR Toluene 80 ^{o}C

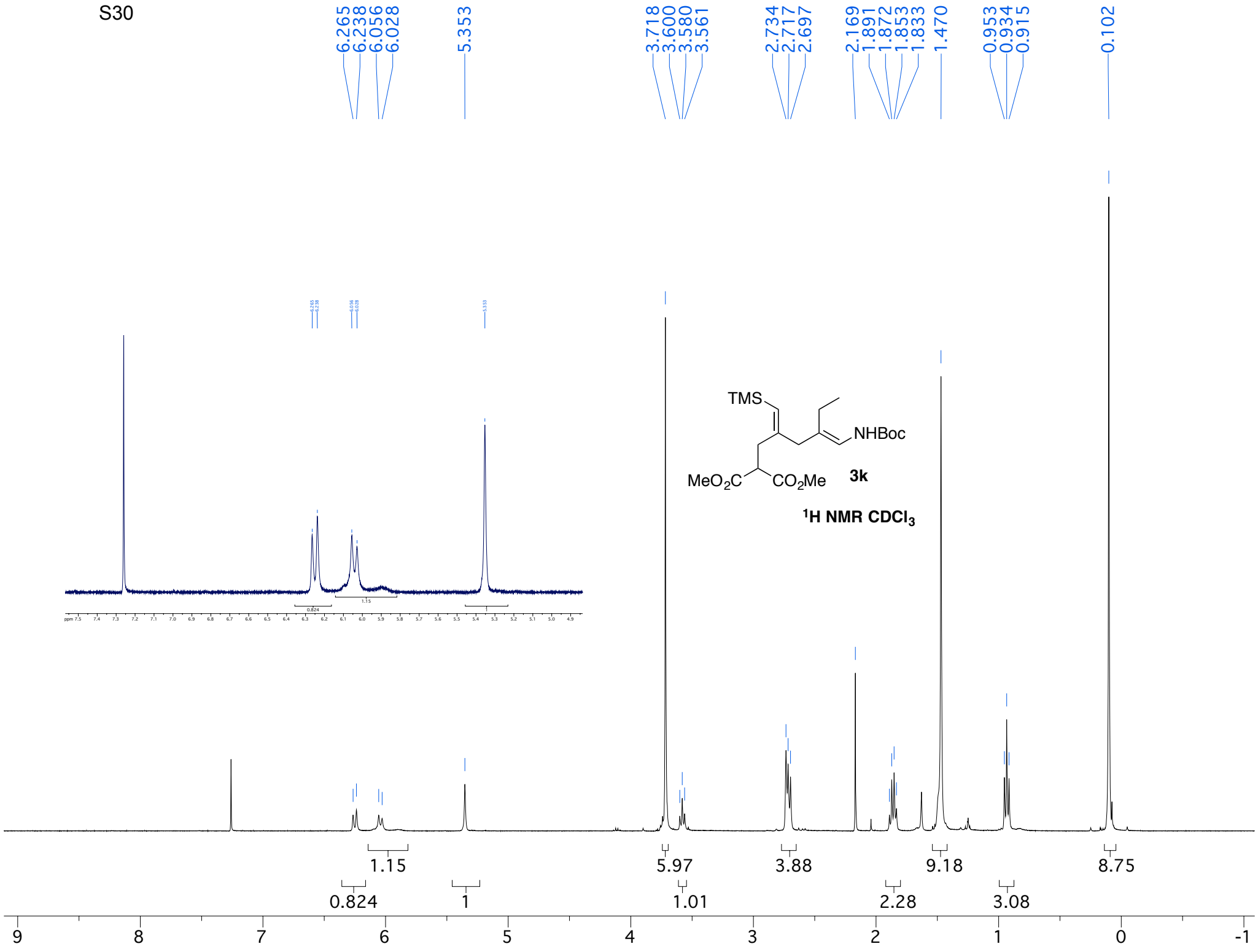

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126.400
119.977
113.417
80.378
63.112
46.828
32.178
31.514
28.438
13.999
0.457
TMS
NHBoc
OH
3i
13C NMR CDCl3
220
200
180
160
140
120
100
80
60
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0
-20

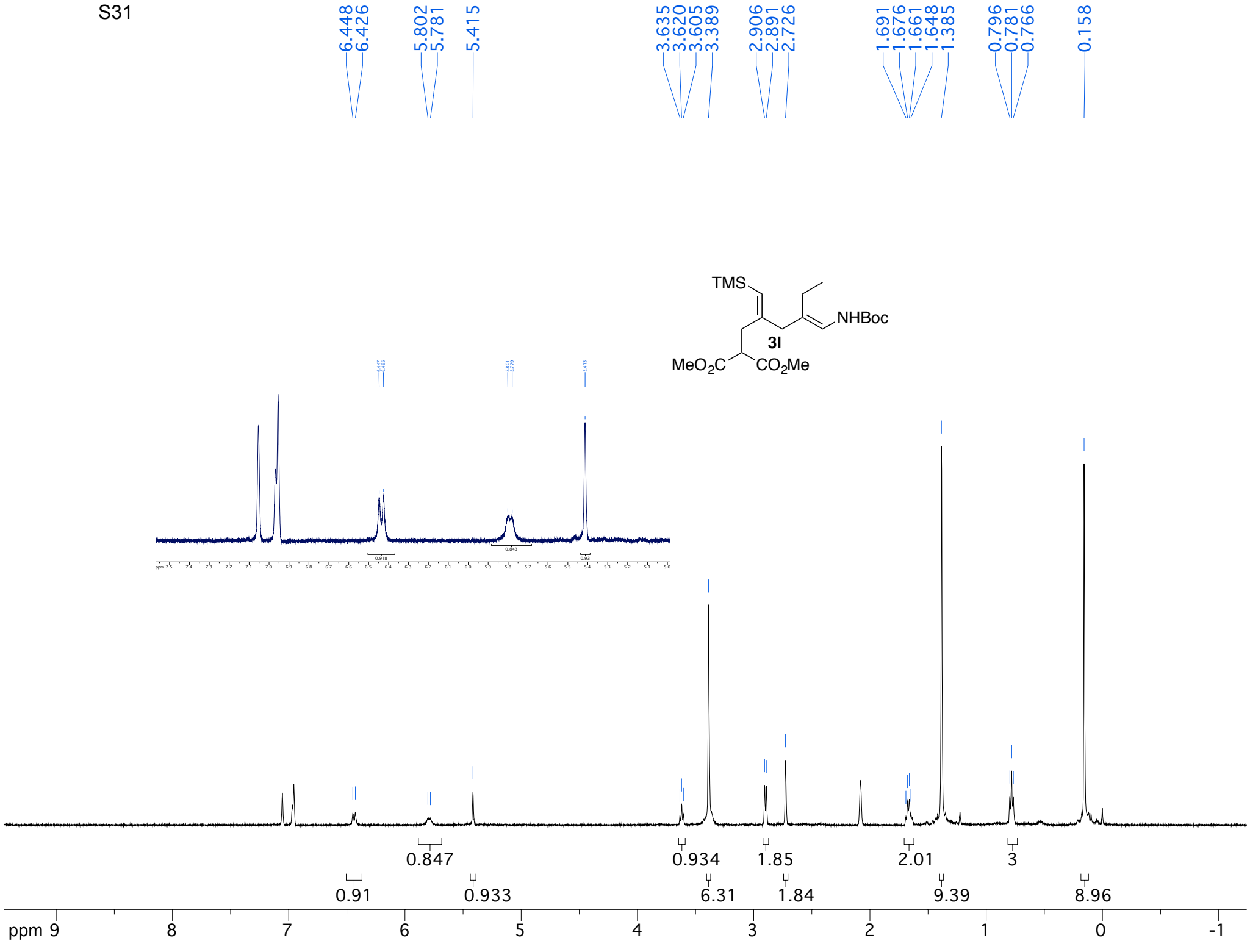

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6.331
6.039
6.018
6.018
5.422
4.086
2.851
1.711
1.495
1.462
0.111
TMS
NHBoc
OH
3j
1H NMR CDCl3
1.01
2.15
1.07
9.14
0.877
1
2.17
3.36
8.87
ppm 9
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5
4
3
2
1
0

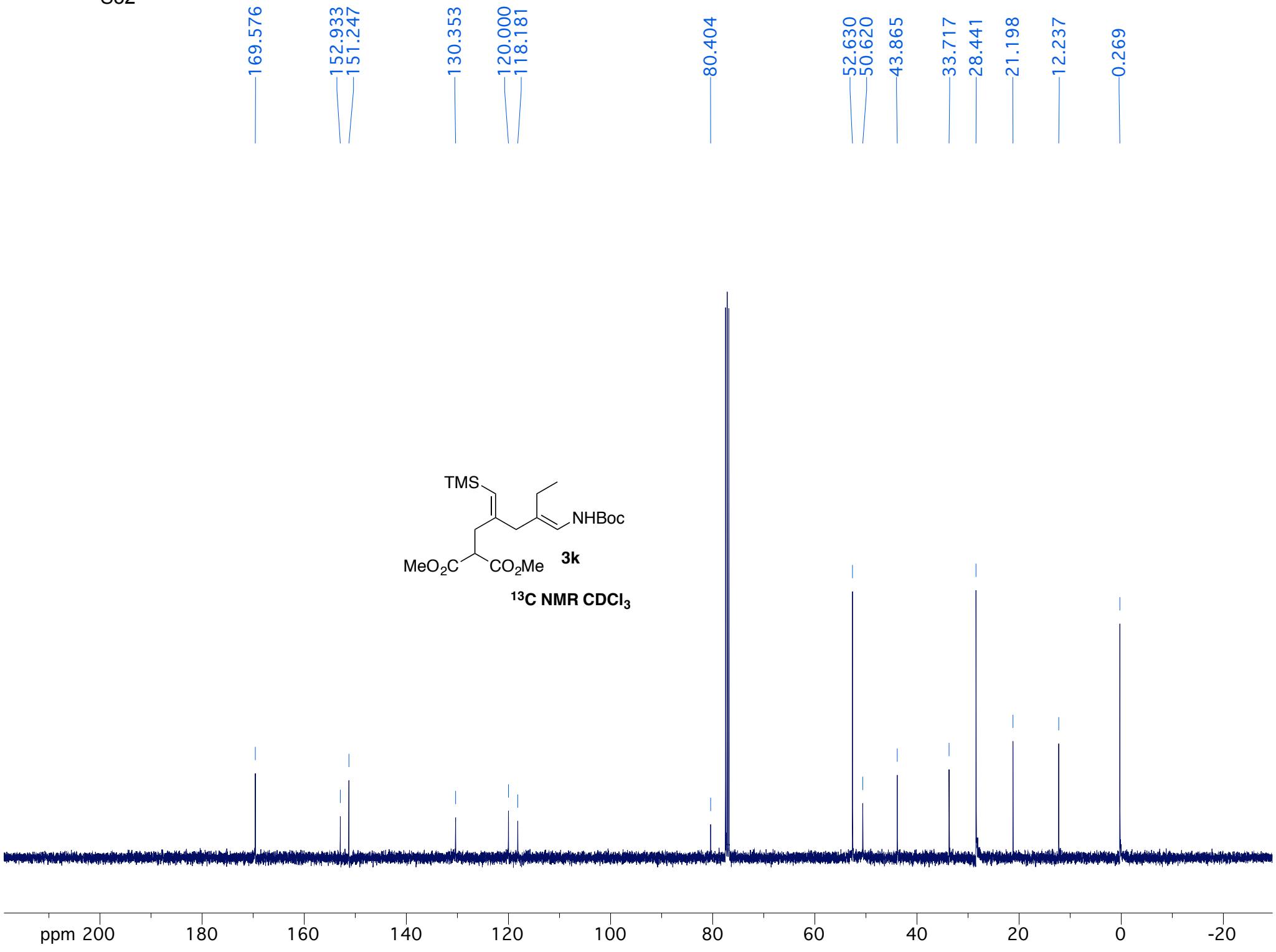

154.785
153.032
129.538
120.231
112.968
80.404
64.262
44.881
28.445
14.199
0.594
TMS
NHBoc
OH
3j
^{13}C NMR CDCl$_3$
220
200
180
160
140
120
100
80
60
40
20
0
-20



^{1}H NMR Toluene 80 ^{o}C

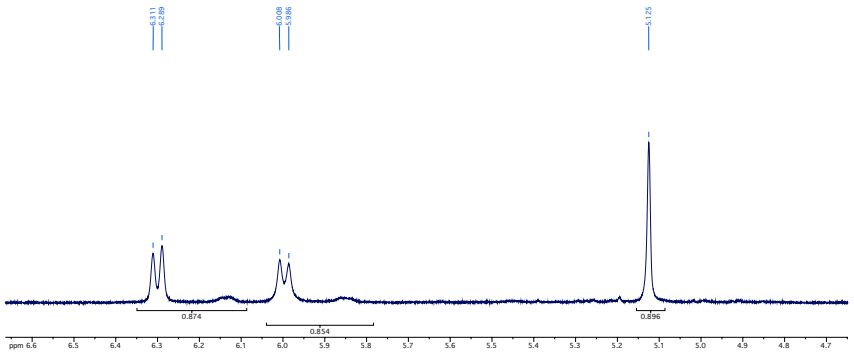

6.265
6.238
6.056
6.028
5.353
3.718
3.600
3.580
3.561
2.734
2.717
2.697
2.169
1.891
1.872
1.853
1.833
1.470
0.953
0.934
0.915
0.102
TMS
NHBoc
MeO2C
CO2Me
3k
1H NMR CDCl3
1.15
5.97
3.88
9.18
8.75
0.824
1
1.01
2.28
3.08
9
8
7
6
5
4
3
2
1
0
-1

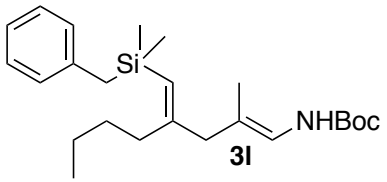

6.448
6.426
5.802
5.781
5.415
3.635
3.620
3.605
3.389
2.906
2.891
2.726
1.691
1.676
1.661
1.648
1.385
0.796
0.781
0.766
0.158
TMS
NHBoc
3l
MeO2C
CO2Me
0.847
0.934
1.85
2.01
3
0.91
0.933
6.31
1.84
9.39
8.96
ppm 9
8
7
6
5
4
3
2
1
0
-1


169.576
152.933
151.247
130.353
120.000
118.181
80.404
52.630
50.620
43.865
33.717
28.441
21.198
12.237
0.269
TMS
NHBoc
MeO2C
CO2Me
3k
13C NMR CDCl3
ppm 200
180
160
140
120
100
80
60
40
20
0
-20

7.199 7.184 7.169 7.065 7.050 7.036 7.001 6.986 6.311 6.289 6.008 5.986 5.125

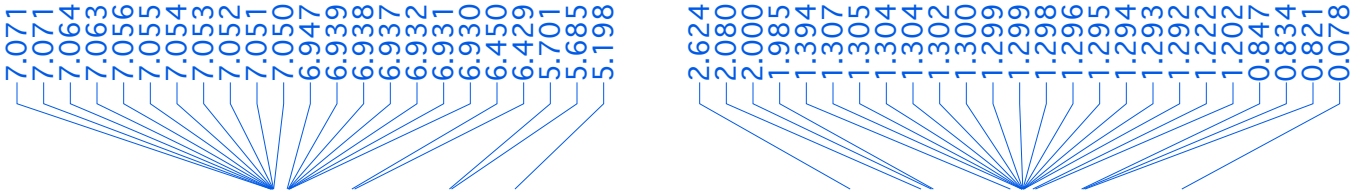
2.714 2.138 1.981 1.968 1.952 1.485 1.444 1.316 1.316 1.315 1.313 1.313 1.298 1.295 1.294 1.294 1.289 1.288 1.276 1.261 1.261 1.255 0.896 0.882 0.869 0.068

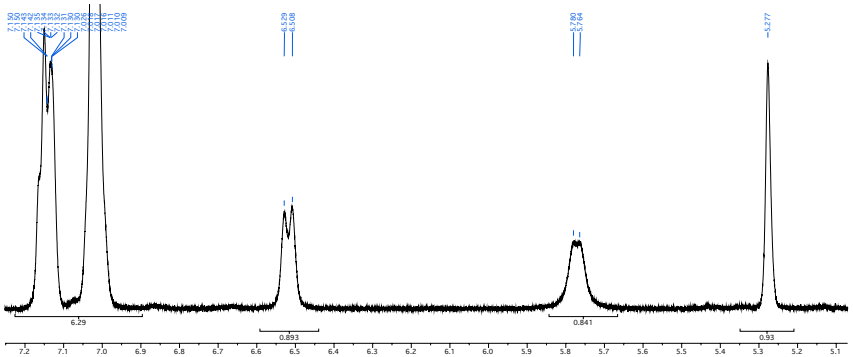


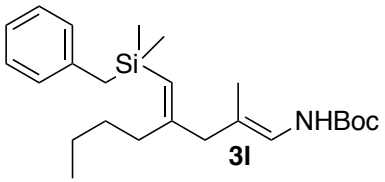


3l

^{1}H NMR $CDCl_3$

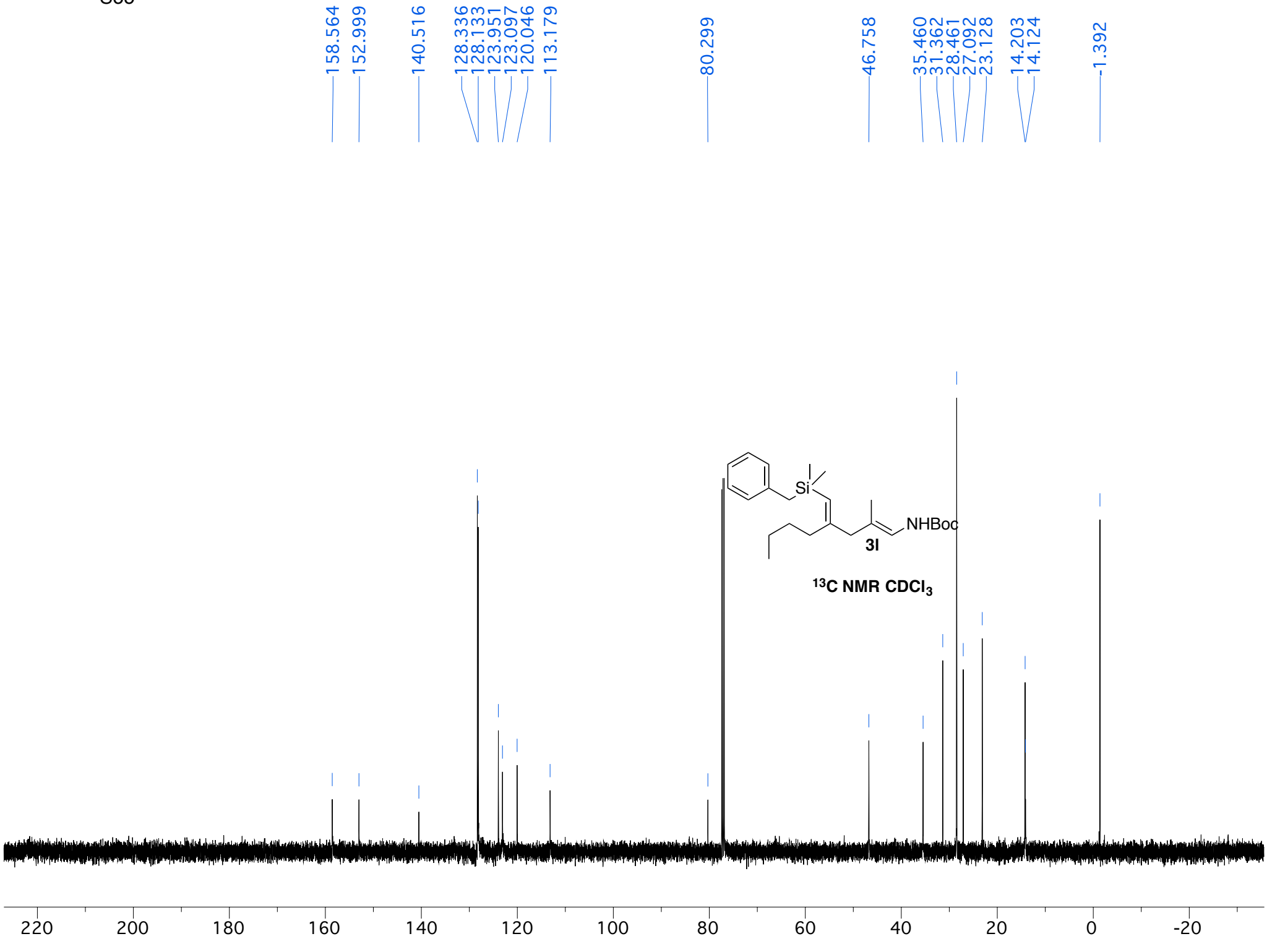


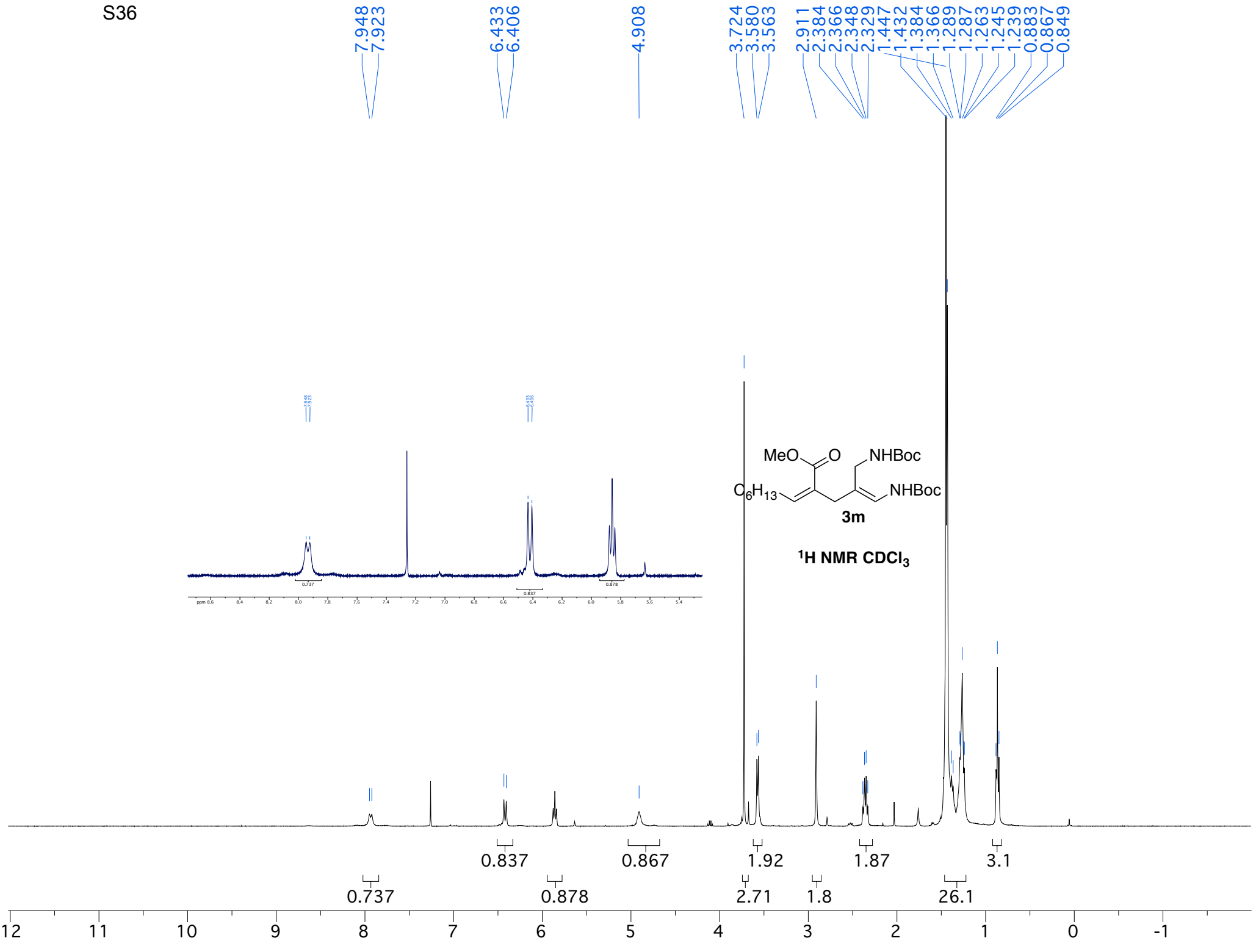


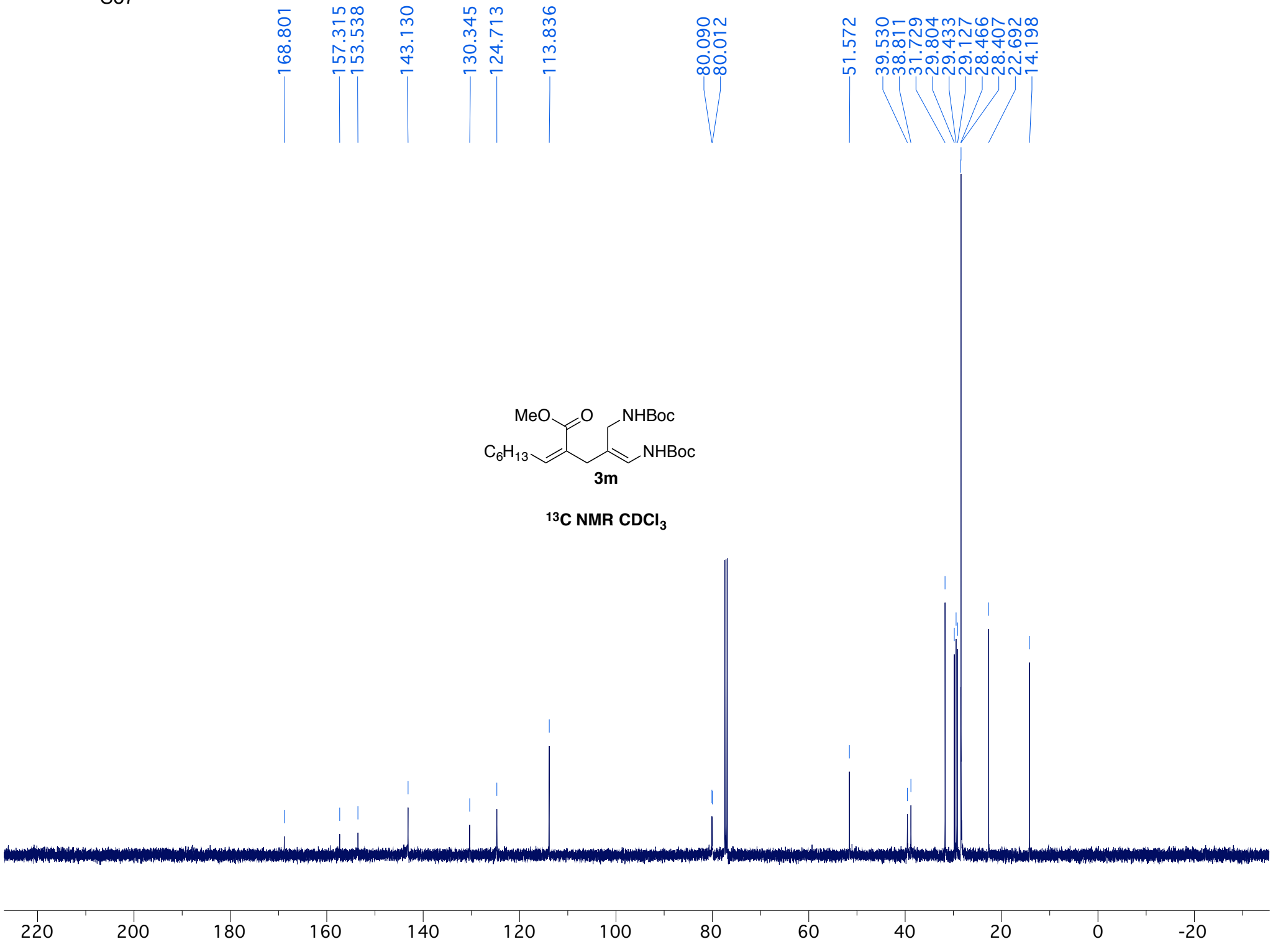


3l

^{1}H NMR Toluene 80 ^{o}C

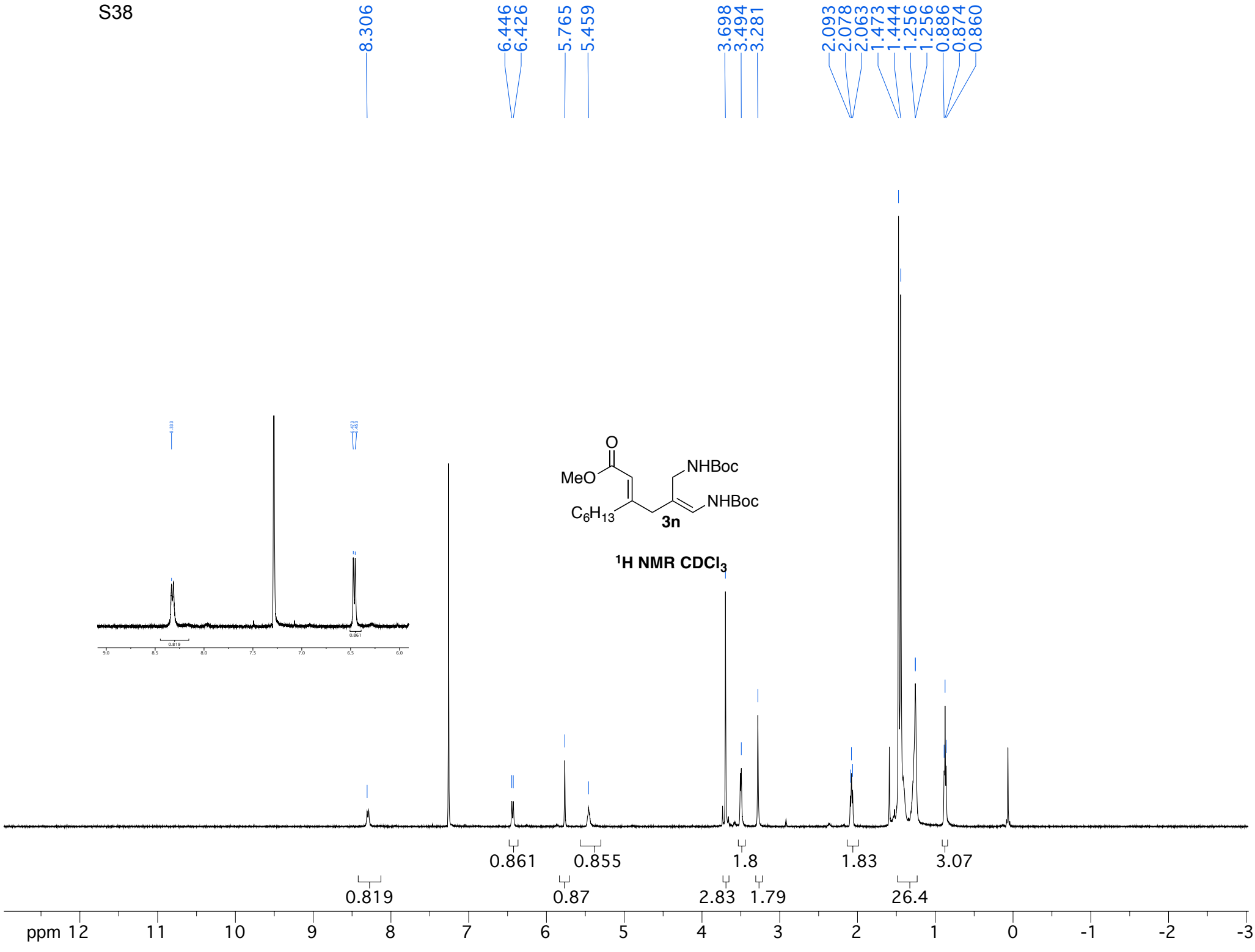

158.564
152.999
140.516
128.336
128.133
123.951
123.097
120.046
113.179
80.299
46.758
35.460
31.362
28.461
27.092
23.128
14.203
14.124
-1.392
Si
NHBoc
3l
13C NMR CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
-20

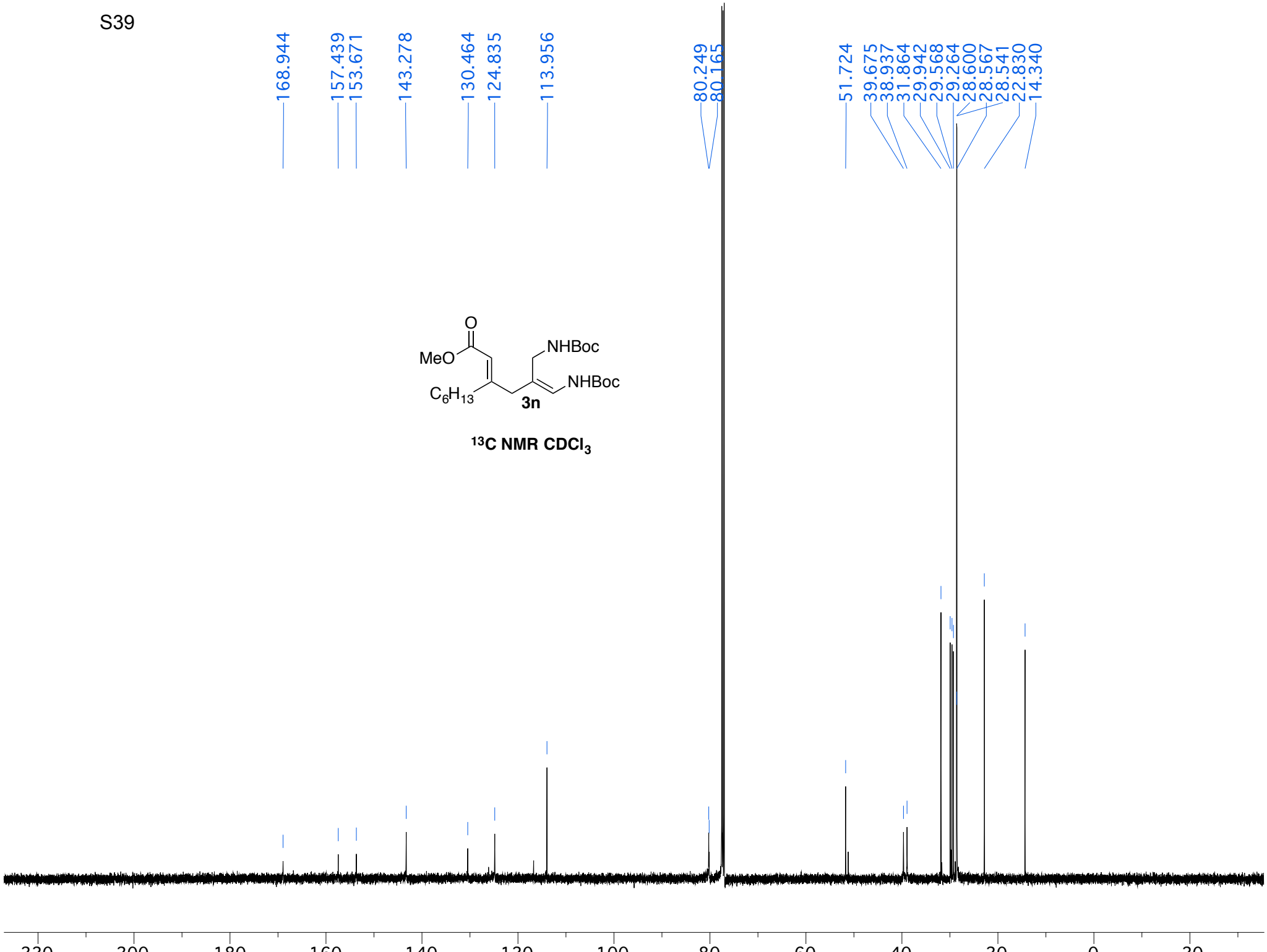

7.948
7.923
6.433
6.406
4.908
3.724
3.580
3.563
2.911
2.384
2.366
2.348
2.329
1.447
1.432
1.384
1.366
1.289
1.287
1.263
1.245
1.239
0.883
0.867
0.849
MeO
O
NHBoc
C6H13
NHBoc
3m
1H NMR CDCl3
0.737
0.878
0.837
0.867
1.92
1.87
3.1
2.71
1.8
26.1
12
11
10
9
8
7
6
5
4
3
2
1
0
-1



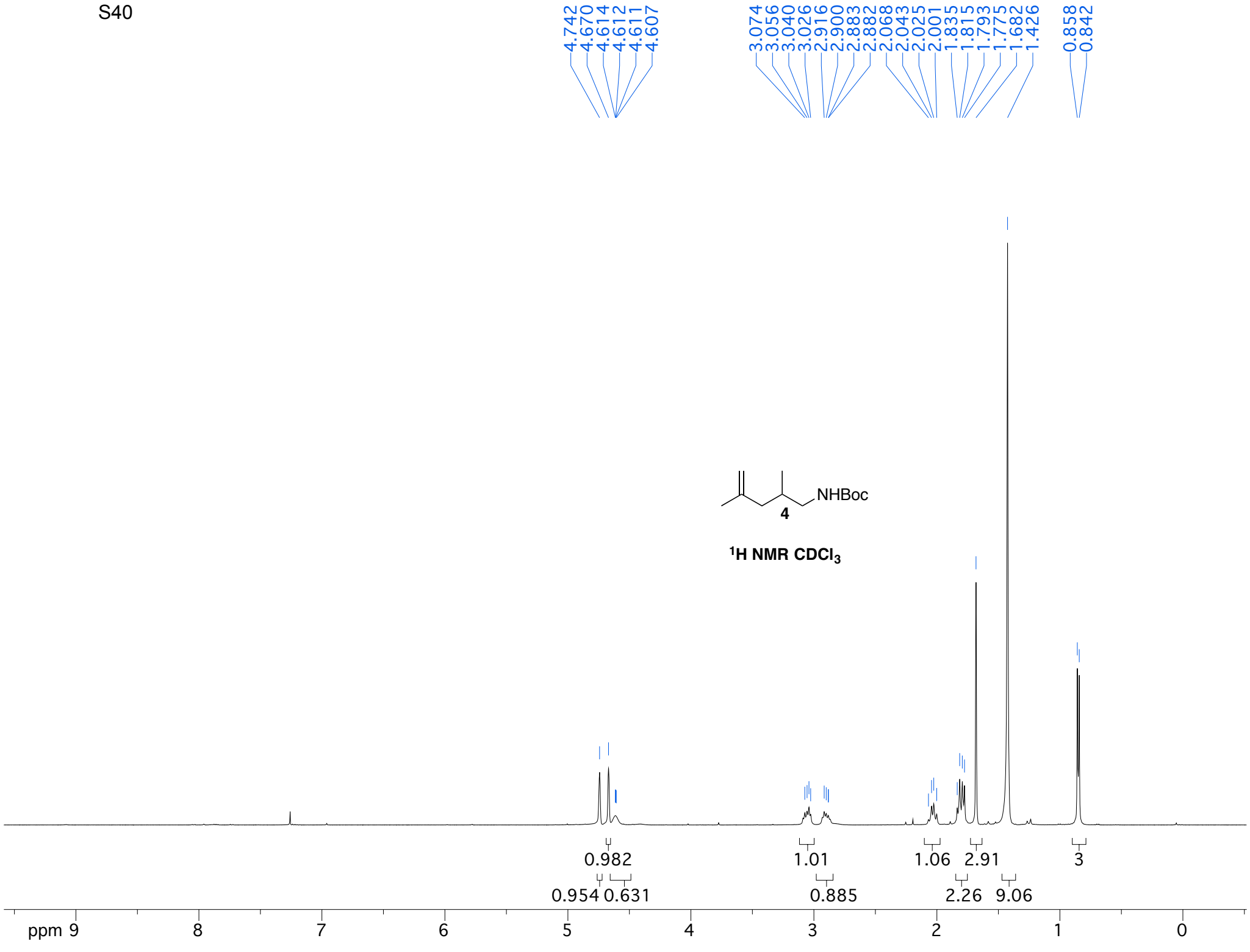
3m

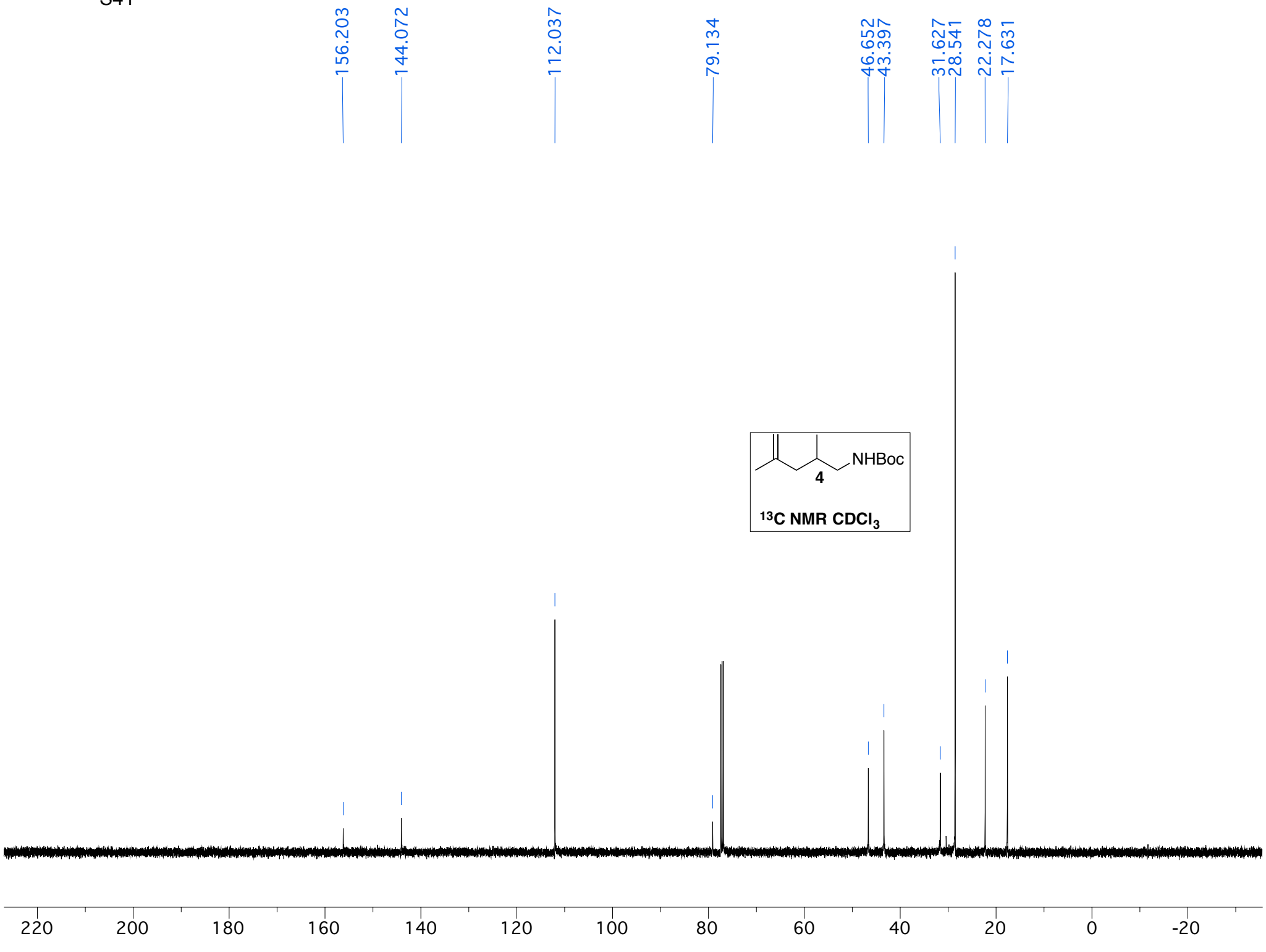
^{13}C NMR $CDCl_3$

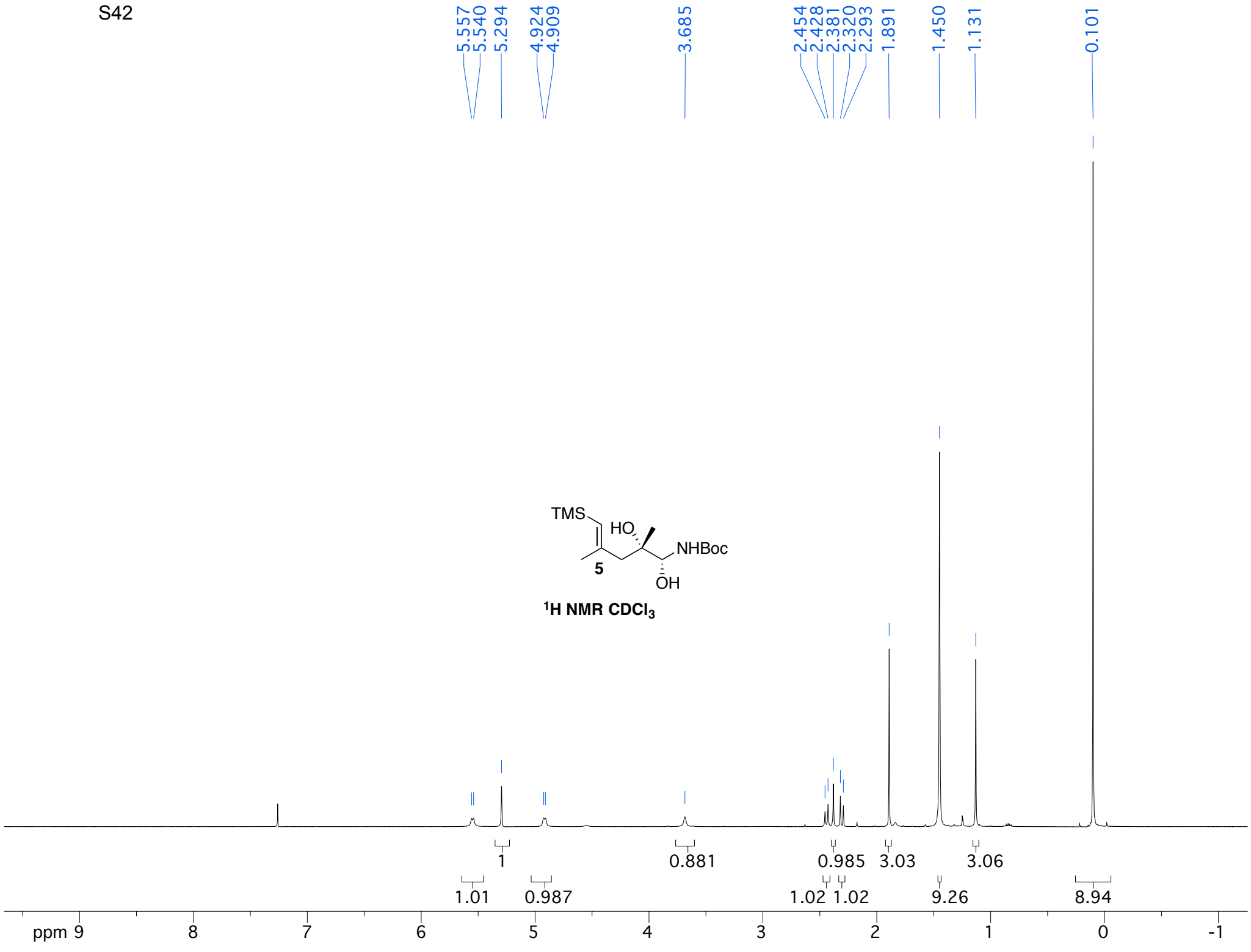

8.306
6.446
6.426
5.765
5.459
3.698
3.494
3.281
2.093
2.078
2.063
1.473
1.444
1.256
1.256
0.886
0.874
0.860
O
MeO
NHBoc
NHBoc
C6H13
3n
1H NMR CDCl3
0.861
0.855
1.8
1.83
3.07
0.819
0.87
2.83
1.79
26.4
ppm 12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3

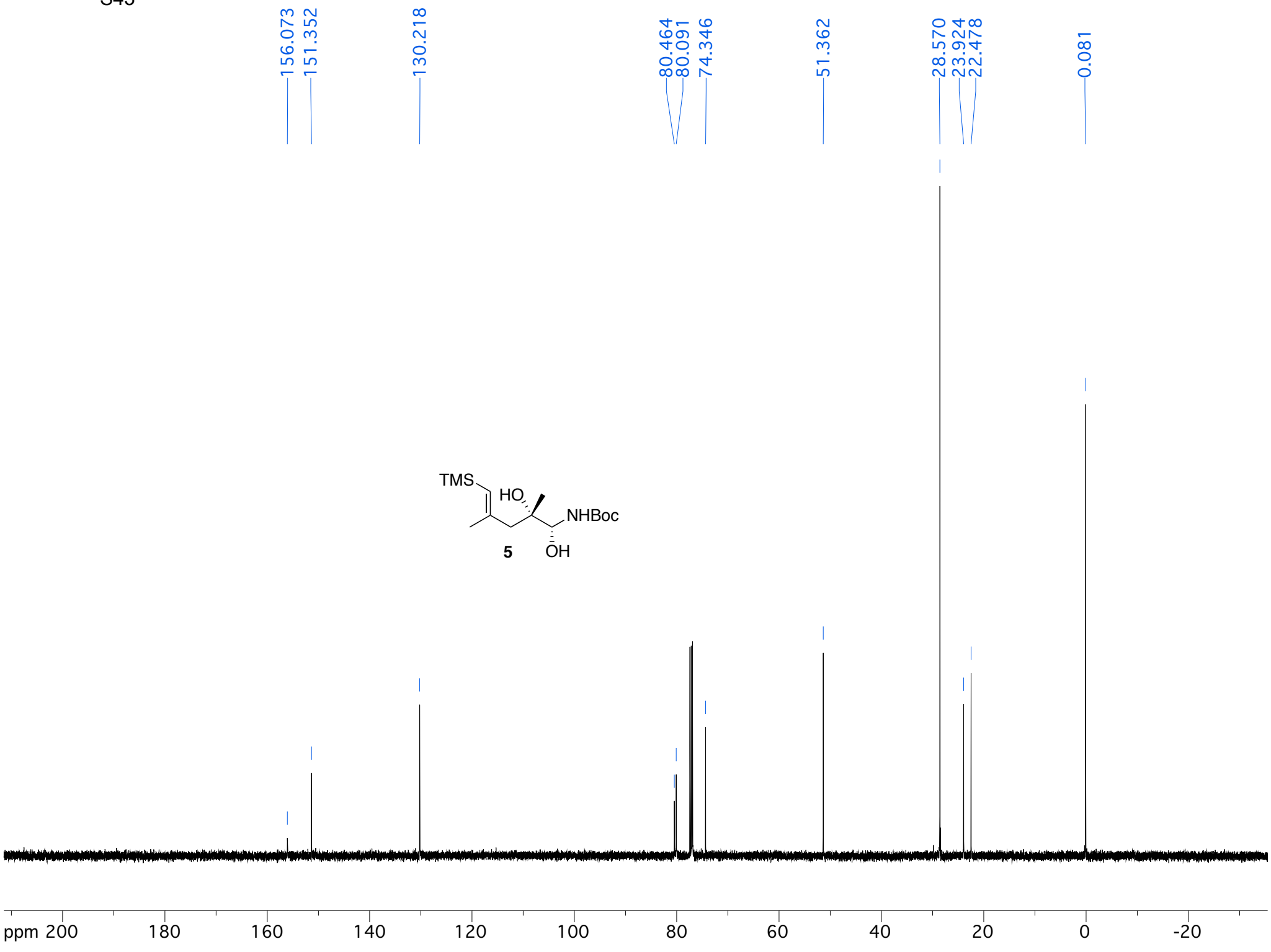


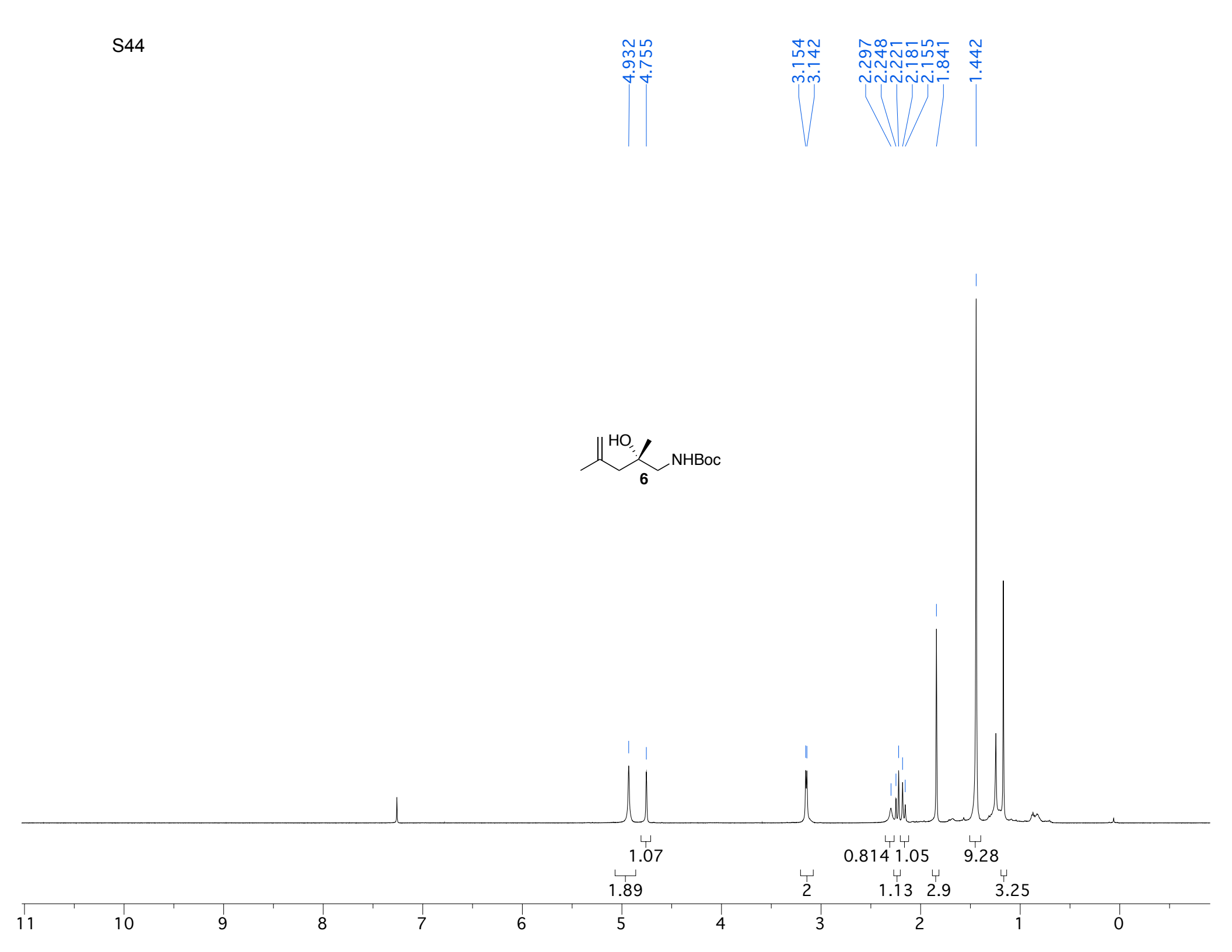
^{13}C NMR $CDCl_3$

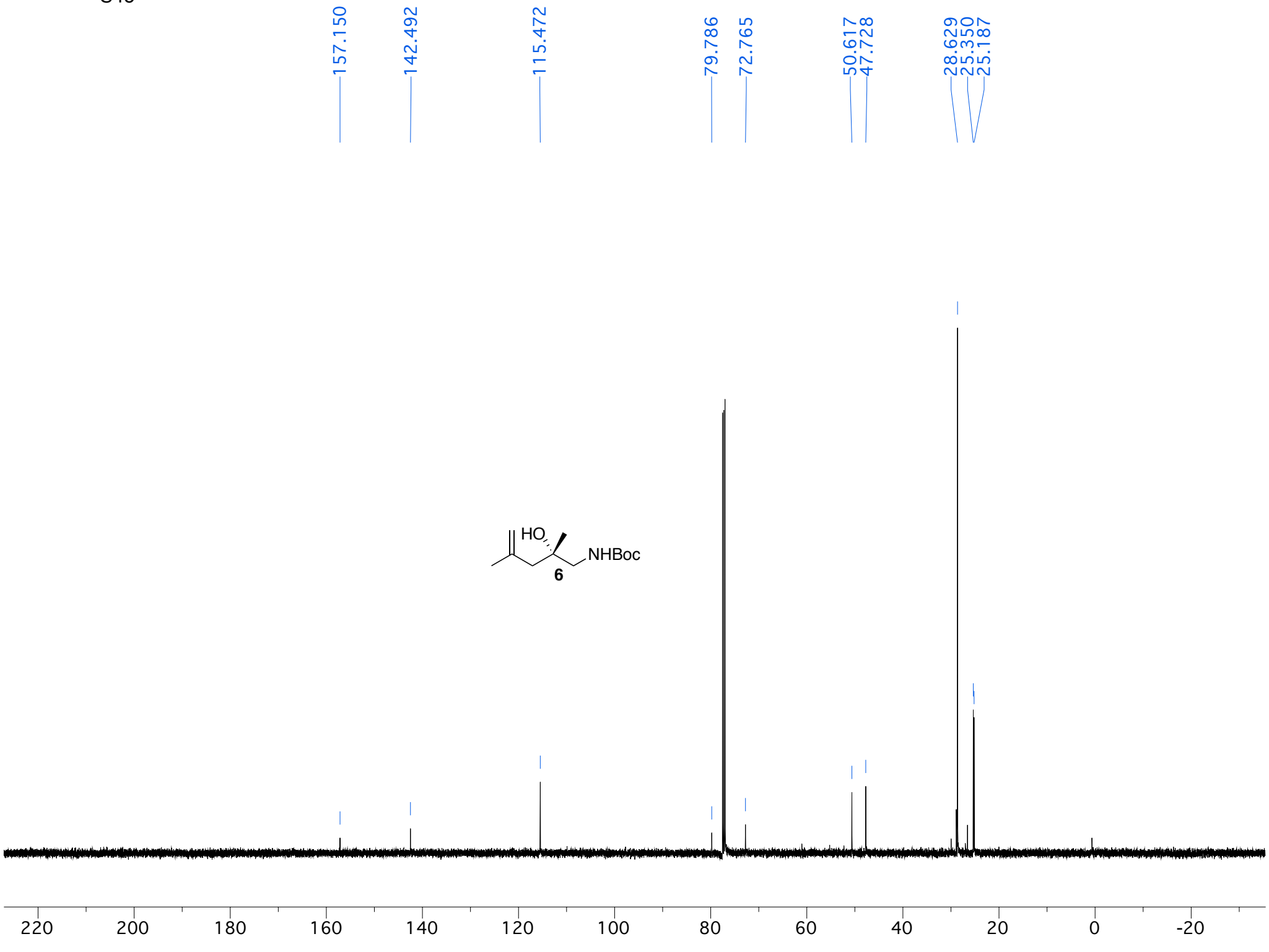

4.742
4.670
4.614
4.612
4.611
4.607
3.074
3.056
3.040
3.026
2.916
2.900
2.883
2.882
2.068
2.043
2.025
2.001
1.835
1.815
1.793
1.775
1.682
1.426
0.858
0.842
NHBoc
4
¹H NMR CDCl₃
0.982
0.954
0.631
1.01
0.885
1.06
2.91
2.26
9.06
3
ppm 9
8
7
6
5
4
3
2
1
0

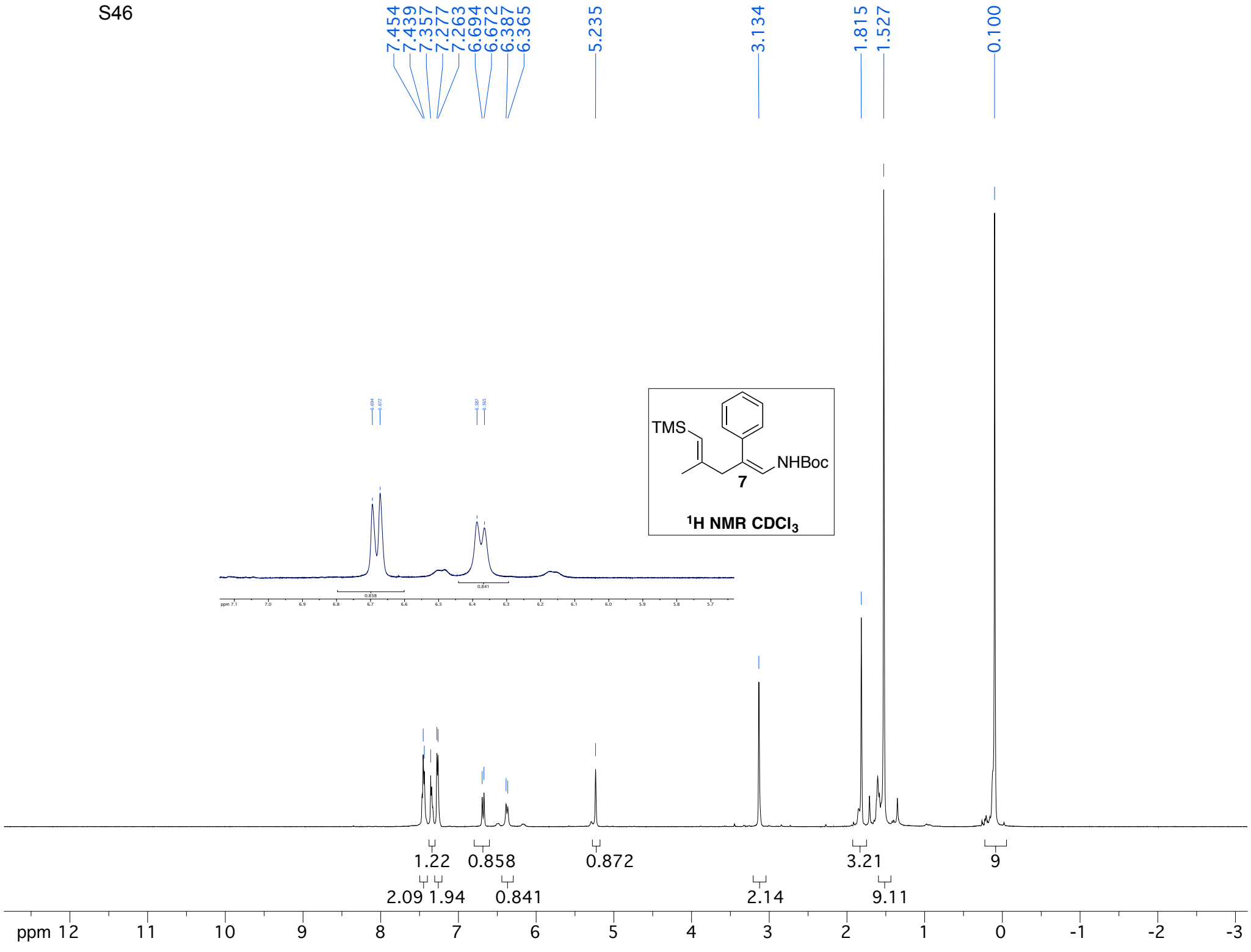

156.203
144.072
112.037
79.134
46.652
43.397
31.627
28.541
22.278
17.631
NHBoc
4
13C NMR CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
-20

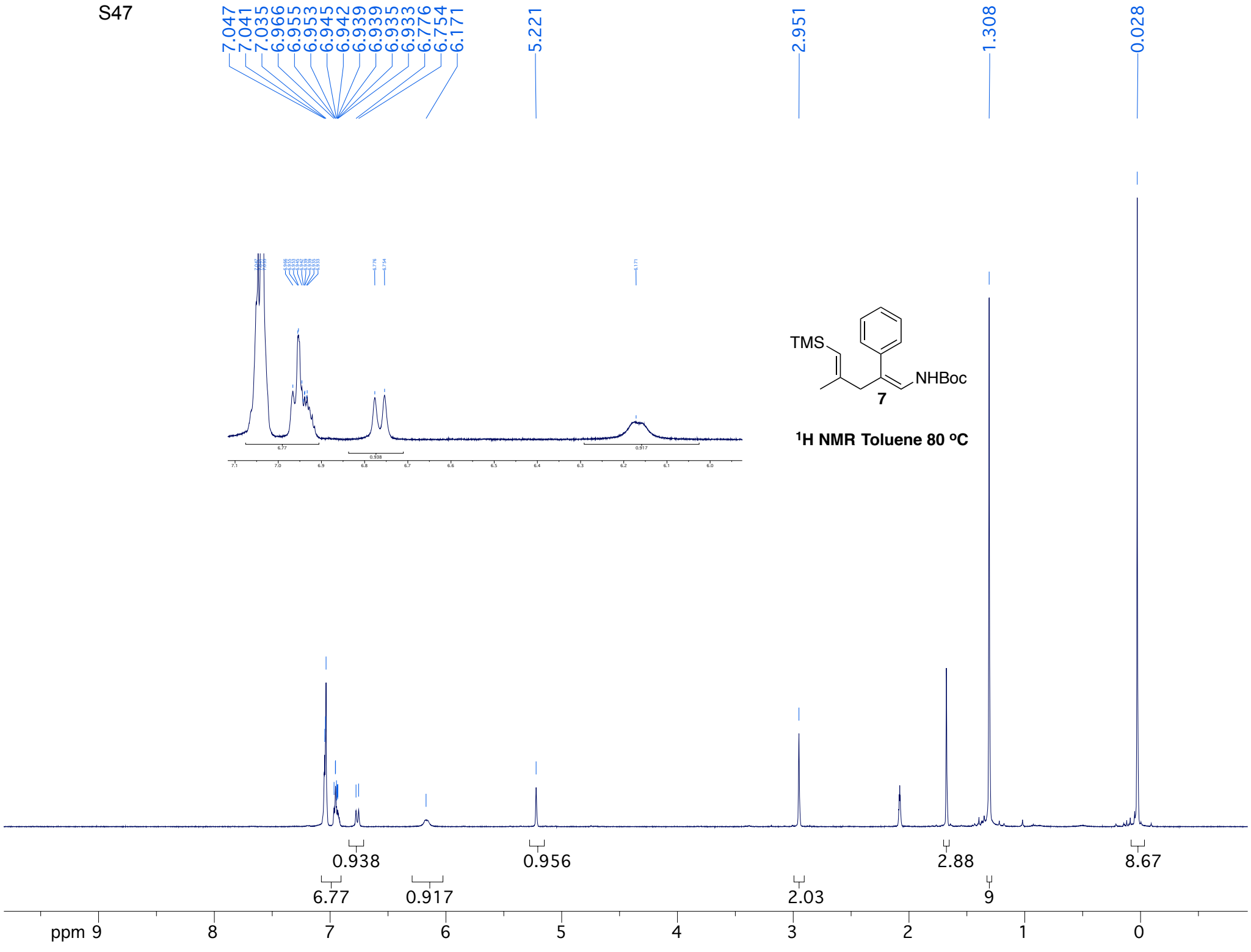

5.557
5.540
5.294
4.924
4.909
3.685
2.454
2.428
2.381
2.320
2.293
1.891
1.450
1.131
0.101
TMS
HO
NHBoc
OH
5
1H NMR CDCl3
1
0.881
0.985
3.03
3.06
1.01
0.987
1.02
1.02
9.26
8.94
ppm 9
8
7
6
5
4
3
2
1
0
-1

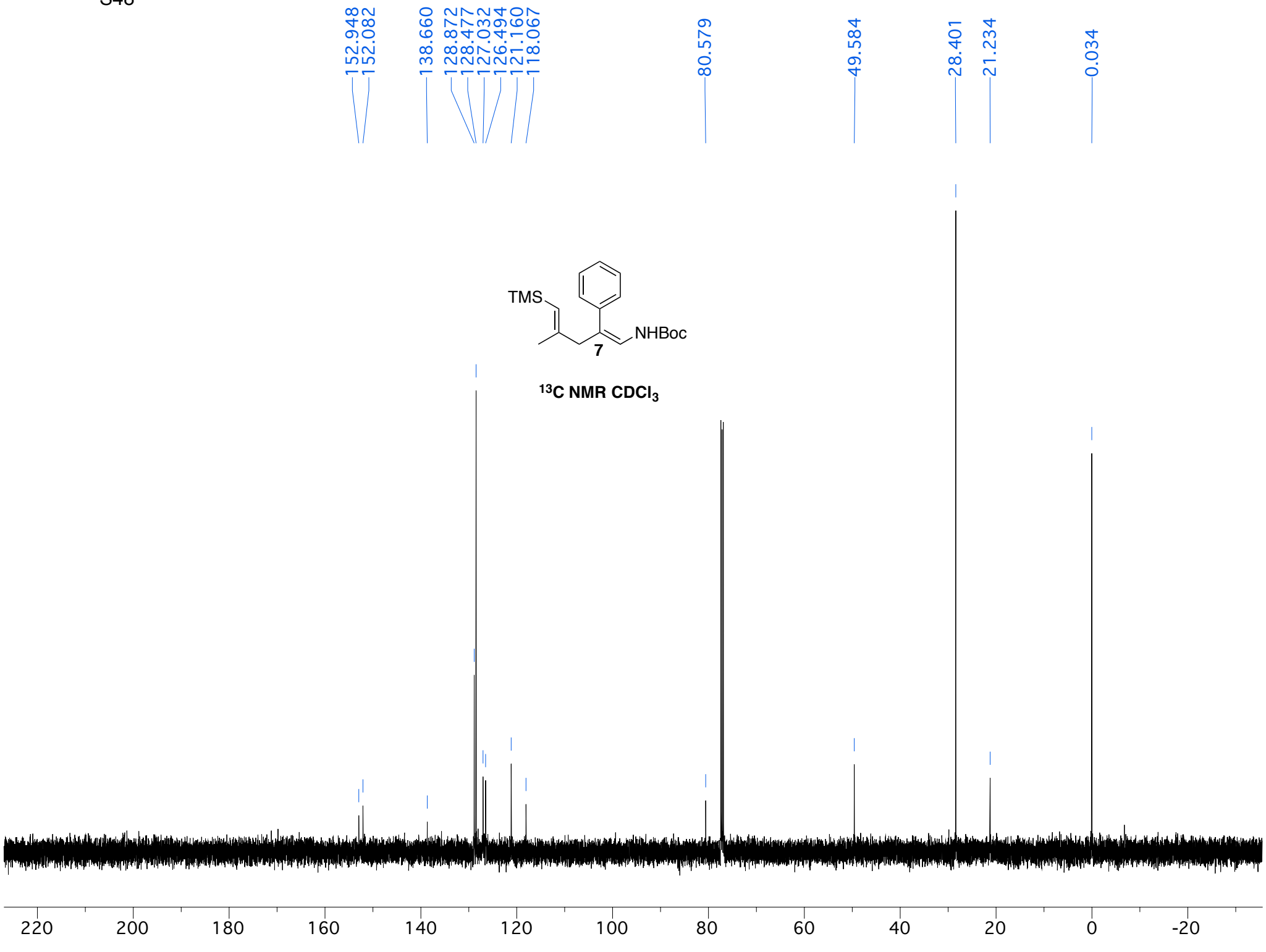

156.073
151.352
130.218
80.464
80.091
74.346
51.362
28.570
23.924
22.478
0.081
TMS
HO
NHBoc
OH
5
ppm 200
180
160
140
120
100
80
60
40
20
0
-20


4.932
4.755
3.154
3.142
2.297
2.248
2.221
2.181
2.155
1.841
1.442
HO
NHBoc
6
1.07
0.814
1.05
9.28
1.89
2
1.13
2.9
3.25
11
10
9
8
7
6
5
4
3
2
1
0

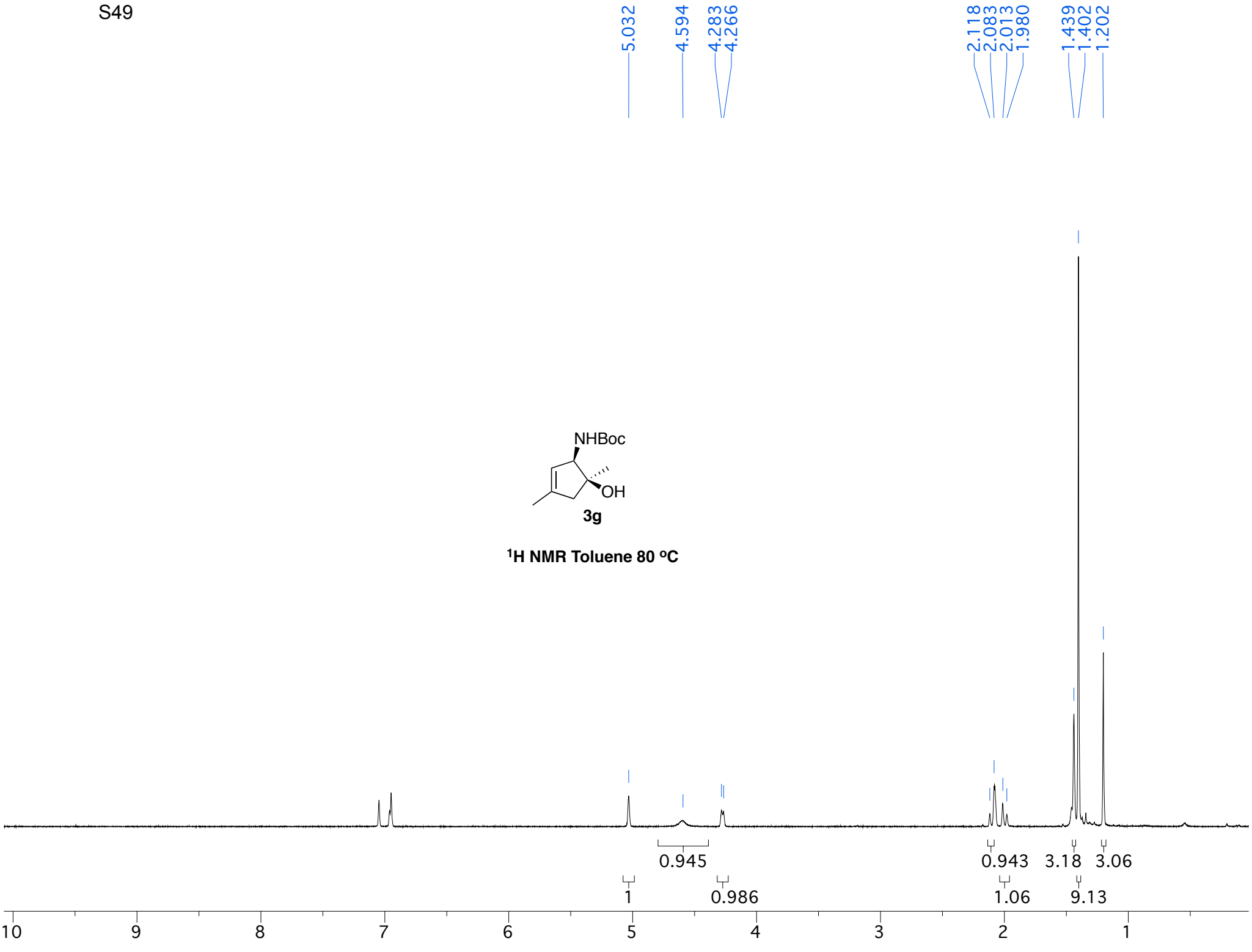

157.150
142.492
115.472
79.786
72.765
50.617
47.728
28.629
25.350
25.187
HO
NHBoc
6
220
200
180
160
140
120
100
80
60
40
20
0
-20


7.454
7.439
7.357
7.277
7.263
6.694
6.672
6.387
6.365
5.235
3.134
1.815
1.527
0.100
TMS
NHBoc
7
^{1}H NMR CDCl$_3$
1.22
0.858
0.872
3.21
9
2.09
1.94
0.841
2.14
9.11
ppm 12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3

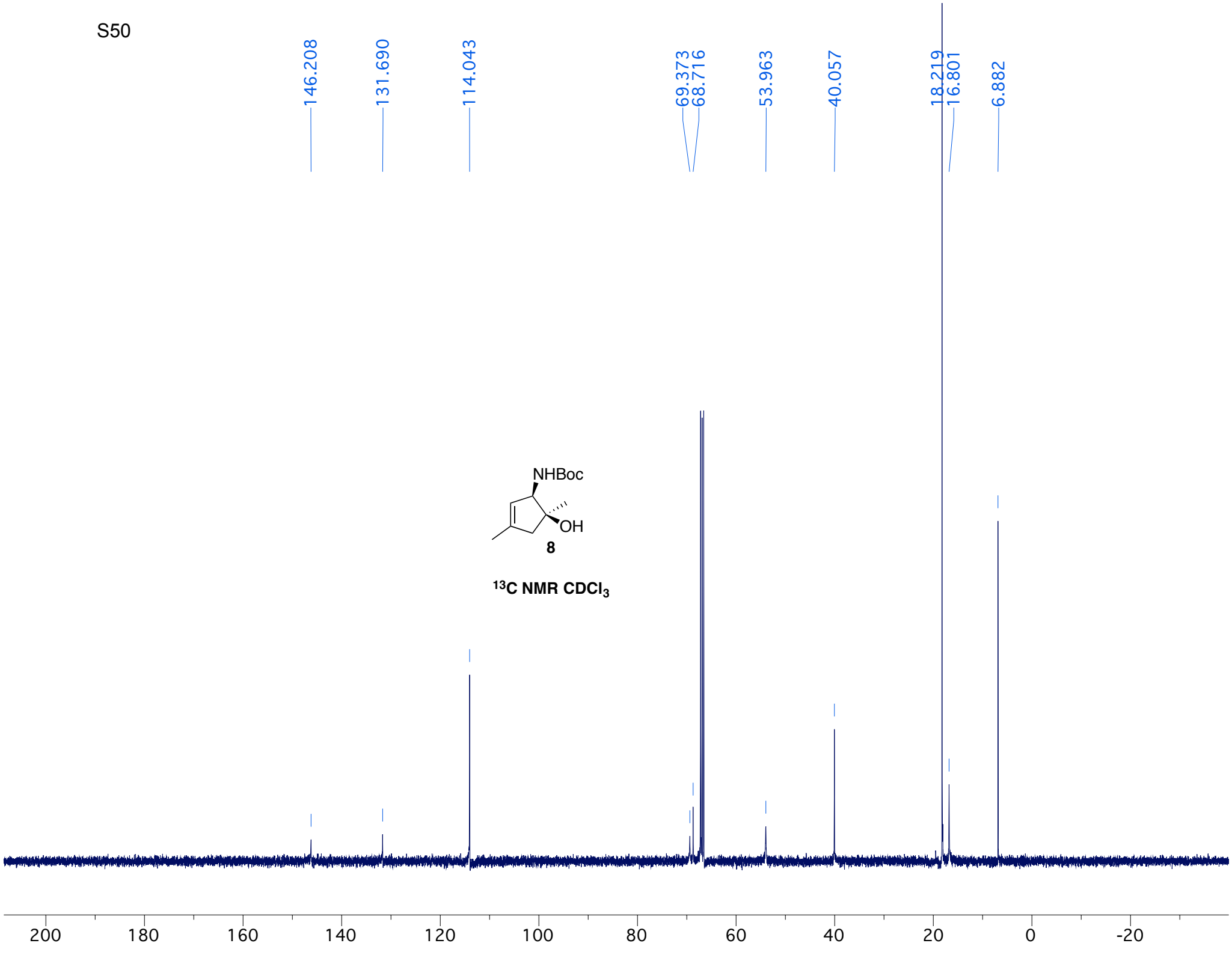

7.047
7.041
7.035
6.966
6.955
6.953
6.945
6.942
6.939
6.939
6.935
6.933
6.776
6.754
6.171
5.221
2.951
1.308
0.028
TMS
NHBoc
7
¹H NMR Toluene 80 °C
0.938
0.956
2.88
8.67
6.77
0.917
2.03
9
ppm 9
8
7
6
5
4
3
2
1
0

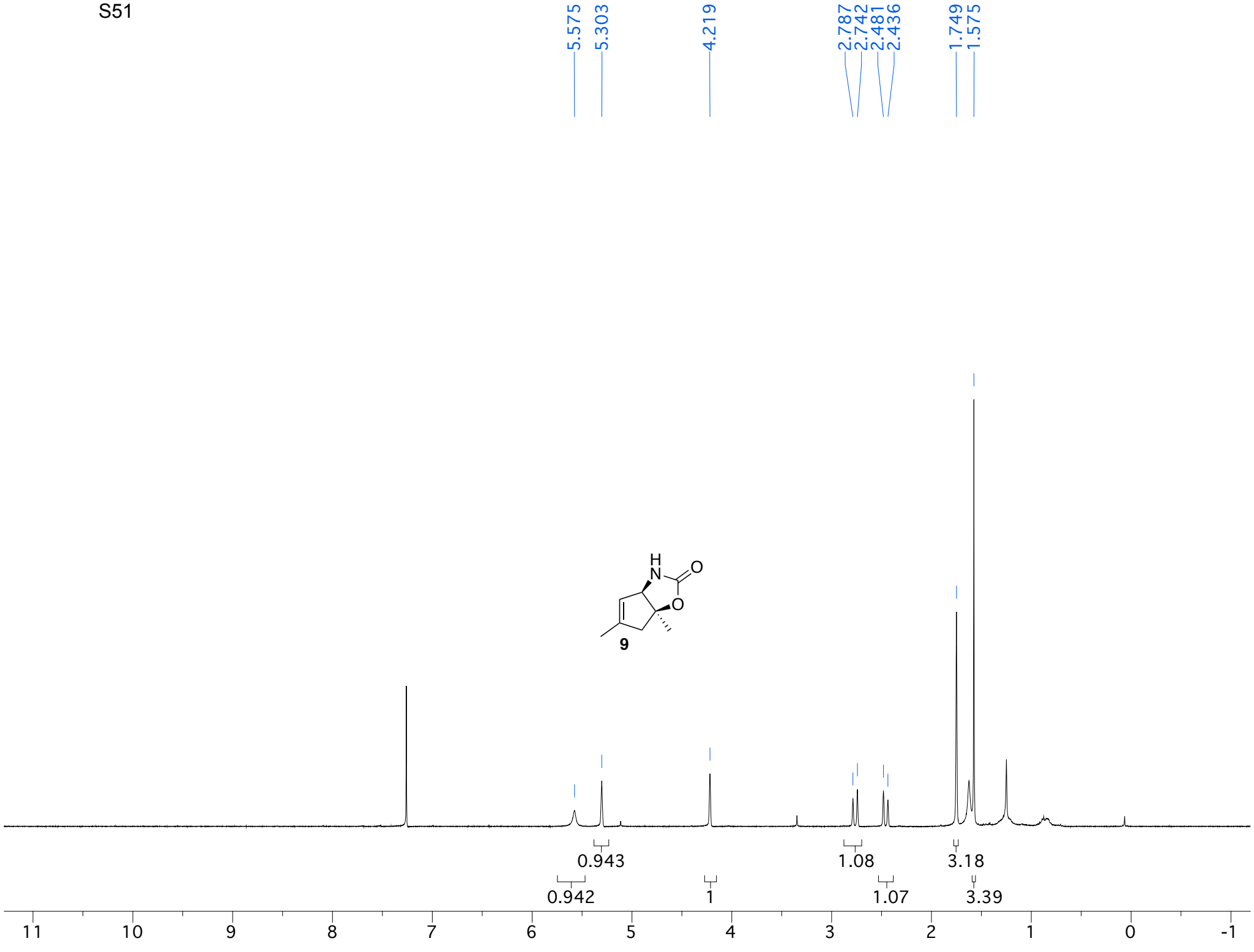


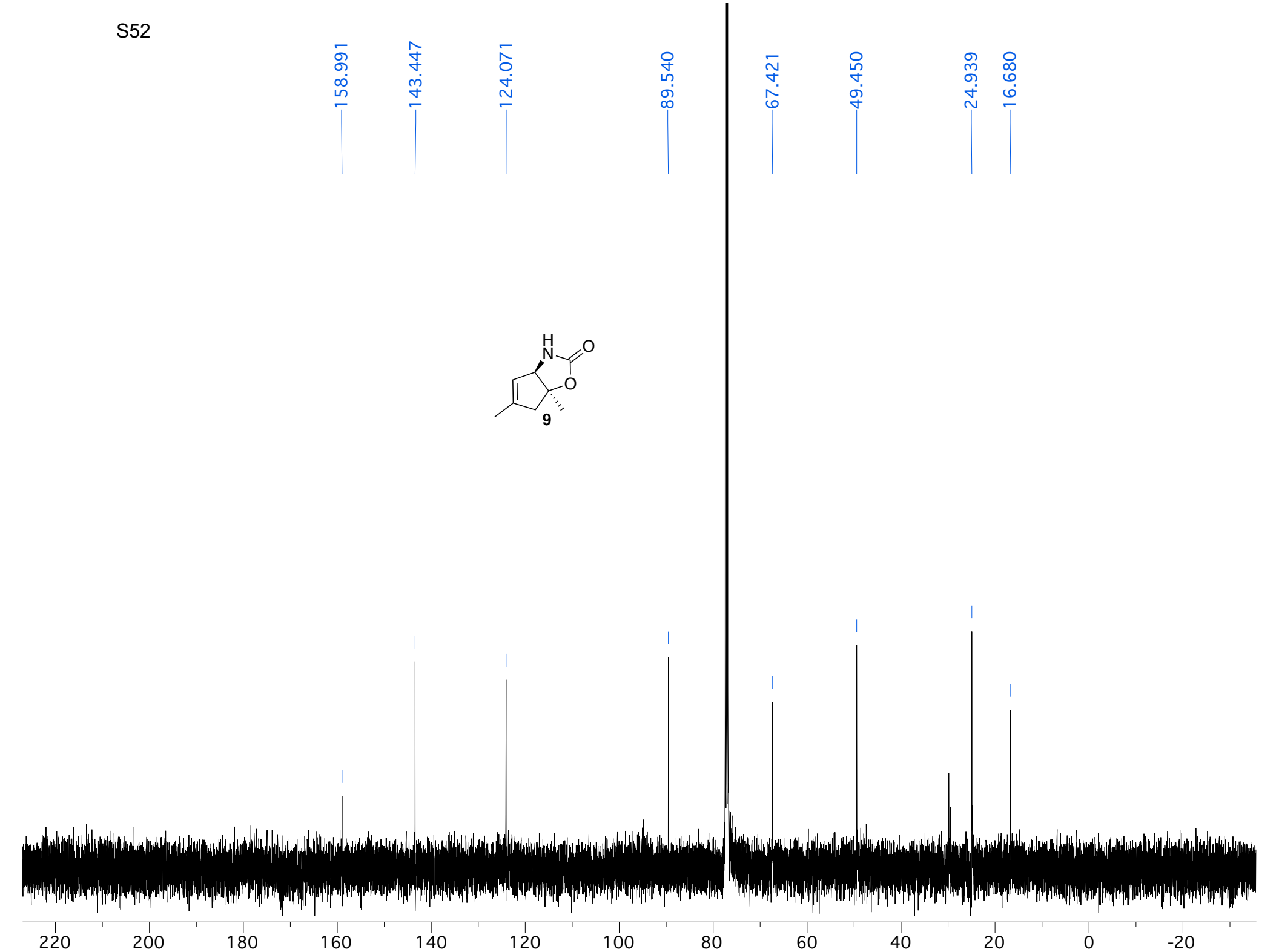
^{13}C NMR $CDCl_3$

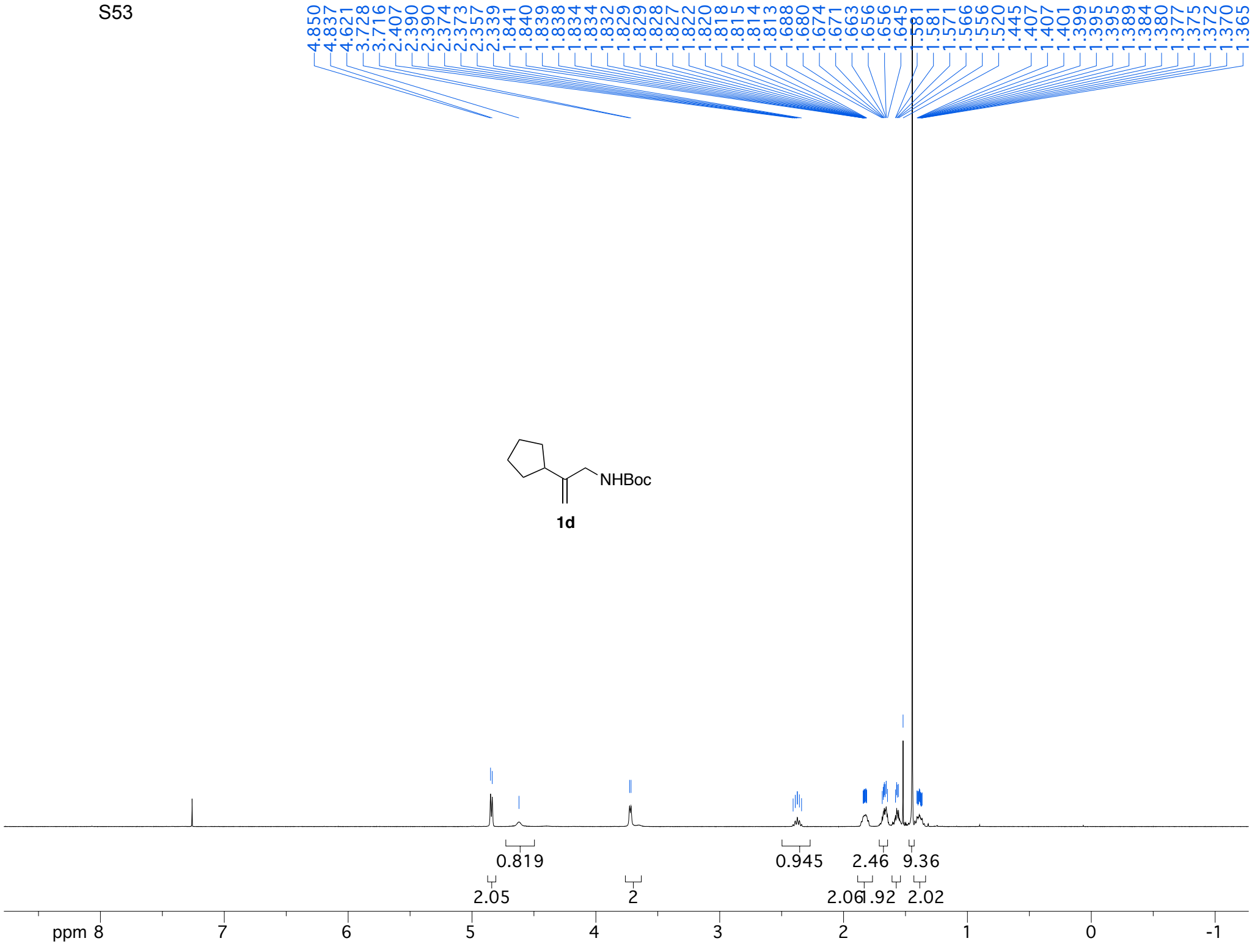


^{1}H NMR Toluene 80 ^{o}C

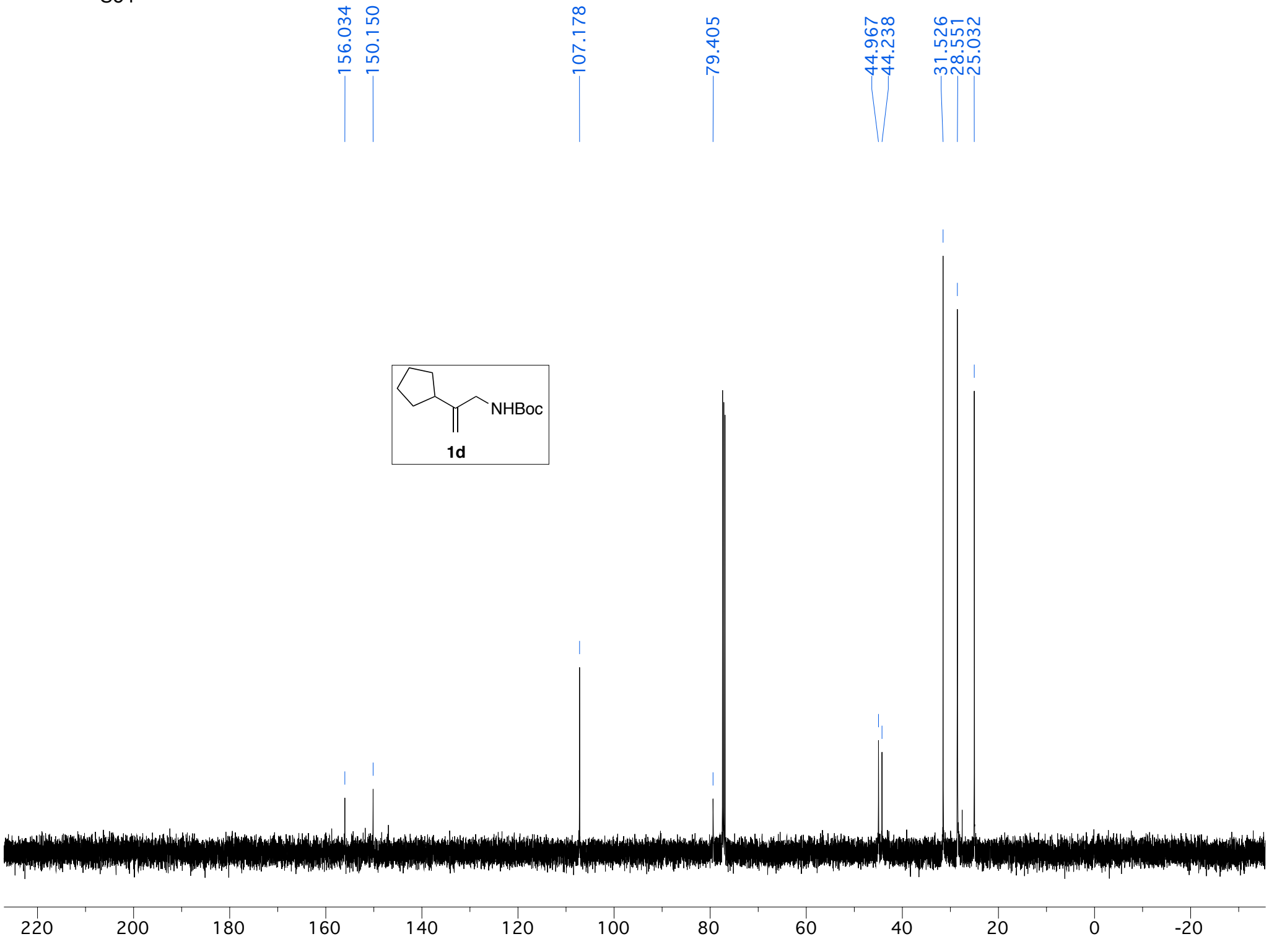

146.208
131.690
114.043
69.373
68.716
53.963
40.057
18.219
16.801
6.882
NHBoc
OH
8
^{13}C NMR CDCl$_3$
200
180
160
140
120
100
80
60
40
20
0
-20

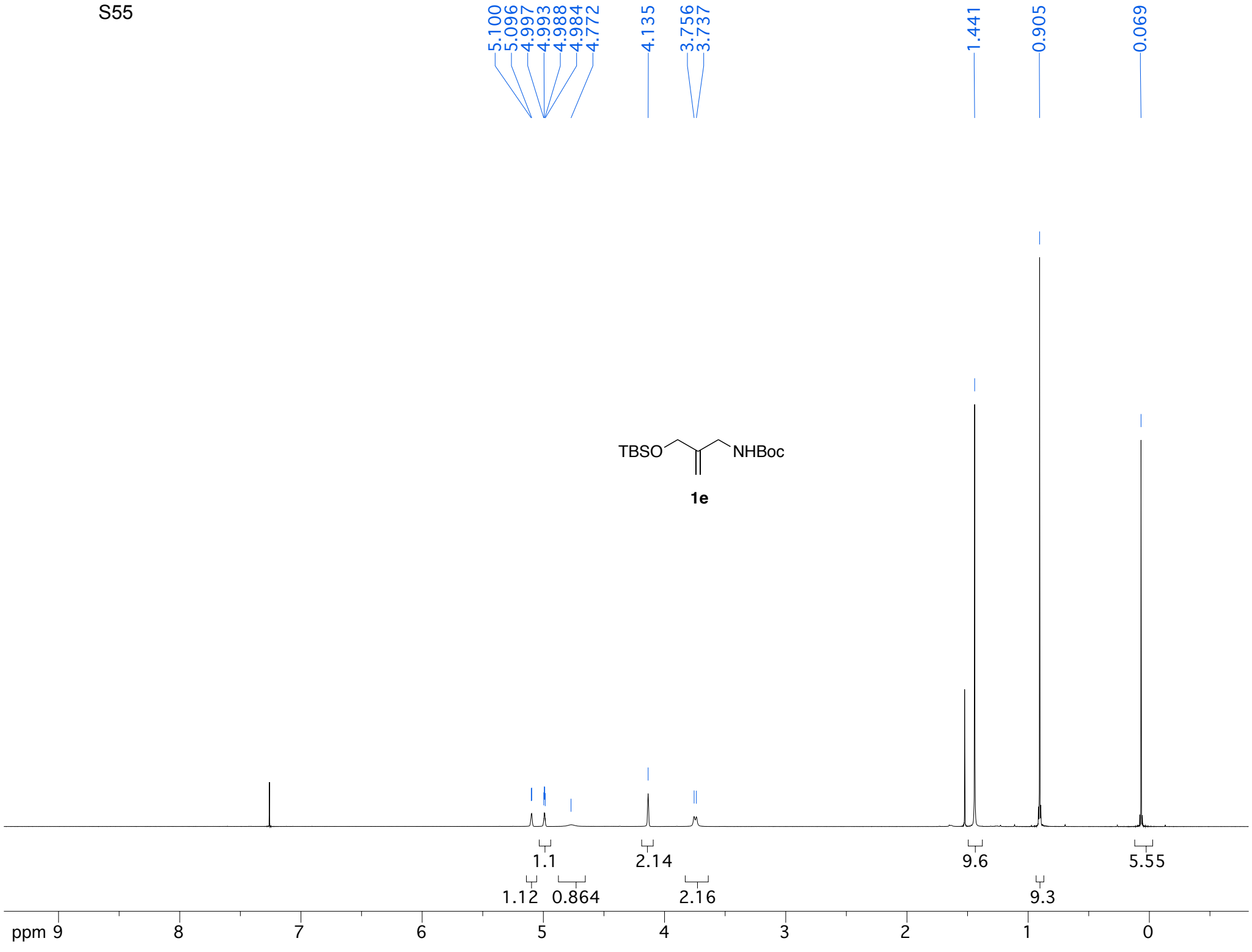

5.575
5.303
4.219
2.787
2.742
2.481
2.436
1.749
1.575
H
N
O
O
9
0.943
1.08
3.18
0.942
1
1.07
3.39
11
10
9
8
7
6
5
4
3
2
1
0
-1

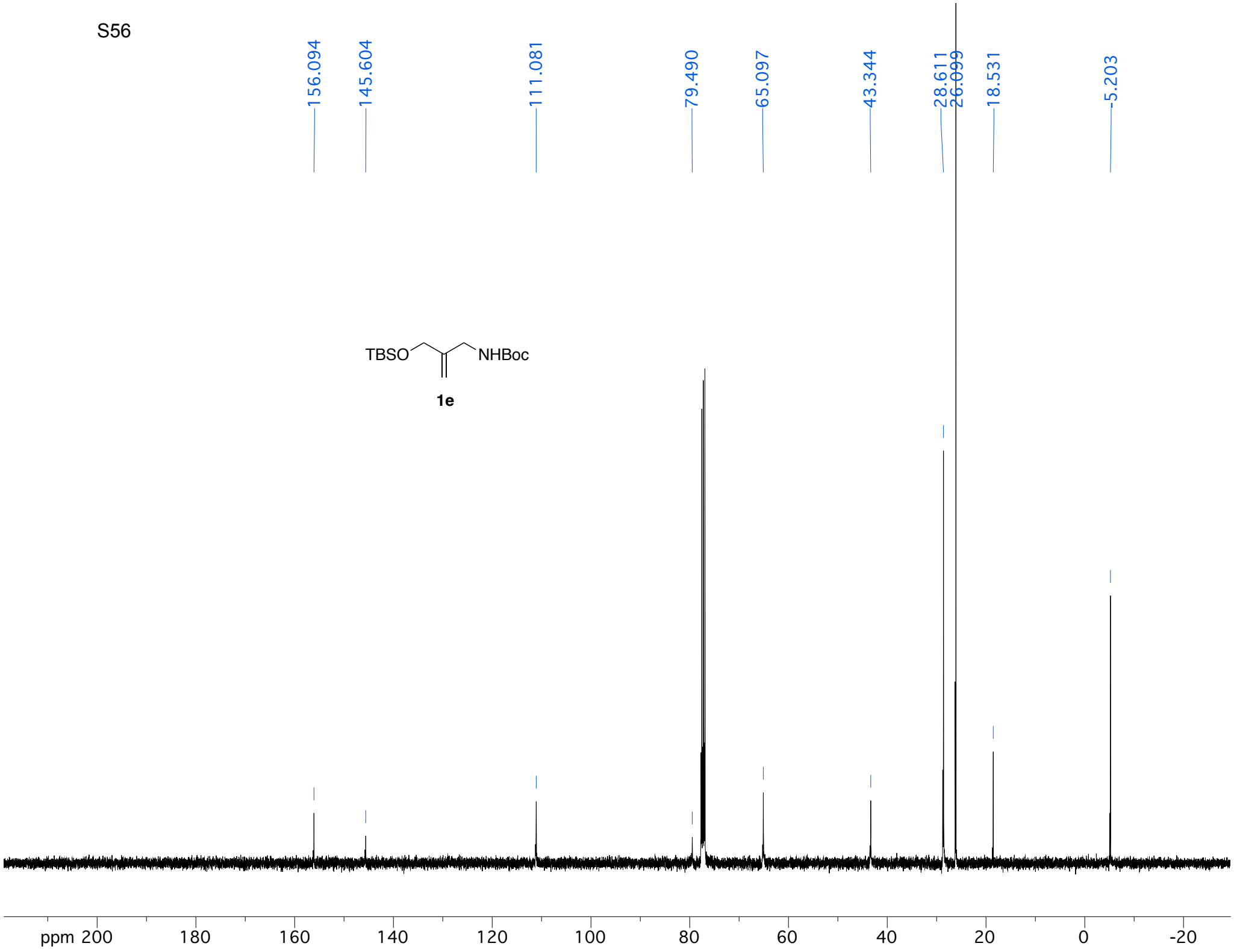

158.991
143.447
124.071
89.540
67.421
49.450
24.939
16.680
H
N
O
O
9
220
200
180
160
140
120
100
80
60
40
20
0
-20

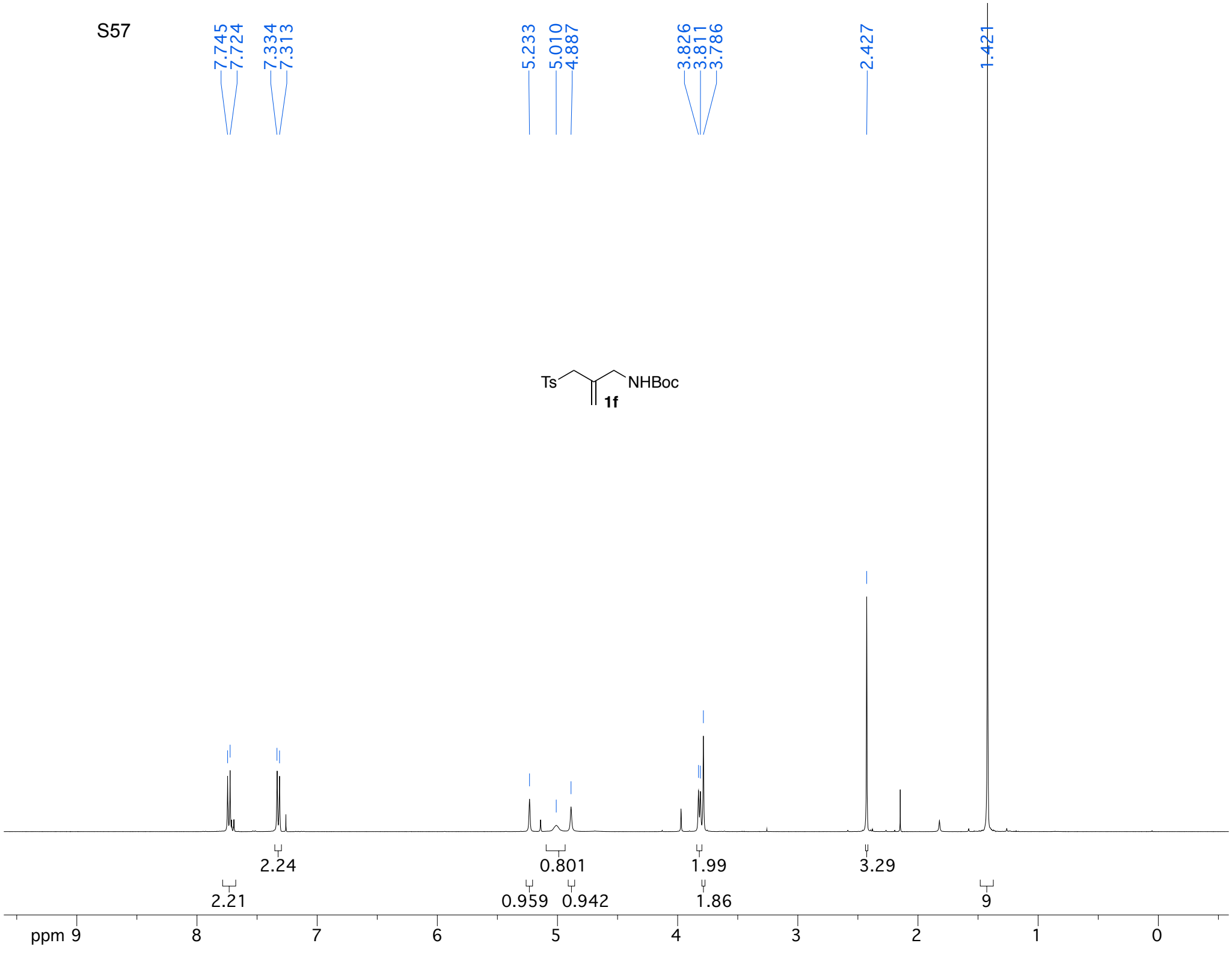

4.850
4.837
4.621
3.728
3.716
2.407
2.390
2.390
2.374
2.373
2.357
2.339
1.841
1.840
1.839
1.838
1.834
1.834
1.832
1.829
1.829
1.828
1.827
1.822
1.820
1.818
1.815
1.814
1.813
1.688
1.680
1.674
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1.663
1.656
1.656
1.645
1.581
1.581
1.571
1.566
1.556
1.520
1.445
1.407
1.407
1.401
1.399
1.395
1.395
1.389
1.384
1.380
1.377
1.375
1.372
1.370
1.365
NHBoc
0.819
0.945
2.46
9.36
2.05
2
2.06
1.92
2.02
ppm 8
7
6
5
4
3
2
1
0
-1

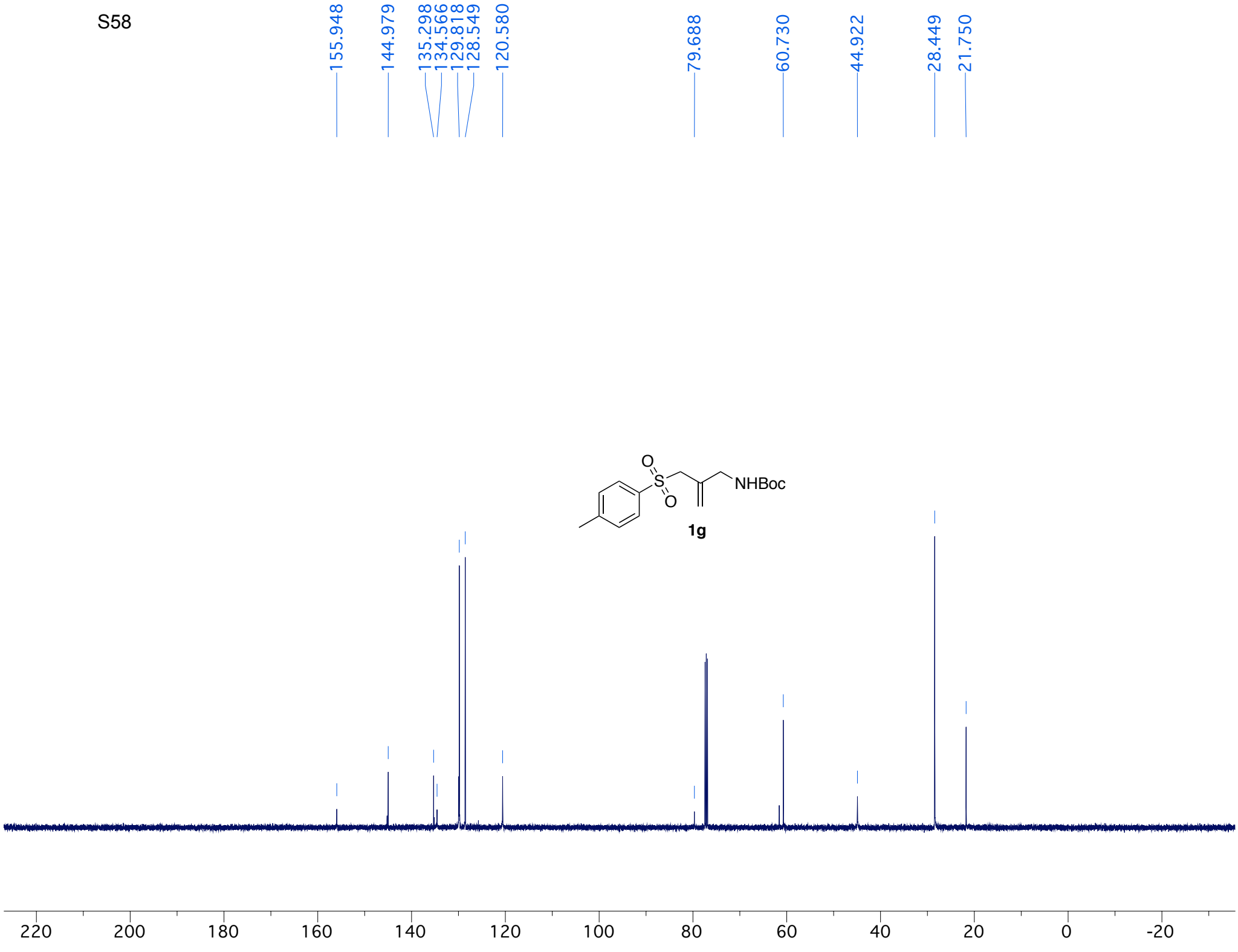
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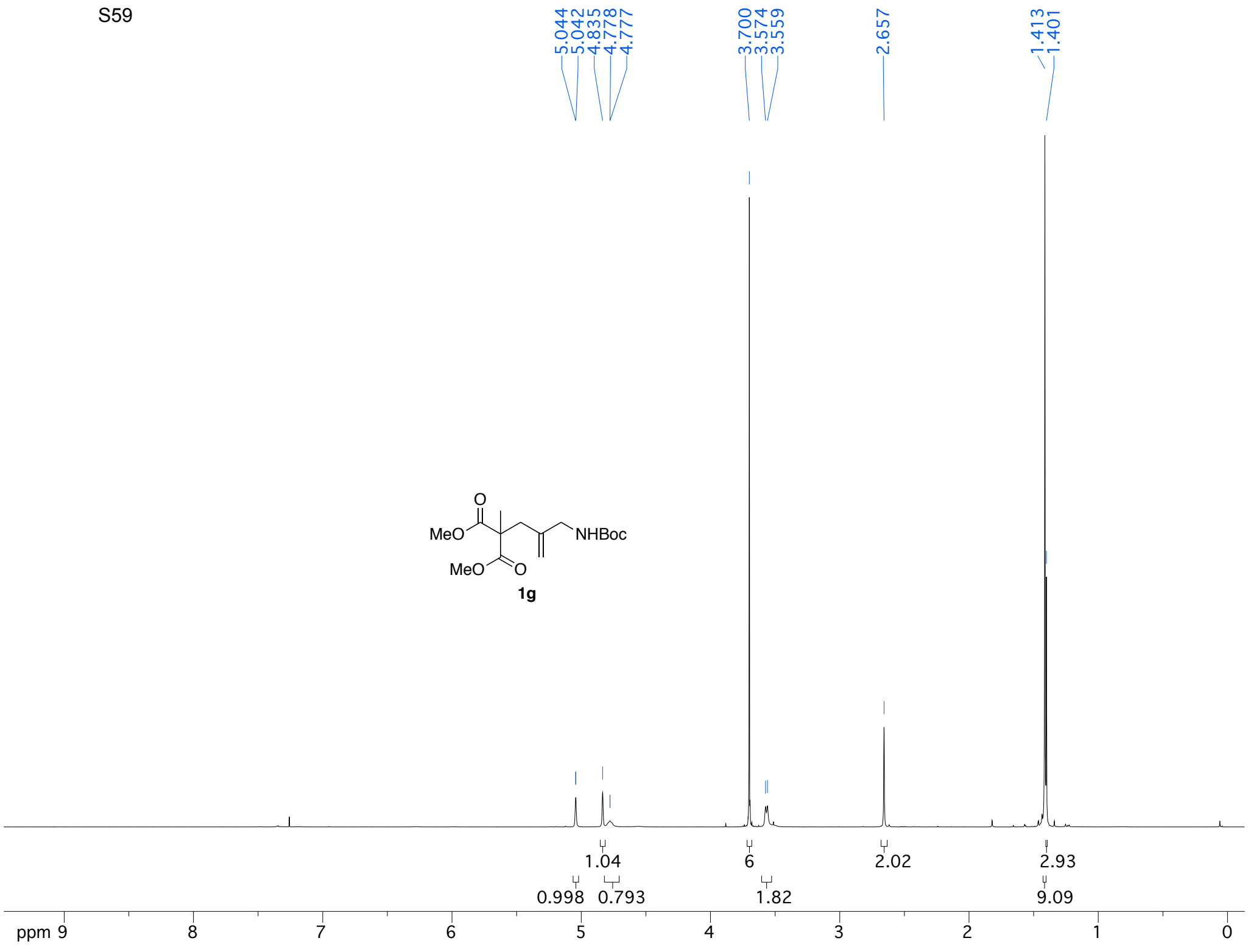

156.034
150.150
107.178
79.405
44.967
44.238
31.526
28.551
25.032
NHBoc
1d
220
200
180
160
140
120
100
80
60
40
20
0
-20

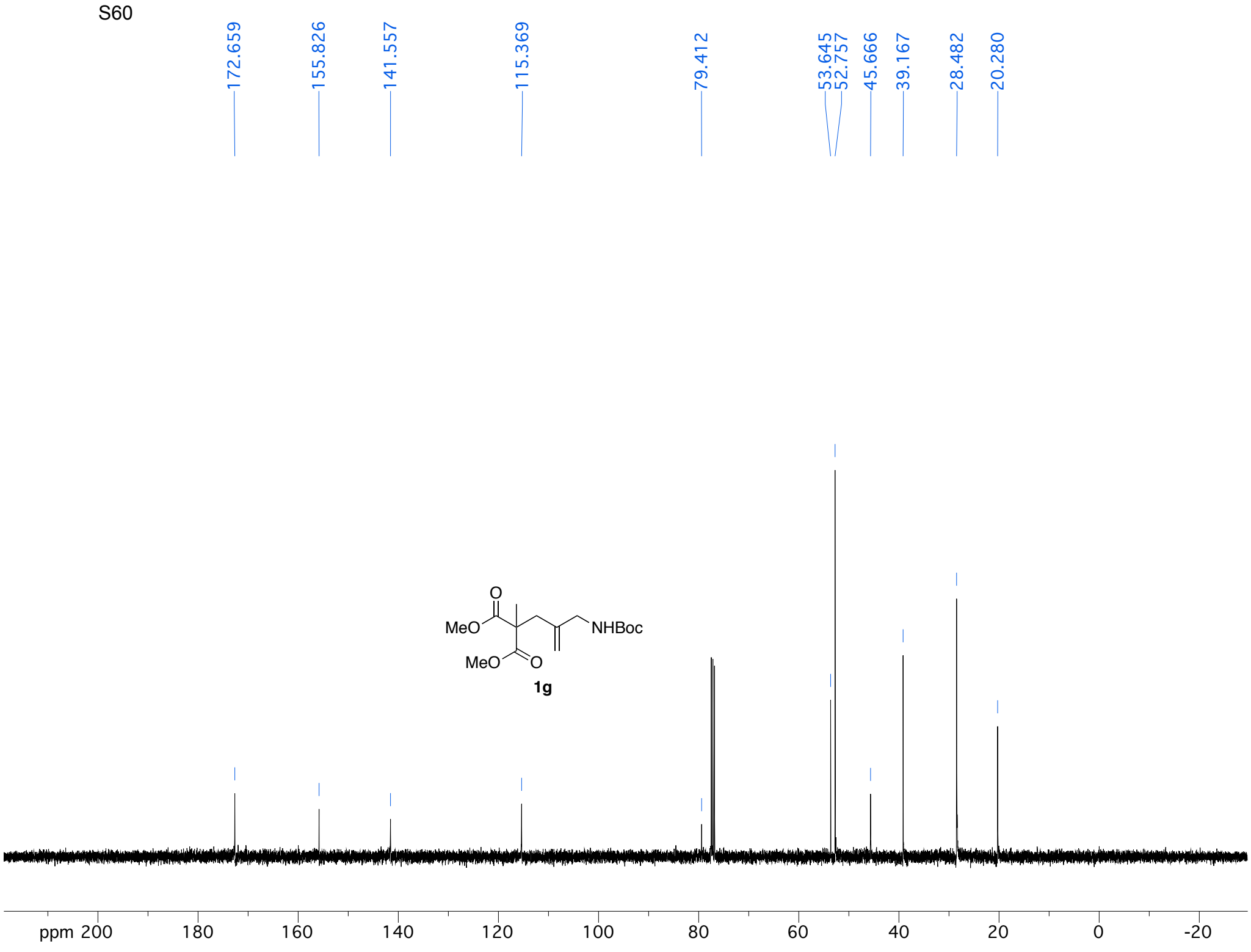

5.100
5.096
4.997
4.993
4.988
4.984
4.772
4.135
3.756
3.737
1.441
0.905
0.069
TBSO
NHBoc
1e
1.1
2.14
9.6
5.55
1.12
0.864
2.16
9.3
ppm 9
8
7
6
5
4
3
2
1
0

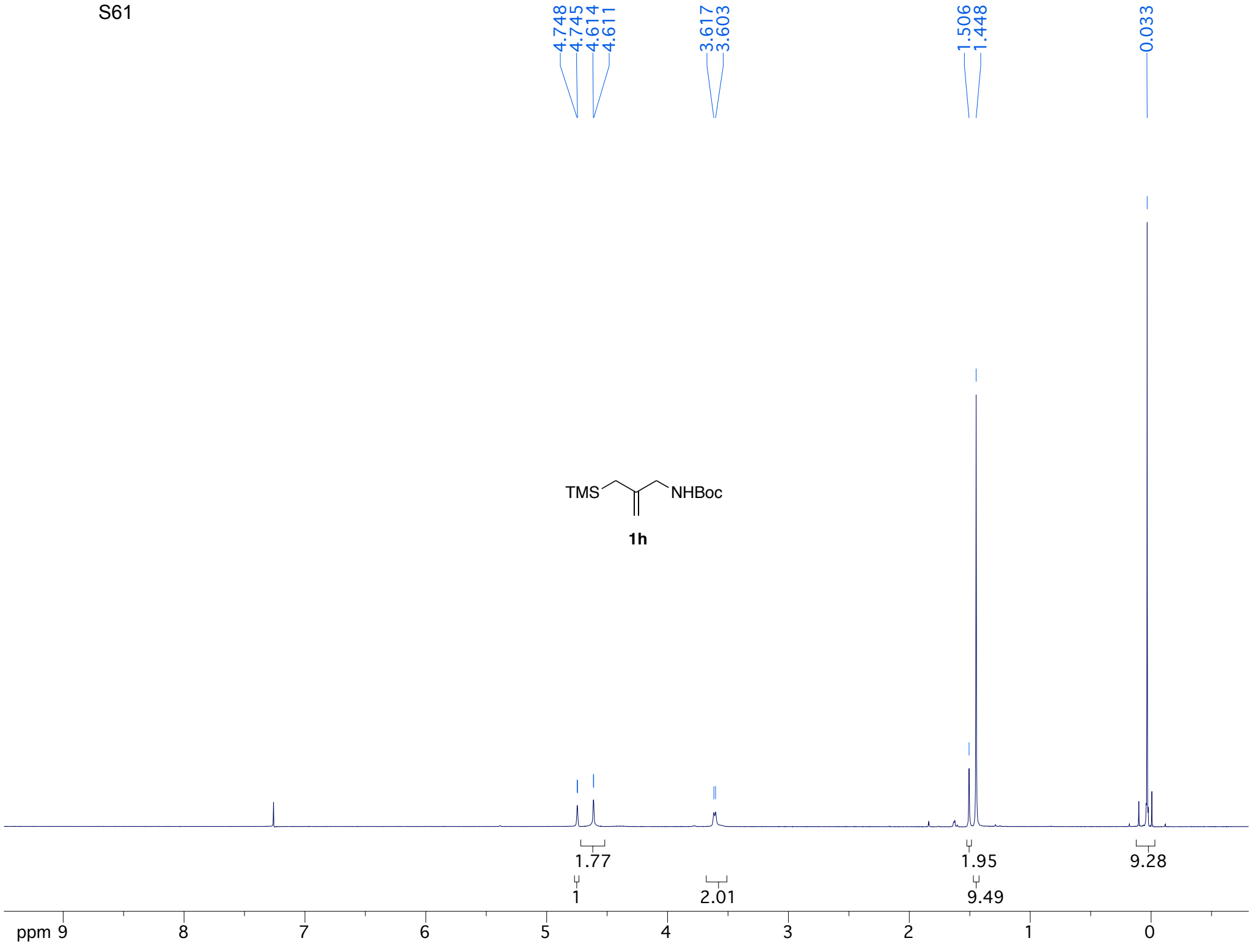

156.094
145.604
111.081
79.490
65.097
43.344
28.611
26.099
18.531
-5.203
TBSO
NHBoc
1e
ppm 200
180
160
140
120
100
80
60
40
20
0
-20

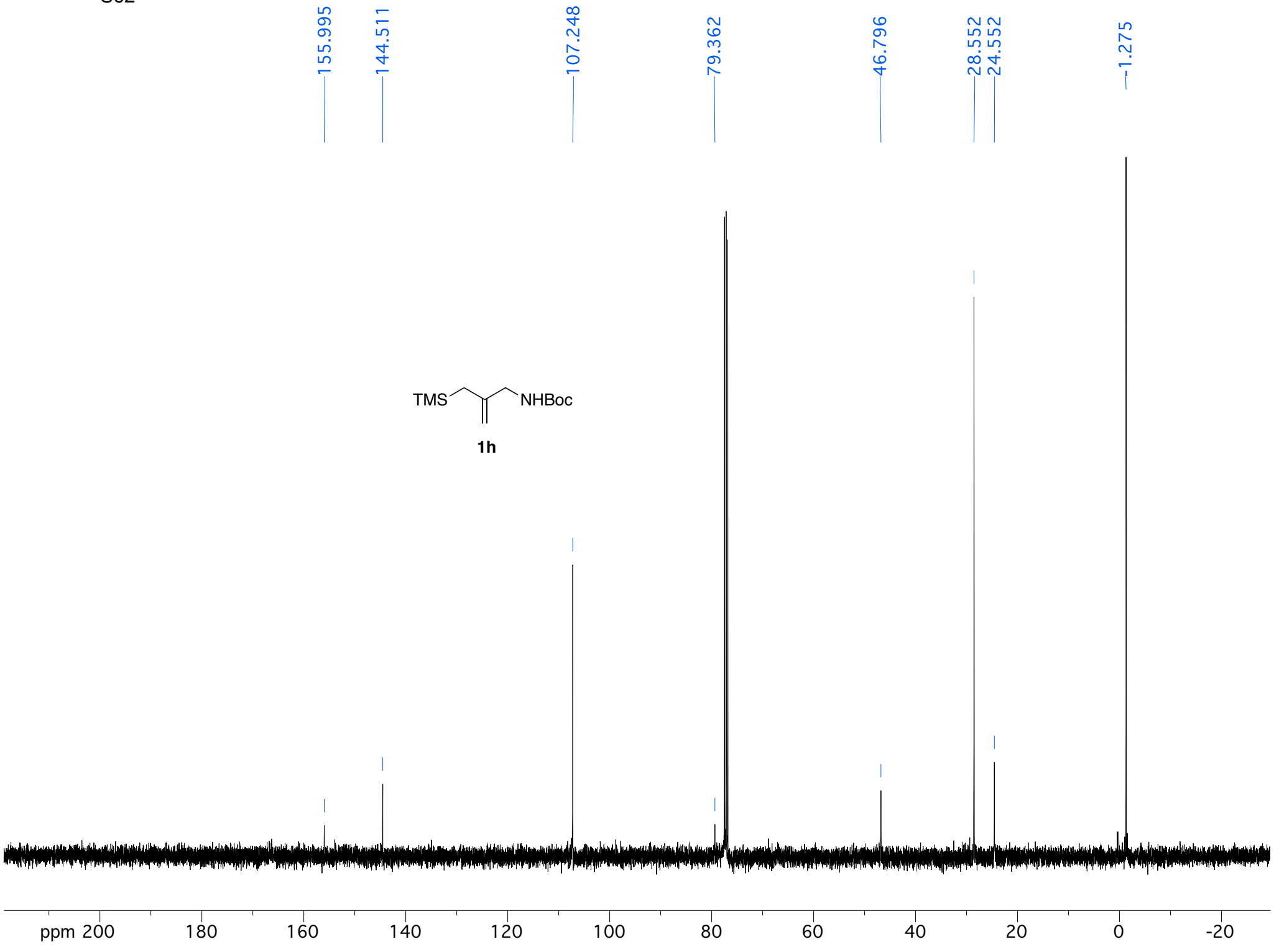

7.745
7.724
7.334
7.313
5.233
5.010
4.887
3.826
3.811
3.786
2.427
1.421
Ts
NHBoc
1f
2.24
0.801
1.99
3.29
2.21
0.959
0.942
1.86
9
ppm 9
8
7
6
5
4
3
2
1
0

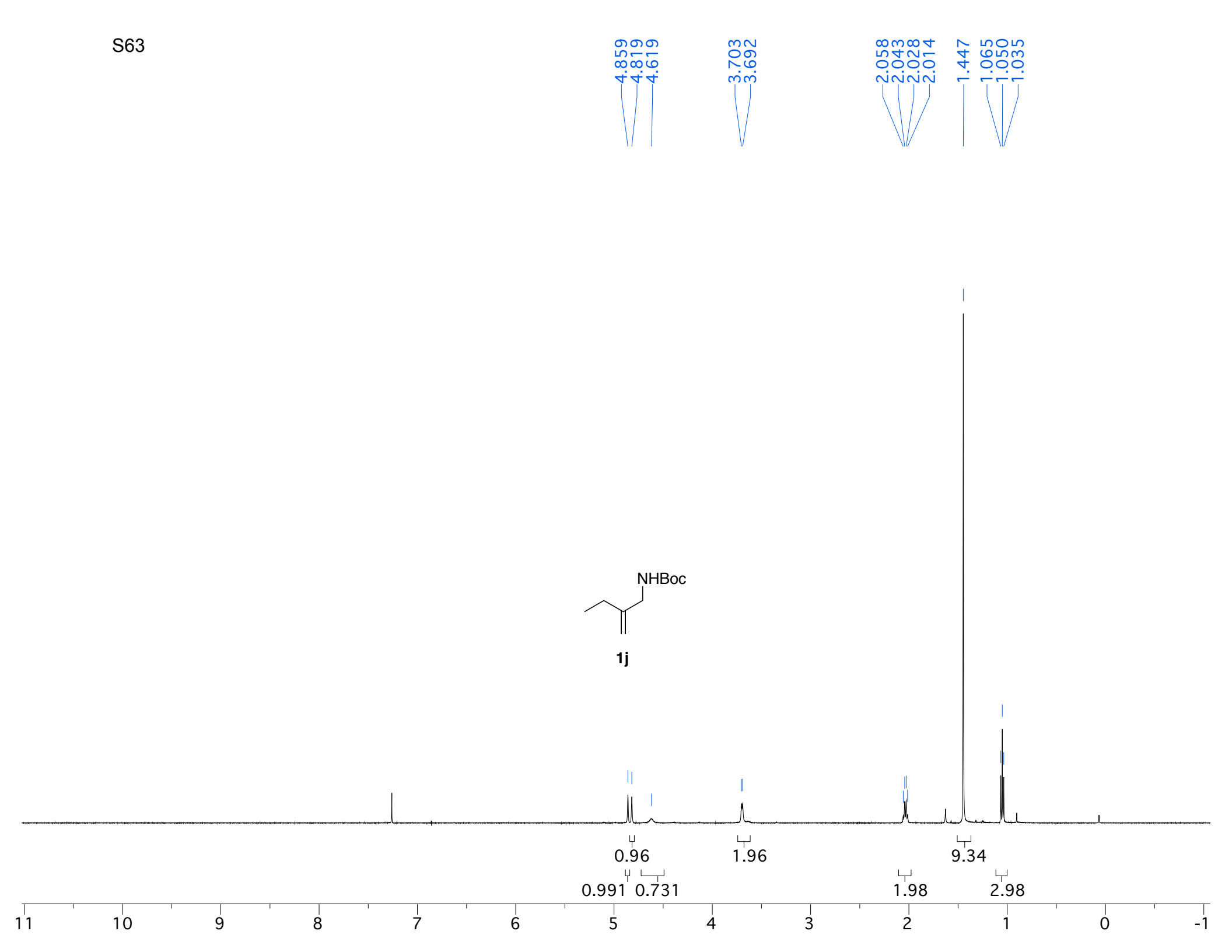

155.948
144.979
135.298
134.566
129.818
128.549
120.580
79.688
60.730
44.922
28.449
21.750
O
S
O
NHBoc
1g
220
200
180
160
140
120
100
80
60
40
20
0
-20

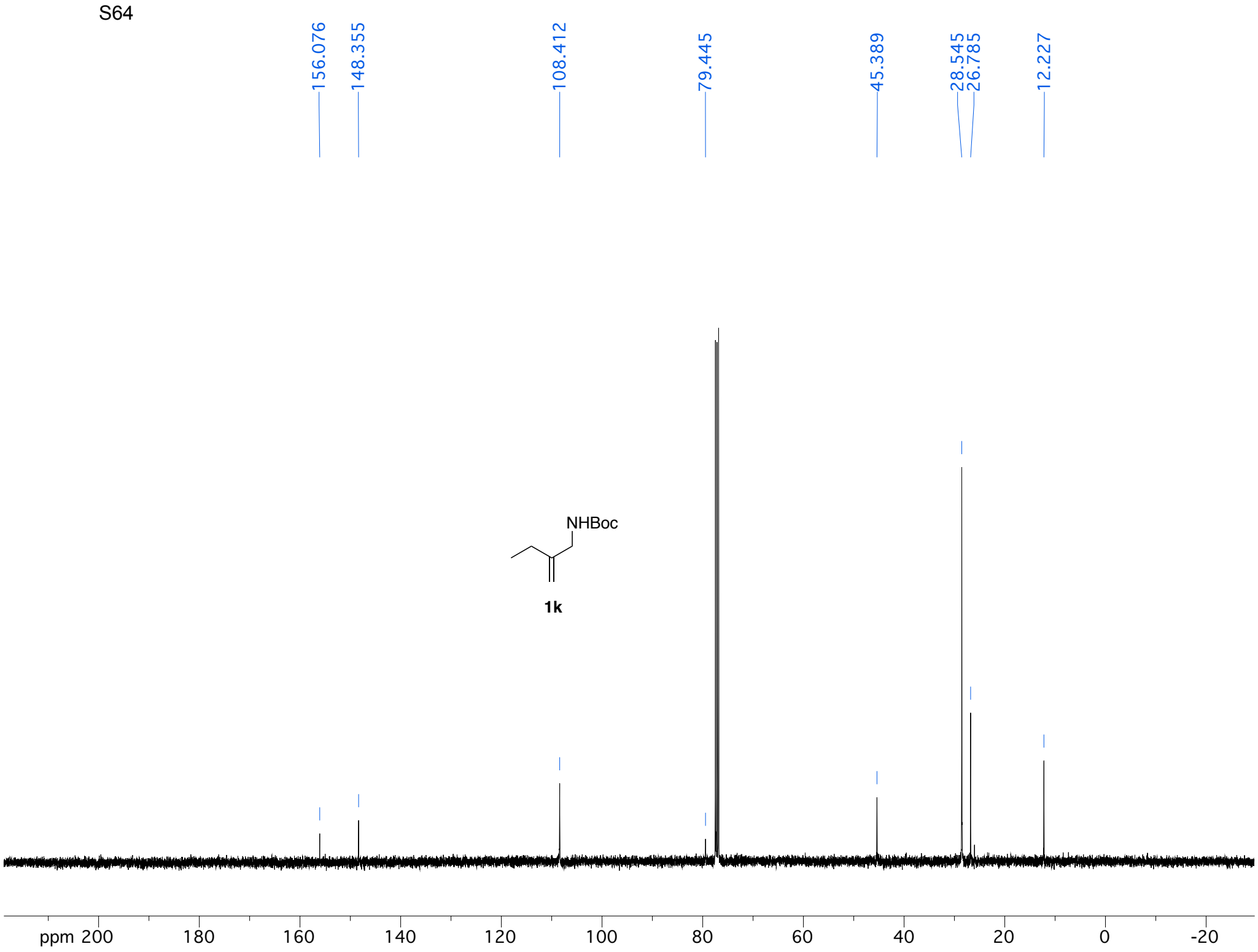

5.044
5.042
4.835
4.778
4.777
3.700
3.574
3.559
2.657
1.413
1.401
O
MeO
NHBoc
MeO
O
1g
1.04
6
2.02
2.93
0.998
0.793
1.82
9.09
ppm 9
8
7
6
5
4
3
2
1
0

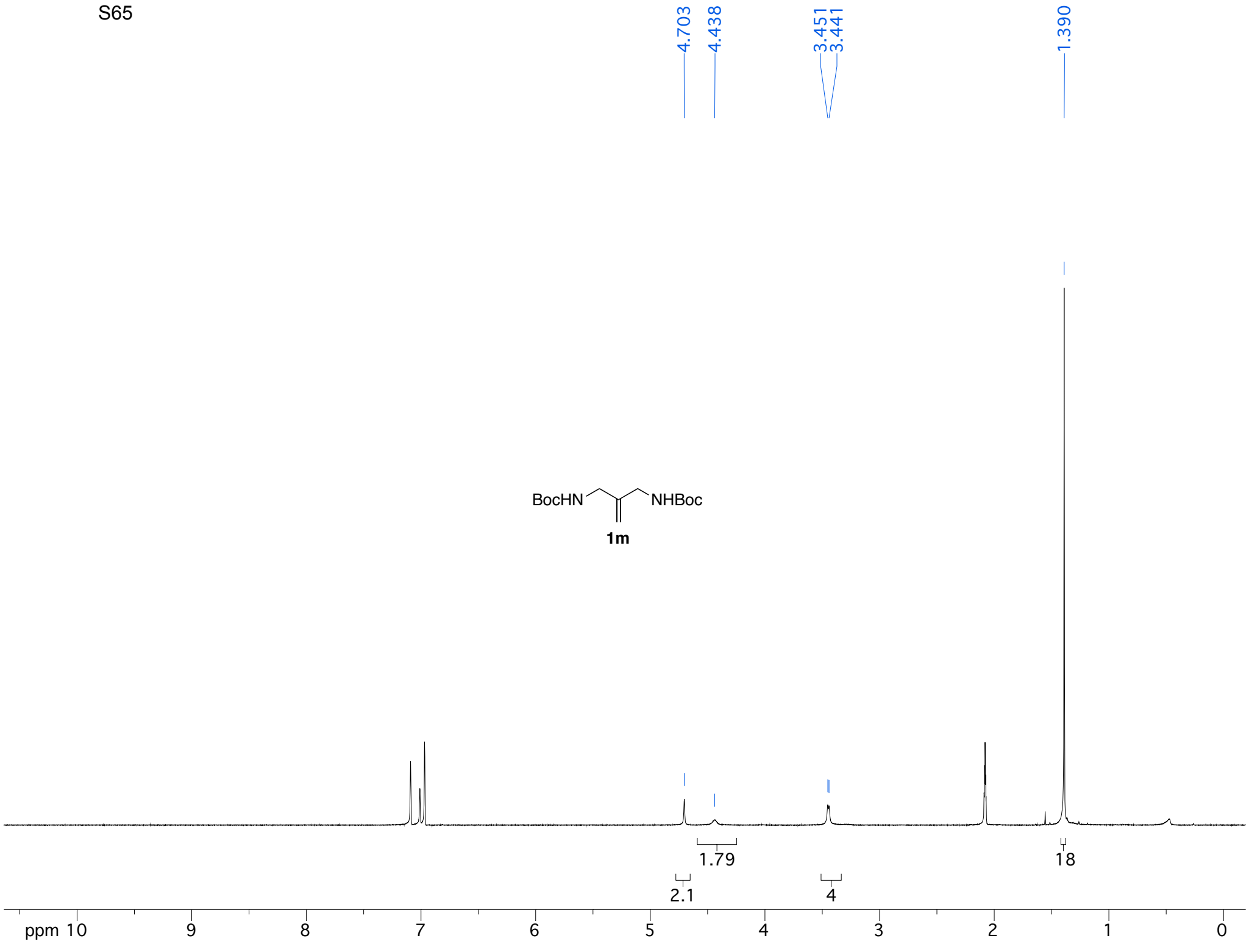

172.659
155.826
141.557
115.369
79.412
53.645
52.757
45.666
39.167
28.482
20.280
MeO
O
NHBoc
MeO
O
1g
ppm 200
180
160
140
120
100
80
60
40
20
0
-20

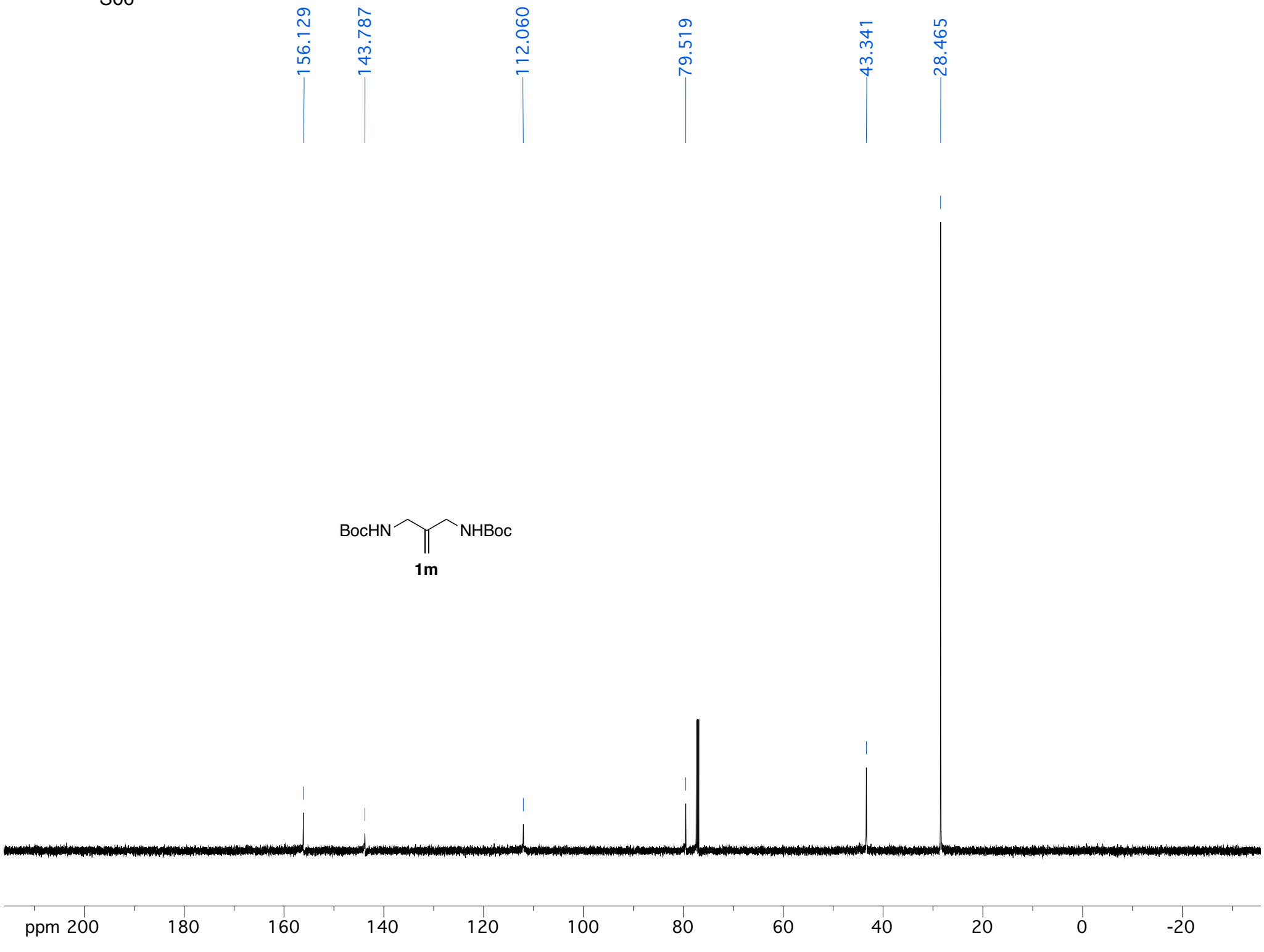

4.748
4.745
4.614
4.611
3.617
3.603
1.506
1.448
0.033
TMS
NHBoc
1h
1.77
1.95
9.28
1
2.01
9.49
ppm 9
8
7
6
5
4
3
2
1
0


155.995
144.511
107.248
79.362
46.796
28.552
24.552
-1.275
TMS
NHBoc
1h
ppm 200
180
160
140
120
100
80
60
40
20
0
-20


4.859
4.819
4.619
3.703
3.692
2.058
2.043
2.028
2.014
1.447
1.065
1.050
1.035
NHBoc
1j
0.96
1.96
9.34
0.991
0.731
1.98
2.98
11
10
9
8
7
6
5
4
3
2
1
0
-1


156.076
148.355
108.412
79.445
45.389
28.545
26.785
12.227
NHBoc
1k
ppm 200
180
160
140
120
100
80
60
40
20
0
-20


4.703
4.438
3.451
3.441
1.390
BocHN
NHBoc
1m
1.79
18
2.1
4
ppm 10
9
8
7
6
5
4
3
2
1
0


156.129
143.787
112.060
79.519
43.341
28.465
BocHN
NHBoc
1m
ppm 200
180
160
140
120
100
80
60
40
20
0
-20