Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Asymmetric Synthesis of (-)-Sedacryptine through Diastereoselective Mannich Process of *N,O*-acetal with Ketone

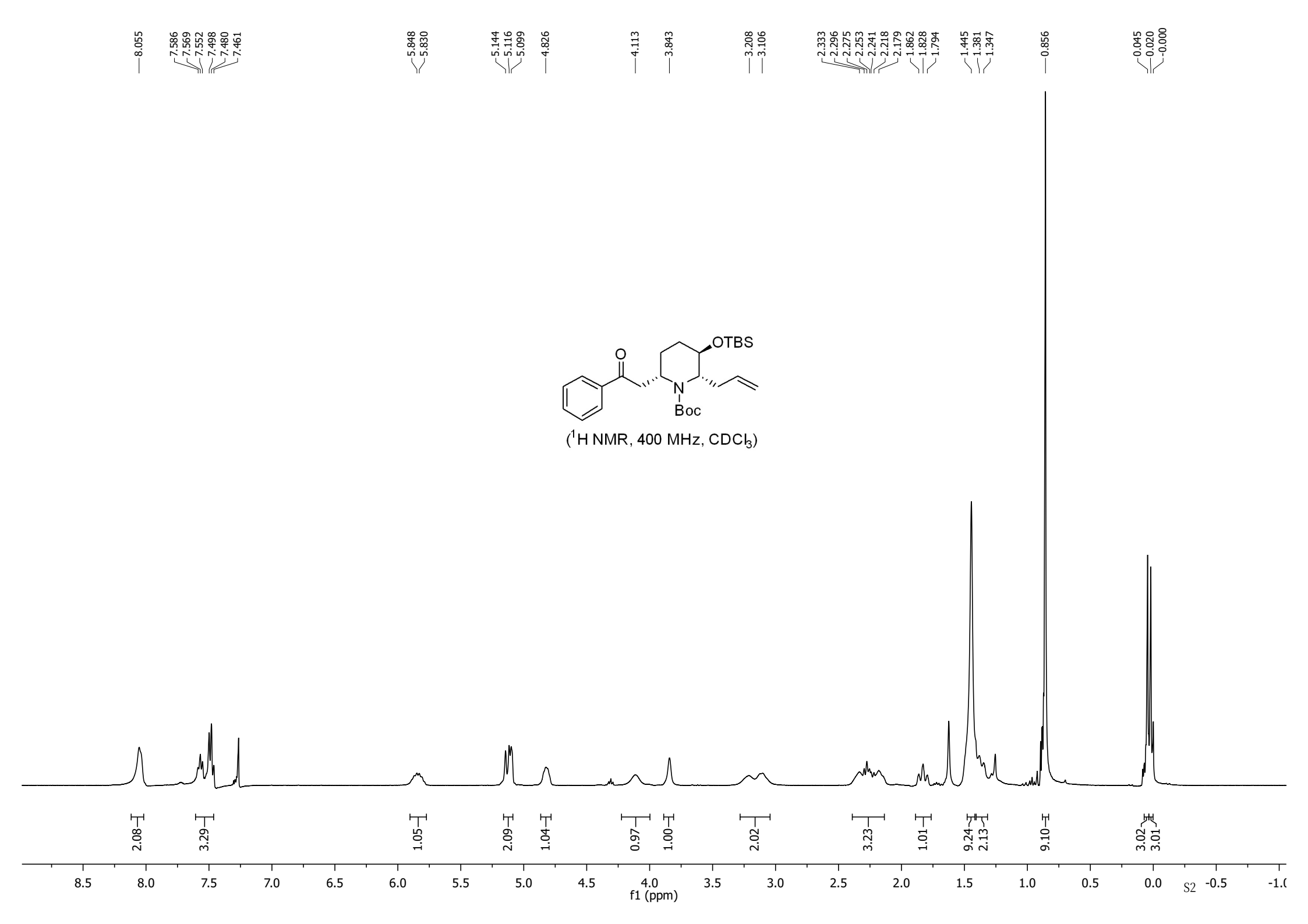
Yi-Wen Liu[a], Rui-Jun Ma[b], Jia-Hang Yan[a], Zhu Zhou[a,*] and Bang-Guo Wei[a,*]

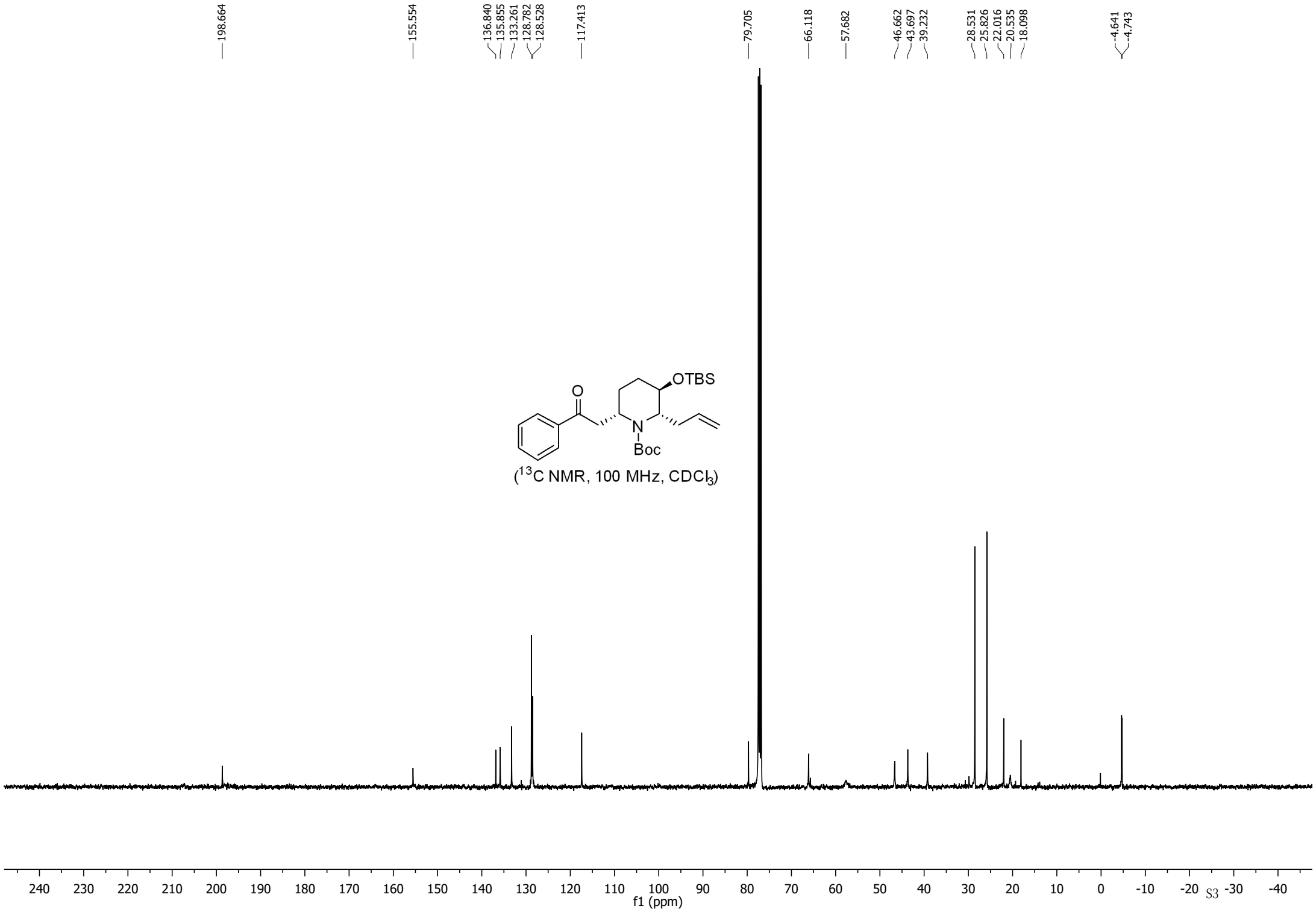
[a] *Institutes of Biomedical Sciences and School of Pharmacy, Fudan University, 130 Dongan Road, Shanghai 200030, China*

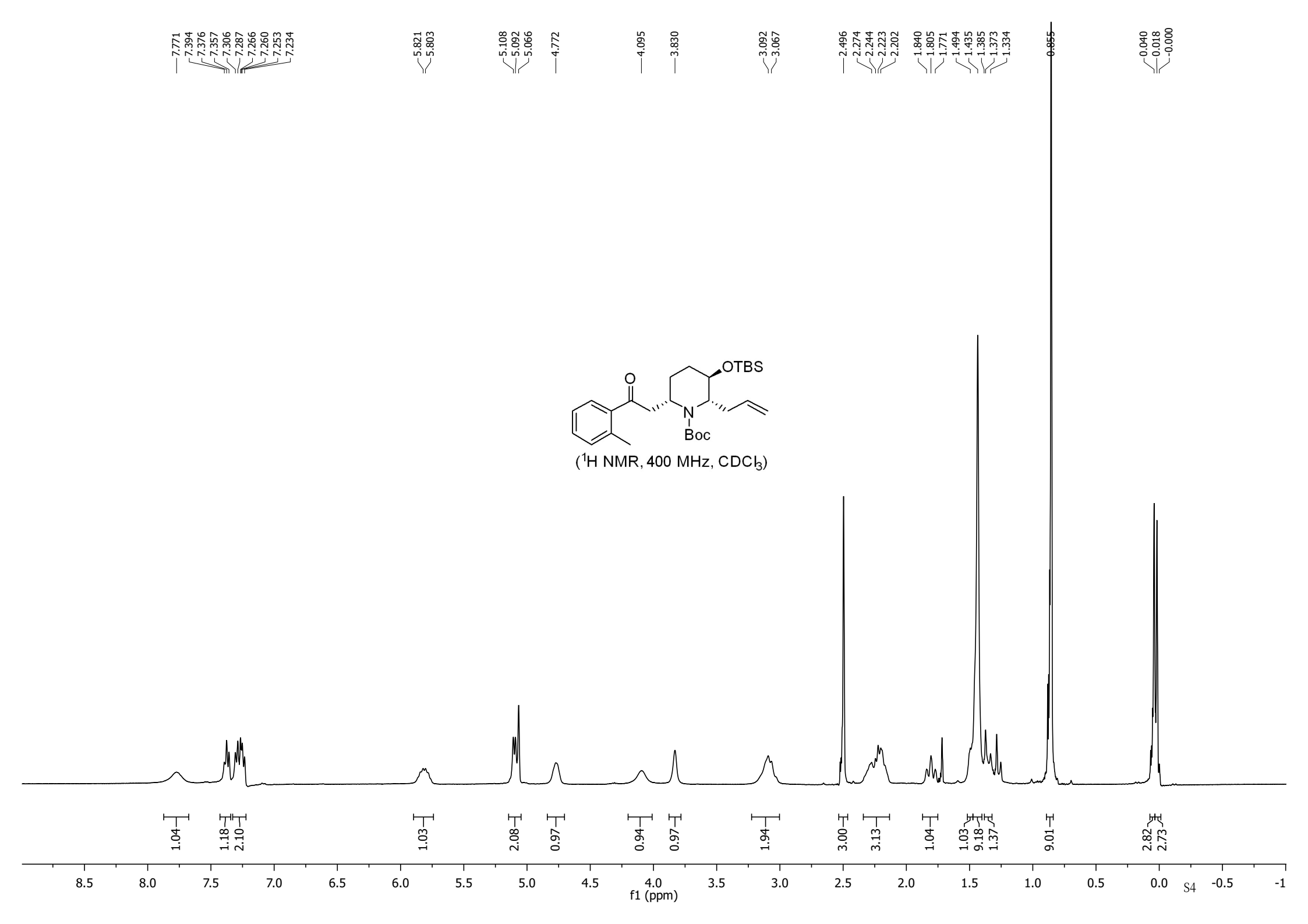
[b] *Center for Gastrointestinal Endoscopy, Shanxi Provincial People's Hospital, 29 Shuangta Road, Taiyuan 030012, China*

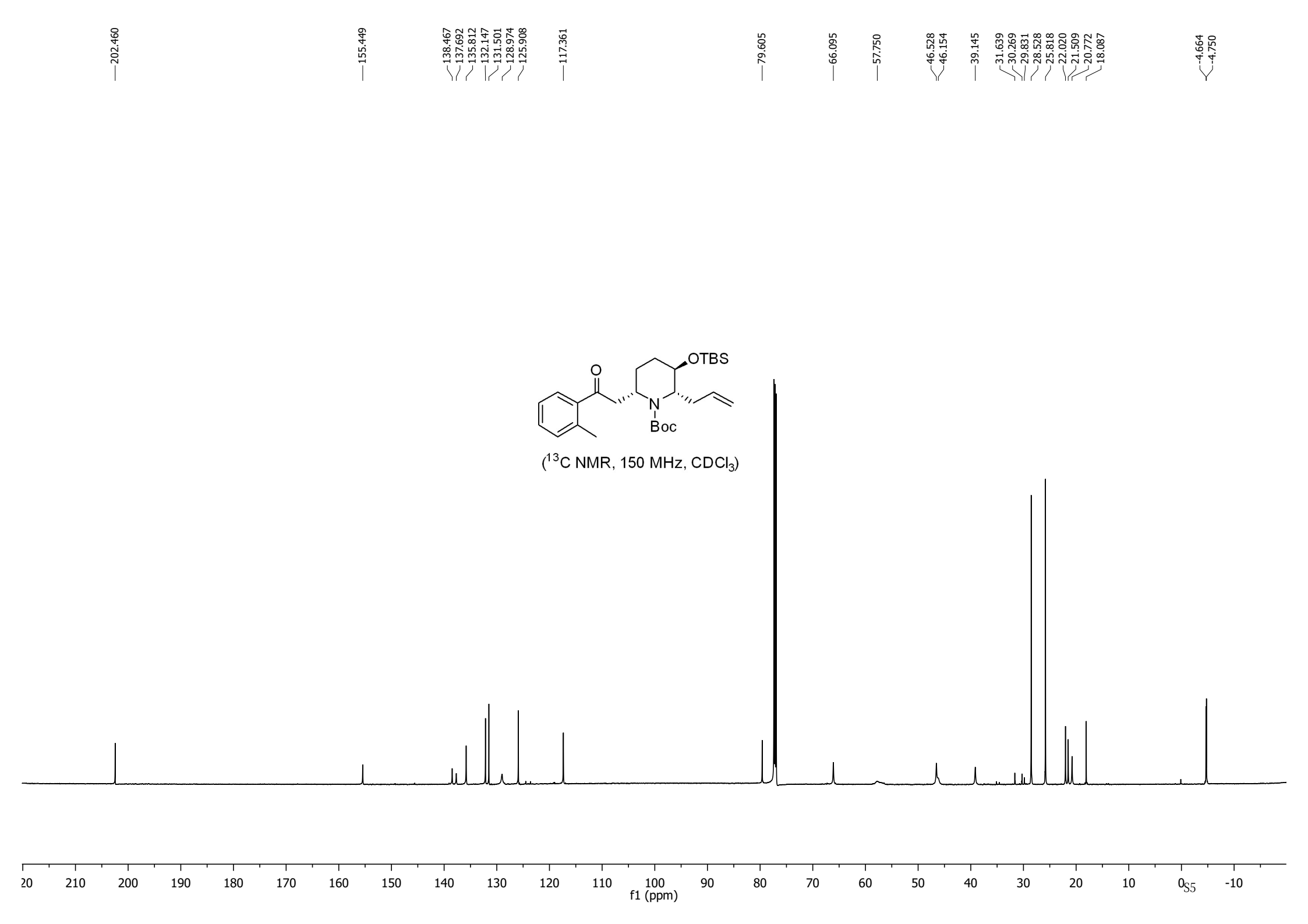
bgwei1974@fudan.edu.cn

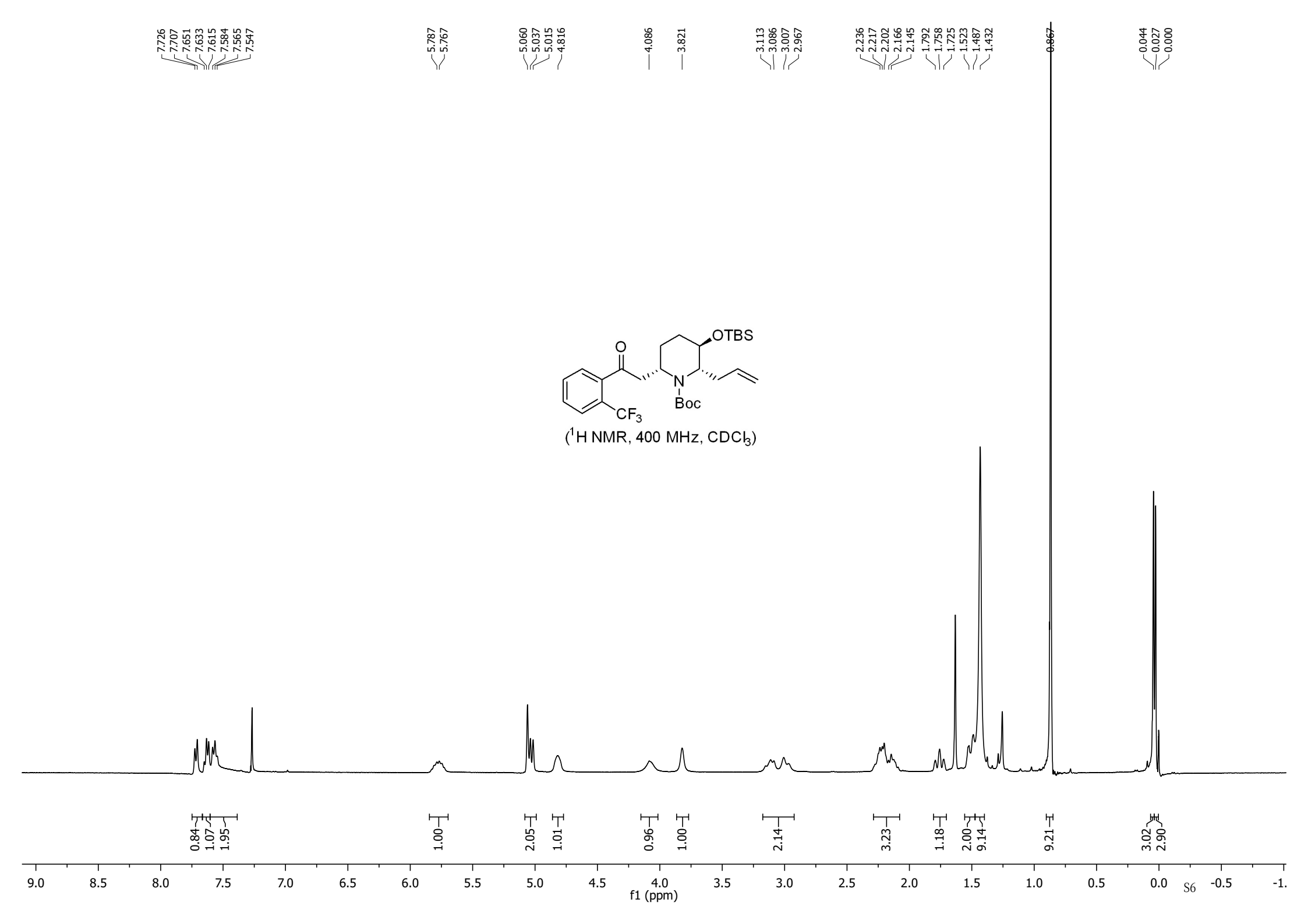
Table of Contents

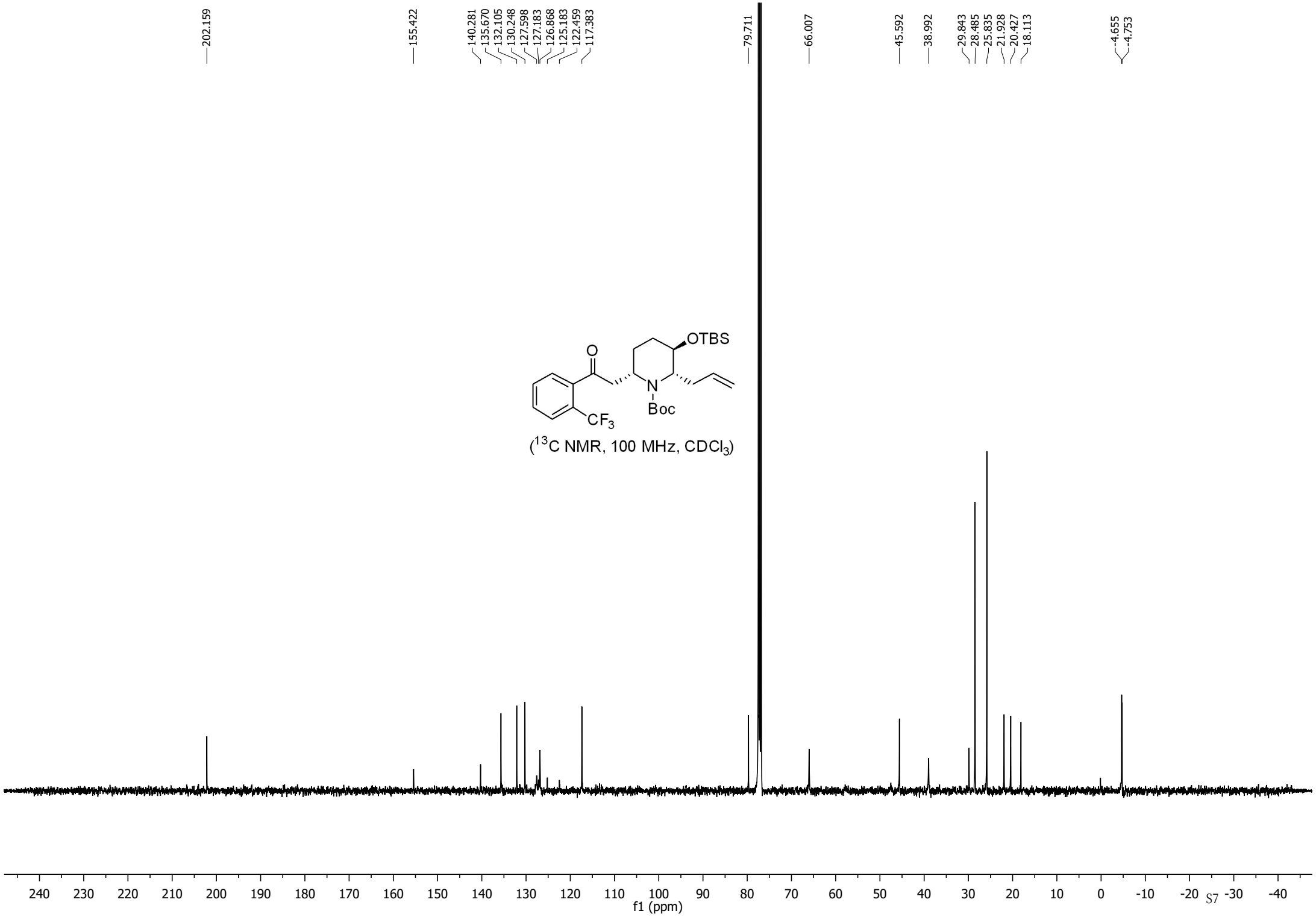

8.055
7.586
7.569
7.552
7.498
7.480
7.461
5.848
5.830
5.144
5.116
5.099
4.826
4.113
3.843
3.208
3.106
2.333
2.296
2.275
2.253
2.241
2.218
2.179
1.862
1.828
1.794
1.445
1.381
1.347
0.856
0.045
0.020
-0.000
OTBS
O
N
Boc
(1H NMR, 400 MHz, CDCl3)
2.08
3.29
1.05
2.09
1.04
0.97
1.00
2.02
3.23
1.01
9.24
2.13
9.10
3.02
3.01
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)

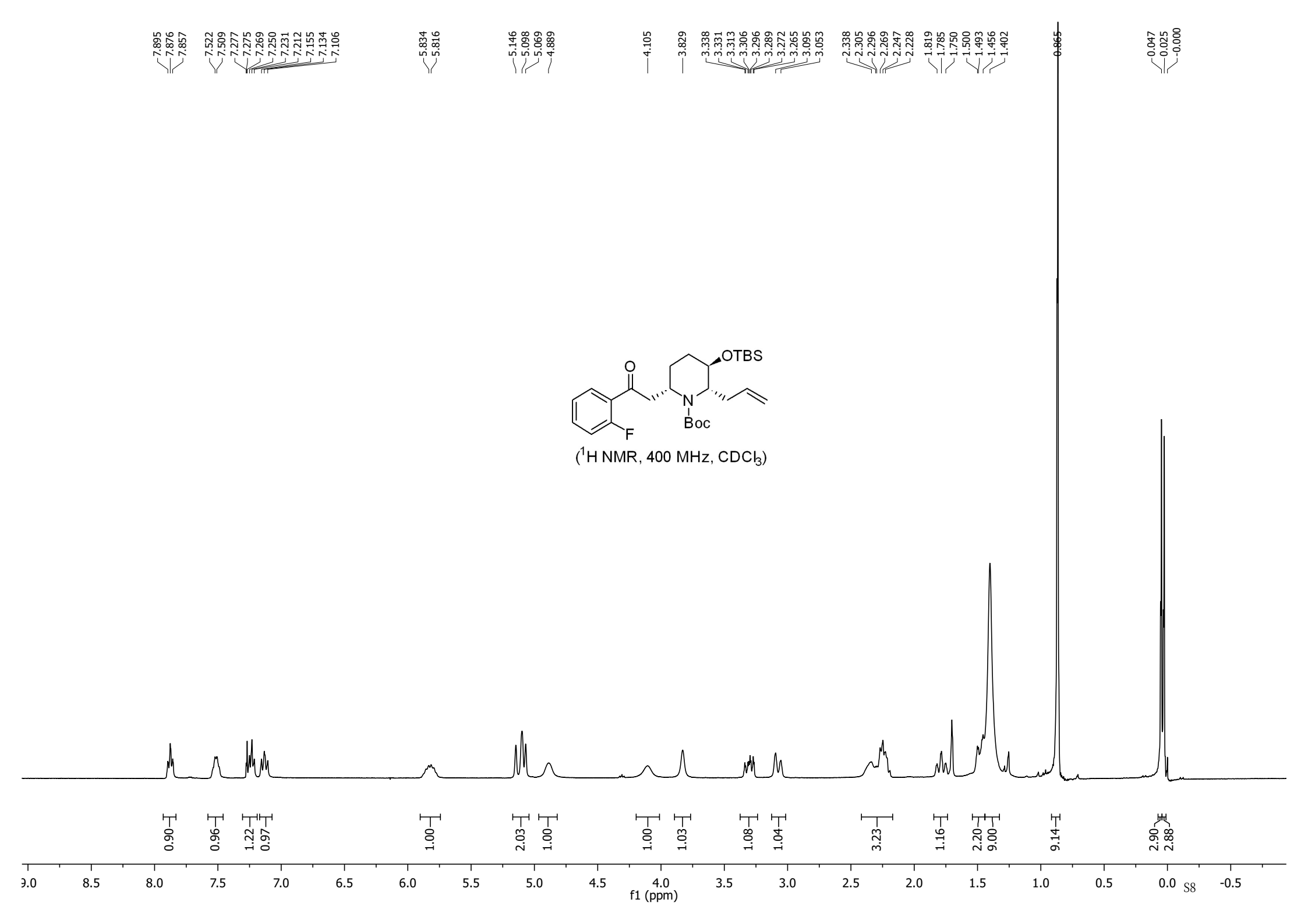

198.664
155.554
136.840
135.855
133.261
128.782
128.528
117.413
79.705
66.118
57.682
46.662
43.697
39.232
28.531
25.826
22.016
20.535
18.098
-4.641
-4.743
OTBS
O
N
Boc
(^{13}C NMR, 100 MHz, $CDCl_3$)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

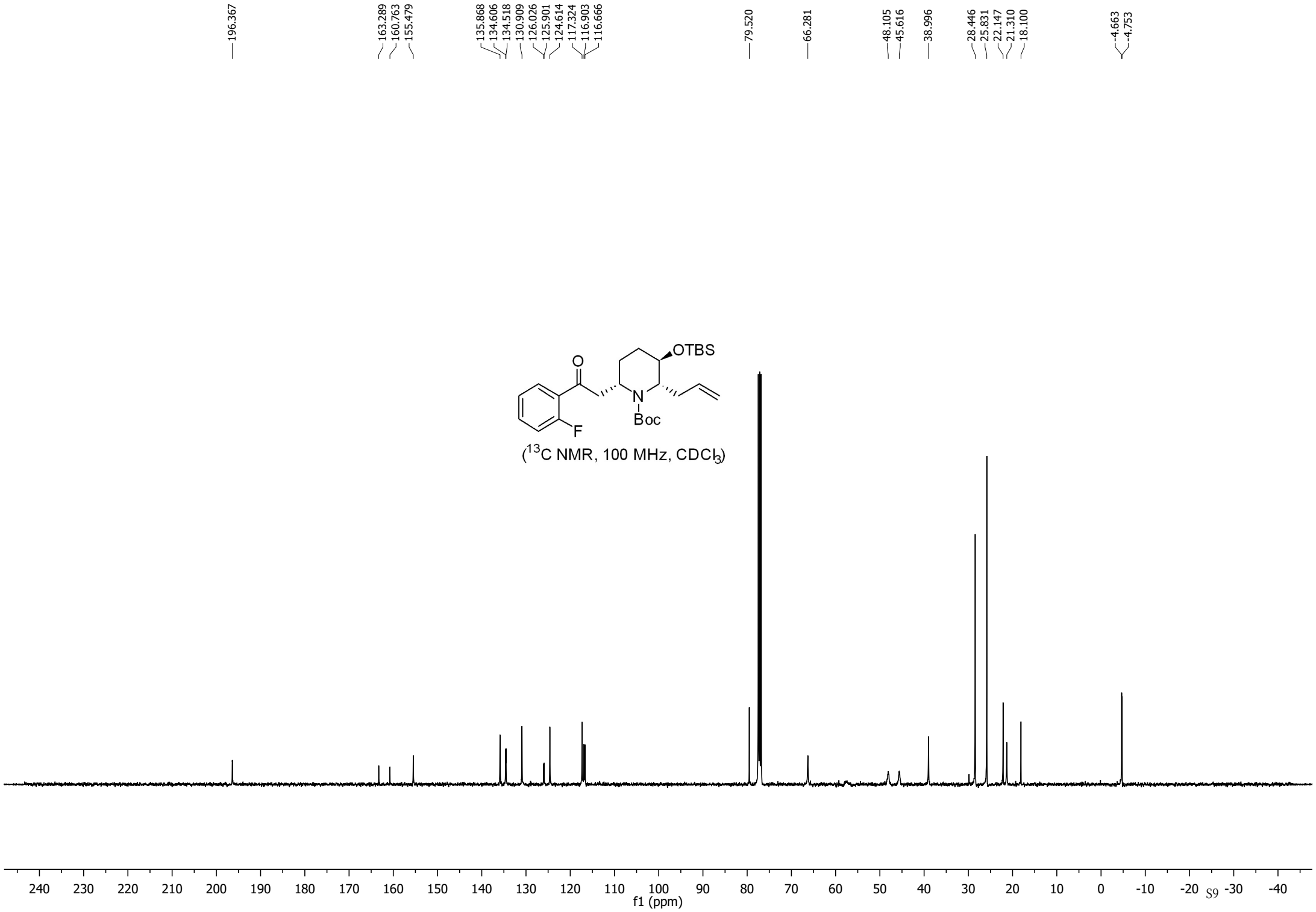

7.771
7.394
7.376
7.357
7.306
7.287
7.266
7.260
7.253
7.234
5.821
5.803
5.108
5.092
5.066
4.772
4.095
3.830
3.092
3.067
2.496
2.274
2.244
2.223
2.202
1.840
1.805
1.771
1.494
1.435
1.385
1.373
1.334
0.855
0.040
0.018
-0.000
OTBS
O
N
Boc
(1H NMR, 400 MHz, CDCl3)
1.04
1.18
2.10
1.03
2.08
0.97
0.94
0.97
1.94
3.00
3.13
1.04
1.03
9.18
1.37
9.01
2.82
2.73
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
-1
f1 (ppm)

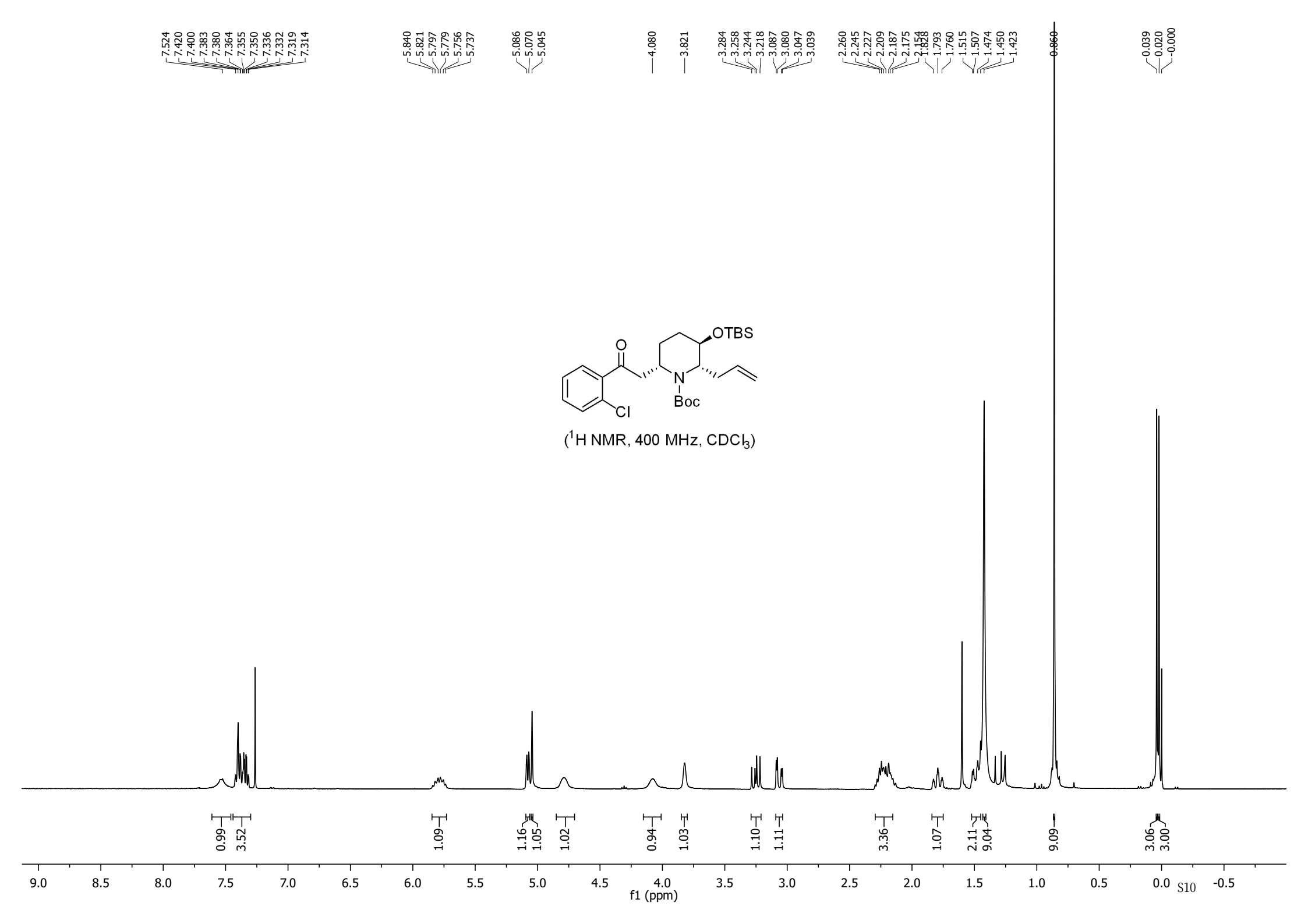

202.460
155.449
138.467
137.692
135.812
132.147
131.501
128.974
125.908
117.361
79.605
66.095
57.750
46.528
46.154
39.145
31.639
30.269
29.831
28.528
25.818
22.020
21.509
20.772
18.087
-4.664
-4.750
OTBS
O
N
Boc
(^{13}C NMR, 150 MHz, $CDCl_3$)
f1 (ppm)

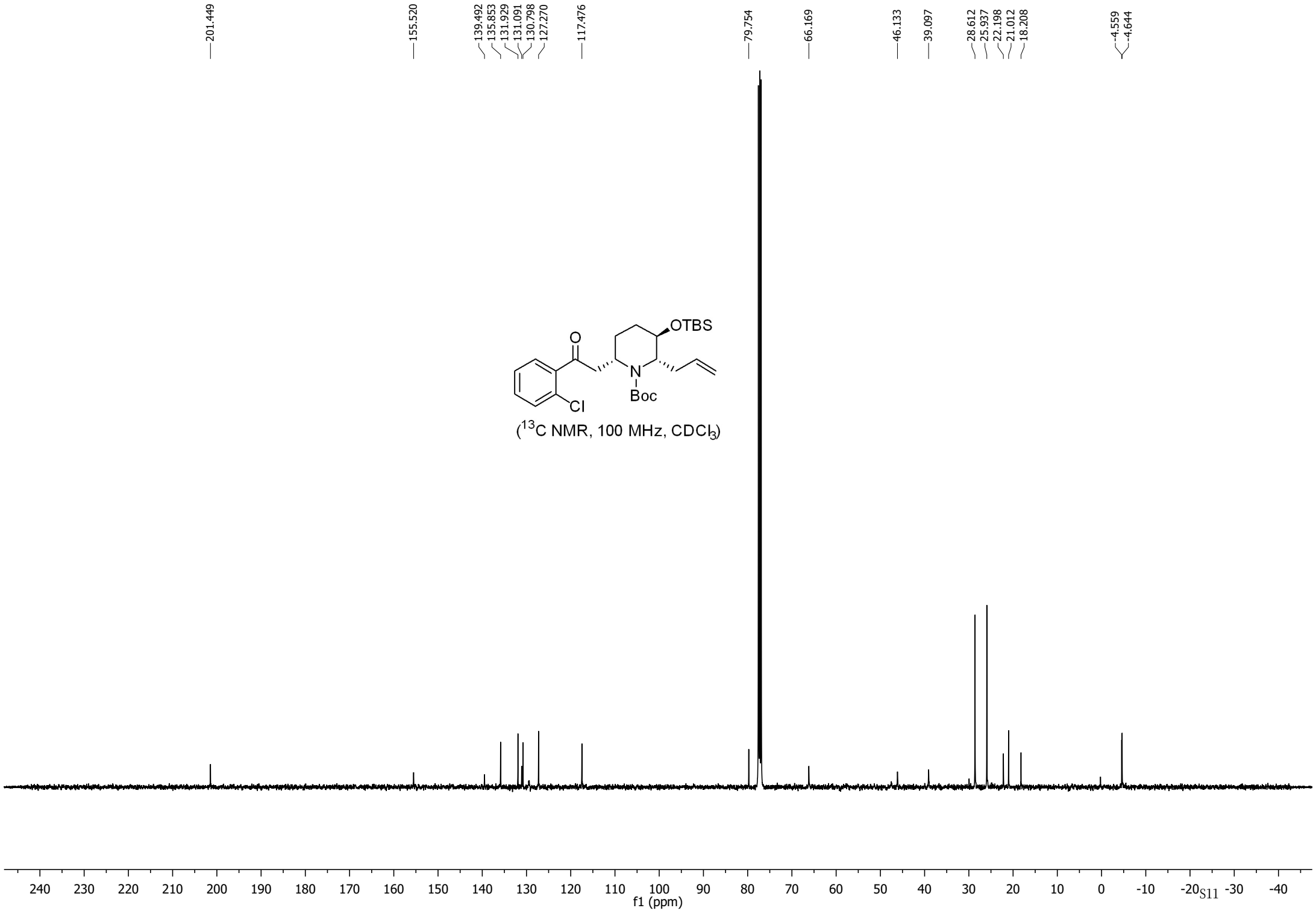

7.726
7.707
7.651
7.633
7.615
7.584
7.565
7.547
5.787
5.767
5.060
5.037
5.015
4.816
4.086
3.821
3.113
3.086
3.007
2.967
2.236
2.217
2.202
2.166
2.145
1.792
1.758
1.725
1.523
1.487
1.432
0.867
0.044
0.027
0.000
OTBS
O
N
Boc
CF3
(1H NMR, 400 MHz, CDCl3)
0.84
1.07
1.95
1.00
2.05
1.01
0.96
1.00
2.14
3.23
1.18
2.00
9.14
9.21
3.02
2.90
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
-1.
f1 (ppm)

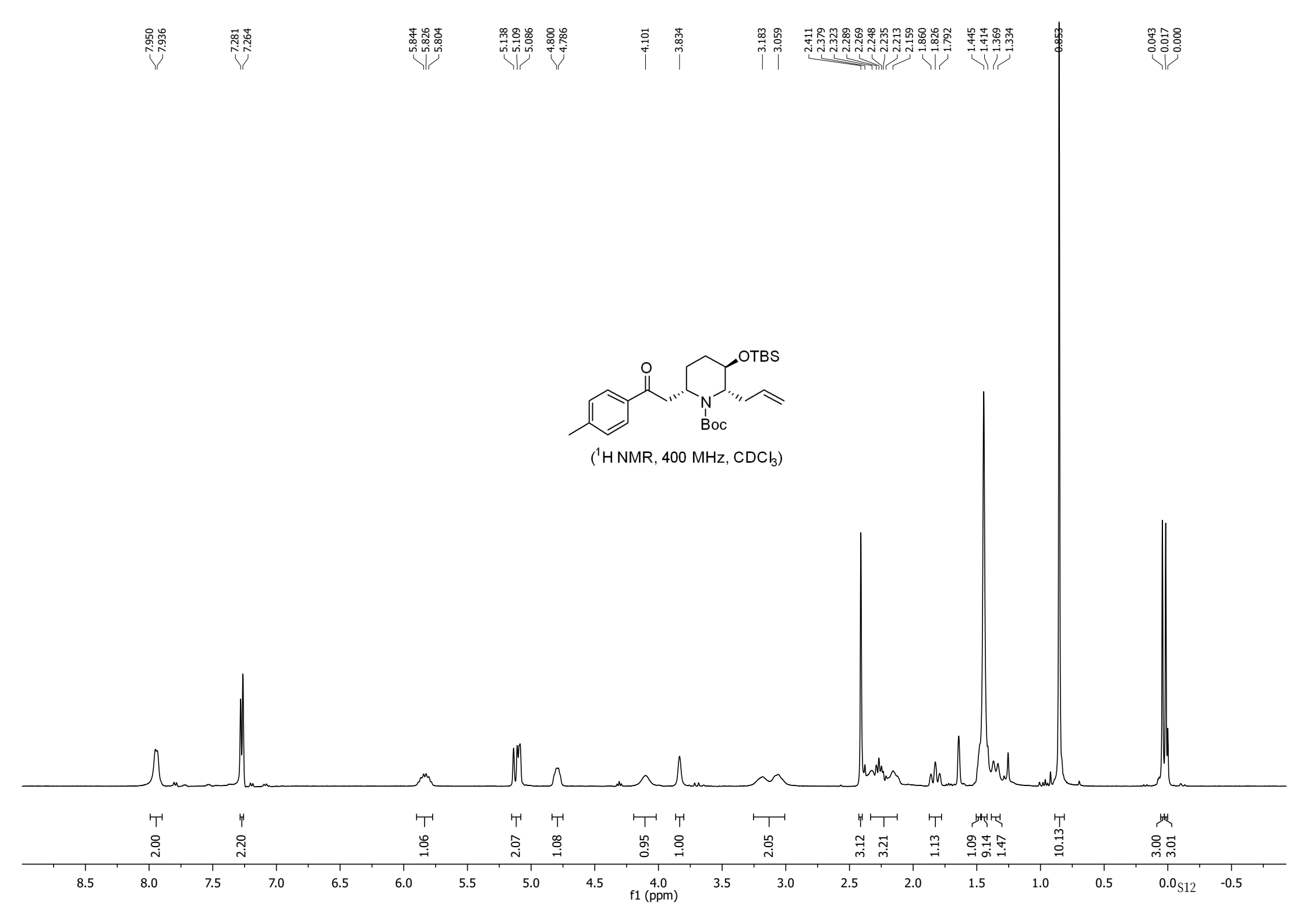

202.159
155.422
140.281
135.670
132.105
130.248
127.598
127.183
126.868
125.183
122.459
117.383
79.711
66.007
45.592
38.992
29.843
28.485
25.835
21.928
20.427
18.113
-4.655
-4.753
OTBS
O
N
Boc
CF3
(13C NMR, 100 MHz, CDCl3)
f1 (ppm)

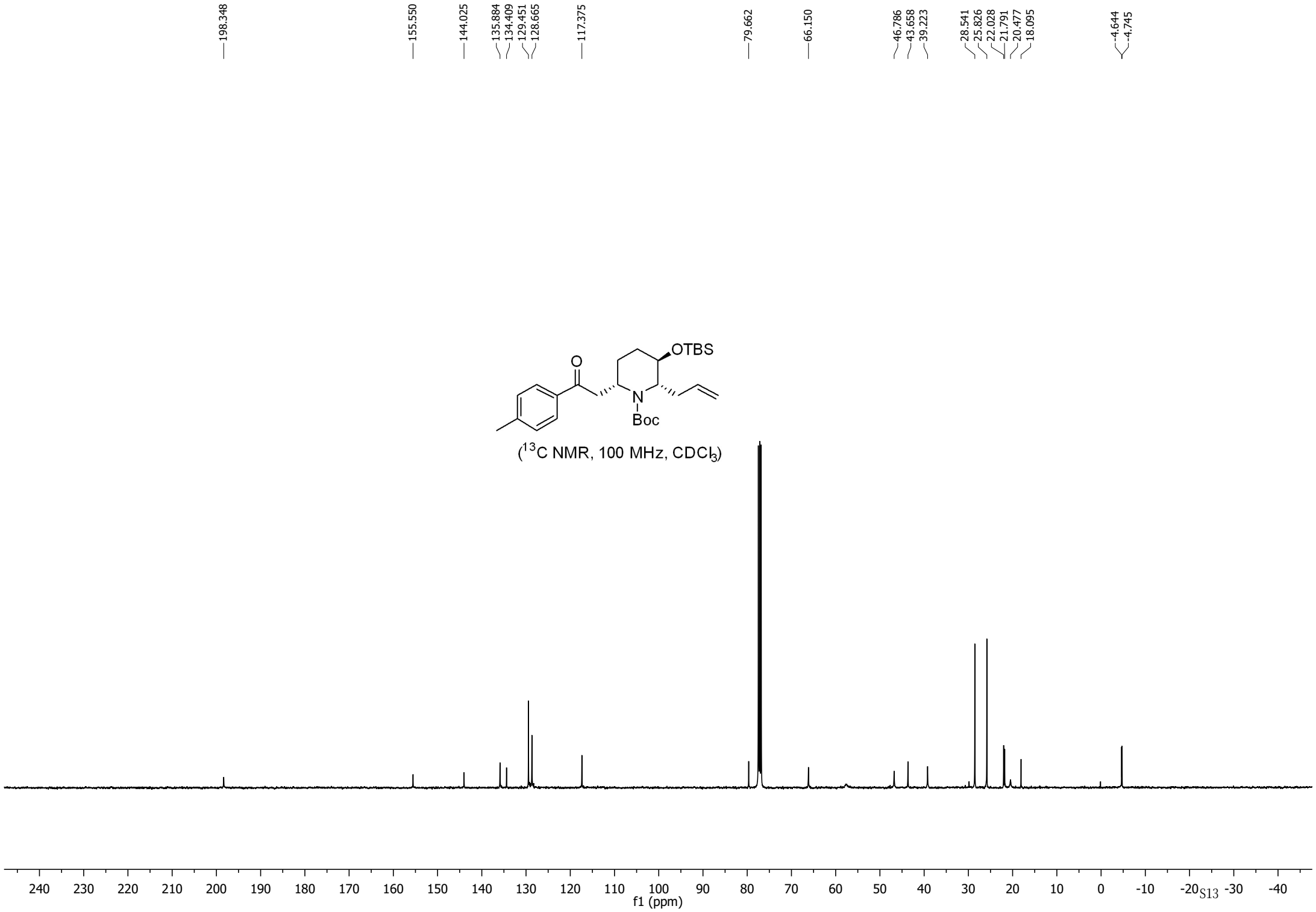

7.895
7.876
7.857
7.522
7.509
7.277
7.275
7.269
7.250
7.231
7.212
7.155
7.134
7.106
5.834
5.816
5.146
5.098
5.069
4.889
4.105
3.829
3.338
3.331
3.313
3.306
3.296
3.289
3.272
3.265
3.095
3.053
2.338
2.305
2.296
2.269
2.247
2.228
1.819
1.785
1.750
1.500
1.493
1.456
1.402
0.865
0.047
0.025
-0.000
OTBS
O
N
Boc
F
(1H NMR, 400 MHz, CDCl3)
0.90
0.96
1.22
0.97
1.00
2.03
1.00
1.00
1.03
1.08
1.04
3.23
1.16
2.20
9.00
9.14
2.90
2.88
f1 (ppm)

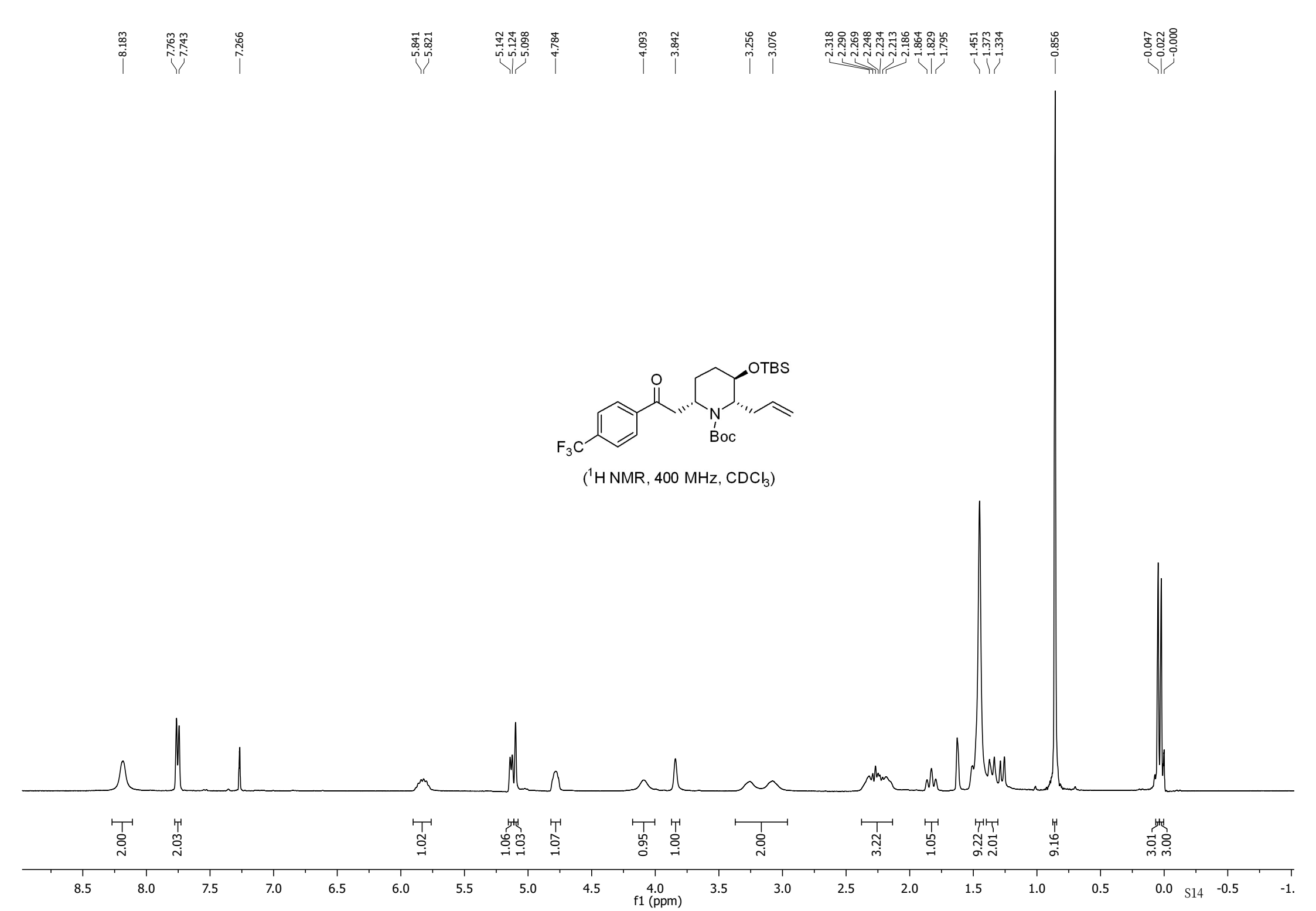

196.367
163.289
160.763
155.479
135.868
134.606
134.518
130.909
126.026
125.901
124.614
117.324
116.903
116.666
79.520
66.281
48.105
45.616
38.996
28.446
25.831
22.147
21.310
18.100
-4.663
-4.753
OTBS
O
N
Boc
F
(13C NMR, 100 MHz, CDCl3)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

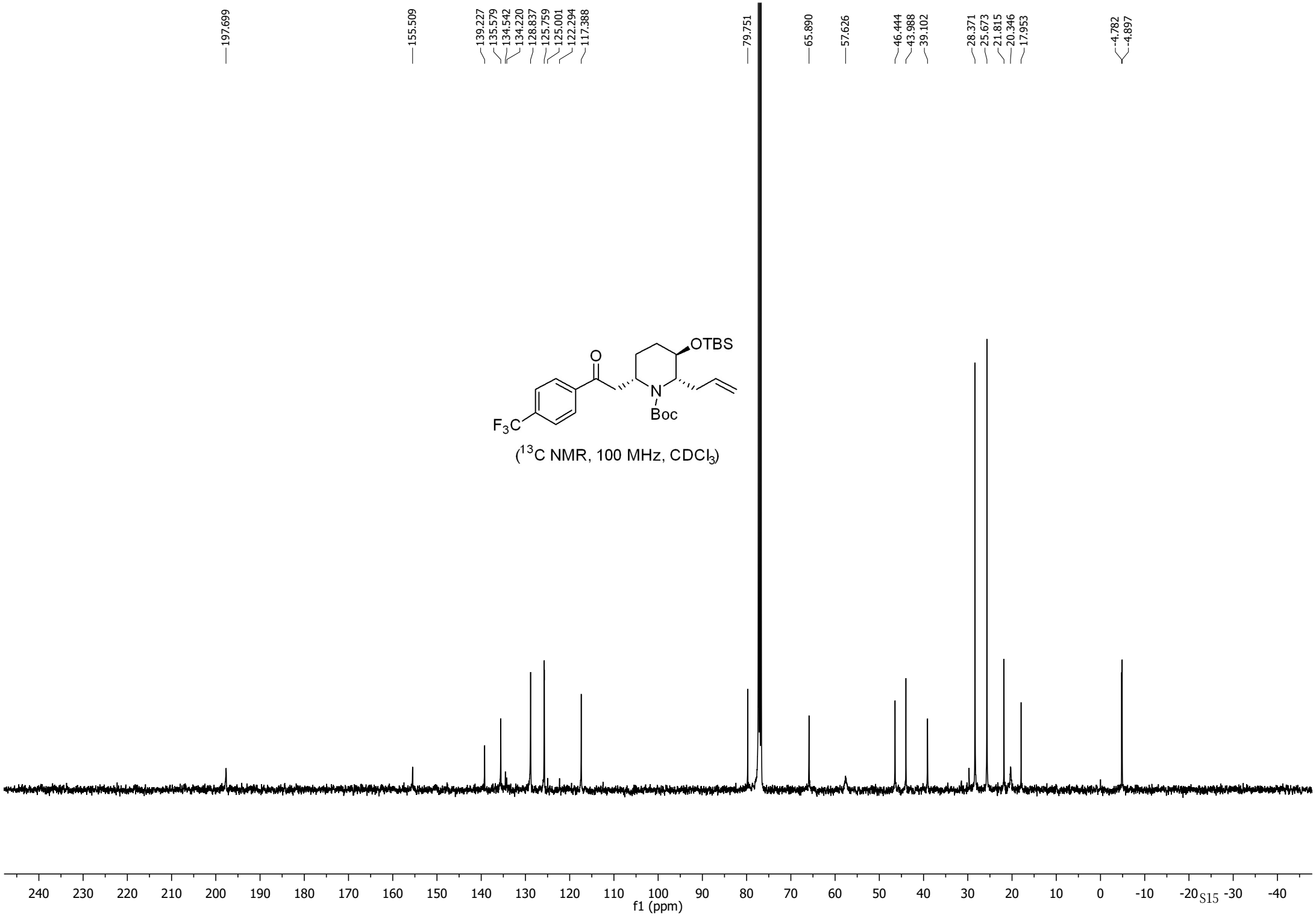

7.524
7.420
7.400
7.383
7.380
7.364
7.355
7.350
7.336
7.332
7.319
7.314
5.840
5.821
5.797
5.779
5.756
5.737
5.086
5.070
5.045
4.080
3.821
3.284
3.258
3.244
3.218
3.087
3.080
3.047
3.039
2.260
2.245
2.227
2.209
2.187
2.175
2.154
1.828
1.793
1.760
1.515
1.507
1.474
1.450
1.423
0.860
0.039
0.020
-0.000
OTBS
O
N
Boc
Cl
(1H NMR, 400 MHz, CDCl3)
0.99
3.52
1.09
1.16
1.05
1.02
0.94
1.03
1.10
1.11
3.36
1.07
2.11
9.04
9.09
3.06
3.00
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)

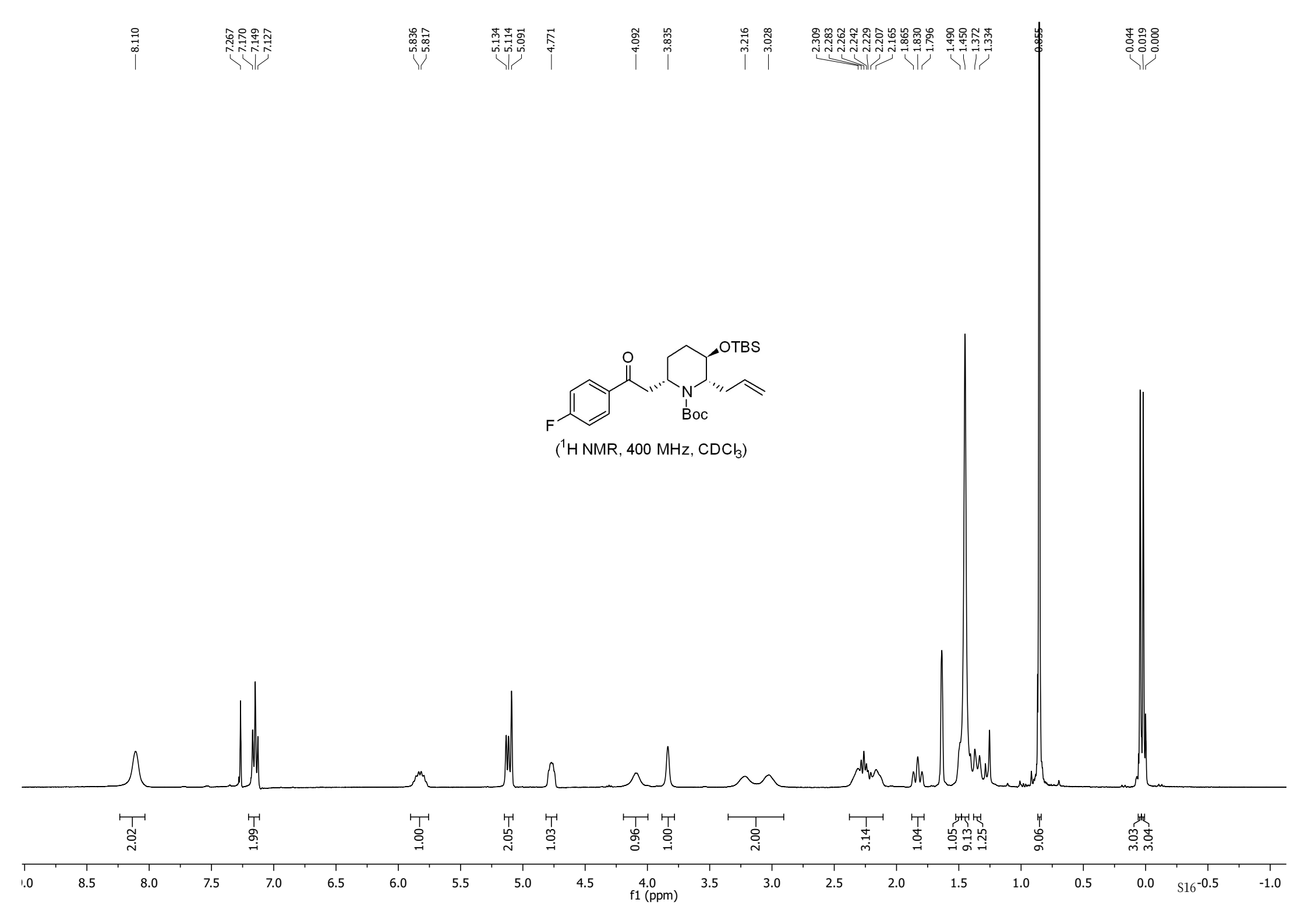

201.449
155.520
139.492
135.853
131.929
131.091
130.798
127.270
117.476
79.754
66.169
46.133
39.097
28.612
25.937
22.198
21.012
18.208
-4.559
-4.644
OTBS
O
N
Boc
Cl
(13C NMR, 100 MHz, CDCl3)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

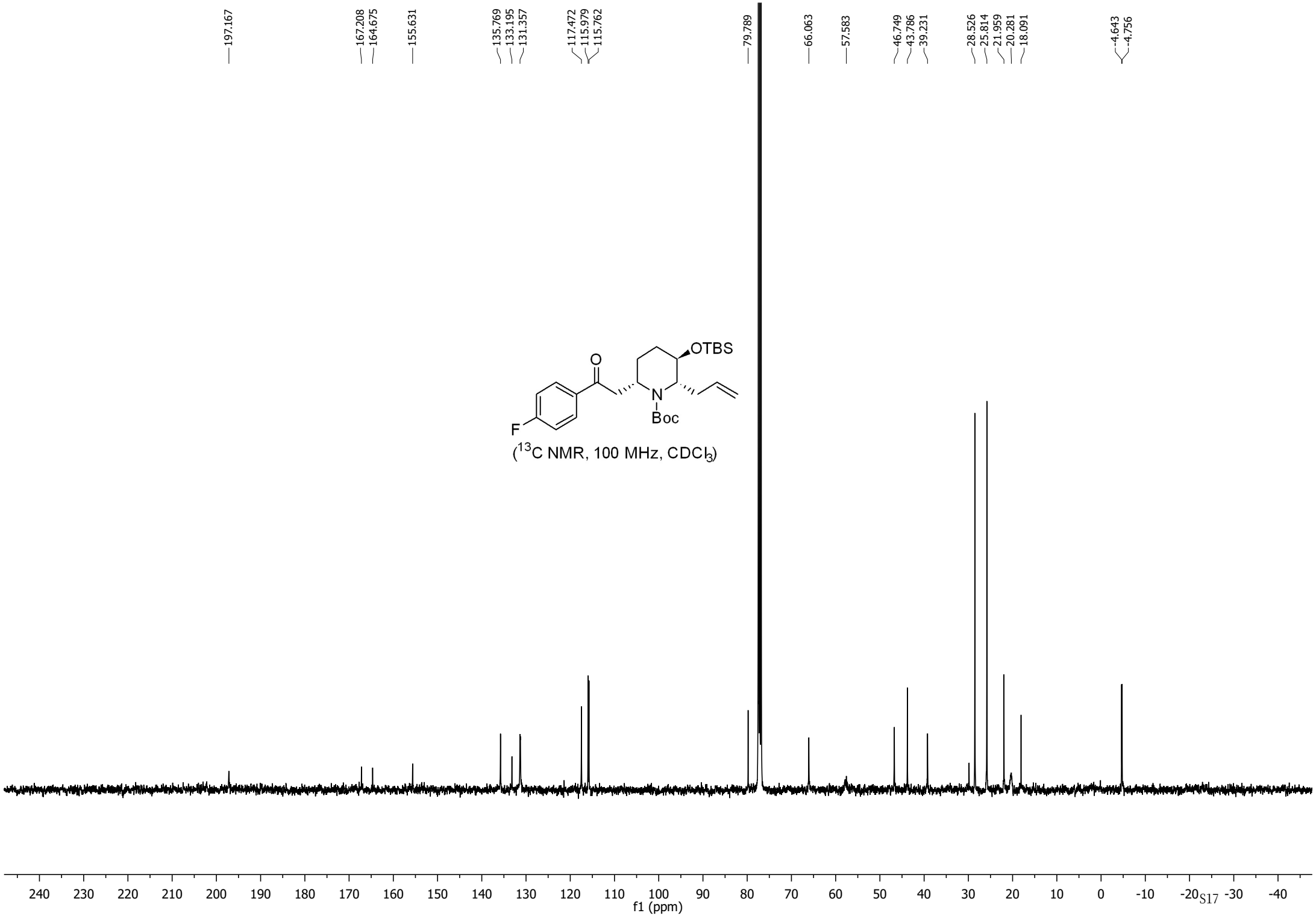

7.950
7.936
7.281
7.264
5.844
5.826
5.804
5.138
5.109
5.086
4.800
4.786
4.101
3.834
3.183
3.059
2.411
2.379
2.323
2.289
2.269
2.248
2.235
2.213
2.159
1.860
1.826
1.792
1.445
1.414
1.369
1.334
0.853
0.043
0.017
0.000
OTBS
O
N
Boc
(1H NMR, 400 MHz, CDCl3)
2.00
2.20
1.06
2.07
1.08
0.95
1.00
2.05
3.12
3.21
1.13
1.09
9.14
1.47
10.13
3.00
3.01
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)

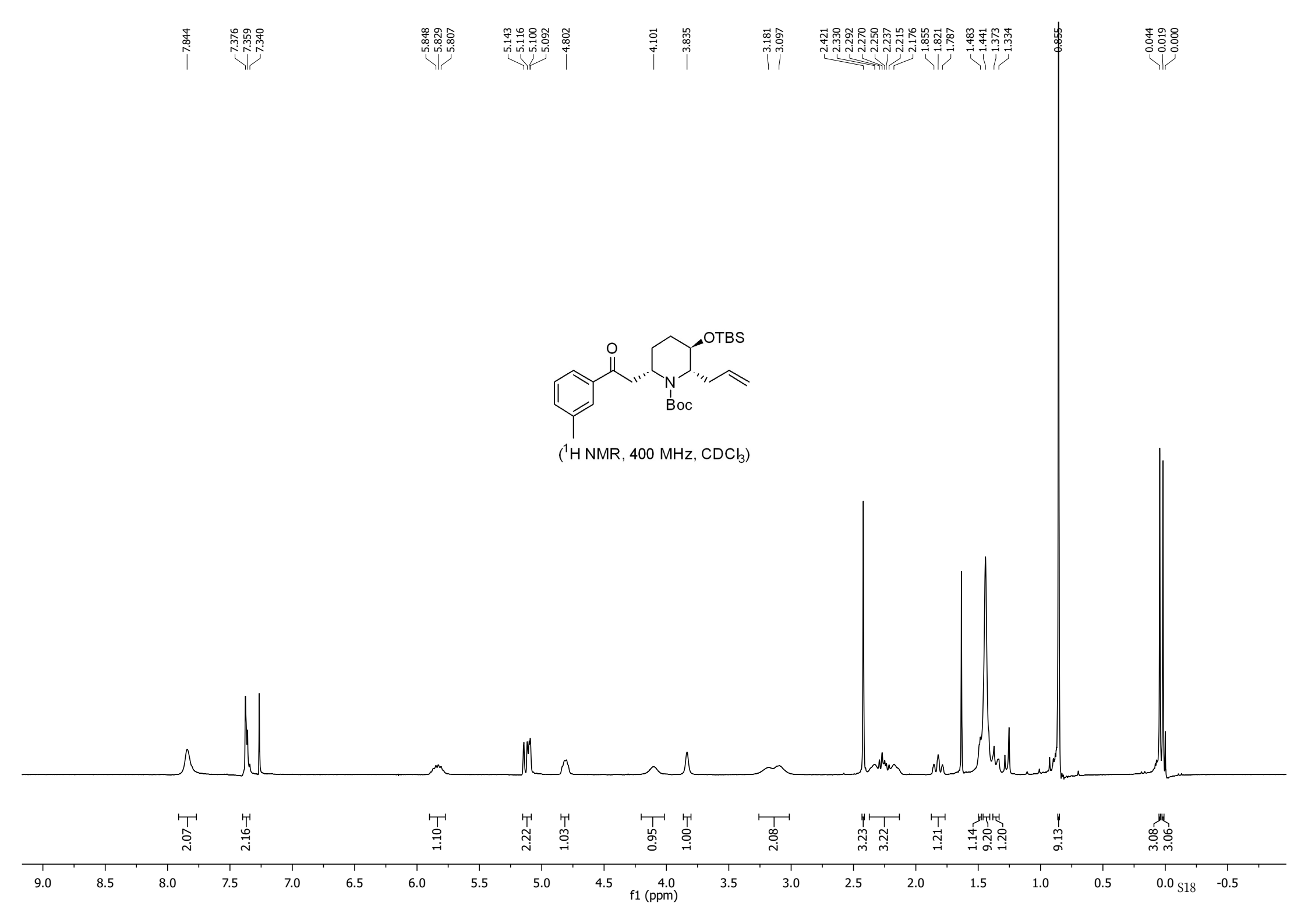

198.348
155.550
144.025
135.884
134.409
129.451
128.665
117.375
79.662
66.150
46.786
43.658
39.223
28.541
25.826
22.028
21.791
20.477
18.095
-4.644
-4.745
OTBS
O
N
Boc
(13C NMR, 100 MHz, CDCl3)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

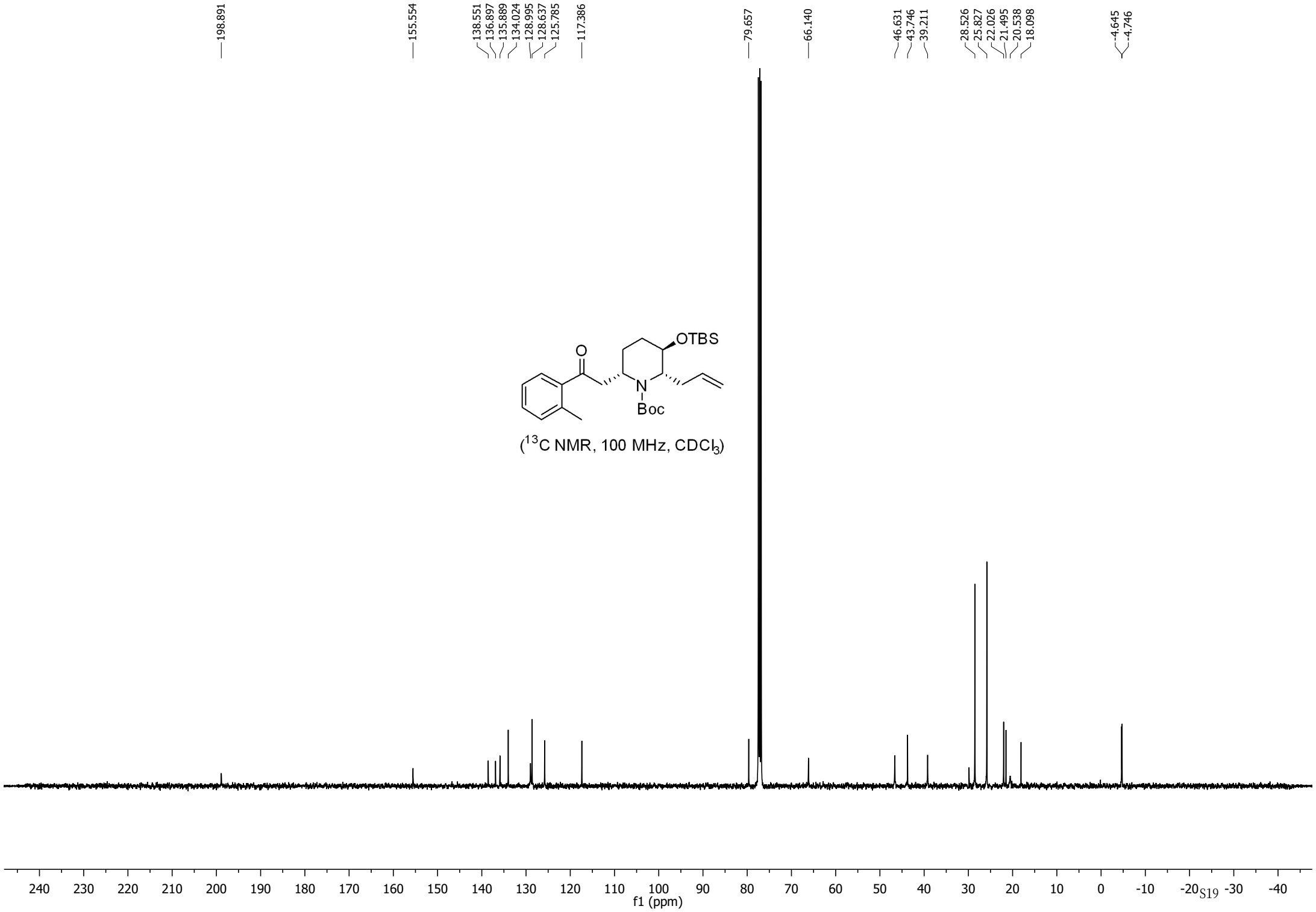

8.183
7.763
7.743
7.266
5.841
5.821
5.142
5.124
5.098
4.784
4.093
3.842
3.256
3.076
2.318
2.290
2.269
2.248
2.234
2.213
2.186
1.864
1.829
1.795
1.451
1.373
1.334
0.856
0.047
0.022
-0.000
OTBS
O
N
Boc
F3C
(1H NMR, 400 MHz, CDCl3)
2.00
2.03
1.02
1.06
1.03
1.07
0.95
1.00
2.00
3.22
1.05
9.22
2.01
9.16
3.01
3.00
f1 (ppm)

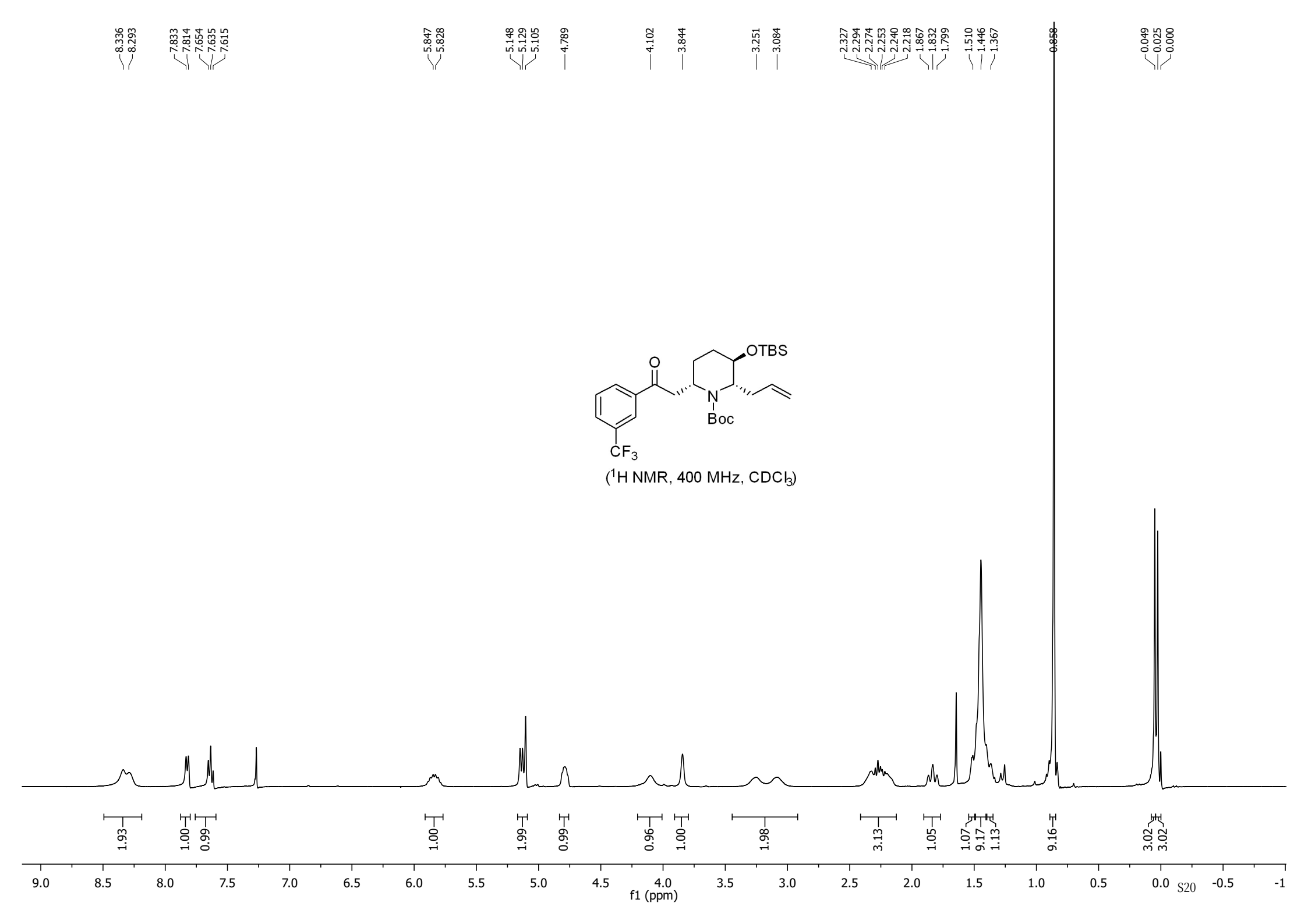

197.699
155.509
139.227
135.579
134.542
134.220
128.837
125.759
125.001
122.294
117.388
79.751
65.890
57.626
46.444
43.988
39.102
28.371
25.673
21.815
20.346
17.953
-4.782
-4.897
OTBS
O
N
Boc
F3C
(13C NMR, 100 MHz, CDCl3)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

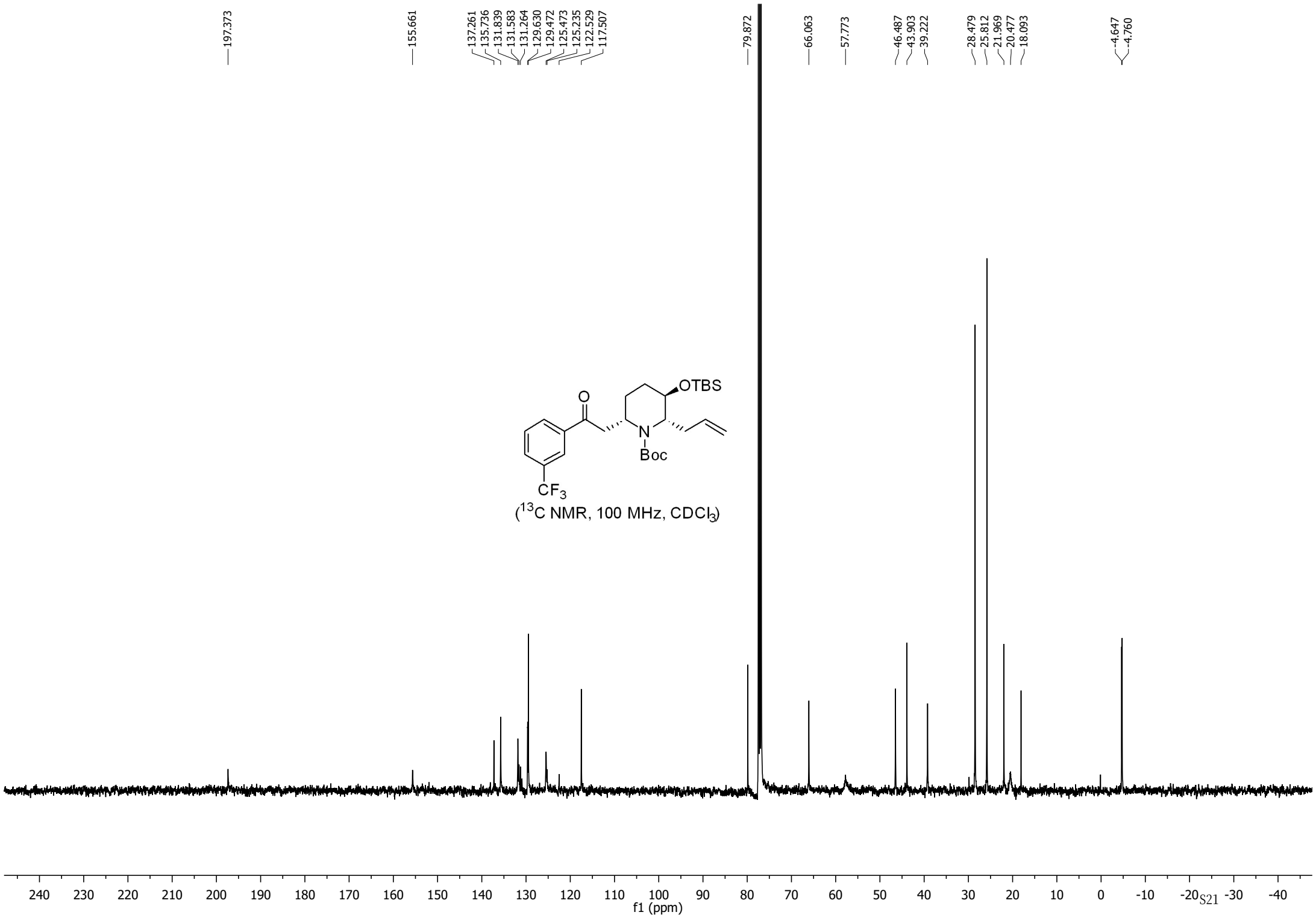

8.110
7.267
7.170
7.149
7.127
5.836
5.817
5.134
5.114
5.091
4.771
4.092
3.835
3.216
3.028
2.309
2.283
2.262
2.242
2.229
2.207
2.165
1.865
1.830
1.796
1.490
1.450
1.372
1.334
0.855
0.044
0.019
0.000
OTBS
O
N
Boc
F
(1H NMR, 400 MHz, CDCl3)
2.02
1.99
1.00
2.05
1.03
0.96
1.00
2.00
3.14
1.04
1.05
9.13
1.25
9.06
3.03
3.04
f1 (ppm)

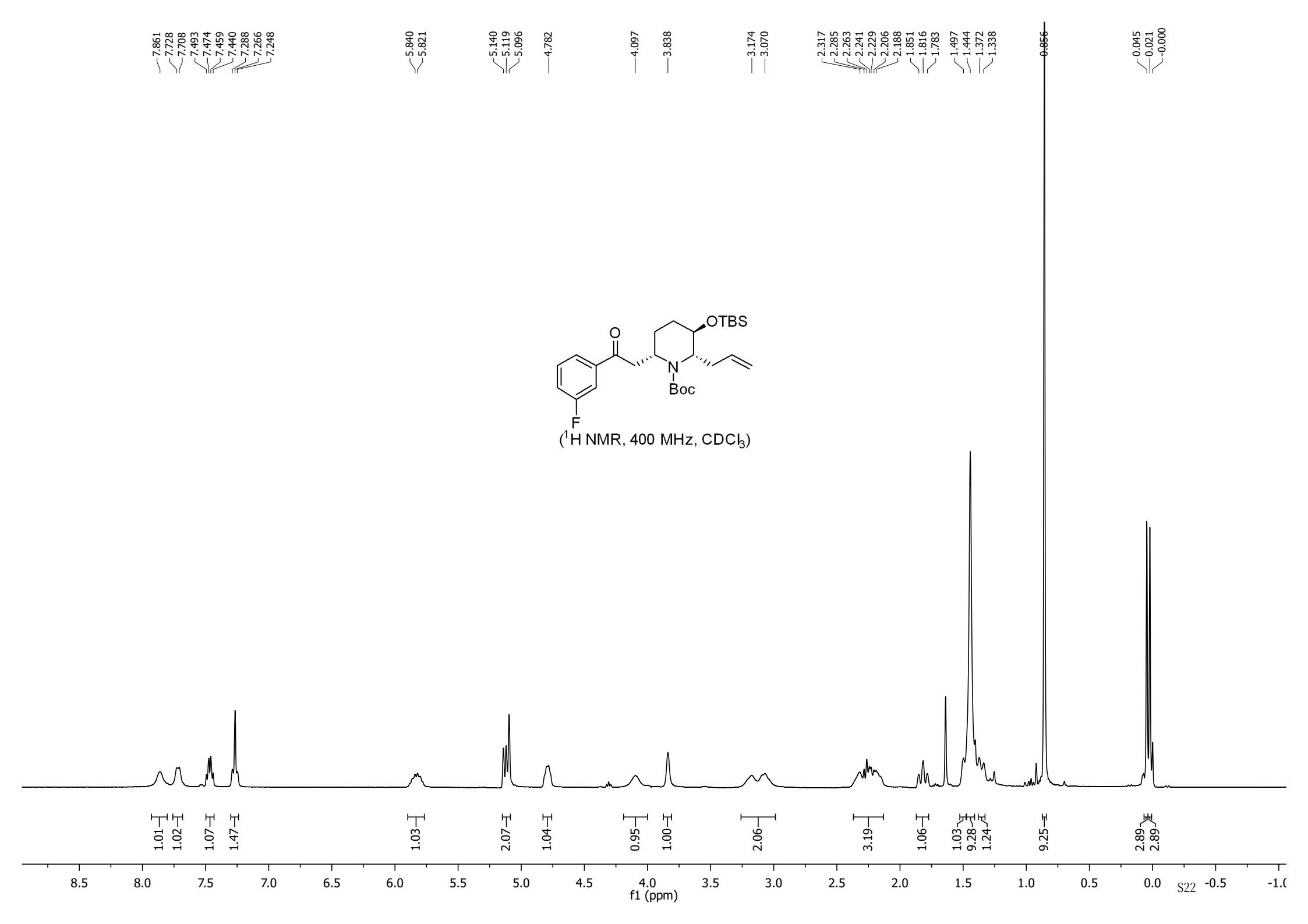

197.167
167.208
164.675
155.631
135.769
133.195
131.357
117.472
115.979
115.762
79.789
66.063
57.583
46.749
43.786
39.231
28.526
25.814
21.959
20.281
18.091
-4.643
-4.756
OTBS
O
N
Boc
F
(13C NMR, 100 MHz, CDCl3)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

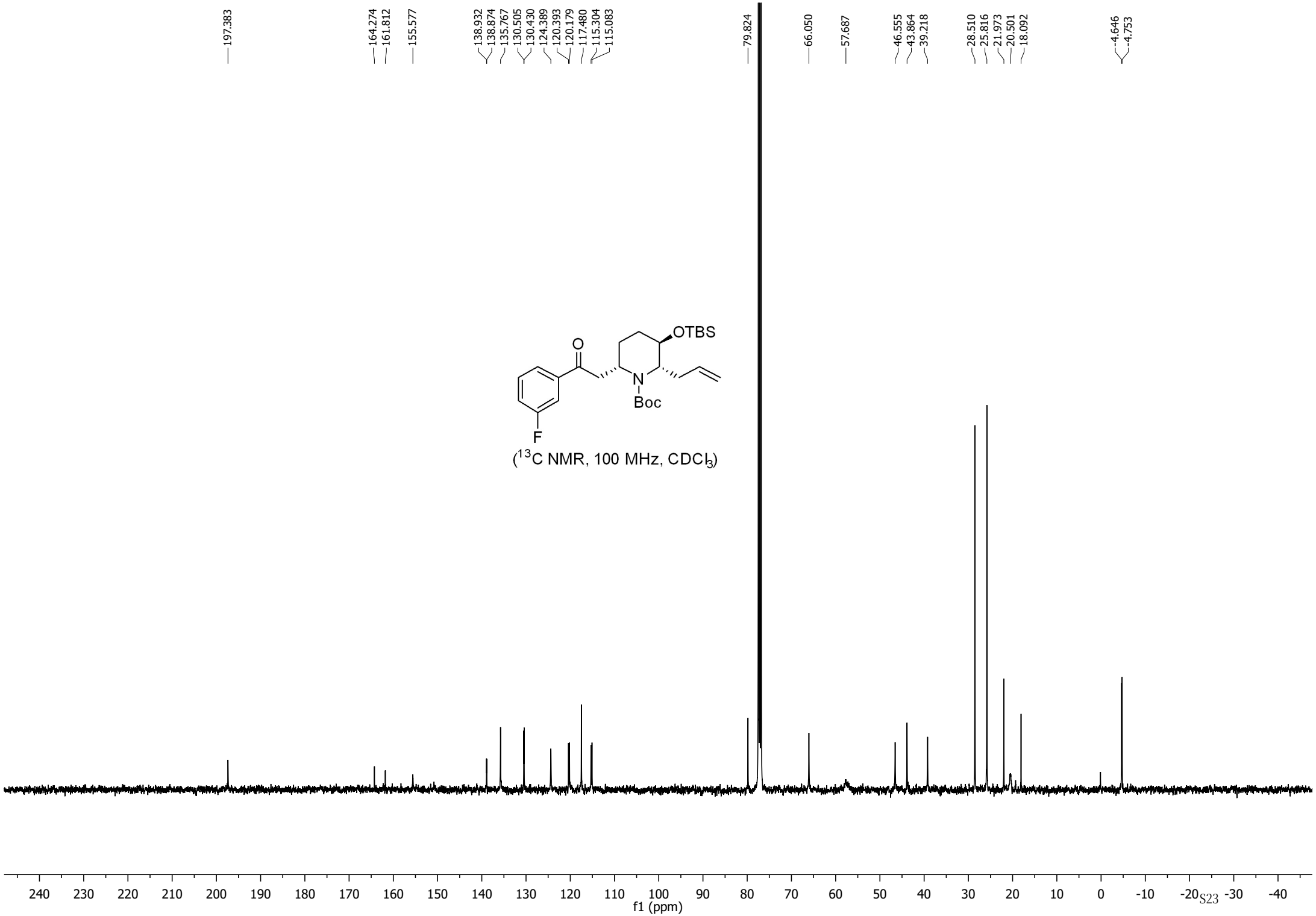

7.844
7.376
7.359
7.340
5.848
5.829
5.807
5.143
5.116
5.100
5.092
4.802
4.101
3.835
3.181
3.097
2.421
2.330
2.292
2.270
2.250
2.237
2.215
2.176
1.855
1.821
1.787
1.483
1.441
1.373
1.334
0.855
0.044
0.019
0.000
OTBS
O
N
Boc
(1H NMR, 400 MHz, CDCl3)
2.07
2.16
1.10
2.22
1.03
0.95
1.00
2.08
3.23
3.22
1.21
1.14
9.20
1.20
9.13
3.08
3.06
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)

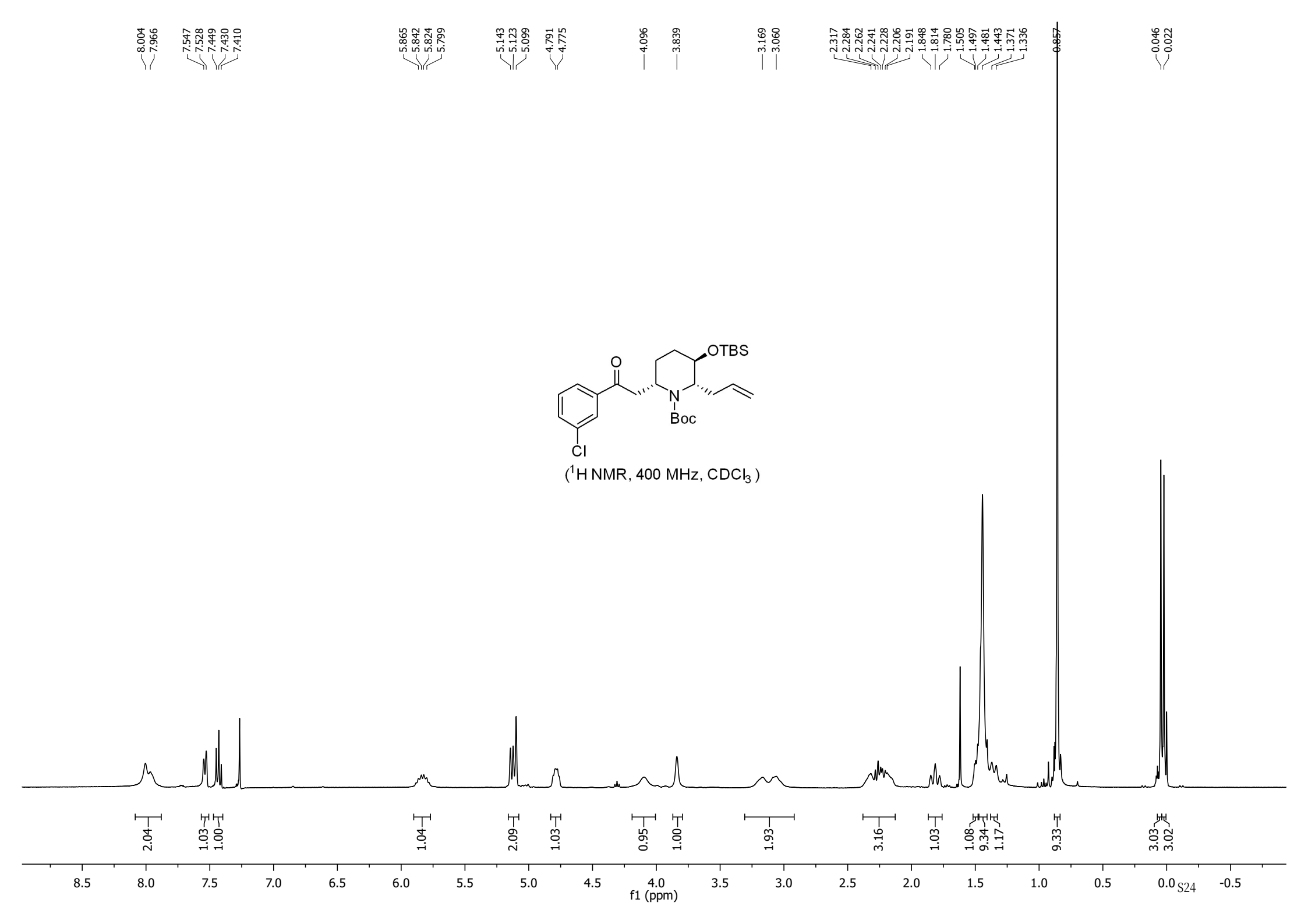

198.891
155.554
138.551
136.897
135.889
134.024
128.995
128.637
125.785
117.386
79.657
66.140
46.631
43.746
39.211
28.526
25.827
22.026
21.495
20.538
18.098
-4.645
-4.746
OTBS
O
N
Boc
(13C NMR, 100 MHz, CDCl3)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

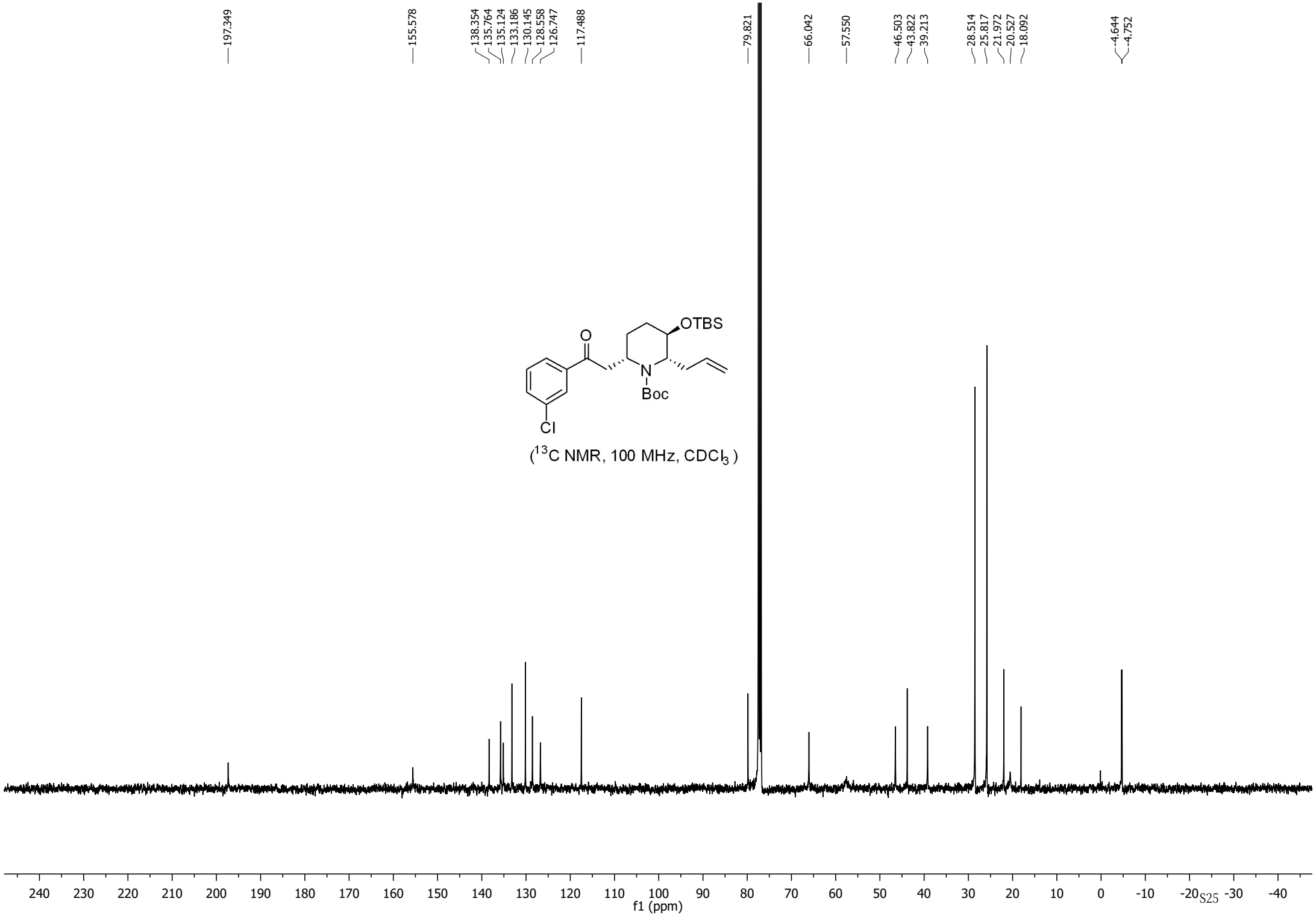

8.336
8.293
7.833
7.814
7.654
7.635
7.615
5.847
5.828
5.148
5.129
5.105
4.789
4.102
3.844
3.251
3.084
2.327
2.294
2.274
2.253
2.240
2.218
1.867
1.832
1.799
1.510
1.446
1.367
0.858
0.049
0.025
0.000
OTBS
O
N
Boc
CF3
(1H NMR, 400 MHz, CDCl3)
1.93
1.00
0.99
1.00
1.99
0.99
0.96
1.00
1.98
3.13
1.05
1.07
9.17
1.13
9.16
3.02
3.02
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
-1
f1 (ppm)

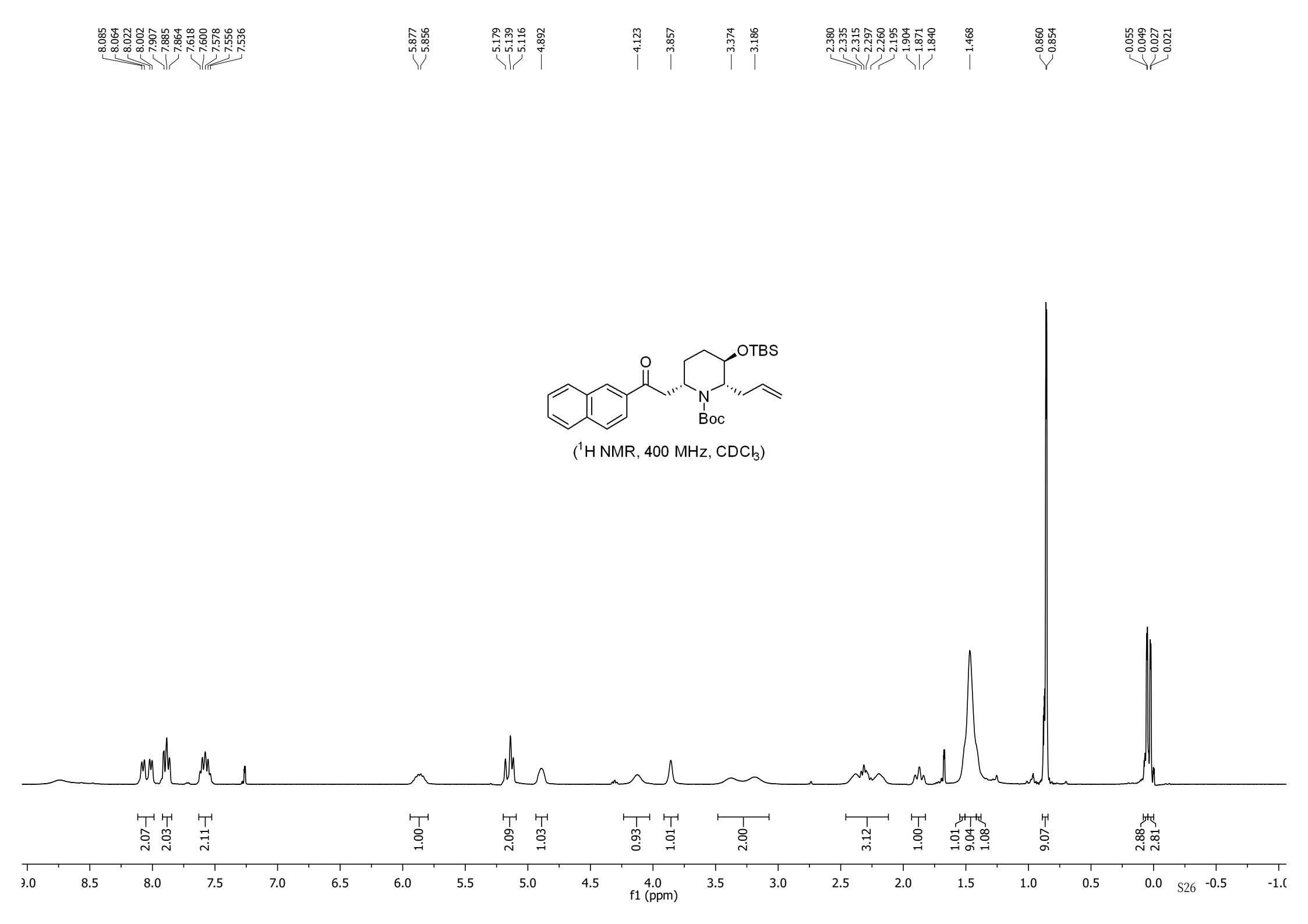

197.373
155.661
137.261
135.736
131.839
131.583
131.264
129.630
129.472
125.473
125.235
122.529
117.507
79.872
66.063
57.773
46.487
43.903
39.222
28.479
25.812
21.969
20.477
18.093
-4.647
-4.760
OTBS
O
N
Boc
CF3
(13C NMR, 100 MHz, CDCl3)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

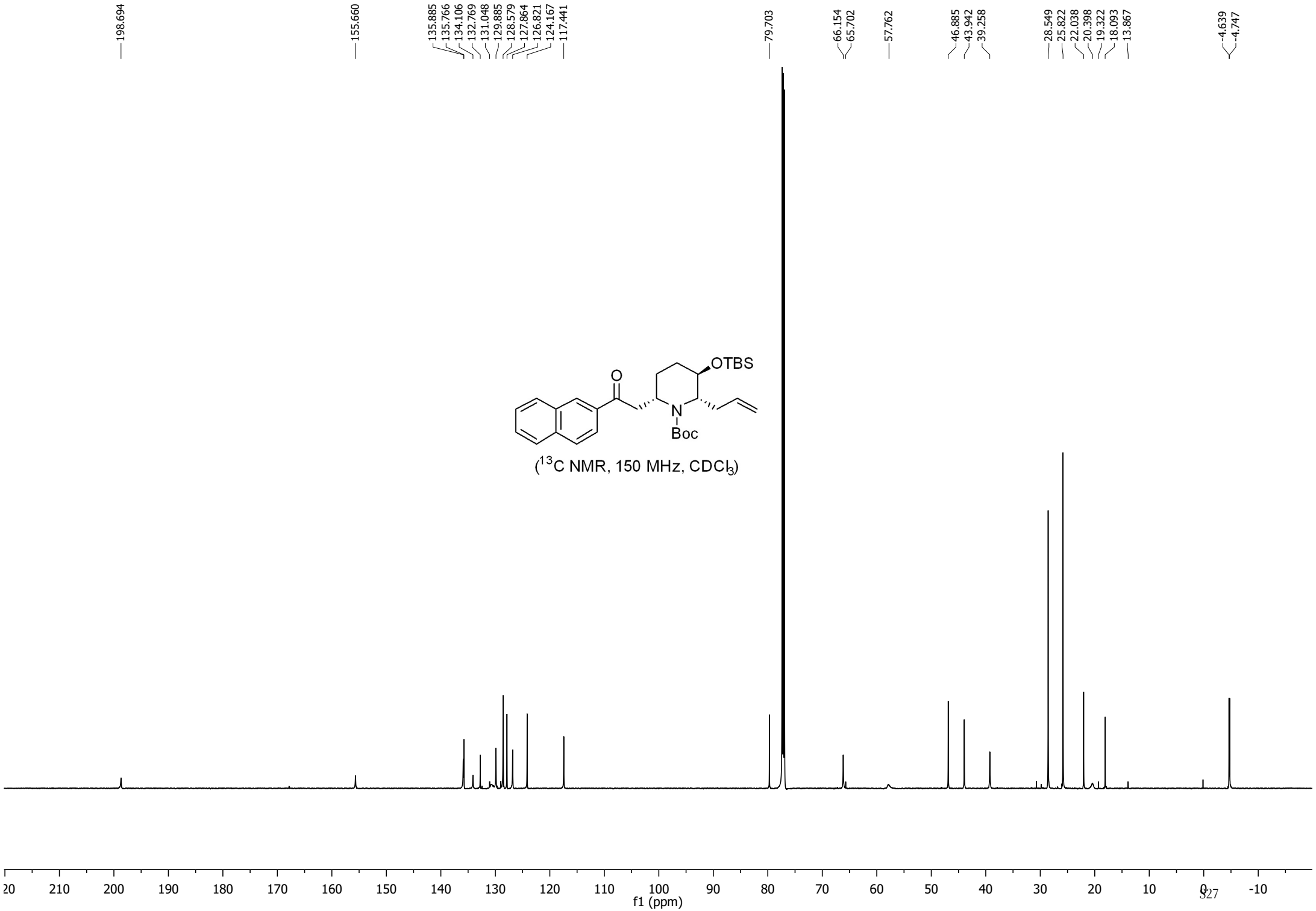

7.861
7.728
7.708
7.493
7.474
7.459
7.440
7.288
7.266
7.248
5.840
5.821
5.140
5.119
5.096
4.782
4.097
3.838
3.174
3.070
2.317
2.285
2.263
2.241
2.229
2.206
2.188
1.851
1.816
1.783
1.497
1.444
1.372
1.338
0.856
0.045
0.021
-0.000
OTBS
O
N
Boc
F
(1H NMR, 400 MHz, CDCl3)
1.01
1.02
1.07
1.47
1.03
2.07
1.04
0.95
1.00
2.06
3.19
1.06
1.03
9.28
1.24
9.25
2.89
2.89
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)

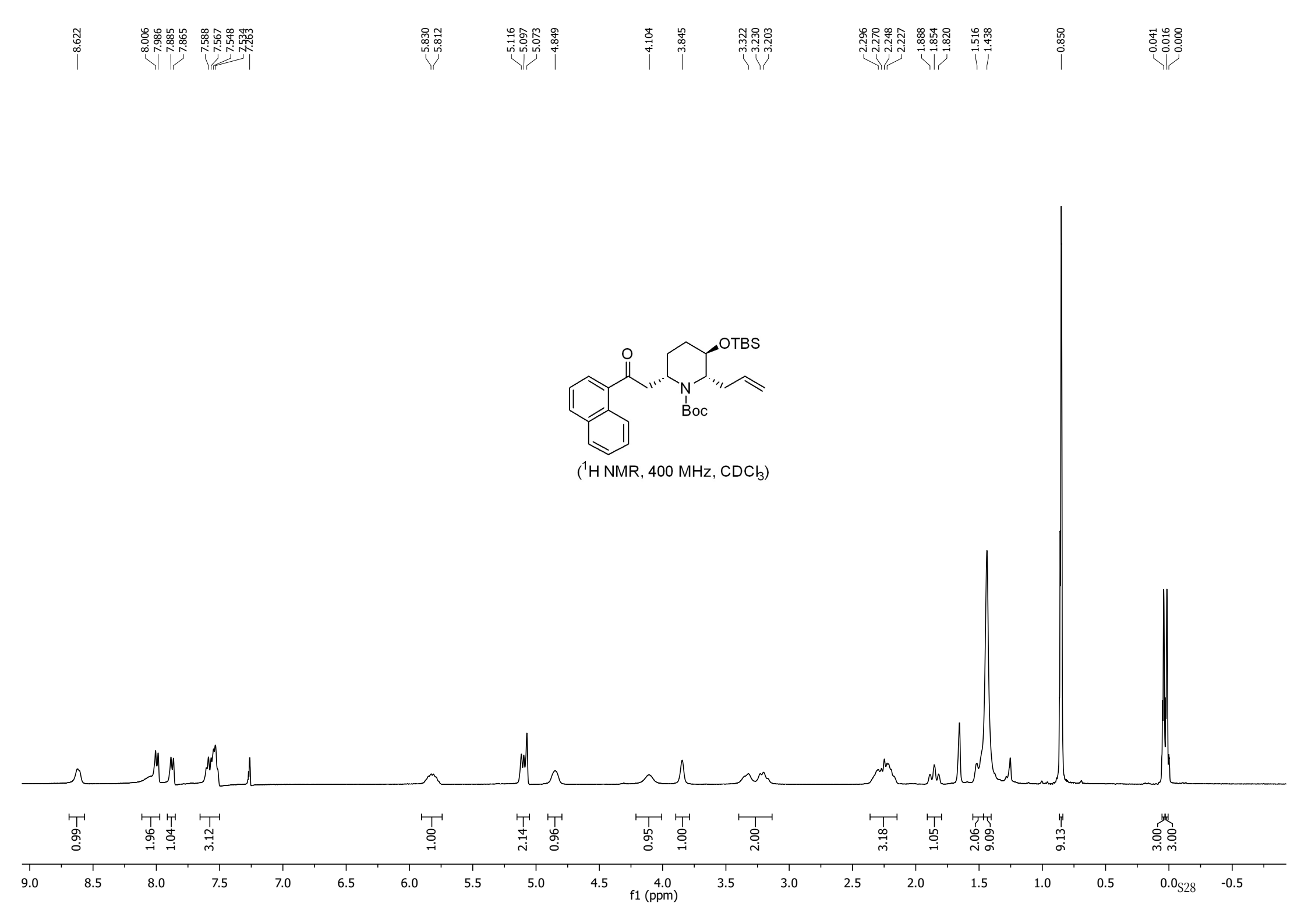

197.383
164.274
161.812
155.577
138.932
138.874
135.767
130.505
130.430
124.389
120.393
120.179
117.480
115.304
115.083
79.824
66.050
57.687
46.555
43.864
39.218
28.510
25.816
21.973
20.501
18.092
-4.646
-4.753
OTBS
O
N
Boc
F
(^{13}C NMR, 100 MHz, $CDCl_3$)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

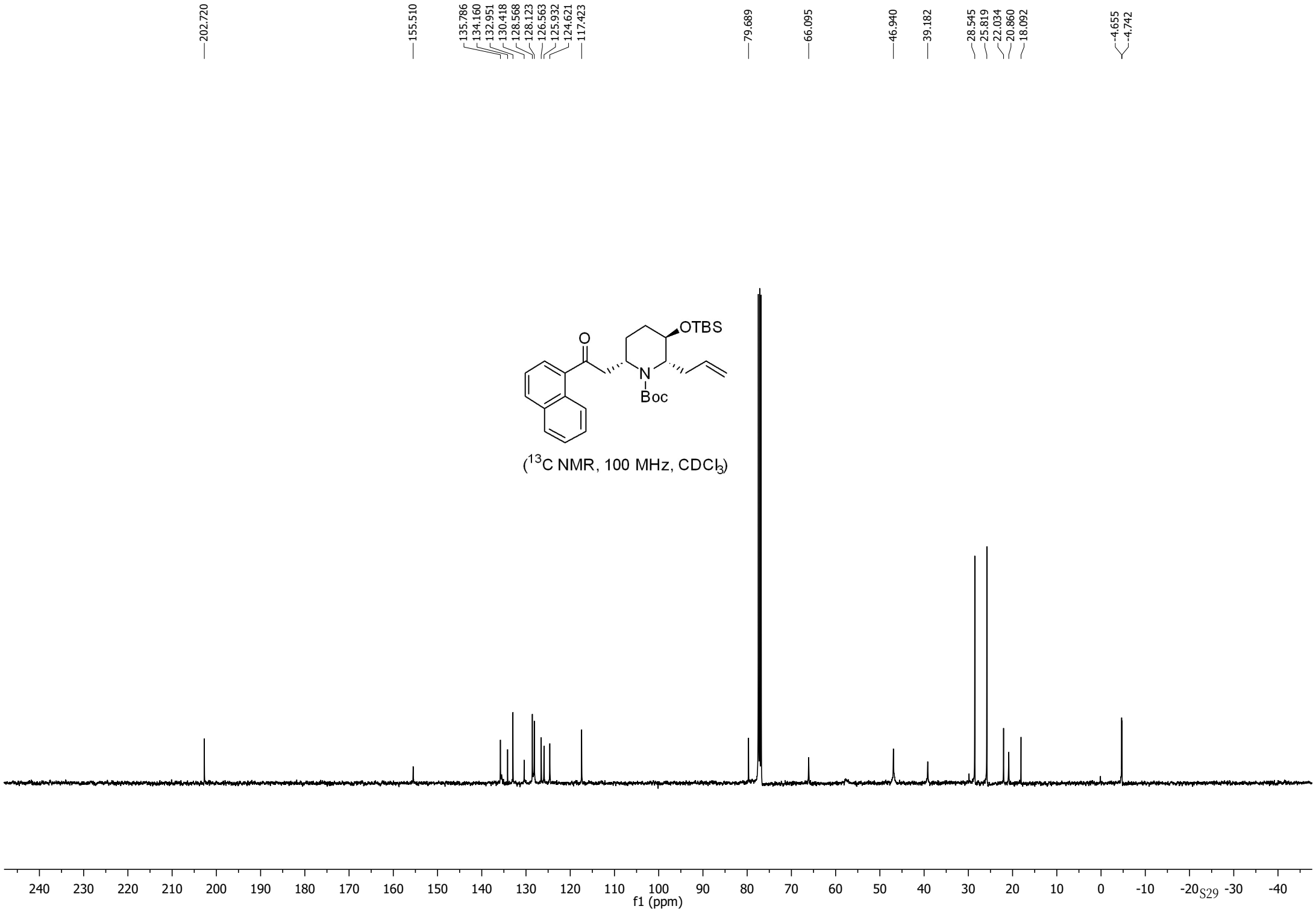

8.004
7.966
7.547
7.528
7.449
7.430
7.410
5.865
5.842
5.824
5.799
5.143
5.123
5.099
4.791
4.775
4.096
3.839
3.169
3.060
2.317
2.284
2.262
2.241
2.228
2.206
2.191
1.848
1.814
1.780
1.505
1.497
1.481
1.443
1.371
1.336
0.857
0.046
0.022
OTBS
O
N
Boc
Cl
(1H NMR, 400 MHz, CDCl3)
2.04
1.03
1.00
1.04
2.09
1.03
0.95
1.00
1.93
3.16
1.03
1.08
9.34
1.17
9.33
3.03
3.02
f1 (ppm)

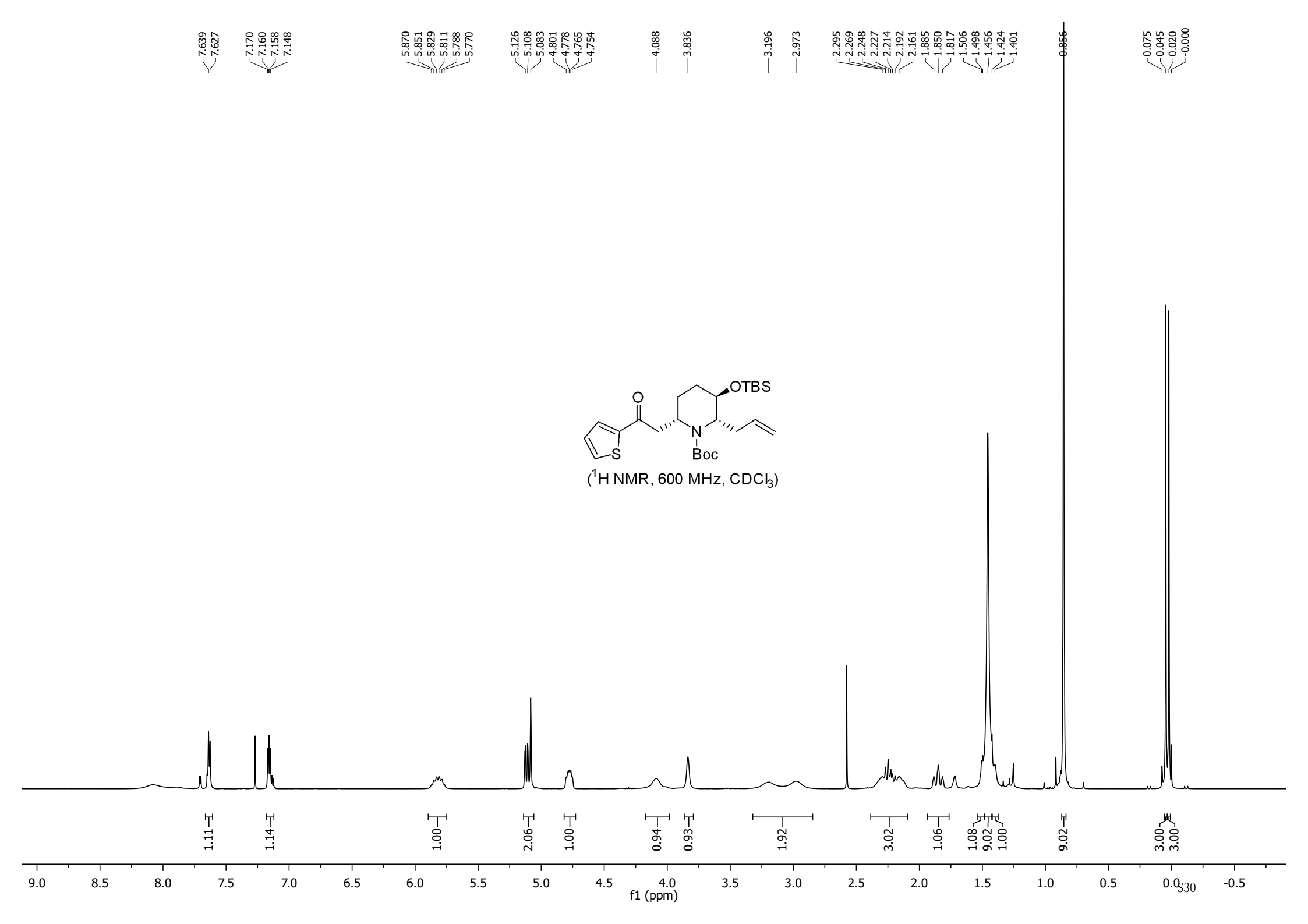

197.349
155.578
138.354
135.764
135.124
133.186
130.145
128.558
126.747
117.488
79.821
66.042
57.550
46.503
43.822
39.213
28.514
25.817
21.972
20.527
18.092
-4.644
-4.752
OTBS
O
N
Boc
Cl
(^{13}C NMR, 100 MHz, $CDCl_3$)
f1 (ppm)

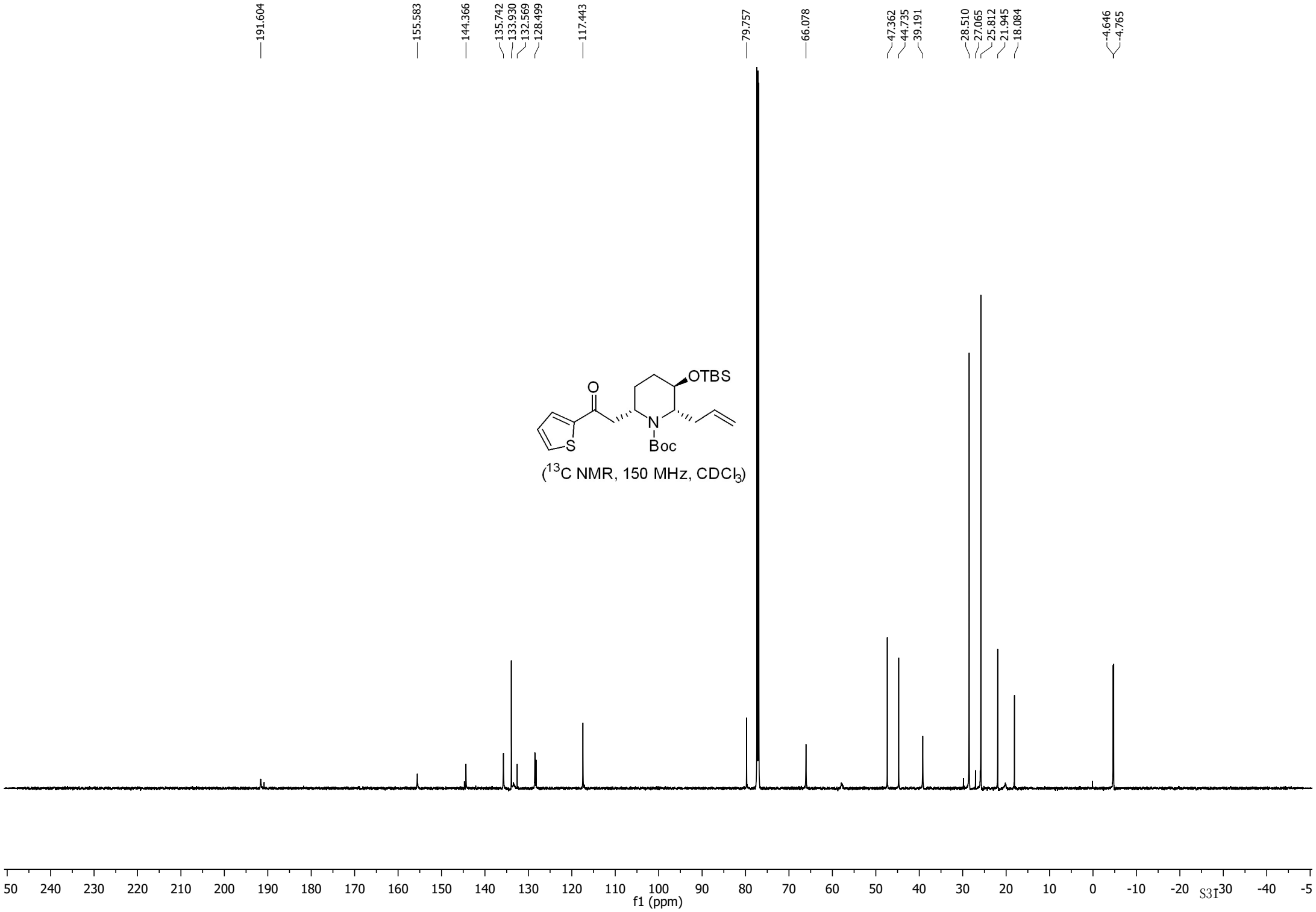

8.085
8.064
8.022
8.002
7.907
7.885
7.864
7.618
7.600
7.578
7.556
7.536
5.877
5.856
5.179
5.139
5.116
4.892
4.123
3.857
3.374
3.186
2.380
2.335
2.315
2.297
2.260
2.195
1.904
1.871
1.840
1.468
0.860
0.854
0.055
0.049
0.027
0.021
OTBS
O
N
Boc
(1H NMR, 400 MHz, CDCl3)
2.07
2.03
2.11
1.00
2.09
1.03
0.93
1.01
2.00
3.12
1.00
1.01
9.04
1.08
9.07
2.88
2.81
f1 (ppm)

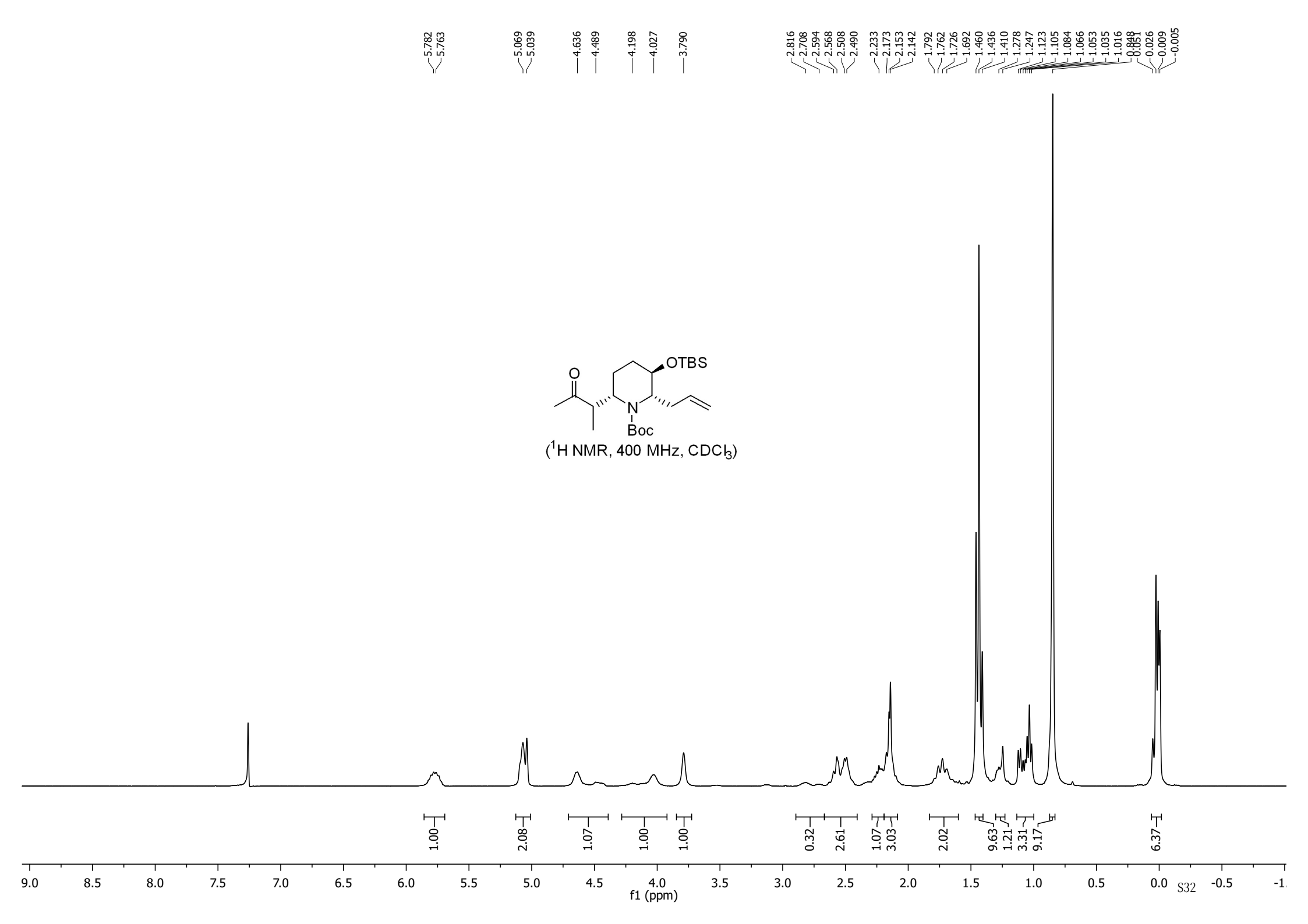

198.694
155.660
135.885
135.766
134.106
132.769
131.048
129.885
128.579
127.864
126.821
124.167
117.441
79.703
66.154
65.702
57.762
46.885
43.942
39.258
28.549
25.822
22.038
20.398
19.322
18.093
13.867
-4.639
-4.747
OTBS
O
N
Boc
(^{13}C NMR, 150 MHz, $CDCl_3$)
f1 (ppm)

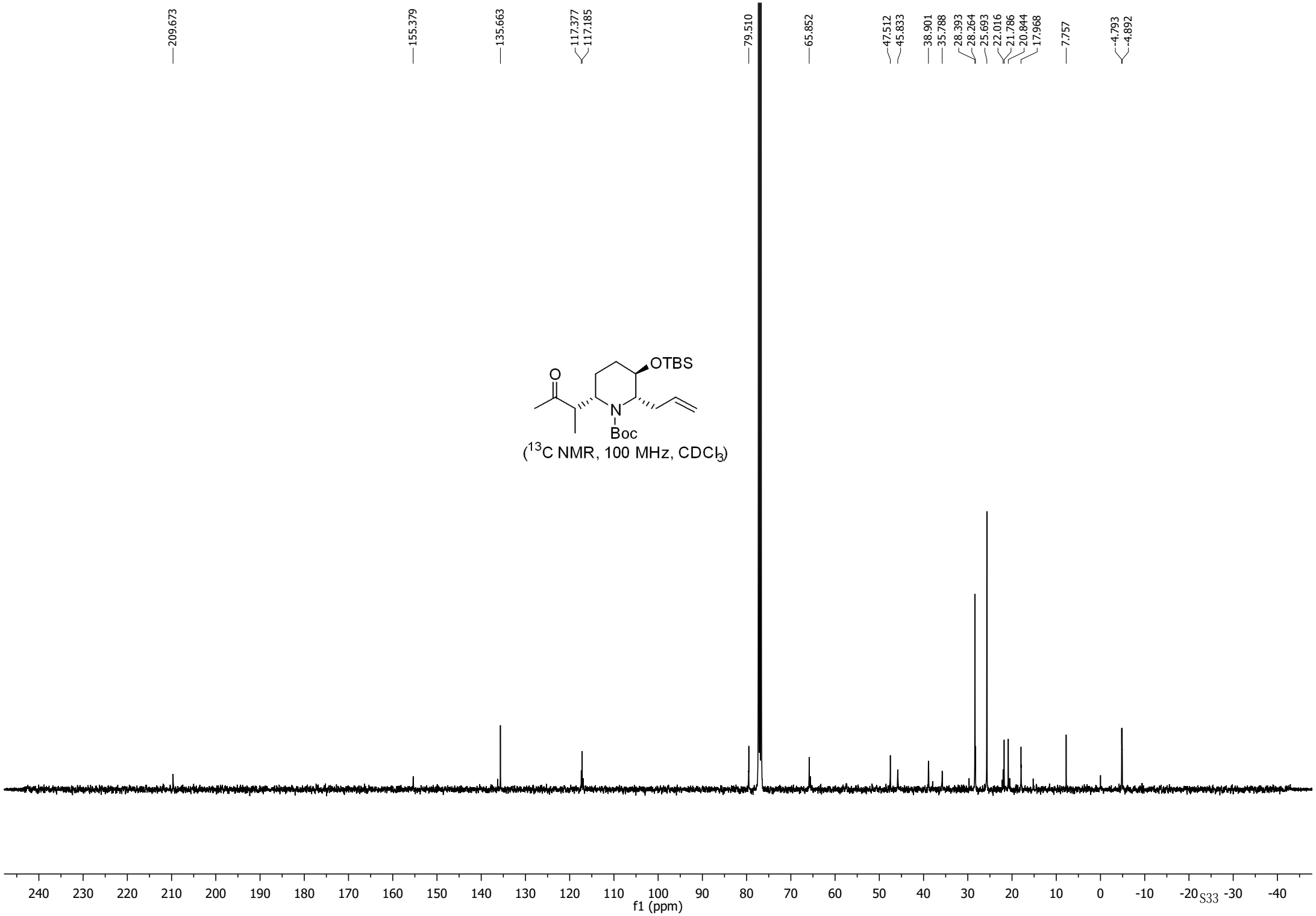

8.622
8.006
7.986
7.885
7.865
7.588
7.567
7.548
7.534
7.263
5.830
5.812
5.116
5.097
5.073
4.849
4.104
3.845
3.322
3.230
3.203
2.296
2.270
2.248
2.227
1.888
1.854
1.820
1.516
1.438
0.850
0.041
0.016
0.000
OTBS
O
N
Boc
(1H NMR, 400 MHz, CDCl3)
0.99
1.96
1.04
3.12
1.00
2.14
0.96
0.95
1.00
2.00
3.18
1.05
2.06
9.09
9.13
3.00
3.00
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)

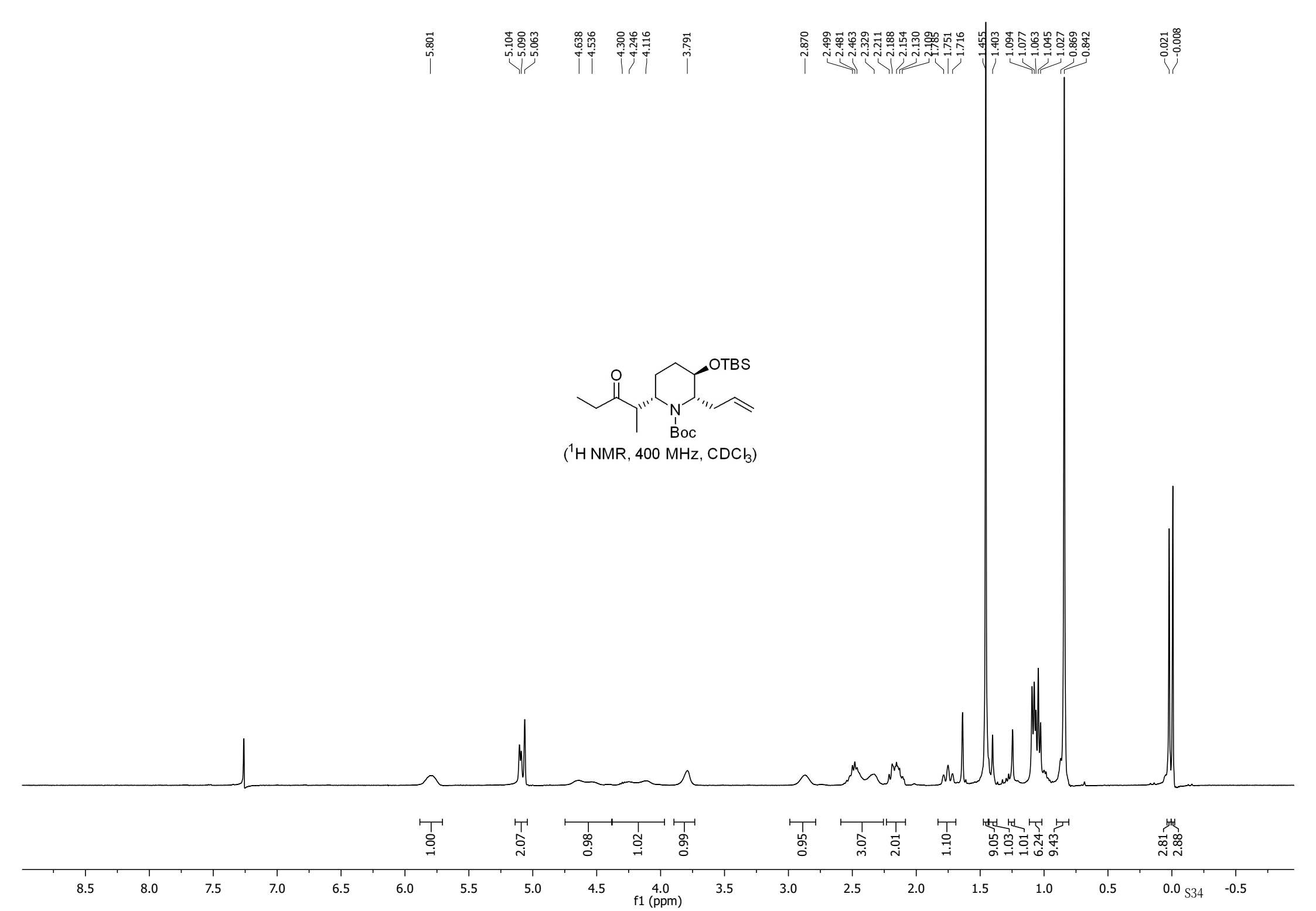

202.720
155.510
135.786
134.160
132.951
130.418
128.568
128.123
126.563
125.932
124.621
117.423
79.689
66.095
46.940
39.182
28.545
25.819
22.034
20.860
18.092
-4.655
-4.742
OTBS
O
N
Boc
(13C NMR, 100 MHz, CDCl3)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

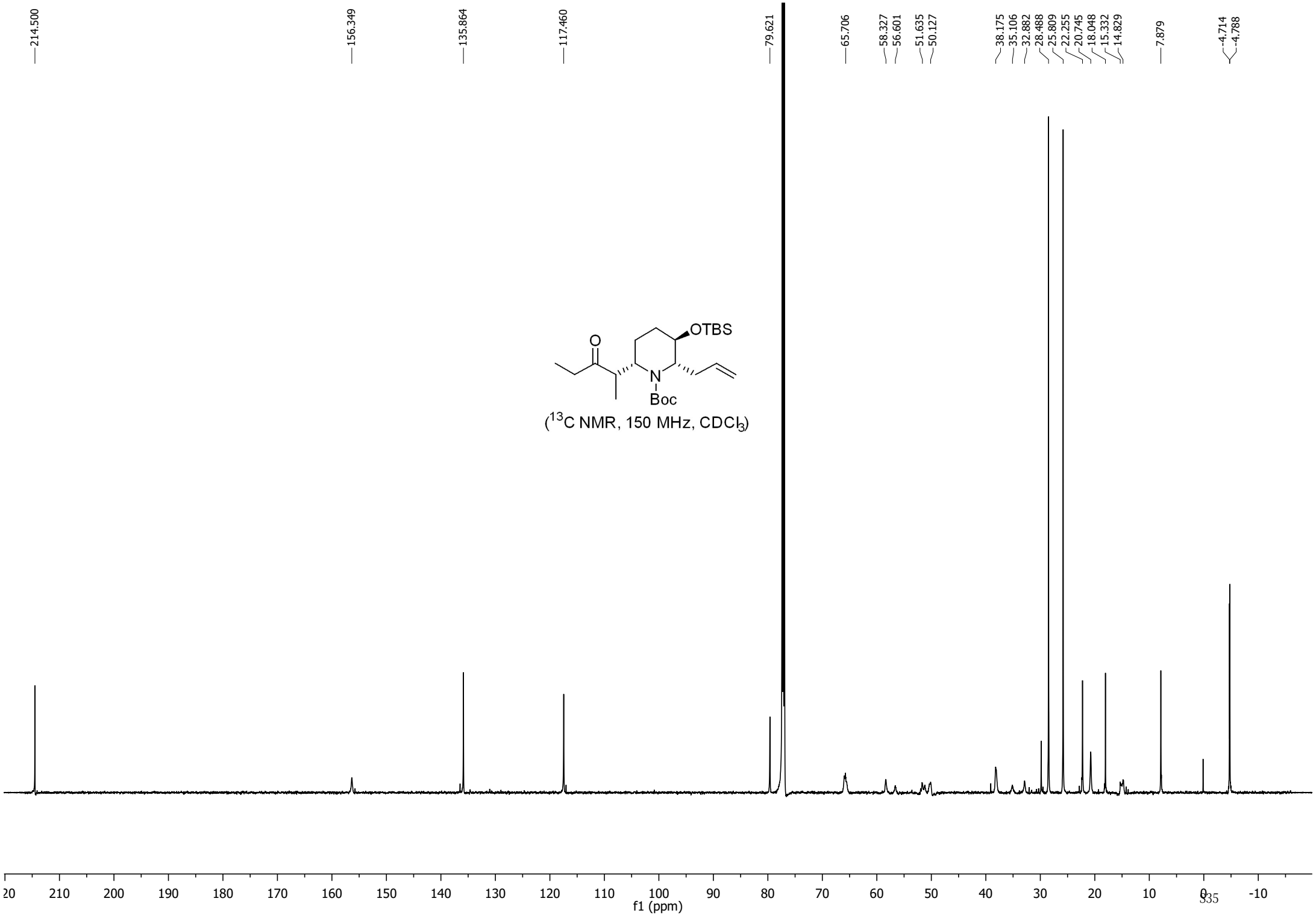

7.639
7.627
7.170
7.160
7.158
7.148
5.870
5.851
5.829
5.811
5.788
5.770
5.126
5.108
5.083
4.801
4.778
4.765
4.754
4.088
3.836
3.196
2.973
2.295
2.269
2.248
2.227
2.214
2.192
2.161
1.885
1.850
1.817
1.506
1.498
1.456
1.424
1.401
0.856
0.075
0.045
0.020
-0.000
OTBS
O
N
S
Boc
(1H NMR, 600 MHz, CDCl3)
1.11
1.14
1.00
2.06
1.00
0.94
0.93
1.92
3.02
1.06
1.08
9.02
1.00
9.02
3.00
3.00
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)

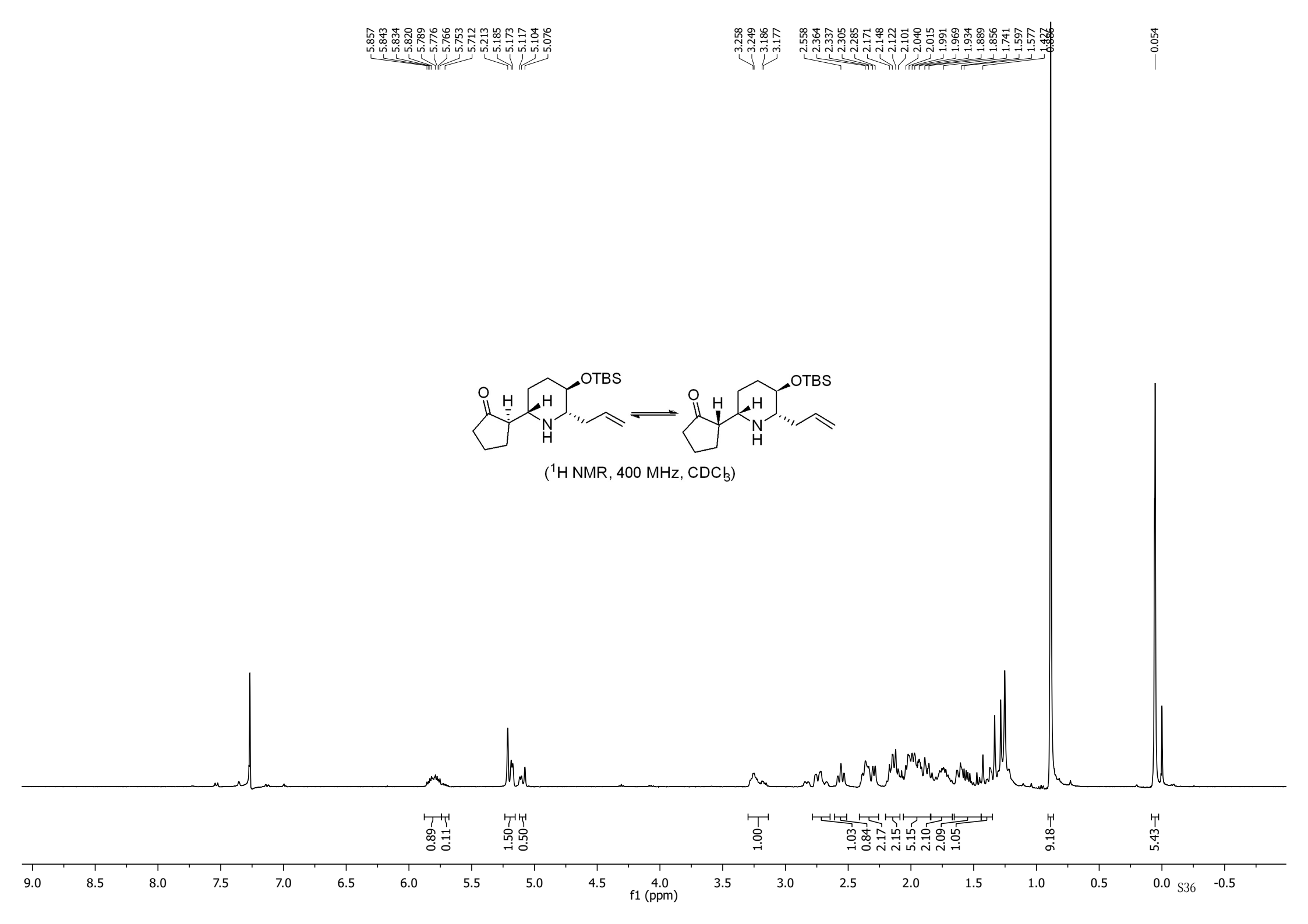

191.604
155.583
144.366
135.742
133.930
132.569
128.499
117.443
79.757
66.078
47.362
44.735
39.191
28.510
27.065
25.812
21.945
18.084
-4.646
-4.765
OTBS
O
N
Boc
S
(^{13}C NMR, 150 MHz, $CDCl_3$)
f1 (ppm)

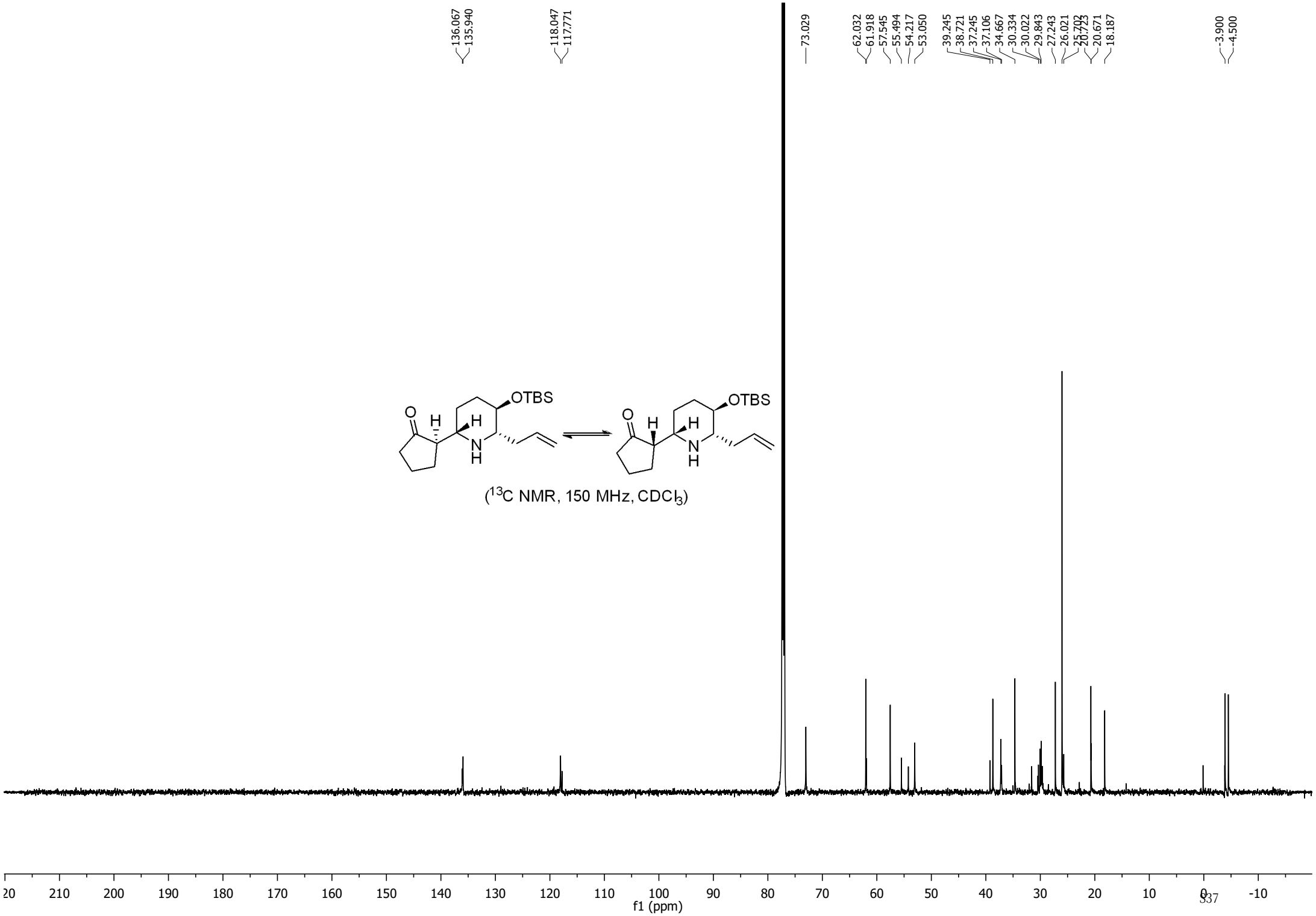

5.782
5.763
5.069
5.039
4.636
4.489
4.198
4.027
3.790
2.816
2.708
2.594
2.568
2.508
2.490
2.233
2.173
2.153
2.142
1.792
1.762
1.726
1.692
1.460
1.436
1.410
1.278
1.247
1.123
1.105
1.084
1.066
1.053
1.035
1.016
0.848
0.831
0.026
0.009
-0.005
OTBS
O
N
Boc
(^{1}H NMR, 400 MHz, $CDCl_3$)
1.00
2.08
1.07
1.00
1.00
0.32
2.61
1.07
3.03
2.02
9.63
1.21
3.31
9.17
6.37
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)


209.673
155.379
135.663
117.377
117.185
79.510
65.852
47.512
45.833
38.901
35.788
28.393
28.264
25.693
22.016
21.786
20.844
17.968
7.757
-4.793
-4.892
OTBS
O
N
Boc
(^{13}C NMR, 100 MHz, $CDCl_3$)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

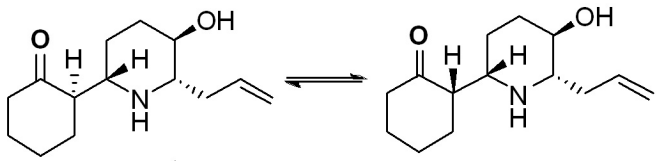

5.801
5.104
5.090
5.063
4.638
4.536
4.300
4.246
4.116
3.791
2.870
2.499
2.481
2.463
2.329
2.211
2.188
2.154
2.130
1.751
1.716
1.455
1.403
1.094
1.077
1.063
1.045
1.027
0.869
0.842
0.021
-0.008
OTBS
O
N
Boc
(1H NMR, 400 MHz, CDCl3)
1.00
2.07
0.98
1.02
0.99
0.95
3.07
2.01
1.10
9.05
1.03
1.01
6.24
9.43
2.81
2.88
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)


214.500
156.349
135.864
117.460
79.621
65.706
58.327
56.601
51.635
50.127
38.175
35.106
32.882
28.488
25.809
22.255
20.745
18.048
15.332
14.829
7.879
-4.714
-4.788
OTBS
O
N
Boc
(^{13}C NMR, 150 MHz, $CDCl_3$)
f1 (ppm)

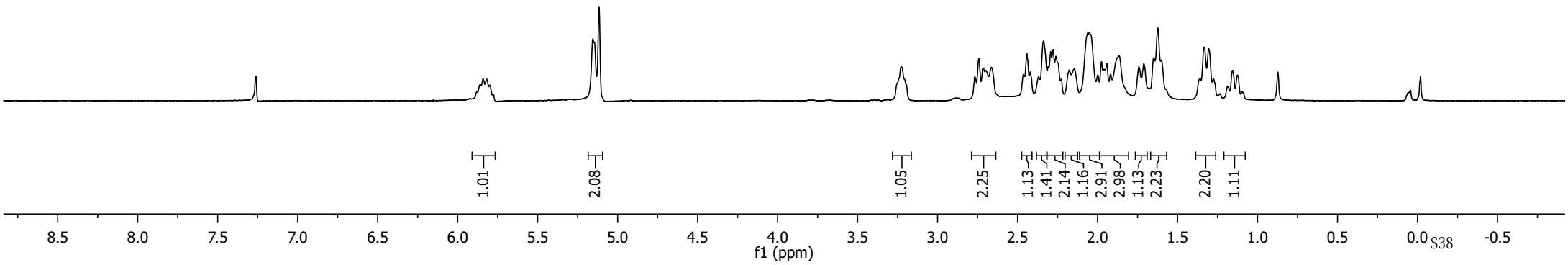

5.857
5.843
5.834
5.820
5.789
5.776
5.766
5.753
5.712
5.213
5.185
5.173
5.117
5.104
5.076
3.258
3.249
3.186
3.177
2.558
2.364
2.337
2.305
2.285
2.171
2.148
2.122
2.101
2.040
2.015
1.991
1.969
1.934
1.889
1.856
1.741
1.597
1.577
1.427
0.054
OTBS
OTBS
(1H NMR, 400 MHz, CDCl3)
0.89
0.11
1.50
0.50
1.00
1.03
0.84
2.17
2.15
5.15
2.10
2.09
1.05
9.18
5.43
f1 (ppm)

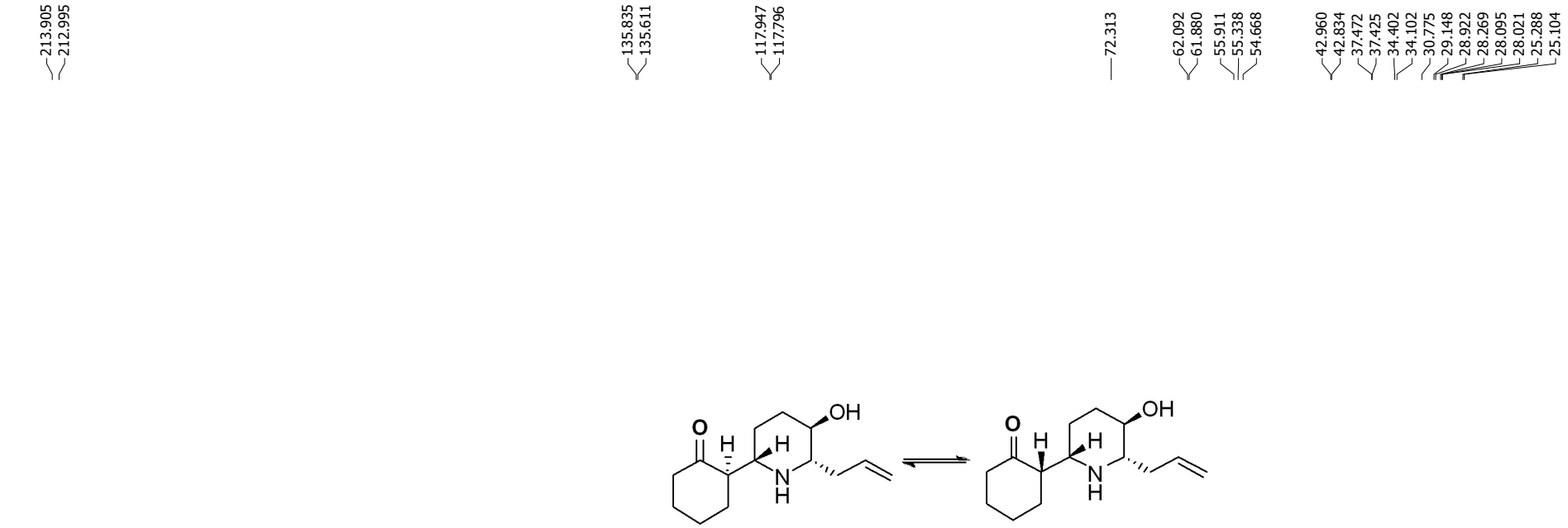


(^{13}C NMR, 150 MHz, $CDCl_3$)

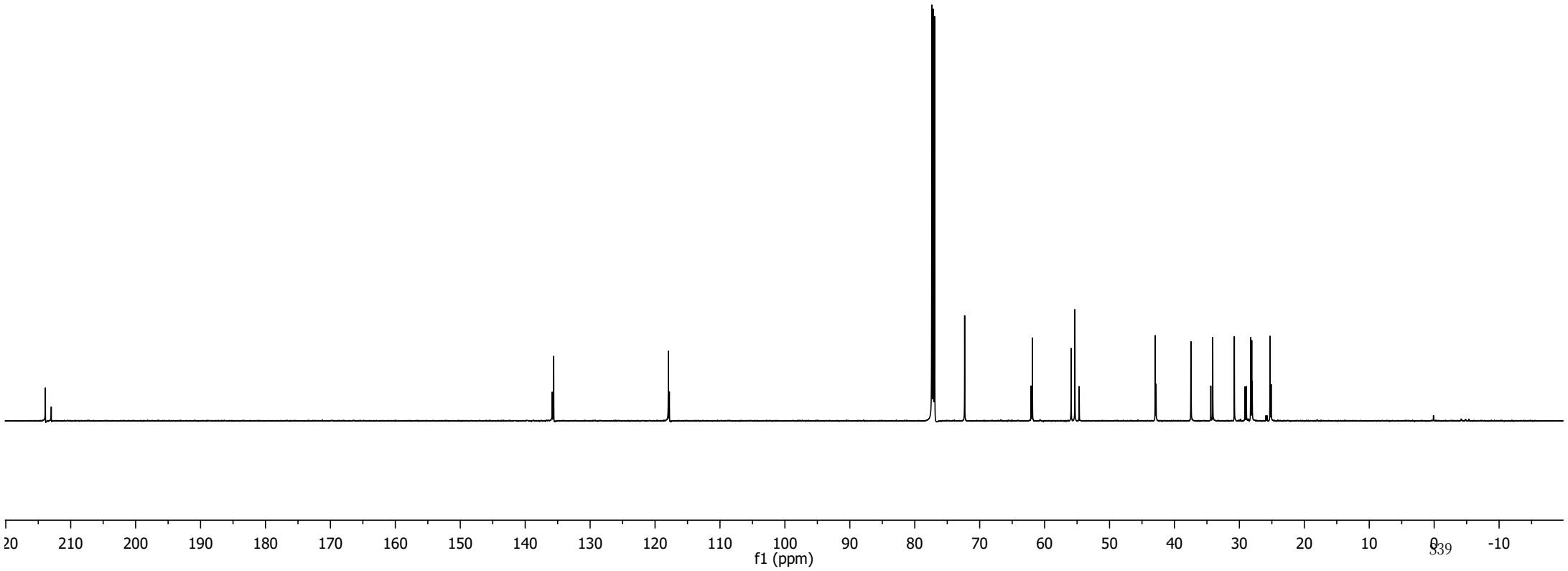


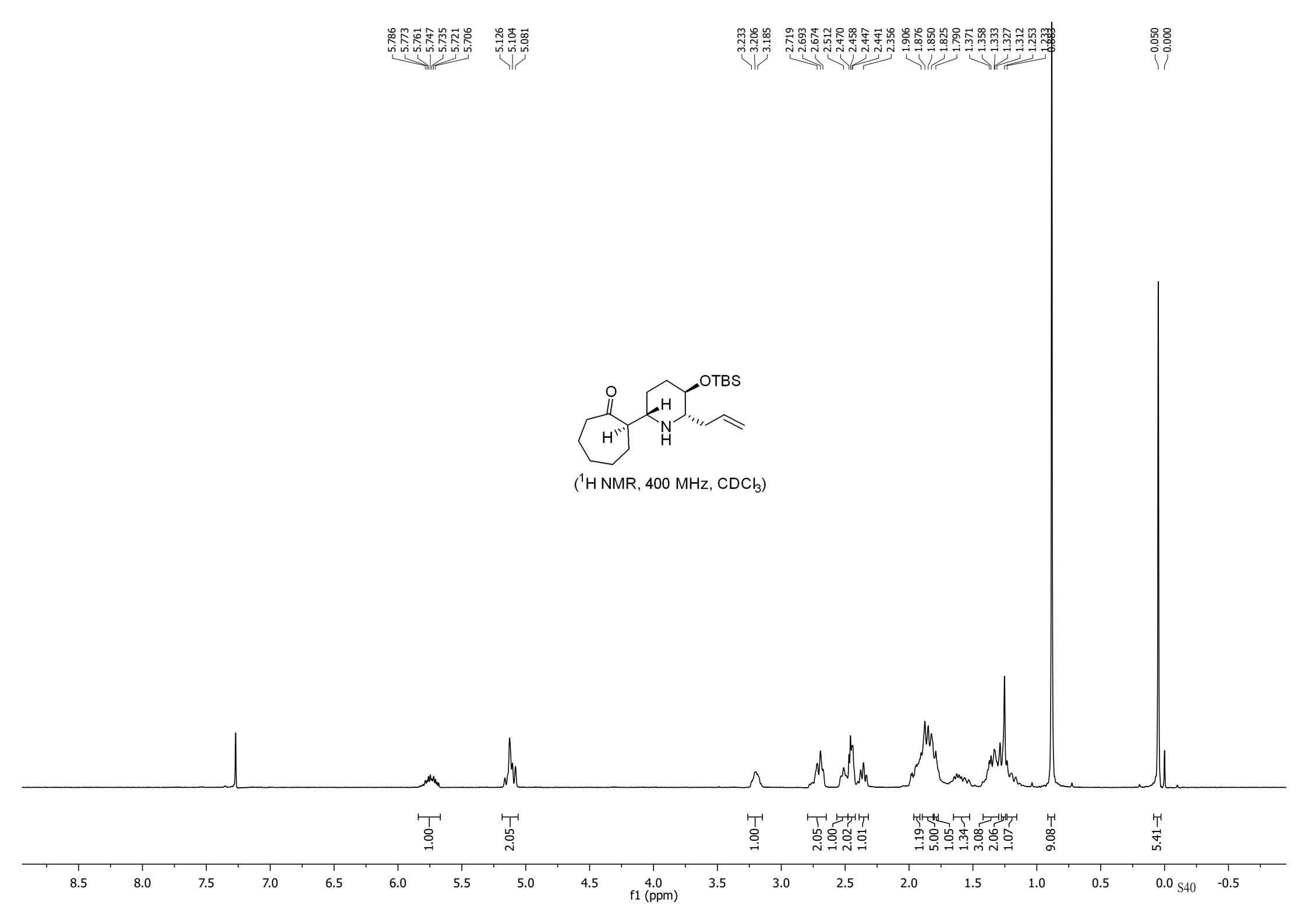
(^{1}H NMR, 100 MHz, $CDCl_3$)

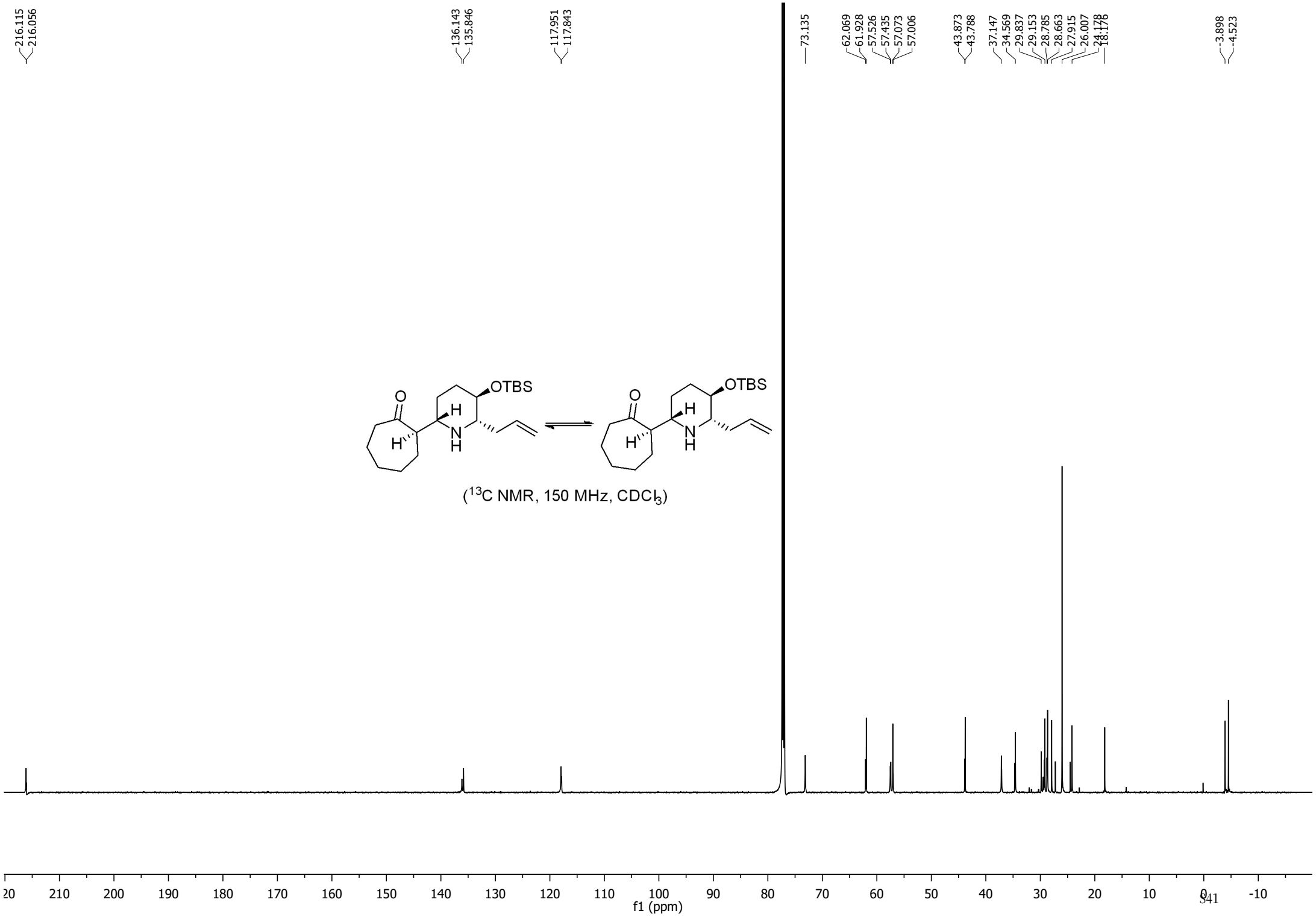




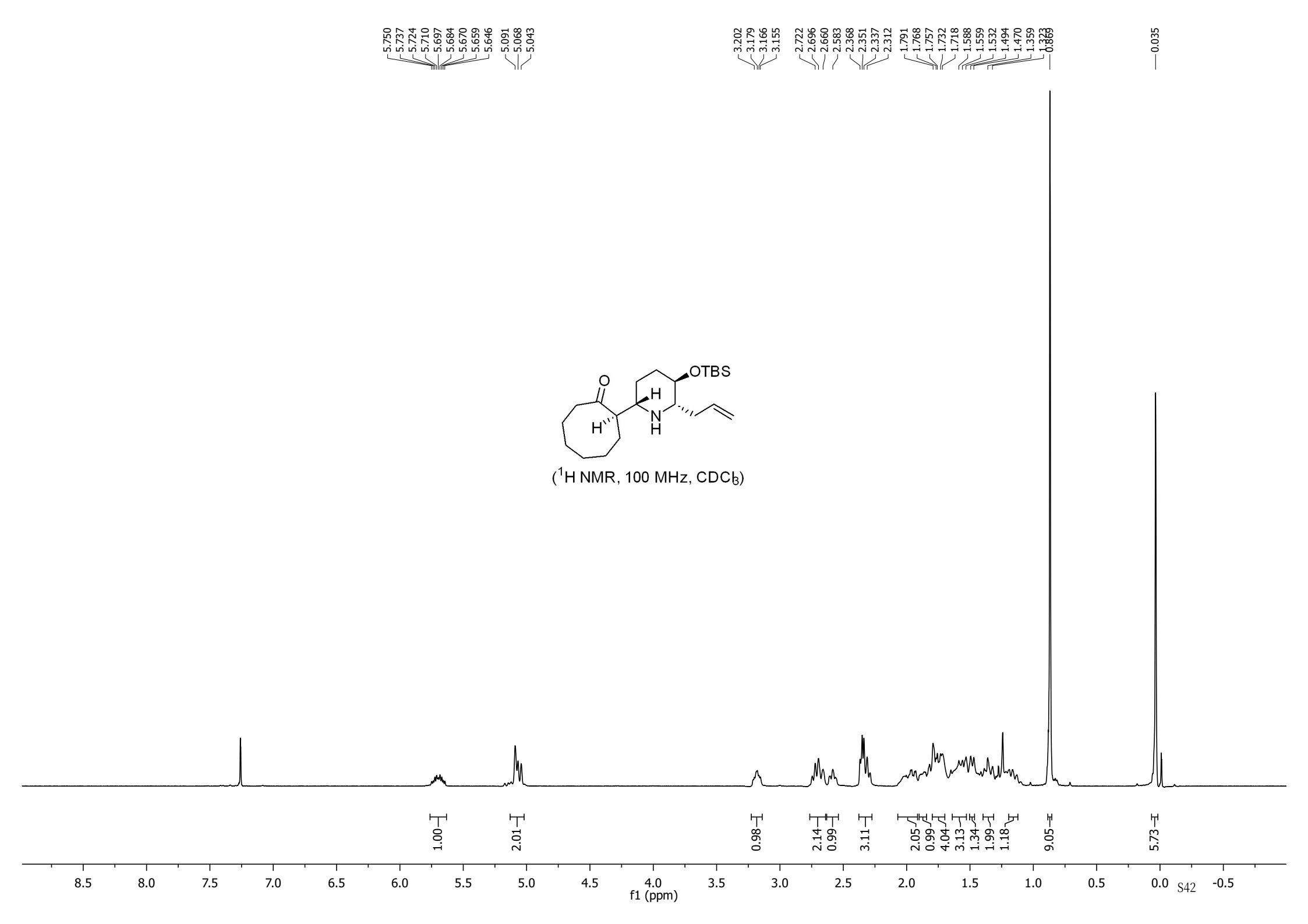
(^{13}C NMR, 150 MHz, $CDCl_3$)

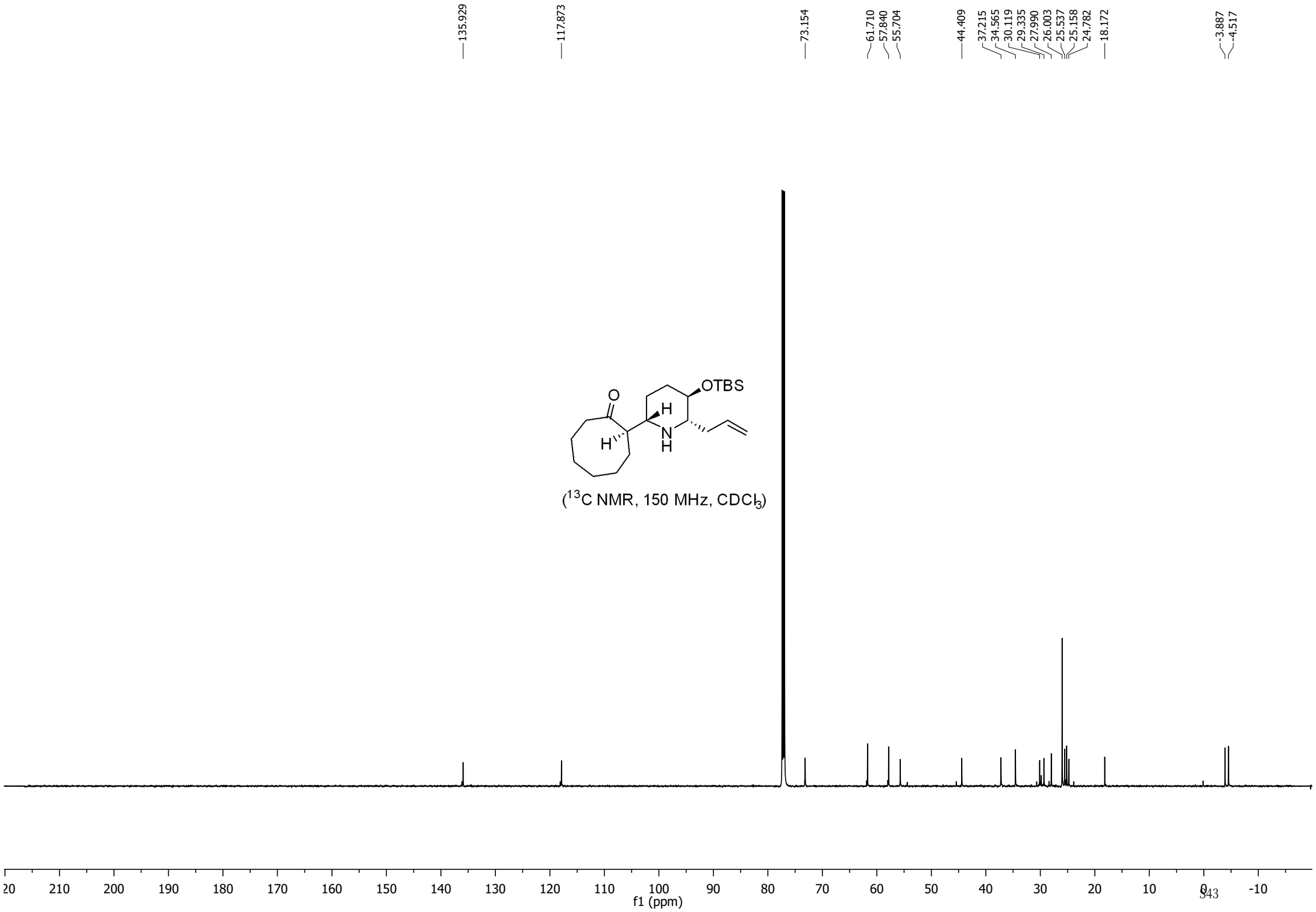


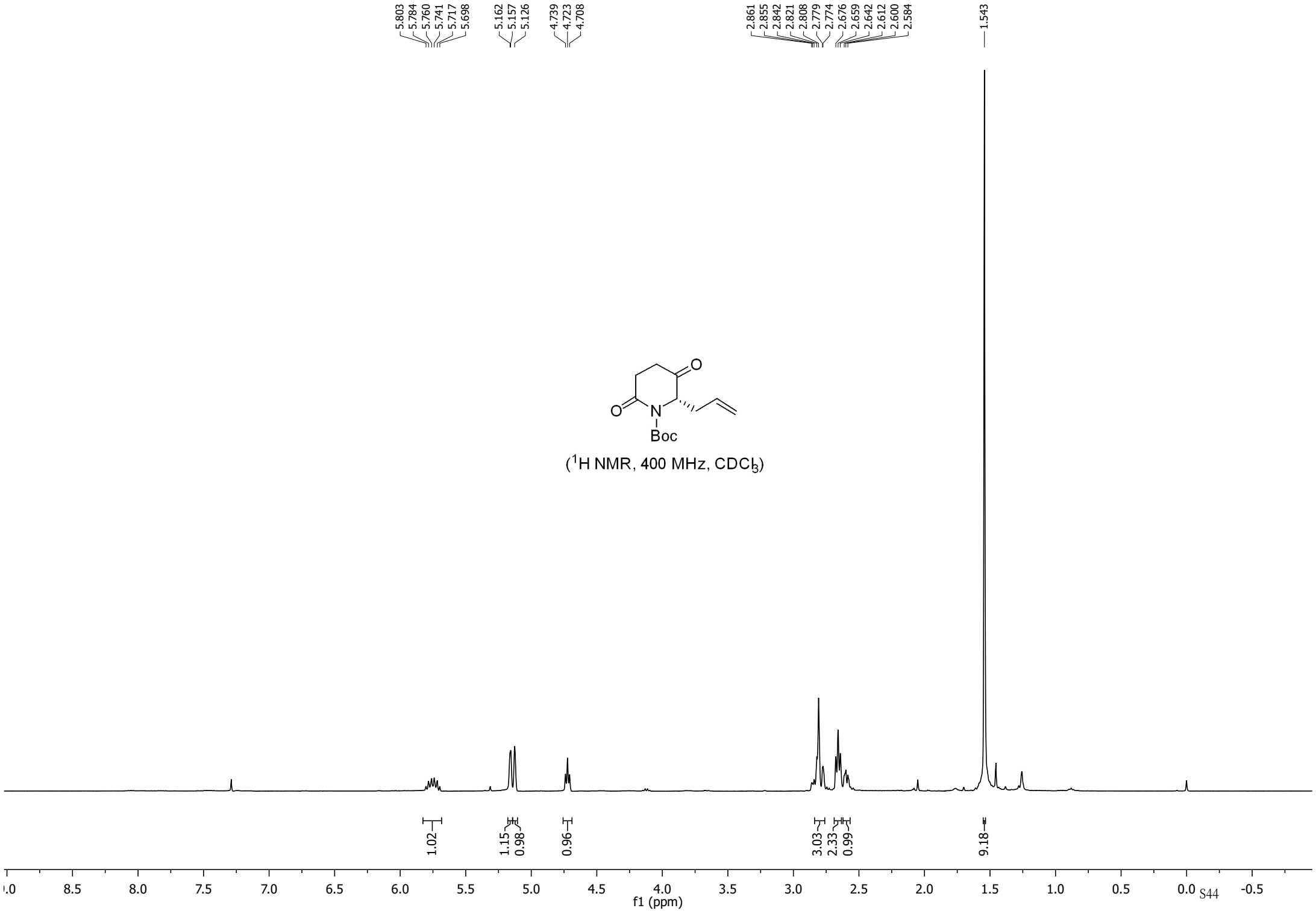

5.786
5.773
5.761
5.747
5.735
5.721
5.706
5.126
5.104
5.081
3.233
3.206
3.185
2.719
2.693
2.674
2.512
2.470
2.458
2.447
2.441
2.356
1.906
1.876
1.850
1.825
1.790
1.371
1.358
1.333
1.327
1.312
1.253
1.233
0.883
0.050
0.000
OTBS
O
H
N
H
H
(1H NMR, 400 MHz, CDCl3)
1.00
2.05
1.00
2.05
1.00
2.02
1.01
1.19
5.00
1.05
1.34
3.08
2.06
1.07
9.08
5.41
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)



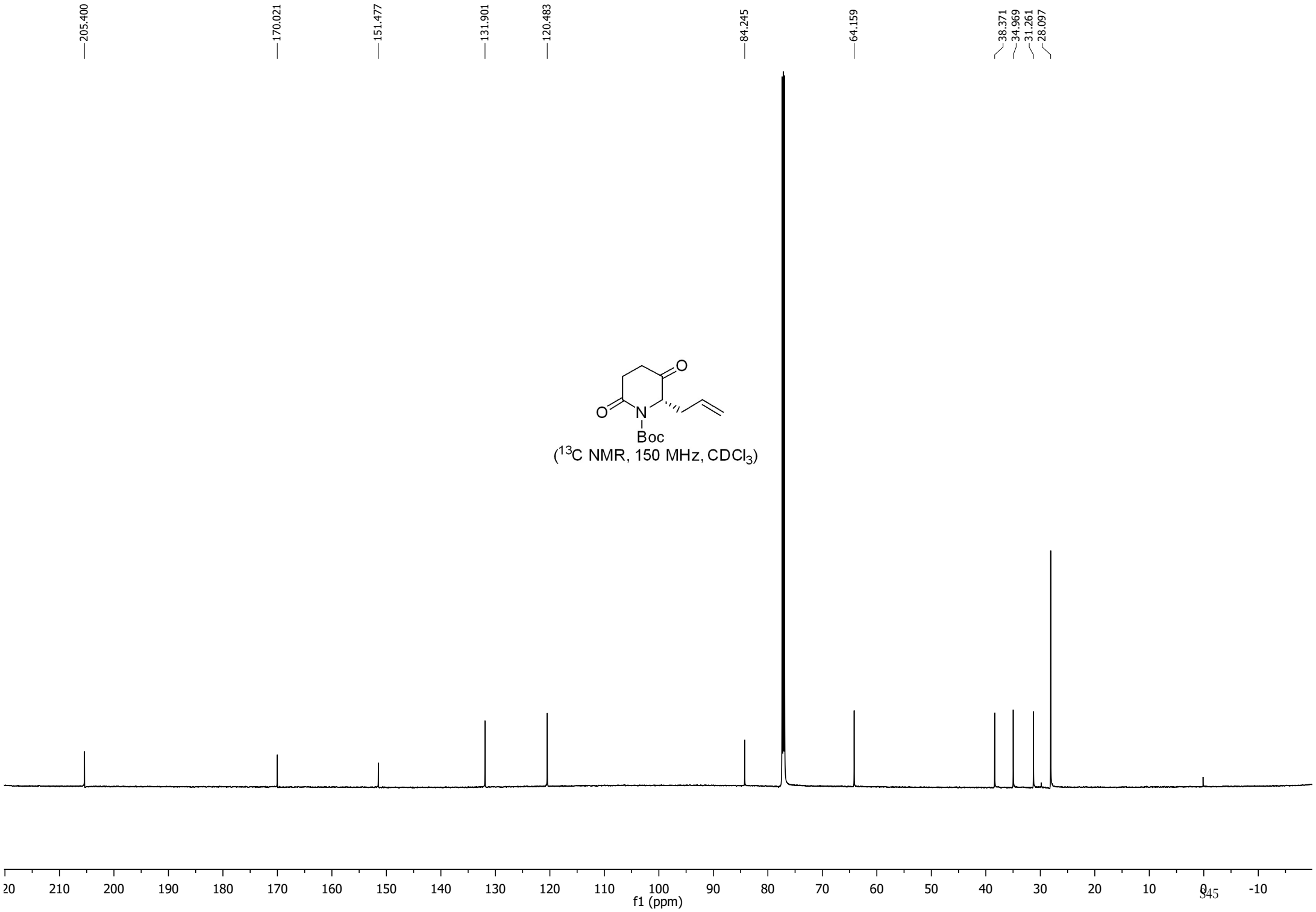
(^{13}C NMR, 150 MHz, $CDCl_3$)

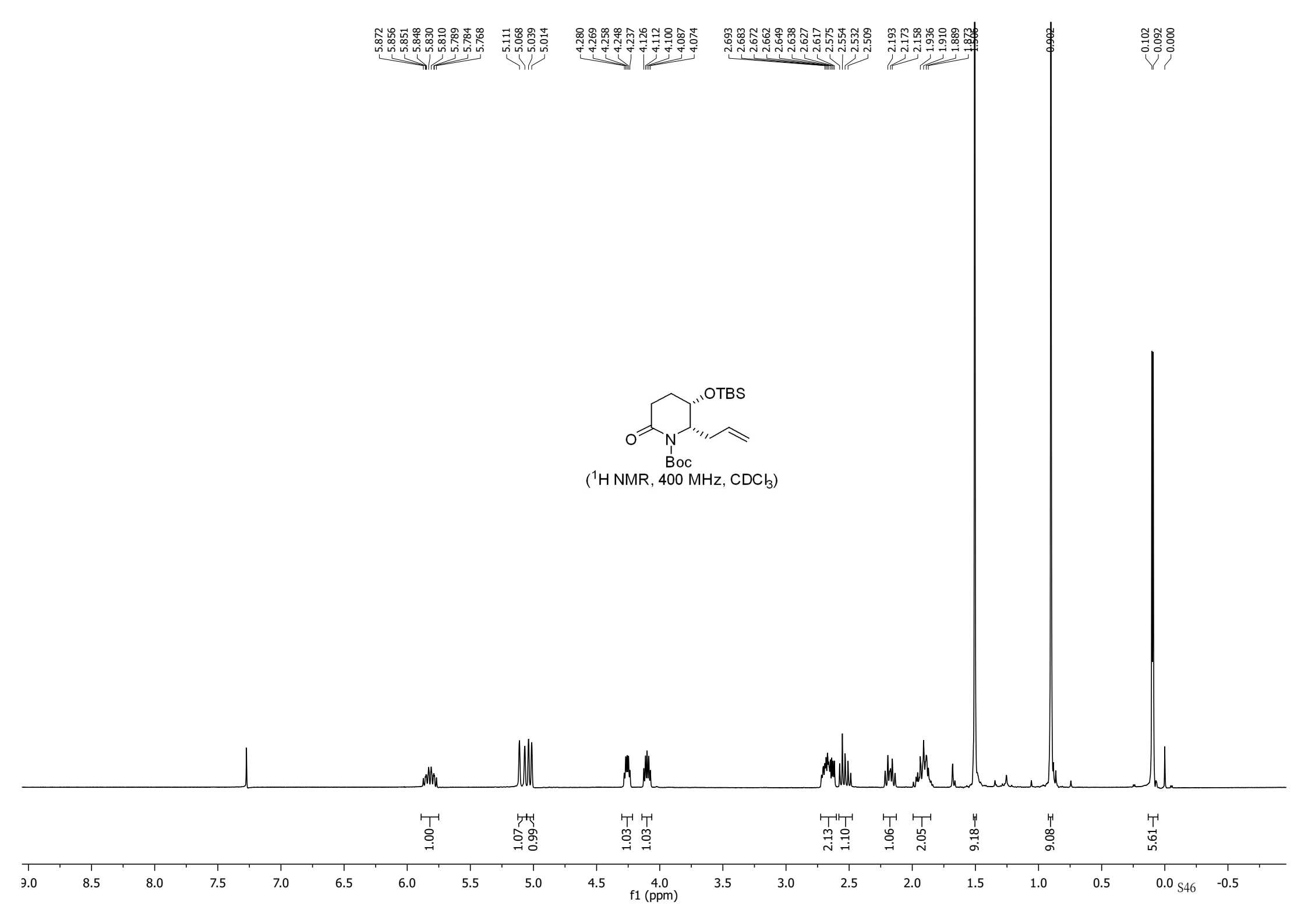

5.750
5.737
5.724
5.710
5.697
5.684
5.670
5.659
5.646
5.091
5.068
5.043
3.202
3.179
3.166
3.155
2.722
2.696
2.660
2.583
2.368
2.351
2.337
2.312
1.791
1.768
1.757
1.732
1.718
1.588
1.559
1.532
1.494
1.470
1.359
0.869
0.035
OTBS
O
H
N
H
H
(1H NMR, 100 MHz, CDCl3)
1.00
2.01
0.98
2.14
0.99
3.11
2.05
0.99
4.04
3.13
1.34
1.99
1.18
9.05
5.73
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)

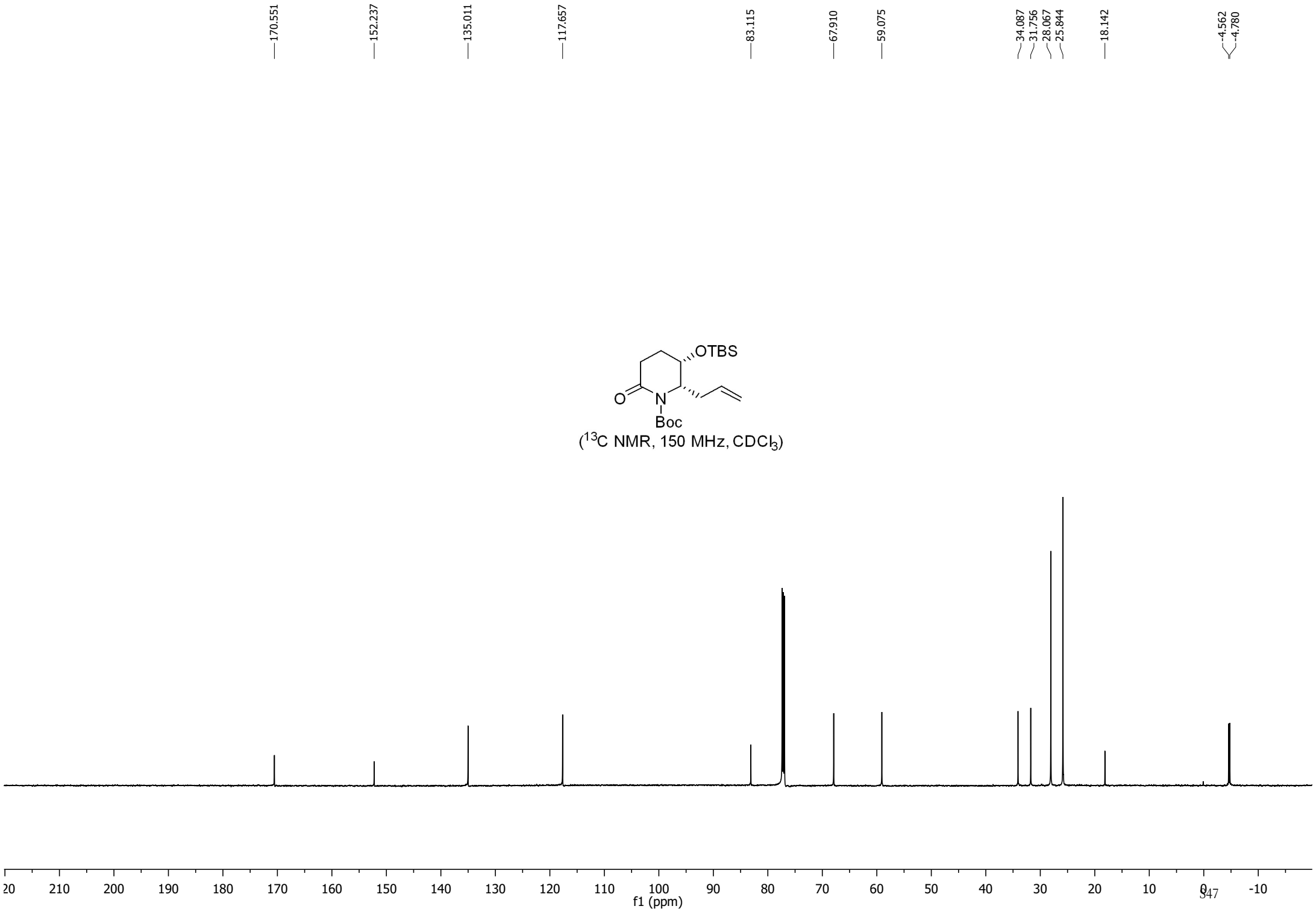

135.929
117.873
73.154
61.710
57.840
55.704
44.409
37.215
34.565
30.119
29.335
27.990
26.003
25.537
25.158
24.782
18.172
-3.887
-4.517
OTBS
O
H
N
H
H
(^{13}C NMR, 150 MHz, $CDCl_3$)
f1 (ppm)

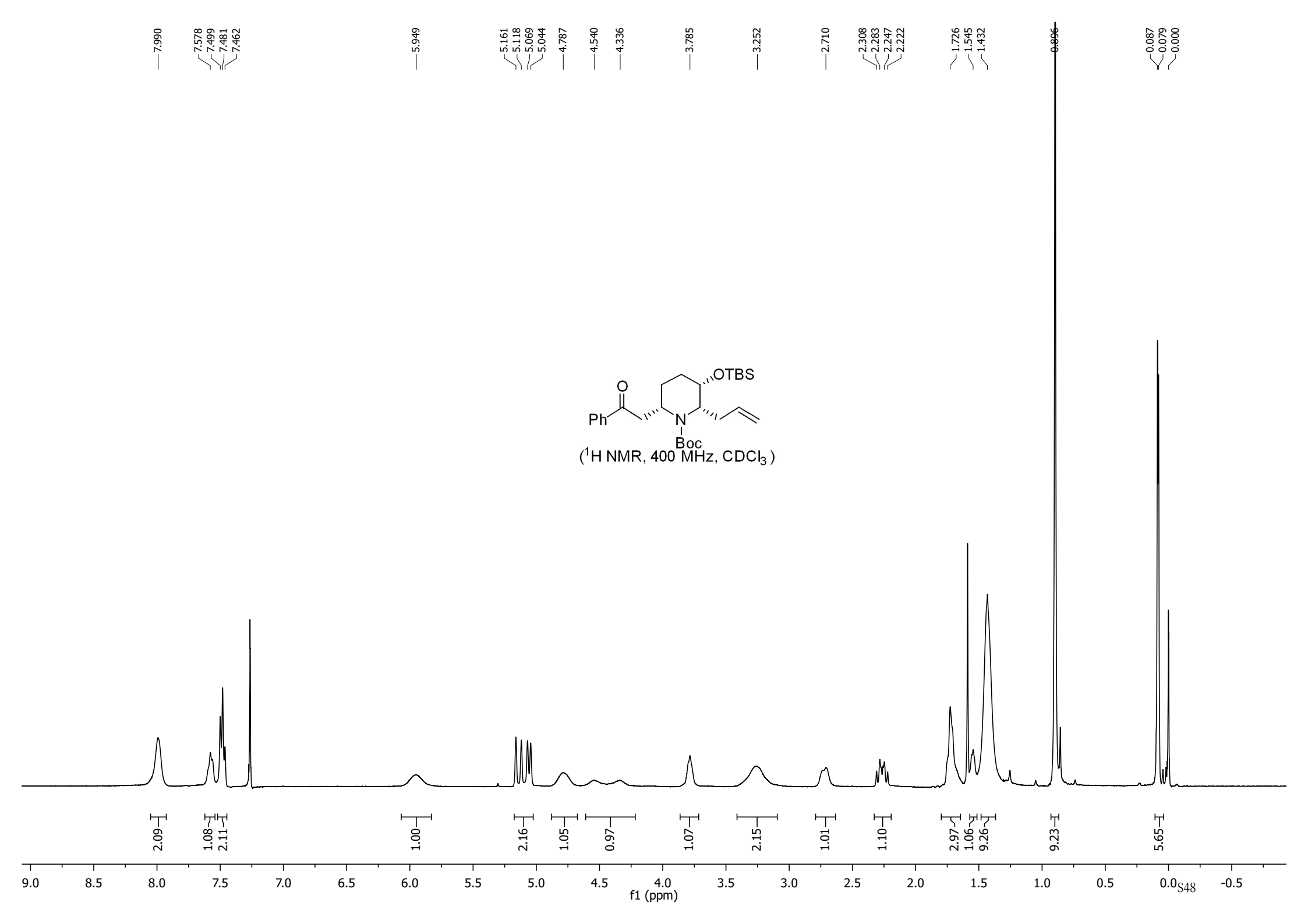


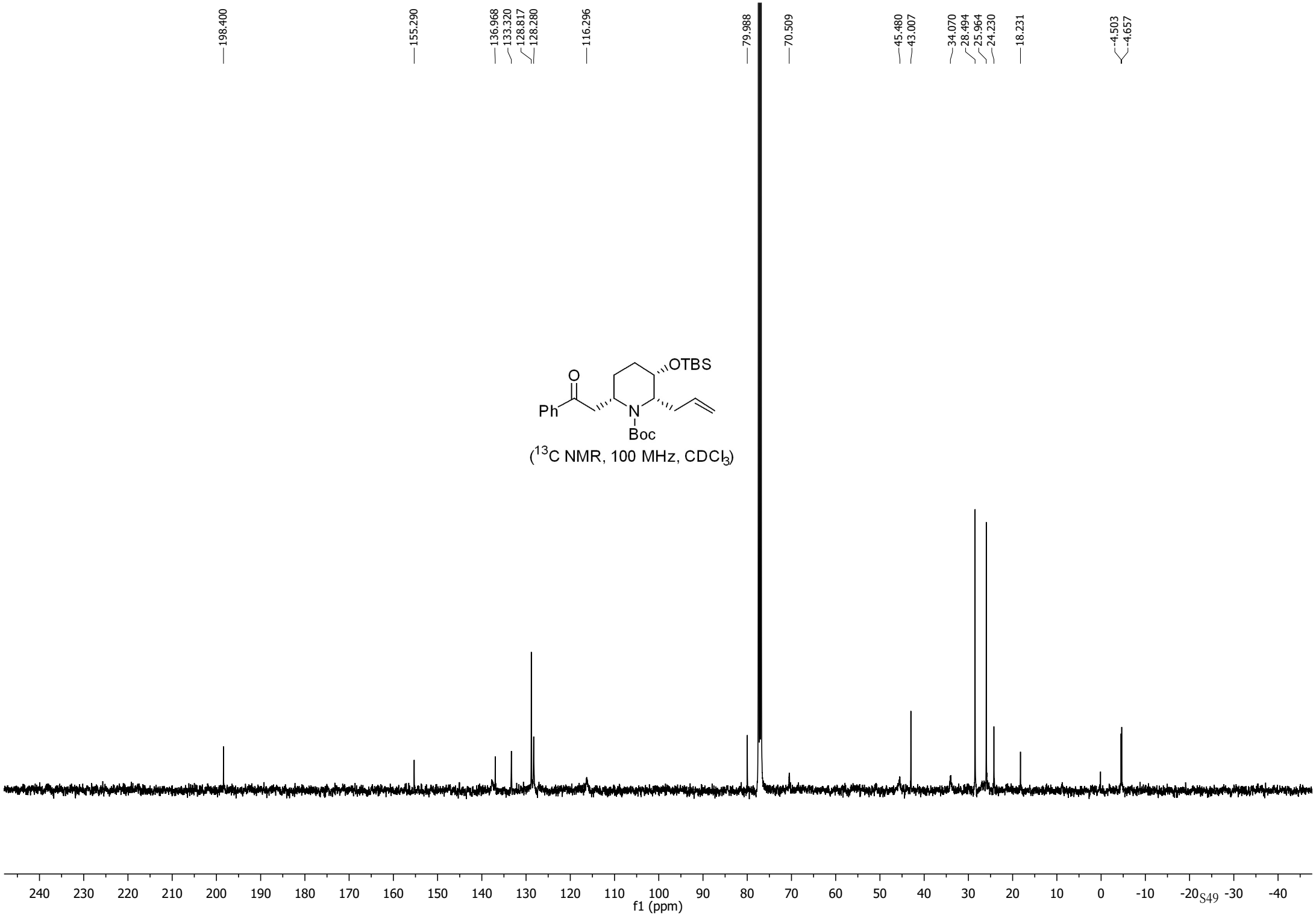
(^{1}H NMR, 400 MHz, $CDCl_3$)

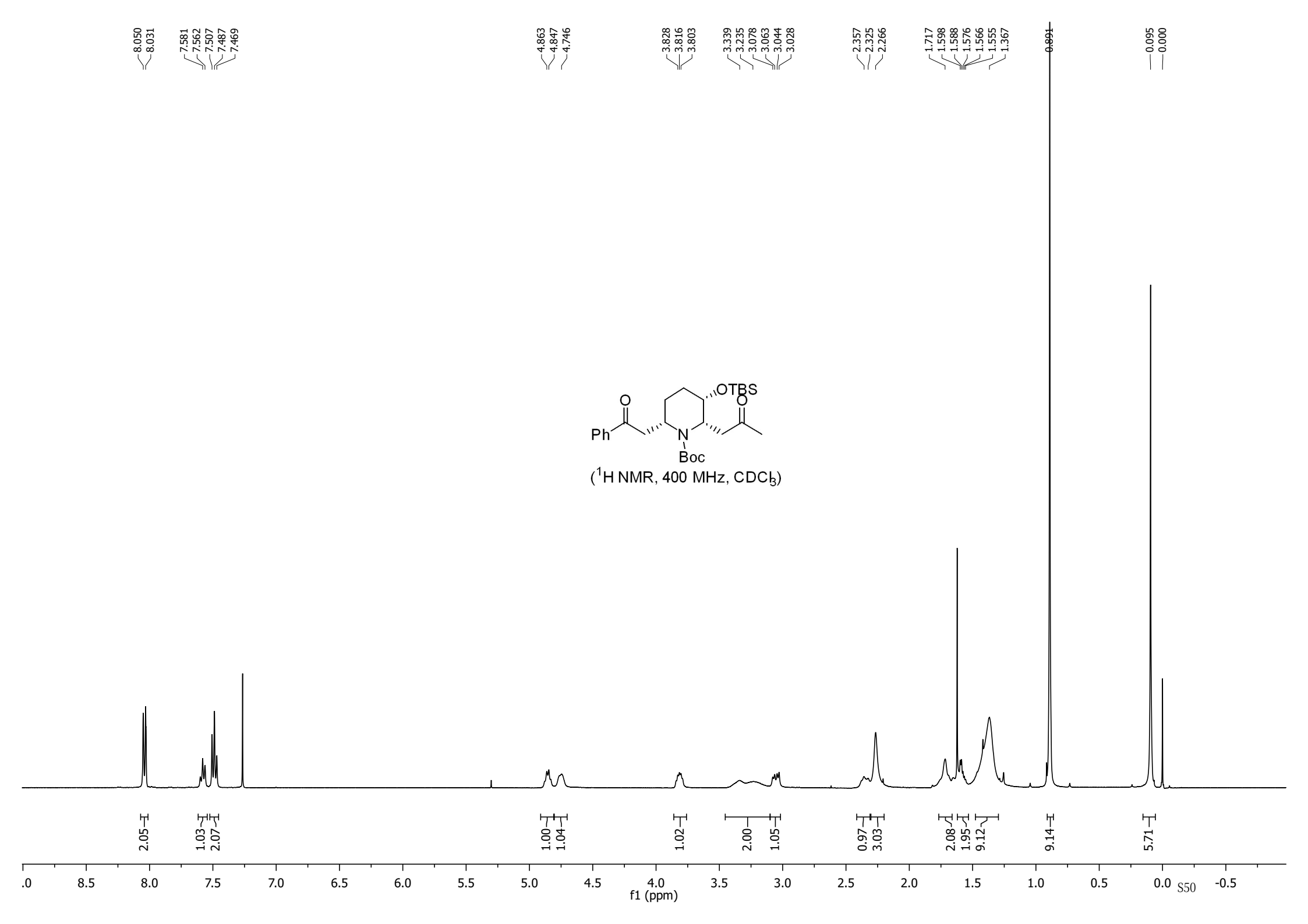

205.400
170.021
151.477
131.901
120.483
84.245
64.159
38.371
34.969
31.261
28.097
O
O
N
Boc
(13C NMR, 150 MHz, CDCl3)
f1 (ppm)

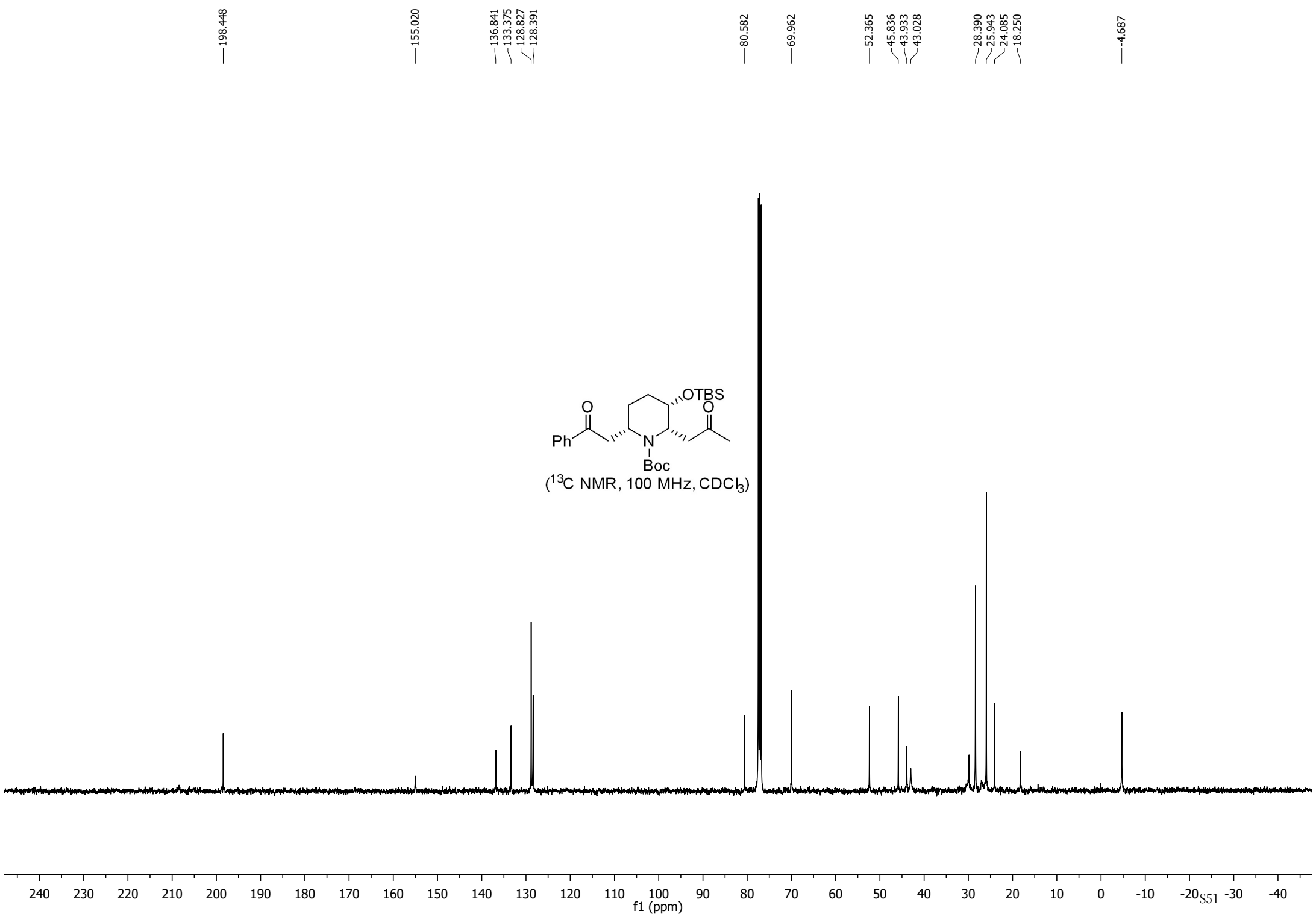

5.872
5.856
5.851
5.848
5.830
5.810
5.789
5.784
5.768
5.111
5.068
5.039
5.014
4.280
4.269
4.258
4.248
4.237
4.126
4.112
4.100
4.087
4.074
2.693
2.683
2.672
2.662
2.649
2.638
2.627
2.617
2.575
2.554
2.532
2.509
2.193
2.173
2.158
1.936
1.910
1.889
1.873
1.506
0.092
0.102
0.092
0.000
OTBS
O
N
Boc
(1H NMR, 400 MHz, CDCl3)
1.00
1.07
0.99
1.03
1.03
2.13
1.10
1.06
2.05
9.18
9.08
5.61
f1 (ppm)

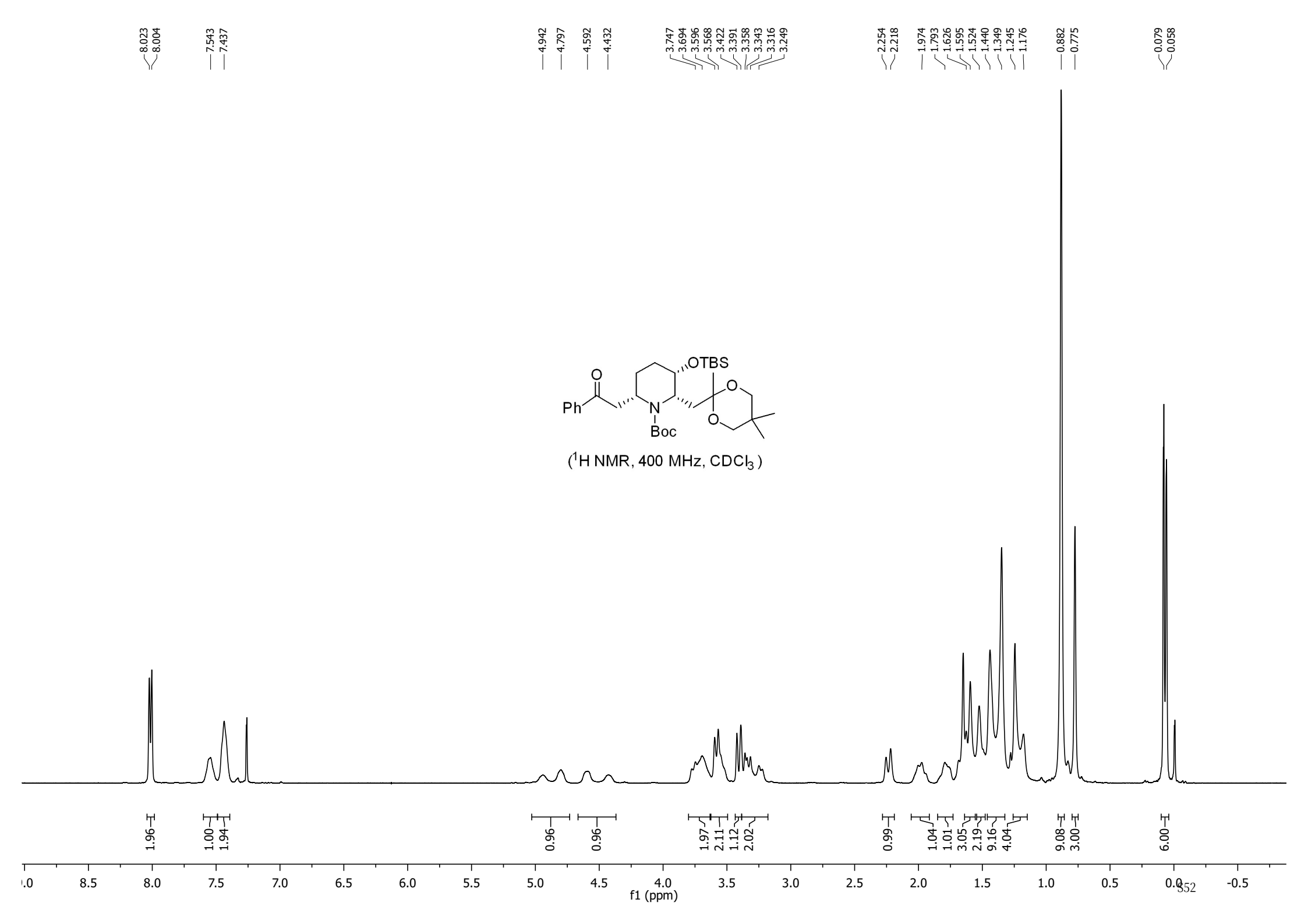

170.551
152.237
135.011
117.657
83.115
67.910
59.075
34.087
31.756
28.067
25.844
18.142
-4.562
-4.780
OTBS
O
N
Boc
(13C NMR, 150 MHz, CDCl3)
f1 (ppm)

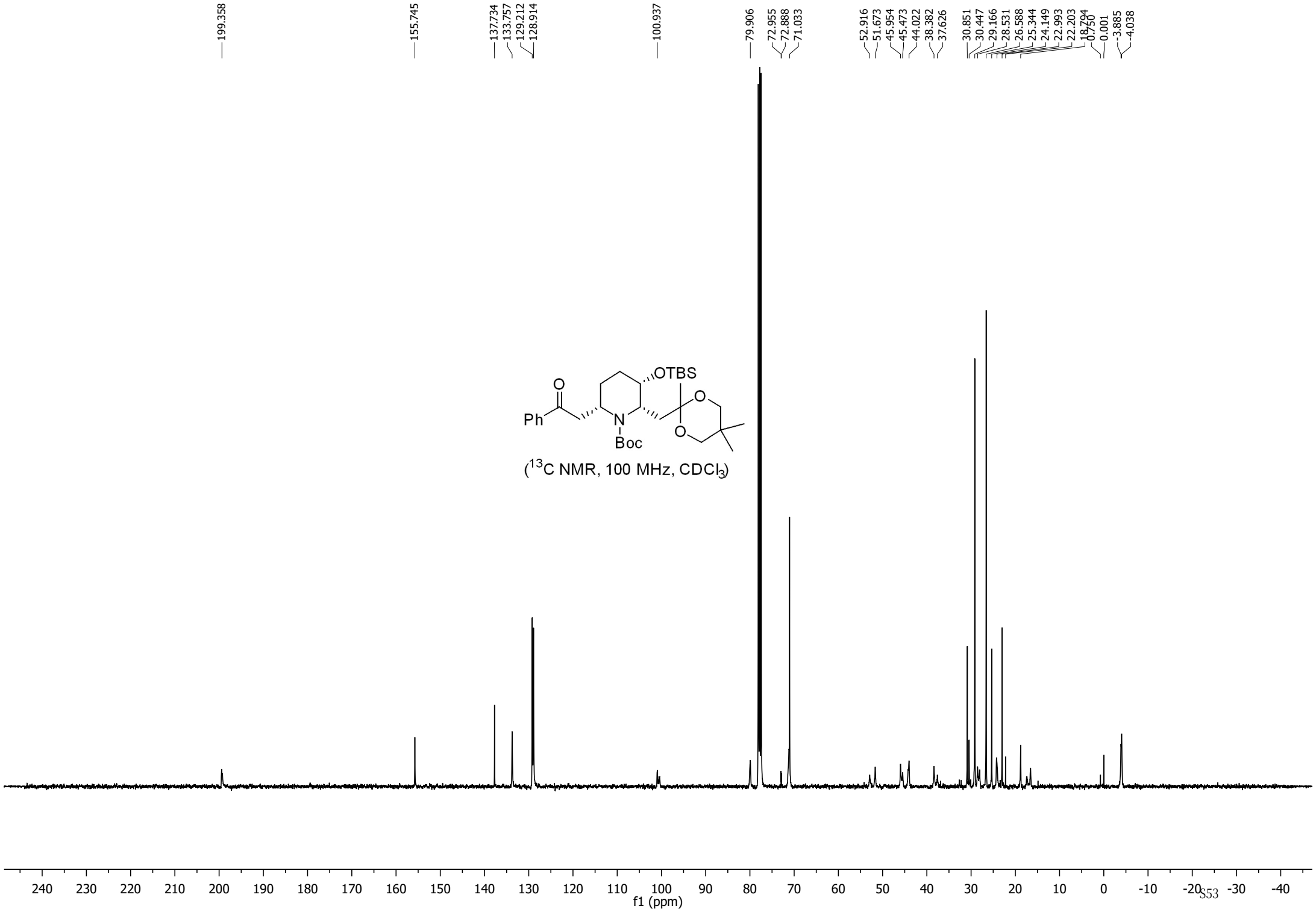

7.990
7.578
7.499
7.481
7.462
5.949
5.161
5.118
5.069
5.044
4.787
4.540
4.336
3.785
3.252
2.710
2.308
2.283
2.247
2.222
1.726
1.545
1.432
0.896
0.087
0.079
0.000
OTBS
O
Ph
N
Boc
(1H NMR, 400 MHz, CDCl3)
2.09
1.08
2.11
1.00
2.16
1.05
0.97
1.07
2.15
1.01
1.10
2.97
1.06
9.26
9.23
5.65
9.0
8.5
8.0
7.5
7.0
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)

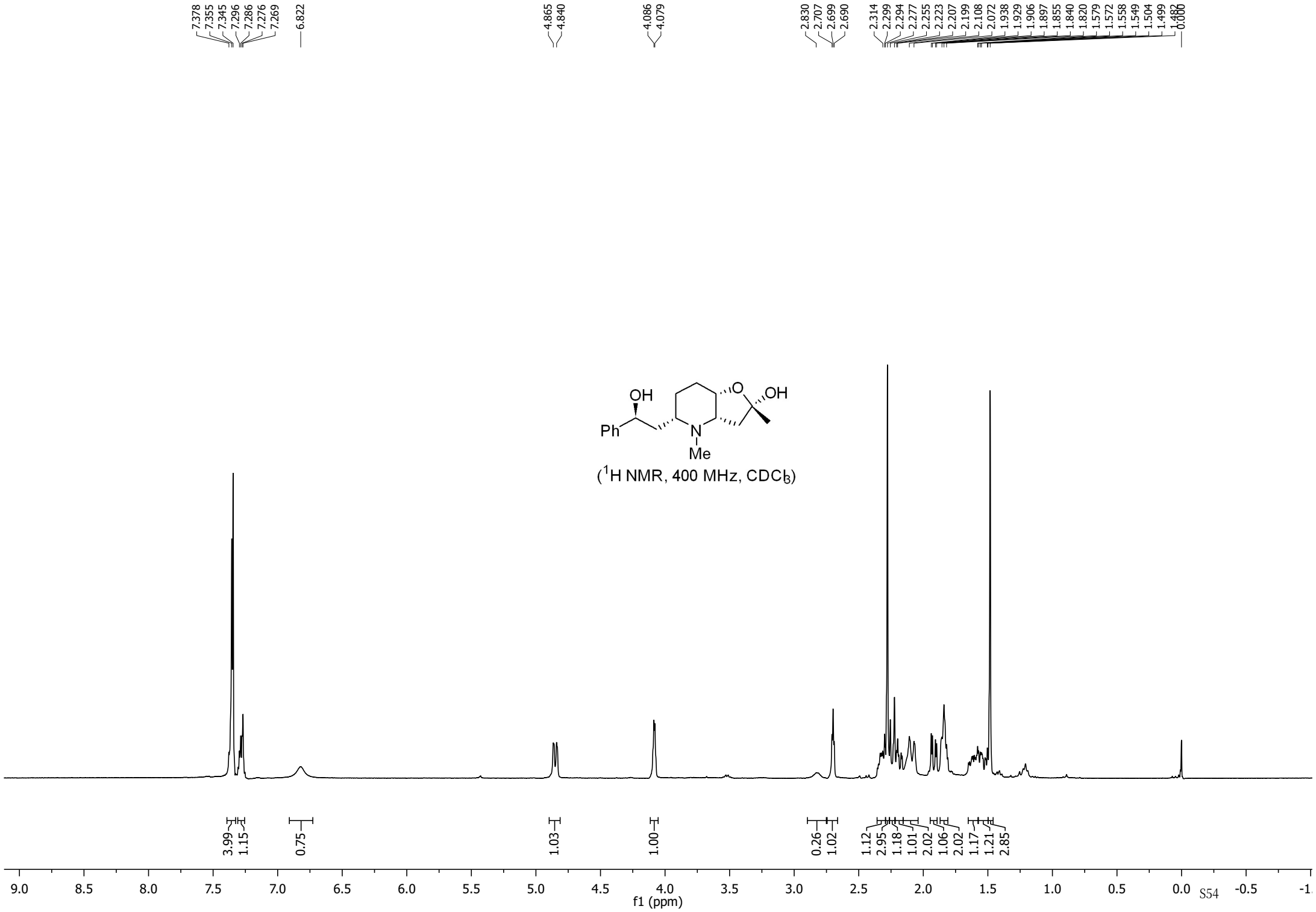

198.400
155.290
136.968
133.320
128.817
128.280
116.296
79.988
70.509
45.480
43.007
34.070
28.494
25.964
24.230
18.231
-4.503
-4.657
OTBS
O
Ph
N
Boc
(13C NMR, 100 MHz, CDCl3)
f1 (ppm)

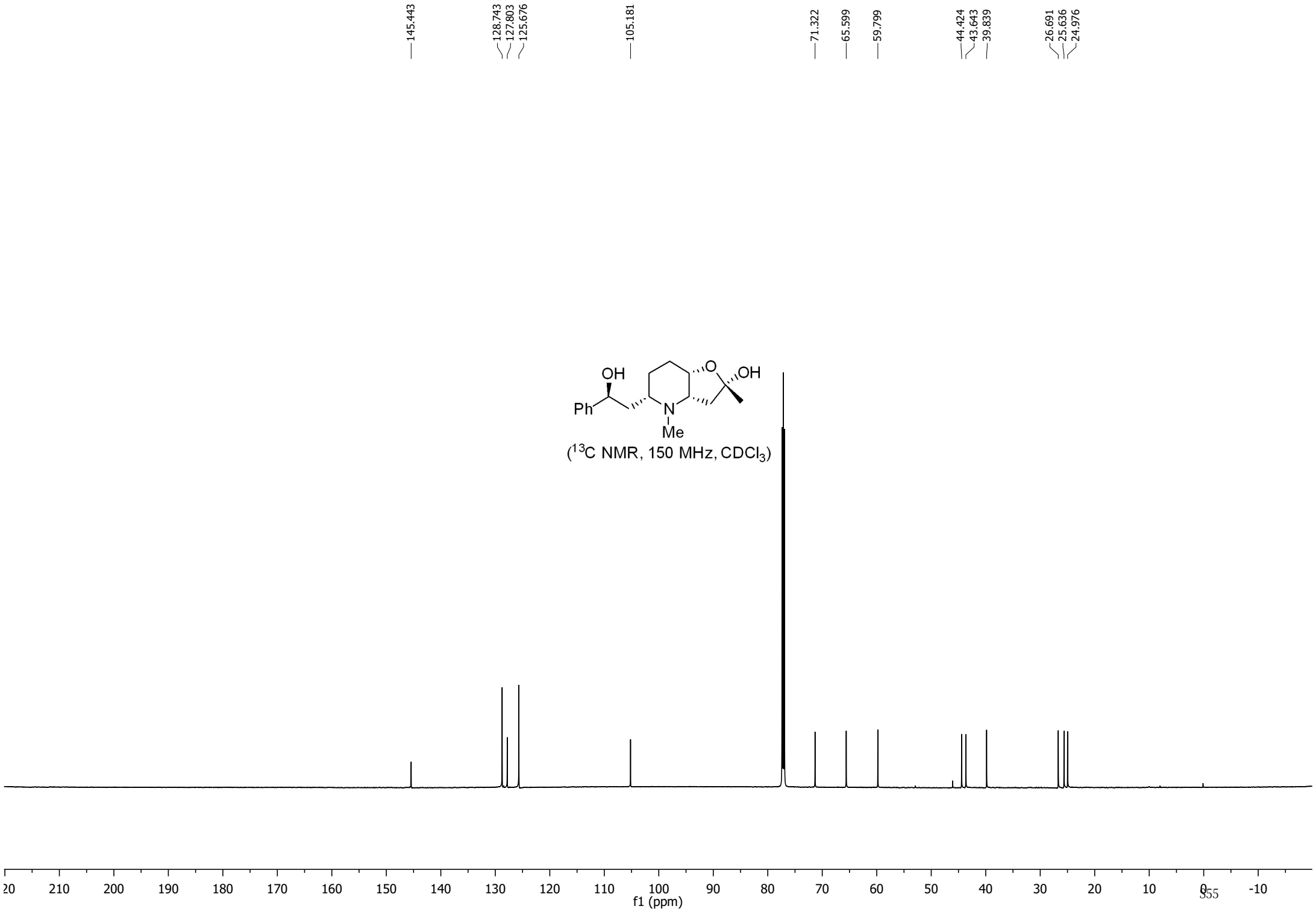

8.050
8.031
7.581
7.562
7.507
7.487
7.469
4.863
4.847
4.746
3.828
3.816
3.803
3.339
3.235
3.078
3.063
3.044
3.028
2.357
2.325
2.266
1.717
1.598
1.588
1.576
1.566
1.555
1.367
0.891
0.095
0.000
OTBS
O
O
Ph
N
Boc
(1H NMR, 400 MHz, CDCl3)
2.05
1.03
2.07
1.00
1.04
1.02
2.00
1.05
0.97
3.03
2.08
1.95
9.12
9.14
5.71
f1 (ppm)


198.448
155.020
136.841
133.375
128.827
128.391
80.582
69.962
52.365
45.836
43.933
43.028
28.390
25.943
24.085
18.250
-4.687
OTBS
O
O
Ph
N
Boc
(13C NMR, 100 MHz, CDCl3)
f1 (ppm)

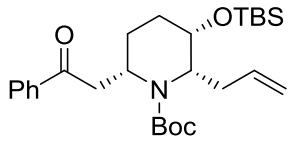

8.023
8.004
7.543
7.437
4.942
4.797
4.592
4.432
3.747
3.694
3.596
3.568
3.422
3.391
3.358
3.343
3.316
3.249
2.254
2.218
1.974
1.793
1.626
1.595
1.524
1.440
1.349
1.245
1.176
0.882
0.775
0.079
0.058
OTBS
O
Ph
N
Boc
O
O
(1H NMR, 400 MHz, CDCl3)
1.96
1.00
1.94
0.96
0.96
1.97
2.11
1.12
2.02
0.99
1.04
1.01
3.05
2.19
9.16
4.04
9.08
3.00
6.00
f1 (ppm)

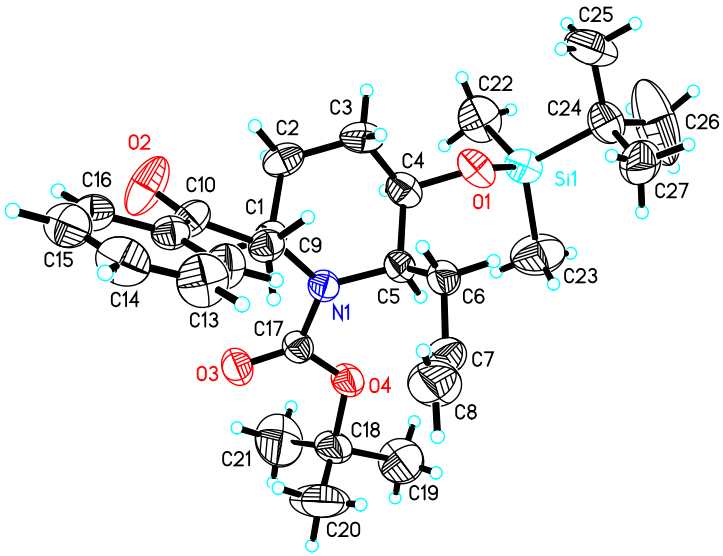

199.358
155.745
137.734
133.757
129.212
128.914
100.937
79.906
72.955
72.888
71.033
52.916
51.673
45.954
45.473
44.022
38.382
37.626
30.851
30.447
29.166
28.531
26.588
25.344
24.149
22.993
22.203
18.794
0.750
0.001
-3.885
-4.038
OTBS
O
Ph
N
Boc
O
O
(^{13}C NMR, 100 MHz, $CDCl_3$)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)


7.378
7.355
7.345
7.296
7.286
7.276
7.269
6.822
4.865
4.840
4.086
4.079
2.830
2.707
2.699
2.690
2.314
2.299
2.294
2.277
2.255
2.223
2.207
2.199
2.108
2.072
1.938
1.929
1.906
1.897
1.855
1.840
1.820
1.579
1.572
1.558
1.549
1.504
1.499
0.000
OH
Ph
O
OH
N
Me
(1H NMR, 400 MHz, CDCl3)
3.99
1.15
0.75
1.03
1.00
0.26
1.02
1.12
2.95
1.18
1.01
2.02
1.06
2.02
1.17
1.21
2.85
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)


145.443
128.743
127.803
125.676
105.181
71.322
65.599
59.799
44.424
43.643
39.839
26.691
25.636
24.976
OH
Ph
N
Me
O
OH
(^{13}C NMR, 150 MHz, $CDCl_3$)
f1 (ppm)

ORTEP drawing of the X-ray crystallographic structure of **(2*S*, 5*S*, 6*S*)-7a**





CCDC1585542 contains the supplementary crystallographic data for this paper.
These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via
www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystal data and structure refinement for mo_d8v17583_0m.

Identification code	mo_d8v17583_0m	
Empirical formula	C27 H43 N O4 Si	
Formula weight	473.71	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2	
Unit cell dimensions	a = 33.6160(19) Å	α= 90 °.
	b = 7.9053(4) Å	β= 91.380(2) °.
	c = 11.1852(7) Å	γ = 90 °.
Volume	2971.5(3) $Å^3$	
Z	4	
Density (calculated)	1.059 Mg/m^3	
Absorption coefficient	0.107 mm^{-1}	
F(000)	1032	
Crystal size	0.180 x 0.160 x 0.130 mm^3	
Theta range for data collection	2.424 to 25.997 °.	
Index ranges	-41<=h<=41, -9<=k<=9, -13<=l<=13	
Reflections collected	34676	
Independent reflections	5776 [R(int) = 0.0320]	
Completeness to theta = 25.242 °	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6943	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5776 / 1 / 307	
Goodness-of-fit on F^2	1.008	
Final R indices [I>2sigma(I)]	R1 = 0.0449, wR2 = 0.1270	
R indices (all data)	R1 = 0.0538, wR2 = 0.1375	
Absolute structure parameter	-0.04(3)	
Largest diff. peak and hole	0.204 and -0.142 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for mo_d8v17583_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Si(1)	7555(1)	2423(1)	7619(1)	79(1)

N(1)	6133(1)	3742(3)	7204(2)	62(1)
O(1)	7217(1)	3428(3)	6809(2)	83(1)
O(2)	5465(1)	3859(3)	3997(3)	121(1)
O(3)	5520(1)	3272(4)	7927(2)	84(1)
O(4)	6059(1)	3449(4)	9166(2)	75(1)
C(1)	5970(1)	3614(4)	5966(2)	64(1)
C(2)	6254(1)	2582(5)	5203(3)	80(1)
C(3)	6686(1)	3098(5)	5364(3)	83(1)
C(4)	6806(1)	2994(4)	6653(3)	75(1)
C(5)	6554(1)	4155(4)	7432(3)	67(1)
C(6)	6654(1)	6042(4)	7263(3)	75(1)
C(7)	6440(1)	7186(5)	8074(4)	99(1)
C(8)	6255(2)	8535(8)	7804(7)	146(2)
C(9)	5862(1)	5334(3)	5429(3)	63(1)
C(10)	5562(1)	5218(4)	4408(3)	69(1)
C(11)	5384(1)	6787(4)	3897(2)	62(1)
C(12)	5508(1)	8390(4)	4253(3)	80(1)
C(13)	5333(2)	9800(5)	3753(5)	102(1)
C(14)	5035(1)	9660(5)	2923(4)	99(1)
C(15)	4910(1)	8070(6)	2551(3)	93(1)
C(16)	5082(1)	6638(5)	3040(3)	75(1)
C(17)	5872(1)	3471(4)	8094(2)	61(1)
C(18)	5832(1)	3312(8)	10264(3)	100(1)
C(19)	6165(2)	3342(13)	11215(4)	155(3)
C(20)	5579(2)	4851(13)	10362(6)	179(4)
C(21)	5613(2)	1711(13)	10295(6)	174(3)
C(22)	7564(2)	143(6)	7232(7)	126(2)
C(23)	7436(2)	2639(10)	9231(4)	150(2)
C(24)	8026(1)	3551(6)	7227(4)	96(1)
C(25)	8099(2)	3361(8)	5893(5)	141(2)
C(26)	8372(2)	2879(17)	7983(12)	265(7)
C(27)	7979(2)	5454(7)	7460(5)	122(2)

Table 3. Bond lengths [Å] and angles [°] for mo_d8v17583_0m.

Si(1)-O(1)	1.641(3)
Si(1)-C(22)	1.854(5)
Si(1)-C(23)	1.864(5)
Si(1)-C(24)	1.879(4)
N(1)-C(17)	1.359(3)
N(1)-C(5)	1.471(4)
N(1)-C(1)	1.481(3)
O(1)-C(4)	1.430(4)
O(2)-C(10)	1.211(4)
O(3)-C(17)	1.202(3)
O(4)-C(17)	1.340(3)
O(4)-C(18)	1.464(3)
C(1)-C(9)	1.527(4)
C(1)-C(2)	1.531(4)
C(1)-H(1)	0.9800
C(2)-C(3)	1.517(5)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-C(4)	1.489(5)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(4)-C(5)	1.533(4)
C(4)-H(4)	0.9800
C(5)-C(6)	1.541(5)
C(5)-H(5)	0.9800
C(6)-C(7)	1.480(5)
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
C(7)-C(8)	1.266(8)
C(7)-H(7)	0.9300
C(8)-H(8A)	0.9300
C(8)-H(8B)	0.9300
C(9)-C(10)	1.508(4)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-C(11)	1.486(4)

C(11)-C(16)	1.384(5)
C(11)-C(12)	1.389(5)
C(12)-C(13)	1.372(5)
C(12)-H(12)	0.9300
C(13)-C(14)	1.354(7)
C(13)-H(13)	0.9300
C(14)-C(15)	1.387(7)
C(14)-H(14)	0.9300
C(15)-C(16)	1.379(5)
C(15)-H(15)	0.9300
C(16)-H(16)	0.9300
C(18)-C(21)	1.466(9)
C(18)-C(20)	1.490(9)
C(18)-C(19)	1.526(6)
C(19)-H(19A)	0.9600
C(19)-H(19B)	0.9600
C(19)-H(19C)	0.9600
C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600
C(21)-H(21A)	0.9600
C(21)-H(21B)	0.9600
C(21)-H(21C)	0.9600
C(22)-H(22A)	0.9600
C(22)-H(22B)	0.9600
C(22)-H(22C)	0.9600
C(23)-H(23A)	0.9600
C(23)-H(23B)	0.9600
C(23)-H(23C)	0.9600
C(24)-C(26)	1.517(8)
C(24)-C(25)	1.525(7)
C(24)-C(27)	1.536(7)
C(25)-H(25A)	0.9600
C(25)-H(25B)	0.9600
C(25)-H(25C)	0.9600
C(26)-H(26A)	0.9600
C(26)-H(26B)	0.9600
C(26)-H(26C)	0.9600

C(27)-H(27A)	0.9600
C(27)-H(27B)	0.9600
C(27)-H(27C)	0.9600

O(1)-Si(1)-C(22)	110.9(2)
O(1)-Si(1)-C(23)	109.1(3)
C(22)-Si(1)-C(23)	108.7(3)
O(1)-Si(1)-C(24)	102.60(15)
C(22)-Si(1)-C(24)	112.8(2)
C(23)-Si(1)-C(24)	112.6(3)
C(17)-N(1)-C(5)	123.0(2)
C(17)-N(1)-C(1)	116.3(2)
C(5)-N(1)-C(1)	120.7(2)
C(4)-O(1)-Si(1)	127.3(2)
C(17)-O(4)-C(18)	120.6(2)
N(1)-C(1)-C(9)	112.7(2)
N(1)-C(1)-C(2)	109.7(2)
C(9)-C(1)-C(2)	113.6(2)
N(1)-C(1)-H(1)	106.8
C(9)-C(1)-H(1)	106.8
C(2)-C(1)-H(1)	106.8
C(3)-C(2)-C(1)	113.6(3)
C(3)-C(2)-H(2A)	108.9
C(1)-C(2)-H(2A)	108.9
C(3)-C(2)-H(2B)	108.9
C(1)-C(2)-H(2B)	108.9
H(2A)-C(2)-H(2B)	107.7
C(4)-C(3)-C(2)	109.6(3)
C(4)-C(3)-H(3A)	109.8
C(2)-C(3)-H(3A)	109.8
C(4)-C(3)-H(3B)	109.8
C(2)-C(3)-H(3B)	109.8
H(3A)-C(3)-H(3B)	108.2
O(1)-C(4)-C(3)	110.0(3)
O(1)-C(4)-C(5)	109.3(3)
C(3)-C(4)-C(5)	112.2(3)
O(1)-C(4)-H(4)	108.4
C(3)-C(4)-H(4)	108.4

C(5)-C(4)-H(4)	108.4
N(1)-C(5)-C(4)	108.1(2)
N(1)-C(5)-C(6)	113.8(3)
C(4)-C(5)-C(6)	112.7(2)
N(1)-C(5)-H(5)	107.3
C(4)-C(5)-H(5)	107.3
C(6)-C(5)-H(5)	107.3
C(7)-C(6)-C(5)	114.0(3)
C(7)-C(6)-H(6A)	108.8
C(5)-C(6)-H(6A)	108.8
C(7)-C(6)-H(6B)	108.8
C(5)-C(6)-H(6B)	108.8
H(6A)-C(6)-H(6B)	107.7
C(8)-C(7)-C(6)	127.7(5)
C(8)-C(7)-H(7)	116.2
C(6)-C(7)-H(7)	116.2
C(7)-C(8)-H(8A)	120.0
C(7)-C(8)-H(8B)	120.0
H(8A)-C(8)-H(8B)	120.0
C(10)-C(9)-C(1)	113.0(2)
C(10)-C(9)-H(9A)	109.0
C(1)-C(9)-H(9A)	109.0
C(10)-C(9)-H(9B)	109.0
C(1)-C(9)-H(9B)	109.0
H(9A)-C(9)-H(9B)	107.8
O(2)-C(10)-C(11)	119.5(3)
O(2)-C(10)-C(9)	120.7(3)
C(11)-C(10)-C(9)	119.8(2)
C(16)-C(11)-C(12)	119.0(3)
C(16)-C(11)-C(10)	118.6(3)
C(12)-C(11)-C(10)	122.4(3)
C(13)-C(12)-C(11)	120.2(3)
C(13)-C(12)-H(12)	119.9
C(11)-C(12)-H(12)	119.9
C(14)-C(13)-C(12)	121.0(4)
C(14)-C(13)-H(13)	119.5
C(12)-C(13)-H(13)	119.5
C(13)-C(14)-C(15)	119.6(3)

C(13)-C(14)-H(14)	120.2
C(15)-C(14)-H(14)	120.2
C(16)-C(15)-C(14)	120.2(4)
C(16)-C(15)-H(15)	119.9
C(14)-C(15)-H(15)	119.9
C(15)-C(16)-C(11)	119.9(4)
C(15)-C(16)-H(16)	120.0
C(11)-C(16)-H(16)	120.0
O(3)-C(17)-O(4)	125.1(2)
O(3)-C(17)-N(1)	123.8(2)
O(4)-C(17)-N(1)	111.1(2)
C(21)-C(18)-O(4)	110.9(4)
C(21)-C(18)-C(20)	114.5(5)
O(4)-C(18)-C(20)	108.1(5)
C(21)-C(18)-C(19)	111.0(6)
O(4)-C(18)-C(19)	101.3(3)
C(20)-C(18)-C(19)	110.3(6)
C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(18)-C(20)-H(20A)	109.5
C(18)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(18)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(18)-C(21)-H(21A)	109.5
C(18)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(18)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
Si(1)-C(22)-H(22A)	109.5
Si(1)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5

Si(1)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
Si(1)-C(23)-H(23A)	109.5
Si(1)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
Si(1)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(26)-C(24)-C(25)	111.8(7)
C(26)-C(24)-C(27)	109.2(7)
C(25)-C(24)-C(27)	106.4(4)
C(26)-C(24)-Si(1)	110.1(4)
C(25)-C(24)-Si(1)	109.7(3)
C(27)-C(24)-Si(1)	109.5(3)
C(24)-C(25)-H(25A)	109.5
C(24)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(24)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(24)-C(26)-H(26A)	109.5
C(24)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(24)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(24)-C(27)-H(27A)	109.5
C(24)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(24)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for mo_d8v17583_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si(1)	85(1)	66(1)	86(1)	10(1)	13(1)	6(1)
N(1)	61(1)	70(1)	55(1)	4(1)	5(1)	-9(1)
O(1)	64(1)	77(1)	110(2)	19(1)	19(1)	4(1)
O(2)	181(3)	54(1)	124(2)	-6(1)	-72(2)	-5(2)
O(3)	58(1)	119(2)	74(1)	5(1)	0(1)	-11(1)
O(4)	60(1)	111(2)	54(1)	10(1)	4(1)	-2(1)
C(1)	76(2)	56(1)	58(1)	2(1)	0(1)	-7(1)
C(2)	107(2)	62(2)	70(2)	-8(2)	2(2)	10(2)
C(3)	101(2)	72(2)	79(2)	-5(2)	27(2)	16(2)
C(4)	70(2)	62(2)	93(2)	8(1)	15(1)	2(1)
C(5)	58(1)	75(2)	66(2)	2(1)	7(1)	-8(1)
C(6)	65(2)	71(2)	89(2)	-12(2)	11(1)	-10(1)
C(7)	107(3)	85(3)	105(3)	-27(2)	18(2)	-12(2)
C(8)	145(4)	97(3)	198(6)	-43(4)	40(4)	4(3)
C(9)	74(2)	53(1)	61(2)	-3(1)	6(1)	-2(1)
C(10)	92(2)	50(1)	64(2)	-3(1)	-5(1)	-5(1)
C(11)	71(2)	59(1)	56(1)	4(1)	9(1)	-1(1)
C(12)	89(2)	55(2)	97(2)	3(2)	-3(2)	-5(2)
C(13)	122(3)	55(2)	128(3)	14(2)	1(3)	0(2)
C(14)	108(3)	82(3)	108(3)	28(2)	12(2)	23(2)
C(15)	93(2)	108(3)	79(2)	17(2)	3(2)	19(2)
C(16)	82(2)	81(2)	63(2)	1(2)	9(1)	2(2)
C(17)	57(1)	66(2)	61(1)	6(1)	3(1)	-1(1)
C(18)	79(2)	166(4)	54(2)	0(2)	15(1)	0(3)
C(19)	134(4)	267(9)	61(2)	18(4)	-12(2)	-2(5)
C(20)	167(6)	262(10)	108(4)	-44(5)	28(4)	84(6)
C(21)	172(6)	247(9)	104(4)	54(5)	30(4)	-79(6)
C(22)	123(4)	69(2)	185(5)	-2(3)	8(3)	13(2)
C(23)	208(6)	154(5)	88(3)	22(3)	31(3)	-4(5)
C(24)	75(2)	97(3)	115(3)	14(2)	-1(2)	5(2)
C(25)	154(4)	115(4)	158(4)	-12(4)	88(4)	-8(3)
C(26)	109(4)	286(13)	395(15)	190(13)	-81(7)	-31(6)
C(27)	143(4)	103(3)	121(4)	-14(3)	15(3)	-40(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for mo_d8v17583_0m.

	x	y	z	U(eq)
H(1)	5722	2967	6005	77
H(2A)	6228	1395	5407	95
H(2B)	6175	2711	4367	95
H(3A)	6853	2354	4901	100
H(3B)	6722	4245	5078	100
H(4)	6769	1826	6922	89
H(5)	6617	3871	8269	80
H(6A)	6938	6200	7392	90
H(6B)	6590	6358	6443	90
H(7)	6440	6878	8876	119
H(8A)	6244	8907	7015	175
H(8B)	6131	9155	8395	175
H(9A)	5756	6049	6049	75
H(9B)	6102	5867	5145	75
H(12)	5709	8508	4831	96
H(13)	5421	10867	3988	122
H(14)	4915	10625	2605	119
H(15)	4709	7969	1968	112
H(16)	4996	5573	2795	90
H(19A)	6368	2548	11005	232
H(19B)	6060	3038	11975	232
H(19C)	6278	4457	11263	232
H(20A)	5745	5840	10367	268
H(20B)	5434	4803	11090	268
H(20C)	5395	4900	9692	268
H(21A)	5420	1682	9648	261
H(21B)	5479	1618	11041	261
H(21C)	5795	785	10218	261
H(22A)	7337	-407	7557	188
H(22B)	7803	-361	7560	188
H(22C)	7559	17	6378	188
H(23A)	7382	3804	9408	225

H(23B)	7658	2256	9714	225
H(23C)	7206	1969	9400	225
H(25A)	8347	3888	5704	211
H(25B)	7886	3895	5445	211
H(25C)	8109	2182	5691	211
H(26A)	8618	3256	7654	397
H(26B)	8365	1665	7985	397
H(26C)	8352	3290	8786	397
H(27A)	7881	5625	8250	183
H(27B)	7794	5925	6883	183
H(27C)	8232	6002	7394	183

Table 6. Torsion angles [°] for mo_d8v17583_0m.

C(22)-Si(1)-O(1)-C(4)	52.3(3)
C(23)-Si(1)-O(1)-C(4)	-67.5(4)
C(24)-Si(1)-O(1)-C(4)	172.9(3)
C(17)-N(1)-C(1)-C(9)	97.5(3)
C(5)-N(1)-C(1)-C(9)	-82.1(3)
C(17)-N(1)-C(1)-C(2)	-135.0(3)
C(5)-N(1)-C(1)-C(2)	45.4(3)
N(1)-C(1)-C(2)-C(3)	-46.3(4)
C(9)-C(1)-C(2)-C(3)	80.7(3)
C(1)-C(2)-C(3)-C(4)	55.6(4)
Si(1)-O(1)-C(4)-C(3)	-134.1(3)
Si(1)-O(1)-C(4)-C(5)	102.2(3)
C(2)-C(3)-C(4)-O(1)	178.2(3)
C(2)-C(3)-C(4)-C(5)	-59.8(3)
C(17)-N(1)-C(5)-C(4)	131.3(3)
C(1)-N(1)-C(5)-C(4)	-49.1(3)
C(17)-N(1)-C(5)-C(6)	-102.6(3)
C(1)-N(1)-C(5)-C(6)	76.9(3)
O(1)-C(4)-C(5)-N(1)	177.0(2)
C(3)-C(4)-C(5)-N(1)	54.7(3)
O(1)-C(4)-C(5)-C(6)	50.3(4)
C(3)-C(4)-C(5)-C(6)	-72.0(4)
N(1)-C(5)-C(6)-C(7)	61.1(4)
C(4)-C(5)-C(6)-C(7)	-175.3(3)
C(5)-C(6)-C(7)-C(8)	-132.7(5)
N(1)-C(1)-C(9)-C(10)	-158.0(2)
C(2)-C(1)-C(9)-C(10)	76.6(3)
C(1)-C(9)-C(10)-O(2)	-8.6(5)
C(1)-C(9)-C(10)-C(11)	171.5(3)
O(2)-C(10)-C(11)-C(16)	6.2(5)
C(9)-C(10)-C(11)-C(16)	-173.9(3)
O(2)-C(10)-C(11)-C(12)	-174.1(4)
C(9)-C(10)-C(11)-C(12)	5.8(4)
C(16)-C(11)-C(12)-C(13)	-0.3(5)
C(10)-C(11)-C(12)-C(13)	180.0(4)
C(11)-C(12)-C(13)-C(14)	1.0(6)

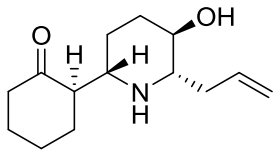
C(12)-C(13)-C(14)-C(15)	-1.5(7)
C(13)-C(14)-C(15)-C(16)	1.4(6)
C(14)-C(15)-C(16)-C(11)	-0.7(5)
C(12)-C(11)-C(16)-C(15)	0.2(5)
C(10)-C(11)-C(16)-C(15)	179.9(3)
C(18)-O(4)-C(17)-O(3)	-5.3(5)
C(18)-O(4)-C(17)-N(1)	175.0(3)
C(5)-N(1)-C(17)-O(3)	173.6(3)
C(1)-N(1)-C(17)-O(3)	-6.0(4)
C(5)-N(1)-C(17)-O(4)	-6.7(4)
C(1)-N(1)-C(17)-O(4)	173.7(2)
C(17)-O(4)-C(18)-C(21)	62.3(6)
C(17)-O(4)-C(18)-C(20)	-63.9(6)
C(17)-O(4)-C(18)-C(19)	-179.9(5)
O(1)-Si(1)-C(24)-C(26)	175.2(7)
C(22)-Si(1)-C(24)-C(26)	-65.4(8)
C(23)-Si(1)-C(24)-C(26)	58.1(8)
O(1)-Si(1)-C(24)-C(25)	-61.3(4)
C(22)-Si(1)-C(24)-C(25)	58.1(4)
C(23)-Si(1)-C(24)-C(25)	-178.5(4)
O(1)-Si(1)-C(24)-C(27)	55.1(4)
C(22)-Si(1)-C(24)-C(27)	174.5(4)
C(23)-Si(1)-C(24)-C(27)	-62.1(4)

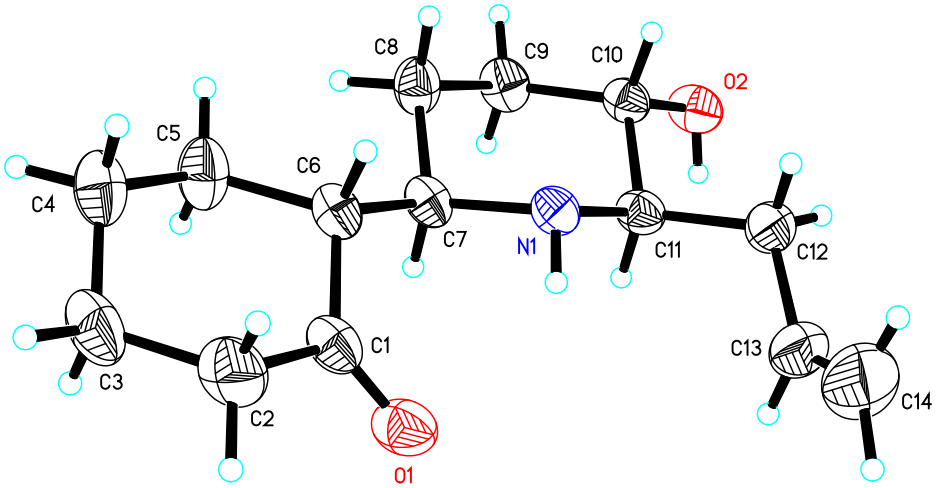
Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for mo_d8v17583_0m [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

ORTEP drawing of the X-ray crystallographic structure of **10b**





CCDC1585539 contains the supplementary crystallographic data for this paper.
These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via
www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystal data and structure refinement for cu_d8v17582_0m.

Identification code	cu_d8v17582_0m	
Empirical formula	C14 H23 N O2	
Formula weight	237.33	
Temperature	296(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 7.7672(2) Å	α= 90 °.
	b = 9.3611(3) Å	β= 90 °.
	c = 19.2665(6) Å	γ = 90 °.
Volume	1400.86(7) $Å^3$	
Z	4	
Density (calculated)	1.125 Mg/m^3	
Absorption coefficient	0.587 mm^{-1}	
F(000)	520	
Crystal size	0.180 x 0.150 x 0.120 mm^3	
Theta range for data collection	6.594 to 70.077 °.	
Index ranges	-9<=h<=7, -10<=k<=11, -18<=l<=23	
Reflections collected	8103	
Independent reflections	2596 [R(int) = 0.0319]	
Completeness to theta = 67.679 °	97.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7533 and 0.5926	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2596 / 0 / 162	
Goodness-of-fit on F^2	1.061	
Final R indices [I>2sigma(I)]	R1 = 0.0448, wR2 = 0.1198	
R indices (all data)	R1 = 0.0484, wR2 = 0.1238	
Absolute structure parameter	0.16(12)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.192 and -0.132 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for cu_d8v17582_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	1742(3)	1244(2)	4207(1)	75(1)
O(2)	4548(2)	6895(2)	2887(1)	63(1)
N(1)	3644(3)	3100(2)	3237(1)	48(1)
C(1)	3097(4)	599(2)	4209(1)	59(1)
C(2)	3191(5)	-968(3)	4384(2)	83(1)
C(3)	4494(5)	-1254(3)	4949(2)	84(1)
C(4)	6216(5)	-643(3)	4763(2)	78(1)
C(5)	6103(4)	961(3)	4611(2)	76(1)
C(6)	4794(3)	1305(2)	4038(1)	53(1)
C(7)	4599(3)	2911(2)	3891(1)	51(1)
C(8)	6316(3)	3679(3)	3820(1)	61(1)
C(9)	6035(4)	5255(3)	3639(1)	62(1)
C(10)	4942(3)	5430(2)	2997(1)	49(1)
C(11)	3256(3)	4601(2)	3067(1)	50(1)
C(12)	2203(3)	4660(3)	2399(1)	62(1)
C(13)	442(4)	4050(4)	2460(2)	87(1)
C(14)	-306(6)	3221(6)	2082(3)	131(2)

Table 3. Bond lengths [Å] and angles [°] for cu_d8v17582_0m.

O(1)-C(1)	1.213(3)
O(2)-C(10)	1.421(3)
N(1)-C(7)	1.473(3)
N(1)-C(11)	1.474(3)
C(1)-C(2)	1.508(3)
C(1)-C(6)	1.510(4)
C(2)-C(3)	1.510(5)
C(3)-C(4)	1.498(5)
C(4)-C(5)	1.532(4)
C(5)-C(6)	1.535(4)
C(6)-C(7)	1.538(3)
C(7)-C(8)	1.521(3)
C(8)-C(9)	1.532(3)
C(9)-C(10)	1.509(3)
C(10)-C(11)	1.528(3)
C(11)-C(12)	1.527(3)
C(12)-C(13)	1.487(4)
C(13)-C(14)	1.213(6)

C(7)-N(1)-C(11)	114.03(17)
O(1)-C(1)-C(2)	121.8(3)
O(1)-C(1)-C(6)	122.6(2)
C(2)-C(1)-C(6)	115.6(3)
C(1)-C(2)-C(3)	111.5(3)
C(4)-C(3)-C(2)	111.0(2)
C(3)-C(4)-C(5)	111.7(3)
C(4)-C(5)-C(6)	112.3(2)
C(1)-C(6)-C(5)	109.2(2)
C(1)-C(6)-C(7)	112.4(2)
C(5)-C(6)-C(7)	113.8(2)
N(1)-C(7)-C(8)	107.93(18)
N(1)-C(7)-C(6)	108.95(18)
C(8)-C(7)-C(6)	113.1(2)
C(7)-C(8)-C(9)	110.5(2)
C(10)-C(9)-C(8)	111.8(2)
O(2)-C(10)-C(9)	110.39(18)

O(2)-C(10)-C(11)	108.56(18)
C(9)-C(10)-C(11)	110.77(18)
N(1)-C(11)-C(12)	109.34(19)
N(1)-C(11)-C(10)	109.15(18)
C(12)-C(11)-C(10)	111.48(18)
C(13)-C(12)-C(11)	114.3(2)
C(14)-C(13)-C(12)	129.7(4)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for cu_d8v17582_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	75(1)	62(1)	89(1)	11(1)	18(1)	-1(1)
O(2)	74(1)	41(1)	73(1)	7(1)	16(1)	3(1)
N(1)	53(1)	42(1)	50(1)	2(1)	2(1)	-6(1)
C(1)	78(2)	46(1)	52(1)	4(1)	10(1)	-1(1)
C(2)	96(2)	51(1)	103(2)	17(1)	9(2)	-7(2)
C(3)	123(3)	55(1)	76(2)	21(1)	12(2)	7(2)
C(4)	104(2)	58(2)	73(2)	12(1)	-12(2)	9(2)
C(5)	94(2)	57(1)	76(2)	11(1)	-21(2)	-3(1)
C(6)	70(1)	44(1)	44(1)	1(1)	5(1)	1(1)
C(7)	67(1)	42(1)	45(1)	1(1)	3(1)	-2(1)
C(8)	69(1)	53(1)	60(1)	6(1)	-13(1)	-7(1)
C(9)	74(2)	49(1)	62(1)	2(1)	-5(1)	-13(1)
C(10)	56(1)	40(1)	52(1)	2(1)	7(1)	0(1)
C(11)	53(1)	44(1)	53(1)	3(1)	9(1)	2(1)
C(12)	56(1)	61(1)	69(2)	16(1)	-1(1)	-1(1)
C(13)	58(2)	107(3)	97(2)	29(2)	-7(2)	-13(2)
C(14)	102(3)	159(4)	132(4)	23(3)	-24(3)	-63(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for cu_d8v17582_0m.

	x	y	z	U(eq)
H(2A)	3505	-1503	3972	100
H(2B)	2067	-1296	4535	100
H(3A)	4098	-832	5380	101
H(3B)	4602	-2276	5019	101
H(4A)	6660	-1133	4357	94
H(4B)	7013	-801	5142	94
H(5A)	7229	1306	4472	91
H(5B)	5777	1460	5032	91
H(6)	5220	861	3610	63
H(7)	3942	3350	4269	61
H(8A)	6994	3226	3459	73
H(8B)	6949	3607	4253	73
H(9A)	5478	5730	4026	74
H(9B)	7142	5710	3565	74
H(10)	5579	5066	2595	59
H(11)	2577	5018	3445	60
H(12A)	2110	5649	2252	75
H(12B)	2820	4146	2039	75
H(13)	-179	4349	2847	105
H(14A)	235	2876	1685	157
H(14B)	-1420	2930	2188	157
H(1)	2730(40)	2660(30)	3273(17)	66(9)
H(2)	5180(40)	7220(30)	2542(18)	70(9)

Table 6. Torsion angles [°] for cu_d8v17582_0m.

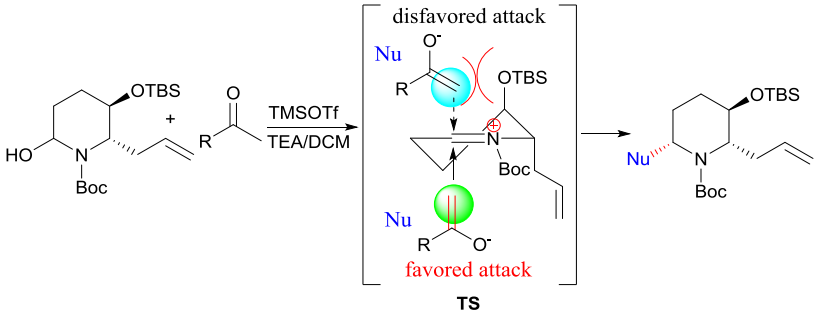
O(1)-C(1)-C(2)-C(3)	-127.2(3)
C(6)-C(1)-C(2)-C(3)	52.7(3)
C(1)-C(2)-C(3)-C(4)	-53.8(4)
C(2)-C(3)-C(4)-C(5)	56.4(4)
C(3)-C(4)-C(5)-C(6)	-56.1(4)
O(1)-C(1)-C(6)-C(5)	129.3(3)
C(2)-C(1)-C(6)-C(5)	-50.7(3)
O(1)-C(1)-C(6)-C(7)	2.0(3)
C(2)-C(1)-C(6)-C(7)	-178.0(2)
C(4)-C(5)-C(6)-C(1)	51.3(3)
C(4)-C(5)-C(6)-C(7)	177.8(2)
C(11)-N(1)-C(7)-C(8)	-61.4(2)
C(11)-N(1)-C(7)-C(6)	175.49(19)
C(1)-C(6)-C(7)-N(1)	-68.2(2)
C(5)-C(6)-C(7)-N(1)	166.9(2)
C(1)-C(6)-C(7)-C(8)	171.76(19)
C(5)-C(6)-C(7)-C(8)	46.9(3)
N(1)-C(7)-C(8)-C(9)	56.6(2)
C(6)-C(7)-C(8)-C(9)	177.2(2)
C(7)-C(8)-C(9)-C(10)	-55.0(3)
C(8)-C(9)-C(10)-O(2)	173.6(2)
C(8)-C(9)-C(10)-C(11)	53.3(3)
C(7)-N(1)-C(11)-C(12)	-177.60(19)
C(7)-N(1)-C(11)-C(10)	60.2(2)
O(2)-C(10)-C(11)-N(1)	-175.57(18)
C(9)-C(10)-C(11)-N(1)	-54.2(2)
O(2)-C(10)-C(11)-C(12)	63.5(2)
C(9)-C(10)-C(11)-C(12)	-175.1(2)
N(1)-C(11)-C(12)-C(13)	67.3(3)
C(10)-C(11)-C(12)-C(13)	-171.9(3)
C(11)-C(12)-C(13)-C(14)	-132.9(5)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for cu_d8v17582_0m [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

The preferred 2,6-*cis* selectivity of forming **7a-7q** can be rationalized by classical transition state **TS**. Due to the steric bulkiness of 3-siloxy group, axial attack of the nucleophile to **TS** would be happened from the same face as that of 2-Allyl group, generating predominantly the 2,6-*cis*-diastereomer (**7a-7q)**.



Proposed transition state for the formation of **(2*S*,3*S*,6*S*)-7a-q**