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

Synthesis of the protected α- amino acid via decarboxylation amination from malonate derivatives

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Table 1
1n
CO2Et
O
O
NHBoc
7.870
7.297
7.279
7.260
7.222
7.204
4.188
4.171
4.153
4.136
3.823
3.804
3.785
3.291
3.272
1.465
1.212
1.194
1.177
0.96
2.22
2.96
2.00
0.98
2.00
9.00
3.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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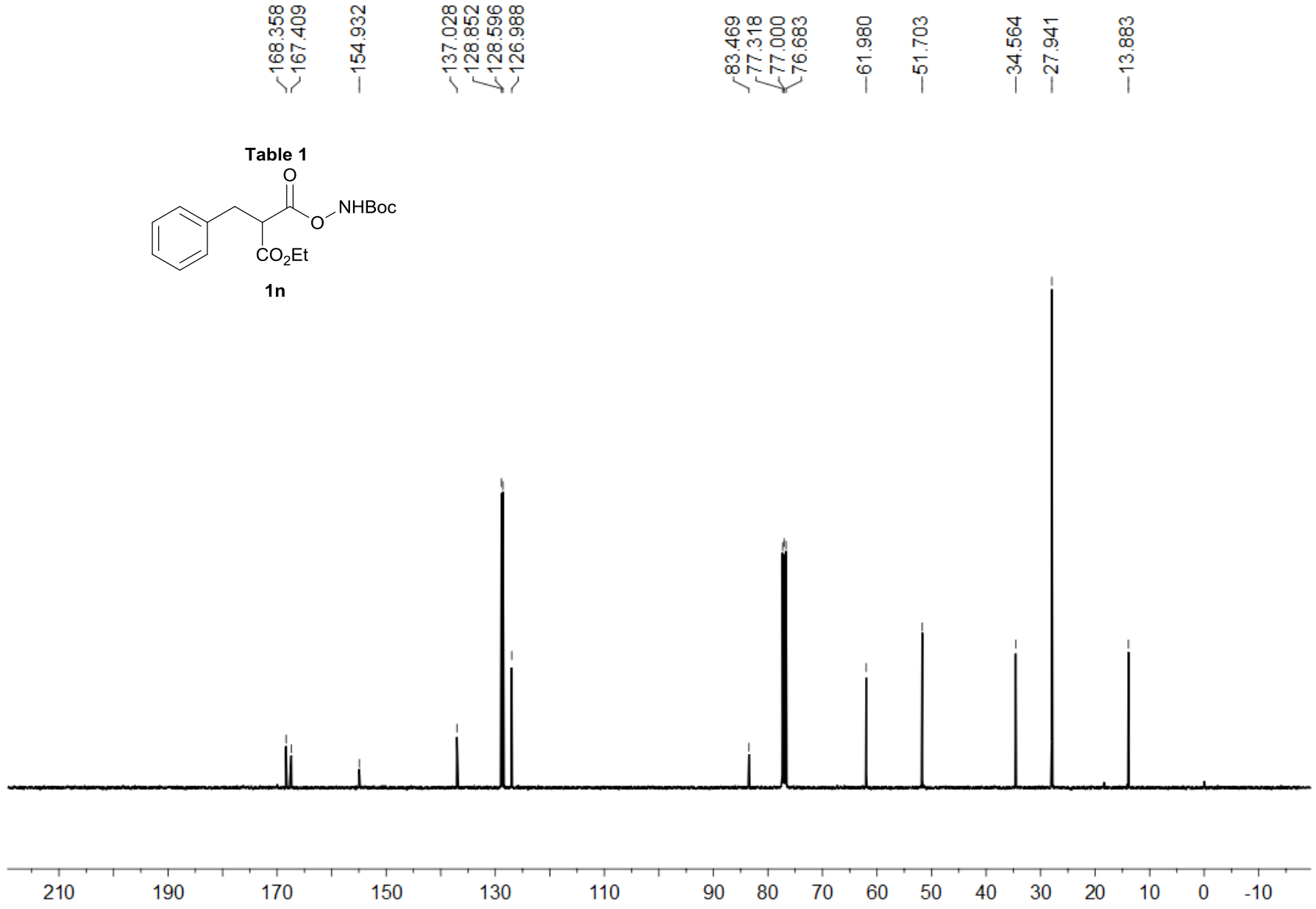
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137.028
128.852
128.596
126.988
83.469
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77.000
76.683
61.980
51.703
34.564
27.941
13.883
Table 1
O
NHBoc
O
CO2Et
1n
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10

Table 2
2a
N
O
N
H
Boc
7.260
5.547
3.949
3.938
3.422
3.404
3.386
3.368
3.269
3.251
3.233
3.215
1.444
1.199
1.181
1.163
1.142
1.124
1.106
0.88
1.91
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2.00
9.00
3.00
3.01
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9.5
9.0
8.5
8.0
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7.0
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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

Table 2
2a
N
O
N
H
Boc
167.247
155.802
79.448
77.318
77.000
76.683
42.117
40.884
40.368
28.336
13.965
12.914
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Table 2
2b
O
N
O
N
H
Boc
7.260
5.485
3.950
3.939
3.681
3.669
3.634
3.621
3.611
3.398
3.385
3.374
1.443
0.94
1.97
4.00
2.00
1.98
9.00
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9.5
9.0
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8.0
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7.0
6.5
6.0
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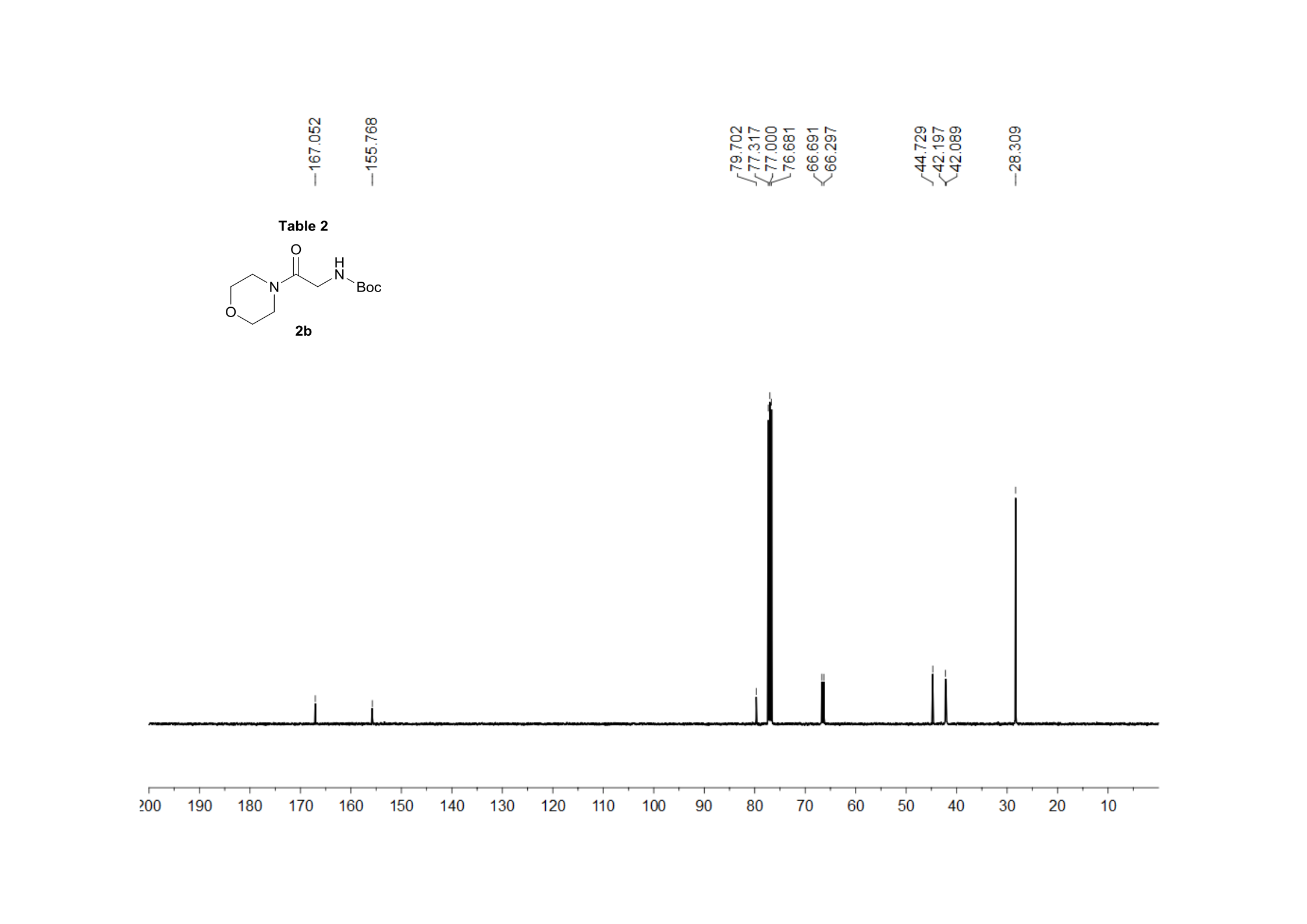
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76.681
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42.197
42.089
28.309
Table 2
O
H
N
N
Boc
O
2b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

Table 2
2c
N
O
N
H
Boc
7.260
5.555
3.934
3.924
3.564
3.550
3.537
3.307
3.293
3.280
1.643
1.631
1.617
1.553
1.540
1.527
1.437
0.95
2.00
2.00
2.00
2.02
4.00
9.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

Table 2
2c
N
O
N
H
Boc
166.322
155.809
79.438
77.317
77.000
76.682
45.323
43.053
42.167
28.332
26.124
25.377
24.343
200
190
180
170
160
150
140
130
120
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50
40
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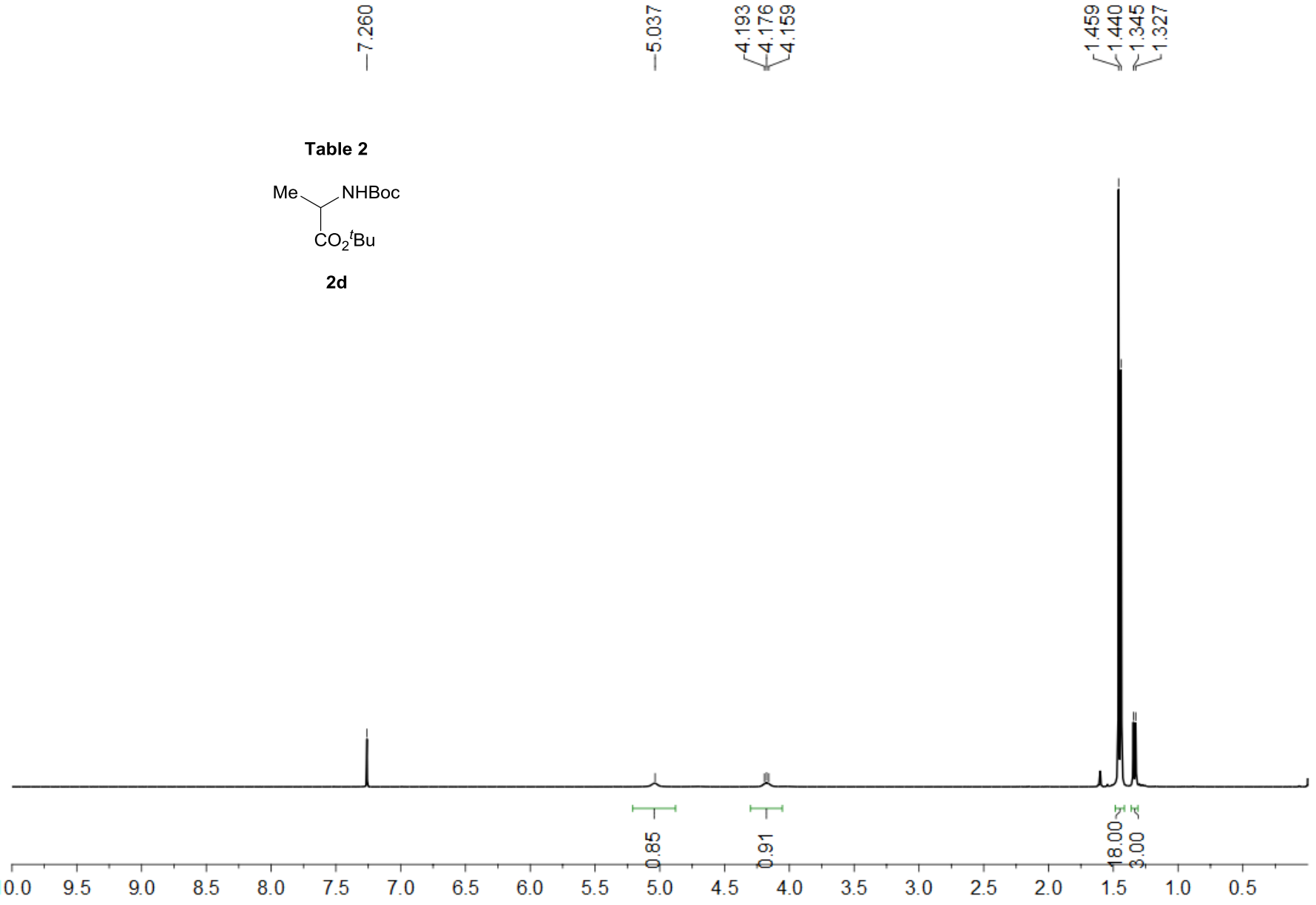
20
10

Table 2

Me
NHBoc
CO2tBu

2d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9.0
8.5
8.0
7.5
7.0
6.5
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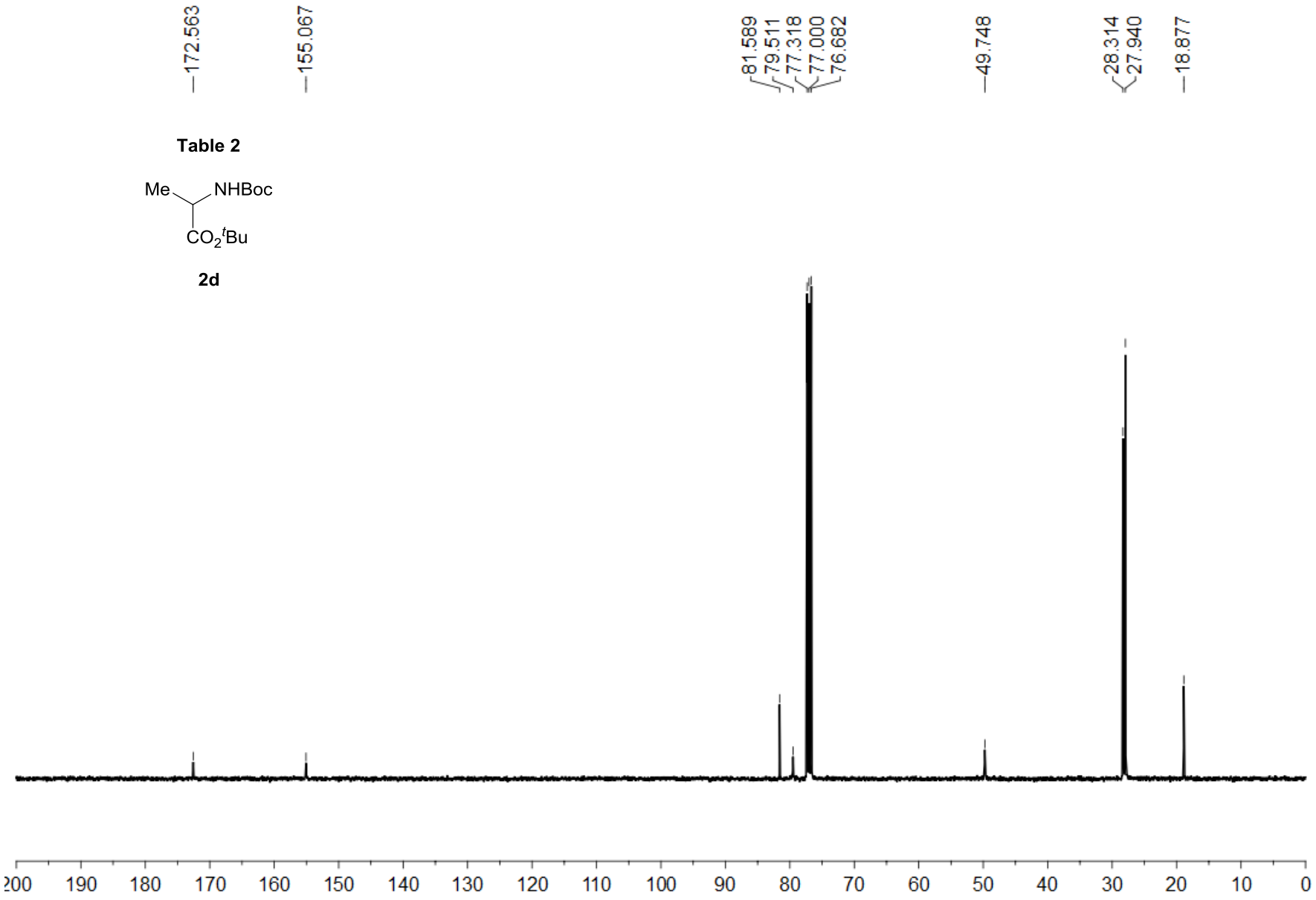
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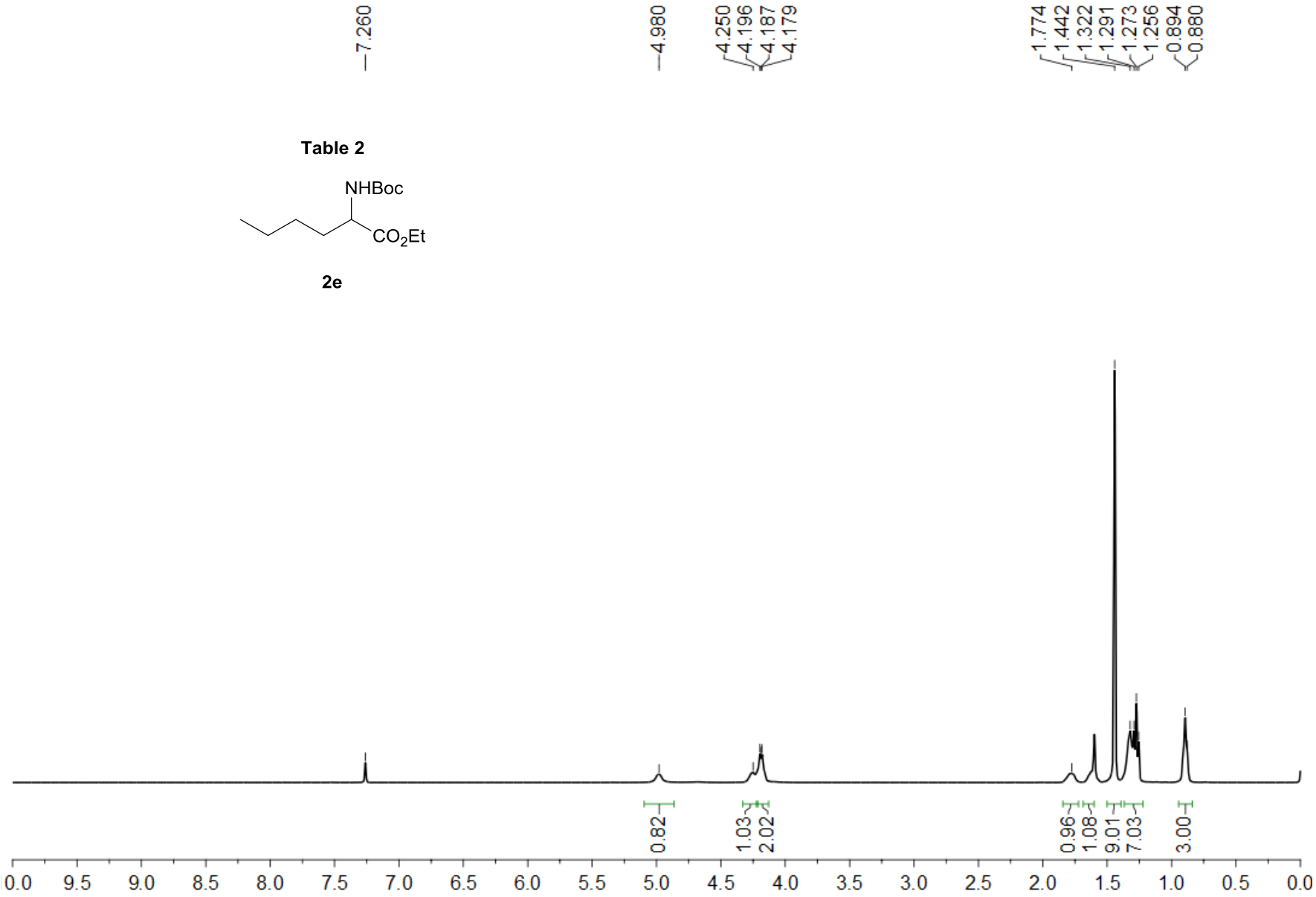
79.511
77.318
77.000
76.682
49.748
28.314
27.940
18.877
Table 2
Me
NHBoc
CO2tBu
2d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Table 2

NHBoc
CO2Et

2e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0.880
0.82
1.03
2.02
0.96
1.08
9.01
7.03
3.00
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

Table 2
2e
NHBoc
CO2Et
173.008
155.371
79.693
77.317
77.000
76.682
61.127
53.474
32.475
28.300
27.334
22.282
14.165
13.825
200
190
180
170
160
150
140
130
120
110
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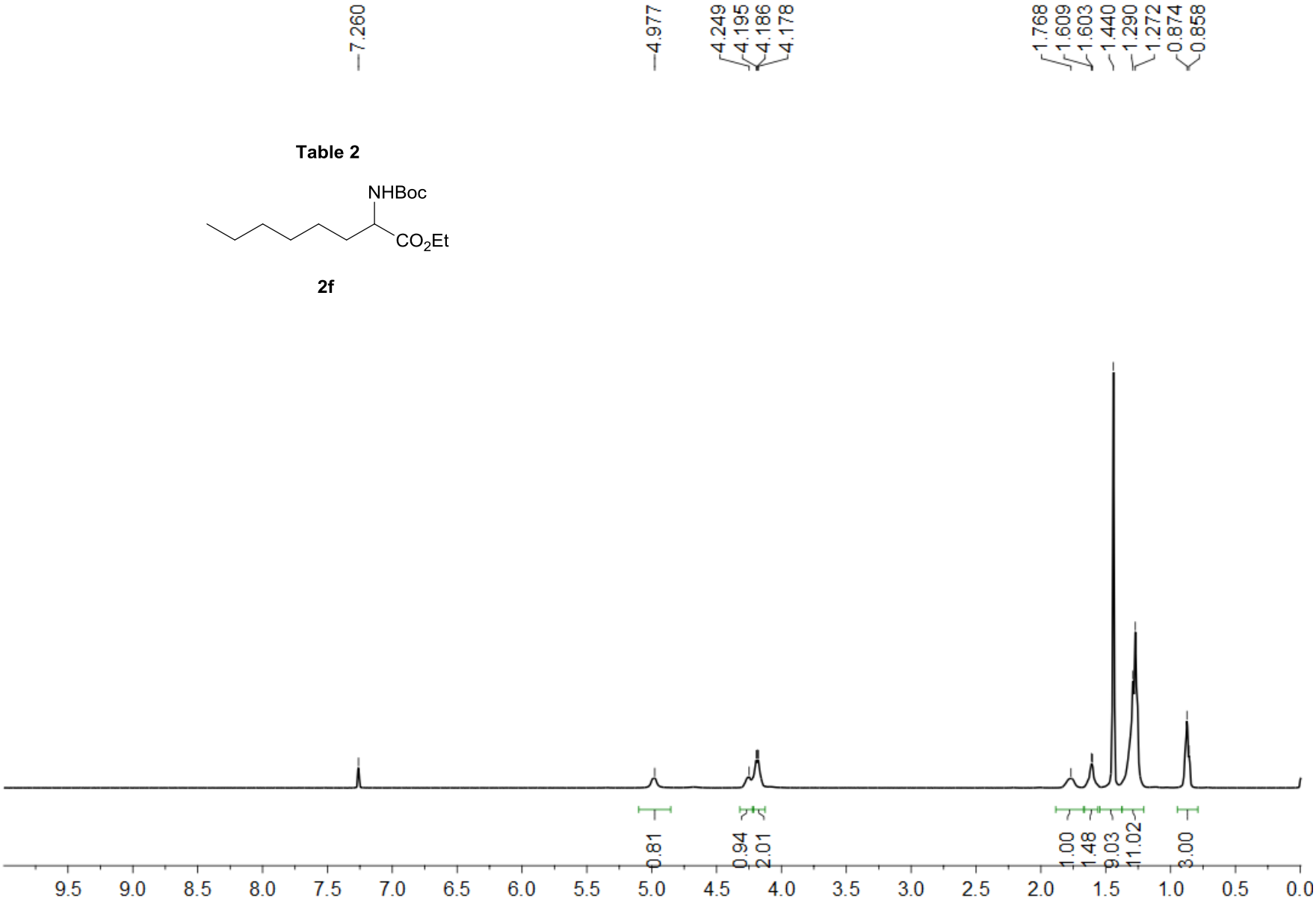
90
80
70
60
50
40
30
20
10
0

Table 2

NHBoc
CO2Et

2f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4.178
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1.609
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1.440
1.290
1.272
0.874
0.858
0.81
0.94
2.01
1.00
1.48
9.03
11.02
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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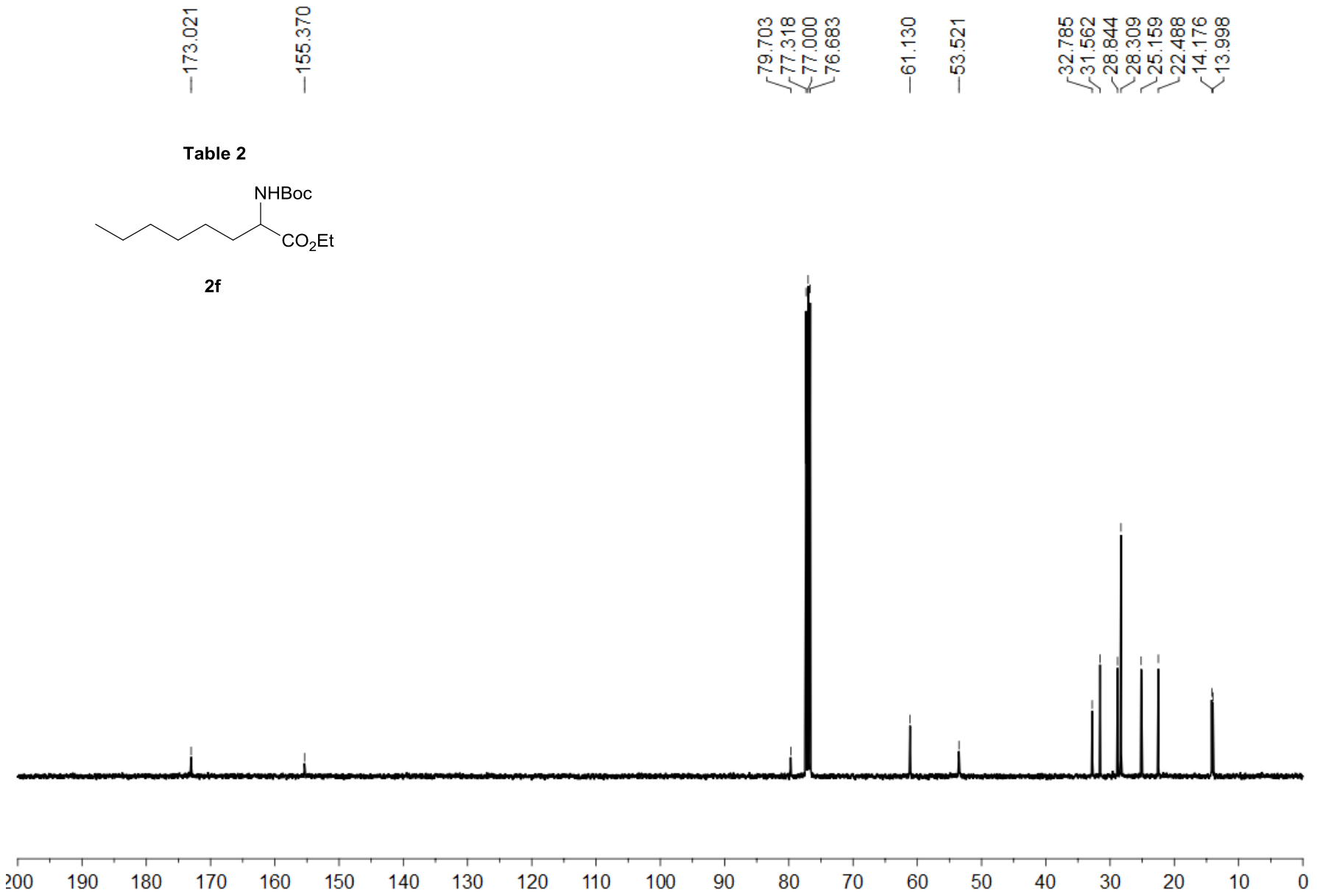
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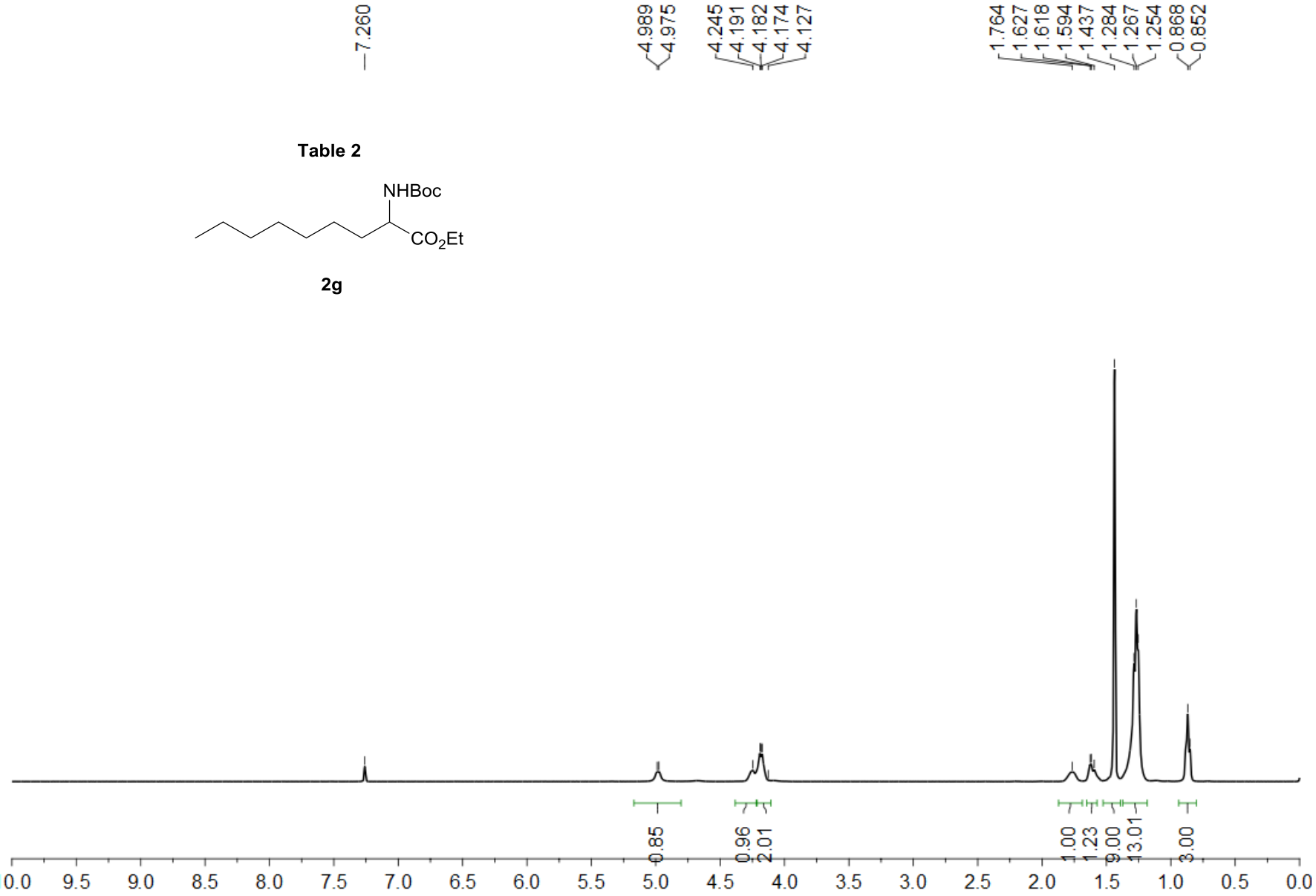
77.000
76.683
61.130
53.521
32.785
31.562
28.844
28.309
25.159
22.488
14.176
13.998
Table 2
NHBoc
CO2Et
2f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Table 2

NHBoc
CO2Et

2g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4.182
4.174
4.127
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1.627
1.618
1.594
1.437
1.284
1.267
1.254
0.868
0.852
0.85
0.96
2.01
1.00
1.23
9.00
13.01
3.00
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9.5
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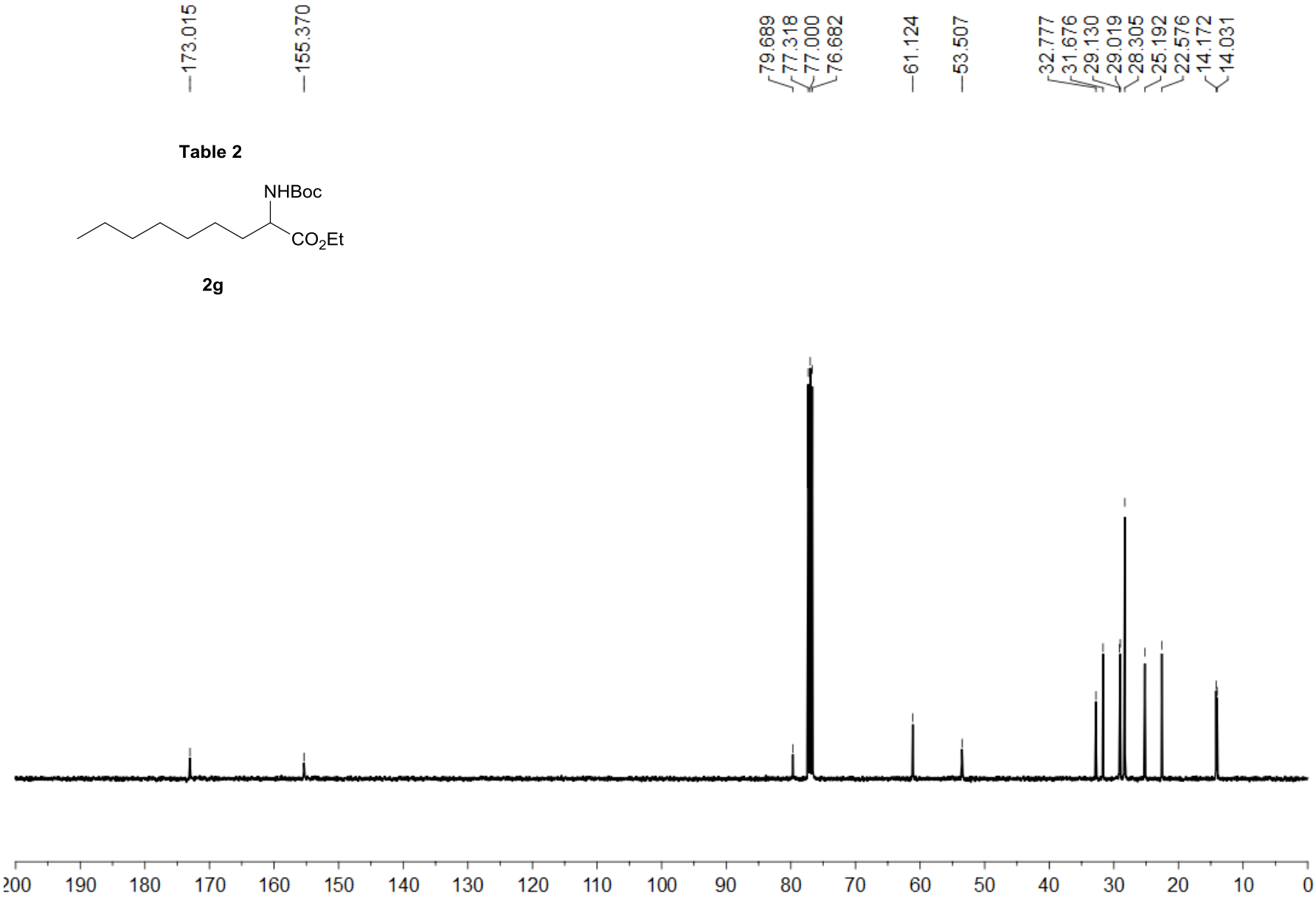
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76.682
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53.507
32.777
31.676
29.130
29.019
28.305
25.192
22.576
14.172
14.031
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Table 2

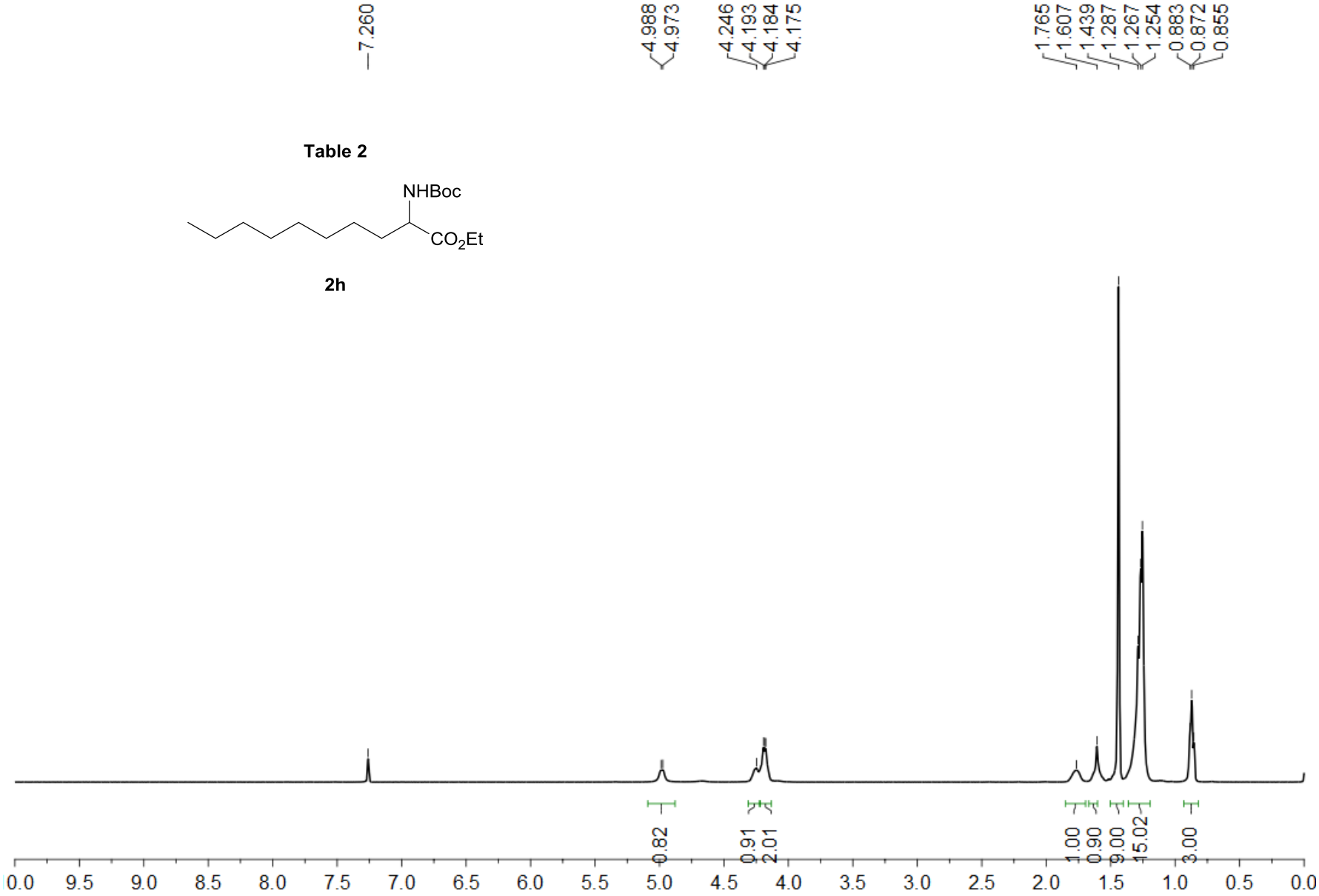
NHBoc
CO2Et

2g

Table 2

NHBoc
CO2Et

2h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4.973
4.246
4.193
4.184
4.175
1.765
1.607
1.439
1.287
1.267
1.254
0.883
0.872
0.855
0.82
0.91
2.01
1.00
0.90
9.00
15.02
3.00
0.0
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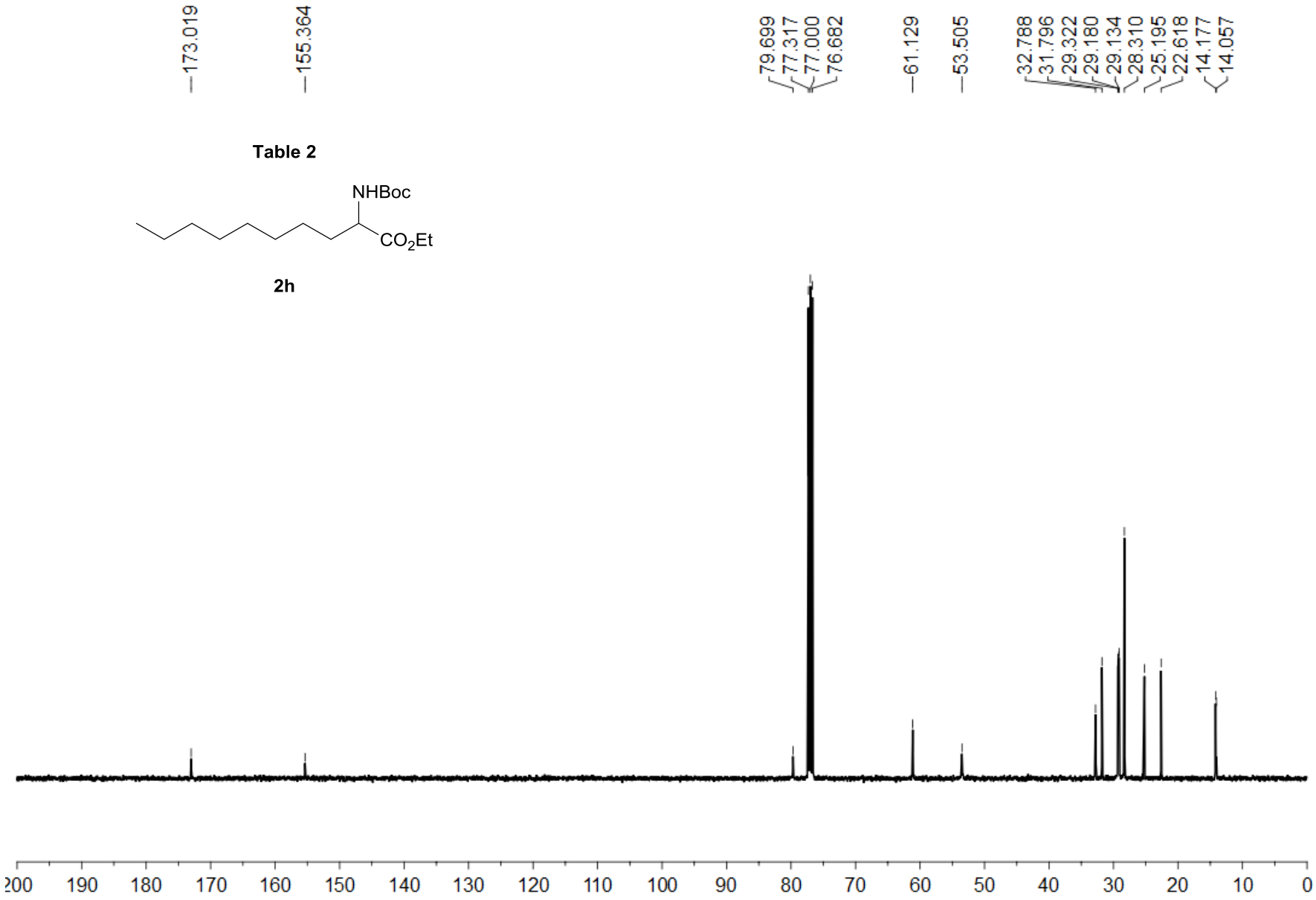
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77.317
77.000
76.682
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32.788
31.796
29.322
29.180
29.134
28.310
25.195
22.618
14.177
14.057
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Table 2

NHBoc
CO2Et

2h

Table 2
2i
Me
Me
NHBoc
CO2tBu
7.260
5.023
5.002
4.108
4.097
4.085
4.074
2.127
2.110
2.098
2.081
2.064
1.460
1.438
0.952
0.935
0.885
0.868
0.85
0.86
1.00
18.00
3.00
3.00

Table 2
2i
Me
Me
NHBoc
CO2tBu
171.510
155.710
81.632
79.455
77.318
77.000
76.683
58.818
31.469
28.308
28.032
18.893
17.446
190
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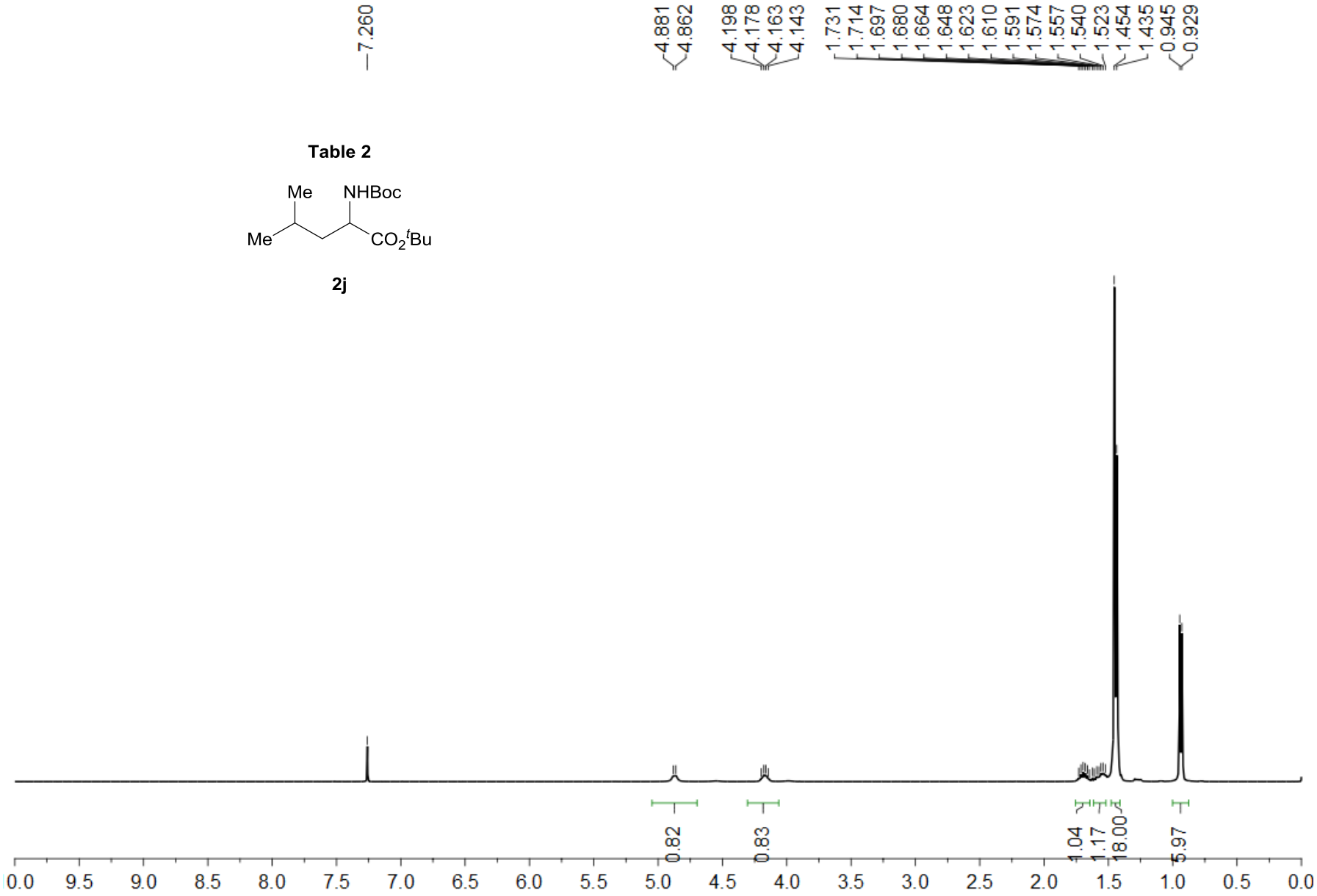
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1.731
1.714
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1.623
1.610
1.591
1.574
1.557
1.540
1.523
1.454
1.435
0.945
0.929
0.82
0.83
1.04
1.17
18.00
5.97
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9.5
9.0
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8.0
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7.0
6.5
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3.5
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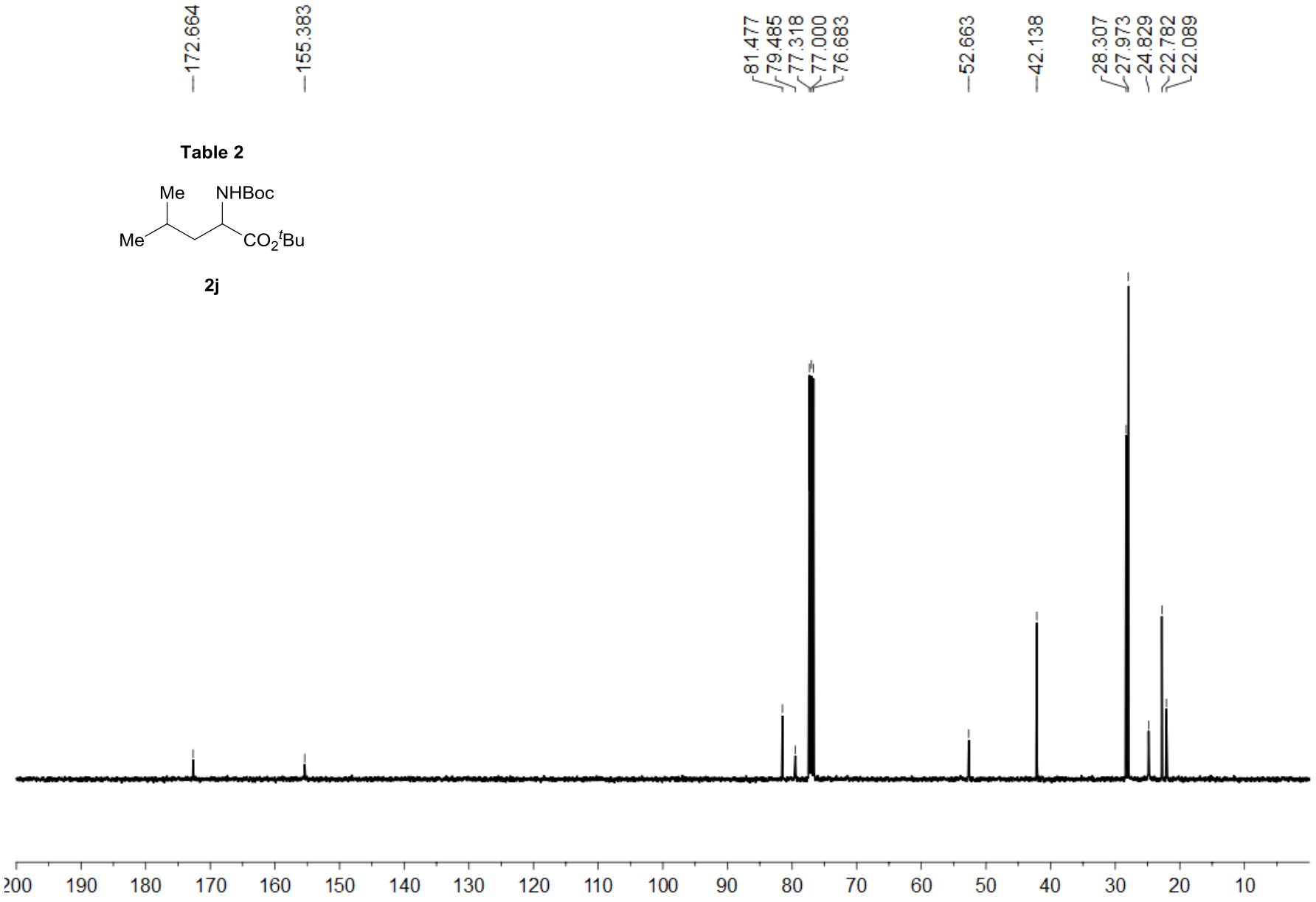
Table 2

Me
NHBoc
Me
CO2tBu

2j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79.485
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77.000
76.683
52.663
42.138
28.307
27.973
24.829
22.782
22.089
Table 2
Me
NHBoc
Me
CO2tBu
2j
200
190
180
170
160
150
140
130
120
110
100
90
80
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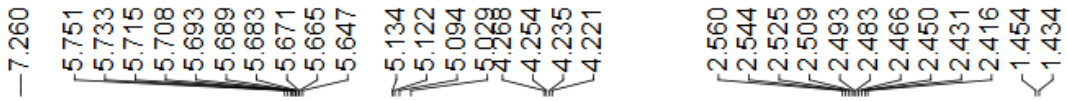
60
50
40
30
20
10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5.715
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5.693
5.689
5.683
5.671
5.665
5.647
5.134
5.122
5.094
4.268
4.254
4.235
4.221
2.560
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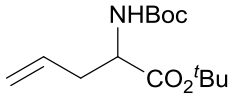
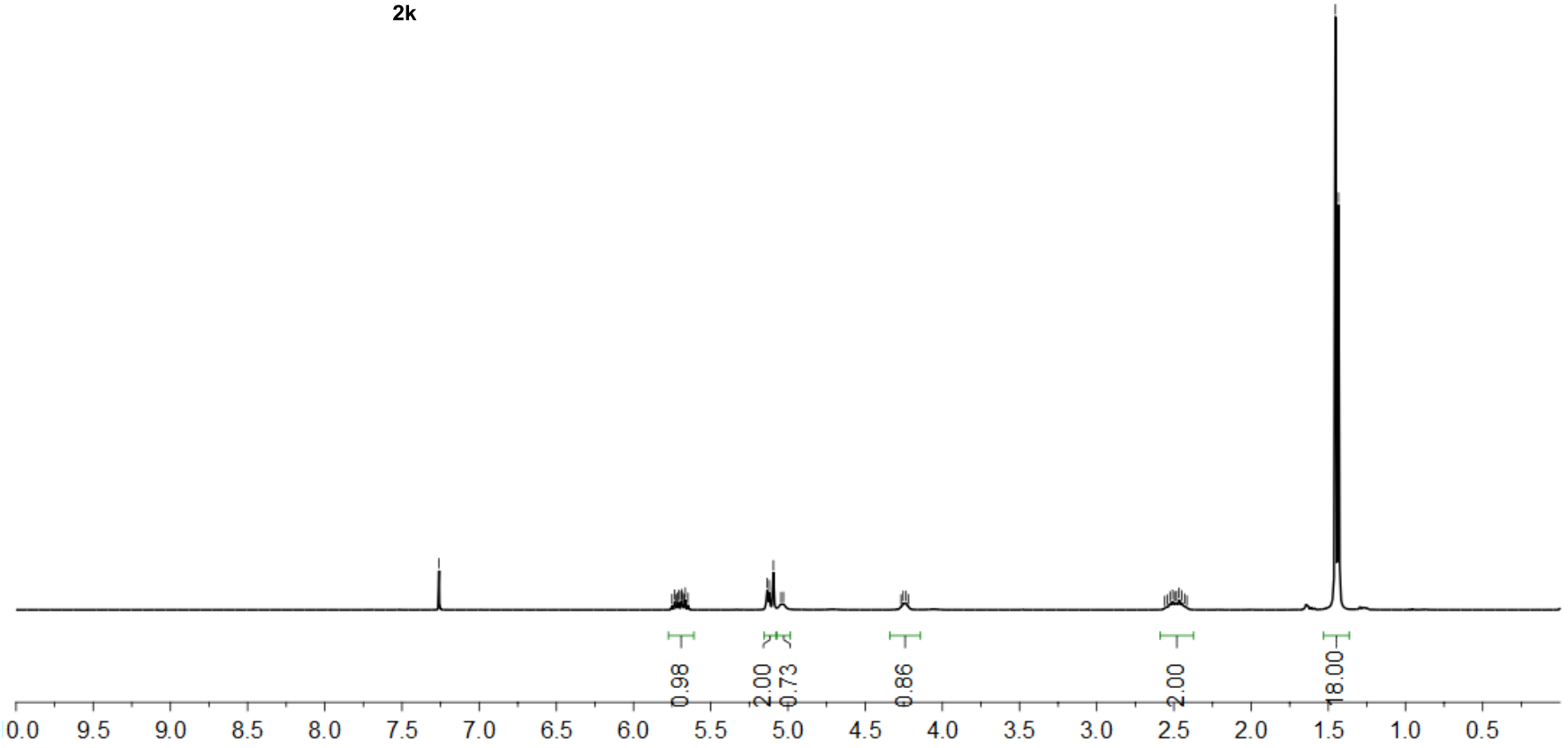
1.454
1.434

Table 2


NHBoc
CO2tBu

2k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8.5
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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

171.118
155.172
132.526
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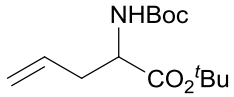
77.000
76.682
53.280
37.046
28.297
28.012

Table 2



2k

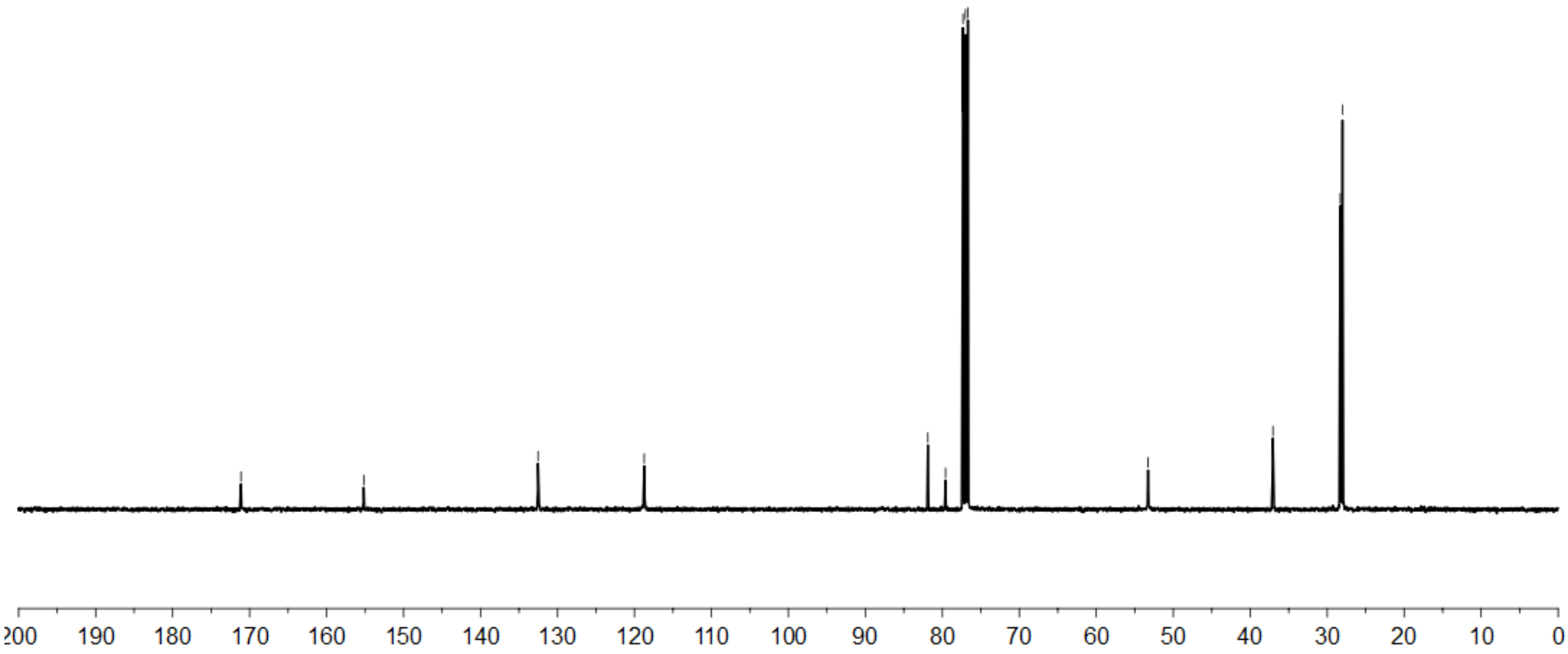
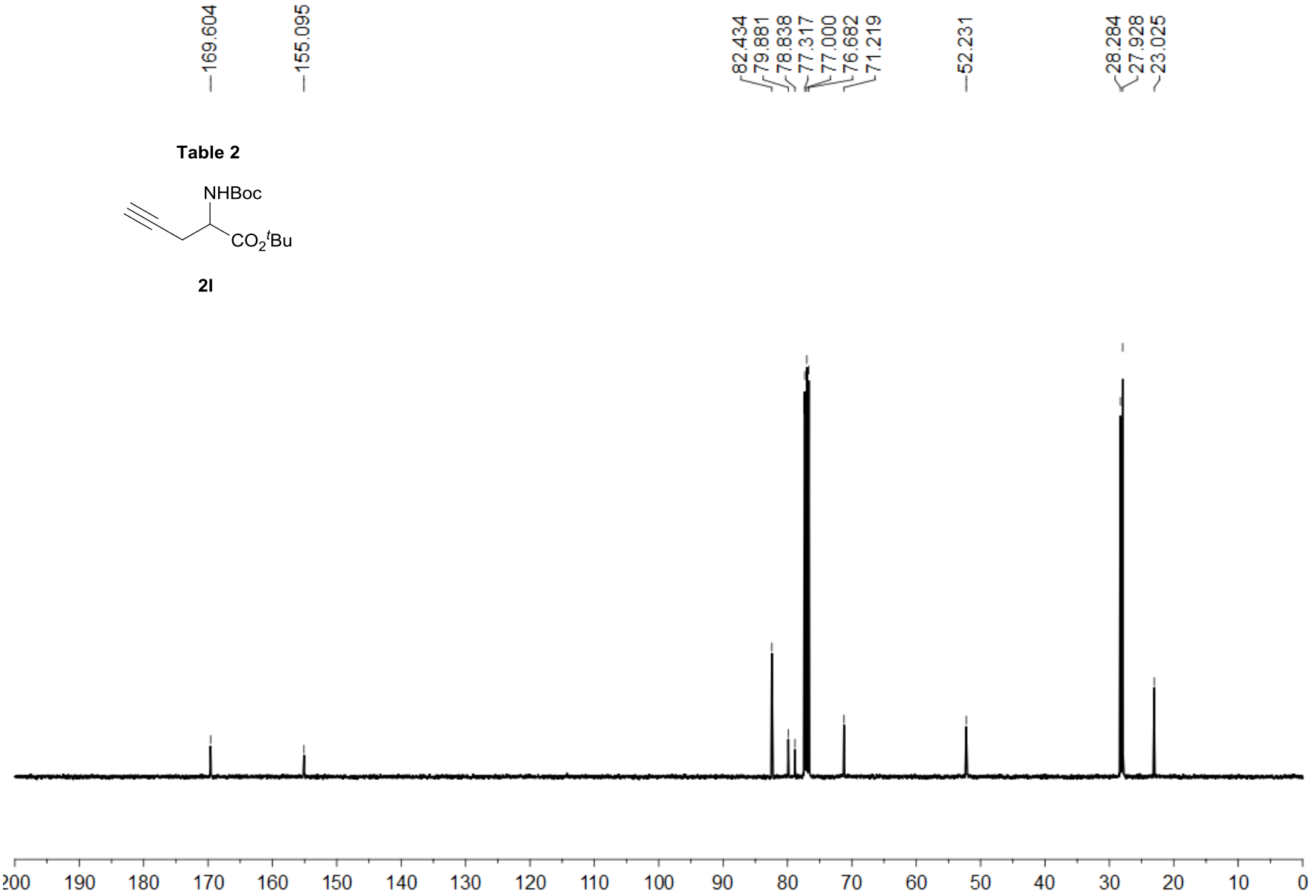


Table 2
2l
NHBoc
CO2tBu
7.260
5.341
5.322
4.353
4.342
4.332
4.322
4.310
4.301
2.745
2.738
2.703
2.696
2.662
2.655
2.017
2.010
2.004
1.479
1.447
0.89
0.92
2.00
1.00
18.00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77.000
76.682
71.219
52.231
28.284
27.928
23.025
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Table 2

NHBoc
CO2tBu

2l

Table 2
2m
NC
NHBoc
CO2tBu
7.260
5.155
4.222
4.211
2.455
2.438
2.432
2.420
2.415
2.404
2.398
2.382
2.355
1.978
1.963
1.956
1.941
1.477
1.444
0.87
0.95
2.00
1.00
1.00
18.00
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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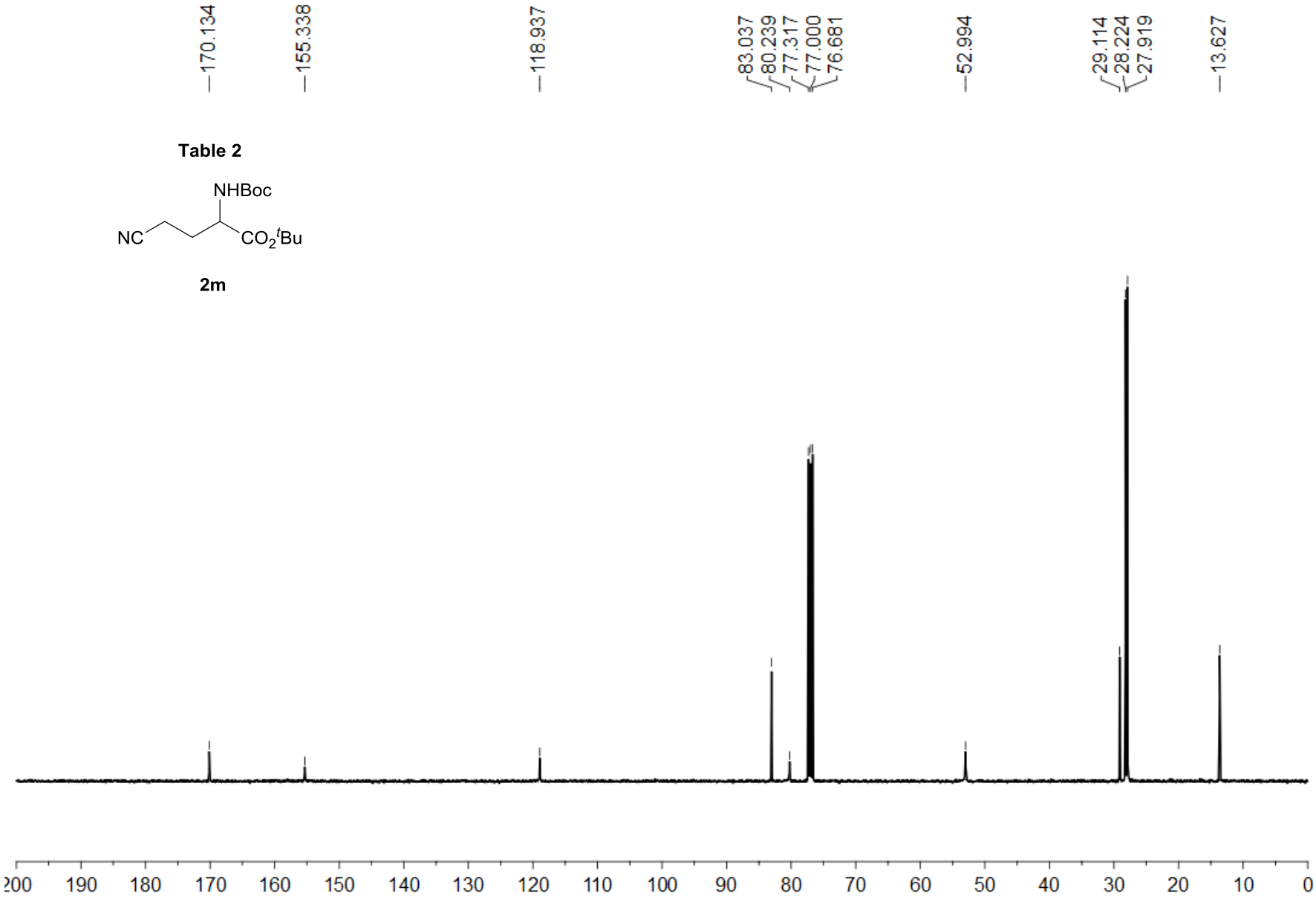
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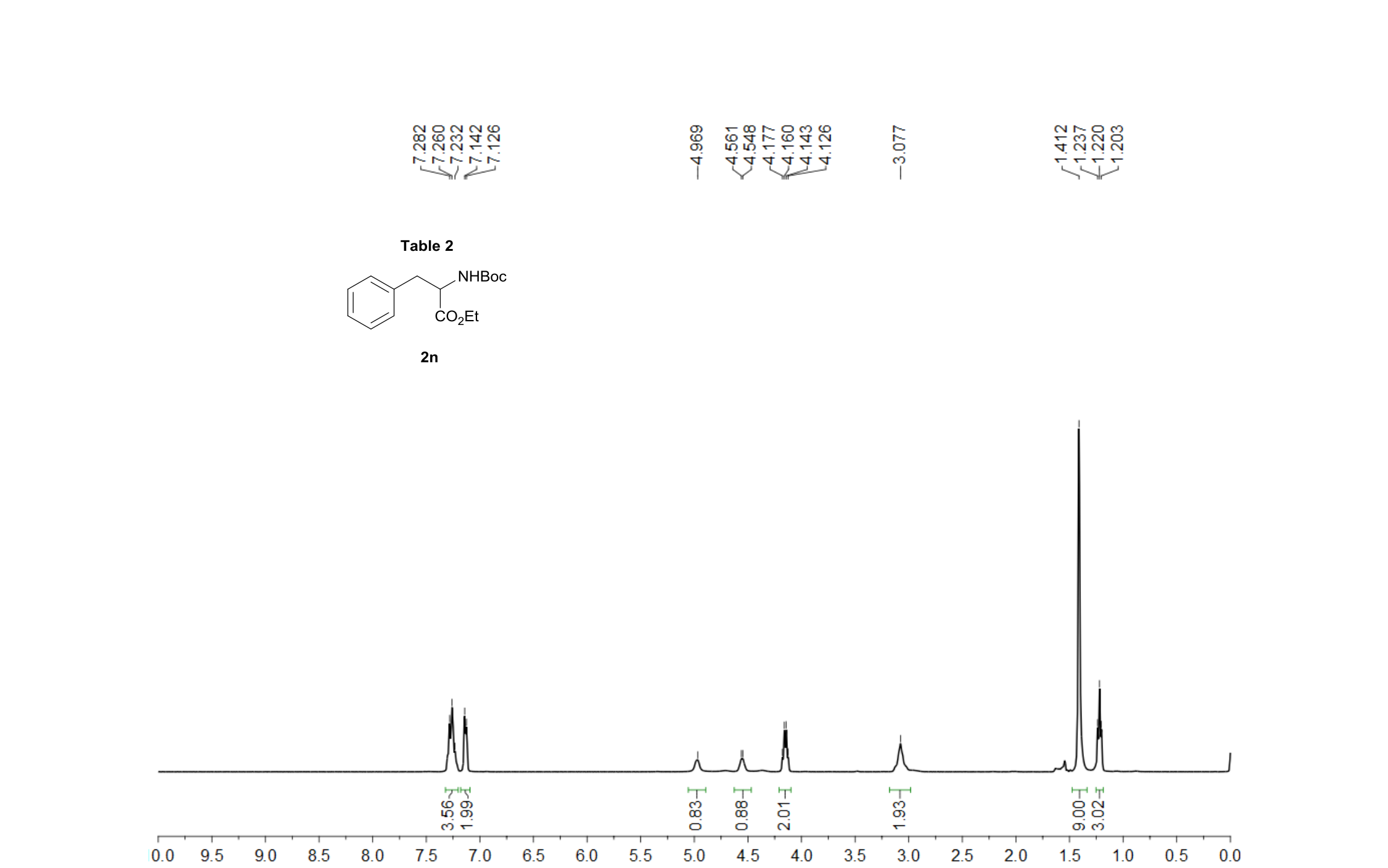
83.037
80.239
77.317
77.000
76.681
52.994
29.114
28.224
27.919
13.627
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Table 2

NHBoc
NC
CO2tBu

2m


7.282
7.260
7.232
7.142
7.126
4.969
4.561
4.548
4.177
4.160
4.143
4.126
3.077
1.412
1.237
1.220
1.203
Table 2
NHBoc
CO2Et
2n
3.56
1.99
0.83
0.88
2.01
1.93
9.00
3.02
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

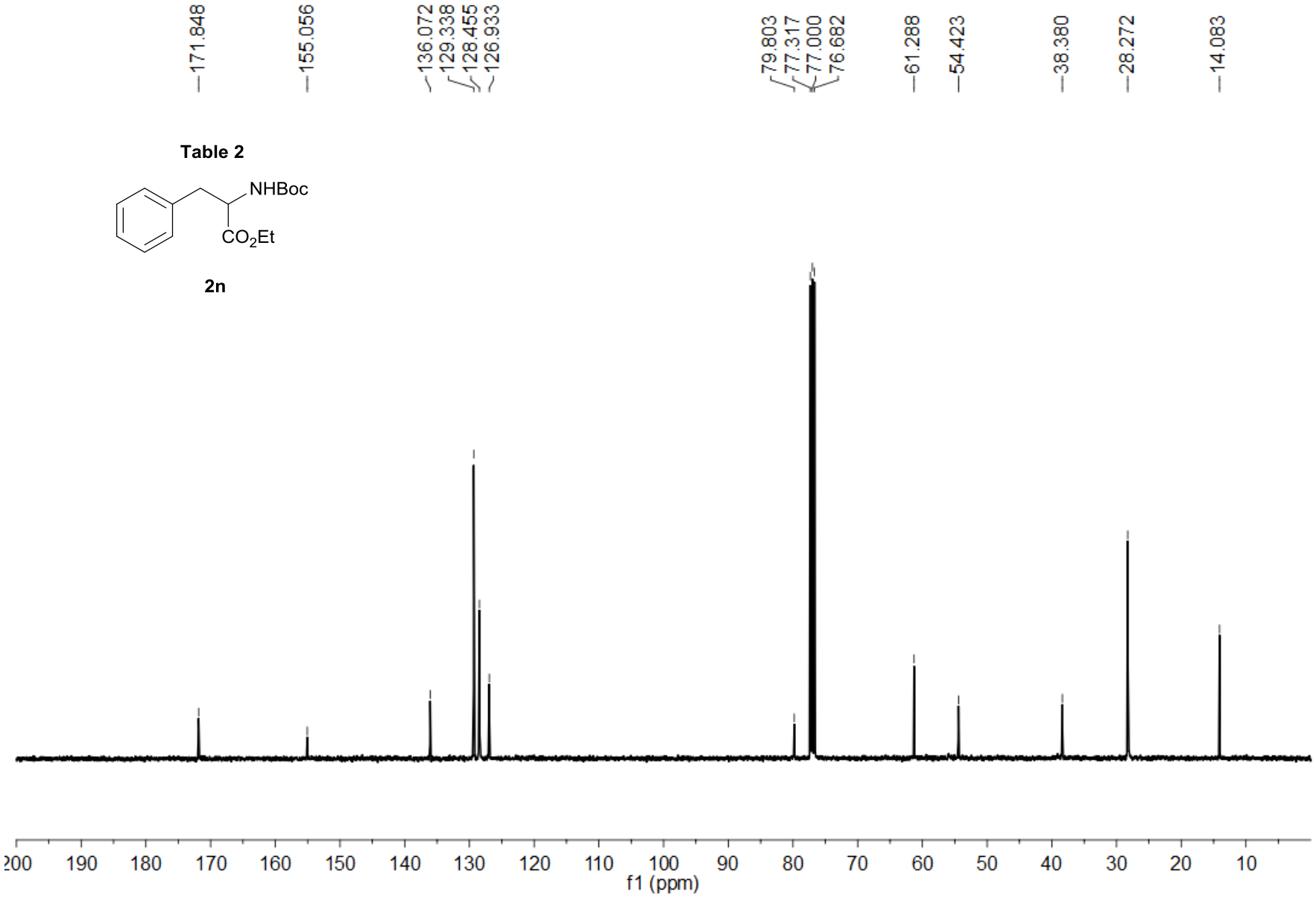
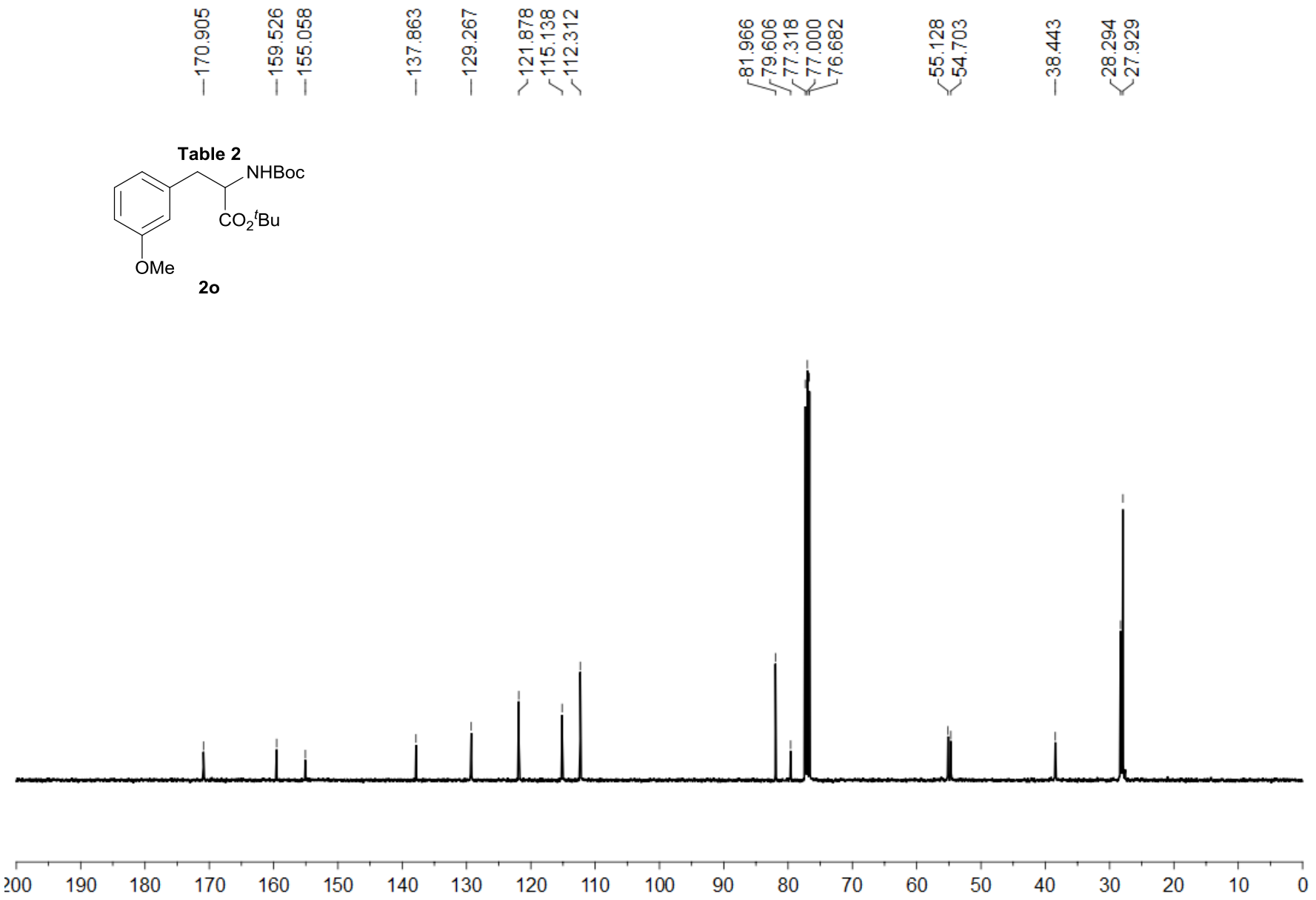
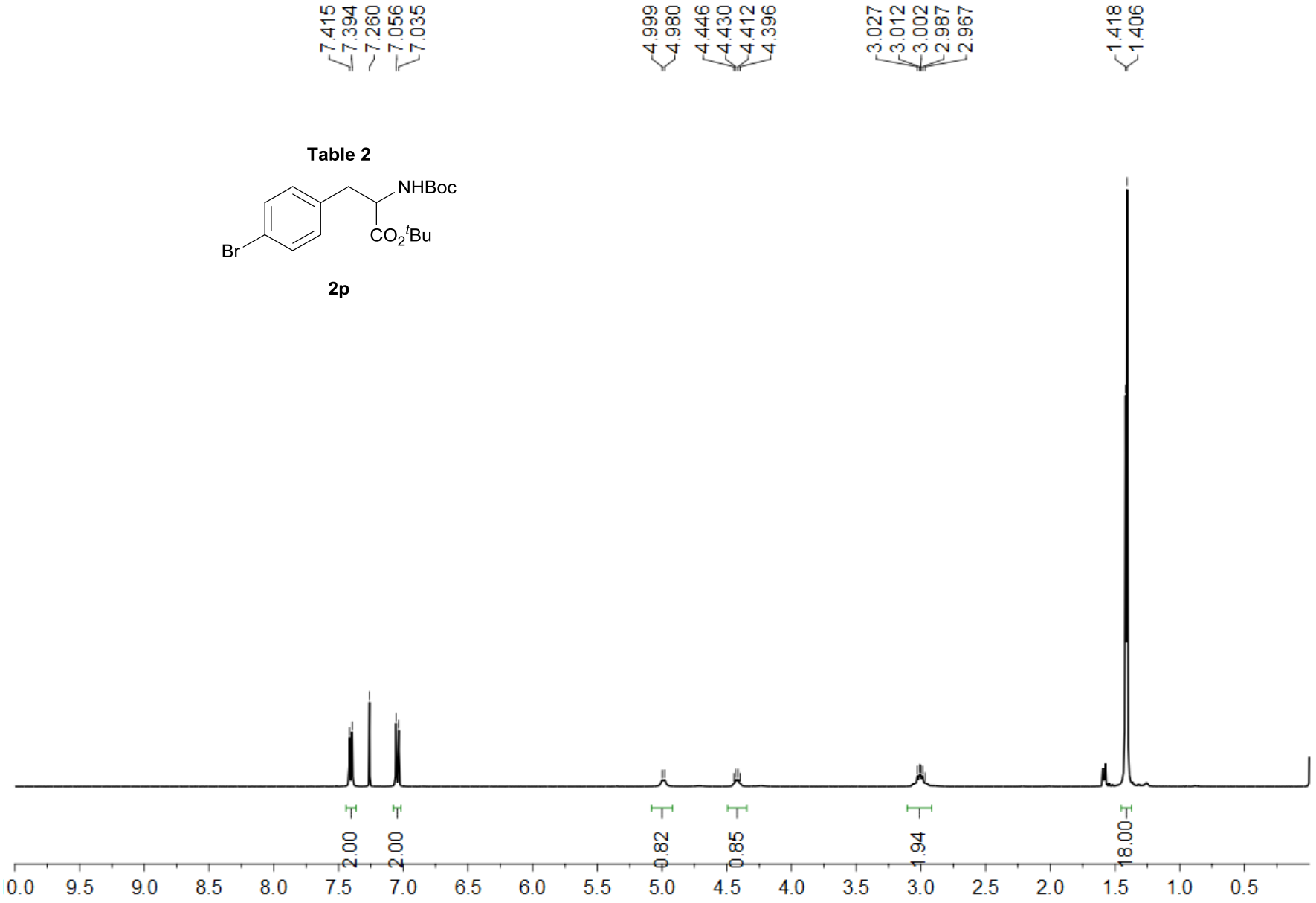

171.848
155.056
136.072
129.338
128.455
126.933
79.803
77.317
77.000
76.682
61.288
54.423
38.380
28.272
14.083
Table 2
NHBoc
CO2Et
2n
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Table 2
OMe
NHBoc
CO2tBu
2o
7.260
6.790
6.783
6.769
6.750
6.715
6.710
4.995
4.975
4.467
4.452
4.433
4.417
3.783
3.037
3.022
1.422
1.408
1.00
2.00
1.00
0.86
0.86
3.00
1.97
18.00


170.905
159.526
155.058
137.863
129.267
121.878
115.138
112.312
81.966
79.606
77.318
77.000
76.682
55.128
54.703
38.443
28.294
27.929
Table 2
NHBoc
CO2tBu
OMe
2o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.415
7.394
7.260
7.056
7.035
4.999
4.980
4.446
4.430
4.412
4.396
3.027
3.012
3.002
2.987
2.967
1.418
1.406
Table 2
NHBoc
Br
CO2tBu
2p
2.00
2.00
0.82
0.85
1.94
18.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

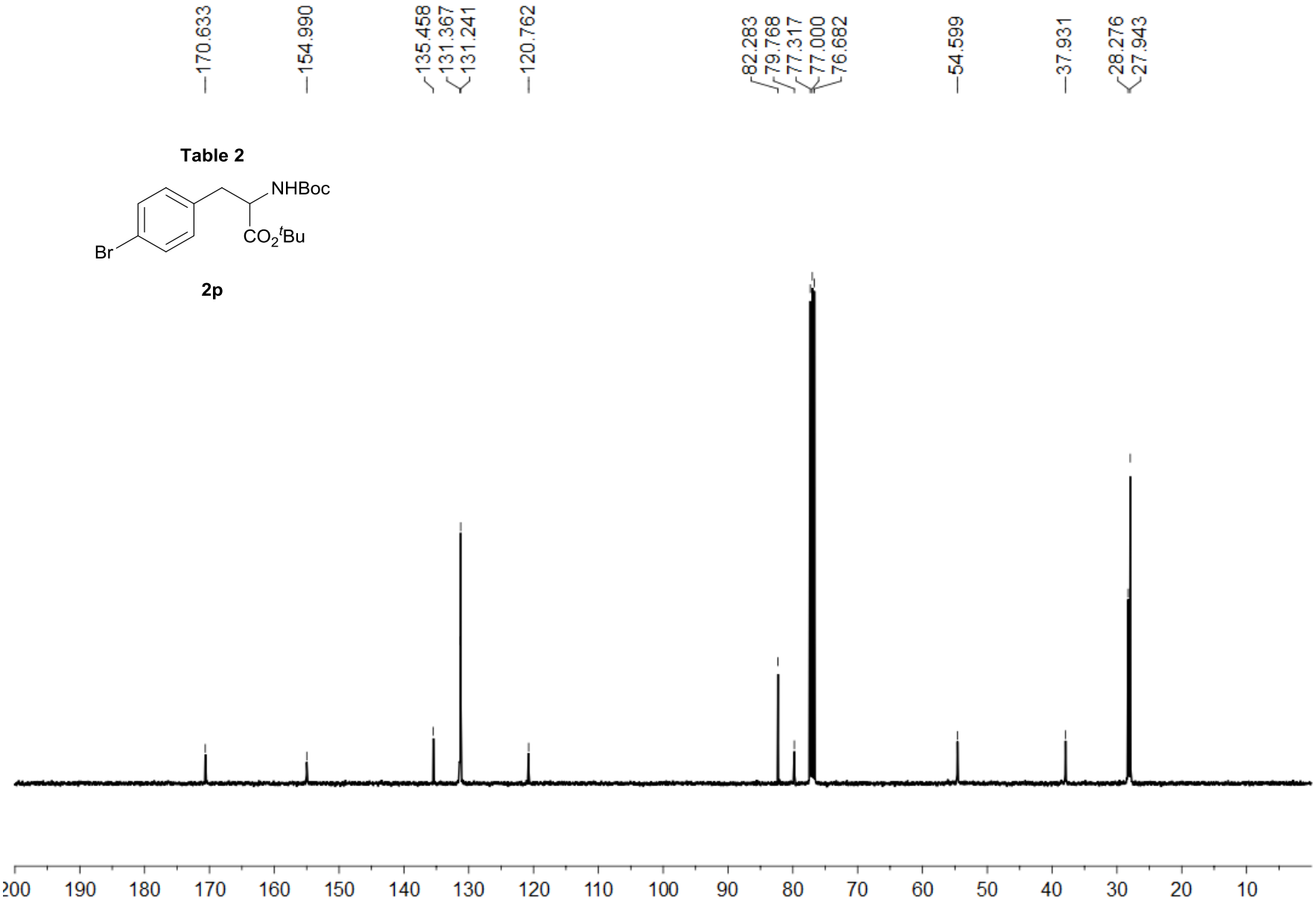
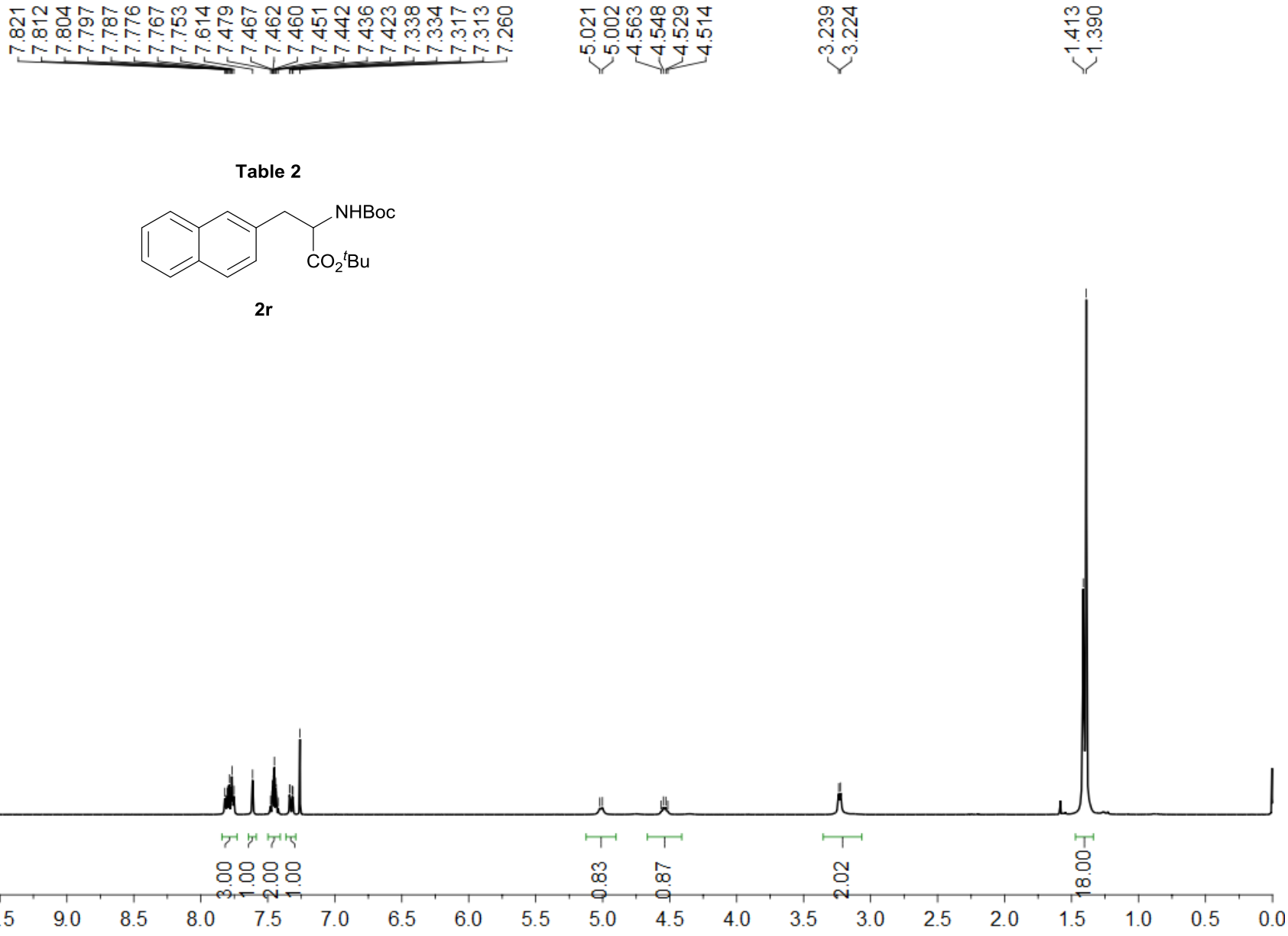
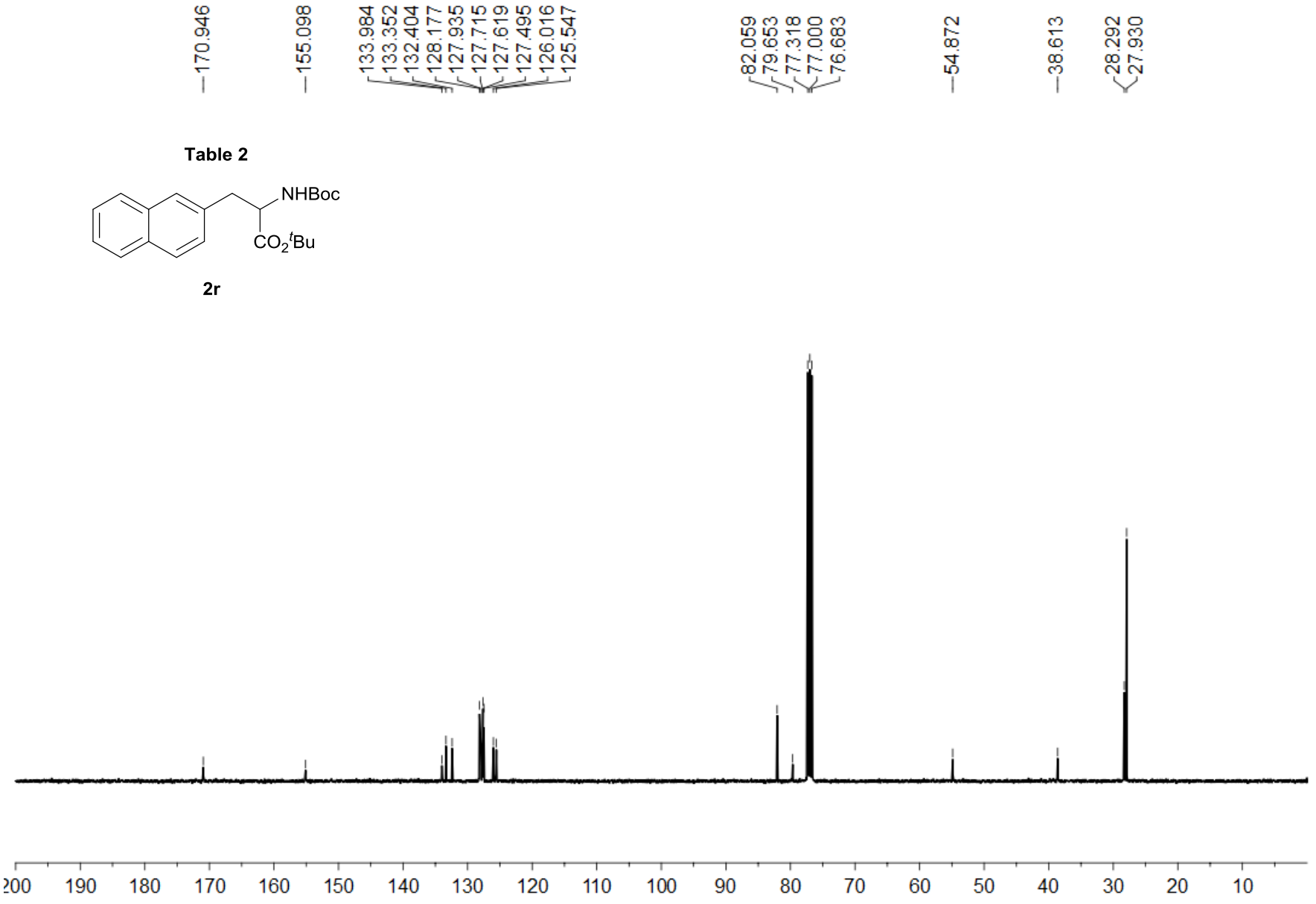

170.633
154.990
135.458
131.367
131.241
120.762
82.283
79.768
77.317
77.000
76.682
54.599
37.931
28.276
27.943
Table 2
NHBoc
CO2tBu
Br
2p
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

Table 2
2q
NO2
CO2tBu
NHBoc
8.121
8.101
8.046
7.538
7.518
7.487
7.467
7.448
7.260
5.092
5.075
4.484
4.467
4.452
3.268
3.253
3.234
3.219
3.148
3.134
3.114
3.100
1.428
1.421
2.01
1.00
1.00
0.90
0.96
1.01
1.02
18.00

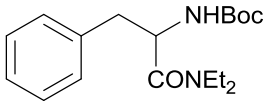
Table 2
2q
NO2
CO2tBu
NHBoc
170.173
154.921
148.127
138.690
135.816
129.185
124.512
121.971
82.855
80.023
77.318
77.000
76.683
54.578
38.152
28.248
27.959
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.821
7.812
7.804
7.797
7.787
7.776
7.767
7.753
7.614
7.479
7.467
7.462
7.460
7.451
7.442
7.436
7.423
7.338
7.334
7.317
7.313
7.260
5.021
5.002
4.563
4.548
4.529
4.514
3.239
3.224
1.413
1.390
Table 2
NHBoc
CO2tBu
2r
3.00
1.00
2.00
1.00
0.83
0.87
2.02
18.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

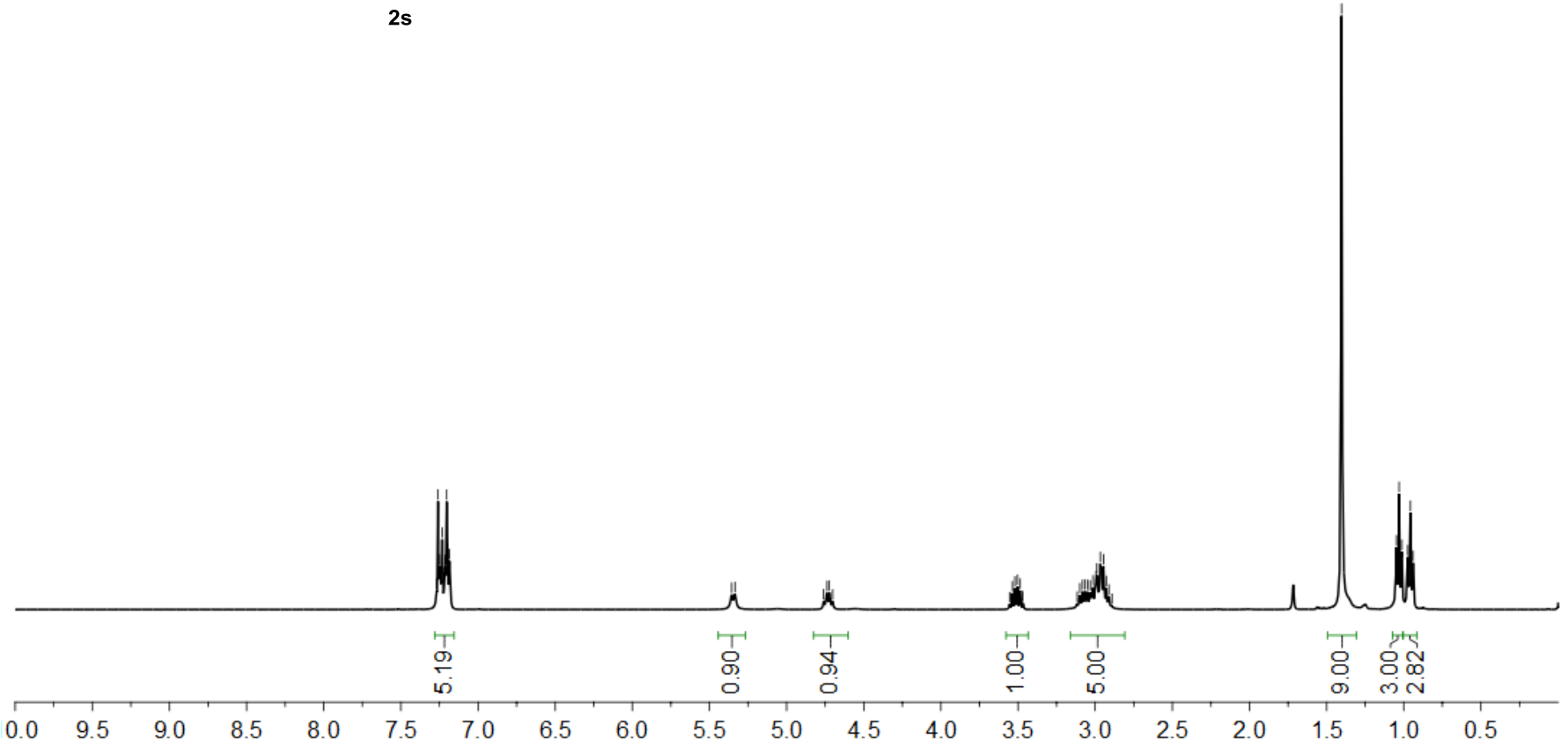

170.946
155.098
133.984
133.352
132.404
128.177
127.935
127.715
127.619
127.495
126.016
125.547
82.059
79.653
77.318
77.000
76.683
54.872
38.613
28.292
27.930
Table 2
NHBoc
CO2tBu
2r
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

7.268
7.260
7.248
7.233
7.213
7.203
7.185
5.356
5.335
4.760
4.738
4.723
4.701
3.555
3.538
3.520
3.504
3.486
3.468
3.082
3.066
3.049
3.032
3.014
2.995
2.989
2.967
2.946
2.928
1.403
1.048
1.030
1.012
0.975
0.957
0.939

Table 2



2s



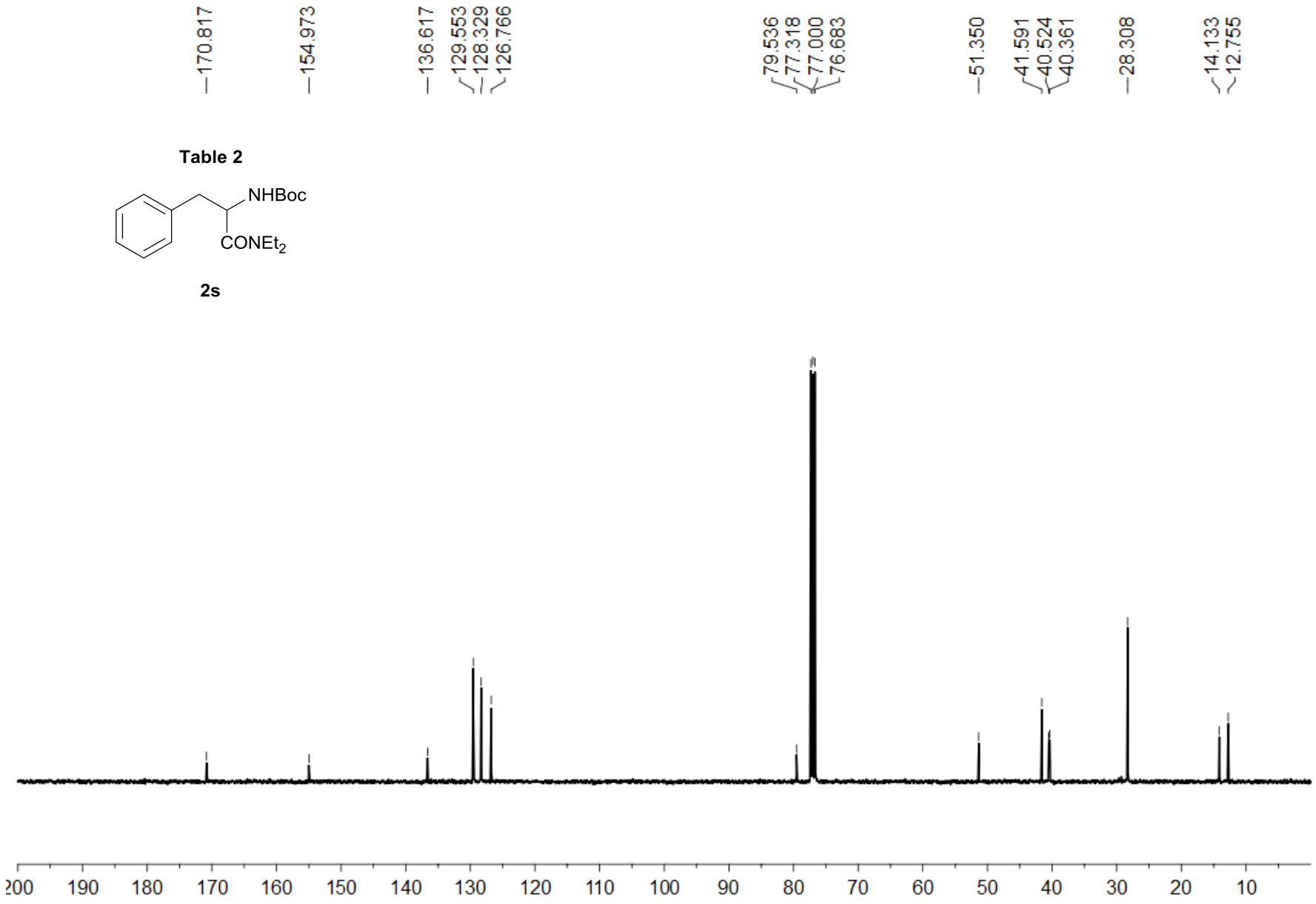

170.817
154.973
136.617
129.553
128.329
126.766
79.536
77.318
77.000
76.683
51.350
41.591
40.524
40.361
28.308
14.133
12.755
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

Table 2

NHBoc
CONEt2

2s

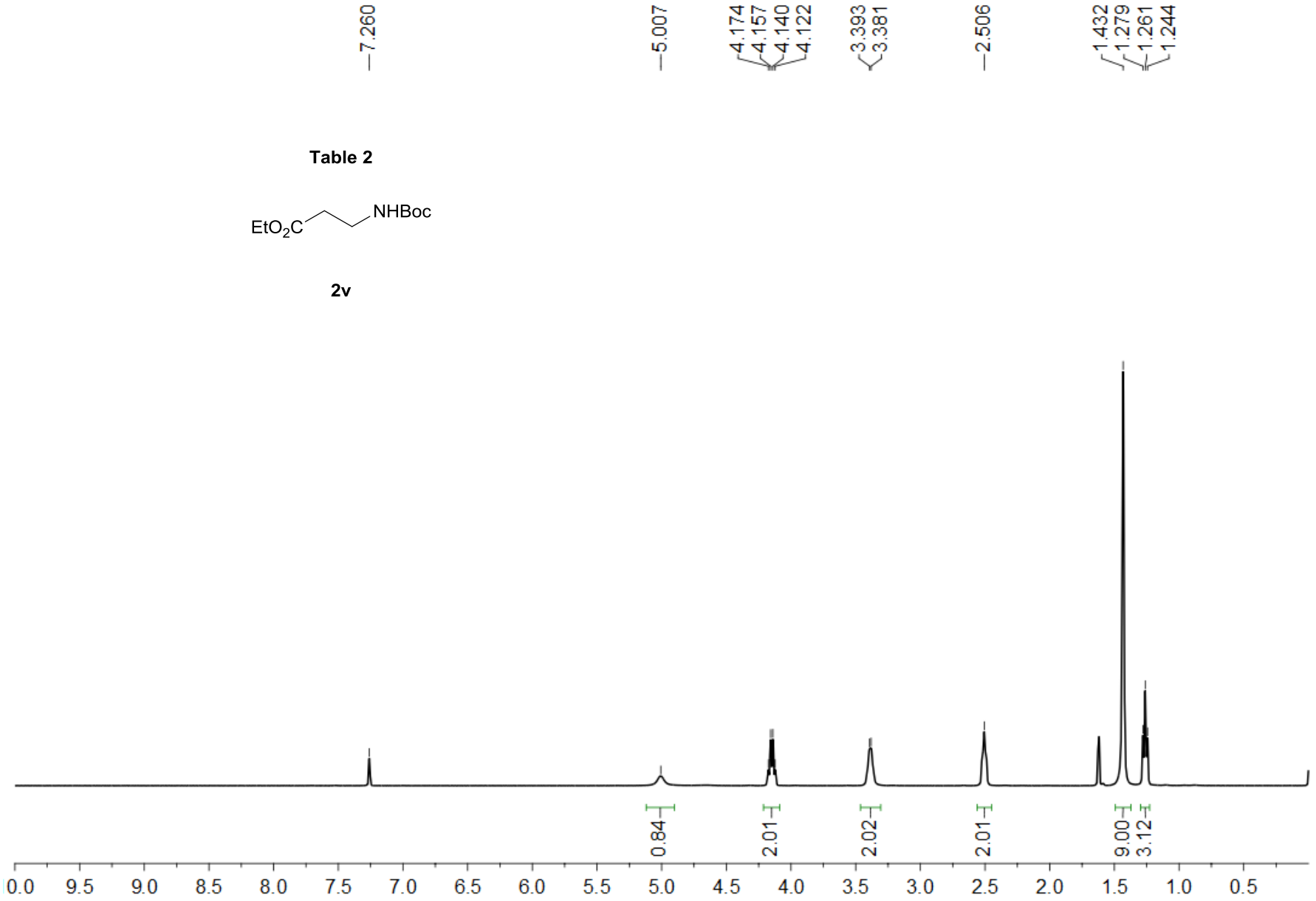

7.260
5.007
4.174
4.157
4.140
4.122
3.393
3.381
2.506
1.432
1.279
1.261
1.244
0.84
2.01
2.02
2.01
9.00
3.12
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

Table 2

EtO2C
NHBoc

2v

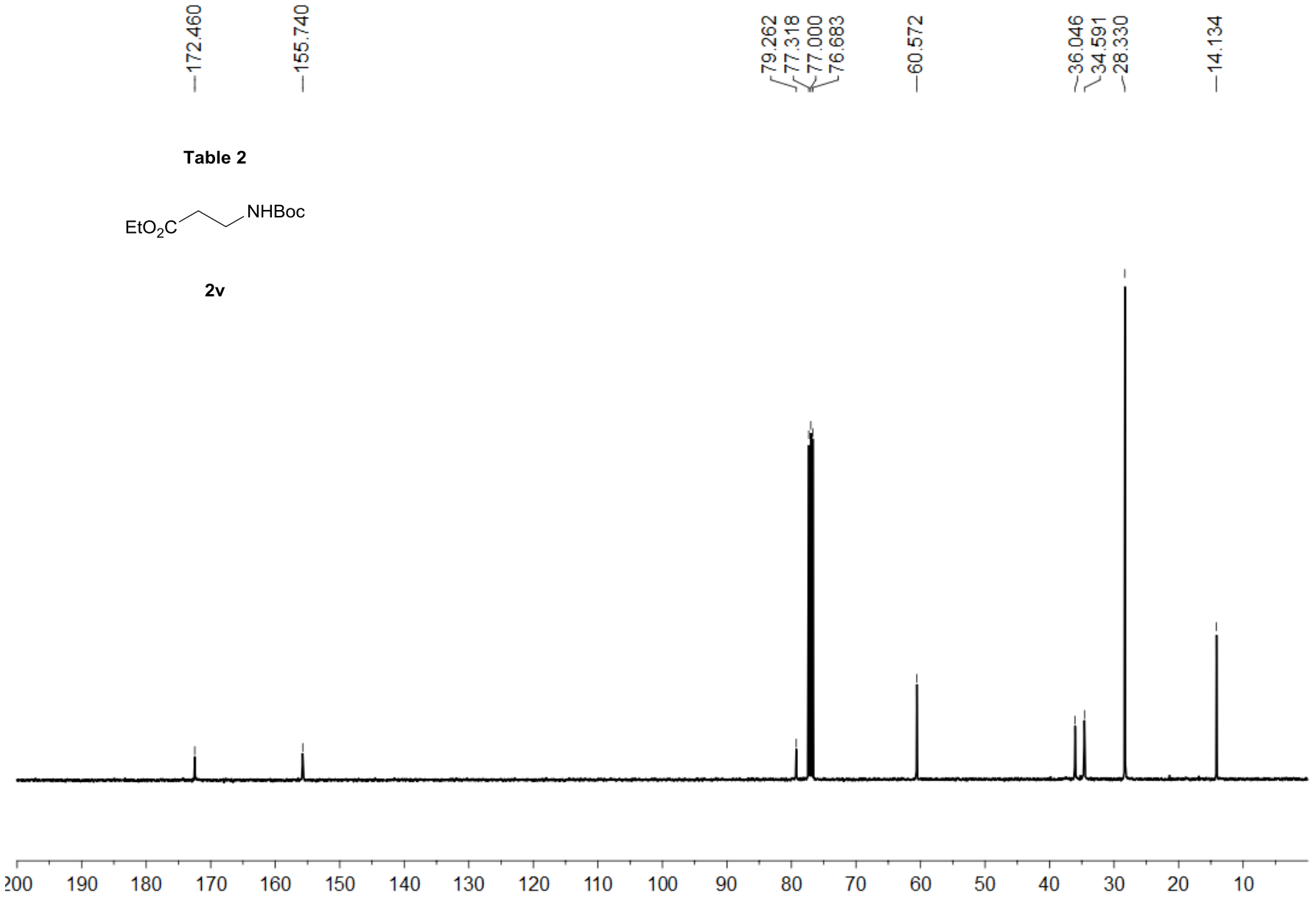

172.460
155.740
79.262
77.318
77.000
76.683
60.572
36.046
34.591
28.330
14.134
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

Table 2

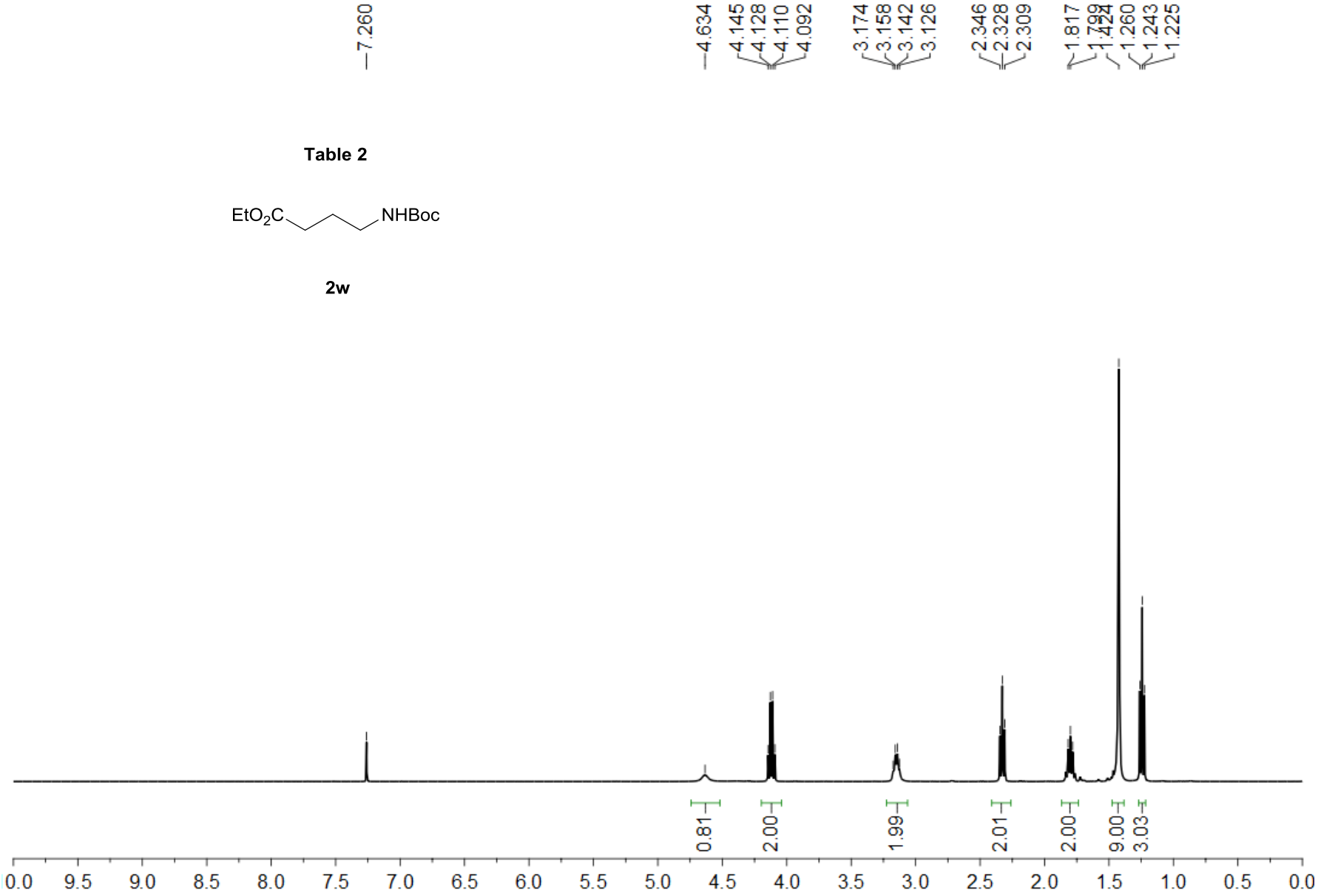
EtO2C
NHBoc

2v

Table 2

EtO2C
NHBoc

2w


7.260
4.634
4.145
4.128
4.110
4.092
3.174
3.158
3.142
3.126
2.346
2.328
2.309
1.817
1.799
1.424
1.260
1.243
1.225
0.81
2.00
1.99
2.01
2.00
9.00
3.03
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

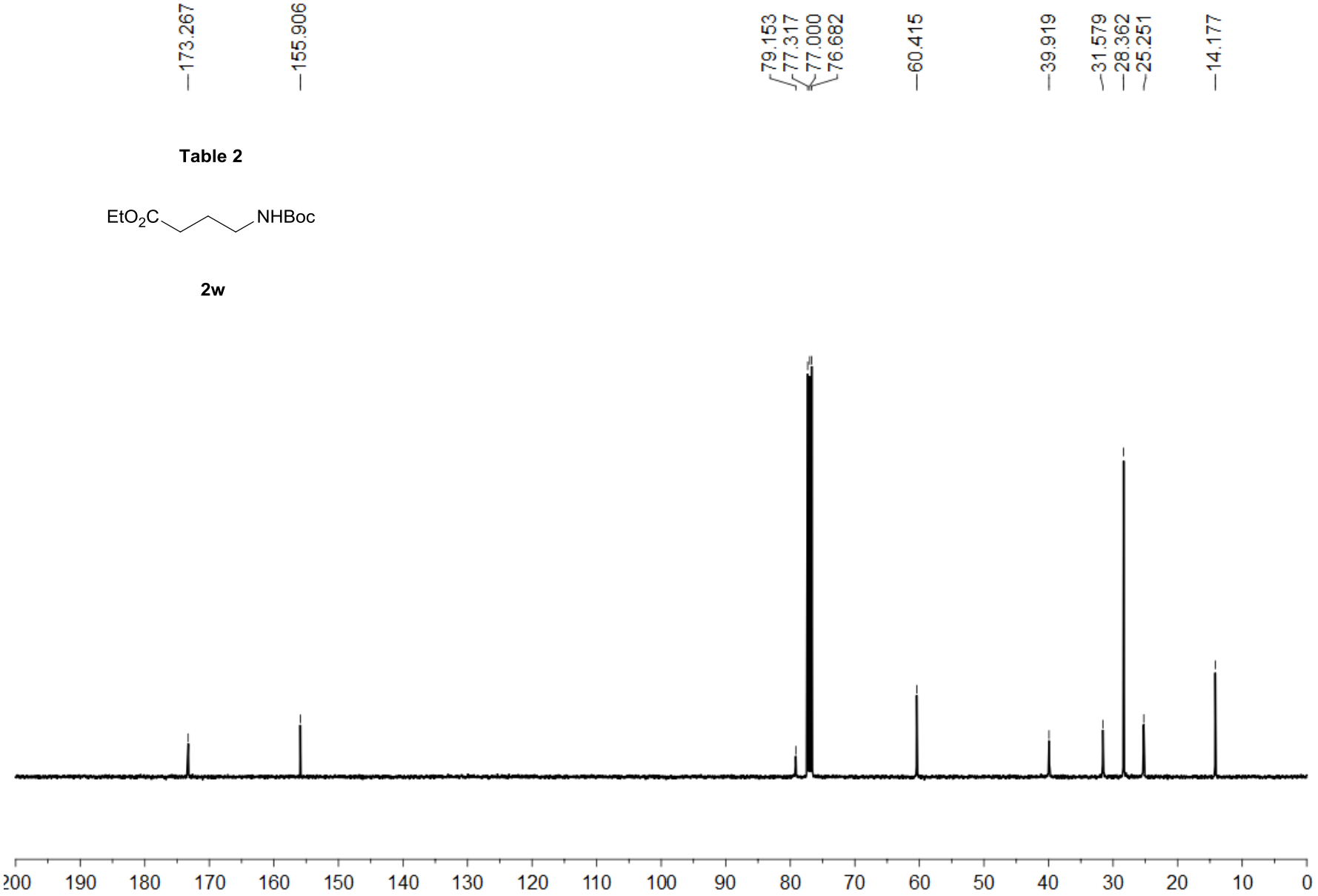

173.267
155.906
79.153
77.317
77.000
76.682
60.415
39.919
31.579
28.362
25.251
14.177
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Table 2

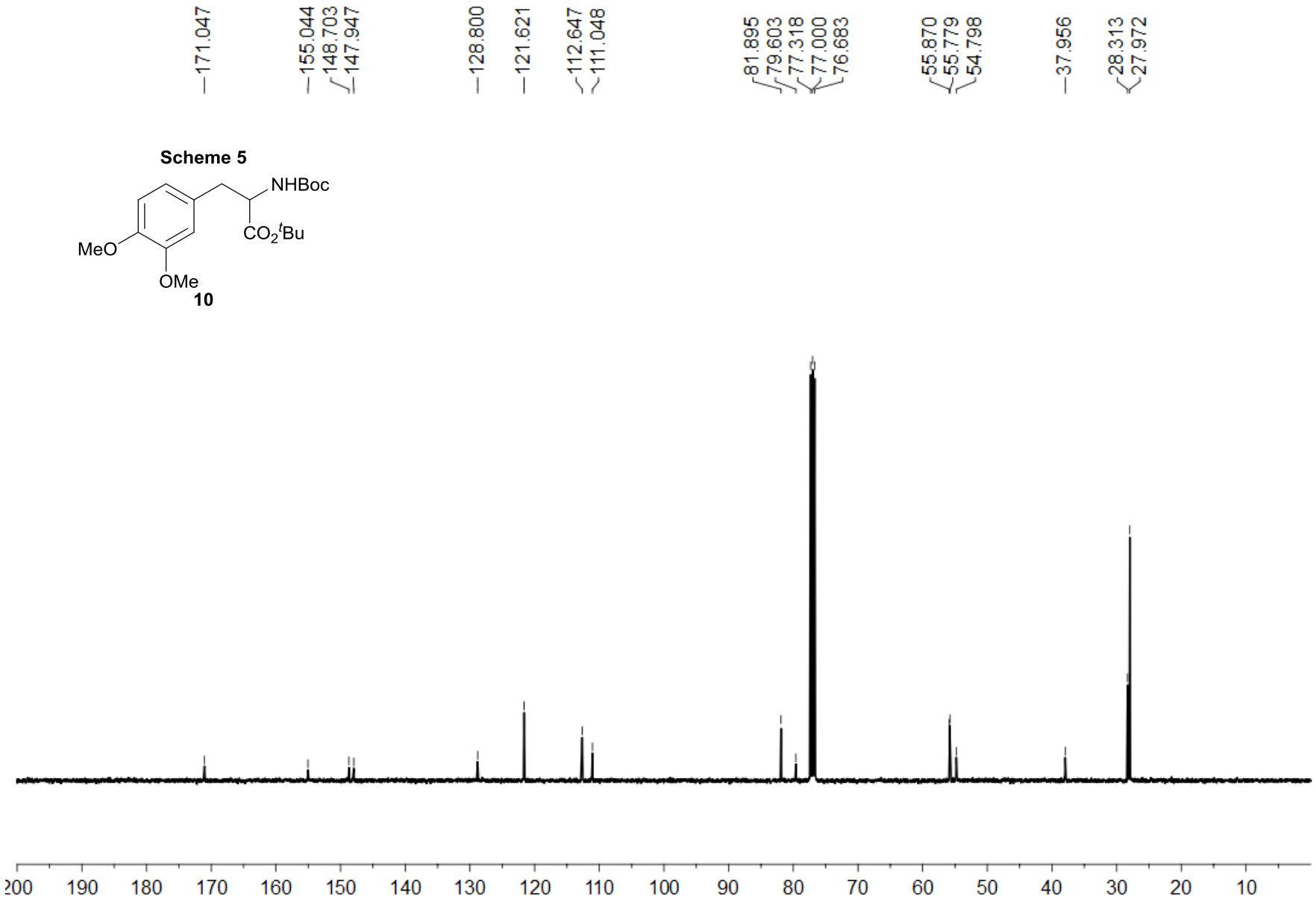
EtO2C
NHBoc

2w

Scheme 4
4
NHBoc
7.260
7.250
7.151
7.142
7.130
7.120
7.110
6.543
6.516
5.923
5.886
1.496
5.05
1.07
1.01
1.00
9.22
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

Scheme 4
4
NHBoc
152.683
136.540
128.560
126.008
125.121
124.252
109.659
80.843
28.229
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

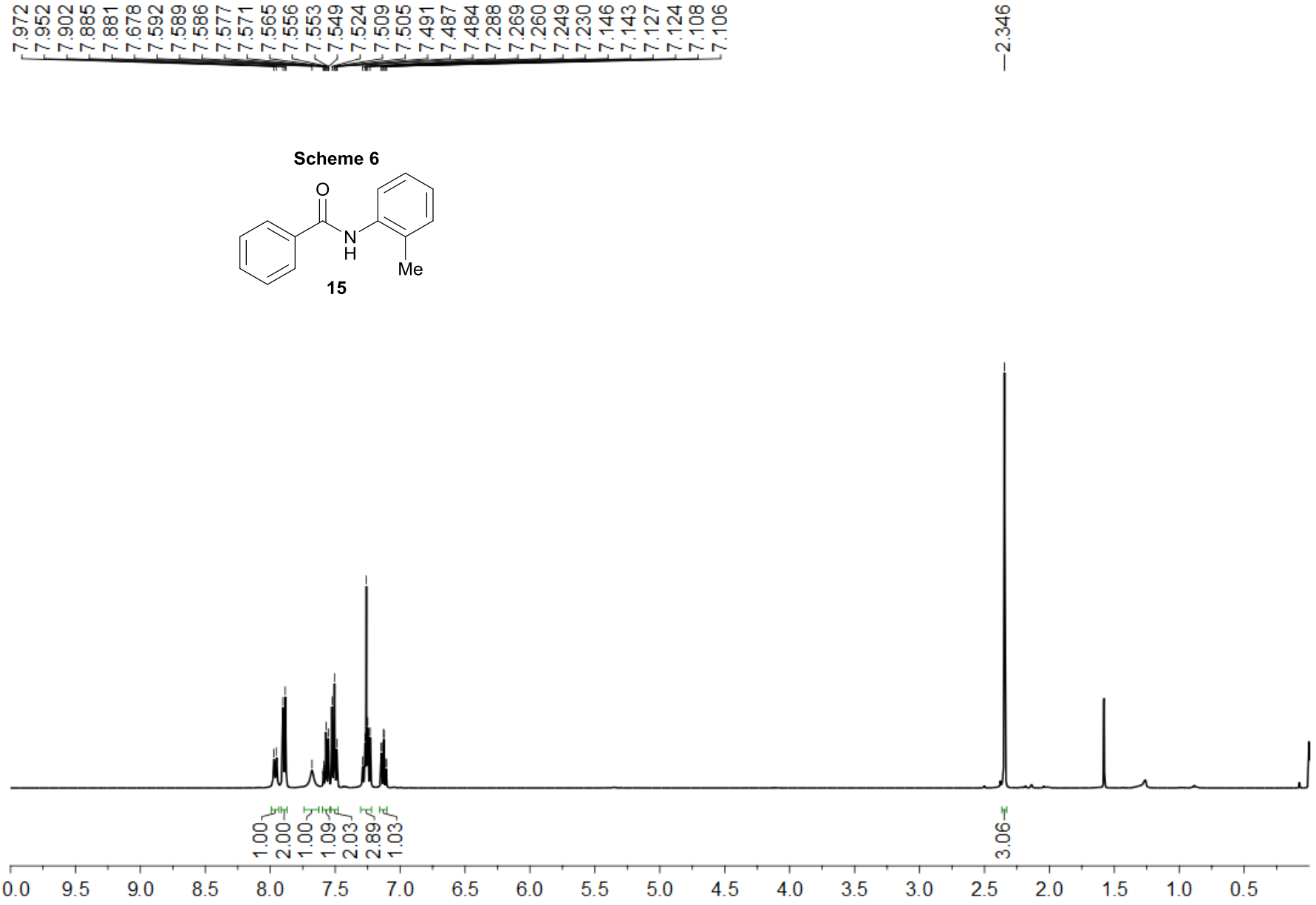
Scheme 5
10
MeO
OMe
CO2tBu
NHBoc
7.260
6.792
6.772
6.712
6.707
6.687
6.682
4.970
4.951
4.444
4.429
4.409
4.394
3.853
3.007
2.993
1.419
1.413
0.99
2.00
0.81
0.82
6.00
2.00
18.00


171.047
155.044
148.703
147.947
128.800
121.621
112.647
111.048
81.895
79.603
77.318
77.000
76.683
55.870
55.779
54.798
37.956
28.313
27.972
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

Scheme 5

NHBoc
CO2tBu
MeO
OMe

10


7.972
7.952
7.902
7.885
7.881
7.678
7.592
7.589
7.586
7.577
7.571
7.565
7.556
7.553
7.549
7.524
7.509
7.505
7.491
7.487
7.484
7.288
7.269
7.260
7.249
7.230
7.146
7.143
7.127
7.124
7.108
7.106
2.346
1.00
2.00
1.00
1.09
2.03
2.89
1.03
3.06
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

Scheme 6

O
N
H
Me

15

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
Scheme 6
15
O
N
H
Me
165.631
135.779
135.036
131.825
130.547
129.219
128.827
127.035
126.903
125.357
123.133
77.318
77.000
76.683
17.804