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Supporting Information

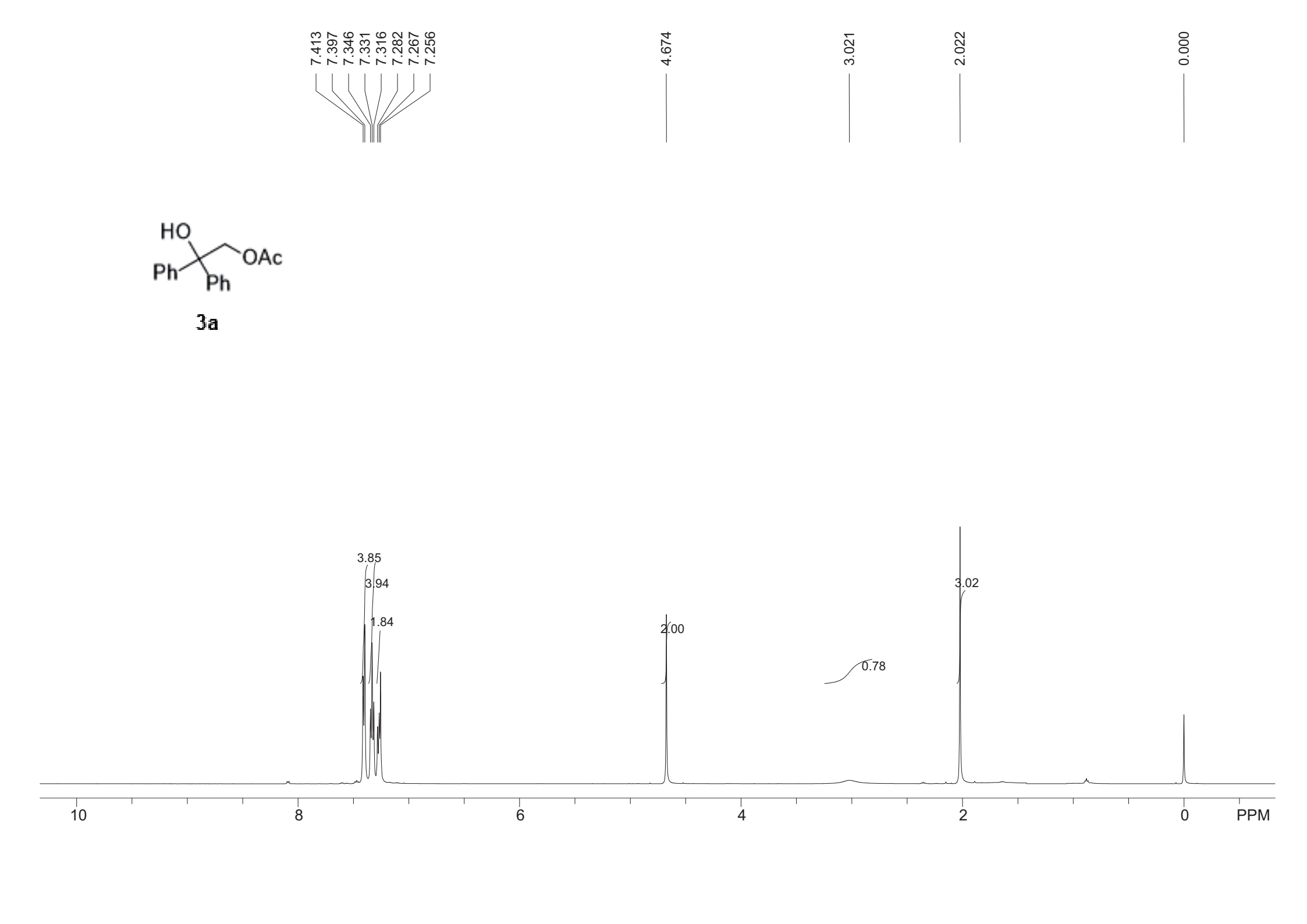
Synthesis of β-Acetoxy Alcohols by $PhI(OAc)_2$-Mediated Metal-Free Diastereoselective β-Acetoxylation of Alcohols

Chun-Yang Zhao[†], Liang-Gui Li[†], Qing-Rong Liu, Cheng-Xue Pan, Gui-Fa Su* and Dong-Liang Mo*

State Key Laboratory for the Chemistry and Molecular Engineering of Medicinal Resources, Ministry of Science and Technology of China; School of Chemistry & Pharmaceutical Sciences, Guangxi Normal University, 15 Yu Cai Road, Guilin 541004, China

Contents

1. NMR spectra of **3a-3x, 4a, 6, 7, 8**, and **9** S-2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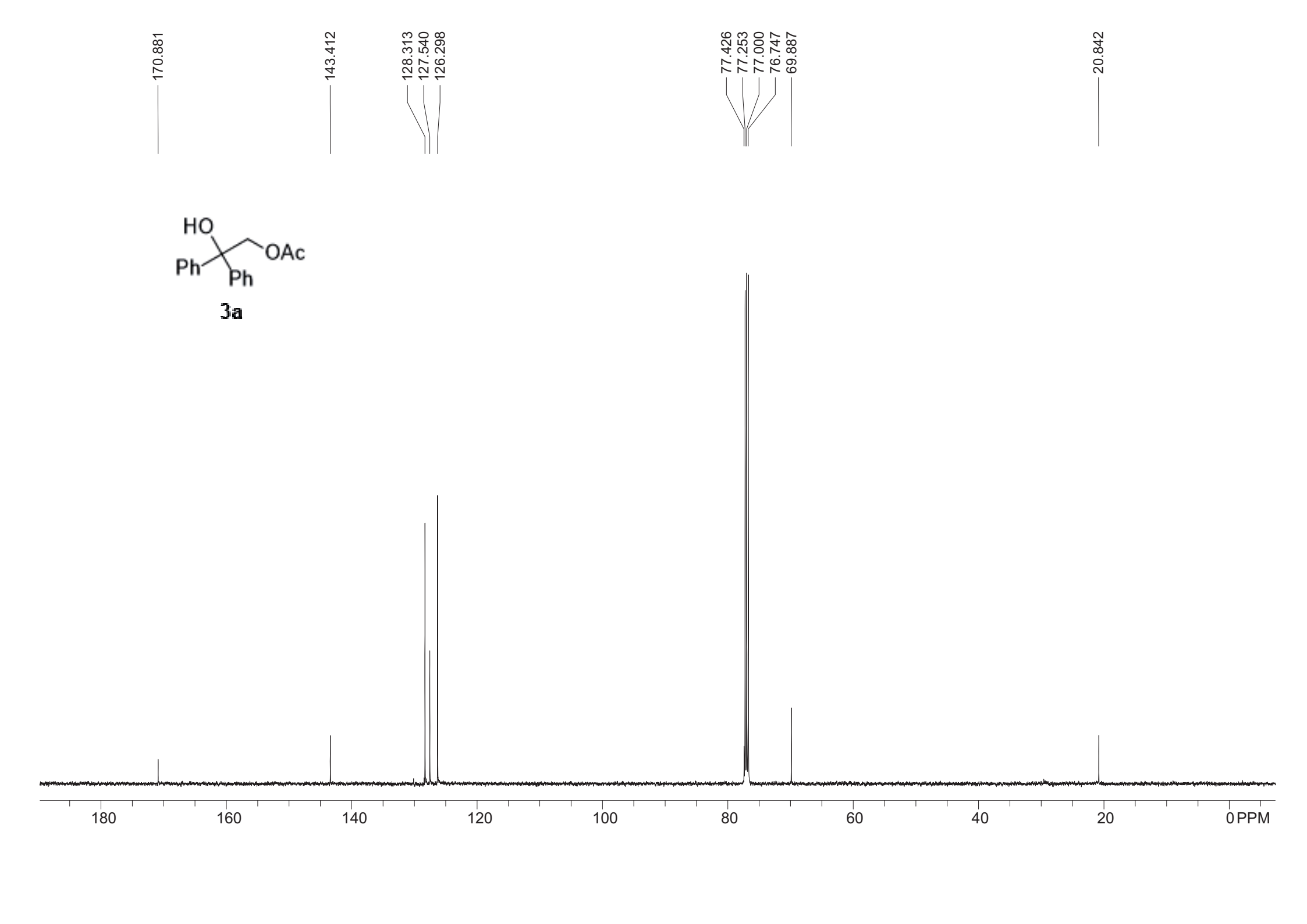
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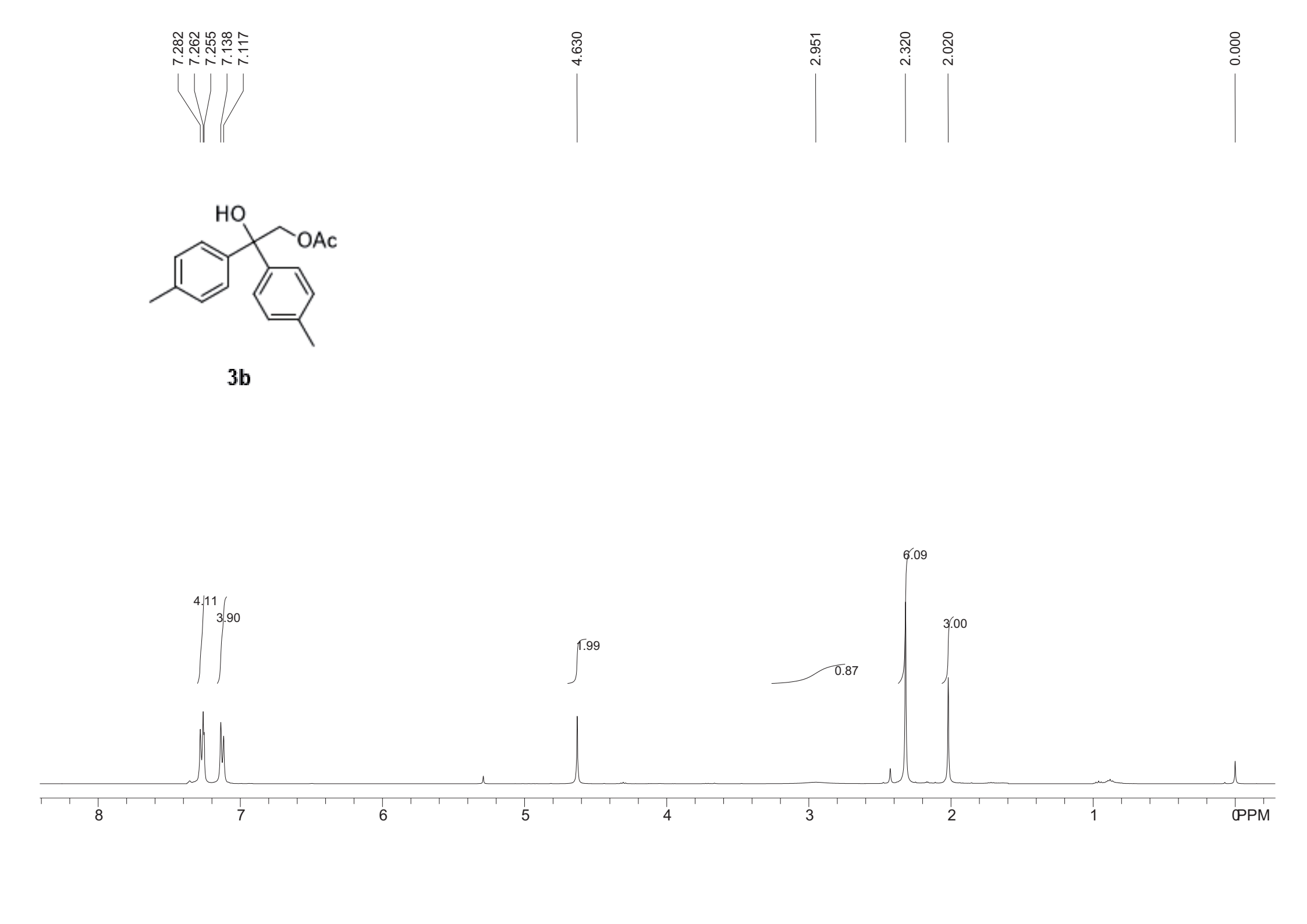
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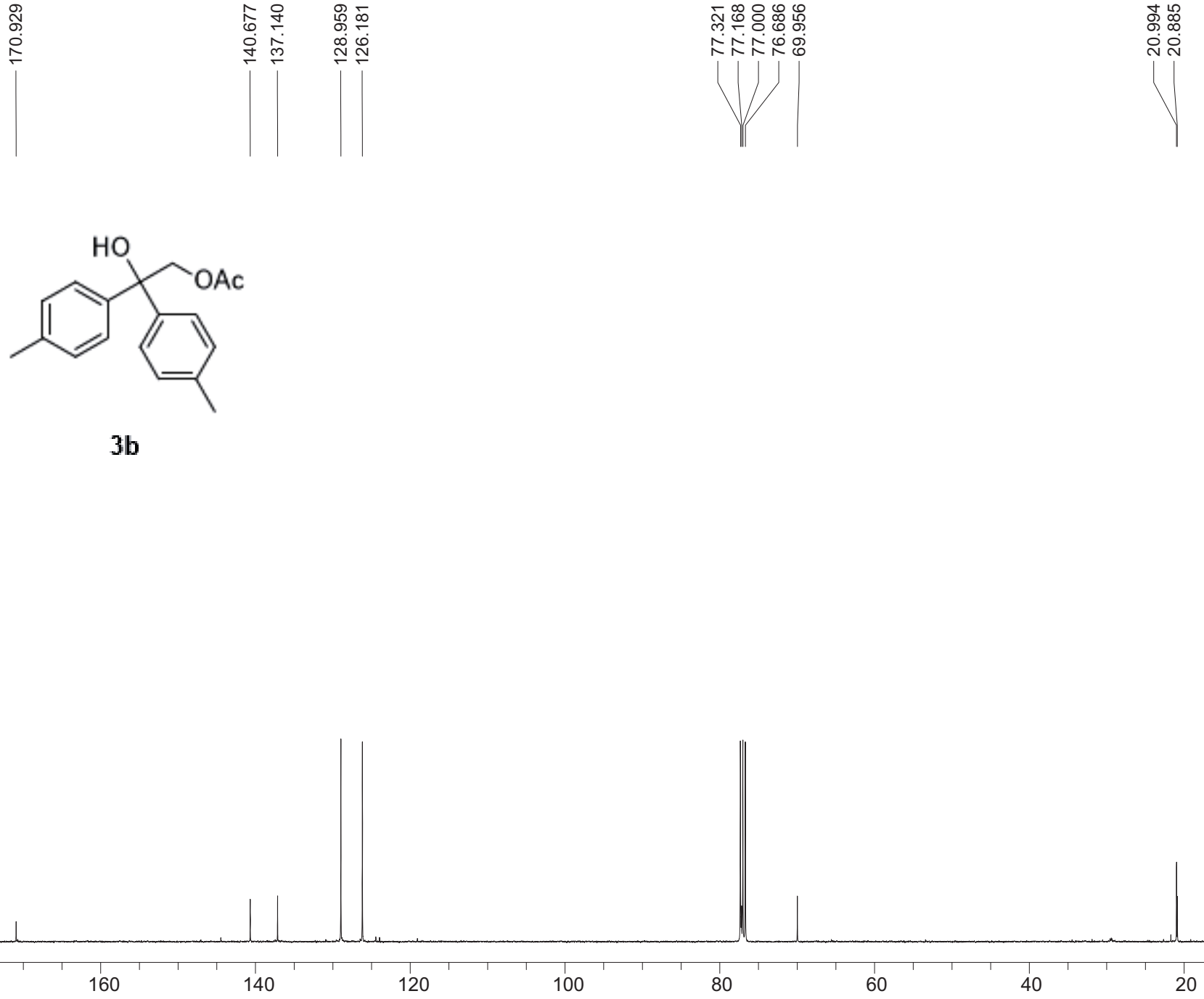
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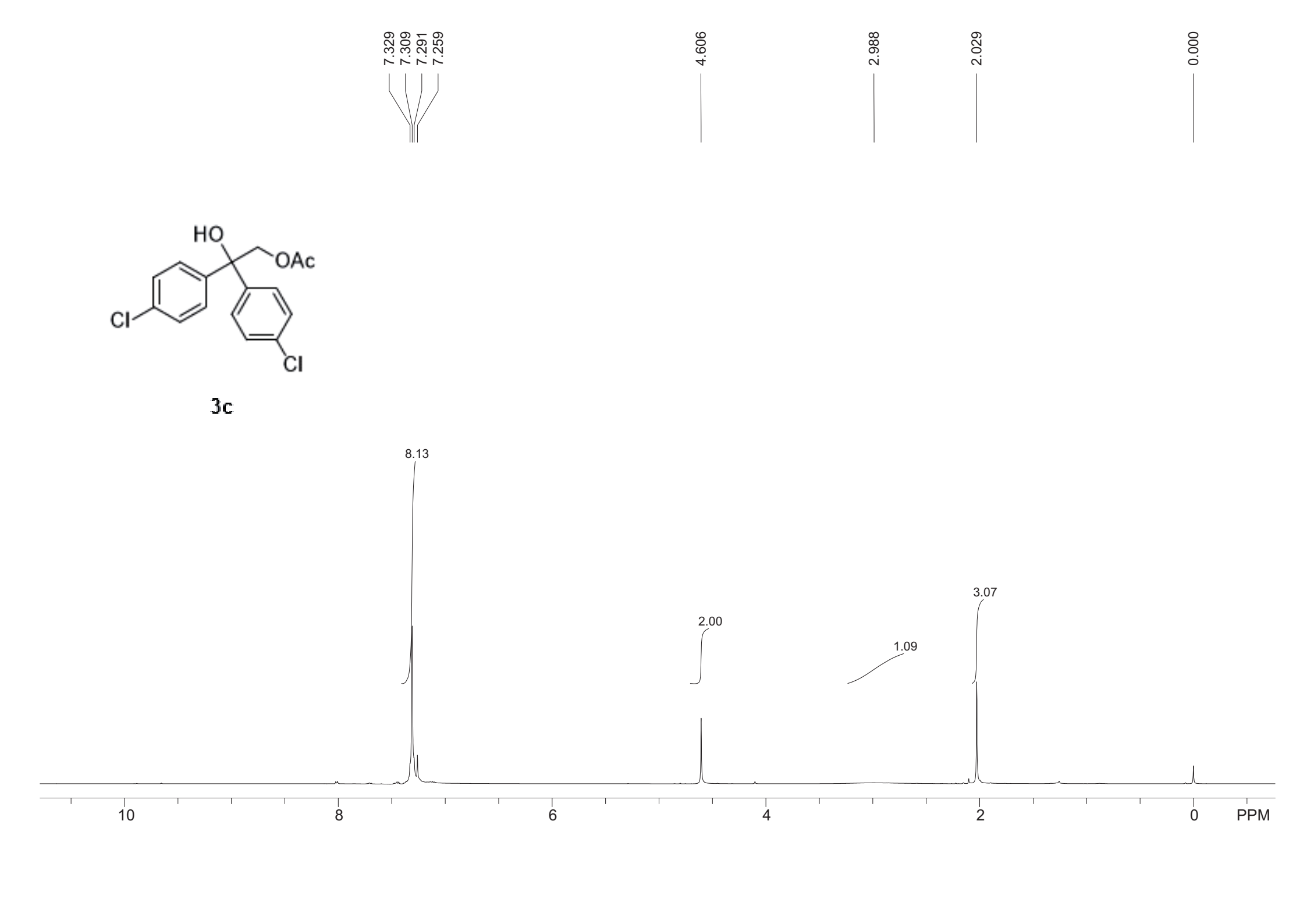
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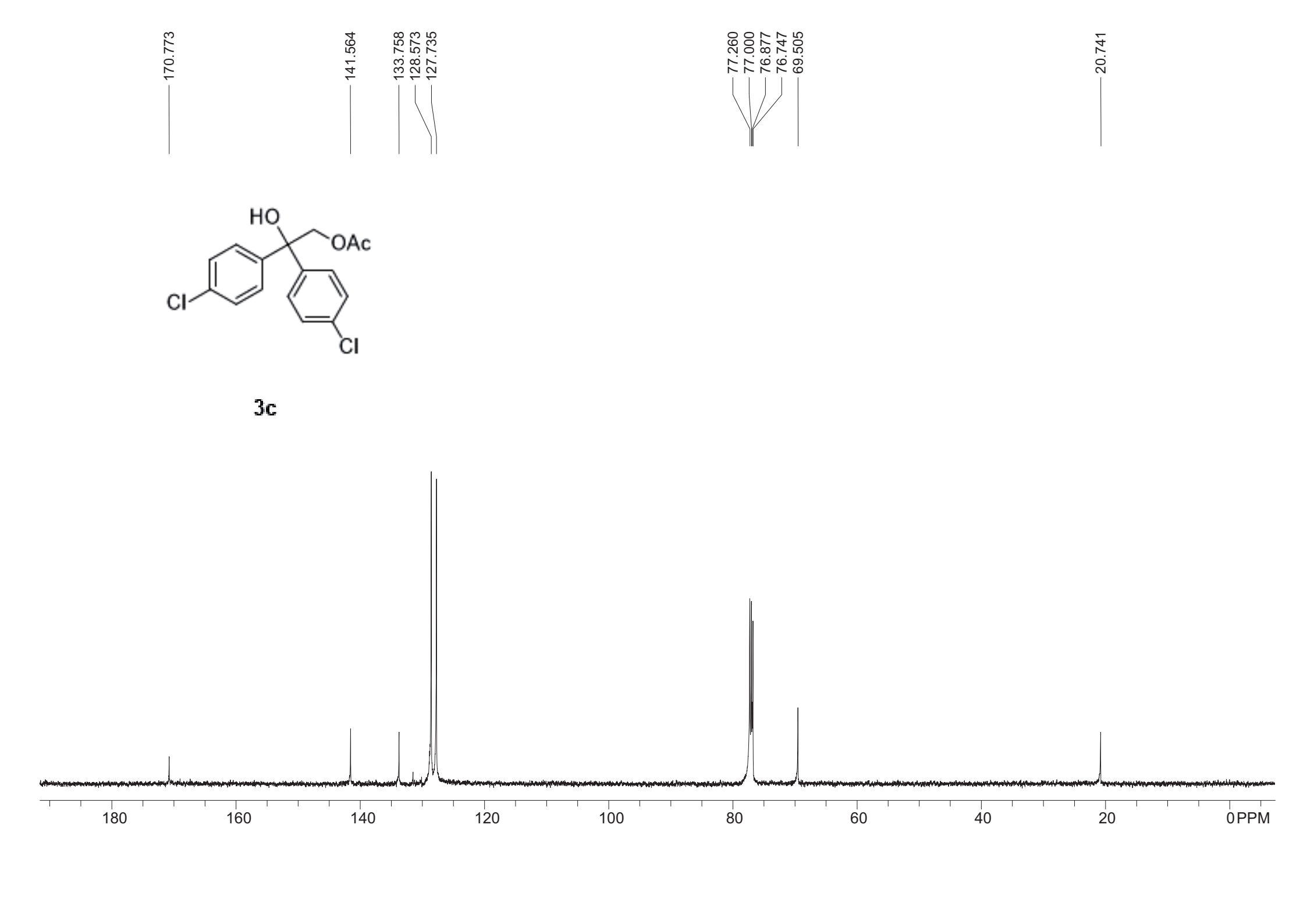
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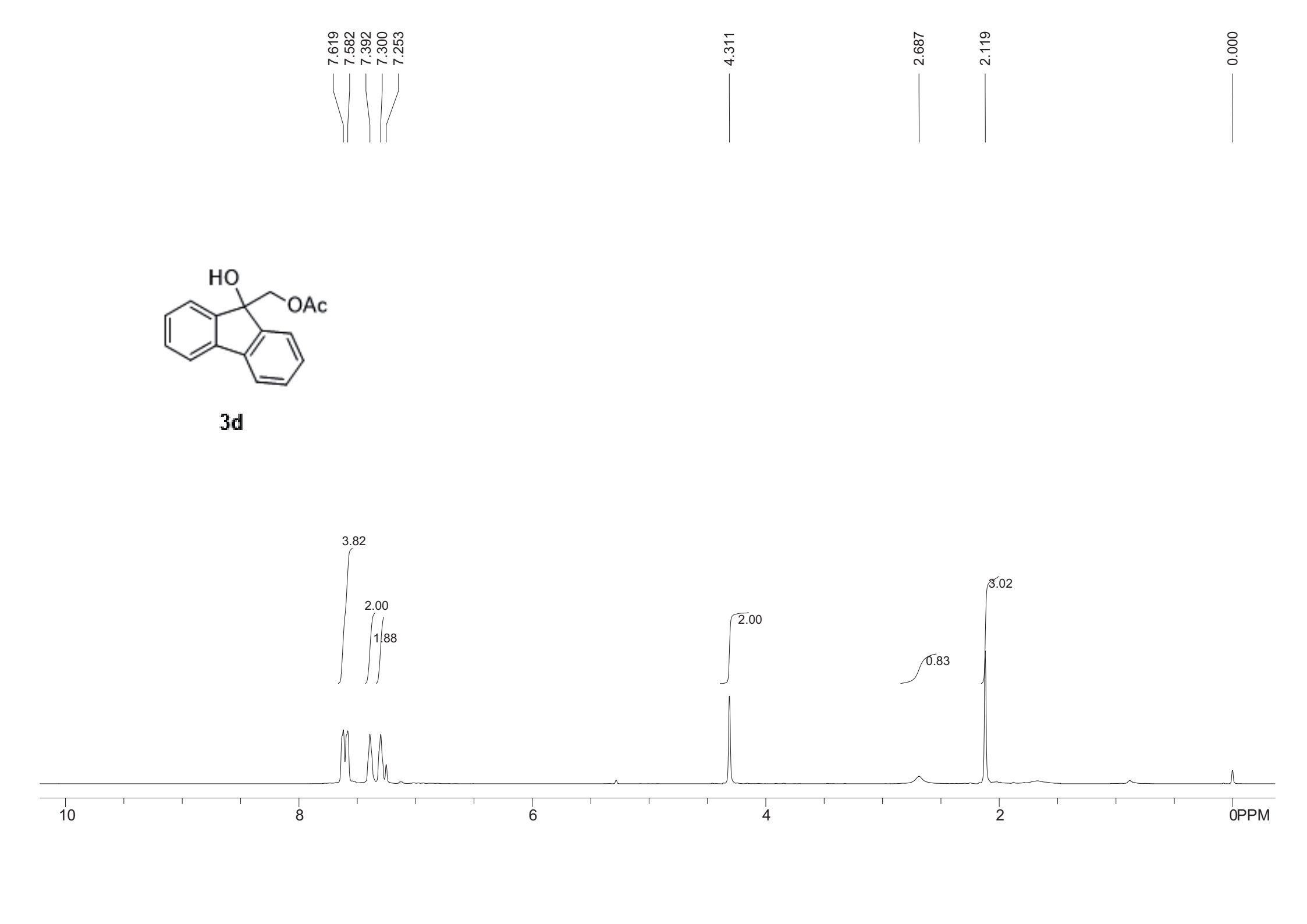
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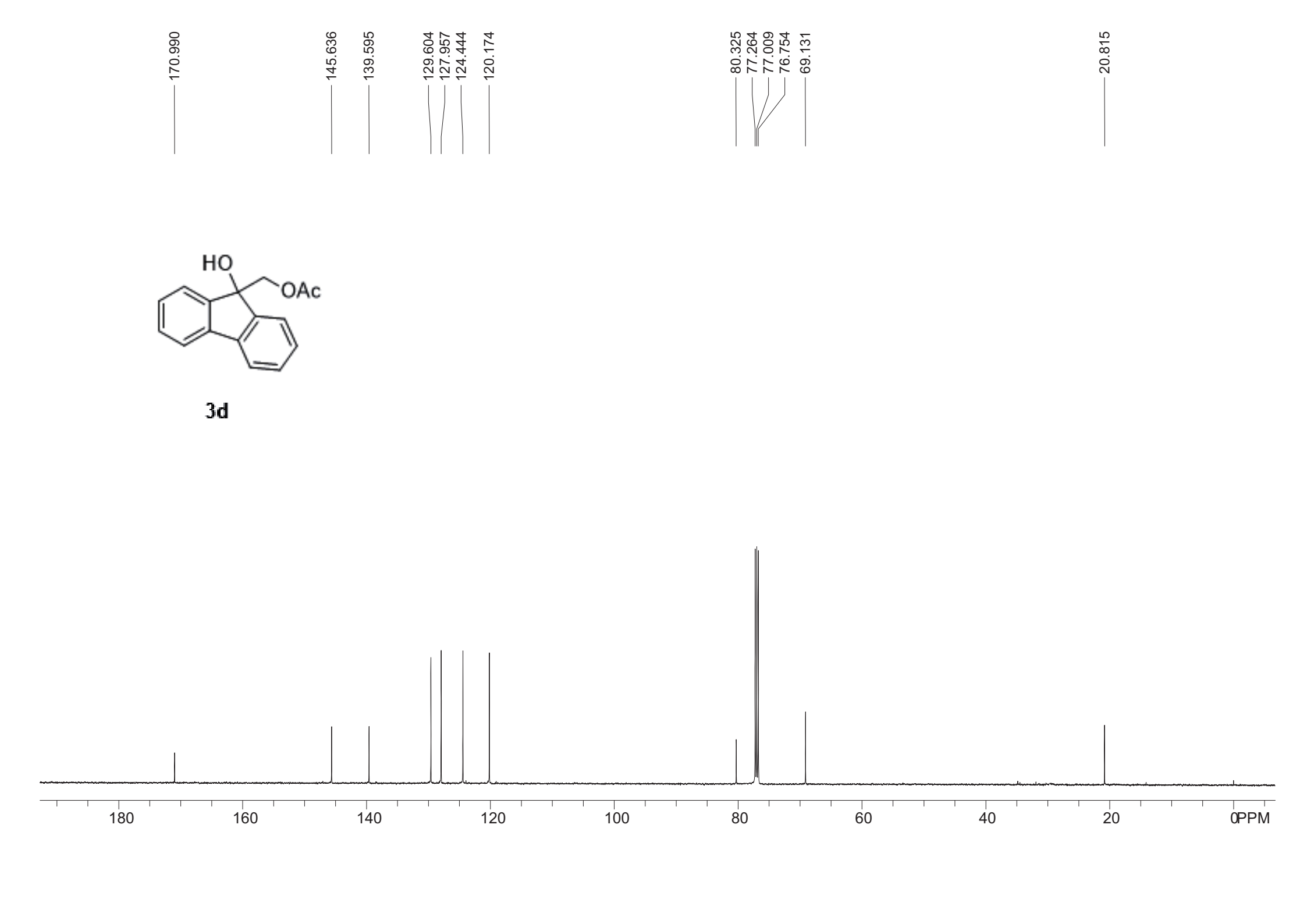
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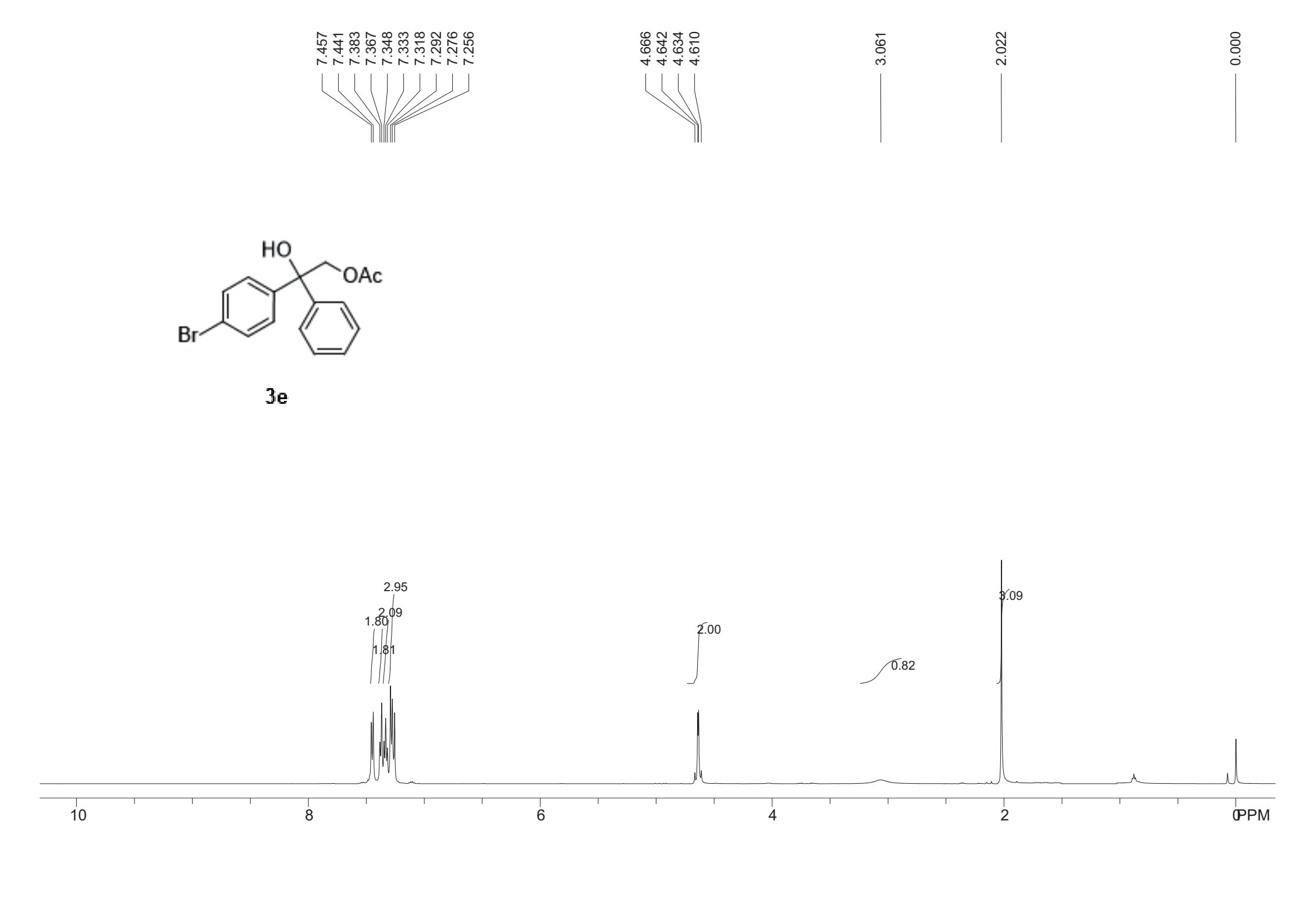
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4
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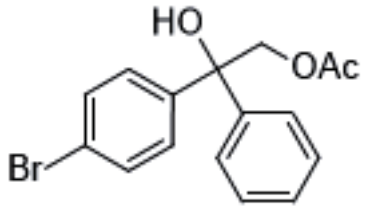
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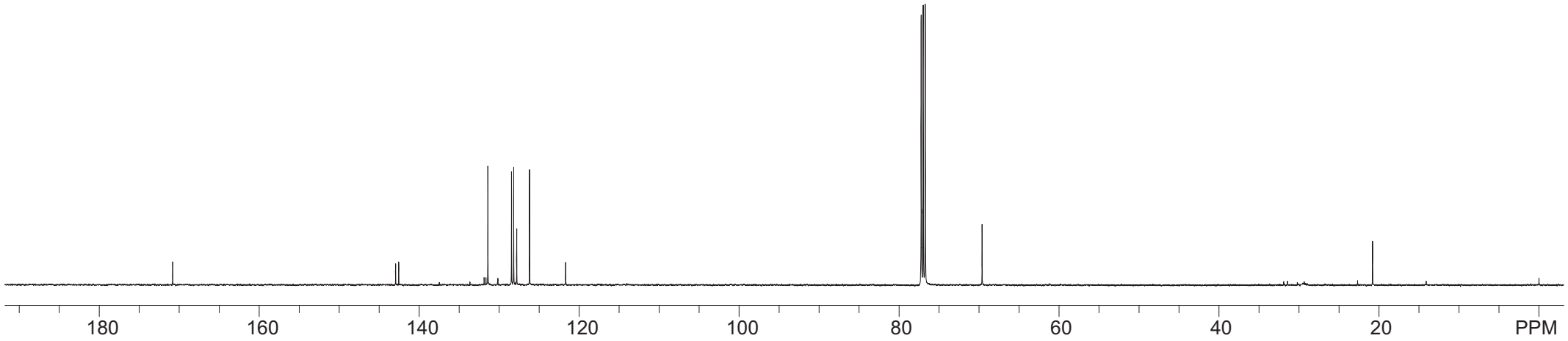
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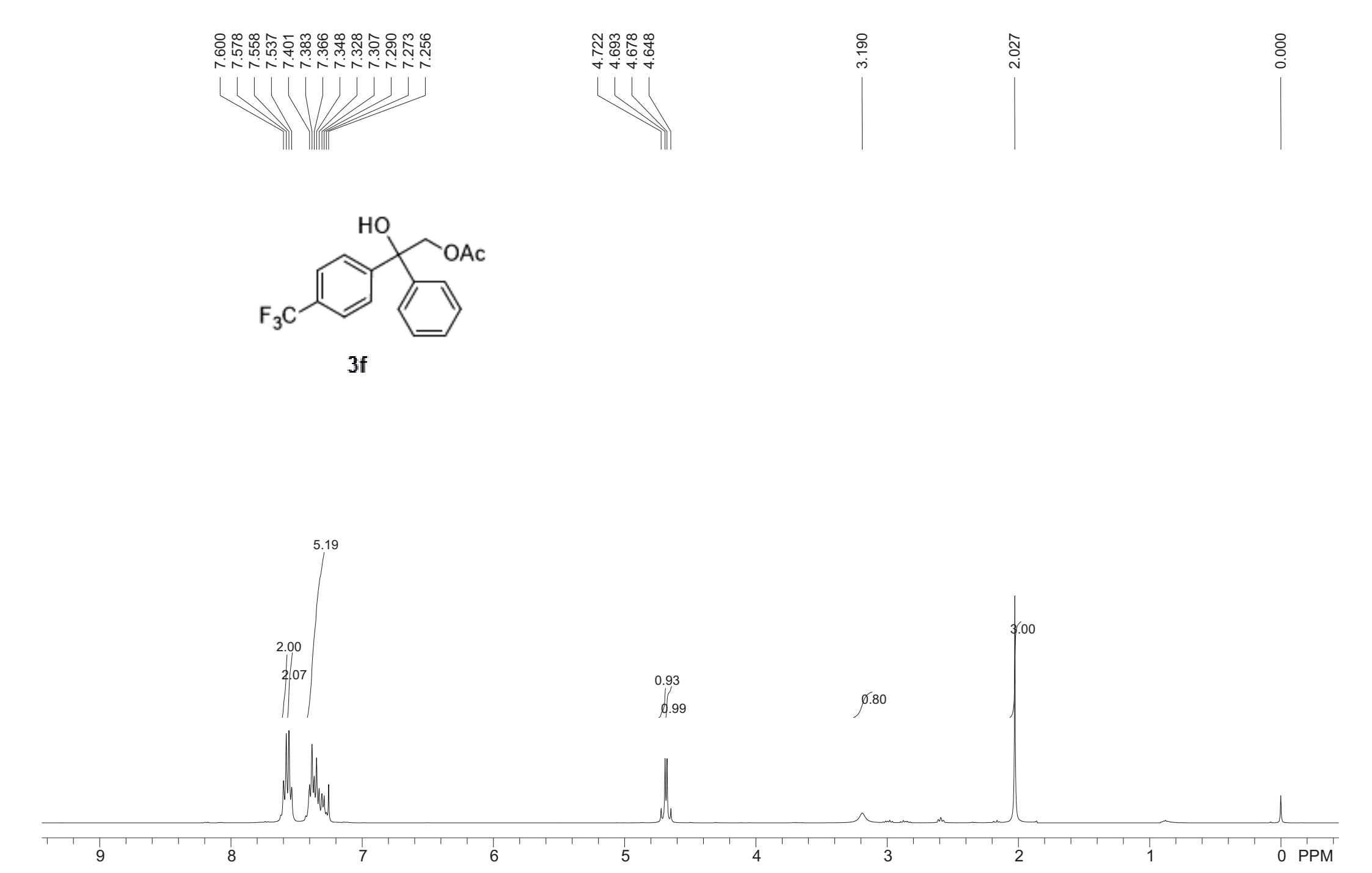
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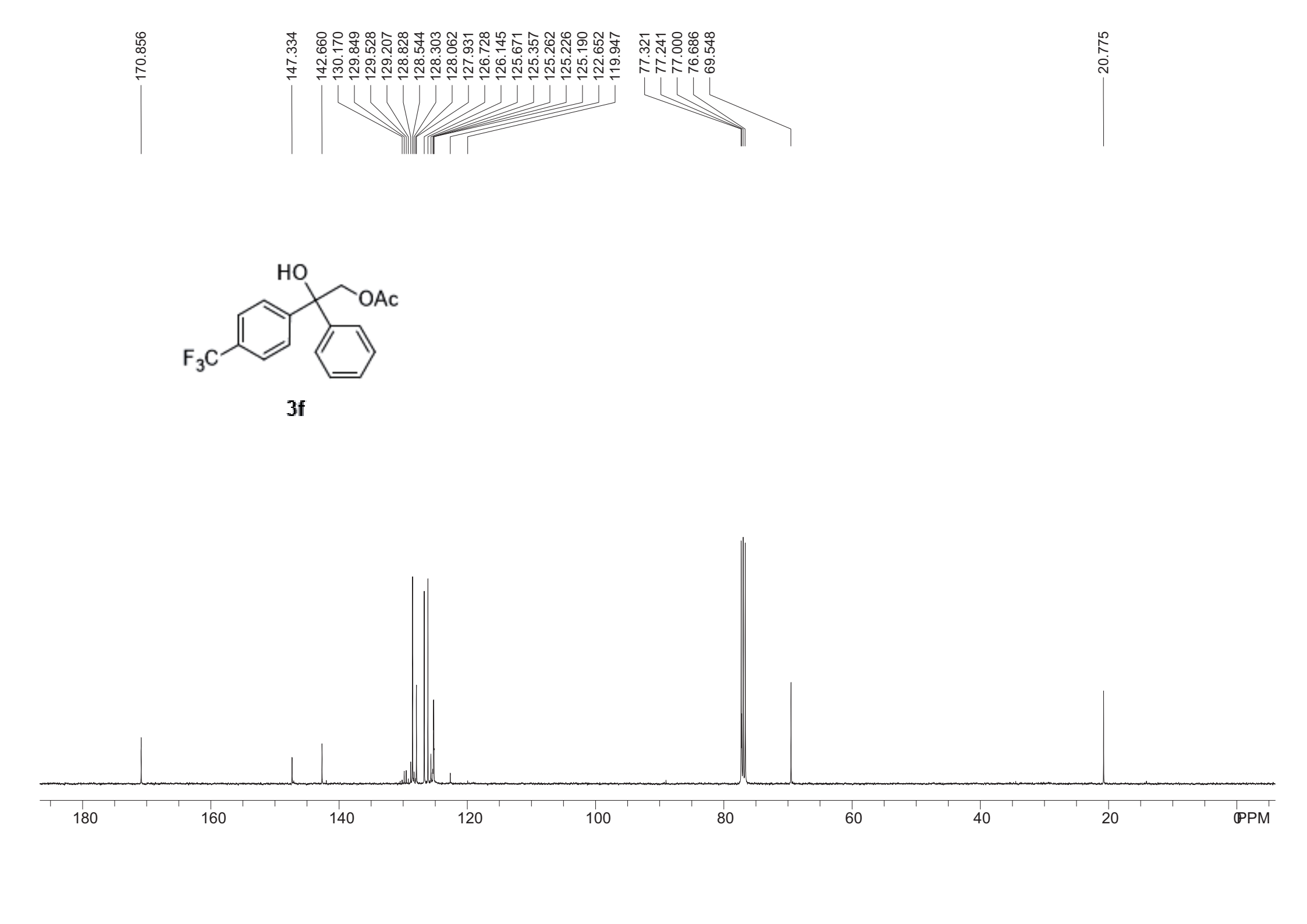
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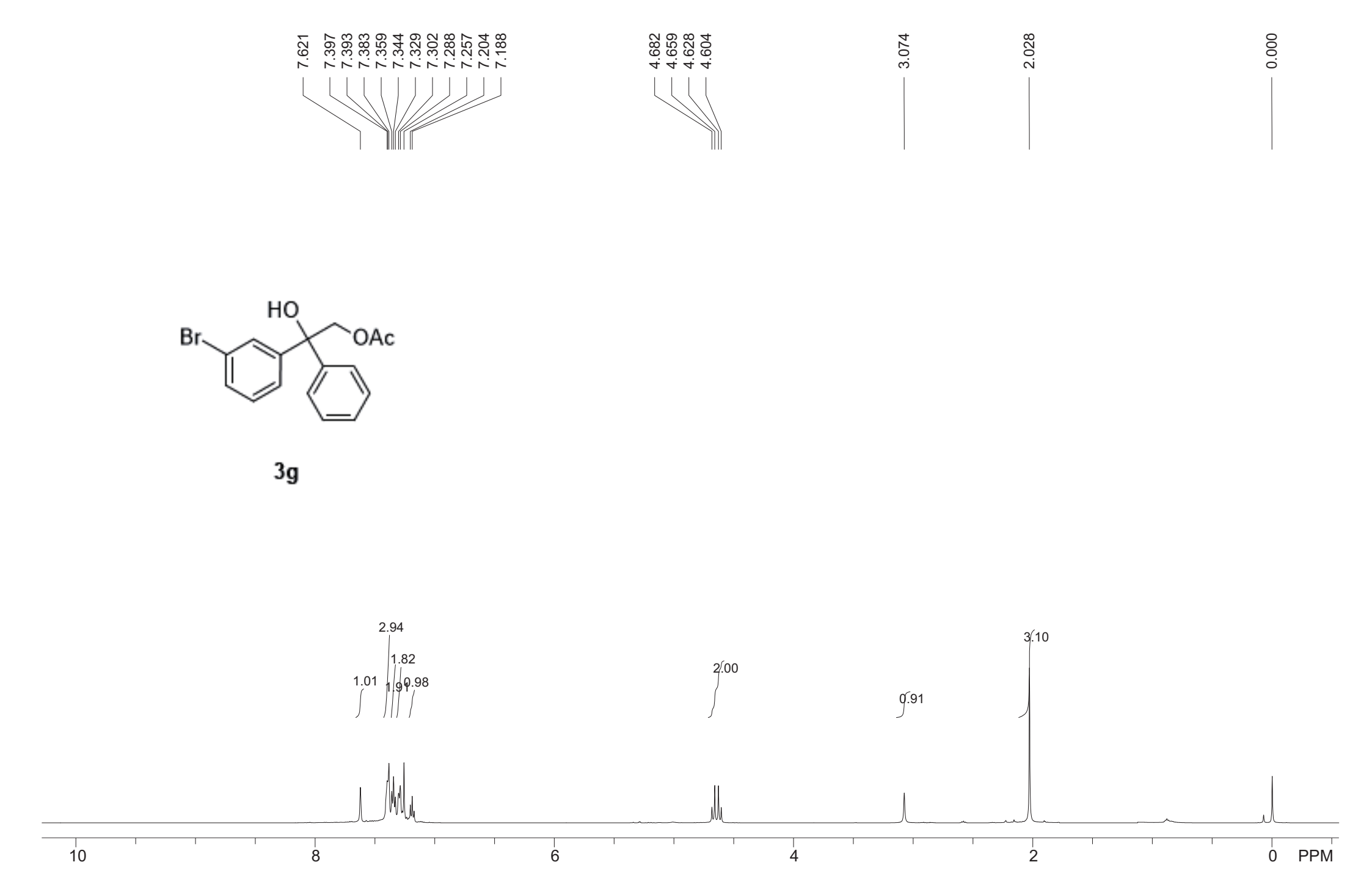
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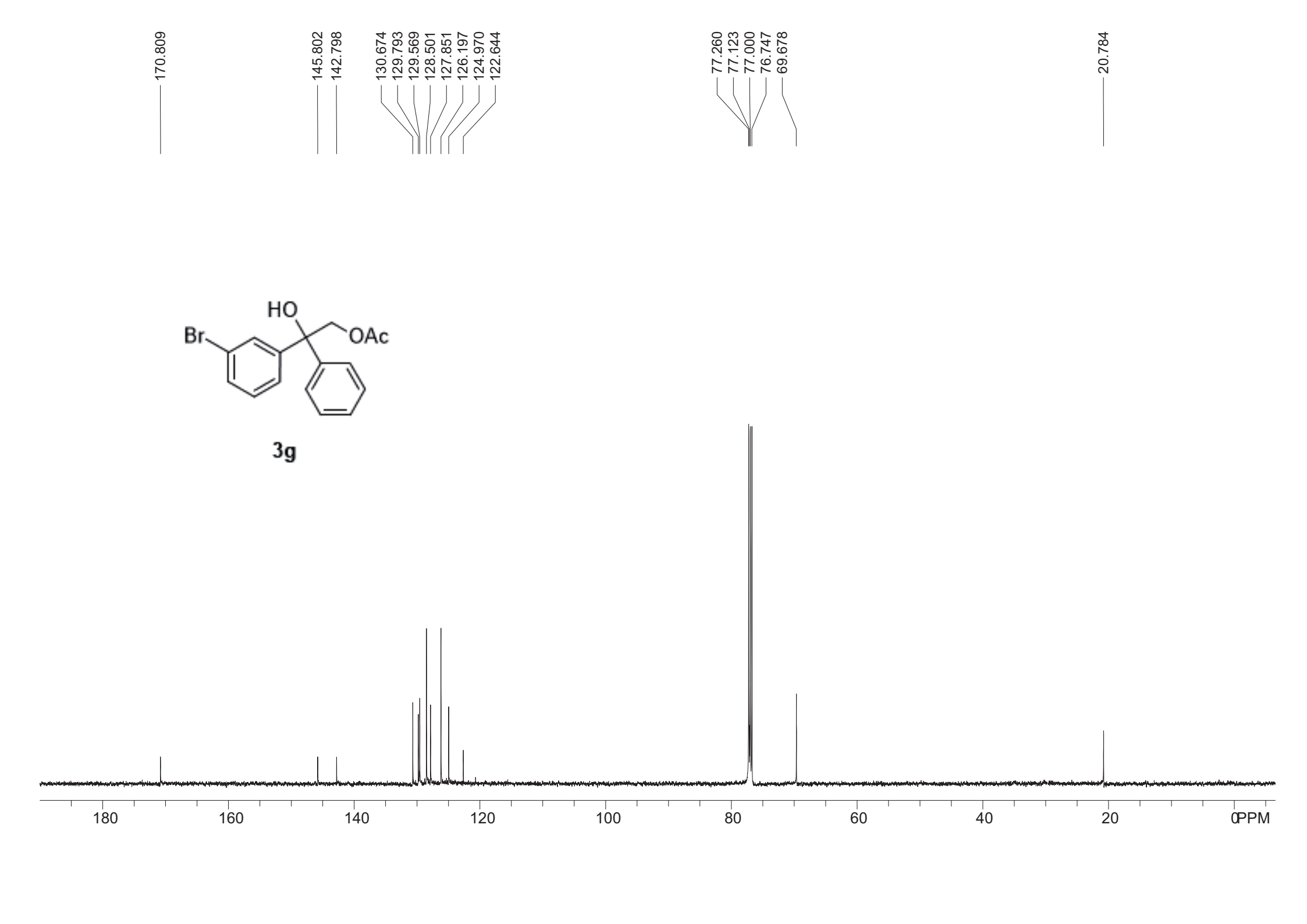
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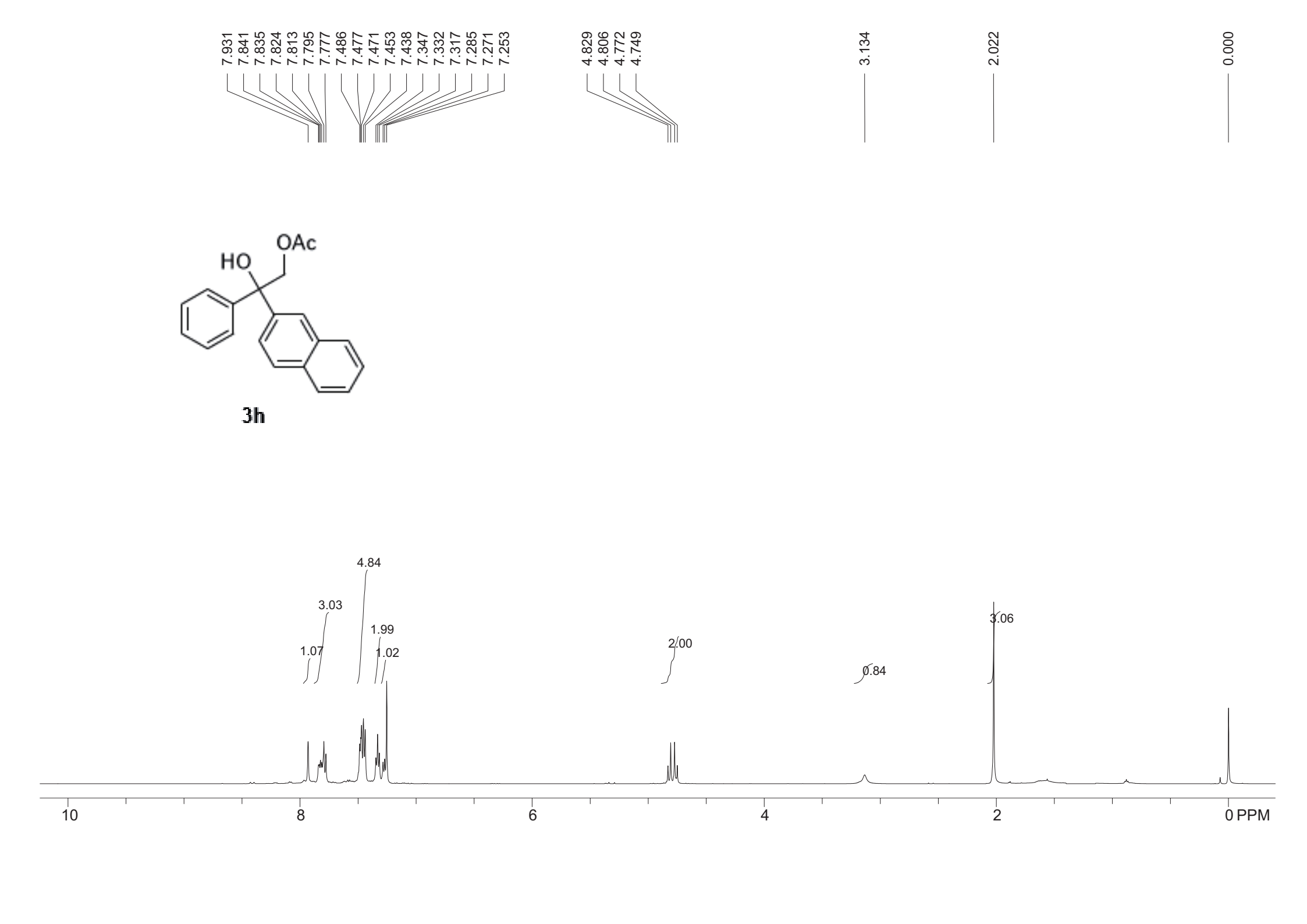
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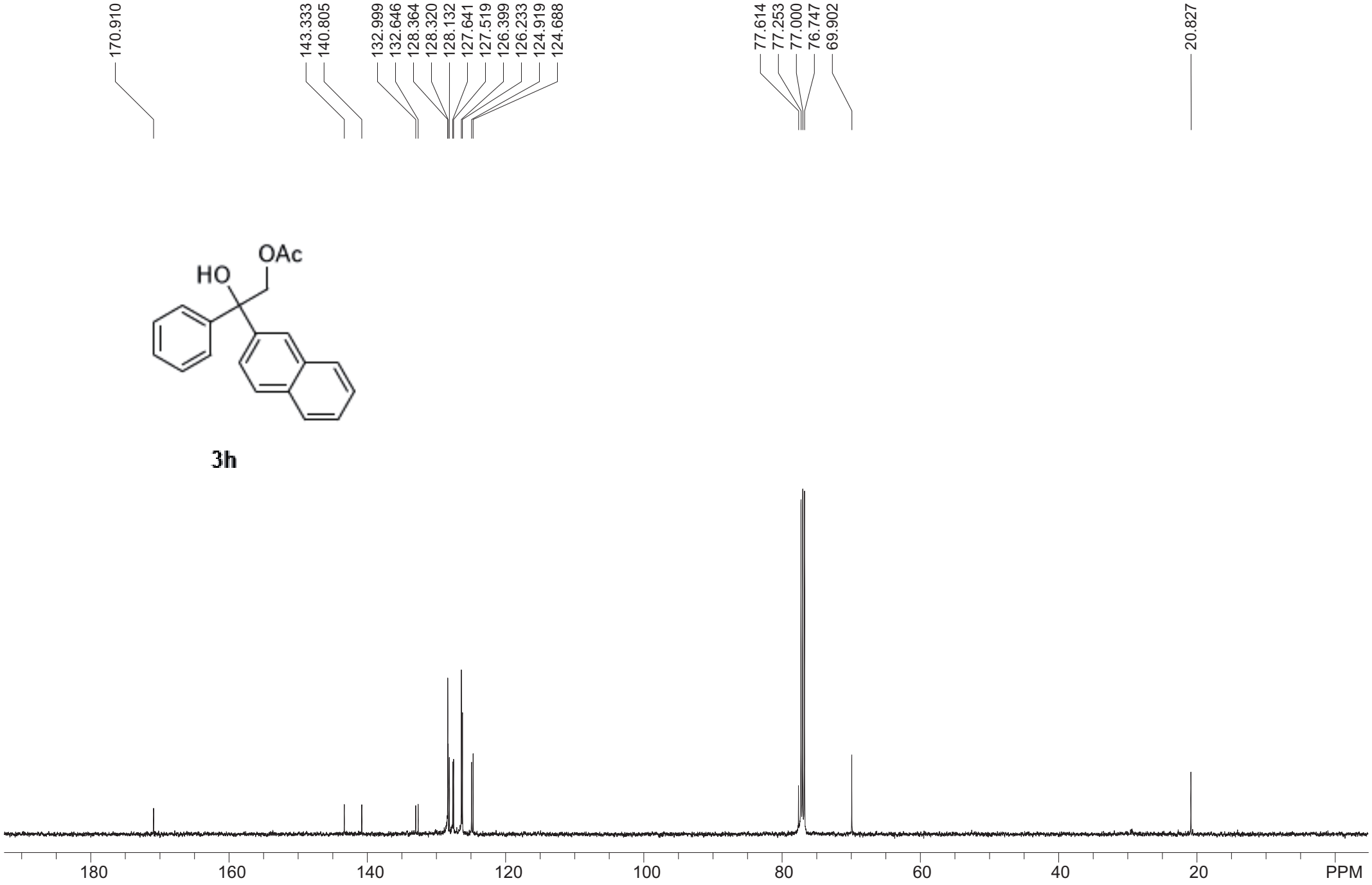
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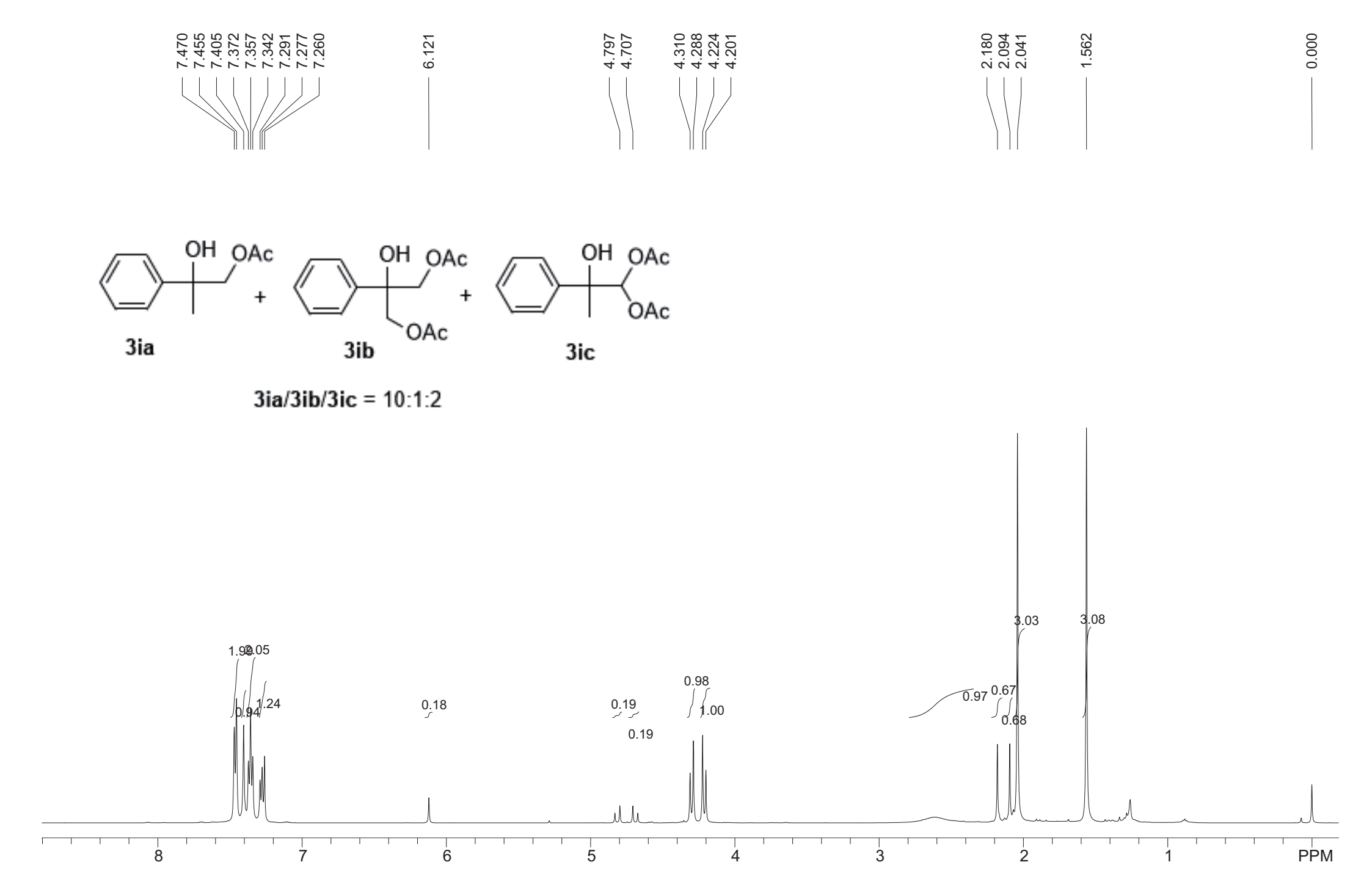
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OAc
OH
OAc
OAc
OH
OAc
OAc
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3ib
3ic
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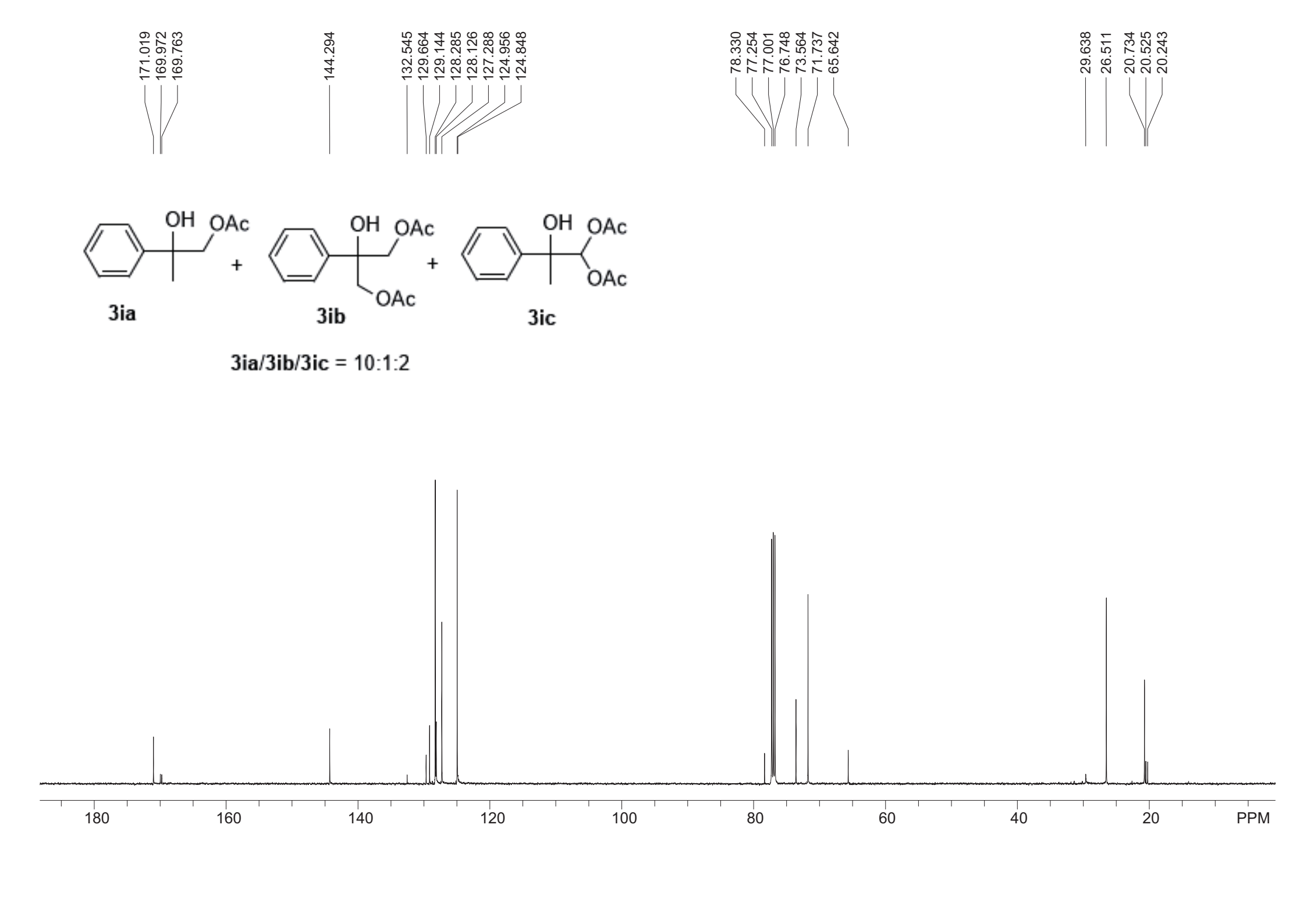
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OAc
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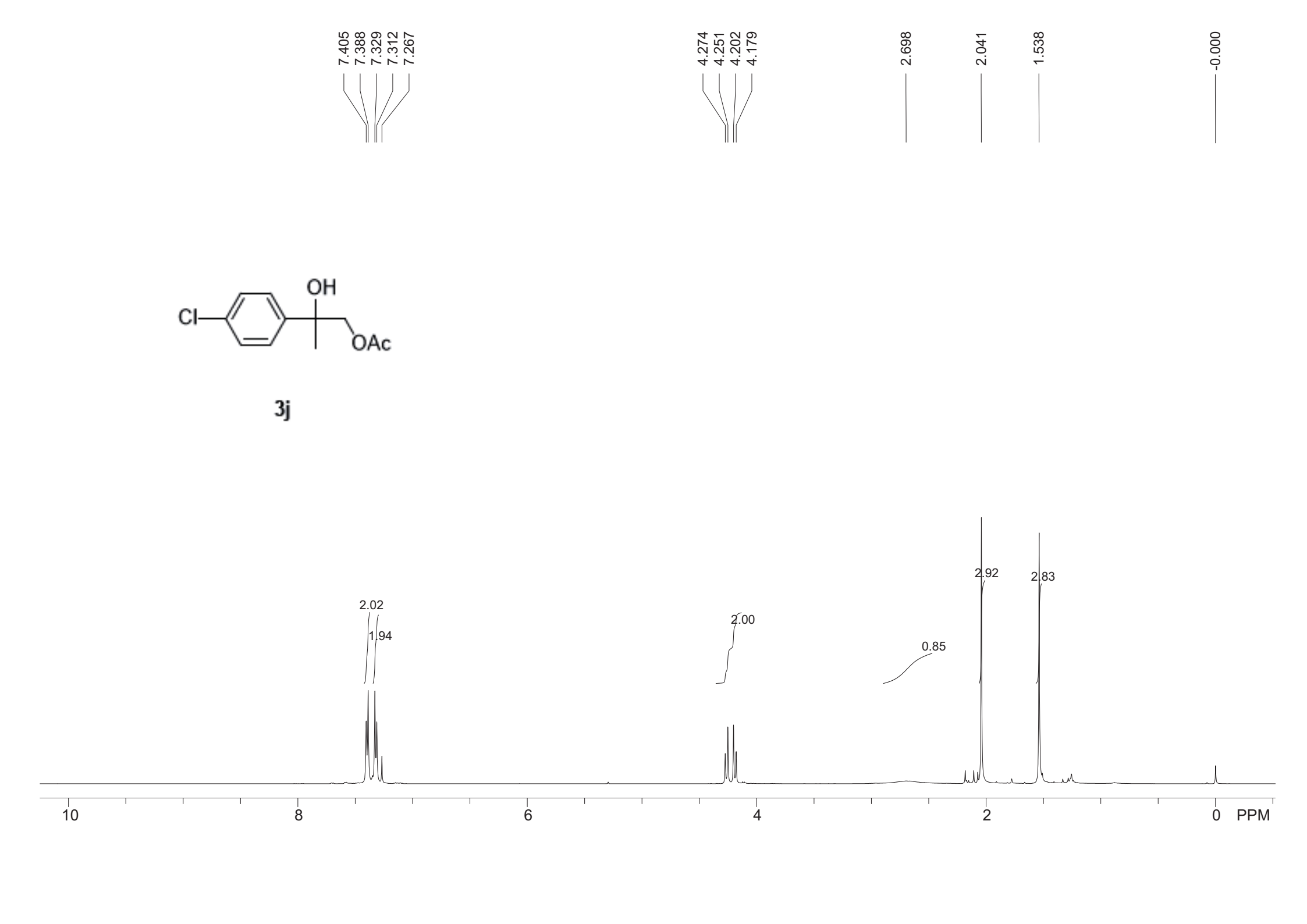
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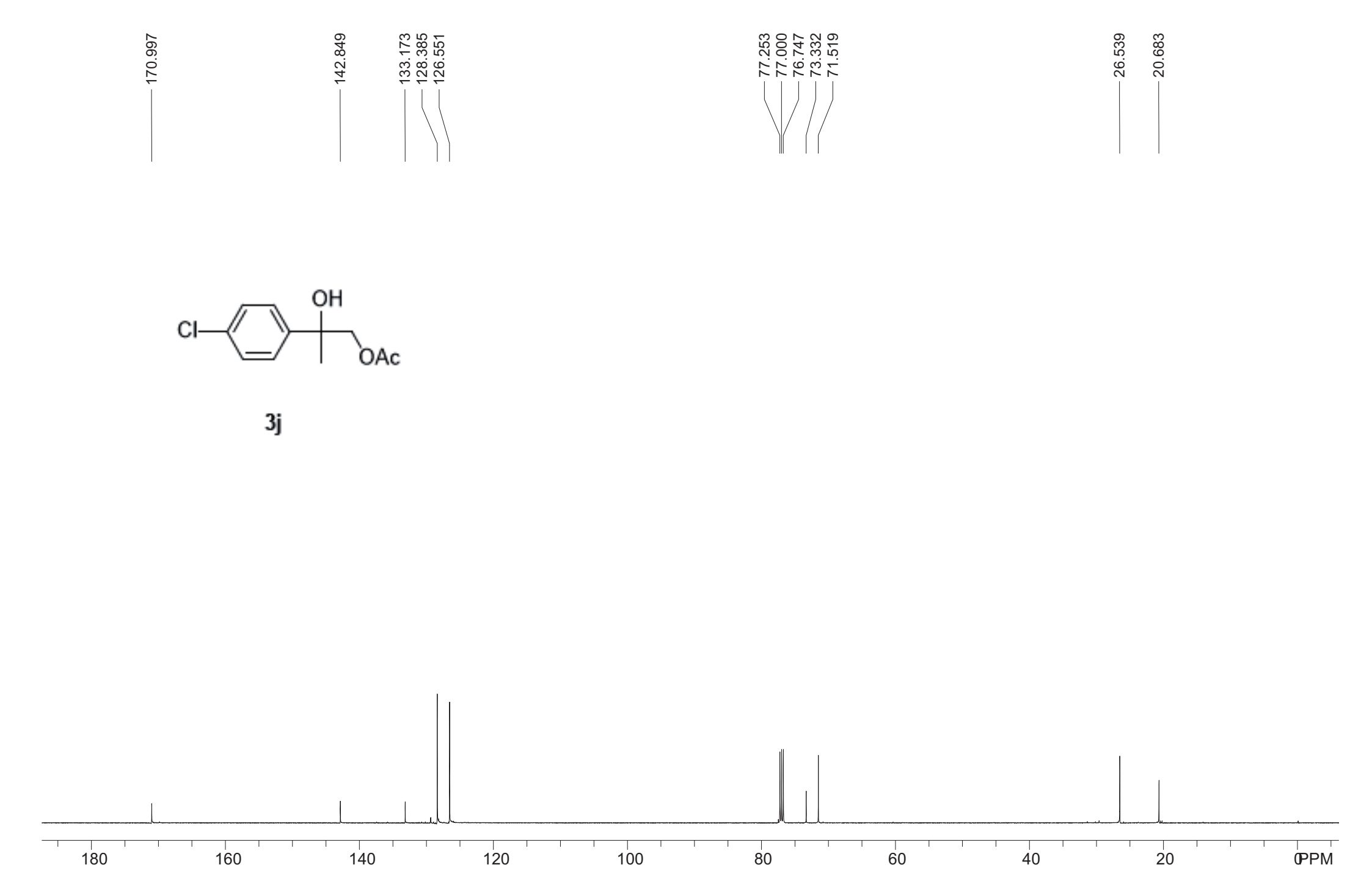
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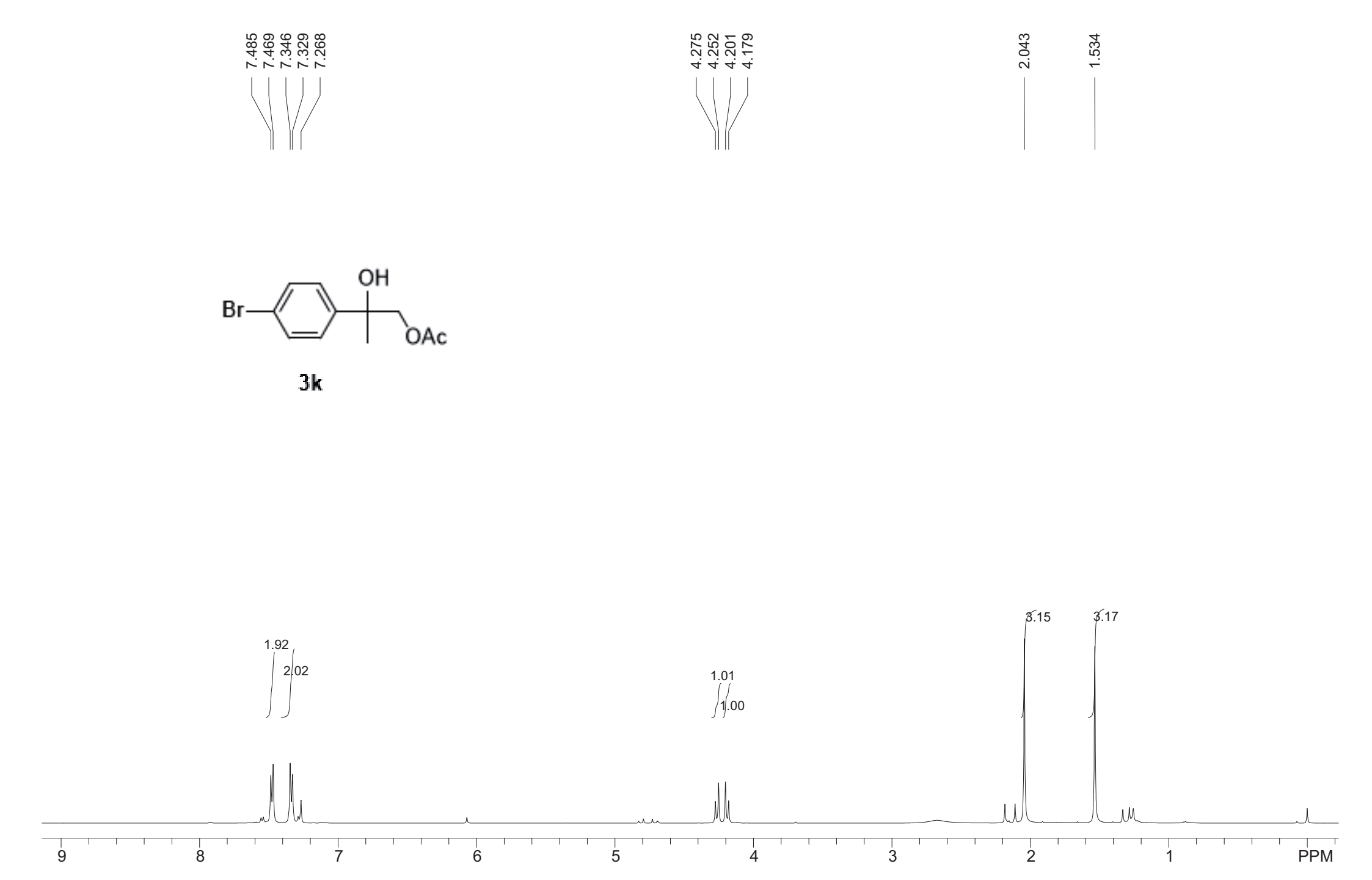
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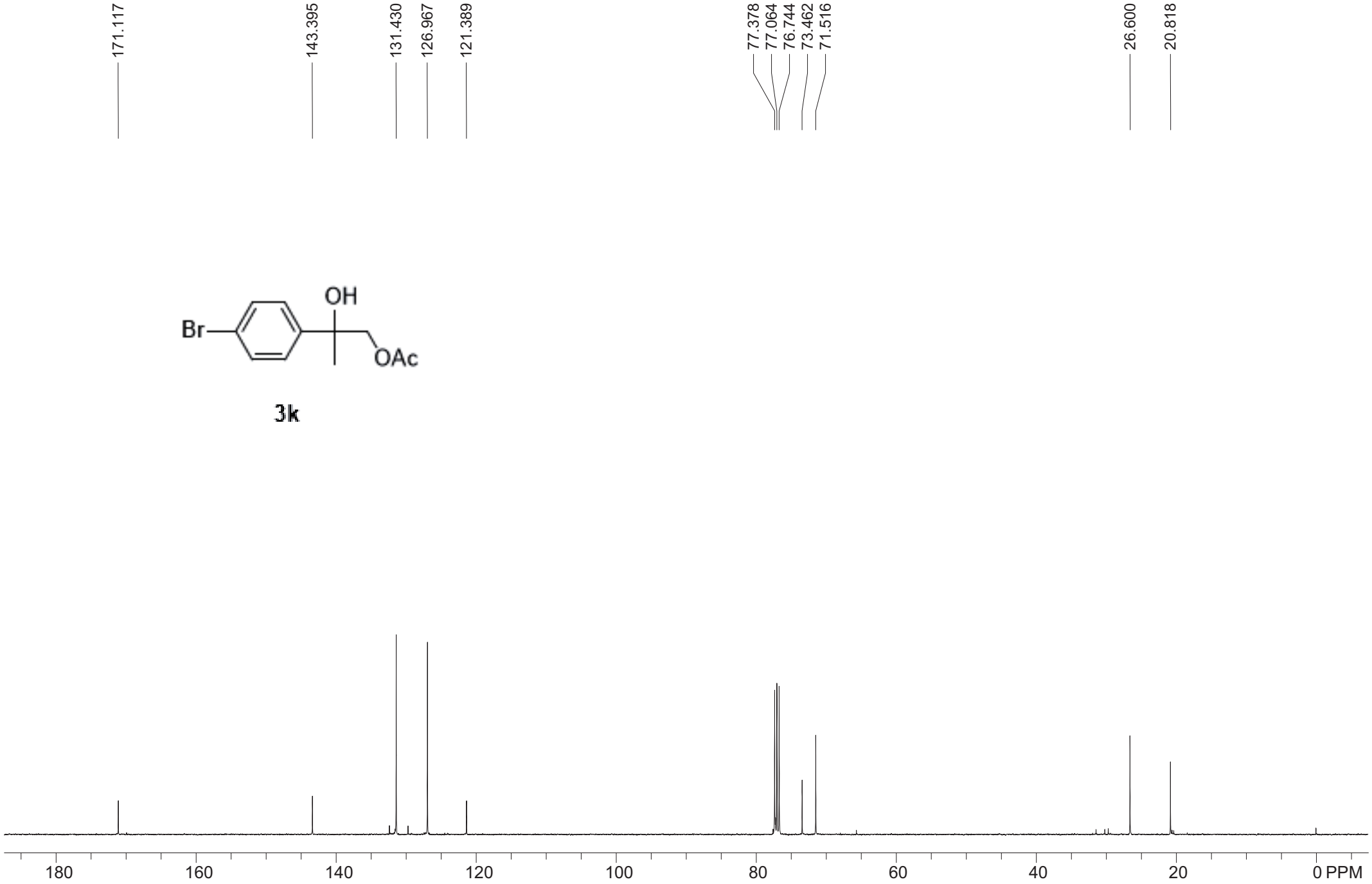
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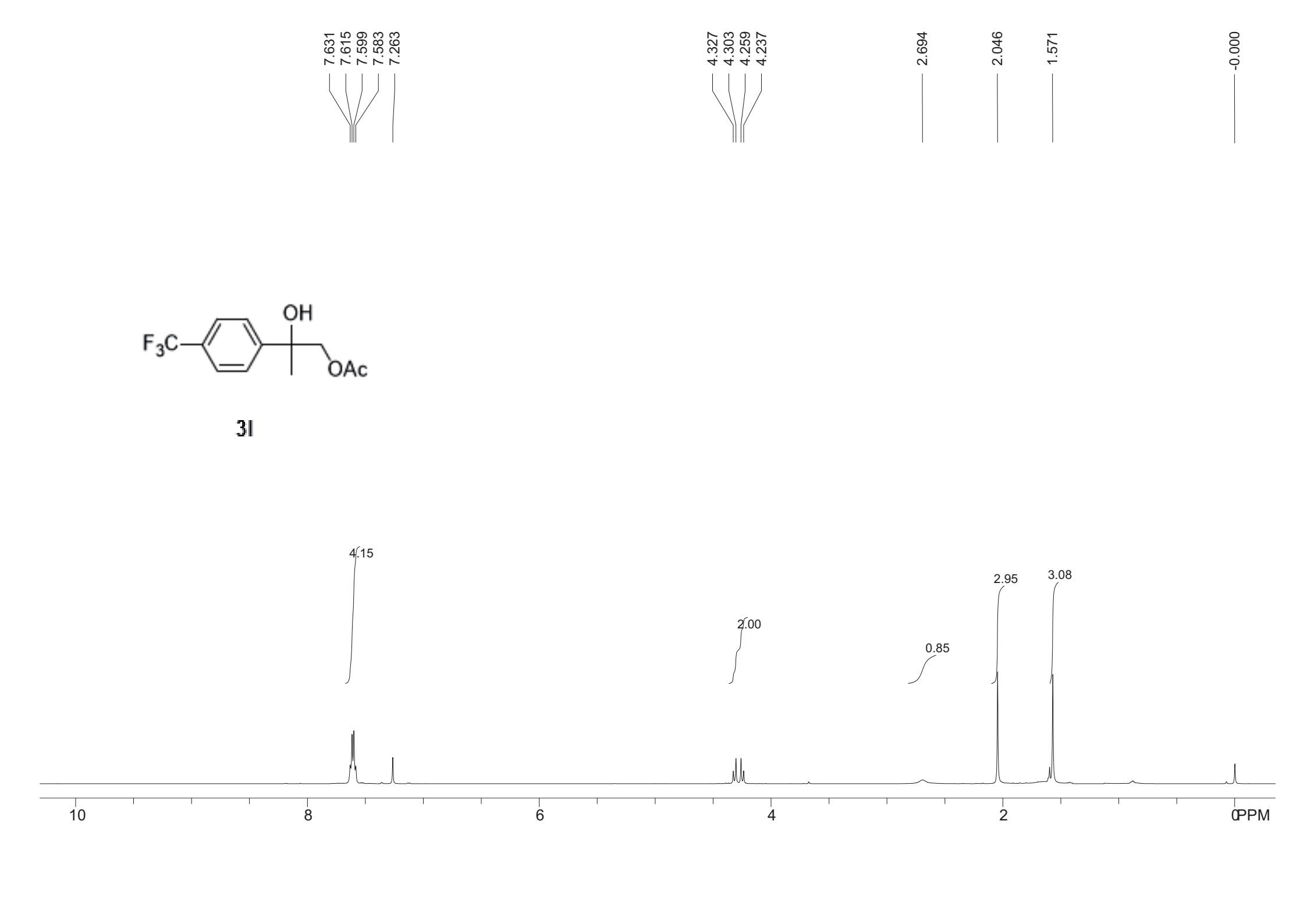
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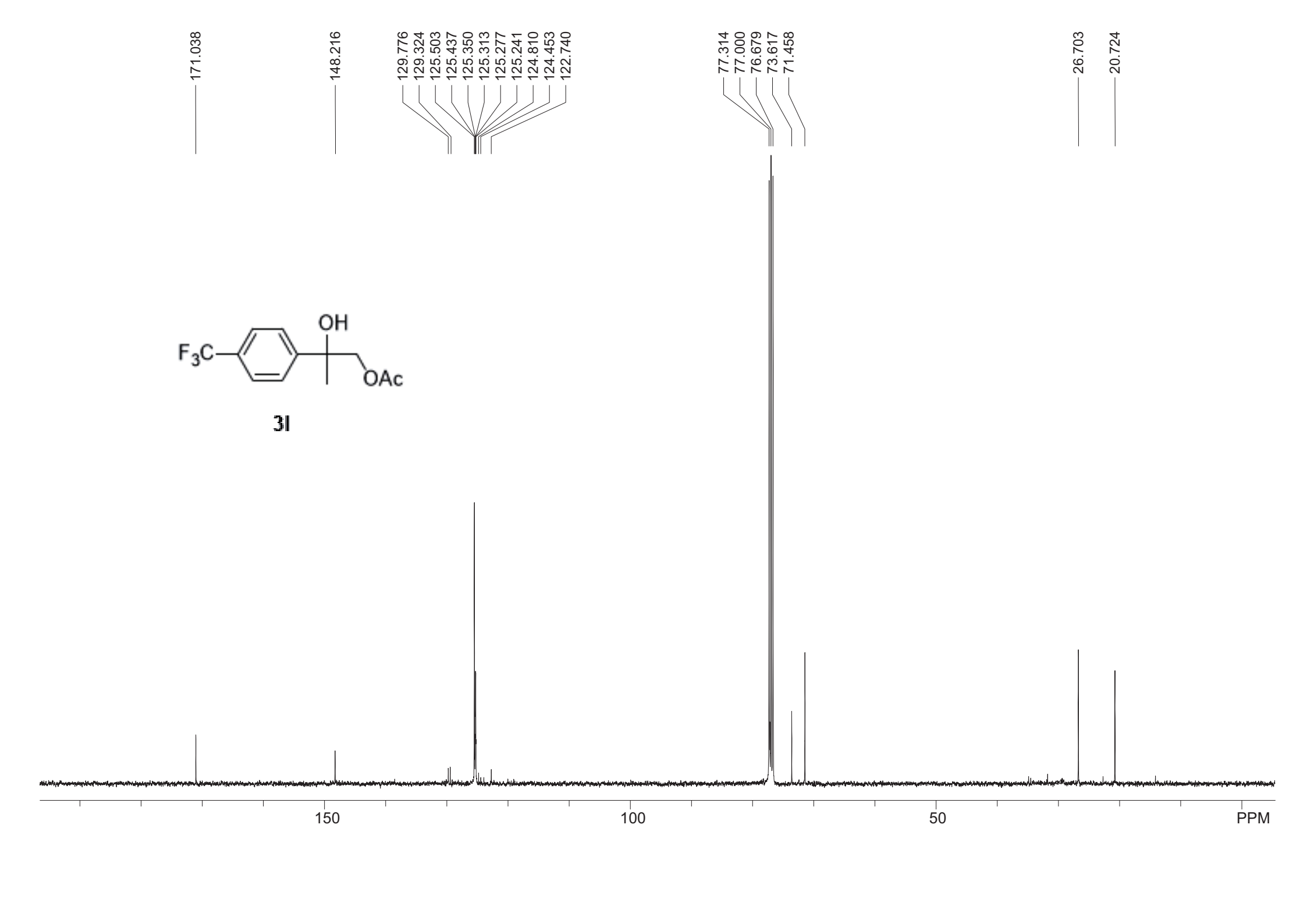
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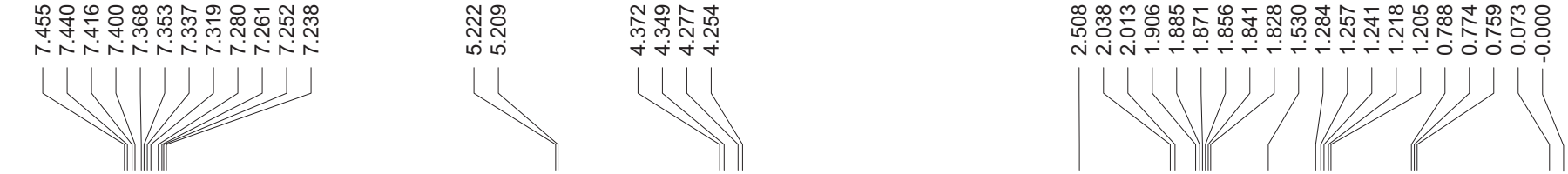

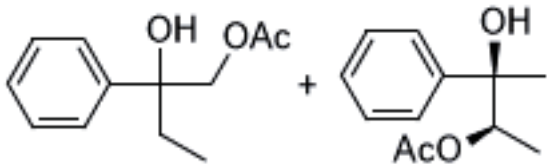

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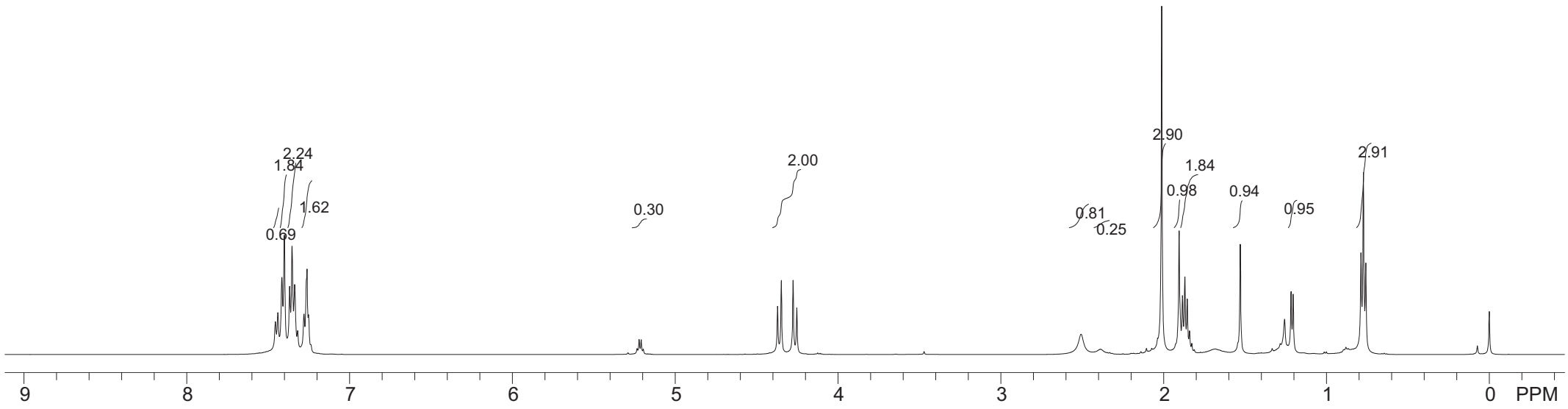

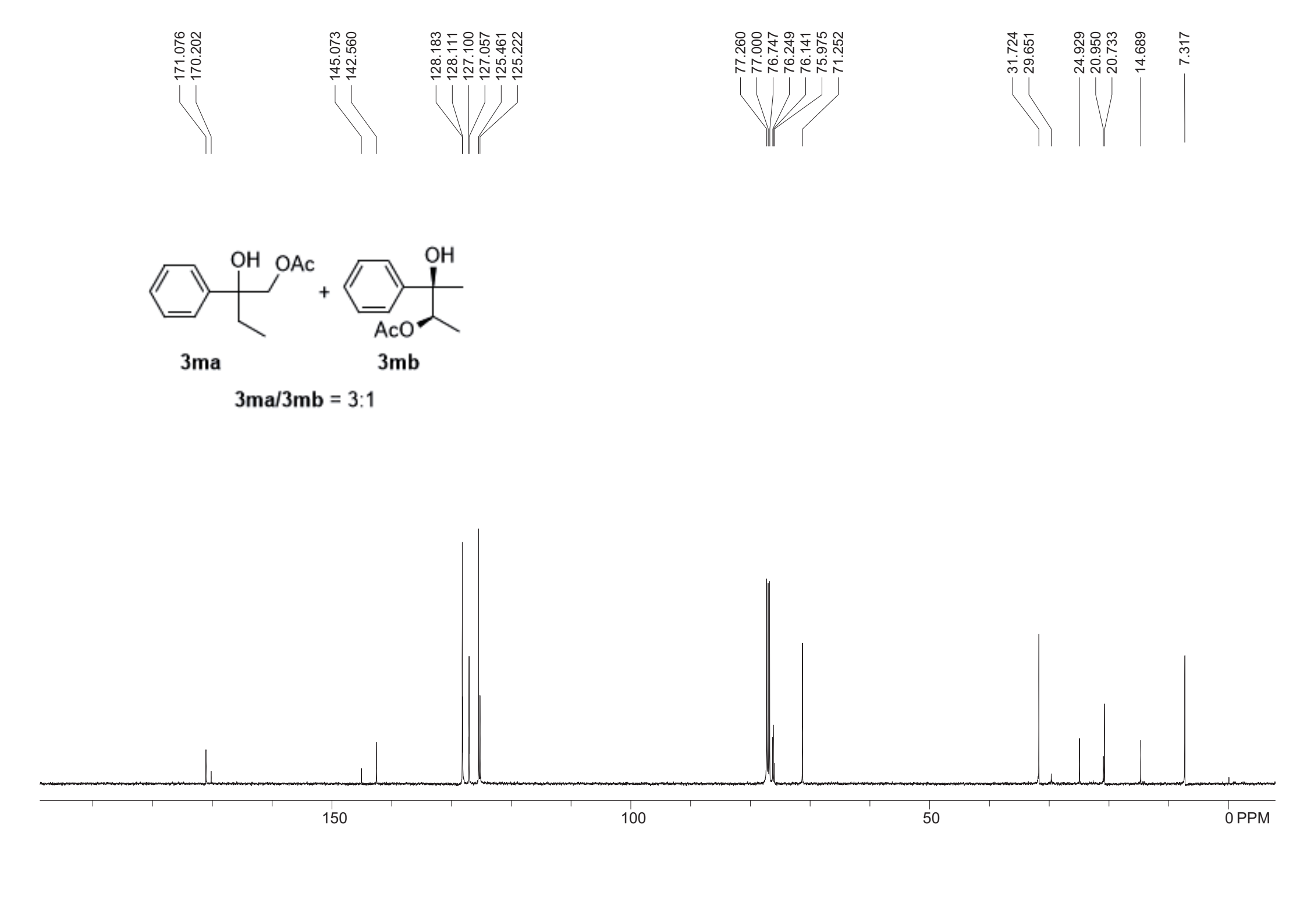
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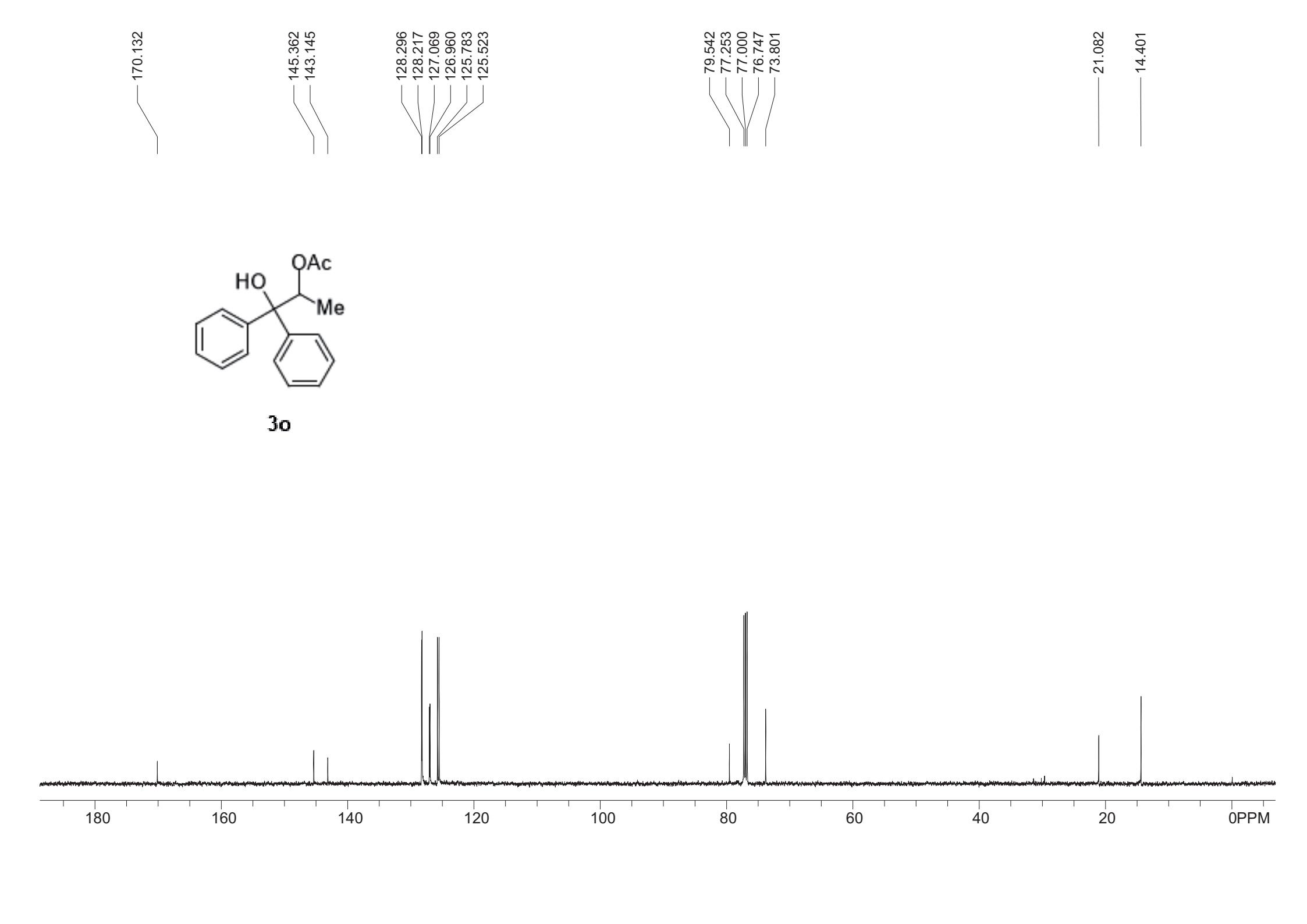
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128.296
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127.069
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125.783
125.523
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77.253
77.000
76.747
73.801
21.082
14.401
OAc
HO
Me
3o
180
160
140
120
100
80
60
40
20
0PPM

7.460
7.441
7.395
7.375
7.221
7.204
7.189
7.124
7.111
7.105
5.858
5.852
5.833
5.827
2.692
1.660
1.642
1.637
1.624
1.618
1.796
1.605
1.600
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1.396
1.390
1.378
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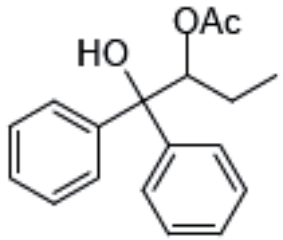
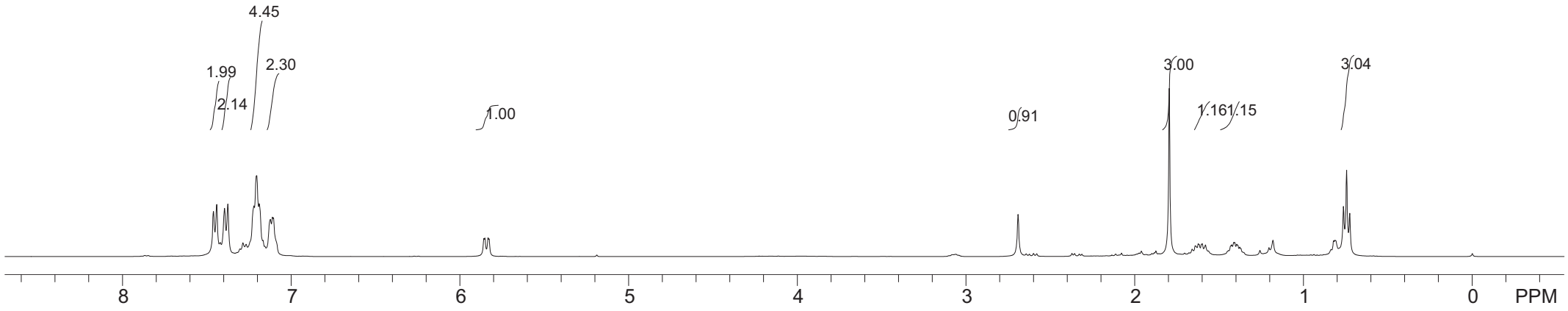
0.745
0.727


OAc
HO

3p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2.14
2.30
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3.04
8
7
6
5
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3
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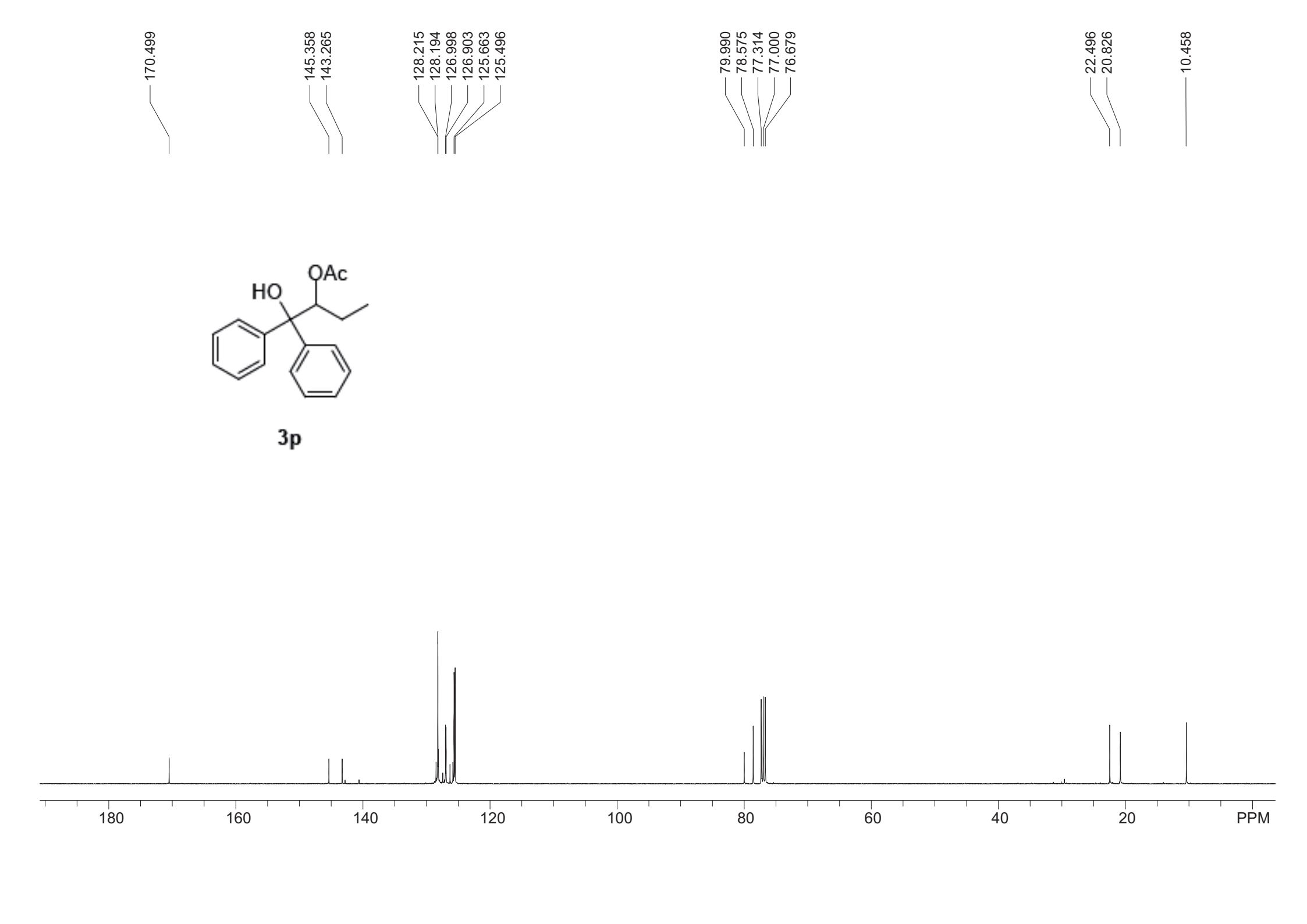
0
PPM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126.903
125.663
125.496
79.990
78.575
77.314
77.000
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22.496
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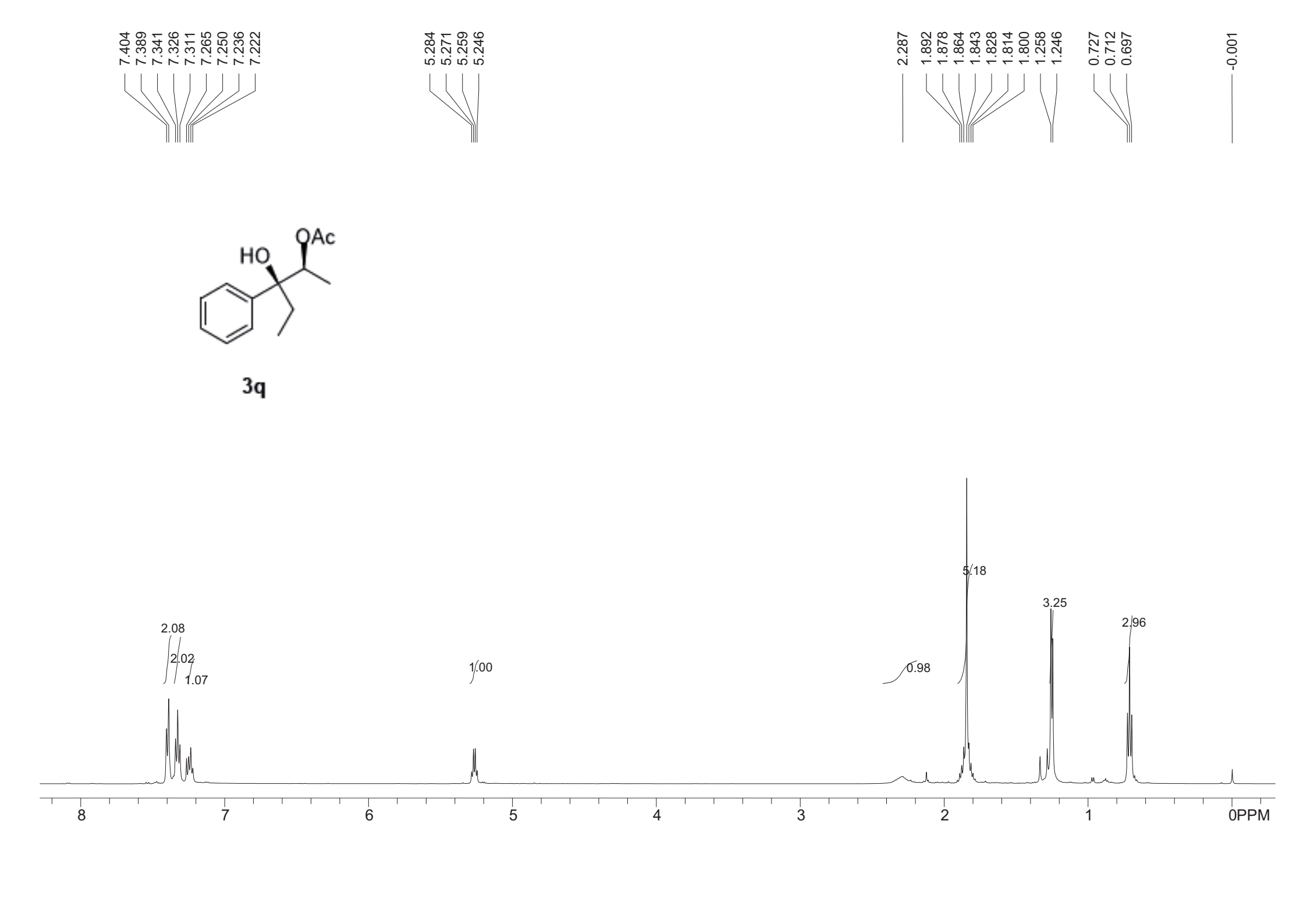
10.458
OAc
HO
3p
180
160
140
120
100
80
60
40
20
PPM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7.389
7.341
7.326
7.311
7.265
7.250
7.236
7.222
5.284
5.271
5.259
5.246
2.287
1.892
1.878
1.864
1.843
1.828
1.814
1.800
1.258
1.246
0.727
0.712
0.697
-0.001
HO
OAc
3q
2.08
2.02
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5.18
3.25
2.96
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6
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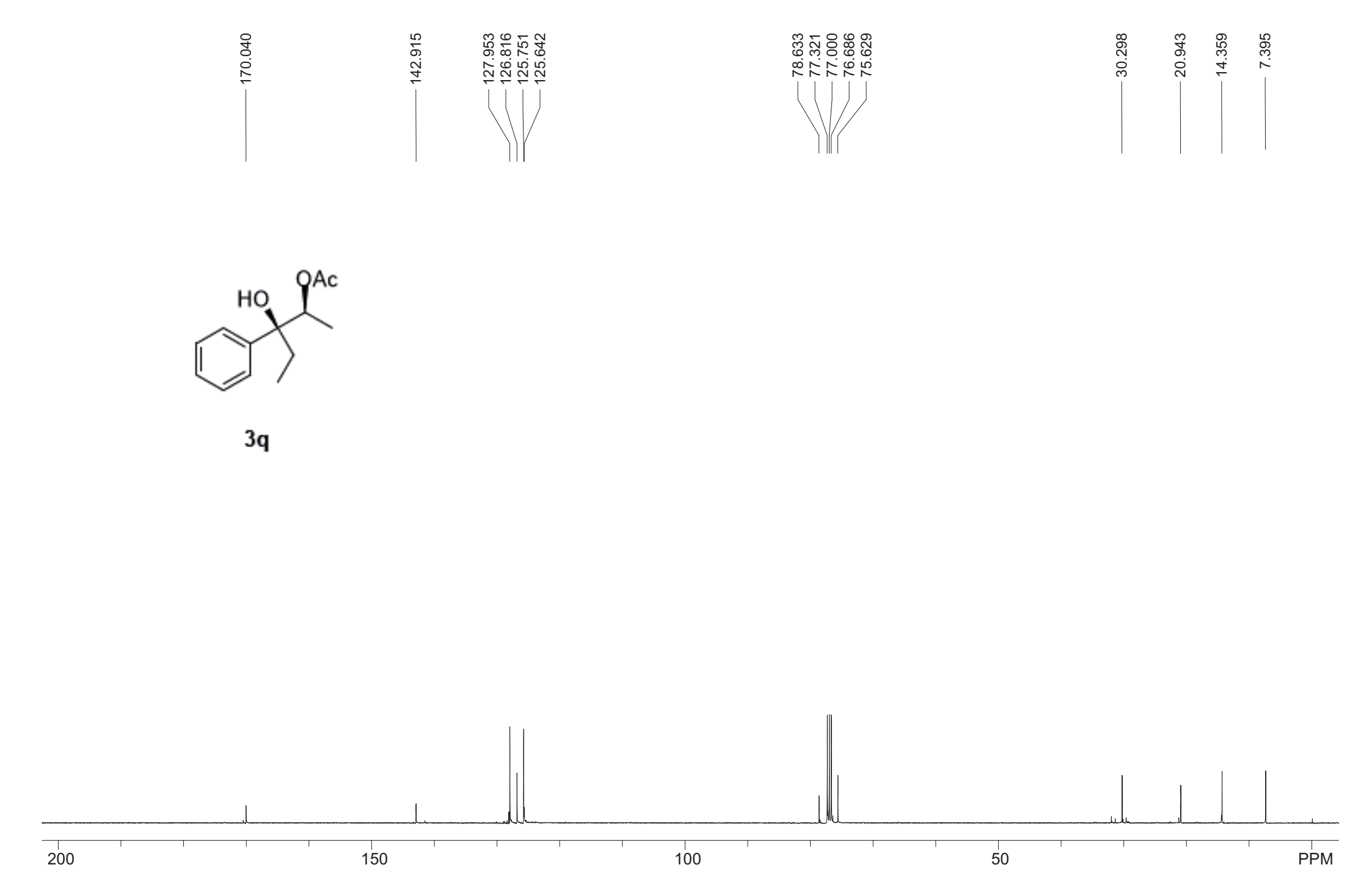
2
1
0PPM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127.953
126.816
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125.642
78.633
77.321
77.000
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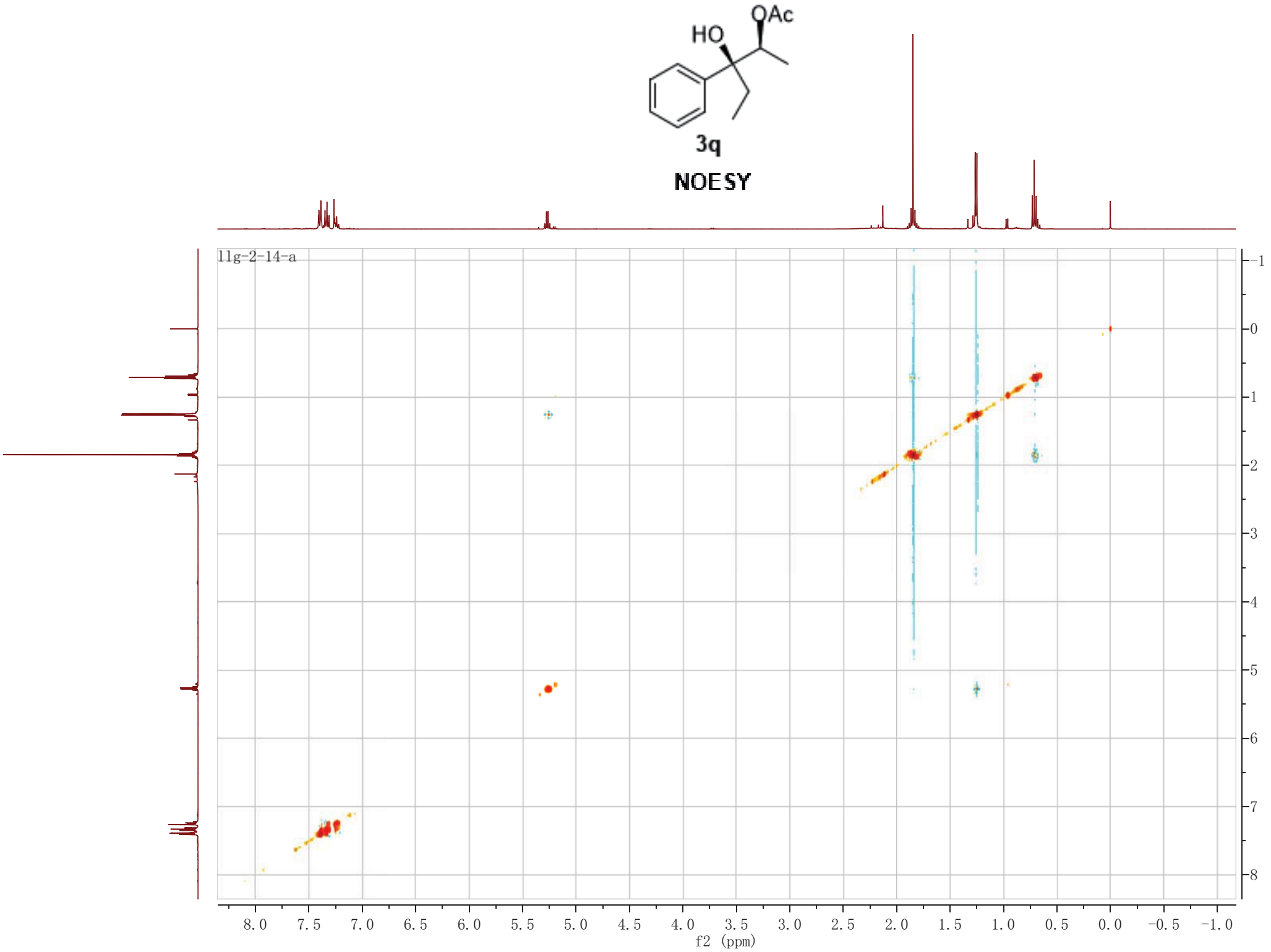
30.298
20.943
14.359
7.395
HO
OAc
200
150
100
50
PPM

3q


OAc
HO
3q
NOESY
11g-2-14-a
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
-1.0
f2 (ppm)
-1
0
1
2
3
4
5
6
7
8
f1 (ppm)

7.650
7.635
7.257
7.252
7.235
7.217
7.202
7.188
7.095
7.080
5.075
5.073
5.063
2.956
2.944
2.937
2.924
2.910
2.903
2.891
2.803
2.794
2.783
2.770
2.759
2.749
2.385
2.298
2.287
2.277
2.271
2.259
2.249
2.237
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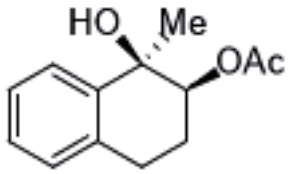
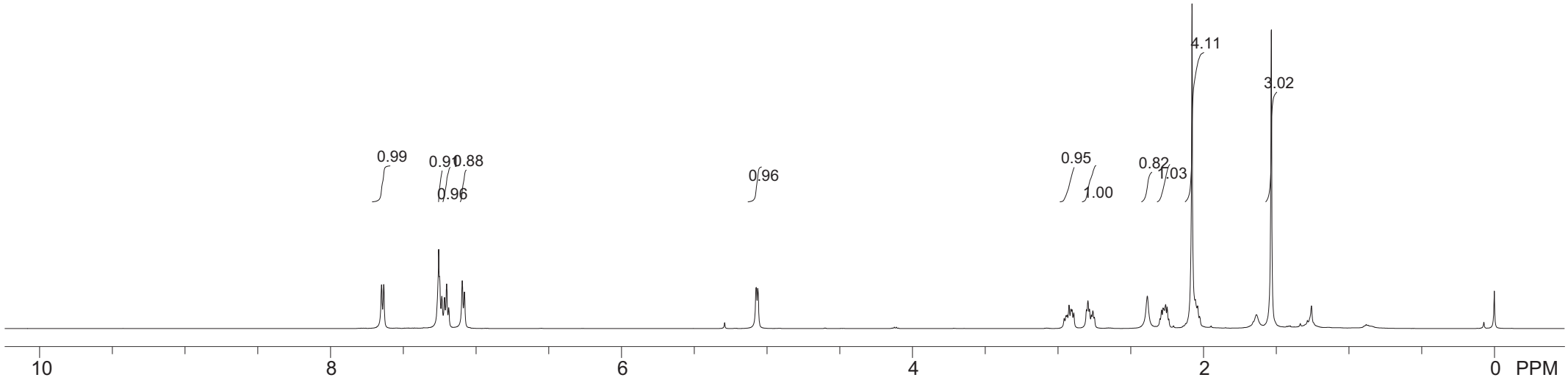
2.039
2.026
1.533
0.000


HO
Me
OAc

3r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0.88
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0.82
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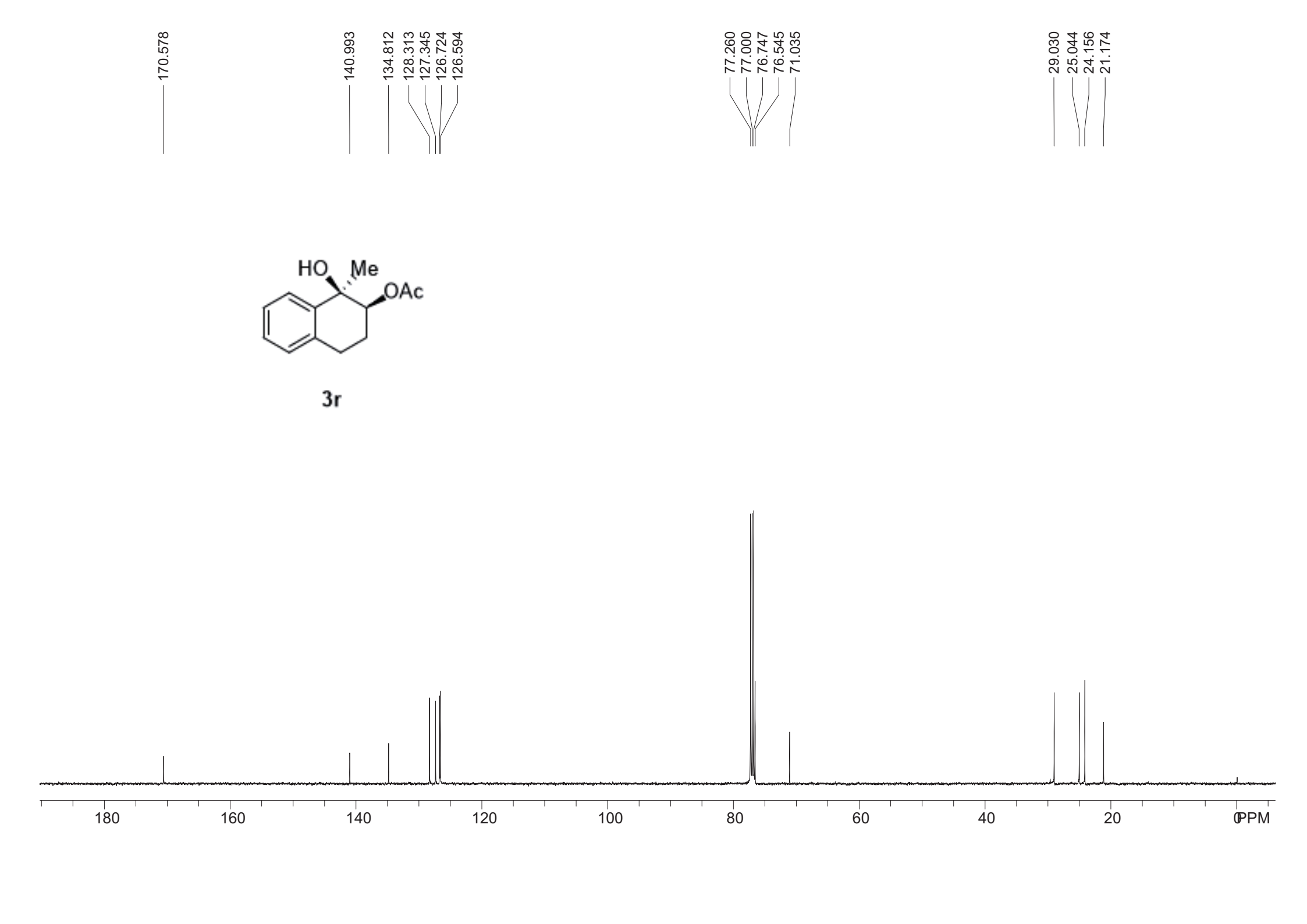
4.11
3.02
10
8
6
4
2
0
PPM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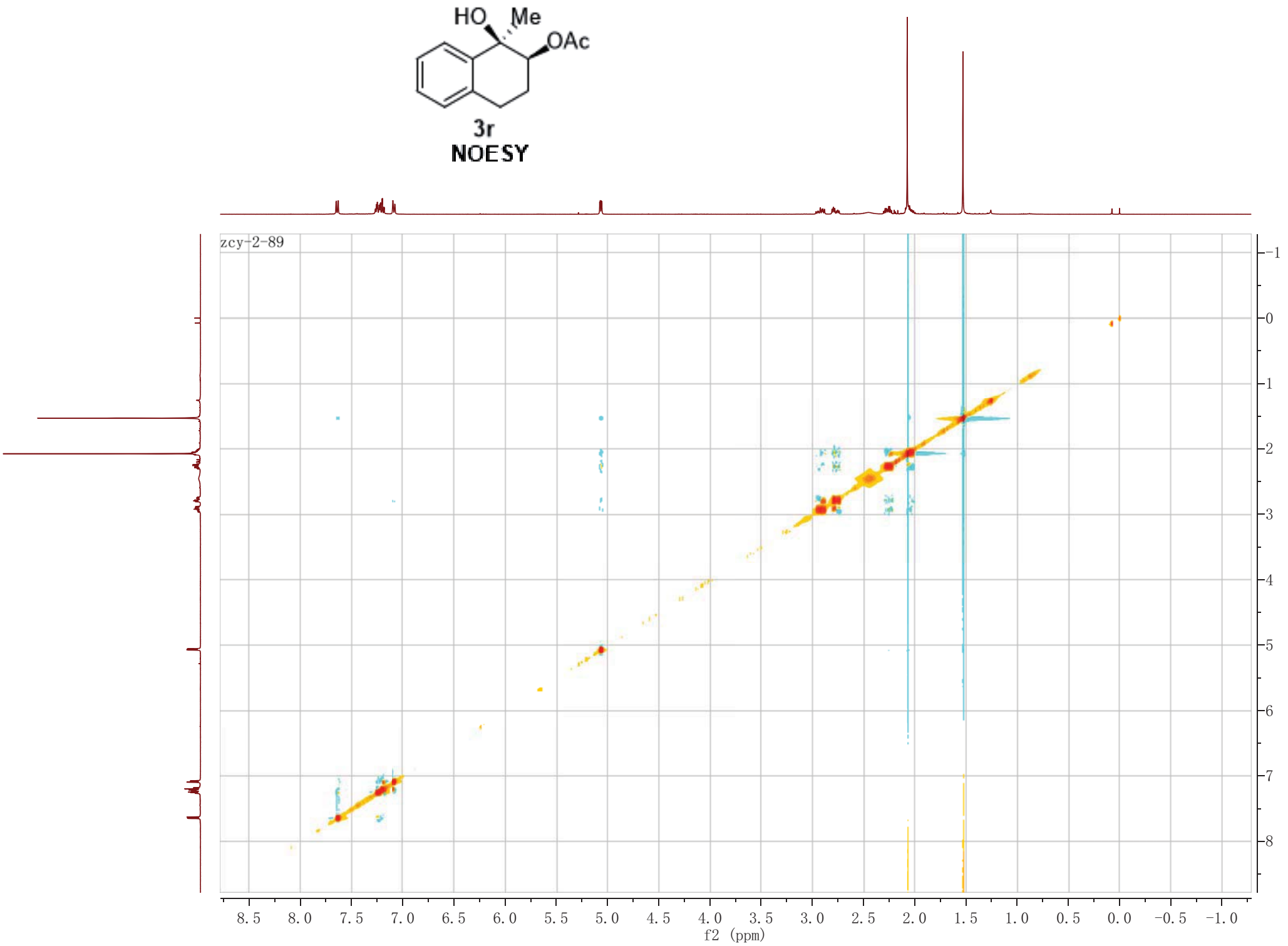
126.594
77.260
77.000
76.747
76.545
71.035
29.030
25.044
24.156
21.174
HO
Me
OAc
3r
180
160
140
120
100
80
60
40
20
0
PPM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Me
OAc
3r
NOESY
zcy-2-89
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f2 (ppm)
-1
0
1
2
3
4
5
6
7
8
f1 (ppm)

7.578
7.563
7.259
7.252
7.236
7.221
7.213
7.198
7.184
7.098
7.084
5.233
5.222
2.917
2.900
2.883
2.868
2.826
2.815
2.804
2.793
2.781
2.769
2.384
2.266
2.253
2.238
2.226
2.215
2.128
2.066
2.040
2.026
2.012
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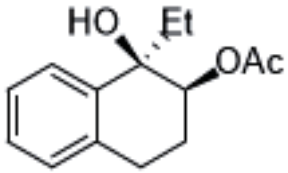
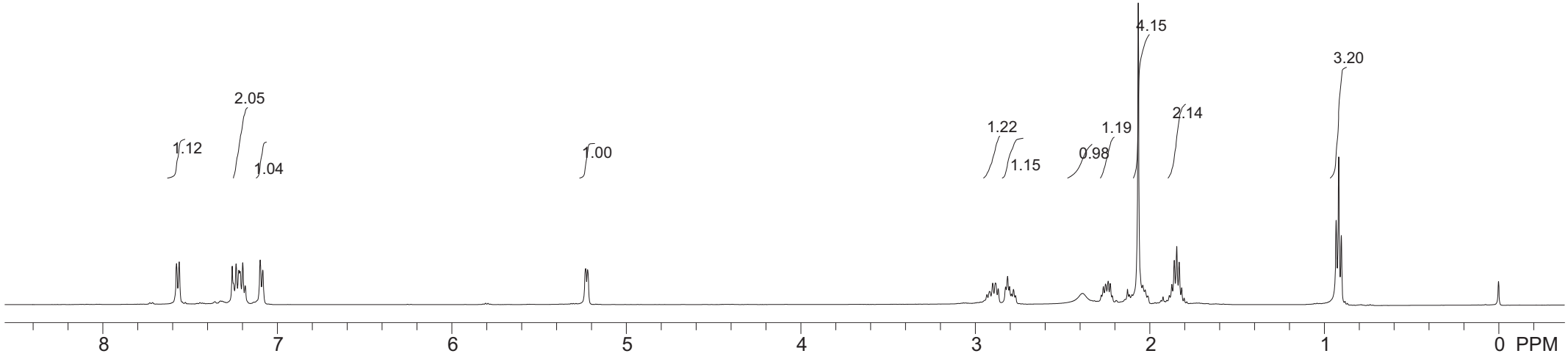
1.859
1.845
1.831
1.817
1.803
0.932
0.917
0.902
0.001


HO
Et
OAc

3s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2.14
1.22
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1.00
1.04
1.15
0.98
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7
6
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2
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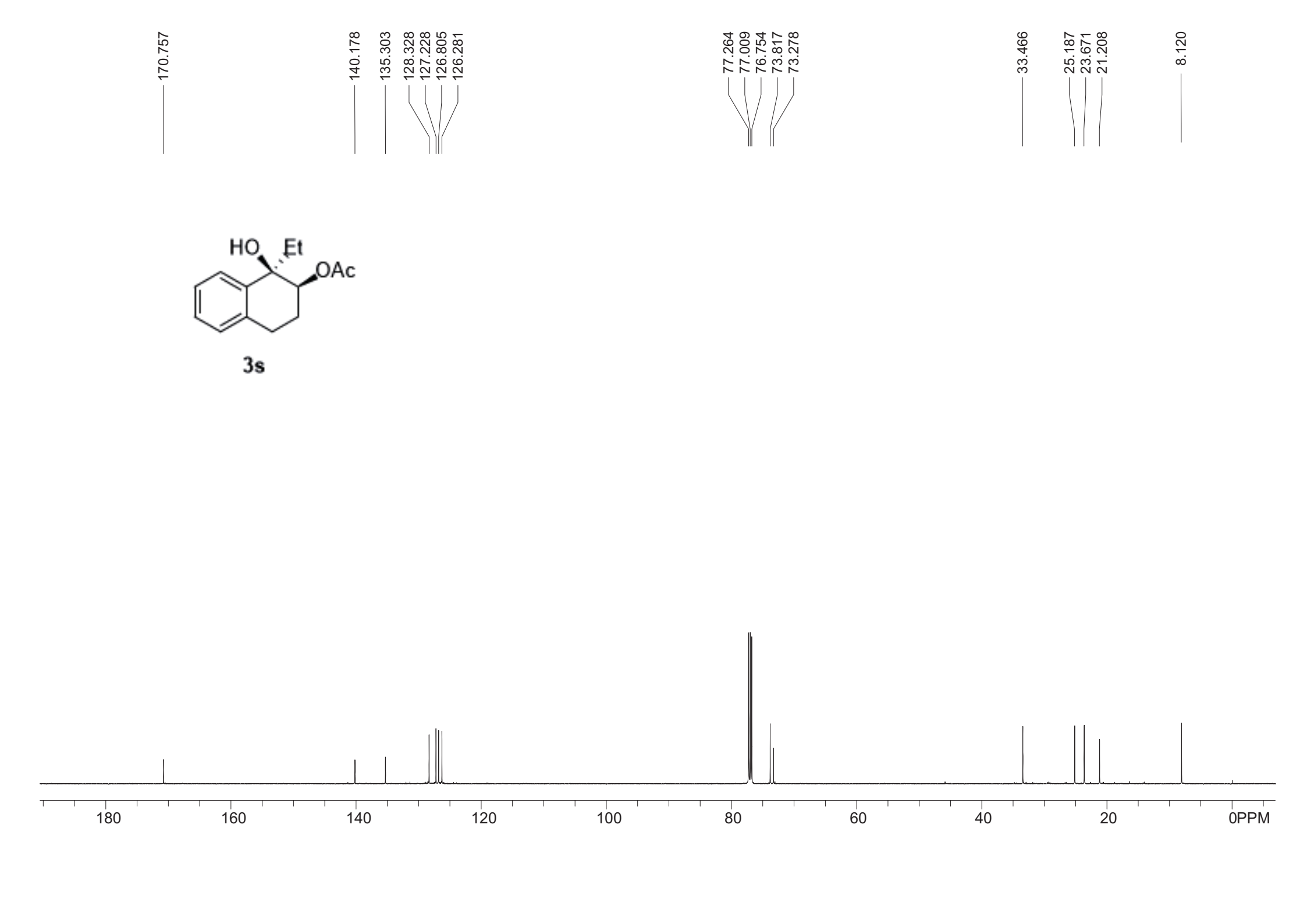
0 PPM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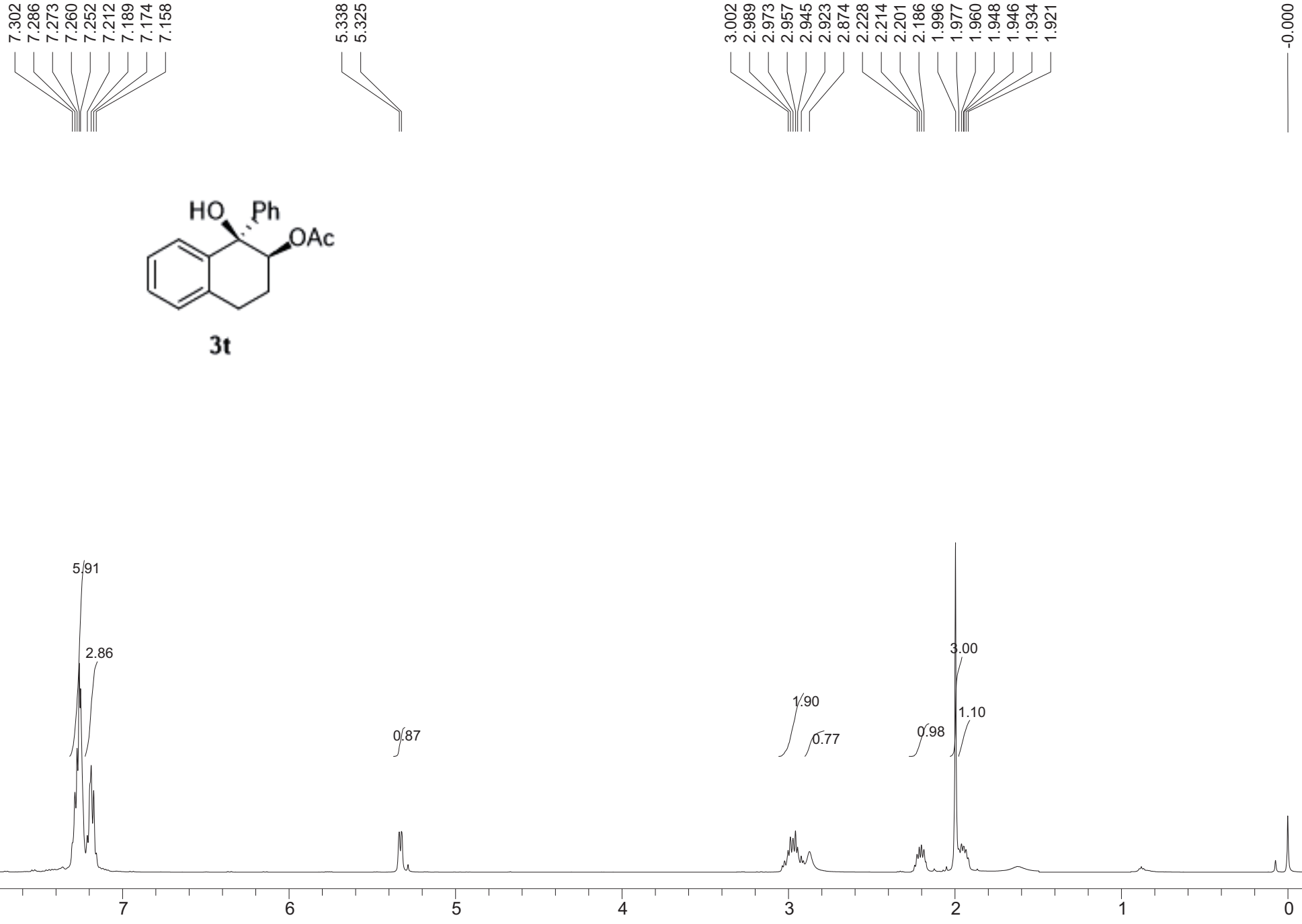
126.805
126.281
77.264
77.009
76.754
73.817
73.278
33.466
25.187
23.671
21.208
8.120
HO
Et
OAc
3s
180
160
140
120
100
80
60
40
20
0PPM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7.286
7.273
7.260
7.252
7.212
7.189
7.174
7.158
5.338
5.325
3.002
2.989
2.973
2.957
2.945
2.923
2.874
2.228
2.214
2.201
2.186
1.996
1.977
1.960
1.948
1.946
1.934
1.921
-0.000
HO
Ph
OAc
3t
5.91
2.86
0.87
1.90
0.77
0.98
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1.10
8
7
6
5
4
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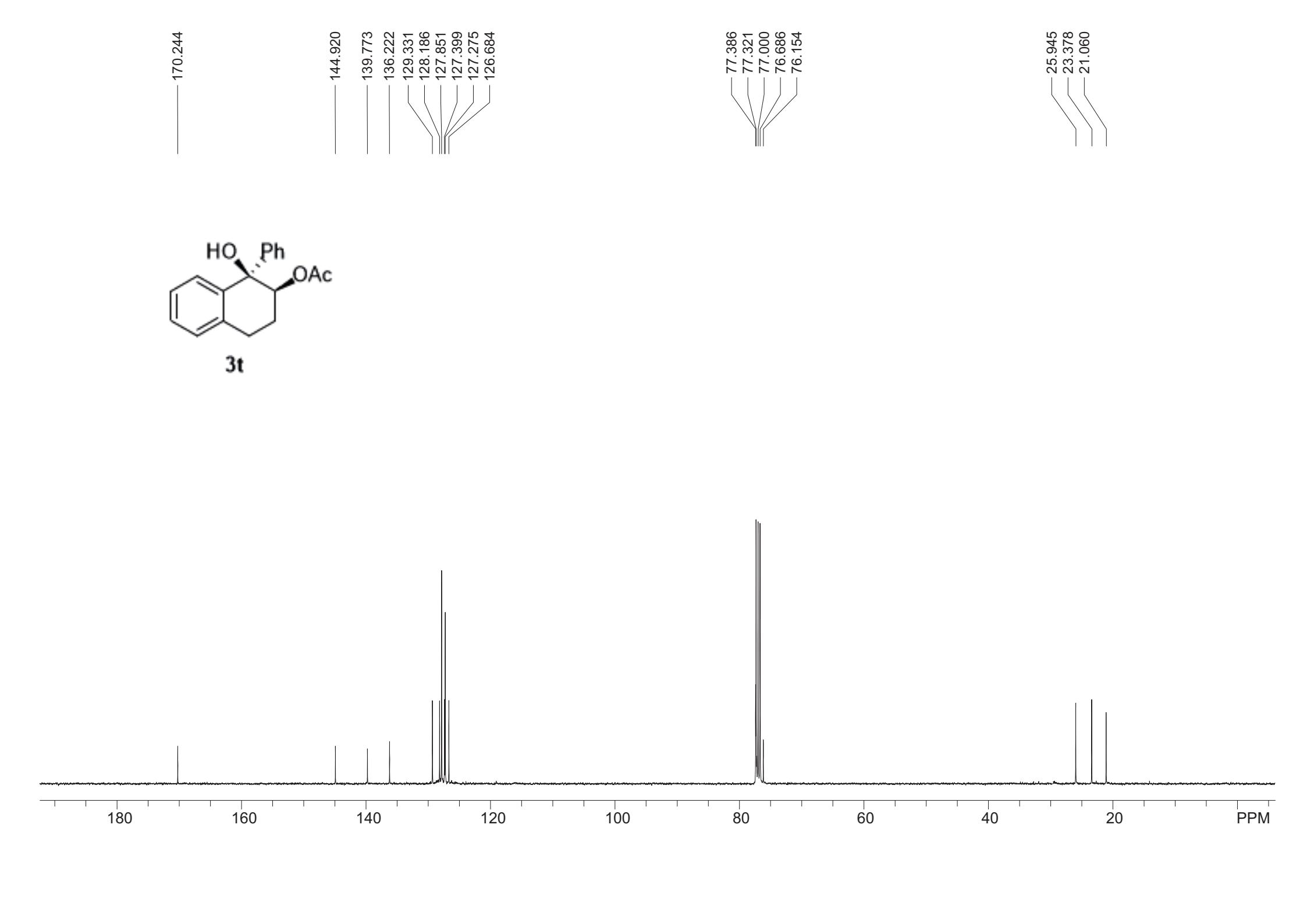
2
1
0 PPM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139.773
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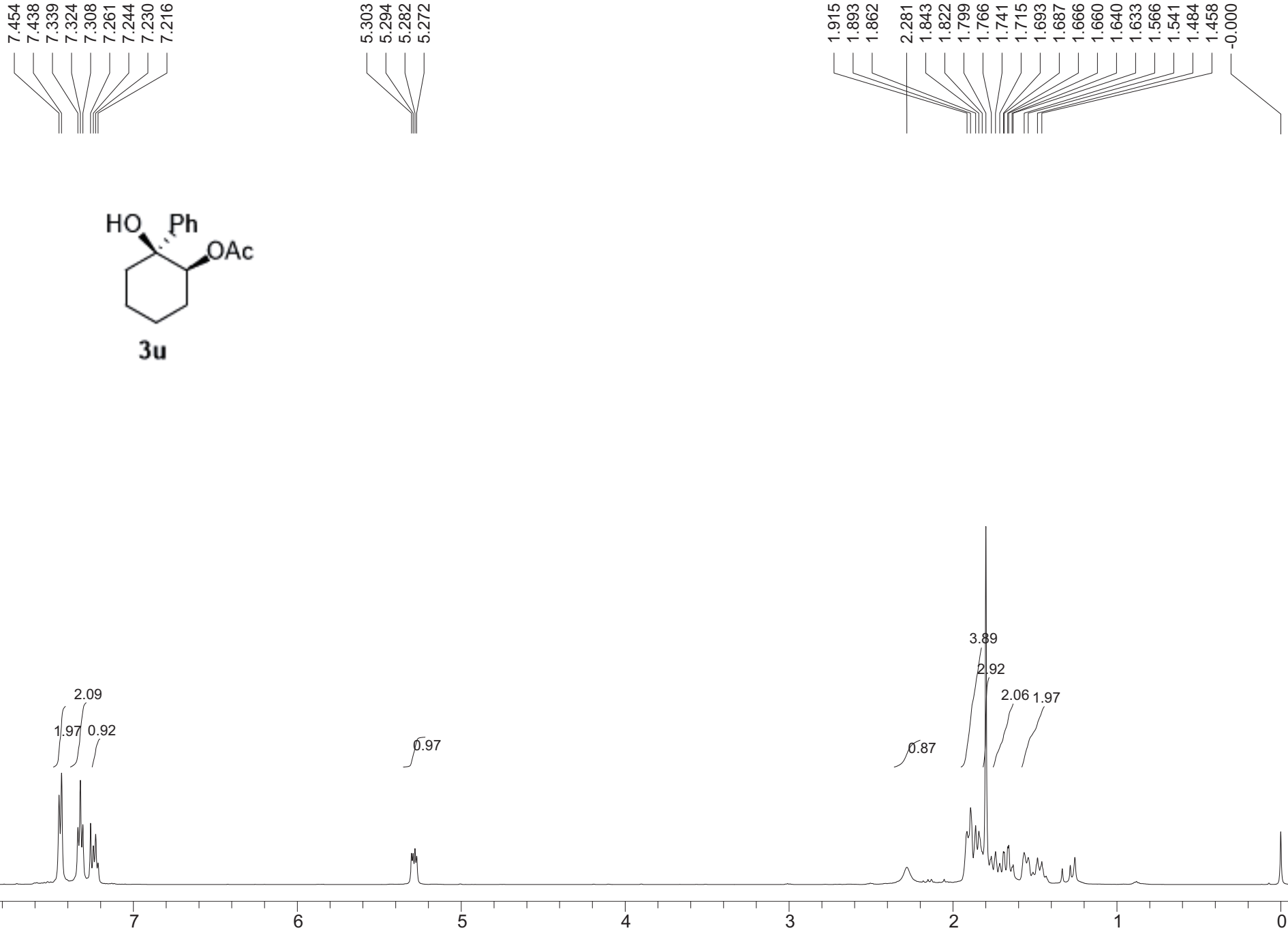
128.186
127.851
127.399
127.275
126.684
77.386
77.321
77.000
76.686
76.154
25.945
23.378
21.060
HO
Ph
OAc
3t
180
160
140
120
100
80
60
40
20
PPM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5.294
5.282
5.272
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1.893
1.862
2.281
1.843
1.822
1.799
1.766
1.741
1.715
1.693
1.687
1.666
1.660
1.640
1.633
1.566
1.541
1.484
1.458
-0.000
HO
Ph
OAc
3u
2.09
1.97
0.92
0.97
0.87
3.89
2.92
2.06
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6
5
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2
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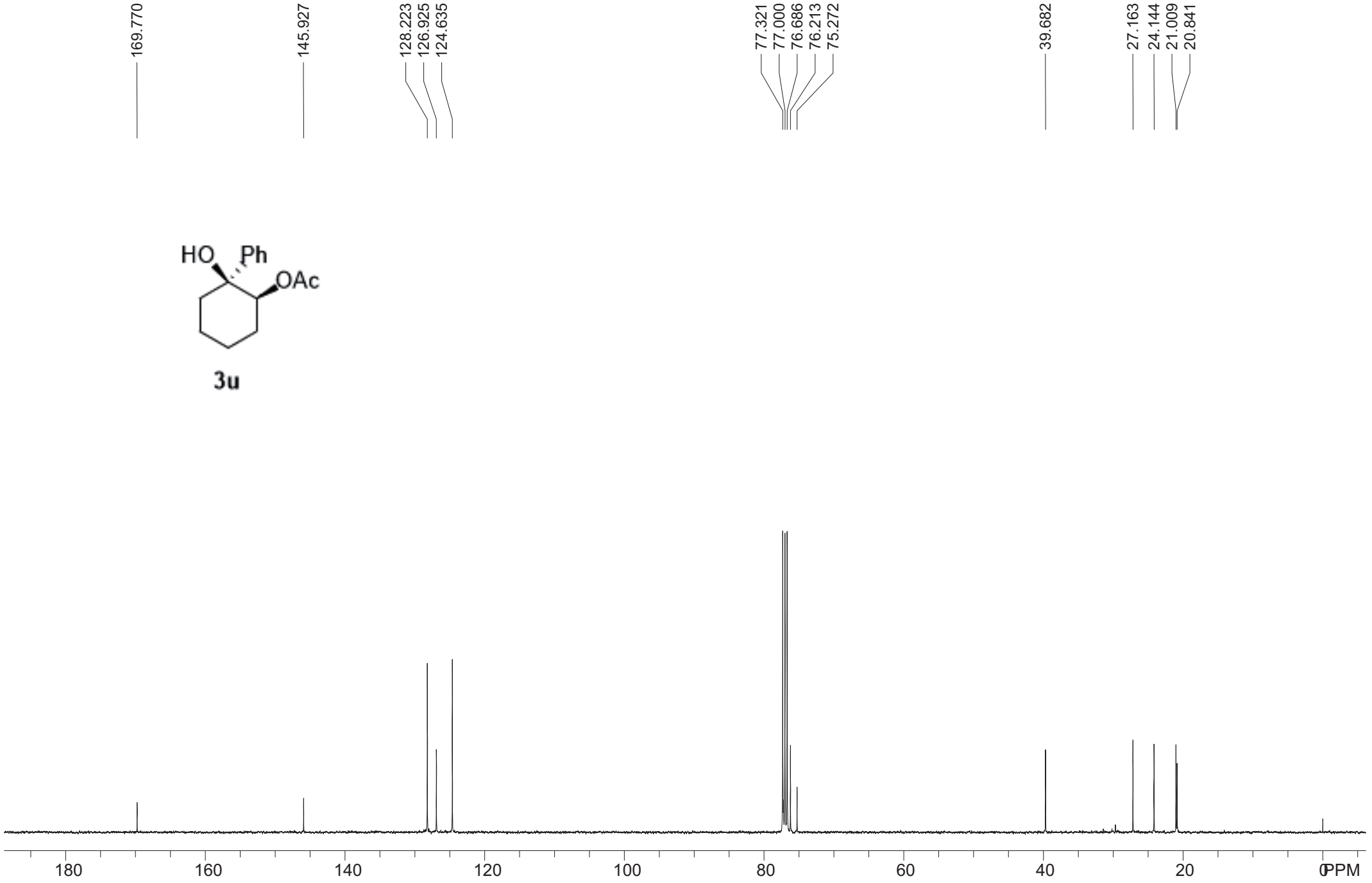
0PPM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77.000
76.686
76.213
75.272
39.682
27.163
24.144
21.009
20.841
HO
Ph
OAc
3u
180
160
140
120
100
80
60
40
20
0
PPM

7.463
7.444
7.350
7.331
7.312
7.262
7.237
5.511
5.499
5.481
5.470
1.881
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1.873
1.846
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1.802
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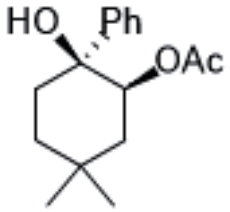
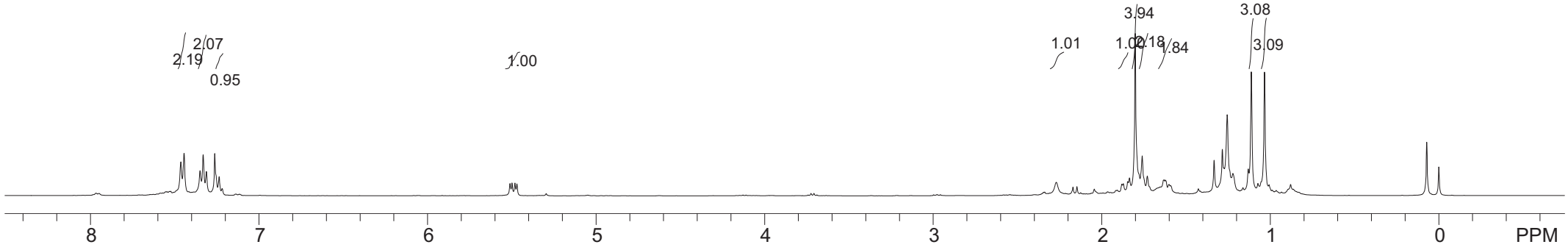

HO
Ph
OAc

3v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3.09
8
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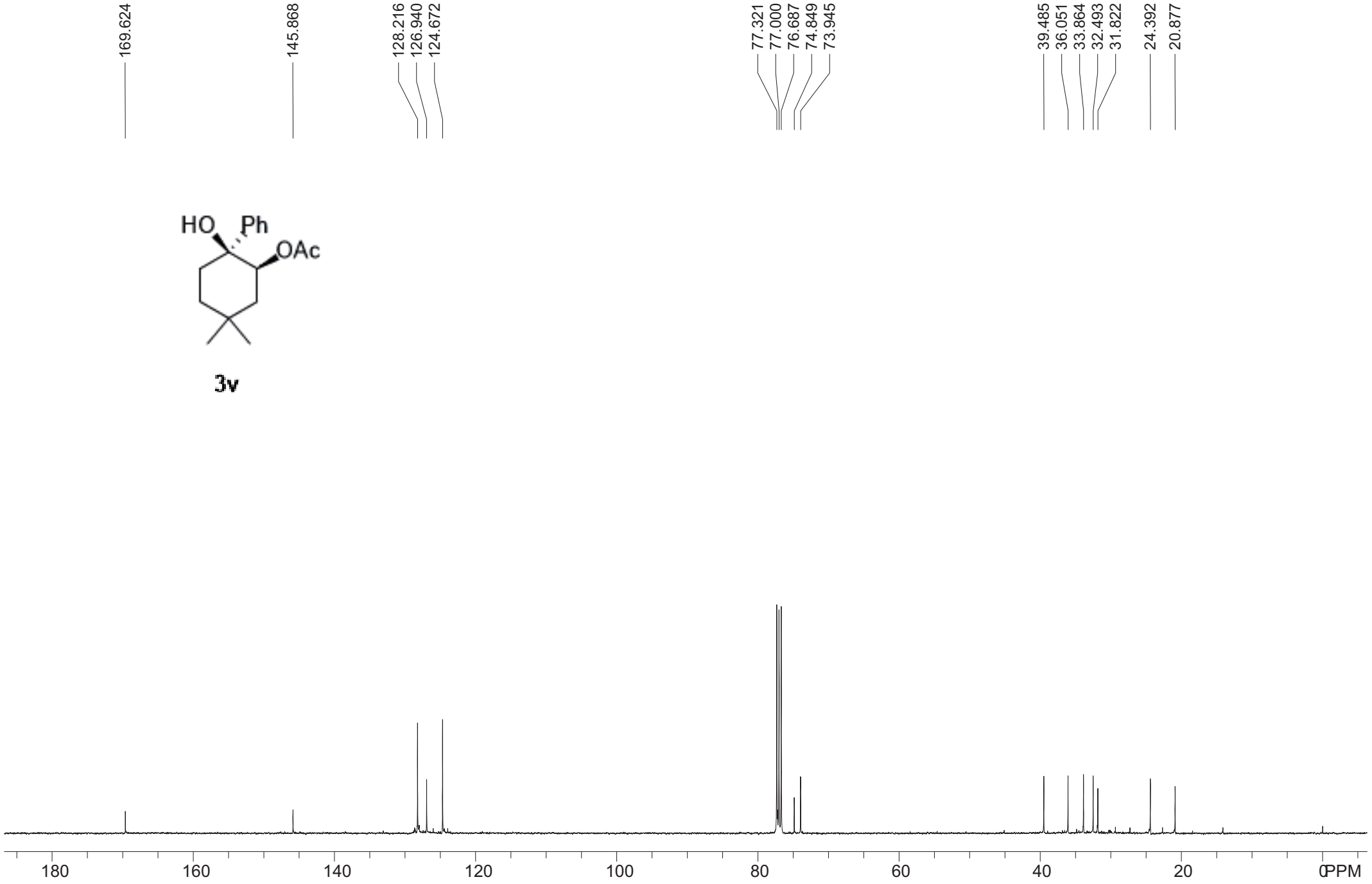
6
5
4
3
2
1
0
PPM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76.687
74.849
73.945
39.485
36.051
33.864
32.493
31.822
24.392
20.877
HO
Ph
OAc
3v
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160
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120
100
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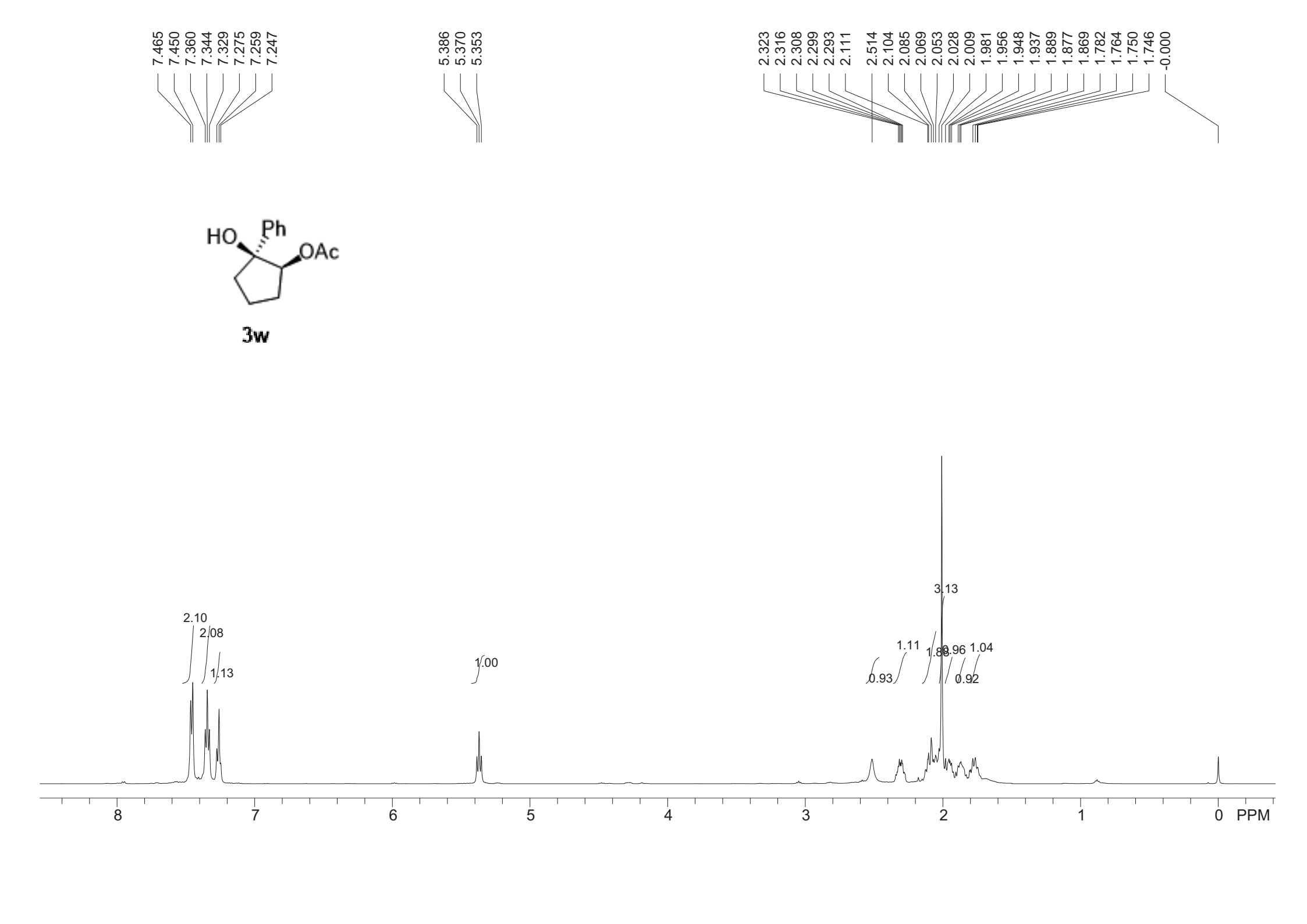
40
20
0
PPM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7.450
7.360
7.344
7.329
7.275
7.259
7.247
5.386
5.370
5.353
2.323
2.316
2.308
2.299
2.293
2.111
2.514
2.104
2.085
2.069
2.053
2.028
2.009
1.981
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1.877
1.869
1.782
1.764
1.750
1.746
-0.000
HO
Ph
OAc
3w
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2.08
1.13
1.00
0.93
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1.04
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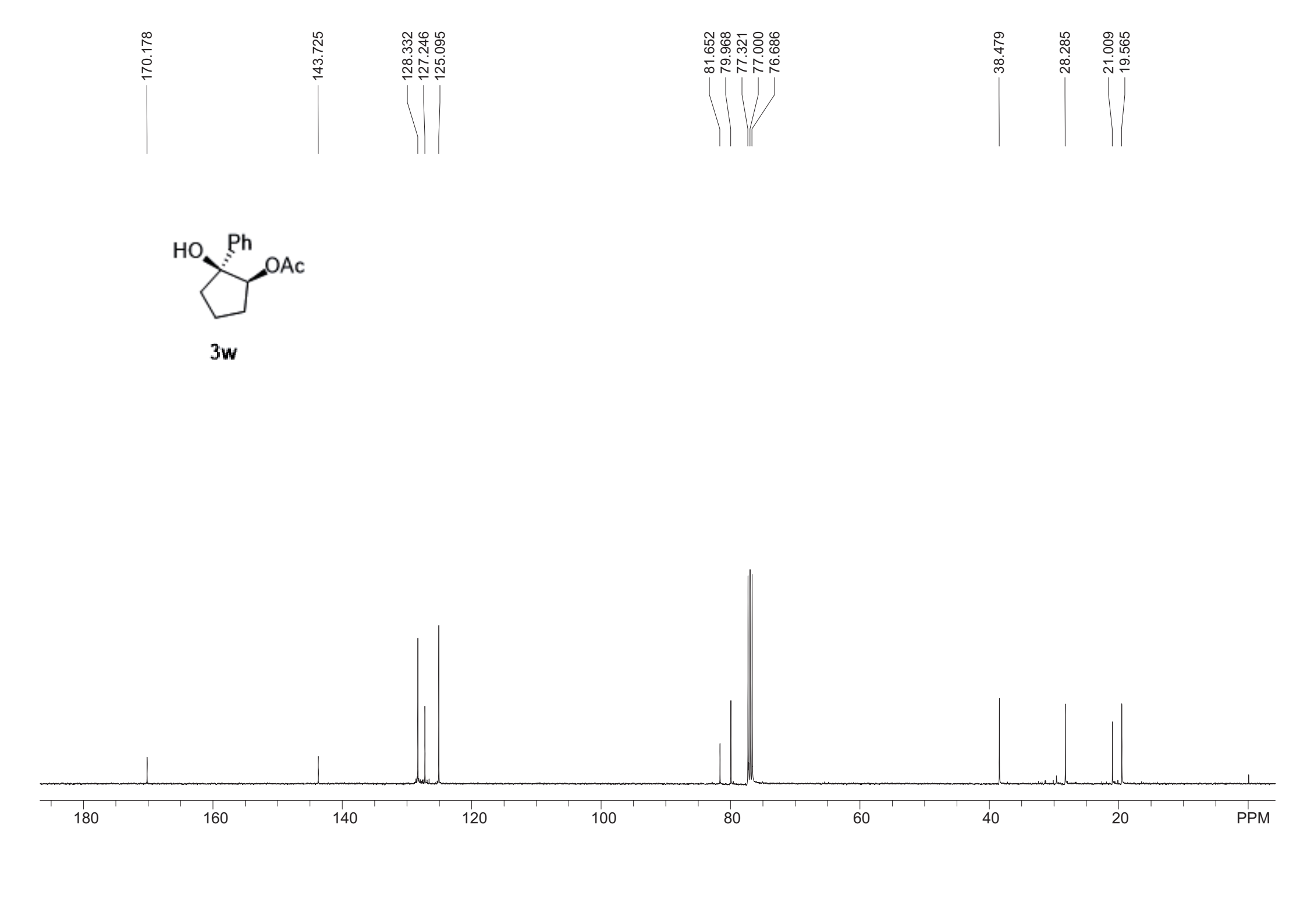
0
PPM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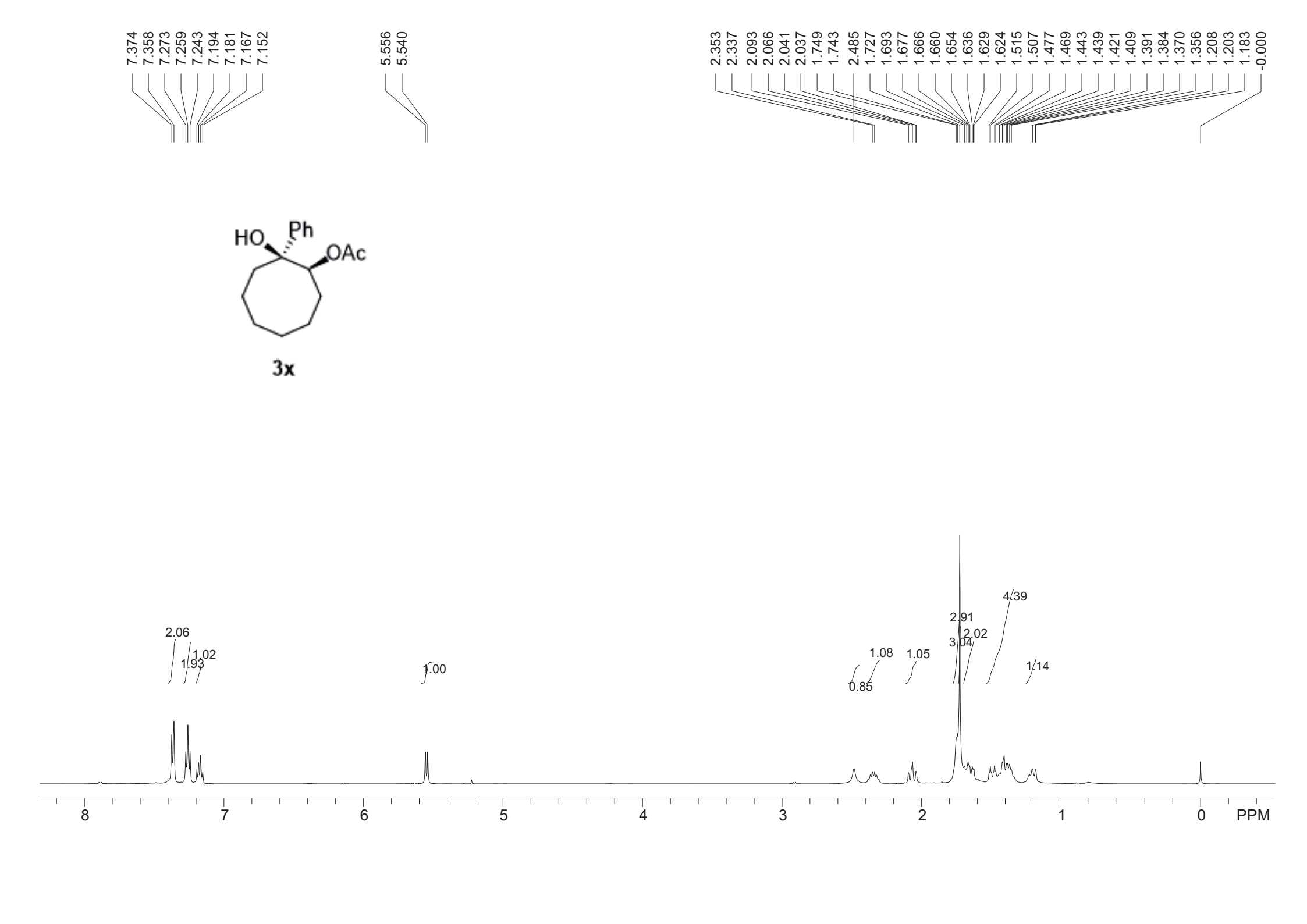
128.332
127.246
125.095
81.652
79.968
77.321
77.000
76.686
38.479
28.285
21.009
19.565
HO
Ph
OAc
3w
180
160
140
120
100
80
60
40
20
PPM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7.167
7.152
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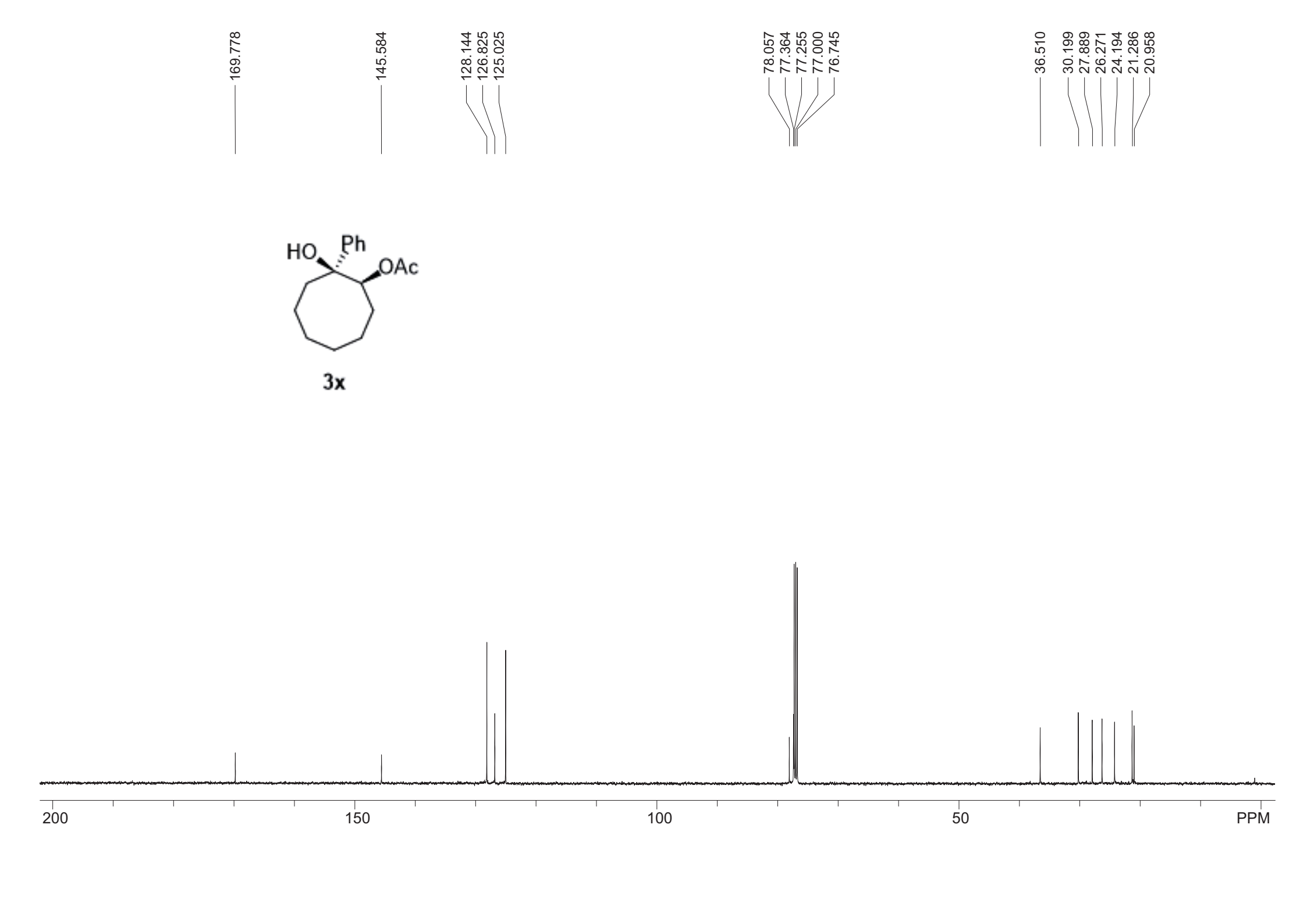
5.540
2.353
2.337
2.093
2.066
2.041
2.037
1.749
1.743
2.485
1.727
1.693
1.677
1.666
1.660
1.654
1.636
1.629
1.624
1.515
1.507
1.477
1.469
1.443
1.439
1.421
1.409
1.391
1.384
1.370
1.356
1.208
1.203
1.183
-0.000
HO
Ph
OAc
3x
2.06
1.93
1.02
1.00
0.85
1.08
1.05
2.91
3.04
2.02
4.39
1.14
8
7
6
5
4
3
2
1
0
PPM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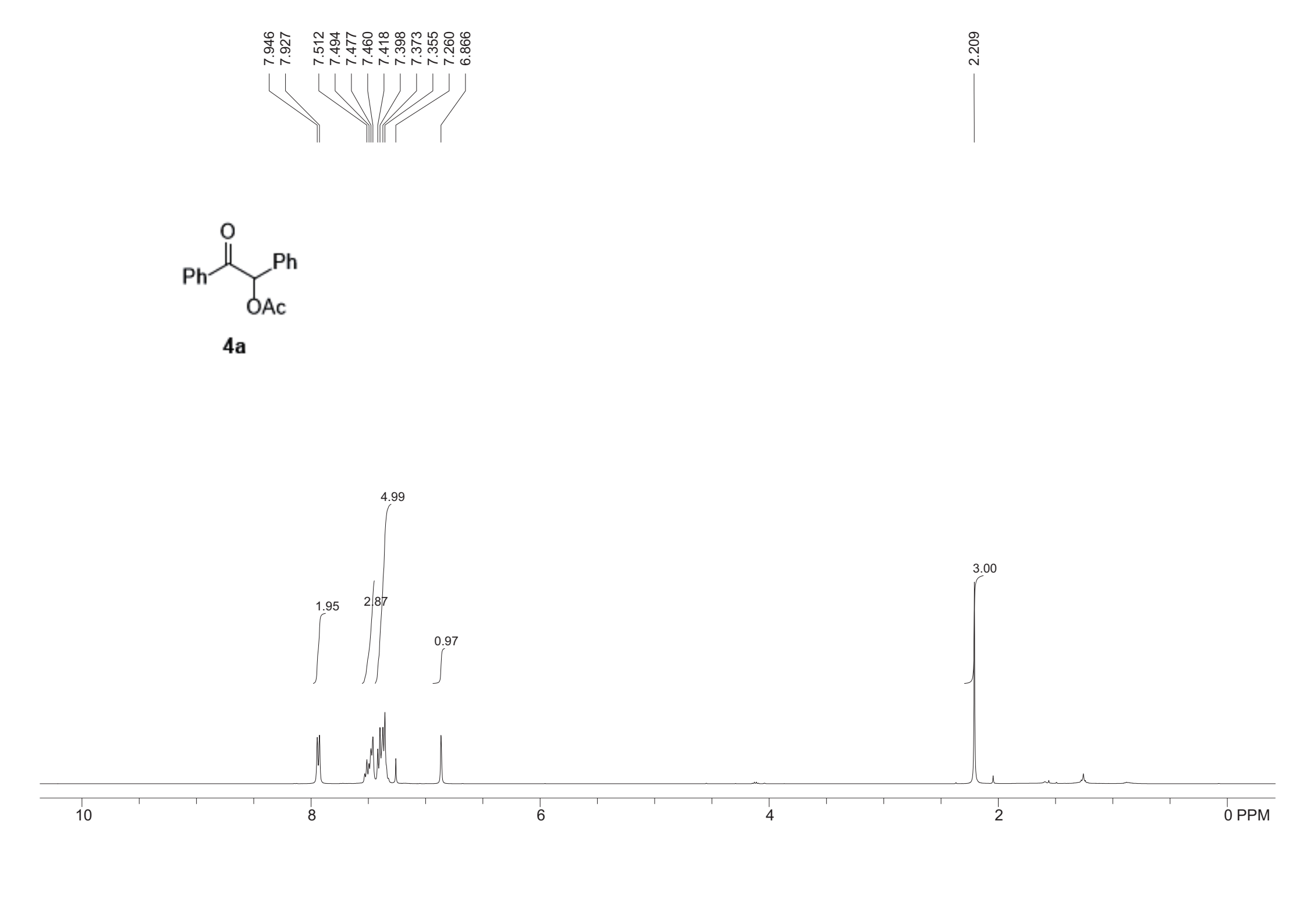
126.825
125.025
78.057
77.364
77.255
77.000
76.745
36.510
30.199
27.889
26.271
24.194
21.286
20.958
HO
Ph
OAc
3x
200
150
100
50
PPM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7.460
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7.398
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7.355
7.260
6.866
2.209
O
Ph
Ph
OAc
4a
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1.95
2.87
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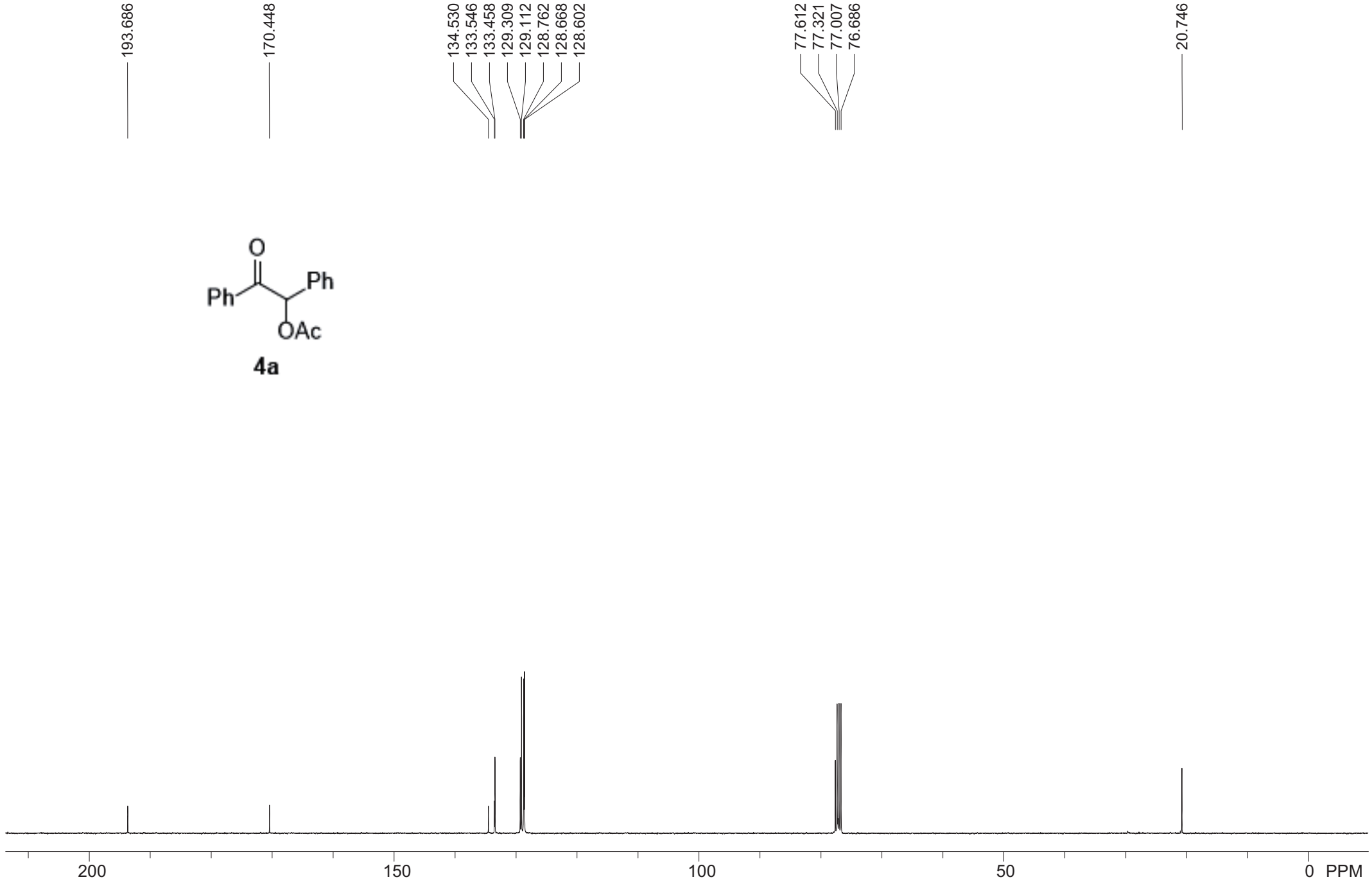
10
8
6
4
2
0 PPM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129.309
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128.762
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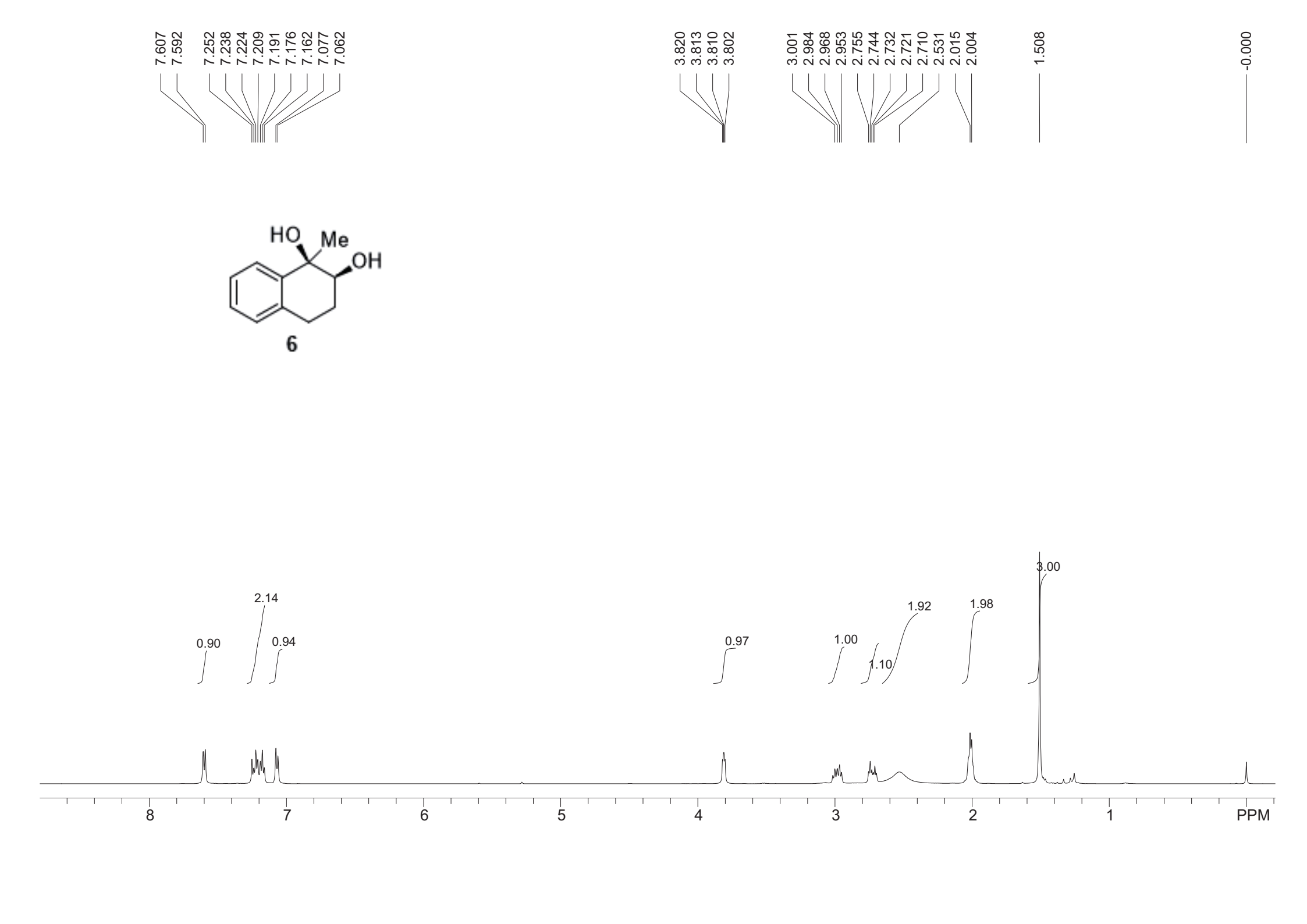
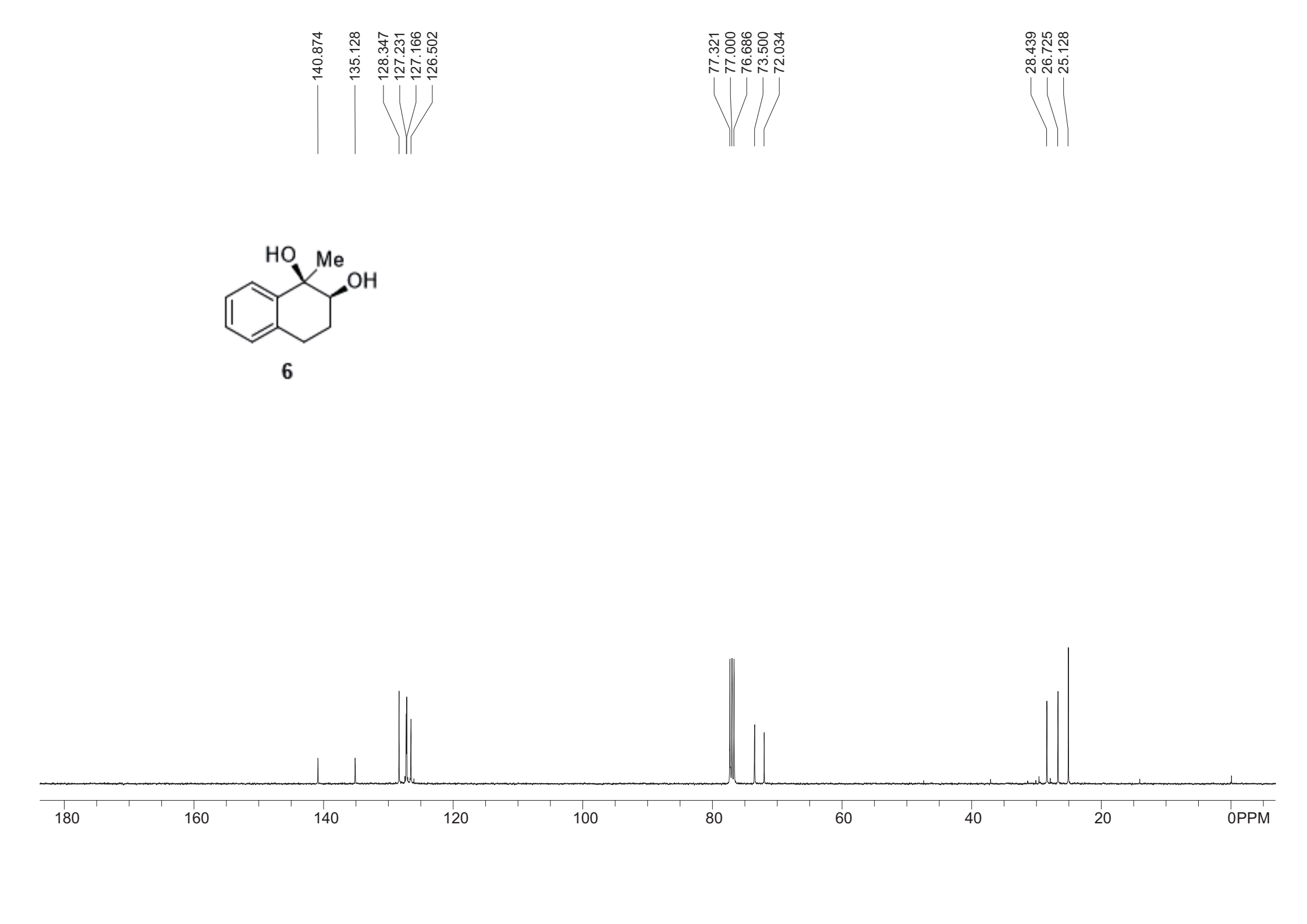
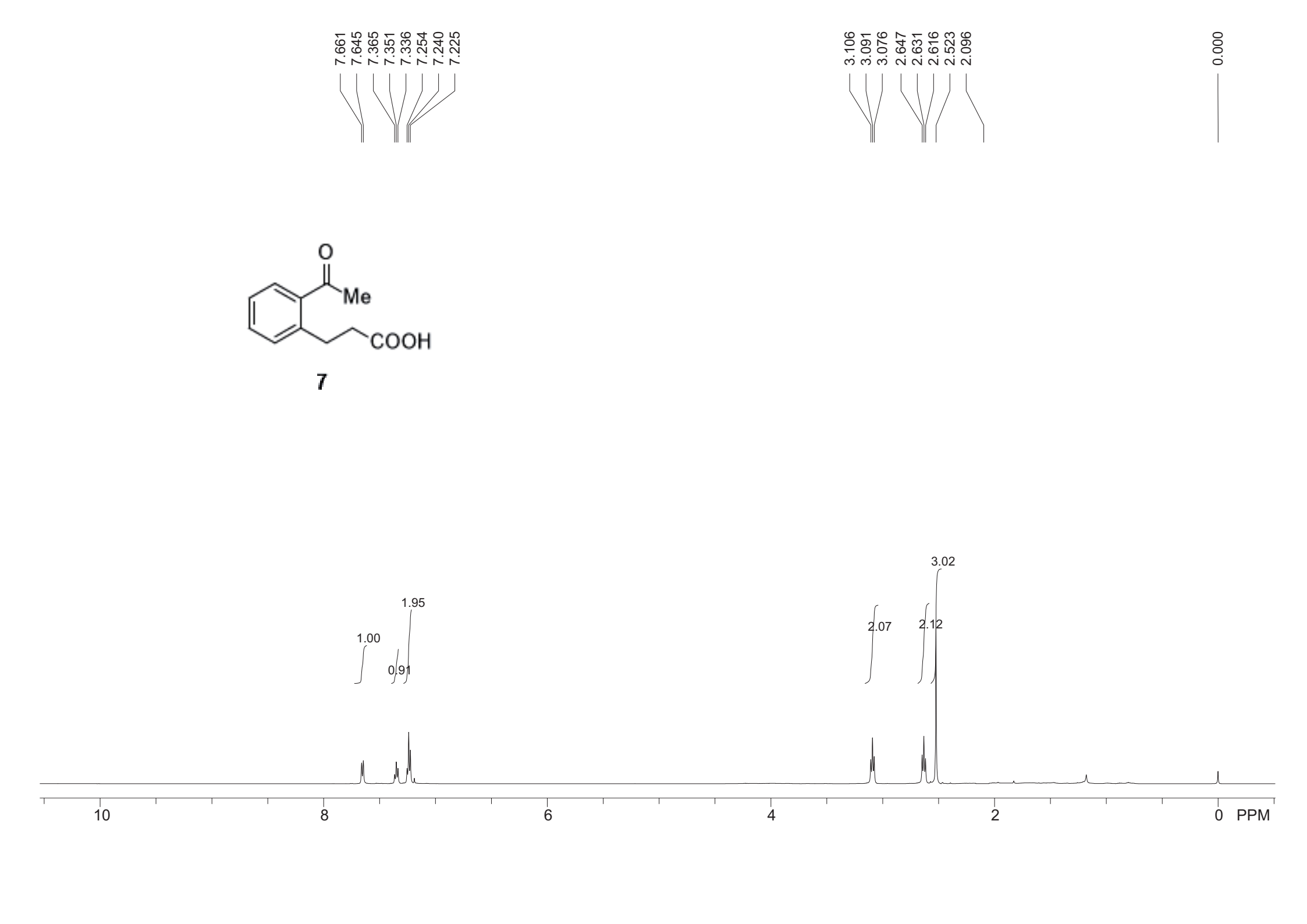
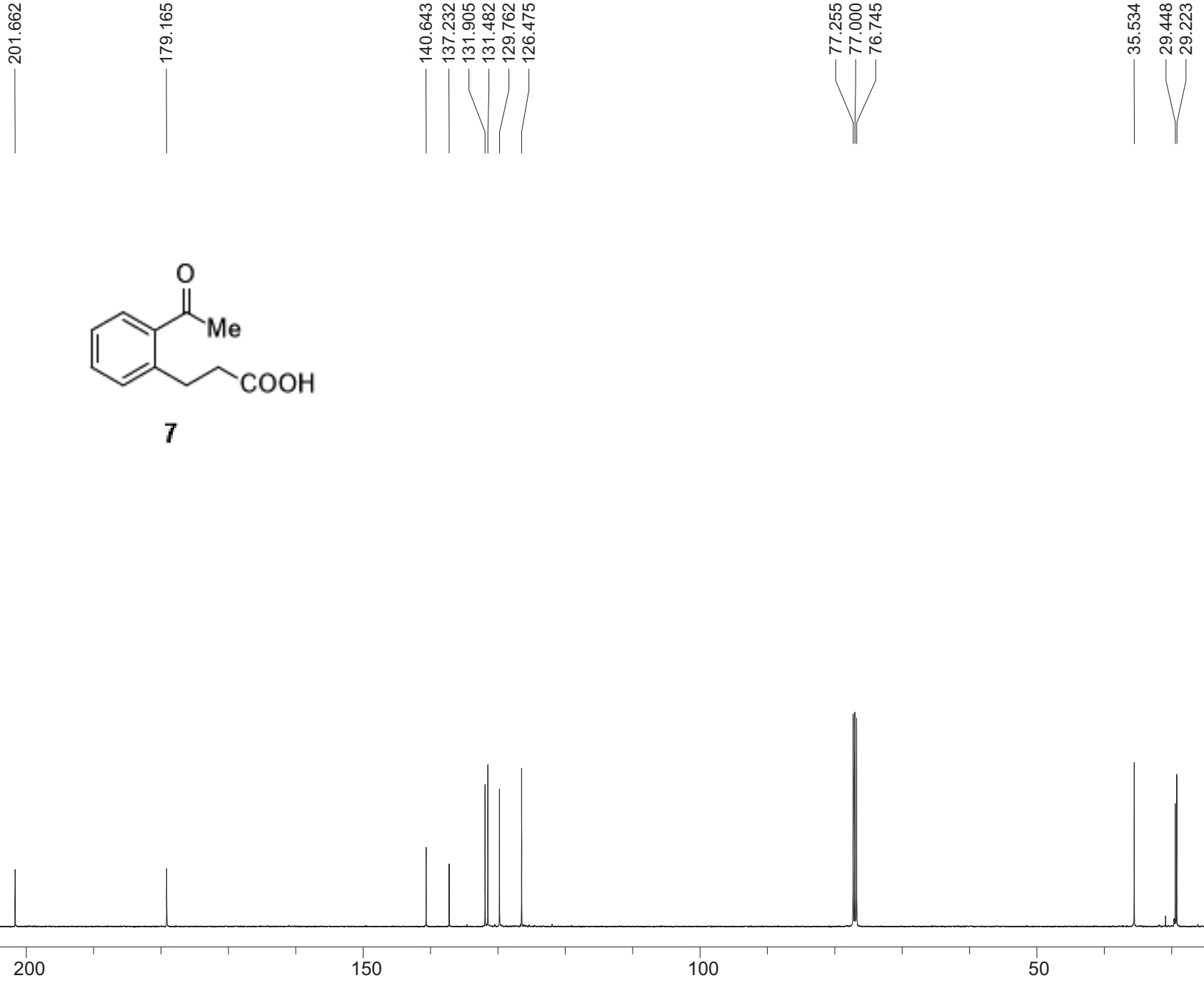
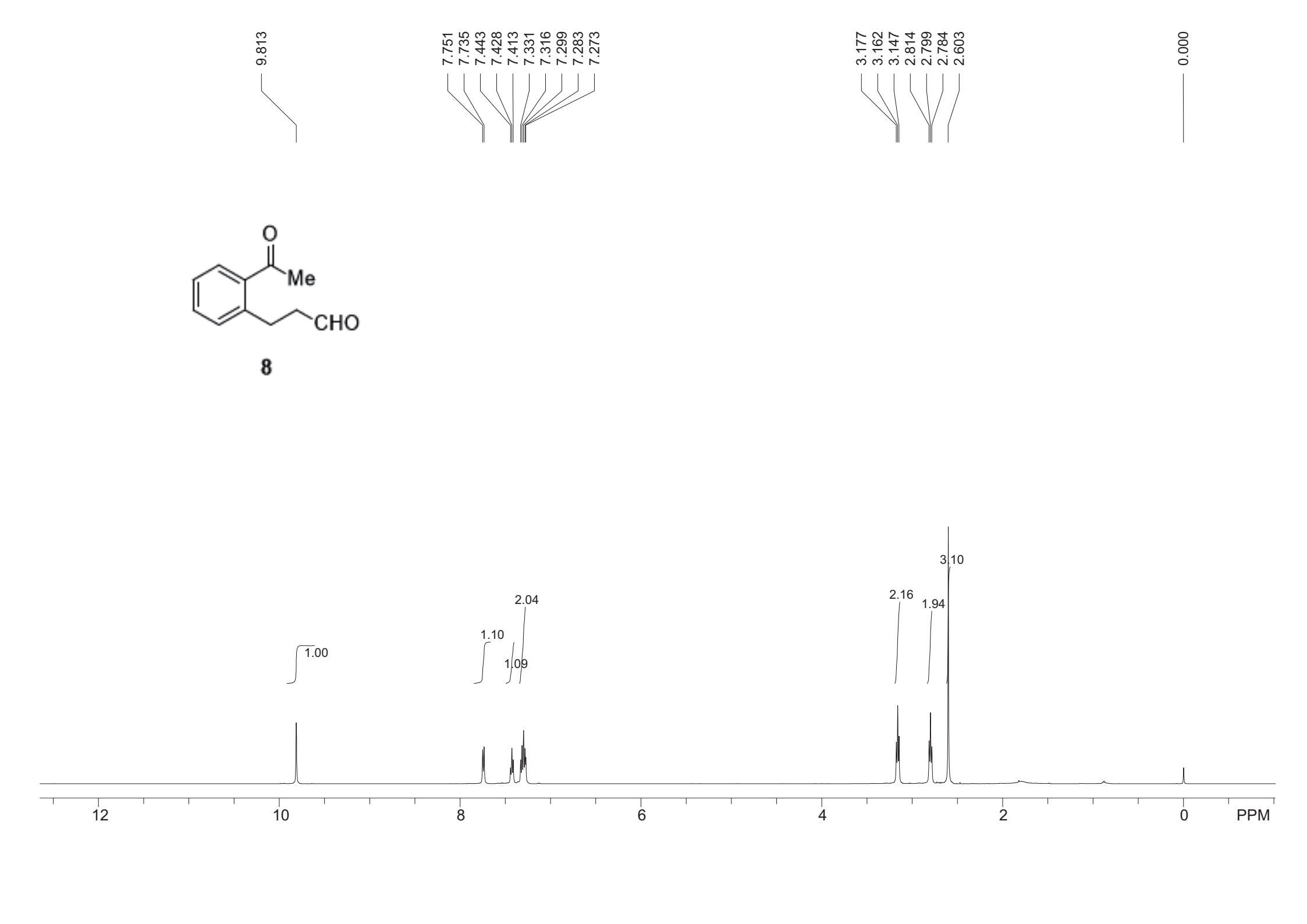
128.602
77.612
77.321
77.007
76.686
20.746
O
Ph
Ph
OAc
4a
200
150
100
50
0
PPM

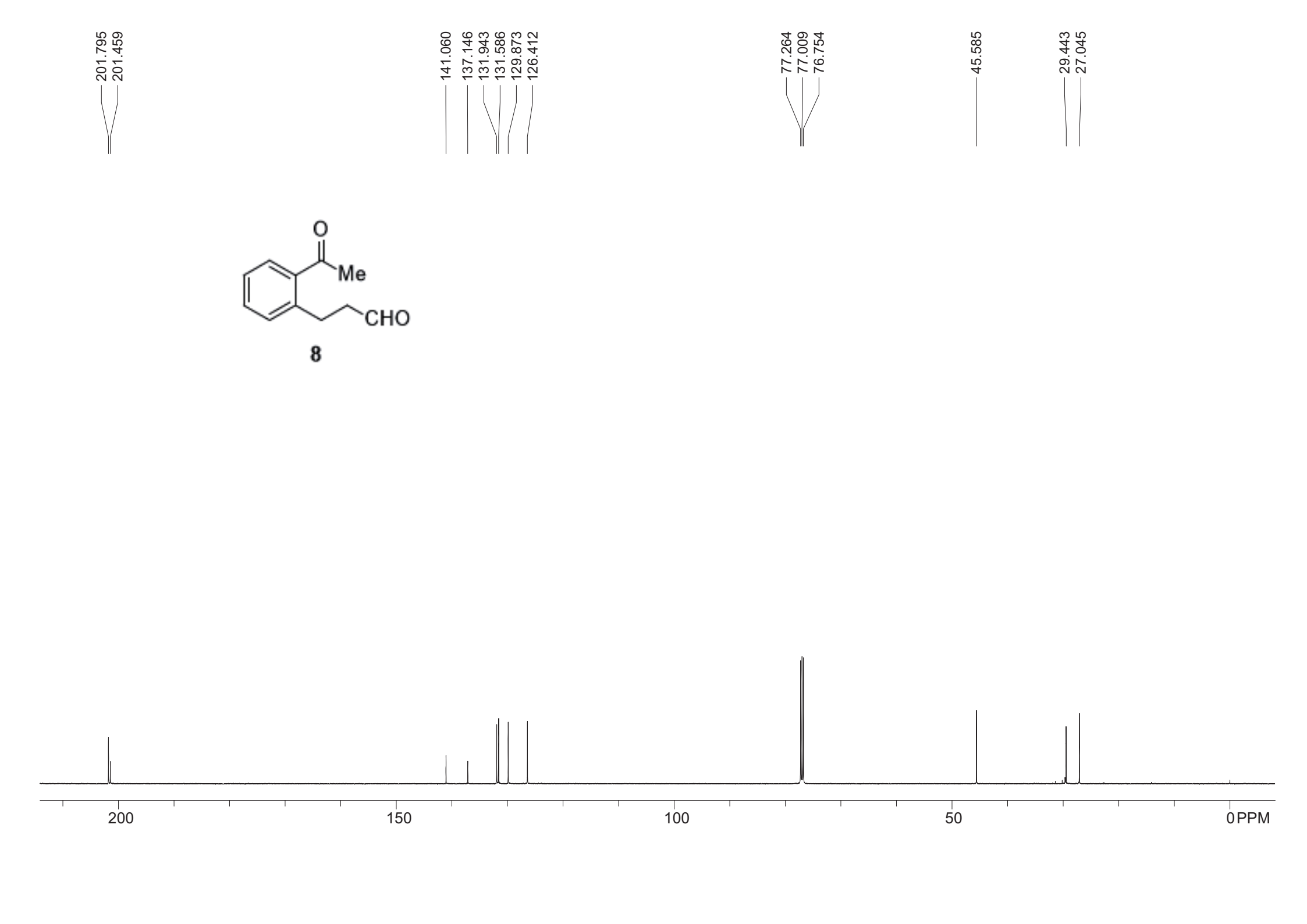

7.607
7.592
7.252
7.238
7.224
7.209
7.191
7.176
7.162
7.077
7.062
3.820
3.813
3.810
3.802
3.001
2.984
2.968
2.953
2.755
2.744
2.732
2.721
2.710
2.531
2.015
2.004
1.508
-0.000
HO
Me
OH
6
0.90
2.14
0.94
0.97
1.00
1.10
1.92
1.98
3.00
8
7
6
5
4
3
2
1
PPM

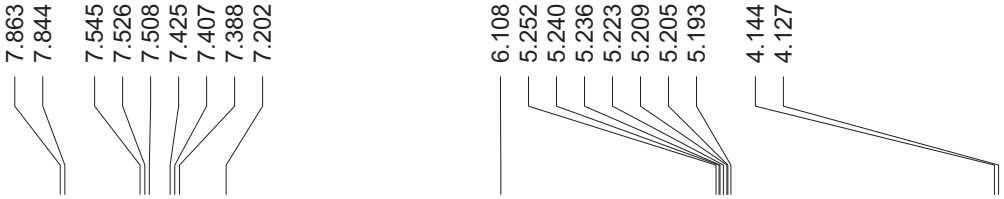

140.874
135.128
128.347
127.231
127.166
126.502
77.321
77.000
76.686
73.500
72.034
28.439
26.725
25.128
HO
Me
OH
6
180
160
140
120
100
80
60
40
20
0PPM

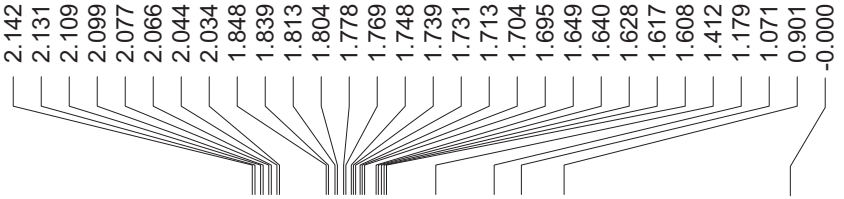

7.661
7.645
7.365
7.351
7.336
7.254
7.240
7.225
3.106
3.091
3.076
2.647
2.631
2.616
2.523
2.096
0.000
O
Me
COOH
7
1.00
0.91
1.95
2.07
2.12
3.02
10
8
6
4
2
0
PPM

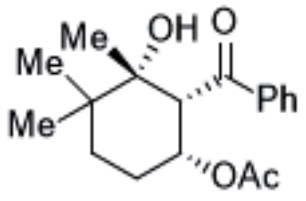

201.662
179.165
140.643
137.232
131.905
131.482
129.762
126.475
77.255
77.000
76.745
35.534
29.448
29.223
O
Me
COOH
7
200
150
100
50
0 PPM


9.813
7.751
7.735
7.443
7.428
7.413
7.331
7.316
7.299
7.283
7.273
3.177
3.162
3.147
2.814
2.799
2.784
2.603
0.000
O
Me
CHO
8
1.00
1.10
1.09
2.04
2.16
1.94
3.10
12
10
8
6
4
2
0
PPM

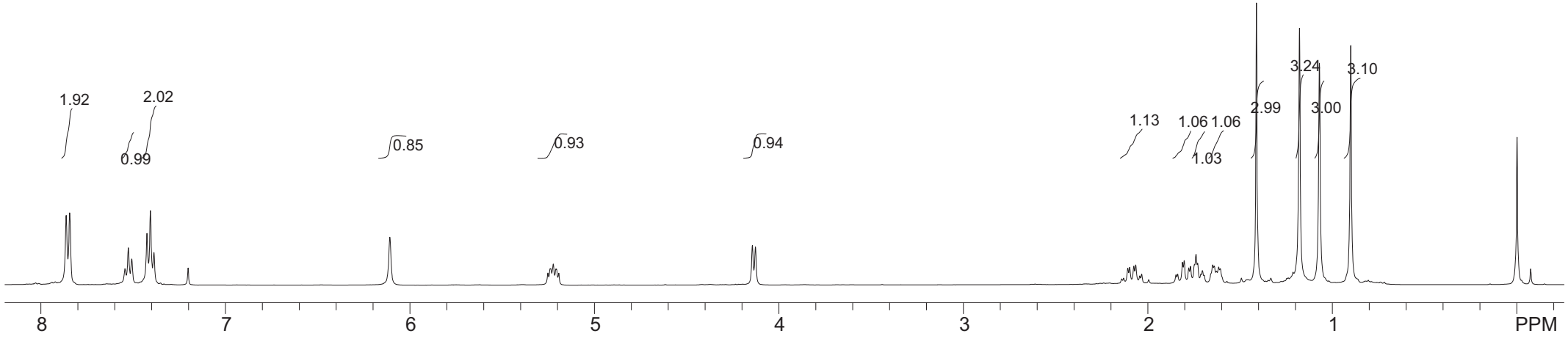

201.795
201.459
141.060
137.146
131.943
131.586
129.873
126.412
77.264
77.009
76.754
45.585
29.443
27.045
O
Me
CHO
8
200
150
100
50
0 PPM


7.863
7.844
7.545
7.526
7.508
7.425
7.407
7.388
7.202
6.108
5.252
5.240
5.236
5.223
5.209
5.205
5.193
4.144
4.127

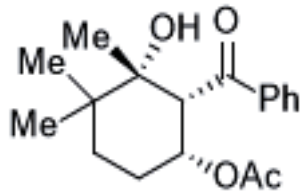

2.142
2.131
2.109
2.099
2.077
2.066
2.044
2.034
1.848
1.839
1.813
1.804
1.778
1.769
1.748
1.739
1.731
1.713
1.704
1.695
1.649
1.640
1.628
1.617
1.608
1.412
1.179
1.071
0.901
-0.000


Me
OH
O
Me
Ph
Me
OAc

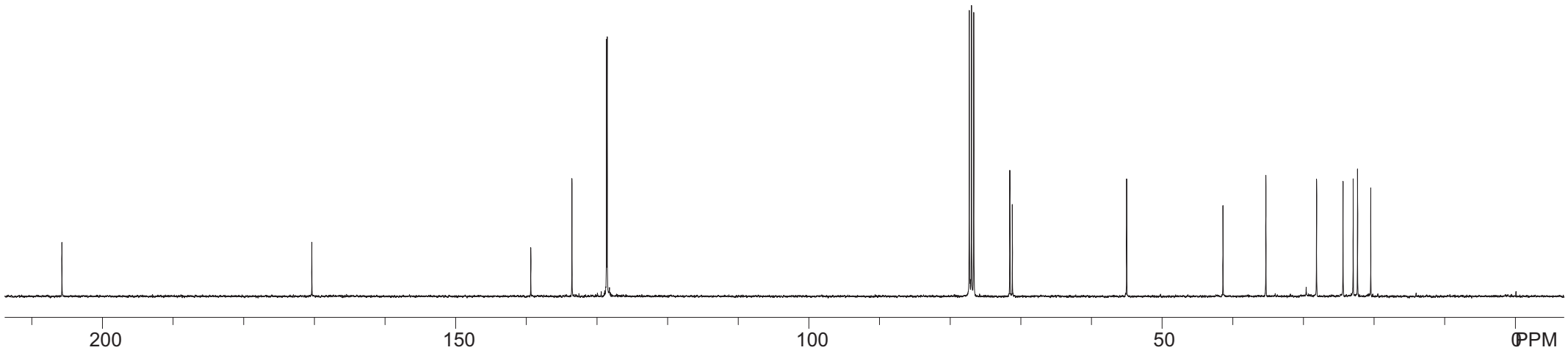
9


1.92
2.02
0.99
0.85
0.93
0.94
1.13
1.06
1.06
1.03
2.99
3.24
3.00
3.10
8
7
6
5
4
3
2
1
PPM

205.732
170.360
139.379
133.553
128.660
128.558
77.321
77.000
76.687
71.575
71.225
55.045
41.410
35.344
28.176
24.421
22.985
22.372
20.498



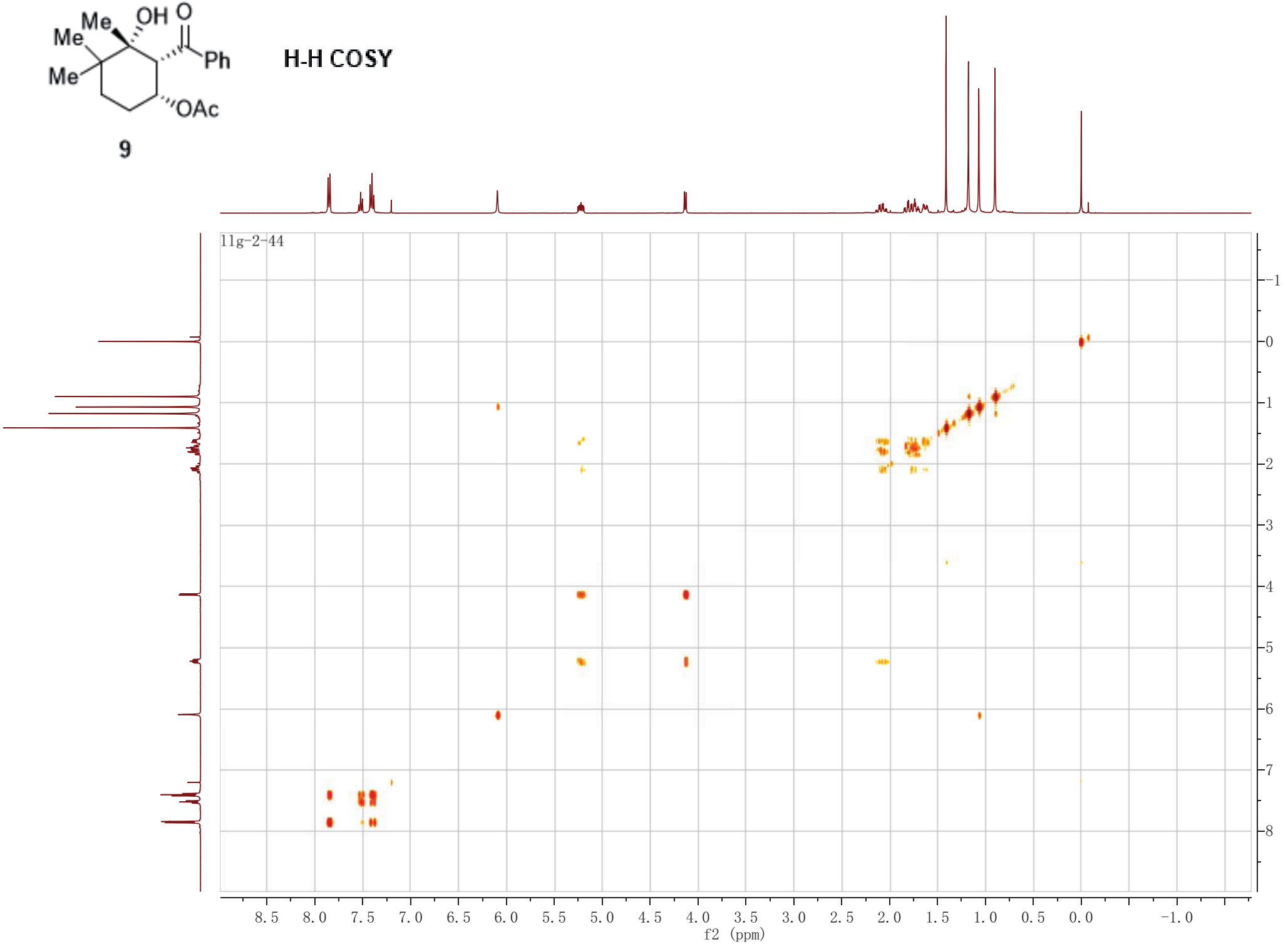
9

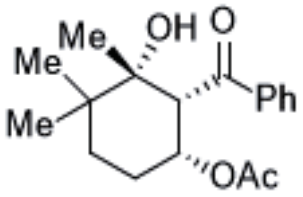


Me
OH
O
Me
Ph
Me
OAc

9

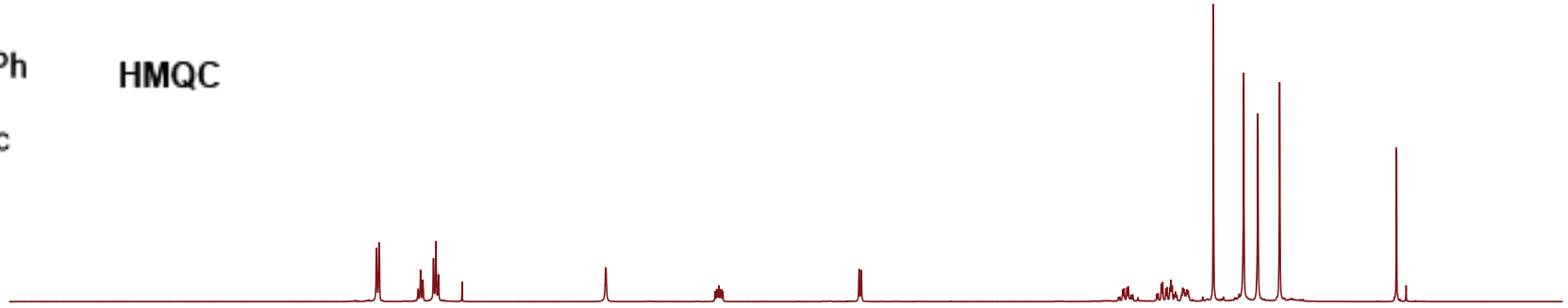
H-H COSY

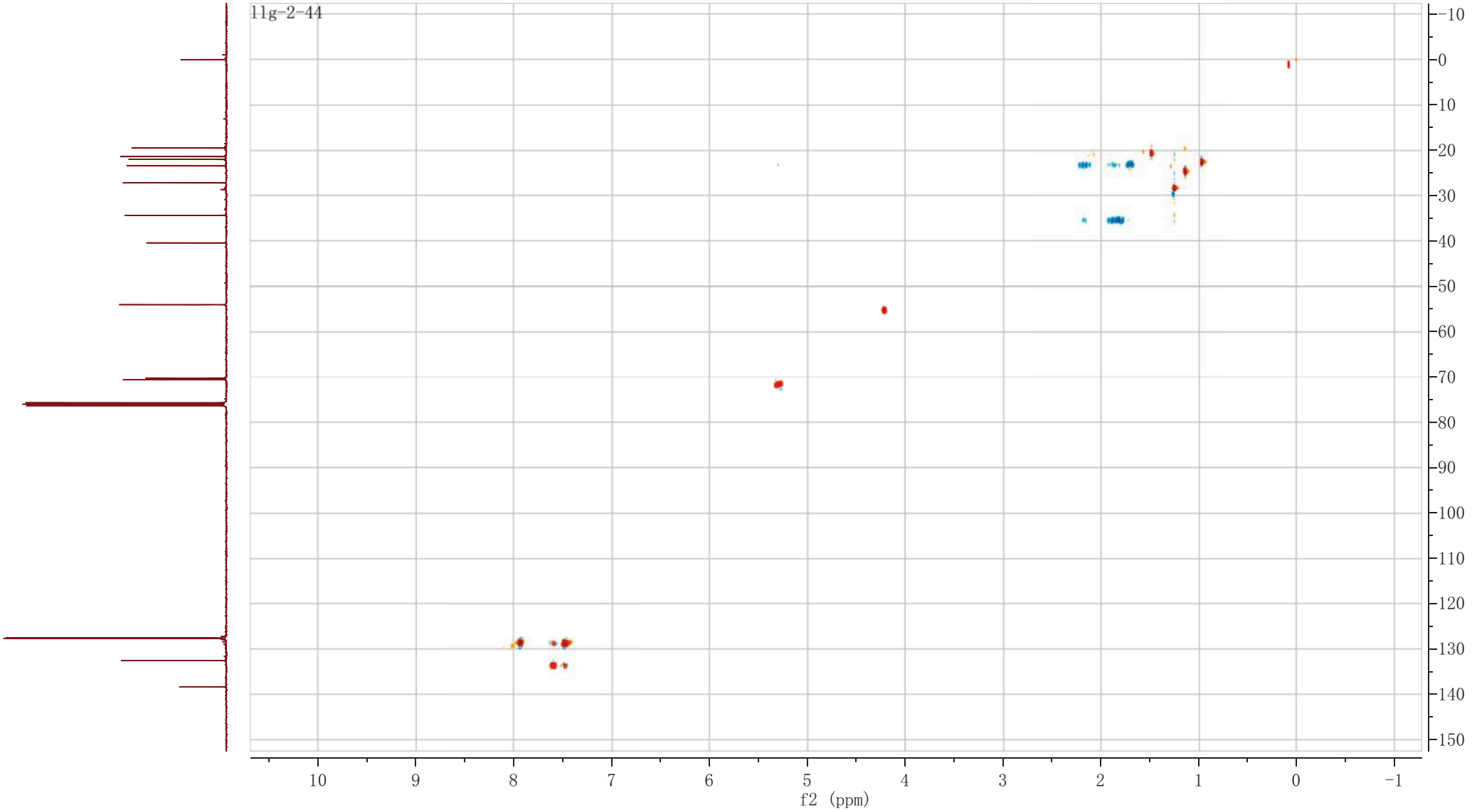

11g-2-44
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f2 (ppm)
-1
0
1
2
3
4
5
6
7
8
f1 (ppm)


Me
OH
O
Me
Ph
Me
OAc

9

HMQC

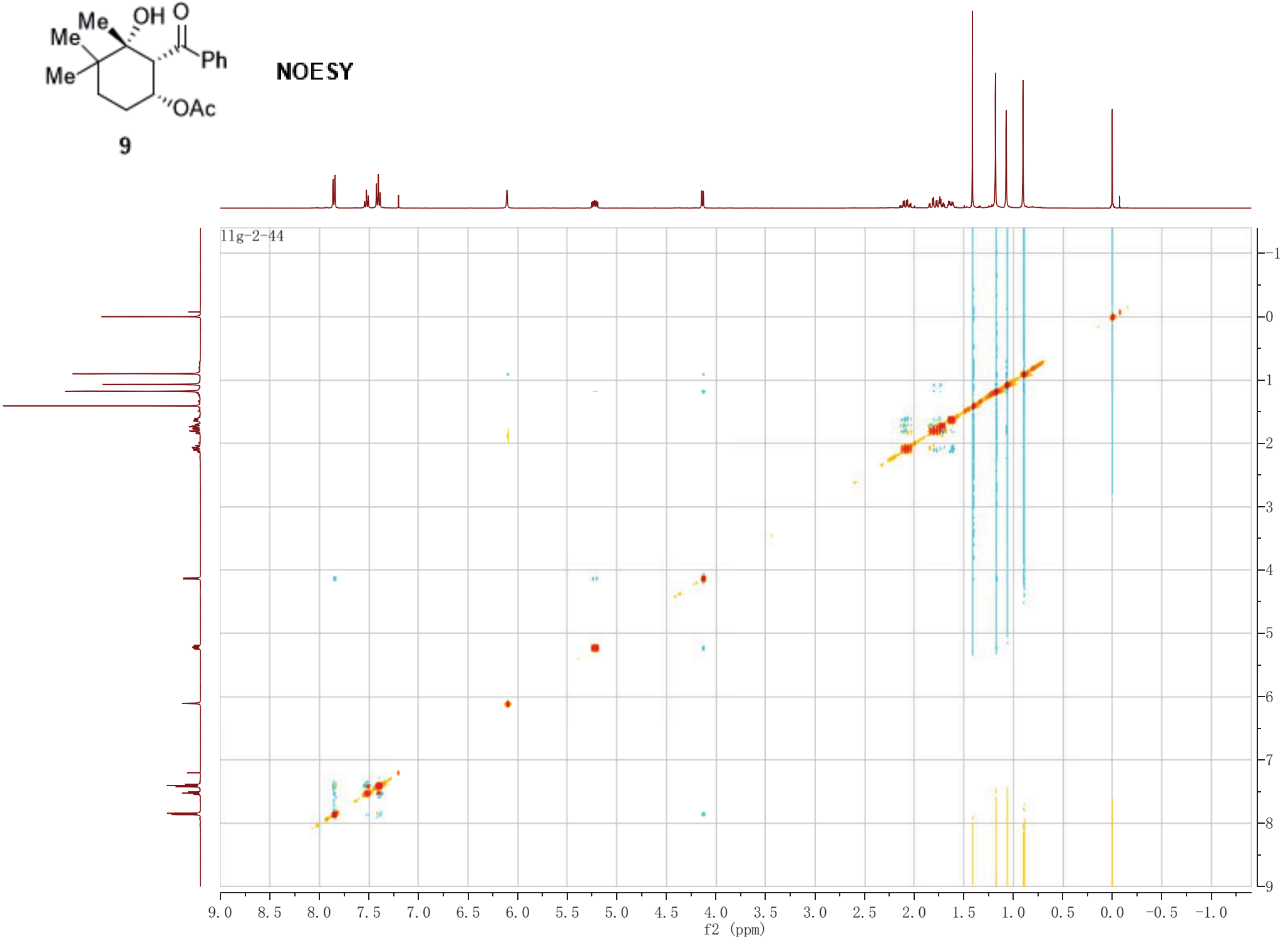


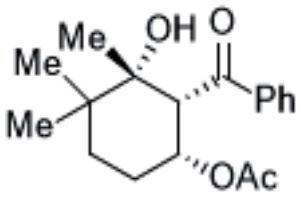

11g-2-44
10
9
8
7
6
5
4
3
2
1
0
−1
f2 (ppm)
−10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)

Me
OH
O
Me
Ph
Me
OAc

9

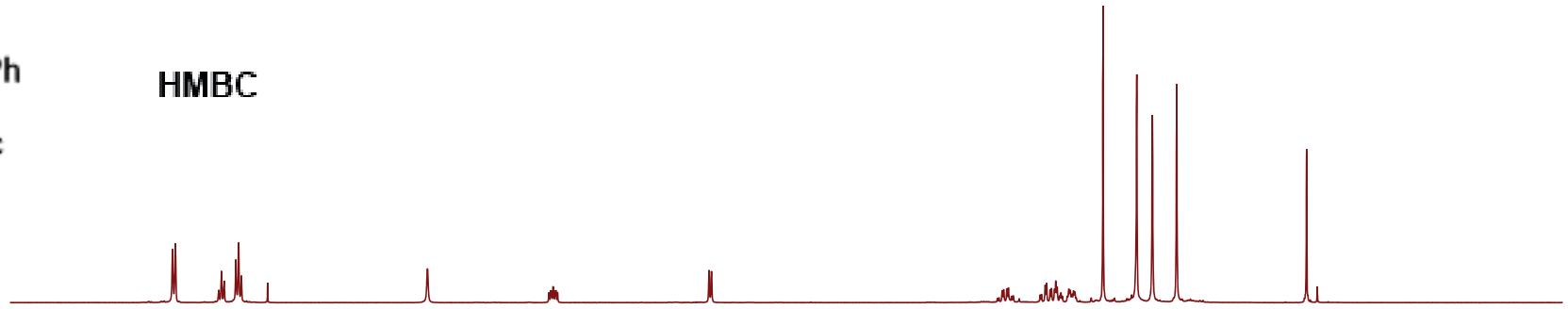
NOESY

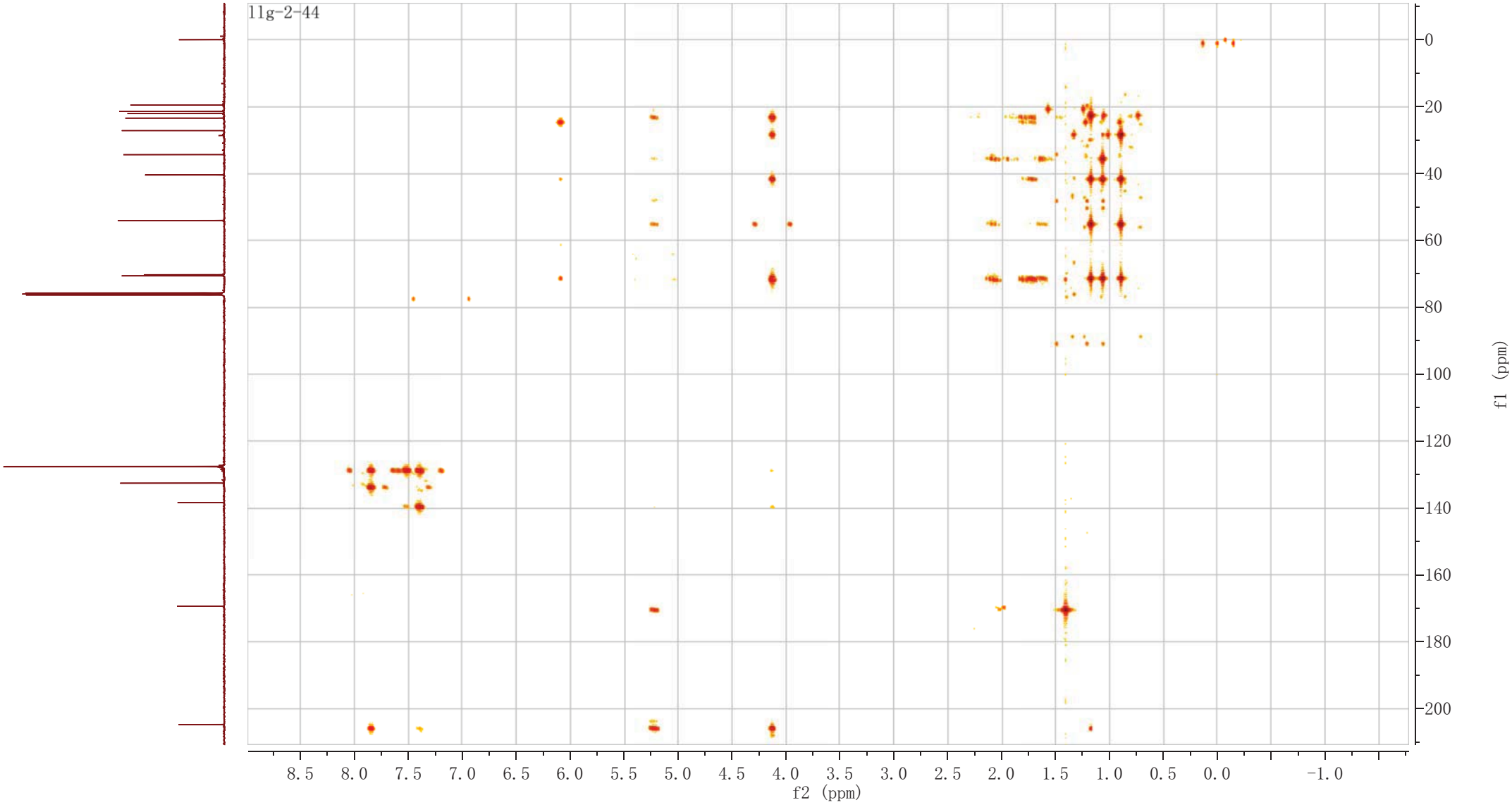

11g-2-44
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f2 (ppm)
-1
0
1
2
3
4
5
6
7
8
9
f1 (ppm)


Me
OH
O
Me
Ph
Me
OAc

9

HMBC




11g-2-44
0
20
40
60
80
100
120
140
160
180
200
f1 (ppm)
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
-1.0
f2 (ppm)