Supporting Information

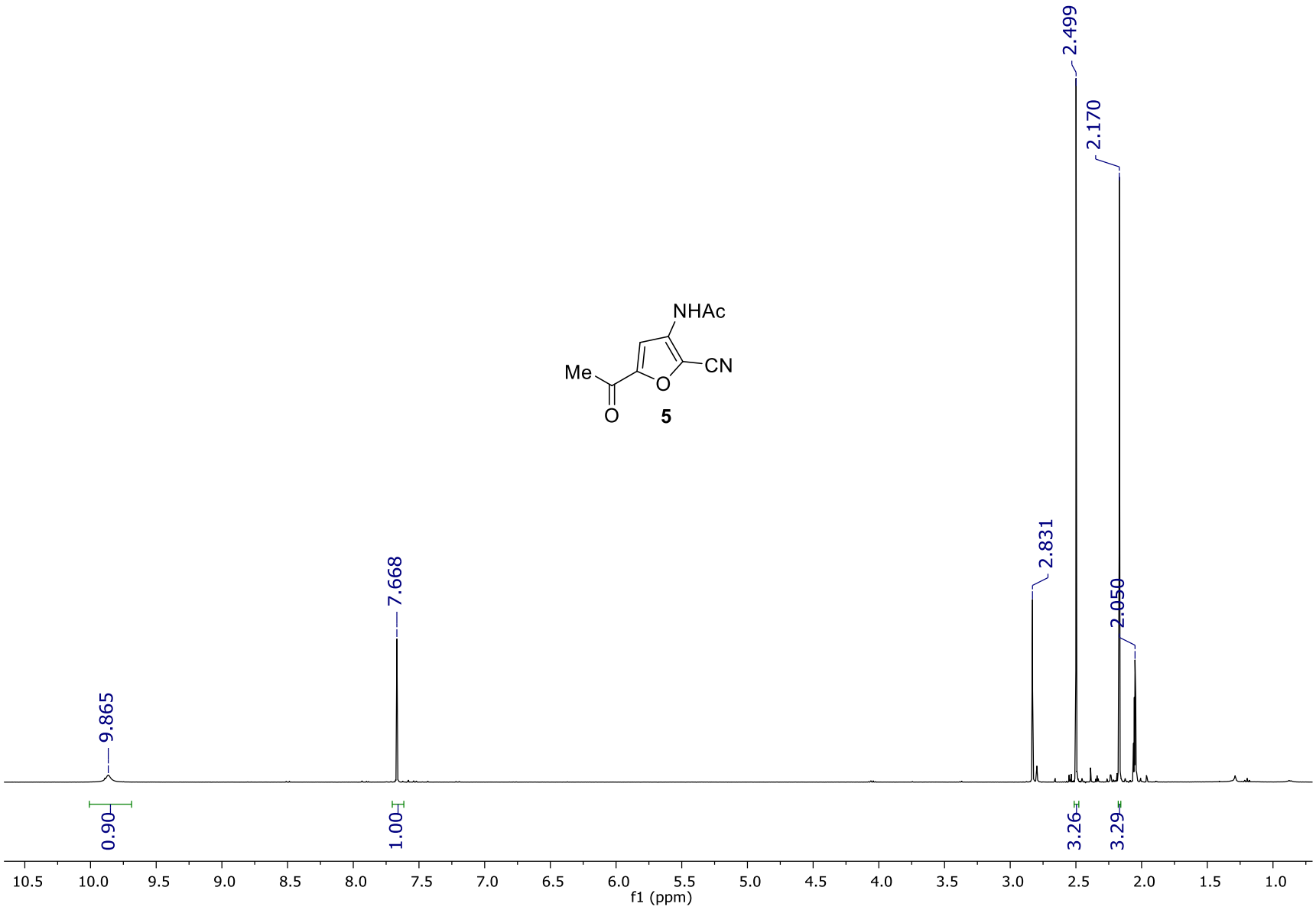
Expanding the Heteroaromatic and 2-Aminosugar Chemical Space Accessible from the Biopolymer Chitin

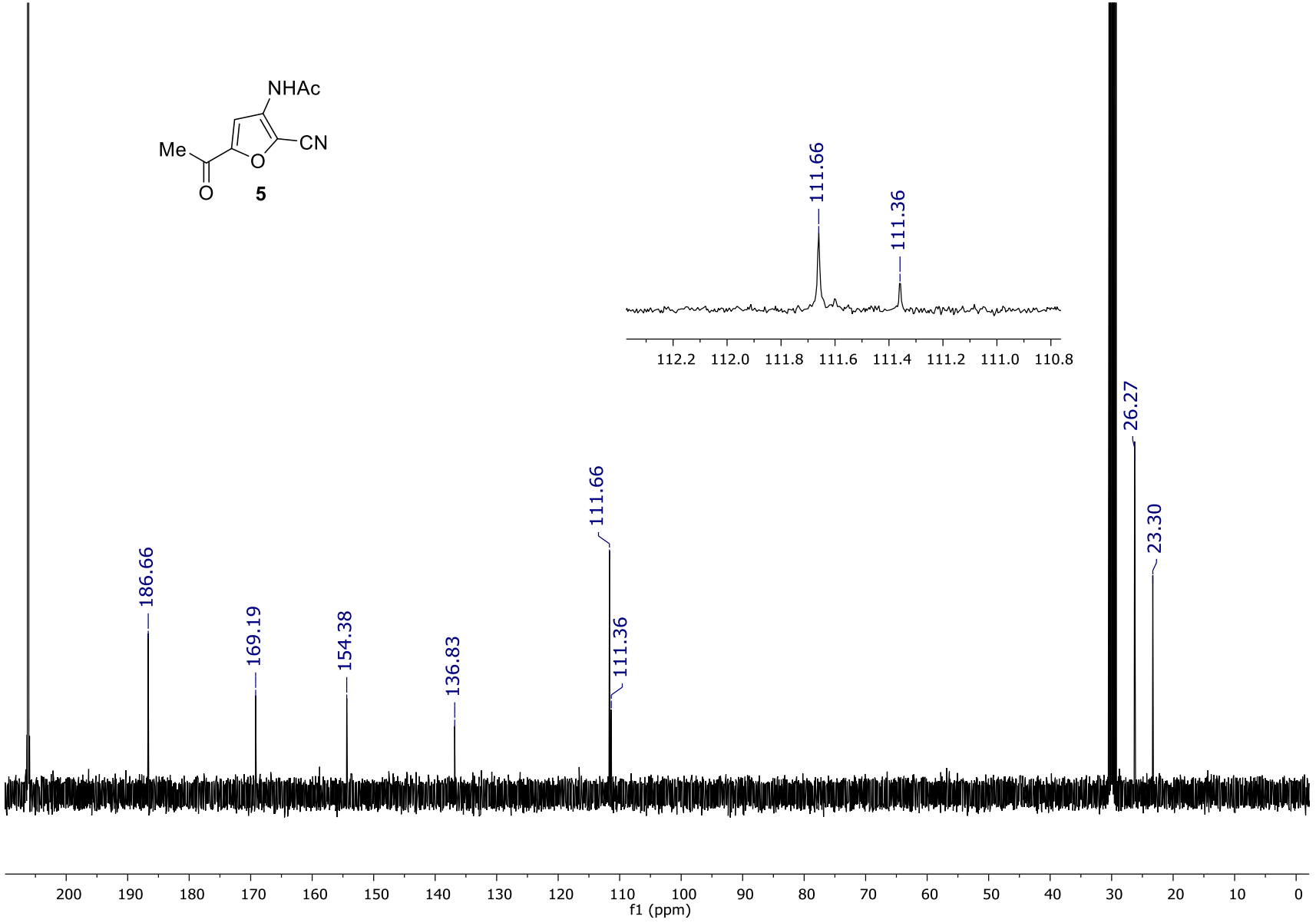
Thaís A. Rossa, Jessica C. Neville, Seongmin Paul Jun, Tilo Söhnel, and Jonathan Sperry*

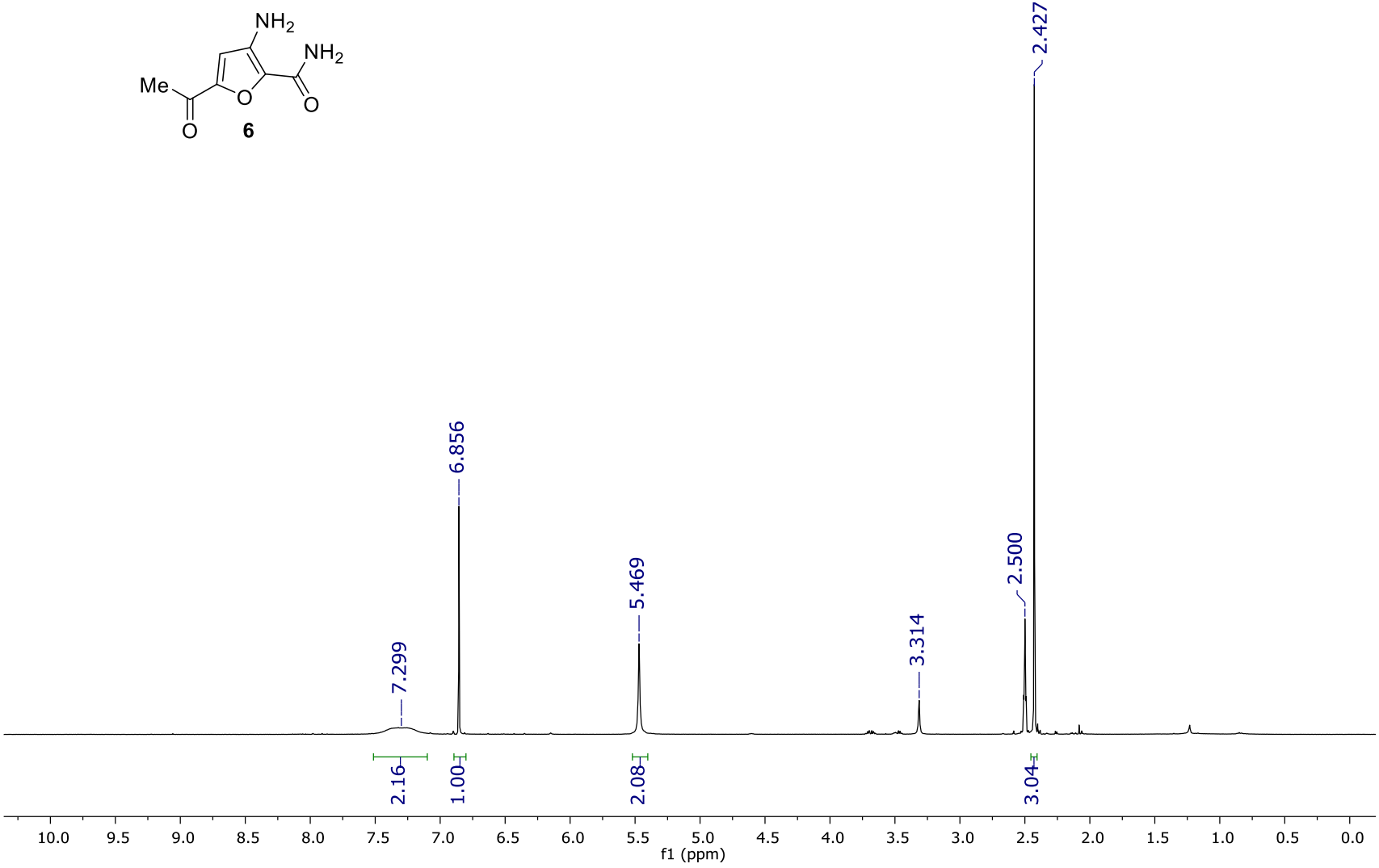
Centre for Green Chemical Science, School of Chemical Sciences, University of Auckland, 23 Symonds Street, Auckland, New Zealand

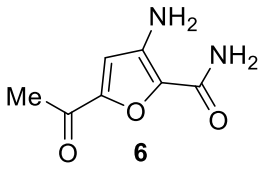
j.sperry@auckland.ac.nz

CONTENTS


NHAc
Me
CN
O
O
5
2.499
2.170
2.831
2.050
7.668
9.865
0.90
1.00
3.26
3.29
10.5
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
f1 (ppm)

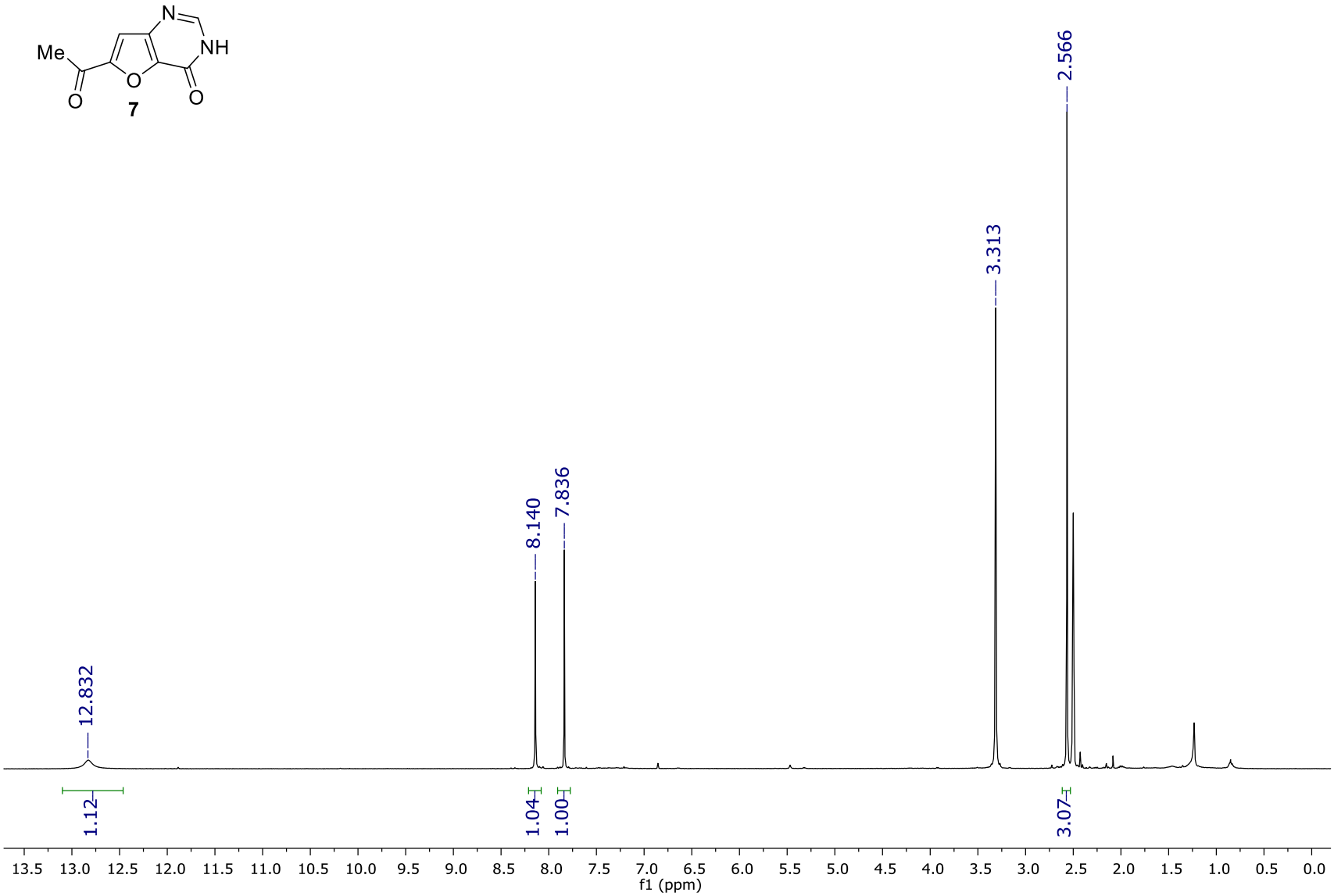

NHAc
CN
Me
O
O
5
111.66
111.36
112.2
112.0
111.8
111.6
111.4
111.2
111.0
110.8
186.66
169.19
154.38
136.83
111.66
111.36
26.27
23.30
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

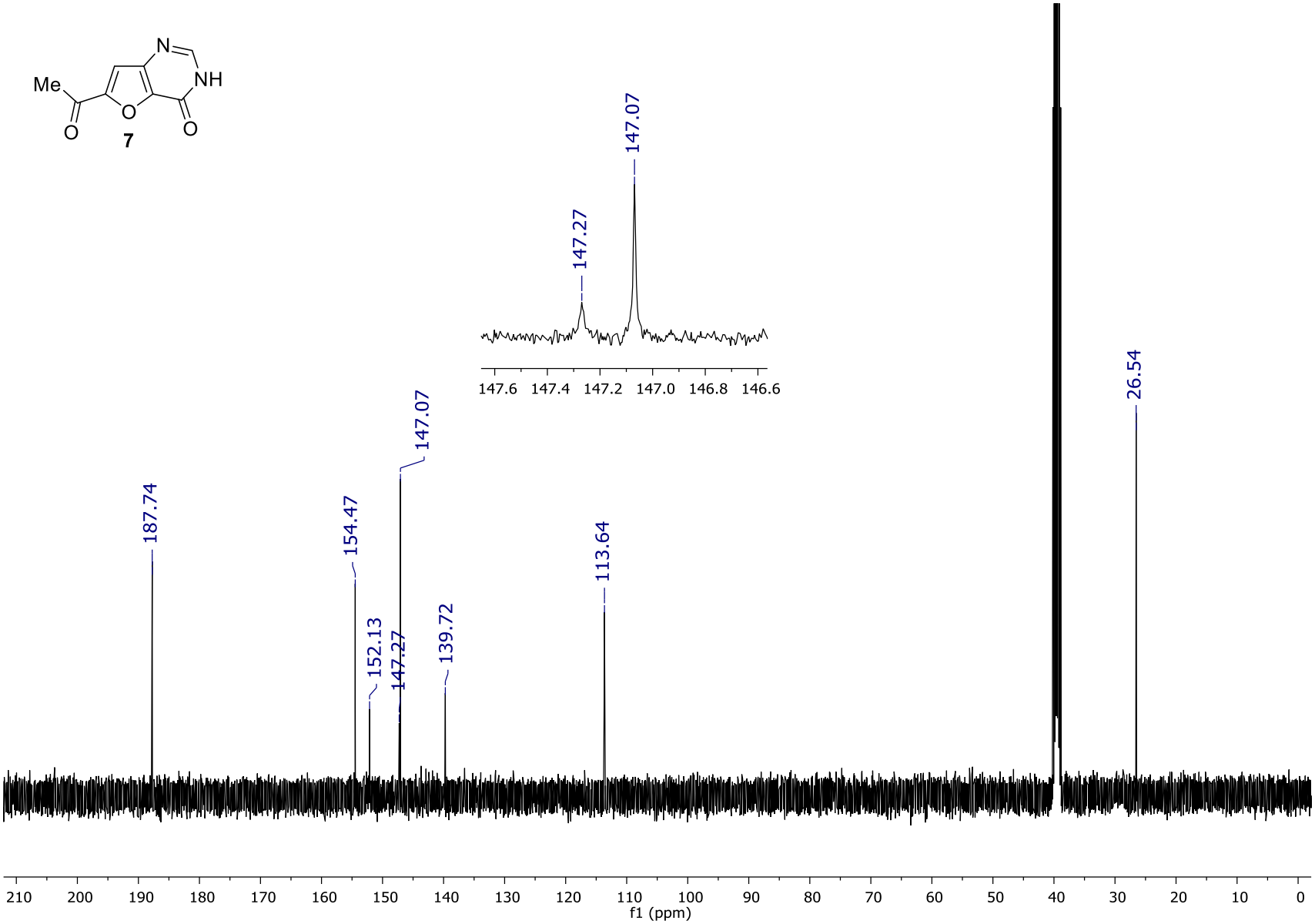

NH2
NH2
Me
O
O
O
6
7.299
6.856
5.469
3.314
2.500
2.427
2.16
1.00
2.08
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

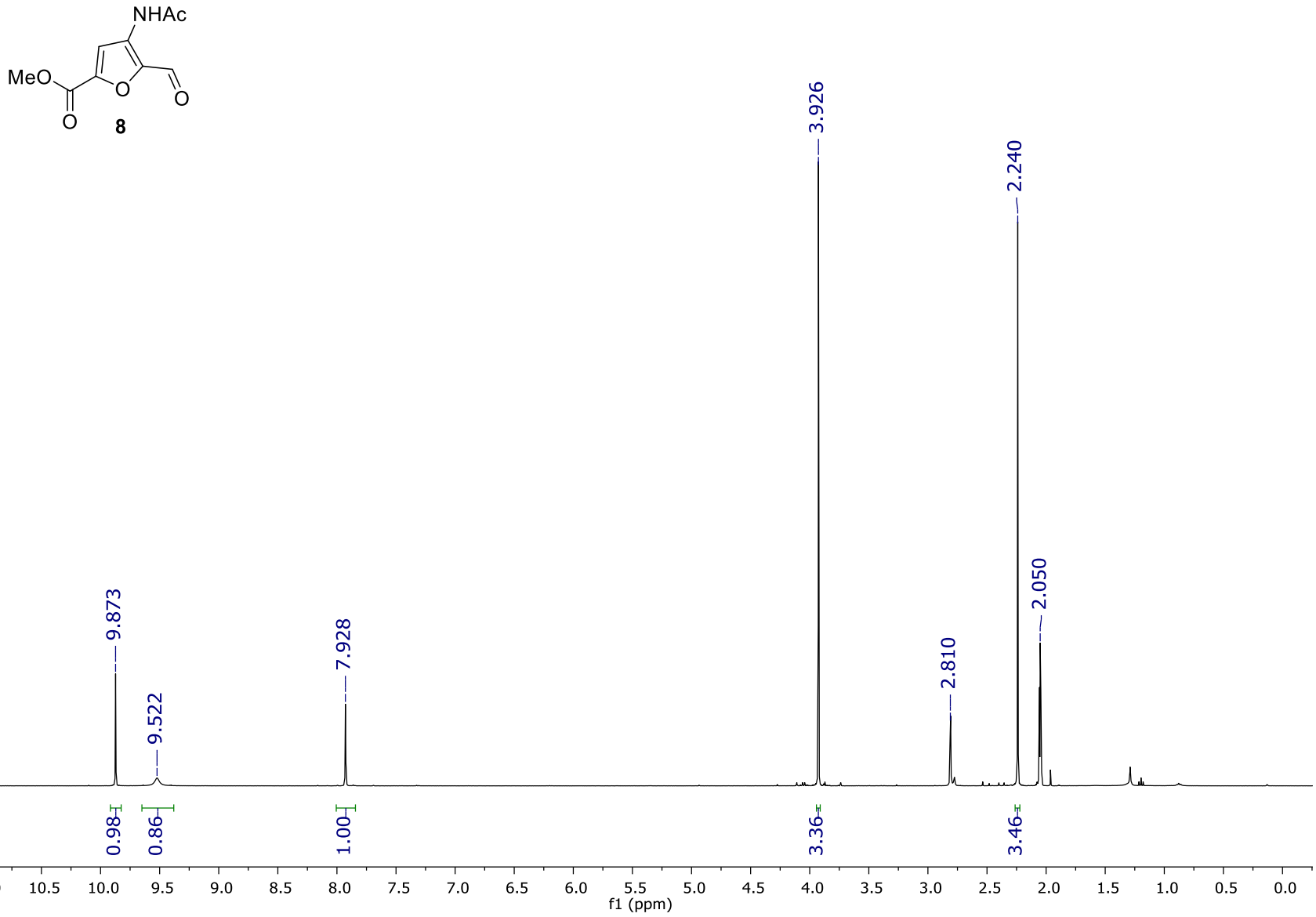

NH2
NH2
Me
O
O
O

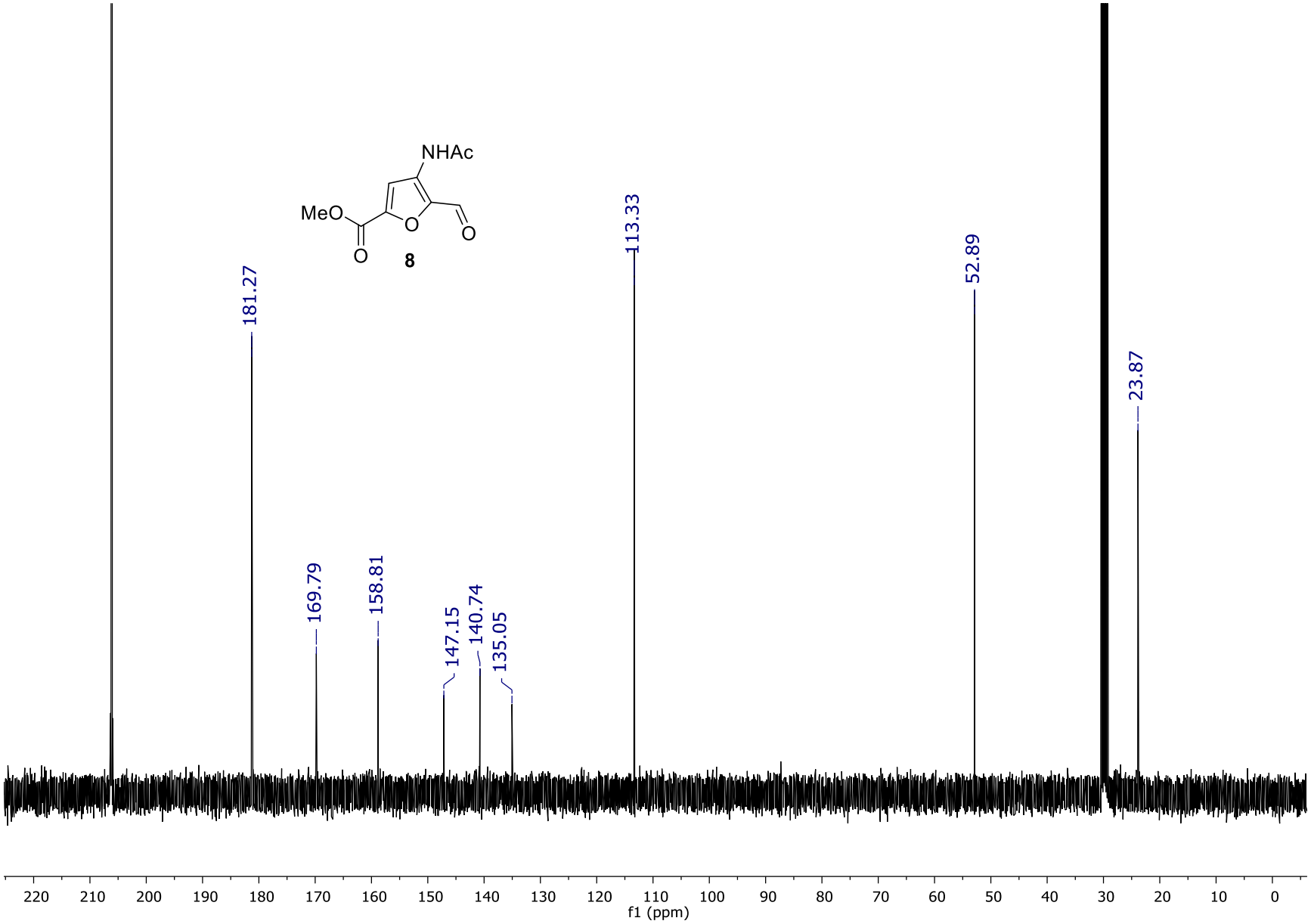
6

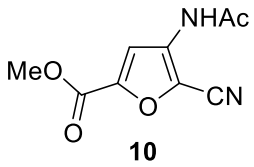
39.52
187.30
162.03
149.32
141.42
128.98
110.19
25.84
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
O
O
N
NH
O
7
12.832
8.140
7.836
3.313
2.566
1.12
1.04
1.00
3.07
13.5 13.0 12.5 12.0 11.5 11.0 10.5 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 0.0
f1 (ppm)

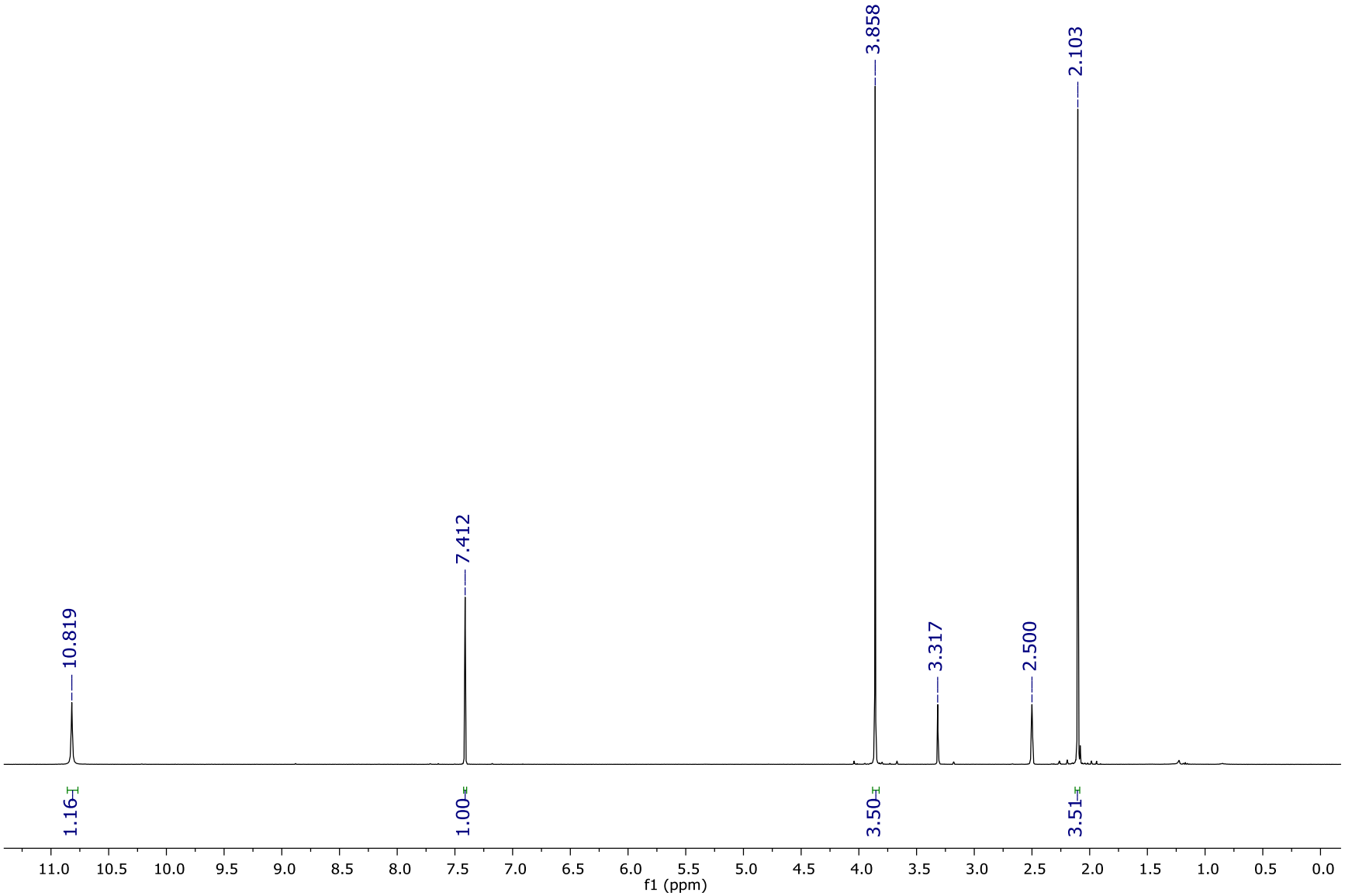

Me
O
O
N
NH
O
7
147.07
147.27
147.6
147.4
147.2
147.0
146.8
146.6
187.74
154.47
152.13
147.27
147.07
139.72
113.64
26.54
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

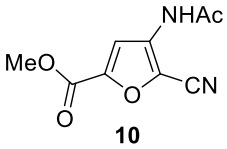

NHAc
MeO
O
O
O
8
3.926
2.240
9.873
9.522
7.928
2.810
2.050
0.98
0.86
1.00
3.36
3.46
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


NHAc
MeO
O
O
O
8
181.27
169.79
158.81
147.15
140.74
135.05
113.33
52.89
23.87
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

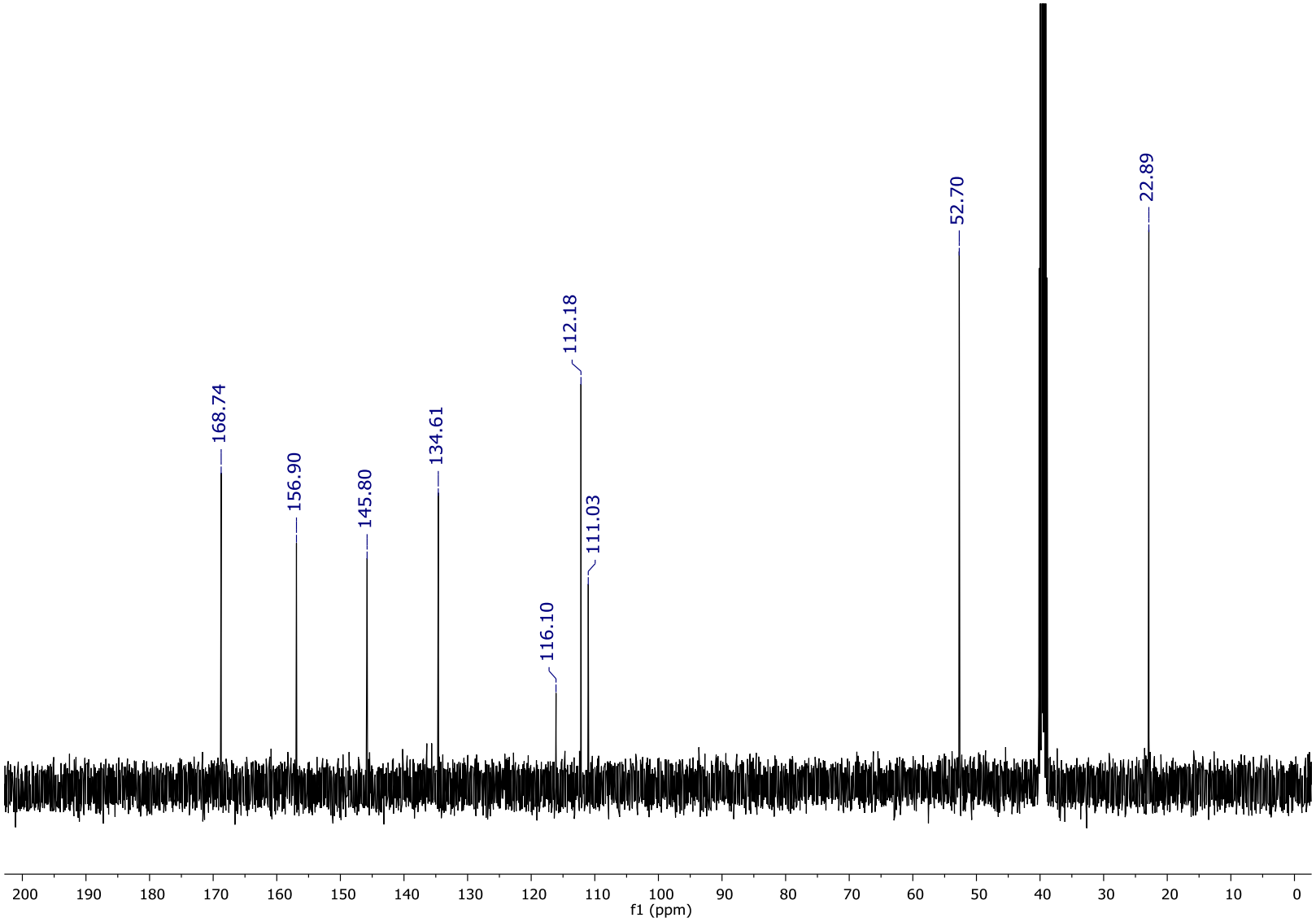

NHAc
MeO
O
O
CN

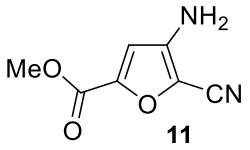
10


3.858
2.103
7.412
10.819
3.317
2.500
1.16
1.00
3.50
3.51
11.0 10.5 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 0.0
f1 (ppm)

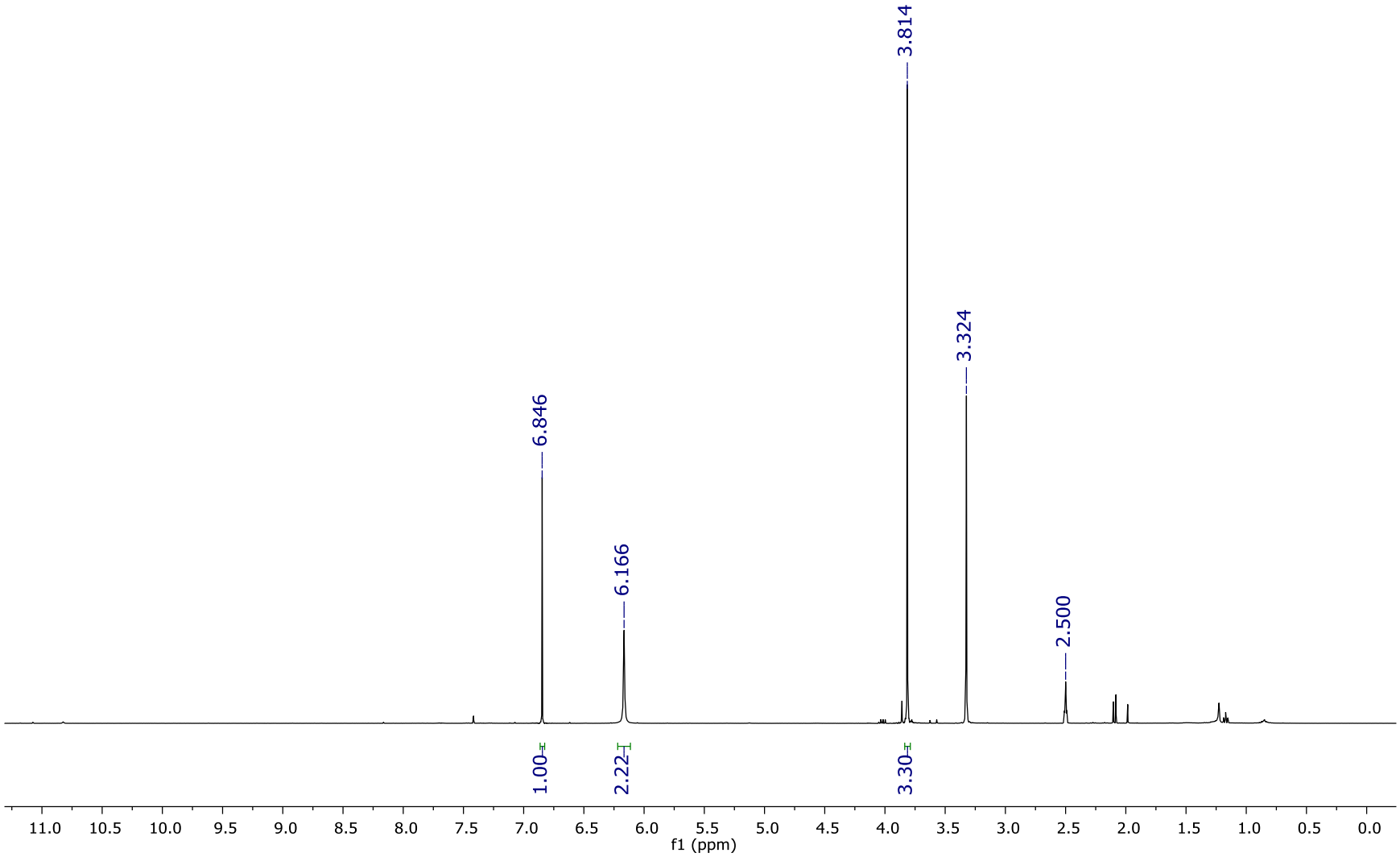

NHAc
MeO
O
O
CN

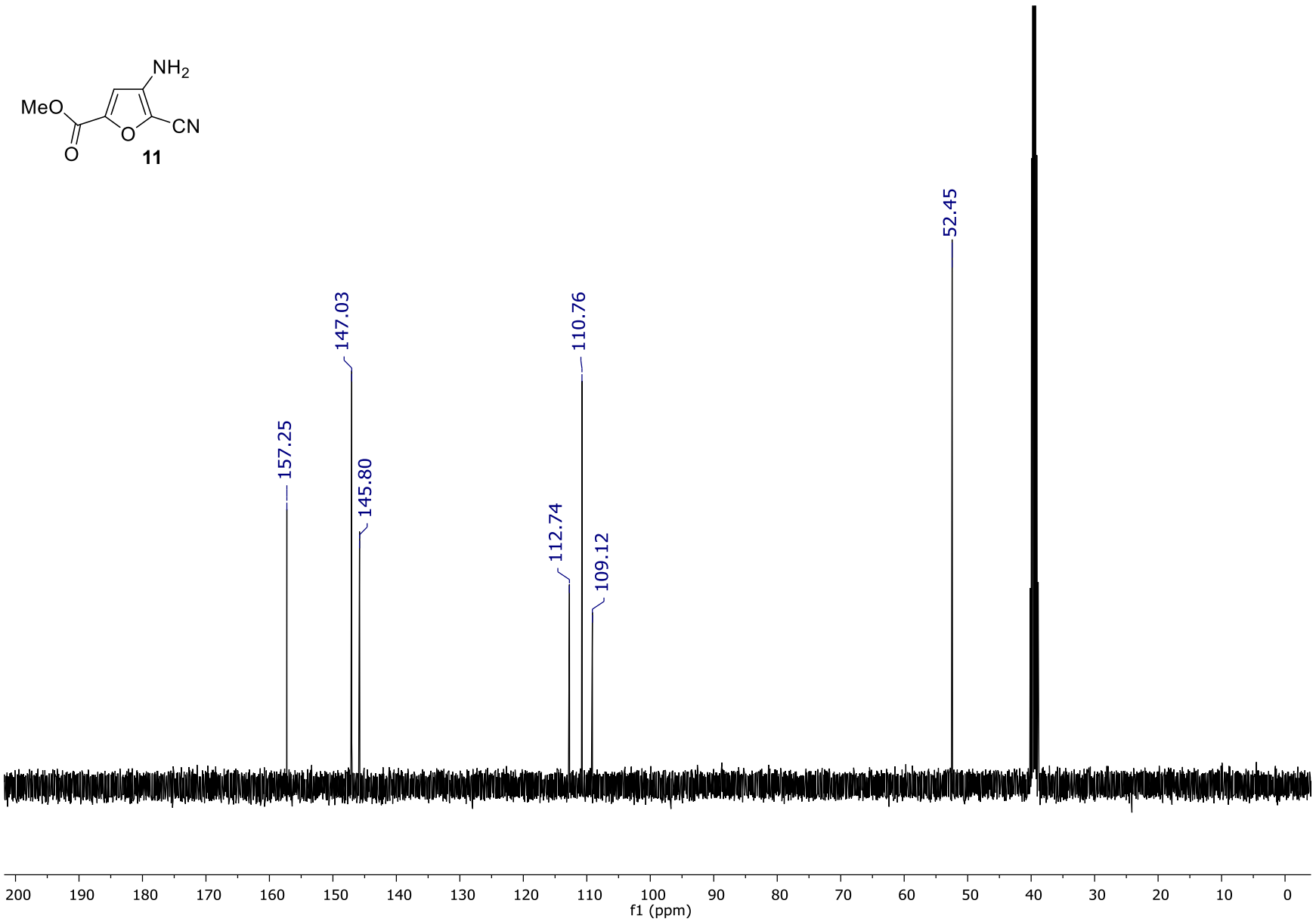
10

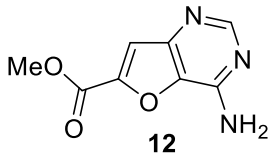

168.74
156.90
145.80
134.61
116.10
112.18
111.03
52.70
22.89
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


NH2
MeO
O
O
CN

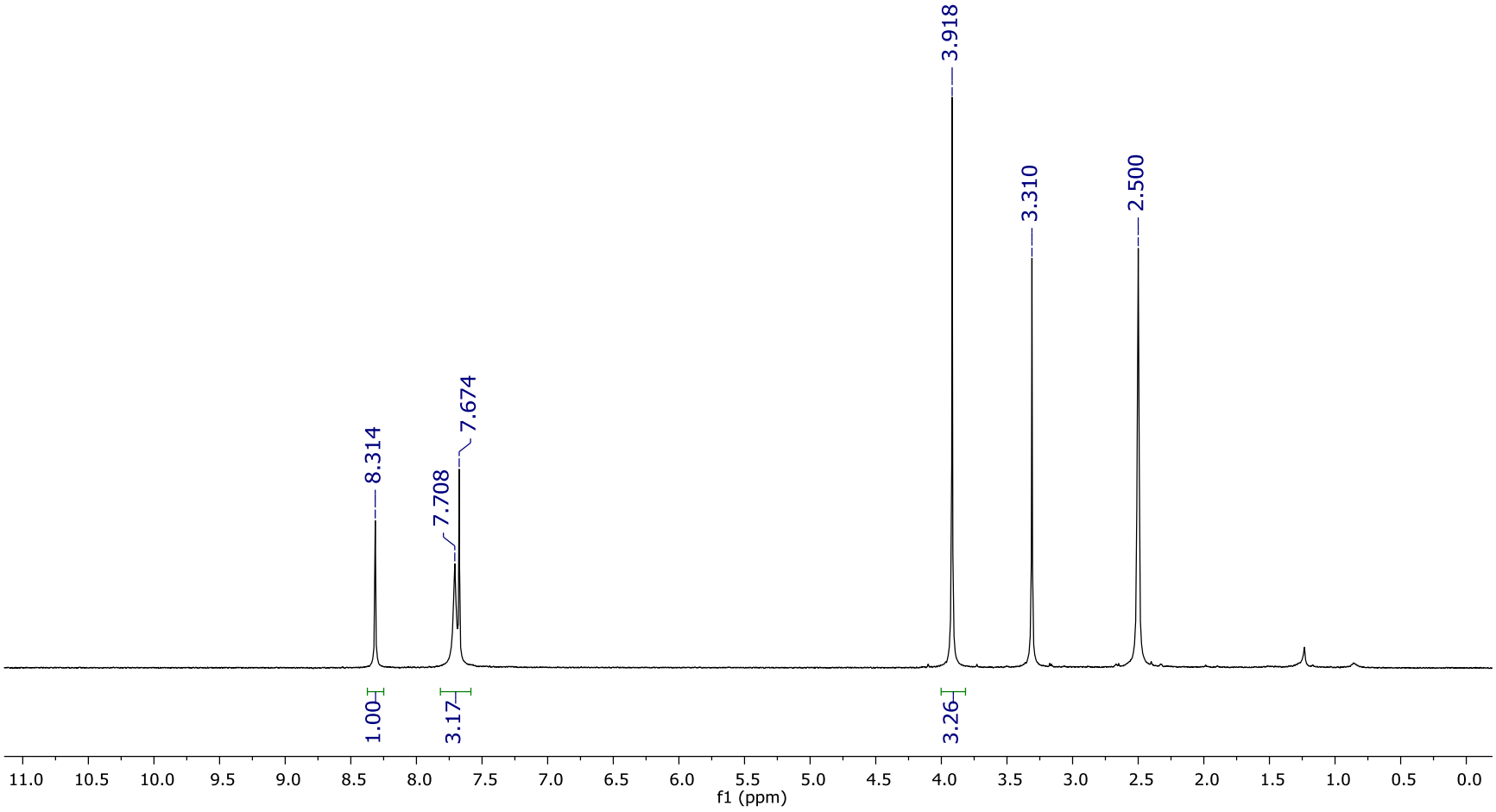
11

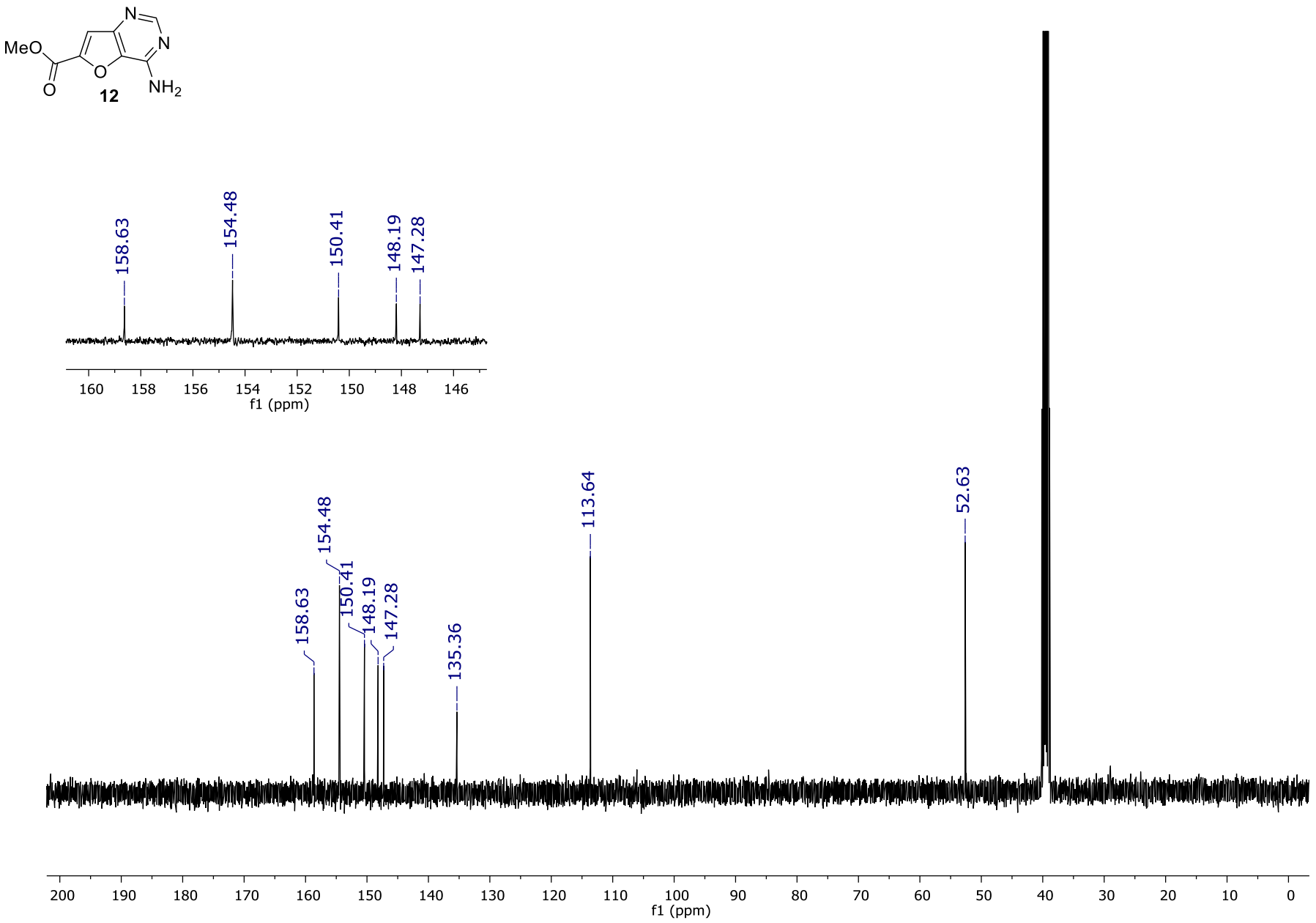

3.814
3.324
6.846
6.166
2.500
1.00
2.22
3.30
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

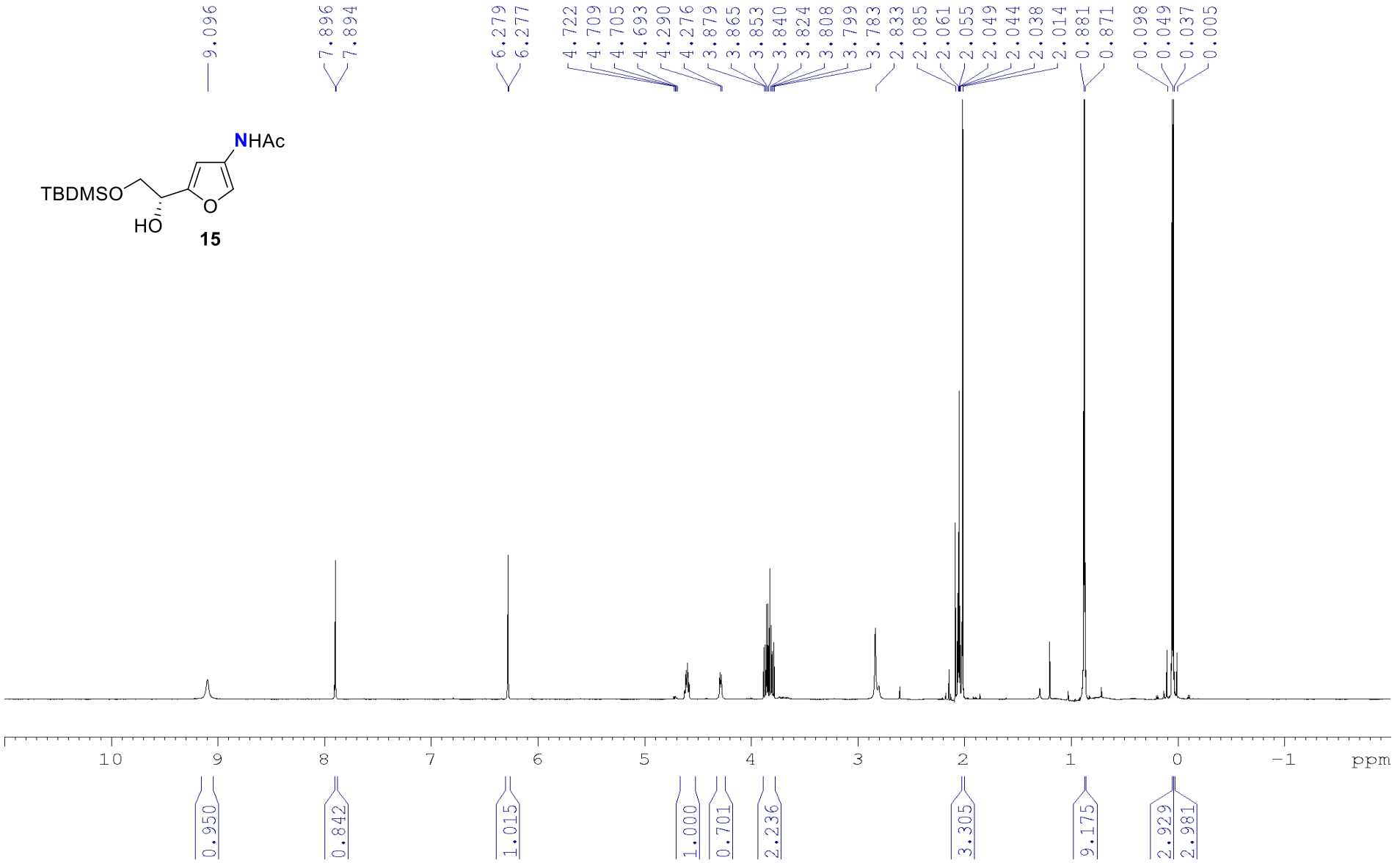

NH2
MeO
O
O
CN
11
157.25
147.03
145.80
112.74
110.76
109.12
52.45
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

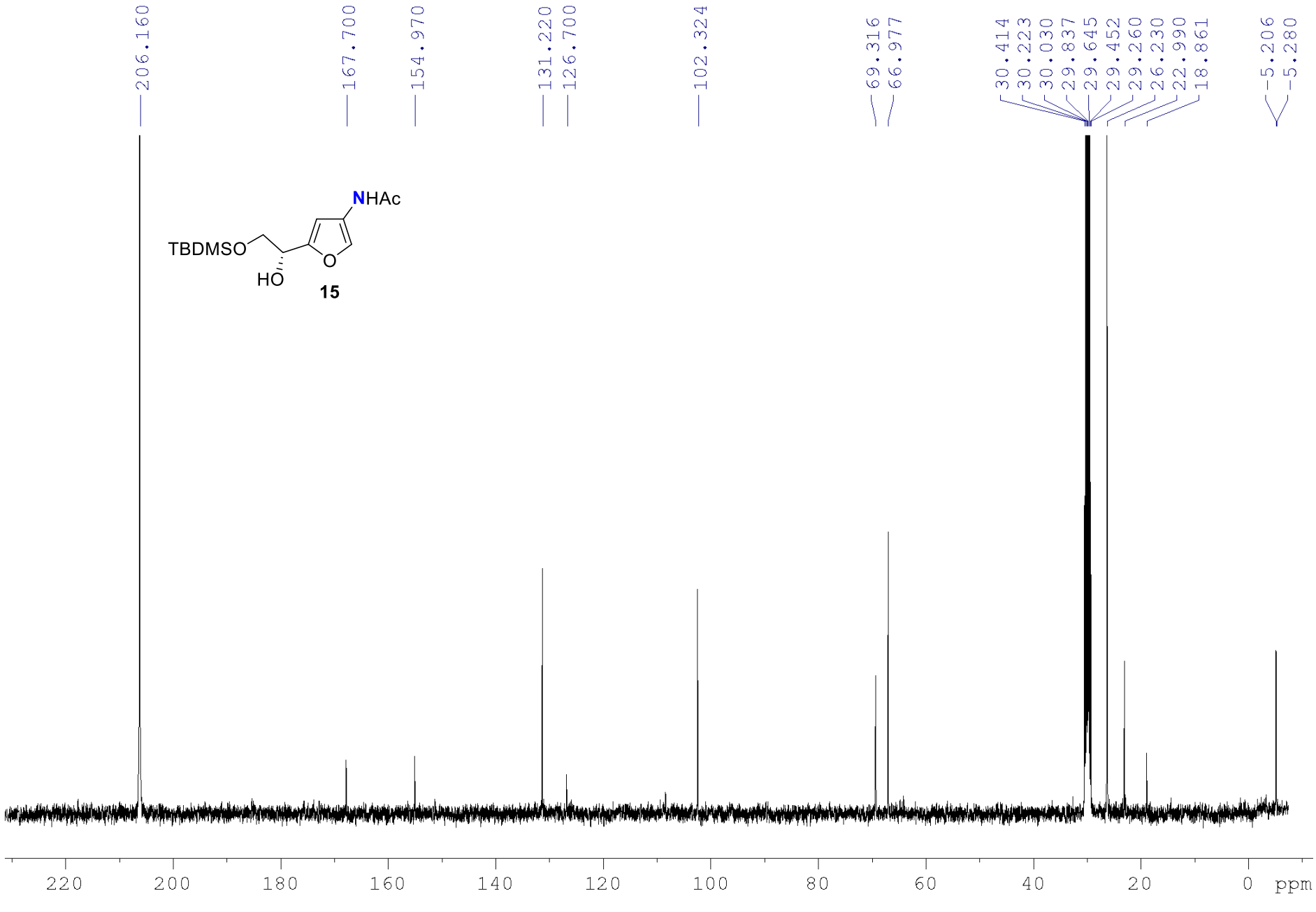

MeO
O
O
N
N
NH2

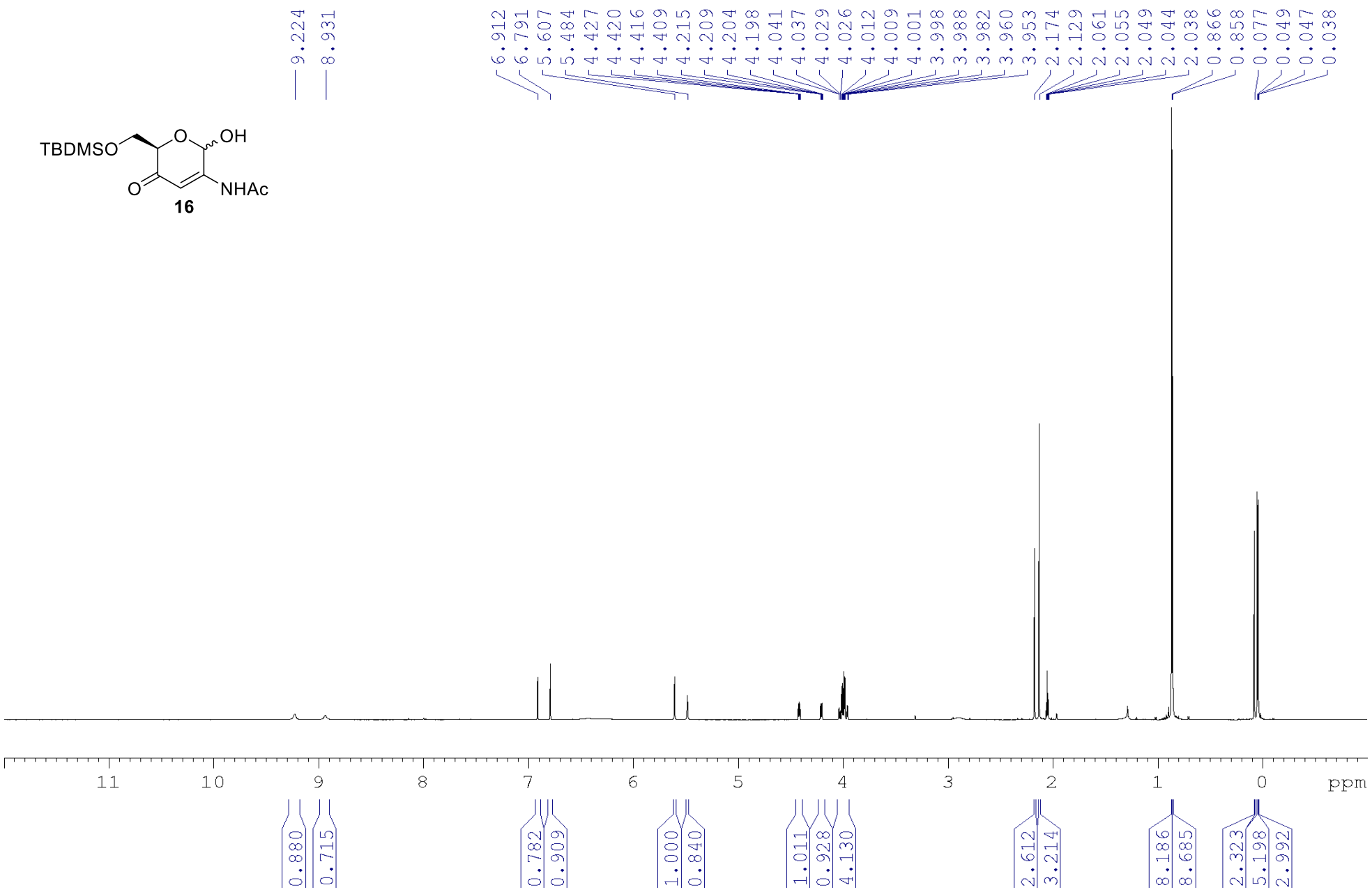
12

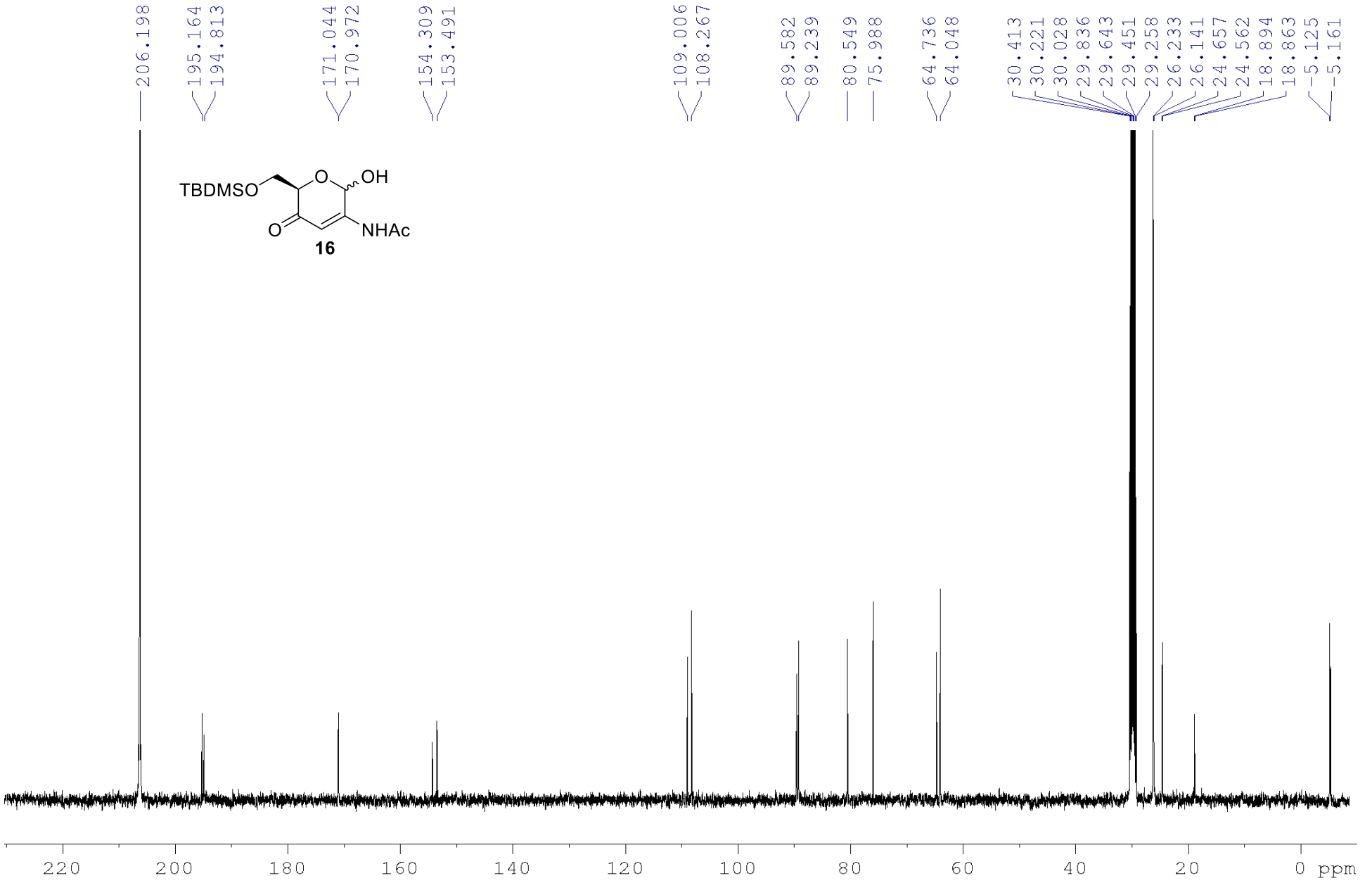

3.918
3.310
2.500
8.314
7.708
7.674
1.00
3.17
3.26
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

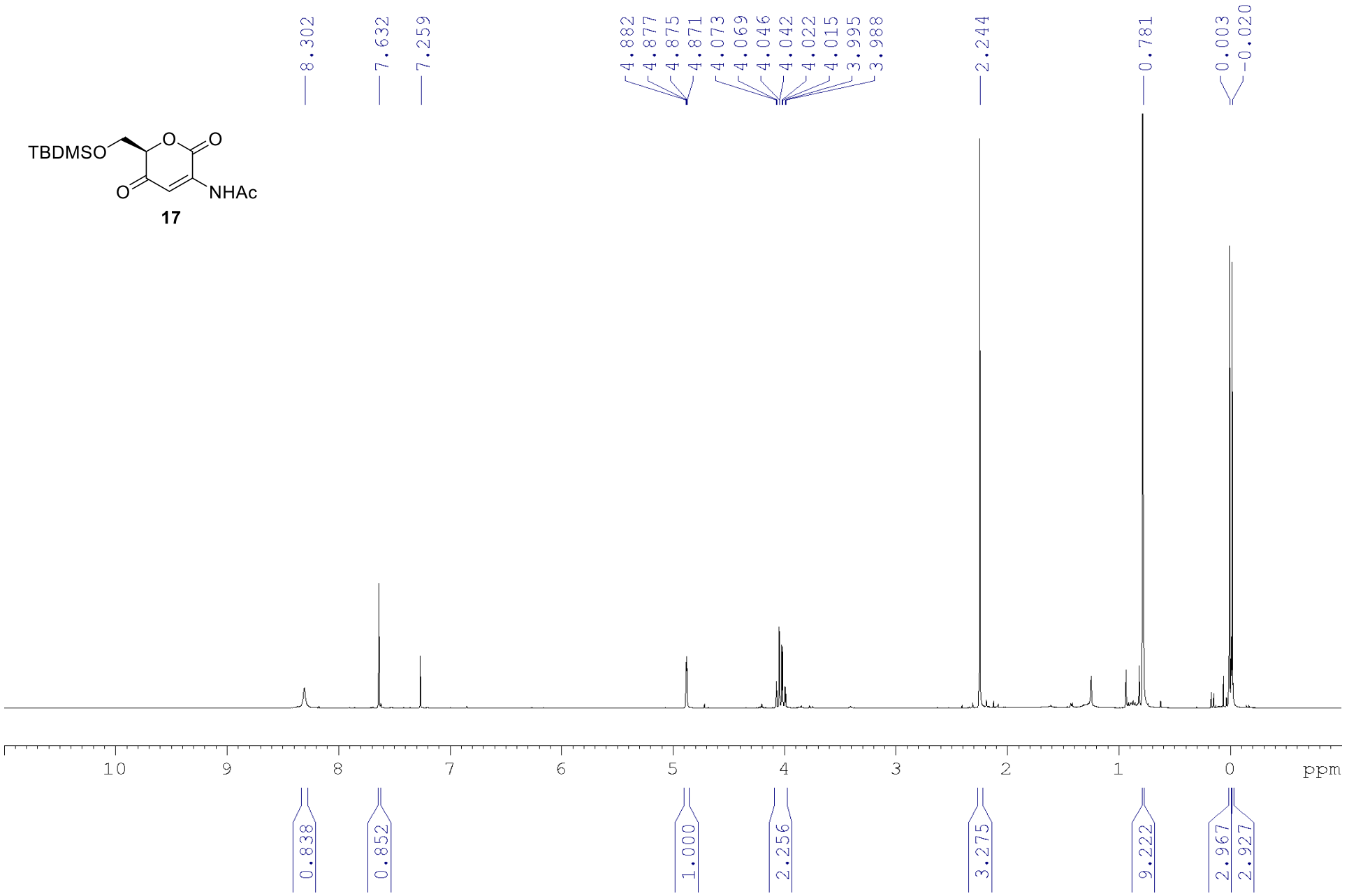

MeO
O
O
N
N
NH2
12
158.63
154.48
150.41
148.19
147.28
160
158
156
154
152
150
148
146
f1 (ppm)
158.63
154.48
150.41
148.19
147.28
135.36
113.64
52.63
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

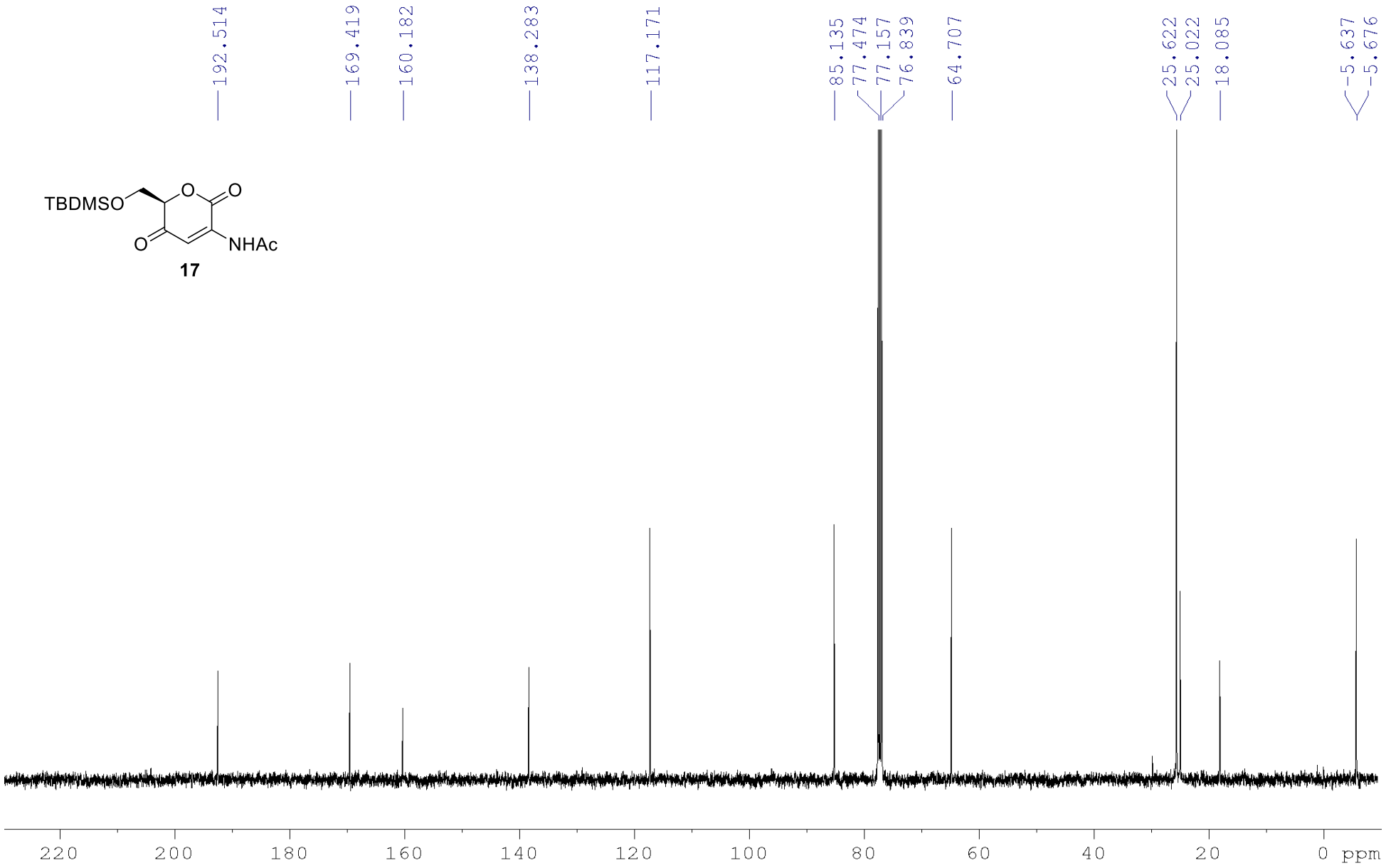

9.096
7.896
7.894
6.279
6.277
4.722
4.709
4.705
4.693
4.290
4.276
3.879
3.865
3.853
3.840
3.824
3.808
3.799
3.783
2.833
2.085
2.061
2.055
2.049
2.044
2.038
2.014
0.881
0.871
0.098
0.049
0.037
0.005
NHAc
TBDMSO
HO
O
15
10
9
8
7
6
5
4
3
2
1
0
−1
ppm
0.950
0.842
1.015
1.000
0.701
2.236
3.305
9.175
2.929
2.981

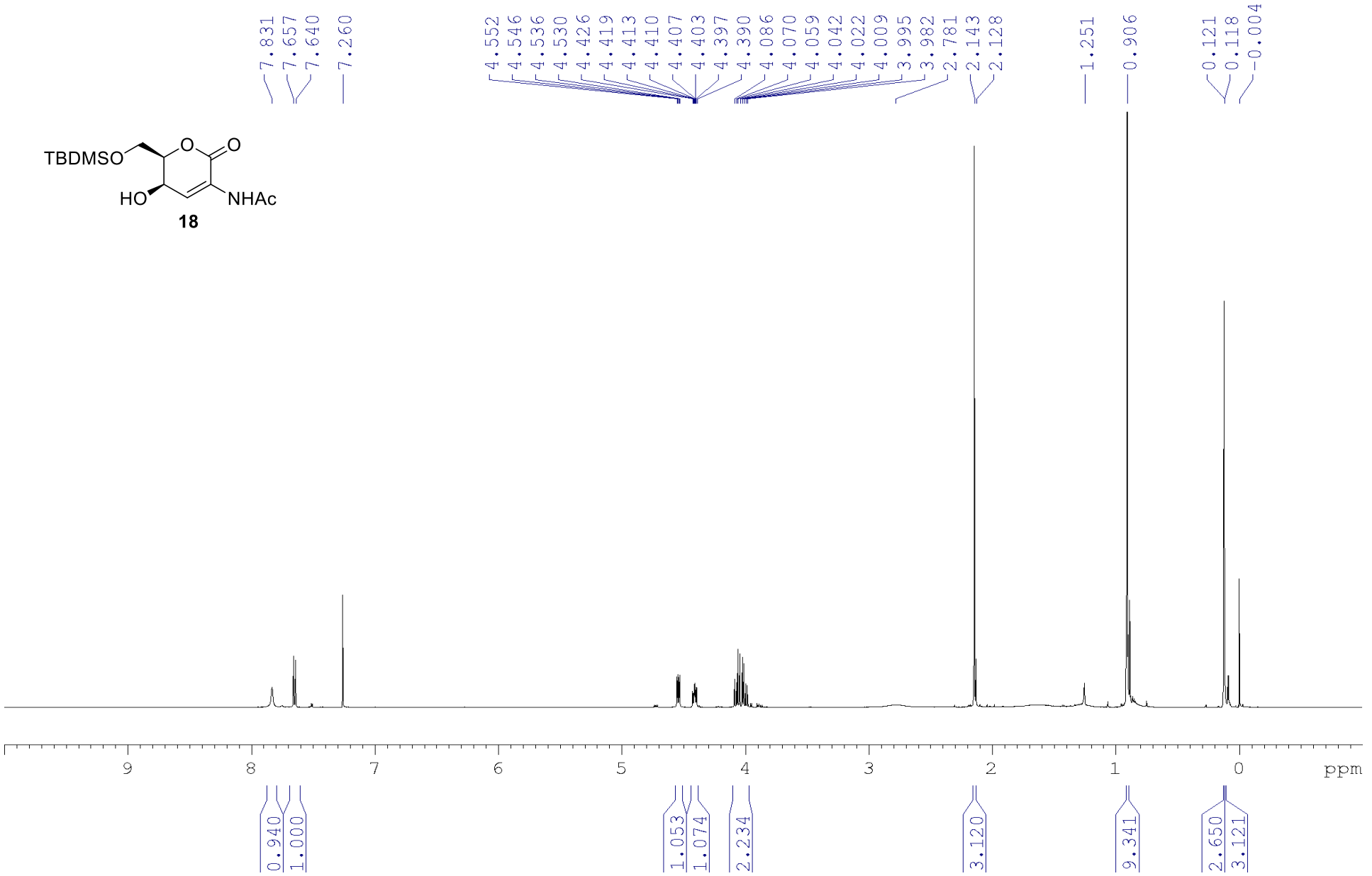

206.160
167.700
154.970
131.220
126.700
102.324
69.316
66.977
30.414
30.223
30.030
29.837
29.645
29.452
29.260
26.230
22.990
18.861
-5.206
-5.280
NHAc
TBDMSO
HO
O
15
220
200
180
160
140
120
100
80
60
40
20
0
ppm

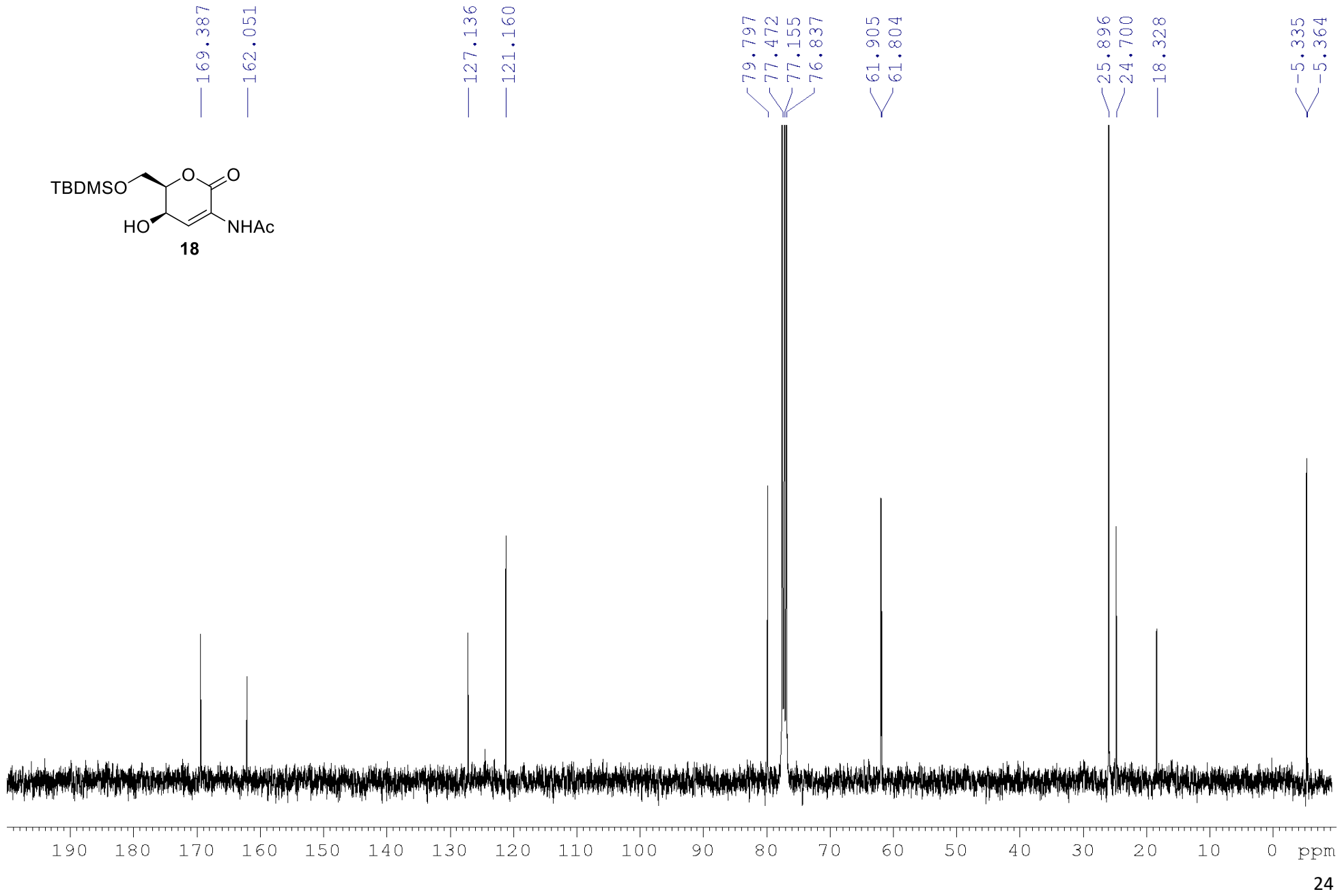

9.224
8.931
6.912
6.791
5.607
5.484
4.427
4.420
4.416
4.409
4.215
4.209
4.204
4.198
4.041
4.037
4.029
4.026
4.012
4.009
4.001
3.998
3.988
3.982
3.960
3.953
2.174
2.129
2.061
2.055
2.049
2.044
2.038
0.866
0.858
0.077
0.049
0.047
0.038
TBDMSO
O
OH
O
NHAc
16
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.880
0.715
0.782
0.909
1.000
0.840
1.011
0.928
4.130
2.612
3.214
8.186
8.685
2.323
5.198
2.992


206.198
195.164
194.813
171.044
170.972
154.309
153.491
109.006
108.267
89.582
89.239
80.549
75.988
64.736
64.048
30.413
30.221
30.028
29.836
29.643
29.451
29.258
26.233
26.141
24.657
24.562
18.894
18.863
-5.125
-5.161
TBDMSO
O
OH
O
NHAc
16
220
200
180
160
140
120
100
80
60
40
20
0 ppm


8.302
7.632
7.259
4.882
4.877
4.875
4.871
4.073
4.069
4.046
4.042
4.022
4.015
3.995
3.988
2.244
0.781
0.003
-0.020
TBDMSO
O
O
O
NHAc
17
10
9
8
7
6
5
4
3
2
1
0
ppm
0.838
0.852
1.000
2.256
3.275
9.222
2.967
2.927


192.514
169.419
160.182
138.283
117.171
85.135
77.474
77.157
76.839
64.707
25.622
25.022
18.085
-5.637
-5.676
TBDMSO
O
O
O
NHAc
17
220
200
180
160
140
120
100
80
60
40
20
0 ppm


7.831
7.657
7.640
7.260
4.552
4.546
4.536
4.530
4.426
4.419
4.413
4.410
4.407
4.403
4.397
4.390
4.086
4.070
4.059
4.042
4.022
4.009
3.995
3.982
2.781
2.143
2.128
1.251
0.906
0.121
0.118
-0.004
TBDMSO
O
O
HO
NHAc
18
9
8
7
6
5
4
3
2
1
0
ppm
0.940
1.000
1.053
1.074
2.234
3.120
9.341
2.650
3.121


169.387
162.051
127.136
121.160
79.797
77.472
77.155
76.837
61.905
61.804
25.896
24.700
18.328
-5.335
-5.364
TBDMSO
O
O
HO
NHAc
18
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Crystal data and structure refinement for 18

Empirical formula	$C_{14}H_{25}NO_5Si$
Formula weight	315.44
Temperature/K	120.01(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	19.8492(11)
b/Å	11.2915(5)
c/Å	7.7679(4)
α/°	90
β/°	98.811(5)
γ/°	90
Volume/Å^3	1720.45(15)
Z	4
ρ_{calc}mg/mm^3	1.218
μ/mm^{-1}	1.381
F(000)	680.0
Crystal size/mm^3	0.25 × 0.05 × 0.02
2Θ range for data collection	9.036 to 145.066°
Index ranges	$-24 \leq h \leq 23$, $-13 \leq k \leq 10$, $-9 \leq l \leq 9$
Reflections collected	12438
Independent reflections	3249[R(int) = 0.0643]
Data/restraints/parameters	3249/0/197
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0615, wR_2 = 0.1641
Final R indexes [all data]	R_1 = 0.0704, wR_2 = 0.1722
Largest diff. peak/hole / e Å^{-3}	0.70/-0.42