Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Synthesis and Structure Revision of Symplocin A

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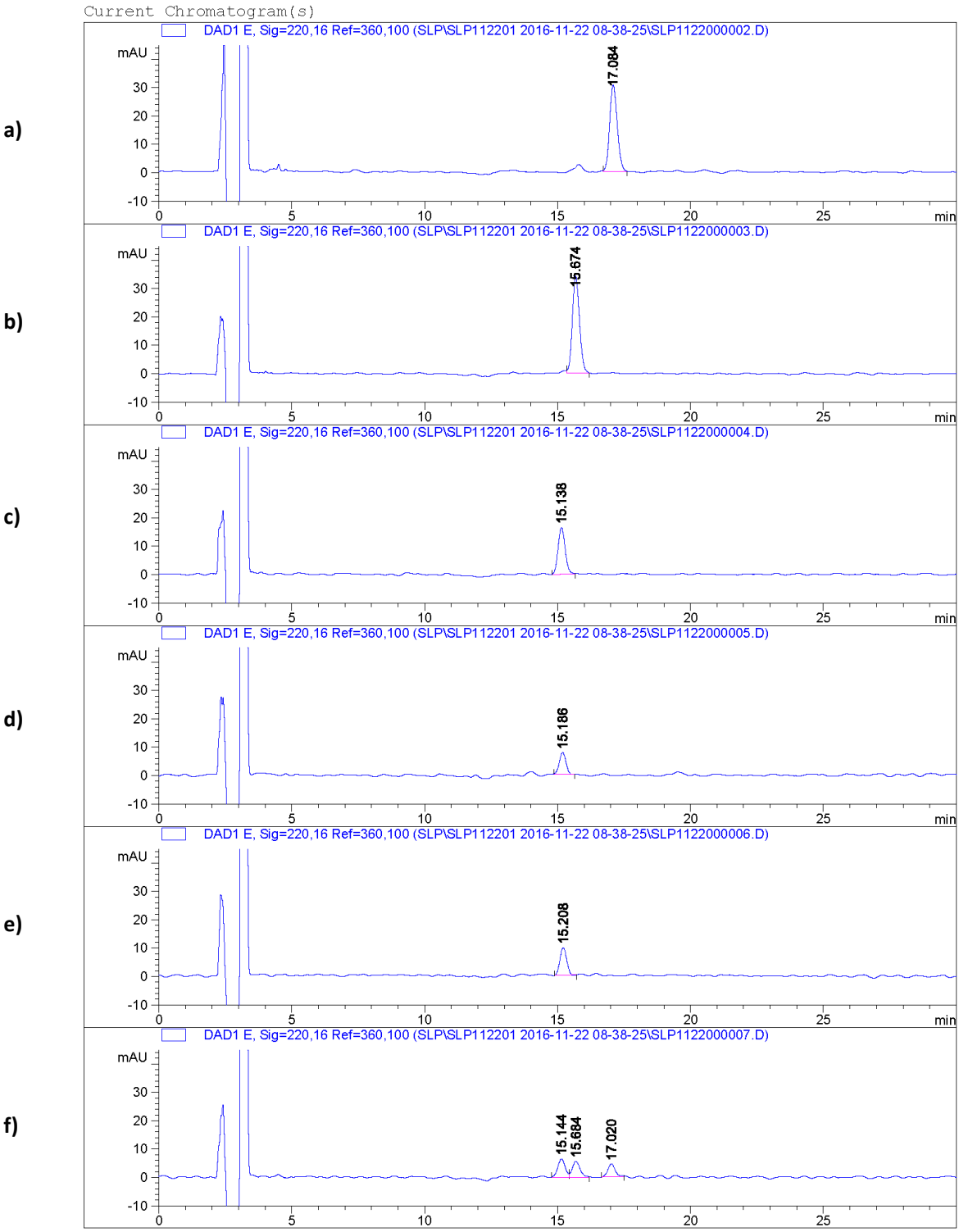
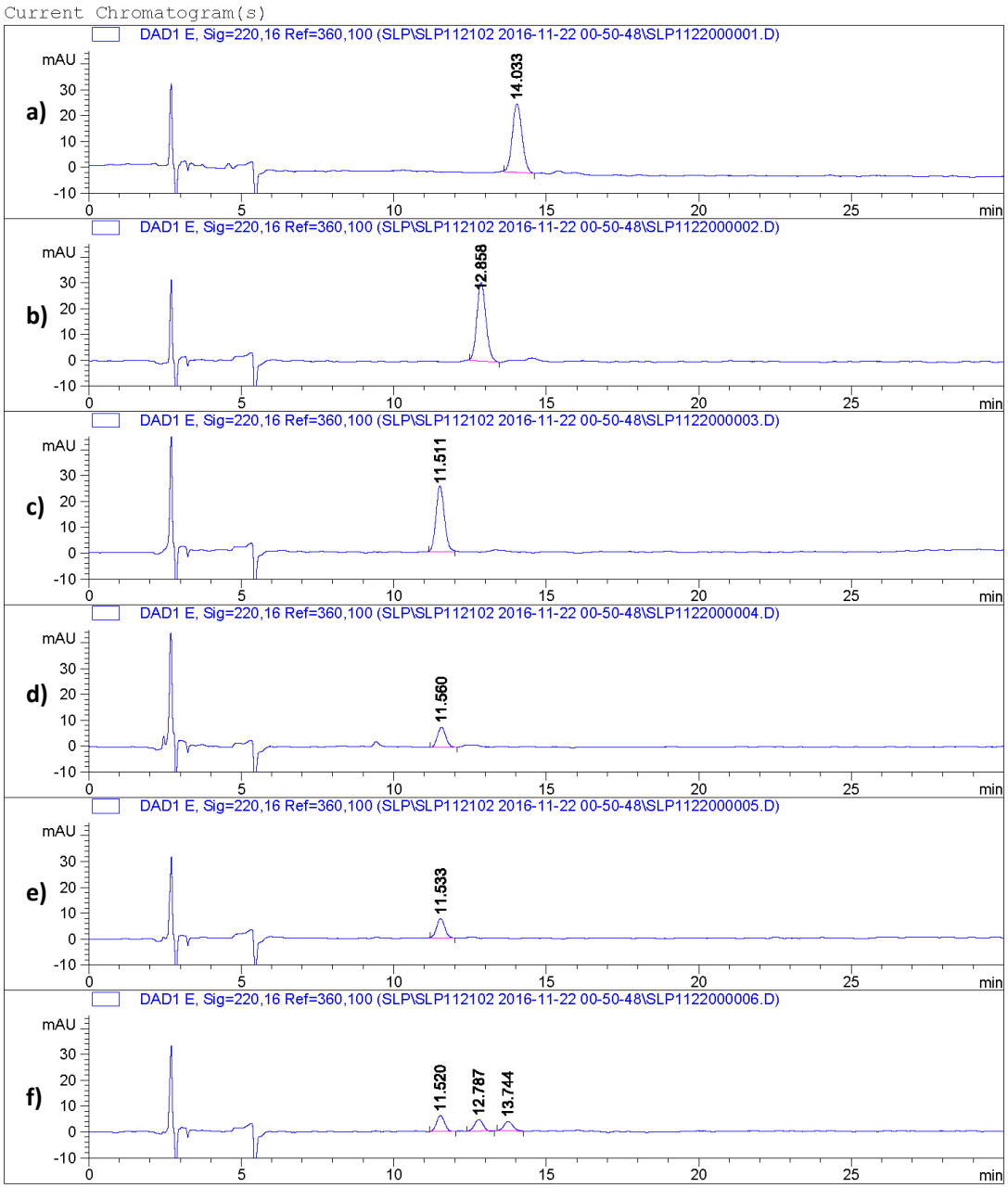
I Comparison HPLC Data of Natural Symplocin A and Synthetic Diastereoisomers

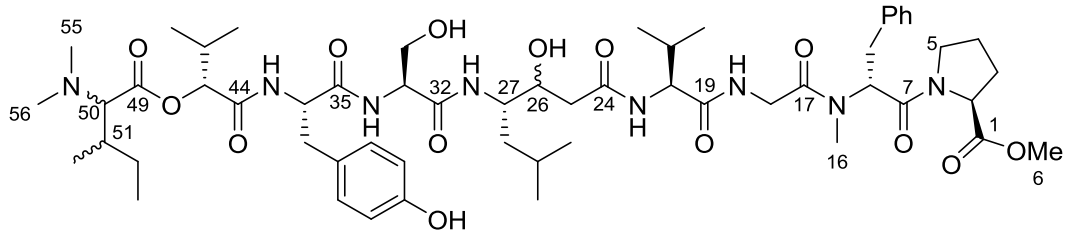


HPLC condition: YMC-Pack ODS-A (4.6 × 250 mm, 5 μm); detected at 220 nm; (CH_3CN + 0.1% TFA(aq.))/ (H_2O + 0.1% TFA(aq.)) = 37/63; flow = 1.0 mL/min. a) synthetic **3b**; b) synthetic **3a**; c) synthetic **3c**; d) natural symplocin A; e) mixture of natural symplocin A and synthetic **3c**; f) mixture of natural symplocin A and synthetic **3a** , **3b**, and **3c**.



HPLC condition: YMC-Pack ODS-A (4.6 × 250 mm, 5 μm); detected at 220 nm; (CH_3OH + 0.1% TFA(aq.))/ (H_2O + 0.1% TFA(aq.)) = 62/38; flow = 1.0 mL/min. a) synthetic **3b**; b) synthetic **3a**; c) synthetic **3c**; d) natural symplocin A; e) mixture of natural symplocin A and synthetic **3c**; f) mixture of natural symplocin A and synthetic **3a** , **3b**, and **3c**.

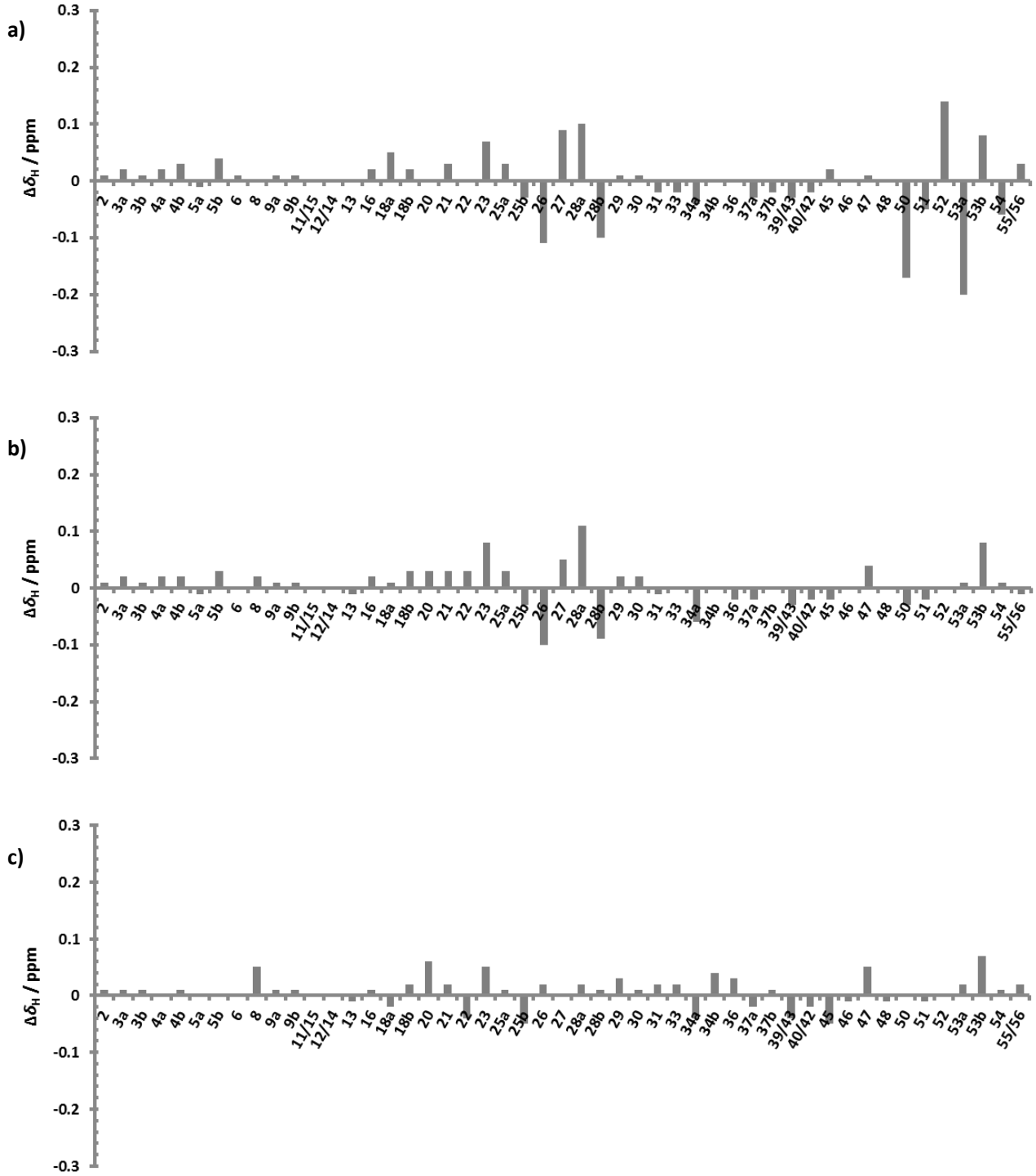
II Comparative NMR Data of Natural Symplocin A and Synthetic diastereoisomers



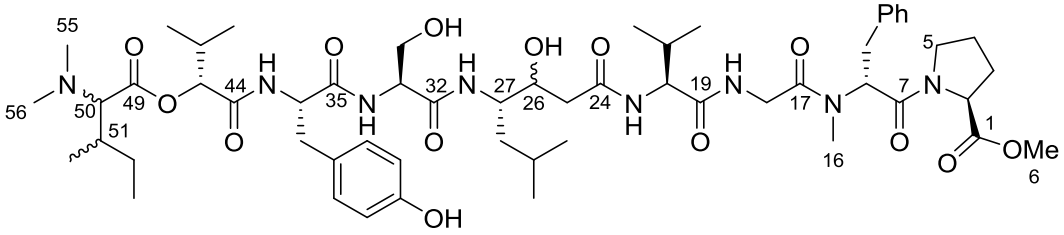
3a: 26*R*, 50*R*, 51*R*
3b: 26*R*, 50*S*, 51*S*
3c: 26*S*, 50*S*, 51*S*

Amino acid	No. [a]	δ_H, mult (*J* in Hz) Natural symplocin	δ_H, mult (*J* in Hz) Synthetic **3a**	$\Delta\delta_H$/ppm Syn.**3a**-Nat.	δ_H, mult (*J* in Hz) Synthetic **3b**	$\Delta\delta_H$/ppm Syn.**3b**-Nat.	δ_H, mult (*J* in Hz) Synthetic **3c**	$\Delta\delta_H$/ppm Syn.**3c**-Nat.
O-Me-Pro	2	4.26, dd (2.3, 5.9)	4.27, dd (8.2, [illegible])	0. 01	4.27, dd (8.4, 5.9)	0. 01	4.27, dd (8.5, [illegible])	0. 01
	3a	1.77, m	1.79, m	0. 02	1.79, m	0. 02	1.78, m	0. 01
	3b	2.12, m	2.13, m	0. 01	2.13, m	0. 01	2.13, m	0. 01
	4a	1.78, m	1.80, m	0. 02	1.80, m	0. 02	1.78, m	0
	4b	1.85, m	1.88, m	0. 03	1.87, m	0. 02	1.86, m	0. 01
	5a	3.31, m	3.30, m	−0. 01	3.30, m	−0. 01	3.31, m	0
	5b	3.31, m	3.35, m	0. 04	3.34, m	0. 03	3.31, m	0
	6	3.65, s	3.66, s	0. 01	3.65, s	0	3.65, s	0
N-MePhe	8	5.42, t (7.1)	5.42, t (7.2)	0	5.44, t (7.6)	0. 02	5.47, t (7.4)	0. 05
	9a	2.75, m	2.76, m	0. 01	2.76, m	0. 01	2.76, m	0. 01
	9b	3.18, m	3.19, m	0. 01	3.19, m	0. 01	3.19, m	0. 01
	11/15	7.23, m	7.23, m	0	7.23, m	0	7.23, m	0
	12/14	7.23, m	7.23, m	0	7.23, m	0	7.23, m	0
	13	7.18, m	7.18, m	0	7.17, m	−0. 01	7.17, m	−0. 01
	16	2.92, s	2.94, s	0. 02	2.94, s	0. 02	2.93, s	0. 01
Gly	18a	3.94, m	3.99, m	0. 05	3.95, m	0. 01	3.92, m	−0. 02
	18b	4.02, m	4.04, m	0. 02	4.05, m	0. 03	4.04, m	0. 02
Val	20	4.12	4.12, m	0	4.15, m	0. 03	4.18, m	0. 06
	21	2.08, m	2.11, m	0. 03	2.11, m	0. 03	2.10, m	0. 02
	22	0.91	0.91, m	0	0.94, m	0. 03	0.87, m	−0. 04
	23	0.86	0.93, m	0. 07	0.94, m	0. 08	0.91, m	0. 05
Sta	25a	2.36, m	2.39, m	0. 03	2.39, m	0. 03	2.37, m	0. 01
	25b	2.42, m	2.39, m	−0. 03	2.39, m	−0. 03	2.37, m	−0. 05
	26	3.92, m	3.81, m	−0. 11	3.82, m	−0. 1	3.94, m	0. 02
	27	3.83, m	3.92, m	0. 09	3.88, m	0. 05	3.83, m	0
	28a	1.29, m	1.39, m	0. 1	1.40, m	0. 11	1.31, m	0. 02
	28b	1.49, m	1.39, m	−0. 1	1.40, m	−0. 09	1.50, m	0. 01
	29	1.57, m	1.58, m	0. 01	1.59, m	0. 02	1.60, m	0. 03
	30	0.88	0.89, m	0. 01	0.90, m	0. 02	0.89, m	0. 01
	31	0.85	0.83, m	−0. 02	0.84, d (6.8)	−0. 01	0.87, m	0. 02
Ser	33	4.31, m	4.29, m	−0. 02	4.31, m	0	4.33, m	0. 02
	34a	3.77, m	3.73, m	−0. 04	3.71, m	−0. 06	3.73, m	−0. 04
	34b	3.77, m	3.77, m	0	3.77, m	0	3.81, m	0. 04
Tyr	36	4.58, m	4.58, m	0	4.56, m	−0. 02	4.61, m	0. 03
	37a	2.81, m	2.78, m	−0. 03	2.79, m	−0. 02	2.79, m	−0. 02
	37b	3.14, m	3.12, m	−0. 02	3.14, m	0	3.15, m	0. 01
	39/43	7.09, d (8.3)	7.06, d (8.4)	−0. 03	7.06, d (8.4)	−0. 03	7.05, d (8.2)	−0. 04
	40/42	6.72, d (8.4)	6.70, d (8.4)	−0. 02	6.70, d (8.4)	−0. 02	6.70, d (8.1)	−0. 02
Valic acid	45	4.87, d (4.1)	4.89, d (4.2)	0. 02	4.85, d (4.4)	−0. 02	4.82, d (4.5)	−0. 05
	46	2.01, m	2.01, m	0	2.01, m	0	2.00, m	−0. 01
	47	0.67, d (6.8)	0.68, d (6.7)	0. 01	0.71, d (6.7)	0. 04	0.72, d (6.7)	0. 05
	48	0.84	0.84, m	0	0.84, d (6.8)	0	0.83, d (6.8)	−0. 01
N,*N*-Me$_2$-[illegible]	50	3.94, d (4.5)	3.77, d (6.4)	−0. 17	3.91, d (4.3)	−0. 03	3.94, d (4.6)	0
	51	2.15, m	2.10, m	−0. 05	2.13, m	−0. 02	2.14, m	−0. 01
	52	0.95	1.09, d (6.8)	0. 14	0.95, m	0	0.95, m	0
	53a	1.32, m	1.12, m	−0. 2	1.33, m	0. 01	1.34, m	0. 02
	53b	1.42, m	1.50, m	0. 08	1.50, m	0. 08	1.49, m	0. 07
	54	0.96	0.90, m	−0. 06	0.97, m	0. 01	0.97, m	0. 01
	55/56	2.83, s	2.86, s	0. 03	2.82, s	−0. 01	2.85, s	0. 02

[a]NH protons are not included.

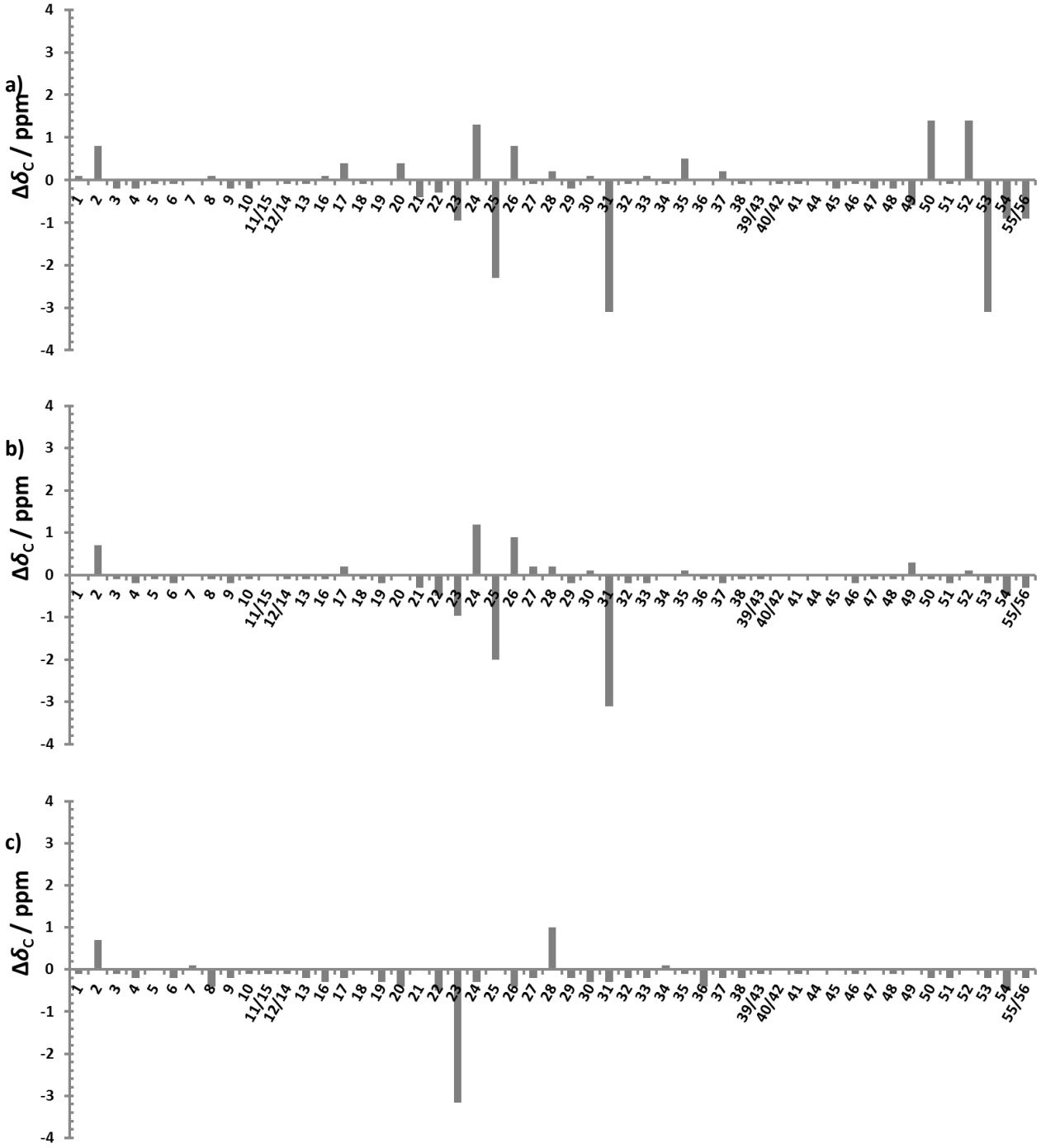


^{1}H NMR chemical shift differences (NH protons are not included) between natural symplocin A and synthetic diastereoisomers. The *x* axis represents the proton number, and the *y* axis shows the chemical shift differences in ppm. a) $\Delta\delta_H$ = Syn.**3a** - Nat., b) $\Delta\delta_H$ = Syn.**3b** - Nat., and c) $\Delta\delta_H$ = Syn.**3c** - Nat..



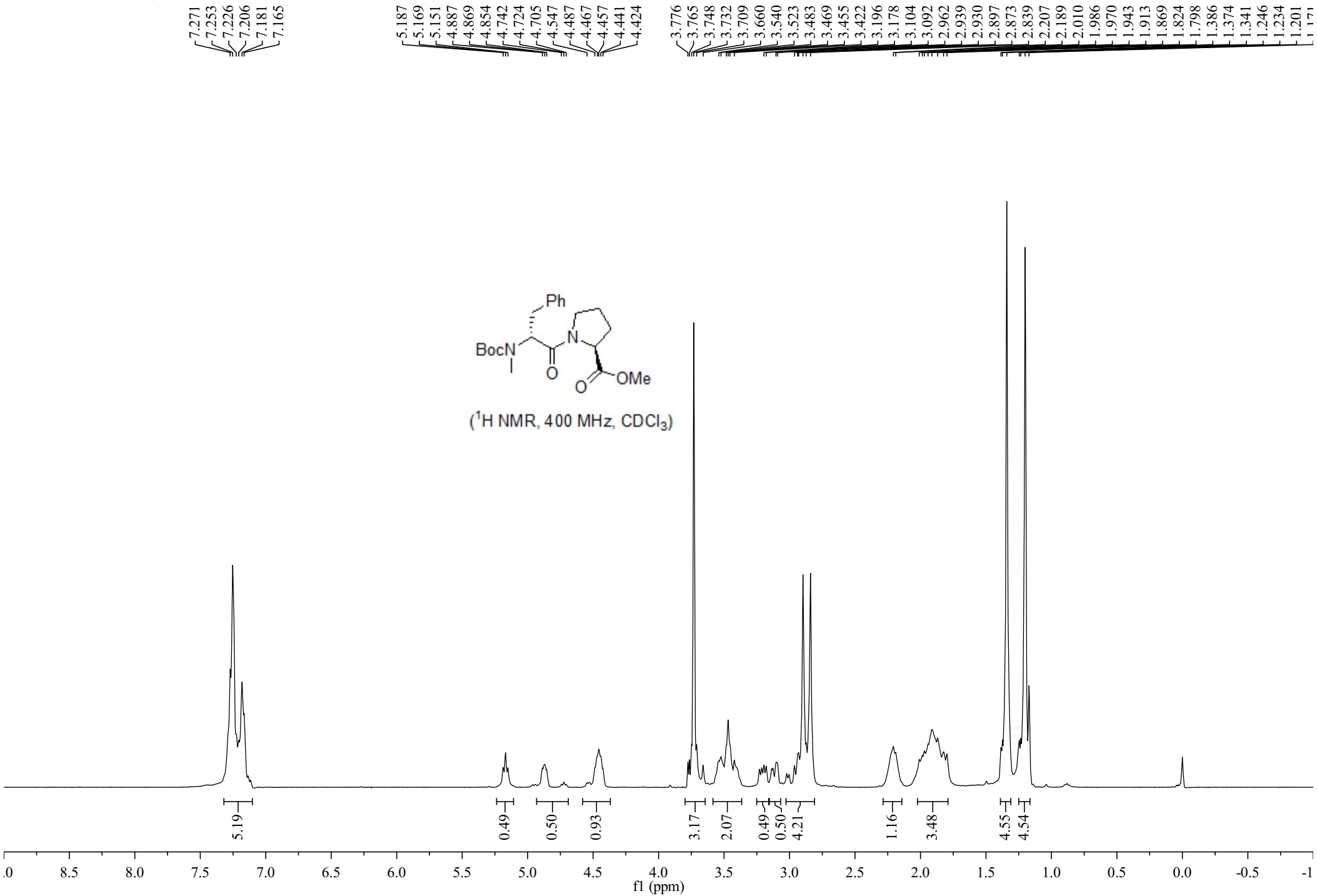
3a: 26*R*, 50*R*, 51*R*
3b: 26*R*, 50*S*, 51*S*
3c: 26*S*, 50*S*, 51*S*

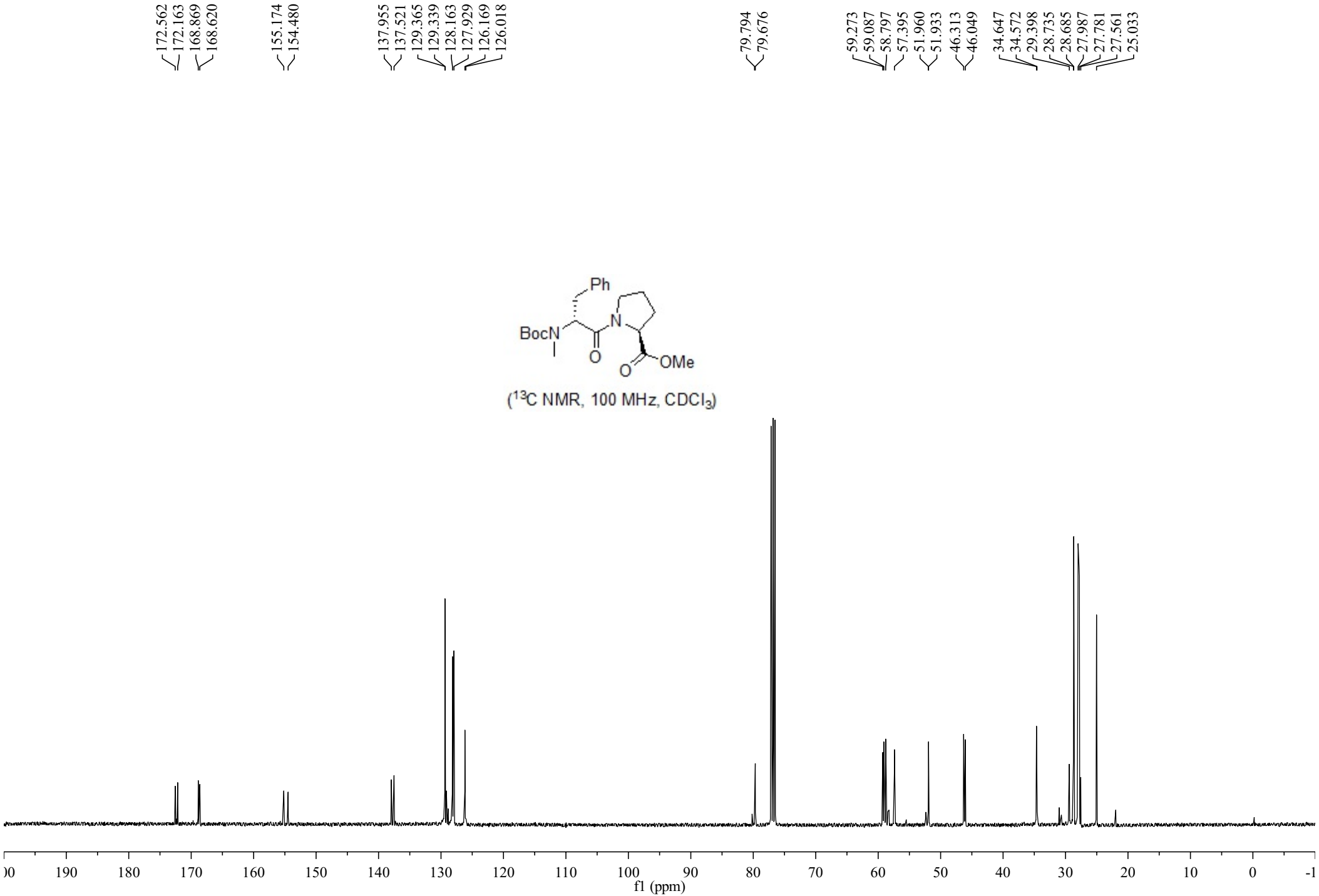
Amino acid	No.	δ_C/ppm Natural symplocin A	δ_C/ppm Synthetic **3a**	$\Delta\,\delta_C$/ppm Syn. **3a**–Nat.	δ_C/ppm Synthetic **3b**	$\Delta\,\delta_C$/ppm Syn. **3b**–Nat.	δ_C/ppm Synthetic **3c**	$\Delta\,\delta_C$/ppm Syn. **3c**–Nat.
O-Me-Pro	1	173.4	173.5	0.1	173.4	0	173.3	-0.1
	2	059.1	59.9	0.8	59.8	0.7	59.8	0.7
	3	029.5	29.3	-0.2	29.4	-0.1	29.4	-0.1
	4	025.7	25.5	-0.2	25.5	-0.2	25.5	-0.2
	5	047.4	47.3	-0.1	47.3	-0.1	47.4	0
	6	052.5	52.4	-0.1	52.3	-0.2	52.3	-0.2
N-MePhe	7	168.7	168.7	0	168.7	0	168.8	0.1
	8	057.5	57.6	0.1	57.4	-0.1	57.1	-0.4
	9	035.3	35.1	-0.2	35.1	-0.2	35.1	-0.2
	10	138.7	138.5	-0.2	138.6	-0.1	138.6	-0.1
	11/15	130.2	130.2	0	130.2	0	130.1	-0.1
	12/14	129.0	128.9	-0.1	128.9	-0.1	128.9	-0.1
	13	127.2	127.1	-0.1	127.1	-0.1	127.0	-0.2
	16	030.6	30.7	0.1	30.5	-0.1	30.3	-0.3
Gly	17	169.5	169.9	0.4	169.7	0.2	169.3	-0.2
	18	041.5	41.4	-0.1	41.4	-0.1	41.5	0
Val	19	172.5	172.5	0	172.3	-0.2	172.2	-0.3
	20	059.9	60.3	0.4	59.9	0	59.5	-0.4
	21	030.9	30.5	-0.4	30.6	-0.3	30.9	0
	22	018.4	18.1	-0.3	17.9	-0.5	17.9	-0.5
	23	022.56	21.6	-0.96	21.6	-0.96	19.4	-3.16
Sta	24	172.7	174.0	1.3	173.9	1.2	172.4	-0.3
	25	041.1	38.8	-2.3	39.1	-2	41.1	0
	26	071.4	72.2	0.8	72.3	0.9	71.0	-0.4
	27	052.5	52.4	-0.1	52.7	0.2	52.3	-0.2
	28	039.7	39.9	0.2	39.9	0.2	40.7	1
	29	025.4	25.2	-0.2	25.2	-0.2	25.2	-0.2
	30	023.6	23.7	0.1	23.7	0.1	23.3	-0.3
	31	022.4	19.3	-3.1	19.3	-3.1	22.1	-0.3
Ser	32	171.8	171.7	-0.1	171.6	-0.2	171.6	-0.2
	33	056.9	57.0	0.1	56.7	-0.2	56.7	-0.2
	34	062.6	62.5	-0.1	62.6	0	62.7	0.1
Tyr	35	172.5	173.0	0.5	172.6	0.1	172.4	-0.1
	36	056.1	56.1	0	56.0	-0.1	55.7	-0.4
	37	036.9	37.1	0.2	36.7	-0.2	36.7	-0.2
	38	129.0	128.9	-0.1	128.9	-0.1	128.8	-0.2
	39/43	131.0	131.0	0	130.9	-0.1	130.9	-0.1
	40/42	115.9	115.8	-0.1	115.9	0	115.9	0
	41	156.6	156.5	-0.1	156.6	0	156.5	-0.1
Valic acid	44	169.4	169.4	0	169.4	0	169.4	0
	45	081.2	81.0	-0.2	81.2	0	81.2	0
	46	031.1	31.0	-0.1	30.9	-0.2	31.0	-0.1
	47	016.8	16.6	-0.2	16.7	-0.1	16.8	0
	48	018.9	18.7	-0.2	18.8	-0.1	18.8	-0.1
N,*N*-Me$_2$-Ile	49	168.0	167.4	-0.6	168.3	0.3	168.0	0
	50	071.8	73.2	1.4	71.7	-0.1	71.6	-0.2
	51	034.1	34.0	-0.1	33.9	-0.2	33.9	-0.2
	52	014.0	15.4	1.4	14.1	0.1	14.0	0
	53	027.5	24.4	-3.1	27.3	-0.2	27.3	-0.2
	54	012.0	11.1	-0.9	11.5	-0.5	11.5	-0.5
	55/56	043.0	42.1	-0.9	42.7	-0.3	42.8	-0.2

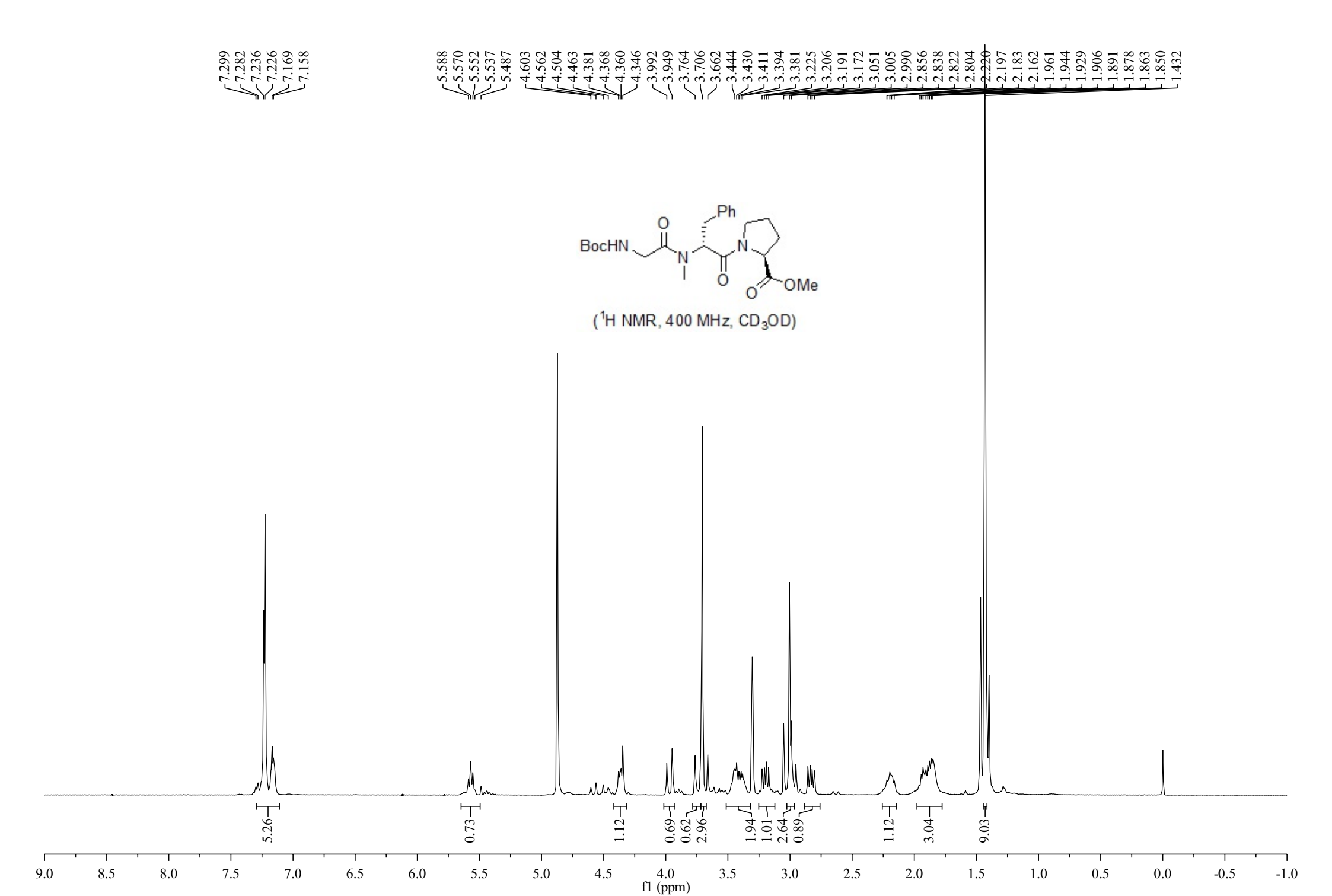


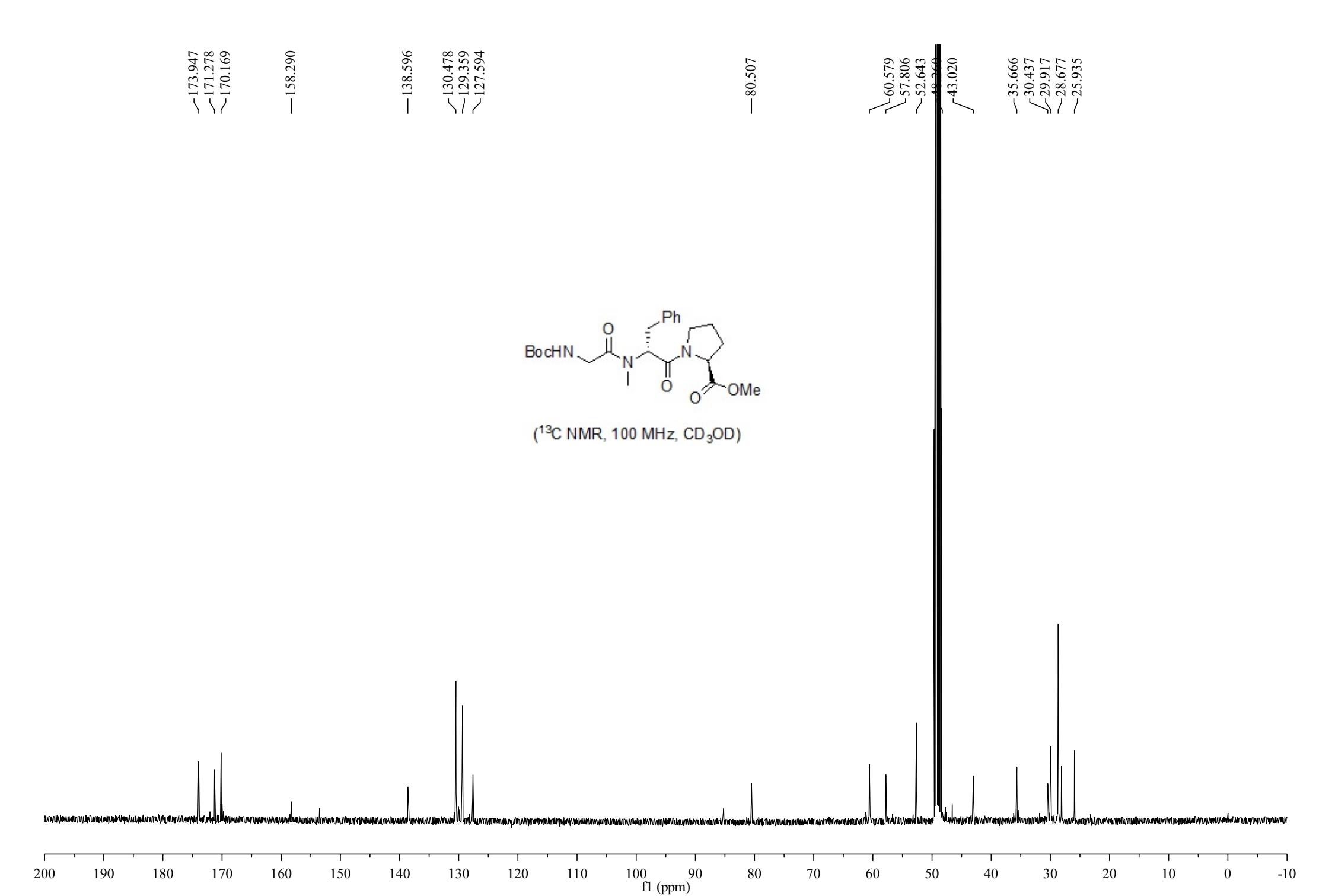
^{13}C NMR chemical shift differences between natural symplocin A and synthetic diastereoisomers. The *x* axis represents the carbon number, and the *y* axis shows the chemical shift differences in ppm. a) $\Delta\delta_C$ = Syn.**3a** - Nat., b) $\Delta\delta_C$ = Syn.**3b** - Nat., and c) $\Delta\delta_C$ = Syn.**3c** - Nat.

III NMR Spectra of coupled products


7.271
7.253
7.226
7.206
7.181
7.165
5.187
5.169
5.151
4.887
4.869
4.854
4.742
4.724
4.705
4.547
4.487
4.467
4.457
4.441
4.424
3.776
3.765
3.748
3.732
3.709
3.660
3.540
3.523
3.483
3.469
3.455
3.422
3.196
3.178
3.104
3.092
2.962
2.939
2.930
2.897
2.873
2.839
2.207
2.189
2.010
1.986
1.970
1.943
1.913
1.869
1.824
1.798
1.386
1.374
1.341
1.246
1.234
1.201
Ph
BocN
N
O
O
OMe
(^{1}H NMR, 400 MHz, $CDCl_3$)
5.19
0.49
0.50
0.93
3.17
2.07
0.49
0.50
4.21
1.16
3.48
4.55
4.54
f1 (ppm)


172.562
172.163
168.869
168.620
155.174
154.480
137.955
137.521
129.365
129.339
128.163
127.929
126.169
126.018
79.794
79.676
59.273
59.087
58.797
57.395
51.960
51.933
46.313
46.049
34.647
34.572
29.398
28.735
28.685
27.987
27.781
27.561
25.033
Ph
BocN
N
O
O
OMe
(13C NMR, 100 MHz, CDCl3)
f1 (ppm)


7.299
7.282
7.236
7.226
7.169
7.158
5.588
5.570
5.552
5.537
5.487
4.603
4.562
4.504
4.463
4.381
4.368
4.360
4.346
3.992
3.949
3.764
3.706
3.662
3.444
3.430
3.411
3.394
3.381
3.225
3.206
3.191
3.172
3.051
3.005
2.990
2.856
2.838
2.822
2.804
2.220
2.197
2.183
2.162
1.961
1.944
1.929
1.906
1.891
1.878
1.863
1.850
1.432
Ph
O
BocHN
N
N
O
O
OMe
(1H NMR, 400 MHz, CD3OD)
5.26
0.73
1.12
0.69
0.62
2.96
1.94
1.01
2.64
0.89
1.12
3.04
9.03
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
f1 (ppm)


173.947
171.278
170.169
158.290
138.596
130.478
129.359
127.594
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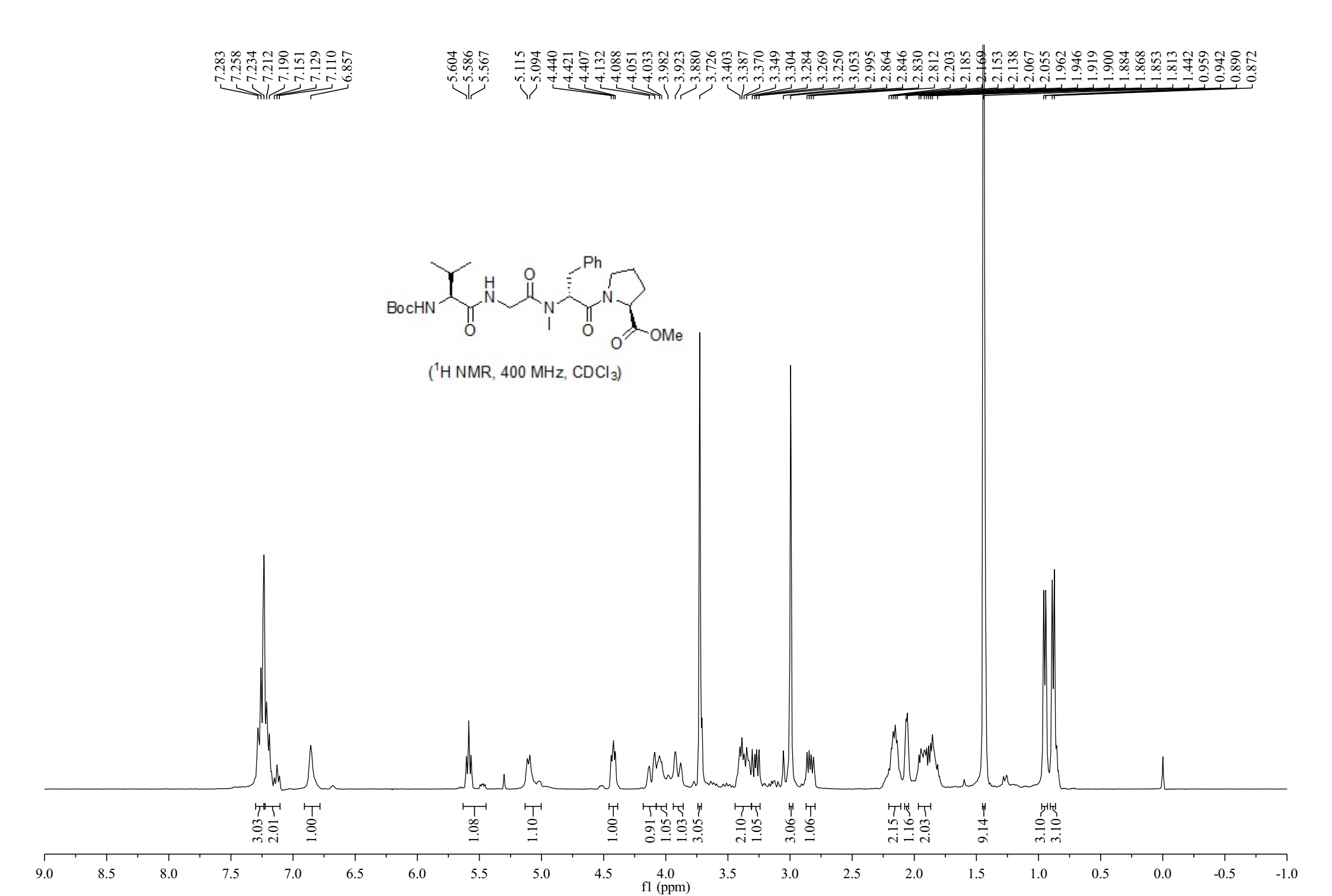
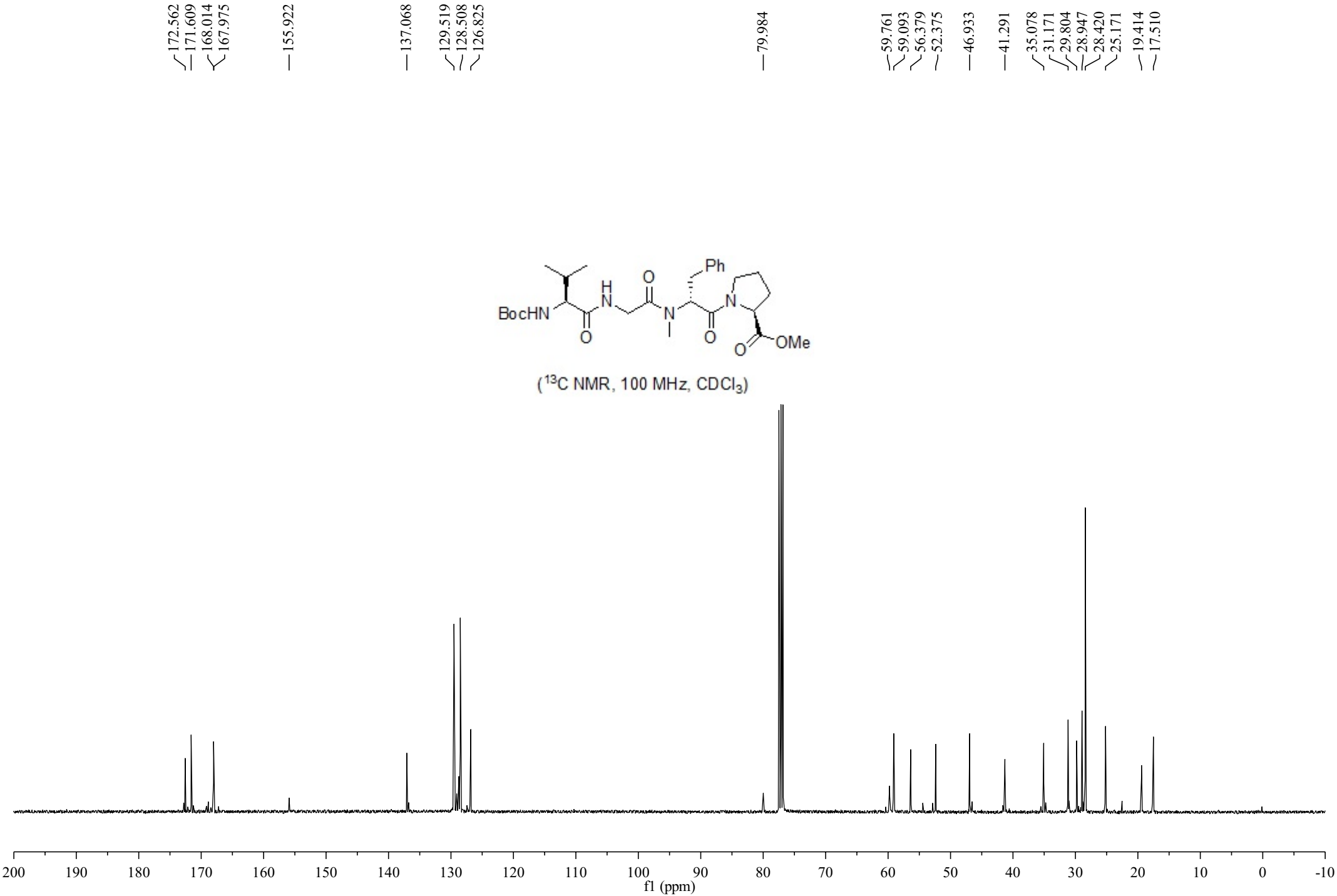
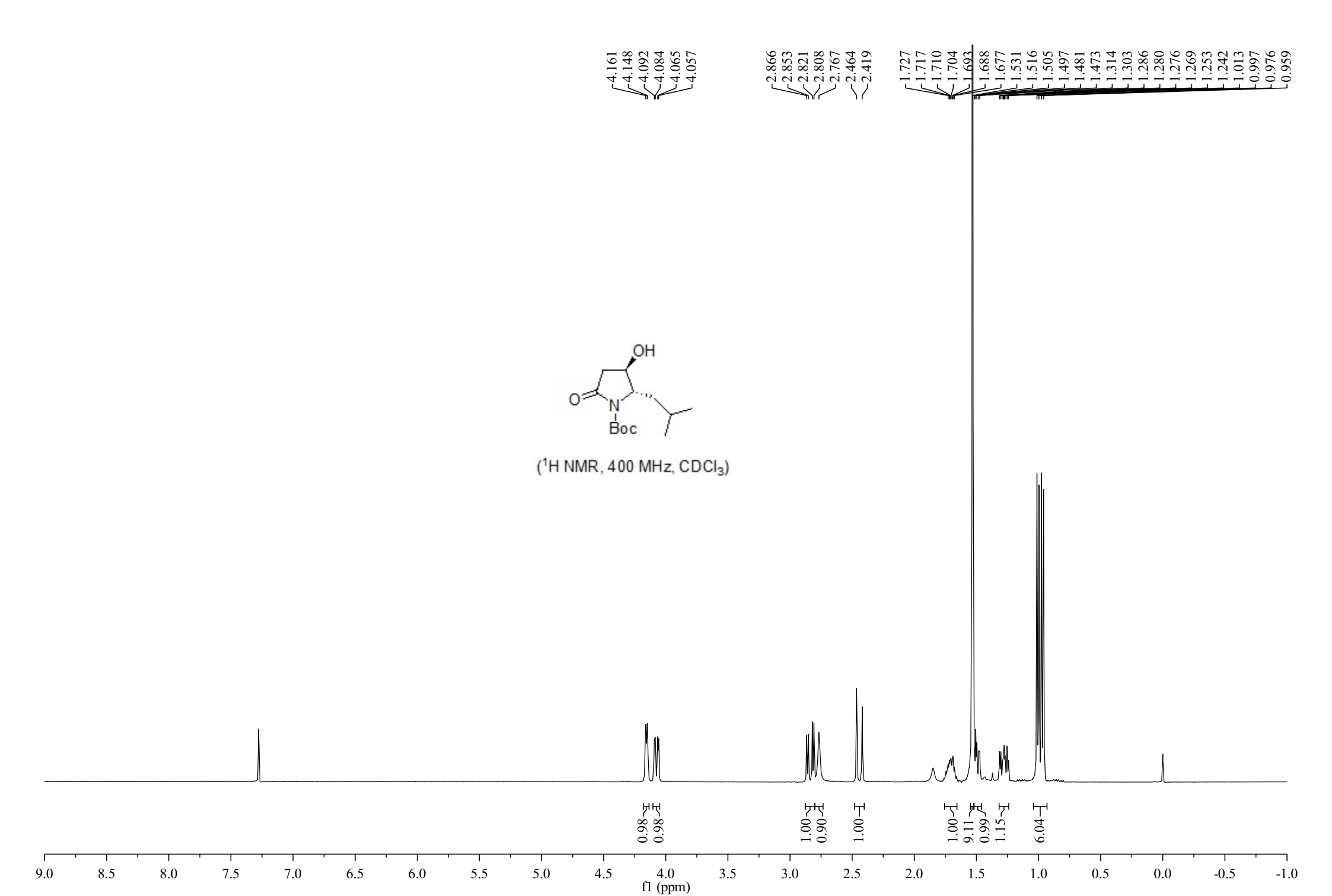
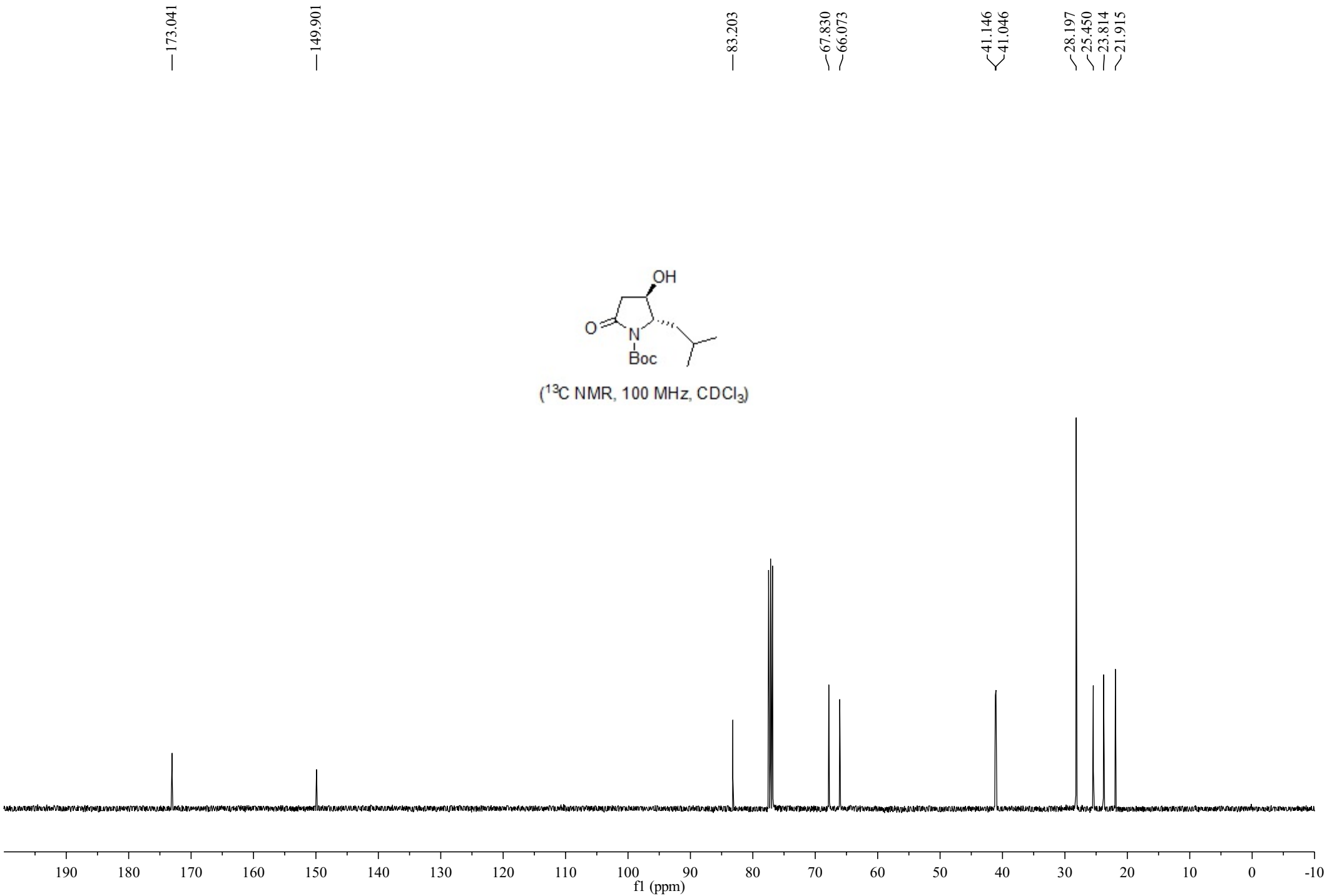
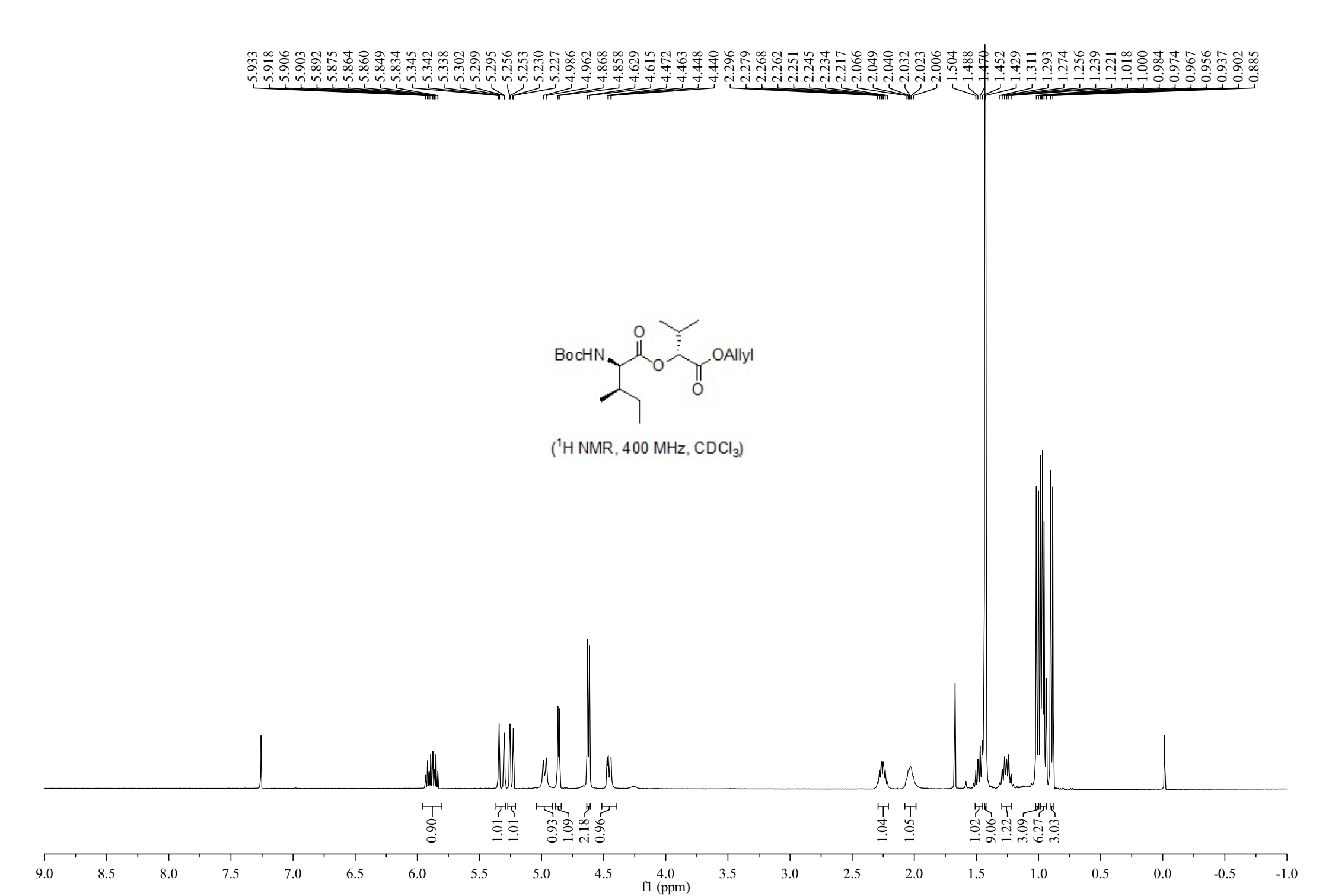
60.579
57.806
52.643
48.360
43.020
35.666
30.437
29.917
28.677
25.935
Ph
O
BocHN
N
N
O
O
OMe
(13C NMR, 100 MHz, CD3OD)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

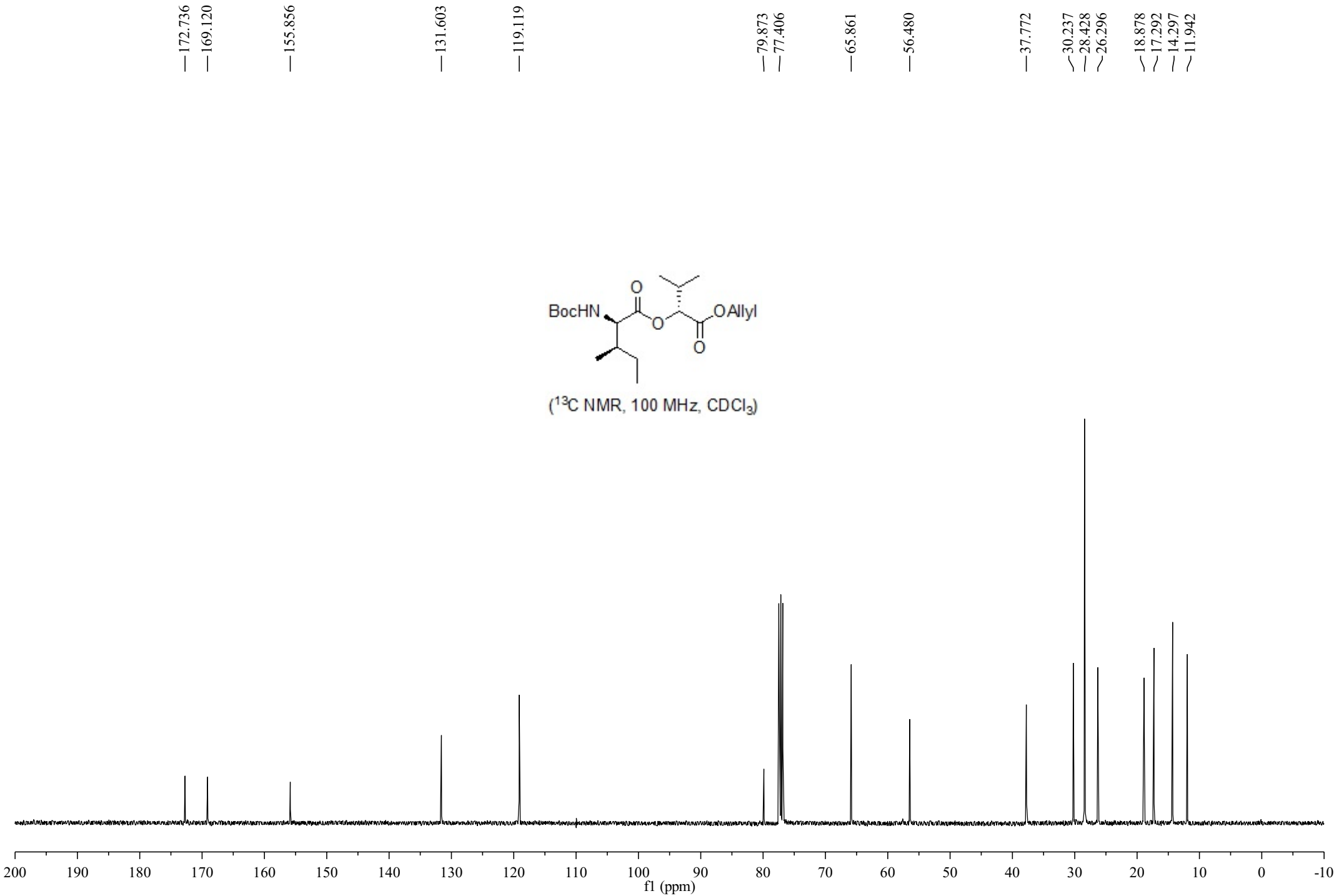

7.283
7.258
7.234
7.212
7.190
7.151
7.129
7.110
6.857
5.604
5.586
5.567
5.115
5.094
4.440
4.421
4.407
4.132
4.088
4.051
4.033
3.982
3.923
3.880
3.726
3.403
3.387
3.370
3.349
3.304
3.284
3.269
3.250
3.053
2.995
2.864
2.846
2.830
2.812
2.203
2.185
2.169
2.153
2.138
2.067
2.055
1.962
1.946
1.919
1.900
1.884
1.868
1.853
1.813
1.442
0.959
0.942
0.890
0.872
BocHN
H
N
O
O
N
Ph
N
O
O
OMe
(1H NMR, 400 MHz, CDCl3)
3.03
2.01
1.00
1.08
1.10
1.00
0.91
1.05
1.03
3.05
2.10
1.05
3.06
1.06
2.15
1.16
2.03
9.14
3.10
3.10
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
f1 (ppm)

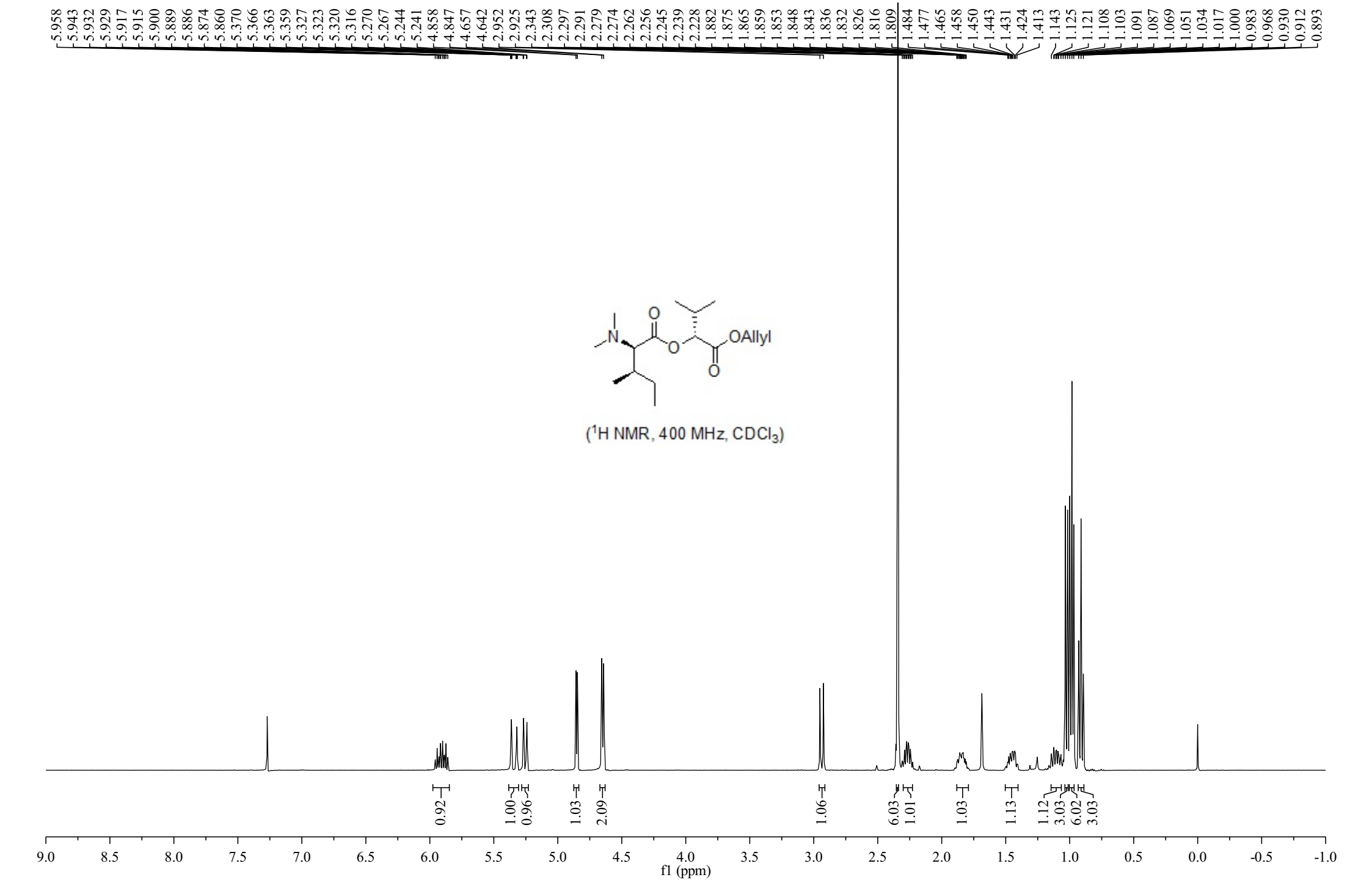

172.562
171.609
168.014
167.975
155.922
137.068
129.519
128.508
126.825
79.984
59.761
59.093
56.379
52.375
46.933
41.291
35.078
31.171
29.804
28.947
28.420
25.171
19.414
17.510
BocHN
H
N
O
O
N
O
N
Ph
O
OMe
(^{13}C NMR, 100 MHz, $CDCl_3$)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

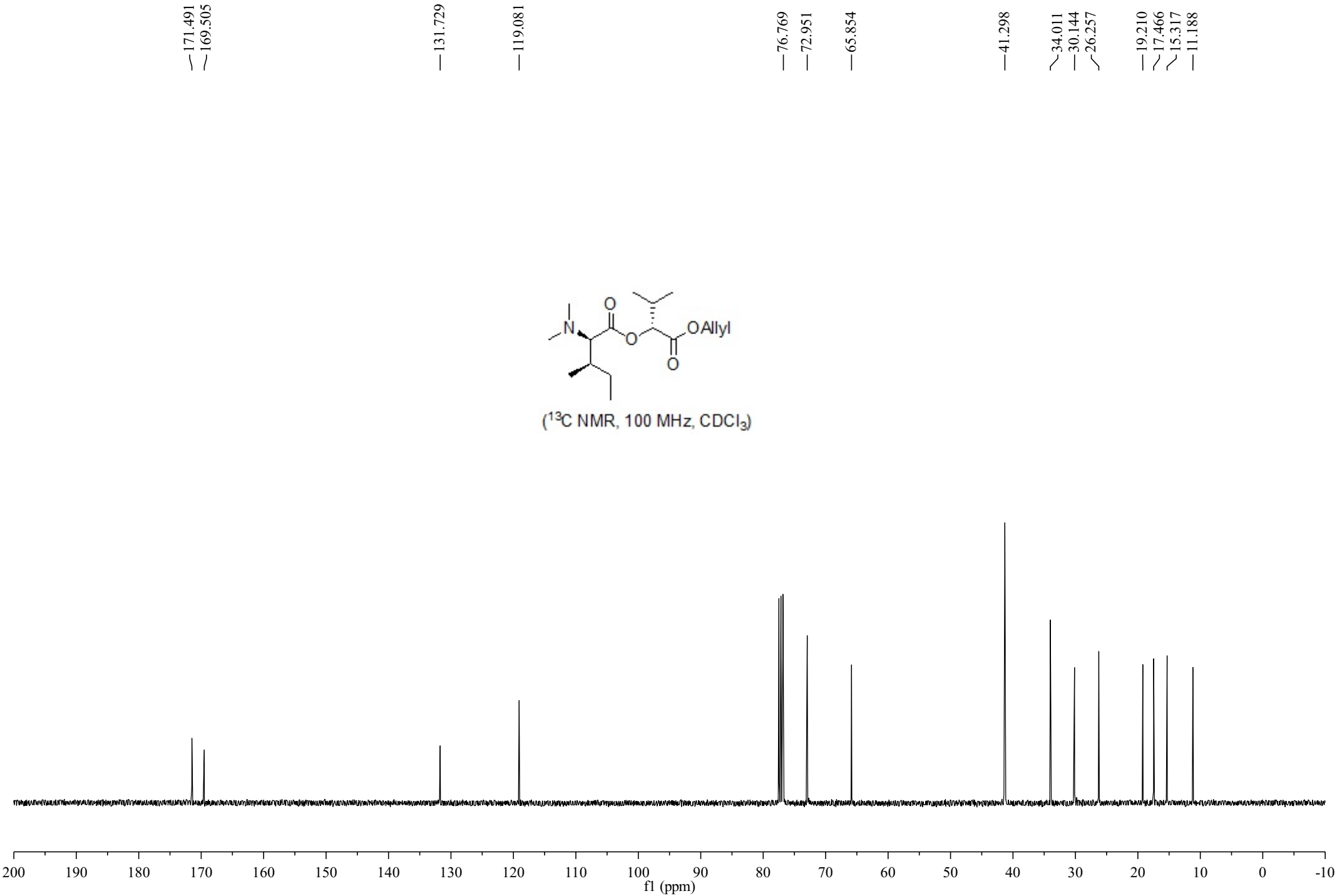

4.161
4.148
4.092
4.084
4.065
4.057
2.866
2.853
2.821
2.808
2.767
2.464
2.419
1.727
1.717
1.710
1.704
1.693
1.688
1.677
1.531
1.516
1.505
1.497
1.481
1.473
1.314
1.303
1.286
1.280
1.276
1.269
1.253
1.242
1.013
0.997
0.976
0.959
OH
O
N
Boc
(1H NMR, 400 MHz, CDCl3)
0.98
0.98
1.00
0.90
1.00
1.00
9.11
0.99
1.15
6.04
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
f1 (ppm)

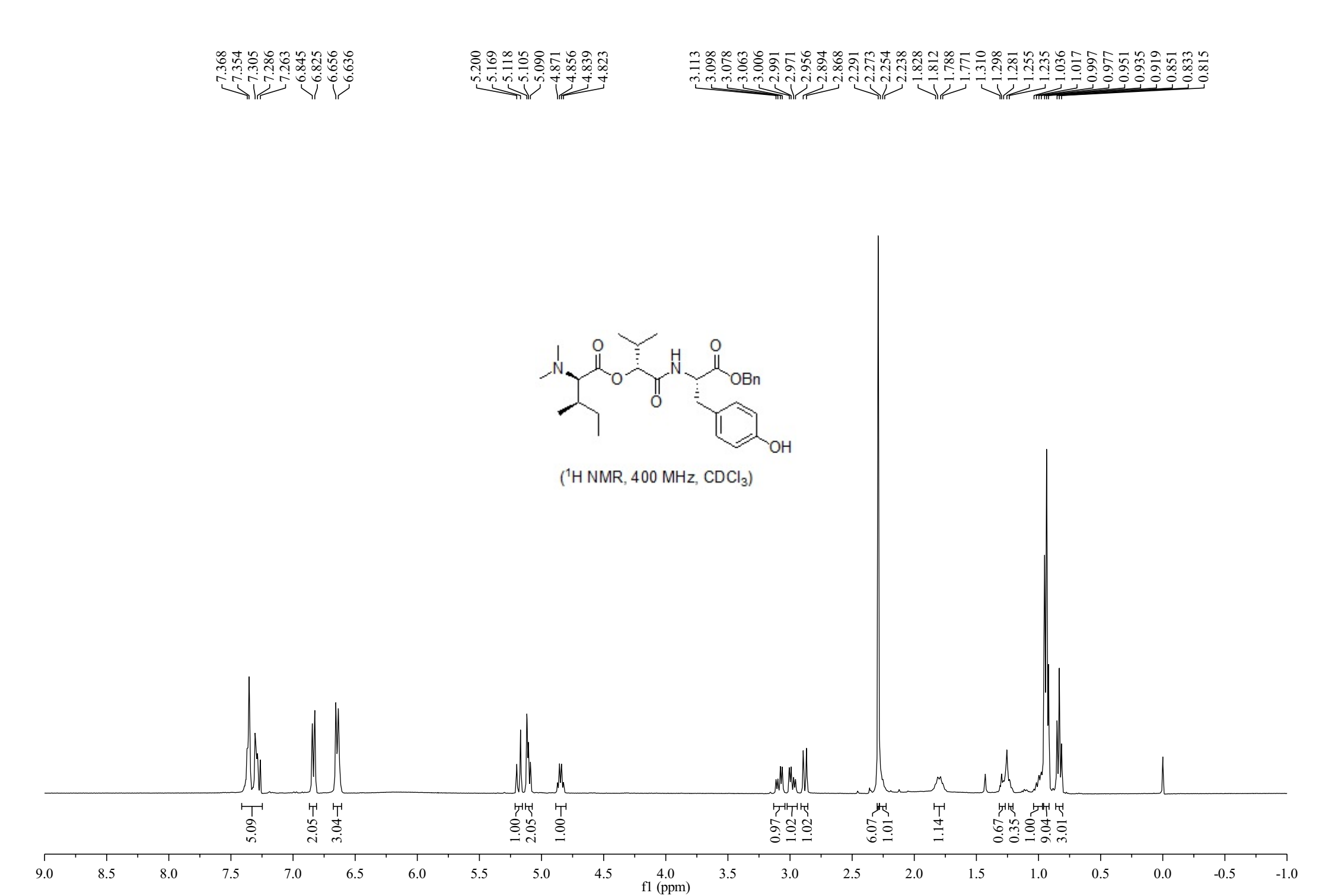

173.041
149.901
83.203
67.830
66.073
41.146
41.046
28.197
25.450
23.814
21.915
OH
O
N
Boc
(13C NMR, 100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


5.933
5.918
5.906
5.903
5.892
5.875
5.864
5.860
5.849
5.834
5.345
5.342
5.338
5.302
5.299
5.295
5.256
5.253
5.230
5.227
4.986
4.962
4.868
4.858
4.629
4.615
4.472
4.463
4.448
4.440
2.296
2.279
2.268
2.262
2.251
2.245
2.234
2.217
2.066
2.049
2.040
2.032
2.023
2.006
1.504
1.488
1.470
1.452
1.429
1.311
1.293
1.274
1.256
1.239
1.221
1.018
1.000
0.984
0.974
0.967
0.956
0.937
0.902
0.885
BocHN
O
O
O
OAllyl
(1H NMR, 400 MHz, CDCl3)
0.90
1.01
1.01
0.93
1.09
2.18
0.96
1.04
1.05
1.02
9.06
1.22
3.09
6.27
3.03
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
f1 (ppm)

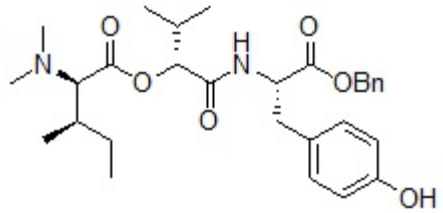

172.736
169.120
155.856
131.603
119.119
79.873
77.406
65.861
56.480
37.772
30.237
28.428
26.296
18.878
17.292
14.297
11.942
BocHN
O
O
O
OAllyl
(13C NMR, 100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


5.958
5.943
5.932
5.929
5.917
5.915
5.900
5.889
5.886
5.874
5.860
5.370
5.366
5.363
5.359
5.327
5.323
5.320
5.316
5.270
5.267
5.244
5.241
4.858
4.847
4.657
4.642
2.952
2.925
2.343
2.308
2.297
2.291
2.279
2.274
2.262
2.256
2.245
2.239
2.228
1.882
1.875
1.865
1.859
1.853
1.848
1.843
1.836
1.832
1.826
1.816
1.809
1.484
1.477
1.465
1.458
1.450
1.443
1.431
1.424
1.413
1.143
1.125
1.121
1.108
1.103
1.091
1.087
1.069
1.051
1.034
1.017
1.000
0.983
0.968
0.930
0.912
0.893
O
N
O
O
OAllyl
O
(1H NMR, 400 MHz, CDCl3)
0.92
1.00
0.96
1.03
2.09
1.06
6.03
1.01
1.03
1.13
1.12
3.03
6.02
3.03
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
f1 (ppm)

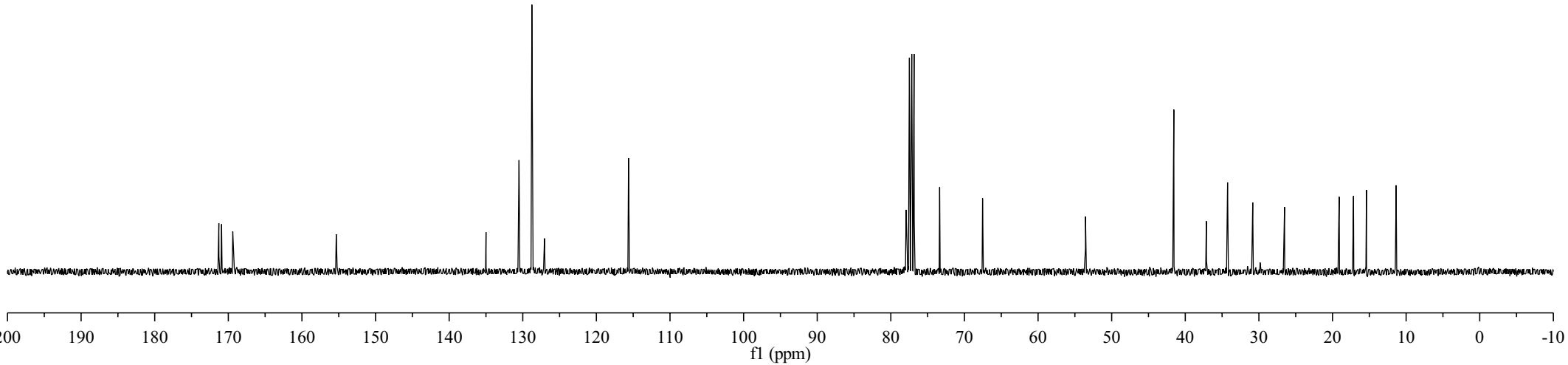

171.491
169.505
131.729
119.081
76.769
72.951
65.854
41.298
34.011
30.144
26.257
19.210
17.466
15.317
11.188
N
O
O
O
OAllyl
(13C NMR, 100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

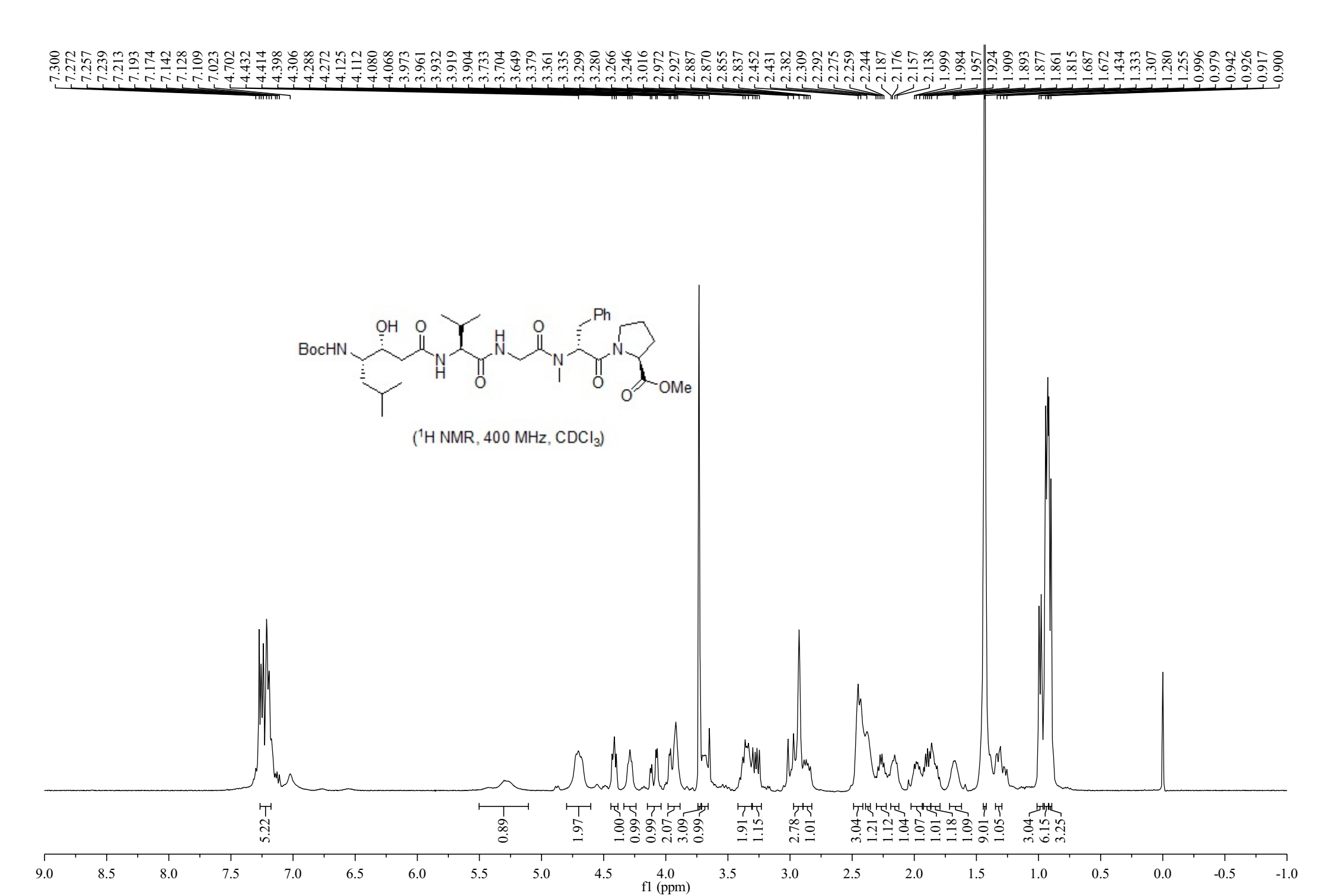

7.368
7.354
7.305
7.286
7.263
6.845
6.825
6.656
6.636
5.200
5.169
5.118
5.105
5.090
4.871
4.856
4.839
4.823
3.113
3.098
3.078
3.063
3.006
2.991
2.971
2.956
2.894
2.868
2.291
2.273
2.254
2.238
1.828
1.812
1.788
1.771
1.310
1.298
1.281
1.255
1.235
1.036
1.017
0.997
0.977
0.951
0.935
0.919
0.851
0.833
0.815
O
N
O
O
H
N
O
OBn
O
OH
(1H NMR, 400 MHz, CDCl3)
5.09
2.05
3.04
1.00
2.05
1.00
0.97
1.02
1.02
6.07
1.01
1.14
0.67
0.35
1.00
9.04
3.01
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
f1 (ppm)

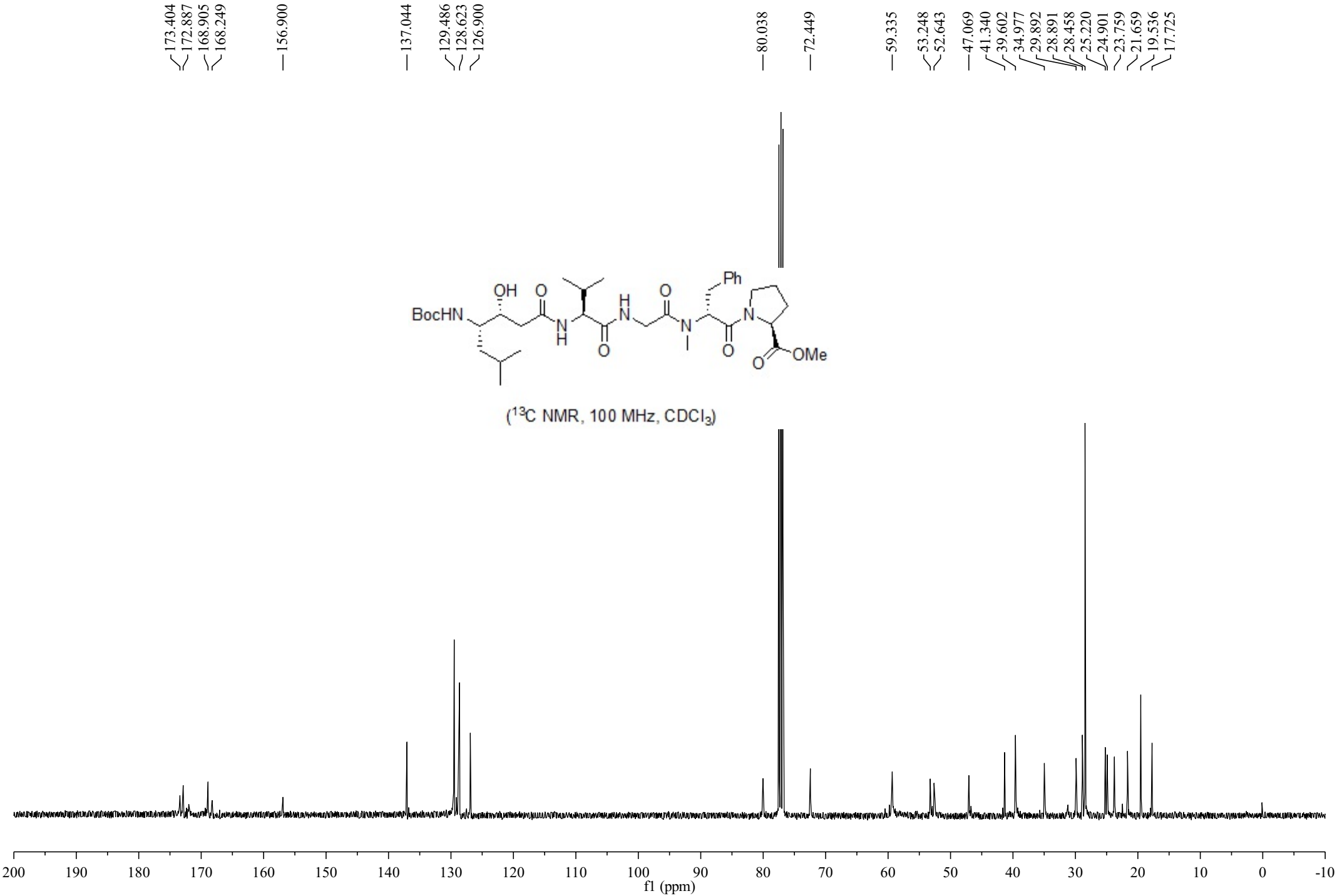
171.288
170.916
169.395
155.339
134.997
130.508
128.763
128.740
127.048
115.636
77.929
73.369
67.538
53.549
41.554
37.139
34.255
30.835
26.512
19.092
17.148
15.388
11.356

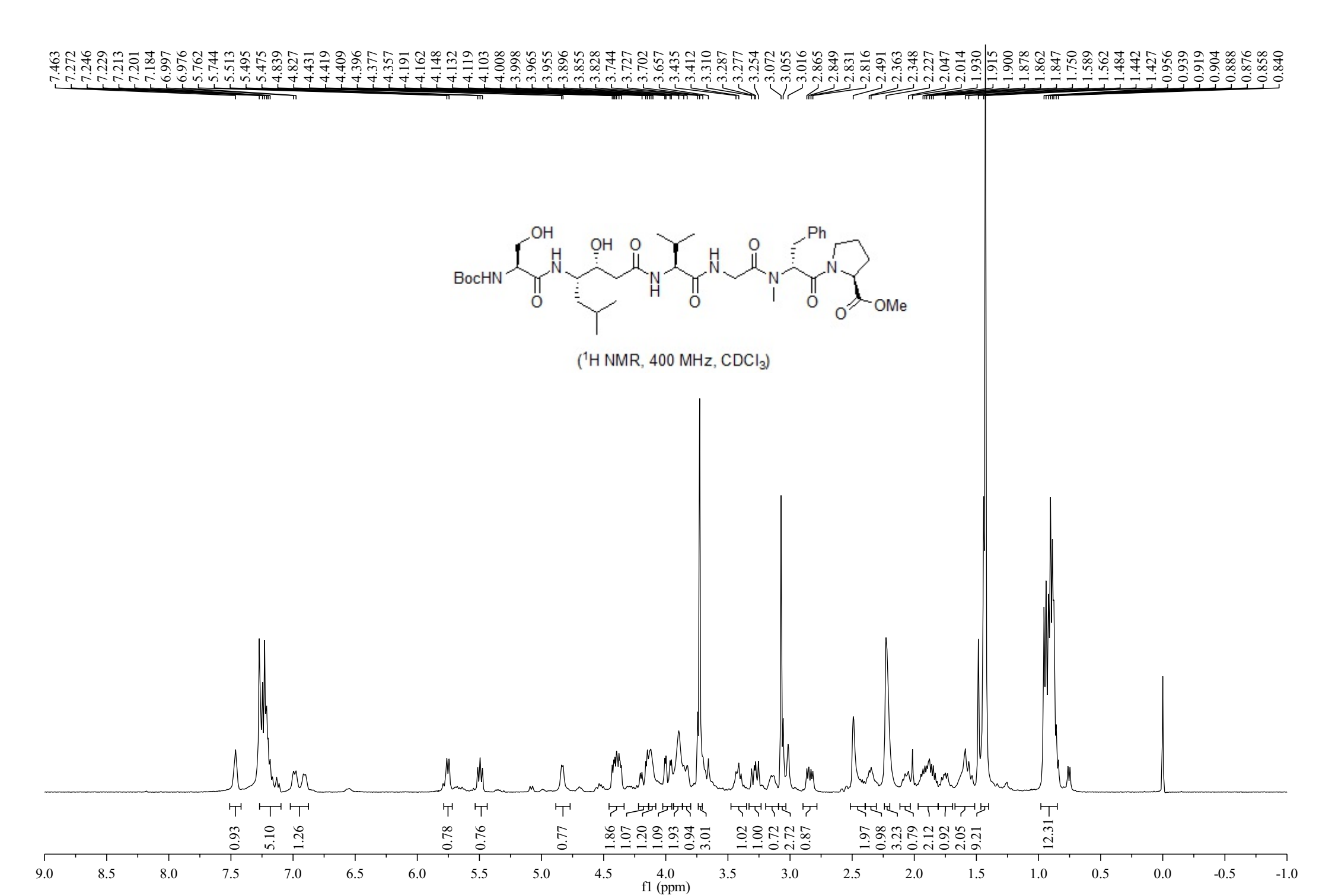


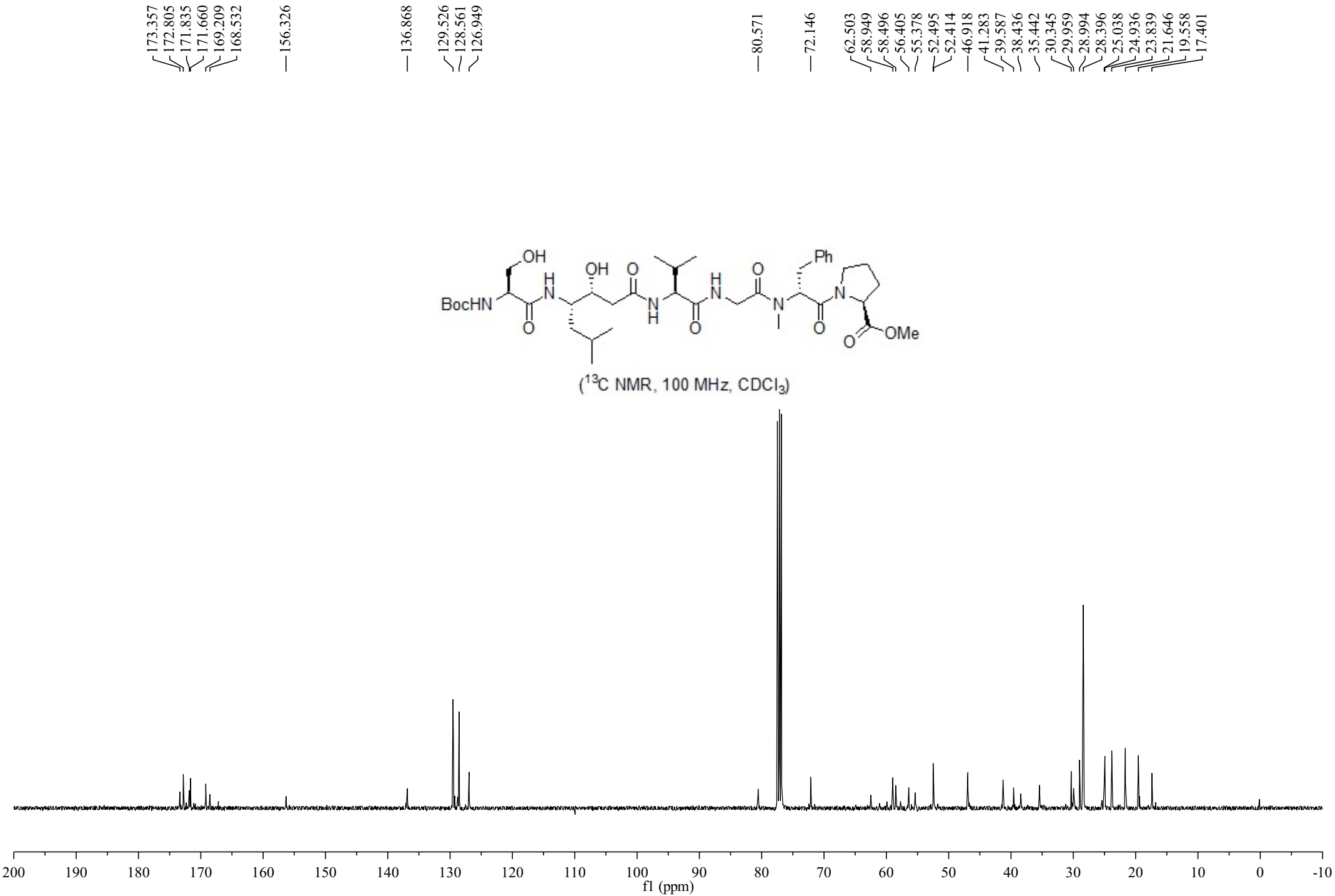
(^{13}C NMR, 100 MHz, $CDCl_3$)

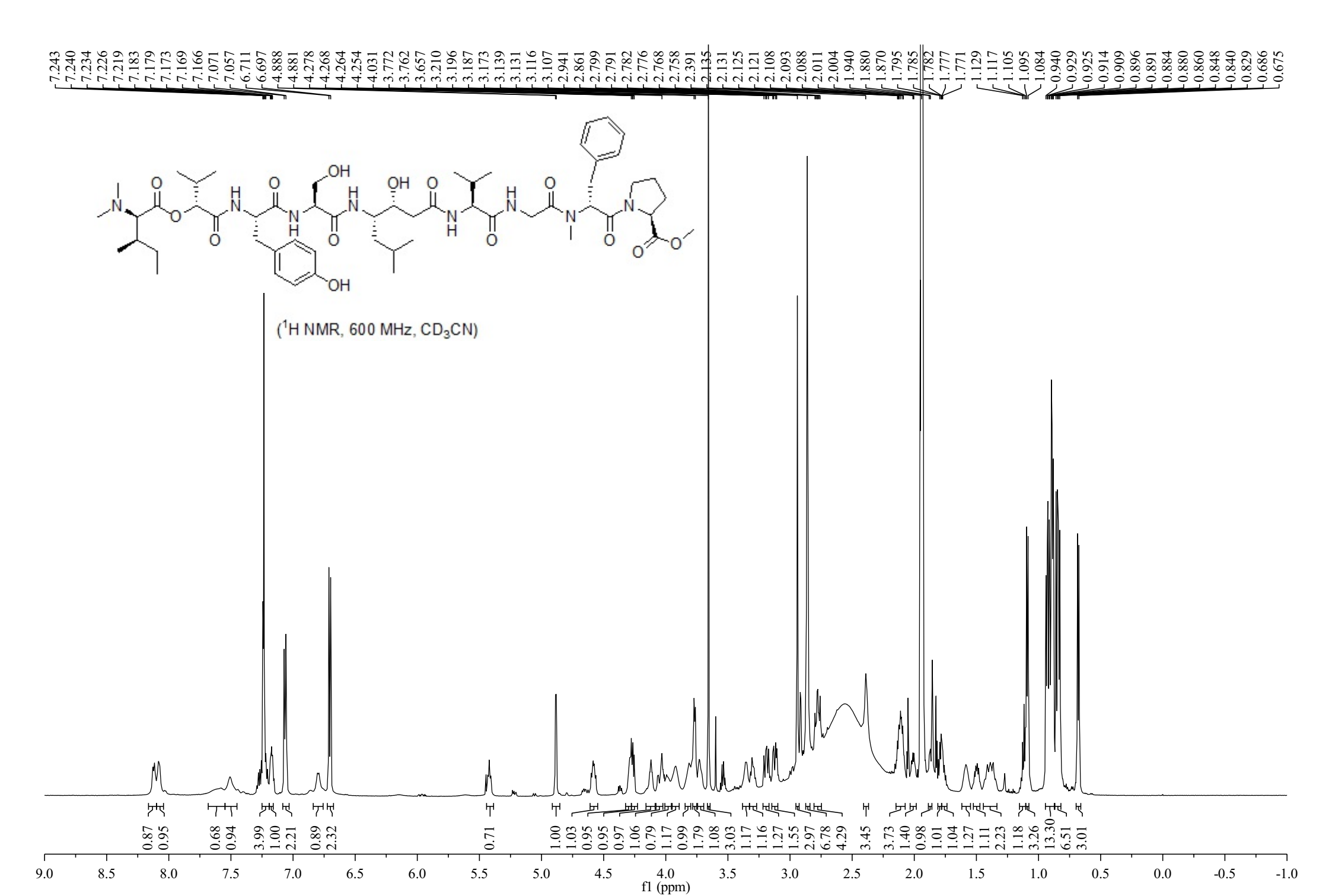


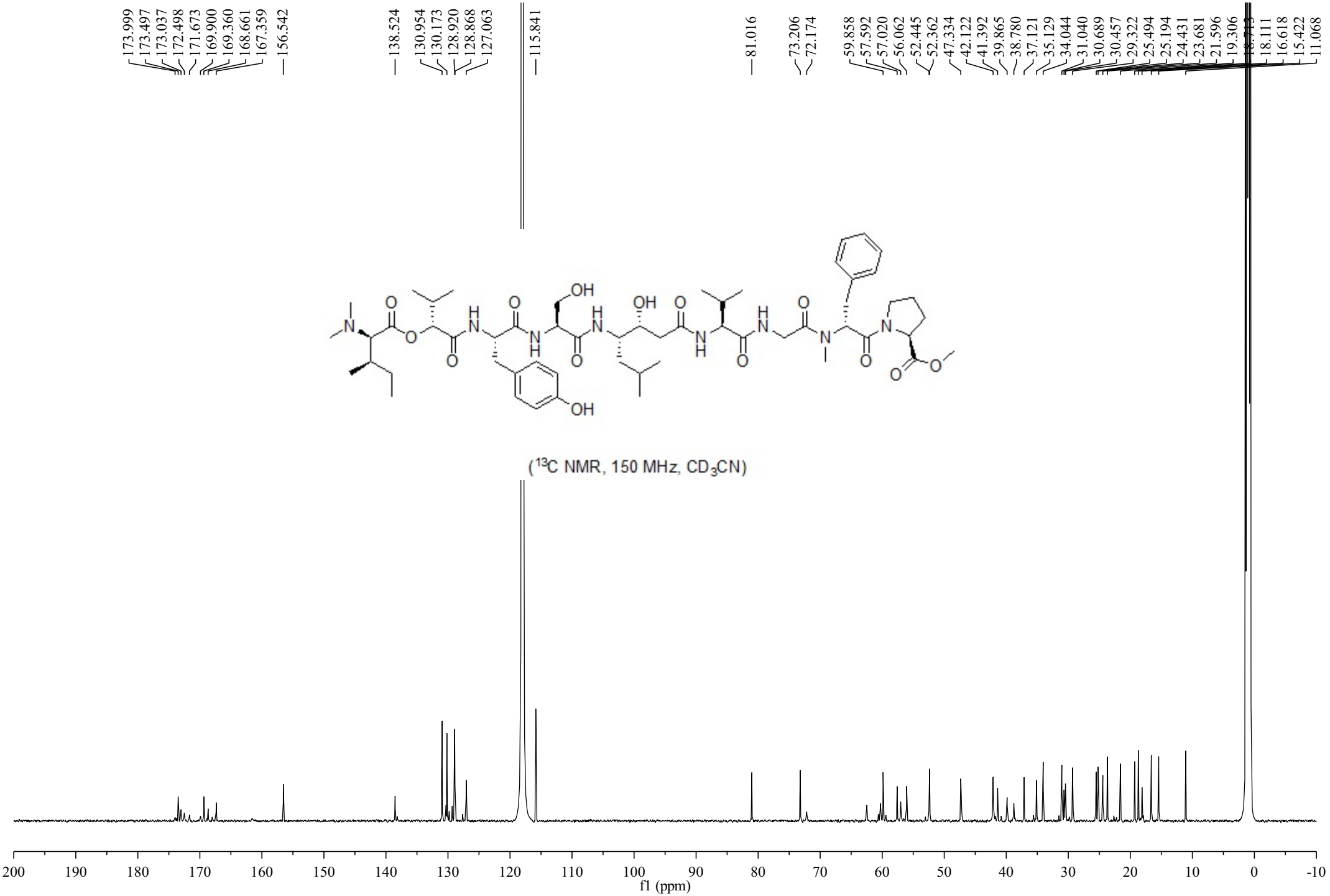

7.300
7.272
7.257
7.239
7.213
7.193
7.174
7.142
7.128
7.109
7.023
4.702
4.432
4.414
4.398
4.306
4.288
4.272
4.125
4.112
4.080
4.068
3.973
3.961
3.932
3.919
3.904
3.733
3.704
3.649
3.379
3.361
3.335
3.299
3.280
3.266
3.246
3.016
2.972
2.927
2.887
2.870
2.855
2.837
2.452
2.431
2.382
2.309
2.292
2.275
2.259
2.244
2.187
2.176
2.157
2.138
1.999
1.984
1.957
1.924
1.909
1.893
1.877
1.861
1.815
1.687
1.672
1.434
1.333
1.307
1.280
1.255
0.996
0.979
0.942
0.926
0.917
0.900
BocHN
OH
O
N
H
O
H
N
O
N
Ph
N
O
O
OMe
(1H NMR, 400 MHz, CDCl3)
5.22
0.89
1.97
1.00
0.99
0.99
2.07
3.09
0.99
1.91
1.15
2.78
1.01
3.04
1.21
1.12
1.04
1.07
1.01
1.18
1.09
9.01
1.05
3.04
6.15
3.25
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
f1 (ppm)

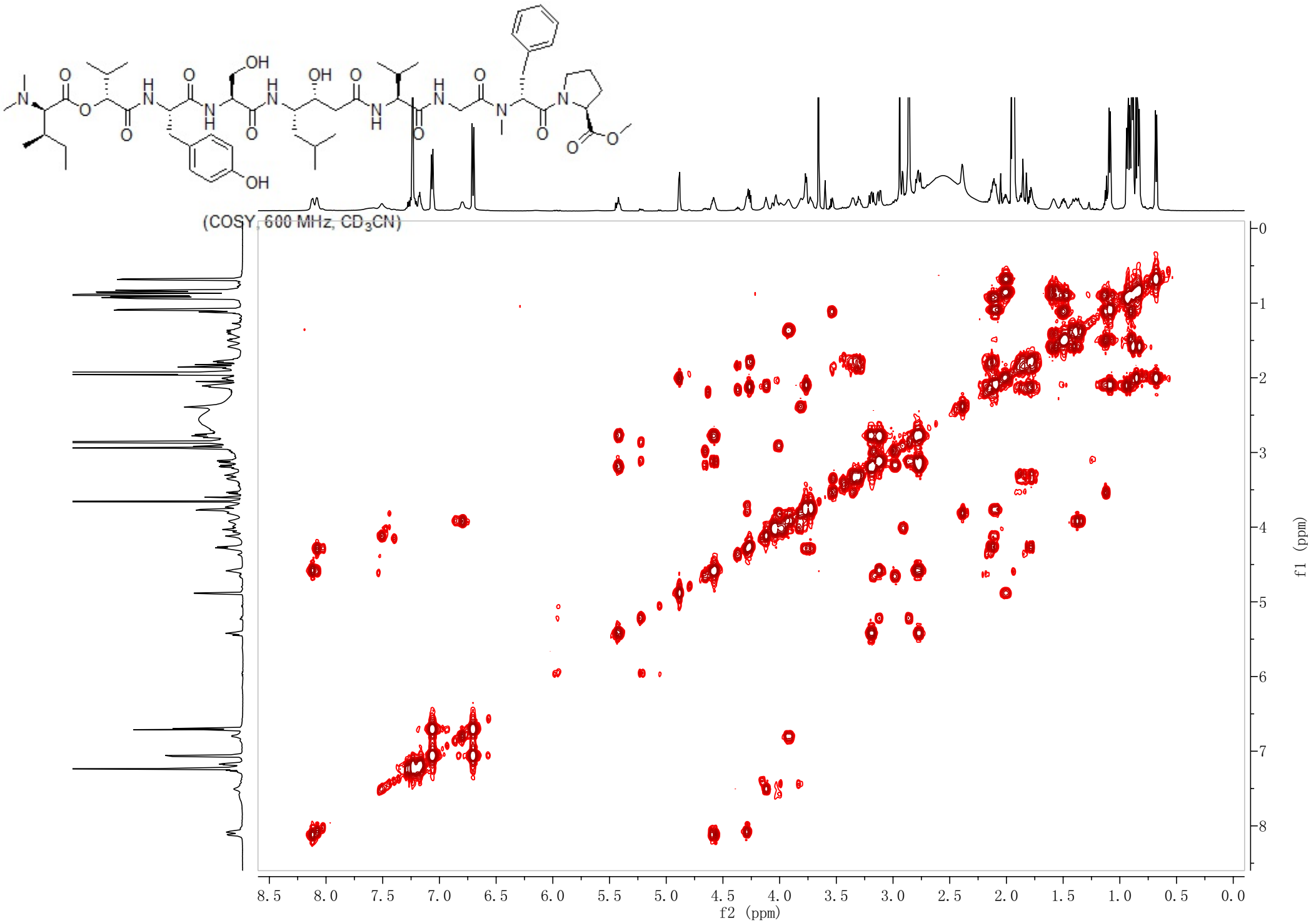

173.404
172.887
168.905
168.249
156.900
137.044
129.486
128.623
126.900
80.038
72.449
59.335
53.248
52.643
47.069
41.340
39.602
34.977
29.892
28.891
28.458
25.220
24.901
23.759
21.659
19.536
17.725
BocHN
OH
O
N
H
H
N
O
N
O
Ph
N
O
O
OMe
(13C NMR, 100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

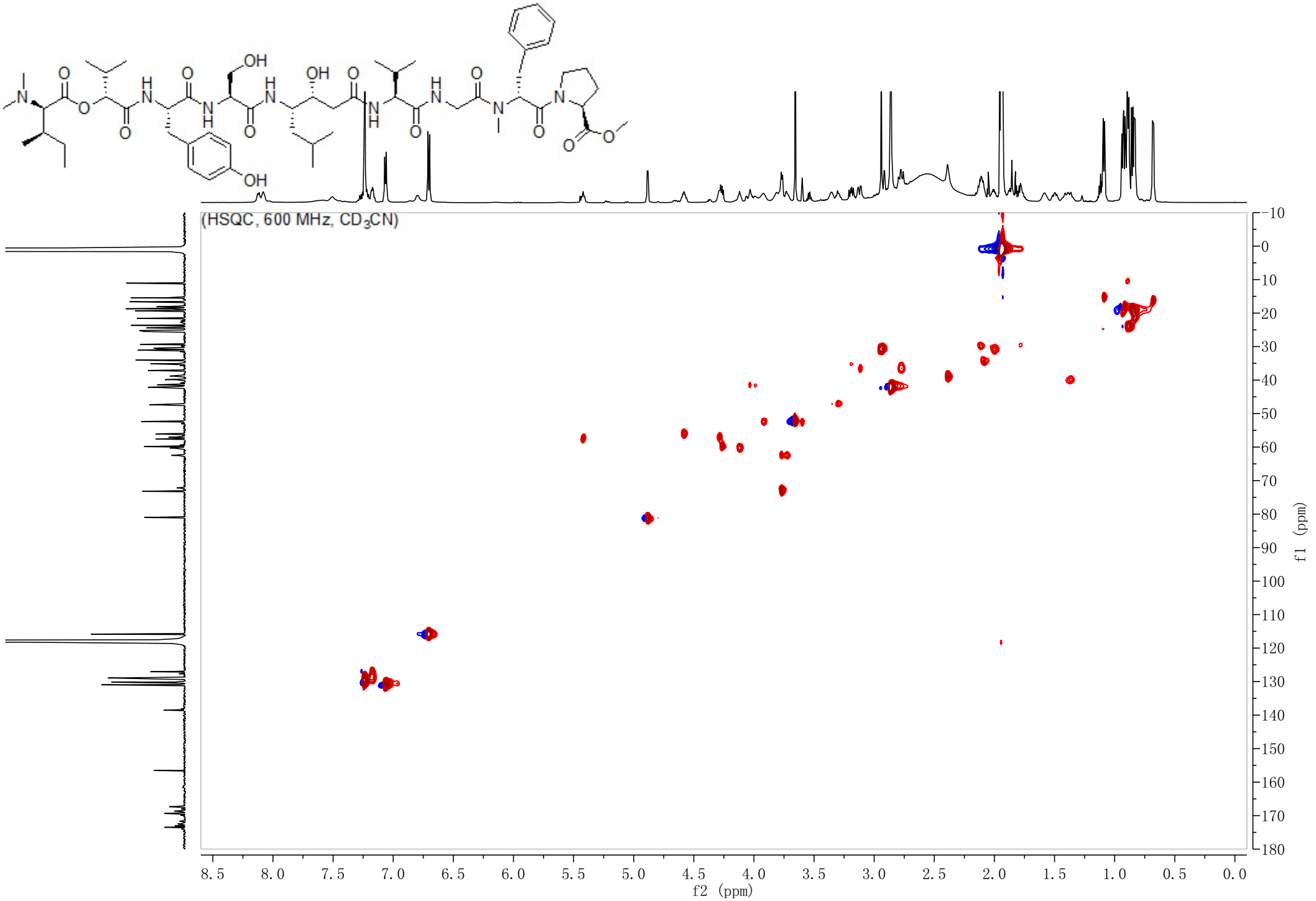

7.463 7.272 7.246 7.229 7.213 7.201 7.184 6.997 6.976 5.762 5.744 5.513 5.495 5.475 4.839 4.827 4.431 4.419 4.409 4.396 4.377 4.357 4.191 4.162 4.148 4.132 4.119 4.103 4.008 3.998 3.965 3.955 3.896 3.855 3.828 3.744 3.727 3.702 3.657 3.435 3.412 3.310 3.287 3.277 3.254 3.072 3.055 3.016 2.865 2.849 2.831 2.816 2.491 2.363 2.348 2.227 2.047 2.014 1.930 1.915 1.900 1.878 1.862 1.847 1.750 1.589 1.562 1.484 1.442 1.427 0.956 0.939 0.919 0.904 0.888 0.876 0.858 0.840
OH
OH
O
Ph
BocHN
H
N
N
H
H
N
N
N
O
O
O
O
O
OMe
(1H NMR, 400 MHz, CDCl3)
0.93 5.10 1.26 0.78 0.76 0.77 1.86 1.07 1.20 1.09 1.93 0.94 3.01 1.02 1.00 0.72 2.72 0.87 1.97 0.98 3.23 0.79 2.12 0.92 2.05 9.21 12.31
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
f1 (ppm)

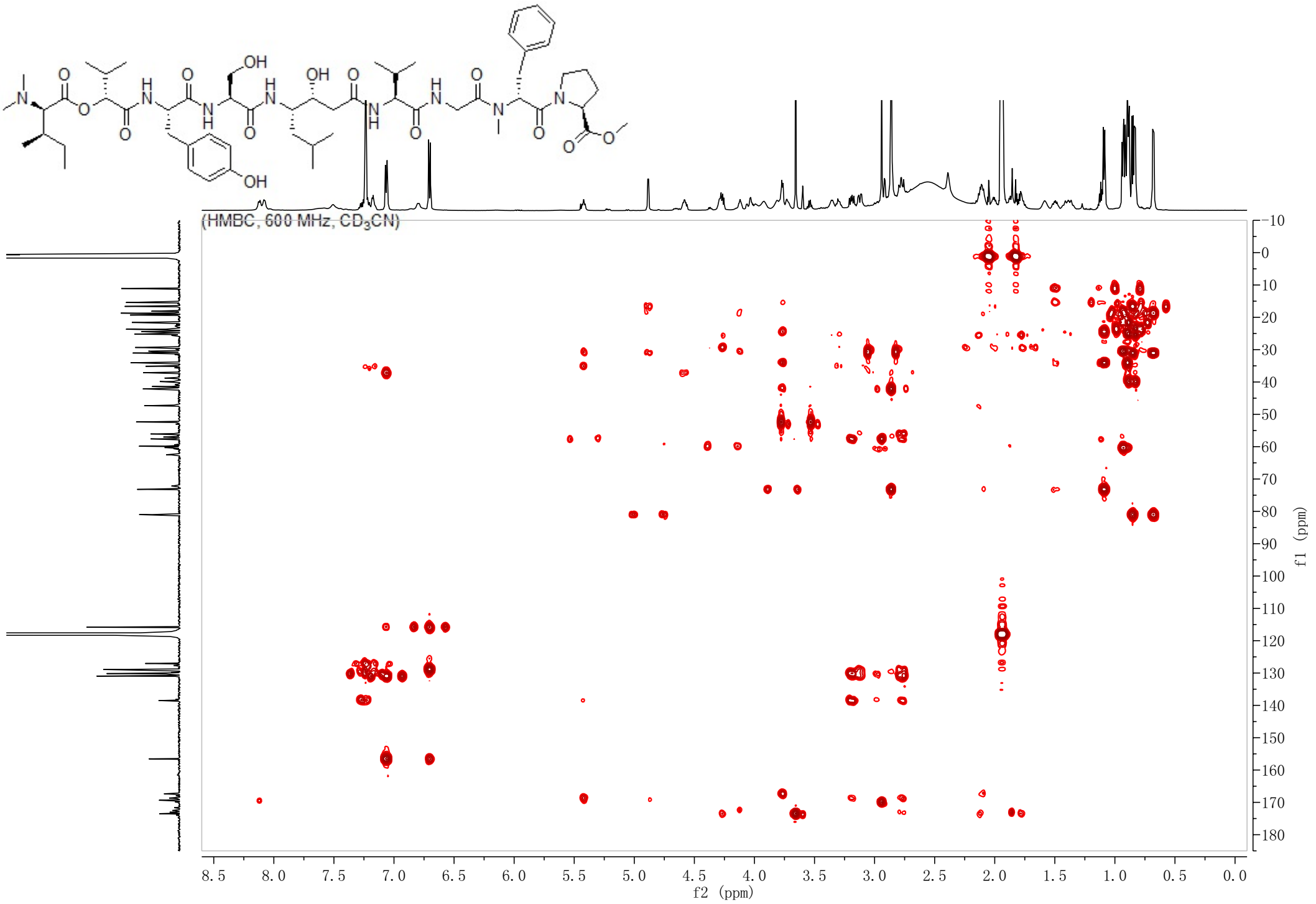

173.357
172.805
171.835
171.660
169.209
168.532
156.326
136.868
129.526
128.561
126.949
80.571
72.146
62.503
58.949
58.496
56.405
55.378
52.495
52.414
46.918
41.283
39.587
38.436
35.442
30.345
29.959
28.994
28.396
25.038
24.936
23.839
21.646
19.558
17.401
BocHN
OH
OH
O
H
N
O
N
H
O
H
N
O
N
Ph
N
O
O
OMe
(^{13}C NMR, 100 MHz, $CDCl_3$)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

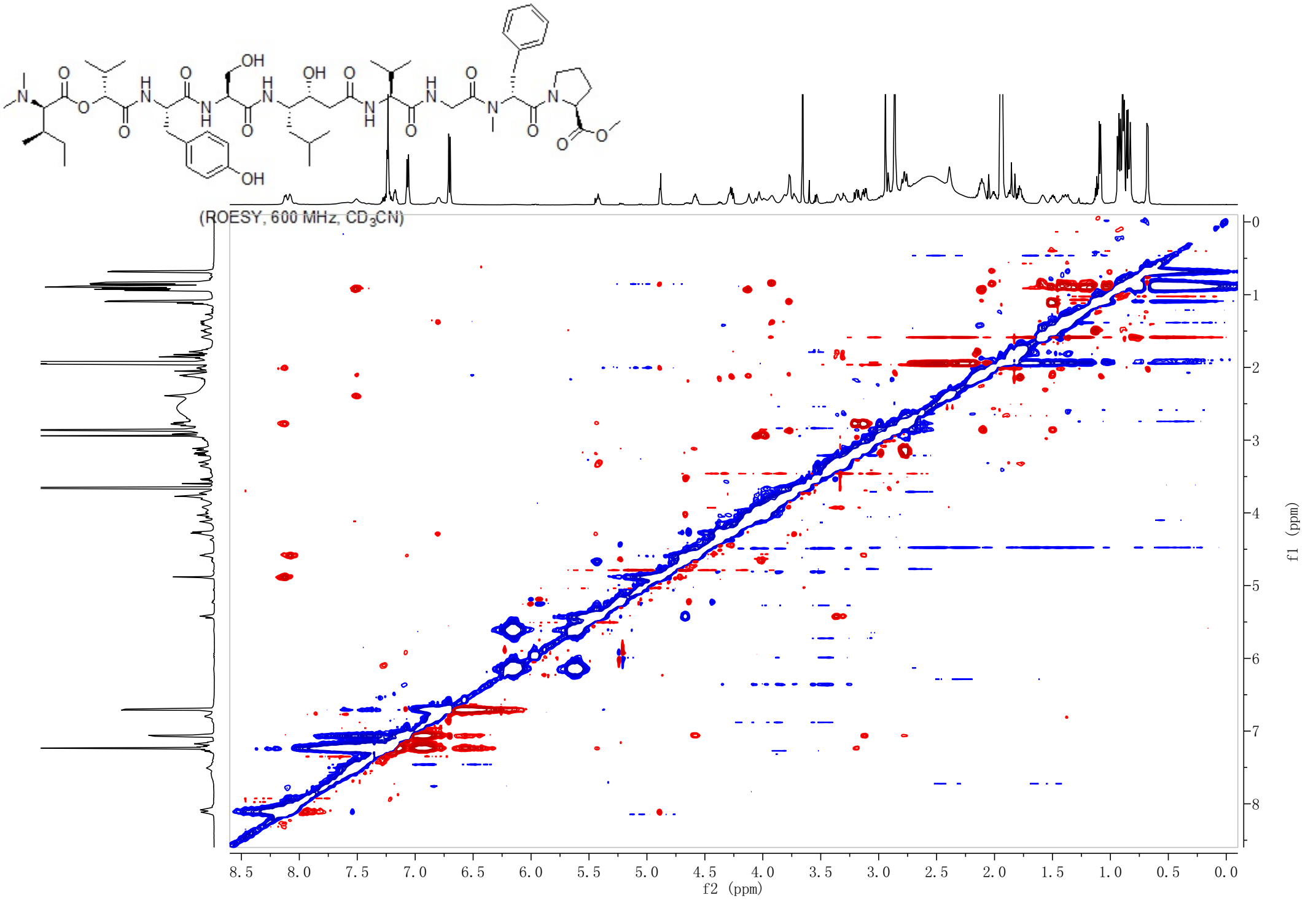

7.243 7.240 7.234 7.226 7.219 7.183 7.179 7.173 7.169 7.166 7.071 7.057 6.711 6.697 4.888 4.881 4.278 4.268 4.264 4.254 4.031 3.772 3.762 3.657 3.210 3.196 3.187 3.173 3.139 3.131 3.116 3.107 2.941 2.861 2.799 2.791 2.782 2.776 2.768 2.758 2.391 2.135 2.131 2.125 2.121 2.108 2.093 2.088 2.011 2.004 1.940 1.880 1.870 1.795 1.785 1.782 1.777 1.771 1.129 1.117 1.105 1.095 1.084 0.940 0.929 0.925 0.914 0.909 0.896 0.891 0.884 0.880 0.860 0.848 0.840 0.829 0.686 0.675
(1H NMR, 600 MHz, CD3CN)
0.87 0.95 0.68 0.94 3.99 1.00 2.21 0.89 2.32 0.71 1.00 1.03 0.95 0.95 0.97 1.06 0.79 1.17 0.99 1.79 1.08 3.03 1.17 1.16 1.27 1.55 2.97 6.78 4.29 3.45 3.73 1.40 0.98 1.01 1.04 1.27 1.11 2.23 1.18 3.26 13.30 6.51 3.01
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
f1 (ppm)

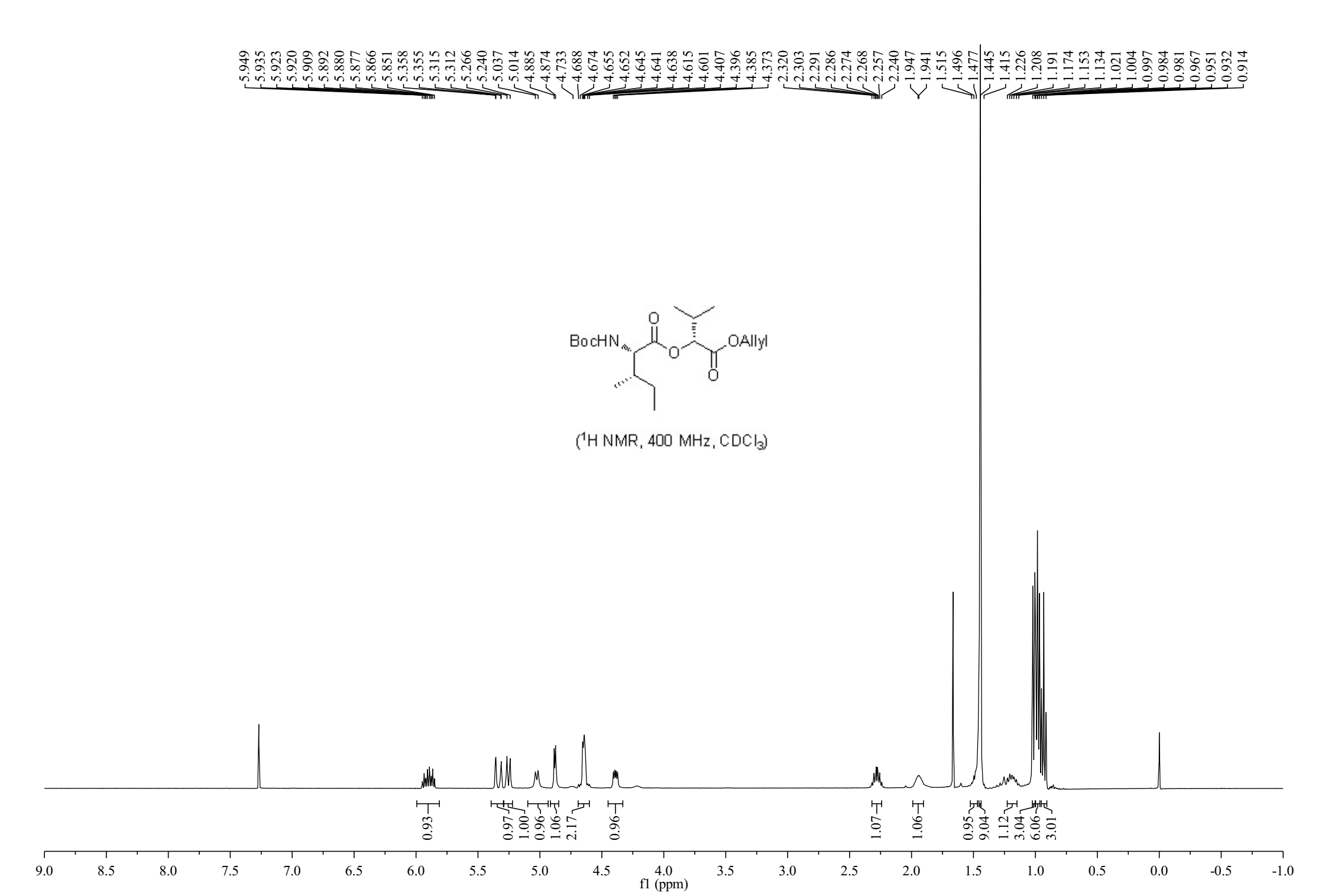

173.999
173.497
173.037
172.498
171.673
169.900
169.360
168.661
167.359
156.542
138.524
130.954
130.173
128.920
128.868
127.063
115.841
81.016
73.206
72.174
59.858
57.592
57.020
56.062
52.445
52.362
47.334
42.122
41.392
39.865
38.780
37.121
35.129
34.044
31.040
30.689
30.457
29.322
25.494
25.194
24.431
23.681
21.596
19.306
18.713
18.111
16.618
15.422
11.068
OH
OH
OH
(^{13}C NMR, 150 MHz, CD_3CN)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

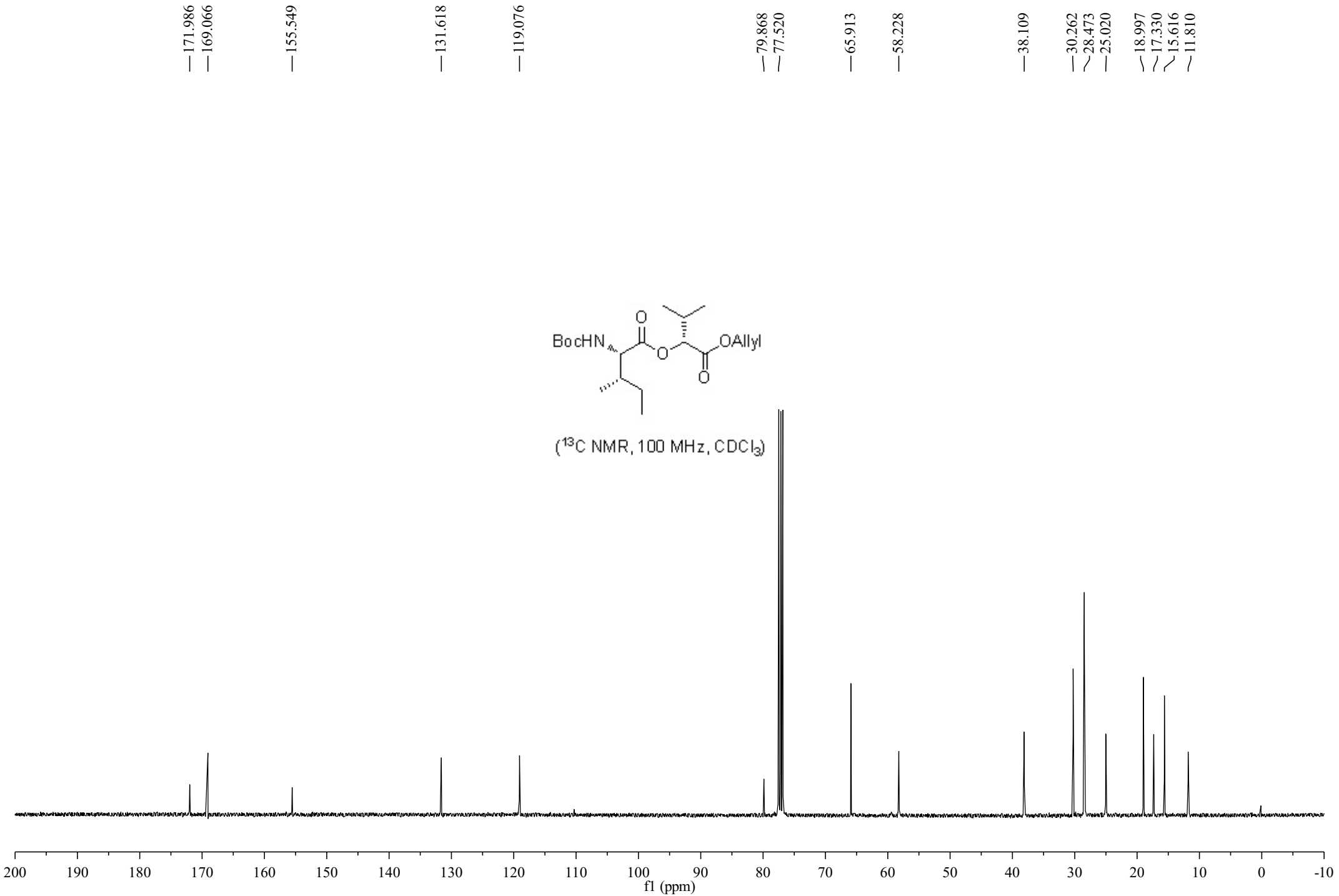

(COSY, 600 MHz, CD_3CN)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)

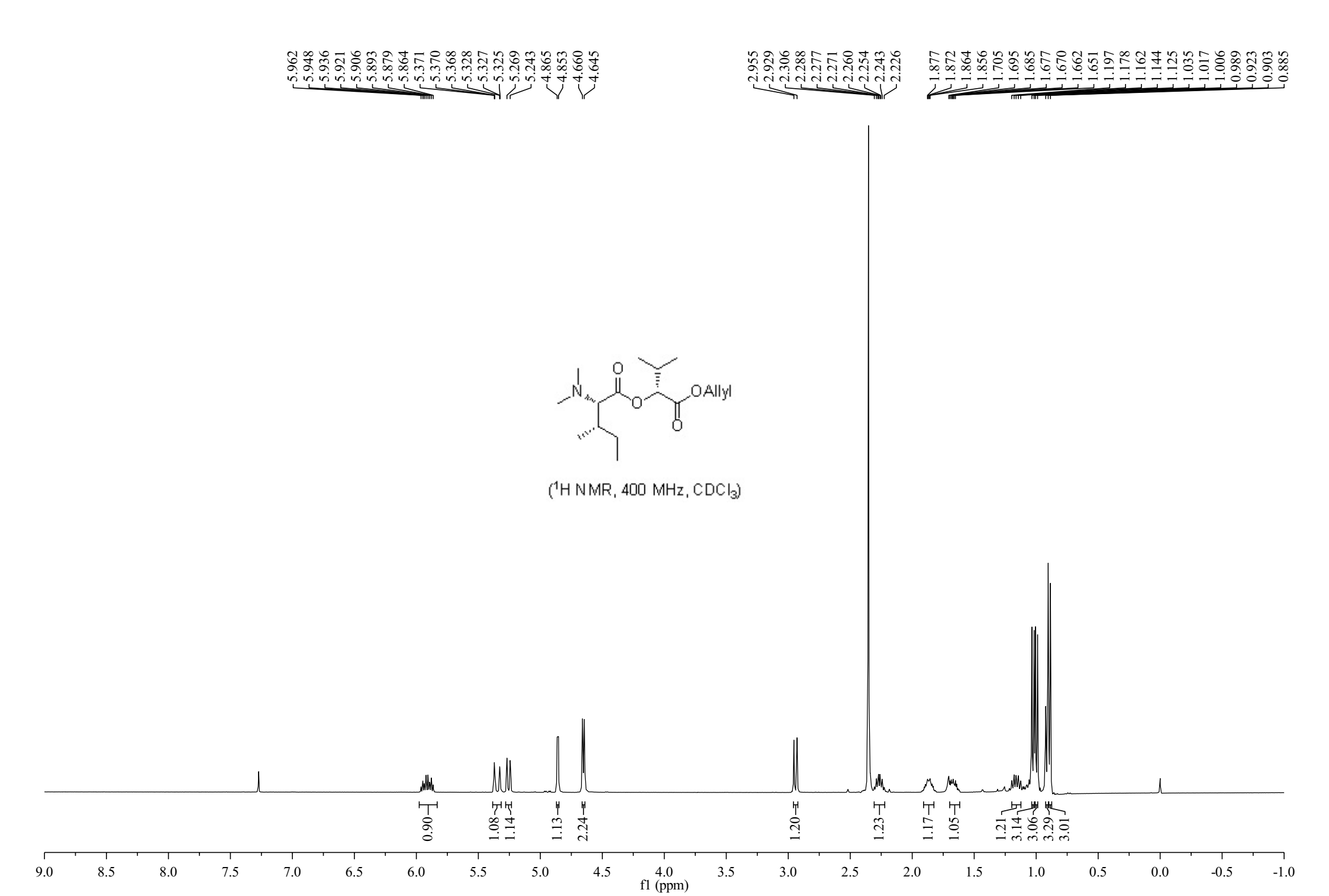

(HSQC, 600 MHz, CD3CN)
f2 (ppm)
f1 (ppm)

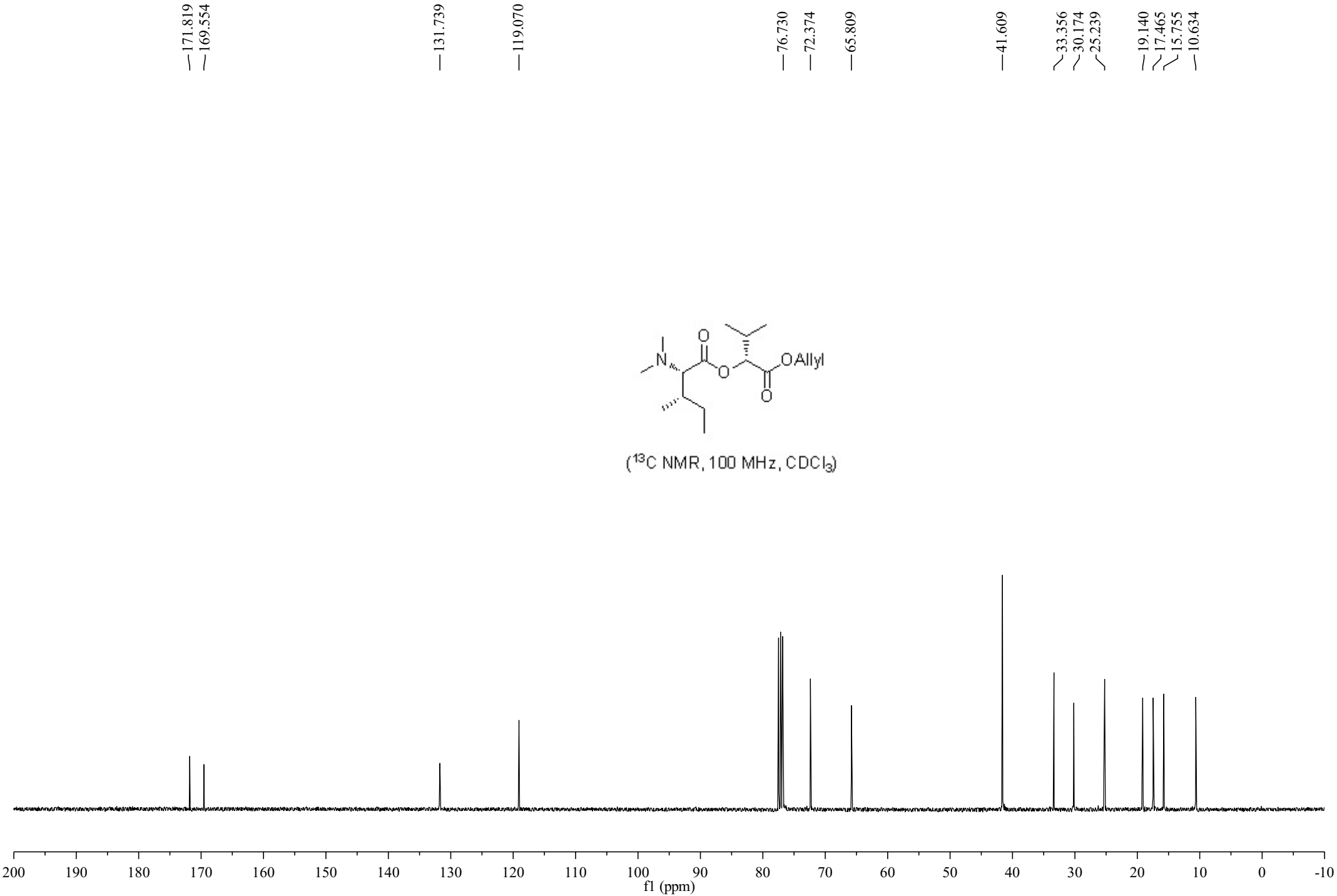

(HMBC, 600 MHz, CD3CN)
f2 (ppm)
f1 (ppm)

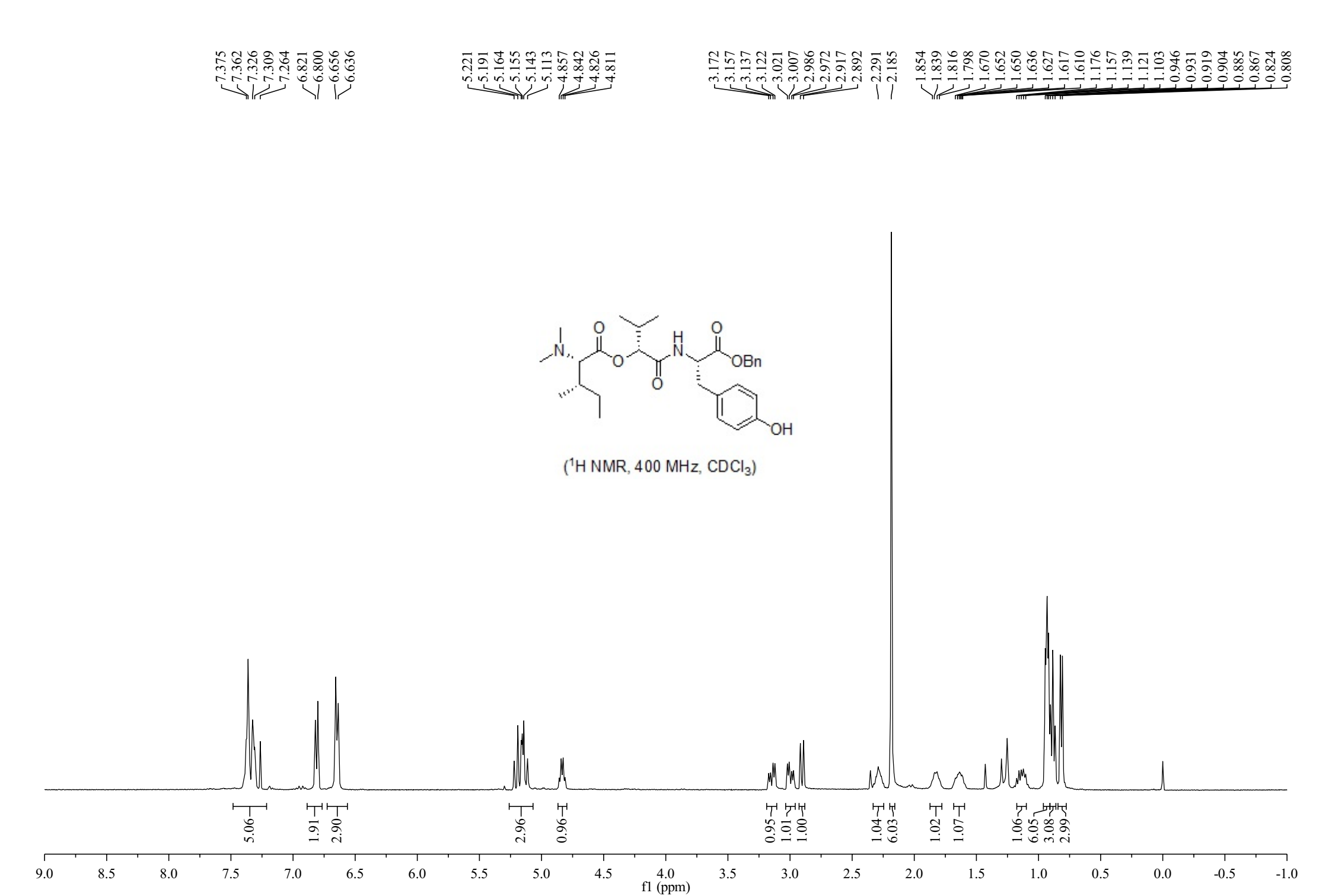

(ROESY, 600 MHz, CD3CN)
f2 (ppm)
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
1
2
3
4
5
6
7
8


5.949
5.935
5.923
5.920
5.909
5.892
5.880
5.877
5.866
5.851
5.358
5.355
5.315
5.312
5.266
5.240
5.037
5.014
4.885
4.874
4.733
4.688
4.674
4.655
4.652
4.645
4.641
4.638
4.615
4.601
4.407
4.396
4.385
4.373
2.320
2.303
2.291
2.286
2.274
2.268
2.257
2.240
1.947
1.941
1.515
1.496
1.477
1.445
1.415
1.226
1.208
1.191
1.174
1.153
1.134
1.021
1.004
0.997
0.984
0.981
0.967
0.951
0.932
0.914
BocHN
O
O
O
OAllyl
(1H NMR, 400 MHz, CDCl3)
0.93
0.97
1.00
0.96
1.06
2.17
0.96
1.07
1.06
0.95
9.04
1.12
3.04
6.06
3.01
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
f1 (ppm)

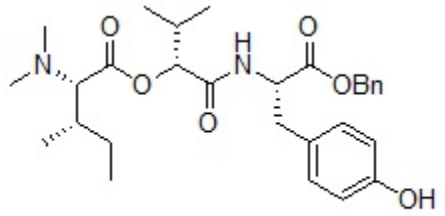

171.986
169.066
155.549
131.618
119.076
79.868
77.520
65.913
58.228
38.109
30.262
28.473
25.020
18.997
17.330
15.616
11.810
BocHN
O
O
O
OAllyl
O
(13C NMR, 100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


5.962
5.948
5.936
5.921
5.906
5.893
5.879
5.864
5.371
5.370
5.368
5.328
5.327
5.325
5.269
5.243
4.865
4.853
4.660
4.645
2.955
2.929
2.306
2.288
2.277
2.271
2.260
2.254
2.243
2.226
1.877
1.872
1.864
1.856
1.705
1.695
1.685
1.677
1.670
1.662
1.651
1.197
1.178
1.162
1.144
1.125
1.035
1.017
1.006
0.989
0.923
0.903
0.885
N
O
O
O
O
OAllyl
(1H NMR, 400 MHz, CDCl3)
0.90
1.08
1.14
1.13
2.24
1.20
1.23
1.17
1.05
1.21
3.14
3.06
3.29
3.01
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
f1 (ppm)

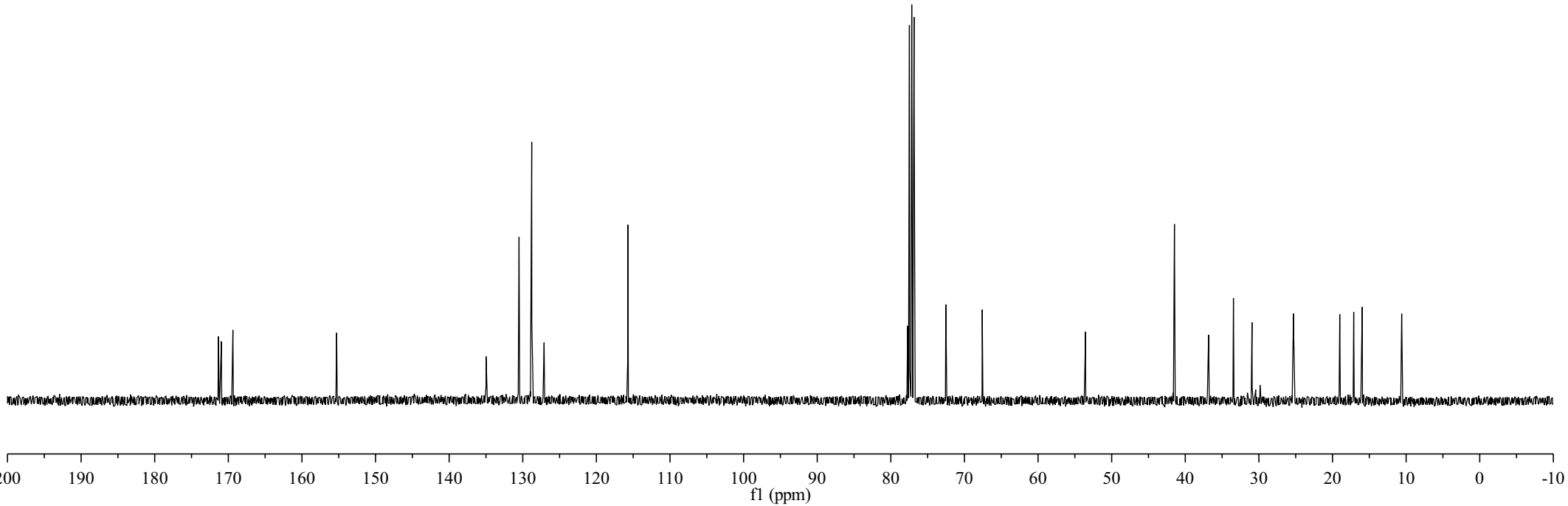

171.819
169.554
131.739
119.070
76.730
72.374
65.809
41.609
33.356
30.174
25.239
19.140
17.465
15.755
10.634
OAllyl
O
N
O
O
O
(13C NMR, 100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

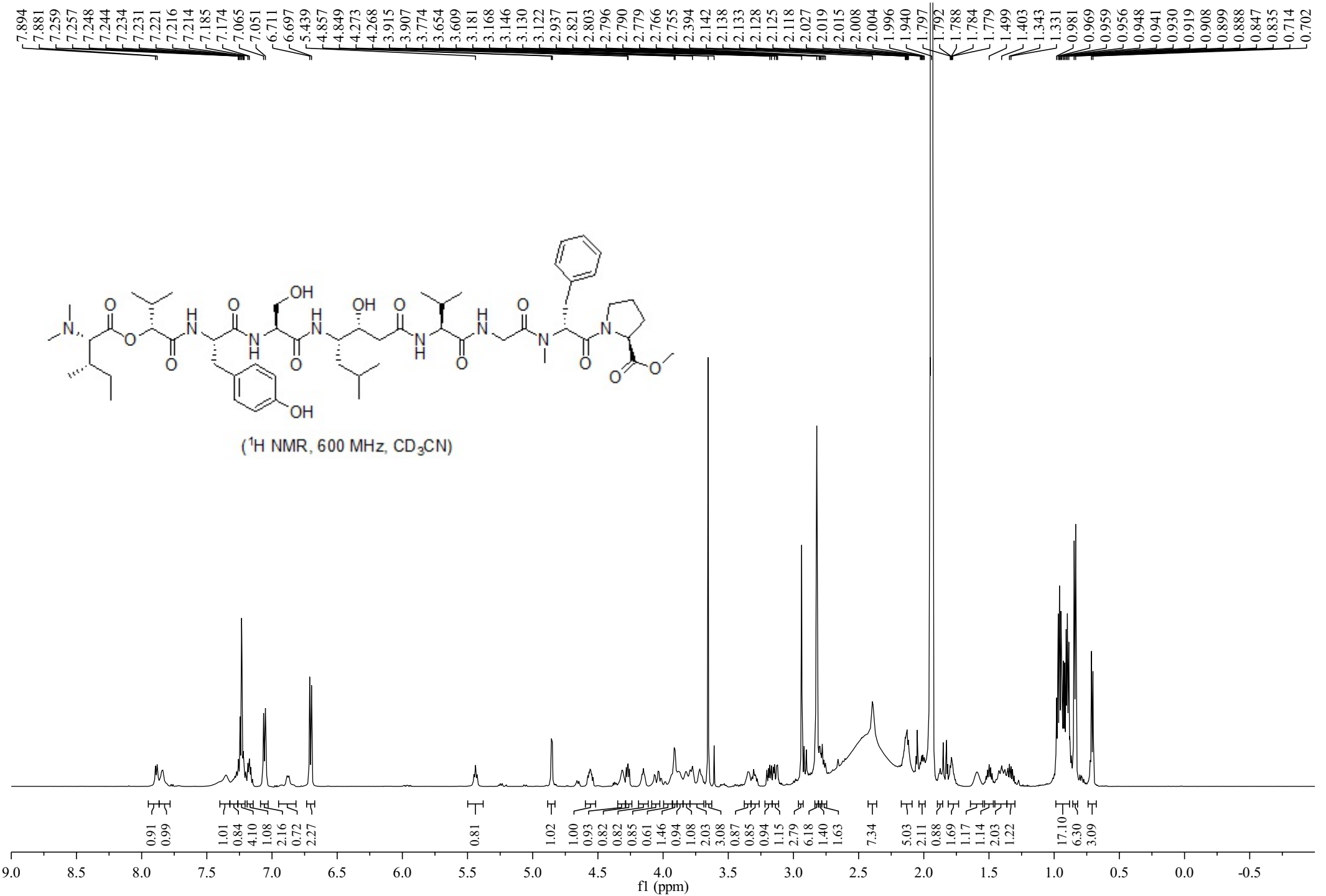

7.375
7.362
7.326
7.309
7.264
6.821
6.800
6.656
6.636
5.221
5.191
5.164
5.155
5.143
5.113
4.857
4.842
4.826
4.811
3.172
3.157
3.137
3.122
3.021
3.007
2.986
2.972
2.917
2.892
2.291
2.185
1.854
1.839
1.816
1.798
1.670
1.652
1.650
1.636
1.627
1.617
1.610
1.176
1.157
1.139
1.121
1.103
0.946
0.931
0.919
0.904
0.885
0.867
0.824
0.808
O
N
O
O
H
N
O
OBn
OH
(1H NMR, 400 MHz, CDCl3)
5.06
1.91
2.90
2.96
0.96
0.95
1.01
1.00
1.04
6.03
1.02
1.07
1.06
6.05
3.08
2.99
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
f1 (ppm)

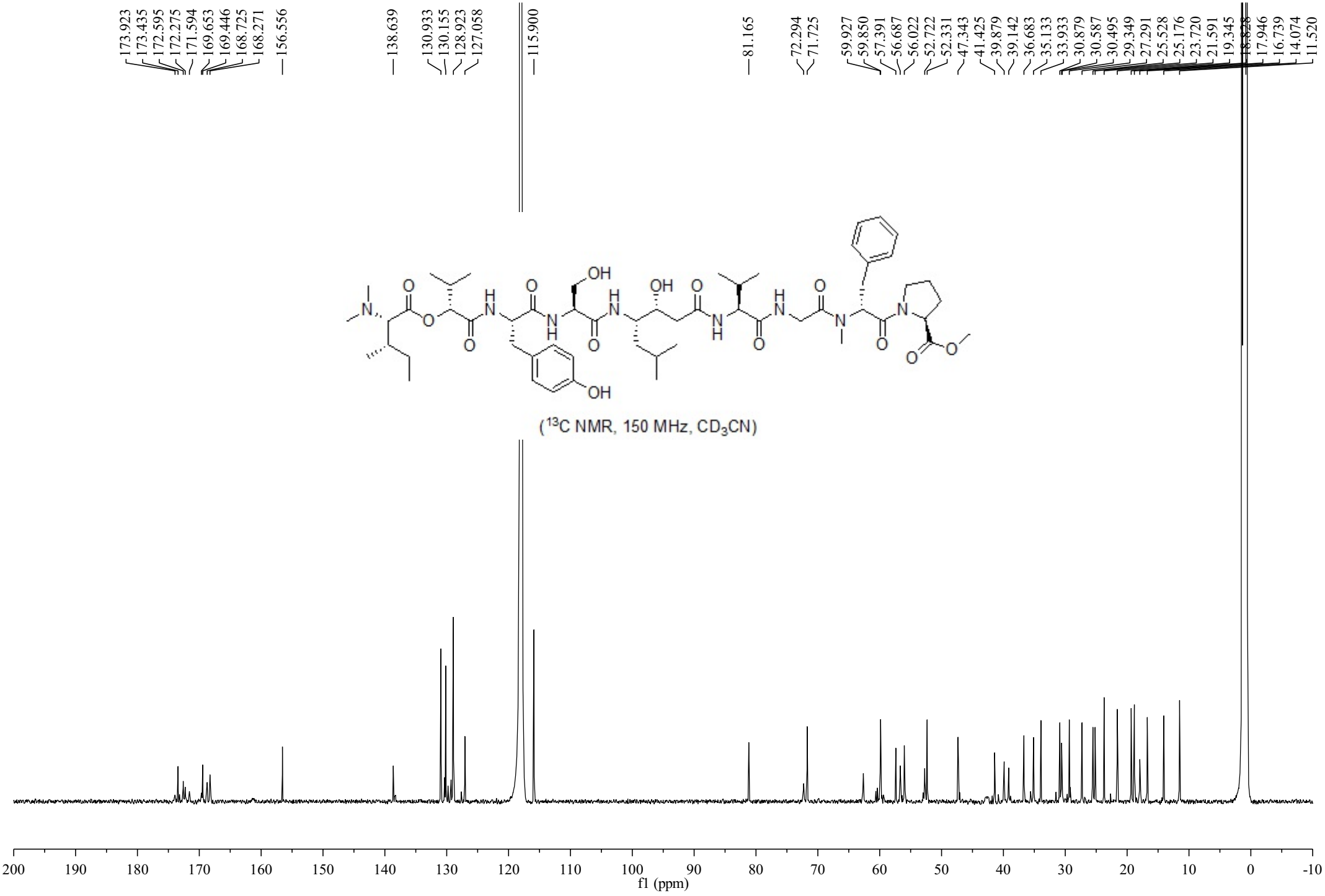
171.337
170.943
169.377
155.287
134.986
130.505
128.802
128.784
127.104
115.727
77.716
72.528
67.582
53.571
41.474
36.828
33.460
30.933
25.299
19.014
17.120
15.964
10.602

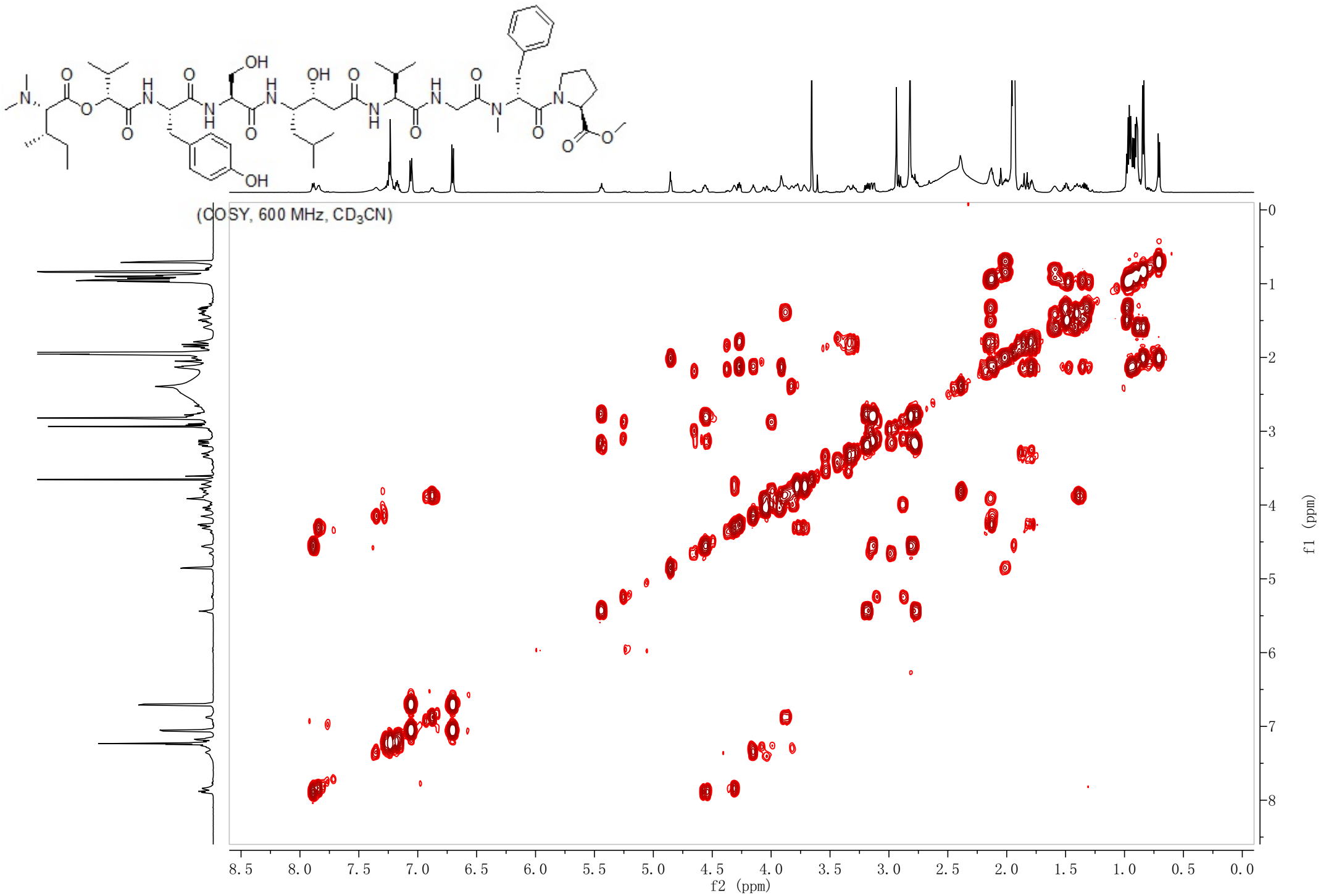


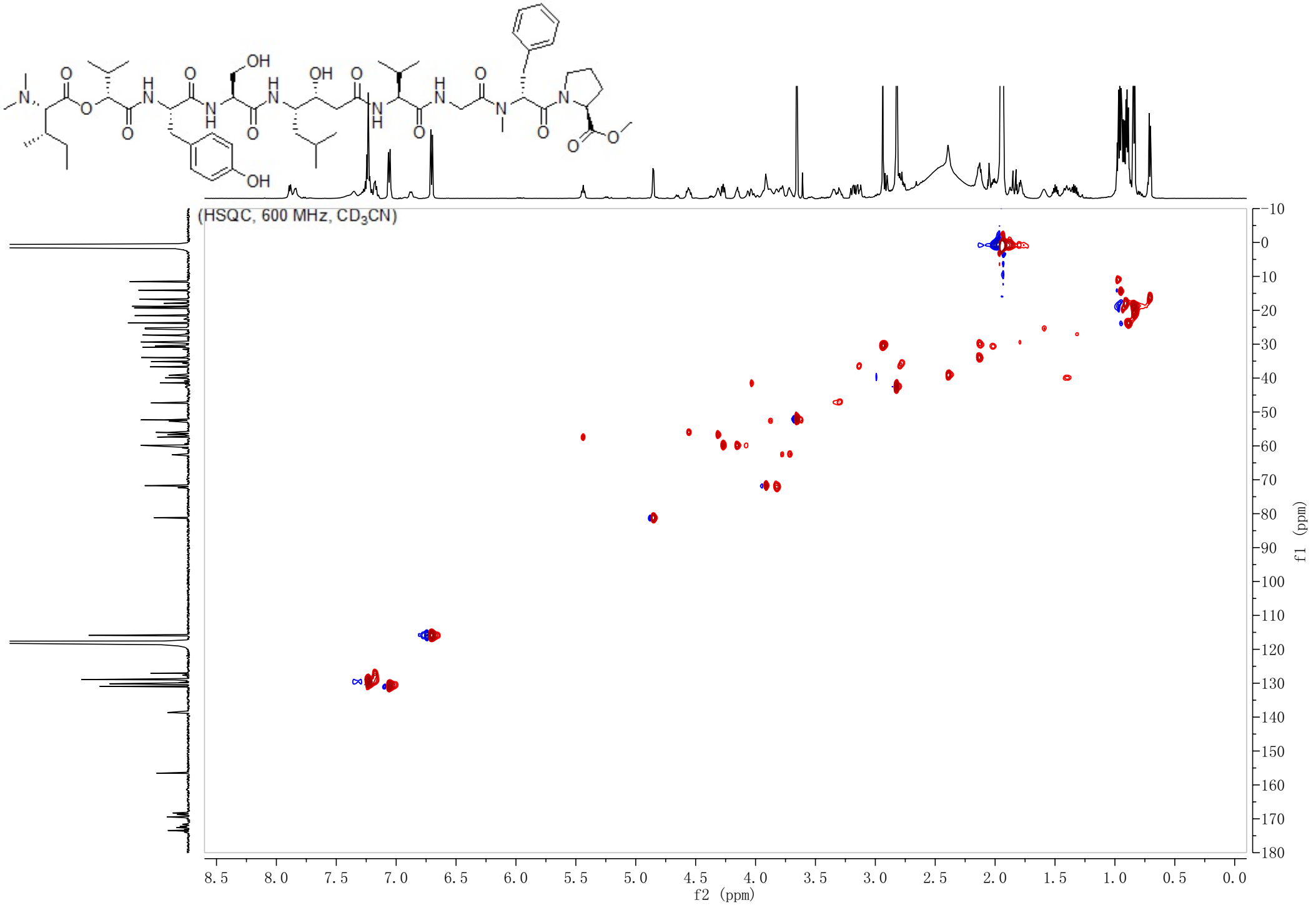
(^{13}C NMR, 100 MHz, $CDCl_3$)

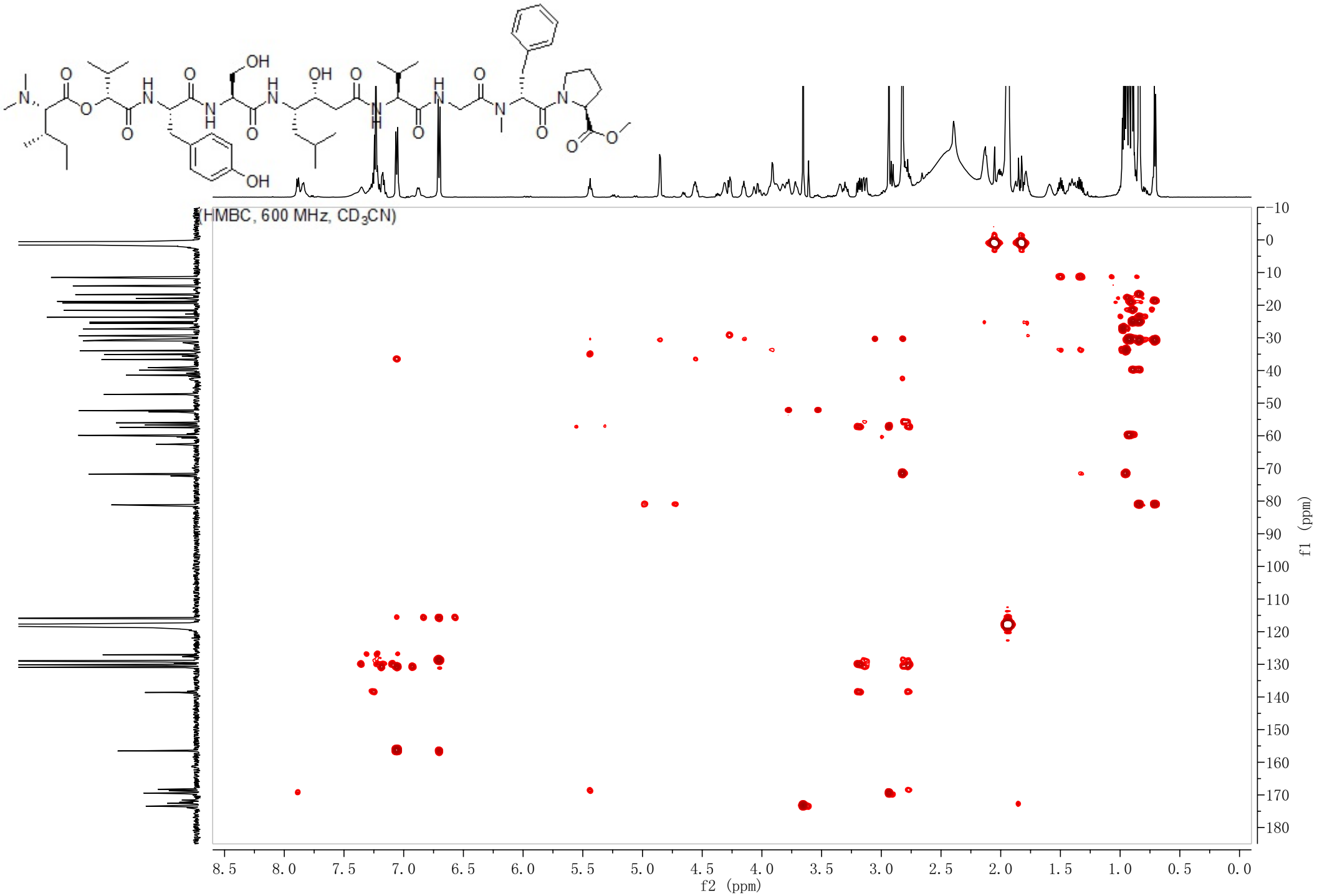


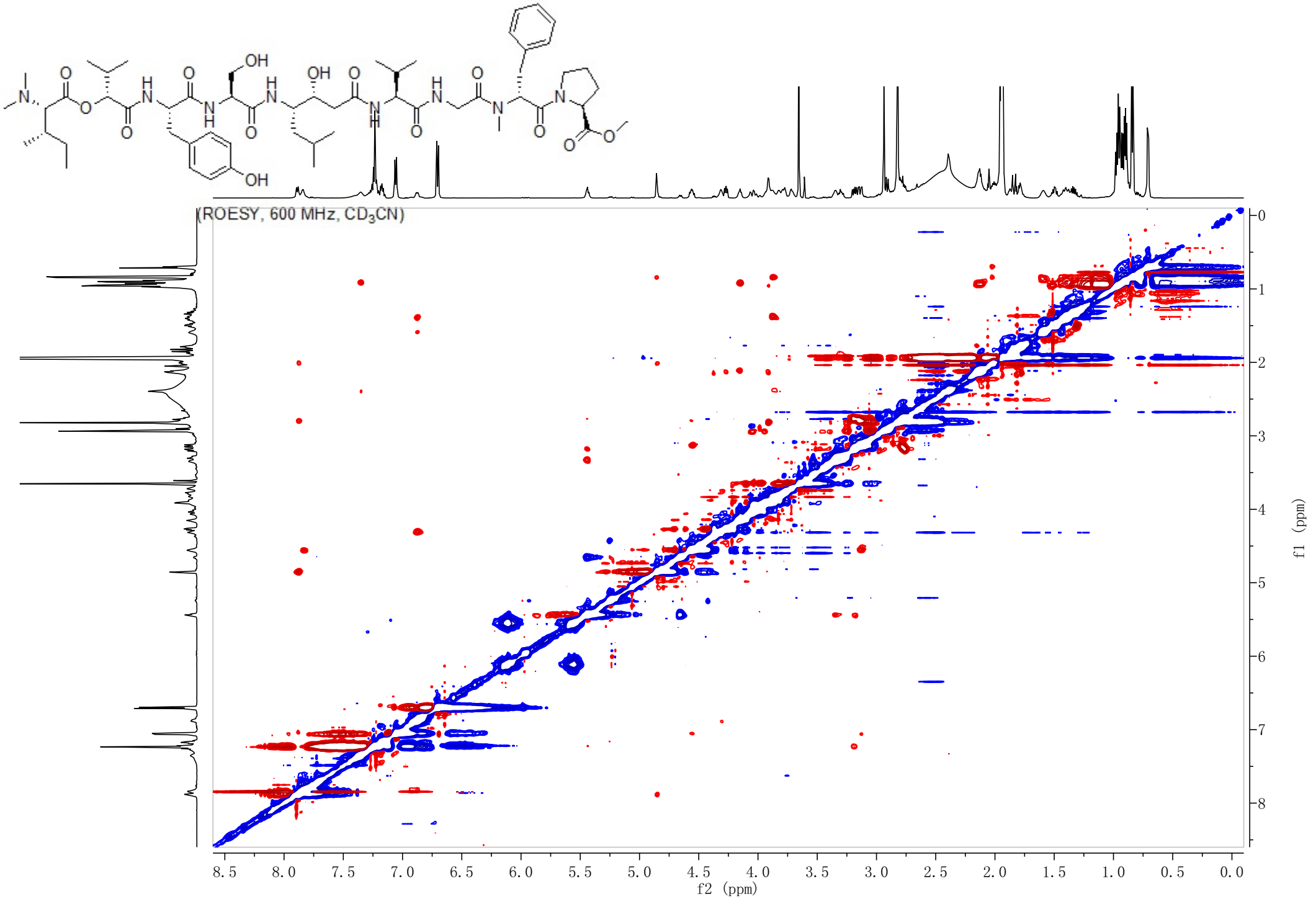

7.894
7.881
7.259
7.257
7.248
7.244
7.234
7.231
7.221
7.216
7.214
7.185
7.174
7.065
7.051
6.711
6.697
5.439
4.857
4.849
4.273
4.268
3.915
3.907
3.774
3.654
3.609
3.181
3.168
3.146
3.130
3.122
2.937
2.821
2.803
2.796
2.790
2.779
2.766
2.755
2.394
2.142
2.138
2.133
2.128
2.125
2.118
2.027
2.019
2.015
2.008
2.004
1.996
1.940
1.797
1.792
1.788
1.784
1.779
1.499
1.403
1.343
1.331
0.981
0.969
0.959
0.956
0.948
0.941
0.930
0.919
0.908
0.899
0.888
0.847
0.835
0.714
0.702
OH
OH
OH
(^{1}H NMR, 600 MHz, CD_3CN)
0.91
0.99
1.01
0.84
4.10
1.08
2.16
0.72
2.27
0.81
1.02
1.00
0.93
0.82
0.82
0.85
0.61
1.46
0.94
1.08
2.03
3.08
0.87
0.85
0.94
1.15
2.79
6.18
1.40
1.63
7.34
5.03
2.11
0.88
1.69
1.17
1.14
2.03
1.22
17.10
6.30
3.09
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)

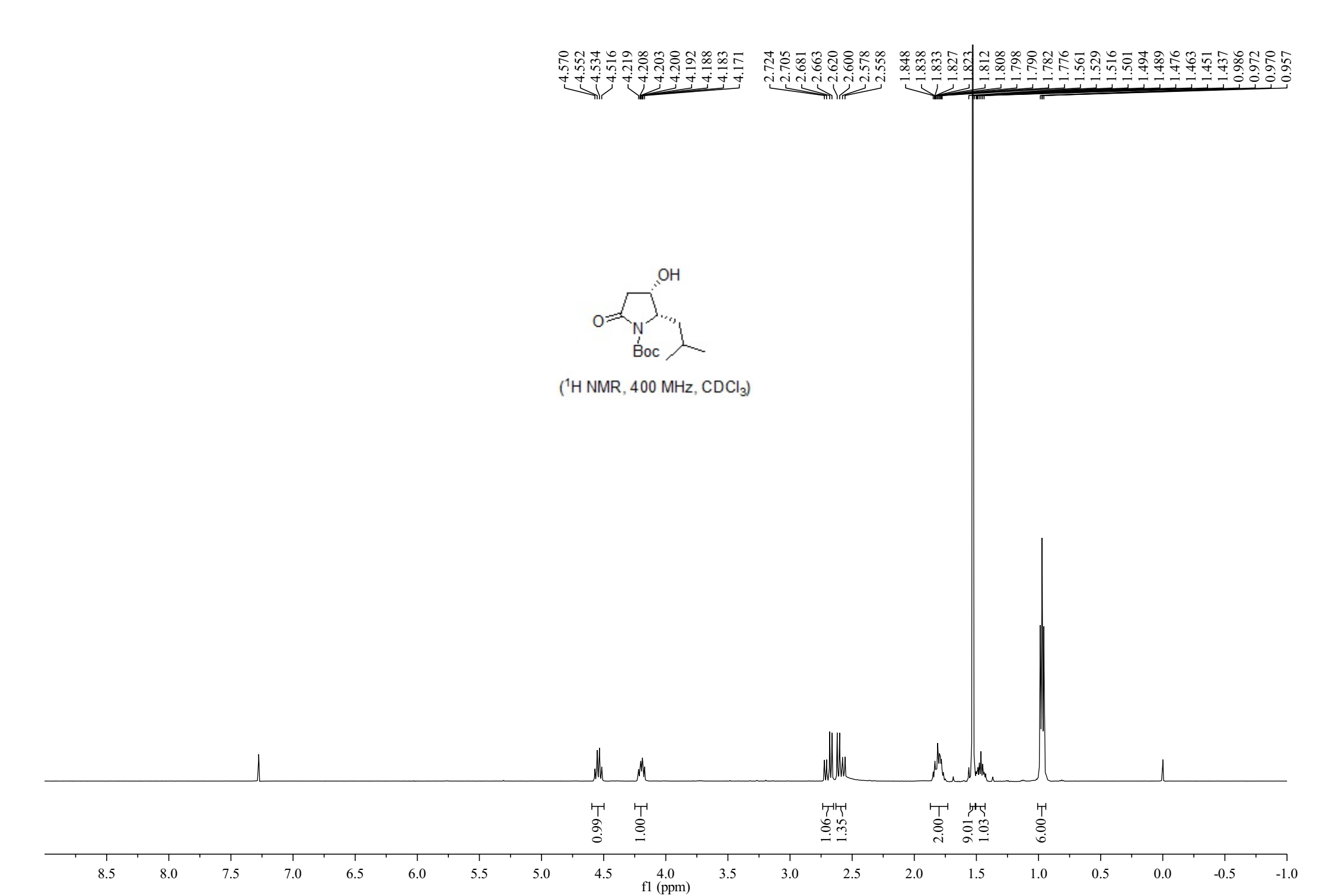

173.923
173.435
172.595
172.275
171.594
169.653
169.446
168.725
168.271
156.556
138.639
130.933
130.155
128.923
127.058
115.900
81.165
72.294
71.725
59.927
59.850
57.391
56.687
56.022
52.722
52.331
47.343
41.425
39.879
39.142
36.683
35.133
33.933
30.879
30.587
30.495
29.349
27.291
25.528
25.176
23.720
21.591
19.345
17.946
16.739
14.074
11.520
OH
OH
OH
(^{13}C NMR, 150 MHz, CD_3CN)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

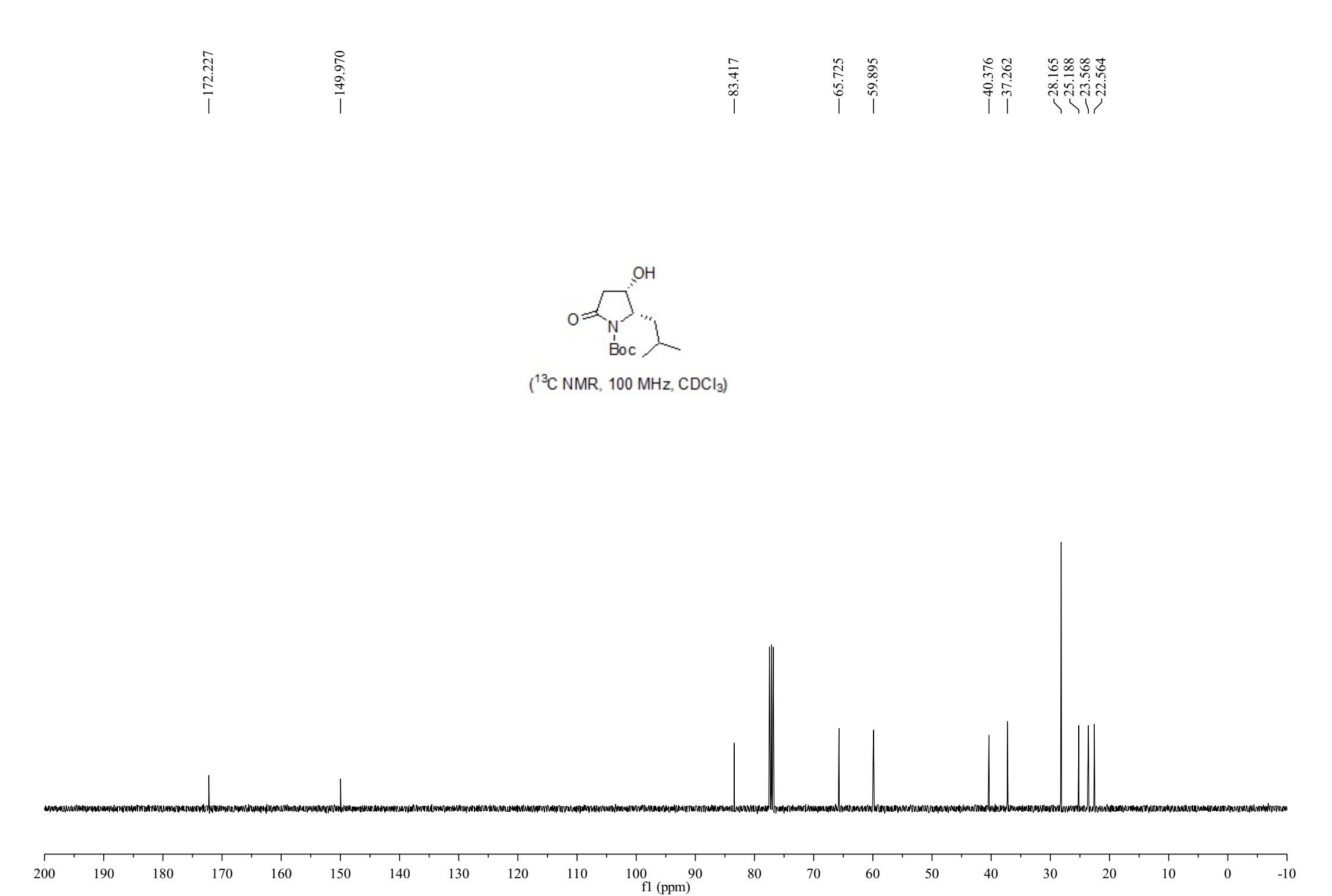

(COSY, 600 MHz, CD_3CN)
f2 (ppm)
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
1
2
3
4
5
6
7
8

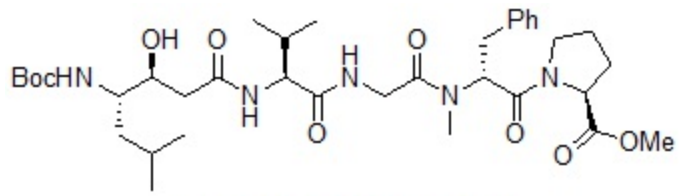

(HSQC, 600 MHz, CD3CN)
f2 (ppm)
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180


HMBC, 600 MHz, CD3CN)
f2 (ppm)
f1 (ppm)

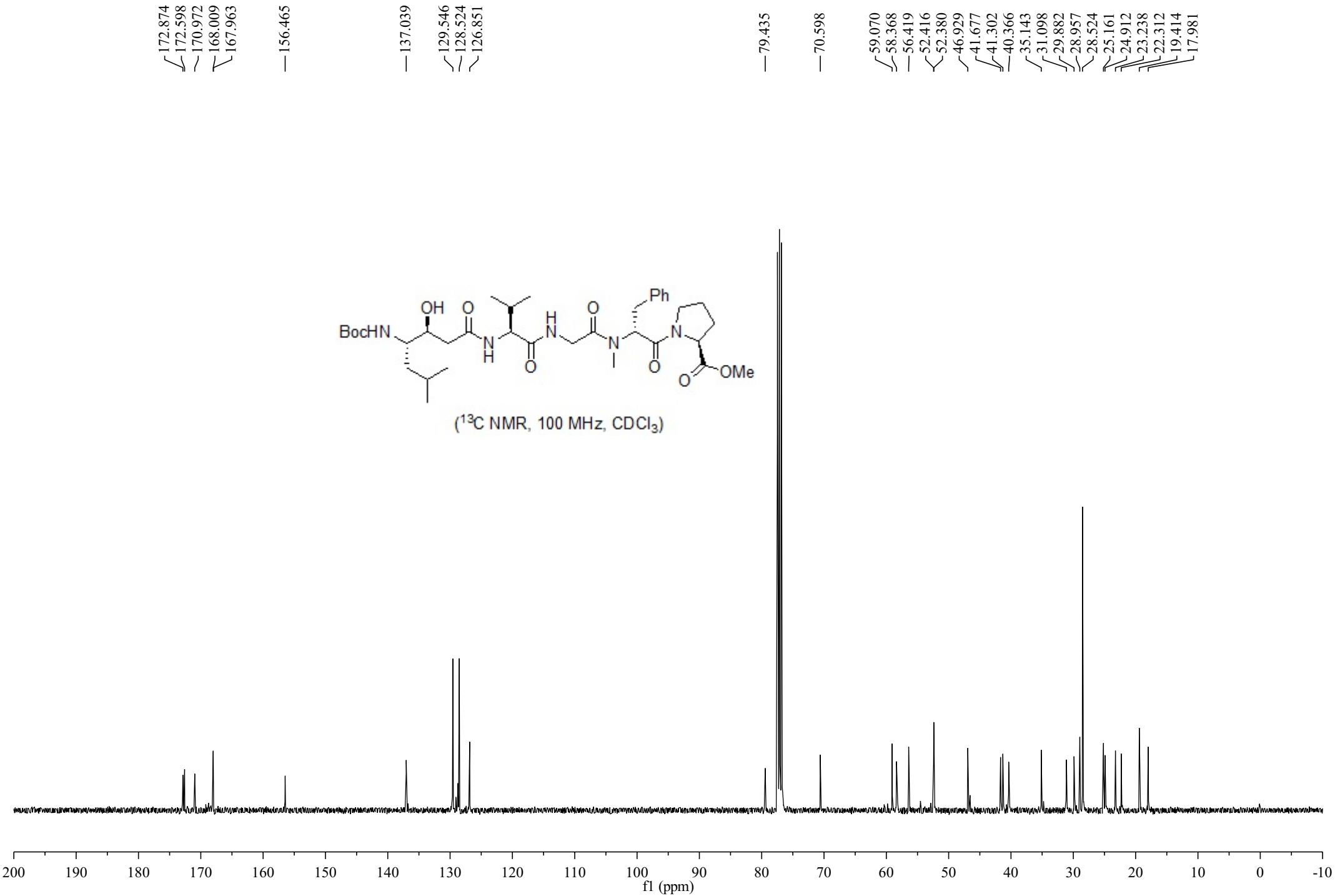

(ROESY, 600 MHz, CD3CN)
f2 (ppm)
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
1
2
3
4
5
6
7
8

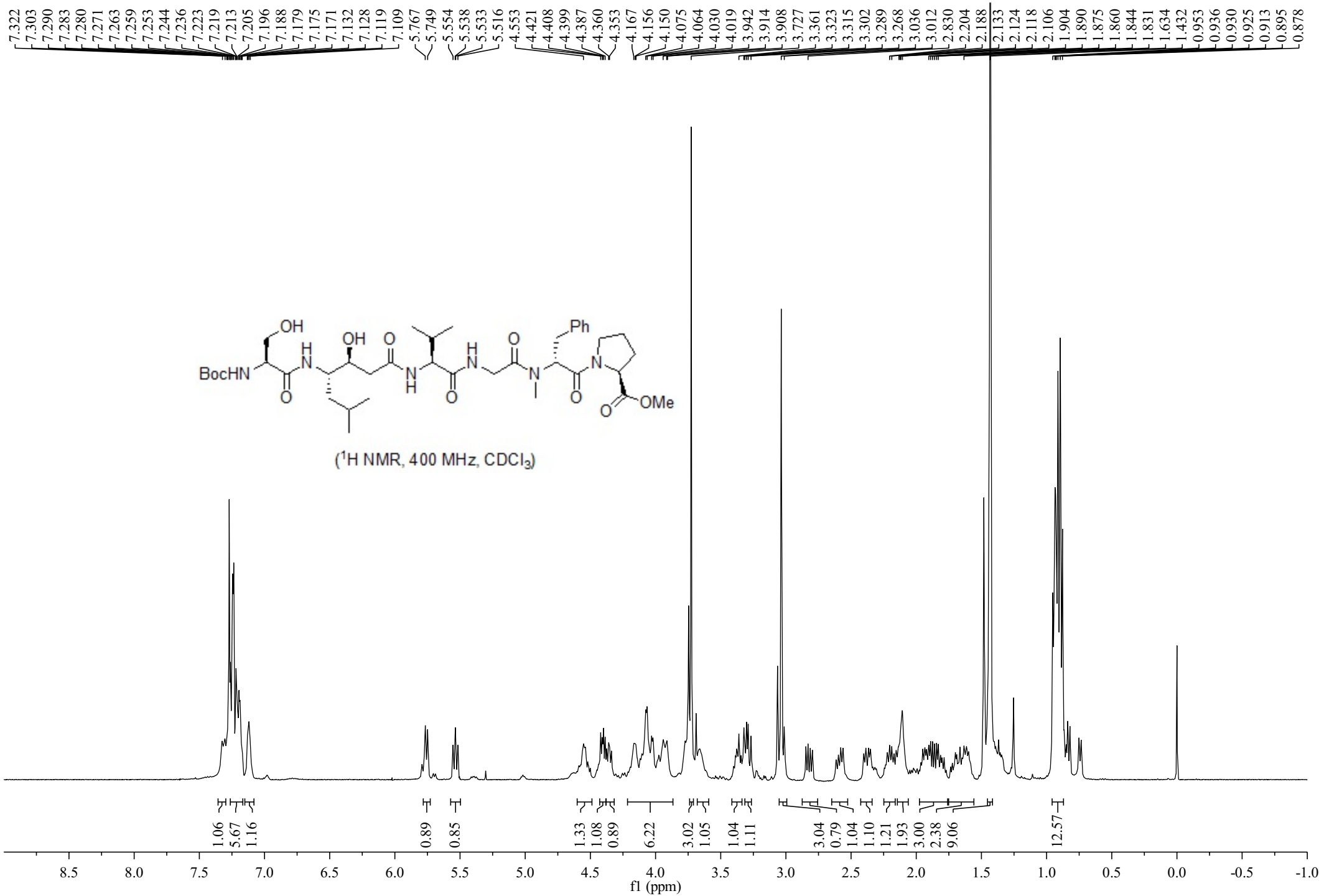

4.570
4.552
4.534
4.516
4.219
4.208
4.203
4.200
4.192
4.188
4.183
4.171
2.724
2.705
2.681
2.663
2.620
2.600
2.578
2.558
1.848
1.838
1.833
1.827
1.823
1.812
1.808
1.798
1.790
1.782
1.776
1.561
1.529
1.516
1.501
1.494
1.489
1.476
1.463
1.451
1.437
0.986
0.972
0.970
0.957
OH
O
N
Boc
(1H NMR, 400 MHz, CDCl3)
0.99
1.00
1.06
1.35
2.00
9.01
1.03
6.00
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
f1 (ppm)

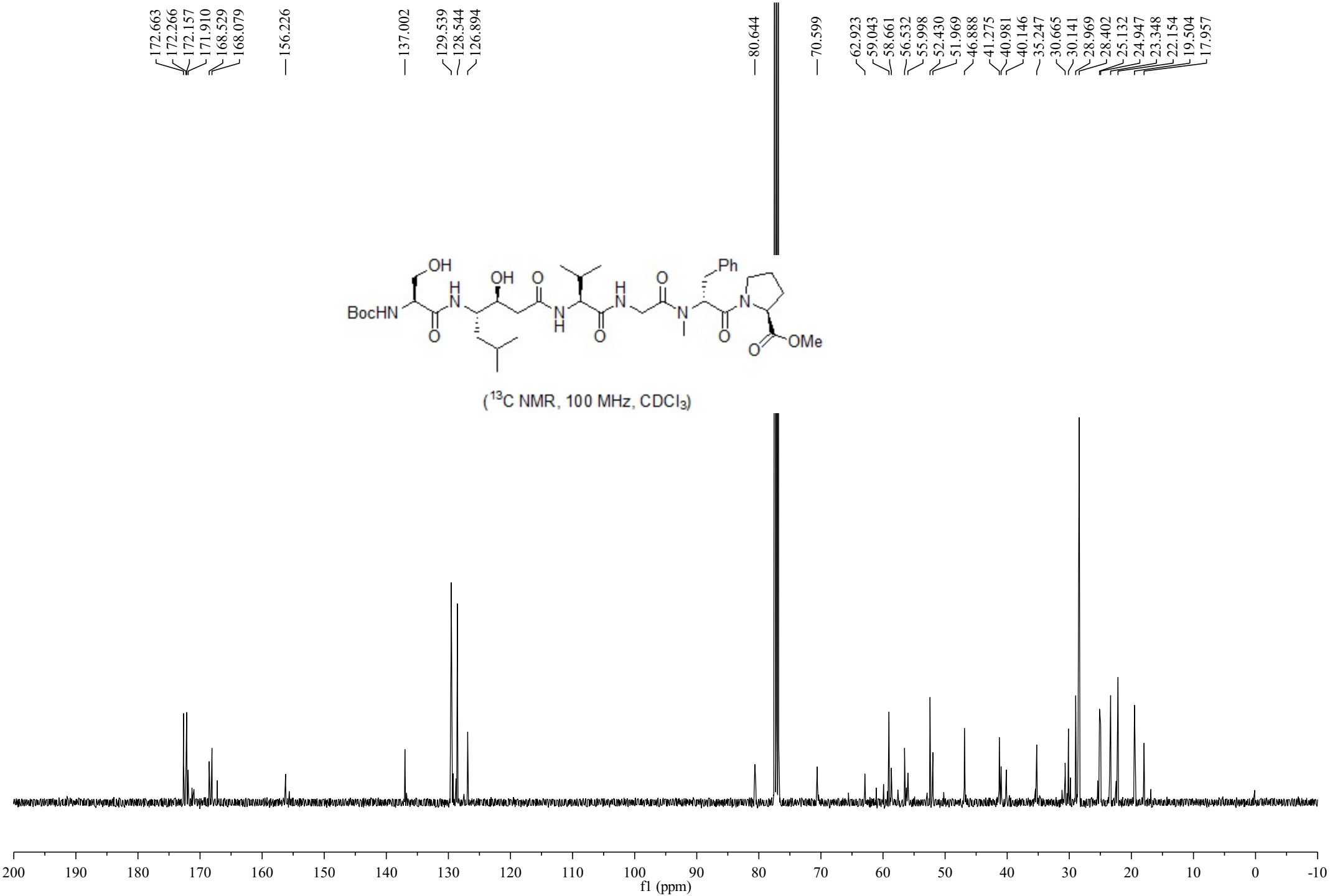

172.227
149.970
83.417
65.725
59.895
40.376
37.262
28.165
25.188
23.568
22.564
OH
O
N
Boc
(13C NMR, 100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

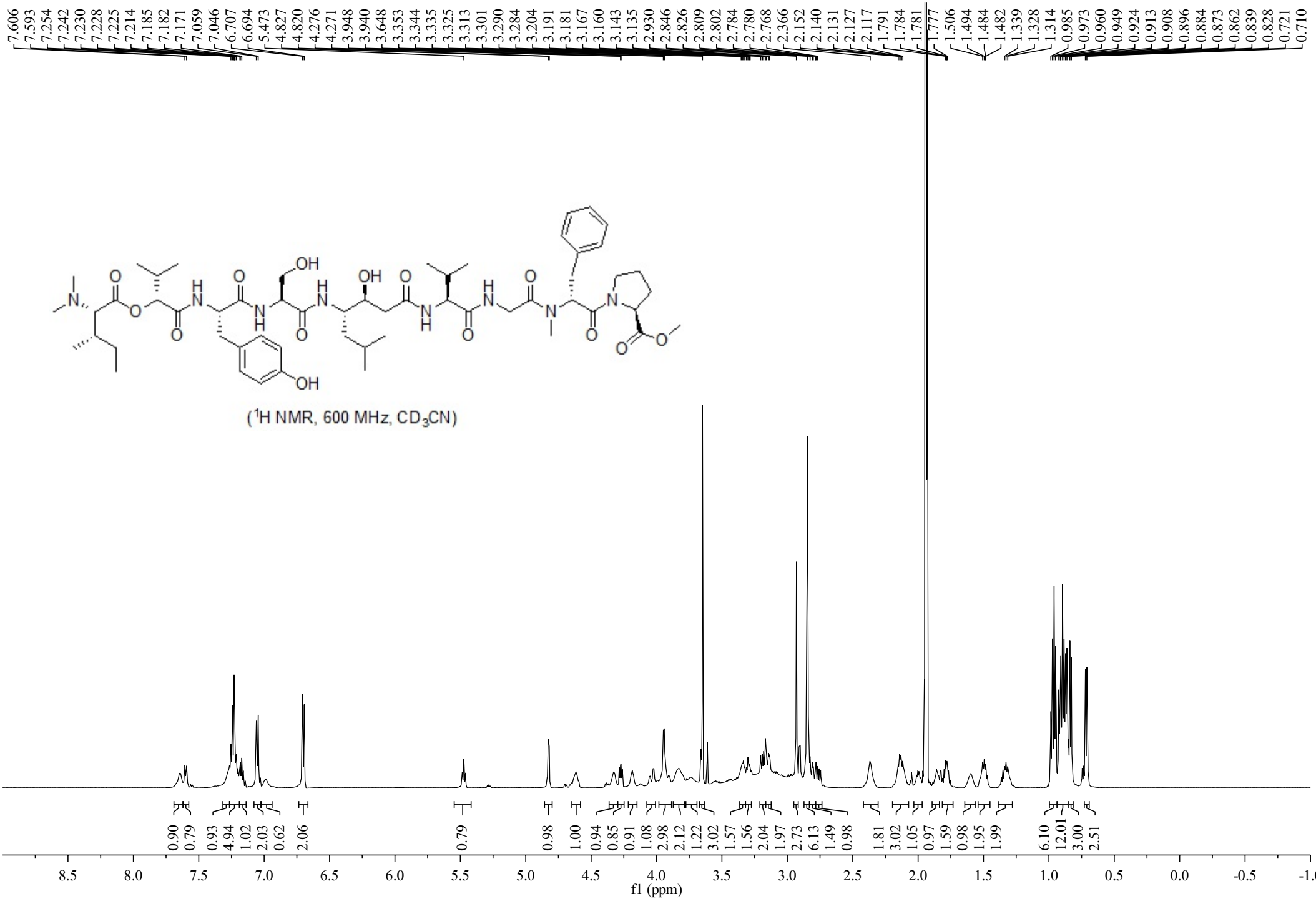


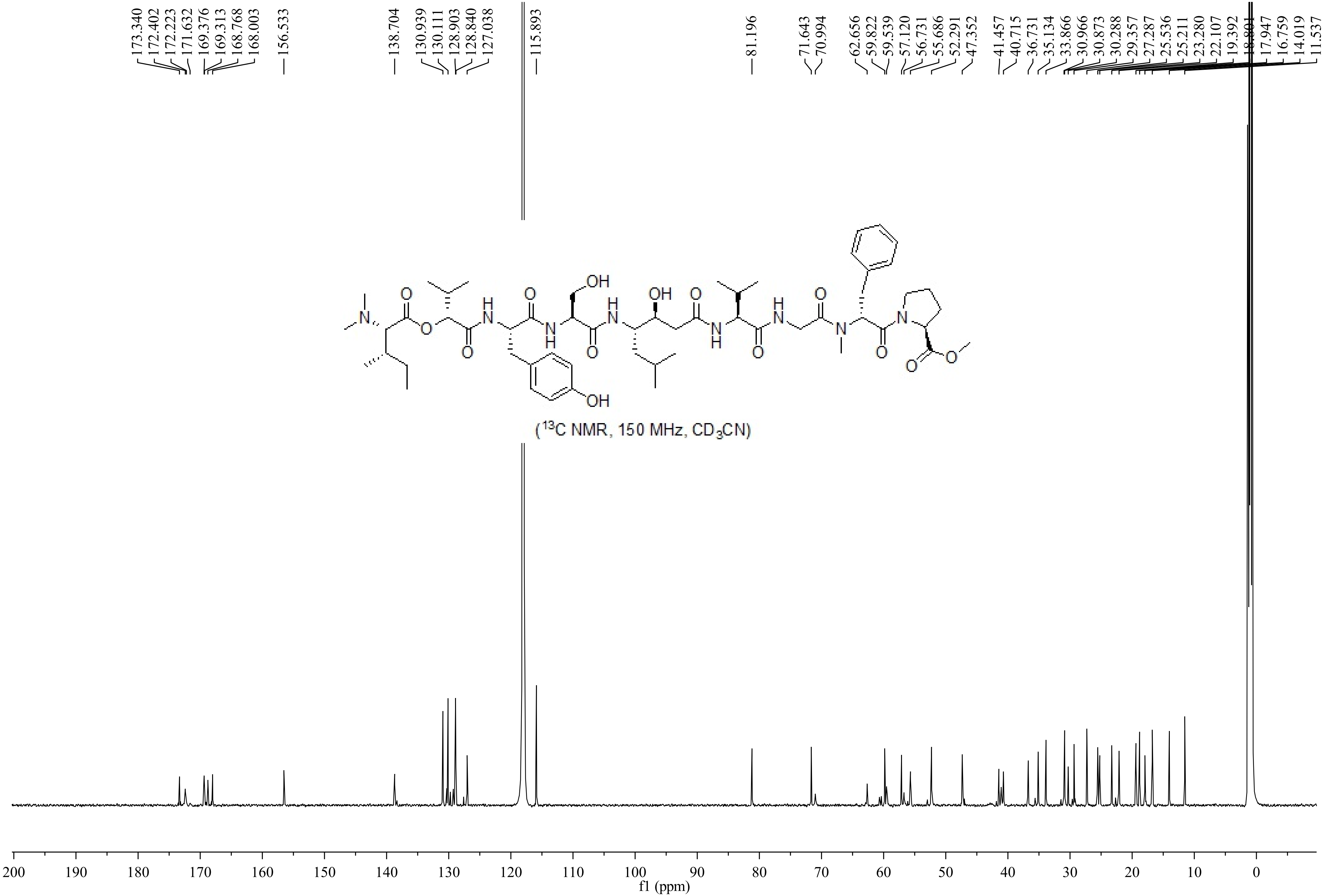
(^{1}H NMR, 400 MHz, $CDCl_3$)

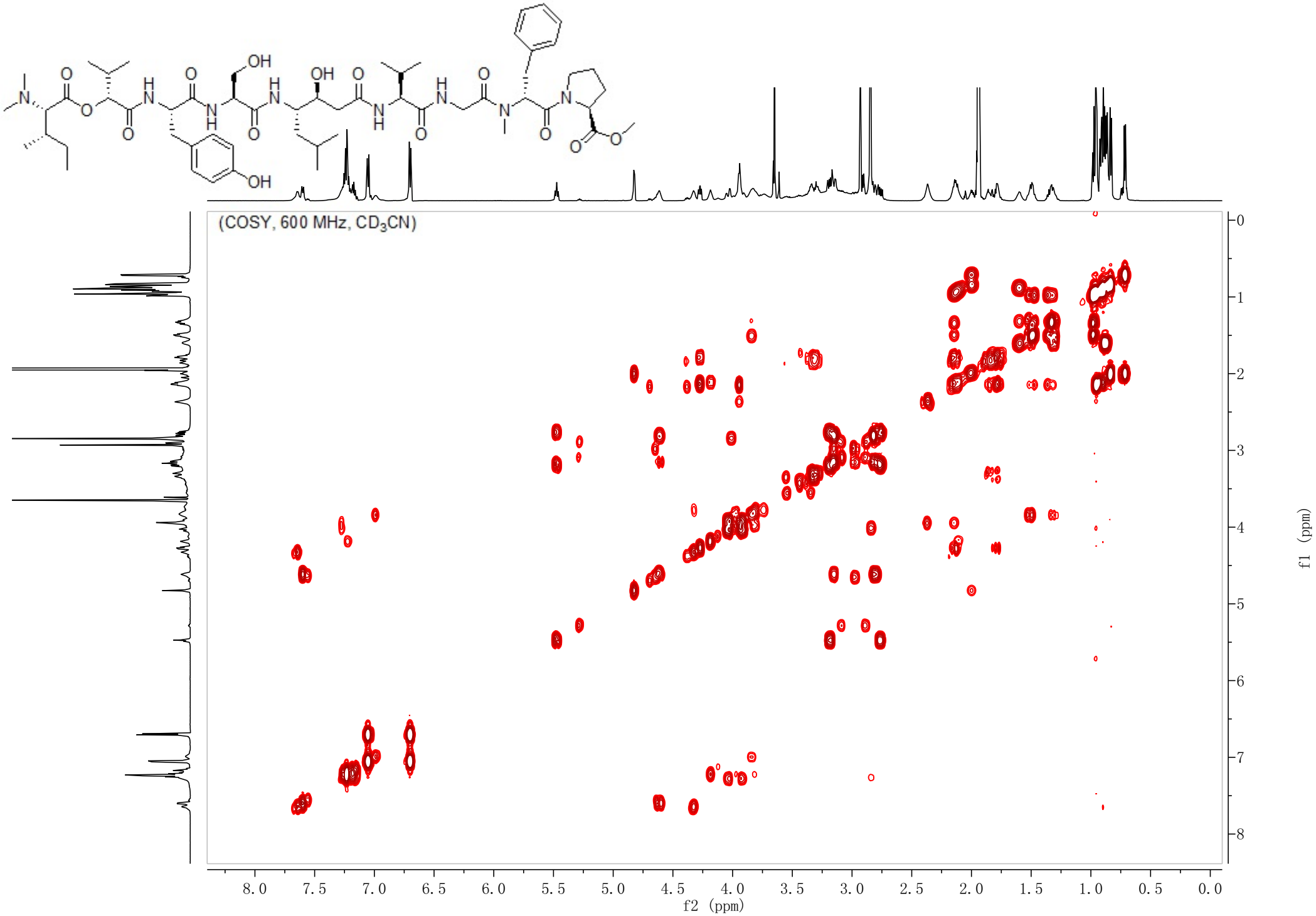

172.874
172.598
170.972
168.009
167.963
156.465
137.039
129.546
128.524
126.851
79.435
70.598
59.070
58.368
56.419
52.416
52.380
46.929
41.677
41.302
40.366
35.143
31.098
29.882
28.957
28.524
25.161
24.912
23.238
22.312
19.414
17.981
BocHN
OH
O
N
H
O
H
N
O
N
O
Ph
N
O
O
OMe
(^{13}C NMR, 100 MHz, $CDCl_3$)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

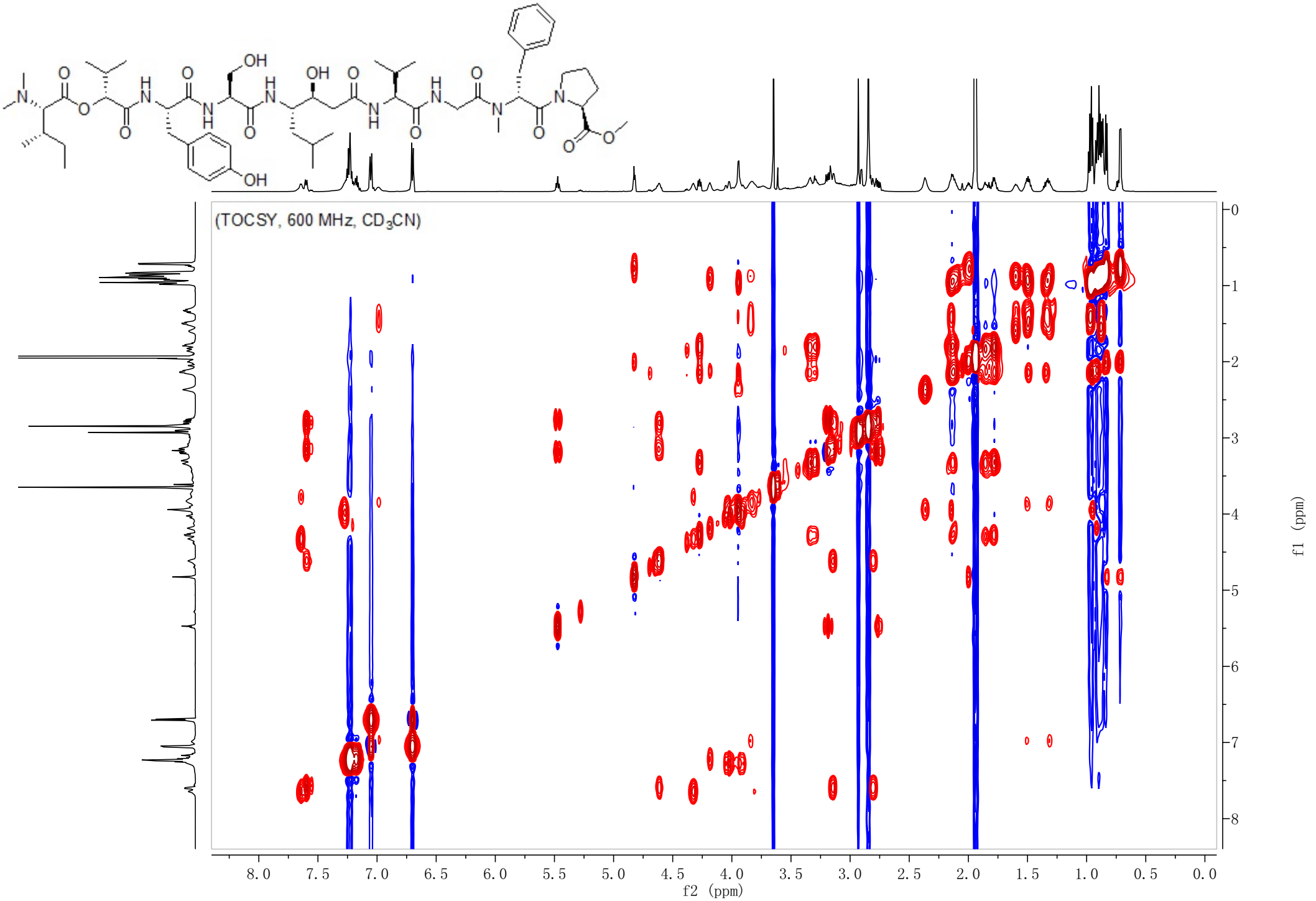

7.322 7.303 7.290 7.283 7.280 7.271 7.263 7.259 7.253 7.244 7.236 7.223 7.219 7.213 7.205 7.196 7.188 7.179 7.175 7.171 7.132 7.128 7.119 7.109
5.767 5.749 5.554 5.538 5.533 5.516
4.553 4.421 4.408 4.399 4.387 4.360 4.353
4.167 4.156 4.150 4.075 4.064 4.030 4.019 3.942 3.914 3.908 3.727 3.361 3.323 3.315 3.302 3.289 3.268 3.036 3.012 2.830 2.204 2.188
2.133 2.124 2.118 2.106 1.904 1.890 1.875 1.860 1.844 1.831 1.634 1.432 0.953 0.936 0.930 0.925 0.913 0.895 0.878
OH
OH
O
Ph
BocHN
H
N
O
N
H
O
H
N
O
N
N
O
O
OMe
O
(1H NMR, 400 MHz, CDCl3)
1.06 5.67 1.16 0.89 0.85 1.33 1.08 0.89 6.22 3.02 1.05 1.04 1.11 3.04 0.79 1.04 1.10 1.21 1.93 3.00 2.38 9.06 12.57
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
f1 (ppm)

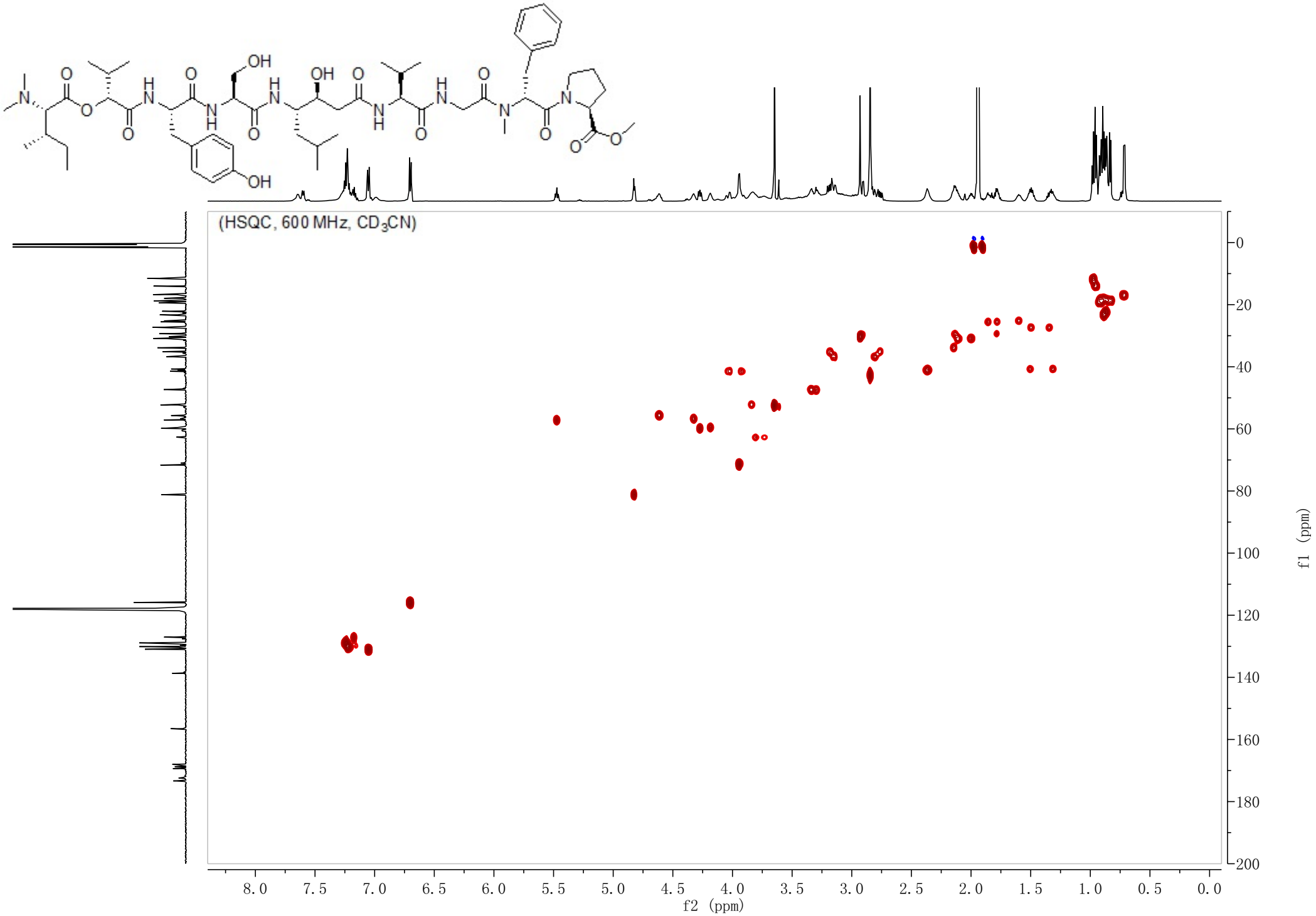

172.663
172.266
172.157
171.910
168.529
168.079
156.226
137.002
129.539
128.544
126.894
80.644
70.599
62.923
59.043
58.661
56.532
55.998
52.430
51.969
46.888
41.275
40.981
40.146
35.247
30.665
30.141
28.969
28.402
25.132
24.947
23.348
22.154
19.504
17.957
BocHN
OH
OH
Ph
OMe
(^{13}C NMR, 100 MHz, $CDCl_3$)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

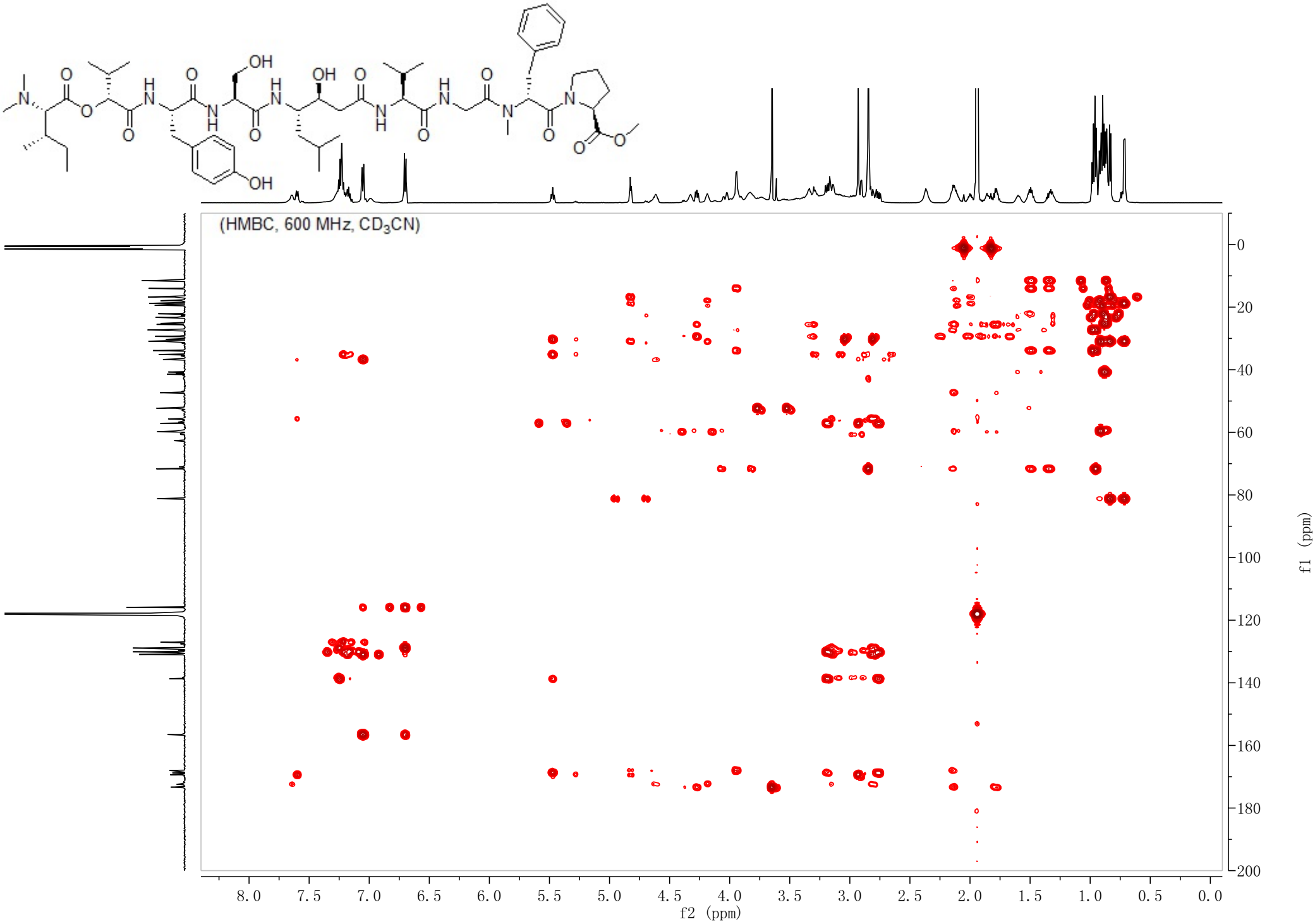

7.606
7.593
7.254
7.242
7.230
7.228
7.225
7.214
7.185
7.182
7.171
7.059
7.046
6.707
6.694
5.473
4.827
4.820
4.276
4.271
3.948
3.940
3.648
3.353
3.344
3.335
3.325
3.313
3.301
3.290
3.284
3.204
3.191
3.181
3.167
3.160
3.143
3.135
2.930
2.846
2.826
2.809
2.802
2.784
2.780
2.768
2.366
2.152
2.140
2.131
2.127
2.117
1.791
1.784
1.781
1.777
1.506
1.494
1.484
1.482
1.339
1.328
1.314
0.985
0.973
0.960
0.949
0.924
0.913
0.908
0.896
0.884
0.873
0.862
0.839
0.828
0.721
0.710
OH
OH
OH
(^{1}H NMR, 600 MHz, CD_3CN)
0.90
0.79
0.93
4.94
1.02
2.03
0.62
2.06
0.79
0.98
1.00
0.94
0.85
0.91
1.08
2.98
2.12
1.22
3.02
1.57
1.56
2.04
1.97
2.73
6.13
1.49
0.98
1.81
3.02
1.05
0.97
1.59
0.98
1.95
1.99
6.10
12.01
3.00
2.51
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
f1 (ppm)

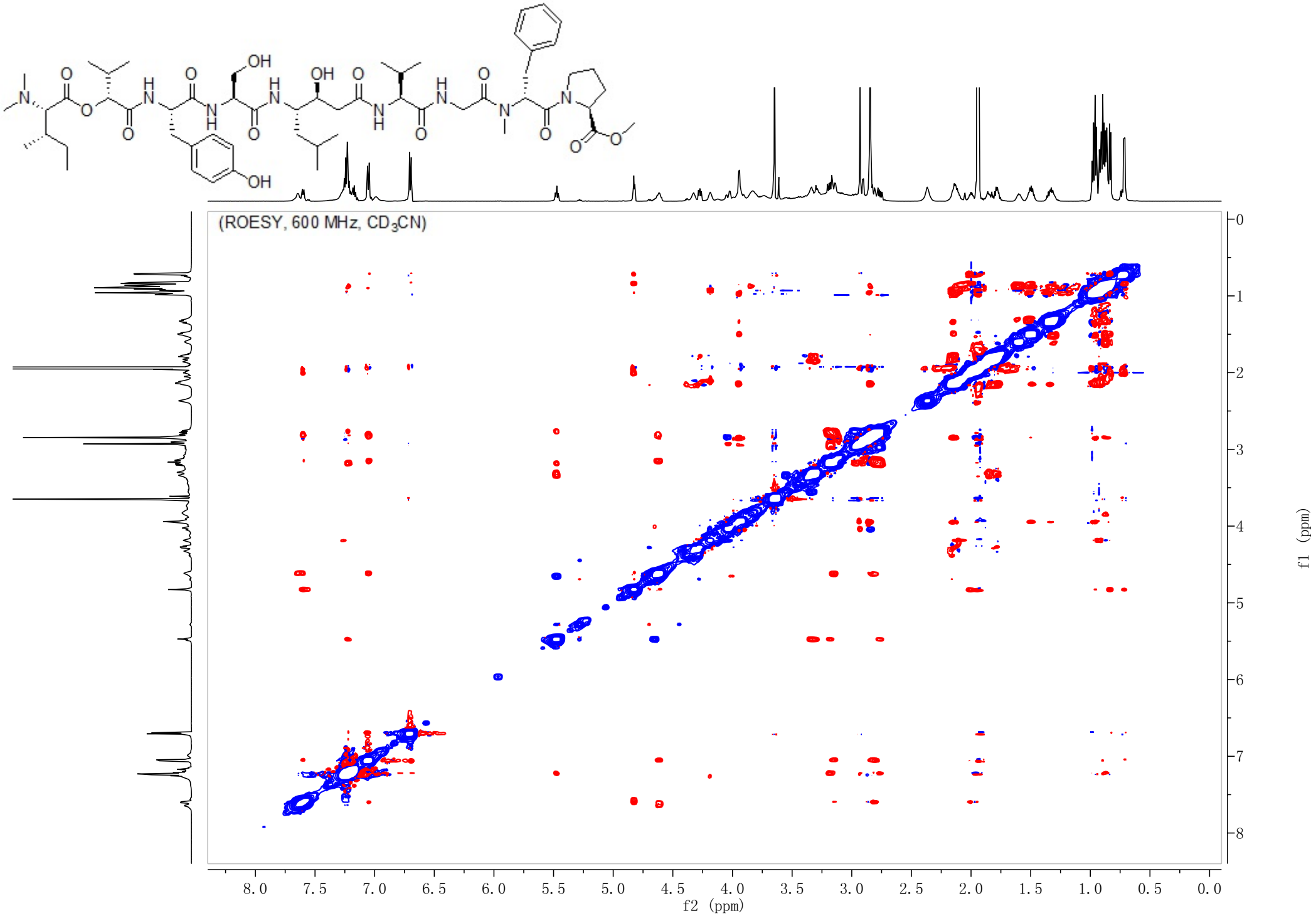

173.340
172.402
172.223
171.632
169.376
169.313
168.768
168.003
156.533
138.704
130.939
130.111
128.903
128.840
127.038
115.893
81.196
71.643
70.994
62.656
59.822
59.539
57.120
56.731
55.686
52.291
47.352
41.457
40.715
36.731
35.134
33.866
30.966
30.873
30.288
29.357
27.287
25.536
25.211
23.280
22.107
19.392
18.801
17.947
16.759
14.019
11.537
(^{13}C NMR, 150 MHz, CD_3CN)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

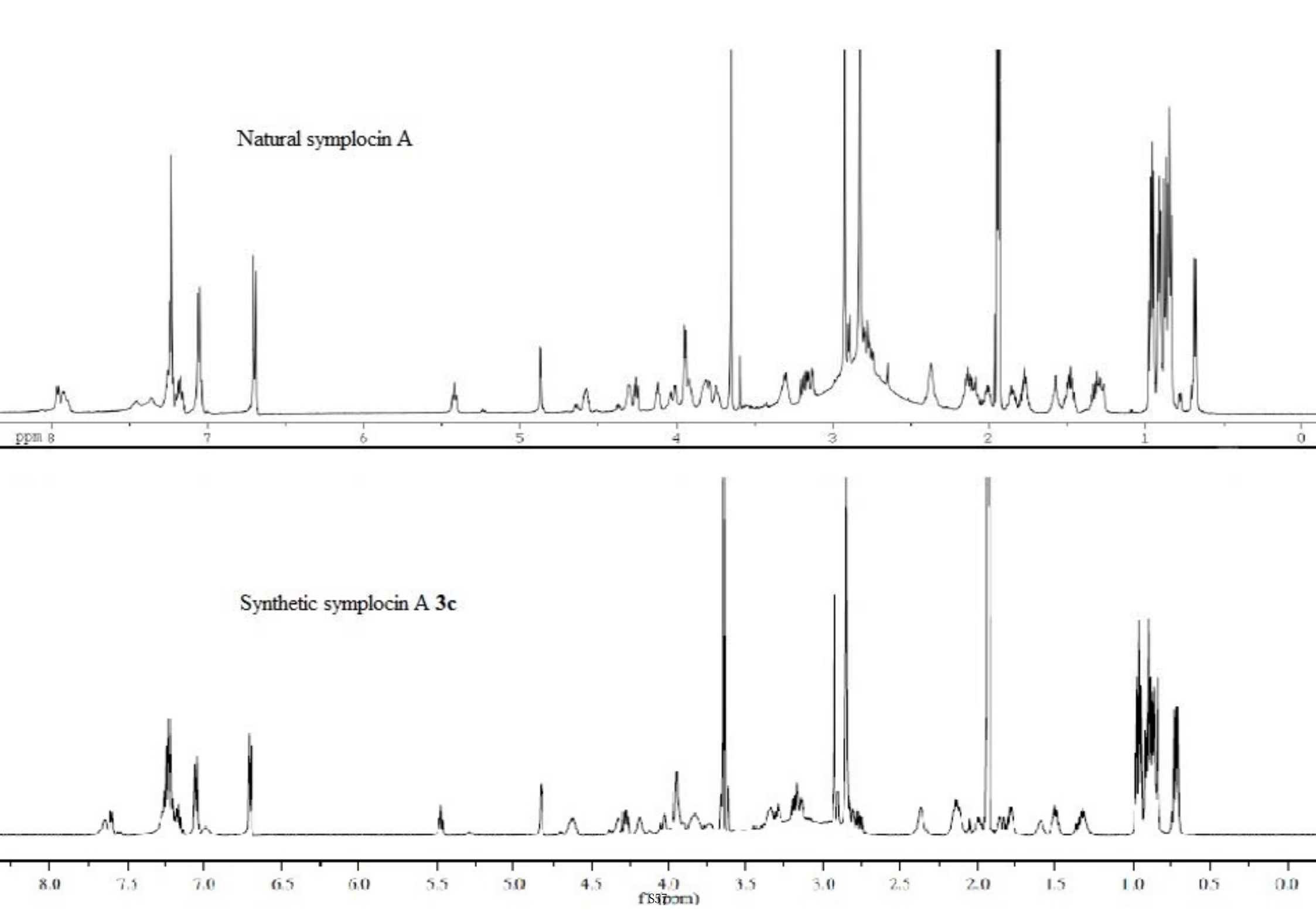

(COSY, 600 MHz, CD3CN)
f2 (ppm)
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
1
2
3
4
5
6
7
8


(TOCSY, 600 MHz, CD3CN)
f2 (ppm)
f1 (ppm)


(HSQC, 600 MHz, CD3CN)
f2 (ppm)
f1 (ppm)
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
20
40
60
80
100
120
140
160
180
200


(HMBC, 600 MHz, CD3CN)
f2 (ppm)
f1 (ppm)
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
20
40
60
80
100
120
140
160
180
200


(ROESY, 600 MHz, CD3CN)
f2 (ppm)
f1 (ppm)
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
1
2
3
4
5
6
7
8


Natural symplocin A
ppm 8
7
6
5
4
3
2
1
0
Synthetic symplocin A 3c
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)