SUPPORTING INFORMATION FOR:

A Formal Total Synthesis of (±)-Kopsihainanine A Using a Raney-Cobalt Mediated Reductive Cyclization Route to Polyhydroquinolines

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Anisotropic Displacement Ellipsoid Plots from the Single-crystal X-ray Analyses of compounds **5**, **6** and **8**. S2

^{1}H and ^{13}C NMR spectra for compounds **2**, **5**, **6**, **8**-**11** and **13**-**17**. S5

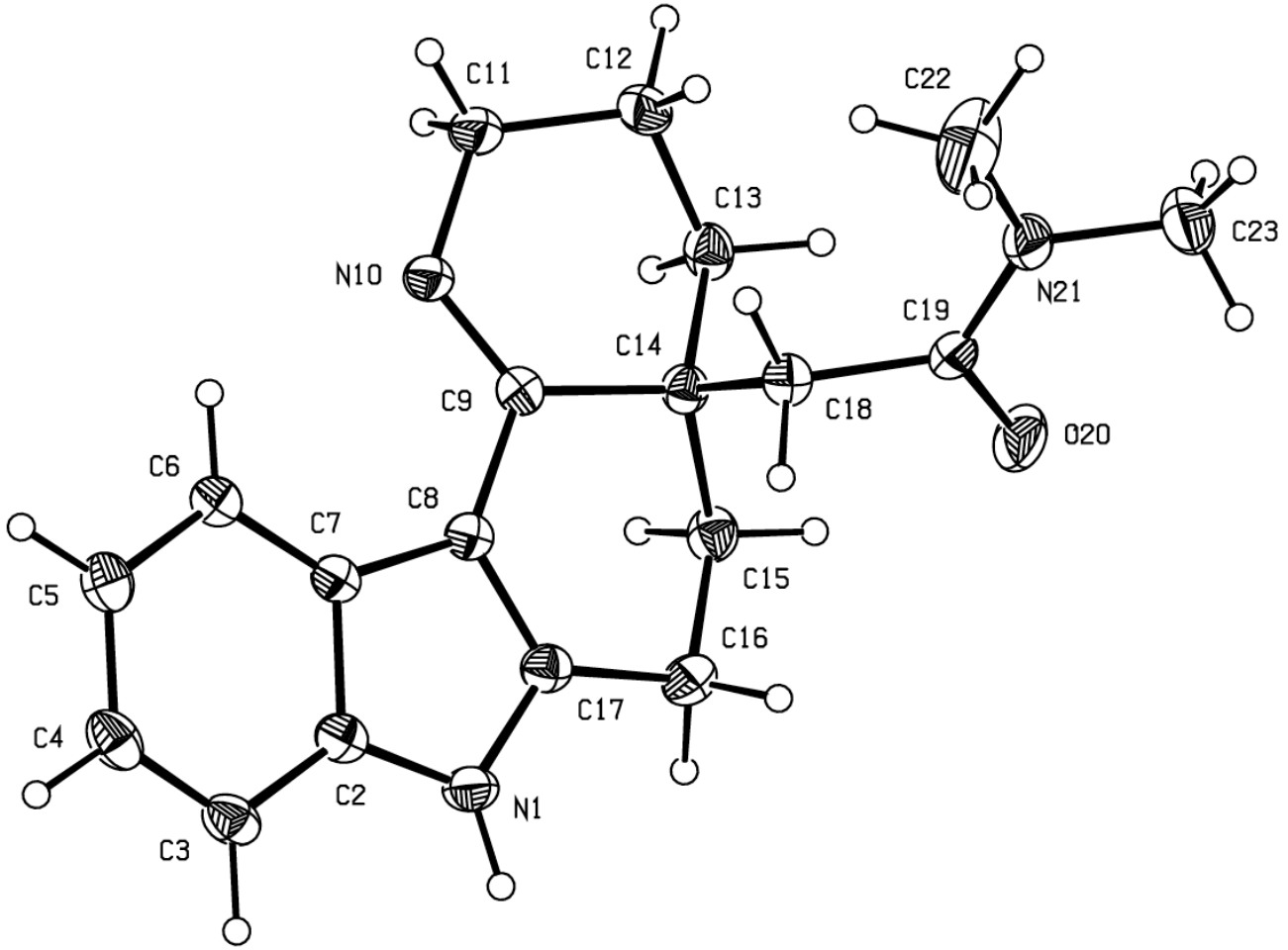


Figure S1: Structure of compound **5** (CCDC 1482202) with labeling of selected atoms. Anisotropic displacement ellipsoids show 30% probability levels. Hydrogen atoms are drawn as circles with small radii.

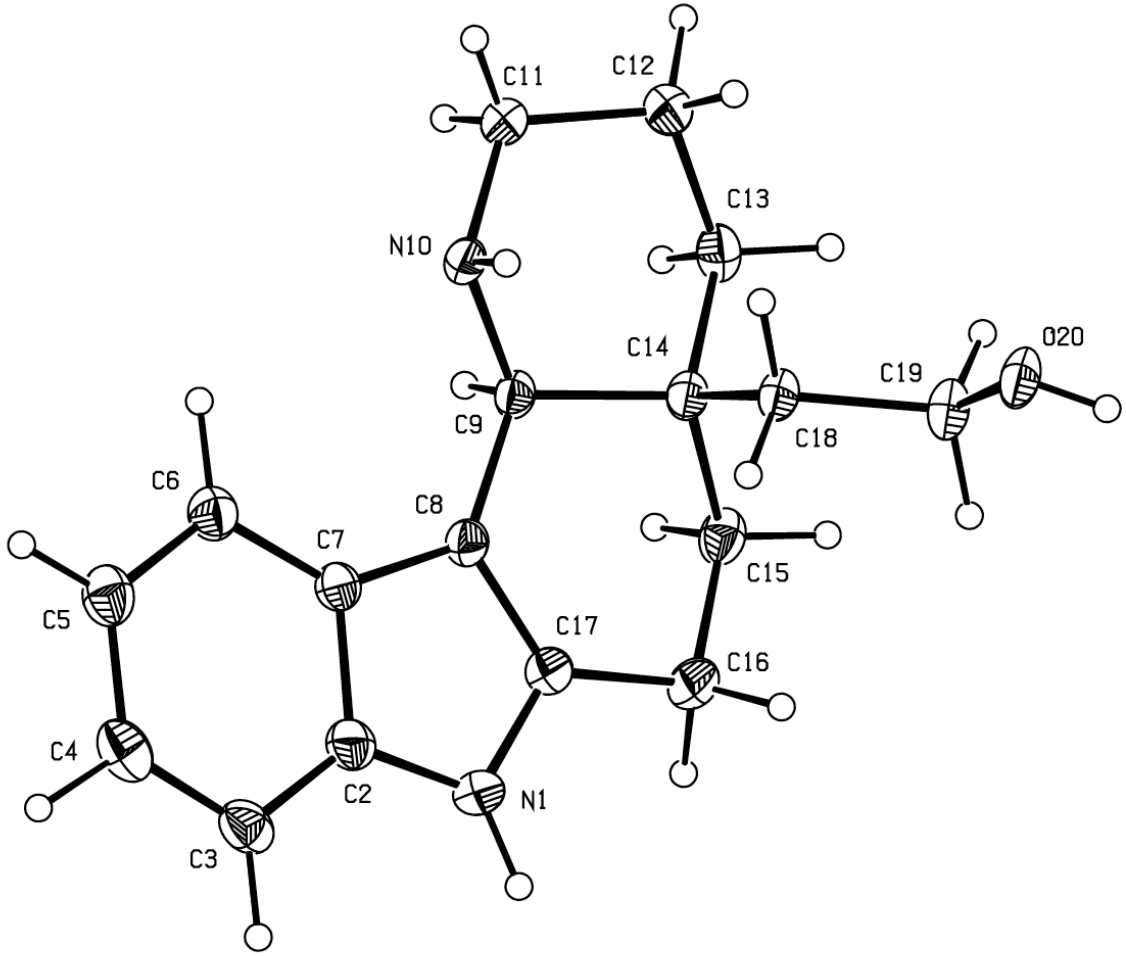


Figure S2: Structure of compound **6** (CCDC 1482203) with labeling of selected atoms. Anisotropic displacement ellipsoids show 30% probability levels. Hydrogen atoms are drawn as circles with small radii.

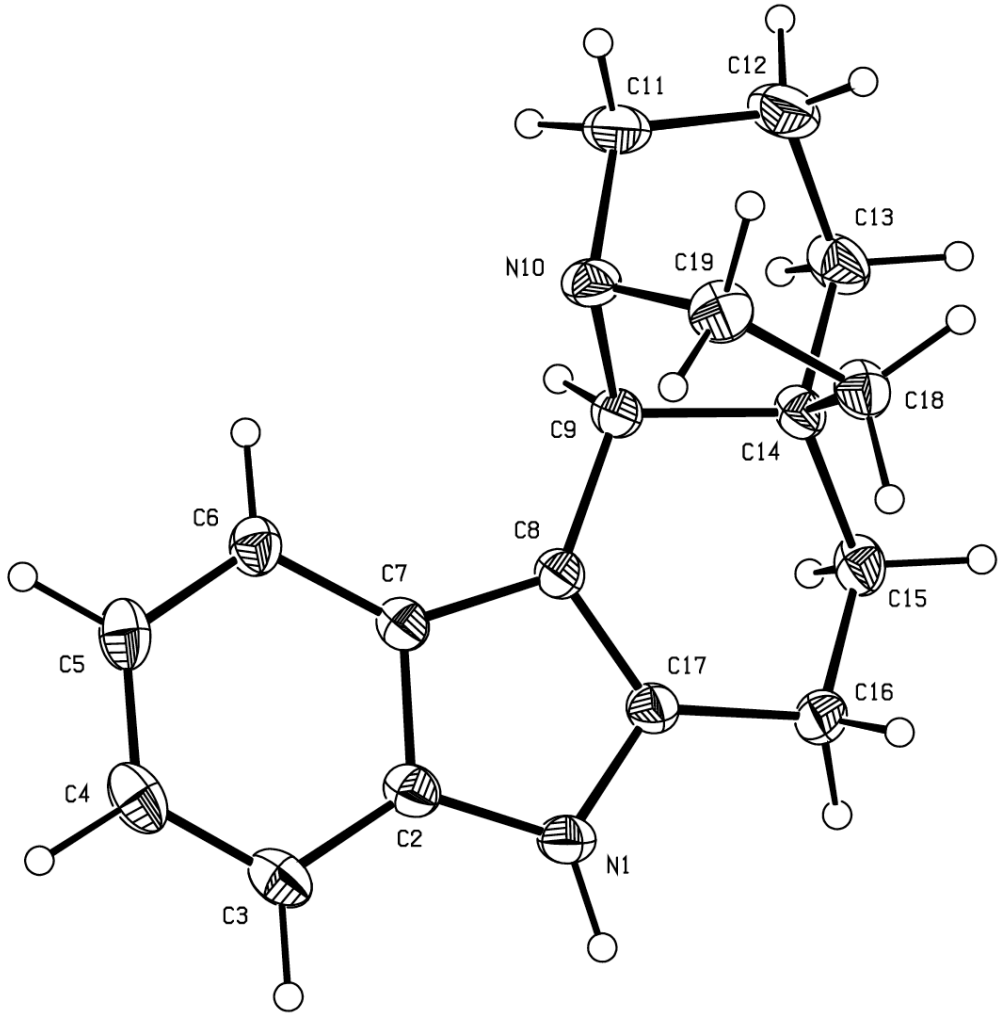
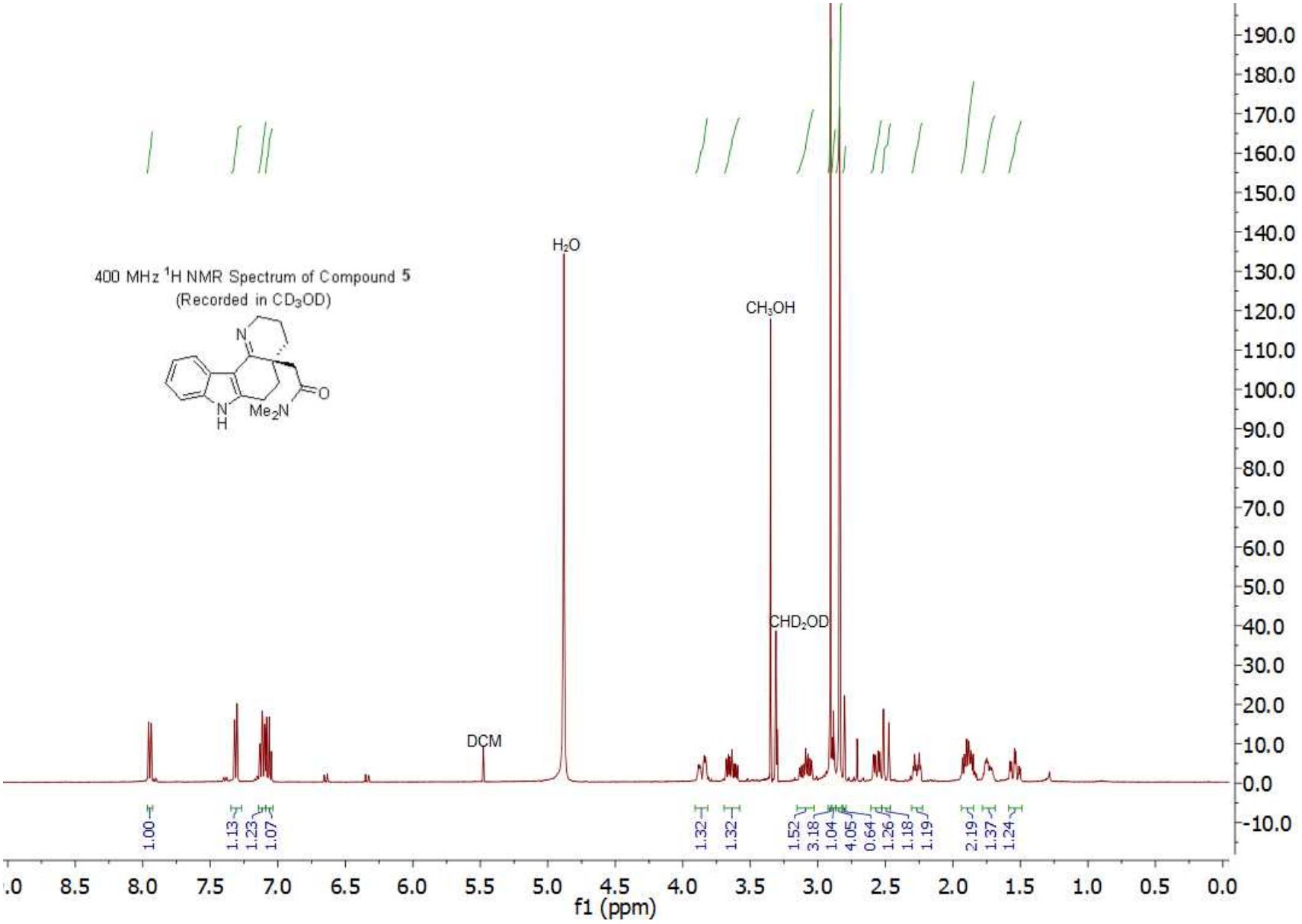
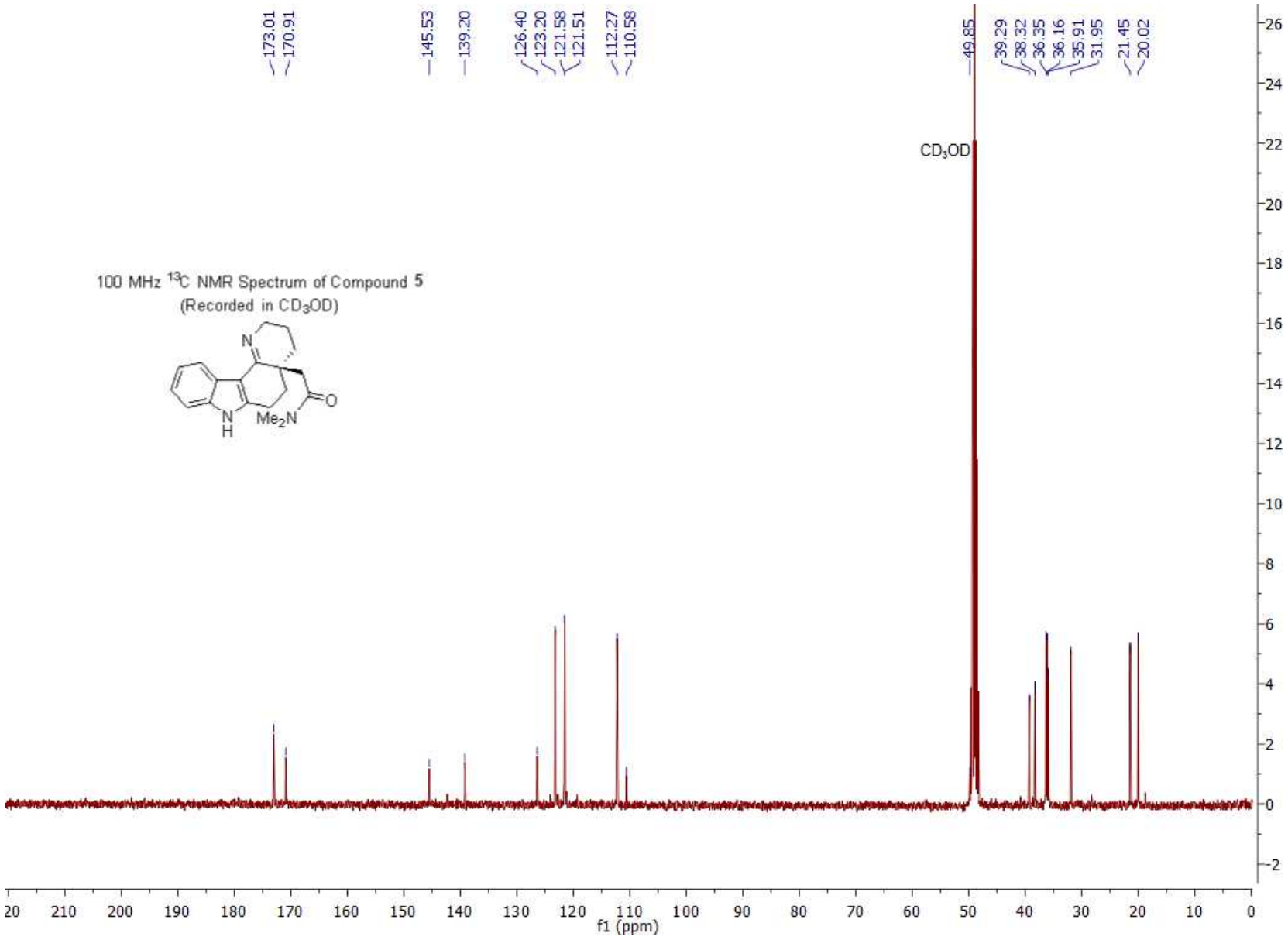
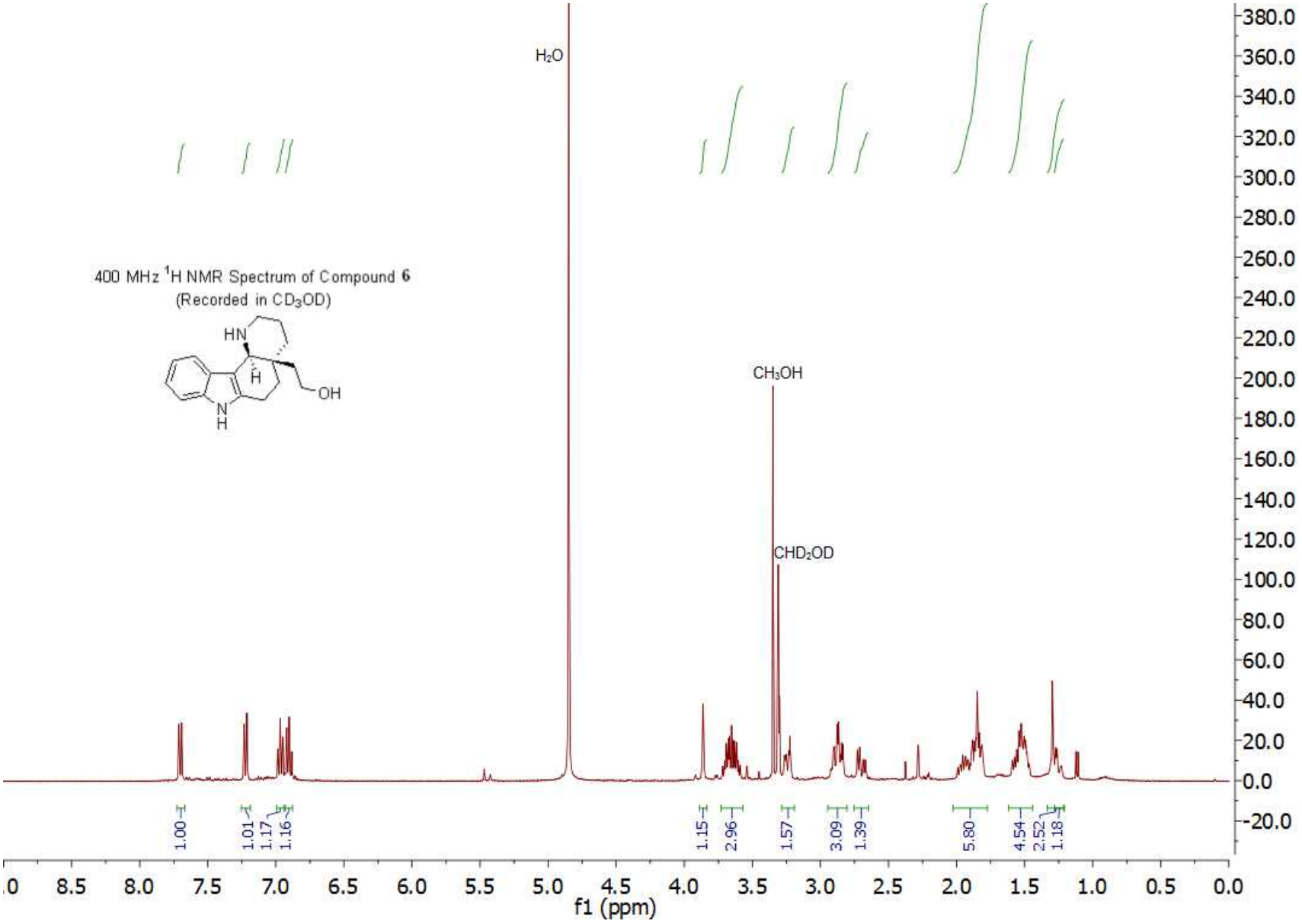
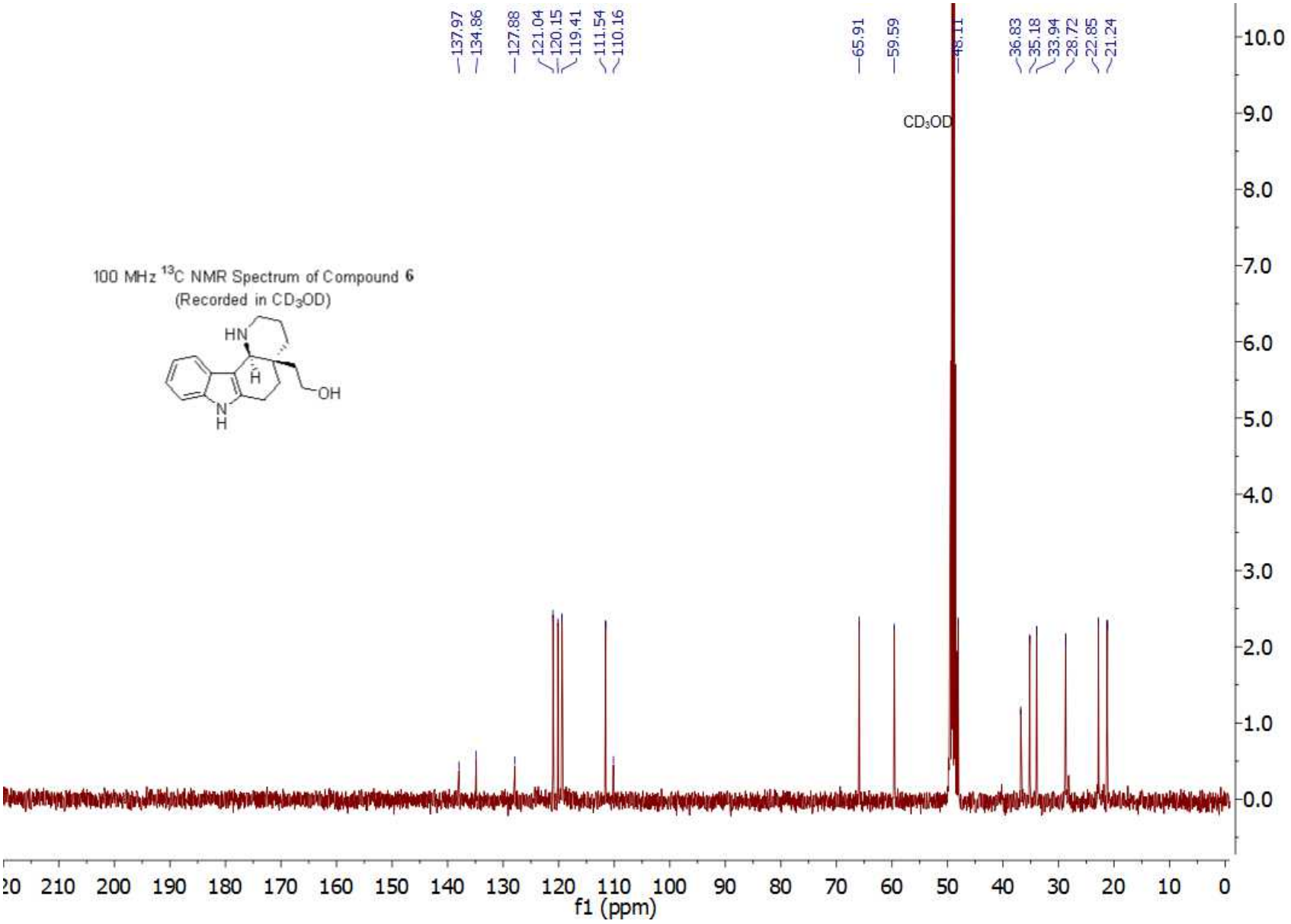


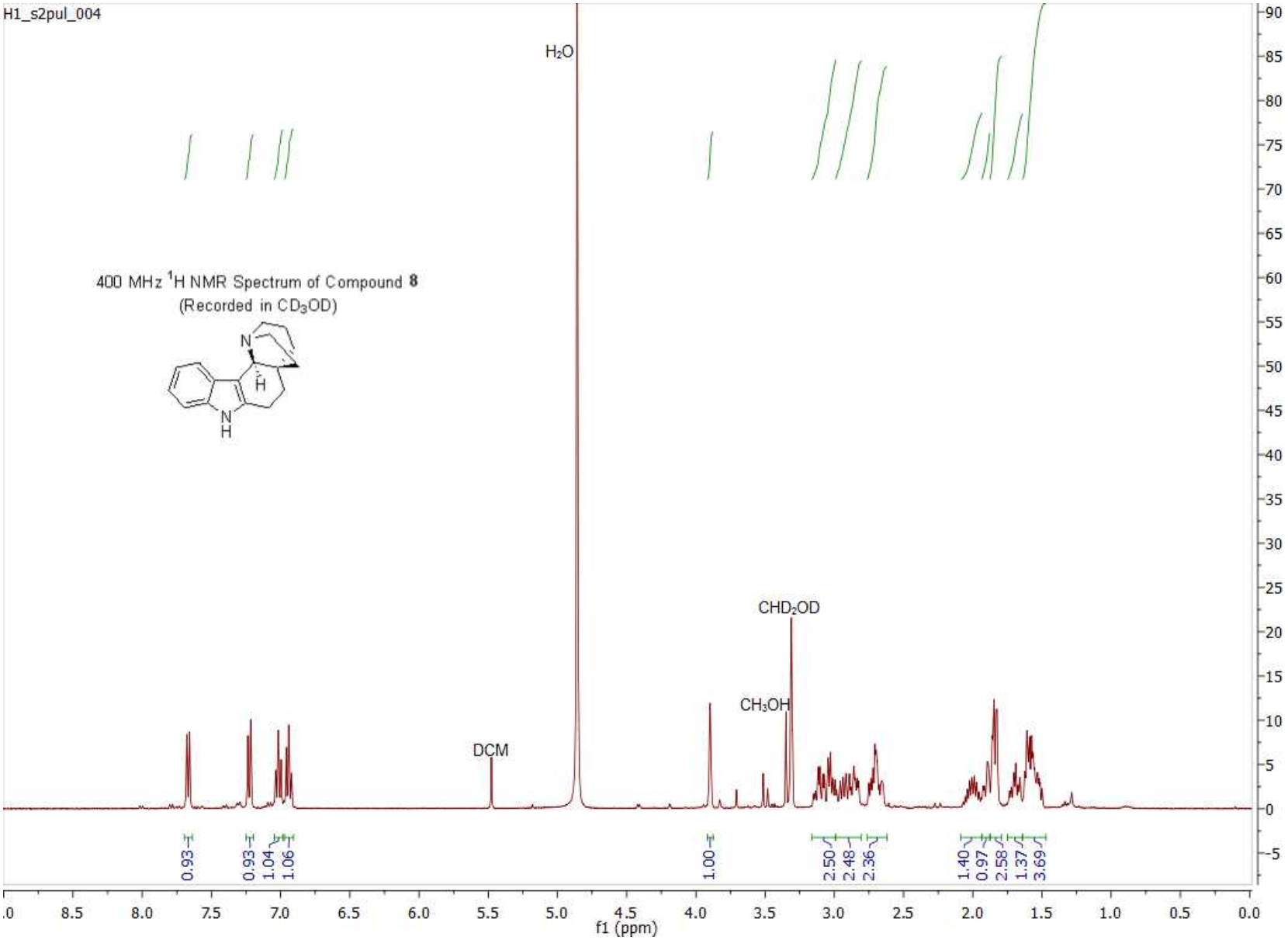
Figure S3: Structure of compound **8** (CCDC 1482204) with labeling of selected atoms. Anisotropic displacement ellipsoids show 30% probability levels. Hydrogen atoms are drawn as circles with small radii.

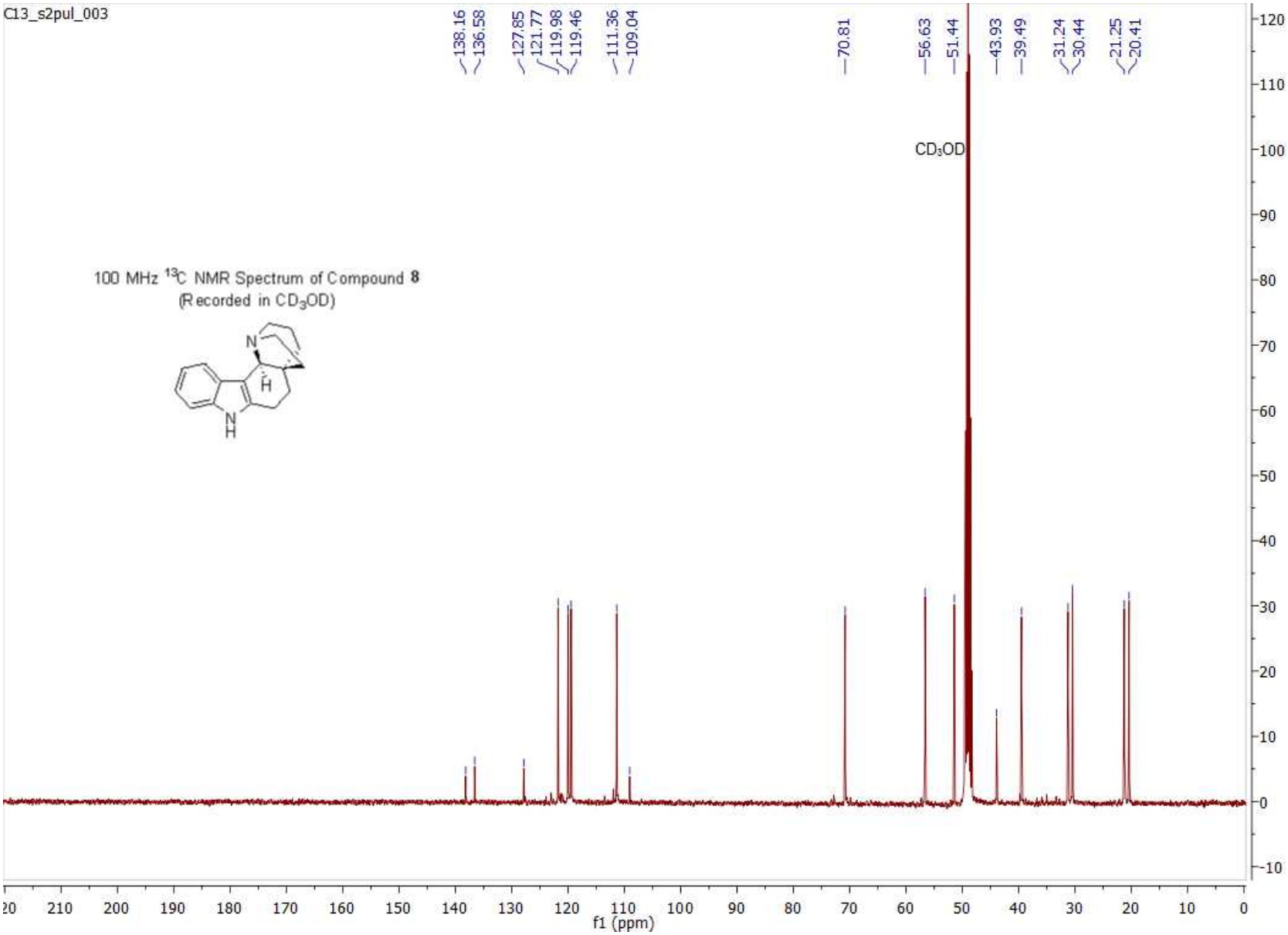

400 MHz ^{1}H NMR Spectrum of Compound 5
(Recorded in CD_3OD)
H_2O
CH_3OH
CHD_2OD
DCM
f1 (ppm)

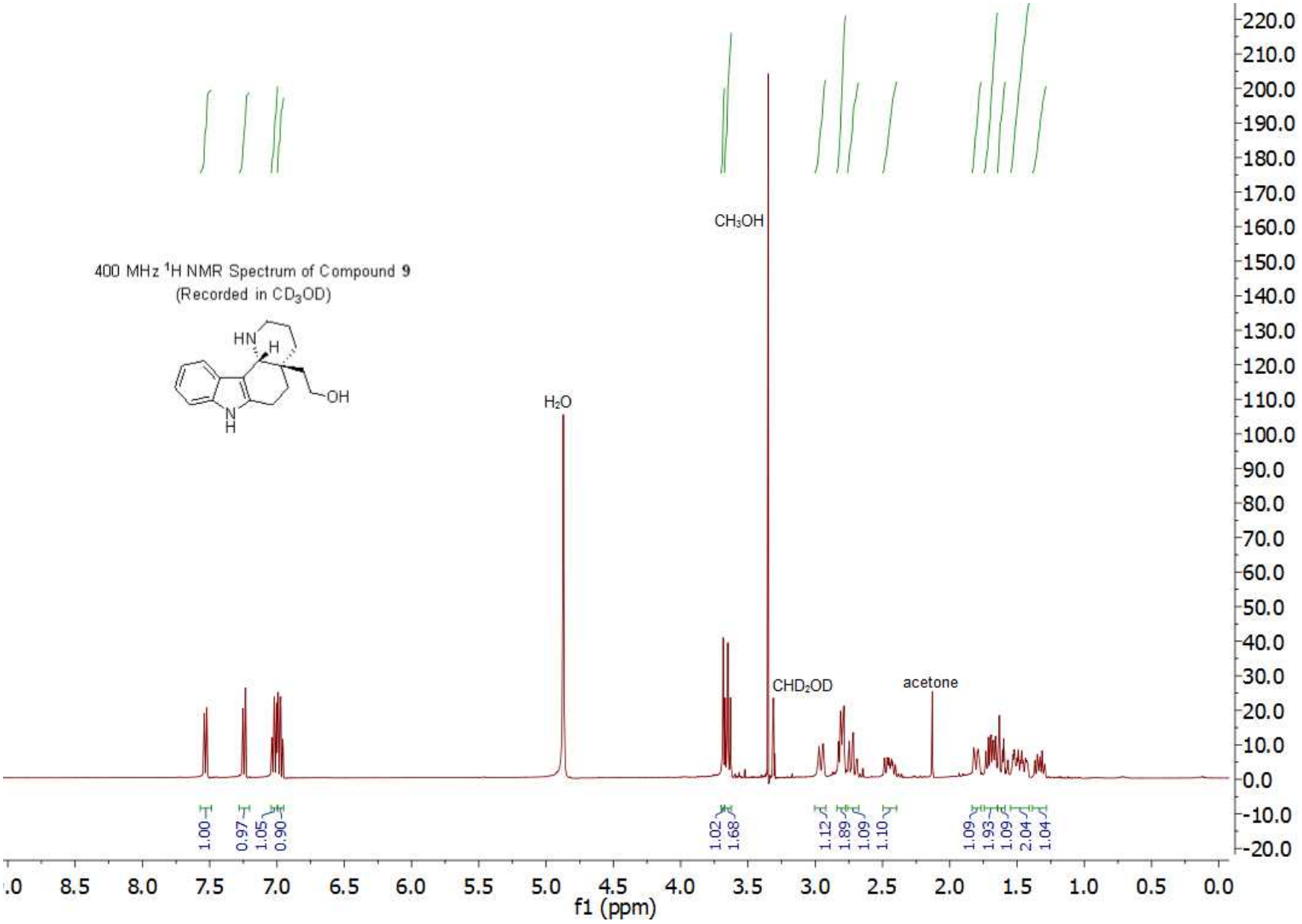

100 MHz ^{13}C NMR Spectrum of Compound 5
(Recorded in CD_3OD)
N
N
H
Me_2N
O
173.01
170.91
145.53
139.20
126.40
123.20
121.58
121.51
112.27
110.58
49.85
39.29
38.32
36.35
36.16
35.91
31.95
21.45
20.02
CD_3OD
f1 (ppm)

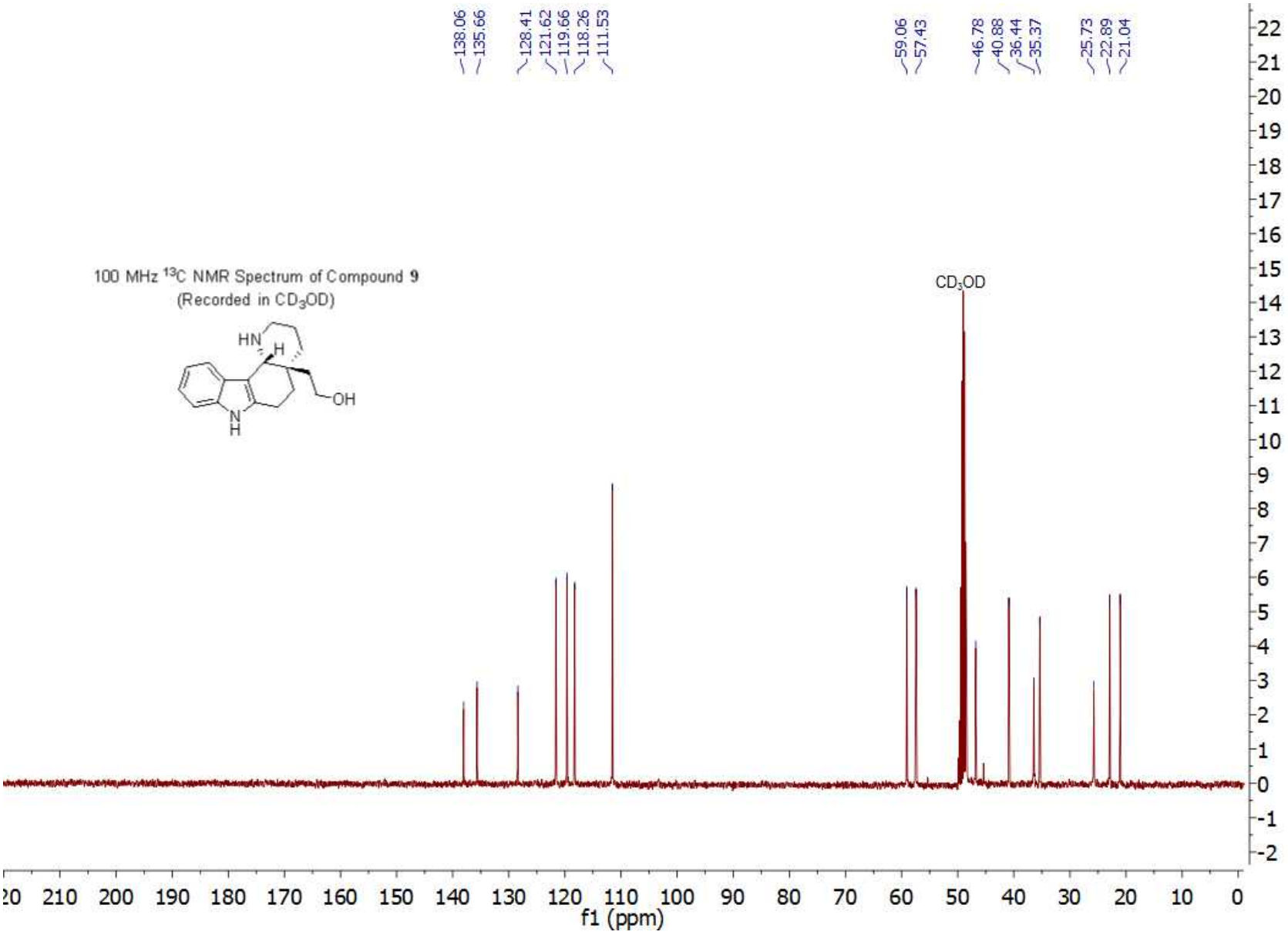

400 MHz ^{1}H NMR Spectrum of Compound 6
(Recorded in CD_3OD)
HN
H
N
H
OH
H_2O
CH_3OH
CHD_2OD
1.00
1.01
1.17
1.16
1.15
2.96
1.57
3.09
1.39
5.80
4.54
2.52
1.18
f1 (ppm)

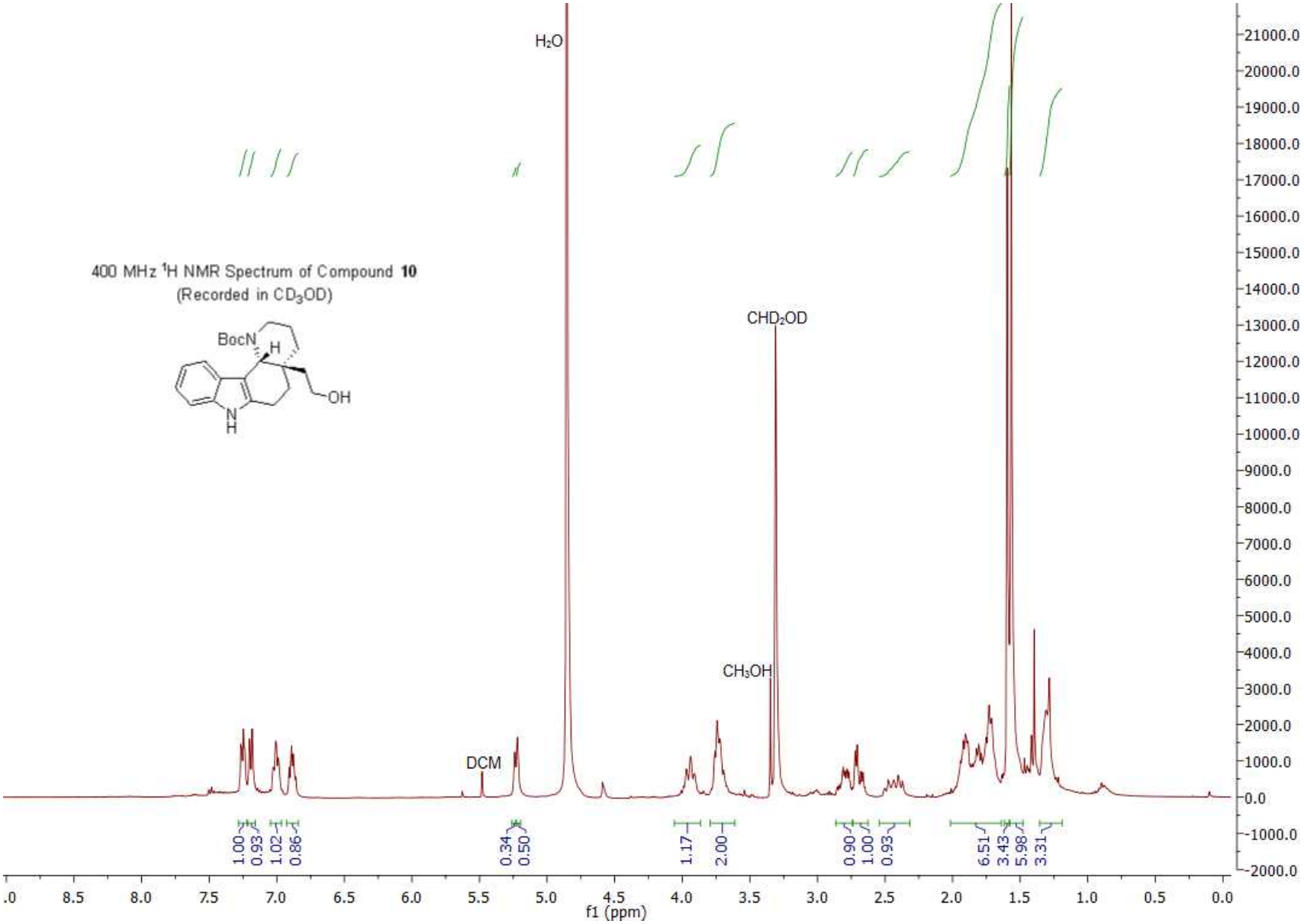

100 MHz ^{13}C NMR Spectrum of Compound 6
(Recorded in CD_3OD)
HN
H
N
H
OH
137.97
134.86
127.88
121.04
120.15
119.41
111.54
110.16
65.91
59.59
48.11
CD_3OD
36.83
35.18
33.94
28.72
22.85
21.24
f1 (ppm)

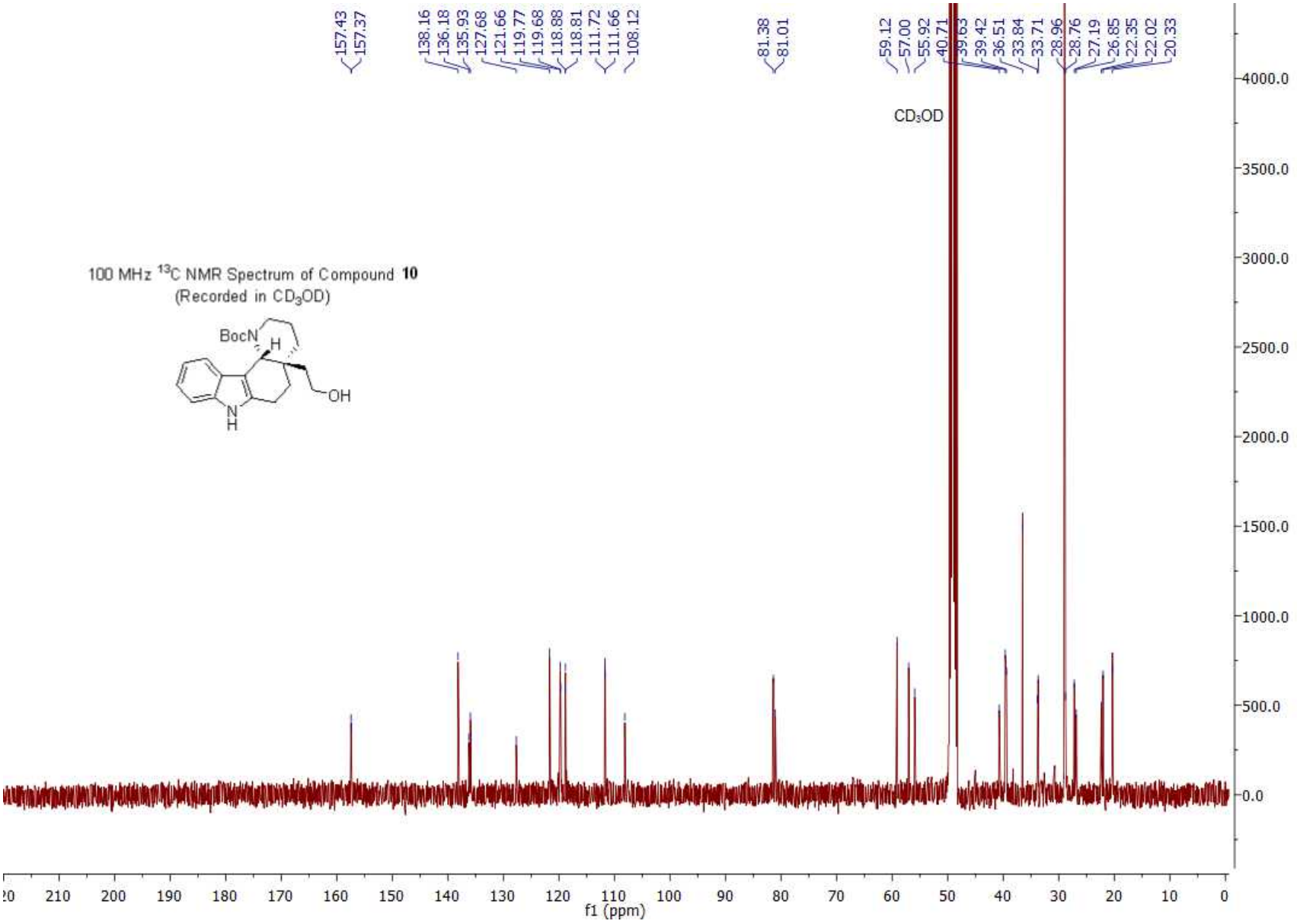

H1_s2pul_004
400 MHz ^{1}H NMR Spectrum of Compound **8**
(Recorded in CD_3OD)
H_2O
DCM
CH_3OH
CHD_2OD
0.93
0.93
1.04
1.06
1.00
2.50
2.48
2.36
1.40
0.97
2.58
1.37
3.69
f1 (ppm)

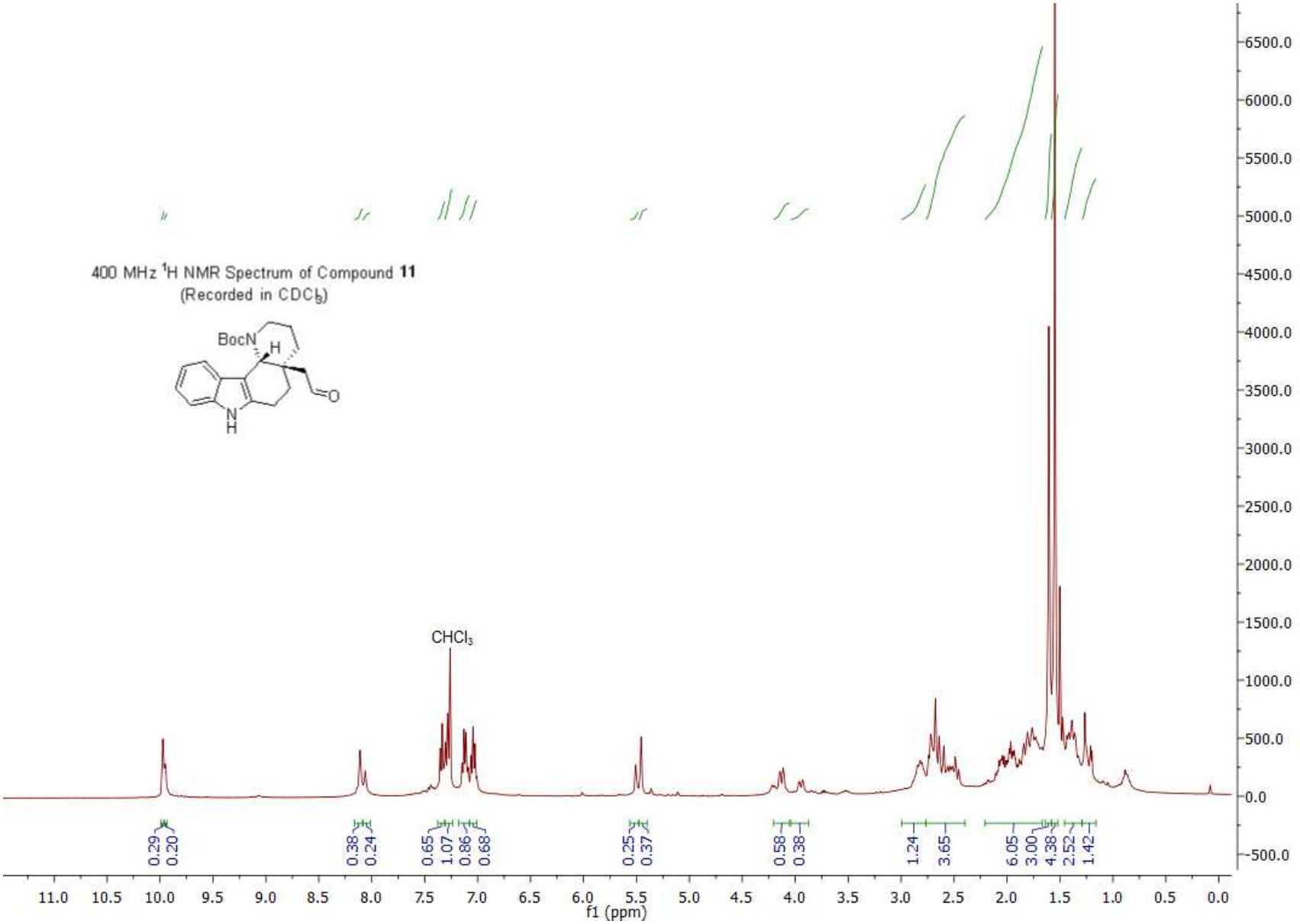

C13_s2pul_003
138.16
136.58
127.85
121.77
119.98
119.46
111.36
109.04
70.81
56.63
51.44
43.93
39.49
31.24
30.44
21.25
20.41
CD3OD
100 MHz 13C NMR Spectrum of Compound 8
(Recorded in CD3OD)
N
H
N
H
f1 (ppm)

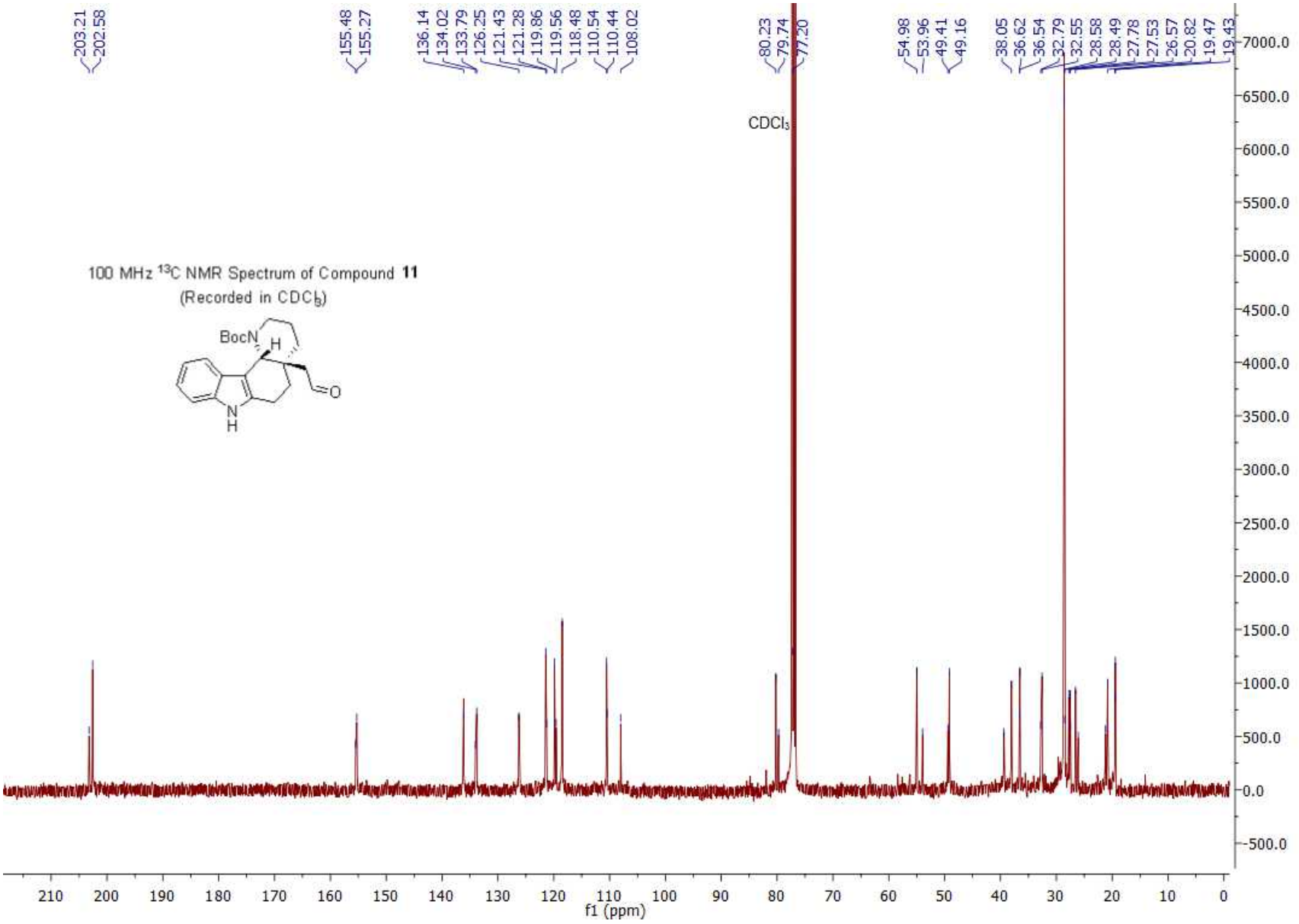

400 MHz ^{1}H NMR Spectrum of Compound 9
(Recorded in CD_3OD)
HN
H
OH
N
H
CH_3OH
H_2O
CHD_2OD
acetone
1.00
0.97
1.05
0.90
1.02
1.68
1.12
1.89
1.09
1.10
1.09
1.93
1.09
2.04
1.04
f1 (ppm)

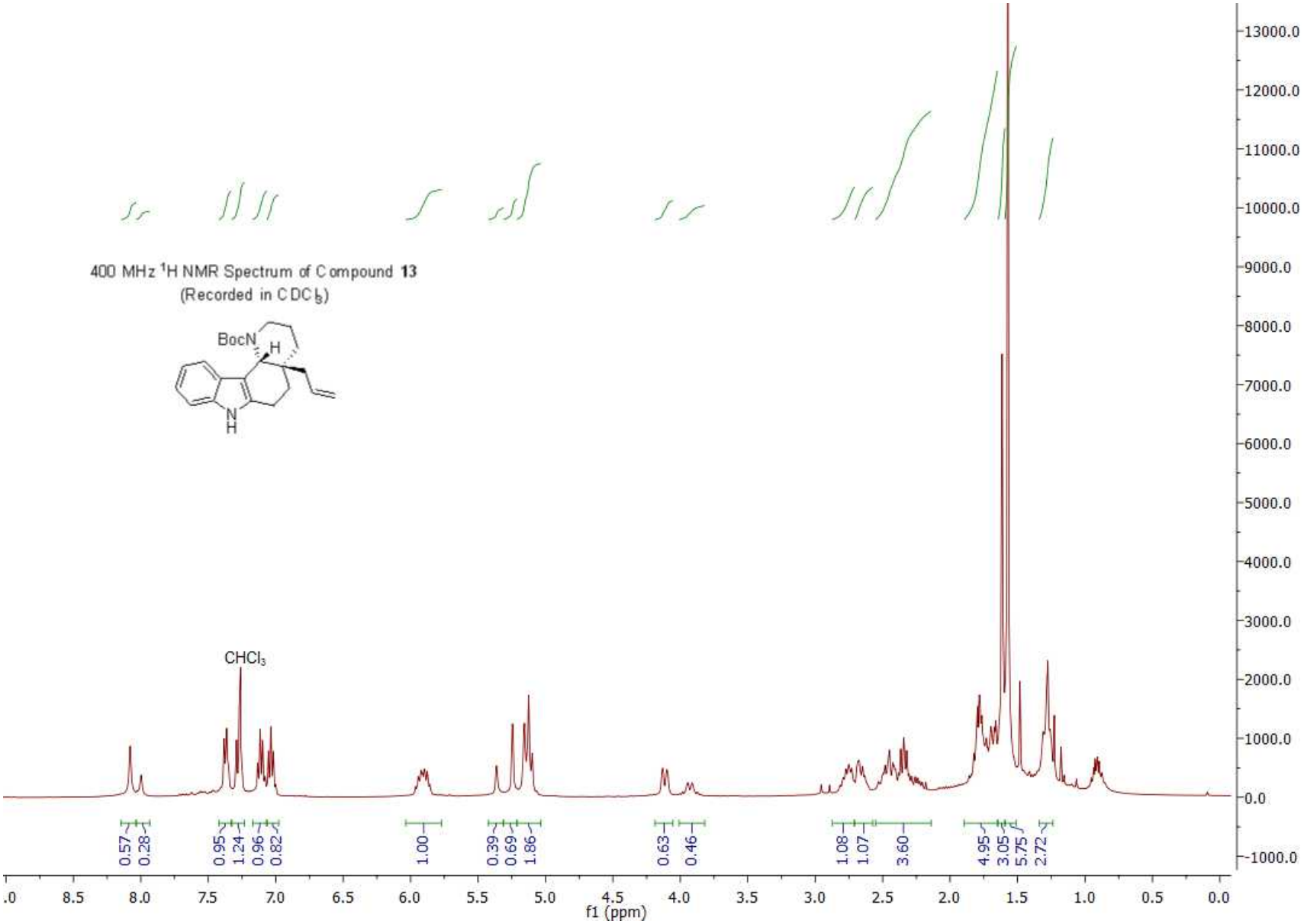

100 MHz ^{13}C NMR Spectrum of Compound 9
(Recorded in CD_3OD)
HN
H
OH
N
H
138.06
135.66
128.41
121.62
119.66
118.26
111.53
59.06
57.43
46.78
40.88
36.44
35.37
25.73
22.89
21.04
CD_3OD
f1 (ppm)

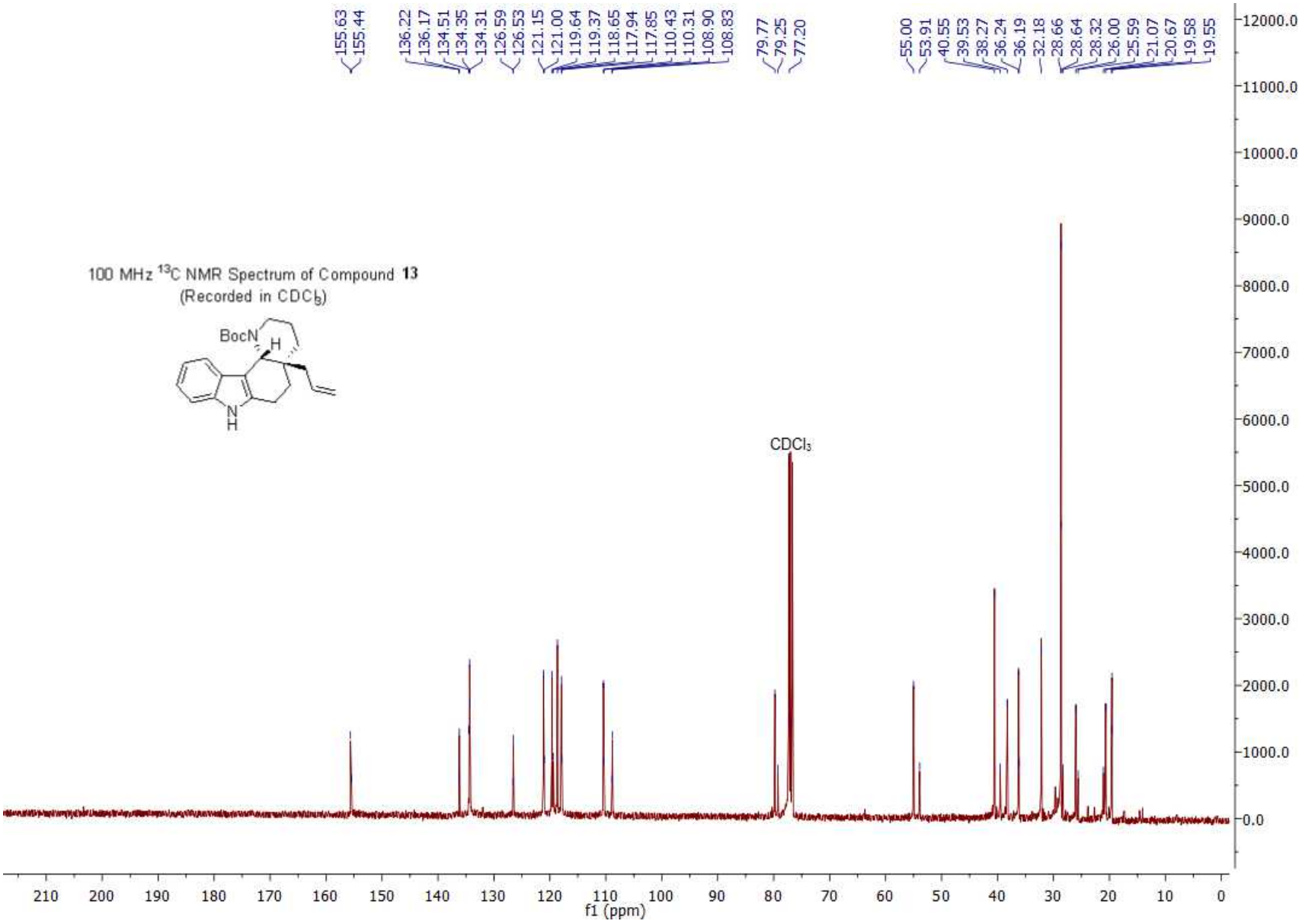

400 MHz ¹H NMR Spectrum of Compound 10
(Recorded in CD3OD)
BocN
H
OH
N
H
H2O
CHD2OD
CH3OH
DCM
1.00
0.93
1.02
0.86
0.34
0.50
1.17
2.00
0.90
1.00
0.93
6.51
3.43
5.98
3.31
f1 (ppm)

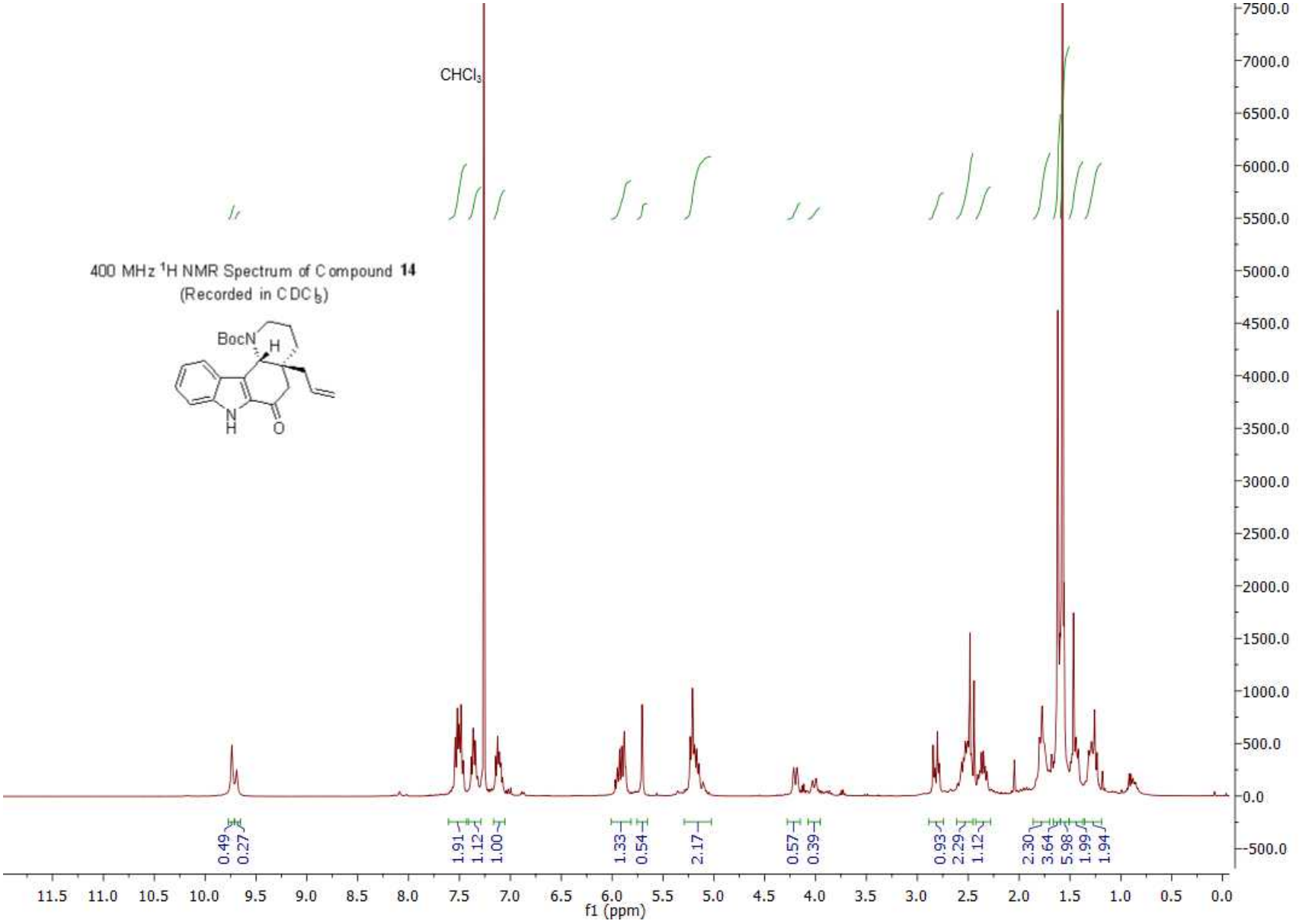

157.43
157.37
138.16
136.18
135.93
127.68
121.66
119.77
119.68
118.88
118.81
111.72
111.66
108.12
81.38
81.01
59.12
57.00
55.92
40.71
39.63
39.42
36.51
33.84
33.71
28.96
28.76
27.19
26.85
22.35
22.02
20.33
CD3OD
100 MHz 13C NMR Spectrum of Compound 10
(Recorded in CD3OD)
BocN
H
OH
N
H
4000.0
3500.0
3000.0
2500.0
2000.0
1500.0
1000.0
500.0
0.0
f1 (ppm)

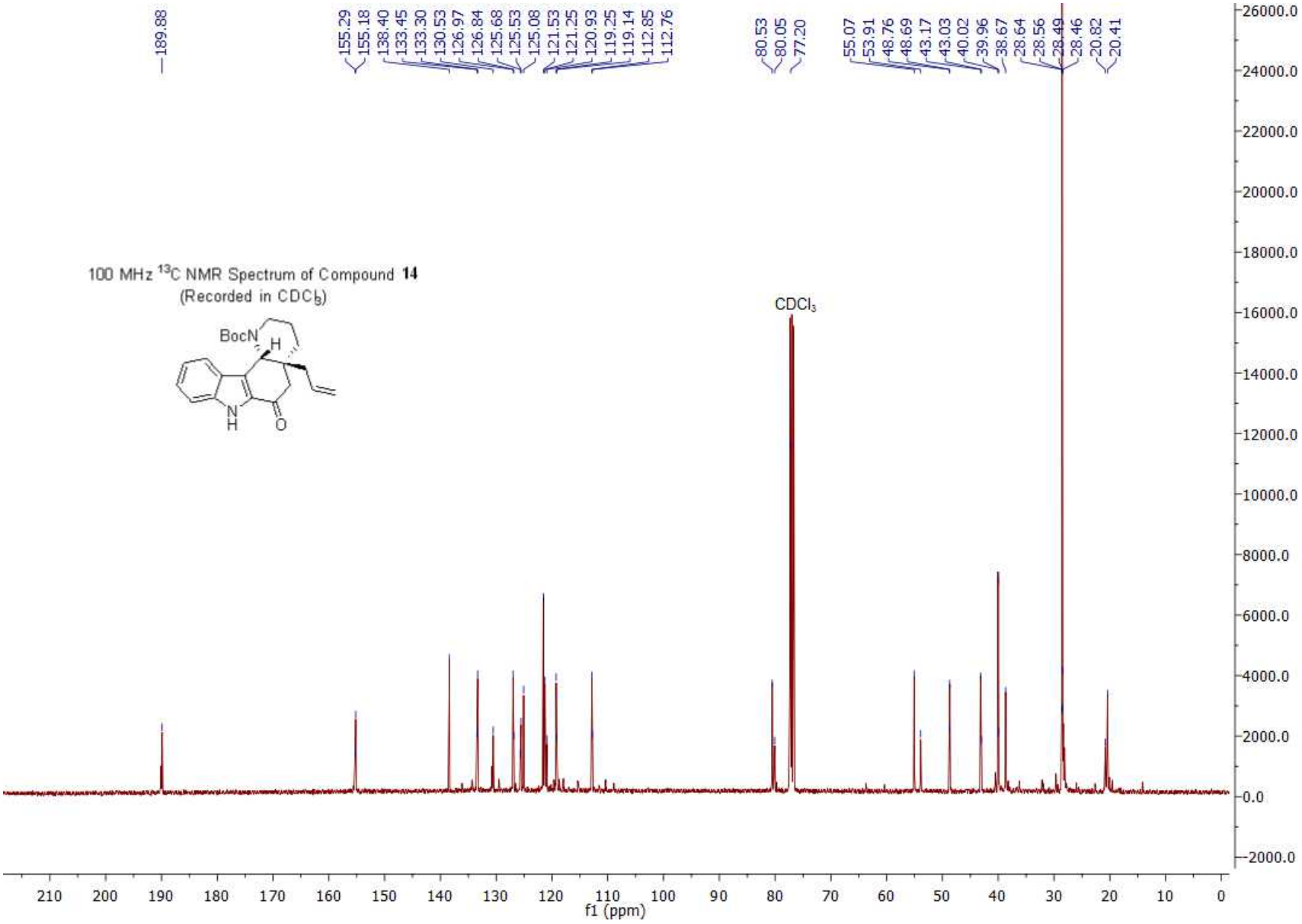

400 MHz ¹H NMR Spectrum of Compound 11
(Recorded in CDCl3)
BocN
H
O
N
H
CHCl3
0.29
0.20
0.38
0.24
0.65
1.07
0.86
0.68
0.25
0.37
0.58
0.38
1.24
3.65
6.05
3.00
4.38
2.52
1.42
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
6500.0
6000.0
5500.0
5000.0
4500.0
4000.0
3500.0
3000.0
2500.0
2000.0
1500.0
1000.0
500.0
0.0
-500.0

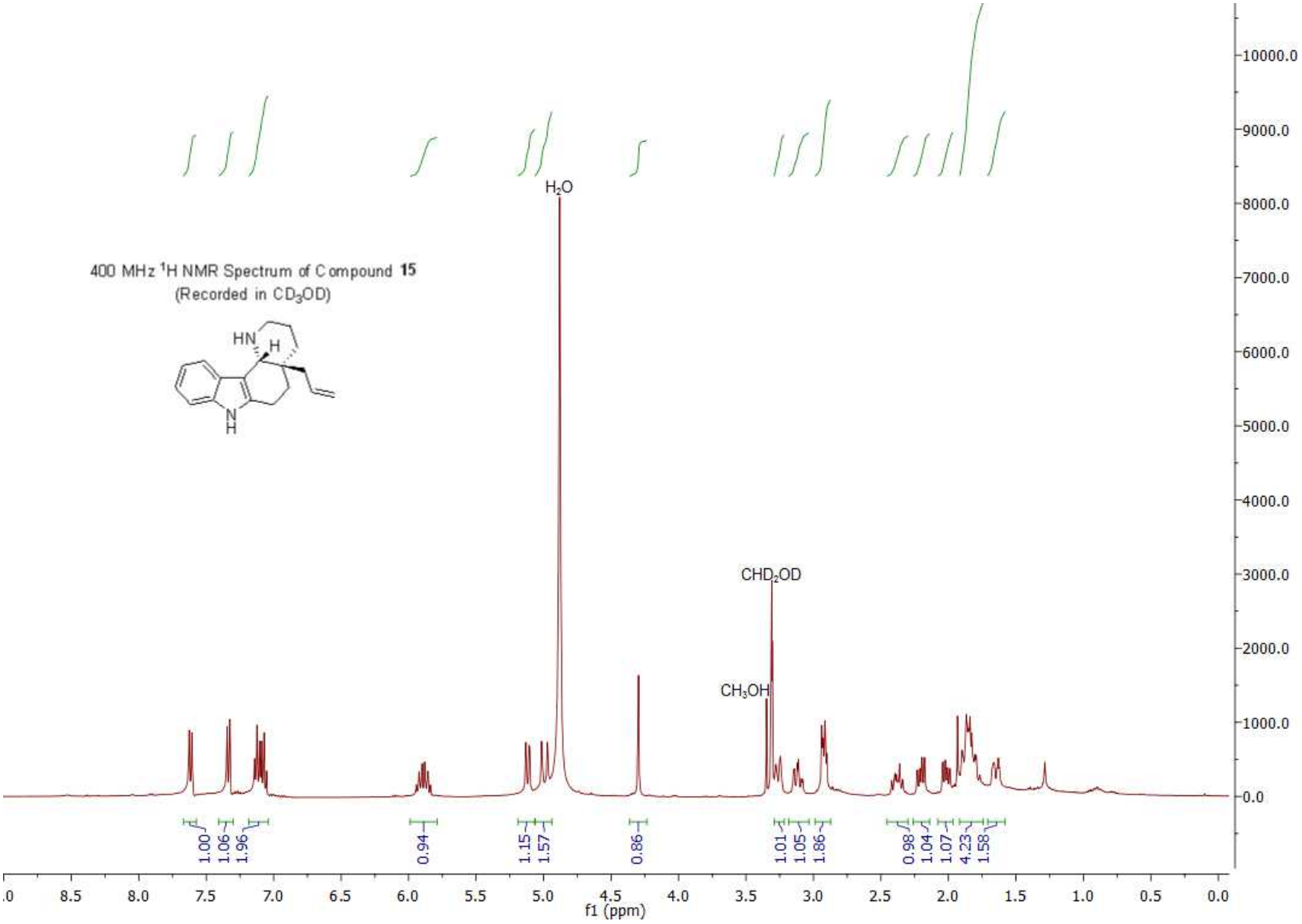

203.21
202.58
155.48
155.27
136.14
134.02
133.79
126.25
121.43
121.28
119.86
119.56
118.48
110.54
110.44
108.02
80.23
79.74
77.20
54.98
53.96
49.41
49.16
38.05
36.62
36.54
32.79
32.55
28.58
28.49
27.78
27.53
26.57
20.82
19.47
19.43
CDCl3
100 MHz 13C NMR Spectrum of Compound 11
(Recorded in CDCl3)
BocN
H
N
H
O
f1 (ppm)

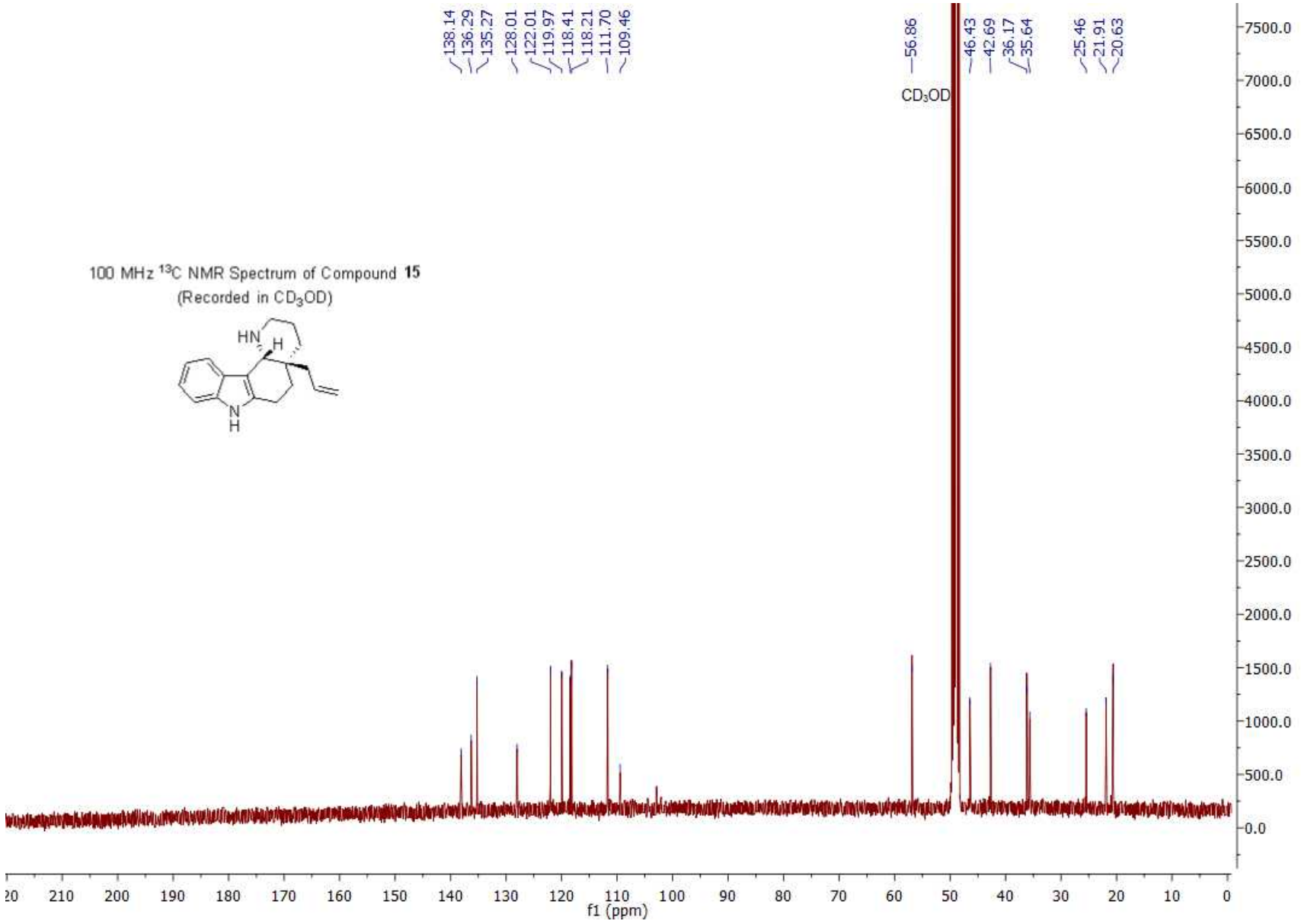

400 MHz ^{1}H NMR Spectrum of Compound **13**
(Recorded in $CDCl_3$)
BocN
H
N
H
$CHCl_3$
0.57
0.28
0.95
1.24
0.96
0.82
1.00
0.39
0.69
1.86
0.63
0.46
1.08
1.07
3.60
4.95
3.05
5.75
2.72
f1 (ppm)

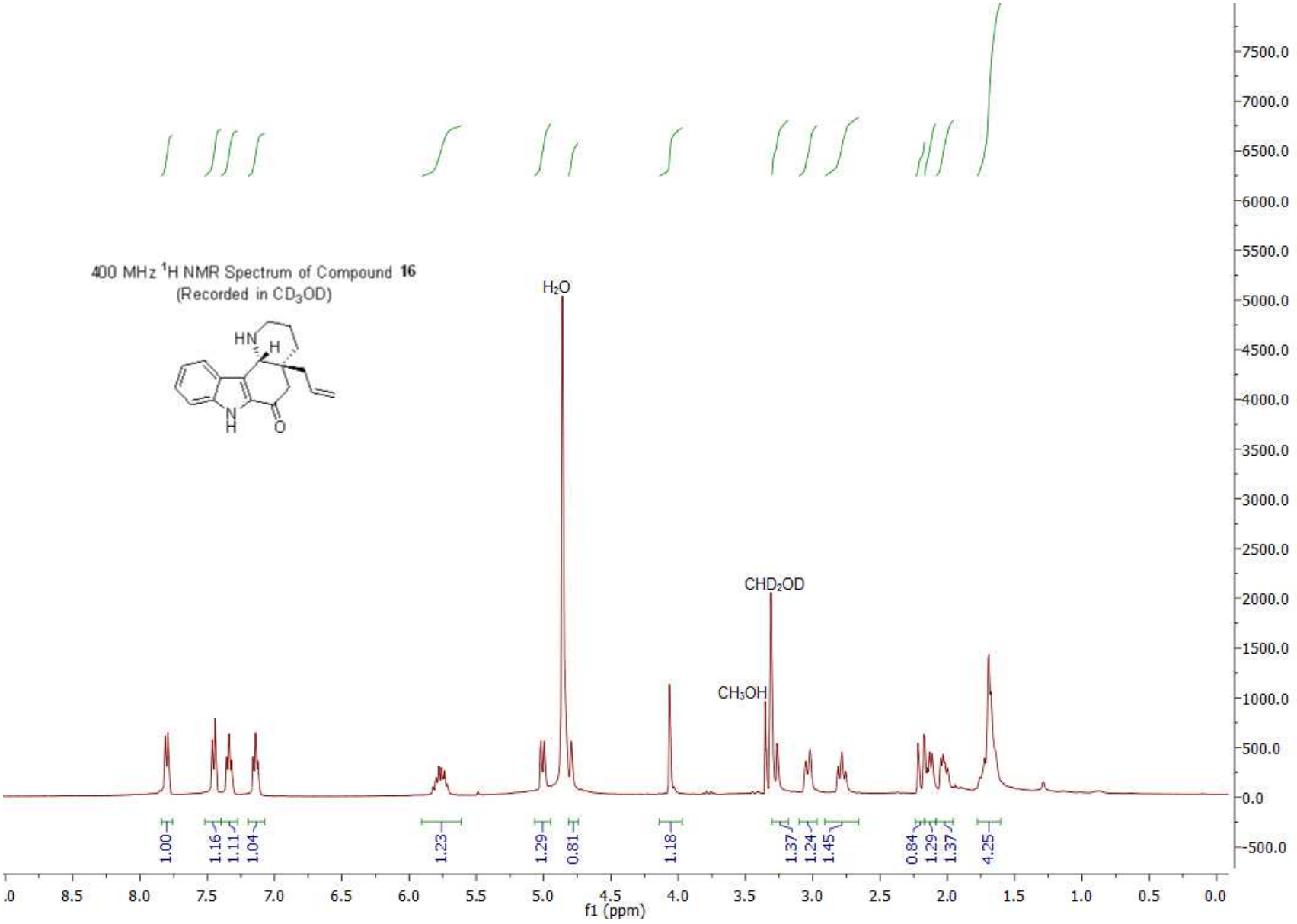

155.63
155.44
136.22
136.17
134.51
134.35
134.31
126.59
126.53
121.15
121.00
119.64
119.37
118.65
117.94
117.85
110.43
110.31
108.90
108.83
79.77
79.25
77.20
55.00
53.91
40.55
39.53
38.27
36.24
36.19
32.18
28.66
28.64
28.32
26.00
25.59
21.07
20.67
19.58
19.55
100 MHz ^{13}C NMR Spectrum of Compound 13
(Recorded in $CDCl_3$)
BocN
H
N
H
$CDCl_3$
12000.0
11000.0
10000.0
9000.0
8000.0
7000.0
6000.0
5000.0
4000.0
3000.0
2000.0
1000.0
0.0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

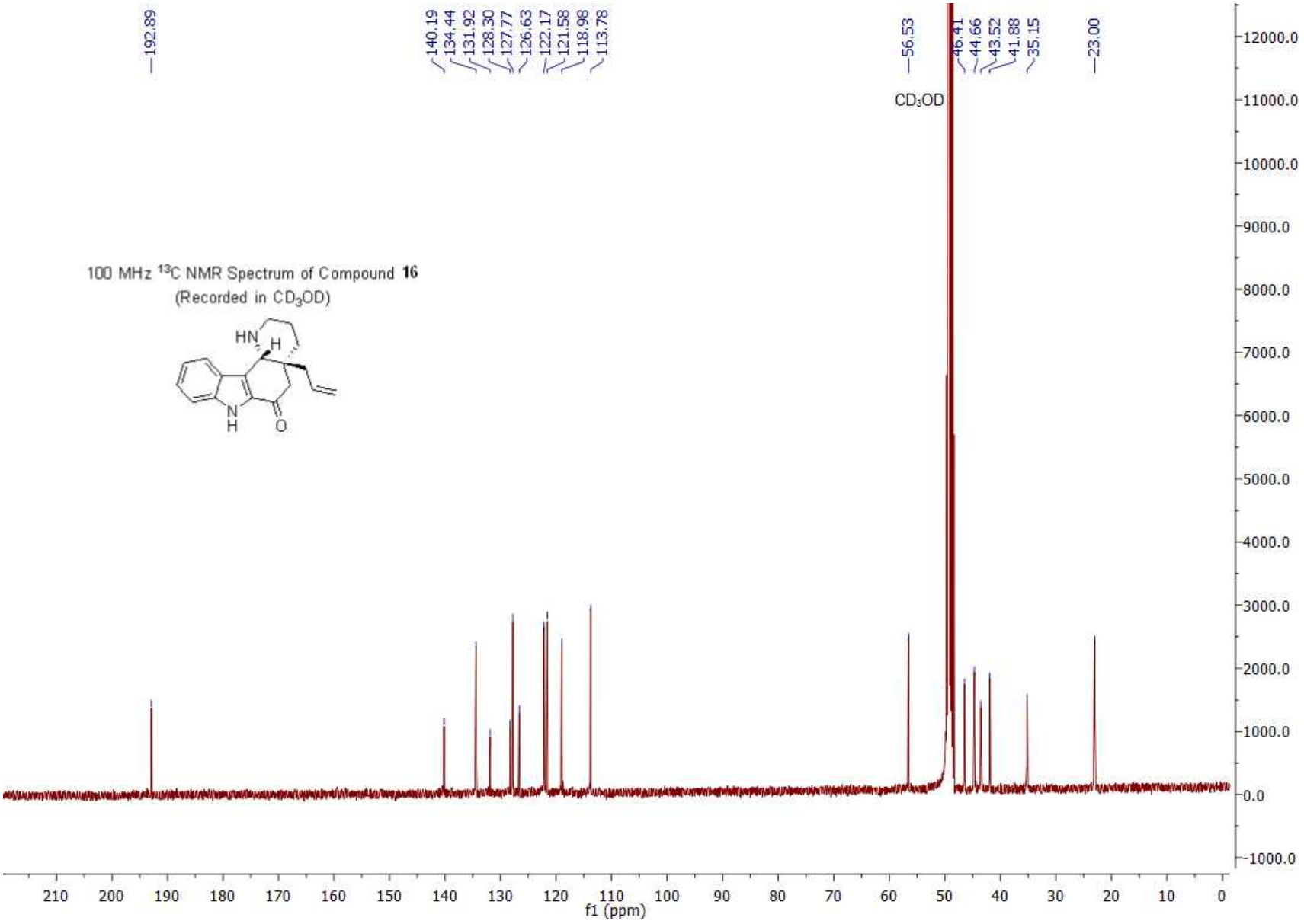

400 MHz ^{1}H NMR Spectrum of Compound **14**
(Recorded in $CDCl_3$)
BocN
H
N
H
O
$CHCl_3$
0.49
0.27
1.91
1.12
1.00
1.33
0.54
2.17
0.57
0.39
0.93
2.29
1.12
2.30
3.64
5.98
1.99
1.94
f1 (ppm)

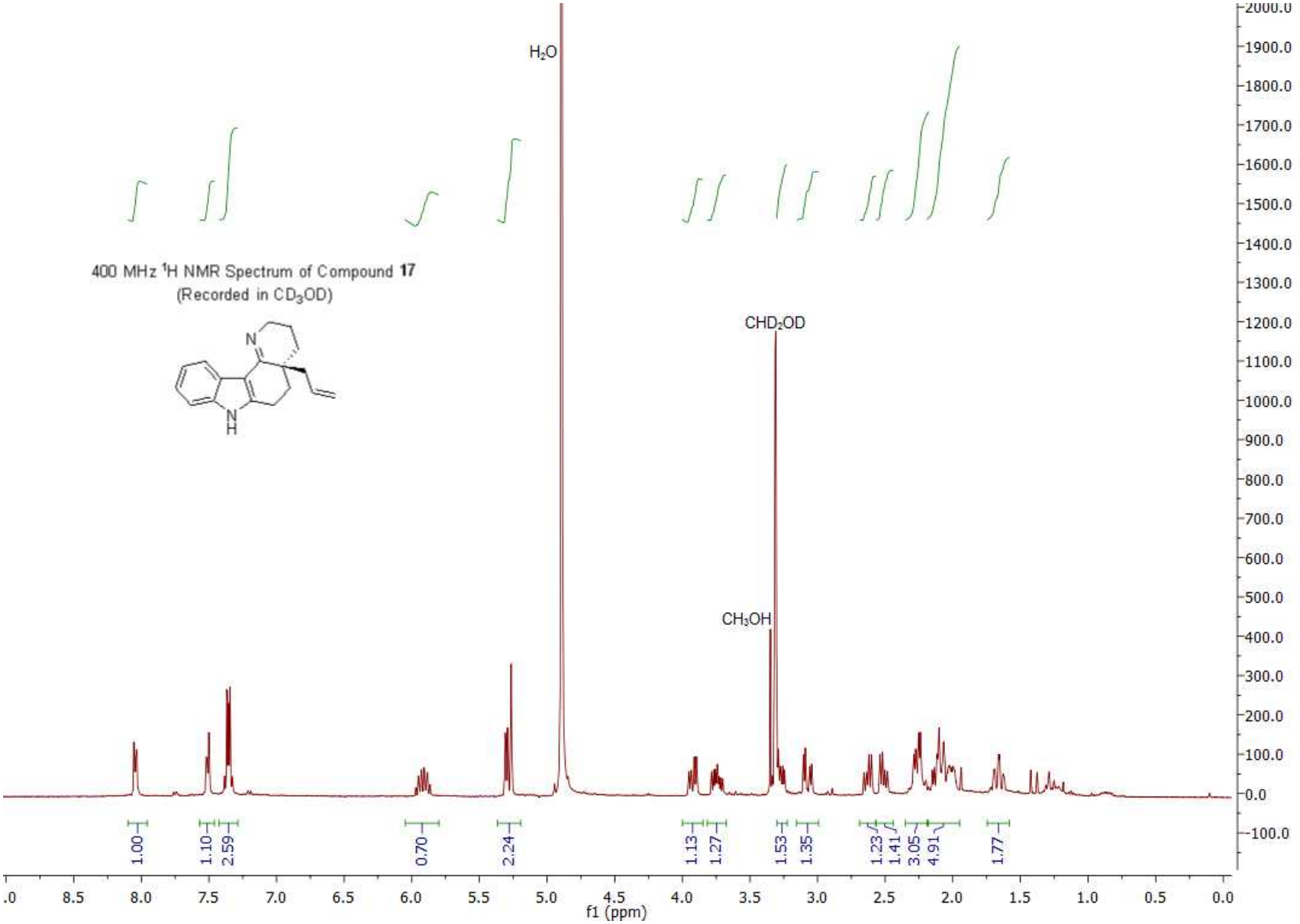

189.88
155.29
155.18
138.40
133.45
133.30
130.53
126.97
126.84
125.68
125.53
125.08
121.53
121.25
120.93
119.25
119.14
112.85
112.76
80.53
80.05
77.20
55.07
53.91
48.76
48.69
43.17
43.03
40.02
39.96
38.67
28.64
28.56
28.49
28.46
20.82
20.41
100 MHz 13C NMR Spectrum of Compound 14
(Recorded in CDCl3)
BocN
H
N
H
O
CDCl3
f1 (ppm)

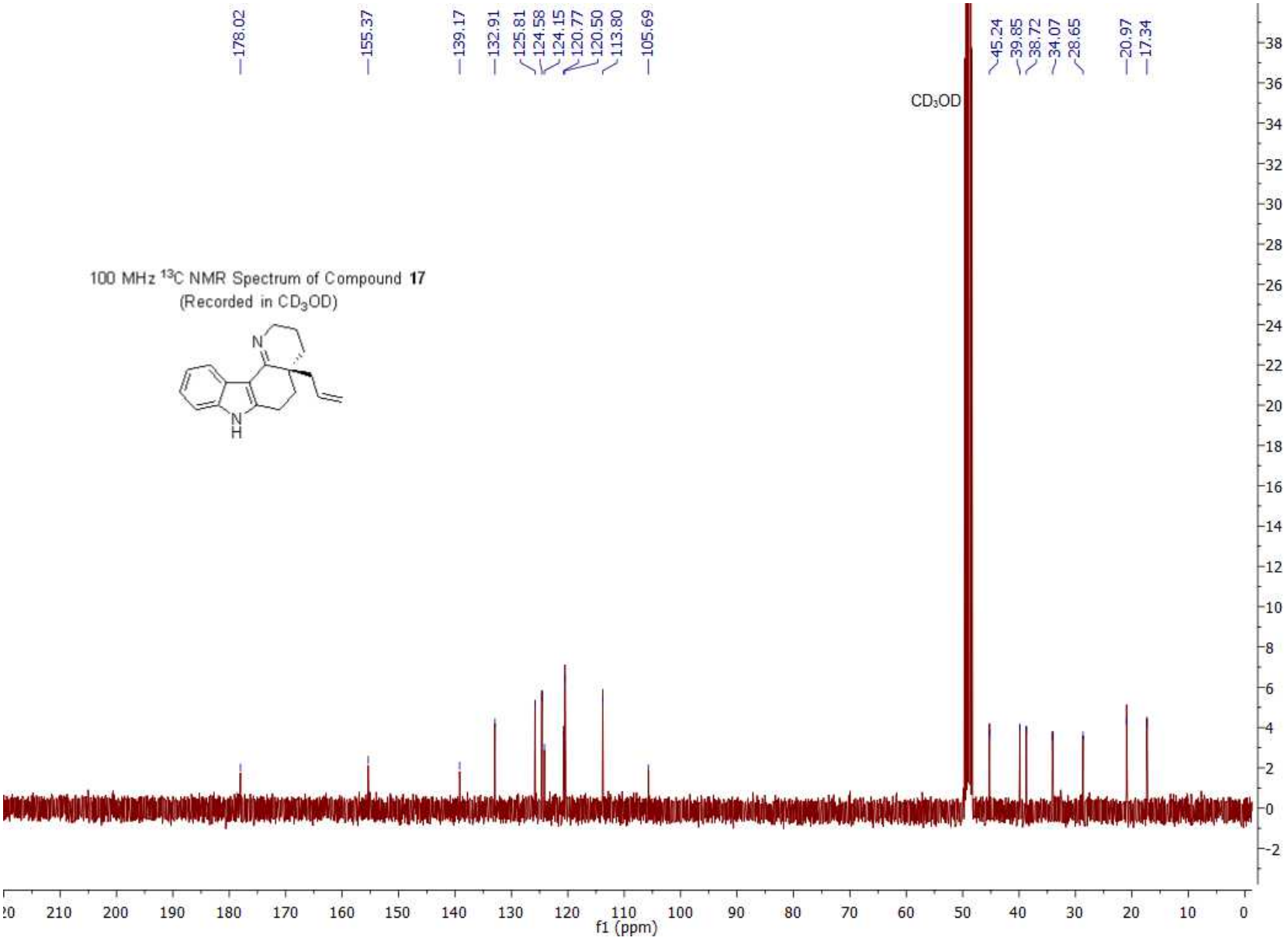

400 MHz ^{1}H NMR Spectrum of Compound **15**
(Recorded in CD_3OD)
HN
H
N
H
H_2O
CHD_2OD
CH_3OH
1.00
1.06
1.96
0.94
1.15
1.57
0.86
1.01
1.05
1.86
0.98
1.04
1.07
4.23
1.58
10000.0
9000.0
8000.0
7000.0
6000.0
5000.0
4000.0
3000.0
2000.0
1000.0
0.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

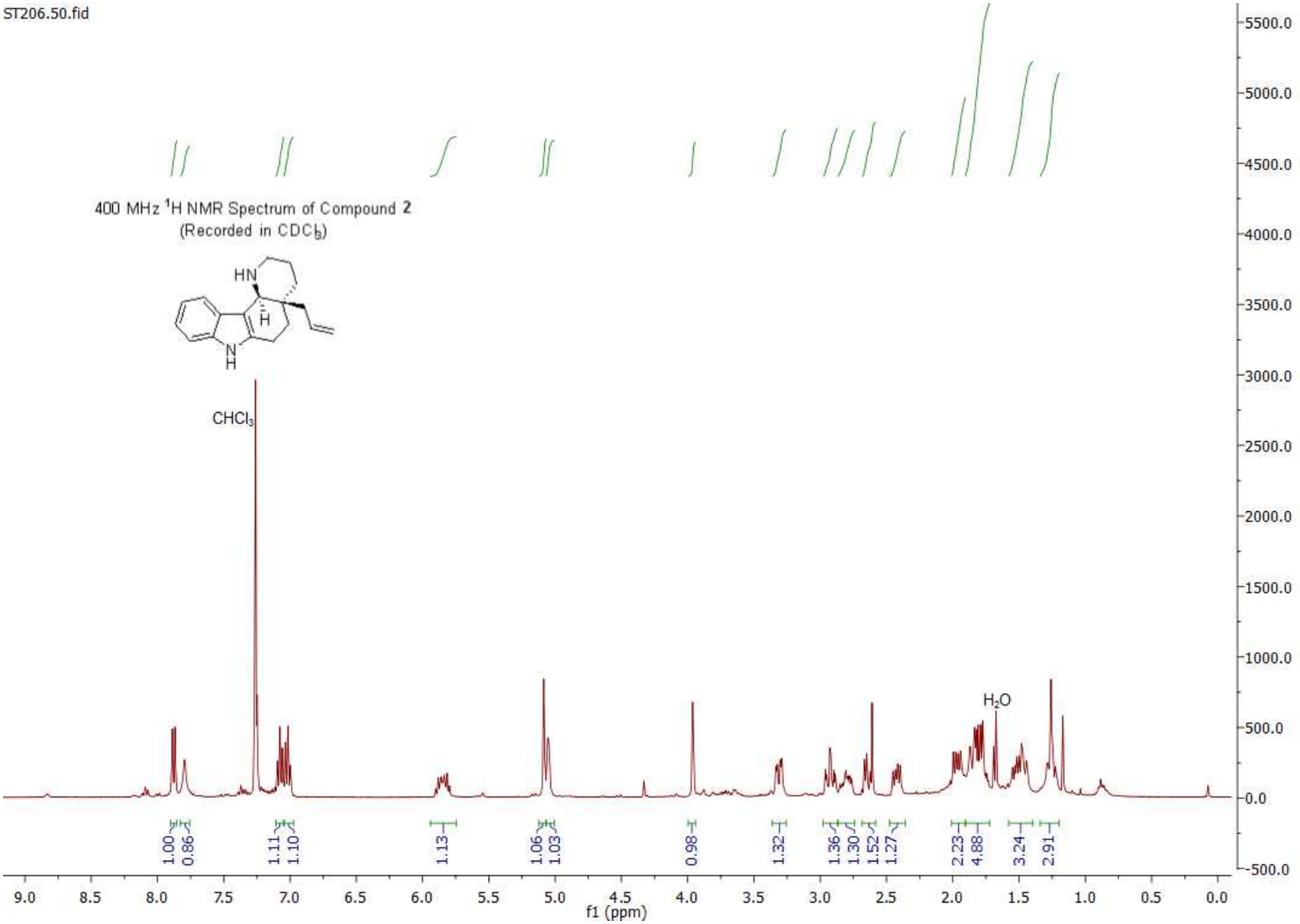

138.14
136.29
135.27
128.01
122.01
119.97
118.41
118.21
111.70
109.46
56.86
CD3OD
46.43
42.69
36.17
35.64
25.46
21.91
20.63
100 MHz 13C NMR Spectrum of Compound 15
(Recorded in CD3OD)
HN
H
N
H
7500.0
7000.0
6500.0
6000.0
5500.0
5000.0
4500.0
4000.0
3500.0
3000.0
2500.0
2000.0
1500.0
1000.0
500.0
0.0
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)


400 MHz ^{1}H NMR Spectrum of Compound **16**
(Recorded in CD_3OD)
HN
H
N
H
O
H_2O
CHD_2OD
CH_3OH
1.00
1.16
1.11
1.04
1.23
1.29
0.81
1.18
1.37
1.24
1.45
0.84
1.29
1.37
4.25
f1 (ppm)


192.89
140.19
134.44
131.92
128.30
127.77
126.63
122.17
121.58
118.98
113.78
56.53
46.41
44.66
43.52
41.88
35.15
23.00
CD3OD
100 MHz 13C NMR Spectrum of Compound 16
(Recorded in CD3OD)
HN
H
N
H
O
f1 (ppm)


400 MHz ¹H NMR Spectrum of Compound 17
(Recorded in CD3OD)
H2O
CHD2OD
CH3OH
1.00
1.10
2.59
0.70
2.24
1.13
1.27
1.53
1.35
1.23
1.41
3.05
4.91
1.77
f1 (ppm)


178.02
155.37
139.17
132.91
125.81
124.58
124.15
120.77
120.50
113.80
105.69
CD3OD
45.24
39.85
38.72
34.07
28.65
20.97
17.34
100 MHz 13C NMR Spectrum of Compound 17
(Recorded in CD3OD)
N
NH
f1 (ppm)


ST206.50.fid
400 MHz ^{1}H NMR Spectrum of Compound **2**
(Recorded in $CDCl_3$)
HN
H
N
H
$CHCl_3$
H_2O
1.00
0.86
1.11
1.10
1.13
1.06
1.03
0.98
1.32
1.36
1.30
1.52
1.27
2.23
4.88
3.24
2.91
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)
5500.0
5000.0
4500.0
4000.0
3500.0
3000.0
2500.0
2000.0
1500.0
1000.0
500.0
0.0
-500.0

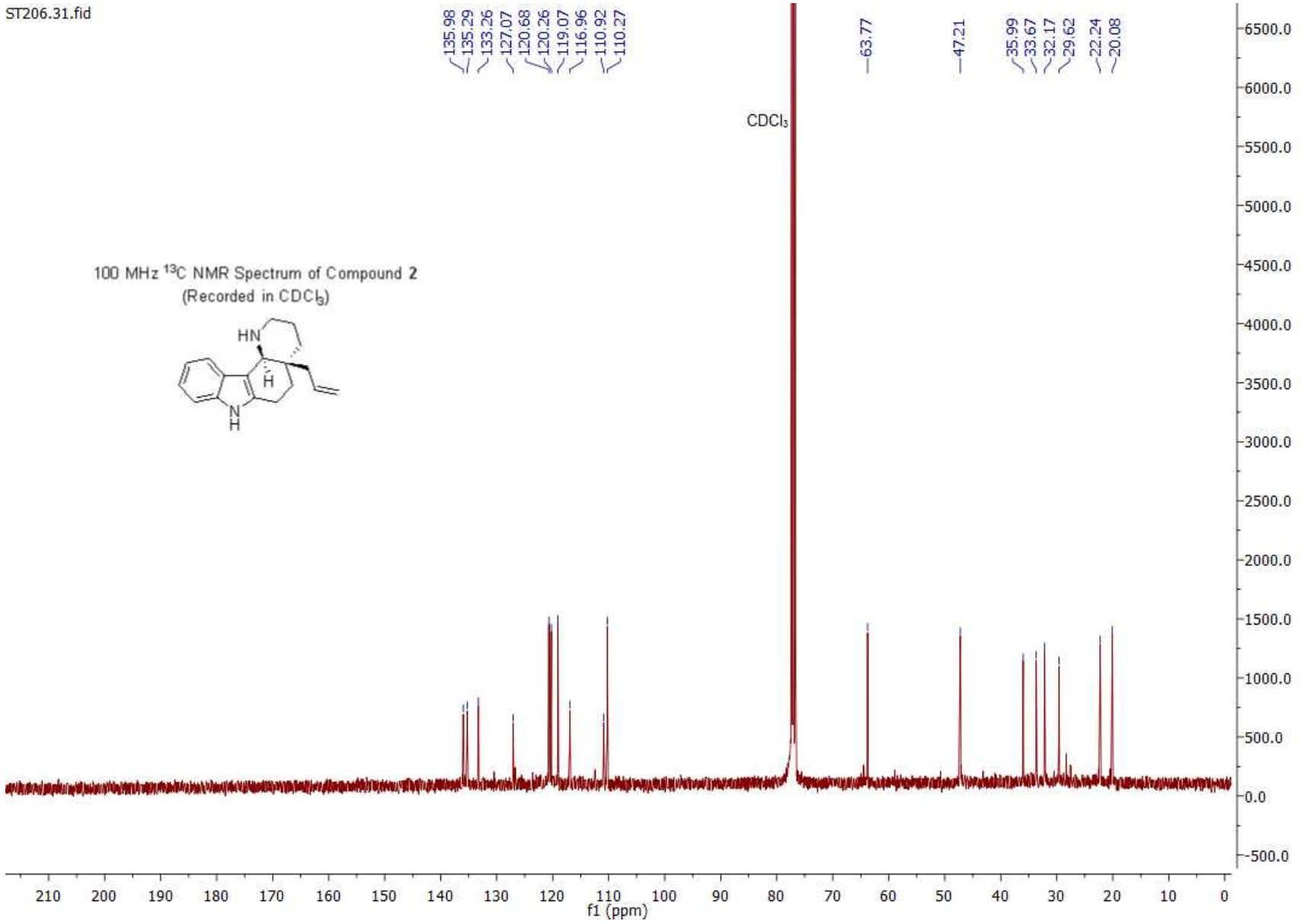

ST206.31.fid
135.98
135.29
133.26
127.07
120.68
120.26
119.07
116.96
110.92
110.27
63.77
47.21
35.99
33.67
32.17
29.62
22.24
20.08
CDCl3
100 MHz 13C NMR Spectrum of Compound 2
(Recorded in CDCl3)
HN
H
N
H
6500.0
6000.0
5500.0
5000.0
4500.0
4000.0
3500.0
3000.0
2500.0
2000.0
1500.0
1000.0
500.0
0.0
-500.0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Table 1: *Comparison of ^{13}C NMR Data Recorded for Compound **2** Obtained by the Route Associated with the Present Study with those Reported by Mukai*[6]

^{13}C NMR Data for Compound **2** (δ_C)[a]	^{13}C NMR Data from Mukai (δ_C)[b]
136.0	135.9
135.3	135.3
133.3	133.3
127.1	127.1
120.7	120.6
120.3	120.2
119.1	119.0
117.0	117.0
110.9	110.9
110.3	110.3
63.8	63.7
47.2	47.2
36.0	35.9
33.7	33.6
32.2	32.1
29.6	29.6
22.2	22.2
20.1	20.0

[a]spectrum recorded in $CDCl_3$ at 100 MHz;
[b]data obtained from reference 6, spectrum recorded in $CDCl_3$ at 100 MHz.