SUPPORTING INFORMATION FOR:

ABC → ABCE/D BASED APPROACHES TO THE PENTACYCLIC RING SYSTEM OF THE *VINCA* ALKALOIDS USING INTRAMOLECULAR HETERO-[2+2]CYCLOADDITION AND GOLD(I)-CATALYSED 6-*ENDO-DIG* CYCLISATION PROTOCOLS

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The Australian National University, Canberra, ACT 0200 (Australia)

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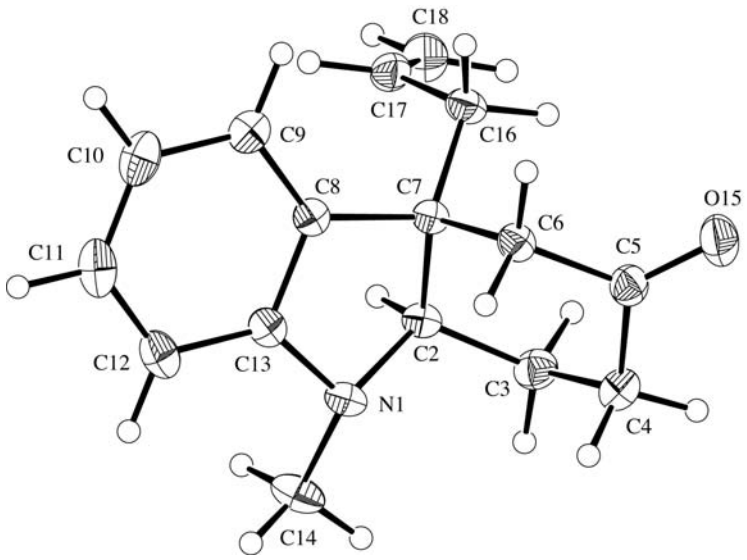


Figure S1. Structure of compound **10** (CCDC990090) with labelling of selected atoms. Anisotropic displacement ellipsoids display 30% probability levels. Hydrogen atoms are drawn as circles with small radii.

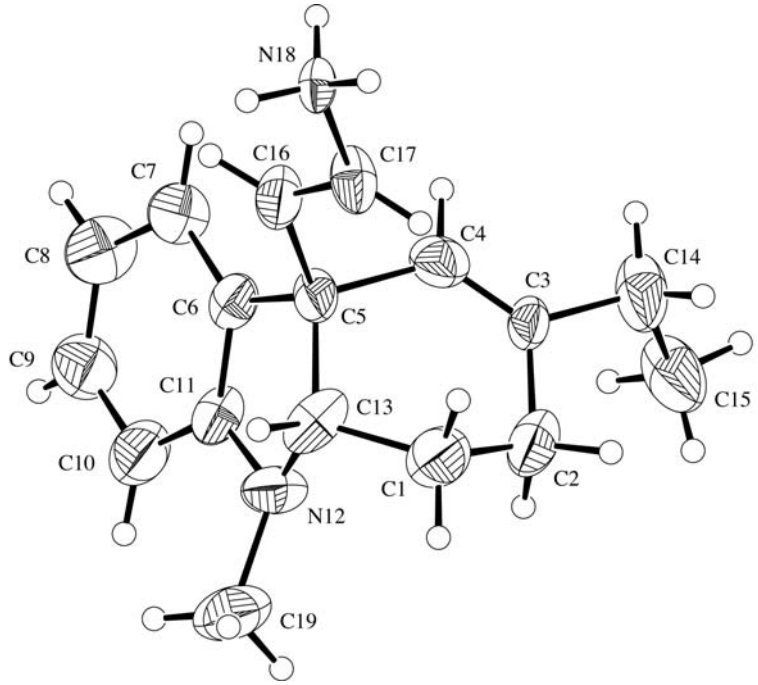


Figure S2. Structure of the cation of the oxalate salt of compound **14** (CCDC990091) with labelling of selected atoms. Anisotropic displacement ellipsoids display 30% probability levels. Hydrogen atoms are drawn as circles with small radii.

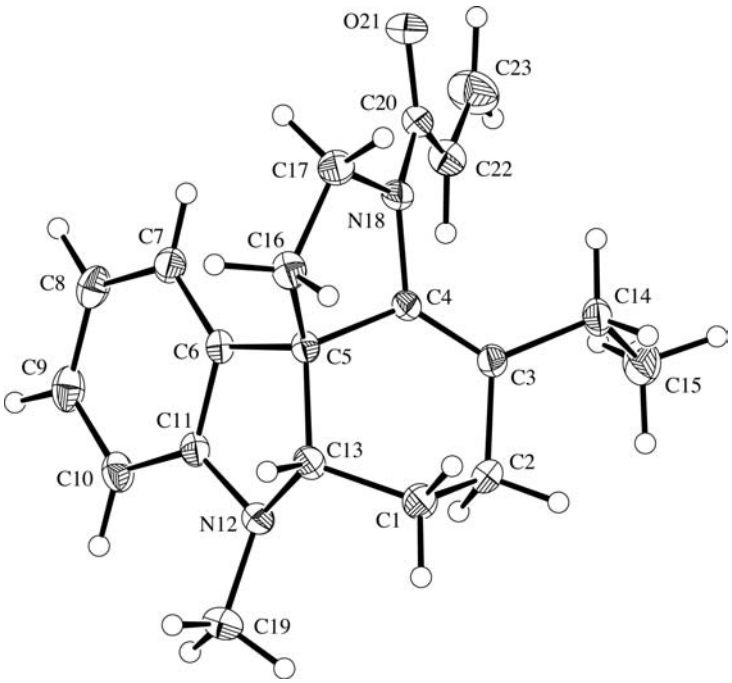
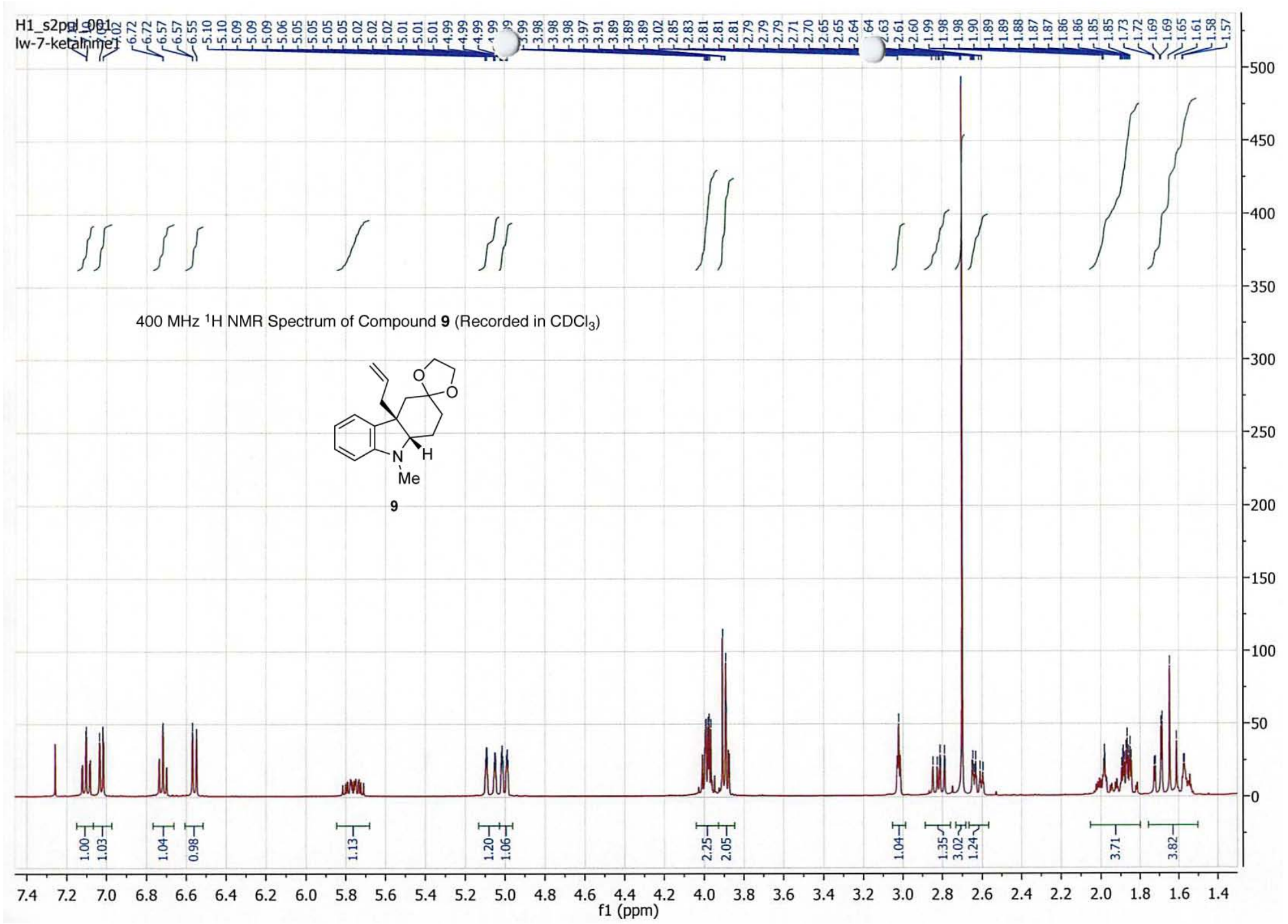
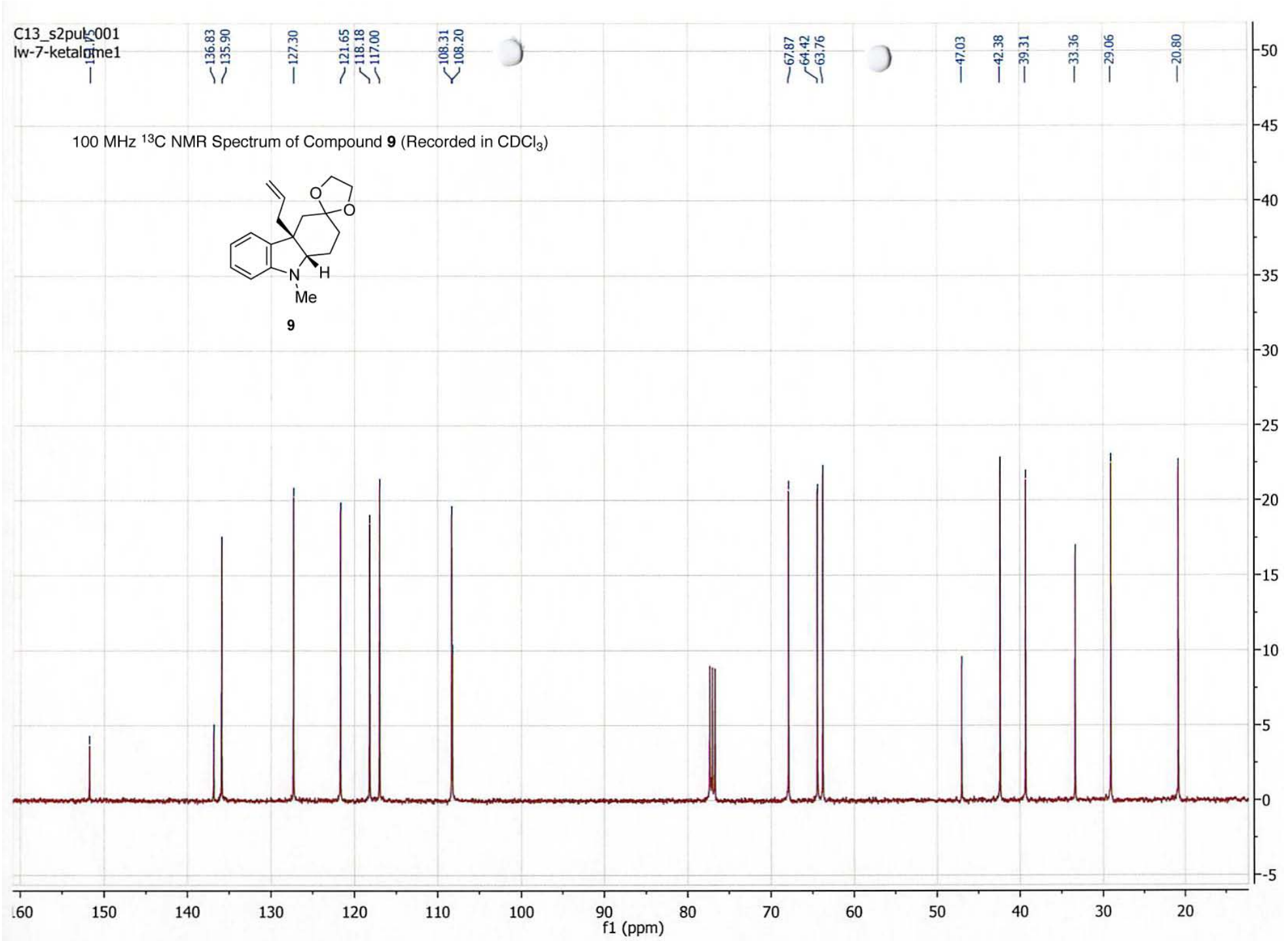
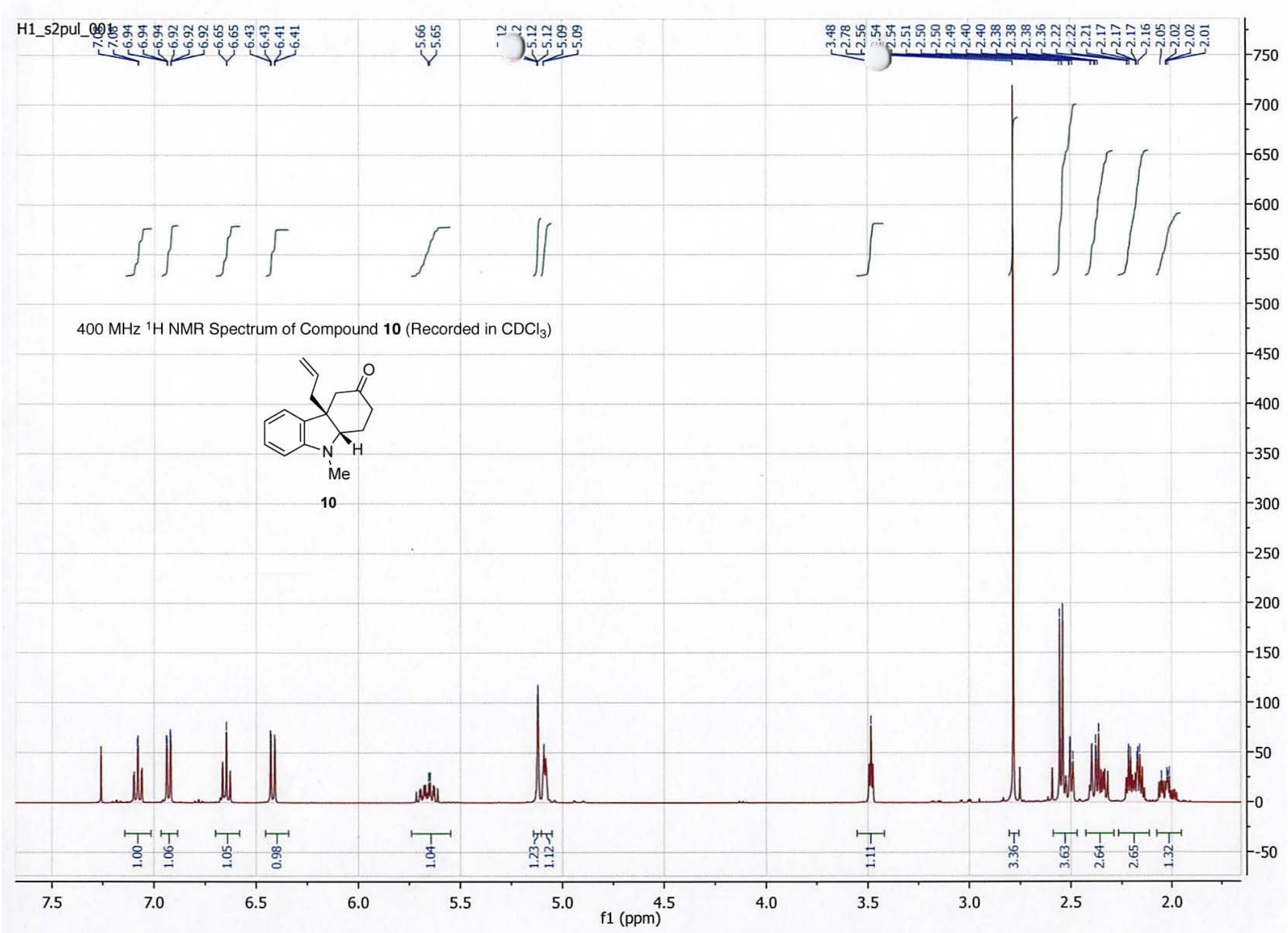
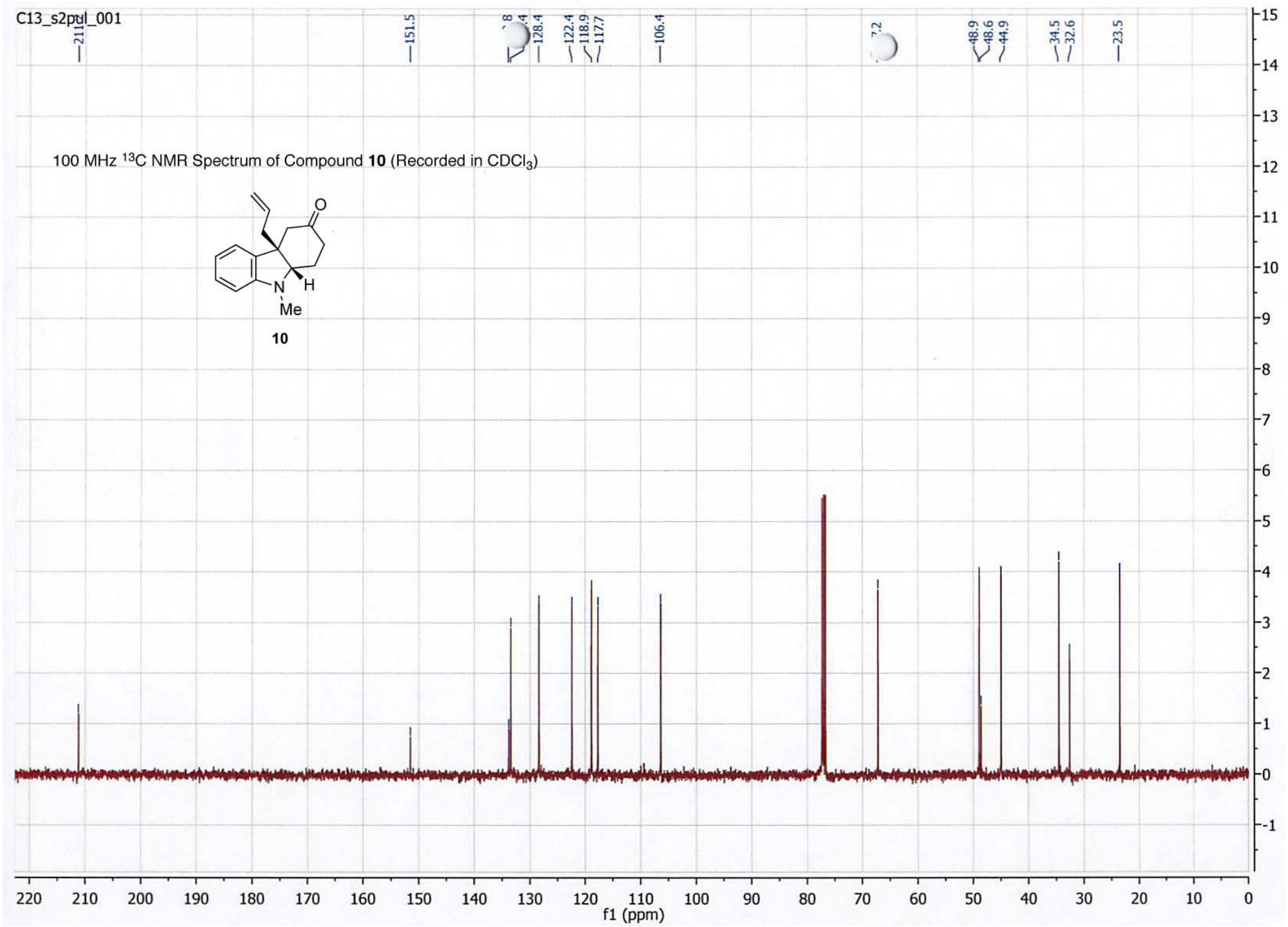


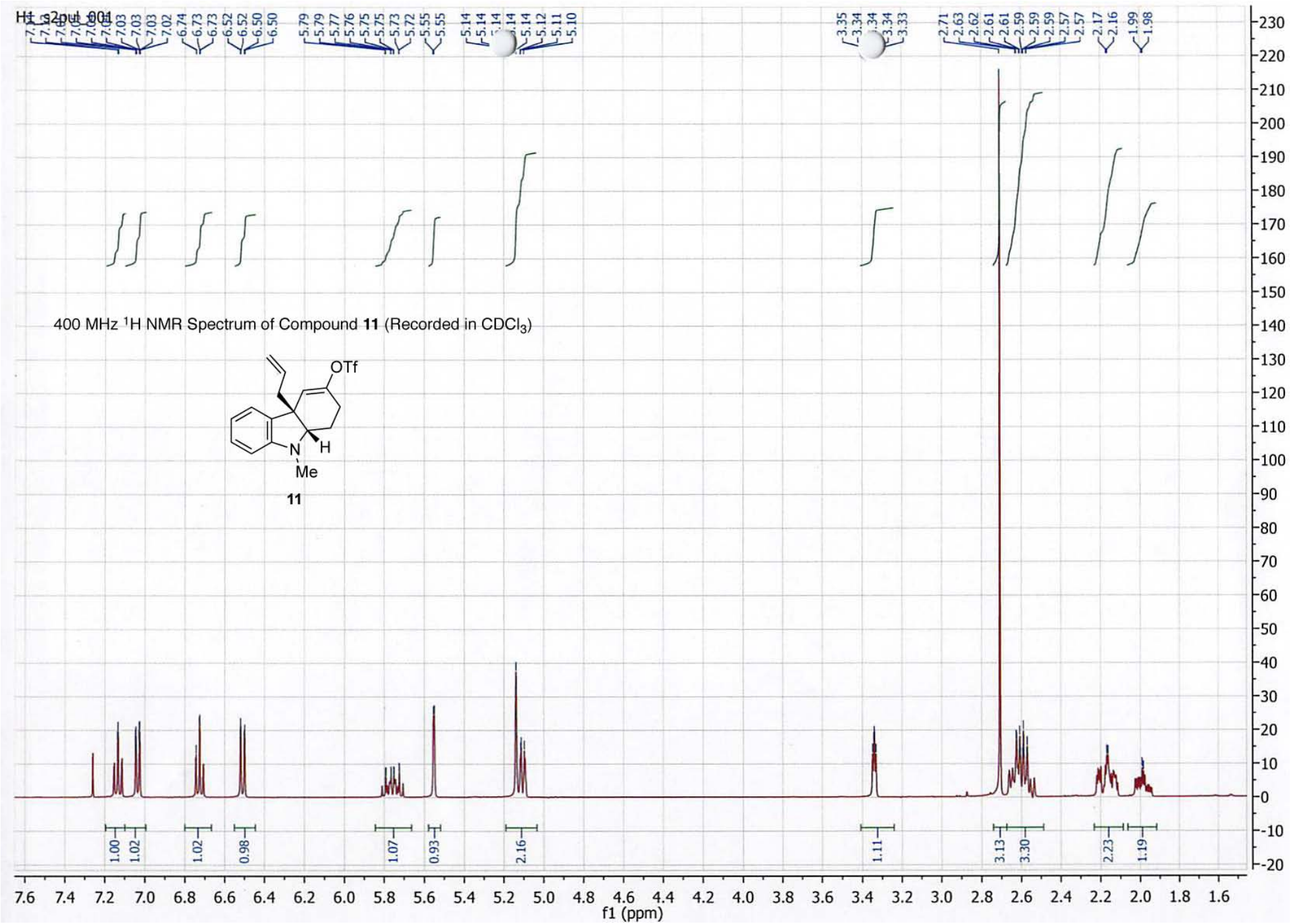
Figure S3. Structure of compound **22** (CCDC990092) with labelling of selected atoms. Anisotropic displacement ellipsoids display 30% probability levels. Hydrogen atoms are drawn as circles with small radii.

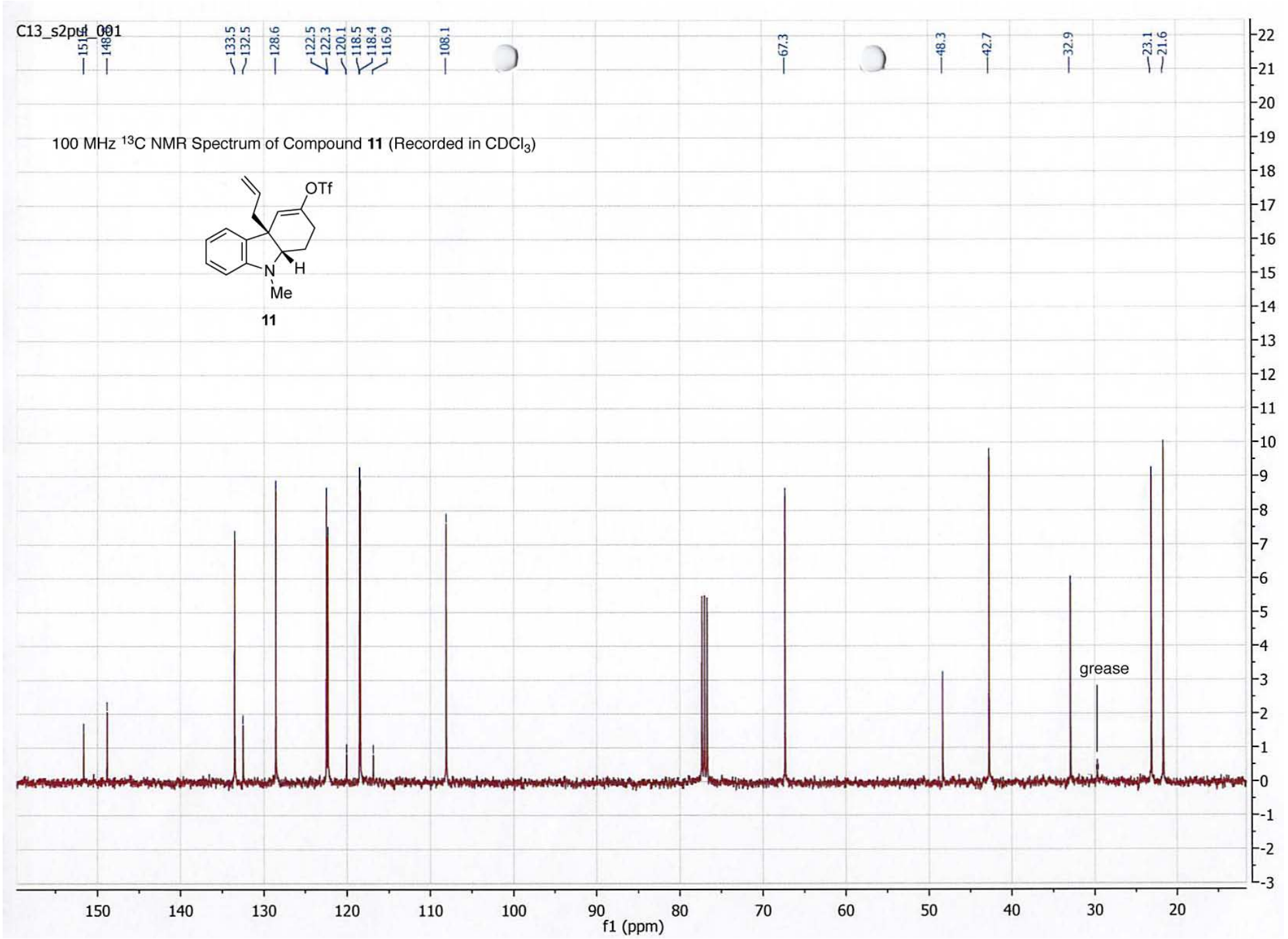

H1_s2pul_001
lw-7-ketalmet
400 MHz ¹H NMR Spectrum of Compound 9 (Recorded in CDCl3)
O
O
N
H
Me
9
f1 (ppm)

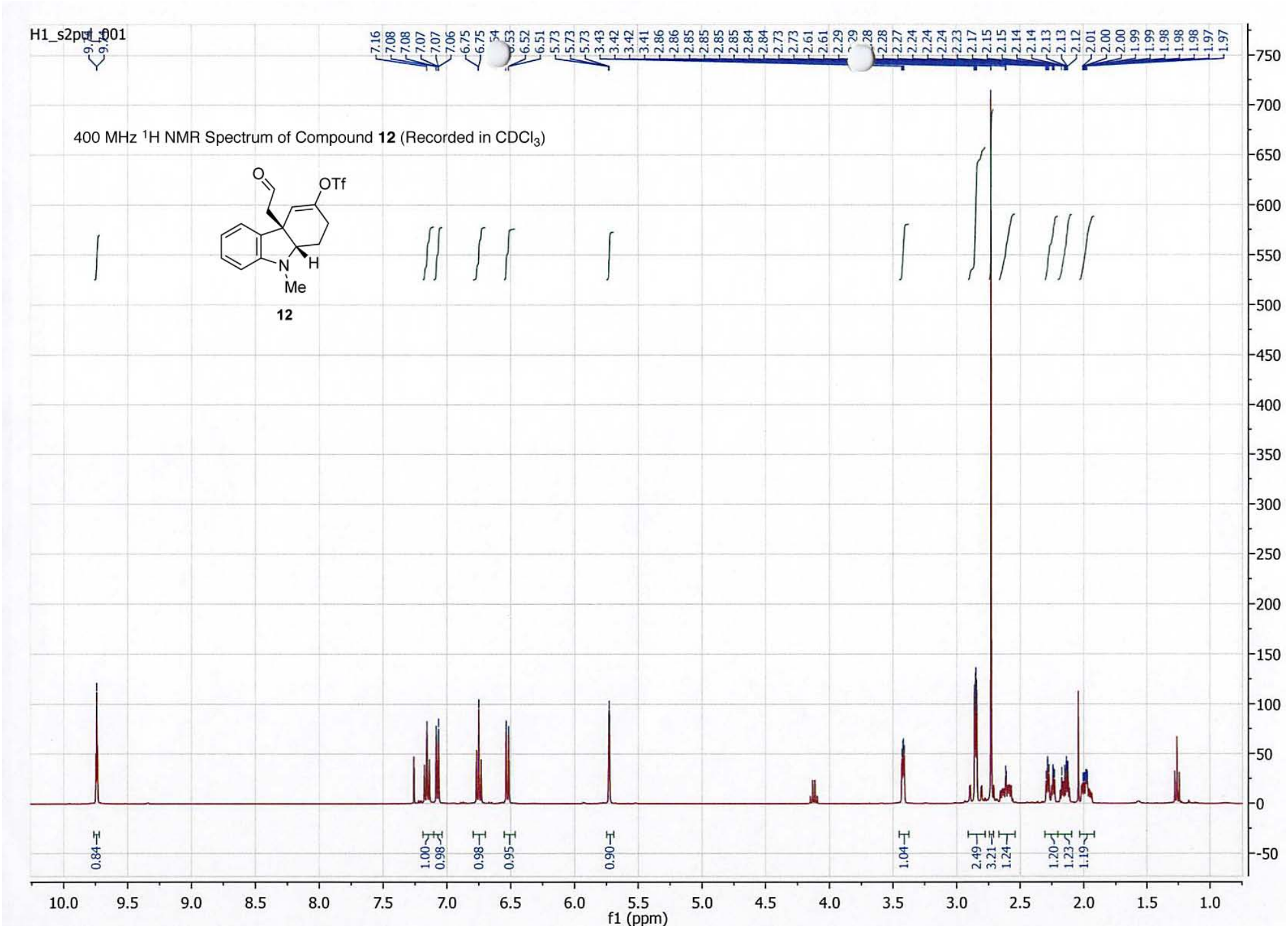

C13_s2pul-001
lw-7-ketalone1
148.47
136.83
135.90
127.30
121.65
118.18
117.00
108.31
108.20
67.87
64.42
63.76
47.03
42.38
39.31
33.36
29.06
20.80
100 MHz 13C NMR Spectrum of Compound 9 (Recorded in CDCl3)
O
O
N
H
Me
9
f1 (ppm)

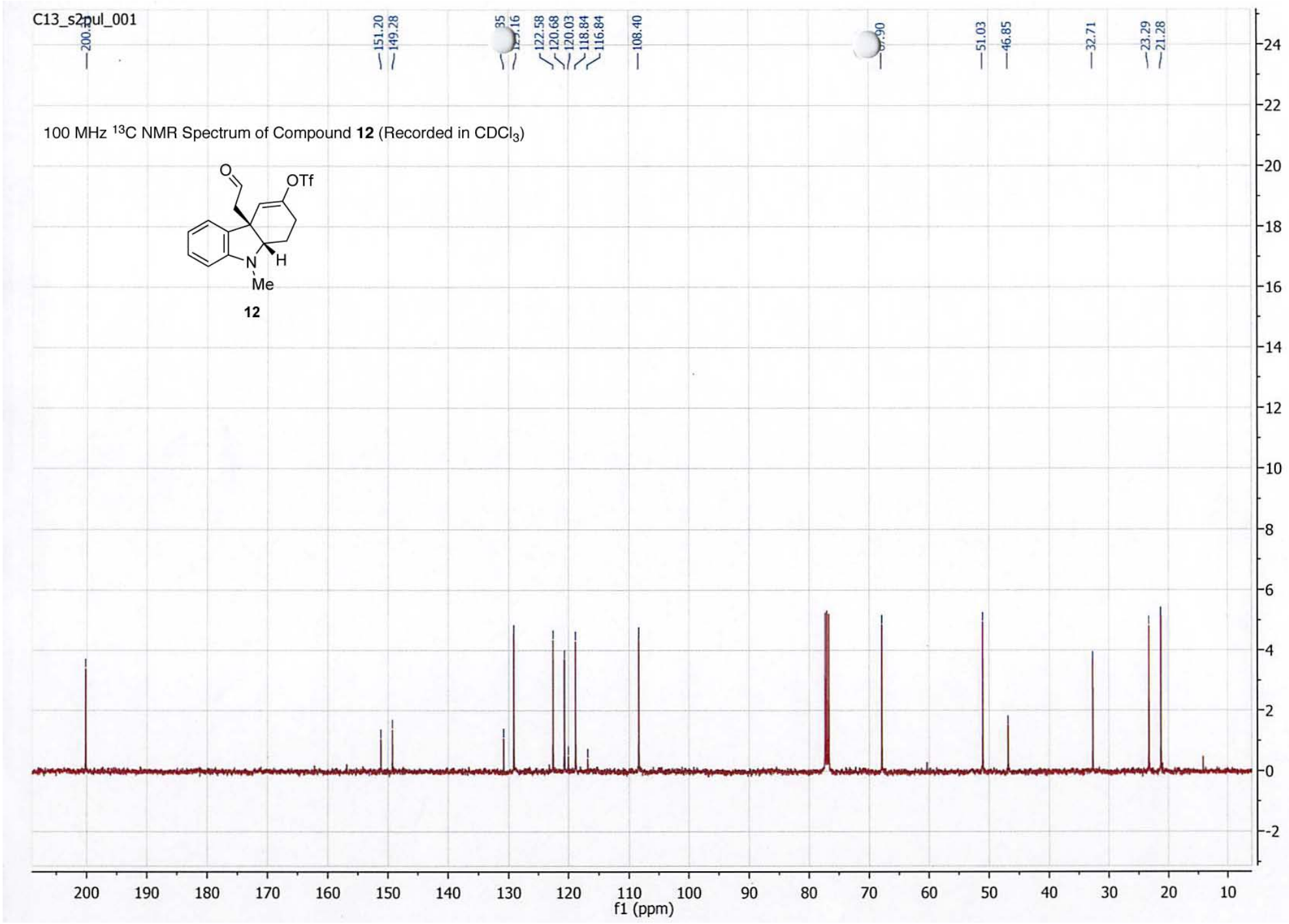

H1_s2pul_001
400 MHz ^{1}H NMR Spectrum of Compound **10** (Recorded in $CDCl_3$)
O
N
H
Me
10
f1 (ppm)

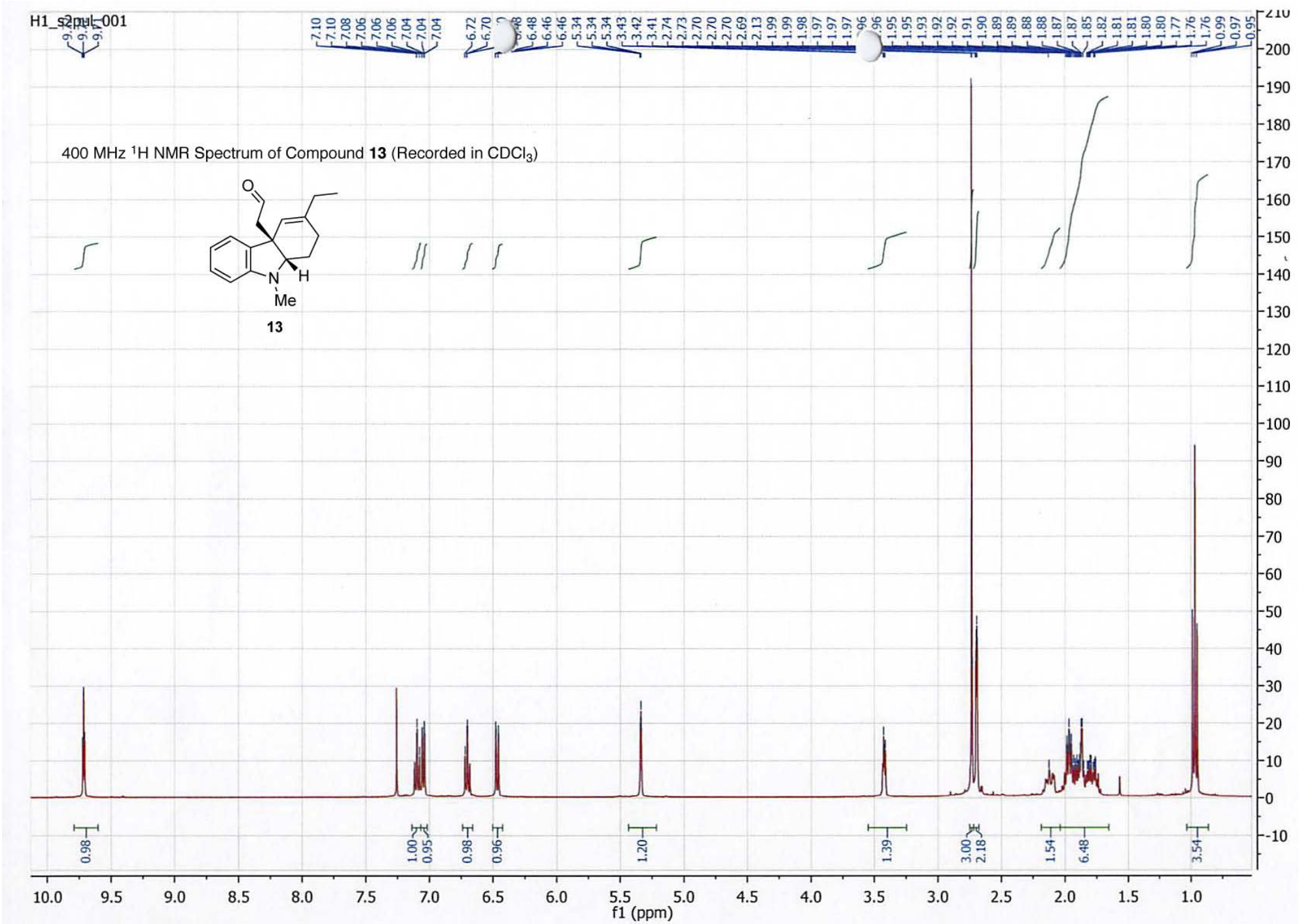

C13_s2pul_001
211
151.5
128.4
122.4
118.9
117.7
106.4
48.9
48.6
44.9
34.5
32.6
23.5
100 MHz ^{13}C NMR Spectrum of Compound **10** (Recorded in $CDCl_3$)
O
N
H
Me
10
f1 (ppm)

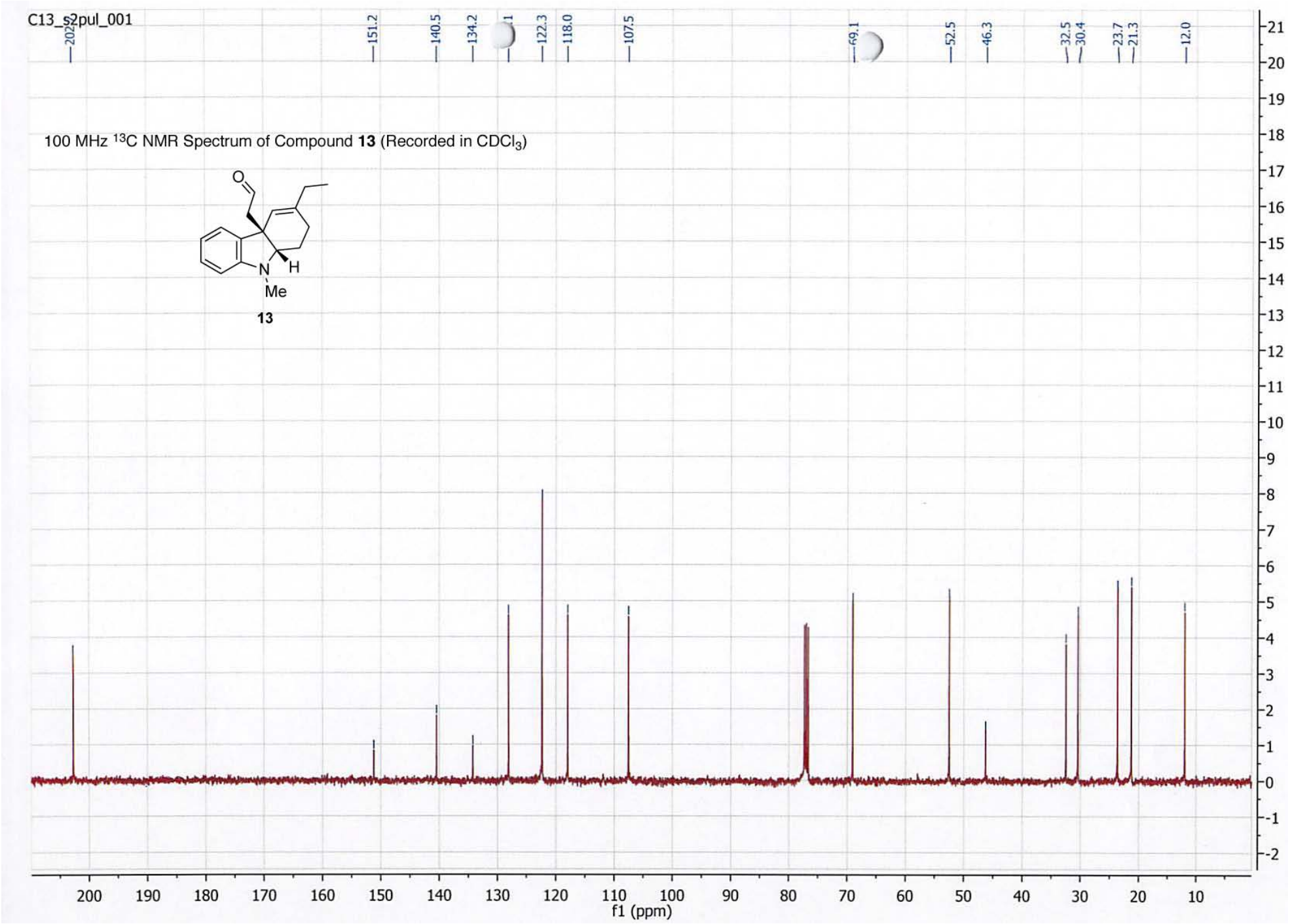

400 MHz ¹H NMR Spectrum of Compound 11 (Recorded in CDCl3)
OTf
N
H
Me
11
f1 (ppm)

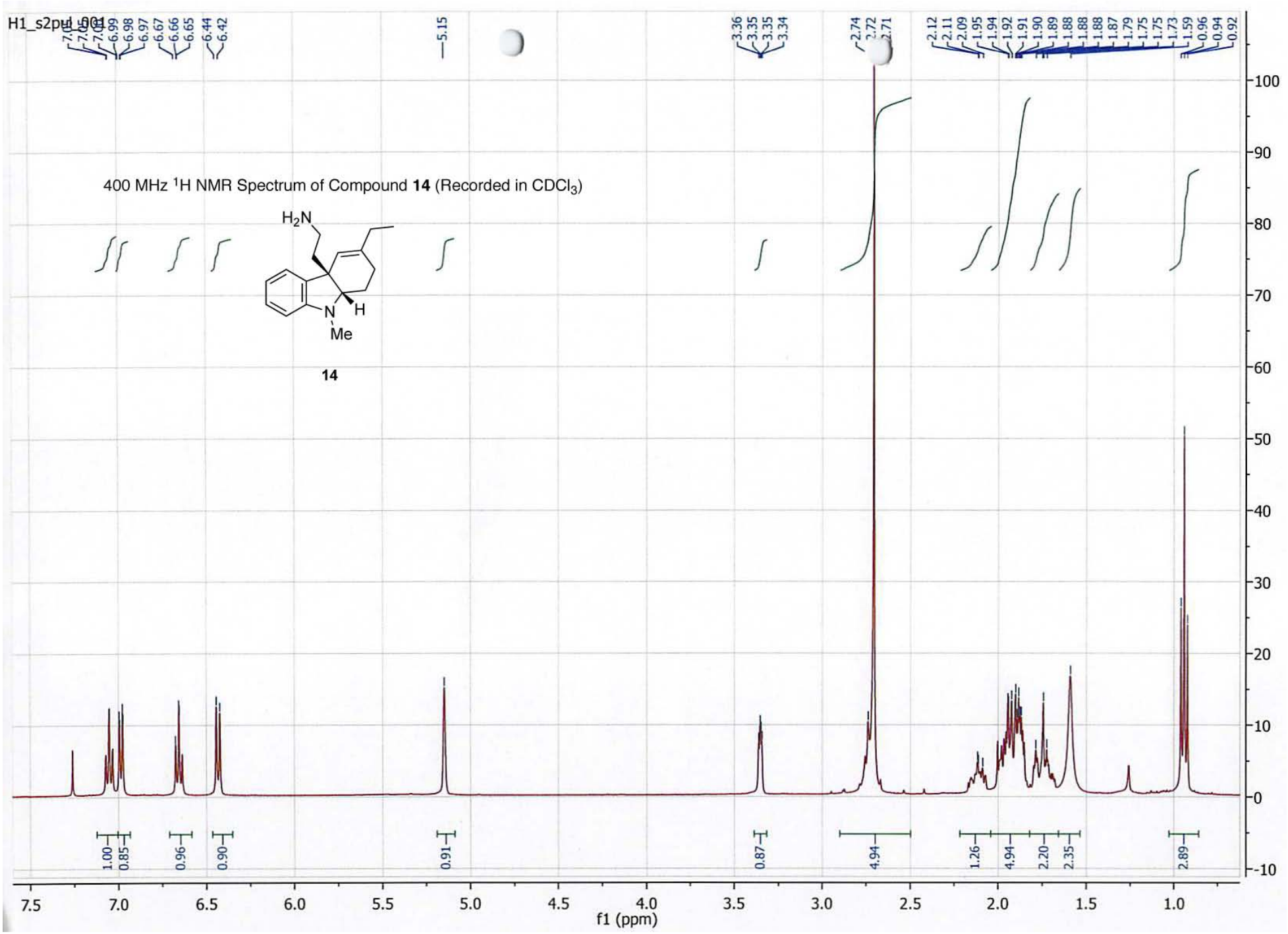

C13_s2pul_001
151.1
148.4
133.5
132.5
128.6
122.5
122.3
120.1
118.5
118.4
116.9
108.1
67.3
48.3
42.7
32.9
23.1
21.6
100 MHz 13C NMR Spectrum of Compound 11 (Recorded in CDCl3)
OTf
N
H
Me
11
grease
f1 (ppm)

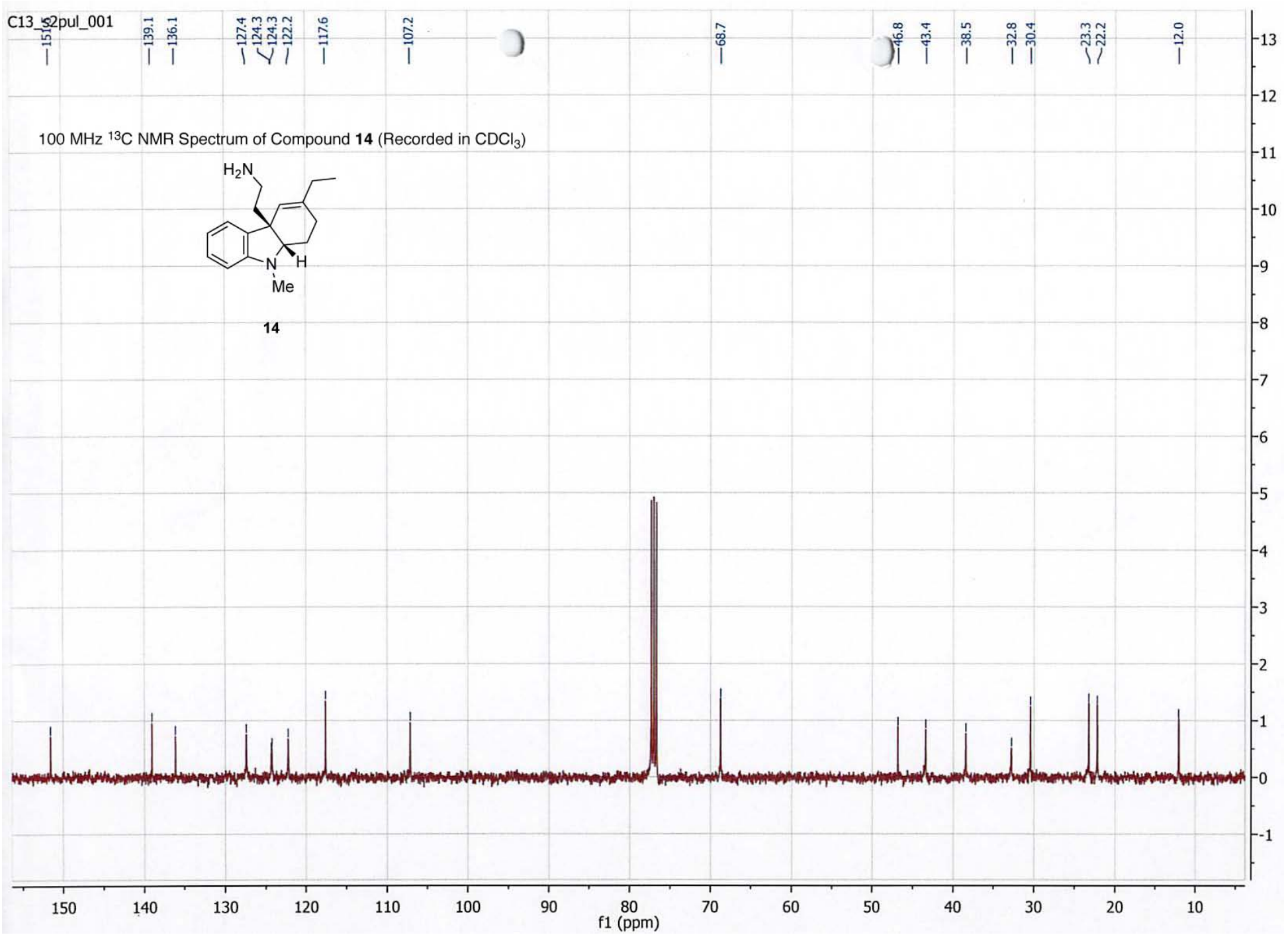

H1_s2pul_001
400 MHz ^{1}H NMR Spectrum of Compound **12** (Recorded in $CDCl_3$)
O
OTf
N
H
Me
12
f1 (ppm)


C13_s2pul_001
200.11
151.20
149.28
129.16
122.58
120.68
120.03
118.84
116.84
108.40
67.90
51.03
46.85
32.71
23.29
21.28
100 MHz ^{13}C NMR Spectrum of Compound **12** (Recorded in $CDCl_3$)
O
OTf
N
H
Me
12
f1 (ppm)


H1_s2pul_001
400 MHz ^{1}H NMR Spectrum of Compound **13** (Recorded in $CDCl_3$)
O
N
H
Me
13
f1 (ppm)

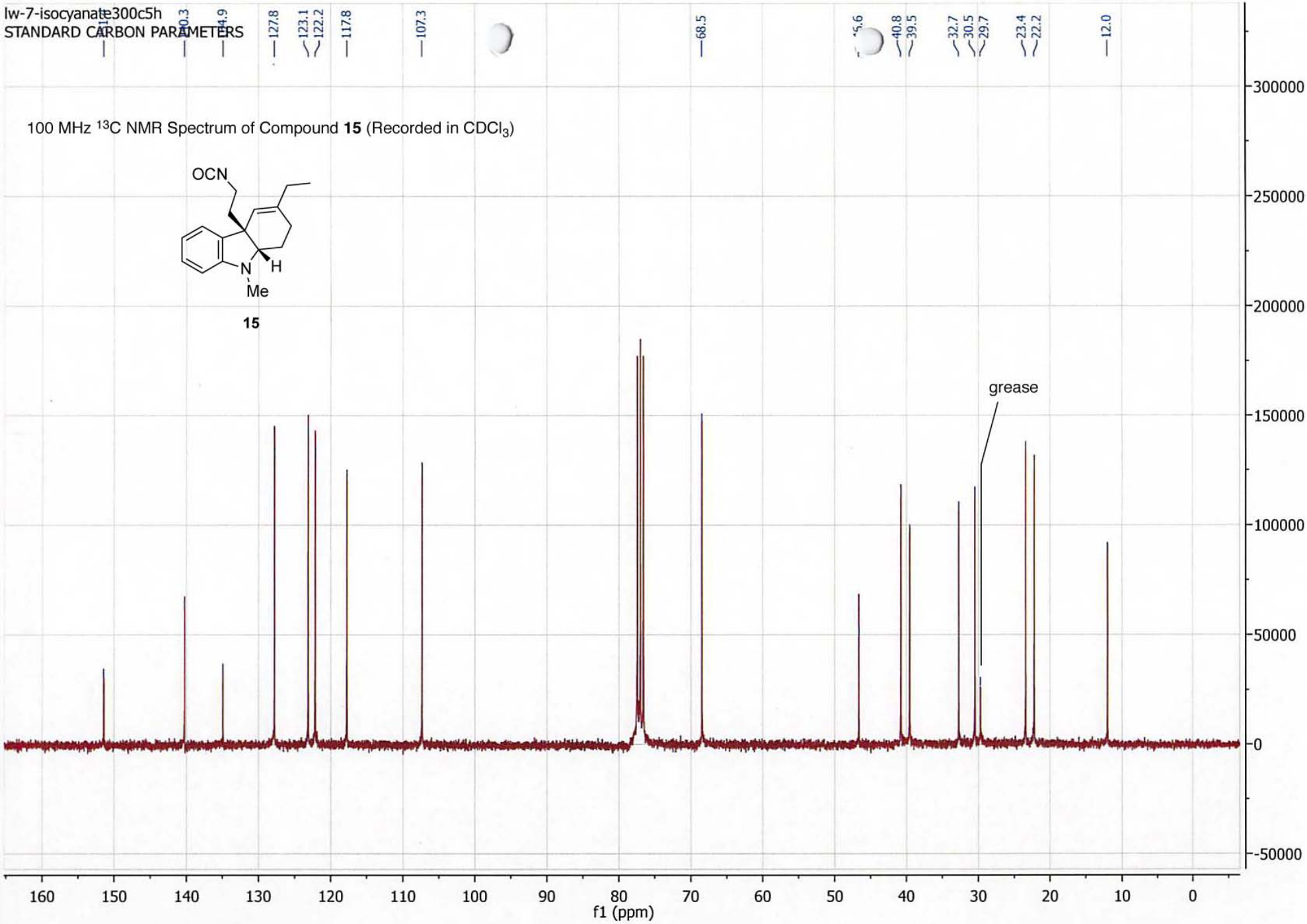

C13_s2pul_001
202.2
151.2
140.5
134.2
122.3
118.0
107.5
69.1
52.5
46.3
32.5
30.4
23.7
21.3
12.0
100 MHz ^{13}C NMR Spectrum of Compound **13** (Recorded in $CDCl_3$)
O
N
H
Me
13
f1 (ppm)

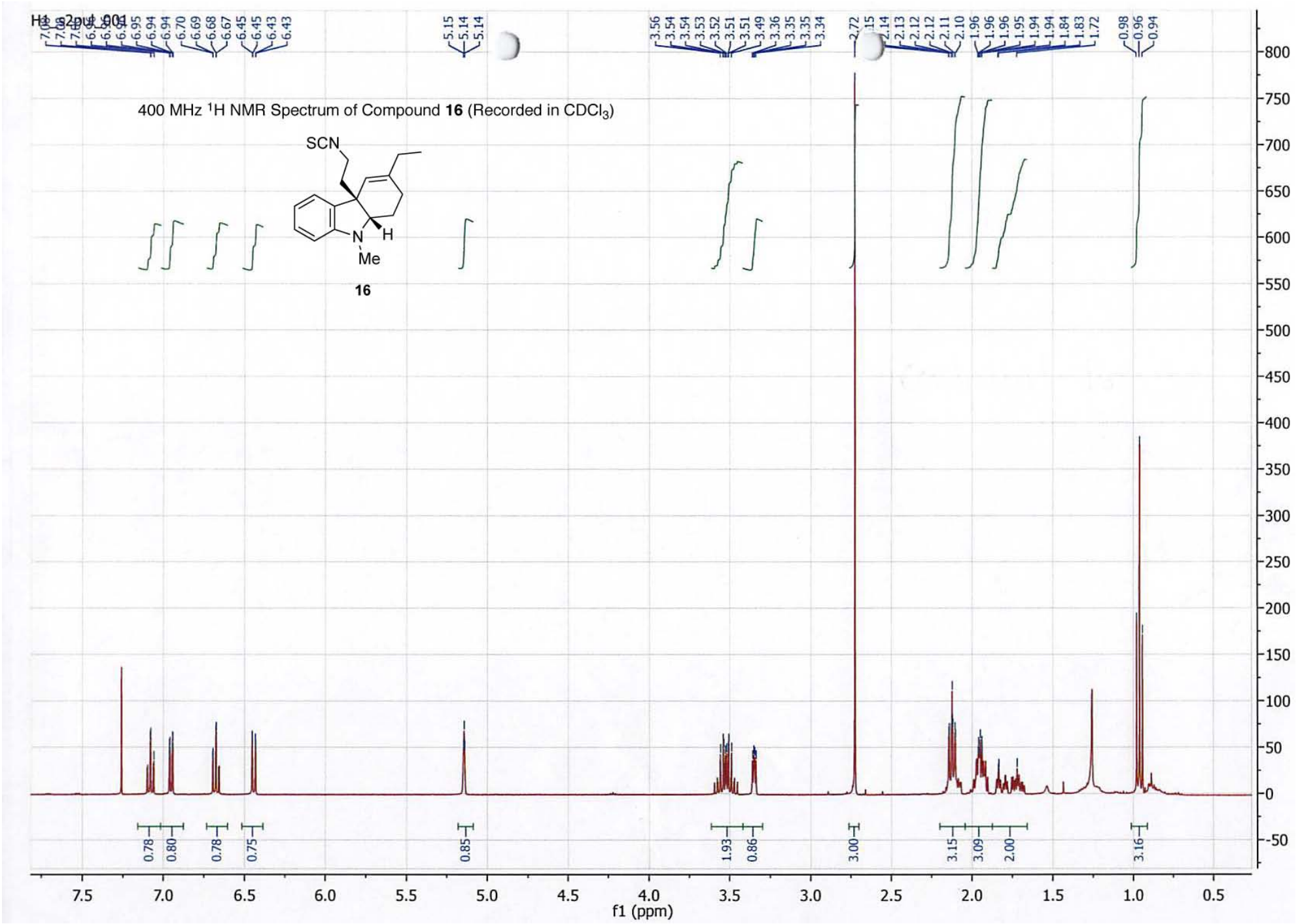

H1_s2pul_001
400 MHz ^{1}H NMR Spectrum of Compound **14** (Recorded in $CDCl_3$)
H_2N
N
H
Me
14
f1 (ppm)

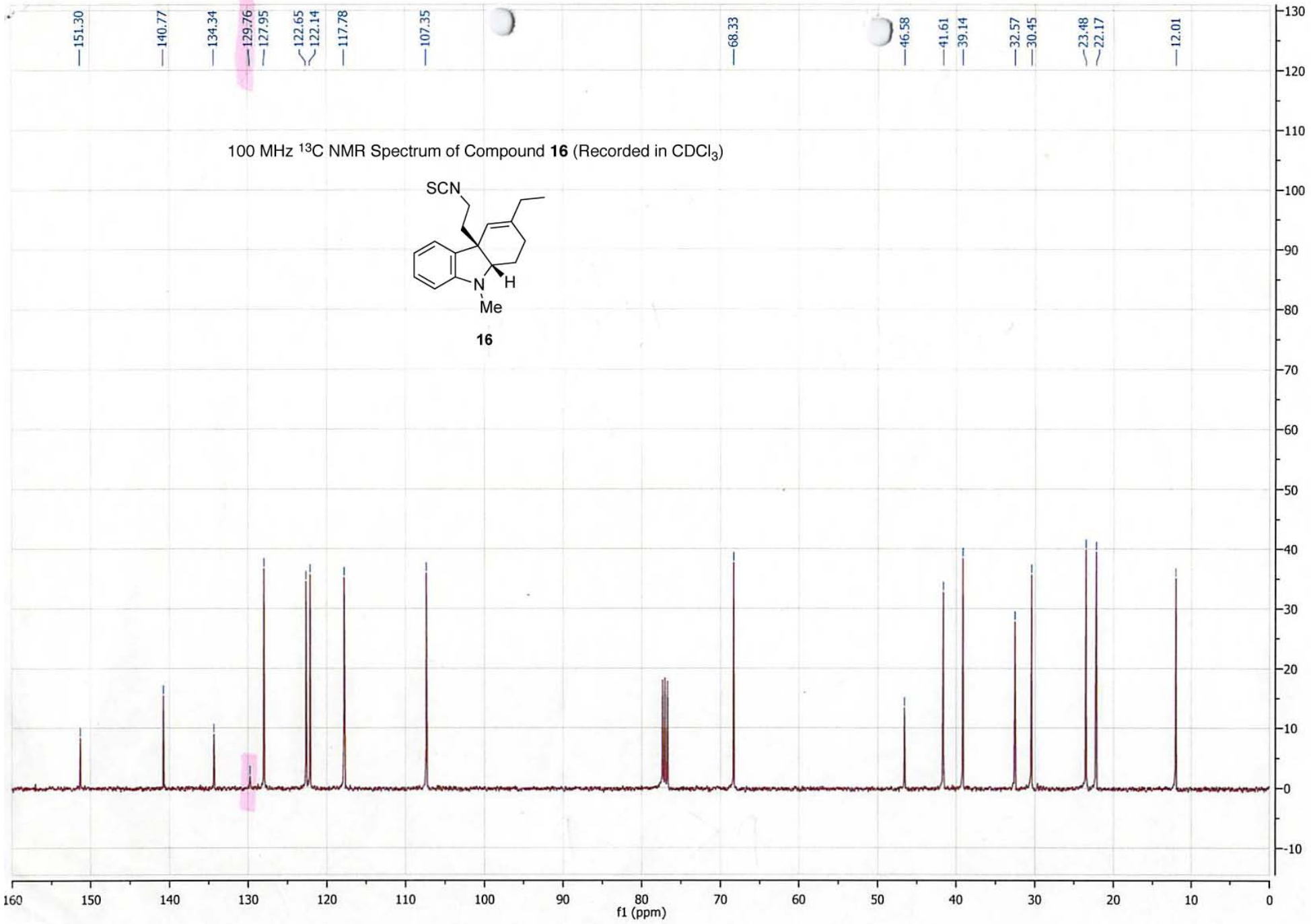

C13_s2pul_001
151.
139.1
136.1
127.4
124.3
124.3
122.2
117.6
107.2
68.7
46.8
43.4
38.5
32.8
30.4
23.3
22.2
12.0
100 MHz 13C NMR Spectrum of Compound 14 (Recorded in CDCl3)
H2N
N
H
Me
14
f1 (ppm)

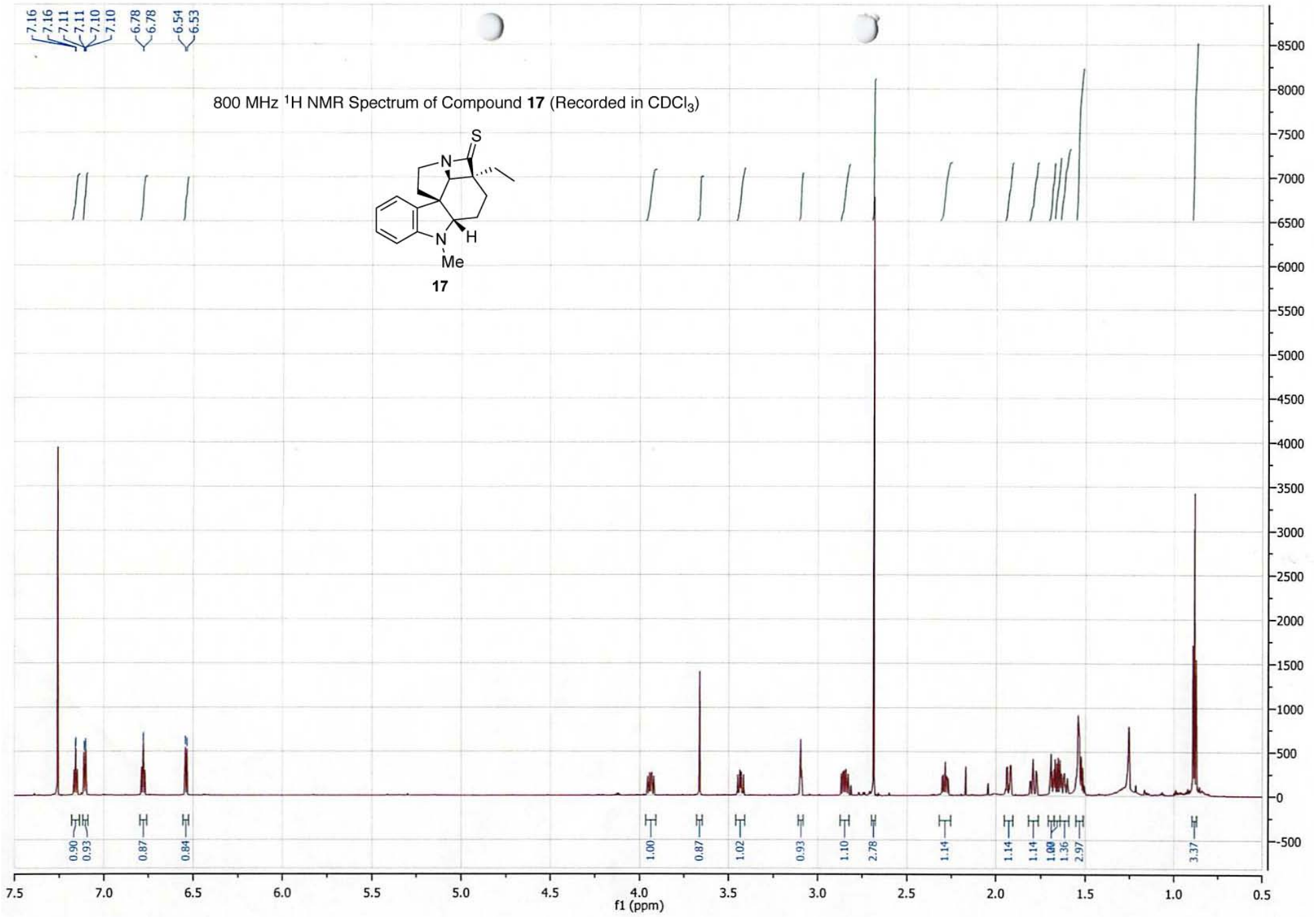
400 MHz ^{1}H NMR Spectrum of Compound **15** (Recorded in $CDCl_3$)

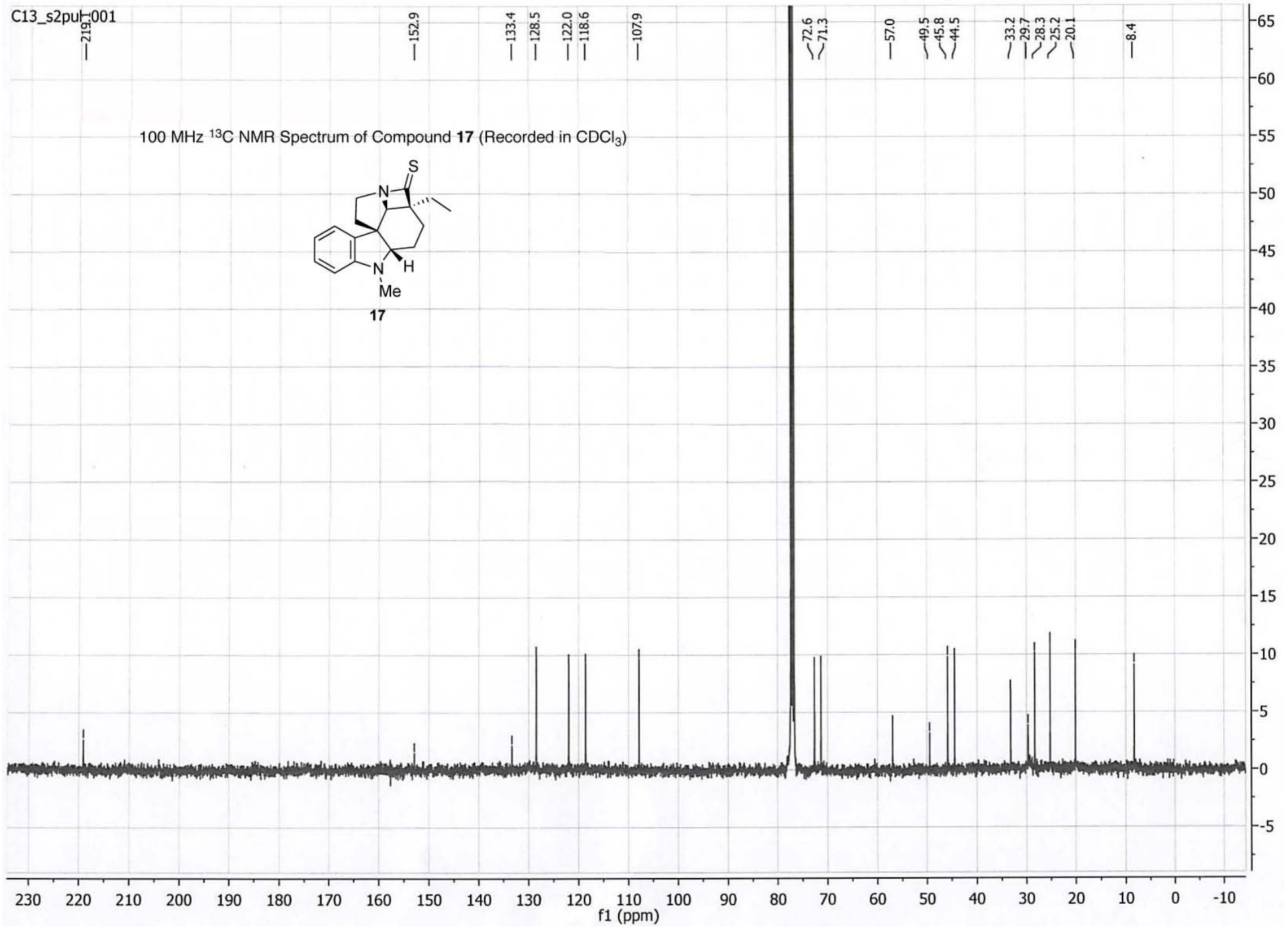
15

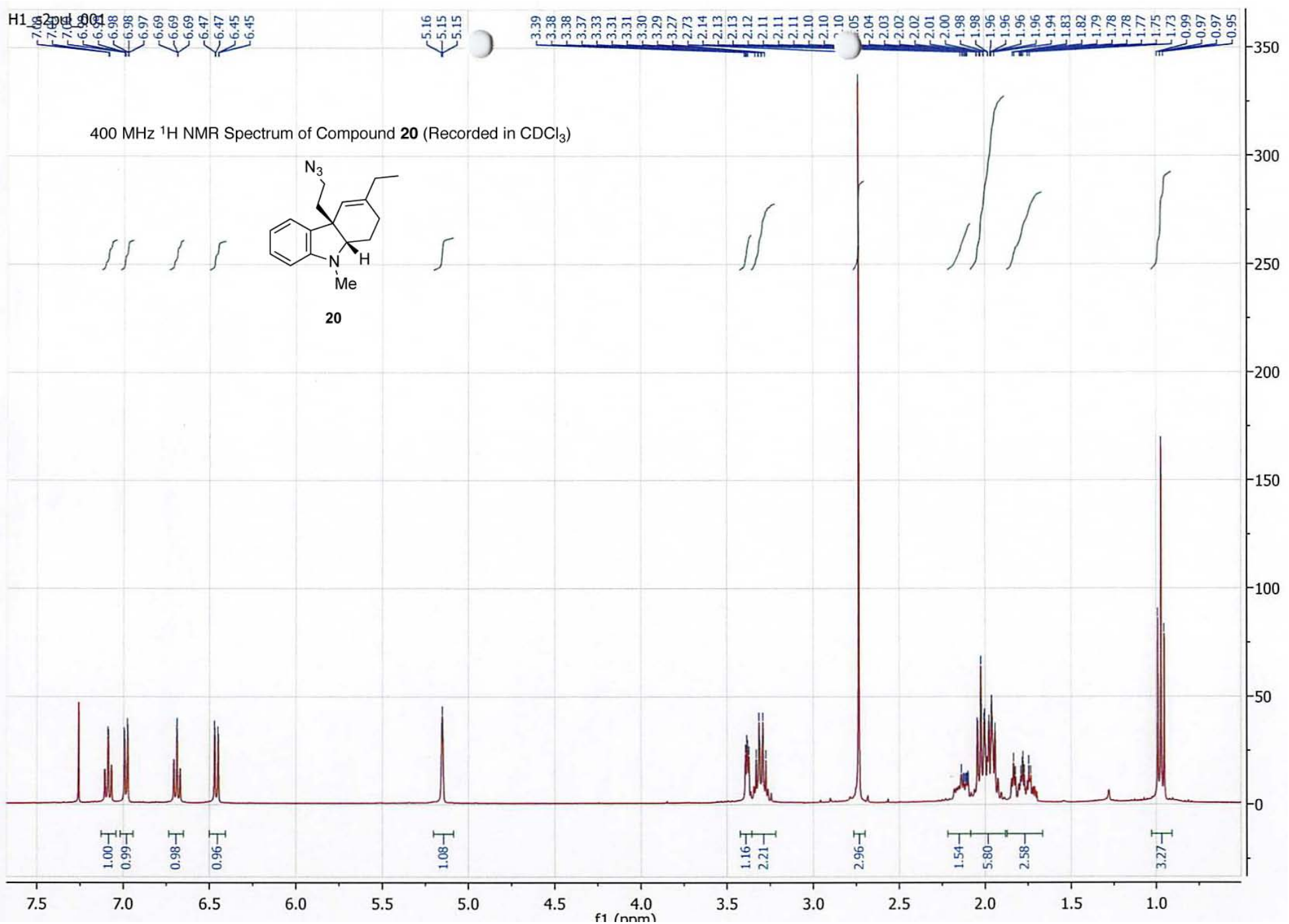

lw-7-isocyanate300c5h
STANDARD CARBON PARAMETERS
127.8
123.1
122.2
117.8
107.3
68.5
40.8
39.5
32.7
30.5
29.7
23.4
22.2
12.0
100 MHz ^{13}C NMR Spectrum of Compound **15** (Recorded in $CDCl_3$)
OCN
N
H
Me
15
grease
300000
250000
200000
150000
100000
50000
0
-50000
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

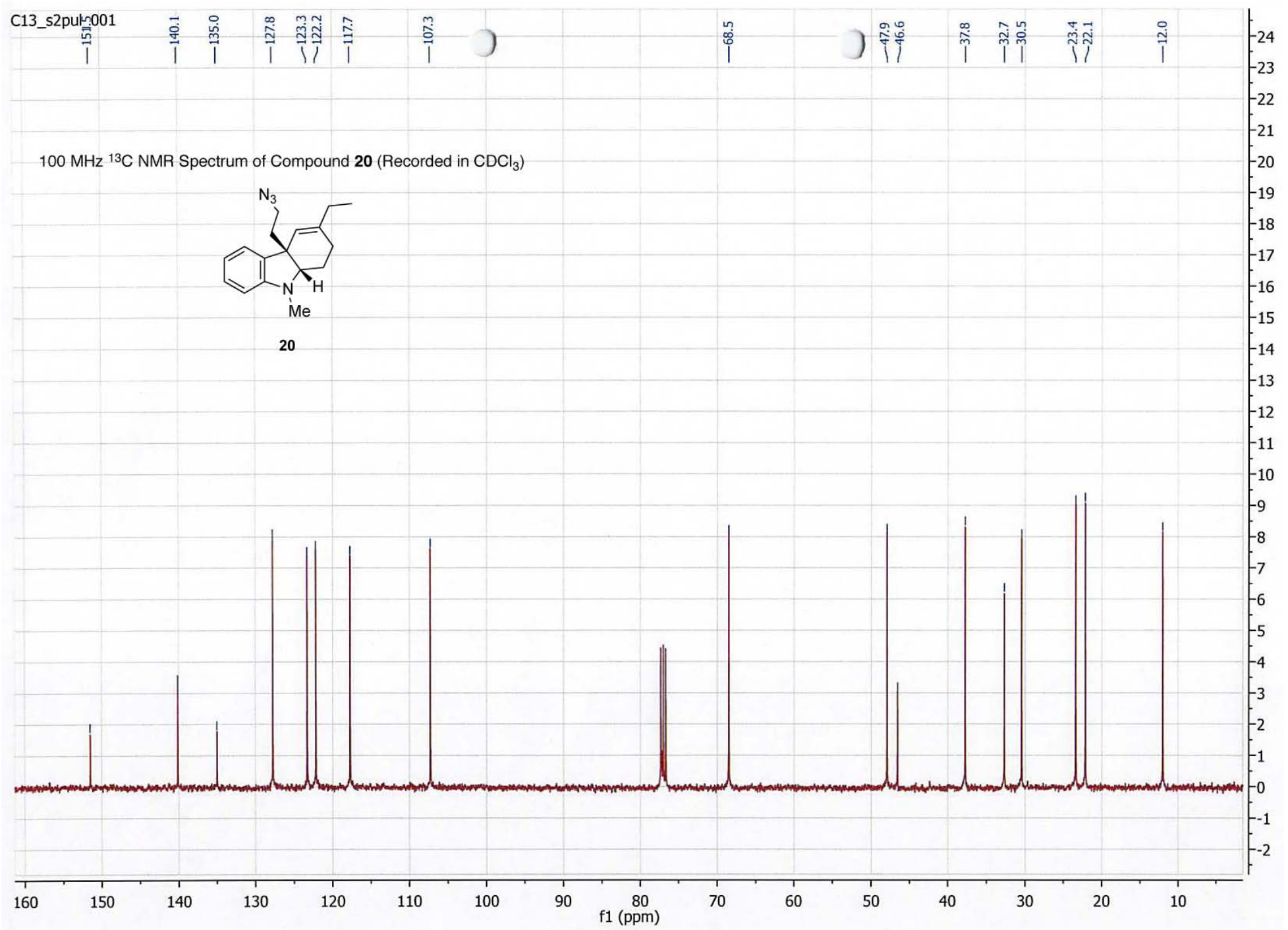

400 MHz ^{1}H NMR Spectrum of Compound **16** (Recorded in $CDCl_3$)
SCN
N
H
Me
16
f1 (ppm)

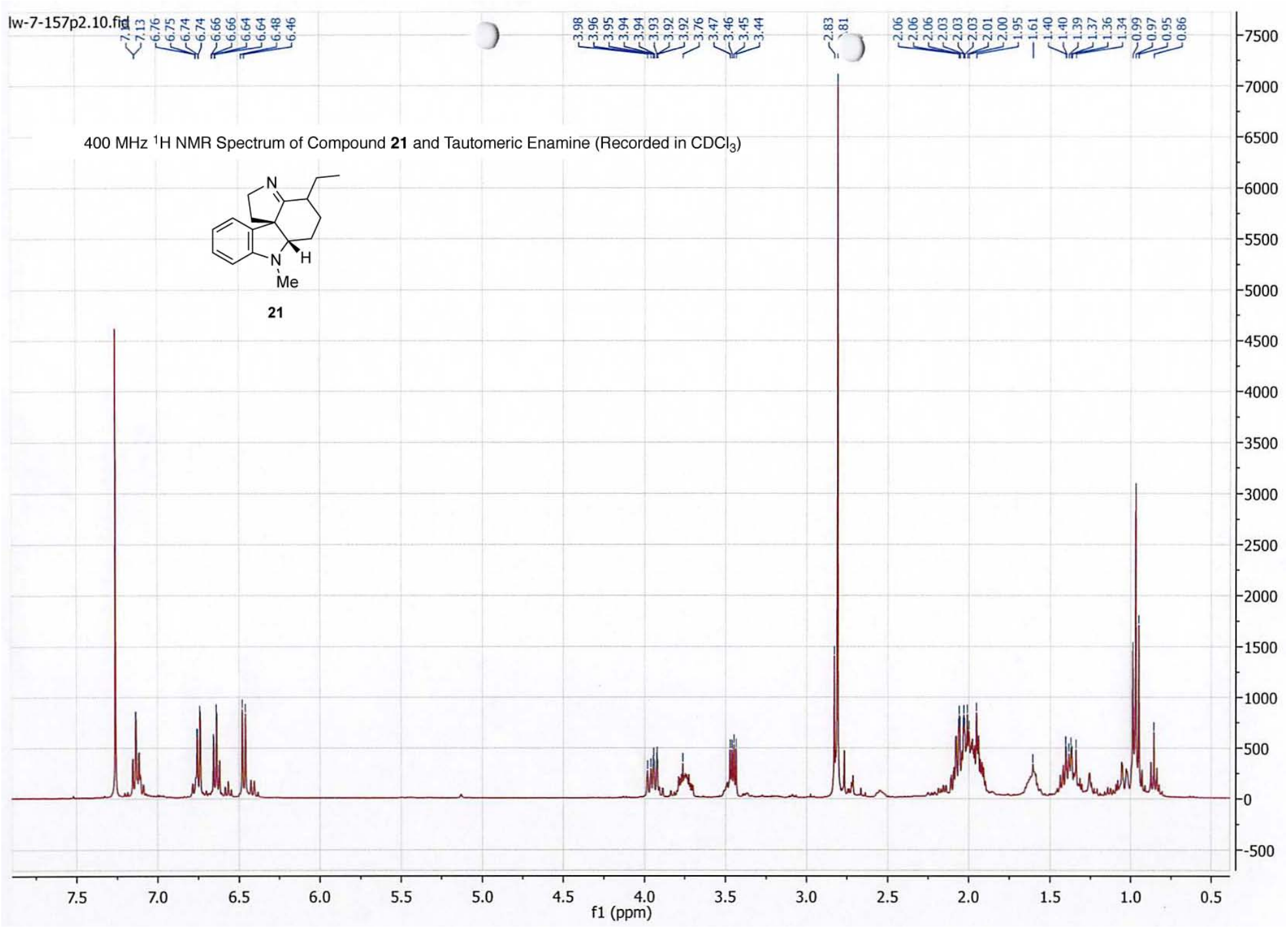

151.30
140.77
134.34
129.76
127.95
122.65
122.14
117.78
107.35
68.33
46.58
41.61
39.14
32.57
30.45
23.48
22.17
12.01
100 MHz ^{13}C NMR Spectrum of Compound **16** (Recorded in $CDCl_3$)
SCN
N
H
Me
16
f1 (ppm)

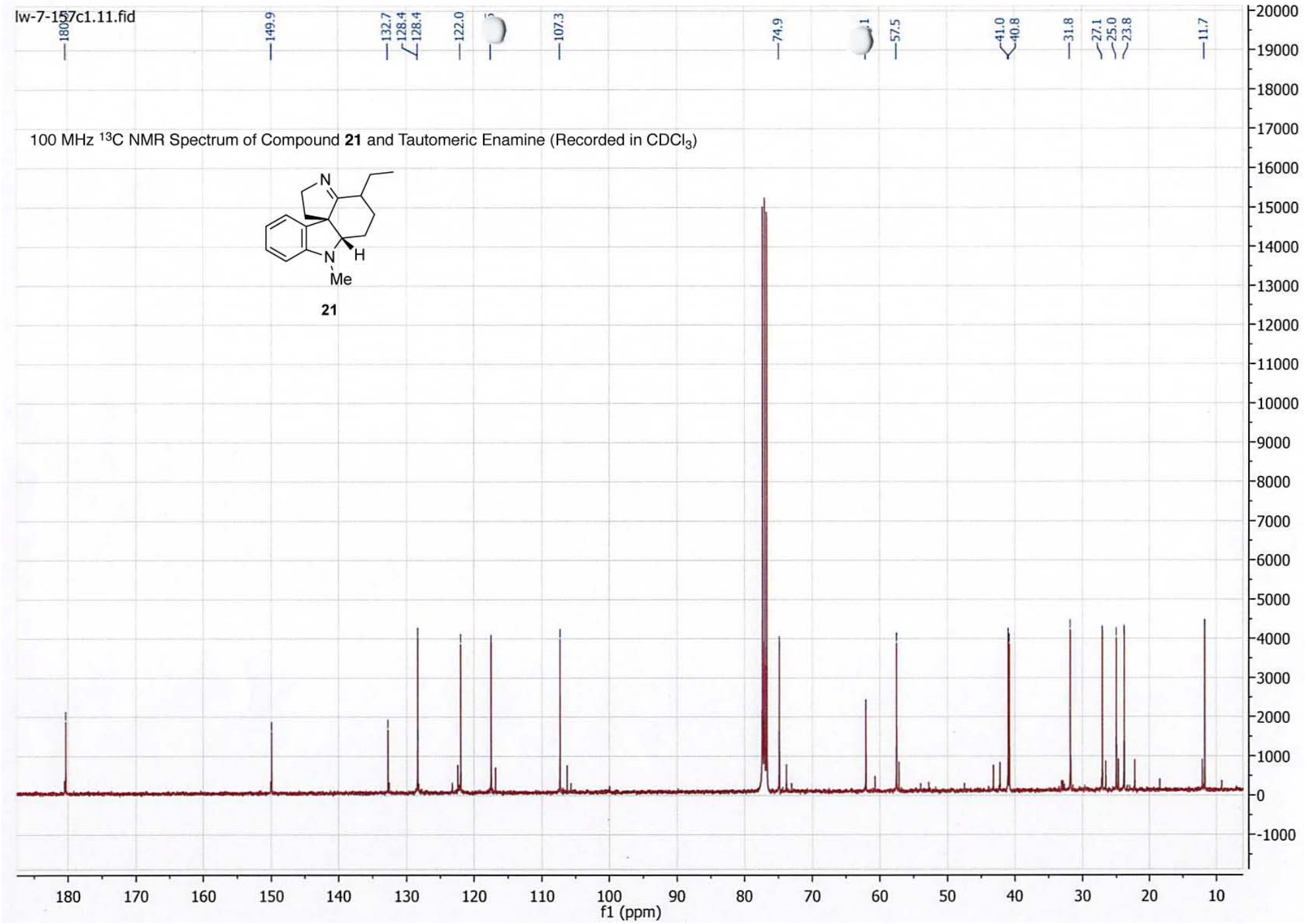

800 MHz ¹H NMR Spectrum of Compound 17 (Recorded in CDCl3)
S
N
N
H
Me
17
f1 (ppm)

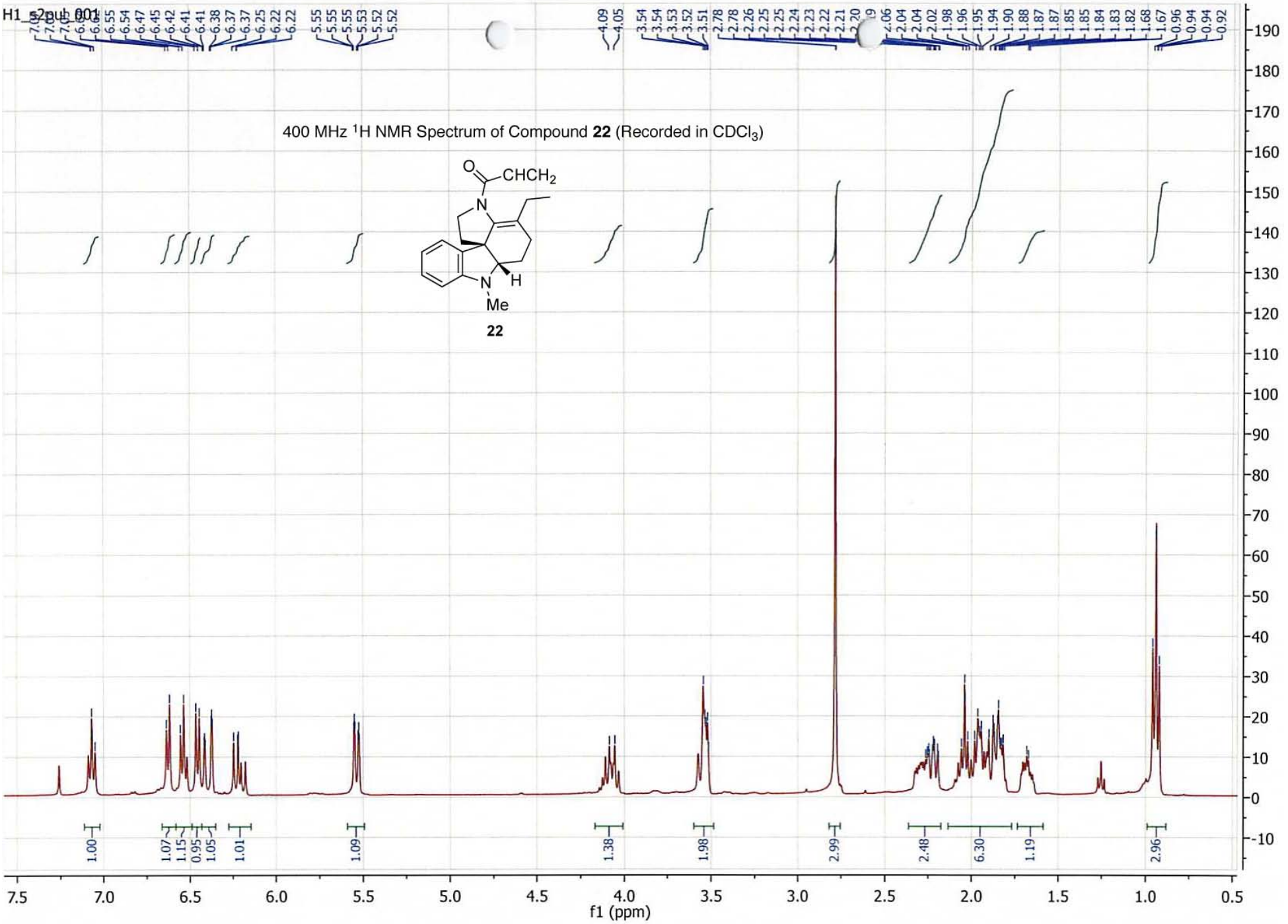

C13_s2pul-001
219.1
152.9
133.4
128.5
122.0
118.6
107.9
72.6
71.3
57.0
49.5
45.8
44.5
33.2
29.7
28.3
25.2
20.1
8.4
100 MHz ^{13}C NMR Spectrum of Compound **17** (Recorded in $CDCl_3$)
S
N
N
H
Me
17
f1 (ppm)

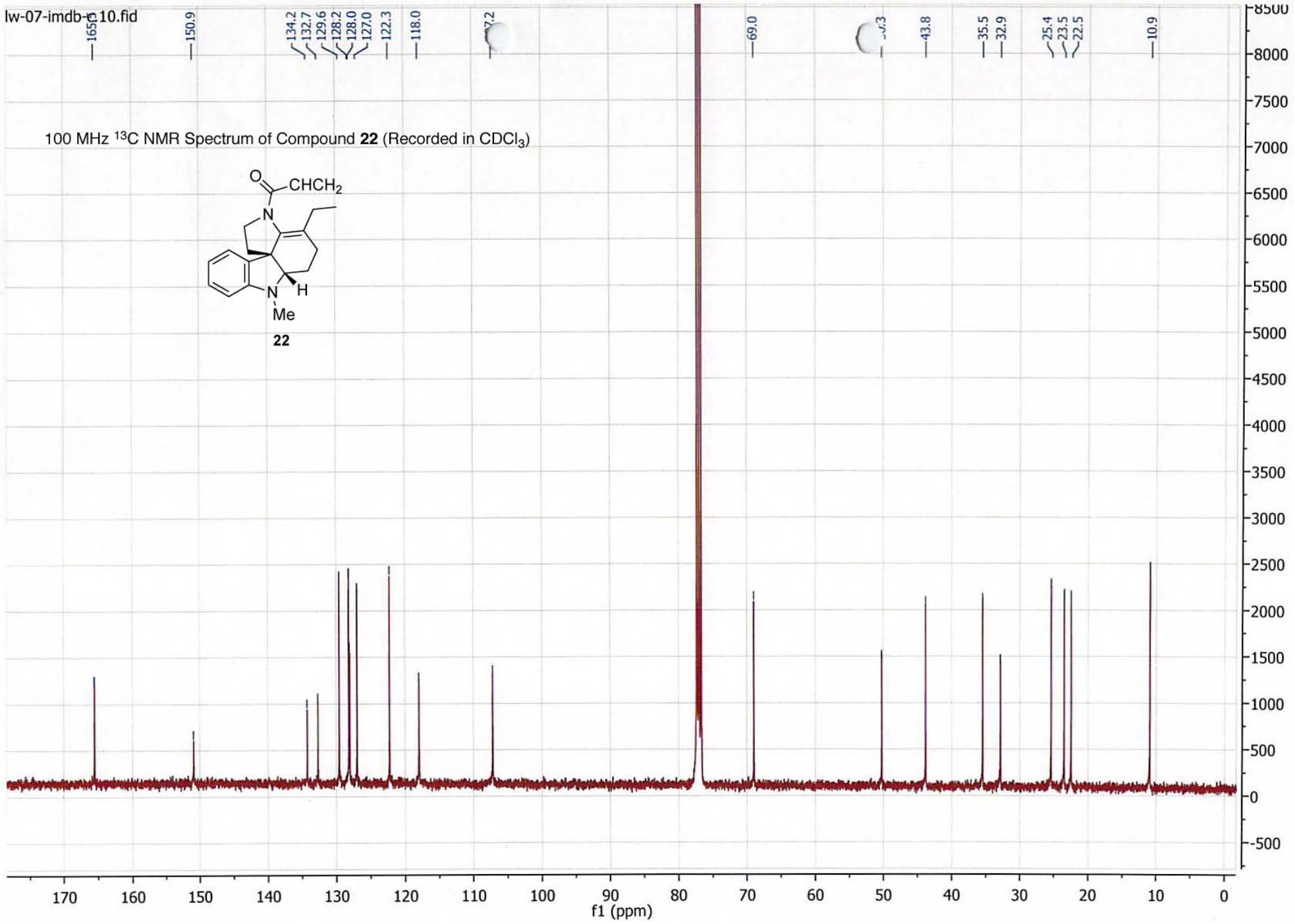

H1_s2pul_001
400 MHz ^{1}H NMR Spectrum of Compound **20** (Recorded in $CDCl_3$)
N_3
N
H
Me
20
f1 (ppm)

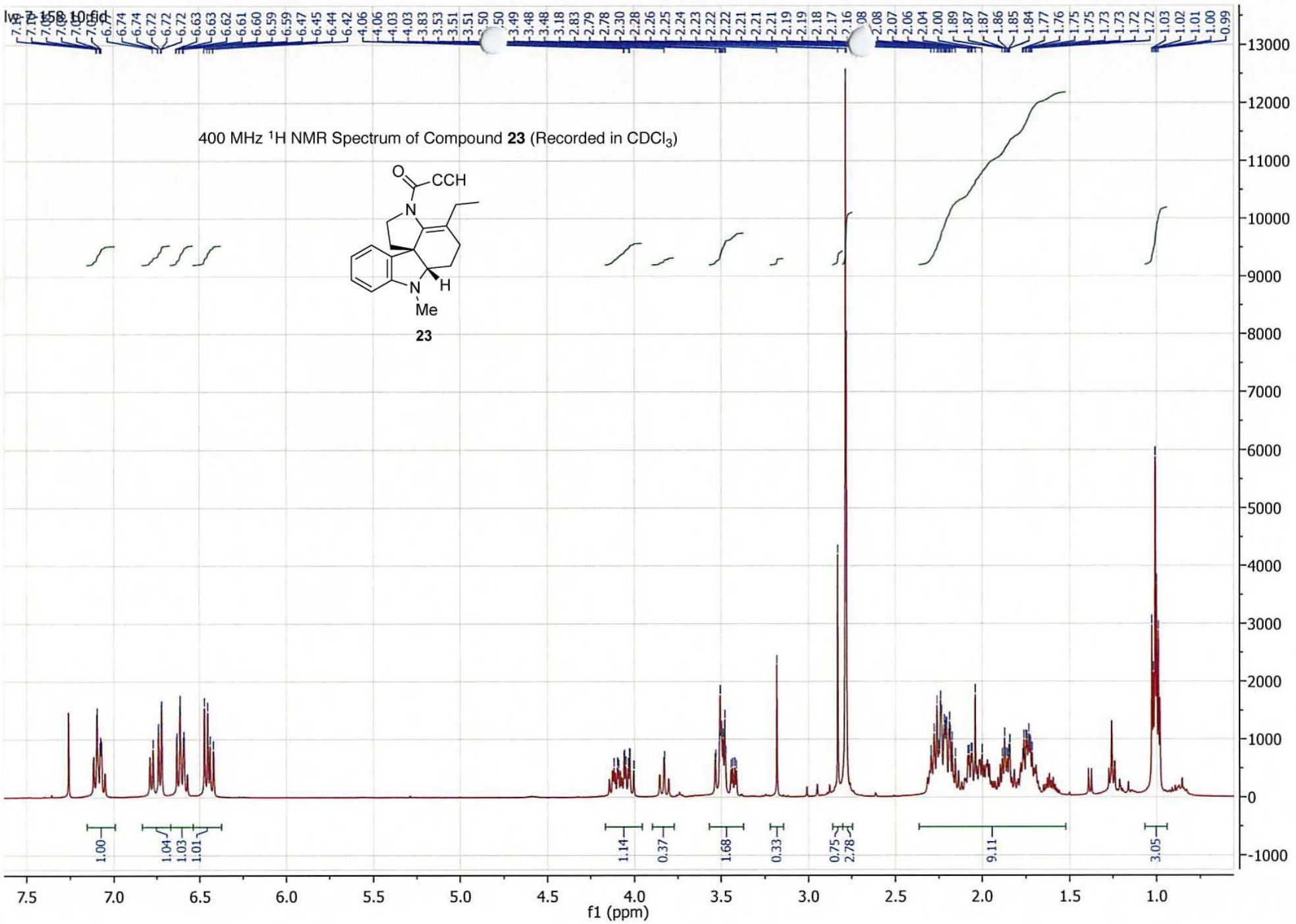

C13_s2pul-001
151.5
140.1
135.0
127.8
123.3
122.2
117.7
107.3
68.5
47.9
46.6
37.8
32.7
30.5
23.4
22.1
12.0
100 MHz ^{13}C NMR Spectrum of Compound **20** (Recorded in $CDCl_3$)
N_3
N
H
Me
20
f1 (ppm)

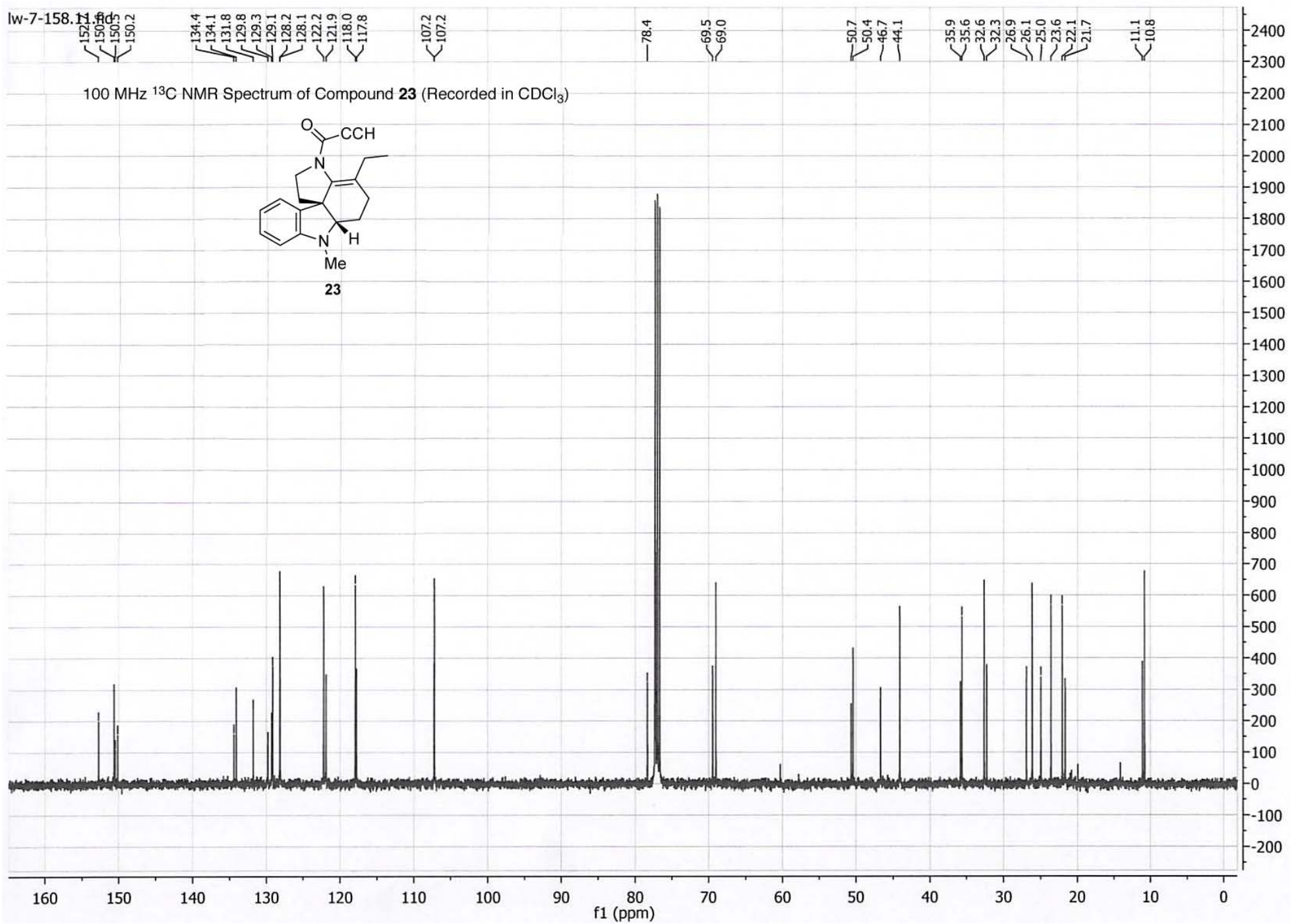

lw-7-157p2.10.fid
7.26
7.13
6.76
6.75
6.74
6.74
6.66
6.66
6.64
6.64
6.48
6.46
3.98
3.96
3.95
3.94
3.94
3.93
3.92
3.76
3.47
3.46
3.45
3.44
2.83
2.81
2.06
2.06
2.06
2.03
2.03
2.03
2.01
2.00
1.95
1.61
1.40
1.40
1.39
1.37
1.36
1.34
0.99
0.97
0.95
0.86
400 MHz ^{1}H NMR Spectrum of Compound **21** and Tautomeric Enamine (Recorded in $CDCl_3$)
N
N
H
Me
21
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
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
f1 (ppm)

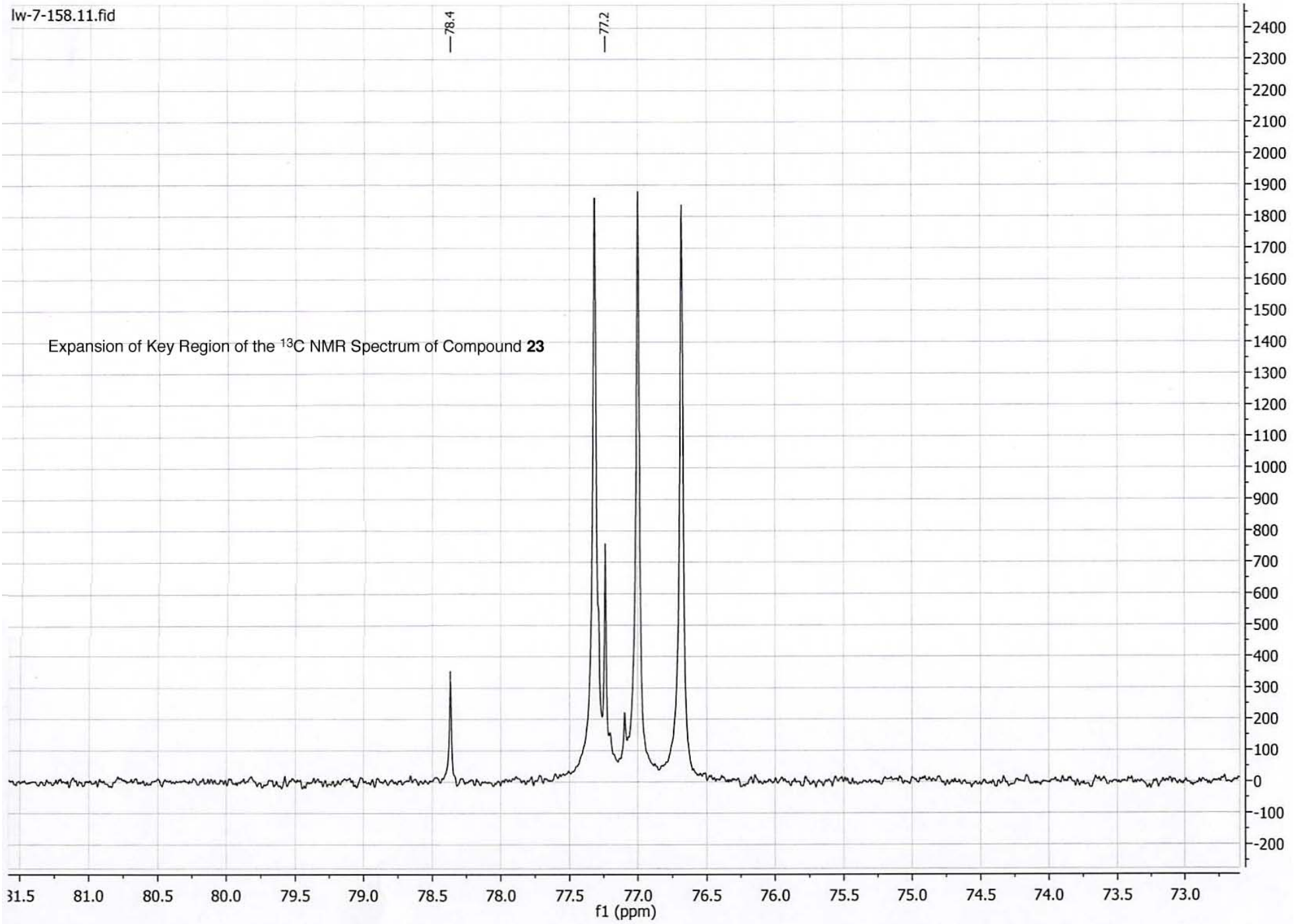

lw-7-157c1.11.fid
180.2
149.9
132.7
128.4
128.4
122.0
107.3
74.9
57.5
41.0
40.8
31.8
27.1
25.0
23.8
11.7
100 MHz ^{13}C NMR Spectrum of Compound **21** and Tautomeric Enamine (Recorded in $CDCl_3$)
N
N
H
Me
21
f1 (ppm)

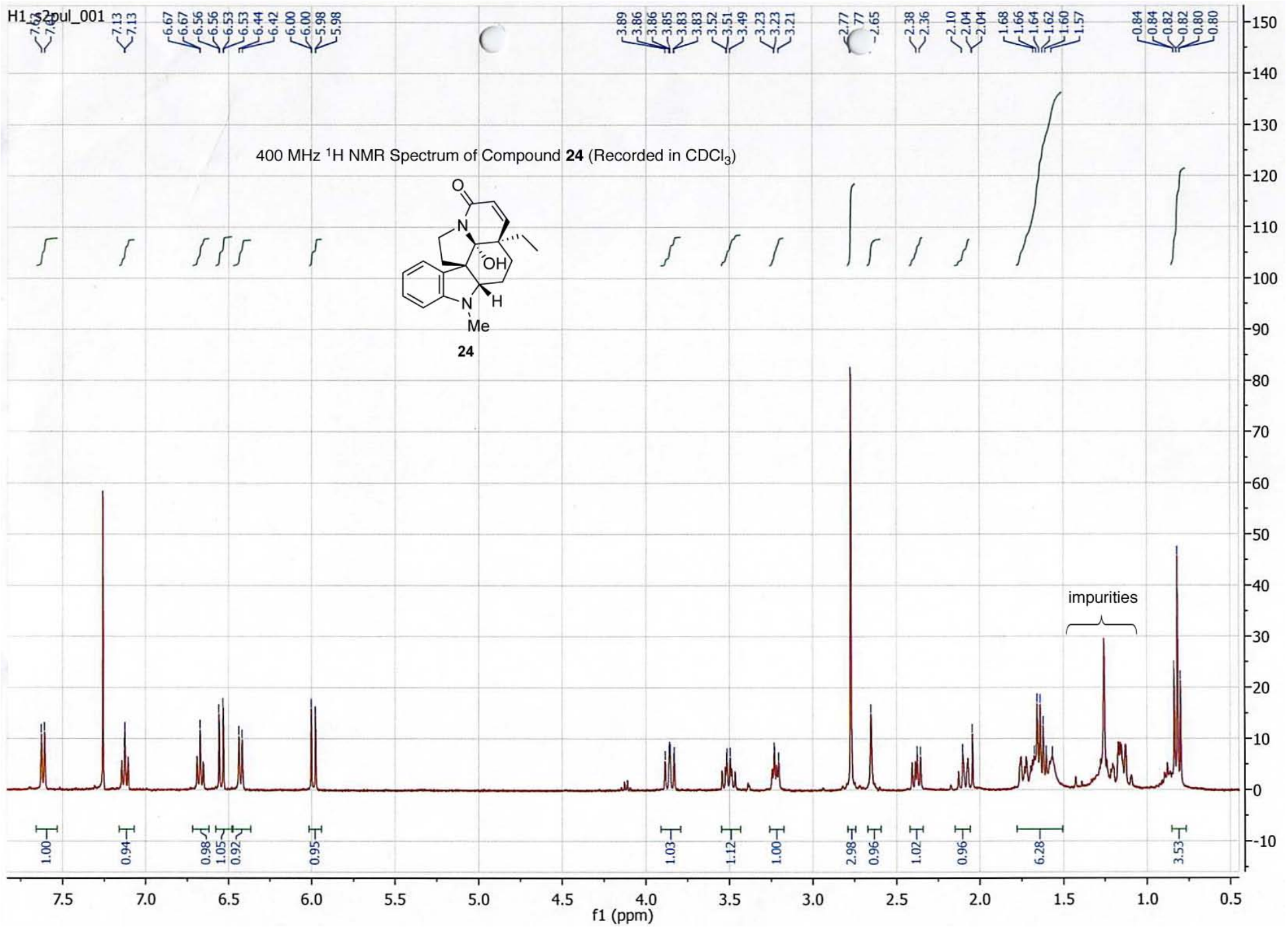

H1_s2pul 001
400 MHz ^{1}H NMR Spectrum of Compound **22** (Recorded in $CDCl_3$)
O
CHCH$_2$
N
N
H
Me
22
f1 (ppm)

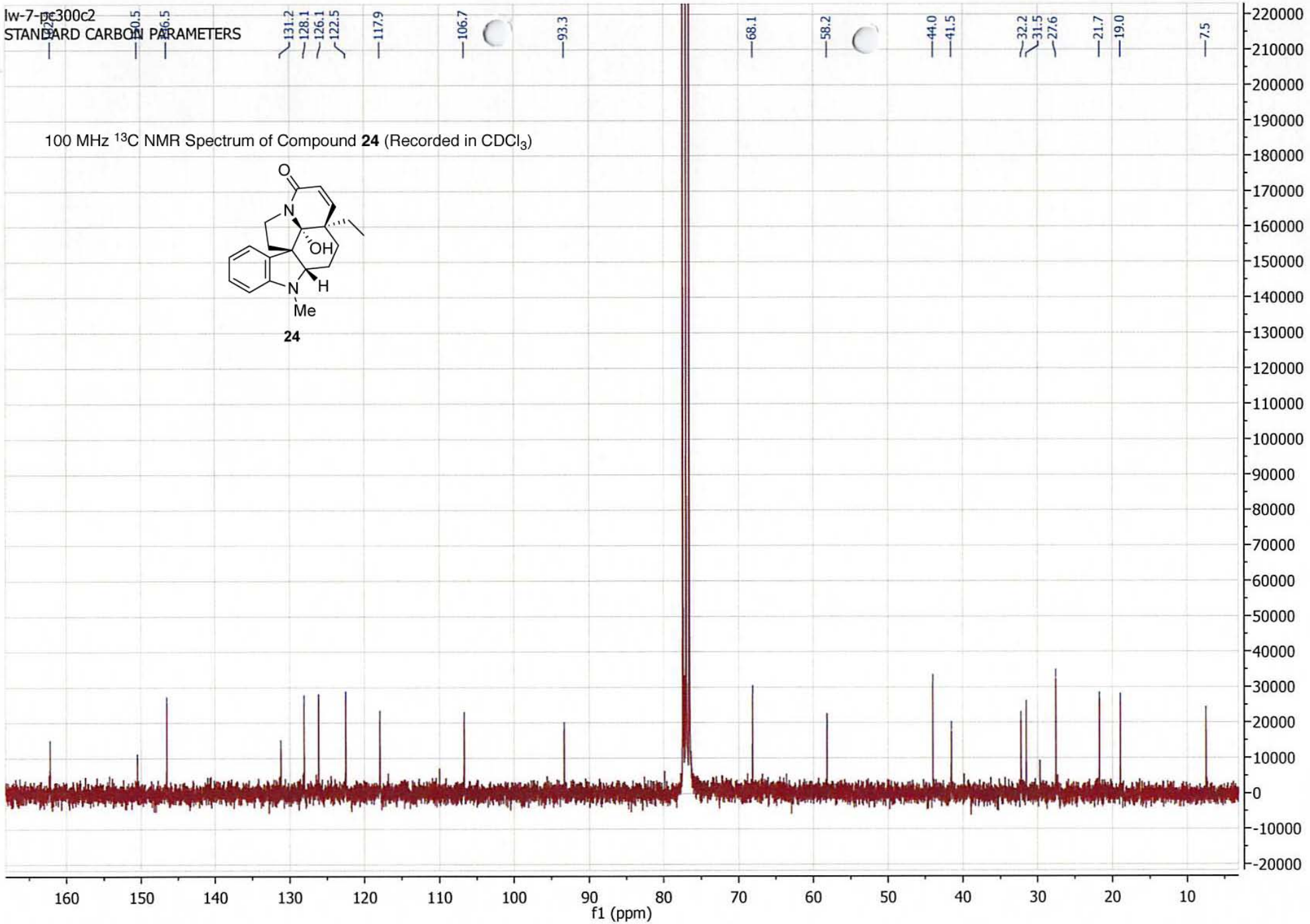

lw-07-imdb-c 10.fid
165.1
150.9
134.2
132.7
129.6
128.2
128.0
127.0
122.3
118.0
69.0
43.8
35.5
32.9
25.4
23.5
22.5
10.9
100 MHz ^{13}C NMR Spectrum of Compound **22** (Recorded in $CDCl_3$)
O
CHCH$_2$
N
N
H
Me
22
f1 (ppm)


400 MHz ^{1}H NMR Spectrum of Compound **23** (Recorded in $CDCl_3$)
O
CCH
N
N
H
Me
23
f1 (ppm)


lw-7-158.11.fid
152.1
150.5
150.5
150.2
134.4
134.1
131.8
129.8
129.3
129.1
128.2
128.1
122.2
121.9
118.0
117.8
107.2
107.2
78.4
69.5
69.0
50.7
50.4
46.7
44.1
35.9
35.6
32.6
32.3
26.9
26.1
25.0
23.6
22.1
21.7
11.1
10.8
100 MHz ^{13}C NMR Spectrum of Compound **23** (Recorded in $CDCl_3$)
O
CCH
N
N
H
Me
23
f1 (ppm)


lw-7-158.11.fid
78.4
77.2
Expansion of Key Region of the ^{13}C NMR Spectrum of Compound **23**
2400
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
81.5
81.0
80.5
80.0
79.5
79.0
78.5
78.0
77.5
77.0
76.5
76.0
75.5
75.0
74.5
74.0
73.5
73.0
f1 (ppm)


H1_s2pul_001
400 MHz ^{1}H NMR Spectrum of Compound **24** (Recorded in $CDCl_3$)
O
N
OH
N
H
Me
24
impurities
f1 (ppm)


lw-7-pc300c2
STANDARD CARBON PARAMETERS
131.2
128.1
126.1
122.5
117.9
106.7
93.3
68.1
58.2
44.0
41.5
32.2
31.5
27.6
21.7
19.0
7.5
100 MHz 13C NMR Spectrum of Compound 24 (Recorded in CDCl3)
O
N
OH
N
H
Me
24
f1 (ppm)