Supporting Information for:

Tunable, Chemoselective Amination *via* Silver Catalysis

Jared W. Rigoli, Cale D. Weatherly, Juliet M. Alderson, Brian T. Vo and Jennifer M. Schomaker*

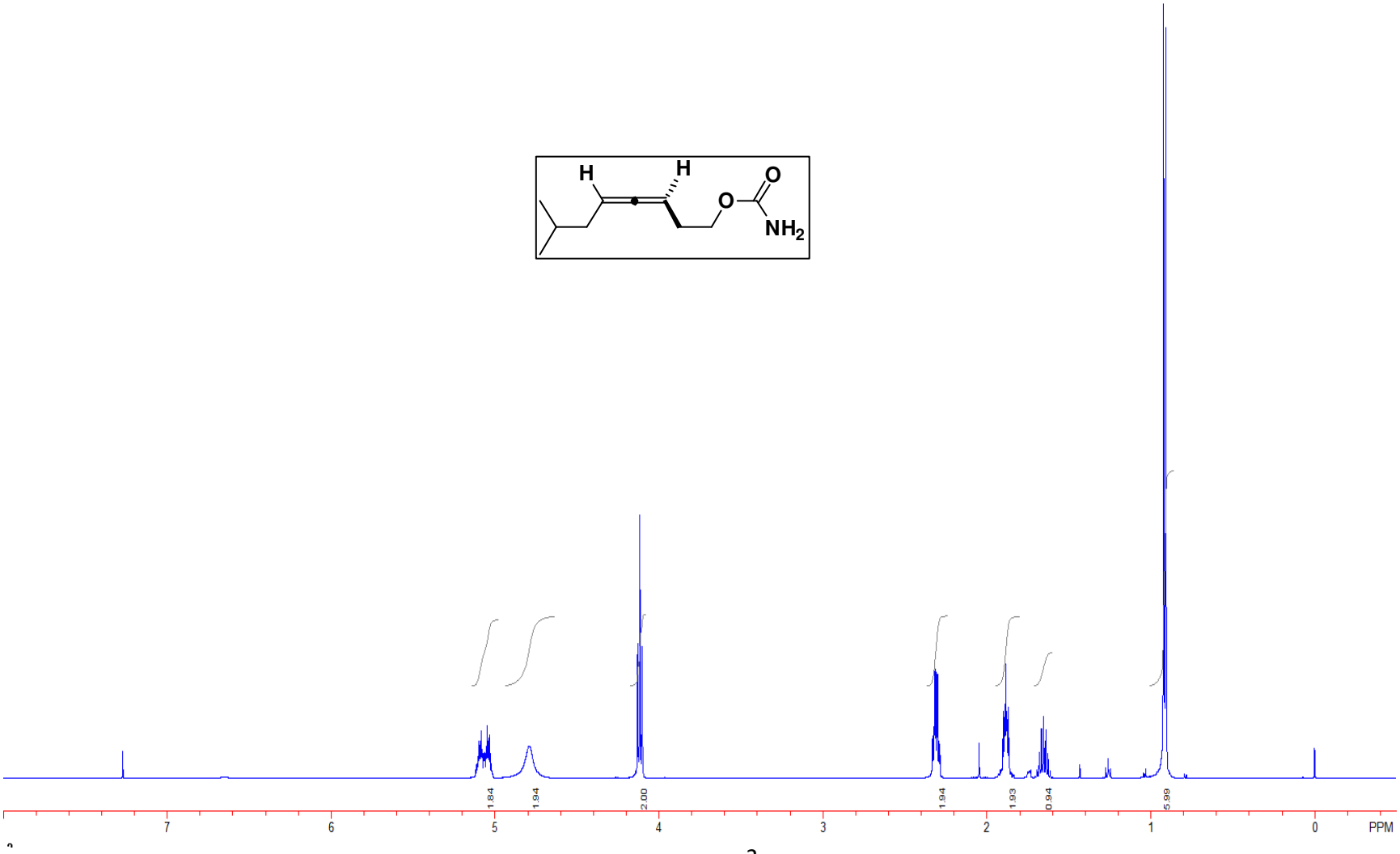
Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue

Madison, Wisconsin, 53706-1396

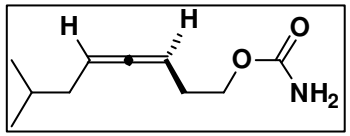
Table of Contents……..……...1

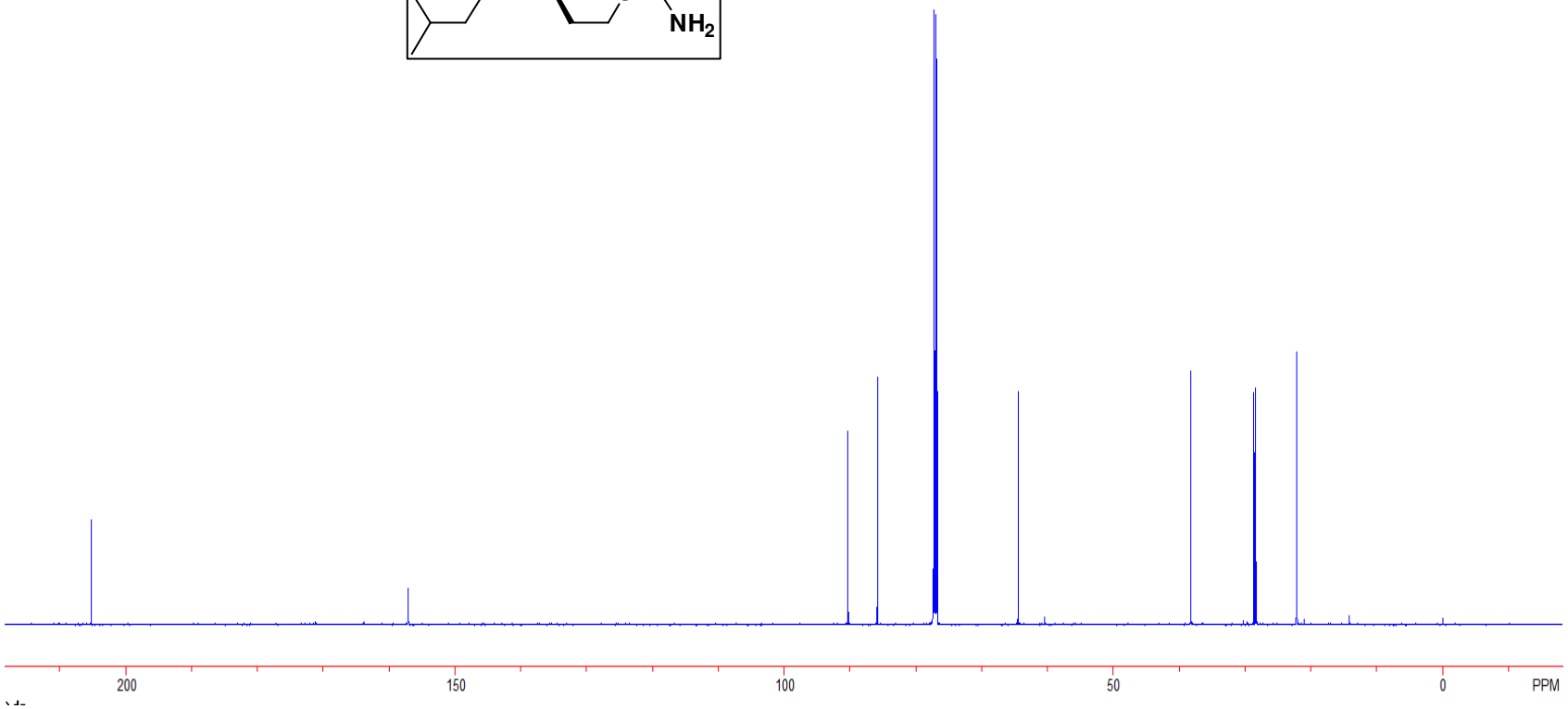
I. NMR Spectra.

Compound 3h.

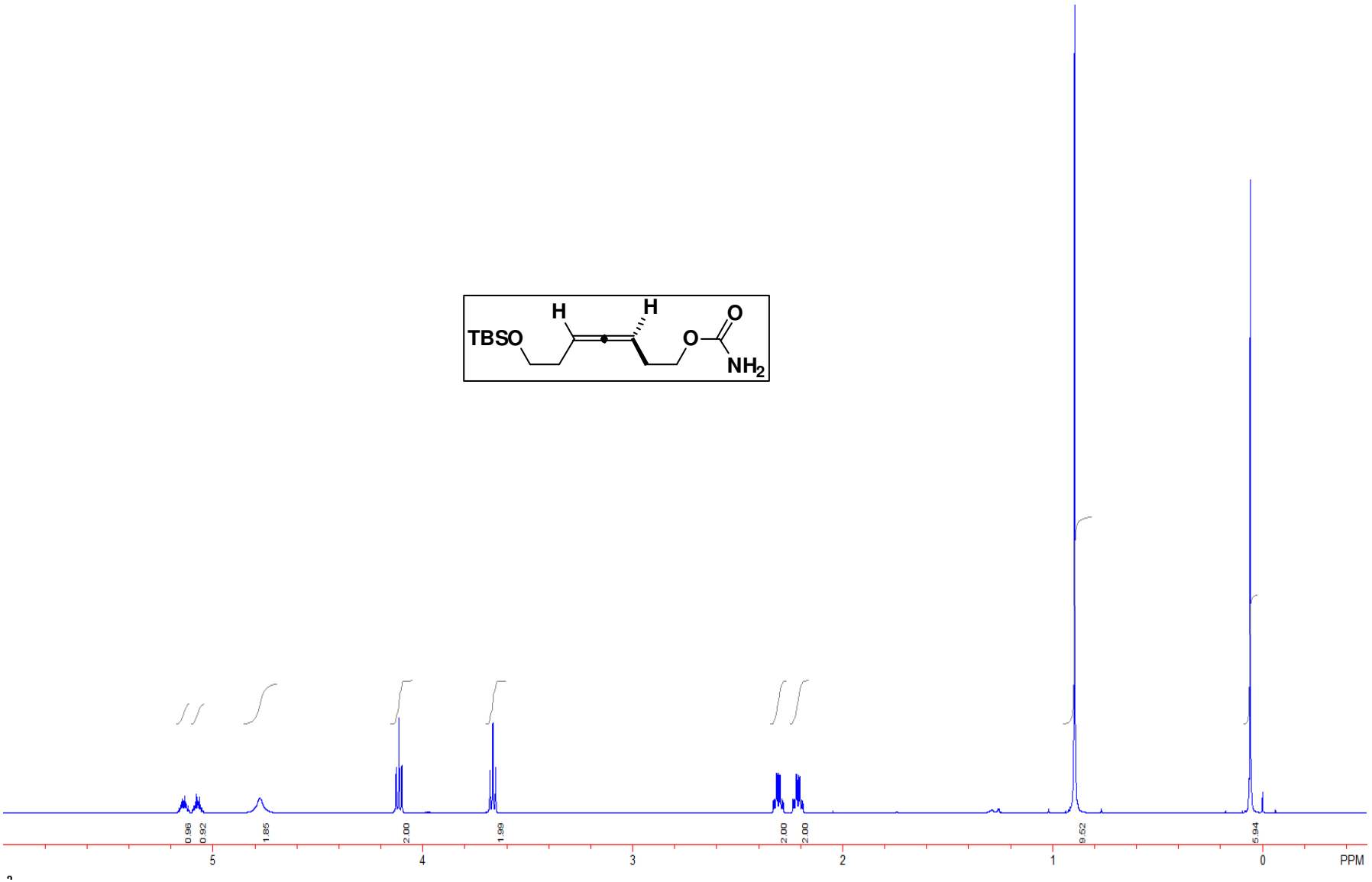


Compound 3h.

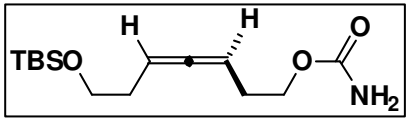


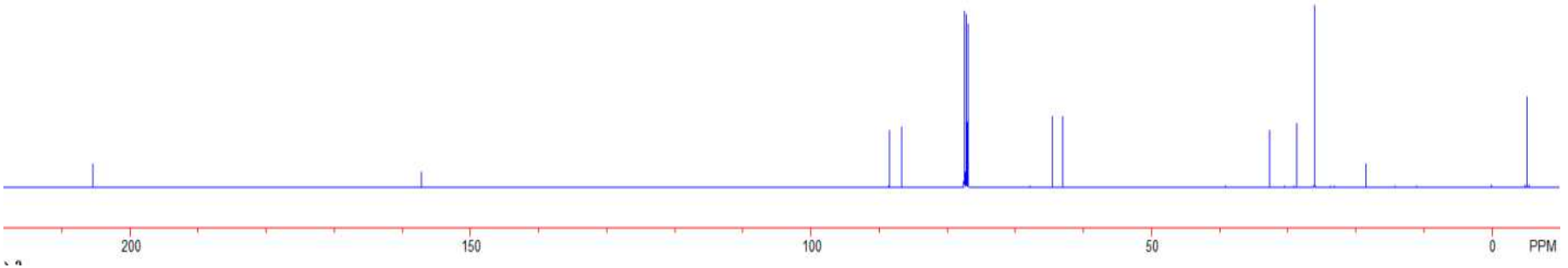


Compound 3j.

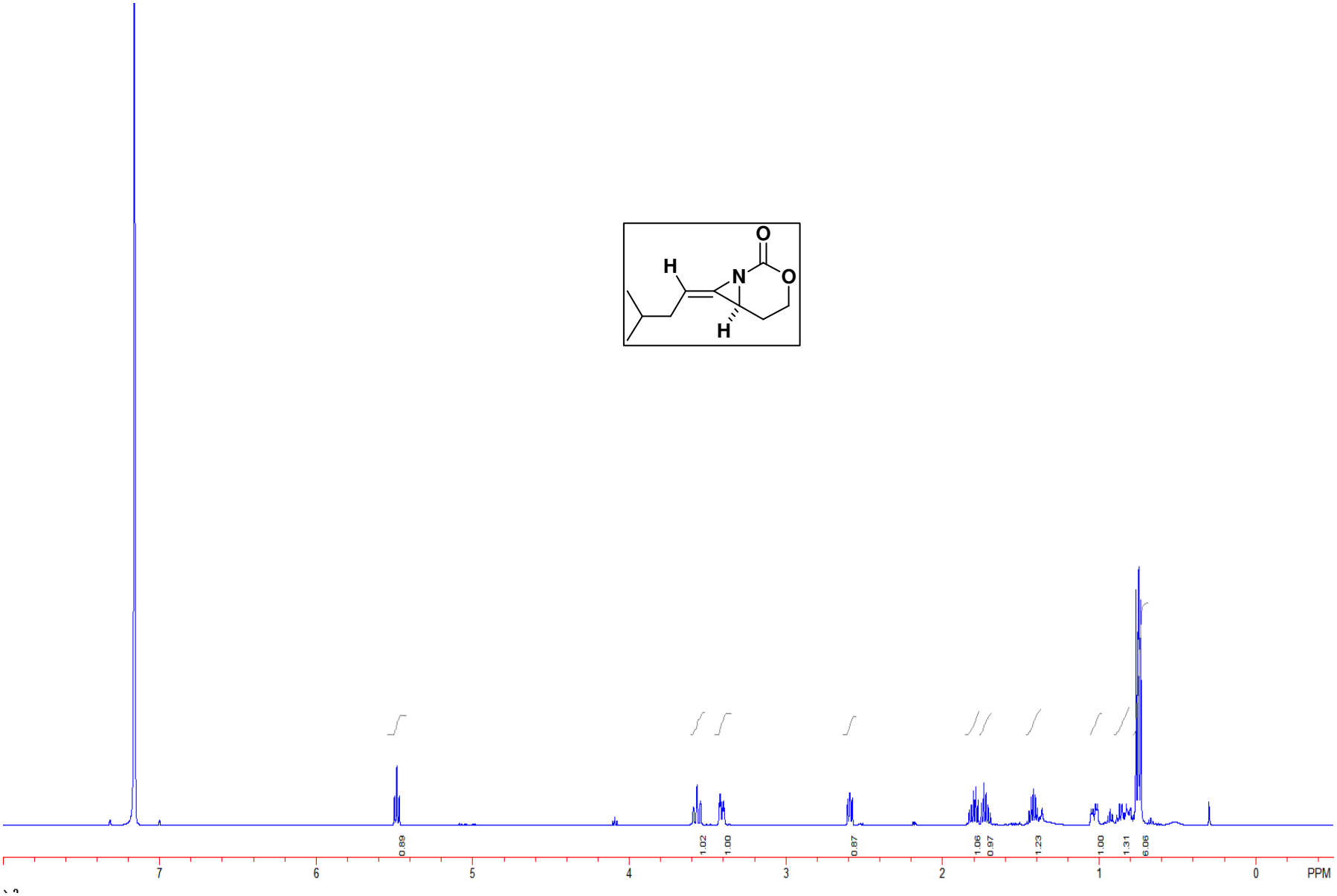


Compound 3j.

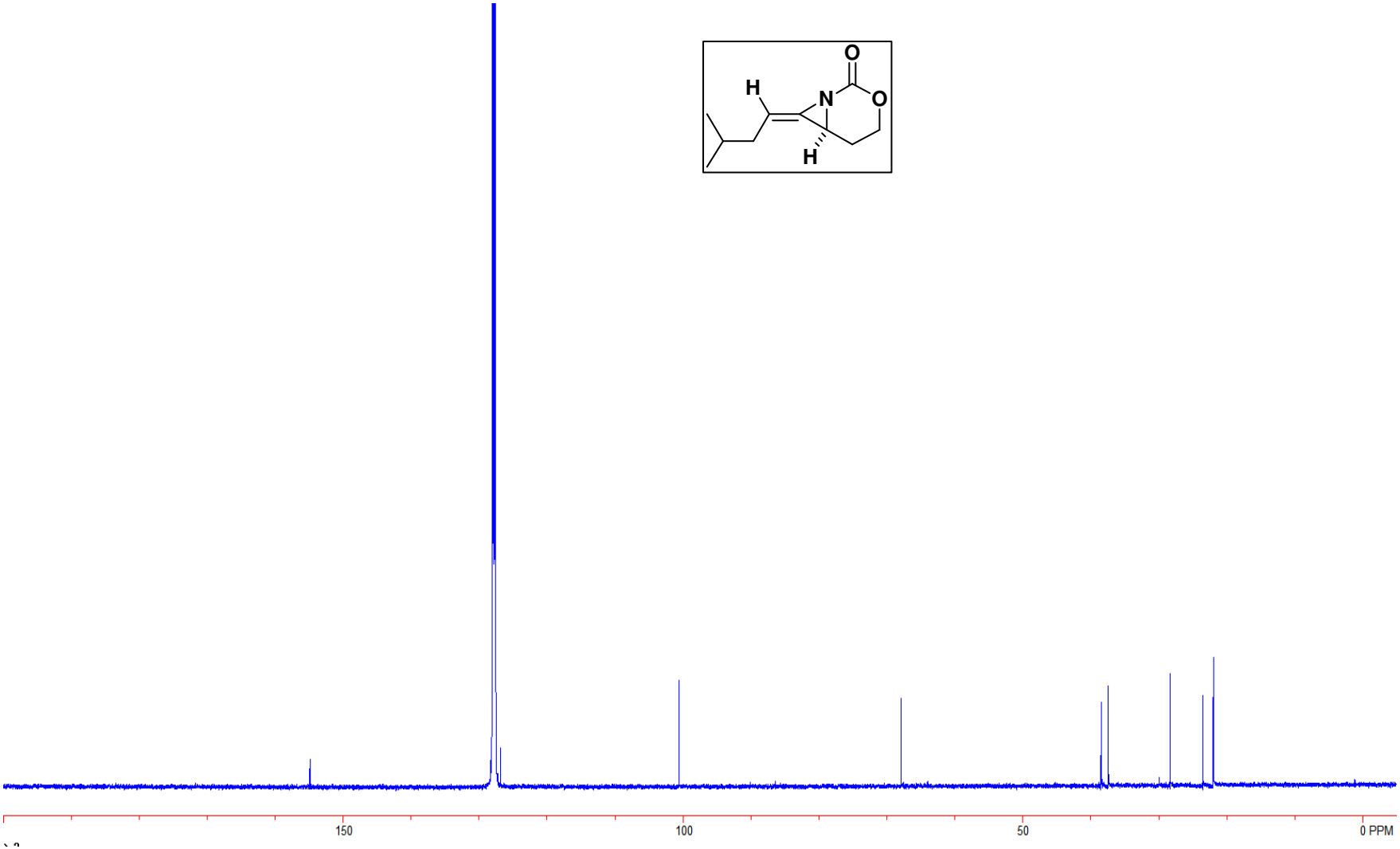




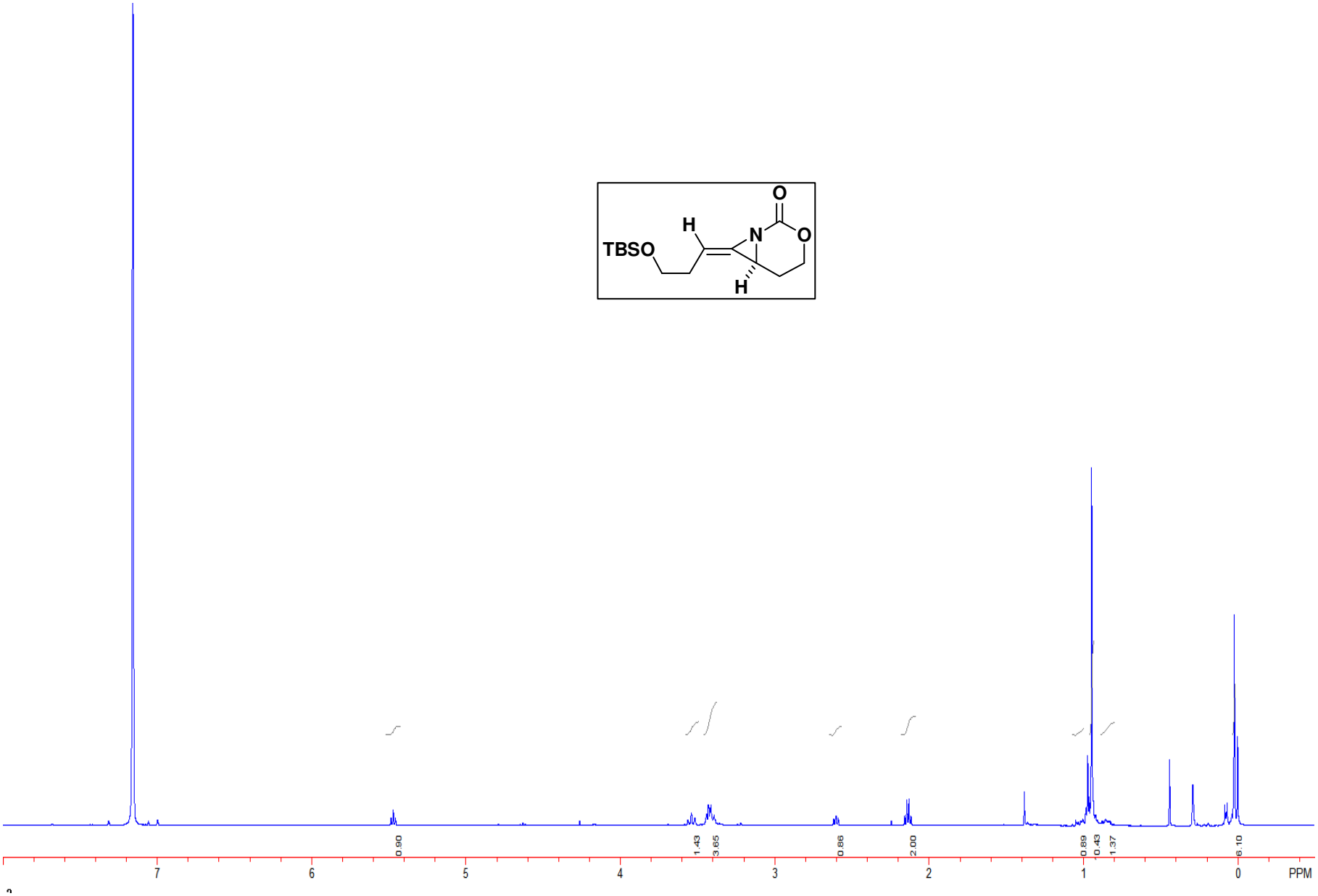
Compound 4h.



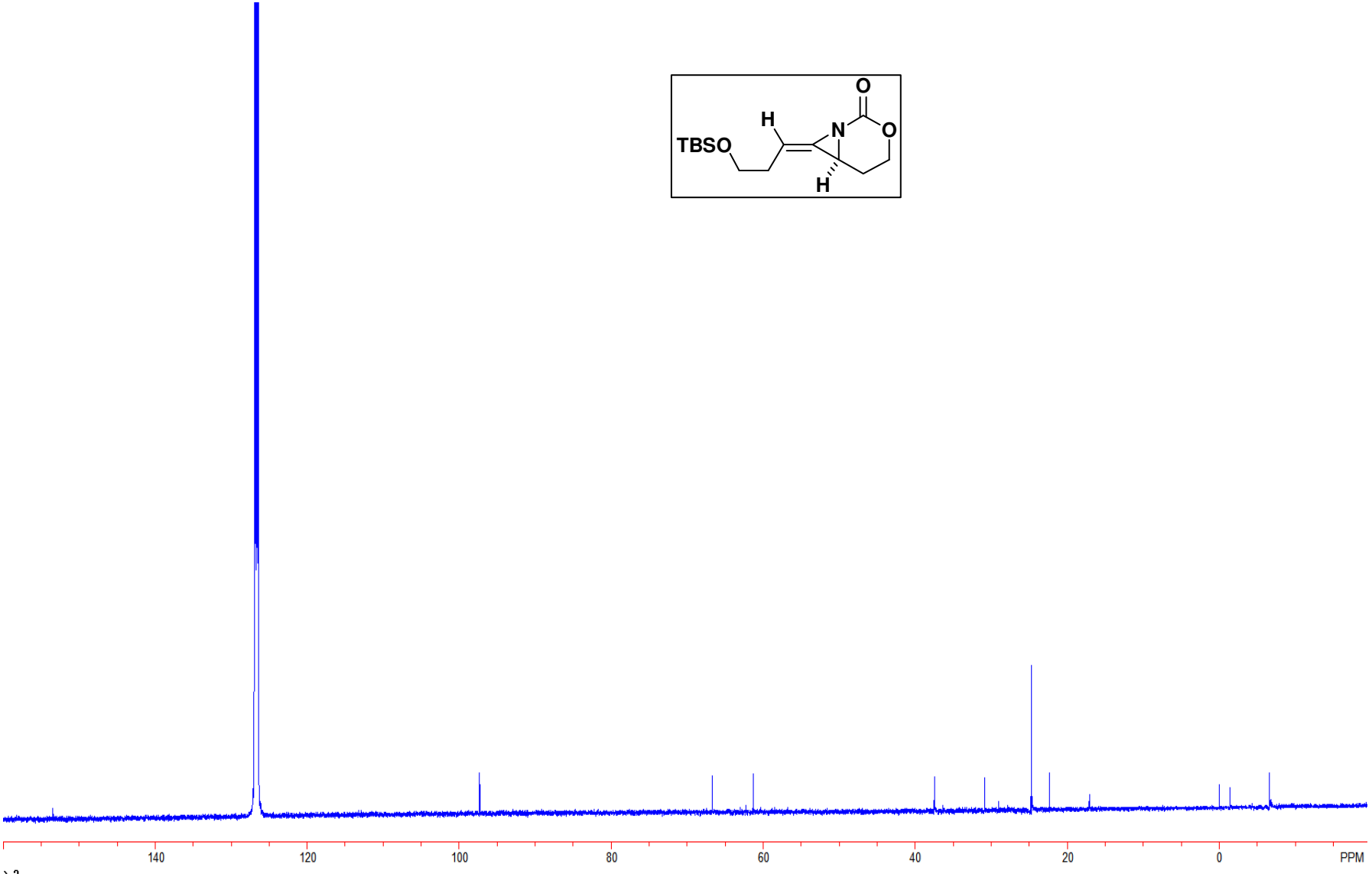
Compound 4h.



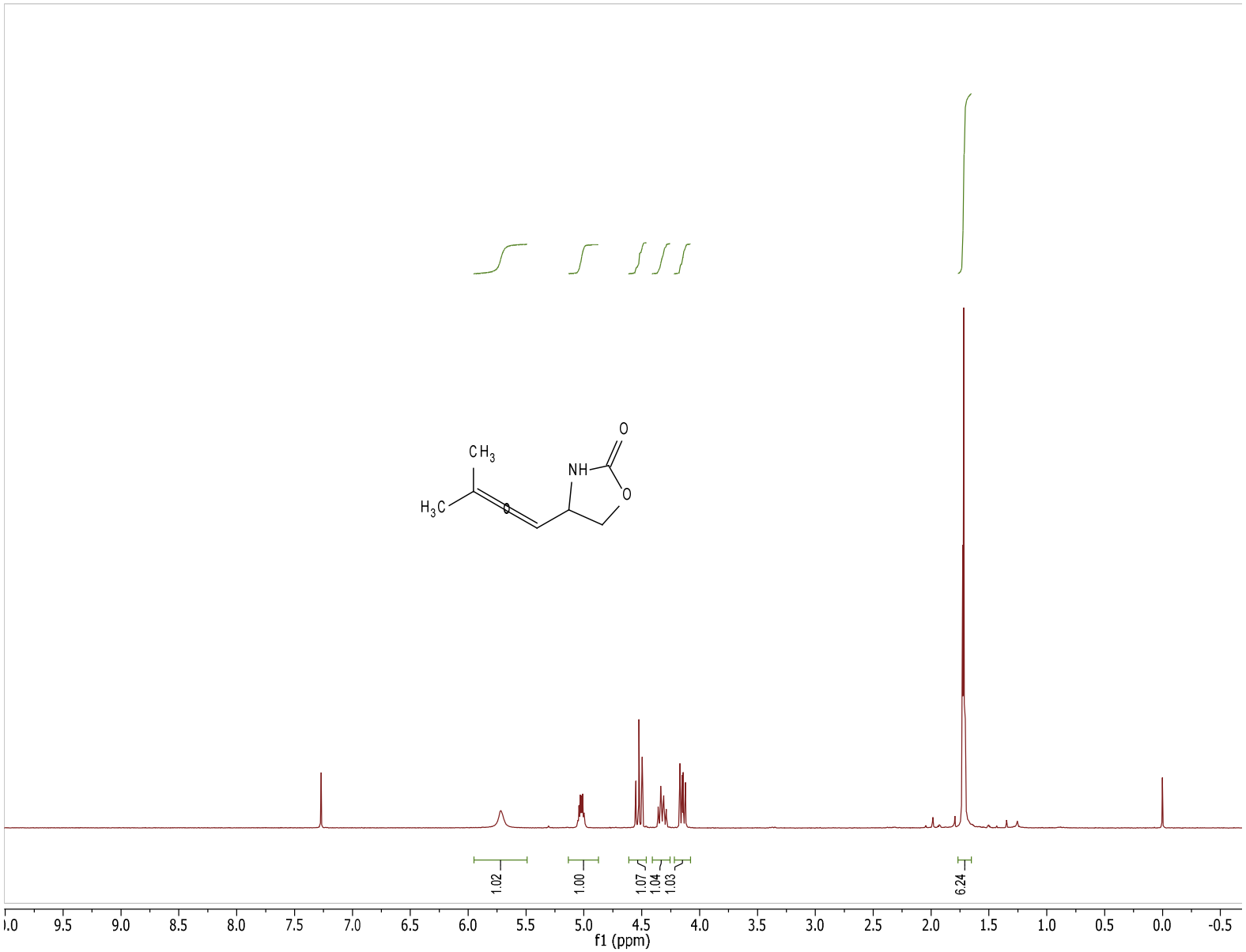
Compound 4j.



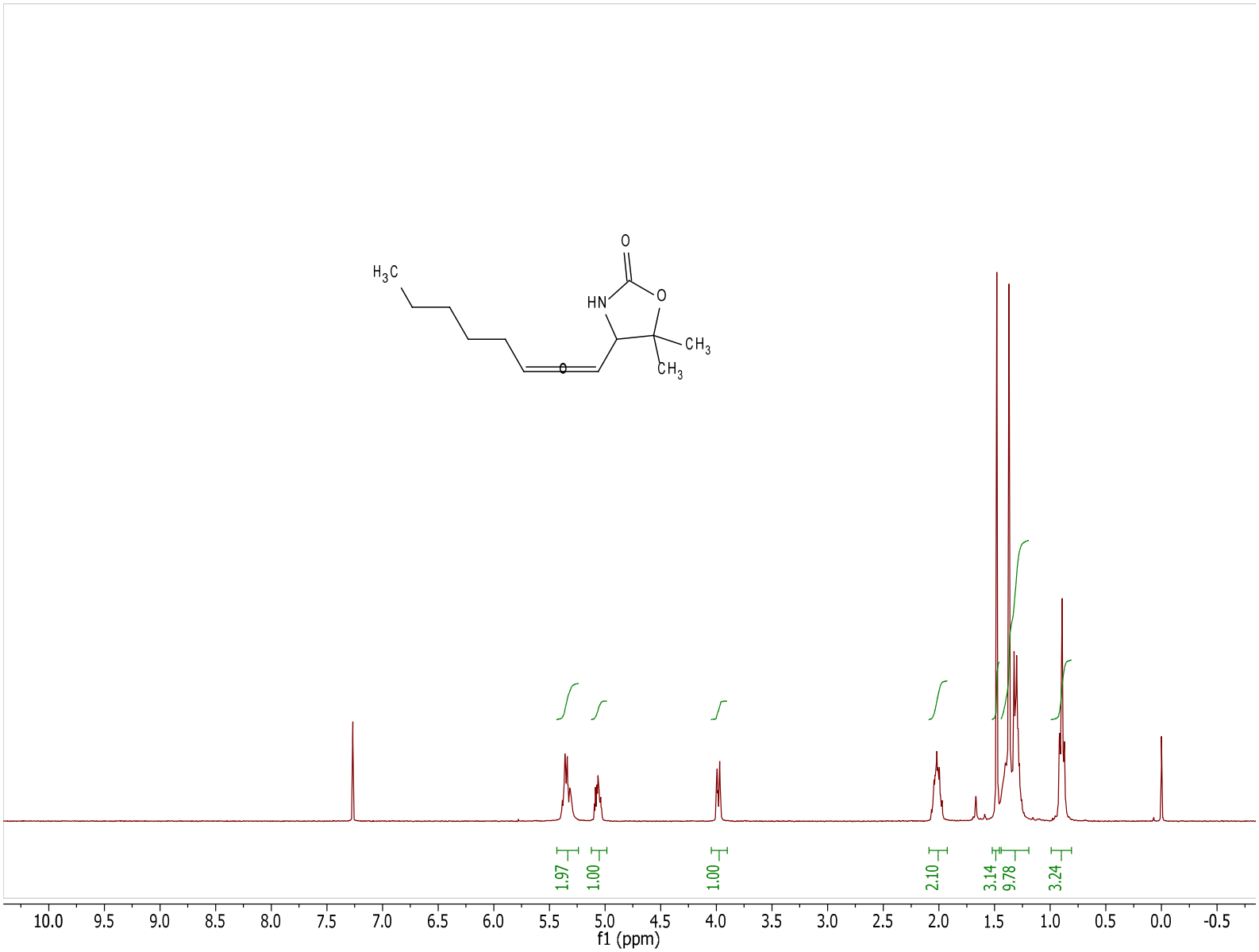
Compound 4j.



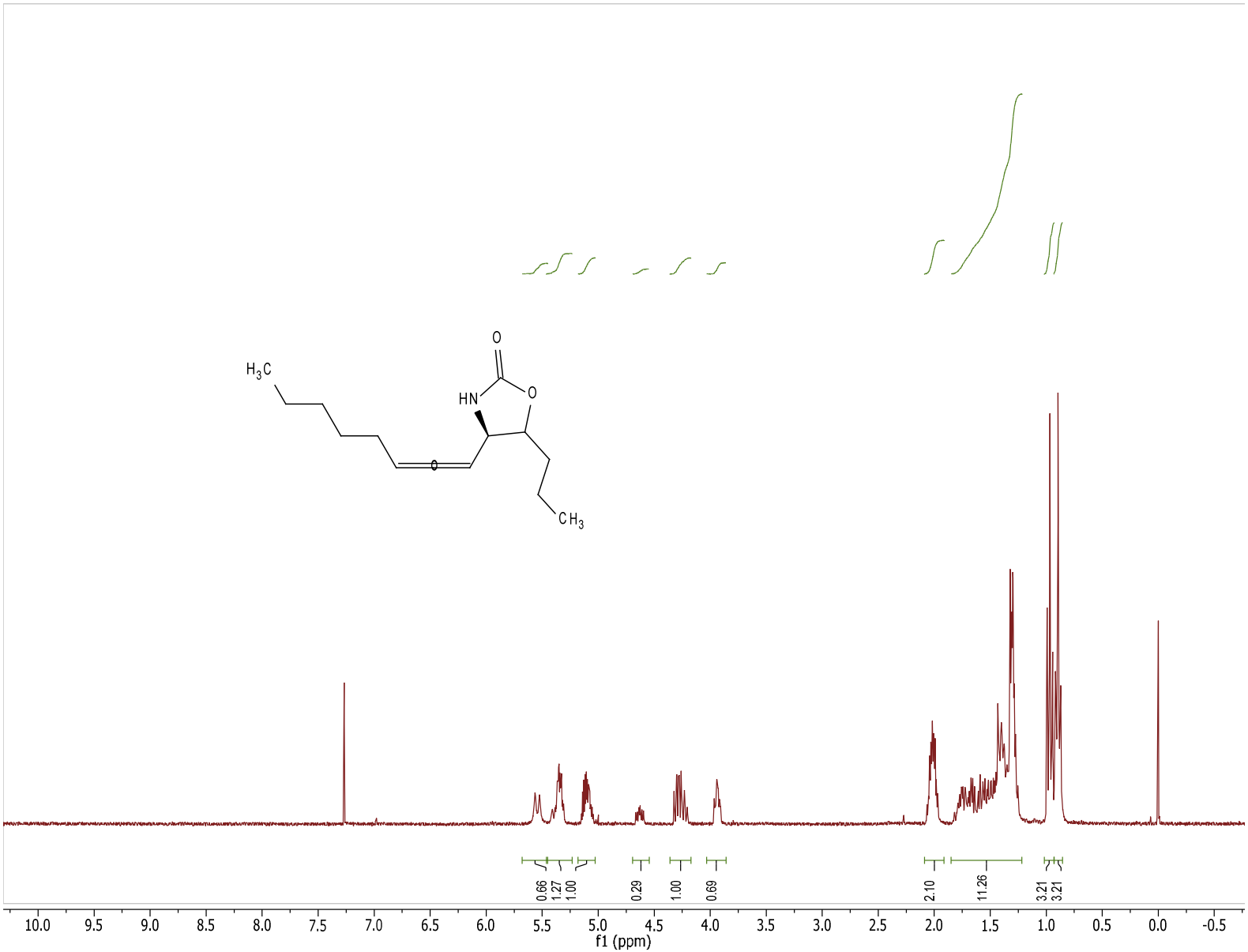
Compound 5a.



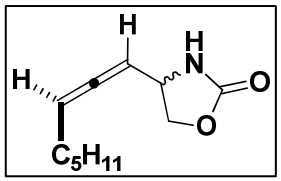
Compound 5b.

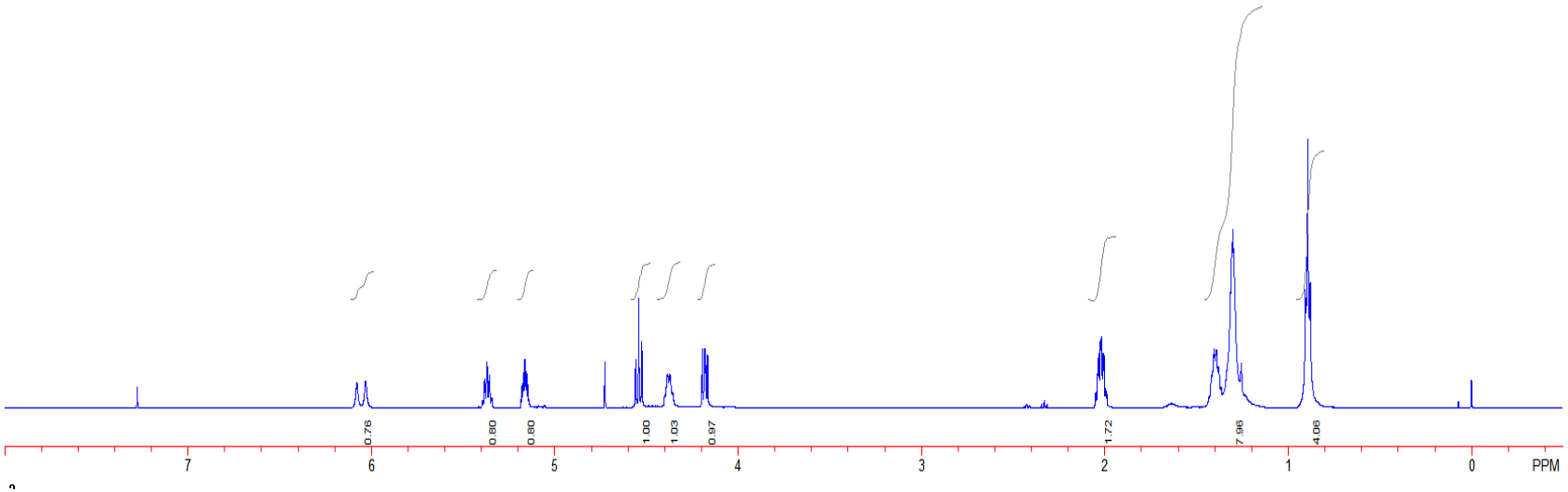

H3C
O
HN
O
CH3
CH3
1.97
1.00
1.00
2.10
3.14
9.78
3.24
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

Compound 5c.

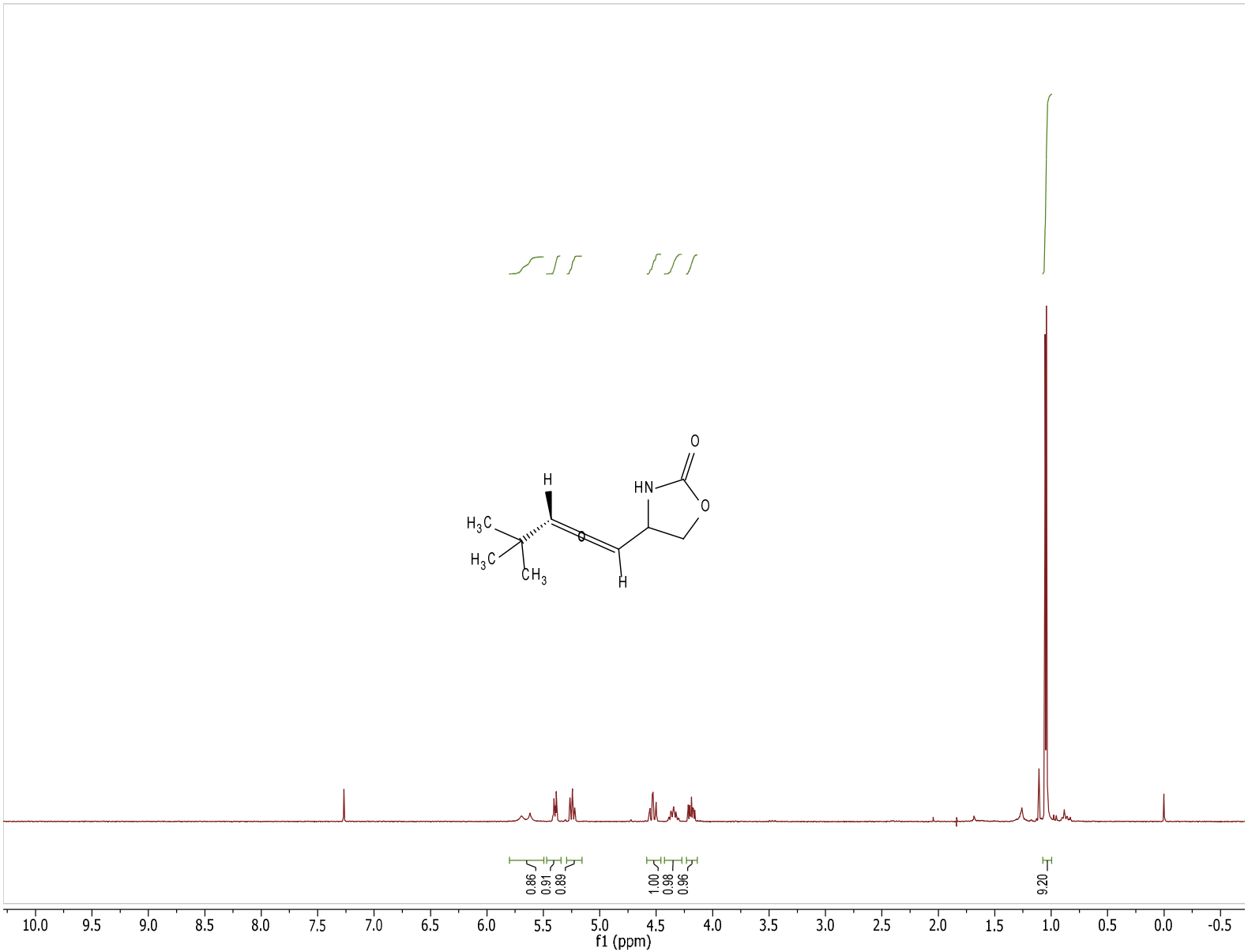

H3C
HN
O
O
O
CH3
0.66
1.27
1.00
0.29
1.00
0.69
2.10
11.26
3.21
3.21
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

Compound 5d.

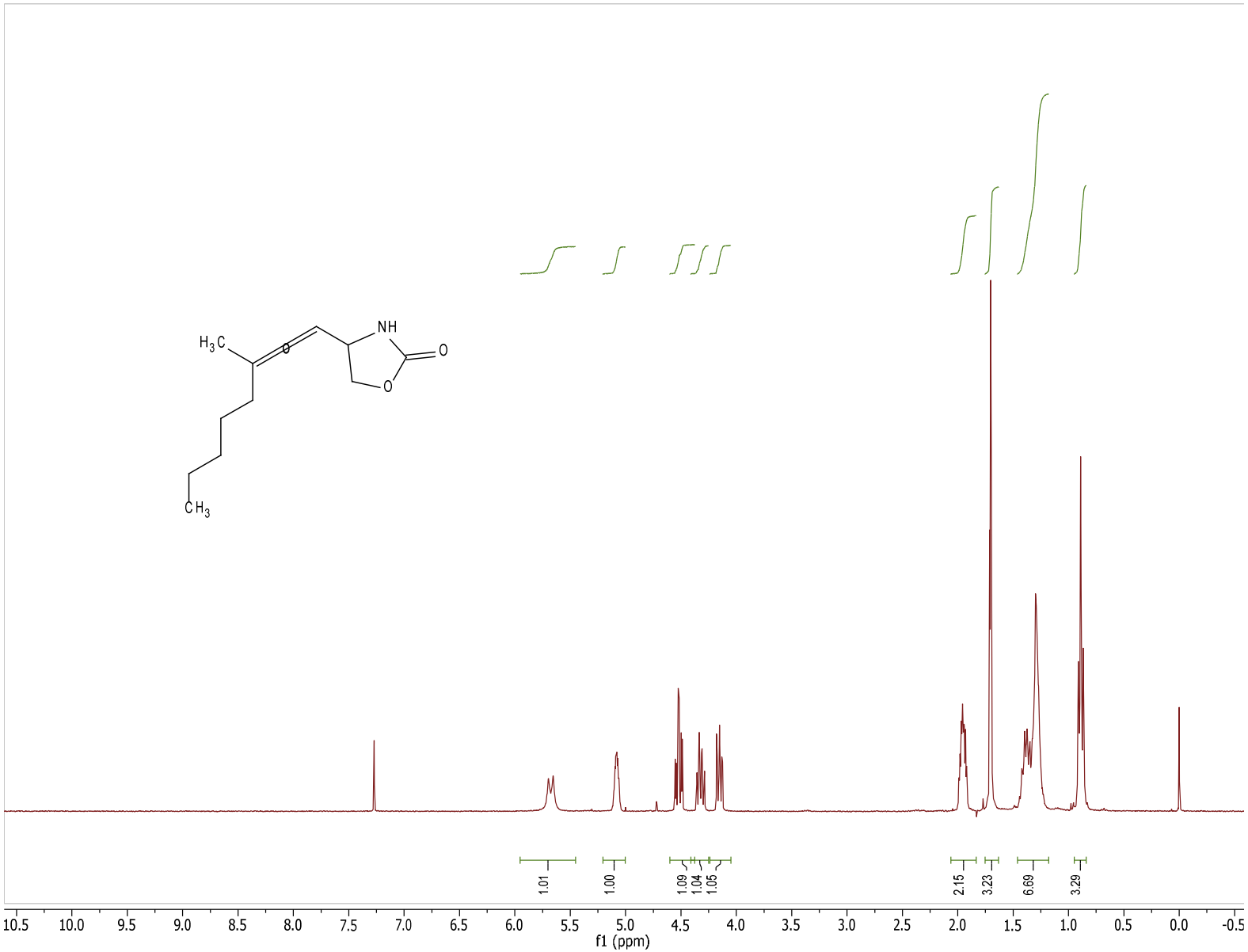




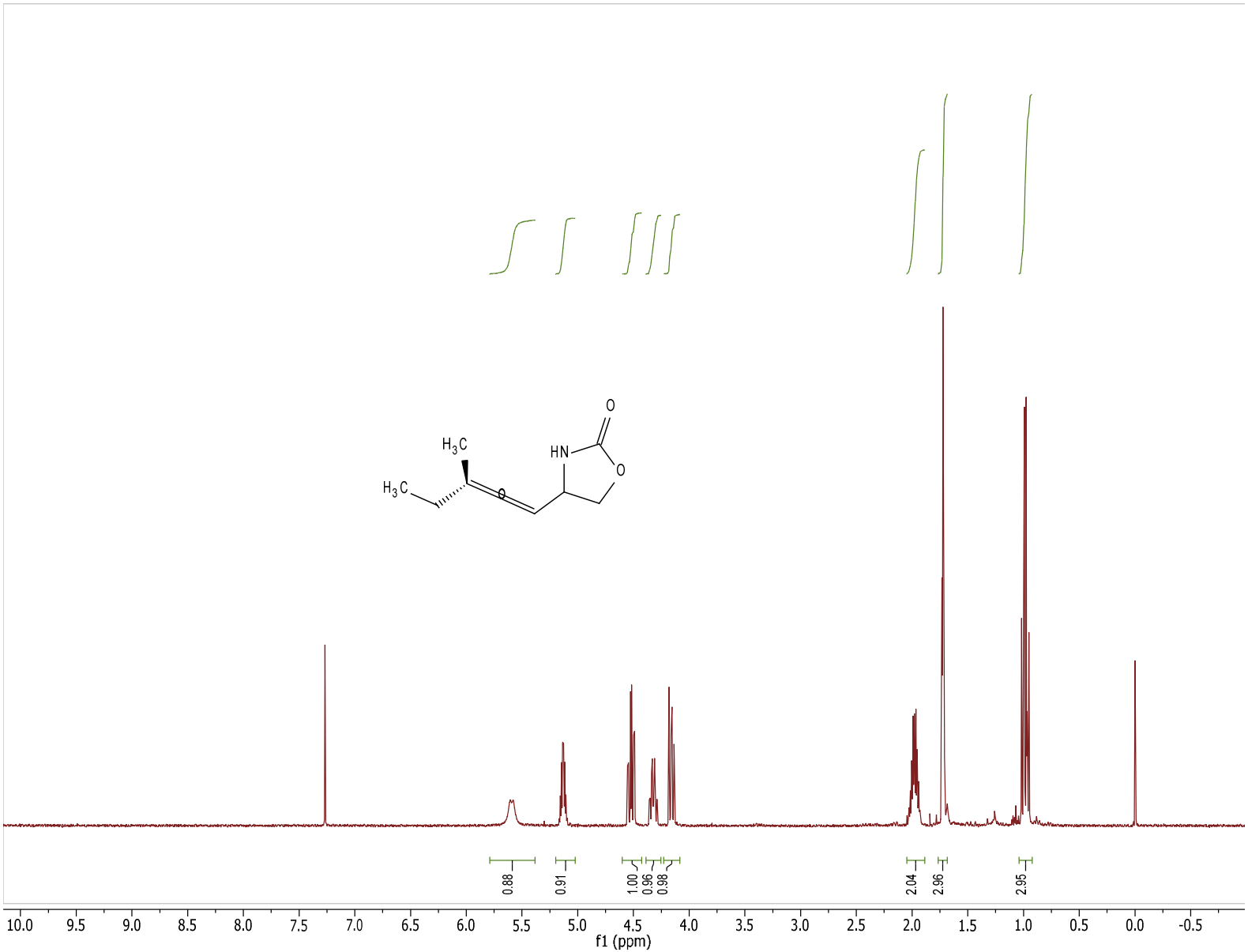
Compound 5e.


O
HN
O
H
H3C
H3C
CH3
H
0.86
0.91
0.89
1.00
0.98
0.96
9.20
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
-0.5
f1 (ppm)

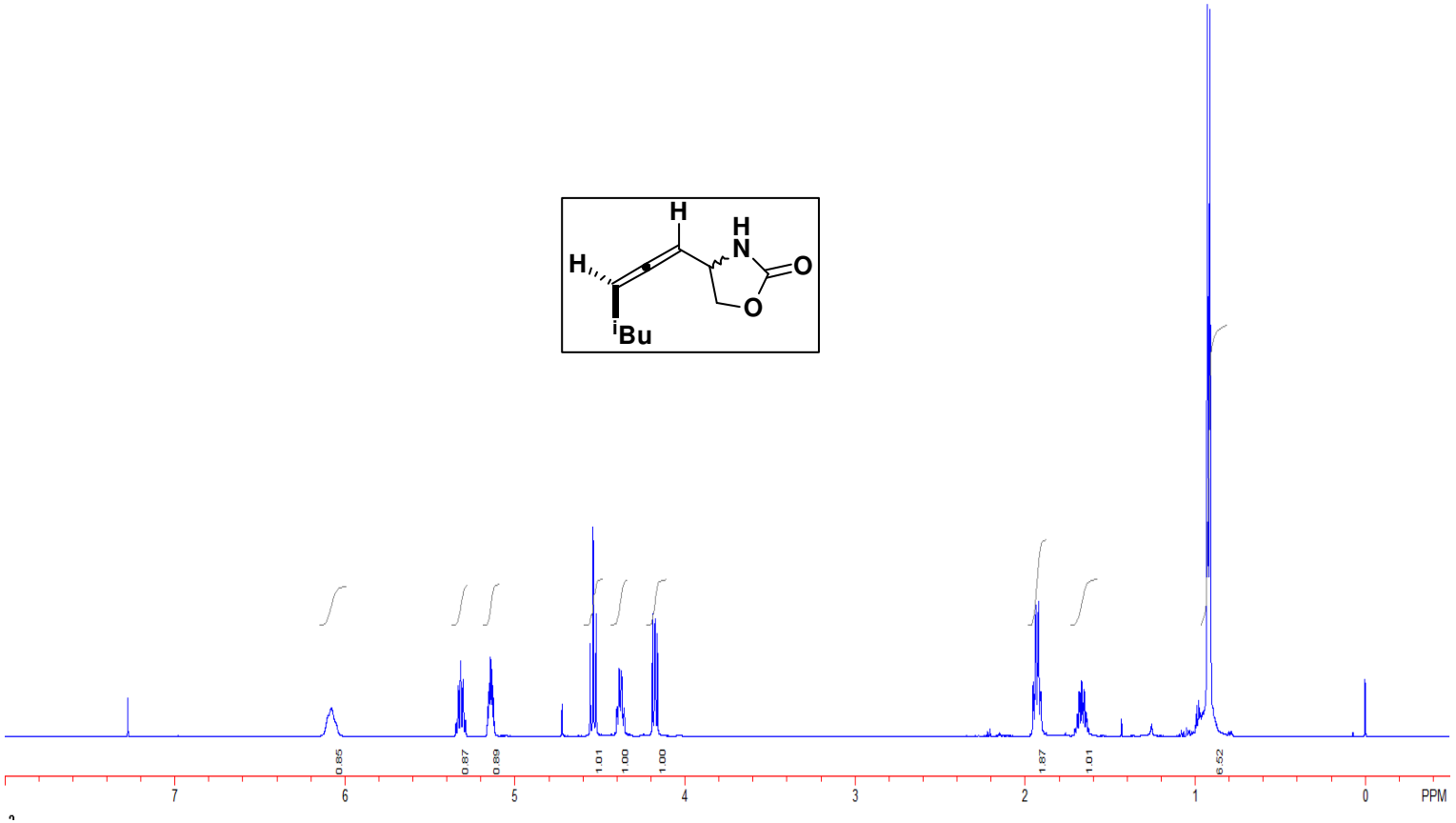
Compound 5f.


H3C
O
NH
O
O
CH3
1.01
1.00
1.09
1.04
1.05
2.15
3.23
6.69
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 0.5 0.0 -0.5
f1 (ppm)

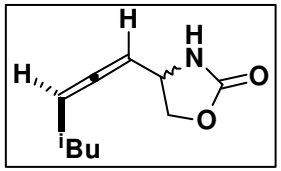
Compound 5g.

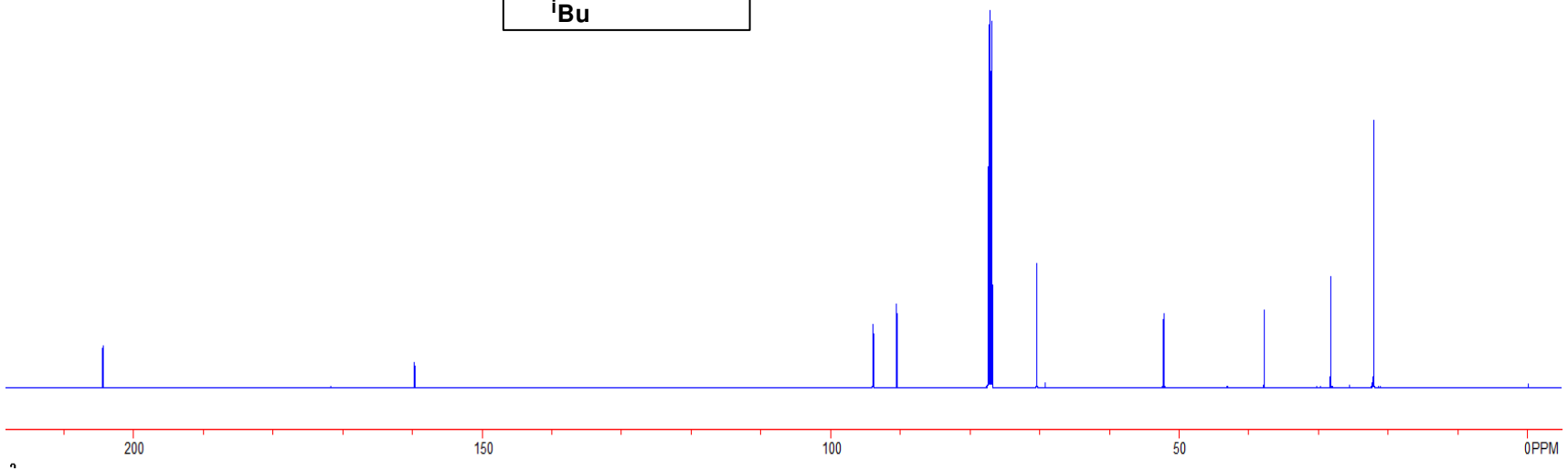

H3C
H3C
HN
O
O
O
0.88
0.91
1.00
0.96
0.98
2.04
2.96
2.95
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

Compound 5h.

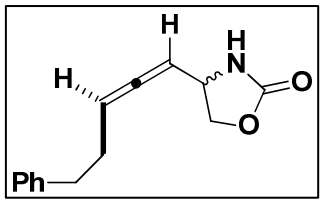


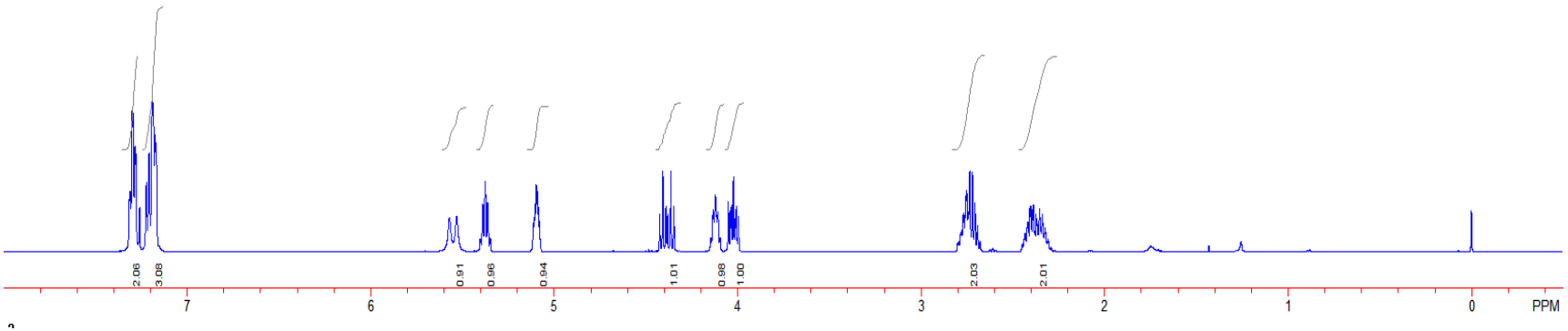
Compound 5h.



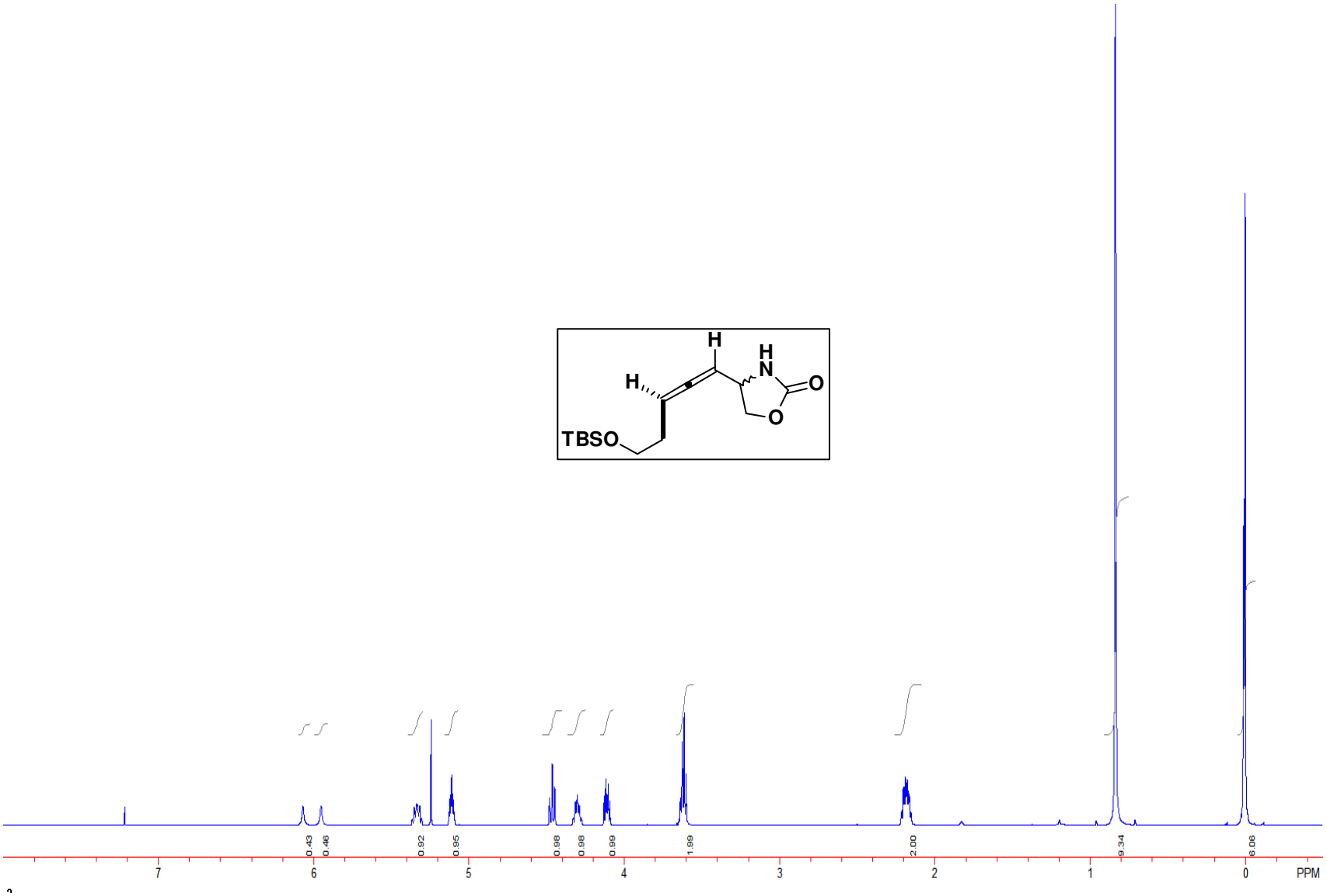


Compound 5i.

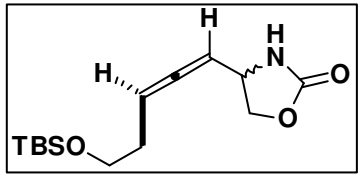


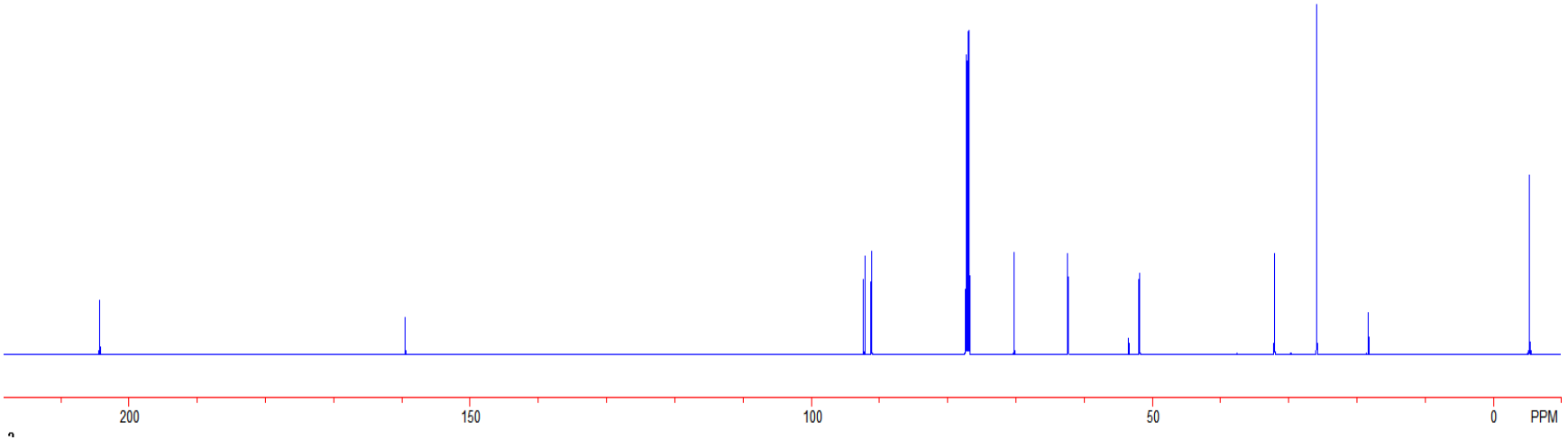


Compound 5j.

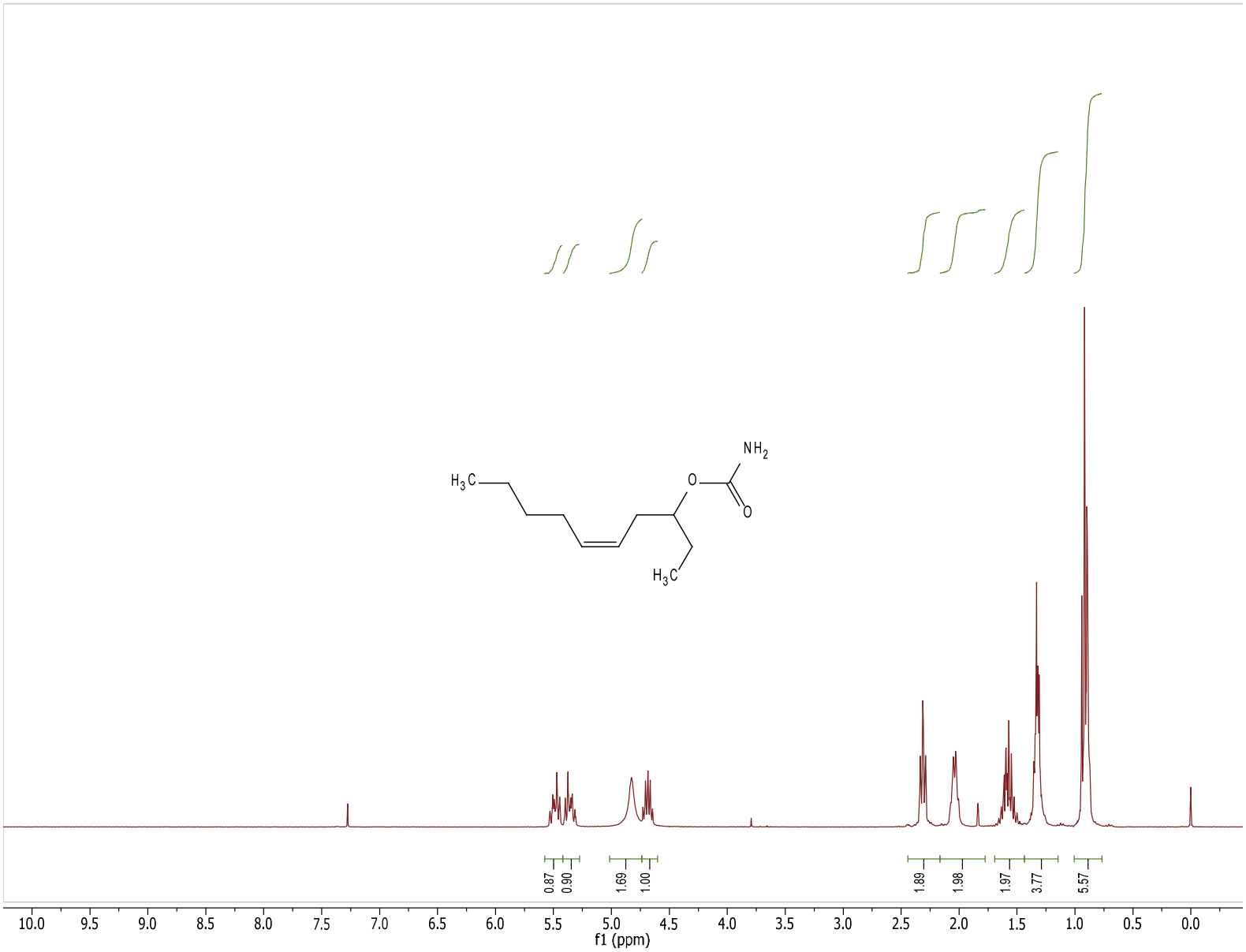

H
H
N
O
H
O
TBSO
0.43
0.46
0.92
0.95
0.98
0.98
0.99
1.99
2.00
9.34
6.06
7
6
5
4
3
2
1
0
PPM

Compound 5j.

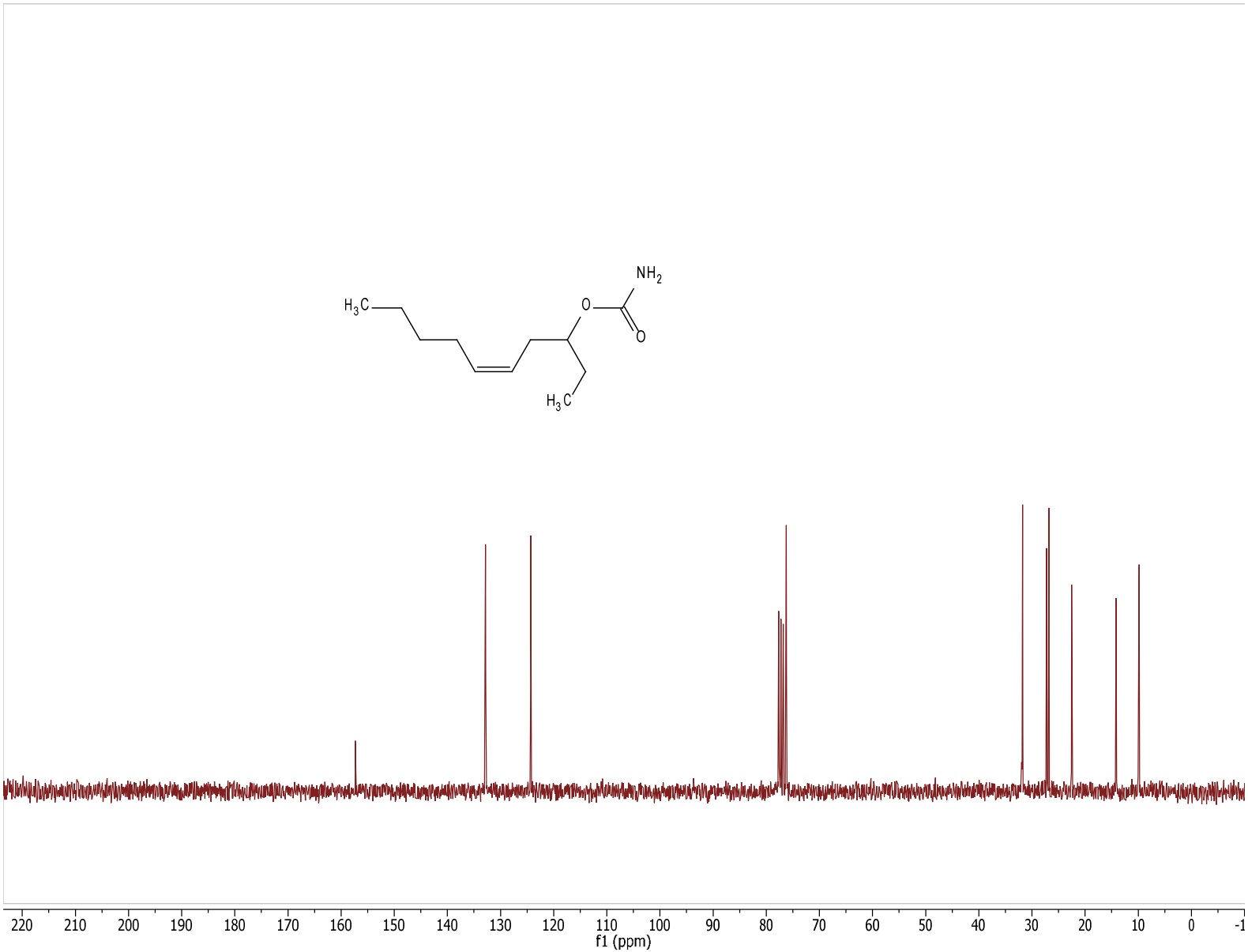




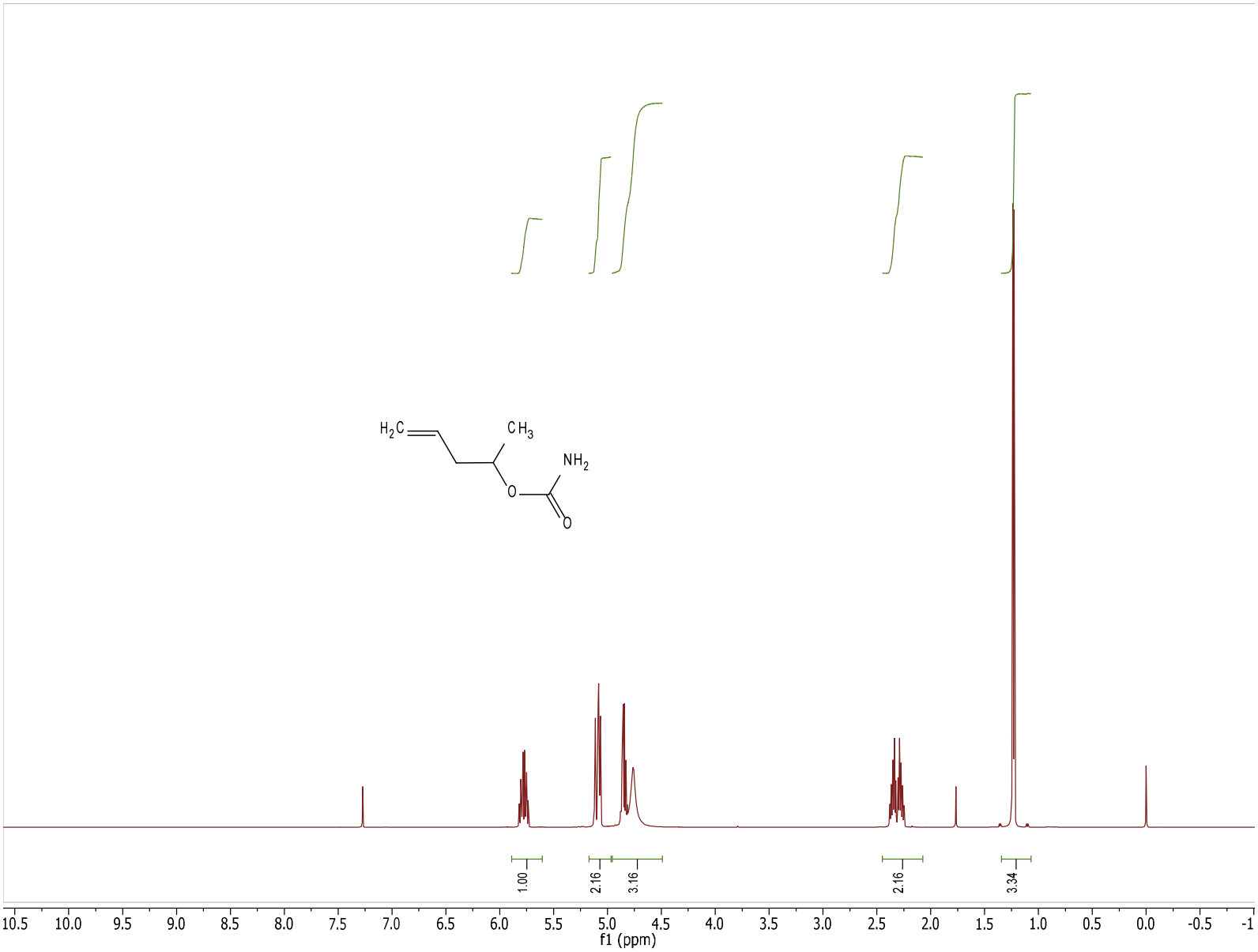
Compound 6b.


NH2
H3C
O
O
H3C
0.87
0.90
1.69
1.00
1.89
1.98
1.97
3.77
5.57
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)

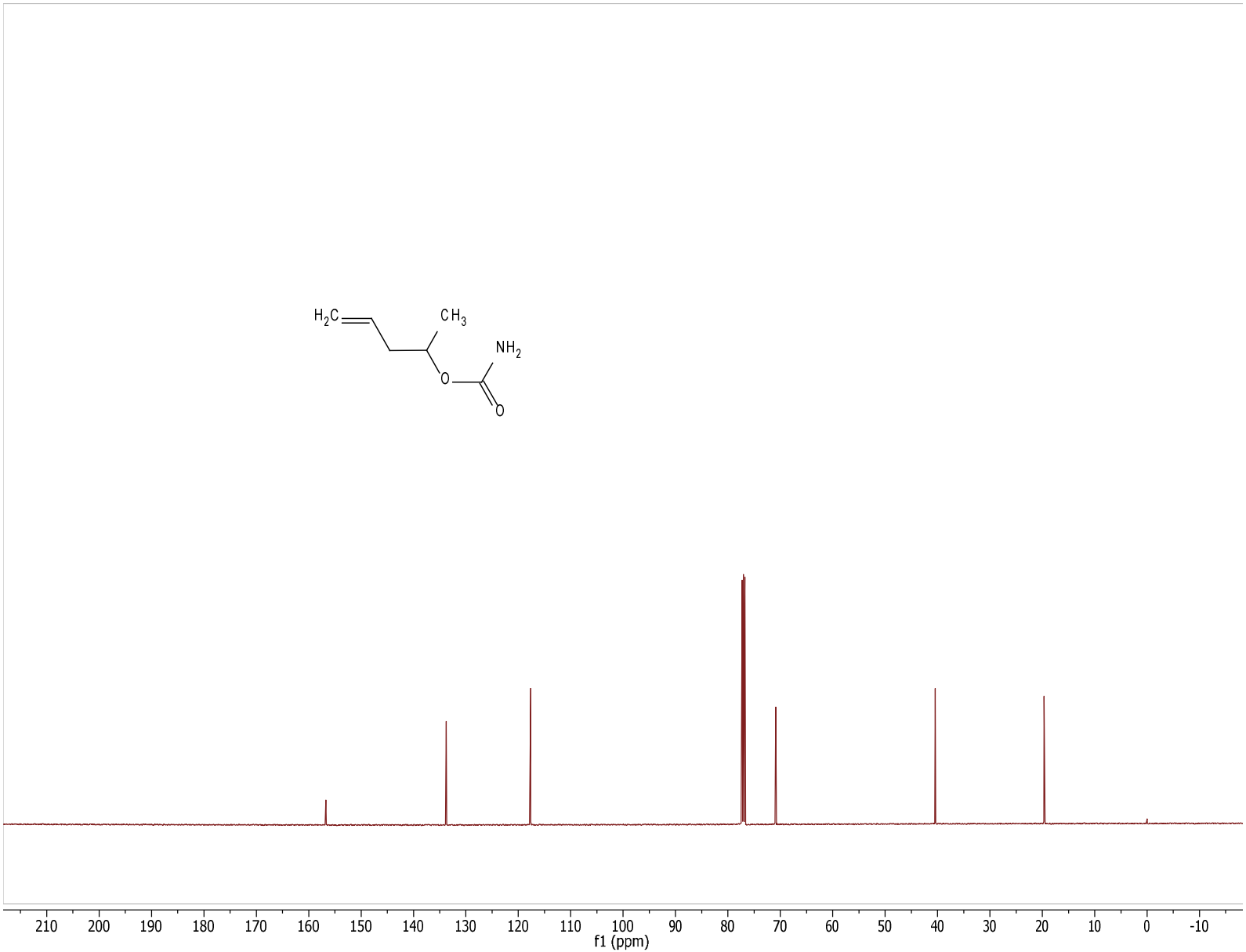
Compound 6b.


NH2
H3C
O
O
H3C
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

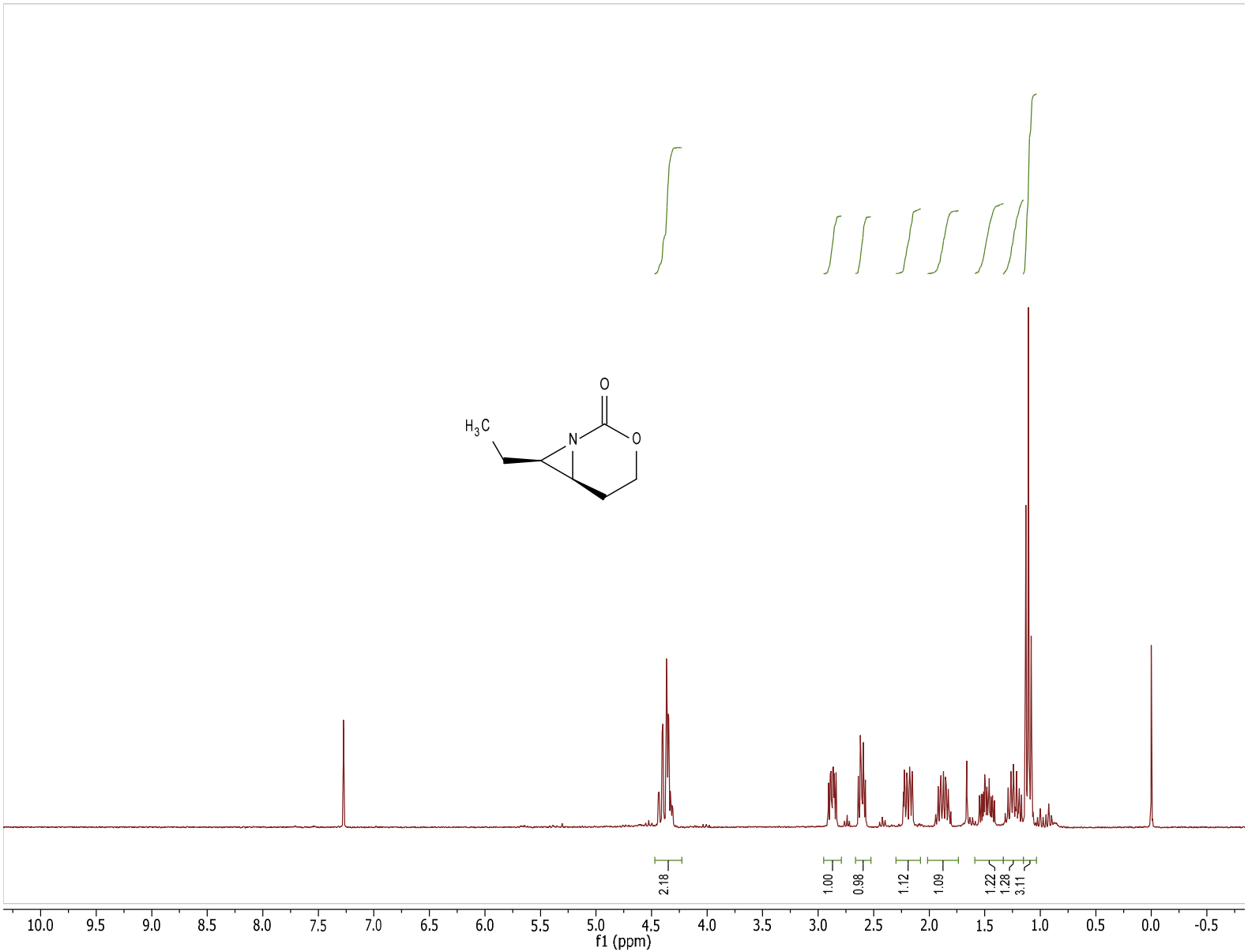
Compound 6e.


H2C
CH3
NH2
O
O
1.00
2.16
3.16
2.16
3.34
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 -0.5 -1
f1 (ppm)

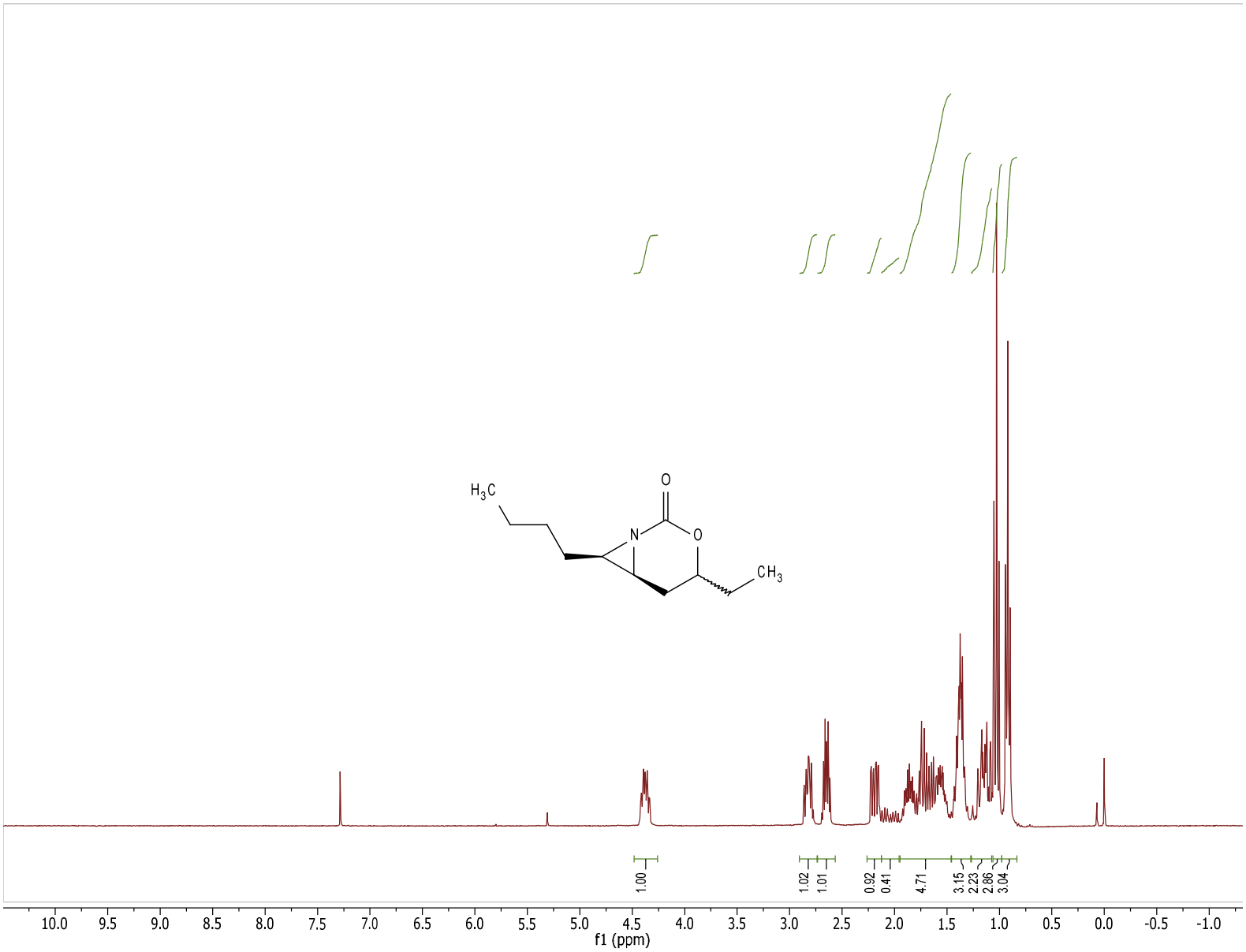
Compound 6e.


H2C
CH3
NH2
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

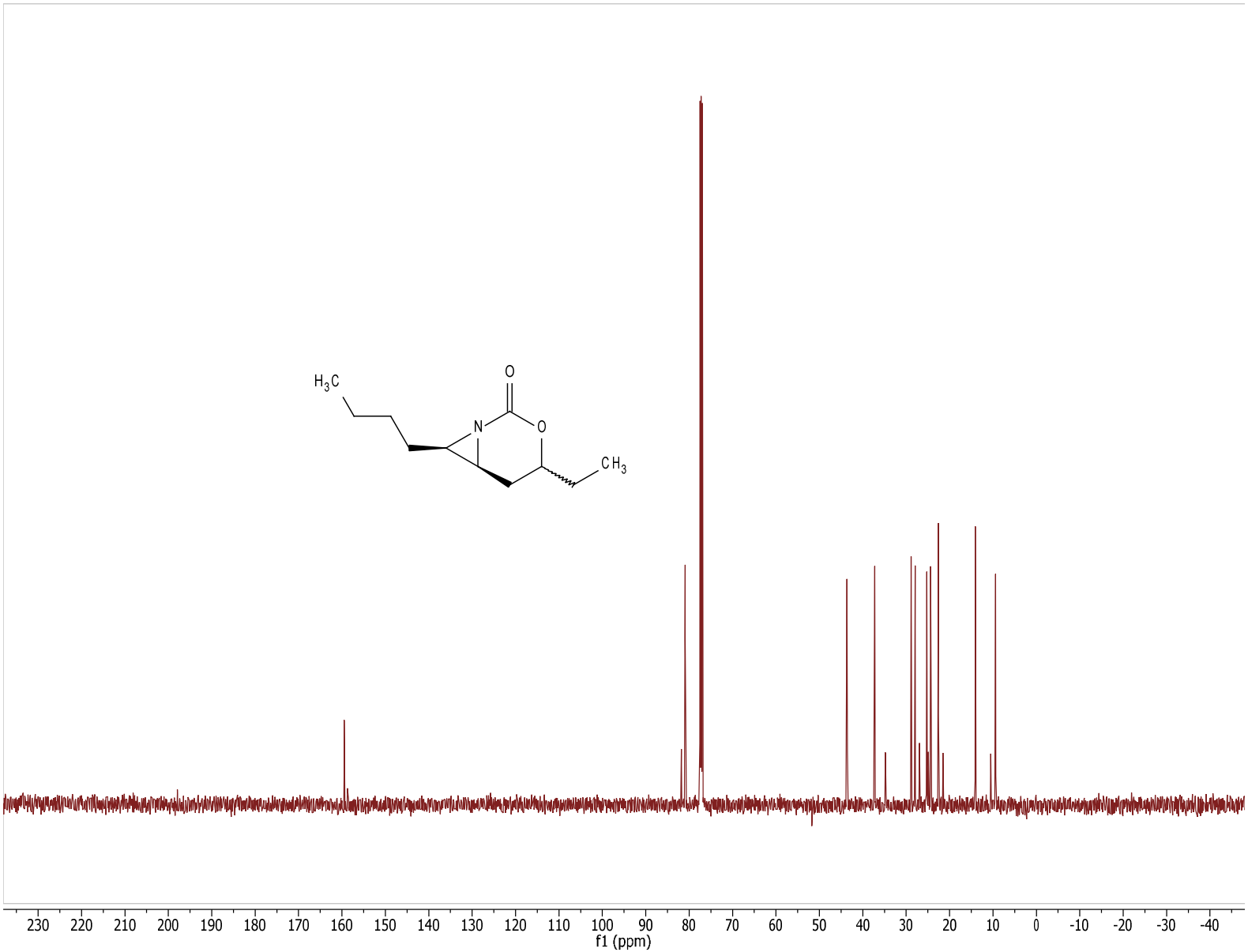
Compound 7a.


O
H3C
N
O
2.18
1.00
0.98
1.12
1.09
1.22
1.28
3.11
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
-0.5
f1 (ppm)

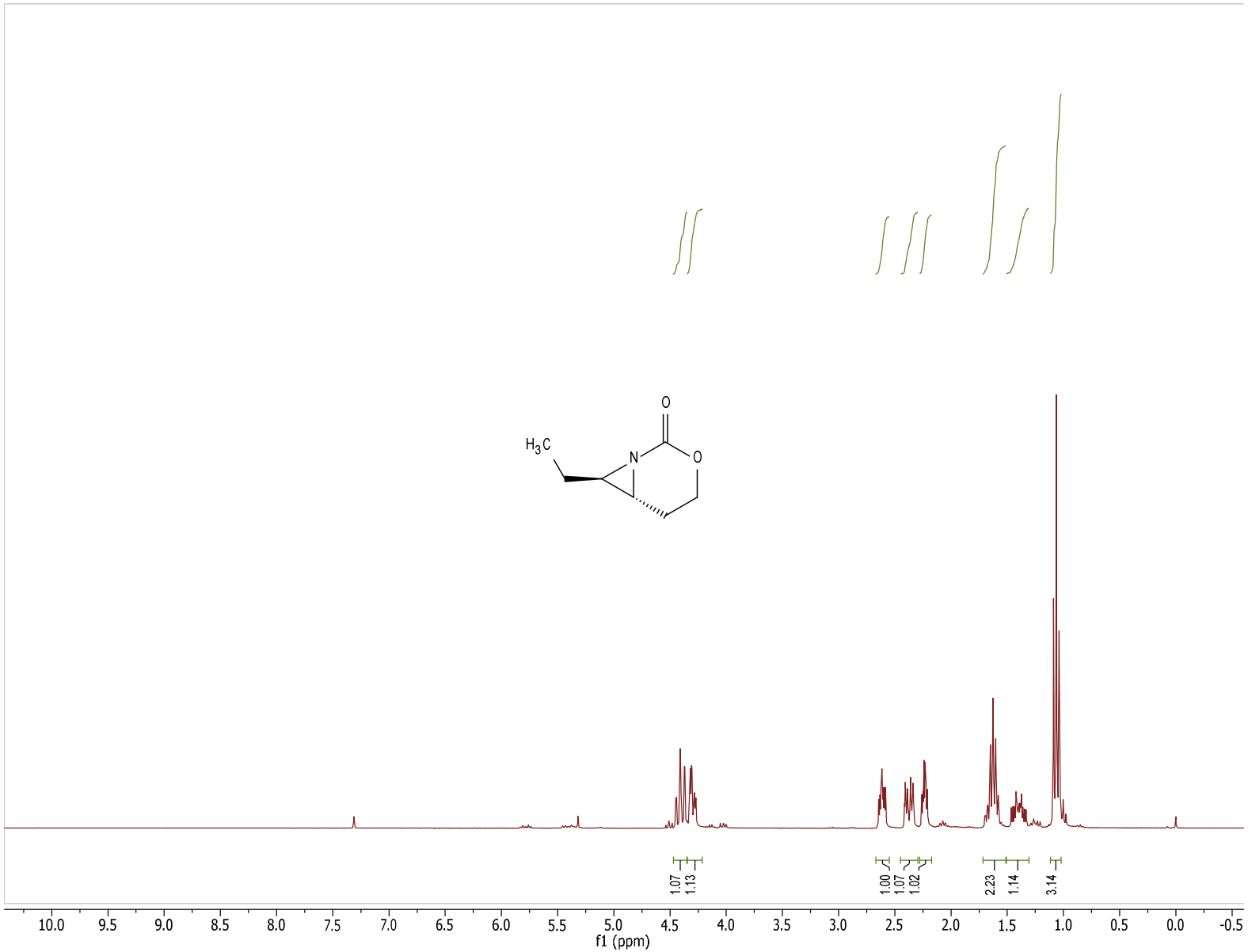
Compound 7b.


H3C
O
N
O
CH3
1.00
1.02
1.01
0.92
0.41
4.71
3.15
2.23
2.86
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
-0.5
-1.0
f1 (ppm)

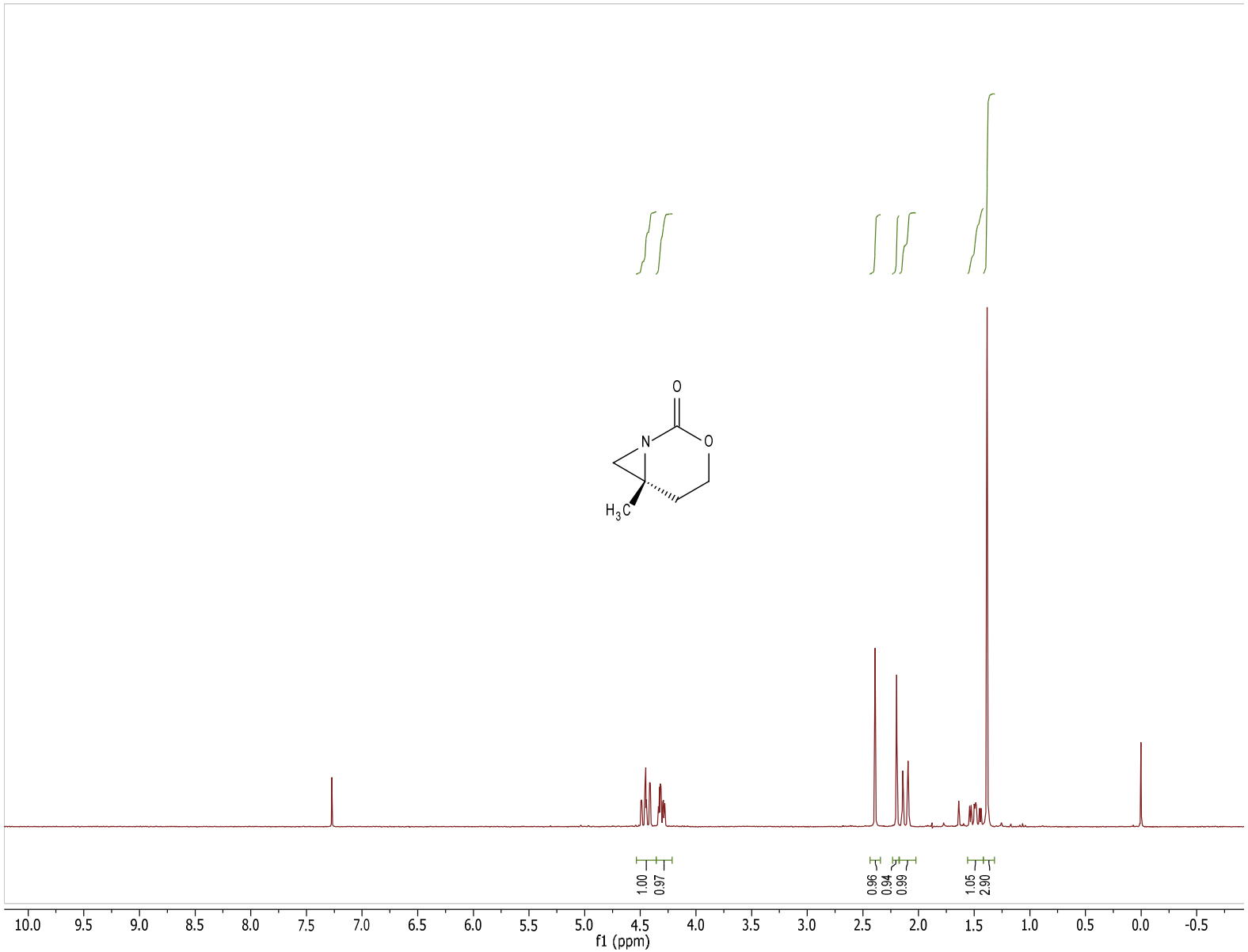
Compound 7b.


H3C
O
N
O
CH3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

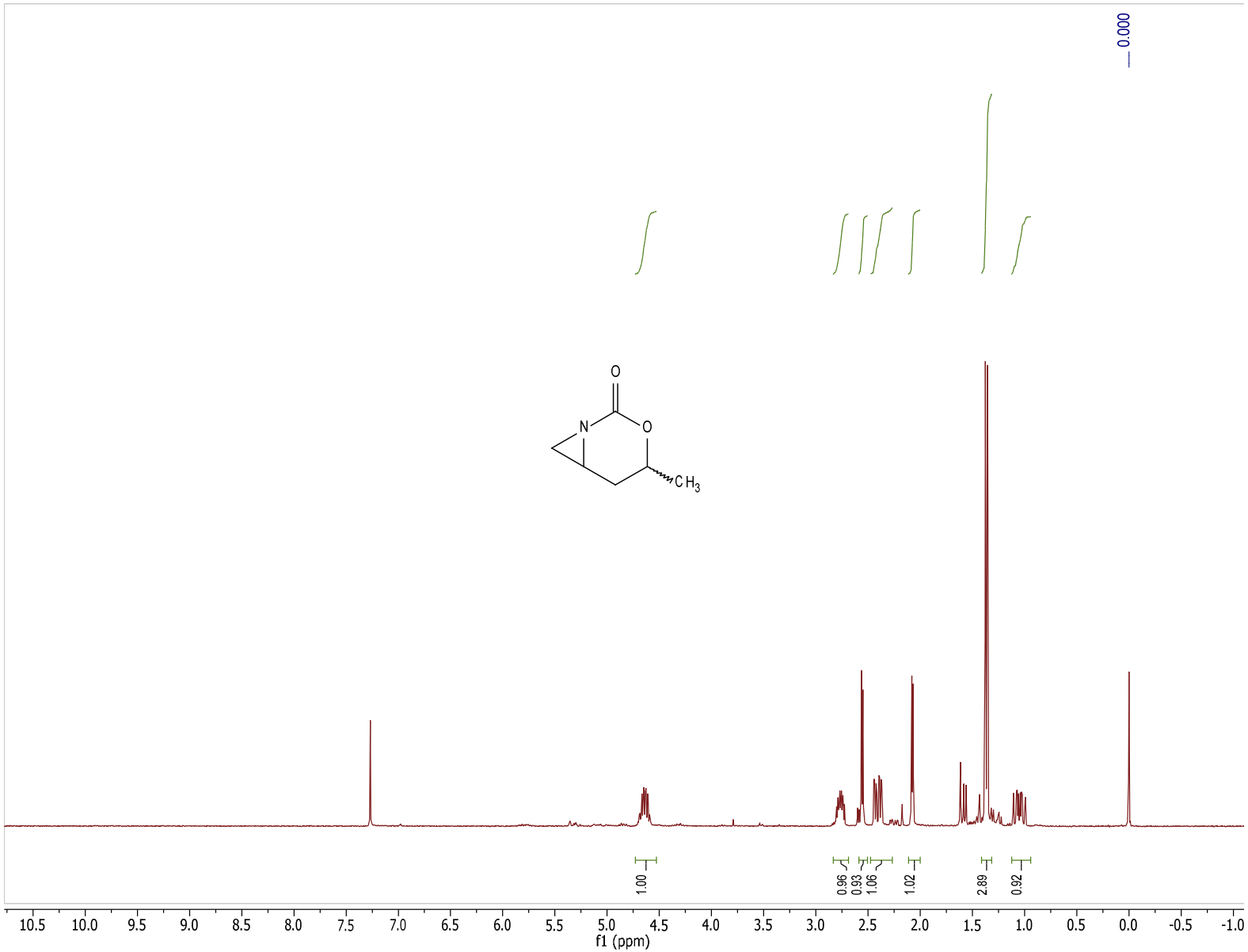
Compound 7c.


O
H3C
N
O
1.07
1.13
1.00
1.07
1.02
2.23
1.14
3.14
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
-0.5
f1 (ppm)

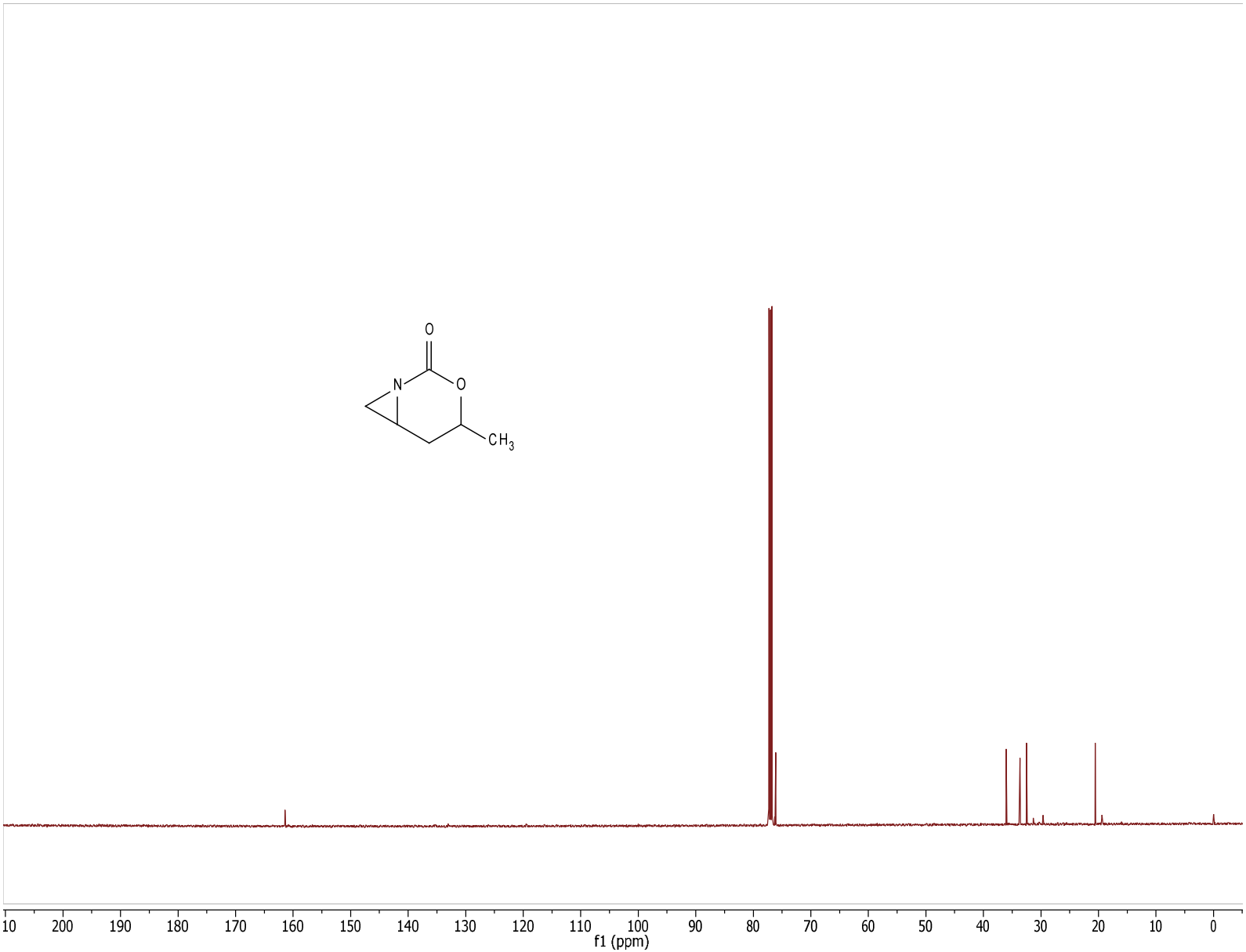
Compound 7d.


O
N
O
H3C
1.00
0.97
0.96
0.94
0.99
1.05
2.90
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
-0.5
f1 (ppm)

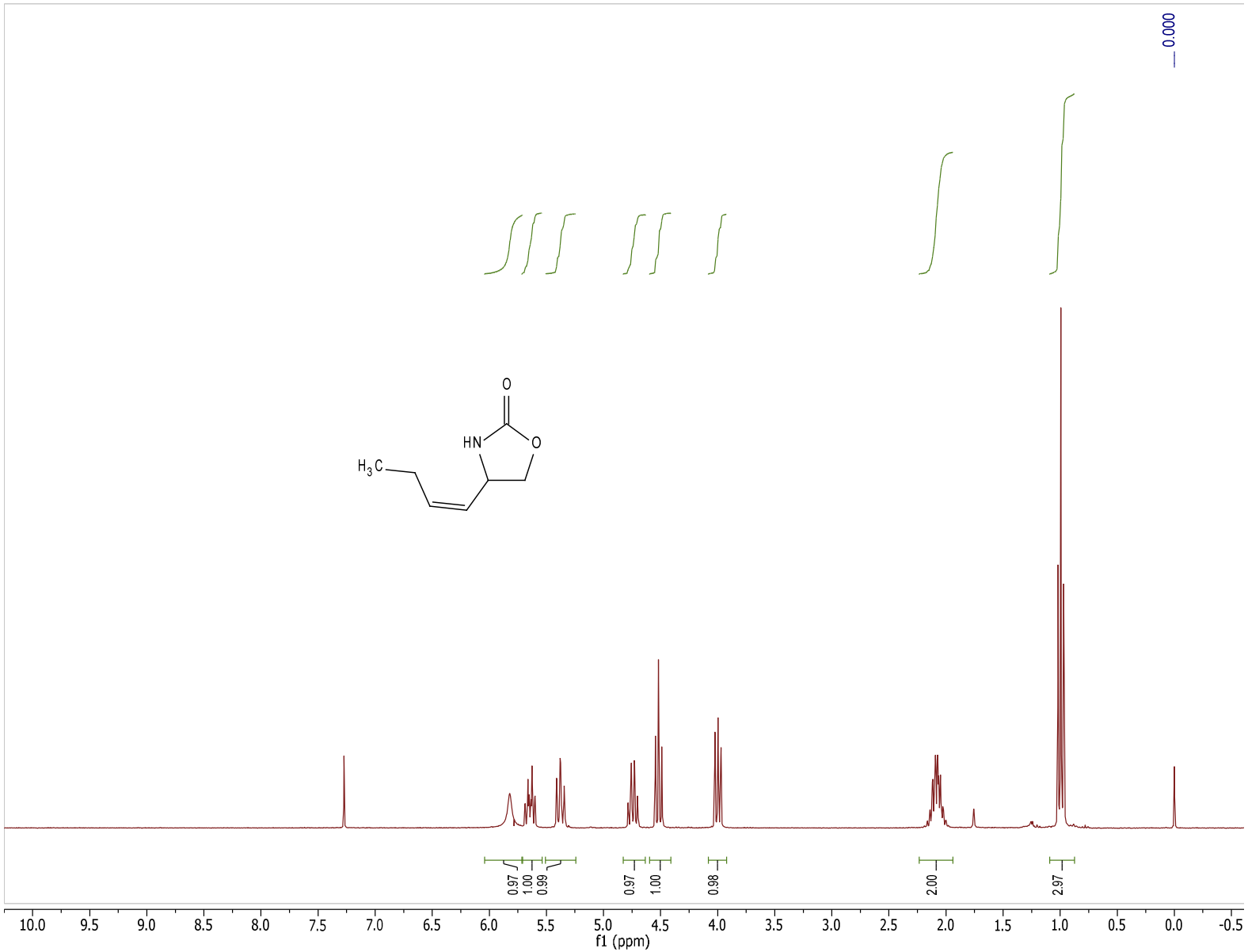
Compound 7e.


0.000
O
N
O
CH3
1.00
0.96
0.93
1.06
1.02
2.89
0.92
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 -0.5 -1.0
f1 (ppm)

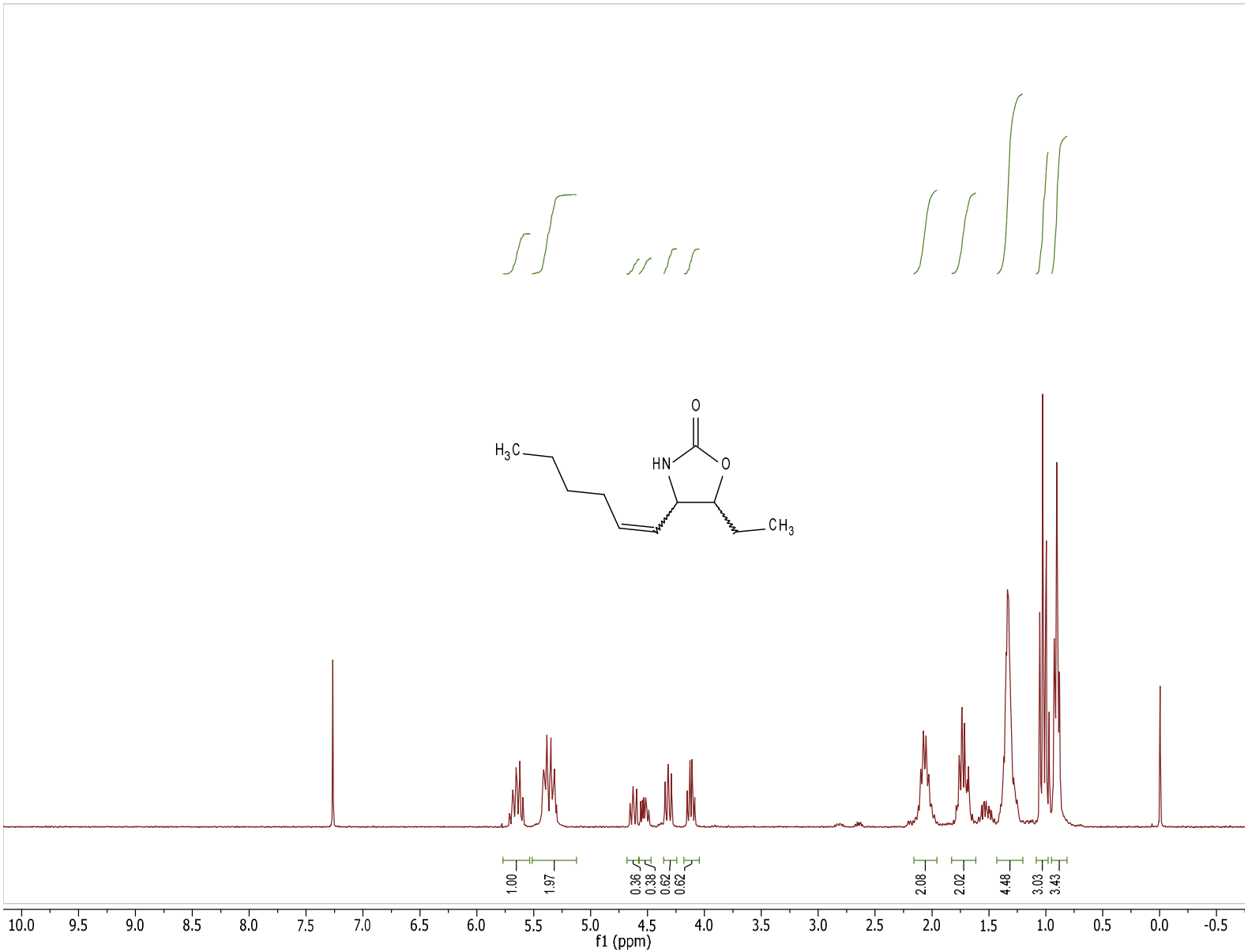
Compound 7e.


O
N
O
CH3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

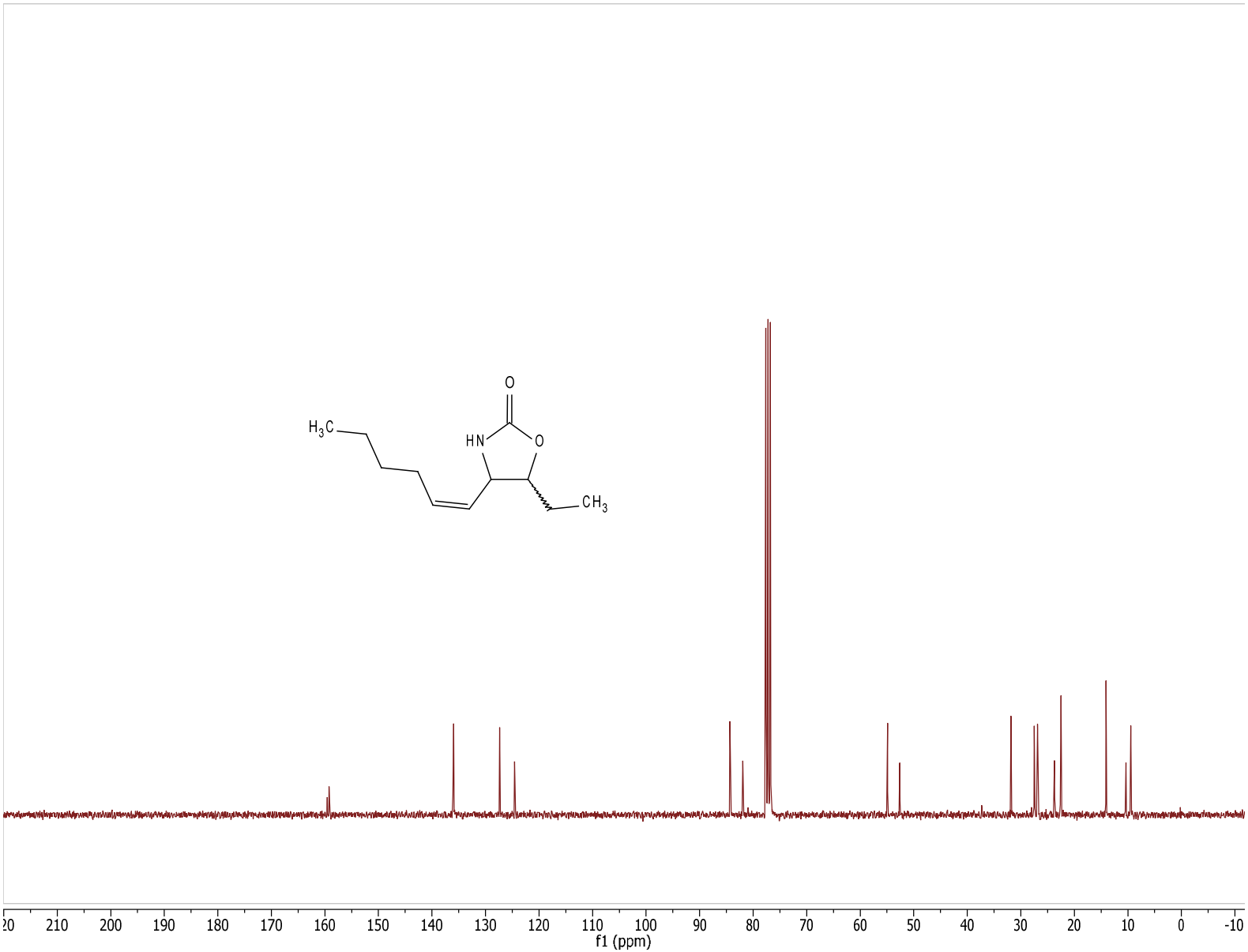
Compound 8a.


0.000
O
HN
O
H3C
0.97
1.00
0.99
0.97
1.00
0.98
2.00
2.97
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
-0.5
f1 (ppm)

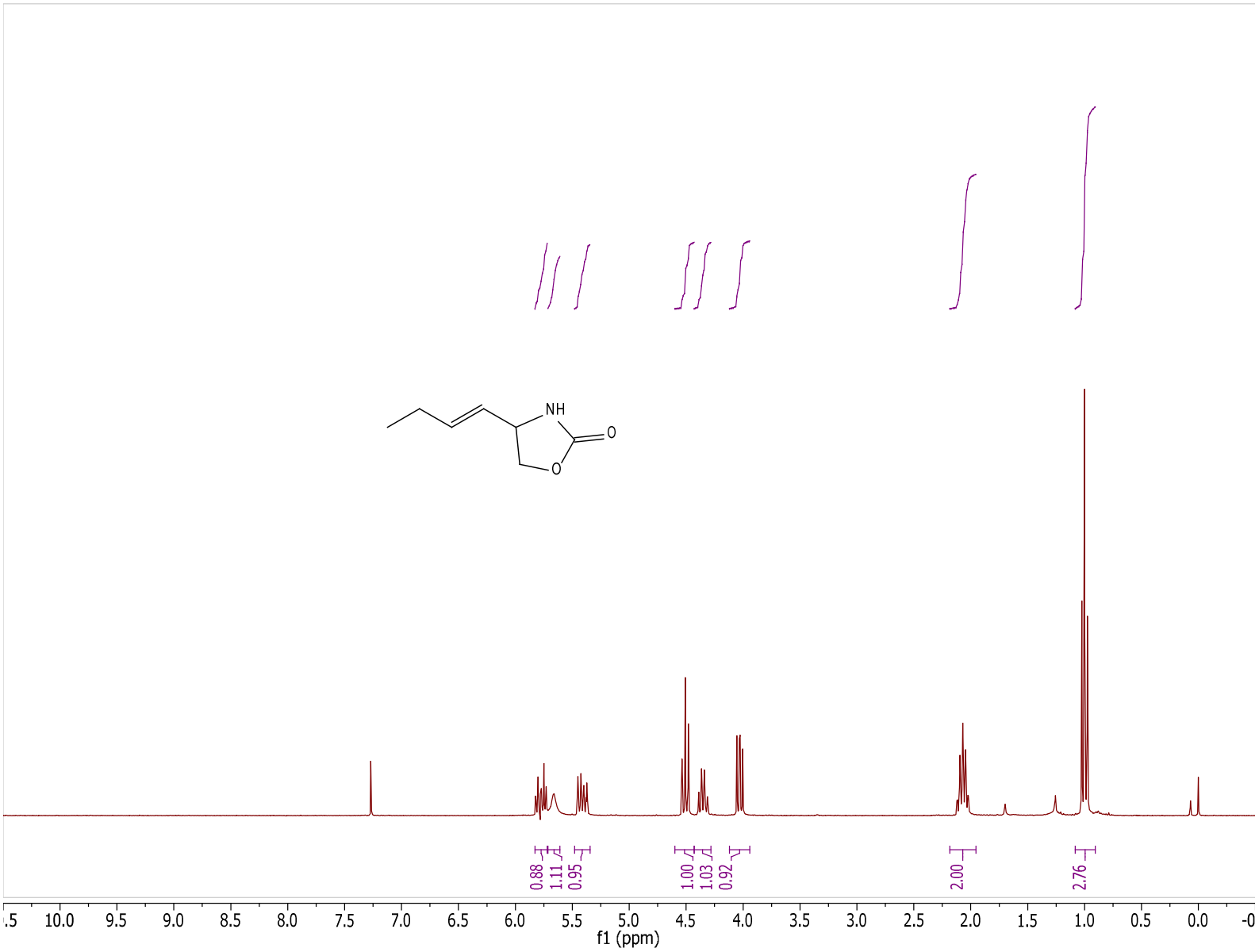
Compound 8b.


O
HN
O
H_3C
CH_3
1.00
1.97
0.36
0.38
0.62
0.62
2.08
2.02
4.48
3.03
3.43
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 -0.5
f1 (ppm)

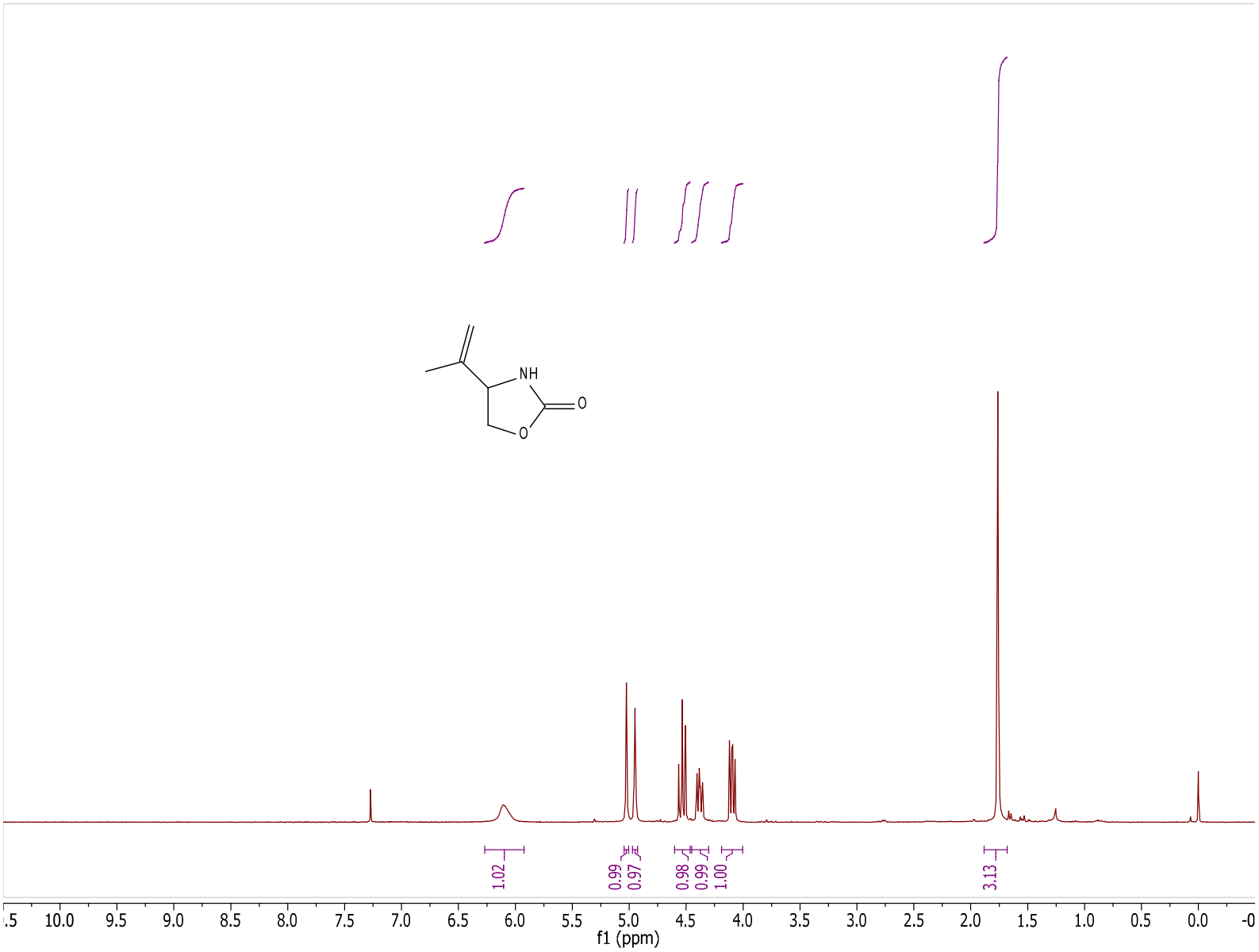
Compound 8b.


O
HN
O
H3C
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

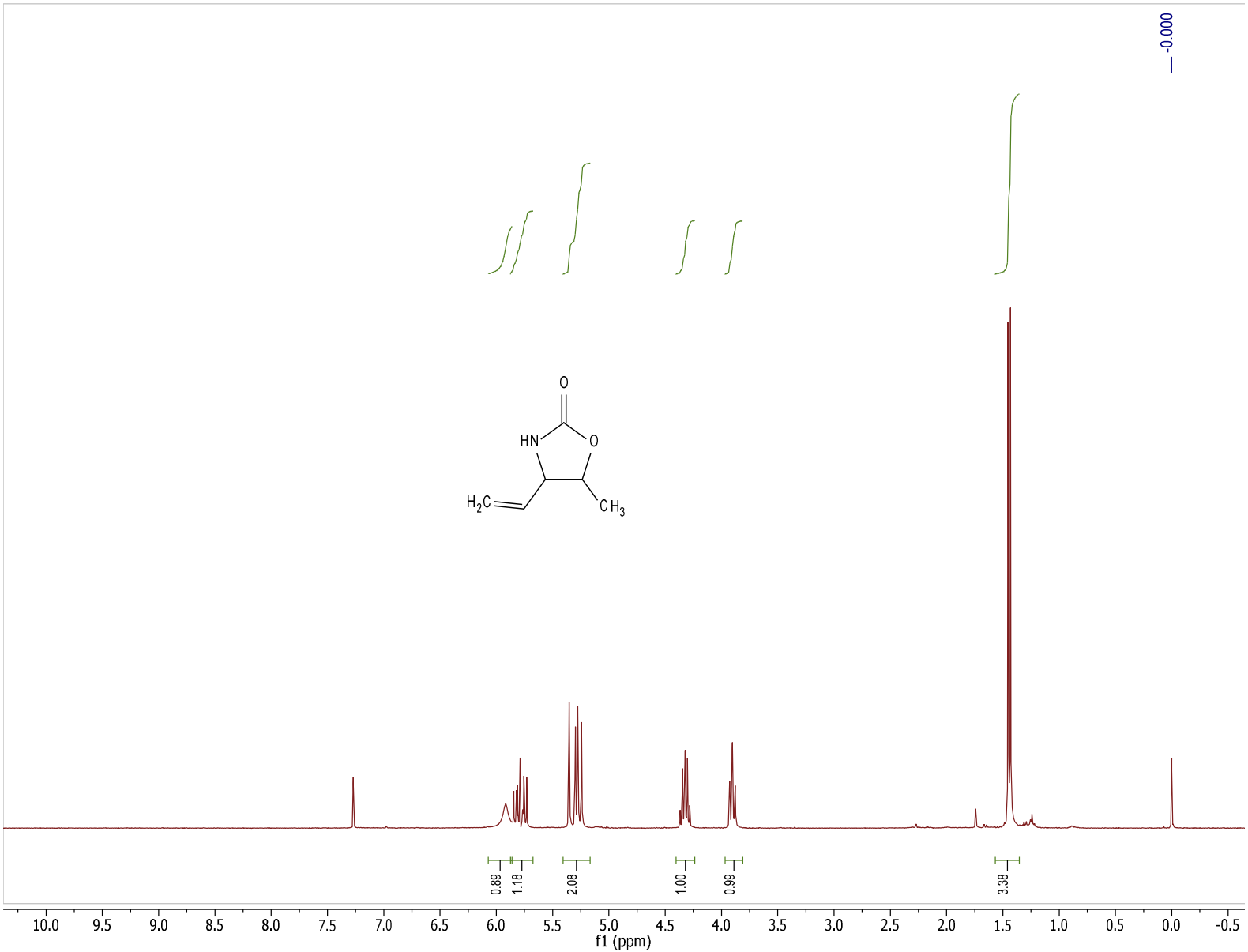
Compound 8c.


NH
O
O
0.88
1.11
0.95
1.00
1.03
0.92
2.00
2.76
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)

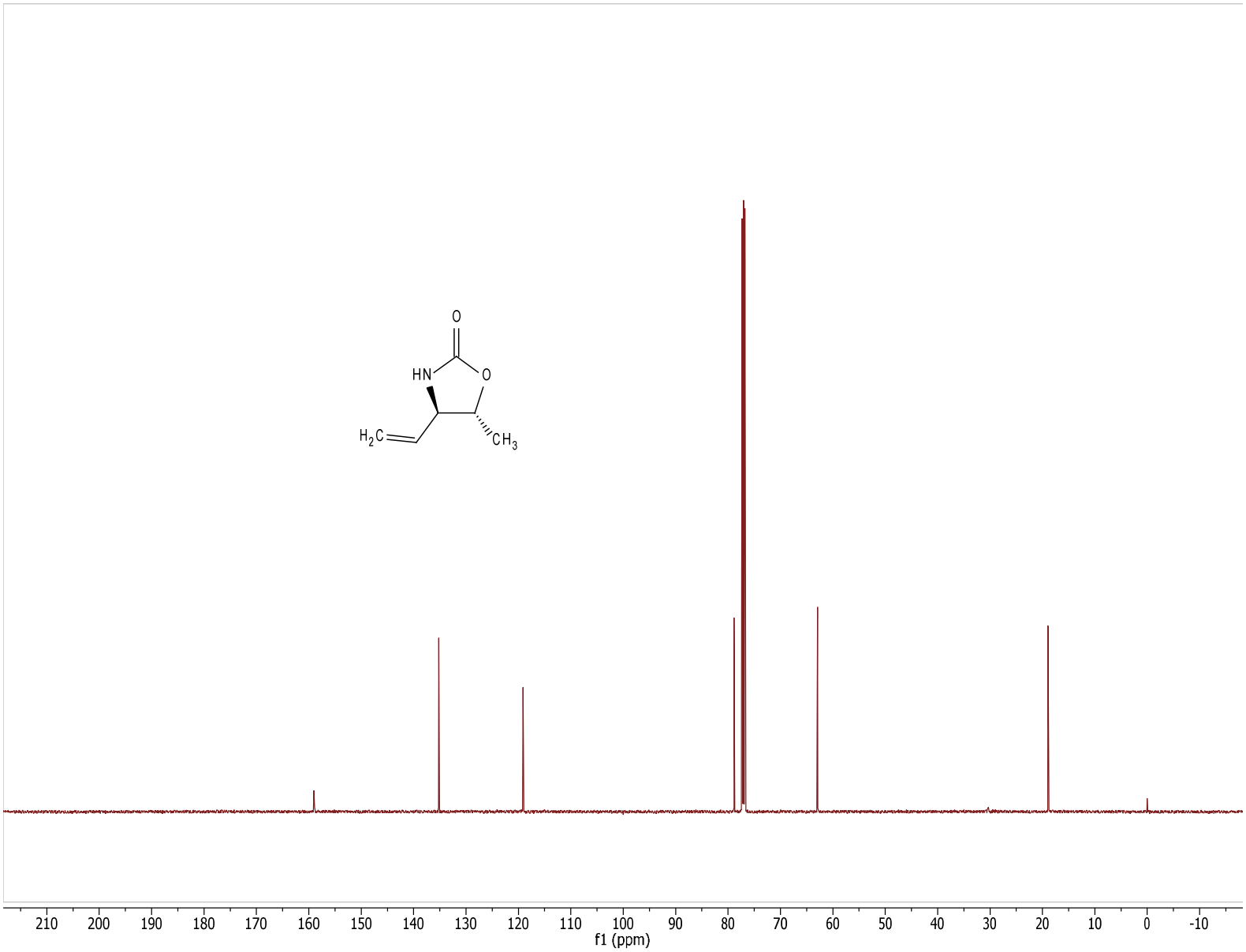
Compound 8d.


NH
O
O
1.02
0.99
0.97
0.98
0.99
1.00
3.13
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)

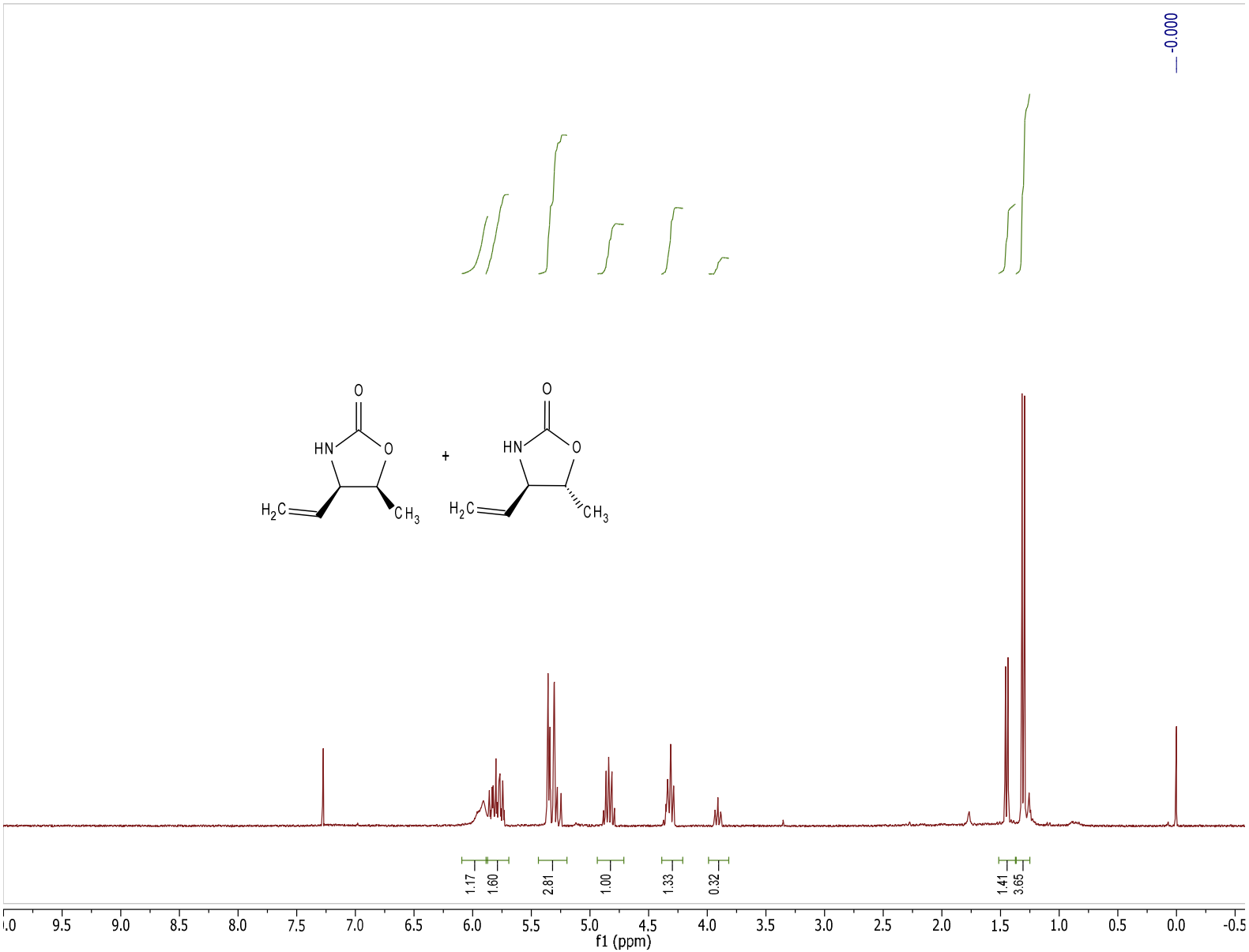
Compound 8e Major.



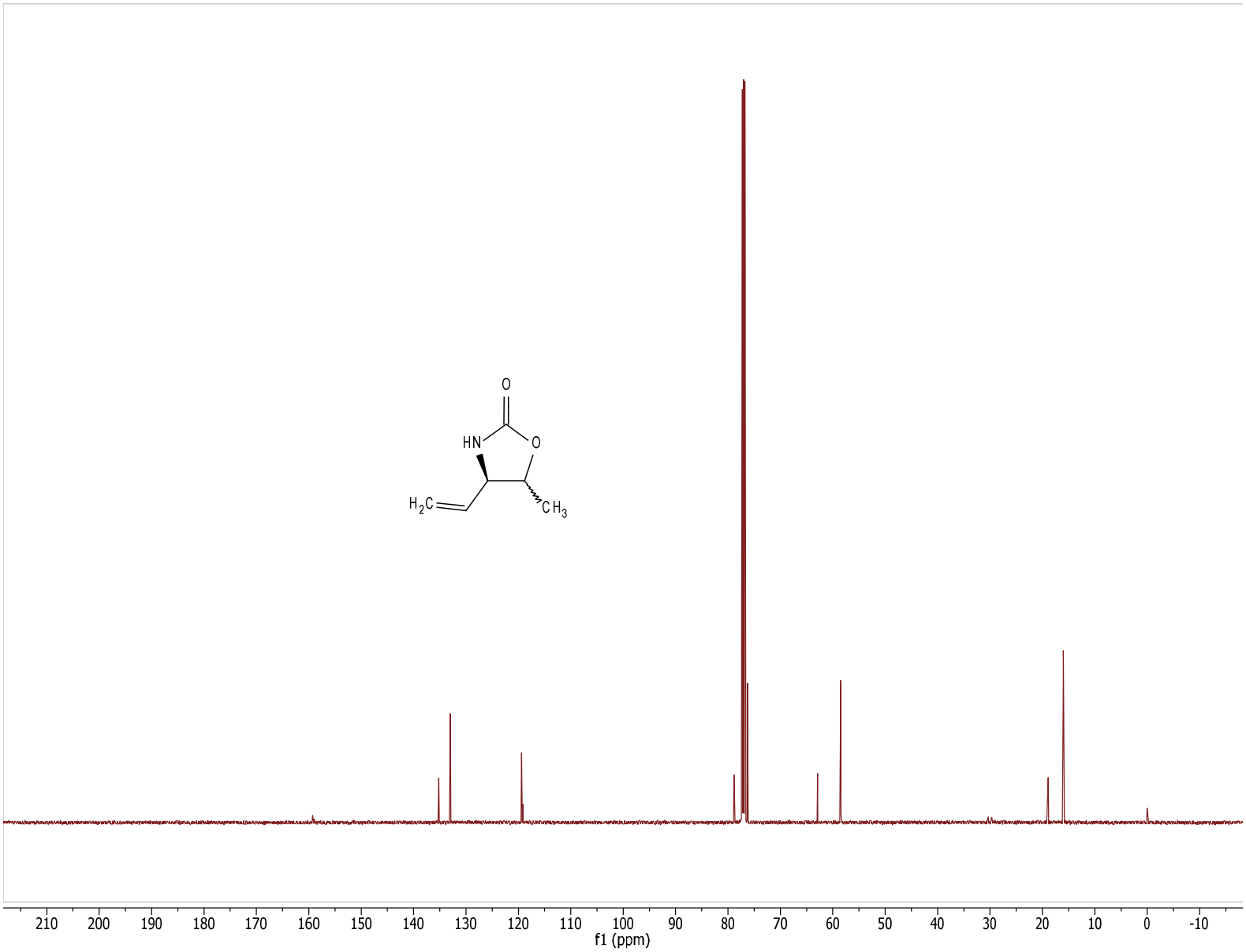
Compound 8e Major.



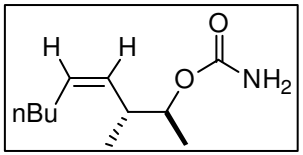
Compound 8e mixture of minor and major isomers.

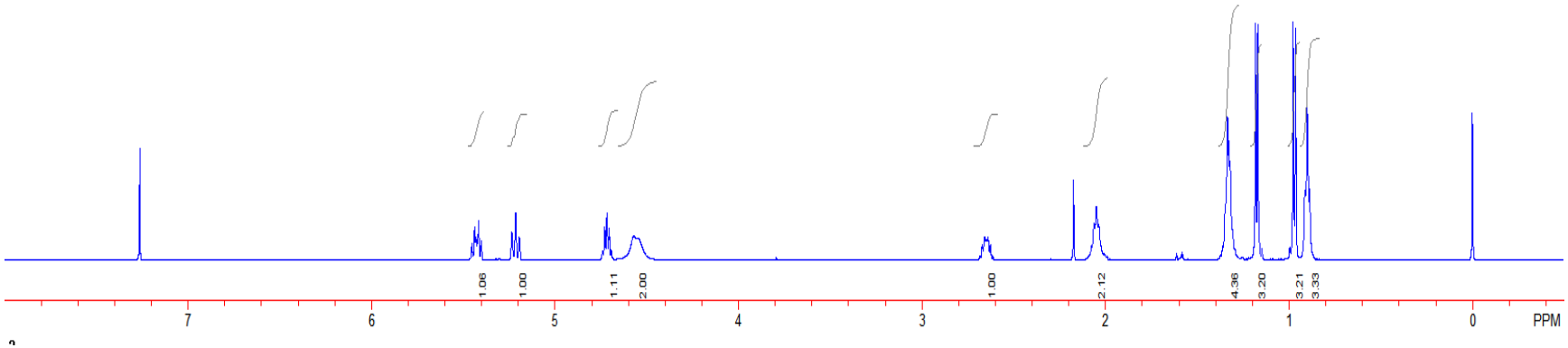


Compound 8e mixture of minor and major isomers.

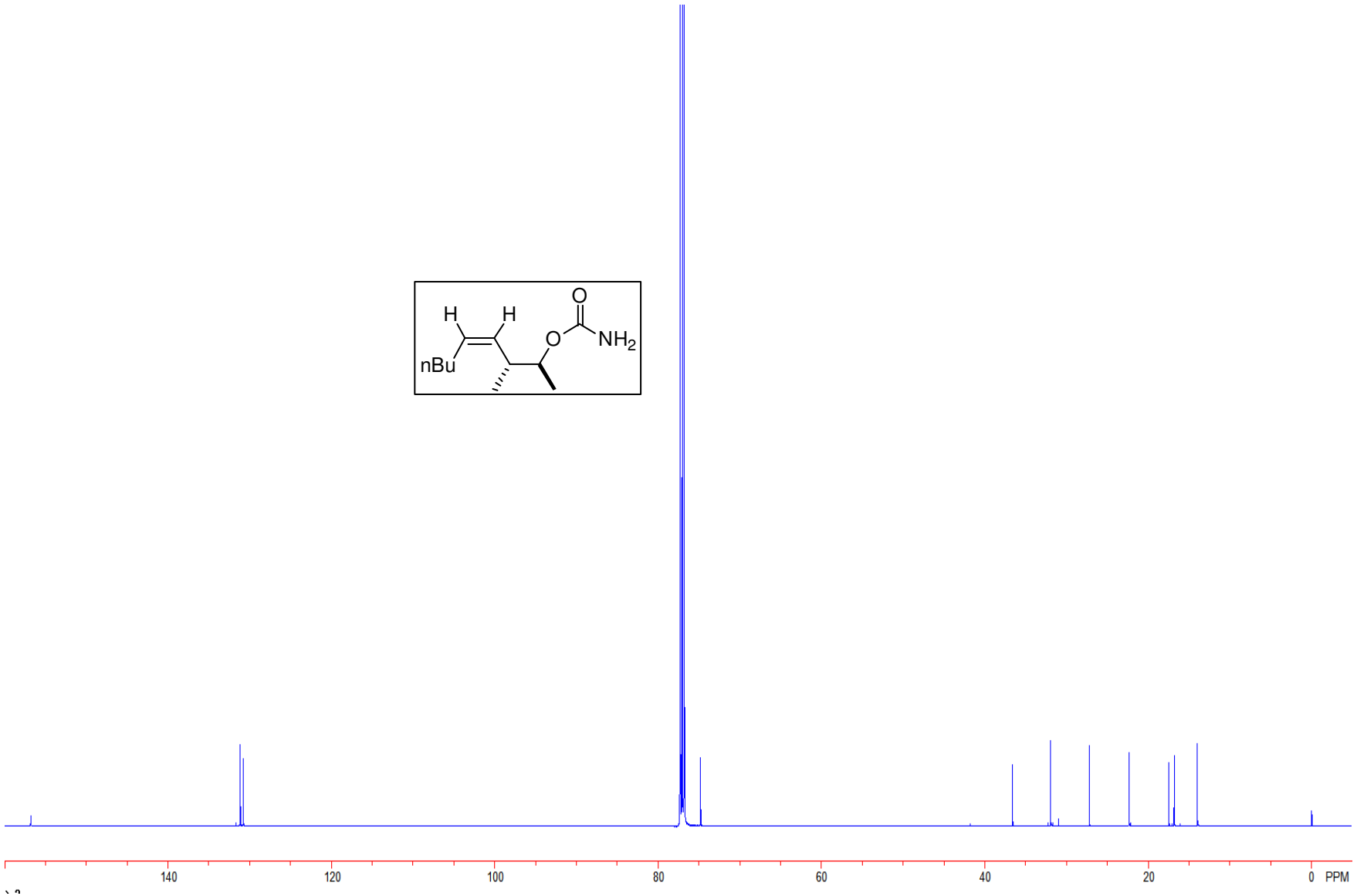


Compound 11.

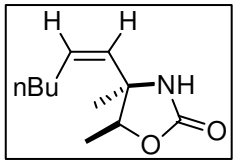

H
H
O
O
NH2
nBu

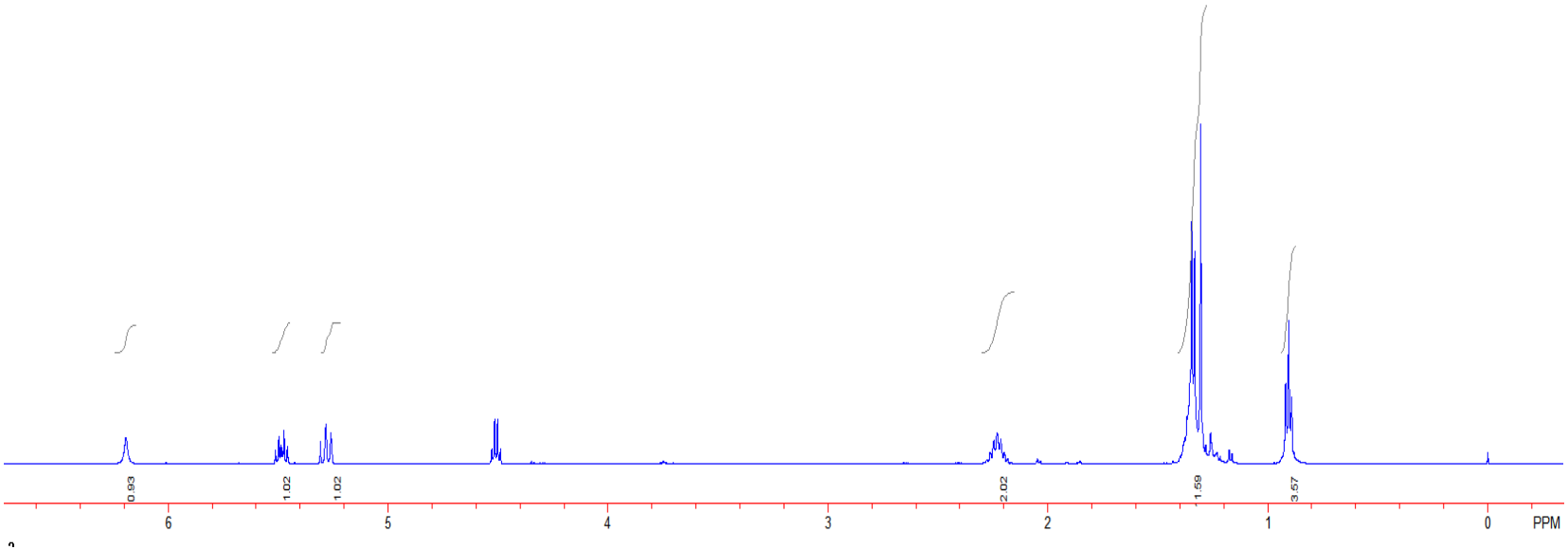

1.06
1.00
1.11
2.00
1.00
2.12
4.96
3.20
3.21
3.33
7
6
5
4
3
2
1
0
PPM

Compound 11.

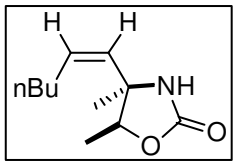


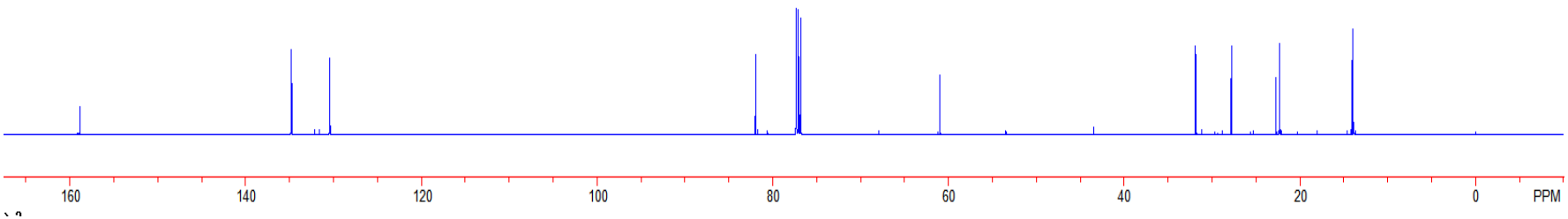
Compound 12.



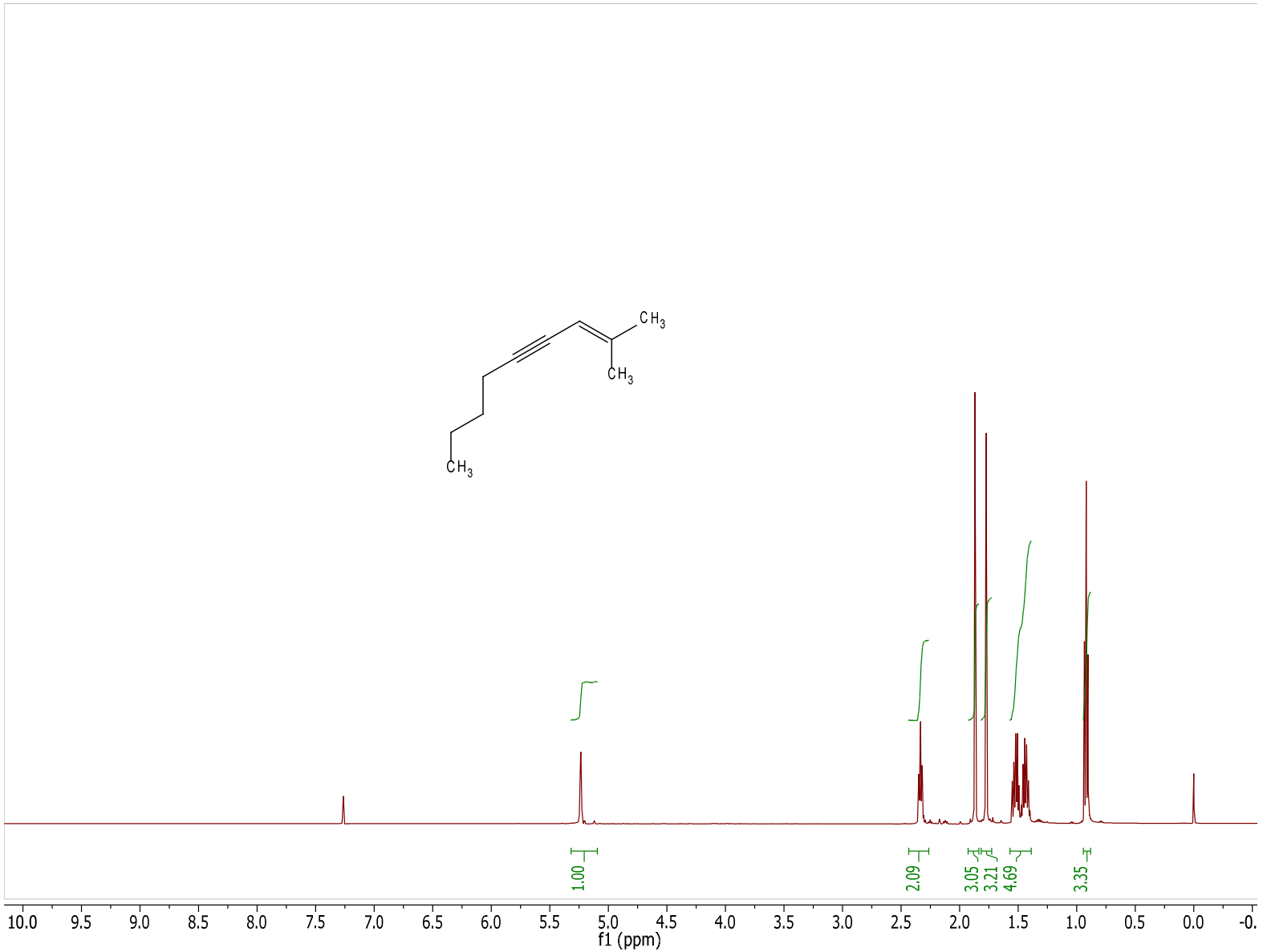


Compound 12.

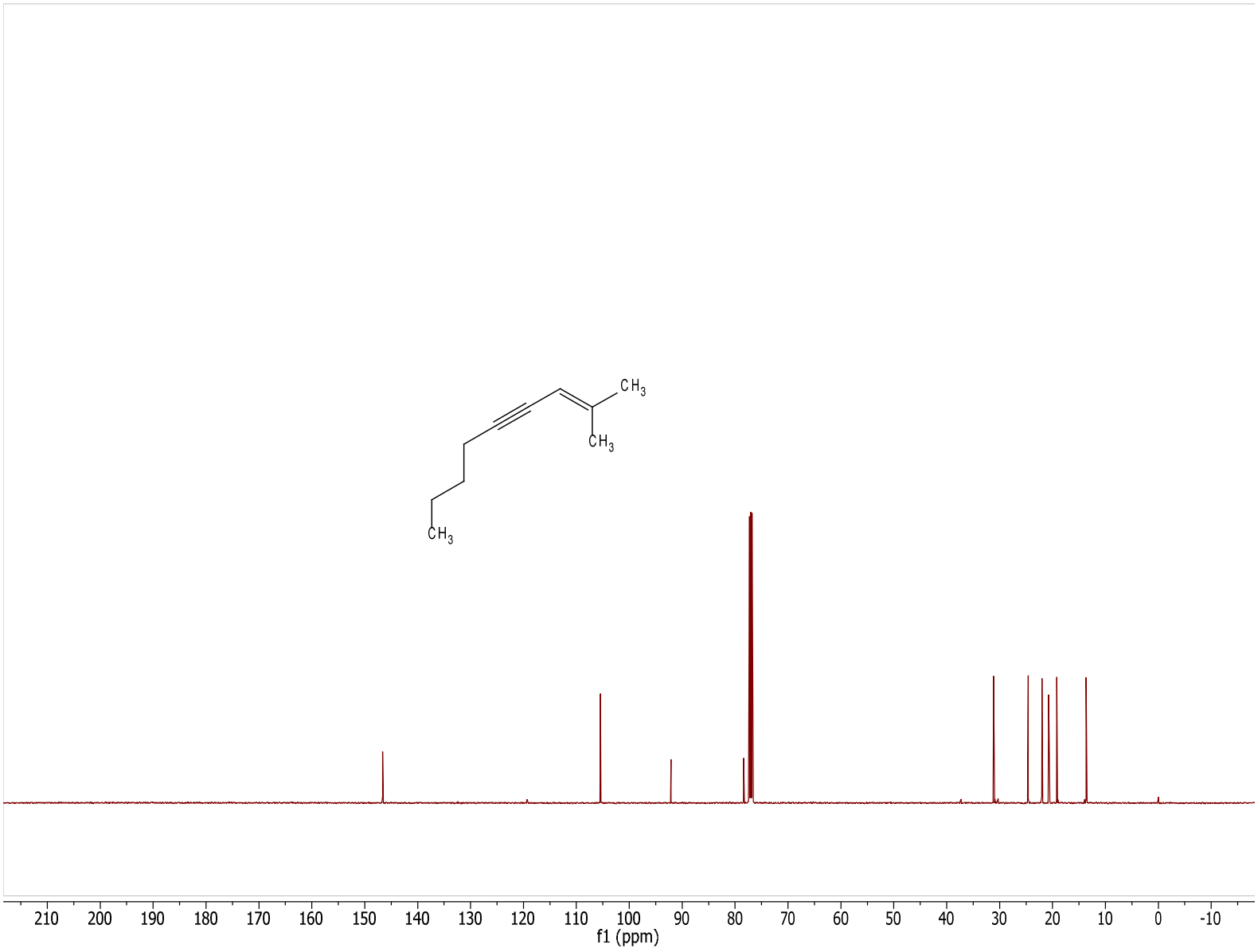




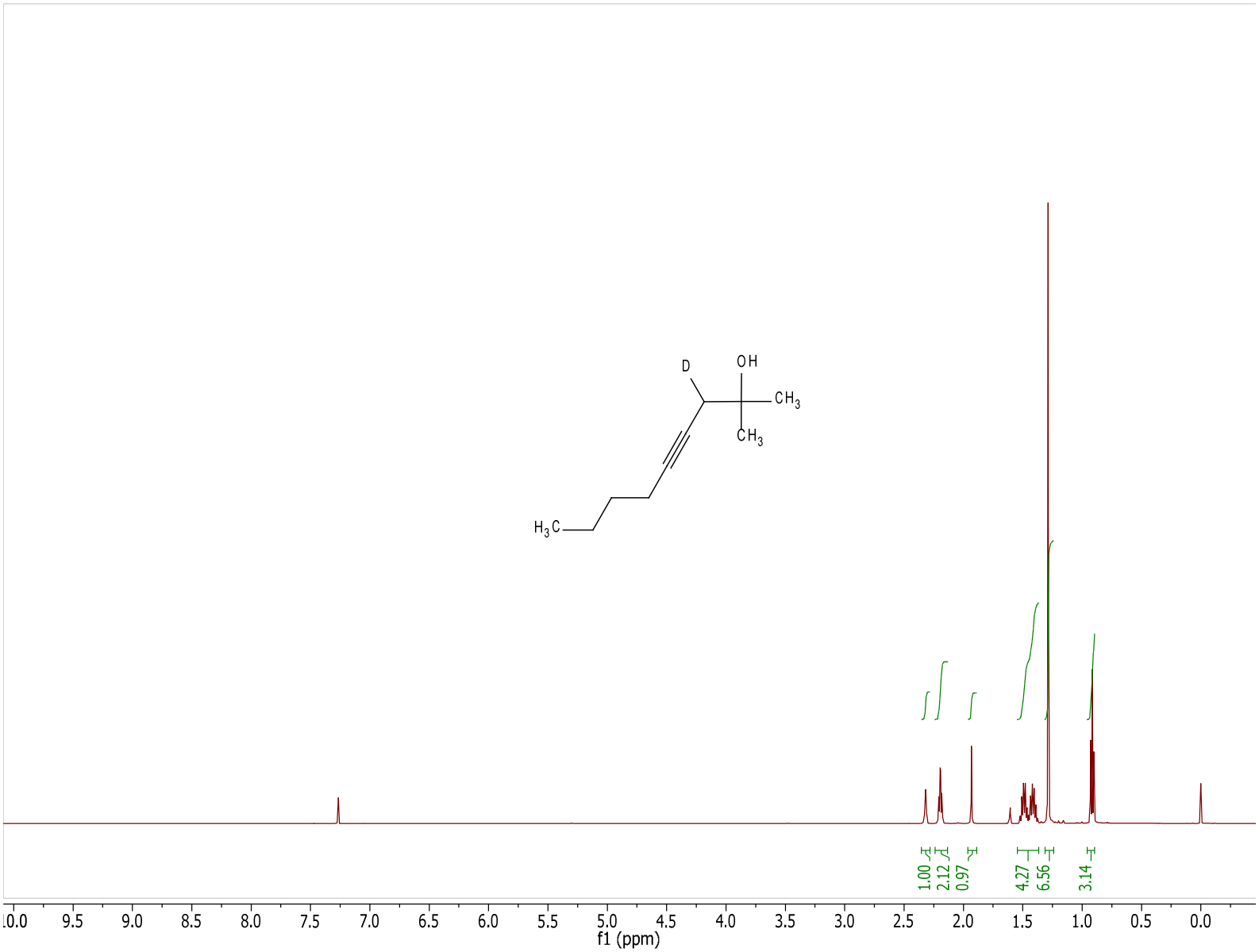
Compound 14-Da.



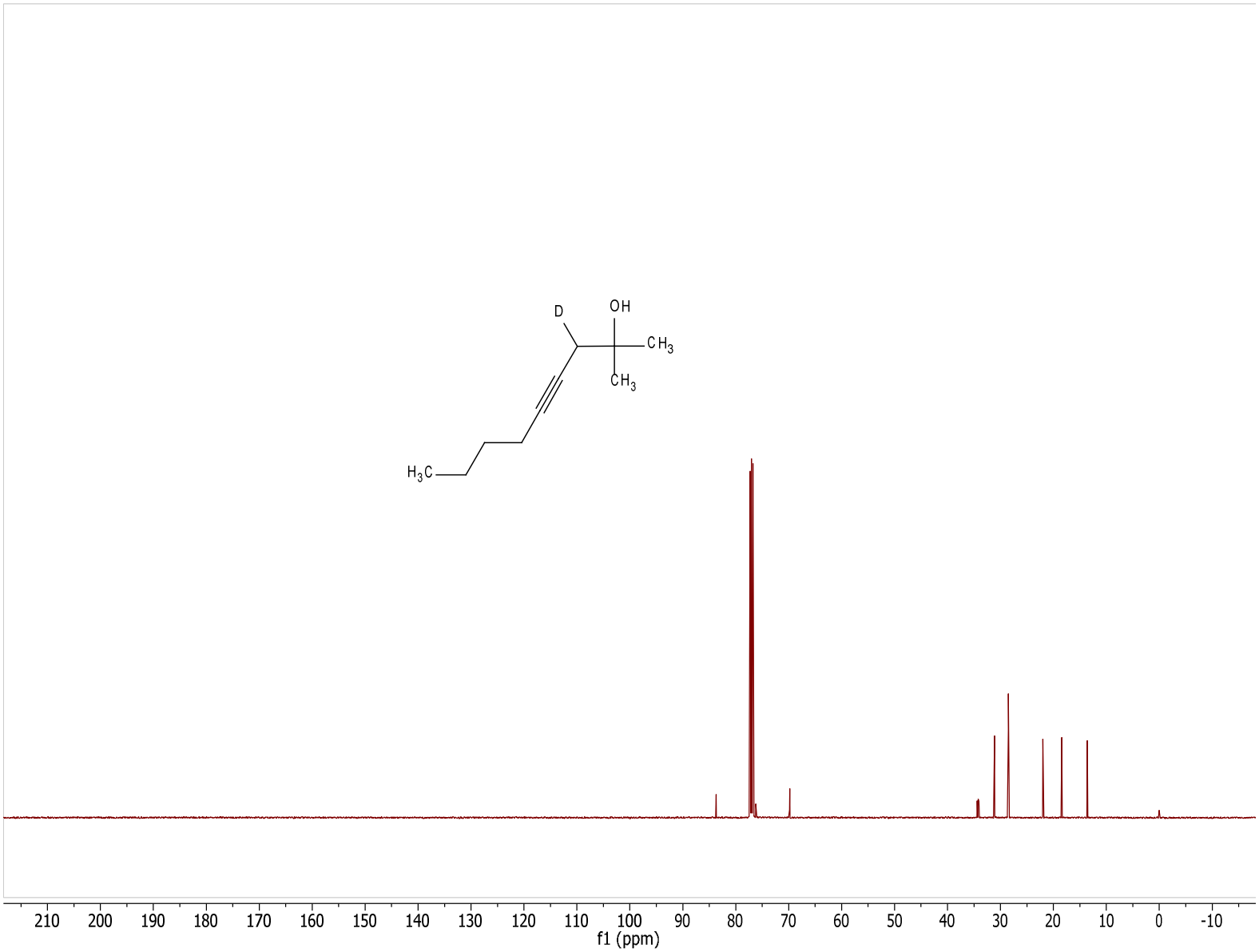
Compound 14-Da.



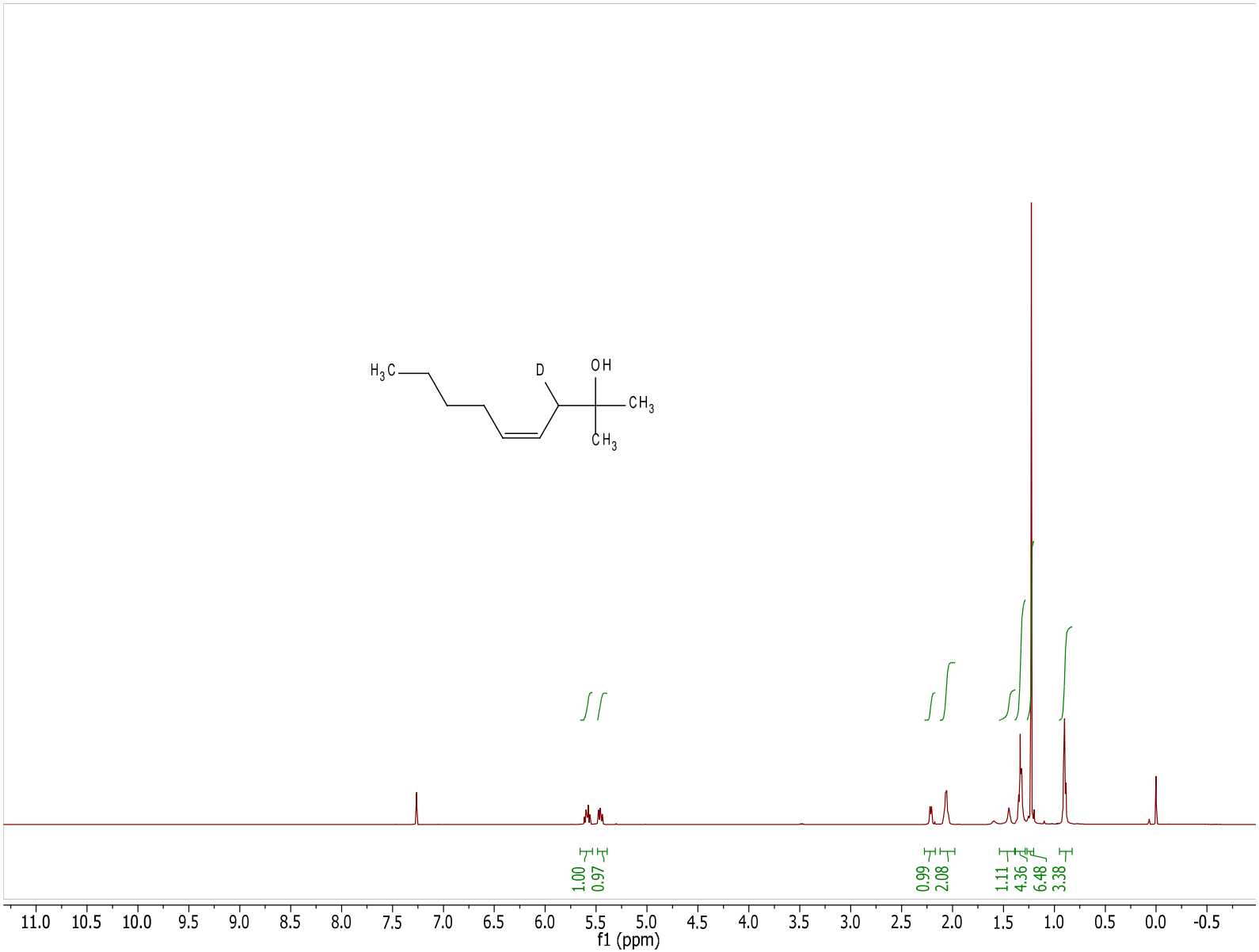
Compound 14-Db.



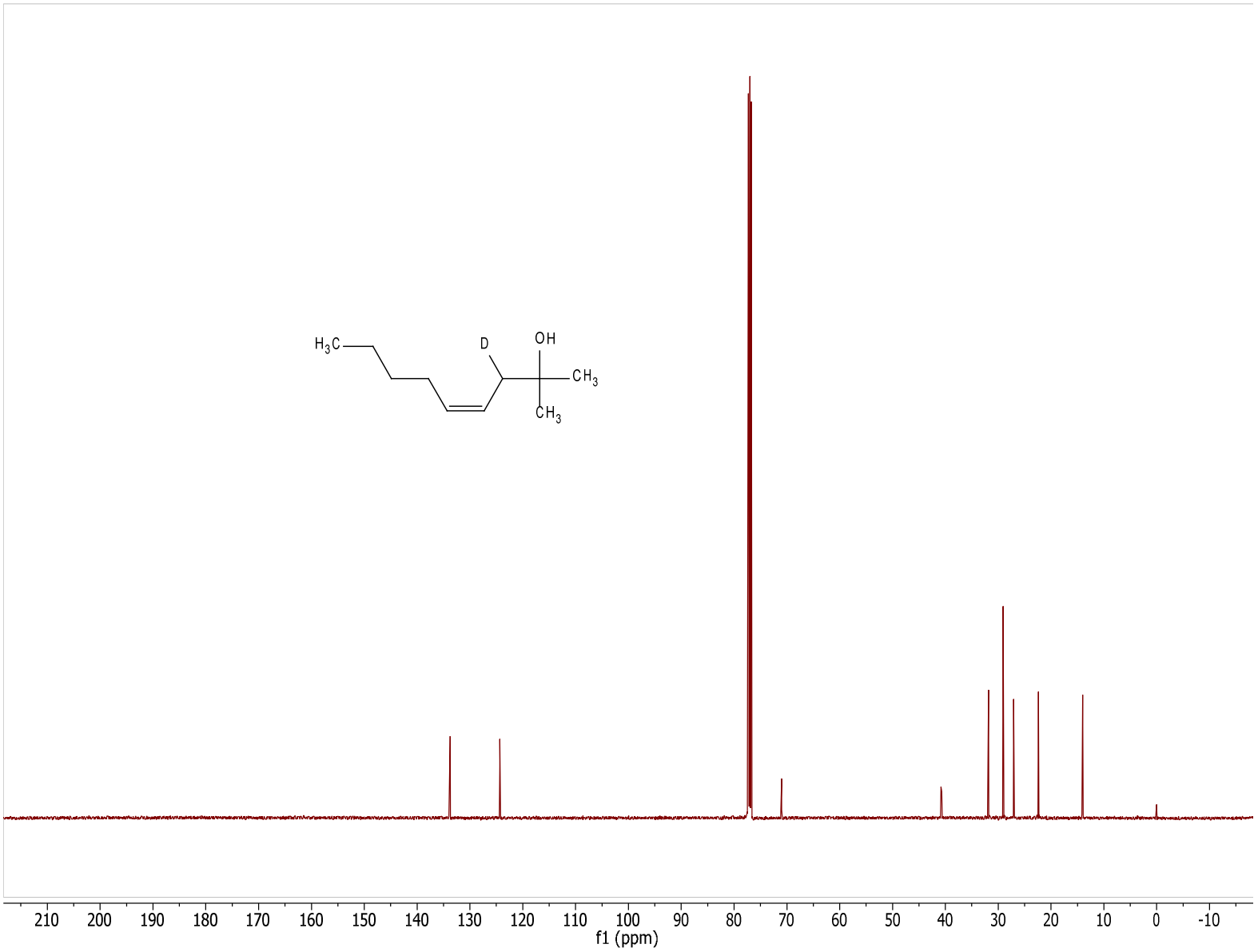
Compound 14-Db.



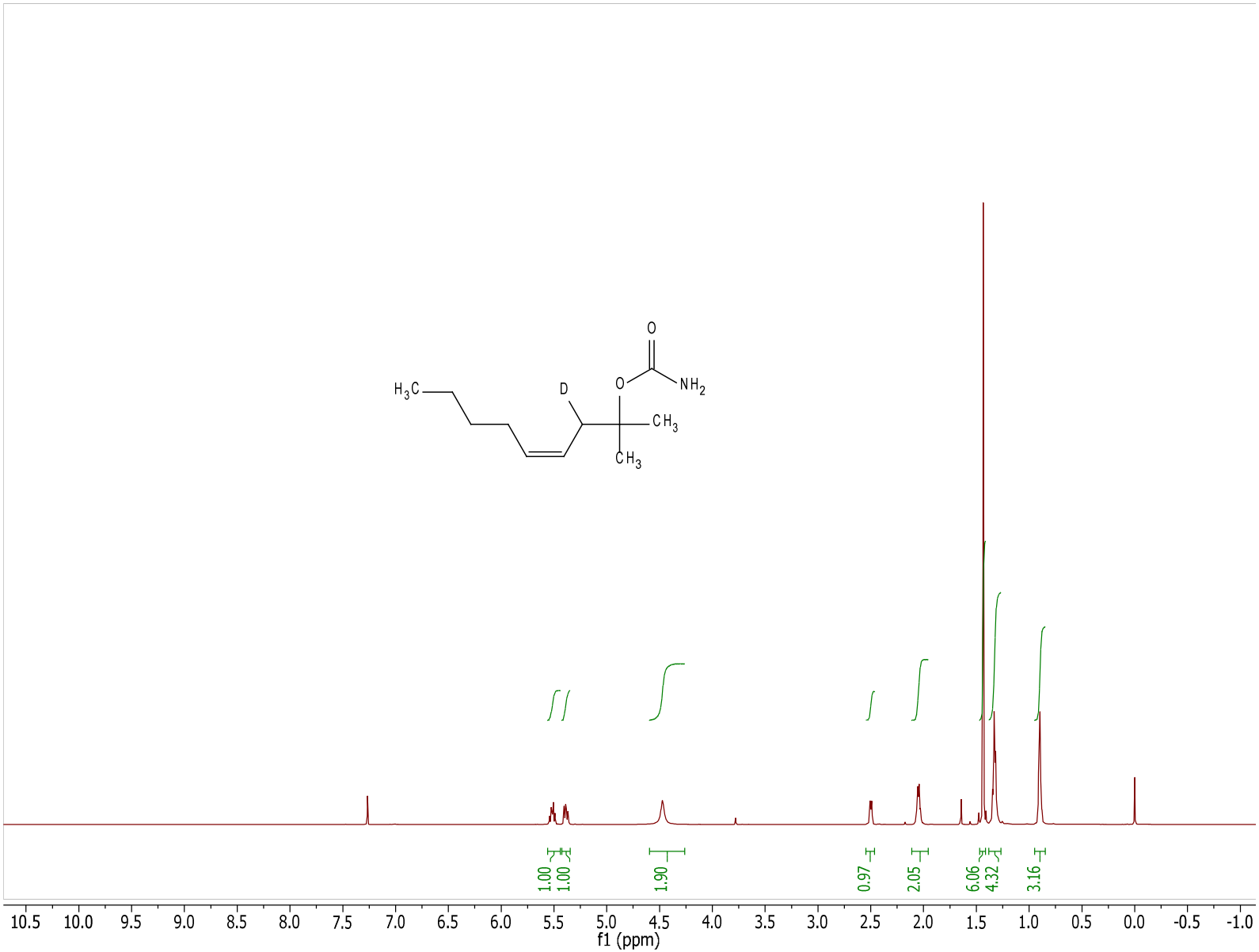
Compound 14-Dc.



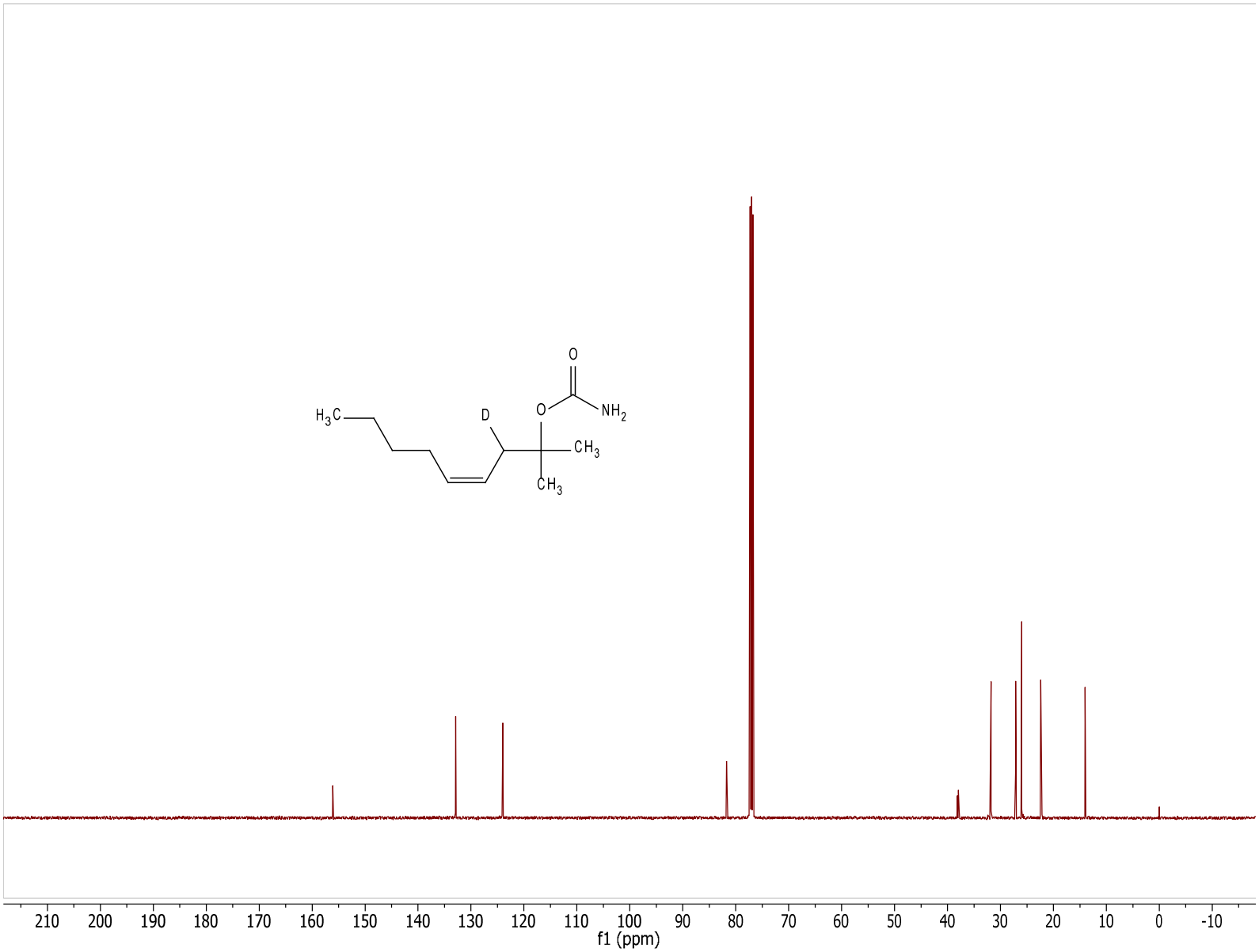
Compound 14-Dc.



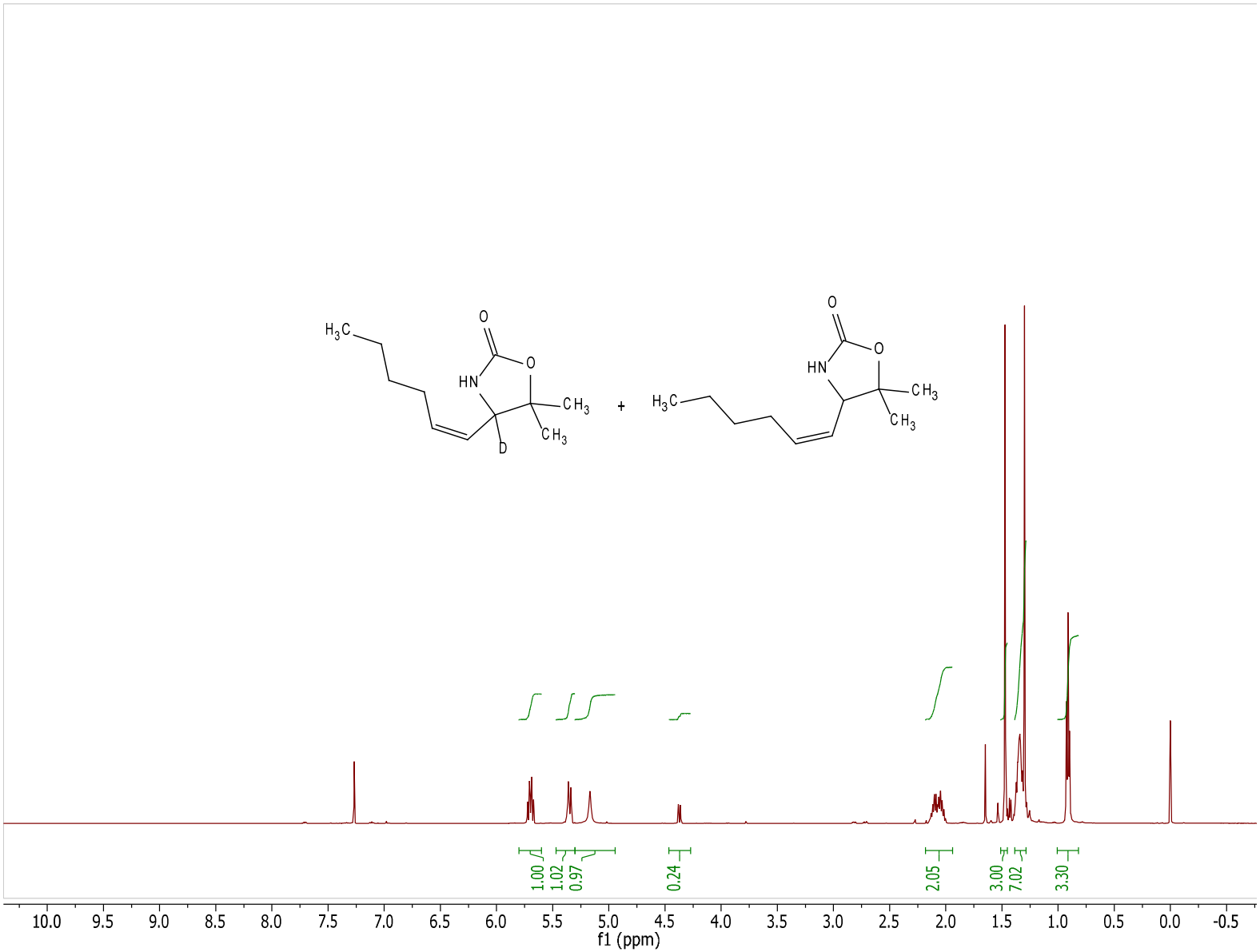
Compound 14-D.



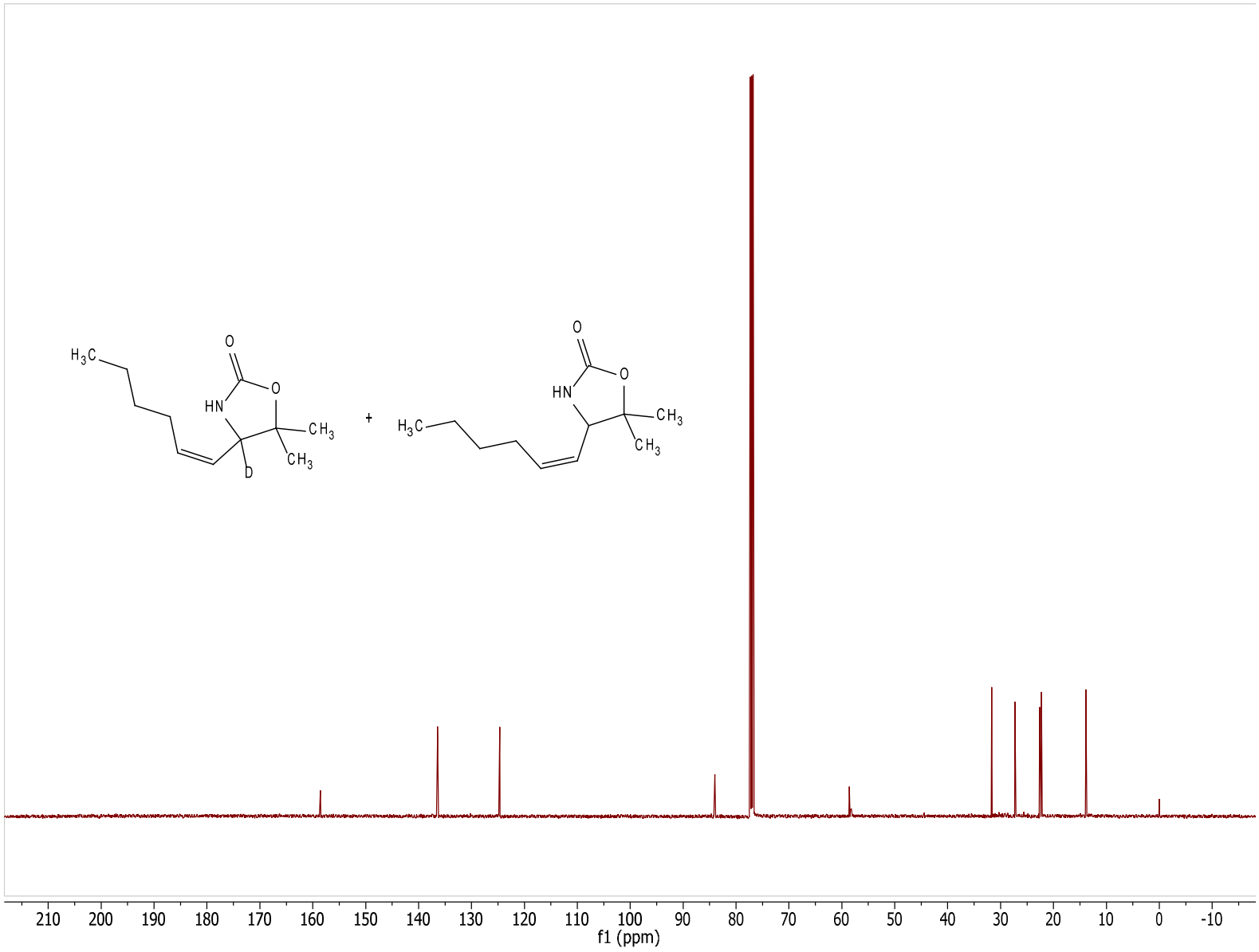
Compound 14-D.



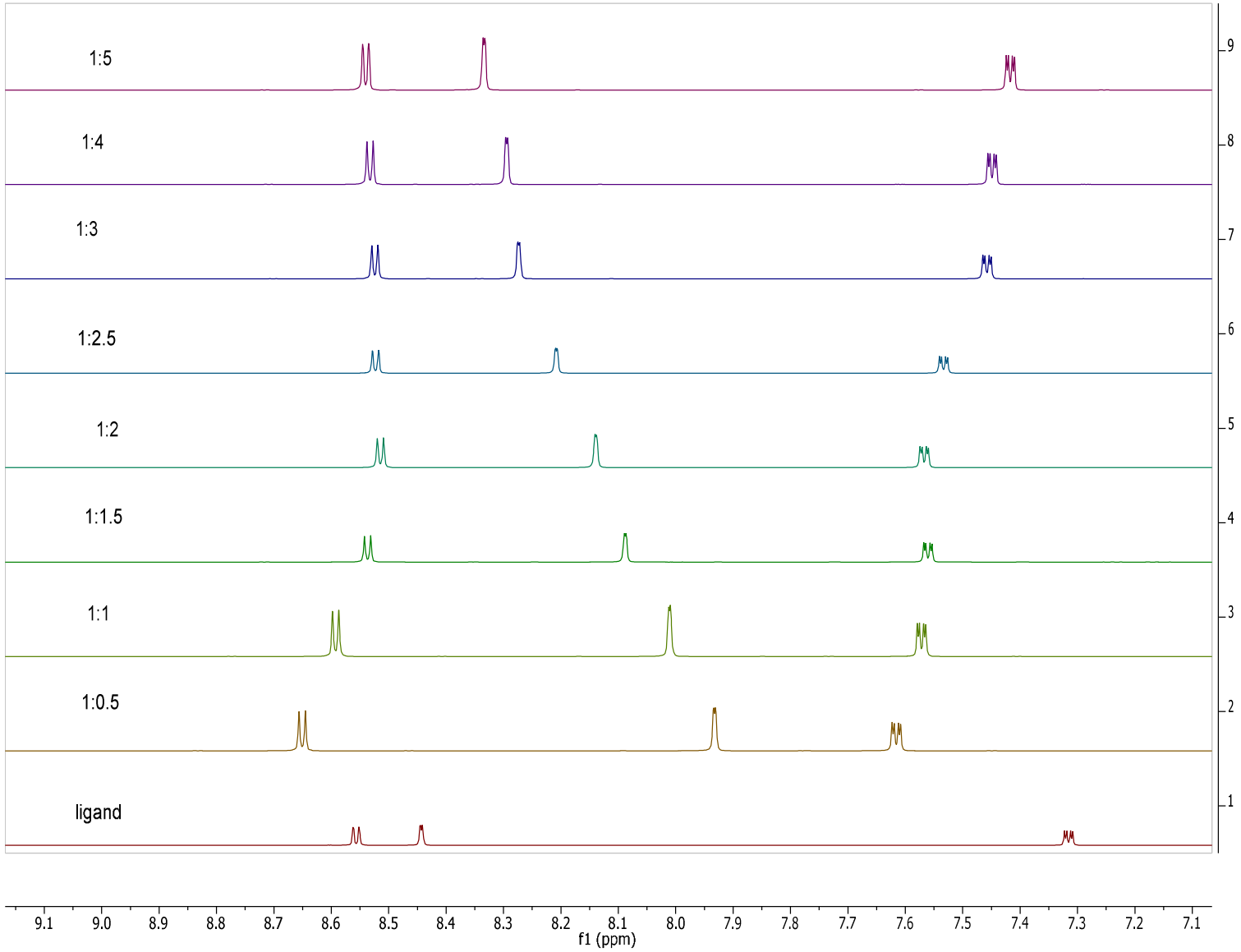
Compound 15-D and 15-H.



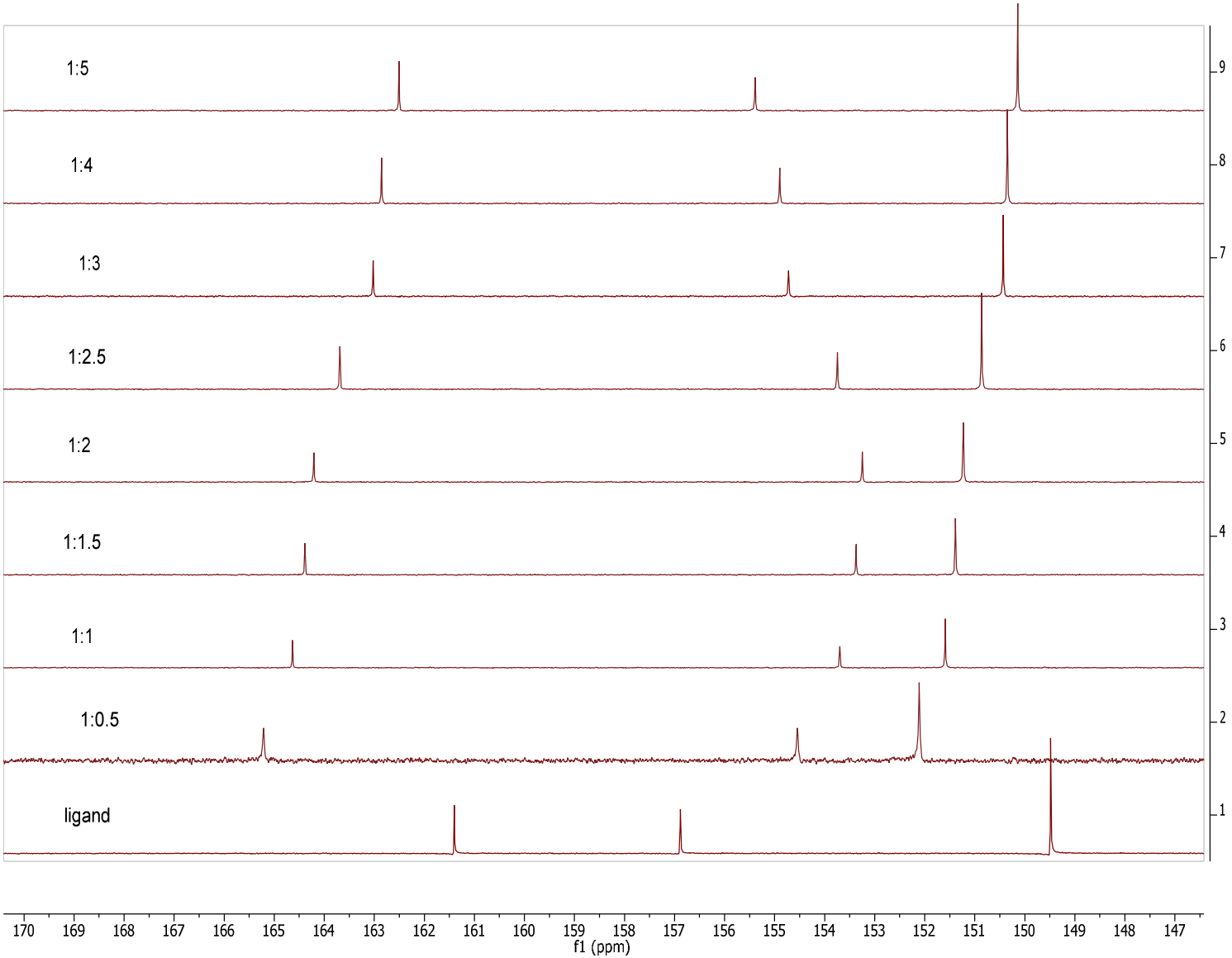
Compound 15-D and 15-H.



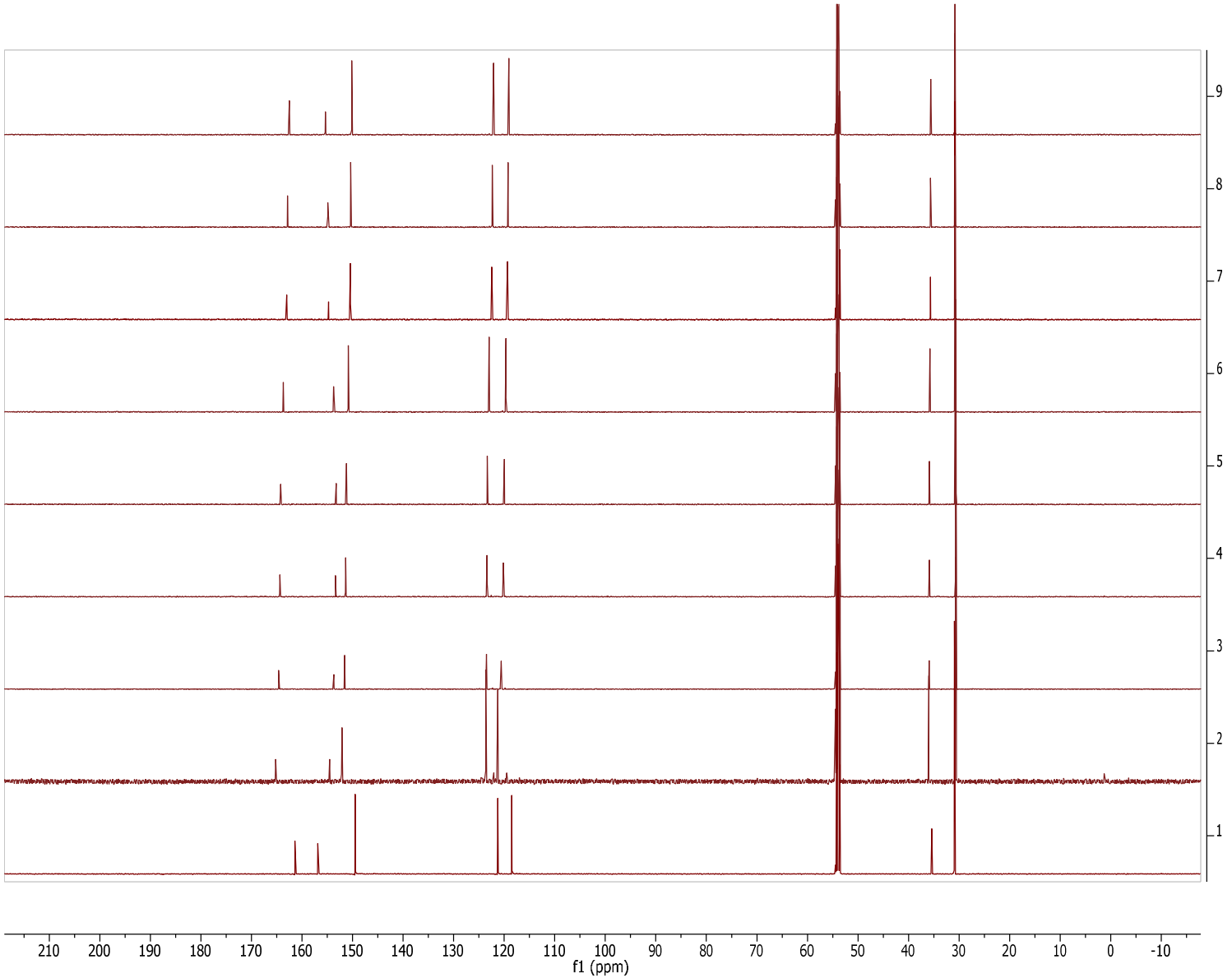
II. Proton NMR of AgOTf:Ligand Titration experiment.



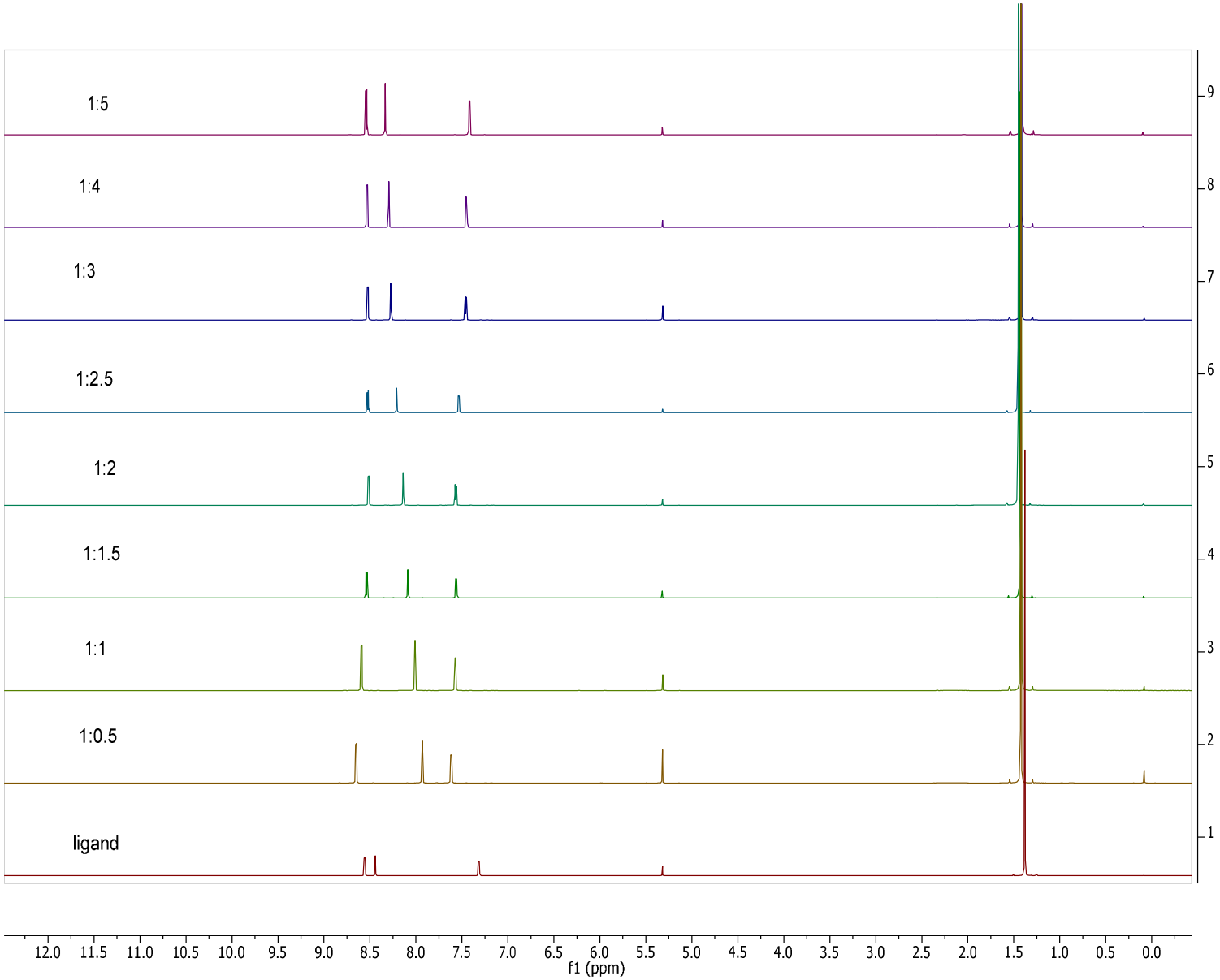
Carbon NMR of AgOTf:Ligand Titration experiment.



Proton NMR of AgOTf:Ligand Titration experiment.

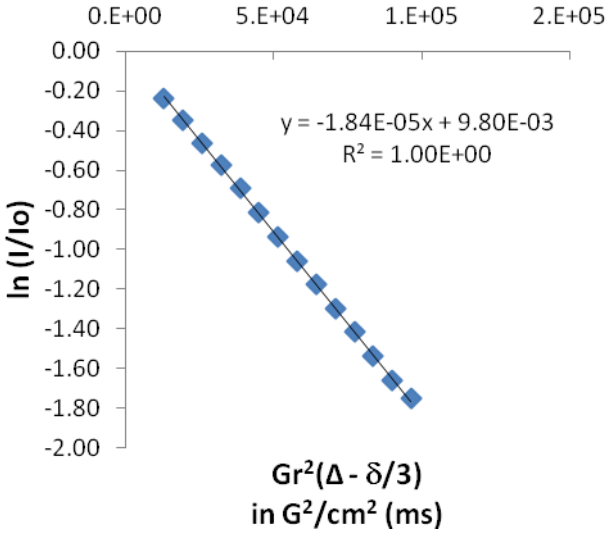


Carbon NMR of AgOTf:Ligand Titration experiment.



III. Pulse Gradient Spin Echo Diffusion Experiments.

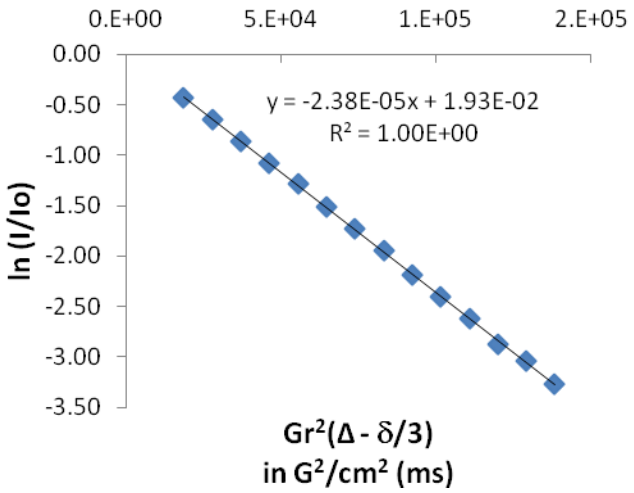
Ag samples were prepared by dissolving AgOTf (10 mg) with the desired ligand (1 or 2 equiv) in d_2-dichloromethane (2 mL). The 1:2 bathophen mixture required an additional 2 mL of solvent to prevent precipitation from occurring. Standard DOSY experiments were used to obtain the data on a 500 mhz NMR spectrometer. Diffusion coefficients were obtained using ICON NMR software.



Rh_2TPA_4 Δ = 46.73, δ = 2.00

Gradient Amplitude (Gr)	$Gr^2(\Delta - \delta/3)$	ln (I/Io)
16.73	12893.55	-0.24
20.48	19321.48	-0.35
23.64	25743.97	-0.46
26.42	32154.82	-0.58
28.94	38581.36	-0.69
31.26	45015.12	-0.81
33.41	51420.16	-0.93
35.44	57858.60	-1.06
37.35	64263.11	-1.17
39.17	70678.55	-1.30
40.92	77135.05	-1.41
42.58	83520.26	-1.54
44.19	89955.66	-1.66
45.74	96376.87	-1.75

	Average	Standard Deviation
Diffusion Coefficient =	6.50E-10	1.05E-11

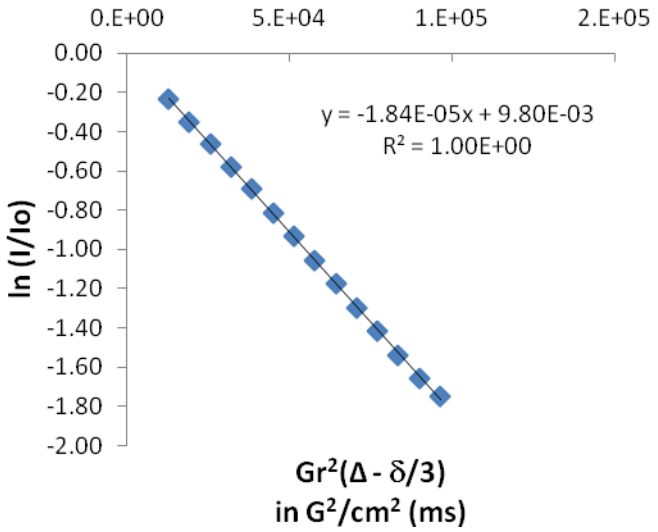


Δ = 66.73

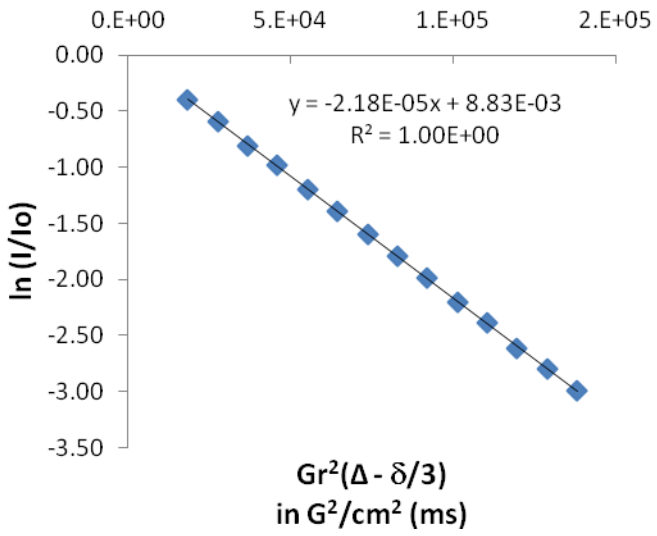
Rh_2esp_2 δ = 2.00

Gradient Amplitude (Gr)	$Gr^2(\Delta - \delta/3)$	ln (I/Io)
16.73	18491.40	-0.43
20.48	27710.09	-0.65
23.64	36920.96	-0.86
26.42	46115.15	-1.08
28.94	55331.83	-1.29
31.26	64558.88	-1.51
33.41	73744.73	-1.73
35.44	82978.47	-1.95
37.35	92163.56	-2.19
39.17	101364.33	-2.41
40.92	110623.98	-2.62
42.58	119781.38	-2.87
44.19	129010.78	-3.04
45.74	138219.82	-3.27

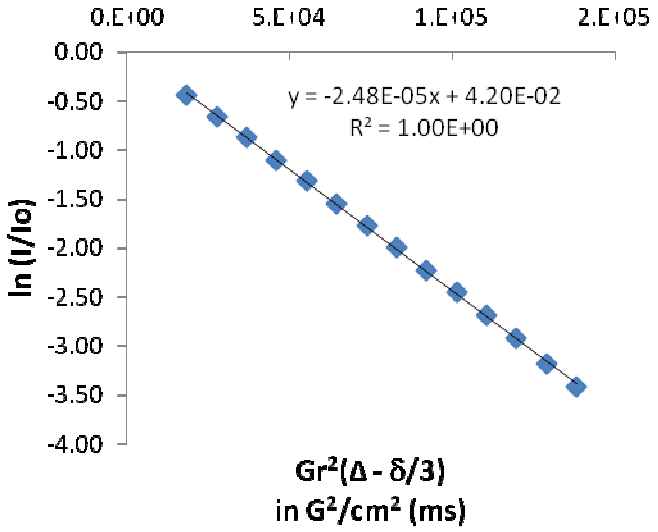
Diffusion Coefficient =	Average 8.04E-10	Standard Deviation 1.00E-11



Ag:^{t}Bubpy 1:1 Gradient	Δ = 66.73 δ = 2.00	
		ln (I/Io)
Amplitude (Gr)	$Gr^2(\Delta - \delta/3)$	
16.73	18491.40	-0.44
20.48	27710.09	-0.68
23.64	36920.96	-0.89
26.42	46115.15	-1.13
28.94	55331.83	-1.35
31.26	64558.88	-1.57
33.41	73744.73	-1.81
35.44	82978.47	-2.01
37.35	92163.56	-2.27
39.17	101364.33	-2.47
40.92	110623.98	-2.71
42.58	119781.38	-2.95
44.19	129010.78	-3.16
45.74	138219.82	-3.40
Diffusion	Average	Stdev
Coefficient =	8.55E-10	1.59E-11



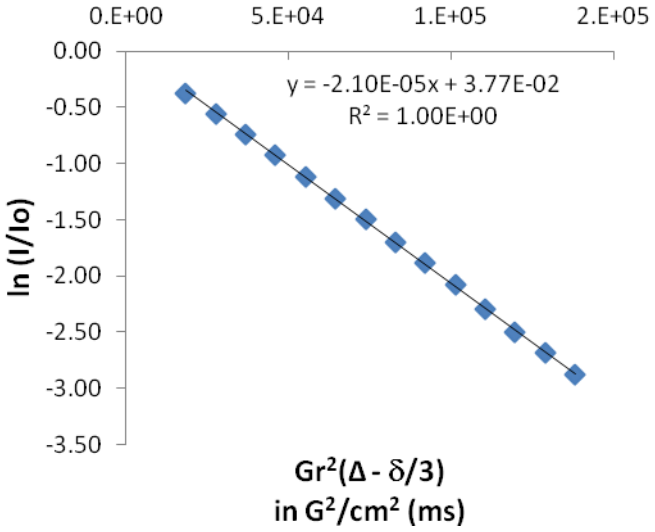
	Δ = 66.73	
Ag:tBubpy 1:2	d = 2.00	
Gradient		
Amplitude (Gr)	Gr2(Δ - d/3)	ln (I/Io)
16.73	18491.40	-0.40
20.48	27710.09	-0.59
23.64	36920.96	-0.81
26.42	46115.15	-0.98
28.94	55331.83	-1.20
31.26	64558.88	-1.39
33.41	73744.73	-1.59
35.44	82978.47	-1.79
37.35	92163.56	-1.98
39.17	101364.33	-2.21
40.92	110623.98	-2.39
42.58	119781.38	-2.62
44.19	129010.78	-2.80
45.74	138219.82	-2.99
Diffusion	Average	Stdev
Coefficient =	7.59E-10	7.74E-12



Δ = 66.73

Ag:bathoPhen 1:1 δ = 2.00

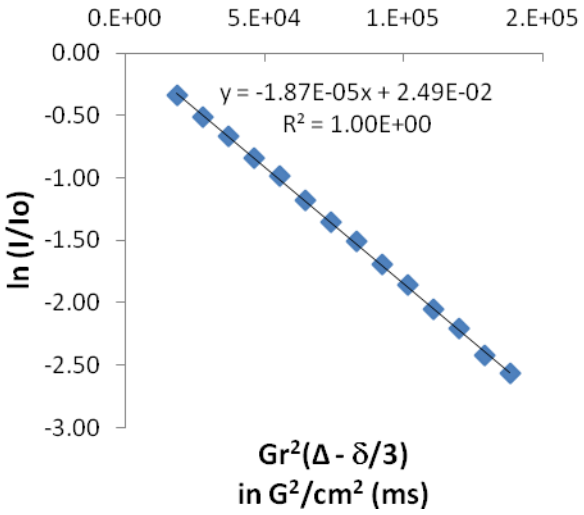
Gradient Amplitude (Gr)	$Gr^2(\Delta - \delta/3)$	ln (I/Io)
16.73	18491.40	-0.44
20.48	27710.09	-0.66
23.64	36920.96	-0.88
26.42	46115.15	-1.11
28.94	55331.83	-1.32
31.26	64558.88	-1.55
33.41	73744.73	-1.77
35.44	82978.47	-2.00
37.35	92163.56	-2.23
39.17	101364.33	-2.46
40.92	110623.98	-2.69
42.58	119781.38	-2.93
44.19	129010.78	-3.19
45.74	138219.82	-3.42
Diffusion	Average	Stdev
Coefficient =	8.14E-10	1.85E-11



Δ = 66.73

Ag:bathoPhen 1:2 δ = 2.00

Gradient Amplitude (Gr)	$Gr^2(\Delta - \delta/3)$	ln (I/Io)
16.73	18491.40	-0.38
20.48	27710.09	-0.56
23.64	36920.96	-0.75
26.42	46115.15	-0.92
28.94	55331.83	-1.12
31.26	64558.88	-1.31
33.41	73744.73	-1.49
35.44	82978.47	-1.70
37.35	92163.56	-1.88
39.17	101364.33	-2.08
40.92	110623.98	-2.29
42.58	119781.38	-2.51
44.19	129010.78	-2.69
45.74	138219.82	-2.88
Diffusion	Average	Stdev
Coefficient =	6.88E-10	1.38E-11

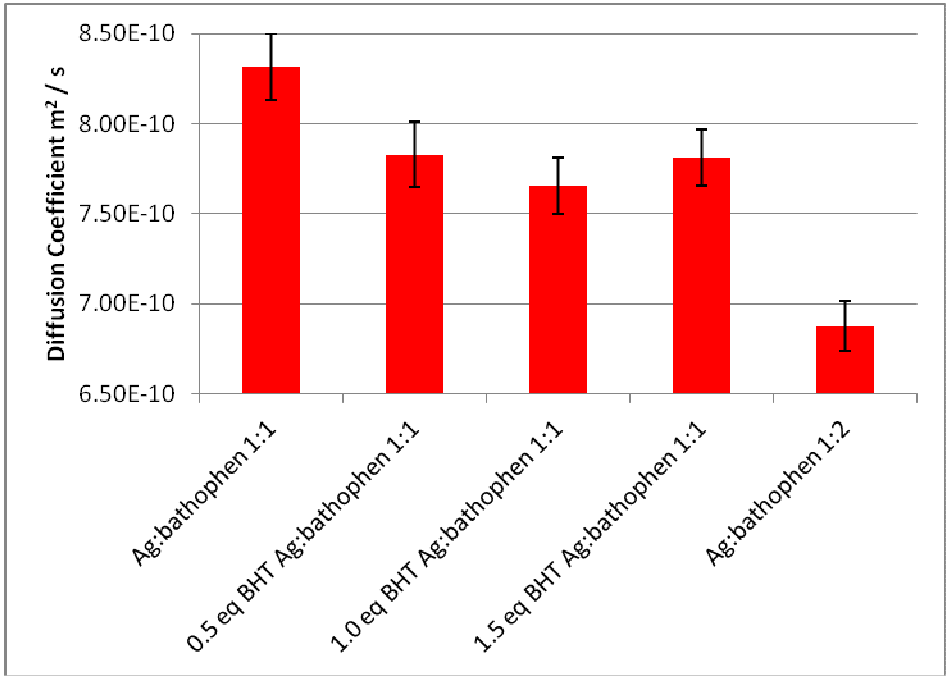


Ag:^{t}Buterpy 1:1 Δ = 66.73

δ = 2.00

Gradient Amplitude (Gr)	$Gr^2(\Delta - \delta/3)$	ln (I/Io)
16.73	18491.40	-0.34
20.48	27710.09	-0.51
23.64	36920.96	-0.66
26.42	46115.15	-0.84
28.94	55331.83	-0.99
31.26	64558.88	-1.18
33.41	73744.73	-1.35
35.44	82978.47	-1.51
37.35	92163.56	-1.69
39.17	101364.33	-1.85
40.92	110623.98	-2.05
42.58	119781.38	-2.20
44.19	129010.78	-2.42
45.74	138219.82	-2.56
Diffusion Coefficient =	Average 6.30E-10	Stdev 5.60E-12

Summary of Pulsed Gradient Spin Echo NMR experiments using BHT as an additive.



PGSE NMR experiments were carried out on mixtures of the indicated amounts of BHT with 1:1 ratios of AgOTf:bathophenanthroline in deuterated dichloromethane. The addition of 0.5 equiv of BHT relative to the catalyst did perturb the equilibrium from mainly AgphenOTf (the 1:1 complex that is formed when no BHT is present) to other species in solution, accounting for the decreased amount of aziridination in the reaction when BHT is added to the reaction. Increasing the amount of BHT further did not perturb this equilibrium to any great extent. The PGSE data also showed that the BHT did not complex directly to either AgOTf or AgphenOTf and appeared to act only to perturb the equilibrium of the AgphenOTf/Ag(phen)$_2$OTf mixture. The fast ligand exchange resulted in an averaged diffusion coefficient between AgphenOTf and Ag(phen)$_2$OTf.