Direct functionalization of (un)protected tetrahydroisoquinolines and isochroman under iron and copper catalysis – two metals, two mechanisms

Michael Ghobrial, Marko D. Mihovilovic and Michael Schnürch*

Institute of Applied Synthetic Chemistry, Vienna University of Technology, Getreidemarkt 9/163-OC, 1060 Vienna, Austria

*E-mail: mschnuerch@ioc.tuwien.ac.at

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1. General

Unless otherwise noted, chemicals were purchased from commercial suppliers and used without further purification. Flash column chromatography was performed on silica gel (40-63µm). For thin layer chromatography (TLC) aluminum coated silica gel was used and signals were visualized with UV light (254nm).

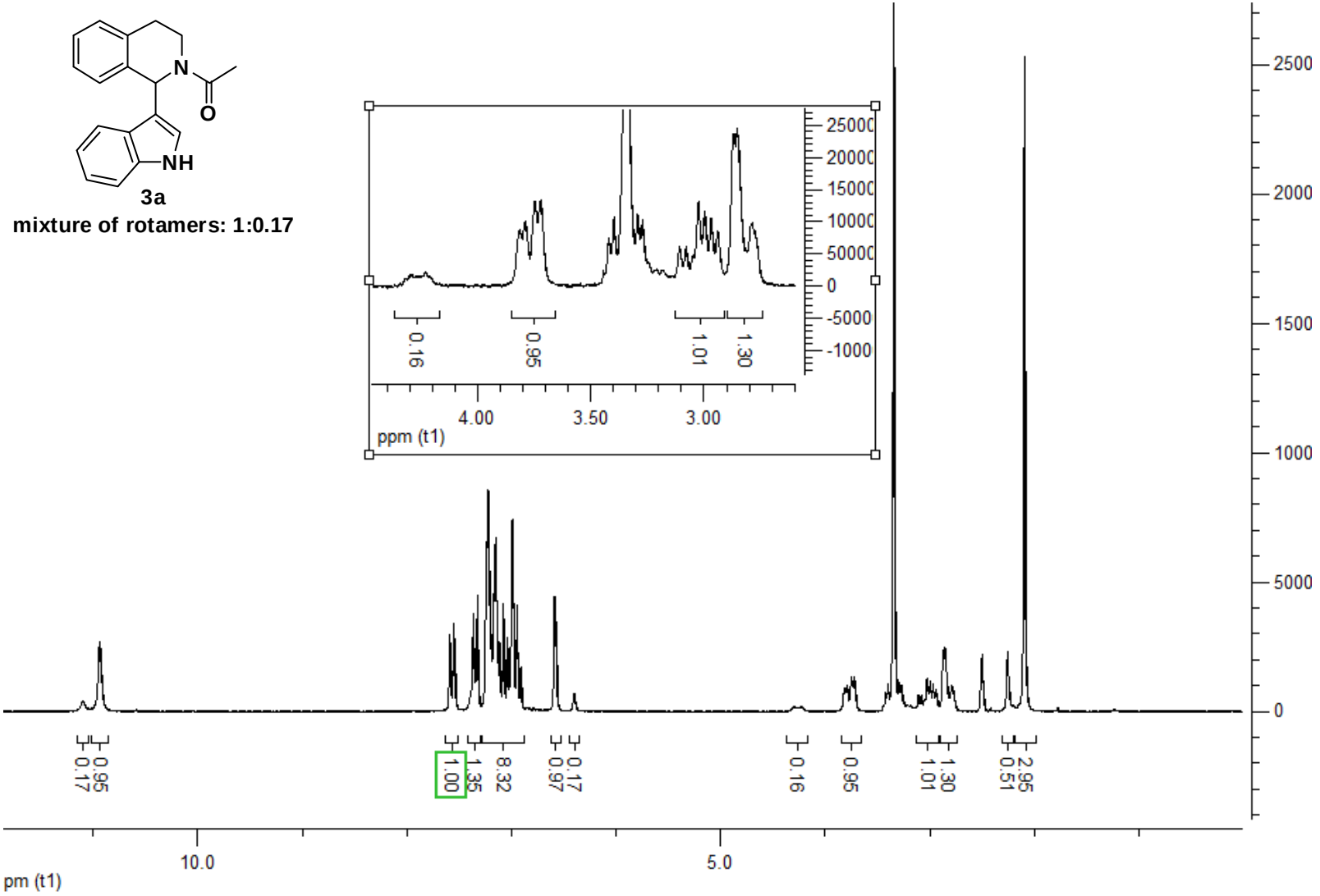
1.1. Caution

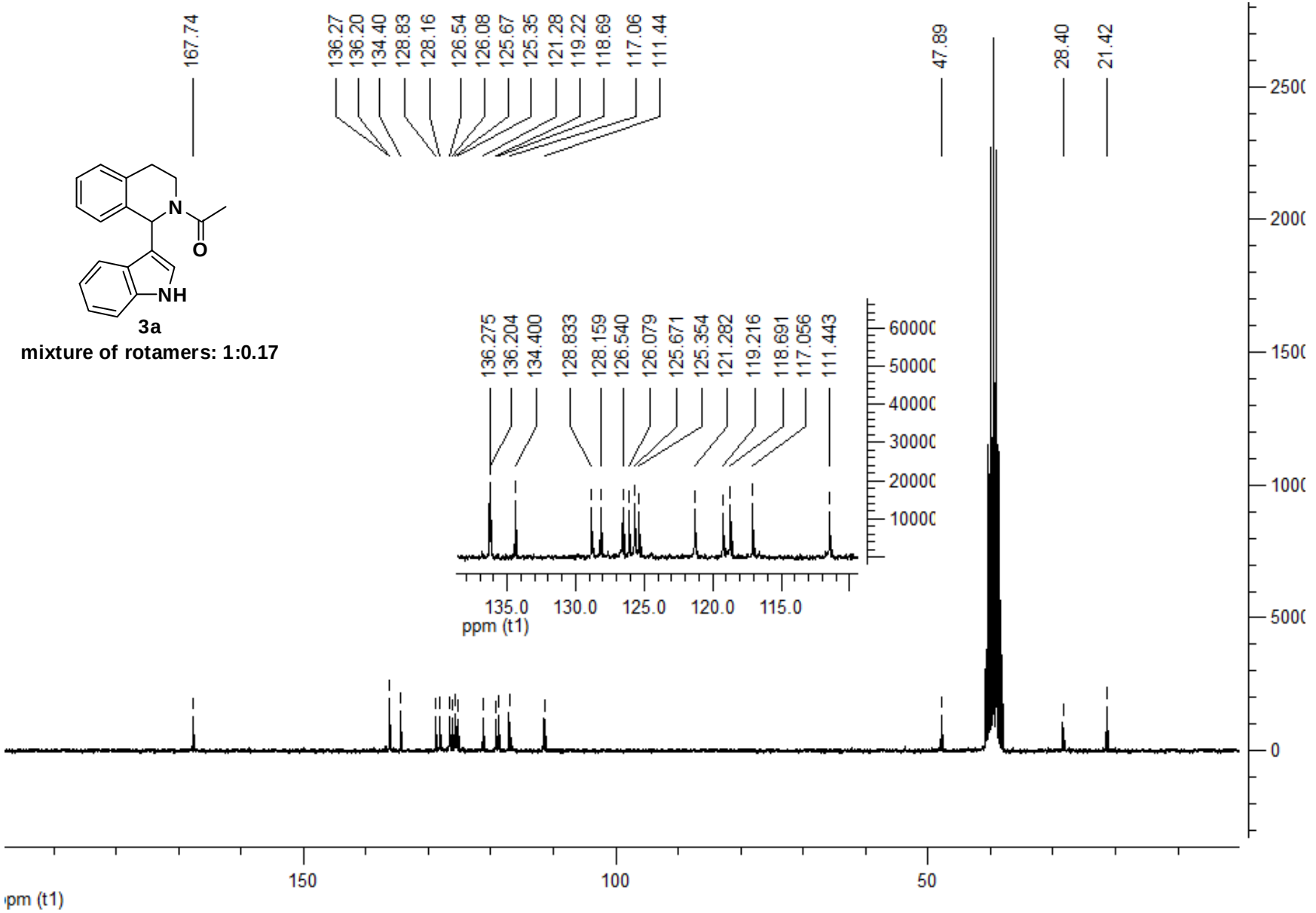
Mixing a metal salt and peroxide can cause explosion. See: Jones, A. K.; Wilson, T. E.; Nikam, S. S. In Encyclopedia of Reagents for Organic Synthesis, Paquette, L. A. Ed.; John Wiley & Sons, Inc. 1995, 2, 880.

1.2. Instrumentation

GC-MS runs were performed using a standard capillary column (30m x 0.32 mm ID), applying the following standardized temperature profile: 2 minutes at 80°C, 10°C/min until 280°C, 15 minutes at 280°C. All samples subjected to HR-MS were analyzed by LC-IT-TOF-MS in only positive ion detection mode upon recording of MS and MS/MS spectra. For the evaluation in the following, only positive ionization spectra were used (where the quasi-molecular ion is the one of [M+H]+), and further data or information were not taken into consideration. Microwave reactions were performed on a BIOTAGE InitiatorTM sixty microwave unit. Melting points were determined using a Kofler-type hot stage microscope and are uncorrected. ^{1}H-NMR and ^{13}C-NMR spectra were recorded either on 200 MHz or 400 MHz spectrometer. Chemical shifts are reported as ppm downfield from TMS (tetramethylsilane) as internal standard with multiplicity, number of protons, allocation, and coupling constant(s) in Hertz.

2. Copies of ^{1}H and ^{13}C-NMR spectra of compounds 3a-3s, 5h-5t, 8a-8d, 10a-10f, and 11a-11d

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117.06
111.44
47.89
28.40
21.42
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O
NH
3a
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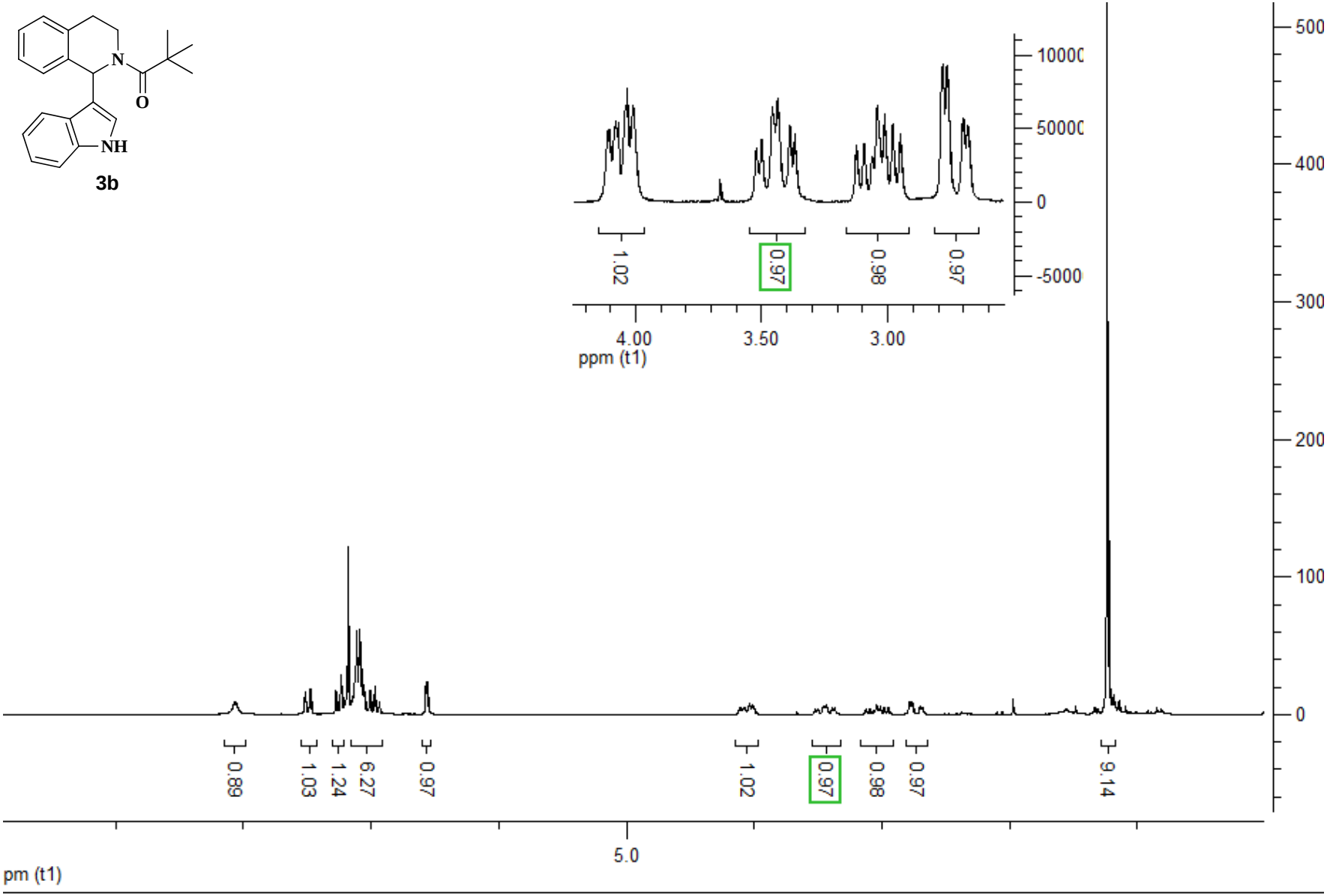
ppm (t1)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400
300
200
100
0
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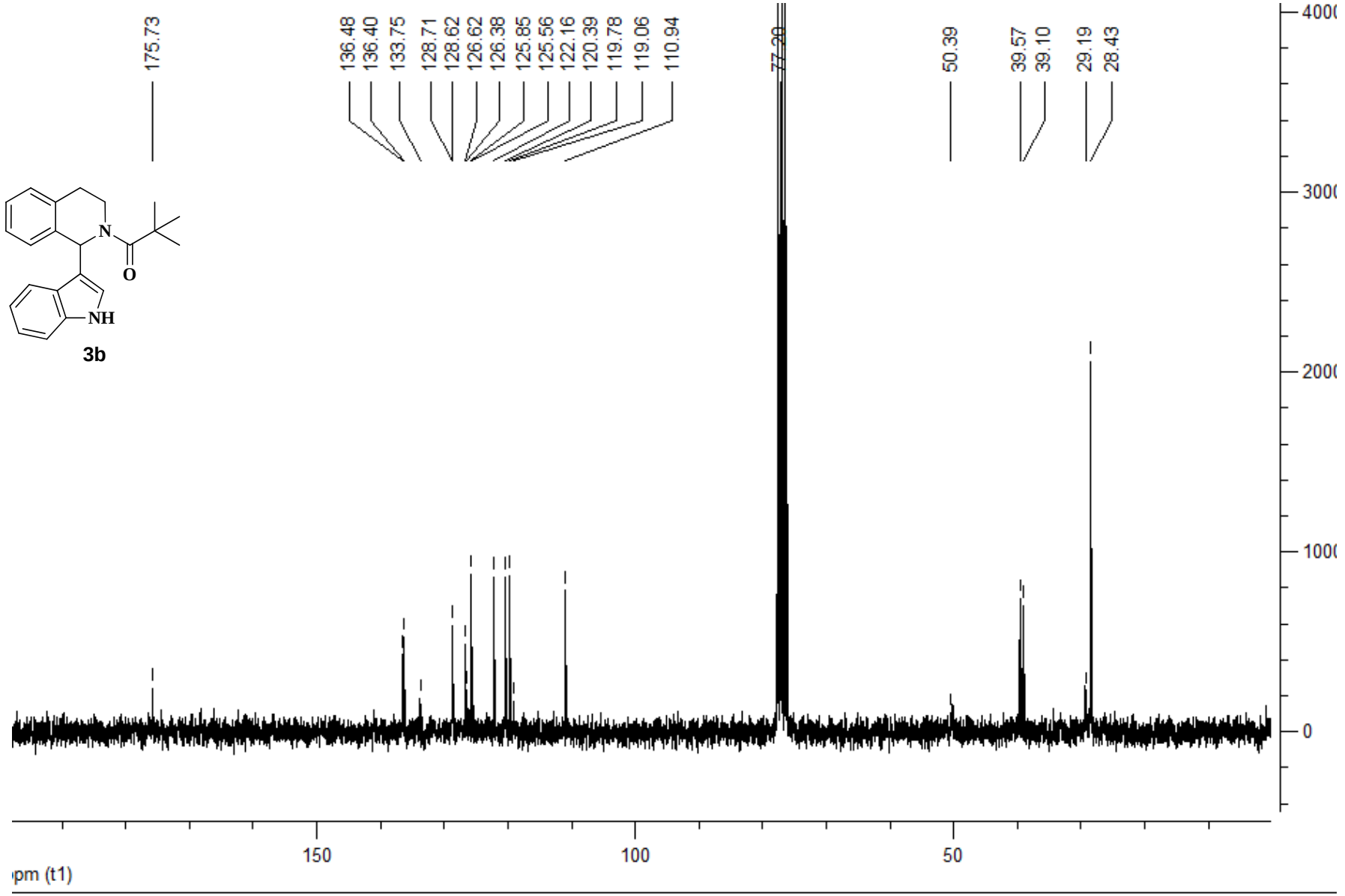
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110.94
77.20
50.39
39.57
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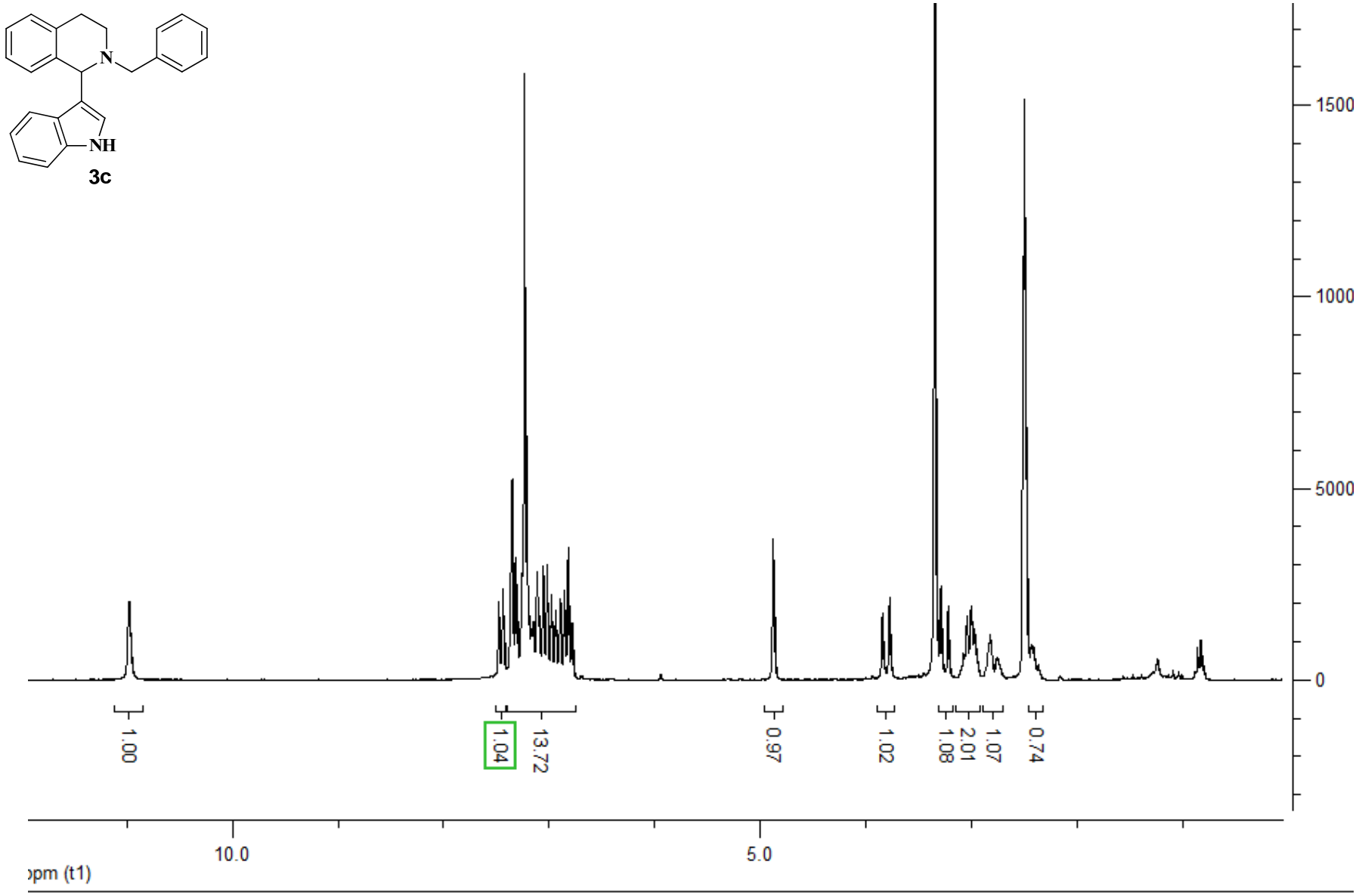
ppm (t1)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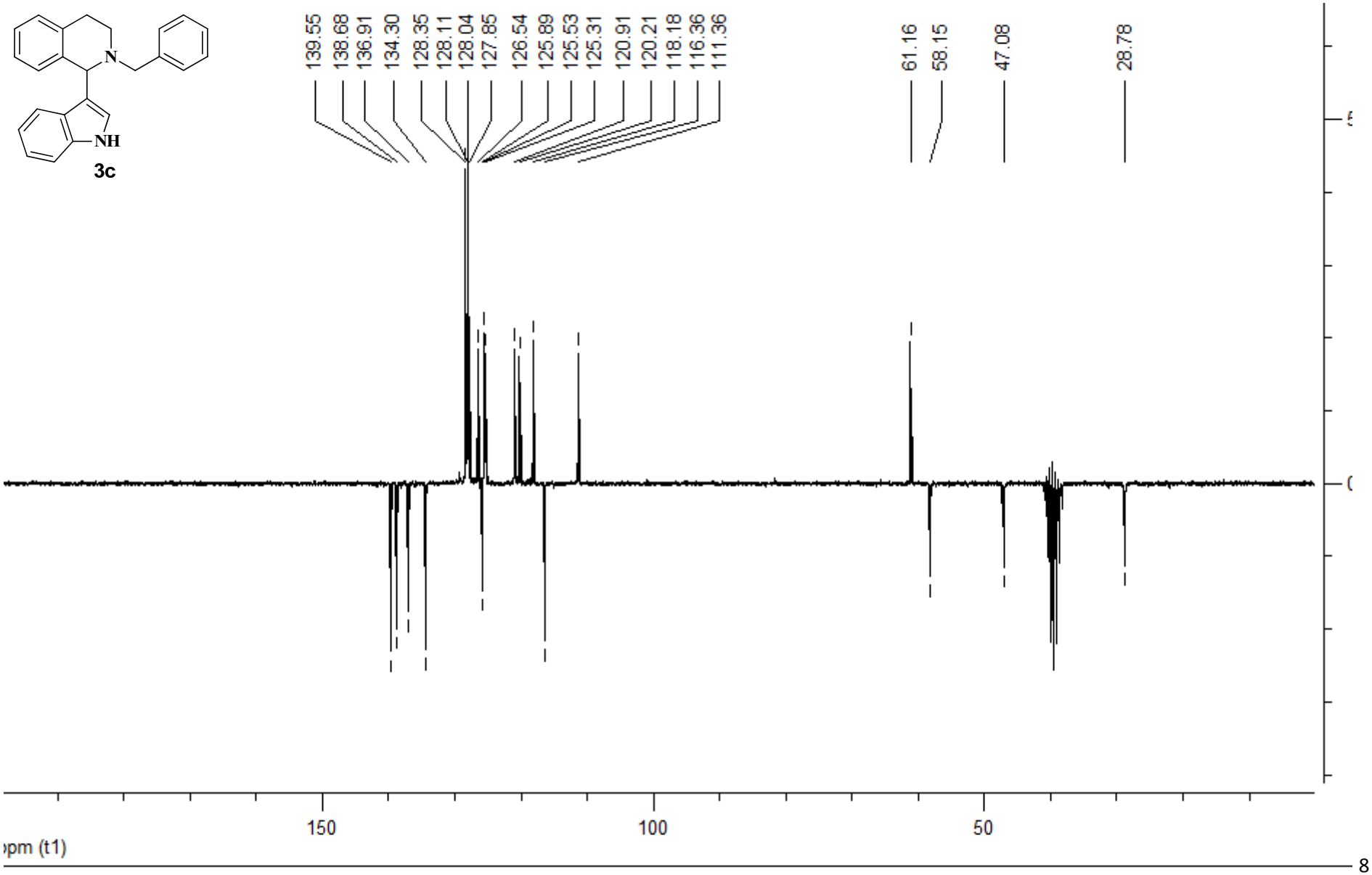
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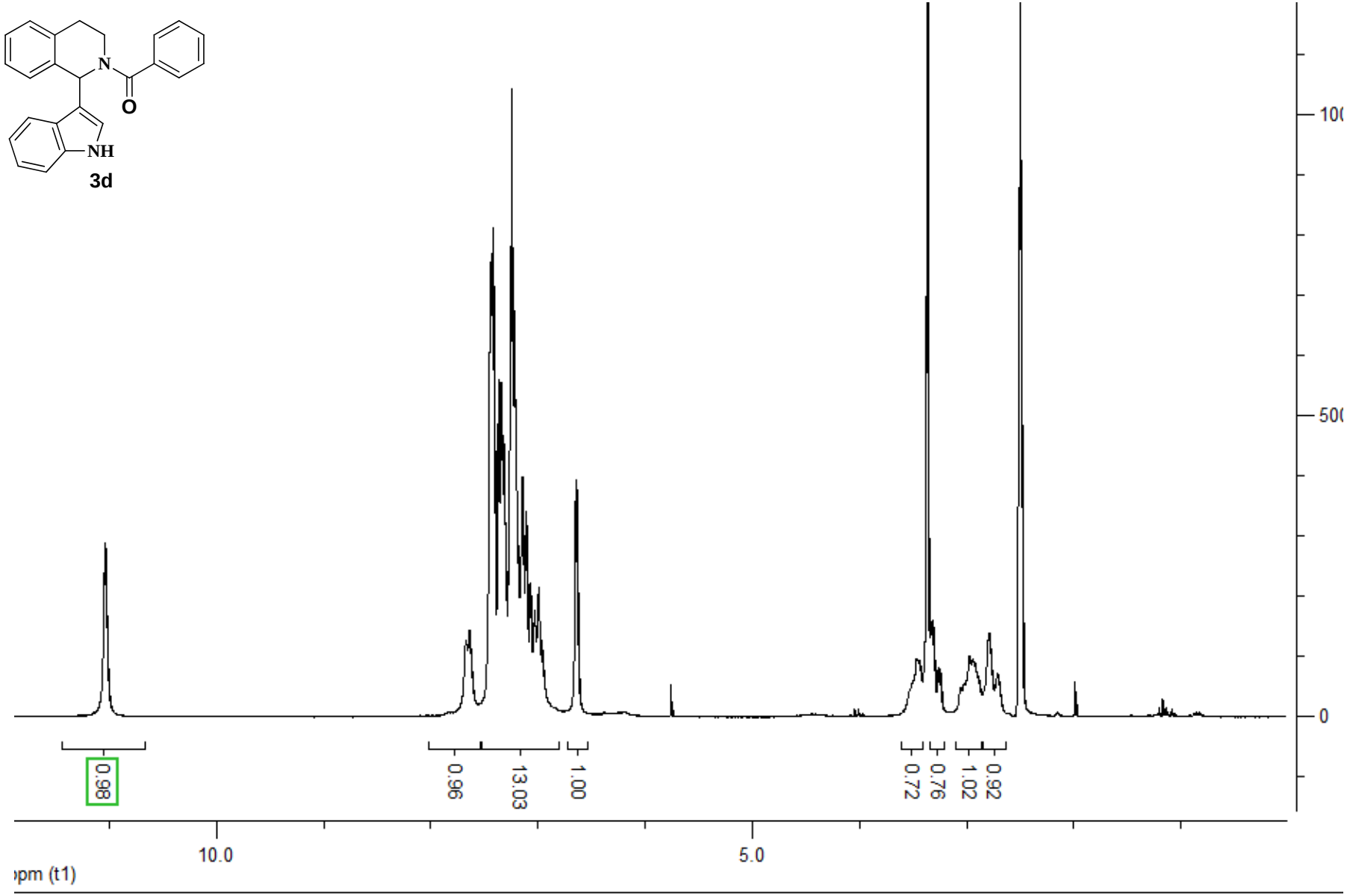
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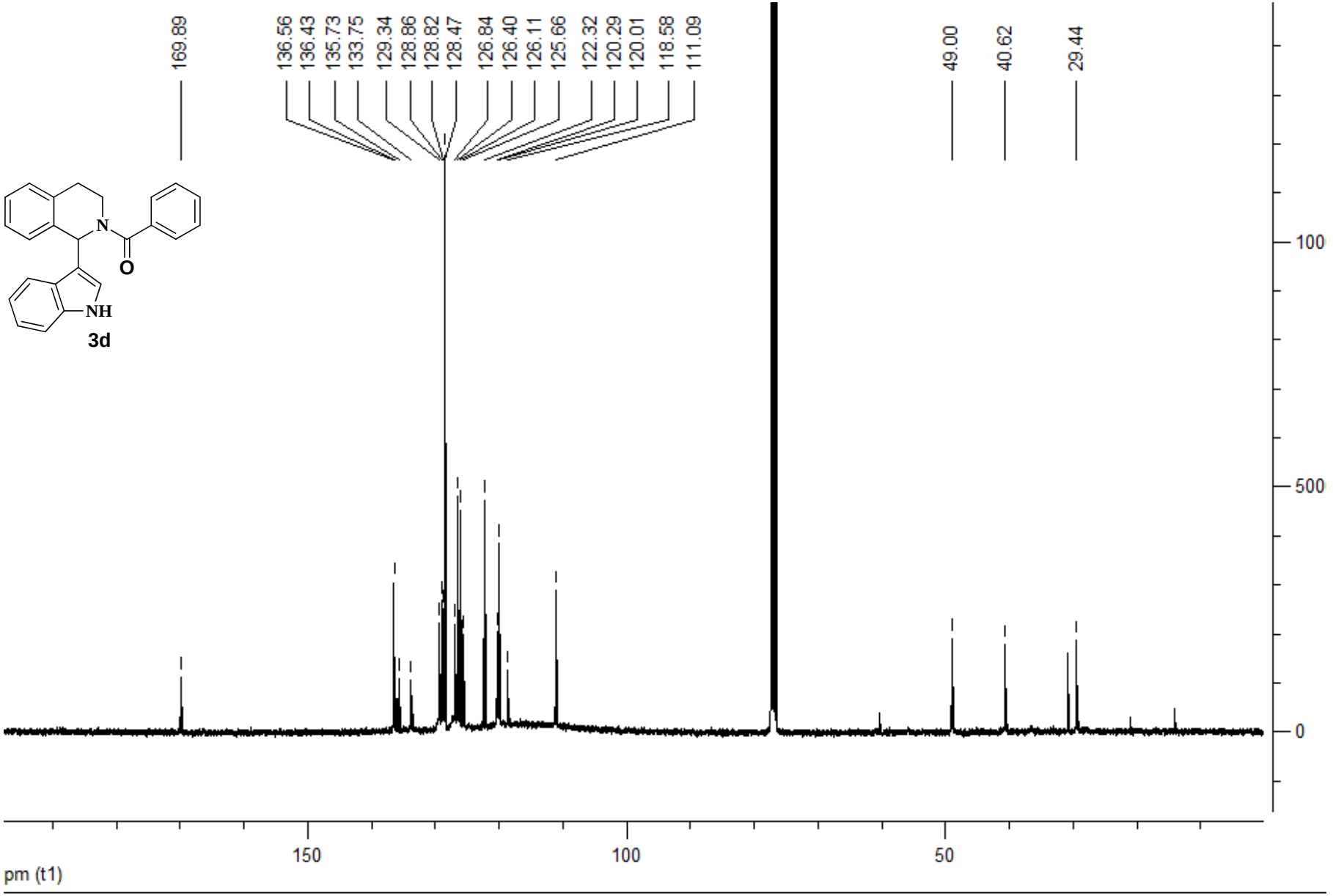
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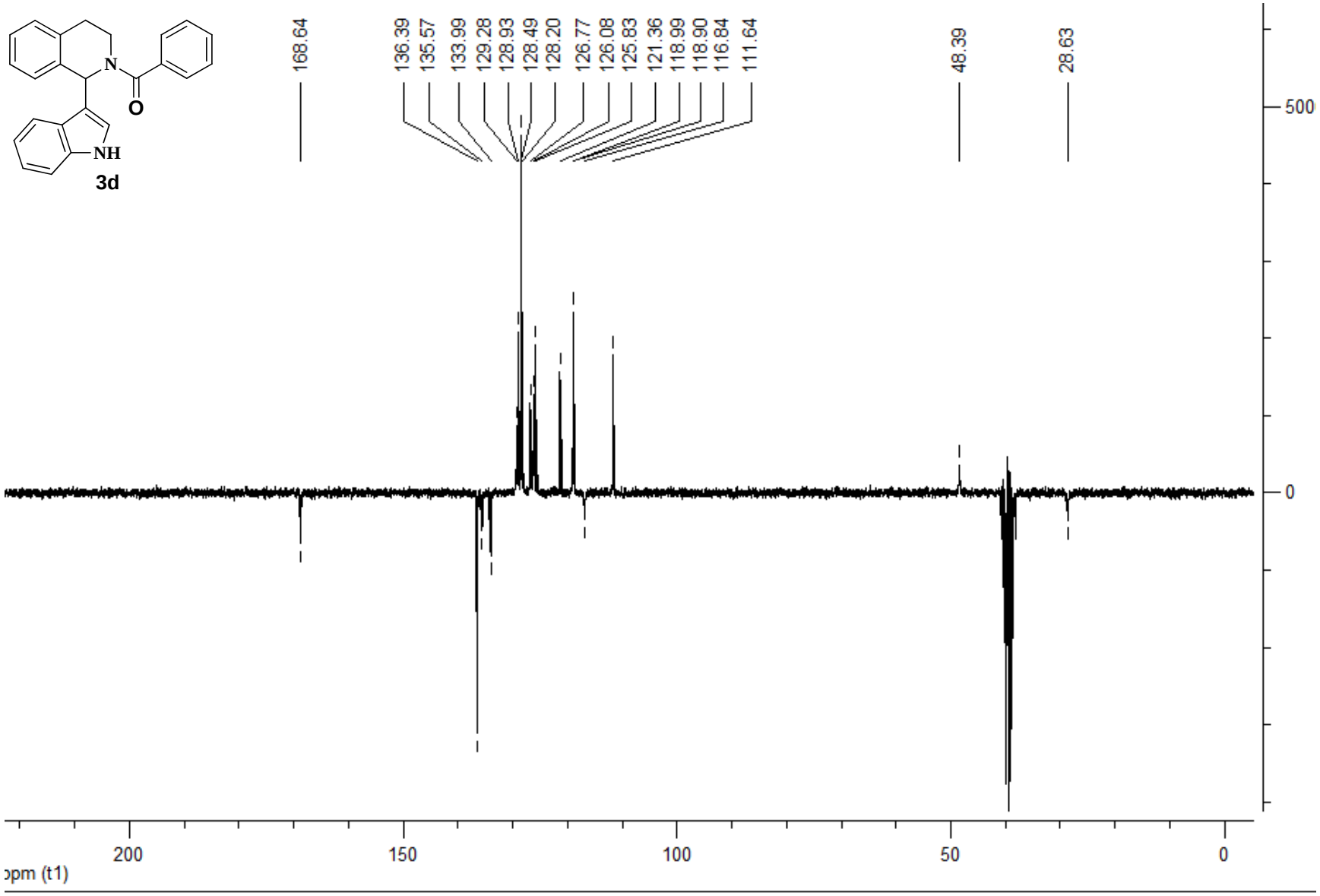
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200
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50
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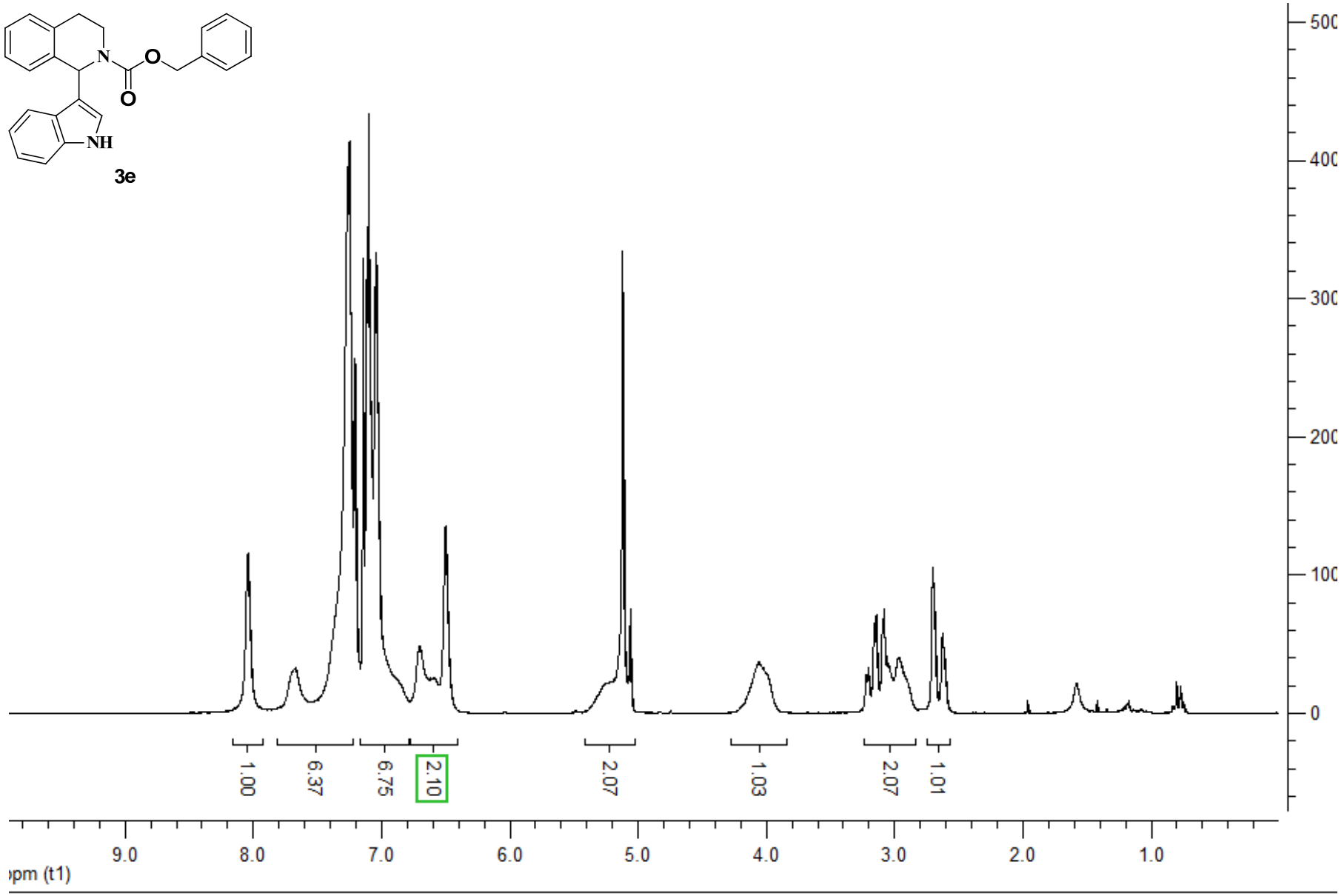
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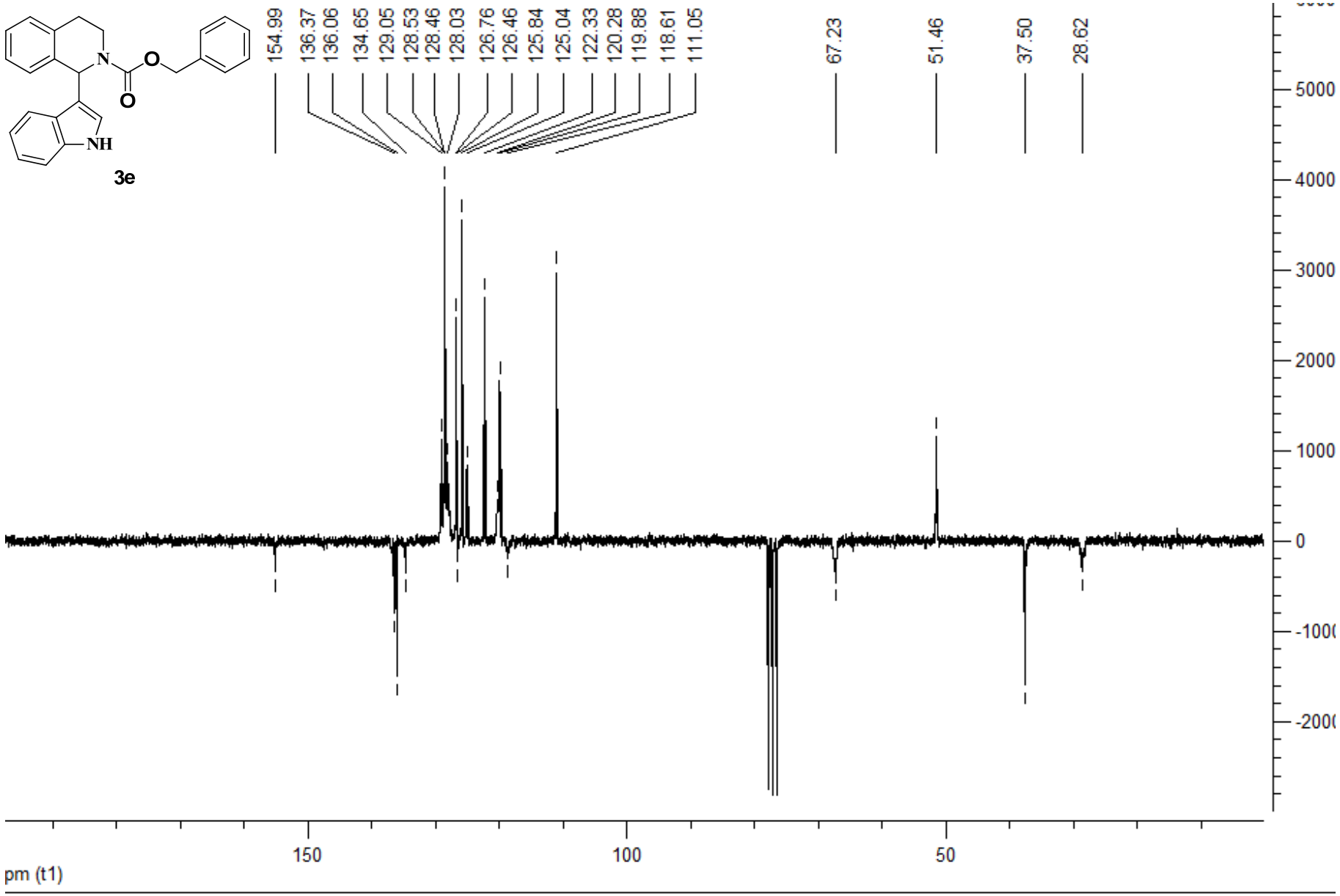
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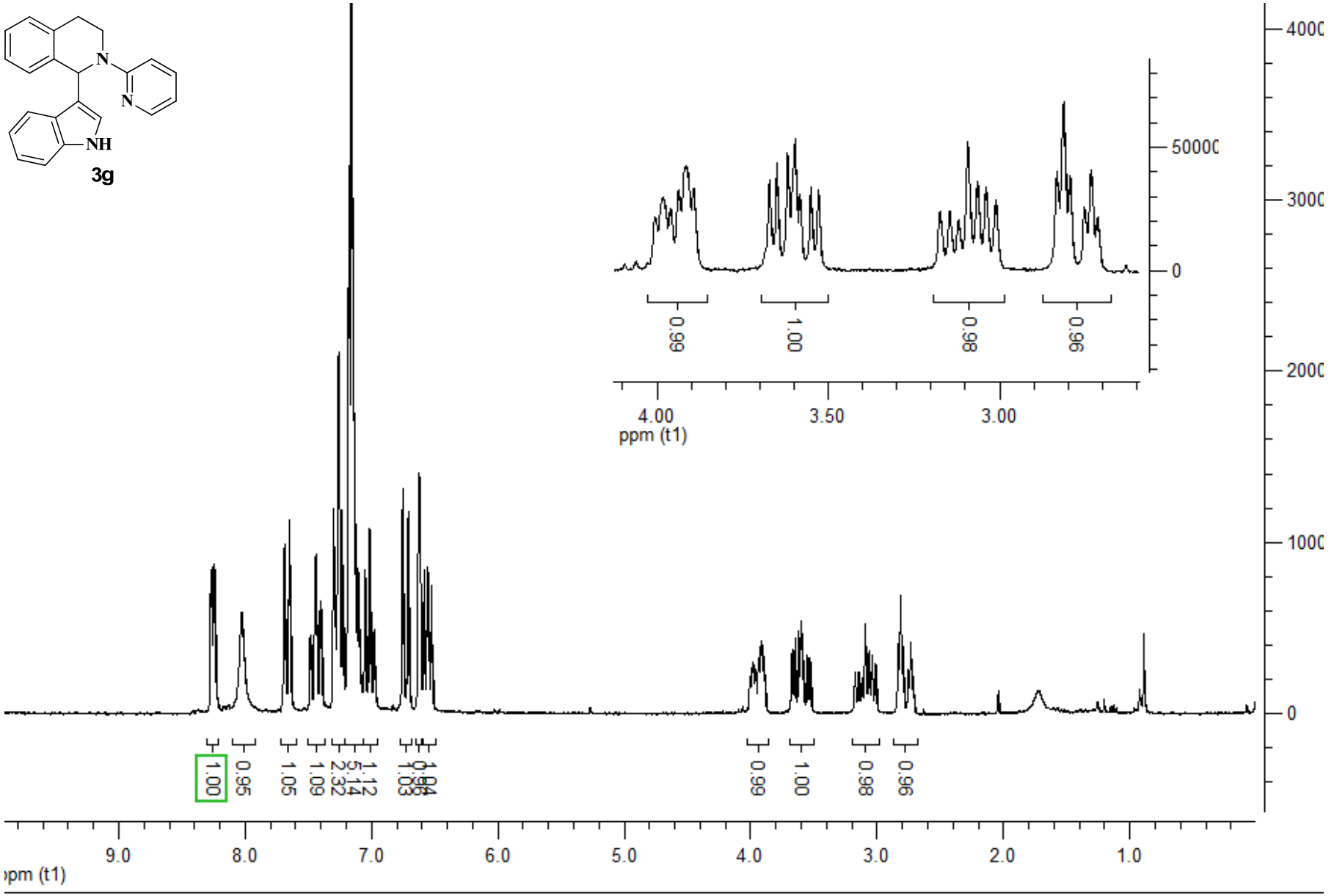
pm (t1)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3.00
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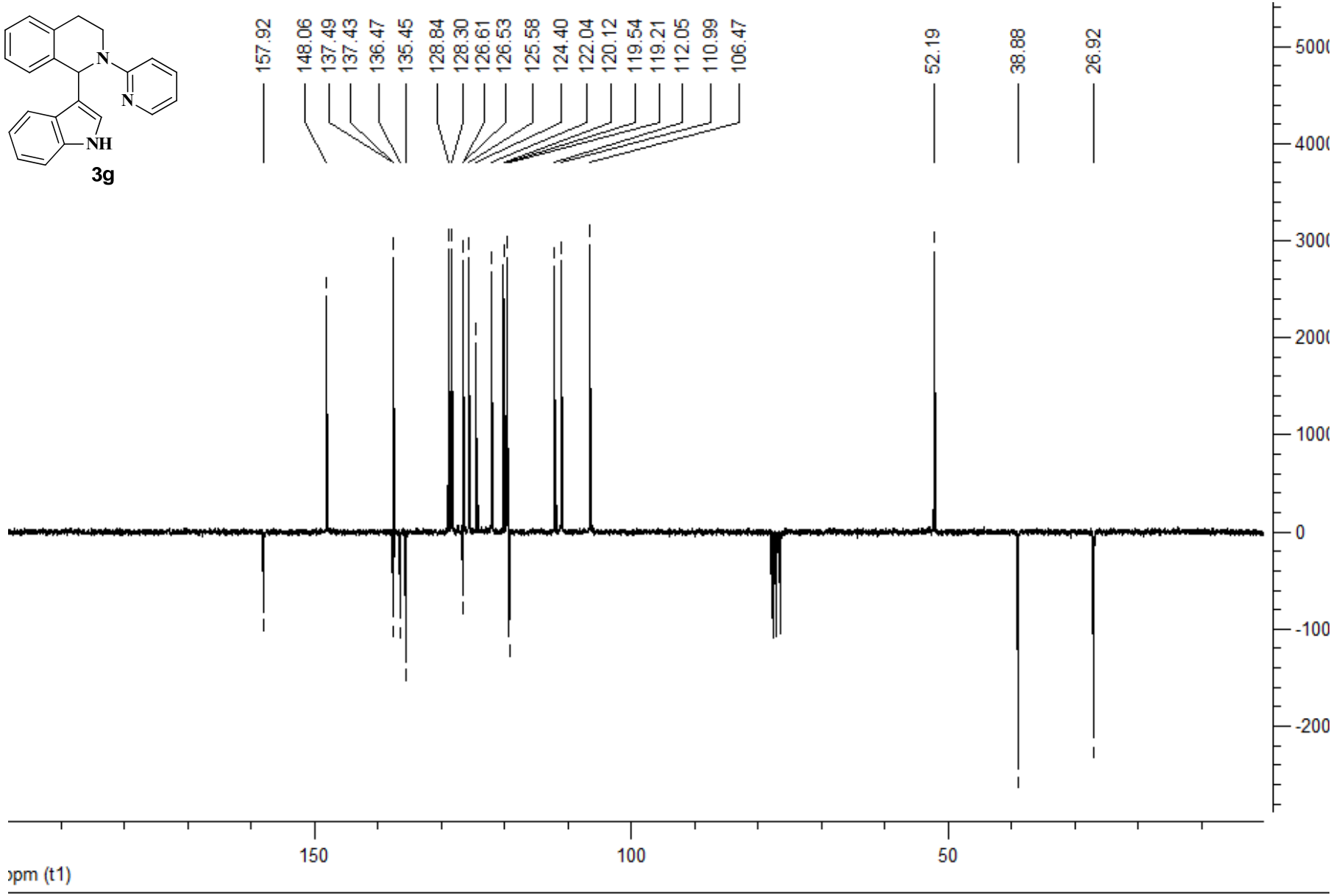
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119.54
119.21
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N
NH
3g
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50
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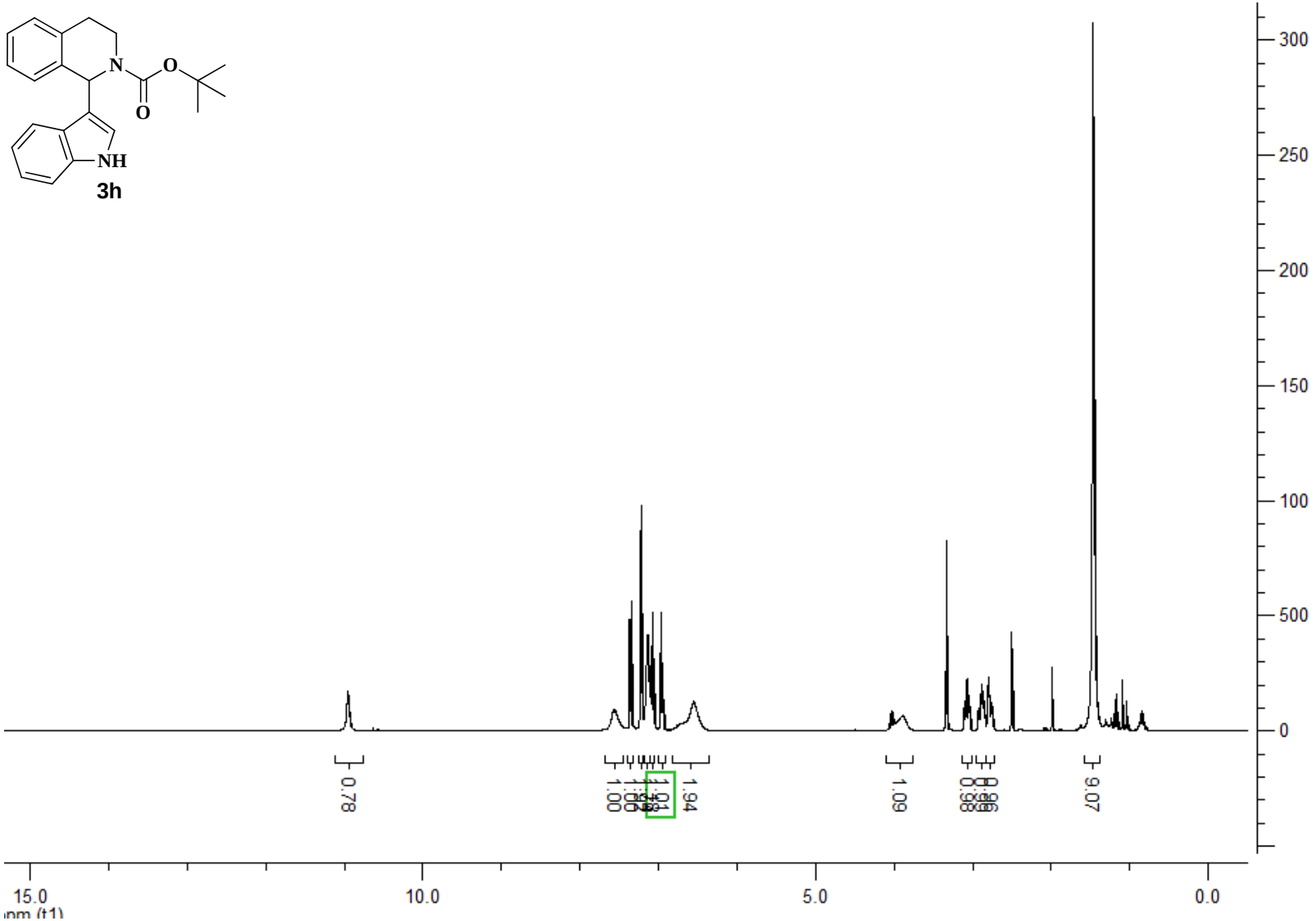
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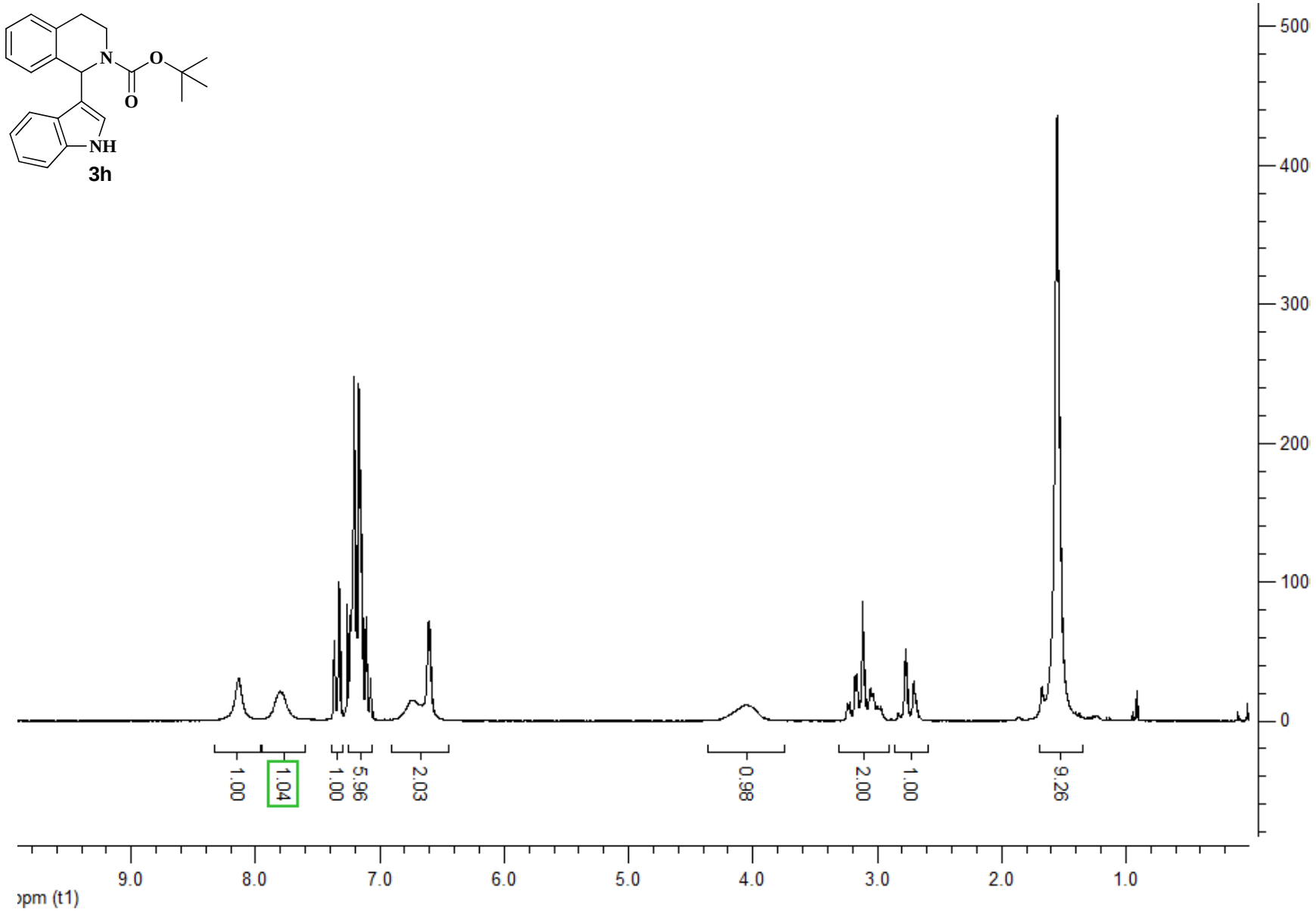
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2.00
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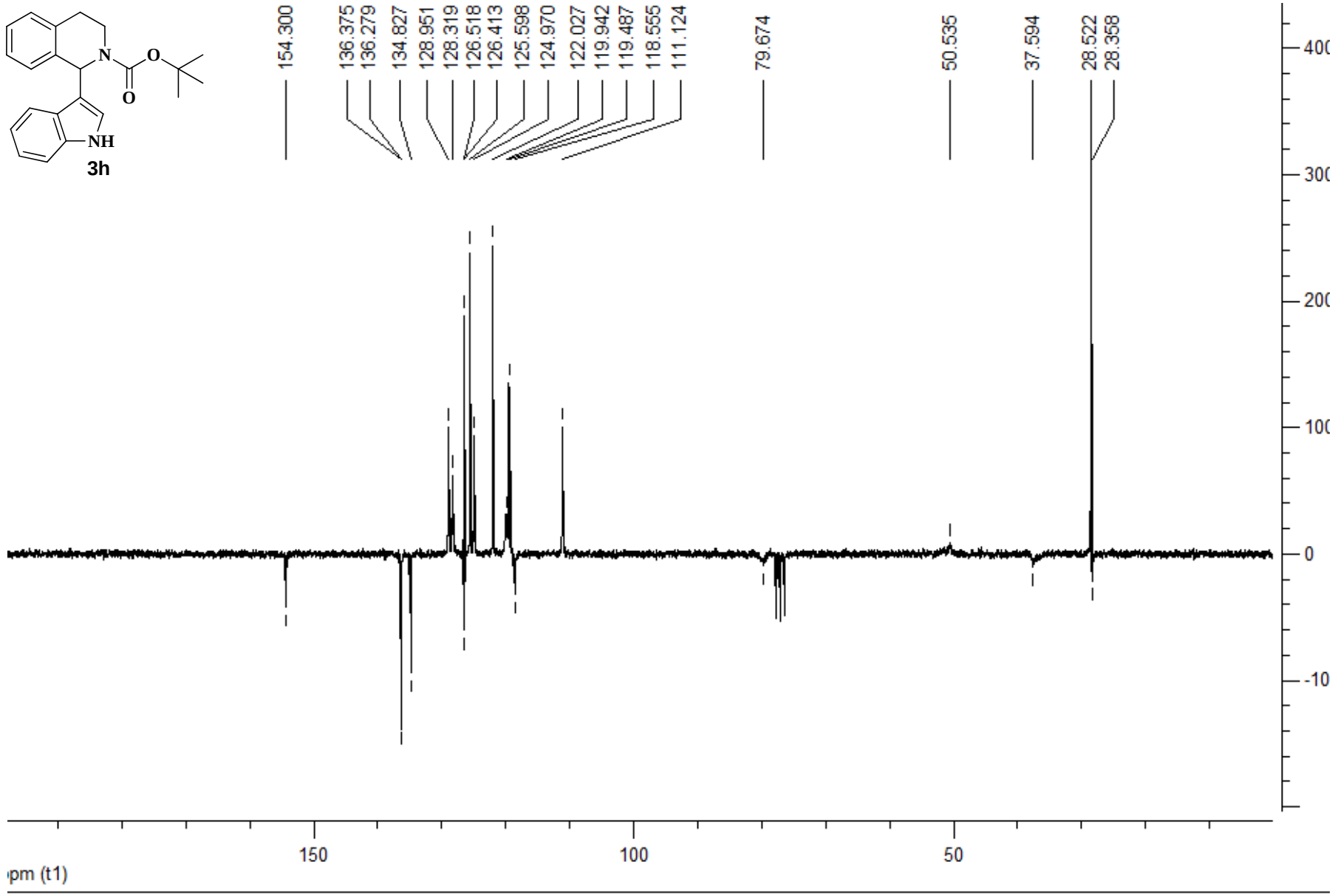
ppm (t1)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119.487
118.555
111.124
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100
50
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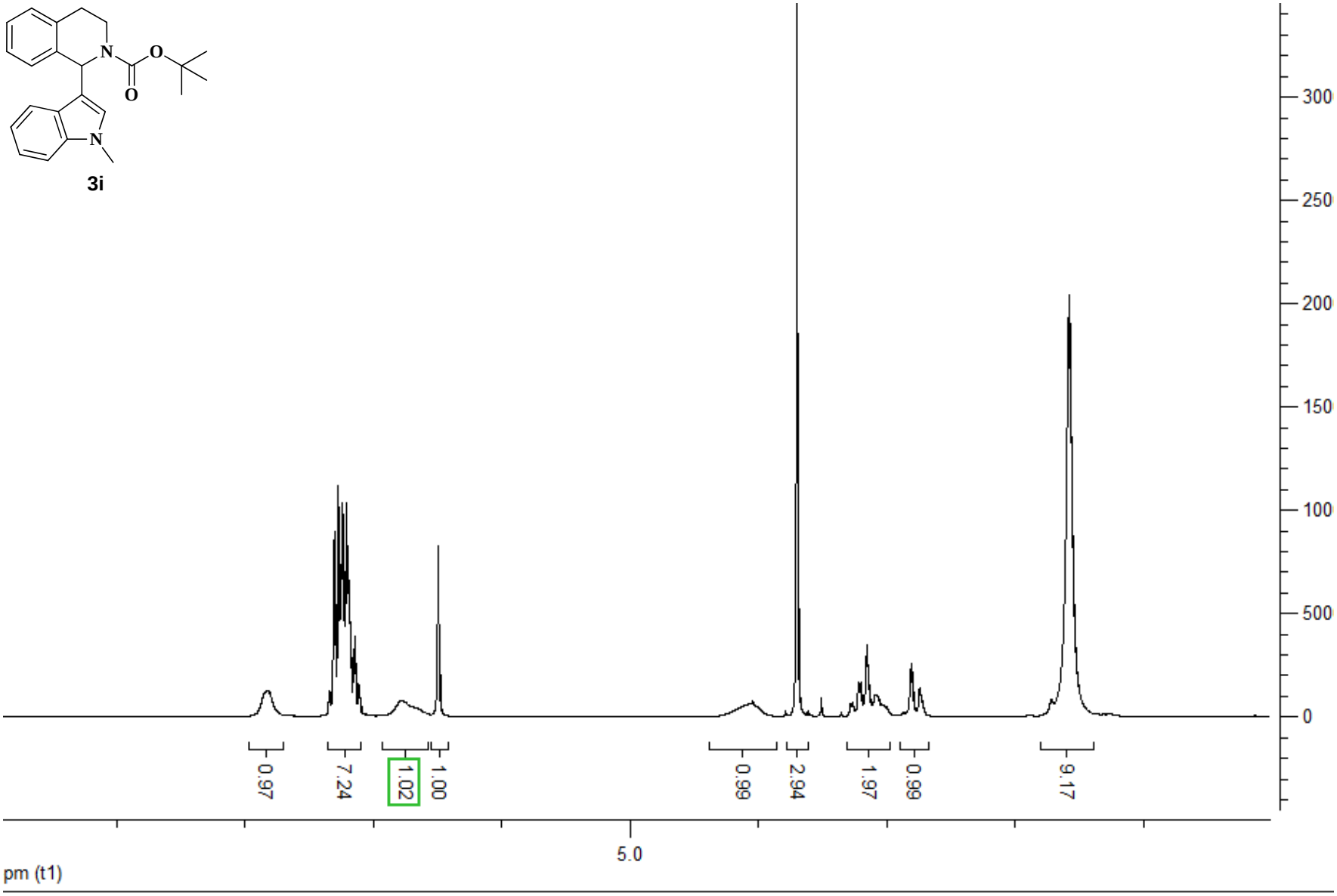
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100
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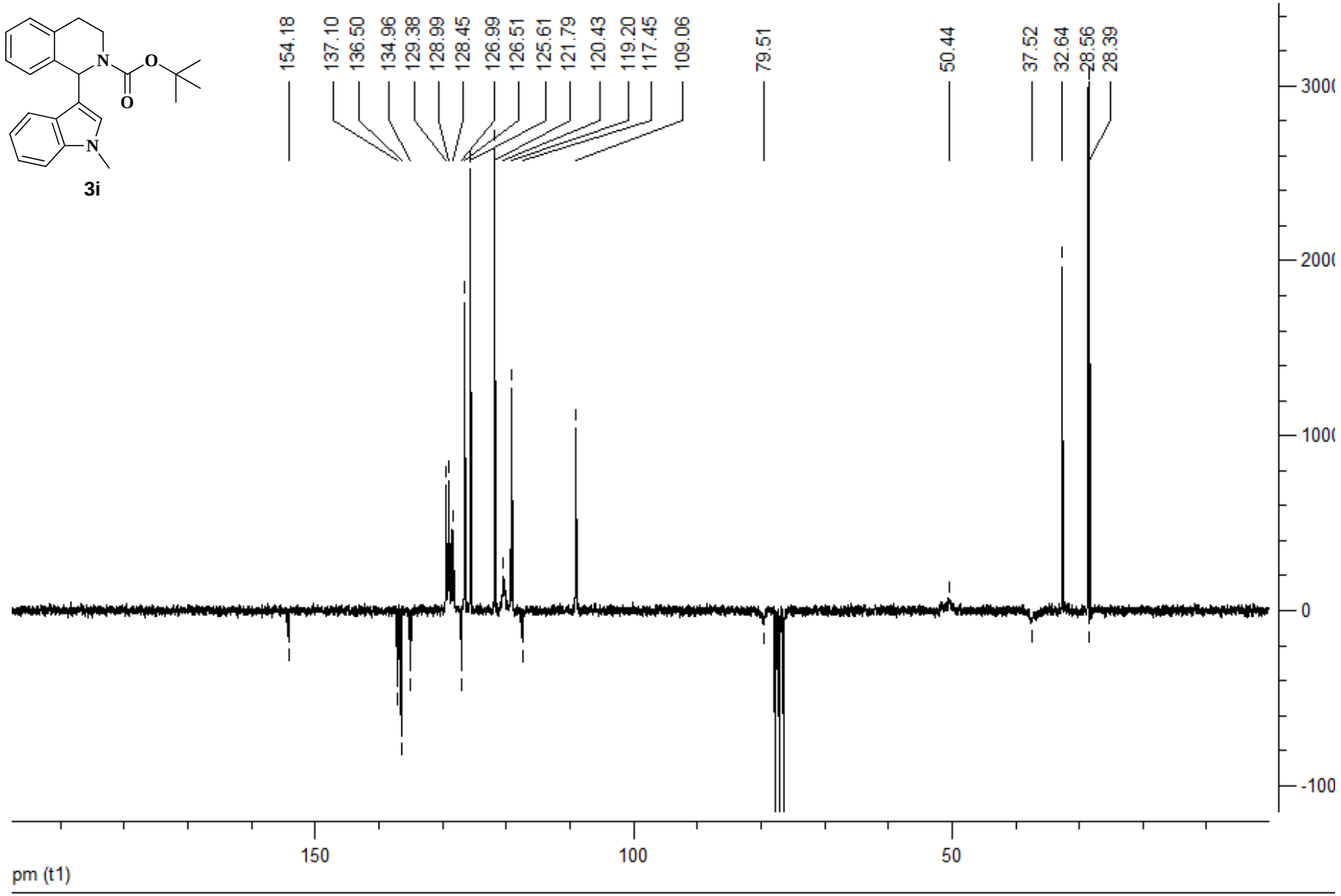
pm (t1)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119.20
117.45
109.06
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2000
1000
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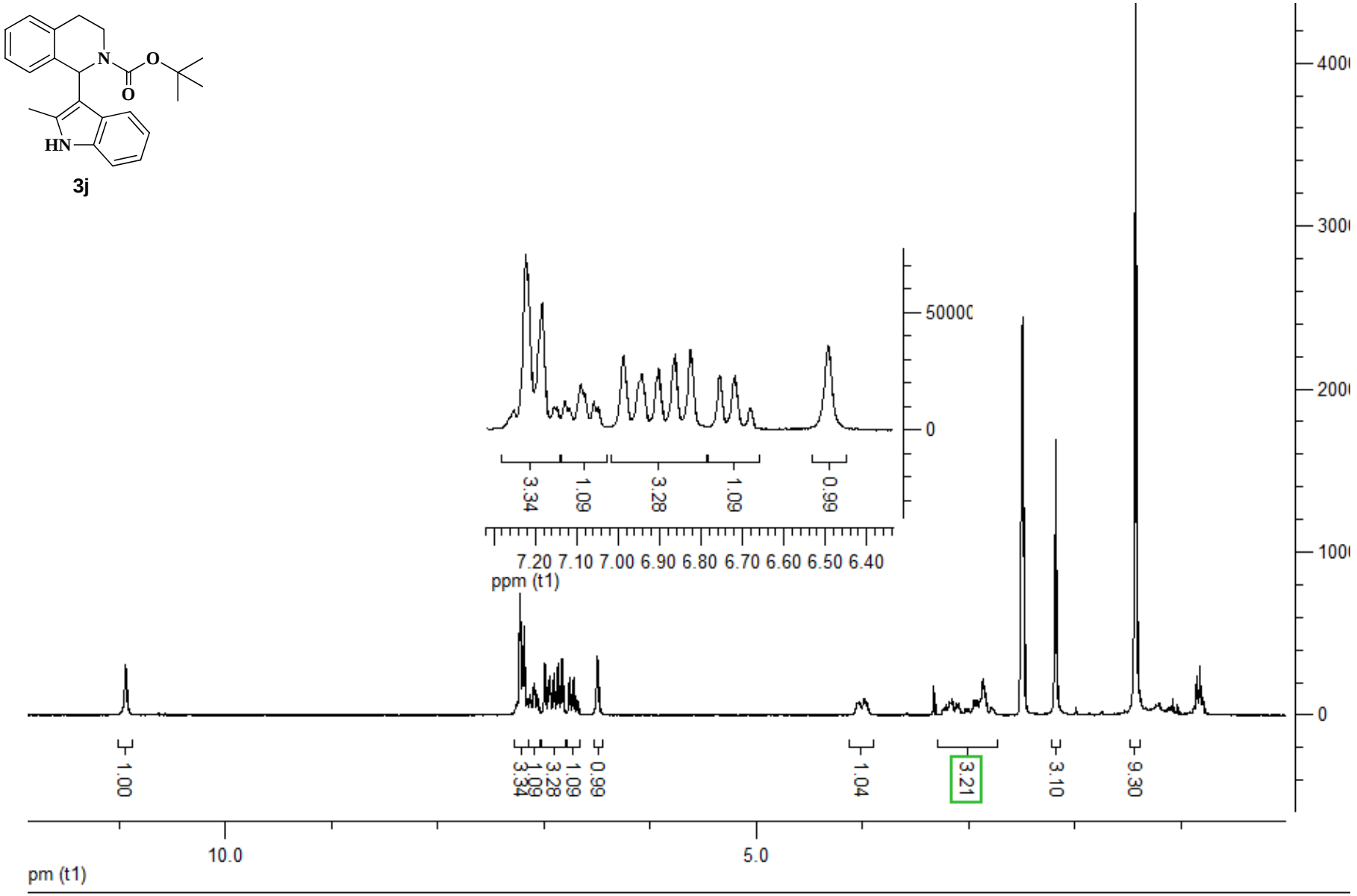
-100
150
100
50
pm (t1)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O
O
HN
3j
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300
200
100
0
50000
0
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1.09
3.28
1.09
0.99
7.20 7.10 7.00 6.90 6.80 6.70 6.60 6.50 6.40
ppm (t1)
1.00
3.34
1.09
3.28
1.09
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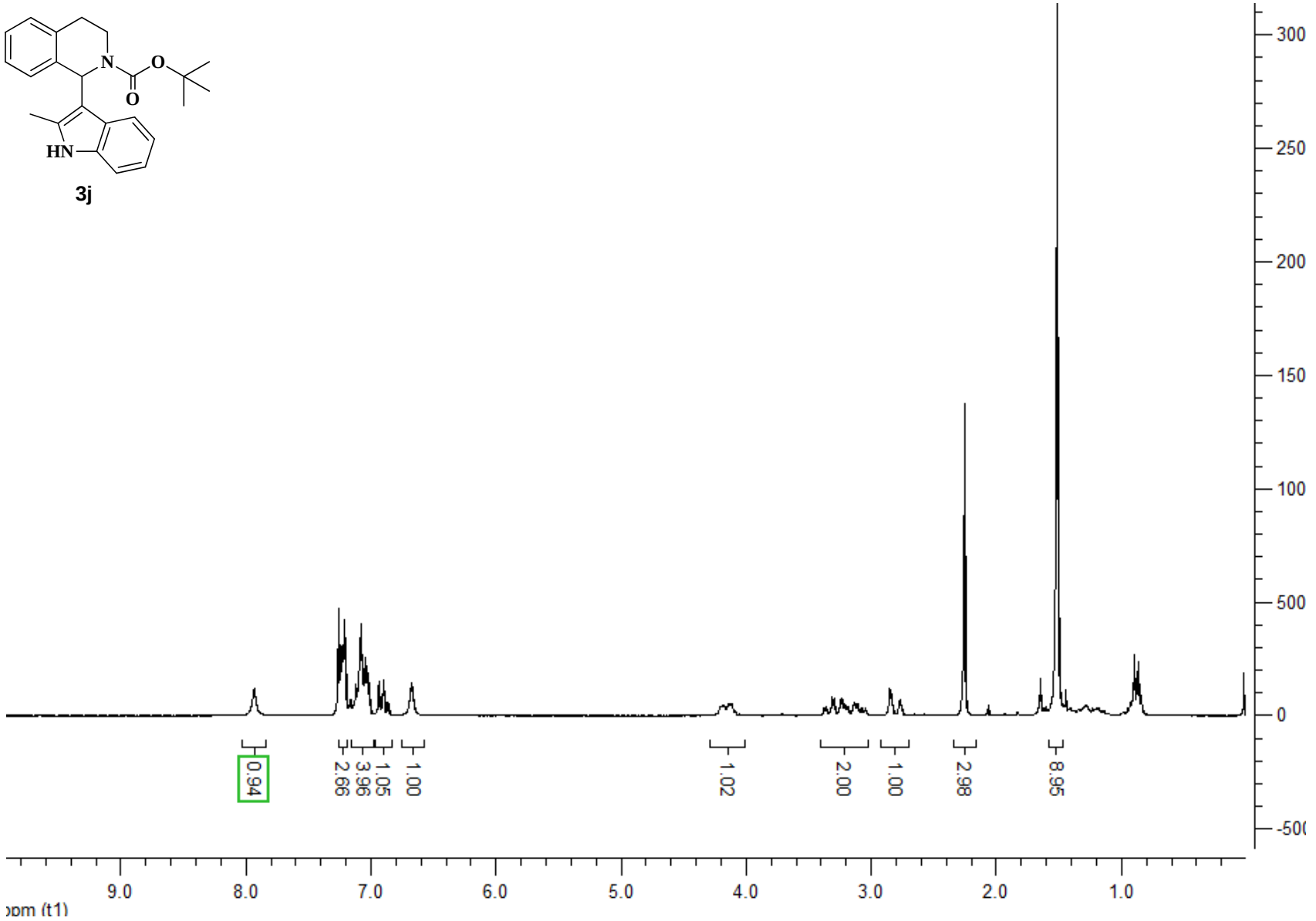
3.21
3.10
9.30
10.0
5.0
pm (t1)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O
O
HN
3j
300
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100
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1.00
1.02
2.00
1.00
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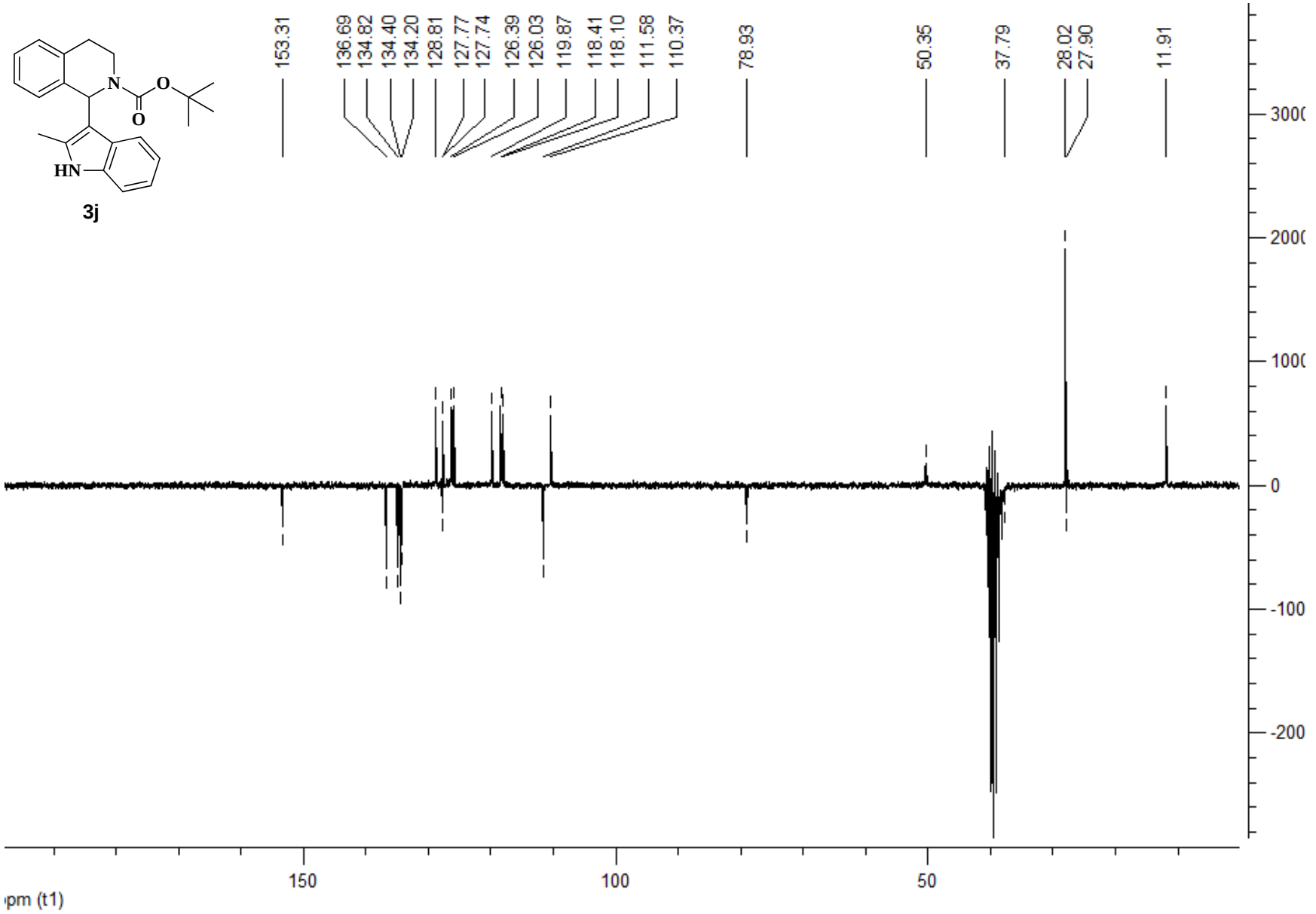
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111.58
110.37
78.93
50.35
37.79
28.02
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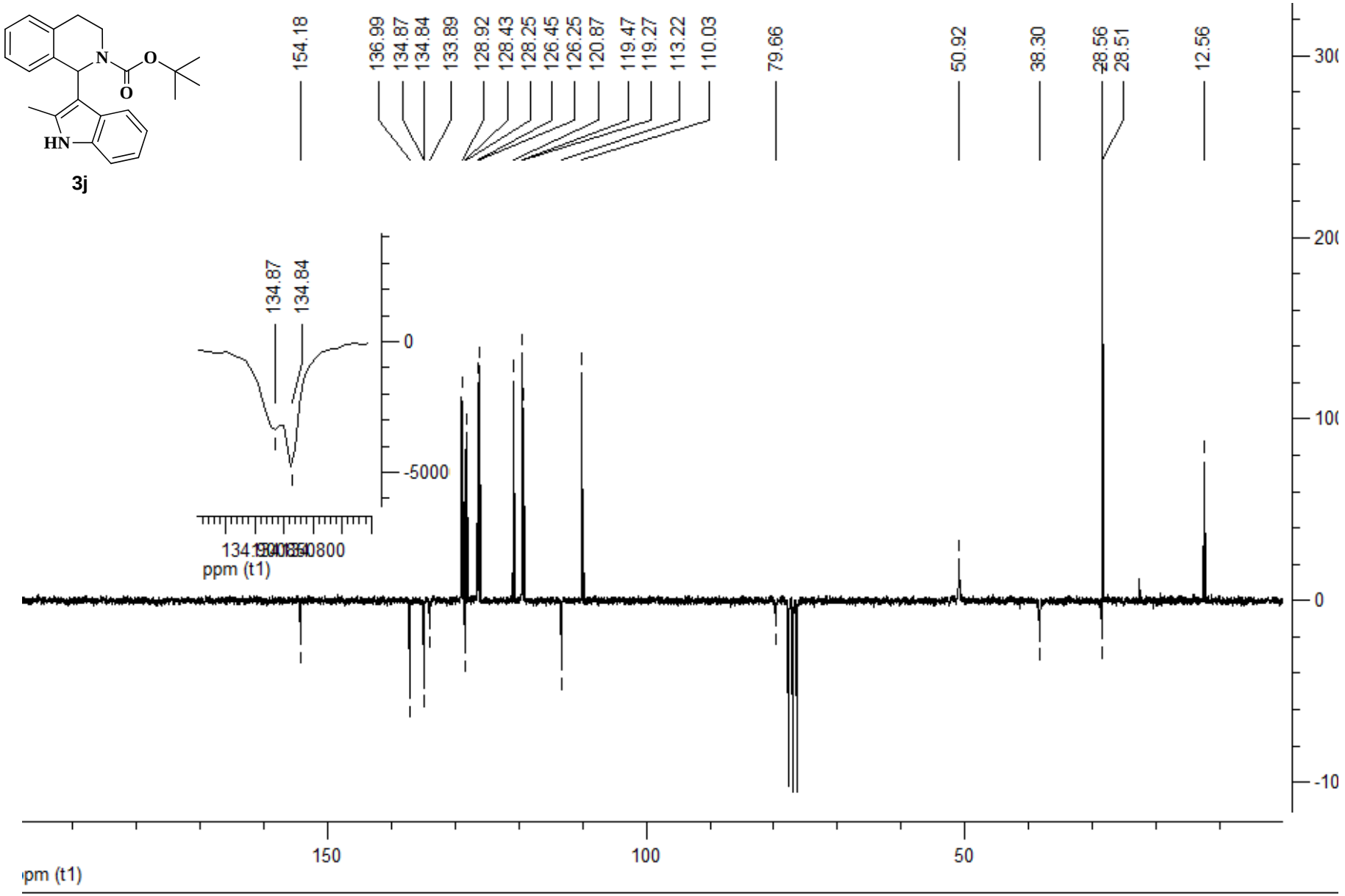
50
ppm (t1)
N
O
O
HN

3j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119.27
113.22
110.03
79.66
50.92
38.30
28.56
28.51
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ppm (t1)
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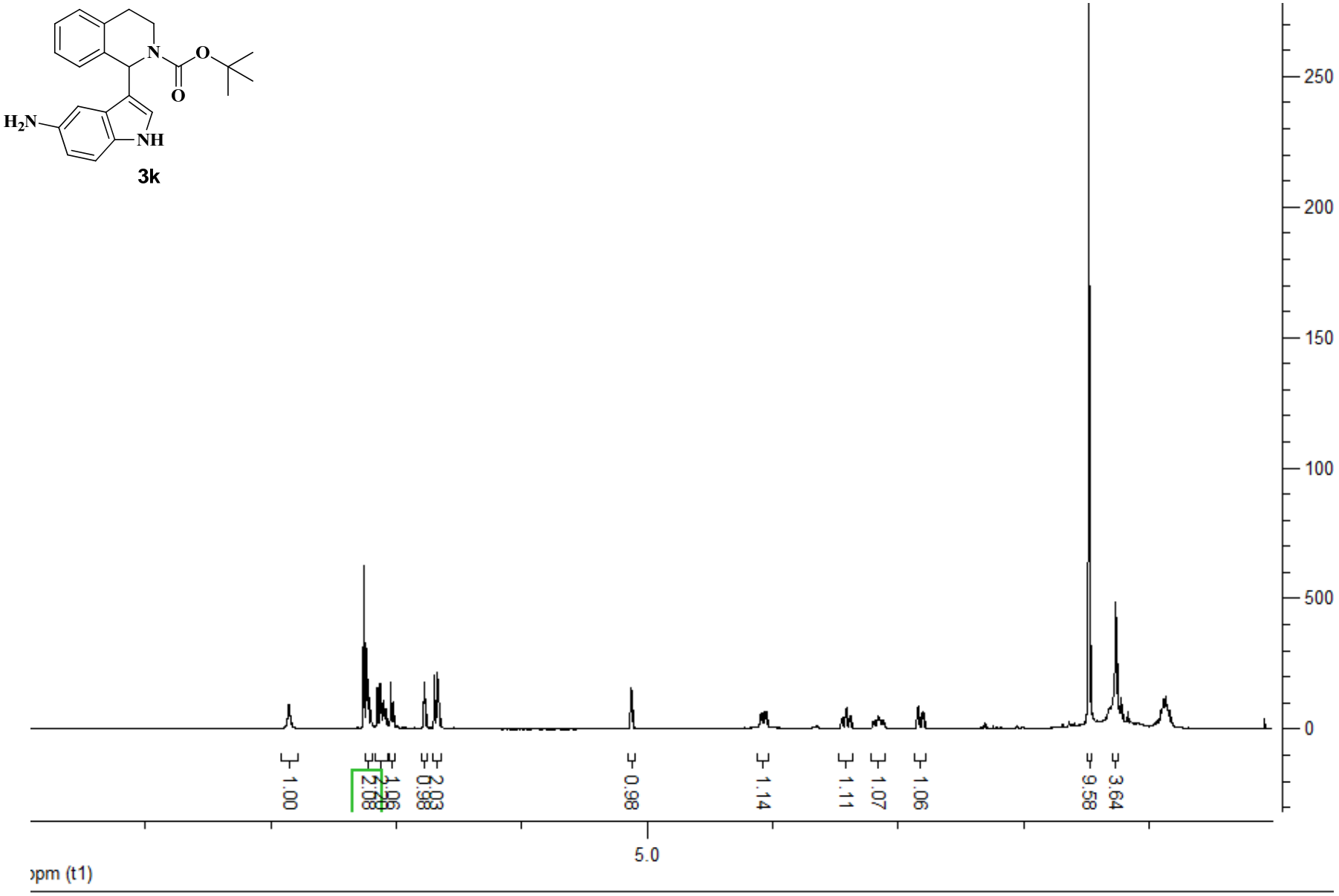
100
0
-10
150
100
50
ppm (t1)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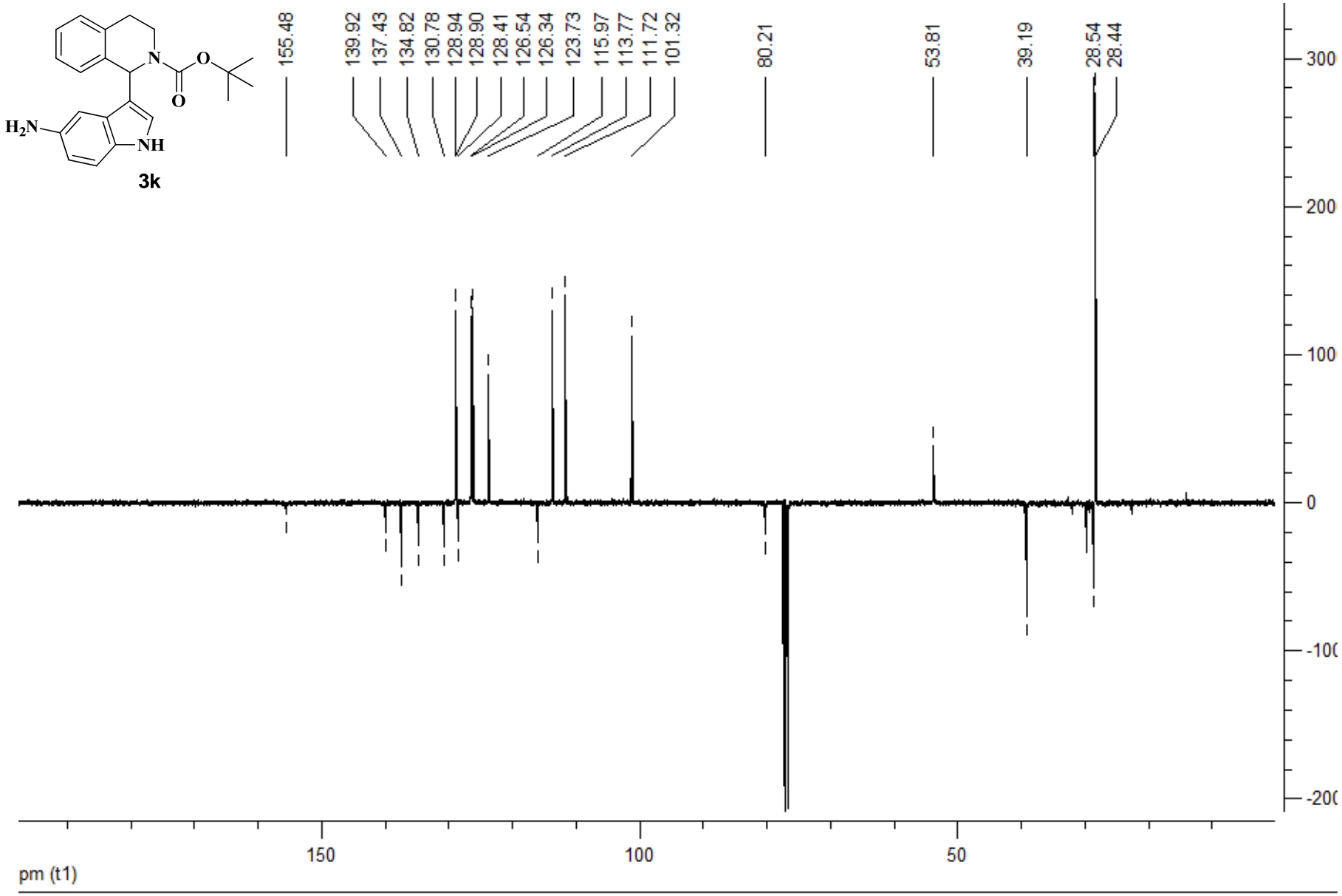
ppm (t1)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123.73
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113.77
111.72
101.32
80.21
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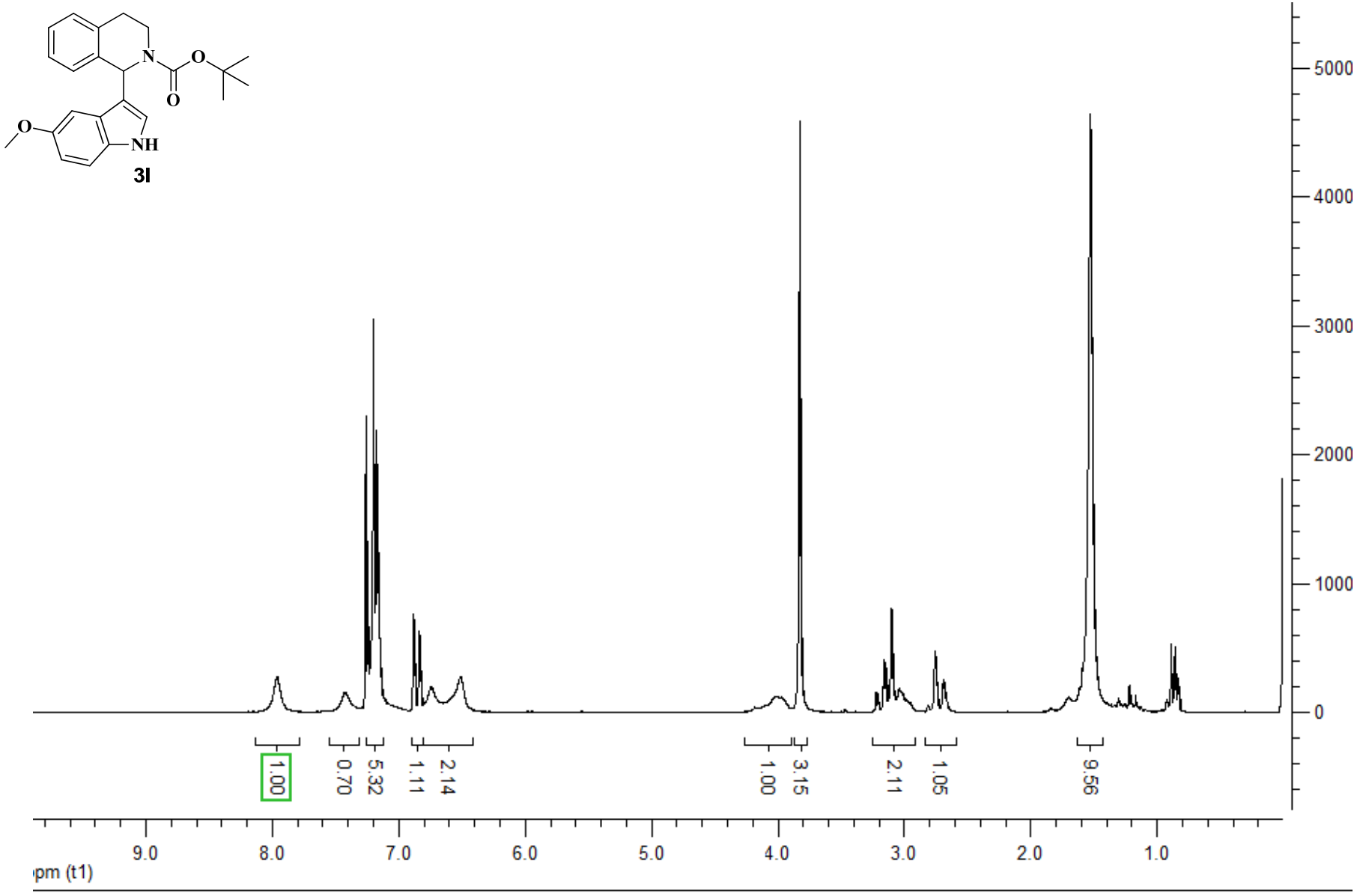
0
-100
-200
150
100
50
pm (t1)

3k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O
O
NH
3l
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1000
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1.00
3.15
2.11
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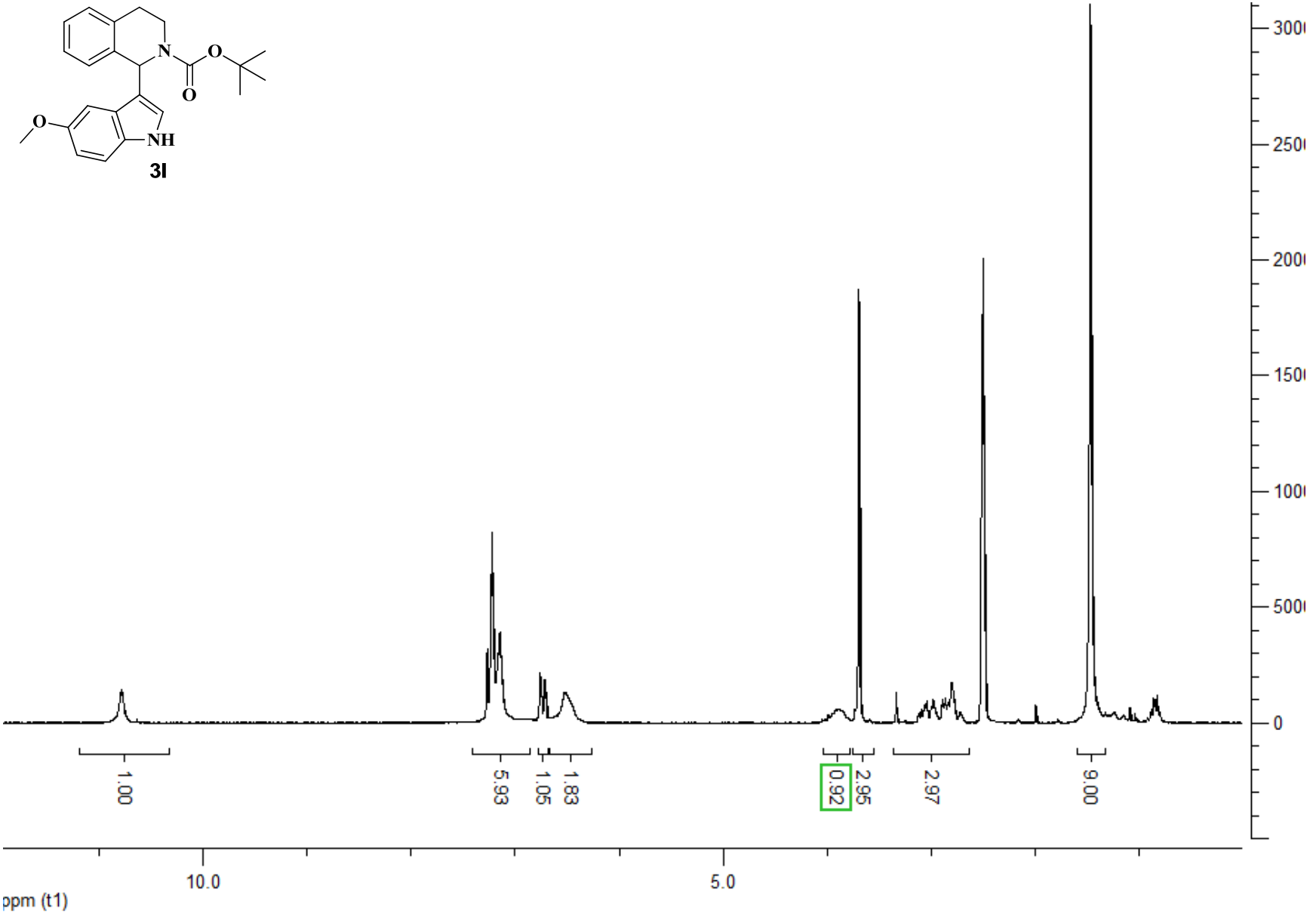
ppm (t1)


O
N
O
O
O
NH
3l
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2.97
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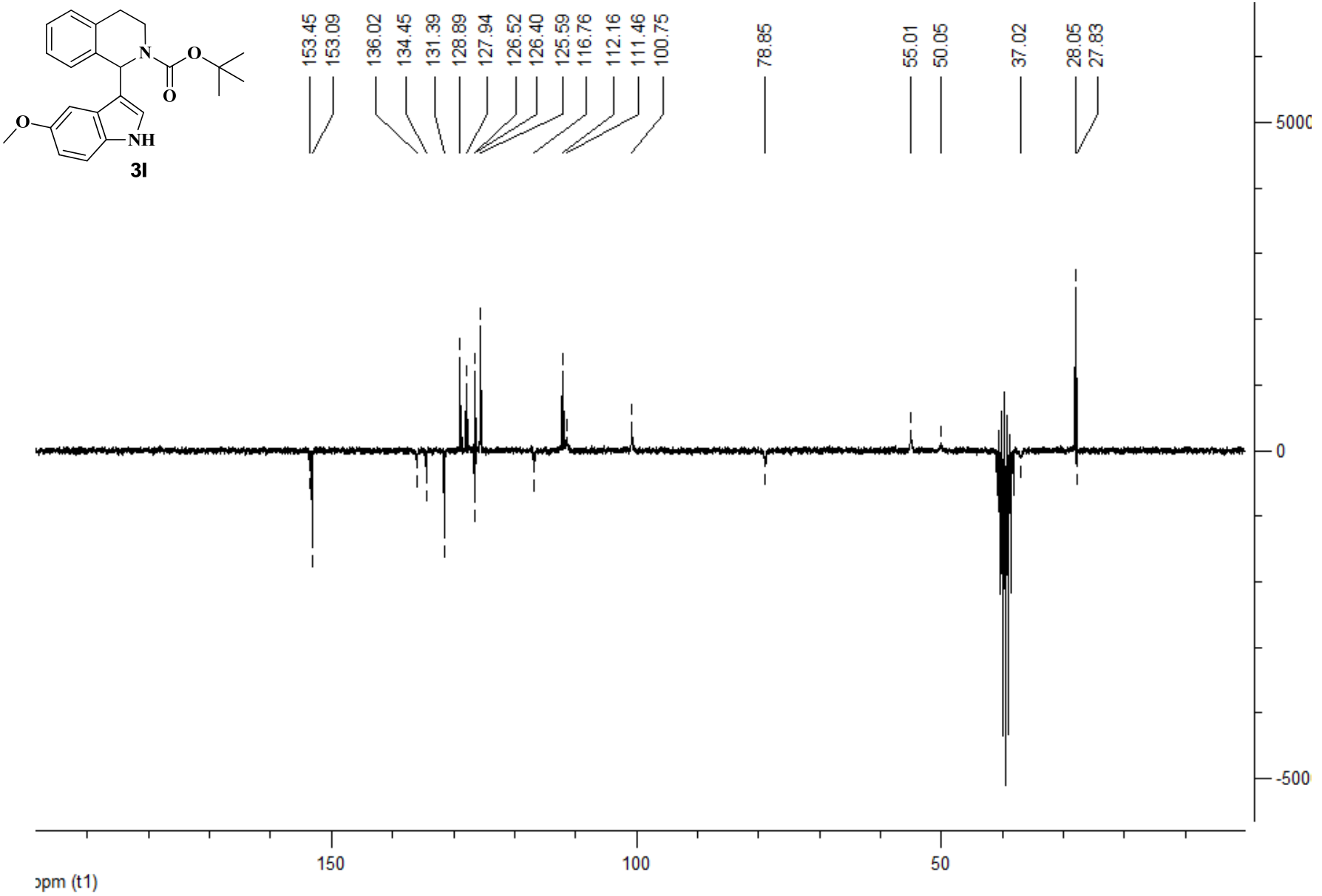
ppm (t1)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112.16
111.46
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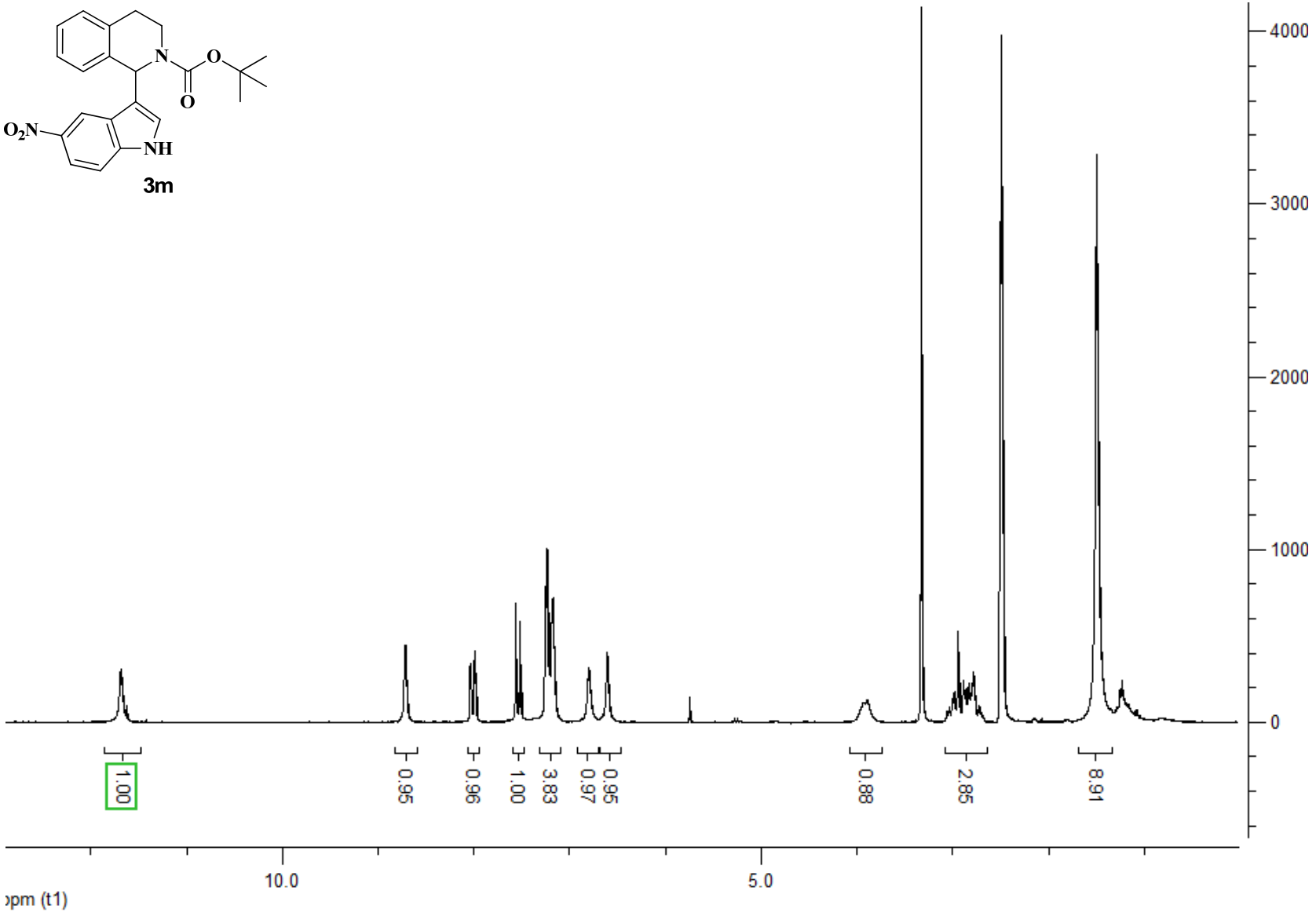
150
100
50
ppm (t1)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N
O
O
3m
4000
3000
2000
1000
0
1.00
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1.00
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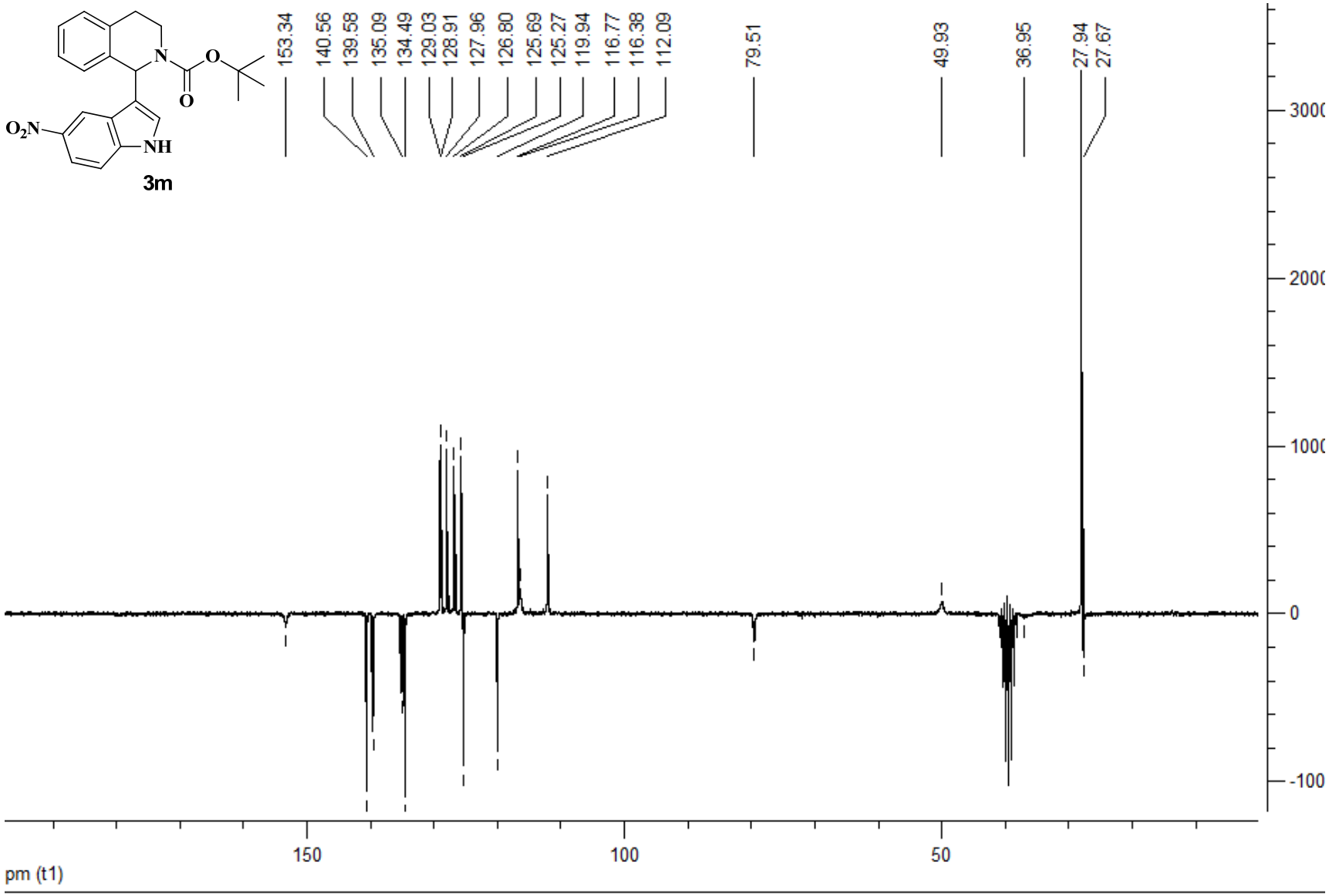
0.97
0.95
0.88
2.85
8.91
10.0
5.0
ppm (t1)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116.38
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27.94
27.67
3000
2000
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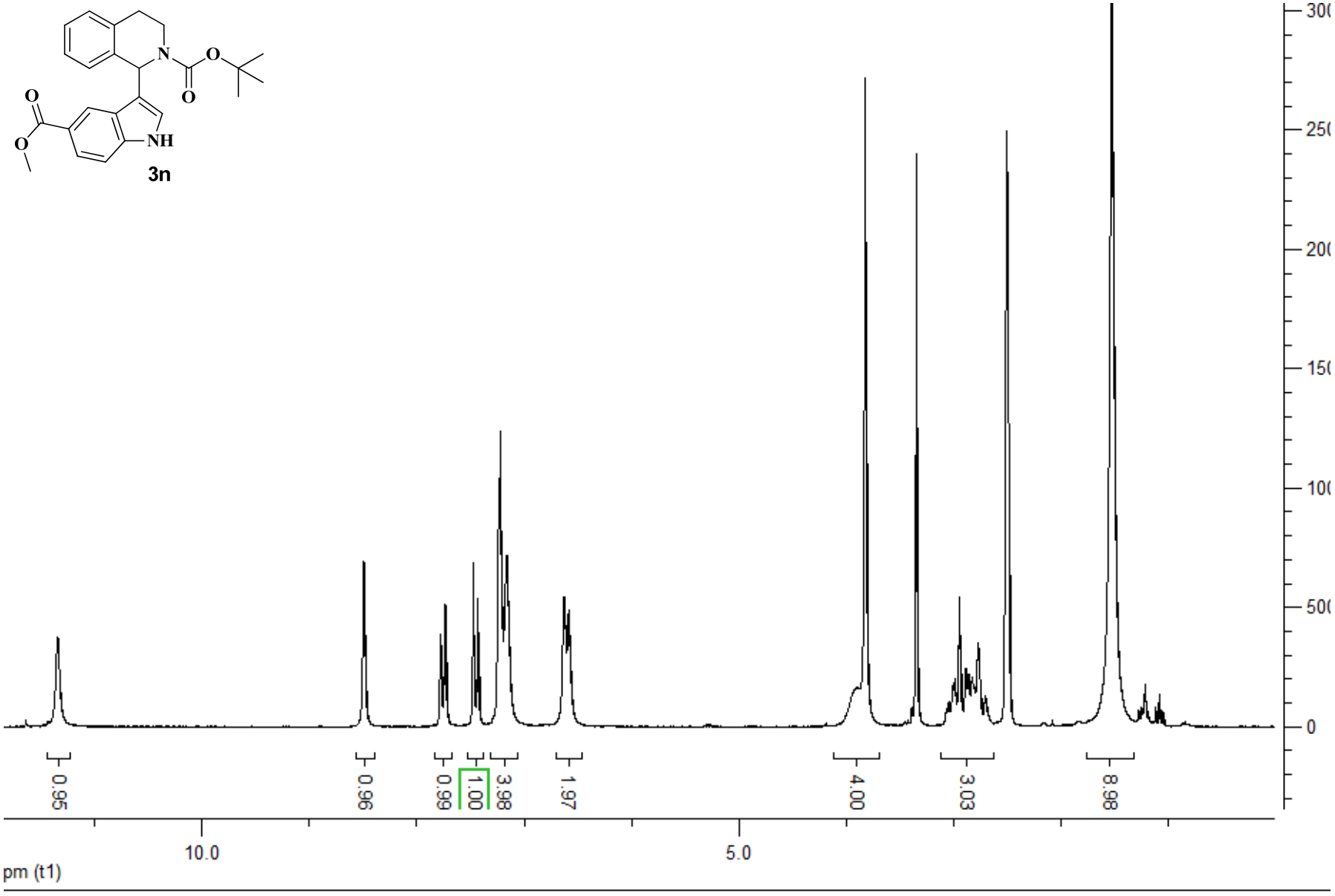
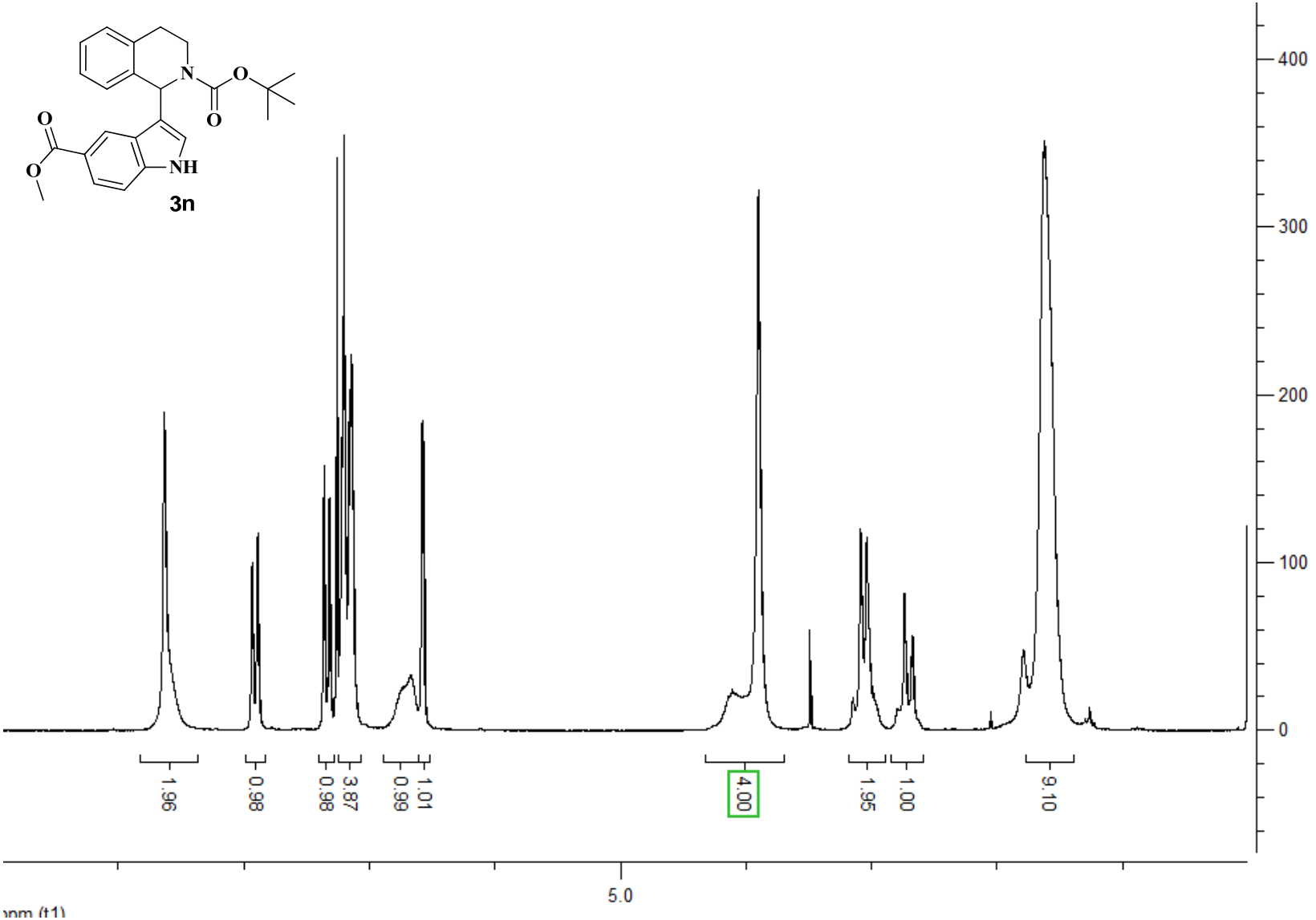
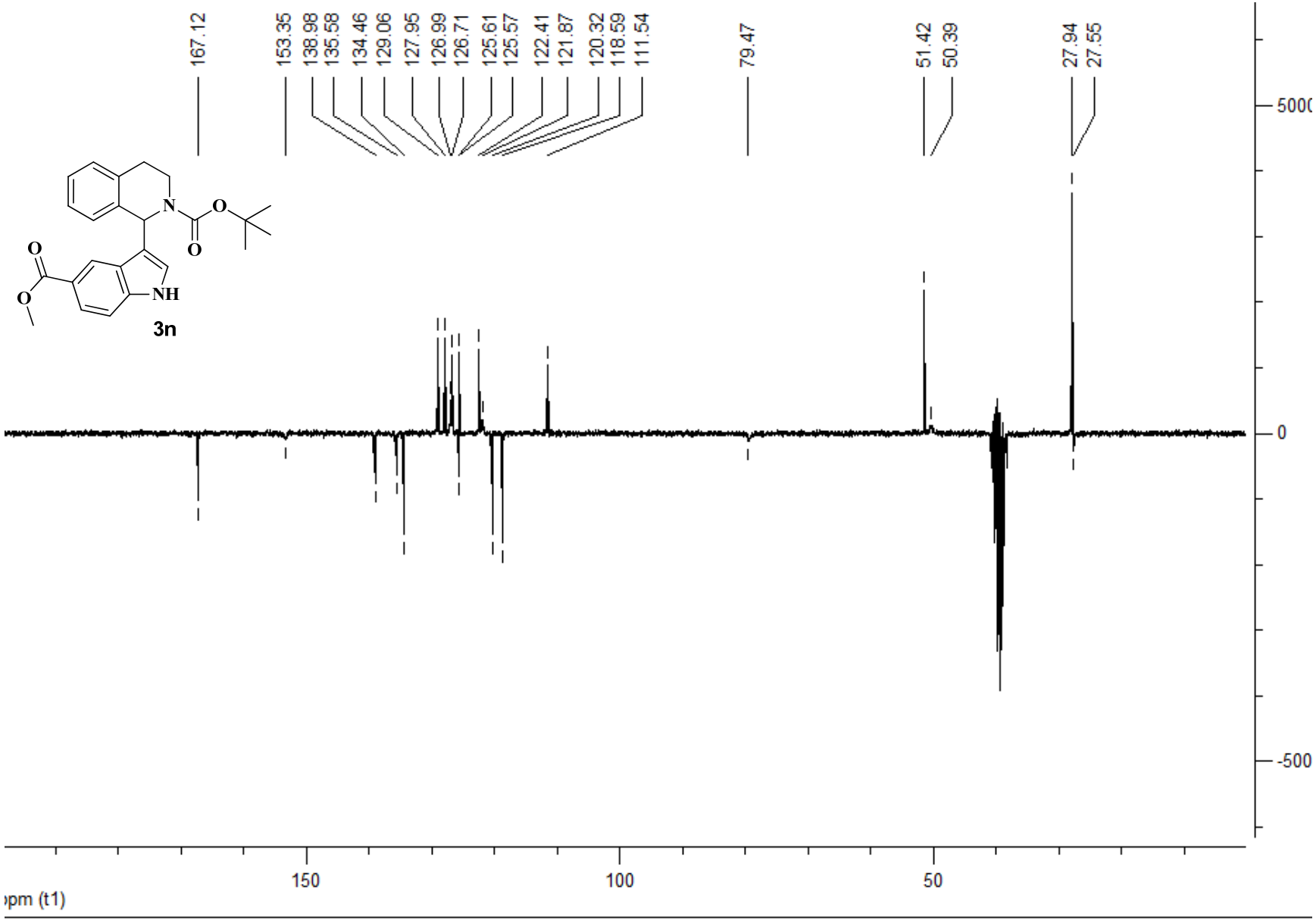
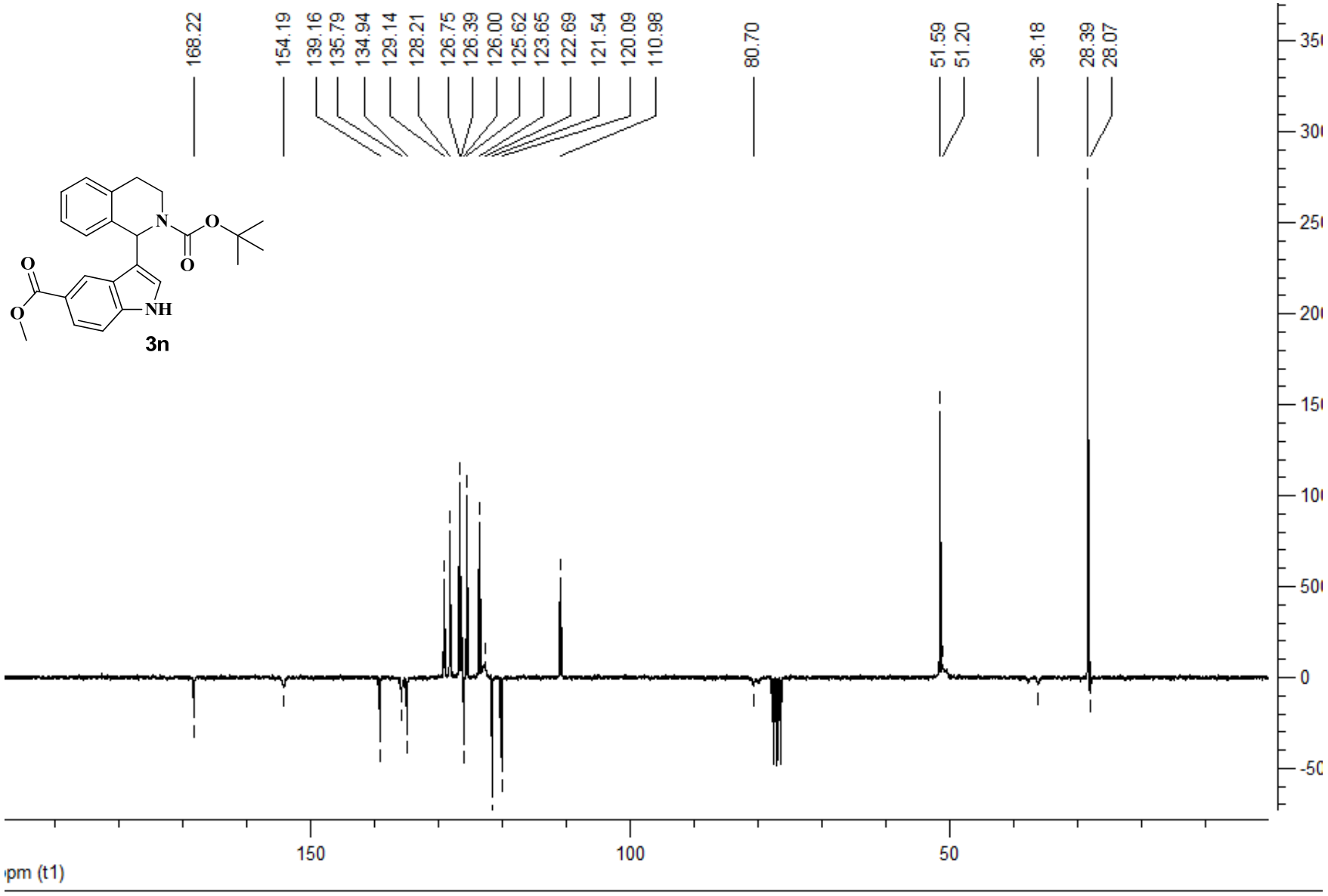
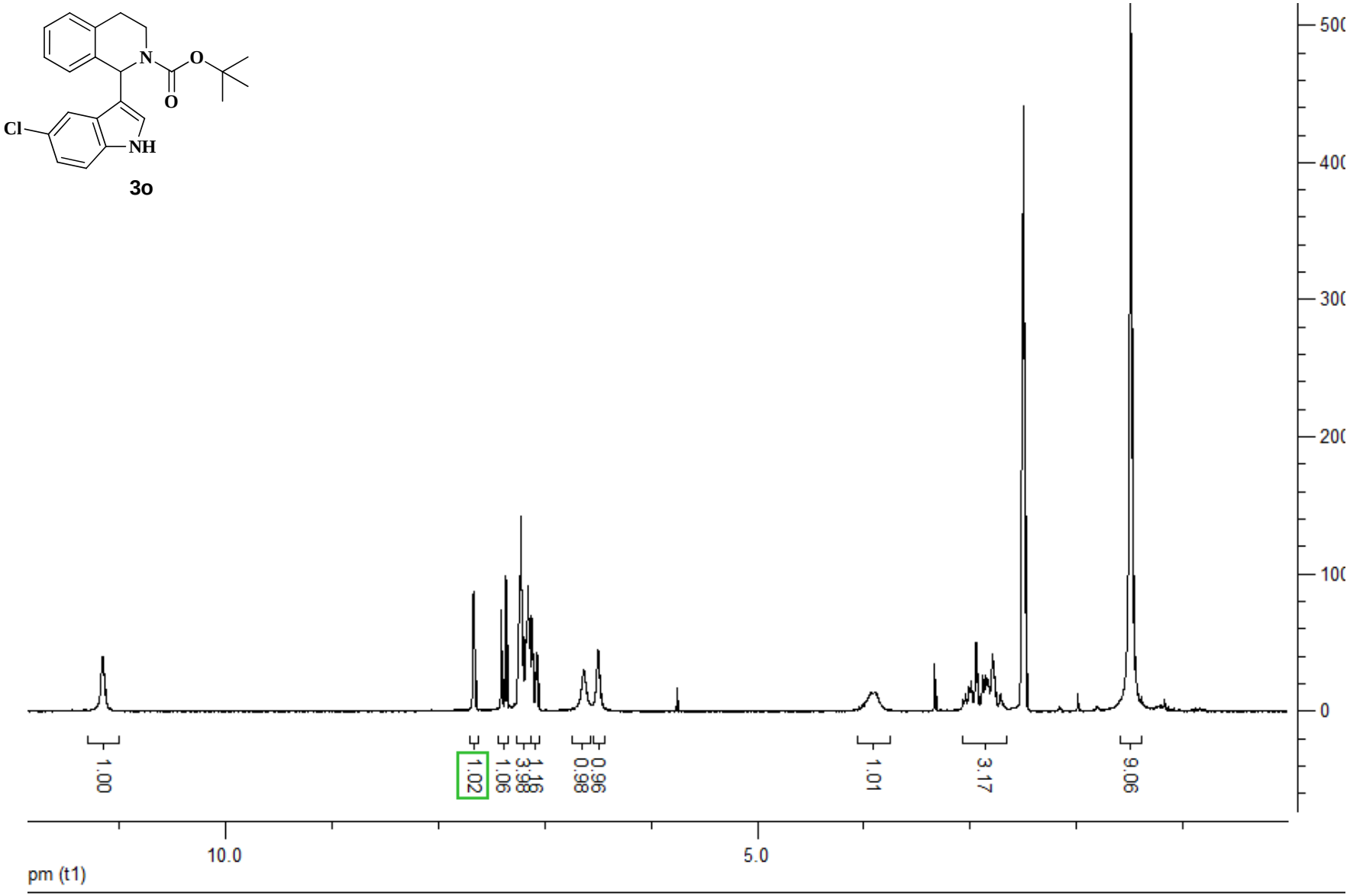
150
100
50
pm (t1)
3m

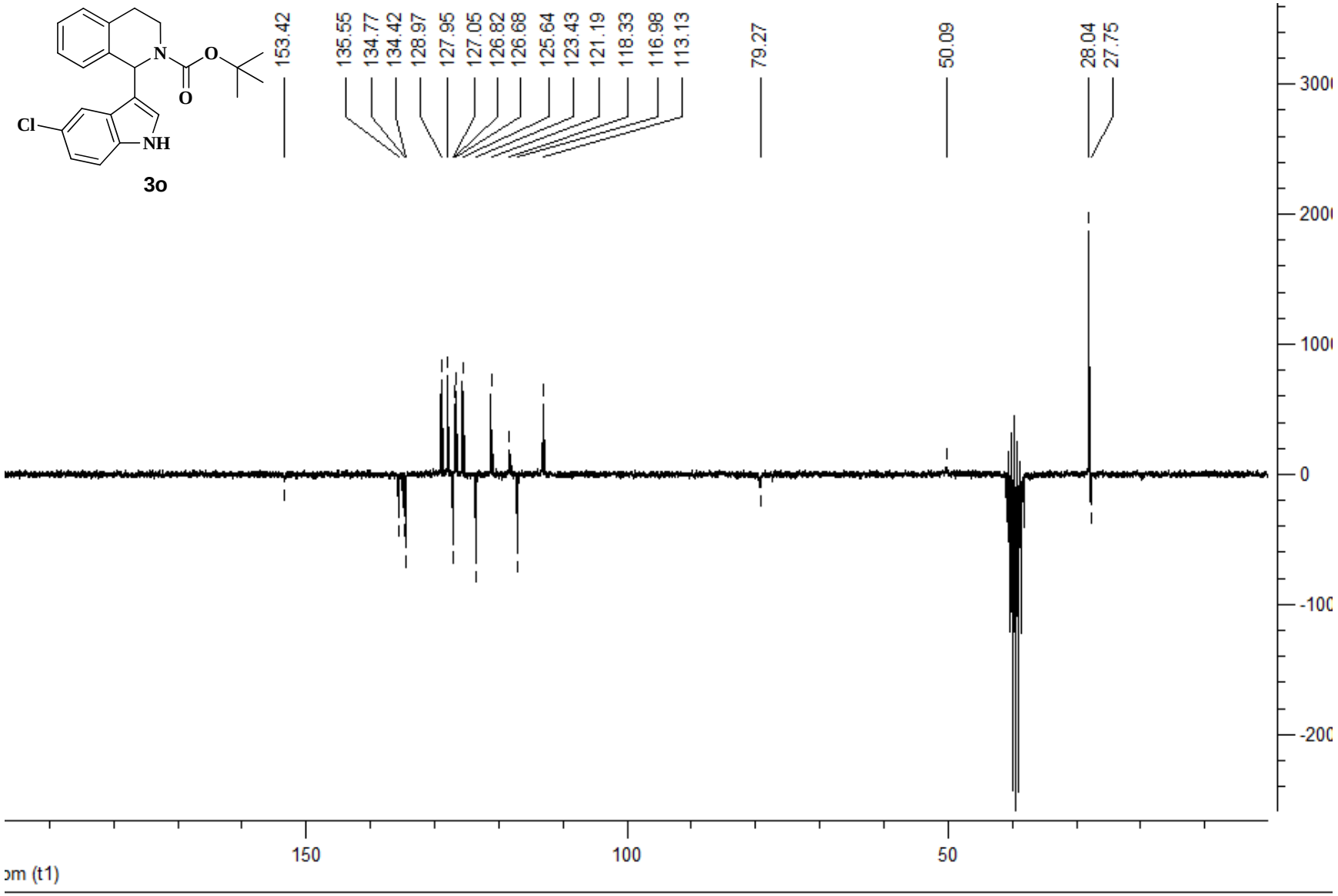

3n
0.95
0.96
0.99
1.00
3.98
1.97
4.00
3.03
8.98
10.0
5.0
pm (t1)

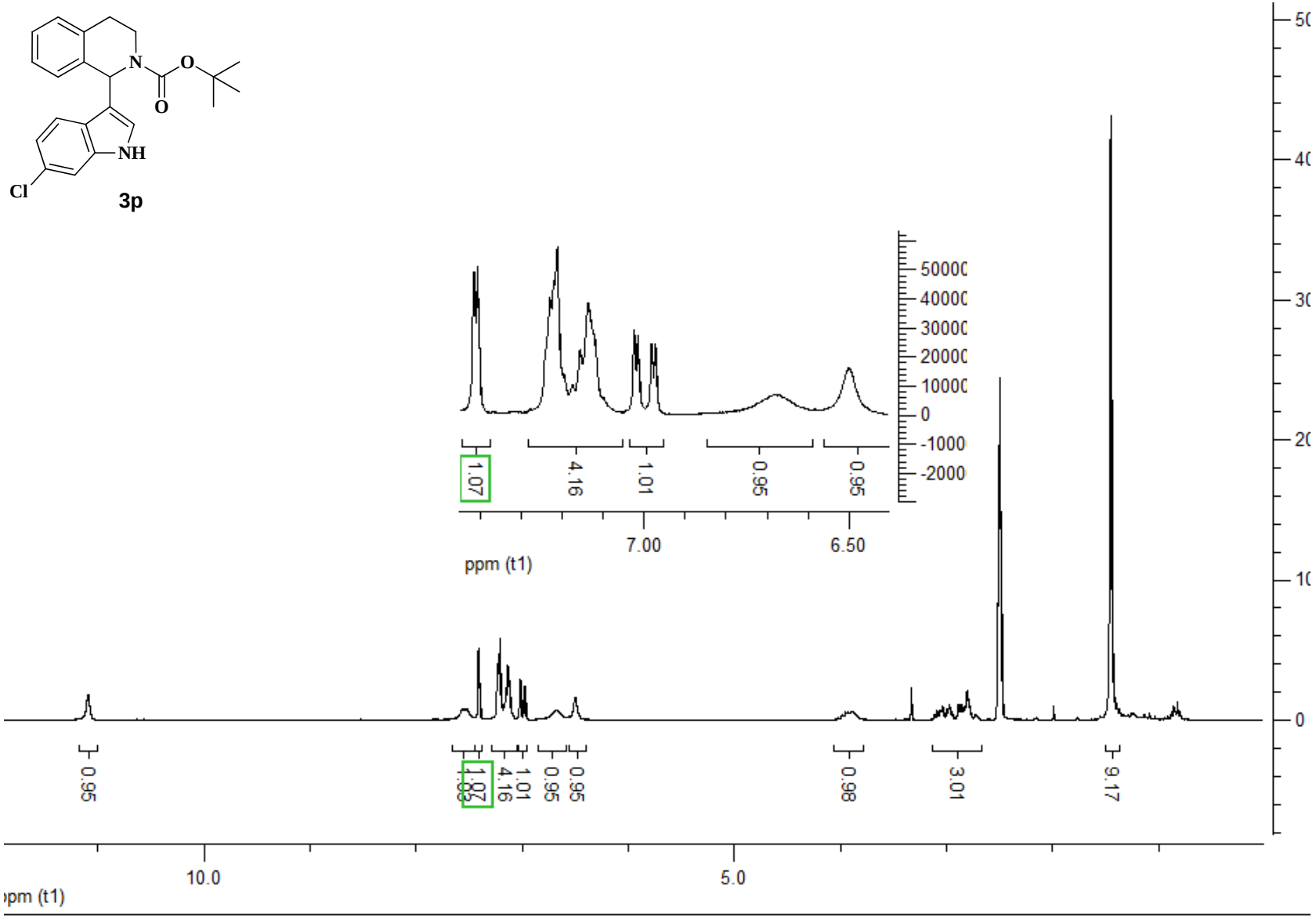

O
O
N
O
O
NH
3n
400
300
200
100
0
1.96
0.98
0.98
3.87
0.99
1.01
4.00
1.95
1.00
9.10
5.0
ppm (t1)

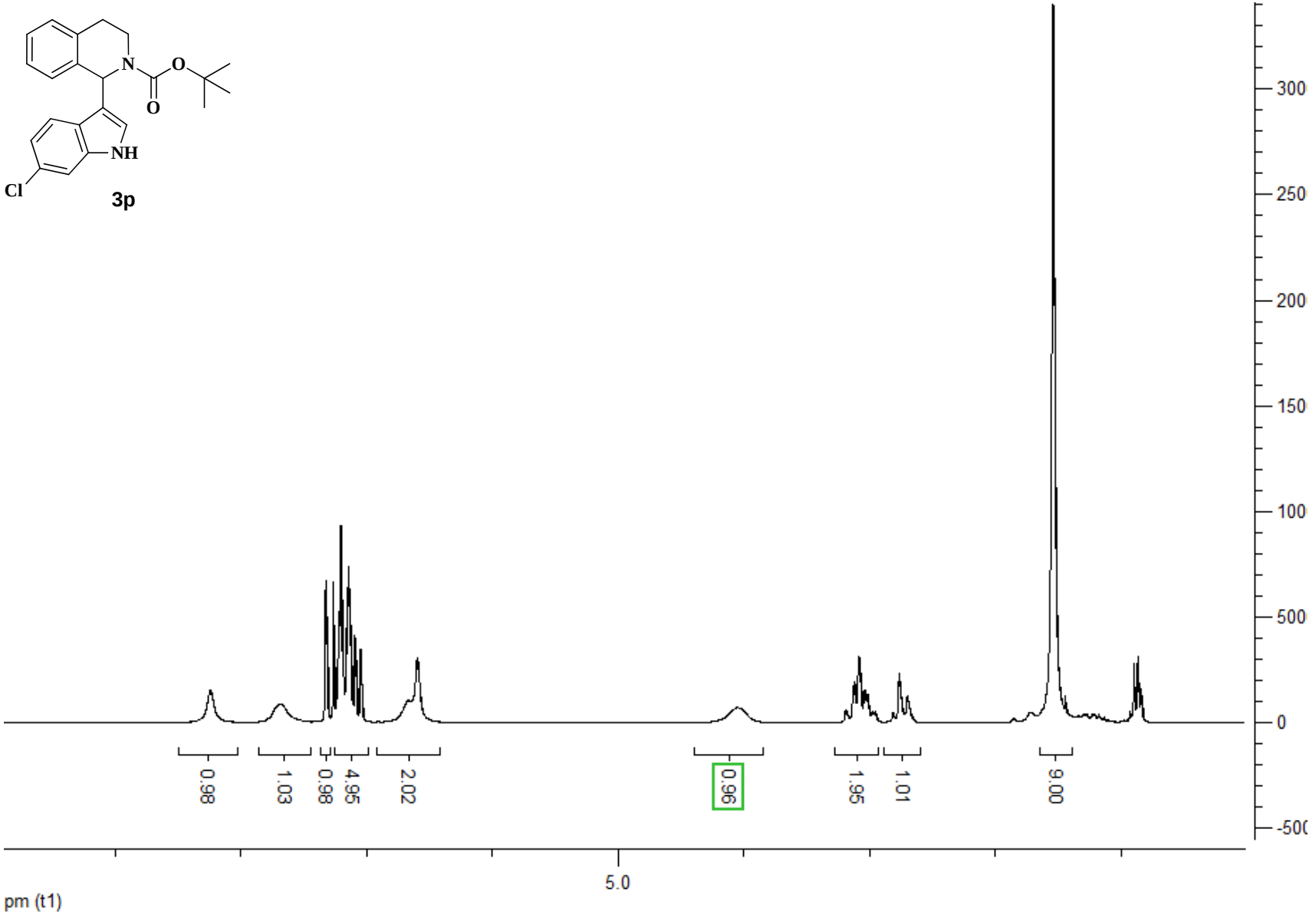

167.12
153.35
138.98
135.58
134.46
129.06
127.95
126.99
126.71
125.61
125.57
122.41
121.87
120.32
118.59
111.54
79.47
51.42
50.39
27.94
27.55
5000
0
-500
150
100
50
ppm (t1)
N
O
O
O
O
NH
3n

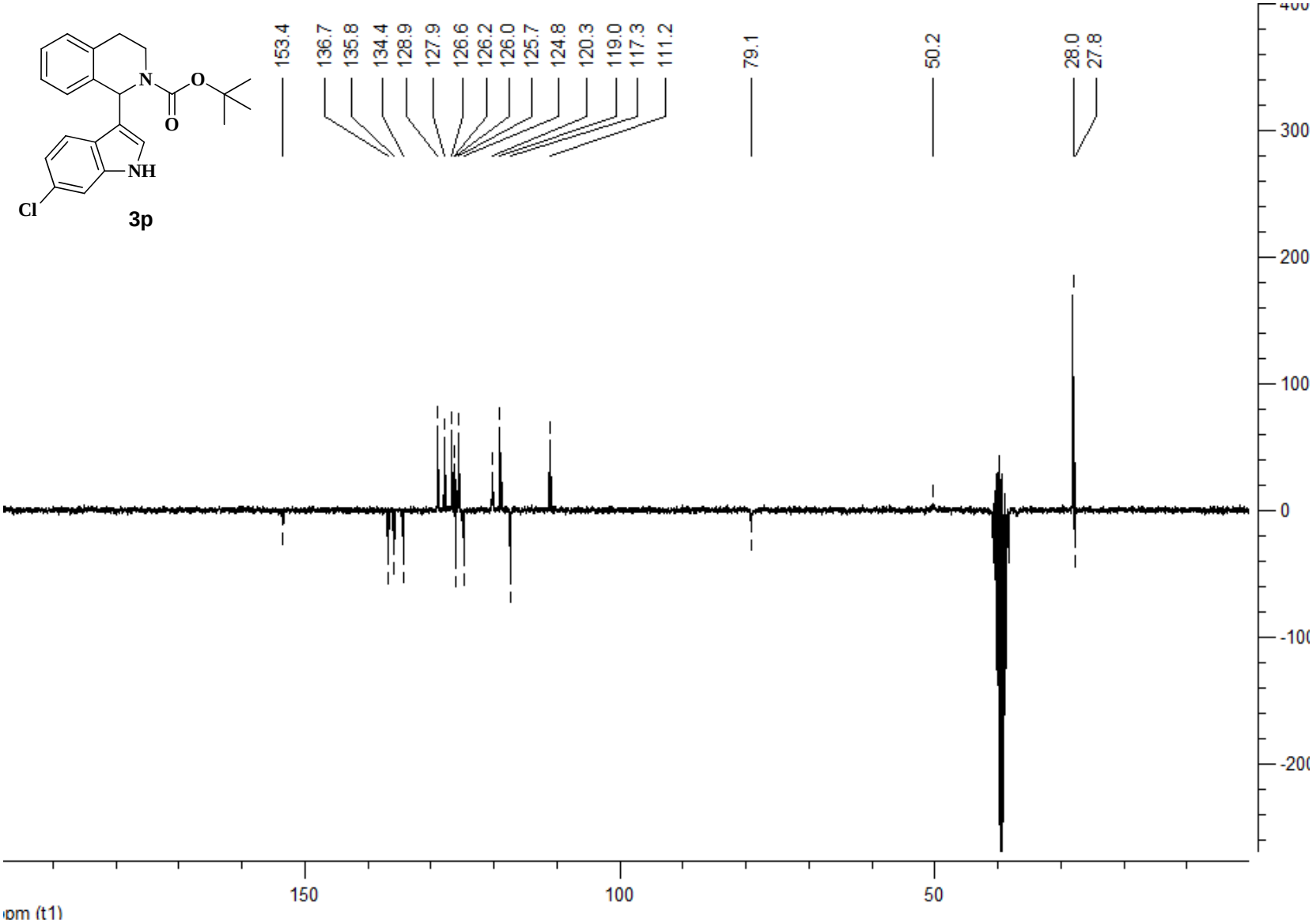

168.22
154.19
139.16
135.79
134.94
129.14
128.21
126.75
126.39
126.00
125.62
123.65
122.69
121.54
120.09
110.98
80.70
51.59
51.20
36.18
28.39
28.07
O
O
O
O
N
NH
3n
150
100
50
ppm (t1)

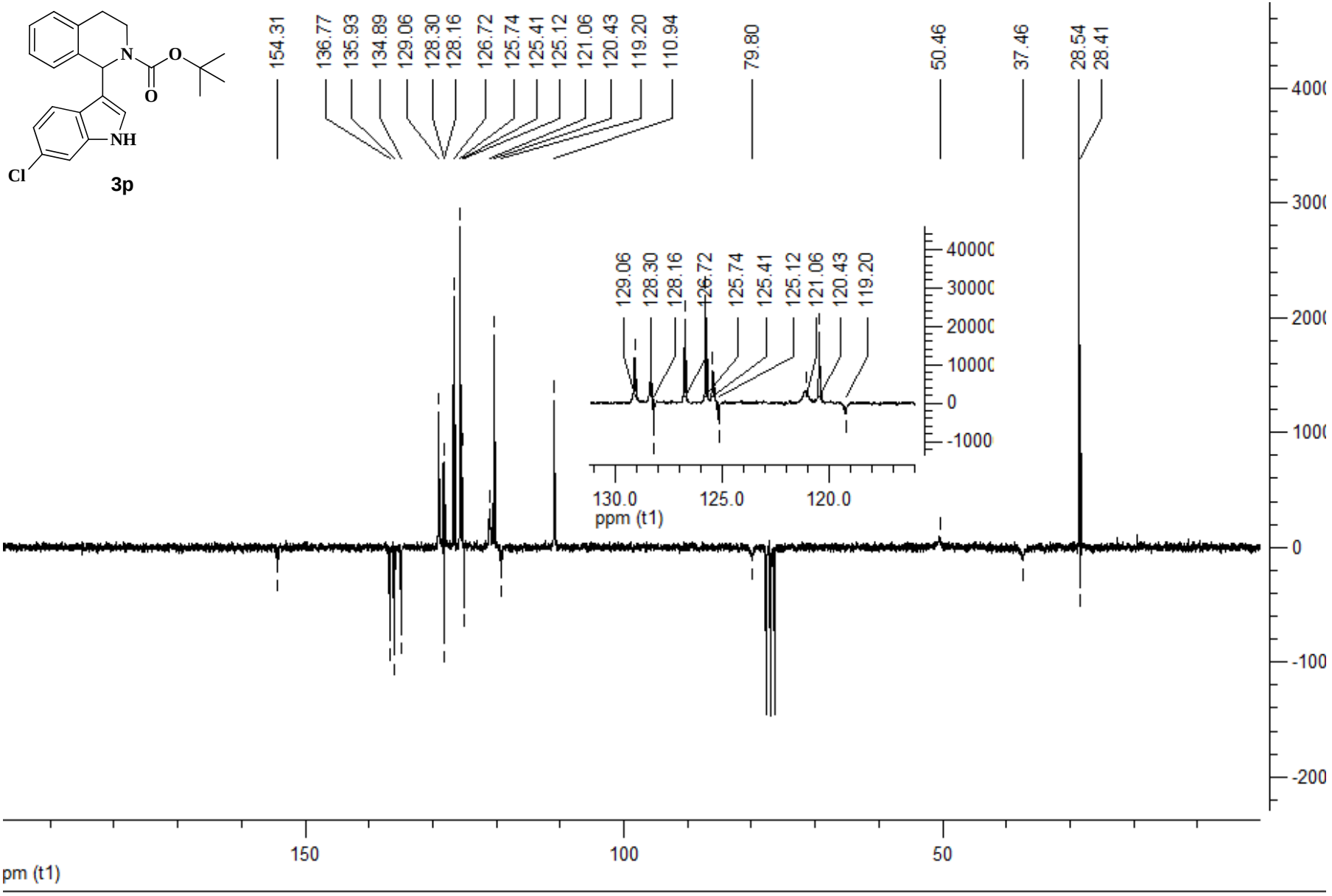

Cl
NH
N
O
O
3o
1.00
1.02
1.06
3.88
3.16
0.98
0.96
1.01
3.17
9.06
10.0
5.0
pm (t1)

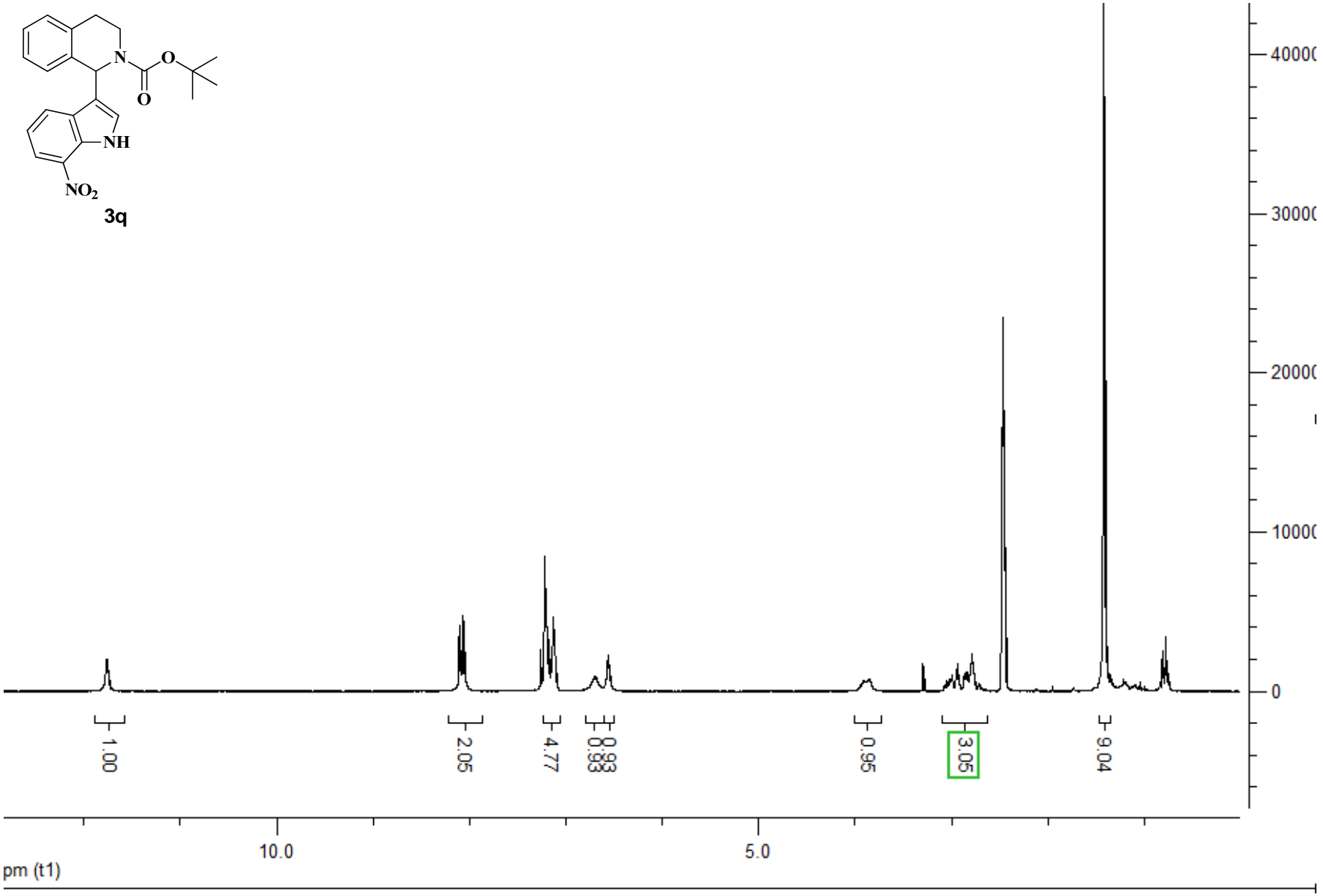

Cl
NH
N
O
O
3o
153.42
135.55
134.77
134.42
128.97
127.95
127.05
126.82
126.68
125.64
123.43
121.19
118.33
116.98
113.13
79.27
50.09
28.04
27.75
300
200
100
0
-100
-200
150
100
50
om (t1)

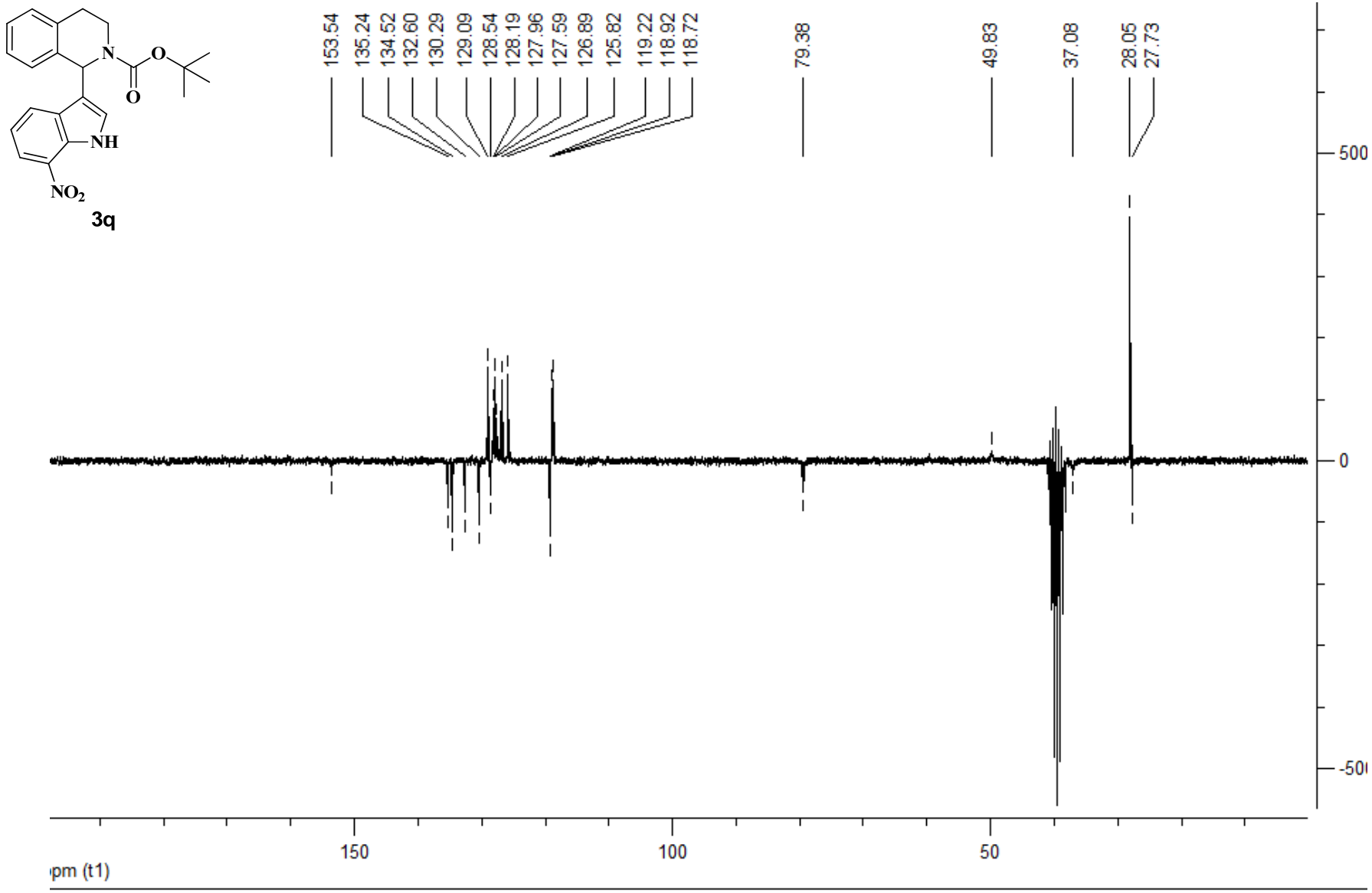

N
O
O
NH
Cl
3p
1.07
4.16
1.01
0.95
0.95
7.00
6.50
ppm (t1)
0.95
1.07
4.16
1.01
0.95
0.95
0.98
3.01
9.17
10.0
5.0
ppm (t1)


N
O
O
NH
Cl
3p
300
250
200
150
100
500
0
-500
0.98
1.03
0.98
4.95
2.02
0.96
1.95
1.01
9.00
5.0
pm (t1)

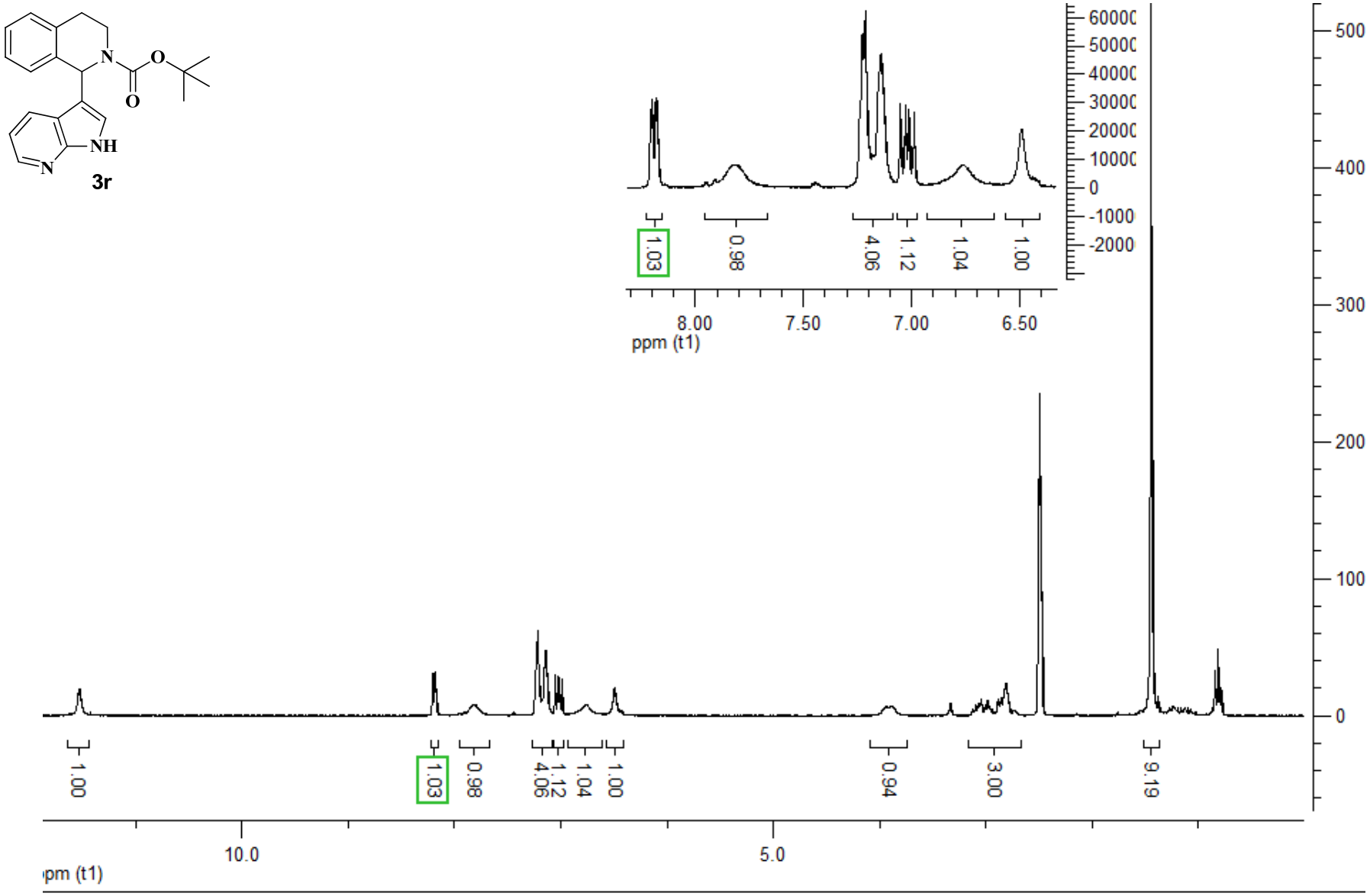

153.4
136.7
135.8
134.4
128.9
127.9
126.6
126.2
126.0
125.7
124.8
120.3
119.0
117.3
111.2
79.1
50.2
28.0
27.8
N
O
O
NH
Cl
3p
300
200
100
0
150
100
50
ppm (t1)

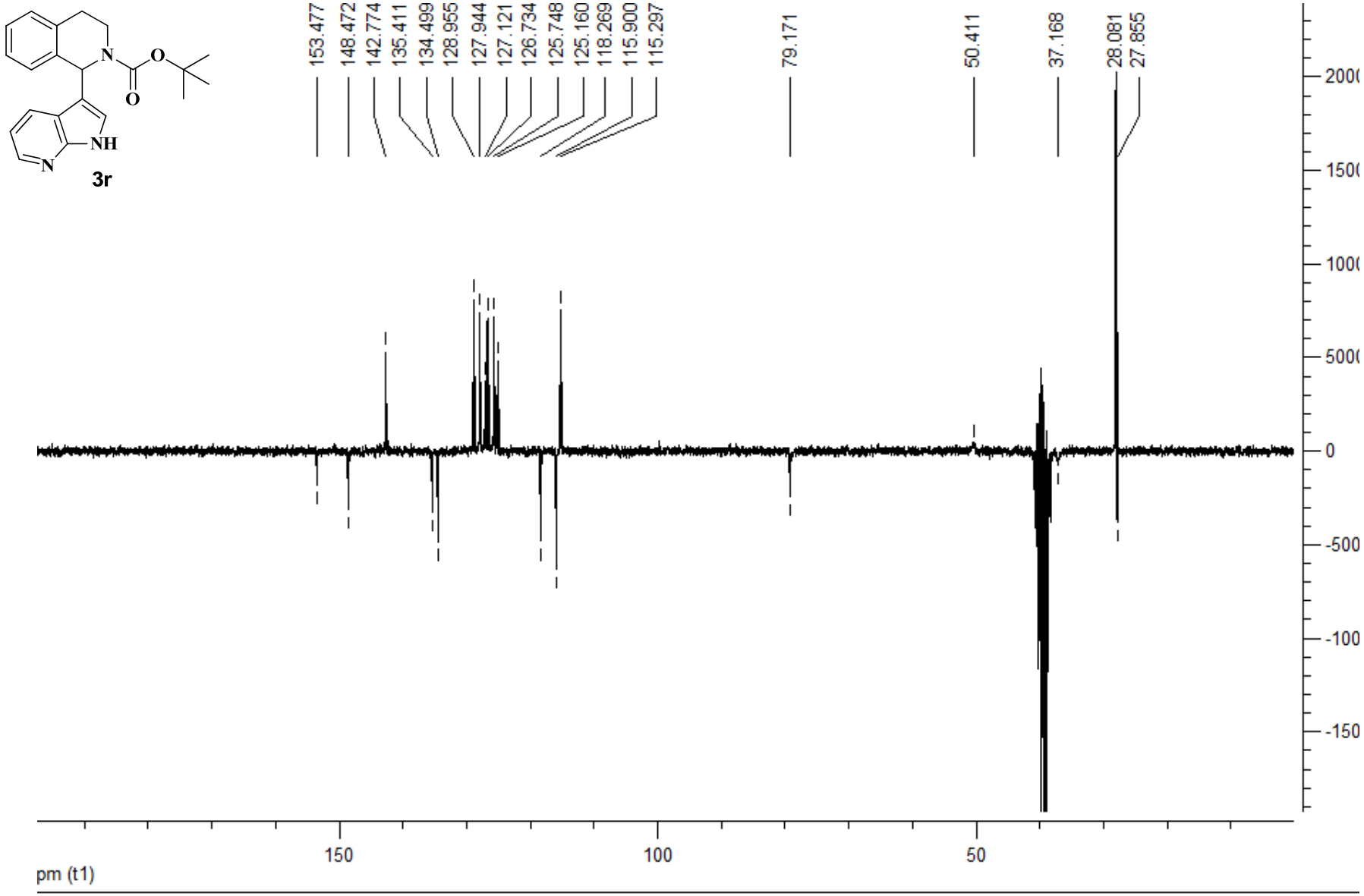

3p
154.31
136.77
135.93
134.89
129.06
128.30
128.16
126.72
125.74
125.41
125.12
121.06
120.43
119.20
110.94
79.80
50.46
37.46
28.54
28.41
130.0
125.0
120.0
ppm (t1)
150
100
50
pm (t1)


N
O
O
NH
NO2
3q
40000
30000
20000
10000
0
1.00
2.05
4.77
0.93
0.93
0.95
3.05
9.04
10.0
5.0
pm (t1)

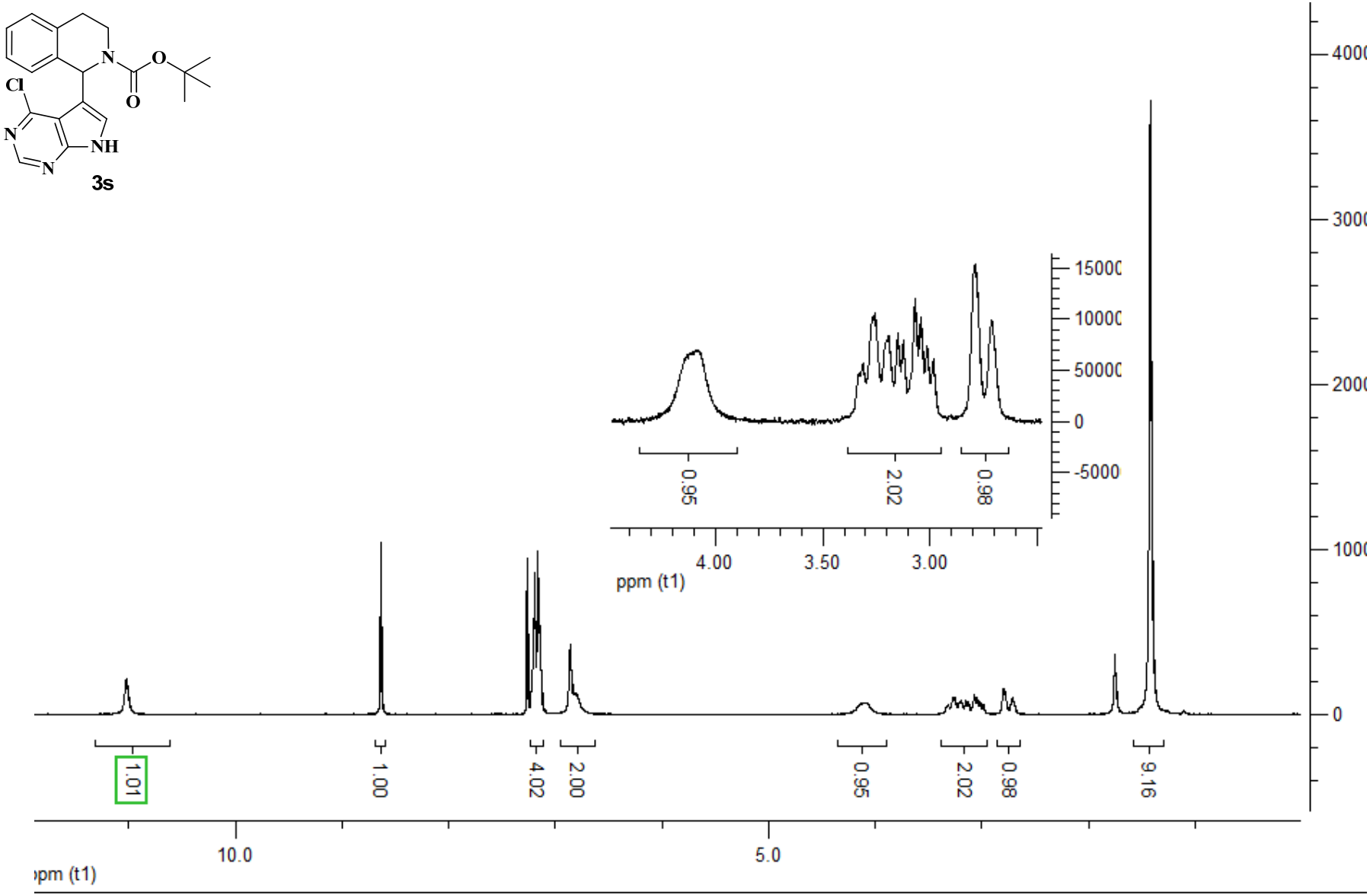

153.54
135.24
134.52
132.60
130.29
129.09
128.54
128.19
127.96
127.59
126.89
125.82
119.22
118.92
118.72
79.38
49.83
37.08
28.05
27.73
N
O
O
NH
NO2
500
0
-50
150
100
50
ppm (t1)

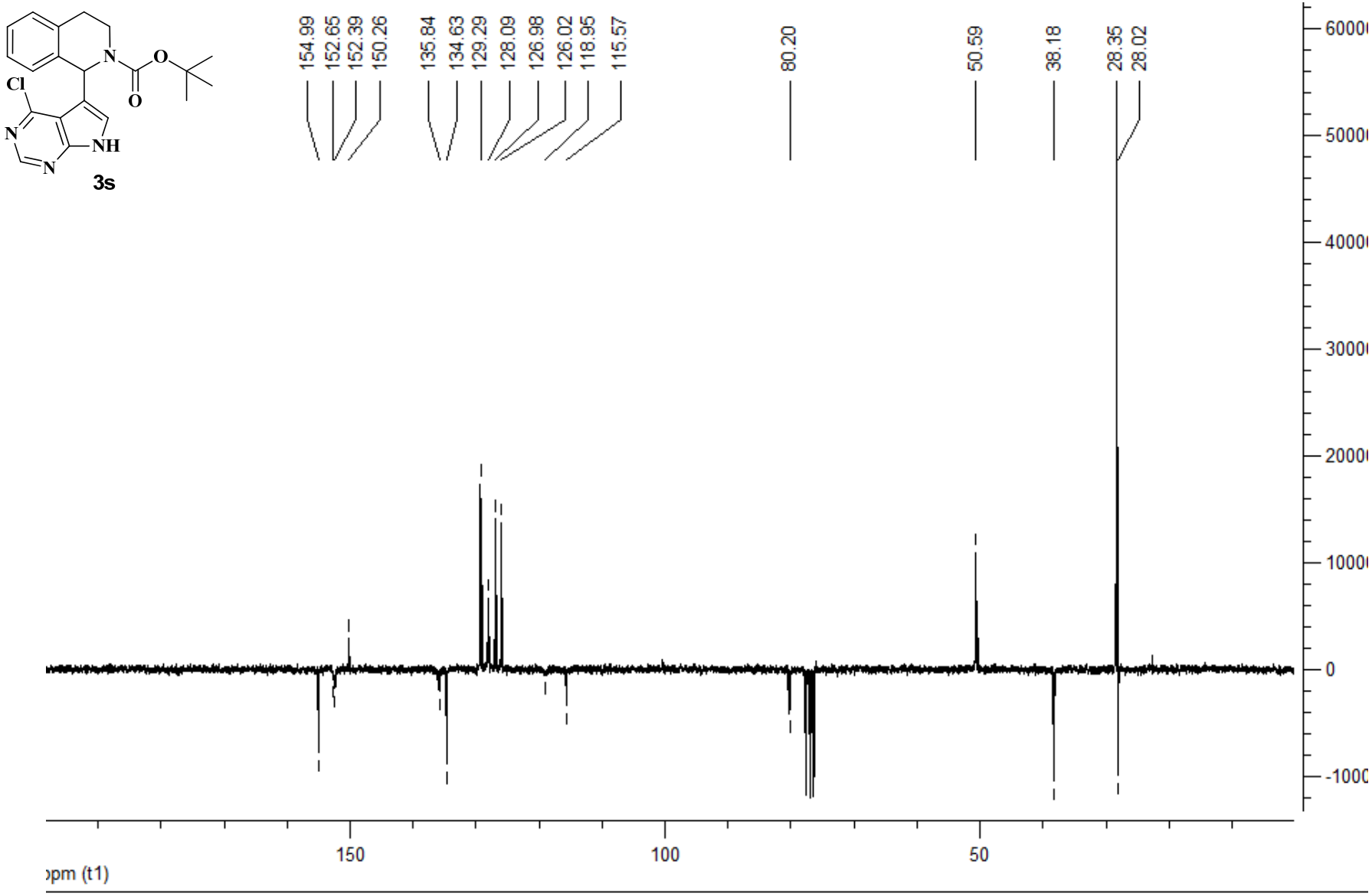
3q

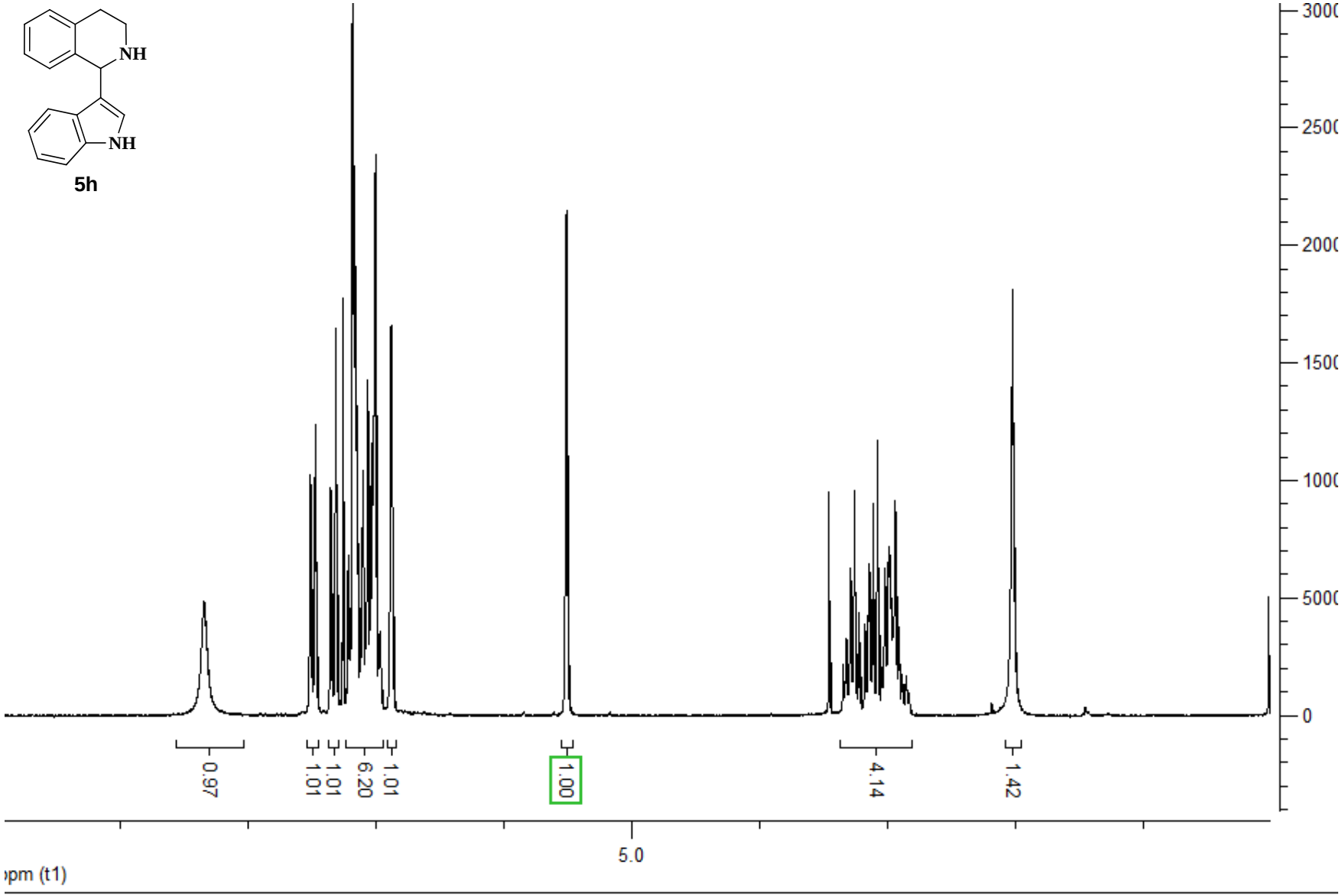

N
O
O
NH
N
3r
1.03
0.98
4.06
1.12
1.04
1.00
8.00
7.50
7.00
6.50
ppm (t1)
60000
50000
40000
30000
20000
10000
0
-1000
-2000
500
400
300
200
100
0
1.00
1.03
0.98
4.06
1.12
1.04
1.00
0.94
3.00
9.19
10.0
5.0
ppm (t1)

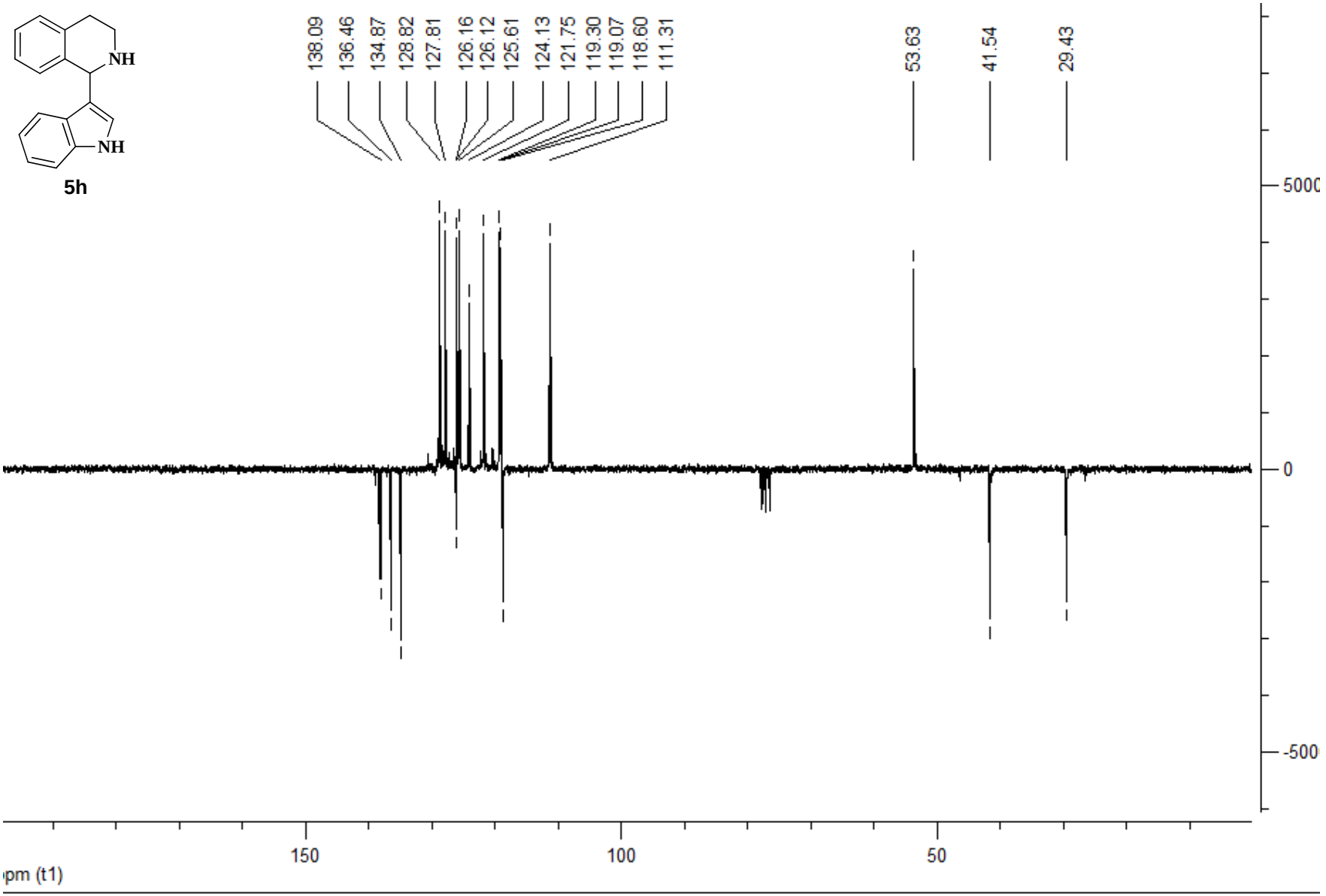

153.477
148.472
142.774
135.411
134.499
128.955
127.944
127.121
126.734
125.748
125.160
118.269
115.900
115.297
79.171
50.411
37.168
28.081
27.855
2000
1500
1000
500
0
-500
-100
-150
150
100
50
pm (t1)

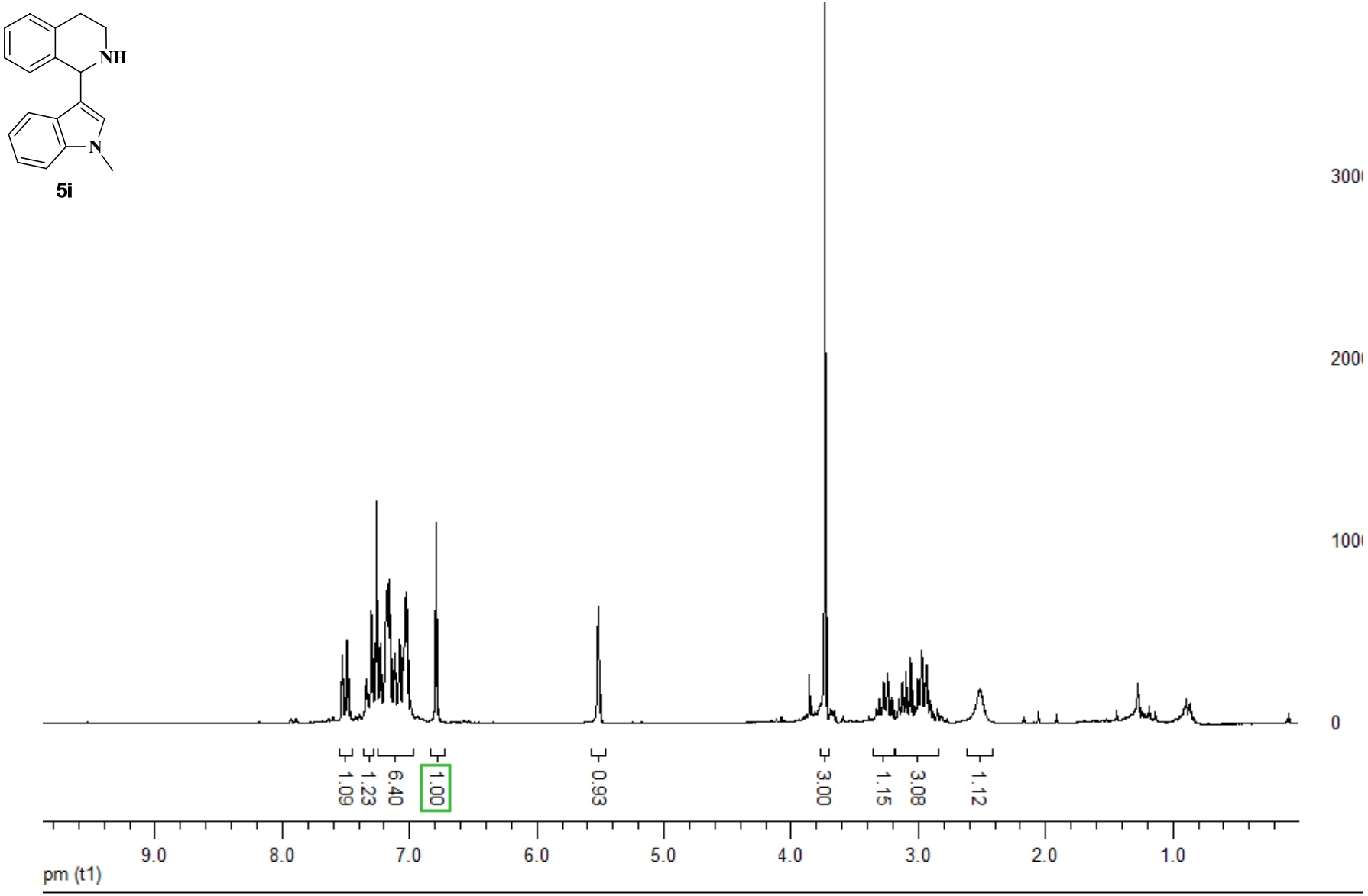
3r

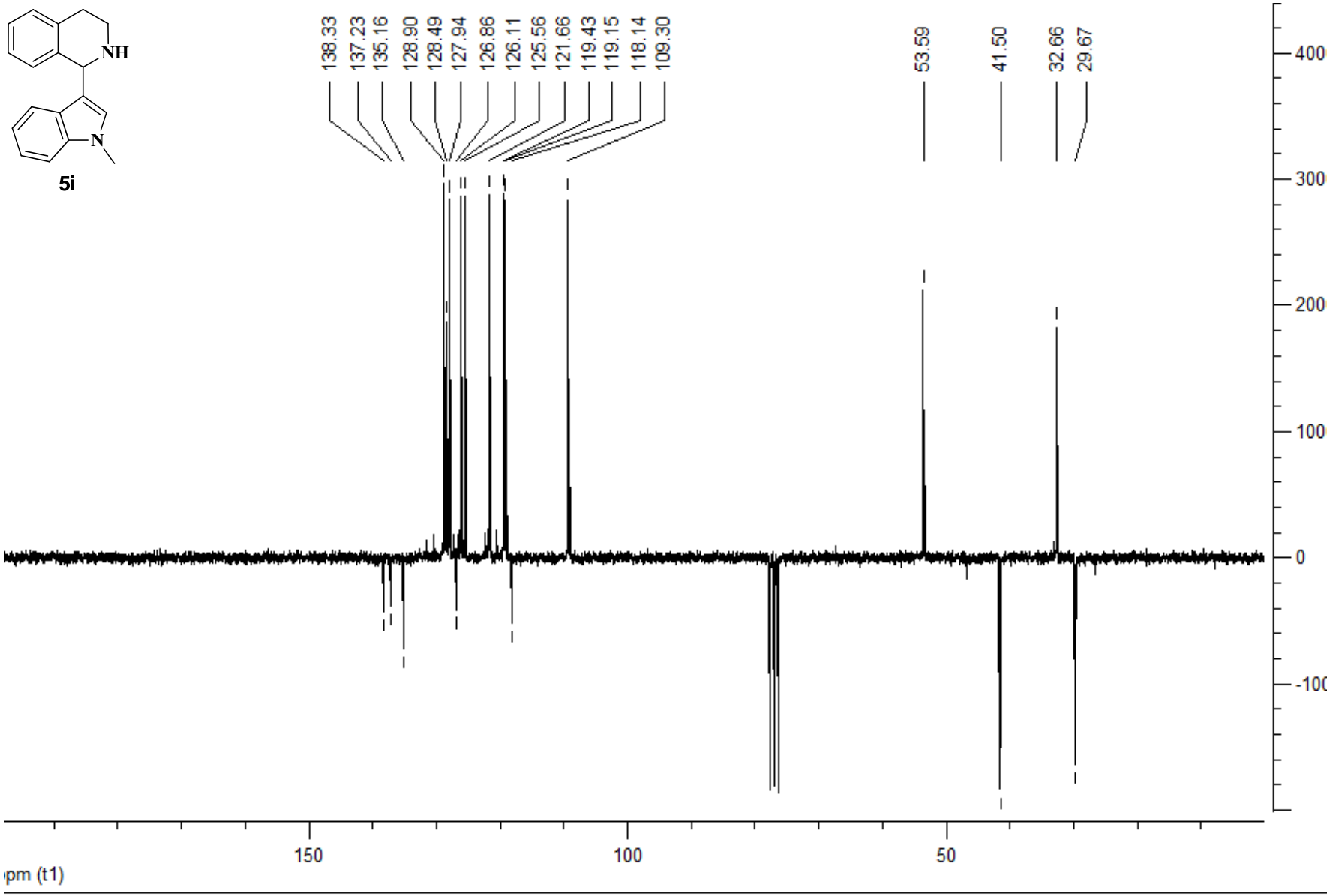

Cl
N
O
O
N
NH
N
3s
4000
3000
2000
1000
0
15000
10000
5000
0
-5000
0.95
2.02
0.98
4.00
3.50
3.00
ppm (t1)
1.01
1.00
4.02
2.00
0.95
2.02
0.98
9.16
10.0
5.0
ppm (t1)

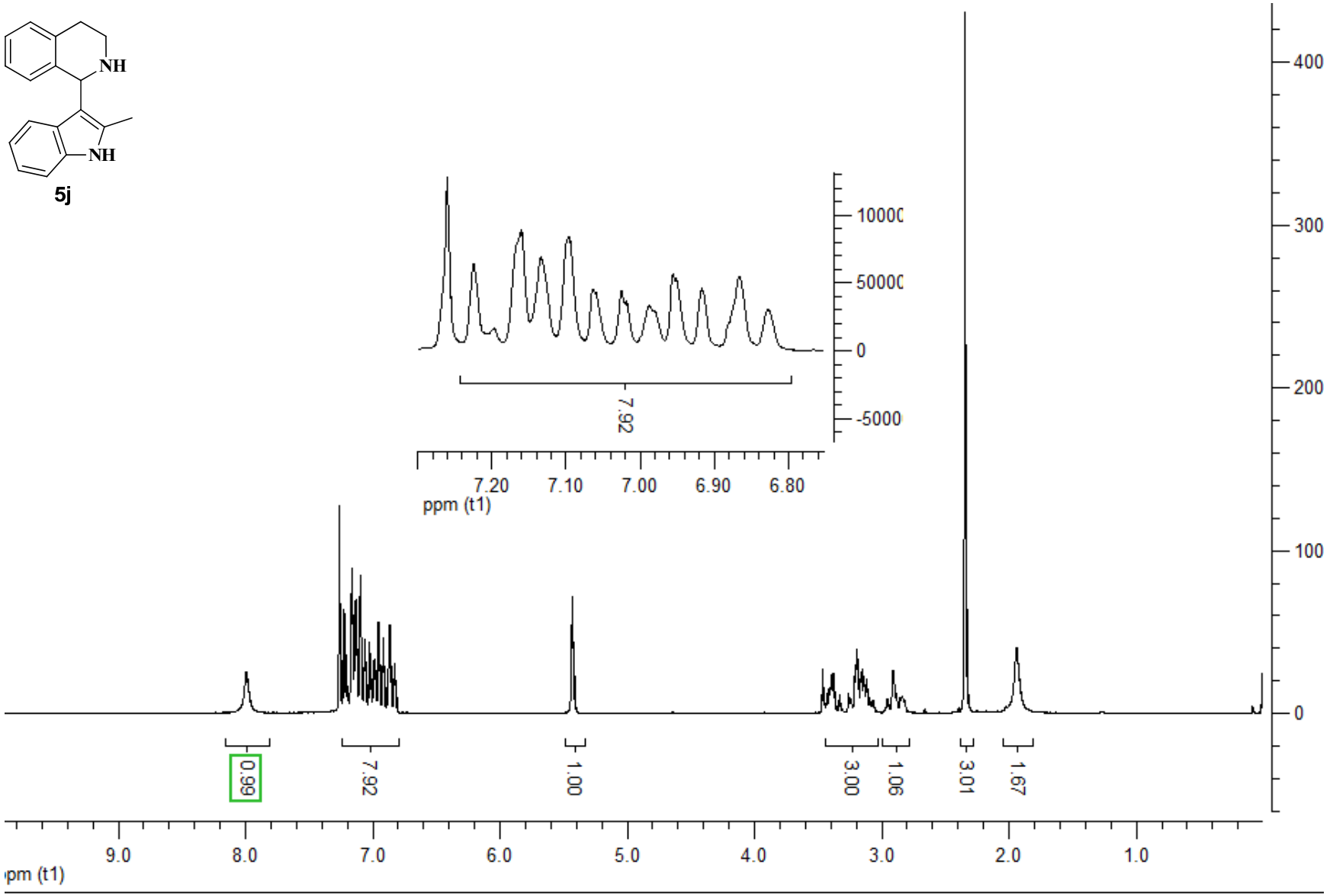

Cl
N
O
O
N
NH
N
3s
154.99
152.65
152.39
150.26
135.84
134.63
129.29
128.09
126.98
126.02
118.95
115.57
80.20
50.59
38.18
28.35
28.02
60000
50000
40000
30000
20000
10000
0
-10000
150
100
50
ppm (t1)

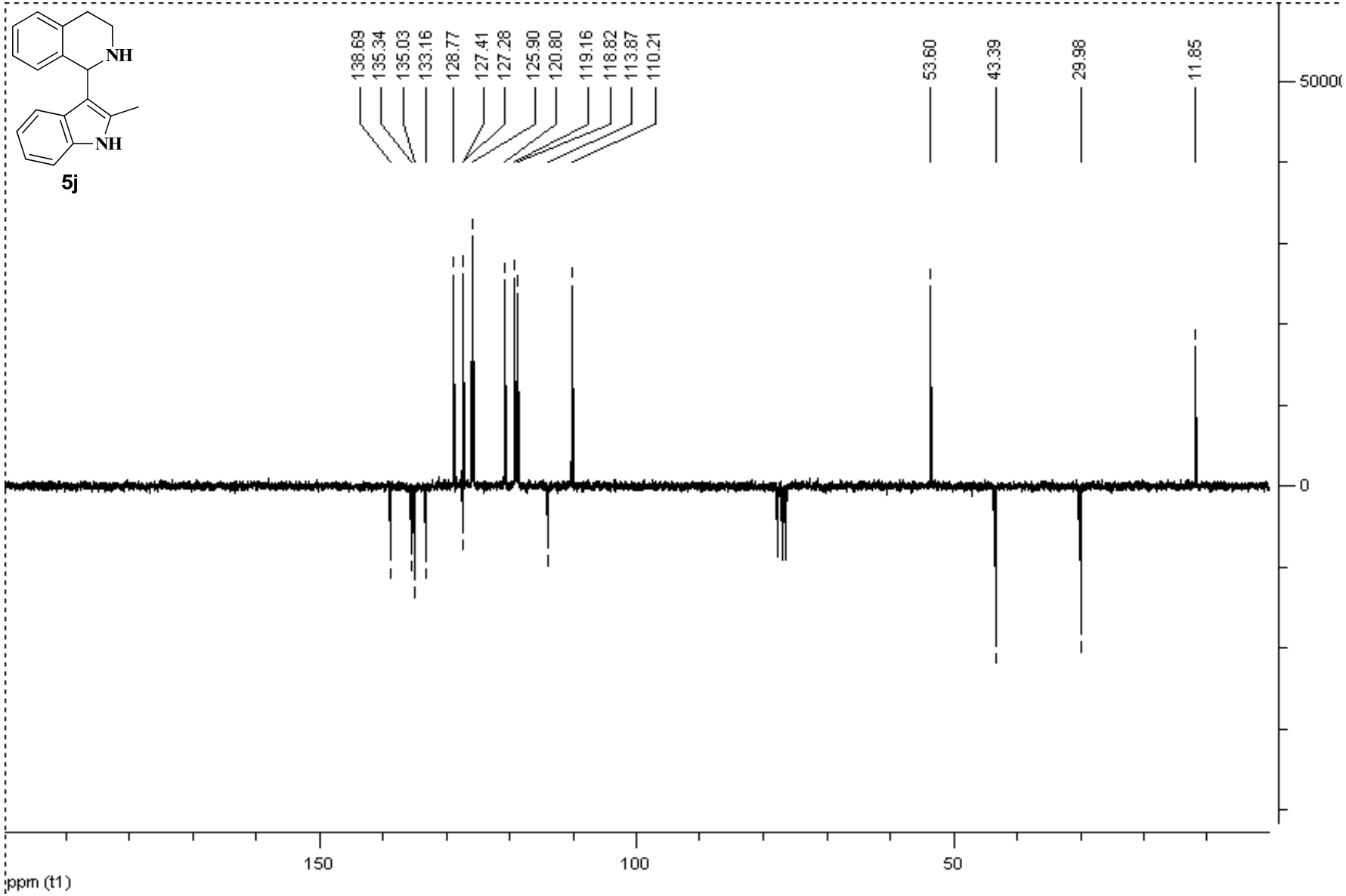

NH
NH
5h
3000
2500
2000
1500
1000
500
0
0.97
1.01
1.01
1.01
6.20
1.01
1.00
4.14
1.42
5.0
ppm (t1)

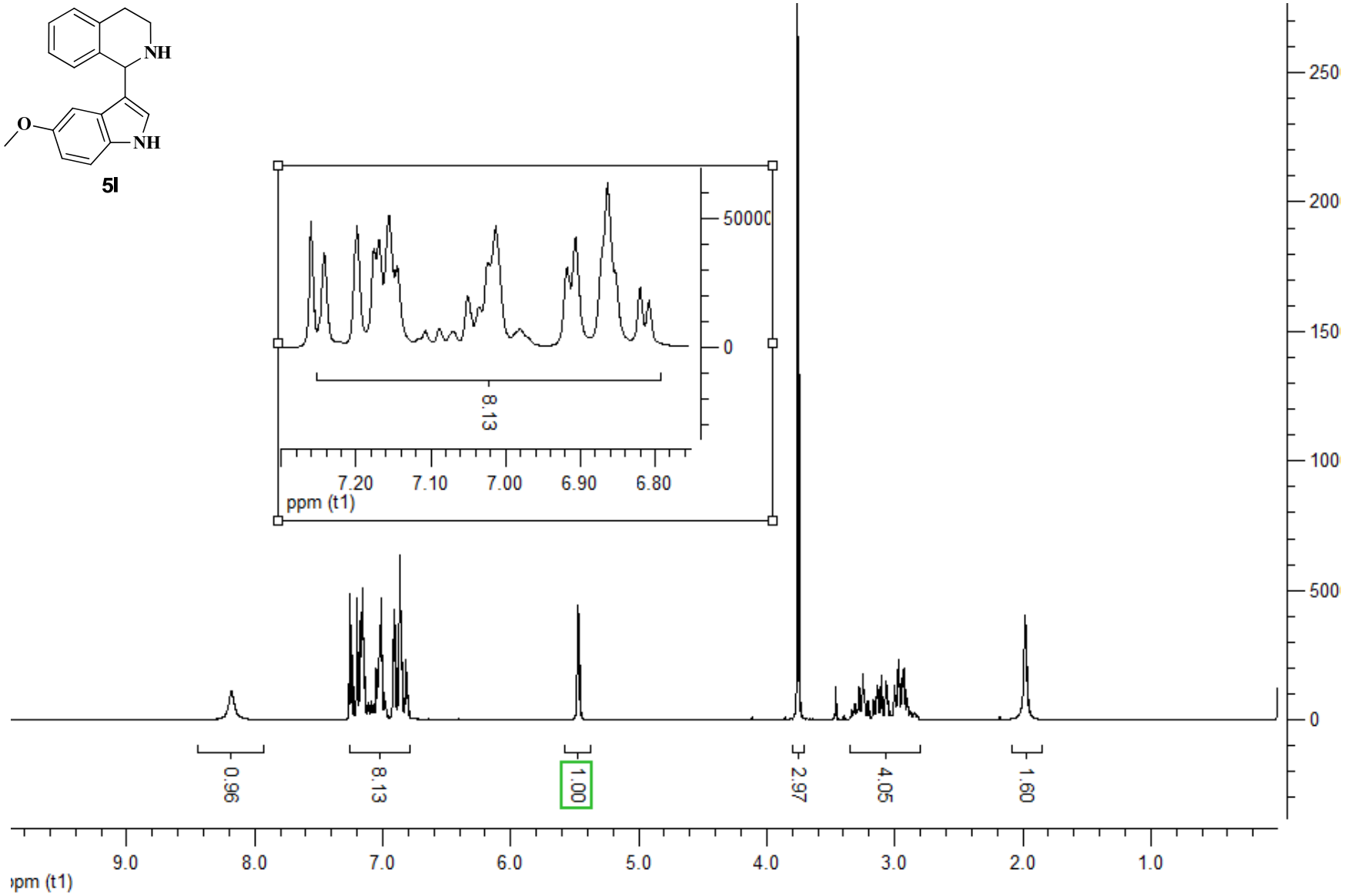

NH
NH
5h
138.09
136.46
134.87
128.82
127.81
126.16
126.12
125.61
124.13
121.75
119.30
119.07
118.60
111.31
53.63
41.54
29.43
5000
0
-500
150
100
50
ppm (t1)

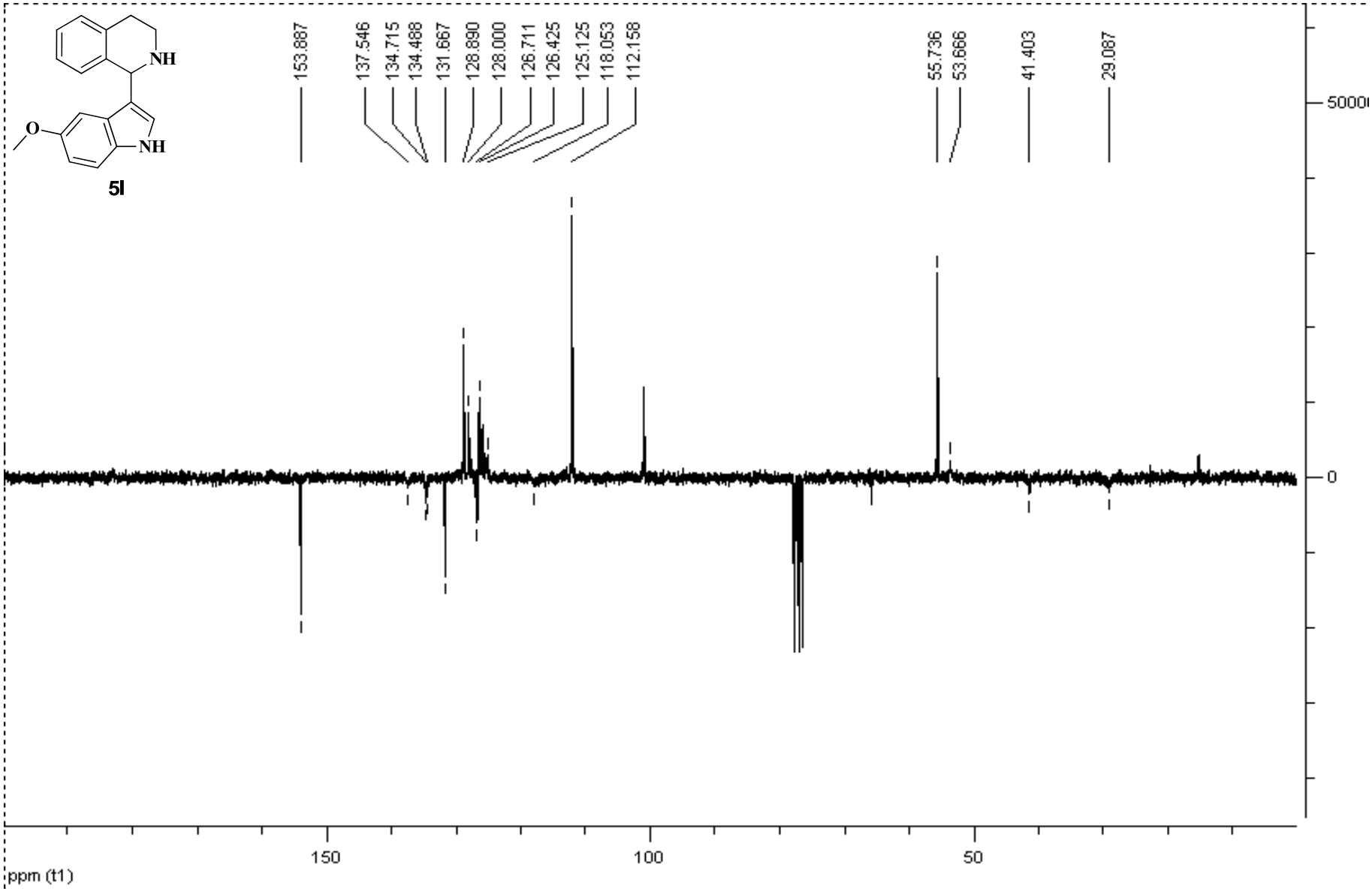

NH
N
5i
3000
2000
1000
0
1.09
1.23
6.40
1.00
0.93
3.00
1.15
3.08
1.12
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
pm (t1)

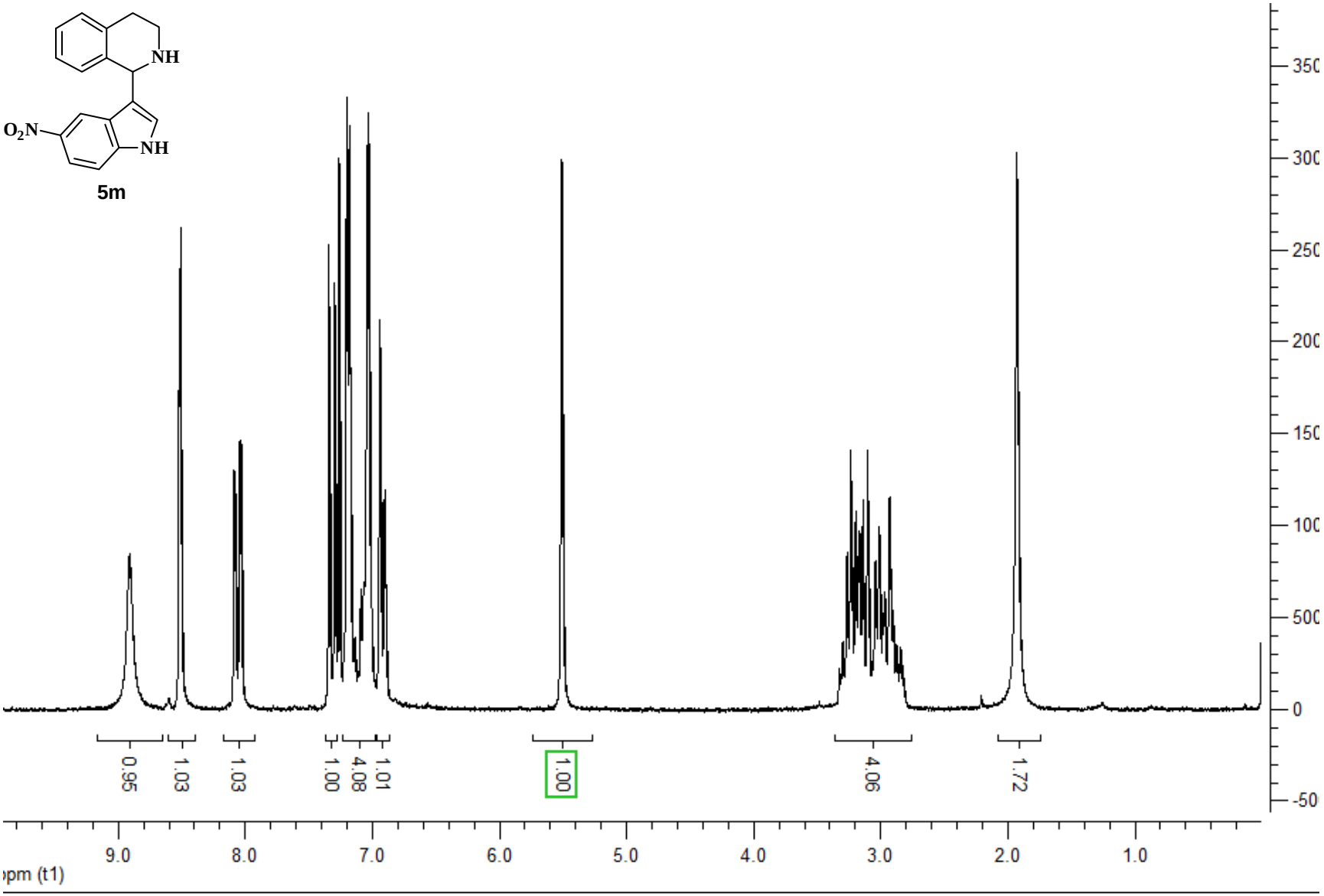

NH
N
5i
138.33
137.23
135.16
128.90
128.49
127.94
126.86
126.11
125.56
121.66
119.43
119.15
118.14
109.30
53.59
41.50
32.66
29.67
400
300
200
100
0
-100
150
100
50
ppm (t1)

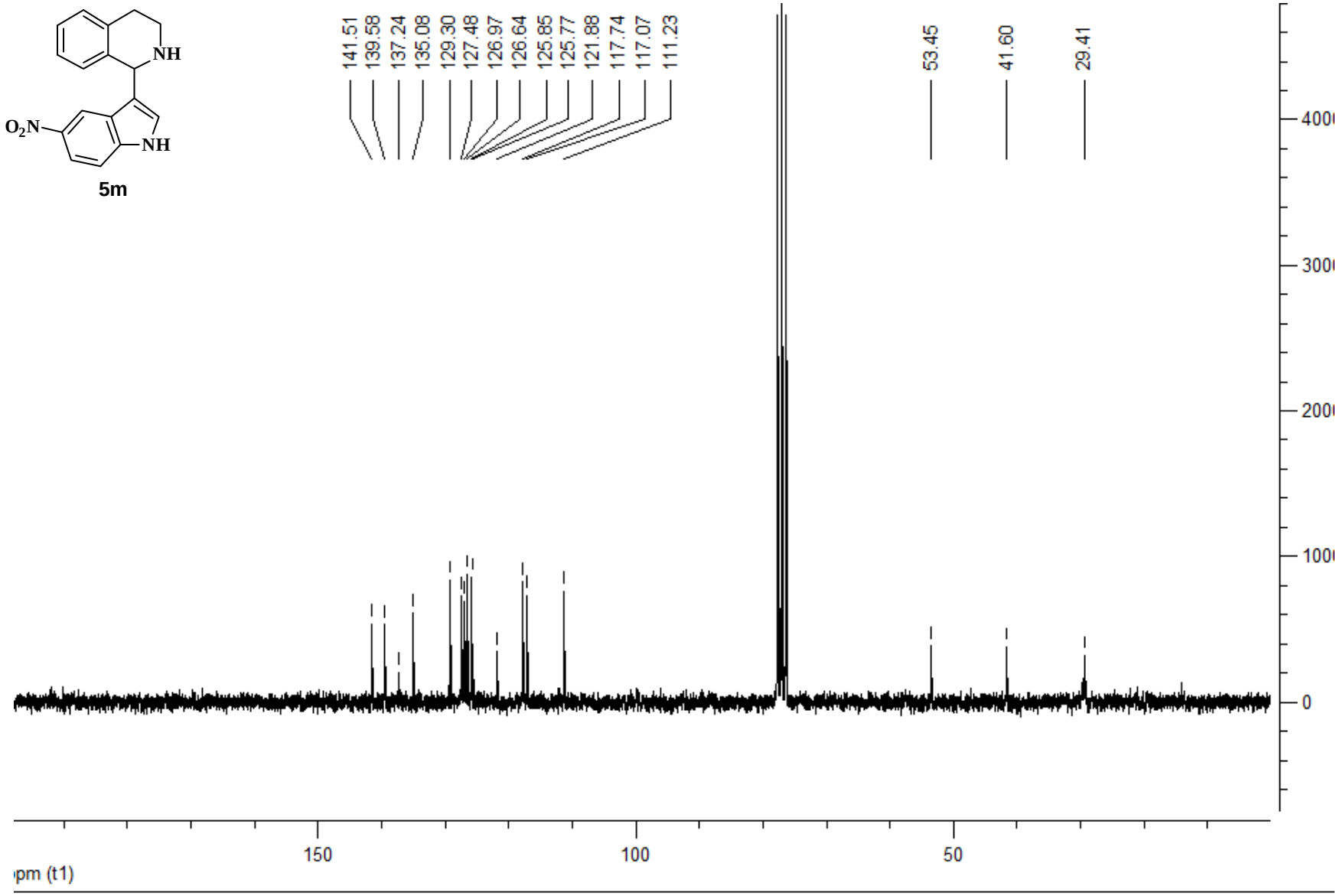

NH
NH
5j
10000
50000
0
-5000
7.92
7.20
7.10
7.00
6.90
6.80
ppm (t1)
400
300
200
100
0
0.99
7.92
1.00
3.00
1.06
3.01
1.67
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

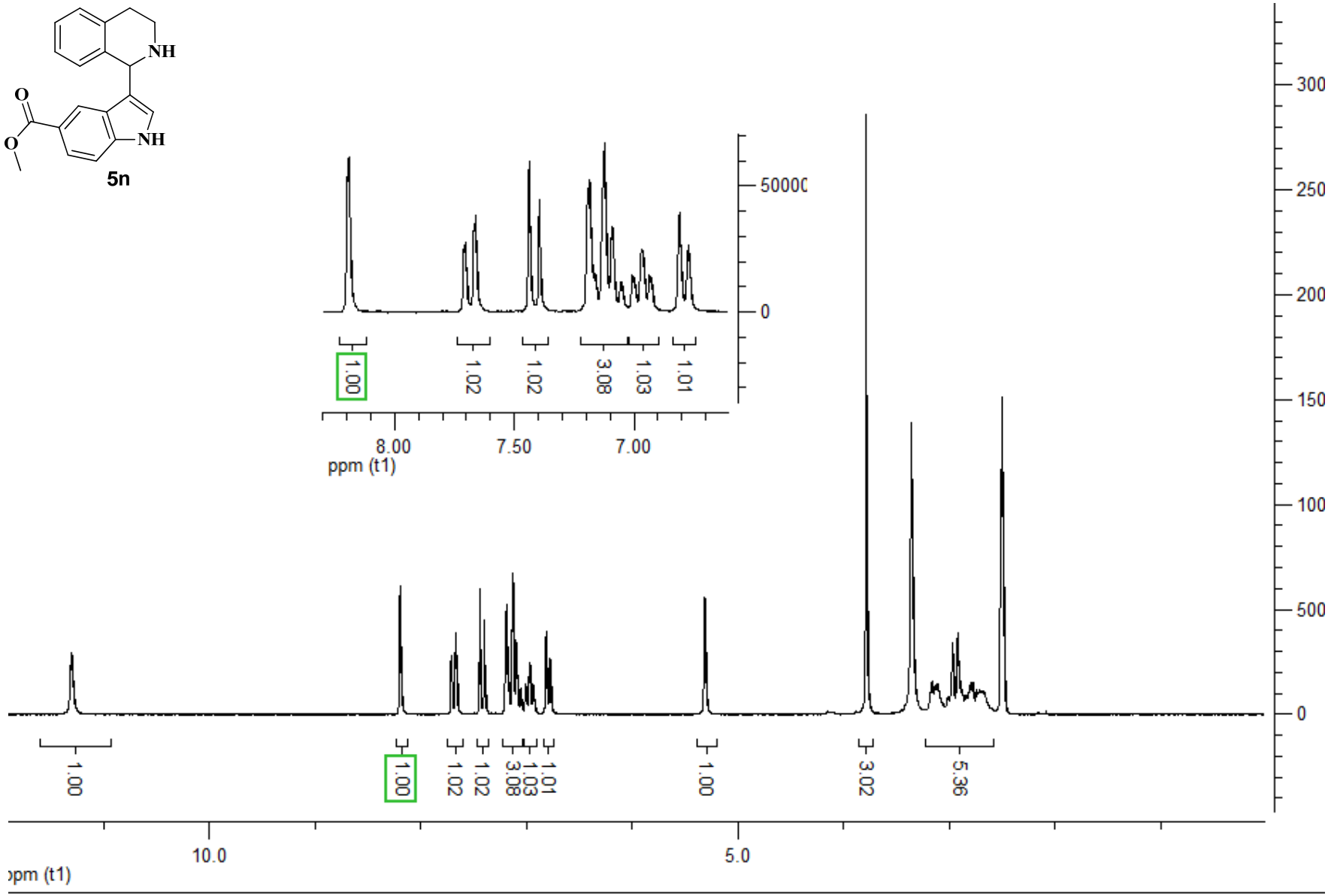

NH
NH
5j
138.69
135.34
135.03
133.16
128.77
127.41
127.28
125.90
120.80
119.16
118.82
113.87
110.21
53.60
43.39
29.98
11.85
50000
0
150
100
50
ppm (t1)

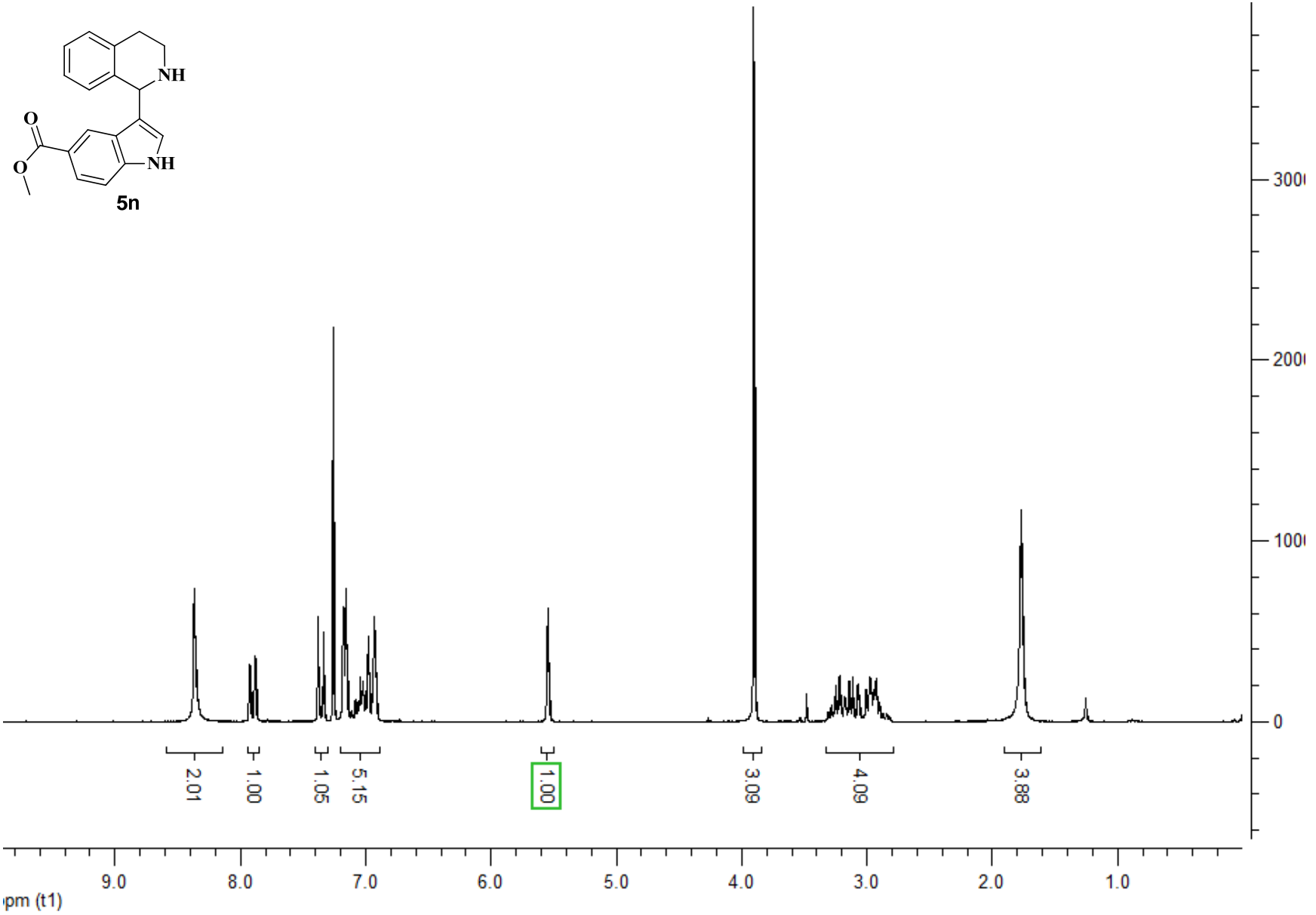

NH
O
NH
5l
50000
0
8.13
7.20
7.10
7.00
6.90
6.80
ppm (t1)
250
200
150
100
500
0
0.96
8.13
1.00
2.97
4.05
1.60
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

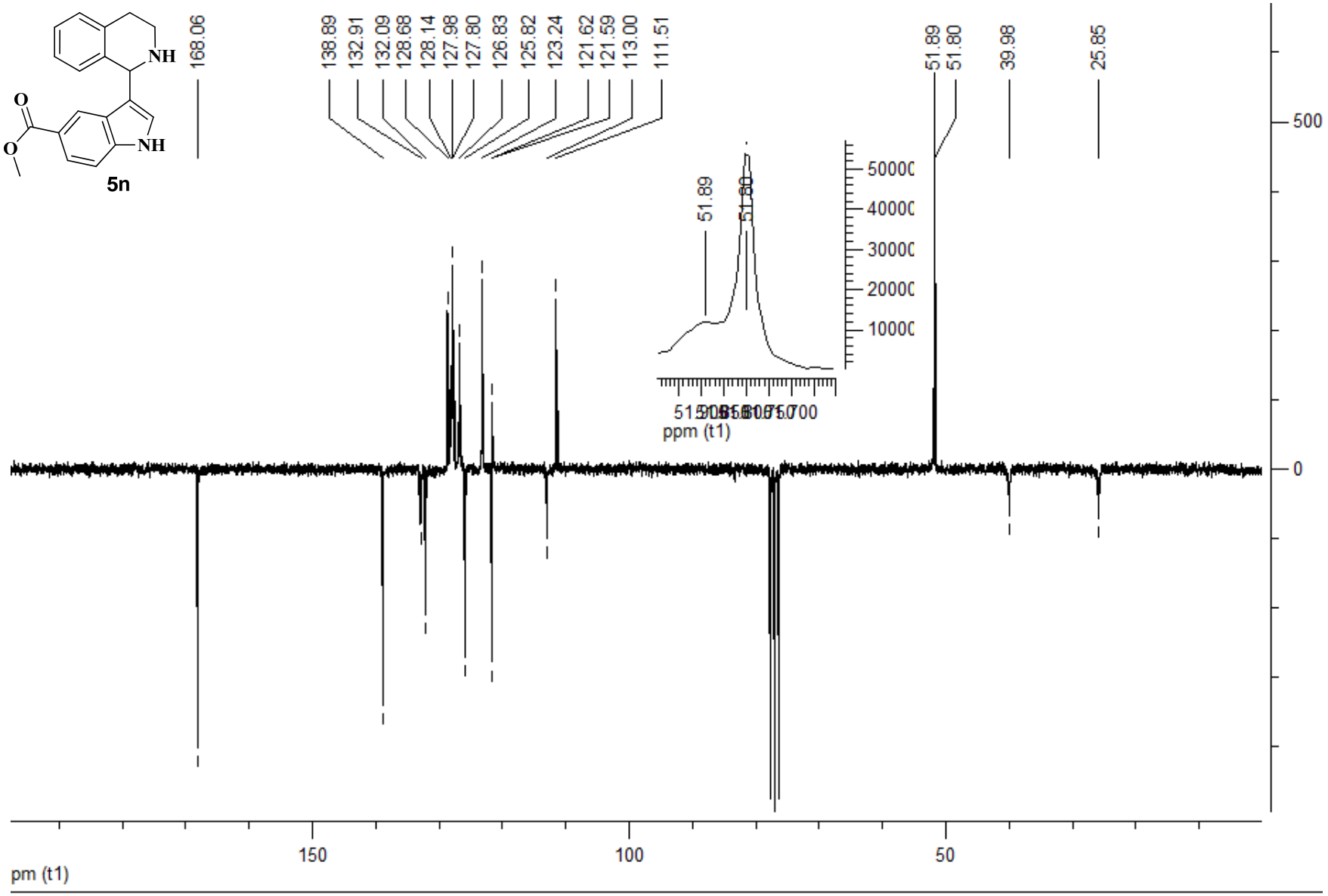

NH
O
NH
5l
153.887
137.546
134.715
134.488
131.667
128.890
128.000
126.711
126.425
125.125
118.053
112.158
55.736
53.666
41.403
29.087
50000
0
150
100
50
ppm (t1)

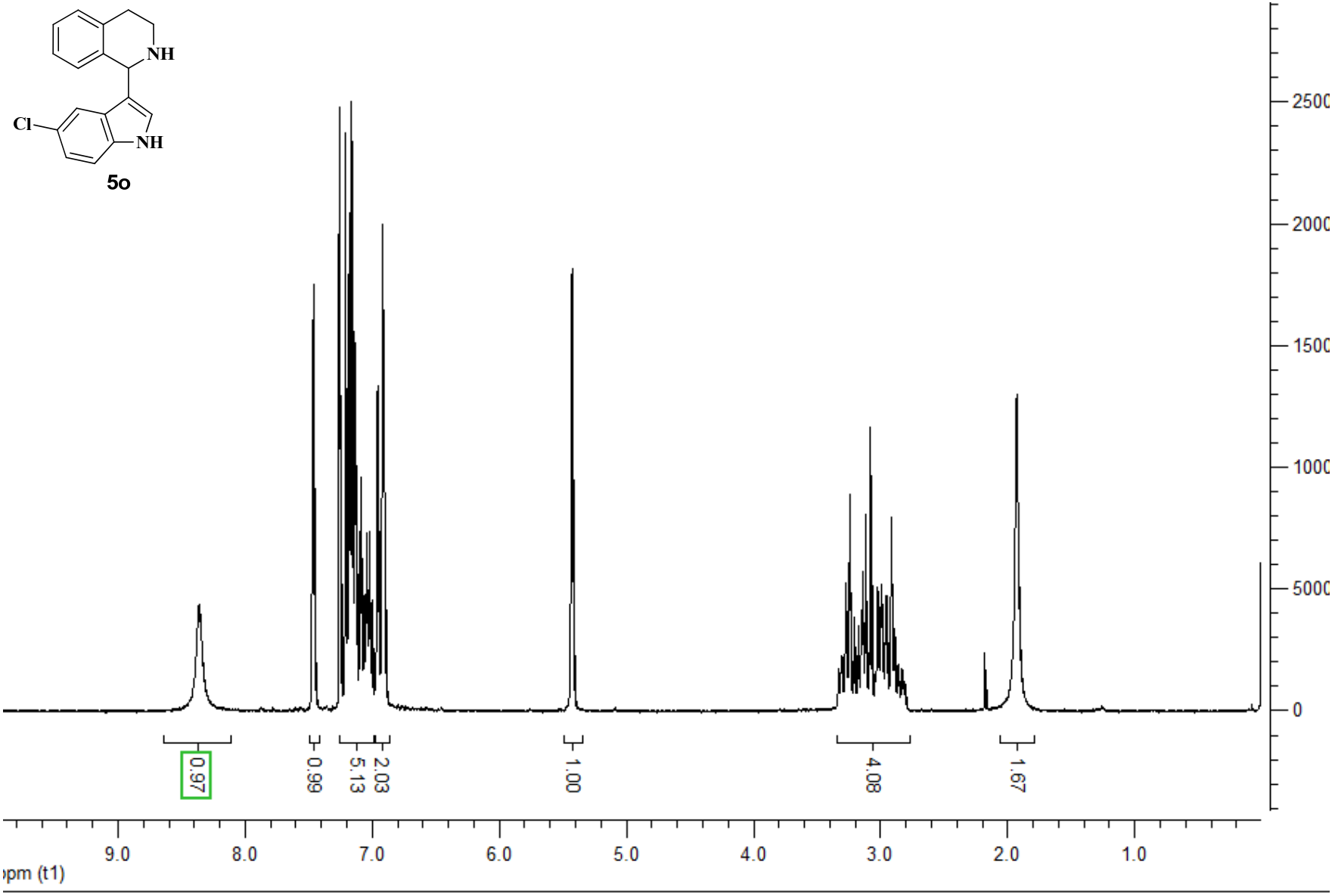

NH
O2N
NH
5m
350
300
250
200
150
100
500
0
-50
0.95
1.03
1.03
1.00
4.08
1.01
1.00
4.06
1.72
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

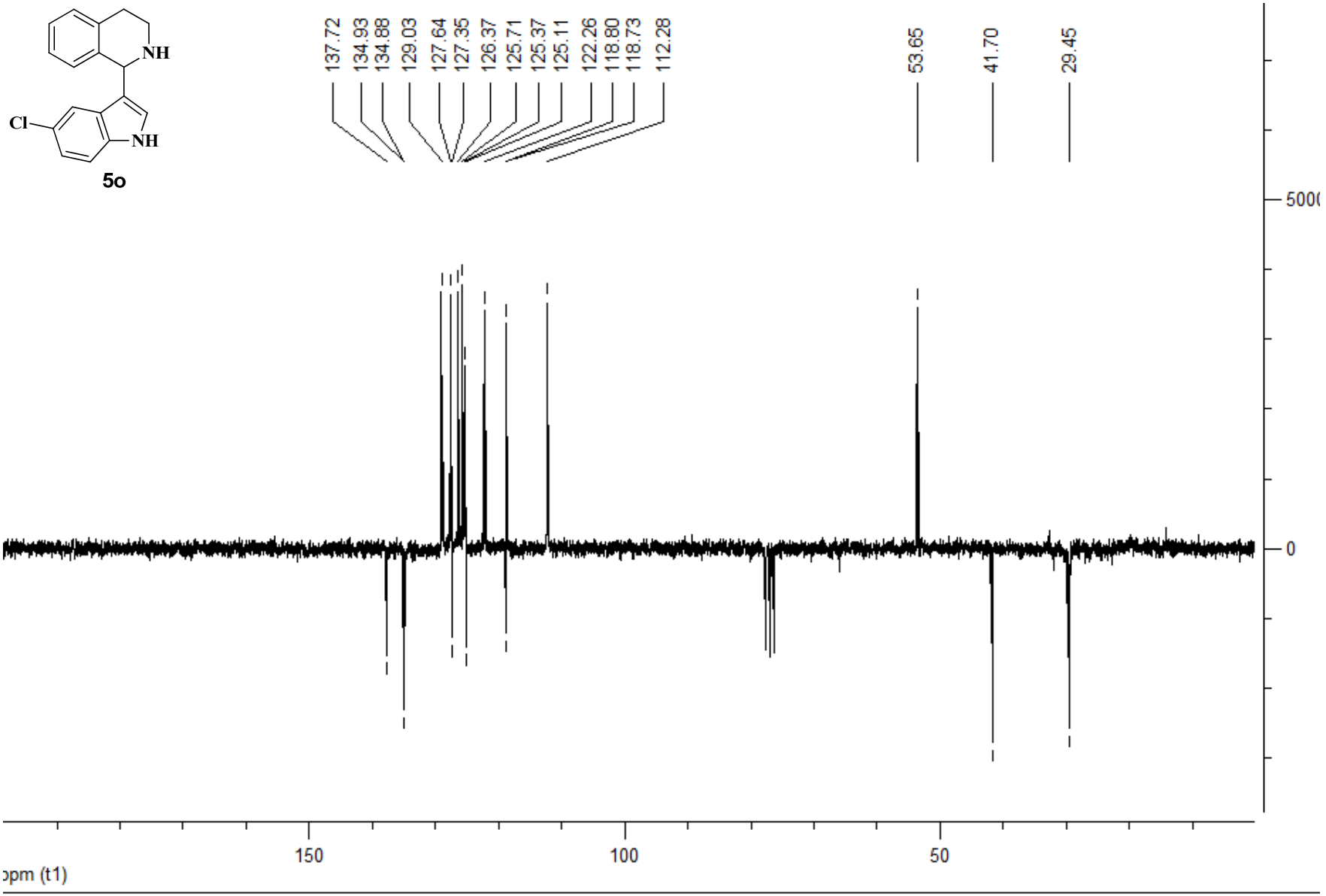

NH
O2N
NH
5m
141.51
139.58
137.24
135.08
129.30
127.48
126.97
126.64
125.85
125.77
121.88
117.74
117.07
111.23
53.45
41.60
29.41
400
300
200
100
0
150
100
50
ppm (t1)

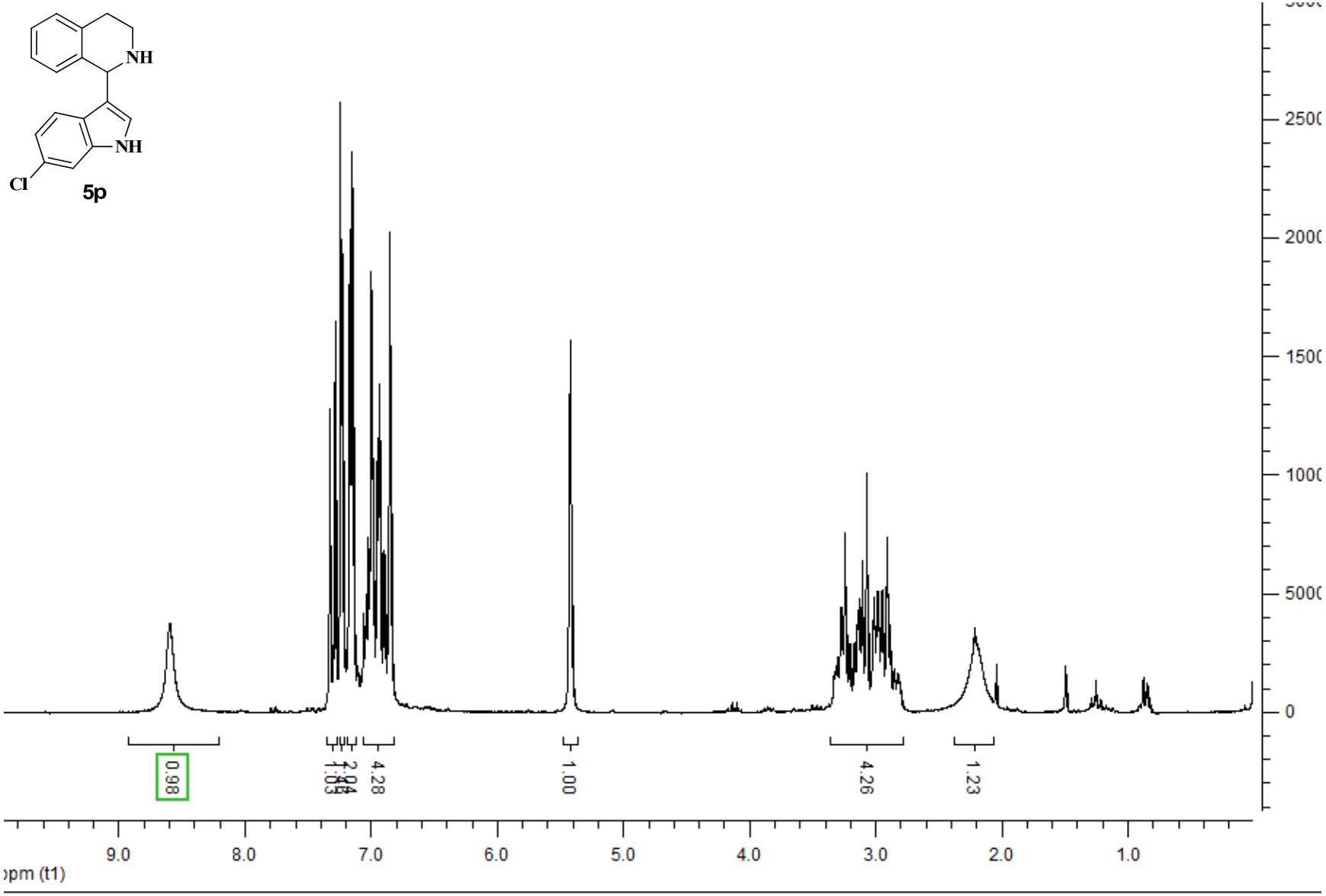

NH
O
O
NH
5n
50000
0
1.00
1.02
1.02
3.08
1.03
1.01
8.00
7.50
7.00
ppm (t1)
300
250
200
150
100
500
0
1.00
1.00
1.02
1.02
3.08
1.03
1.01
1.00
3.02
5.36
10.0
5.0
ppm (t1)

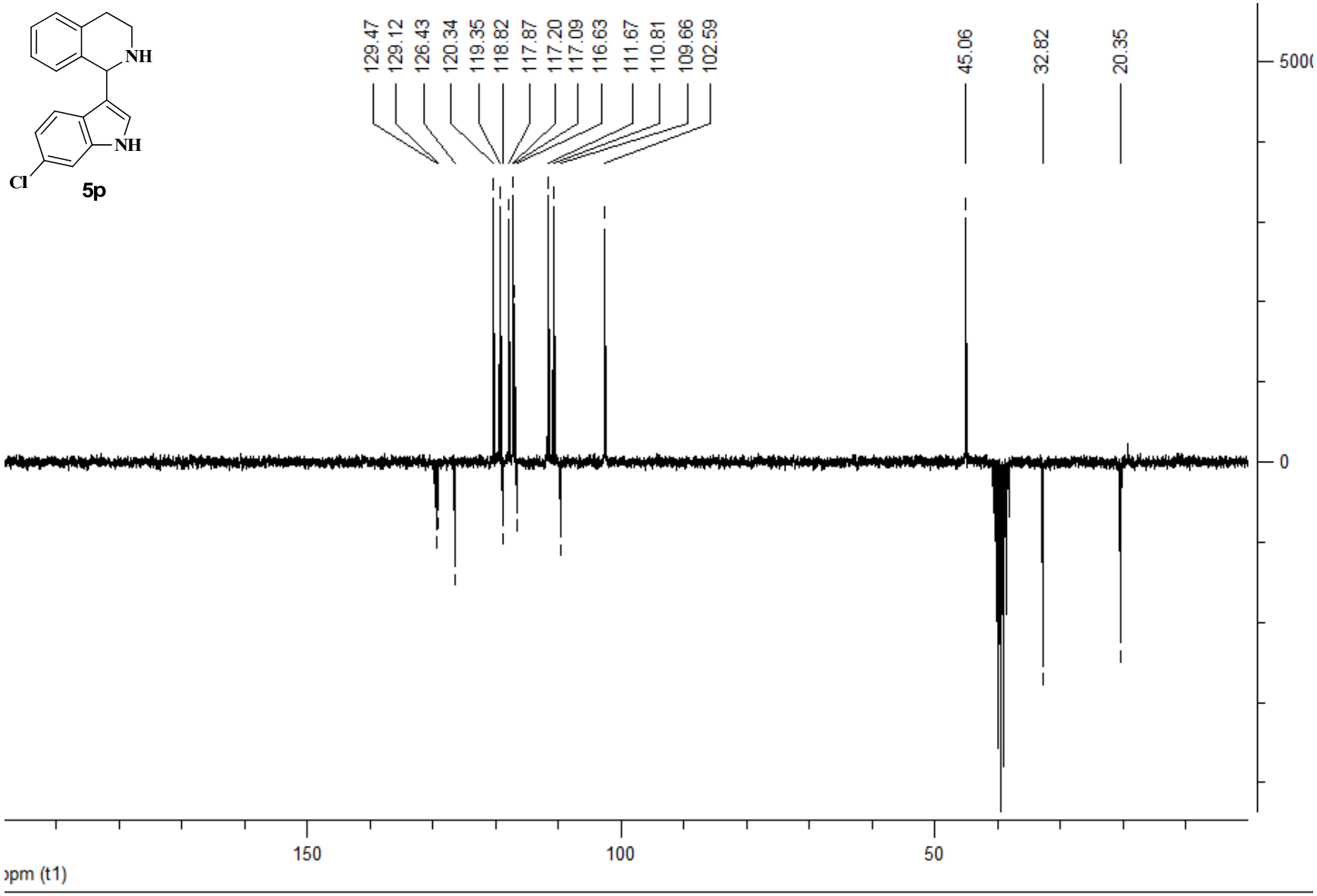

NH
O
O
NH
5n
2.01
1.00
1.05
5.15
1.00
3.09
4.09
3.88
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
pm (t1)

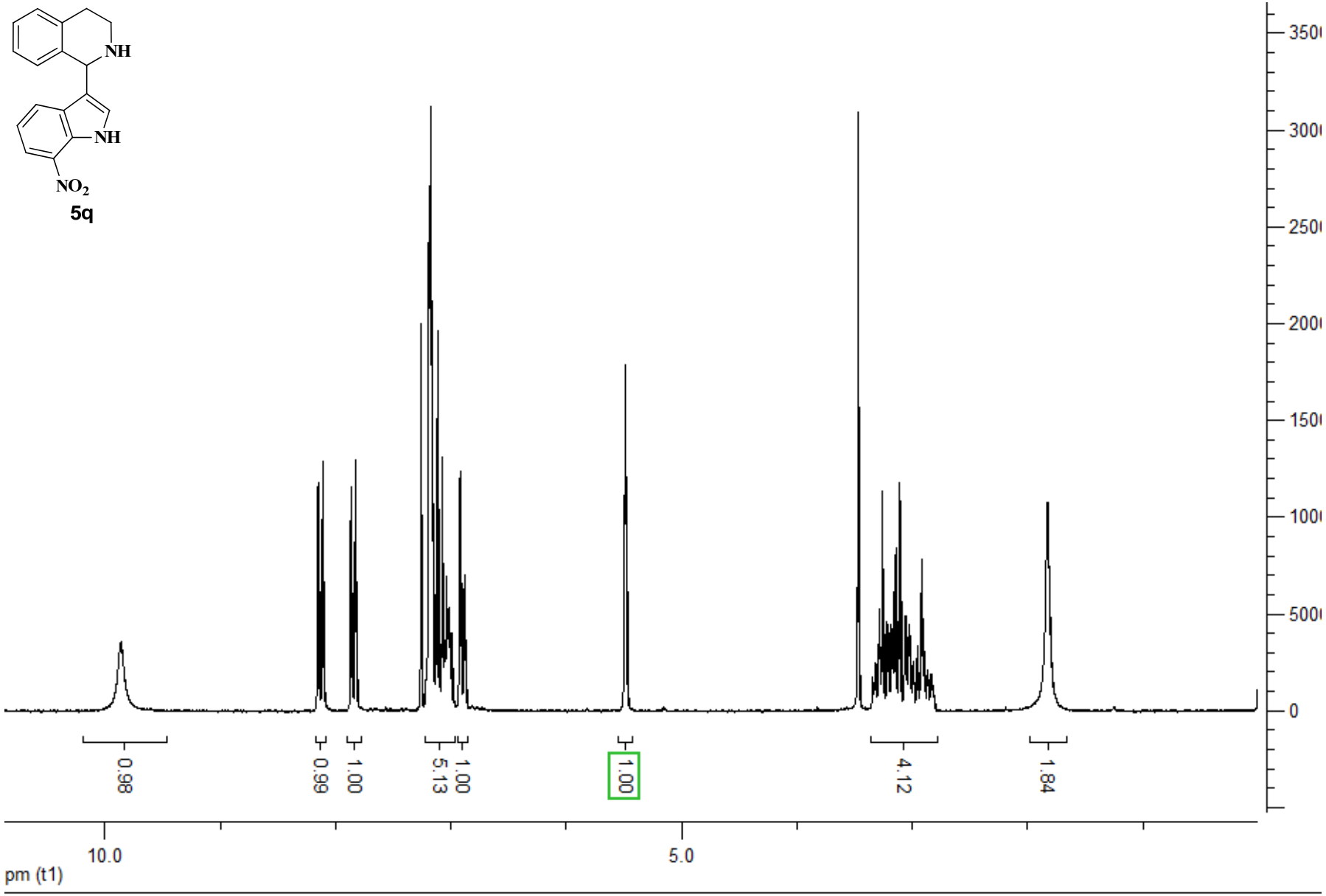

NH
O
O
NH
5n
168.06
138.89
132.91
132.09
128.68
128.14
127.98
127.80
126.83
125.82
123.24
121.62
121.59
113.00
111.51
51.89
51.80
39.98
25.85
51.89
51.80
50000
40000
30000
20000
10000
ppm (t1)
500
0
150
100
50
pm (t1)

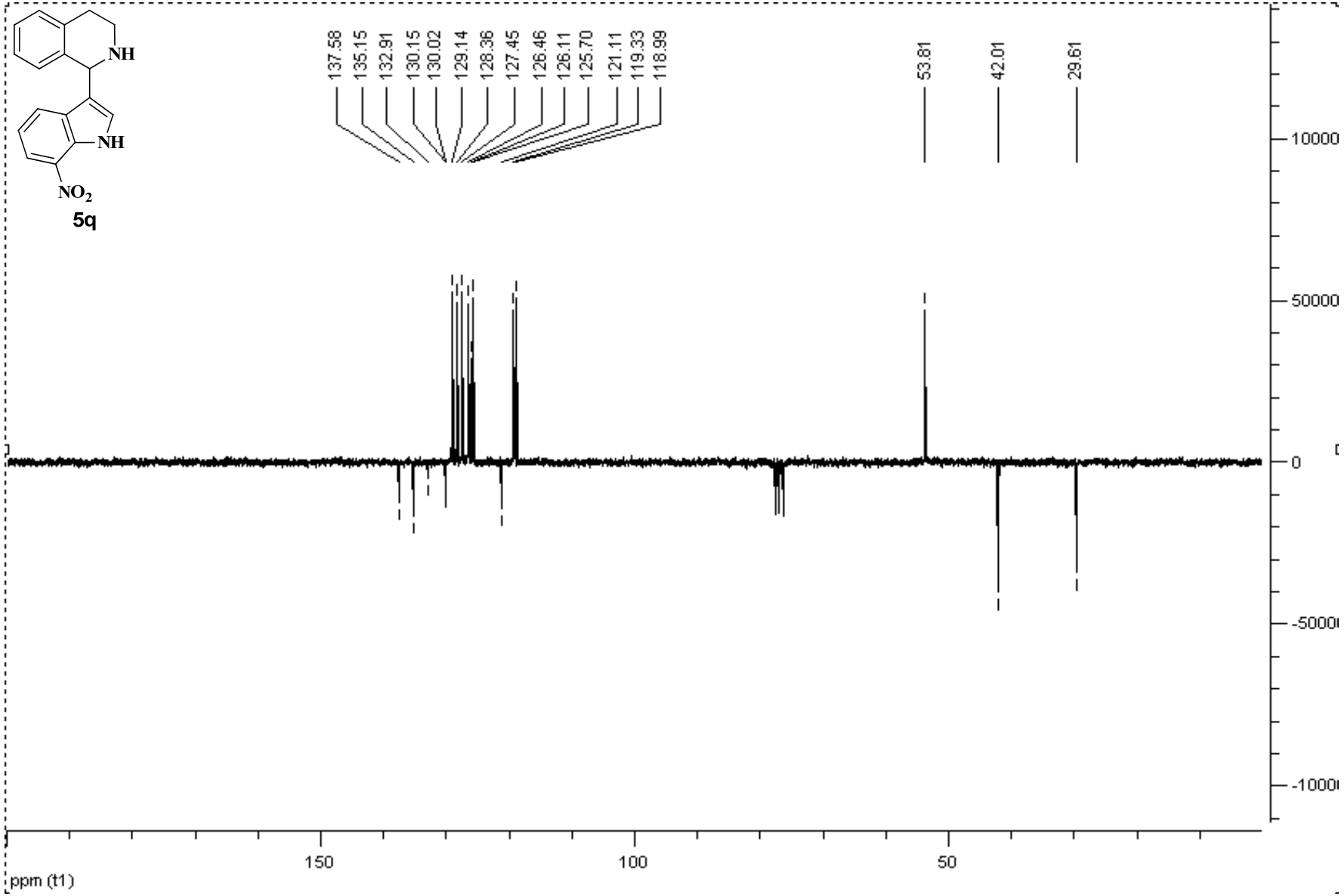

NH
Cl
NH
5o
2500
2000
1500
1000
5000
0
0.97
0.99
5.13
2.03
1.00
4.08
1.67
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

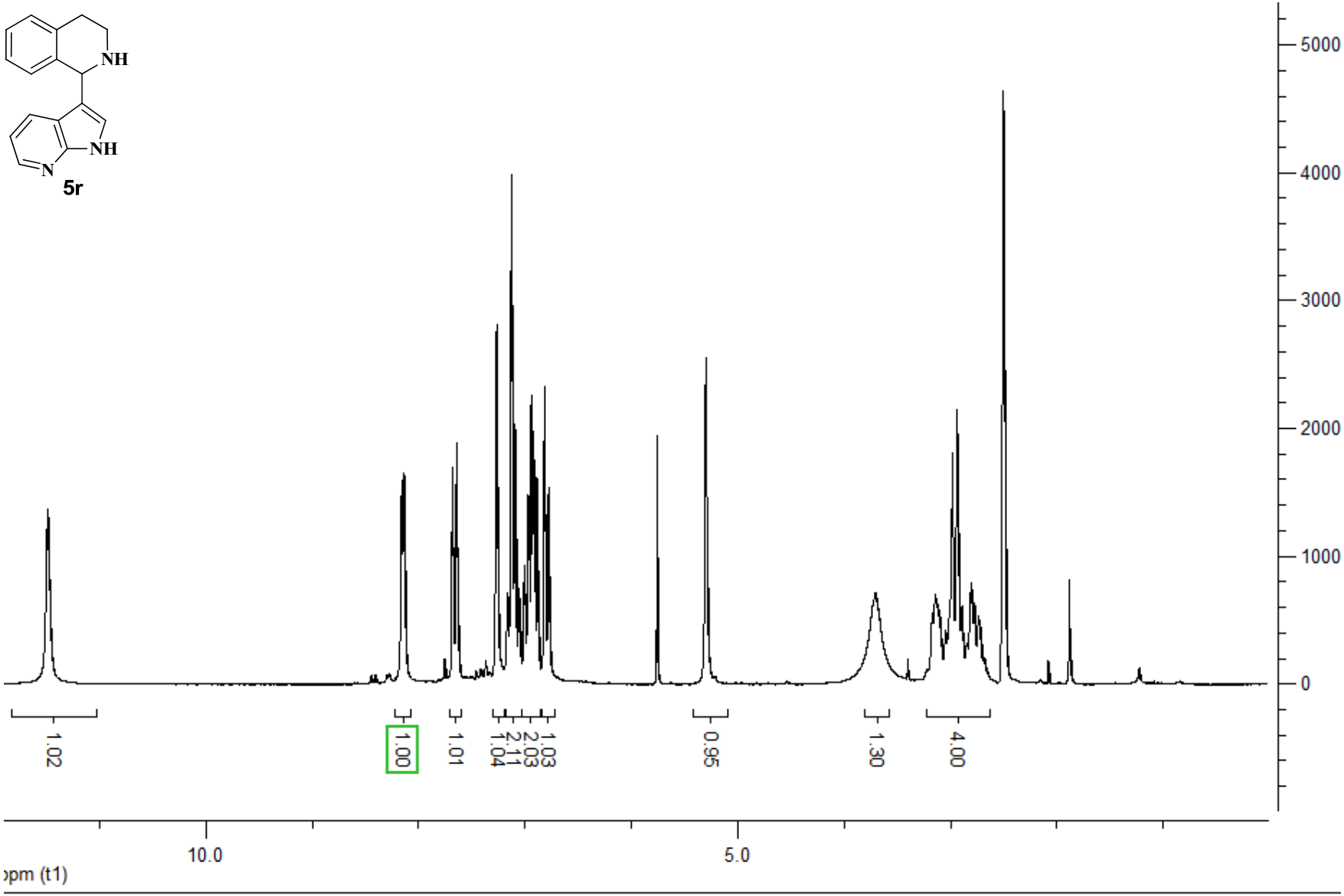

NH
Cl
NH
5o
137.72
134.93
134.88
129.03
127.64
127.35
126.37
125.71
125.37
125.11
122.26
118.80
118.73
112.28
53.65
41.70
29.45
5000
0
150
100
50
ppm (t1)

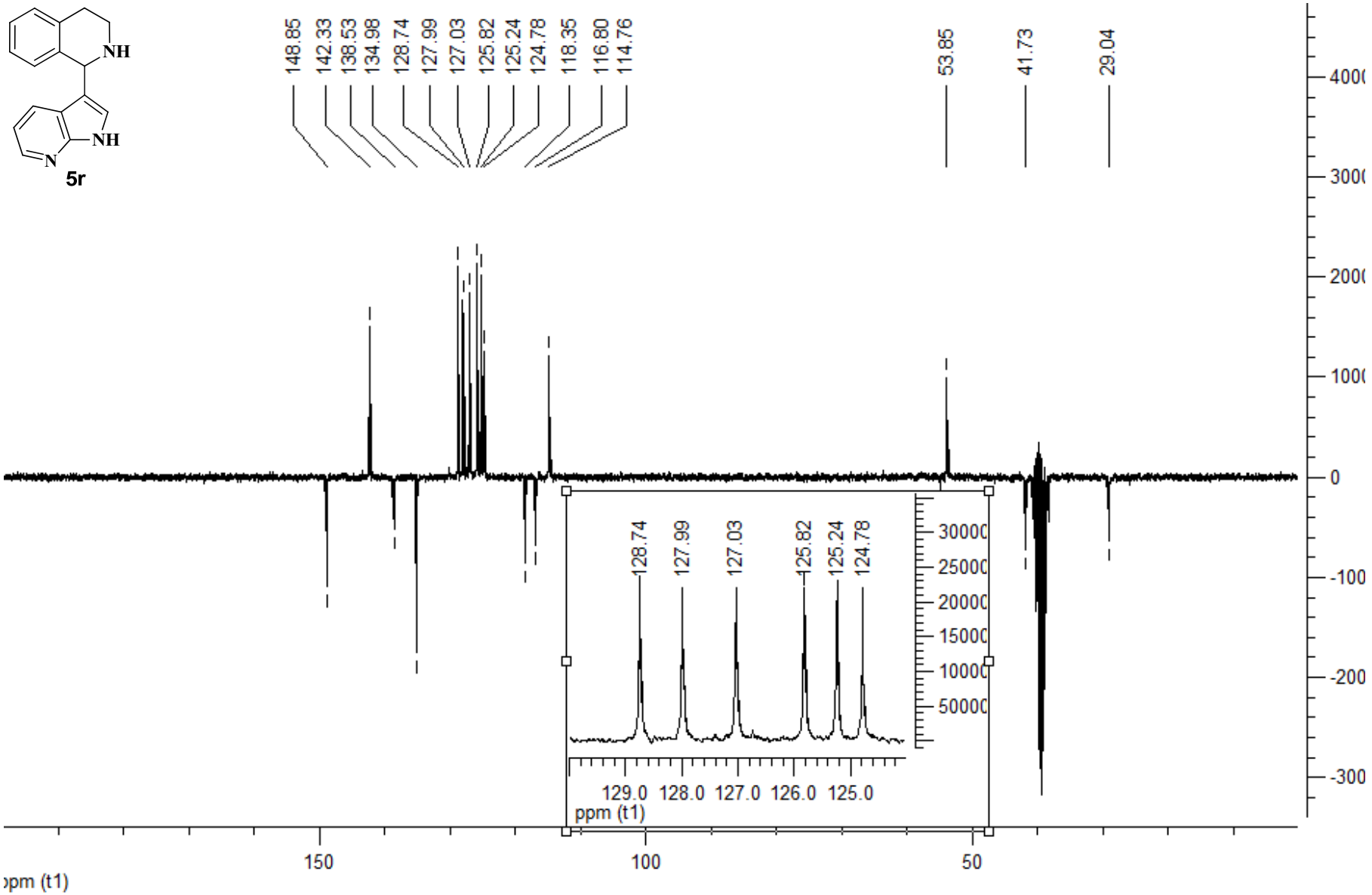

NH
NH
Cl
5p
2500
2000
1500
1000
5000
0
0.98
4.28
1.00
4.26
1.23
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

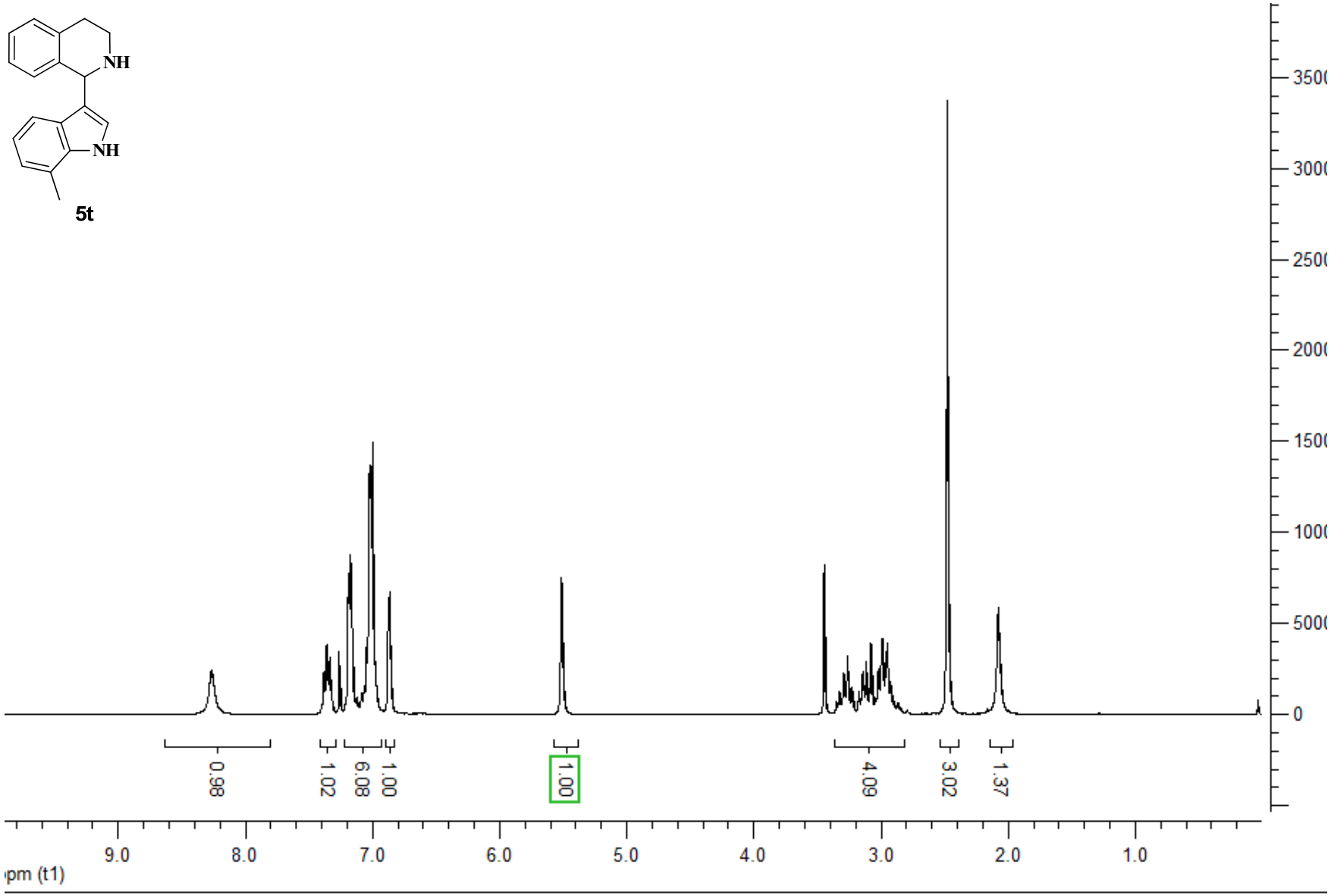

NH
NH
Cl
5p
129.47
129.12
126.43
120.34
119.35
118.82
117.87
117.20
117.09
116.63
111.67
110.81
109.66
102.59
45.06
32.82
20.35
5000
0
150
100
50
ppm (t1)

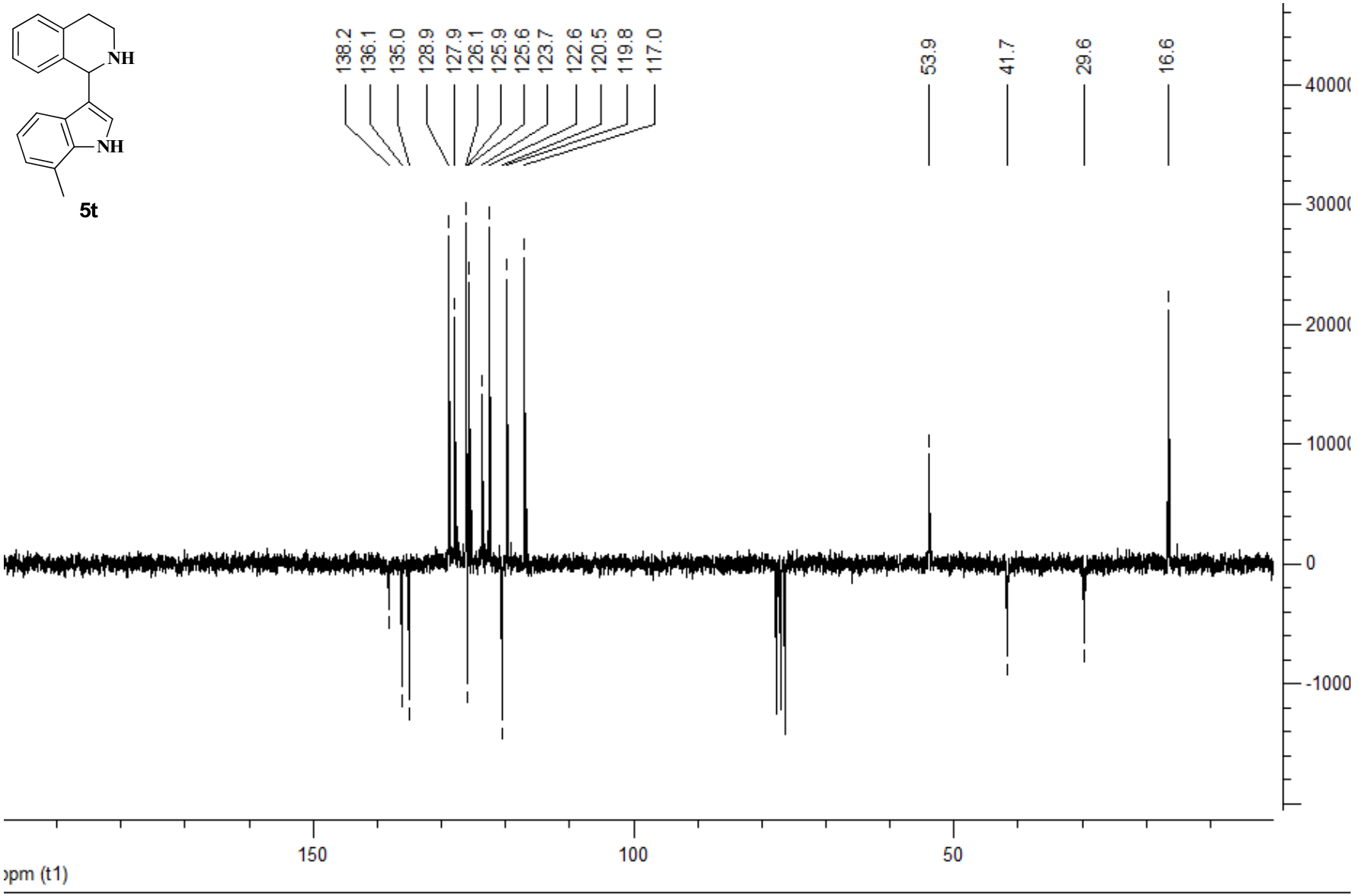

NH
NH
NO2
5q
350
300
250
200
150
100
500
0
0.98
0.99
1.00
5.13
1.00
1.00
4.12
1.84
10.0
5.0
pm (t1)

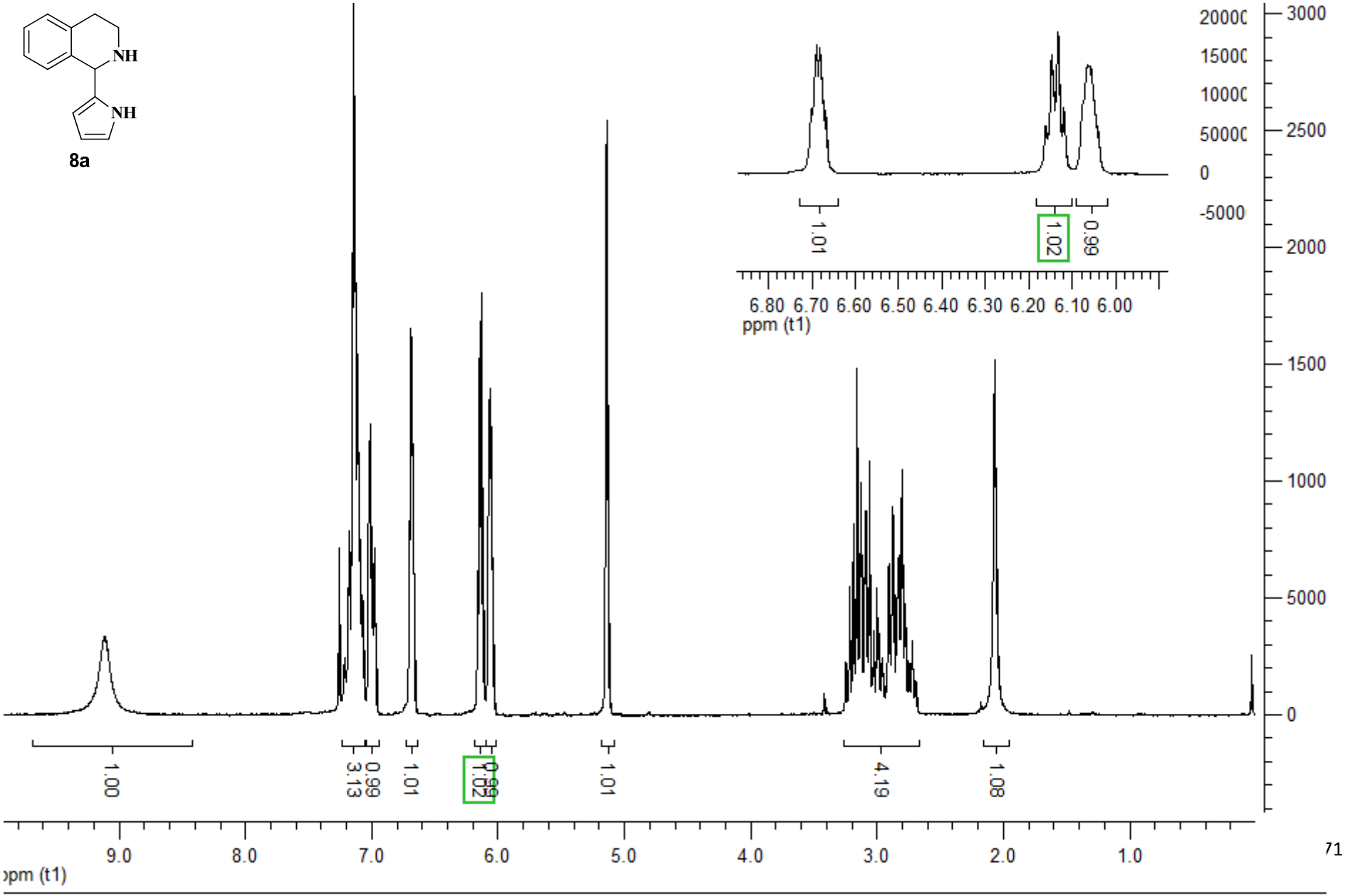

NH
NH
NO2
5q
137.58
135.15
132.91
130.15
130.02
129.14
128.36
127.45
126.46
126.11
125.70
121.11
119.33
118.99
53.81
42.01
29.61
10000
50000
0
-5000
-1000
150
100
50
ppm (t1)

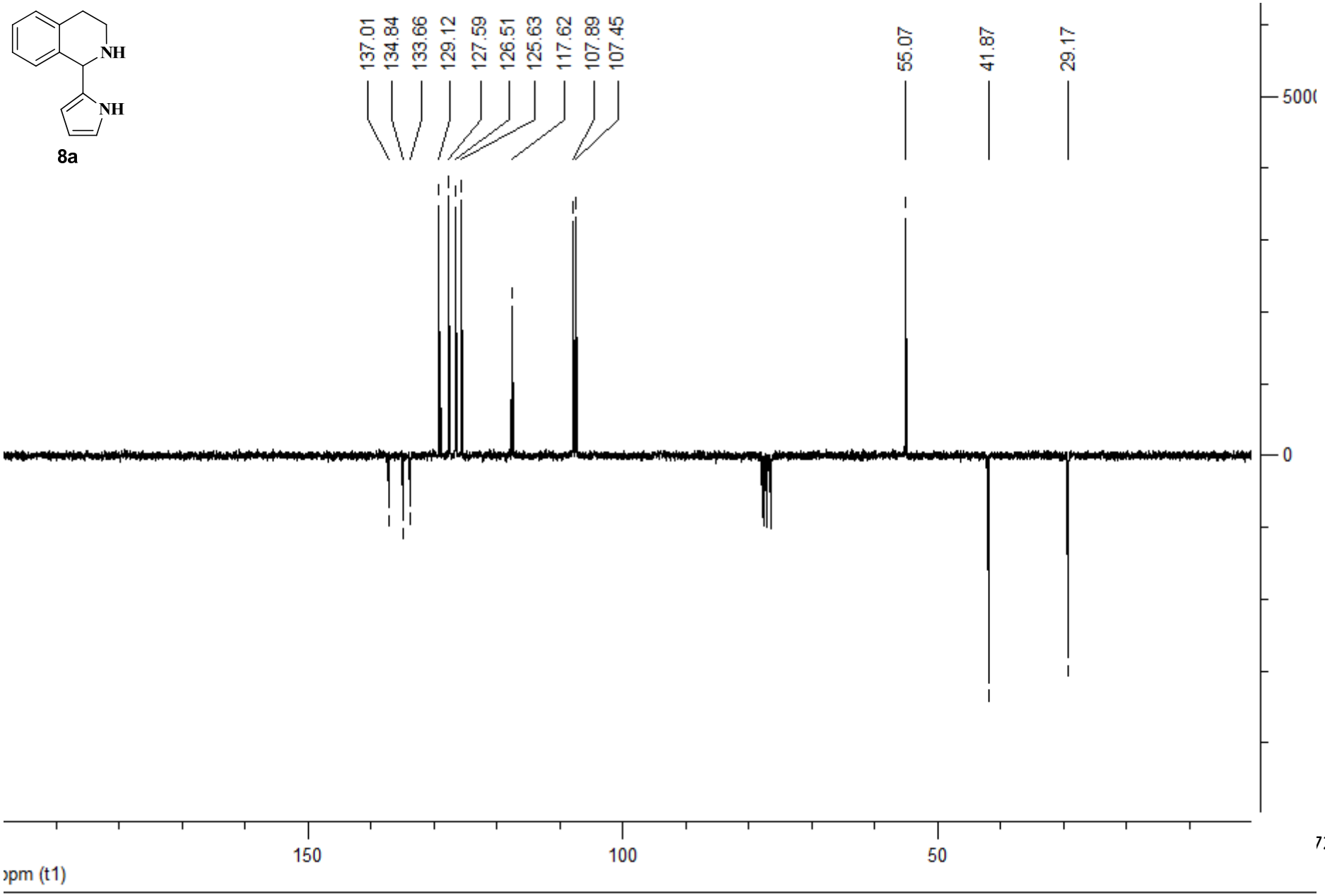

NH
NH
N
5r
5000
4000
3000
2000
1000
0
1.02
1.00
1.01
1.11
1.04
2.03
1.03
0.95
1.30
4.00
10.0
5.0
ppm (t1)

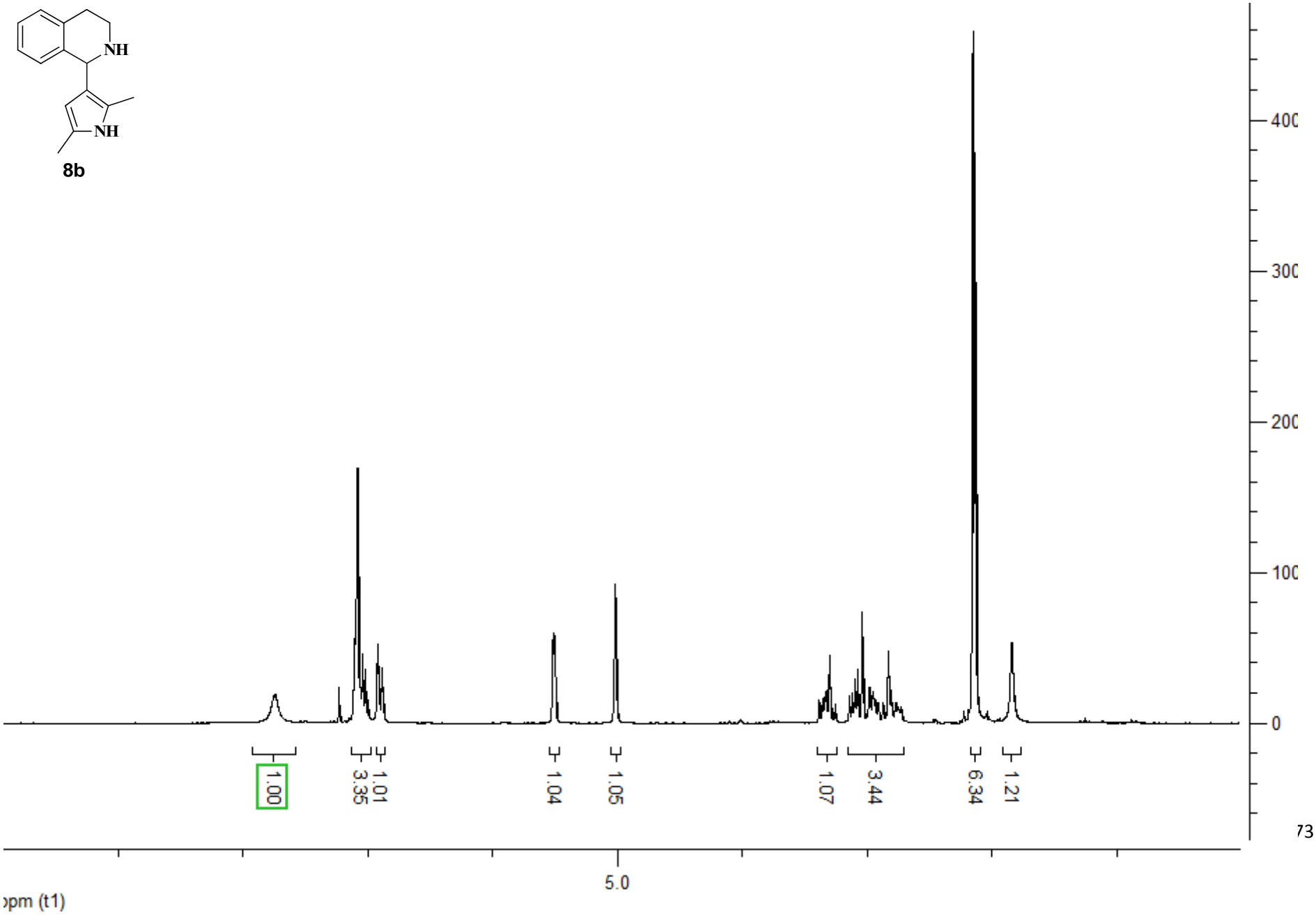

NH
NH
N
5r
148.85
142.33
138.53
134.98
128.74
127.99
127.03
125.82
125.24
124.78
118.35
116.80
114.76
53.85
41.73
29.04
4000
3000
2000
1000
0
-100
-200
-300
128.74
127.99
127.03
125.82
125.24
124.78
30000
25000
20000
15000
10000
5000
129.0 128.0 127.0 126.0 125.0
ppm (t1)
150
100
50
ppm (t1)

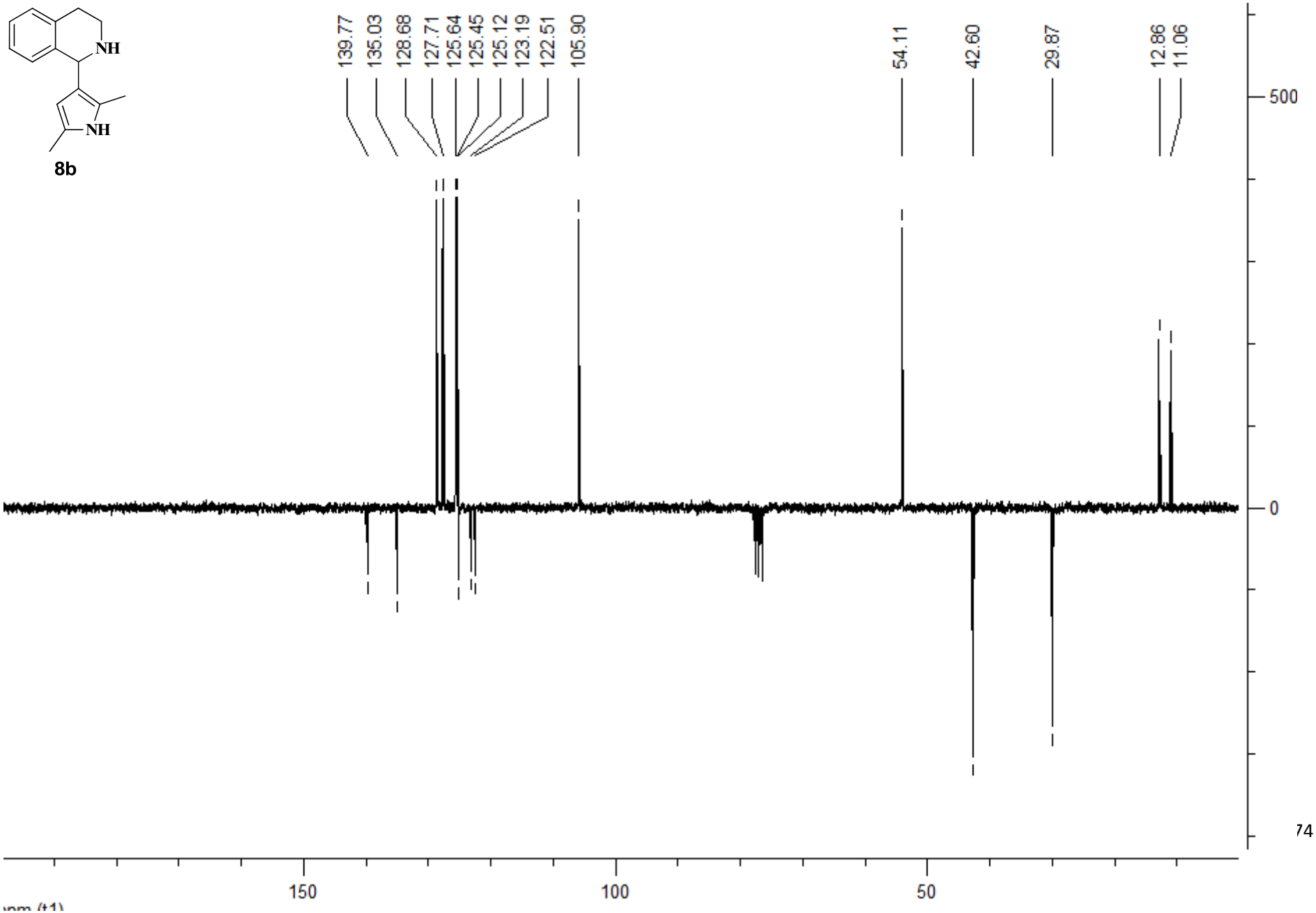

NH
NH
5t
0.98
1.02
6.08
1.00
1.00
4.09
3.02
1.37
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
pm (t1)

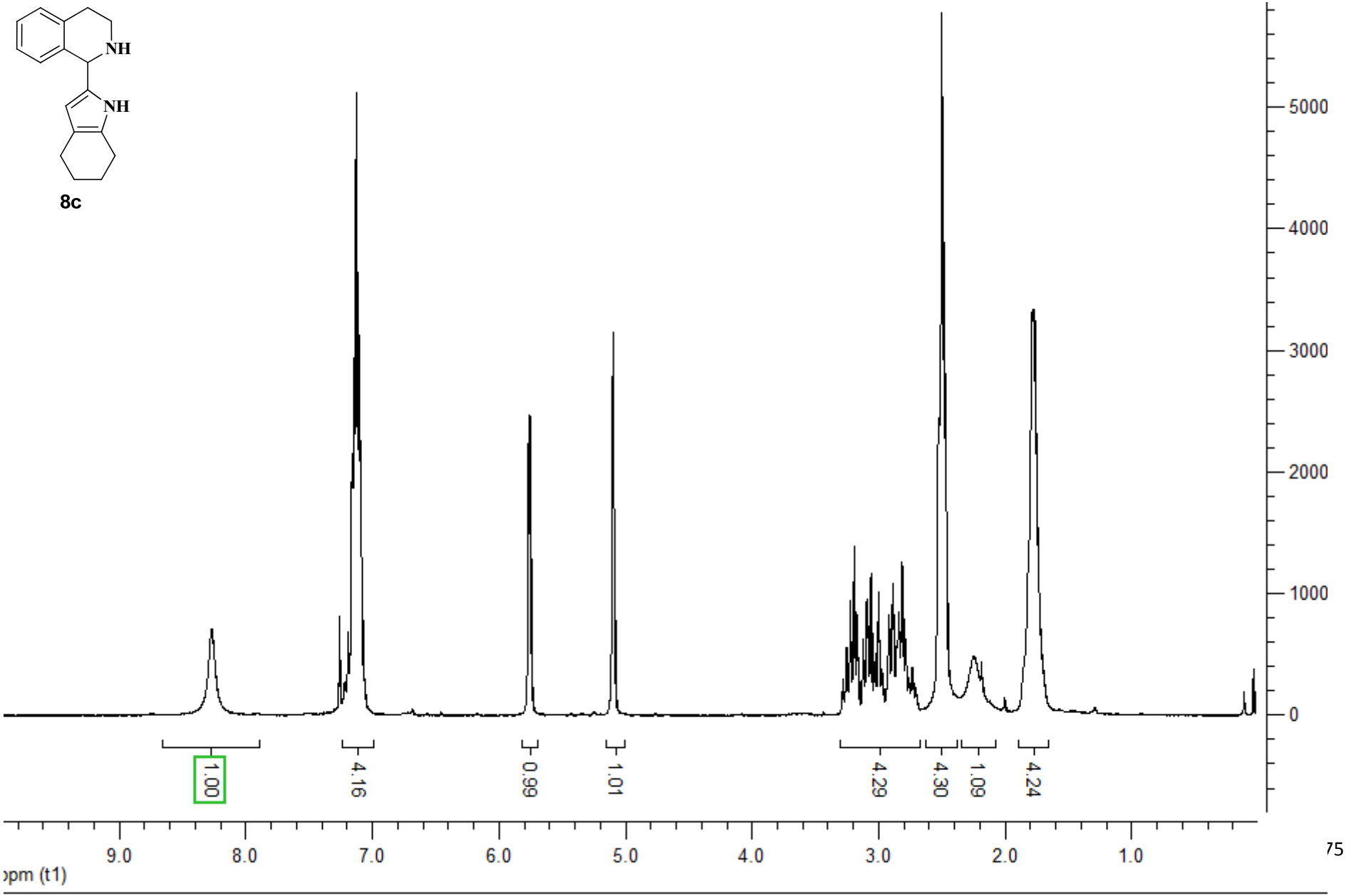

NH
NH
5t
138.2
136.1
135.0
128.9
127.9
126.1
125.9
125.6
123.7
122.6
120.5
119.8
117.0
53.9
41.7
29.6
16.6
40000
30000
20000
10000
0
-10000
150
100
50
ppm (t1)

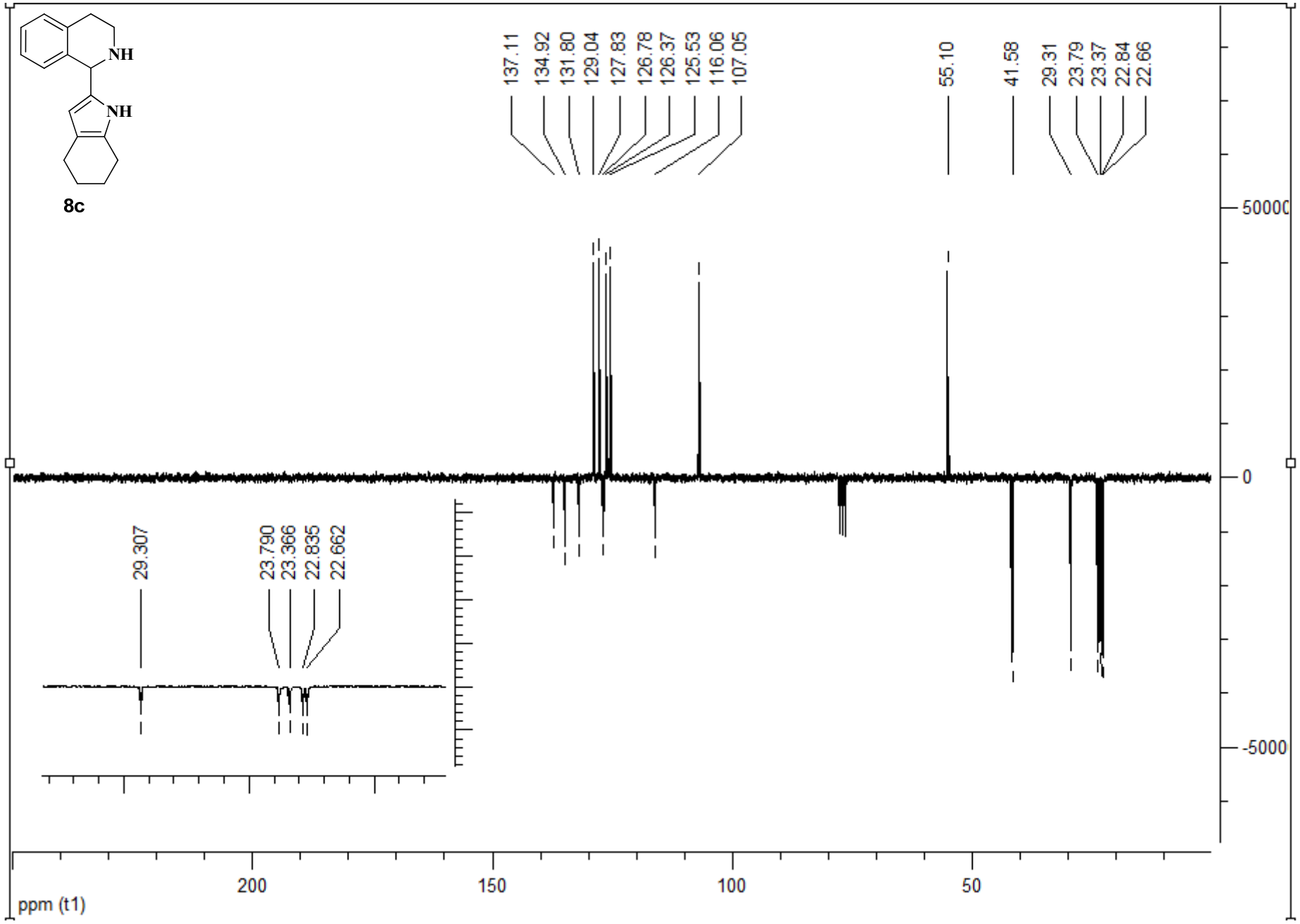

NH
NH
8a
1.01
1.02
0.99
6.80 6.70 6.60 6.50 6.40 6.30 6.20 6.10 6.00
ppm (t1)
20000
15000
10000
5000
0
-5000
3000
2500
2000
1500
1000
5000
0
1.00
3.13
0.99
1.01
1.02
0.99
1.01
4.19
1.08
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

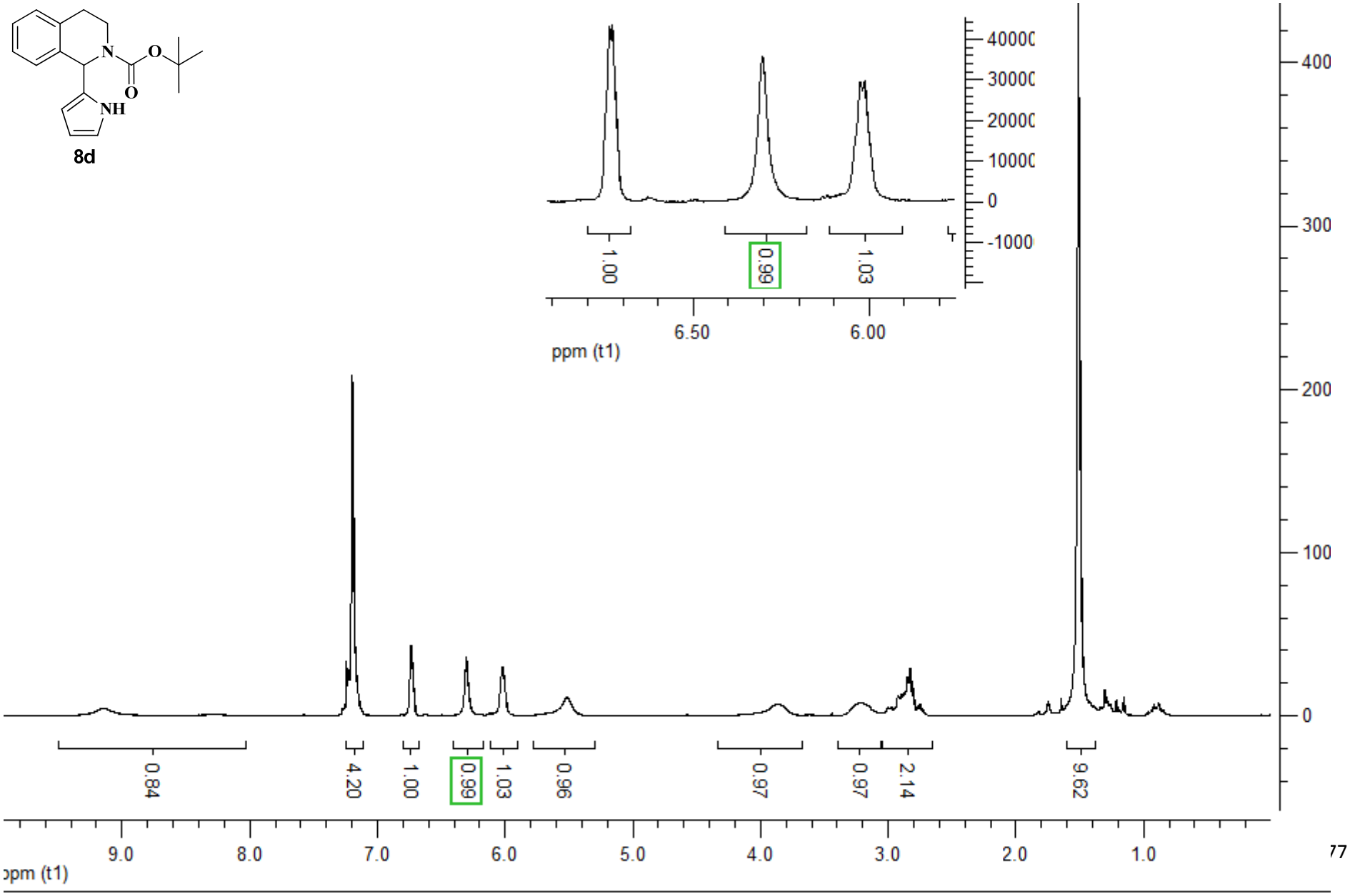

NH
NH
8a
137.01
134.84
133.66
129.12
127.59
126.51
125.63
117.62
107.89
107.45
55.07
41.87
29.17
5000
0
150
100
50
ppm (t1)

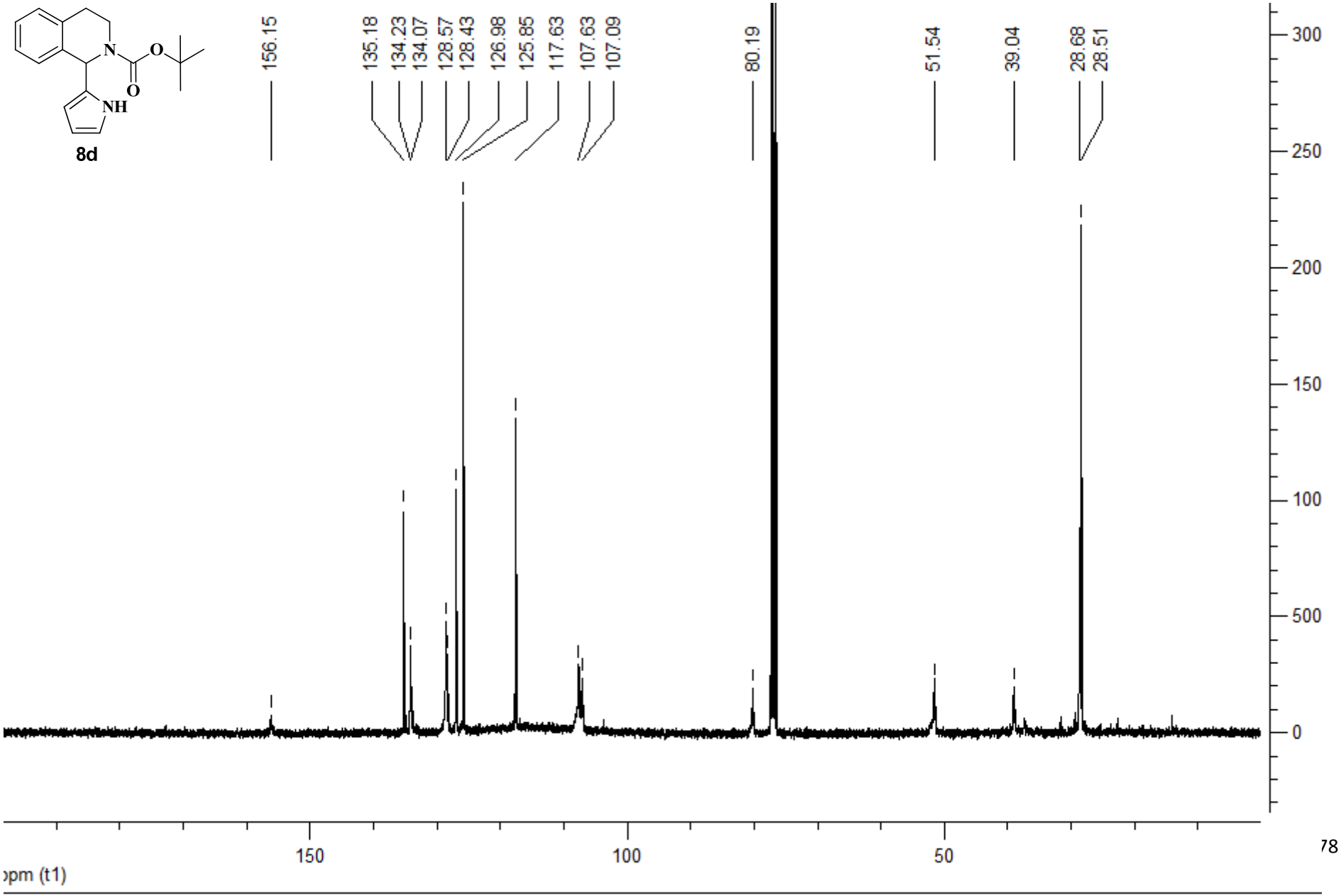

NH
NH
8b
400
300
200
100
0
1.00
3.35
1.01
1.04
1.05
1.07
3.44
6.34
1.21
5.0
ppm (t1)

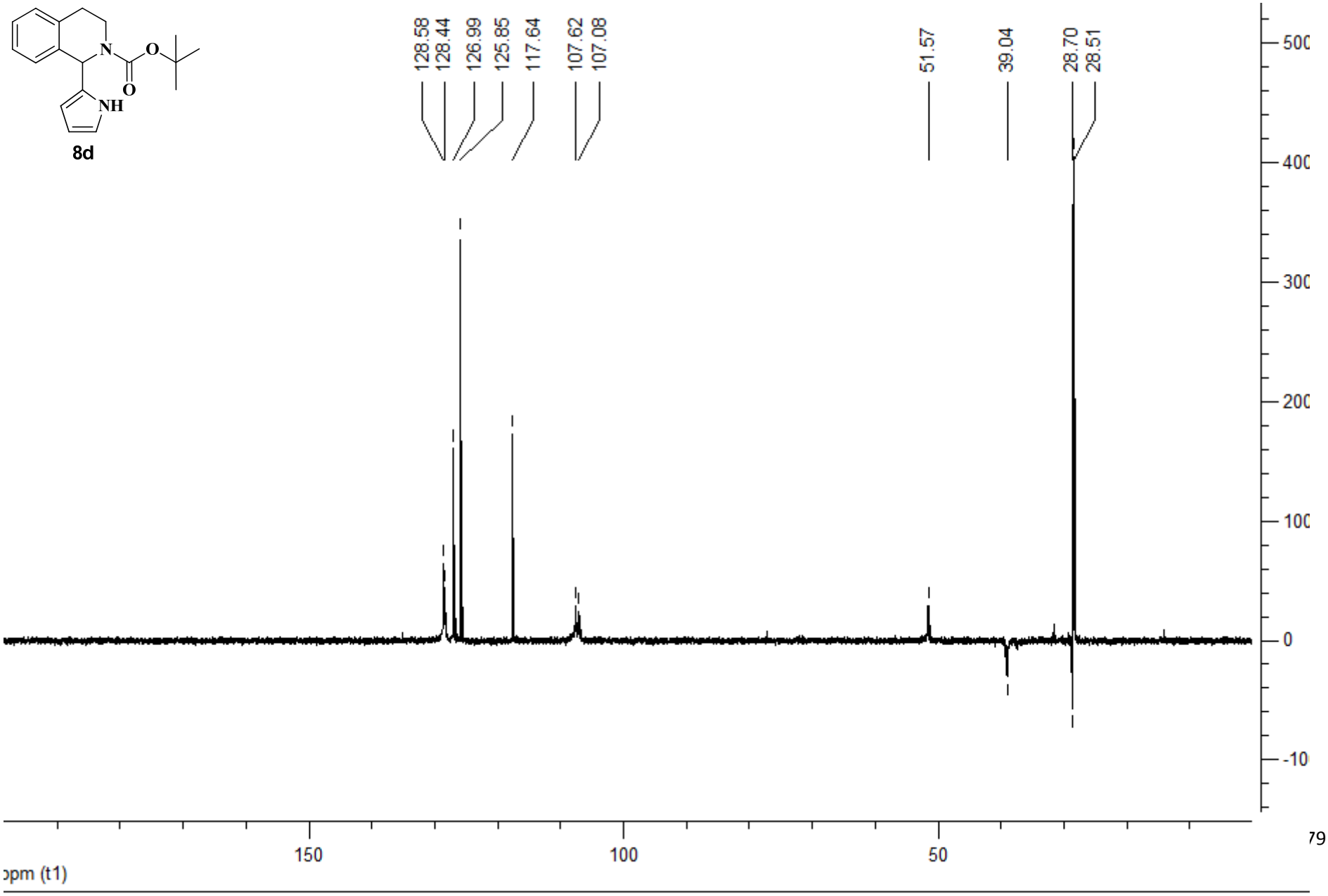

NH
NH
8b
139.77
135.03
128.68
127.71
125.64
125.45
125.12
123.19
122.51
105.90
54.11
42.60
29.87
12.86
11.06
500
0
150
100
50

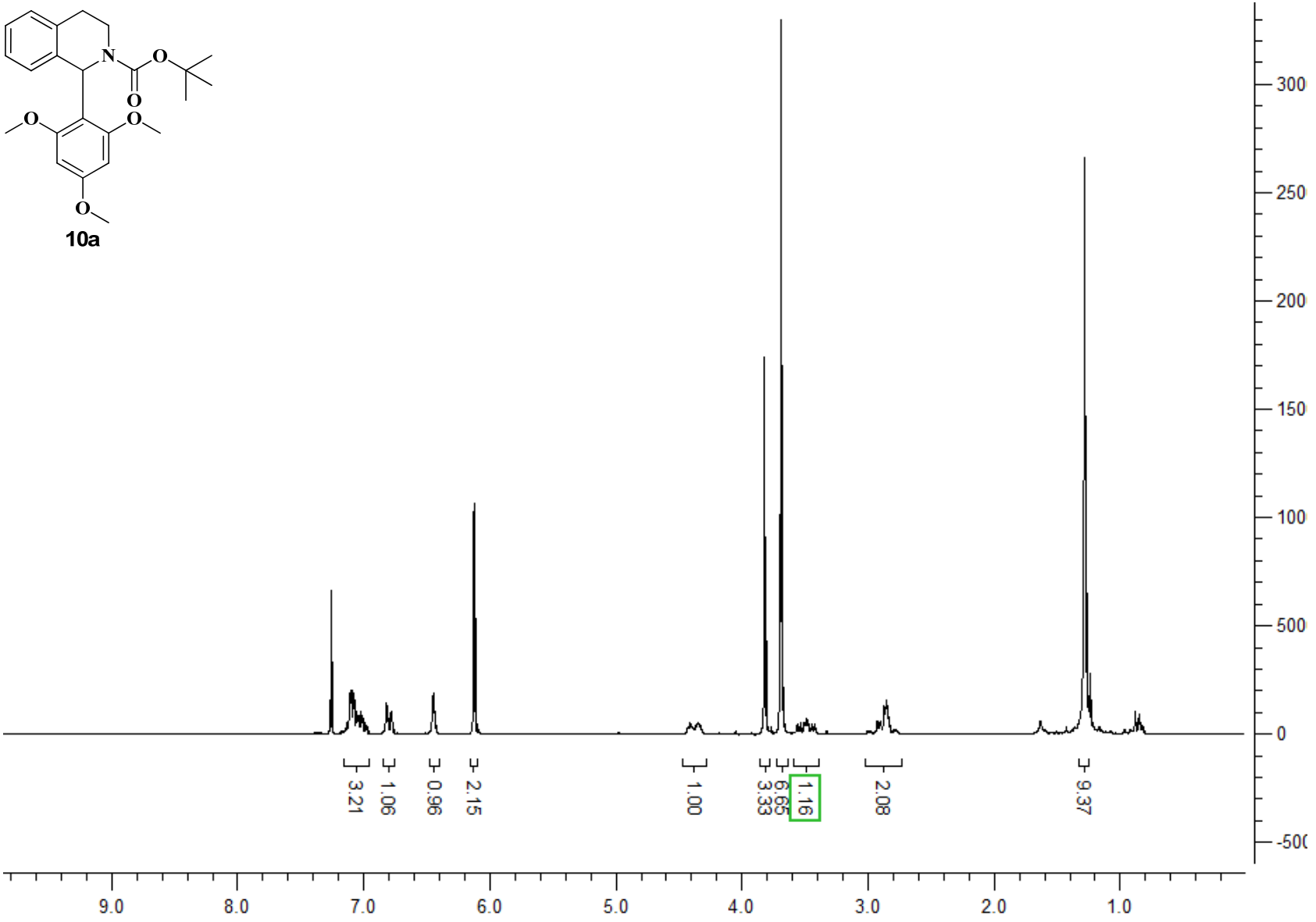

NH
NH
8c
5000
4000
3000
2000
1000
0
1.00
4.16
0.99
1.01
4.29
4.30
1.09
4.24
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

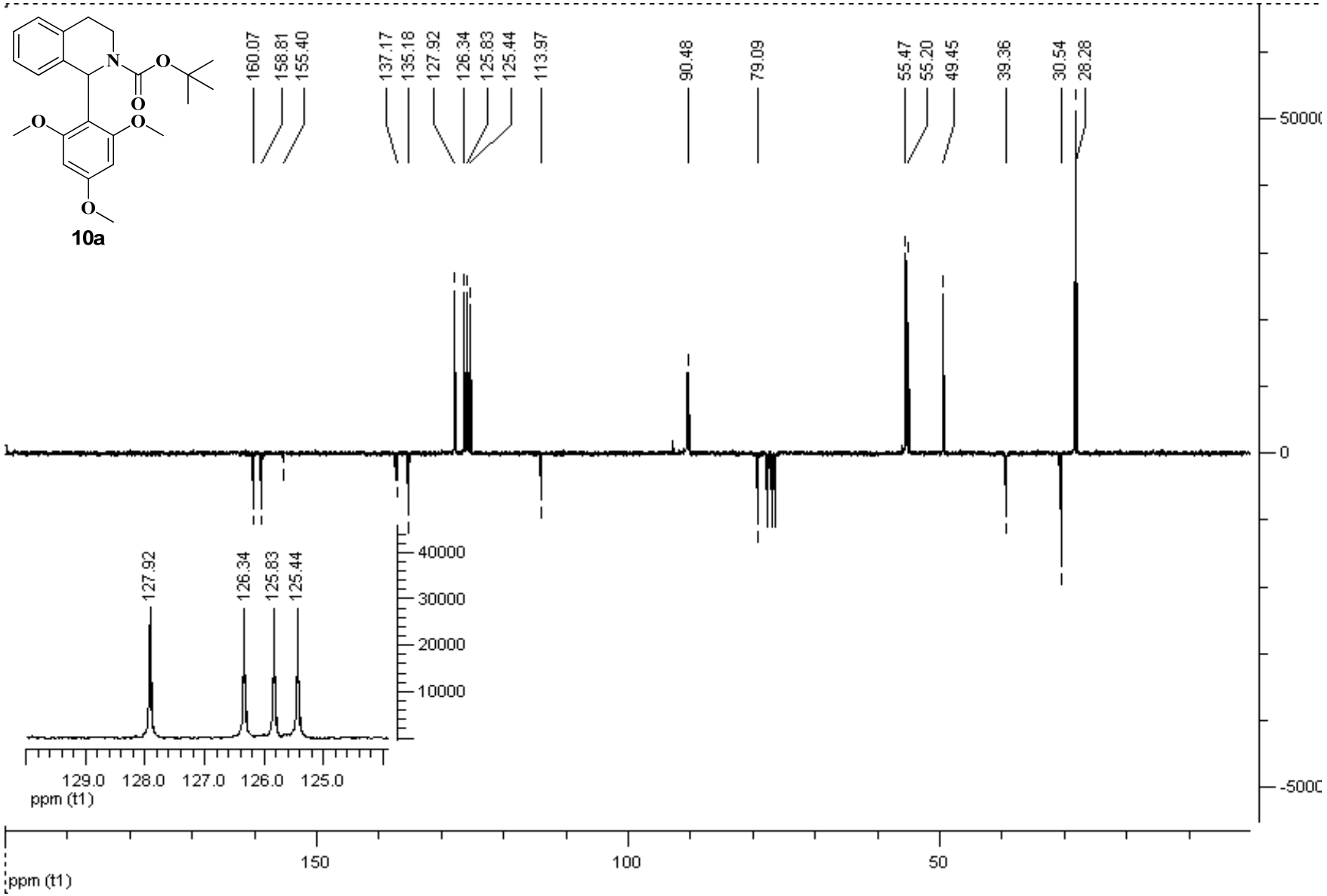

NH
NH
8c
137.11
134.92
131.80
129.04
127.83
126.78
126.37
125.53
116.06
107.05
55.10
41.58
29.31
23.79
23.37
22.84
22.66
29.307
23.790
23.366
22.835
22.662
50000
0
-5000
200
150
100
50
ppm (t1)

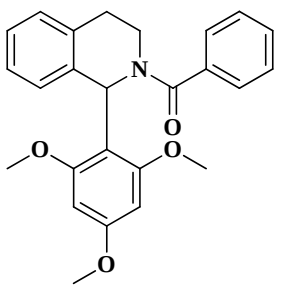

8d
N
O
O
NH
40000
30000
20000
10000
0
-1000
1.00
0.99
1.03
6.50
6.00
ppm (t1)
400
300
200
100
0
0.84
4.20
1.00
0.99
1.03
0.96
0.97
0.97
2.14
9.62
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


8d
156.15
135.18
134.23
134.07
128.57
128.43
126.98
125.85
117.63
107.63
107.09
80.19
51.54
39.04
28.68
28.51
300
250
200
150
100
500
0
150
100
50
ppm (t1)


8d
128.58
128.44
126.99
125.85
117.64
107.62
107.08
51.57
39.04
28.70
28.51
500
400
300
200
100
0
-10
150
100
50
ppm (t1)

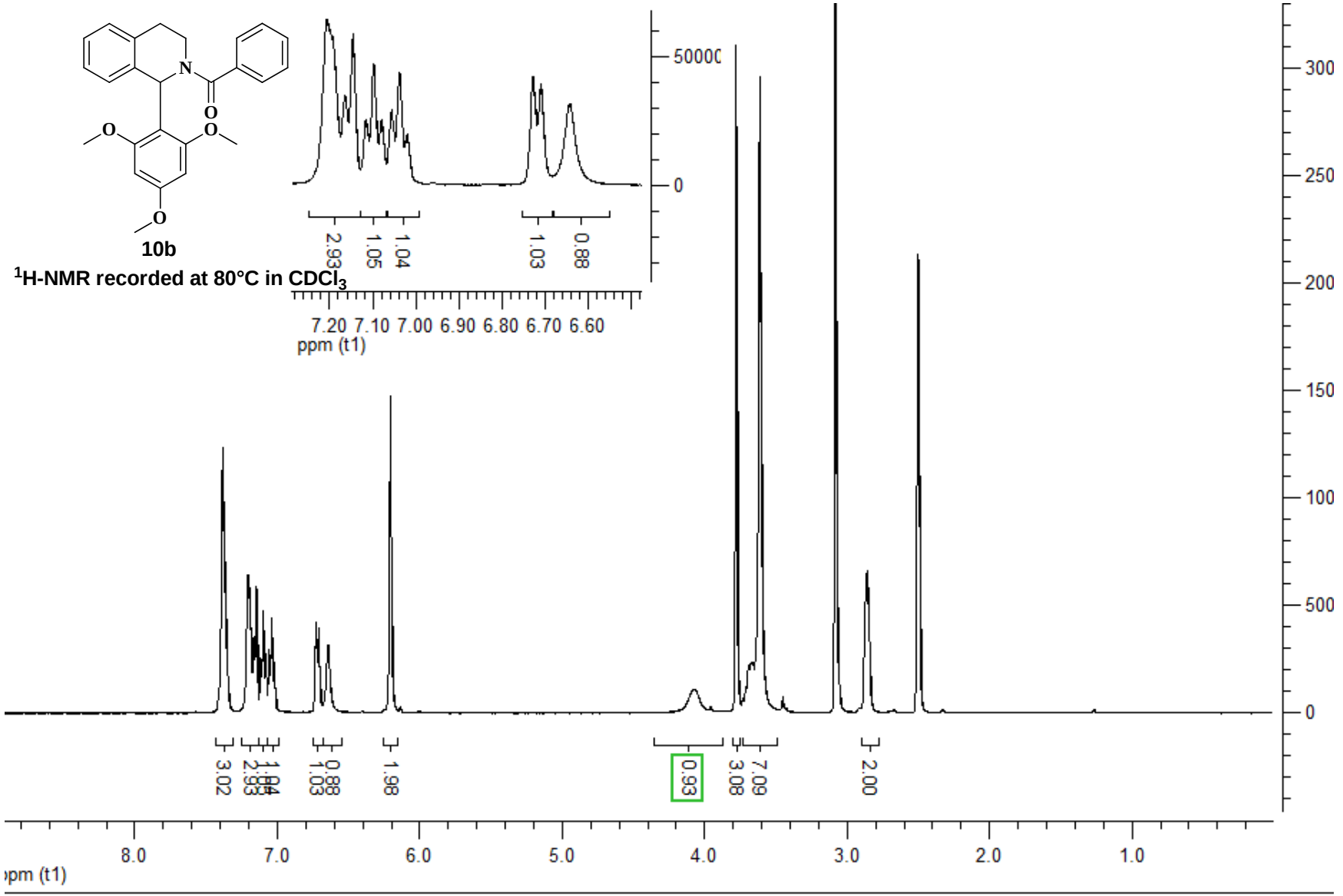

10a
3.21
1.06
0.96
2.15
1.00
3.33
6.65
1.16
2.08
9.37
300
250
200
150
100
500
0
-500
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

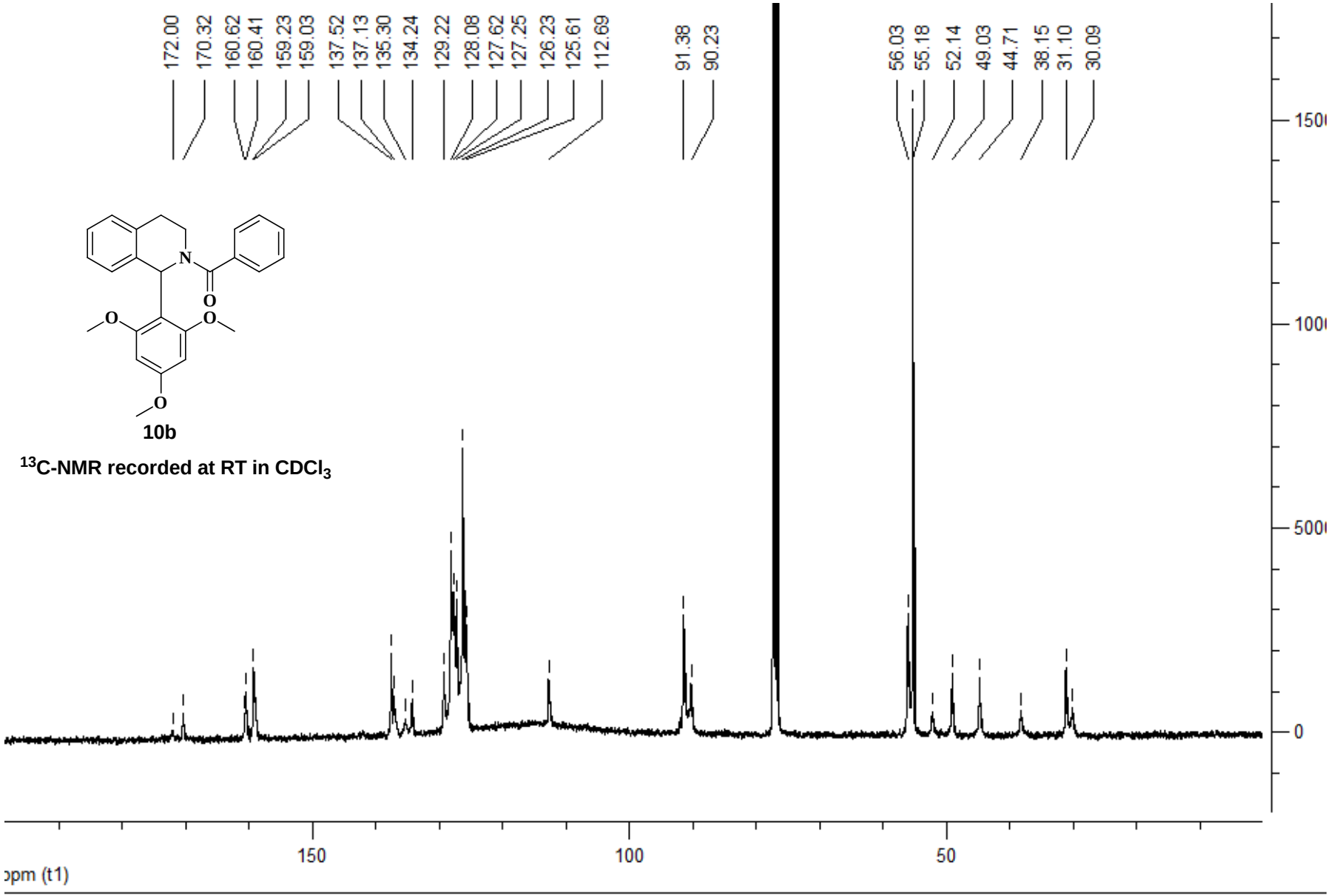

10a
160.07
158.81
155.40
137.17
135.18
127.92
126.34
125.83
125.44
113.97
90.48
79.09
55.47
55.20
49.45
39.36
30.54
28.28
50000
0
-5000
40000
30000
20000
10000
129.0
128.0
127.0
126.0
125.0
ppm (t1)
150
100
50
ppm (t1)



10b

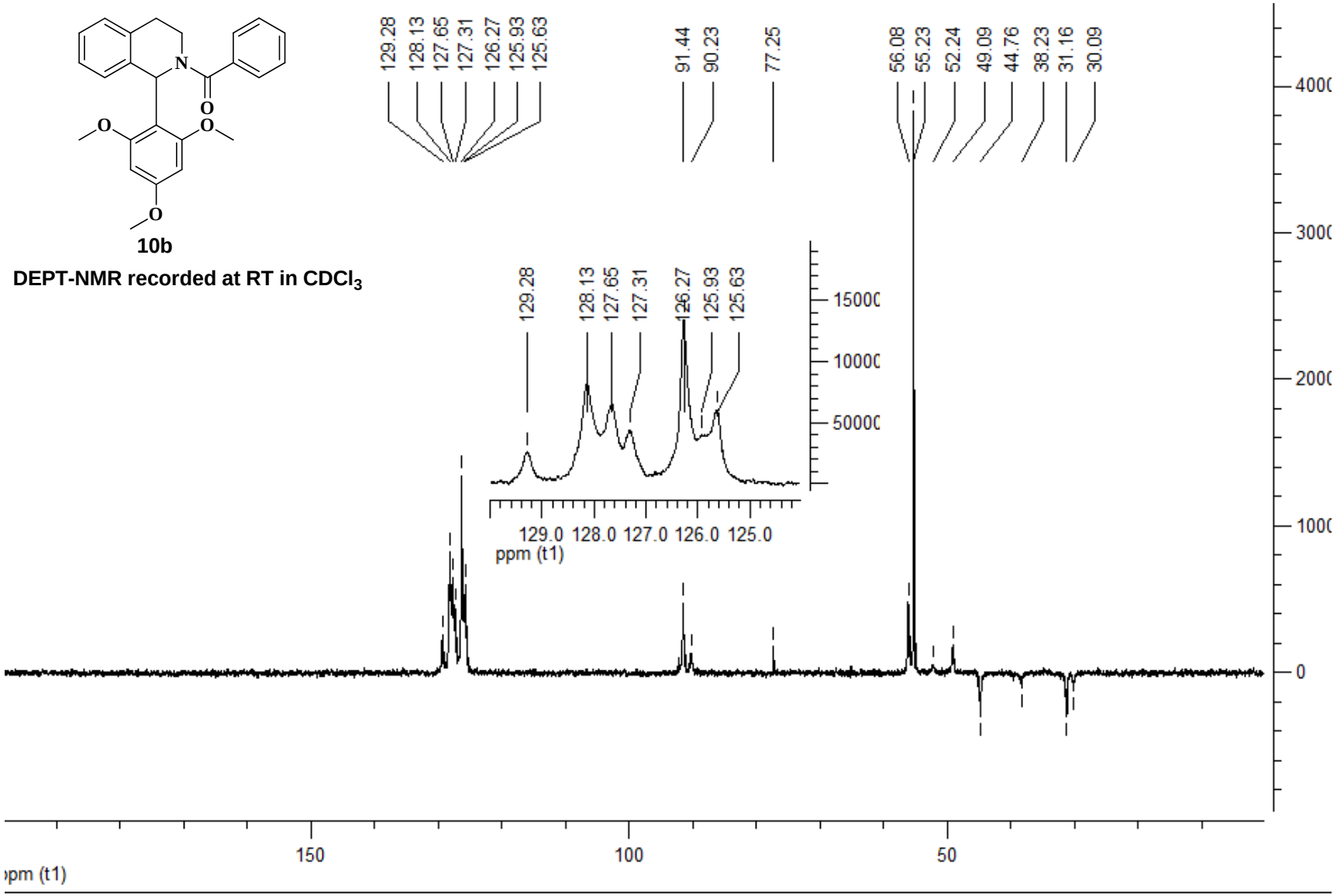
^{1}H-NMR recorded at RT in $CDCl_3$

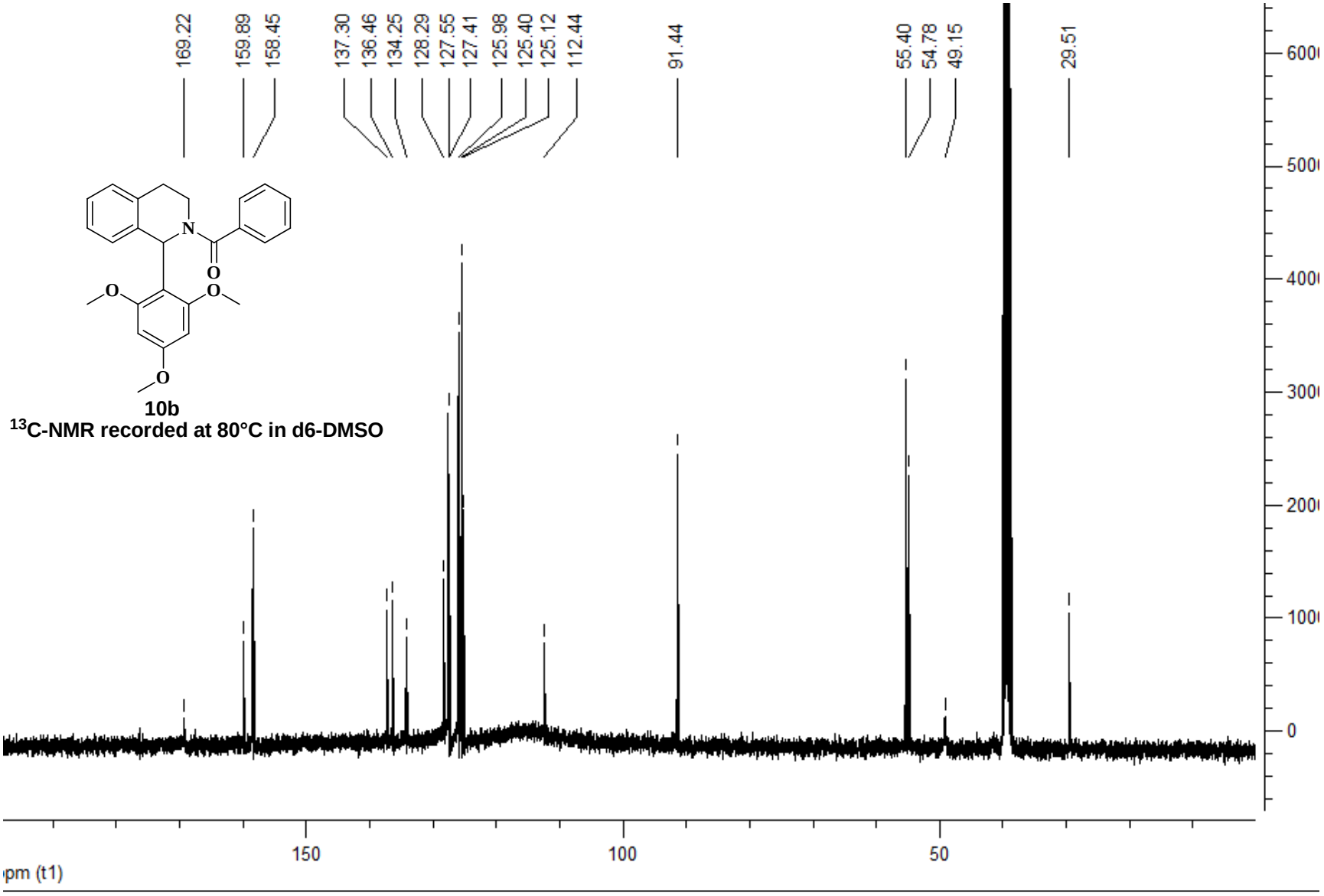

10b
1H-NMR recorded at 80°C in CDCl3
50000
0
2.93
1.05
1.04
1.03
0.88
7.20 7.10 7.00 6.90 6.80 6.70 6.60
ppm (t1)
300
250
200
150
100
500
0
3.02
2.93
1.03
0.88
1.98
0.93
3.08
7.09
2.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)



10b

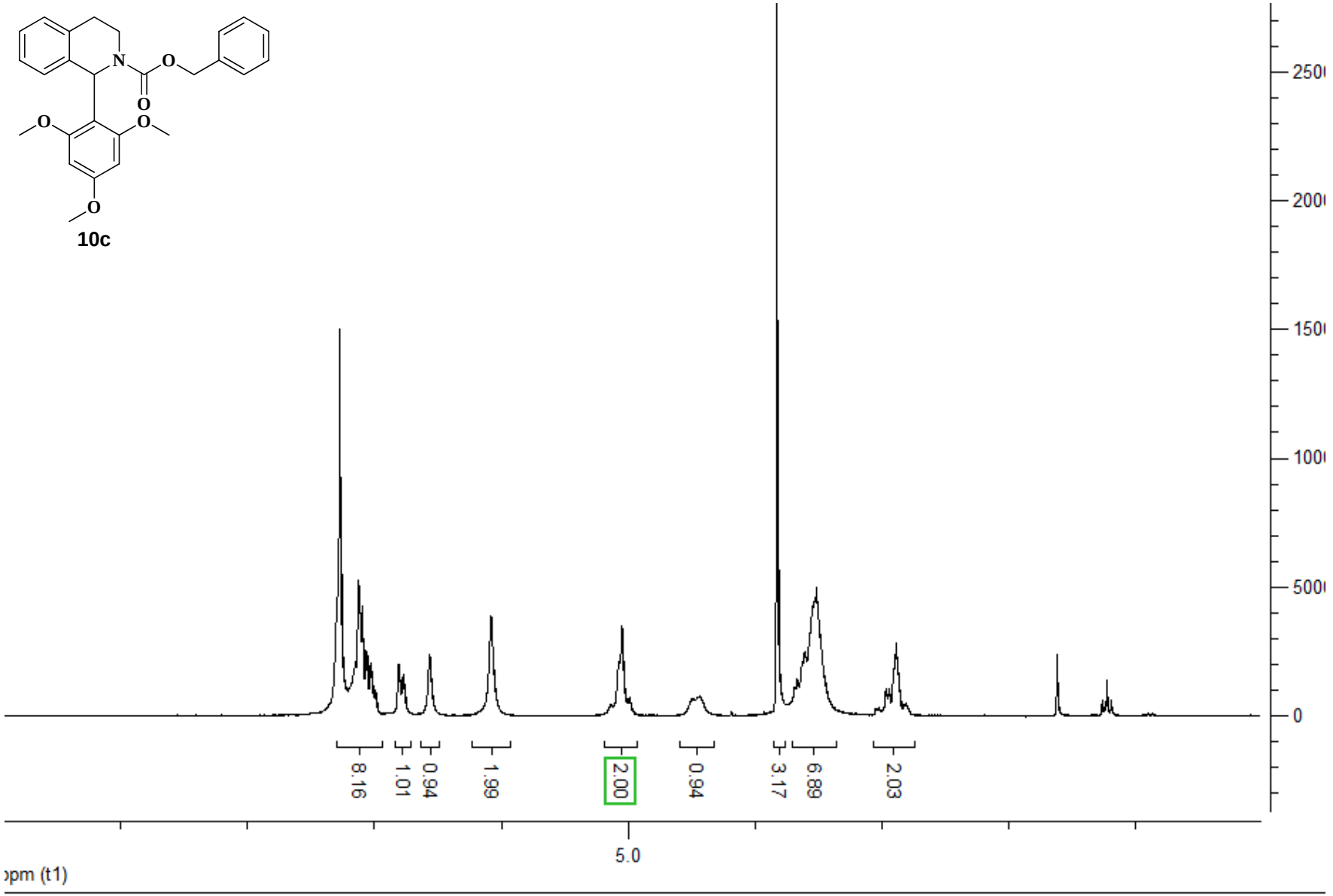
^{13}C-NMR recorded at RT in $CDCl_3$

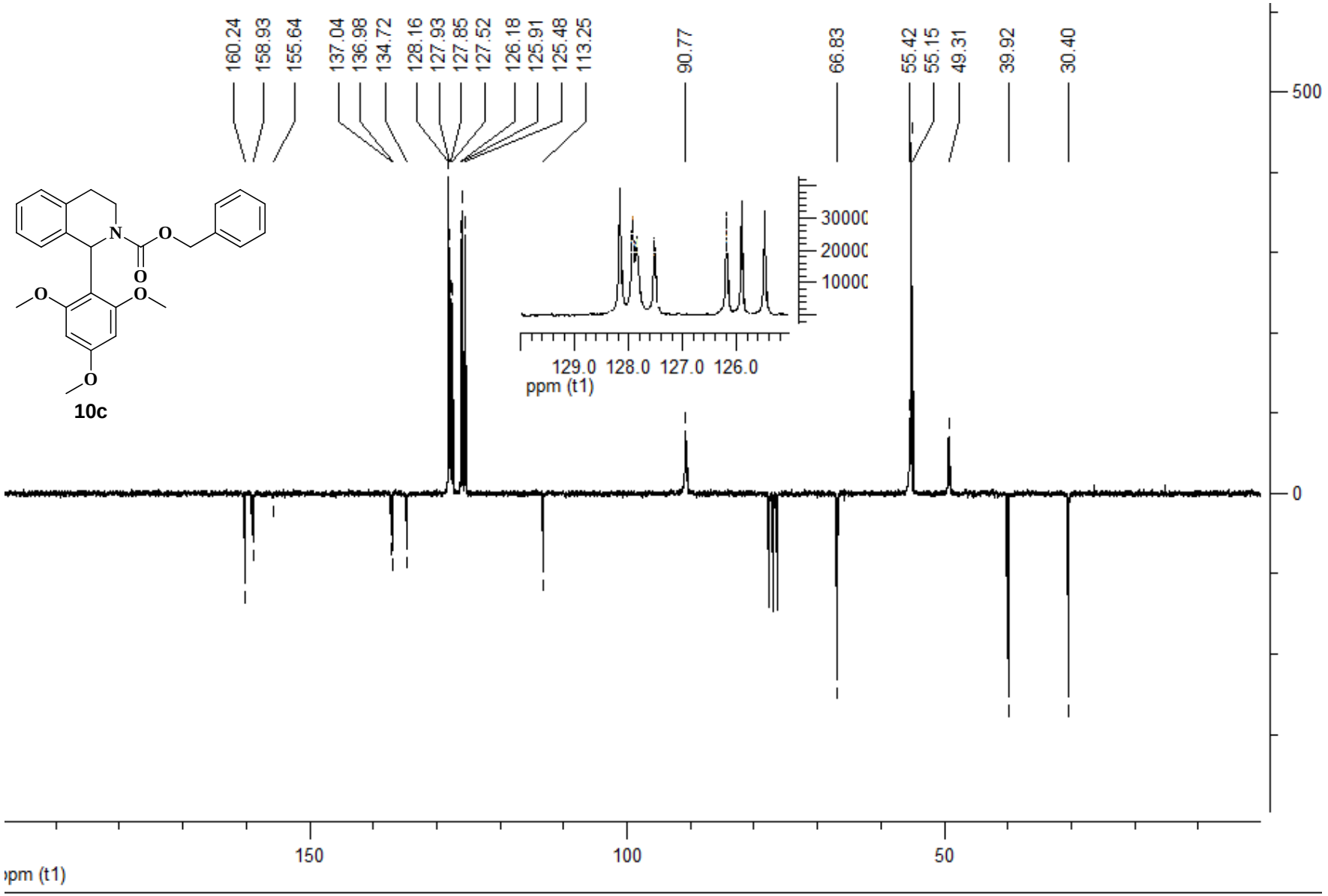

10b
DEPT-NMR recorded at RT in CDCl3
129.28
128.13
127.65
127.31
126.27
125.93
125.63
91.44
90.23
77.25
56.08
55.23
52.24
49.09
44.76
38.23
31.16
30.09
129.0 128.0 127.0 126.0 125.0
ppm (t1)
150
100
50
ppm (t1)



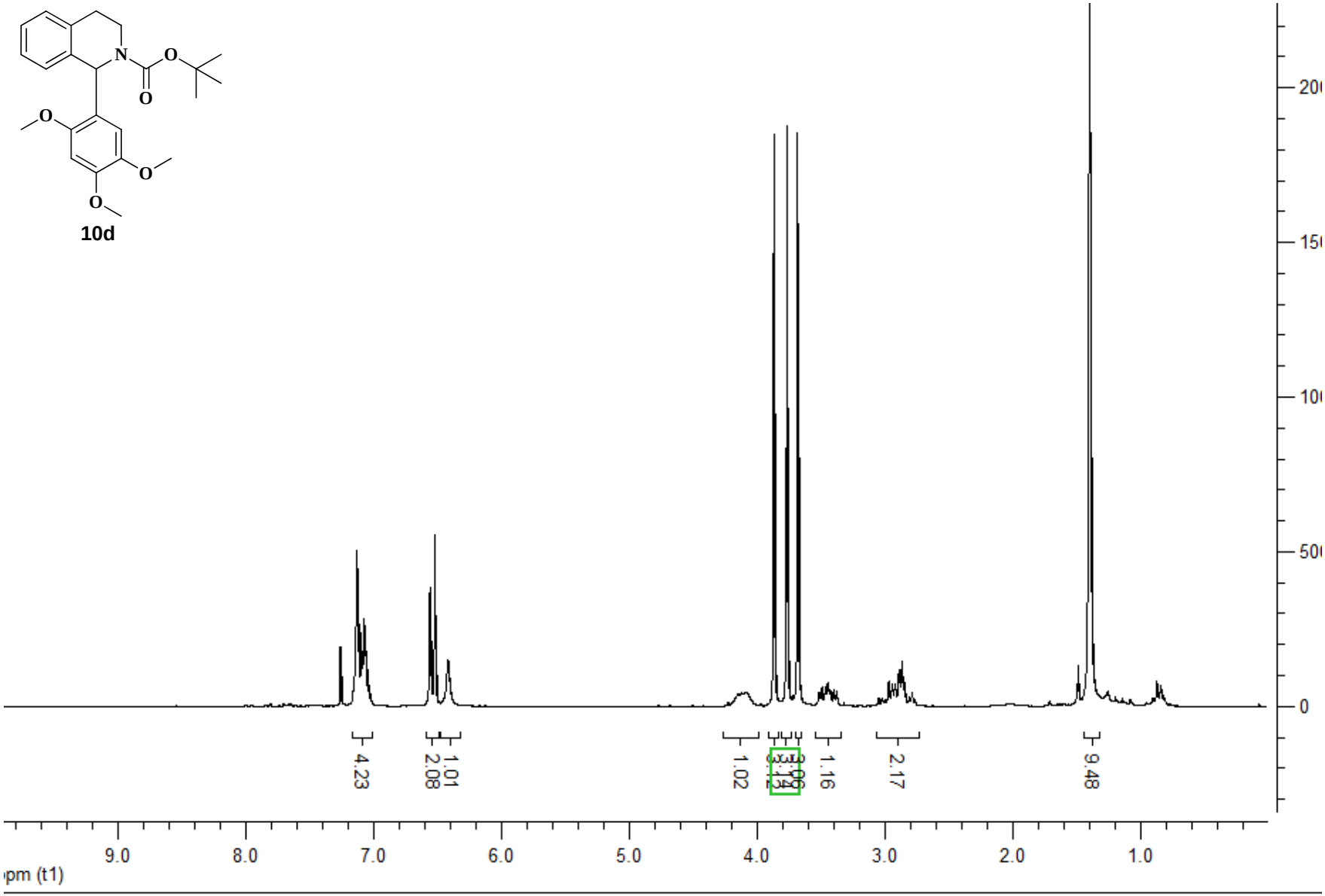
10b

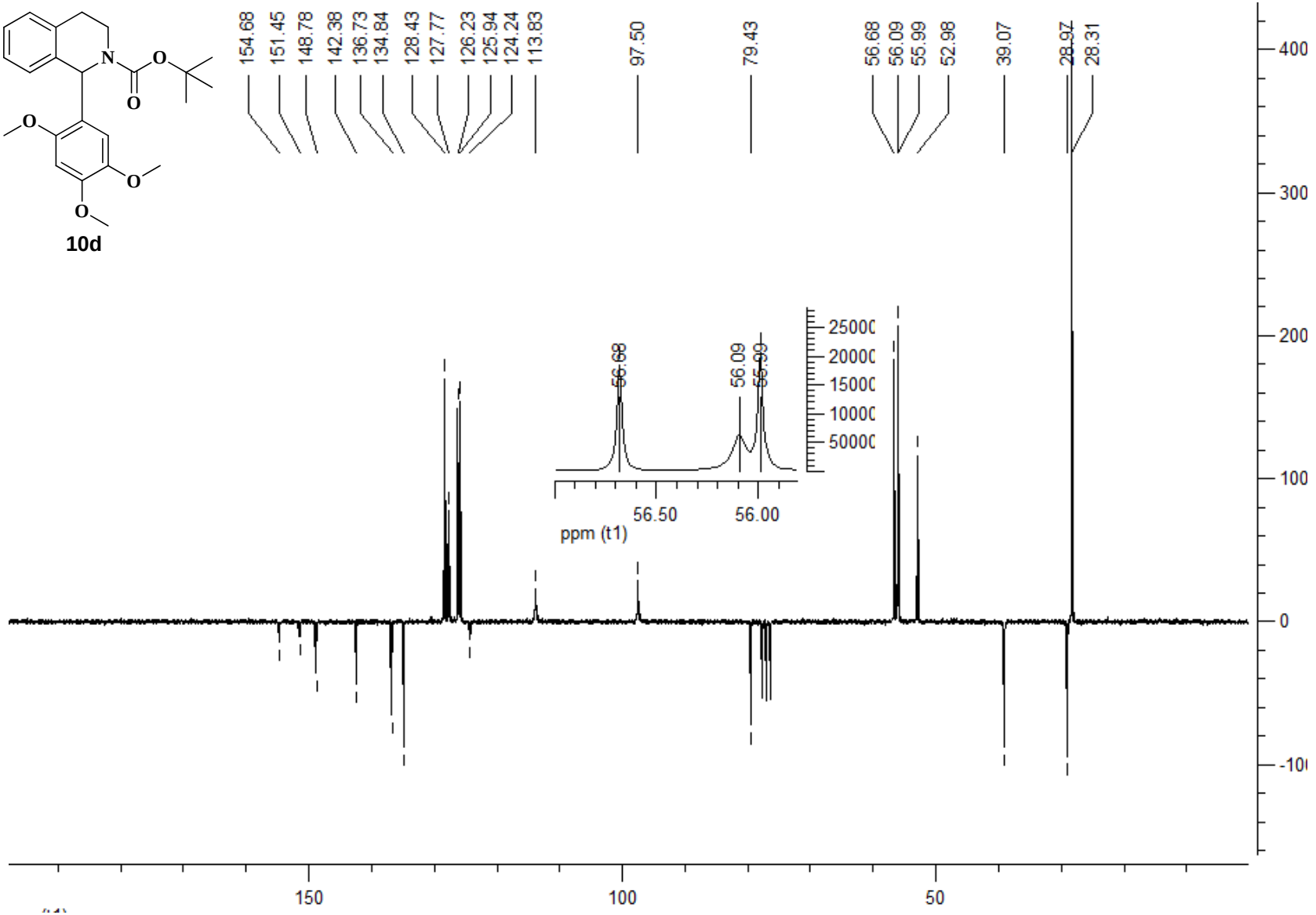
^{13}C-NMR recorded at 80°C in d6-DMSO

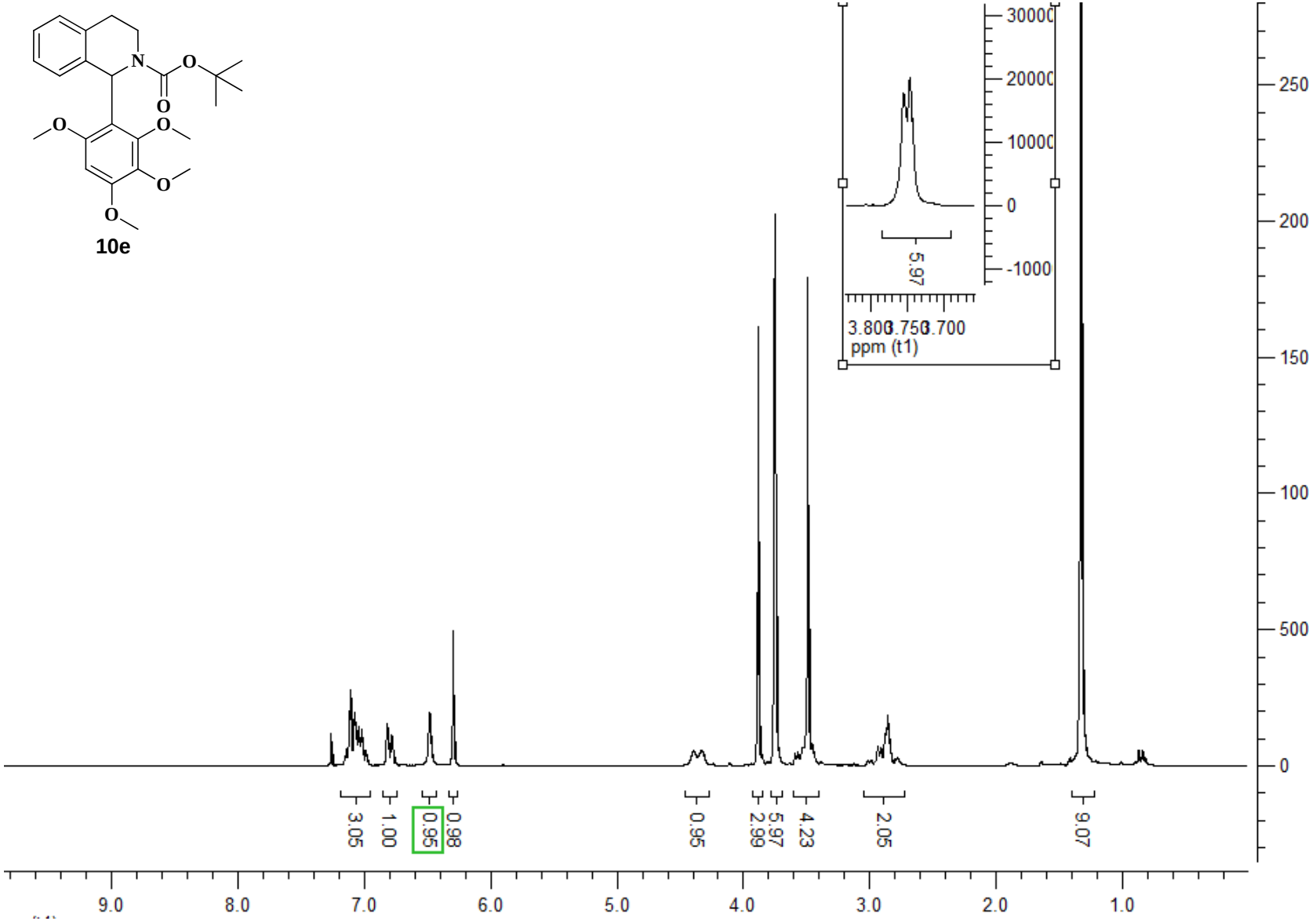

10c
8.16
1.01
0.94
1.99
2.00
0.94
3.17
6.89
2.03
5.0
ppm (t1)

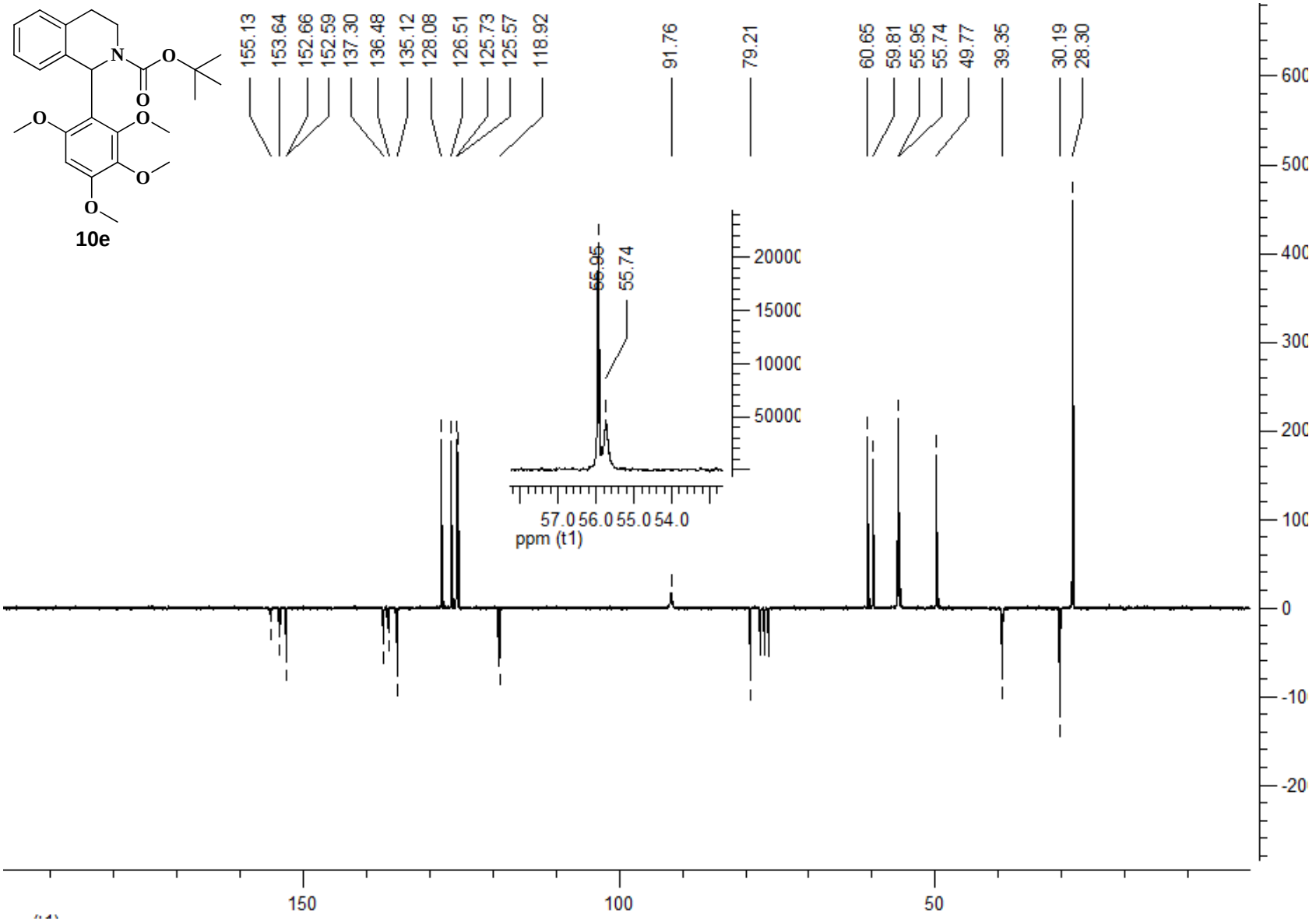

160.24
158.93
155.64
137.04
136.98
134.72
128.16
127.93
127.85
127.52
126.18
125.91
125.48
113.25
90.77
66.83
55.42
55.15
49.31
39.92
30.40
500
0
30000
20000
10000
129.0 128.0 127.0 126.0
ppm (t1)
150
100
50
ppm (t1)

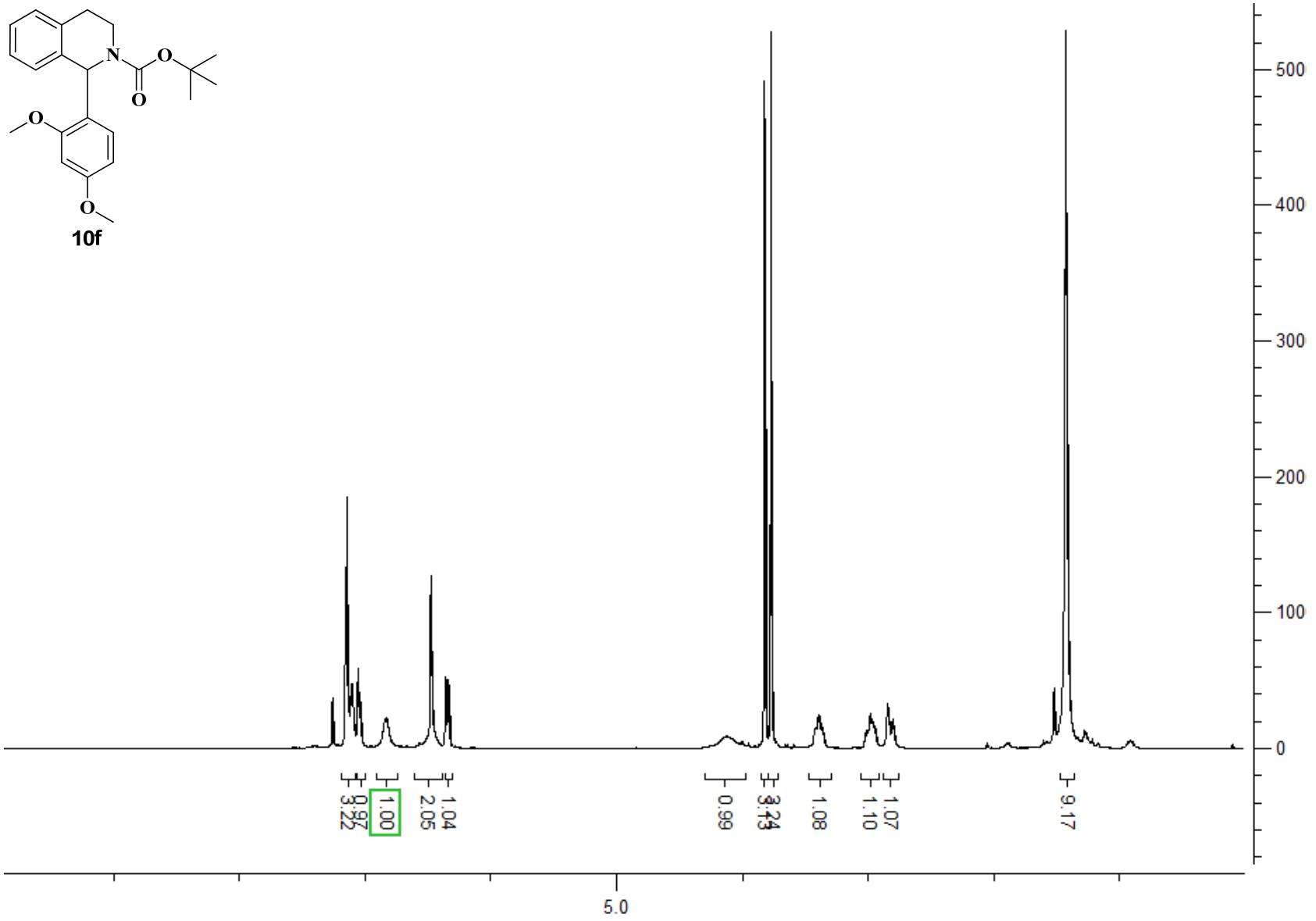
10c

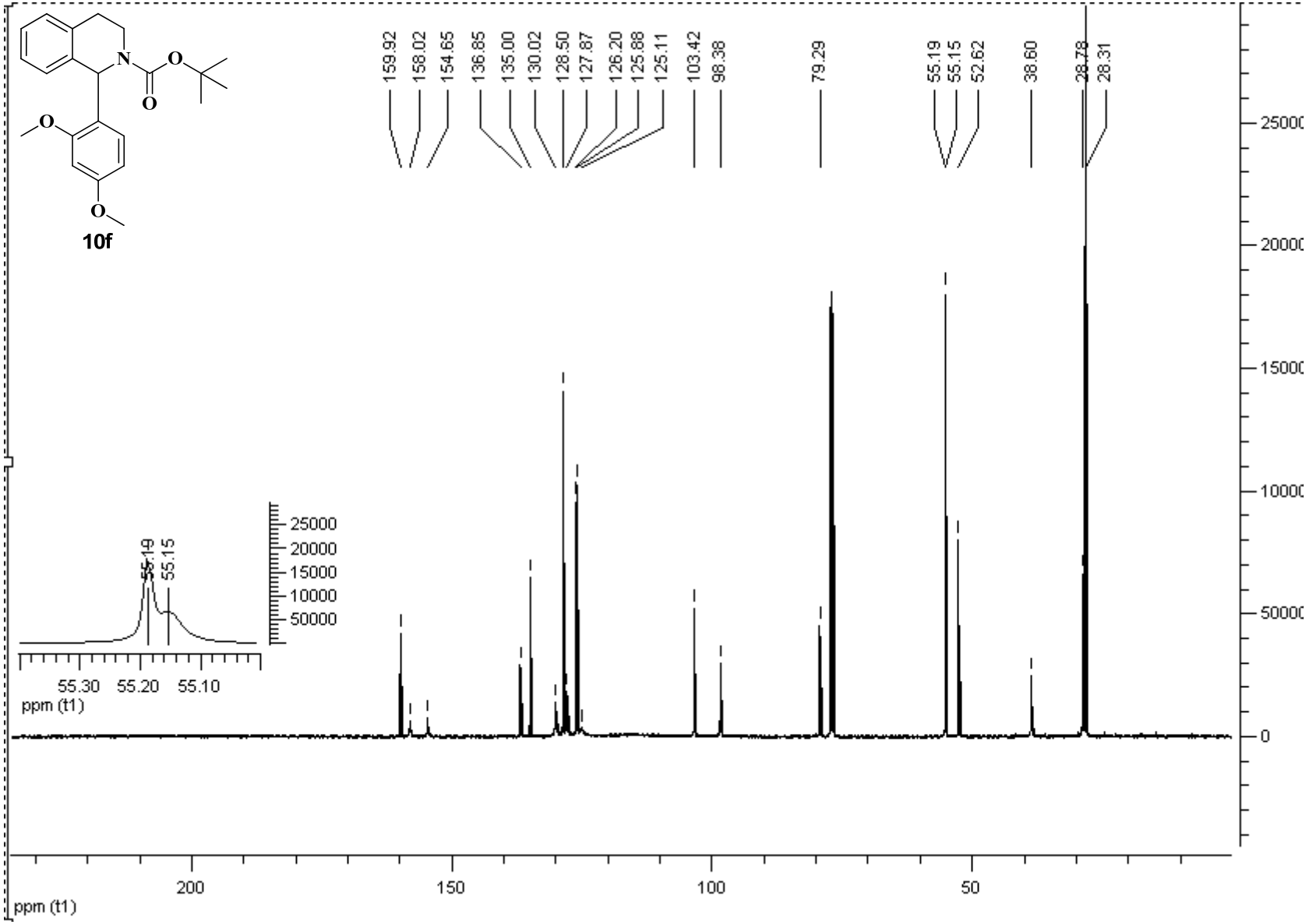

10d
4.23
2.08
1.01
1.02
3.13
3.14
3.00
1.16
2.17
9.48
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

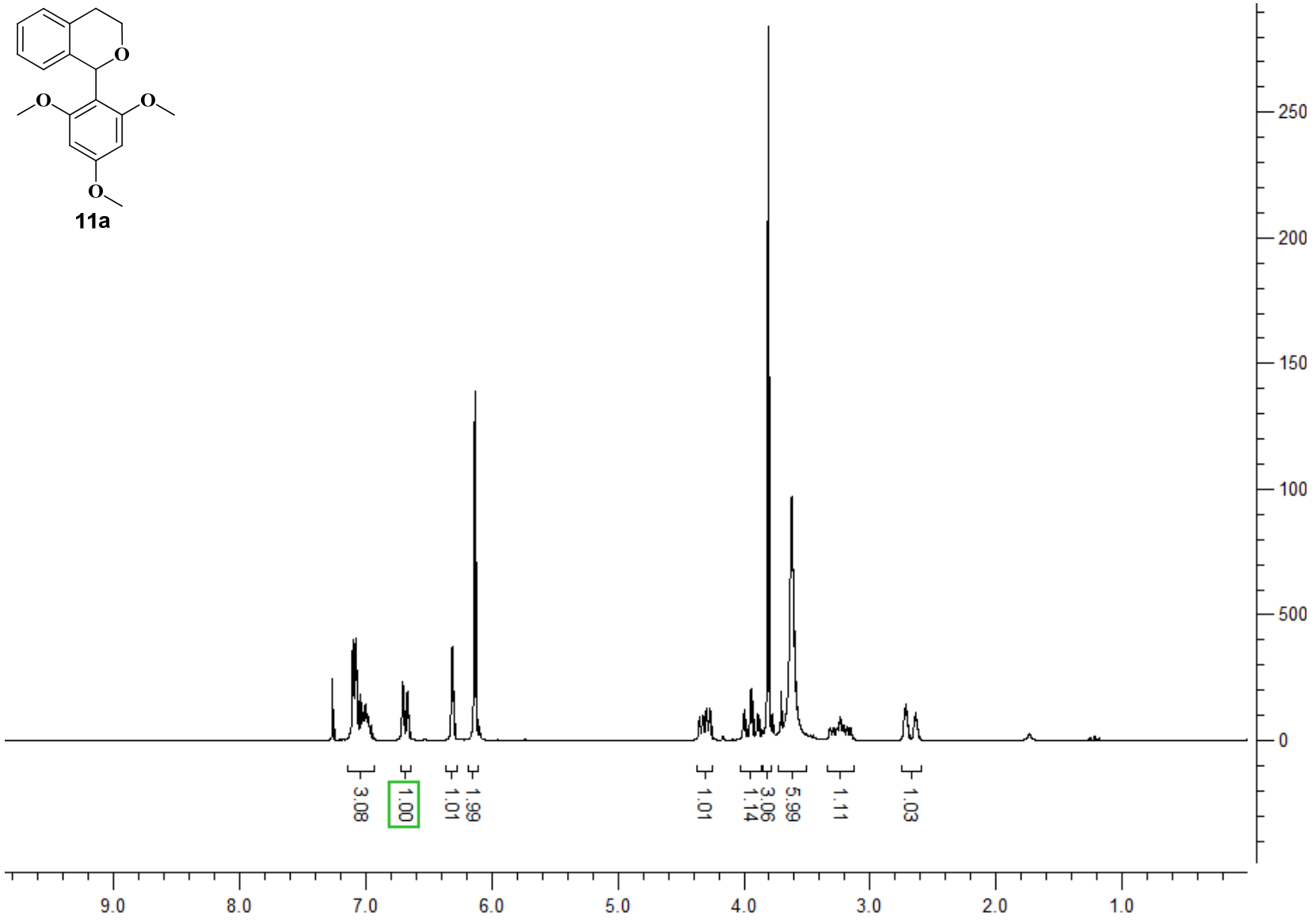

10d
154.68
151.45
148.78
142.38
136.73
134.84
128.43
127.77
126.23
125.94
124.24
113.83
97.50
79.43
56.68
56.09
55.99
52.98
39.07
28.97
28.31
56.68
56.09
55.99
56.50
56.00
ppm (t1)
25000
20000
15000
10000
5000
400
300
200
100
0
-10
150
100
50

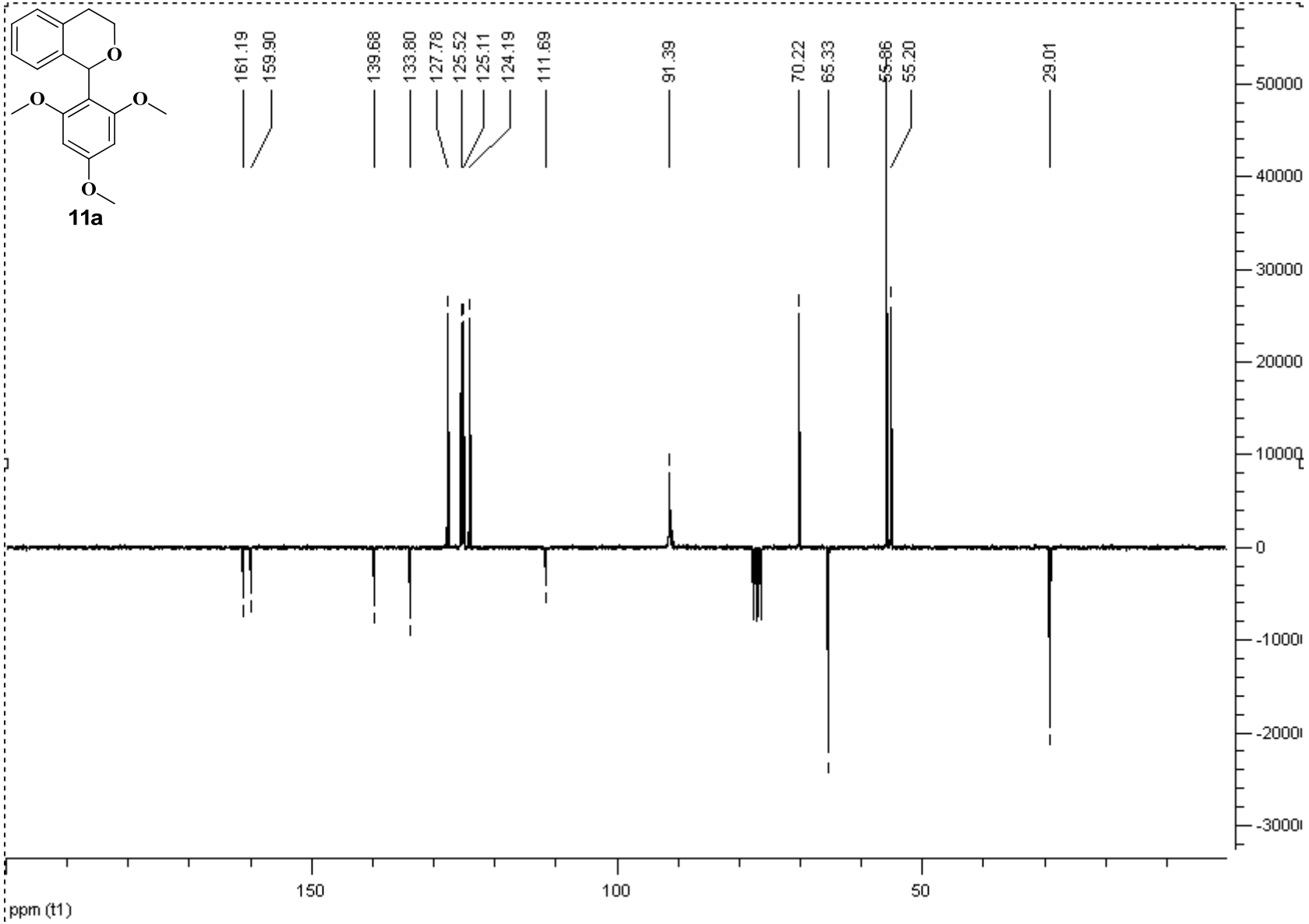

10e
3.05
1.00
0.95
0.98
0.95
2.99
5.97
4.23
2.05
9.07
5.97
3.800
3.750
3.700
ppm (t1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

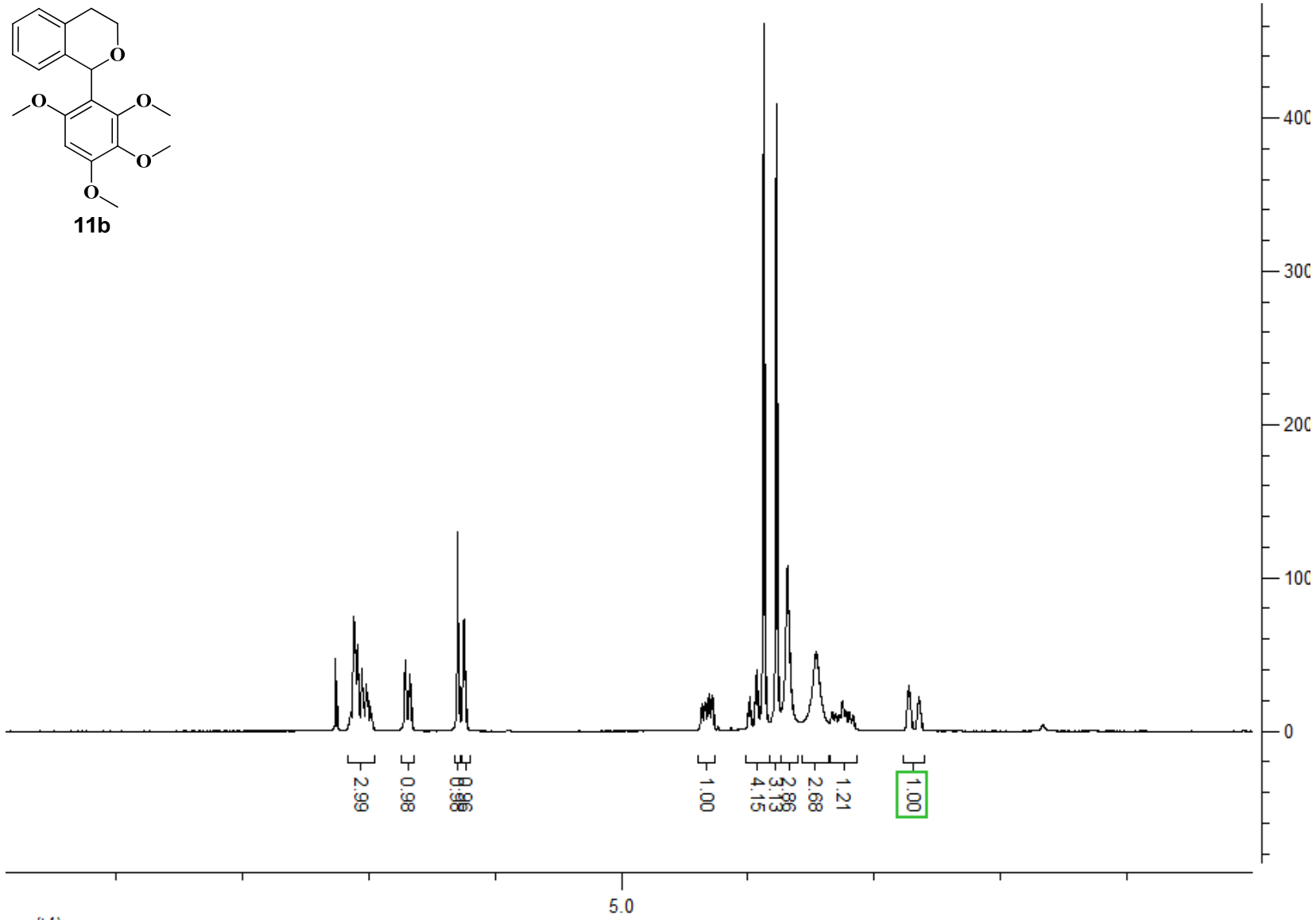

155.13
153.64
152.66
152.59
137.30
136.48
135.12
128.08
126.51
125.73
125.57
118.92
91.76
79.21
60.65
59.81
55.95
55.74
49.77
39.35
30.19
28.30
10e
55.95
55.74
57.0 56.0 55.0 54.0
ppm (t1)
150
100
50

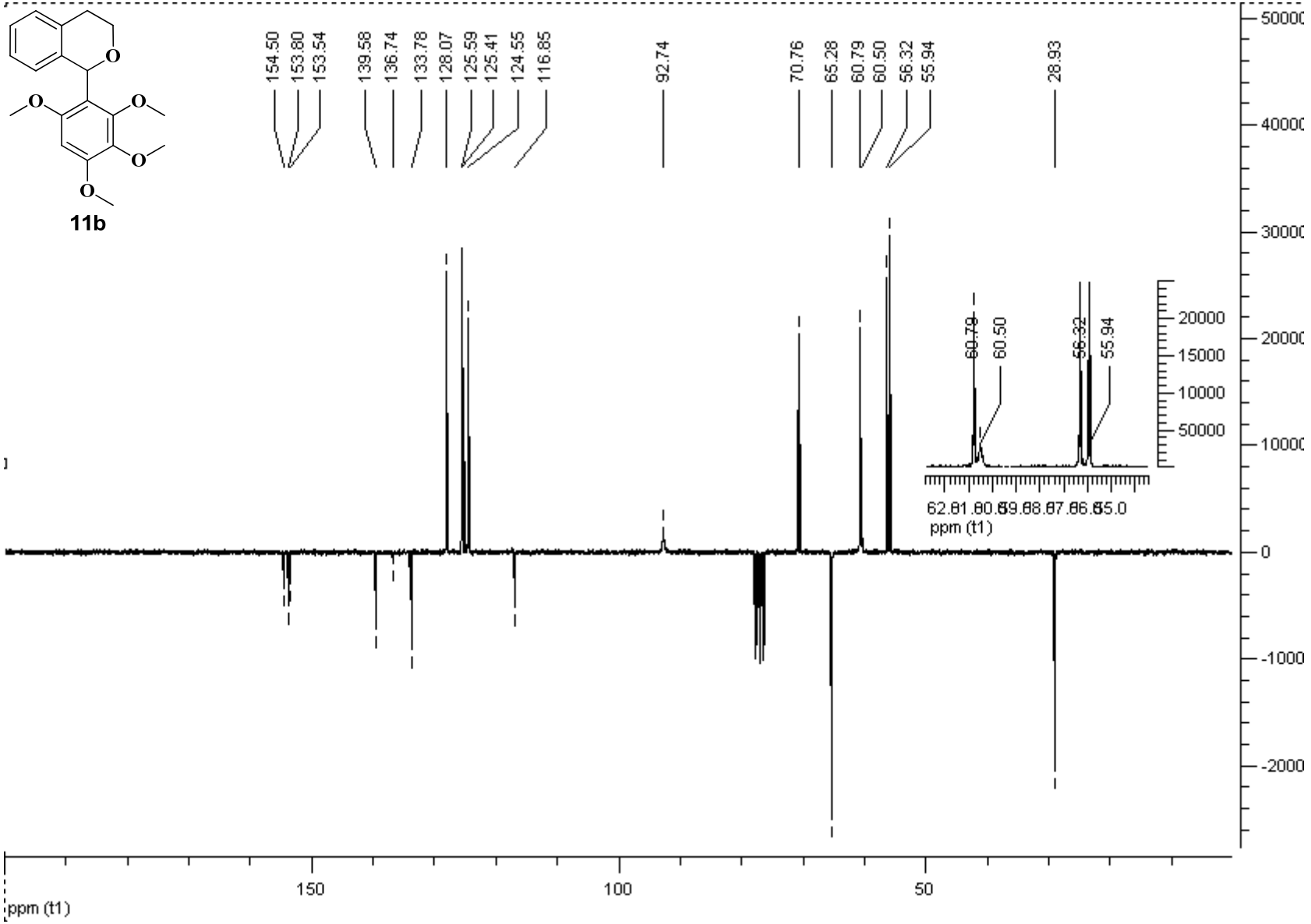

10f
500
400
300
200
100
0
3.22
0.97
1.00
2.05
1.04
0.99
3.24
1.08
1.10
1.07
9.17
5.0

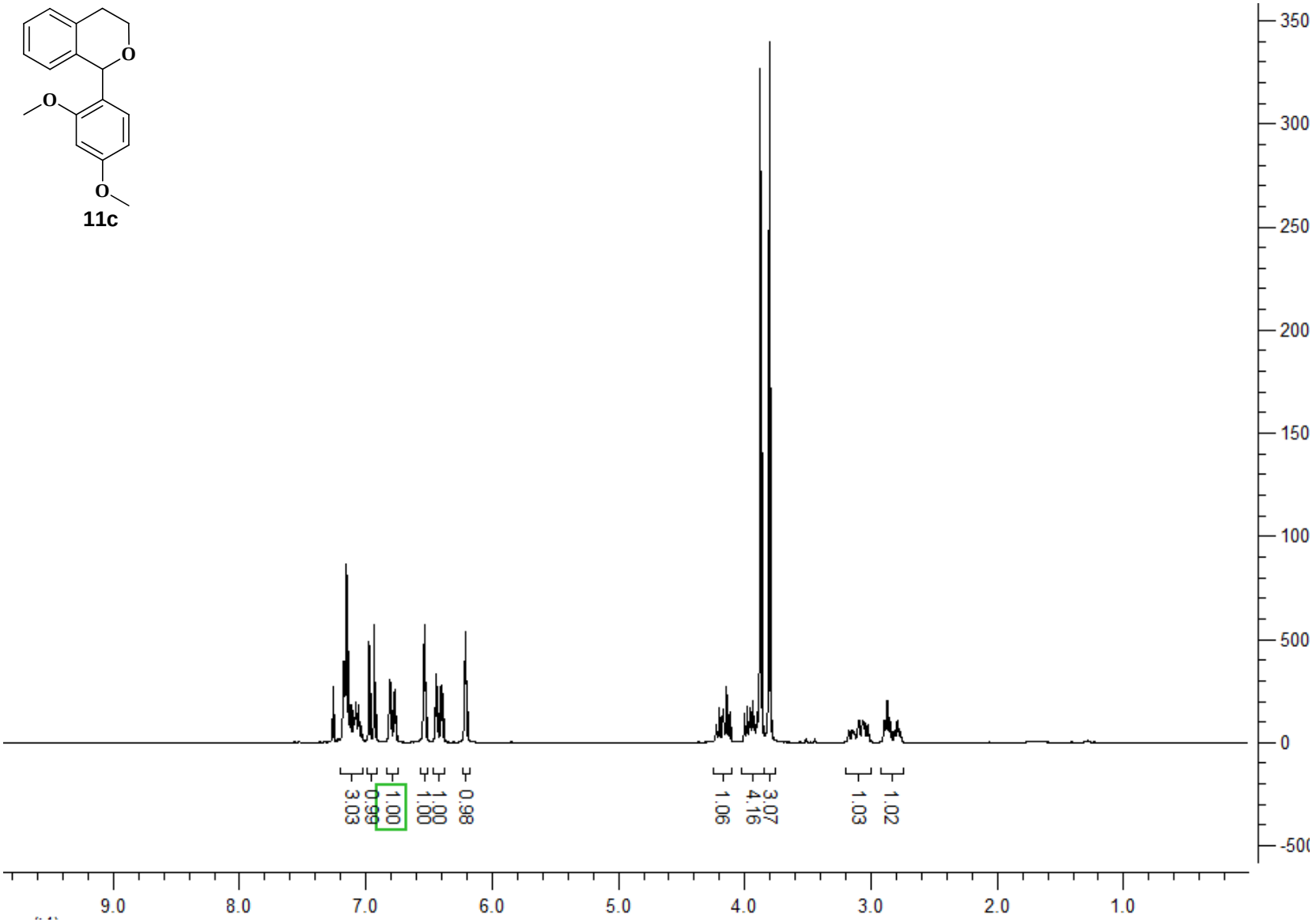

10f
159.92
158.02
154.65
136.85
135.00
130.02
128.50
127.87
126.20
125.88
125.11
103.42
98.38
79.29
55.19
55.15
52.62
38.60
28.78
28.31
25000
20000
15000
10000
50000
0
55.19
55.15
55.30
55.20
55.10
ppm (t1)
200
150
100
50
ppm (t1)

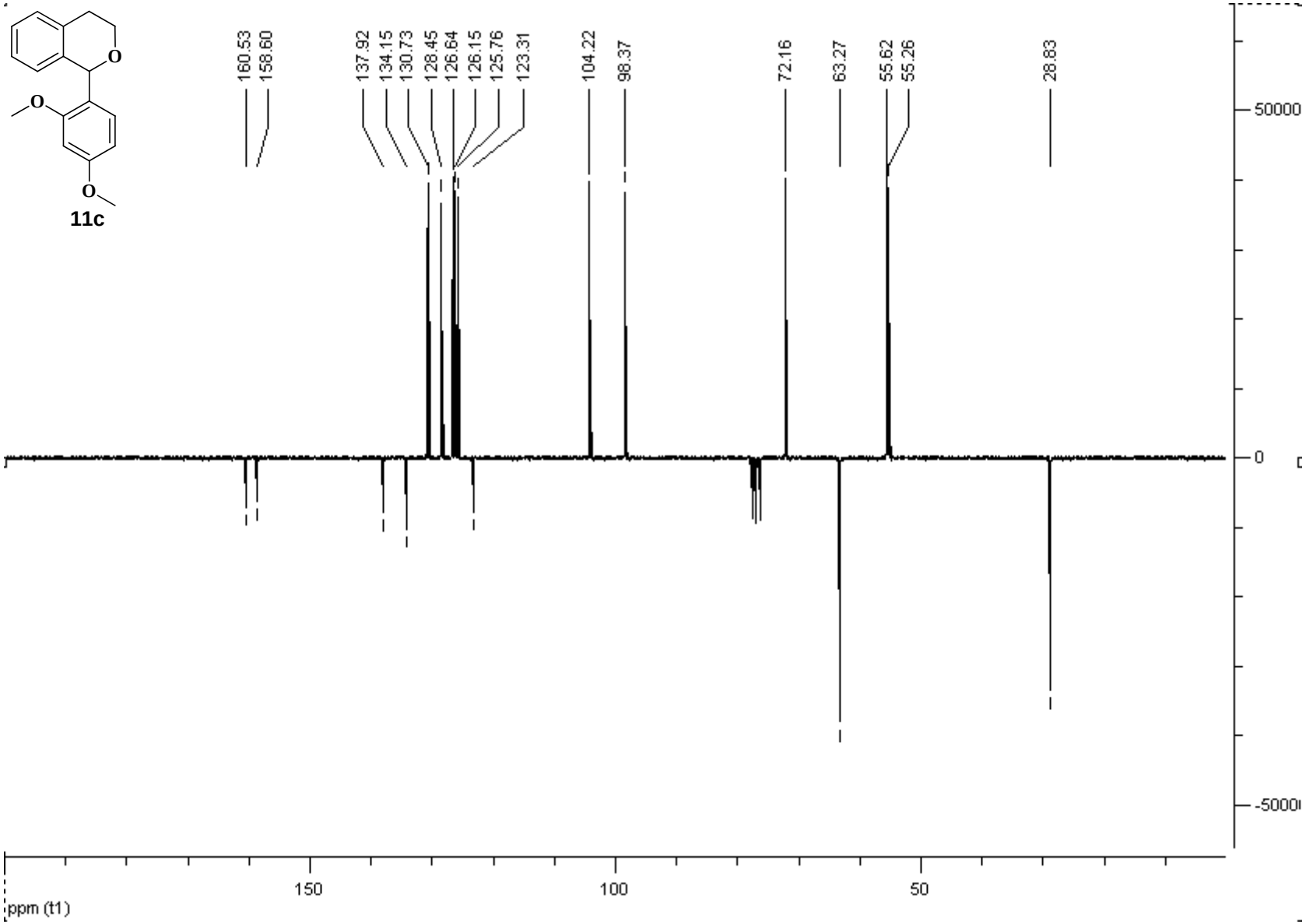

11a
250
200
150
100
500
0
3.08
1.00
1.01
1.99
1.01
1.14
3.06
5.99
1.11
1.03
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

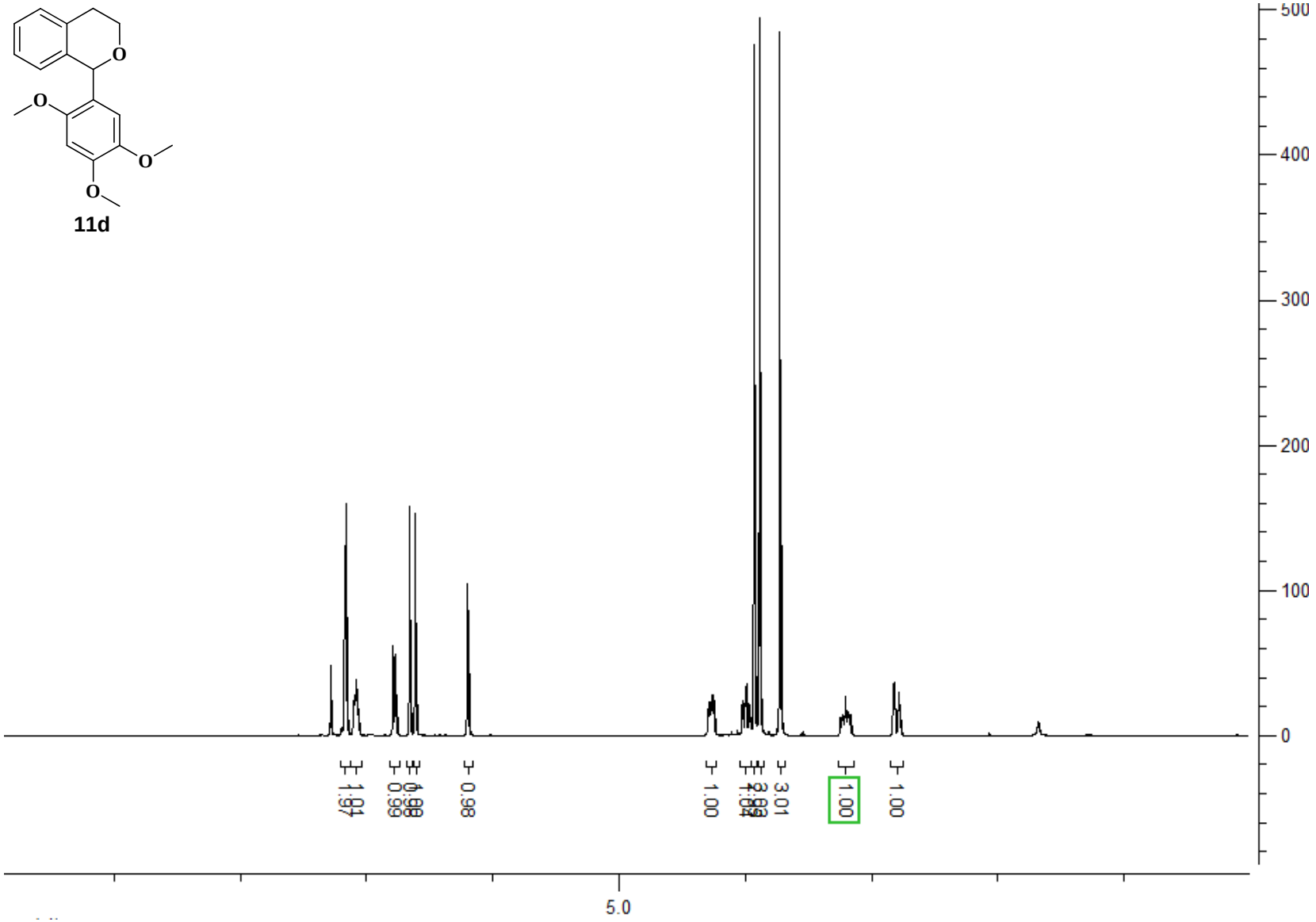

11a
161.19
159.90
139.68
133.80
127.78
125.52
125.11
124.19
111.69
91.39
70.22
65.33
55.86
55.20
29.01
50000
40000
30000
20000
10000
0
-10000
-20000
-30000
150
100
50
ppm (t1)

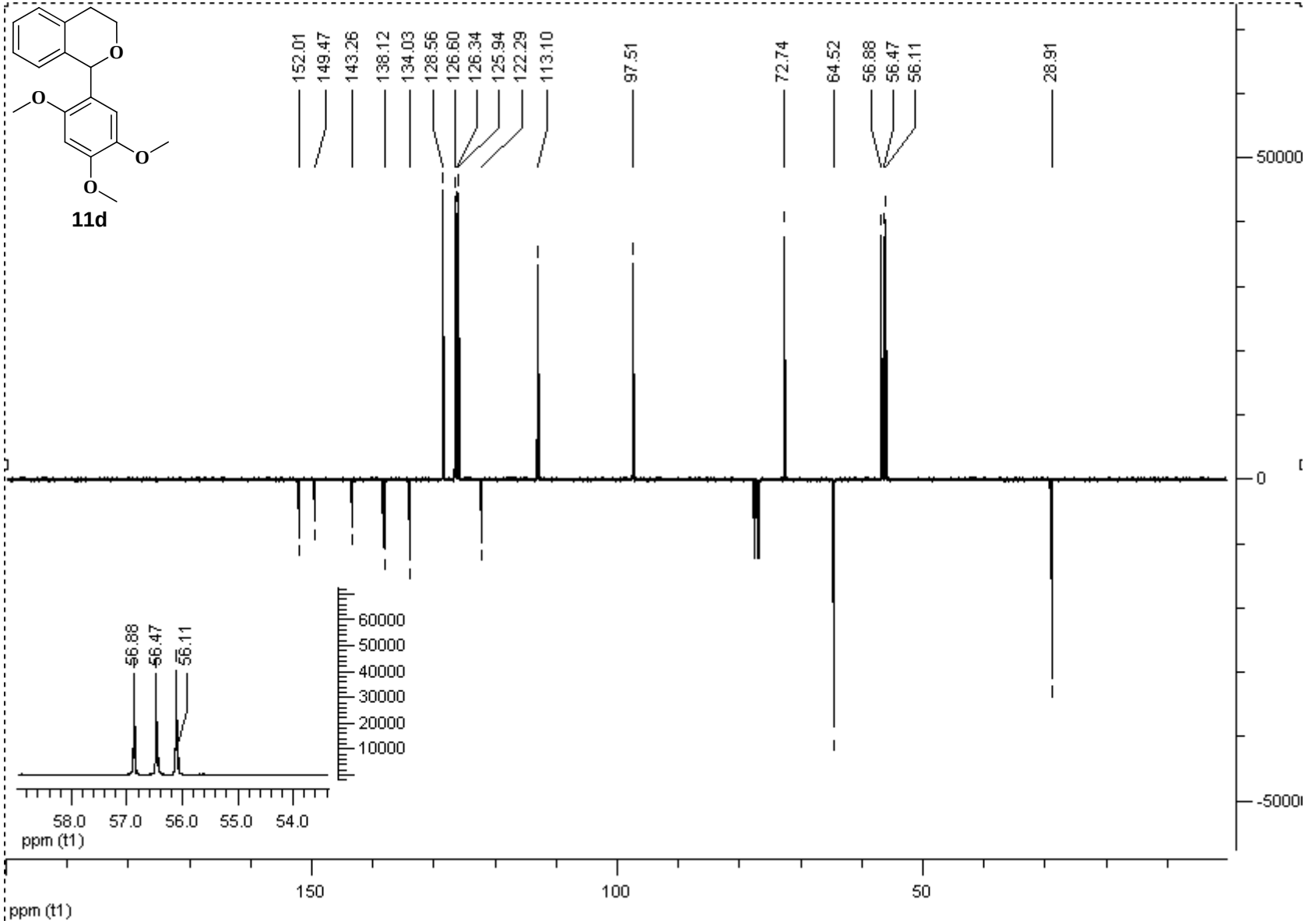

11b
400
300
200
100
0
2.99
0.98
1.00
4.15
2.68
1.21
1.00
5.0


11b
154.50
153.80
153.54
139.58
136.74
133.78
128.07
125.59
125.41
124.55
116.85
92.74
70.76
65.28
60.79
60.50
56.32
55.94
28.93
ppm (t1)
150
100
50
50000
40000
30000
20000
10000
0
-1000
-2000
20000
15000
10000
50000


11c
350
300
250
200
150
100
500
0
-500
3.03
0.99
1.00
1.00
0.98
1.06
4.16
3.07
1.03
1.02
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


11c
160.53
158.60
137.92
134.15
130.73
128.45
126.64
126.15
125.76
123.31
104.22
98.37
72.16
63.27
55.62
55.26
28.83
50000
0
-50000
150
100
50
ppm (t1)


11d
500
400
300
200
100
0
1.00
3.01
1.00
1.00
0.98
1.00
5.0


11d
152.01
149.47
143.26
138.12
134.03
128.56
126.60
126.34
125.94
122.29
113.10
97.51
72.74
64.52
56.88
56.47
56.11
28.91
50000
0
-50000
60000
50000
40000
30000
20000
10000
58.0
57.0
56.0
55.0
54.0
ppm (t1)
150
100
50
ppm (t1)