Supplementary Information

Assignment of ^{1}H and ^{13}C NMR spectra

Due to the nature of the project it was essential that we were certain of the structure of the compounds that were prepared. It was our aim was to unambiguously assign the proton and carbon signals in every molecule prepared. This involved numerous NMR experiments and a representative example of the analysis performed on amine **27** (Figure 1) is outlined below.

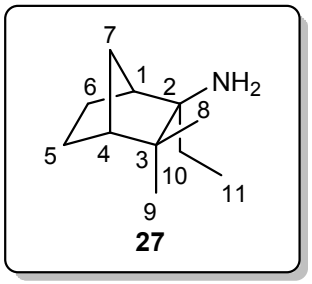


Figure 1 NMR assignment for amine 27

A HSQC (heteronuclear single quantum coherence) experiment was performed (Figure 2). This allows the construction of a large portion of Table 1 which displays the direct connectivity of proton and carbon signals. The chemical shift for the quaternary carbons was taken from the standard ^{13}C 1-D spectrum. (Figure 3) The DEPT 135 (distortionless enhancement by polarization transfer) experiment displayed on the y-axis in Figure 2 facilitated identification of the CH_2 carbon signals which were phase shifted by 180°. It was possible to distinguish between CH and CH_3 carbon signals from a DEPT 90 experiment (not shown). The area highlighted in Figure 2 is shown in greater detail in Figure 4 which allowed one to distinguish between the ^{1}H signals for carbon 5 and 6 which were separated by 0.1 ppm in the ^{13}C spectrum.

The information required to complete the 'position' column in Table 1 will be outlined in due course.

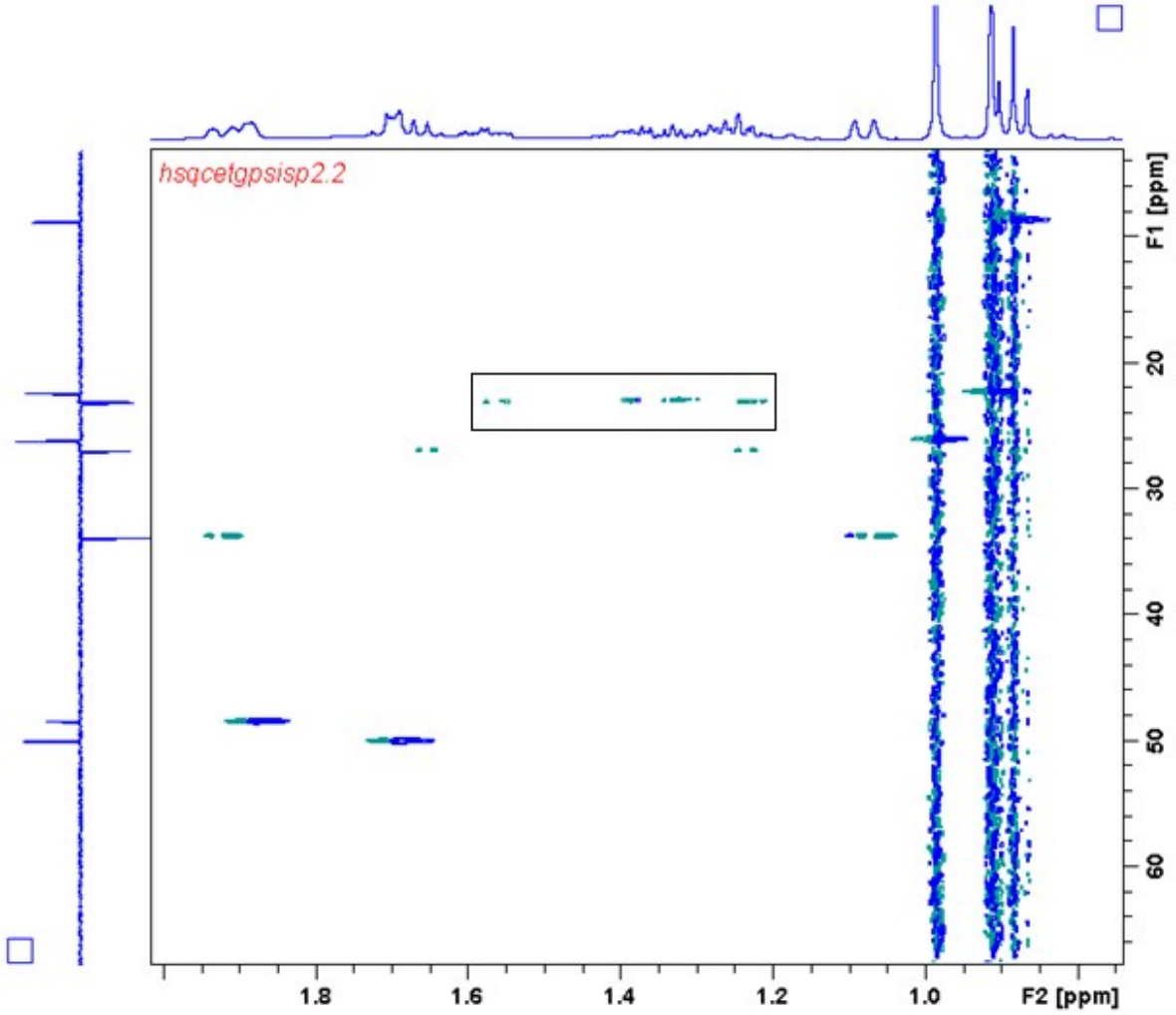


Figure 2: HSQC experiment: ^{1}H NMR on x axis and DEPT 135 on y-axis

Table 1 Complete NMR assignment of amine 27

Carbon (ppm)	Type	Proton (ppm)	Position
8.9	CH3 (t)	0.88	11
22.4	CH3 (s)	0.91	9
23.0	CH2 (m)	1.29-1.40	6
23.1	CH2 (m)	1.19-1.27 and 1.54-1.62	5
26.2	CH3 (s)	0.99	8
27.0	CH2 (m)	1.20-1.27 and 1.62-1.70	10
33.8	CH2 (m)	1.04-1.11 and 1.89-1.96	7
43.0	q		3
48.5	CH (m)	1.86-1.90	1
50.1	CH (m)	1.68-1.72	4
61.5	q		2

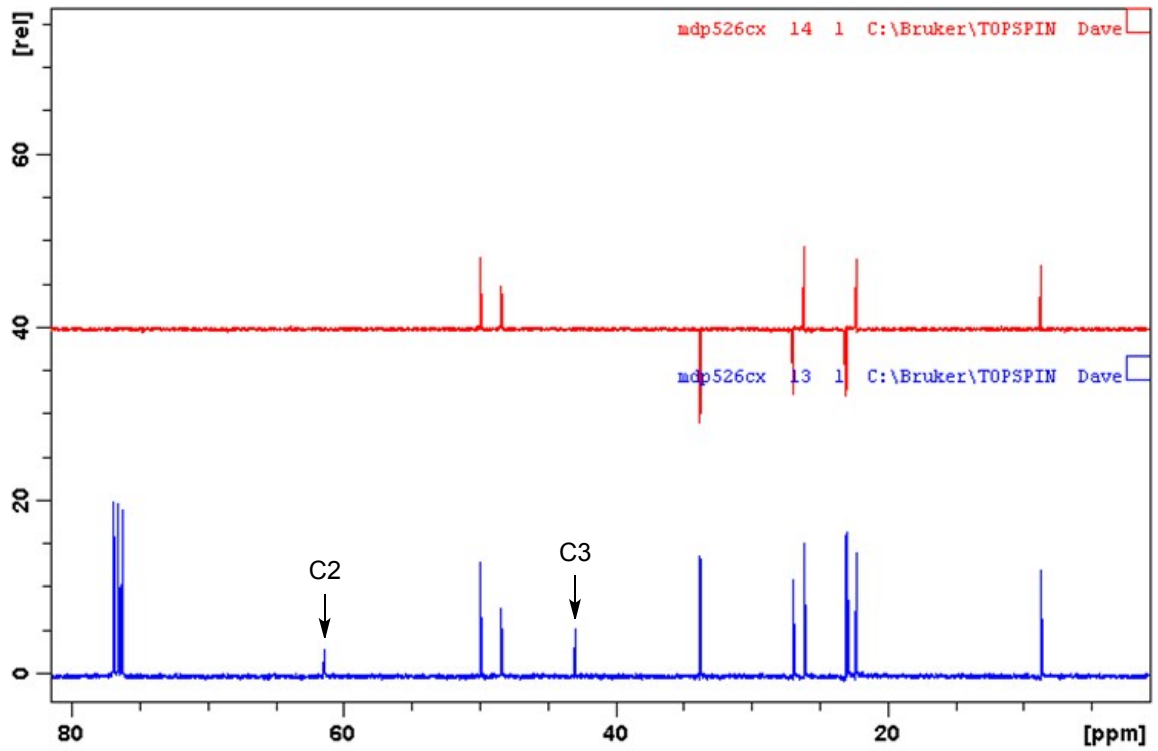


Figure 3: 13C and DEPT 135 experiments for amine 27

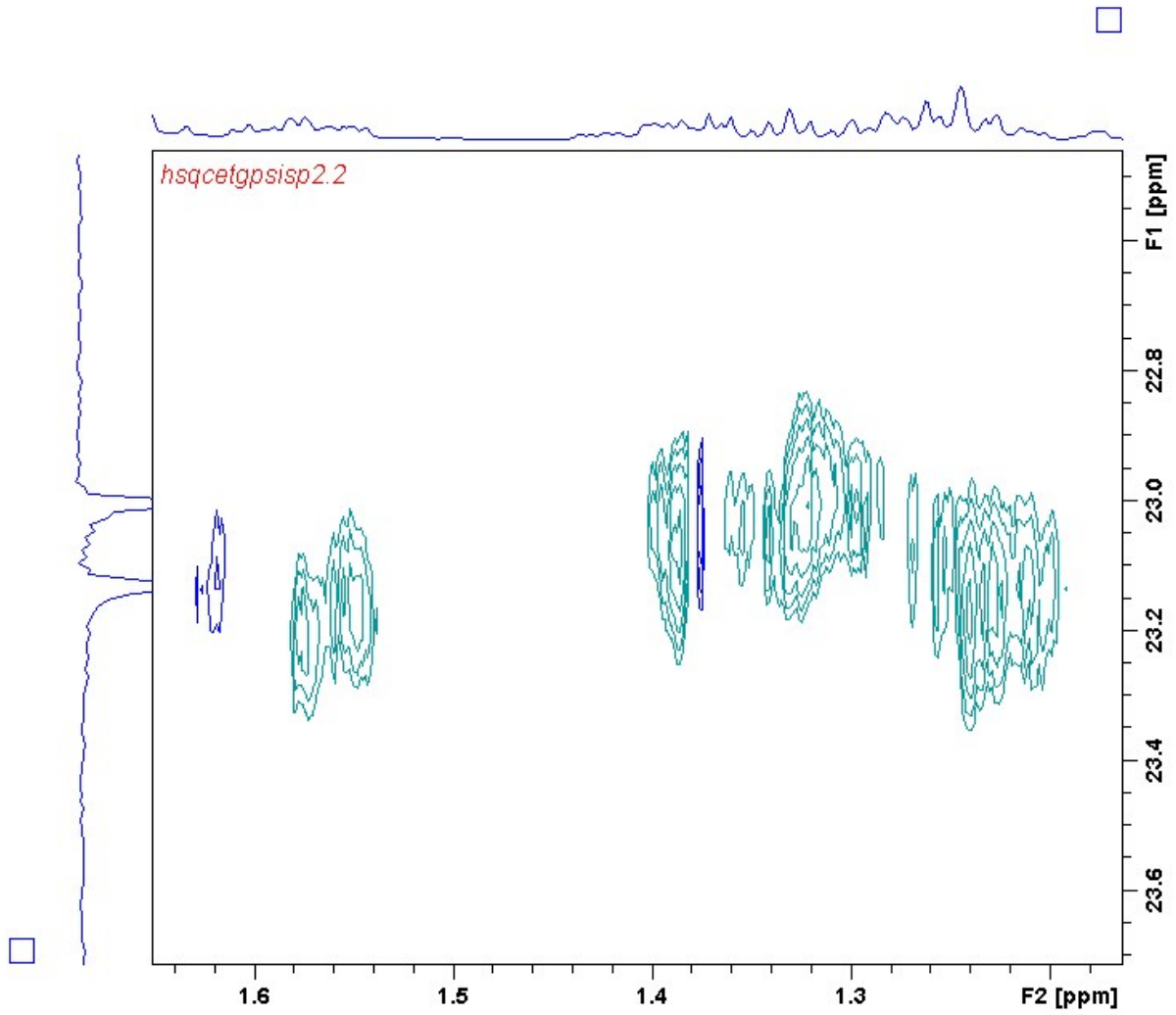


Figure 4: Magnification of a portion of the HSQC response for amine 27

A TOCSY (total correlation spectroscopy) experiment was performed to analyse the interactions between protons on adjacent carbons (or on the same carbon if the protons were diastereotopic).

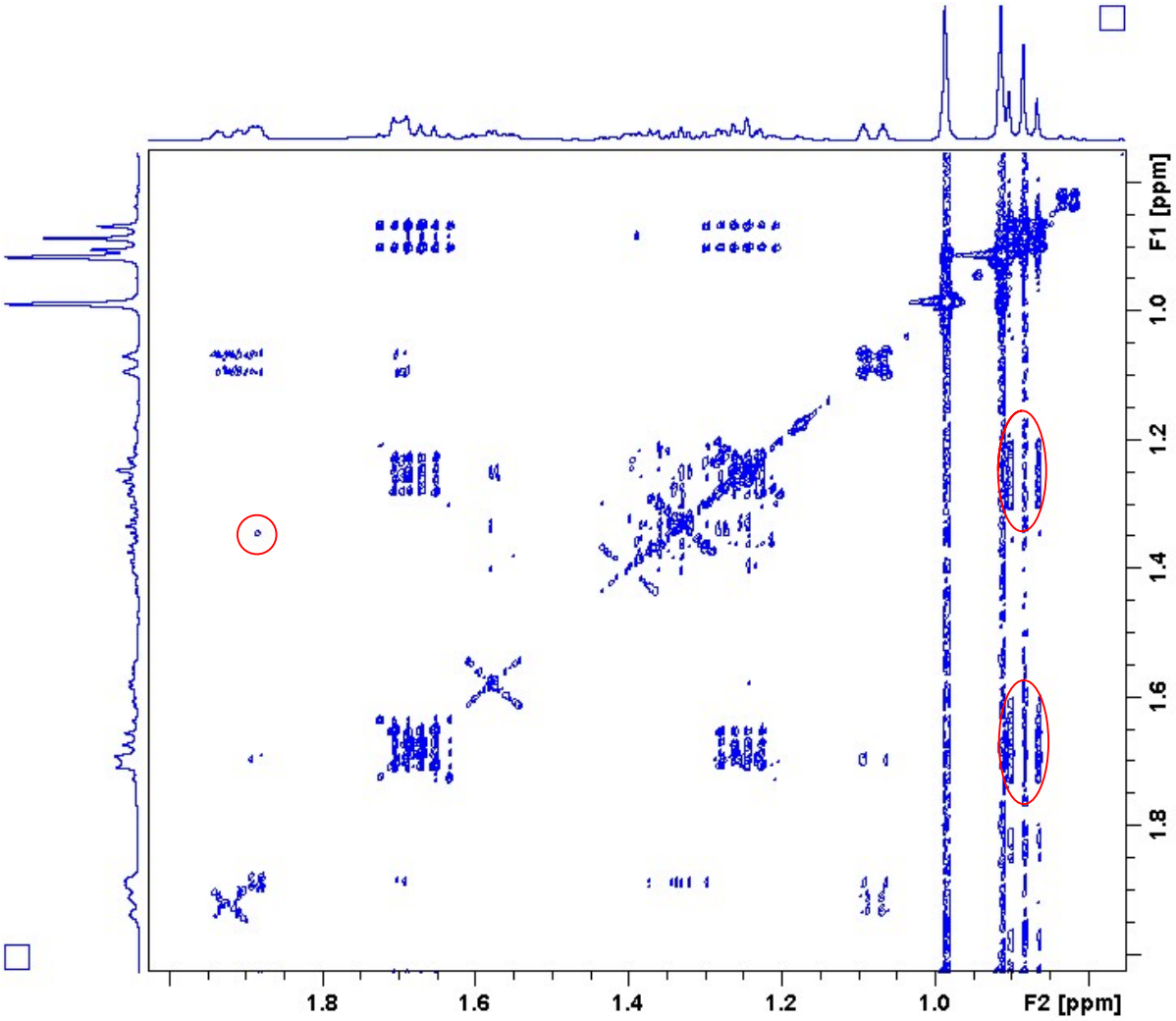


Figure 5: TOCSY experiment: ^{1}H NMR on both x and y axes

The methyl triplet signal at 0.88 ppm showed a response at 1.20-1.27 ppm and 1.62-1.70 ppm which corresponds to the CH_2 at 27.0 ppm. Hence, carbons 10 and 11 were assigned. Also evident, is an interaction between the CH at 1.86-1.90 ppm and the CH_2 at 1.29-1.40 although unambiguous assignment of these signals was not yet possible. As a result, a HMBC (heteronulcear multiple bond coherence) experiment was performed to analyse long range carbon-hydrogen interactions in an attempt to characterise the relevant CH position.

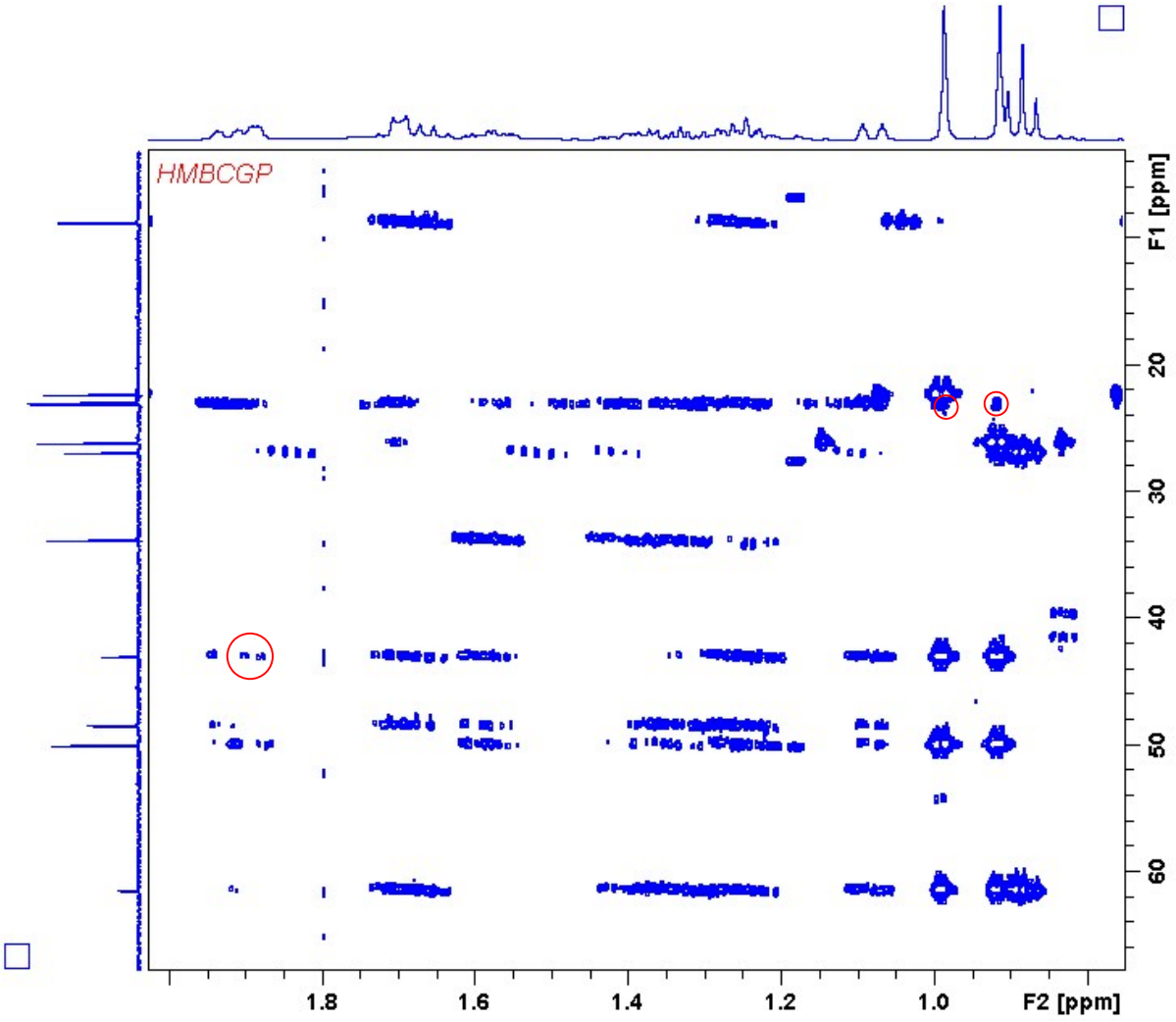


Figure 6: HMBC experiment on amine 27: ^{1}H NMR on x axis and ^{13}C NMR on y axis

An interaction was observed between the quaternary carbon 3 and the CH at 1.86-1.90 ppm. HMBC responses are generally strongest between atoms separated by three bonds, implying the CH in question is at position 1. The HH-COSY interaction (Figure 5) observed for this signal implies that the CH_2 at 1.29-1.40 ppm is at position 6. A number of the remaining signals could also be identified at this point. The second CH (51.1 ppm) was assigned to position 4. It was thought to be highly likely that carbons 5 and 6 would have very similar chemical shifts allowing the CH_2 at 23.1 ppm to be assigned to position 5. Further evidence to support this claim was available from the HMBC experiment (Figure 6) which shows an interaction between both methyl singlets and the CH_2 at 23.1 ppm (C5). The remaining CH_2 was attributed to position 7.

In order to confirm the proposed characterization and also to define the stereochemistry in this system, a series of nOe (nuclear Overhauser effect) experiments were performed in order to analyse the 'through space' interactions for a selected number of protons.

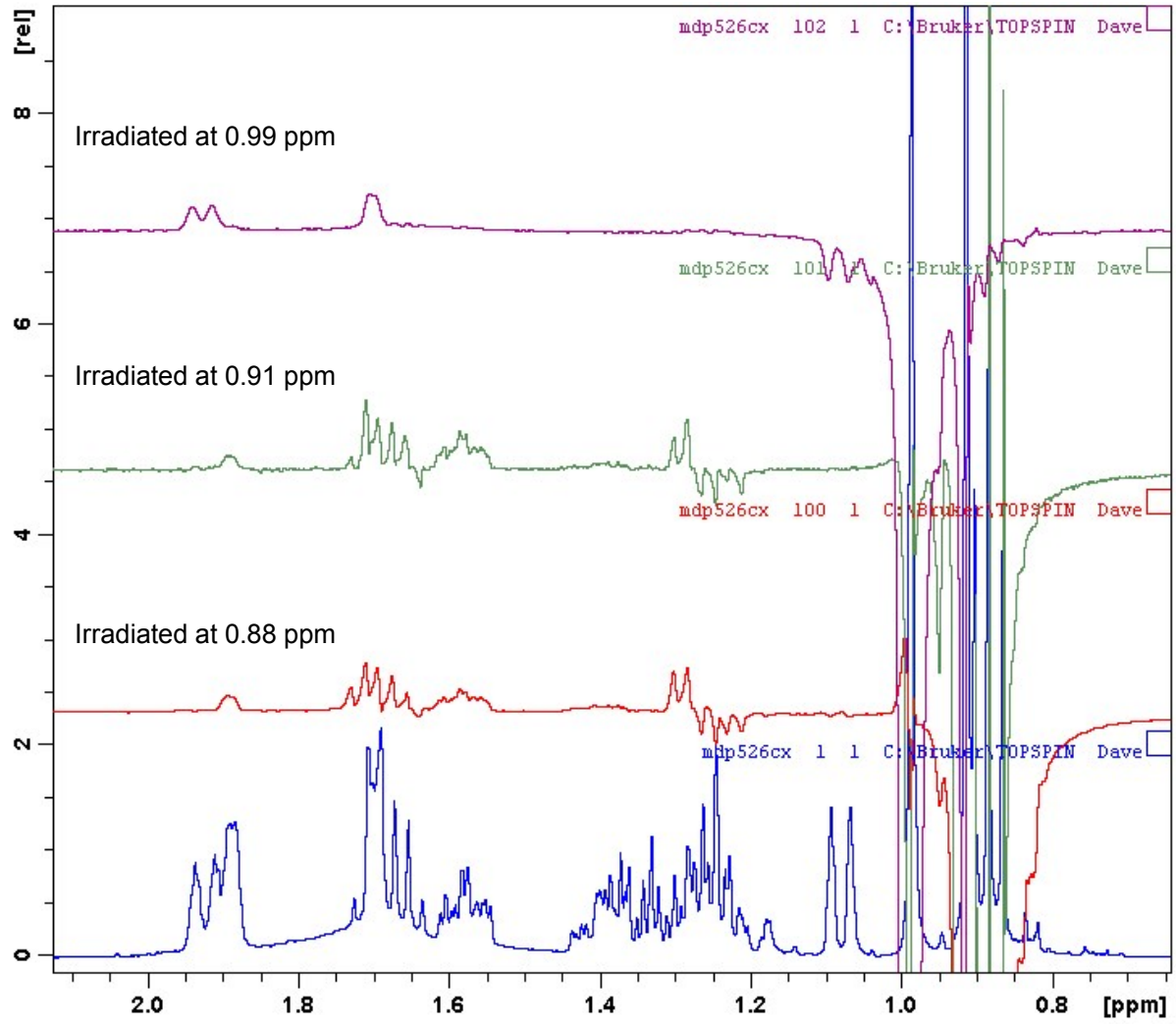


Figure 7: nOe experiments irradiating the methy substituents in amine 27 and original ^{1}H NMR

In the spectrum for the experiment irradiating at 0.99 ppm, the response visible for the CH at 1.68 - 1.72 ppm confirms the earlier assignment of position 4. The response at 1.89-1.96 ppm corresponds to the interaction shown in Figure 8.

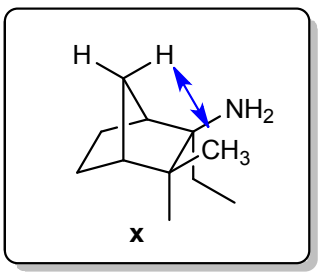


Figure 8: nOe response between H8 and H7b in amine 27

This confirms the assignment of position 7 and allows unambiguous assignment of the *exo* methyl substituent. The nOe experiments irradiating the two remaining methyl groups proved to be less informative, as their chemical shifts were too close to allow selective irradiation of each signal individually. Vitally however, there was clearly no response observed with the NOE experiments irradiating at 0.91 or 0.88 ppm for the signal at 1.89-1.96 ppm, thereby confirming these substituents reside in an *endo* orientation.

This methodical approach was applied to every compound synthesised. Analysis of the stereochemistry of the alkyl substituents at positions 2 and 3 was generally carried out only for one of the azide, amine or methylated amine of each analogue as it was known that the stereochemistry was immutable throughout these transformations.

In certain cases, unambiguous stereochemical assignment was not possible. This generally arose in the case of 3,3-diethyl compounds, in which nOe analysis of the type described above was prevented by the fact that the ^{1}H NMR signals for CH_2 protons on ethyl substituents tended to give rise to overlapping multiplets that could not be selectively irradiated. In these cases, the ethyl substituents were assigned arbitrarily. An example is shown in Figure 9.

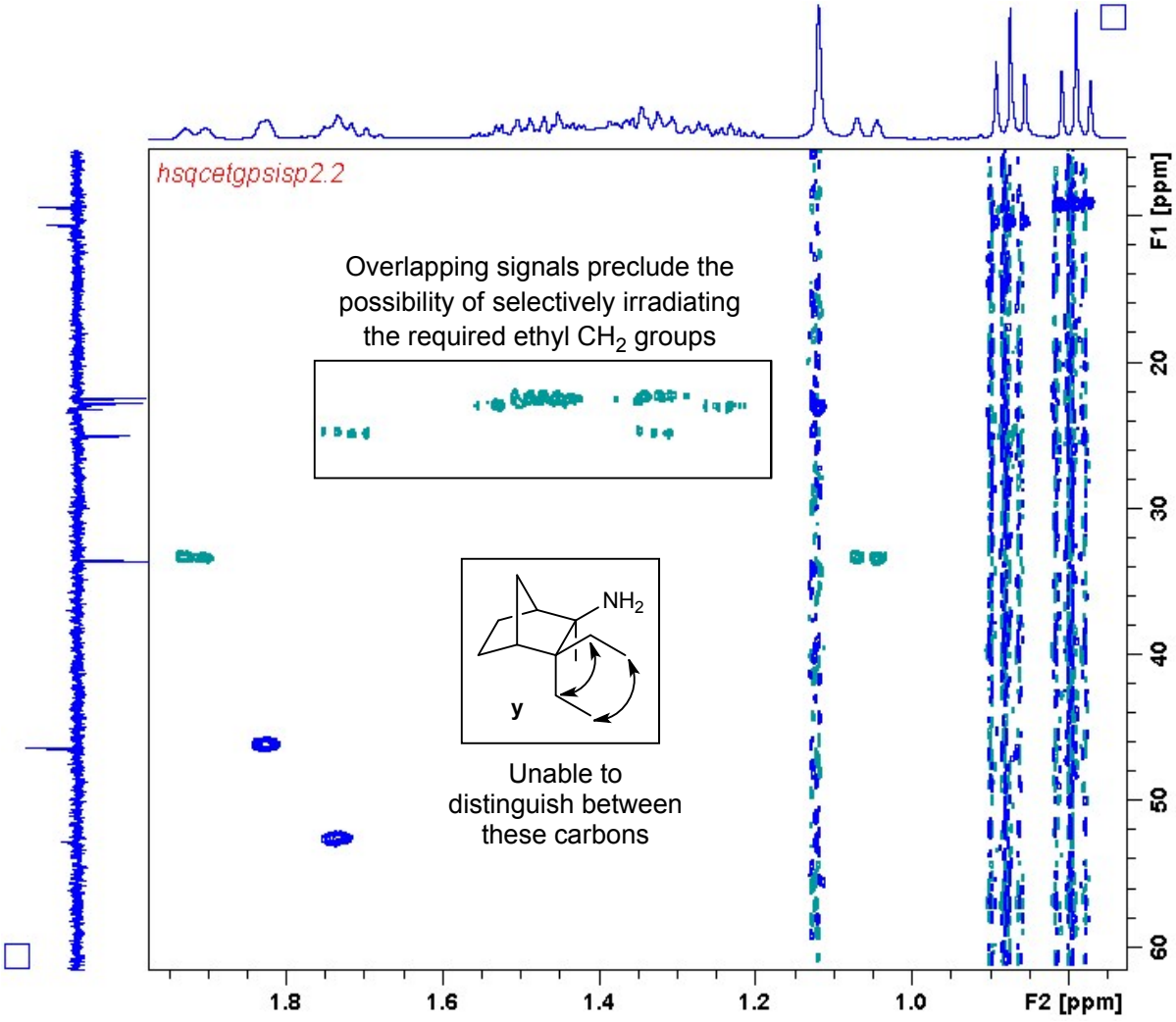
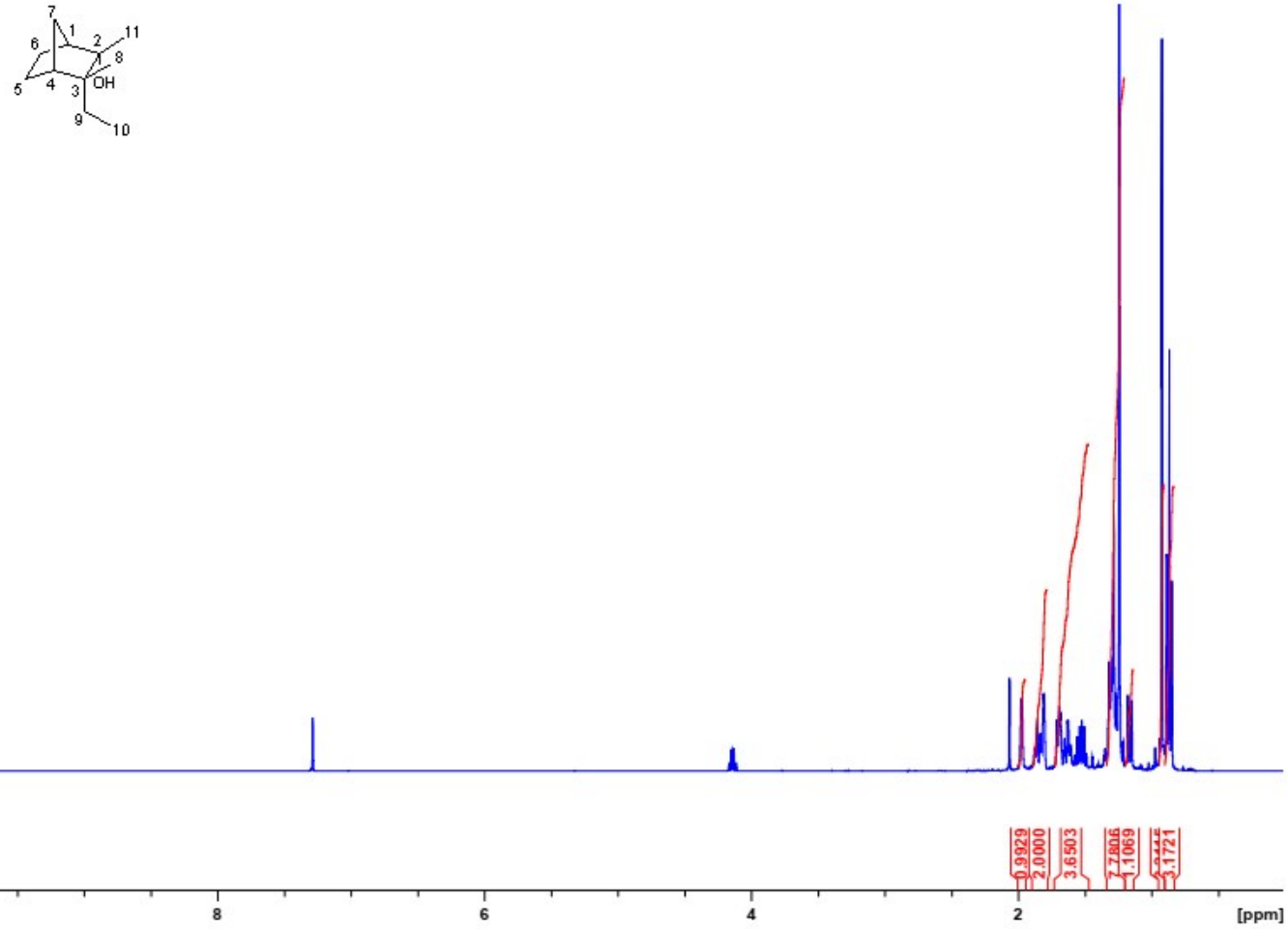


Figure 9: Inability to unambiguously assign NMR spectra in amine 27

NMR spectra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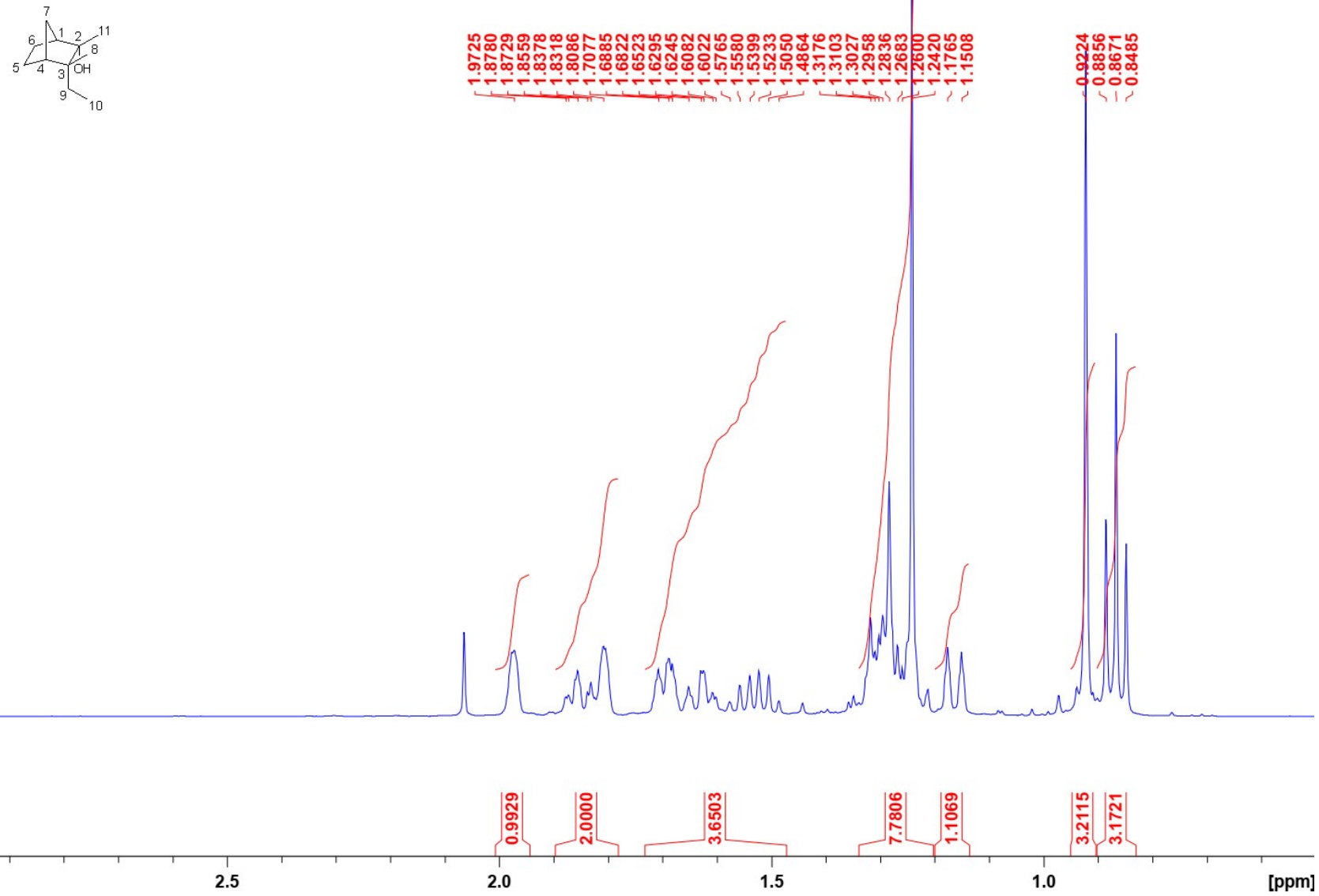
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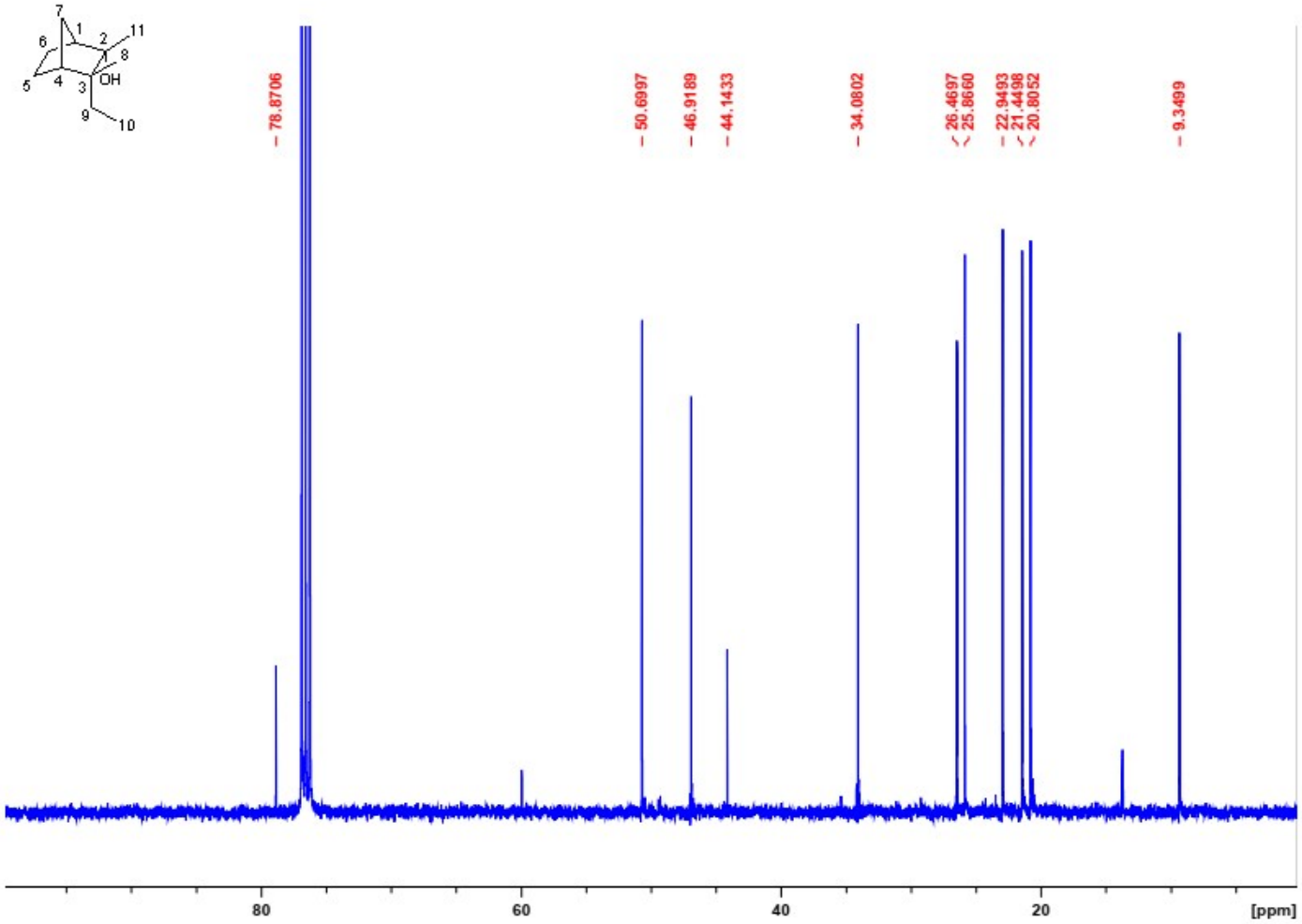
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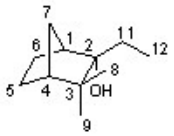
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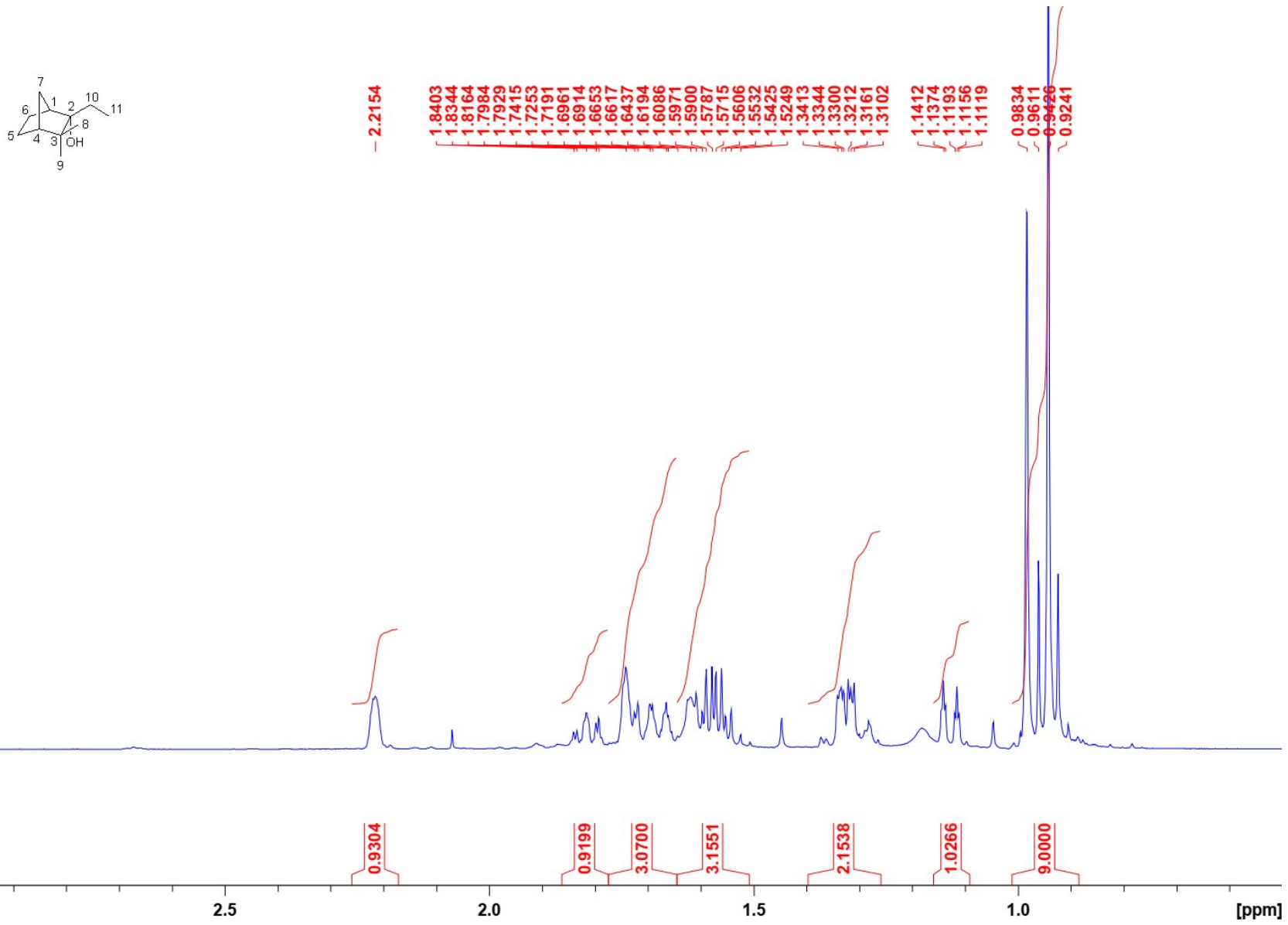
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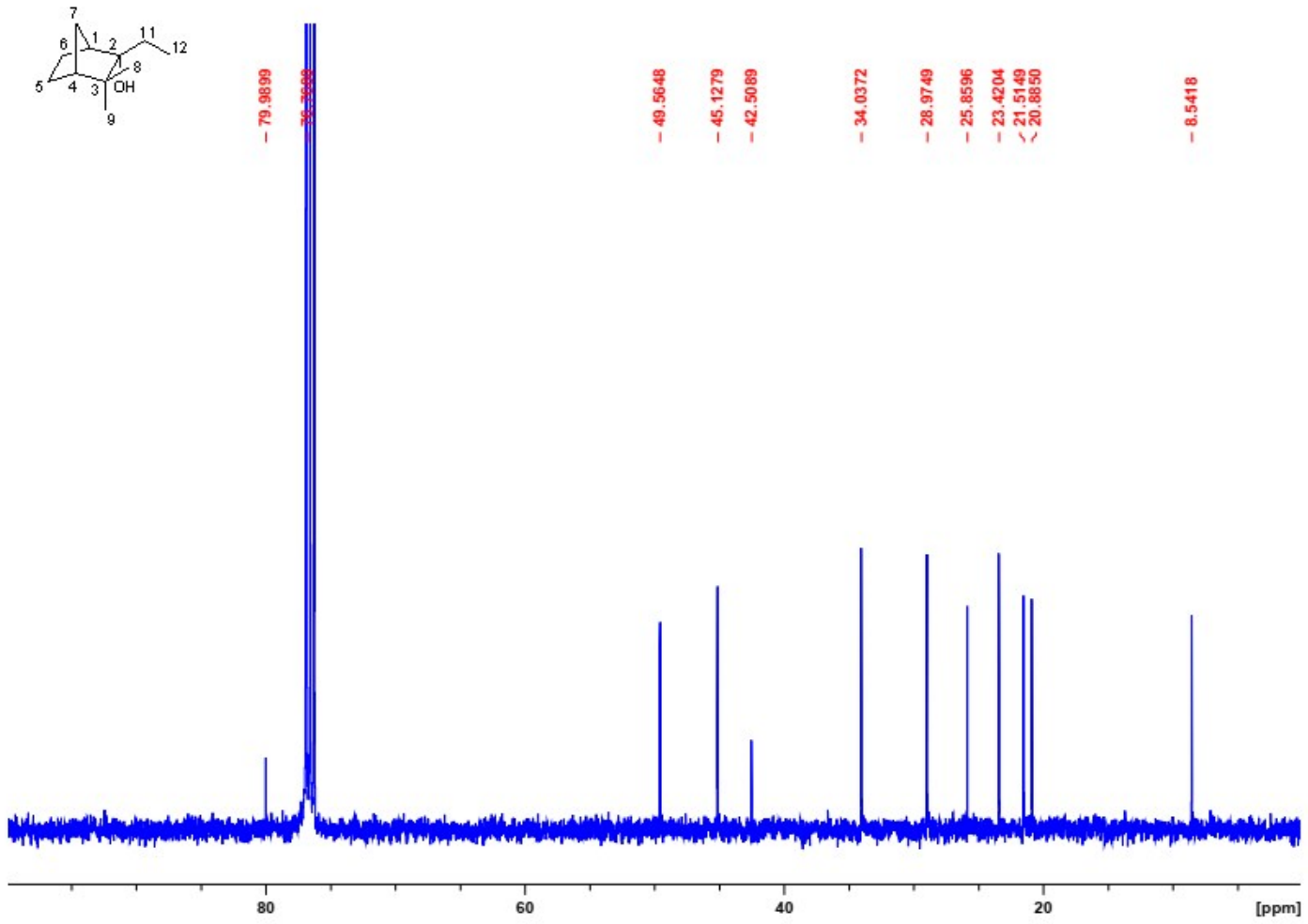
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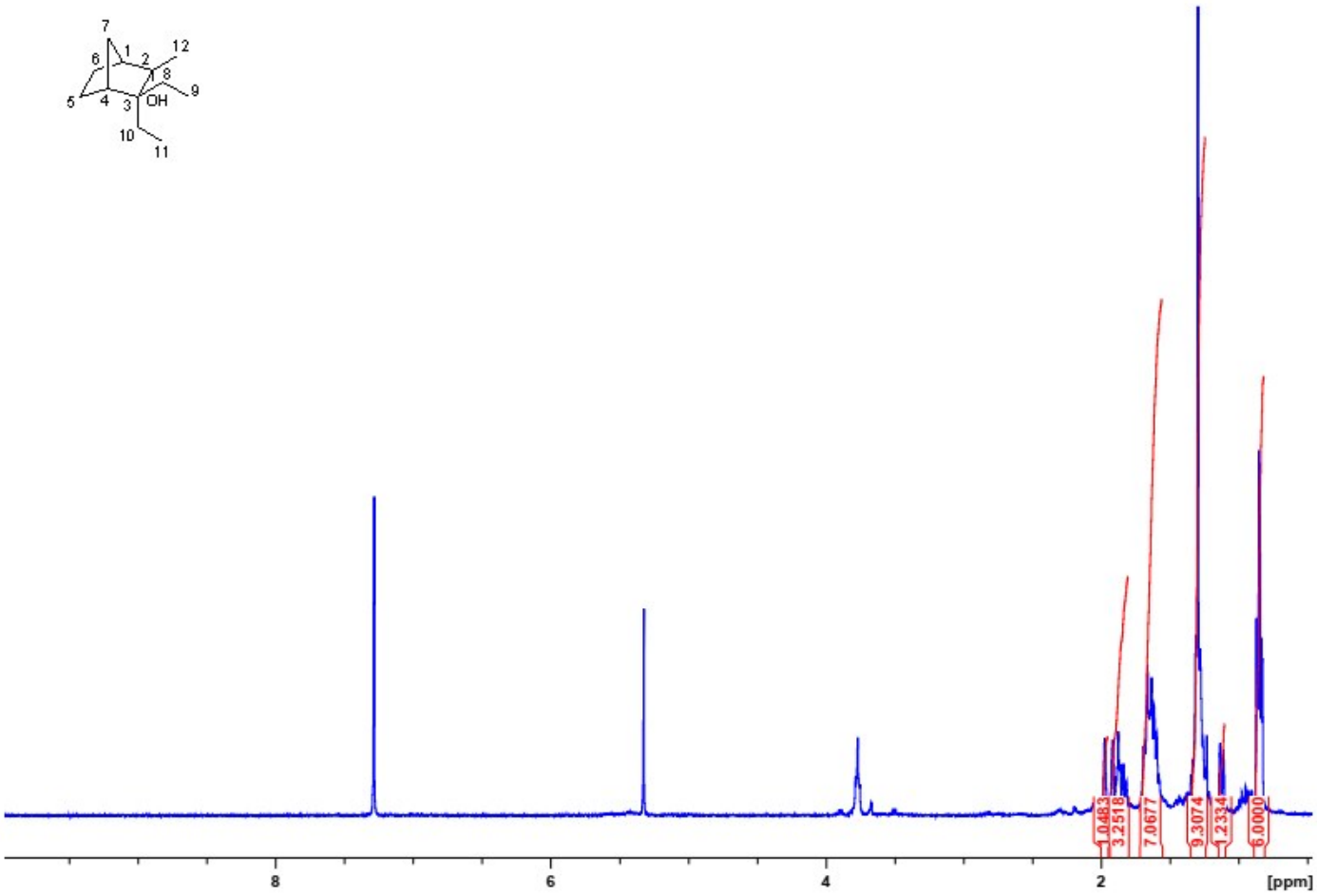
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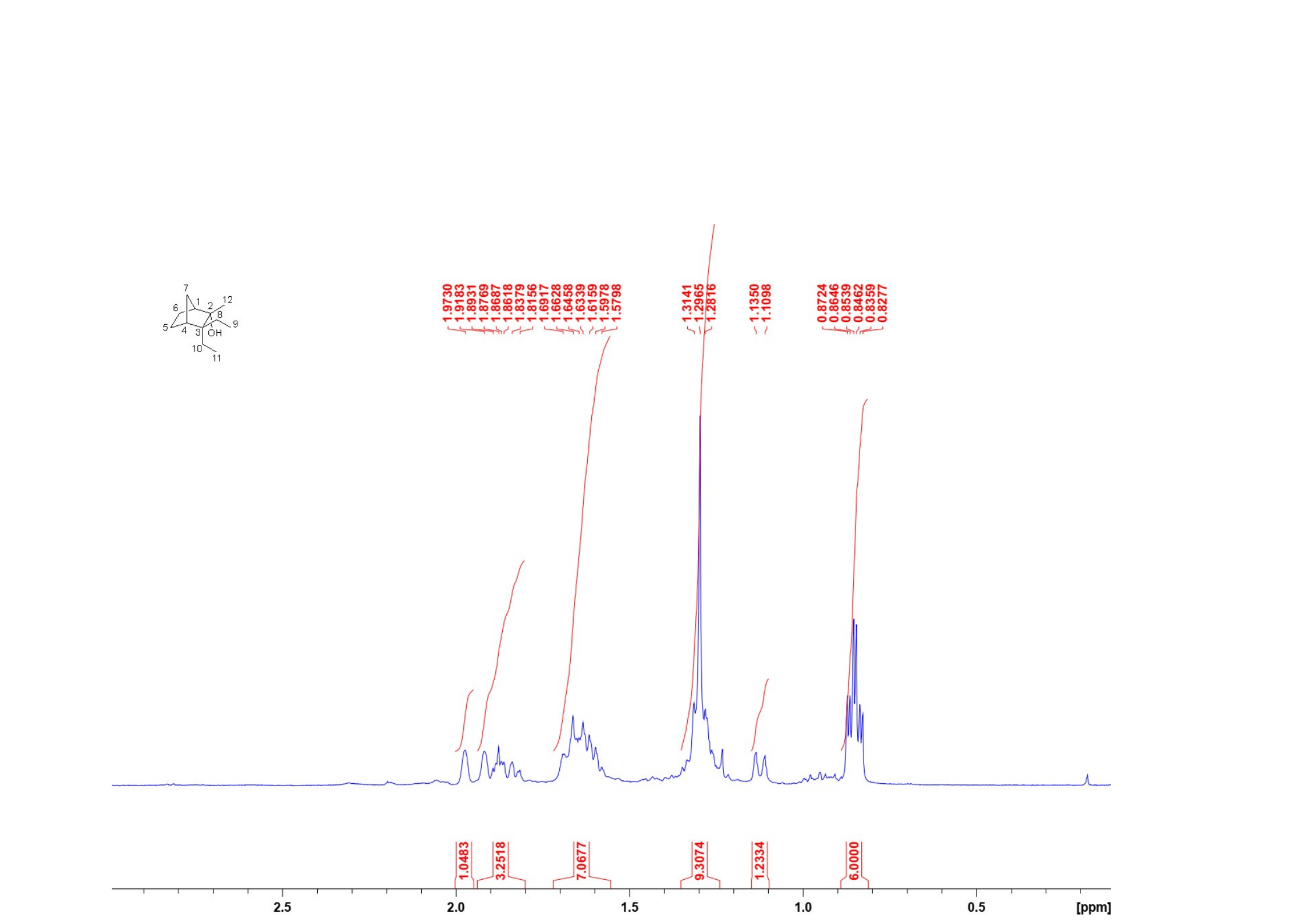
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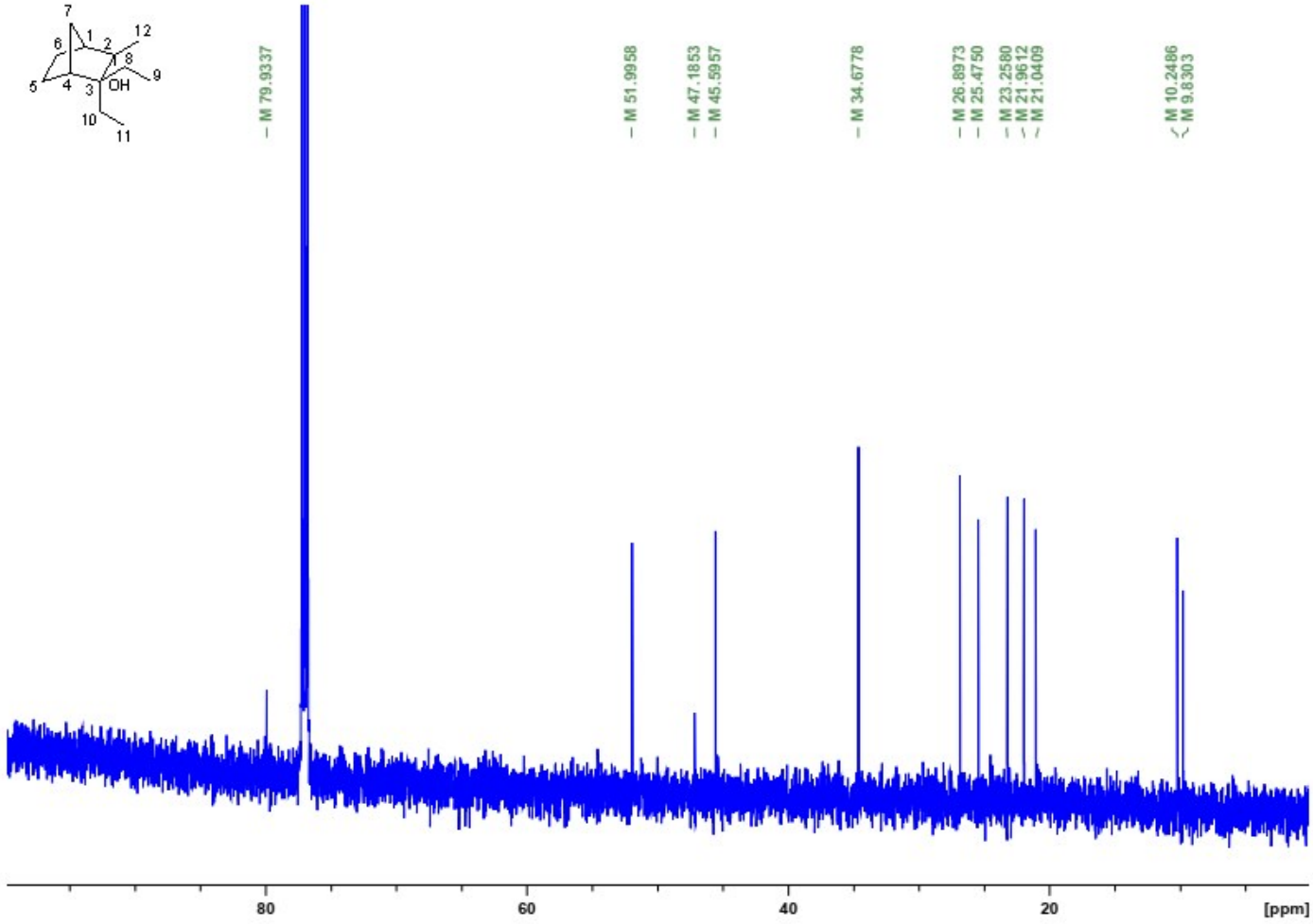
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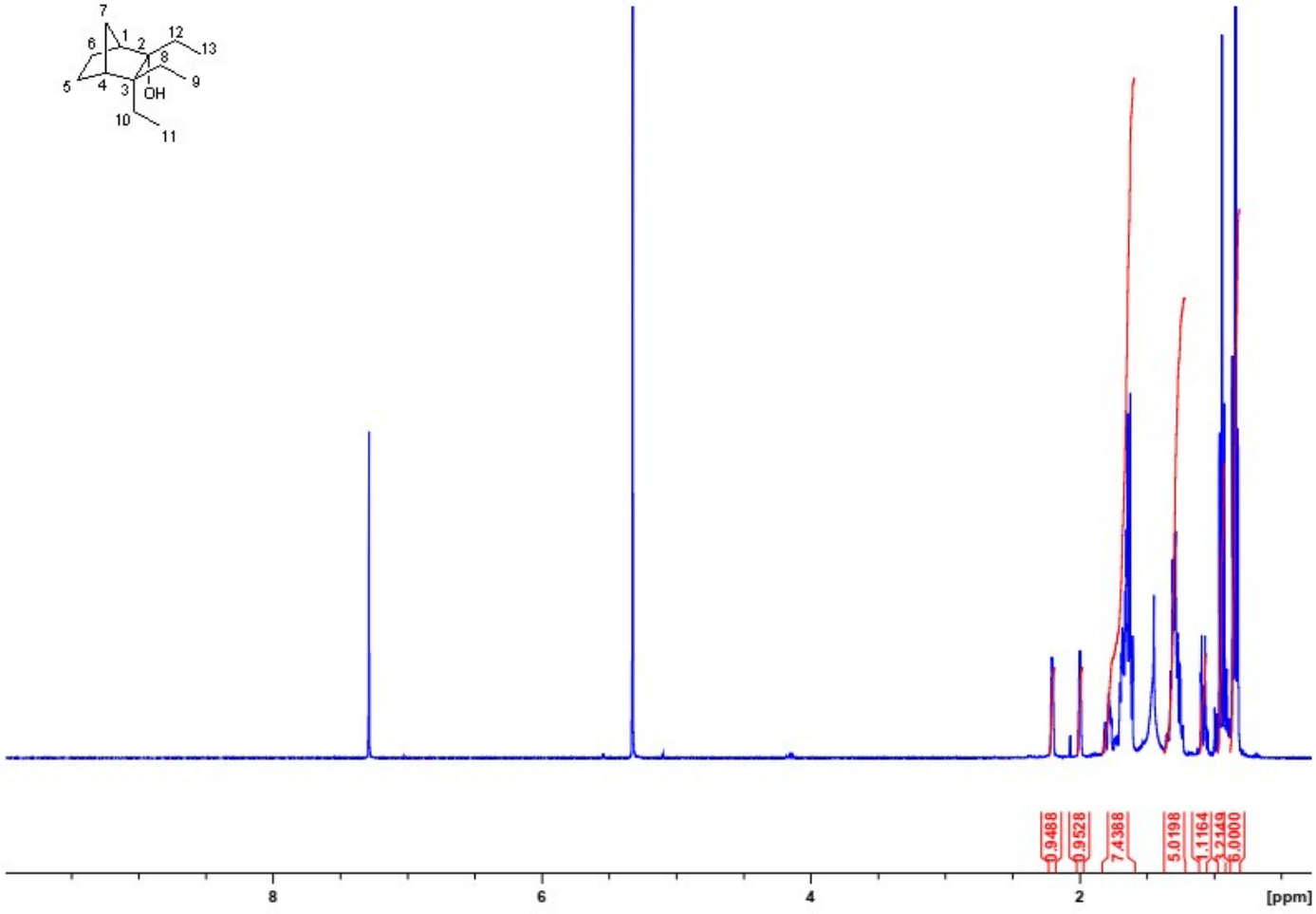
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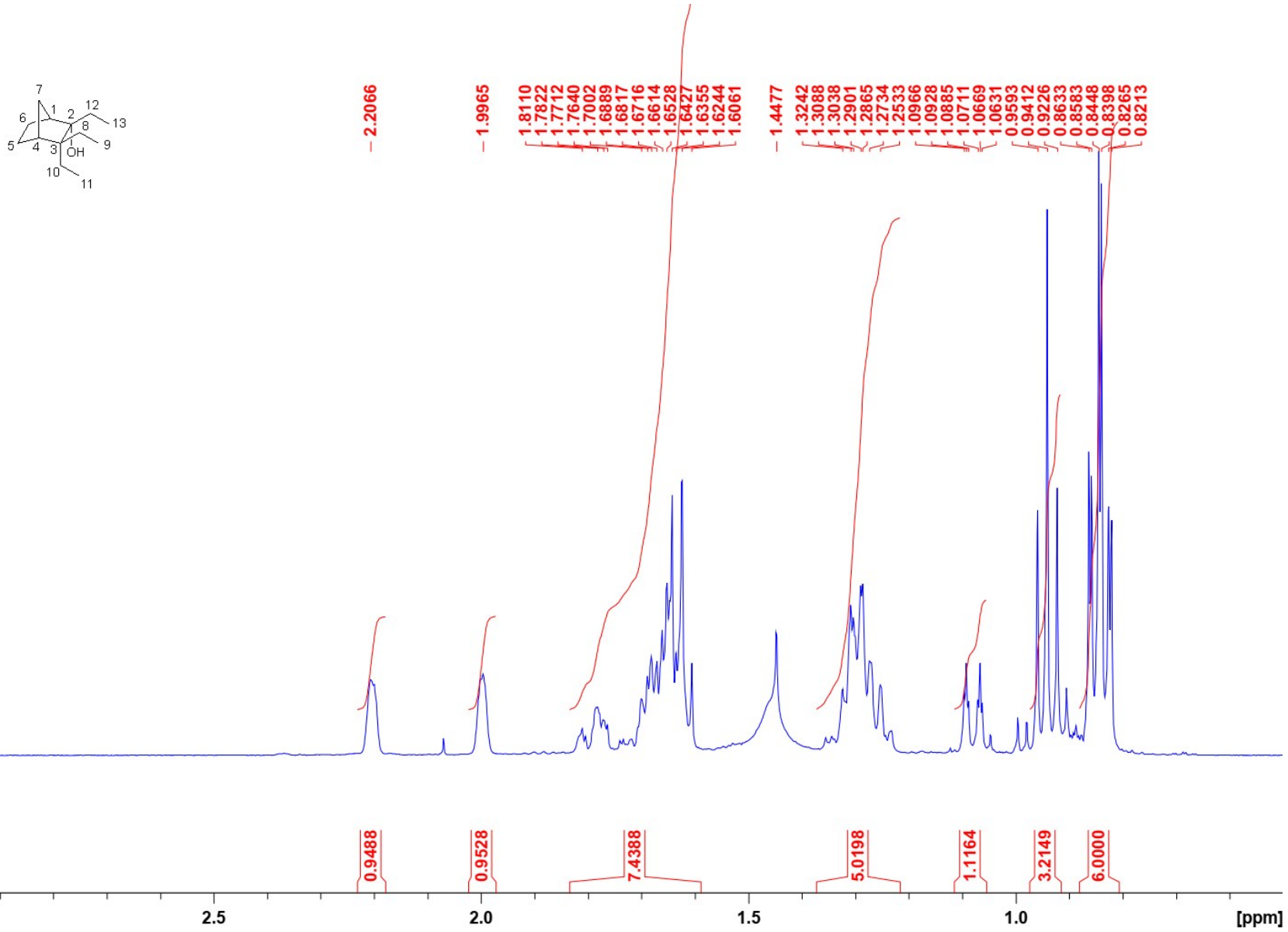
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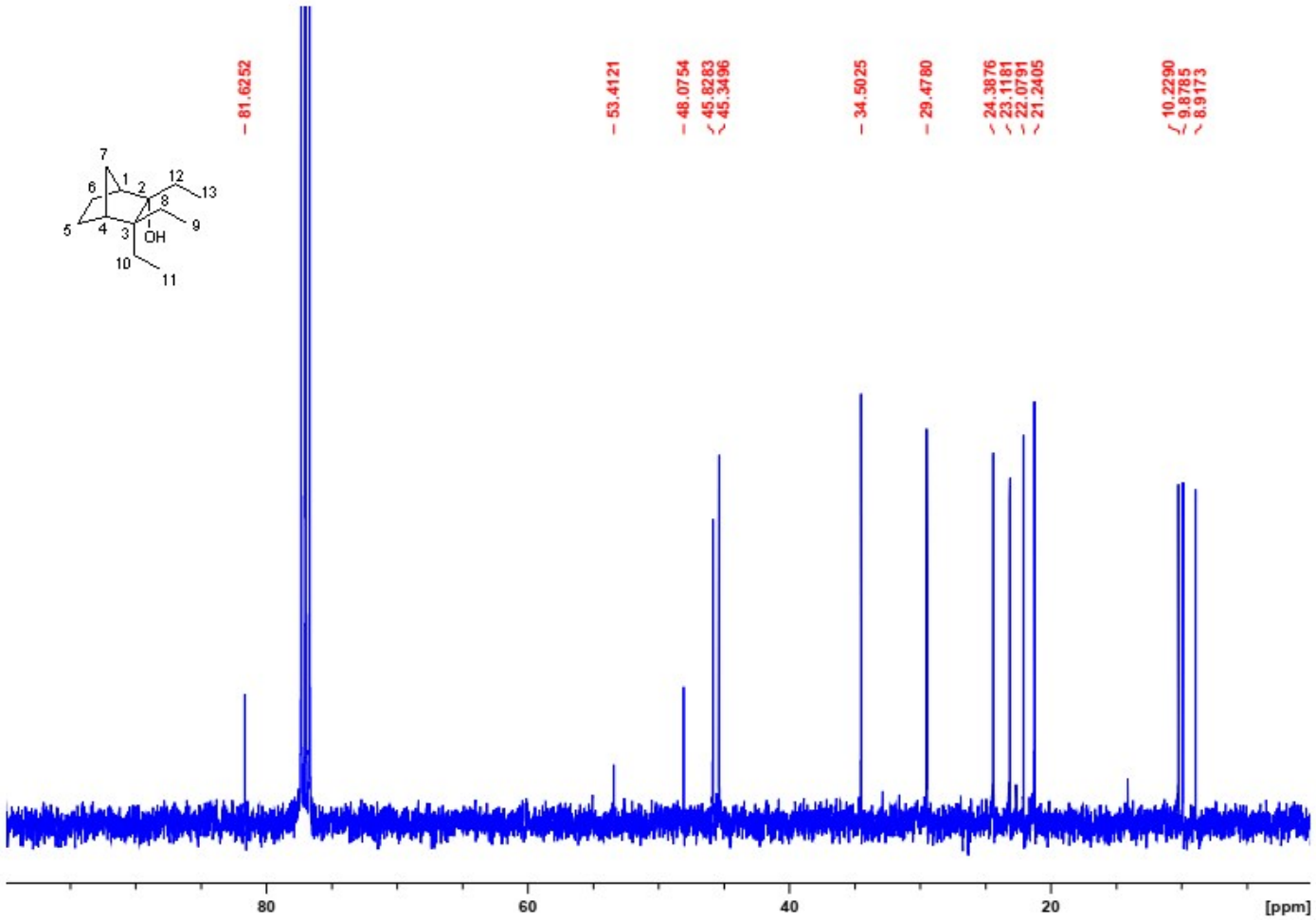
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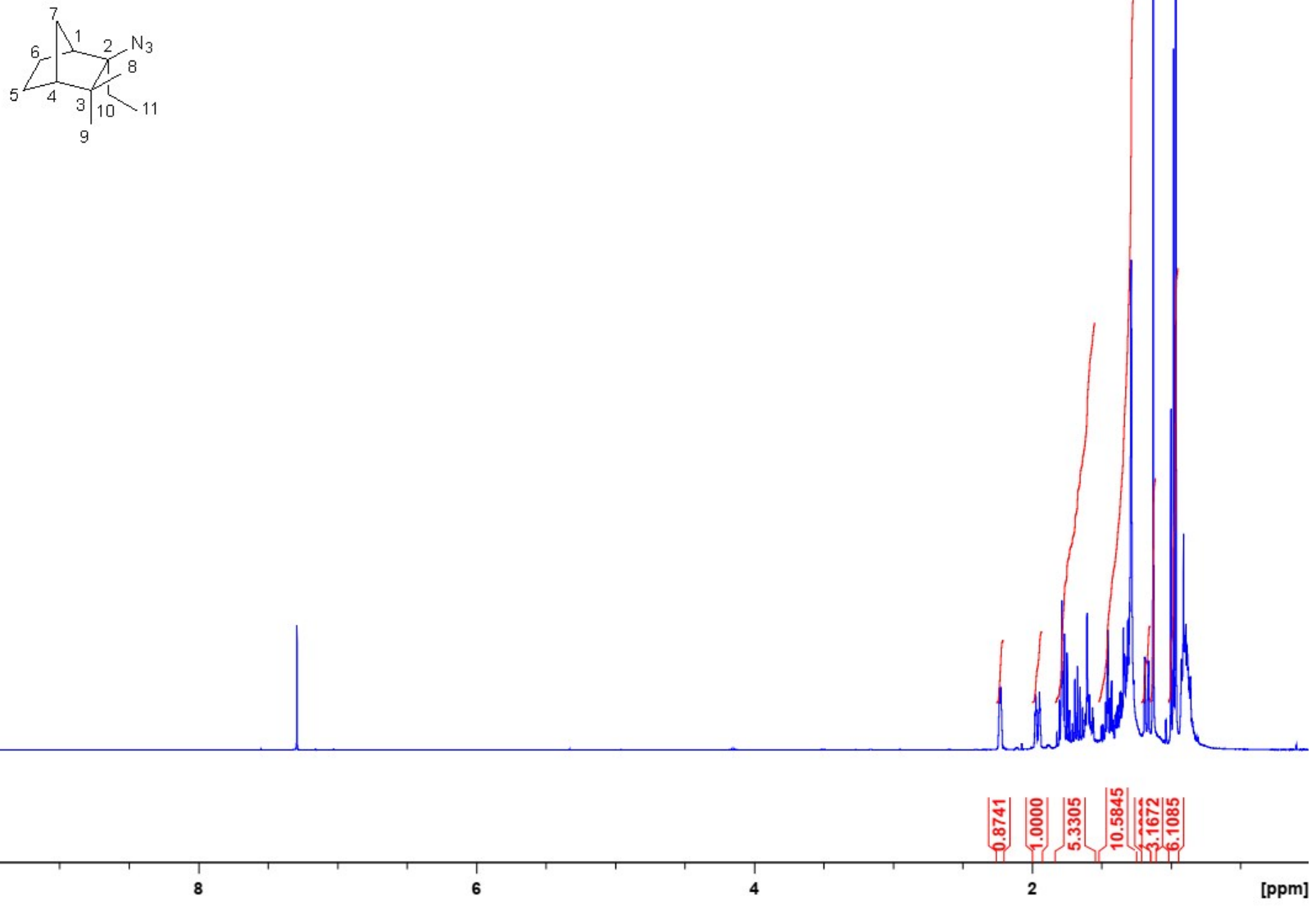
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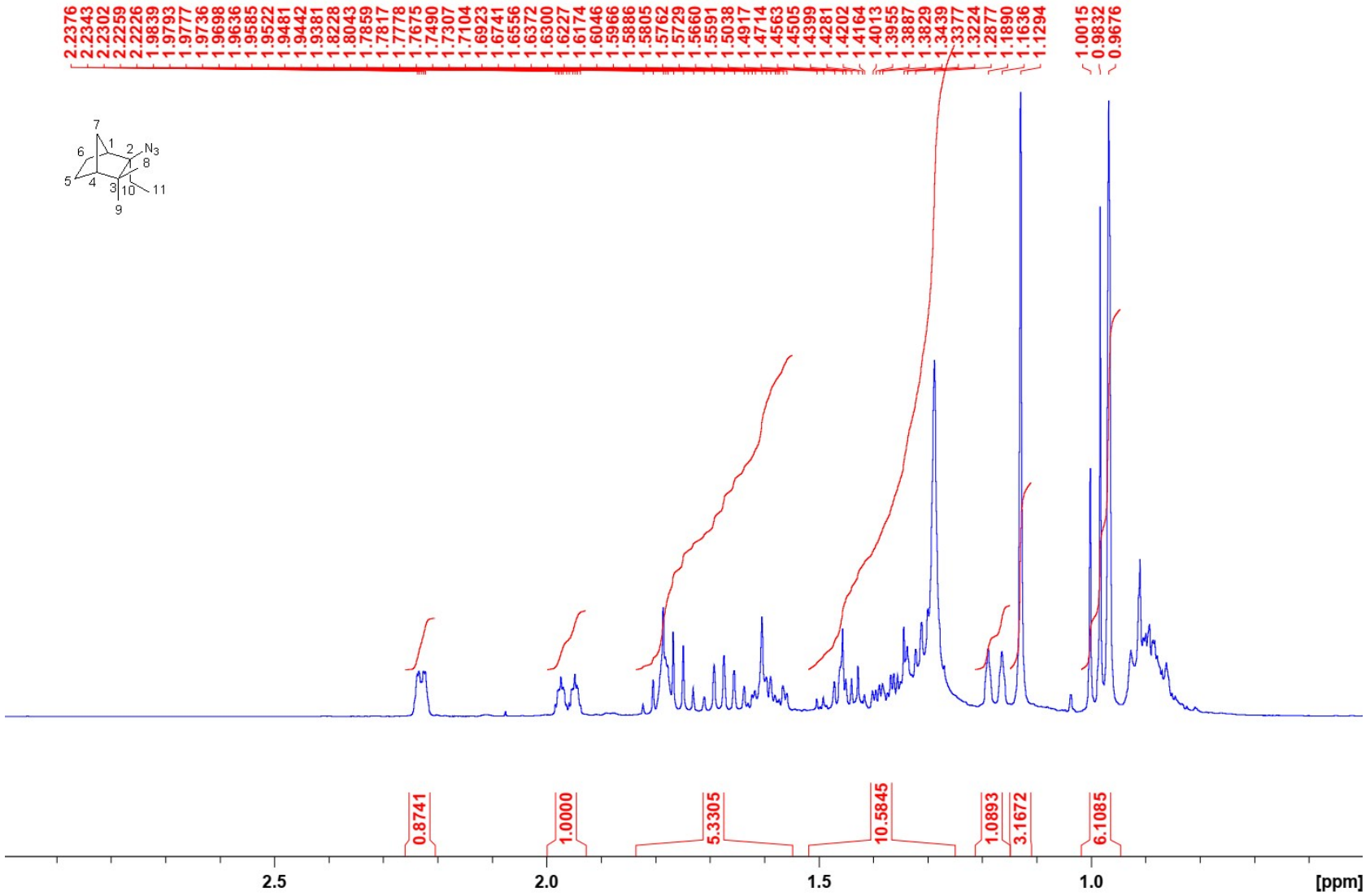
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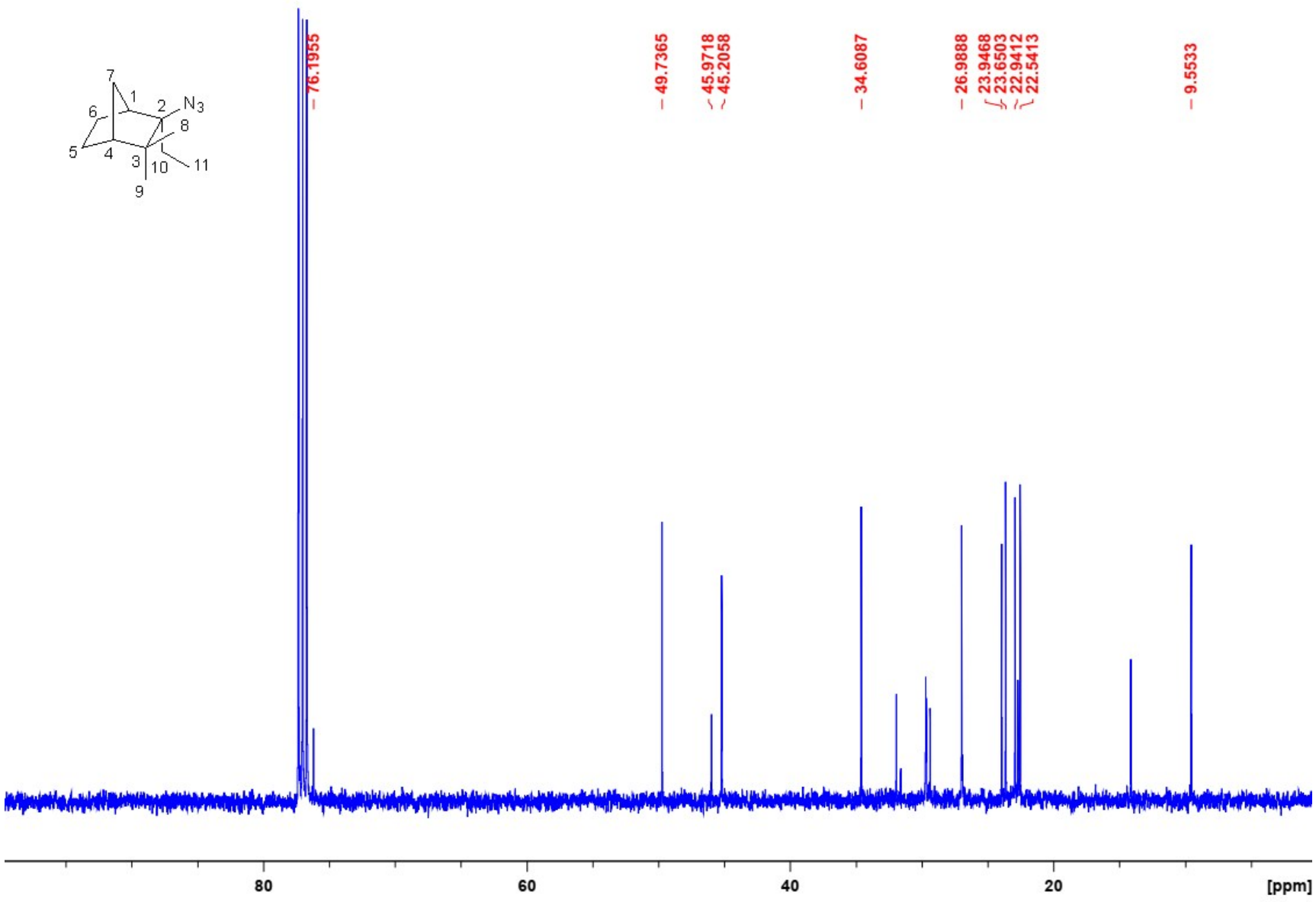
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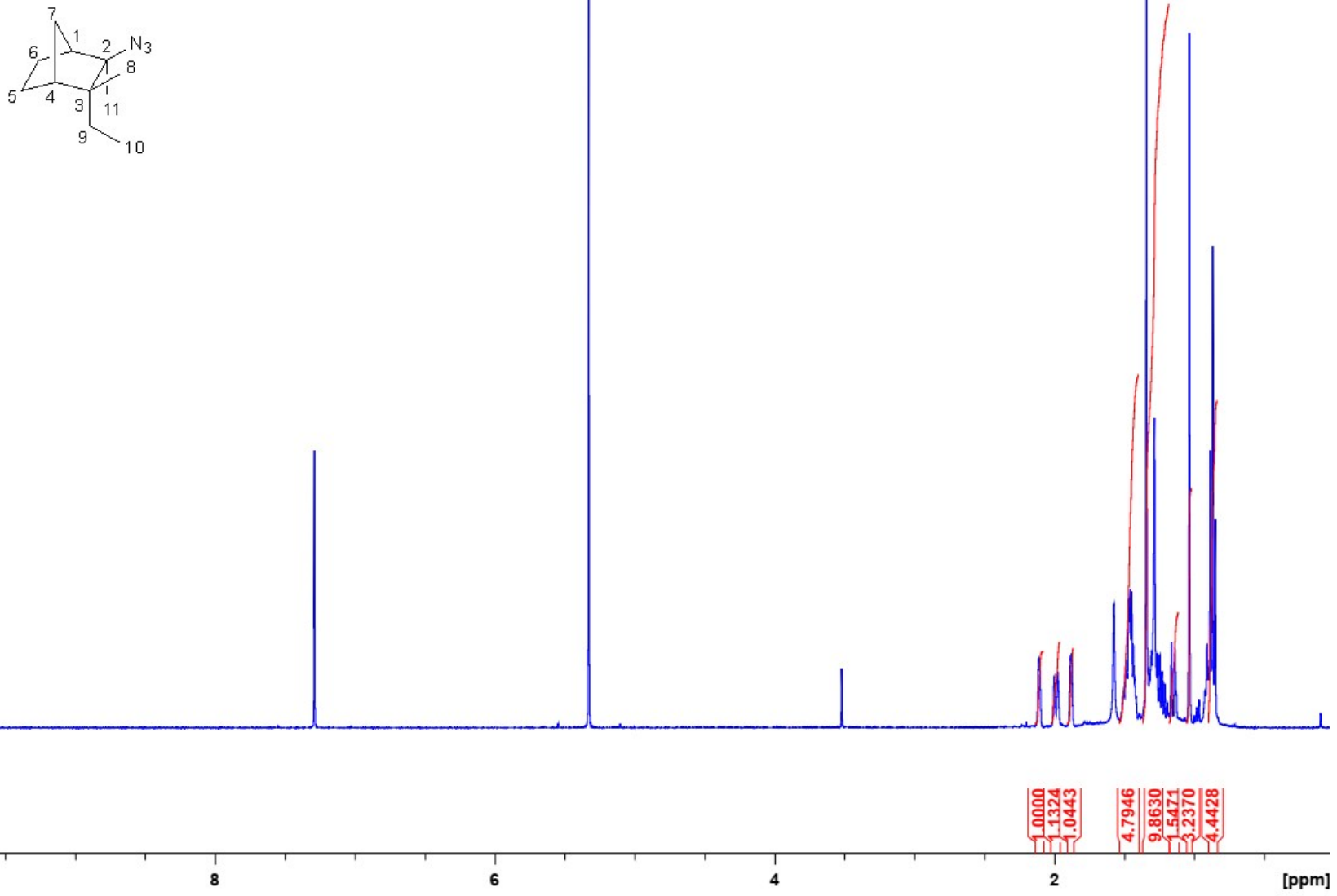
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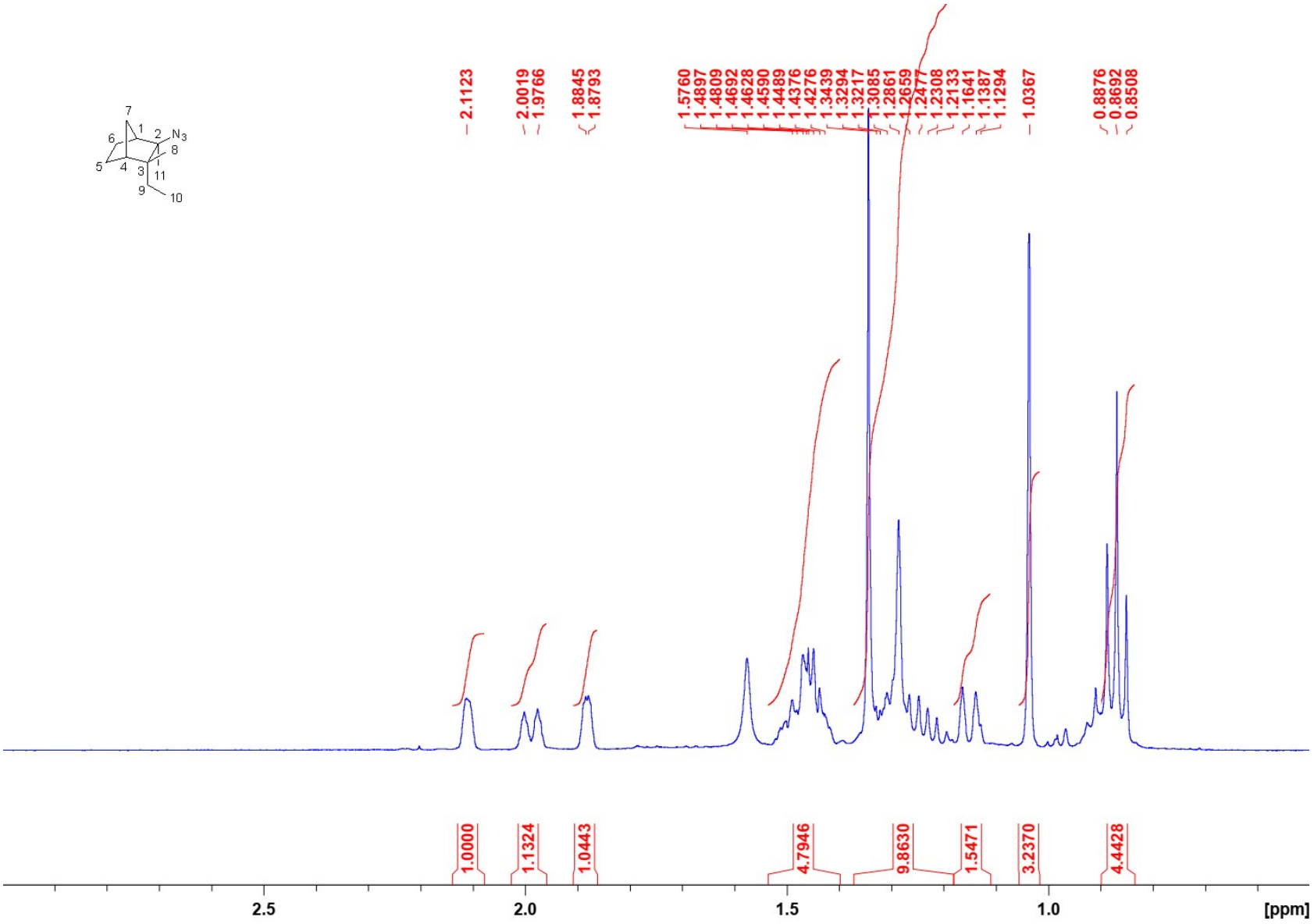
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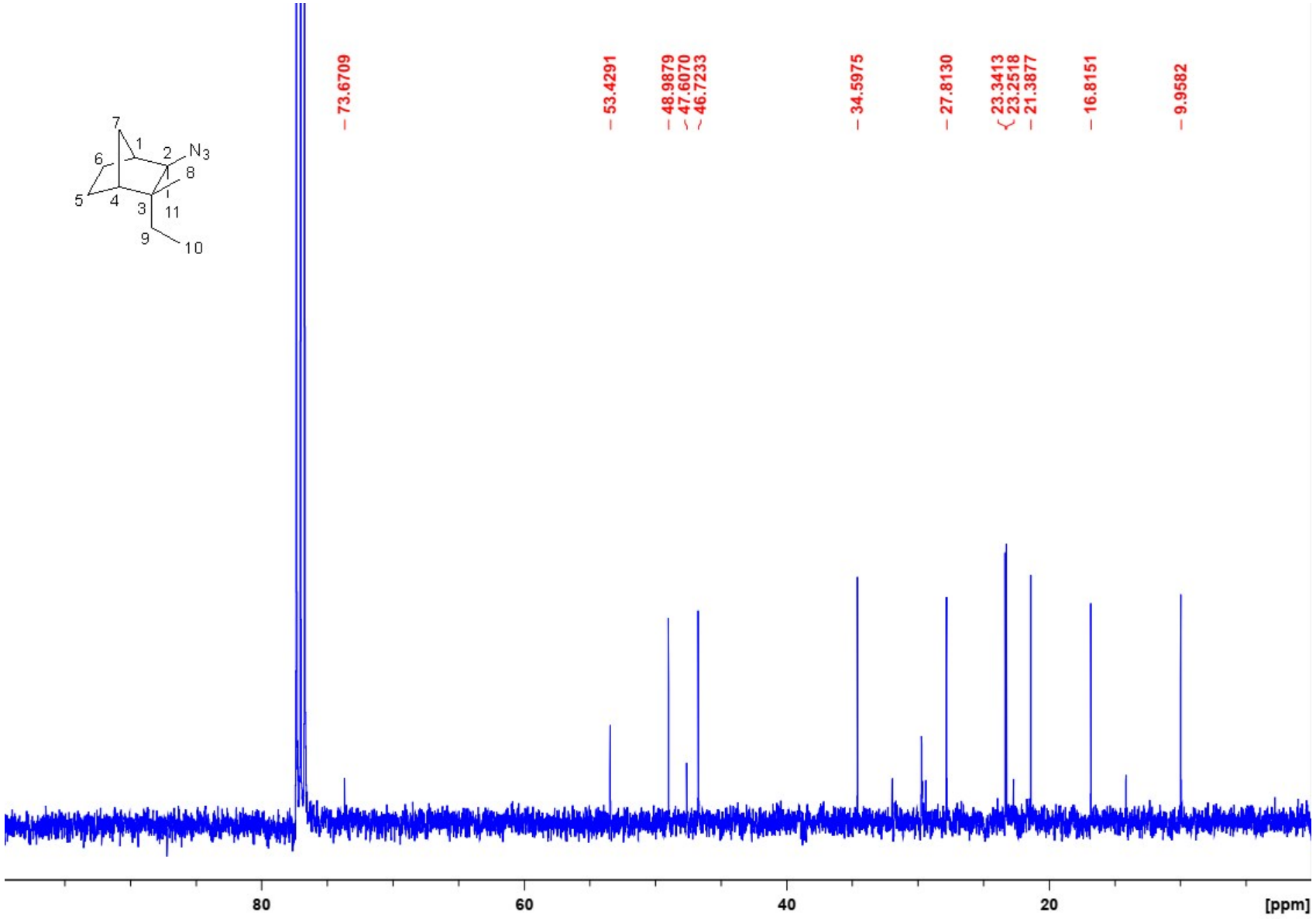
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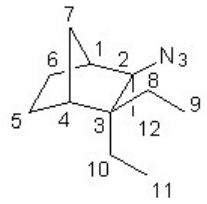
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N3
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3
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10
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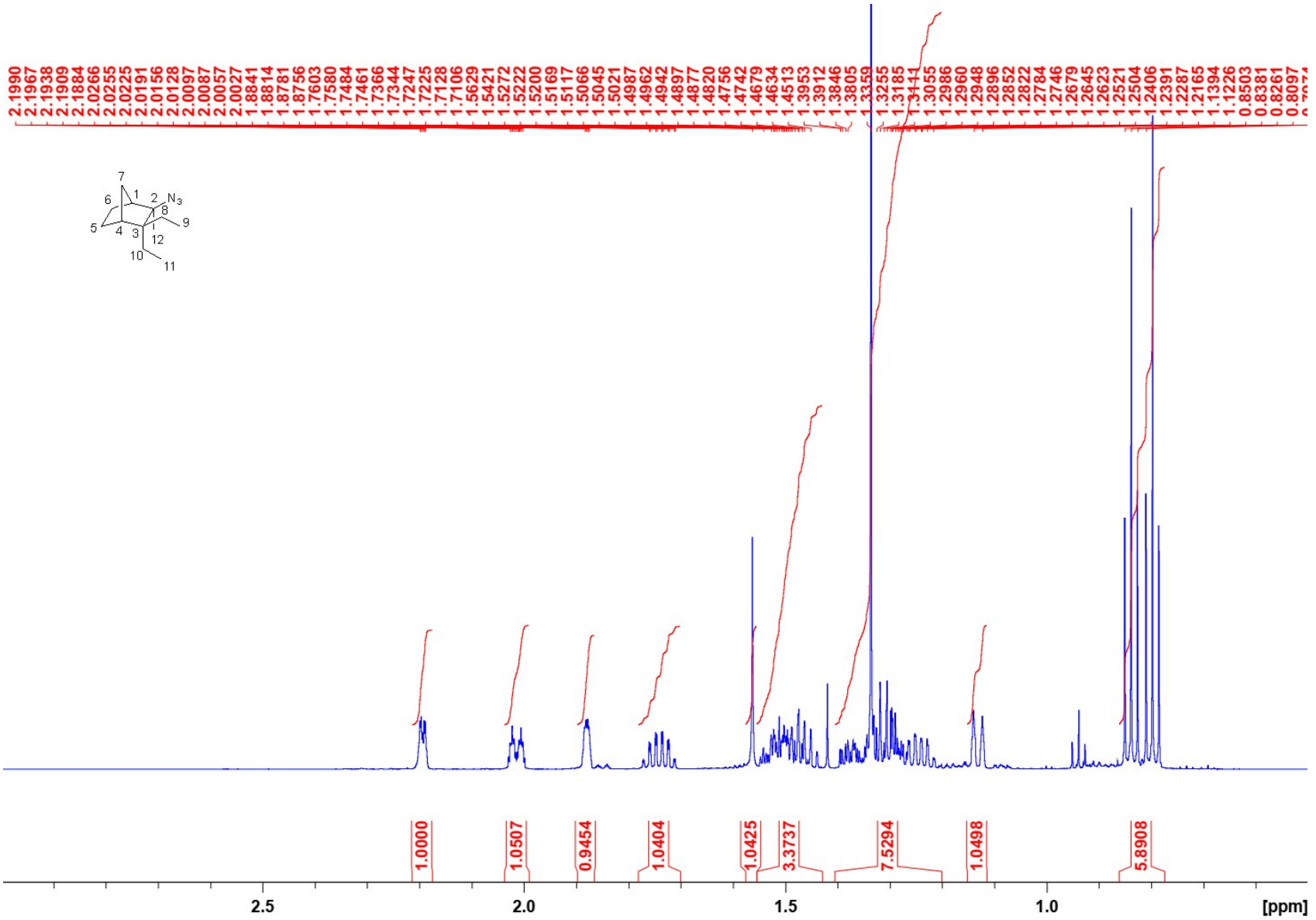
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N3
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5
4
3
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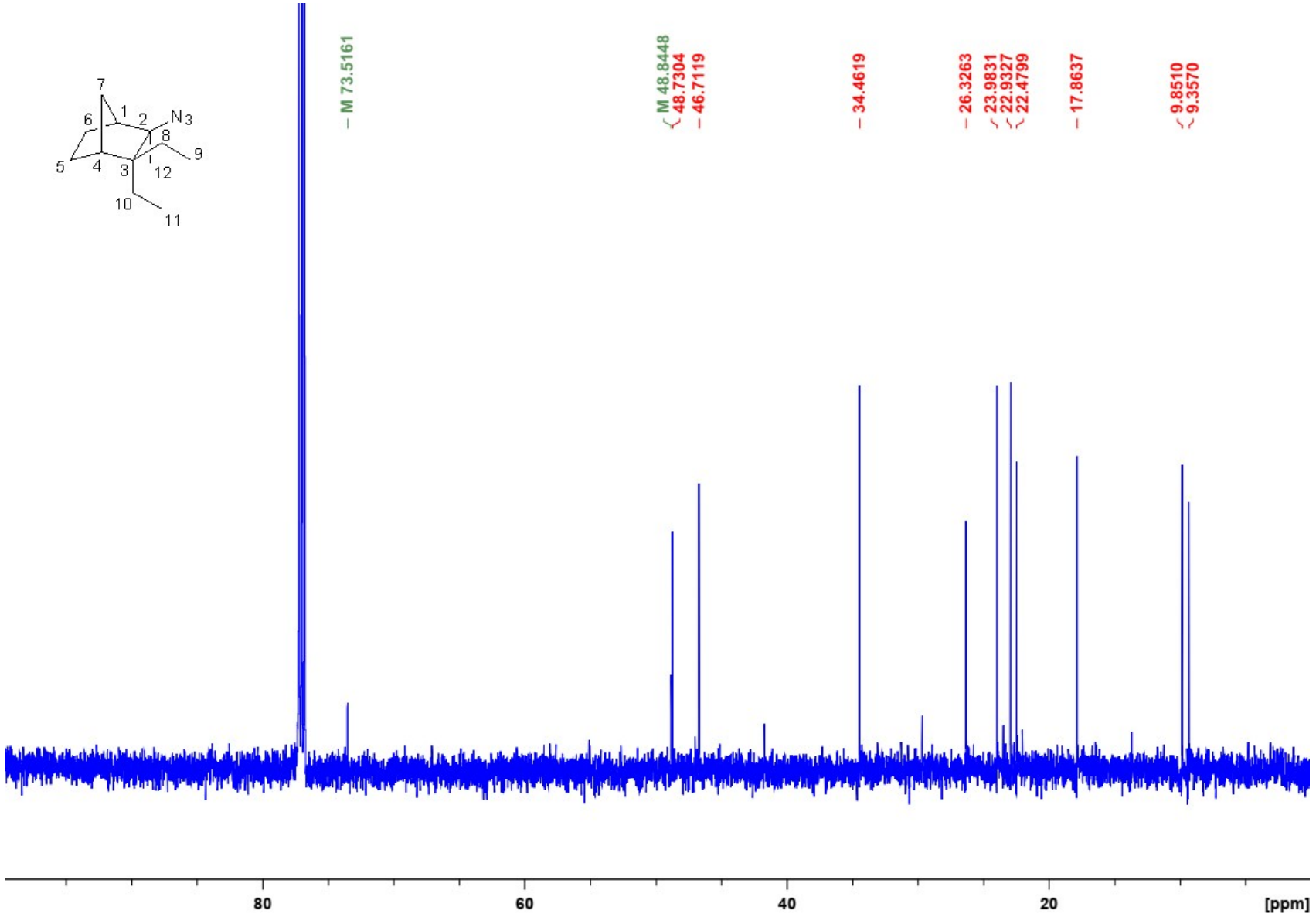
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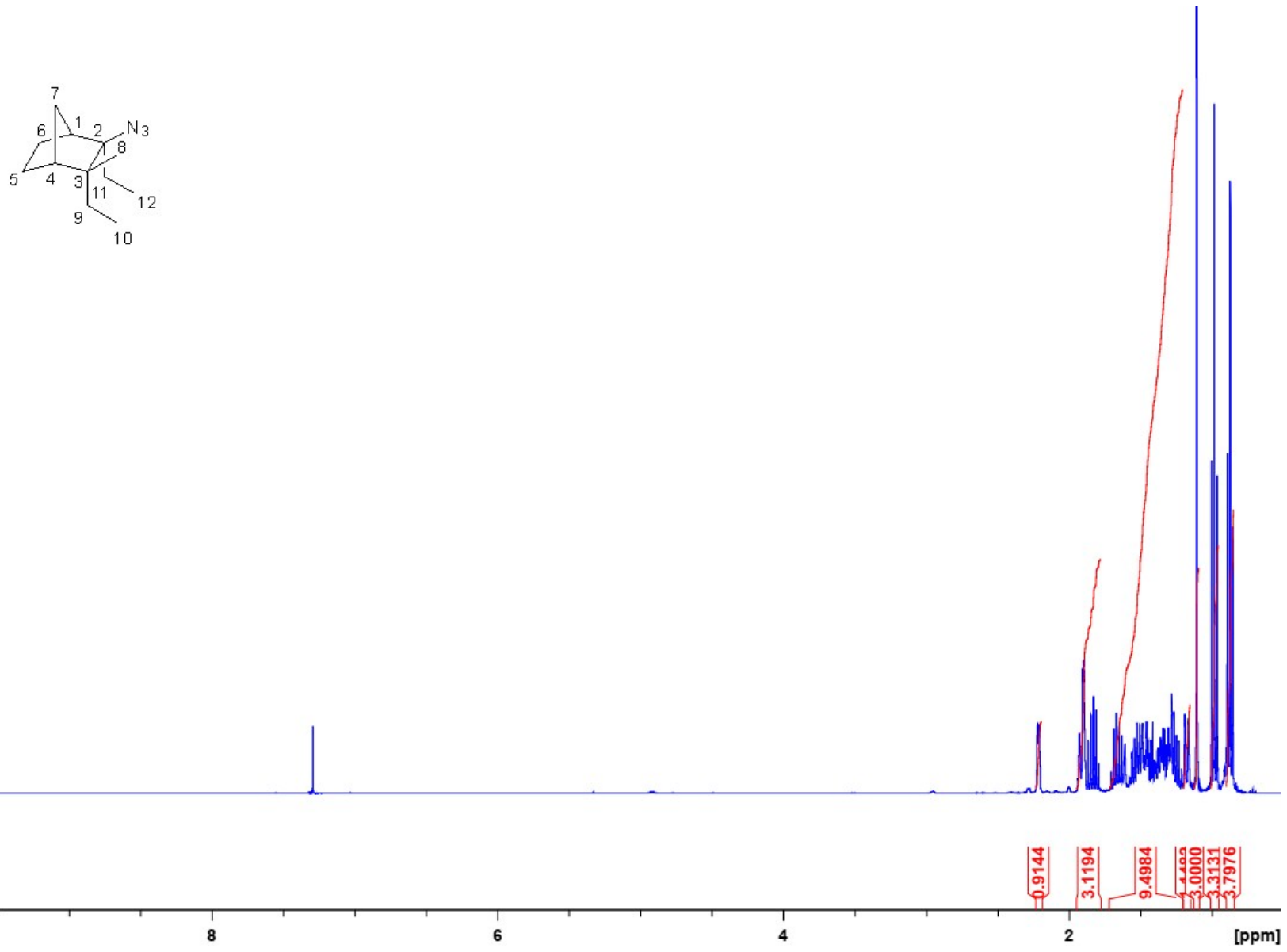
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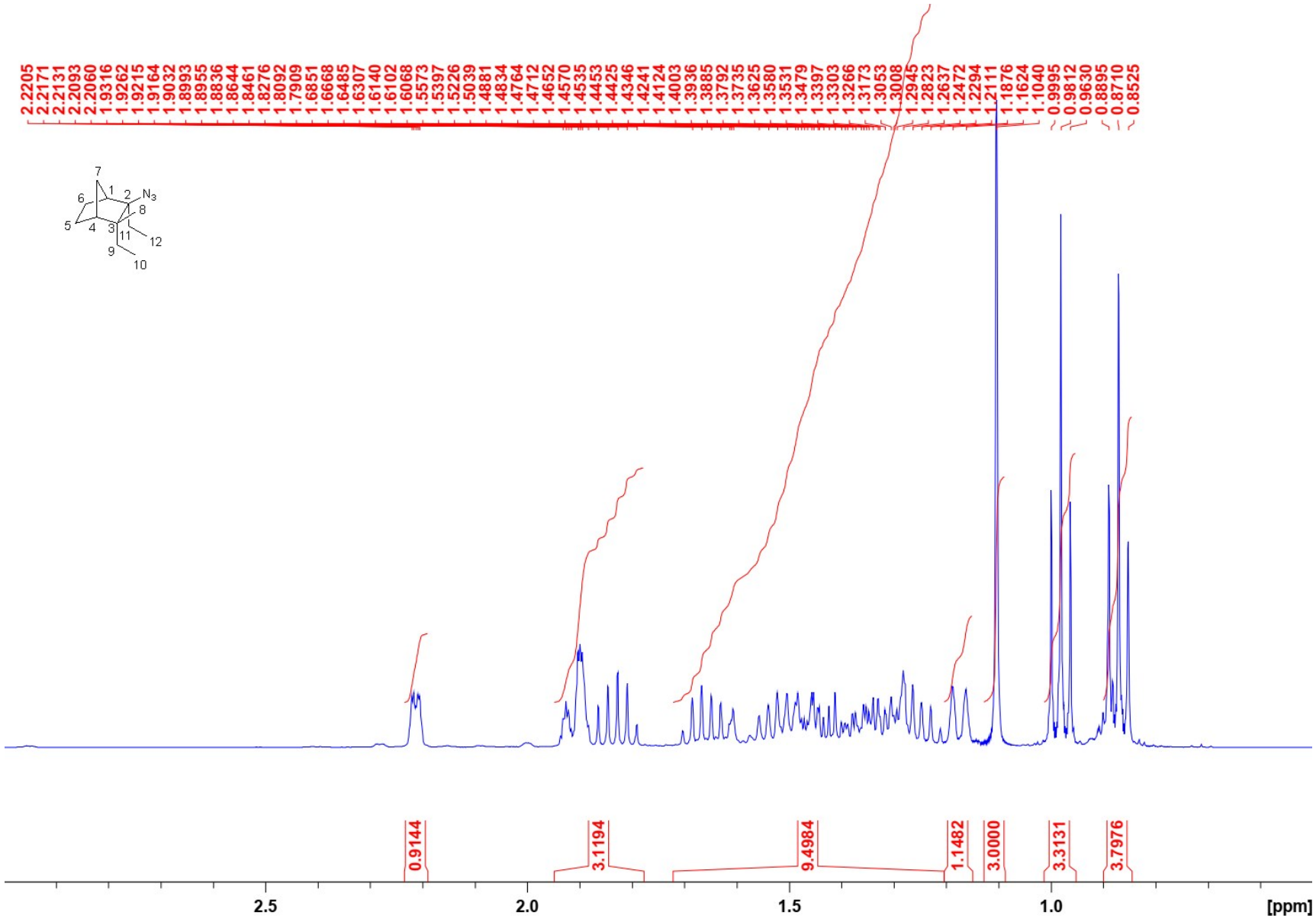
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1.5226
1.5039
1.4881
1.4834
1.4764
1.4712
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1.4570
1.4535
1.4453
1.4425
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1.3792
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1.3625
1.3580
1.3531
1.3479
1.3397
1.3303
1.3266
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1.2945
1.2823
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1.2111
1.1876
1.1624
1.1040
0.9995
0.9812
0.9630
0.8895
0.8710
0.8525
7
1
2
N3
8
6
5
4
3
11
12
9
10
0.9144
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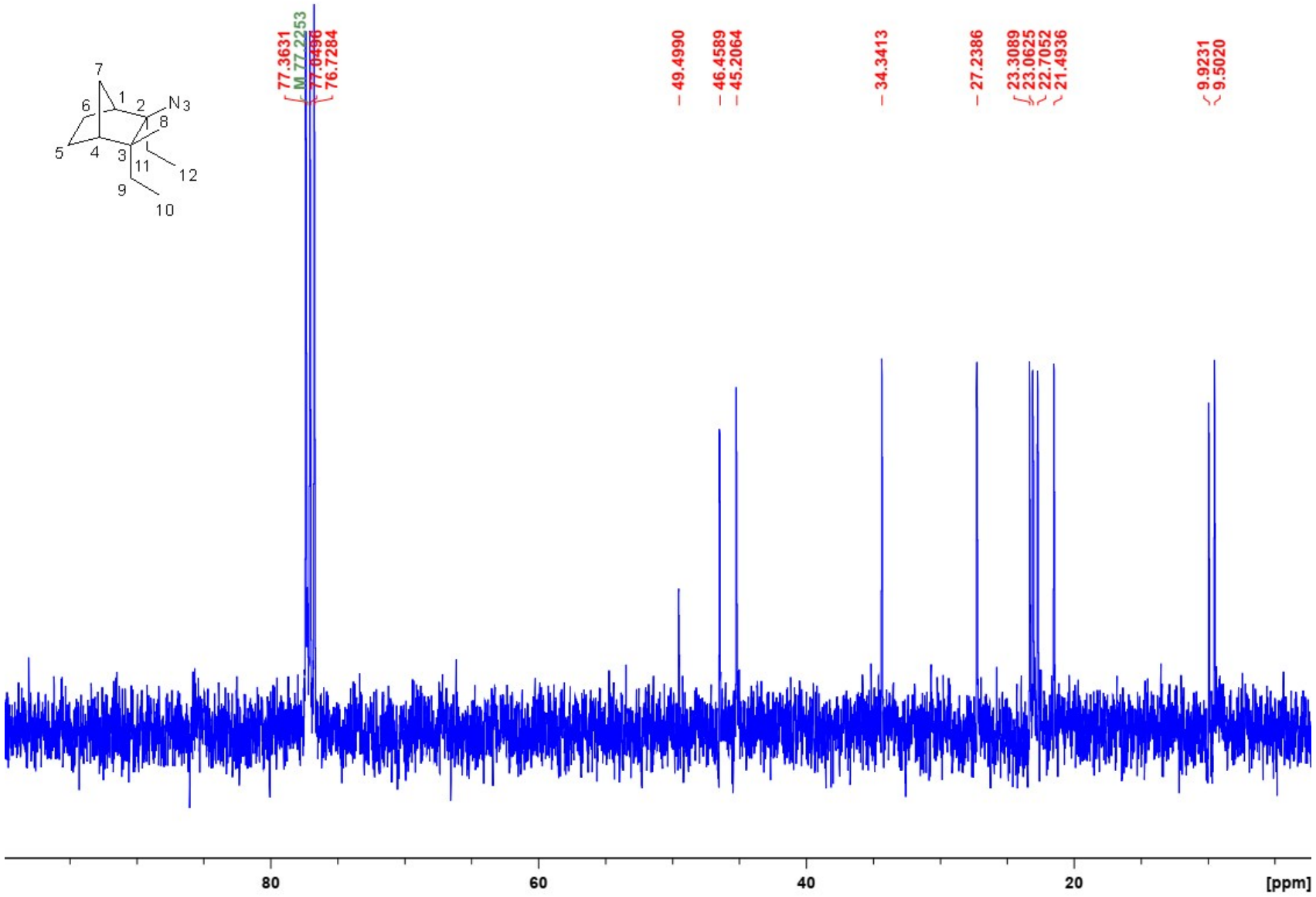
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22.7052
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9.9231
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N3
8
5
4
3
11
12
9
10
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60
40
20
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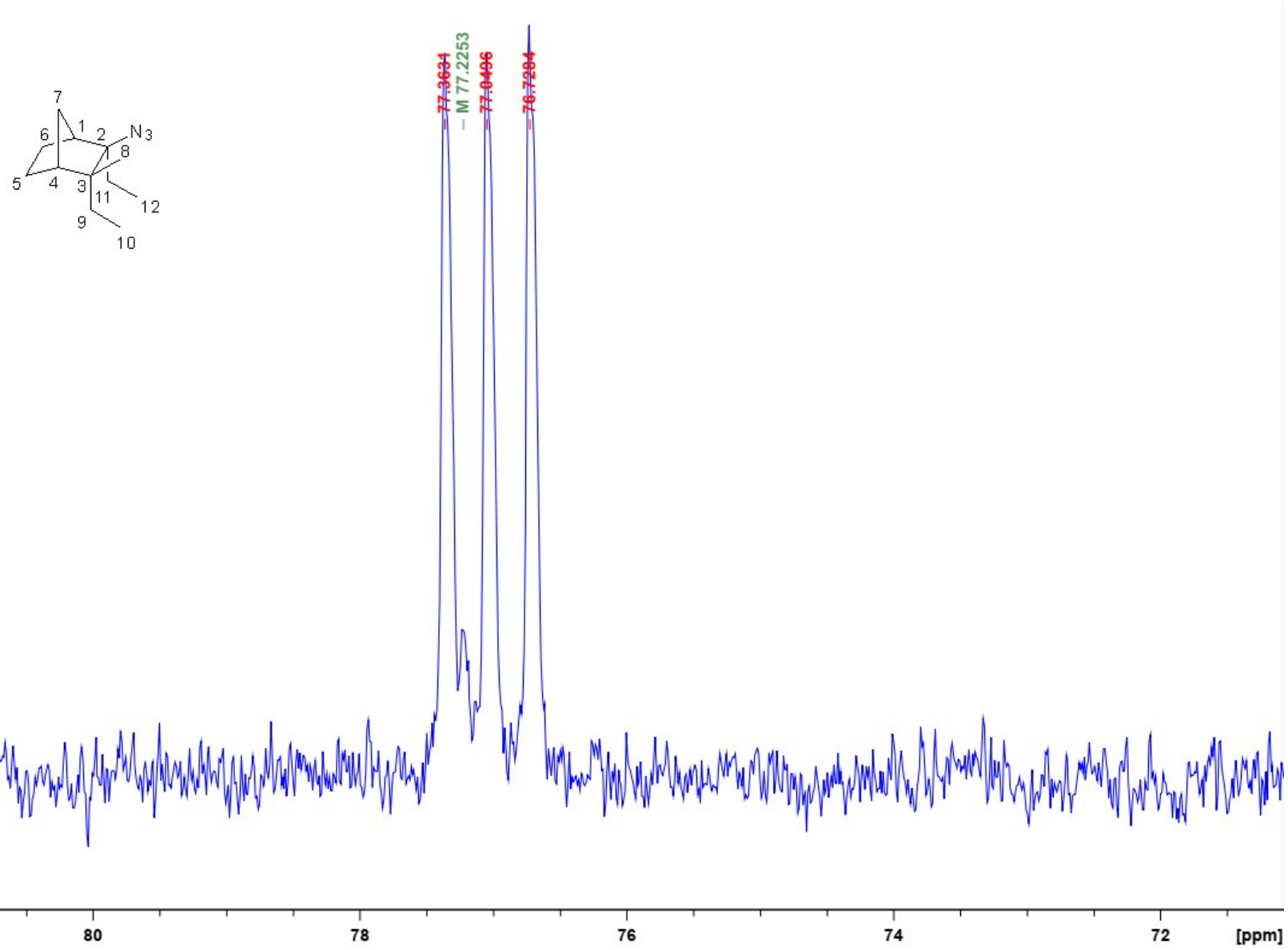
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N3
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11
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10
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76
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72
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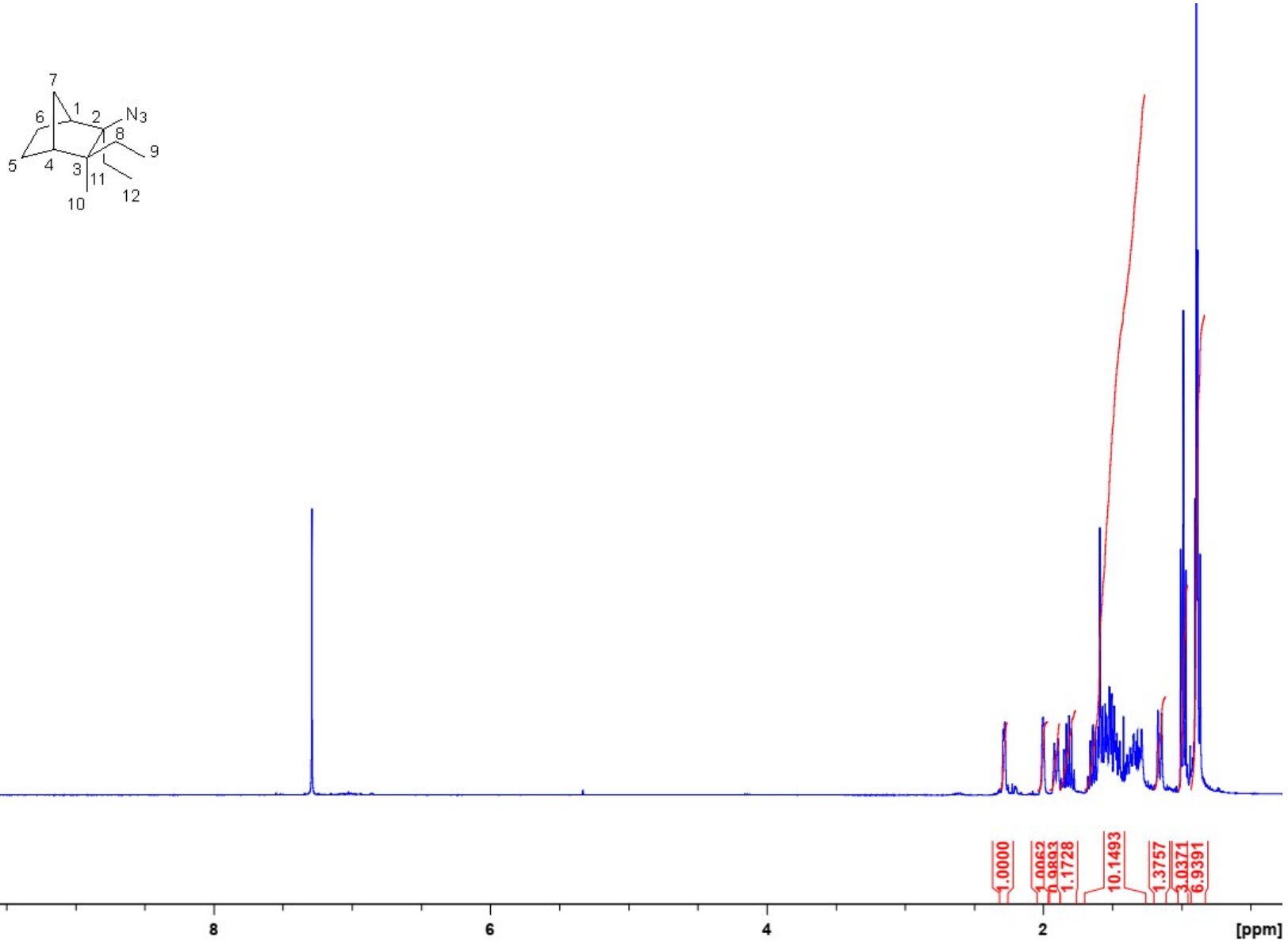
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N3
8
9
5
4
3
11
10
12
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8
6
4
2
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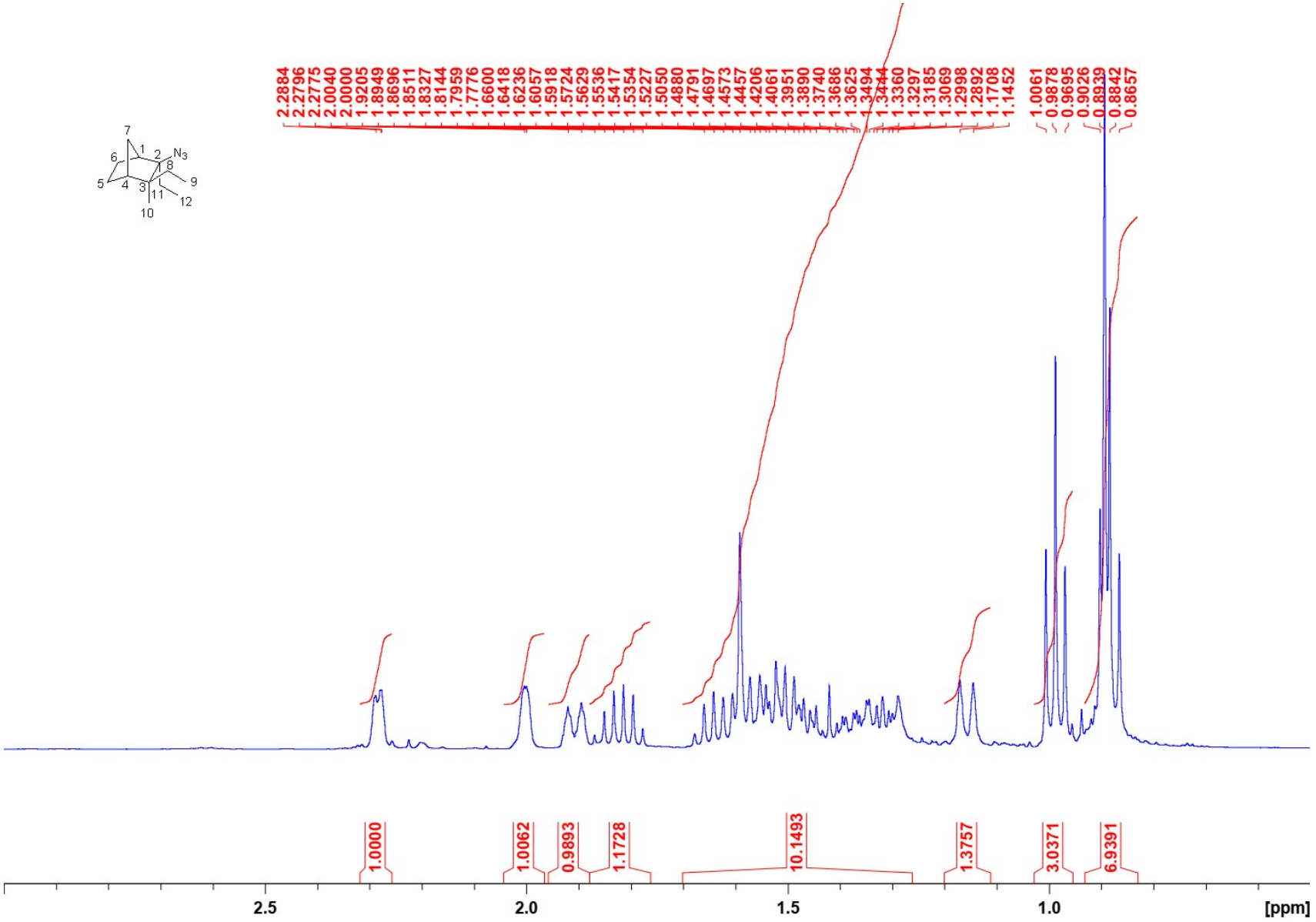
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1
2
N3
8
9
6
5
4
3
11
12
10
1.0000
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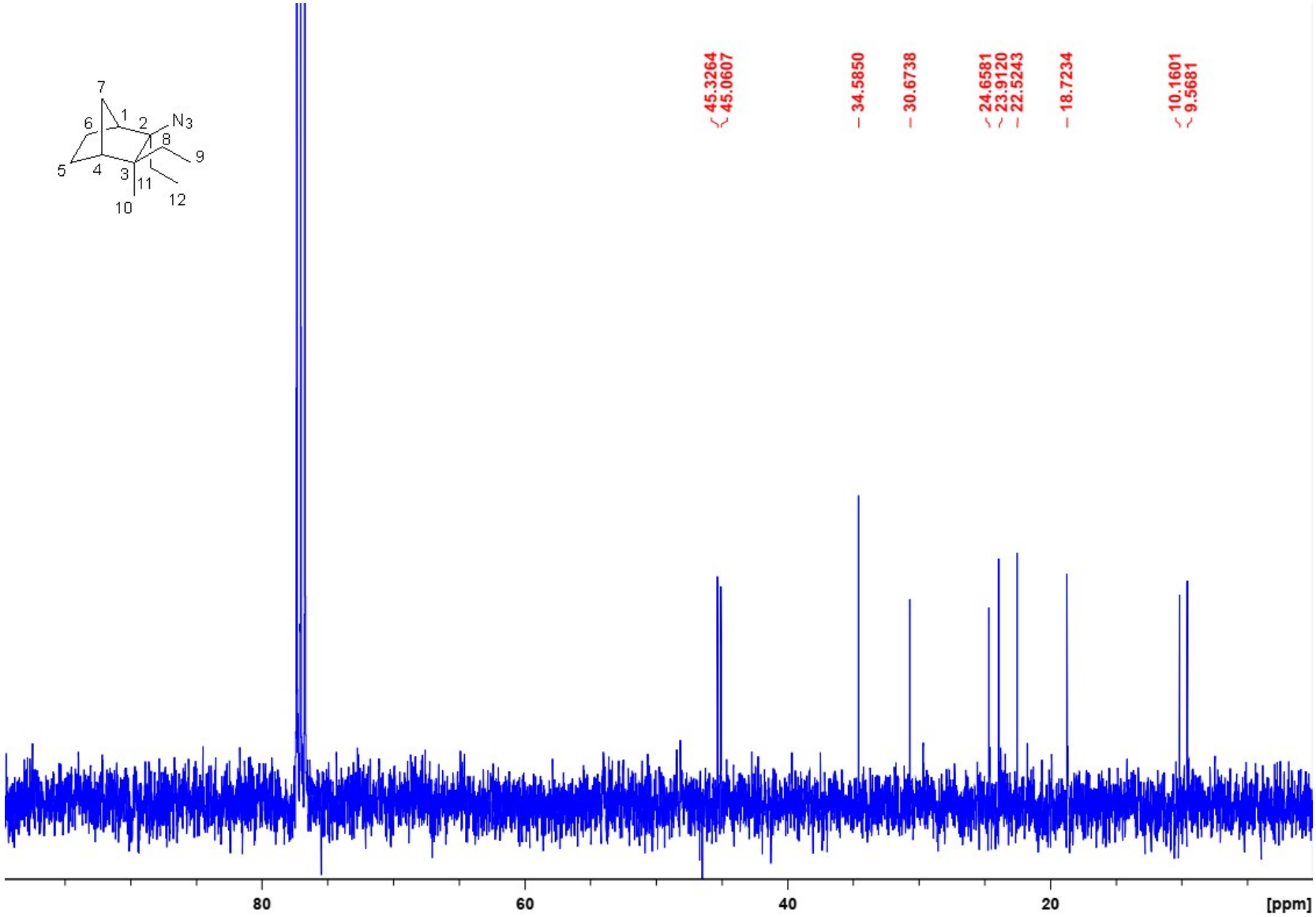
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4
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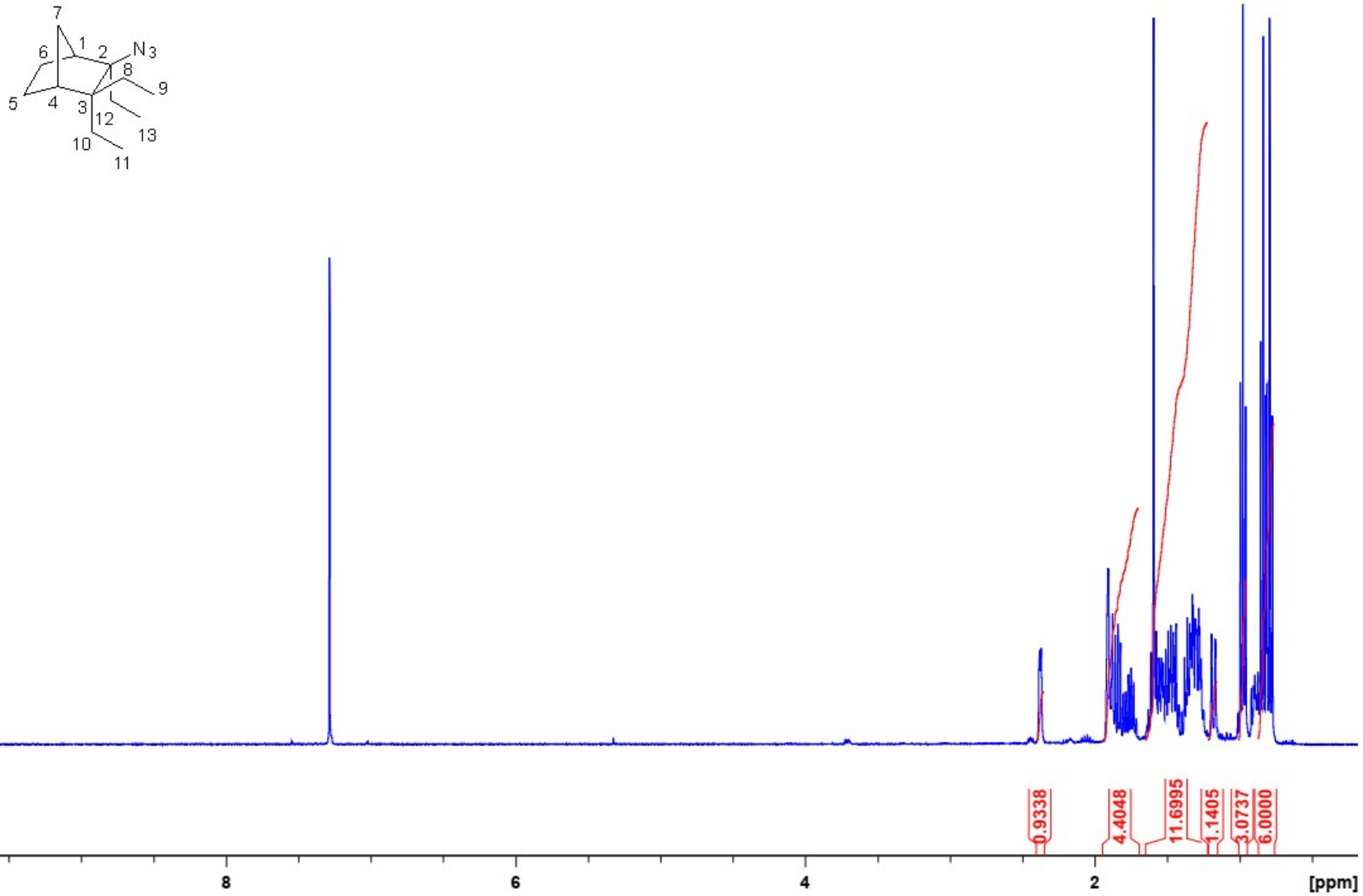
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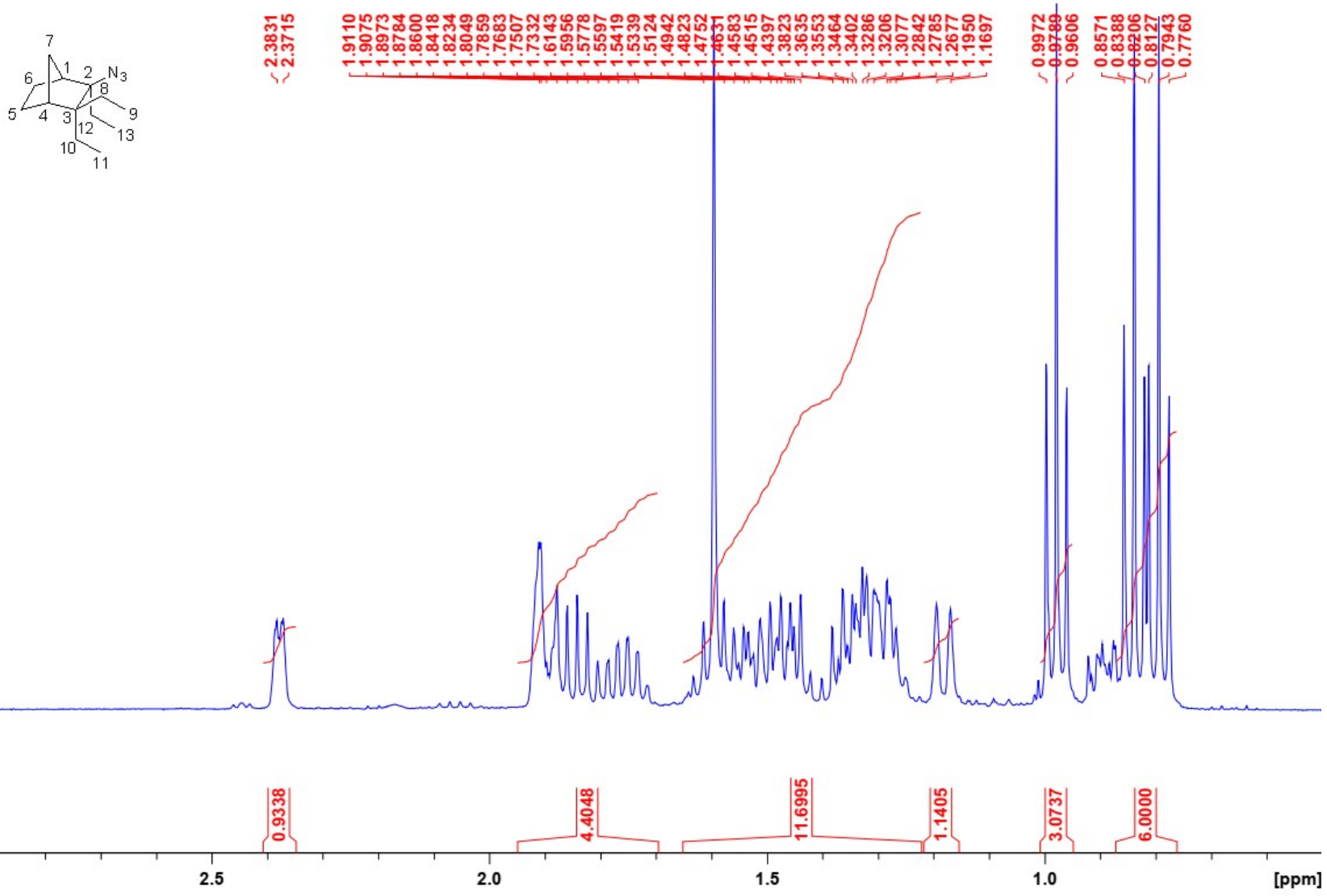
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10
11
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1.3464
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1.3206
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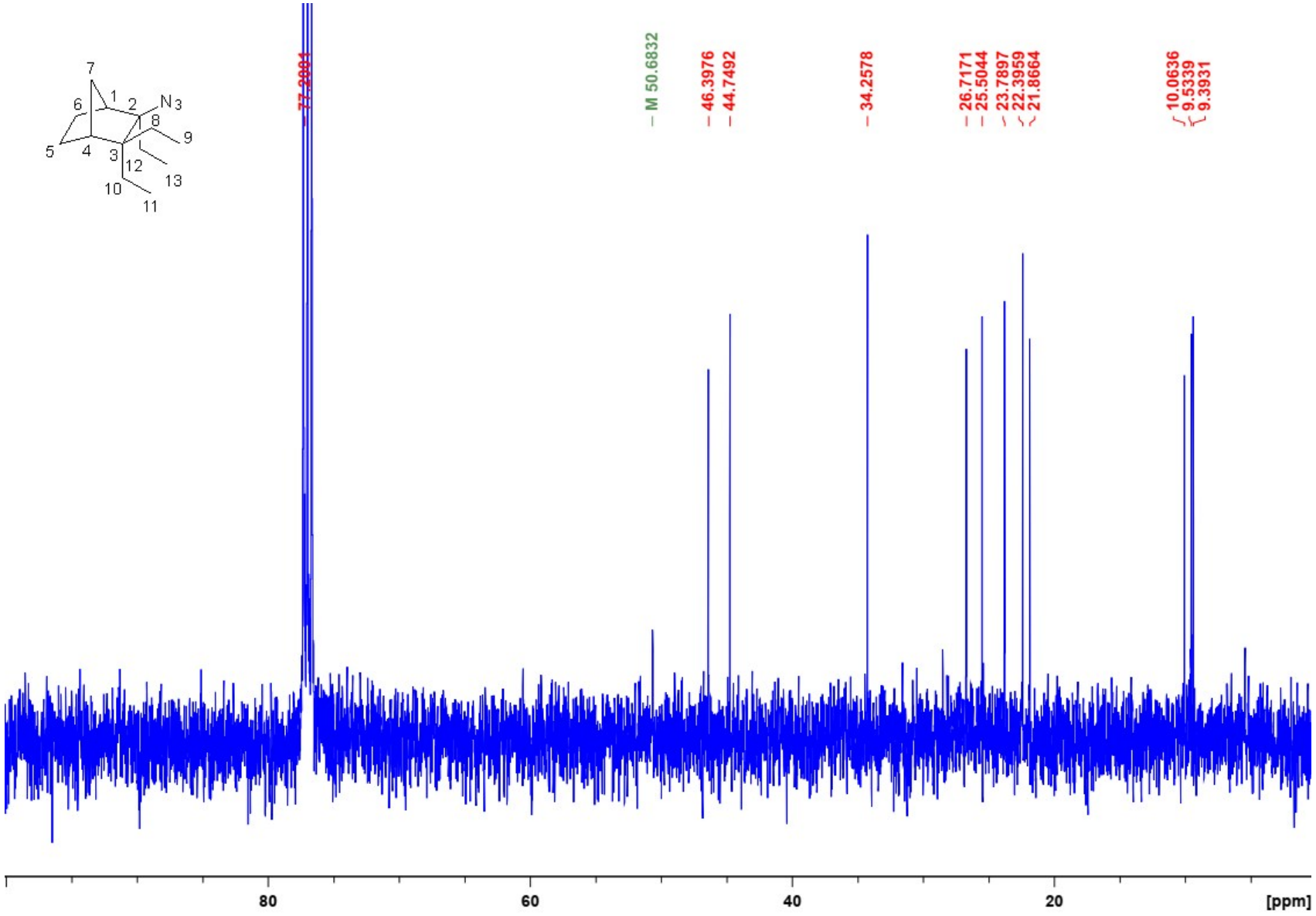
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13
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11
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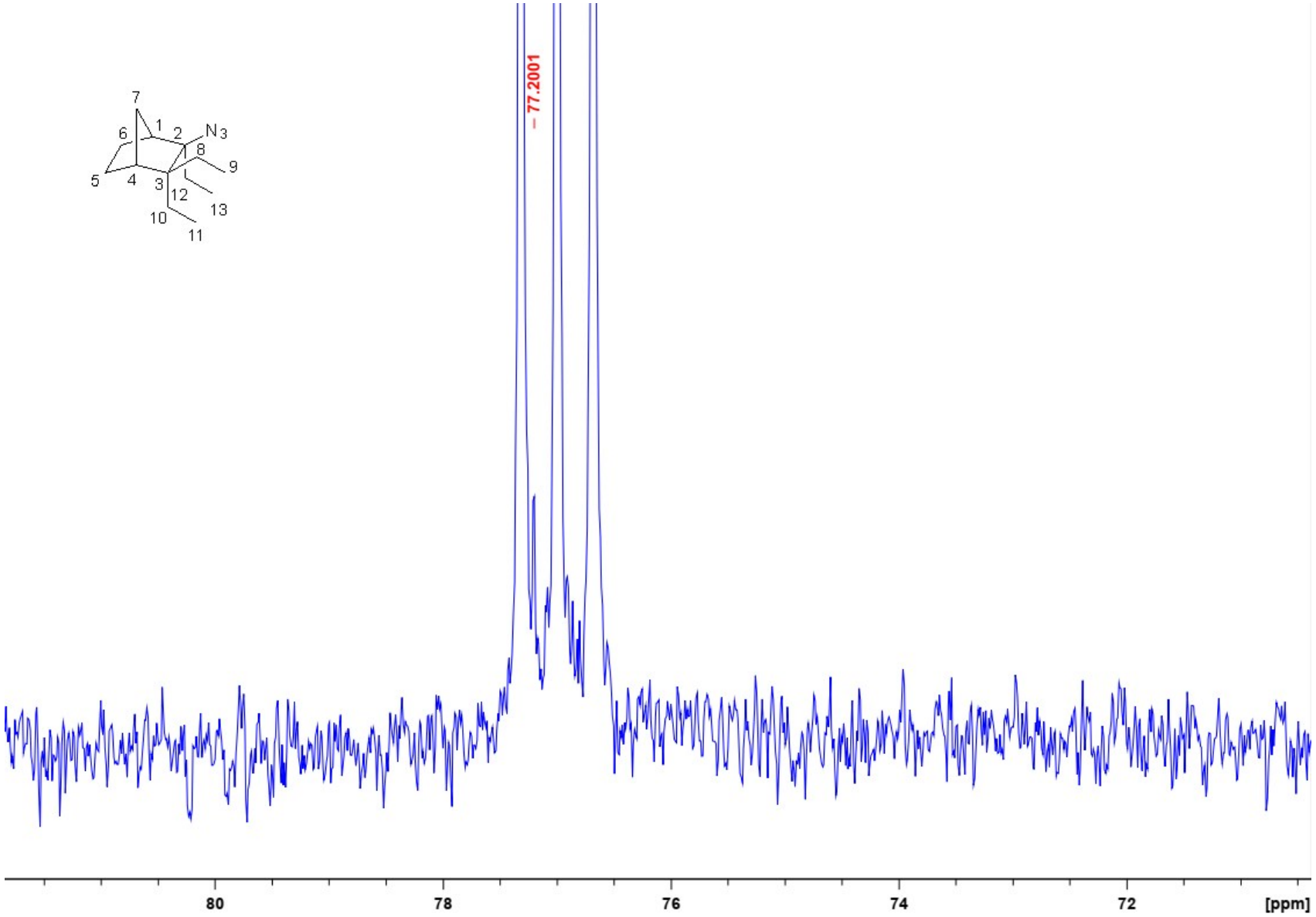
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N3
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4
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12
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10
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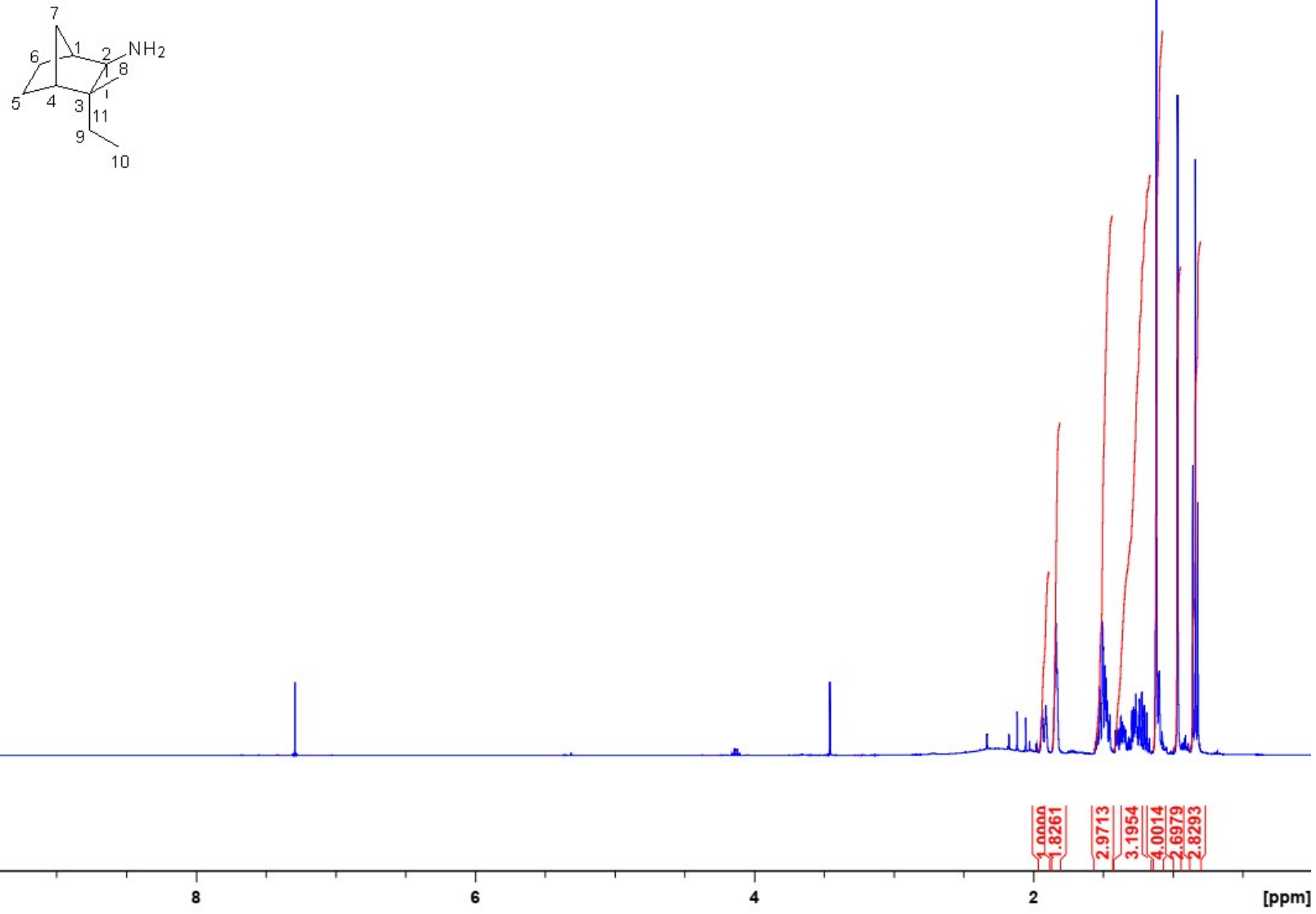
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NH2
6
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4
3
11
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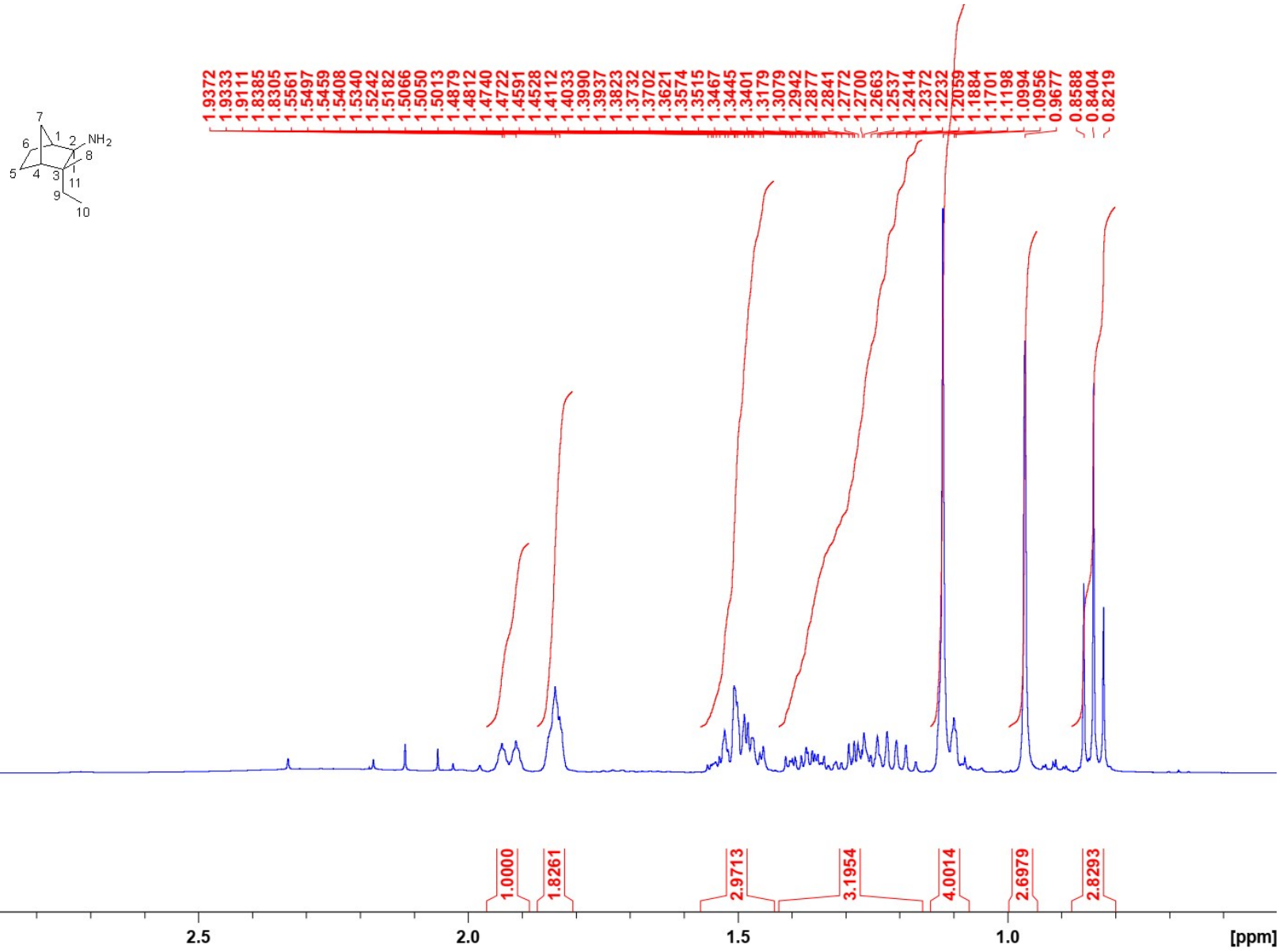
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1.4812
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1.4722
1.4591
1.4528
1.4112
1.4033
1.3990
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1.3401
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1.2877
1.2841
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1.2700
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1.2537
1.2414
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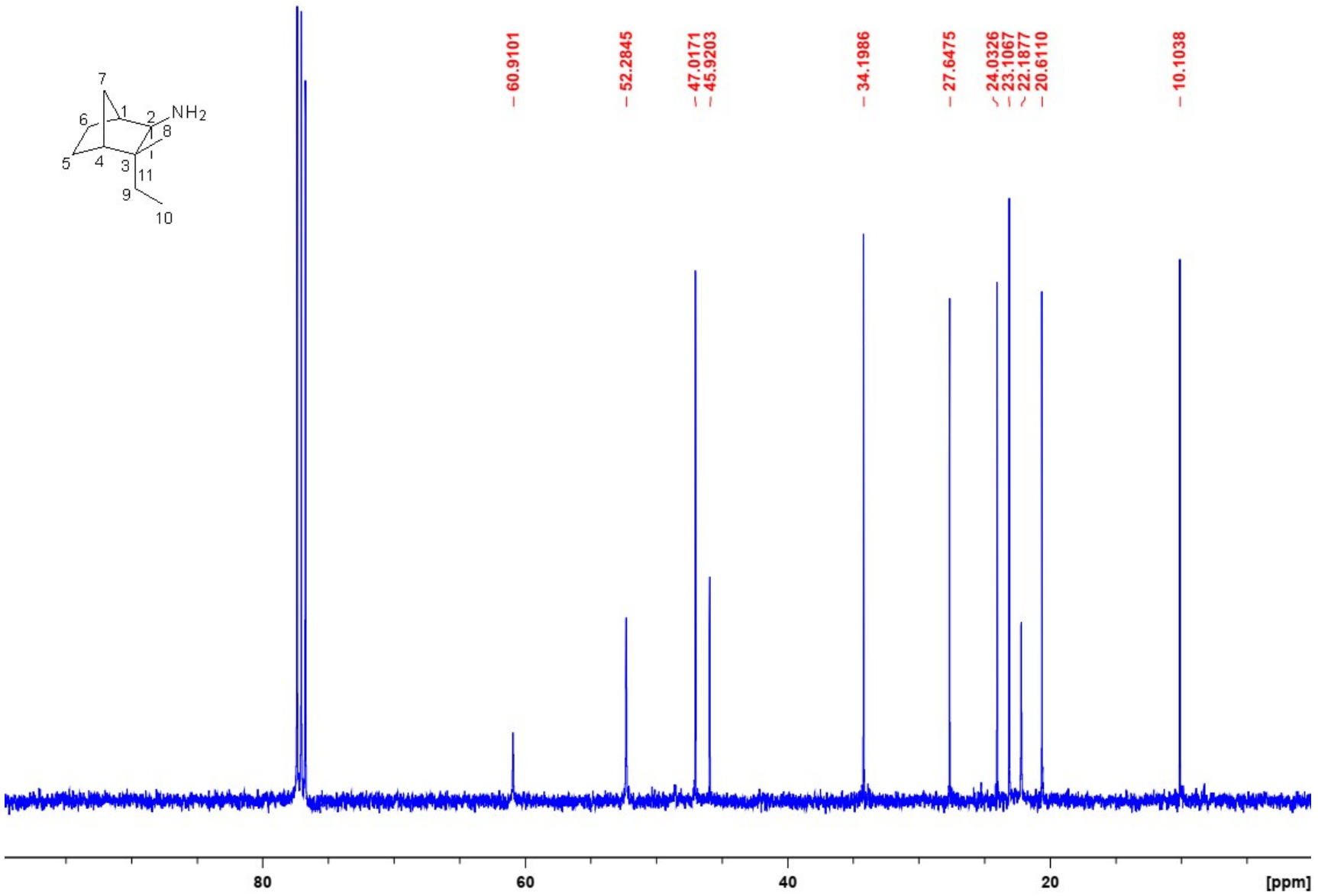
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20
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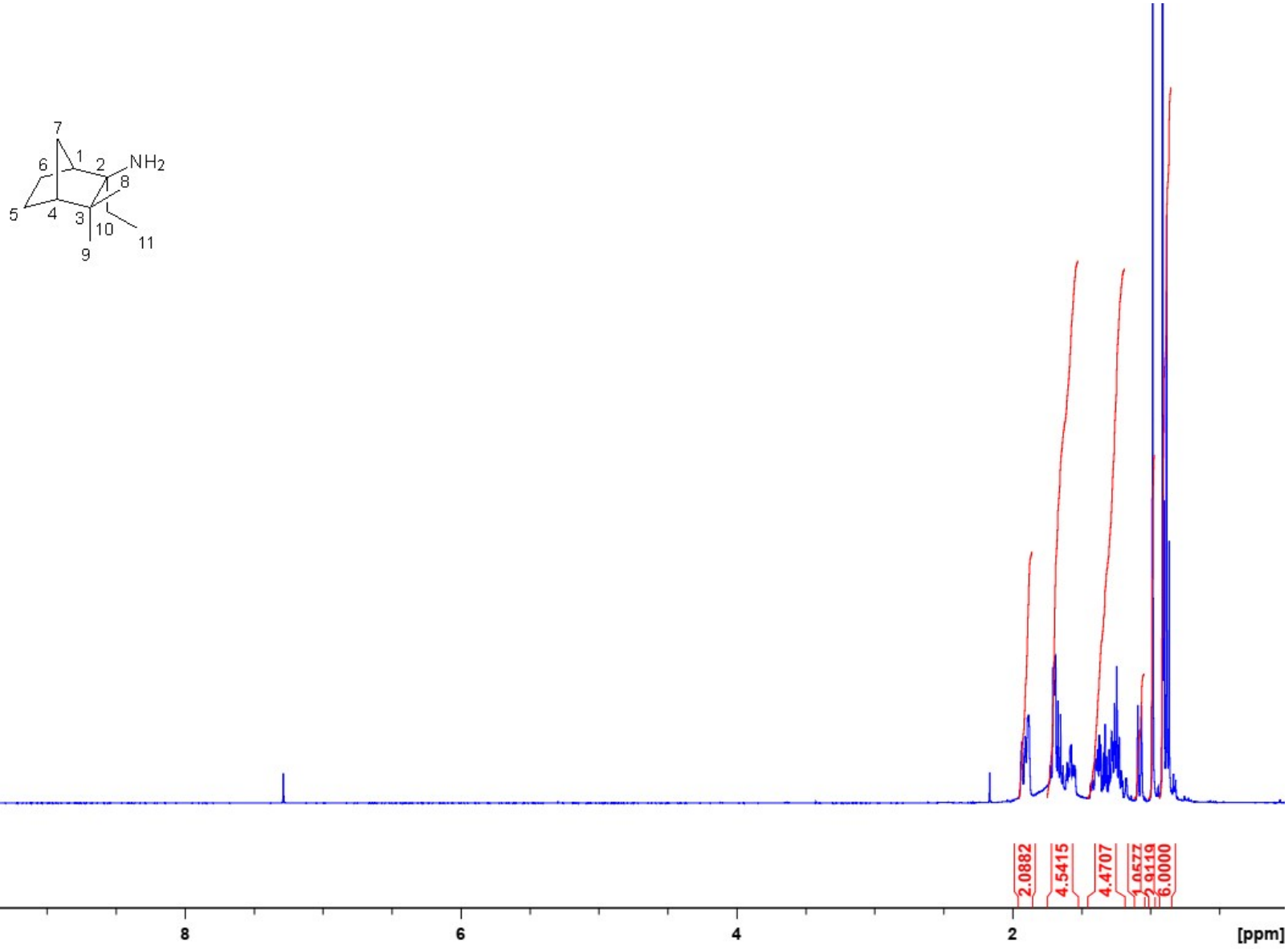
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4
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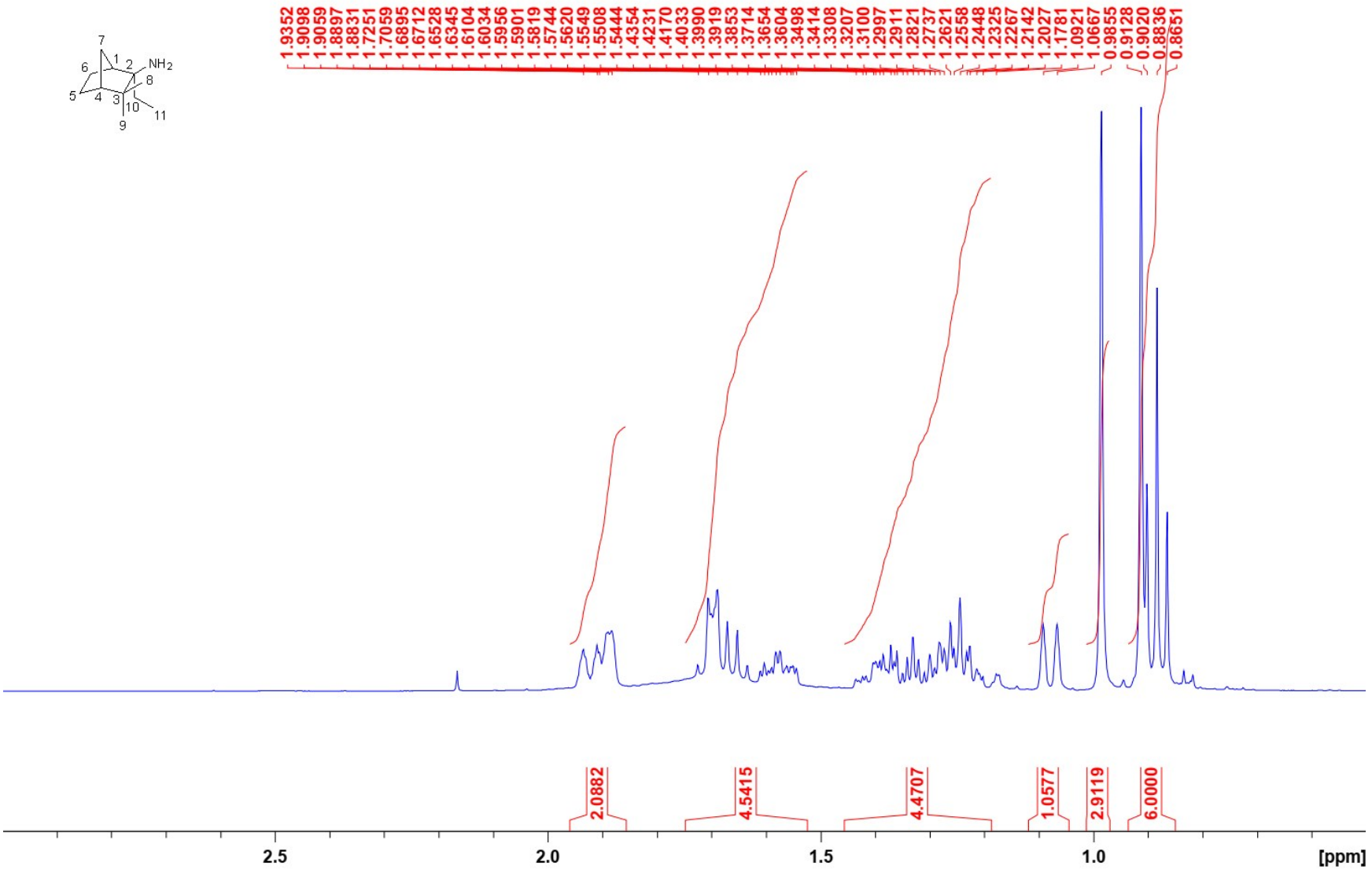
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10
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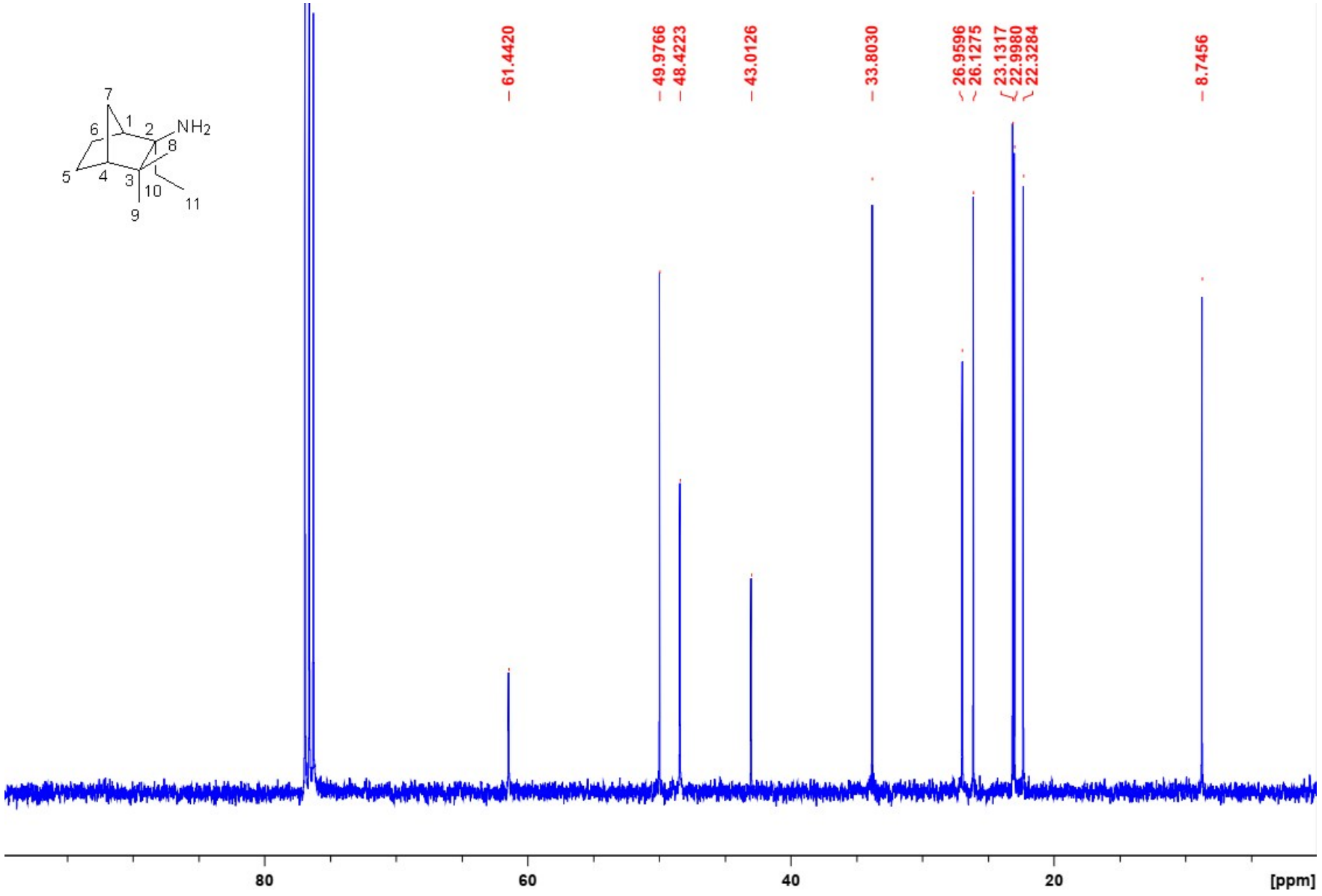
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80
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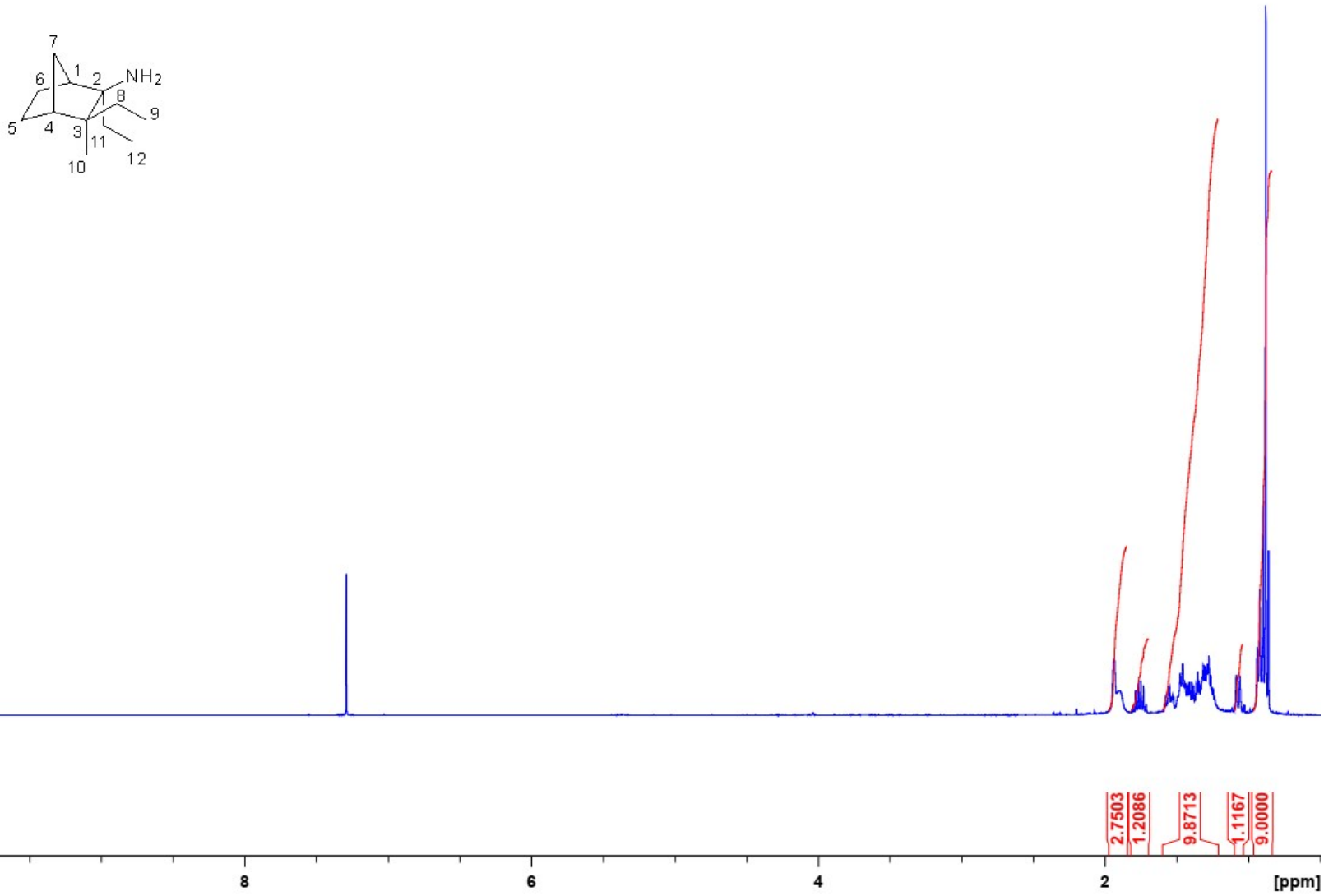
40
20
[ppm]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NH2
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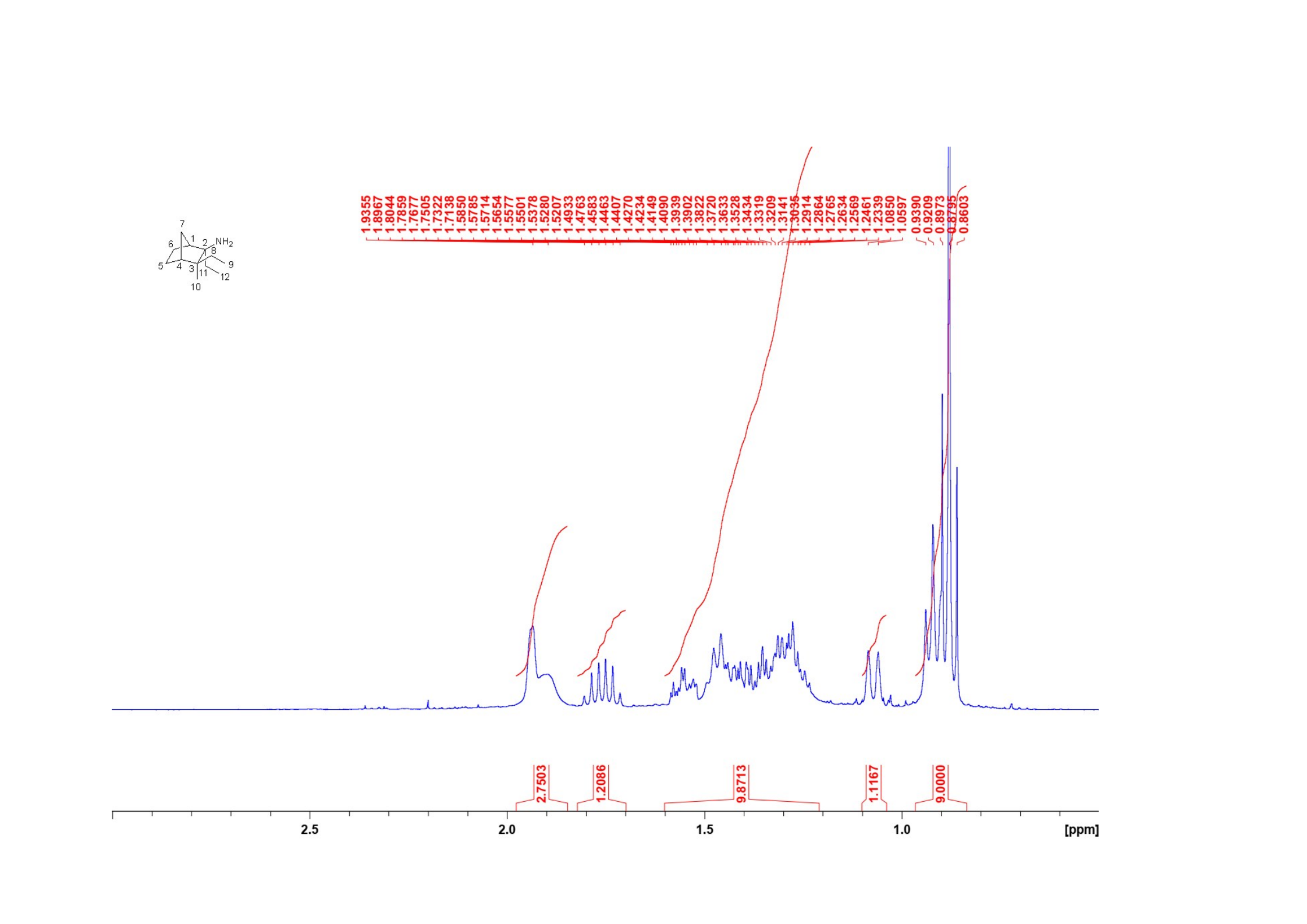
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NH2
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12
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1.3528
1.3434
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1.3141
1.3035
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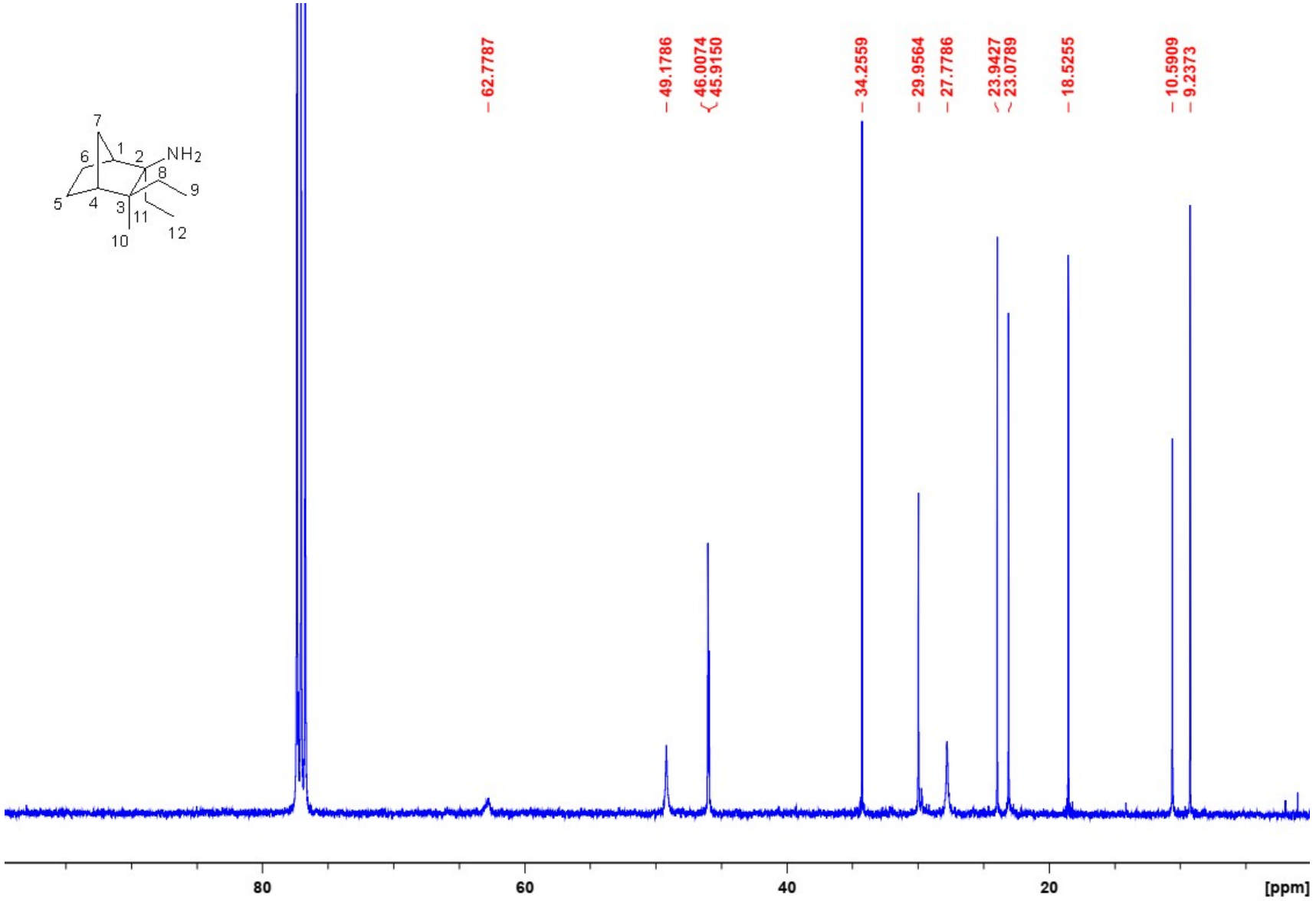
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9.2373
NH2
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7
8
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11
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40
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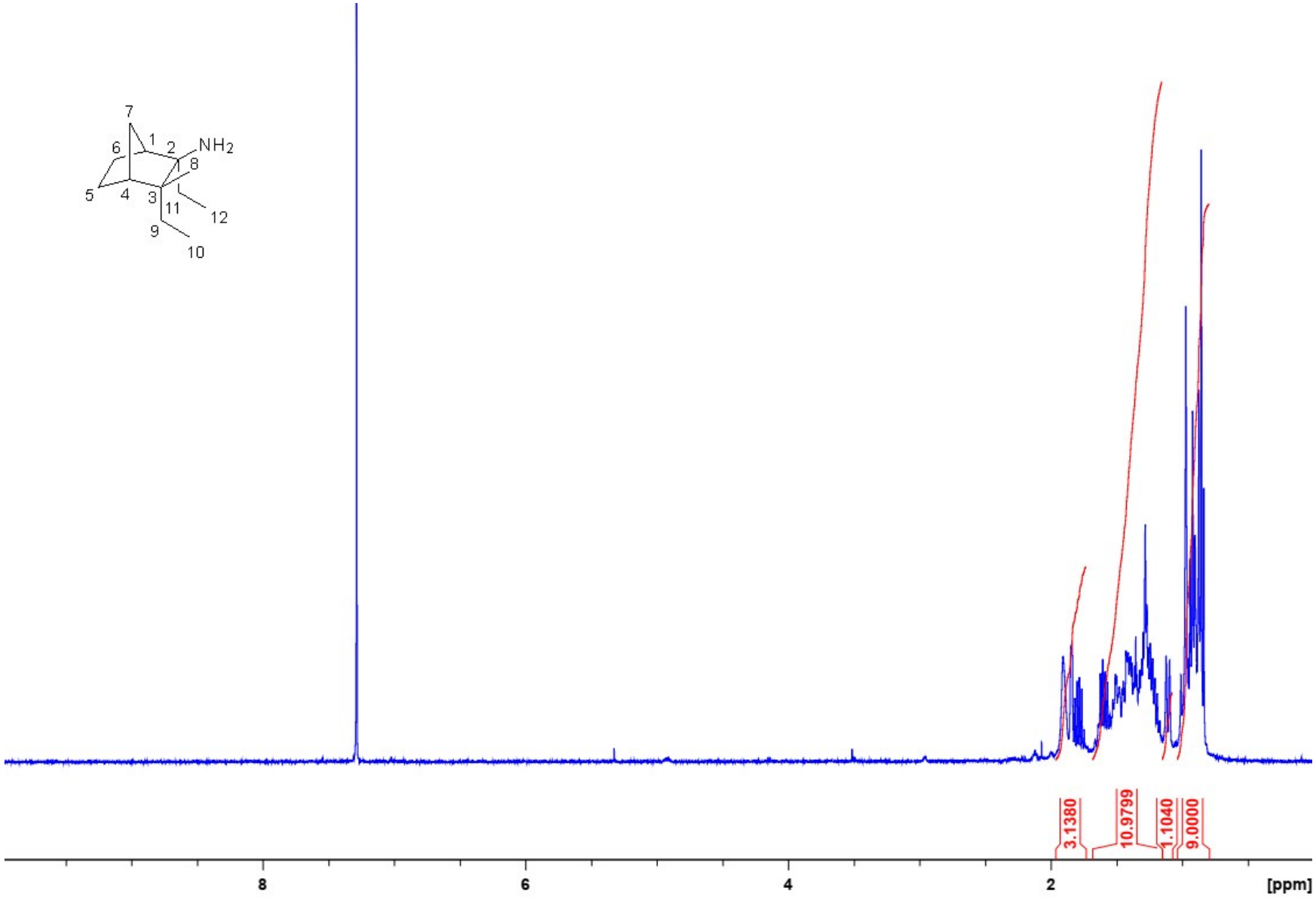
7
6
1
2
NH2
8
5
4
3
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12
9
10
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1.1040
9.0000
8
6
4
2
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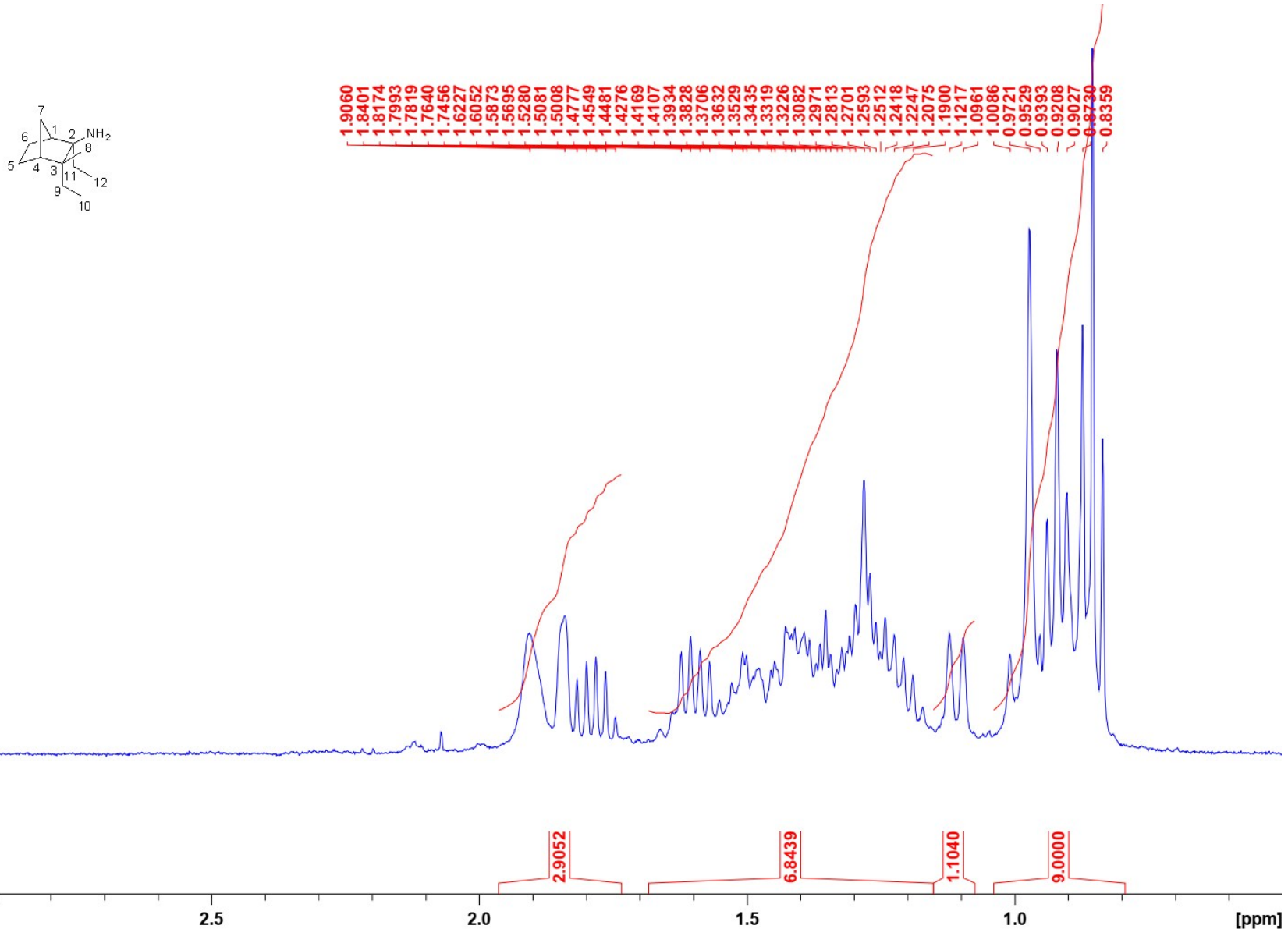
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2
NH2
8
6
5
4
3
11
12
9
10
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1.8401
1.8174
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1.7640
1.7456
1.6227
1.6052
1.5873
1.5695
1.5280
1.5081
1.5008
1.4777
1.4549
1.4481
1.4276
1.4169
1.4107
1.3934
1.3828
1.3706
1.3632
1.3529
1.3435
1.3319
1.3226
1.3082
1.2971
1.2813
1.2701
1.2593
1.2512
1.2418
1.2247
1.2075
1.1900
1.1217
1.0961
1.0086
0.9721
0.9529
0.9393
0.9208
0.9027
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6.8439
1.1040
9.0000
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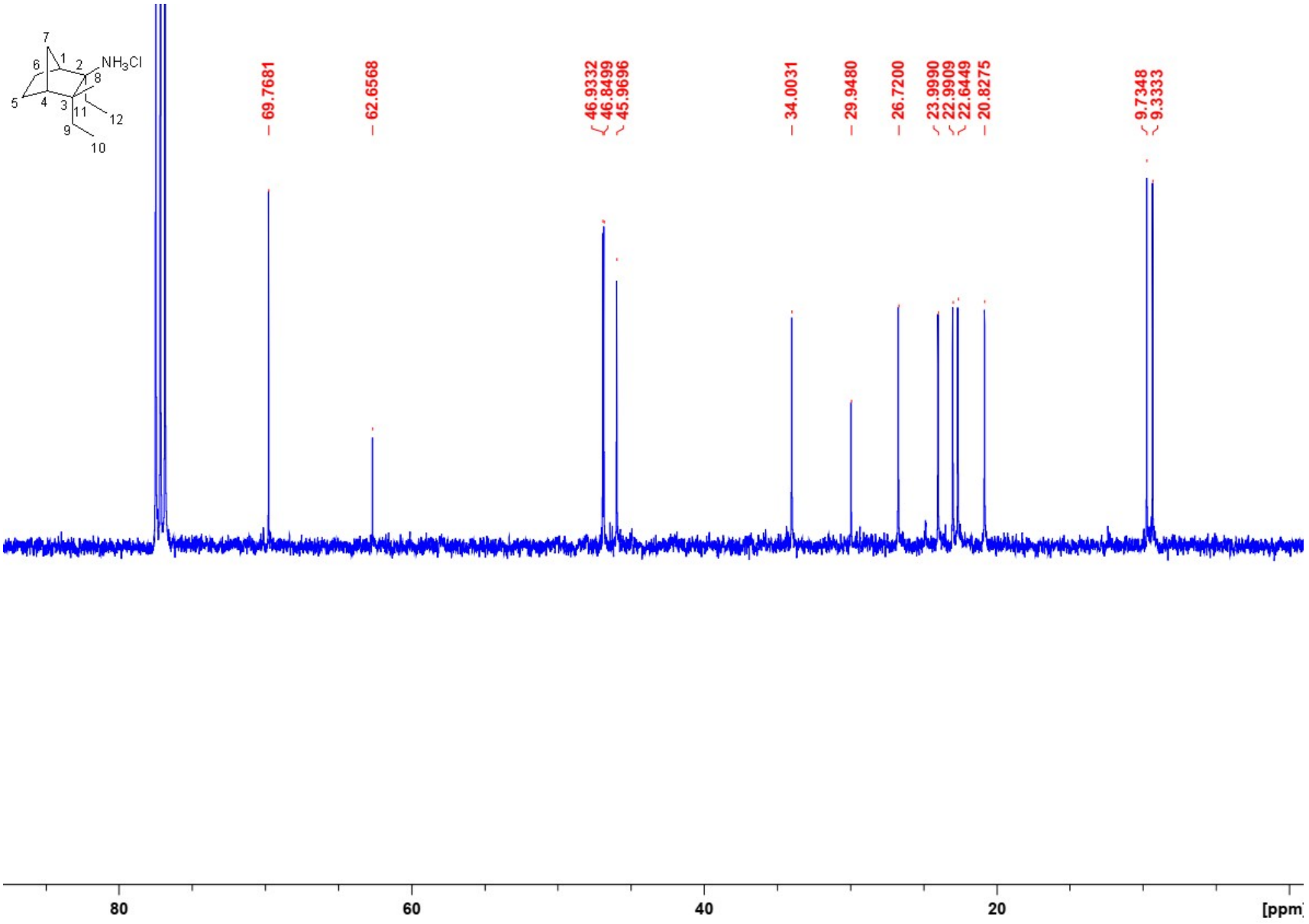
1.5
1.0
[ppm]


7
6
1
2
NH3Cl
8
5
4
3
11
12
9
10
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62.6568
46.9332
46.8499
45.9696
34.0031
29.9480
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22.9909
22.6449
20.8275
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9.3333
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40
20
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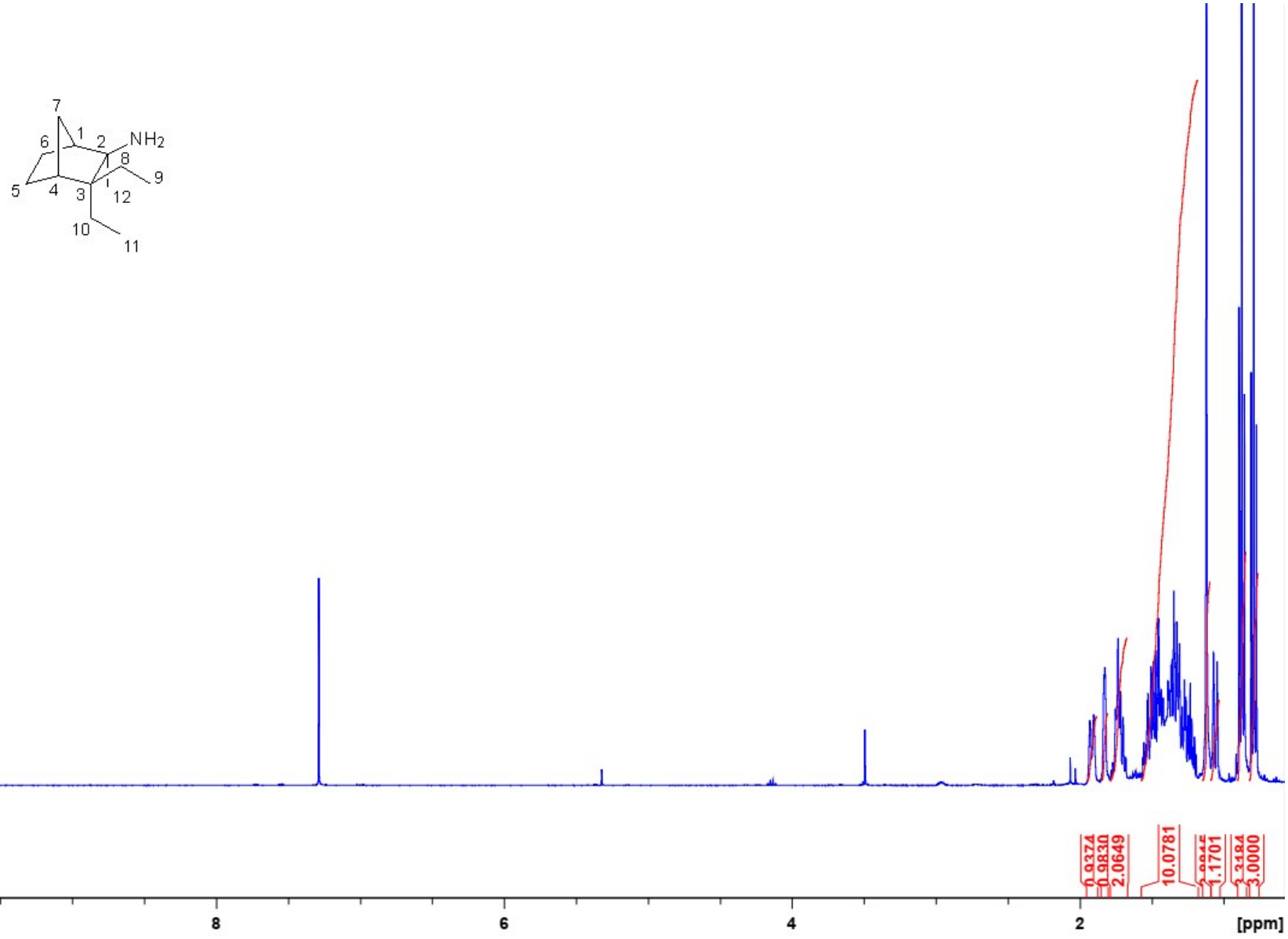
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6
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NH2
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5
4
3
12
10
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3.0000
8
6
4
2
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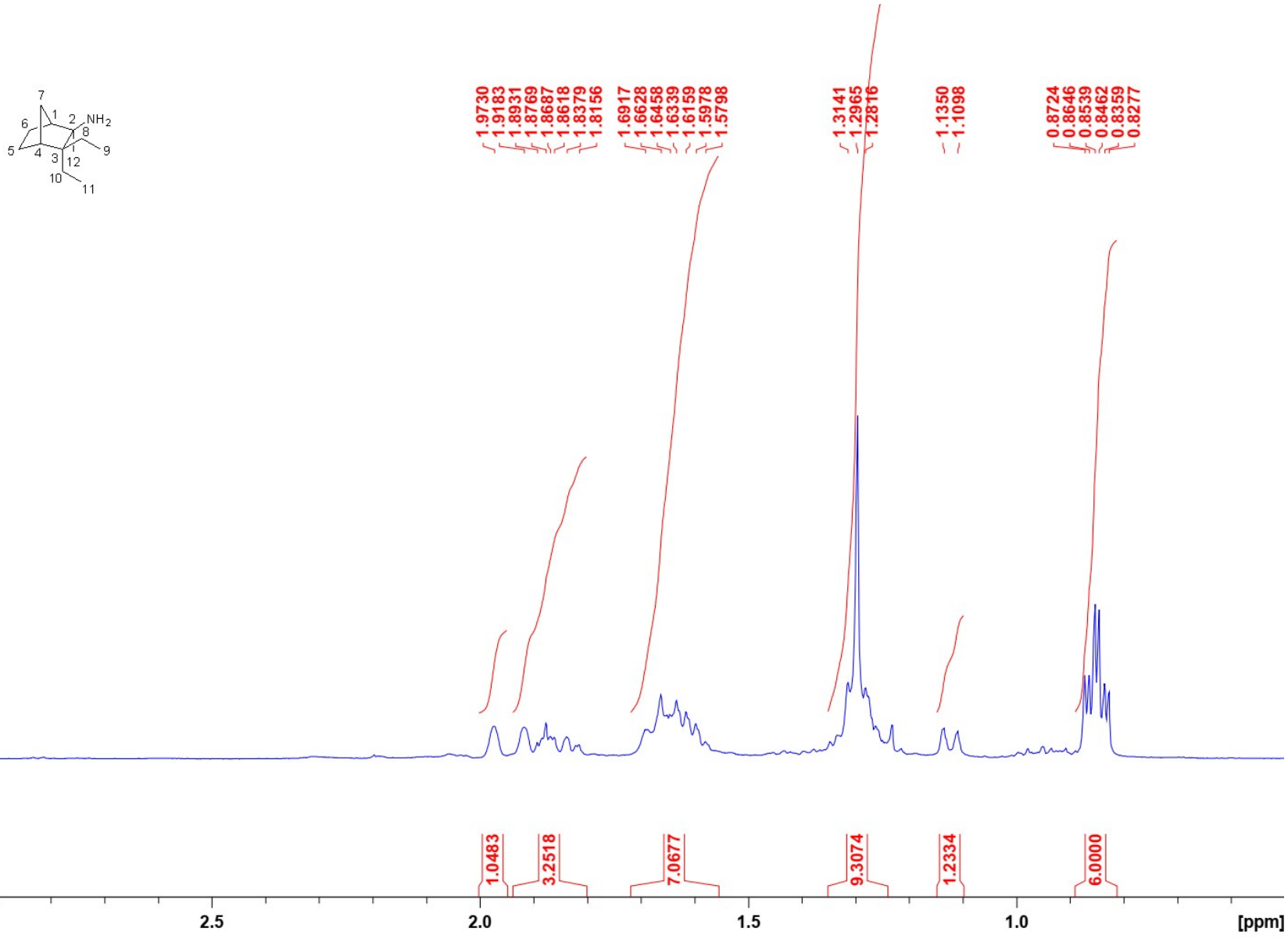
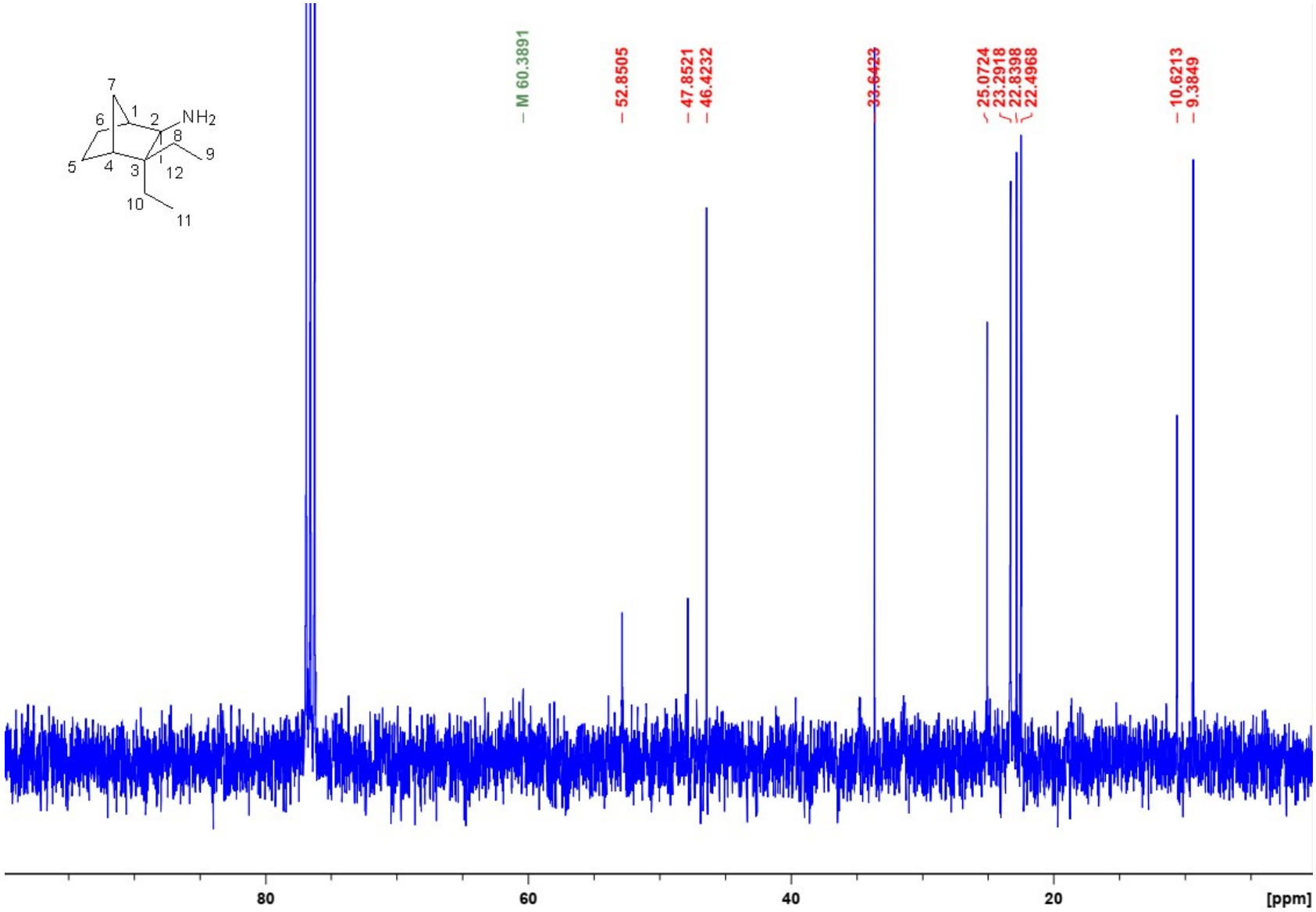

7
1
2
NH2
6
8
5
4
3
9
12
10
11
1.9730
1.9183
1.8931
1.8769
1.8687
1.8618
1.8379
1.8156
1.6917
1.6628
1.6458
1.6339
1.6159
1.5978
1.5798
1.3141
1.2965
1.2816
1.1350
1.1098
0.8724
0.8646
0.8539
0.8462
0.8359
0.8277
1.0483
3.2518
7.0677
9.3074
1.2334
6.0000
2.5
2.0
1.5
1.0
[ppm]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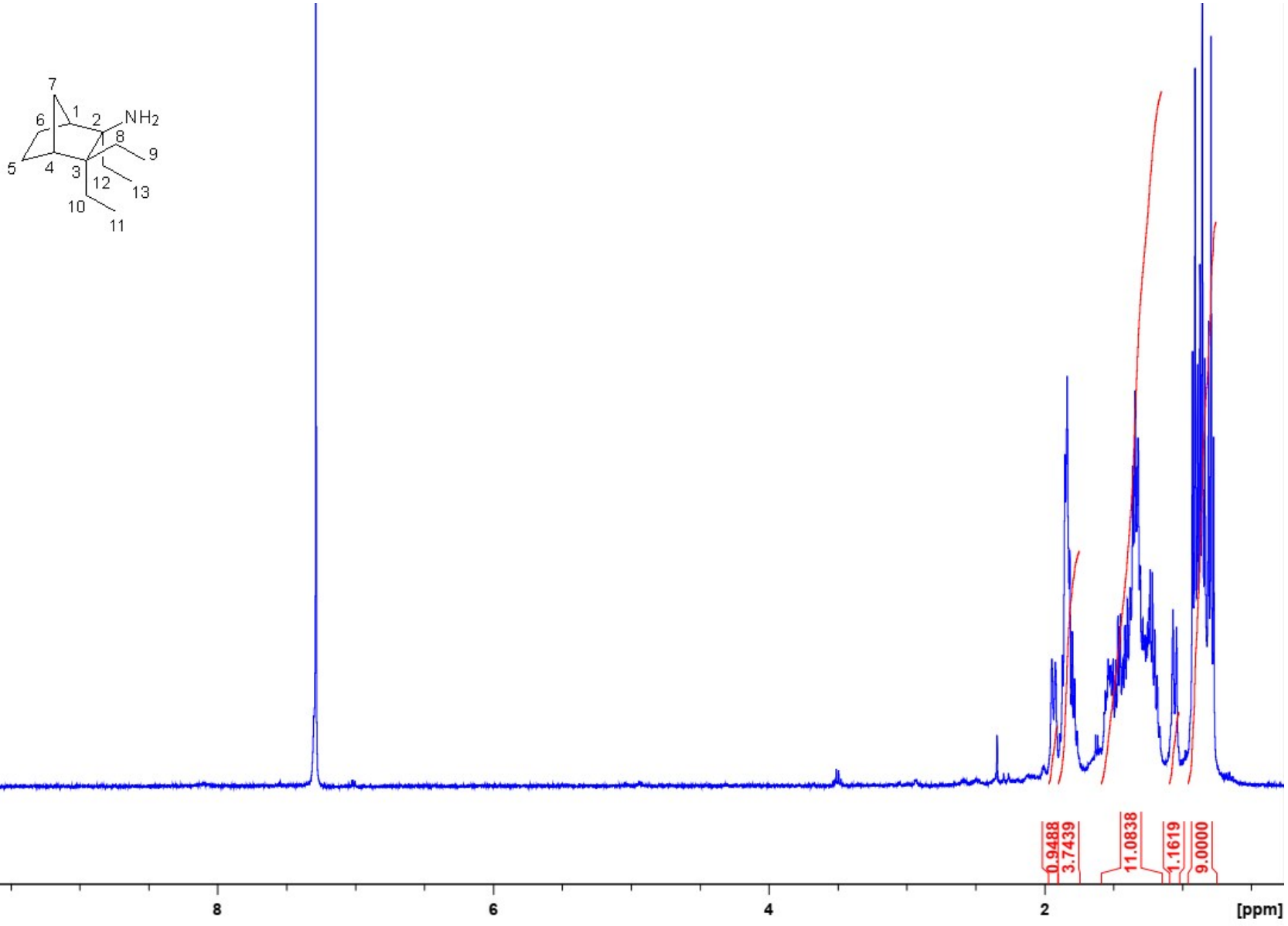
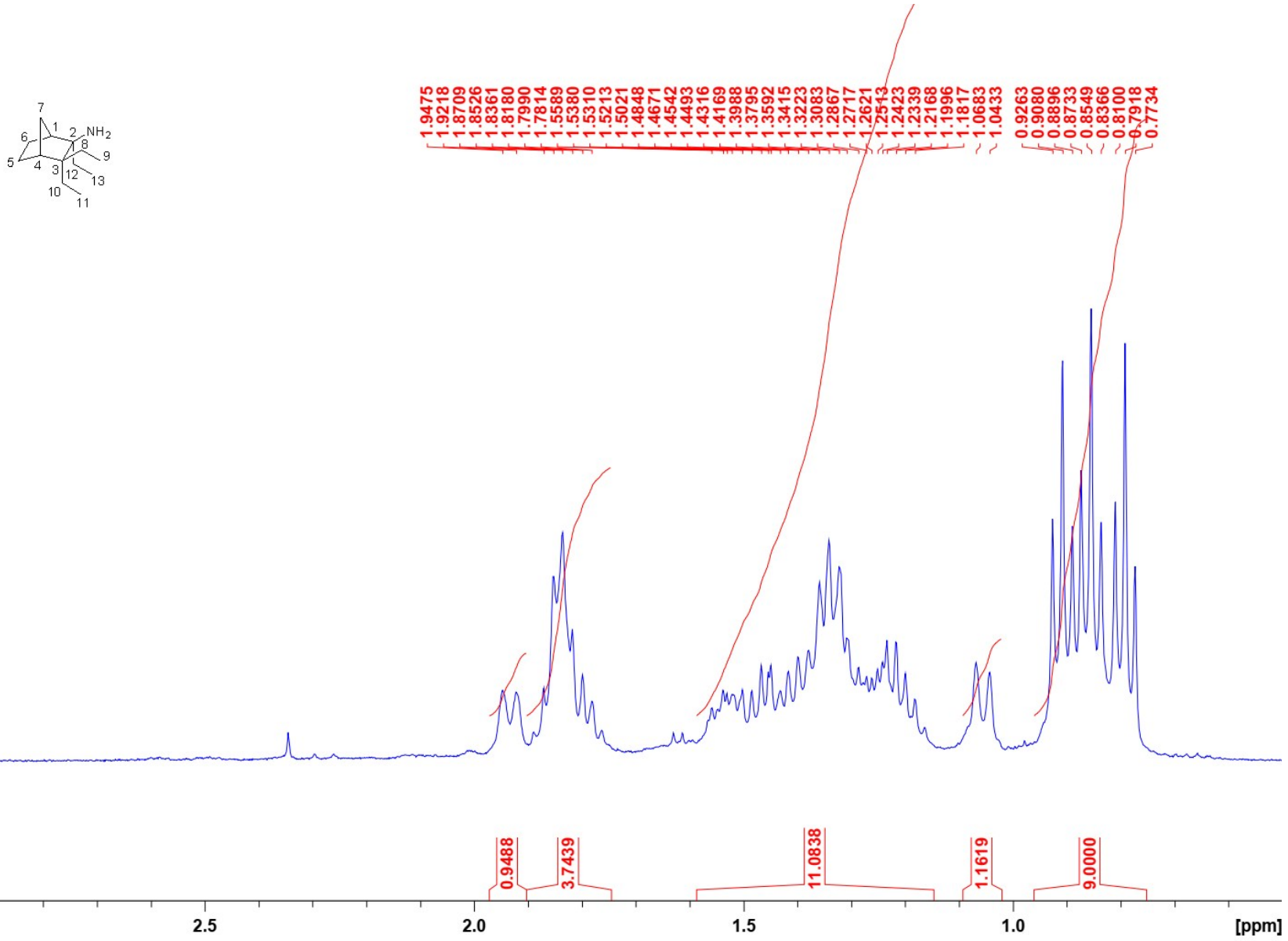
52.8505
47.8521
46.4232
33.6423
25.0724
23.2918
22.8398
22.4968
10.6213
9.3849
NH2
1
2
3
4
5
6
7
8
9
10
11
12
80
60
40
20
[ppm]


7
1
2
NH2
6
8
9
5
4
3
12
13
10
11
0.9488
3.7439
11.0838
1.1619
9.0000
8
6
4
2
[ppm]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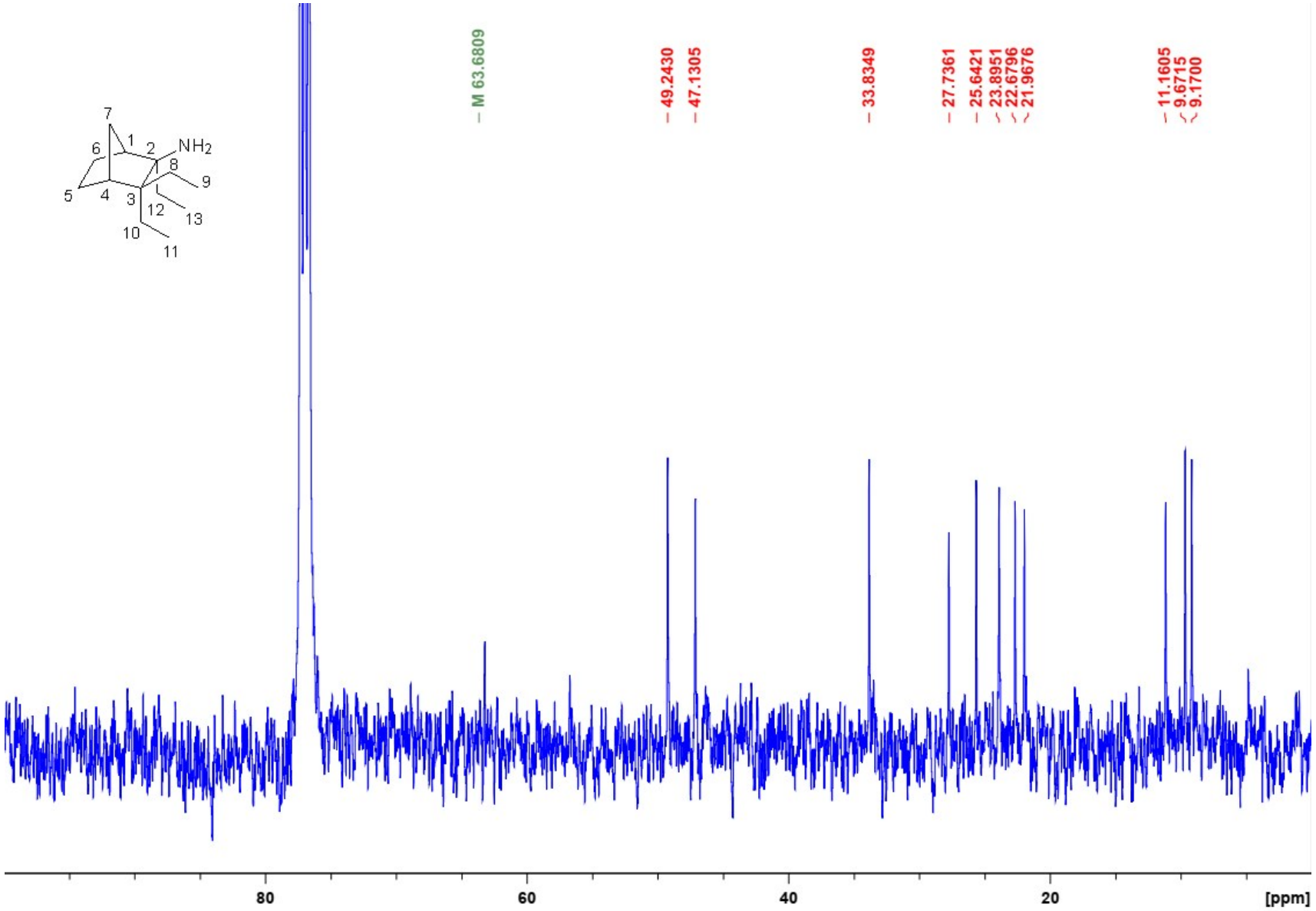
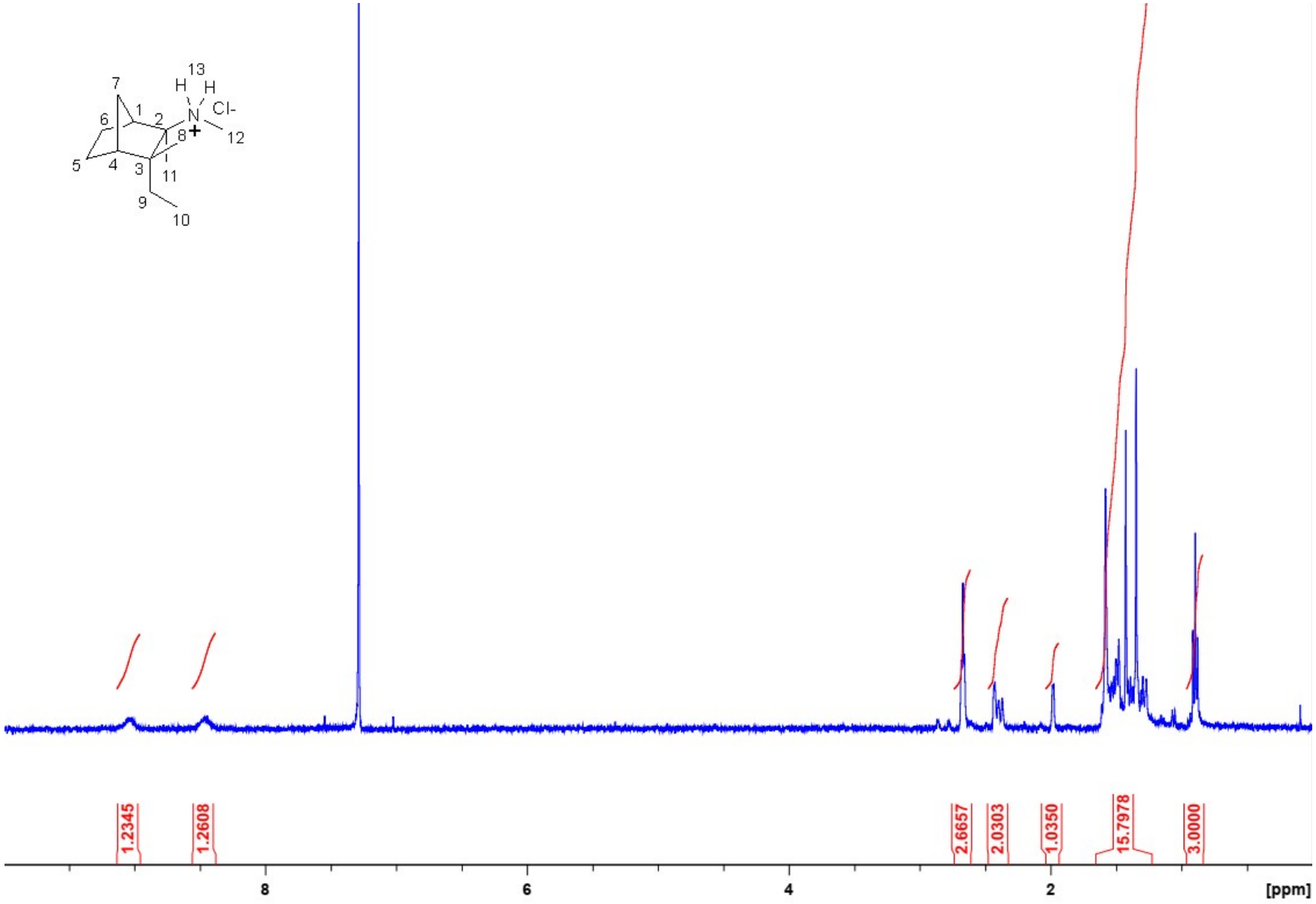
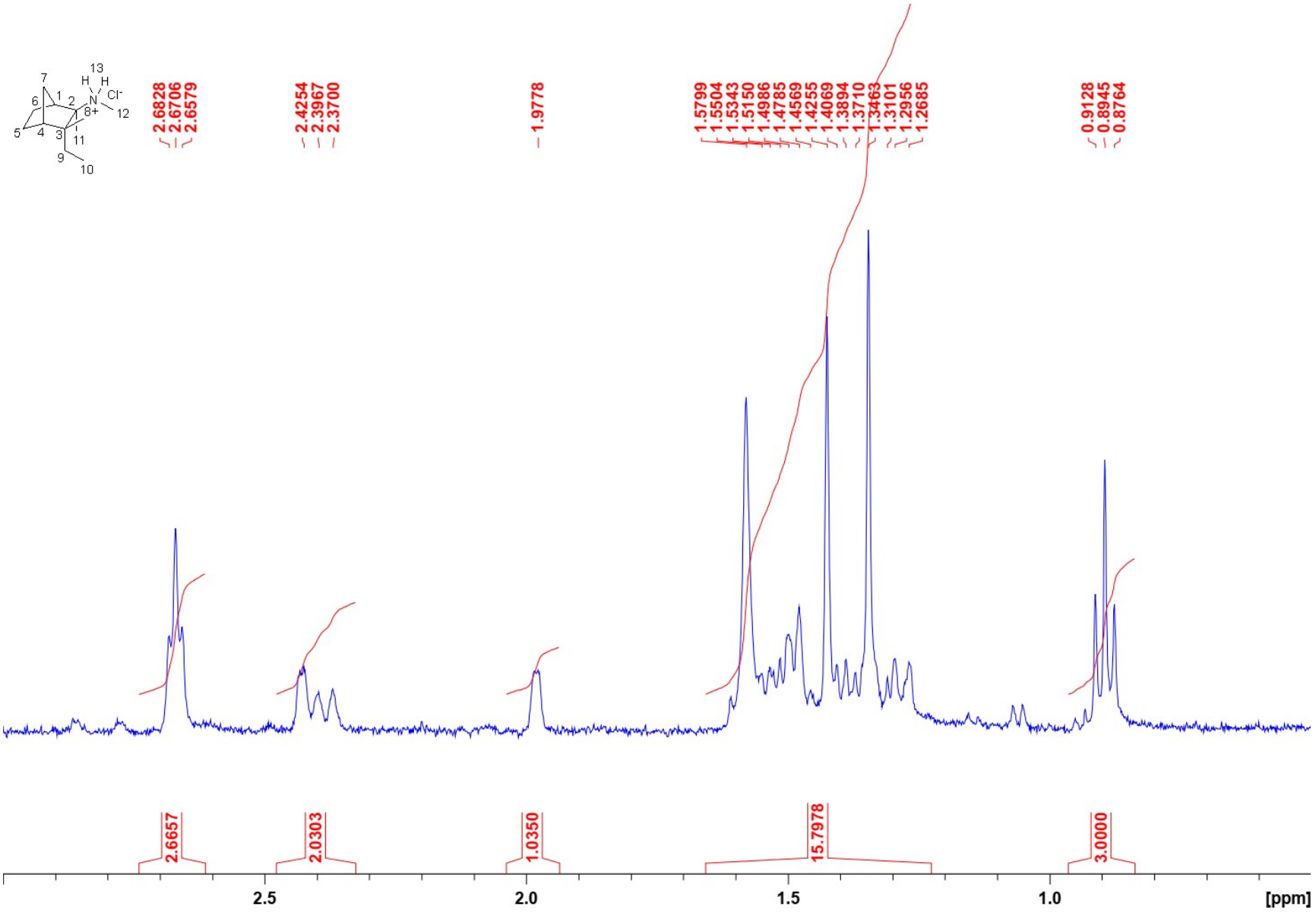
1
2
NH2
6
8
9
5
4
3
12
13
10
11
1.9475
1.9218
1.8709
1.8526
1.8361
1.8180
1.7990
1.7814
1.5589
1.5380
1.5310
1.5213
1.5021
1.4848
1.4671
1.4542
1.4493
1.4316
1.4169
1.3988
1.3795
1.3592
1.3415
1.3223
1.3083
1.2867
1.2717
1.2621
1.2513
1.2423
1.2339
1.2168
1.1996
1.1817
1.0683
1.0433
0.9263
0.9080
0.8896
0.8733
0.8549
0.8366
0.8100
0.7918
0.7734
0.9488
3.7439
11.0838
1.1619
9.0000
2.5
2.0
1.5
1.0
[ppm]


M 63.6809
49.2430
47.1305
33.8349
27.7361
25.6421
23.8951
22.6796
21.9676
11.1605
9.6715
9.1700
NH2
1
2
3
4
5
6
7
8
9
10
11
12
13
80
60
40
20
[ppm]


7
13
H
H
1
2
N
Cl-
6
8
+
12
5
4
3
11
9
10
1.2345
1.2608
2.6657
2.0303
1.0350
15.7978
3.0000
8
6
4
2
[ppm]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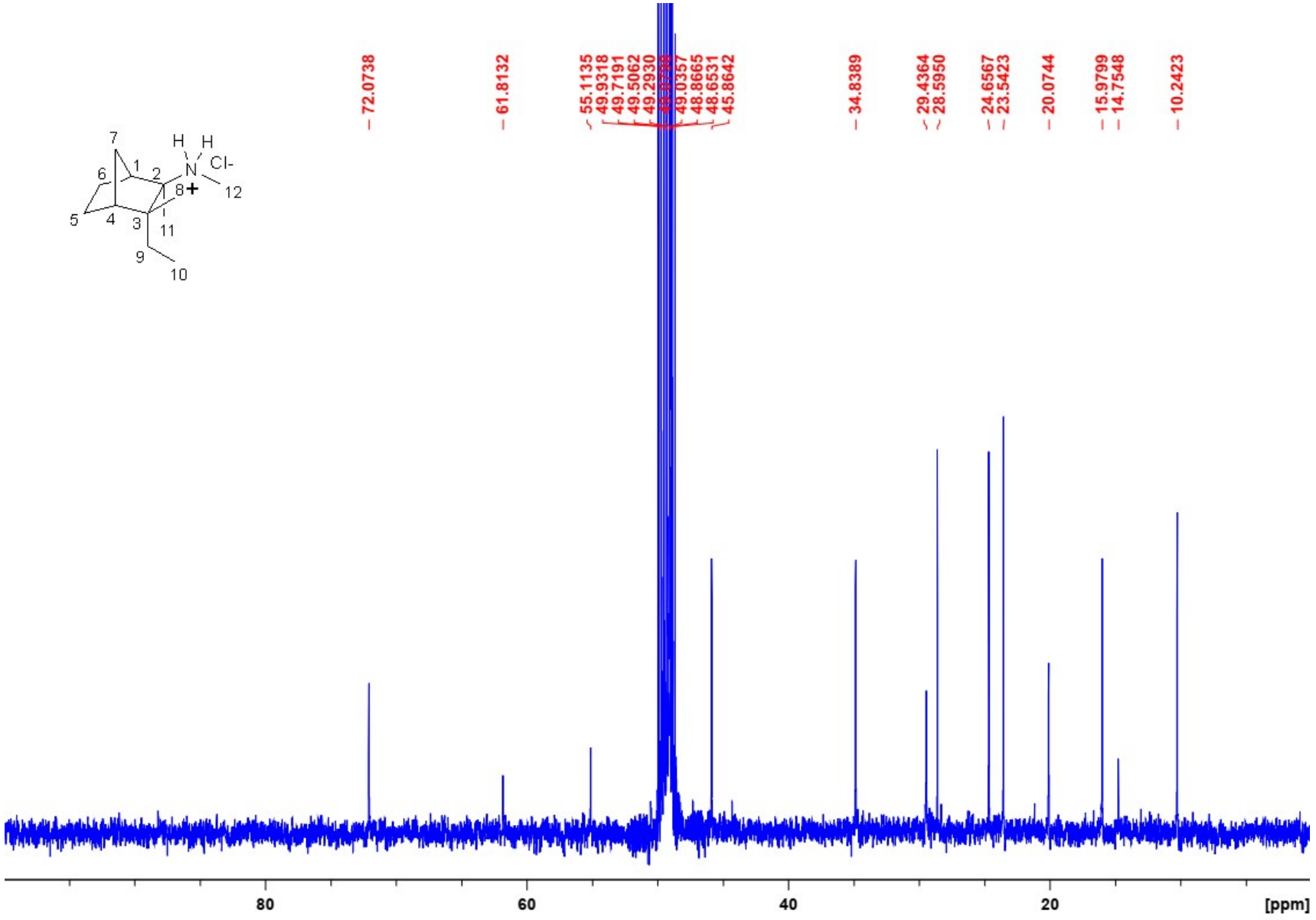
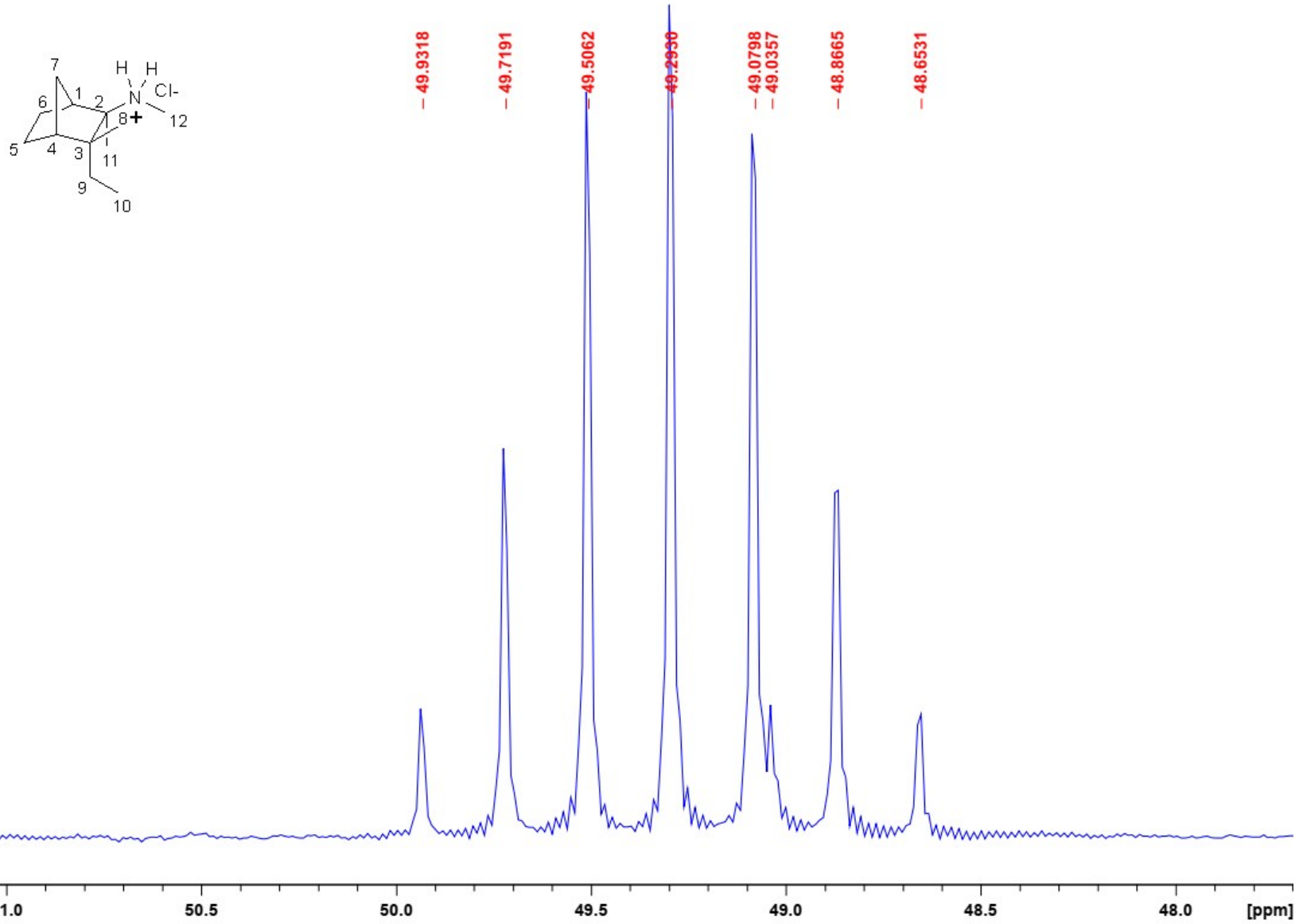
2.6706
2.6579
2.4254
2.3967
2.3700
1.9778
1.5799
1.5504
1.5343
1.5150
1.4986
1.4785
1.4569
1.4255
1.4069
1.3894
1.3710
1.3463
1.3101
1.2956
1.2685
0.9128
0.8945
0.8764
2.6657
2.0303
1.0350
15.7978
3.0000
2.5
2.0
1.5
1.0
[ppm]


72.0738
61.8132
55.1135
49.9318
49.7191
49.5062
49.2930
49.0357
48.8665
48.6531
45.8642
34.8389
29.4364
28.5950
24.6567
23.5423
20.0744
15.9799
14.7548
10.2423
H
H
N
Cl-
12
7
1
2
6
8+
5
4
3
11
9
10
80
60
40
20
[ppm]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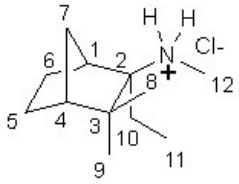
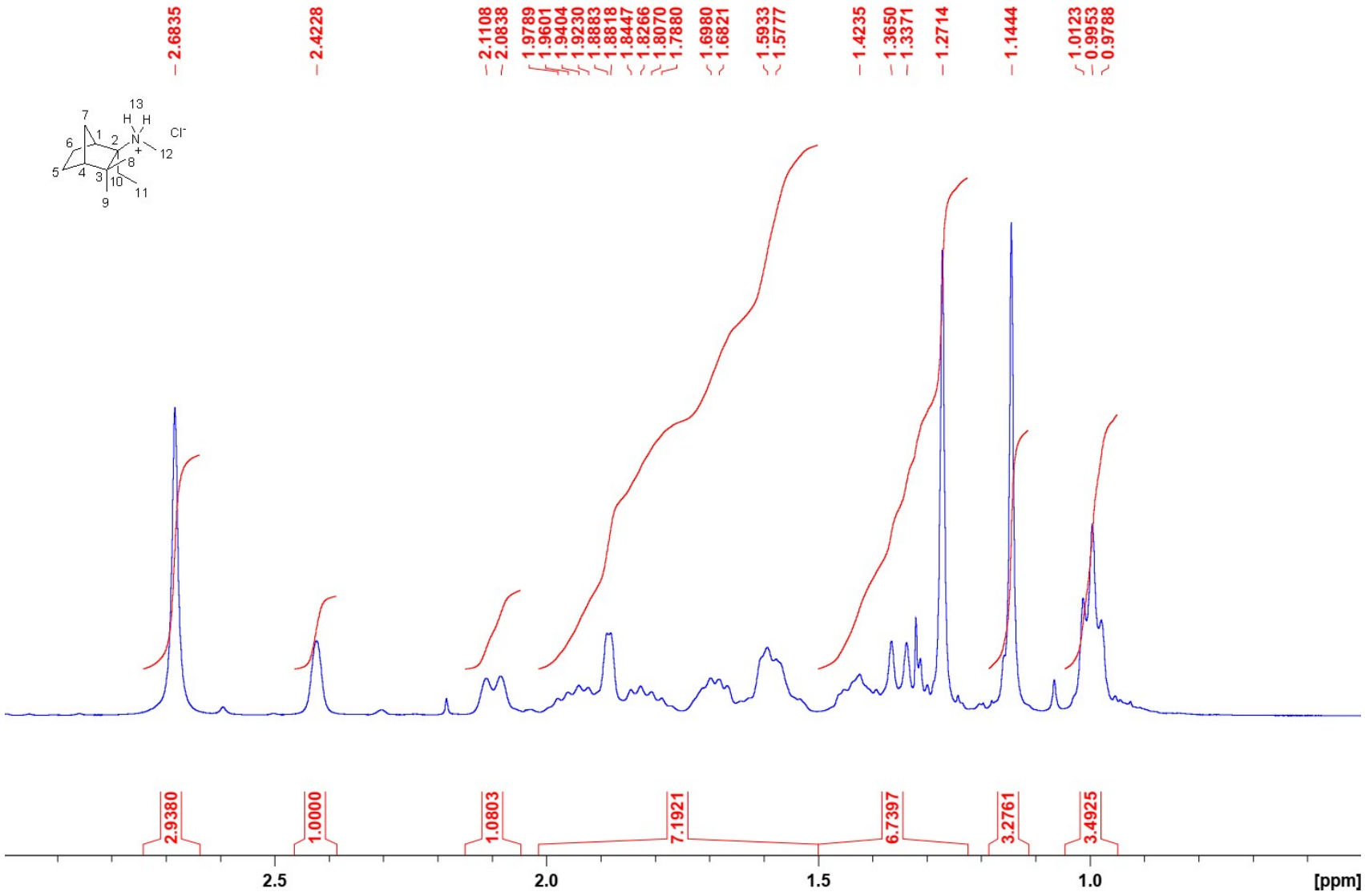
49.7191
49.5062
49.2930
49.0798
49.0357
48.8665
48.6531
51.0
50.5
50.0
49.5
49.0
48.5
48.0
[ppm]


7
H
H
1
2
6
N
Cl-
8
12
5
4
3
10
9
11

2.9380
1.0000
1.0803
7.1921
6.7397
3.2761
3.4925
8
6
4
2
[ppm]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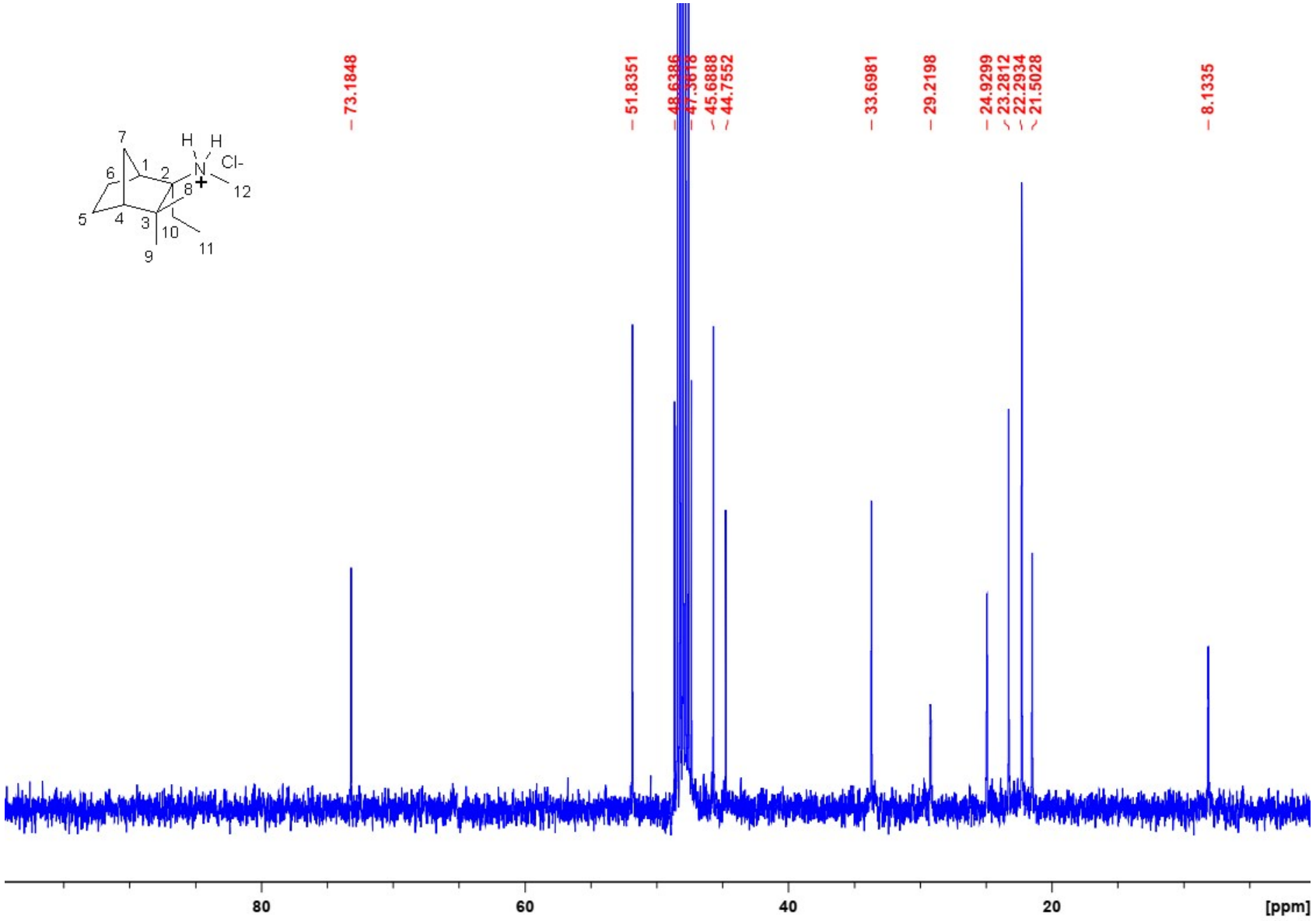
2.4228
2.1108
2.0838
1.9789
1.9601
1.9404
1.9230
1.8883
1.8818
1.8447
1.8266
1.8070
1.7880
1.6980
1.6821
1.5933
1.5777
1.4235
1.3650
1.3371
1.2714
1.1444
1.0123
0.9953
0.9788
2.9380
1.0000
1.0803
7.1921
6.7397
3.2761
3.4925
2.5
2.0
1.5
1.0
[ppm]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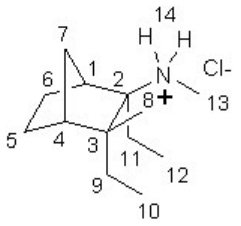
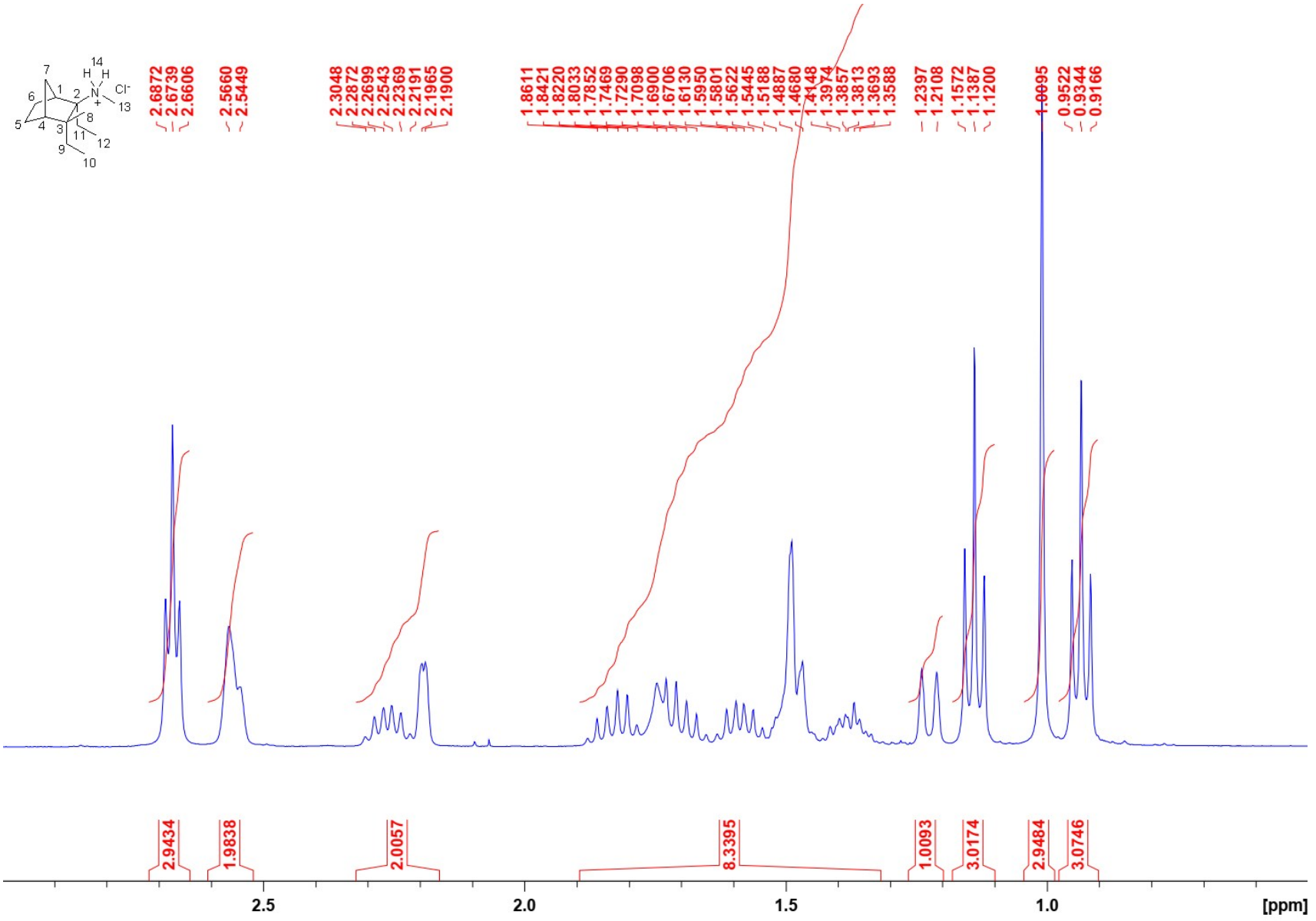
47.3618
45.6888
44.7552
33.6981
29.2198
24.9299
23.2812
22.2934
21.5028
8.1335
H
H
N
Cl-
+
1
2
3
4
5
6
7
8
9
10
11
12
80
60
40
20
[ppm]


14
H
H
7
1
2
N
Cl-
13
6
8+
5
4
3
11
12
9
10

1.0000
0.9578
2.9434
1.9838
2.0057
8.3395
1.0093
3.0174
2.0484
3.0746
8
6
4
2
[ppm]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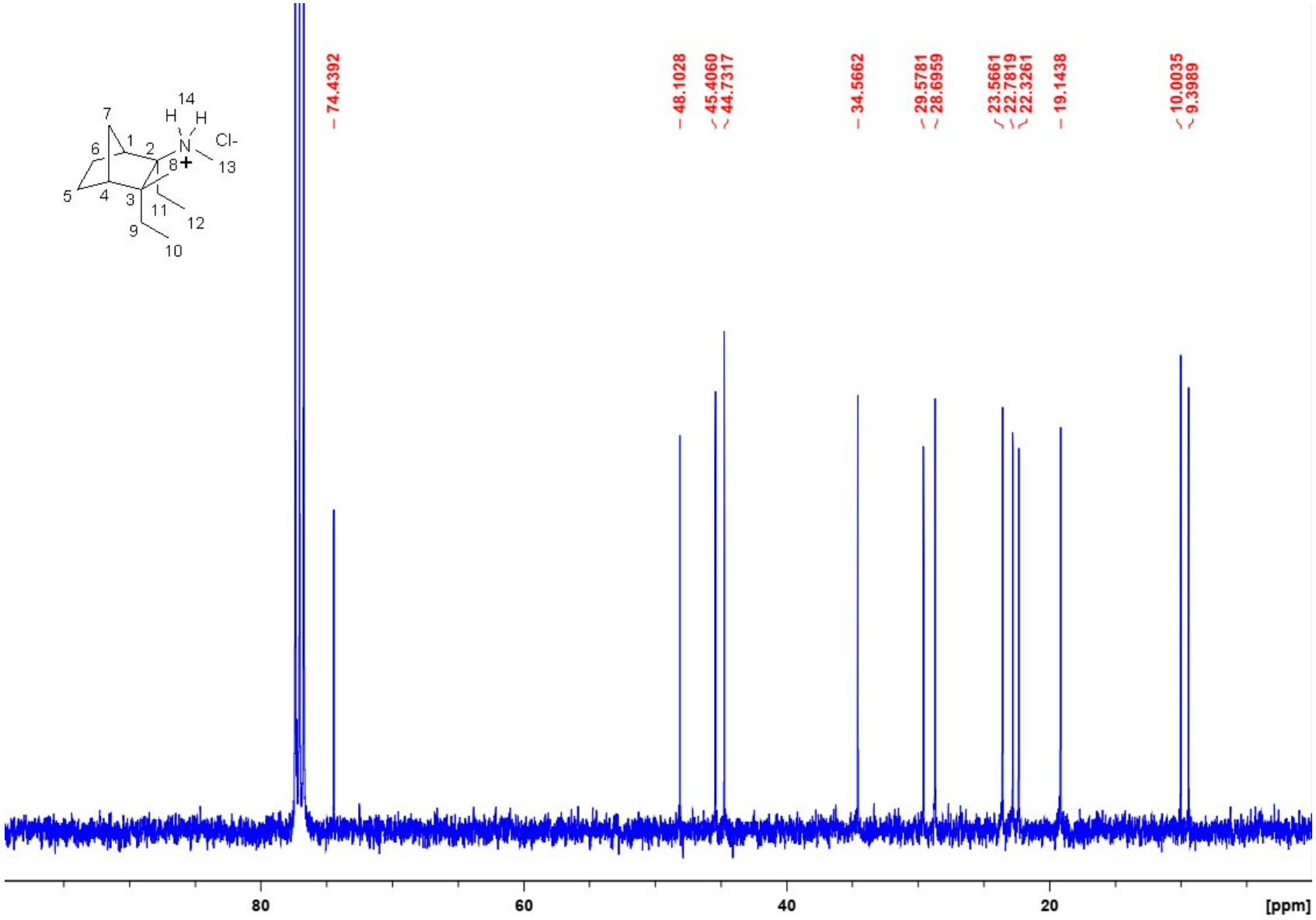
2.5660
2.5449
2.3048
2.2872
2.2699
2.2543
2.2369
2.2191
2.1965
2.1900
1.8611
1.8421
1.8220
1.8033
1.7852
1.7469
1.7290
1.7098
1.6900
1.6706
1.6130
1.5950
1.5801
1.5622
1.5445
1.5188
1.4887
1.4680
1.4148
1.3974
1.3857
1.3813
1.3693
1.3588
1.2397
1.2108
1.1572
1.1387
1.1200
1.0095
0.9522
0.9344
0.9166
2.9434
1.9838
2.0057
8.3395
1.0093
3.0174
2.9484
3.0746
2.5
2.0
1.5
1.0
[ppm]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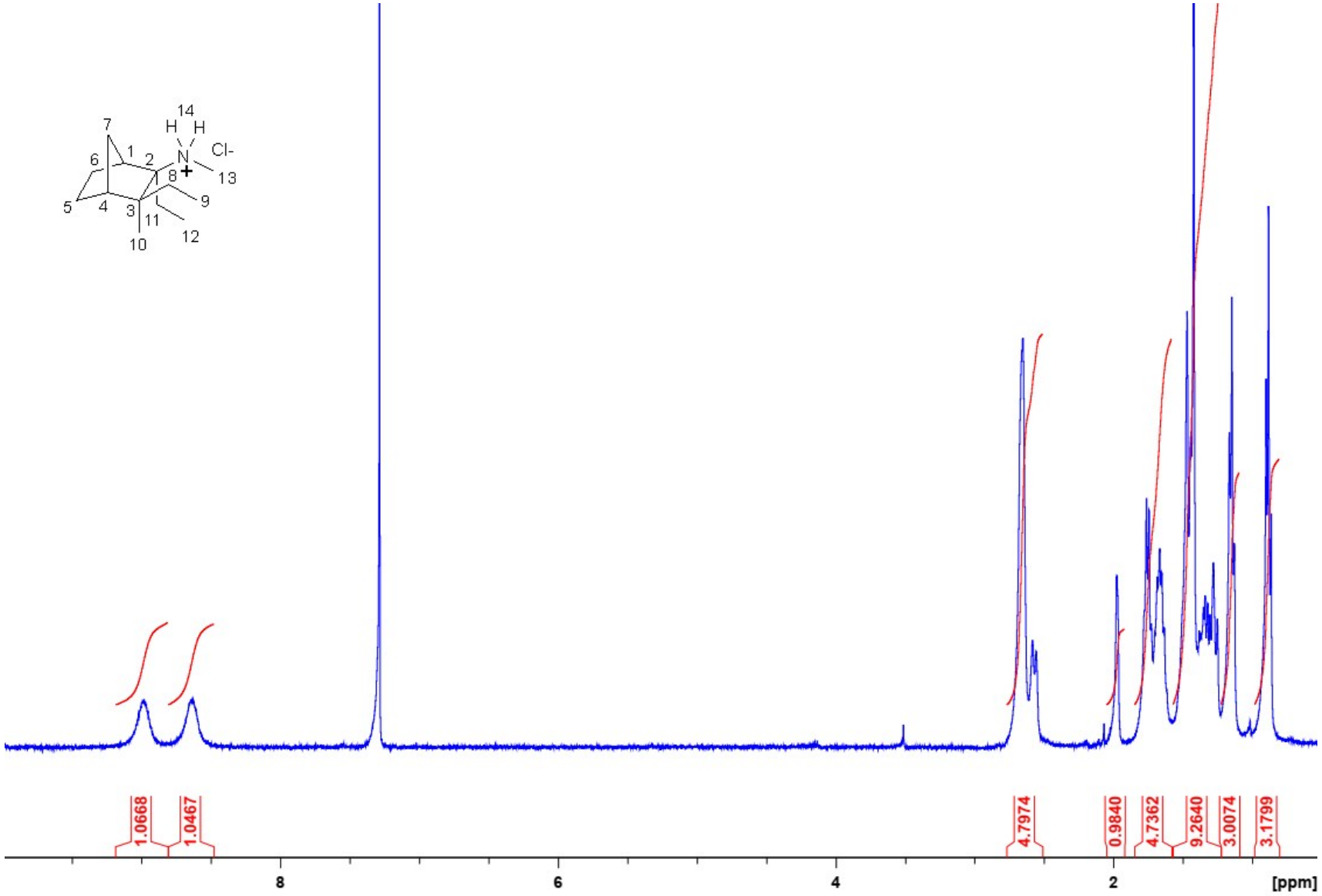
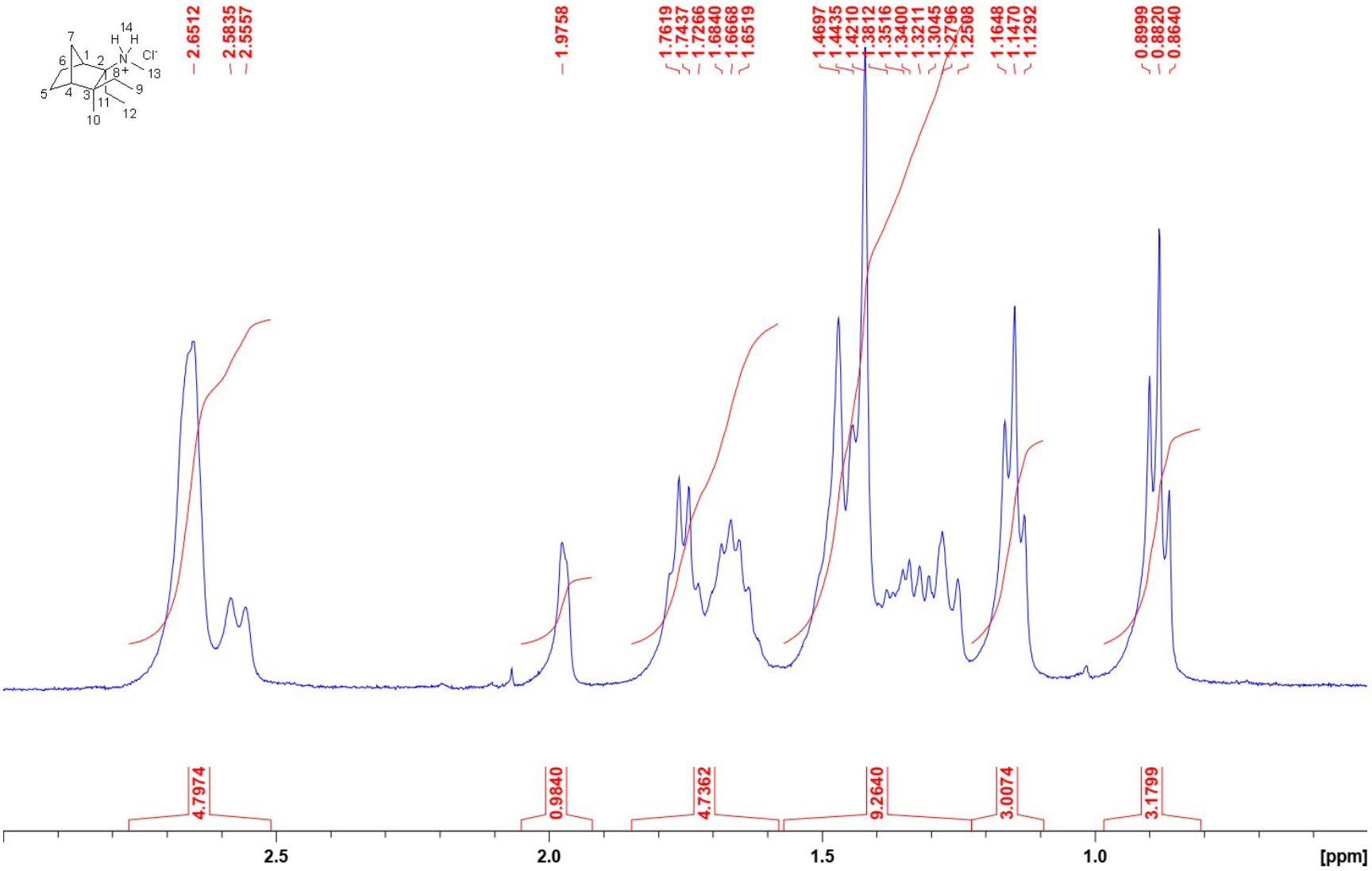
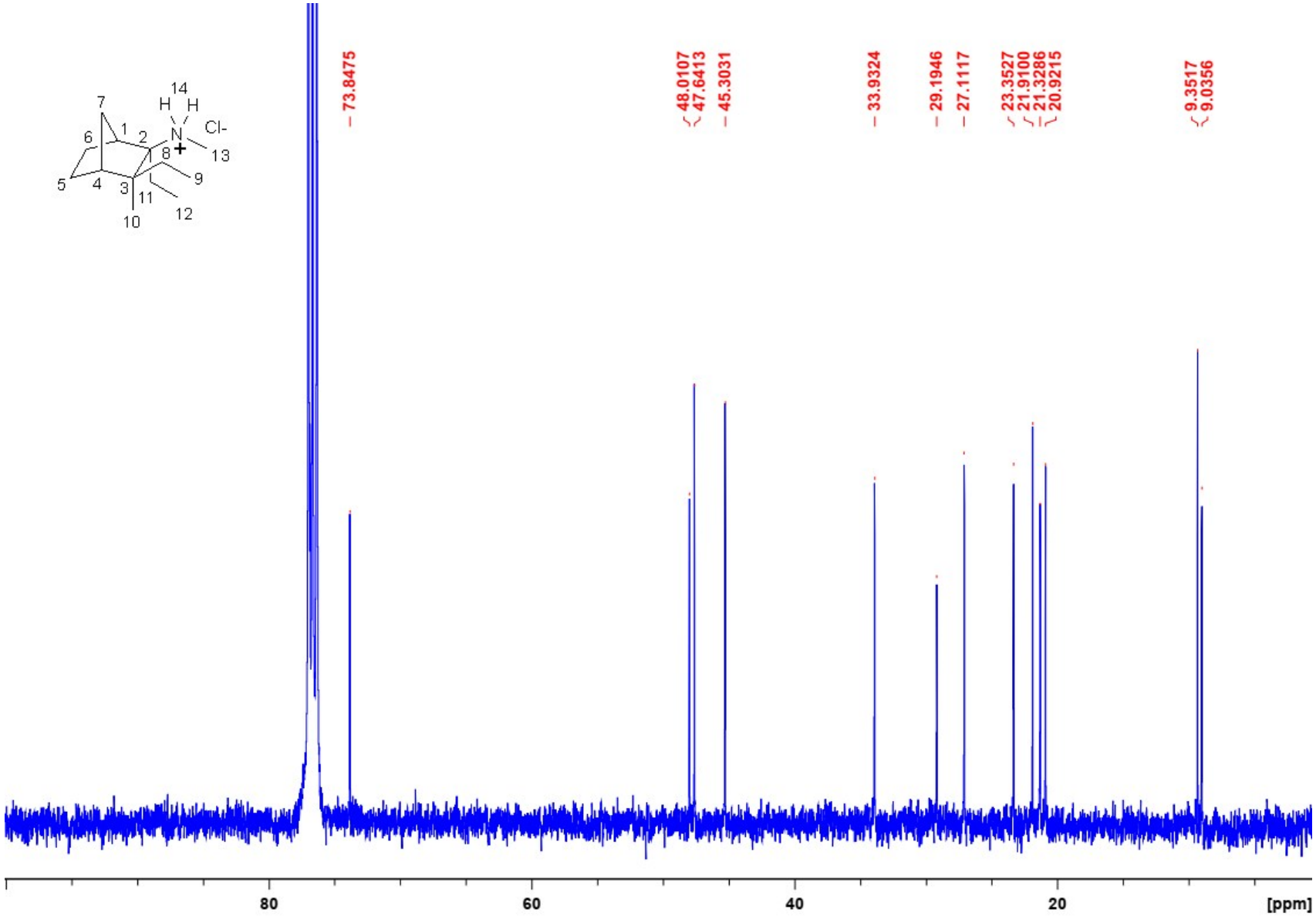
45.4060
44.7317
34.5662
29.5781
28.6959
23.5661
22.7819
22.3261
19.1438
10.0035
9.3989
14
H
H
7
1
2
N
Cl-
6
8+
13
5
4
3
11
12
9
10
80
60
40
20
[ppm]


14
H H
7
1
2
N
Cl-
13
6
8
+
9
5
4
3
11
12
10
1.0668
1.0467
4.7974
0.9840
4.7362
9.2640
3.0074
3.1799
8
6
4
2
[ppm]


2.6512
2.5835
2.5557
1.9758
1.7619
1.7437
1.7266
1.6840
1.6668
1.6519
1.4697
1.4435
1.4210
1.3812
1.3516
1.3400
1.3211
1.3045
1.2796
1.2508
1.1648
1.1470
1.1292
0.8999
0.8820
0.8640
4.7974
0.9840
4.7362
9.2640
3.0074
3.1799
2.5
2.0
1.5
1.0
[ppm]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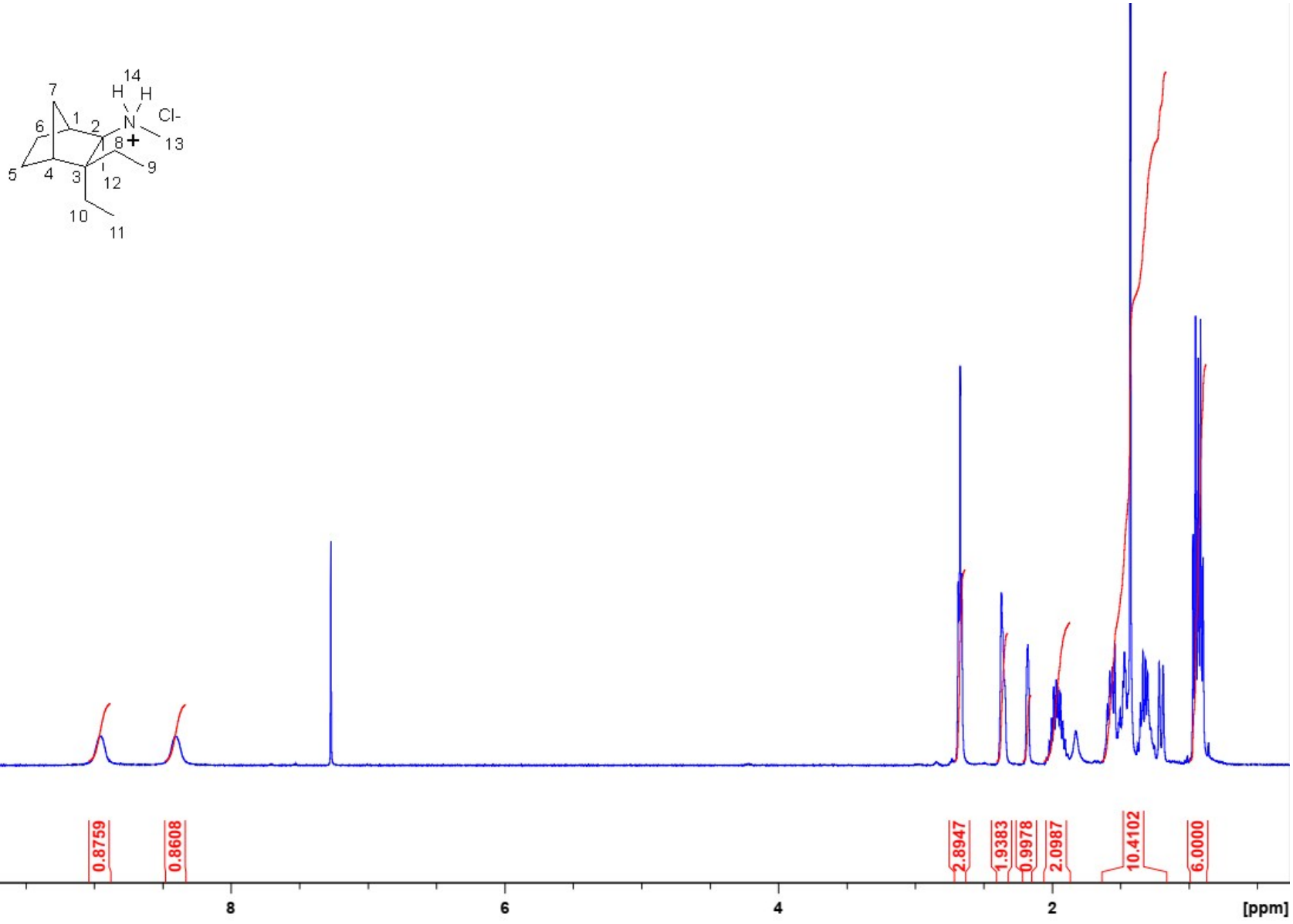
47.6413
45.3031
33.9324
29.1946
27.1117
23.3527
21.9100
21.3286
20.9215
9.3517
9.0356
80
60
40
20
[ppm]


14
H
H
7
1
2
N
Cl-
13
6
8
+
9
5
4
3
12
10
11
0.8759
0.8608
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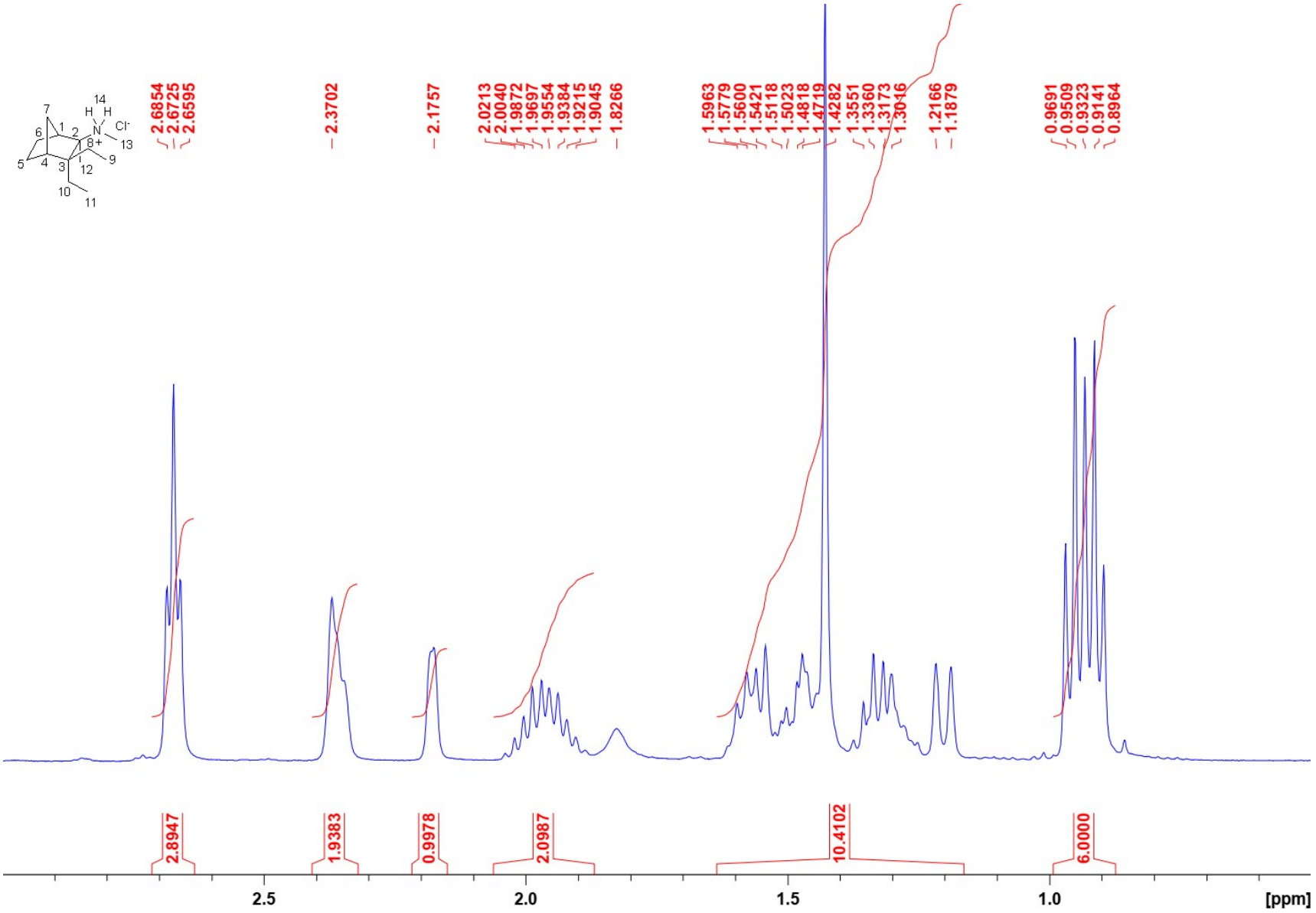
1.9383
0.9978
2.0987
10.4102
6.0000
8
6
4
2
[ppm]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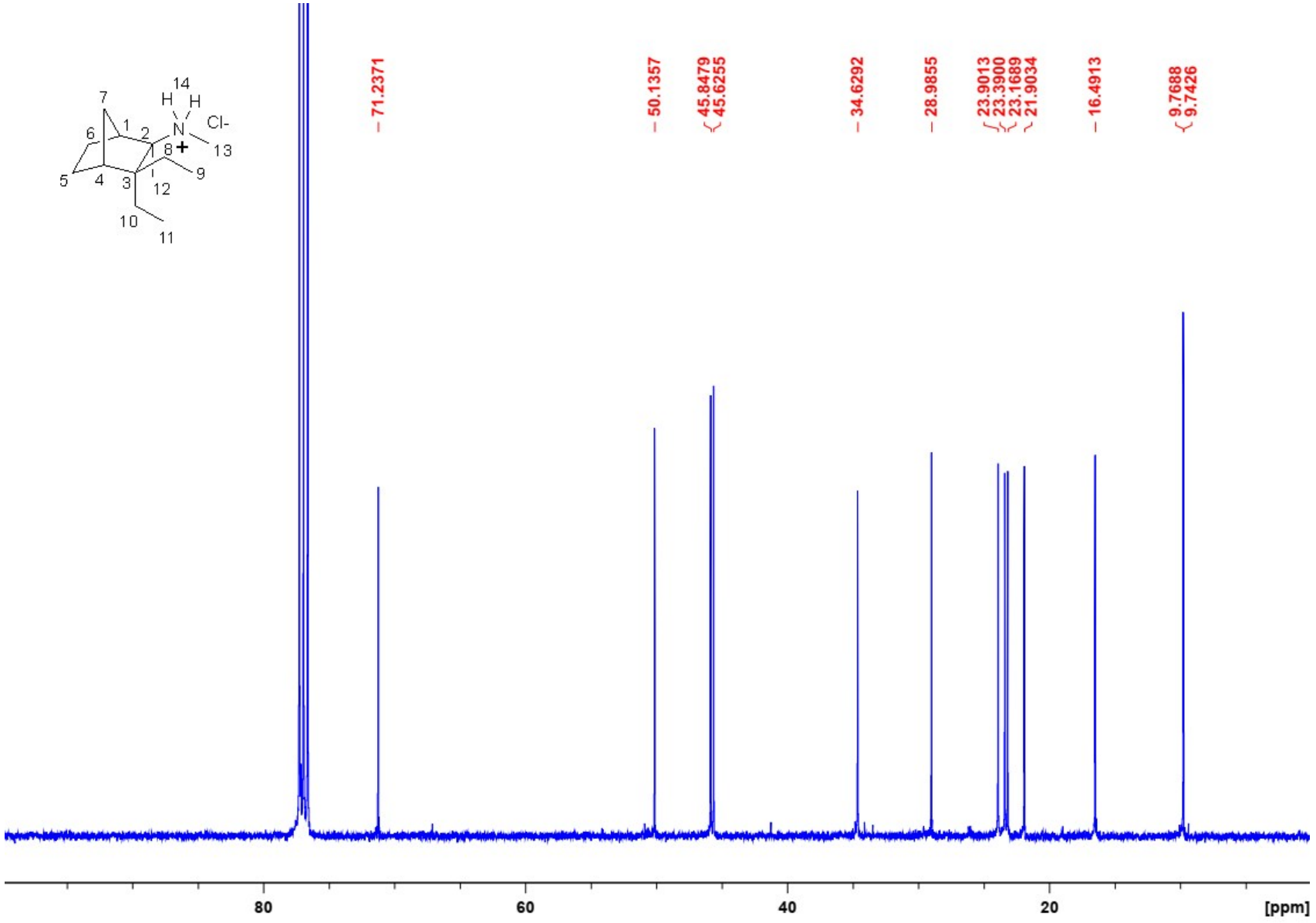
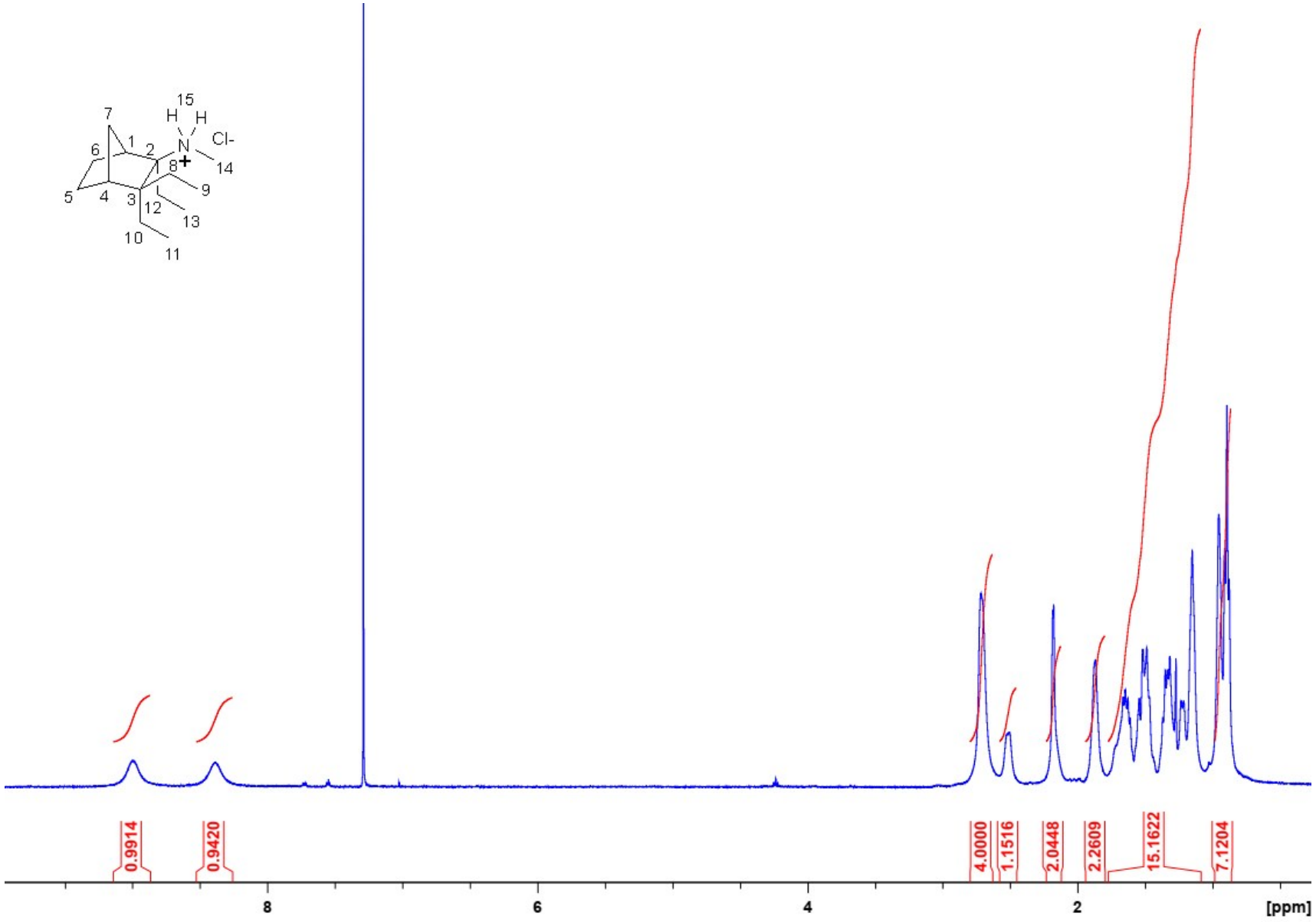
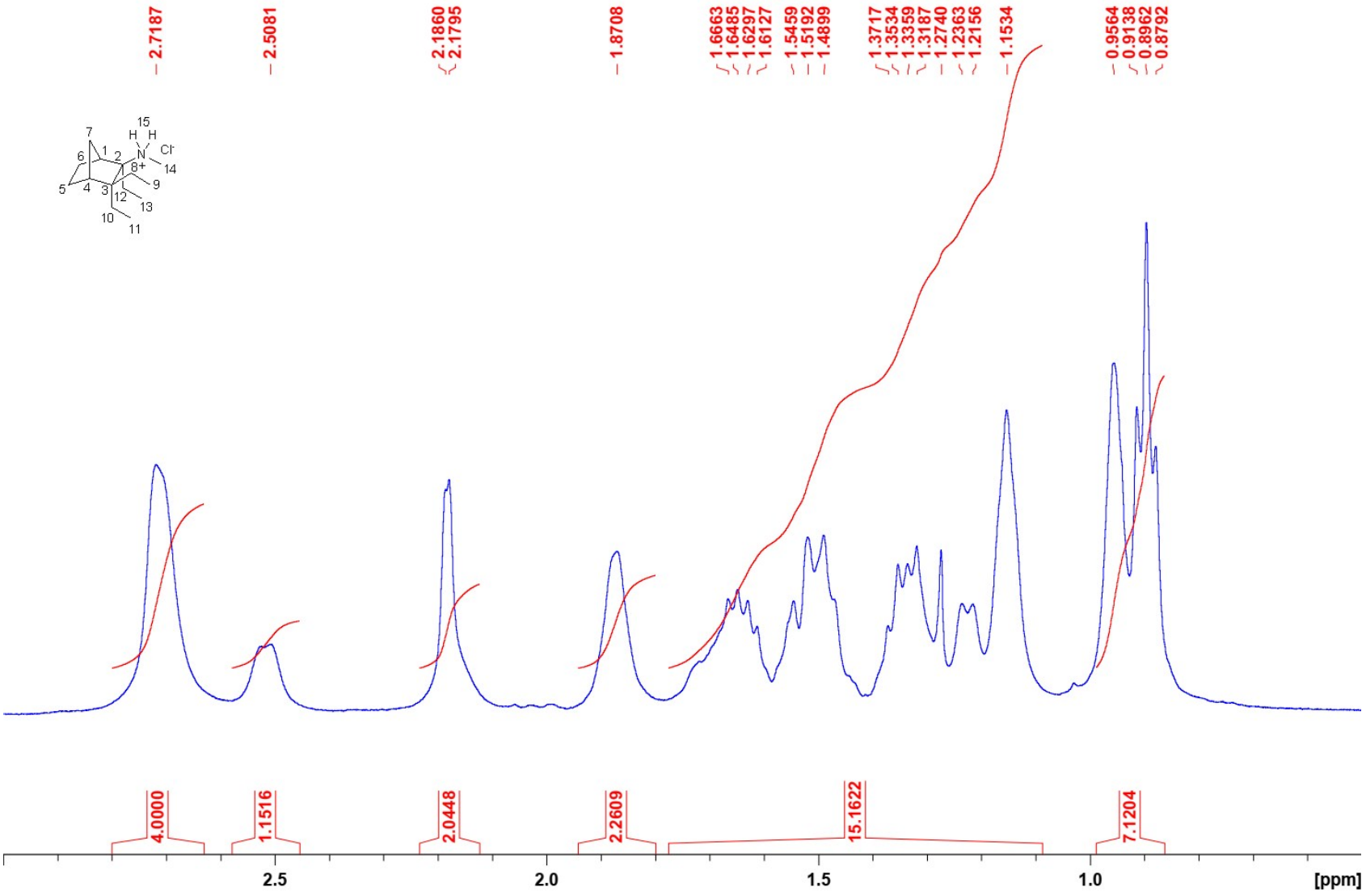
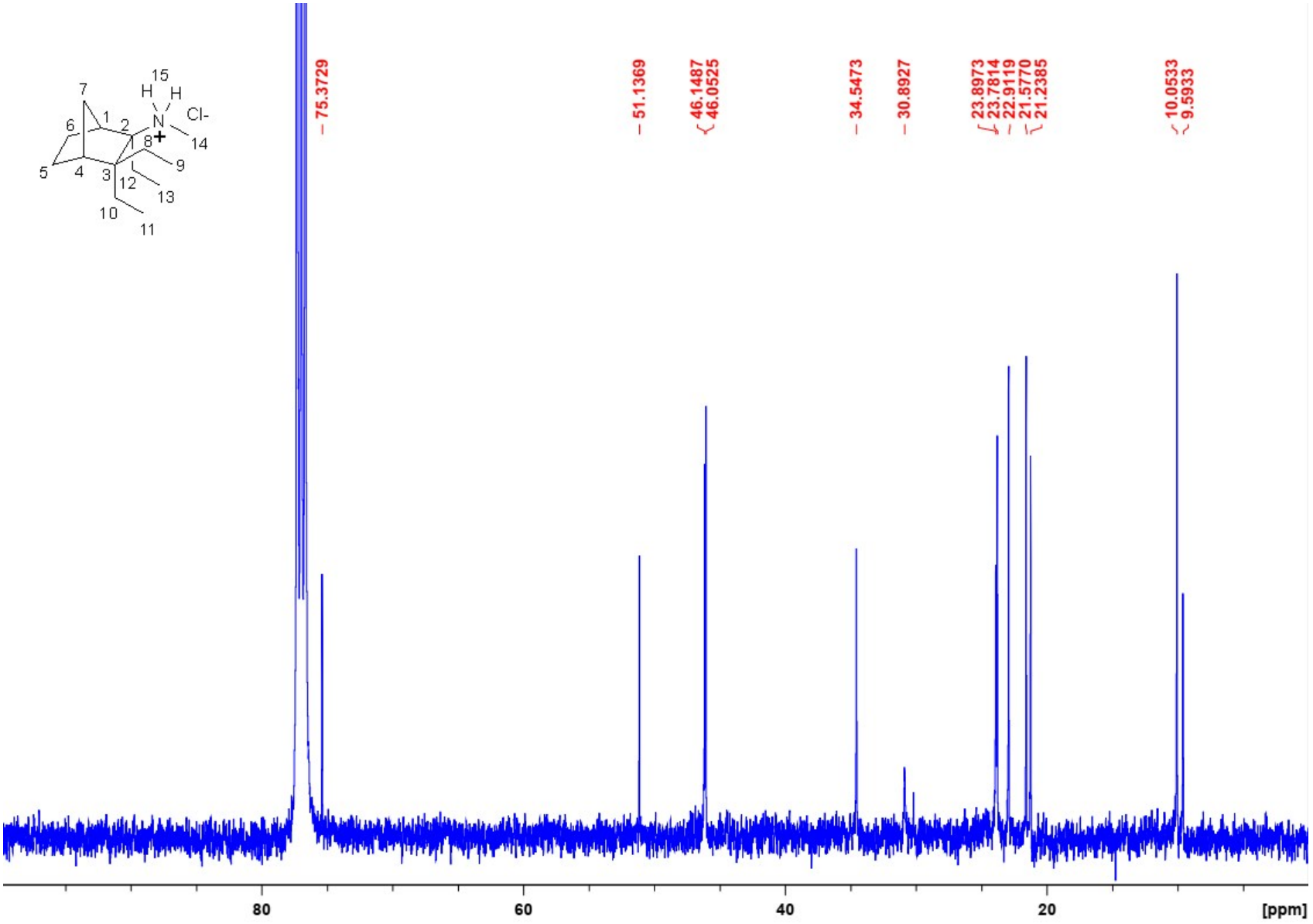
2.6725
2.6595
2.3702
2.1757
2.0213
2.0040
1.9872
1.9697
1.9554
1.9384
1.9215
1.9045
1.8266
1.5963
1.5779
1.5600
1.5421
1.5118
1.5023
1.4818
1.4719
1.4282
1.3551
1.3360
1.3173
1.3046
1.2166
1.1879
0.9691
0.9509
0.9323
0.9141
0.8964
2.8947
1.9383
0.9978
2.0987
10.4102
6.0000
2.5
2.0
1.5
1.0
[ppm]

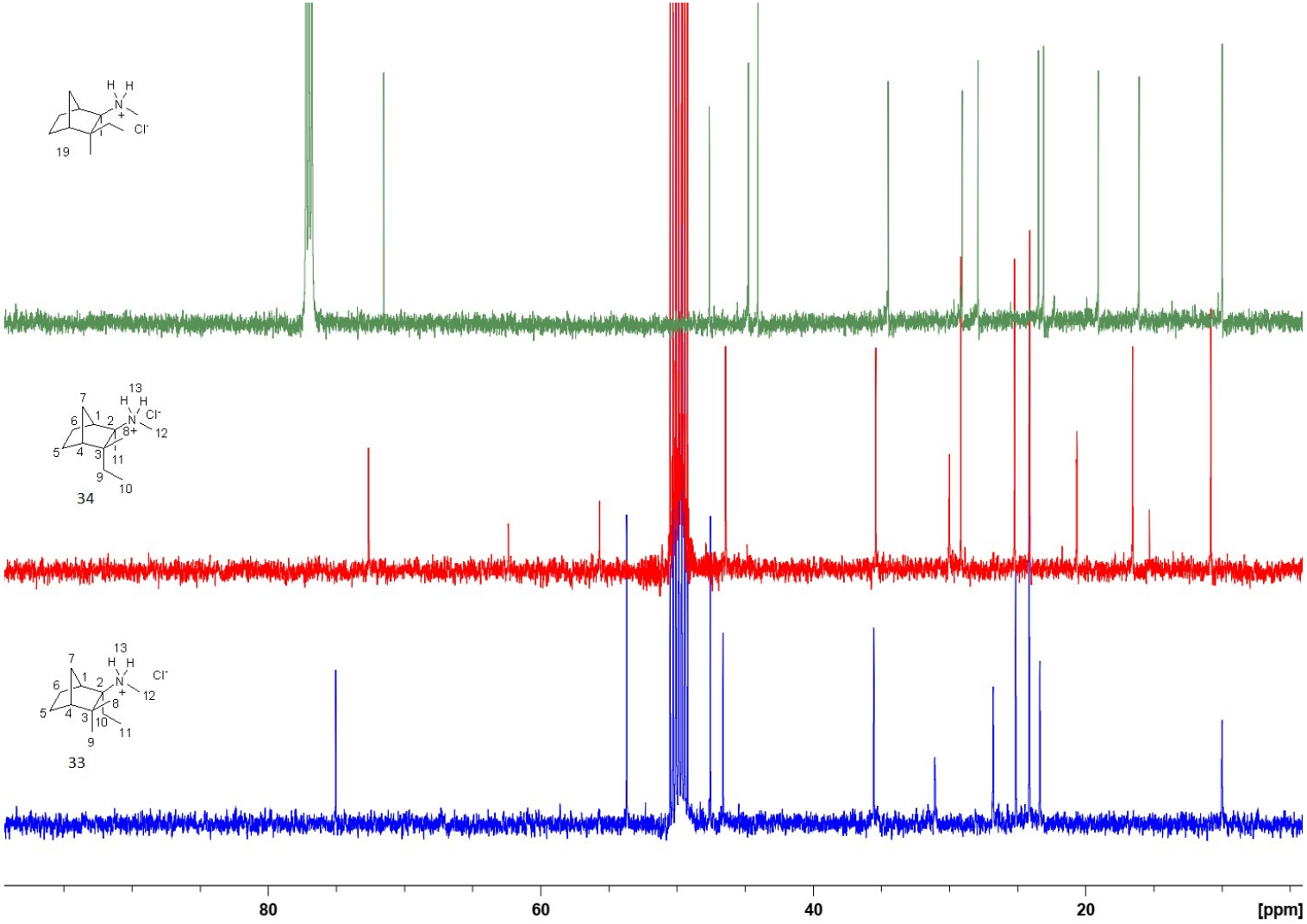

71.2371
50.1357
45.8479
45.6255
34.6292
28.9855
23.9013
23.3900
23.1689
21.9034
16.4913
9.7688
9.7426
80
60
40
20
[ppm]

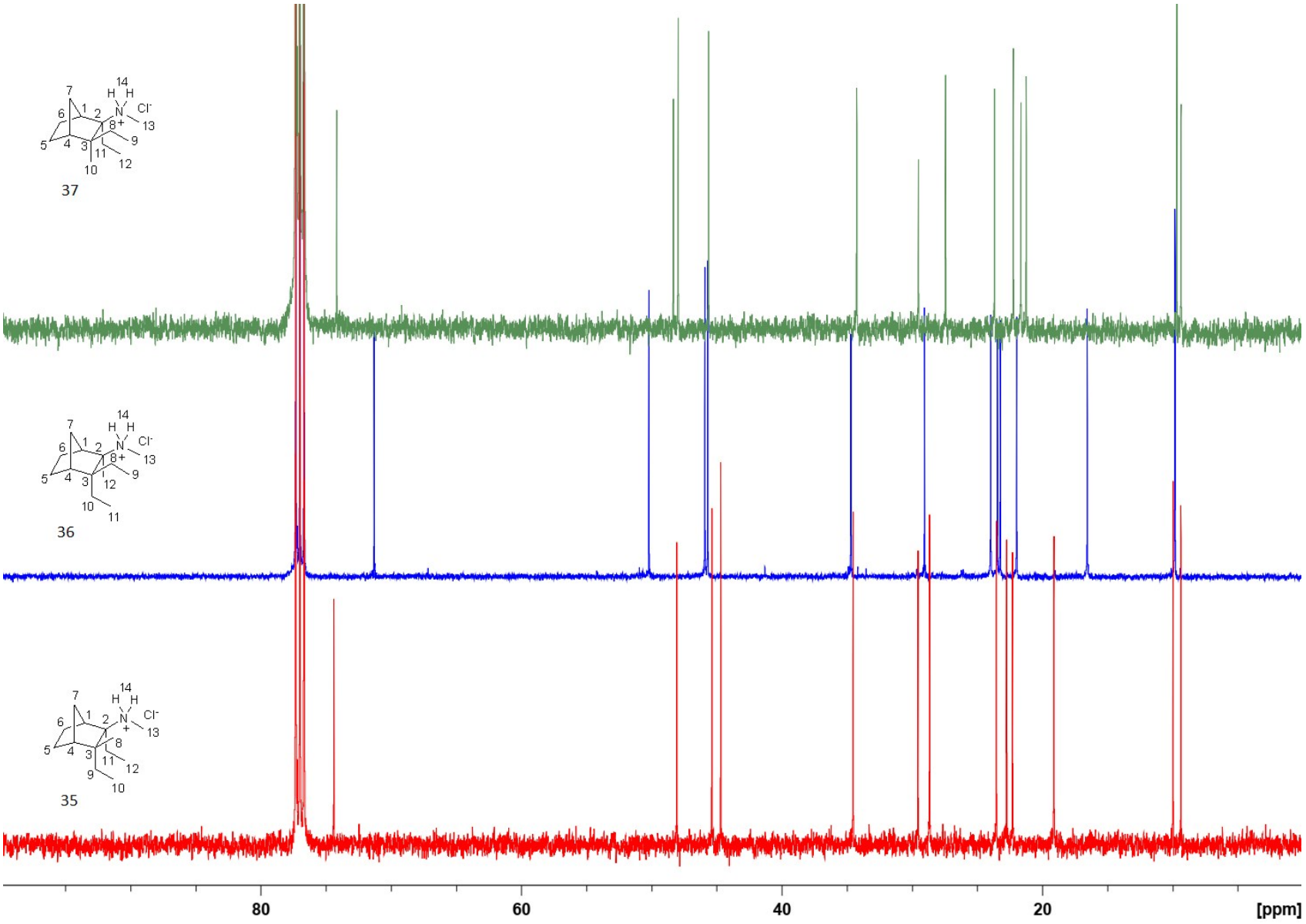

15
H
H
7
1
2
N
Cl-
6
8
14
5
4
3
9
12
13
10
11
0.9914
0.9420
4.0000
1.1516
2.0448
2.2609
15.1622
7.1204
8
6
4
2
[ppm]


2.7187
2.5081
2.1860
2.1795
1.8708
1.6663
1.6485
1.6297
1.6127
1.5459
1.5192
1.4899
1.3717
1.3534
1.3359
1.3187
1.2740
1.2363
1.2156
1.1534
0.9564
0.9138
0.8962
0.8792
4.0000
1.1516
2.0448
2.2609
15.1622
7.1204
2.5
2.0
1.5
1.0
[ppm]


75.3729
51.1369
46.1487
46.0525
34.5473
30.8927
23.8973
23.7814
22.9119
21.5770
21.2385
10.0533
9.5933
80
60
40
20
[ppm]
15
H
H
7
1
2
N
Cl-
6
8
14
5
4
3
9
12
13
10
11

The nature of the formation of azides is such that there is a concern of cross contamination with mixtures of isomeric compounds being tested. To highlight that this is not the case (at least to the limit of 13C detection) stack plots of the appropriate final compounds from the dimethylethyl series (**19**, **33**, **34**) and the diethylmethyl series (**35**, **36**, **37**) are shown below. Compound **19**[25] (unfortunately in a different solvent) is included for the sake of completeness.




37
36
35
80
60
40
20
[ppm]