Supporting Information

Glass engineering of aminotriazine-based materials with sub-ambient T_g and high kinetic stability

Zeinab Kara Ali,[†] Anna Iankovitch,[‡] Mahboubeh Jokar,[‡] Thierry Maris,[†] Olivier Lebel,[‡,*] Christian Pellerin[†,*]

[†] *Département de chimie, Université de Montréal, Montréal, QC, H3C 3J7, Canada*
[‡] *Department of Chemistry and Chemical Engineering, Royal Military College of Canada, Kingston, ON, K7K 7B4, Canada*

[*]Corresponding authors: c.pellerin@umontreal.ca; olivier.lebel@rmc.ca

Synthesis

Compounds $\mathbf{1}_{NHMe}$ and $\mathbf{1}_{NMe2}$ were synthesized following the same procedure as compoLe und $\mathbf{1}_{Et}$ from 2-methylamino-4,6-dichloro-1,3,5-triazine and 2-dimethylamino-4,6-dichloro-1,3,5-triazine, respectively.

Synthesis of 2-methylamino-4,6-bis(N-methylphenylamino)-1,3,5-triazine ($\mathbf{1}_{NHMe}$)

Yield: 52 %; T_g 7 °C; FT-IR (ATR) 3430, 3278, 3169, 3060, 3034, 2937, 1601, 1582, 1537, 1490, 1445, 1381, 1329, 1308, 1286, 1213, 1171, 1126, 1104, 1028, 997, 905, 809, 764, 695 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (m, 8H), 7.17 (m, 2H), 4.90 (br s, 1H), 3.47 (s, 6H), 2.84 (d, J = 4.5 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 165.4, 144.9, 128.2, 126.4, 124.8, 37.2, 27.3 ppm; HRMS (ESI, MH^+) calcd. for $C_{18}H_{21}N_6$ *m/z*: 321.1822, found: 321.1827.

Synthesis of 2-dimethylamino-4,6-bis(N-methylphenylamino)-1,3,5-triazine ($\mathbf{1}_{NMe2}$)

Yield: 78 %; T_g -12 °C; FT-IR (ATR) 3060, 3037, 2927, 2865, 2791, 1601, 1533, 1494, 1440, 1382, 1330, 1310, 1287, 1238, 1177, 1105, 1074, 1051, 1029, 904, 808, 764, 695 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (m, 8H), 7.13 (t, J = 6.8 Hz, 2H), 3.47 (s, 6H), 3.02 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 144.9, 128.0, 126.2, 124.6, 37.1, 35.7 ppm; HRMS (ESI, MH^+) calcd. for $C_{19}H_{23}N_6$ *m/z*: 335.1979, found: 335.1985.

Synthesis of 2-dimethylamino-4-(N-methylcyclohexylamino)-6-(N-methylphenylamino)-1,3,5-triazine ($\mathbf{2}_{NMe2}$)

Compound $\mathbf{2}_{NMe2}$ was synthesized following the same procedure as compound $\mathbf{2}_{NHMe}$ with aqueous dimethylamine (40 wt%). Yield: 84 %; T_g -5 °C, T_m 97 °C; FT-IR (ATR) 3059, 3028, 2925, 2853, 2793, 1600, 1541, 1527, 1492, 1442, 1380, 1349, 1331, 1259, 1245, 1221, 1174, 1128, 1103, 1049, 1030, 1003, 935, 895, 867, 839, 808, 785, 763, 736, 696, 663 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.8 Hz, 2H), 7.35 (t, J = 7.4 Hz, 2H), 7.16 (t, J = 7.1 Hz, 1H), 4.43 (br d, 1H), 3.56 (s, 3H), 3.11 (s, 6H), 2.99 (s, 3H), 1.83 (m, 2H), 1.71 (m, 3H), 1.44 (m, 4H), 1.15 (m, 1H) ppm; ^{13}C NMR (100 MHz, CDClB) δ 165.7, 165.3, 165.0, 145.4, 127.8, 126.2, 124.1, 53.4, 36.8, 35.6, 29.9, 27.7, 26.0, 25.7 ppm; HRMS (ESI, MH^+) calcd. for $C_{19}H_{29}N_6$ *m/z*: 327.2292, found: 327.2288.

Compounds **3_{OMe}**, **3_{NHMe}** and **3_{NMe2}** were synthesized following the same procedure as compound **3_{Et}** from 2-methoxy-4,6-dichloro-1,3,5-triazine, 2-methylamino-4,6-dichloro-1,3,5-triazine and 2-dimethylamino-4,6-dichloro-1,3,5-triazine, respectively.

Synthesis of 2-methoxy-4,6-bis(N-methylcyclohexylamino)-1,3,5-triazine (3_{OMe})

Yield: 66 %; T_g 4 °C, T_m 67 °C; FT-IR (ATR) 2927, 2853, 2803, 1569, 1521, 1491, 1453, 1401, 1378, 1358, 1329, 1258, 1221, 1199, 1167, 1134, 1085, 1049, 998, 894, 870, 811, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.56 (br d, 2H), 3.86 (s, 3H), 2.97 (s, 6H), 1.80 (m, 4H), 1.69 (m, 6H), 1.42 (m, 8H), 1.11 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 165.9, 54.5, 53.3, 30.0, 28.2, 25.7 ppm; HRMS (ESI, MH^+) calcd. for $C_{18}H_{32}N_5O$ *m/z*: 334.2601, found: 334.2604.

Synthesis of 2-methylamino-4,6-bis(N-methylcyclohexylamino)-1,3,5-triazine (3_{NHMe})

Yield: 42 %; T_g 32 °C, T_m 94 °C; FT-IR (ATR) 3465, 3279, 3169, 2928, 2853, 2793, 1560, 1528, 1501, 1450, 1399, 1384, 1348, 1327, 1253, 1202, 1154, 1112, 1047, 998, 894, 871, 838, 810, 755 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.69 (br s, 1H), 4.53 (br s, 2H), 2.96 (s, 6H), 2.91 (d, J = 4.2 Hz, 3H) 1.81 (m, 4H), 1.69 (m, 6H), 1.41 (m, 8H), 1.12 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 165.1, 53.4, 30.0, 27.8, 27.4, 26.1, 25.9 ppm; HRMS (ESI, MH^+) calcd. for $C_{18}H_{33}N_6$ *m/z*: 333.2761, found: 333.2768.

Synthesis of 2-dimethylamino-4,6-bis(N-methylcyclohexylamino)-1,3,5-triazine (3_{NMe2})

Yield: 55 %; T_g -9 °C, T_m 54 °C; FT-IR (ATR) 2926, 2853, 2791, 1568, 1534, 1491, 1449, 1395, 1348, 1330, 1310, 1260, 1246, 1209, 1172, 1123, 1047, 1006, 982, 894, 867, 842, 808, 739, 675 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.54 (br s, 2H), 3.09 (s, 6H), 2.97 (s, 6H), 1.81 (m, 4H), 1.70 (m, 6H), 1.42 (m, 8H), 1.13 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.2, 53.5, 36.3, 35.7, 30.0, 27.8, 26.2, 25.9 ppm; HRMS (ESI, MH^+) calcd. for $C_{19}H_{35}N_6$ *m/z*: 347.2918, found: 347.2923.

Table S1. Crystallographic parameters for single crystals of compounds 3_{Et}, 3_{OMe}, 2_{NMe2}, and 3_{NMe2}, crystallized by slow evaporation from methanol or from chloroform.

Compound	3_{Et}	3_{OMe}	2_{NMe2}	3_{NMe2}
Molecular Formula	$C_{19}H_{33}N_5$	$C_{18}H_{31}N_5O$	$C_{19}H_{28}N_6$	$C_{19}H_{34}N_6$
M (g/mol)	331.50	333.48	340.47	346.52
Space Group	*Pbca*	*Pbca*	$Pca2_1$	$P2_1/m$
a (Å)	15.0700(3)	14.7113(3)	14.6085(5)	5.7373(3)
b (Å)	10.3551(2)	10.5414(2)	12.2750(4)	30.1441(16)
c (Å)	24.4042(5)	24.3585(6)	10.4746(4)	6.1322(3)
β (°)	90	90	90	109.223(3)
V (Å^3)	3808.31(13)	3777.46(14)	1878.30(11)	1001.41(9)
Z	8	8	4	2
F(000)	1456	1456	736	380
ρ_{calc} (g cm^{-3})	1.156	1.173	1.204	1.149
T (K)	150	150	150	150
Radiation	GaKα	GaKα	GaKα	GaKα
λ (Å)	1.34139	1.34139	1.34139	1.34139
μ (mm^{-1})	0.347	0.379	0.375	0.352
Measured Refl.	34870	30234	15250	12348
Ind. Refl.	4386	4341	1836	1861
R_{int}	0.0379	0.0273	0.0978	0.0752
R_σ	0.0227	0.0176	0.0316	0.0407
Obs. Refl.	3894	4124	1570	1244
R_1 (I > 2σ)	0.0451	0.0470	0.0795	0.0768
wR_2 (I > 2σ)	0.1125	0.1181	0.1938	0.2032
R_1 (all data)	0.0505	0.0484	0.0915	0.1088
wR_2 (all data)	0.1173	0.1199	0.2022	0.2351
GOF	1.065	1.095	1.175	1.062
Packing Index (%)	67.6	66.5	67.4	66.2

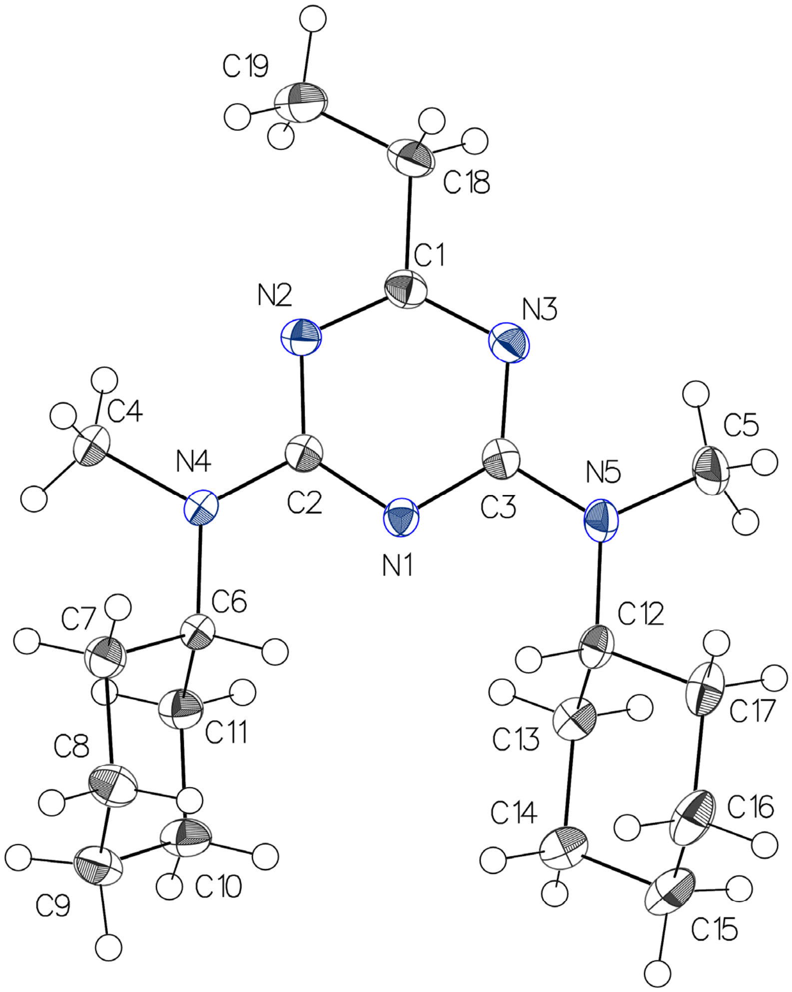


Figure S1. Thermal atomic displacement ellipsoid plot of the structure of **3_{Et}**. The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level, and hydrogen atoms are represented by a sphere of arbitrary size.

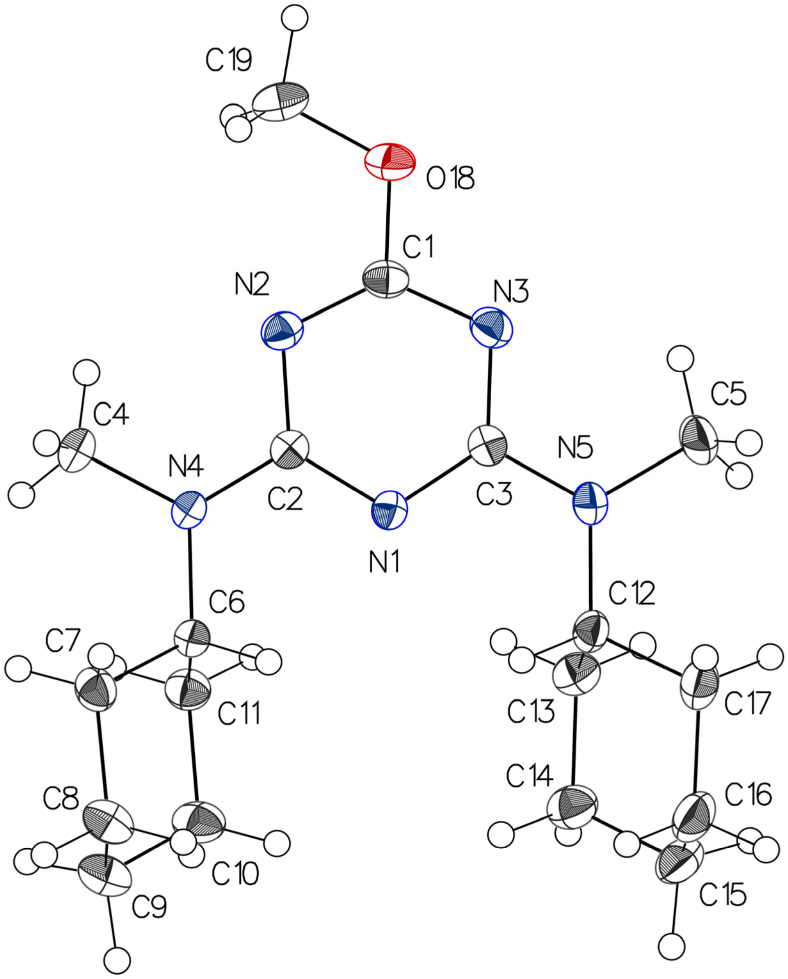


Figure S2. Thermal atomic displacement ellipsoid plot of the structure of **3**$_{\mathbf{OMe}}$. The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level, and hydrogen atoms are represented by a sphere of arbitrary size.

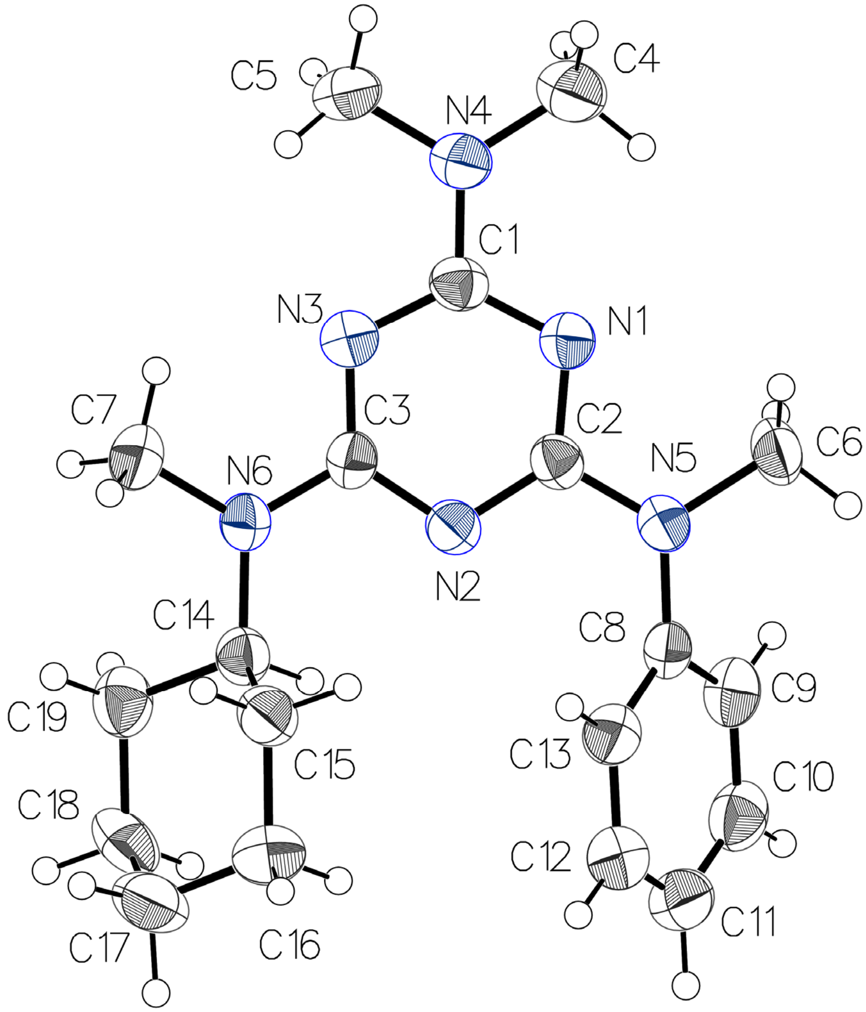


Figure S3. Thermal atomic displacement ellipsoid plot of the structure of $\mathbf{2_{NMe2}}$. The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level, and hydrogen atoms are represented by a sphere of arbitrary size.

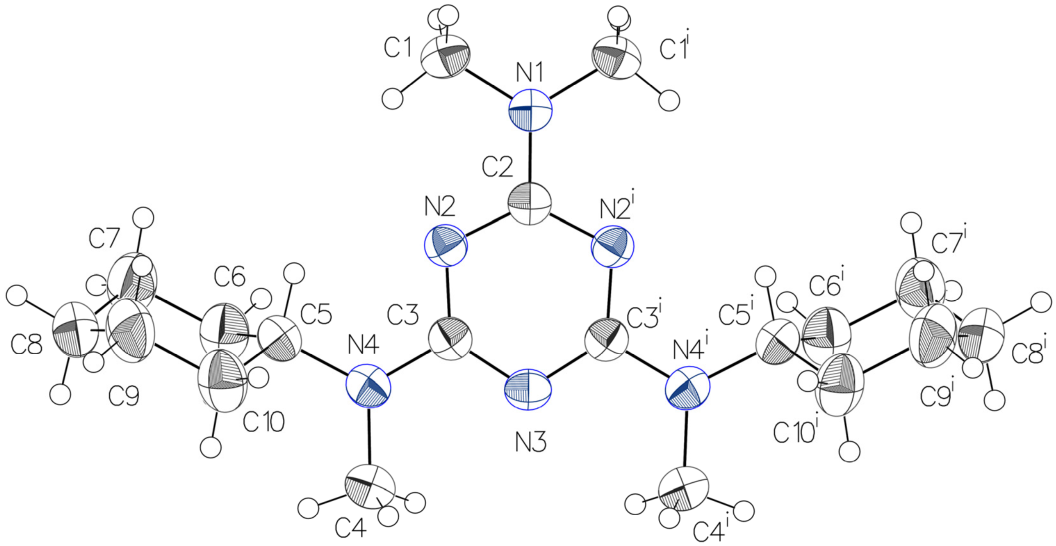
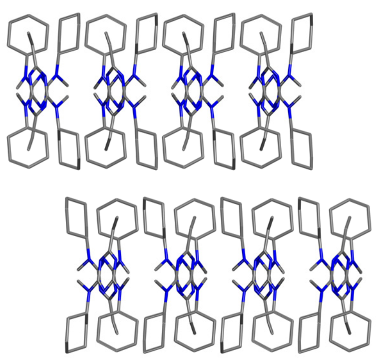
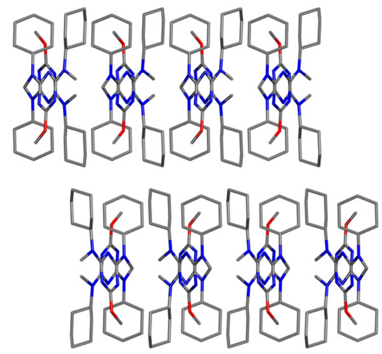
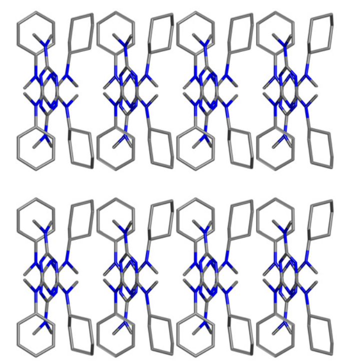


Figure S4. Thermal atomic displacement ellipsoid plot of the structure of **3_{NMe2}**. The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level, and hydrogen atoms are represented by a sphere of arbitrary size.



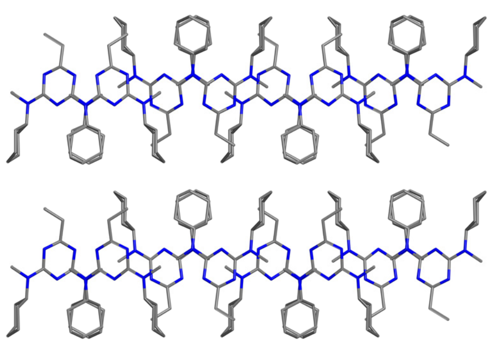




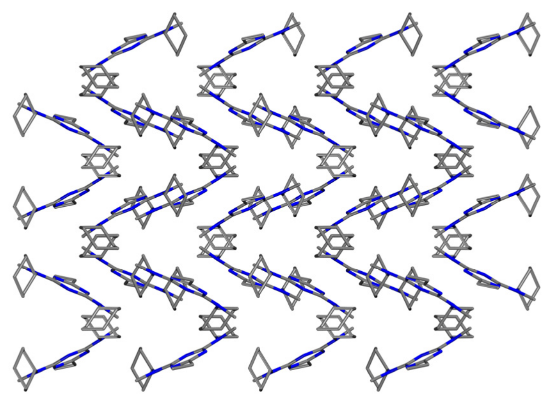
3_{Et} along the *a*-axis

3_{OMe} along the *a*-axis

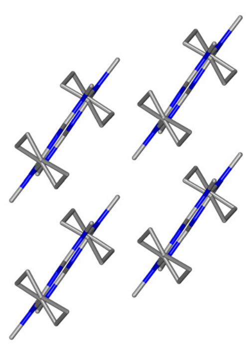
2_{NMe2} along the *a*-axis



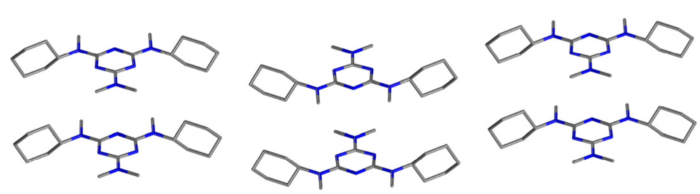
3_{Et} along the *b*-axis



3_{Et} along the *c*-axis



3_{NMe2} along the *b*-axis



3_{NMe2} along the *c*-axis

Figure S5. Different view of the crystal structures of **3_{Et}**, **3_{OMe}**, **2_{NMe2}** and **3_{NMe2}**

Table S2. Relative energy (kJ/mol) for the three stable conformers of $\mathbf{1}_{HG}$ and $\mathbf{3}_{HG}$. Top and bottom refer to the conformations of the ancillary groups along or opposite to the headgroup, respectively.

Compound	Conformation	HG = Et	HG = OMe	HG = NMe_2	HG = NHMe
$\mathbf{1}_{HG}$	bottom-bottom	0	0.9	1.7	0.4
	top-bottom	0.4	0	0.6	0
	top-top	1.5	1.8	0	0.2
$\mathbf{3}_{HG}$	bottom-bottom	3.1	2.4	0.1	1.3
	top-bottom	1.2	1.1	0	0.2
	top-top	0	0	0.8	0

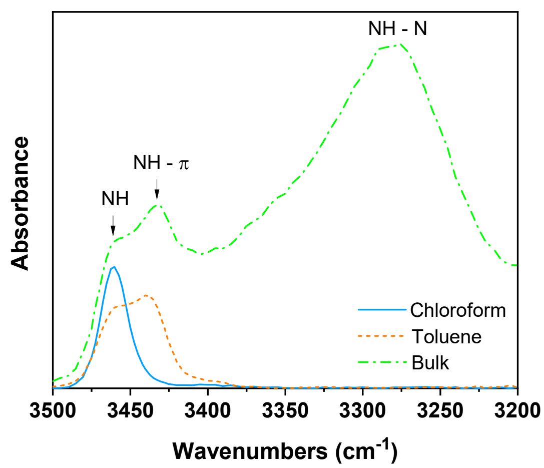


Figure S6. IR spectra of $\mathbf{2}_{NHMe}$ in the bulk state, and in 1 mM solutions in toluene and chloroform. The bands due to NH groups engaged in hydrogen bonding (NH – N), NH – π interactions, and weak van der Waals interactions (NH) are indicated.

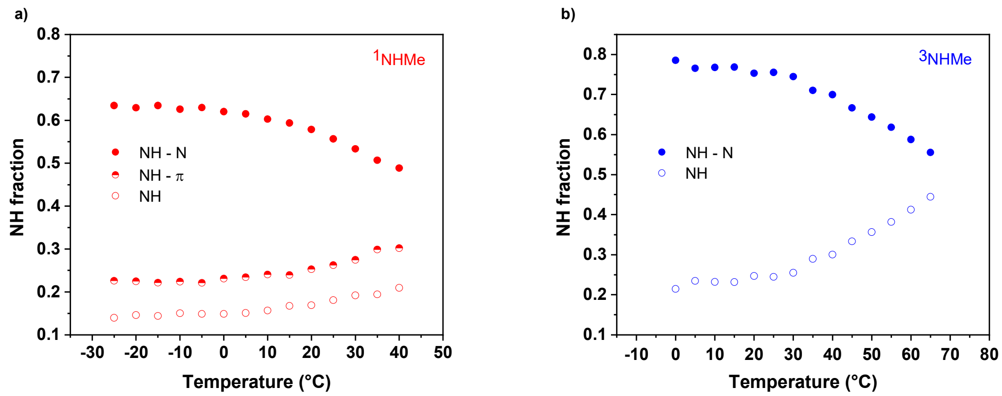


Figure S7. Fractions of NH groups engaged in hydrogen bonding (NH – N), NH – π interactions, and weak van der Waals interactions (NH) as a function of temperature for compounds a) $\mathbf{1}_{\mathbf{NHMe}}$ and b) $\mathbf{3}_{\mathbf{NHMe}}$, as determined by IR spectroscopy and chemometrics analysis.

Table S3. Average fraction of bonded NH (± standard deviation for three measurements) at different temperatures relative to T_g for the compounds studied by variable-temperature IR spectroscopy.

Compound	Temperature (°C)	NH – N	NH – π	NH
$\mathbf{1}_{\mathbf{NHMe}}$	T_g + 33	0.49 ± 0.01	0.30 ± 0.01	0.21 ± 0.02
	T_g - 2	0.61 ± 0.04	0.23 ± 0.01	0.15 ± 0.03
	T_g - 32	0.63 ± 0.04	0.23 ± 0.02	0.14 ± 0.03
$\mathbf{2}_{\mathbf{NHMe}}$	T_g + 33	0.49 ± 0.03	0.29 ± 0.07	0.23 ± 0.09
	T_g - 2	0.66 ± 0.02	0.20 ± 0.06	0.14 ± 0.04
	T_g - 32	0.70 ± 0.03	0.18 ± 0.06	0.11 ± 0.04
$\mathbf{3}_{\mathbf{NHMe}}$	T_g + 33	0.56 ± 0.04	–	0.44 ± 0.04
	T_g - 2	0.74 ± 0.04	–	0.26 0.04
	T_g - 32	0.79 ± 0.03	–	0.21 ± 0.03

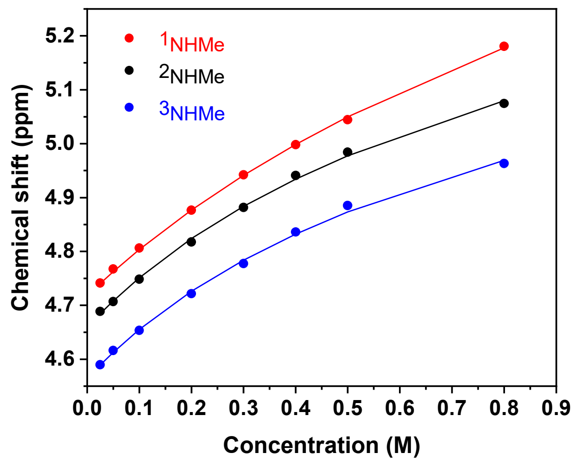
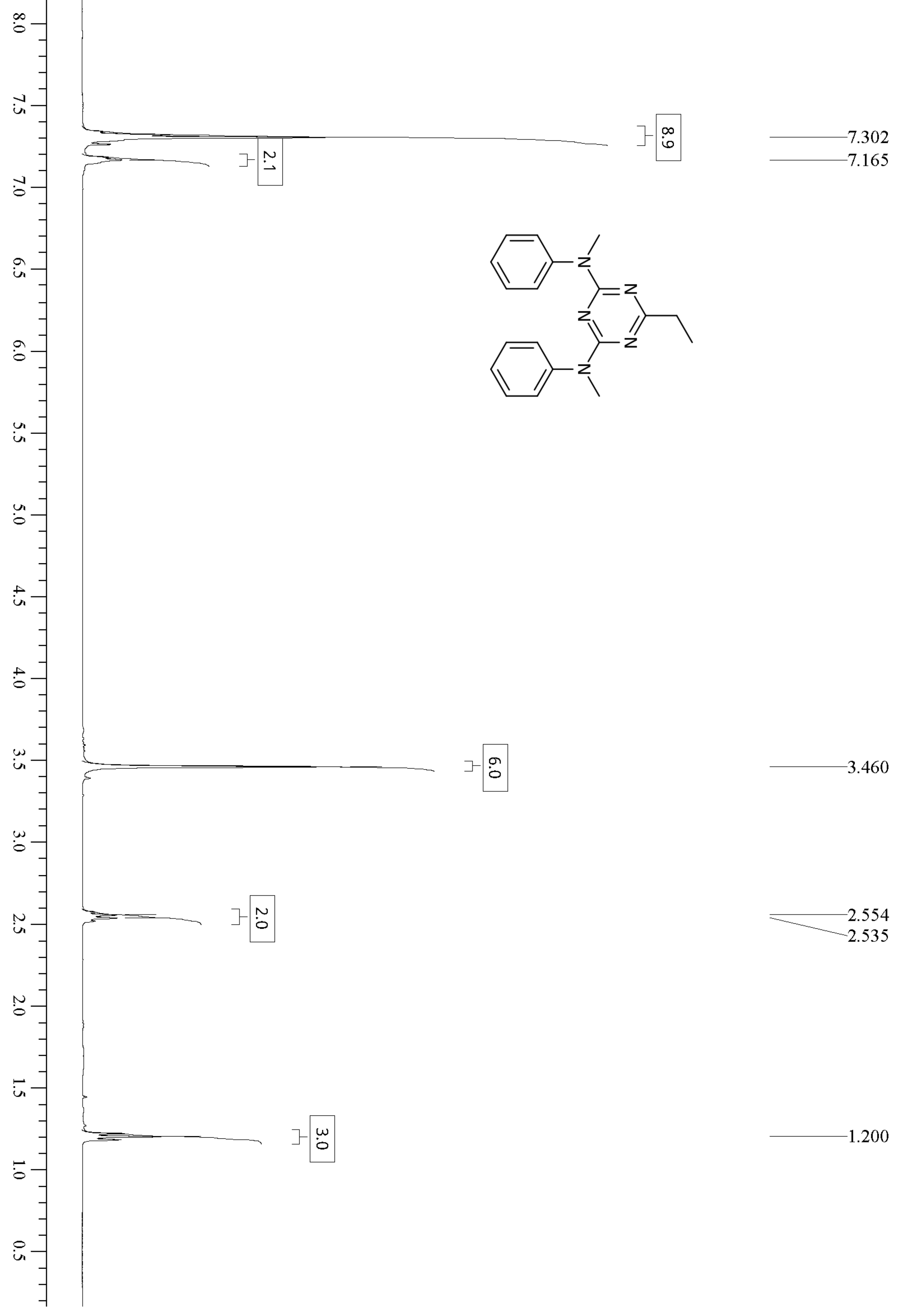


Figure S8. Evolution of NH peak chemical shift with concentration in $CDCl_3$ for $\mathbf{1}_{NHMe}$, $\mathbf{2}_{NHMe}$ and $\mathbf{3}_{NHMe}$, fitted to a curve using a monomer–dimer model (lines).[1]

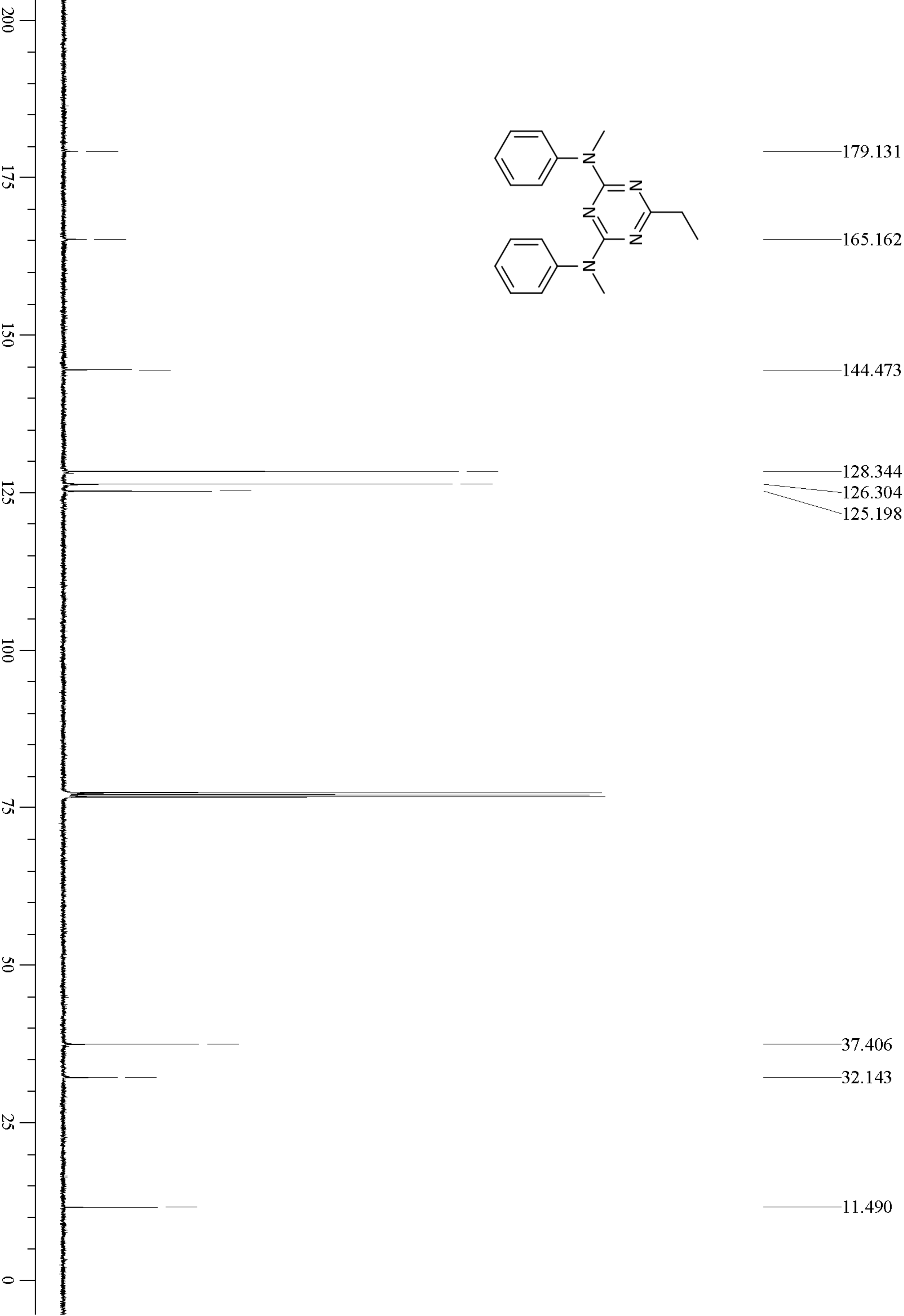
Reference

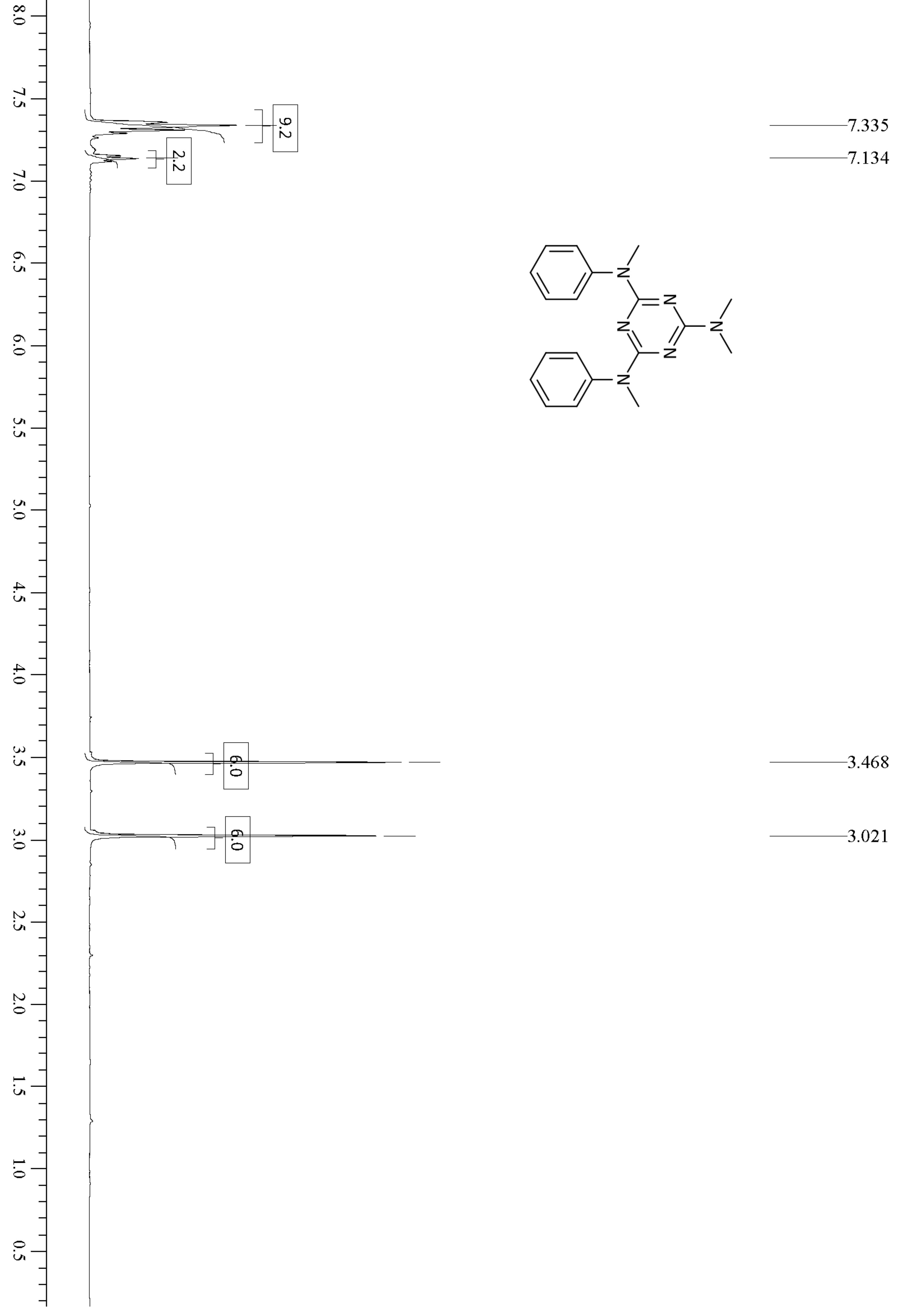
1. K.M. Psutka and K.E. Maly, *RSC Adv.*, 2016, **6**, 78784-78790.

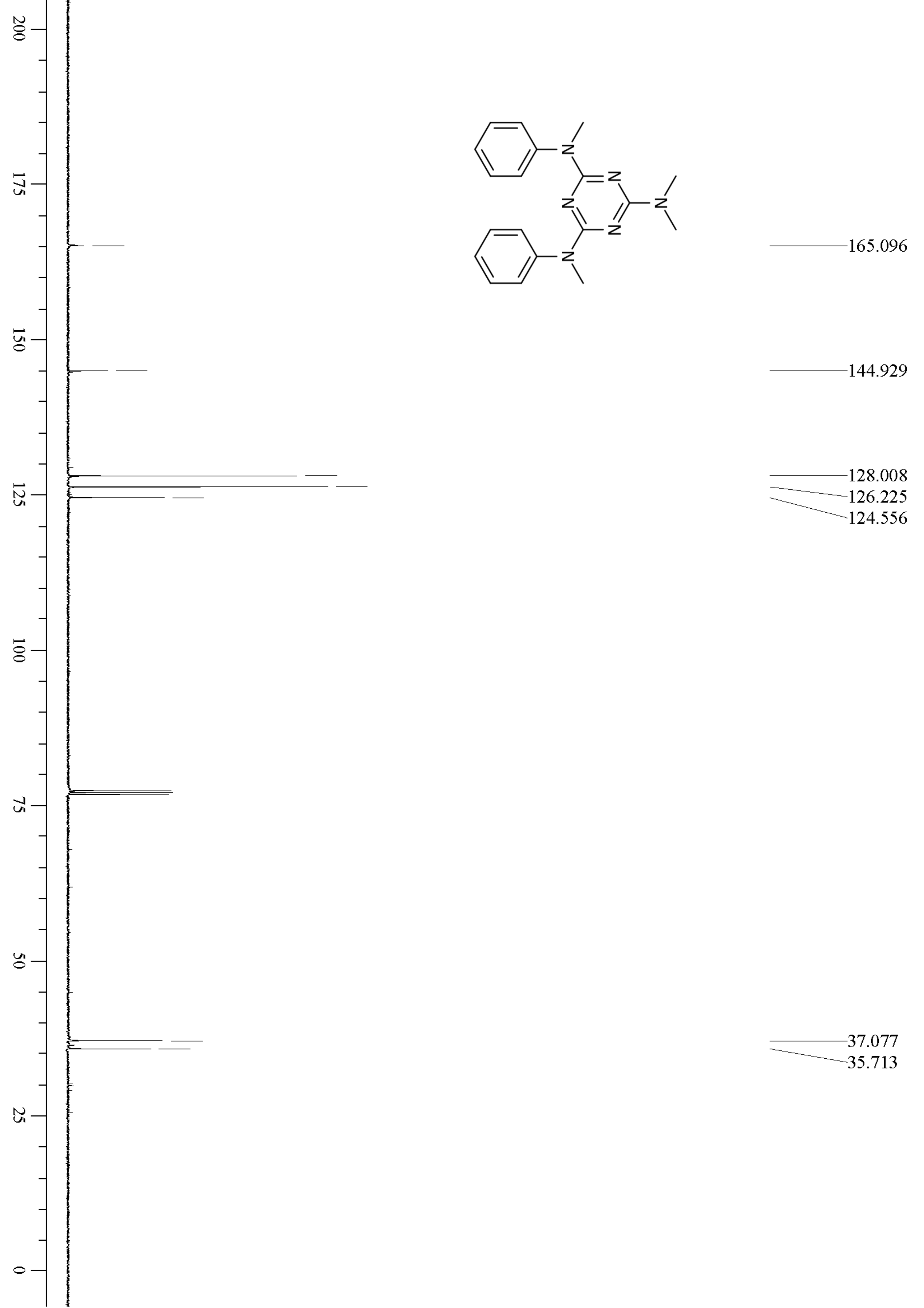
NMR Spectra of Compounds 1-5

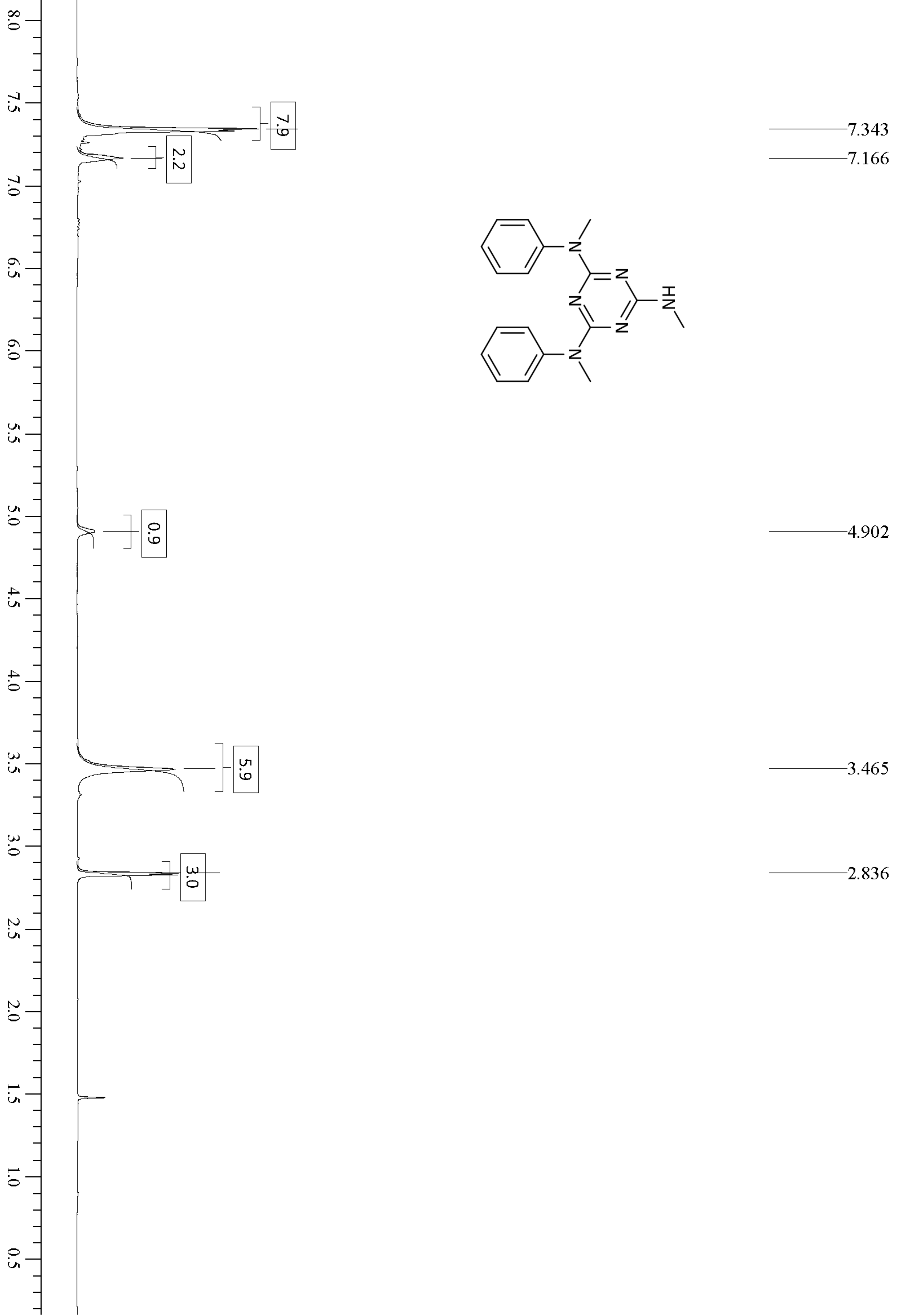


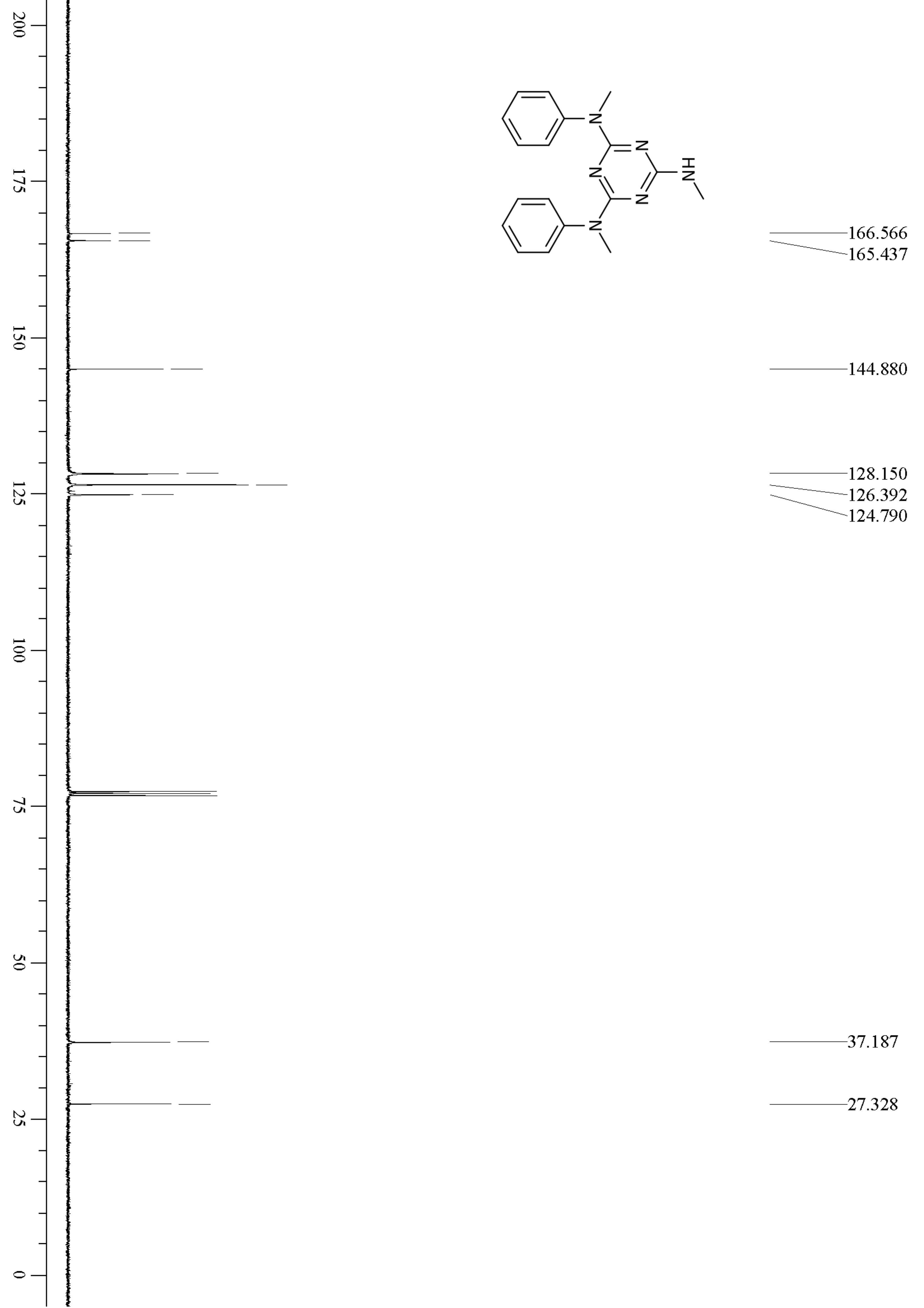
7.302
7.165
3.460
2.554
2.535
1.200
8.9
2.1
6.0
2.0
3.0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


179.131
165.162
144.473
128.344
126.304
125.198
37.406
32.143
11.490
200
175
150
125
100
75
50
25
0

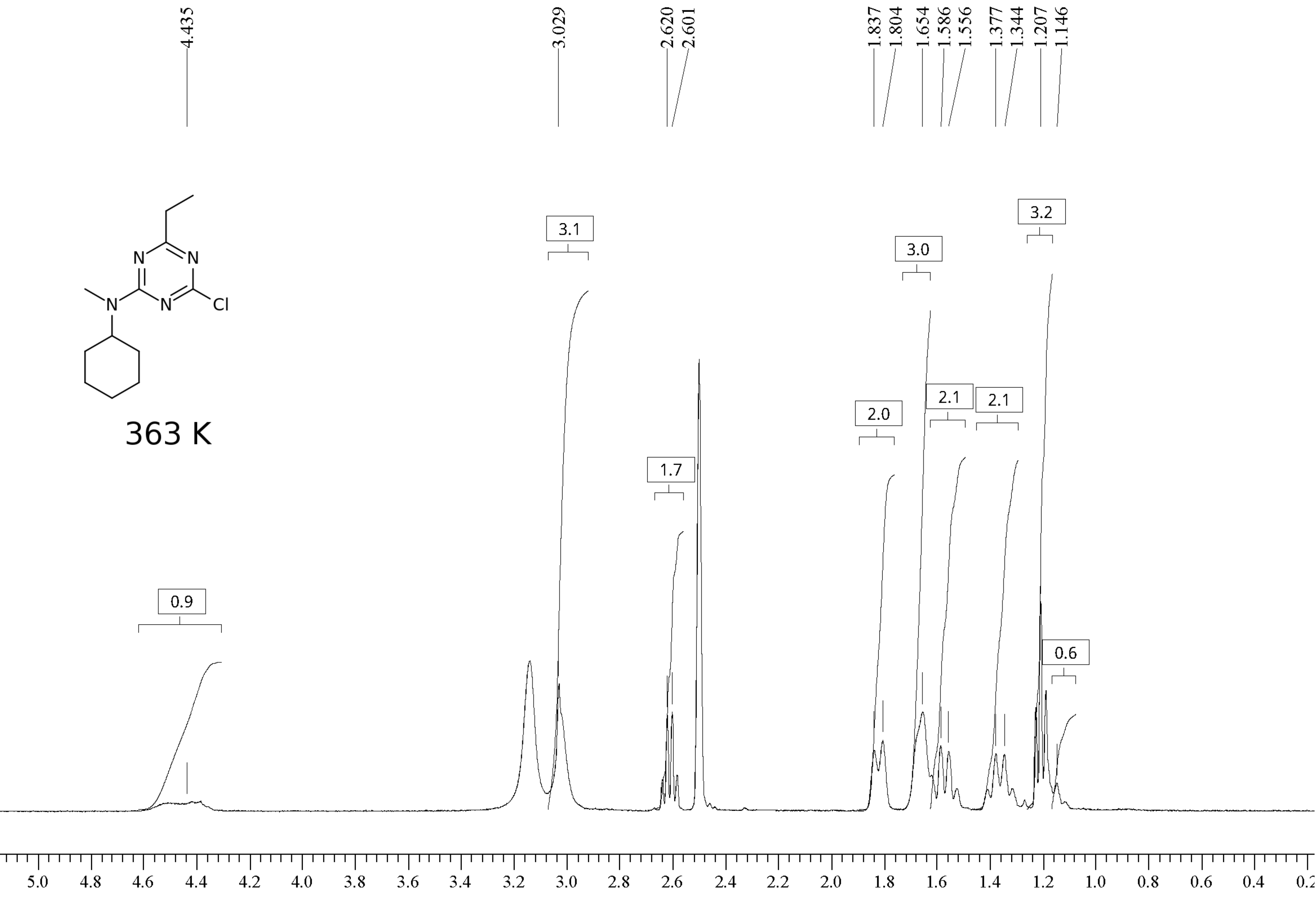

7.335
7.134
3.468
3.021
9.2
2.2
6.0
6.0


165.096
144.929
128.008
126.225
124.556
37.077
35.713
200
175
150
125
100
75
50
25
0

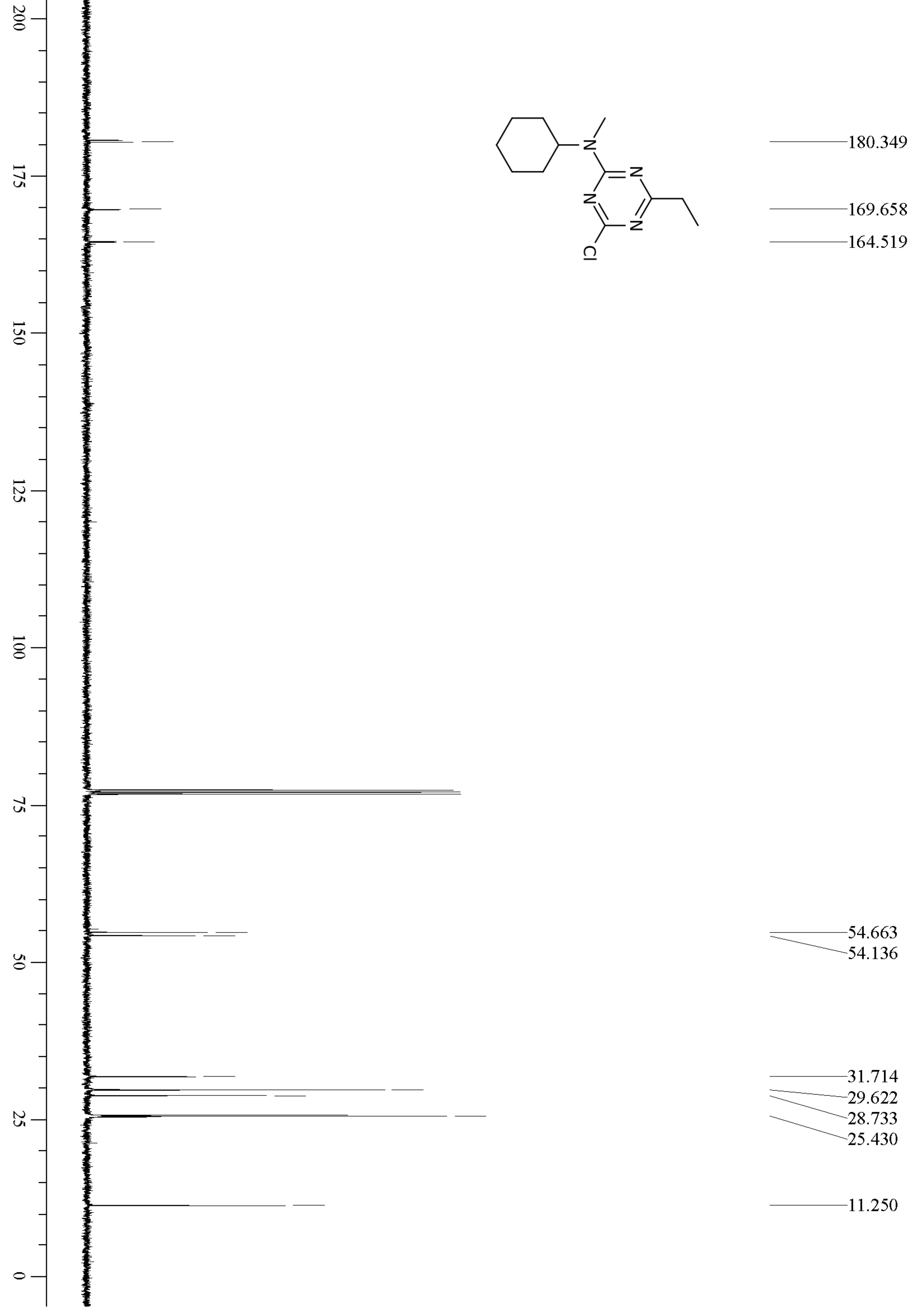

7.343
7.166
4.902
3.465
2.836
7.9
2.2
0.9
5.9
3.0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
N
HN



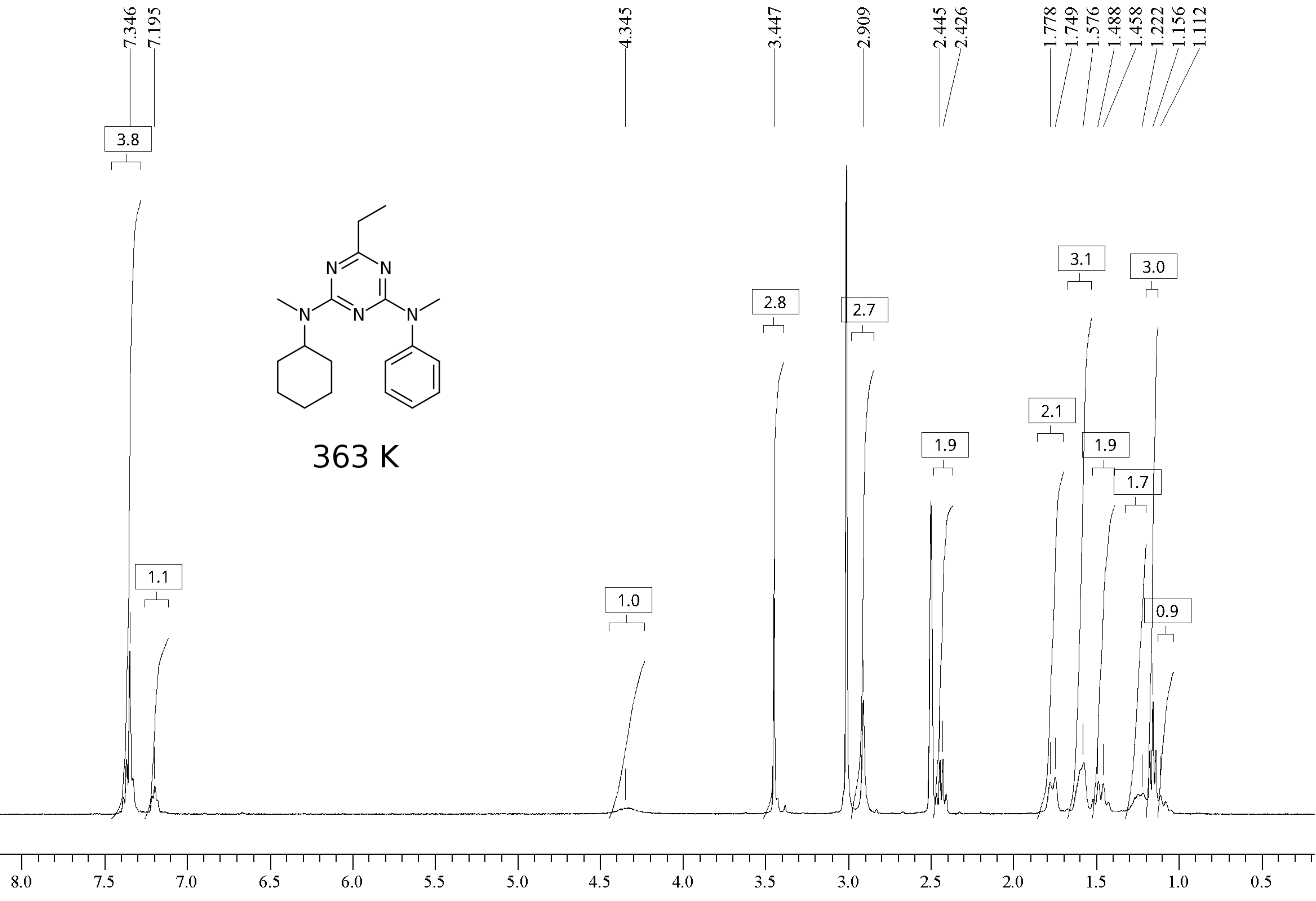
166.566
165.437
144.880
128.150
126.392
124.790
37.187
27.328
200
175
150
125
100
75
50
25
0
N
HN



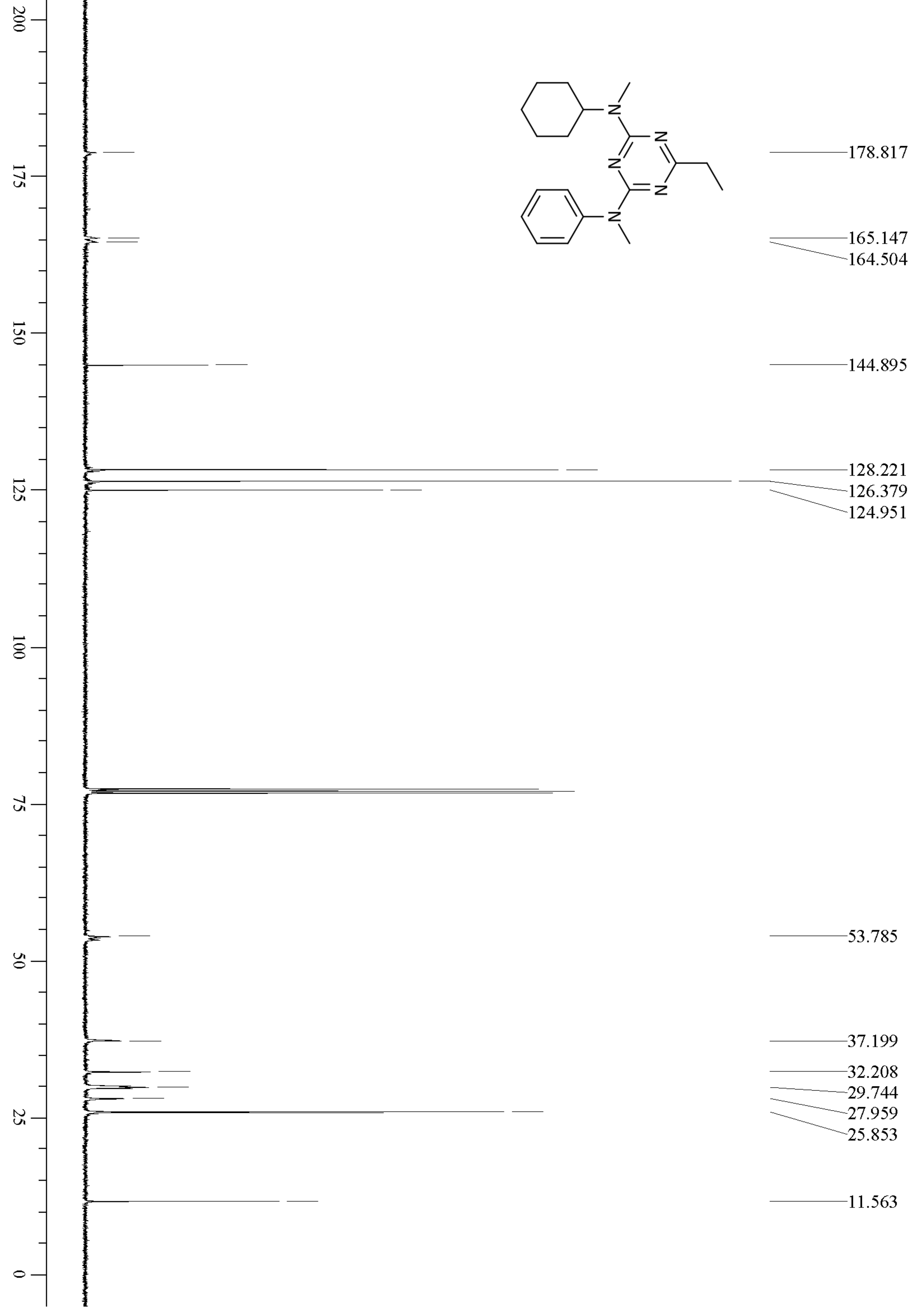
4.435
3.029
2.620
2.601
1.837
1.804
1.654
1.586
1.556
1.377
1.344
1.207
1.146
N
N
N
N
Cl
363 K
0.9
3.1
1.7
2.0
3.0
2.1
2.1
3.2
0.6
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2

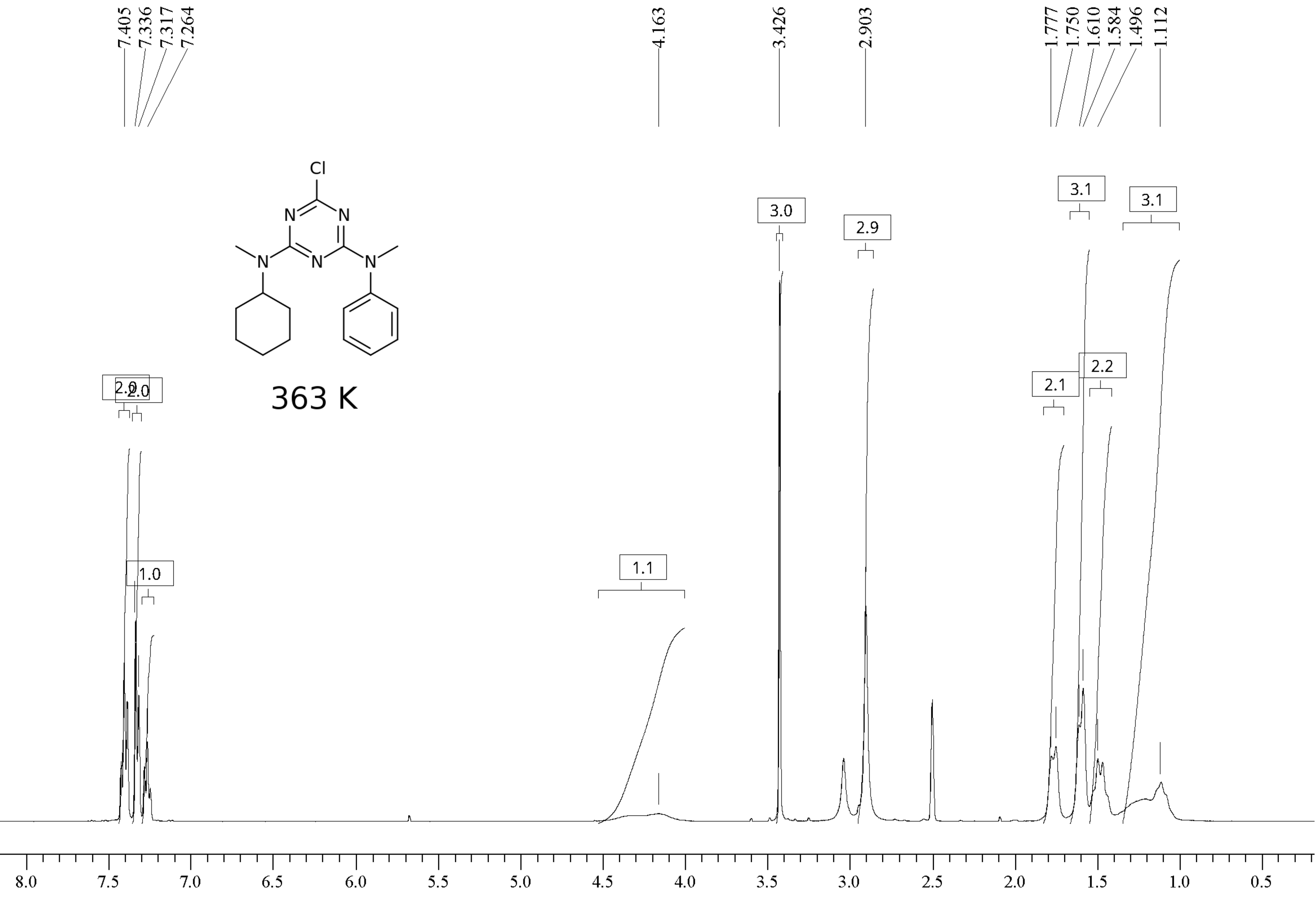


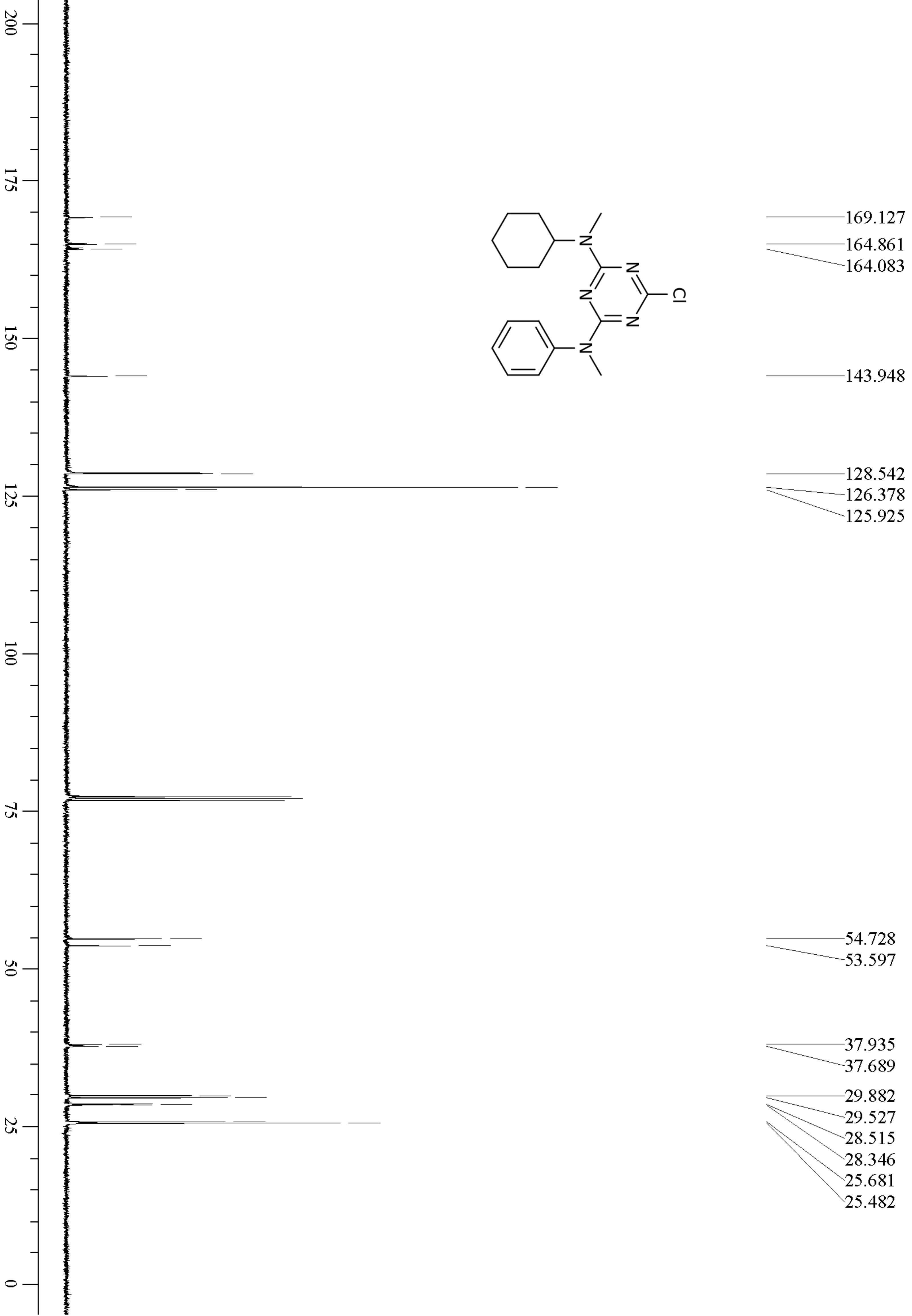
N
N
N
N
Cl
180.349
169.658
164.519
54.663
54.136
31.714
29.622
28.733
25.430
11.250
200
175
150
125
100
75
50
25
0

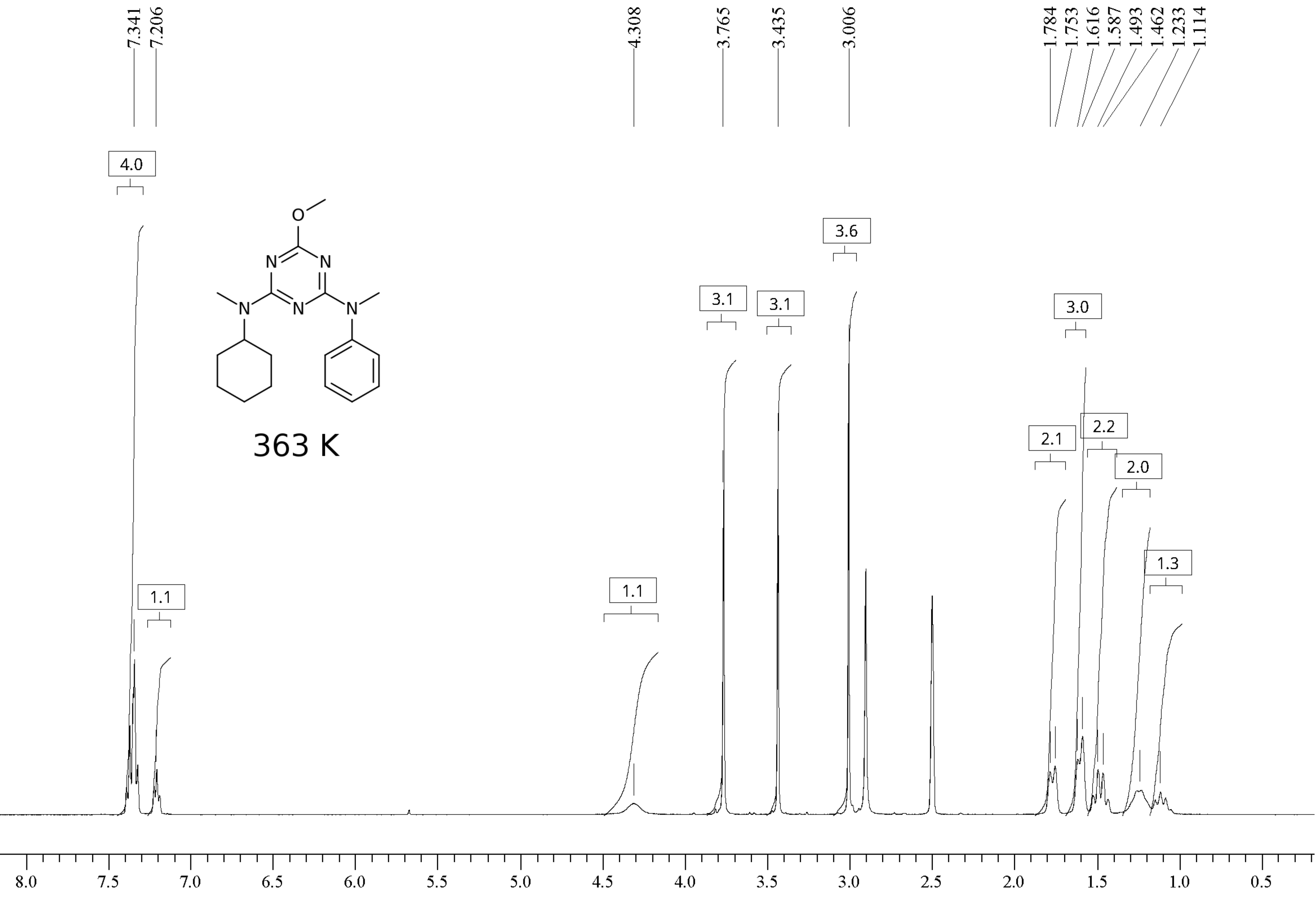


7.346
7.195
4.345
3.447
2.909
2.445
2.426
1.778
1.749
1.576
1.488
1.458
1.222
1.156
1.112
3.8
1.1
1.0
2.8
2.7
1.9
2.1
3.1
1.9
1.7
3.0
0.9
N
N
N
N
N
363 K
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

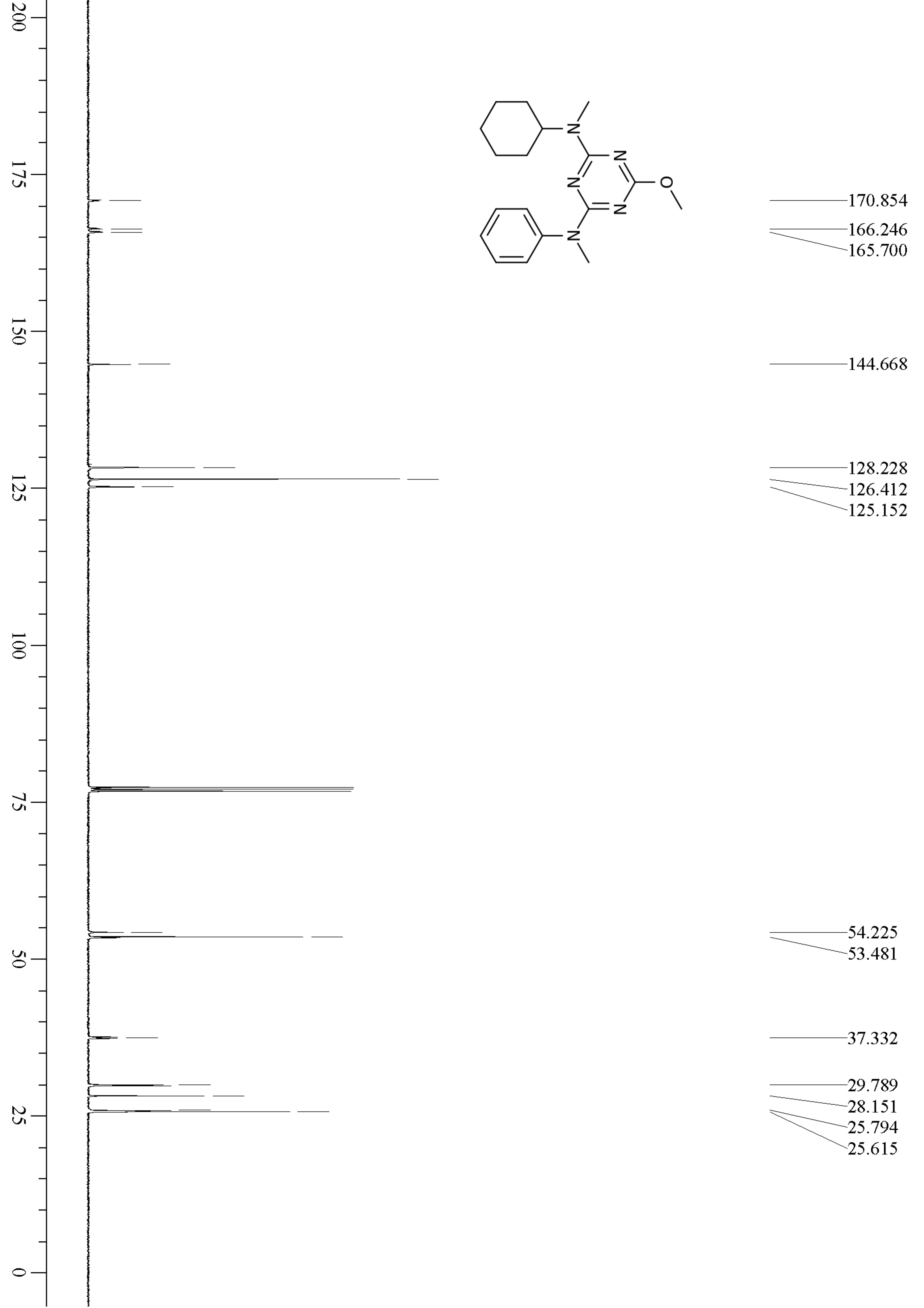

178.817
165.147
164.504
144.895
128.221
126.379
124.951
53.785
37.199
32.208
29.744
27.959
25.853
11.563
200
175
150
125
100
75
50
25
0
N
N
N
N
N


7.405
7.336
7.317
7.264
4.163
3.426
2.903
1.777
1.750
1.610
1.584
1.496
1.112
Cl
N
363 K
2.0
2.0
1.0
1.1
3.0
2.9
2.1
3.1
2.2
3.1
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

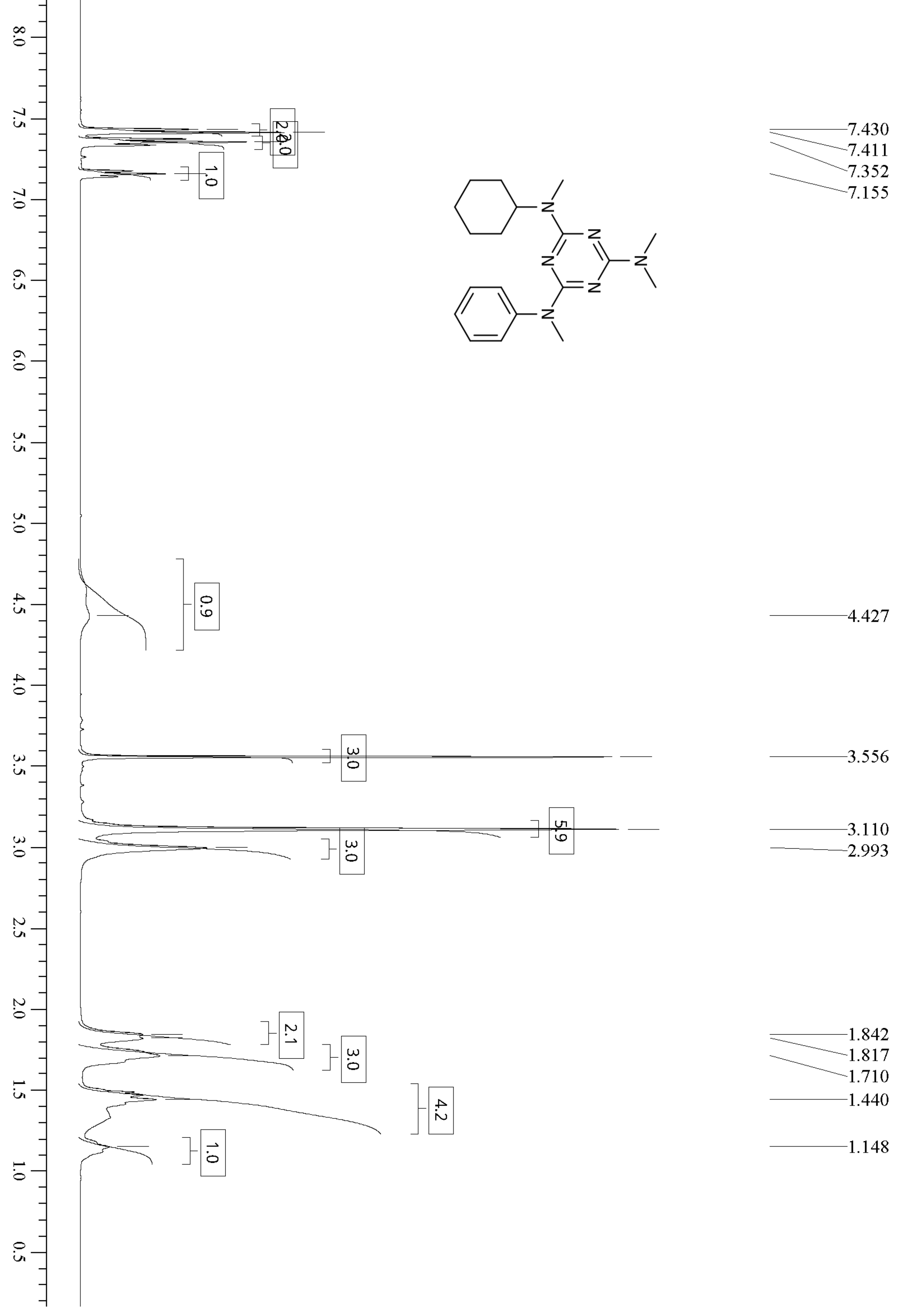

169.127
164.861
164.083
143.948
128.542
126.378
125.925
54.728
53.597
37.935
37.689
29.882
29.527
28.515
28.346
25.681
25.482
N
N
N
N
N
Cl
200
175
150
125
100
75
50
25
0



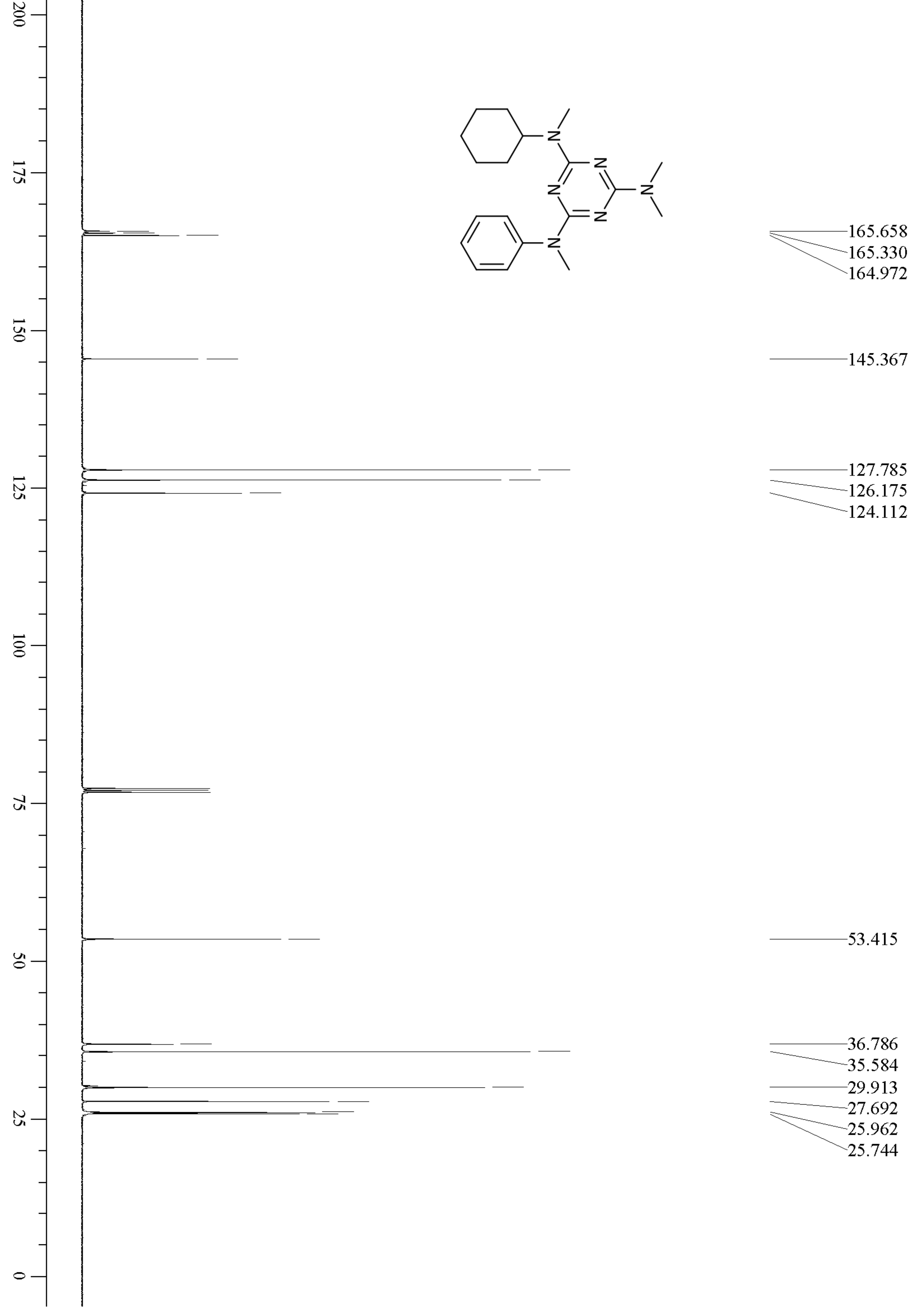
7.341
7.206
4.308
3.765
3.435
3.006
1.784
1.753
1.616
1.587
1.493
1.462
1.233
1.114
4.0
1.1
1.1
3.1
3.1
3.6
3.0
2.1
2.2
2.0
1.3
O
N
N
N
N
N
363 K
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5



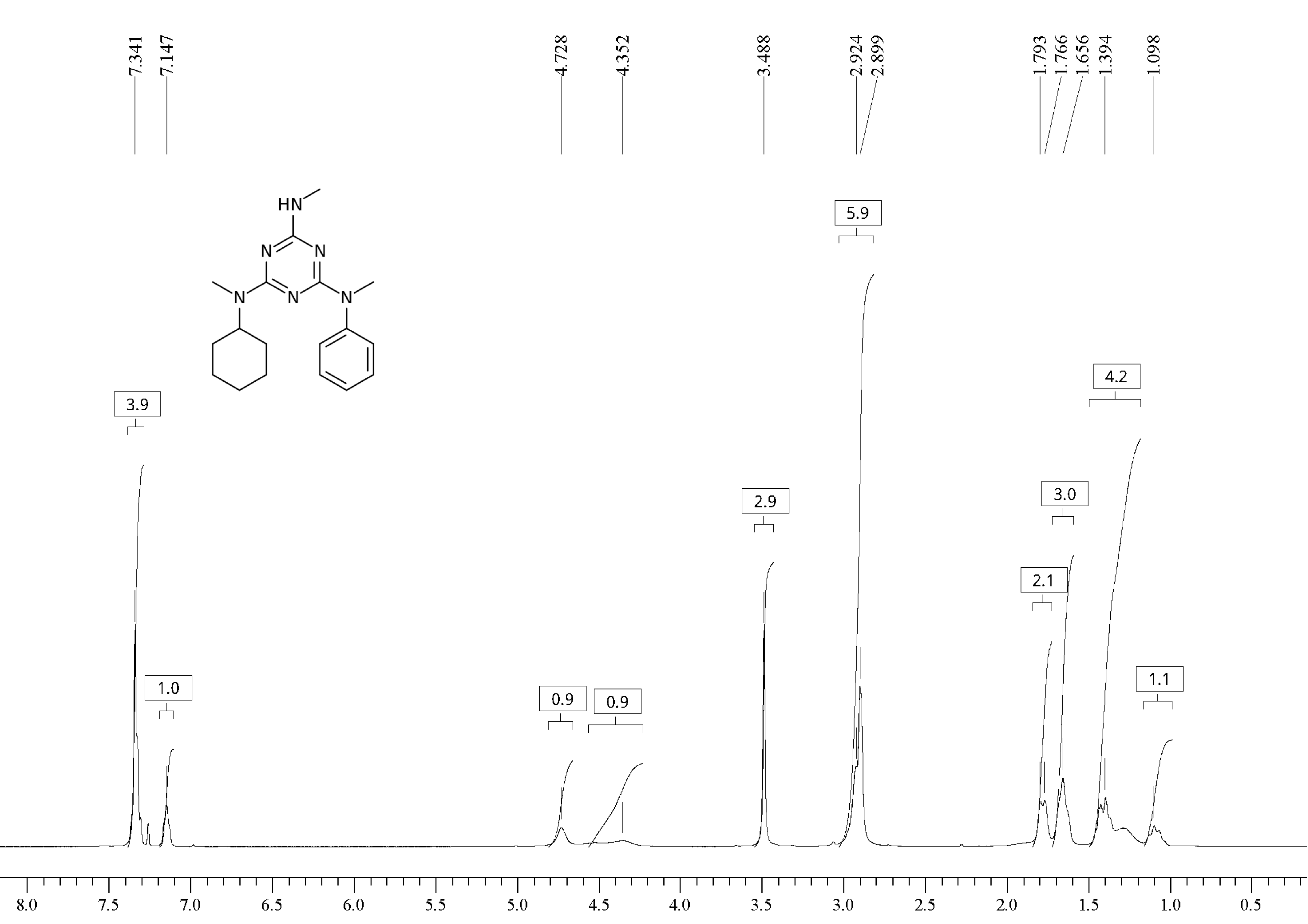
170.854
166.246
165.700
144.668
128.228
126.412
125.152
54.225
53.481
37.332
29.789
28.151
25.794
25.615
200
175
150
125
100
75
50
25
0



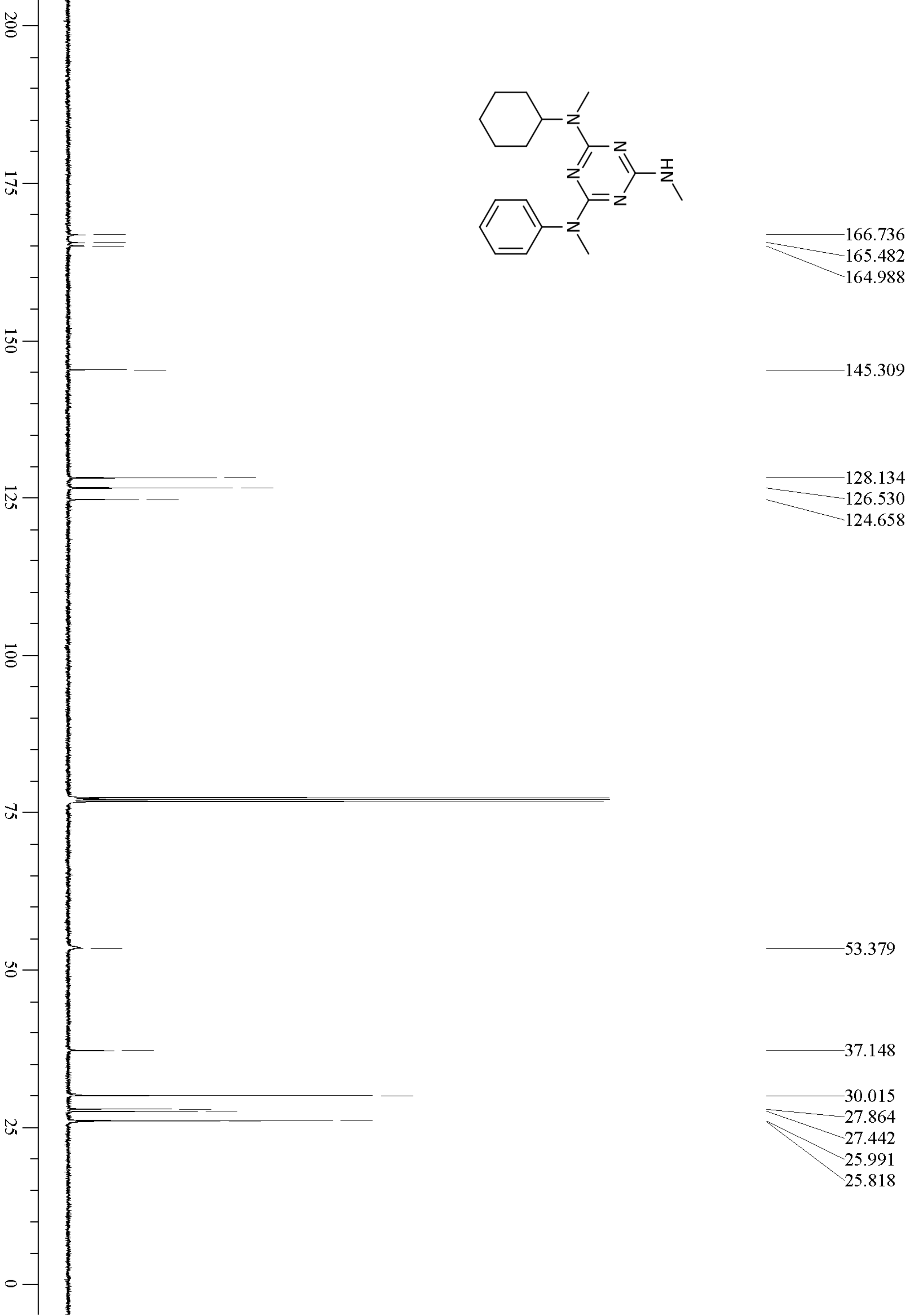
7.430
7.411
7.352
7.155
4.427
3.556
3.110
2.993
1.842
1.817
1.710
1.440
1.148
2.0
1.0
0.9
3.0
5.9
3.0
2.1
3.0
4.2
1.0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
N



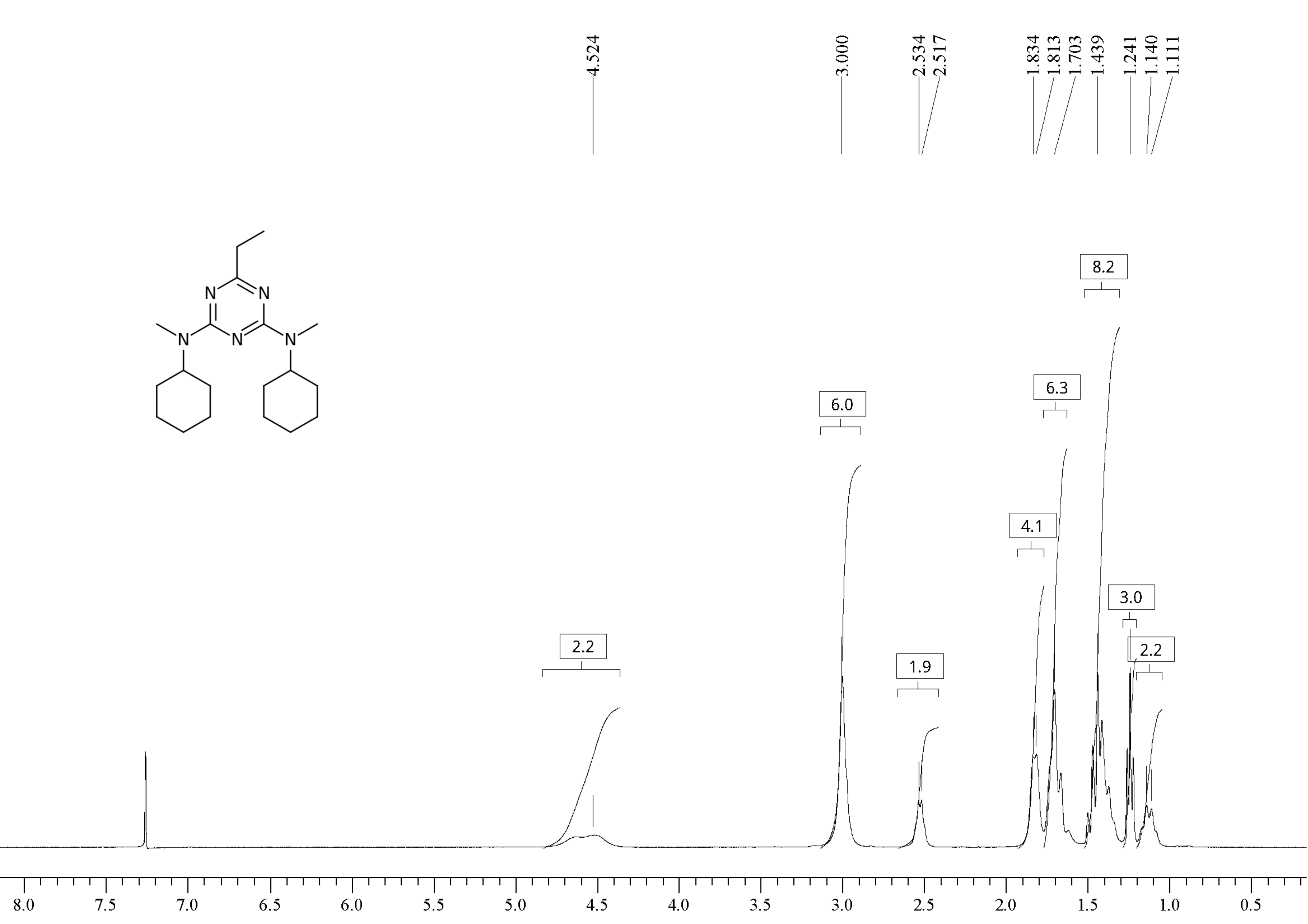
165.658
165.330
164.972
145.367
127.785
126.175
124.112
53.415
36.786
35.584
29.913
27.692
25.962
25.744
200
175
150
125
100
75
50
25
0



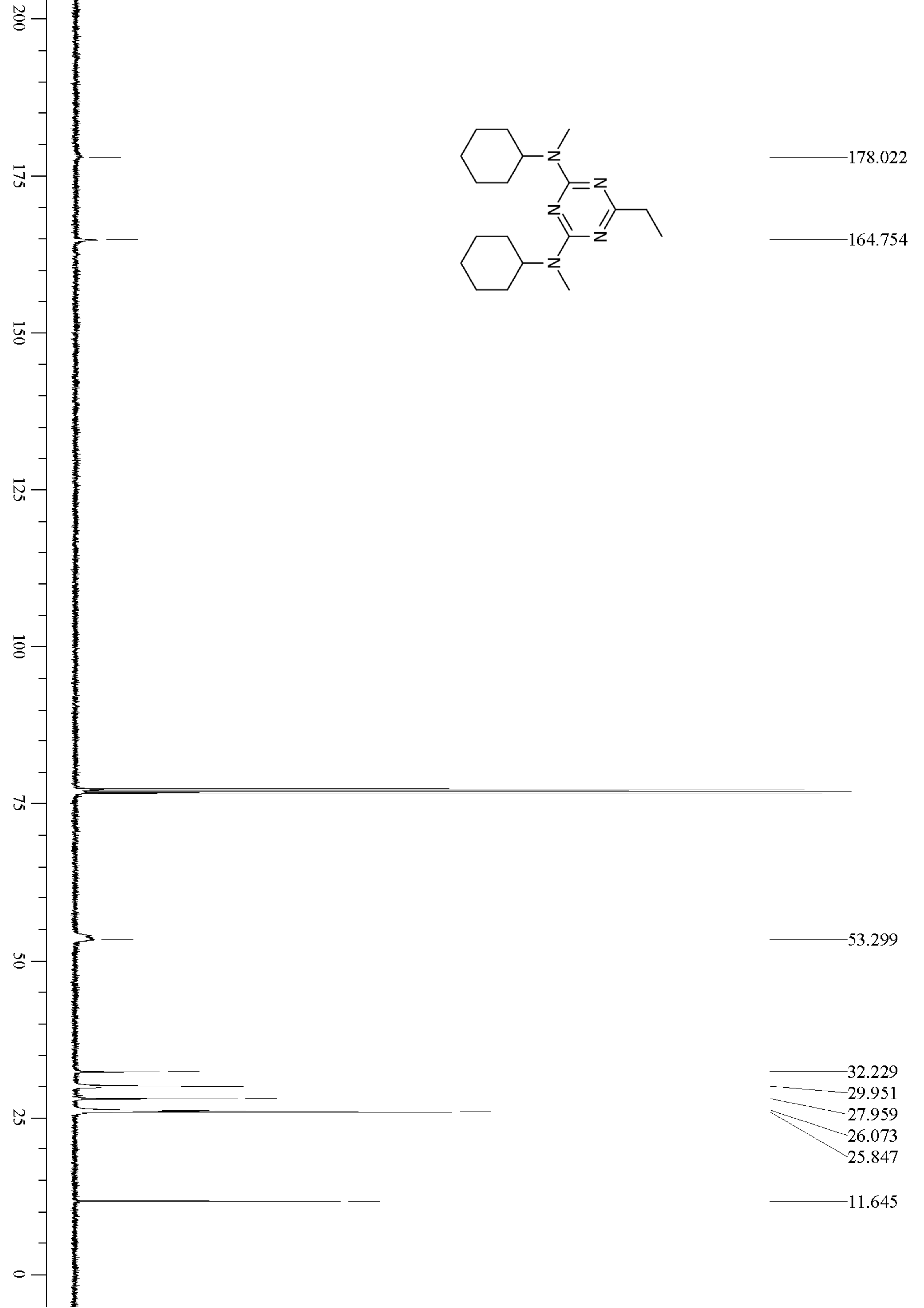
7.341
7.147
4.728
4.352
3.488
2.924
2.899
1.793
1.766
1.656
1.394
1.098
HN
N
N
N
N
N
3.9
1.0
0.9
0.9
2.9
5.9
2.1
3.0
4.2
1.1
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5



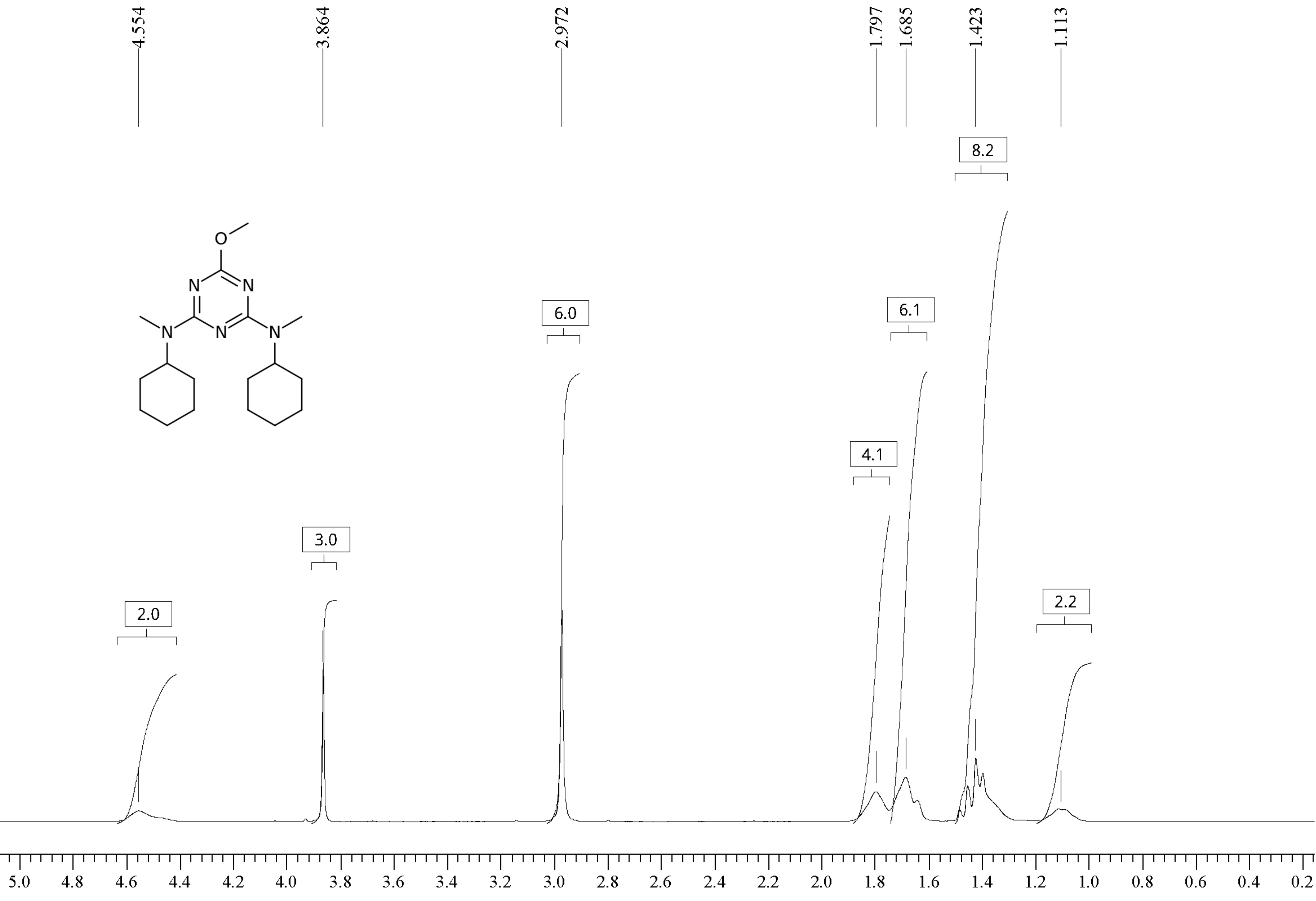
166.736
165.482
164.988
145.309
128.134
126.530
124.658
53.379
37.148
30.015
27.864
27.442
25.991
25.818
200
175
150
125
100
75
50
25
0



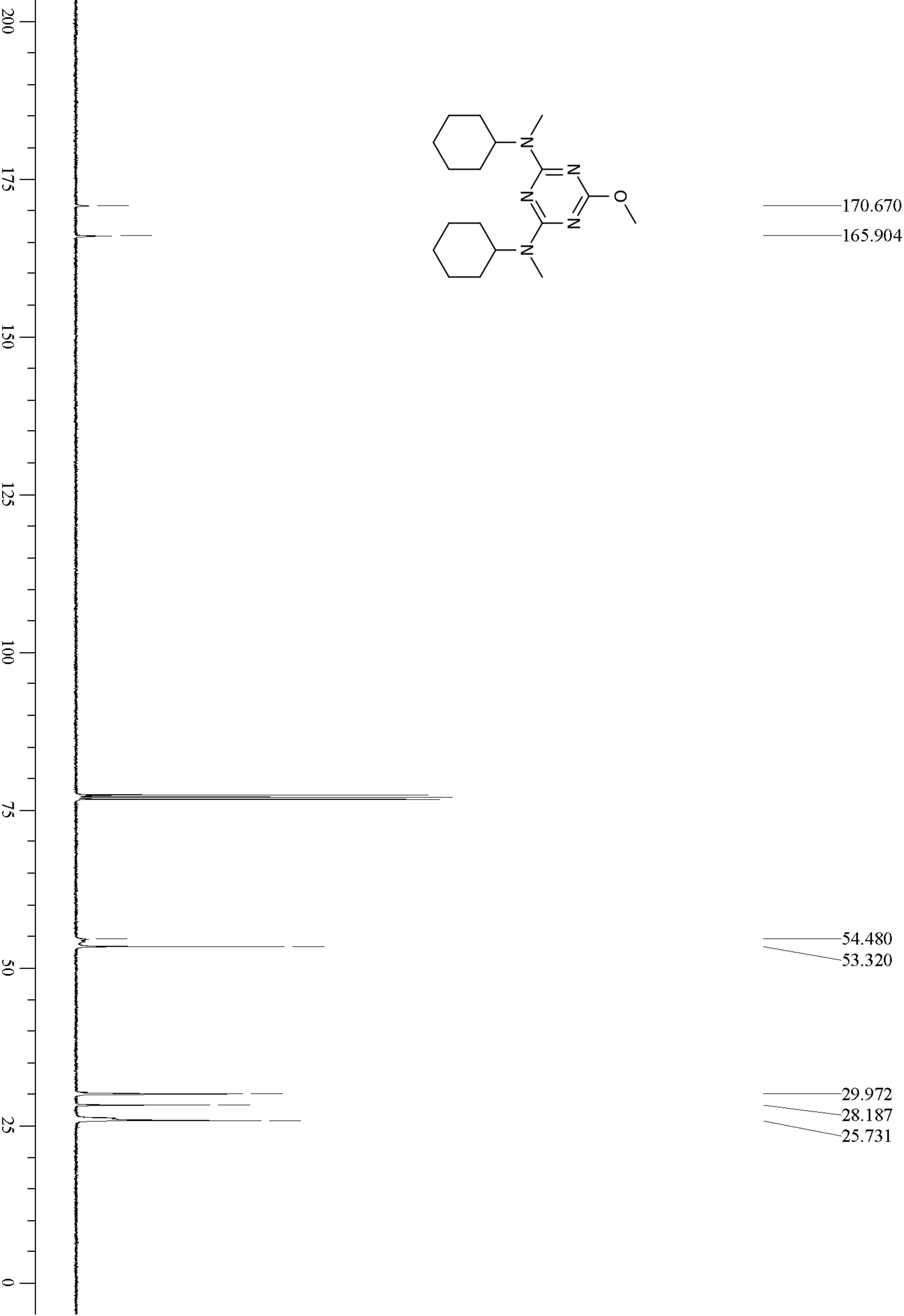
4.524
3.000
2.534
2.517
1.834
1.813
1.703
1.439
1.241
1.140
1.111
8.2
6.3
6.0
4.1
3.0
2.2
1.9
2.2
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5



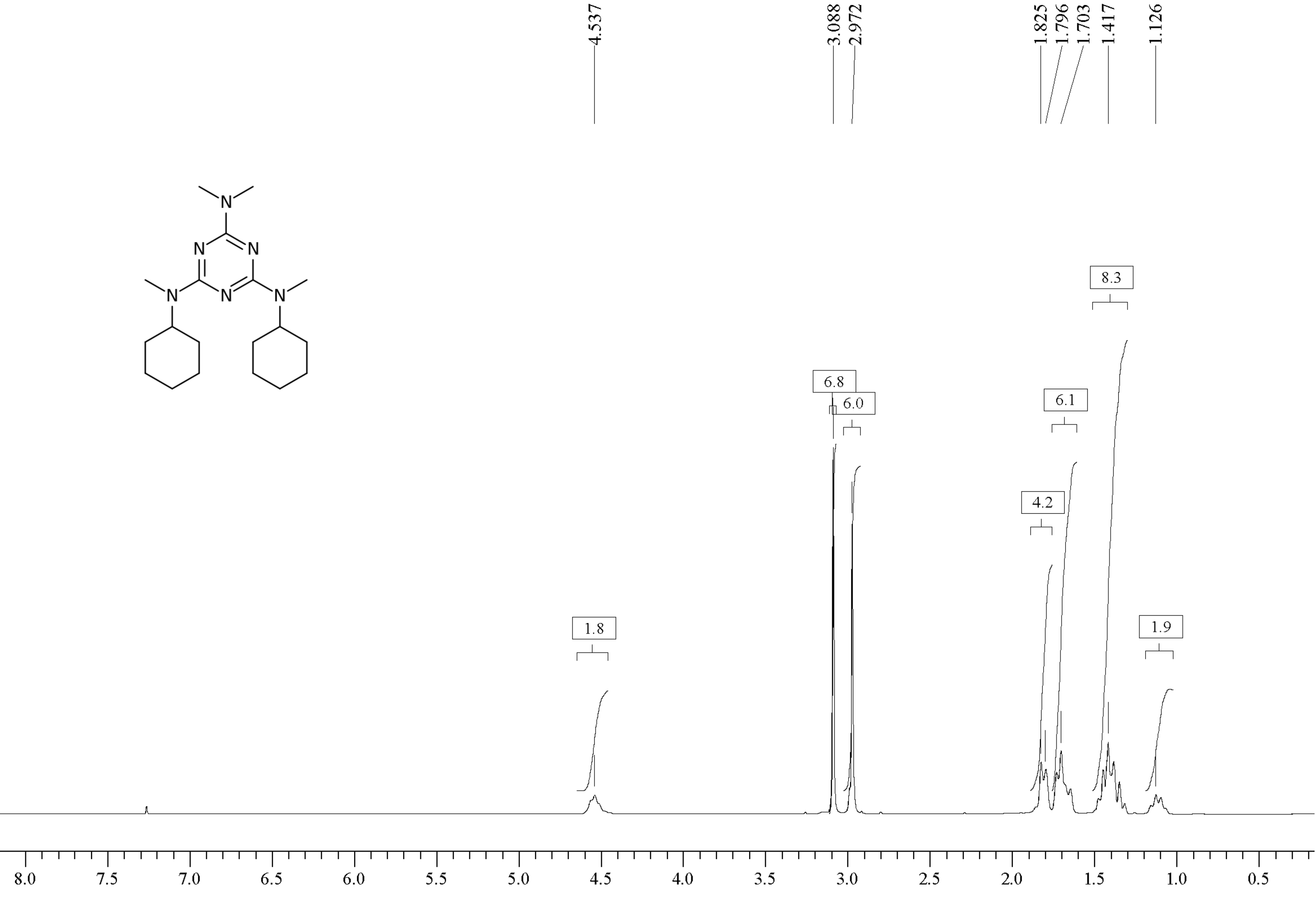
178.022
164.754
53.299
32.229
29.951
27.959
26.073
25.847
11.645
200
175
150
125
100
75
50
25
0
N

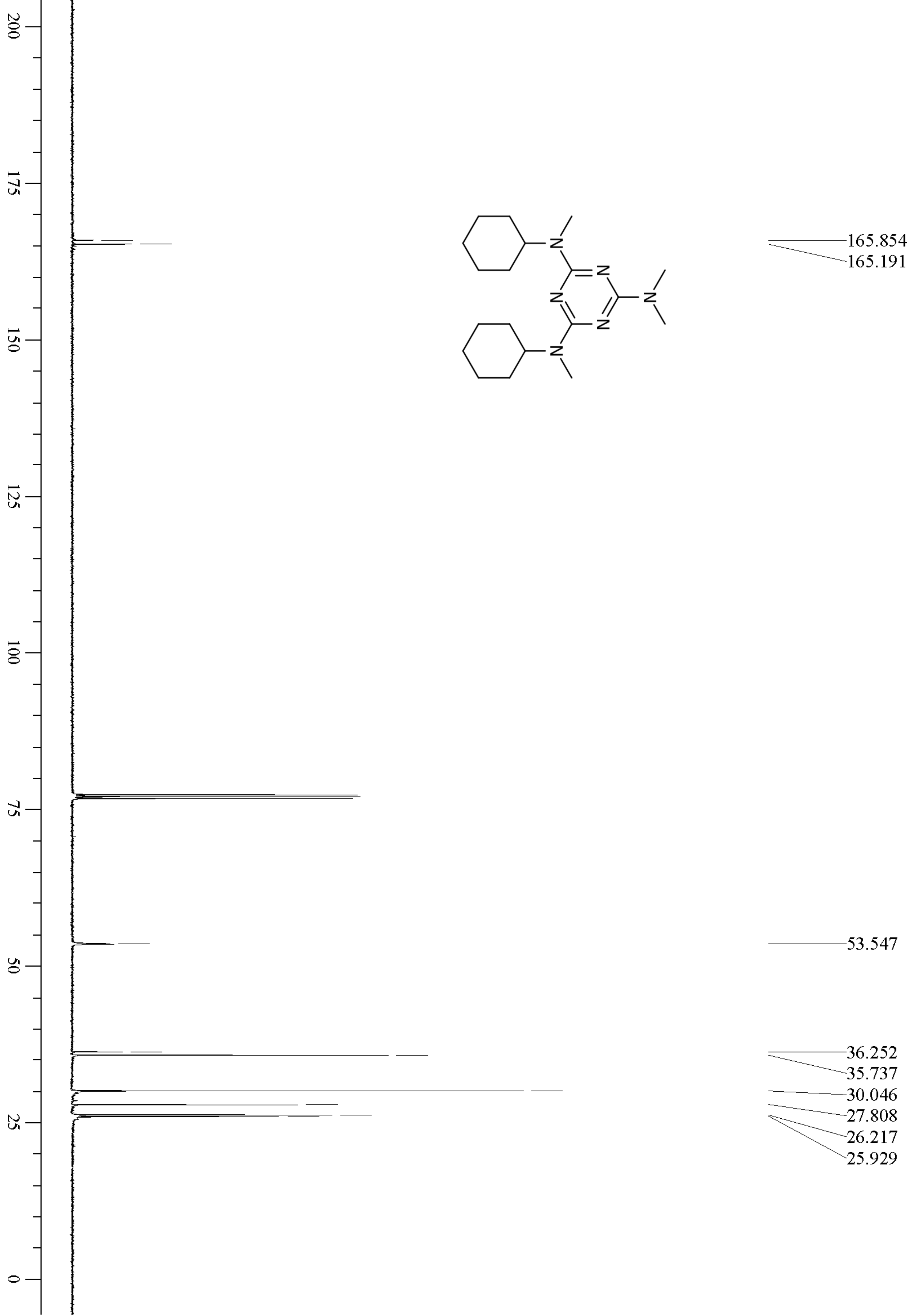


4.554
3.864
2.972
1.797
1.685
1.423
1.113
8.2
6.0
6.1
4.1
3.0
2.0
2.2
O
N
N
N
N
N
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2

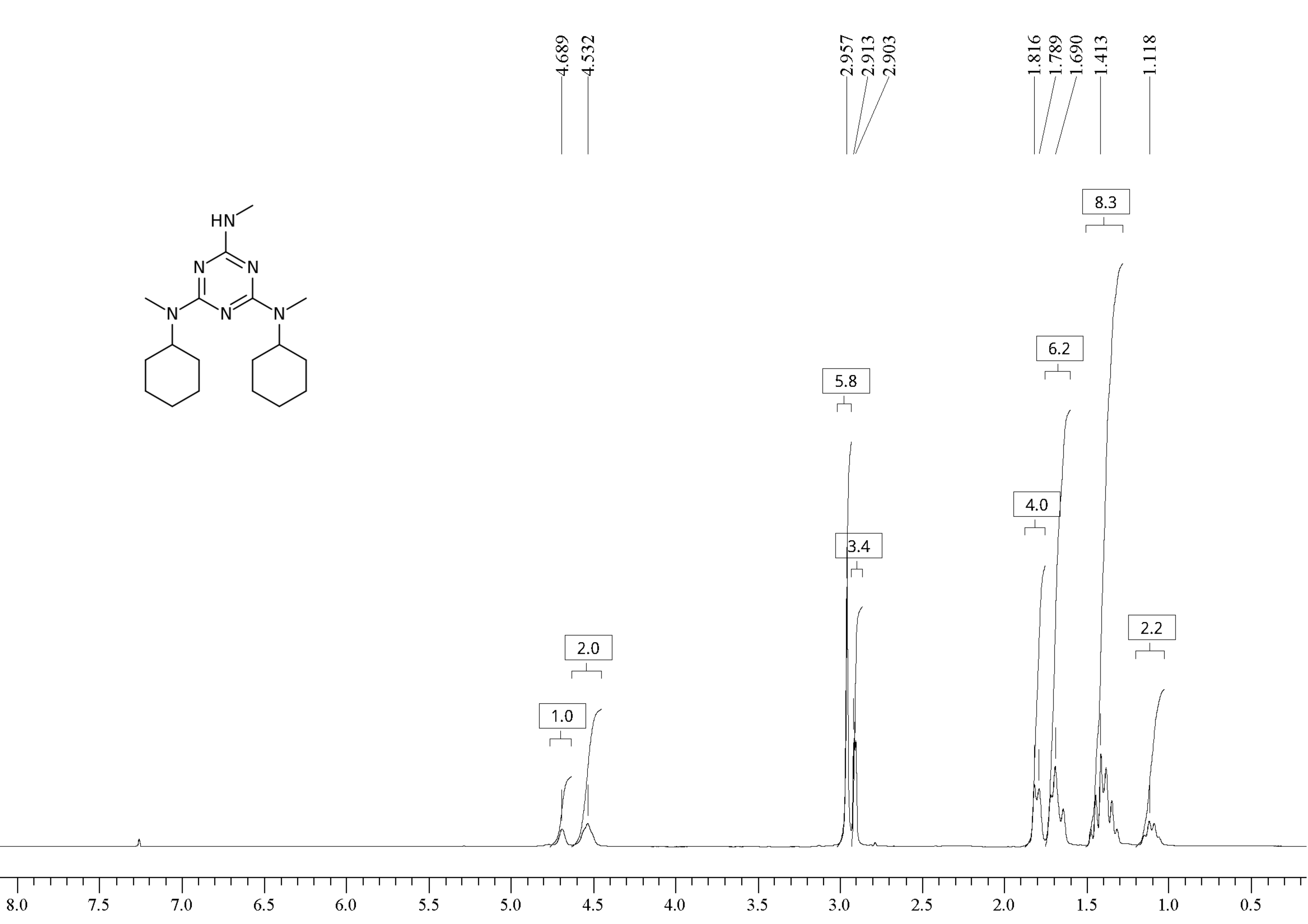


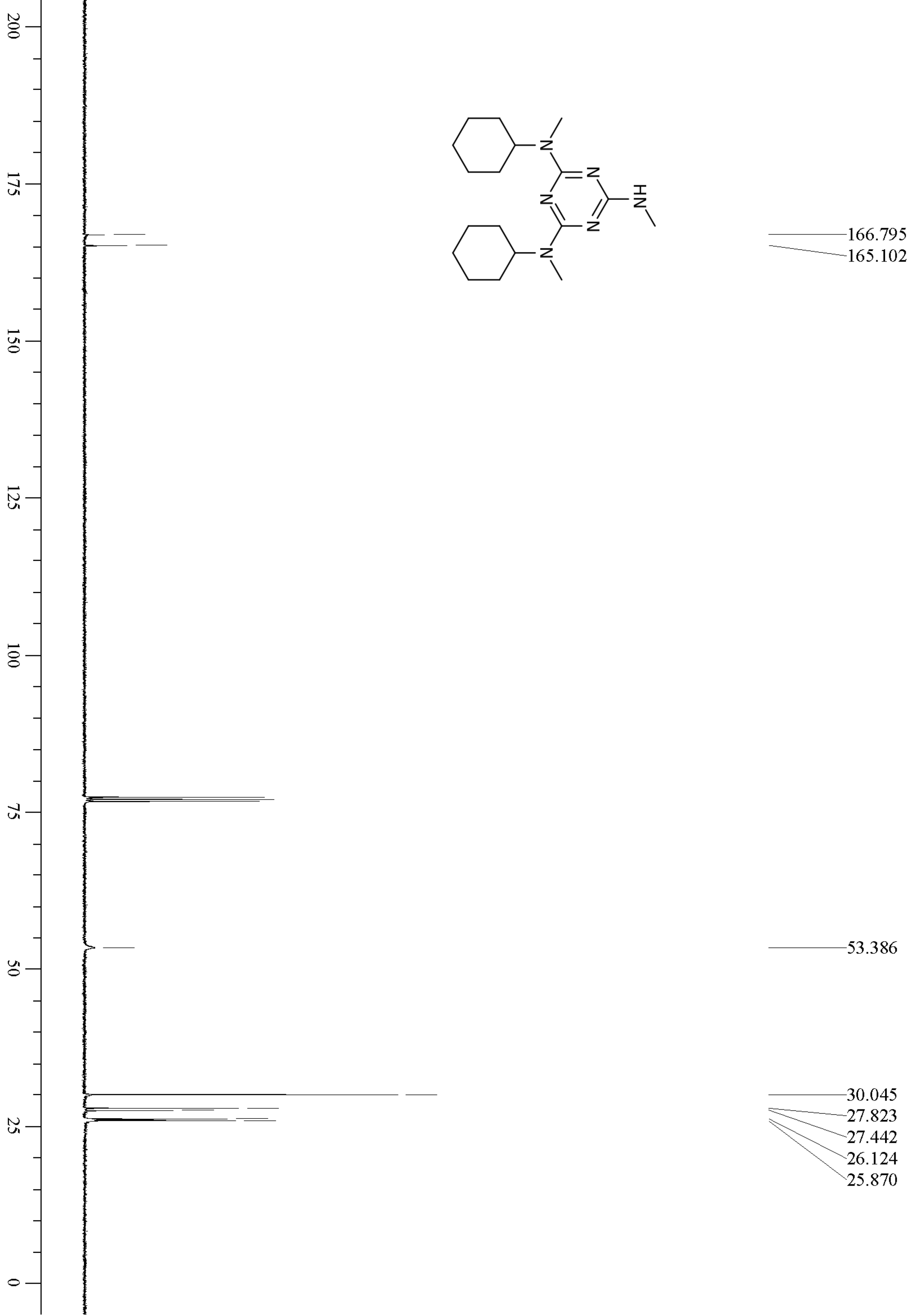
170.670
165.904
54.480
53.320
29.972
28.187
25.731
200
175
150
125
100
75
50
25
0


4.537
3.088
2.972
1.825
1.796
1.703
1.417
1.126
N
1.8
6.8
6.0
4.2
6.1
8.3
1.9
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



165.854
165.191
53.547
36.252
35.737
30.046
27.808
26.217
25.929
N
N
N
N
N
N
200
175
150
125
100
75
50
25
0


4.689
4.532
2.957
2.913
2.903
1.816
1.789
1.690
1.413
1.118
1.0
2.0
5.8
3.4
4.0
6.2
8.3
2.2
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



166.795
165.102
53.386
30.045
27.823
27.442
26.124
25.870
200
175
150
125
100
75
50
25
0