Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

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

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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}; ^1H 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}; ^1H 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}; ^1H 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 $\mathbf{3_{OMe}}$, $\mathbf{3_{NHMe}}$ and $\mathbf{3_{NMe2}}$ were synthesized following the same procedure as compound $\mathbf{3_{Et}}$ 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 ($\mathbf{3_{OMe}}$)

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 ($\mathbf{3_{NHMe}}$)

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 ($\mathbf{3_{NMe2}}$)

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	GaK_α	GaK_α	GaK_α	GaK_α
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
***w*R_2 (I > 2σ)**	0.1125	0.1181	0.1938	0.2032
R_1 (all data)	0.0505	0.0484	0.0915	0.1088
***w*R_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

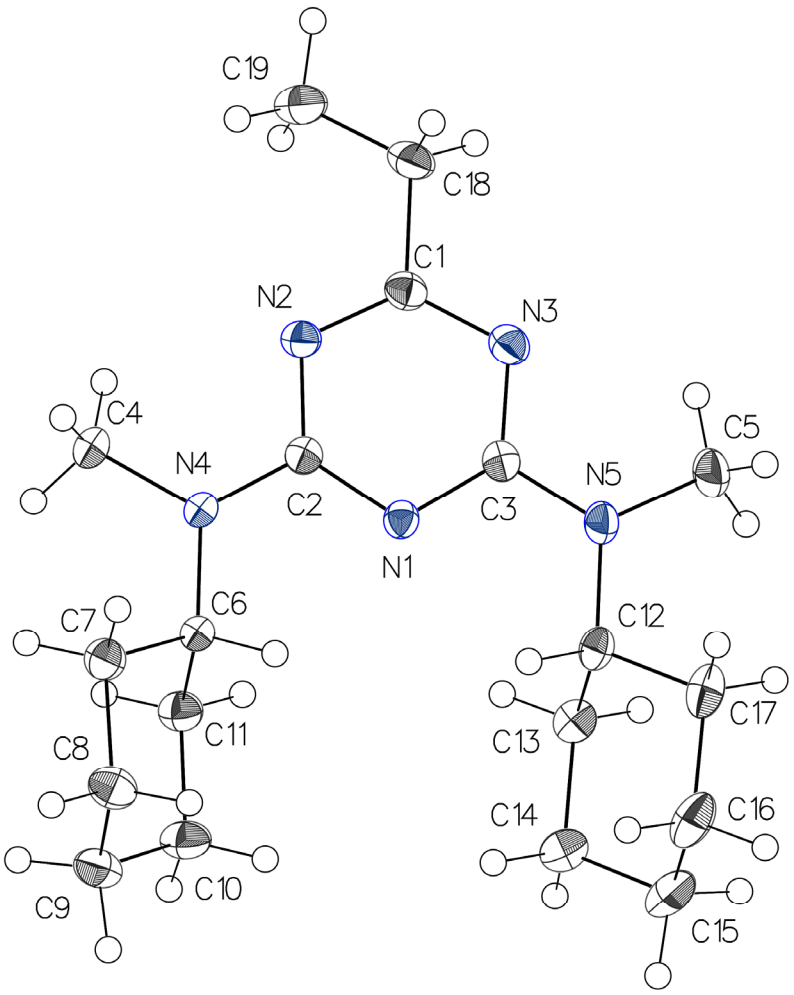


Figure S1. Thermal atomic displacement ellipsoid plot of the structure of $\mathbf{3}_{Et}$. The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level, and hydrogen atoms are represented by a sphere of arbitrary size.

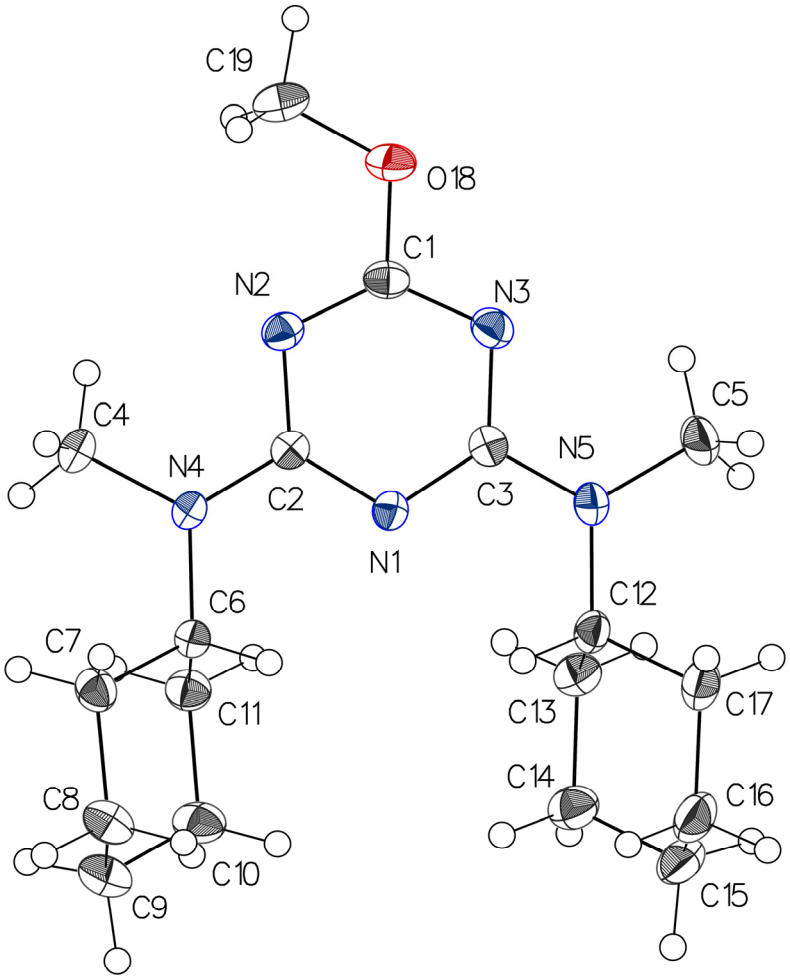


Figure S2. Thermal atomic displacement ellipsoid plot of the structure of $\mathbf{3}_{\mathbf{OMe}}$. The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level, and hydrogen atoms are represented by a sphere of arbitrary size.

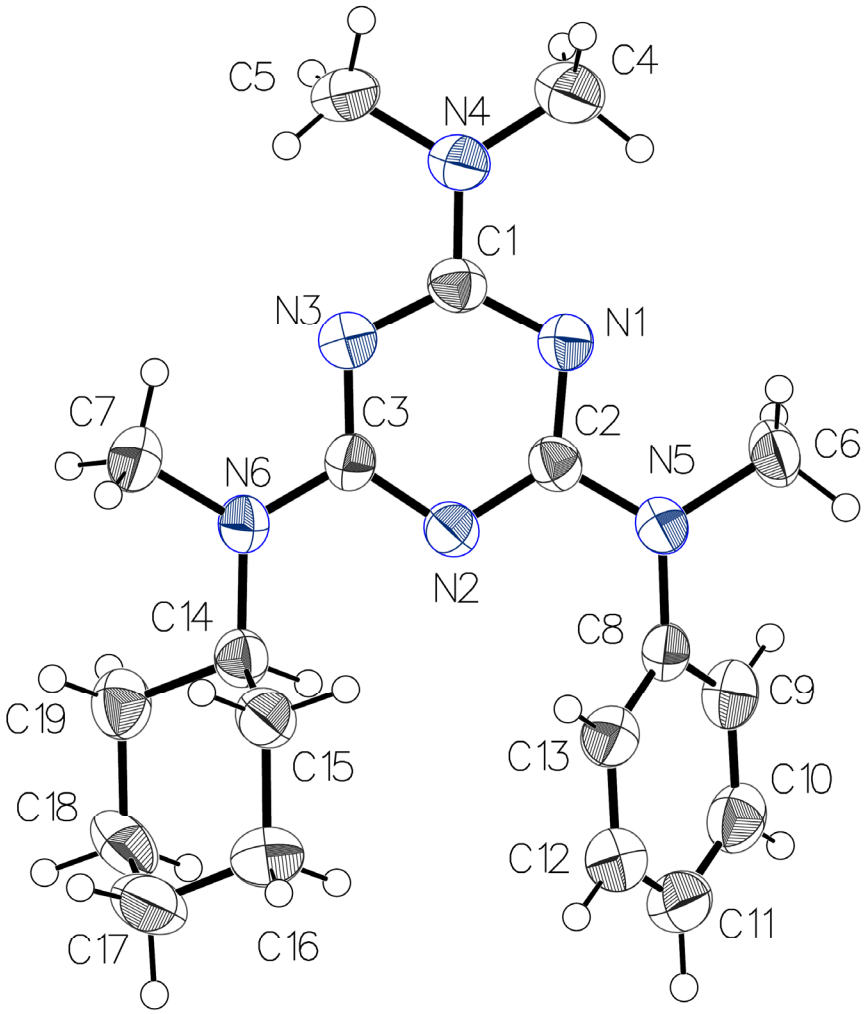


Figure S3. Thermal atomic displacement ellipsoid plot of the structure of $\mathbf{2}_{\mathbf{NMe2}}$. The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level, and hydrogen atoms are represented by a sphere of arbitrary size.

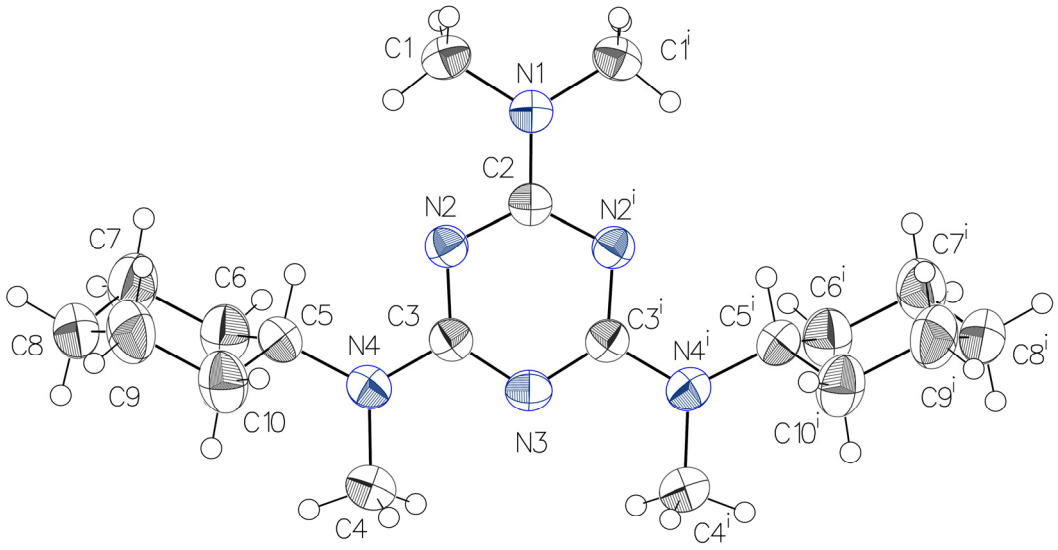
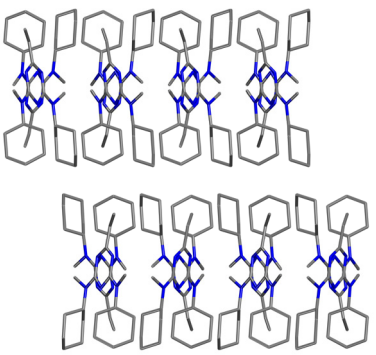
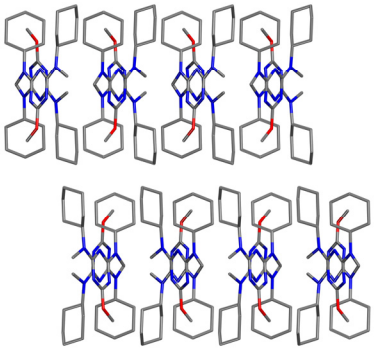


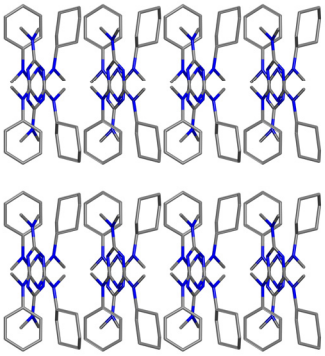
Figure S4. Thermal atomic displacement ellipsoid plot of the structure of $\mathbf{3}_{\mathbf{NMe2}}$. The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level, and hydrogen atoms are represented by a sphere of arbitrary size.



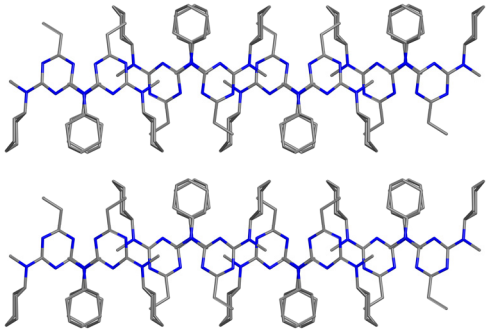
3_{Et} along the *a*-axis



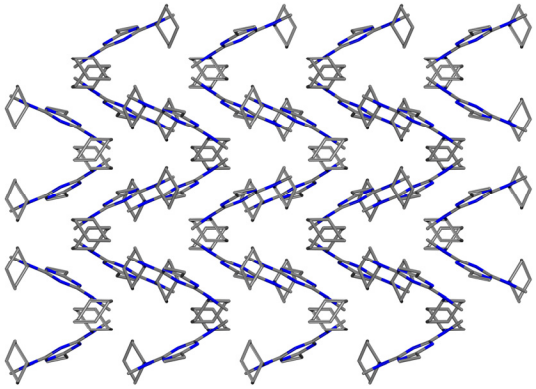
3_{OMe} along the *a*-axis



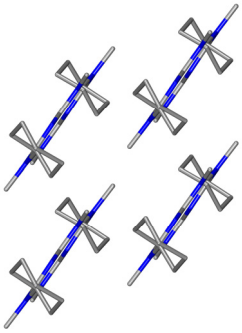
2_{NMe2} along the *a*-axis



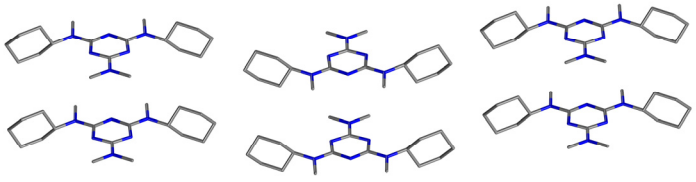
3_{Et} along the *b*-axis



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

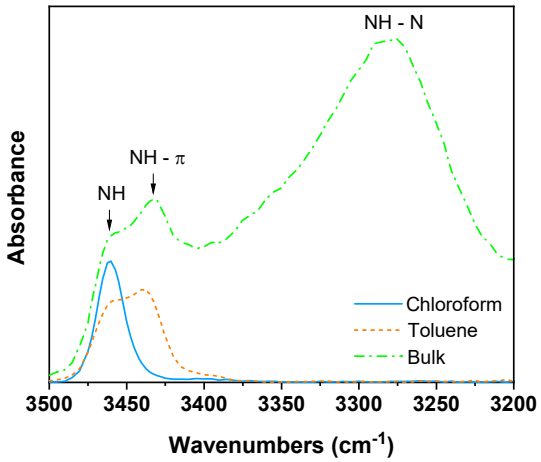


Figure S6. IR spectra of $\mathbf{2}_{NHMe}$ in the bulk state, and in 1 mM solutions in toluene and chloroform. The bands due to NH groups engaged in hydrogen bonding (NH – N), NH – π interactions, and weak van der Waals interactions (NH) are indicated.

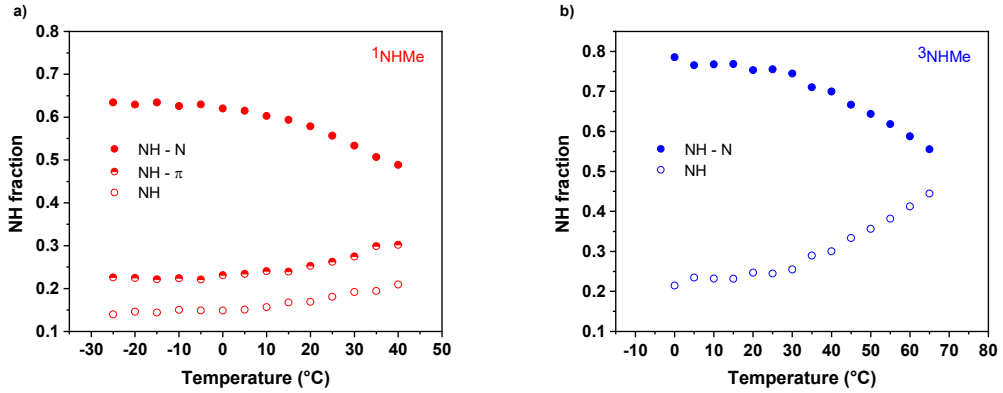


Figure S7. Fractions of NH groups engaged in hydrogen bonding (NH – N), NH – π interactions, and weak van der Waals interactions (NH) as a function of temperature for compounds a) $\mathbf{1}_{\mathbf{NHMe}}$ and b) $\mathbf{3}_{\mathbf{NHMe}}$, as determined by IR spectroscopy and chemometrics analysis.

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

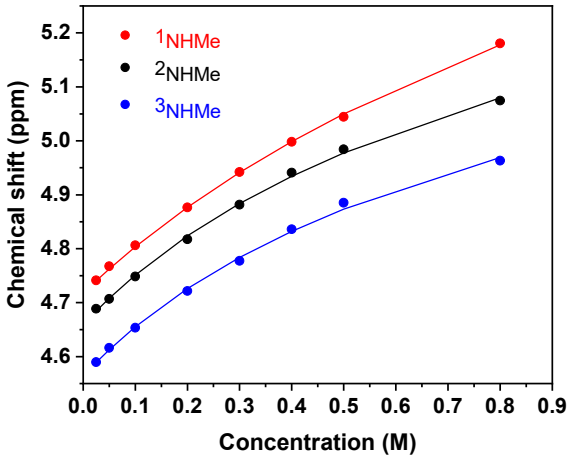
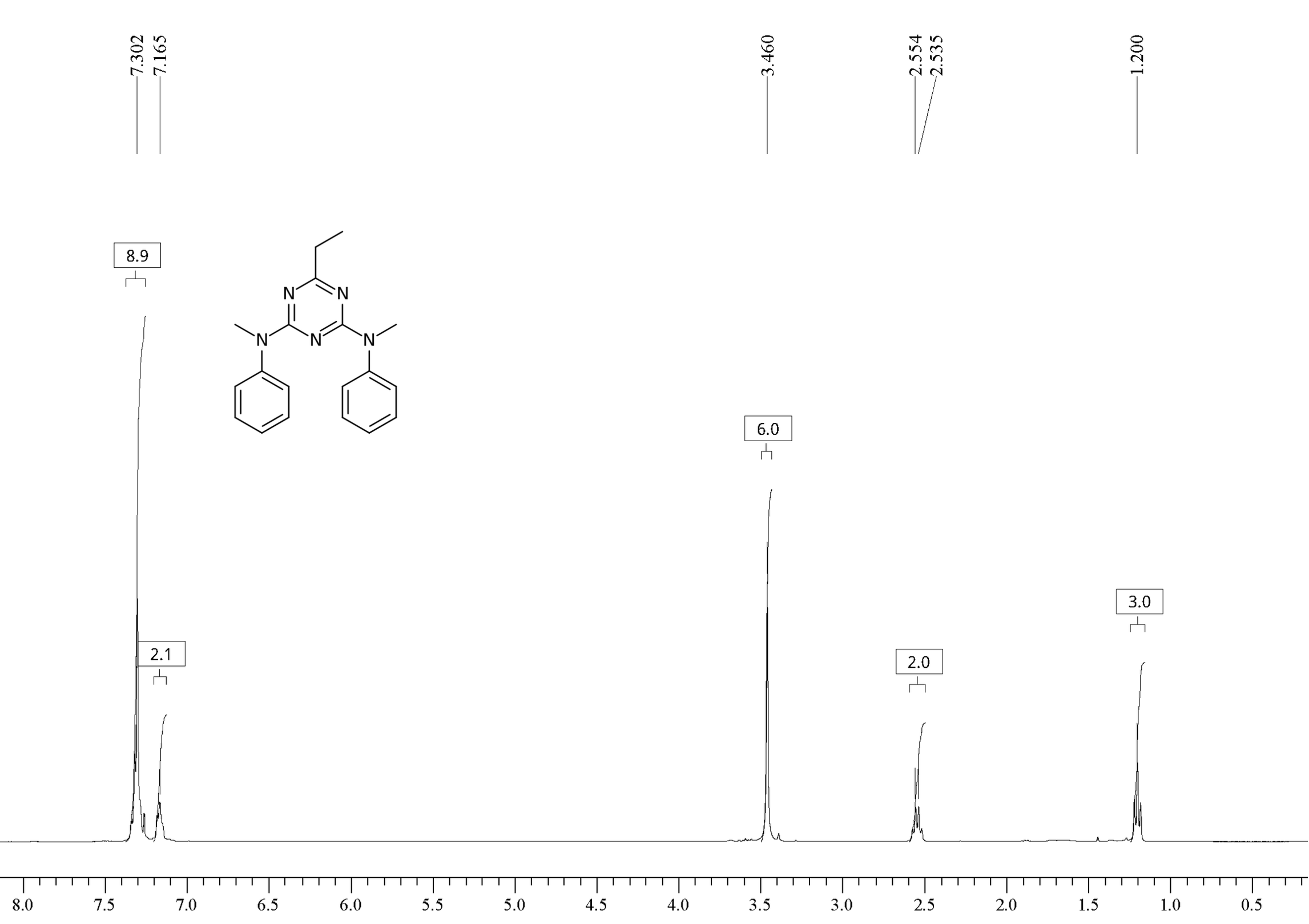


Figure S8. Evolution of NH peak chemical shift with concentration in $CDCl_3$ for $\mathbf{1}_{NHMe}$, $\mathbf{2}_{NHMe}$ and $\mathbf{3}_{NHMe}$, fitted to a curve using a monomer–dimer model (lines).[1]

Reference

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

NMR Spectra of Compounds 1-5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2.554
2.535
1.200
8.9
2.1
6.0
2.0
3.0
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N
N
N
N
8.0
7.5
7.0
6.5
6.0
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3.0
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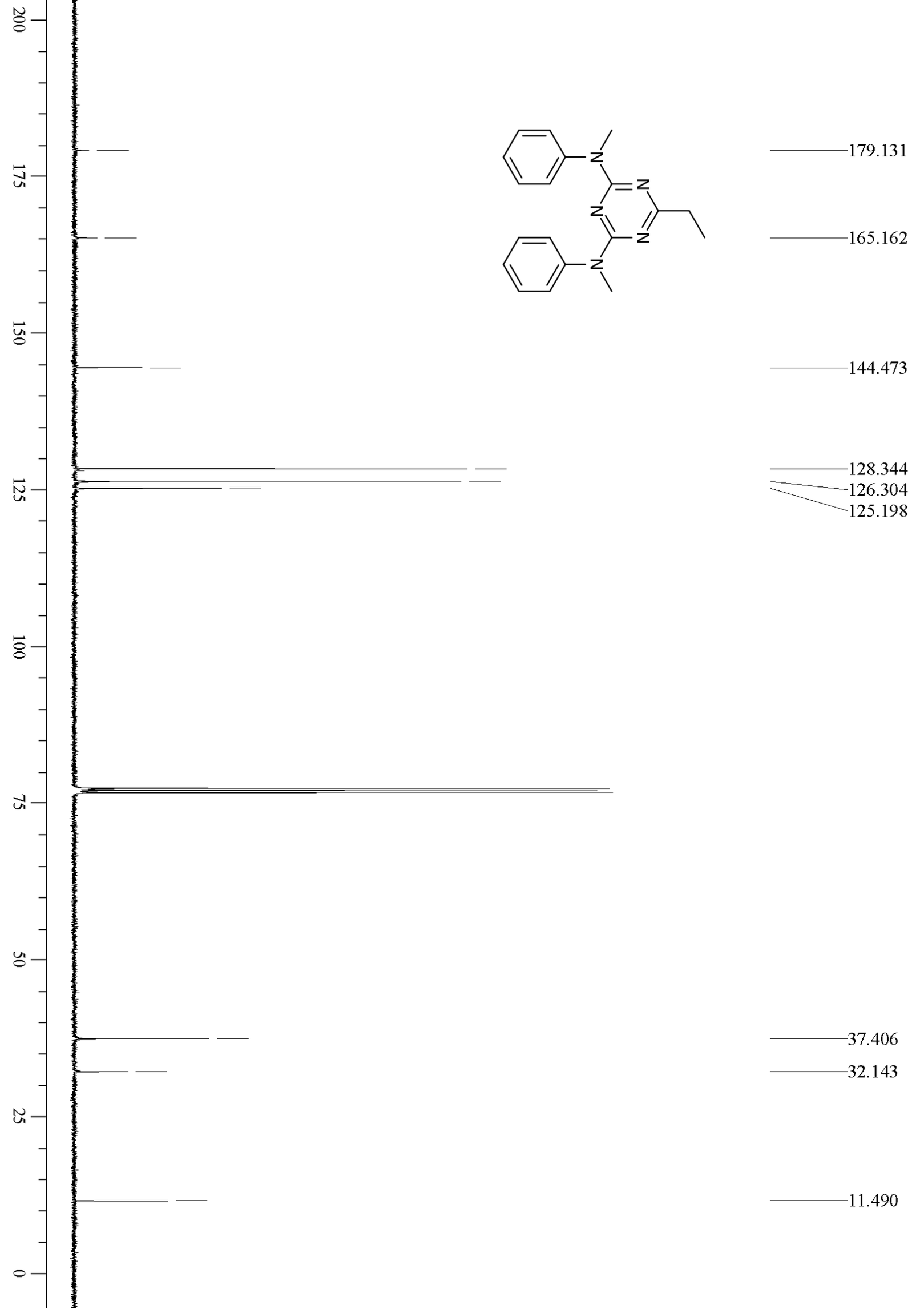
0.5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175
150
125
100
75
50
25
0
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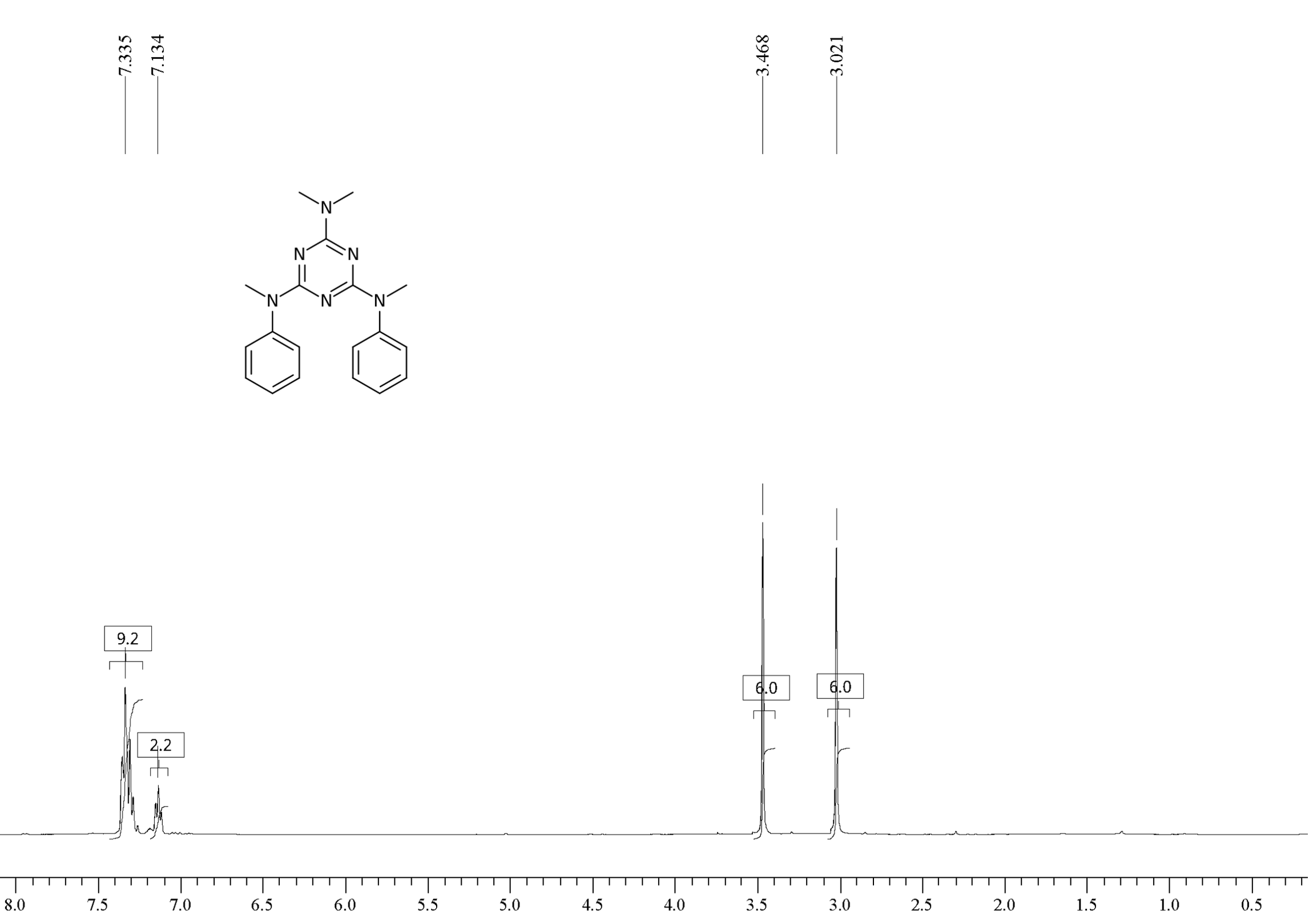
125.198
37.406
32.143
11.490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9.2
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6.0
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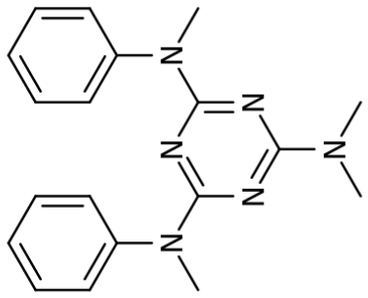
1.5
1.0
0.5



165.096

144.929

128.008

126.225

124.556

37.077

35.713

200

175

150

125

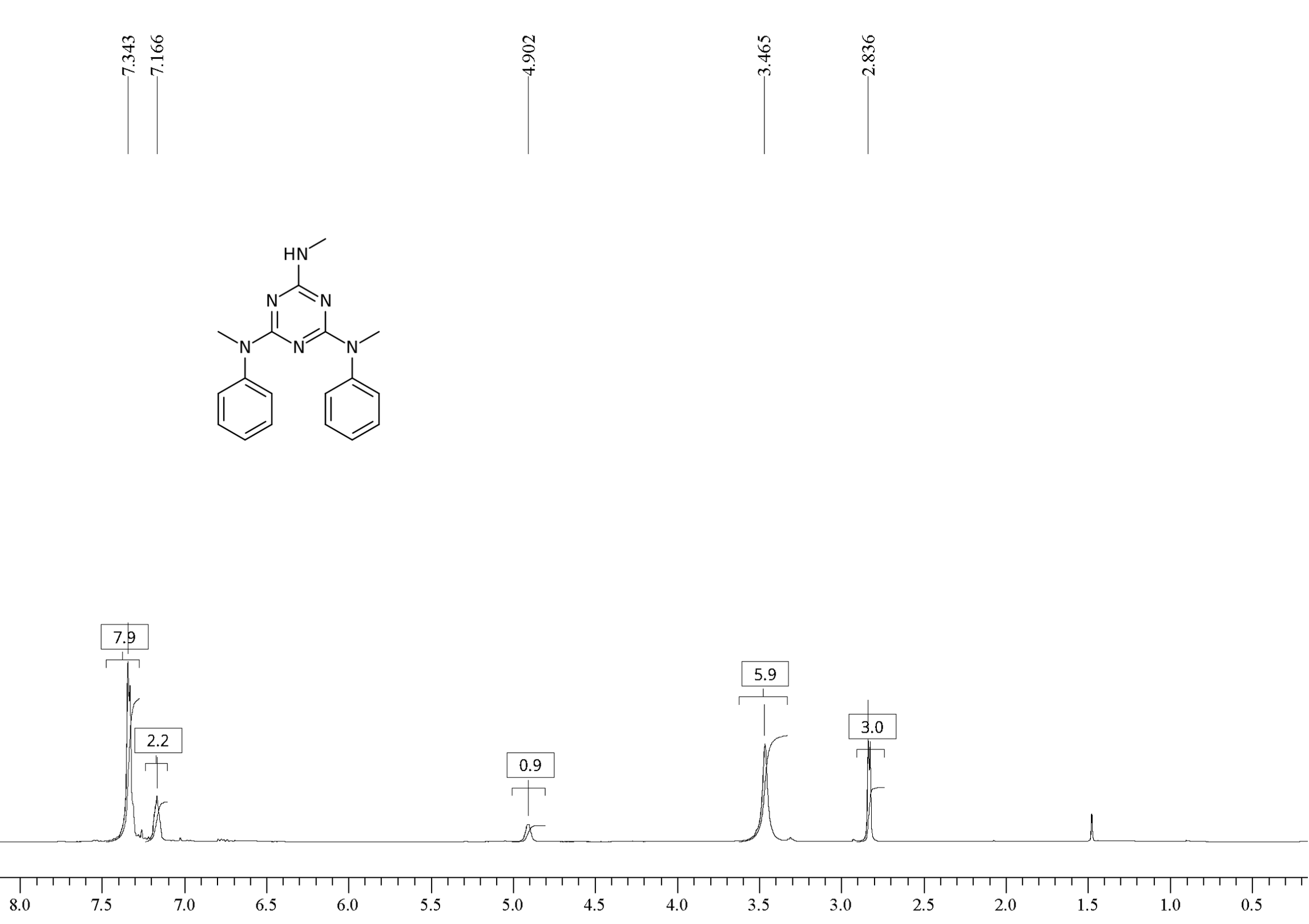
100

75

50

25

0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2.836
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N
N
N
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8.0
7.5
7.0
6.5
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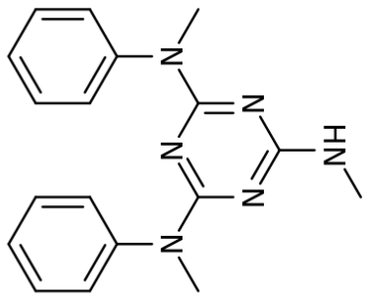

166.566
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126.392
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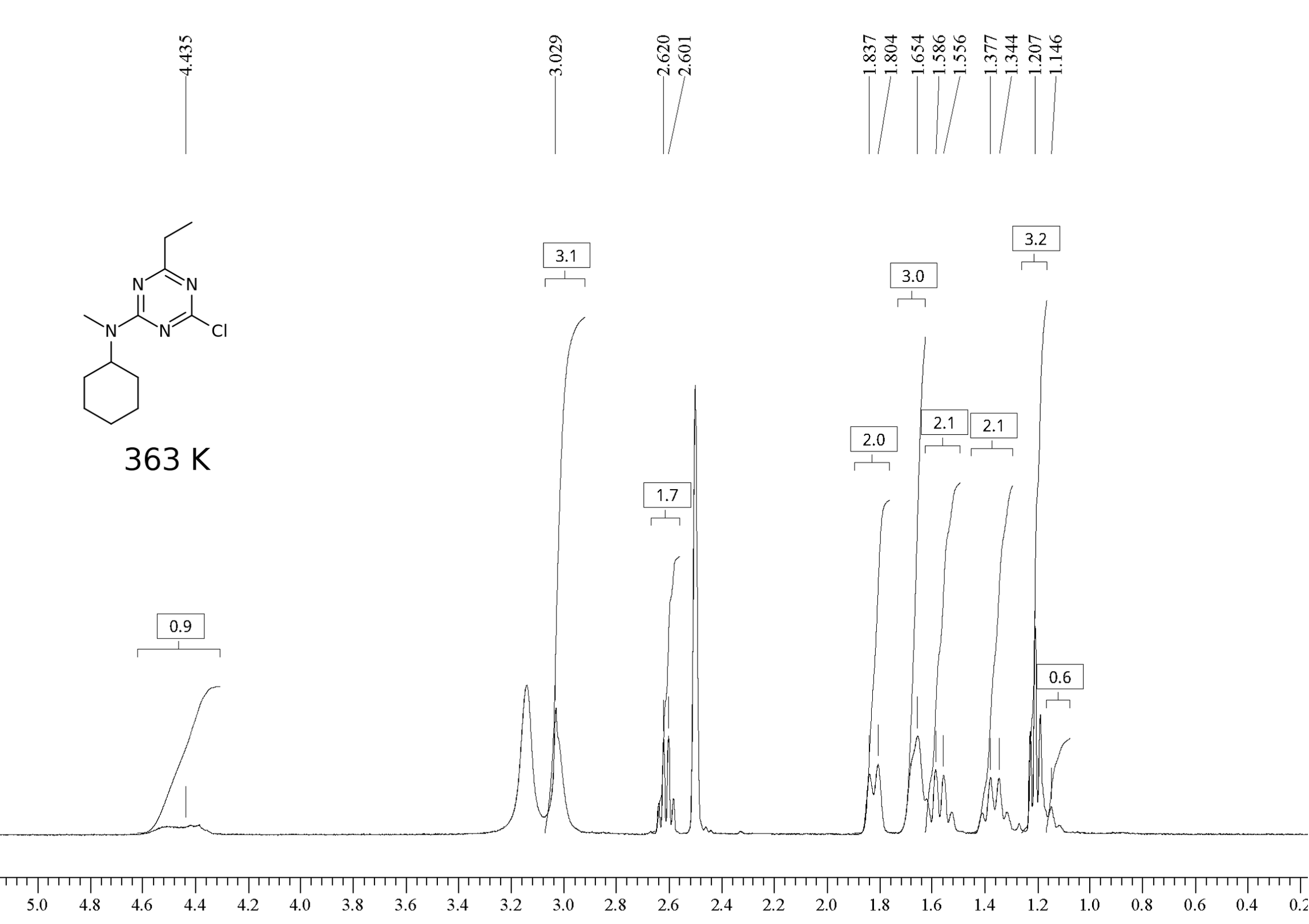
37.187
27.328

200
175
150
125
100
75
50
25
0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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
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3.8
3.6
3.4
3.2
3.0
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2.6
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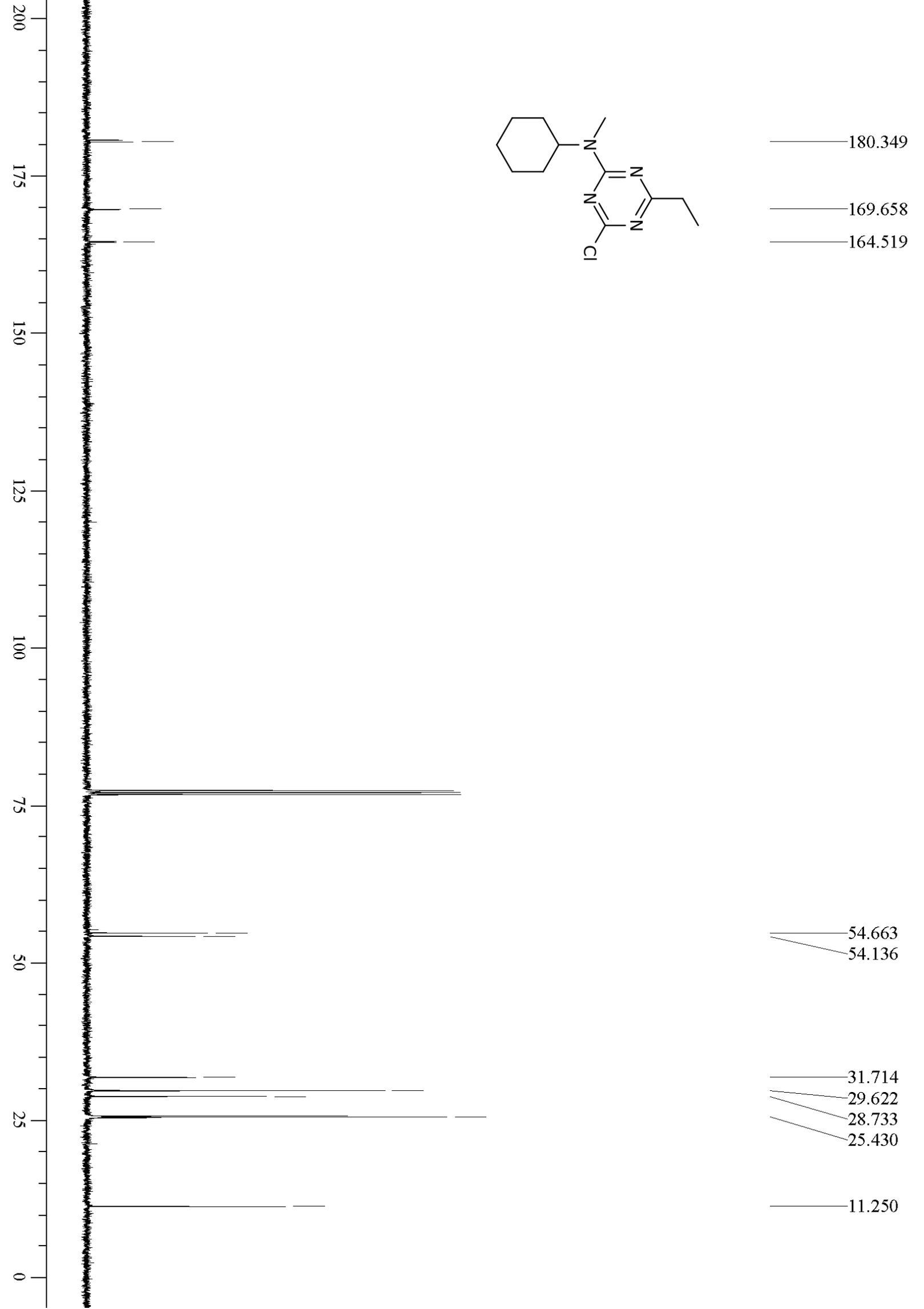
200
175
150
125
100
75
50
25
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N
N
N
N
Cl
180.349
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31.714
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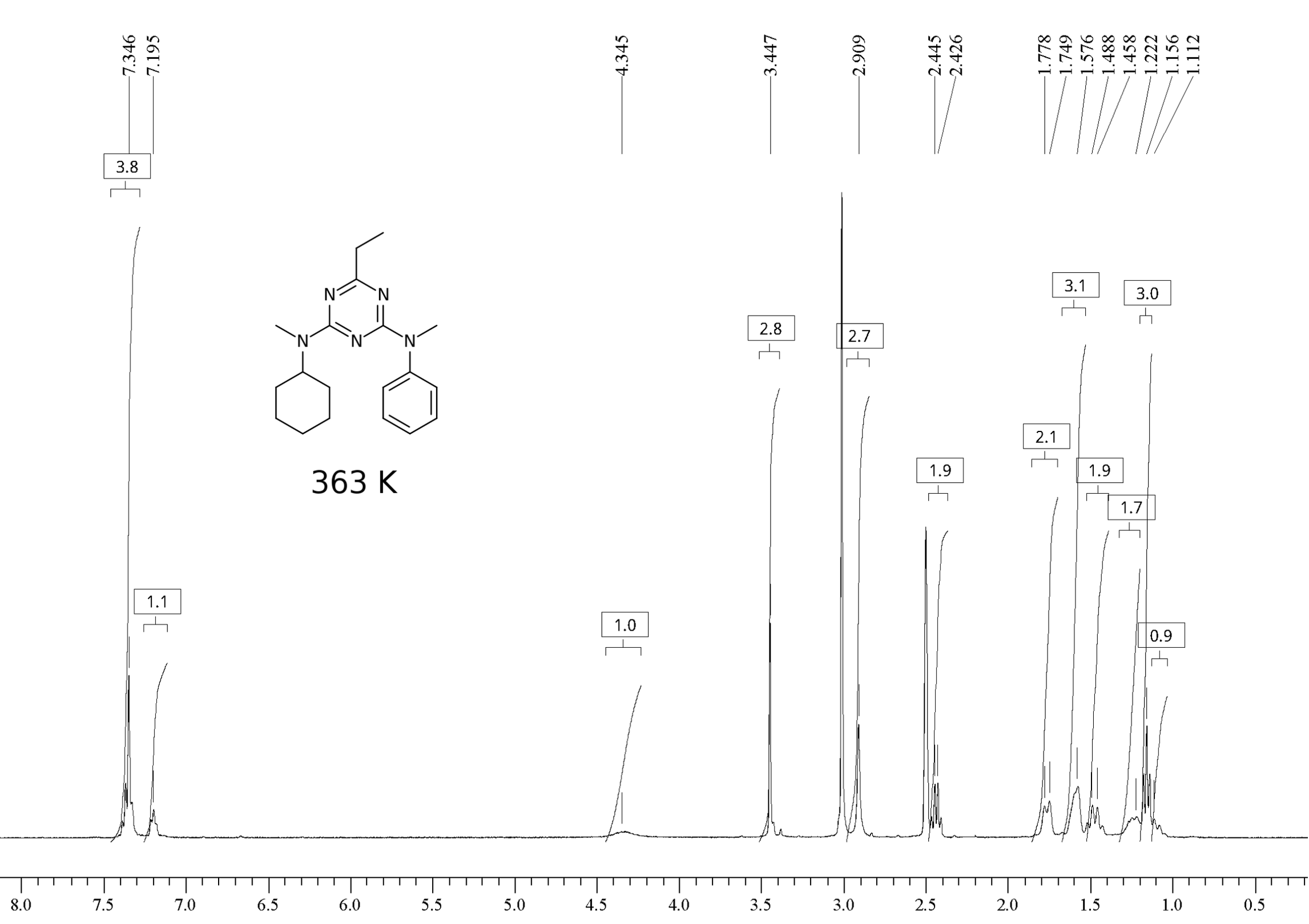
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2.7
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2.1
3.1
1.9
1.7
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0.9
363 K
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7.5
7.0
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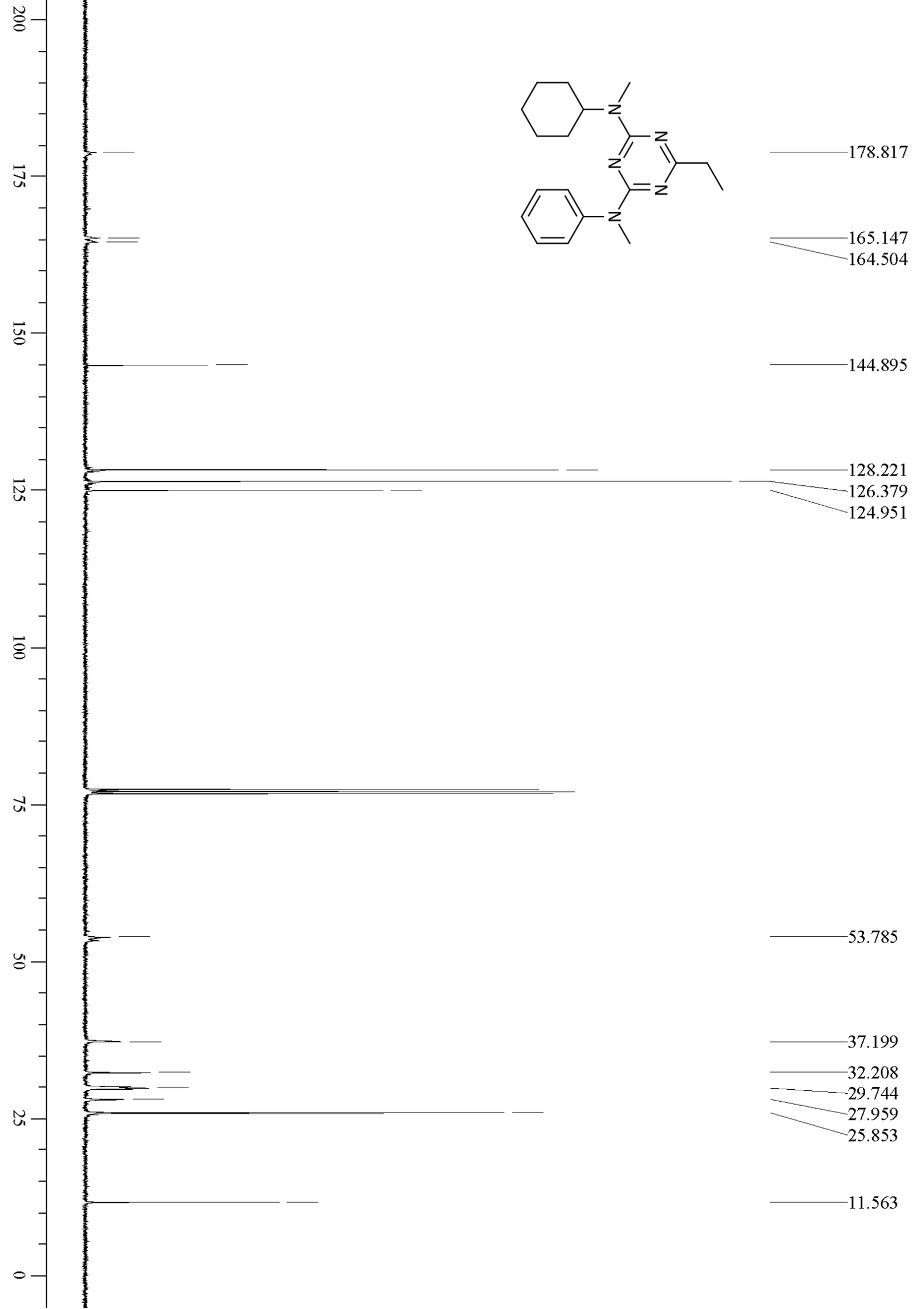
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75
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53.785
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32.208
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27.959
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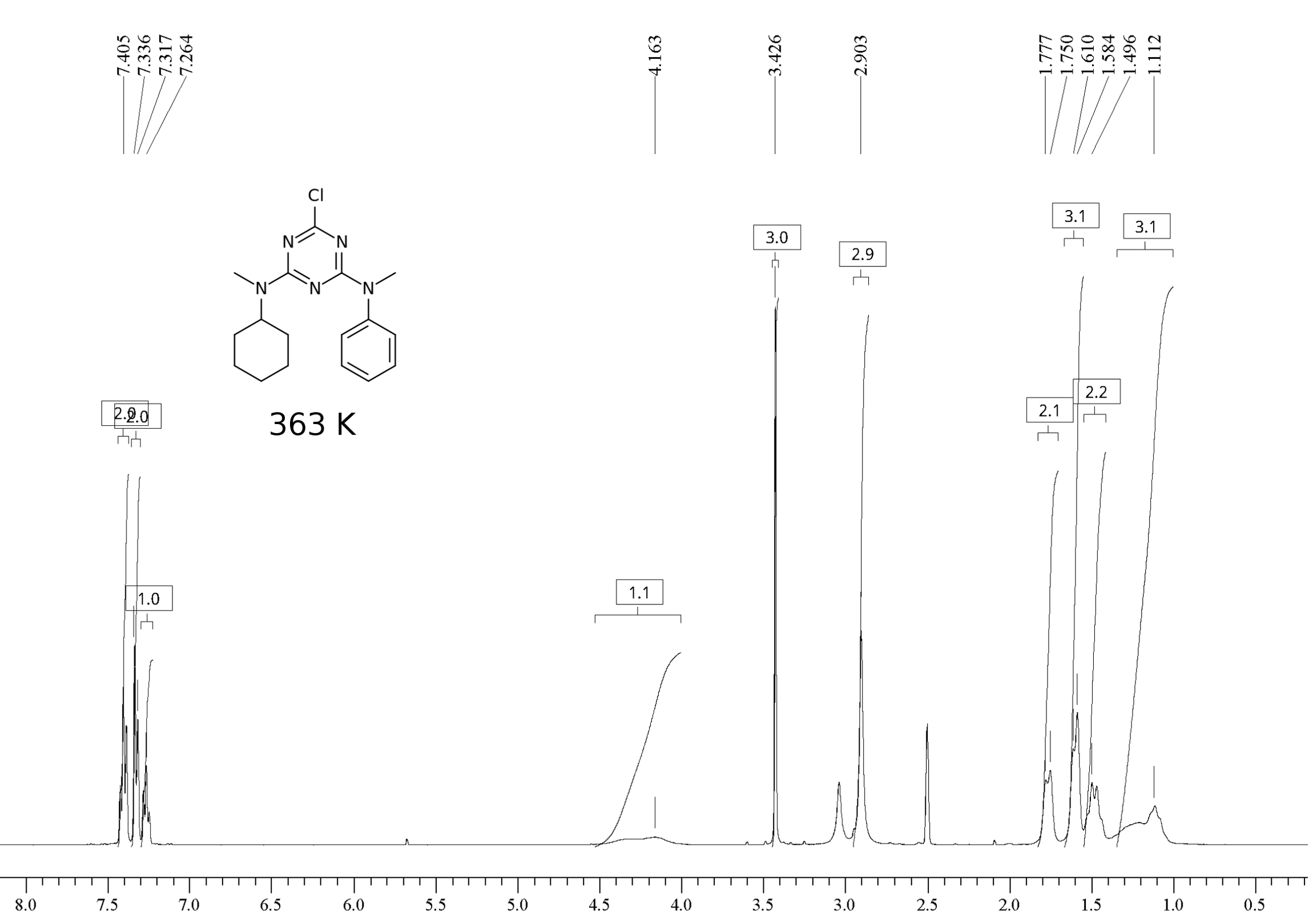
11.563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1.112
Cl
N
N
N
N
N
363 K
2.0
2.0
1.0
1.1
3.0
2.9
3.1
3.1
2.1
2.2
8.0
7.5
7.0
6.5
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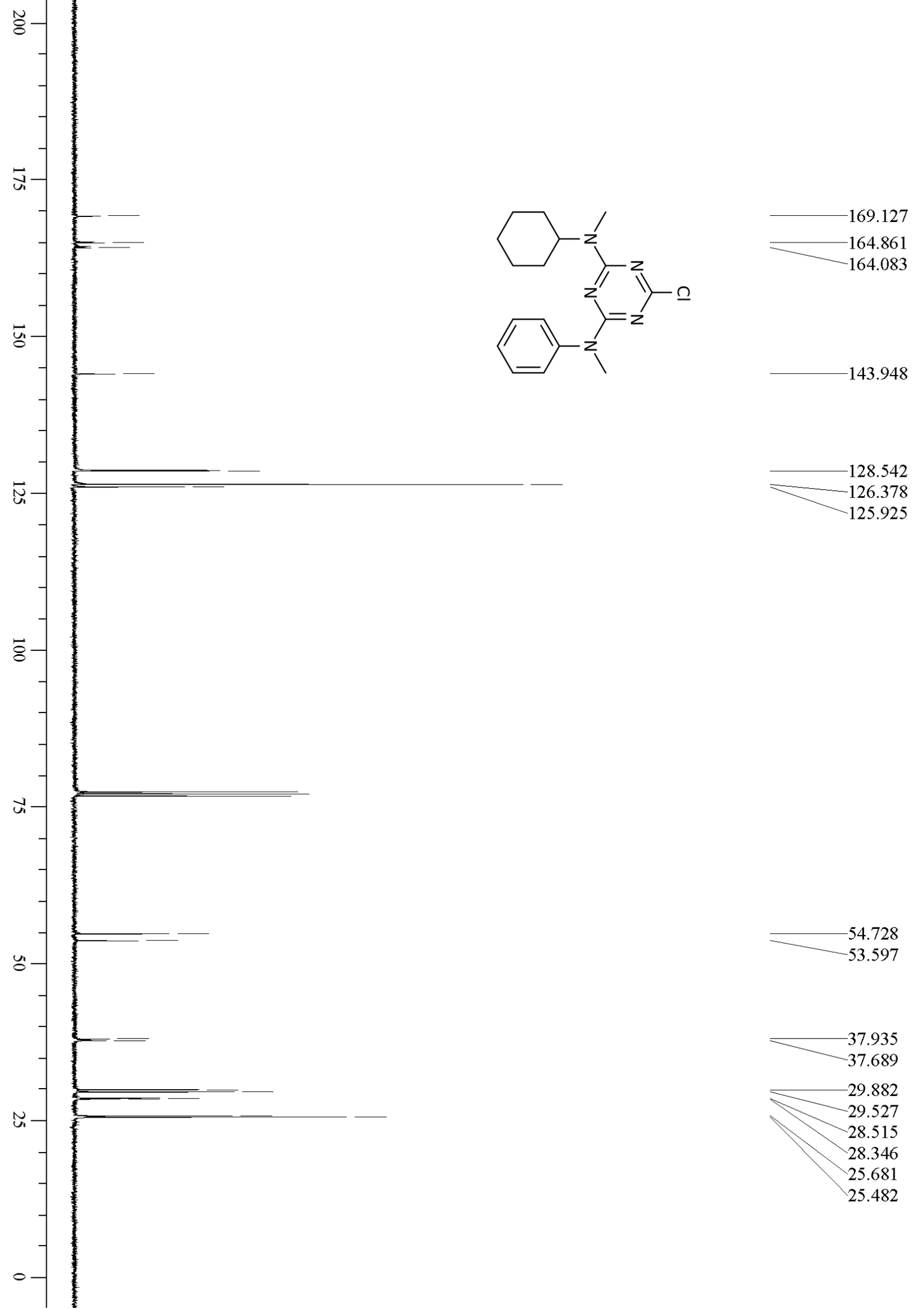
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N
N
N
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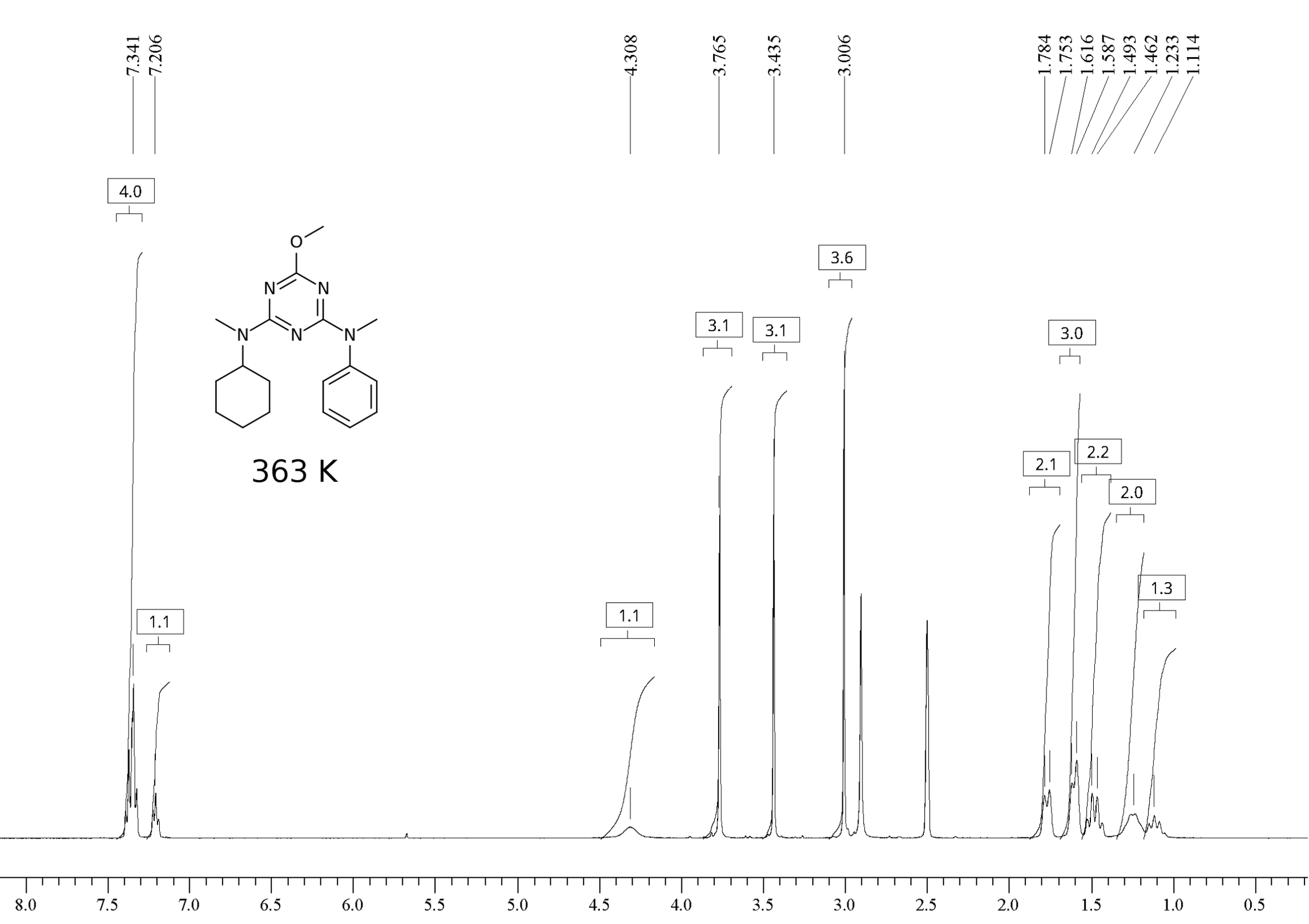
25.482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1.233
1.114
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1.1
1.1
3.1
3.1
3.6
3.0
2.1
2.2
2.0
1.3
363 K
8.0
7.5
7.0
6.5
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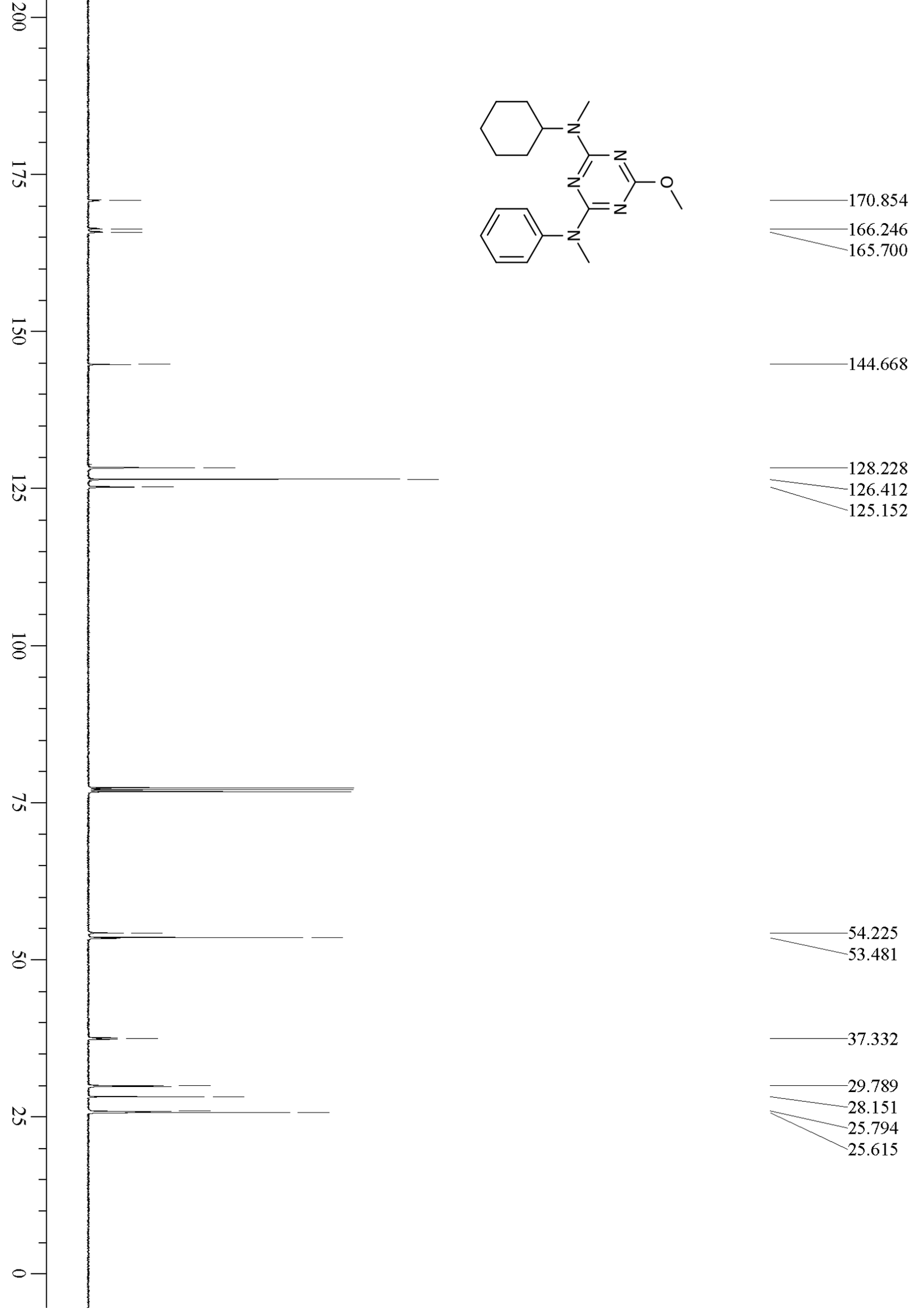
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N
N
N
N
O
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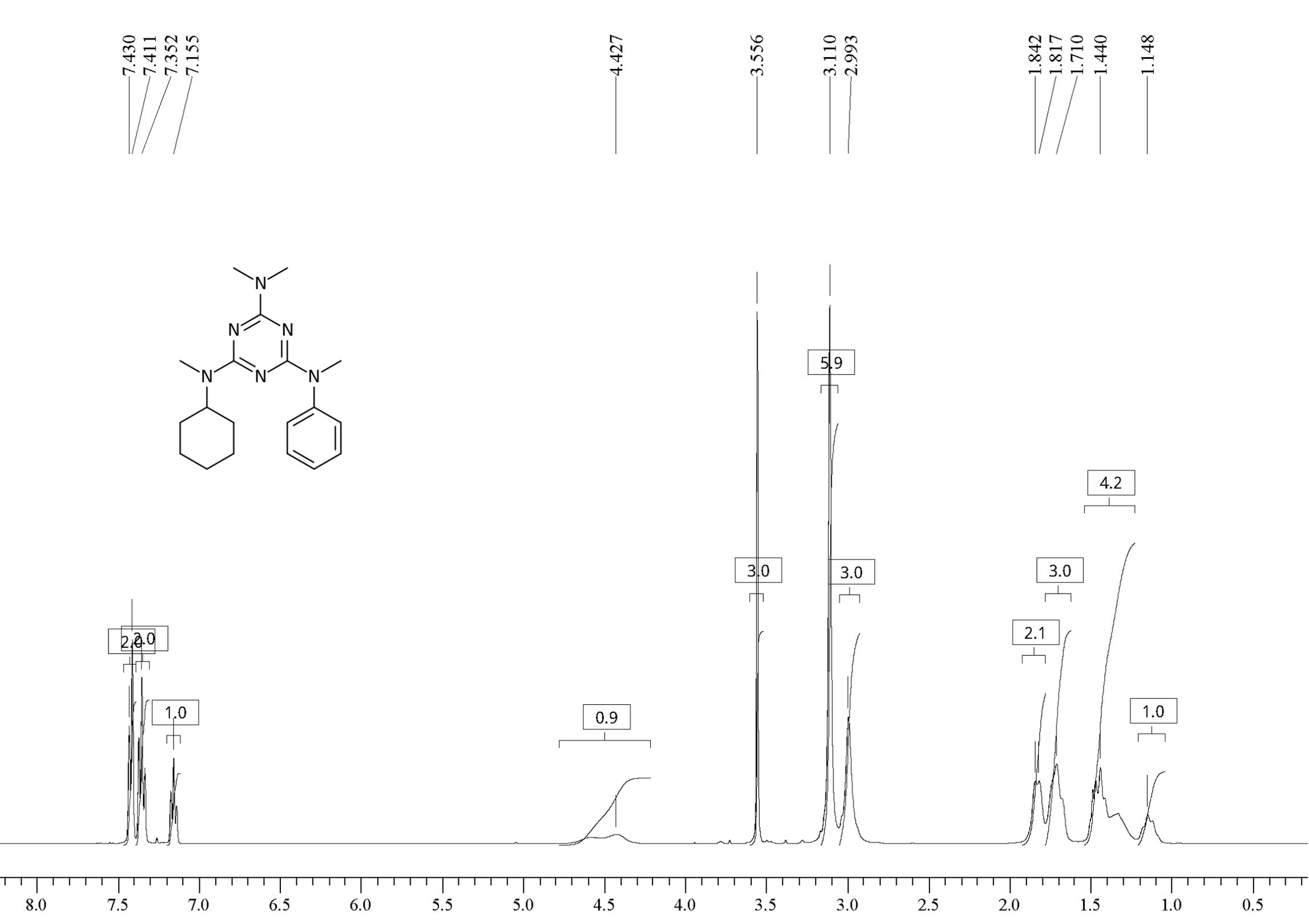
25.615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1.148
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5.9
3.0
2.1
3.0
4.2
1.0
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7.0
6.5
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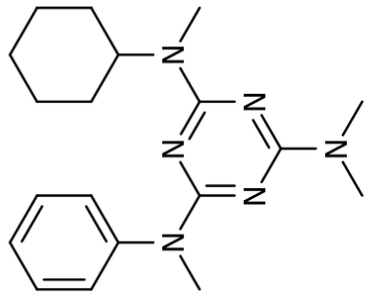

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124.112
53.415
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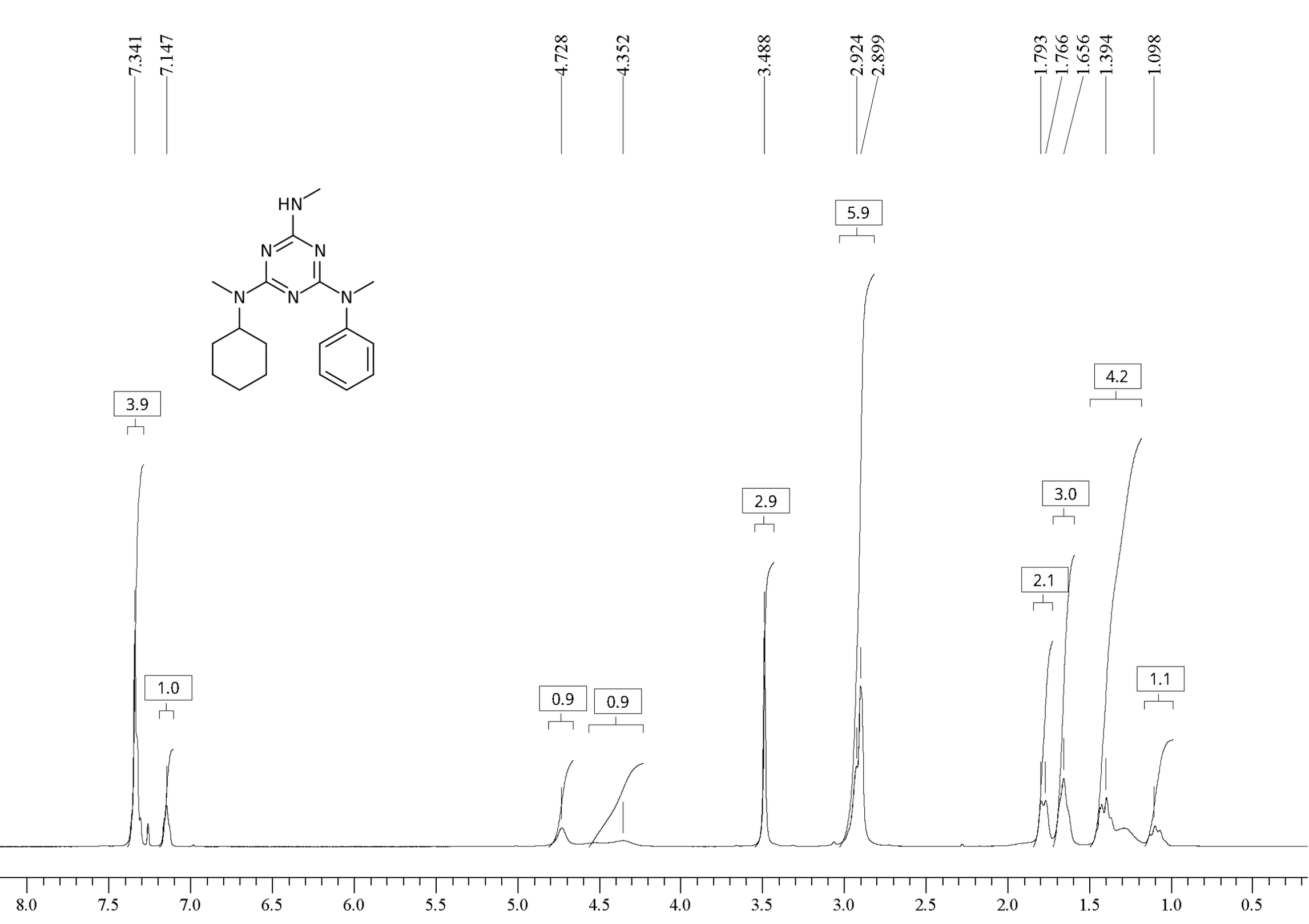
29.913
27.692
25.962
25.744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0.9
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5.9
2.1
3.0
4.2
1.1
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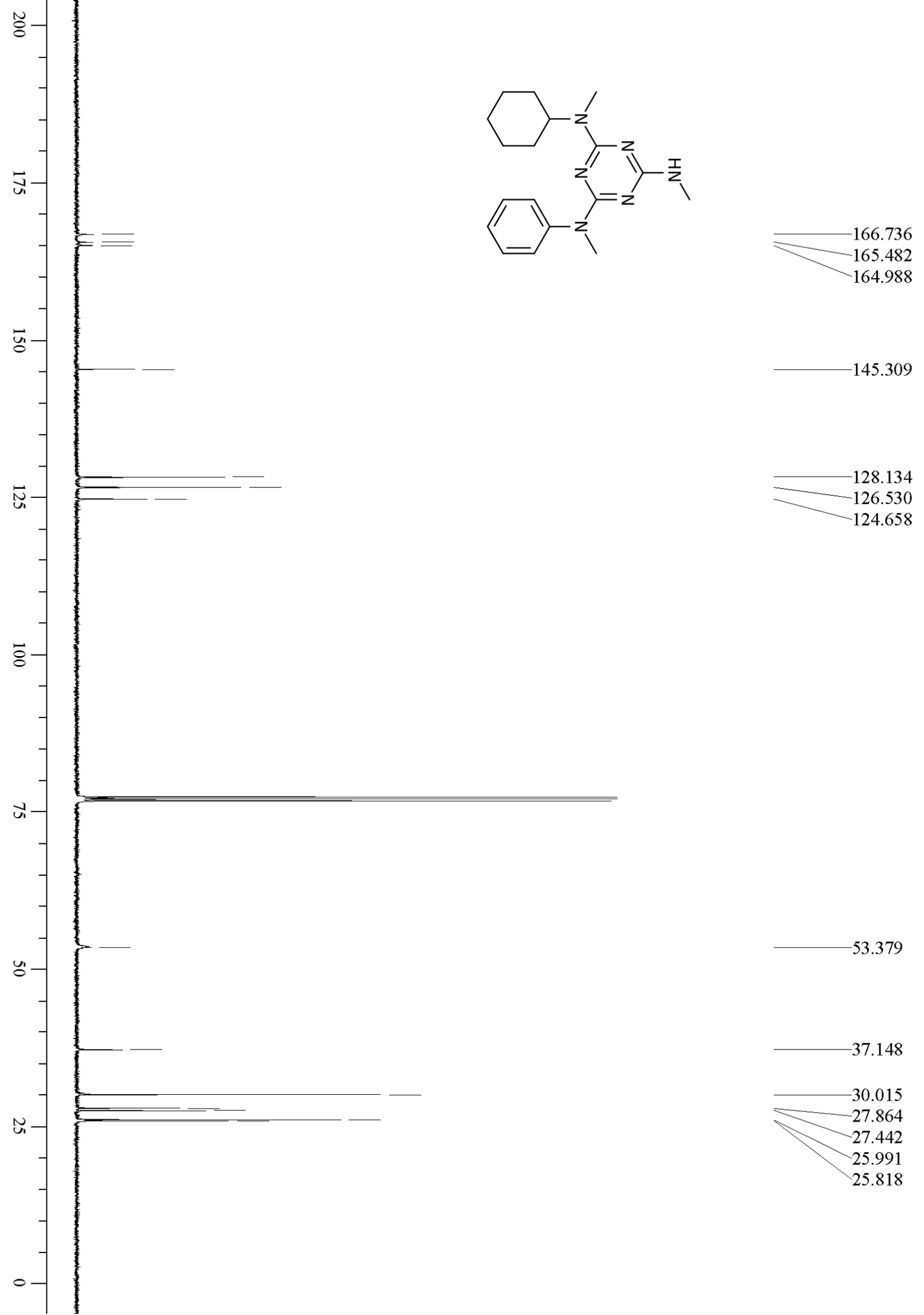
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30.015
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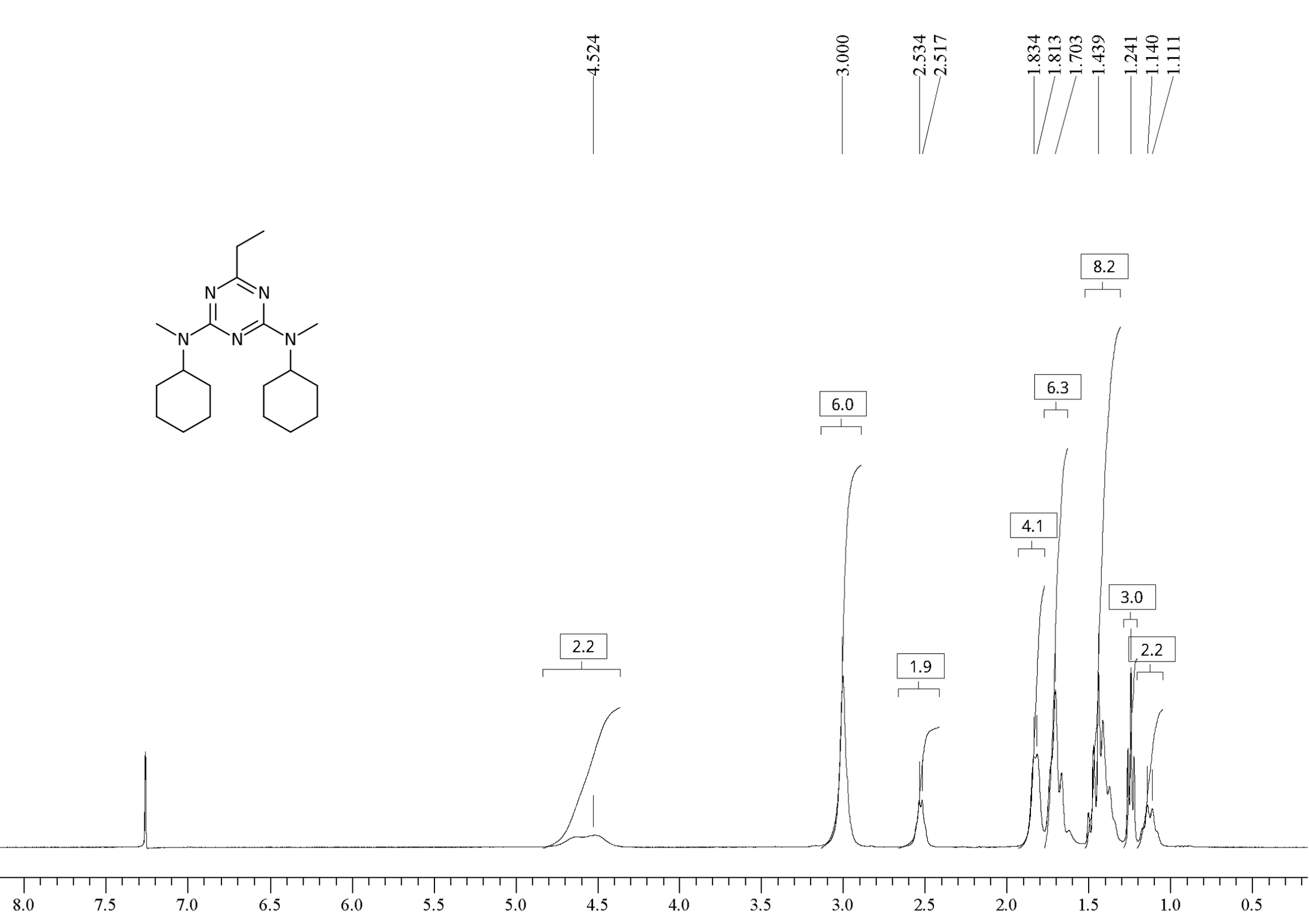
27.442
25.991
25.818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1.439
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1.111
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6.3
6.0
4.1
3.0
2.2
2.2
1.9
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N
N
N
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7.0
6.5
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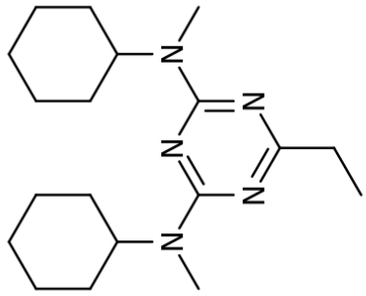

178.022

164.754

53.299

32.229

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27.959

26.073

25.847

11.645

200

175

150

125

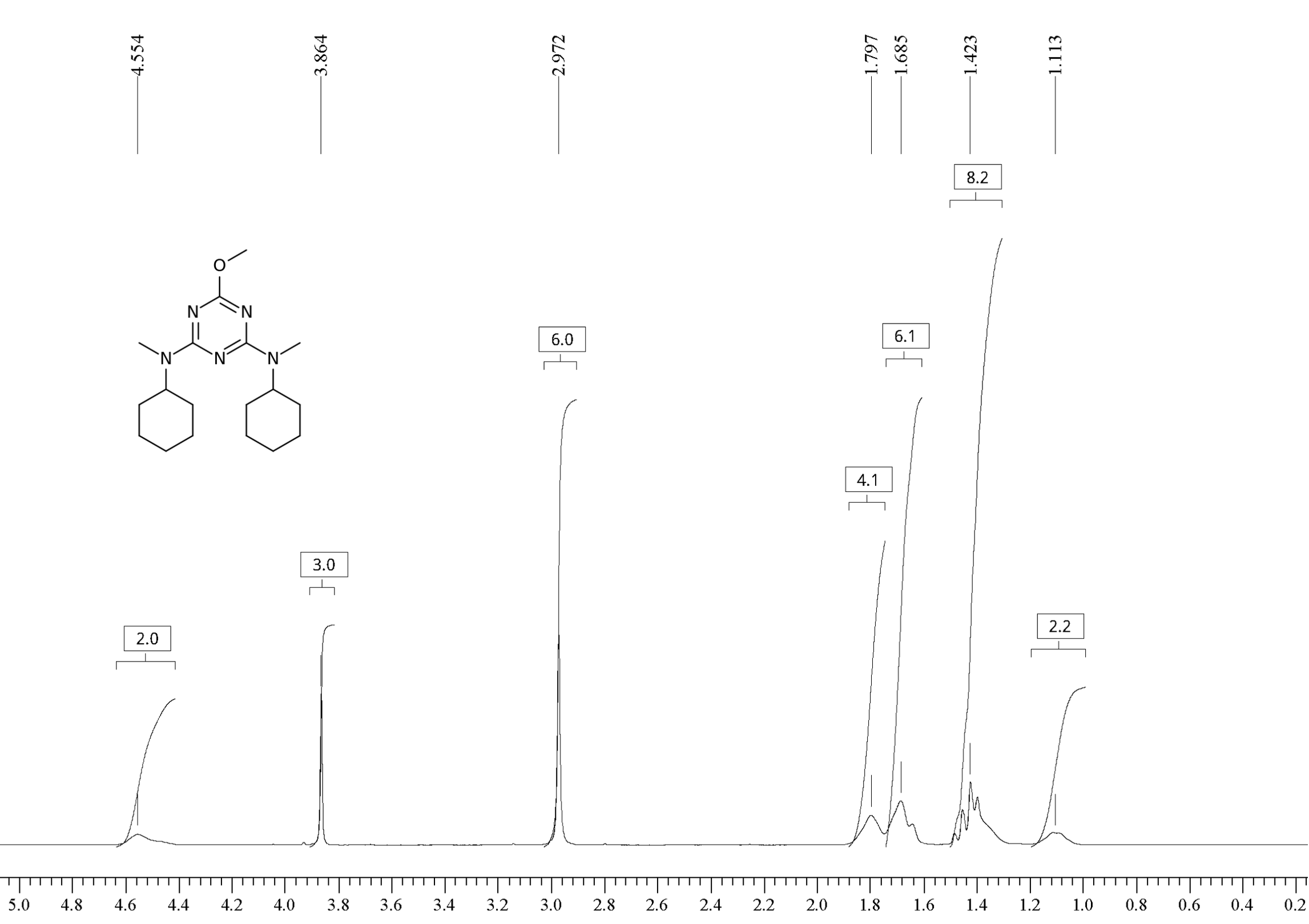
100

75

50

25

0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2.0
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O
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4.6
4.4
4.2
4.0
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3.6
3.4
3.2
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2.6
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1.4
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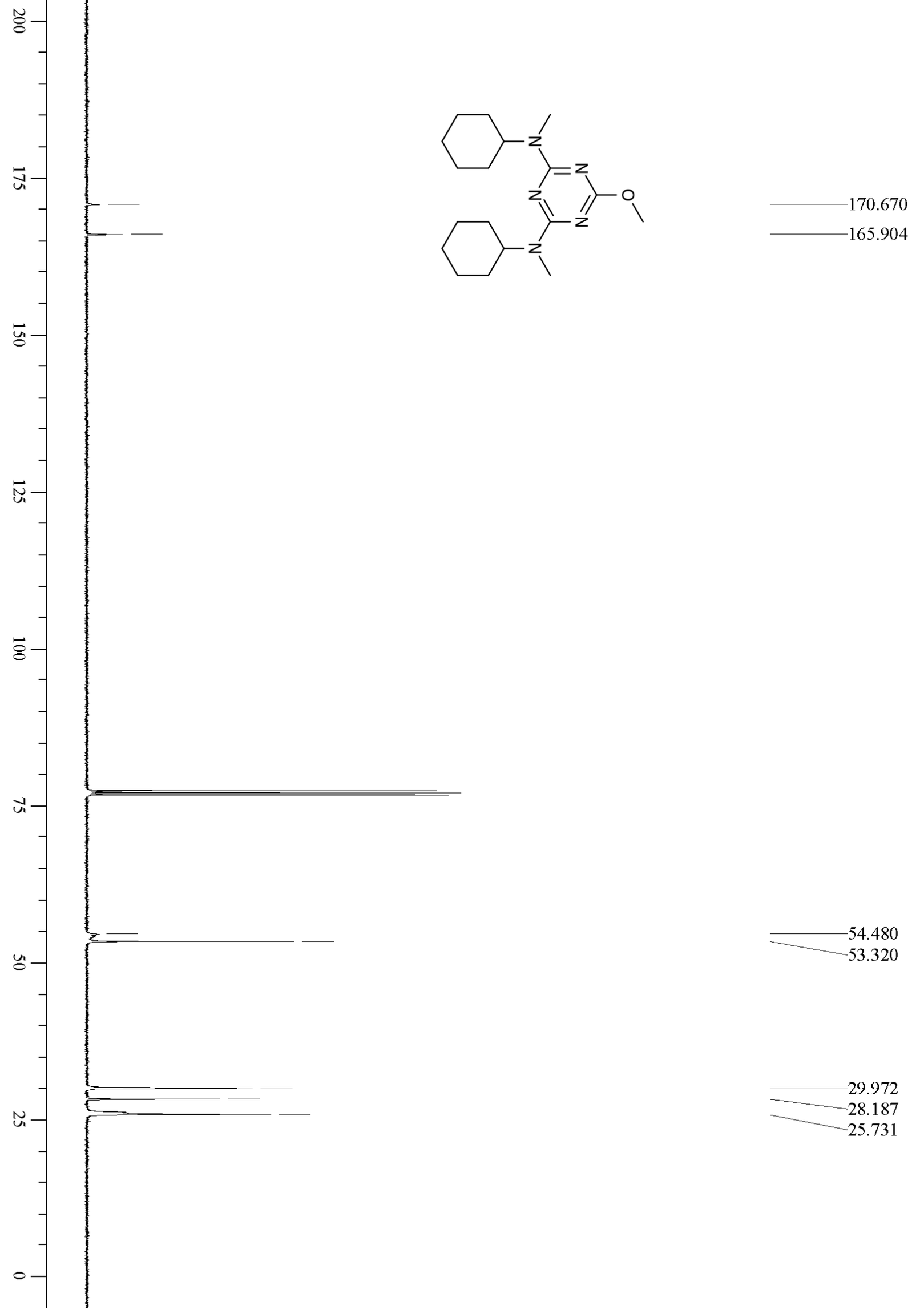
0.4
0.2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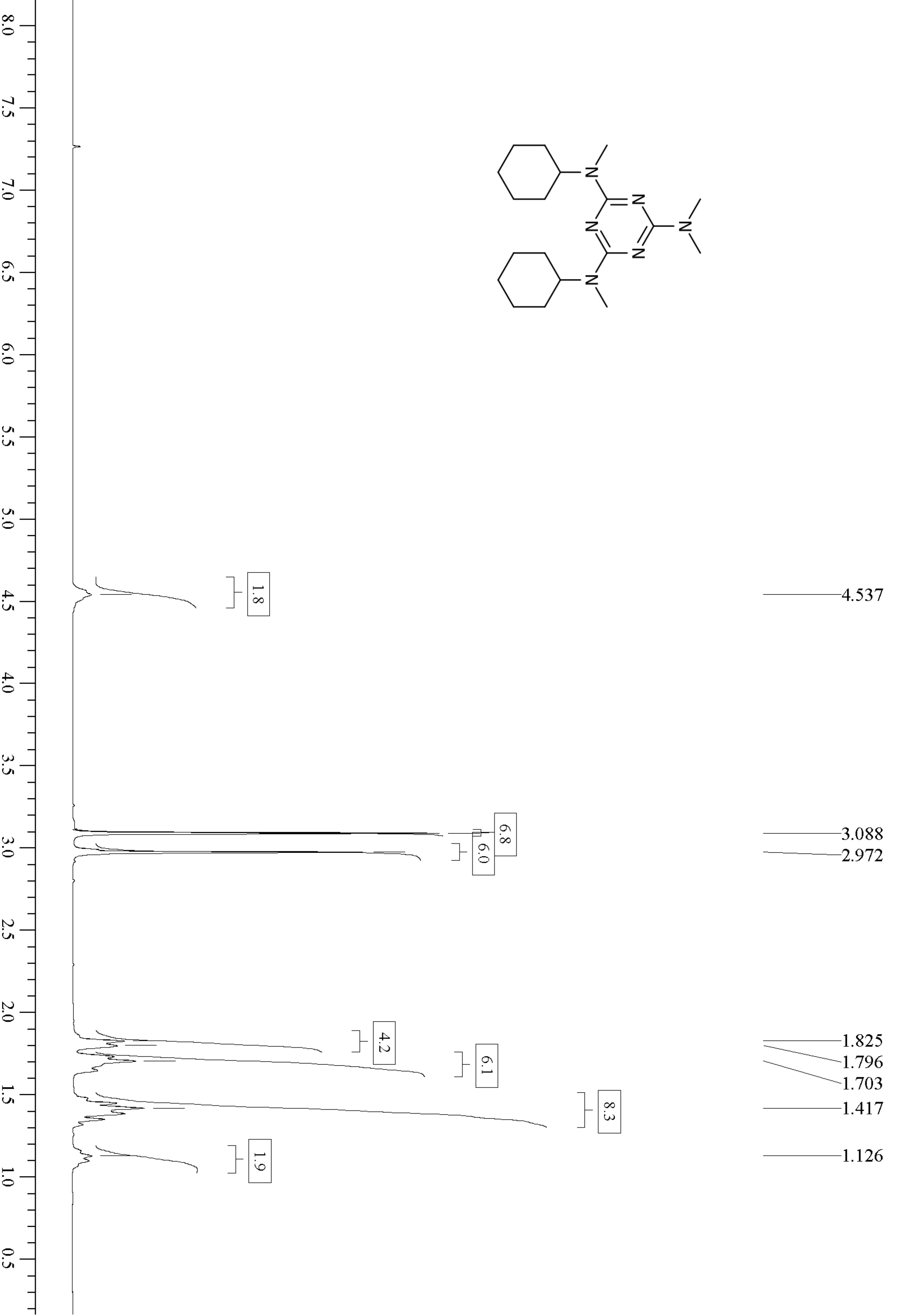
25.731



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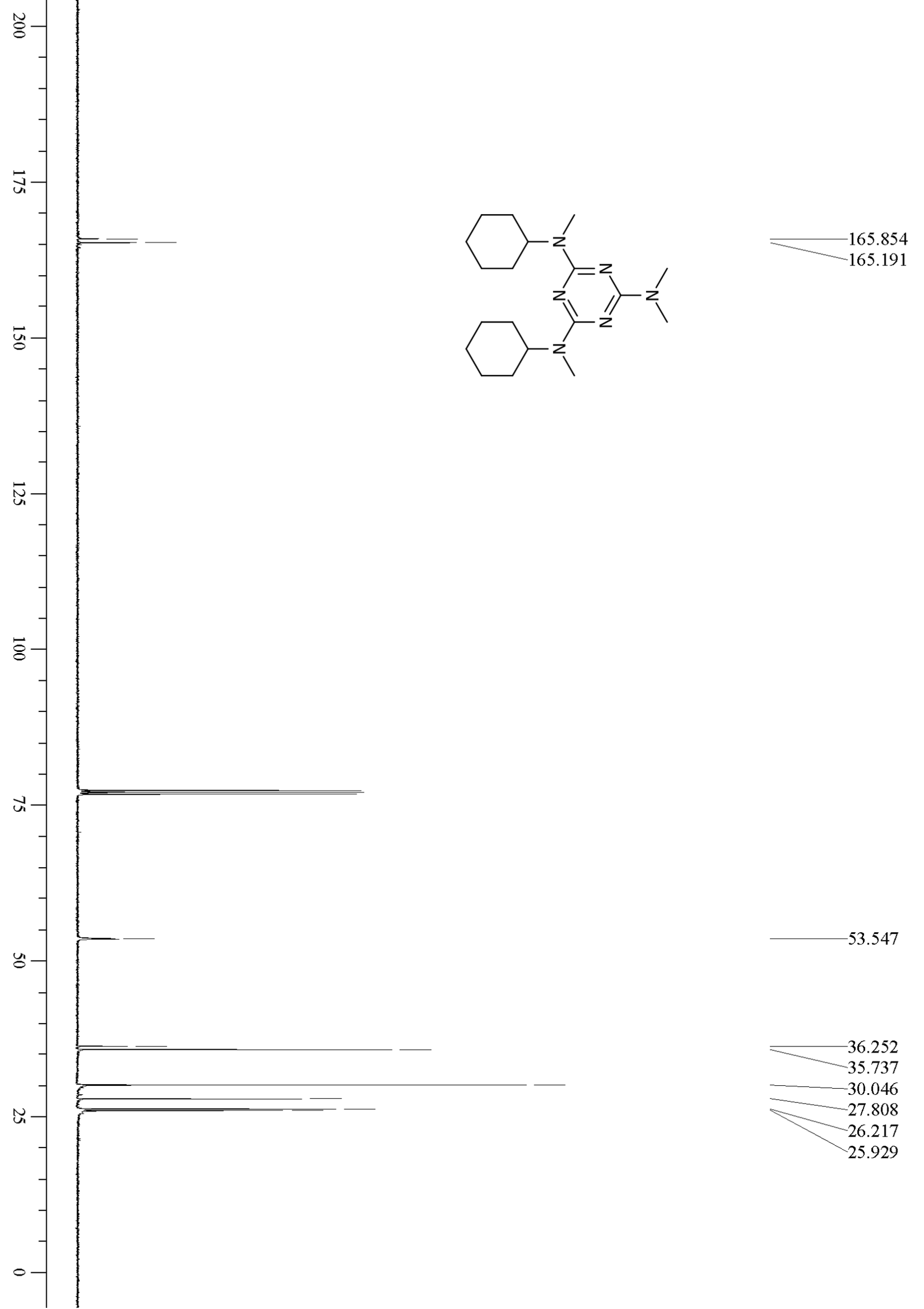
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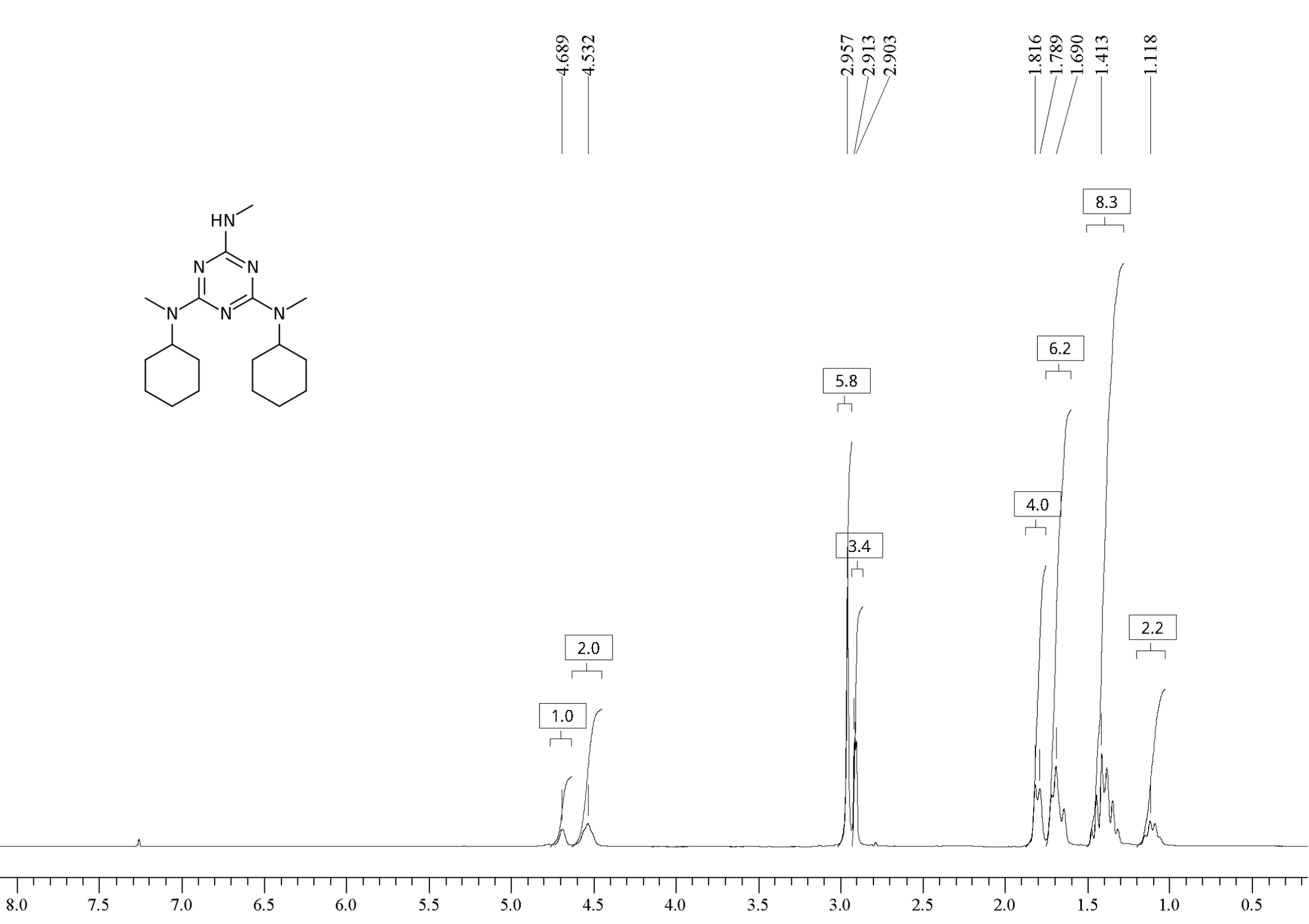
26.217
25.929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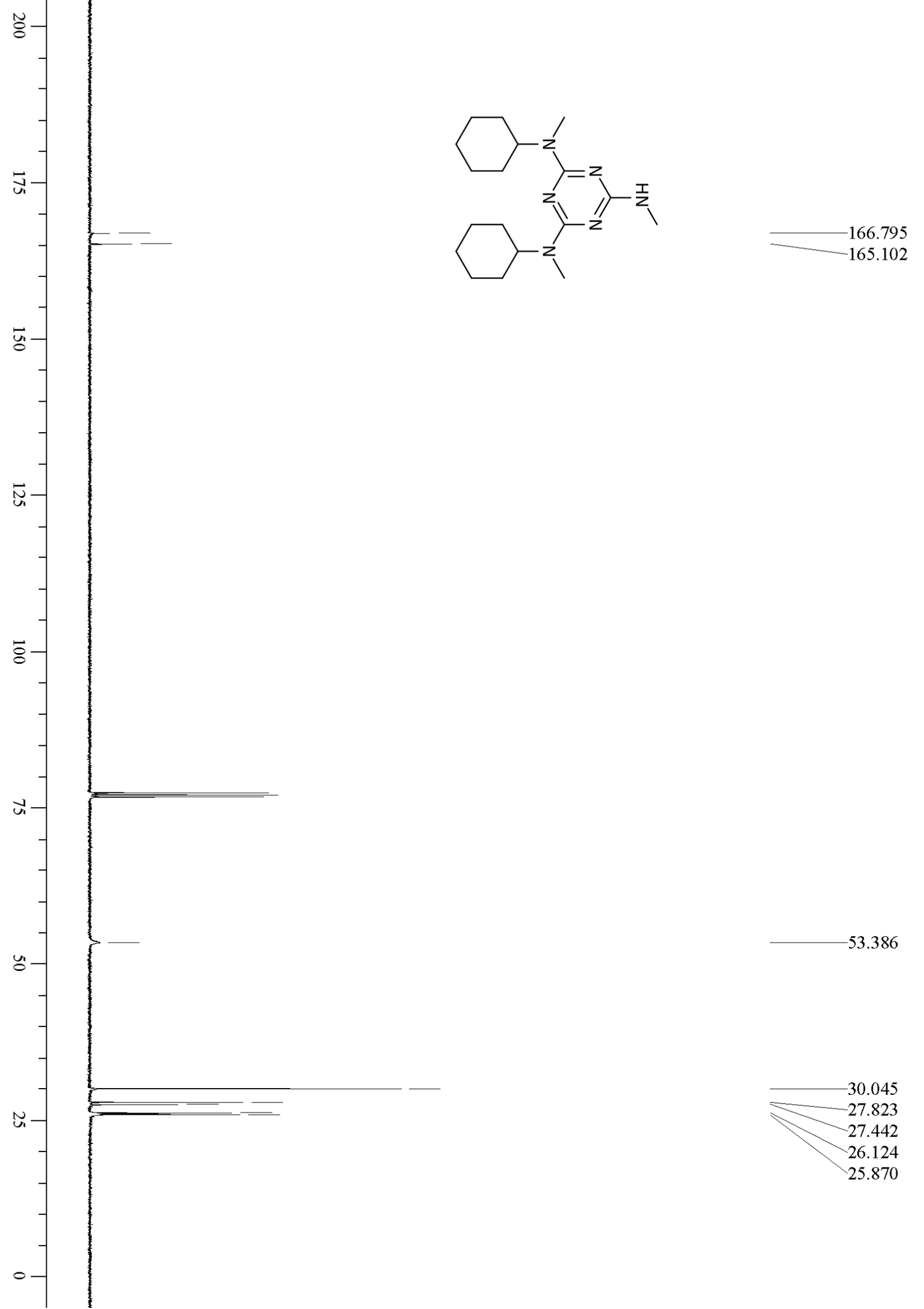
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