

Unraveling the interplay between hydrogen bonding and rotational energy barrier to fine-tune the properties of triazine molecular glasses

Supporting Information

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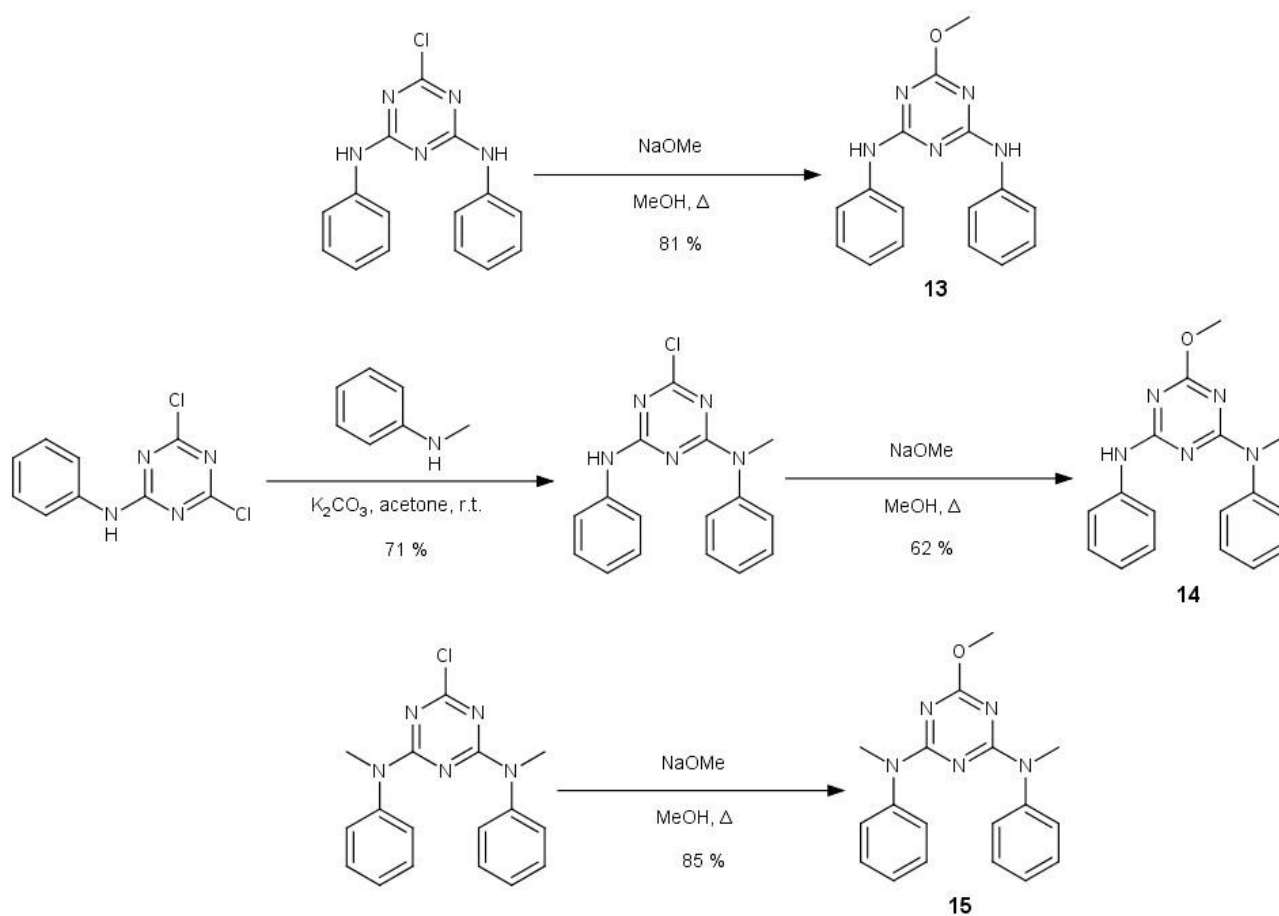
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Synthesis of compounds 13-15

To confirm the observed trends in the thermal behavior of compounds **1-12**, analogues **13-15** where both methylamino ancillary groups are replaced by phenylamino groups were synthesized in 62-85 % yield from the corresponding bis(phenylamino)chlorotriazines and sodium methoxide in methanol (Scheme S1) following a previously published procedure.¹



Scheme S1.

2-Methoxy-4-phenylamino-6-(N-methylphenylamino)-1,3,5-triazine (**14**)

2-Phenylamino-4,6-dichloro-1,3,5-triazine (1.00 g, 4.15 mmol) was dissolved in acetone (20 mL) in a round-bottomed flask equipped with a magnetic stirrer. K₂CO₃ (0.574 g, 4.15 mmol) was added, then the flask was placed in an ice bath. A solution of N-methylaniline (0.450 mL, 0.445 g, 4.15 mmol) in acetone (10 mL) was then slowly added at 0-5 °C under vigorous

stirring, after which the ice bath was removed and the mixture was stirred for 18h at ambient temperature, after which H₂O was added. The product was extracted with ethyl ether, the organic layer was washed successively with 1M aqueous HCl, aqueous NaHCO₃ and brine, dried over Na₂SO₄, filtered, and the solvent was evaporated under reduced pressure. Recrystallization from hot hexanes afforded 0.914 g 2-chloro-4-phenylamino-6-(N-methylphenylamino)-1,3,5-triazine (2.93 mmol, 71 %). T_m 126 °C; FT-IR (ATR/CH₂Cl₂) 3393, 3275, 3204, 3166, 3121, 3094, 3061, 3037, 2952, 2929, 2870, 1602, 1574, 1524, 1497, 1446, 1404, 1388, 1353, 1317, 1250, 1228, 1162, 1114, 1097, 1027, 976, 931, 900, 837, 800, 757, 735, 695, 627 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆, 363 K) δ 9.76 (s, 1H), 7.53 (d, ³*J* = 7.8 Hz, 2H), 7.47 (t, ³*J* = 8.1 Hz, 2H), 7.37 (m, 3H), 7.18 (t, ³*J* = 7.6 Hz, 2H), 6.99 (t, ³*J* = 7.1 Hz, 2H), 3.48 (s, 3H) ppm; ¹³C NMR (75 MHz, DMSO-*d*₆) δ 168.7, 165.5, 163.2, 143.9, 139.1, 129.5, 128.8, 127.3, 127.1, 123.2, 120.1, 38.6 ppm; HRMS (ESI, MNa⁺) calcd. for C₁₆H₁₄ClNaN₅ *m/e*: 334.0835, found: 334.0839.

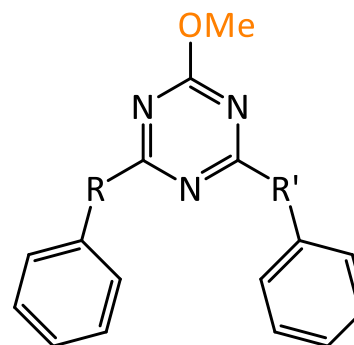
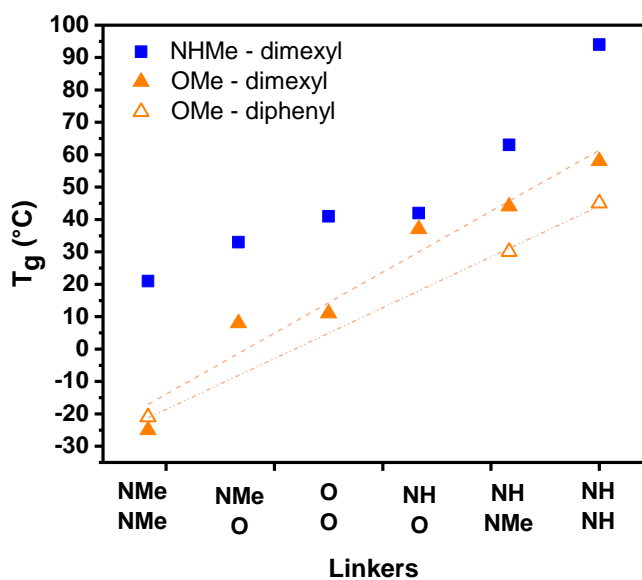
2-chloro-4-phenylamino-6-(N-methylphenylamino)-1,3,5-triazine (0.814 g, 2.61 mmol) was dissolved in methanol (20 mL) in a round-bottomed flask equipped with a magnetic stirrer and a water-jacketed condenser. A methanolic NaOMe solution (25 wt%, 0.846 mL, 3.92 mmol) was added, and the mixture was refluxed for 18 h. The volatiles were concentrated under vacuum, then CH₂Cl₂ and H₂O were added, and both layers were separated. The organic layer was recovered, dried over Na₂SO₄, filtered, and the solvent was evaporated under reduced pressure. Recrystallization from hot hexanes afforded 0.494 g of pure compound **14** (1.61 mmol, 62 %). T_g 30 °C, T_c 102 °C, T_m 141 °C; FT-IR (ATR/CH₂Cl₂) 3391, 3275, 3191, 3158, 3100, 3061, 3033, 3011, 2994, 2951, 2906, 2868, 1610, 1602, 1577, 1561, 1539, 1494, 1462, 1443, 1405, 1389, 1358, 1299, 1265, 1245, 12010, 1180, 1156, 1120, 1097, 1052, 1028, 989, 961, 901, 853, 810, 756, 736, 694, 670 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆, 363 K) δ 9.17 (br s, 1H), 7.61 (d, ³*J* = 8.1 Hz, 2H), 7.43 (t, ³*J* = 8.1 Hz, 2H), 7.37 (d, ³*J* = 7.1 Hz, 2H), 7.29 (t, ³*J* = 7.1 Hz, 1H), 7.17 (t, ³*J* = 8.1 Hz, 2H), 6.94 (t, ³*J* = 7.3 Hz, 1H), 3.86 (s, 3H), 2.50 (s, 3H) ppm; ¹³C NMR (75 MHz, DMSO-*d*₆) δ 170.9, 166.8, 165.1, 144.6, 140.1, 129.2, 128.6, 127.3, 126.4, 122.4, 120.0, 54.1, 38.1 ppm; HRMS (ESI, MNa⁺) calcd. for C₁₇H₁₇NaN₅O *m/e*: 330.1331, found: 330.1336.

2-Methoxy-4,6-bis(N-methylphenylamino)-1,3,5-triazine (15)

2-chloro-4,6-bis(N-methylphenylamino)-1,3,5-triazine (1.44 g, 4.43 mmol) was dissolved in methanol (30 mL) in a round-bottomed flask equipped with a magnetic stirrer and a water-jacketed condenser. A methanolic NaOMe solution (25 wt%, 1.44 mL, 6.65 mmol) was added, and the mixture was refluxed for 18 h. The volatiles were concentrated under vacuum, then CH₂Cl₂ and H₂O were added, and both layers were separated. The organic layer was recovered, dried over Na₂SO₄, filtered, and the solvent was evaporated under reduced pressure and dried thoroughly to yield 1.22 g of compound 15 (3.79 mmol, 85 %). T_g -21 °C; FT-IR (ATR/CH₂Cl₂) 3090, 3061, 3035, 3010, 2980, 2948, 2895, 2866, 2808, 2790, 1603, 1561, 1528, 1494, 1477, 1460, 1444, 1385, 1358, 1299, 1270, 1212, 1162, 1105, 1028, 996, 977, 955, 906, 835, 810, 764, 735, 696 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, 298 K) δ 7.30 (m, 8H), 7.17 (t, ³J = 7.0 Hz, 2H), 3.78 (s, 3H), 3.45 (s, 6H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 170.7, 166.3, 144.3, 128.5, 126.4, 125.5, 53.8, 37.7 ppm; HRMS (ESI, MNa⁺) calcd. for C₁₈H₁₉NaN₅O *m/e*: 344.1487, found: 344.1493.

Table S1. Comparison of the glass transition temperature (T_g), crystallisation temperature (T_c) and melting temperature (T_m) of compounds **1-12**.

Linkers	Headgroup							
	NHMe				OMe			
		T_g (°C)	T_c (°C)	T_m (°C)		T_g (°C)	T_c (°C)	T_m (°C)
NH, NH	1	94	-	-	2	58	-	168
O,O	5	41	58, 100	180	3	11	98	129
NH, O	4	42	122	178	6	37	-	-
NH, NMe	7	63	-	-	9	44	126	148
NMe, NMe	8	21	-	-	10	-25	-	-
NMe, O	11	33	126	152	12	8	-	129



Linker: R, R' = NH or NMe

Figure S1. Evolution of T_g according to their headgroup and linkers. Compounds bearing an OMe headgroup and diphenyl moieties as shown on the right (dashed-dotted line, shown at the right of the figure and represented by open symbols) follow the trend of the dimexyl (dashed line) for the Ome headgroup series of compounds.

Chemometrics processing of the spectra

From the experimental spectral input data, the algorithm first defines the pure variables (the wavenumbers that present the highest ratio of standard deviation to the mean)² to enable the calculation of the pure component spectra, *i.e.* the spectra that would be equivalent to a totally “free” NH species and a totally “bonded” NH species in our case (see Figure S2). These two spectra can then be used in a linear combination to reproduce the experimental spectral input data. Principal component analysis (PCA) was conducted prior to the SMMA and revealed that, for all compounds, two components account for 97 to 99% of the variance of the experimental spectral input data, meaning that our system can be reasonably well described using solely the “free” and “bonded” components.^{2,3,4}

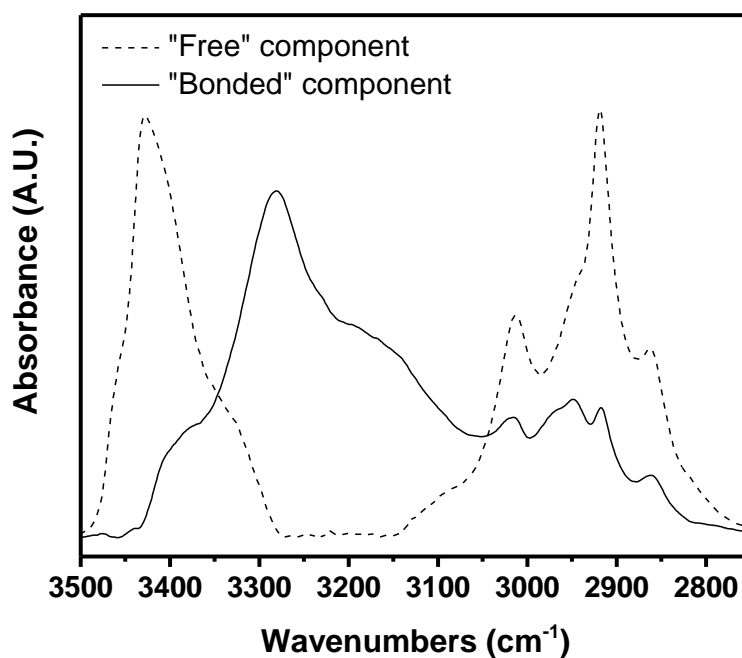


Figure S2. Pure components spectra corresponding to the “free” NH species and the “bonded” NH species extracted from the variable-temperature IR spectra of the NHMe/NH,NH compound **1**.

Figure S3 compares the original (experimental) and the reconstructed data. In all cases, the calculated relative root sum of square difference (rrssq, which calculates the difference between the two data sets) lies between 0.003 and 0.015, indicating an excellent agreement

between the two sets of spectra and confirming the uselessness of considering a third component to describe the system. Indeed, the intensity of the residuals is two orders of magnitude lower than the intensity of the original spectra. Sometimes, residuals show what could be considered as structured data, where a derivative-shaped band showed in between the “free” and the “bonded” bands (around 3325 cm^{-1} for the NHMe/NH,NH compound **1**, see the right panel of Figure S3). A similar third component was observed in other H-bonded systems and defined as the intermediate case between the two species by Šašić *et al.*, among others.² In the present case, and in the cases reported in the literature, this component does not contribute significantly to the data, accounting for less than 1% of the original spectra. A two-component representation was thus chosen as a suitable model for the systems (without ruling out the existence of a minor third species in the real system). The fractions of each species displayed in Figure 3 of the main text correspond to the multiplying factor needed to reconstruct the spectral data from the two corresponding pure component spectra. It must be emphasized that we do not claim that these fractions, although absolute (versus relative), stand as the “real” numbers. Indeed, Dupuy *et al.* have demonstrated that quantification with this SMMA method leads to a relative error of 10%.⁵ However, we believe that the comparison of this quantification is still meaningful because the data processing was done identically for all compounds.

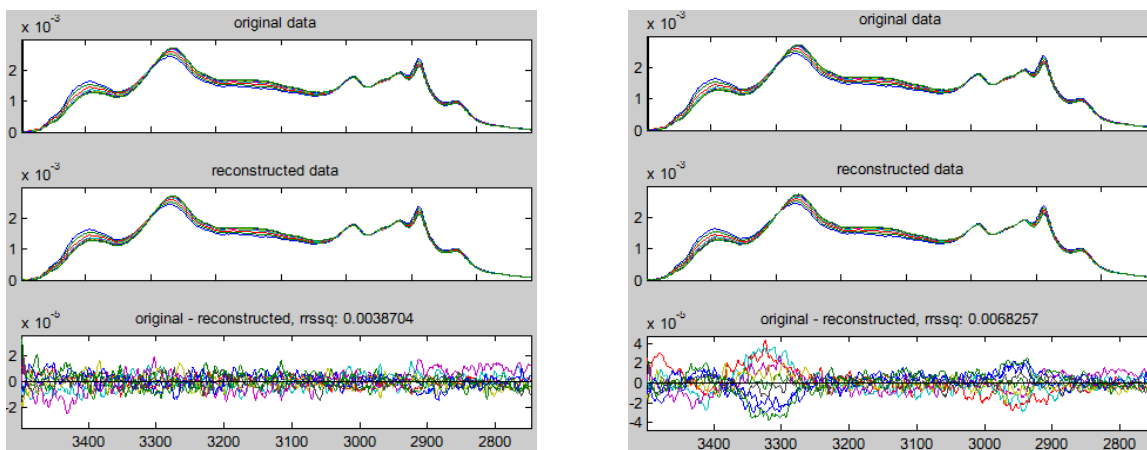


Figure S3. Reconstructed original spectra of NHMe/NH,NH compound **1** for two independent samples using two pure component spectra. In the left panel, no evidence of a residual component is found while a small contribution, larger at extreme temperatures, is found around 3325 cm^{-1} in the right panel.

Table S2. Average fraction of bonded NH (\pm standard deviation for three measurements) at different temperatures for the compounds studied by variable-temperature IR spectroscopy.

Linkers	Headgroup							
	NHMe				OMe			
		$T_g - 20$	T_g	$T_g + 40$		$T_g - 20$	T_g	$T_g + 40$
NH, NH	1	0.77 ± 0.02	0.74 ± 0.01	0.66 ± 0.01	2	0.85 ± 0.01	0.83 ± 0.01	0.76 ± 0.01
O, O	5	-	-	-	3	-	-	-
NH, O	4	-	0.86 ± 0.01	0.79 ± 0.02	6	-	0.85 ± 0.01	0.75 ± 0.01
NH, NMe	7	0.77 ± 0.02	0.73 ± 0.02	0.60 ± 0.03	9	-	0.8 ± 0.1	0.72 ± 0.1
NMe, NMe	8	0.73 ± 0.02	0.71 ± 0.01	0.55 ± 0.02	10	-	-	-
NMe, O	11	-	0.81 ± 0.02	0.67 ± 0.01	12	-	-	-

Calculation of the enthalpy of H-bond formation

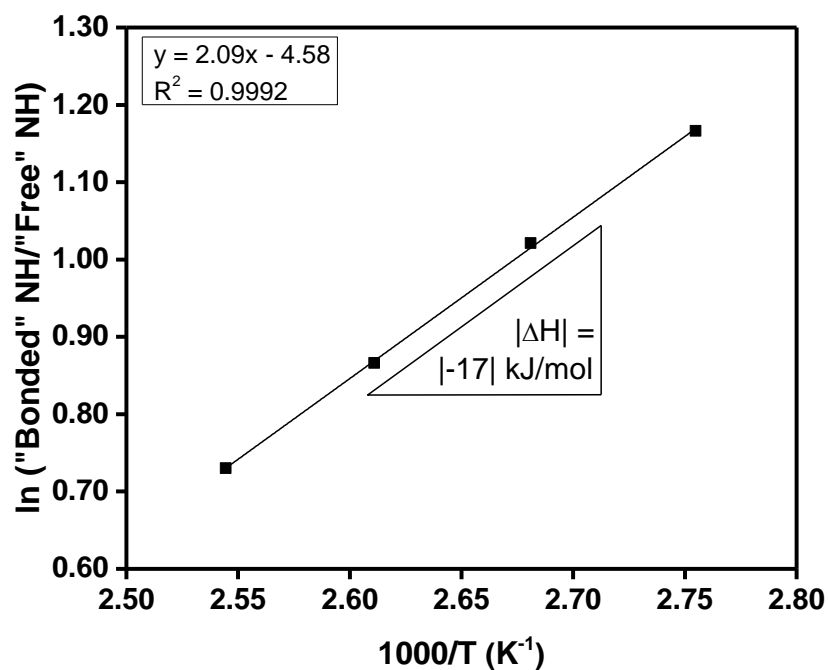


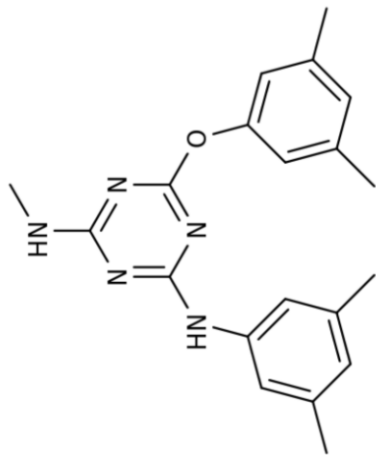
Figure S4. Construction of the van't Hoff plot from the “bonded” and “free” NH fractions of the NHMe/NH,NH (1). The value of the slope gives access to the ΔH of H-bonds formation.

Table S3. Enthalpy of H-bond formation (\pm standard deviation for three measurements) for the compounds studied by variable-temperature IR spectroscopy.

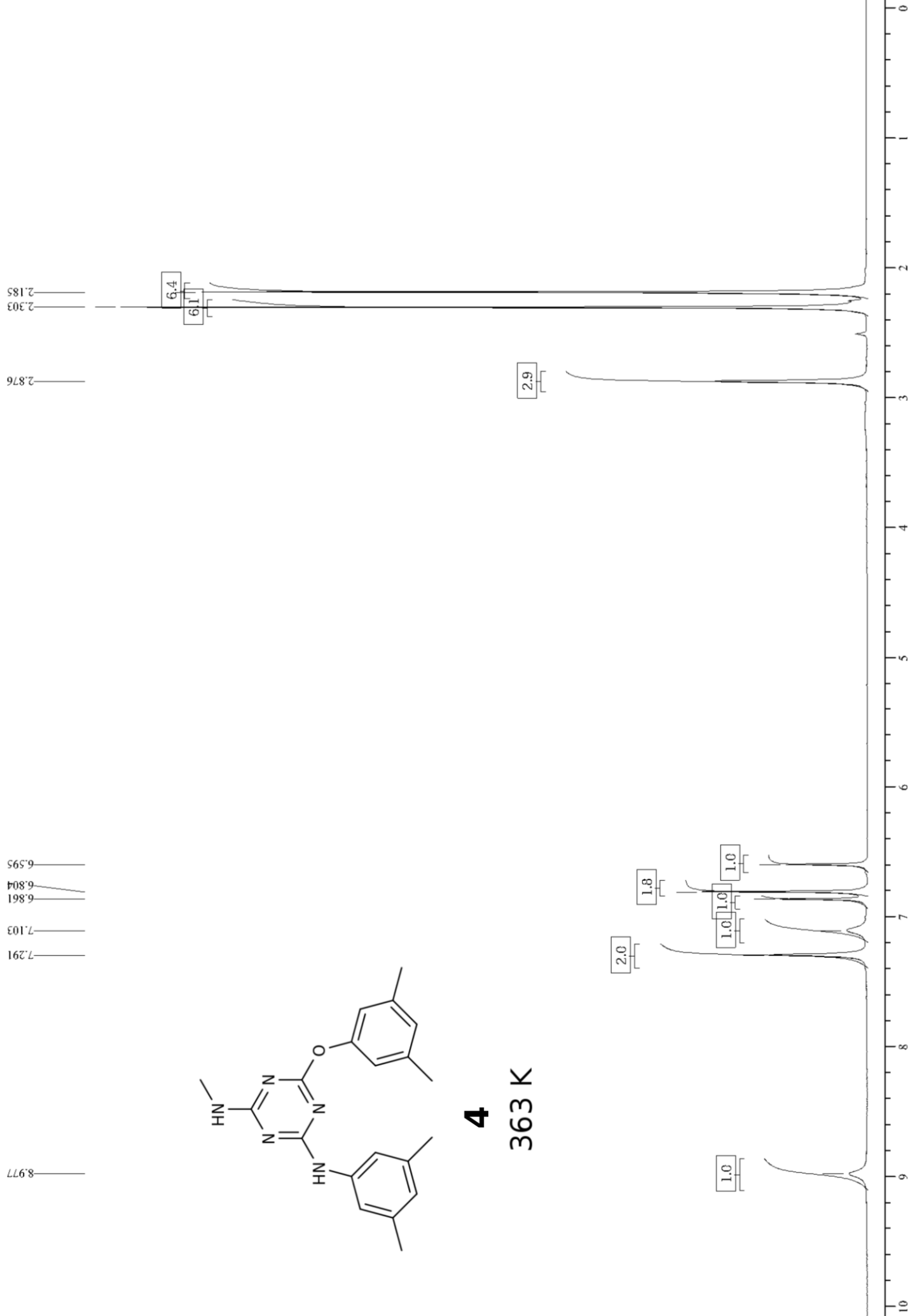
Linkers	Headgroup			
	NHMe		OMe	
	kJ/mol		kJ/mol	
NH, NH	1	17 ± 2	2	12 ± 1
O,O	5	-	3	-
NH, O	4	16 ± 1	6	16 ± 1
NH, NMe	7	17.8 ± 0.4	9	13 ± 2
NMe, NMe	8	23 ± 2	10	-
NMe, O	11	19 ± 2	12	-

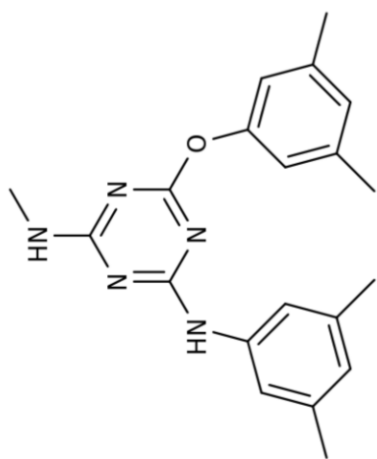
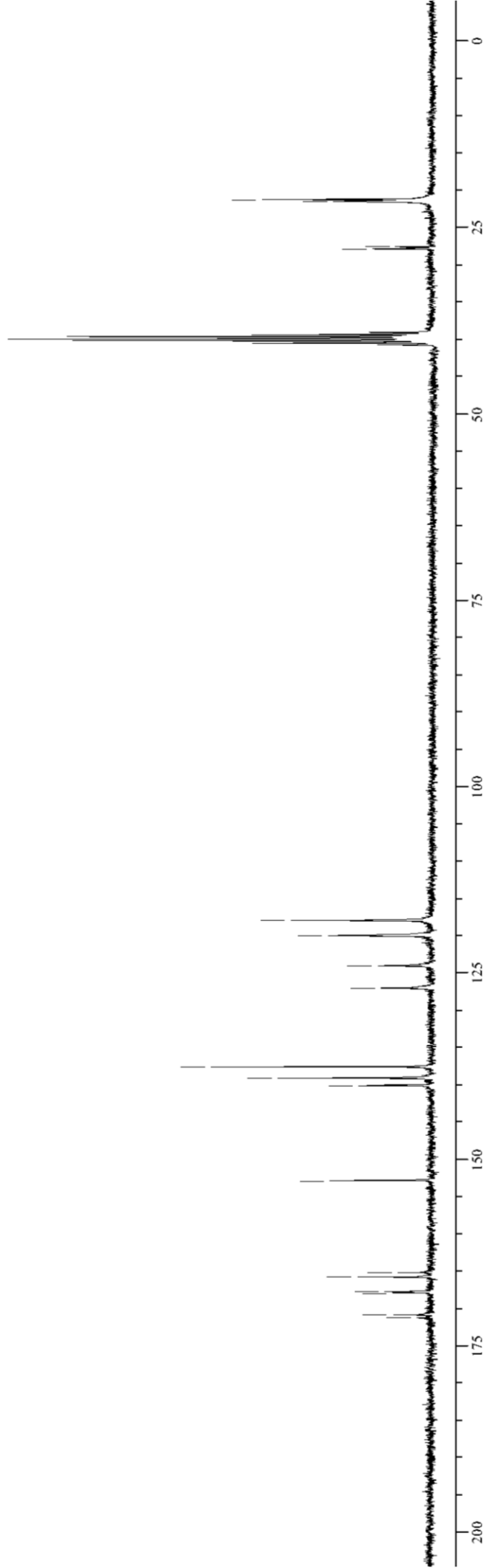
References

1. Lebel, O., Maris, T., Perron, M.-È., Demers, E., Wuest, J. D. *J. Am. Chem. Soc.* **2006**, *128*, 10372.
2. Šašić, S., Segtnan, V. H., Ozaki, Y. *J. Phys. Chem. A* **2002**, *106*, 760.
3. Libnau, F. O., Toft, J., Christy, A. A., Kvalheim, O. M. *J. Am. Chem. Soc.* **1994**, *116*, 8311.
4. Segtnan, V. H., Šašić, Š., Isaksson, T., Ozaki, Y. *Anal. Chem.* **2001**, *73*, 3153.
5. Dupuy, N., Batonneau, Y. *Anal. Chim. Acta* **2003**, *495*, 205.



4
363 K





4

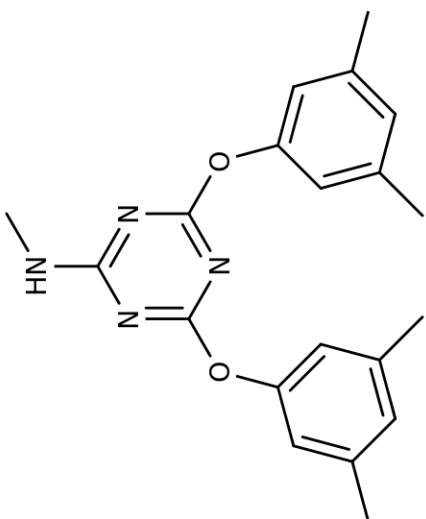
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171.232



5

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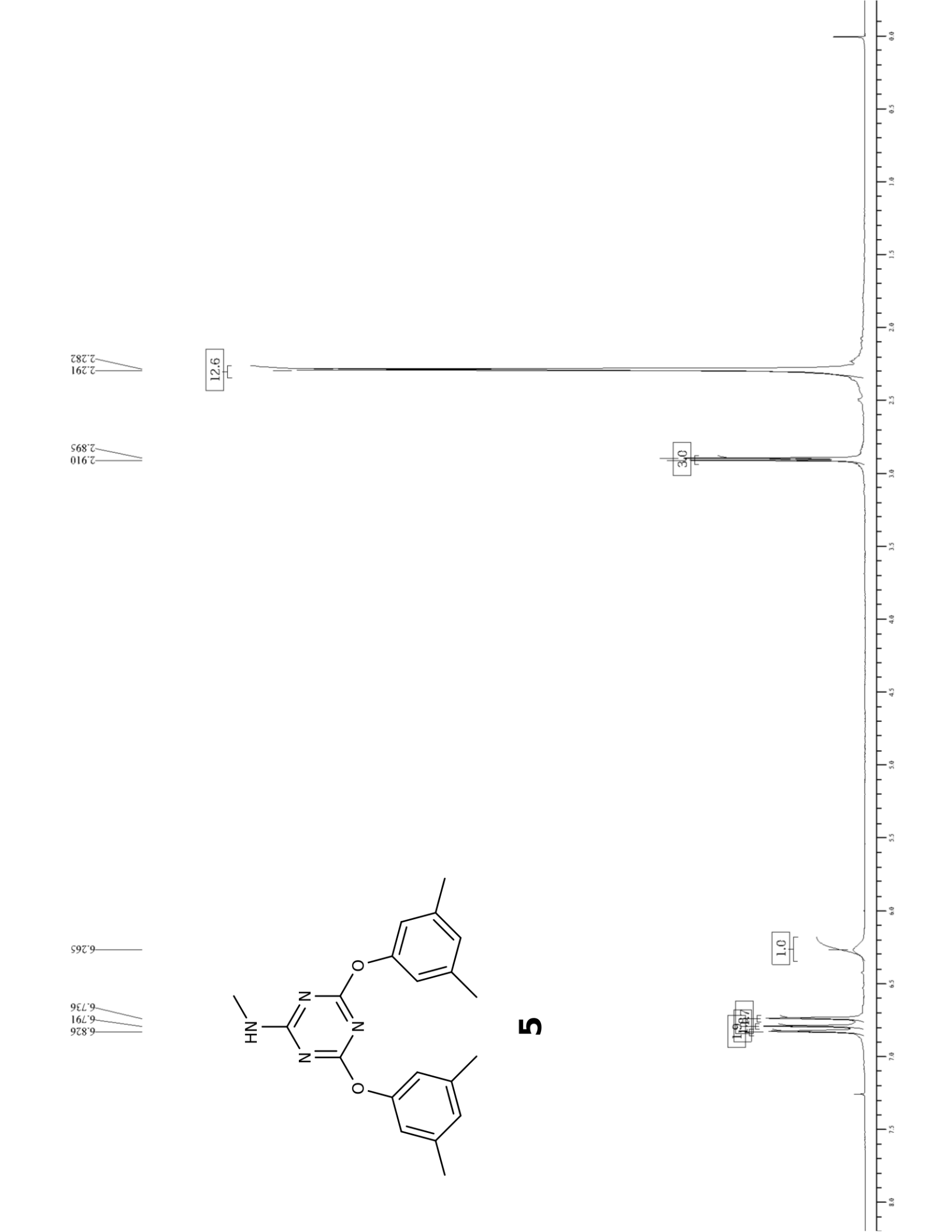
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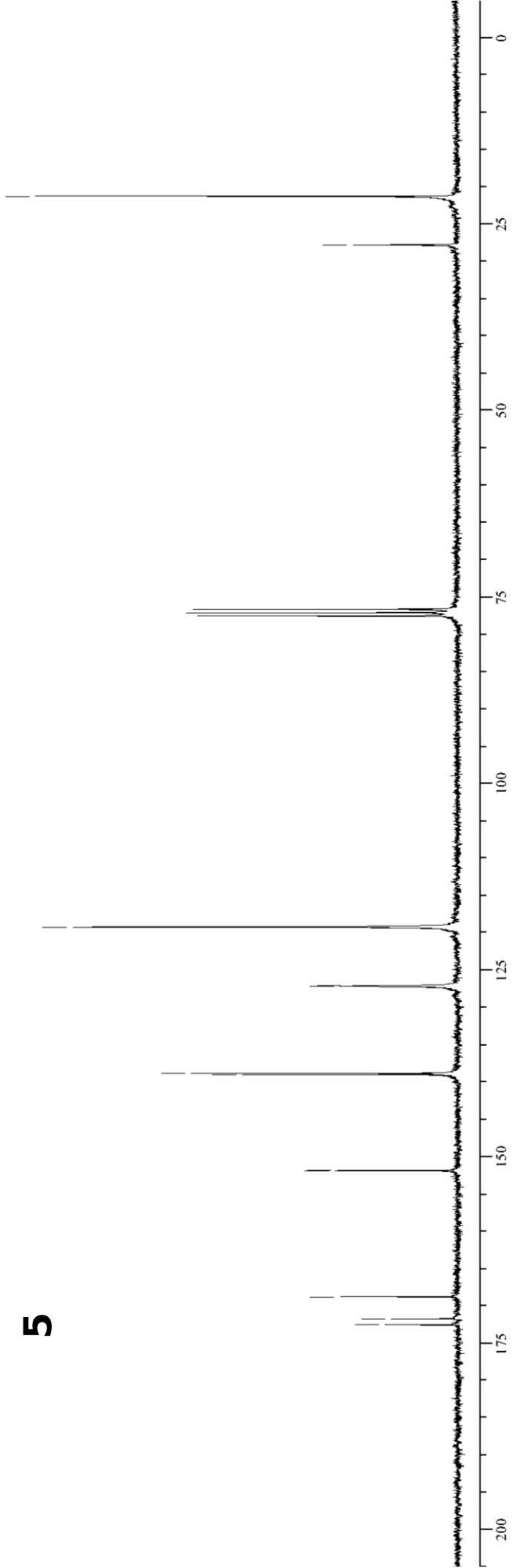
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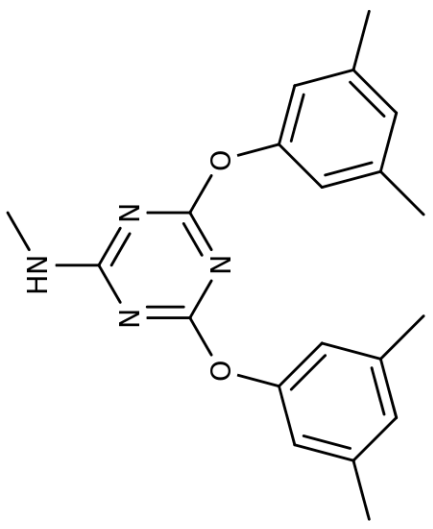
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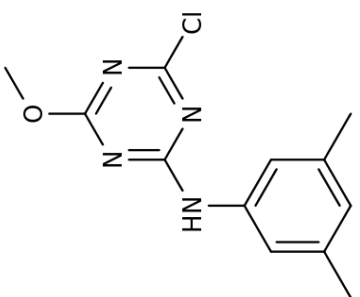
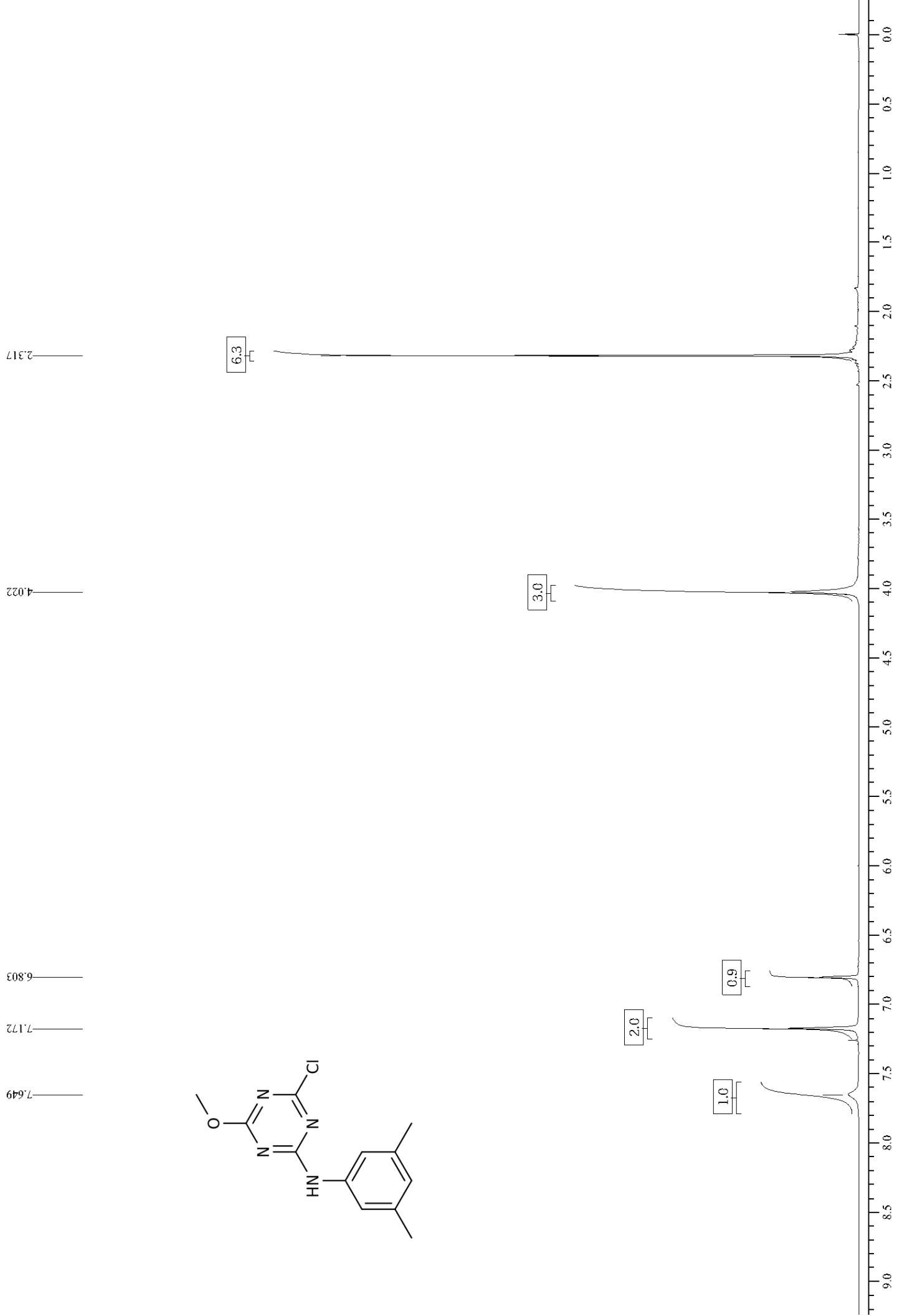
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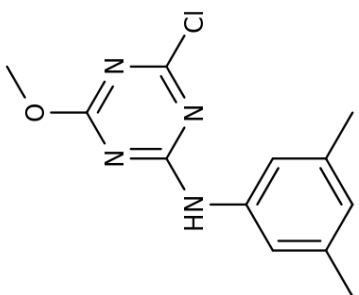
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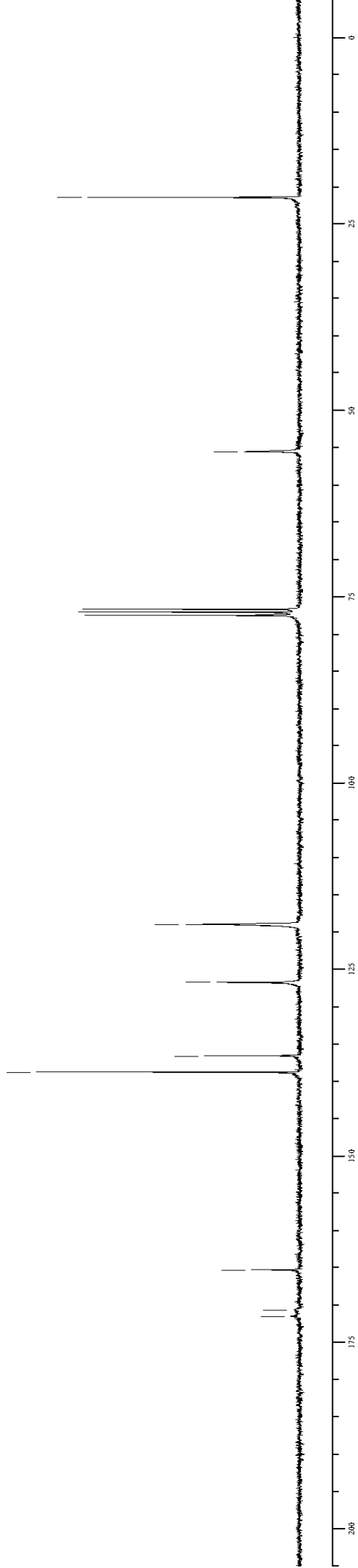
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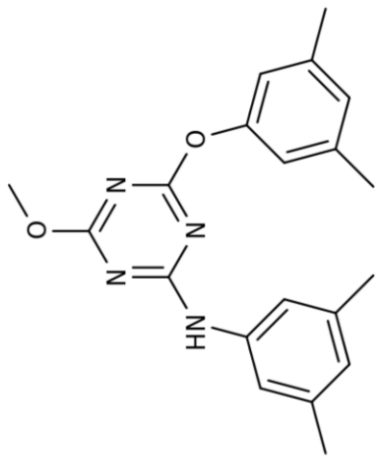
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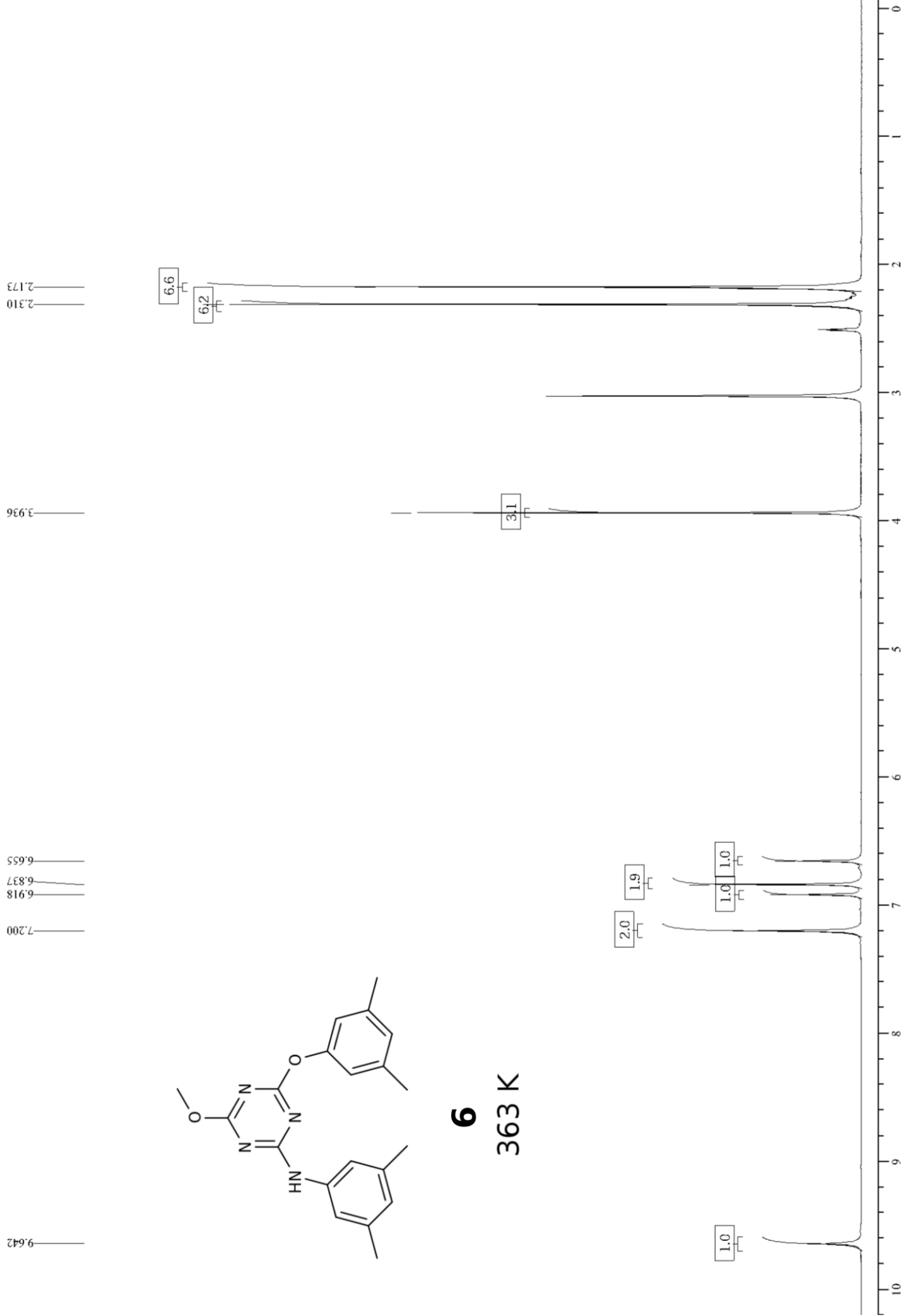
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363 K



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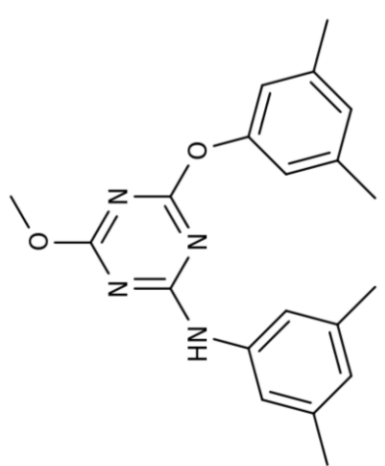
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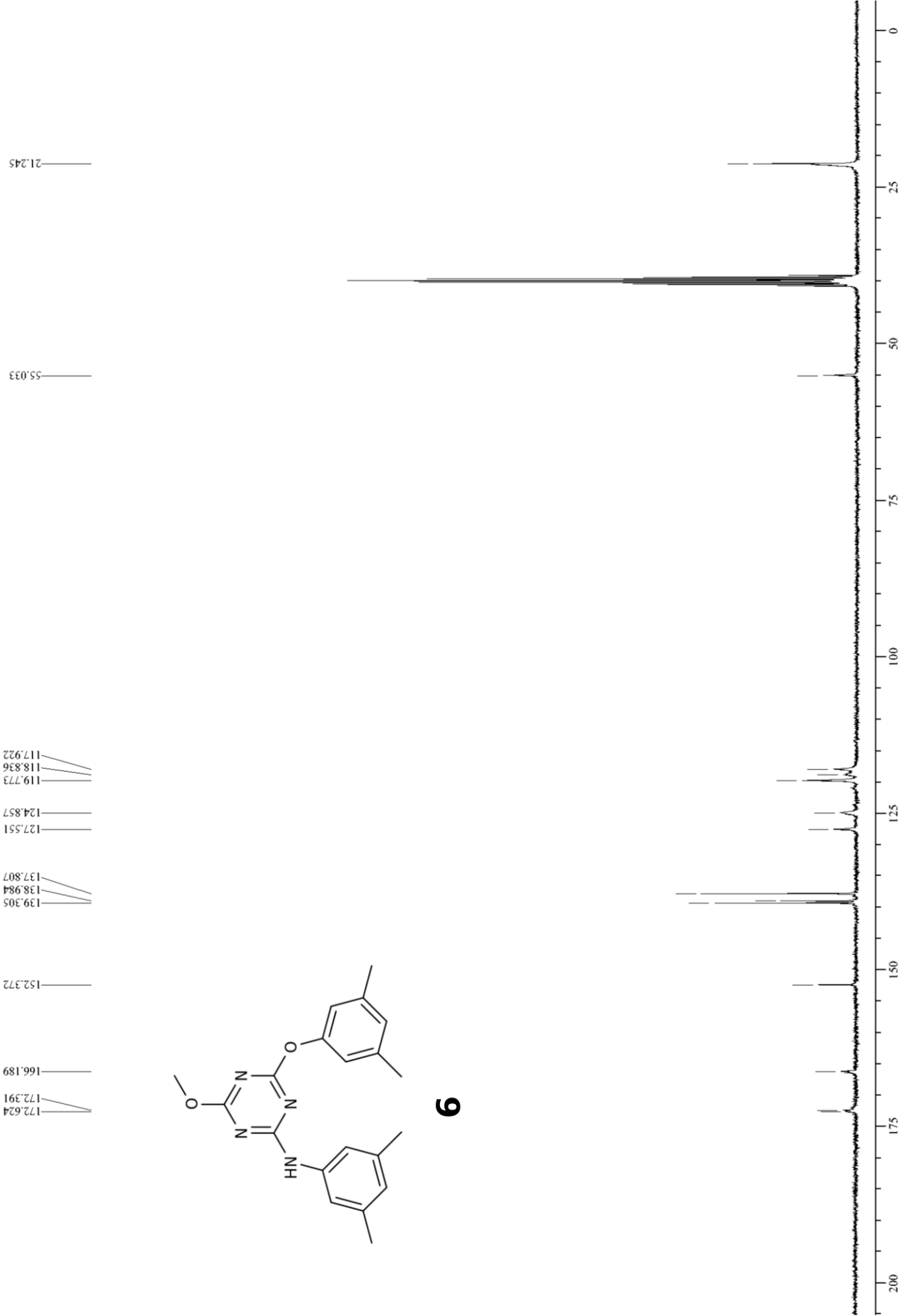
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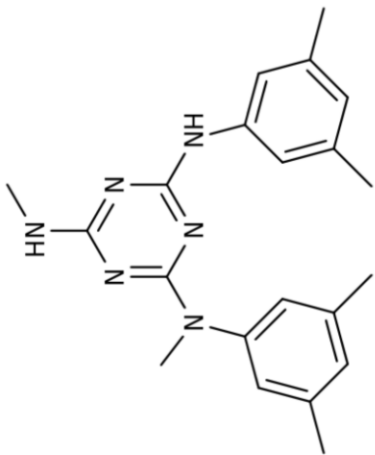
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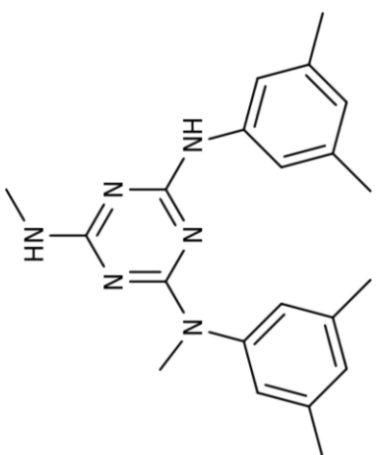




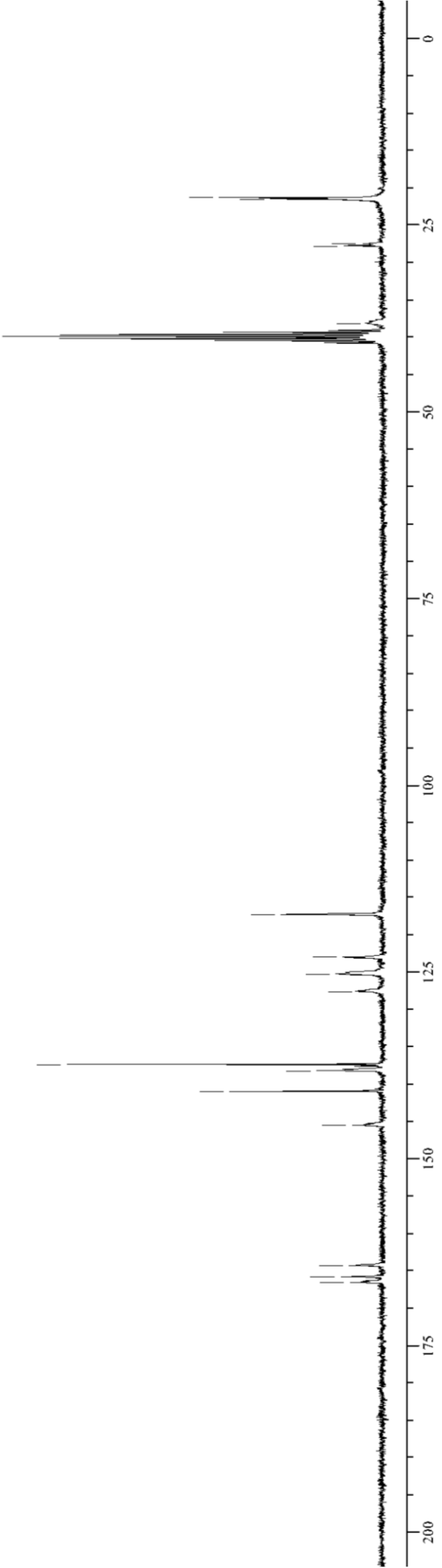
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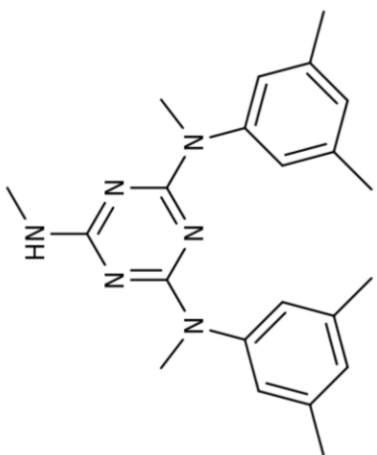
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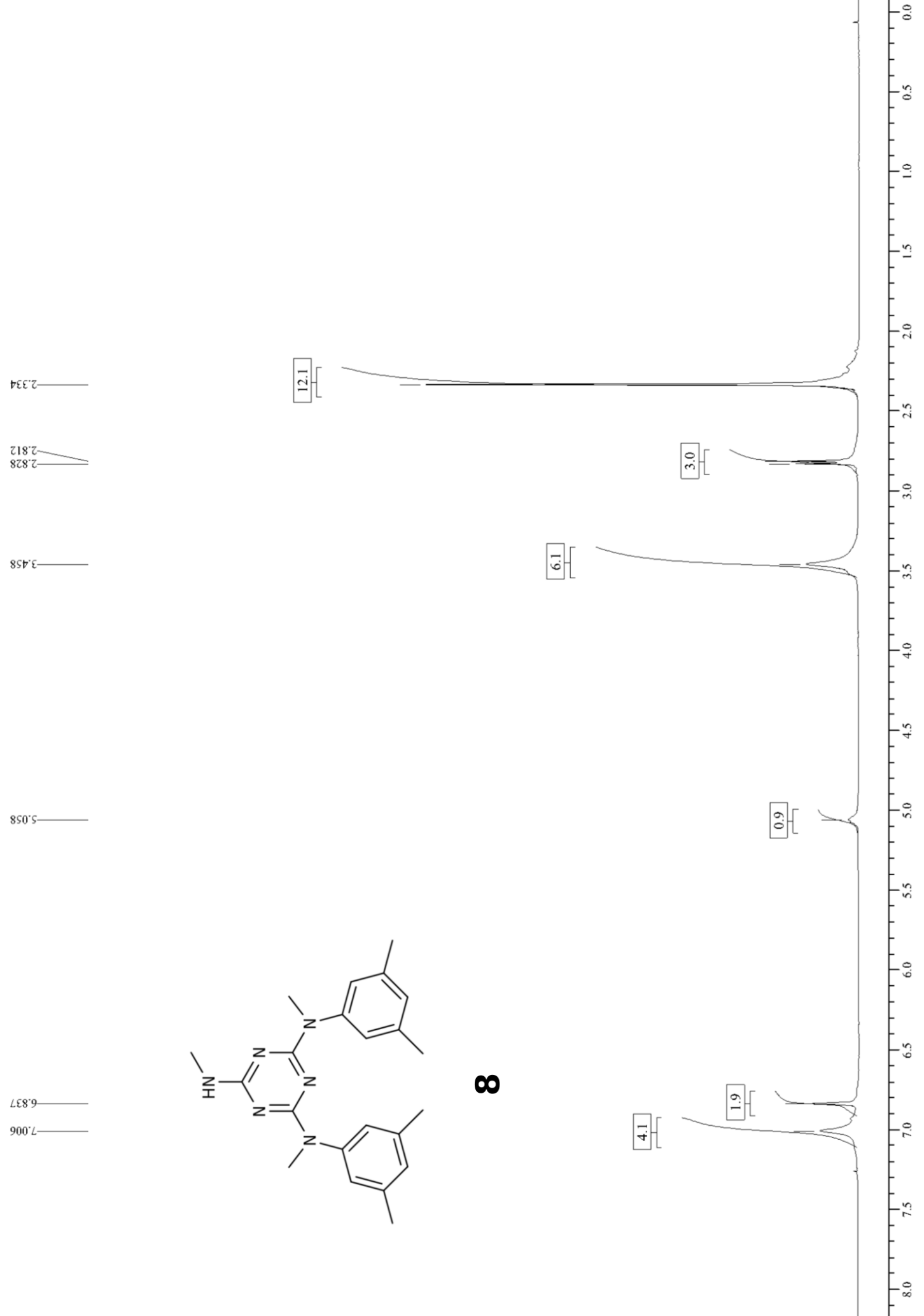
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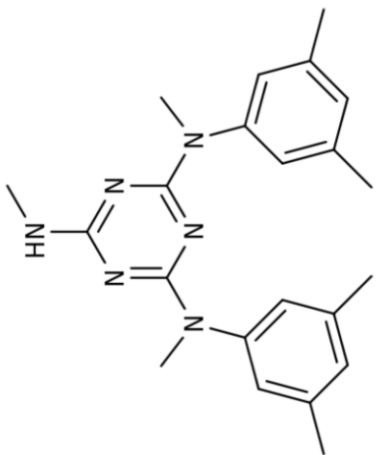
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8

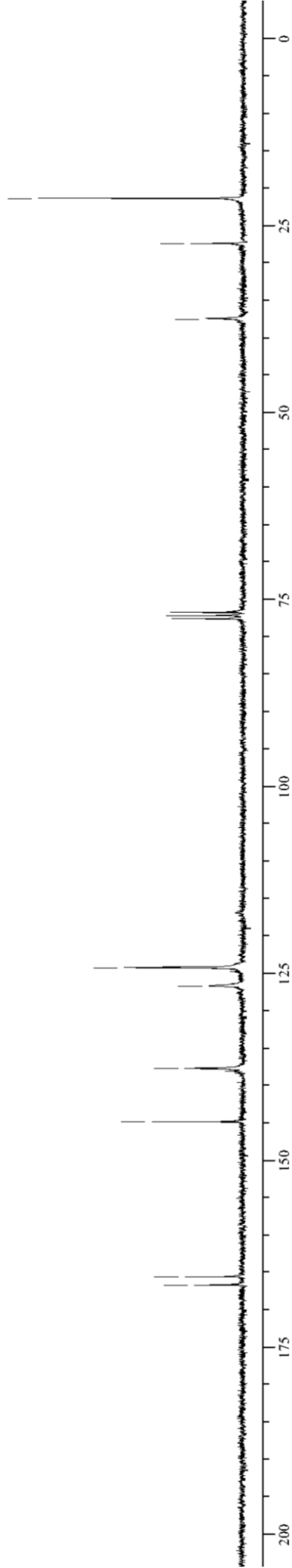


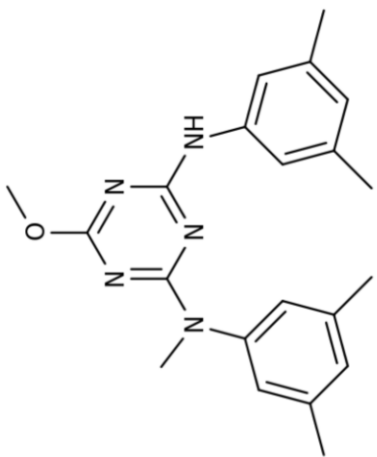


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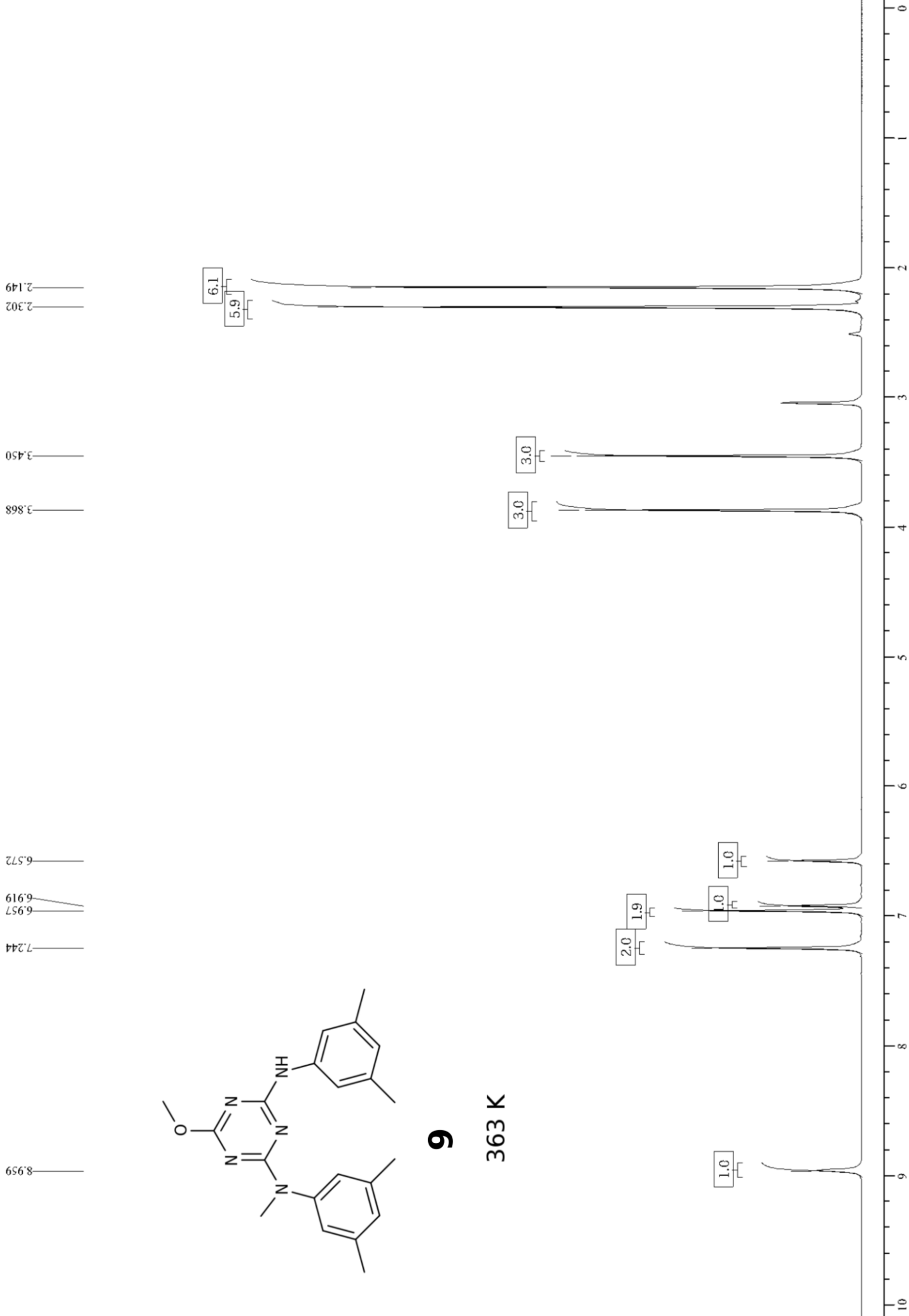
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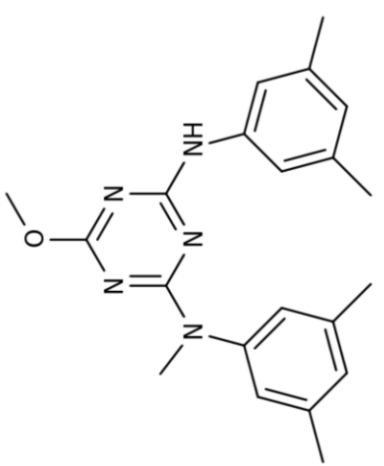
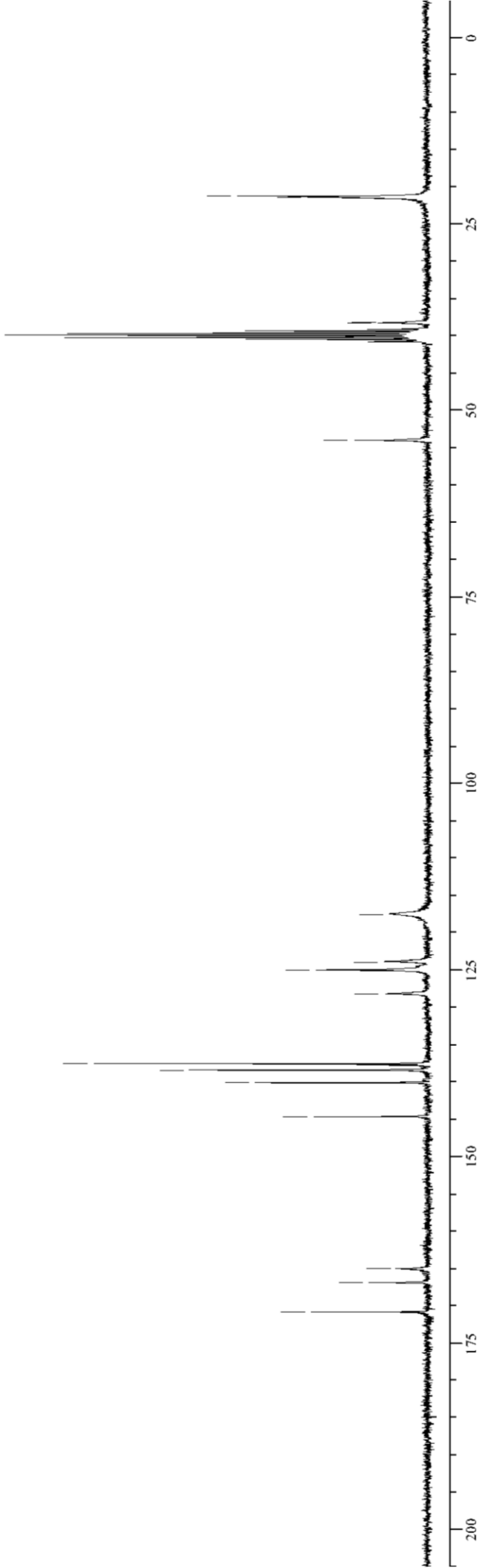




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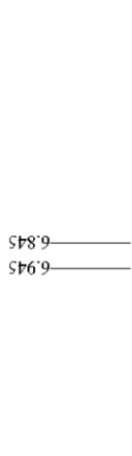
363 K





6

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- 165.003
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- 125.000
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- 21.259



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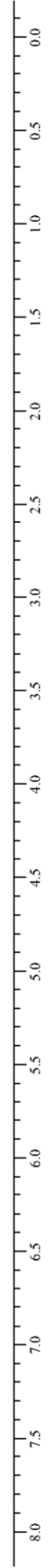
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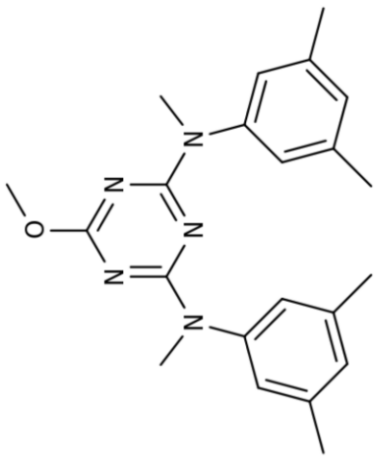
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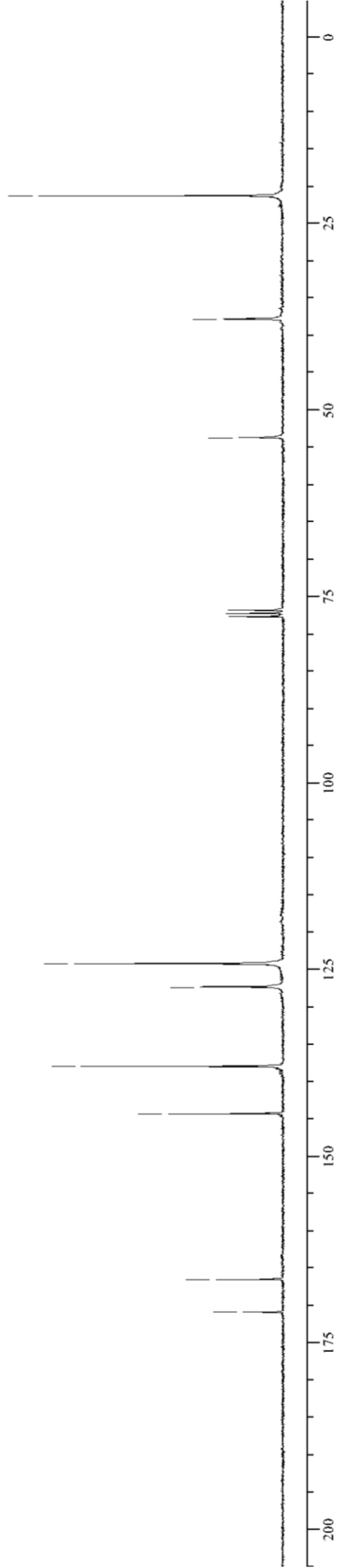
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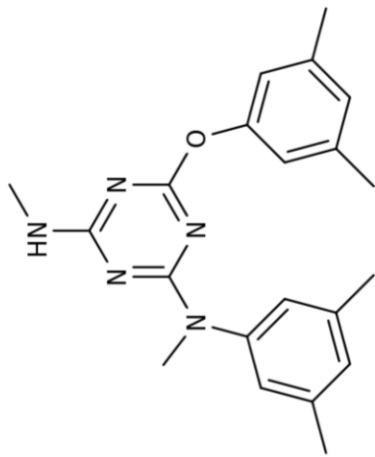




10



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11

363 K

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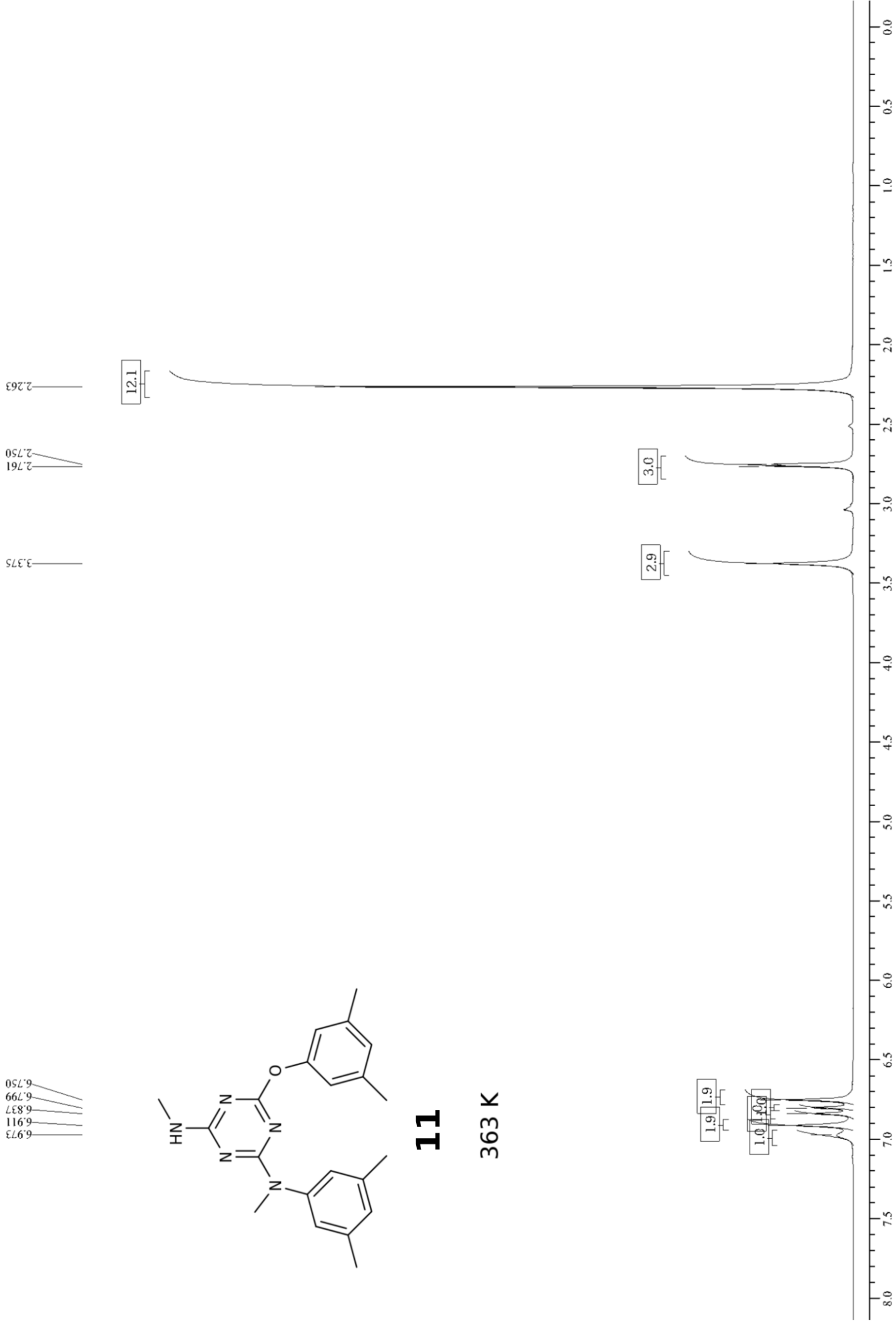
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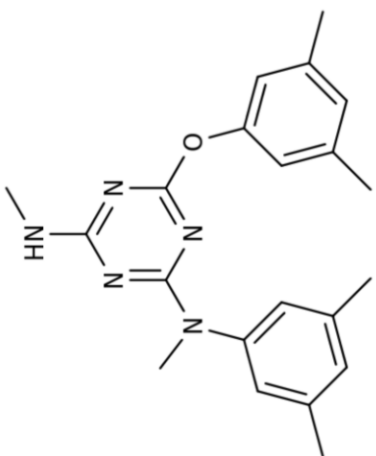
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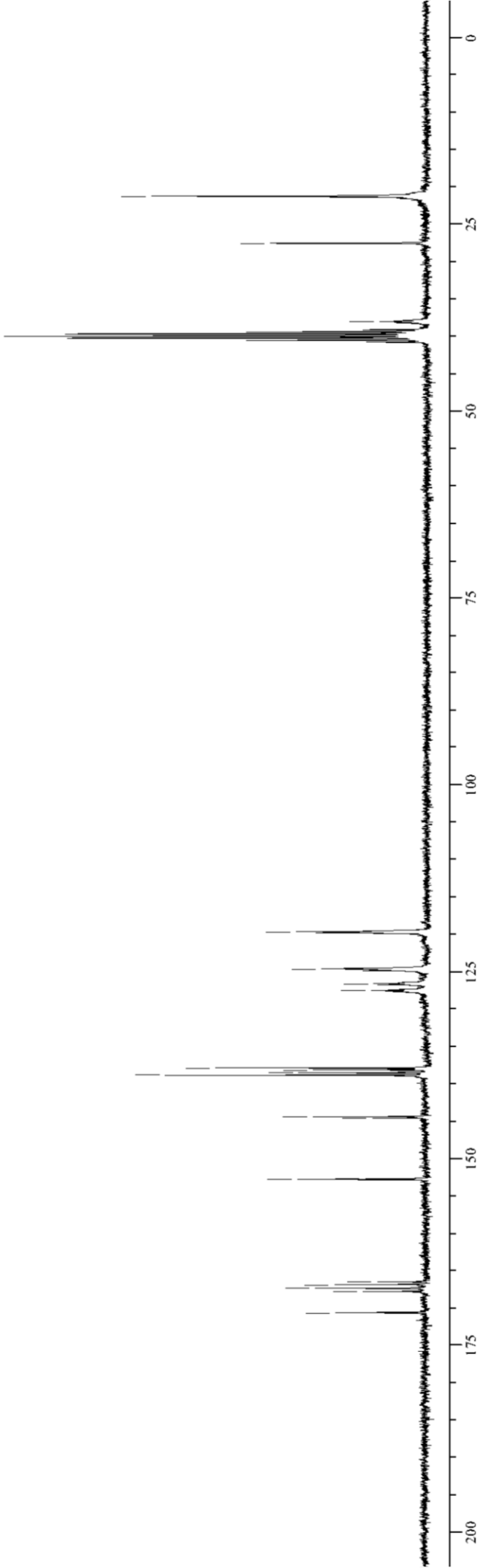
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1.0 1.0



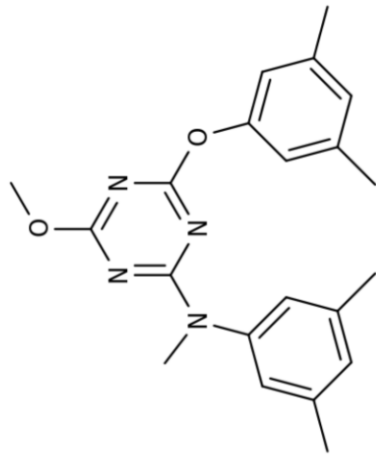


11



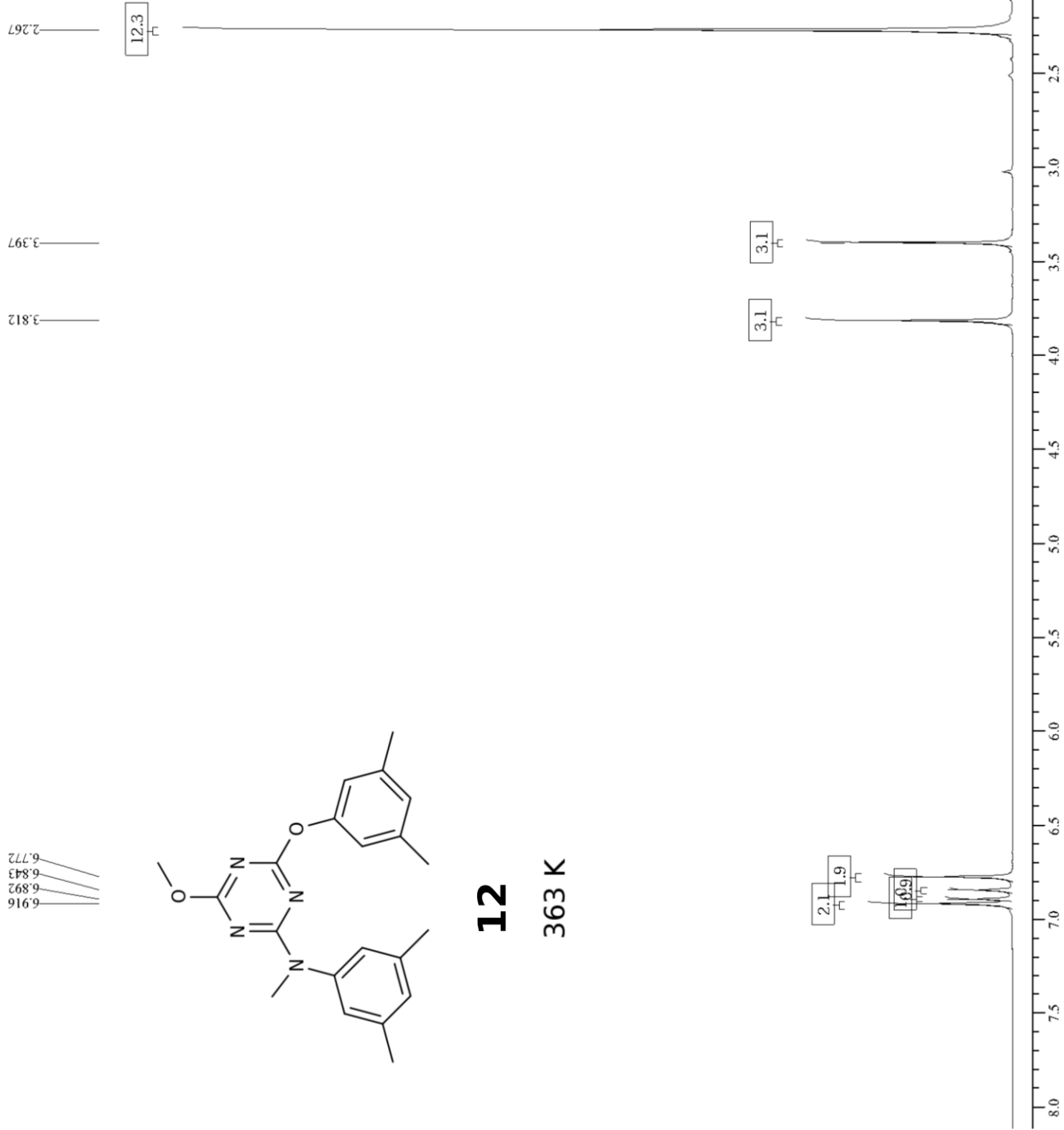
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7.499
7.229

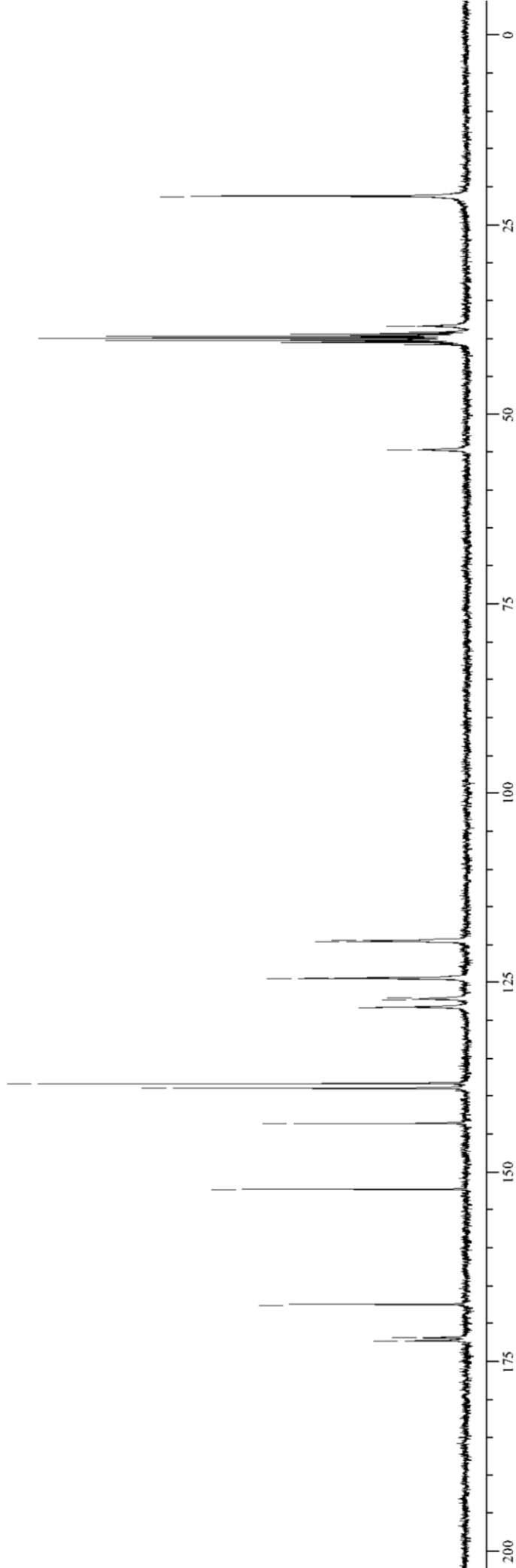
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167.788
167.334
166.851
166.485
152.787
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138.851
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138.117
137.865
127.523
126.595
124.603
119.649



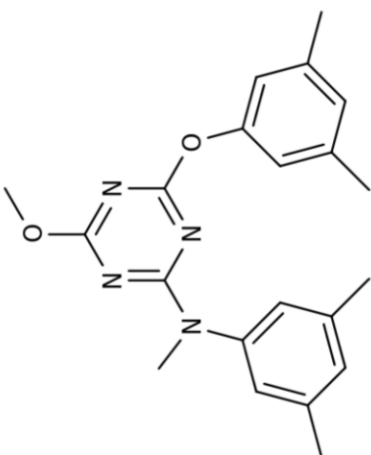
12

363 K

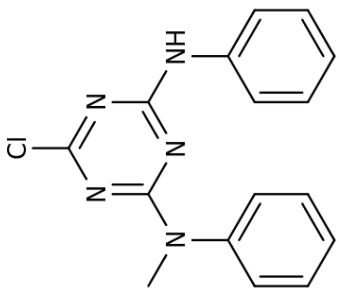




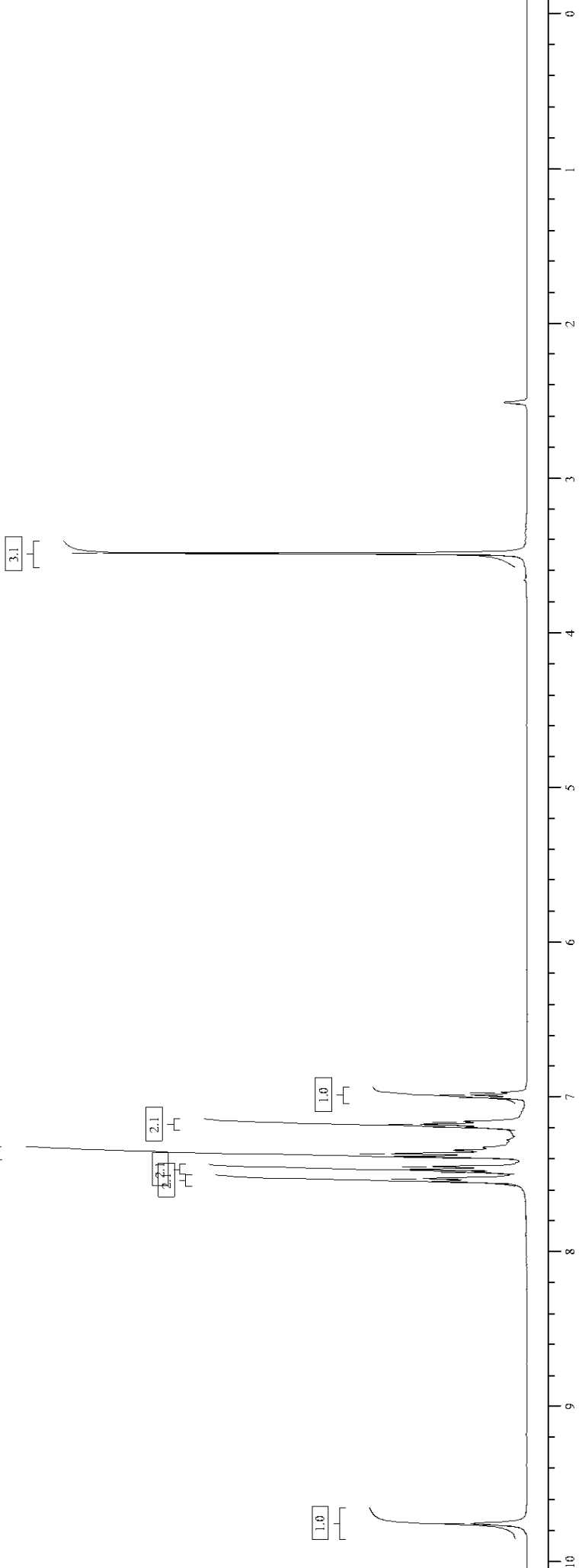
12



- 172.214
- 171.815
- 167.454
- 152.244
- 143.551
- 138.907
- 138.278
- 128.241
- 128.139
- 127.155
- 127.020
- 124.445
- 124.327
- 119.534
- 119.416
- 54.727
- 38.405
- 38.312
- 21.214



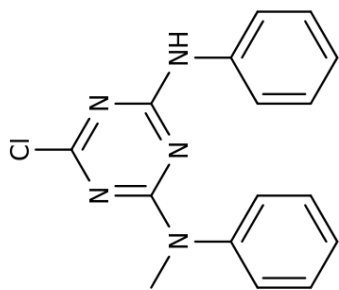
363 K



7.545
7.526
7.485
7.467
7.447
7.365
7.194
7.176
7.157
7.004
6.986
6.969

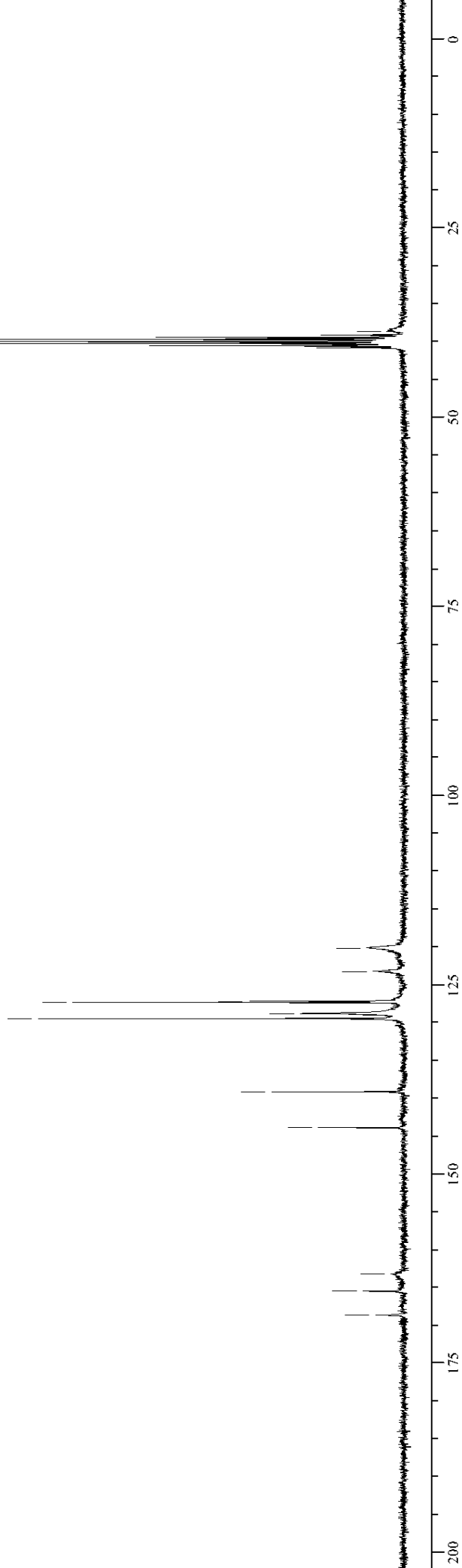
3.484

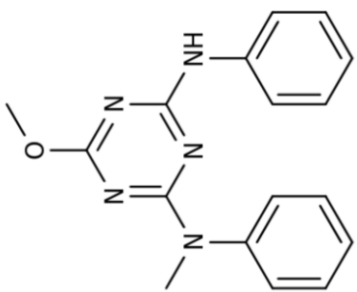
9.757



168.650
165.505
163.204
143.887
139.115
129.471
128.768
127.304
127.128
123.216
120.091

38.566





14

363 K

3.856
3.495

7.624
7.604
7.454
7.434
7.415
7.378
7.360
7.306
7.288
7.270
7.186
7.167
7.147
6.956
6.938
6.920

9.171

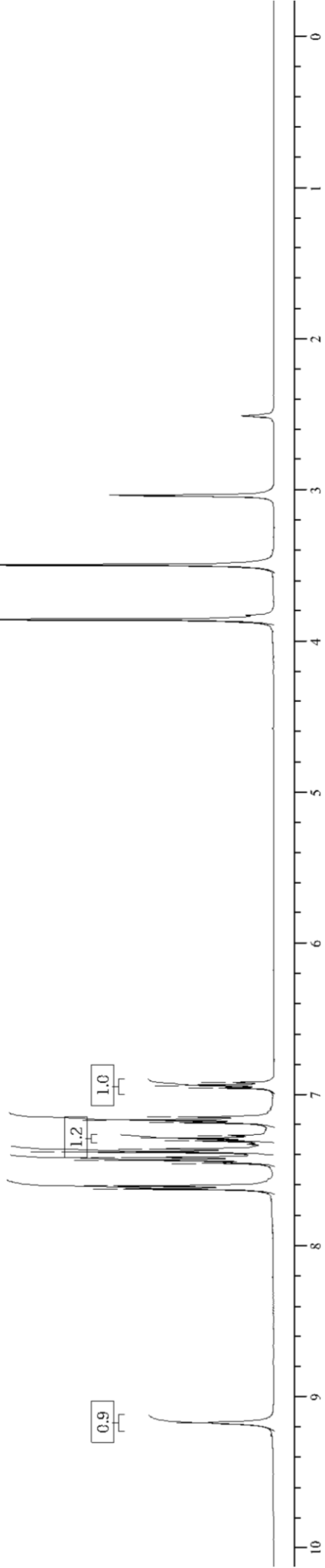
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2.0
2.0

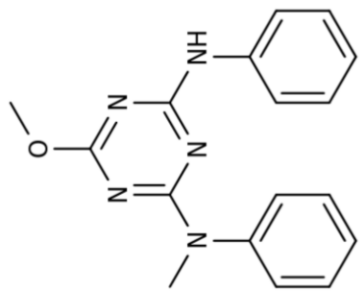
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1.2

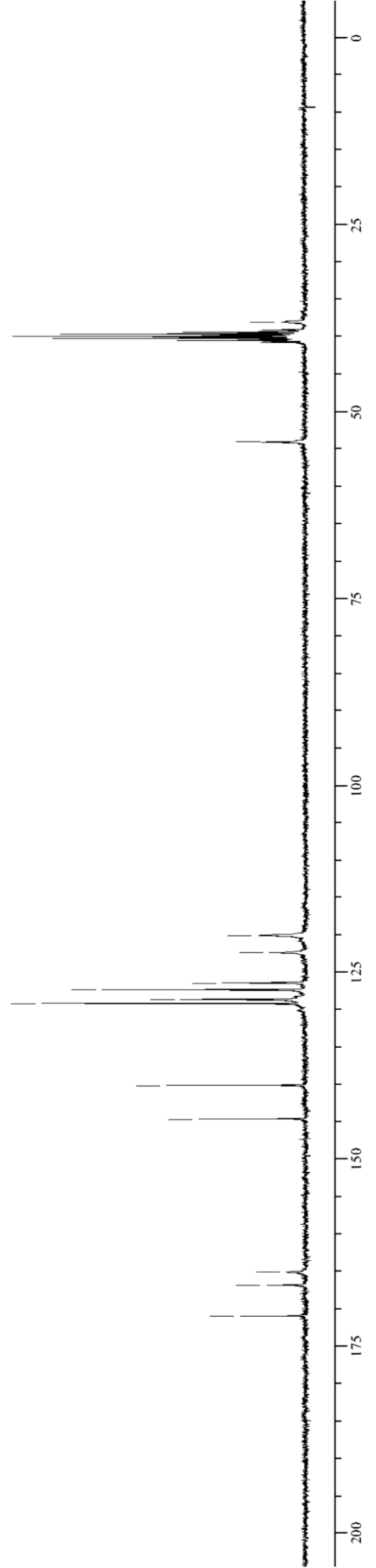
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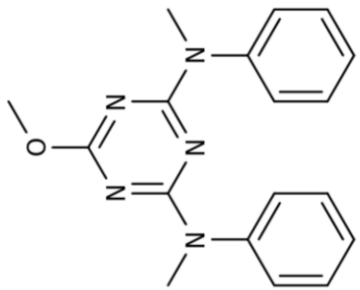
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3.0



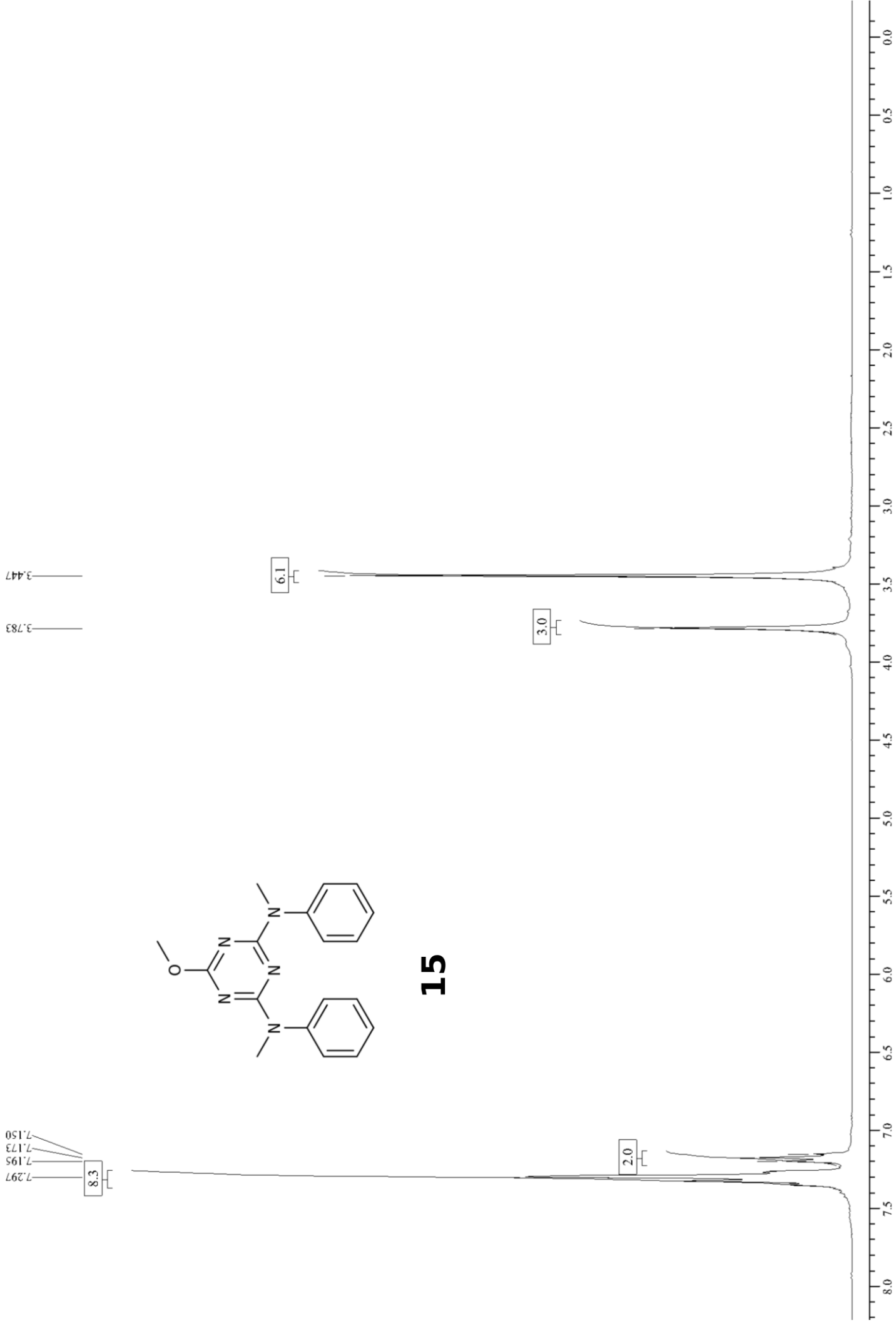


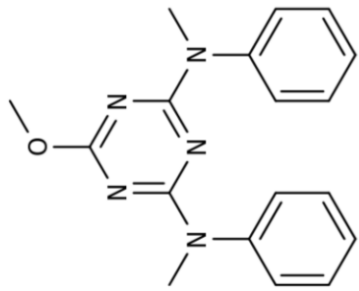
14





15





15

