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Supporting Information

Surface relief grating growth in thin films of mexylaminotriazine-functionalized glass-forming azobenzene derivatives

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I. Synthetic procedures and spectral data for compounds 4b-e

Synthesis of Azo Glass 4b

Glass **4b** was synthesized from 4-(N-(2-hydroxyethyl)-N-ethylamino)-3',5'-dichloroazobenzene by a procedure similar to that used for compound **4a**. Yield: 90 %; T_g 68 °C; FTIR (CH_2Cl_2/KBr) 3300, 3052, 2955, 2919, 2848, 1709, 1629, 1598, 1577, 1568, 1536, 1515, 1451, 1384, 1358, 1244, 1192, 1140, 1125, 1101, 957, 887, 855, 822, 809, 798, 725, 671, 656 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.83 (br s, 1H), 7.79 (d, ^3J = 8.8 Hz, 2H), 7.69 (d, ^4J = 2.0 Hz, 2H), 7.53 (t, ^4J = 2.0 Hz, 1H), 7.36 (s, 2H), 6.93 (br s, 3H), 6.88 (d, ^3J = 9.0 Hz, 2H), 6.62 (s, 1H), 4.19 (t, ^3J = 6.0 Hz, 2H), 3.66 (t, ^3J = 6.0 Hz, 2H), 3.52 (q, ^3J = 7.1 Hz, 2H), 3.42 (br s, 2H), 3.25 (q, ^3J = 5.8 Hz, 2H), 2.86 (s, 3H), 2.24 (s, 6H), 1.18 (t, ^3J = 7.1 Hz, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 164.4, 162.8, 156.6, 154.6, 151.7, 142.6, 140.2, 137.6, 135.2, 128.4, 126.3, 123.9, 120.7, 118.1, 111.8, 61.5, 49.2, 45.5, 40.4, 40.4, 27.7, 21.6, 12.4 ppm; UV-Vis (CH_2Cl_2): λ_{max} (ε) 435 nm (20 000); HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{31}H_{37}Cl_2N_{10}O_2$: 651.2473, found: 651.2473.

Synthesis of Azo Glass 4c

Glass **4c** was synthesized from 4-(N-(2-hydroxyethyl)-N-ethylamino)-4'-phenylazoazobenzene by a procedure similar to that used for compound **4a**. Yield: 94 %; T_g 64 °C; FTIR (CH_2Cl_2/KBr) 3405, 3283, 3059, 2969, 2924, 2855, 1709, 1599, 1563, 1512, 1442, 1392, 1353, 1320, 1241, 1189, 1143, 1124, 1000, 851, 822, 810, 768, 735, 687 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.29 (br s, 1H), 8.03 (d, ^3J = 8.3 Hz, 2H), 7.95 (d, ^3J = 9.6 Hz, 2H), 7.92 (d, ^3J = 8.1 Hz, 2H), 7.84 (d, ^3J = 8.8 Hz, 2H), 7.59 (m, 3H), 7.41 (s, 2H), 6.90 (d, ^3J = 8.8 Hz, 2H), 6.86 (br s, 1H), 6.57 (s, 1H), 6.40 (br s, 1H), 6.33 (br s, 1H), 4.21 (t, ^3J = 5.8 Hz, 2H), 3.67 (t, ^3J = 6.8 Hz, 2H), 3.52 (q, ^3J = 5.8 Hz, 2H), 3.43 (q, ^3J = 5.8 Hz, 2H), 3.26 (q, ^3J = 5.8 Hz, 2H), 2.84 (d, ^3J = 4.5 Hz, 3H), 2.24 (s, 6H), 1.19 (t, ^3J = 6.8 Hz, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.5, 166.1, 164.4, 156.7, 154.4, 152.5, 152.2, 151.3, 143.3, 141.0, 137.4, 132.1, 129.9, 126.0, 124.2, 123.3, 123.1, 117.6, 111.8, 61.6, 49.2, 45.5, 40.4, 40.4, 27.7, 21.7, 12.4 ppm; UV-Vis (CH_2Cl_2): λ_{max} (ε) 475 nm (28 000); HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{37}H_{43}N_{12}O_2$: 709.3446, found: 709.3453.

Synthesis of Azo Glass 4d

To a stirred suspension of N,N'-carbonyldiimidazole (0.700 g, 4.32 mmol) in dry DMF (3 mL) in a dry round-bottomed flask equipped with a magnetic stirrer was slowly added a solution of 2-[4-(N-(2-hydroxyethyl)-N-ethylamino)phenylazo]-6-nitrobenzothiazole (1.07 g, 2.88 mmol) in dry DMF (7 mL) at ambient temperature, then the mixture was stirred for 18 h under nitrogen atmosphere. The mixture was poured in water-saturated ethyl ether, then the precipitate was collected by filtration and washed with ethyl ether. The crude residue was redissolved in THF (20 mL), then 2-methylamino-4-mexylamino-6-(2-aminoethylamino)-1,3,5-triazine (0.993 g, 3.46 mmol) was added and the mixture was refluxed for 18 h. The solvent was evaporated, then 1M aqueous HCl was added, then the precipitated product was collected by filtration and washed with 1M aq. HCl and H_2O until the effluent was colorless. The residue was dissolved in acetone, then CH_2Cl_2 and aq. $NaHCO_3$ were added. The layers were separated, the organic layer was dried over Na_2SO_4, filtered, and the volatiles were thoroughly evaporated under reduced pressure. The crude product was filtered on a short silica pad with 10% acetone/$CHCl_3$ as eluent to yield, after thorough drying, 1.46 g of compound **4d** (2.13 mmol, 74%). T_g 72 °C; FTIR (CH_2Cl_2/KBr) 3407, 3304, 2970, 2923, 2857, 1709, 1600, 1566, 1517, 1437, 1354, 1329, 1309, 1271, 1192, 1140, 1114, 1074, 1043, 1014, 997, 911, 887, 826, 810, 752, 737 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.92 (d, ^4J = 1.8 Hz, 1H), 8.28 (d, ^3J = 9.1 Hz, ^4J = 2.0 Hz, 1H), 8.26 (br s, 1H), 8.11 (d, ^3J =9.1 Hz, 1H), 7.88 (d, ^3J = 9.1 Hz, 2H), 7.39 (s, 2H), 6.99 (d, ^3J = 9.1 Hz, 2H), 6.85 (br s, 1H), 6.55 (s, 1H), 6.36 (br s, 1H), 6.30 (br s, 1H), 4.24 (t, ^3J = 5.5 Hz, 2H), 3.77 (t, ^3J = 6.8 Hz, 2H), 3.61 (q, ^3J = 5.8 Hz, 2H), 3.41 (q, ^3J = 5.5 Hz, 2H), 3.24 (q, ^3J = 5.5 Hz, 2H), 2.84 (d, ^3J = 4.5 Hz, 3H), 2.23 (s, 6H), 1.22 (t, ^3J = 6.8 Hz, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 182.3, 166.5, 166.0, 164.4, 157.0, 156.5, 154.4, 144.8, 142.7, 141.0, 137.4, 134.3, 123.7, 123.0, 122.0, 119.6, 117.6, 113.1, 61.5, 49.6, 46.1, 40.4, 40.4, 27.7, 21.7, 12.5 ppm; UV-Vis (CH_2Cl_2): λ_{max} (ε) 539 nm (24 000); HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{32}H_{37}N_{12}O_4S$: 685.2776, found: 685.2780.

Synthesis of Azo Glass 4e

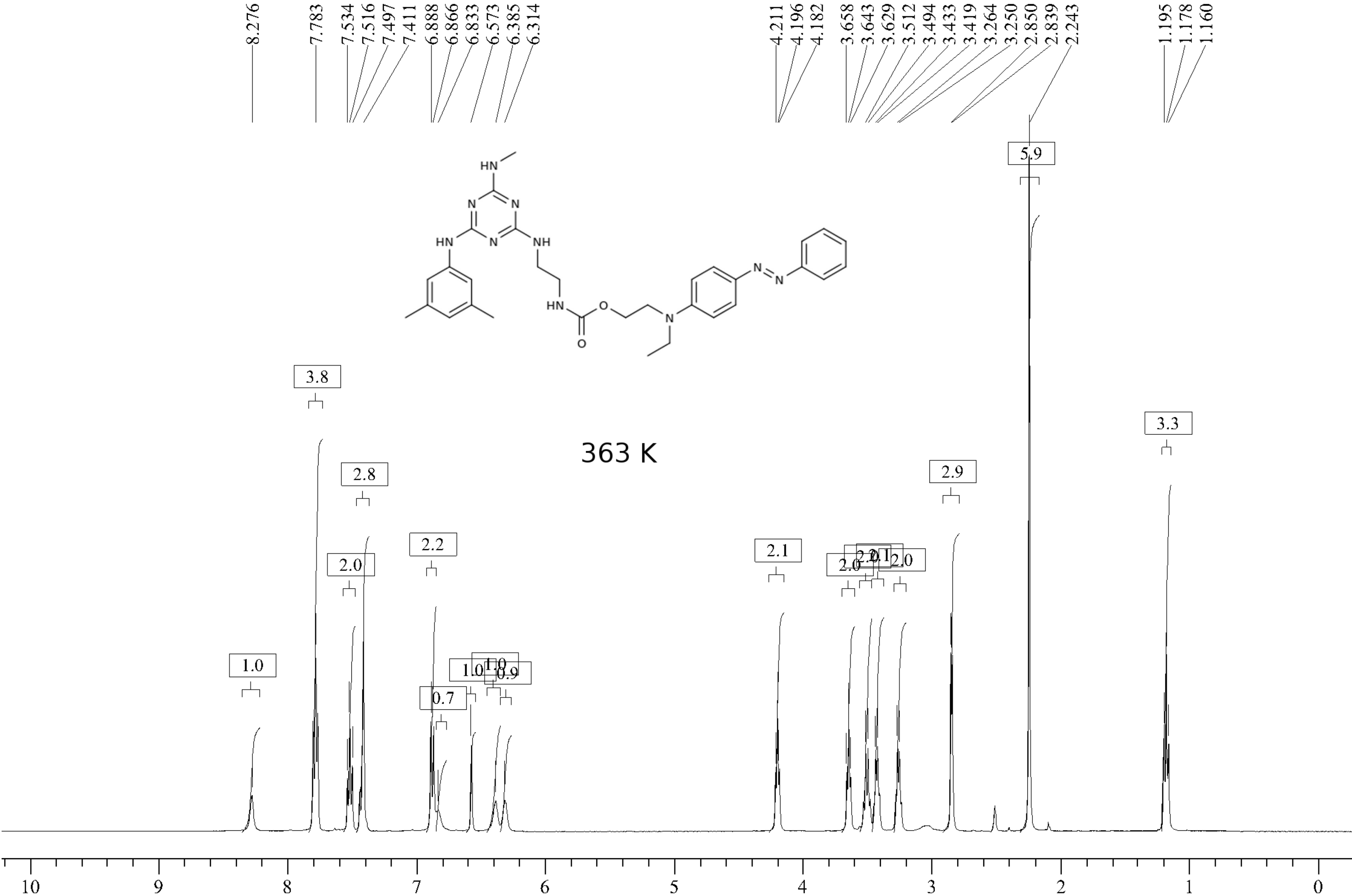
To a stirred suspension of N,N'-carbonyldiimidazole (0.757 g, 4.67 mmol) in dry DMF (3 mL) in a dry round-bottomed flask equipped with a magnetic stirrer was slowly added a solution of 2-[4-(N-(2-hydroxyethyl)-N-ethylamino)phenylazo]-5-nitrothiazole (1.00 g, 3.11 mmol) in dry DMF (7 mL) at ambient temperature, then the mixture was stirred for 18 h under nitrogen atmosphere. The mixture was poured in water, NaCl (0.1 g) was added, and the mixture was stirred for 5 min, after which a dark blue precipitate had formed. The precipitate was collected by filtration and washed with water. The crude residue was redissolved in THF (20 mL), then 2-methylamino-4-mexylamino-6-(2-aminoethylamino)-1,3,5-triazine (1.07 g, 3.73 mmol) was added and the mixture was refluxed for 18 h. The solvent was evaporated, then 1M aqueous HCl was added, then the precipitated product was collected by filtration and washed with 1M aq. HCl and H_2O until the effluent was colorless. The residue was dissolved in acetone, then CH_2Cl_2 and aq. $NaHCO_3$ were added. The layers were separated, the organic layer was dried over Na_2SO_4, filtered, and the volatiles were thoroughly evaporated under reduced pressure. The crude product was redissolved in CH_2Cl_2 and filtered to remove insoluble precipitate, then the filtrate was recovered and the volatiles were thoroughly removed under reduced pressure to give 1.44 g of compound **4e** (2.27 mmol, 73%). T_g 73 °C; FTIR (CH_2Cl_2/KBr) 3395, 3283, 3094, 2971, 2932, 2860, 1710, 1626, 1600, 1561, 1517, 1442, 1336, 1290, 1238, 1188, 1133, 1116, 1072, 997, 887, 839, 828, 810, 788, 735, 698, 687 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.75 (s, 1H), 8.26 (br s, 1H), 7.86 (d, ^3J = 8.8 Hz, 2H), 7.38 (s, 2H), 7.02 (d, ^3J = 9.3 Hz, 2H), 6.85 (br s, 1H), 6.56 (s, 1H), 6.36 (br s, 1H), 6.30 (br s, 1H), 4.24 (t, ^3J = 5.5 Hz, 2H), 3.80 (t, ^3J = 5.7 Hz, 2H), 3.64 (q, ^3J = 7.1 Hz, 2H), 3.38 (q, ^3J = 5.5 Hz, 2H), 3.21 (q, ^3J = 6.0 Hz, 2H), 2.82 (d, ^3J = 4.5 Hz, 3H), 2.23 (s, 6H), 1.23 (t, ^3J = 7.0 Hz, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 181.5, 164.0, 162.7, 162.0, 156.5, 155.5, 155.2, 145.9, 145.5, 142.6, 139.9, 137.7, 124.1, 118.1, 113.7, 61.6, 49.7, 46.3, 40.4, 40.4, 27.7, 21.6 ppm; UV-Vis (CH_2Cl_2): λ_{max} (ε) 571 nm (18 000); HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{28}H_{35}N_{12}O_4S$: 657.2439, found: 657.2444.

II. Additional data on SRG growth for compounds 1 and 4a-e

Table S1. Final diffraction efficiencies for SRG of compounds **1** and **4a**-**e**. Wavelengths and irradiances used are indicated.

Wavelength (nm)	Irradiance (mW/cm^2)	Compound	Diffraction Efficiency (%)
488	80	**1**	10.2
		4a	4.2
		4b	4.3
		4c	4.8
496.5	31	**1**	4.5
		4a	2.1
		4b	3.4
		4c	5.2
514	95	**1**	10.1
		4a	1.4
		4b	2.8
		4c	5.9
532	157	**1**	11.5
		4a	0.88
		4b	5.1
		4c	7.1
532	344	**1**	10.6
		4a	3.1
		4b	4.3
		4c	5.6
532	521	**1**	6.5
		4a	3.3
		4b	6.3
		4c	4.2
532	809	**4d**	0.83
		4e	0.055
532	1509	**4d**	0.20
		4e	0.0090
632	76	**1**	8.6
		4c	6.3

III. NMR spectra of compounds 4a-e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6.866
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4.211
4.196
4.182
3.658
3.643
3.629
3.512
3.494
3.433
3.419
3.264
3.250
2.850
2.839
2.243
1.195
1.178
1.160
363 K
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3.8
2.8
2.0
2.2
0.7
1.0
1.0
0.9
2.1
2.0
2.1
2.0
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5.9
3.3
10
9
8
7
6
5
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1
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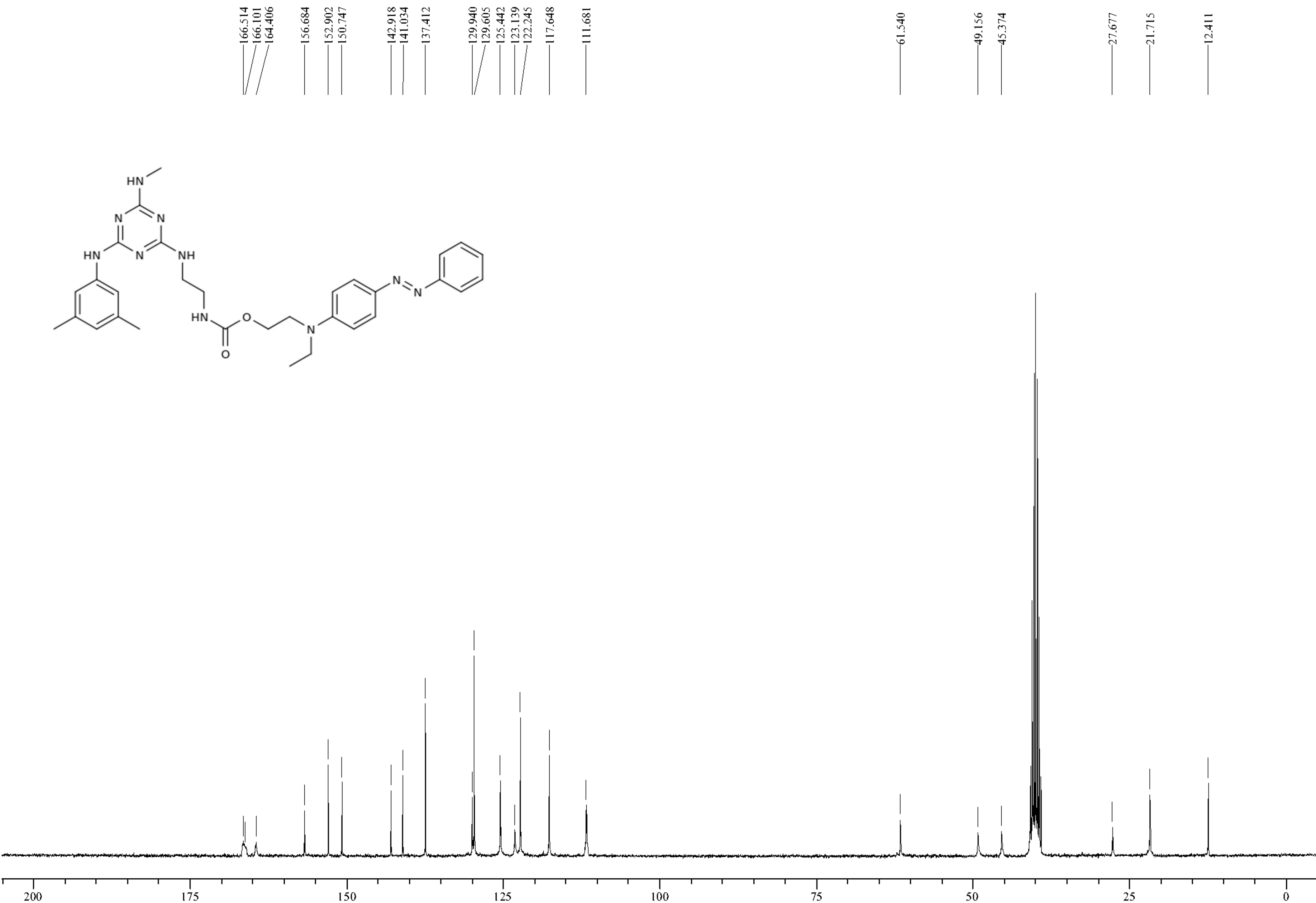
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123.139
122.245
117.648
111.681
61.540
49.156
45.374
27.677
21.715
12.411
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50
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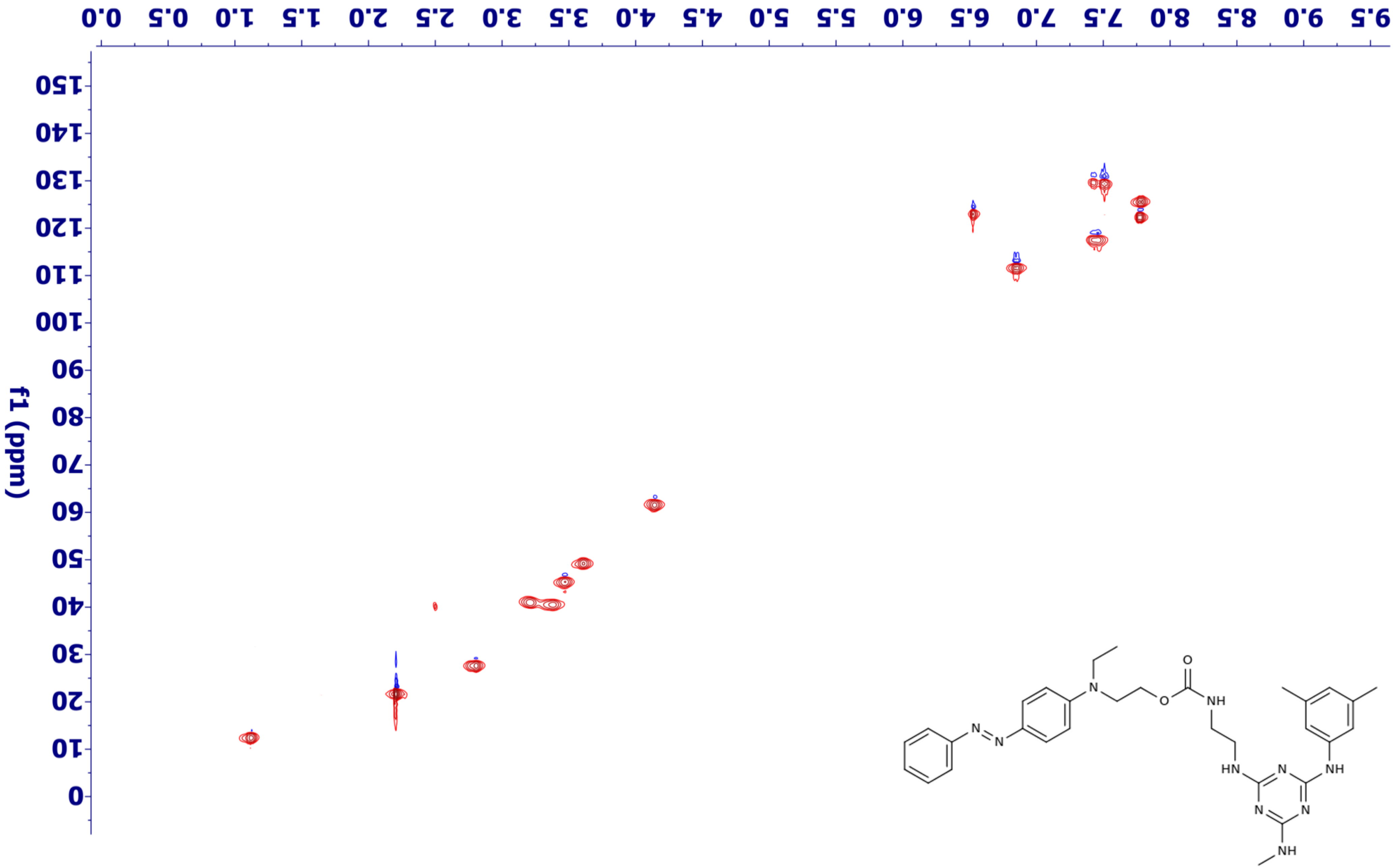
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N
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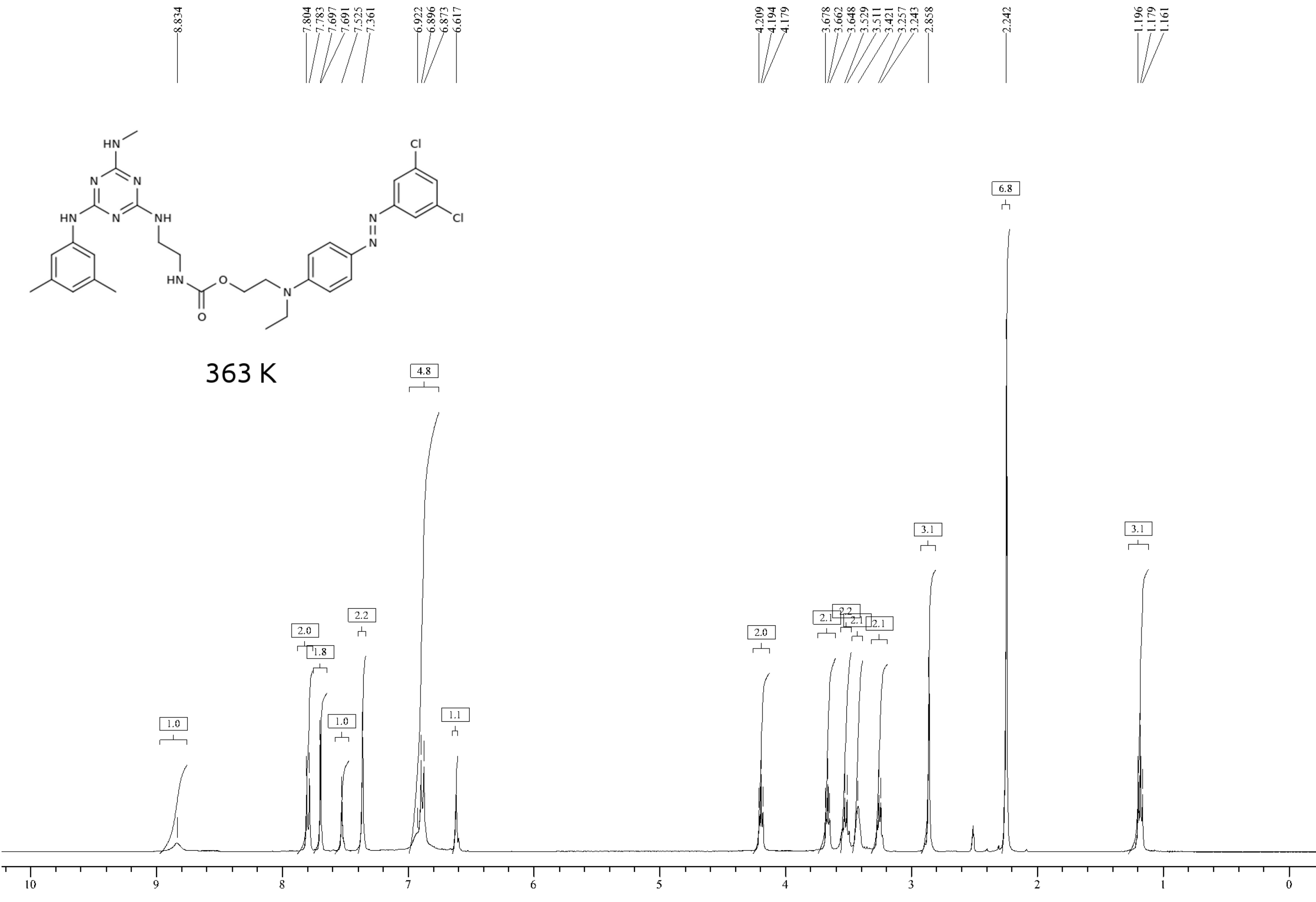
NH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4.179
3.678
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3.648
3.529
3.511
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N
HN
N
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HN
O
O
N
N
N
Cl
Cl
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1.0
2.2
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1.1
2.0
2.1
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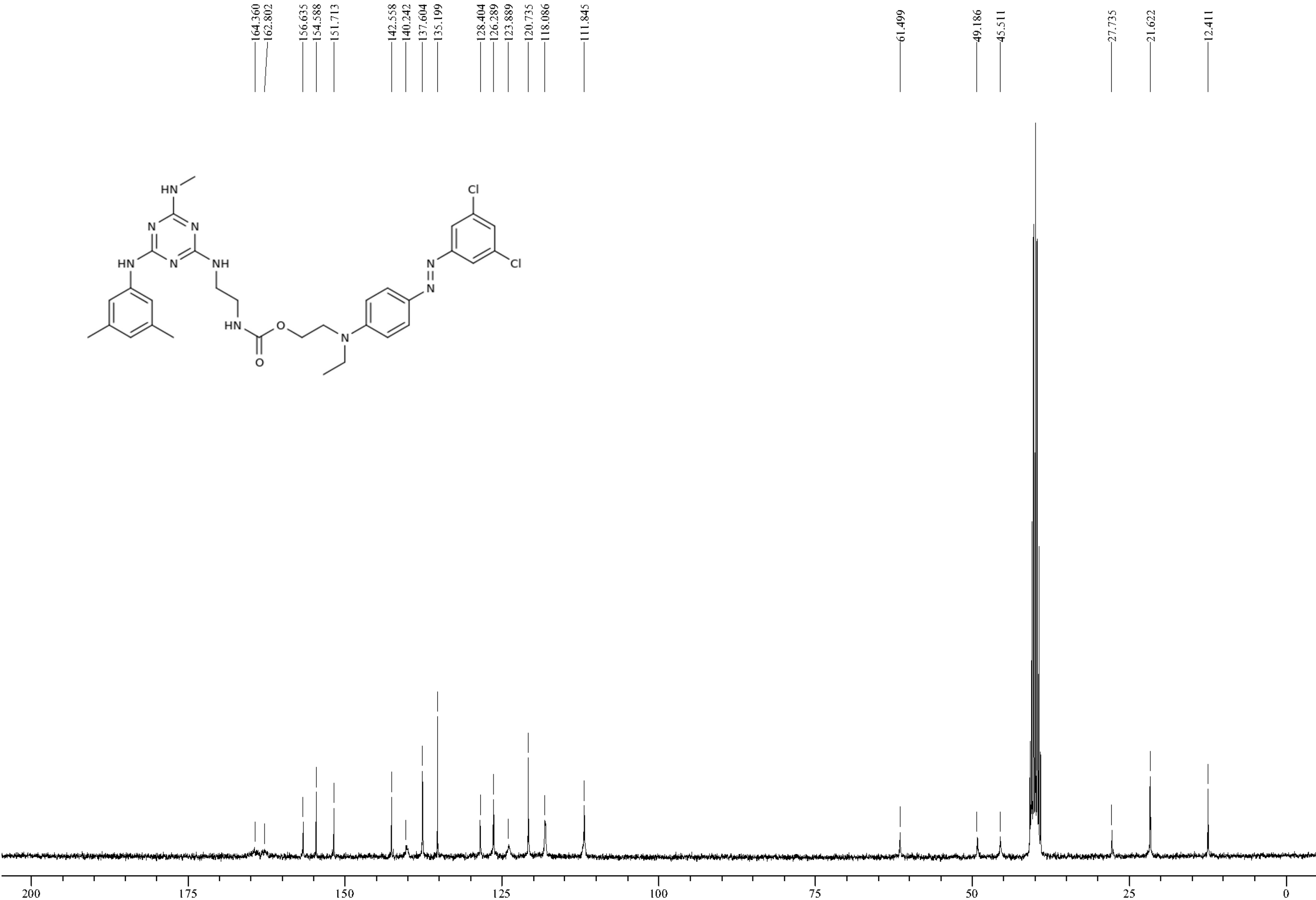
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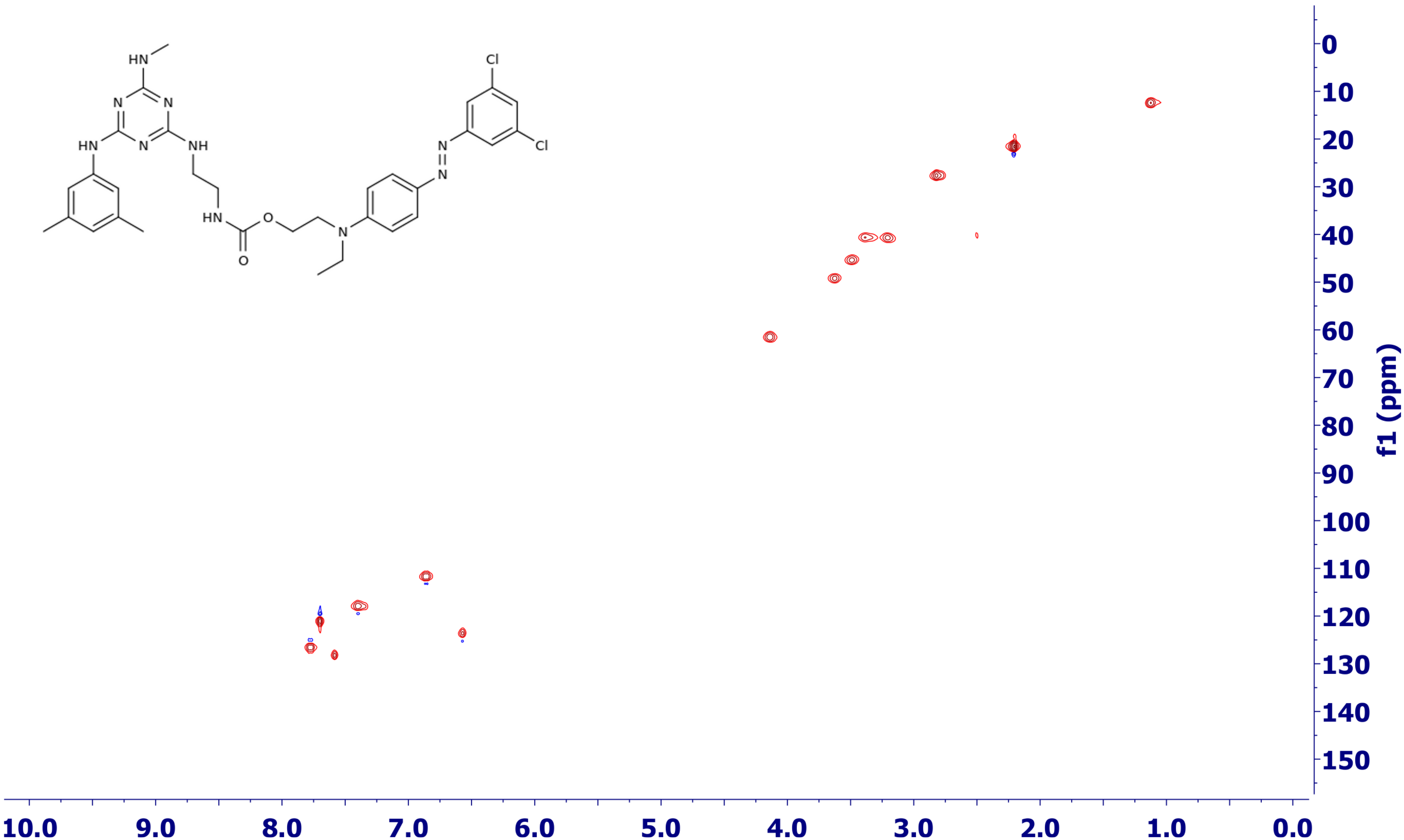

HN
N
N
HN
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NH
HN
O
O
N
N
N
Cl
Cl
f1 (ppm)
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30
40
50
60
70
80
90
100
110
120
130
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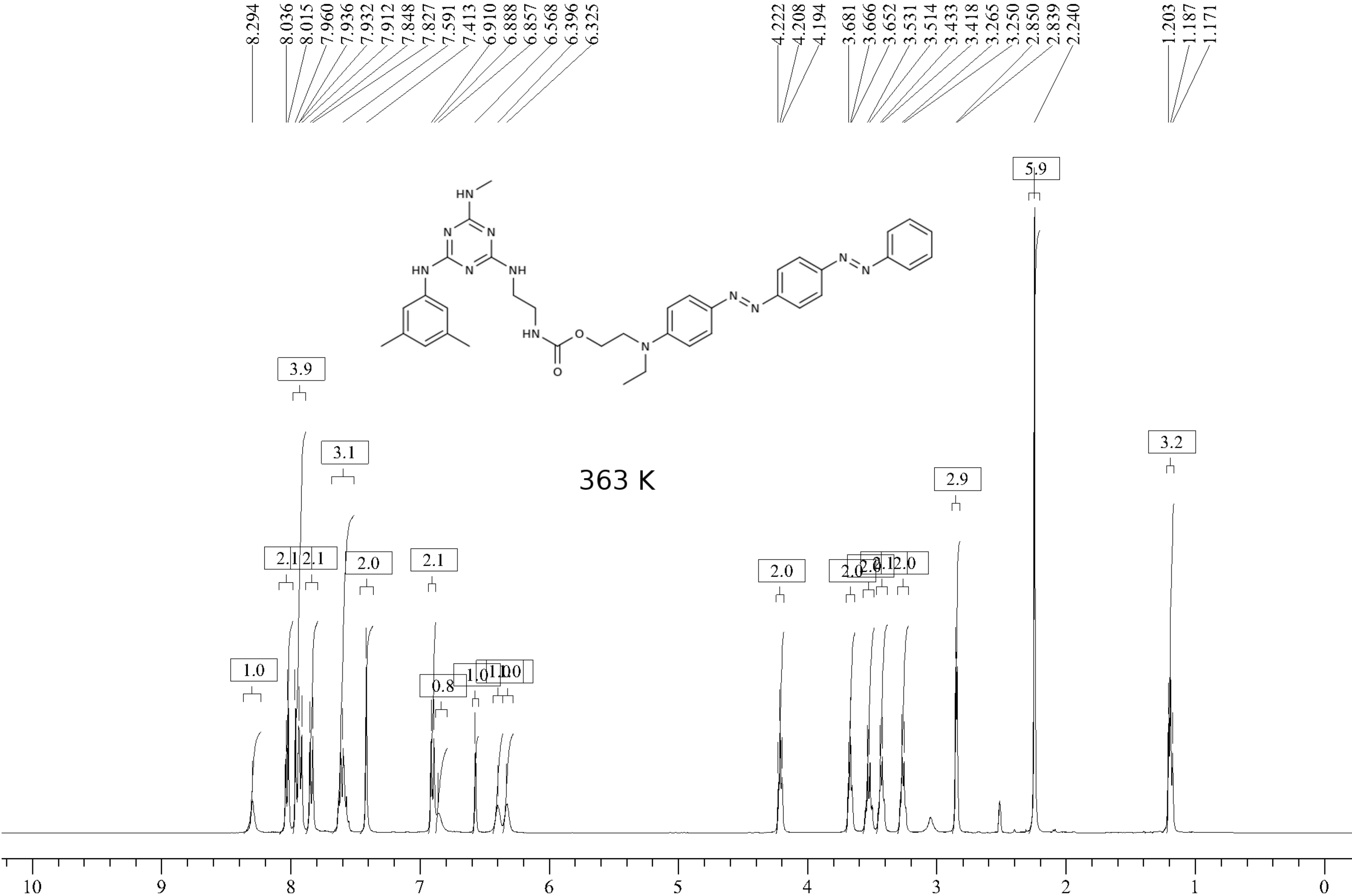
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6.568
6.396
6.325
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4.208
4.194
3.681
3.666
3.652
3.531
3.514
3.433
3.418
3.265
3.250
2.850
2.839
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363 K
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8
7
6
5
4
3
2
1
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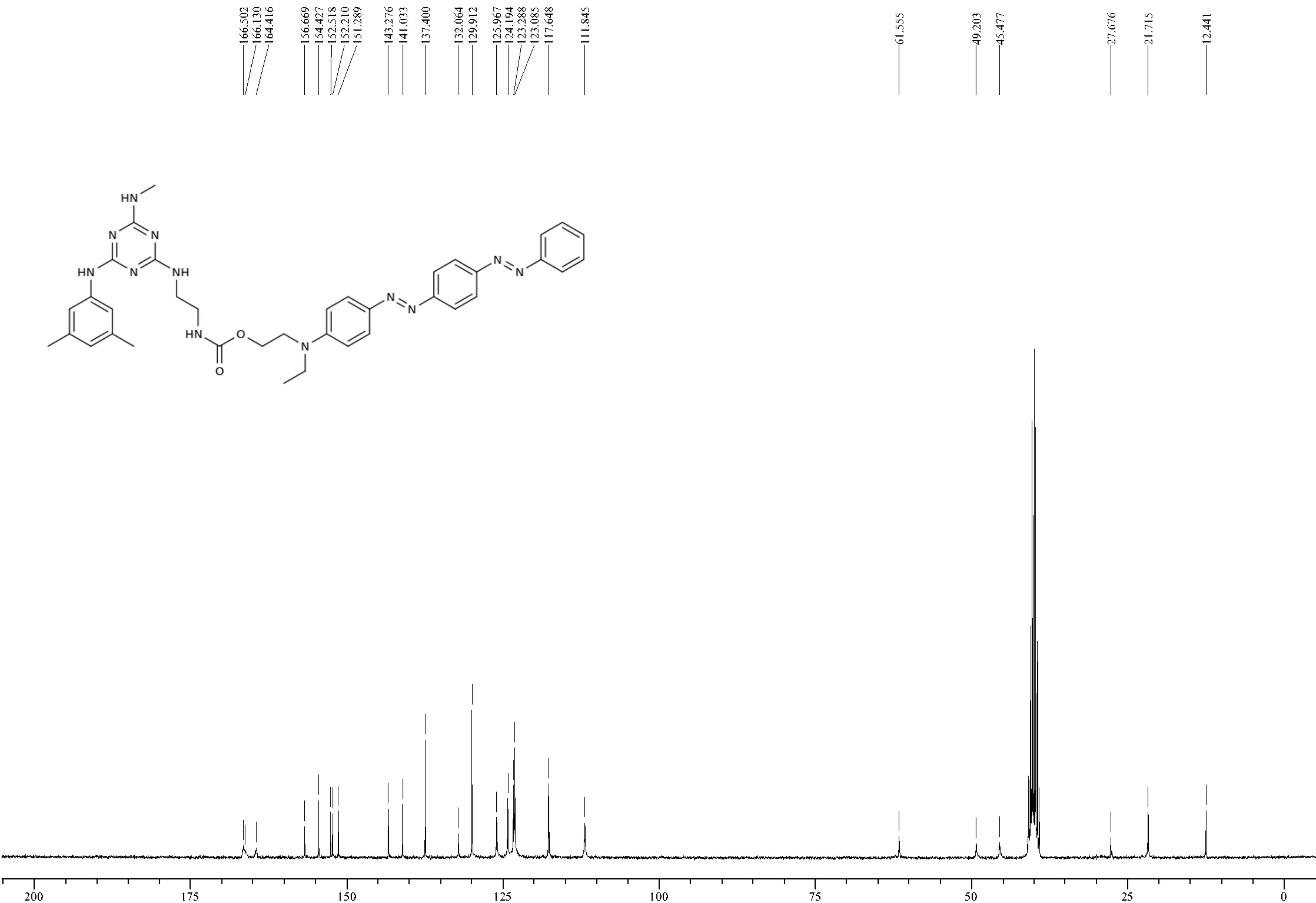
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125.967
124.194
123.288
123.085
117.648
111.845
61.555
49.203
45.477
27.676
21.715
12.441
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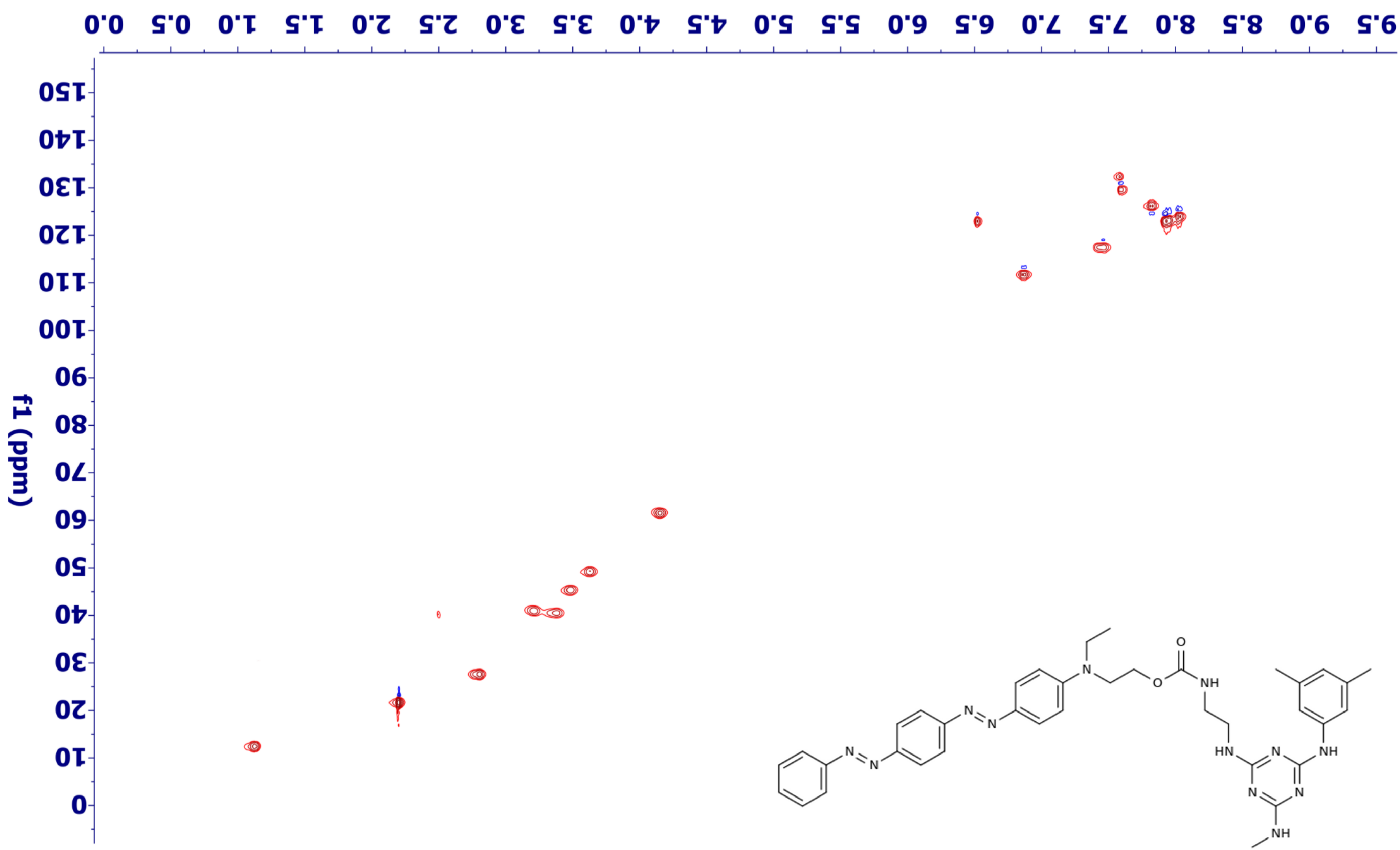
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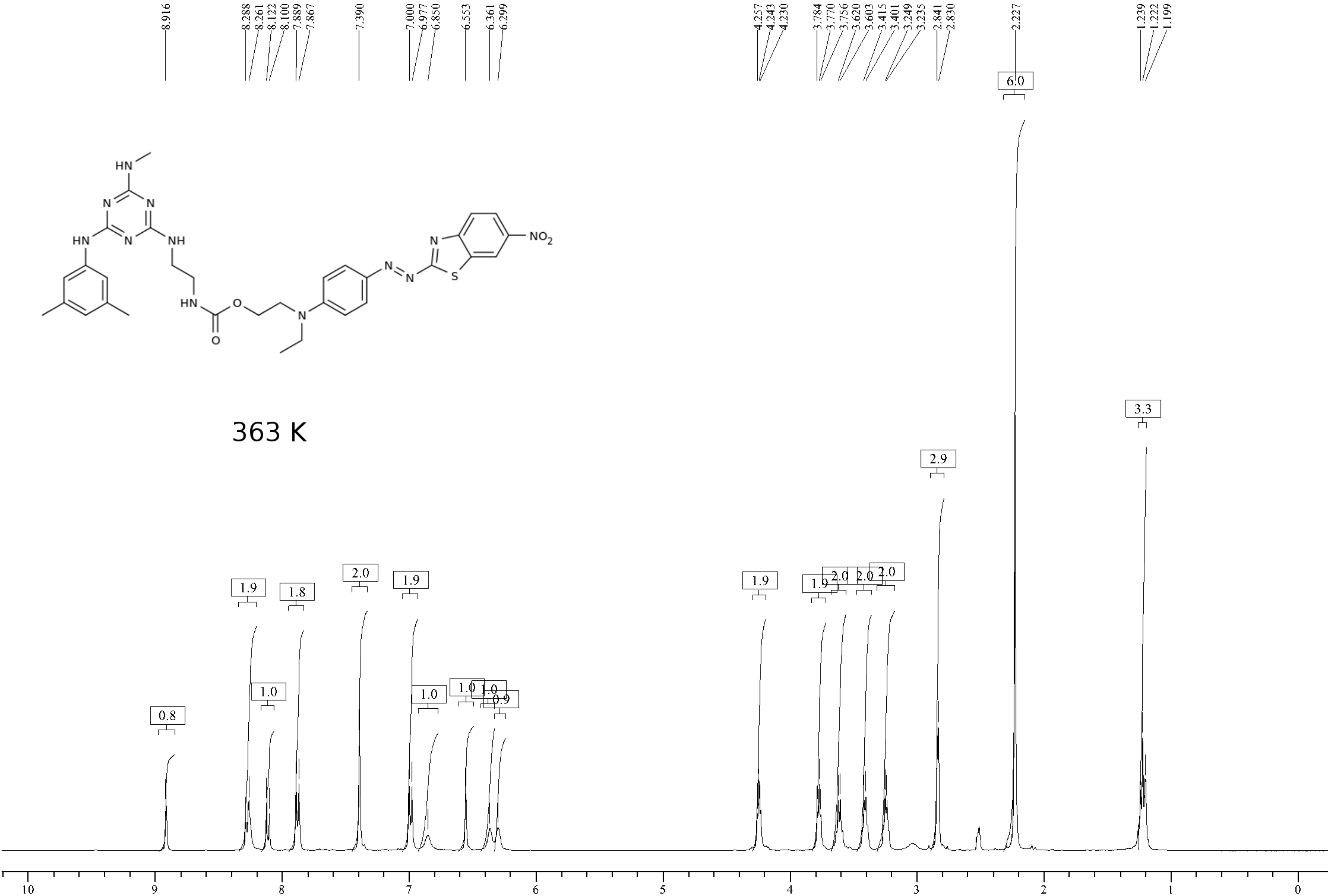

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6.553
6.361
6.299
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4.243
4.230
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3.770
3.756
3.620
3.603
3.415
3.401
3.249
3.235
2.841
2.830
2.227
1.239
1.222
1.199
363 K
0.8
1.9
1.0
1.8
2.0
1.9
1.0
1.0
1.0
0.9
1.9
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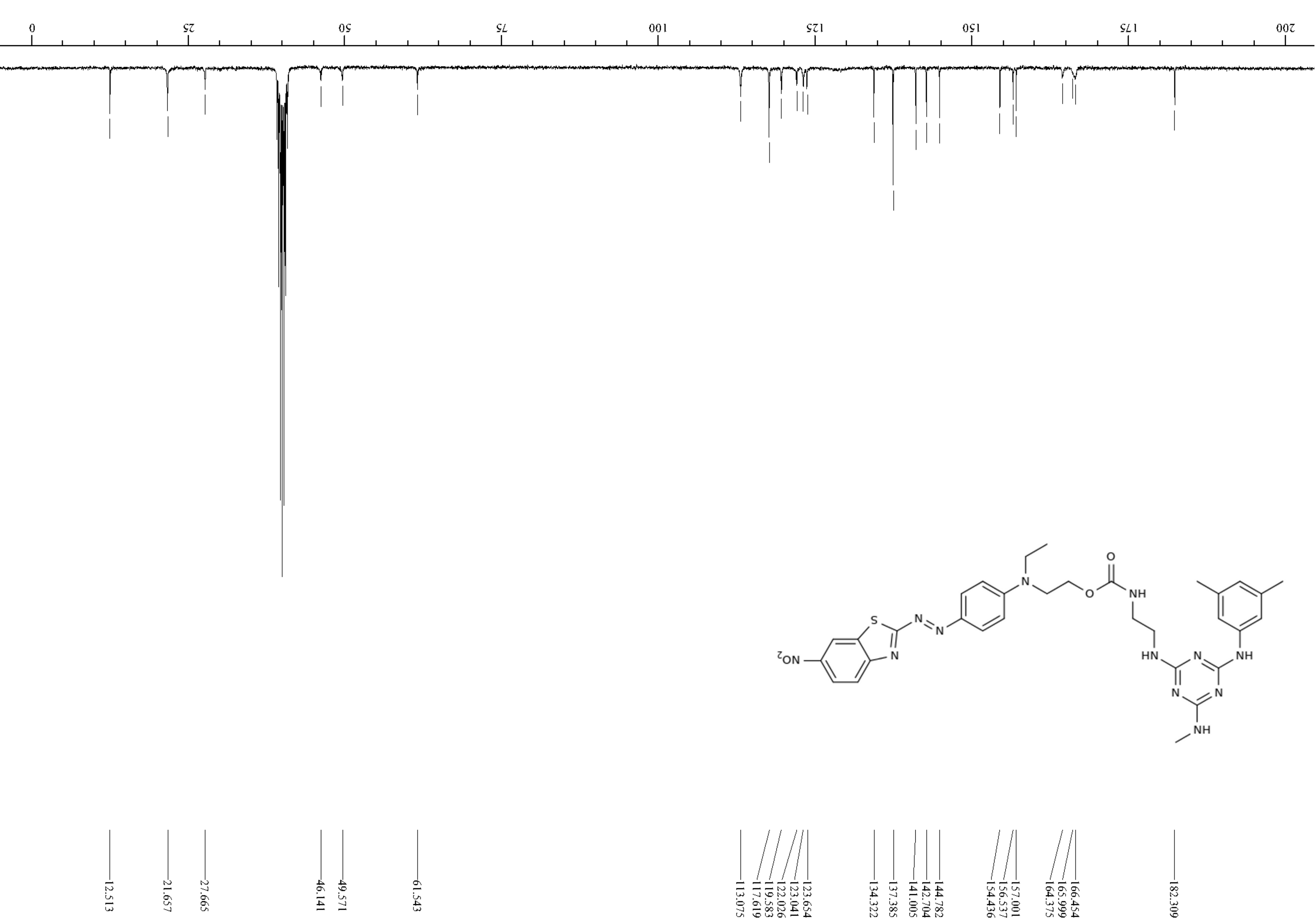

0
25
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150
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200
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117.619
119.583
122.026
123.041
123.654
134.322
137.385
141.005
142.704
144.782
154.436
156.537
157.001
164.375
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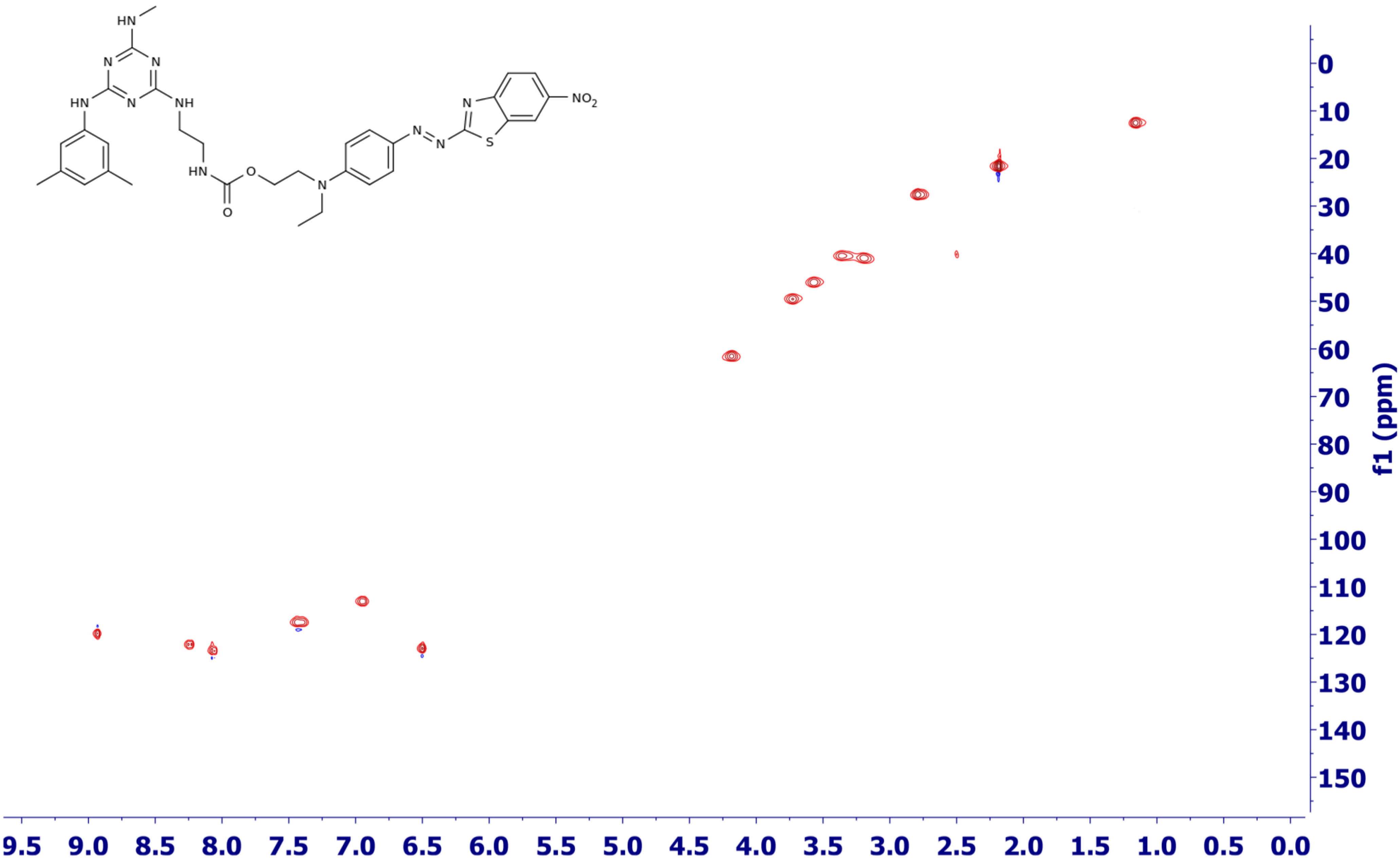
NH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N
NH
HN
O
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N
N
S
NO2
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7.5
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4.5
4.0
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2.0
1.5
1.0
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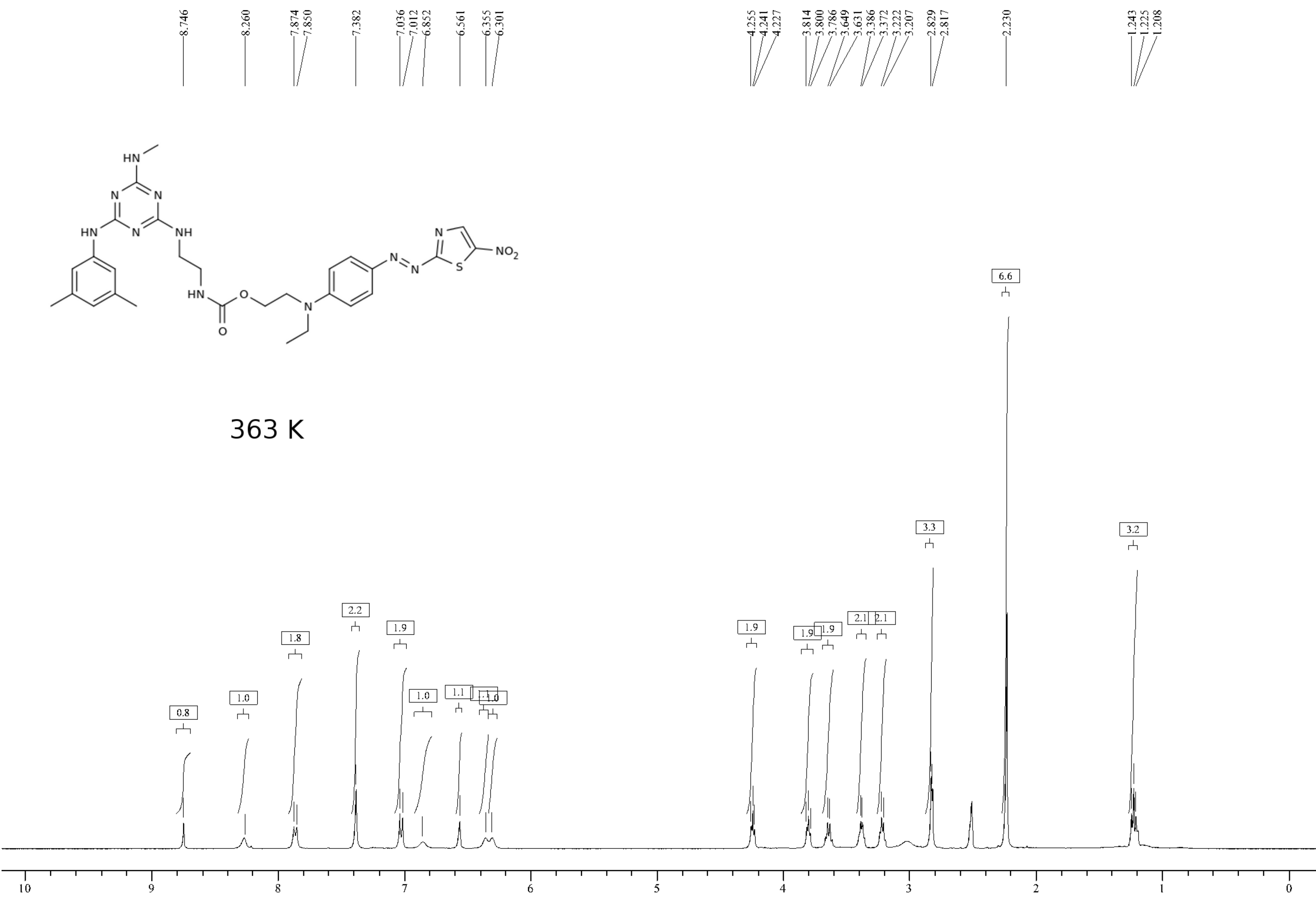
f1 (ppm)



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7.012
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4.227
3.814
3.800
3.786
3.649
3.631
3.386
3.372
3.222
3.207
2.829
2.817
2.230
1.243
1.225
1.208
0.8
1.0
1.8
2.2
1.9
1.0
1.1
1.1
1.0
1.9
1.9
1.9
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6
5
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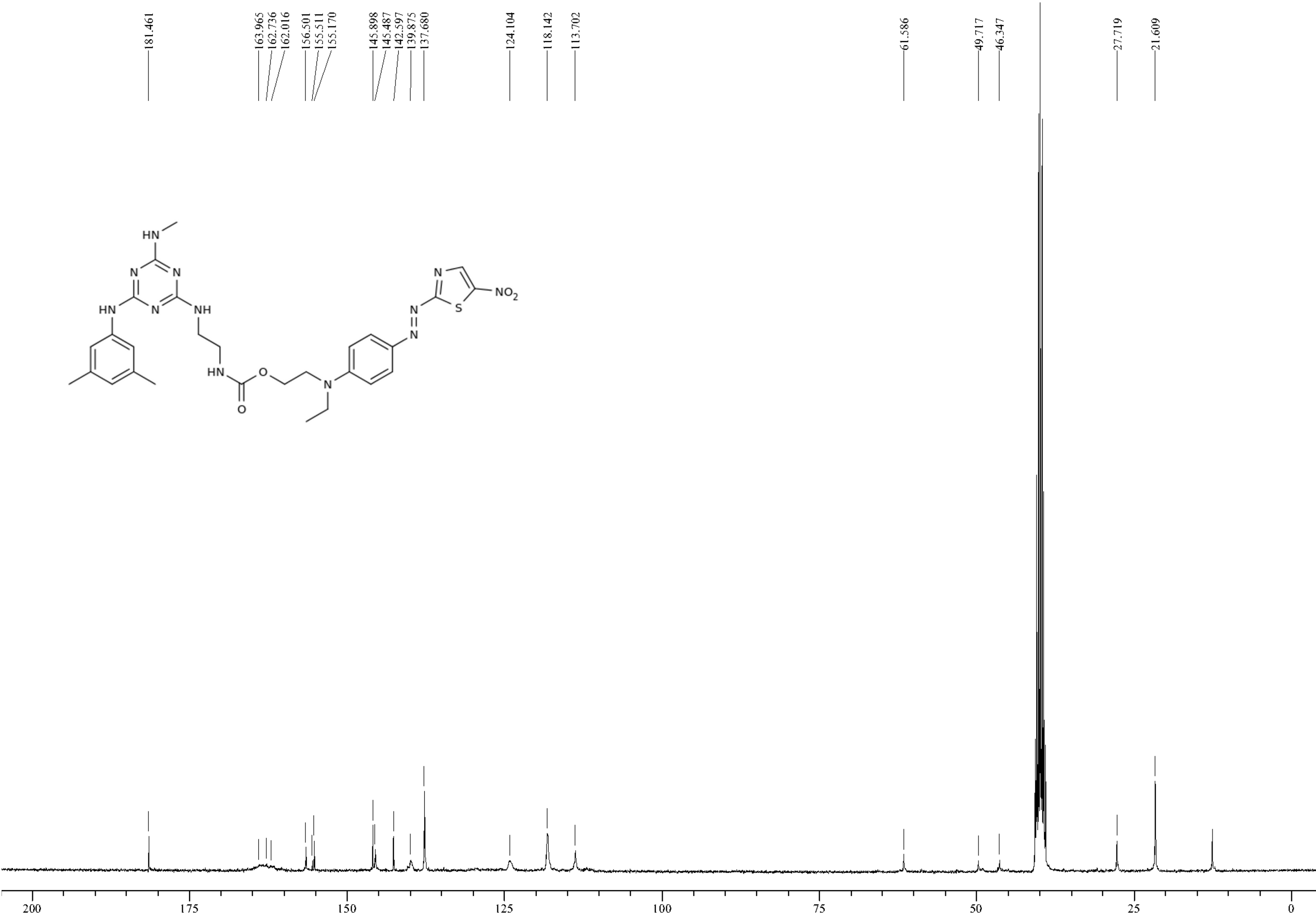
3
2
1
0

363 K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61.586
49.717
46.347
27.719
21.609
HN
N
N
N
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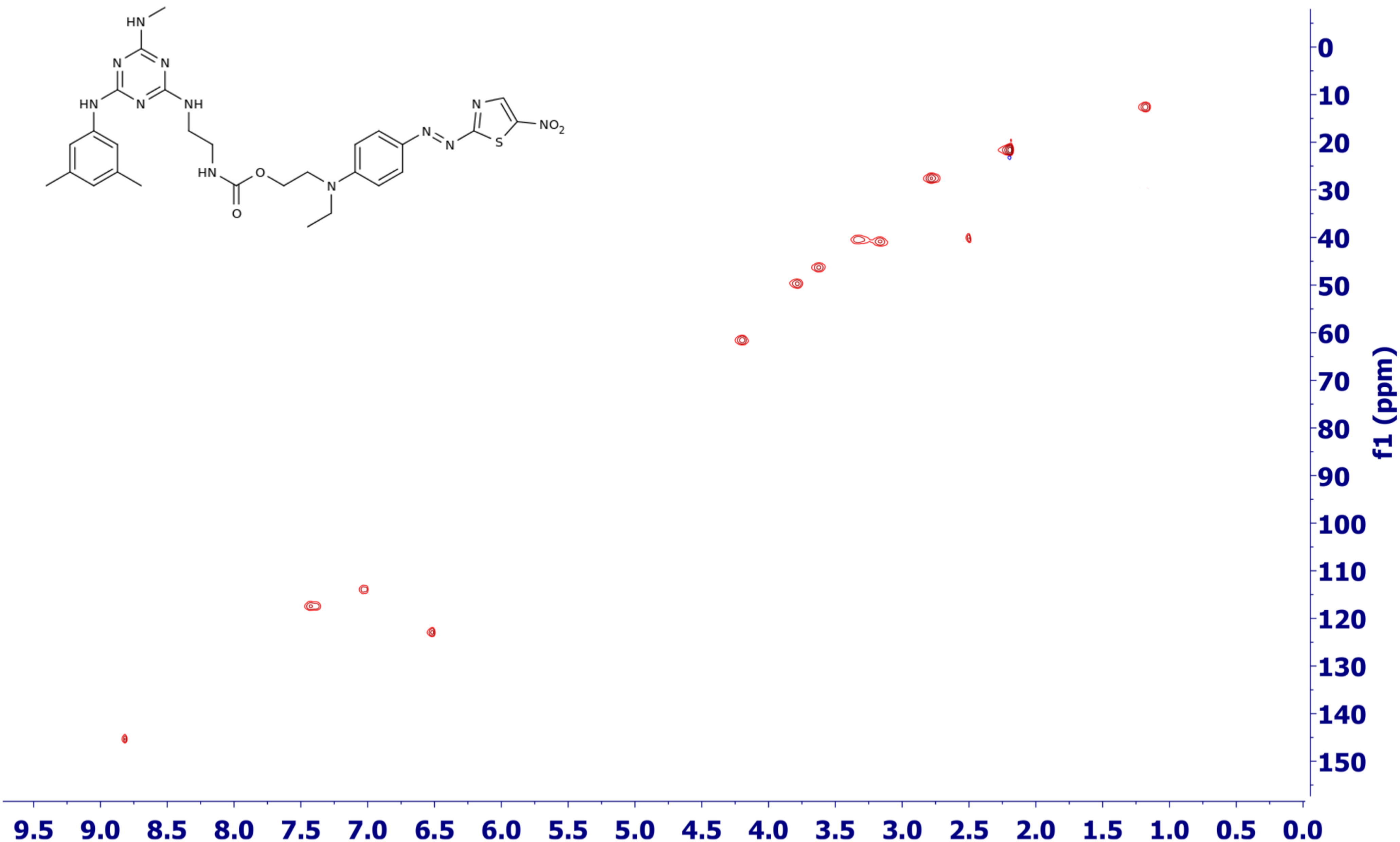
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N
N
HN
N
NH
HN
O
O
N
N
N
N
S
NO2
f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0