Supplementary material (ESI) for Journal of Materials Chemistry

Supplementary Information for
“Highly fluorescent donor–acceptor purines”

Roslyn S. Butler, Andrea K. Myers, Prabhu Bellarmine, Khalil A. Abboud,
*and Ronald K. Castellano**
Department of Chemistry, University of Florida, Gainesville, FL 32611

Experimental

General. Reagents and solvents were purchased from Aldrich, Fluka, or Acros and used without further purification unless otherwise specified. THF, ether, CH_2Cl_2, and DMF were degassed in 20 L drums and passed through two sequential purification columns (activated alumina; molecular sieves for DMF) under a positive argon atmosphere. Flash chromatography (FC) was performed on Purasil SiO_2-60, 230−400 mesh from Whatman. Thin layer chromatography (TLC) was performed on SiO_2-60 F_{254} aluminum plates from EMD Chemicals with visualization by UV light or staining (e.g. $KMnO_4$). Melting points (m.p.) were determined on a Mel-temp electrothermal melting point apparatus and are uncorrected. ^{1}H (300) and ^{13}C NMR (75 MHz) spectra were recorded on Varian Mercury 300, Gemini 300, and VXR 300 spectrometers. Chemical shifts (δ) are given in parts per million (ppm) relative to residual protonated solvent ($CHCl_3$: δ_H 7.26 ppm, δ_C 77.00 ppm). Abbreviations used are s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), b (broad), and m (multiplet). UV-Visible absorption spectra were obtained on a Perkin-Elmer Lambda 25 dual beam absorption spectrometer and a Cary 100 Bio spectrophotometer using 1 cm quartz cells. Steady-state fluorescence emission spectra were recorded on a SPEX Fluoromax spectrophotometer. Fluorescence lifetime measurements were obtained on a Photon Technology International, Inc. Time Master Fluorescence Lifetime system. High resolution mass spectra (HRMS) were obtained by the University of Florida Mass Spectrometry Services using a Finnigan MAT95Q Hybrid

Sector spectrometer. Purines **3a**[1], **3d**[2], and **4a**[3] were obtained as described in the literature with some modification.

Synthesis of Compounds

General Method A (*C(8) bromination of purines; conversion of **3** to **4***)[4]

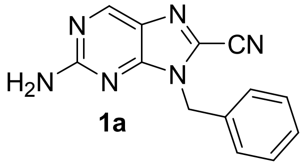
To a solution (6 mM) of starting material in CH_2Cl_2 was added bromine (33 equiv.) dropwise and the mixture was stirred at room temperature for 1 h to 24 h. The reaction mixture was poured into 10% aqueous $Na_2S_2O_3$. The organic layer was separated and washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (1% MeOH/CH_2Cl_2) to give the C(8) brominated product.

General Method B (*coupling of bromopurines with zinc cyanide; conversion of **4** to **1***)[5]

To a solution (0.16 M) of bromopurine **4** in NMP was added tetrakis(triphenylphosphine)palladium(0) (20–40 mol %), which was purified by washing with benzene and methanol. After stirring at 90 °C for 20 min a mixture of zinc cyanide (2 equiv.) suspended in NMP (0.90 mM) was added dropwise to the reaction (10 drops every 30 min for 4 h). The reaction was stirred at 90 °C overnight and then cooled and treated with aqueous ammonia (2 N, 15 mL). The mixture was extracted with ethyl acetate (3 x 100 mL). The combined organic extracts were washed with 2 N NH_4OH and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (0.5% MeOH/CH_2Cl_2).

General Method C (*methanolysis of C(8) cyanopurines; conversion of **1** to **2***)[6]

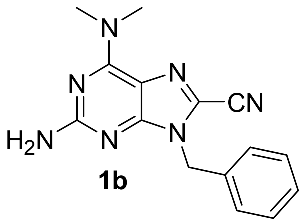
A solution of methanolic ammonia (7 N) and cyanopurine **1** was stirred at room temperature overnight. The residue, after evaporation, was stirred in methanol while 1 N aqueous HCl was added dropwise. The solution was stirred for 2 h at room temperature, neutralized with Dowex 1 (OH^-) resin, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (1% $MeOH/CH_2Cl_2$).



1a

2-Amino-8-cyano-9-benzylpurine (1a)

Compound **4a** (0.10 g, 0.33 mmol) was reacted under the conditions of general method **B** to yield a white solid (0.065 g, 80%): m.p. 139−142 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 5.40 (s, 2H), 7.26 (m, 7H), 8.88 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 46.62, 112.17, 124.40, 126.58, 127.87, 128.87, 128.90, 129.67, 136.11. HRMS calcd for $C_{13}H_{10}N_6$ [M^+]: 250.0967, found: 250.0973.

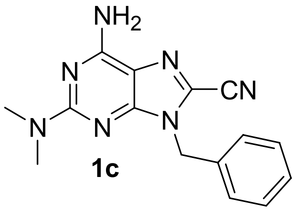


1b

2-Amino-6-dimethylamino-8-cyano-9-benzylpurine (1b)

Compound **4b** (0.20 g, 0.58 mmol) was reacted under the conditions of general method **B** to yield a white solid (0.15 g, 91%): m.p. 175−176°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.40 (bs, 6H), 5.33 (s, 2H), 6.44 (s, 2H), 7.33 (m, 5H). ^{13}C NMR (75 MHz, DMSO-d_6) δ

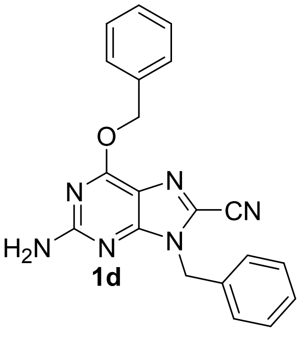
47.56, 112.08, 114.91, 117.72, 126.90, 127.90, 128.78, 135.82, 152.77, 154.86, 161.50. HRMS calcd for $C_{15}H_{16}N_7$ $[M+H]^+$: 294.1467, found: 294.1479.



1c

2-Dimethylamino-6-amino-8-cyano-9-benzylpurine (1c)

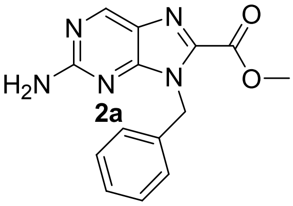
Compound **4c** (0.10 g, 0.29 mmol) was reacted under the conditions of general method **B** to yield a white solid (85 mg, 77 %): m.p. 205−209 ° C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.12 (s, 6H), 5.33 (s, 2H), 7.34 (m, 7H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 36.90, 46.02, 112.25, 113.92, 118.50, 127.67, 128.10, 135.86, 136.00, 151.49, 156.28, 161.02. HRMS calcd for $C_{15}H_{16}N_7$ $[M+H]^+$: 294.1467, found: 294.1492.



1d

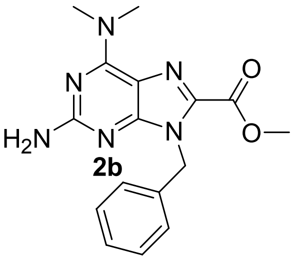
2-Amino-6-benzyloxy-8-cyano-9-benzylpurine (1d)

Compound **4d** (0.30 g, 0.73 mmol) was reacted under the conditions of general method **B** to yield a white solid (0.14 g, 54%): m.p. 246−248 ° C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 5.37 (s, 2H), 5.52 (s, 2H), 7.14, (s, 2H) 7.38 (m, 10H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 46.22, 67.61, 111.58, 114.62, 121.17, 127.01, 128.07, 128.25, 128.42, 128.64, 128.88, 135.48, 135.89, 153.69, 161.10, 161.79. HRMS calcd for $C_{20}H_{17}N_6O$ $[M+H]^+$: 357.1464, found: 357.1432.



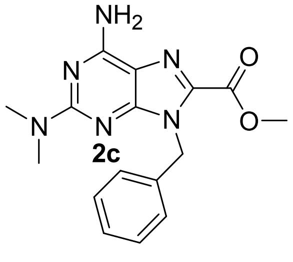
2-Amino-8-methylester-9-benzylpurine (2a)

Compound **1a** (0.10 g, 0.40 mmol) was reacted under the conditions of general method **C** to yield a white solid (0.068 g, 60%): m.p. 226–228 ° C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.97 (s, 3H), 5.27 (s, 2H), 5.74 (s, 2H), 7.29 (m, 5H), 8.84 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 47.05, 53.22, 127.18, 127.92, 128.13, 128.87, 136.71, 151.75, 153.26, 159.86, 161.43. HRMS calcd for $C_{14}H_{13}N_5O_2$ [M+H]$^+$: 283.1069, found: 283.1086.



2-Amino-6-dimethylamino-8-methylester-9-benzylpurine (2b)

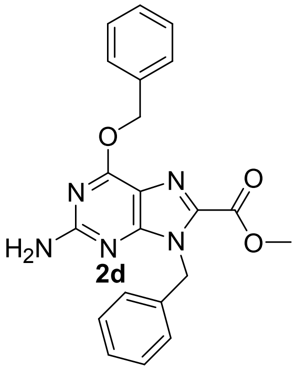
Compound **1b** (0.062 g, 0.21 mmol) was reacted under the general method **C** to yield a white solid (0.054 g, 86%): m.p. 175−180 ° C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.51 (bs, 6H) 3.91 (s, 3H) 4.77 (s, 2H) 5.70 (s, 2H) 7.26 (m, 5H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 37.00, 46.12, 52.02, 114.23, 126.49, 127.12, 128.41, 132.89, 137.89, 137.60, 154.38, 155.46, 159.28, 161.02. HRMS calcd for $C_{16}H_{19}N_6O_2$ [M+H]$^+$: 327.1569, found: 327.1583.



2c

2-Dimethylamino-6-amino-8-methylester-9-benzylpurine (2c)

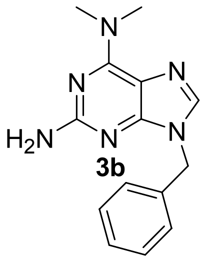
Compound **1c** (0.10 g, 0.34 mmol) was reacted under the conditions of general method **C** to yield a white solid (0.067 g, 60%): m.p. 250−252 ° C. ^{1}H NMR (300 MHz, DMSO-*d*$_6$) δ 3.10 (s, 6H), 3.80 (s, 3H), 5.55 (s, 2H), 7.26 (m, 7H). ^{13}C NMR (75 MHz, DMSO-*d*$_6$) δ 36.91, 46.25, 51.94, 113.12, 127.30, 128.39, 133.75, 137.67, 153.04, 156.83, 159.39, 160.58. HRMS calcd For $C_{16}H_{18}N_6O_2$ [M$^+$]: 326.1491, found: 326.1488.



2d

2-Amino-6-benzyloxy-8-methylester-9-benzylpurine (2d)

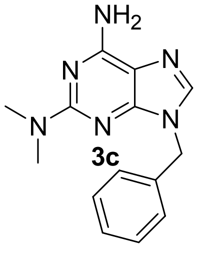
Compound **1d** (0.037 g, 0.10 mmol) was reacted under the conditions of general method **C** to yield a white solid (0.038 g, 95%): m.p. 180−185 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.90 (s, 3H), 5.03 (s, 2H), 5.53 (s, 2H), 5.70 (s, 2H), 7.31 (m, 10H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 47.20, 52.64, 68.46, 115.51, 127.52, 127.69, 128.18, 128.37, 128.53, 128.65, 135.90, 136.74, 137.13, 155.26, 159.70, 160.53, 162.56. HRMS calcd for $C_{21}H_{19}N_5O_3$ [M+H]$^+$: 390.1566, found: 390.1544.



3b

2-Amino-6-dimethylamino-9-benzylpurine (3b)

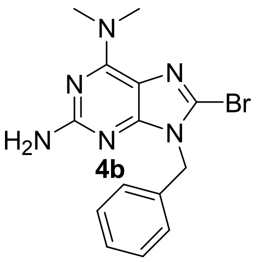
Dimethylamine (4.0 mL, 33% in abs ethanol) was added to 2-amino-6-chloro-9-benzylpurine[7] (1.0 g, 3.9 mmol) in abs ethanol (40 mL) and the solution was heated to 60 °C for 20 h. The reaction mixture was evaporated to dryness and triturated with deionized H_2O. The white crystals (0.95 g, 92%) were then collected by vacuum filtration and dried under high vacuum: m.p. 170−173 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 3.46 (s, 6H), 4.61 (s, 2H), 5.21 (s, 2H), 7.27 (m, 5H), 7.42 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 38.22, 46.39, 114.98, 127.49, 127.93, 128.82, 135.87, 136.36, 152.91, 155.39, 159.40. HRMS Calcd for $C_{14}H_{17}N_5$ $[M+H]^+$: 269.1509, found: 269.1516.



3c

2-Dimethylamino-6-amino-9-benzylpurine (3c)

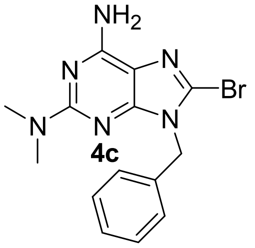
Dimethylamine (10 mL, 33% in abs ethanol) was added to 2-chloro-6-amino-9-benzyl purine (0.30 g, 1.2 mmol) in a sealed tube. The reaction was stirred at 100 °C for 20 h, and then concentrated under reduced pressure. The crude solid was purified by silica gel column chromatography (1% $MeOH/CH_2Cl_2$) to afford a white solid (0.31 g, 99%): m.p. 168−171 °C. ^1H NMR (300 MHz, DMSO-d_6) δ 3.07 (s, 6H), 5.19 (s, 2H), 6.73 (s, 2H), 7.34 (m, 5H), 7.82 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 37.00, 45.64, 112.39, 127.50, 127.77, 128.48, 137.35, 137.56, 151.60, 155.54, 159.48. HRMS calcd for $C_{14}H_{17}N_6$ $[M+H]^+$: 269.1509, found: 269.1515.



4b

2-Amino-6-dimethylamino-8-bromo-9-benzylpurine (4b)

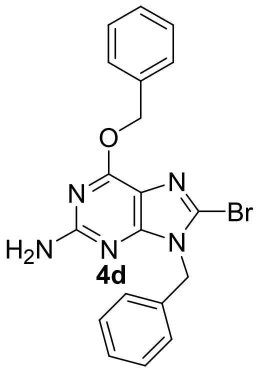
Compound **3b** (0.50 g, 1.8 mmol) was reacted under the conditions of general method **A** to yield a white solid (0.52 g, 81%): m.p. 168−169 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.42 (s, 6H), 4.69 (s, 2H), 5.24 (s, 2H), 7.28 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 38.27, 46.69, 115.54, 121.10, 127.40, 127.77, 128.63, 135.87, 154.13, 154.21, 159.19. HRMS calcd for $C_{14}H_{15}BrN_6$ $[M+H]^+$: 347.0620, found: 347.0618.



4c

2-Dimethylamino-6-amino-8-bromo-9-benzylpurine (4c)

Compound **3c** (0.59 g, 2.2 mmol) was reacted under the conditions of general method **A** to yield a white solid (0.52 g, 68%): m.p. 195−197 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.15 (s, 6H), 5.21 (bs, 2H), 5.23 (s, 2H), 7.29 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.33, 46.11, 46.90, 113.31, 122.36, 127.90, 128.06, 128.61, 136.03, 153.87, 159.77. HRMS calcd for $C_{14}H_{16}BrN_6$ $[M+H]^+$: 347.0614, found: 347.0626.



4d

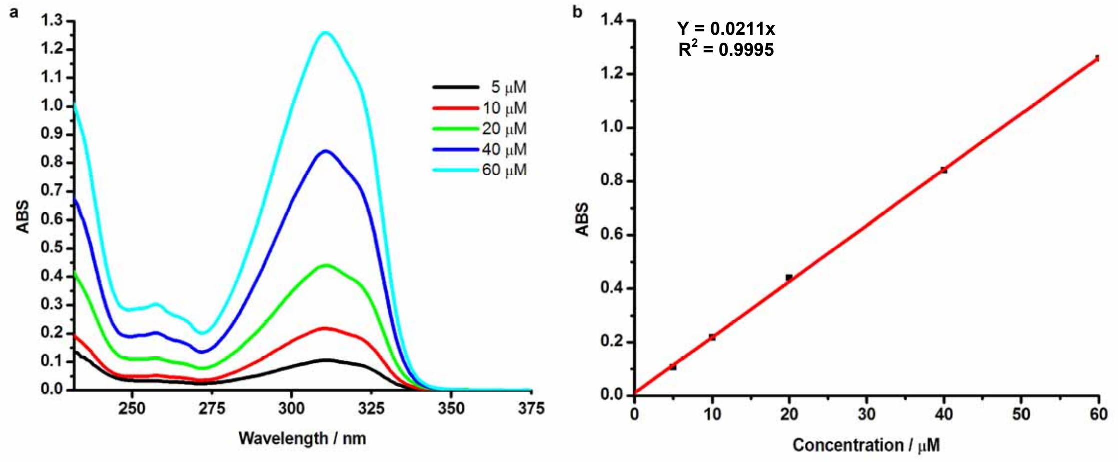
2-Amino-6-benzyloxy-8-bromo-9-benzylpurine (4d)

Compound **3d** (0.38 g, 0.93 mmol) was reacted under the conditions of general method **A** to yield a white solid (0.44 g, 77%): m.p. 164−166 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (m, 2H), 7.30 (m, 8H), 5.53 (s, 2H), 5.26 (s, 2H), 4.90 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 47.11, 68.25, 115.85, 125.56, 127.50, 128.03, 128.07, 128.39, 128.75, 135.37, 136.20, 155.29, 159.17, 159.85. HRMS calcd for $C_{19}H_{17}BrN_6O$ $[M+H]^+$: 410.0616, found: 410.0627.

Optical Studies

UV-Visible Data

The absorbance was measured for 5, 10, 20, 40, and 60 μM solutions on the Cary 100 Bio UV-Visible spectrophotometer (thermostatted at 25 °C) using dried and degassed methylene chloride (CH_2Cl_2). The absorbance intensity at λ_{max} was then plotted against the concentration to confirm, by linearity, that the compounds followed Beer's law. Once confirmed, molar extinction coefficients (ε) were determined from the linear plot for each compound (where $A = \varepsilon bc$). An example of this procedure is shown below for **1d**.



The slope of the line is then multiplied by 10^6 (this accounts for the concentration) to generate ε. This is then displayed as log ε.

Fluorescence Data

Fluorescence Lifetime Measurements

Fluorescence lifetime measurements were performed on a Photon Technology International, Inc. Time Master Fluorescence Lifetime system. Excitation was performed via a nitrogen laser at 337 nm (pulse width approximately 800 ps), and a quartz fiber optic was used to convey light to the sample chamber. Samples for fluorescence lifetime measurements of compounds **1a**–**d** and **2a**–**d** were prepared by making ~ 5 μM solutions of each compound in dried and degassed methylene chloride. Each compound was excited at 337 nm and the monochromater was set to the corresponding $\lambda_{\mathrm{em(max)}}$ for each compound. After the measurement of each compound, a scattering agent (Ludox® AM-30 colloidal silica, 30% wt. % suspension in water) was measured under the same parameters as the compound in order to find the instrument response time. The instrument response time along with the data collected for each sample was placed into the Time Master software to generate the fluorescence lifetime data.[8,9,10]

Table 1: Lifetime Values and Parameters

Compound	Lifetime of the excited state [ns] (λ_{ex} = 373 nm)	χ^2	DW	Z
1a	0.51 ±0.23	1.049	0.727	-1.454
1b	1.59 ±0.25	1.158	1.158	-1.577
1c	3.15 ±0.25	0.885	0.870	-0.980
1d	3.05 ±0.16	1.041	0.463	-2.534
2a	1.75 ±0.18	1.333	0.937	-2.336
2b	3.06 ±0.27	1.219	0.398	-1.911
2c	3.25 ±0.08	0.968	1.451	-1.714
2d	2.54 ±0.07	1.092	2.414	-0.564

Deviations from the best fit are characterized by the reduced chi-square statistic, χ^2. Good results typically produce χ^2's of 0.9 to 1.2. Most of the χ^2 values displayed in the table above are within the range indicated, those that are not are very close. The Durbin-Watson (DW) parameter was introduced to test for correlations. The fit is likely satisfactory if the value of DW is greater than 1.7 for single exponential fits. Most of the values are well below the satisfactory value of DW, however, the correlation is looking for structured patterns around the baseline, and can be sensitive to radio-frequency (RF) noise. The runs test determines the number of positive and negative groups of the residuals. A value of $-1.96 < Z$ indicates a satisfactory fit at the 95% confidence level. The general structure of each analysis program is the same so there is considerable similarity in running the programs.

Fluorescence Quantum Yield Measurements

Fluorescence quantum yield measurements were performed by collecting correlating absorption and steady-state emission spectra on a Perkin-Elmer Lambda 25 dual beam absorption spectrometer and a SPEX Fluoromax spectrophotometer, respectively. The unknowns and standards were prepared with dried and degassed solvent at or below a 10 μM concentration and absorbance below an intensity of 0.1. The equation used to calculate the quantum yield values follows,

$$\Phi_{F(x)} = (A_s/A_x)(F_x/F_s)(\eta_x/\ \eta_s)^2\,\Phi_{F(s)}$$

where Φ_F is the fluorescence quantum yield, A is the absorbance at the excitation wavelength, F is the area under the emission curve, and η is the refractive index of the solvent used. Subscripts s and x refer to the standard and unknown, respectively. Quantum yields were calculated using several different solutions of three different standards (shown in the table below).

Table 2: **Fluorescence Quantum Yield (Φ_F) Data in CH_2Cl_2 Calculated Using Three Different Standards**

Standards[a]	**1a**	**1b**	**1c**	**1d**	**2a**	**2b**	**2c**	**2d**
DPA 1	0.194	0.302	0.976	0.820	0.419	> 1	> 1	0.986
DPA 2	0.148	0.320	–	0.871	0.445	> 1	> 1	0.749
Q3	0.176	0.299	0.886	0.744	0.380	0.939	> 1	0.894
Q4	0.197	0.300	0.993	0.834	0.426	> 1	> 1	> 1
Q5	0.193	0.301	0.972	0.816	0.417	> 1	> 1	0.981
Q6	0.193	0.302	0.972	0.817	0.417	> 1	> 1	0.982
Q7	0.193	0.306	0.969	0.814	0.416	> 1	> 1	0.979
A1	0.193	0.273	0.973	0.816	0.418	> 1	> 1	0.982
A3	0.194	0.307	0.976	0.819	0.419	> 1	> 1	0.986
A4	0.194	0.300	0.977	–	0.420	> 1	> 1	0.987
A5	0.197	0.300	0.991	0.832	0.426	> 1	> 1	> 1

[a] DPA = 9,10-diphenylanthracene in cyclohexane (Φ_F = 0.90);[11] Q = quinine sulfate in 0.05 M H_2SO_4 (Φ_F = 0.546);[10,12] A = anthracene in ethanol. The numbers after the standards indicate different solutions.

Table 3: Absorption and Emission Data for Donor-Acceptor Purines in Methanol (10^{-6} M)

Compound	$\lambda_{(max)}$	**log** ε	$\lambda_{em(max)}$ **excited at 320 nm**
1a	222, 318	4.4, 3.2	399
1b	248, 327	4.2, 4.2	382
1c	291, 338	4.2, 4.2	412
1d	208, 318	4.3, 4.1	383
2a	248, 335	3.9, 4.1	409
2b	249, 331	4.2, 4.2	419
2c	226, 345	4.2, 4.1	436
2d	209, 321	4.6, 4.3	405

X-ray Crystallography

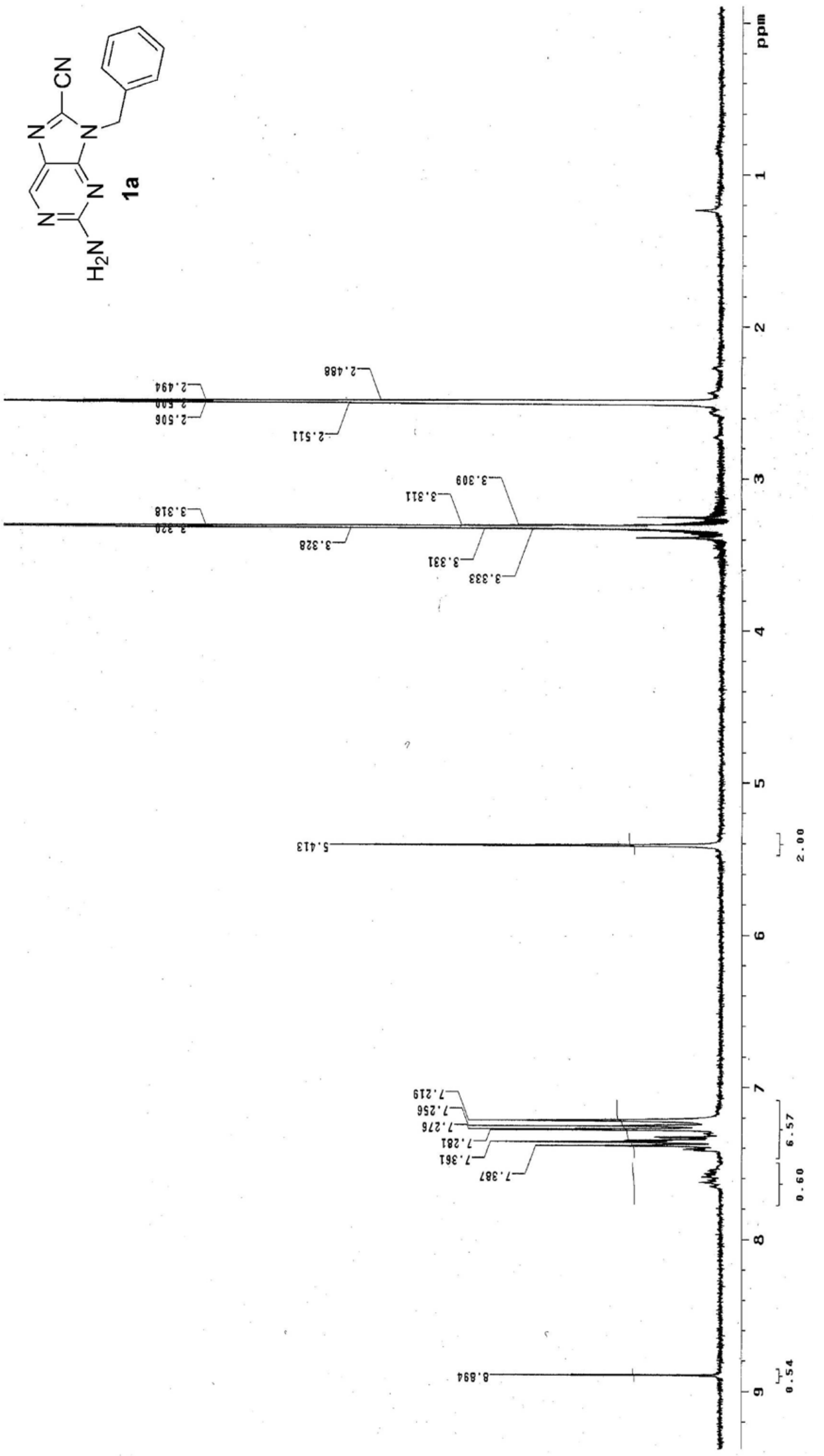
General: Data were collected at 173 K on a Siemens SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing MoK$_\alpha$ radiation (λ = 0.71073 Å). Cell parameters were refined using up to 8192 reflections. A full sphere of data (1850 frames) was collected using the ω-scan method (0.3° frame width). The first 50 frames were re-measured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was < 1 %). Absorption corrections by integration were applied based on measured indexed crystal faces.

The structures were solved by the Direct Methods in *SHELXTL6*,[13] and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms.

Compound 1b: The methyl H atoms on C(14) and C(15) are disordered and each set was refined in two parts and in a riding model with their site occupation factors fixed at 50%. A total of 208 parameters were refined in the final cycle of refinement using 4656 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 3.83% and 10.27%, respectively. Refinement was done using F^2.

Compound 1c: A total of 207 parameters were refined in the final cycle of refinement using 3304 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 4.75% and 12.0%, respectively. Refinement was done using F^2.

^{1}H NMR Spectra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N
CN
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2.506
2.511
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3.311
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3.320
3.328
3.331
3.333
5.413
7.219
7.256
7.276
7.281
7.361
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2
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6
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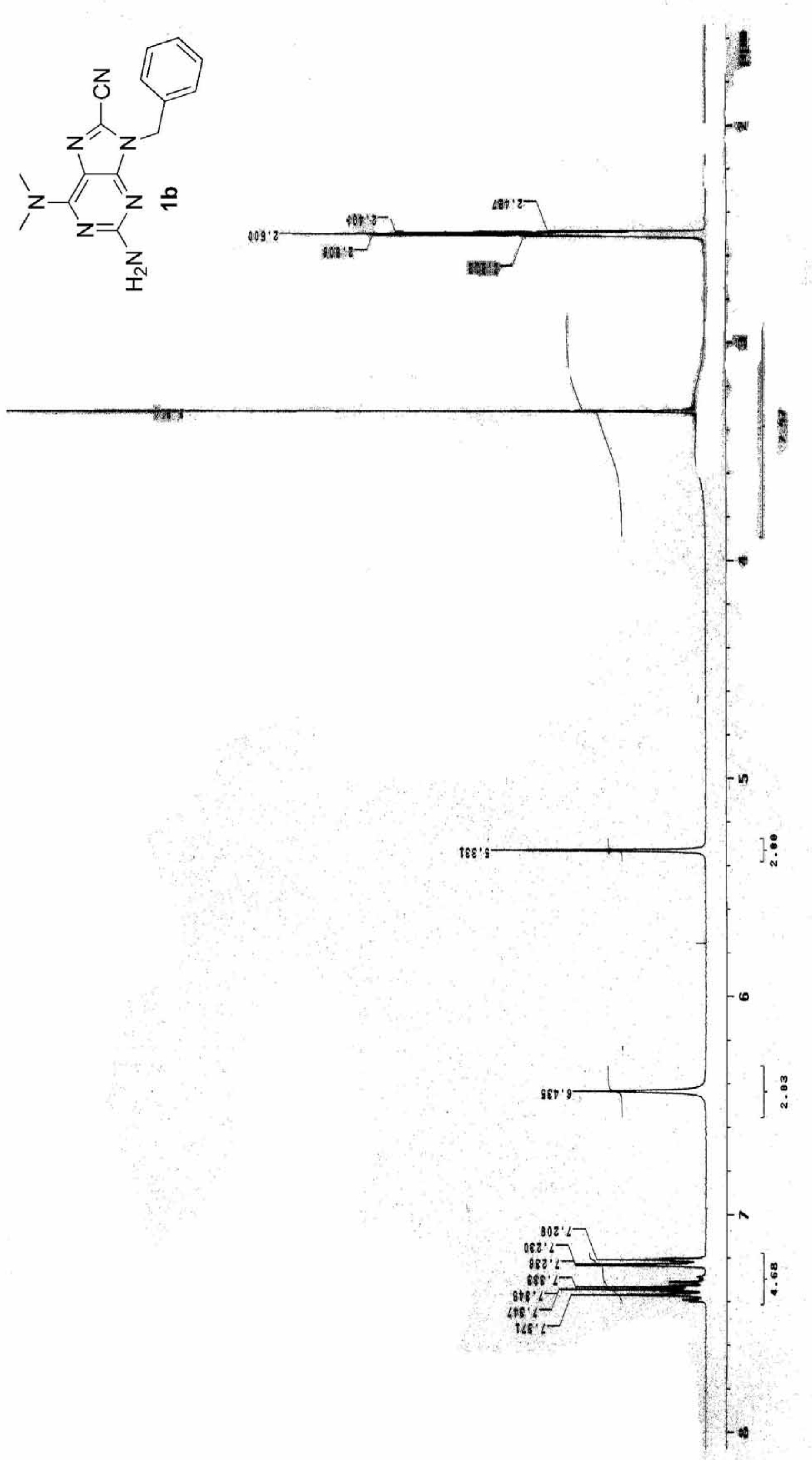
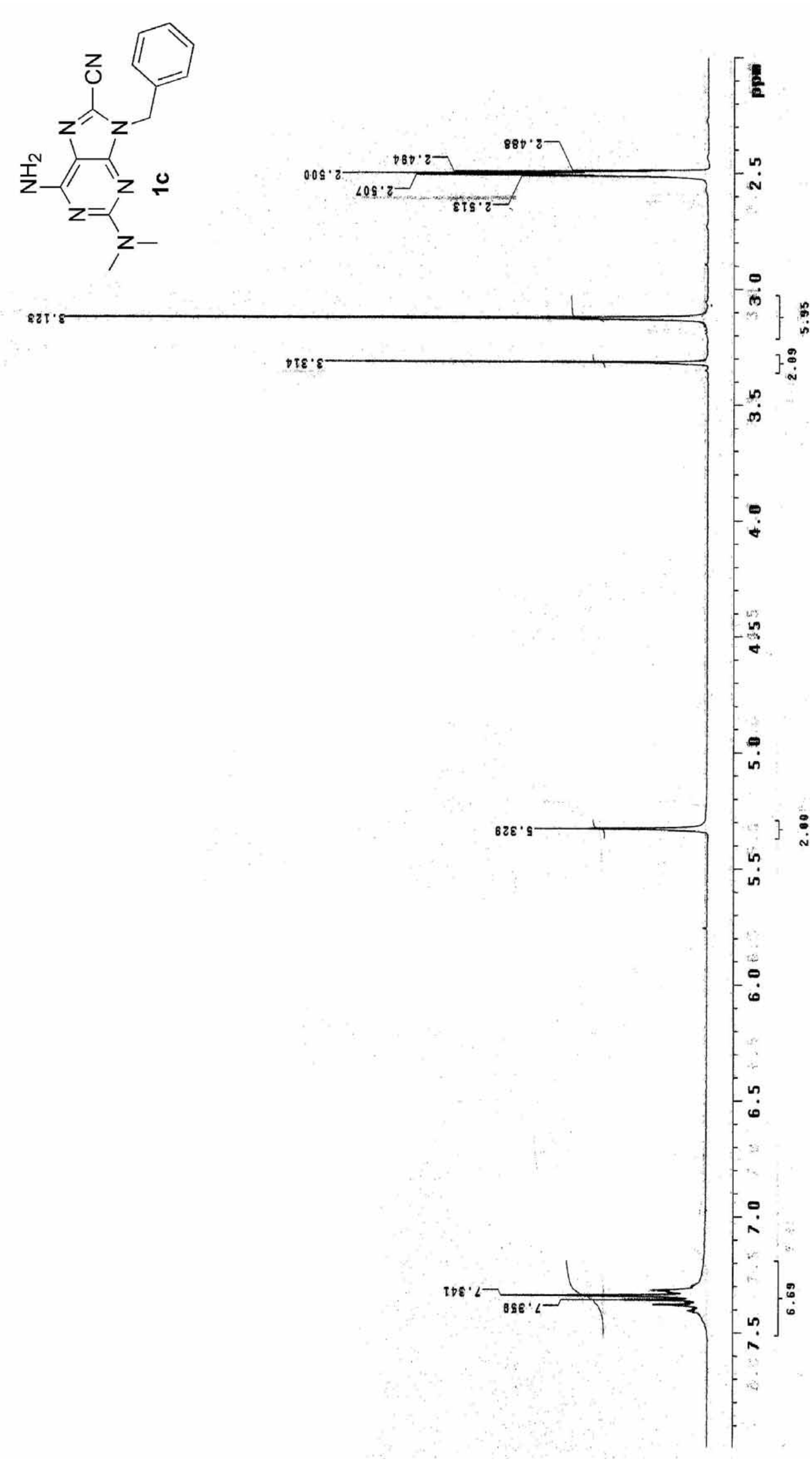
8
9


CN
N
N
N
N
H2N
1b
2.500
2.494
2.508
2.487
5.331
6.435
7.208
7.230
7.238
7.339
7.345
7.347
7.371
2.00
2.03
4.68
3
4
5
6
7
8


NH2
CN
N
1c
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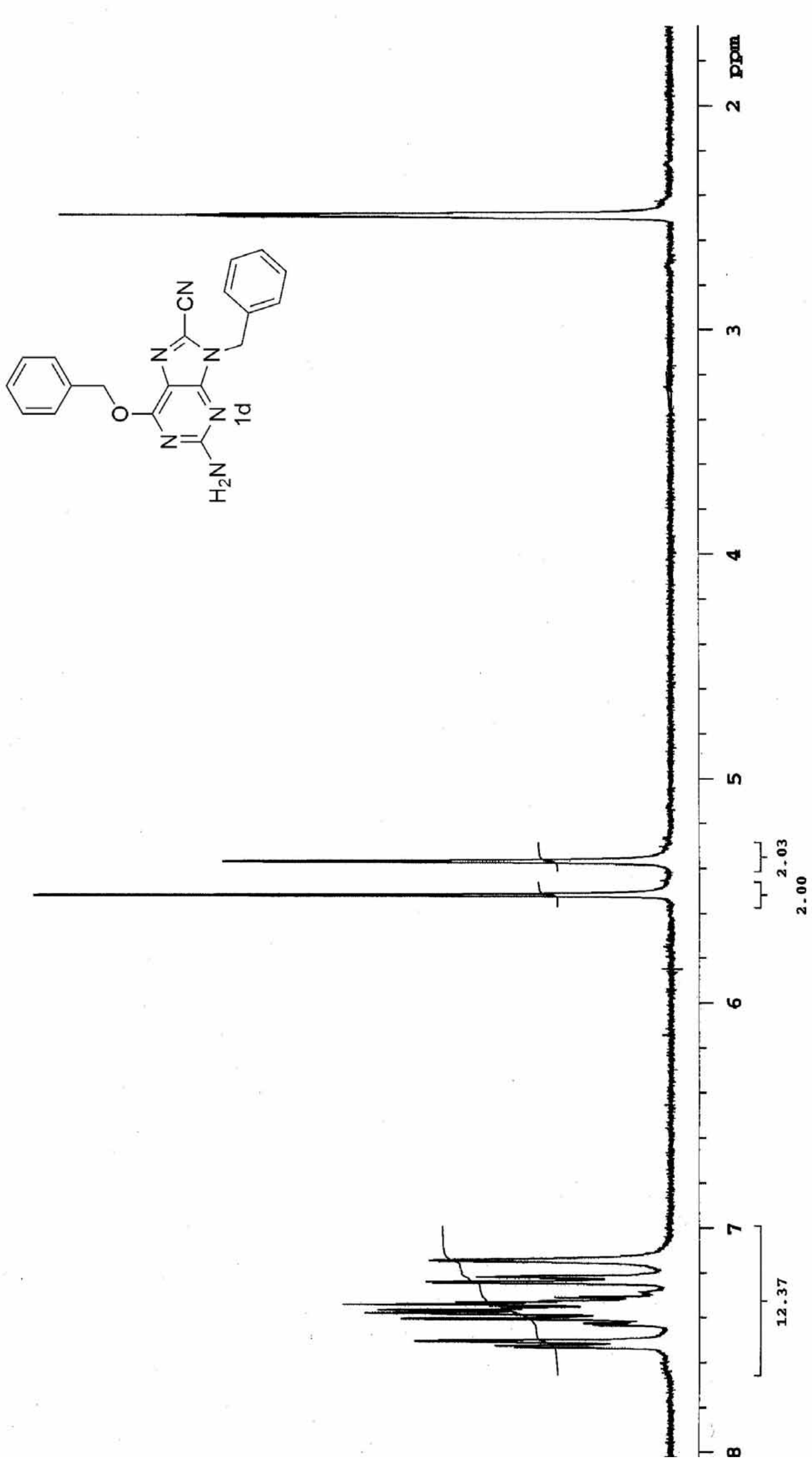
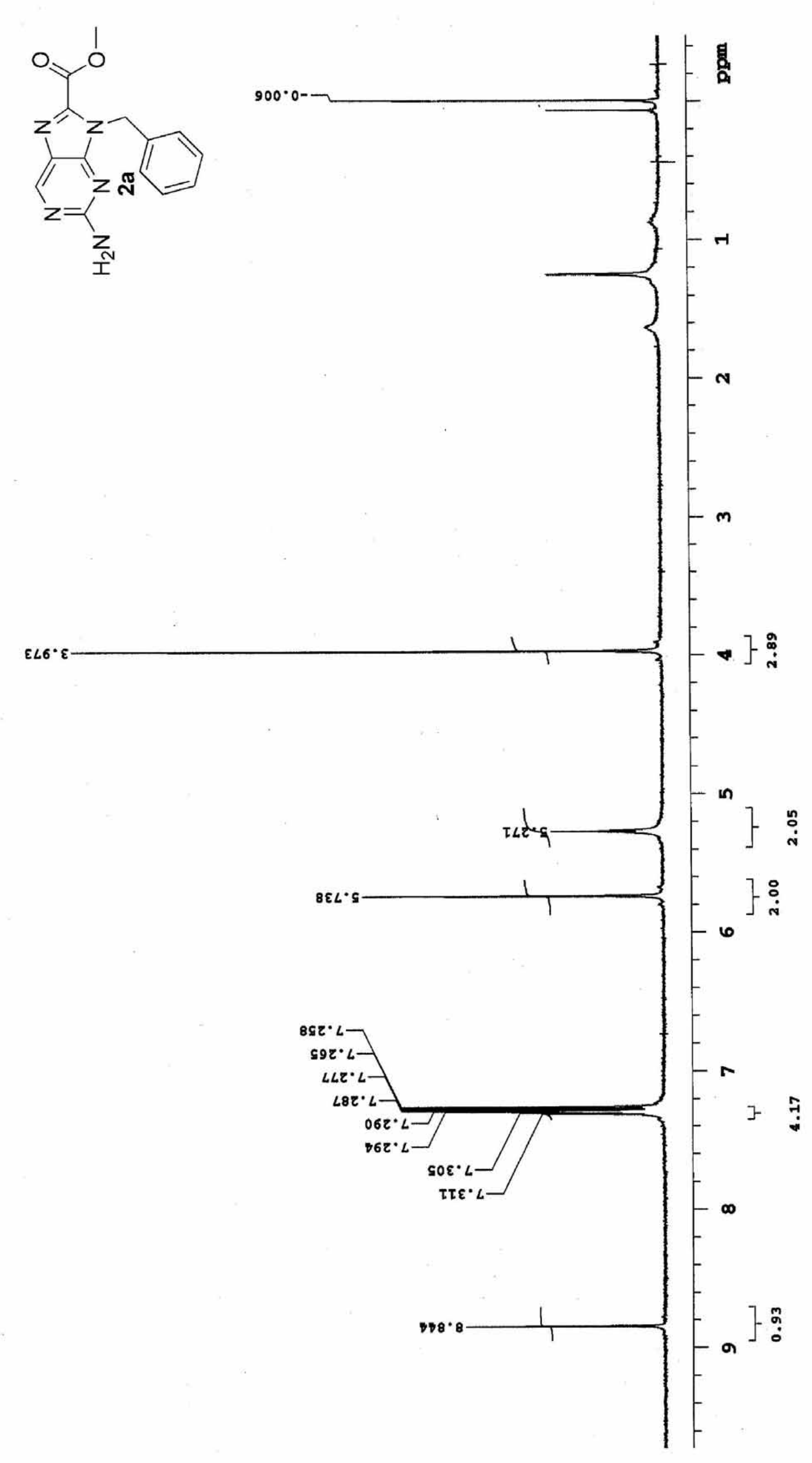
2.484
2.500
2.507
2.513
3.123
3.314
5.328
7.341
7.358
ppm
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
5.95
2.09
2.00
6.69


ppm
2
3
4
5
6
7
8
2.03
2.00
12.37
H$_2$N
O
CN
N
1d


2a
H2N
N
O
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3.973
5.271
5.738
7.258
7.265
7.277
7.287
7.290
7.294
7.305
7.311
8.844
2.89
2.05
2.00
4.17
0.93
ppm
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2
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4
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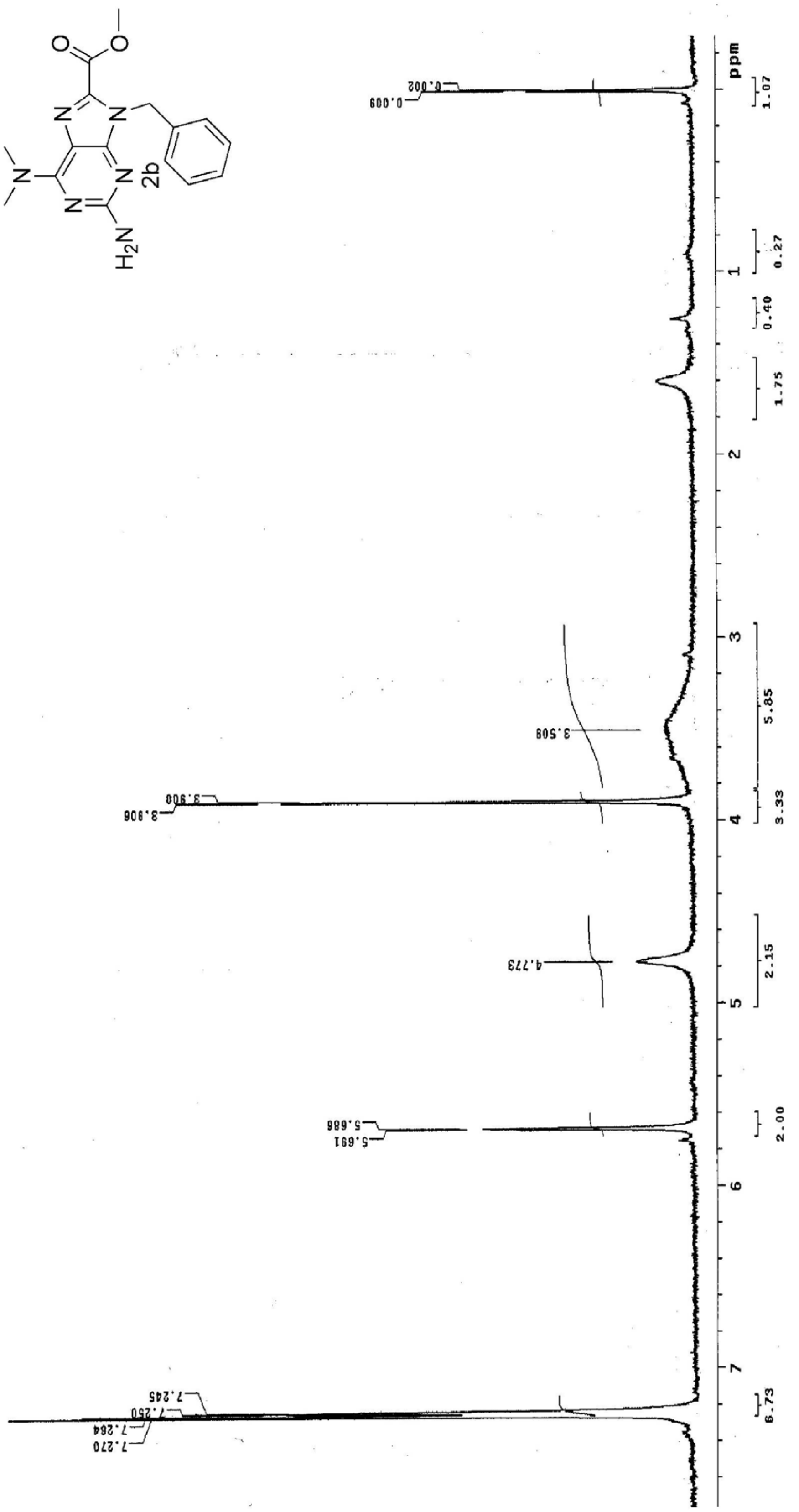
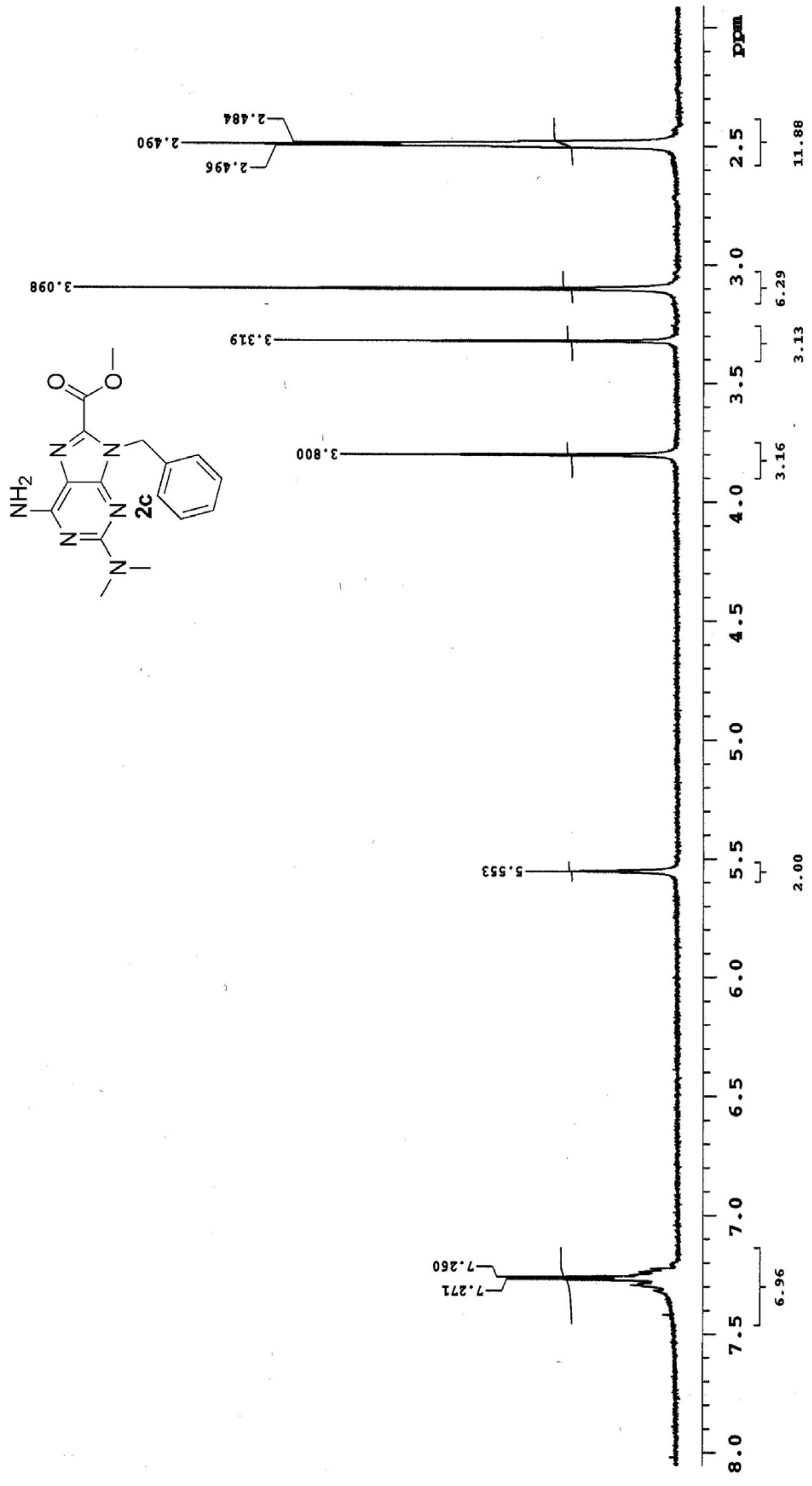
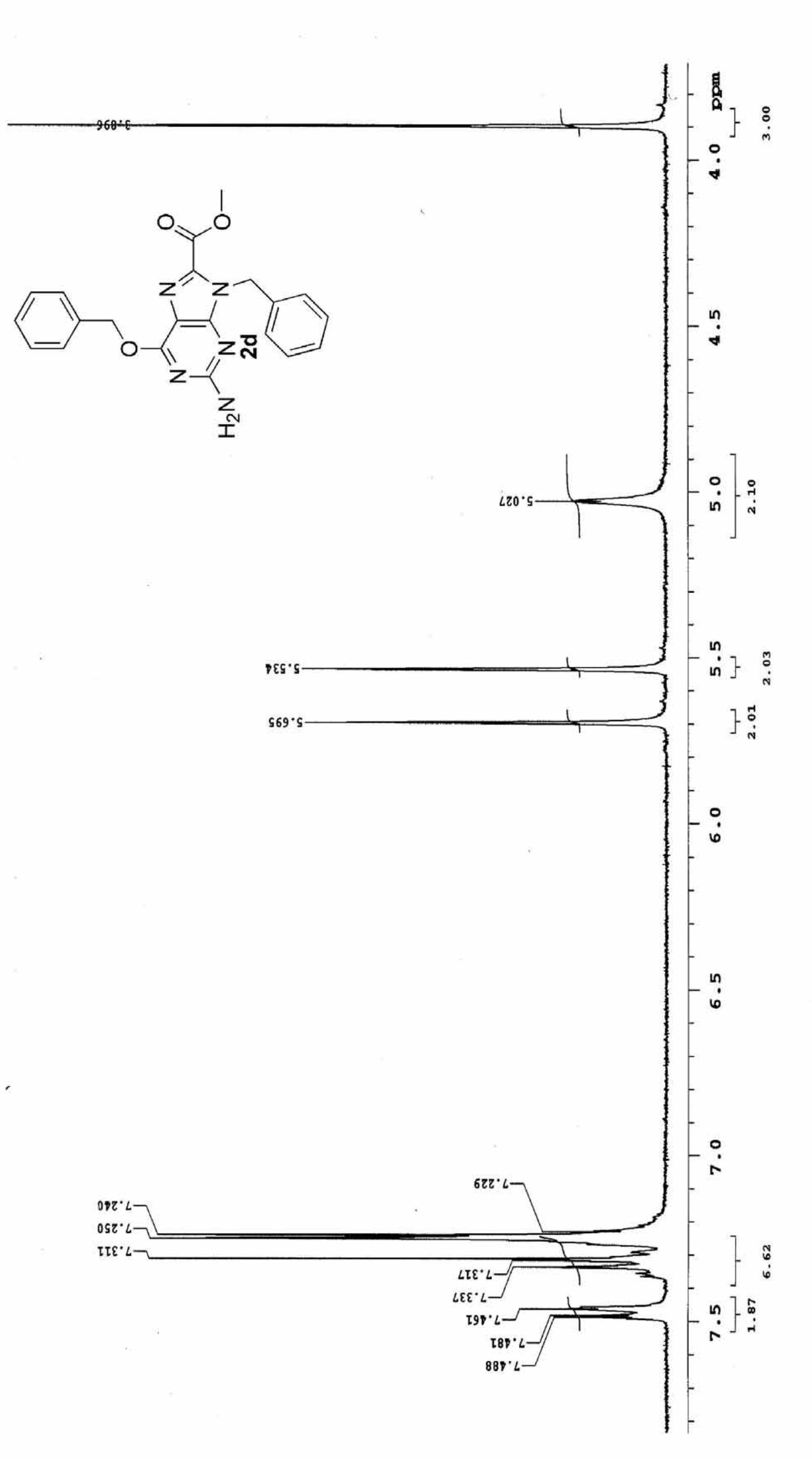
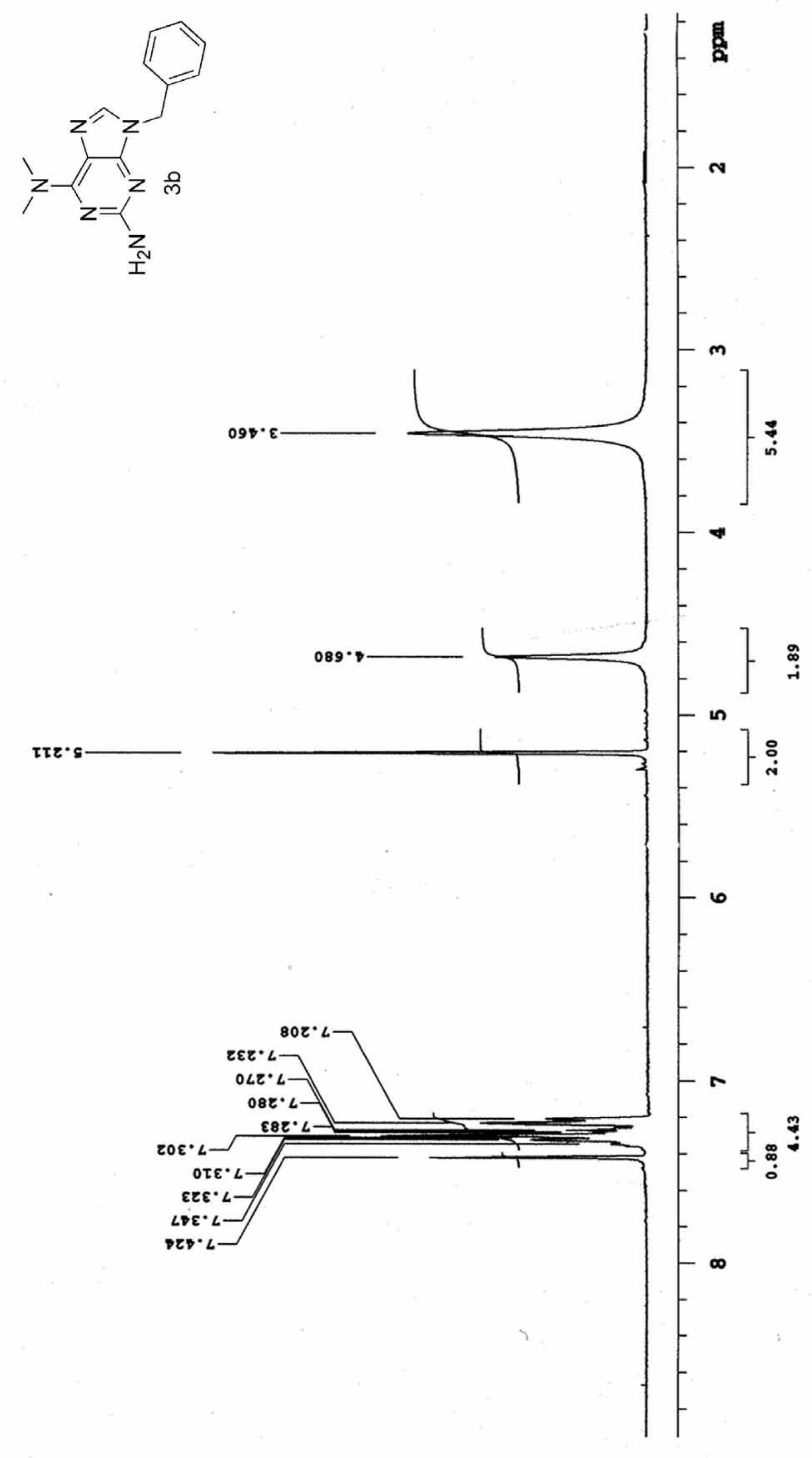
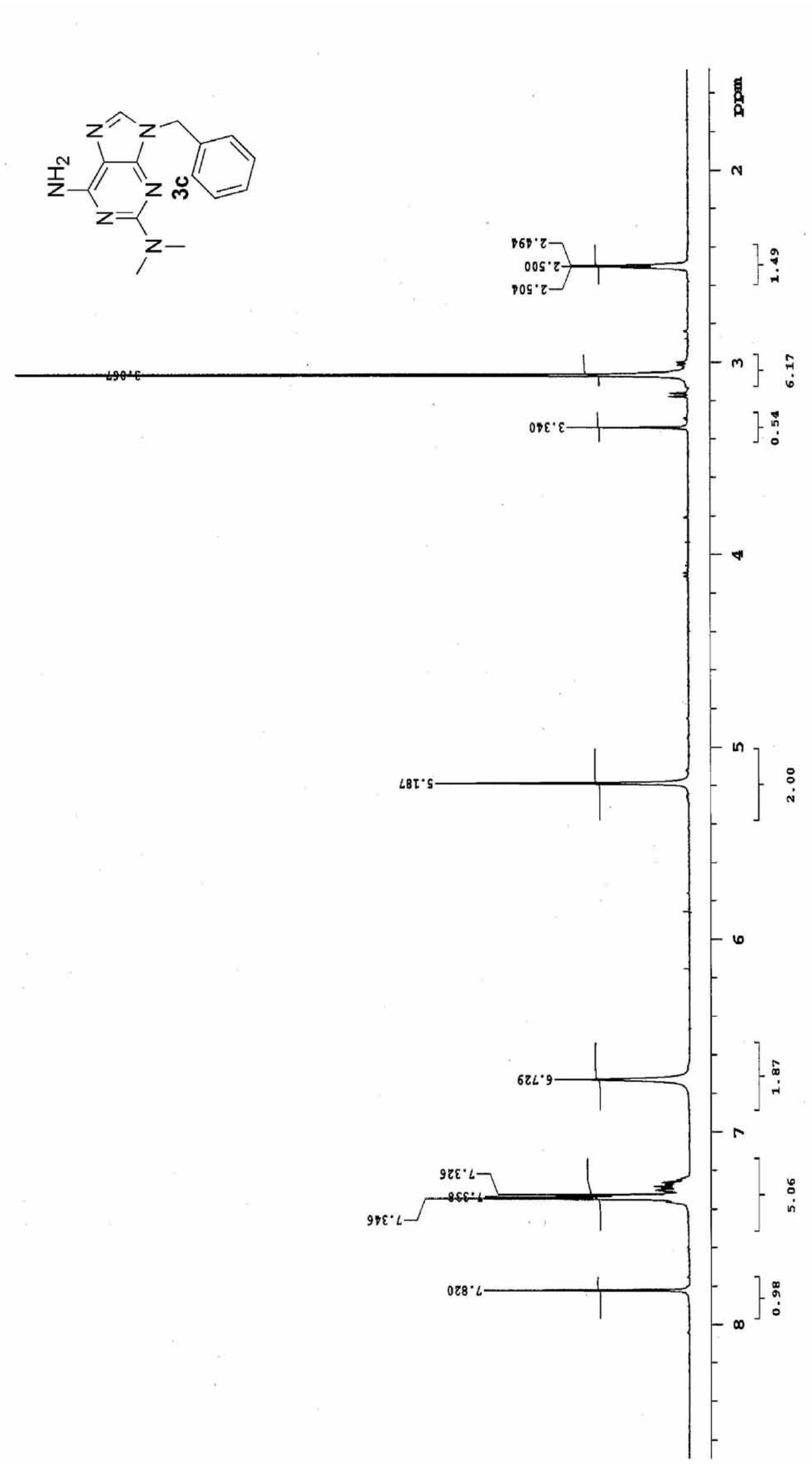
6
7
8
9

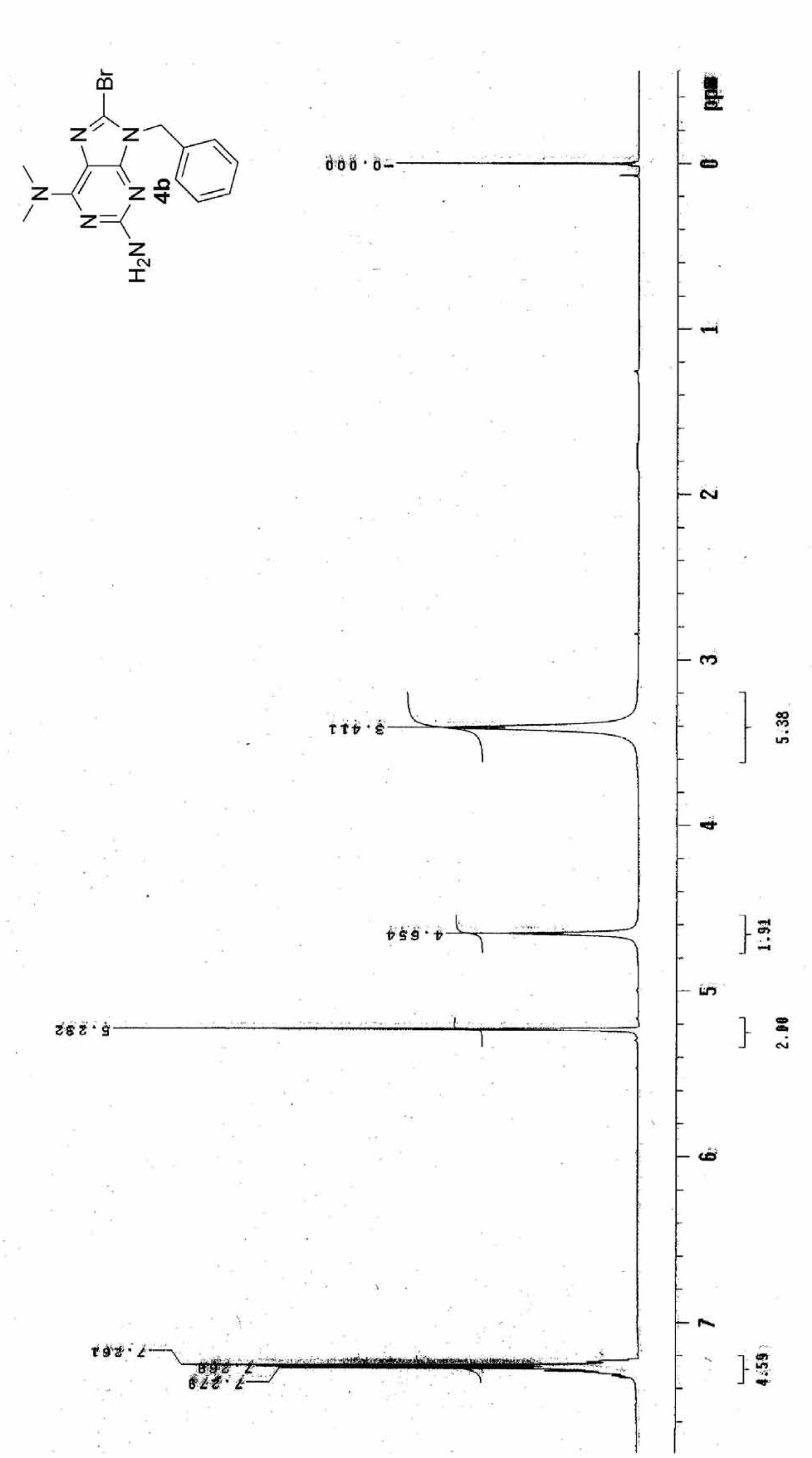

2b
H2N
N
O
0.002
0.009
3.509
3.900
3.906
4.773
5.686
5.691
7.245
7.250
7.264
7.270
ppm
1
2
3
4
5
6
7
1.07
0.27
0.40
1.75
5.85
3.33
2.15
2.00
6.73


2c
NH2
2.484
2.490
2.496
3.098
3.319
3.800
5.553
7.260
7.271
ppm
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
11.88
6.29
3.13
3.16
2.00
6.96


2d
H2N
N
O
3.896
5.027
5.534
5.695
7.229
7.240
7.250
7.311
7.317
7.337
7.461
7.481
7.488
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
ppm
3.00
2.10
2.03
2.01
6.62
1.87


3b
H2N
N
5.211
4.680
3.460
7.208
7.232
7.270
7.280
7.283
7.302
7.310
7.323
7.347
7.424
ppm
2
3
4
5
6
7
8
5.44
1.89
2.00
0.88
4.43


NH2
N
N
N
N
N
3c
2.494
2.500
2.504
3.067
3.340
5.187
6.729
7.326
7.338
7.346
7.820
1.49
6.17
0.54
2.00
1.87
5.06
0.98
2
3
4
5
6
7
8
ppm


Br
N
H2N
4b
-0.000
3.411
4.654
5.282
7.261
7.268
7.279
5.38
1.91
2.00
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ppm
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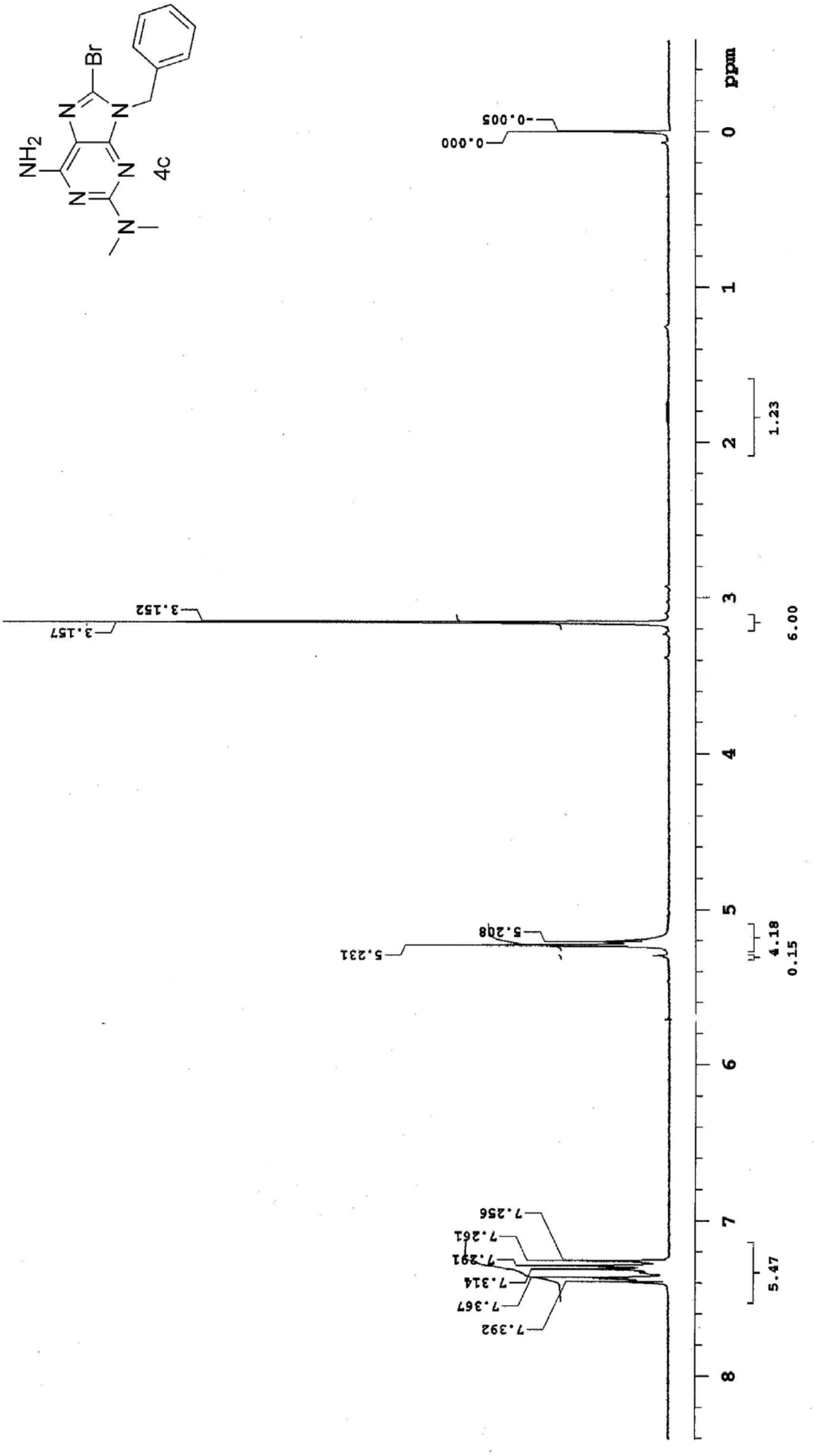
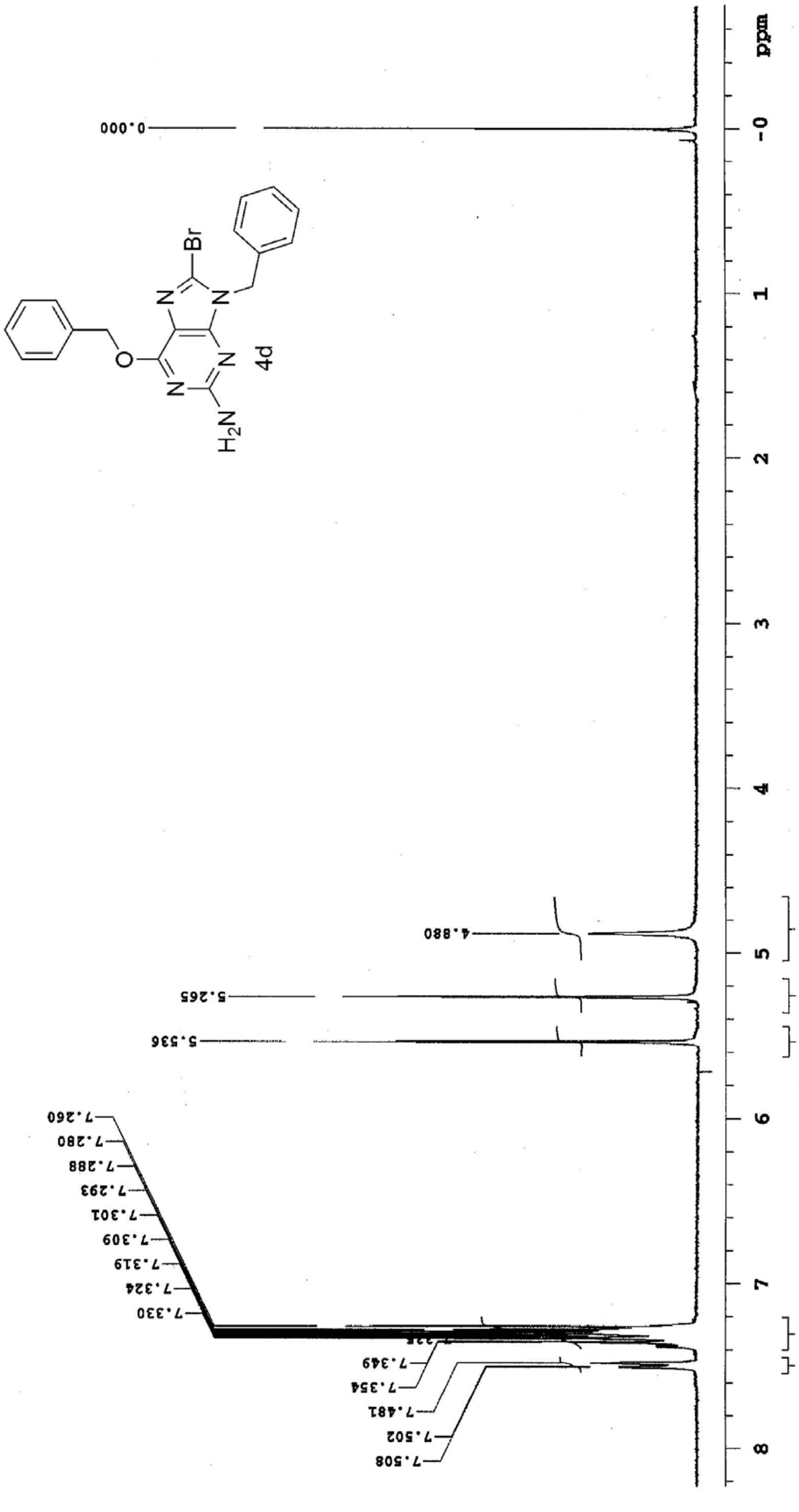
2
3
4
5
6
7


4c
NH2
Br
N
ppm
0
1
2
3
4
5
6
7
8
-0.005
0.000
3.152
3.157
5.208
5.231
7.256
7.261
7.291
7.314
7.367
7.392
1.23
6.00
4.18
0.15
5.47


0.000
4.880
5.265
5.536
7.260
7.280
7.288
7.293
7.301
7.309
7.319
7.324
7.330
7.349
7.354
7.481
7.502
7.508
2.17
2.14
2.00
1.75
8.17
ppm
-0
1
2
3
4
5
6
7
8
Br
N
O
H2N

4d

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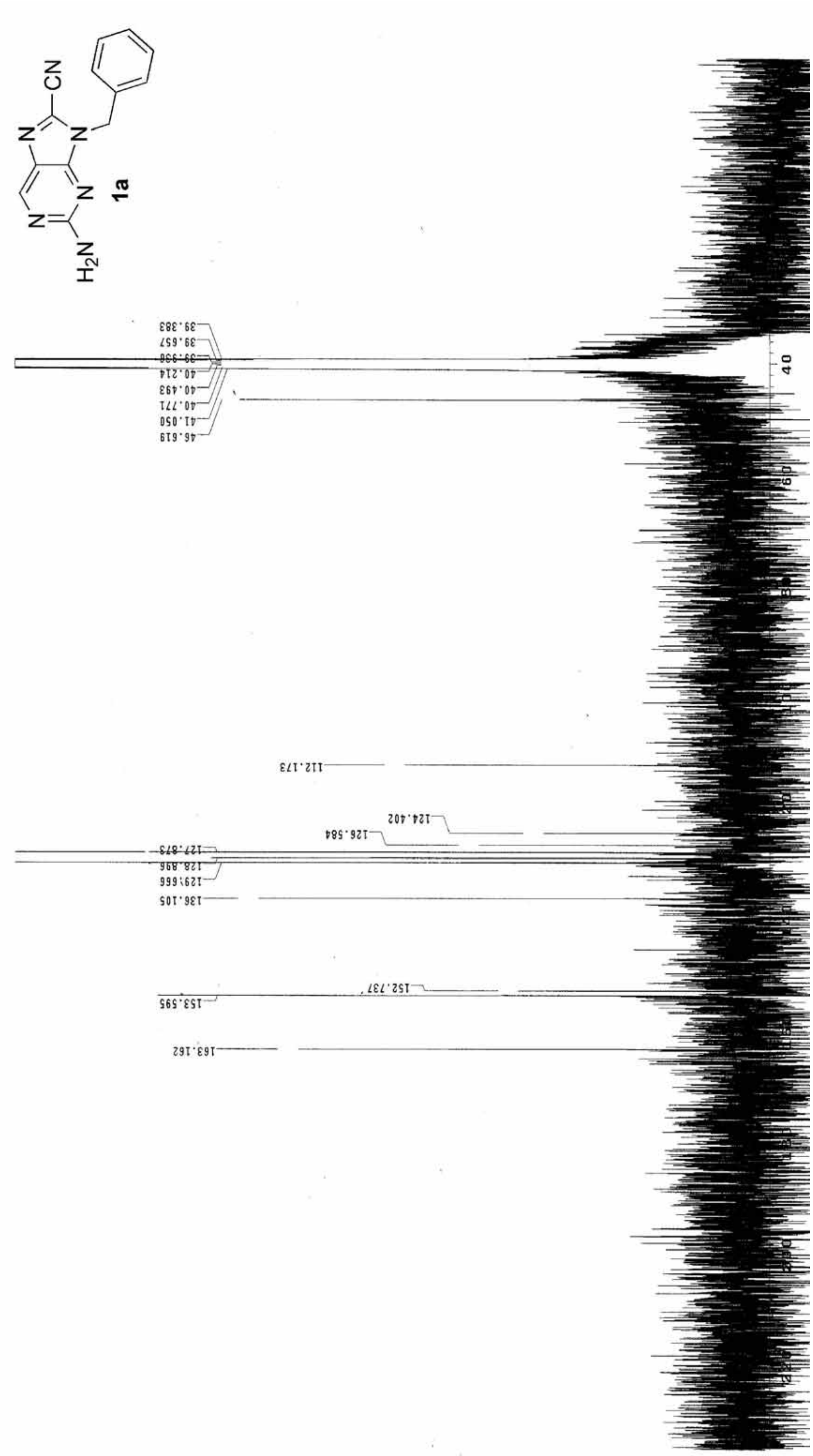
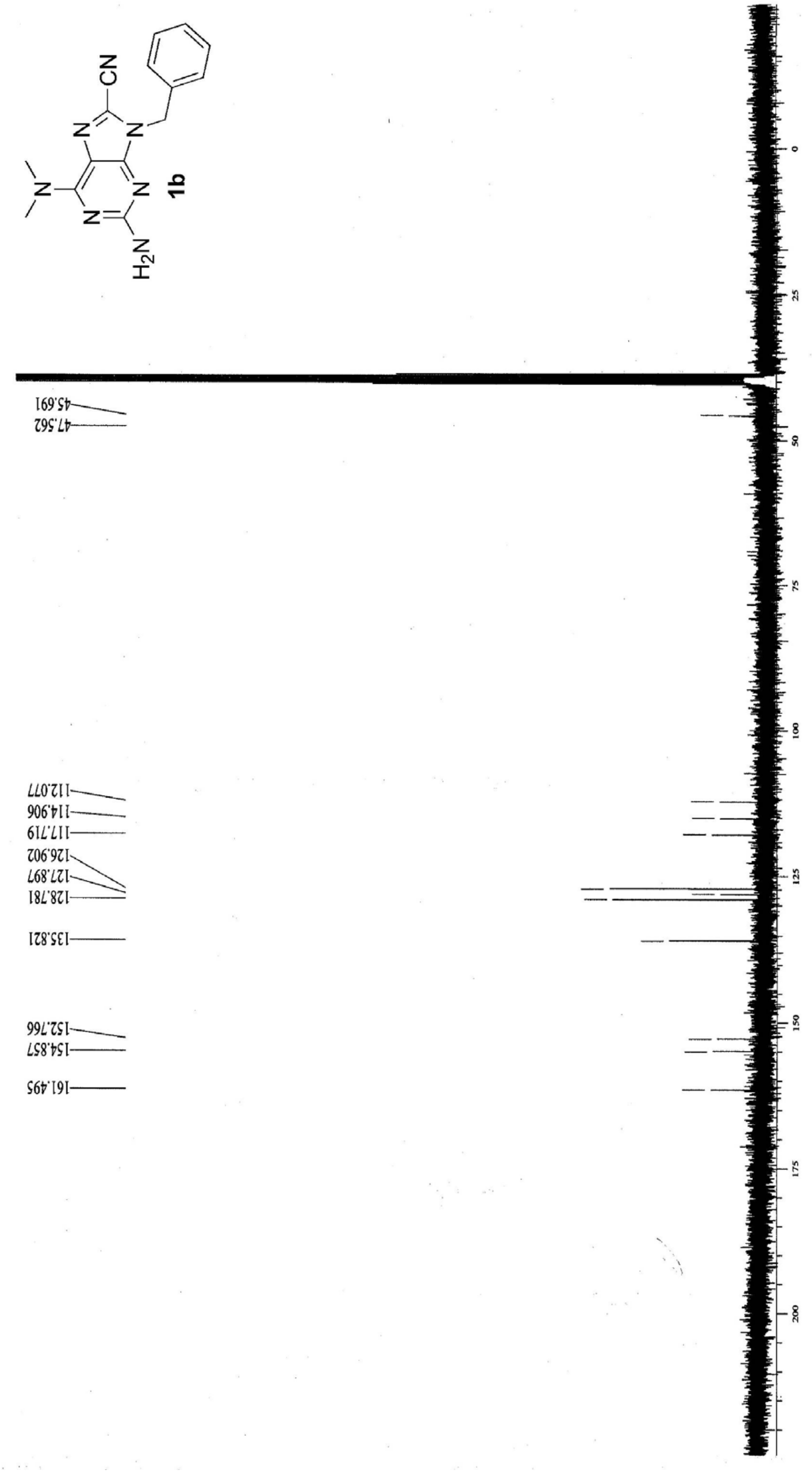
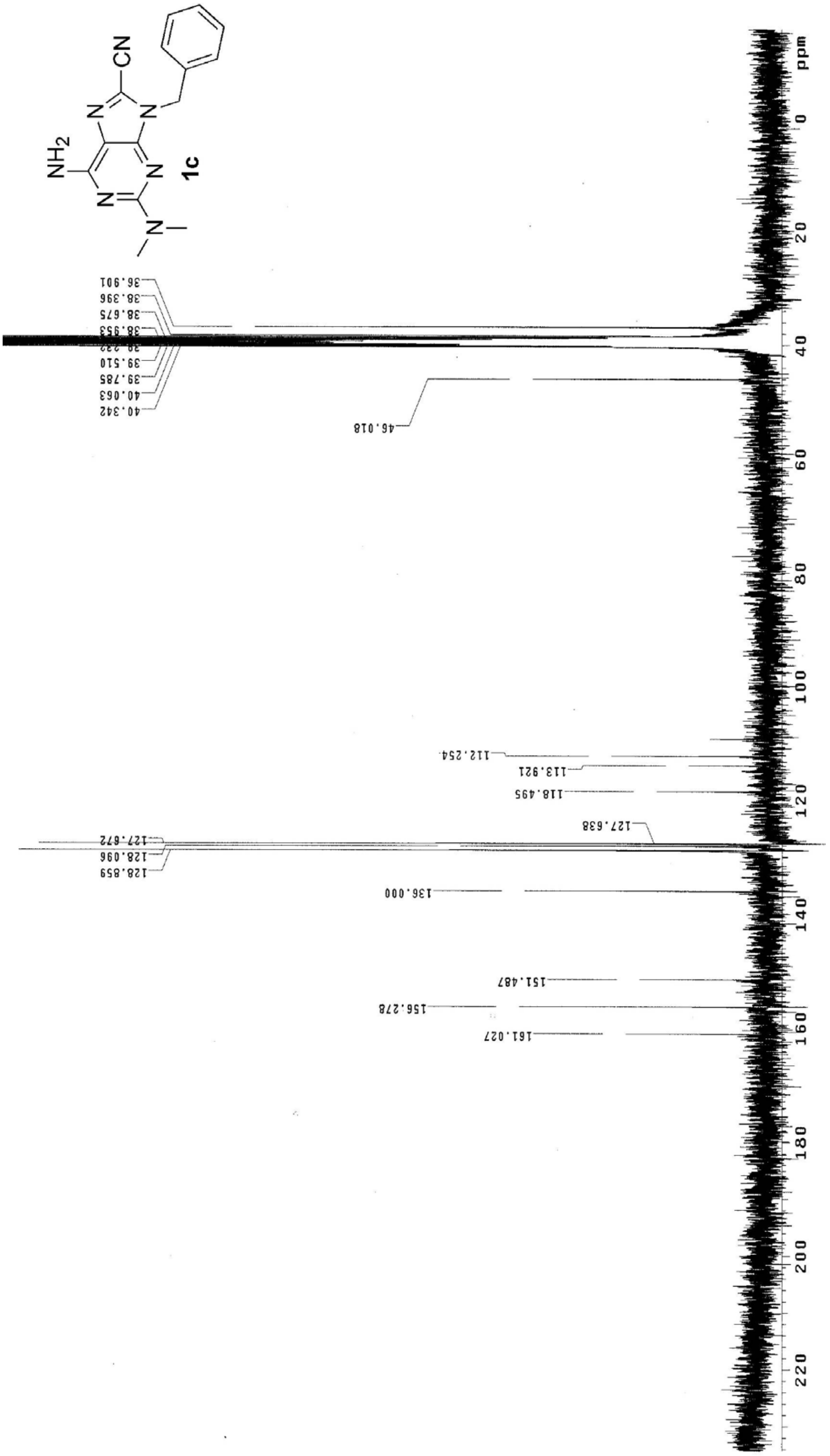
^{13}C NMR Spectra

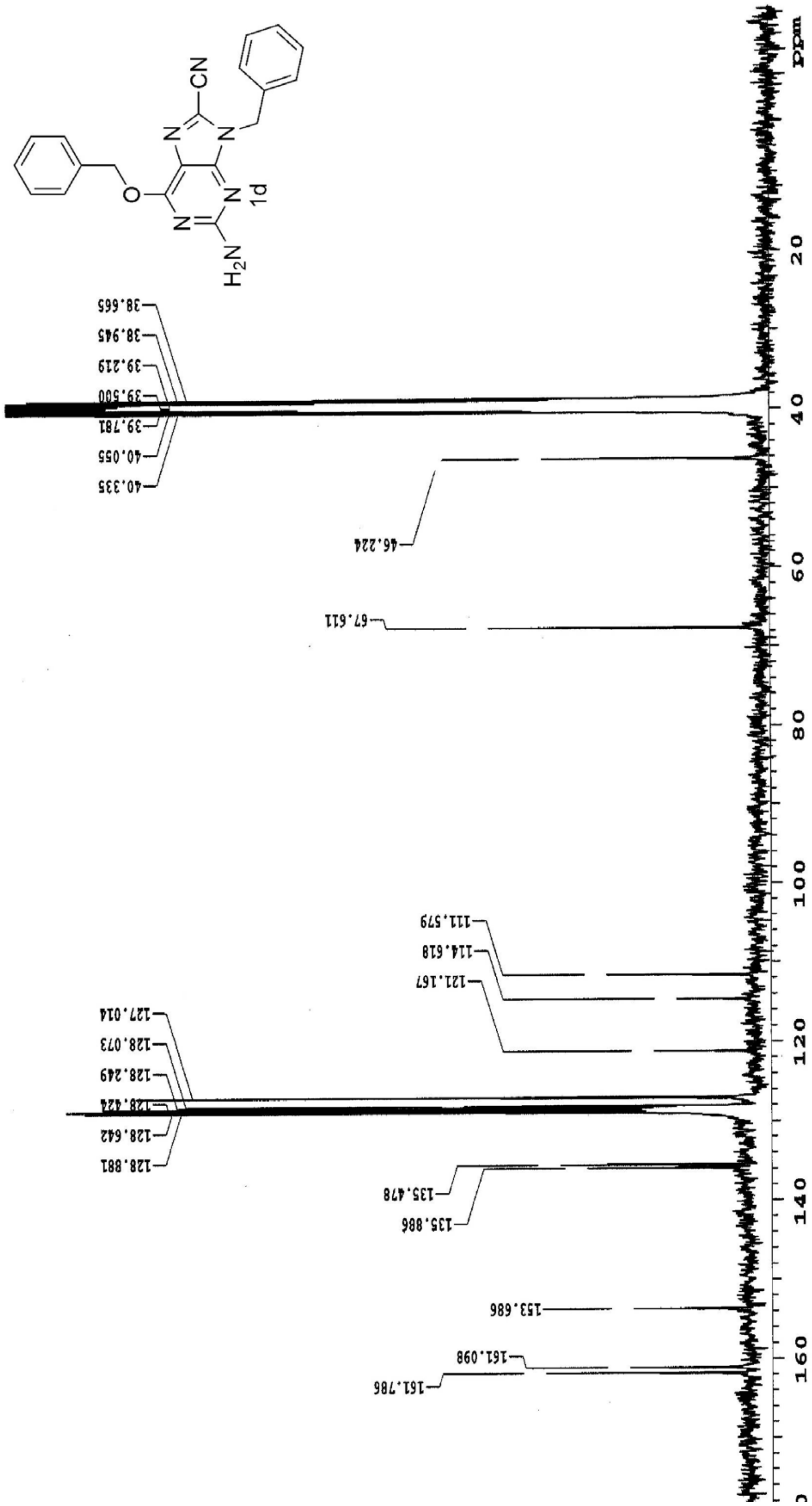



CN
N
N
N
N
N
H2N
1b
45.691
47.562
112.077
114.906
117.719
126.902
127.897
128.781
135.821
152.766
154.857
161.495
0
25
50
75
100
125
150
175
200



1c

NH2
CN
N
36.901
38.396
38.675
38.953
39.232
39.510
39.785
40.063
40.342
46.018
112.254
113.921
118.495
127.638
127.672
128.096
128.859
136.000
151.487
156.278
161.027
ppm
0
20
40
60
80
100
120
140
160
180
200
220


H2N
N
N
O
N
N
CN
1d
38.665
38.945
39.219
39.500
39.781
40.055
40.335
46.224
67.611
111.579
114.618
121.167
127.014
128.073
128.249
128.424
128.642
128.881
135.478
135.886
153.686
161.098
161.786
ppm
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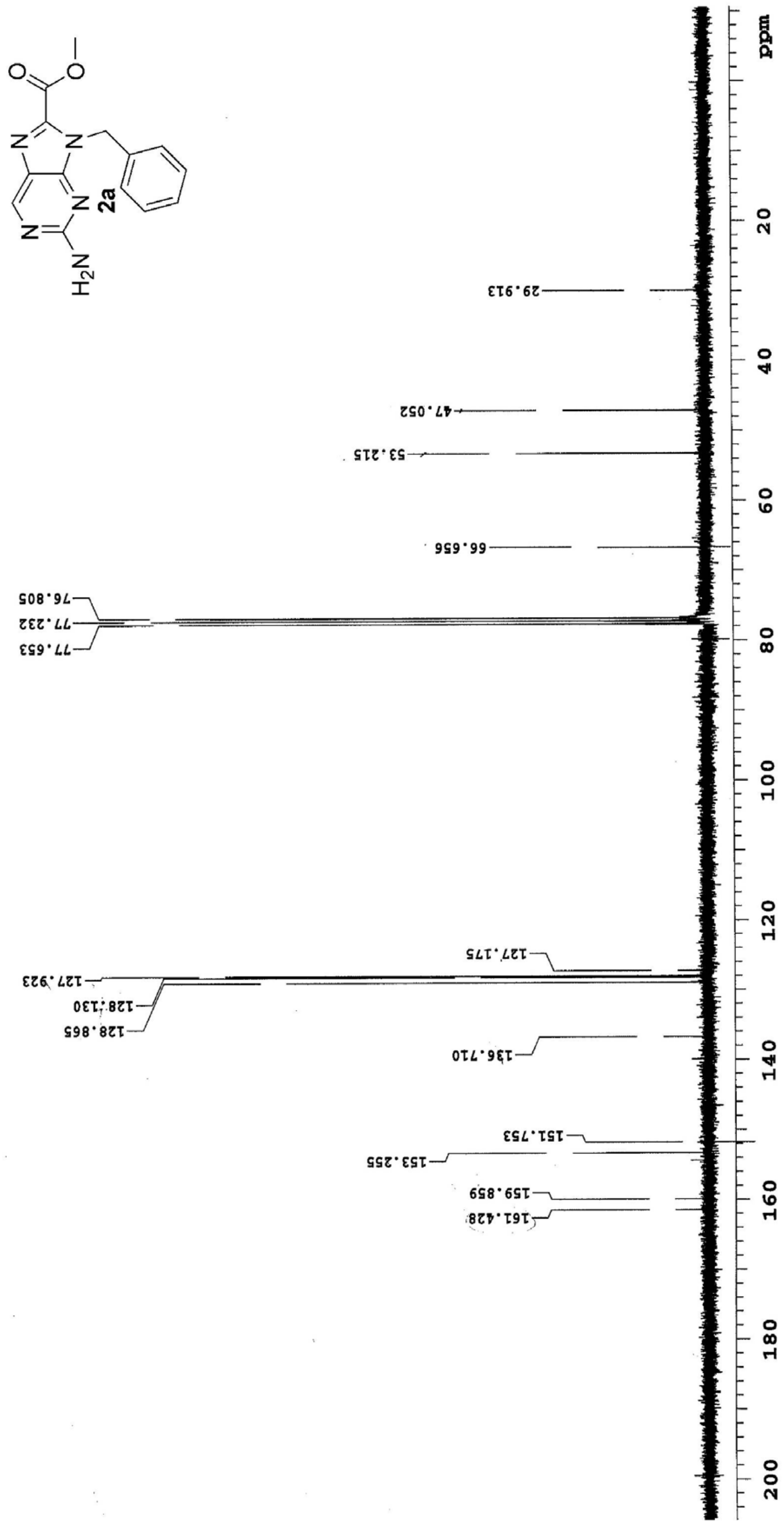
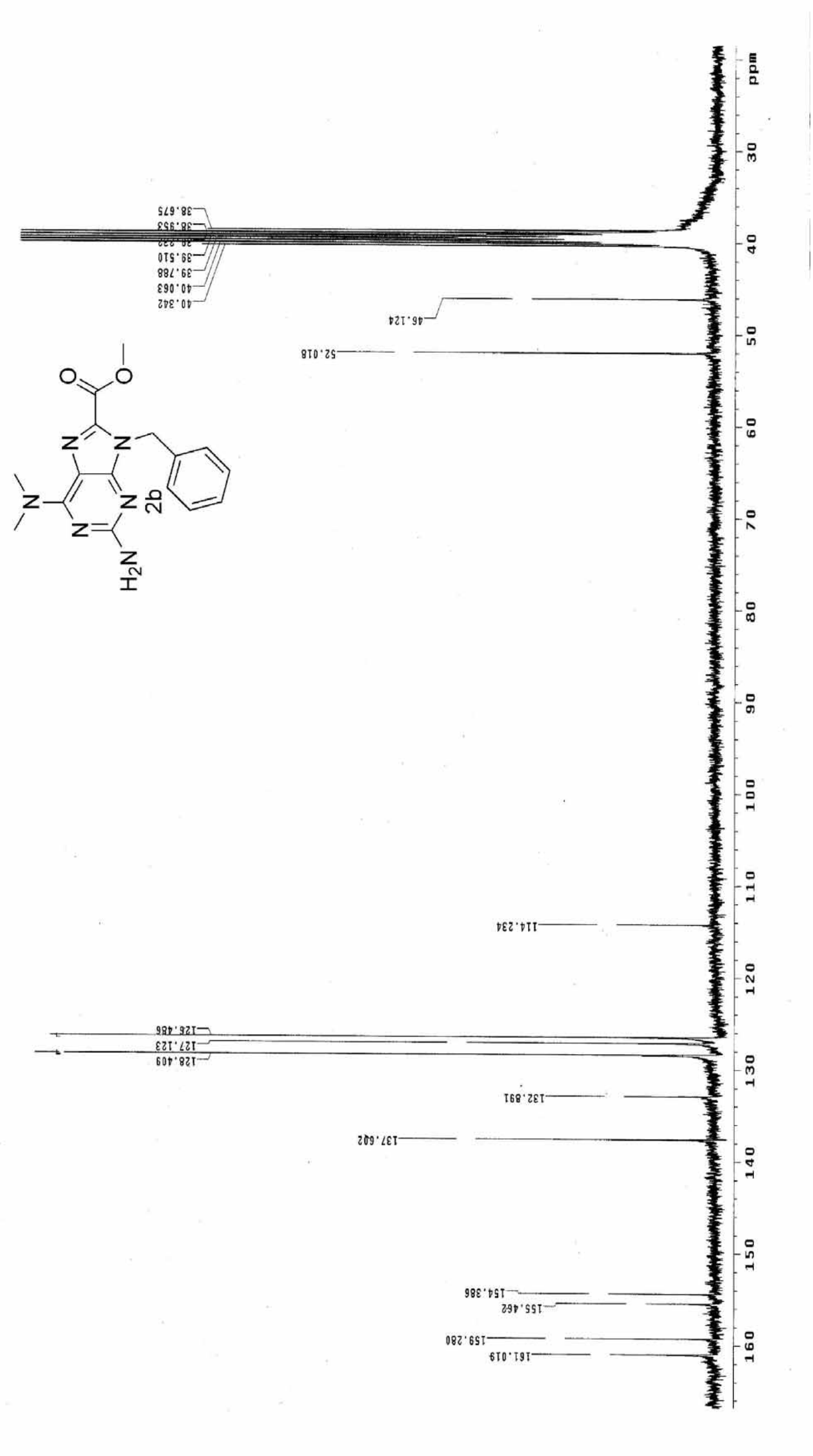
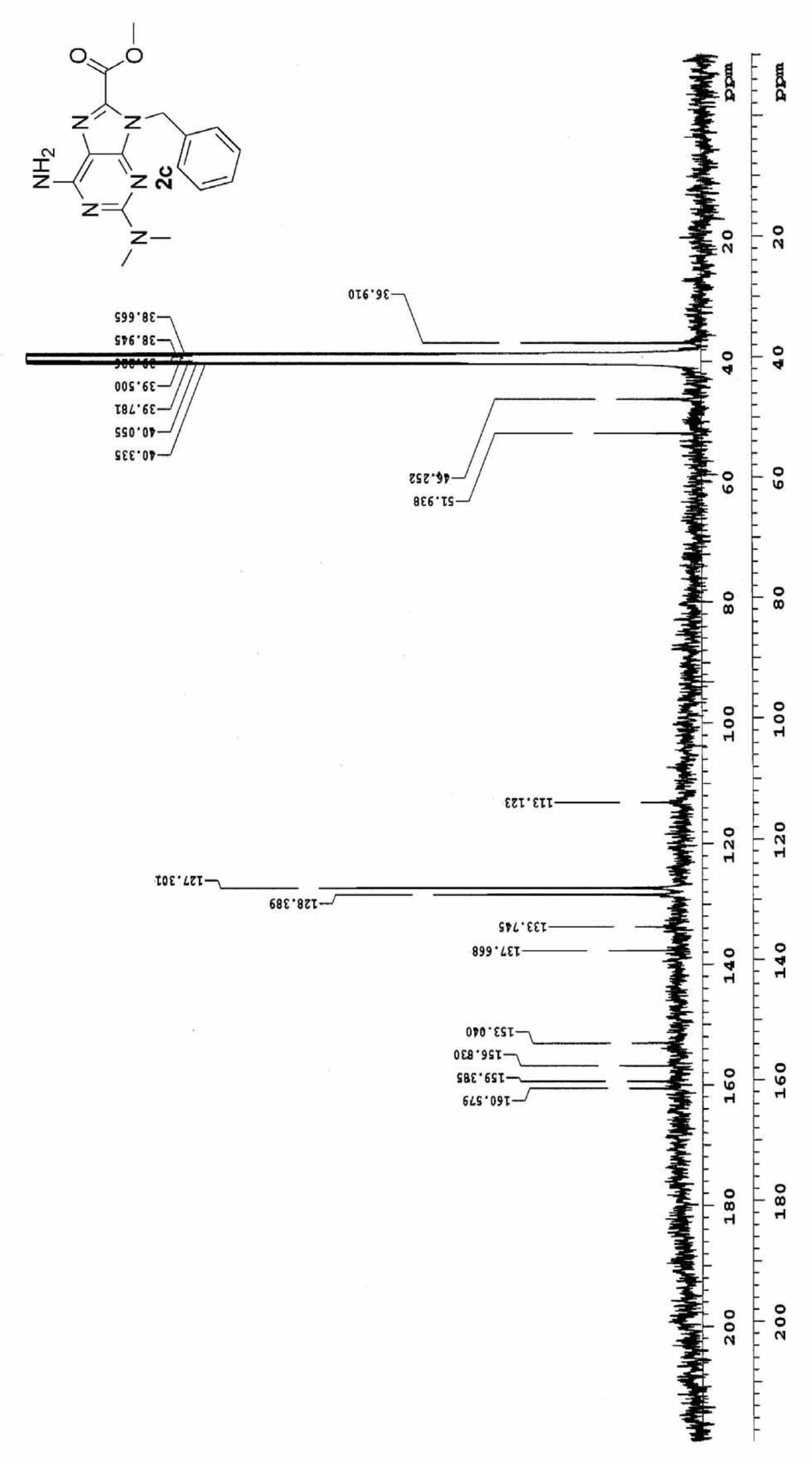
60
80
100
120
140
160


O
O
N
N
N
N
H_2N
29.913
47.052
53.215
66.656
76.805
77.232
77.653
127.175
127.923
128.130
128.865
136.710
151.753
153.255
159.859
161.428
20
40
60
80
100
120
140
160
180
200
ppm

2a


38.675
38.953
39.232
39.510
39.788
40.063
40.342
46.124
52.018
114.234
126.486
127.123
128.409
132.891
137.602
154.386
155.462
159.280
161.019
ppm
30
40
50
60
70
80
90
100
110
120
130
140
150
160
2b


NH2
N
N
N
N
N
O
O
2c
36.910
38.665
38.945
39.500
39.781
40.055
40.335
46.252
51.938
113.123
127.301
128.389
133.745
137.668
153.040
156.830
159.385
160.579
ppm
20
40
60
80
100
120
140
160
180
200

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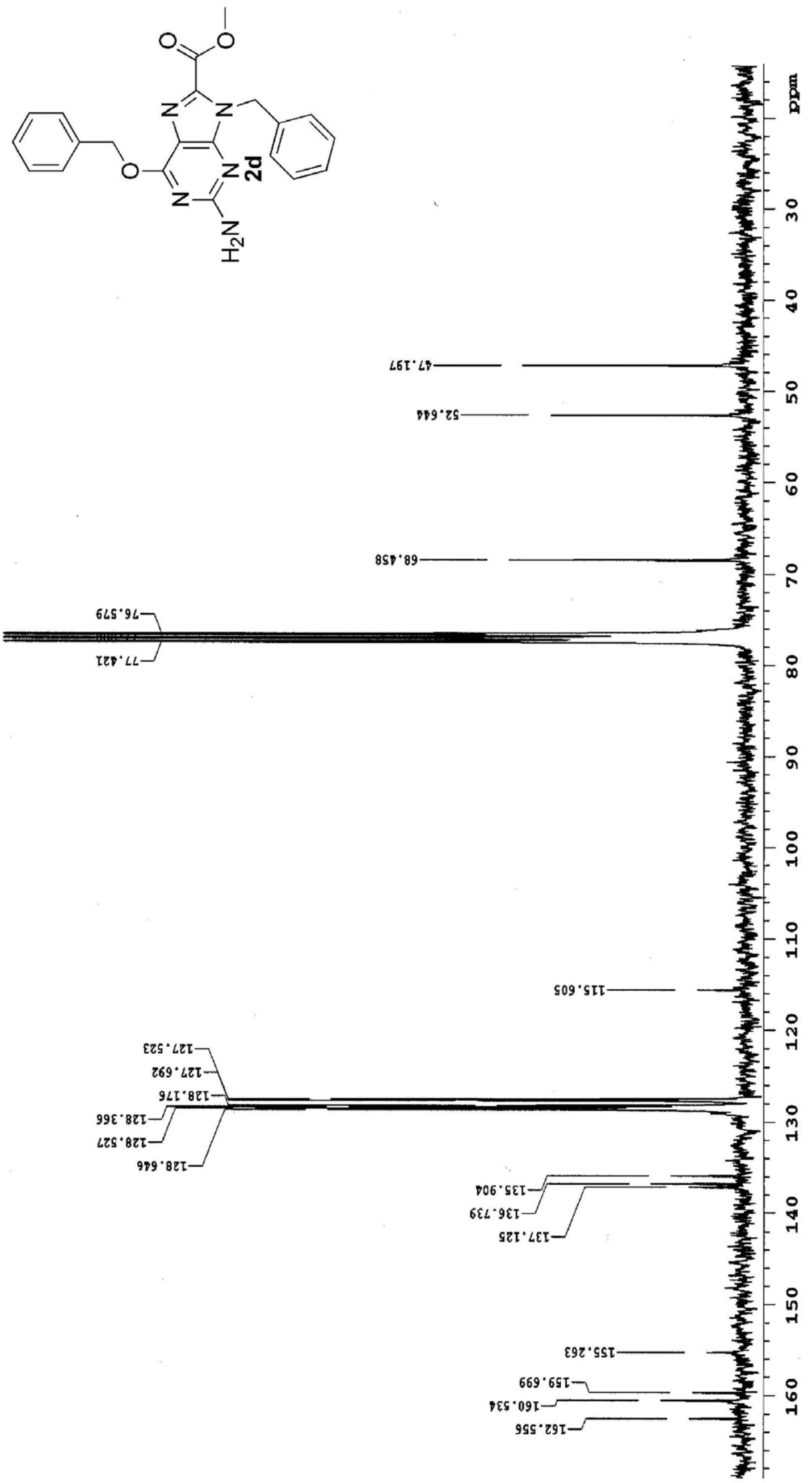

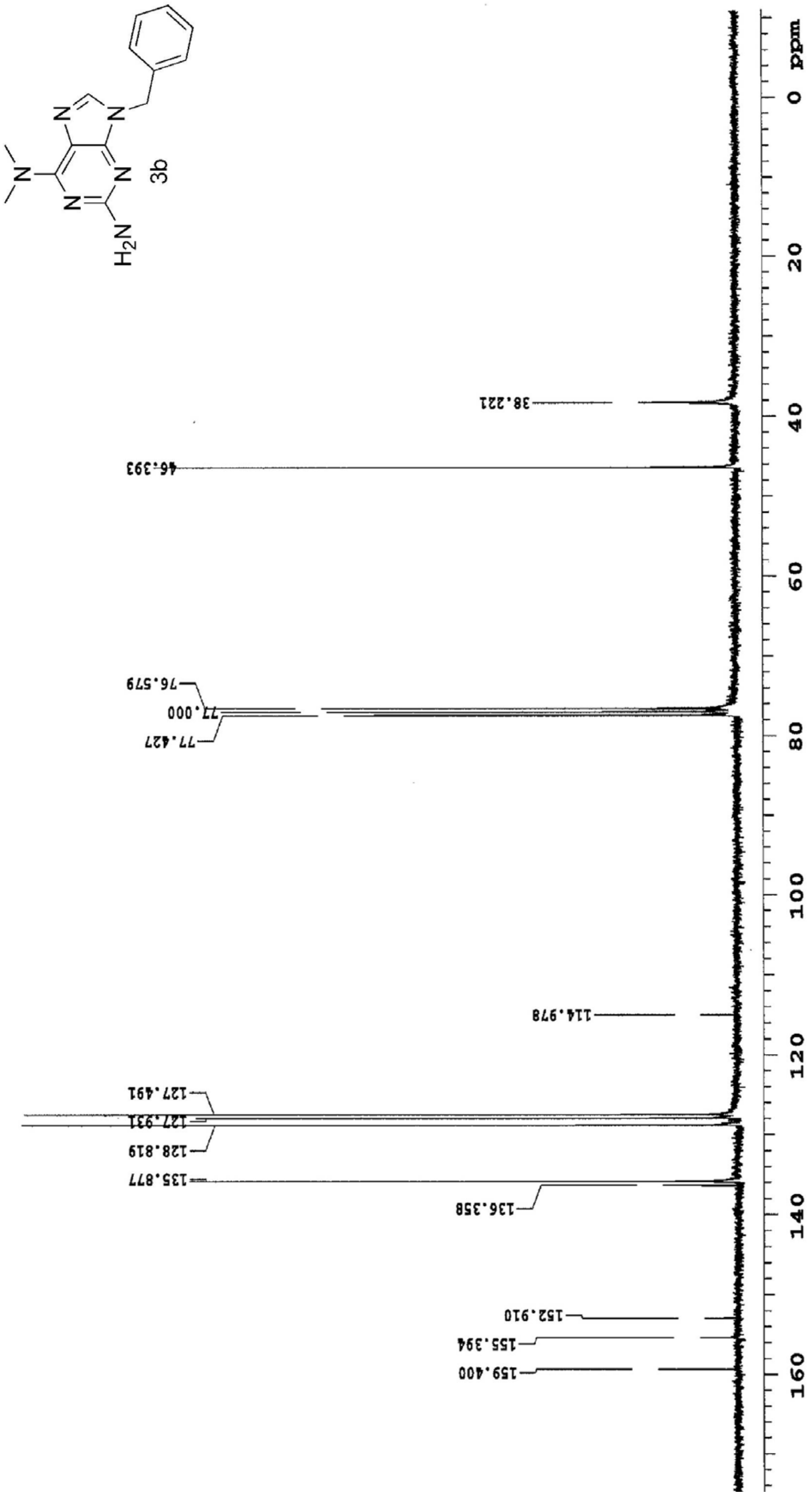
3b
H2N
N
38.221
46.393
76.579
77.000
77.427
114.978
127.491
127.931
128.819
135.877
136.358
152.910
155.394
159.400
ppm
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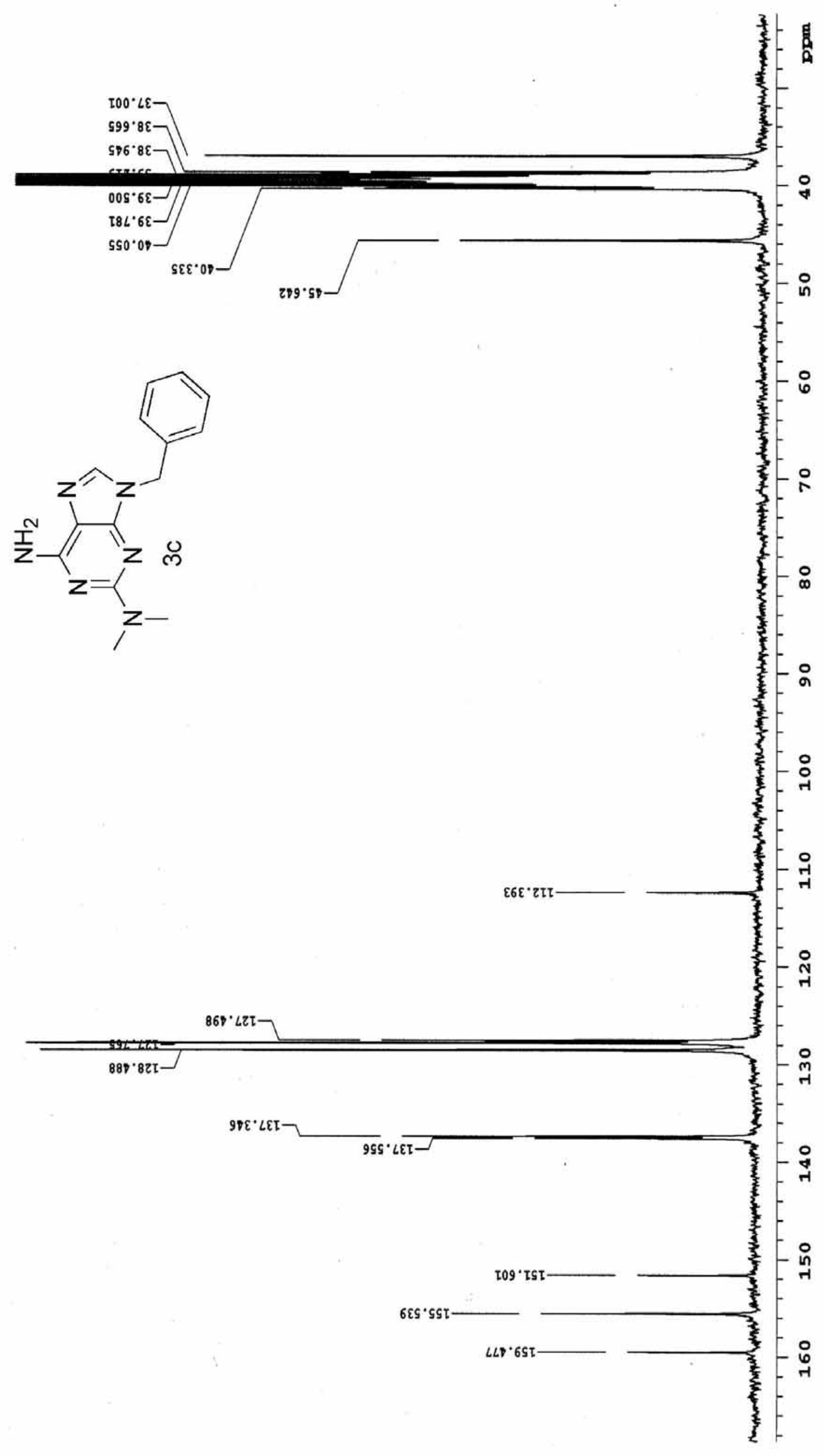
20
40
60
80
100
120
140
160


NH2
N
N
N
N
N
3c
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38.665
38.945
39.500
39.781
40.055
40.335
45.642
112.393
127.498
127.765
128.488
137.346
137.556
151.601
155.539
159.477
ppm
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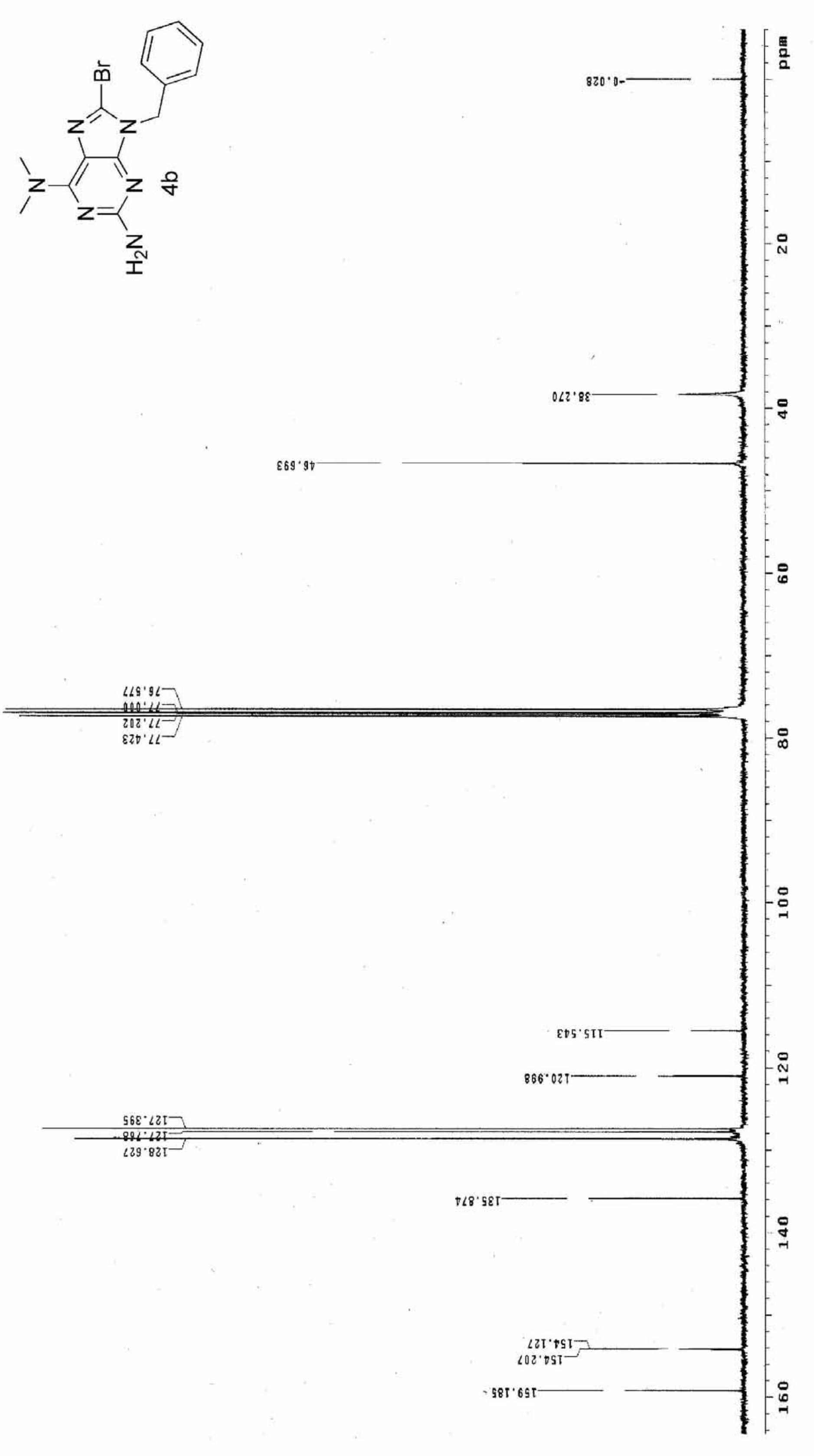
50
60
70
80
90
100
110
120
130
140
150
160


Br
N
N
N
N
H$_2$N
4b
ppm
20
40
60
80
100
120
140
160
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38.270
46.693
76.577
77.000
77.202
77.423
115.543
120.998
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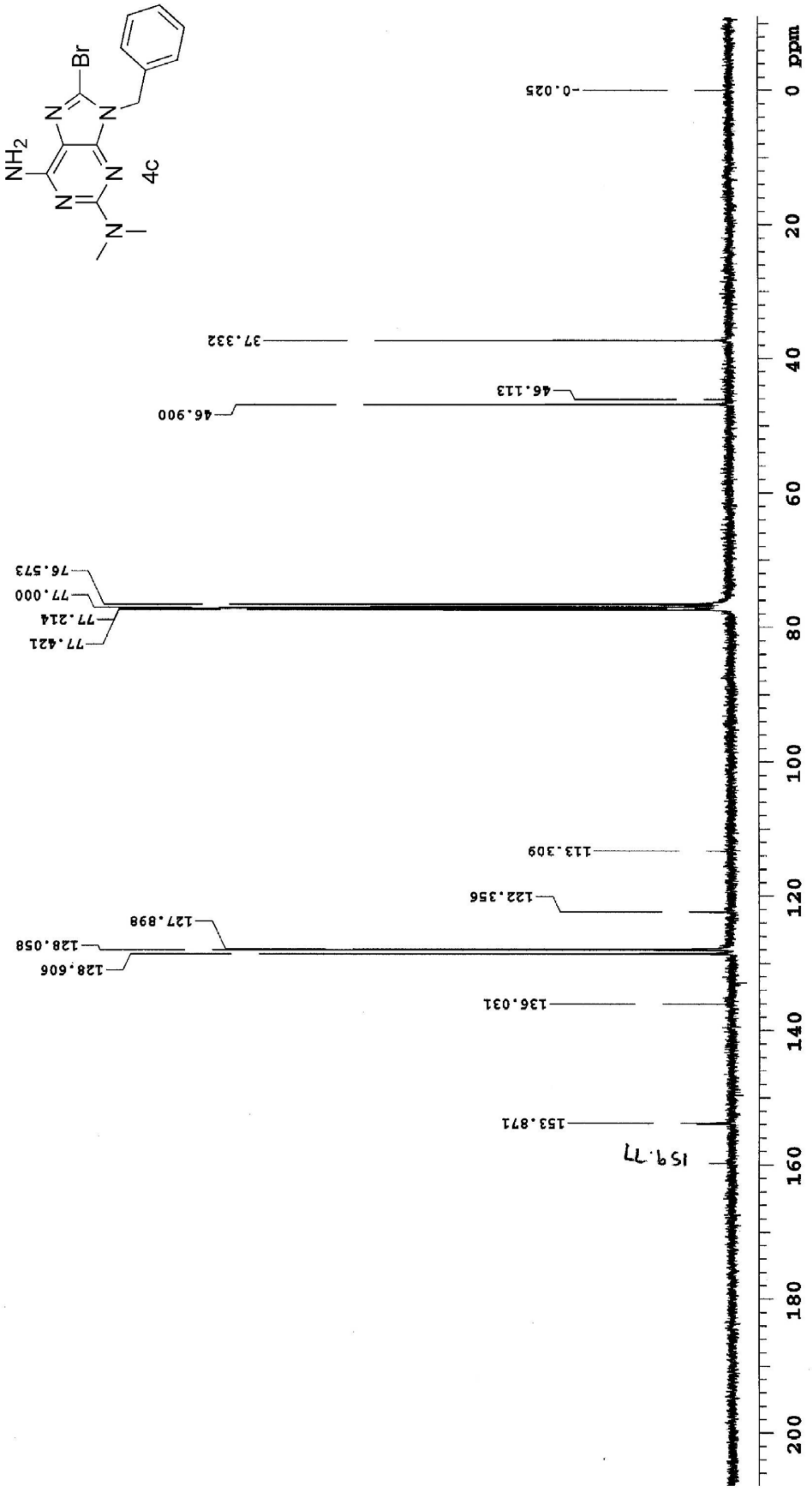
127.768
128.627
135.874
154.127
154.207
159.185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Br
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4c
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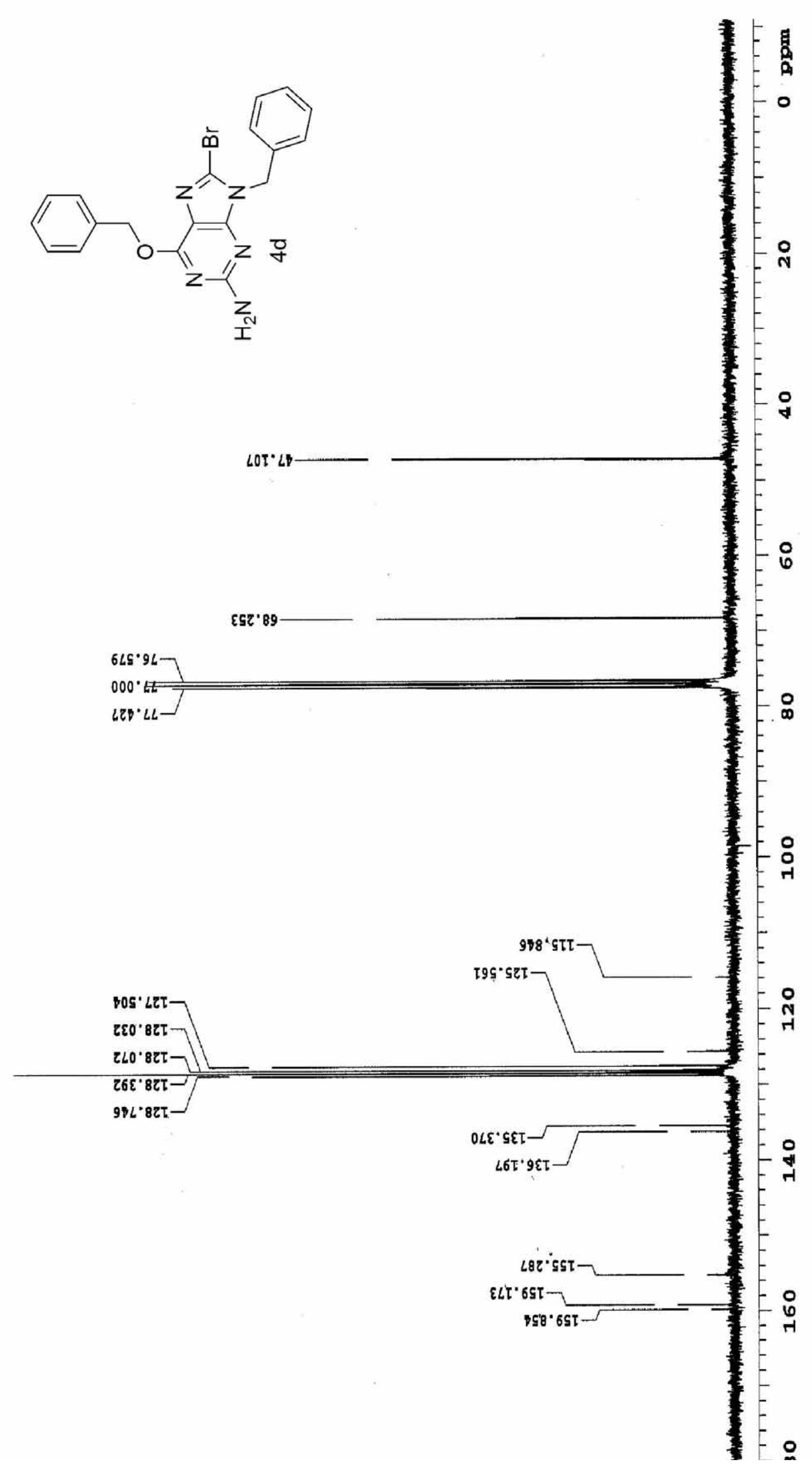
77.000
77.214
77.421
113.309
122.356
127.898
128.058
128.606
136.031
153.871
159.77
0 ppm
20
40
60
80
100
120
140
160
180
200


Br
N
N
N
N
O
H2N
4d
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68.253
76.579
77.000
77.427
115.846
125.561
127.504
128.032
128.072
128.392
128.746
135.370
136.197
155.287
159.173
159.854
0
20
40
60
80
100
120
140
160
ppm

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