Experimental

All commercially obtained chemicals were used as received. Anhydrous acetonitrile and methanol were purchased from Aldrich in sure seal bottles and used as received. Methylene chloride and pyridine were freshly distilled from calcium hydride. THF was freshly distilled from a sodium/benzophenone ketyl. Benzene and toluene were freshly distilled from sodium. All reactions were performed under an argon atmosphere. Melting points were measured on a MelTemp 3.0 apparatus and are uncorrected. Proton and carbon-13 NMR data were recorded at 300 and 75 MHz, respectively in $CDCl_3$ unless otherwise noted. Chemical shifts are reported in ppm downfield from TMS (δ=0); coupling constants are given in Hertz. Optical rotations were measured on a Rudolph Research Autopol polarimeter. High-resolution FAB mass spectra were obtained from the University of Notre Dame Mass Spectrometry Centers using nitrobenzyl alcohol (NBA) as the matrix. Absorbance spectra were measured on a Shimadzu 2101 UV-vis spectrophotometer. Fluorescence spectra were measured on an ISS Model PC1 spectrofluorimeter.

Bis-trimethylsilylalloxazine. A suspension of alloxazine (1.0 g, 4.67 mmol) and chlorotrimethylsilane (1.11 g, 10.3 mmol) in dry benzene (40 mL) was cooled to 0^{o}C, then triethylamine (1.16 g, 11.5 mmol) was added dropwise. The reaction was stirred at room temperature for 48 h, then the precipitate was removed by filtration. The filtrate was evaporated to give bis-trimethylsilylalloxazine (1.6 g, 96% yield), which was used in next step without further purification.

1-(2’,3’,5’-triacetyl-β-D-ribofuranosyl)benzo[g]pteridine-2,4-(1H,3H)-dione (8). A solution of **6** (50 mg, 0.16 mmol) and bis-trimethylsilylalloxazine alloxazine (110 mg, 0.31 mmol) in dry acetonitrile (5 mL) was cooled to 0^{o}C, then tin tetrachloride (210 mg, 0.80 mmol) was added dropwise. After the additional was complete, the reaction was warm to room temperature and stirred for an addition 2 h, then poured into saturated sodium bicarbonate solution (20 mL), and extracted with ethyl acetate (4 x 20 mL). The combined organic extracts were successively washed with 5% HCl, saturated brine, saturated sodium bicarbonate, and saturated brine, then dried over sodium sulfate, filtered and evaporated. Purification by flash chromatography on silica, eluting with 1% methanol in chloroform, gave **8** (64 mg, 85% yield) as a yellow solid, mp 126-128° C. ^{1}H NMR (DMSO-d$_6$) δ 12.0 (br s, 1H), 8.22 (d, *J*= 8.4 Hz, 1H), 8.11 (d, *J*= 7.8 Hz, 1H), 8.01 (t, *J*=7.7 Hz, 1H), 7.87 (t, *J*=7.7 Hz, 1H), 6.80 (d, *J*= 2.4 Hz, 1H), 6.09 (t, *J*= 7.3 Hz, 1H), 6.00 (dd, *J*= 6.5, 2.6 Hz, 1H), 4.44 (dd, *J*= 11.9, 3.6 Hz, 1H), 4.31-4.26 (m, 1H), 4.18 (dd, *J*= 11.9, 5.7 Hz, 1H), 2.09 (s, 3H), 2.08 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (DMSO-d$_6$) δ 169.5, 169.0, 168.9, 158.5, 149.1, 144.7, 140.8, 138.8, 133.4, 131.5, 129.7, 129.1, 126.7, 86.4, 77.6, 72.3, 69.2, 62.4, 19.9, 19.8, 19.7.

3-(2',3',5'-triacetyl-β-D-ribofuranosyl)benzo[g]pteridine-2,4-(1H,3H)-dione (7). A solution of **6** (1.8 g, 5.66 mmol) and bis-trimethylsilylalloxazine (2.5 g, 6.98 mmol) in dry dichloromethane (180 mL) was cooled to –78 °C, then tin tetrachloride (3.3 mL, 28.3 mmol) was added dropwise. After the addition was complete, the reaction was warm to -20° C and stirred for an additional 15 min, then poured into saturated sodium bicarbonate (200 mL) and extracted with ethyl acetate (3x). The combined organic extracts were successively washed with 5% HCl, saturated brine, saturated sodium bicarbonate, and saturated brine, then dried over sodium sulfate, filtered and evaporated. Purification by chromatography on silica, eluting with 1% methanol in chloroform gave **7** (2.5 g, 95% yield) as a yellow solid, mp 103-105°C; $[\alpha]^{23}_{D}$ +8.5° (*c* 0.66, CHCl$_3$); ^{1}H NMR (CDCl$_3$) δ 10.22 (br, s, 1H), 8.24 (d, *J*= 8.0 Hz, 1H), 8.18 (d, *J*= 8.0 Hz, 1H), 7.94 (t, *J*= 8.0 Hz, 1H), 7.77 (t, *J*= 8.0 Hz, 1H), 6.53 (d, *J*= 2.5 Hz, 1H), 5.94 (dd, *J*= 7.0, 2.5 Hz, 1H), 5.72 (t, *J*= 7.0 Hz, 1H), 4.57 (dd, *J*= 11.7, 2.7 Hz, 1H), 4.40-4.33 (m, 1H), 4.27 (dd, *J*= 11.7, 7.0 Hz, 1H), 2.14 (s, 3H), 2.13 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (CDCl$_3$) δ 170.8, 173.2, 169.6, 159.2, 148.8, 144.2, 143.4, 141.0, 134.8, 131.0, 129.7, 129.1, 127.5, 87.7, 79.5, 73.3, 70.5, 63.6, 20.8, 20.7, 20.5; HRMS (FAB) *m/z* calcd for $C_{21}H_{21}N_4O_9$ (M+H) 473.1309, found 473.1301.

3-(β-D-ribofuranosyl)benzo[g]pteridine-2,4-(1H,3H)-dione (4a). A solution of **7** (2.2 g, 4.66 mmol) in 0.1 M methanolic sodium methoxide (150 mL) was stirred for 10 min, then neutralized with Dowex 50 (WX8, H^+ form) ion exchange resin. The resin was removed by filtration and washed with methanol. The filtrate was evaporated under reduced pressure to give **4a** (1.6 g, 99% yield) as a yellow solid, mp 230^o C (dec.) (lit.[5] >240 °C (dec.)). $[\alpha]^{23}_D$ -37° (*c* 0.29, $CHCl_3$/MeOH=1:1); ^1H NMR (DMSO-d_6) δ 12.3 (br s, 1H), 8.18 (d, *J*= 8.4 Hz, 1H), 7.95-7.93 (m, 1H), 7.82-7.76 (m, 1H), 6.20 (d, *J*= 3.1 Hz, 1H), 5.07 (d, *J*= 5.0 Hz, 1H, exchangeable with D_2O), 4.95 (d, *J*= 6.7 Hz, 1H, exchangeable with D_2O), 4.60-4.51 (m, 2H), 4.25-4.18 (m, 1H), 4.38-3.72 (m, 1H), 3.69-3.63 (m, 1H), 3.53-3.46 (m, 1H); ^{13}C NMR (DMSO-d_6) δ 160.2, 150.0, 146.1, 143.2, 139.8, 133.9, 131.3, 130.5, 128.9, 127.4, 89.2, 84.8, 71.7, 70.5, 62.7; HRMS (FAB) *m/z* calcd for $C_{15}H_{15}N_4O_6$ (M+H) 347.0992, found 347.0994.

3-[3’,5’-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxanediyl)-β-D-ribofuranosyl]-benzo[g]pteridine-2,4-(1H,3H)-dione (11). 3-(β-D-ribofuranosyl)benzo[g]pteridine-2,4-(1H,3H)-dione (1.6 g, 2.6 mmol) was dried by evaporation from 50 mL of dry benzene, then dissolved in pyridine (80 mL). The solution was cooled to 0° C, then 1, 3-dichloro-1, 1, 3, 3-tetraisopropyldisiloxane (1.60 g, 5.0 mmol) was added dropwise. The reaction was stirred for 5 h at room temperature. Pyridine was evaporated under reduced pressure and the residue partitioned between ethyl acetate and water. The aqueous phase was extracted with ethyl acetate. The combined organic extracts were successively washed with 5% HCl, saturated brine, saturated sodium bicarbonate and saturated brine, then dried with sodium sulfate, filtered and evaporated. Purification by chromatography on silica gel, eluted with 20% ethyl acetate in hexanes, gave **11** (2.5 g, 92% yield) as a yellow solid, mp 130-132ºC; $[\alpha]^{23}_{D}$ -57° (*c* 1.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 9.24 (br s, 1H), 8.34 (dd, *J*= 8.5, 1.0 Hz, 1H), 8.10 (dd, *J*= 8.5, 1.0 Hz, 1H), 7.92 (ddd, *J*= 8.5, 6.9, 1.0 Hz, 1H), 7.78 (ddd, *J*= 8.5, 6.9, 1.0 Hz, 1H), 6.49 (d, *J*= 1.4 Hz, 1H), 5.07 (t, *J*= 7.0 Hz, 1H), 4.72 (dd, *J*= 7.0, 1,4 Hz, 1H), 4.08-4.06 (m, 2H), 4.00-3.93 (m, 1H), 3.42 (br, s, OH, exchangeable with D_2O), 1.17-1.00 (m, 28 H); ^{13}C NMR ($CDCl_3$) δ 159.3, 149.2, 144.3, 143.3, 141.1, 134.5, 131.1, 129.5, 127.5, 89.5, 82.7, 73.6, 72.8, 63.7, 17.5, 17.4, 17.3, 17.1, 13.2, 13.1, 12.7; HRMS (FAB) *m/z* calcd for $C_{27}H_{40}N_4O_7Si_2Na$ (M+Na) 611.2333, found 611.2316.

2,2'-Anhydronucleoside 14. A solution of **11** (60 mg, 0.102 mmol), Ph_3P (30 mg, 0.114) and DIAD (25 mg, 0.122 mmol) in toluene (2 mL) was heated at reflux for 6 h. The solvent were removed under reduced pressure and the residue purified by flash chromatography on silica, eluting with 20% ethyl acetate in hexanes, to give **14** (55 mg, 94% yield) as a yellow solid, mp 110-112ºC; $[\alpha]^{23}_{D}$ -174° (*c* 0.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 8.29 (d, *J*= 8.4 Hz, 1H), 8.08 (d, *J*= 8.4 Hz, 1H), 7.87 (ddd, *J*= 8.4, 6.9, 1.3 Hz, 1H), 7.76 (ddd, *J*= 8.4, 6.9, 1.3 Hz, 1H), 6.55 (d, *J*= 5.9 Hz, 1H), 5.44 (dd, *J*= 5.9, 3.4 Hz, 1H), 4.64 (dd, *J*= 7.3, 3.4 Hz, 1H), 4.07-3.90 (m, 3H), 1.16-0.91 (m, 28H); ^{13}C NMR ($CDCl_3$) δ 157.9, 156.8, 152.2, 145.1, 141.3, 133.6, 132.3, 130.5, 130.0, 128.8, 89.7, 84.3, 83.1, 77.4, 61.7, 17.3, 17.2, 17.1, 17.0, 16.9, 16.8, 16.7, 13.2, 13.0, 12.6, 12.4; HRMS (FAB) *m/z* calcd for $C_{27}H_{39}N_4O_6Si_2$ (M+H) 571.2408, found 571.2439.

3-[3',5'-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxanediyl)-β-D-2'-bromo-2'-deoxyribo-furanosyl]benzo[g]pteridine-2,4-(1H,3H)-dione (15). Acetyl bromide (0.29 mL, 3.85 mmol) was added to a solution of methanol (0.32 mL) in ethyl acetate (60 mL) at 0º C followed by addition of **14** (1.1 g, 1.93 mmol). The mixture was heated at reflux for 15 min, then cooled to 0º C and neutralized with sodium bicarbonate. The phases were separated and the aqueous phase extracted with ethyl acetate. The combined organic extracts were washed with saturated brine, dried over sodium sulfate, filtered and evaporated. Purification by flash chromatography on silica, eluting with 10% ethyl acetate in hexanes, gave **15** (1.1 g, 85% yield) as a yellow solid, mp 123-125°C. $[\alpha]^{23}_{D}$ -35° (*c* 0.57, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 10.33 (s, 1H), 8.32 (d, *J*= 8.4 Hz, 1H), 8.25 (d, *J*= 8.4 Hz, 1H), 7.93 (ddd, *J*= 8.4, 6.9, 1.3 Hz, 1H), 7.79 (ddd, *J*= 8.4, 6.9, 1.3 Hz, 1H), 6.96 (d, *J*= 3.0 Hz, 1H), 5.21 (dd, *J*= 7.0, 3.0 Hz, 1H), 4.99 (t, *J*= 7.4 Hz, 1H), 4.18-4.02 (m, 2H), 4.00-3.95 (m, 1H), 1.13-1.02 (m, 28H); ^{13}C NMR ($CDCl_3$) δ 159.1, 148.9, 144.2, 143.2, 141.1, 134.8, 131.1, 129.7, 129.4, 127.4, 89.8, 81.9, 69.4, 61.5, 54.1, 17.4, 17.3, 17.2, 17.1, 17.0, 13.3, 13.0, 12.8, 12.7; HRMS (FAB) *m/z* calcd for $C_{27}H_{40}BrN_4O_6Si_2$ (M+H) 651.1670, found 651.1695.

3-[3’,5’-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxanediyl)-β-D-2’-deoxyribofuranosyl]-benzo[g]pteridine-2,4-(1H,3H)-dione (16). A solution of **15** (60 mg, 0.092 mmol), tributyltin hydride (54 mg, 0.184 mmol) and AIBN (3 mg) in toluene (2 mL) was degassed by bubbling argon through the solution for 30 min. The solution was heated at reflux for 1 h, then cooled to room temperature and the solvent removed under reduced pressure. Purification by flash chromatography on silica, eluting with 10% ethyl acetate in hexanes, gave **16** (48 mg, 91% yield) as a yellow powder, mp 135-137° C. $[\alpha]^{23}_{D}$ -44°(*c* 1.75, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 8.98 (s, 1H), 8.35 (d, *J*= 8.0 Hz, 1H), 8.07 (d, *J*= 8.0 Hz, 1H), 7.92 (ddd, *J*= 8.0, 6.9, 1.3 Hz, 1H), 7.78 (ddd, *J*= 8.0, 6.9, 1.3 Hz, 1H), 6.83 (dd, *J*= 9.7, 3.2 Hz, 1H), 5.13 (m, 1H), 4.13-4.00 (m, 2H), 3.94-3.87 (m, 1H), 2.93 (ddd, *J*= 13.5, 8.8, 3.2 Hz, 1H), 2.51 (ddd, *J*= 13.5, 9.7, 7.1 Hz, 1H), 1.18-0.98 (m, 28H); ^{13}C NMR ($CDCl_3$) δ 159.2, 149.3, 144.3, 143.3, 141.0, 134.4, 131.1, 129.8, 129.4, 127.4, 86.0, 81.8, 74.0, 64.4, 39.2, 17.6, 17.5, 17.4, 17.3, 17.2, 17.1, 13.3, 13.2, 12.7, 12.6.

3-(β-D-2’-deoxyribofuranosyl)benzo[g]pteridine-2,4-(1H,3H)-dione (4b). To a stirred solution of **16** (48 mg, 0.084 mmol) in dry THF (1 mL), was added TBAF in THF (0.17 mmol, 1.0 M in THF). The mixture was stirred for 6 h at room temperature after which time, the solvent was evaporated under reduced pressure. Purification by flash chromatography on silica, eluting with 10% methanol in chloroform, gave **4b** (25 mg, 90% yield) as a yellow powder, mp 190-191° C (dec.); $[\alpha]^{23}_{D}$ -21° (*c* 0.865, $CHCl_3$/MeOH=1:1); ^1HNMR (DMSO-d_6) δ 12.2 (s, 1H), 8.18-8.15 (m, 1H), 7.95-7.90

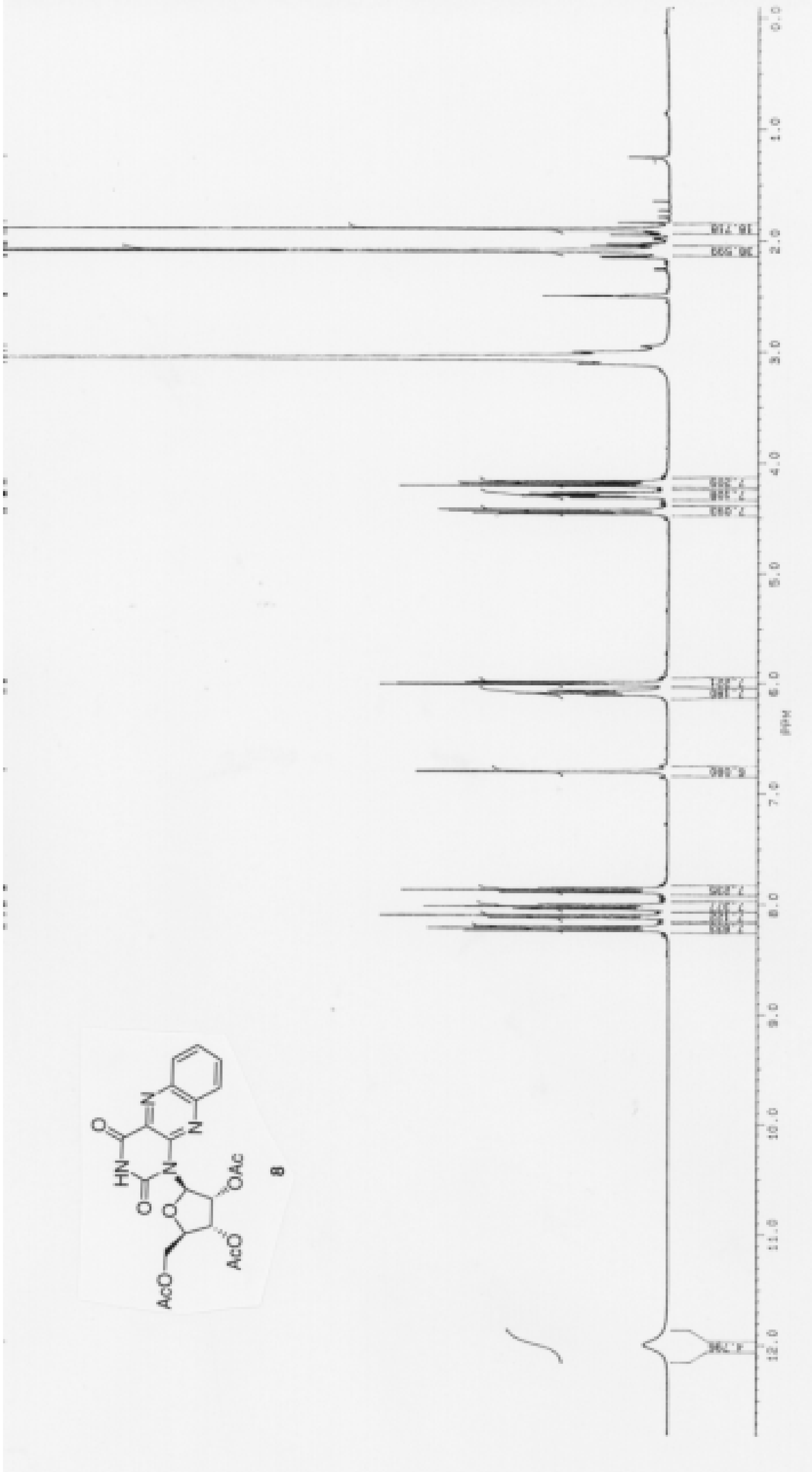
(m, 2H), 7.81-7.75 (m, 1H), 6.65 (dd, *J*= 8.2, 6.0 Hz, 1H), 5.14 (br, s, 1H), 4.56 (br, s, 1H), 4.41-4.35 (m, 1H), 3.74-3.63 (m, 2H), 3.55-3.48 (m, 1H), 2.79 (ddd, *J*= 13.2, 7.4, 6.0 Hz, 1H), 2.04 (ddd, *J*= 13.2, 8.2, 5.0 Hz, 1H); ^{13}C NMR (DMSO-d_6) δ 159.7, 149.6, 145.5, 142.8, 139.5, 133.5, 131.1, 130.2, 128.5, 127.0, 87.5, 82.1, 71.1, 62.3, 36.7; HRMS (FAB) *m/z* calcd for $C_{15}H_{15}N_4O_5$(M+H) 331.1042, found 331.1054.

Fluorescence Measurements. Optical densities (OD) for **4b**, **16** and quinine sulfate at the excitation wavelength were determined by UV spectroscopy. Fluorescence emission spectra were recorded on each sample, with an optical density less than 0.11, at the excitation wavelength at room temperature using a 1 x 1 cm quartz cuvette. The fluorescence spectra were exported as an ACSII text file to Kaleidagraph 3.08d (Synergy Software, Inc.)where the emission spectra were integrated and referenced to quinine sulfate (*Q*= 0.51). Quantum yields were calculated according to the following equation:

$$Q=c \bullet A/OD$$

Where *Q* is the quantum yield, *OD* is the optical density, *A* is the area under the fluorescence emission spectra curve, and *c* is a constant, which was determined for quinine sulfate.

	Quinine sulfate	**4b**	**16**
concentration	1.0 x 10^5 M in H_2O	1.0 x 10^5 M in H_2O	1.0 x 10^5 M in CH_3CN
Excitation wavelength	332 nm	332 nm	321 nm
Emission wavelength	390 nm	455 nm	427 nm
OD	0.102	0.061	0.080
A	6.7 x 10^6	4.6 x 10^5	1.8 x 10^5
Q	0.51	0.06	0.02



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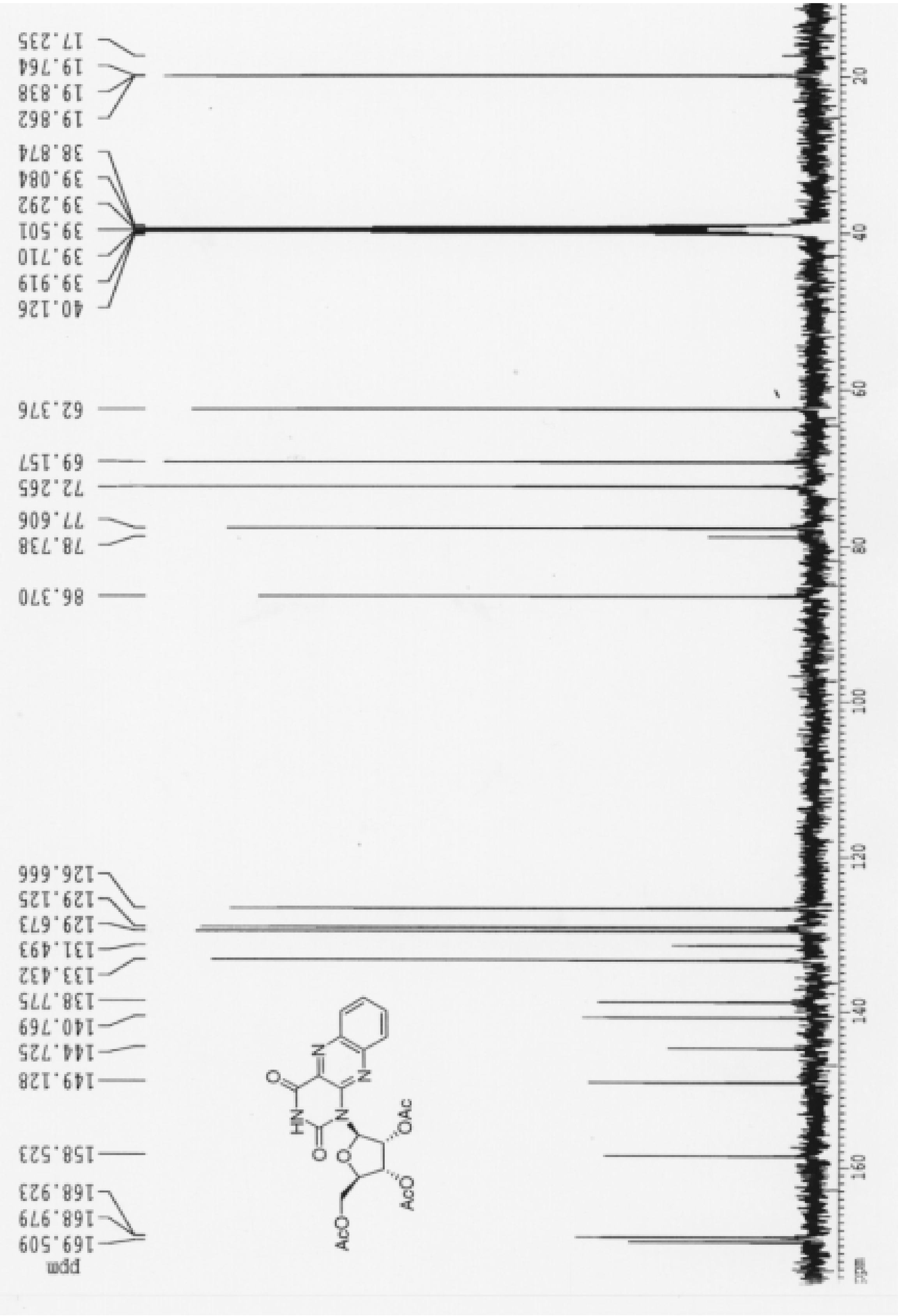
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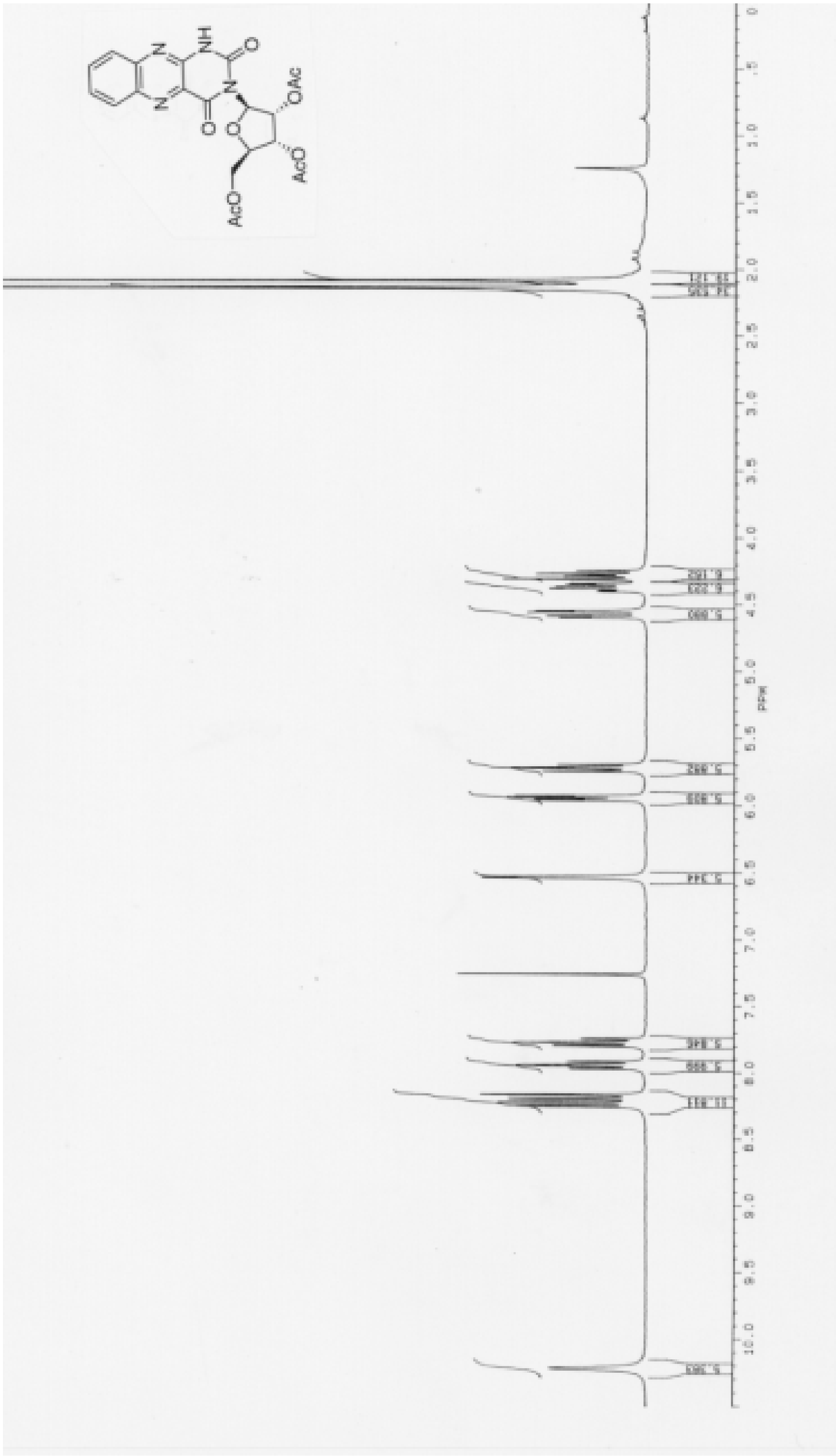

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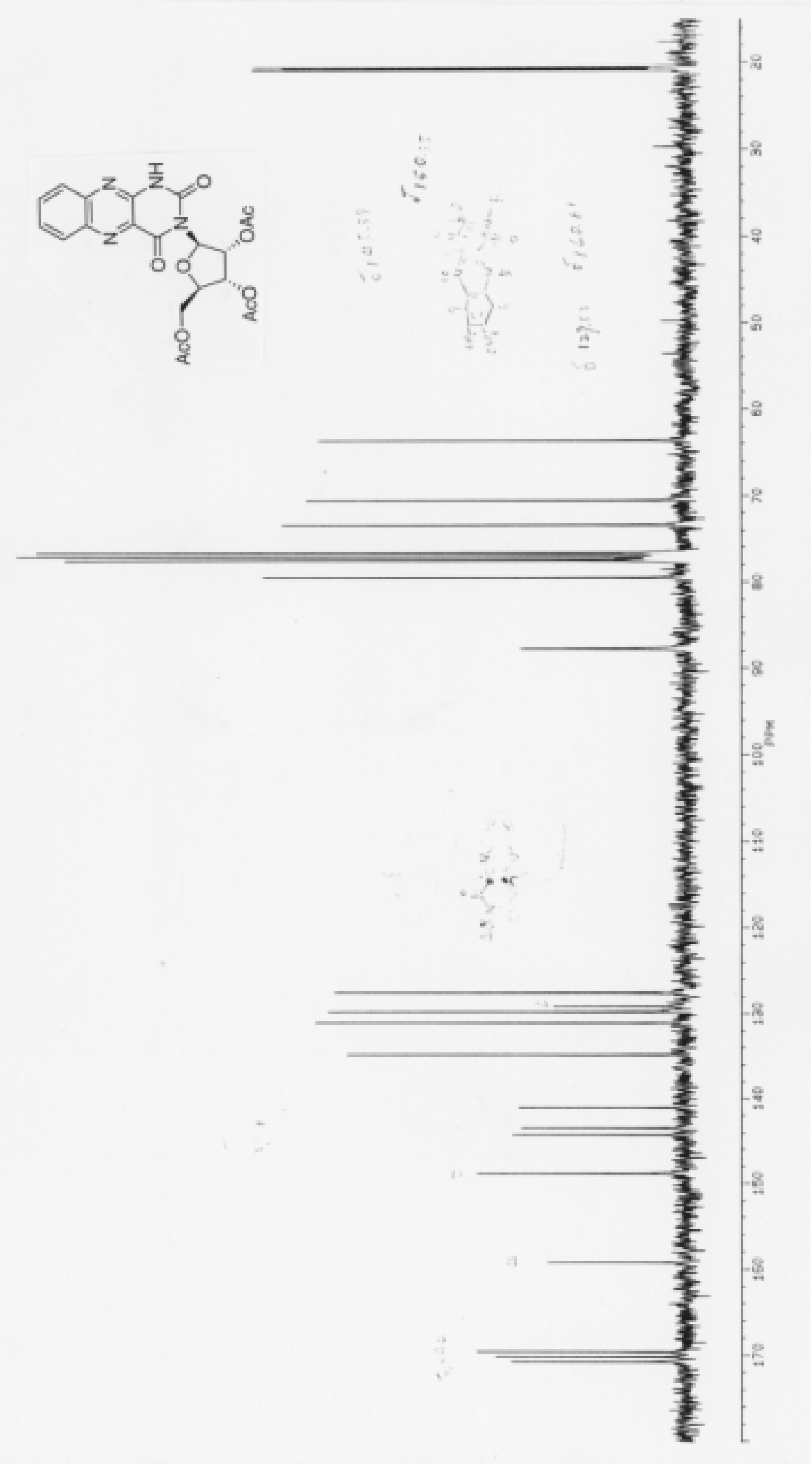
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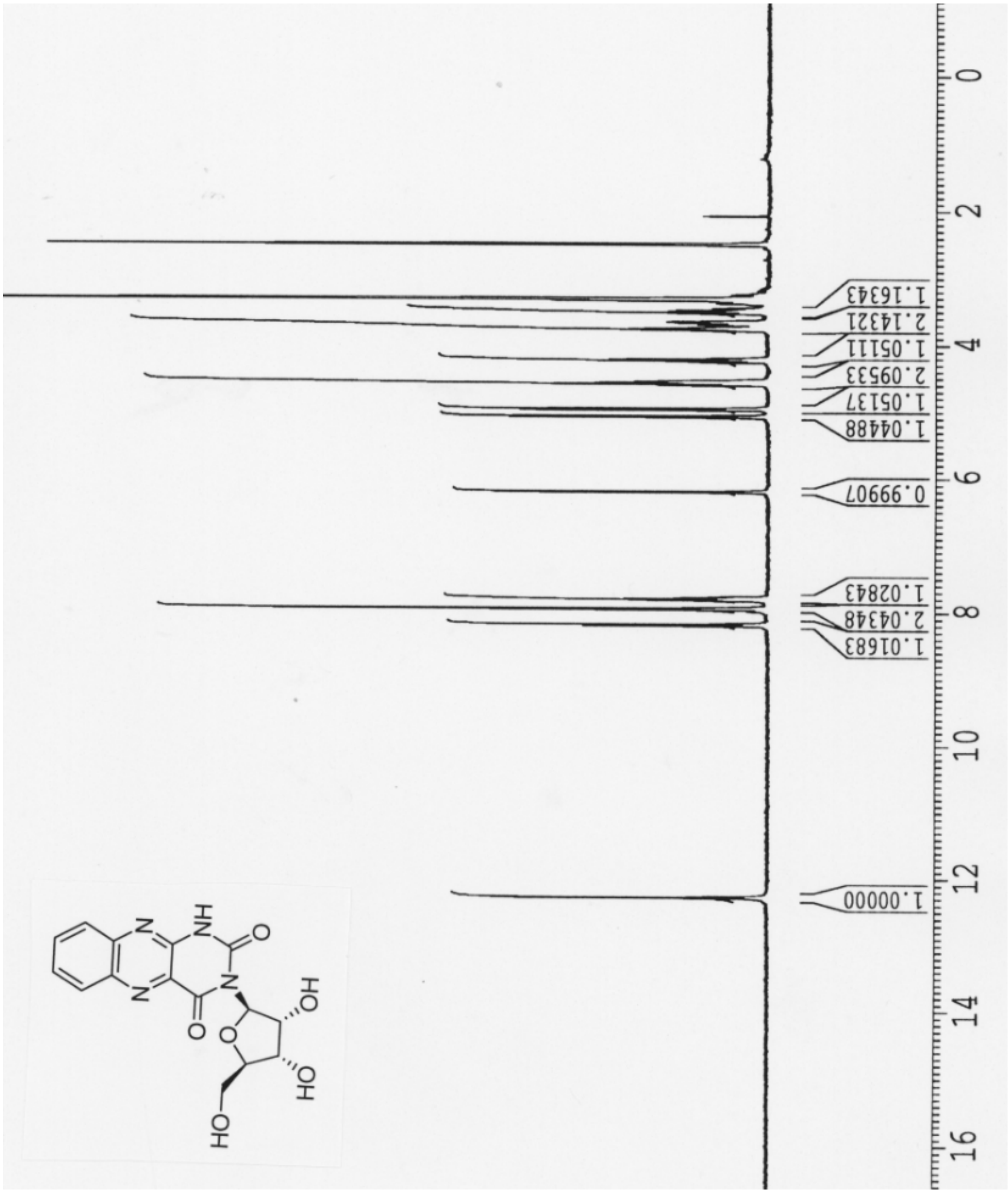
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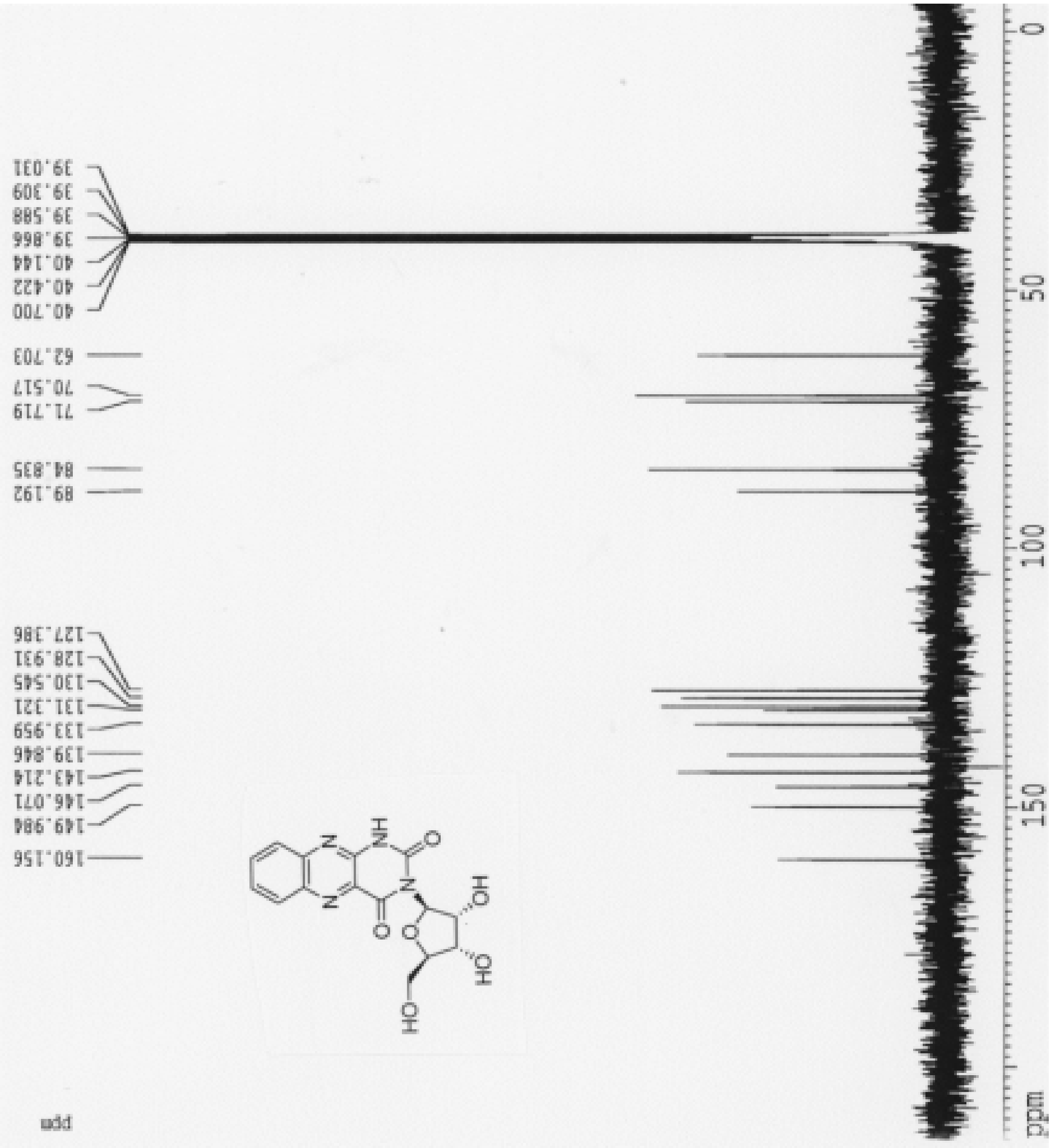
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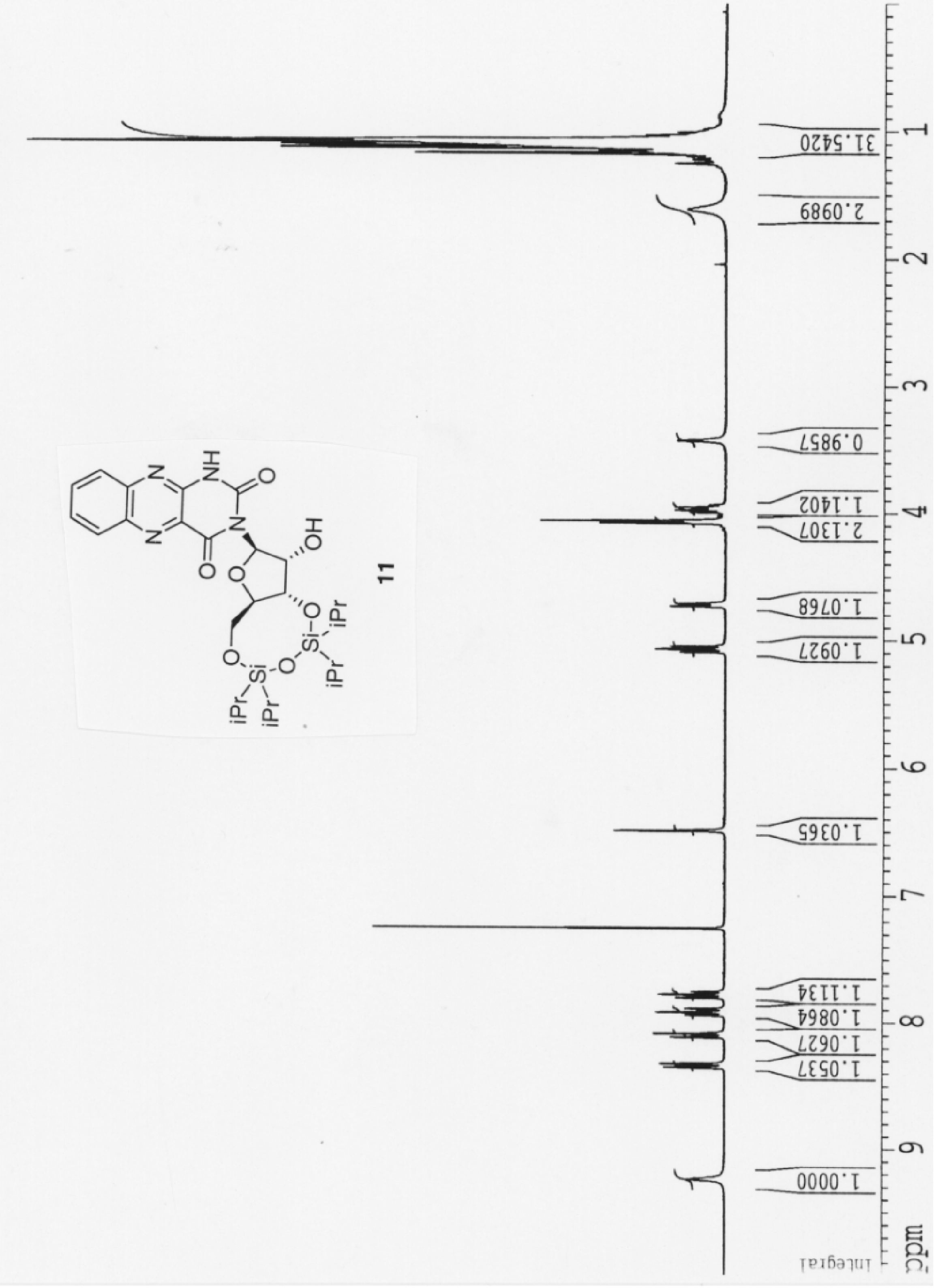
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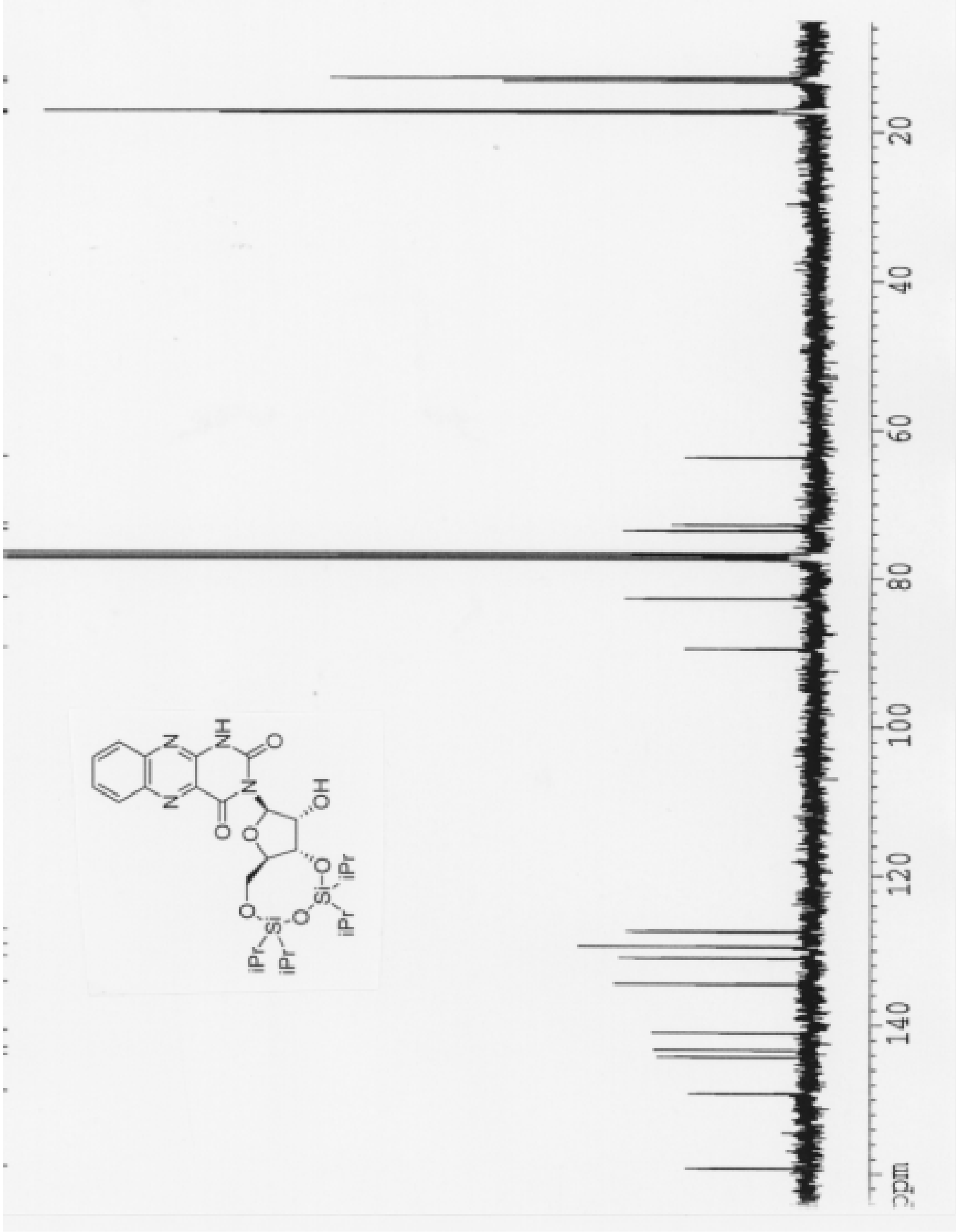
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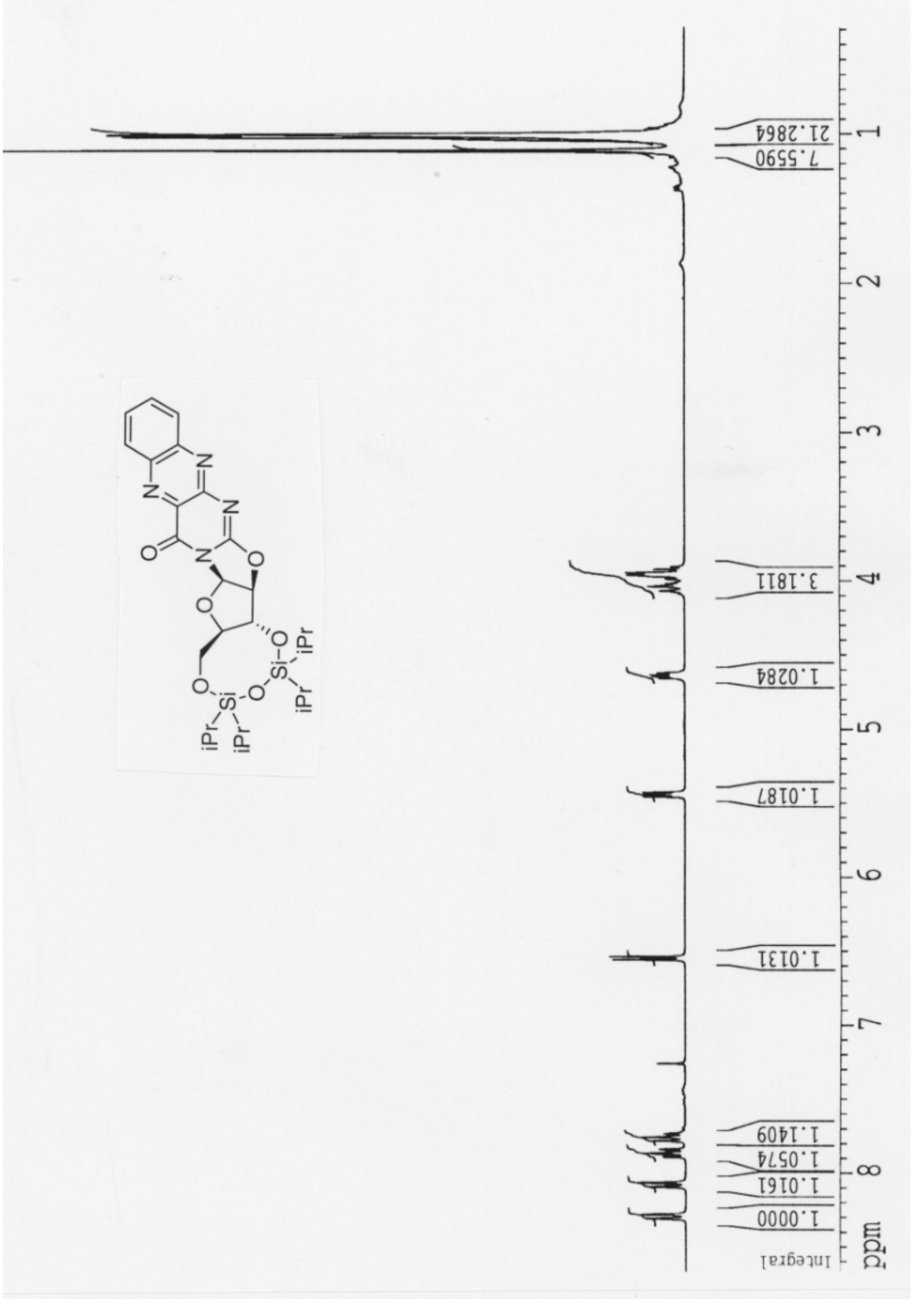

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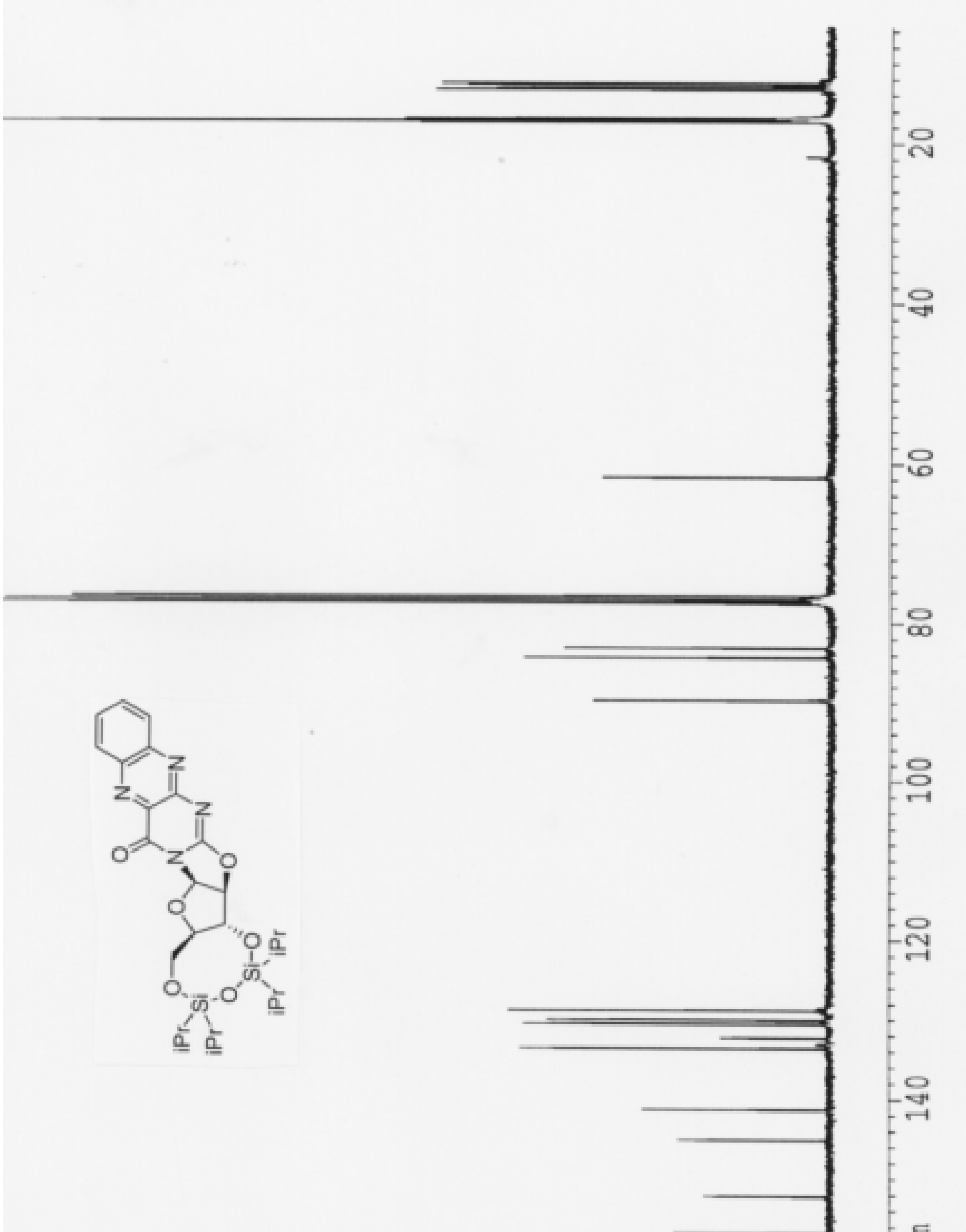
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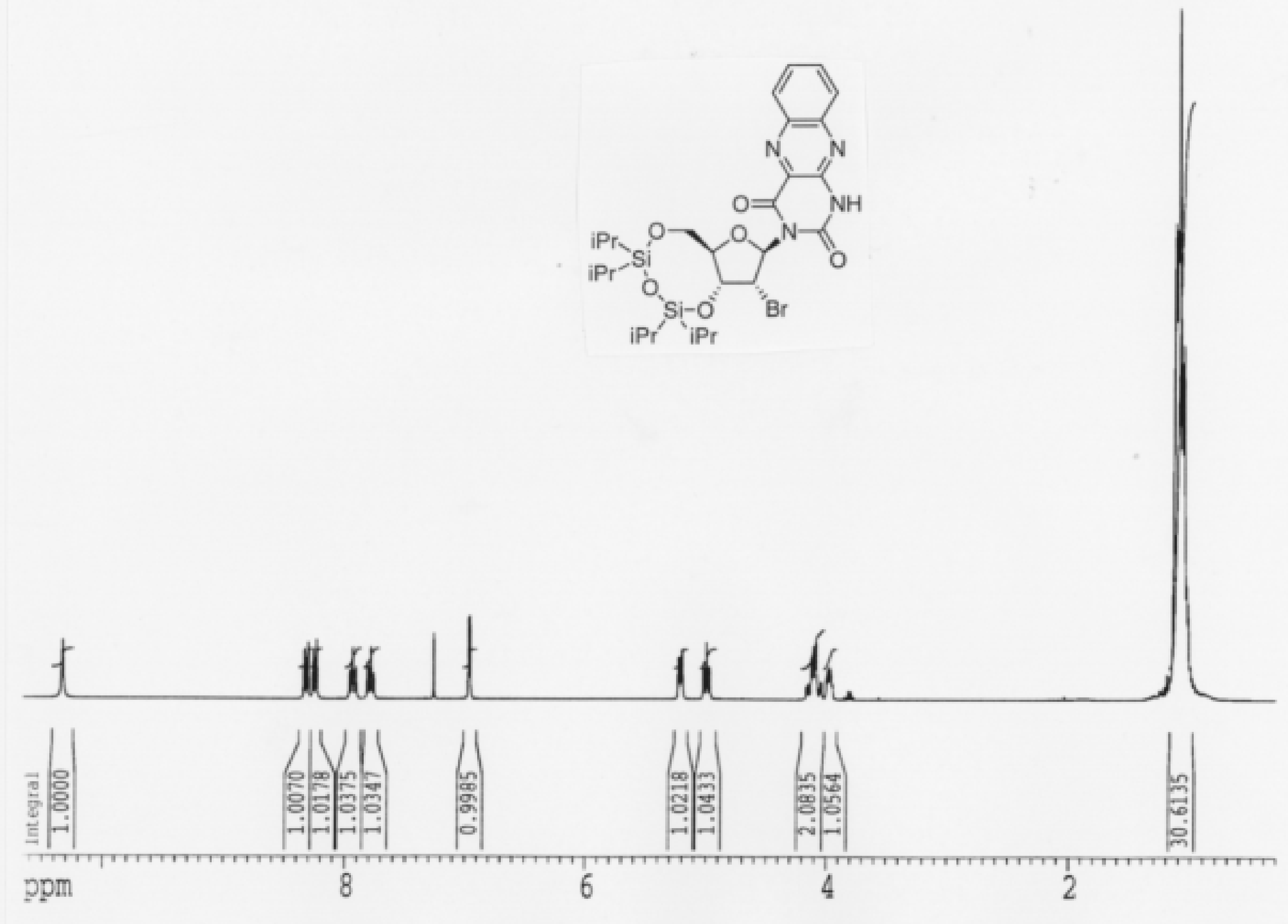
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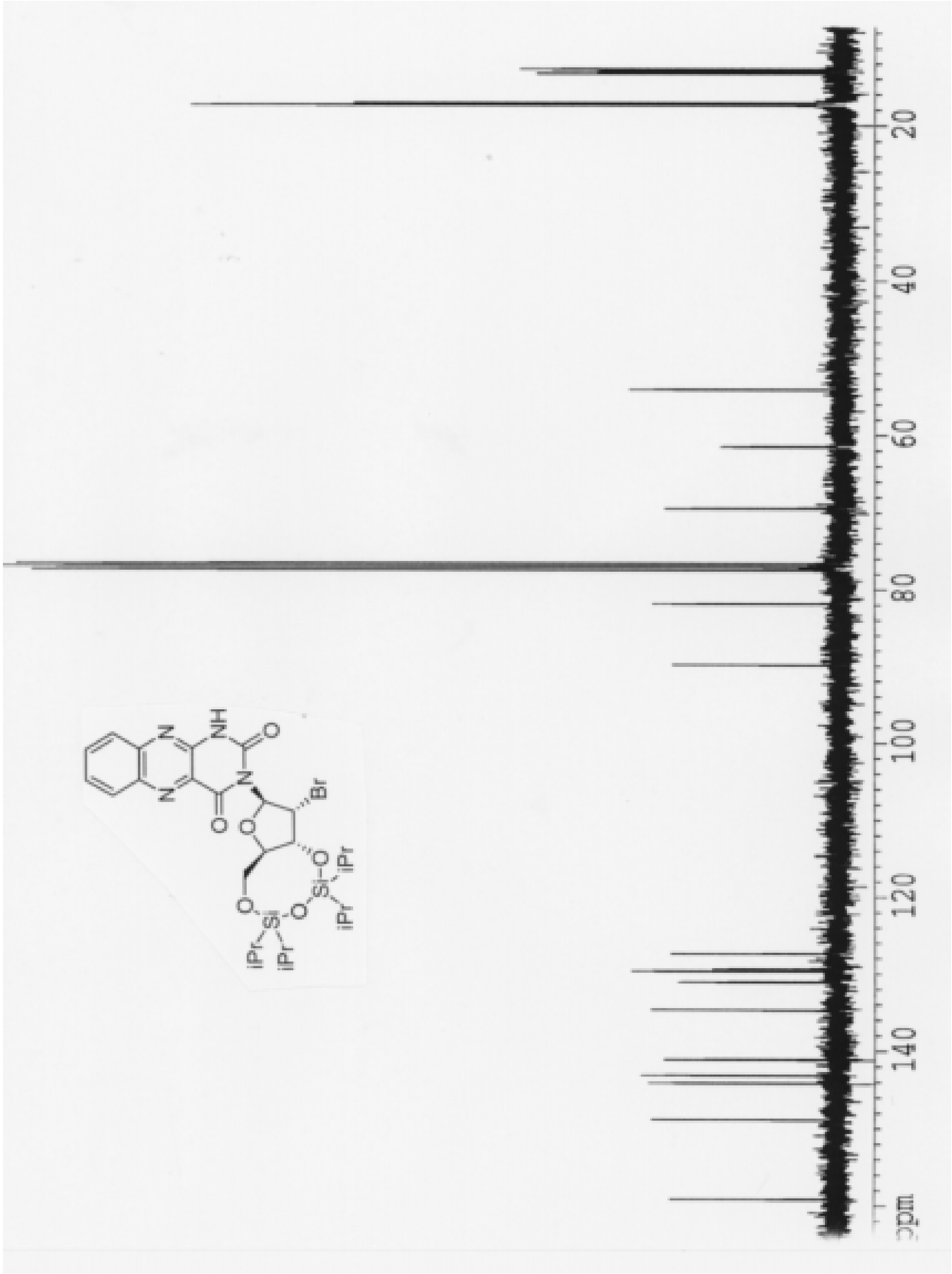

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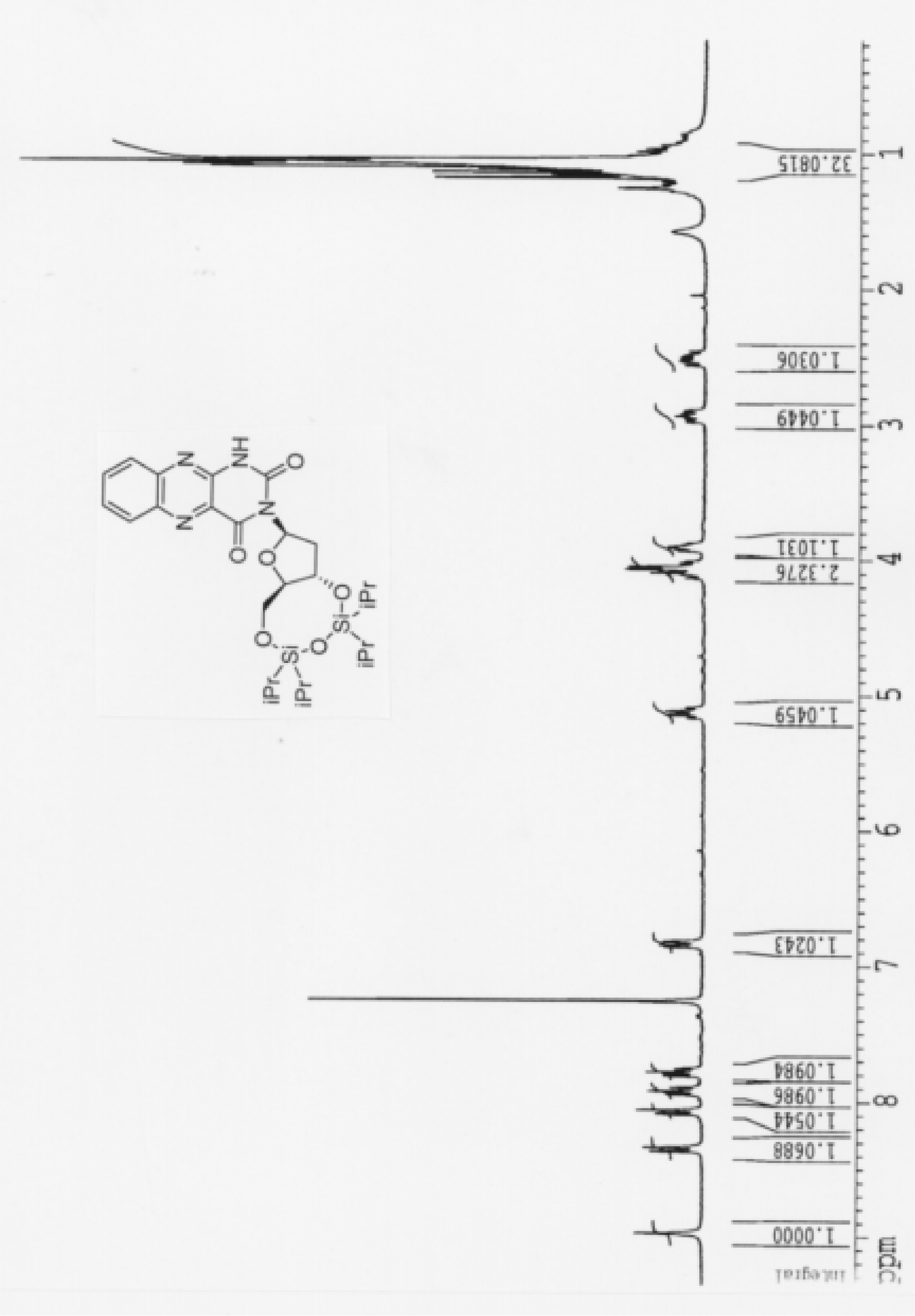
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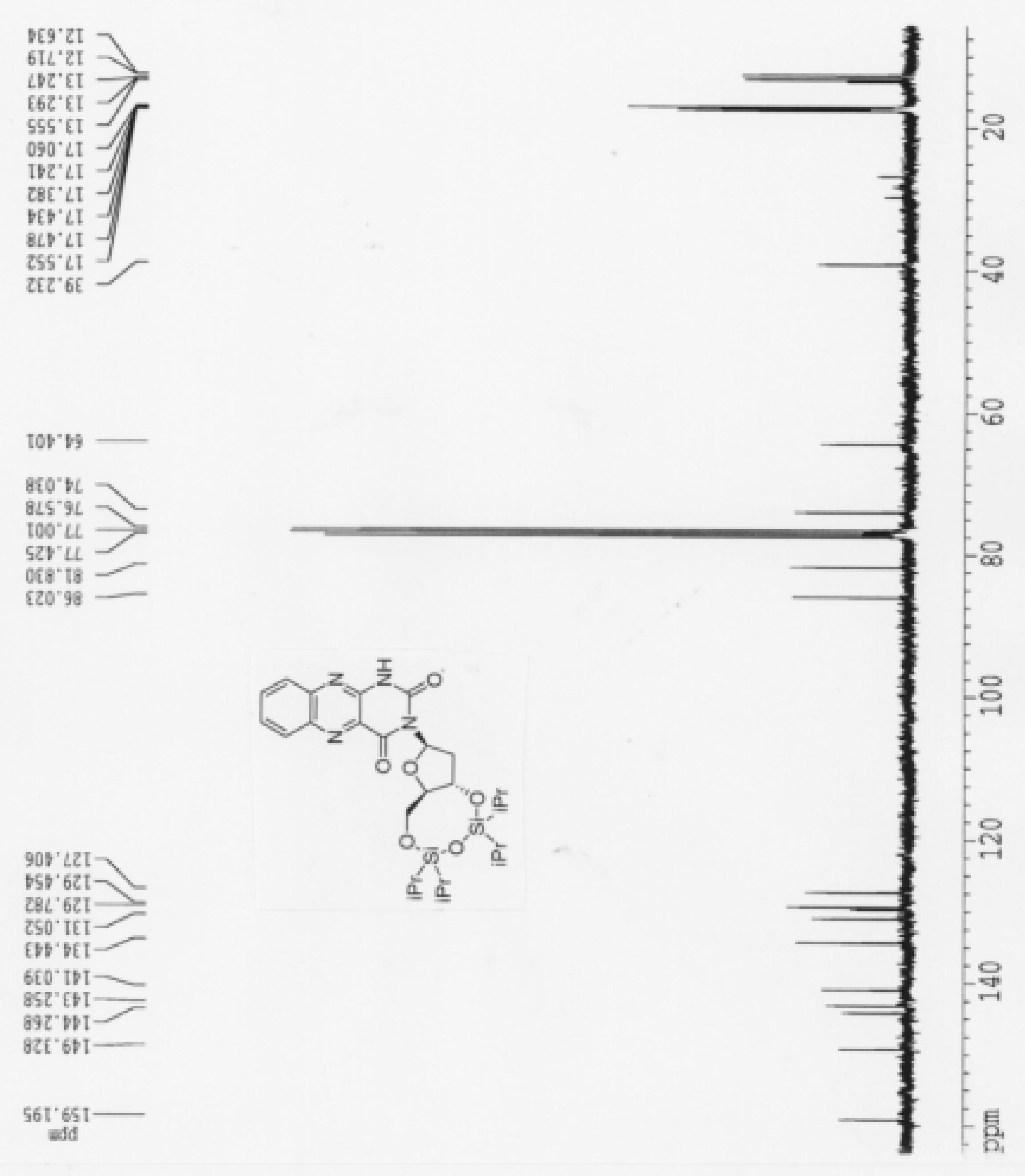
1.0984
1.0986
1.0544
1.0688
1.0000
integral
ppm
1
2
3
4
5
6
7
8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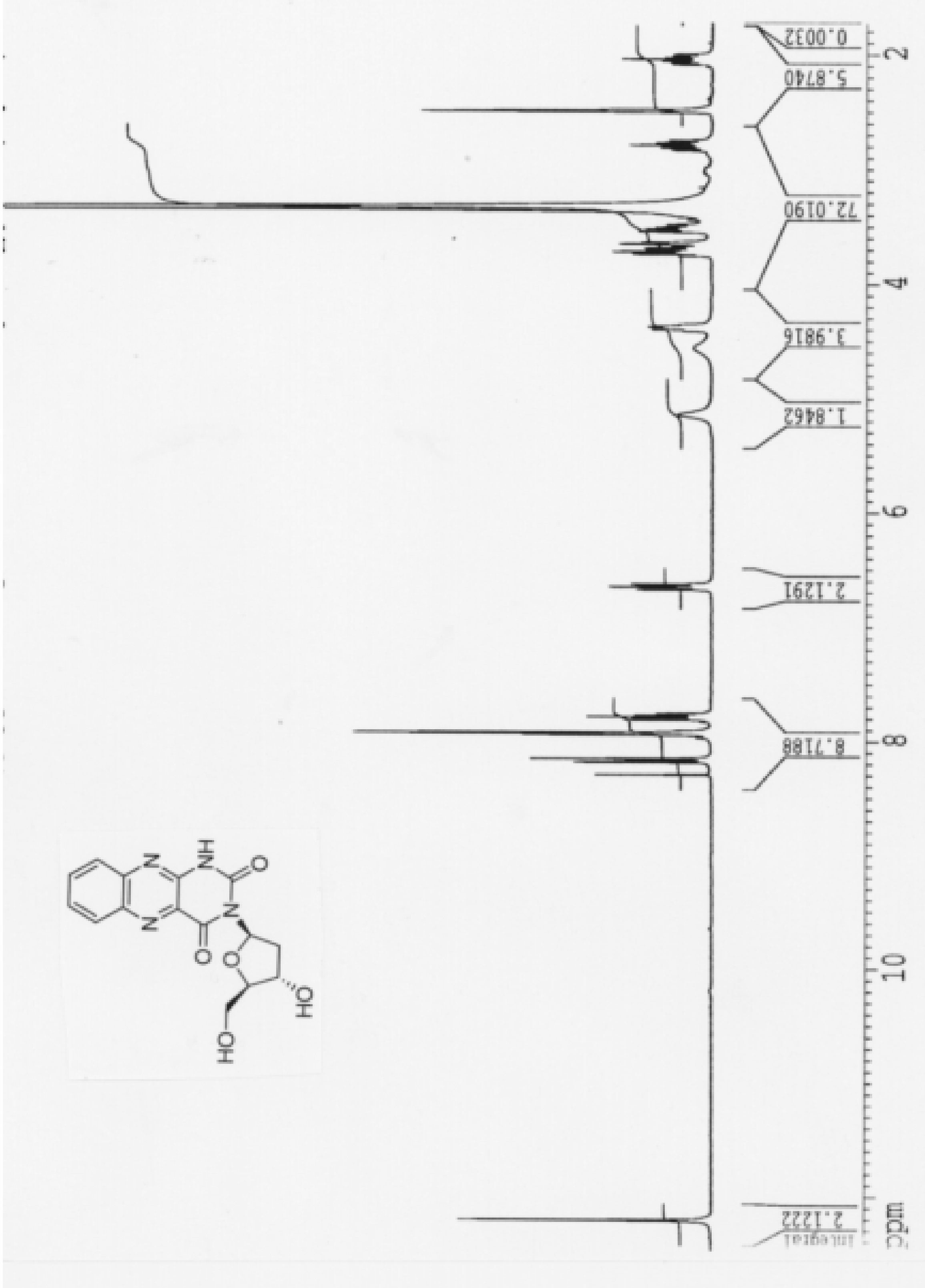
12.719
13.247
13.293
13.555
17.060
17.241
17.382
17.434
17.478
17.552
39.232
64.401
74.038
76.578
77.001
77.425
81.830
86.023
127.406
129.454
129.782
131.052
134.443
141.039
143.258
144.268
149.328
159.195
ppm
20
40
60
80
100
120
140
ppm
N
NH
O
iPr
Si
O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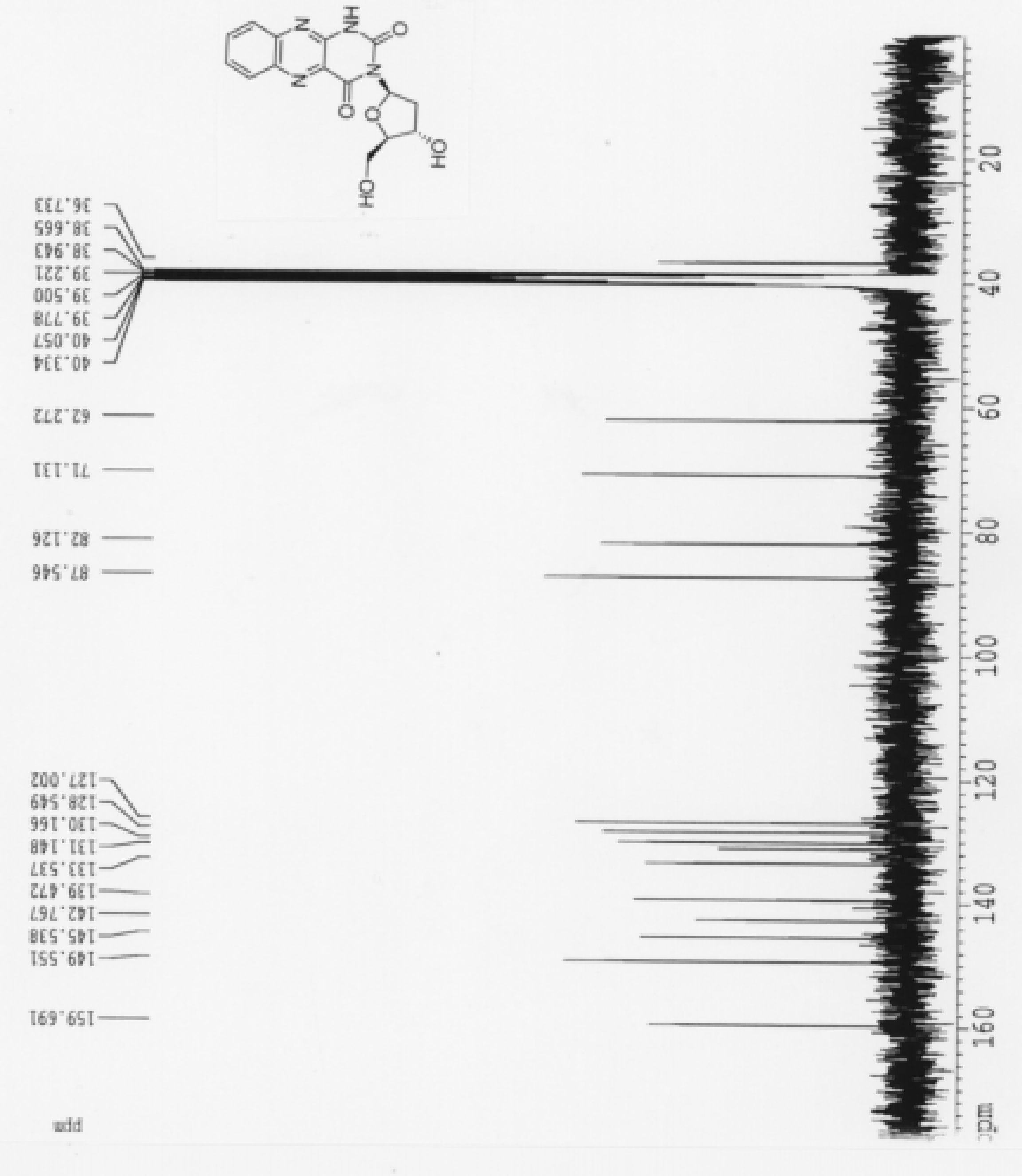
5.8740
72.0190
3.9816
1.8462
2.1291
8.7188
2.1222
Integral
ppm
2
4
6
8
10
HN
N
O
HO
OH


N
NH
O
O
N
N
OH
HO
36.733
38.665
38.943
39.221
39.500
39.778
40.057
40.334
62.272
71.131
82.126
87.546
127.002
128.549
130.166
131.148
133.537
139.472
142.767
145.538
149.551
159.691
ppm
20
40
60
80
100
120
140
160
ppm

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