Electronic Supplementary Material (ESI) for RSC Advances.


# Supporting Information (SI)

## Stereoselective Synthesis of 2′-Modified Nucleosides by Using *ortho*-Alkynyl Benzoate as A Gold(I)-Catalyzed Removable Neighboring Participation Group

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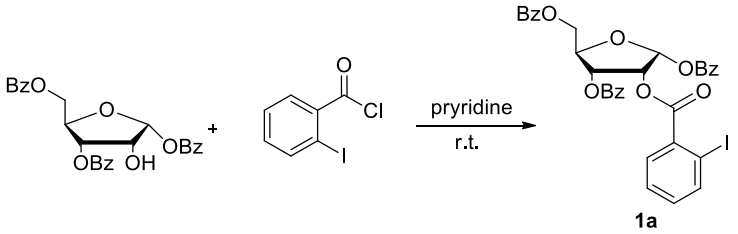
## 1. General information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvent were treated according to general methods. Flash column chromatography was performed using 300-400 mesh silica gel. Analytical thin-layer chromatography (TLC) was performed using glass plates pre-coated with 200-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20Torr (house vacuum) at 30–40°C. Commercial reagents and solvents were used as received. The $^{1}H$ and $^{13}C$ NMR spectra were recorded on a Bruker AV-400 Spectrometer. Chemical shifts (δ) were given in ppm and are referenced to residual solvent peaks ($CDCl_3$: δ 7.26 ppm $^{1}H$; δ 77.7 ppm $^{13}C$). Coupling constants (*J*) were reported in Hertz. High resolution mass spectra were obtained using a Bruker Dalton micro TOFQ II spectrometer.

## 2. Preparation of substrates

### 2.1 Synthesis of 2-*O*-(2-iodobenzoyl) -1,3,5-tri-*O*–benzoyl-α-D-ribofuranoside(1a)

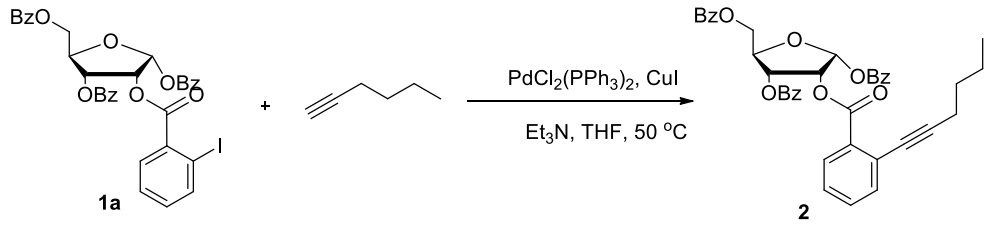



**1a**

To a solution of 1,3,5-tri-*O*-benzoyl-*β*-D-ribofuranoside (4.62 g, 10.0 mmol) in pyridine was added 2-iodobenzoyl chloride (4.00 g, 15.0 mmol) dropwise in an ice-water bath. The reaction mixture was stirred and allowed to warm to room temperature. After reaction completed, the solvent was removed in *vacuo* and added $CH_2Cl_2$. Then, the mixture was sequentially washed with distilled water (2 × 30 mL) and brine (2 × 30 mL), The Organic layer was dried over $Na_2SO_4$ and filtered. The solution was concentrated in *vacuo* and the residue was purified by column chromatography on silica gel (eluted with PE/EA = 5 : 1, V:V) to give the product **1a** as a yellow syrup (6.51 g, 94% yield). $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.02

(m, 6H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.69 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.62 – 7.55 (m, 3H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.42 – 7.34 (m, 4H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.08 (td, *J* = 7.6, 1.3 Hz, 1H), 6.98 (d, *J* = 4.4 Hz, 1H), 5.95 (dd, *J* = 6.5, 2.0 Hz, 1H), 5.72 – 5.70 (m, 1H), 4.91 – 4.90 (m, 1H), 4.78 (dd, *J* = 12.2, 3.0 Hz, 1H), 4.68 (dd, *J* = 12.2, 3.5 Hz, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.1, 164.7, 164.1, 163.5, 140.7, 132.6, 132.5, 132.4, 132.3, 131.7, 130.4, 129.0, 128.9, 128.8, 128.6, 128.4, 128.2, 127.6, 127.5, 127.4, 126.7, 93.7, 93.7, 81.9, 71.0, 69.6, 63.0; HRMS ($ESI^+$): *m/z* calcd for: $C_{33}H_{25}IO_9$ $[M+Na]^+$: 715.0441, found:715.0454.

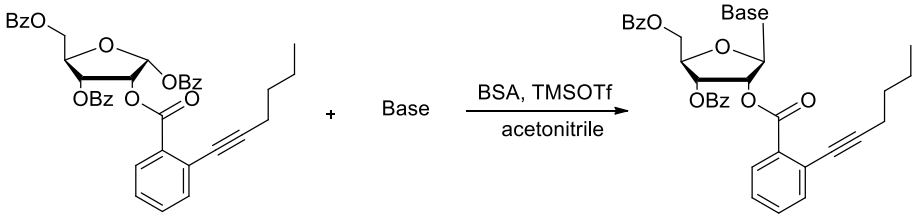
## 2.2 Synthesis of 2-*O*-(2-hexynylbenzoyl)-1,3,5-tri-*O*-benzoyl-α-D-ribofuranoside (2)




A mixture solvent of THF/ $Et_3N$ (3:1, V:V) was added to a mixture of **1a** ( 3.46 g, 5.0 mmol), CuI (47.6 mg, 0.25 mmol), $PdCl_2(PPh_3)_2$ (175.5 mg, 0.25 mmol) in a round bottom flask under argon atmosphere. The mixture was stirred at room temperature and hex-1-yne (493 mg, 6.0 mmol) was added dropwise. After 30 min, the reaction mixture was then heated to 50 ºC for 3h. After completion of the reaction as indicated by TLC, the reaction mixture was diluted with distilled water (100 mL) and extracted into $CH_2Cl_2$ (2 × 50 mL). The combined organics were dried ($Na_2SO_4$), filtered, and concentrated in *vacuo.* The residue was purified by flash column chromatography (eluted with PE/EA = 10:1 to 5:1, V:V) to afford product **2** as a yellow syrup (2.73 g, 84%). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.4 Hz, 2H), 8.08 (t, *J* = 7.1 Hz, 4H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.62 – 7.52 (m, 3H), 7.50 – 7.44 (m, 3H), 7.42 – 7.31 (m, 5H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 4.3 Hz, 1H), 5.93 (dd, *J* = 6.5, 2.0 Hz, 1H), 5.72 –5.70 (m, 1H), 4.91 – 4.90 (m, 1H), 4.79 (dd, *J* = 12.1, 2.9 Hz, 1H), 4.70 (dd, *J* = 12.1, 3.5 Hz, 1H), 2.36 (t, *J* = 7.0 Hz, 2H), 1.60 – 1.48 (m, 2H), 1.48 – 1.37 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H); $^{13}$C NMR (101 MHz,

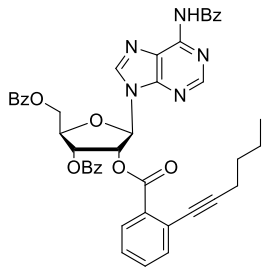
$CDCl_3$) δ 166.1, 165.8, 165.2, 164.2, 134.5, 133.6, 133.5, 133.4, 132.1, 130.1, 130.0, 129.9, 129.8, 129.7, 129.5, 129.3, 128.6, 128.5, 128.4, 126.9, 125.6, 97.1, 94.9, 82.9, 78.8, 71.6, 70.9, 64.1, 30.6, 22.0, 19.4, 13.6; HRMS ($ESI^+$): *m/z* calcd for: $C_{39}H_{34}O_9$ $[M+Na]^+$: 669.2101, found: 669.2107.

**2.3 General procedure for synthesis of substrates(3a-3i)**




To a suspension of Base (1.2 mmol, 1.2 eq) in dry acetonitrile (15 mL) was added BSA (4.0 mmol, 4 eq) under argon atmosphere and heated at 60 ºC for 30 min. After cooling, compound **2** (1.0 mmol, 1.0 eq) dissolved in dry acetonitrile (2 mL) was added. TMSOTf (4.0 mmol, 4.0 eq) was then added dropwise to the reaction mixture at 0 ºC. The resulting solution was stirred for 20 min before heating to 80 °C for 3 h and poured into cold *sat*. $NaHCO_3$(30 mL). The mixture was extracted with $CH_2Cl_2$ (2 × 30 mL). The combined organic layers were washed with *sat*. aq $NaHCO_3$ (2 × 30 mL) and brine (2 × 30 mL), and dried ($Na_2SO_4$), filtered, and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (eluted with $CH_2Cl_2$/MeOH, 100:1 to 30:1, v:v) to afford compound **3(a-i)**.

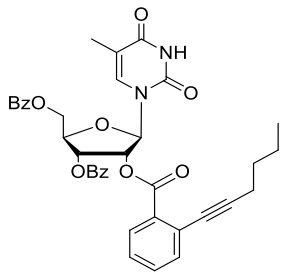
## 3. Characterization data of the substrates (3a-3i)




$N^6$-benzoyl-9-[2-*O*-(2-hexynylbenzoyl)-3,5-di-*O*-benzoyl-*β*-D-ribofuranosyl]adenine (**3a**)

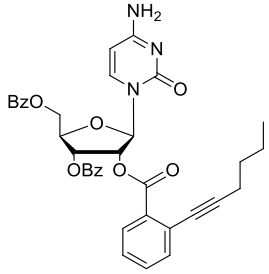
Yield: 74%; White solid; $^1H$ NMR (400 MHz, $CDCl_3$): δ 9.11 (s, 1H), 8.72 (s, 1H), 8.16 (s, 1H), 8.11 – 8.05 (m, 2H), 8.04 – 7.98 (m, 4H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.62

– 7.54 (m, 3H), 7.50 (t, *J* = 8.1 Hz, 3H), 7.47 – 7.36 (m, 5H), 7.22 (t, *J* = 6.4 Hz, 1H), 6.49 (d, *J* = 4.8 Hz, 1H), 6.41(t, *J* = 5.2 Hz, 1H), 6.32 (t, *J* = 5.5 Hz, 1H), 4.91 (dd, *J* = 12.1, 3.2 Hz, 1H), 4.85 – 4.82 (m, 1H), 4.70 (dd, *J* = 12.2, 4.4 Hz, 1H), 2.38 (t, *J* = 7.1 Hz, 2H), 1.58 – 1.48 (m, 2H), 1.46 – 1.48 (m, 2H),), 0.88 (t, *J* = 7.3 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.3, 164.6, 152.9, 151.6, 149.8, 141.7, 134.6, 133.6, 133.3, 132.7, 132.3, 130.5, 129.8, 129.7, 129.5, 129.3, 128.7, 128.5, 127.9, 127.1, 125.3, 123.6, 97.0, 87.2, 80.8, 79.0, 74.1, 71.3, 63.5, 30.6, 22.0, 19.4, 13.5; HRMS (ESI$^+$): *m/z* calcd for: $C_{44}H_{37}N_5O_8$ $[M+H]^+$: 764.2720, found: 764.2718.



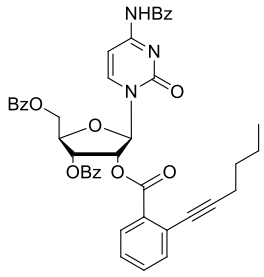

N-[2-*O*-(2-hexynylbenzoyl)-3,5-di-*O*-benzoyl-*β*-D-ribofuranosyl]thymine (**3b**)

Yield: 82%; syrup; $^1$H NMR (400 MHz, $CDCl_3$): δ 9.94 (s, 1H), 8.13 (d, *J* = 7.7 Hz, 2H), 7.98 (d, *J* = 7.9 Hz, 2H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.49 – 7.45 (m, 3H), 7.43 – 7.33 (m, 3H), 7.25 –7.10 (m, 2H), 6.42 (d, *J* = 5.9 Hz, 1H), 5.94 (d, *J* = 5.6 Hz, 1H), 5.79 (t, *J* = 5.9 Hz, 1H), 4.88 (d, *J* = 10.2 Hz, 1H), 4.69 – 4.64 (m, 2H), 2.40 (t, *J* = 7.1 Hz, 2H), 1.59 (s, 3H), 1.55 – 1.50(m, 2H), 1.45 – 1.39(m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ 166.0, 165.5, 164.6, 164.0, 150.6, 135.3, 134.6, 133.6, 132.4, 130.7, 130.1, 129.9, 129.7, 129.4, 129.3, 128.8, 128.7, 128.5, 128.3, 127.2, 125.4, 112.1, 97.1, 87.3, 80.6, 79.0, 73.5, 71.2, 63.9, 30.6, 22.0, 19.5, 13.6, 12.1; HRMS (ESI$^+$): *m/z* calcd for: $C_{37}H_{34}N_2O_9$ $[M+H]^+$: 651.2343, found: 651.2339.



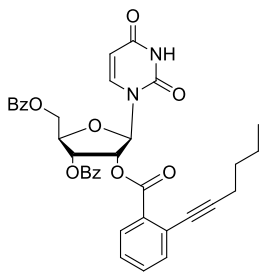

N-[2-*O*-(2-hexynylbenzoyl)-3,5-di-*O*-benzoyl-*β*-D-ribofuranosyl]cytosine (**3c**)

Yield: 80%; syrup; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.03 (d, *J* = 7.5 Hz, 2H), 7.95 (d, *J* = 7.6 Hz, 2H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 2H), 7.49 – 7.34 (m, 6H), 7.23 (t, *J* = 7.6 Hz, 1H), 6.26 (d, *J* = 4.0 Hz, 1H), 6.14 (d, *J* = 7.6 Hz, 1H), 5.86 (t, *J* = 5.3 Hz, 1H), 5.84 – 5.76 (m, 1H), 4.74 – 4.56 (m, 3H), 2.33 (t, *J* = 7.0 Hz, 2H), 1.54 – 1.43 (m, 2H), 1.42 – 1.32 (m, 2H), 0.84 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.1, 165.2, 164.6, 164.1, 154.1, 141.6, 134.7, 133.8, 133.6, 132.5, 130.8, 129.9, 129.7, 129.5, 129.2, 128.8, 128.6, 127.4, 125.3, 97.0, 96.9, 89.8, 80.6, 79.2, 74.5, 71.1, 63.7, 30.6, 22.0, 19.5, 13.7; HRMS (ESI$^+$): *m/z* calcd for: $C_{36}H_{33}N_3O_8$ $[M+H]^+$: 636.2346, found: 636.2342.



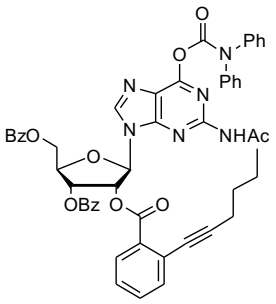

N$^4$-benzoyl-[2-*O*-(2-hexynylbenzoyl)-3,5-tri-*O*-benzoyl-*β*-D-ribofuranosyl)]cytosine (**3d**)

Yield: 81%; syrup;$^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.08 (s, 1H), 8.14 – 8.06 (m, 2H), 8.03 (d, *J* = 7.5 Hz, 1H), 7.93 – 7.86 (m, 5H), 7.62 – 7.36 (m, 10H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.24 – 7.17 (m, 1H), 6.39 (d, *J* = 3.4 Hz, 1H), 6.01 – 5.82 (m, 2H), 4.91 – 4.77 (m, 2H), 4.72 (dd, *J* = 12.1, 3.9 Hz, 1H), 2.36 (t, *J* = 6.9 Hz, 2H), 1.58 – 1.46 (m, 2H), 1.45 – 1.32 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.1, 165.3, 164.5, 162.8, 154.5, 144.4, 134.6, 133.6, 133.5, 133.2, 132.3, 130.9, 129.9, 129.7, 129.7, 129.3, 129.0, 128.7, 128.4, 127.7, 127.2, 125.3, 97.4, 96.9, 90.1, 80.4, 79.3, 74.8, 70.5, 63.4, 30.6, 22.1, 19.5, 13.7; HRMS (ESI$^+$): *m/z* calcd for: $C_{43}H_{37}N_3O_9$ $[M+Na]^+$: 762.2427, found: 762.2421.



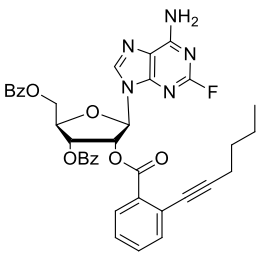

N-[2-*O*-(2-hexynylbenzoyl)-3,5-di-*O*-benzoyl-*β*-D-ribofuranosyl]uracil (**3e**)

Yield: 82%; syrup; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.09 (d, *J* = 7.6 Hz, 2H), 7.98 (d, *J* = 7.6 Hz, 2H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.67 – 7.52 (m, 2H), 7.52 – 7.34 (m, 7H), 7.21 (t, *J* = 7.6 Hz, 1H), 6.30 (d, *J* = 4.9 Hz, 1H), 5.89 (t, *J* = 5.3 Hz, 1H), 5.78 (t, *J* = 5.4 Hz, 1H), 5.60 (d, *J* = 8.1 Hz, 1H), 4.84 (d, *J* = 11.6 Hz, 1H), 4.71 – 4.65 (m, 2H), 2.40 (t, *J* = 7.0 Hz, 2H), 1.58 – 1.51(m, 2H), 1.47 – 1.38(m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.2, 165.5, 164.7, 162.9, 150.1, 139.9, 134.8, 133.8, 133.7, 132.5, 130.8, 130.0, 129.8, 129.6, 129.4, 128.8, 128.7, 128.6, 127.3, 125.5, 103.4, 97.2, 88.5, 80.6, 79.2, 74.0, 71.0, 63.7, 30.7, 22.2, 19.6, 13.7; HRMS (ESI$^+$): *m/z* calcd for: $C_{36}H_{32}N_2O_9$ $[M+Na]^+$: 659.2006, found: 659.2021.



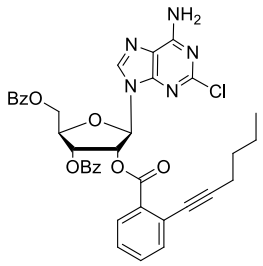

2-Acetamido-6-diphenylcarbamate-9-[2-*O*-(2-hexynylbenzoyl)-3,5-di-*O*-benzoyl-*β*-D-ribofuranosyl]guanine (**3f**)

Yield: 75%; syrup; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.14 (s, 1H), 7.99 (t, *J* = 7.6 Hz, 4H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.59 – 7.32 (m, 18H), 7.19 (t, *J* = 7.6 Hz, 1H), 6.39 – 6.38 (m, 1H), 6.33 (d, *J* = 3.5 Hz, 1H), 6.28 – 6.26 (m, 1H), 4.96 – 4.81 (m, 2H), 4.75 (dd, *J* = 11.5, 4.7 Hz, 1H), 2.43 (s, 3H), 2.36 (t, *J* = 7.1 Hz, 2H), 1.55 – 1.48 (m, 2H), 1.45 – 1.36 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 169.9, 166.2, 165.3, 164.5, 156.3, 154.0, 152.4, 150.1, 142.4, 141.7, 134.7, 133.6, 133.4, 132.4, 130.5, 129.9, 129.6, 129.5, 129.3, 128.8, 128.5, 127.1, 125.3, 120.8, 97.1, 87.9, 80.5, 79.0, 77.2, 74.4, 71.2, 63.5, 30.6, 25.1, 22.0, 19.5, 13.6; HRMS (ESI$^+$): m/z calcd for: $C_{52}H_{46}N_6O_{10}$ $[M+Na]^+$: 937.3173, found: 937.3108.



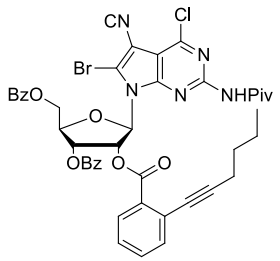
2-Fluoro-9-[2-*O*-(2-hexynylbenzoyl)-3,5-di-*O*-benzoyl-*β*-D-ribofuranosyl]adenine (**3g**)

Yield: 70%; syrup; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.04 (m, 2H), 8.00 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.96 (s, 1H), 7.84 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 2H), 7.50 – 7.36 (m, 6H), 7.21 (td, *J* = 7.8, 1.3 Hz, 1H), 6.65 (brs, 2H), 6.39 (d, *J* = 4.3 Hz, 1H), 6.26 – 6.16 (m, 2H), 4.87 (dd, *J* = 12.1, 3.1 Hz, 1H), 4.82 – 4.79 (m, 1H), 4.72 (dd, *J* = 12.1, 4.3 Hz, 1H), 2.38 (t, *J* = 7.0 Hz, 2H), 1.57 – 1.47 (m, 2H), 1.46 – 1.34 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.2, 165.4, 164.6, 160.4, 158.3, 157.4, 157.2, 151.2, 151.0, 138.9, 134.7, 133.7, 133.5, 132.4, 130.6, 129.9, 129.7, 128.8, 128.6, 128.5, 127.1, 125.3, 118.0, 117.9, 97.1, 86.7, 80.8, 79.0, 74.3, 71.2, 63.6, 30.6, 22.1, 19.5, 13.6; HRMS ($ESI^+$): *m/z* calcd for: $C_{37}H_{32}FN_5O_8$ $[M+Na]^+$: 700.2183, found: 700.2179.




2-Chloro-9-[2-*O*-(2-hexynylbenzoyl)-3,5-di-*O*-benzoyl-*β*-D-ribofuranosyl]adenine (**3h**)

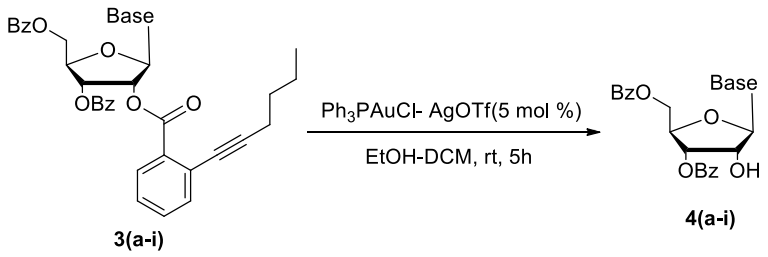
Yield: 73%; white solid; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.04 (m, 2H), 8.03 – 7.99 (m, 2H), 7.96 (s, 1H), 7.89 – 7.82 (m, 1H), 7.56 (t, *J* = 7.4 Hz, 2H), 7.51 – 7.36 (m, 6H), 7.25 – 7.18 (m, 1H), 6.53 (s, 2H), 6.45 (d, *J* = 4.3 Hz, 1H), 6.21 – 6.16 (m, 2H), 4.89 (dd, *J* = 12.0, 3.2 Hz, 1H), 4.82 – 4.80 (m, 1H), 4.72 (dd, *J* = 12.0, 4.4 Hz, 1H), 2.38 (t, *J* = 7.1 Hz, 3H), 1.59 – 1.47 (m, 2H), 1.47 – 1.35 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.2, 165.5, 164.7, 156.4, 154.7, 150.9, 139.0, 134.7, 133.8, 133.5, 132.5, 130.8, 130.0, 129.8, 129.6, 129.4, 128. 9, 128.7, 128.6, 127.2, 125.5, 118.9, 97.2, 86.6, 81.1, 79.1, 74.6, 71.5, 63.8, 30.7, 22.1, 19.6, 13.7; HRMS ($ESI^+$): m/z calcd for: $C_{37}H_{32}ClN_5O_8$ $[M+Na]^+$: 716.1888 found: 716.1890.




$N^2$-pivaloyl-6-chloro-7-cyano-8-bromo-9-[2-*O*-(2-hexynylbenzoyl)-3,5-di-*O*-benzoyl-*β*-D-ribofuranosyl]pyrrolo[2,3-*d*]pyrimidine (**3i**)

Yield: 73%; white solid; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.04 (d, *J* = 7.3 Hz, 2H), 7.79 (d, *J* = 7.3 Hz, 3H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.55 –7.53 (m, 2H), 7.44 (q, *J* = 7.8 Hz, 3H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.00 – 6.96 (m, 1H), 6.64 (dd, *J* = 5.5, 1.3 Hz, 1H), 6.29 (d, *J* = 1.3 Hz, 1H), 4.90 – 4.86 (m, 2H), 4.66 (dd, *J* = 13.2, 5.8 Hz, 1H), 2.43 (t, *J* = 7.1 Hz, 2H), 1.61 – 1.54 (m, 2H), 1.50 – 1.42 (m, 2H), 1.34 (s, 9H), 0.92 (t, *J* = 7.3 Hz, 3H); $^{13}$C NMR (101 MHz, DMSO) δ 175.2, 166.0, 165.6, 164.9, 152.9, 152.5, 151.0, 134.8, 133.6, 133.4, 132.5, 130.5, 129.9, 129.7, 129.3, 128.9, 128.6, 128.4, 127.2, 125.3, 124.9, 112.7, 112.3, 102.0, 97.0, 91.0, 90.5, 79.6, 79.1, 74.4, 71.0, 62.6, 40.4, 30.7, 27.2, 22.1, 19.6, 13.7; HRMS ($ESI^+$): *m/z* calcd for: $C_{44}H_{39}BrClN_5O_8$ $[M+H]^+$: 882.1749, found: 882.1721.

## 4. General experimental procedure for 4(a-i)

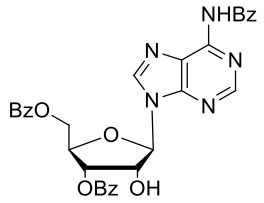



**3(a-i)** **4(a-i)**

To a solution of **3(a-i)** (0.5 mmol, 1.0 eq )in $CH_2Cl_2$ was added $H_2O$ (1.0 eq), and ethanol(6.0 eq) under argon atmosphere. The mixture was stirred at room temperature for 20 minutes. The freshly prepared solution of $Ph_3PAuOTf$ in $CH_2Cl_2$ (0.05 N, 0.5 mL) was added, and the stirring was continued at room temperature for 3 hours until **3(a-i)** was consumed as monitored by TLC. The solvent was removed under reduced pressure, the resulting residue was purified by silica gel column

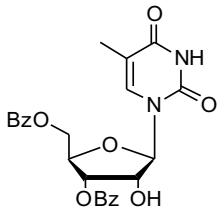
chromatography (eluted with $CH_2Cl_2$/MeOH, 50:1 to 30:1, V:V) to afford compound **4(a-i)** as solid.

## 5. Characterization data of the products




$N^6$-benzoyl-9-(3,5-di-*O*-benzoyl-*β*-D-ribofuranosyl)adenine (**4a**)

Yield: 96%; Solid; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.36 (s, 1H), 8.06 (d, *J* = 7.8 Hz, 2H), 7.94 (t, *J* = 7.2 Hz, 4H), 7.59 – 7.37 (m, 7H), 7.33 (t, *J* = 7.7 Hz, 2H), 6.21 (d, *J* = 5.9 Hz, 1H), 5.87 – 5.71 (m, 1H), 5.33 – 5.29 (m, 1H), 4.76 (dd, *J* = 11.8, 3.2 Hz, 1H), 4.70 – 4.69 (m, 1H), 4.61 (dd, *J* = 11.9, 4.1 Hz, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ 166.2, 165.9, 165.2, 152.2, 151.3, 149.1, 142.2, 133.6, 133.4, 133.3, 132.9, 129.8, 129.6, 129.3, 129.0, 128.8, 128.5, 128.0, 122.5, 89.4, 81.0, 73.5, 73.2, 63.8; HRMS (ESI$^+$): *m/z* calcd for: $C_{31}H_{25}N_5O_7$ $[M+H]^+$:580.1832, found: 580.1821.

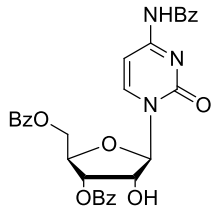



N-(3,5-di-*O*-benzoyl-*β*-D-ribofuranosyl)thymine (**4b**)

Yield: 95%; Solid; $^1$H NMR (400 MHz, $CDCl_3$): δ 10.56 (s, 1H), 8.15 (d, *J* = 7.8 Hz, 2H), 8.06 (d, *J* = 7.8 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.24 (s, 1H), 6.28 (d, *J* = 6.1 Hz, 1H), 5.56 – 5.44 (m, 1H), 4.80 (d, *J* = 11.3 Hz, 1H), 4.68 – 4.51 (m, 3H), 1.44 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ 166.1, 164.2, 151.3, 134.6, 133.7, 133.6, 130.1, 129.6, 129.1, 128.9, 128.8, 128.4, 111.8, 88.2, 80.7, 74.1, 72.7, 63.9, 12.1; HRMS (ESI$^+$): *m/z* calcd for: $C_{24}H_{22}N_2O_8$ $[M+Na]^+$: 489.1274, found: 489.1278.

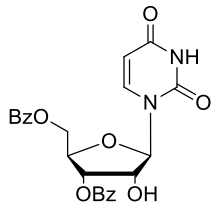


1



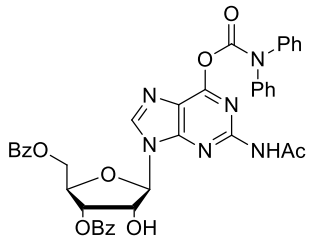

$N^4$-benzoyl-(3,5-tri-*O*-benzoyl-*β*-D-ribofuranosyl)cytosine (**4d**)

Yield: 97%; Solid; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.22 (brs, 1H), 8.12 (d, *J* = 7.5 Hz, 1H), 8.08 – 8.03 (m, 2H), 7.97 (m, 2H), 7.93 – 7.88 (m, 2H), 7.59 – 7.52 (m, 3H), 7.50 – 7.38 (m, 7H), 6.02 (d, *J* = 4.0 Hz, 1H), 5.48 (t, *J* = 5.3 Hz, 1H), 4.84 – 4.76 (m, 2H), 4.70 (dd, *J* = 5.3, 4.3 Hz, 1H), 4.64 (dd, *J* = 12.1, 3.3 Hz, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.1, 165.8, 162.6, 155.8, 144.0, 133.7, 133.6, 133.3, 132.8, 130.0, 129.6, 129.1, 129.0, 128.7, 128.5, 127.9, 97.2, 93.0, 81.2, 75.1, 72.7, 63.4; HRMS ($ESI^+$): *m/z* calcd for: $C_{30}H_{25}N_3O_8$ $[M+H]^+$: 578.1539, found: 578.1556.



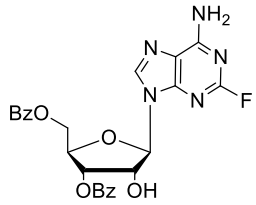

N-(3,5-di-*O*-benzoyl-*β*-D-ribofuranosyl)uracil (**4e**)

Yield: 96%; Solid; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.40 (s, 1H), 8.09 (d, *J* = 7.5 Hz, 2H), 8.02 (d, *J* = 7.5 Hz, 2H), 7.59 – 7.51 (m, 3H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 6.10 (d, *J* = 4.4 Hz, 1H), 5.46 (d, *J* = 8.0 Hz, 1H), 5.39 (t, *J* = 5.2 Hz, 1H), 4.76 (dd, *J* = 13.3, 3.7 Hz, 1H), 4.67 – 4.62 (m, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.1, 165.8, 162.6, 155.8, 144.0, 133.7, 133.6, 133.3, 132. 8, 123.0, 129.6, 129.1, 129.0, 128.7, 128.5, 127.9, 97.2, 93.0, 81.2, 75.1, 72.7, 63.4; HRMS ($ESI^+$): *m/z* calcd for: $C_{23}H_{20}N_2O_8$ $[M+H]^+$:453.1298, found: 453.1302.



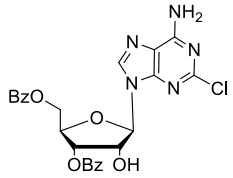

2-Acetamido-6-diphenylcarbamate-9-(3,5-di-*O*-benzoyl-*β*-D-ribofuranosyl)guanine (**4f**)

Yield: 93%; Solid; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.11 – 8.10 (m, 3H), 7.74 (d, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.50 – 7.20 (m, 12H), 7.16 (t, *J* = 7.6 Hz, 2H), 6.06 (d, *J* = 6.0 Hz, 1H), 5.77 (d, *J* = 5.2 Hz, 1H), 5.14 (t, *J* = 5.7 Hz, 1H), 4.74 – 4.71 (m, 2H), 4.54 (d, *J* = 8.4 Hz, 1H), 2.09 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 168.4, 165.5, 165.4, 155.5, 153.1, 150.8, 149.9, 142.1, 141.1, 132.9, 132.8, 129.5, 128.9, 128.7, 128.5, 127.9, 127.8, 120.4, 91.0, 82.6, 74.2, 74.1, 63.3, 24.3; HRMS ($ESI^+$): *m/z* calcd for: $C_{39}H_{34}N_6O_9[M+Na]^+$:753.2285, found: 753.2290.




2-Fluoro-9-(3,5-di-*O*-benzoyl-*β*-D-ribofuranosyl)adenine (**4g**)

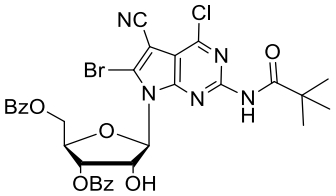
Yield: 93%; Solid; $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ 8.37 (s, 1H), 8.11 (d, *J* = 7.2 Hz, 2H), 8.01 (d, *J* = 7.2 Hz, 2H), 7.95 (brs, 2H), 7.73 – 7.66 (m, 2H), 2H), 7.59 (t, *J* = 7.7 Hz, 2H), 7.52 (t, *J* = 7.7 Hz, 2H), 6.11 (d, *J* = 6.1 Hz, 1H), 6.02 (d, *J* = 6.1 Hz, 1H), 5.71 (d, *J* = 5.5 Hz, 1H), 5.18 (q, *J* = 6.0 Hz, 1H), 4.74 – 4.59 (m, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 166.0, 165.5, 160.2, 158.3, 158.1, 151.2, 151.01, 140.8, 134.1, 134.0, 130.0, 129.8, 129.8, 129.2, 118.2, 88.2, 79.8, 73.4, 71.5, 64.4; HRMS ($ESI^+$): *m/z* calcd for: $C_{24}H_{20}FN_5O_6$ $[M+H]^+$:494.1476, found: 494.1465.




2-Chloro-9-(3,5-di-*O*-benzoyl-*β*-D-ribofuranosyl)adenine (**4h**)

Yield: 95%; Solid; $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ 8.39 (s, 1H), 8.14 – 8.08 (m, 2H), 8.00 – 7.95 (m, 2H), 7.91 (brs, 2H), 7.74 – 7.64 (m, 2H), 7.57 (t, *J* = 7.7 Hz, 2H), 7.51 (t, *J* = 7.8 Hz, 2H), 6.11 (d, *J* = 6.2 Hz, 1H), 6.02 (d, *J* = 6.1 Hz, 1H), 5.69 (dd, *J* = 5.6, 3.4 Hz, 1H), 5.12 (q, *J* = 6.0 Hz, 1H), 4.73 – 4.58 (m, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 165.5, 165.0, 156.9, 153.3, 150.4, 140.2, 140.1, 133.6, 133.5, 129.6,

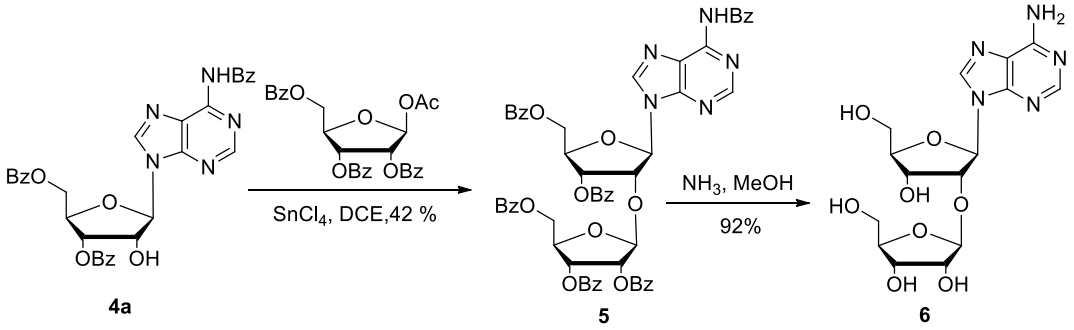
129.4, 129.3, 128.8, 128.7, 118.3, 87.6, 79.4, 73.0, 71.3, 64.0, 54.9; HRMS ($ESI^+$): *m/z* calcd for: $C_{24}H_{20}ClN_5O_6$ $[M+H]^+$:510.1180, found: 510.1182.




$N^2$-pivaloyl-6-chloro-7-cyano-8-bromo-9-(3,5-di-*O*-benzoyl-*β*-D-ribofuranosyl)pyrrolo[2,3-*d*]pyrimidine (**4i**)

Yield: 94%; Solid; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.08 (d, *J* = 7.3 Hz, 2H), 7.80 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.31– 7.27 (m, 2H), 6.08 – 6.05 (m, 2H), 5.90 (t, *J* = 5.4 Hz, 1H), 4.74 – 4.65 (m, 2H), 4.60 – 4.56 (m, 1H), 1.29 (s, 9H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 176.2, 166.0, 165.8, 152.1, 152.0, 151.0, 133.6, 133.3, 129.9, 129.4, 129.3, 129.2, 128.5, 128.3, 125.9, 112.6, 112.2, 91.2, 91.0, 80.7, 73.8, 71.5, 63.3, 40.5, 27.2; HRMS ($ESI^+$): *m/z* calcd for: $C_{31}H_{27}BrClN_5O_7$ $[M+Na]^+$:720.0662, found: 720.0675.

## 6 Synthesis of 2′ -O-β-D- ribofuranosylnucleoside




### 6.1 Synthesis of $N^6$-benzoyl-9-[3,5-di-*O*-benzoyl-2-*O*-(2,3,5-tri-*O*-benzoyl-*β*-D-ribofuranosyl)- *β*-D-ribofuranosyl]adenine (5)

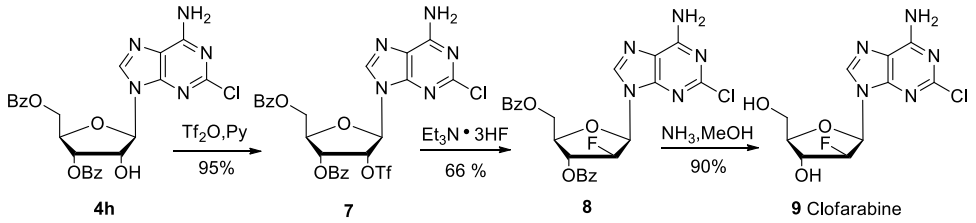
1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose (242 mg, 0.48 mmol) and **4a** (232 mg, 0.4 mmol) were dissolved in 1,2-dichloroethane (15 mL). The reaction mixture was stirred at 0 °C under $N_2$ atmosphere. Subsequently, the solution of tin tetrachloride (156 mg, 0.60 mmol) was added in one portion. After 7 hour at 0°C, the reaction mixture was diluted with saturated *aq.* $NaHCO_3$(30 mL) and extracted with $CH_2Cl_2$ (2 × 20 mL). The combined organic layers were washed with saturated *sat*. aq

$NaHCO_3$ (2 × 30 mL) and brine (2 × 30 mL), and dried ($Na_2SO_4$), filtered, and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (eluted with $CH_2Cl_2$) to afford white solid **5** (172 mg, 42%). $^1$H NMR (400 MHz, $CDCl_3$) δ 9.26 (brs, 1H), 8.66 (s, 1H), 8.14 (s, 1H), 8.03 – 7.79 (m, 6H), 7.92 (d, *J* = 7.3 Hz, 2H), 7.83 – 7.74 (m, 4H), 7.57 – 7.28 (m, 17H), 7.25-7.24 (m, 1H), 6.24 (d, *J* = 4.4 Hz, 1H), 5.93 (t, *J* = 5.8 Hz, 1H), 5.69 (t, *J* = 5.1 Hz, 1H), 5.58 – 5.51 (m, 2H), 5.43-5.42 (m, 1H), 4.79 – 4.74 (m, 1H), 4.60 – 4.47 (m, 3H), 4.49 (dd, *J* = 11.9, 3.8 Hz, 1H), 4.14 (dd, *J* = 12.0, 4.4 Hz, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.1, 166.0, 165.9, 165.2, 164.7, 152.9, 151.4, 149.3, 142.7, 133.8, 133.6, 133.5, 133.4, 132.7, 129.9, 129.8, 129.7, 129.6, 129.4, 129.3, 128.8, 128.7, 128.6, 128.5, 128.4, 128.0, 123.7, 106.8, 88.8, 80.6, 79.8, 78.6, 75.2, 72.2, 71.3, 64.3, 63.2, 60.4; HRMS ($ESI^+$): *m/z* calcd for: $C_{57}H_{45}N_5O_{14}$ $[M+H]^+$:1024.3041, found: 1024.3058.

**6.2 Synthesis of 9-(2-*O*-*β*-D-ribofuranosyl-*β*-D-ribofuranosyl)adenine (6)**

A solution of 5 (200 mg, 0.2 mmol) in methanolic ammonia (MeOH saturated with $NH_3$ at 0°C, 10mL) was placed in an autoclave and stirred at 40 0°C for 12h. The reaction mixture was concentrated to dryness and the residue was extracted with $CH_2Cl_2$ (10 mL) and water (10 mL). The aqueous layers were washed with $CH_2Cl_2$ (2 × 10 mL) and concentrated in *vacuo*. The residue was purified by Sephadex LH-20 column chromatography (eluted with MeOH) to afford white solid **6** (72 mg, 92%). $[a]_{20}^{D}$ -95°(c 0.50, DMSO); $^1$H NMR (400 MHz, $D_2O$) δ 8.26 (s, 1H), 8.11 (s, 1H), 6.06 (d, *J* = 6.3 Hz, 1H), 5.02 (s, 1H), 4.71 (t, *J* = 5.7 Hz, 1H), 4.51 (dd, *J* = 5.0, 3.4 Hz, 1H), 4.27 – 4.24 (m, 1H), 4.10 (d, *J* = 4.5 Hz, 1H), 3.96 (dd, *J* = 7.4, 4.6 Hz, 1H), 3.90 (dd, *J* = 12.9, 2.6 Hz, 1H), 3.85 – 3.75 (m, 2H), 3.29 (dd, *J* = 12.0, 3.6 Hz, 1H), 2.72 (dd, *J* = 12.0, 6.7 Hz, 1H); δ$^{13}$C NMR (101 MHz, $D_2O$) δ 156.0, 153.0, 148.6, 141.0, 119.3, 106.4, 87.4, 86.7, 83.1, 78.7, 74.7, 71.3, 69.4, 63.1, 61.8; HRMS ($ESI^+$): *m/z* calcd for: $C_{15}H_{21}N_5O_8$ $[M+H]^+$:400.1468, found: 400.1472.

## 7. Synthesis of Clofarabine




### 7.1 2-Chloro-9-(2-*O*-trifyl-3,5-di-*O*-benzoyl-*β*-D-ribofuranosyl)adenine (7)

To a solution of **4h** (1.02 g, 2.0 mmol) in dichloromethane was added dry pyridine (0.4 mL, 5.0 mmol). The mixture was cooled to -20°C and the trifluoromethanesulfonic anhydride (0.42 mL, 2.5 mmol) was added slowly via syringe. After 5 hour at -20°C, the reaction mixture was diluted with saturated *aq.* $NaHCO_3$(30 mL) and extracted with $CH_2Cl_2$ (2 × 20 mL). The combined organic layers were washed with saturated *sat*. aq $NaHCO_3$ (2 × 30 mL) and brine (2 × 30 mL), and dried ($Na_2SO_4$), filtered, and concentrated in *vacuo.* The residue was purified by silica gel column chromatography (eluted with PE/EtOAc = 2 : 1, V:V) to afford white solid **7** (1.22 g, 95%). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.5 Hz, 2H), 7.96 (d, *J* = 7.7 Hz, 3H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.39 (t, *J* = 7.7 Hz, 2H), 6.73 (brs, 2H), 6.32 (d, *J* = 2.8 Hz, 1H), 6.31 – 6.24 (m, 1H), 6.19 – 6.17 (m, 1H), 4.86 (dd, *J* = 12.3, 3.2 Hz, 1H), 4.80 – 4.77 (m, 1H), 4.67 (dd, *J* = 12.3, 4.3 Hz, 1H); $^{13}$C NMR (101 MHz, CDCl3) *δ* 166.0, 165.0, 156.3, 154.8, 150.2, 139.2, 134.2, 133.5, 130.1, 129.6, 129.1, 128.7, 128.6, 128.0, 119.9, 119.0, 116.7, 87.1, 84.2, 79.8, 69.7, 62.6; HRMS ($ESI^+$): *m/z* calcd for: $C_{15}H_{21}N_5O_8$ $[M+H]^+$:642.0673, found: 642.0675.

### 7.2 2-Chloro-9-(2-fluoro-3,5-di-*O*-benzoyl-*β*-D-ribofuranosyl)adenine(8)

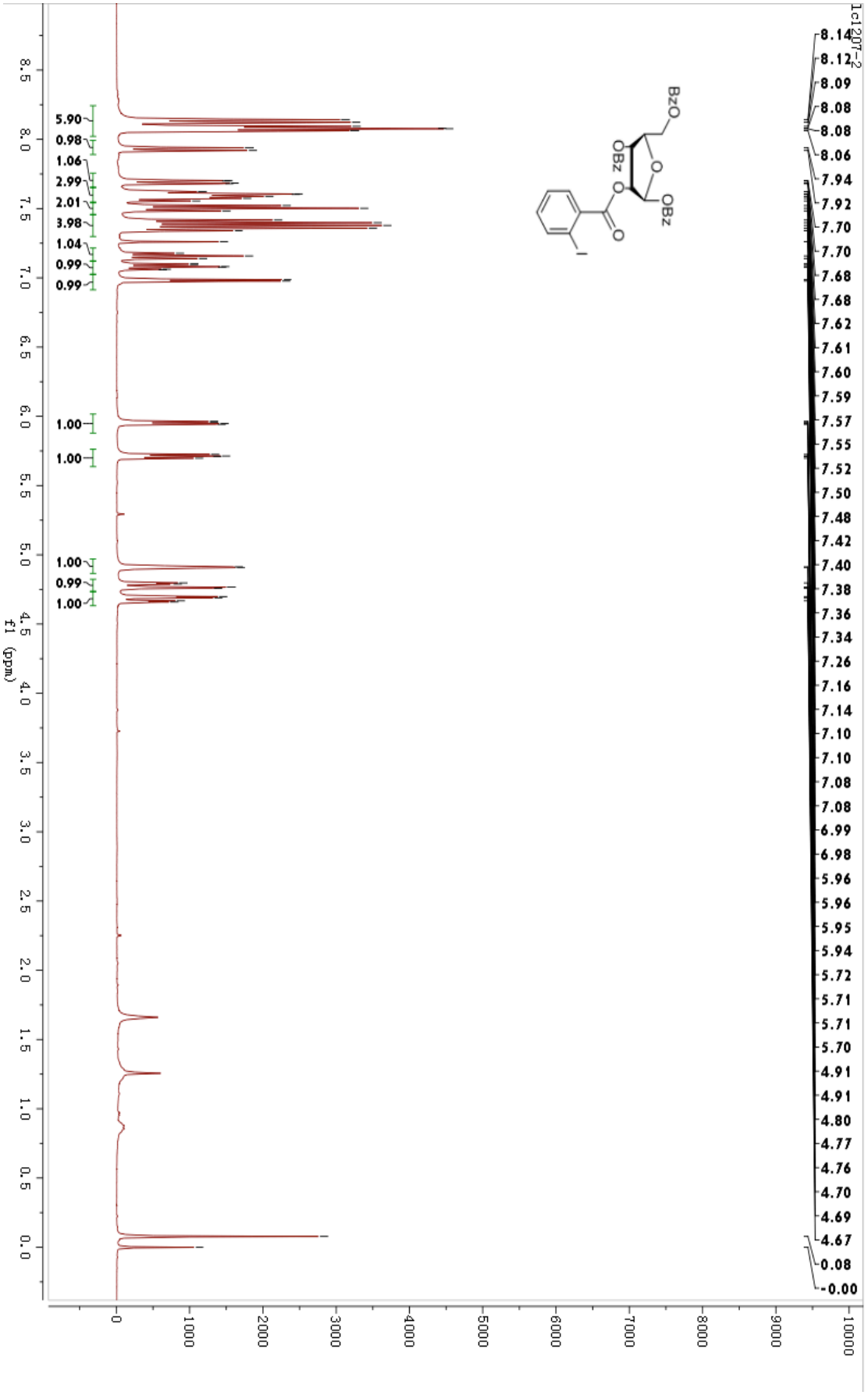
To a solution of **7** (0.90 g, 1.4 mmol) in ethyl acetate (20 mL) was added triethylamine trihydrofluoride (0.57 mL, 5.6 mmol) under $N_2$ atmosphere. The reaction mixture was heated to 70°C for 24 h. After completion of the reaction as indicated by TLC, the reaction mixture was diluted with saturated *aq.* $NaHCO_3$(30 mL) and extracted with EtOAc (2 × 20 mL). The combined organic layers were washed with saturated *sat*. aq $NaHCO_3$ (2 × 30 mL) and brine (2 × 30 mL), and dried

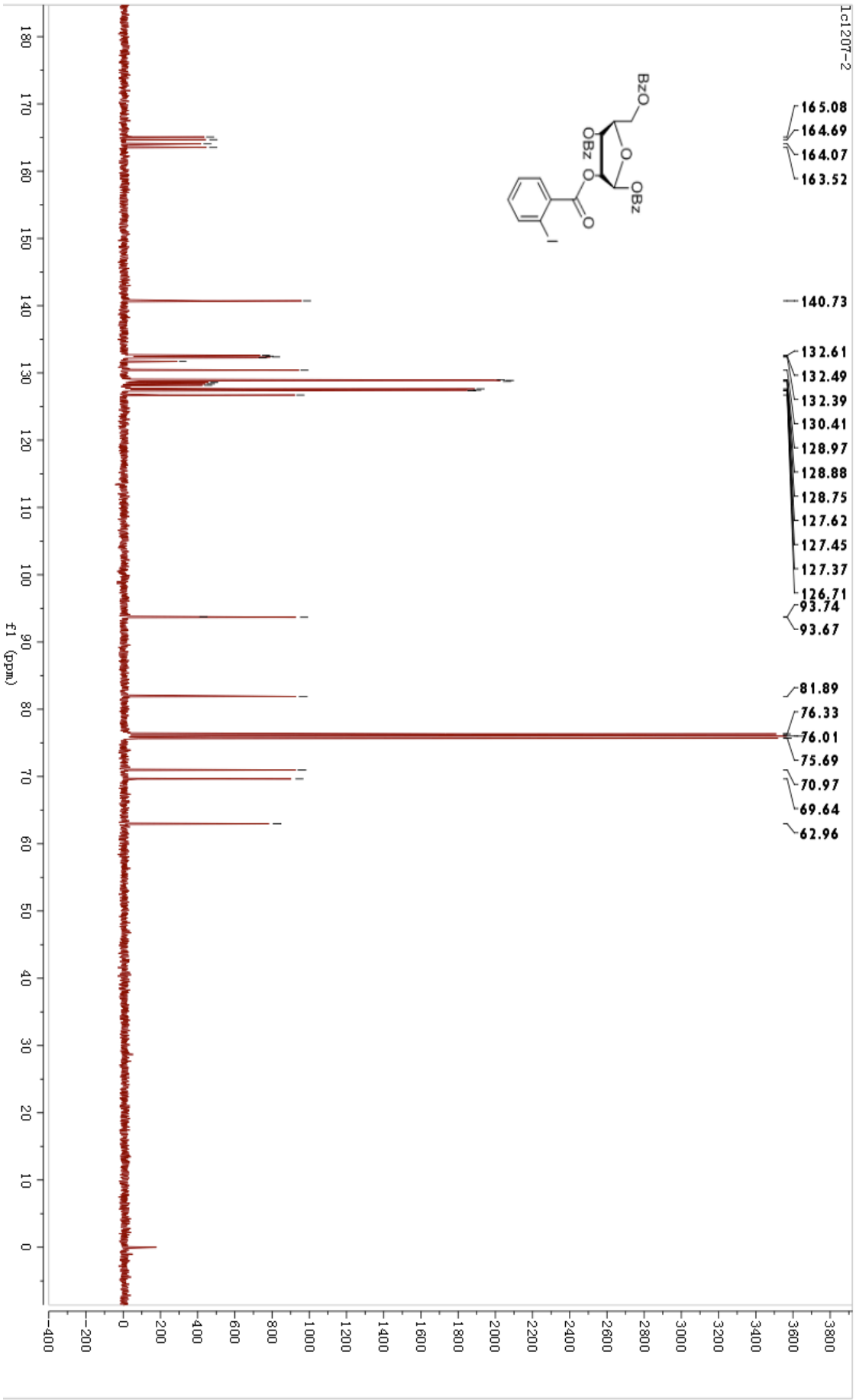
($Na_2SO_4$), filtered, and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (eluted with PE/EtOAc = 2 : 1, V:V) to afford white solid **8** (473 mg, 66%). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.03 (m, 5H), 7.66 (t, $J$ = 7.4 Hz, 1H), 7.58 (t, $J$ = 7.4 Hz, 1H), 7.52 (t, $J$ = 7.8 Hz, 2H), 7.45 (t, $J$ = 7.7 Hz, 2H), 6.58 (dd, $J_{C\text{-}F}$ = 22.4, 2.5 Hz, 1H), 6.39 (brs, 2H), 5.75 (dd, $J_{C\text{-}F}$ = 17.0, 2.6 Hz, 1H), 5.37 (dd, $J_{C\text{-}F}$ = 49.8, 2.5 Hz, 1H), 4.81 (d, $J$ = 4.5 Hz, 2H), 4.57 (dd, $J$ = 7.3, 4.3 Hz, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.2, 165.2, 156.0, 154.6, 150.5, 140.2, 140.1, 134.3, 133.5, 130.1, 129.8, 129.4, 128.8, 128.6, 128.1, 117.3, 93.6, 91.7, 83.7, 83.6, 81.4, 77.2, 76.9, 76.6, 63.3; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -197.8; HRMS ($ESI^+$): *m/z* calcd for: $C_{24}H_{19}ClFN_5O_5$ $[M+Na]^+$:534.0956, found: 534.0953.

### 7.3 Synthesis of Clofarabine (9)

A solution of **8** (307 mg, 0.6 mmol) in methanolic ammonia (MeOH saturated with $NH_3$ at 0°C, 10mL) was placed in an autoclave and stirred at 40 0°C for 6h. The reaction mixture was concentrated to dryness and the residue was purified by silica gel column chromatography (eluted with $CH_2Cl_2$/MeOH, 10:1,V:V) to afford white solid **9** (164 mg, 90%). $^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.28 (d, $J$ = 1.7 Hz, 1H), 7.90 (brs, 2H), 6.32 (dd, $J$ = 13.7, 4.6 Hz, 1H), 5.97 (d, $J$ = 5.2 Hz, 1H), 5.23 (dt, $J_{C\text{-}F}$ = 52.6, 4.3 Hz, 1H), 5.10 (t, $J$ = 5.7 Hz, 1H), 4.47 – 4.38 (m, 1H), 3.84 (q, 4.8 Hz, 1H), 3.74 – 3.56 (m, 2H); $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 157.3, 153.7, 150.6, 140.5, 117.8, 96.8, 94.9, 84.0, 83.9, 82.0, 81.8, 73.1, 72.9, 60.8; $^{19}$F NMR (376 MHz, DMSO-$d_6$) δ -198.1; HRMS ($ESI^+$): *m/z* calcd for: $C_{10}H_{12}ClFN_5O_3$ $[M+Na]^+$:326.0432, found: 306.0420.

## 8. 1 H and 13C NMR spectra of the products

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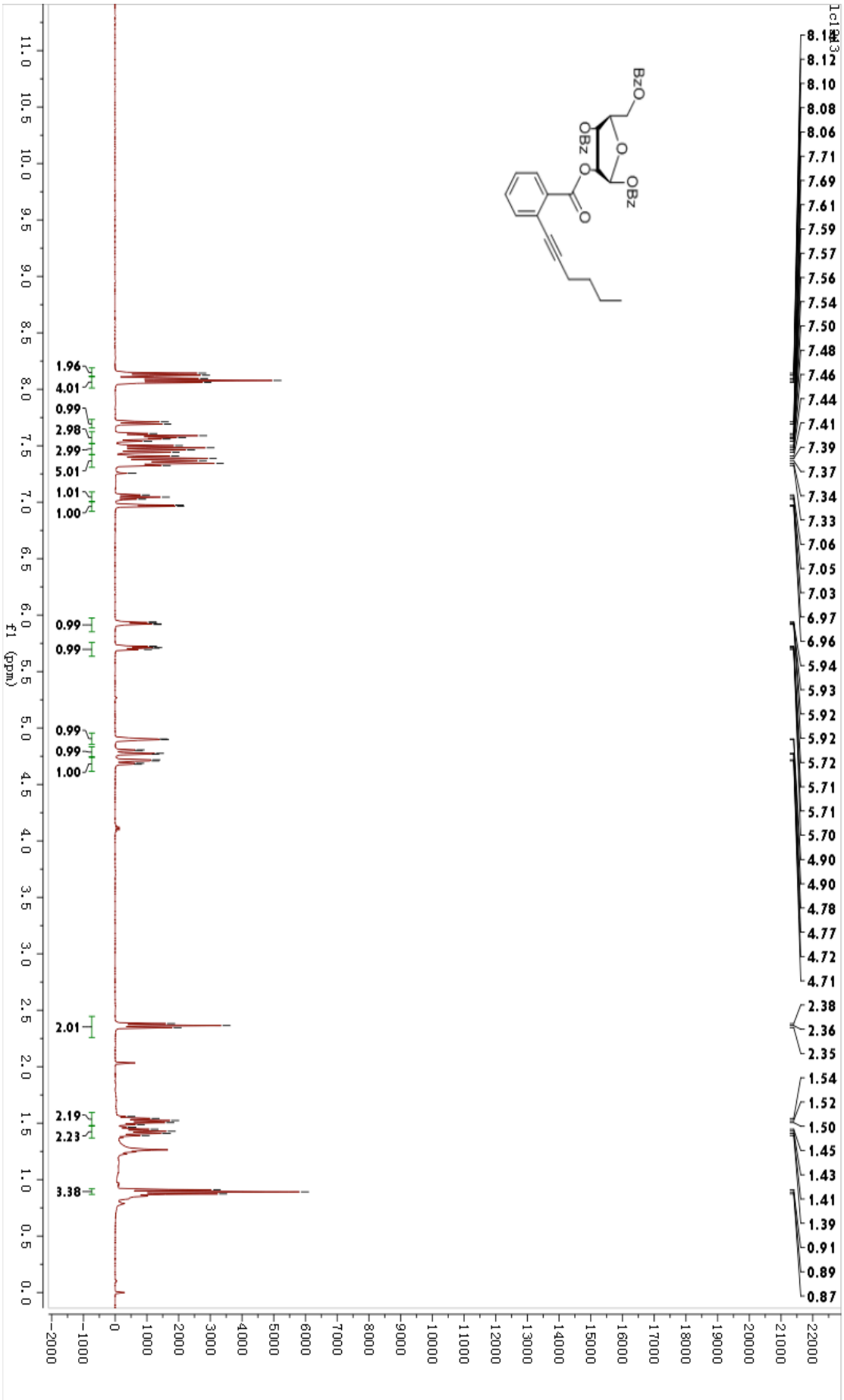
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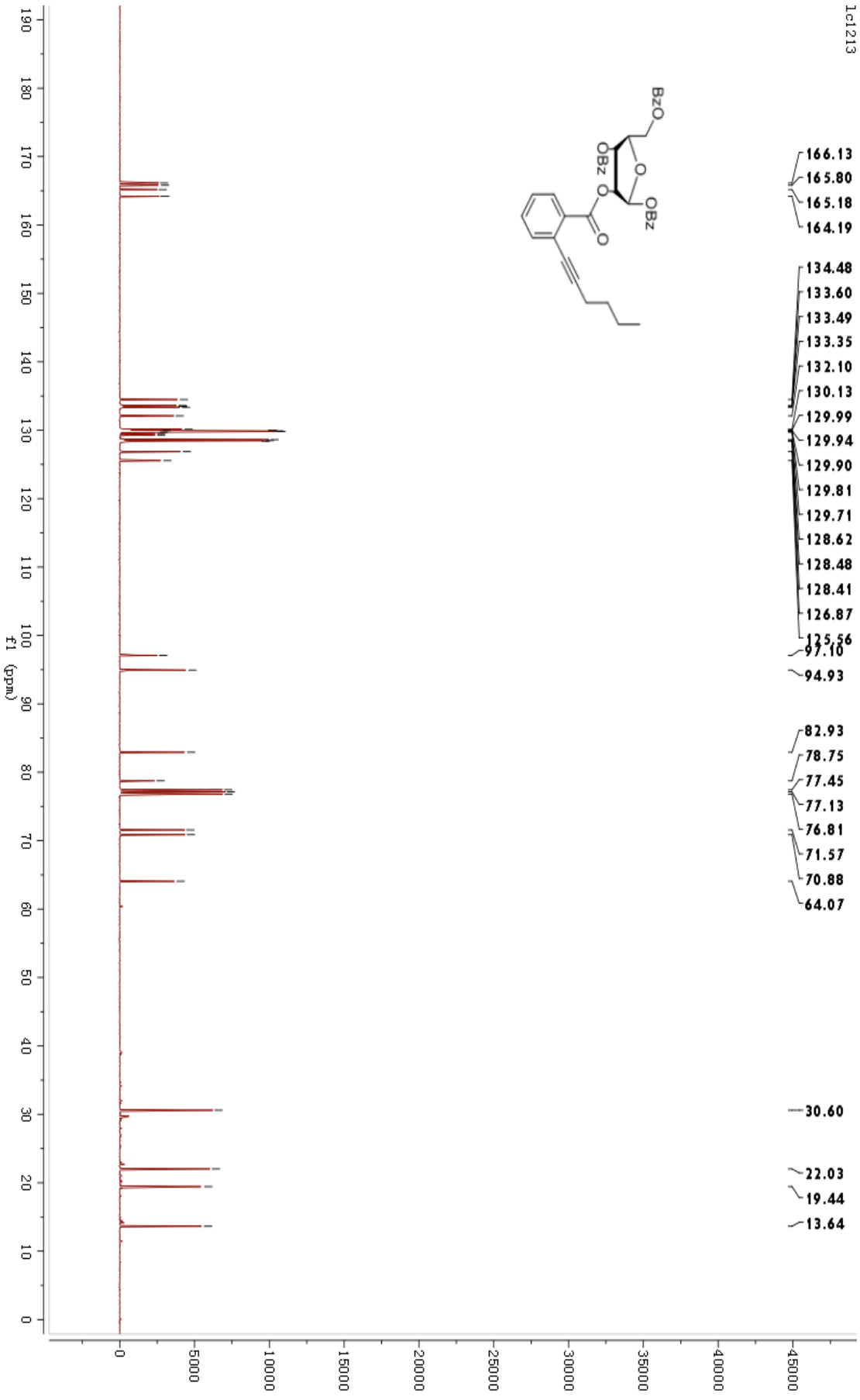
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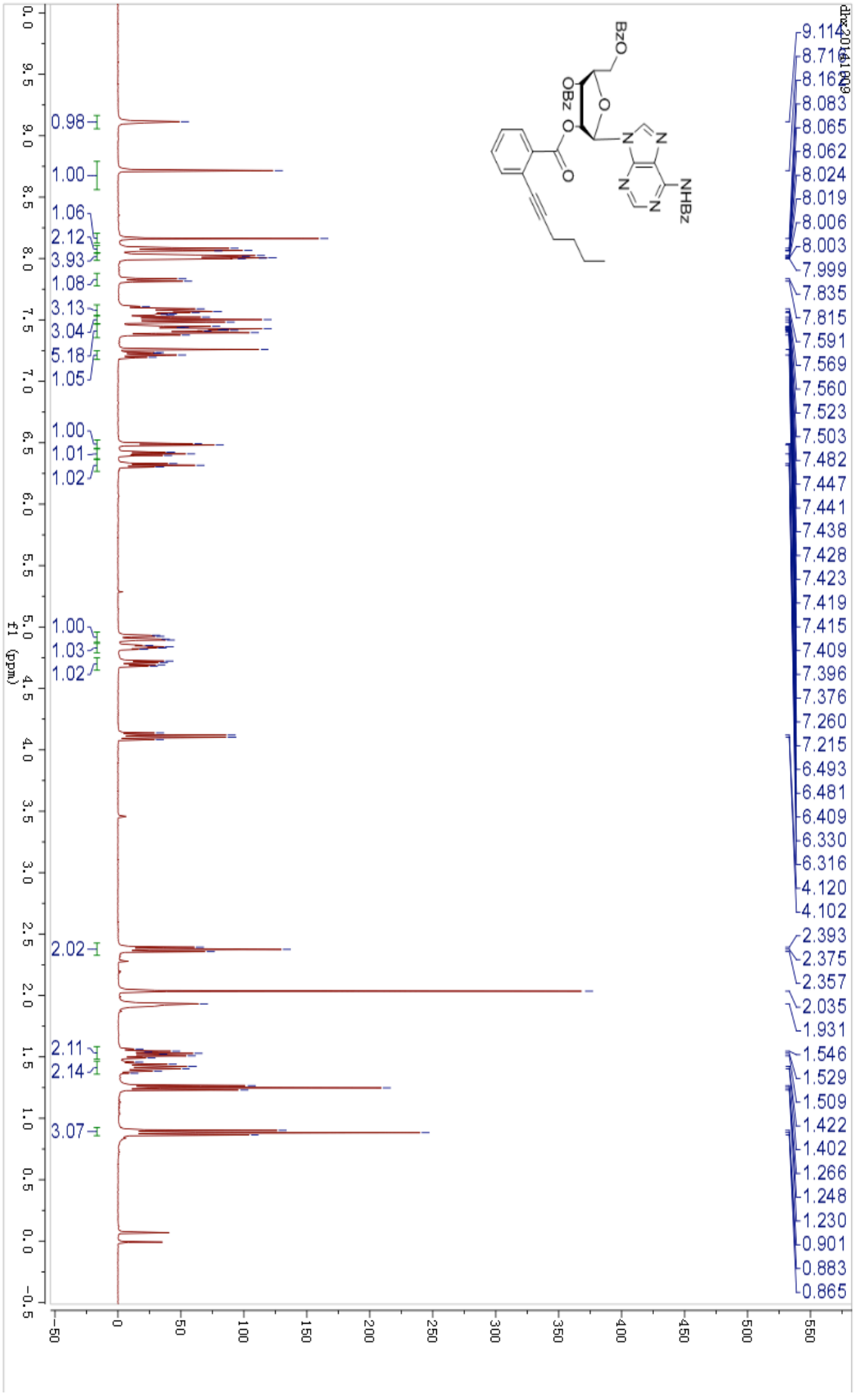
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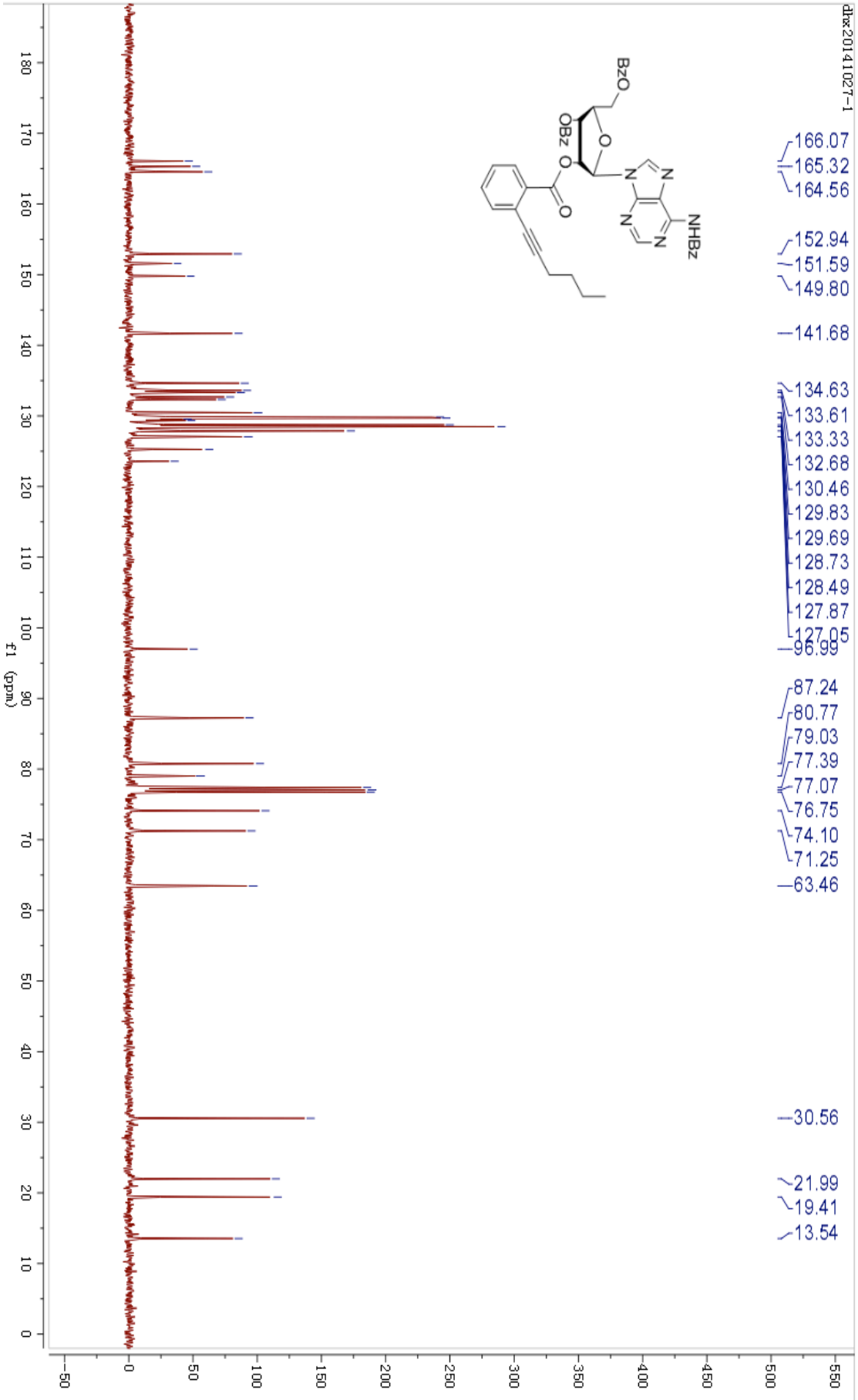
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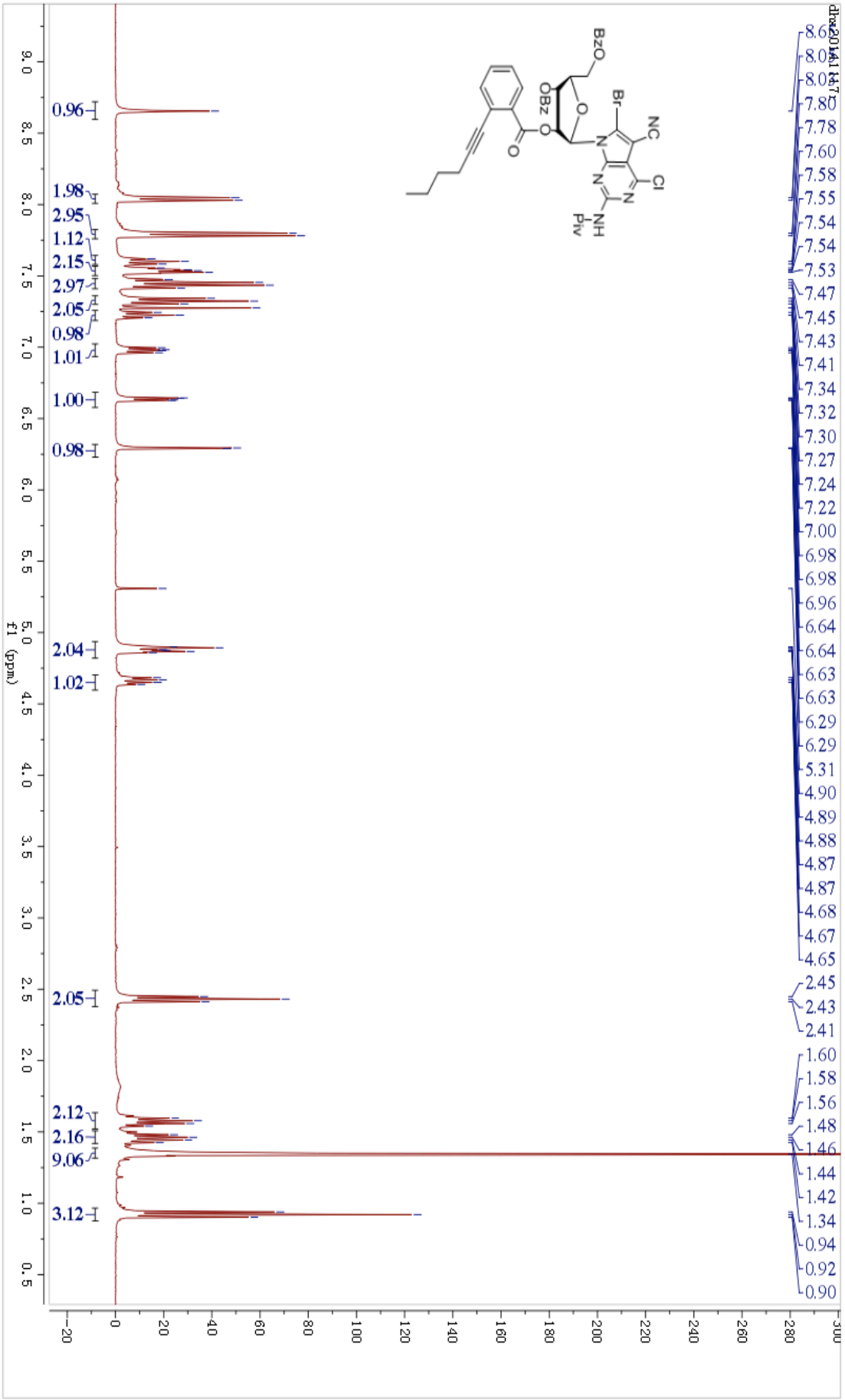
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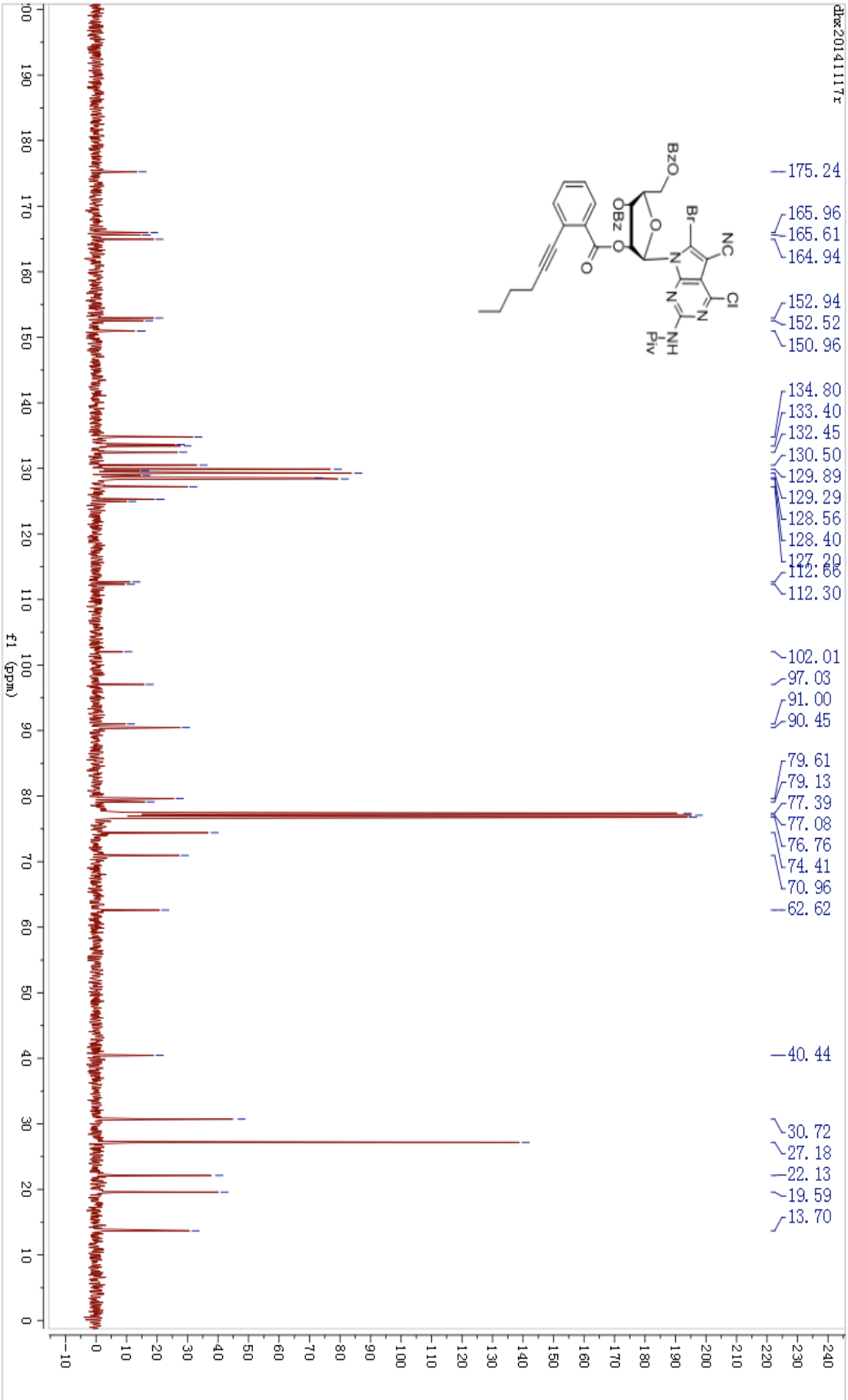
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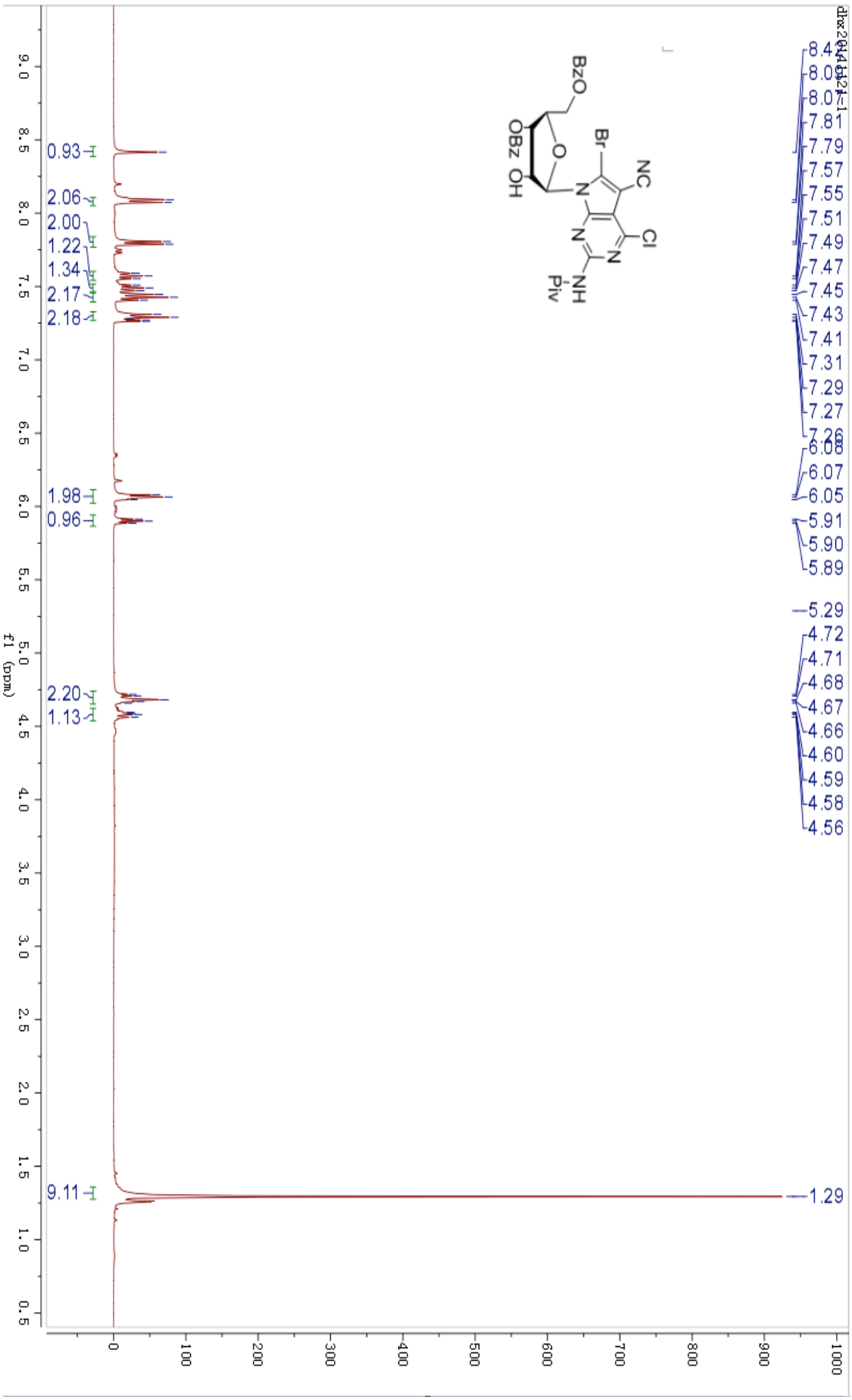
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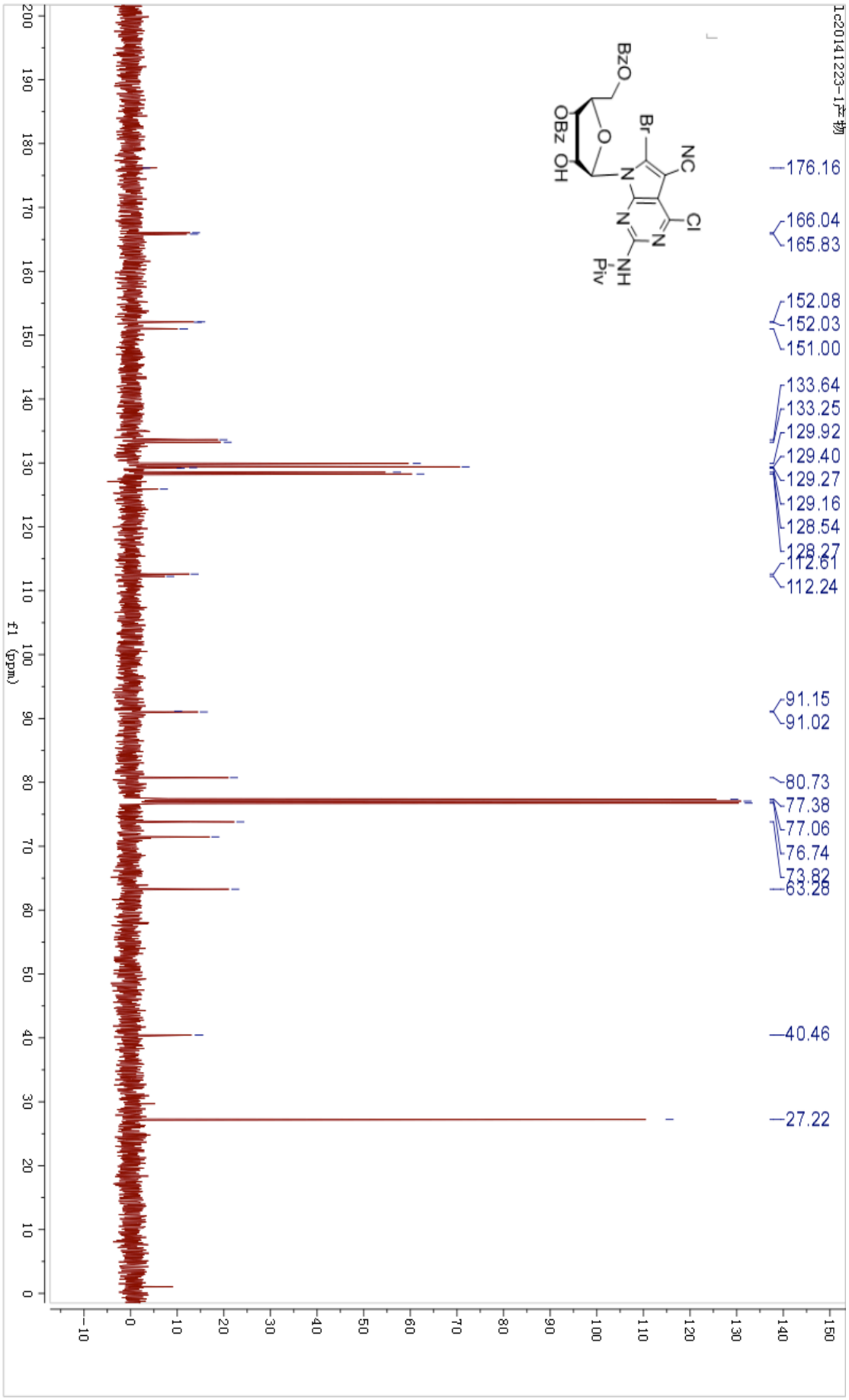
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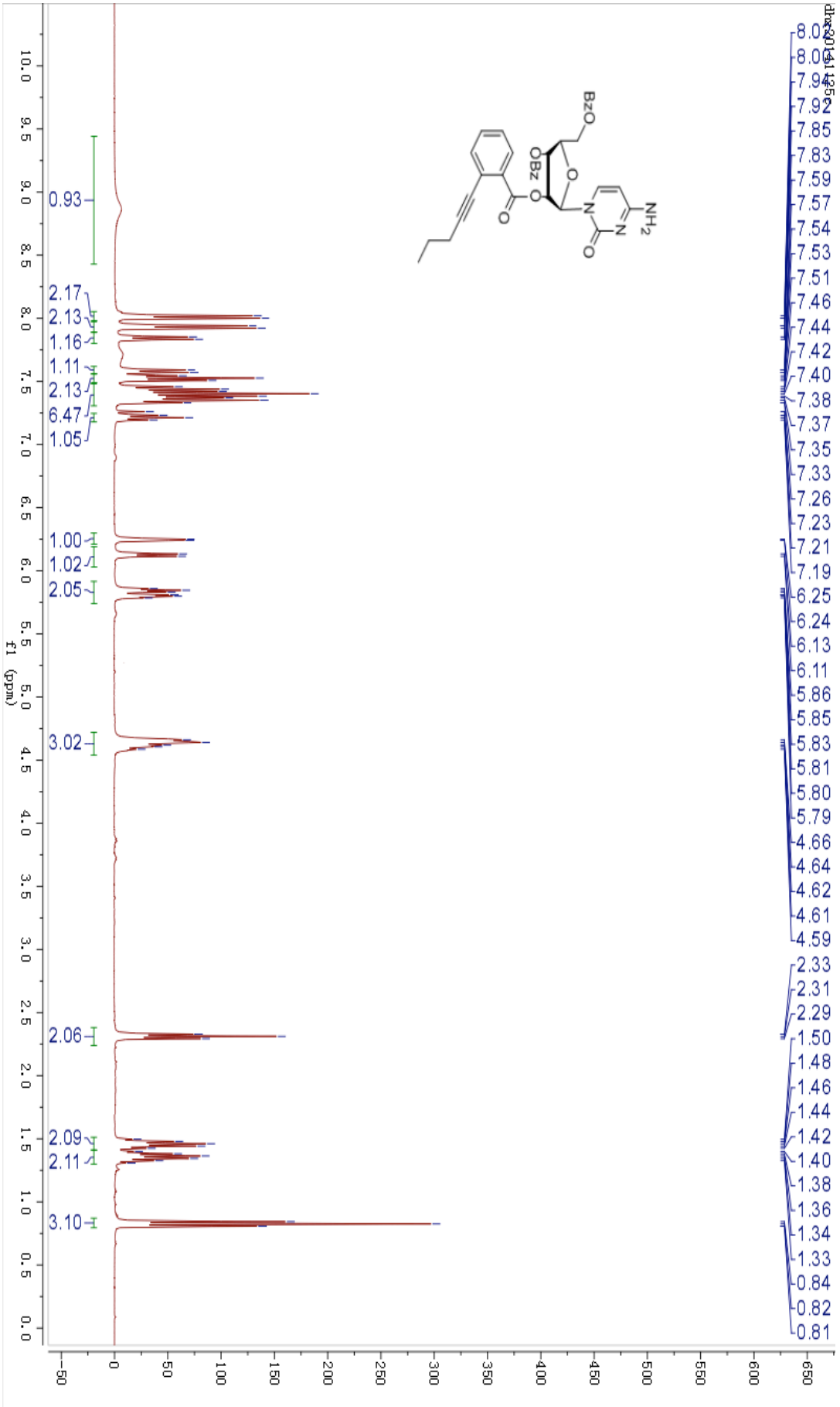
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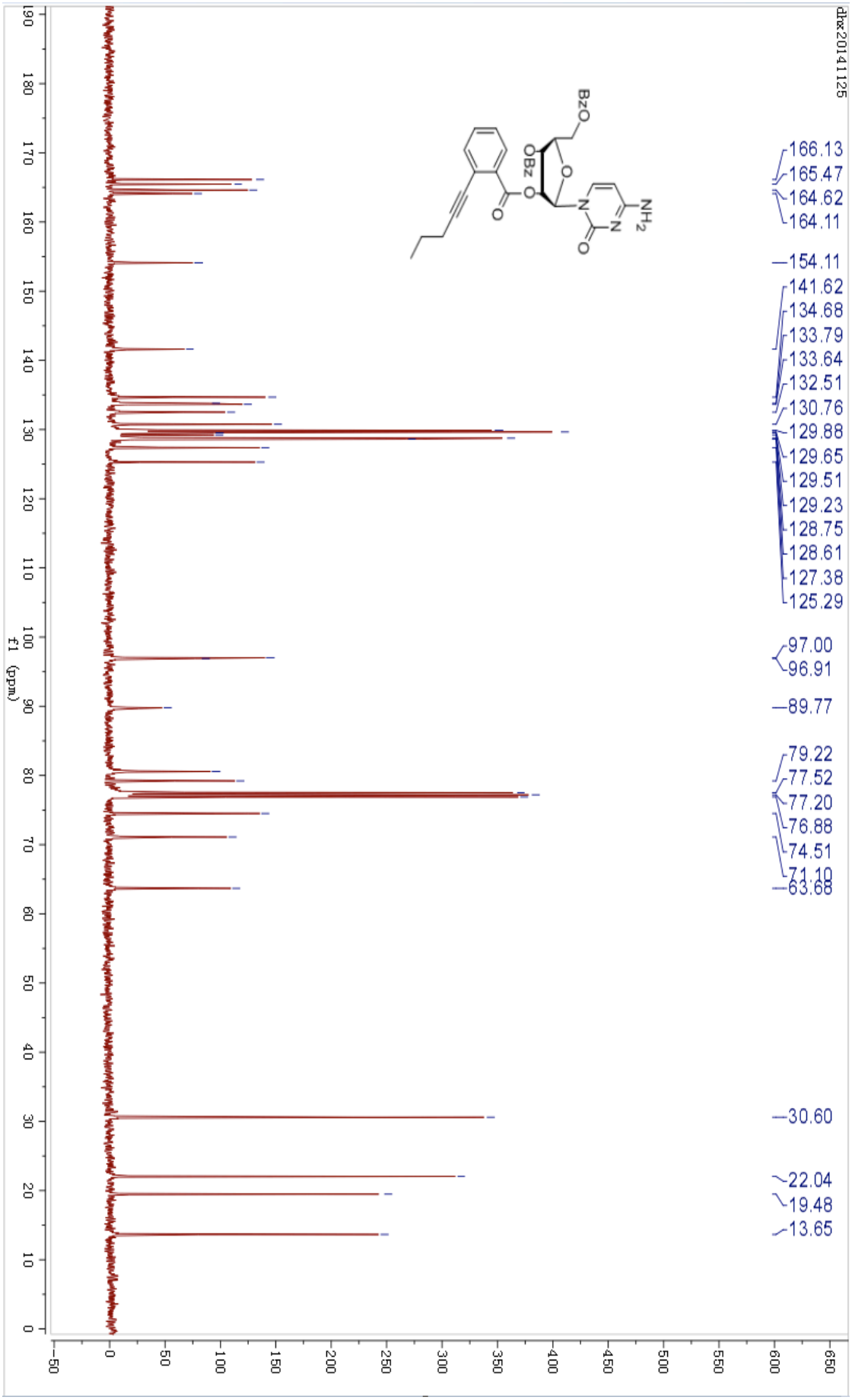
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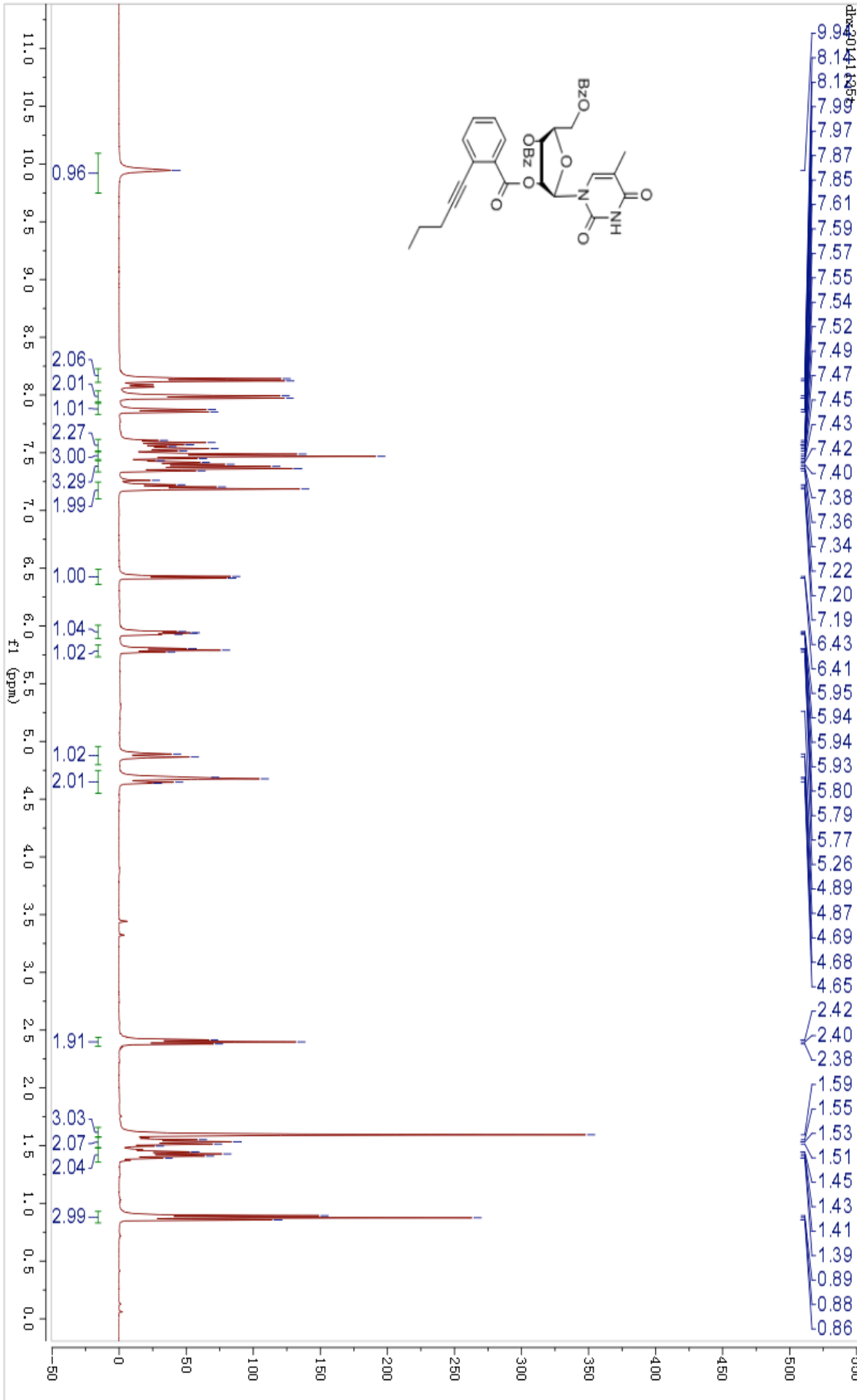
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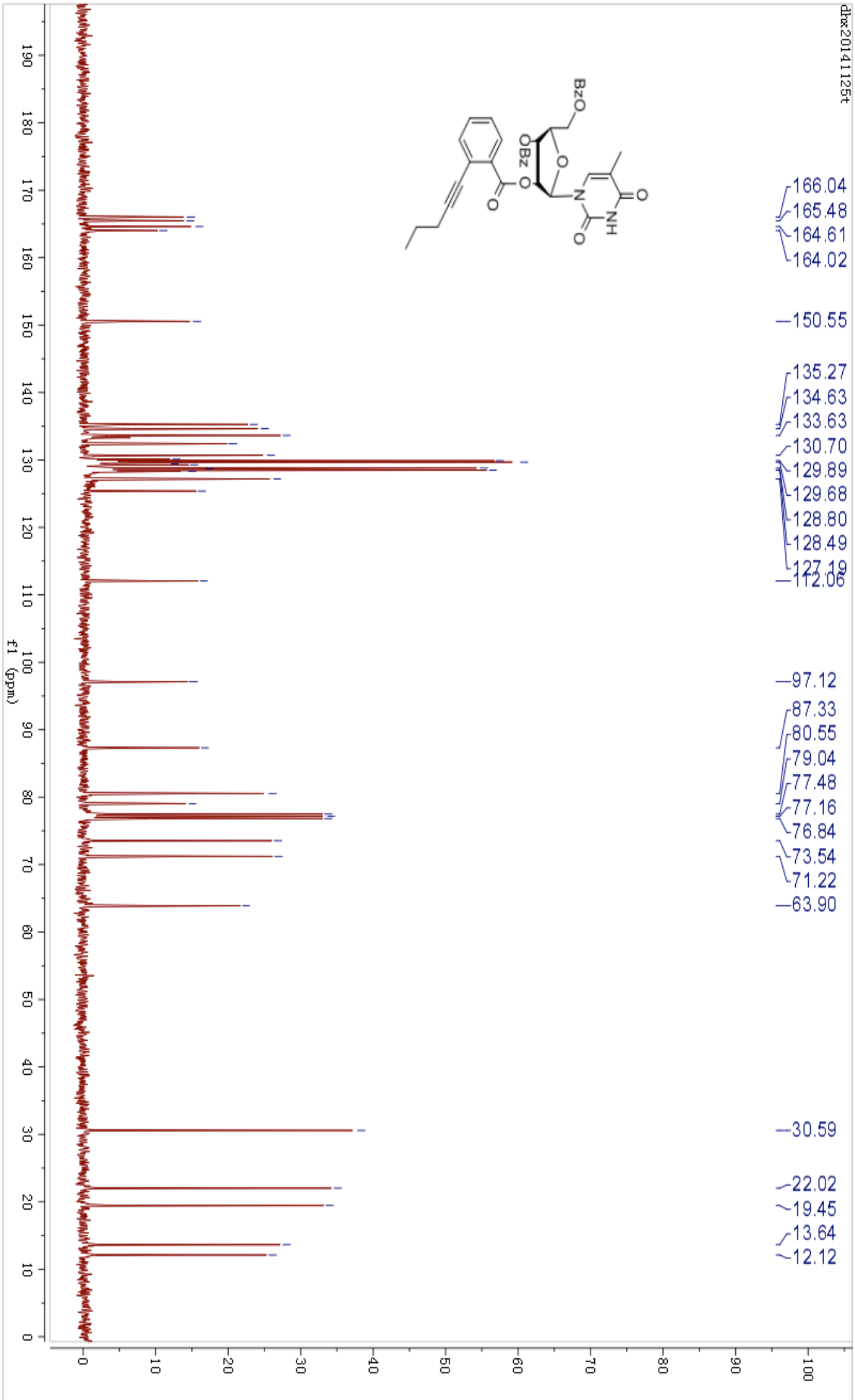
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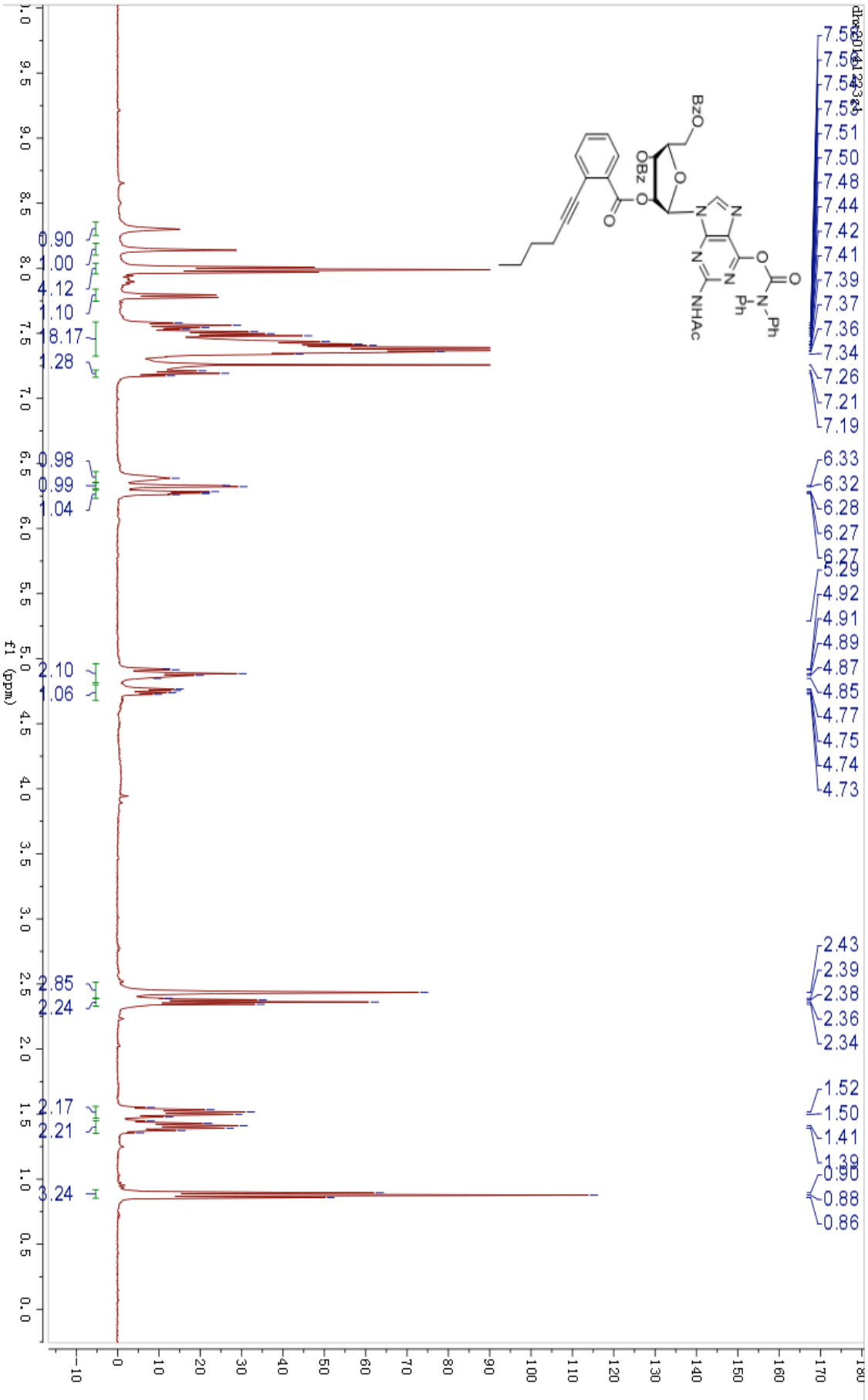
190



1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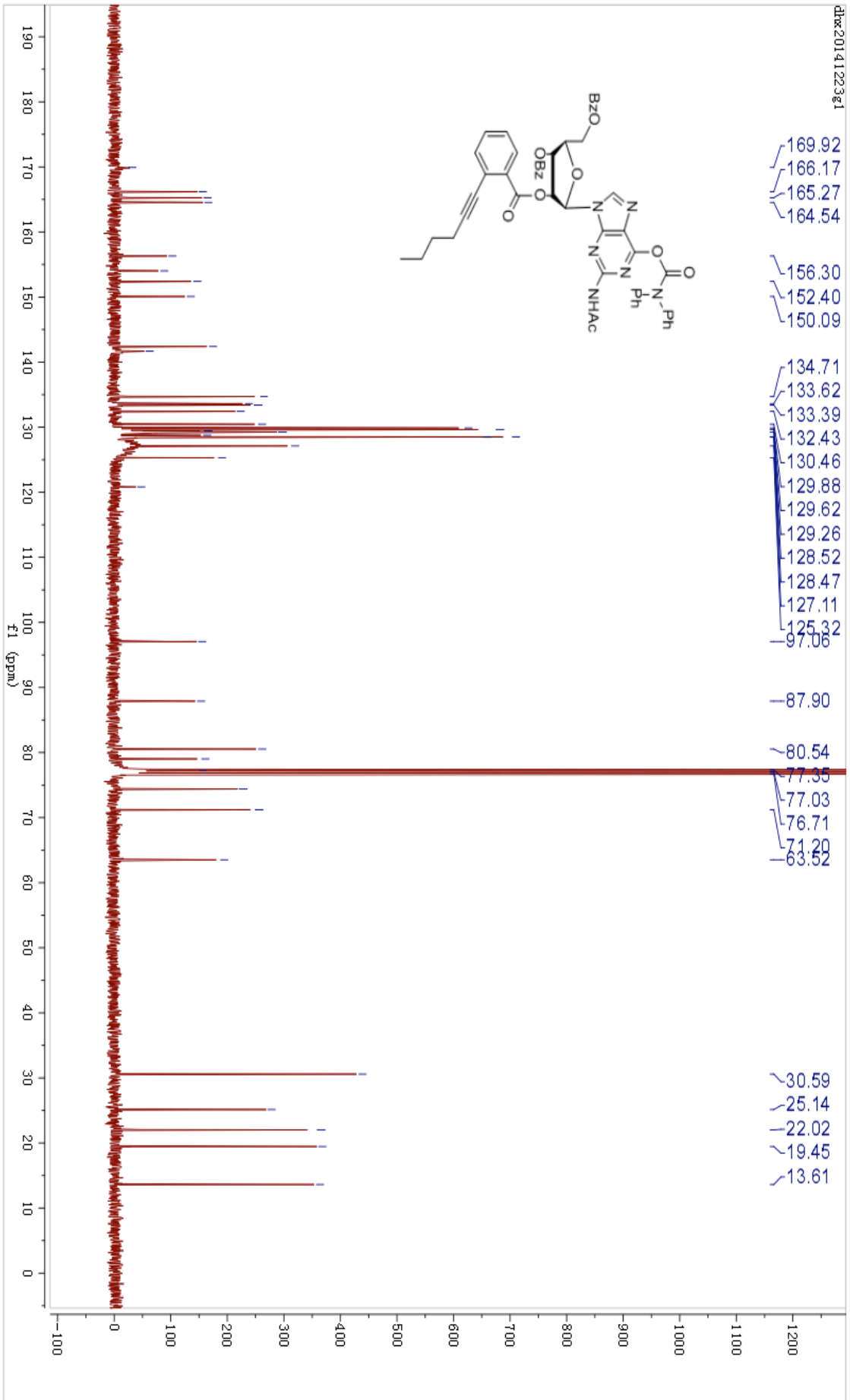
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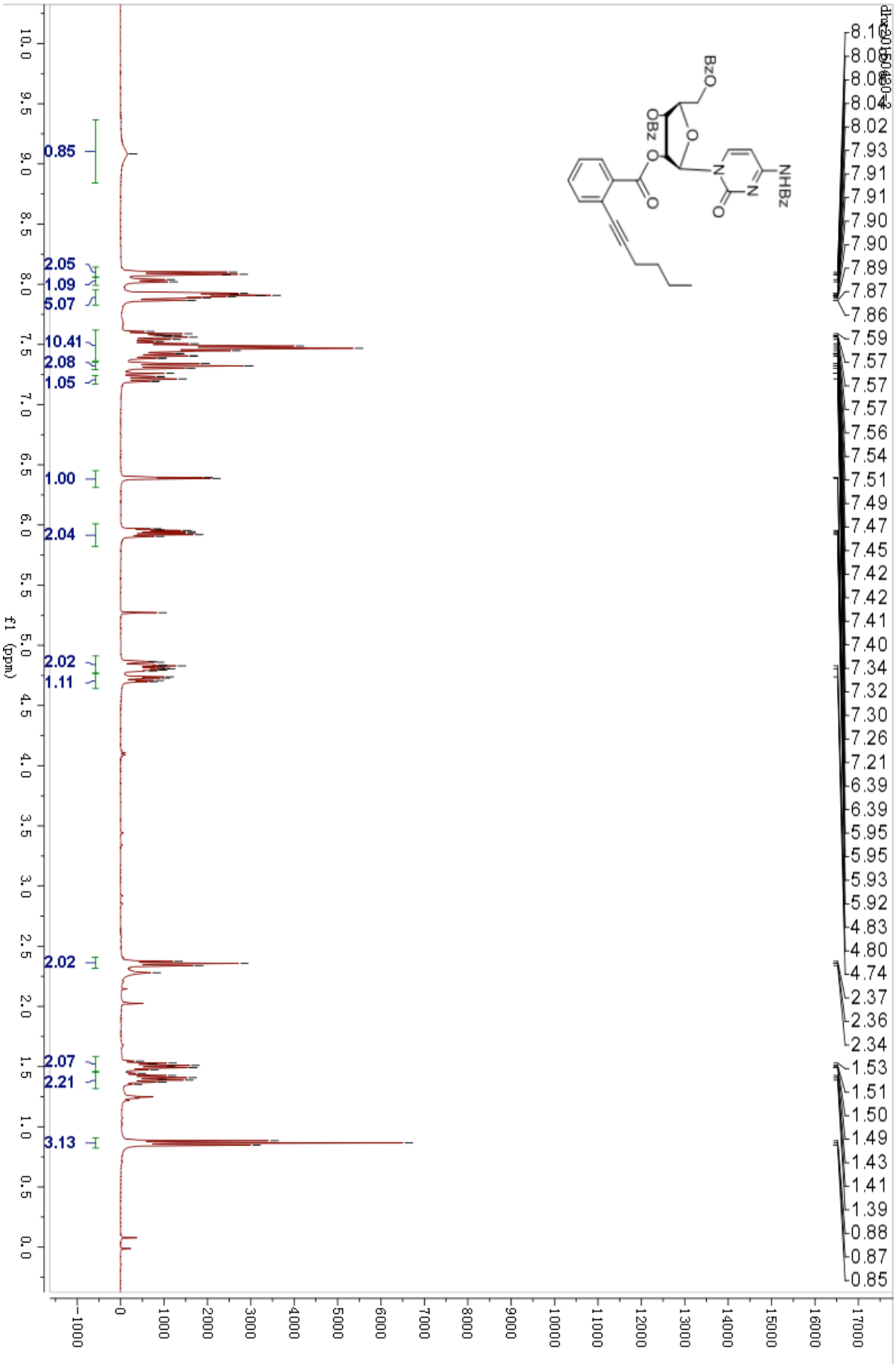
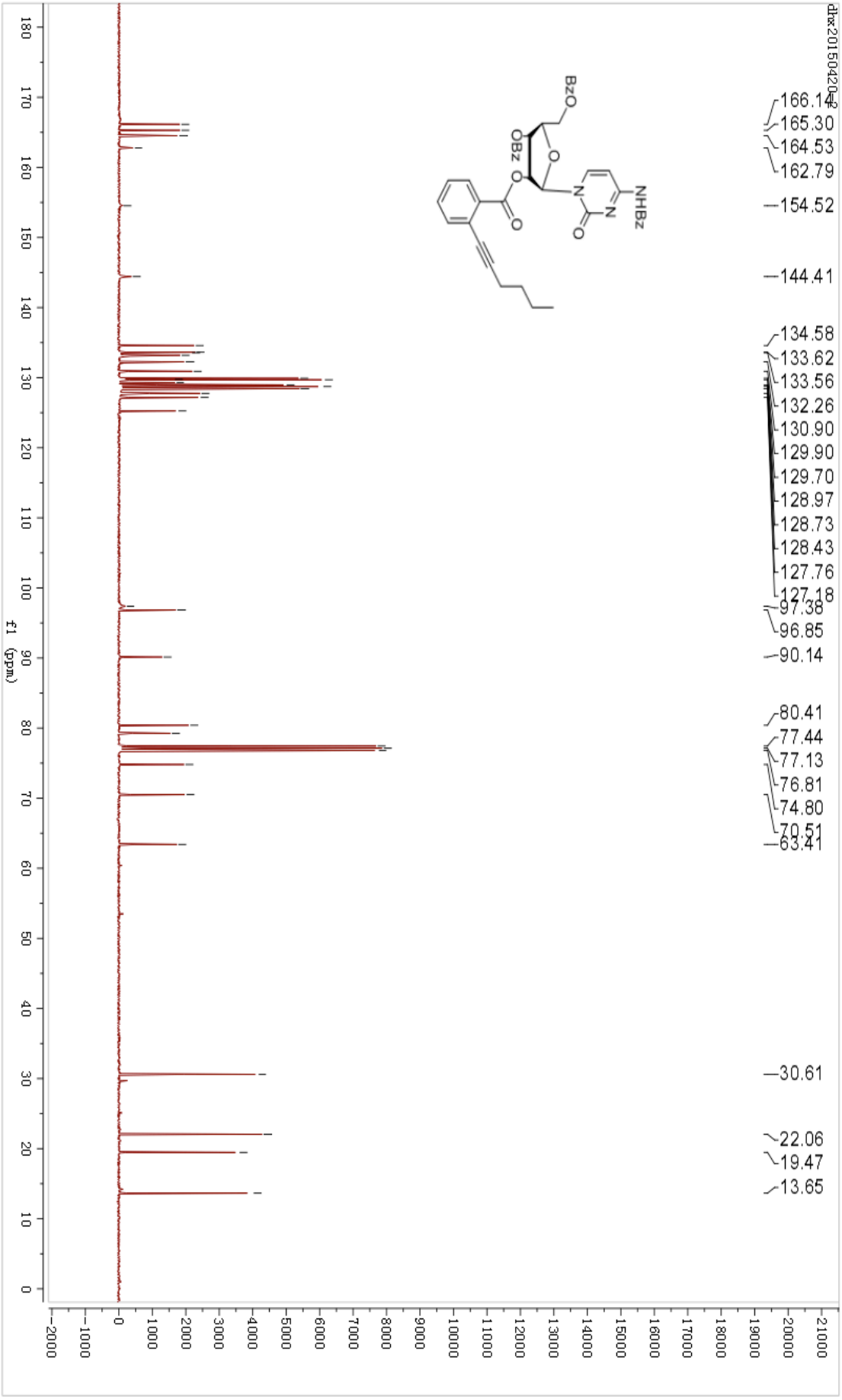
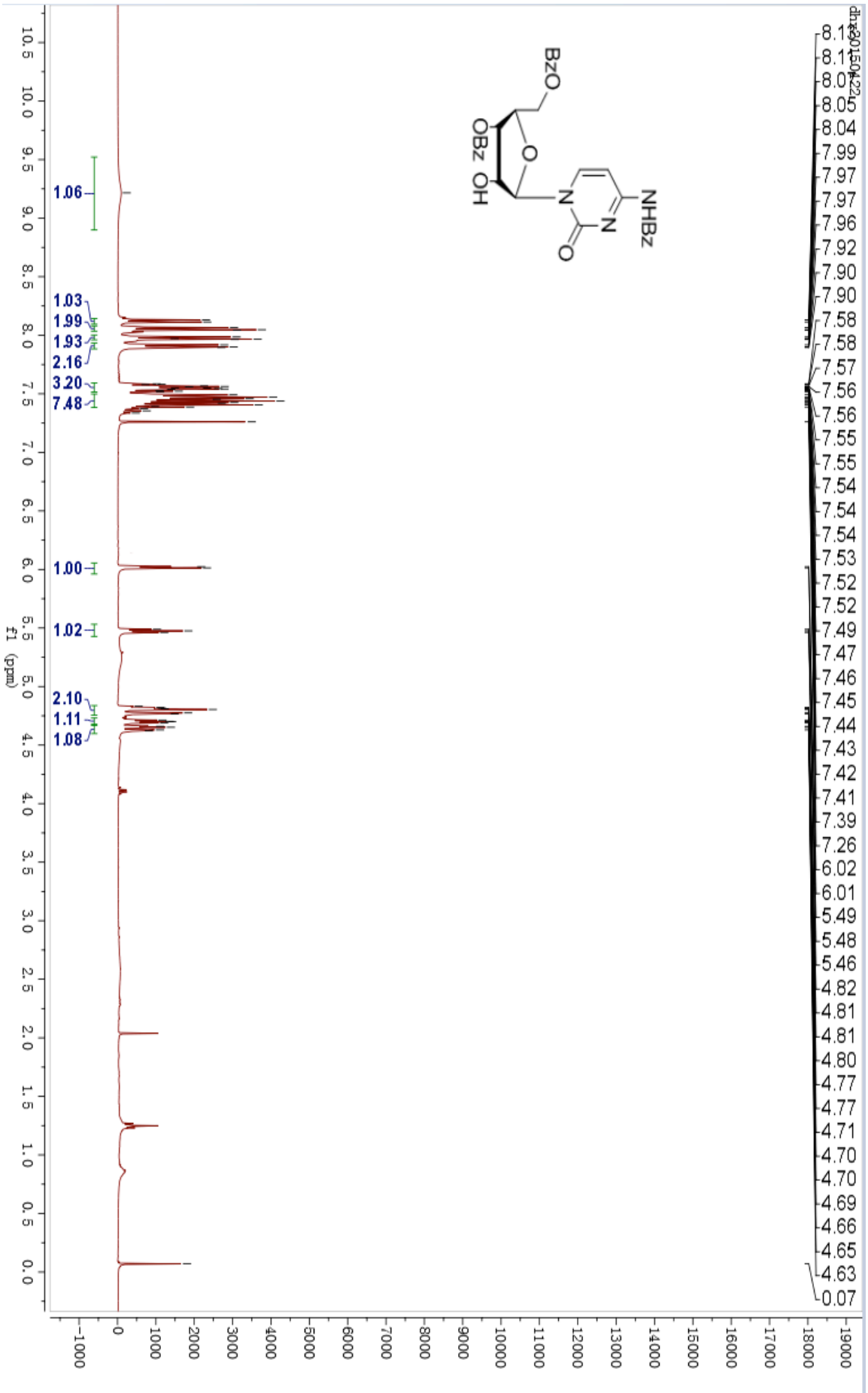
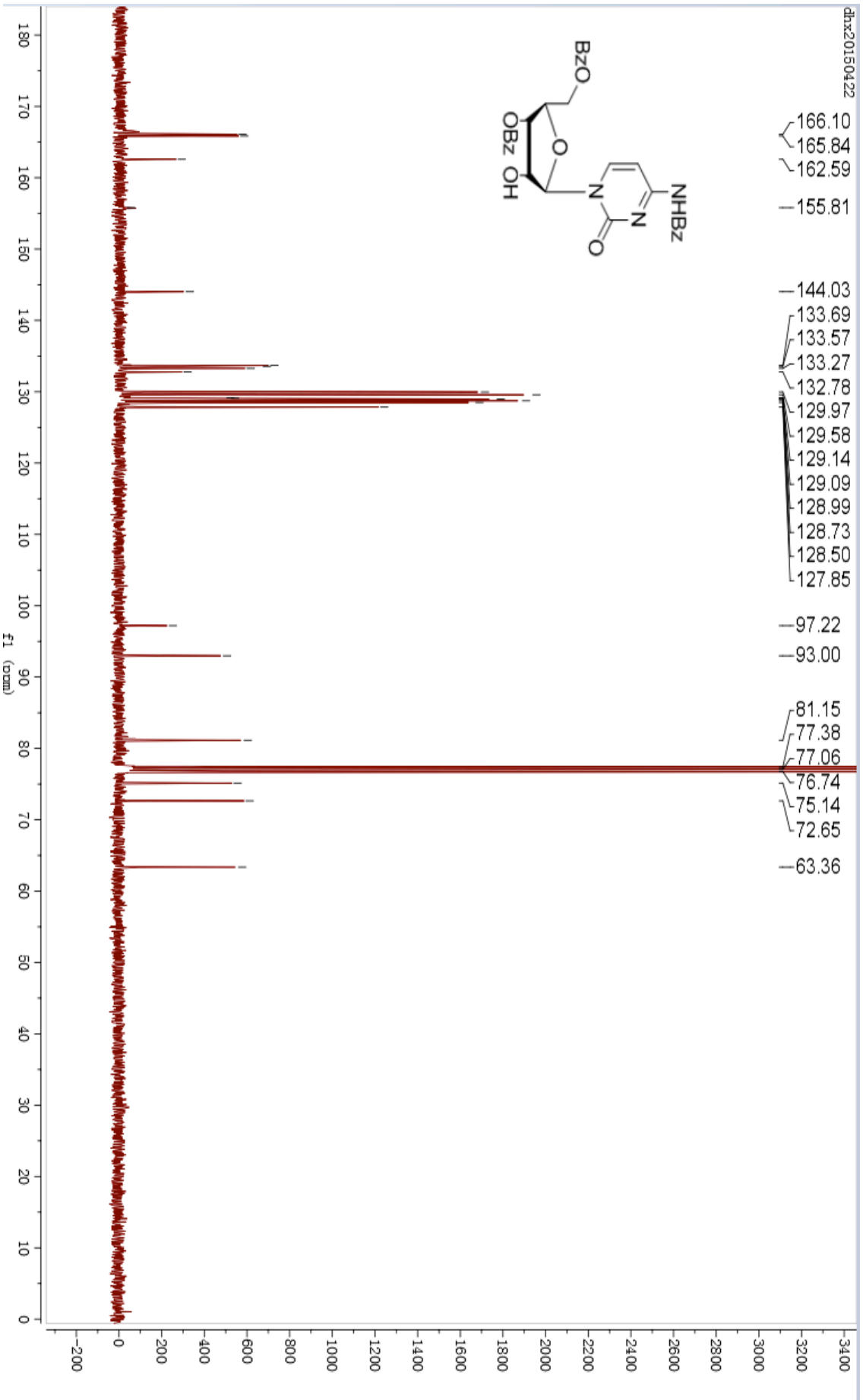
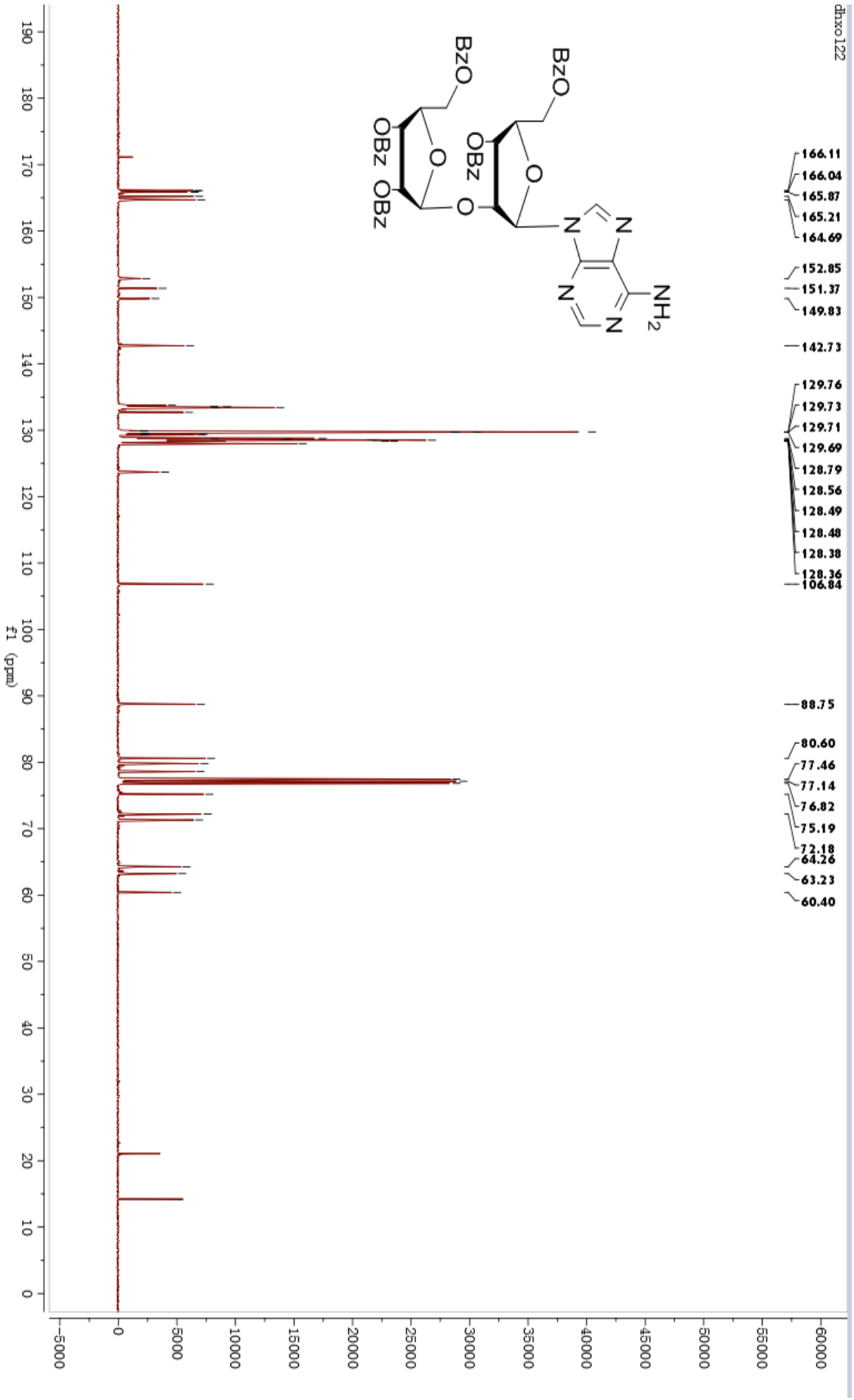
152.40
150.09
134.71
133.62
133.39
132.43
130.46
129.88
129.62
129.26
128.52
128.47
127.11
125.32
97.06
87.90
80.54
77.35
77.03
76.71
71.20
63.52
30.59
25.14
22.02
19.45
13.61
f1 (ppm)

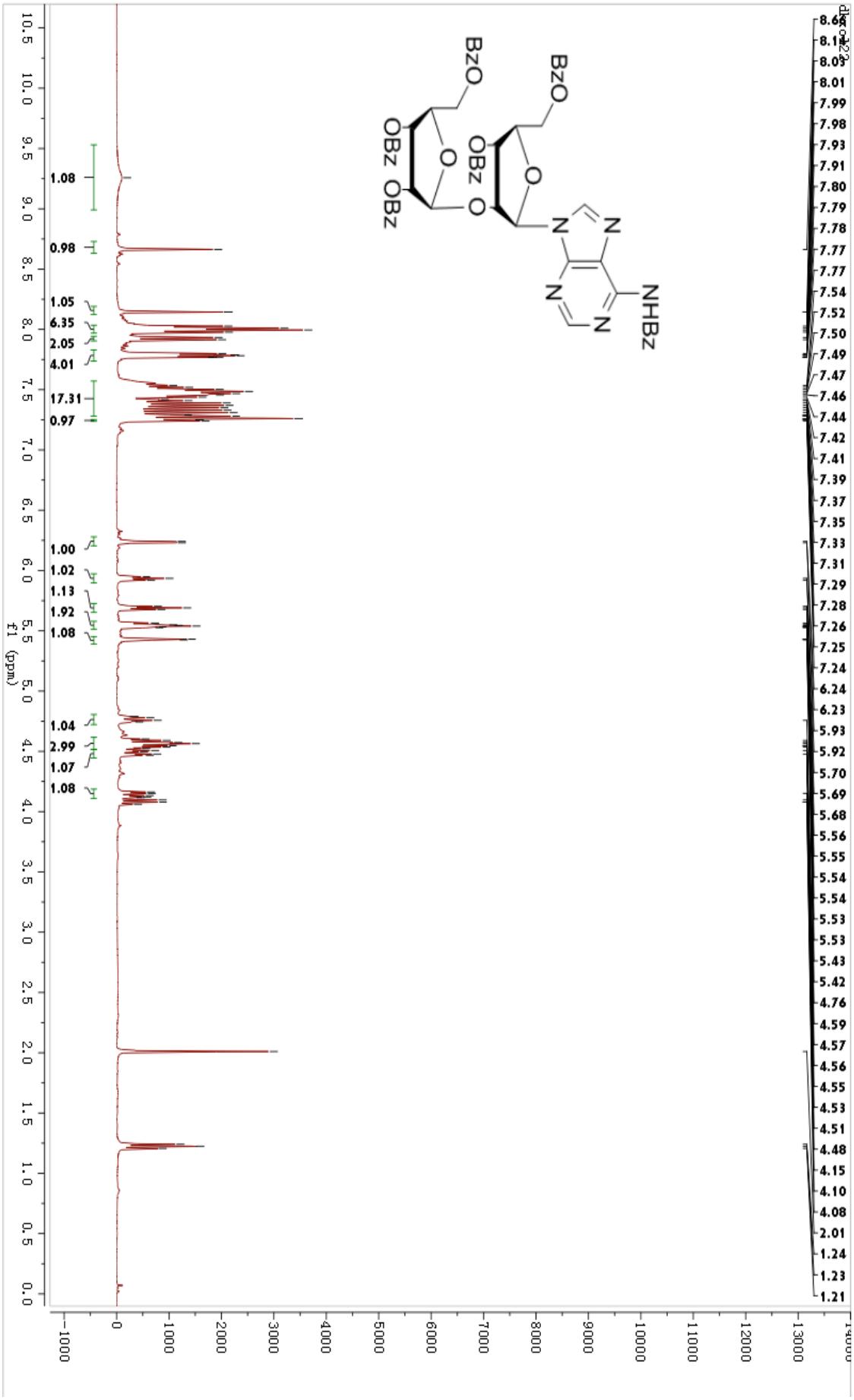

BzO
OBz
O
O
N
N
O
NHBz
0.85
2.05
1.09
5.07
10.41
2.08
1.05
1.00
2.04
2.02
1.11
2.02
2.07
2.21
3.13
f1 (ppm)

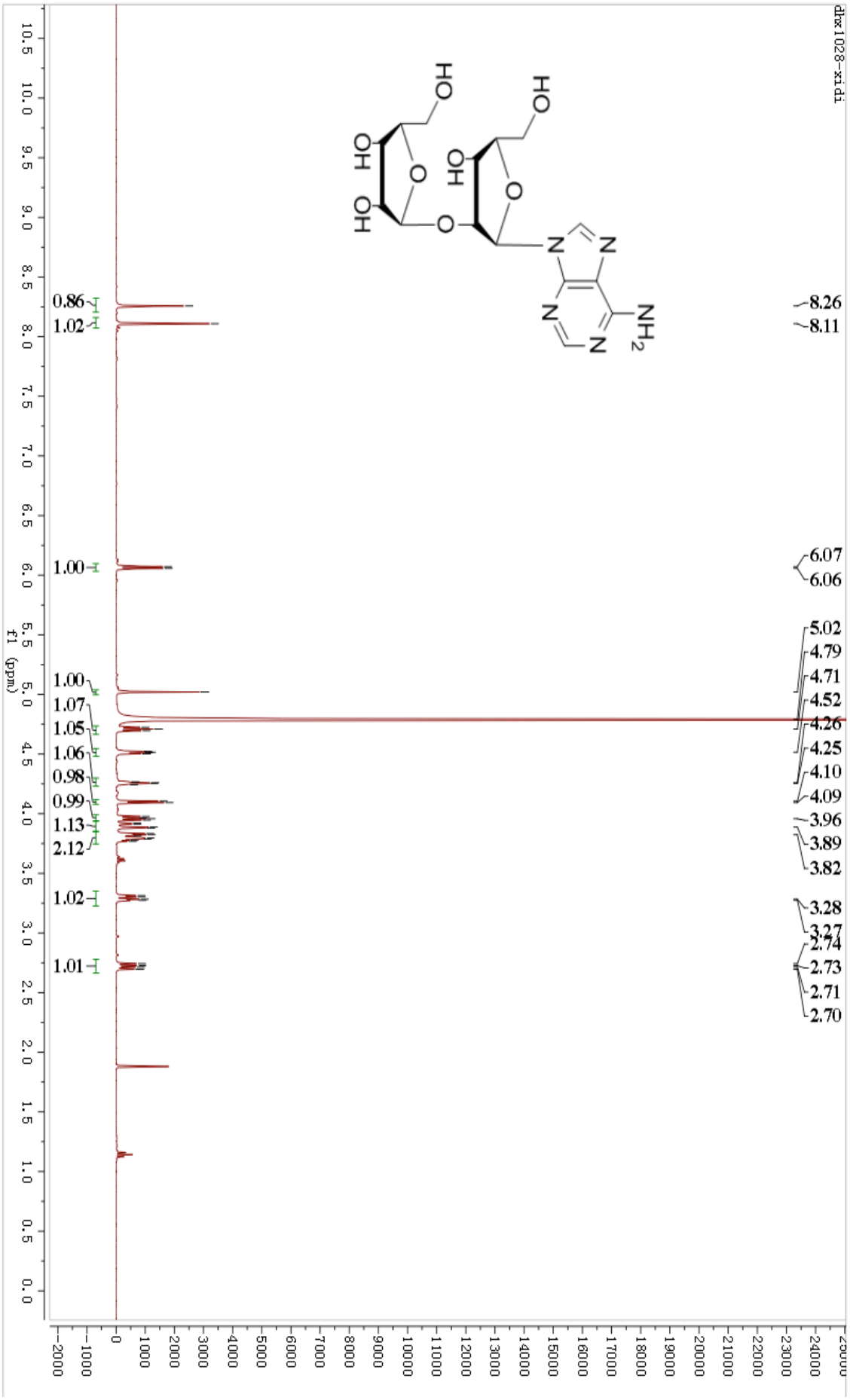

dtx20150420_3
166.14
165.30
164.53
162.79
154.52
144.41
134.58
133.62
133.56
132.26
130.90
129.90
129.70
128.97
128.73
128.43
127.76
127.18
97.38
96.85
90.14
80.41
77.44
77.13
76.81
74.80
70.51
63.41
30.61
22.06
19.47
13.65
BzO
OBz
O
N
N
O
NHBz
f1 (ppm)


BzO
OBz
OH
O
N
N
NHBz
O
1.06
1.03
1.99
1.93
2.16
3.20
7.48
1.00
1.02
2.10
1.11
1.08
f1 (ppm)


dhx20150422
BzO
OBz
OH
O
N
N
O
NHBz
166.10
165.84
162.59
155.81
144.03
133.69
133.57
133.27
132.78
129.97
129.58
129.14
129.09
128.99
128.73
128.50
127.85
97.22
93.00
81.15
77.38
77.06
76.74
75.14
72.65
63.36
f1 (ppm)

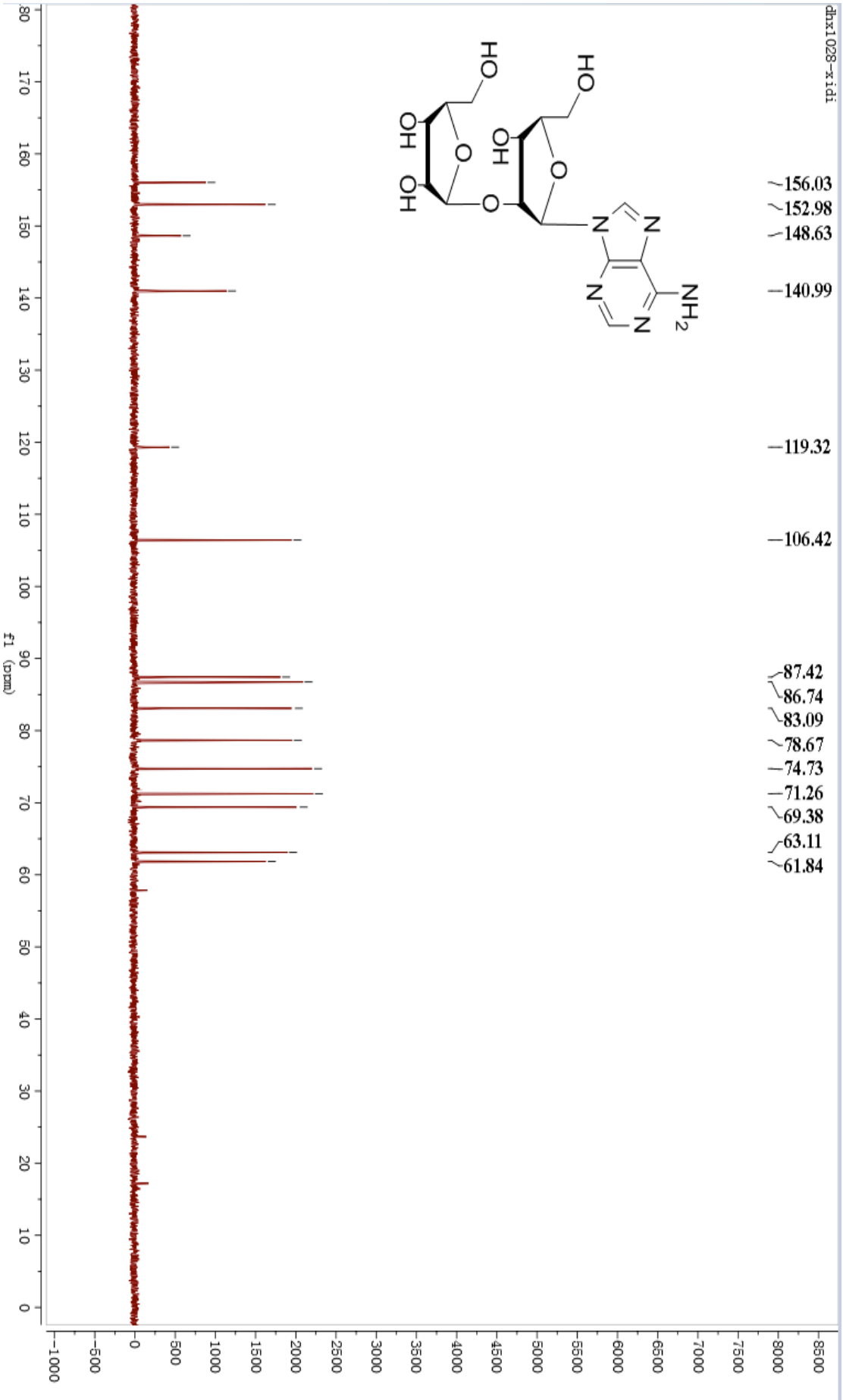

dhxo122
166.11
166.04
165.87
165.21
164.69
152.85
151.37
149.83
142.73
129.76
129.73
129.71
129.69
128.79
128.56
128.49
128.48
128.38
128.36
106.84
88.75
80.60
77.46
77.14
76.82
75.19
72.18
64.26
63.23
60.40
BzO
OBz
OBz
O
O
BzO
OBz
O
N
N
N
N
NH2
f1 (ppm)

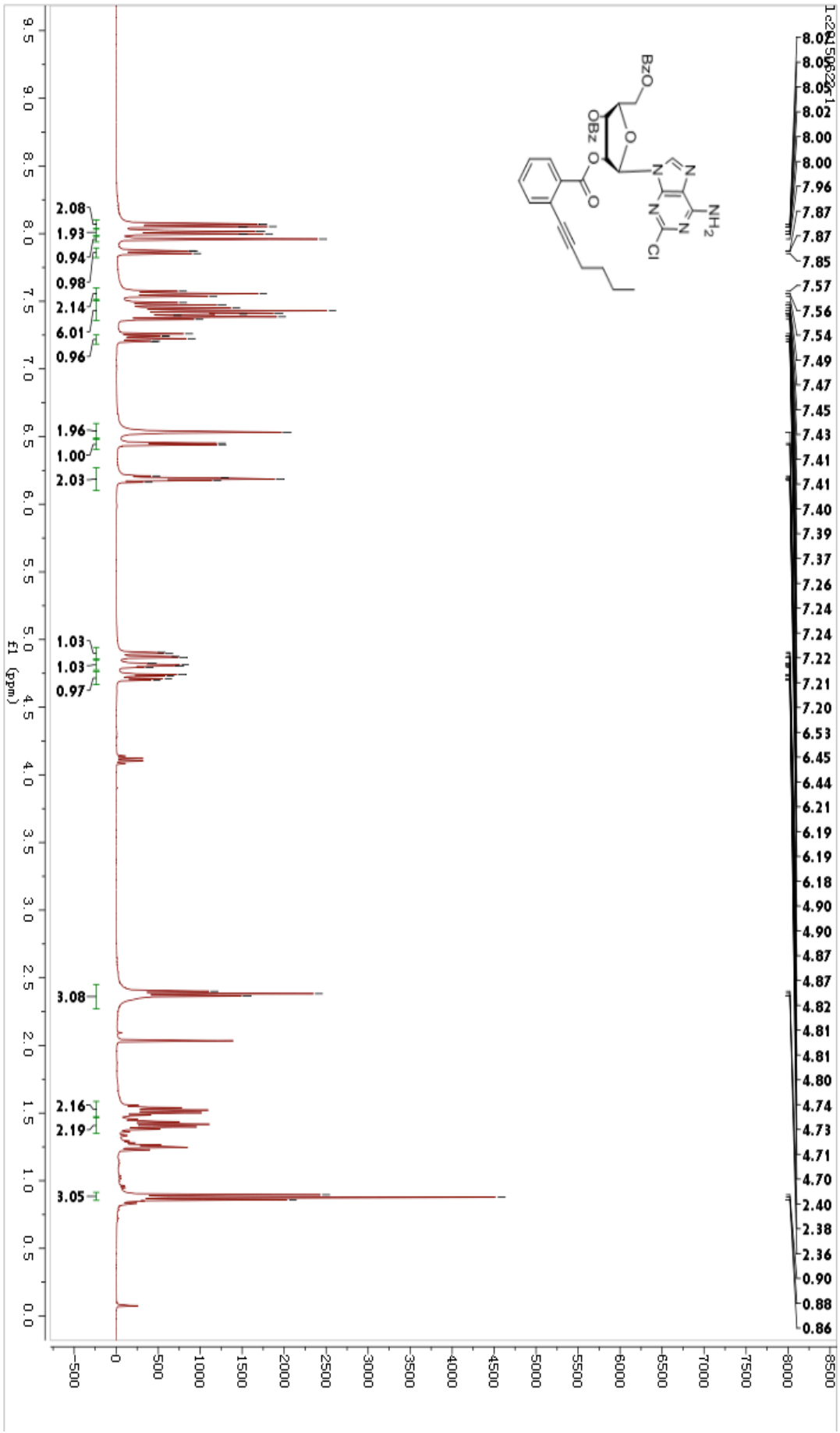

BzO
OBz
OBz
O
BzO
OBz
O
N
N
N
N
N
NHBz
f1 (ppm)
1.08
0.98
1.05
6.35
2.05
4.01
17.31
0.97
1.00
1.02
1.13
1.92
1.08
1.04
2.99
1.07
1.08


dhx1028-xidi
f1 (ppm)
8.26
8.11
6.07
6.06
5.02
4.79
4.71
4.52
4.26
4.25
4.10
4.09
3.96
3.89
3.82
3.28
3.27
2.74
2.73
2.71
2.70
0.86
1.02
1.00
1.00
1.07
1.05
1.06
0.98
0.99
1.13
2.12
1.02
1.01
HO
HO
HO
O
O
HO
O
N
N
N
N
NH2



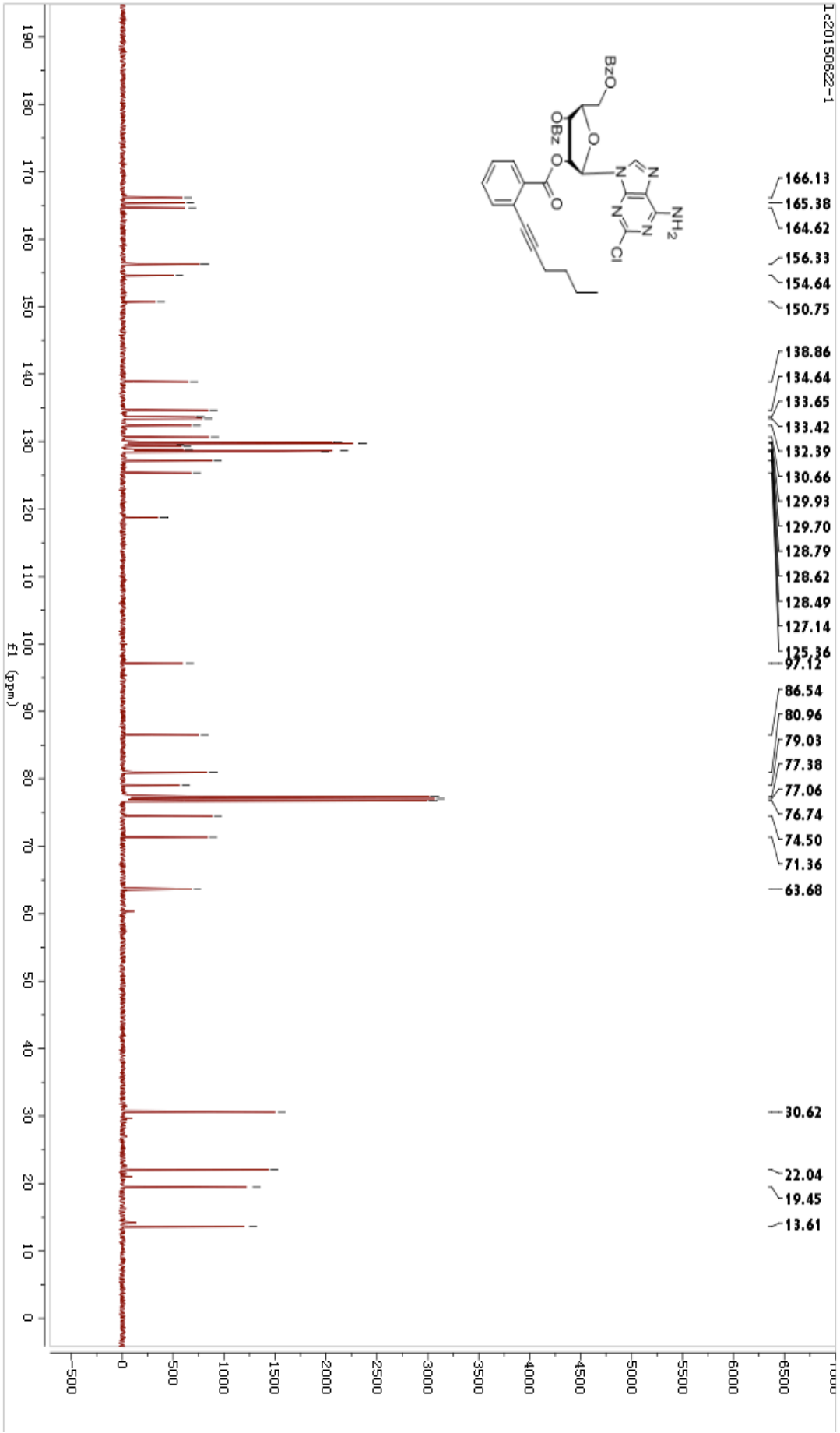
0

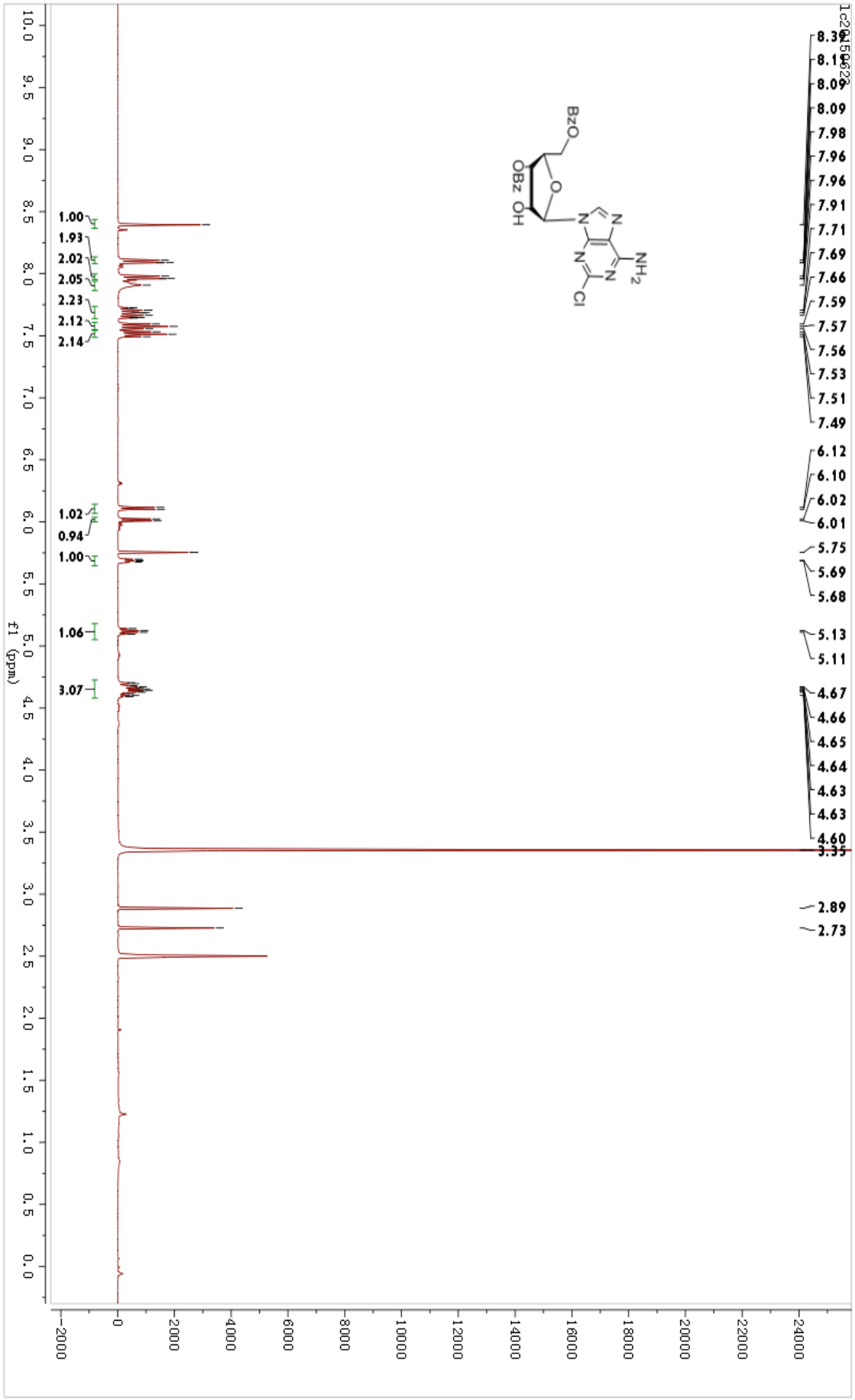

dhx1028-xidi
156.03
152.98
148.63
140.99
119.32
106.42
87.42
86.74
83.09
78.67
74.73
71.26
69.38
63.11
61.84
f1 (ppm)

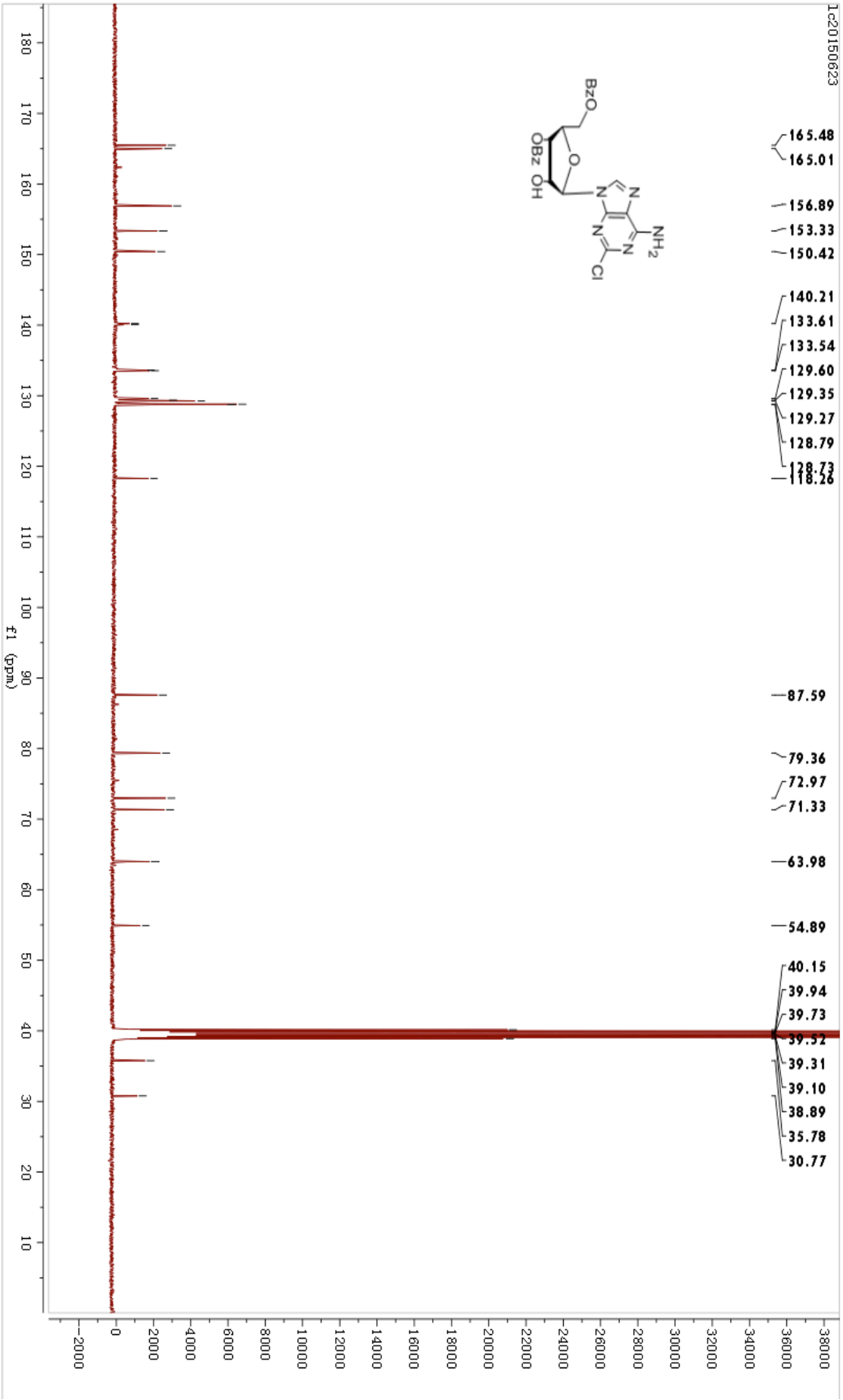

f1 (ppm)
2.08
1.93
0.94
0.98
2.14
6.01
0.96
1.96
1.00
2.03
1.03
1.03
0.97
3.08
2.16
2.19
3.05
BzO
OBz
O
N
N
N
N
NH2
Cl
8.07
8.05
8.02
8.00
8.00
7.96
7.87
7.87
7.85
7.57
7.56
7.54
7.49
7.47
7.45
7.43
7.41
7.41
7.40
7.39
7.37
7.26
7.24
7.24
7.22
7.21
7.20
6.53
6.45
6.44
6.21
6.19
6.19
6.18
4.90
4.90
4.87
4.87
4.82
4.81
4.81
4.80
4.74
4.73
4.71
4.70
2.40
2.38
2.36
0.90
0.88
0.86

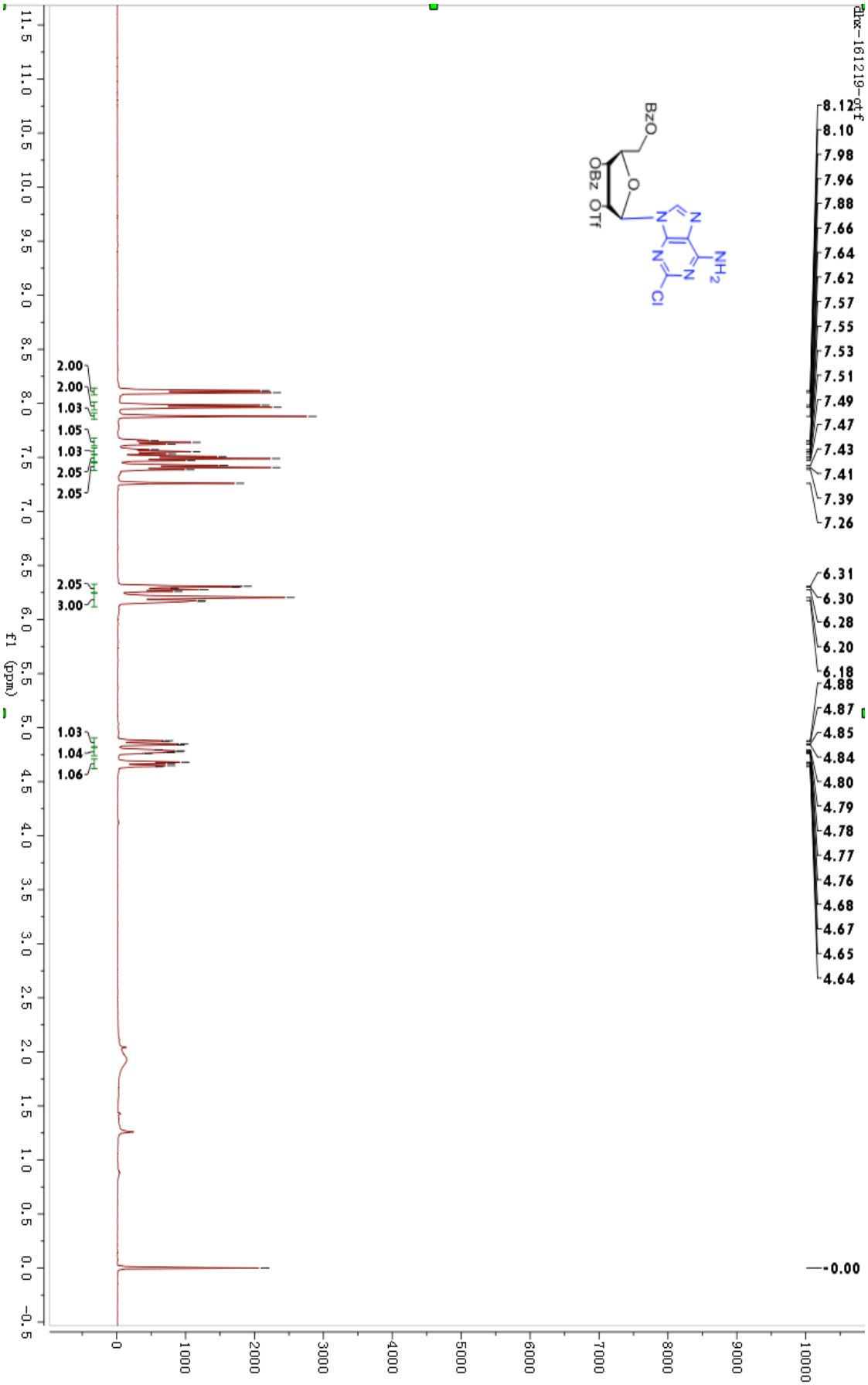


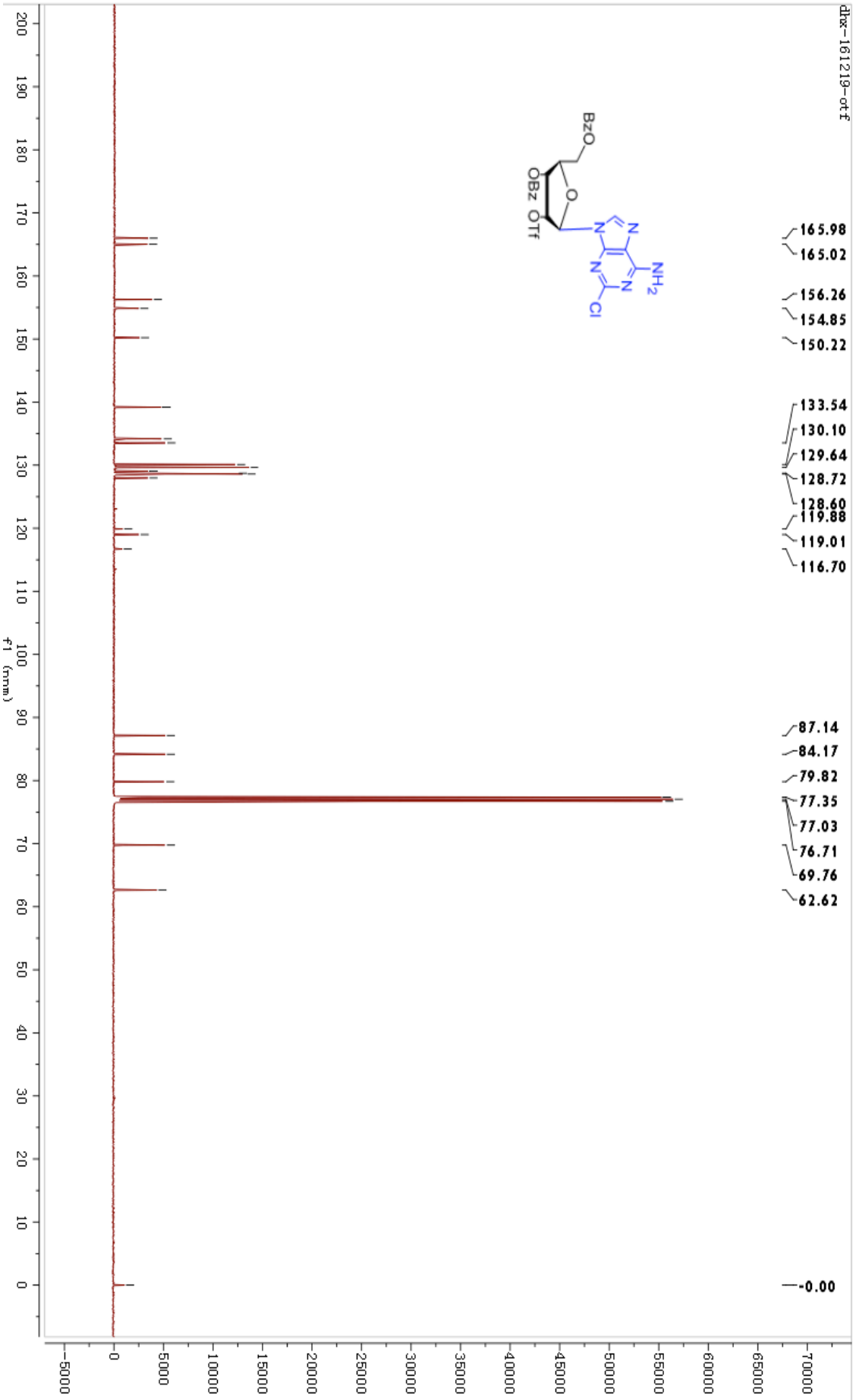
2

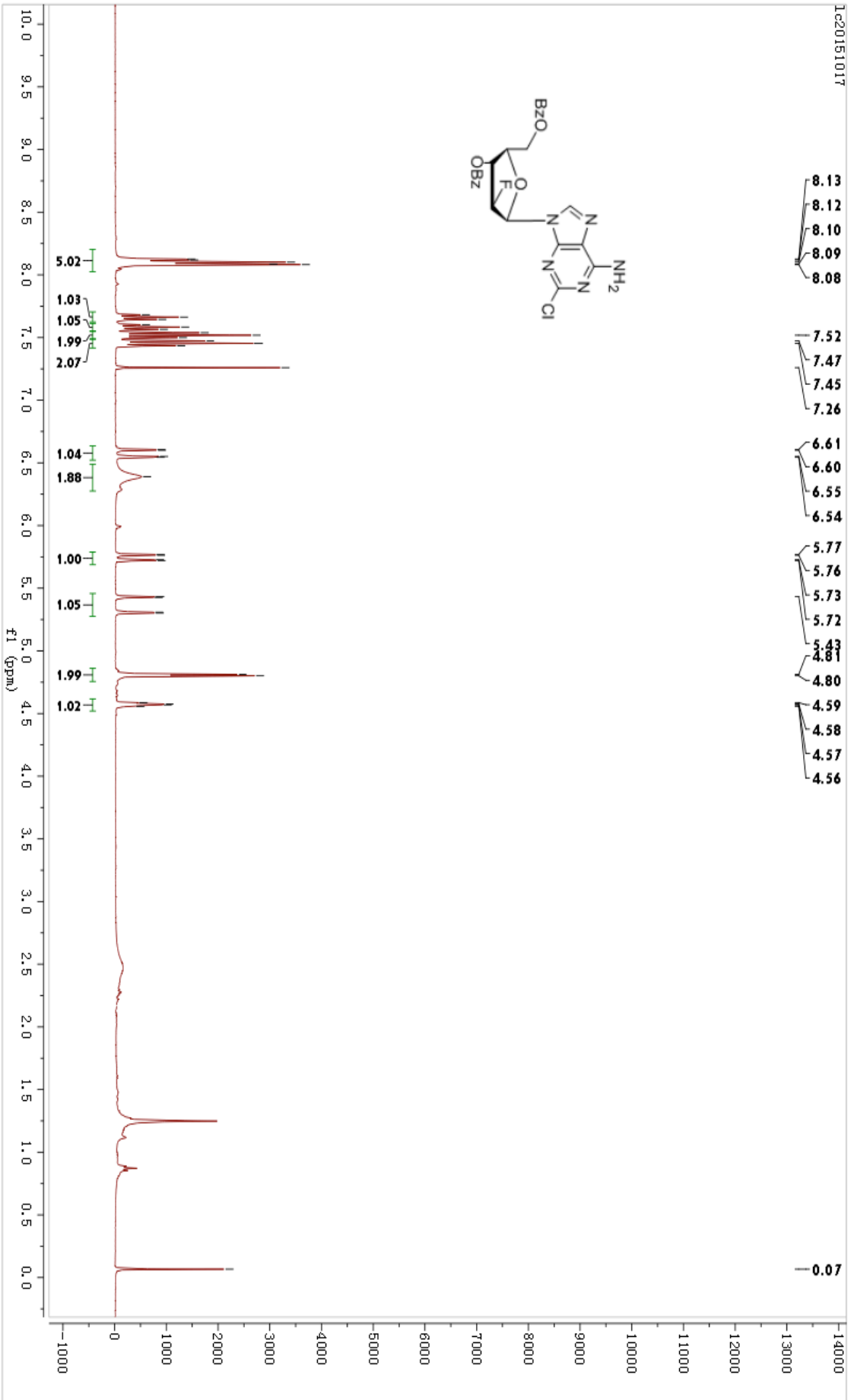

1c20150622-1
166.13
165.38
164.62
156.33
154.64
150.75
138.86
134.64
133.65
133.42
132.39
130.66
129.93
129.70
128.79
128.62
128.49
127.14
125.36
97.12
86.54
80.96
79.03
77.38
77.06
76.74
74.50
71.36
63.68
30.62
22.04
19.45
13.61
f1 (ppm)
BzO
OBz
NH2
Cl

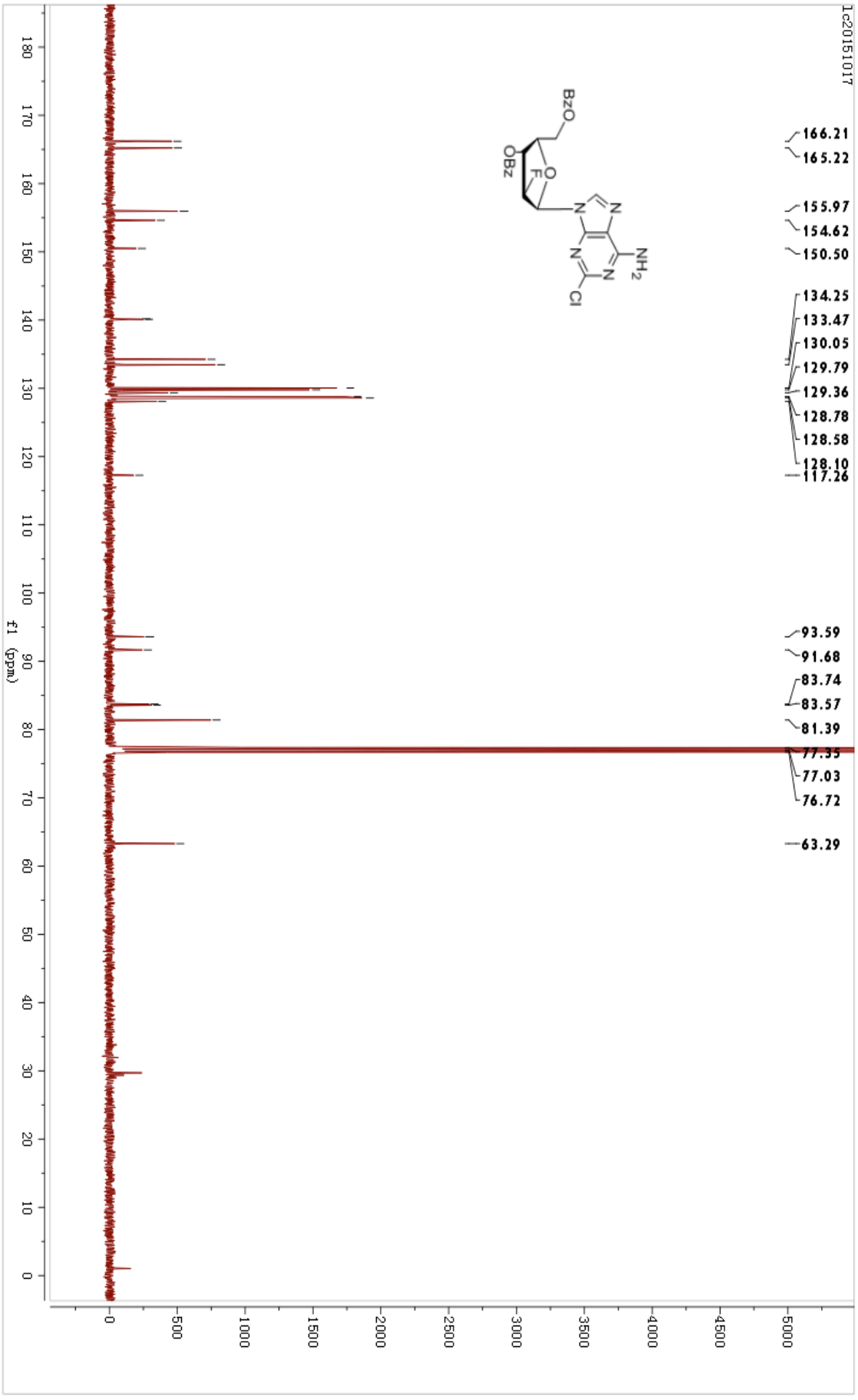

BzO
OBz
OH
O
N
N
N
N
NH2
Cl
1.00
1.93
2.02
2.05
2.23
2.12
2.14
1.02
0.94
1.00
1.06
3.07
8.39
8.12
8.09
8.09
7.98
7.96
7.96
7.91
7.71
7.69
7.66
7.59
7.57
7.56
7.53
7.51
7.49
6.12
6.10
6.02
6.01
5.75
5.69
5.68
5.13
5.11
4.67
4.66
4.65
4.64
4.63
4.63
4.60
3.35
2.89
2.73
f1 (ppm)

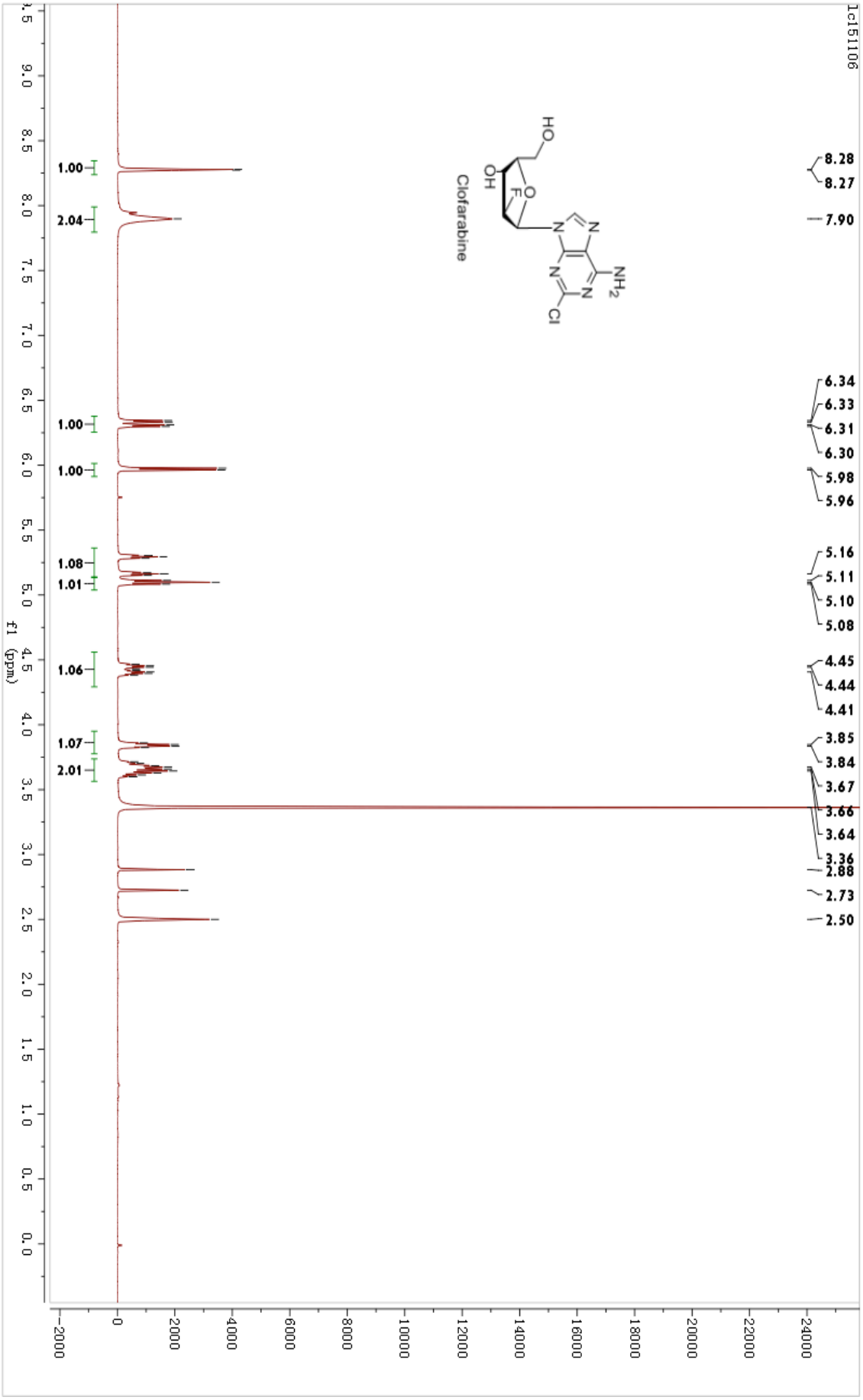

1c20150623
BzO
OBz OH
O
N
N
N
N
NH2
Cl
165.48
165.01
156.89
153.33
150.42
140.21
133.61
133.54
129.60
129.35
129.27
128.79
128.73
118.26
87.59
79.36
72.97
71.33
63.98
54.89
40.15
39.94
39.73
39.52
39.31
39.10
38.89
35.78
30.77
f1 (ppm)


zhx-161219-otf
f1 (ppm)
BzO
OBz OTf
NH2
Cl
8.12
8.10
7.98
7.96
7.88
7.66
7.64
7.62
7.57
7.55
7.53
7.51
7.49
7.47
7.43
7.41
7.39
7.26
6.31
6.30
6.28
6.20
6.18
4.88
4.87
4.85
4.84
4.80
4.79
4.78
4.77
4.76
4.68
4.67
4.65
4.64
0.00
2.00
2.00
1.03
1.05
1.03
2.05
2.05
2.05
3.00
1.03
1.04
1.06


dhx-161219-otf
BzO
OBz OTf
NH2
Cl
165.98
165.02
156.26
154.85
150.22
133.54
130.10
129.64
128.72
128.60
119.88
119.01
116.70
87.14
84.17
79.82
77.35
77.03
76.71
69.76
62.62
0.00
f1 (ppm)

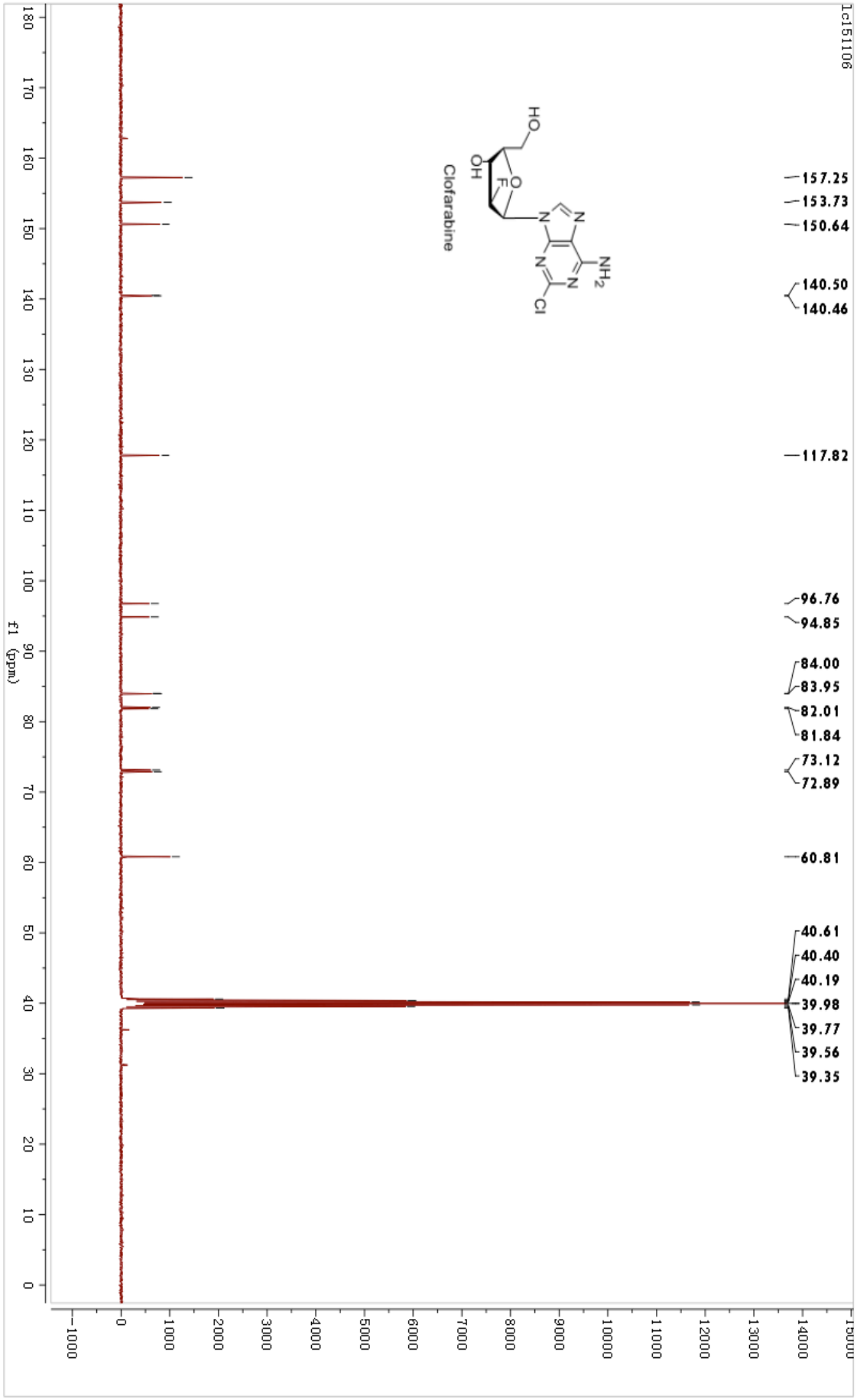

1c20151017
8.13
8.12
8.10
8.09
8.08
7.52
7.47
7.45
7.26
6.61
6.60
6.55
6.54
5.77
5.76
5.73
5.72
5.43
4.81
4.80
4.59
4.58
4.57
4.56
0.07
5.02
1.03
1.05
1.99
2.07
1.04
1.88
1.00
1.05
1.99
1.02
BzO
OBz
O
F
N
N
N
N
NH2
Cl
f1 (ppm)


1c20151017
166.21
165.22
155.97
154.62
150.50
134.25
133.47
130.05
129.79
129.36
128.78
128.58
128.10
117.26
93.59
91.68
83.74
83.57
81.39
77.35
77.03
76.72
63.29
BzO
OBz
F
O
N
N
N
N
NH2
Cl
f1 (ppm)


1cl51106
Clofarabine
8.28
8.27
7.90
6.34
6.33
6.31
6.30
5.98
5.96
5.16
5.11
5.10
5.08
4.45
4.44
4.41
3.85
3.84
3.67
3.66
3.64
3.36
2.88
2.73
2.50
1.00
2.04
1.00
1.00
1.08
1.01
1.06
1.07
2.01
f1 (ppm)



0


1c151106
Clofarabine
157.25
153.73
150.64
140.50
140.46
117.82
96.76
94.85
84.00
83.95
82.01
81.84
73.12
72.89
60.81
40.61
40.40
40.19
39.98
39.77
39.56
39.35
f1 (ppm)