Supporting Information for:

Protecting-Group-Free Synthesis of Glycosyl 1-Phosphates

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General Methods:

Solvents were removed under vacuum at approximately 50 °C. Extra dry dimethylformamide (DMF) (Acros Organics), 2-methyl-2-oxazoline (Sigma-Aldrich), anhydrous cupric chloride (Sigma-Aldrich), and crystalline phosphoric acid (Sigma-Aldrich) were all used as supplied. All glassware and stir bars were oven dried prior to use. All reactions were performed under a constant flow of $N_{2(g)}$.

Instrumentation:

Rotary evaporation was performed using a Heidolph rotary evaporator. ^{1}H, ^{13}C, and ^{31}P nuclear magnetic resonance (NMR) spectra were recorded using either a Varian 400 MHz or Bruker 400 MHz spectrometer at 25 °C. One dimensional proton and carbon chemical shifts are reported in parts per million and referenced to residual proton signals of NMR solvents (CD_3OD; δ 3.31 ppm, D_2O; δ 4.80 ppm for proton and δ 49.0 for carbon ppm). Proton NMR assignments were determined using gCOSY. ^{1}H spectra used for determining diastereomeric ratios of products were recorded using a Varian 400 MHz spectrometer at 40 °C. All coupling constants (*J* values) are reported in hertz (Hz) and multiplicity of protons are described as either s = singlet, d = doublet, dd = doublet of doublets, t = triplet, m = multiplet. NMR data is reported in the following order/format; chemical shift (multiplicity, integration, coupling constant, assignment). High resolution mass spectra were recorded using a ABI/Sciex Qstar mass spectrometer (electrospray ionization).

Screen of reaction additives:

A spatula tip of cupric chloride was dissolved in dry DMF (~1 mL). A reaction additive was then added (1 drop for liquids, 1 spatula tip for solids) and the mixture was shaken. A spatula tip of GSH donor **1** was then added to the mixture and the vial was shaken. Samples with additives that reduced or prevented the oxidative competency of Cu(II) towards the GSH donor did not effervesce. Samples were inspected for effervescence over a 10 minute period.

All additives produced a colour change except where otherwise indicated.

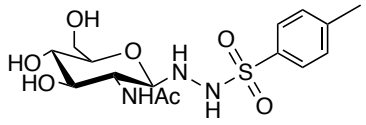
Table S1.

Additive	Effervescence Observed [a]
None	++
Isonicotimamide	-
Pyridine	- [b]
Imidazole	+++
2-methyl-2-oxazoline	+++
Aniline	+
4-Nitroaniline	+
Ethylenediamine	+
Diisopropylethylamine	+
p-hydroxybenzenethiol	- [b]
Acetonitrile	+
p-toluenesulfonamide	++ [c]
p-toluenesulfonic acid	++ [c]
Triphenylphosphine	-

[a] "-" indicates no effervescence, "+", "++", and "+++" indicate minimal, moderate, and vigorous effervescence respectively
[b] Insoluble precipitate was produced
[c] No colour change observed

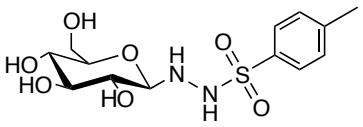
Experimental Procedures and Spectral Assignments:

N'-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-p-toluenesulfono-hydrazide (1)



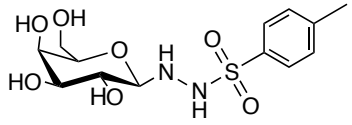
N-acetyl-D-glucosamine (5.00 g, 22.6 mmol) and *p*-toluenesulfonyl hydrazide (4.64 g, 24.9 mmol) were suspended in DMF (10 mL) and distilled H_2O (5 mL) in a 50 mL polypropylene tube. Glacial acetic acid (1.0 mL, 18 mmol) was then added and the mixture was incubated at 37 °C (without stirring) until all solids had dissolved (1.5 days). The clear homogeneous solution was then poured into diethyl ether (800 mL) and stirred vigorously for 18 hours. The precipitate was collected, dissolved in distilled H_2O (20 mL), and subsequently freeze-dried, affording compound **1** (8.18 g, 21.0 mmol) as a white solid in good purity. ^{1}H NMR (400 MHz, CD_3OD): δ 7.74 (d, 2H, J = 8.3 Hz, Ar), 7.38 (d, 2H, J = 8.3 Hz, Ar), 3.94 (d, 1H, $J_{1,2}$ = 9.2 Hz, H-1), 3.89 (dd, 1H, $J_{6a,6b}$ = 11.7, $J_{5,6a}$ = 1.7 Hz, H-6a), 3.60 (m, 1H, H-6b), 3.46 (t, 1H, $J_{2,3}$ = 10.1 Hz, H-2), 3.42-3.37 (m, 1H, H-3), 3.20-3.18 (m, 2H, H-4, H-5), 2.43 (s, 3H, PhCH_3), 2.01 (s, 3H, Ac); ^{13}C NMR (100 MHz, CD_3OD): δ 173.9, 145.1, 137.2, 130.5 (2), 129.1 (2), 91.9, 78.9, 76.2, 72.4, 63.2, 55.0, 23.0, 21.5; HRMS *m*/*z* calcd. for $C_{15}H_{23}N_2O_7NaS$ (M^+Na^+) 412.1148, found 412.1156.

N'-(β-D-glucopyranosyl)-p-toluenesulfono-hydrazide (2)



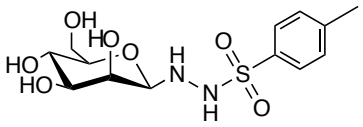
Glucose (5.00 g, 27.8 mmol) and *p*-toluenesulfonyl hydrazide (5.60 g, 30.5 mmol) were suspended in DMF (10 mL) and distilled H_2O (5 mL) in a 50 mL polypropylene tube. Glacial acetic acid (1.0 mL, 18 mmol) was then added and the mixture was incubated at 37 °C (without stirring) until all solids had dissolved (1.5 days). The clear homogeneous solution was then poured into diethyl ether (800 mL) and stirred vigorously for 18 hours. The precipitate was collected, dissolved in distilled H_2O (20 mL), and subsequently freeze-dried, affording compound **2** (8.70 g, 25.0 mmol) as a white solid in good purity. ^{1}H NMR (400 MHz, CD_3OD): δ 7.81 (d, 2H, J = 8.3 Hz, Ar), 7.40 (d, 2H, J = 8.3 Hz, Ar), 3.86 (dd, 1H, $J_{6a,6b}$ = 11.6, $J_{5,6a}$ = 1.9 Hz, H-6a), 3.67 (d, 1H, $J_{1,2}$ = 8.5 Hz, H-1), 3.58 (dd, 1H, $J_{6a,6b}$ = 11.7, $J_{5,6b}$ = 6.2 Hz, H- 6b), 3.34 (under CD_3OD peak, t, 1H, H-3), 3.29 (under CD_3OD peak, 1H, H-4), 3.20-3.11 (m, 2H, H-2, H-5), 2.44 (s, 3H, PhCH_3); ^{13}C NMR (100 MHz, CD_3OD): δ 145.1, 137.4, 130.6 (2), 129.1 (2), 91.5, 79.2, 78.2, 71.8 (2), 63.2, 21.5; HRMS *m*/*z* calcd. for $C_{13}H_{20}N_2O_7NaS$ (M^+Na^+) 371.0883, found 371.0901.

N'-(β-D-galactopyranosyl)-p-toluenesulfono-hydrazide (3)



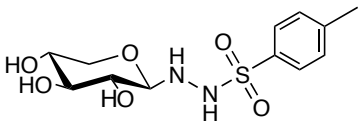
Galactose (5.00 g, 27.8 mmol) and *p*-toluenesulfonyl hydrazide (5.60 g, 30.5 mmol) were suspended in DMF (10 mL) and distilled H_2O (5 mL) in a 50 mL polypropylene tube. Glacial acetic acid (1.0 mL, 17.47 mmol) was then added and the mixture was incubated at 37 °C (without stirring) until all solids had dissolved (1.5 days). The clear homogeneous solution was then poured into diethyl ether (800 mL) and stirred vigorously for 18 hours. The precipitate was collected, dissolved in distilled H_2O (20 mL), and subsequently freeze-dried, affording compound **3** (8.12 g, 23.3 mmol) as a white solid in good purity. ^{1}H NMR (400 MHz, D_2O): δ 7.84 (d, 2H, J = 8.4 Hz, Ar), 7.50 (d, 2H, J = 8.1 Hz, Ar), 3.87 (d, 1H, $J_{5,6a}$ = 2.4 Hz, H-6a), 3.73-3.67 (m, 3H, H-1, H-3, H-5), 3.54-3.47 (m, 3H, H-2, H-4, H-6b), 2.46 (s, 3H, PhCH_3); ^{13}C NMR (100 MHz, D_2O): δ 145.8, 133.6, 130.1 (2), 127.9 (2), 90.4, 76.2, 73.3, 68.9, 68.2, 61.5, 20.9; ESI HRMS *m*/*z* calcd. for $C_{13}H_{21}N_2O_7S$ (M^+H^+) 349.1063, found 349.1056.

N'-(β-D-mannopyranosyl)-p-toluenesulfono-hydrazide (4)



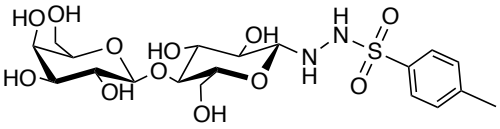
Mannose (5.00 g, 27.8 mmol) and p-toluenesulfonyl hydrazide (5.60 g, 30.5 mmol) were suspended in DMF (10 mL) and distilled H_2O (5 mL) in a 50 mL polypropylene tube. Glacial acetic acid (1.0 mL, 18 mmol) was then added and the mixture was incubated at 37 °C (without stirring) until all solids had dissolved (1.5 days). The clear homogeneous solution was then poured into diethyl ether (800 mL) and stirred vigorously for 18 hours. The precipitate was collected, dissolved in distilled H_2O (20 mL), and subsequently freeze-dried, affording compound **4** (8.10 g, 23.3 mmol) as a white solid in good purity. ^{1}H NMR (400 MHz, D_2O): δ 7.82 (d, 2H, J = 8.4 Hz, Ar), 7.50 (d, 2H, J = 8.04 Hz, Ar), 3.91 (dd, 1H, $J_{6a,6b}$ = 12.0, $J_{5,6a}$ = 2.0 Hz, H-6a), 3.80 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-2), 3.74 (s, 1H, H-1), 3.68 (dd, 1H, $J_{6a,6b}$ = 12.0, $J_{5,6b}$ = 6.8 Hz, H-6b), 3.46 (t, 1H, $J_{4,5}$ = 9.6 Hz, H-4), 3.38 (dd, 1H, $J_{2,3}$ = 3.2, $J_{3,4}$ = 9.6 Hz, H-3), 3.13 (ddd, 1H, H-5), 2.45 (s, 3H, PhCH_3); ^{13}C NMR (100 MHz, D_2O): δ 145.8, 133.7, 130.1 (2), 127.7 (2), 87.3, 77.4, 73.5, 69.6, 66.9, 61.2, 48.9, 20.7; HRMS *m*/*z* calcd. for $C_{13}H_{21}N_2O_7S$ (M^+H^+) 349.1063, found 349.1047.

N'-(β-D-xylopyranosyl)-p-toluenesulfono-hydrazide (5)



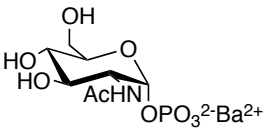
Xylose (5.00 g, 33.3 mmol) and p-toluenesulfonyl hydrazide (6.82 g, 36.6 mmol) were suspended in DMF (10 mL) and distilled H_2O (5 mL) in a 50 mL polypropylene tube. Glacial acetic acid (1.0 mL, 17.47 mmol) was then added and the mixture was incubated at 37 °C (without stirring) until all solids had dissolved (1.5 days). The clear homogeneous solution was then poured into diethyl ether (800 mL) and stirred vigorously for 18 hours. The precipitate was collected, dissolved in distilled H_2O (20 mL), and subsequently freeze-dried, affording compound **5** (8.76 g, 27.5 mmol) as a white, partially crystalline solid in good purity. ^{1}H NMR (400 MHz, CD_3OD): *δ* 7.79 (d, 2H, *J* = 8.3 Hz, Ar), 7.39 (d, 2H, *J* = 8.3 Hz, Ar), 3.79 (dd, 1H, $J_{5a,5b}$ = 11.3, $J_{4,5a}$ = 5.4 Hz, H-5a), 3.70 (d, 1H, $J_{1,2}$ = 8.7 Hz, H-1), 3.47-3.40 (m, 2H, H-2, H-4), 3.28 (under CD_3OD peak, 1H, H-3), 3.07 (dd, 1H, $J_{5a,5b}$ = 11.3, $J_{4,5b}$ = 10.7, H-5b), 2.43 (s, 3H, PhCH_3); ^{13}C NMR (100 MHz, CD_3OD): *δ* 145.1, 137.1, 130.6 (2), 129.1 (2), 92.4, 78.2, 71.4, 71.2, 68.3, 21.5; HRMS *m*/*z* calcd. for $C_{12}H_{18}N_2O_6NaS$ (M^+Na^+) 341.0777, found 341.0788.

N'-(β-D-lactopyranosyl)-p-toluenesulfono-hydrazide (6)



Lactose (5.00 g, 14.6 mmol) and p-toluenesulfonyl hydrazide (2.99 g, 16.1 mmol) were suspended in DMF (10 mL) and distilled H_2O (5 mL) in a 50 mL polypropylene tube. Glacial acetic acid (1.0 mL, 18 mmol) was then added and the mixture was incubated at 37 °C (without stirring) until all solids had dissolved (1.5 days). The clear homogeneous solution was then poured into diethyl ether (800 mL) and stirred vigorously for 18 hours. The precipitate was collected, dissolved in distilled H_2O (20 mL), and subsequently freeze-dried, affording compound **6** (6.72 g, 13.2 mol) as a white solid in good purity. ^{1}H NMR (400 MHz, CD_3OD): *δ* 7.81 (d, 2H, *J* = 8.4 Hz, Ar), 7.40 (d, 2H, *J* = 8.0 Hz, Ar), 4.32 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-1'), 3.91 (dd, 1H, $J_{6a,6b}$ = 12.0, $J_{5,6a}$ = 2.4 Hz, H-6a), 3.81-3.67 (m, 5H, H-1', H-6'a, H-4', H-6'b, H-6b), 3.58-3.42 (m, 6H, H-2, H-4, H-3, H-2', H-5, H-3'), 3.31 (under CD_3OD peak, 1H, H-5'), 2.44 (s, 3H, PhCH_3); ^{13}C NMR (100 MHz, CD_3OD): *δ* 145.3, 137.5, 130.8 (2), 129.2 (2), 105.2, 91.6, 80.8, 77.8, 77.3, 76.7, 75.0, 72.6, 71.5, 70.4, 62.6, 62.4, 21.6; HRMS *m*/*z* calcd. for $C_{19}H_{31}N_2O_{12}S$ (M^+H^+) 511.1592, found 511.1588.

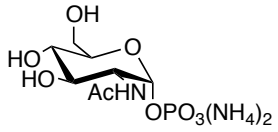
***Barium acetamido-2-deoxy-α-D-glucopyranosyl-1-phosphate* (7)**



A dry 250 mL round bottom flask was charged with activated spherical 4 Å molecular sieves (~1 g), a dry magnetic stir bar, and GSH donor **1** (557 mg, 1.43 mmol). Dry DMF (20 mL) was added to the flask and the mixture was stirred for 15 minutes under $N_{2(g)}$ atmosphere at 23 °C. Anhydrous cupric chloride (790 mg, 5.9 mmol) was placed in a dry scintillation vial and dissolved in dry DMF (5 mL). 2-methyl-2-oxazoline (0.50 mL, 5.9 mmol) was added to the cupric chloride solution and the mixture was shaken vigorously. Crystalline phosphoric acid (2.25 g, 23.0 mmol) was placed in a separate dry scintillation vial, dissolved in dry DMF (5 mL), and subsequently added to the cupric chloride-oxazoline solution. This mixture was shaken vigorously for 30 seconds and then added rapidly to the solution containing the GSH donor *via* syringe at 23 °C. After stirring for 18 hours the crude reaction mixture was poured into dichloromethane (150 mL) and the resultant precipitate was collected *via* vacuum filtration. The precipitate was dissolved in a minimal amount of dry DMF (~ 15 mL) followed by dilution with absolute ethanol (75 mL). A aqueous saturated solution of barium hydroxide was then added dropwise (with shaking) to the DMF/ethanol mixture until litmus paper indicated the pH was approximately 8-9. The resulting precipitate was filtered off and washed with ~75 mL of

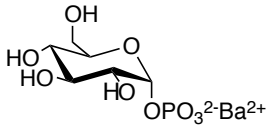
hot distilled H_2O (~ 70 °C). The combined filtrate was concentrated *via* rotary evaporation. The resultant solid was dissolved in a minimal volume of distilled H_2O (~5 mL) and re-precipitated *via* addition of absolute ethanol (~ 20 mL). Precipitate was isolated *via* centrifugation. The dissolution-precipitation was repeated three times, after which the desired glycosyl 1-phosphate **7** (375 mg, 0.86 mmol, white solid) was obtained in approximately 80% purity as a 6.7:1 mixture of α:β anomers. ^{1}H and ^{13}C NMR data was consistent with previous literature reports.[33,34] ^{31}P NMR (162 MHz, D_2O) δ 3.90. HRMS *m*/*z* calcd. for $C_8H_{15}NO_9P$ (M-) 300.0489, found 300.0504.

Ammonium acetamido-2-deoxy-α-D-glucopyranosyl-1-phosphate (7A)



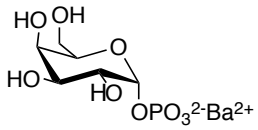
A column (1.5 cm diameter, 18 cm length) was loaded with DEAE-Sephadex A-25 (40-125 μM, 3-4 meq/g) attached to a Gilson 1250 HPLC with a UV detector. The column was equilibrated with NH_4HCO_3 (500 mM, 500 mL) at a flow rate of 1 mL/min. After equilibration the column was washed with dH_2O (200 mL). The barium salt of compound 7 (40 mg) was suspended in dH_2O (2 mL) and injected onto the column, *via* a 10 mL loop, through a 2 μM syringe filter. The sample failed to completely dissolve before injection likely due to minor copper and barium salt impurities. The glycosyl 1-phosphate was then eluted with the following gradient program at 1 mL/min: 10 min water wash, 10-60 min linear gradient 1-500 mM NH_4HCO_3, 60-100 min 500 mM NH_4HCO_3. Glycosyl-1-phosphates eluted at approximately 85 minutes which could be visualized *via* monitoring UV at 215 nm or on TLC by charring after a 5% H_2SO_4/MeOH dip. The fractions containing the glycosyl 1-phoshphates were lyophilized to give the glycosyl 1-phosphate ammonium salts as fluffy white powder (30 mg). ^{1}H NMR on pg. S22 indicates that all hemiacetal related peaks were removed from the sample

***Barium α-D-Glucopyranosyl-1-phosphate* (8)**



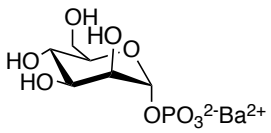
A dry 250 mL round bottom flask was charged with activated spherical 4 Å molecular sieves (~1 g), a dry magnetic stir bar, and GSH donor **2** (497 mg, 1.43 mmol). Dry DMF (20 mL) was added to the flask and the mixture was stirred for 15 minutes under $N_{2(g)}$ atmosphere at 23 °C. Anhydrous cupric chloride (790 mg, 5.9 mmol) was placed in a dry scintillation vial and dissolved in dry DMF (5 mL). 2-methyl-2-oxazoline (0.50 mL, 5.9 mmol) was added to the cupric chloride solution and the mixture was shaken vigorously. Crystalline phosphoric acid (2.25 g, 23.0 mmol) was placed in a separate dry scintillation vial, dissolved in dry DMF (5 mL), and subsequently added to the cupric chloride-oxazoline solution. This mixture was shaken vigorously for 30 seconds and then added rapidly to the solution containing the GSH donor *via* syringe at 23 °C. After stirring for 18 hours the crude reaction mixture was poured into dichloromethane (150 mL) and the resultant precipitate was collected *via* vacuum filtration. The precipitate was dissolved in a minimal amount of dry DMF (~ 15 mL) followed by dilution with absolute ethanol (75 mL). A aqueous saturated solution of barium hydroxide was then added dropwise (with shaking) to the DMF/ethanol mixture until litmus paper indicated the pH was approximately 8-9. The resulting precipitate was filtered off and washed with ~75 mL of hot distilled H_2O (~ 70 °C). The combined filtrate was concentrated *via* rotary evaporation. The resultant solid was dissolved in a minimal volume of distilled H_2O (~5 mL) and re-precipitated *via* addition of absolute ethanol (~ 20 mL). Precipitate was isolated *via* centrifugation. The dissolution-precipitation was repeated three times, after which the desired glycosyl-1-phosphate **8** (360 mg, 0.91 mmol, white solid) was obtained in approximately 80% purity as a 3.5:1 mixture of α:β anomers. ^{1}H and ^{13}C NMR data was consistent with previous literature reports.[29] ^{31}P NMR (162 MHz, D_2O) δ 0.84. HRMS *m*/*z* calcd. for $C_8H_{12}O_9P$ (M-) 259.0224, found 259.0217.

***Barium α-D-Galactopyranosyl-1-phosphate* (9)**



A dry 250 mL round bottom flask was charged with activated spherical 4 Å molecular sieves (~1 g), a dry magnetic stir bar, and GSH donor **3** (497 mg, 1.43 mmol). Dry DMF (20 mL) was added to the flask and the mixture was stirred for 15 minutes under $N_{2(g)}$ atmosphere at 23 °C. Anhydrous cupric chloride (790 mg, 5.9 mmol) was placed in a dry scintillation vial and dissolved in dry DMF (5 mL). 2-methyl-2-oxazoline (0.50 mL, 5.9 mmol) was added to the cupric chloride solution and the mixture was shaken vigorously. Crystalline phosphoric acid (2.25 g, 23.0 mmol) was placed in a separate dry scintillation vial, dissolved in dry DMF (5 mL), and subsequently added to the cupric chloride-oxazoline solution. This mixture was shaken vigorously for 30 seconds and then added rapidly to the solution containing the GSH donor *via* syringe at 23 °C. After stirring for 18 hours the crude reaction mixture was poured into dichloromethane (150 mL) and the resultant precipitate was collected *via* vacuum filtration. The precipitate was dissolved in a minimal amount of dry DMF (~15 mL) followed by dilution with absolute ethanol (75 mL). A aqueous saturated solution of barium hydroxide was then added dropwise (with shaking) to the DMF/ethanol mixture until litmus paper indicated the pH was approximately 8-9. The resulting precipitate was filtered off and washed hot dH_2O (~75 mL, ~ 70 °C). The combined filtrate was concentrated *via* rotary evaporation. The resultant solid was dissolved in a minimal volume of distilled H_2O (~5 mL) and re-precipitated *via* addition of absolute ethanol (~ 20 mL). Precipitate was isolated *via* centrifugation. The dissolution-precipitation was repeated three times, after which the desired glycosyl 1-phosphate **9** (350.76 mg, 0.89 mmol, white solid) was obtained in approximately 80% purity as a 7:1 mixture of α:β anomers. ^{1}H, ^{13}C NMR data was consistent with previous literature reports.[29] ^{31}P NMR (162 MHz, D_2O) δ 1.83. HRMS *m*/*z* calcd. for $C_8H_{12}O_9P$ (M-) 259.0224, found 259.0223.

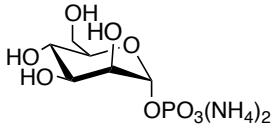
***Barium α-D-Mannopyranosyl-1-phosphate* (10)**



A dry 250 mL round bottom flask was charged with activated spherical 4 Å molecular sieves (~1 g), a dry magnetic stir bar, and GSH donor **4** (497.0 mg, 1.43 mmol). Dry DMF (20 mL) was added to the flask and the mixture was stirred for 15 minutes under $N_{2(g)}$ atmosphere at 23 °C. Anhydrous cupric chloride (793.0 mg, 5.9 mmol) was placed in a dry scintillation vial and dissolved in dry DMF (5 mL). 2-methyl-2-oxazoline (0.50 mL, 5.9 mmol) was added to the cupric chloride solution and the mixture was shaken vigorously. Crystalline phosphoric acid (2.25 g, 23.0 mmol) was placed in a separate dry scintillation vial, dissolved in dry DMF (5 mL), and subsequently added to the cupric chloride-oxazoline solution. This mixture was shaken vigorously for 30 seconds and then added rapidly to the solution containing the GSH donor *via* syringe at 23 °C. After stirring for 18 hours the crude reaction mixture was poured into dichloromethane (150 mL) and the resultant precipitate was collected *via* vacuum filtration. The precipitate was dissolved in a minimal amount of dry DMF (~ 15 mL) followed by dilution with absolute ethanol (75 mL). A aqueous saturated solution of barium hydroxide was then added dropwise (with shaking) to the DMF/ethanol mixture until litmus paper indicated the pH was approximately 8-9. The resulting precipitate was filtered off and washed with ~75 mL of hot distilled H_2O (~ 70 °C). The combined filtrate was concentrated *via* rotary evaporation. The resultant solid was dissolved in a minimal volume of distilled H_2O (~5 mL) and re-precipitated *via* addition of absolute ethanol (~ 20 mL). Precipitate was isolated *via* centrifugation. The dissolution-precipitation was repeated three times, after which the desired glycosyl α-1-phosphate **10** (254.39 mg, 0.64 mmol, white solid) was obtained in approximately 80% purity.

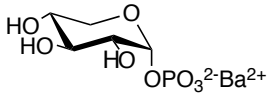
^{1}H, ^{13}C NMR data was consistent with previous literature reports.[35] ^{31}P NMR (162 MHz, D_2O) δ 1.48.

***Ammonium α-D-Mannopyranosyl-1-phosphate* (10A)**



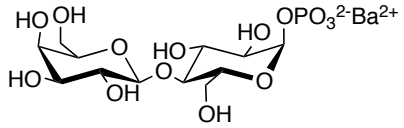
Using an identical procedure to the ion-exchange preformed on compound **7**, compound **10** (40 mg) was further purified to give the desired ammonium salt (15 mg).

***Barium α-D-Xylopyranosyl-1-phosphate* (11)**



A dry 250 mL round bottom flask was charged with activated spherical 4 Å molecular sieves (~1 g), a dry magnetic stir bar, and GSH donor **5** (455 mg, 1.43 mmol). Dry DMF (20 mL) was added to the flask and the mixture was stirred for 15 minutes under $N_{2(g)}$ atmosphere at 23 °C. Anhydrous cupric chloride (790 mg, 5.9 mmol) was placed in a dry scintillation vial and dissolved in dry DMF (5 mL). 2-methyl-2-oxazoline (0.50 mL, 5.9 mmol) was added to the cupric chloride solution and the mixture was shaken vigorously. Crystalline phosphoric acid (2.25 g, 23.0 mmol) was placed in a separate dry scintillation vial, dissolved in dry DMF (5 mL), and subsequently added to the cupric chloride-oxazoline solution. This mixture was shaken vigorously for 30 seconds and then added rapidly to the solution containing the GSH donor *via* syringe at 23 °C. After stirring for 18 hours the crude reaction mixture was poured into dichloromethane (150 mL) and the resultant precipitate was collected *via* vacuum filtration. The precipitate was dissolved in a minimal amount of dry DMF (~ 15 mL) followed by dilution with absolute ethanol (75 mL). A aqueous saturated solution of barium hydroxide was then added dropwise (with shaking) to the DMF/ethanol mixture until litmus paper indicated the pH was approximately 8-9. The resulting precipitate was filtered off and washed with hot dH_2O (~75 mL, ~ 70 °C). The combined filtrate was concentrated *via* rotary evaporation. The resultant solid was dissolved in a minimal volume of distilled H_2O (~5 mL) and re-precipitated *via* addition of absolute ethanol (~ 20 mL). Precipitate was isolated *via* centrifugation. The dissolution-precipitation was repeated three times, after which the desired glycosyl-1-phosphate **11** (266 mg, 0.73 mmol, white solid) was obtained in approximately 80% purity as a 5:1 mixture of α:β anomers. The crude precipitate was purified via an ion-exchange procedure similar to that outlined for compound **7** to yield ammonium α-D-xylopyranosyl-1-phosphate (**11A**). ^{1}H NMR (400 MHz, D_2O): *δ* 5.34 (dd, 1H, *J* = 8.0, *J* = 4.0 Hz, H-1α), 4.77 (app. t, 0.27H, *J* = 8 Hz, H-1β), 3.90 (dd, 0.27H, *J* = 8.0, *J* = 4.0 Hz, H-5aβ), 3.69-3.60 (m, 3.27H, H-5bα, H-5aα, H-3α, H-3β), 3.59-3.51 (m, 1.27H, H-4α, H-4β), 3.44-3.40 (m, 1.27H, H-2α, H-5bβ), 3.30-3.22 (m, 0.54H, H-5bβ, H-2β). ^{13}C NMR (100 MHz, D_2O) δ 98.0 (d, *J* = 4.0 Hz), 94.2 (d, *J* = 5 Hz), 75.7, 74.3 (d, *J* = 7 Hz), 73.4, 72.2 (d, *J* = 7 Hz), 69.7, 69. 4, 65.5, 61. 8. ^{31}P NMR (162 MHz, D_2O) δ 1.06. HRMS *m*/*z* calcd. for $C_{12}H_{22}O_{14}P$ (M-) 421.0752, found 421.0749.

***Barium α-D-Lactopyranosyl-1-phosphate* (12)**

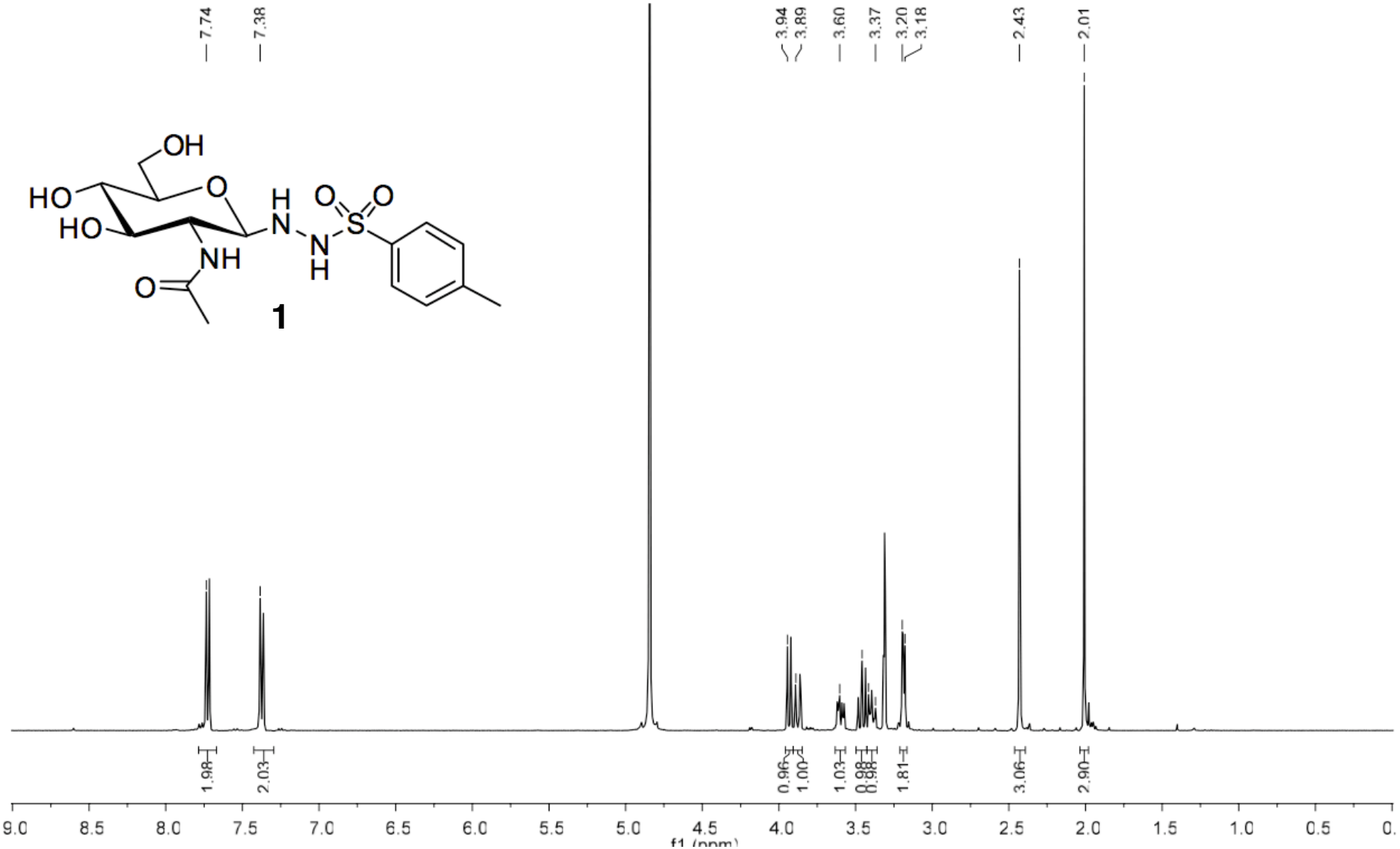


A dry 250 mL round bottom flask was charged with activated spherical 4 Å molecular sieves (~1 g), a dry magnetic stir bar, and GSH donor **6** (730.0 mg, 1.43 mmol). Dry DMF (20 mL) was added to the flask and the mixture was stirred for 15 minutes under $N_{2(g)}$ atmosphere at 23 °C. Anhydrous cupric chloride (793.0 mg, 5.9 mmol) was placed in a dry scintillation vial and dissolved in dry DMF (5 mL). 2-methyl-2-oxazoline (0.50 mL, 5.9 mmol) was added to the cupric chloride solution and the mixture was shaken vigorously. Crystalline phosphoric acid (2.25 g, 23.0 mmol) was placed in a separate dry scintillation vial,

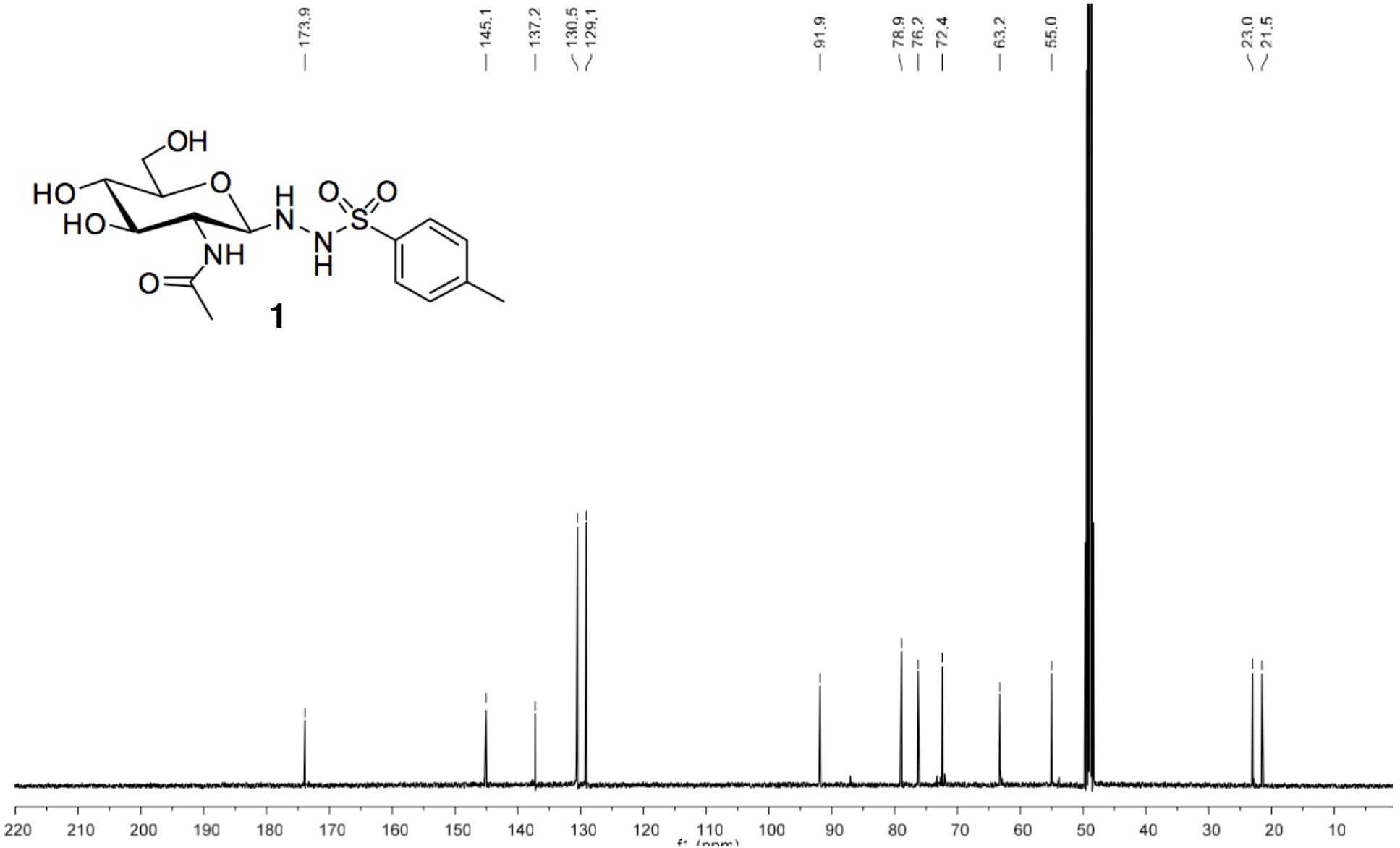
dissolved in dry DMF (5 mL), and subsequently added to the cupric chloride-oxazoline solution. This mixture was shaken vigorously for 30 seconds and then added rapidly to the solution containing the GSH donor *via* syringe at 23 °C. After stirring for 18 hours the crude reaction mixture was poured into dichloromethane (150 mL) and the resultant precipitate was collected *via* vacuum filtration. The precipitate was dissolved in a minimal amount of dry DMF (~ 15 mL) followed by dilution with absolute ethanol (75 mL). A aqueous saturated solution of barium hydroxide was then added dropwise (with shaking) to the DMF/ethanol mixture until litmus paper indicated the pH was approximately 8-9. The resulting precipitate was filtered off and washed with ~75 mL of hot distilled H_2O (~ 70 °C). The combined filtrate was concentrated *via* rotary evaporation. The resultant solid was dissolved in a minimal volume of distilled H_2O (~5 mL) and re-precipitated *via* addition of absolute ethanol (~ 20 mL). Precipitate was isolated *via* centrifugation. The dissolution-precipitation was repeated three times, after which the desired glycosyl 1-phosphate **12** (583 mg, 1.04 mmol, white solid) was obtained in approximately 80% purity as a 3:1 mixture of α:β anomers. The crude precipitate was purified *via* an ion-exchange procedure similar to that outlined for compound **7** to yield ammonium α-D-lactopyranosyl-1-phosphate (**12A**).^{1}H NMR (400 MHz, D_2O): 5.31 (dd, 1H, *J* = 8.0, *J* = 4.0 Hz, H-1α), 4.79 (app. t, 0.25H, *J* = 8.0 Hz, H-1β), 4.31 (d, 1H, *J* = 8.0 Hz, H-1'α), 4.30 (d, 0.25H, *J* = 8.0 Hz, H-1'β), 3.92-3.87 (m, 1H, H-5'α), 3.87-3.84 (m, 0.25H, H-6aβ), 3.80-3.73 (m, 3.25H, H-6aα, H-6a'α, H-6a'β, H-3α), 3.72-3.61 (m, 3.50H, H-6b'α, H-6b'β, H-6bα, H-6bβ, H-5α), 3.55-3.47 (m, 4.25H, H-4α, H-3β, H-5β, H-5'β, H-3'α, H-3'β, H-4'α, H-4'β), 3.44-3.37 (m, 2.50H, H-2'α, H-2'β, H-4β, H-2α), 3.25-3.21 (m, 0.25H, H-2β). ^{13}C NMR (100 MHz, D_2O) δ 102.8, 93.2, 78.6, 78.4, 75.3, 72.4, 71.7, 70.9, 70.6, 68.5, 60.9, 59.9. ^{31}P NMR (162 MHz, D_2O) δ 2.04. HRMS *m*/*z* calcd. for $C_8H_{12}O_9P$ (M-) 259.0224, found 259.0217.

(33) Derappe, C.; Bauvy, C.; Lemonnier, M.; Lhermitte, M.; Platzer, N.; Egge, H.; Peter Katalinić, J.; van Halbeek, H.; Kamerling, J. P.; Vliegenthart, F. G. *Carbohydr. Res.* **1986**, *1*, 273-284.
(34) Sabesan, S.; Neira, S. *Carbohydr. Res.* **1992**, *223*, 169-185.
(35) Poláková, M.; Roslund, M. U.; Ekholm, F. S.; Saloranta, T.; Leino, R. *Eur. J. Org. Chem.* **2009**, 870-888.

^{1}H NMR 400 MHz (CD_3OD, 25 °C)



^{13}C NMR 100 MHz (CD_3OD, 25 °C)



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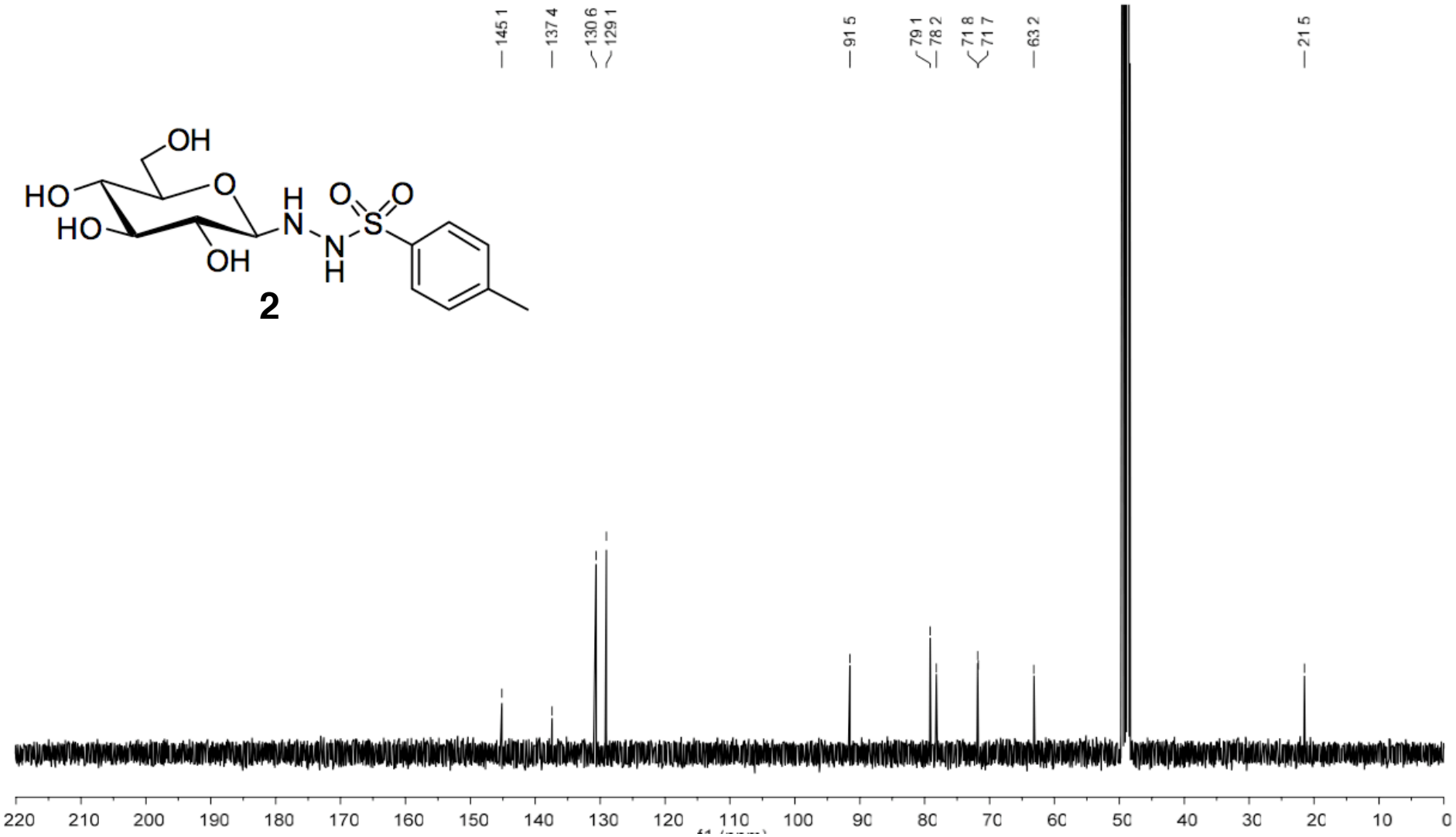
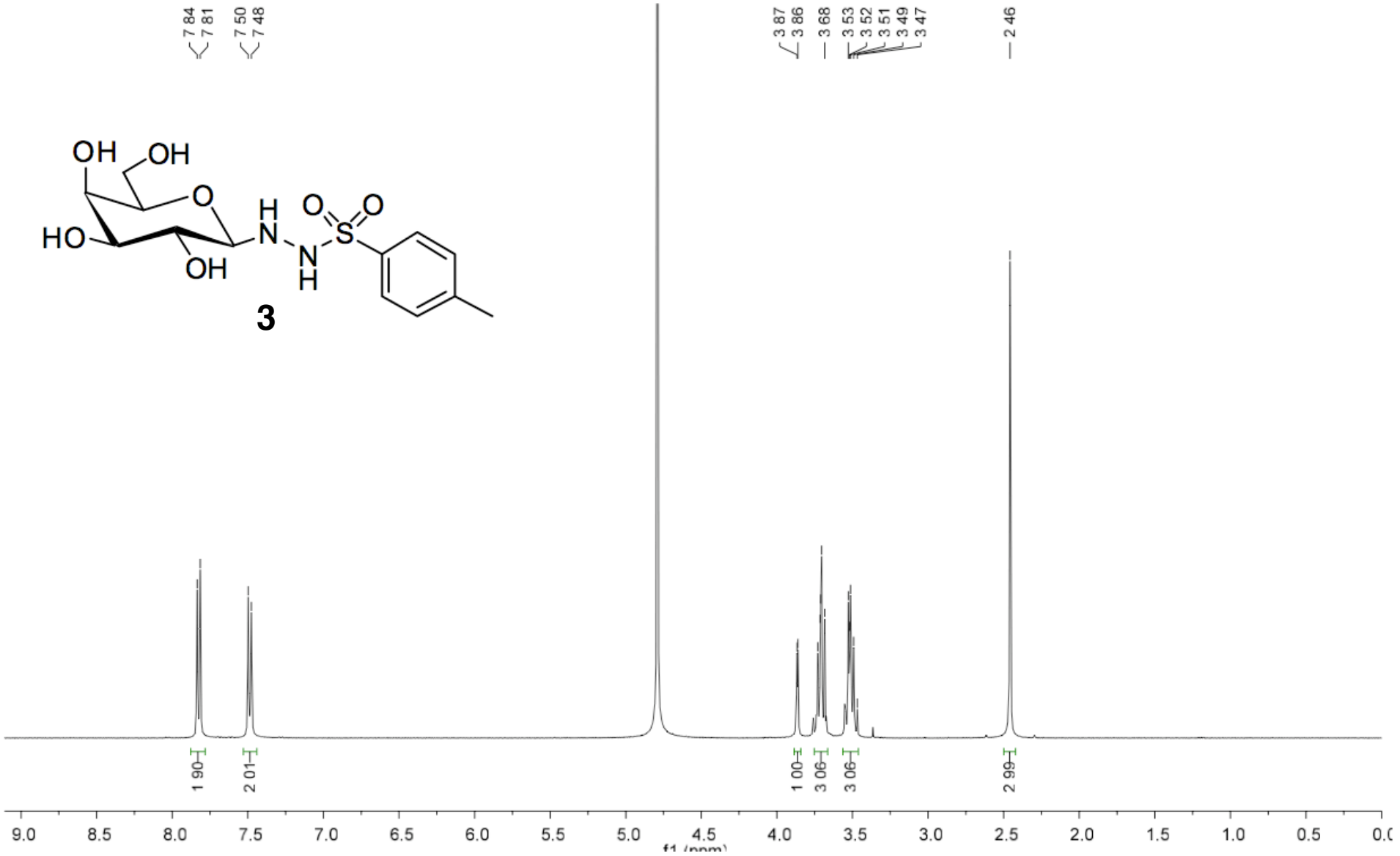
^{13}C NMR 100 MHz (CD_3OD, 25 °C)



^{1}H NMR 400 MHz (D_2O, 25 °C)



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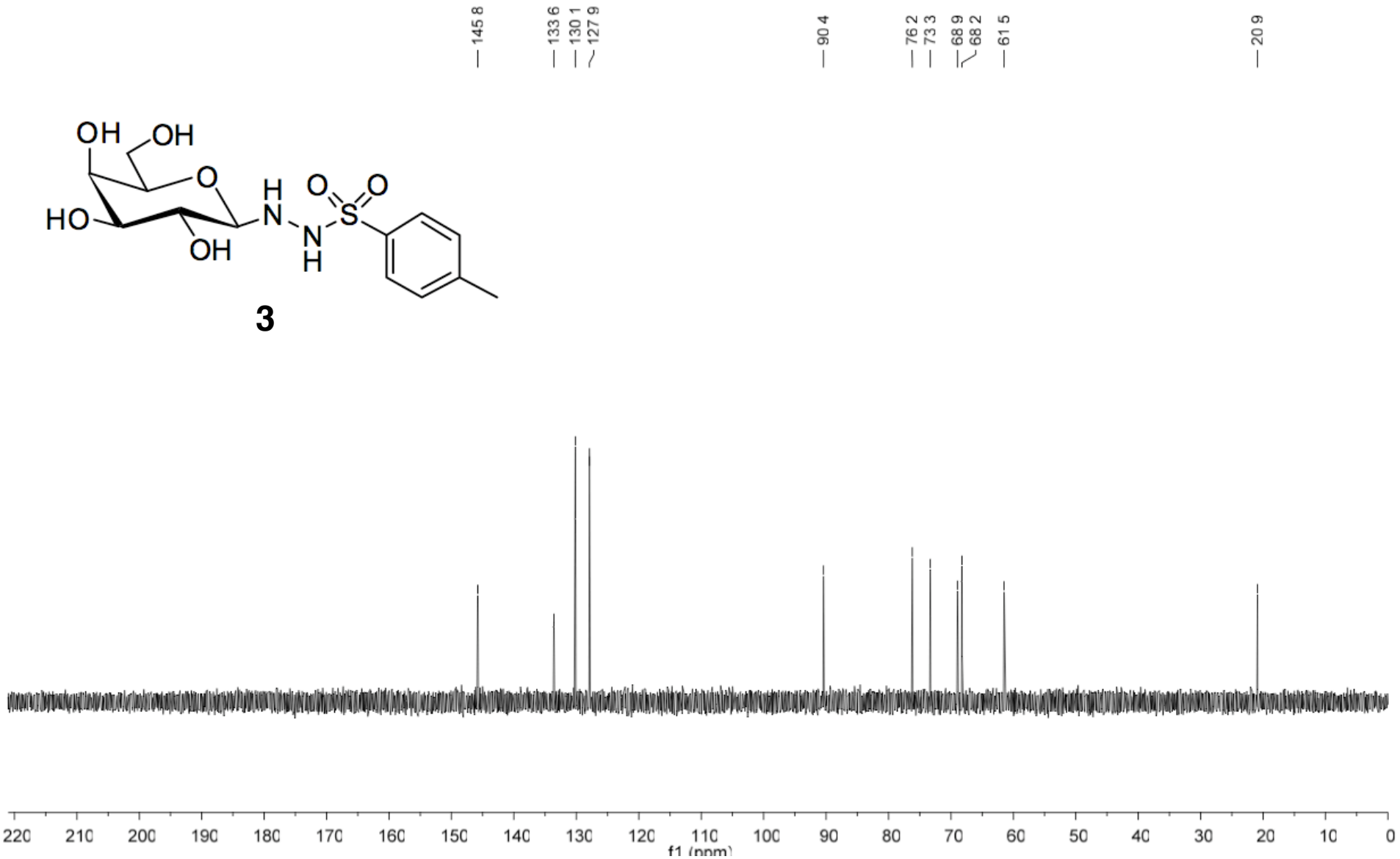

3

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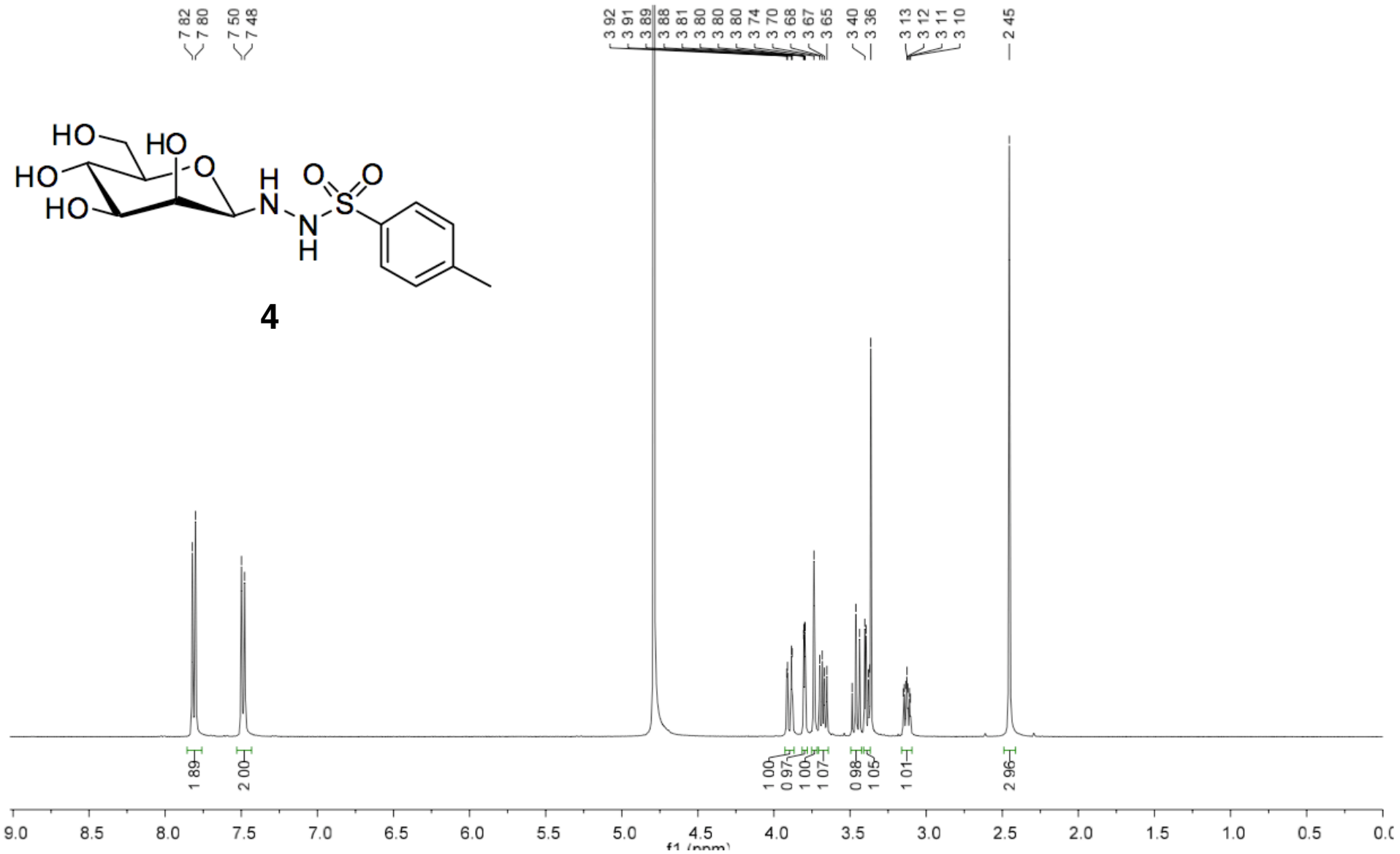

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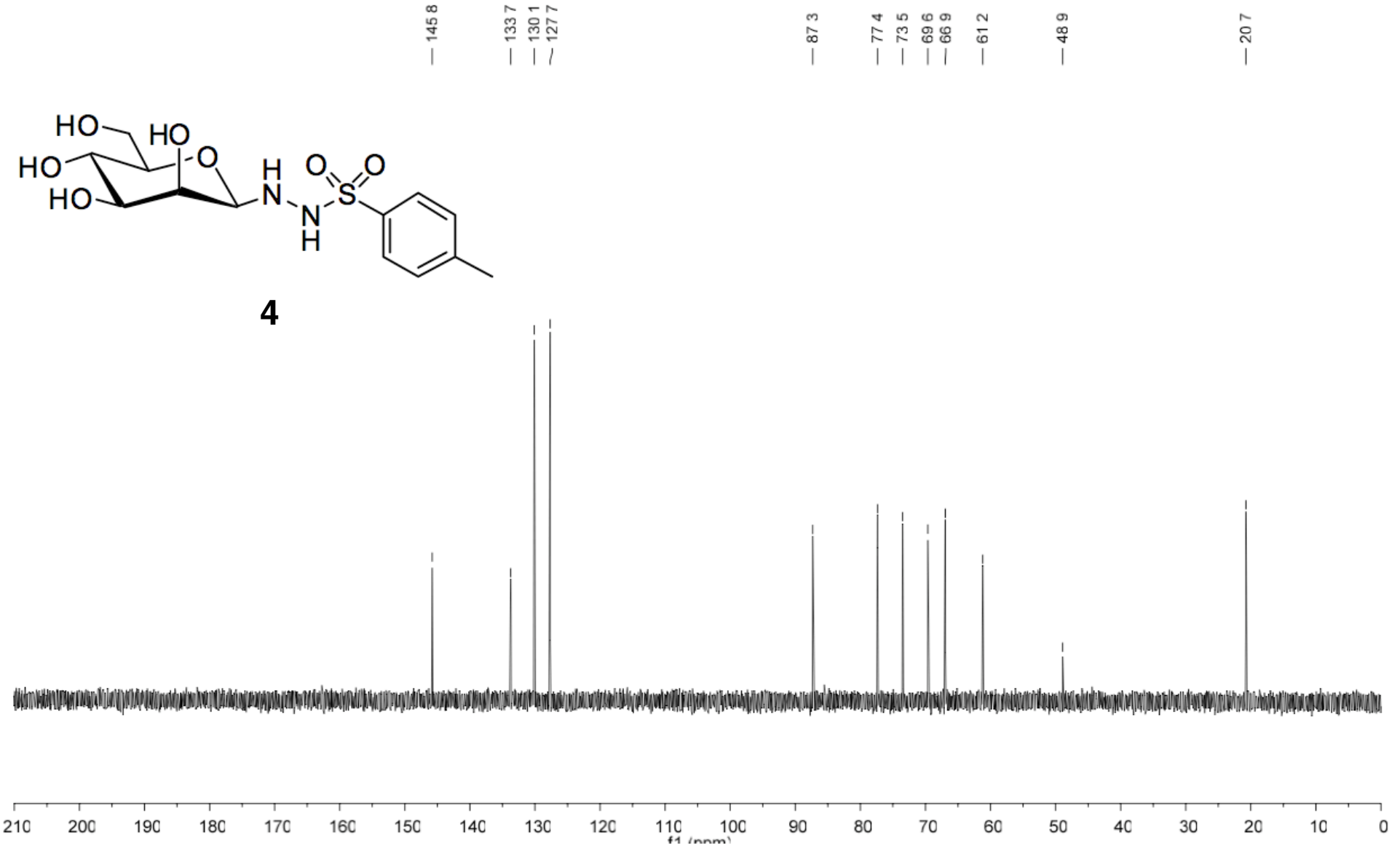

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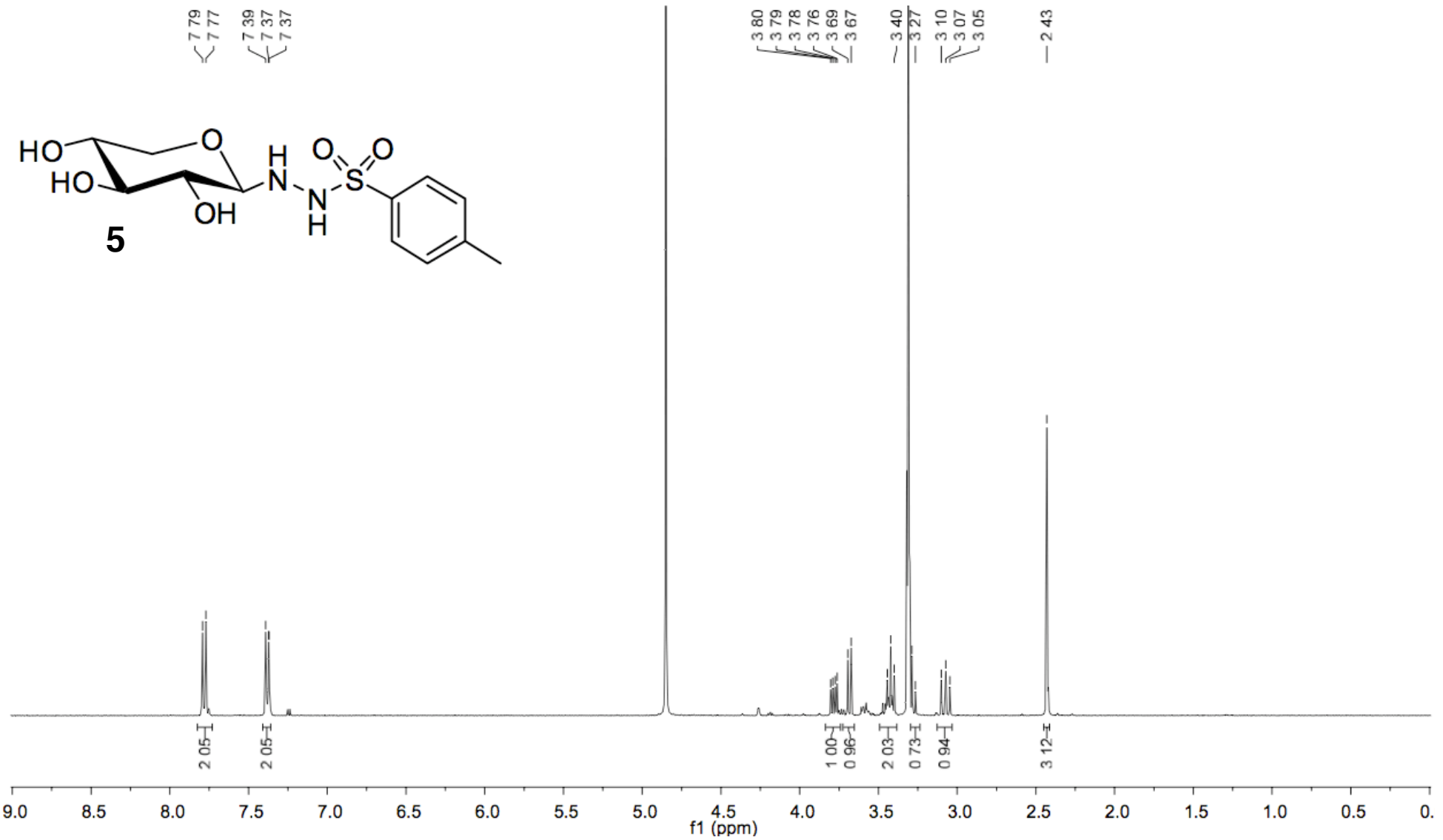

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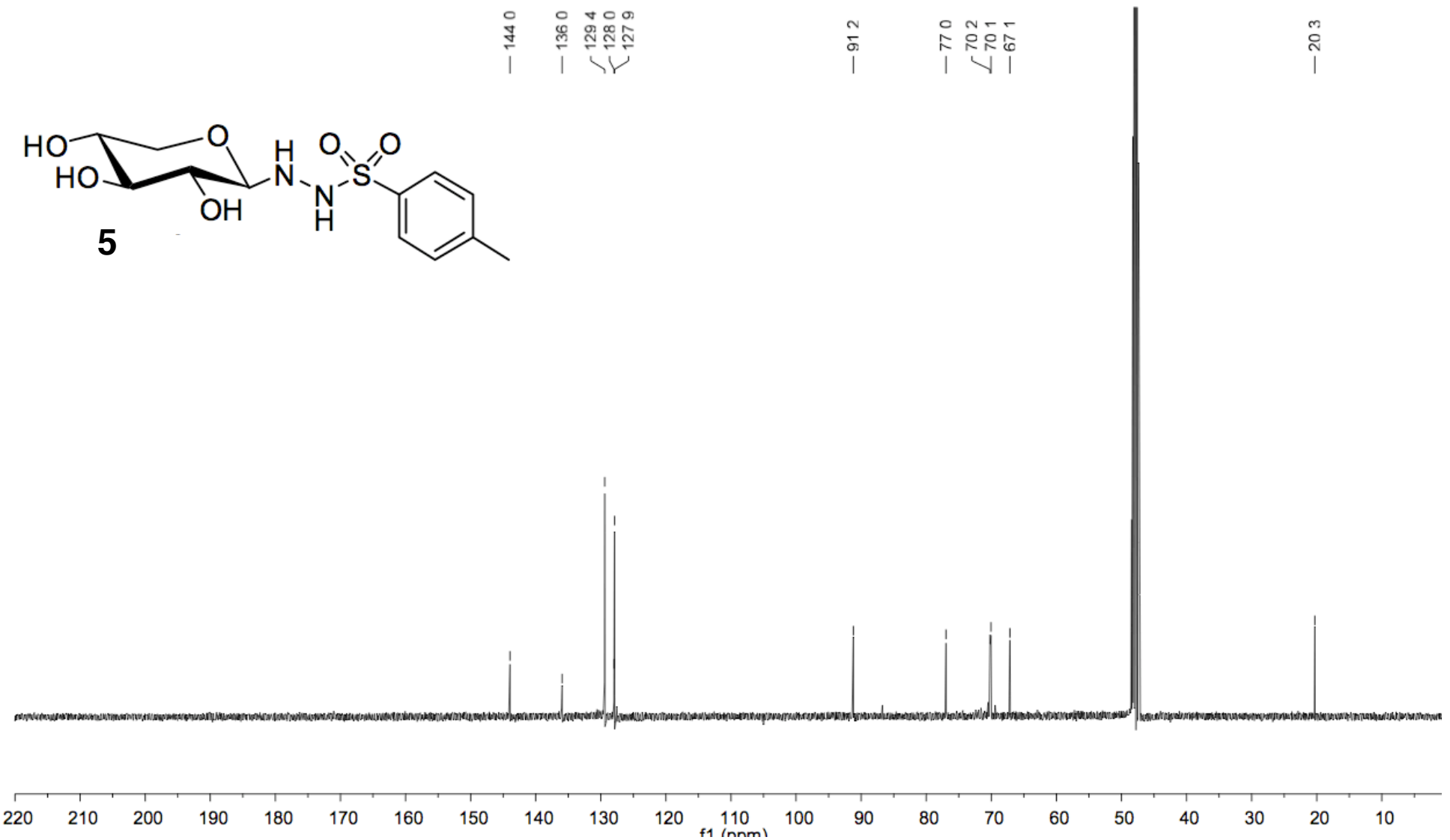

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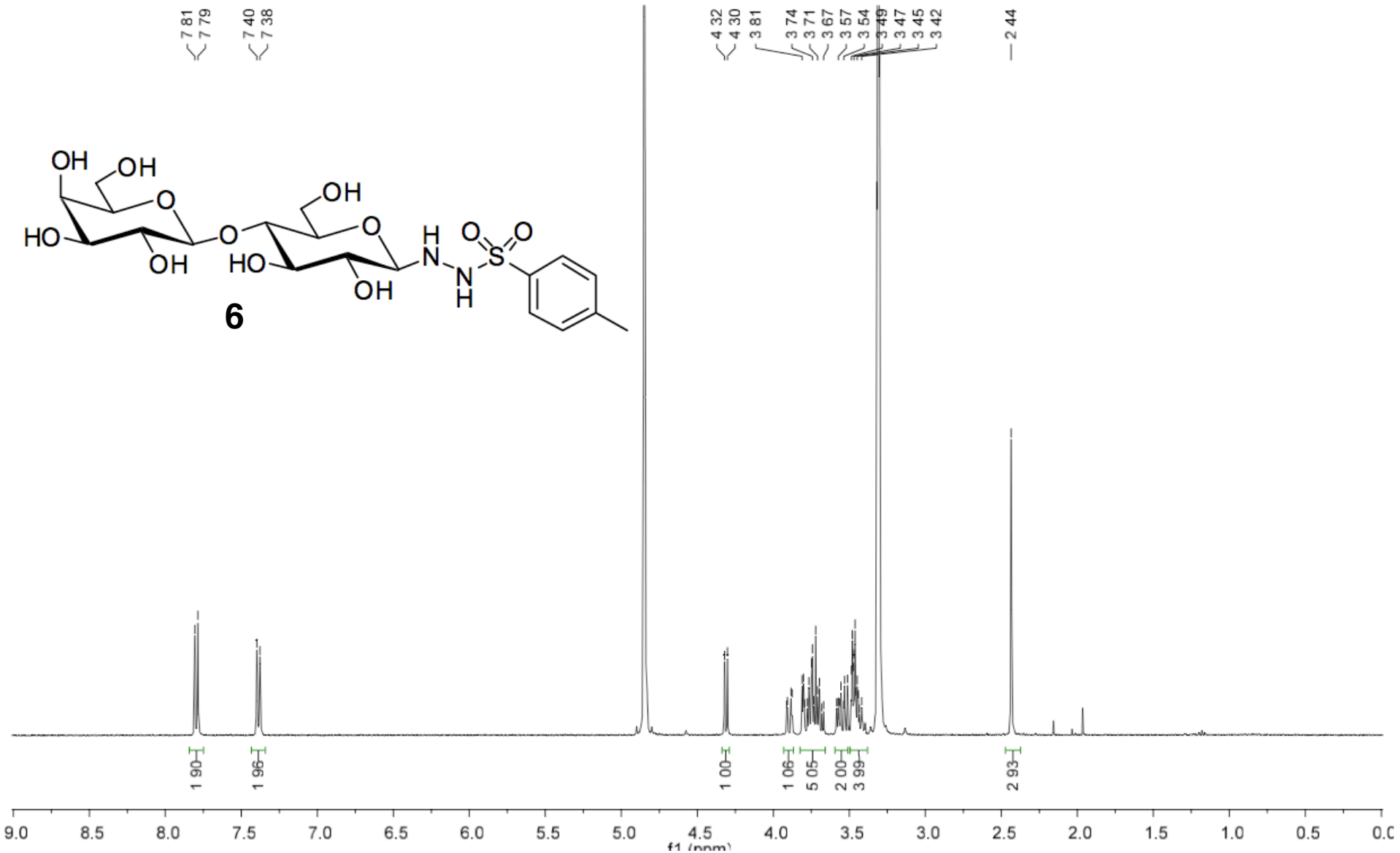

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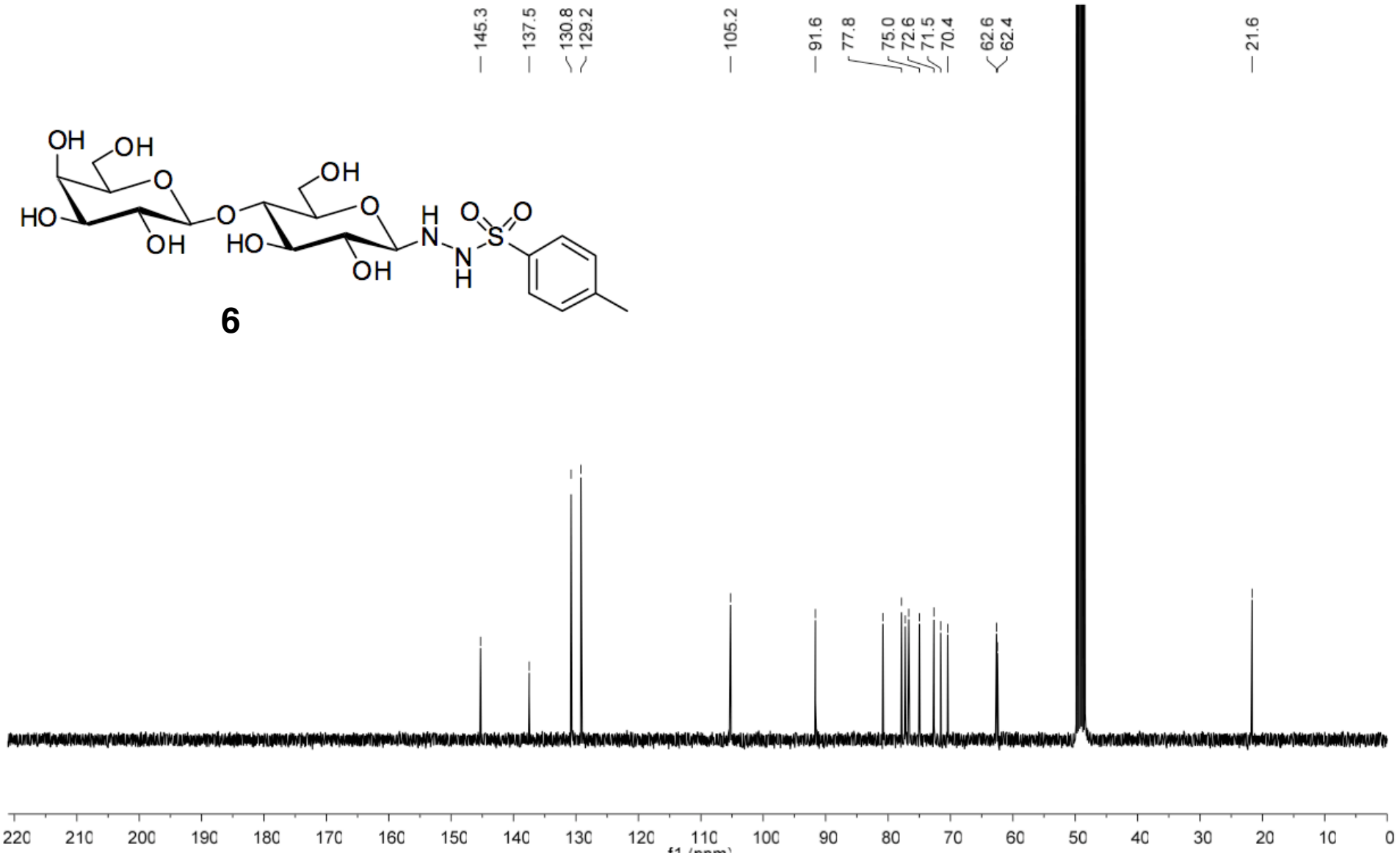

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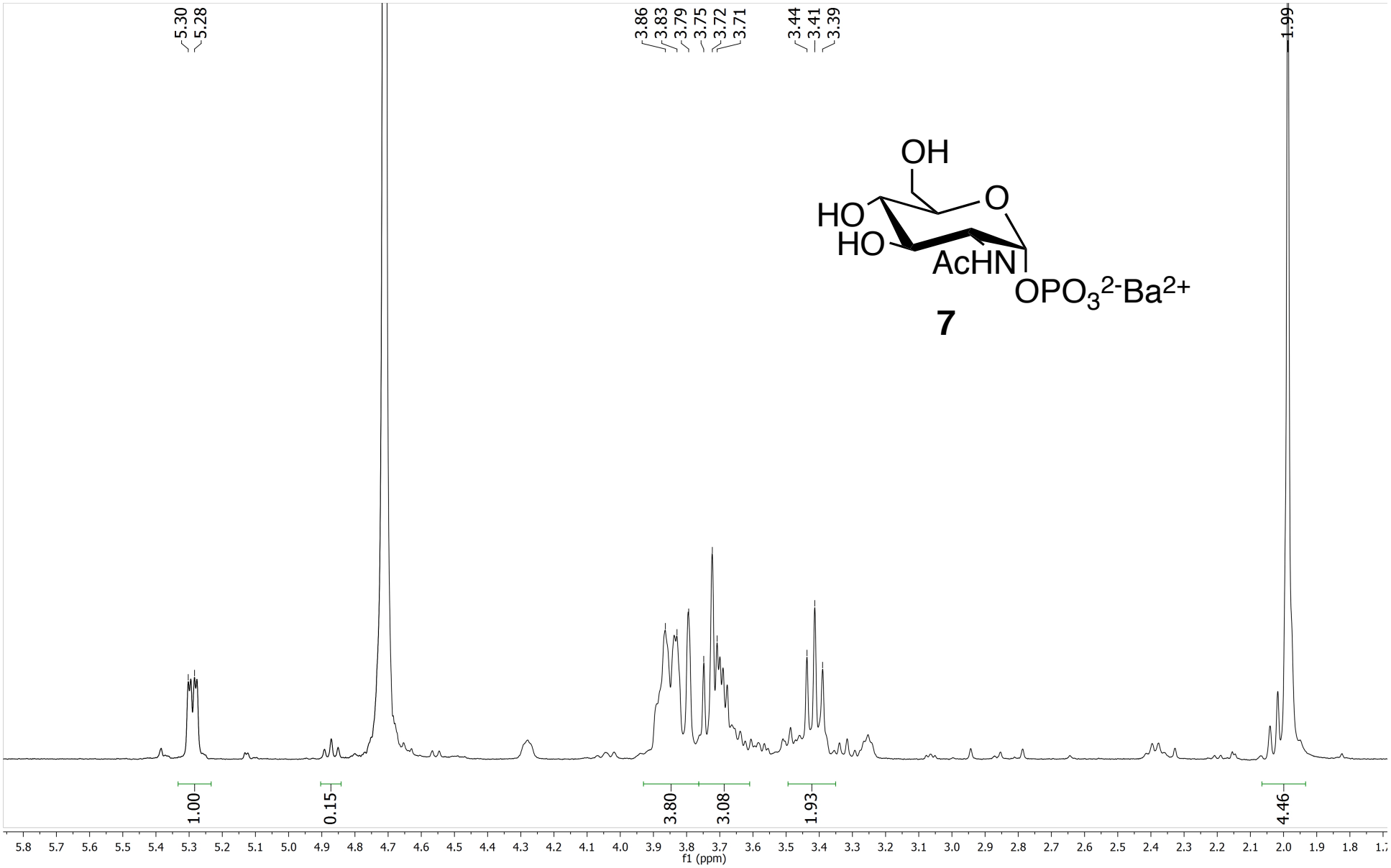

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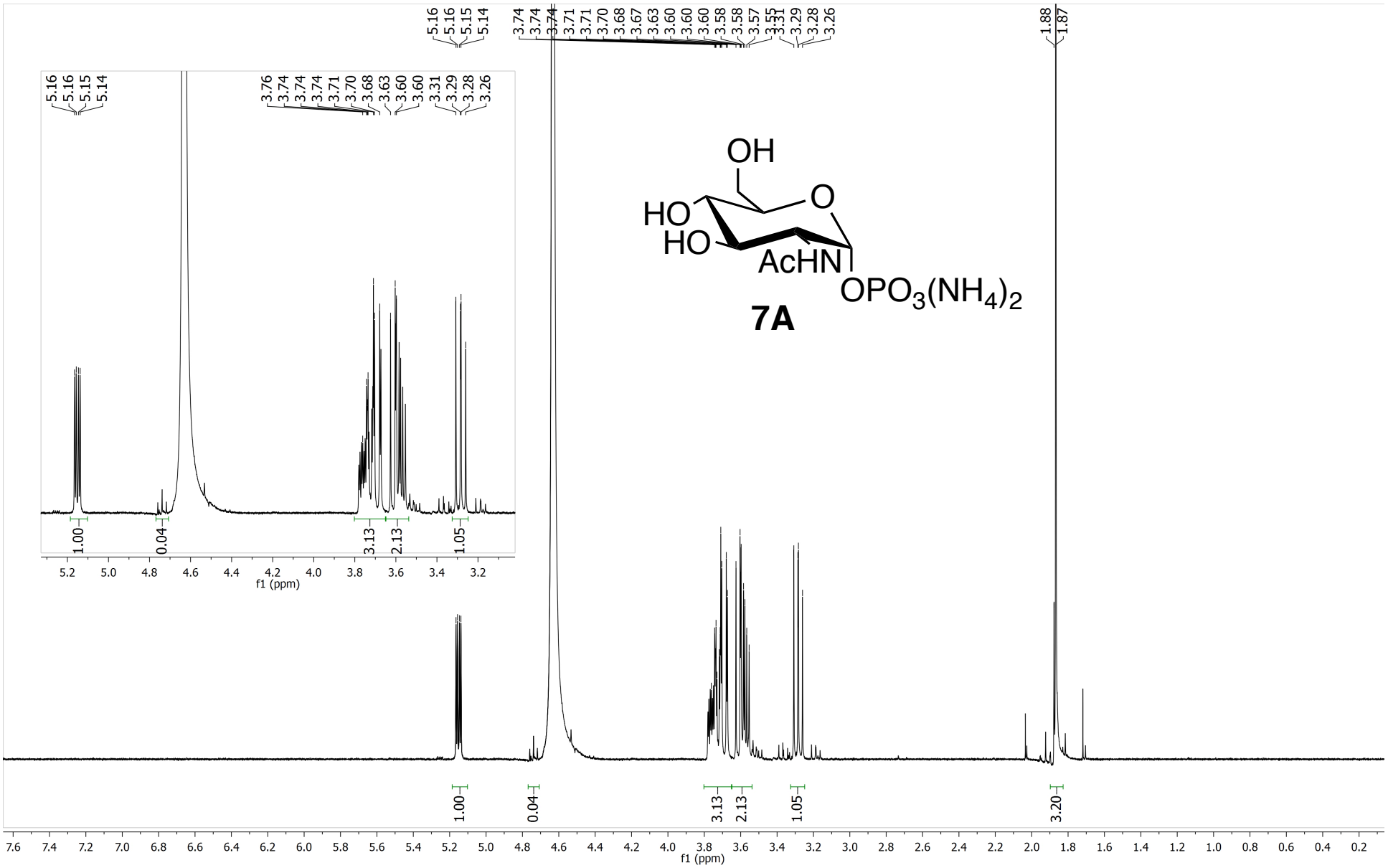
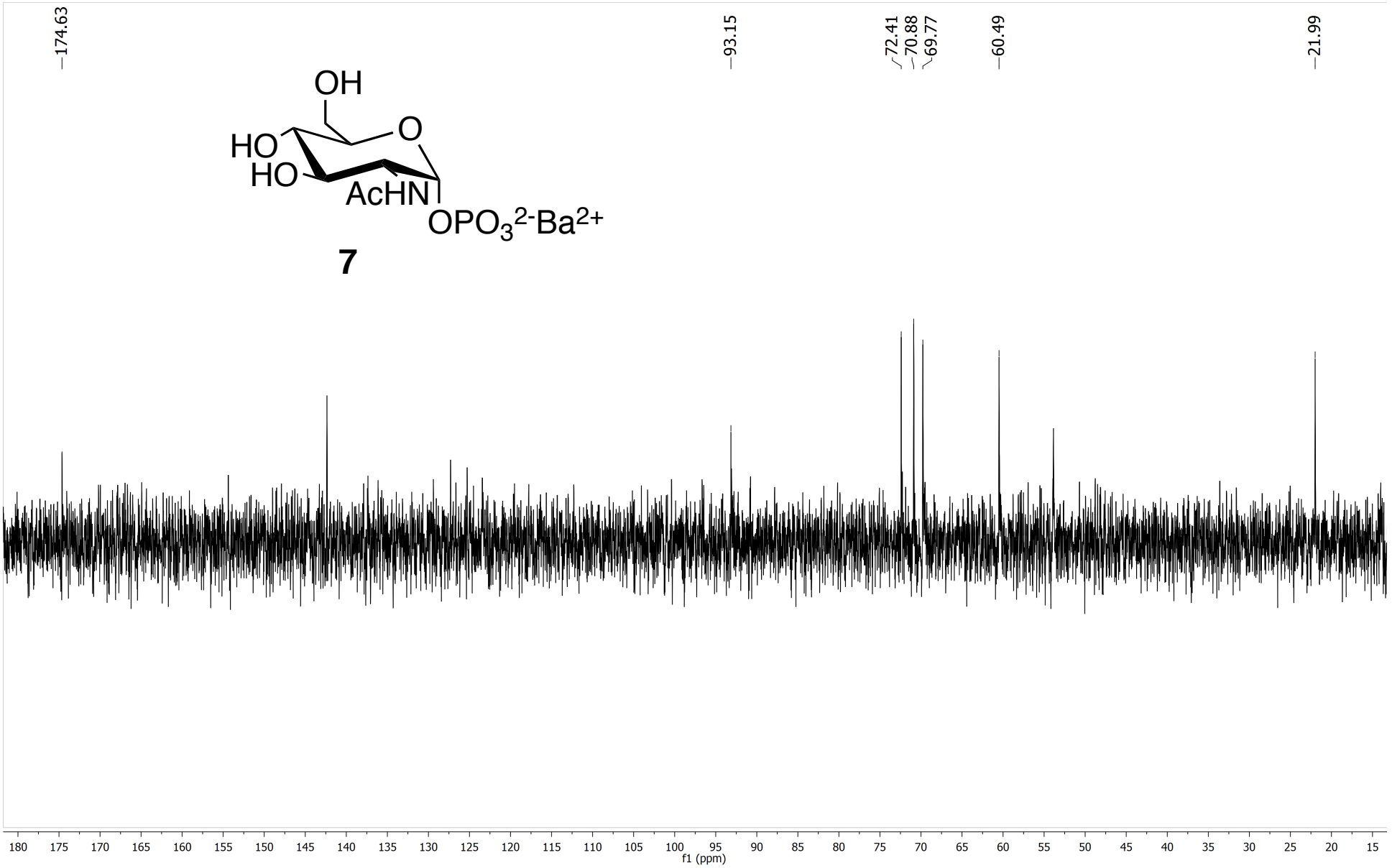
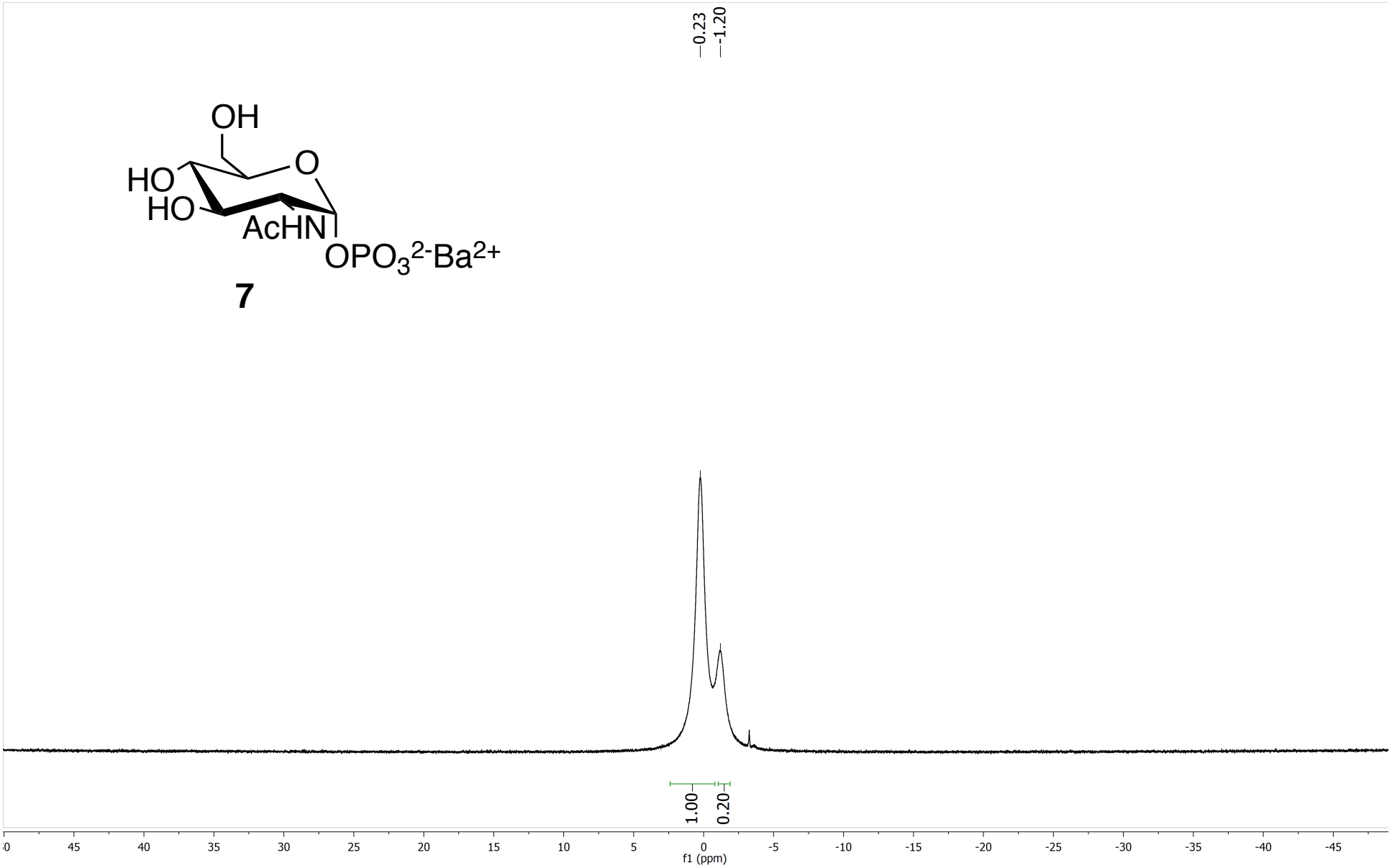


^{13}C NMR 100 MHz (D_2O, 25 °C)



^{31}P NMR 162 MHz (D_2O, 25 °C)



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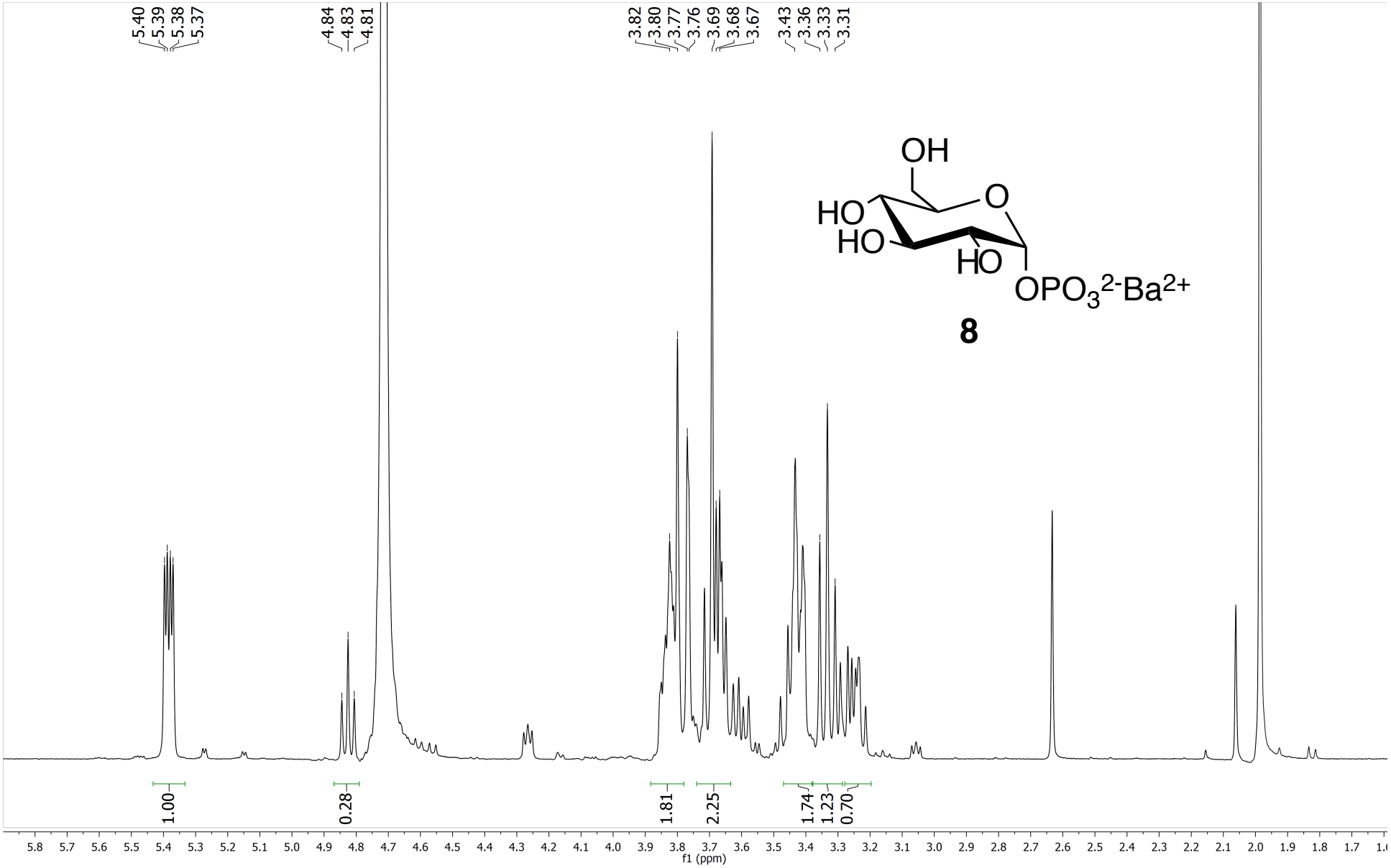

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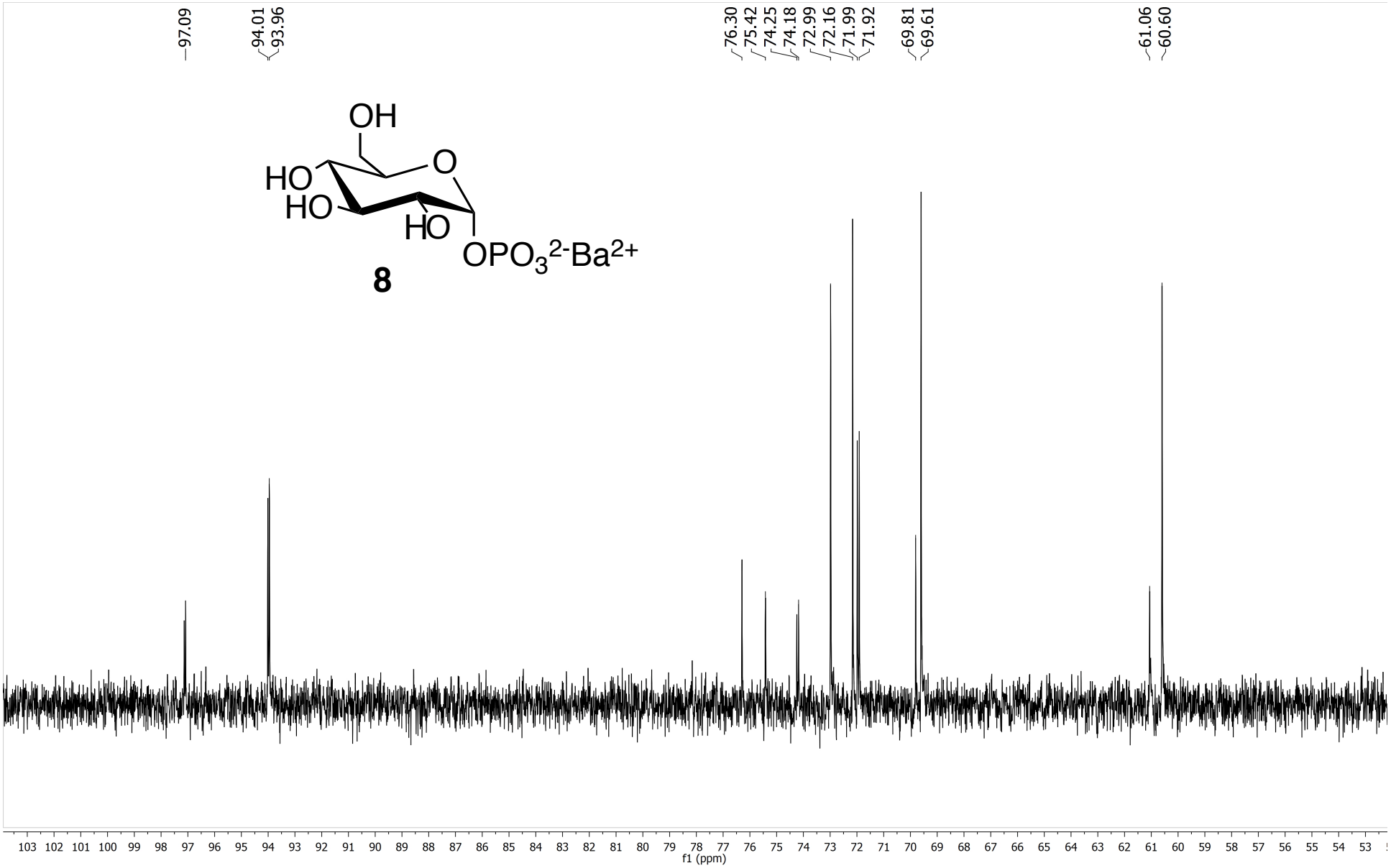

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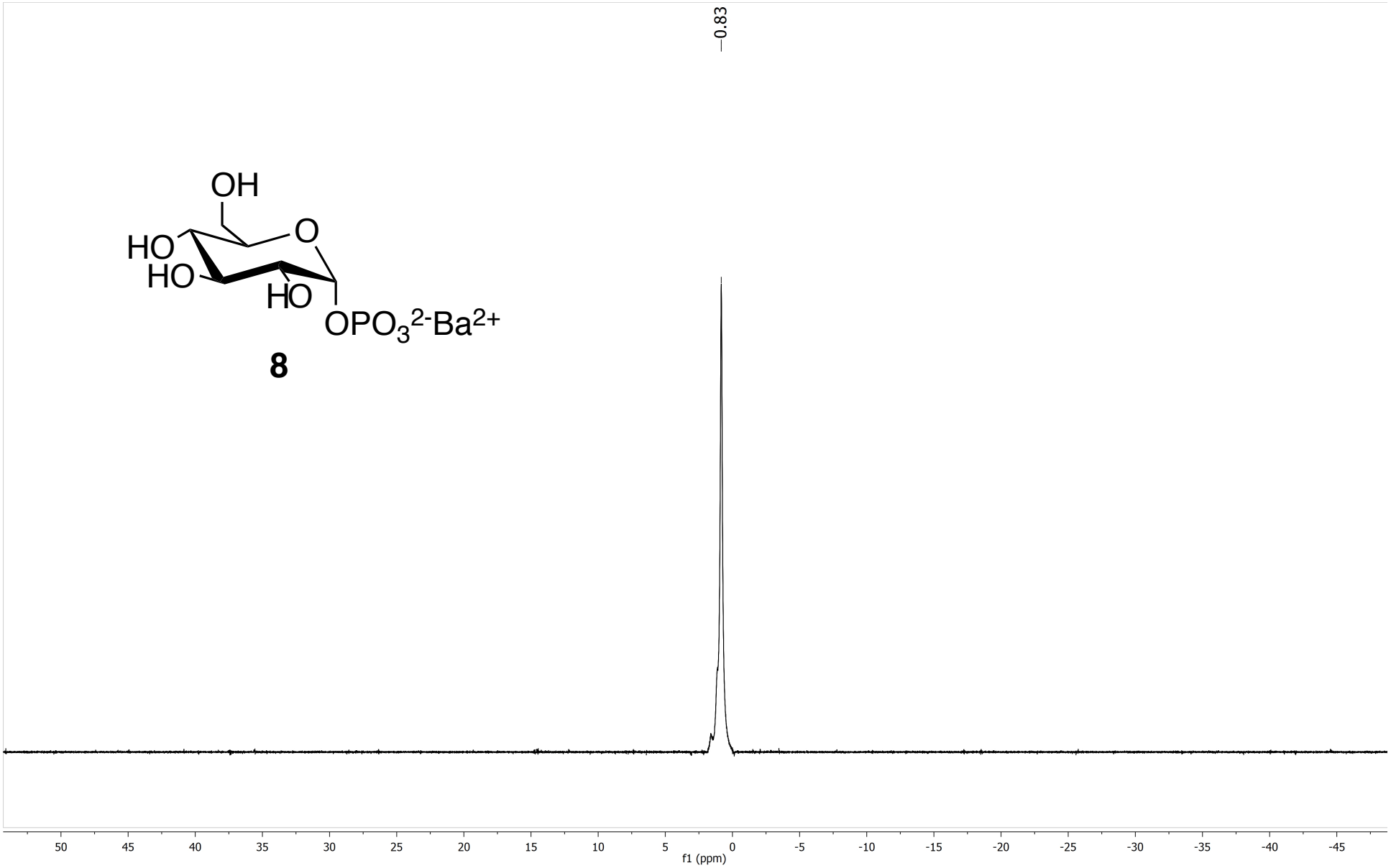

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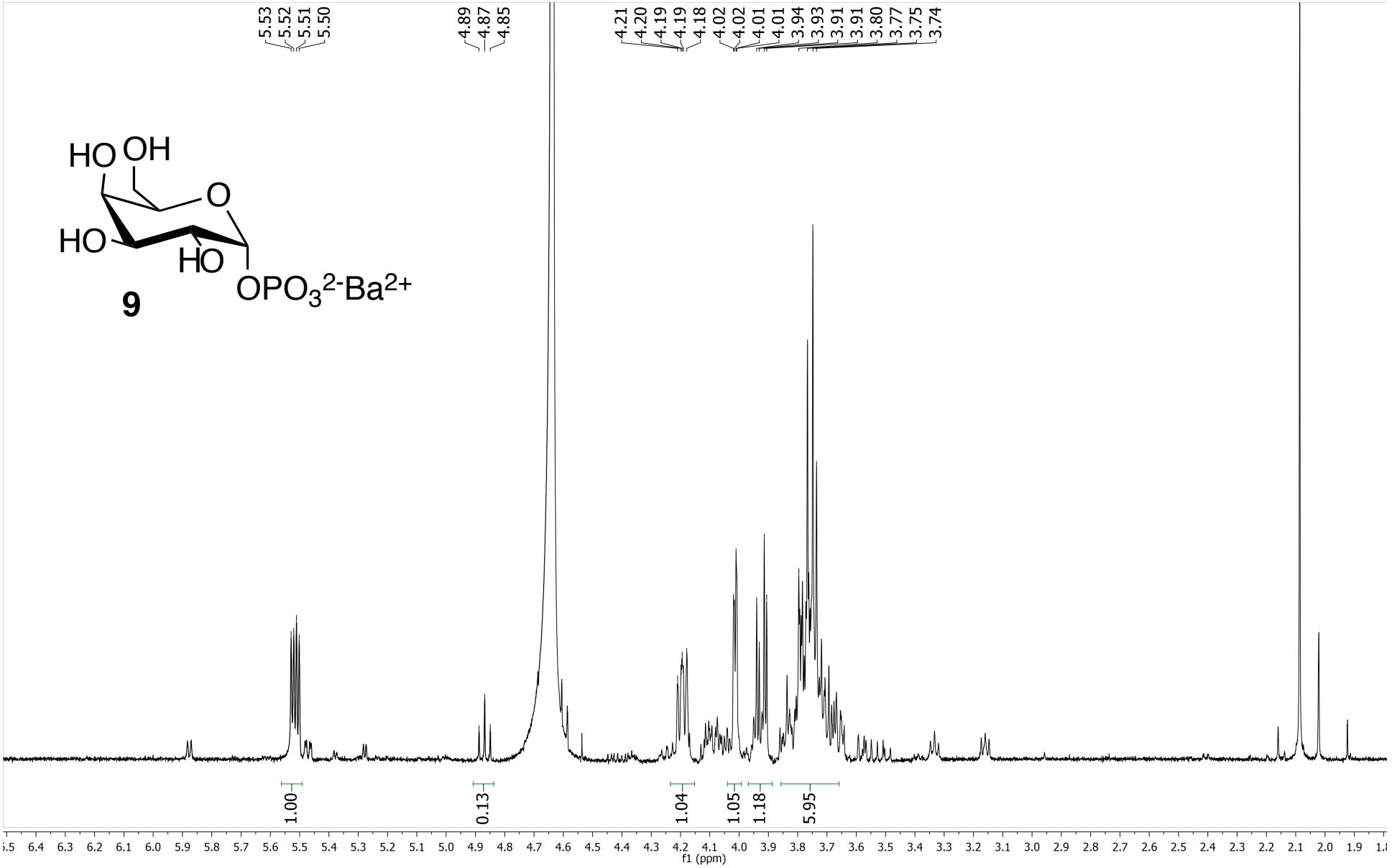

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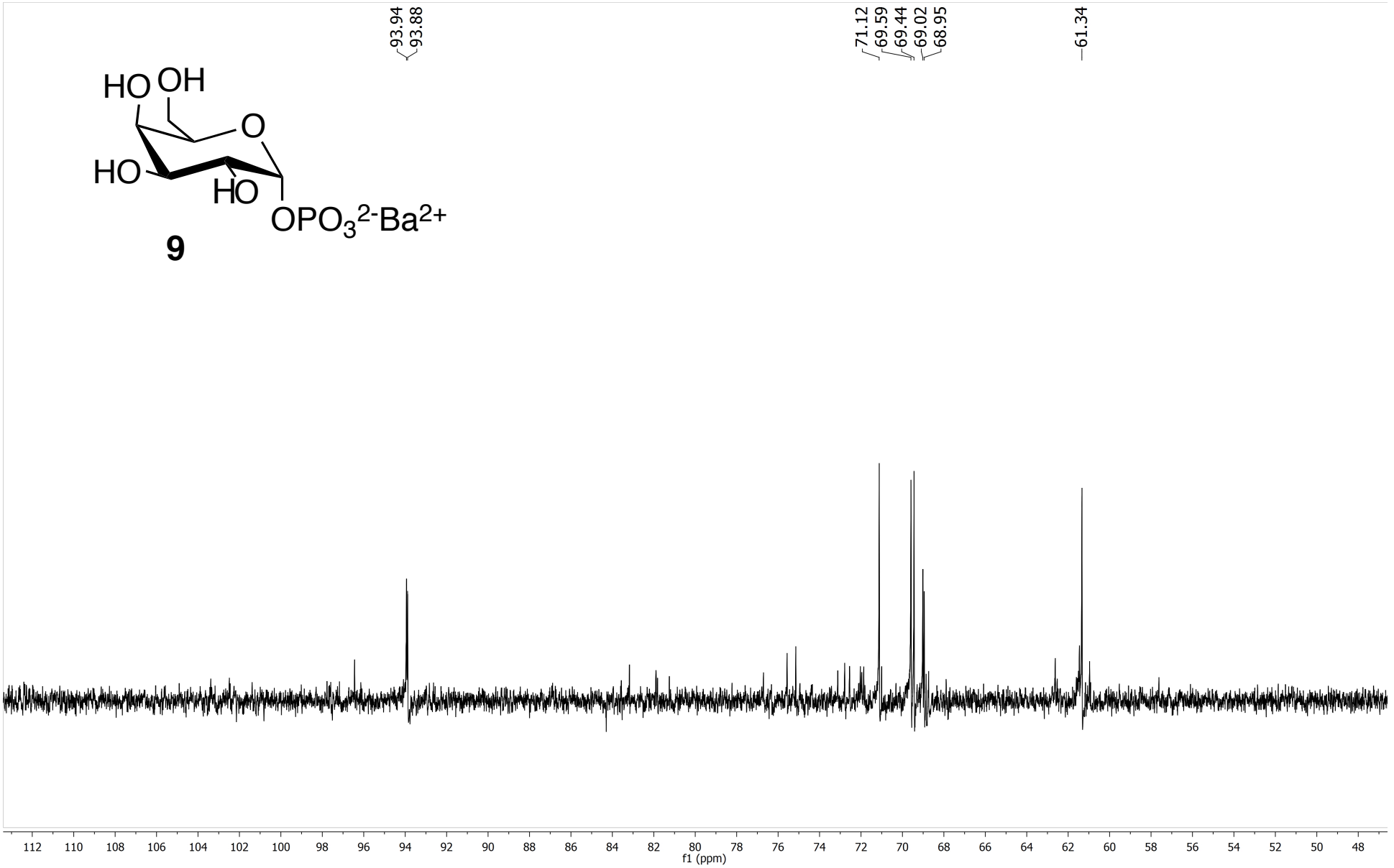

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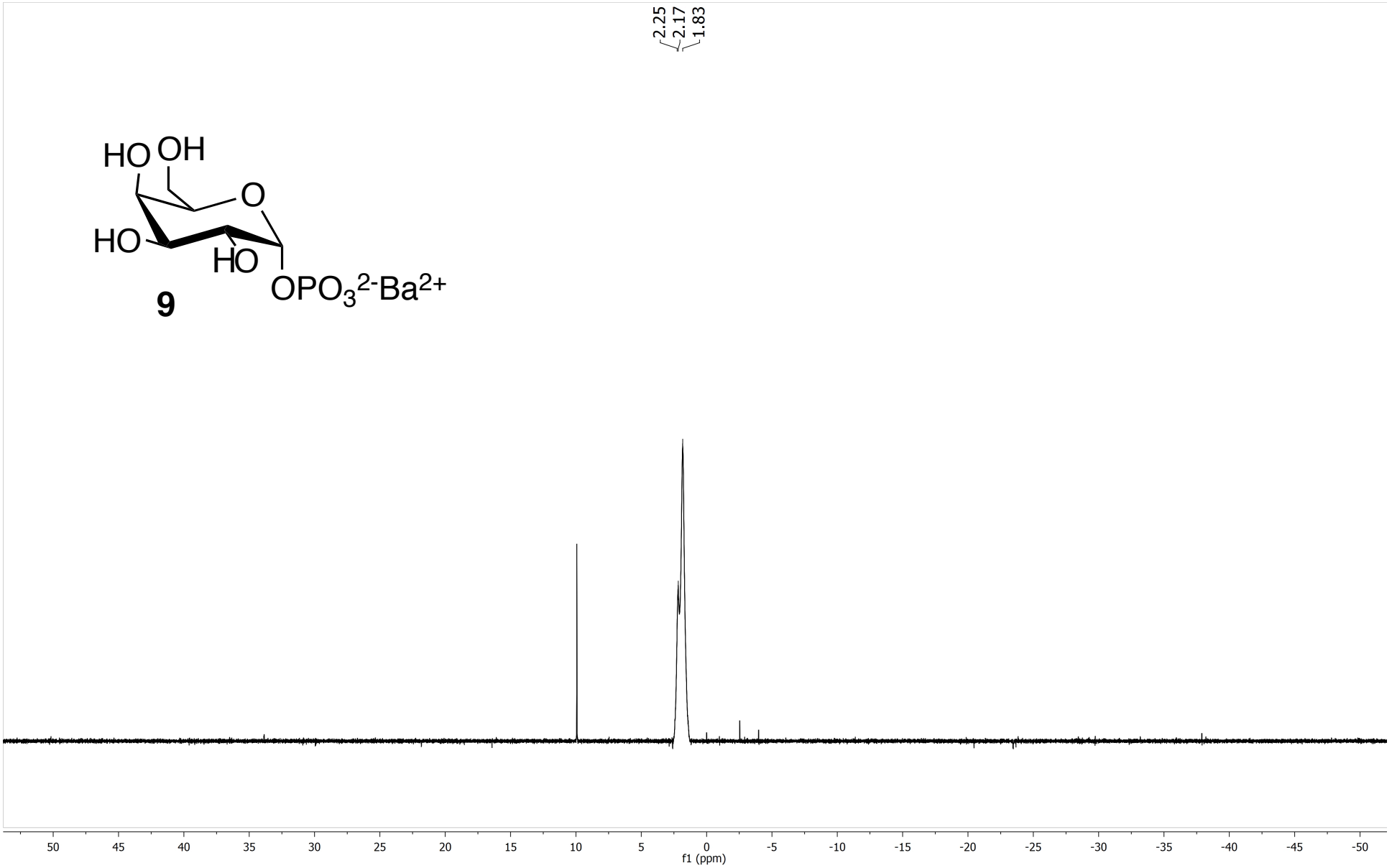

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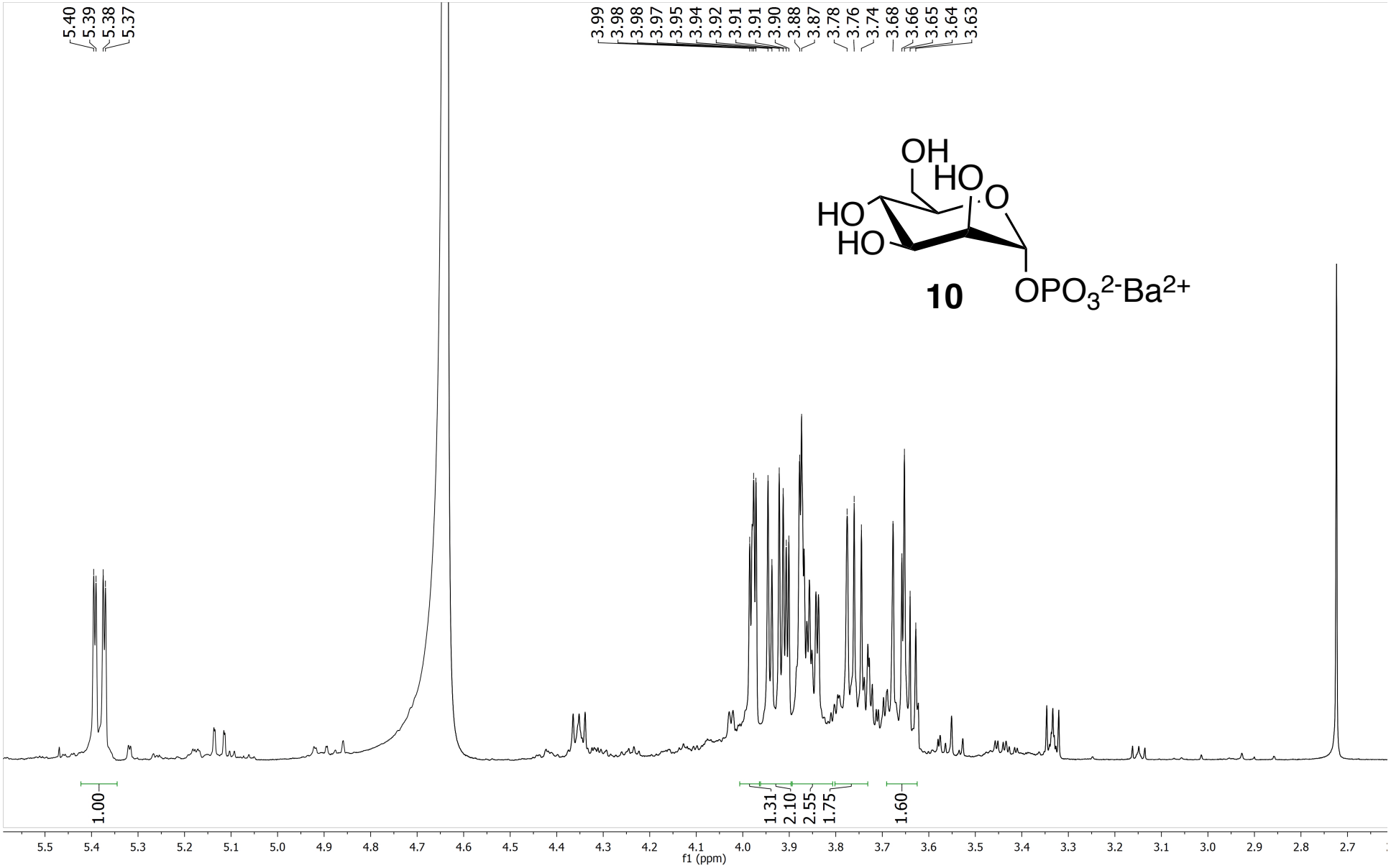

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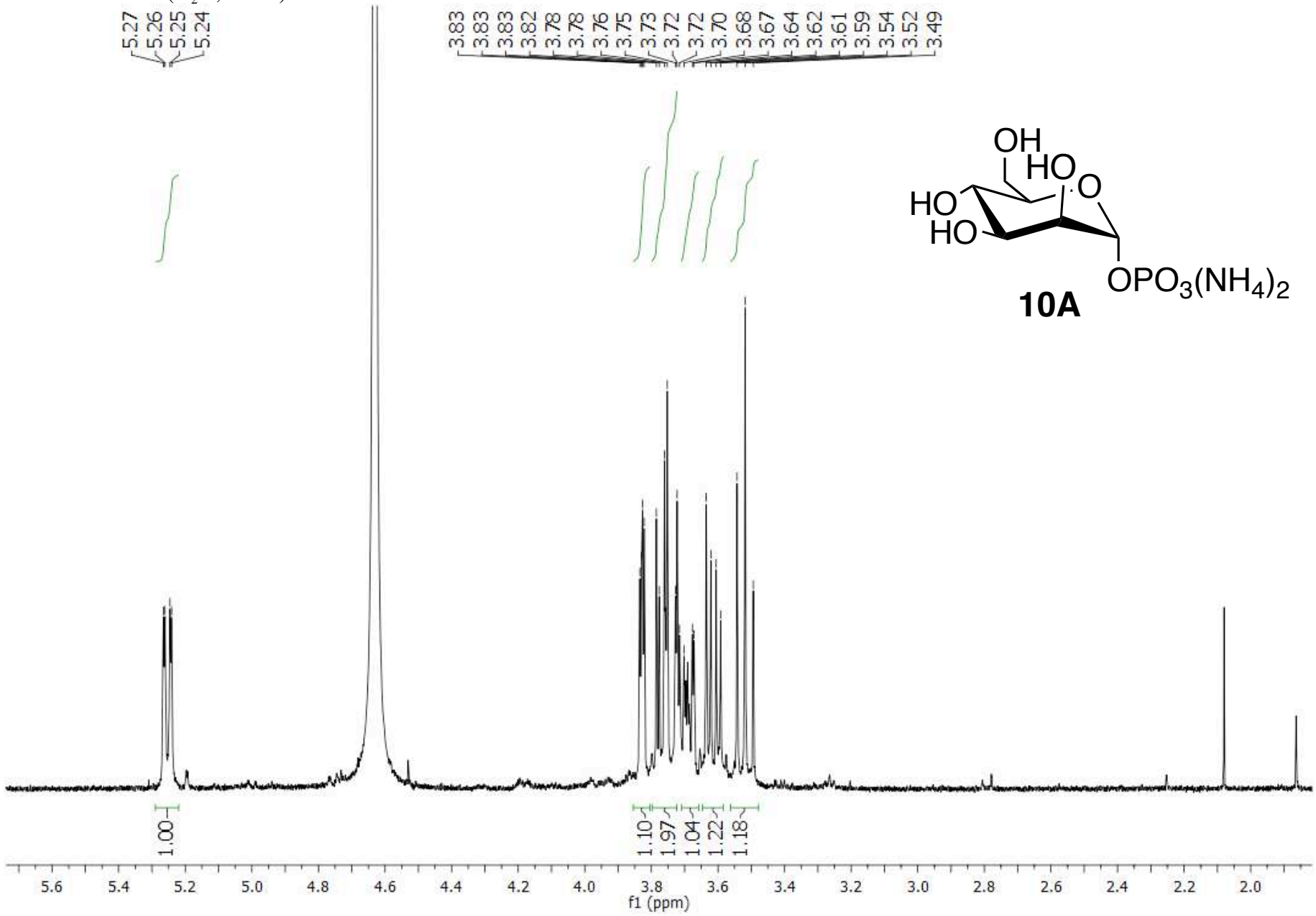

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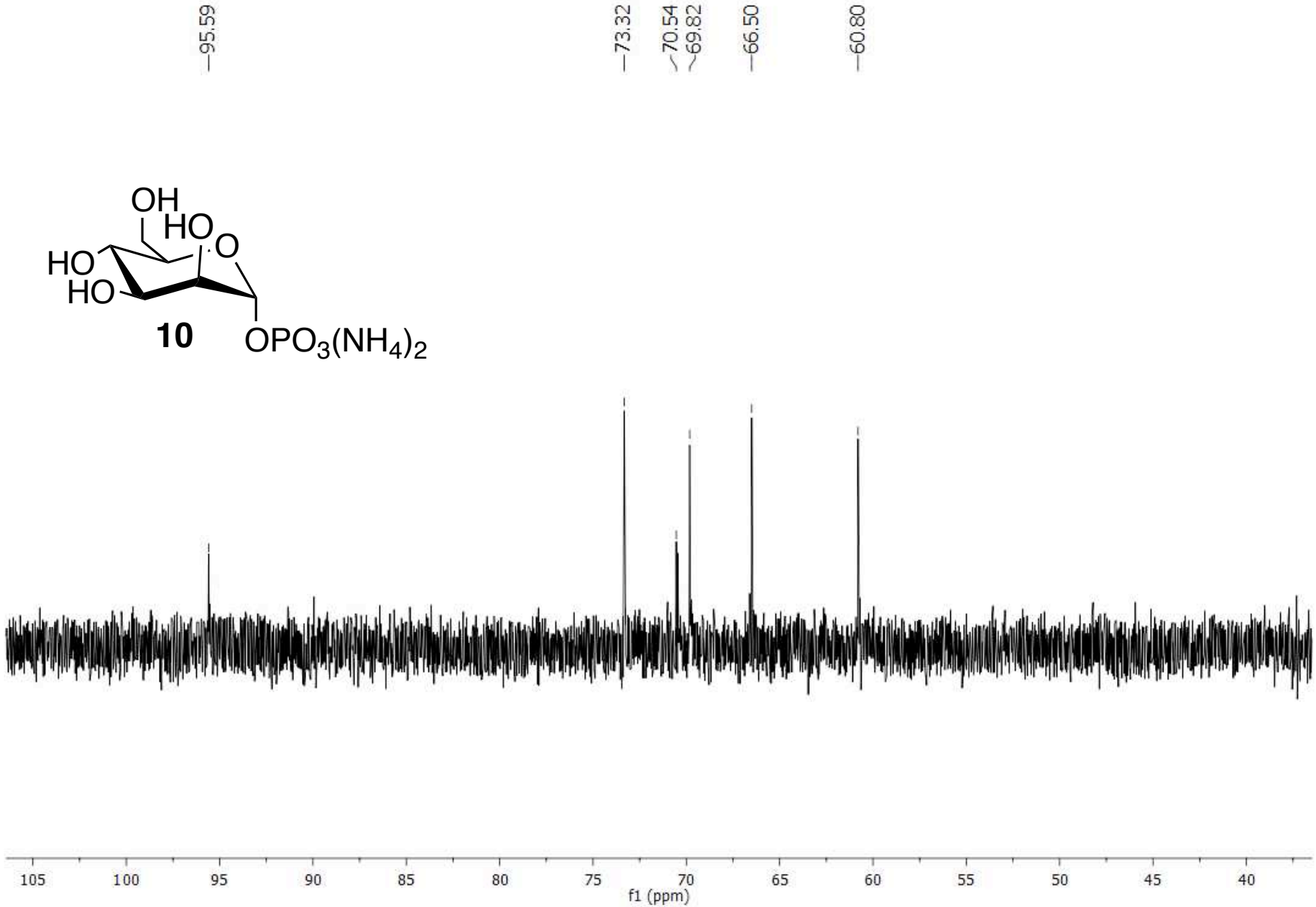

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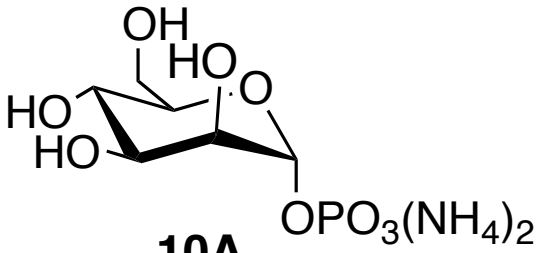
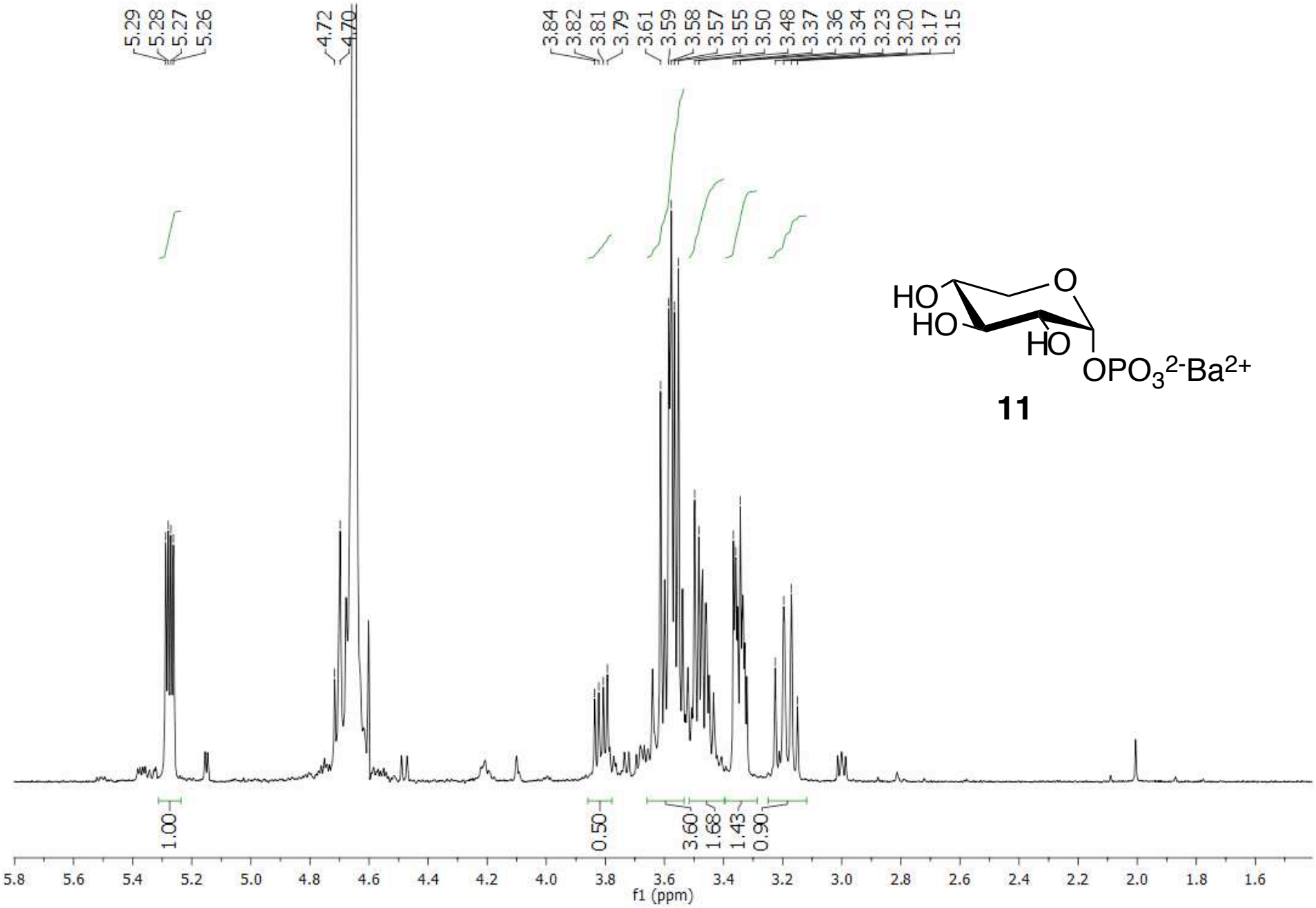


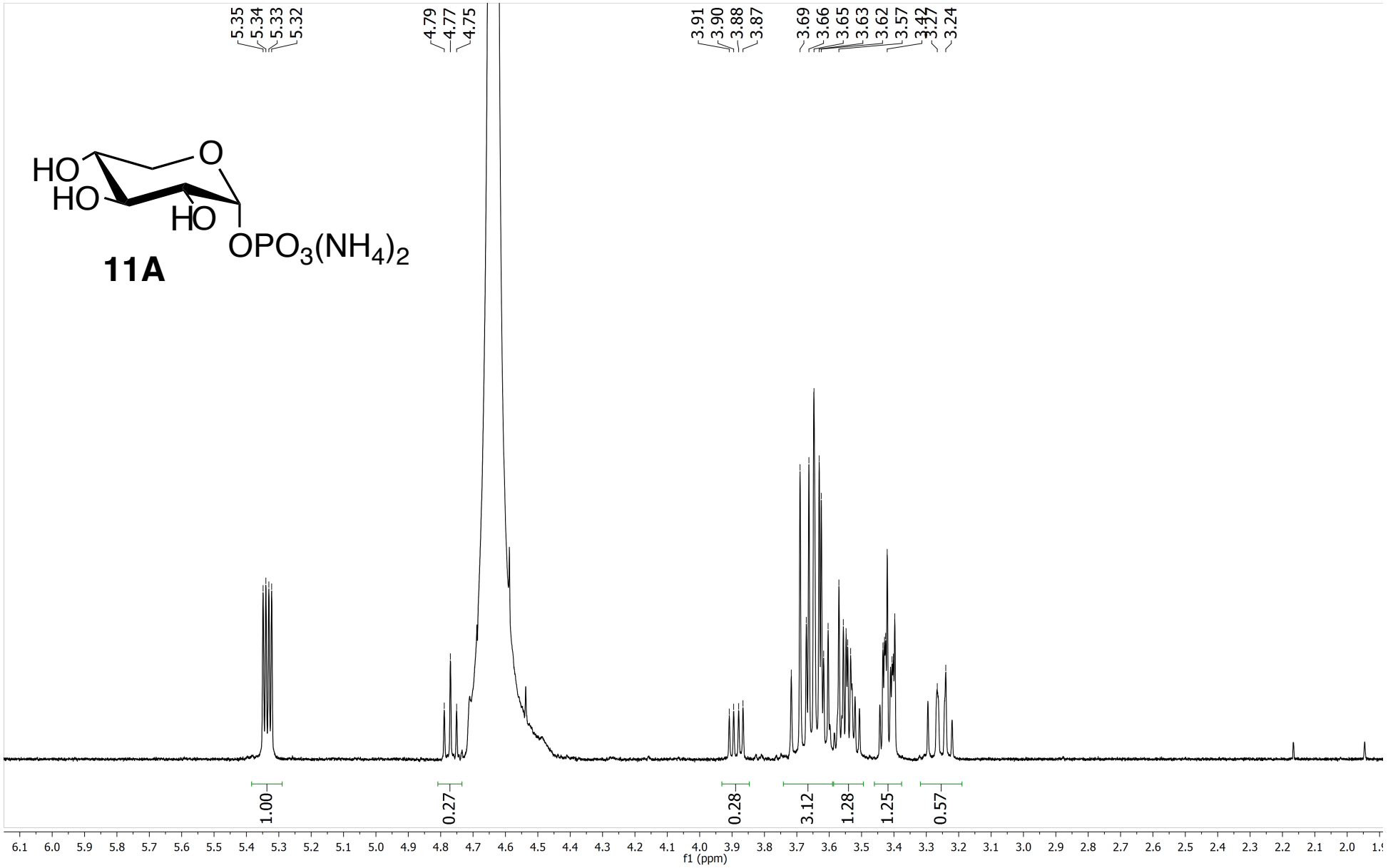
10A

^{1}H NMR 400 MHz (D_2O, 25 °C)



11

^{1}H NMR 400 MHz (D_2O, 40 °C)



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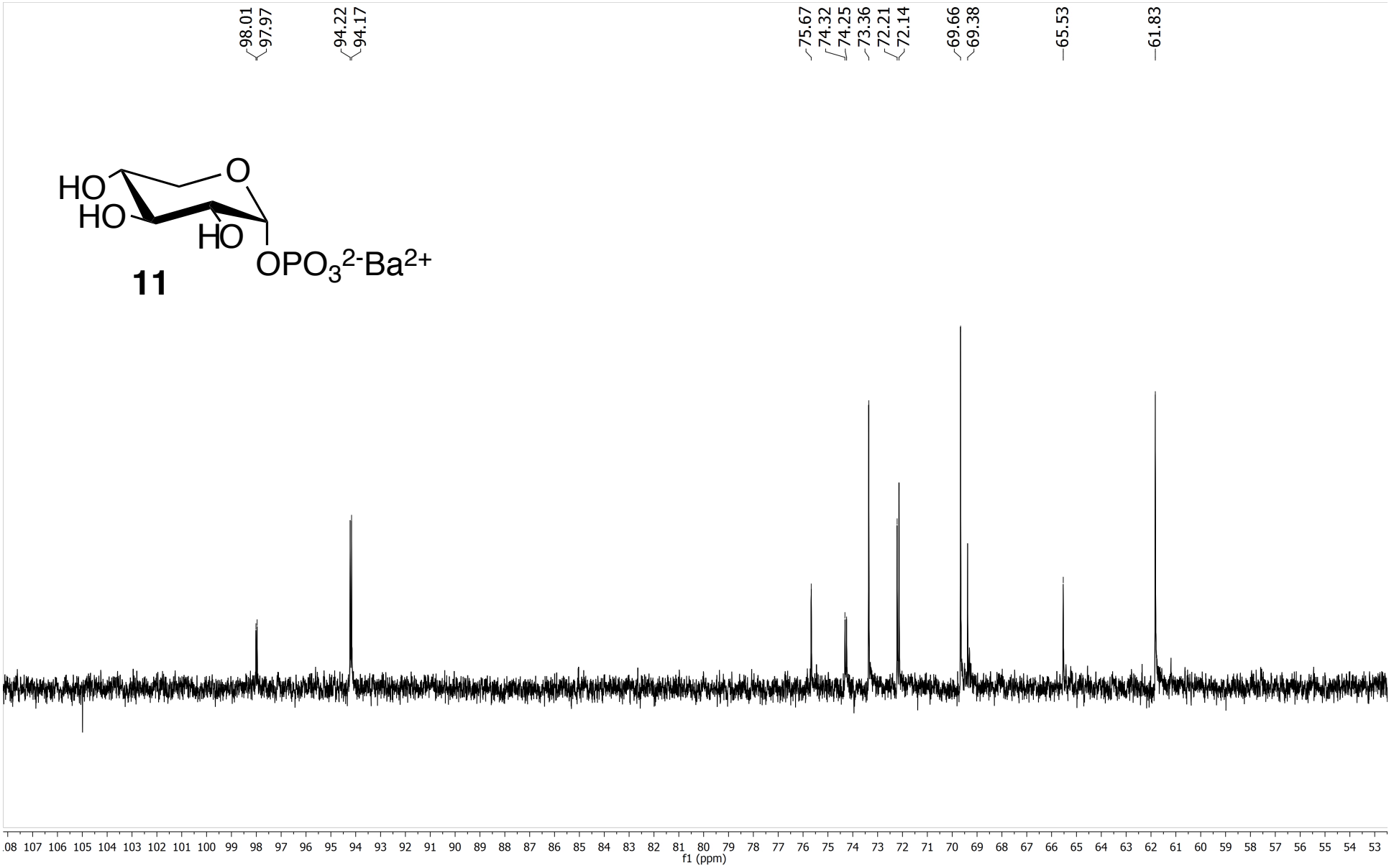
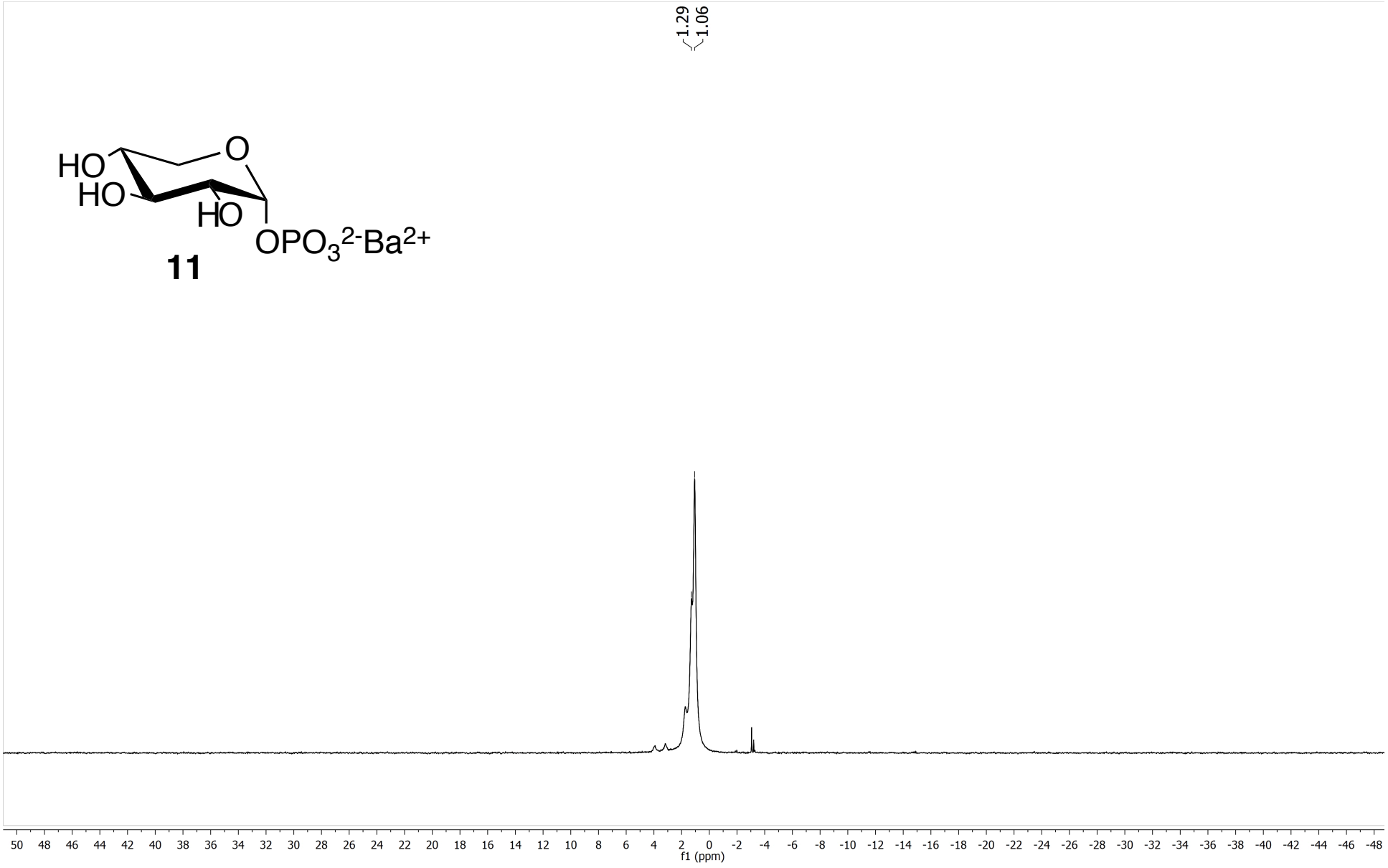


^{31}P NMR 162 MHz (D_2O, 25 °C)



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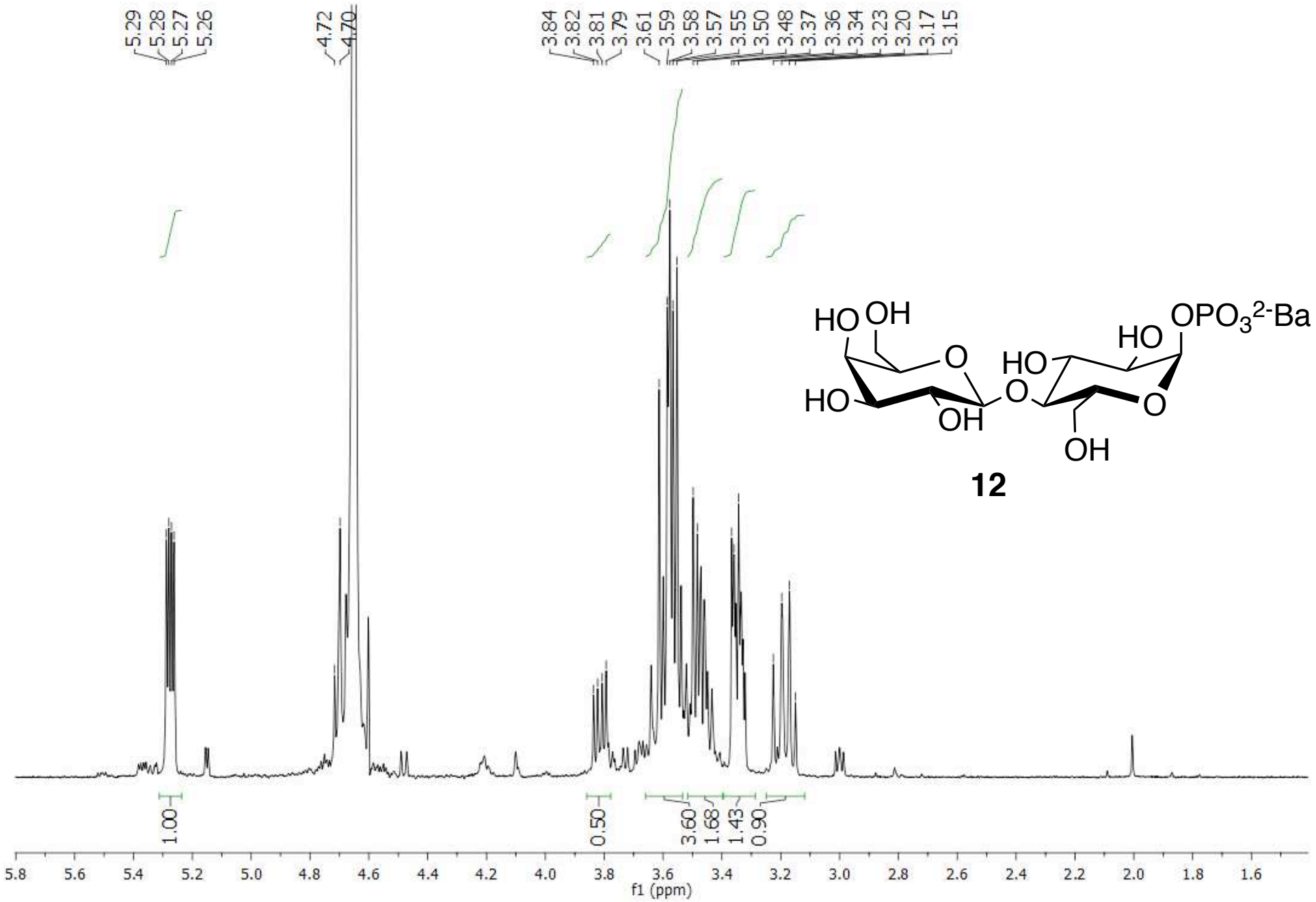

12

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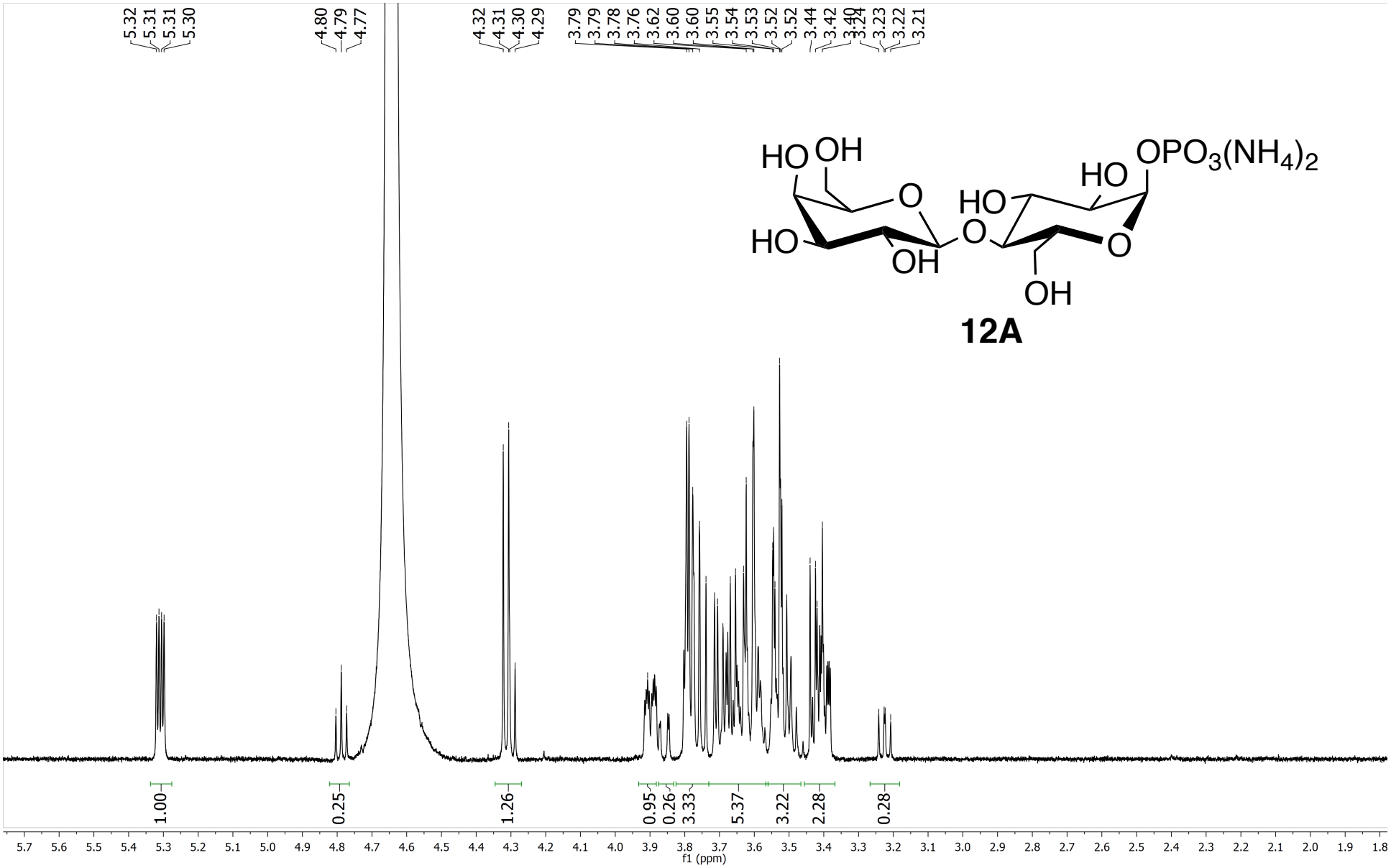

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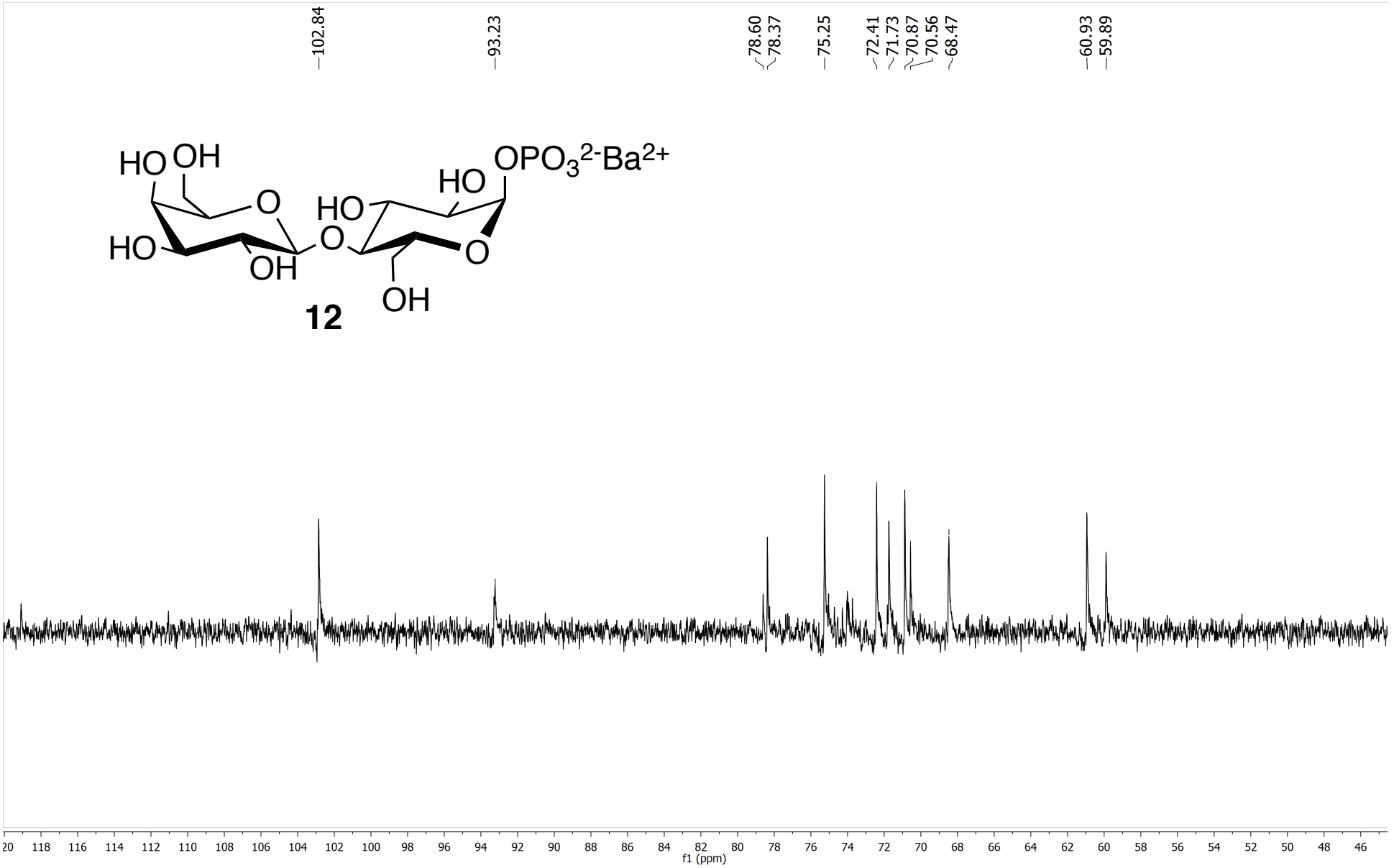

^{31}P NMR 162 MHz (D_2O, 25 °C)