*Supporting Information*

# *O*-Aryl-glycoside ice recrystallization inhibitors as novel cryoprotectants – A structure-function study

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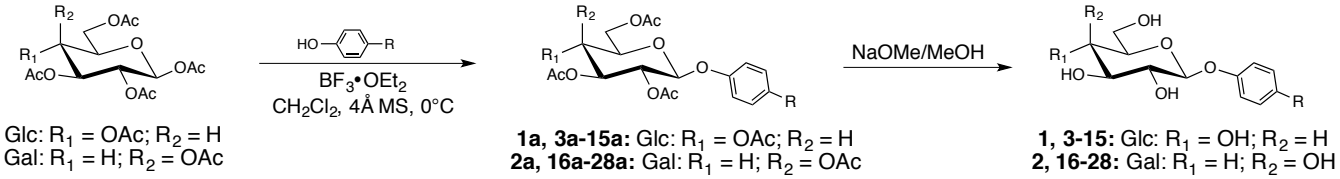
***General Experimental***

All anhydrous reactions were performed in flame-dried glassware under a positive pressure of dry argon. Air or moisture-sensitive reagents and anhydrous solvents were transferred with oven-dried syringes or cannulae. All flash chromatography was performed with E. Merck silica gel 60 (230-400 mesh). All solution phase reactions were monitored using analytical thin layer chromatography (TLC) with 0.2 mm pre-coated silica gel aluminum plates 60 F254 (E. Merck). Components were visualized by illumination with a short-wavelength (254 nm) ultra-violet light and/or staining (ceric ammonium molybdate, potassium permanganate, or phosphomolybdate stain solution). All solvents used for anhydrous reactions were distilled. Tetrahydrofuran (THF) and diethyl ether ($Et_2O$) were distilled from sodium/benzophenone under nitrogen. Dichloromethane (DCM) was distilled from calcium hydride. *N*,*N*-dimethylformamide (DMF) was stored over activated 4Å molecular sieves under argon. $^1H$ (400 or 500 MHz) and $^{13}C$ NMR (100 or 125 MHz) spectra were recorded at ambient temperature on a Bruker Avance 400, Bruker Avance 500, or Varian Inova 500 spectrometer. Deuterated chloroform ($CDCl_3$) or water ($D_2O$) were used as NMR solvents, unless otherwise stated. Chemical shifts are reported in ppm using the solvent residual peak as an internal standard. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet and br, broad. Low resolution mass spectrometry (LRMS) was performed on a Micromass Quatro-LC Electrospray spectrometer with a pump rate of 20 μL/min using electrospray ionization (ESI).

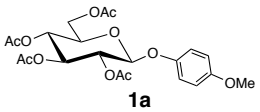
Compounds below are in order of appearance in the manuscript. Intermediates that were not numbered in the manuscript received numbers beginning with **51**. NMR spectra for novel compounds and final compounds assessed for IRI activity are provided. Compounds **1**-**2**, **4**-**7**, **9**, **29**, **30**, **35** and **39** were prepared as described previously by our laboratory.[1]

***General Synthetic Scheme for the preparation of O-aryl-glycosides***




**Scheme S1.** General synthetic scheme for the preparation of *O*-aryl-glucosides and –galactosides **1**-**28**.

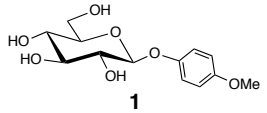
***4-Methoxyphenyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (1a)***




**1a**

To a mixture of 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (15 g, 38.4 mmol), 4-methoxyphenol (6.7 g, 53.8 mmol) and 4 Å MS in anhydrous $CH_2Cl_2$ (100 mL) stirring at 0 °C under Ar, was slowly added boron trifluoride diethyl etherate (9.64 mL, 76.8 mmol). The reaction mixture was stirred overnight, then diluted with $CH_2Cl_2$ and quenched with sodium bicarbonate. The solution was filtered through Celite®, then extracted with $CH_2Cl_2$. The organic layer was washed with sodium bicarbonate, water, saturated brine, then dried over $MgSO_4$ and concentrated. Flash column chromatography (6:4 hexanes/ethyl acetate) afforded **1a** as a white powder (13.6 g, 78%).[1] $^1H$ NMR (300 MHz, $CDCl_3$): δ 6.97-6.92 (m, 2H), 6.84-6.78 (m, 2H), 5.31-5.20 (m, 2H), 5.16 (t, *J* = 9.6 Hz, 1H), 4.95 (d, *J* = 7.6 Hz, 1H), 4.29 (dd, *J* = 12.3, 5.2 Hz, 1H), 4.18 (dd, *J* = 12.3, 2.5 Hz, 1H), 3.83-3.79 (m, 1H), 3.77 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H) 2.03 (s, 3H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 170.6, 170.3, 169.4, 169.3, 155.8, 150.9, 118.7, 114.5, 100.3, 72.7, 71.9, 71.2, 68.3, 61.9, 55.6, 20.7, 20.7, 20.6, 20.6. LRMS (ESI): *m*/*z* calcd. for $C_{21}H_{30}NO_{11}$ $[M+NH_4]^+$ 472.5; found, 472.2; *m*/*z* calcd. for $C_{21}H_{26}NaO_{11}$ $[M+Na]^+$ 477.4; found, 477.1.

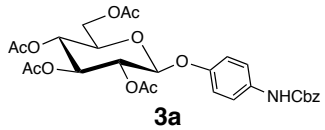
***4-Methoxyphenyl-β-D-glucopyranoside (1)***




**1**

Compound **1a** (6.75 g, 14.9 mmol) was dissolved in a solution of sodium methoxide in methanol (25 mL) and stirred for one hour at room temperature. The solution was then neutralized with Amberlite® IR-120 ($H^+$) ion-exchange resin, filtered and concentrated. The filtrate was concentrated and the product was lyophilized to yield **1** as a white powder (4.1 g, 95%).[1] $^1$H NMR (400 MHz, $D_2O$): δ 7.14-7.10 (m, 2H), 7.01-6.96 (m, 2H), 5.01 (d, *J* = 7.6 Hz, 1H), 3.92 (dd, *J* = 12.4, 2.2 Hz, 1H), 3.81 (s, 3H), 3.75 (dd, *J* = 12.4, 5.7 Hz, 1H), 3.62-3.54 (m, 3H), 3.48 (dd, *J* = 9.6, 9.2 Hz, 1H). $^{13}$C NMR (101 MHz, $D_2O$): δ 154.7, 150.9, 118.2, 115.0, 101.2, 76.1, 75.5, 72.9, 69.4, 60.5, 55.8. LRMS (ESI): *m/z* calcd. for $C_{13}H_{18}NaO_7$ $[M+Na]^+$ 309.3; found, 309.3.

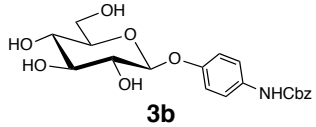
***4-(benzyloxycarbonyl)aminophenyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (3a)***




**3a**

Compound **3a** was prepared in a similar manner as **1a** from 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (300 mg, 0.77 mmol), 4-(benzyloxycarbonyl)aminophenol (206 mg, 0.85 mmol) and boron trifluoride diethyl etherate (482 μL, 3.84 mmol) with 4 Å MS in anhydrous $CH_2Cl_2$ (15 mL) at 0 °C**.** Column chromatography (7:3 hexanes/ethyl acetate) afforded **3a** (372 mg, 84%) as a yellow oil. $^1$H NMR (300 MHz, $CDCl_3$) δ 2.03 (s, 3H), 2.04 (s, 3H), 2.06 (s, 3H), 2.07 (s, 3H), 3.79-3.86 (m, 1H), 4.15 (dd, J=12.3, 2.4 Hz, 1H), 4.28 (dd, J=12.2, 5.4 Hz, 1H), 5.00 (d, J=7.6 Hz, 1H), 5.12-5.17 (m, 1H), 5.19 (s, 2H), 5.23-5.29 (m, 2H), 6.69 (br s, 1H), 6.95 (d, J=9.0 Hz, 2H), 7.30 (d, J=8.9 Hz, 2H), 7.35-7.42 (m, 5H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 20.47, 20.50, 20.53, 20.59, 61.88, 68.21, 71.15, 71.83, 172.68, 99.52, 117.70, 120.19, 128.17, 128.25, 128.52, 133.60, 136.02, 152.85, 166.19, 169.52, 170.30, 170.74, 175.63 LRMS (ESI): *m/z* calcd. for $C_{28}H_{30}NO_{12}$ $[M-H]^-$ 572.2; found 572.0.

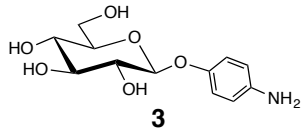
***4-(benzyloxycarbonyl)aminophenyl-β-D-glucopyranoside (3b)***




**3b**

Compound **3a** (370 mg, 0.645 mmol) and potassium carbonate (9 mg, 0.0645 mmol) were dissolved in methanol (10 mL) in a 50 mL round bottom flask and stirred overnight at room temperature. Amberlite IRC-76 resin (H+ form, pH=4) was pre-rinsed with MeOH and then added to the mixture, which was stirred for an additional 10 minutes until a pH of 5 to 6. The mixture was filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (90:10 $CH_2Cl_2$:MeOH) to afford white crystals (142 mg, 54%). $^1$H NMR (300 MHz, MeOD) δ 3.36-3.46 (m, 4H), 3.96 (dd, J= 11.9, 4.9 Hz, 1H), 3.89 (d, J=11.9 Hz, 1H), 4.83 (d, J=7.6 Hz, 1H), 7.04 (d, J=9.0 Hz, 2H), 7.28- 7.43 (m, 7H). $^{13}$C NMR (75 MHz, MeOD) δ 62.69, 67.01, 71.37, 74.79, 77.92, 77.97, 102.67, 118.11, 120.61, 129.01, 129.05, 129.48, 134.73, 138.18, 154.71, 154.86. LRMS (ESI): *m/z* calcd. for $C_{20}H_{22}NO_8$ $[M-H]^-$ 404.1; found 403.9.

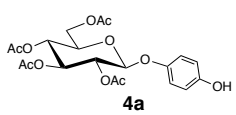
***4-aminophenyl-β-D-glucopyranoside (3)***



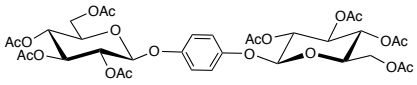
**3**

Compound **3b** (142 mg, 0.35 mmol) was dissolved in methanol (10 mL) in a 50 mL flame-dried round bottom flask. 20% palladium (II) hydroxide on carbon (25 mg, 0.0350 mmol) was added, the atmosphere was removed from the flask using a water aspirator, and a positive pressure of hydrogen gas was added. The contents were stirred overnight at room temperature, after which the mixture was filtered over a bed of celite and the solvent evaporated under reduced pressure to give light brown crystals (96 mg, 98%). $^{1}$H NMR (300 MHz, $D_2O$) δ 3.42-3.61 (m, 4H), 3.72 (dd, J=12.3, 5.3 Hz, 1H), 3.90 (dd, J=12.4, 2.2 Hz, 1H), 4.95 (d, J=7.6 Hz, 1H), 6.80 (d, J=9.0 Hz, 2H), 6.98 (d, J=8.9 Hz, 1H). $^{13}$C NMR (75 MHz, $D_2O$) δ 61.17, 70.07, 73.60, 76.21, 76.64, 101.99, 118.16, 118.79, 142.32, 150.72. LRMS (ESI): *m/z* calcd. for $C_{12}H_{16}NO_6$ $[M-H]^-$ 270. 1; found 269.8.

***4-Hydroxyphenyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (4a) and 1,4-Bis-(2,3,4,6- tetra-O-acetyl-β-D-glucopyranosyl)benzene (48a)***



**4a**



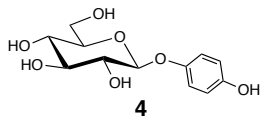
**48a**

Compounds **4a** and **48a** were prepared in a similar manner as **1a** from 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (1 g, 2.56 mmol), hydroquinone (211 mg, 1.92 mmol) with boron trifluoride diethyl etherate (482 μL, 3.84 mmol)**.** Flash column chromatography (7:3 hexanes/ethyl acetate) afforded both **4a**[2] (339 mg, 40%) and **48a**[3] (491 mg, 33%) as white powders.

Characterization data for **4a**:[2]
$^{1}$H NMR (400 MHz, $CDCl_3$): δ 6.90-6.86 (m, 2H), 6.77-6.72 (m, 2H), 5.30-5.20 (m, 2H), 5.16 (t, *J* = 9.5 Hz, 2H), 4.93 (d, *J* = 7.6 Hz, 1H), 4.28 (dd, *J* = 12.3, 5.1 Hz, 1H), 4.16 (dd, *J* = 12.3, 2.5 Hz, 1H), 3.79 (ddd, *J* = 9.9, 5.1, 2.5 Hz, 1H), 2.09 (d, *J* = 1.5 Hz, 3H), 2.07-2.05 (m, 5H), 2.02 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 170.7, 170.3, 169.5, 169.4, 151.8, 150.8, 118.9, 116.0, 100.3, 72.7, 71.9, 71.2, 68.3, 61.9, 20.7, 20.7, 20.6, 20.6. LRMS (ESI): *m/z* calcd. for $C_{20}H_{24}NaO_{11}$ $[M+Na]^+$ 463.4; found, 463.2.

Characterization data for **48a**:[3]
$^{1}$H NMR (400 MHz, $CDCl_3$): δ 6.92 (s, 4H), 5.30-5.21 (m, 4H), 5.16 (t, *J* = 9.6 Hz, 2H), 4.98 (d, *J* = 7.6 Hz, 2H), 4.28 (dd, *J* = 12.3, 5.1 Hz, 2H), 4.16 (dd, *J* = 12.3, 2.5 Hz, 2H), 3.81 (ddd, *J* = 9.9, 5.1, 2.5 Hz, 2H), 2.07 (s, 6H), 2.06 (s, 6H), 2.04 (s, 7H), 2.03 (s, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 170.5, 170.2, 169.3, 169.2, 152.8, 118.4, 99.8, 72.6, 72.0, 71.1, 68.2, 61.8, 20.7, 20.6, 20.6, 20.6. LRMS (ESI): *m/z* calcd. for $C_{34}H_{42}KO_{20}$ $[M+K]^+$ 809.9; found, 809.2.

***4-Hydroxyphenyl-β-D-glucopyranoside (4)***

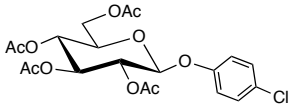


**4**

Compound **4a** (200 mg, 0.45 mmol) was dissolved in a solution of sodium methoxide in methanol (5 mL) and stirred for one hour at room temperature. The solution was then neutralized with Amberlite® IR-120 ($H^+$) ion-exchange resin, filtered and concentrated. The filtrate was concentrated and the product was lyophilized to yield **4** as a white powder (122 mg, 98%). $^{1}$H NMR (400 MHz, $D_2O$): δ 7.07-7.03 (m, 2H), 6.89-6.85 (m, 2H), 4.99 (d, *J* = 7.6 Hz, 1H), 3.92 (dd, *J* = 12.4, 2.2 Hz, 1H), 3.75 (dd, *J* = 12.5, 5.6 Hz, 1H), 3.61-3.52 (m, 3H), 3.48 (dd, *J* = 9.7, 8.9 Hz, 1H). $^{13}$C NMR (101

MHz, $D_2O$): δ 151.2, 150.4, 118.4, 116.2, 101.3, 76.0, 75.5, 73.0, 69.4, 60.5. LRMS (ESI): *m/z* calcd. for $C_{12}H_{16}NaO_7$ $[M+Na]^+$ 295.3; found, 295.2.

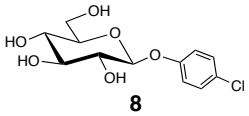
***4-Chlorophenyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (8a)***




**8a**

Compound **8a** was prepared in a similar manner as **1a** from 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (500 mg, 1.28 mmol), 4-chlorophenol (230 mg, 1.79 mmol) with boron trifluoride diethyl etherate (803 μL, 6.4 mmol). Flash column chromatography (3:2 hexanes/ethyl acetate) afforded **8a** as a white powder (234 mg, 40%). Characterization data is consistent with that previously reported.[4] $^1$H NMR (400 MHz, $CDCl_3$): δ 7.27-7.23 (m, 4H), 6.95-6.91 (m, 2H), 5.31-5.23 (m, 2H), 5.16 (t, *J* = 9.6 Hz, 1H), 5.03 (d, *J* = 7.6 Hz, 1H), 4.28 (dd, *J* = 12.3, 5.4 Hz, 1H), 4.18-4.15 (m, 1H), 3.84 (ddd, *J* = 9.9, 5.3, 2.4 Hz, 1H), 2.08 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 170.5, 170.2, 169.3, 169.2, 155.3, 129.5, 128.5, 118.4, 99.2, 72.6, 72.1, 71.1, 68.2, 61.9, 20.7, 20.6, 20.6, 20.6. LRMS (ESI): *m/z* calcd. for $C_{20}H_{27}ClNO_{10}$ $[M+NH_4]^+$ 476.9; found, 476.3.

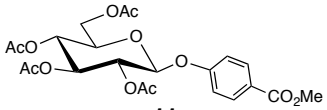
***4-Chlorophenyl-β-D-glucopyranoside (8)***




**8**

Compound **8a** (150 mg, 0.33 mmol) was dissolved in a solution of sodium methoxide in methanol (5 mL) and stirred for one hour at room temperature. The solution was then neutralized with Amberlite® IR-120 ($H^+$) ion-exchange resin, filtered and concentrated. The filtrate was concentrated and the product was lyophilized to yield **8** as a white powder (92 mg, 97%). $^1$H NMR (400 MHz, $D_2O$): δ 7.39-7.35 (m, 2H), 7.12-7.08 (m, 2H), 5.09 (d, *J* = 7.5 Hz, 1H), 3.92 (dd, *J* = 12.5, 2.2 Hz, 1H), 3.74 (dd, *J* = 12.4, 5.7 Hz, 1H), 3.64-3.53 (m, 3H), 3.49 (t, *J* = 9.3 Hz, 1H). $^{13}$C NMR (101 MHz, $D_2O$): δ 155.2, 129.6, 127.5, 118.0, 100.3, 76.1, 75.5, 72.9, 69.4, 60.5. LRMS (ESI): *m/z* calcd. for $C_{12}H_{15}ClNaO_6$ $[M+Na]^+$ 313.7; found, 313.1.

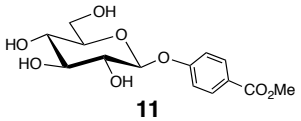
***4-(Methoxycarbonyl)phenyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (11a)***




**11a**

Compound **11a** was prepared in a similar manner as **1a** from 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (500 mg, 1.28 mmol), 4-(methoxycarbonyl)phenol (234 mg, 1.53 mmol) with boron trifluoride diethyl etherate (209 μL, 1.66 mmol)**.** Flash column chromatography (3:2 hexanes/EtOAc) afforded **11a** as a white powder (258 mg, 77%). $^1$H NMR (400 MHz, $CDCl_3$): δ 8.02-7.99 (m, 2H), 7.03-6.99 (m, 2H), 5.35-5.28 (m, 2H), 5.20-5.15 (m, 2H), 4.29 (dd, *J* = 12.3, 5.5 Hz, 1H), 4.18 (dd, *J* = 12.3, 2.4 Hz, 1H), 3.92 (m, 1H), 3.90 (s, 3H), 2.08 (d, *J* = 5.8 Hz, 3H), 2.05 (s, 6H), 2.05 (d, *J* = 5.6 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 170.5, 170.2, 169.4, 169.2, 166.4, 160.1, 131.6, 116.1, 98.2, 72.6, 72.2, 71.0, 68.2, 61.9, 52.0, 20.7, 20.7, 20.6, 20.6. LRMS (ESI): *m/z* calcd. for $C_{22}H_{26}NaO_{12}$ $[M+Na]^+$ 505.4; found, 505.3.

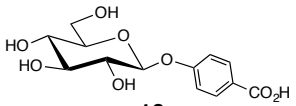
***4-(Methoxycarbonyl)phenyl-β-D-glucopyranoside (11)***




**11**

Compound **11a** (150 mg, 0.31 mmol) was dissolved in a solution of sodium methoxide in methanol (5 mL) and stirred for one hour at room temperature. The solution was then neutralized with Amberlite® IR-120 ($H^+$) ion-exchange resin, filtered and concentrated. The filtrate was concentrated and the product was lyophilized to yield **11** as a white powder (87 mg, 89%). $^1$H NMR (400 MHz, $D_2O$): δ 8.01 (d, *J* = 8.8 Hz, 2H), 7.18 (d, *J* = 8.9 Hz, 2H), 5.23 (d, *J* = 7.0 Hz, 1H), 3.95-3.92 (m, 1H), 3.90 (s, 3H), 3.75 (dd, *J* = 12.4, 5.6 Hz, 1H), 3.69-3.65 (m, 1H), 3.62-3.58 (m, 2H), 3.50 (t, *J* = 9.3 Hz, 1H). $^{13}$C NMR (101 MHz, $D_2O$): δ 169.6, 161.2, 132.4, 124.7, 116.8, 100.1, 76.9, 76.1, 73.5, 70.0, 61.1, 53.2. LRMS (ESI): *m/z* calcd. for $C_{14}H_{18}NaO_8$ $[M+Na]^+$ 337.3; found, 337.2.

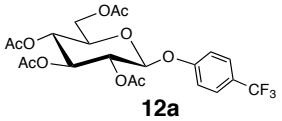
***4-(β-D-glucopyranosyloxy)-benzoic acid (10)***




**10**

Compound **11** (150 mg, 0.477 mmol) and lithium hydroxide (34 mg, 1.413 mmol) was dissolved in a 3:1 mixture of $H_2O$:THF (10 mL) in a 50 mL round bottom flask. The reaction mixture was stirred for 3 hours at room temperature. Amberlite IR-120 resin (H+ form, pH=4) was pre-rinsed with MeOH and then added to the mixture, which was stirred for an additional 10 minutes until a pH of 5 to 6. The mixture was filtered and the solvent evaporated under reduced pressure. The crude product was dissolved in a minimum of methanol and precipitated with diethyl ether to afford white crystals (136 mg, 95%). $^1$H NMR (500 MHz, $D_2O$) δ 3.53 (dd, J=9.2, 9.2 Hz, 1H), 3.59-3.71 (m, 3H), 3.78 (dd, J=12.5, 5.6 Hz, 1H), 3.96, (dd, J=12.2, 1.8 Hz, 1H), 5.23 (d, J= 7.4 Hz, 1H), 7.17 (d, J= 8.7 Hz, 2H), 7.91 (d, J=8.7 Hz, 2H). $^{13}$C NMR (125 MHz, $D_2O$) δ 61.12, 70.02, 73.51, 76.13, 76.76, 100.27, 116.43, 130.21, 131.75, 159.72, 174.71. LRMS (ESI): *m/z* calcd. for $C_{13}H_{15}O_8$ $[M-H]^-$ 299.1; found 298.9.

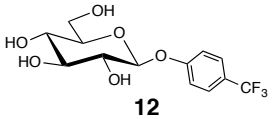
***4-Trifluoromethylphenyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (12a)***




**12a**

Compound **12a** was prepared in a similar manner as **1a** from 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (500 mg, 1.28 mmol), 4-trifluoromethylphenol (290 mg, 1.79 mmol) with boron trifluoride diethyl etherate (1.6 mL, 12.8 mmol)**.** Flash column chromatography (3:2 hexanes/EtOAc) afforded **12a** as a white powder (189 mg, 30%). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 5.34-5.27 (m, 2H), 5.20-5.14 (m, 2H), 4.29 (dd, *J* = 12.3, 5.4 Hz, 1H), 4.18 (dd, *J* = 12.3, 2.4 Hz, 1H), 3.92-3.87 (m, 1H), 2.07 (s, 3H), 2.06 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 170.5, 170.2, 169.4, 169.2, 127.1, 127.0, 127.0, 127.0, 116.7, 98.4, 72.5, 72.2, 71.0, 68.1, 61.9, 20.7, 20.6, 20.6. LRMS (ESI): *m/z* calcd. for $C_{21}H_{23}F_3NaO_{10}$ $[M+Na]^+$ 515.4; found, 515.2.

***4-Trifluoromethylphenyl-β-D-glucopyranoside (12)***

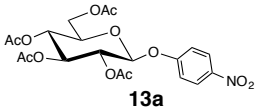



**12**

Compound **12a** (117 mg, 0.24 mmol) was dissolved in a solution of sodium methoxide in methanol (5 mL) and stirred for one hour at room temperature. The solution was then neutralized with Amberlite® IR-120 ($H^+$) ion-exchange resin, filtered and concentrated. The filtrate was concentrated and the product was lyophilized to yield **12** as a white powder

(74 mg, 96%). $^{1}$H NMR (400 MHz, $D_2O$): δ 7.70 (d, *J* = 8.7 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 5.21 (d, *J* = 7.6 Hz, 1H), 3.93 (dd, *J* = 12.4, 2.2 Hz, 1H), 3.75 (dd, *J* = 12.4, 5.7 Hz, 1H), 3.69-3.65 (m, 1H), 3.62-3.60 (m, 2H), 3.50 (t, *J* = 9.4 Hz, 1H). $^{13}$C NMR (101 MHz, $D_2O$): δ 159.0, 127.3, 127.2, 127.2, 127.2, 116.5, 99.6, 76.2, 75.5, 72.8, 69.4, 60.5. LRMS (ESI): *m/z* calcd. for $C_{13}H_{15}F_3NaO_6$ $[M+Na]^+$ 347.2; found, 347.1.

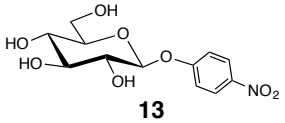
***4-Nitrophenyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (13a)***




**13a**

Compound **13a** was prepared in a similar manner as **1a** from 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (420 mg, 1.08 mmol), 4-nitrophenol (210 mg, 1.51 mmol) with boron trifluoride diethyl etherate (180 μL, 1.40 mmol)**.** Flash column chromatography (8:2 hexanes/EtOAc) afforded **13a** as a white powder (347 mg, 68%). Characterization data is consistent with that previously reported in the literature.[5] $^{1}$H NMR (500 MHz, $CDCl_3$): δ 8.23-8.20 (m, 2H), 7.09-7.06 (m, 2H), 5.16-5.11 (m, 3H), 5.09 (d, *J* = 3.7 Hz, 1H), 4.28 (dd, *J* = 12.3, 5.2 Hz, 1H), 4.18 (dd, *J* = 12.3, 2.3 Hz, 1H), 3.86-3.82 (m, 1H), 2.07 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 170.7, 170.2, 169.7, 169.3, 160.8, 140.9, 124.7, 115.5, 98.1, 74.7, 73.9, 71.2, 68.1, 61.9, 20.9, 20.7, 20.6, 20.5. LRMS (ESI): *m/z* calcd. for $C_{20}H_{22}NO_{12}$ $[M-H]^-$ 468.4; found, 468.2.

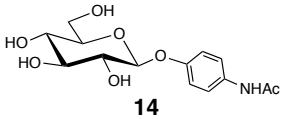
***4-Nitrophenyl -β-D-glucopyranoside (13)***




**13**

Compound **13a** (250 mg, 0.53 mmol) was dissolved in a solution of sodium methoxide in methanol (4 mL) and stirred for one hour at room temperature. The solution was then neutralized with Amberlite® IR-120 ($H^+$) ion-exchange resin, filtered and concentrated. The product was purified by column chromatography (4:1:1:1 EtOAc/ACN/$H_2O$/MeOH) to afford **13** as a white powder (128 mg, 80%). $^{1}$H NMR (400 MHz, $D_2O$): δ 8.28-8.24 (m, 2H), 7.26-7.22 (m, 2H), 5.27 (d, *J* = 7.7 Hz, 1H), 3.93 (dd, *J* = 12.3, 2.1 Hz, 1H), 3.75 (dd, *J* = 12.3, 5.7 Hz, 1H), 3.71-3.67 (m, 1H), 3.63-3.61 (m, 2H), 3.51 (t, *J* = 9.4 Hz, 1H). $^{13}$C NMR (101 MHz, $D_2O$): δ 161.7, 142.6, 126.1, 116.4, 99.4, 76.3, 75.4, 72.7, 69.3, 60.4. LRMS (ESI): *m/z* calcd. for $C_{12}H_{14}NO_8$ $[M-H]^-$ 300.3; found, 300.5. LRMS (ESI): *m/z* calcd. for $C_{24}H_{28}N_2O_{16}$ $[M-H]^-$ Dimer 601.5; found, 601.0.

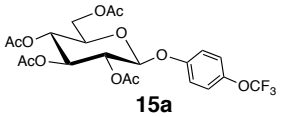
***4-Acetamidophenyl-β-D-glucopyranoside (14)***




**14**

Compound **3** (86 mg, 0.320 mmol) was dissolved in water (3 mL) in a 50 mL round bottom flask. Acetic anhydride (32 μL, 0.337 mmol) was added, and the solution was stirred overnight at room temperature. The reaction mixture was concentrated under reduced pressure, and the crude product was dissolved in a minimum of methanol and precipitated with ether to afford light brown crystals (73 mg, 74%). $^{1}$H NMR (300 MHz, $D_2O$): δ 2.14 (s, 3H), 3.45-3.65 (m, 4H), 3.74 (dd, J=12.4, 5.7 Hz, 1H), 3.92 (dd, J=12.4, 2.2 Hz, 1H), 5.10 (d, J=7.5 Hz, 1H), 7.12 (d, J=9.0 Hz, 2H), 7.35 (d, J=9.0 Hz, 2H). $^{13}$C NMR (75 MHz, $D_2O$): δ 22.46, 60.43, 69.33, 72.83, 75.44, 76.03, 100.28, 116.98, 124.06, 131.79, 154.03, 172.97. LRMS (ESI): *m/z* calcd. for $C_{14}H_{18}NO_7$ $[M-H]^-$ 312.1; found 312.03.

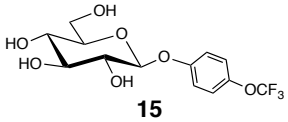
***4-Trifluoromethoxyphenyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (15a)***



**15a**

Compound **15a** was prepared in a similar manner as **1a** from 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (250 mg, 0.64 mmol), 4-trifluoromethoxyphenol (116 $\mu$L, 0.90 mmol) with boron trifluoride diethyl etherate (161 $\mu$L, 1.28 mmol)**.** Flash column chromatography (4:1 hexanes/EtOAc) afforded **15a** as a white powder (291 mg, 89%). $^{1}$H NMR (300 MHz, $CDCl_3$): δ 7.15 (d, *J* = 8.9 Hz, 2H), 7.00 (d, *J* = 9.0 Hz, 2H), 5.33-5.23 (m, 2H), 5.16 (t, *J* = 9.5 Hz, 1H), 5.06 (d, *J* = 7.3 Hz, 1H), 4.28 (dd, *J* = 12.3, 5.3 Hz, 1H), 4.16 (dd, *J* = 12.3, 2.3 Hz, 1H), 3.88-3.82 (m, 1H), 2.07 (s, 6H), 2.05 (s, 3H), 2.03 (s, 3H). $^{13}$C NMR (76 MHz, $CDCl_3$): δ 170.5, 170.2, 169.4, 169.2, 155.1, 144.6, 122.5, 118.1, 99.1, 72.6, 72.1, 71.1, 68.1, 61.8, 20.6, 20.6, 20.6. LRMS (ESI): *m/z* calcd. for $C_{21}H_{22}F_3NaO_{11}$ $[M-H]^-$ 507.4; found, 507.2.

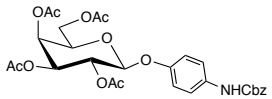
***4-Trifluoromethoxyphenyl-β-D-glucopyranoside (15)***



**15**

Compound **15a** (180 mg, 0.35 mmol) was dissolved in a solution of sodium methoxide in methanol (5 mL) and stirred for one hour at room temperature. The solution was then neutralized with Amberlite® IR-120 ($H^+$) ion-exchange resin, filtered and concentrated. The filtrate was concentrated and the product was lyophilized to yield **15** as a white powder (110 mg, 91%). $^{1}$H NMR (500 MHz, $D_2O$): δ 7.30 (d, *J* = 9.1 Hz, 2H), 7.17-7.15 (m, 2H), 5.09 (d, *J* = 7.3 Hz, 1H), 3.91 (dd, *J* = 12.5, 2.1 Hz, 1H), 3.73 (t, *J* = 9.0 Hz, 1H), 3.62-3.55 (m, 3H), 3.48 (d, *J* = 9.2 Hz, 1H). $^{13}$C NMR (126 MHz, $D_2O$): δ 155.0, 144.1, 122.6, 119.2, 117.6, 100.3, 76.1, 75.4, 72.8, 69.3, 60.4. LRMS (ESI): *m/z* calcd. for $C_{13}H_{14}F_3NaO_7$ $[M-H]^-$ 339.2; found, 339.1.

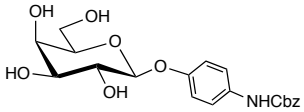
***4-(benzyloxycarbonyl)aminophenyl-2,3,4,6-tetra-O-acetyl-β-D-galactopyranoside (16a)***



**16a**

Compound **16a** was prepared in a similar manner as **1a** from 1,2,3,4,6-penta-O-acetyl-β-D-galactopyranoside (300 mg, 0.769 mmol) and 4-(benzyloxycarbonyl)aminophenol (206 mg, 0.845 mmol) with boron trifluoride diethyl etherate (1.09 mL, 15.37 mmol). Flash column chromatography (75:25 - 70:30 (Hexanes:EtOAc) afforded **16a** as a yellow oil (327 mg, 74%). $^{1}$H NMR (300 MHz, CDCl3) δ 1.94 (s, 3H), 1.97 (s, 3H), 2.01 (s, 3H), 2.09 (s, 3H), 3.97 (dd, J=6.7, 6.6 Hz, 1H), 4.08-4.18 (m, 2H), 4.93 (d, J=8.0 Hz, 1H), 5.08 (dd, J= 10.4, 3.3 Hz, 1H), 5.12 (s, 2H), 5.39-5.40 (m, 1H), 5.41 (dd, J=10.4, 8.0 Hz, 1H), 6.90 (d, J=9.0 Hz, 2H), 7.24-7.33 (m, 7H). $^{13}$C NMR (75 MHz, CDCl3) δ 20.38, 20.40, 20.43, 20.53, 61.25, 66.68, 66.86, 68.57, 70.64, 70.76, 99.91, 117.51, 120.07, 128.05, 128.12, 128.41, 133.54, 136.00, 152.81, 153.60, 169.34, 169.96, 170.21, 170.27. LRMS (ESI): *m/z* calcd. for $C_{28}H_{30}NO_{12}$ $[M-H]^-$ 572.2; found 572.0.

***4-(benzyloxycarbonyl)aminophenyl-β-D-glucopyranoside (16b)***

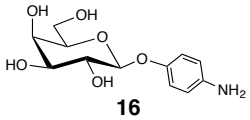


**16b**

Compound **16a** (325 mg, 0.567 mmol) and potassium carbonate (8 mg, 0.0567 mmol) were dissolved in methanol (10 mL) in a 50 mL round bottom flask and stirred overnight at room temperature. Amberlite IRC-76 resin (H+ form, pH=4) was pre-rinsed with MeOH and then added to the mixture, which was stirred for an additional 10 minutes until a pH of 5 to 6. The mixture was filtered and the solvent was removed under reduced pressure. The crude product was purified by

recrystallization in EtOAc to yield white crystals (122 mg, 53%). $^1$H NMR (300 MHz, $(CD_3)CO_2$) δ 3.61 (dd, J=9.4, 3.4 Hz, 1H), 3.69-3.82 (m, 4H), 3.94-3.97 (m, 1H), 4.83 (d, J=7.7 Hz, 1H), 5.15 (s, 2H), 7.03 (d, J=9.0 Hz, 2H), 7.29-7.48 (m, 7H), 8.62 (br s, 1H). $^{13}$C NMR (75 MHz, $(CD_3)CO_2$) δ 62.35, 66.76, 69.82, 72.14, 74.67, 76.44, 103.01, 117.91, 120.39, 128.80, 128.90, 129.27, 134.51, 138.00, 154.48, 154.62. LRMS (ESI): *m/z* calcd. for $C_{20}H_{22}NO_8$ $[M-H]^-$ 404.1, Found 404.0.

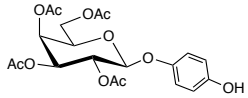
***4-aminophenyl-β-D-glucopyranoside (16)***



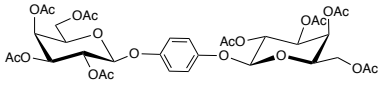

**16**

Compound **16b** (110 mg, 0.271 mmol) was dissolved in methanol (10 mL) in a 50 mL flame-dried round bottom flask. 20% palladium (II) hydroxide on carbon (19 mg, 0.0271 mmol) was added, the atmosphere was removed from the flask using a water aspirator, and a positive pressure of hydrogen gas was added. The contents were stirred overnight at room temperature, after which the mixture was filtered over a bed of celite and the solvent evaporated under reduced pressure to yield the title compound as light brown crystals (56 mg, 100%). $^1$H NMR (300 MHz, $D_2O$) δ 3.71-3.79 (m, 5H), 3.96 (m, 1H), 4.88 (d, J=7.8 Hz, 1H), 6.80 (d, J=9.0 Hz, 2H), 6.98 (d, J=9.0 Hz, 2H). $^{13}$C NMR (75 MHz, $D_2O$) δ 61.38, 69.11, 71.24, 73.23, 75.93, 102.58, 118.17, 118.71, 142.22, 150.90. LRMS (ESI): *m/z* calcd. for $C_{12}H_{16}NO_6$ $[M-H]^-$ 270.1, Found 270.0.

***4-Hydroxyphenyl-2,3,4,6-tetra-O-acetyl-β-D-galactopyranoside (17a) and 1,4-Bis-(2,3,4,6- tetra-O-acetyl-β-D-galactopyranosyl)benzene (50a)***




**17a**




**50a**

Compounds **17a** and **50a** were prepared in a similar manner as **1a** from 1,2,3,4,6-penta-*O*-acetyl-β-D-galactopyranose (1 g, 2.56 mmol), hydroquinone (211 mg, 1.92 mmol) with boron trifluoride diethyl etherate (482 μL, 3.84 mmol). Flash column chromatography (7:3 hexanes/ethyl acetate) afforded both **17a**[2] (185 mg, 22%) and **50a**[3] (451 mg, 30%) as white powders.

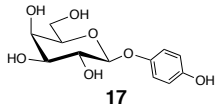
Characterization data for **17a**:[2]

$^1$H NMR (400 MHz, $CDCl_3$): δ 6.92-6.88 (m, 2H), 6.77-6.73 (m, 2H), 5.47-5.43 (m, 2H), 5.08 (dd, *J* = 10.5, 3.4 Hz, 1H), 4.90 (d, *J* = 8.0 Hz, 1H), 4.24 (dd, *J* = 11.3, 6.9 Hz, 1H), 4.17-4.11 (m, 1H), 4.00 (td, *J* = 6.7, 1.0 Hz, 1H), 2.18 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 170.4, 170.3, 170.2, 169.5, 151.7, 151.0, 118.8, 116.0, 100.8, 70.9, 70.9, 68.8, 66.9, 61.3, 20.8, 20.7, 20.6. LRMS (ESI): *m/z* calcd. for $C_{20}H_{24}NaO_{11}$ $[M+Na]^+$ 463.4; found, 463.3.

Characterization data for **50a**:[3]

$^1$H NMR (400 MHz, $CDCl_3$): δ 6.94 (s, 4H), 5.48-5.44 (m, 4H), 5.11-5.07 (m, 2H), 4.95 (d, *J* = 7.9 Hz, 2H), 4.25-4.20 (m, 2H), 4.17-4.12 (m, 2H), 4.03-4.00 (m, 2H), 2.18 (s, 6H), 2.07 (s, 6H), 2.05 (s, 6H), 2.01 (s, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 170.3, 170.2, 170.1, 169.3, 152.9, 118.3, 100.4, 71.0, 70.8, 68.6, 66.8, 61.2, 20.7, 20.7, 20.6. LRMS (ESI): *m/z* calcd. for $C_{34}H_{46}NO_{20}$ $[M+NH_4]^+$ 788.8; found, 788.6.

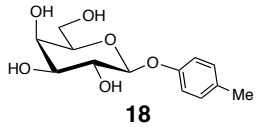
***4-Hydroxyphenyl-β-D-galactopyranoside (17)***



**17**

Compound **17a** (95 mg, 0.22 mmol) was dissolved in a solution of sodium methoxide in methanol (5 mL) and stirred for one hour at room temperature. The solution was then neutralized with Amberlite® IR-120 ($H^+$) ion-exchange resin, filtered and concentrated. The filtrate was concentrated and the product was lyophilized to yield **17** as a white powder (41 mg, 70%). $^1$H NMR (400 MHz, $D_2O$): δ 7.07-7.02 (m, 2H), 6.88-6.83 (m, 2H), 4.91 (d, *J* = 7.6 Hz, 1H), 3.97 (d, *J* = 2.6 Hz, 1H), 3.82-3.71 (m, 5H). $^{13}$C NMR (101 MHz, $D_2O$): δ 151.1, 150.6, 118.3, 116.2, 101.9, 75.3, 72.6, 70.6, 68.5, 60.7. LRMS (ESI): *m/z* calcd. for $C_{12}H_{16}NaO_7$ $[M+Na]^+$ 295.3; found, 295.2.

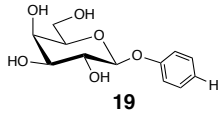
***4-Methylphenyl-β-D-galactopyranoside (18)***



**18**

Compound **18** was prepared in a similar manner as **1a** from 1,2,3,4,6-penta-O-acetyl-β-D-galactopyranoside (1 g, 2.56 mmol) and 4-methylphenol (305 mg, 2.82 mmol) with boron trifluoride diethyl etherate (0.46 mL, 3.84 mmol). 100 mg of the crude mixture was dissolved into 4:1 methanol: sodium methoxide then stirred for 2h. The solution was concentrated under vacuo. and re-dissolved in minimum methanol. Ether was added to recrystallize and afford **18** as a yellowish-white crystalline solid (42mg, 48% over two steps). $^1$H NMR (500 MHz, $D_2O$) δ 7.16 (d, *J* = 8.68 Hz, 2H), 7.00 (d, *J* = 8.54 Hz, 2H), 4.96 (d, *J* = 7.21 Hz, 1H), 3.94 (d, *J* = 3.08 Hz, 2H), 3.82-3.78 (m, 1H), 3.70 (m, 5H). $^{13}$C NMR (126 MHz, $D_2O$) δ 154.44, 133.04, 130.10, 116.45, 100.96, 75.27, 72.48, 70.49, 70.48, 68.39, 60.66. LRMS (ESI): *m/z* calcd. for $C_{13}H_{18}NaO_6$ $[M+Na]^+$ 293.1; found 293.1.

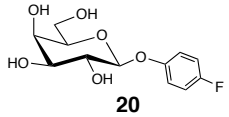
***Phenyl-β-D-galactopyranoside (19)***



**19**

Compound **19** was prepared in a similar manner as **1a** from 1,2,3,4,6-penta-O-acetyl-β-D-galactopyranoside (1 g, 2.56 mmol) and phenol (265 mg, 2.82 mmol) with boron trifluoride diethyl etherate (0.46 mL, 3.84 mmol). 100 mg of the crude mixture was dissolved into 4:1 methanol: sodium methoxide then stirred for 2h. The solution was concentrated under vacuo. and re-dissolved in minimum methanol. Ether was added to recrystallize and afford **19** as a white solid (39 mg, 41% over two steps). $^1$H NMR (500 MHz, $D_2O$) δ 7.40-7.35 (2H, m), 7.15-7.09 (3H, m), 5.05 (1H, d, *J* = 7.4 Hz), 4.80 (1H, m) 3.98 (1H, dd, *J* = 3.2, 0.8 Hz), 3.85 (1H, ddd, *J* = 6.6, 5.6, 0.9 Hz), 3.78 (1H, dd, *J* = 9.9, 7.4 Hz), 3.75 (1H, dd, *J* = 5.3, 3.4 Hz), 3.74 (1H, dd, *J* = 10.0, 3.4 Hz). $^{13}$C NMR (126 MHz, $D_2O$) δ 156.6, 129.8, 123.1, 116.4, 100.6, 75.3, 72.5, 70.5, 68.4, 60.6. LRMS (ESI): *m/z* calcd. for $C_{12}H_{16}NaO_6$ $[M+Na]^+$ 279.1; found 279.1.

***4-Fluoropenyl-β-D-galactopyranoside (20)***

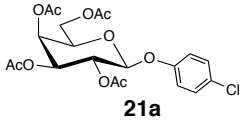


**20**

Compound **20** was prepared in a similar manner as **1a** from 1,2,3,4,6-penta-O-acetyl-β-D-galactopyranoside (100 mg, 0.26 mmol) and 4-fluorophenol (172 mg, 1.53 mmol) with boron trifluoride diethyl etherate (0.1 mL, 0.76 mmol). The crude mixture was dissolved into 4:1 methanol: sodium methoxide then stirred for 2h. The solution was concentrated under vacuo. and re-dissolved in minimum methanol. Ether was added to recrystallize and afford **20** as a white solid

(105 mg, 75% over two steps). $^1$H NMR (500 MHz, $D_2O$) δ 7.15-7.02 (4H, m), 4.94 (1H, d, *J* = 7.6 Hz), 3.97 (1H, d, *J* = 3.3 Hz), 3.87-3.72 (4H, m), 3.73 (1H, dd, *J* = 10.0, 3.3 Hz). $^{13}$C NMR (126 MHz, $D_2O$) δ 158.8, 153.2, 118.5 (d, $J_{C\text{-}F}$ = 8.46 Hz), 116.5 (d, $J_{C\text{-}F}$ = 23.44 Hz, C), 101.9, 75.8, 72.9, 71.0, 68.9, 61.1. LRMS (ESI): *m/z* calcd. for $C_{12}H_{15}FNaO_6$ $[M+Na]^+$ 297.1; found 297.1.

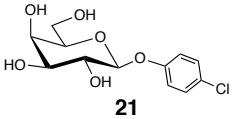
***4-Chlorophenyl-2,3,4,6-tetra-O-acetyl-β-D-galactopyranoside (21a)***




**21a**

Compound **21a** was prepared in a similar manner as **1a** from 1,2,3,4,6-penta-*O*-acetyl-β-D-galactopyranose (500 mg, 1.28 mmol), 4-chlorophenol (197 mg, 1.54 mmol) with boron trifluoride diethyl etherate (209 μL, 1.66 mmol)**.** Flash column chromatography (3:2 hexanes/ethyl acetate) afforded **21a** as a white powder (294 mg, 50%). Characterization data is consistent with that previously reported.[4] $^1$H NMR (400 MHz, $CDCl_3$): δ 7.27-7.23 (m, 2H), 6.96-6.92 (m, 2H), 5.49-5.44 (m, 2H), 5.10 (dd, *J* = 10.4, 3.4 Hz, 1H), 4.99 (d, *J* = 7.9 Hz, 1H), 4.22 (dd, *J* = 11.3, 7.0 Hz, 1H), 4.15 (dd, *J* = 11.3, 6.2 Hz, 1H), 4.06-4.03 (m, 1H), 2.18 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 170.3, 170.2, 170.1, 169.3, 155.4, 129.5, 128.4, 118.3, 99.7, 71.1, 70.7, 68.5, 66.8, 61.3, 20.7, 20.6, 20.6. LRMS (ESI): *m/z* calcd. for $C_{20}H_{27}ClNO_{10}$ $[M+NH_4]^+$ 476.9; found, 476.3.

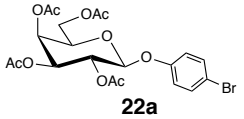
***4-Chlorophenyl-β-D-galactopyranoside (21)***




**21**

Compound **21a** (250 mg, 0.55 mmol) was dissolved in a solution of sodium methoxide in methanol (5 mL) and stirred for one hour at room temperature. The solution was then neutralized with Amberlite® IR-120 ($H^+$) ion-exchange resin, filtered and concentrated. The filtrate was concentrated and the product was lyophilized to yield **21** as a white powder (146 mg, 92%). $^1$H NMR (400 MHz, $D_2O$): δ 7.39-7.35 (m, 2H), 7.13-7.09 (m, 2H), 5.03 (d, *J* = 7.2 Hz, 1H), 3.99 (dd, *J* = 3.1, 0.8 Hz, 1H), 3.86 (t, *J* = 6.5 Hz, 1H), 3.82-3.74 (m, 4H). $^{13}$C NMR (101 MHz, $D_2O$): δ 156.1, 130.2, 128.1, 118.7, 101.5, 76.1, 73.2, 71.2, 69.1, 61.4. LRMS (ESI): *m/z* calcd. for $C_{12}H_{15}ClNaO_6$ $[M+Na]^+$ 313.7; found, 313.2.

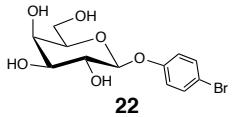
***4-Bromophenyl-2,3,4,6-tetra-O-acetyl-β-D-galactopyranoside (22a)***




**22a**

Compound **22a** was prepared in a similar manner as **1a** from 1,2,3,4,6-penta-*O*-acetyl-β-D-galactopyranose (500 mg, 1.28 mmol), 4-bromophenol (266 mg, 1.54 mmol) with boron trifluoride diethyl etherate (209 μL, 1.66 mmol)**.** Flash column chromatography (3:2 hexanes/ethyl acetate) afforded **22a** as a white powder (406 g, 63%). Characterization data is consistent with that previously reported.[6] $^1$H NMR (400 MHz, $CDCl_3$): δ 7.41-7.37 (m, 2H), 6.90-6.86 (m, 2H), 5.49-5.44 (m, 2H), 5.10 (dd, *J* = 10.4, 3.4 Hz, 1H), 4.99 (d, *J* = 7.9 Hz, 1H), 4.21 (dd, *J* = 11.3, 7.1 Hz, 1H), 4.15 (dd, *J* = 11.3, 6.2 Hz, 1H), 4.06-4.03 (m, 1H), 2.18 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 170.3, 170.2, 170.0, 169.3, 155.9, 132.4, 118.7, 115.8, 99.6, 71.1, 70.7, 68.5, 66.8, 61.3, 20.7, 20.6, 20.6. LRMS (ESI): *m/z* calcd. for $C_{20}H_{27}BrNO_{10}$ $[M+NH_4]^+$ 521.4; found, 522.2.

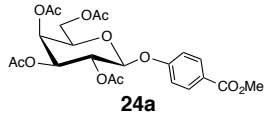
***4-Bromophenyl-β-D-galactopyranoside (22)***



**22**

Compound **22a** (300 mg, 0.60 mmol) was dissolved in a solution of sodium methoxide in methanol (5 mL) and stirred for one hour at room temperature. The solution was then neutralized with Amberlite® IR-120 ($H^+$) ion-exchange resin, filtered and concentrated. The filtrate was concentrated and the product was lyophilized to yield **22** as a white powder (159 mg, 80%). $^1$H NMR (400 MHz, $D_2O$): δ 7.54-7.50 (m, 2H), 7.08-7.04 (m, 2H), 5.03 (d, *J* = 7.3 Hz, 1H), 3.99 (d, *J* = 2.8 Hz, 1H), 3.88-3.84 (m, 1H), 3.82-3.73 (m, 4H). $^{13}$C NMR (101 MHz, $D_2O$): δ 155.9, 132.5, 118.4, 114.8, 100.7, 75.4, 72.5, 70.5, 68.4, 60.7. LRMS (ESI): *m/z* calcd. for $C_{12}H_{15}BrNaO_6$ $[M+Na]^+$ 357.0; found, 357.2.

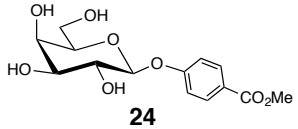
***4-(Methoxycarbonyl)phenyl-2,3,4,6-tetra-O-acetyl-β-D-galactopyranoside (24a)***



**24a**

Compound **24a** was prepared in a similar manner as **1a** from 1,2,3,4,6-penta-*O*-acetyl-β-D-galactopyranose (600 mg, 1.57 mmol), 4-(methoxycarbonyl)phenol (257 mg, 1.69 mmol) with boron trifluoride diethyl etherate (420 μL, 3.3 mmol)**.** Flash column chromatography (8:2 hexanes/EtOAc) afforded **24a** as a white powder (411 mg, 55%). $^1$H NMR (300 MHz, $CDCl_3$): δ 2.02 (s, 3H), 2.06 (s, 3H), 2.07 (s, 3H), 2.18 (s, 3H), 3.89 (s, 3H), 4.06-4.26 (m, 3H), 5.12 (dd, 1H, J=10.5, 3.4Hz), 5.13 (d, 1H, J=7.9Hz), 5.47 (dd, 1H, J=3.5, 1.0Hz), 5.51 (dd, 1H, J=10.5, 7.9Hz), 7.01 (dd, 2H, J=8.9, 2.0Hz), 8.00 (dd, 2H, J=8.9, 2.0Hz). $^{13}$C NMR (75 MHz, $CDCl_3$): δ 20.71, 20.79, 20.81, 20.86, 52.21, 61.54, 66.93, 68.60, 70.87, 71.40, 98.92, 116.27, 125.18, 131.71, 160.37, 166.60, 169.47, 170.23, 170.33, 170.49. LRMS (ESI): *m/z* calcd. for $C_{22}H_{26}KO_{12}$ $[M+K]^+$ 521.2; found, 521.2.

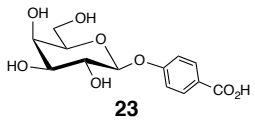
***4-(Methoxycarbonyl)phenyl-β-D-galactopyranoside (24)***



**24**

Compound **24a** (409 mg, 0.848 mmol) and potassium carbonate (12 mg, 0.0848 mmol) were dissolved in methanol (15 mL) in a 100 mL round bottom flask. The contents were stirred for two hours at room temperature. Amberlite IR resin (H+ form, pH=4) was pre-rinsed with MeOH and then added to the mixture, which was stirred for an additional 10 minutes until a pH of 5 to 6. The mixture was filtered and the solvent was removed under reduced pressure. The product was recrystallized in MeOH/$CH_2Cl_2$ to afford white crystals (181 mg, 68%). $^1$H NMR (300 MHz, $D_2O$): δ 3.74-3.86 (m, 4H), 3.88 (s, 3H), 3.91 (m, 1H), 4.00 (d, 1H, J= 3.16Hz), 5.15 (d, 1H, J=7.5Hz), 7.18 (dd, 2H, J=8.9Hz, 1.8Hz), 7.99 (dd, 2H, J=8.9, 1.8Hz). $^{13}$C NMR (75 MHz, $D_2O$): δ 52.45, 60.64, 68.36, 70.36, 72.42, 75.48, 99.94, 116.00, 123.79, 131.61, 160.63, 168.90. LRMS (ESI): *m/z* calcd. for $C_{14}H_{18}KO_8$ $[M+K]^+$ 353.2; found, 353.1.

***4-(β-D-glucopyranosyloxy)-benzoic acid (23)***

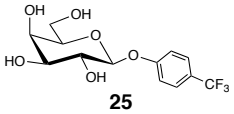


**23**

Compound **24** (160 mg, 0.509 mmol) and lithium hydroxide (37 mg, 1.527 mmol) were dissolved in a 2:1 mixture of $H_2O$:THF (10 mL) in a 50 mL flame-dried round bottom flask. The reaction mixture was stirred for 3 hours at room temperature. Amberlite IR-120 resin (H+ form, pH=4) was pre-rinsed with MeOH and then added to the mixture, which was stirred for an additional 10 minutes until a pH of 5 to 6. The mixture was filtered and the solvent evaporated under

reduced pressure to yield the desired product as white crystals (153 mg, 99%). $^1$H NMR (300 MHz, $D_2O$) δ 3.73-3.87 (m, 4H), 3.90 (dd, 1H, J=6.0Hz, 1.0Hz), 4.00 (dd, 1H, J=3.2Hz, 0.9Hz), 5.14, (d, 1H, J=7.3Hz), 7.16 (dd, 2H, 8.9Hz, 2.0Hz), 7.96 (dd, 2H, 8.9Hz, 2.0Hz). $^{13}$C NMR (75 MHz, $D_2O$) δ 60.63, 68.40, 70.38, 72.44, 75.47, 100.00, 115.92, 125.29, 131.70, 160.33, 171.07. LRMS (ESI): *m/z* calcd. for $C_{13}H_{15}KO_8$ $[M+K]^+$ 339.2; found 339.1.

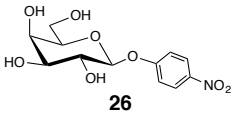
***4-Trifluoromethylphenyl-β-D-galactopyranoside (25)***




**25**

Compound **25** was prepared in a similar manner as **1a** from 1,2,3,4,6-penta-O-acetyl-β-D-galactopyranoside (100 mg, 0.26 mmol) and 4-(trifluoromethyl)phenol (46 mg, 0.28 mmol) with boron trifluoride diethyl etherate (0.1 mL, 0.76 mmol). The crude mixture was dissolved into 4:1 methanol: sodium methoxide then stirred for 2h. The solution was concentrated under vacuo. and re-dissolved in minimum methanol. Ether was added to recrystallize and afford **25** as a white solid (13 mg, 19% over two steps). $^1$H NMR (500 MHz, $D_2O$) δ 7.75 (2H, d, *J* = 8.4 Hz), 7.30 (2H, d, *J* = 8.5 Hz), 5.19 (1H, d, *J* = 7.8 Hz), 4.06 (1H, d, *J* = 2.7 Hz), 3.95 (1H, dd, *J* = 6.1, 5.6 Hz), 3.89 (1H, dd, *J* = 9.0, 8.5 Hz), 3.85-3.80 (3H, m). $^{13}$C NMR (126 MHz, $D_2O$) δ 159.1, 127. 17, 127.14, 127.11, 116.3, 100.1, 75.4, 72.4, 70.4, 68.3, 60.6. LRMS (ESI): *m/z* calcd. for $C_{13}H_{15}F_3NaO_6$ $[M+Na]^+$ 347.1; found 347.1.

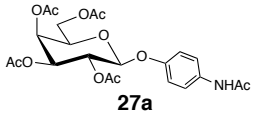
***4-Nitrophenyl -β-D-galactopyranoside (26)***




**26**

Compound **26** was prepared in a similar manner as **1a** from 1,2,3,4,6-penta-O-acetyl-β-D-galactopyranoside (100 mg, 0.26 mmol) and 4-nitrophenol (42 mg, 0.28 mmol) with boron trifluoride diethyl etherate (0.1 mL, 0.76 mmol). The crude mixture was dissolved into 4:1 methanol: sodium methoxide then stirred for 2h. The solution was concentrated under vacuo. and re-dissolved in minimum methanol. Ether was added to recrystallize and afford **26** as a white solid (15 mg, 19% over two steps). $^1$H NMR (500 MHz, $D_2O$) δ 8.24 (2H, d, *J* = 9.2 Hz), 7.22 (2H, d, *J* = 9.3 Hz), 5.18 (1H, d, *J* = 7.6 Hz), 3.99 (1H, d, *J* = 3.0 Hz), 3.91 (1H, dd, *J* = 6.0, 5.9 Hz), 3.83 (1H, dd, *J* = 9.9, 7.6 Hz), 3.78-3.74 (3H, m). $^{13}$C NMR (126 MHz, $D_2O$) δ 161.8, 142.5, 126.1, 116.4, 100.0, 75.6, 72.4, 70.3, 68.4, 60.7. LRMS (ESI): *m/z* calcd. for $C_{12}H_{16}NO_8$ $[M+H]^+$ 302.1; found 302.1.

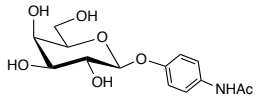
***4-Acetamidophenyl-2,3,4,6-tetra-O-acetyl-β-D-galatcopyranoside (27a)***




**27a**

Compound **27a** was prepared in a similar manner as **1a** from 1,2,3,4,6-penta-*O*-acetyl-β-D-galactopyranose (300 mg, 0.77 mmol), 4-*N*-acetylphenol (128 mg, 0.85 mmol) with boron trifluoride diethyl etherate (180 μL, 1.40 mmol)**.** Flash column chromatography (6:4 hexanes/EtOAc) afforded **27a** as a colourless oil (148 mg, 40%). $^1$H NMR (300 MHz, $CDCl_3$): δ 1.99 (s, 3H), 2.04 (s, 3H), 2.05 (s, 3H), 2.11 (s, 3H), 2.14 (s, 3H), 4.03 (dd, J=6.6 Hz, 1H), 4.10-4.18 (m, 2H), 5.05 (d, J=7.9 Hz, 1H), 5.09 (dd, J=10.3, 3.4 Hz, 1H), 5.45 (dd, J=10.2, 7.8 Hz, 1H), 5.42 (m, 1H), 6.91 (d, J=9.0 Hz, 2H), 7.39 (d, J=9.0 Hz, 2H), 7.63 (br s, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ 20.73, 20.81, 20.82, 20.89, 24.55, 61.49, 67.08, 68.79, 70.95, 71.17, 100.26, 117.77, 121.71, 133.52, 153.73, 168.41, 169.57, 170.27, 170.40, 170.53. LRMS (ESI): *m/z* calcd. for $C_{22}H_{27}NNaO_{11}$ $[M+Na]^+$ 504.1; found, 504.3.

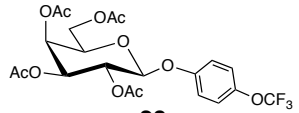
***4-Acetamidophenyl-β-D-glucopyranoside (27)***




**27**

Compound **27a** (25 mg, 0.051 mmol) and potassium carbonate (7 mg, 0.0051 mmol) were dissolved in methanol (10 mL) in a 50 mL round bottom flask and stirred overnight at room temperature. Amberlite IRC-76 resin (H+ form, pH=4) was pre-rinsed with MeOH and then added to the mixture, which was stirred for an additional 10 minutes until a pH of 5 to 6. The mixture was filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (85:15 $CH_2Cl_2$) to yield white crystals (8 mg, 53%). $^1$H NMR (300 MHz, $D_2O$) δ 2.15 (s, 3H), 3.76-3.81 (m, 4H), 3.86 (dd, J=12.1, 6.1 Hz, 1H), 4.00 (d, J=3.1 Hz, 1H), 5.04 (d, J=7.2 Hz, 1H), 7.14 (d, J=9.0 Hz, 2H), 7.35 (d, J=9.0 Hz, 2H). $^{13}$C NMR (75 MHz, $D_2O$) δ 30.87, 61.38, 69.11, 71.18, 73.19, 76.07, 101.57, 117.66, 124.83, 132.41, 154.93, 173.86. LRMS (ESI): *m/z* calcd. for $C_{14}H_{19}NNaO_7$ $[M+Na]^+$ 336.1; found 336.2.

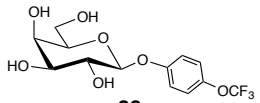
***4-Trifluoromethoxyphenyl-2,3,4,6-tetra-O-acetyl-β-D-galactopyranoside (28a)***




**28a**

Compound **28a** was prepared in a similar manner as **1a** from 1,2,3,4,6-penta-*O*-acetyl-β-D-galactopyranose (154 mg, 0.40 mmol), 4-trifluoromethoxyphenol (61 μL, 0.47 mmol) with boron trifluoride diethyl etherate (69 μL, 0.55 mmol)**.** Flash column chromatography (4:1 hexanes/EtOAc) afforded **28a** as a white powder (125 mg, 89%). $^1$H NMR (300 MHz, $CDCl_3$): δ 7.15 (d, *J* = 9.1 Hz, 2H), 7.03-6.98 (m, 2H), 5.48-5.45 (m, 2H), 5.10 (dd, *J* = 10.4, 3.4 Hz, 1H), 5.01 (d, *J* = 7.9 Hz, 1H), 4.26-4.12 (m, 2H), 4.05 (td, *J* = 6.6, 1.0 Hz, 1H), 2.18 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H). $^{13}$C NMR (76 MHz, $CDCl_3$): δ 170.3, 170.2, 170.1, 169.3, 155.2, 144.6, 122.4, 122.1, 118.7, 118.0, 99.7, 77.2, 71.1, 70.7, 68.5, 66.8, 61.3, 20.7, 20.6, 20.5. LRMS (ESI): *m/z* calcd. for $C_{21}H_{22}F_3NaO_{11}$ $[M-H]^-$ 507.4; found, 507.2.

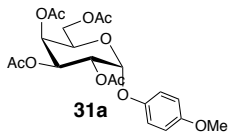
***4-Trifluoromethoxyphenyl-β-D-galactopyranoside (28)***




**28**

Compound **28a** (125 mg, 0.25 mmol) was dissolved in a solution of sodium methoxide in methanol (5 mL) and stirred for one hour at room temperature. The solution was then neutralized with Amberlite® IR-120 ($H^+$) ion-exchange resin, filtered and concentrated. The filtrate was concentrated and the product was lyophilized to yield **28** as a white powder (77 mg, 92%). $^1$H NMR (500 MHz, $D_2O$): δ 7.35-7.33 (m, 2H), 7.21 (d, *J* = 9.2 Hz, 2H), 5.07 (d, *J* = 7.5 Hz, 1H), 4.02 (d, *J* = 3.2 Hz, 1H), 3.89 (t, *J* = 6.2 Hz, 1H), 3.85-3.77 (m, 4H). $^{13}$C NMR (126 MHz, $D_2O$): δ 155.2, 122.6, 117.6, 116.1, 100.9, 75.4, 72.4, 70.4, 68.4, 60.6. LRMS (ESI): *m/z* calcd. for $C_{13}H_{14}F_3NaO_7$ $[M-H]^-$ 339.2; found, 339.1.

***4-Methoxyphenyl-2,3,4,6-tetra-O-acetyl-α-D-galactopyranoside (31a)***

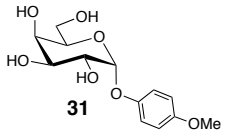



**31a**

Compound **31a** was prepared in a similar manner as **1a** from 1,2,3,4,6-penta-*O*-acetyl-β-D-galactopyranose (2 g, 5.12 mmol), 4-methoxyphenol (1.91 g, 15.4 mmol) with boron trifluoride diethyl etherate (2.6 mL, 20.5 mmol)**.** The reaction

mixture was refluxed for 2 days, and following quenching, washing and concentration the crude mixture showed a 1.6:1 ratio of α:β-linked products. Flash column chromatography (4:1 hexanes/EtOAc) afforded **31a** as a white powder (1.4 g, 60%). Characterization data is consistent with that previously reported in the literature.[7] $^1$H NMR (300 MHz, $CDCl_3$): δ 7.00-6.96 (m, 2H), 6.85-6.81 (m, 2H), 5.65 (d, *J* = 3.7 Hz, 1H), 5.58-5.51 (m, 2H), 5.26 (dd, *J* = 10.4, 3.6 Hz, 1H), 4.39 (t, *J* = 6.7 Hz, 1H), 4.10 (t, *J* = 6.6 Hz, 2H), 3.77 (s, 3H), 2.16 (s, 3H), 2.08 (s, 3H), 2.02 (s, 3H), 1.97 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 170.5, 170.5, 170.3, 170.2, 155.6, 150.4, 118.2, 114.8, 95.9, 68.1, 68.0, 67.7, 67.1, 61.7, 55.8, 20.9, 20.8, 20.8, 20.8. LRMS (ESI): *m/z* calcd. for $C_{21}H_{30}NO_{11}$ $[M+NH_4]^+$ 472.5; found, 472.0.

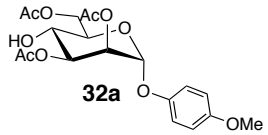
***4-Methoxyphenyl-α-D-galactopyranoside (31)***



**31**

Compound **31a** (1.4 g, 3.15 mmol) was dissolved in a solution of sodium methoxide in methanol (15 mL) and stirred for one hour at room temperature. The solution was then neutralized with Amberlite® IR-120 ($H^+$) ion-exchange resin, filtered and concentrated. The filtrate was concentrated and the product was lyophilized to yield **31** as a white powder (600 mg, 67%). $^1$H NMR (300 MHz, $D_2O$): δ 7.17-7.12 (m, 2H), 7.01-6.97 (m, 2H), 5.53 (d, *J* = 3.8 Hz, 1H), 4.12 (t, *J* = 6.2 Hz, 1H), 4.08-4.03 (m, 2H), 3.99-3.94 (m, 1H), 3.81 (s, 3H), 3.72-3.70 (m, 2H). $^{13}$C NMR (76 MHz, $D_2O$): δ 154.6, 150.4, 119.1, 115.0, 98.5, 71.6, 69.4, 69.1, 68.1, 61.0, 55.7. LRMS (ESI): *m/z* calcd. for $C_{13}H_{17}O_7$ $[M-H]^-$ 285.3; found, 285.1.

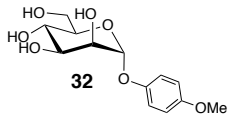
***4-Methoxyphenyl-2,3,4,6-Tetra-O-Acetyl-α-D-Mannopyranoside (32a)***



**32a**

Compound **32a** was prepared in a similar manner as **1a** from 1,2,3,4,6-penta-*O*-acetyl-α-D-mannopyranose (250 mg, 0.64 mmol), 4-methoxyphenol (95 mg, 0.77 mmol) with boron trifluoride diethyl etherate (113 μL, 0.9 mmol)**.** Flash column chromatography (3:2 hexanes/EtOAc) afforded **32a** as a white powder (124 mg, 43%). Characterization data is consistent with that previously reported.[8] $^1$H NMR (500 MHz, $CDCl_3$): δ 7.03-7.00 (m, 2H), 6.84-6.80 (m, 2H), 5.54 (dd, *J* = 10.0, 3.5 Hz, 1H), 5.43 (dd, *J* = 3.5, 1.8 Hz, 1H), 5.41 (d, *J* = 1.8 Hz, 1H), 5.35 (t, *J* = 10.1 Hz, 1H), 4.28 (dd, *J* = 12.2, 5.3 Hz, 1H), 4.13 (ddd, *J* = 10.1, 5.3, 2.2 Hz, 1H), 4.08 (dd, *J* = 12.1, 2.3 Hz, 1H), 3.77 (s, 3H), 2.19 (s, 3H), 2.05 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 170.6, 170.0, 169.9, 169.8, 155.4, 149.6, 117.7, 114.6, 96.6, 69.5, 69.0, 68.9, 66.0, 62.2, 55.6, 20.9, 20.7, 20.7. LRMS (ESI): *m/z* calcd. for $C_{21}H_{30}NO_{11}$ $[M+NH_4]^+$ 472.5; found, 472.4.

***4-Methoxyphenyl-α-D-Mannopyranoside (32)***

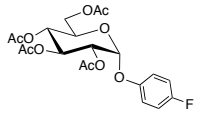


**32**

Compound **32a** (103 mg, 3.15 mmol) was dissolved in a solution of sodium methoxide in methanol (5 mL) and stirred for one hour at room temperature. The solution was then neutralized with Amberlite® IR-120 ($H^+$) ion-exchange resin, filtered and concentrated. The filtrate was concentrated and the product was lyophilized to yield **32** as a white powder (61 mg, 94%). $^1$H NMR (500 MHz, $D_2O$): δ 7.13-7.09 (m, 2H), 6.98-6.94 (m, 2H), 5.47 (d, *J* = 1.8 Hz, 1H), 4.14 (dd, *J* = 3.4, 1.8 Hz, 1H), 4.00 (dd, *J* = 8.9, 3.4 Hz, 1H), 3.78-3.74 (m, 1H), 3.78 (s, 3H), 3.75-3.69 (m, 3H). $^{13}$C NMR (76

MHz, $D_2O$): δ 154.5, 149.5, 118.7, 114.9, 99.2, 73.3, 70.3, 69.9, 66.5, 60.6, 55.7. LRMS (ESI): *m/z* calcd. for $C_{13}H_{17}O_7$ $[M-H]^-$ 285.3; found, 285.2.

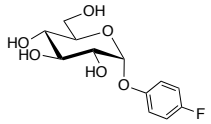
***4-Fluorophenyl-2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside (33a)***




**33a**

Compound **33a** was prepared in a similar manner as **1a** from 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (10 g, 25.6 mmol), 4-fluorophenol (3.45 g, 30.8 mmol) with boron trifluoride diethyl etherate (4.5 mL, 35.8 mmol)**.** The reaction mixture was refluxed for 2 days, and following quenching, washing and concentration the crude mixture showed a 1:4 ratio of α:β-linked products. Flash column chromatography (4:1 hexanes/EtOAc) afforded **33a** as a white powder (1.02 g, 9%). $^1$H NMR (300 MHz, $CDCl_3$): δ 7.03-6.99 (m, 4H), 5.71-5.64 (m, 2H), 5.14 (t, *J* = 9.7 Hz, 1H), 5.02 (dd, *J* = 10.3, 3.7 Hz, 1H), 4.24 (dd, *J* = 11.9, 4.4 Hz, 1H), 4.15-4.04 (m, 2H), 2.07 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.04 (s, 3H). $^{13}$C NMR (76 MHz, $CDCl_3$): δ 170.5, 170.1, 169.6, 160.2, 157.0, 152.2, 152.1, 118.0, 117.9, 116.3, 116.0, 94.8, 70.4, 69.9, 68.3, 68.0, 61.6, 20.7, 20.6, 20.6. LRMS (ESI): *m/z* calcd for $C_{20}H_{27}FNO_{10}$ $[M+NH_4]^+$ 460.5; found, 460.4.

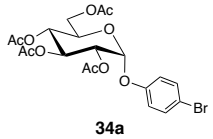
***4-Fluorophenyl-α-D-glucopyranoside (33)***




**33**

Compound **33a** (15 mg, 0.033 mmol) was dissolved in a solution of sodium methoxide in methanol (2 mL) and stirred for one hour at room temperature. The solution was then neutralized with Amberlite® IR-120 ($H^+$) ion-exchange resin, filtered and concentrated. The filtrate was concentrated and the product was lyophilized to yield **33** as a white powder (6 mg, 66%). $^1$H NMR (300 MHz, $D_2O$): δ 7.18-7.07 (m, 4H), 5.55 (d, *J* = 3.7 Hz, 1H), 3.90 (t, *J* = 9.5 Hz, 1H), 3.82-3.69 (m, 5H), 3.50 (t, *J* = 9.4 Hz, 1H). $^{13}$C NMR (76 MHz, $D_2O$): δ 148.9, 118.2, 118.2, 116.2, 114.4, 97.1, 75.5, 72.9, 72.3, 69.4, 60.5. LRMS (ESI): *m/z* calcd. for $C_{12}H_{15}FNaO_6$ $[M+Na]^+$ 297.2; found, 297.3.

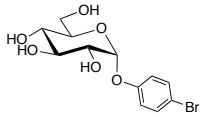
***4-Bromophenyl-2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside (34a)***




**34a**

Compound **34a** was prepared in a similar manner as **1a** from 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (8 g, 20.5 mmol), 4-bromophenol (4.25 mg, 24.6 mmol) with boron trifluoride diethyl etherate (3.86 mL, 30.8 mmol)**.** The reaction mixture was refluxed for 2 days, and following quenching, washing and concentration the crude mixture showed a 1:6 ratio of α:β-linked products. Flash column chromatography (4:1 hexanes/EtOAc) afforded **34a** as a white powder (1.14 g, 11%). Characterization data is consistent with that previously reported in the literature.[9] $^1$H NMR (300 MHz, $CDCl_3$): δ 7.39 (d, *J* = 9.0 Hz, 2H), 6.96 (d, *J* = 9.0 Hz, 2H), 5.69-5.62 (m, 2H), 5.13 (t, *J* = 9.8 Hz, 1H), 5.01 (dd, *J* = 10.3, 3.6 Hz, 1H), 4.22 (dd, *J* = 12.1, 4.6 Hz, 1H), 4.09-4.01 (m, 2H), 2.05 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H). $^{13}$C NMR (76 MHz, $CDCl_3$): δ 170.5, 170.2, 169.3, 169.2, 155.3, 129.5, 128.5, 118.4, 94.6, 72.6, 72.1, 71.1, 68.2, 61.9, 20.7, 20.6, 20.6, 20.6. LRMS (ESI): *m/z* calcd. for $C_{20}H_{27}BrNO_{10}$ $[M+NH_4]^+$ 521.4; found, 522.2.

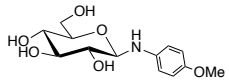
***4-Bromophenyl-α-D-glucopyranoside (34)***



**34**

Compound **34a** (25 mg, 0.050 mmol) was dissolved in a solution of sodium methoxide in methanol (2 mL) and stirred for one hour at room temperature. The solution was then neutralized with Amberlite® IR-120 ($H^+$) ion-exchange resin, filtered and concentrated. The filtrate was concentrated and the product was lyophilized to yield **34** as a white powder (17 mg, 98%). $^1$H NMR (300 MHz, $D_2O$): δ 7.51 (d, *J* = 9.0 Hz, 2H), 7.09 (d, *J* = 9.1 Hz, 2H), 5.61 (d, *J* = 3.8 Hz, 1H), 3.90 (t, *J* = 9.4 Hz, 1H), 3.77-3.69 (m, 4H), 3.50 (t, *J* = 9.5 Hz, 1H). $^{13}$C NMR (76 MHz, $D_2O$): δ 155.7, 151.5, 132.6, 128.4, 118.5, 115.0, 114.3, 110.8, 100.2, 92.2, 76.1, 75.5, 72.9, 71.9, 71.3, 69.4, 68.7, 65.2, 60.5, 56.3. LRMS (ESI): *m/z* calcd. for $C_{12}H_{15}BrNaO_6$ $[M+Na]^+$ 357.0; found, 357.2.

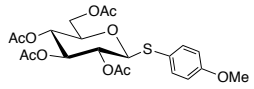
***N-(4-Methoxyphenyl)-1-β-D-glucopyranoside (37)***



**37**

To a solution of D-glucose (50 mg, 0.28 mmol) in ethanol (2 mL) was added *para*-anisidine. The solution was refluxed for 1 h, cooled to room temperature, then 0°C to precipitate the product. The product was filtered and lyophilized to yield **37** as a white powder (68 mg, 86%). $^1$H NMR (500 MHz, $D_2O$): δ 6.81-6.79 (m, 2H), 6.76-6.73 (m, 2H), 4.55 (d, *J* = 8.8 Hz, 1H), 3.74 (dd, *J* = 12.4, 2.3 Hz, 1H), 3.66 (s, 3H), 3.57 (dd, *J* = 12.4, 5.7 Hz, 1H), 3.45 (t, *J* = 9.1 Hz, 1H), 3.40 (ddd, *J* = 9.8, 5.7, 2.3 Hz, 1H), 3.32-3.26 (m, 2H). $^{13}$C NMR (126 MHz, $D_2O$): δ 152.4, 139.7, 115.9, 115.2, 85.7, 76.8, 76.4, 72.7, 69.7, 60.7, 55.8. LRMS (ESI): *m/z* calcd. for $C_{13}H_{19}NO_6$ $[M+K]^+$ 324.3; found, 324.2.

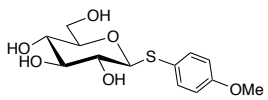
***4-Methoxyphenyl-2,3,4,6-tetra-O-acetyl-1-thio-β-D-glucopyranoside (38a)***



**38a**

Compound **38a** was prepared in a similar manner as **1a** from 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (200 mg, 0.51 mmol), 4-methoxythiophenol (76 μL, 0.62 mmol) with boron trifluoride diethyl etherate (97 μL, 0.77 mmol)**.** Flash column chromatography (7:3 hexanes/EtOAc) afforded **38a** as a white powder (188 mg, 78%). Characterization data is consistent with that previously reported in the literature.[10] $^1$H NMR (500 MHz, $CDCl_3$): δ 7.46-7.43 (m, 2H), 6.86-6.83 (m, 2H), 5.20 (t, *J* = 9.3 Hz, 1H), 5.00 (t, *J* = 9.8 Hz, 1H), 4.89 (dd, *J* = 10.0, 9.3 Hz, 1H), 4.55 (d, *J* = 10.0 Hz, 1H), 4.20-4.18 (m, 2H), 3.82 (s, 3H), 3.69-3.66 (m, 1H), 2.11 (s, 2H), 2.08 (s, 2H), 2.01 (s, 2H), 1.98 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 170.6, 170.2, 169.4, 169.3, 136.6, 120.8, 114.4, 85.7, 75.7, 74.0, 69.8, 68.1, 62.0, 55.3, 20.2, 20.8, 20.8. LRMS (ESI): *m/z* calcd. for $C_{21}H_{27}O_{10}S$ $[M+H]^+$ 471.5; found, 471.3.

***4-Methoxyphenyl-1-thio-β-D-glucopyranoside (38)***

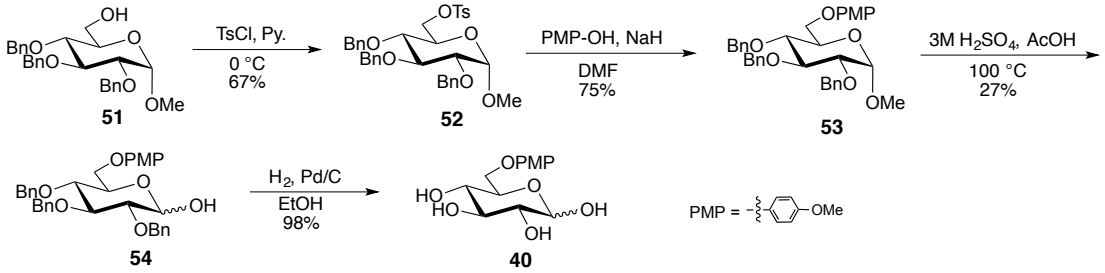


**38**

Compound **38a** (108 mg, 0.23 mmol) was dissolved in a solution of sodium methoxide in methanol (5 mL) and stirred for one hour at room temperature. The solution was then neutralized with Amberlite® IR-120 ($H^+$) ion-exchange resin,

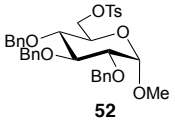
filtered and concentrated. The filtrate was concentrated and the product was lyophilized to yield **38** as a white powder (59 mg, 85%). $^{1}$H NMR (500 MHz, $D_2O$): δ 7.54 (dd, *J* = 8.9, 0.6 Hz, 2H), 6.99 (dd, *J* = 9.0, 0.6 Hz, 2H), 4.60 (d, *J* = 9.8 Hz, 2H), 3.87-3.84 (m, 1H), 3.83 (dd, *J* = 10.6, 1.2 Hz, 3H), 3.70-3.66 (m, 1H), 3.47 (td, *J* = 9.0, 0.6 Hz, 1H), 3.42-3.38 (m, 1H), 3.35-3.31 (m, 1H), 3.23 (td, *J* = 9.4, 0.6 Hz, 1H). $^{13}$C NMR (126 MHz, $D_2O$): δ 159.4, 135.1, 122.0, 114.7, 87.7, 79.8, 77.1, 71.5, 69.3, 60.7, 55.4. LRMS (ESI): *m/z* calcd. for $C_{13}H_{17}O_6S$ $[M-H]^-$ 302.3; found, 302.0.

***Synthetic scheme for the preparation of C6-O-PMP-Glc (40)***




**Scheme S2.** Preparation of C6-*O*-PMP-Glc **40**.

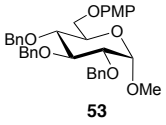
**Methyl-2,3,4-tri-*O*-Benzyl-6-*O*-(4-methylbenzenesulfonyl)-α-D-glucopyranoside (52)**



52

To a solution of methyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (122 mg, 0.26 mmol) (**51**, prepared as described previously)[11] and pyridine (47 $\mu$L, 0.58 mmol) in dry $CH_2Cl_2$ stirring at 0°C under argon was added TsCl (86 mg, 0.45 mmol). The reaction mixture was stirred overnight, then diluted with $CH_2Cl_2$. The organic layer was washed with water, brine, then dried over $MgSO_4$ and concentrated. Flash column chromatography (19:1 toluene/EtOAc) afforded **52** as a white powder (143 mg, 88%). Characterization data is consistent with that previously reported.[12] $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.36-7.28 (m, 15H), 7.15 (dt, *J* = 4.8, 2.3 Hz, 2H), 4.98 (d, *J* = 10.9 Hz, 1H), 4.80 (td, *J* = 14.6, 8.3 Hz, 3H), 4.64 (d, *J* = 12.1 Hz, 1H), 4.53 (d, *J* = 3.5 Hz, 1H), 4.44 (d, *J* = 10.7 Hz, 1H), 4.20 (qd, *J* = 9.8, 3.2 Hz, 2H), 3.96 (t, *J* = 9.3 Hz, 1H), 3.76 (ddd, *J* = 10.1, 3.9, 2.1 Hz, 1H), 3.49-3.43 (m, 2H), 3.32 (s, 3H), 2.40 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 144.8, 138.5, 137.9, 137.7, 132.8, 129.8, 128.5, 128.4, 128.1, 128.0, 127.9, 127.9, 127.9, 127.8, 127.6, 98.0, 81.8, 79.6, 76.8, 75.7, 74.9, 73.4, 68.5, 68.4, 55.3, 21.6. LRMS (ESI): *m/z* calcd. for $C_{35}H_{38}NaO_8S[M+Na]^+$ 657.7; found, 657.5.

**Methyl-2,3,4-tri-*O*-Benzyl-6-*O*-(4-methoxyphenyl)-α-D-glucopyranoside (53)**

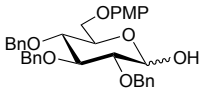


53

To a stirred solution of 66% sodium hydride (9 mg, 0.23 mmol) in dry DMF under argon was added *para*-methoxyphenol (26 mg, 0.21mmol). The mixture was stirred for 20 min and **52** (65 mg, 0.11 mmol) was added and the reaction mixture was stirred overnight. The reaction was quenched with brine, diluted with ethyl acetate and the organic layer was washed with saturated sodium thiosulfate, water, brine, then dried over $MgSO_4$ and concentrated. Flash column chromatography (9:1 pet. ether/EtOAc) afforded **53** as a white powder (45 mg, 75%). $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.39-7.18 (m, 15H), 6.85-6.80 (m, 4H), 5.02 (d, *J* = 10.8 Hz, 1H), 4.86 (dt, *J* = 15.5, 10.6 Hz, 3H), 4.70 (d, *J*

= 12.1 Hz, 1H), 4.66 (d, *J* = 3.5 Hz, 1H), 4.53 (d, *J* = 10.9 Hz, 1H), 4.12-4.03 (m, 3H), 3.91 (dt, *J* = 10.0, 2.8 Hz, 1H), 3.77 (s, 3H), 3.75 (t, *J* = 7.7 Hz, 1H), 3.62 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.40 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 153.9, 152.7, 138.7, 138.1, 138.0, 128.4, 128.4, 128.1, 128.0, 127.9, 127.7, 127.6, 115.5, 114.5, 98.2, 82.1, 79.8, 77.4, 75.8, 75.2, 73.4, 69.3, 67.1, 55.6, 55.2. LRMS (ESI): *m/z* calcd. for $C_{35}H_{38}NaO_7$ $[M+K]^+$ 609.7; found, 609.5.

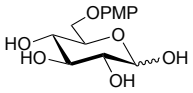
**2,3,4-tri-*O*-Benzyl-6-*O*-(4-methoxyphenyl)-D-glucopyranoside (54)**




**54**

A solution of **53** (45 g, 0.08 mmol) in 3 M $H_2SO_4$ in acetic acid (1.2 mL) was refluxed gently for 2 h. Following this, the mixture was cooled to room temperature, diluted with water and extracted with ethyl acetate. The organic layer was extract with water, brine, then dried over $MgSO_4$ and concentrated**.** Flash column chromatography (4:1 hexanes/ethyl acetate) afforded **54** as a white solid (12 mg, 27%). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.36-7.28 (m, 20H), 7.24 (d, *J* = 1.5 Hz, 5H), 7.18-7.16 (m, 5H), 6.84-6.79 (m, 8H), 5.26 (d, *J* = 3.6 Hz, 1H), 4.97 (d, *J* = 10.9 Hz, 3H), 4.89-4.85 (m, 4H), 4.80 (d, *J* = 11.8 Hz, 2H), 4.71 (d, *J* = 11.7 Hz, 1H), 4.55 (t, *J* = 10.3 Hz, 1H), 4.18 (dt, *J* = 10.0, 2.8 Hz, 1H), 4.09 (d, *J* = 2.9 Hz, 2H), 4.02 (t, *J* = 9.3 Hz, 2H), 3.79-3.75 (m, 9H), 3.64 (dd, *J* = 9.4, 3.6 Hz, 2H), 3.47-3.43 (m, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 154.0, 152.75, 152.69, 138.57, 138.42, 138.24, 137.97, 137.81, 137.74, 128.54, 128.46, 128.41, 128.40, 128.15, 128.12, 128.07, 128.04, 128.02, 127.93, 127.87, 127.77, 127.67, 97.6, 91.4, 84.5, 83.1, 81.7, 80.0, 77.46, 77.39, 75.76, 75.72, 75.21, 75.14, 74.8, 74.0, 73.4, 69.8, 67.6, 67.2, 55.7. LRMS (ESI): *m/z* calcd. for $C_{34}H_{36}NaO_7$ $[M+Na]^+$ 579.6; found, 579.4.

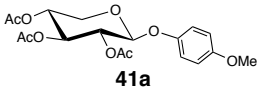
**6-*O*-(4-methoxyphenyl)-D-glucopyranoside (40)**




**40**

To a solution of **54** (8 mg, 0.15mmol) in ethanol (2 mL) was added Pd/C (5 mol %) and the reaction mixture was purged three times with $H_2$ under closed atmosphere. The mixture was stirred under $H_2$ atmosphere overnight, filtered over Celite and the solvent was evaporated to afforded **40** as a white powder (4 mg, 98%)**.** $^1$H NMR (500 MHz, $D_2O$): δ 7.02-6.96 (m, 8H), 5.24 (d, *J* = 3.8 Hz, 1H), 4.67 (dd, *J* = 8.0, 0.6 Hz, 1H), 4.31-4.29 (m, 1H), 4.24 (dd, *J* = 10.9, 2.0 Hz, 1H), 4.17 (ddd, *J* = 18.6, 11.1, 5.4 Hz, 2H), 4.10-4.07 (m, 1H), 3.79 (d, *J* = 19.4 Hz, 6H), 3.73 (t, *J* = 9.6 Hz, 2H), 3.60-3.55 (m, 3H), 3.52-3.49 (m, 1H), 3.28 (dd, *J* = 9.0, 8.1 Hz, 1H). $^{13}$C NMR (126 MHz, $D_2O$): δ 153.6, 153.5, 152.4, 152.3, 116.3, 116.3, 115.1, 96.0, 92.1, 75.6, 74.1, 74.0, 72.7, 71.4, 69.7, 69.5, 69.5, 68.0, 67.8, 55.8. LRMS (ESI): *m/z* calcd. for $C_{13}H_{18}KO_7$ $[M+K]^+$ 325.3; found, 325.1.

***4-Methoxyphenyl-2,3,4-tri-O-acetyl-β-D-xylopyranoside (41a)***

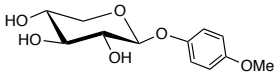



**41a**

Compound **41a** was prepared in a similar manner as **1a** from 1,2,3,4-penta-*O*-acetyl-β-D-xylopyranose (340 mg, 1.07 mmol), 4-methoxyphenol (186 mg, 1.5 mmol) with boron trifluoride diethyl etherate (402 μL, 3.2 mmol). Flash column chromatography (7:3 hexanes/ethyl acetate) afforded **41a** as a white powder (228 mg, 60%). Characterization data is consistent with that previously reported.[13] $^1$H NMR (500 MHz, $CDCl_3$): δ 6.94 (d, *J* = 9.1 Hz, 2H), 6.82 (d, *J* = 9.1 Hz, 2H), 5.22 (t, *J* = 8.1 Hz, 1H), 5.15 (dd, *J* = 8.2, 6.4 Hz, 1H), 5.03-4.99 (m, 2H), 4.20 (dd, *J* = 12.0, 4.8 Hz, 1H), 3.77 (s, 3H), 3.47 (dd, *J* = 12.0, 8.1 Hz, 1H), 2.09 (s, 3H), 2.07 (s, 3H), 2.07 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 167.0,

169.8, 169.4, 155.6, 150.6, 118.5, 114.6, 99.8, 71.0, 70.4, 68.6, 61.9, 55.6, 20.7, 20.7. LRMS (ESI): *m/z* calcd. for $C_{18}H_{22}NaO_9$ $[M+Na]^+$ 405.4; found, 405.3.

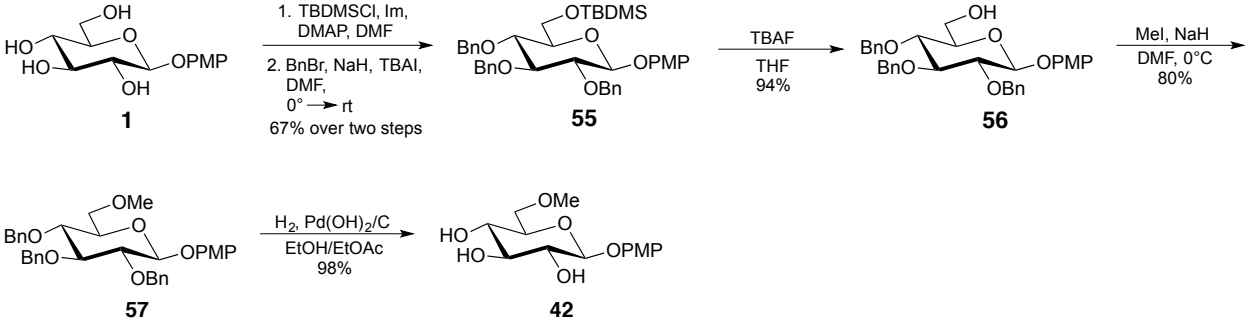
***4-Methoxyphenyl-β-D-xylopyranoside (41)***



**41**

Compound **41a** (74 mg, 0.19 mmol) was dissolved in a solution of sodium methoxide in methanol (5 mL) and stirred for one hour at room temperature. The solution was then neutralized with Amberlite® IR-120 ($H^+$) ion-exchange resin, filtered and concentrated. The filtrate was concentrated and the product was lyophilized to yield **41** as a white powder (44 mg, 89%). Characterization data is consistent with that previously reported.[14] $^1$H NMR (500 MHz, $D_2O$): δ 7.12-7.09 (m, 2H), 7.00-6.97 (m, 2H), 4.97 (d, *J* = 7.5 Hz, 1H), 4.00 (dd, *J* = 11.6, 5.5 Hz, 1H), 3.82 (s, 3H), 3.72-3.68 (m, 1H), 3.56-3.50 (m, 2H), 3.43 (dd, *J* = 11.5, 10.6 Hz, 1H). $^{13}$C NMR (126 MHz, $D_2O$): δ 154.8, 150.6, 118.3, 115.0, 101.8, 75.5, 72.8, 69.0, 65.1, 55.7. LRMS (ESI): *m/z* calcd. for $C_{12}H_{16}NaO_6$ $[M+Na]^+$ 279.2; found, 279.4.

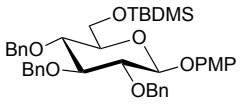
***Synthetic scheme for the preparation of C6-O-Me-β-PMP-Glc (42)***




**1** **55** **56** **57** **42**

**Scheme S3.** Preparation of C6-*O*-Me- β-PMP-Glc **42**.

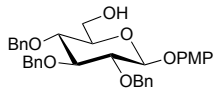
***para*-Methoxyphenyl-2,3,4-tri-*O*-Benzyl-6-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranoside (55)**



**55**

To a mixture of **1** (6.71 g, 23.4 mmol) in dry DMF (50 mL) under argon was added *tert*-butyldimethylsilyl chloride (4.24 g, 28.1 mmol), 4-dimethylaminopyridine (286 mg, 2.34 mmol) and imidazole (3.51 g, 51.5 mmol). The reaction mixture was stirred overnight, then evaporated to a syrup that was dissolved in ethyl acetate and washed with 10% HCl, saturated $NaHCO_3$, water and brine, then dried over $MgSO_4$ and concentrated. The crude silylated product was dissolved in 10 mL dry DMF and added dropwise over 30 min to a mixture of 66% sodium hydride (2.46 g, 61.8 mmol), benzyl bromide (10 mL, 84.2 mmol) and tetrabutylammonium iodide (692 mg, 1.87 mmol) stirring at 0°C under argon. The reaction mixture was slowly warmed to room temperature and stirred overnight. The reaction was quenched with brine, then diluted with ethyl acetate and extracted. The aqueous layer was washed twice with ethyl acetate, and the combined organic extracts were dried over $MgSO_4$ and concentrated. Flash column chromatography (9:1 hexanes/ethyl acetate) afforded **55** as a white solid (10.4 g, 83%). $^1$H NMR (300 MHz, $CDCl_3$): δ 7.39-7.30 (m, 15H), 7.07-7.02 (m, 2H), 6.85-6.79 (m, 2H), 5.06 (d, *J* = 10.9 Hz, 1H), 4.94 (d, *J* = 10.8 Hz, 1H), 4.89-4.81 (m, 4H), 4.68 (d, *J* = 10.9 Hz, 1H), 3.88 (dd, *J* = 11.3, 1.8 Hz, 1H), 3.80-3.74 (m, 1H), 3.78 (s, 3H) 3.72-3.62 (m, 3H), 3.39 (ddd, *J* = 9.3, 4.9, 1.8 Hz, 1H), 0.90 (s, 9H), 0.05 (d, *J* = 9.5 Hz, 6H). $^{13}$C NMR (76 MHz, $CDCl_3$): δ 151.6, 138.5, 138.4, 138.2, 128.4, 128.4, 128.1, 128.0, 128.0, 127.8, 127.7, 127.7, 118.7, 114.5, 103.0, 84.7, 82.3, 77.5, 76.1, 75.9, 75.0, 62.3, 55.6, 25.9, 18.3, -5.1, -5.4. LRMS (ESI): *m/z* calcd. for $C_{40}H_{54}NO_7Si$ $[M+NH_4]^+$ 688.4; found, 688.3.

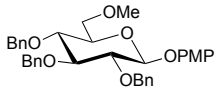
***para*-Methoxyphenyl-2,3,4-tri-*O*-Benzyl-β-D-glucopyranoside (56)**




**56**

To a solution of **55** (10.4 g, 15.5 mmol) in dry THF under argon was added tetrabutylammonium fluoride (8.1 g, 30.9 mmol). The reaction mixture was stirred overnight at room temperature, then diluted with ethyl acetate and extracted. The organic phase was washed with brine, dried over $MgSO_4$, and concentrated. Recrystallization with hot chloroform and hexanes afforded **56** as a white solid (8.1 g, 94%). Characterization data is consistent with that previously reported.[15] $^1$H NMR (300 MHz, $CDCl_3$): δ 7.35-7.28 (m, 15H), 7.00-6.96 (m, 2H), 6.86-6.82 (m, 2H), 5.03 (d, *J* = 10.9 Hz, 1H), 4.97-4.95 (m, 2H), 4.90-4.80 (m, 3H), 4.66 (d, *J* = 10.9 Hz, 1H), 3.89 (ddd, *J* = 12.0, 6.1, 2.6 Hz, 1H), 3.77 (s, 3H), 3.75-3.62 (m, 4H), 3.47 (ddd, *J* = 9.6, 4.5, 2.6 Hz, 1H), 1.87 (t, *J* = 6.9, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 155.4, 151.2, 138.4, 138.1, 137.9, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 118.1, 114.7, 102.5, 84.4, 82.1, 75.7, 75.3, 75.1, 75.1, 62.0, 55.6. LRMS (ESI): *m/z* calcd. for $C_{34}H_{40}NO_7$ $[M+NH_4]^+$ 574.8; found, 574.2.

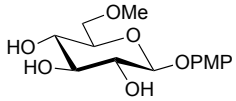
***para*-Methoxyphenyl-6-*O*-Methyl-2,3,4-tri-*O*-Benzyl-β-D-glucopyranoside (57)**




**57**

To a stirred solution of 66% sodium hydride (21 mg, 0.54 mmol) in dry DMF under argon at 0°C was added **56**. The mixture was stirred at 0°C for 20 min and methyl iodide (31 μL, 0.49 mmol) was added and the reaction mixture was stirred overnight. The reaction was quenched with brine, diluted with ethyl acetate and the organic layer was washed with saturated sodium thiosulfate, water, brine, then dried over $MgSO_4$ and concentrated. Flash column chromatography (4:1 hexanes/EtOAc) afforded **57** as a white powder (206 mg, 80%). $^1$H NMR (300 MHz, $CDCl_3$): δ 7.36-7.29 (m, 15H), 7.06-7.00 (m, 2H), 6.87-6.82 (m, 2H), 5.06 (d, *J* = 10.9 Hz, 1H), 4.96 (d, *J* = 11.0 Hz, 1H), 4.91-4.81 (m, 4H), 4.65 (d, *J* = 10.9 Hz, 1H), 3.79 (s, 3H), 3.72-3.60 (m, 5H), 3.54-3.50 (m, 1H), 3.39 (s, 3H). $^{13}$C NMR (76 MHz, $CDCl_3$): δ 155.2, 151.5, 138.5, 138.2, 138.1, 128.4, 128.4, 128.2, 128.0, 127.8, 127.7, 127.6, 118.3, 114.5, 102.8, 84.5, 82.0, 75.7, 75.08, 75.02, 74.8, 71.1, 59.4, 55.6. LRMS (ESI): *m/z* calcd. for $C_{35}H_{38}NaO_7$ $[M+Na]^+$ 593.7; found, 593.4.

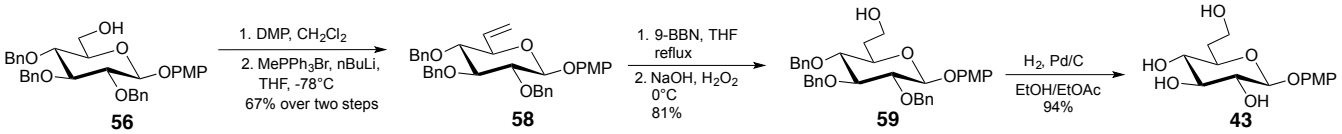
***para*-Methoxyphenyl-6-*O*-Methyl-β-D-glucopyranoside (42)**




**42**

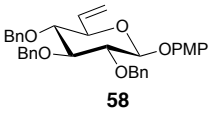
To a solution of **57** (142 mg, 0.25 mmol) in ethanol (4 mL) was added palladium hydroxide (5 mol %) and the reaction mixture was purged three times with $H_2$ under closed atmosphere. The mixture was stirred under $H_2$ atmosphere overnight, filtered over Celite and the solvent was evaporated to afforded **42** as a white powder (74 mg, 98%)**.** $^1$H NMR (500 MHz, $D_2O$): δ 7.10-7.07 (m, 2H), 6.97-6.94 (m, 2H), 4.98 (d, *J* = 7.6 Hz, 1H), 3.79 (s, 3H), 3.78-3.75 (m, 1H), 3.68-3.62 (m, 2H), 3.59-3.50 (m, 2H), 3.47 (t, *J* = 9.2 Hz, 1H), 3.37 (s, 3H). $^{13}$C NMR (126 MHz, $D_2O$): δ 154.6, 150.8, 118.0, 114.9, 101.1, 75.4, 74.6, 72.8, 70.8, 69.5, 58.5, 55.7. LRMS (ESI): *m/z* calcd. for $C_{14}H_{20}NaO_7$ $[M+Na]^+$ 323.3; found, 323.1.

***Synthetic scheme for the preparation of compound 43***




**Scheme S4.** Preparation of β-PMP-Glc derivative **43**.

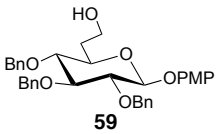
***para*-Methoxyphenyl-6,7-Dideoxy-2,3,4-tri-*O*-Benzyl-β-D-*Gluco*-hept-6-enopyranose (58)**




To a stirred suspension of **56** (1.6 g, 2.87 mmol) in $CH_2Cl_2$ (15 mL) was added Dess-Martin periodinane (1.46 g, 3.45 mmol) and the reaction mixture was stirred at room temperature for 3 h. The reaction mixture was quenched with a 1:1 mixture of 1 M sodium thiosulfate/sat. $NaHCO_3$ until both organic and aqueous layers were clear. The solution was extracted with $CH_2Cl_2$, washed with saturated $NaHCO_3$, dried over $MgSO_4$ and concentrated. The crude aldehyde was then azeotroped three times with toluene and used in the subsequent reaction without further purification.

To a flame dried flask under argon, methyltriphenylphosphonium bromide (1.54 g, 4.31 mmol) was dissolved in dry THF (50 mL) and cooled to -78°C. A 2.55 M solution of *n*-butyllithium (nBuLi) in THF (1.67 mL, 4.31 mmol) was added dropwise to this mixture and stirred for 30 min at -78°C. The concentration of *n*BuLi was determined by titration with diphenylacetic acid (DPA) as described previously.[16] After stirring for 30 min at -78°C the reaction mixture was warmed slowly to 0°C and stirred for 1 h, and a solution of the crude aldehyde in dry THF (10 mL) was transferred dropwise to this solution at 0°C. The reaction was stirred overnight, slowly warming to room temperature, and then was quenched with saturated ammonium chloride, extracted with hexanes. The mixture was subsequently washed with ammonium chloride, $NaHCO_3$, water and brine, then dried over $MgSO_4$ and concentrated. Flash column chromatography (19:1 hexanes/ethyl acetate) afforded **58** as a white solid (1.03 g, 65%). $^1$H NMR (400 MHz, $C_6D_6$): δ 7.42-7.35 (m, 4H), 7.28-7.26 (m, 2H), 7.20-7.08 (m, 11H), 6.72-6.68 (m, 2H), 5.99 (ddd, *J* = 17.3, 10.7, 5.3 Hz, 1H), 5.50 (dt, *J* = 17.2, 1.6 Hz, 1H), 5.14 (d, *J* = 11.4 Hz, 1H), 5.12-5.08 (m, 1H), 5.00 (d, *J* = 11.4 Hz, 1H), 4.92 (d, *J* = 7.7 Hz, 1H), 4.86 (d, *J* = 11.4 Hz, 2H), 4.74 (d, *J* = 11.3 Hz, 1H), 4.50 (d, *J* = 11.2 Hz, 1H), 3.82 (dd, *J* = 9.1, 7.8 Hz, 1H), 3.68 (t, *J* = 9.0 Hz, 2H), 3.33 (t, *J* = 9.3 Hz, 1H), 3.28 (s, 3H). $^{13}$C NMR (76 MHz, $C_6D_6$): δ 156.0, 152.2, 139.5, 139.3, 139.0, 135.1, 128.6, 128.5, 128.5, 128.0, 127.8, 119.1, 117.1, 115.0, 103.5, 84.6, 82.6, 82.5, 75.6, 75.6, 75.1, 75.1, 55.2. LRMS (ESI): *m/z* calcd. for $C_{35}H_{36}NaO_6$ $[M+Na]^+$ 575.7; found, 575.5.

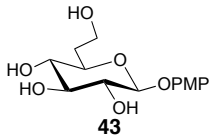
***para*-Methoxyphenyl-6-deoxy-2,3,4-tri-*O*-Benzyl-β-D-*Gluco*-heptopyranose (59)**




To a solution of **58** (267 mg, 0.48 mmol) in dry THF (10 mL), was added a solution of 9-BBN (4.8 mL of 0.5 M solution in THF, 2.4 mmol). The resulting solution was heated under reflux for 5 h., then cooled to room temperature, and then to 0°C and 10% NaOH (5 mL) and followed by 35% $H_2O_2$ (5 mL) were added slowly. The resulting biphasic reaction mixture was stirred for 30 min then diluted with $CH_2Cl_2$. The aqueous layer was then extracted with $CH_2Cl_2$ and combined organic layers were washed with 10% sodium metabisulfite, water, brine, then dried over $MgSO_4$, filtered and concentrated**.** Flash column chromatography (7:3 hexanes/ethyl acetate) afforded **59** as a white solid (223 mg, 81%). $^1$H NMR (300 MHz, $C_6D_6$): δ 7.41-7.34 (m, 4H), 7.27-7.18 (m, 4H), 7.14-7.04 (m, 6H), 6.79-6.73 (m, 2H), 5.13 (d, *J* = 11.3 Hz, 1H), 5.03 (d, *J* = 11.4 Hz, 1H), 4.85 (td, *J* = 10.7, 7.4 Hz, 4H), 4.46 (d, *J* = 11.4 Hz, 1H), 3.80 (dd, *J* = 9.1, 7.8

Hz, 1H), 3.64 (dt, *J* = 15.4, 7.3 Hz, 2H), 3.56-3.48 (m, 1H), 3.45-3.38 (m, 1H), 3.28 (dt, *J* = 5.7, 3.6 Hz, 1H), 3.29 (s, 3H) 1.96 (dddd, *J* = 13.9, 8.2, 5.4, 2.5 Hz, 1H), 1.62-1.51 (m, 1H), 1.22 (dd, *J* = 6.2, 4.3 Hz, 1H). $^{13}$C NMR (76 MHz, $C_6D_6$): δ 156.0, 151.9, 139.5, 139.2, 139.1, 128.6, 128.6, 128.1, 127.9, 127.9, 118.7, 115.1, 103.0, 84.9, 82.6, 81.8, 75.6, 75.1, 75.0, 73.6, 59.8, 55.2, 36.7, 34.7. LRMS (ESI): *m/z* calcd. for $C_{35}H_{34}NO_7$ $[M+NH_4]^+$ 588.8; found, 588.2.

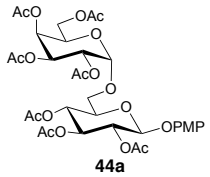
**_para_-Methoxyphenyl-6-deoxy-β-D-_Gluco_-heptopyranose (43)**



**43**

To a solution of **59** in ethanol (4 mL) was added Pd/C (5 mol %) and the reaction mixture was purged three times with $H_2$ under closed atmosphere. The mixture was stirred under $H_2$ atmosphere overnight, filtered over Celite and the solvent was evaporated to afford **43** as a white powder (103 mg, 94%)**.** $^1$H NMR (300 MHz, $D_2O$): δ 7.09-7.03 (m, 2H), 6.99-6.94 (m, 2H), 4.97 (d, *J* = 7.7 Hz, 1H), 3.79 (s, 3H), 3.74-3.63 (m, 2H), 3.60-3.50 (m, 3H), 3.31 (t, *J* = 9.3 Hz, 1H), 2.19-2.08 (m, 1H), 1.72-1.60 (m, 1H). $^{13}$C NMR (76 MHz, $D_2O$): δ 154.6, 150.7, 117.9, 115.0, 100.8, 75.4, 73.3, 73.1, 72.6, 57.8, 55.7, 33.3. LRMS (ESI): *m/z* calcd. for $C_{14}H_{20}NaO_7$ $[M+Na]^+$ 323.3; found, 323.2.

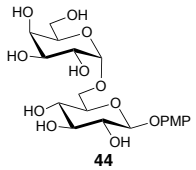
**4-Methoxyphenyl-6-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-2,3,4-tri-*O*-acetyl-β-D-glucopyranoside (44a)**



**44a**

Compound **44a** was prepared in a similar manner as **1a** from 6-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranoside[17] (175 mg, 0.26 mmol), 4-methoxyphenol (45 mg, 0.36 mmol) with boron trifluoride diethyl etherate (42 μL, 0.34 mmol)**.** Flash column chromatography (1:1 hexanes/EtOAc) afforded **44a** as a white powder (150 mg, 78%). $^1$H NMR (400 MHz, $CDCl_3$): δ 6.93-6.87 (m, 4H), 5.35-5.23 (m, 3H), 5.17 (dd, *J* = 9.7, 7.9 Hz, 1H), 5.10-5.00 (m, 4H), 4.15-4.12 (m, 1H), 3.89-3.88 (m, 2H), 3.84-3.74 (m, 5H), 3.54-3.51 (m, 1H), 2.09 (s, 5H), 2.05 (s, 6H), 2.01 (s, 3H), 1.98 (s, 3H), 1.94 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 170.47, 170.31, 170.22, 170.19, 169.8, 169.43, 169.35, 155.7, 150.4, 117.7, 114.7, 98.9, 96.0, 77.2, 72.7, 71.2, 68.8, 68.1, 67.3, 66.43, 66.32, 61.5, 55.6, 20.82, 20.66, 20.65, 20.61, 20.58. LRMS (ESI): *m/z* calcd. for $C_{33}H_{44}NO_{19}$ $[M+NH_4]^+$ 761.7; found, 761.2.

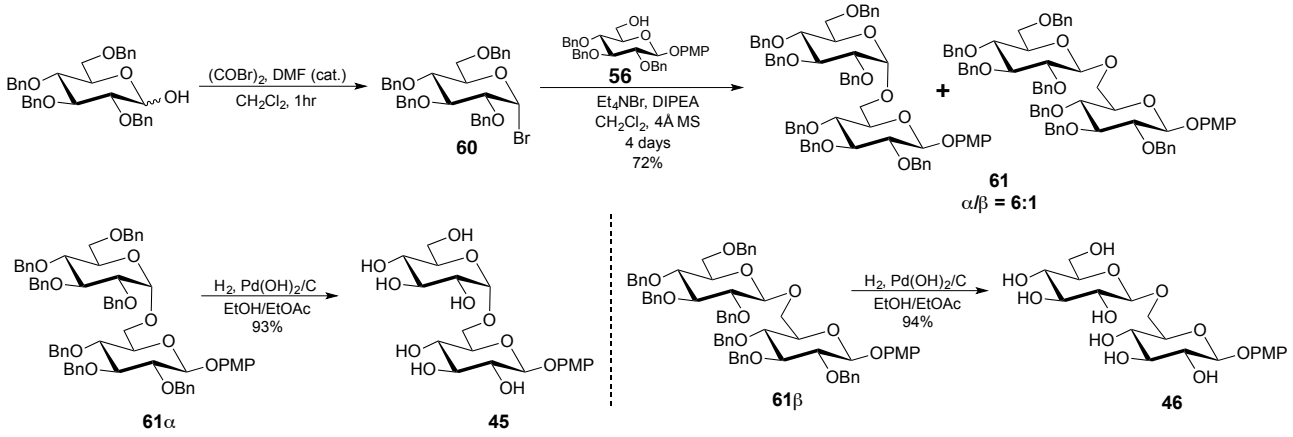
**4-Methoxyphenyl-6-*O*-(α-D-galactopyranosyl)-β-D-glucopyranoside (44)**



**44**

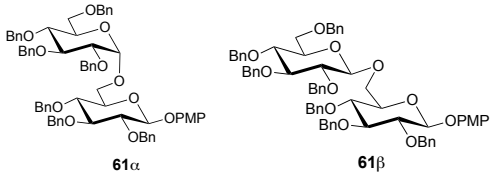
Compound **44a** (66 mg, 0.089 mmol) was dissolved in a solution of sodium methoxide in methanol (2 mL) and stirred for one hour at room temperature. The solution was then neutralized with Amberlite® IR-120 ($H^+$) ion-exchange resin, filtered and concentrated. The filtrate was concentrated and the product was lyophilized to yield **44** as a white powder (28 mg, 70%). $^1$H NMR (500 MHz, $D_2O$): δ 7.11 (dd, *J* = 9.2, 1.1 Hz, 2H), 6.99 (dd, *J* = 9.2, 1.1 Hz, 2H), 5.12 (d, *J* = 7.7 Hz, 1H), 4.95 (s, 1H), 3.89-3.86 (m, 1H), 3.82 (s, 3H), 3.79-3.74 (m, 6H), 3.66-3.50 (m, 6H). $^{13}$C NMR (126 MHz, $D_2O$): δ 154.5, 150.3, 117.7, 114.9, 100.0, 97.5, 75.7, 74.5, 72.9, 70.6, 69.6, 69.3, 69.1, 68.2, 65.4, 61.0, 55.8. LRMS (ESI): *m/z* calcd. for $C_{19}H_{27}O_{12}$ $[M-H]^-$ 447.4; found, 447.2.

***Synthetic scheme for the preparation of disaccharides 45-46***




**Scheme S5.** Preparation of PMP-disaccharide derivatives **45** and **46**.

**4-Methoxyphenyl-6-*O*-(2,3,4,6-tetra-*O*-Benzyl-D-glucopyranosyl)-2:3,4-tri-*O*-benzyl-β-D-glucopyranoside (61α and 61β)**




Compound **60** (273mg, 0.51 mmol) was prepared as described previously.[18,19] The crude bromide **60** was azeotroped three times with toluene and then dissolved dry $CH_2Cl_2$ (1 mL) and added dropwise to a mixture of **56** (140 mg, 0.25 mmol), tetraethylammonium bromide (106 mg, 0.51 mmol) and DIPEA (88 $\mu$L, 0.51 mmol) stirring in dry $CH_2Cl_2$ (5 mL) with 4Å molecular sieves under argon. The reaction mixture was stirred for 4 days, then diluted with $CH_2Cl_2$, washed with brine, dried over $MgSO_4$ and concentrated. Flash column chromatography over a gradient (9:1 then 7:3 hexanes/ethyl acetate) afforded a mixture of **61α/β** (6:1) as a white solid (195 mg, 72%). Further purification with flash chromatography (50:50:1 $CH_2Cl_2$/hexanes/acetone) afforded pure **61α** (154 mg, 57%) and pure **61β** (18 mg, 7%).

**Characterization data for 61α:**

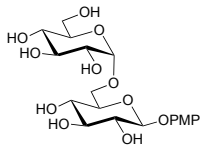
$^1$H NMR (500 MHz, $CDCl_3$): δ 7.39-7.22 (m, 30H), 7.10 (dd, *J* = 6.5, 2.8 Hz, 2H), 7.04-7.03 (m, 2H), 6.79-6.77 (m, 2H), 5.00-4.95 (m, 3H), 4.93-4.90 (m, 2H), 4.85-4.77 (m, 5H), 4.73 (dd, *J* = 11.5, 6.4 Hz, 2H), 4.66 (d, *J* = 11.1 Hz, 1H), 4.59 (d, *J* = 12.1 Hz, 1H), 4.45 (dd, *J* = 18.9, 11.6 Hz, 2H), 3.97 (t, *J* = 9.3 Hz, 1H), 3.85-3.82 (m, 2H), 3.77 (dd, *J* = 11.4, 1.4 Hz, 1H), 3.71-3.63 (m, 4H), 3.61-3.54 (m, 7H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 155.4, 151.4, 138.8, 138.5, 138.5, 138.4, 138.3, 138.1, 137.9, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 127.6, 127.5, 119.0, 114.6, 103.1, 97.3, 82.1, 81.8, 80.0, 77.6, 75.7, 75.1, 75.0, 74.9, 74.7, 73.3, 72.5, 70.1, 68.4, 66.0, 55.4. LRMS (ESI): *m/z* calcd. for $C_{68}H_{70}KO_{12}$ $[M+K]^+$ 1118.3; found, 1118.5.

**Characterization data for 61β:**

$^1$H NMR (500 MHz, $CDCl_3$): δ 7.36-7.28 (m, 30H), 7.02-6.99 (m, 2H), 6.68-6.67 (m, 2H), 5.05 (d, *J* = 10.9 Hz, 1H), 4.97-4.91 (m, 4H), 4.81 (ddd, *J* = 11.0, 7.1, 4.0 Hz, 5H), 4.67 (d, *J* = 11.0 Hz, 1H), 4.60-4.58 (m, 2H), 4.53-4.44 (m, 4H), 4.18 (d, *J* = 9.3 Hz, 1H), 3.76-3.68 (m, 7H), 3.60 (s, 4H), 3.56 (m, 1H), 3.47 (dd, *J* = 9.8, 7.0 Hz, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 156.2, 150.7, 138.8, 138.5, 138.5, 138.4, 138.3, 138.1, 137.9, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 127.6, 127.5, 118.2, 114.8, 103.1, 99.8, 82.1, 81.2, 80.4, 77.6, 75.7,

75.1, 75.0, 74.9, 74.7, 73.9, 72.5, 71.1, 67.4, 66.0, 56.4. LRMS (ESI): *m/z* calcd. for $C_{68}H_{70}NaO_{12}$ $[M+K]^+$ 1102.3; found, 1102.0.

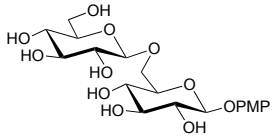
**4-Methoxyphenyl-6-*O*-(α-D-glucopyranosyl)-β-D-glucopyranoside (45)**




**45**

To a solution of **61α** (117 mg, 0.11 mmol) in ethanol (4 mL) was added palladium hydroxide (5 mol %) and the reaction mixture was purged three times with $H_2$ under closed atmosphere. The mixture was stirred under $H_2$ atmosphere overnight, filtered over Celite and the solvent was evaporated to afforded **45** as a white powder (45 mg, 93%)**.** $^1$H NMR (500 MHz, $D_2O$): δ 7.14-7.10 (m, 2H), 7.00-6.97 (m, 2H), 5.06 (d, *J* = 7.4 Hz, 1H), 4.93 (d, *J* = 3.7 Hz, 1H), 3.95 (dd, *J* = 11.4, 5.4 Hz, 1H), 3.81 (s, 3H), 3.78 (dd, *J* = 6.2, 2.2 Hz, 2H), 3.75-3.62 (m, 4H), 3.60-3.53 (m, 4H), 3.41 (t, *J* = 9.4 Hz, 1H). $^{13}$C NMR (126 MHz, $D_2O$): δ 154.6, 150.7, 117.9, 115.0, 100.8, 97.8, 75.7, 74.4, 73.05, 72.89, 71.7, 71.4, 69.31, 69.28, 65.6, 60.3, 55.8. LRMS (ESI): *m/z* calcd. for $C_{19}H_{28}NaO_{12}$ $[M+Na]^+$ 471.4; found, 471.2.

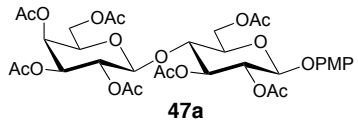
**4-Methoxyphenyl-6-*O*-(β-D-glucopyranosyl)-β-D-glucopyranoside (46)**




**46**

To a solution of **61β** (117 mg, 0.11 mmol) in ethanol (4 mL) was added palladium hydroxide (5 mol %) and the reaction mixture was purged three times with $H_2$ under closed atmosphere. The mixture was stirred under $H_2$ atmosphere overnight, filtered over Celite and the solvent was evaporated to afforded **46** as a white powder (45 mg, 93%)**.** $^1$H NMR (500 MHz, $D_2O$): δ 7.15-7.11 (m, 2H), 7.01-6.98 (m, 2H), 5.06 (d, *J* = 7.9 Hz, 1H), 4.47 (d, *J* = 7.9 Hz, 1H), 4.19 (dd, *J* = 12.0, 1.7 Hz, 1H), 3.91-3.86 (m, 2H), 3.82 (s, 3H), 3.79-3.77 (m, 1H), 3.68 (dd, *J* = 12.4, 5.9 Hz, 1H), 3.60-3.52 (m, 3H), 3.44-3.26 (m, 4H). $^{13}$C NMR (126 MHz, $D_2O$): δ 154.7, 150.7, 118.2, 115.0, 102.4, 100.9, 75.8, 75.59, 75.42, 75.33, 73.05, 72.86, 69.6, 69.3, 68.1, 60.6, 55.8. LRMS (ESI): *m/z* calcd. for $C_{19}H_{28}NaO_{12}$ $[M+Na]^+$ 471.4; found, 471.0.

**4-Methoxyphenyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (47a)**

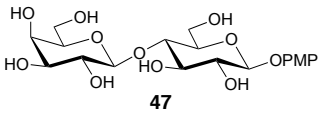



**47a**

Compound **47a** was prepared in a similar manner as **1a** from 4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-1,2,3,6-tetra-*O*-acetyl-β-D-glucopyranoside[17] (500 mg, 0.74 mmol), 4-methoxyphenol (128 mg, 1.03 mmol) with boron trifluoride diethyl etherate (460 μL, 3.68 mmol)**.** Flash column chromatography (1:1 hexanes/EtOAc) afforded **47a** as a white powder (461 mg, 84%). $^1$H NMR (500 MHz, $CDCl_3$): δ 6.94-6.90 (m, 2H), 6.82-6.79 (m, 2H), 5.35 (dd, *J* = 3.4, 0.9 Hz, 1H), 5.26 (t, *J* = 9.1 Hz, 1H), 5.16-5.10 (m, 2H), 4.96 (dd, *J* = 10.4, 3.4 Hz, 1H), 4.92 (d, *J* = 7.8 Hz, 1H), 4.51-4.49 (m, 2H), 4.16-4.12 (m, 2H), 4.08 (dd, *J* = 11.1, 7.4 Hz, 1H), 3.90-3.86 (m, 2H), 3.77 (s, 3H), 3.72 (ddd, *J* = 9.9, 5.6, 2.1 Hz, 1H), 2.16 (s, 3H), 2.10 (s, 3H), 2.07 (s, 6H), 2.07 (s, 3H), 2.05 (s, 3H), 1.97 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 170.37, 170.32, 170.15, 170.08, 169.77, 169.63, 169.1, 155.7, 150.8, 118.6, 114.5, 101.1, 99.9, 76.2, 72.78,

72.68, 71.5, 70.9, 70.7, 69.0, 66.5, 61.9, 60.8, 55.6, 20.83, 20.73, 20.67, 20.65, 20.54. LRMS (ESI): *m/z* calcd. for $C_{33}H_{44}NO_{19}$ $[M+NH_4]^+$ 761.7; found, 761.5.

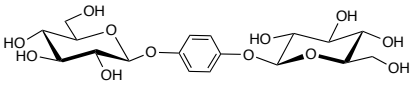
**4-Methoxyphenyl-4-*O*-(β-D-galactopyranosyl)-β-D-glucopyranoside (47)**




**47**

Compound **47a** (171 mg, 0.23 mmol) was dissolved in a solution of sodium methoxide in methanol (2 mL) and stirred for one hour at room temperature. The solution was then neutralized with Amberlite® IR-120 ($H^+$) ion-exchange resin, filtered and concentrated. The filtrate was concentrated and the product was lyophilized to yield **47** as a white powder (83 mg, 80%). $^1$H NMR (500 MHz, $D_2O$): δ 6.95-6.93 (m, 2H), 6.82-6.80 (m, 2H), 4.87 (d, *J* = 7.9 Hz, 1H), 4.30 (d, *J* = 7.8 Hz, 1H), 3.82-3.79 (m, 1H), 3.75 (d, *J* = 3.4 Hz, 1H), 3.67 (d, *J* = 4.3 Hz, 1H), 3.63 (s, 3H), 3.61-3.55 (m, 6H), 3.49 (dd, *J* = 10.0, 3.4 Hz, 1H), 3.42-3.36 (m, 3H). $^{13}$C NMR (126 MHz, $D_2O$): δ 154.6, 150.7, 118.1, 114.9, 102.8, 100.9, 77.9, 75.3, 74.8, 74.1, 72.55, 72.39, 70.8, 68.4, 60.9, 59.7, 55.7. LRMS (ESI): *m/z* calcd. for $C_{19}H_{28}NaO_{12}$ $[M+NaH]^+$ 471.4; found, 471.0.

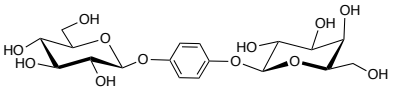
***1,4-Bis-(β-D-glucopyranosyl)benzene (48)***




**48**

Compound **48a** (300 mg, 0.4 mmol) was dissolved in a solution of sodium methoxide in methanol (5 mL) and stirred for one hour at room temperature. The solution was then neutralized with Amberlite® IR-120 ($H^+$) ion-exchange resin, filtered and concentrated. The filtrate was concentrated and the product was lyophilized to yield **48** as a white powder (160 mg, 95%). $^1$H NMR (400 MHz, $D_2O$): δ 7.11 (s, 4H), 5.04 (d, *J* = 7.5 Hz, 2H), 3.91 (dd, *J* = 12.4, 2.2 Hz, 2H), 3.74 (dd, *J* = 12.5, 5.7 Hz, 2H), 3.61-3.45 (m, 8H). $^{13}$C NMR (101 MHz, $D_2O$): δ 152.3, 118.0, 100.8, 76.1, 75.5, 72.9, 69.4, 60.5. LRMS (ESI): *m/z* calcd. for $C_{18}H_{26}NaO_{12}$ $[M+Na]^+$ 457.4; found, 457.2.

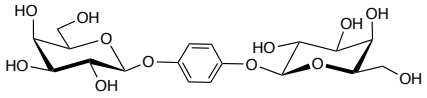
***1-O-(β-D-glucopyranosyl)-4-O-(β-D-galactopyranosyl)-benzene (49)***




**49**

Compound **49a** (10 mg, 0.013 mmol) was dissolved in a solution of sodium methoxide in methanol (5 mL) and stirred for one hour at room temperature. The solution was then neutralized with Amberlite® IR-120 ($H^+$) ion-exchange resin, filtered and concentrated. The filtrate was concentrated and the product was lyophilized to yield **49** as a white powder (5 mg, 94%). $^1$H NMR (400 MHz, $D_2O$): δ 7.14-7.12 (m, 4H), 5.05 (d, *J* = 7.5 Hz, 1H), 4.99 (d, *J* = 7.2 Hz, 1H), 3.99 (dd, *J* = 3.0, 0.7 Hz, 1H), 3.92 (dd, *J* = 12.4, 2.2 Hz, 1H), 3.84-3.81 (m, 1H), 3.79-3.72 (m, 6H), 3.62-3.46 (m, 6H). $^{13}$C NMR (101 MHz, $D_2O$): δ 152.49, 152.33, 152.24, 118.01, 117.94, 101.4, 100.9, 76.1, 75.55, 75.39, 72.9, 72.6, 70.6, 69.4, 68.5, 60.8, 60.5. LRMS (ESI): *m/z* calcd. for $C_{18}H_{26}NaO_{12}$ $[M+Na]^+$ 457.4; found, 457.0.

***1,4-Bis-(β-D-galactopyranosyl)benzene (50)***



**50**

Compound **50a** (100 mg, 0.13 mmol) was dissolved in a solution of sodium methoxide in methanol (5 mL) and stirred for one hour at room temperature. The solution was then neutralized with Amberlite® IR-120 ($H^+$) ion-exchange resin, filtered and concentrated. The filtrate was concentrated and the product was lyophilized to yield **50** as a white powder (53 mg, 94%). $^1$H NMR (400 MHz, $D_2O$): δ 7.11 (s, 4H), 4.98 (d, *J* = 7.0 Hz, 2H), 3.98 (d, *J* = 2.8 Hz, 2H), 3.85-3.72 (m, 11H). $^{13}$C NMR (101 MHz, $D_2O$): δ 152.4, 117.9, 101.4, 75.4, 72.5, 70.6, 68.5, 60.7. LRMS (ESI): *m/z* calcd. for $C_{18}H_{26}NaO_{12}$ $[M+Na]^+$ 457.4; found, 457.3.

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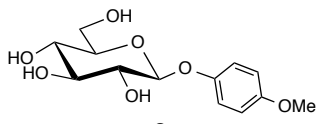
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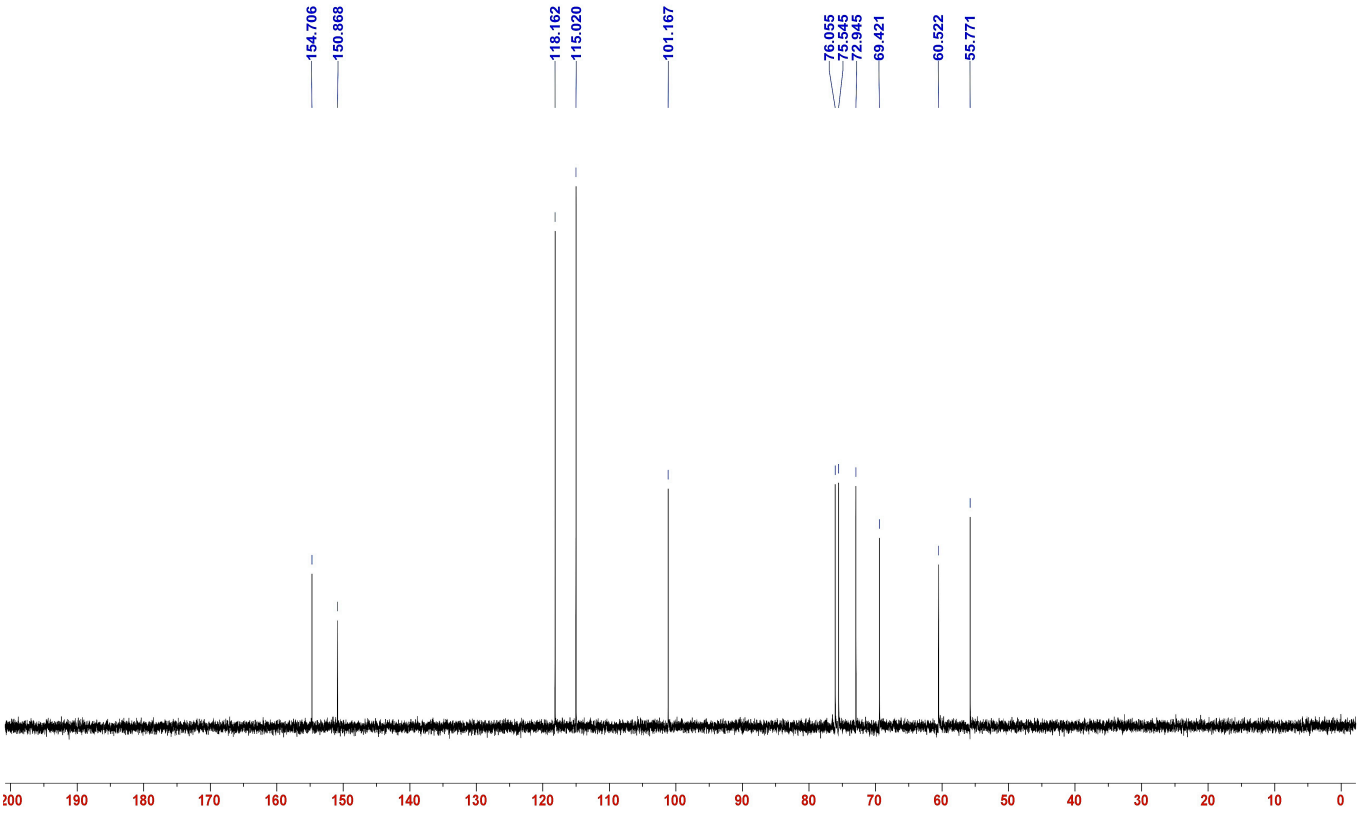
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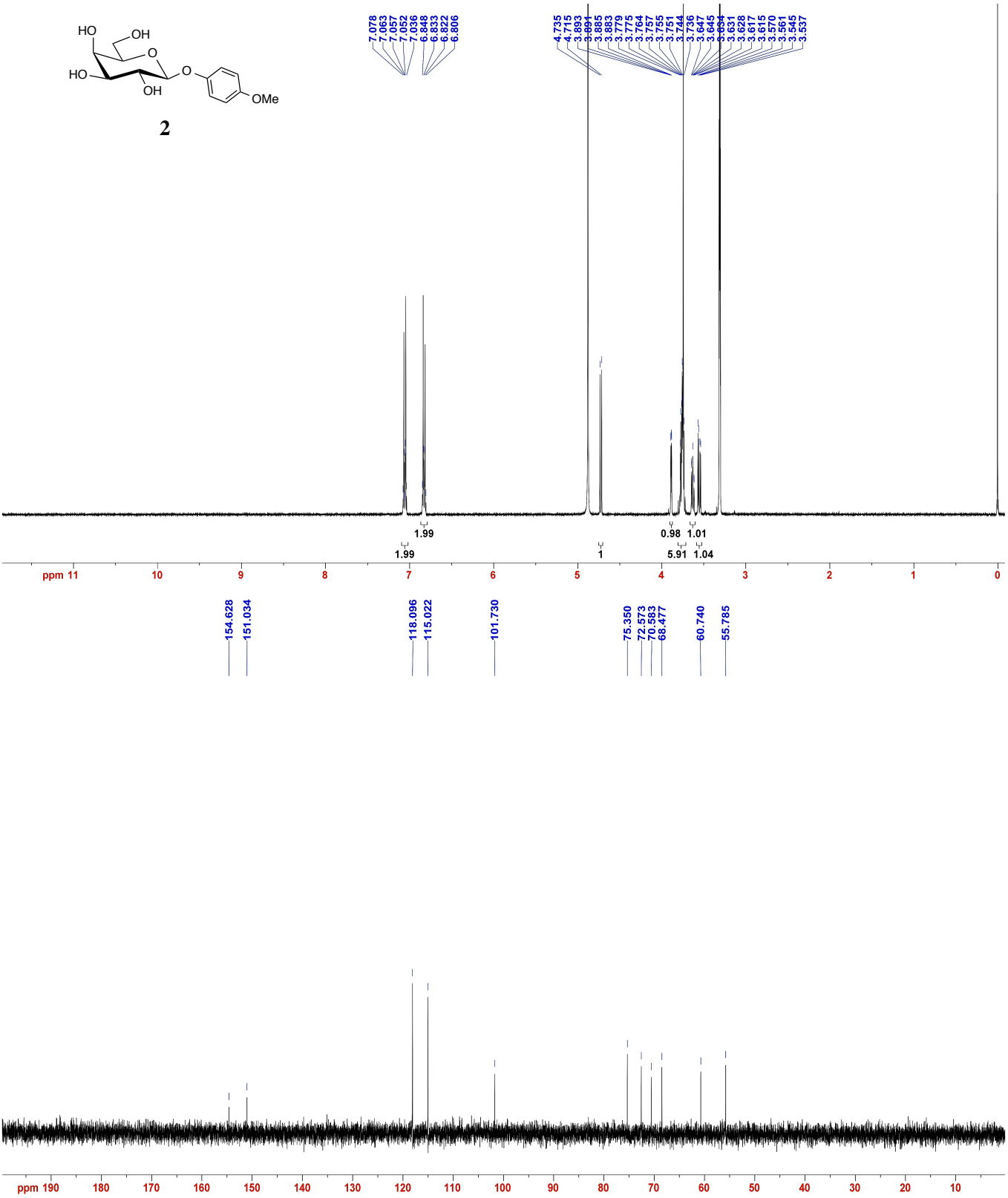
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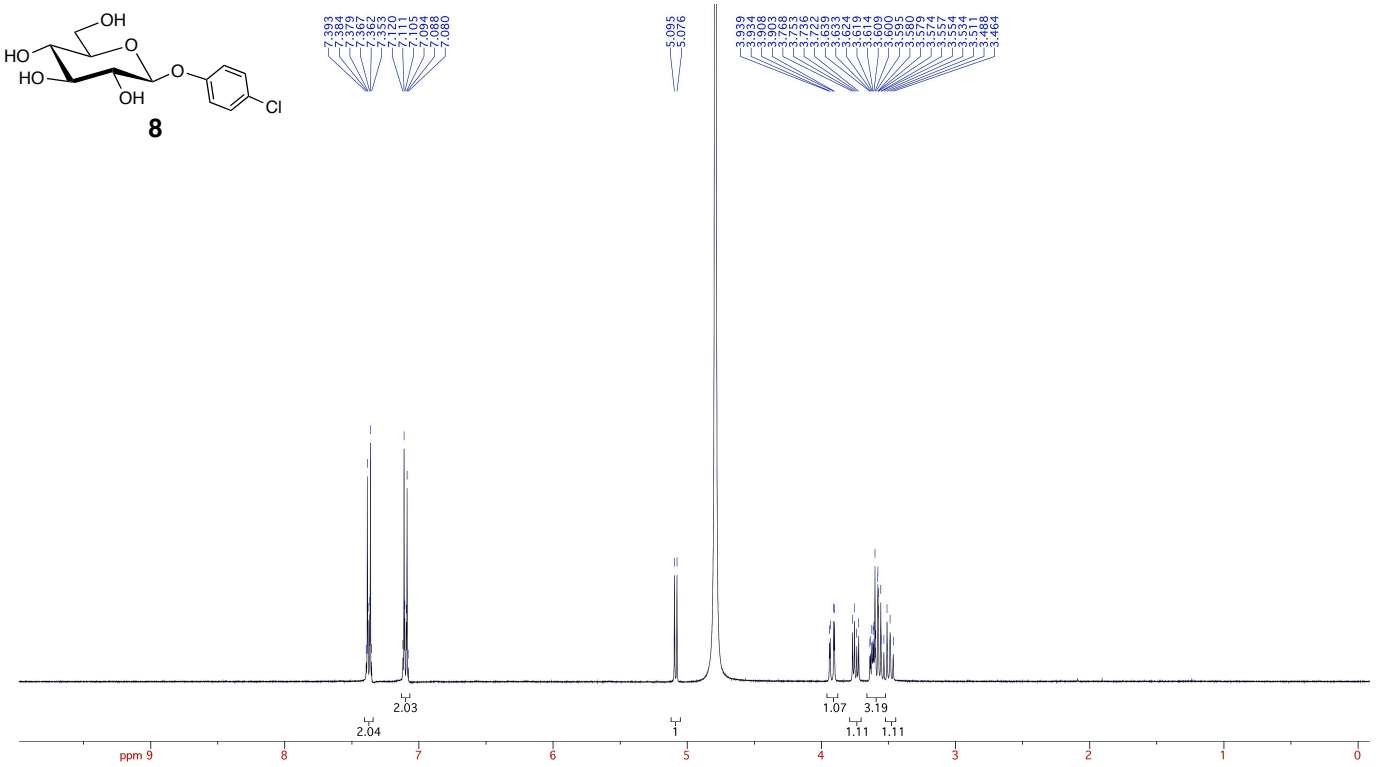
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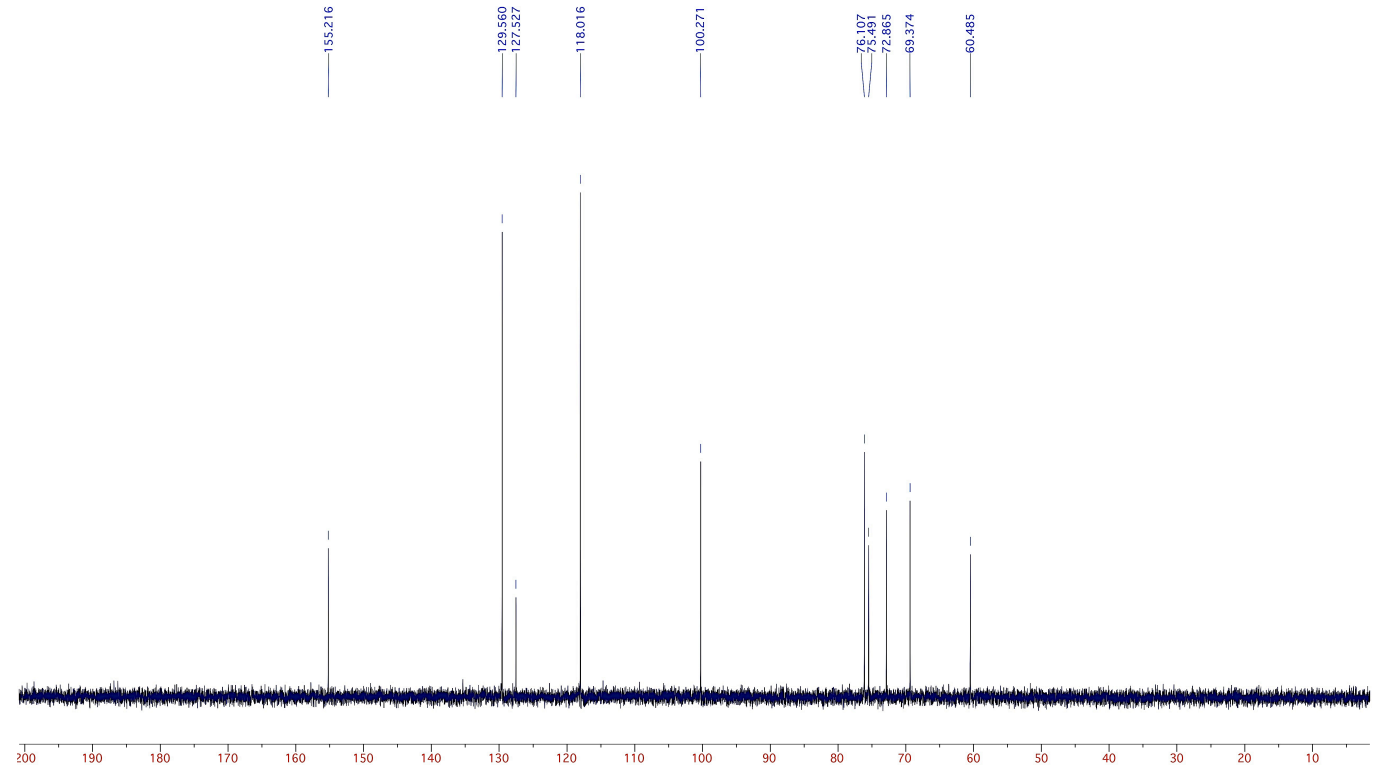
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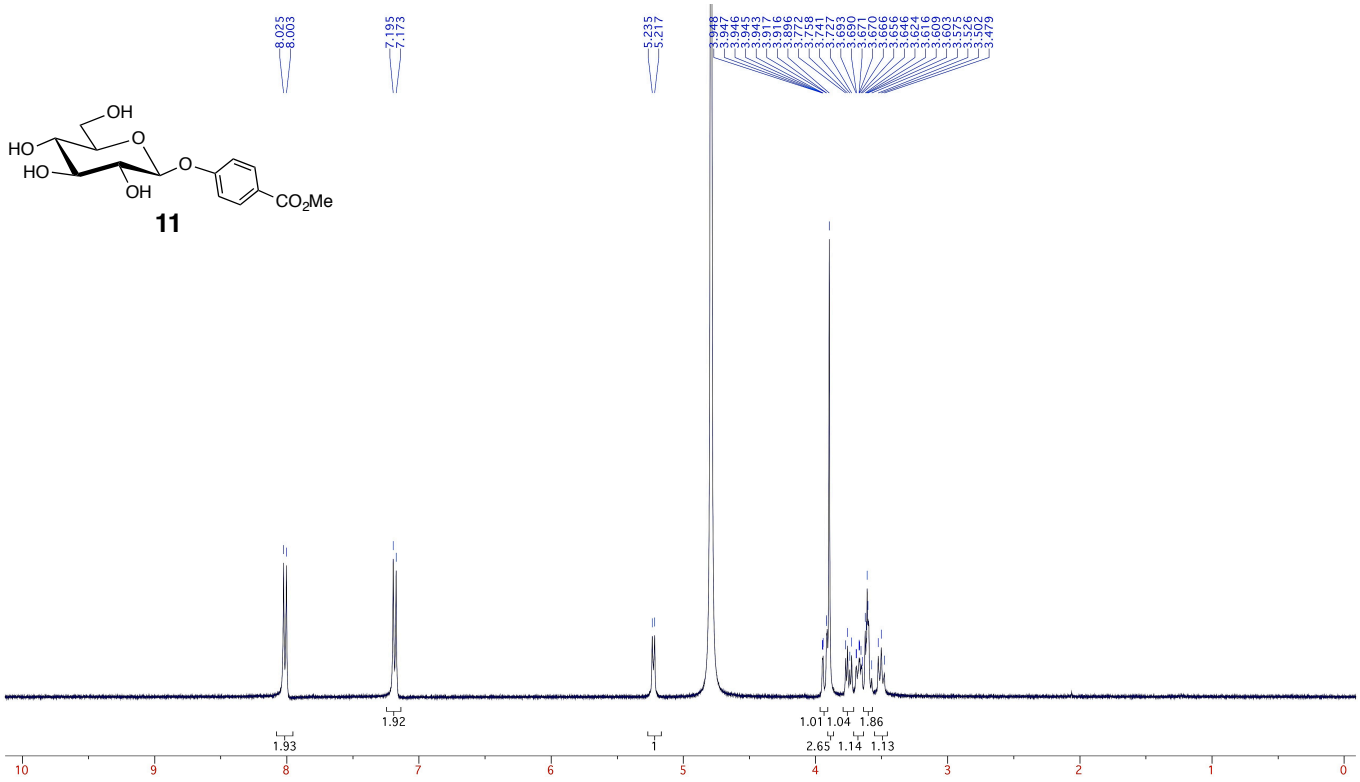
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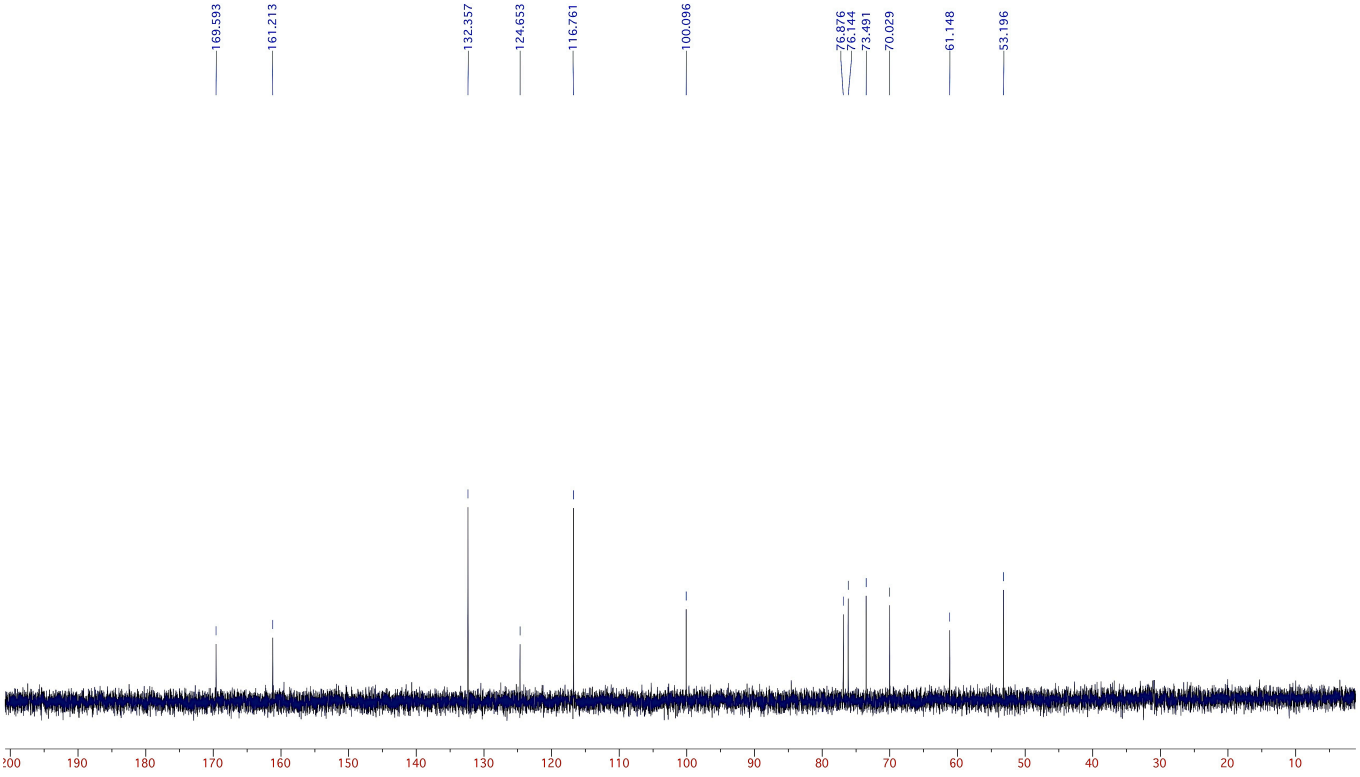
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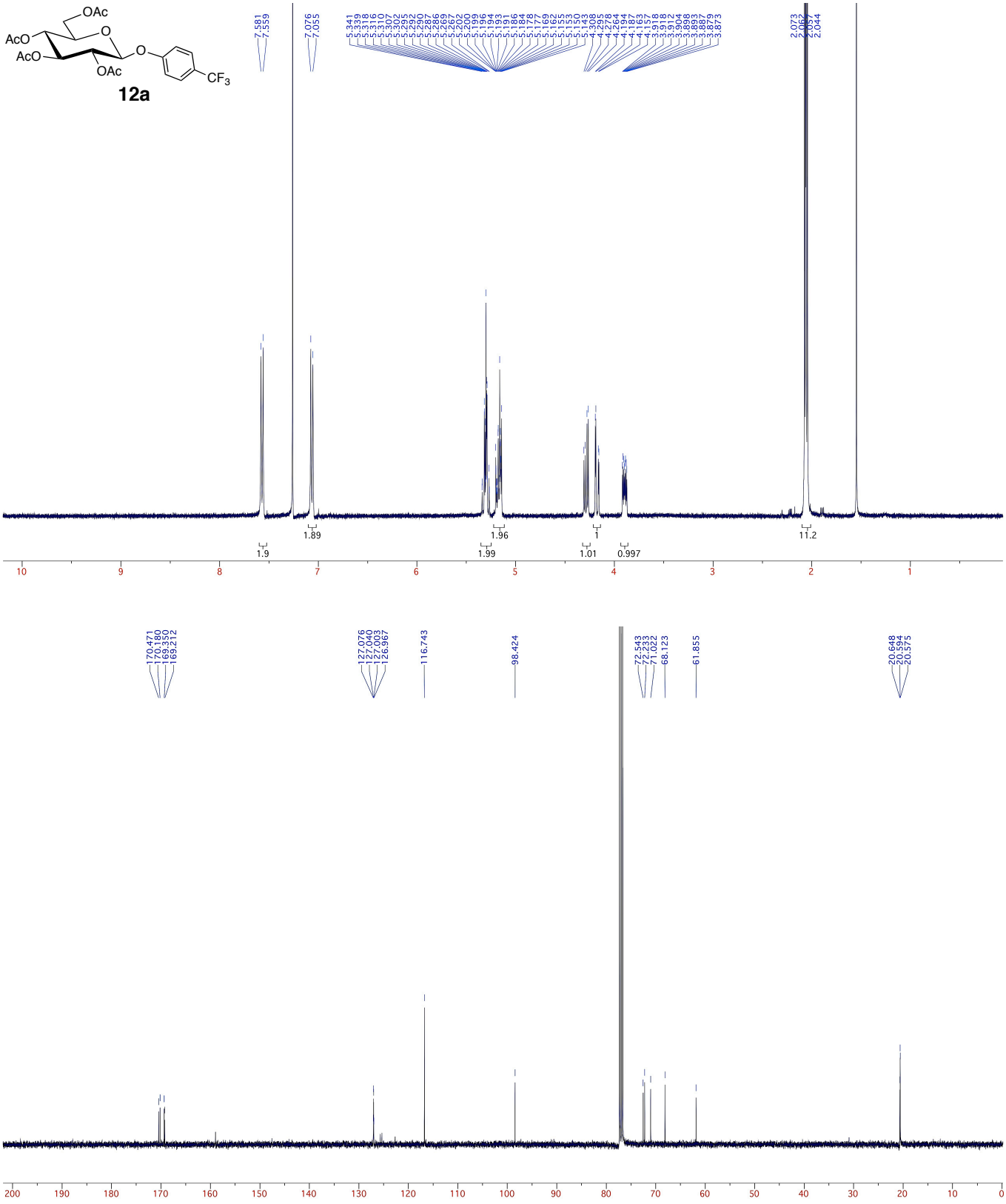
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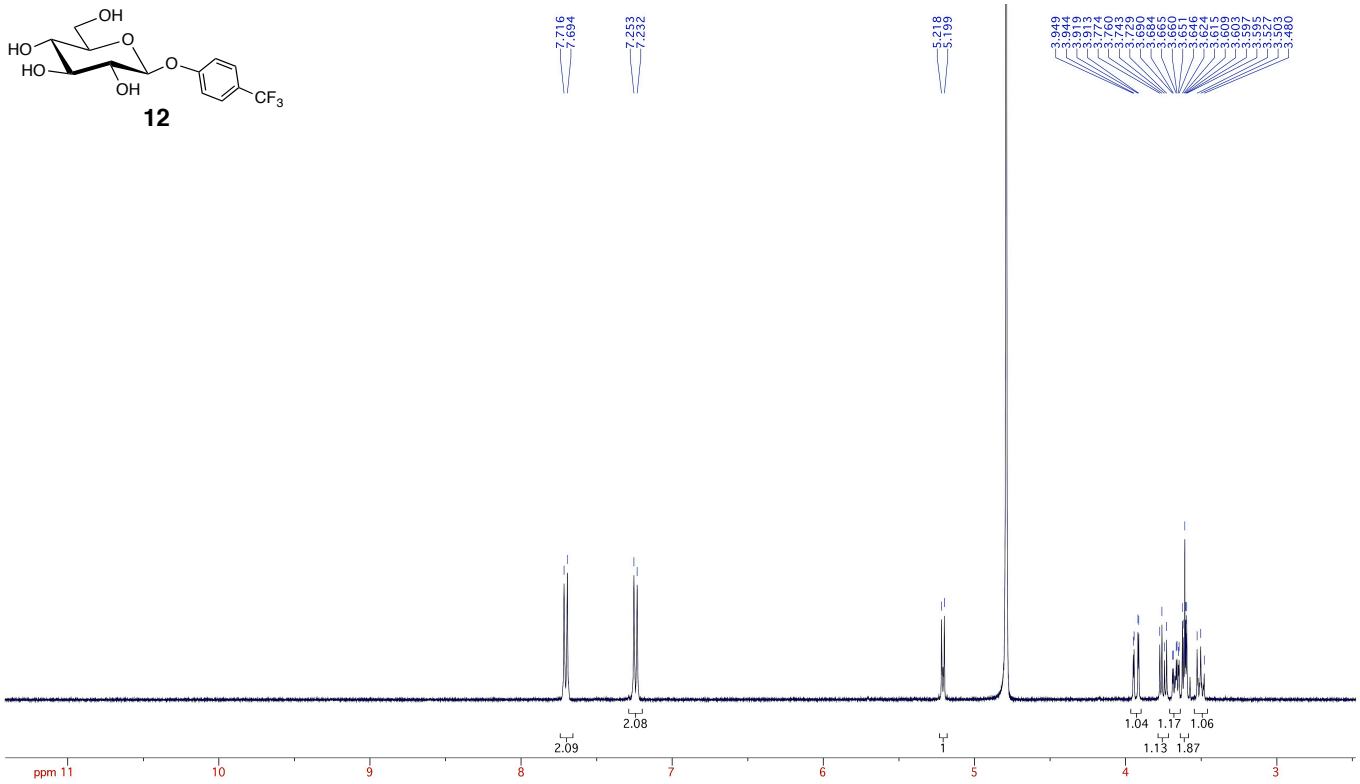
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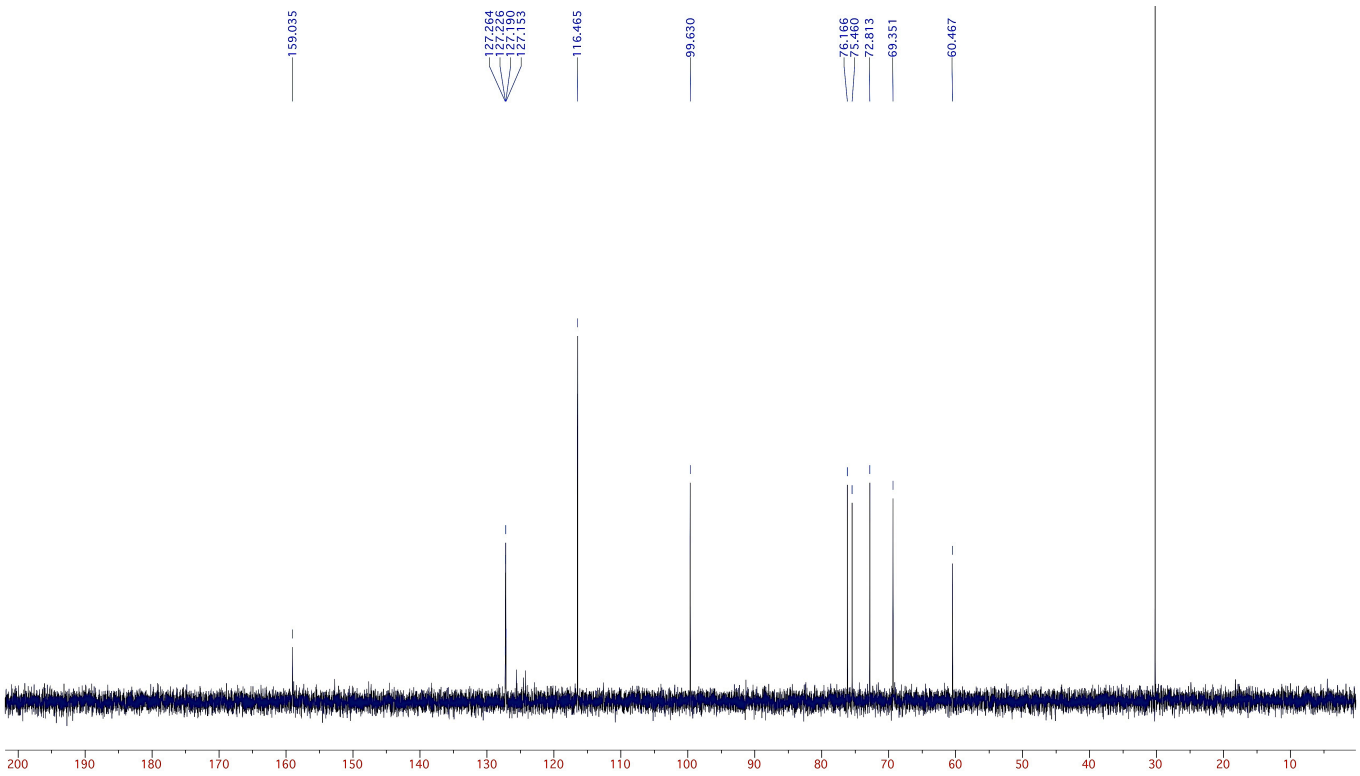
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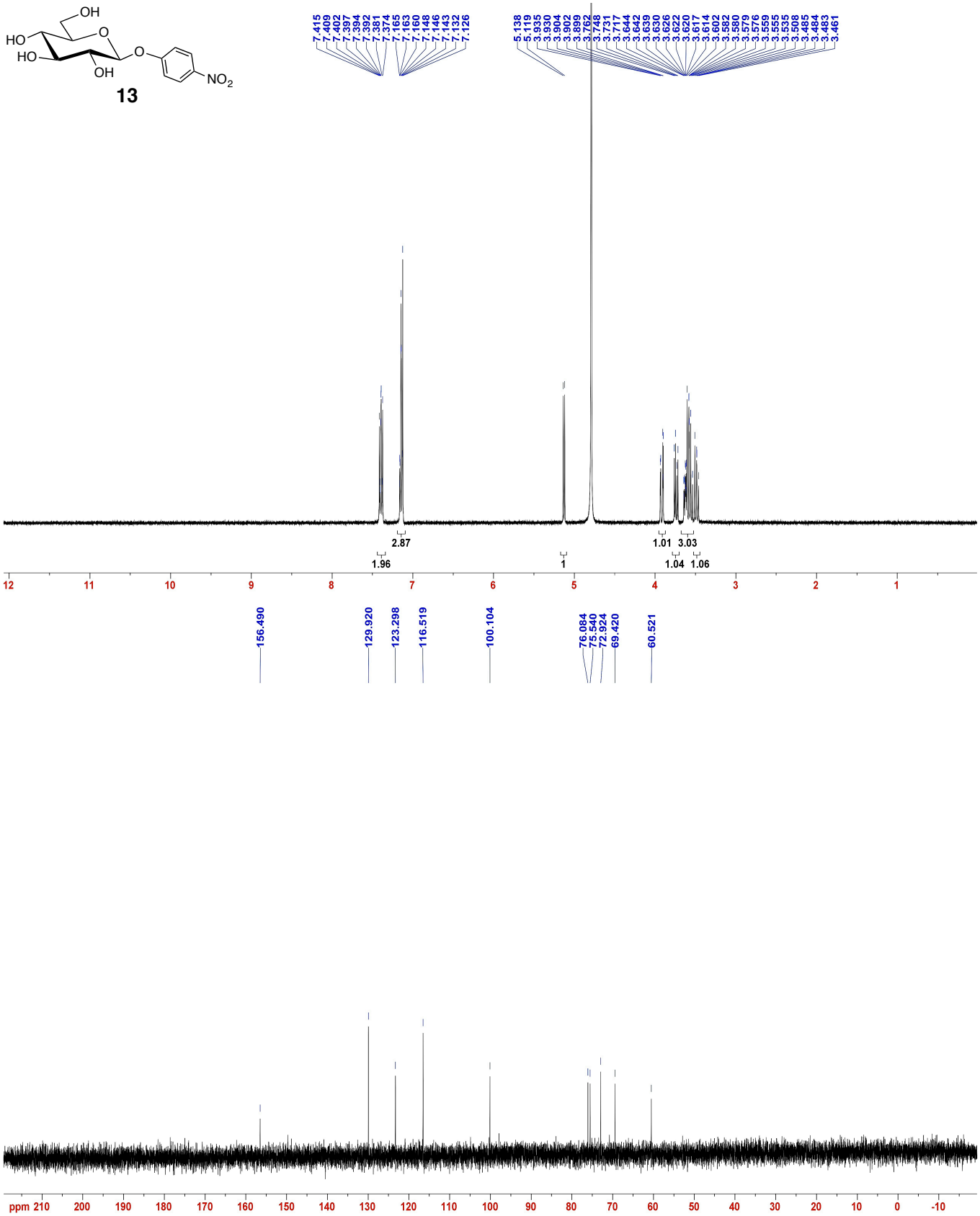
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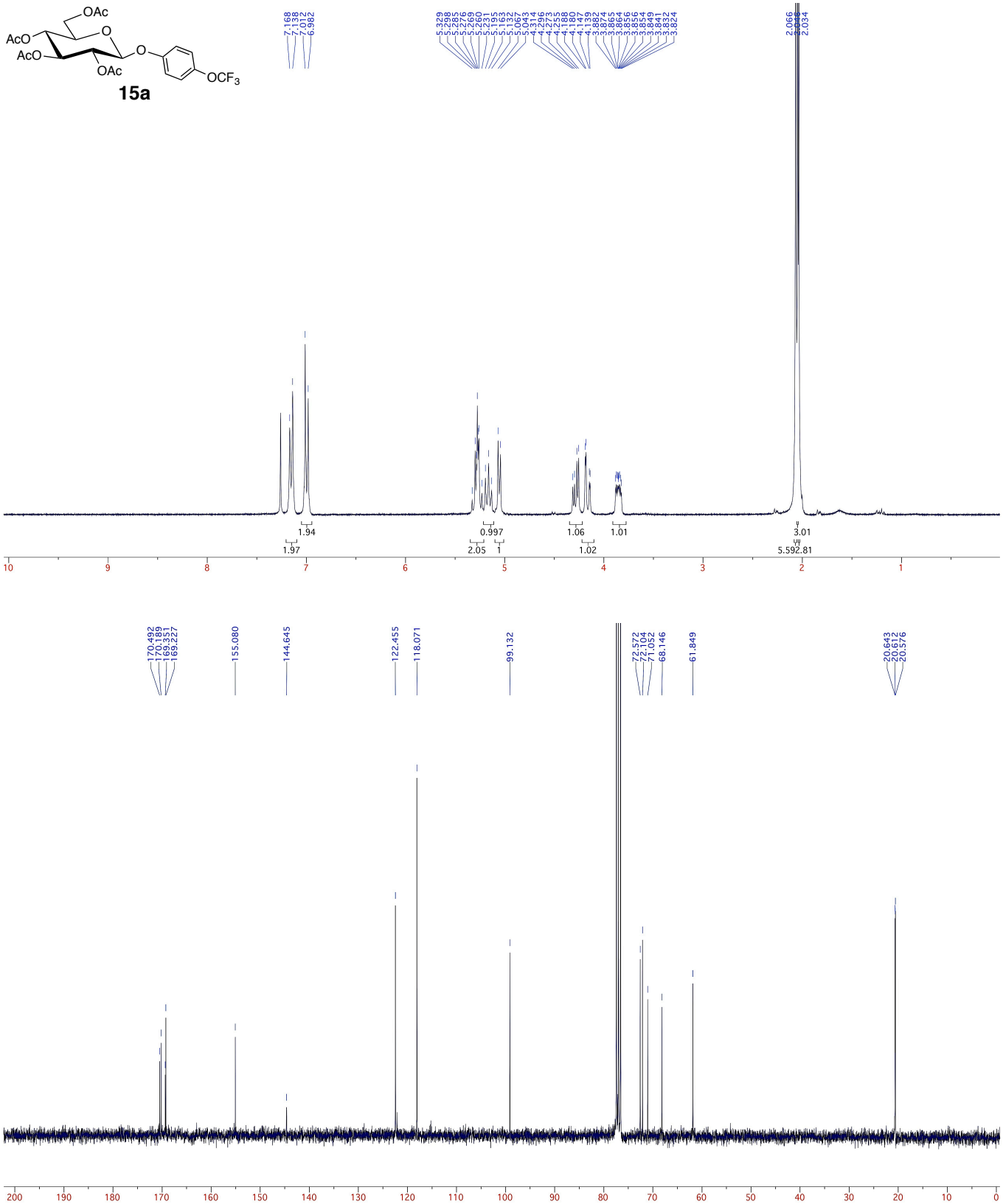
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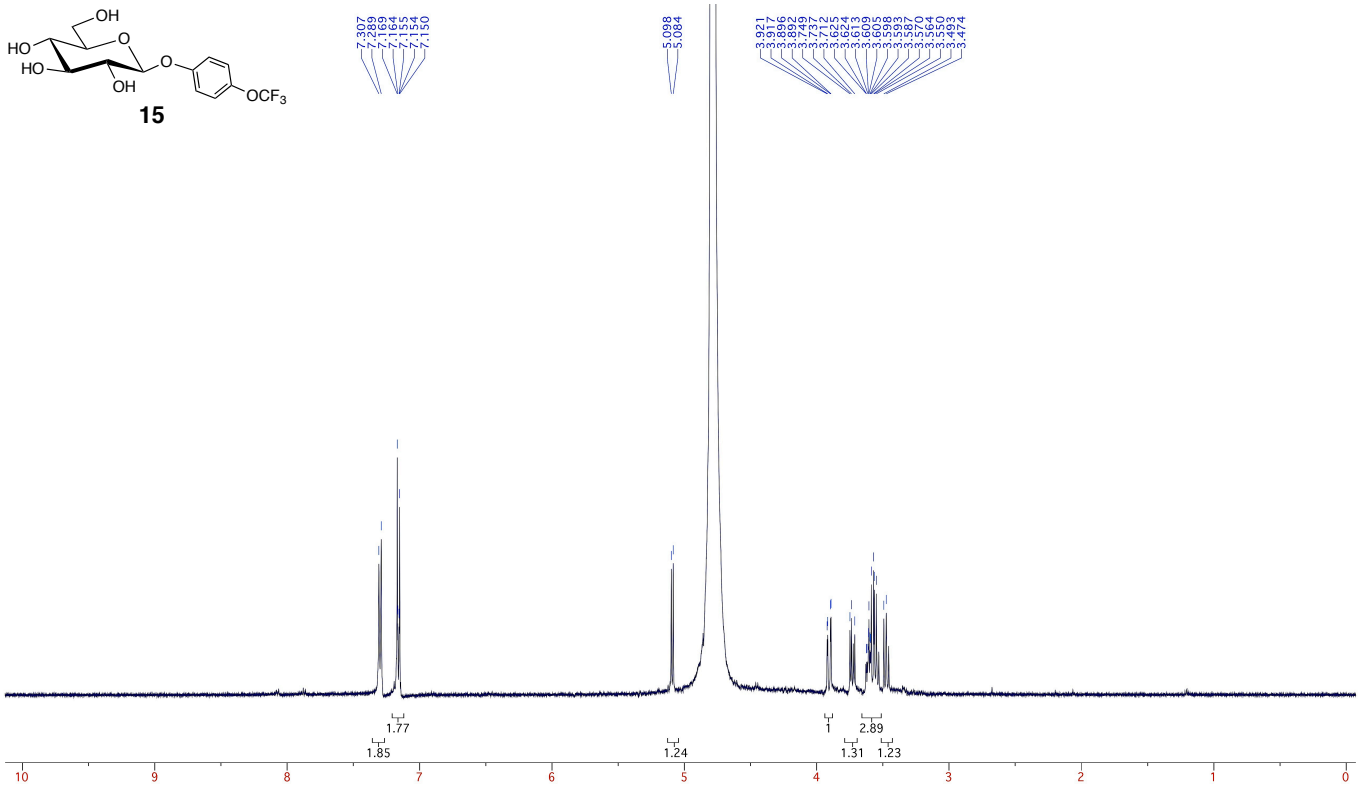
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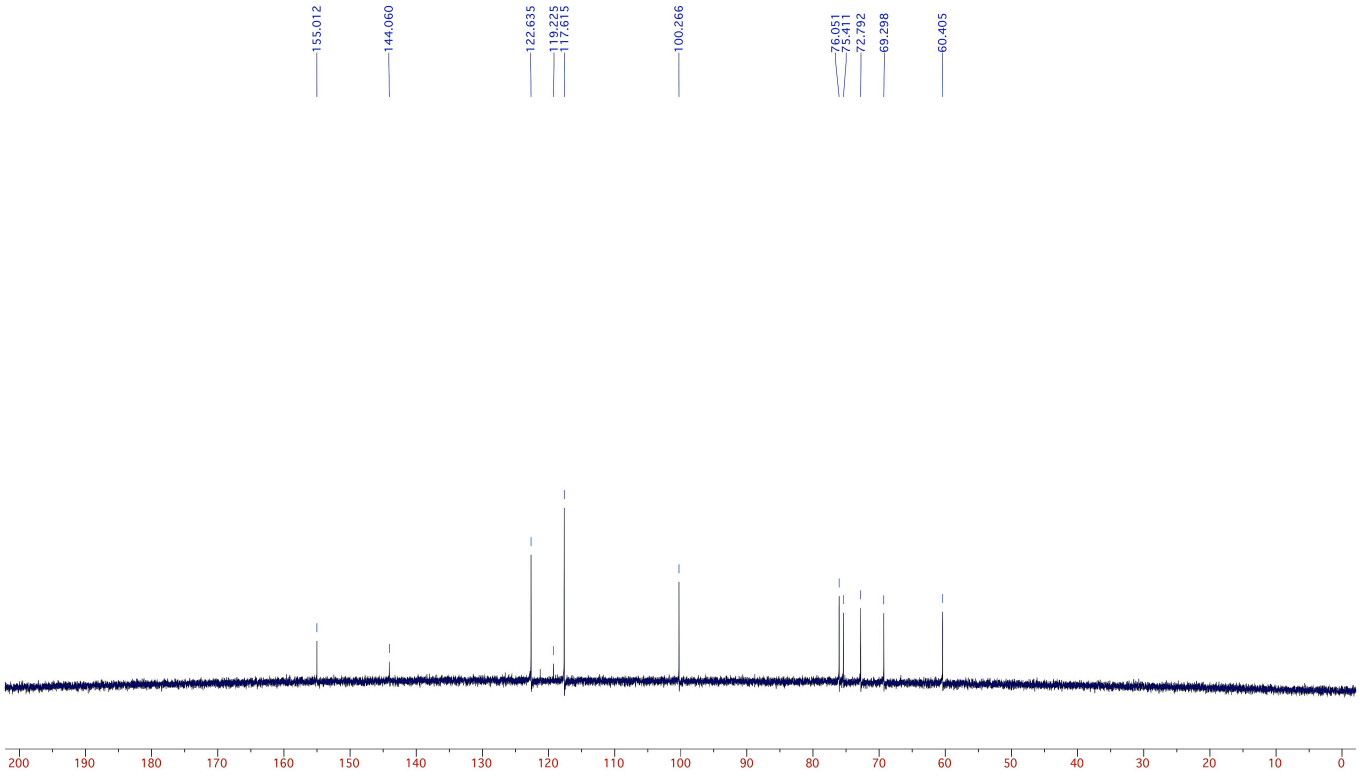
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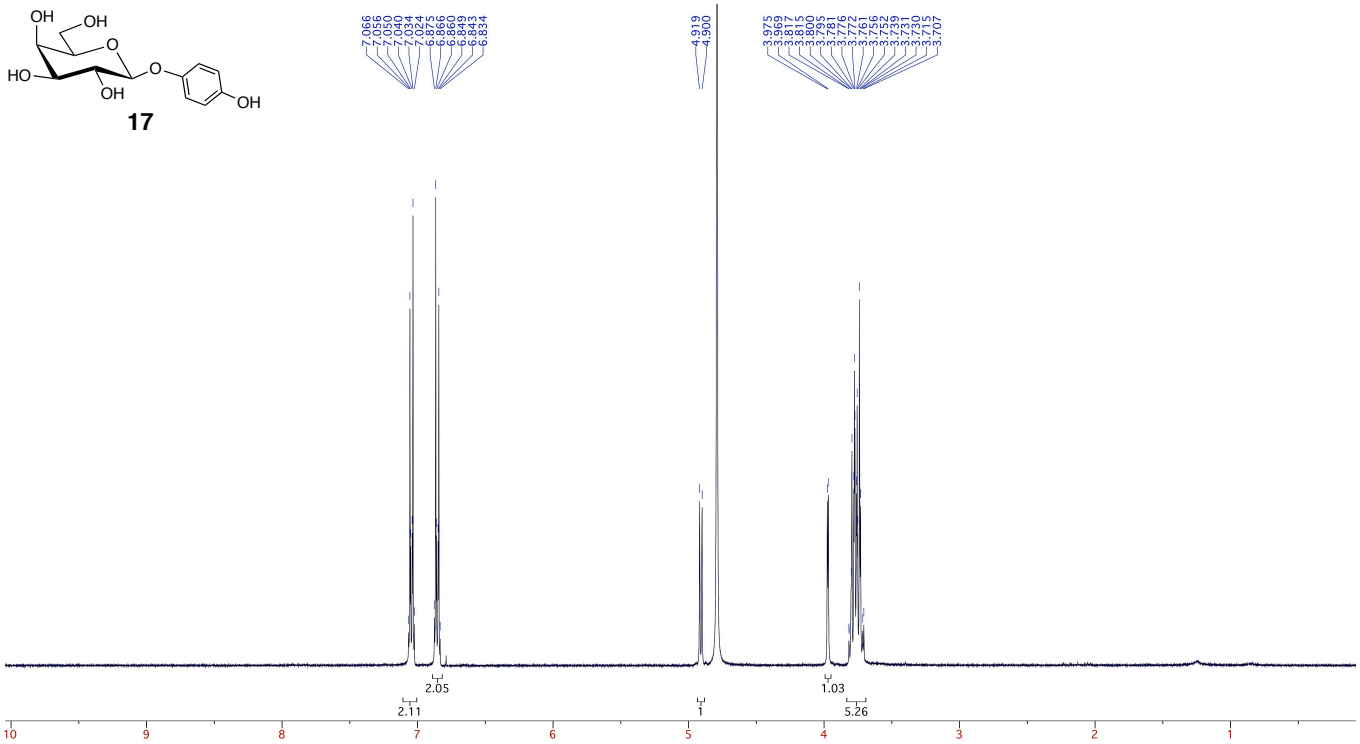
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OH
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6.843
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3.815
3.800
3.795
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3.731
3.730
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2
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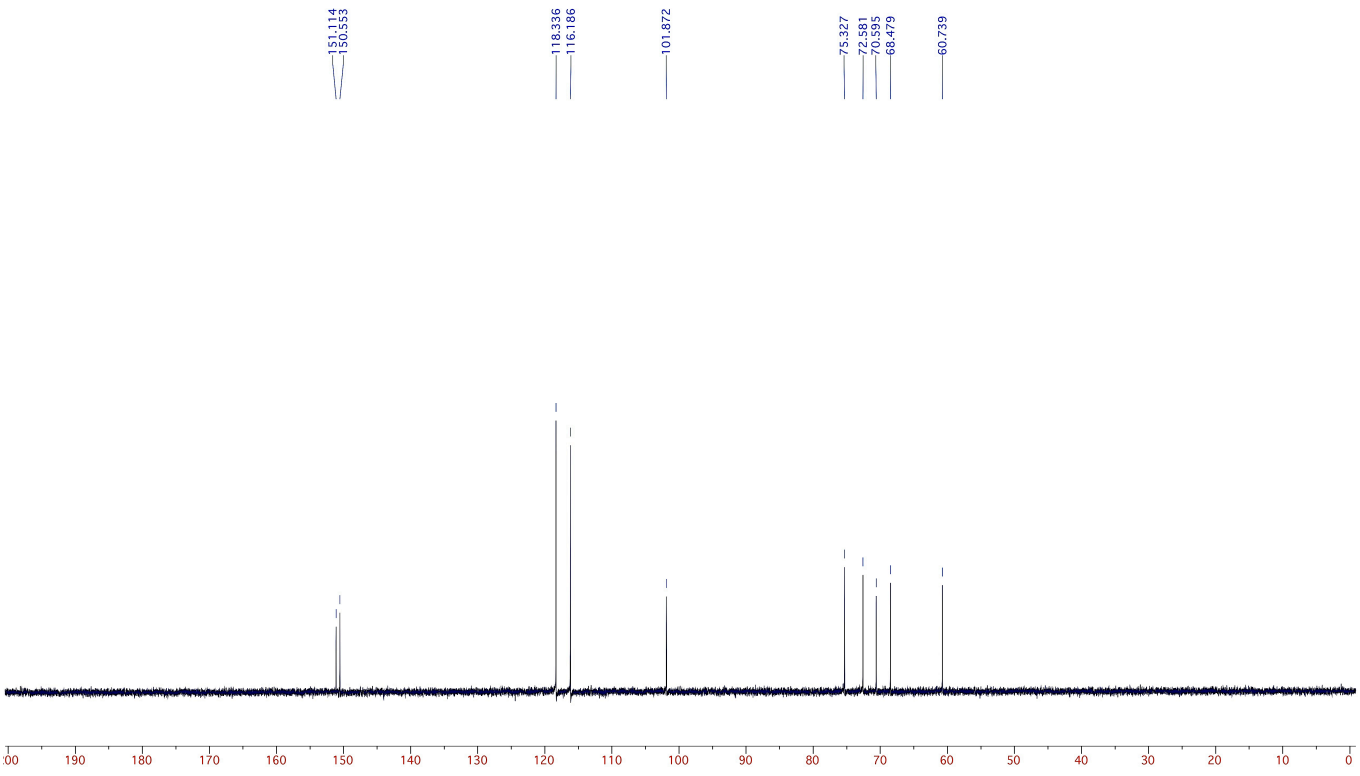
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150
140
130
120
110
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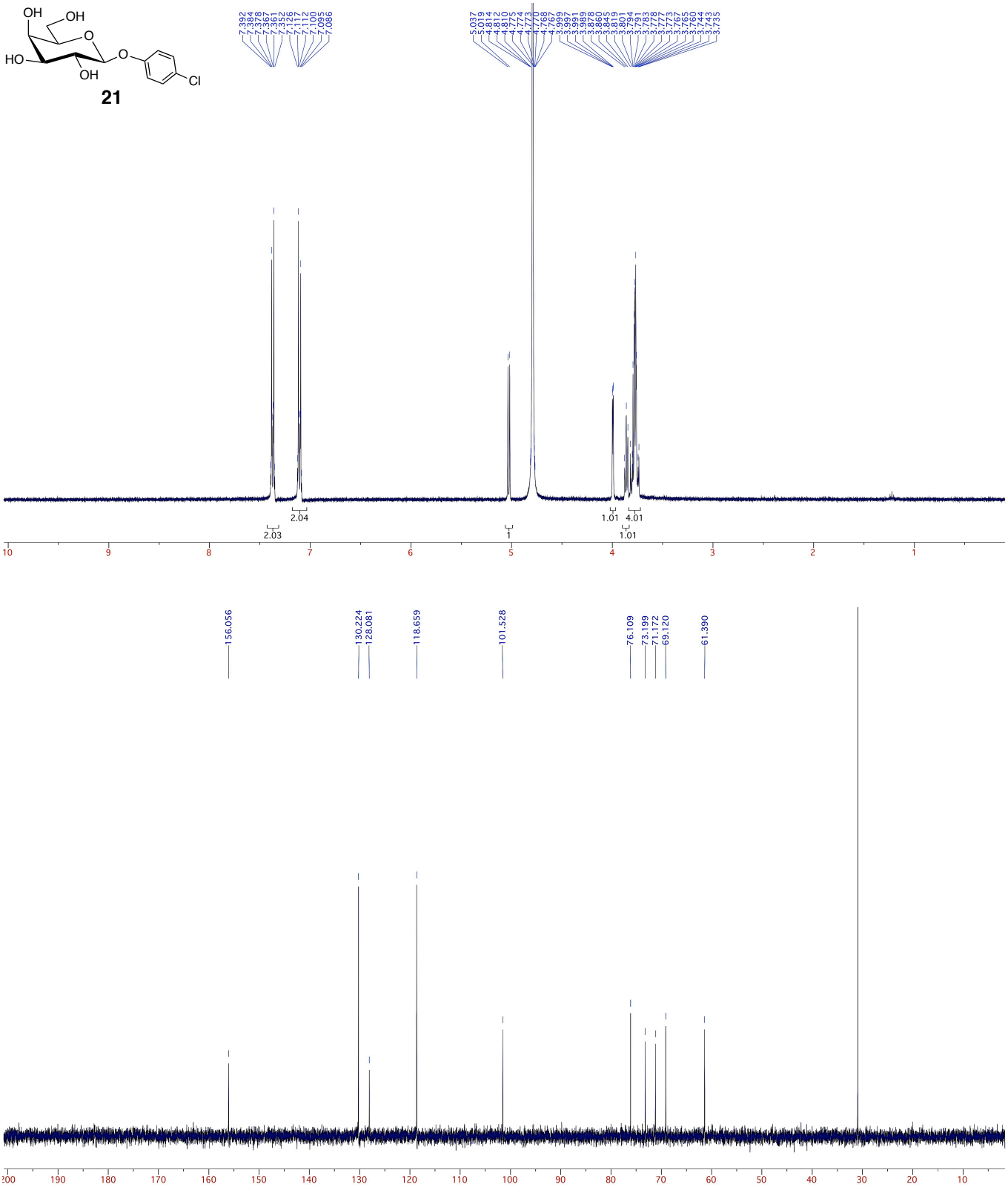
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OH
O
HO
O
OH
Cl
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7.112
7.100
7.090
7.086
5.037
5.019
4.814
4.812
4.810
4.775
4.773
4.770
4.768
4.767
3.997
3.997
3.991
3.989
3.878
3.860
3.845
3.819
3.801
3.794
3.791
3.783
3.778
3.777
3.773
3.767
3.765
3.760
3.744
3.743
3.735
2.03
2.04
1
1.01
1.01
4.01
10
9
8
7
6
5
4
3
2
1
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130.224
128.081
118.659
101.528
76.109
73.199
71.172
69.120
61.390
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160
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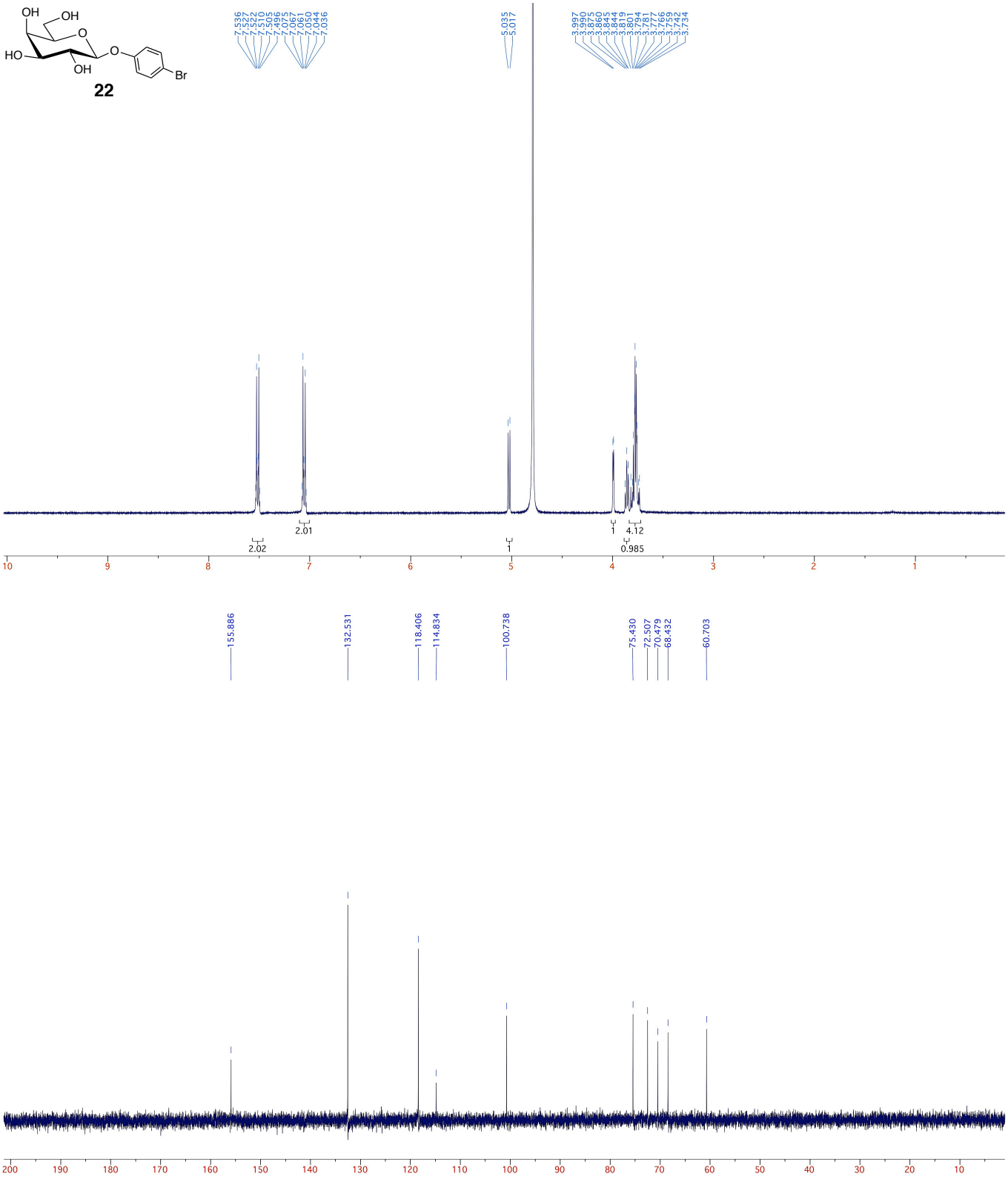
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OH
O
HO
O
OH
Br
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7.522
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7.067
7.061
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7.044
7.036
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3.860
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3.781
3.777
3.766
3.759
3.742
3.734
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2.01
1
1
4.12
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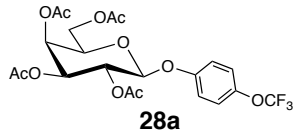
OAc
OAc
O
AcO
O
OAc
OCF3

**28a**


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6.992
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5.457
5.447
5.125
5.114
5.091
5.075
5.026
5.000
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4.234
4.229
4.220
4.210
4.196
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4.177
4.156
4.139
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4.076
4.073
4.056
4.052
4.032
4.029
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2.070
2.050
2.010
2
2.03
2.03
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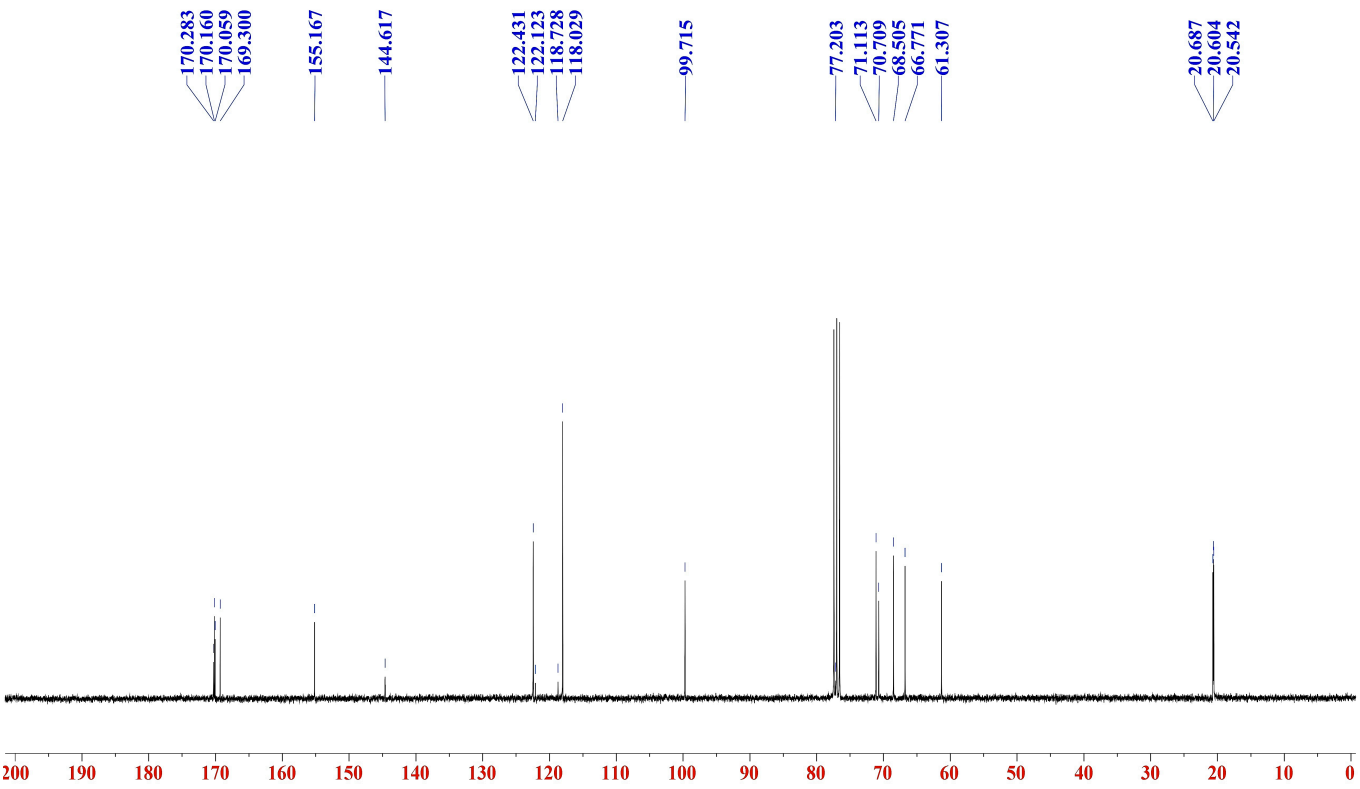
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122.123
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118.029
99.715
77.203
71.113
70.709
68.505
66.771
61.307
20.687
20.604
20.542
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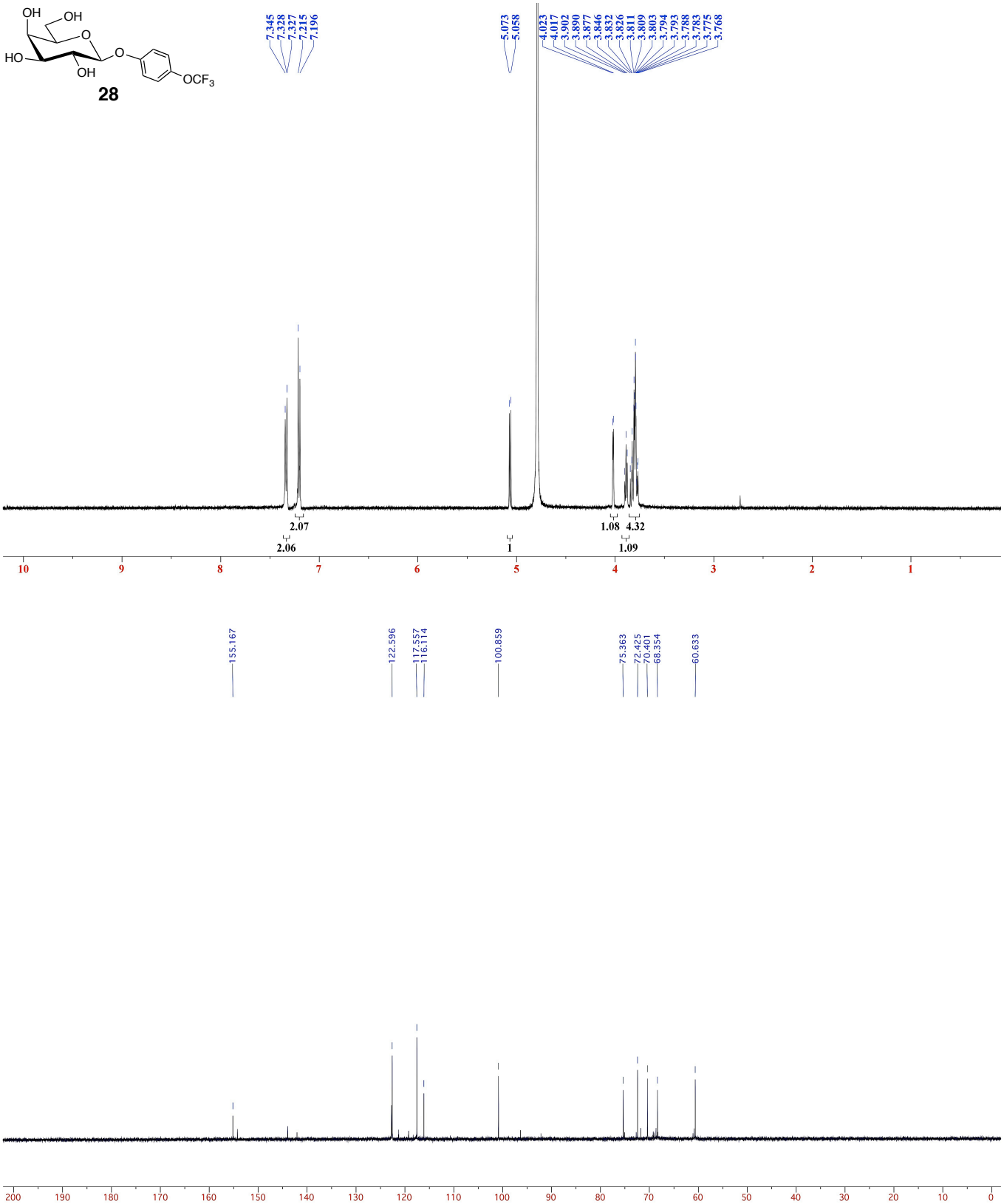
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HO
O
O
OH
OCF3
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5.058
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4.017
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3.890
3.877
3.846
3.832
3.826
3.811
3.809
3.803
3.794
3.793
3.788
3.783
3.775
3.768
2.07
2.06
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1.08
4.32
1.09
10
9
8
7
6
5
4
3
2
1
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122.596
117.557
116.114
100.859
75.363
72.425
70.401
68.354
60.633
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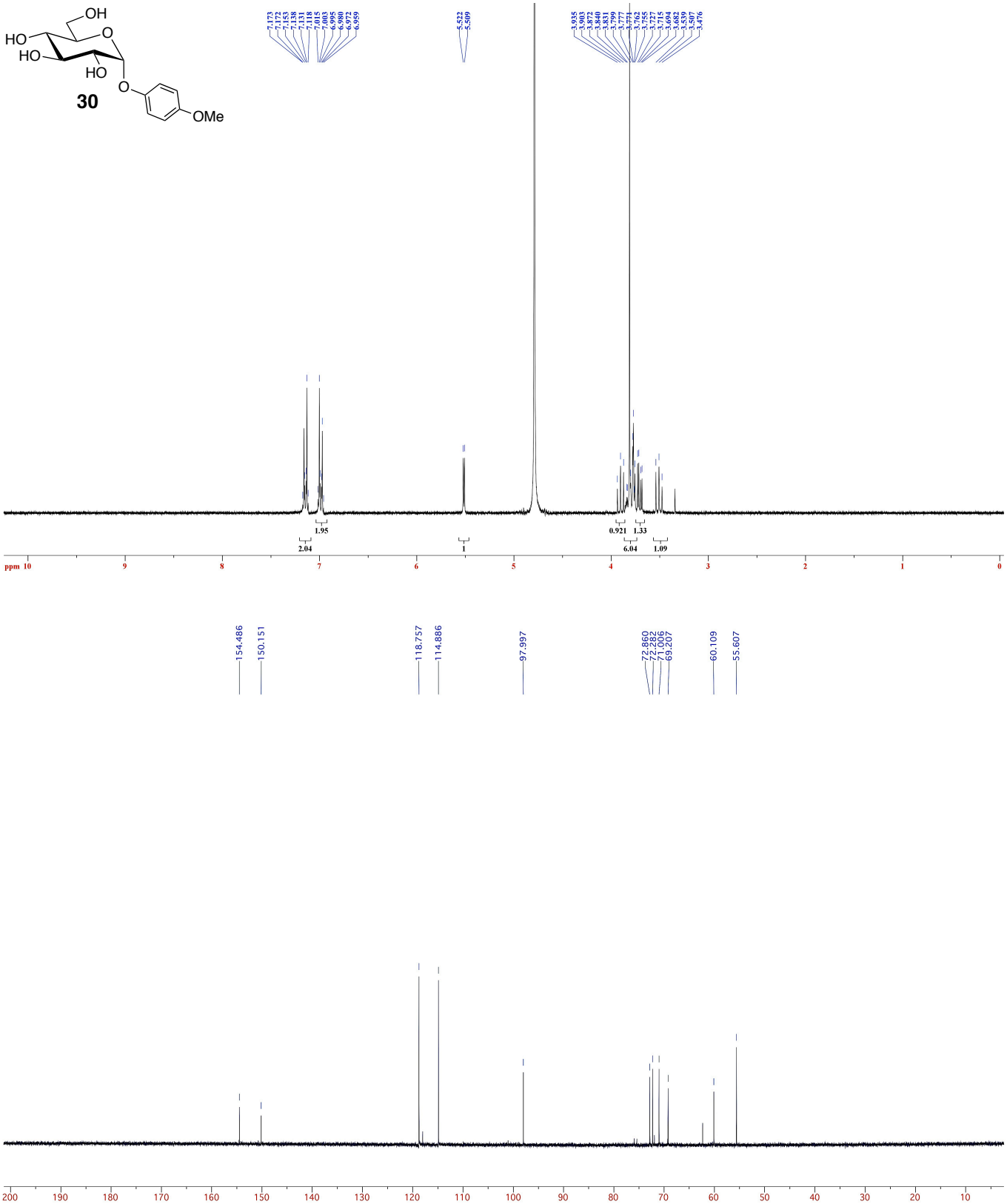
OH
HO
HO
HO
O
O
OMe
30
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7.172
7.153
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7.131
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7.015
7.003
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6.980
6.972
6.959
5.522
5.509
3.935
3.901
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3.831
3.799
3.777
3.771
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3.507
3.476
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1.33
6.04
1.09
ppm 10
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7
6
5
4
3
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0
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71.006
69.207
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55.607
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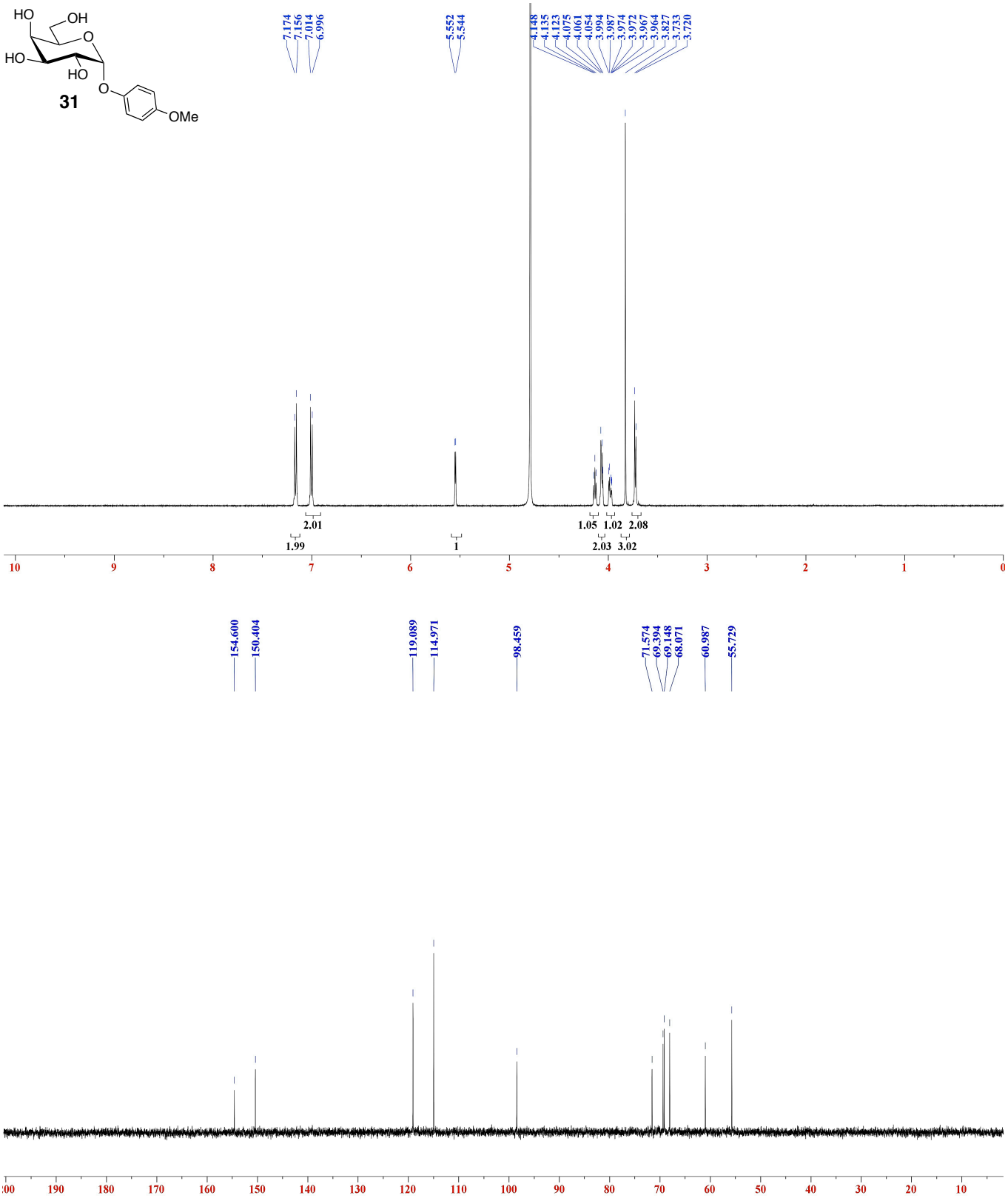
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OH
O
HO
HO
O
OMe
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7.014
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5.544
4.148
4.135
4.123
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4.061
4.054
3.994
3.987
3.974
3.972
3.967
3.964
3.827
3.733
3.720
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1.99
1
1.05
1.02
2.08
2.03
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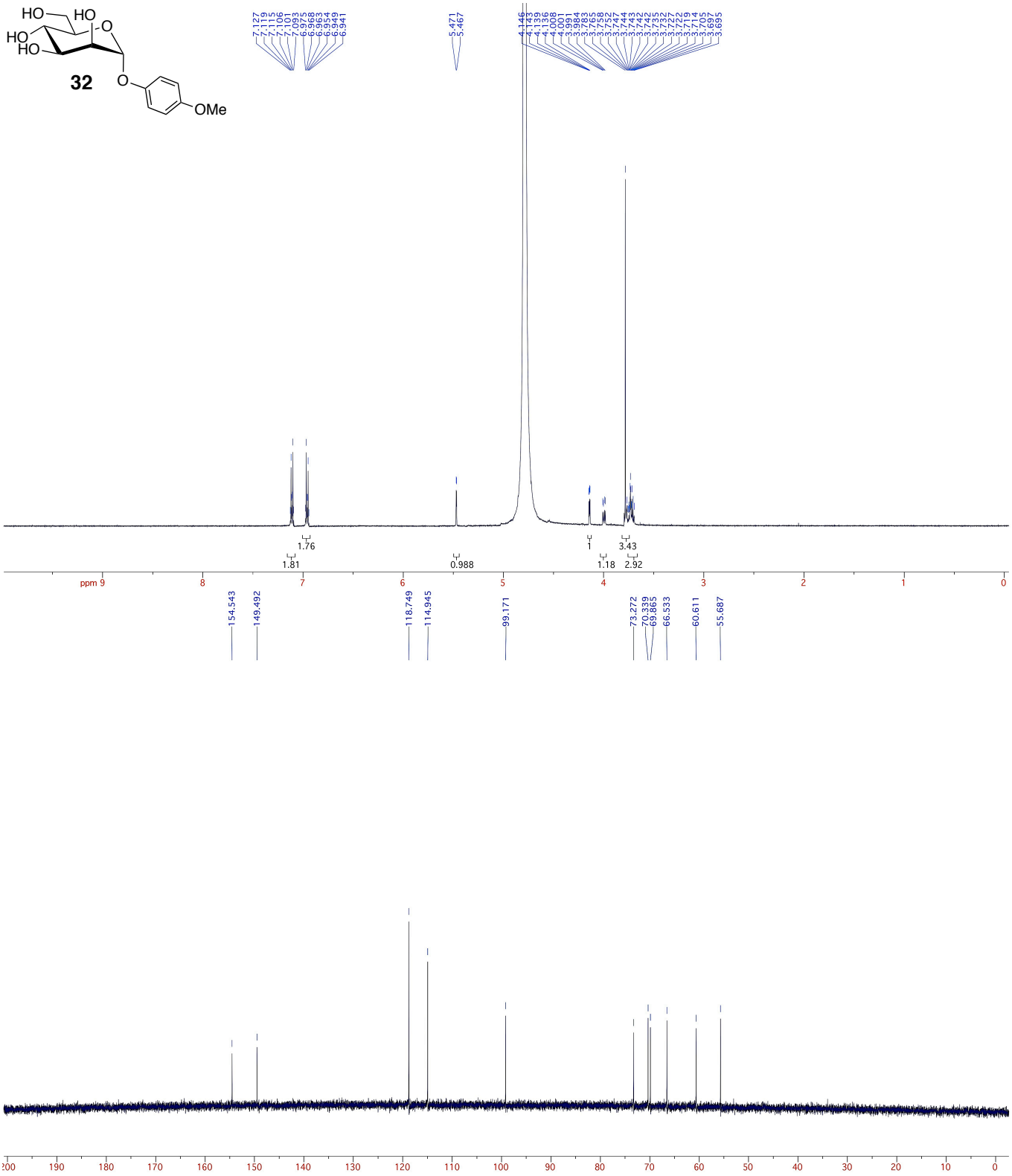
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HO
HO
HO
O
O
OMe
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7.101
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6.954
6.949
6.941
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5.467
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4.143
4.139
4.136
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4.001
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3.758
3.752
3.747
3.744
3.743
3.742
3.735
3.732
3.727
3.722
3.719
3.714
3.705
3.697
3.695
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1.76
0.988
1
1.18
3.43
2.92
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5
4
3
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114.945
99.171
73.272
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69.865
66.533
60.611
55.687
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150
140
130
120
110
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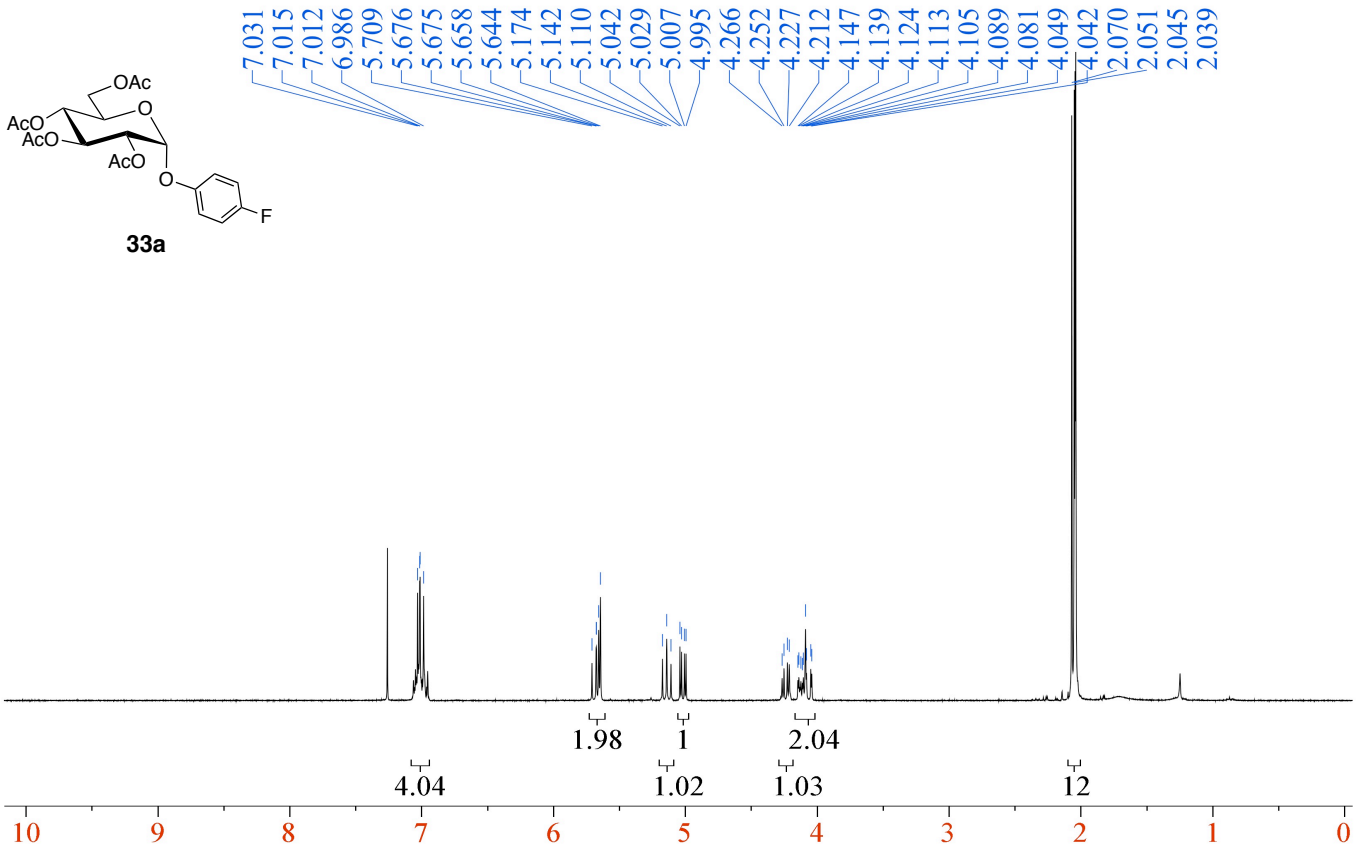
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5.029
5.007
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4.227
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4.147
4.139
4.124
4.113
4.105
4.089
4.081
4.049
4.042
2.070
2.051
2.045
2.039
OAc
AcO
AcO
AcO
O
O
F
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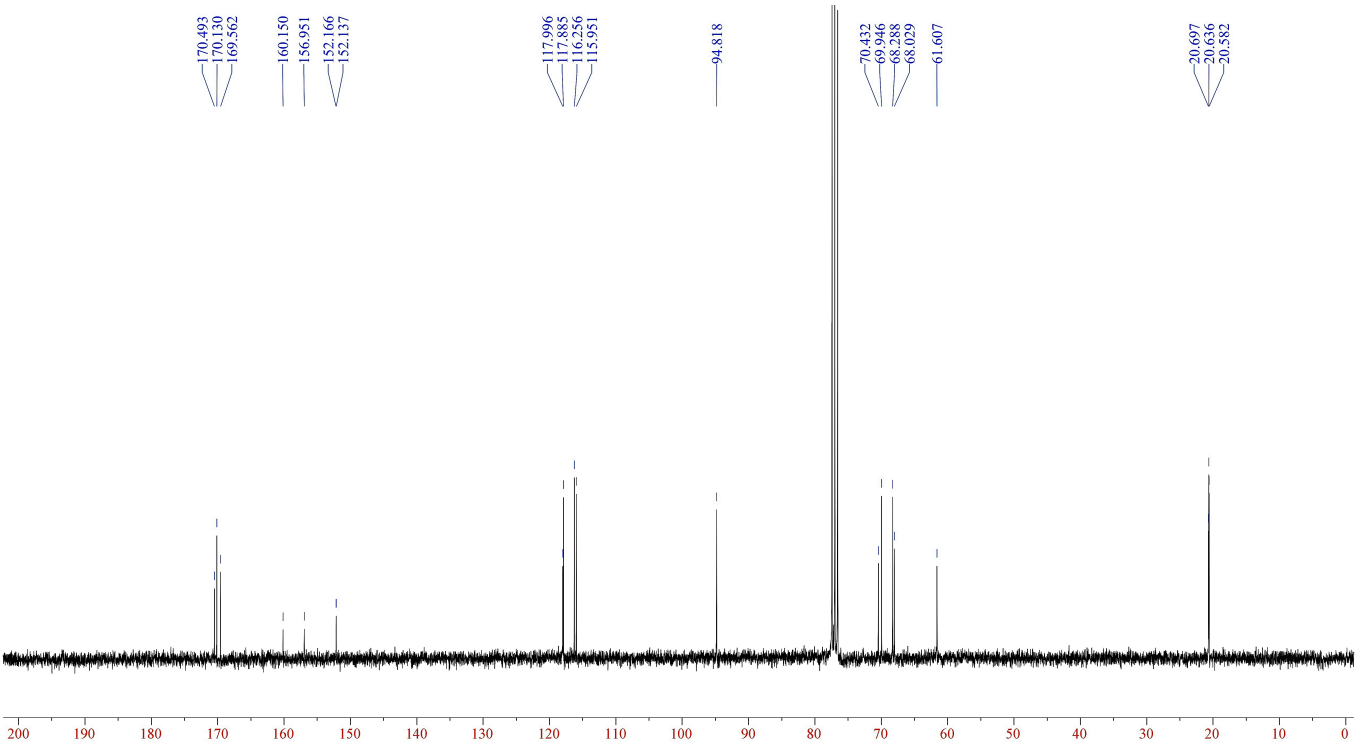
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20.697
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20.582
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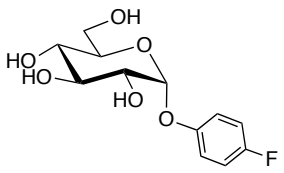
OH
HO
HO
HO
O
O
F

**33**


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7.144
7.141
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7.125
7.123
7.115
7.104
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7.073
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5.547
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4.004
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3.823
3.807
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3.774
3.765
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3.741
3.732
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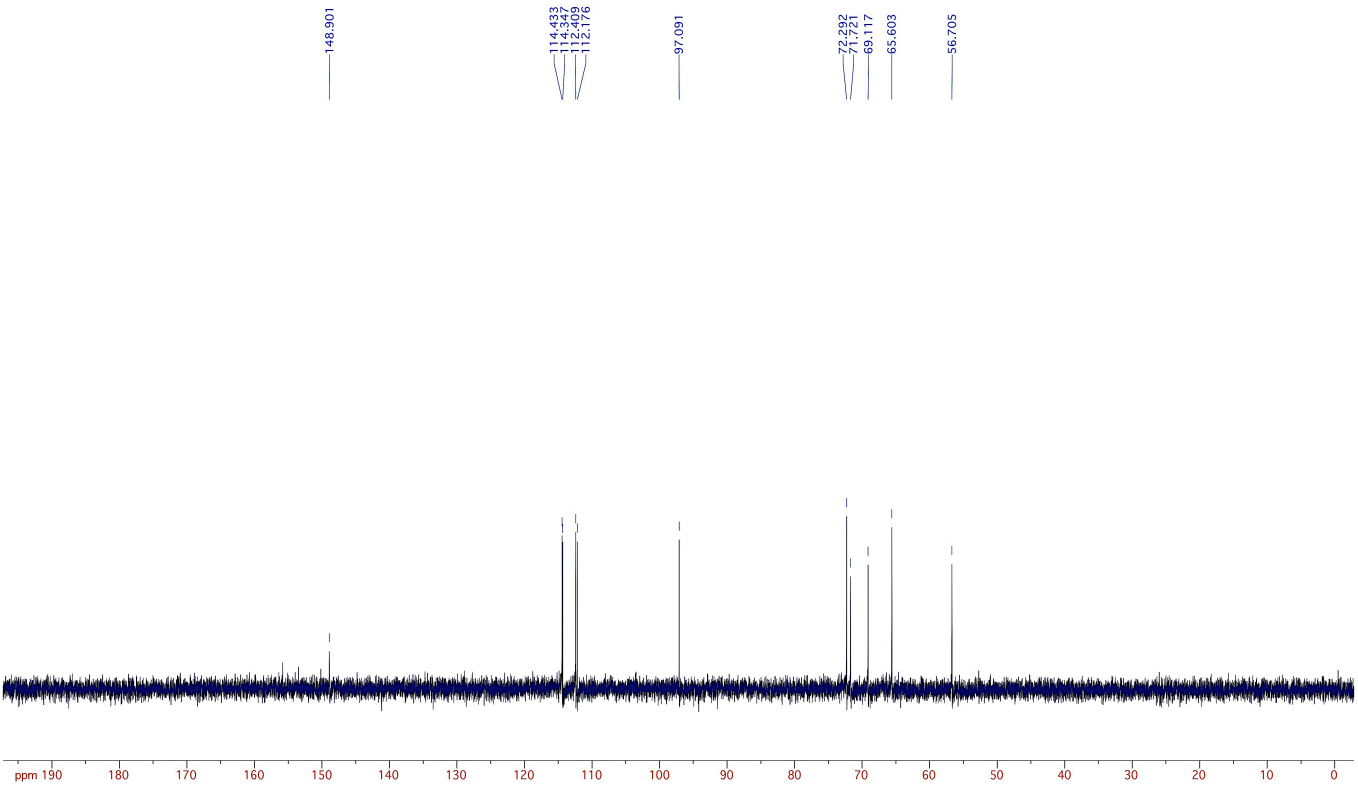
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56.705
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20
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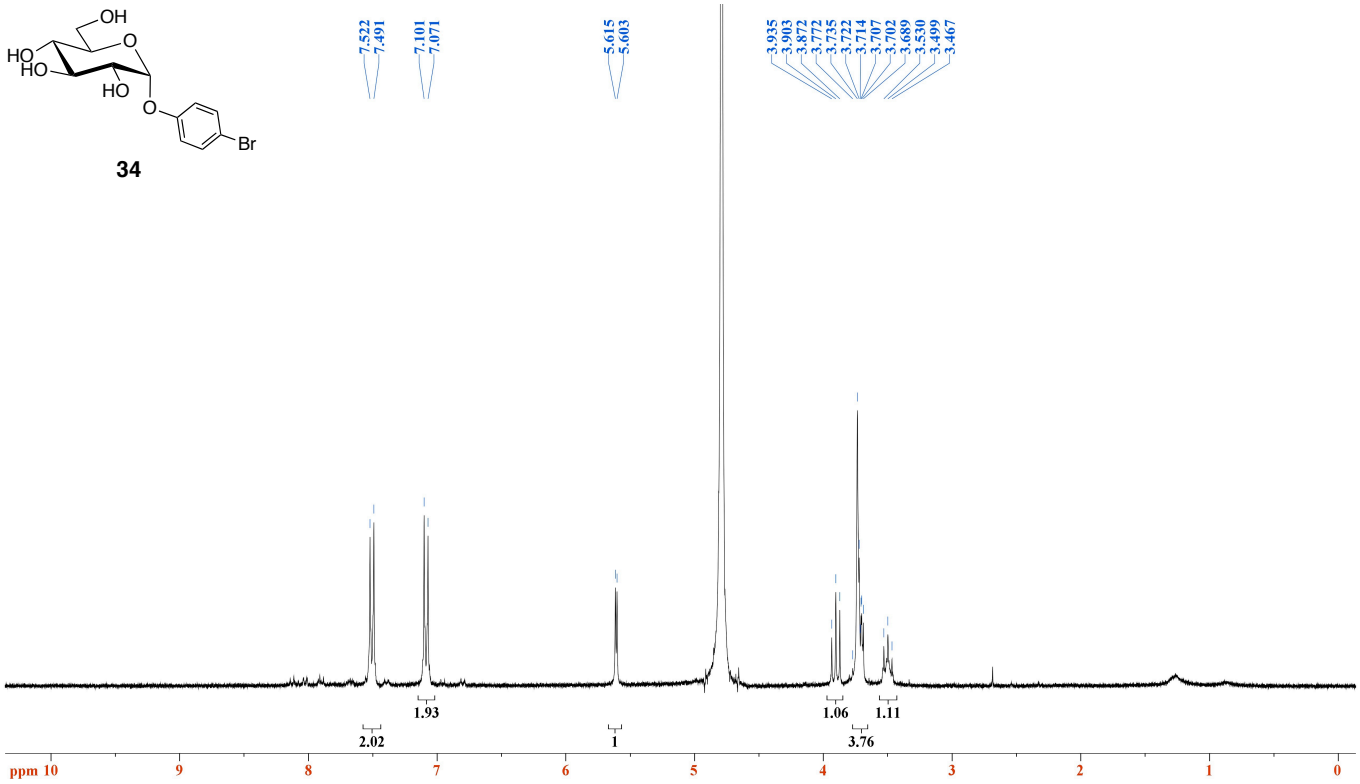
OH
HO
HO
HO
O
O
Br
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7.071
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5.603
3.935
3.903
3.872
3.772
3.735
3.722
3.714
3.707
3.702
3.689
3.530
3.499
3.467
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1.06
3.76
1.11
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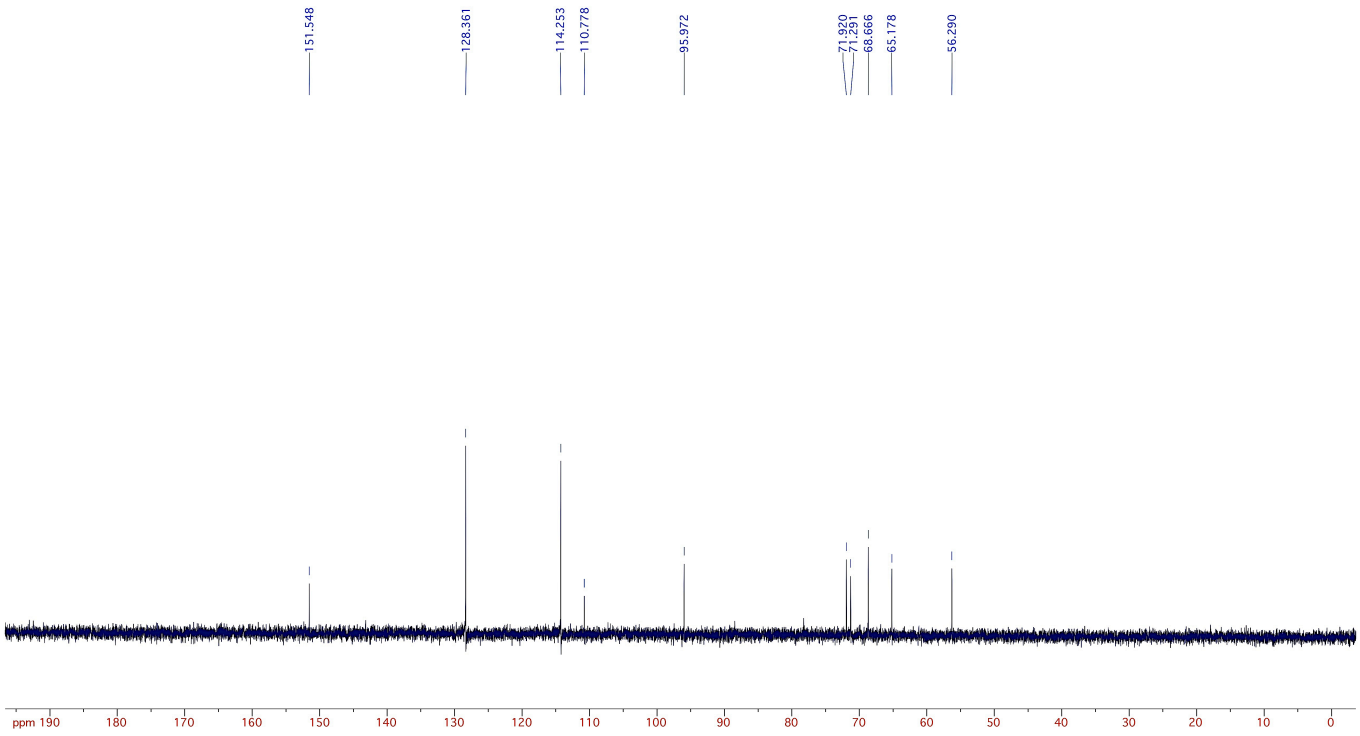
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56.290
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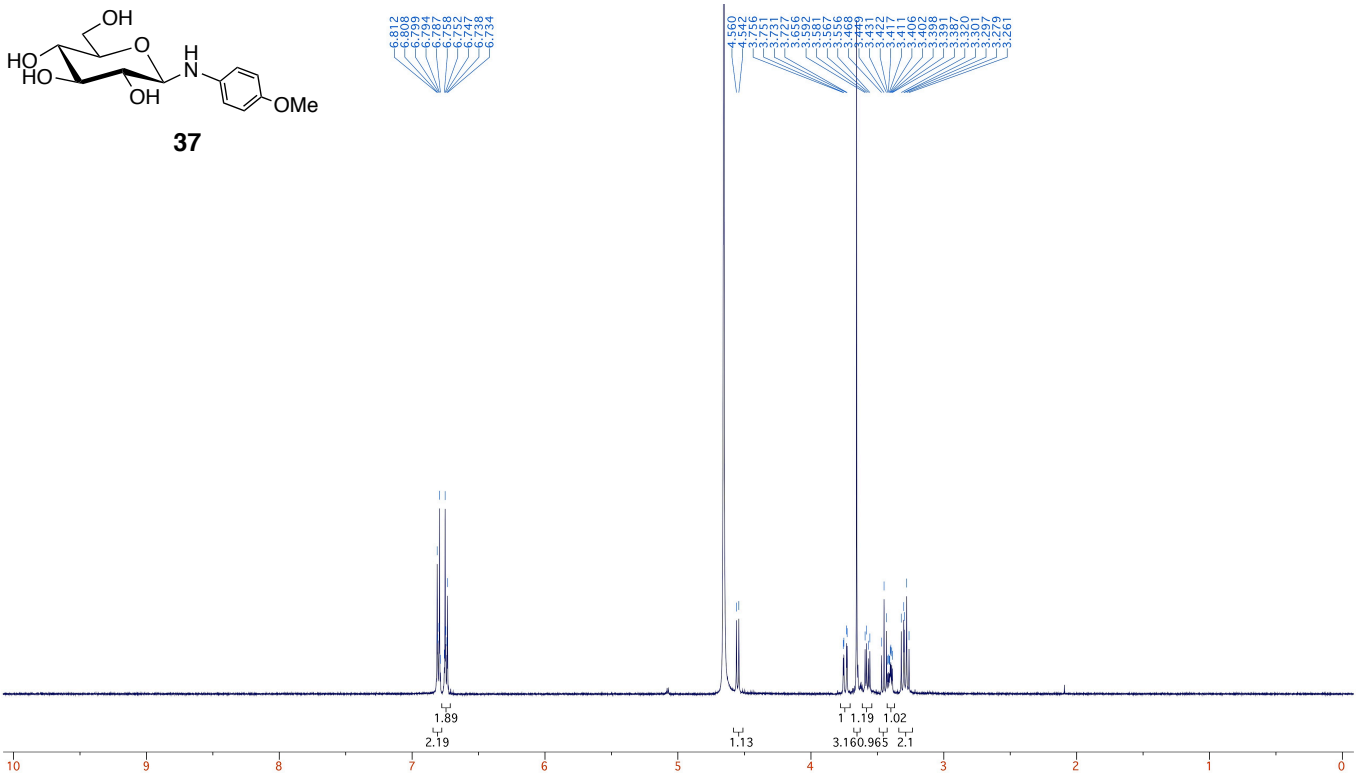
OH
HO
HO
O
OH
H
N
OMe
37
6.812
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6.799
6.794
6.787
6.783
6.755
6.747
6.738
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3.398
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3.279
3.261
1.89
2.19
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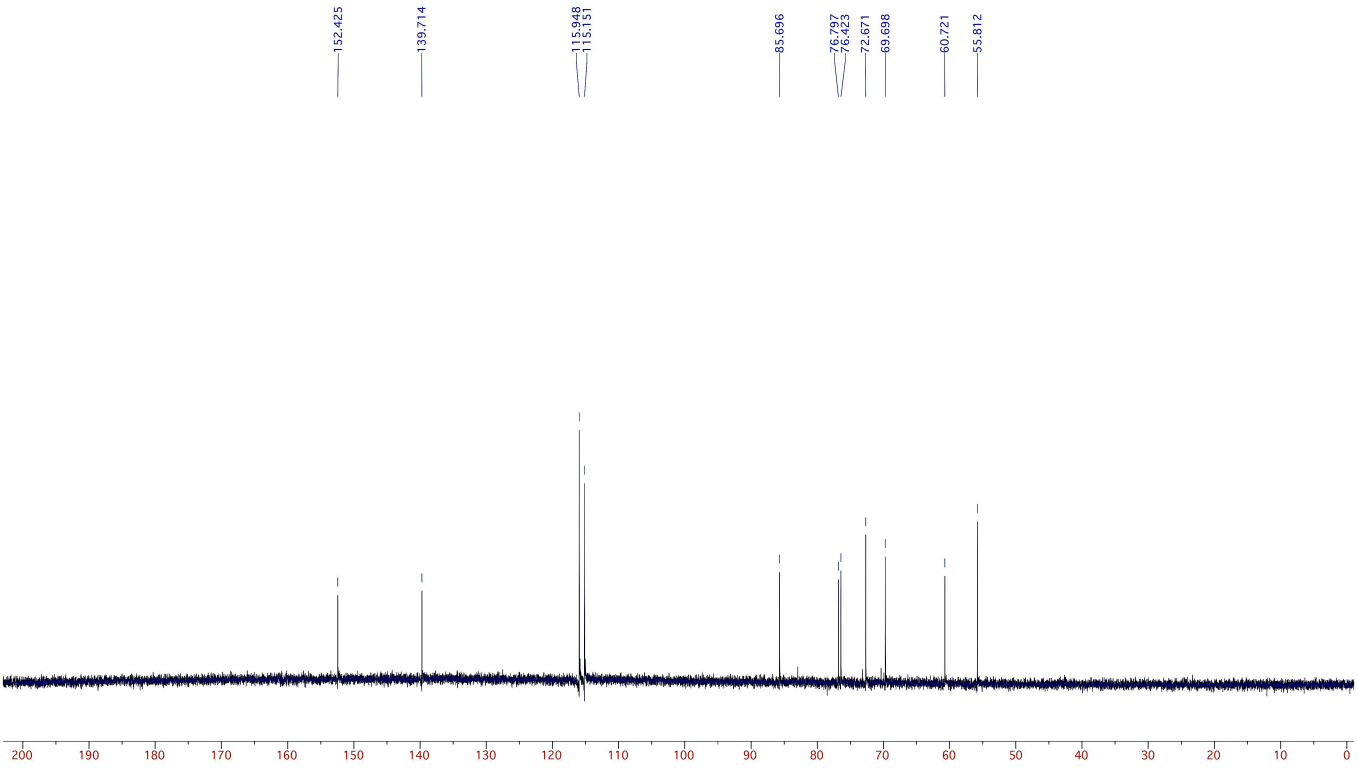
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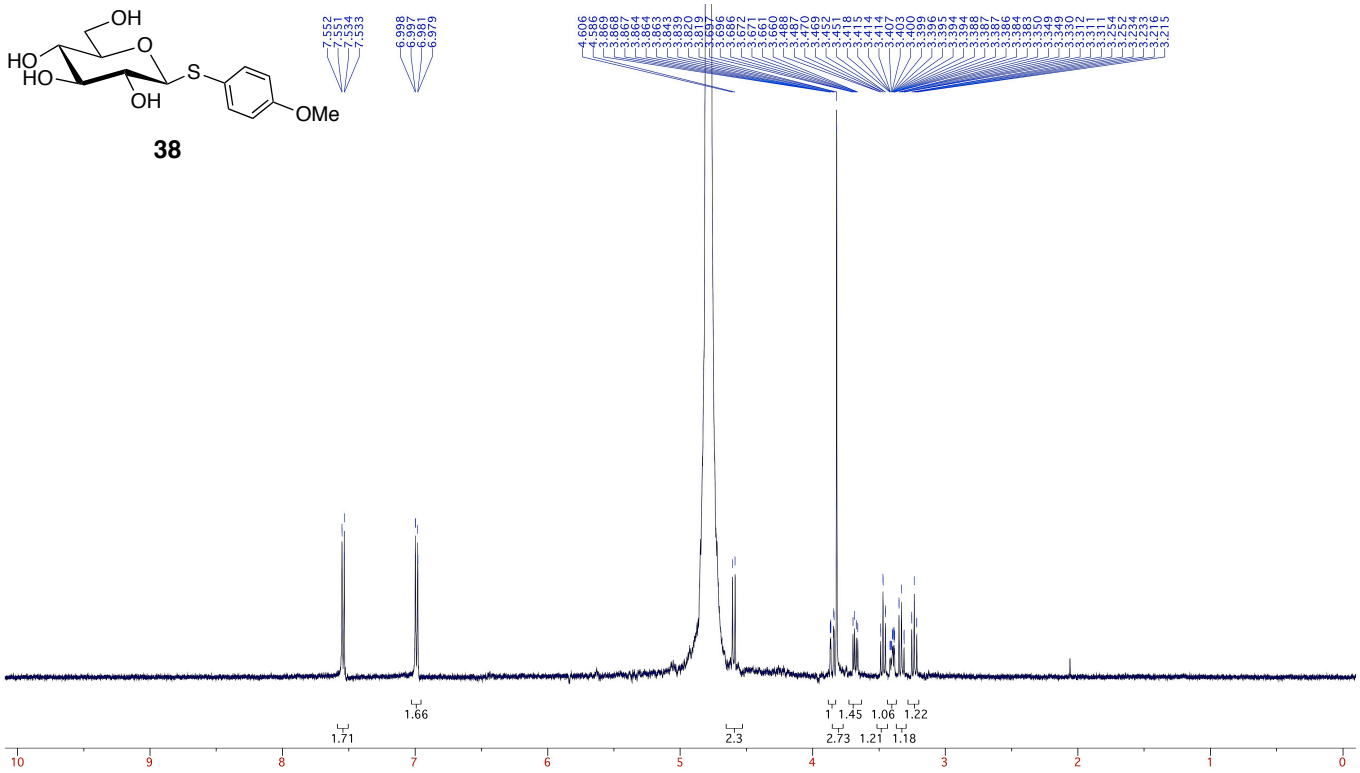
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S
OH
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3.394
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3.387
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3.349
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3.311
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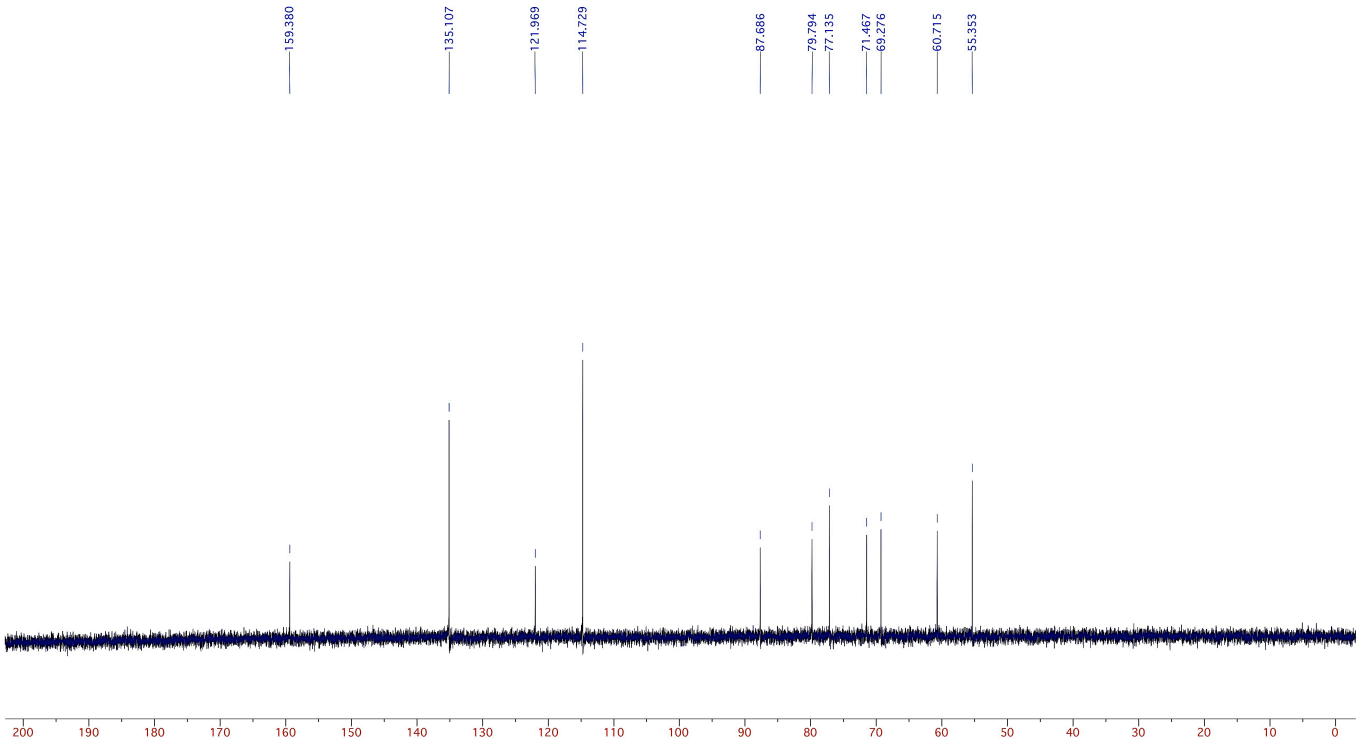
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77.135
71.467
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55.353
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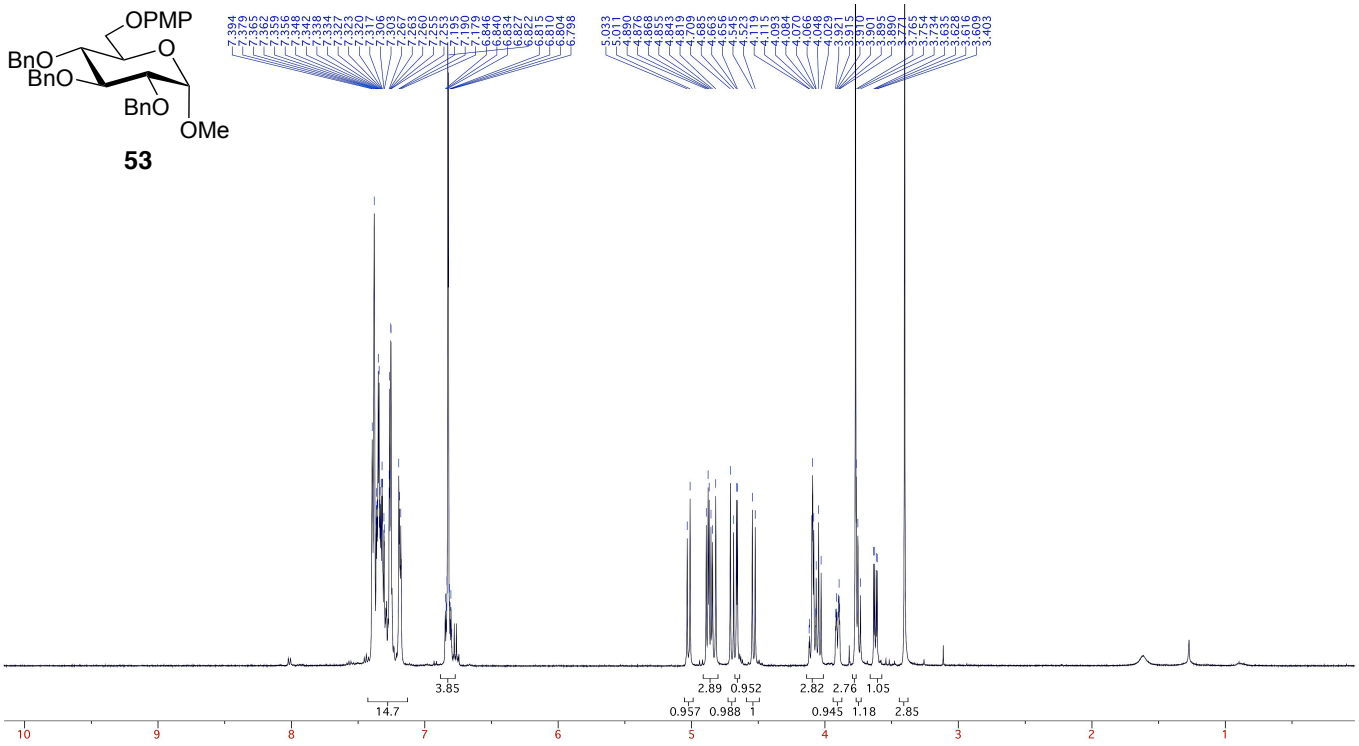
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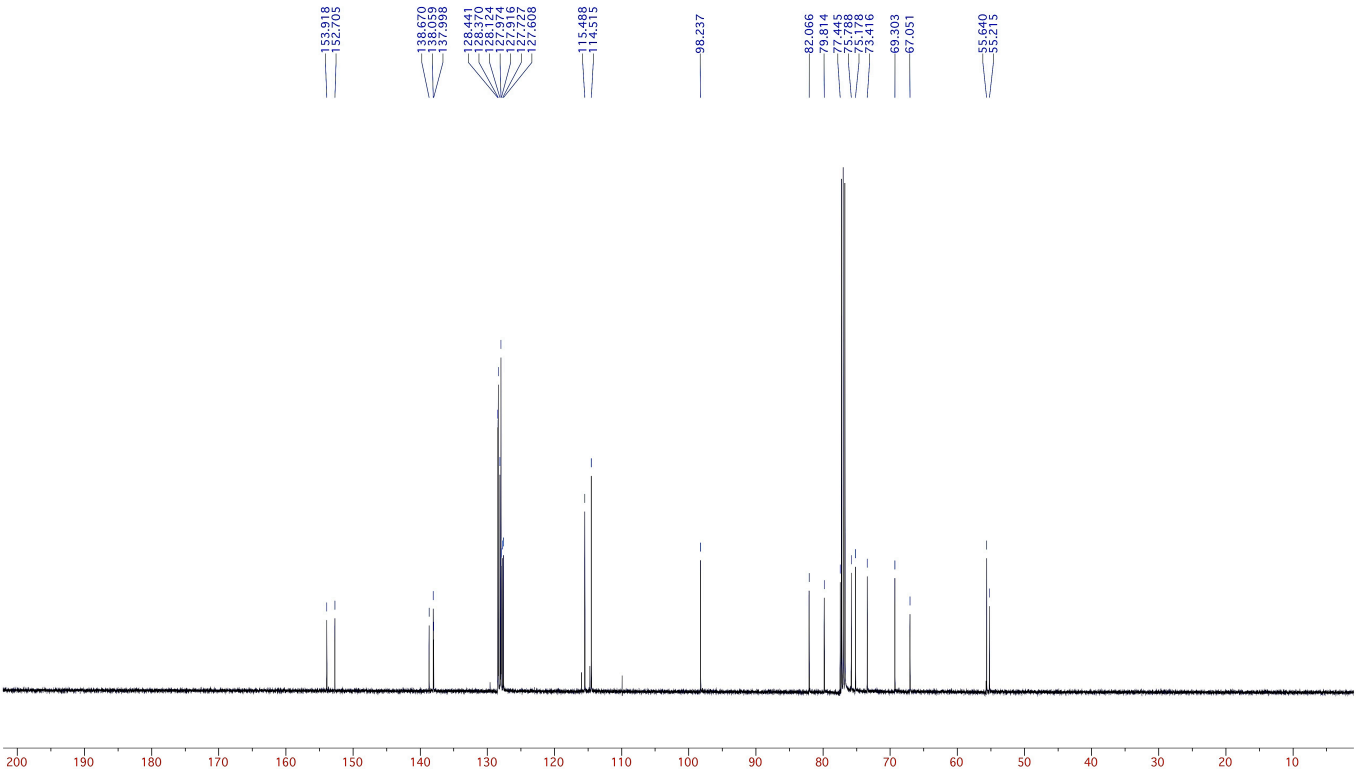
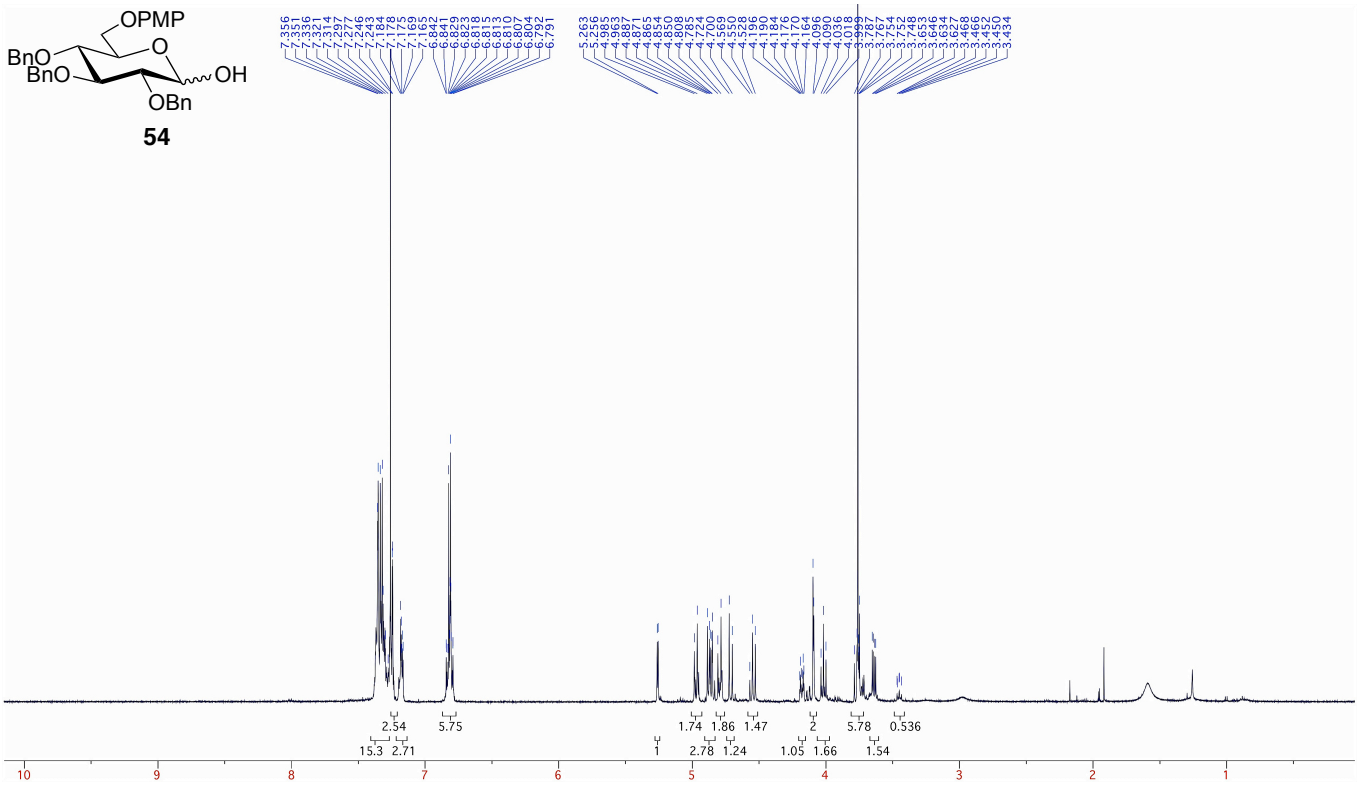
BnO
BnO
BnO
OMe
53

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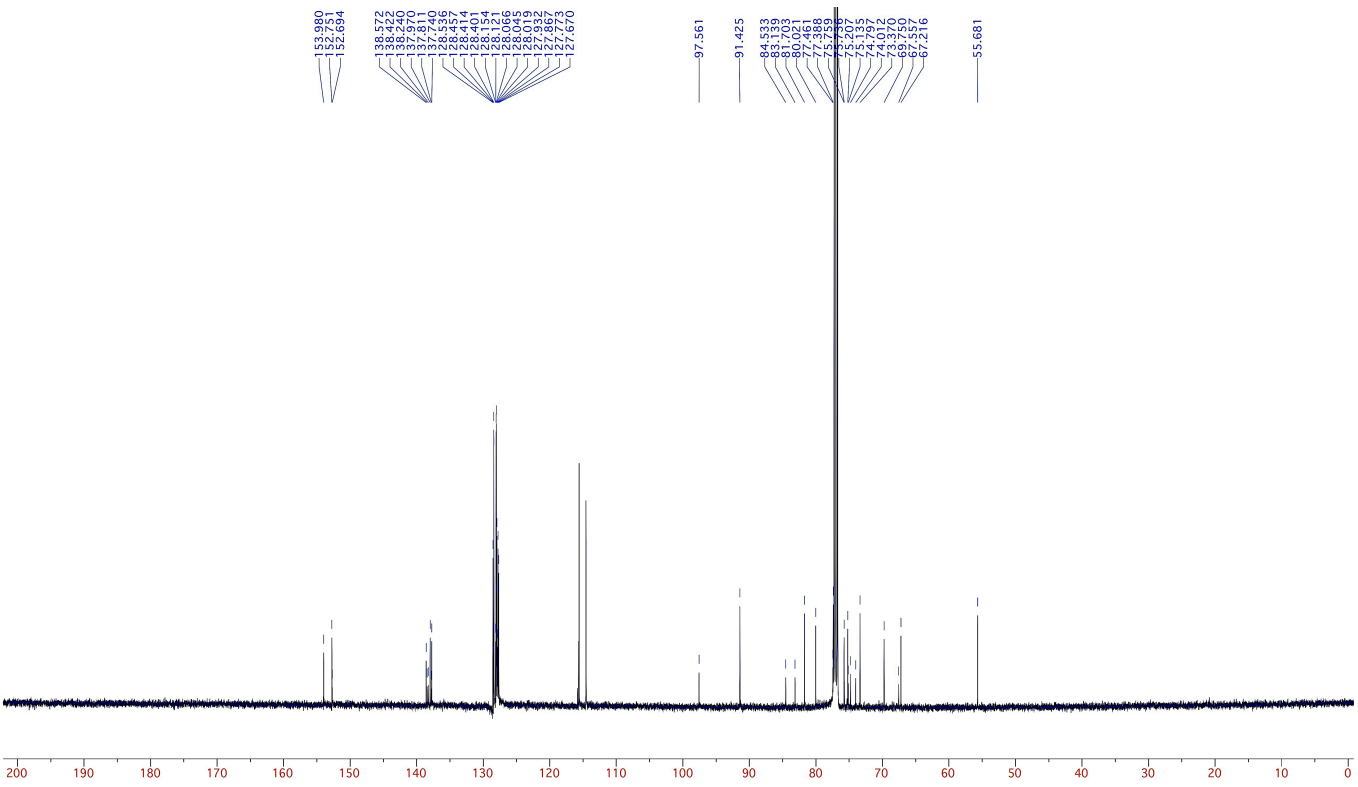
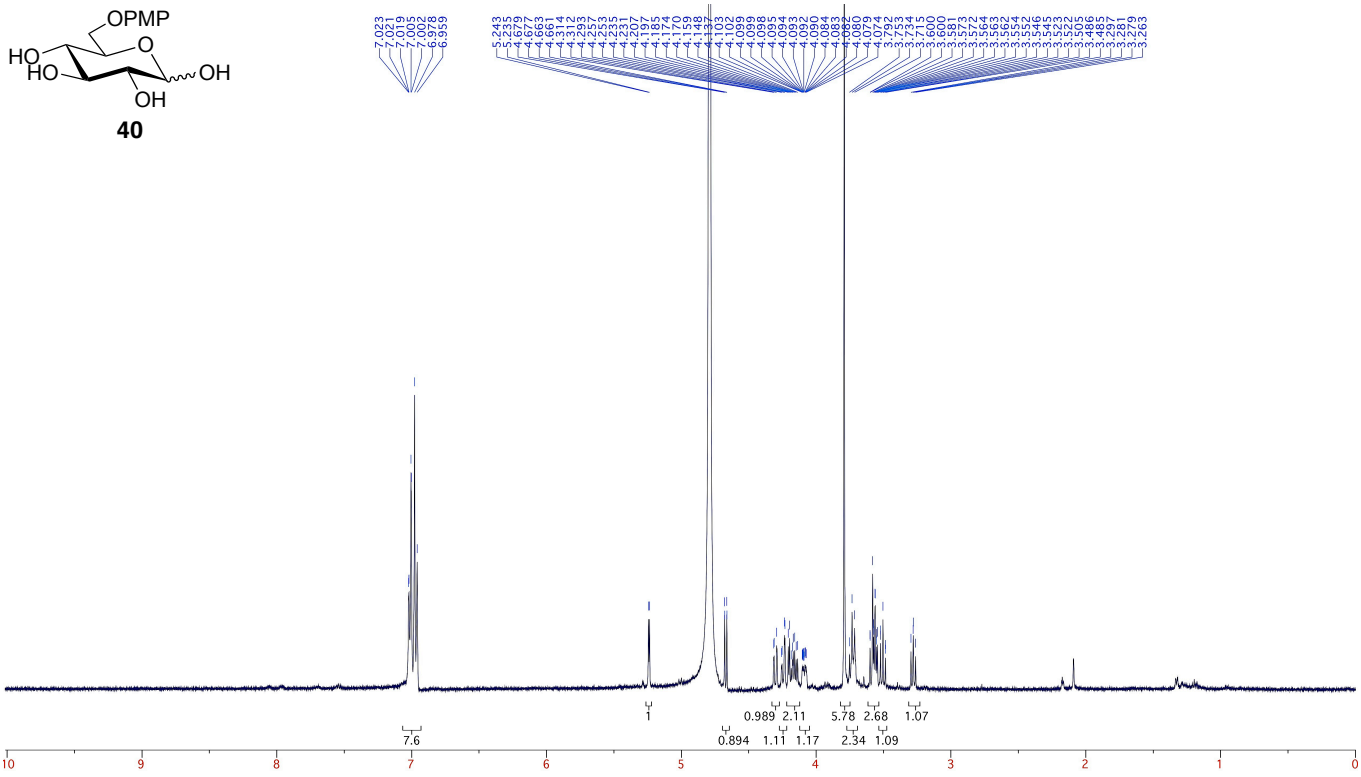
BnO
BnO
OH
OBn
54




OPMP
HO
HO
O
OH
OH
40
7.023
7.021
7.019
7.005
7.002
6.978
6.959
5.243
5.235
5.229
4.677
4.663
4.661
4.314
4.312
4.293
4.257
4.253
4.235
4.231
4.207
4.197
4.185
4.174
4.170
4.160
4.158
4.148
4.137
4.103
4.102
4.096
4.099
4.098
4.095
4.094
4.093
4.092
4.091
4.084
4.083
4.082
4.080
4.079
4.074
3.792
3.733
3.734
3.715
3.600
3.601
3.591
3.573
3.572
3.564
3.563
3.562
3.554
3.552
3.546
3.545
3.523
3.522
3.502
3.501
3.486
3.485
3.297
3.281
3.279
3.263
1
0.989
2.11
5.78
2.68
1.07
7.6
0.894
1.11
1.17
2.34
1.09
10
9
8
7
6
5
4
3
2
1
0
153.546
153.518
153.369
152.969
152.322
116.311
116.275
116.262
111.062
95.991
92.129
75.629
74.066
73.995
72.985
72.855
71.185
69.729
69.535
69.482
67.986
67.806
55.805
200
190
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150
140
130
120
110
100
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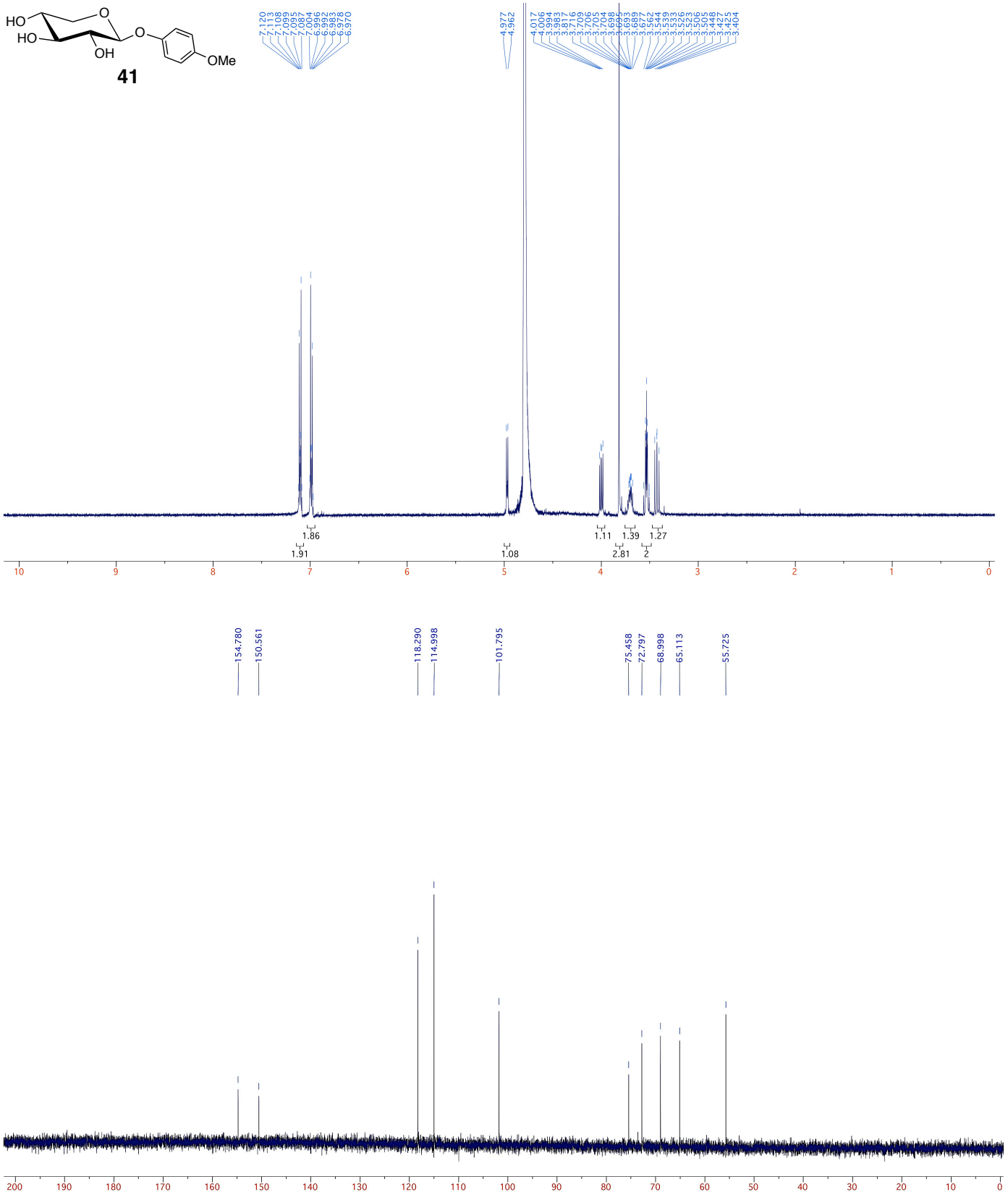
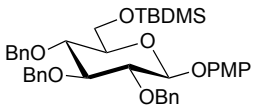
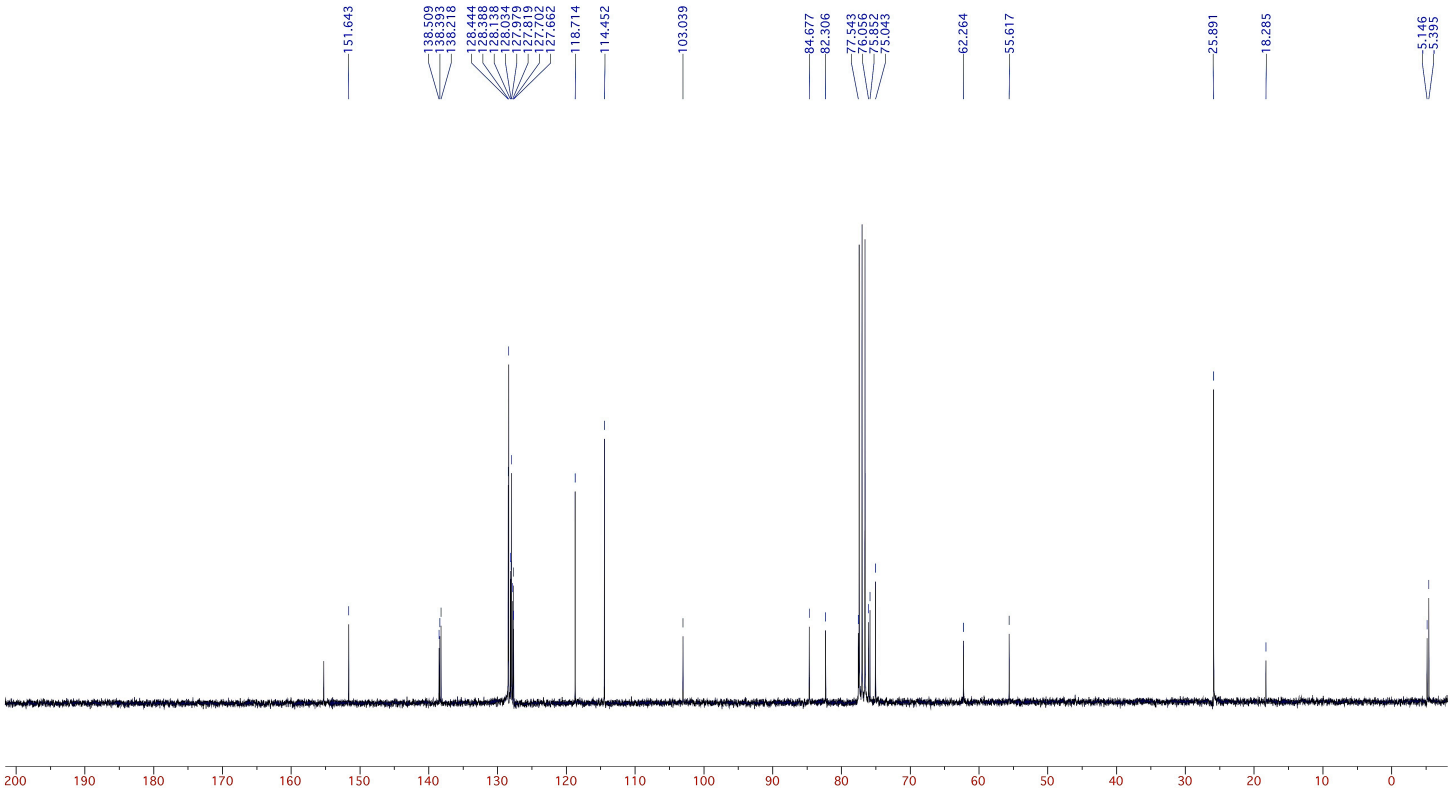
70
60
50
40
30
20
10
0


HO
HO
OH
O
O
OMe
41
7.120
7.113
7.108
7.099
7.095
7.087
7.004
6.996
6.992
6.983
6.978
6.970
4.977
4.962
4.017
4.006
3.994
3.984
3.817
3.716
3.709
3.706
3.705
3.704
3.698
3.693
3.689
3.677
3.562
3.544
3.539
3.533
3.526
3.523
3.506
3.505
3.448
3.427
3.425
3.404
1.86
1.91
1.08
1.11
1.39
2.81
1.27
2
10
9
8
7
6
5
4
3
2
1
0
154.780
150.561
118.290
114.998
101.795
75.458
72.797
68.998
65.113
55.725
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


OTBDMS
O
BnO
OPMP
BnO
OBn

**55**


7.389
7.356
7.340
7.320
7.313
7.302
7.297
7.058
7.051
7.036
7.028
7.018
6.846
6.834
6.826
6.811
6.801
6.792
5.084
5.048
4.961
4.925
4.894
4.858
4.851
4.844
4.837
4.814
4.807
4.698
4.661
3.897
3.891
3.859
3.854
3.799
3.784
3.771
3.766
3.761
3.745
3.722
3.704
3.667
3.652
3.639
3.620
3.419
3.413
3.403
3.397
3.388
3.372
3.366
0.904
0.064
0.032
2.02
14.7
2.01
0.974
3.96
0.976
1
0.944
3.06
4.25
0.995
9.21
5.99
10
9
8
7
6
5
4
3
2
1
0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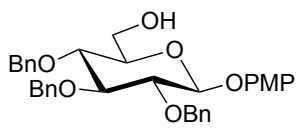
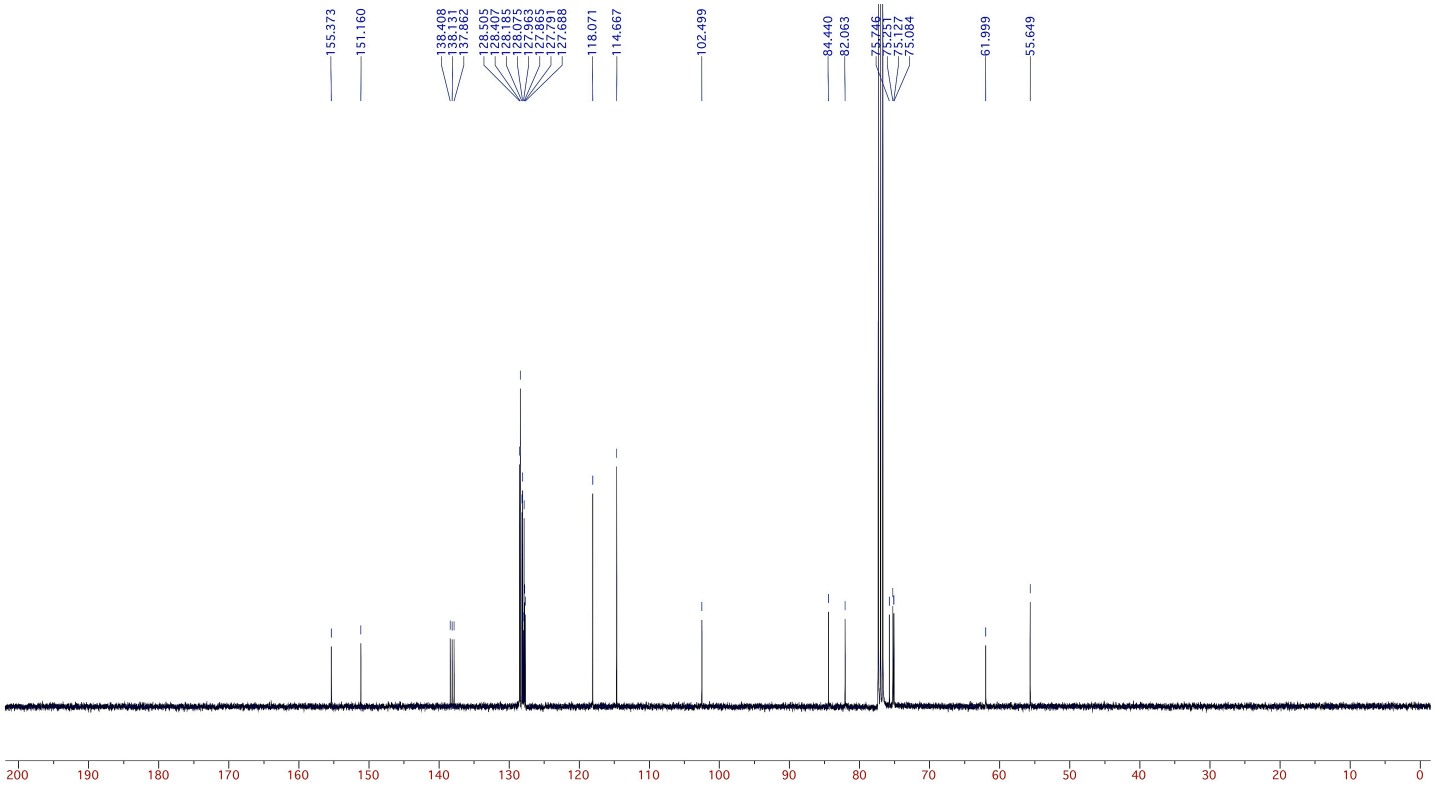
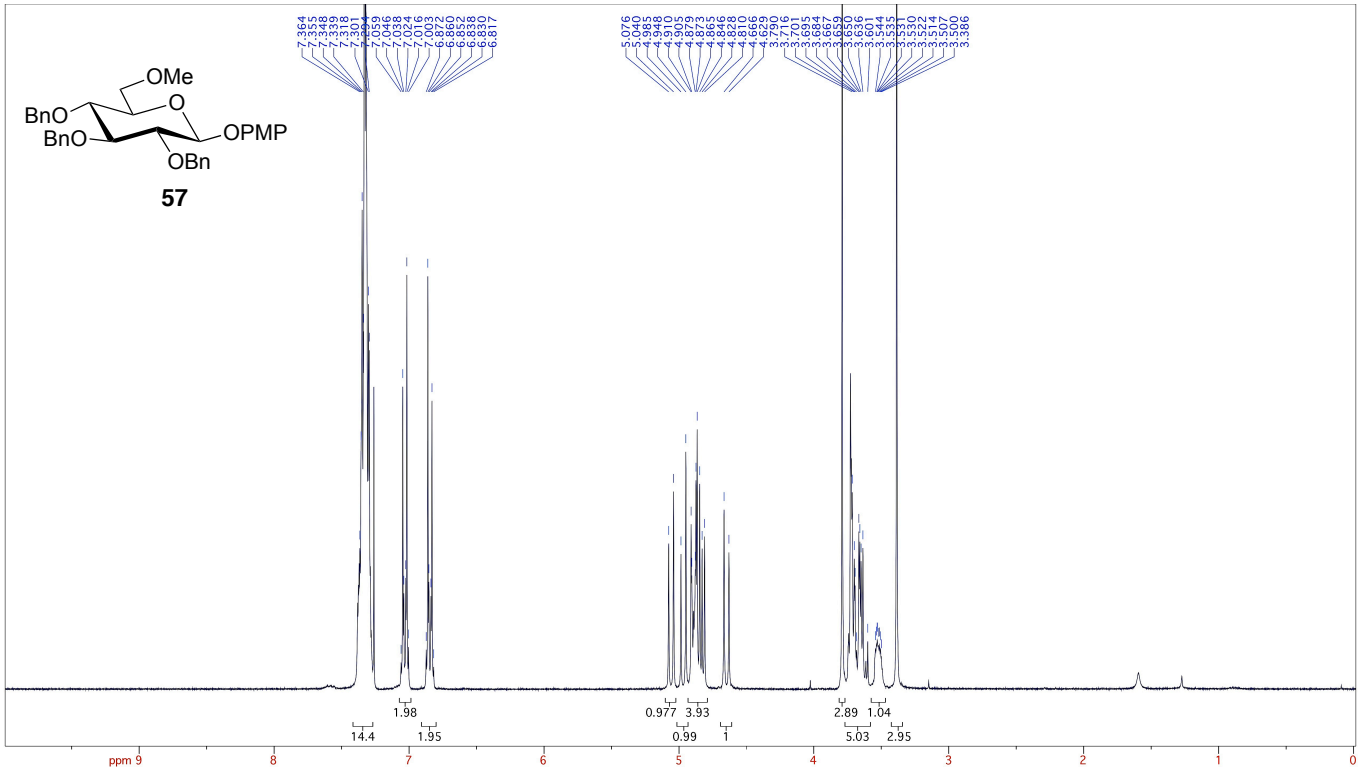
138.509
138.393
138.218
128.444
128.388
128.138
128.034
127.979
127.819
127.702
127.662
118.714
114.452
103.039
84.677
82.306
77.543
76.056
75.852
75.043
62.264
55.617
25.891
18.285
5.146
5.395
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

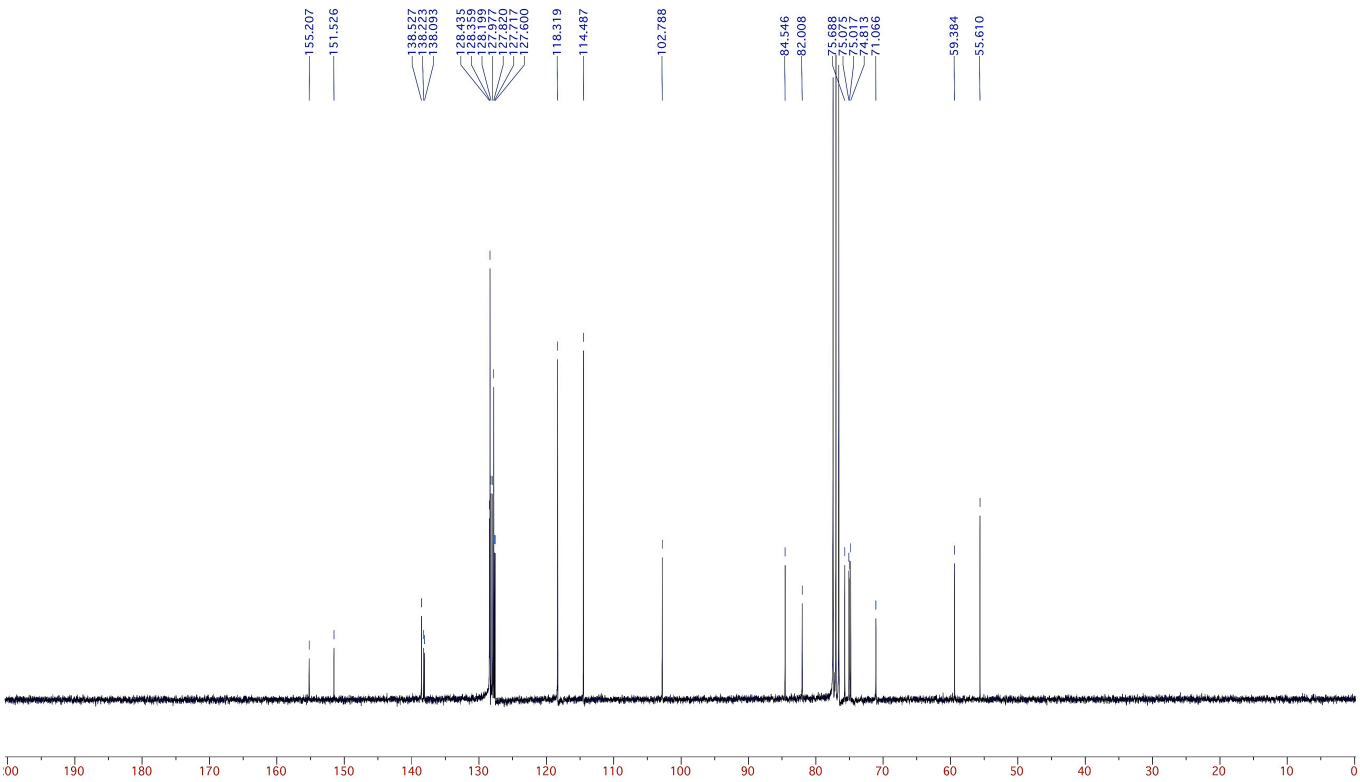


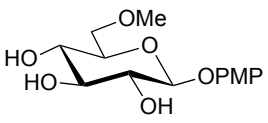

**56**





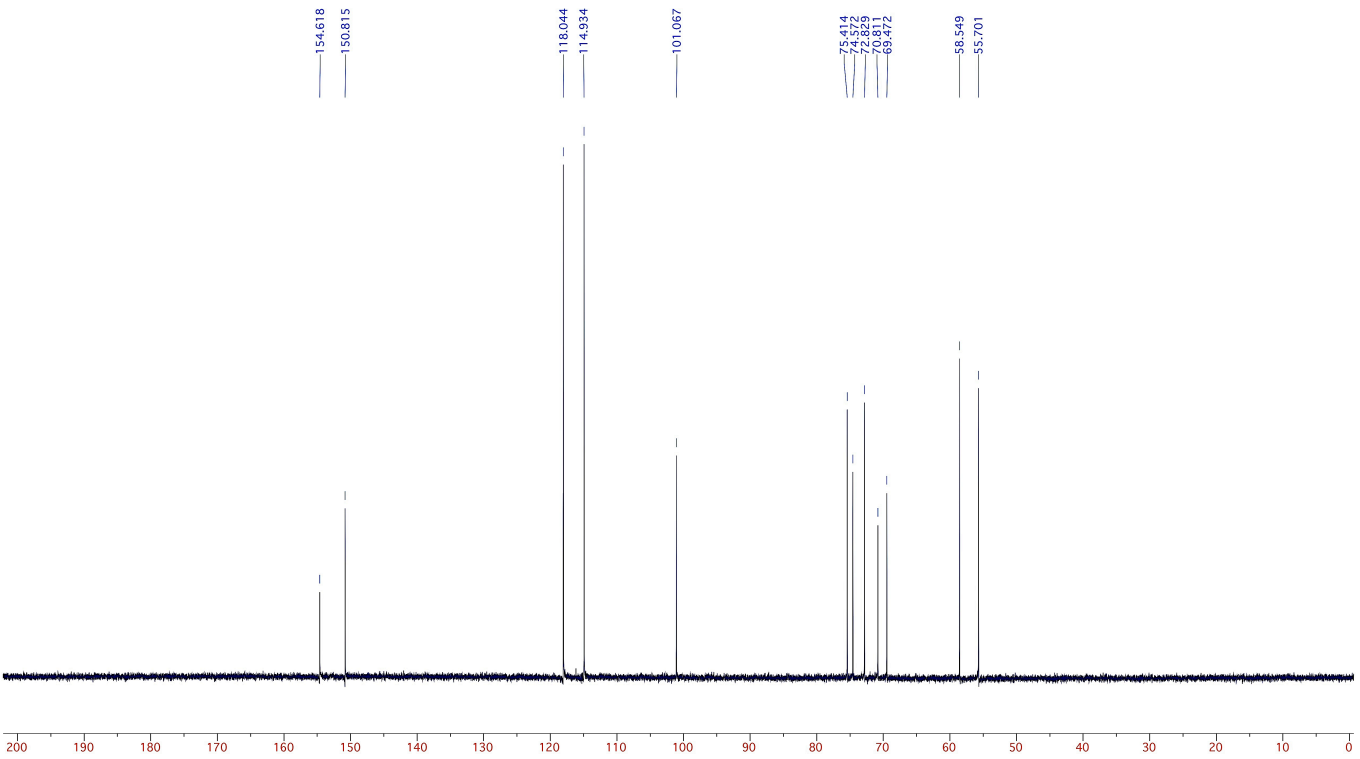

OMe
O
BnO
BnO
OPMP
OBn
57
7.364
7.355
7.348
7.339
7.318
7.301
7.294
7.059
7.046
7.038
7.014
7.003
6.872
6.862
6.850
6.838
6.830
6.817
5.076
5.040
4.945
4.944
4.910
4.905
4.873
4.865
4.846
4.828
4.810
4.666
4.629
3.790
3.716
3.701
3.695
3.684
3.665
3.659
3.650
3.636
3.601
3.544
3.535
3.531
3.520
3.522
3.514
3.507
3.500
3.386
1.98
0.977
3.93
2.89
1.04
14.4
1.95
0.99
1
5.03
2.95
ppm 9
8
7
6
5
4
3
2
1
0

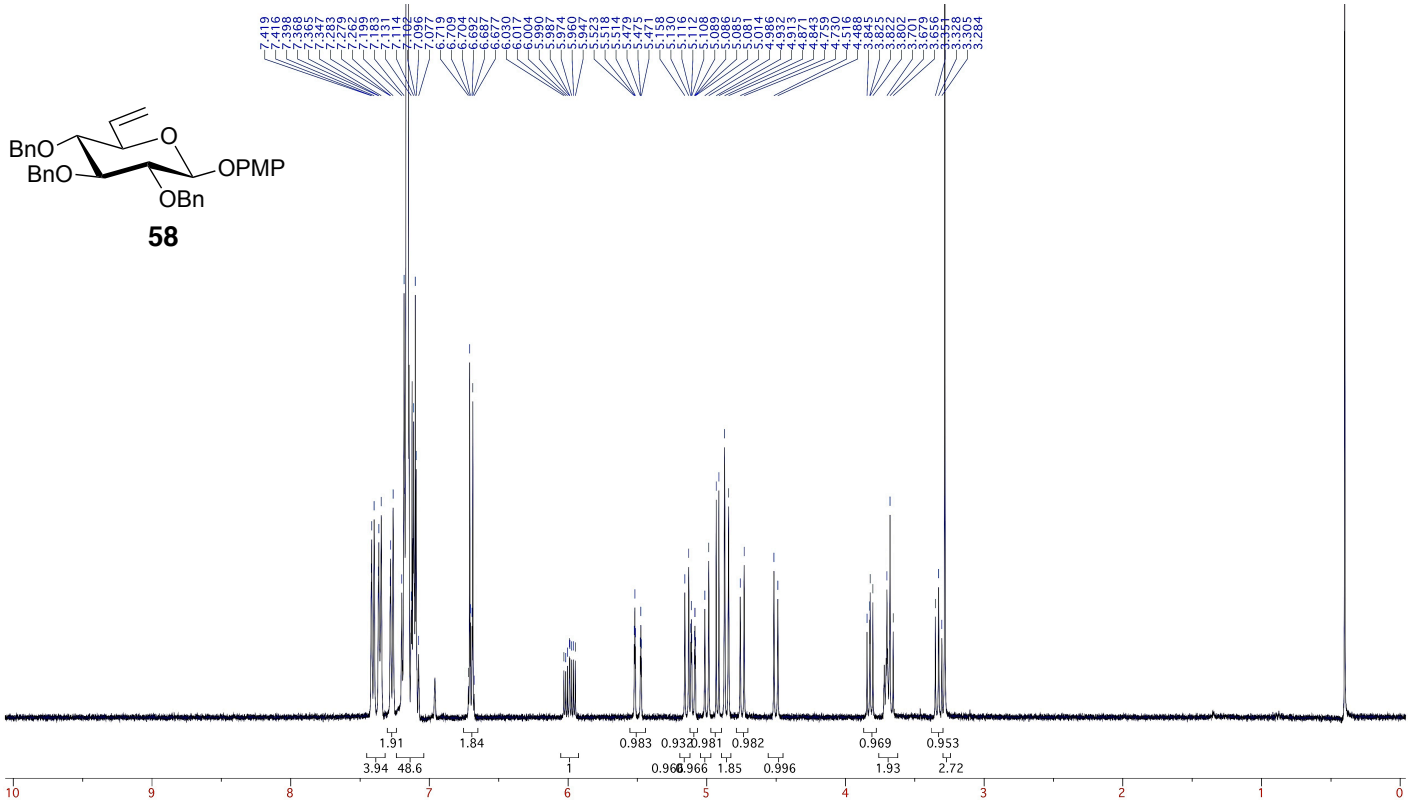

155.207
151.526
138.527
138.273
138.093
128.435
128.359
128.199
128.077
127.820
127.717
127.600
118.319
114.487
102.788
84.546
82.008
75.688
75.475
75.017
74.813
71.066
59.384
55.610
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


OMe
O
HO
HO
OPMP
OH

**42**

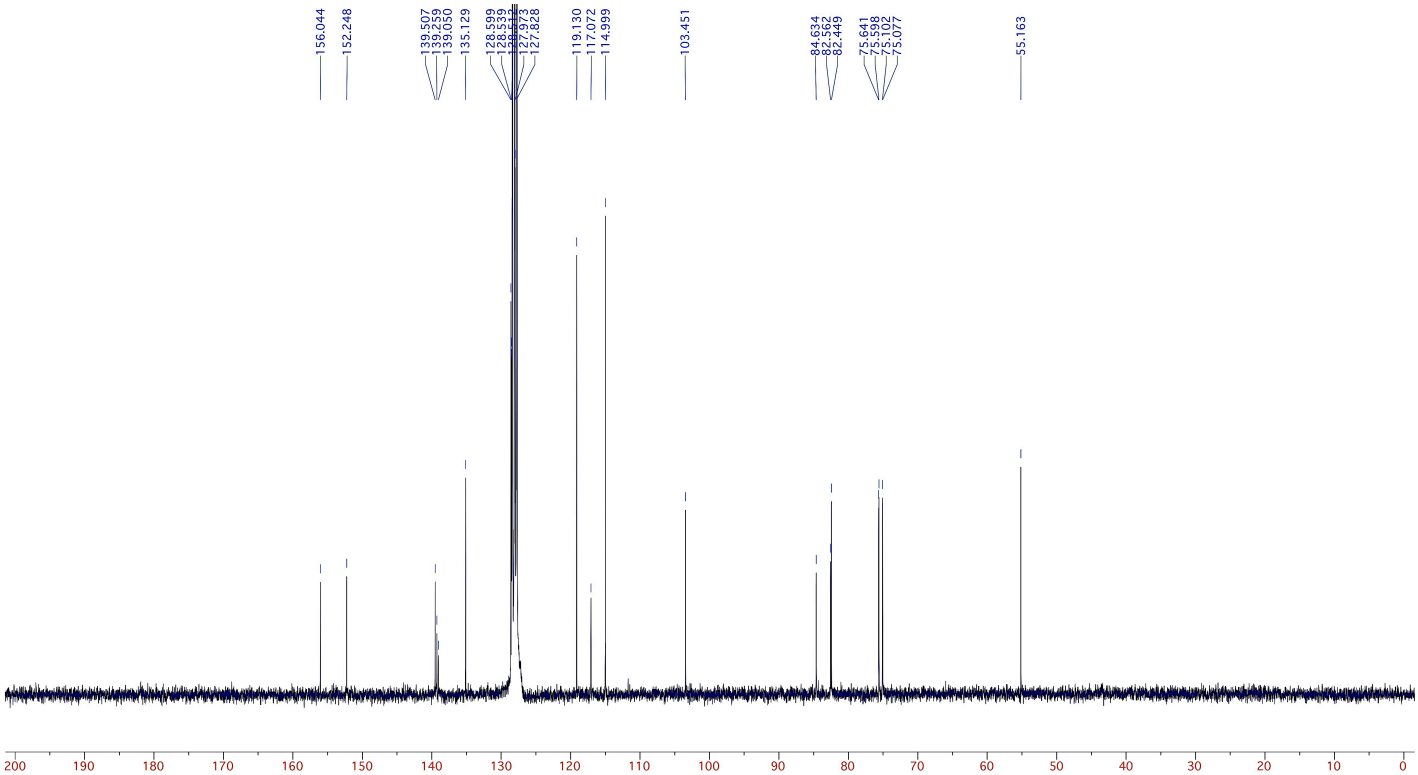

7.099
7.091
7.087
7.078
7.073
7.065
6.973
6.966
6.962
6.952
6.948
6.940
4.985
4.970
3.790
3.779
3.760
3.757
3.750
3.681
3.669
3.666
3.662
3.657
3.642
3.635
3.624
3.591
3.541
3.539
3.523
3.520
3.505
3.487
3.468
3.450
3.368
2.01
2.03
1
3
2.17
1.09
2.13
1.05
3.06
ppm 9
8
7
6
5
4
3
2
1
0

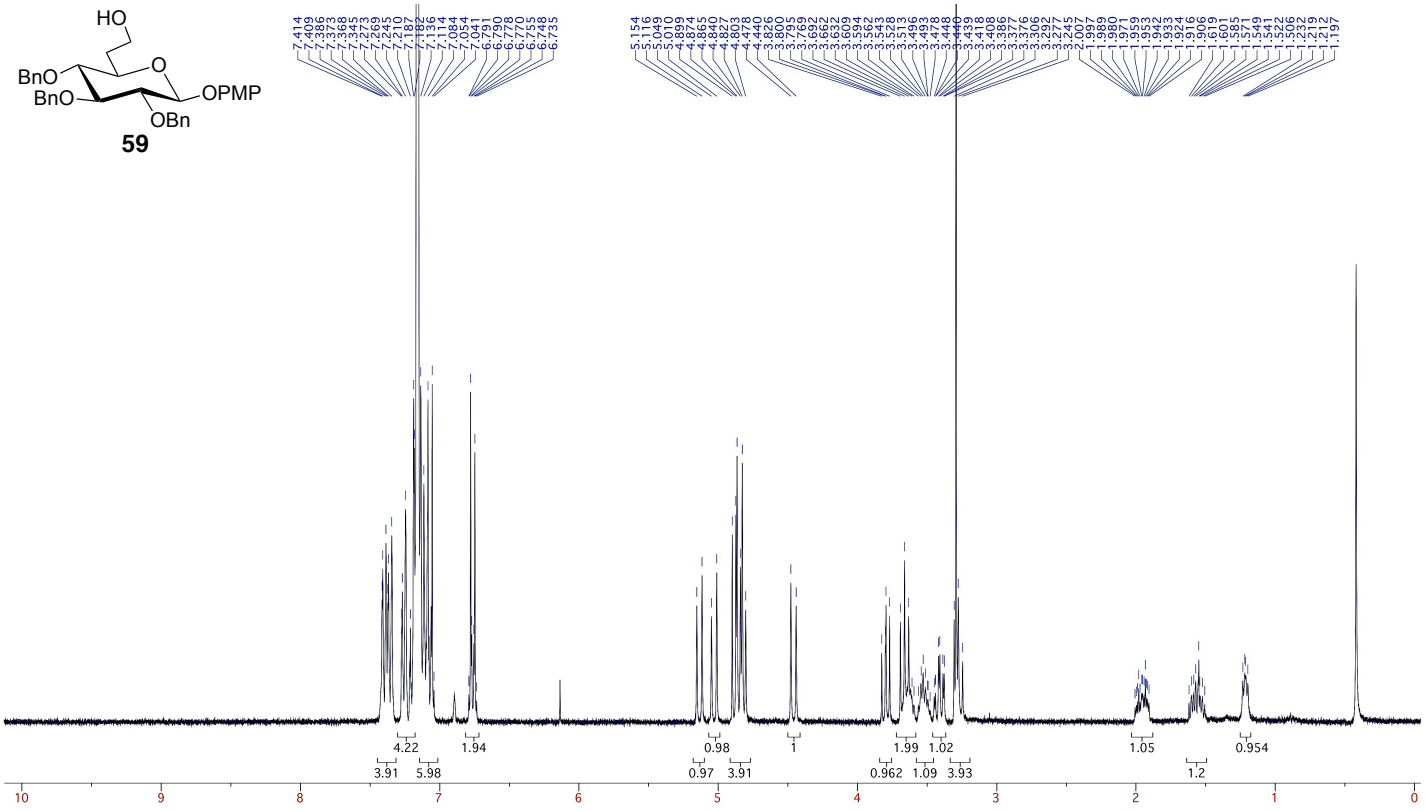

154.618
150.815
118.044
114.934
101.067
75.414
74.572
72.829
70.811
69.472
58.549
55.701
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



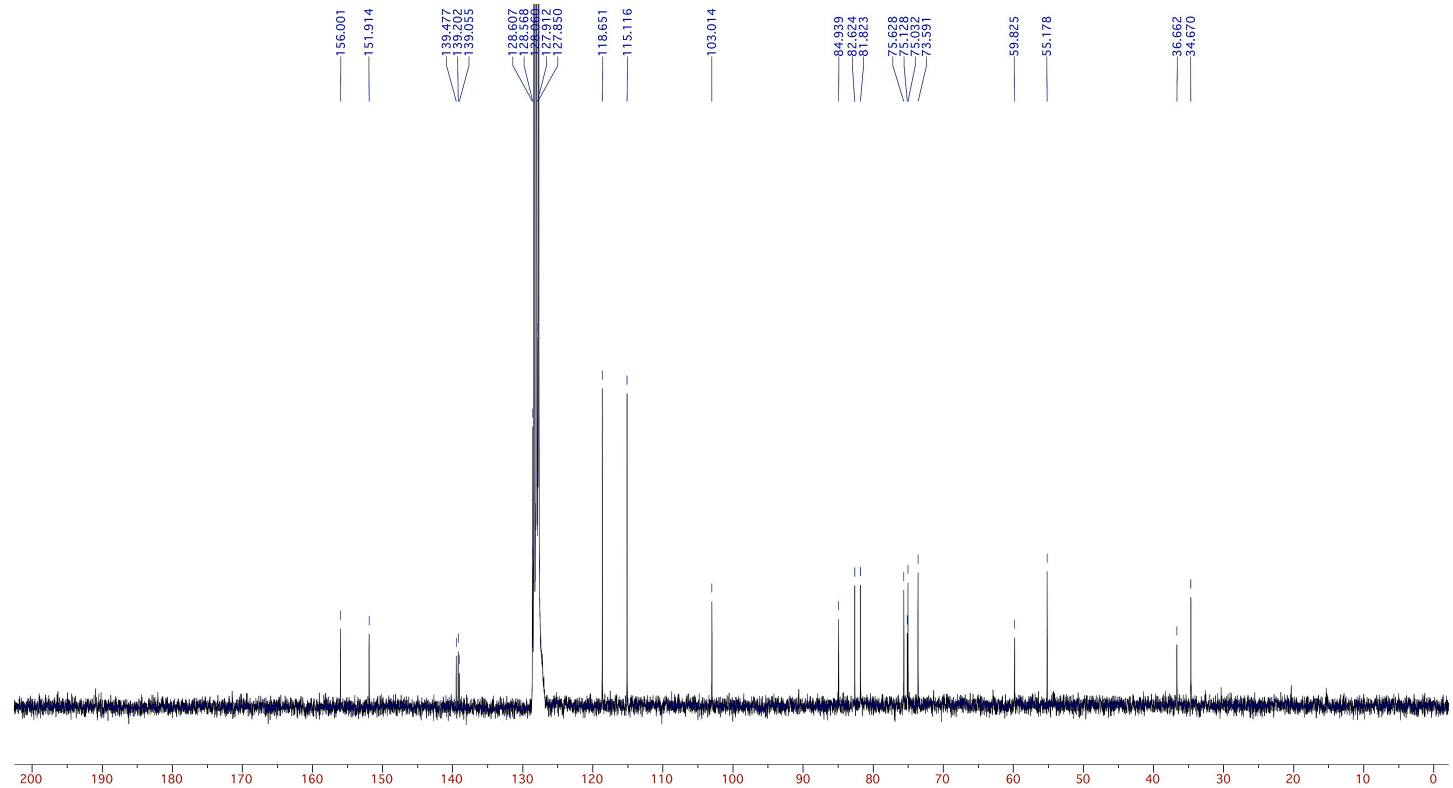

**58**

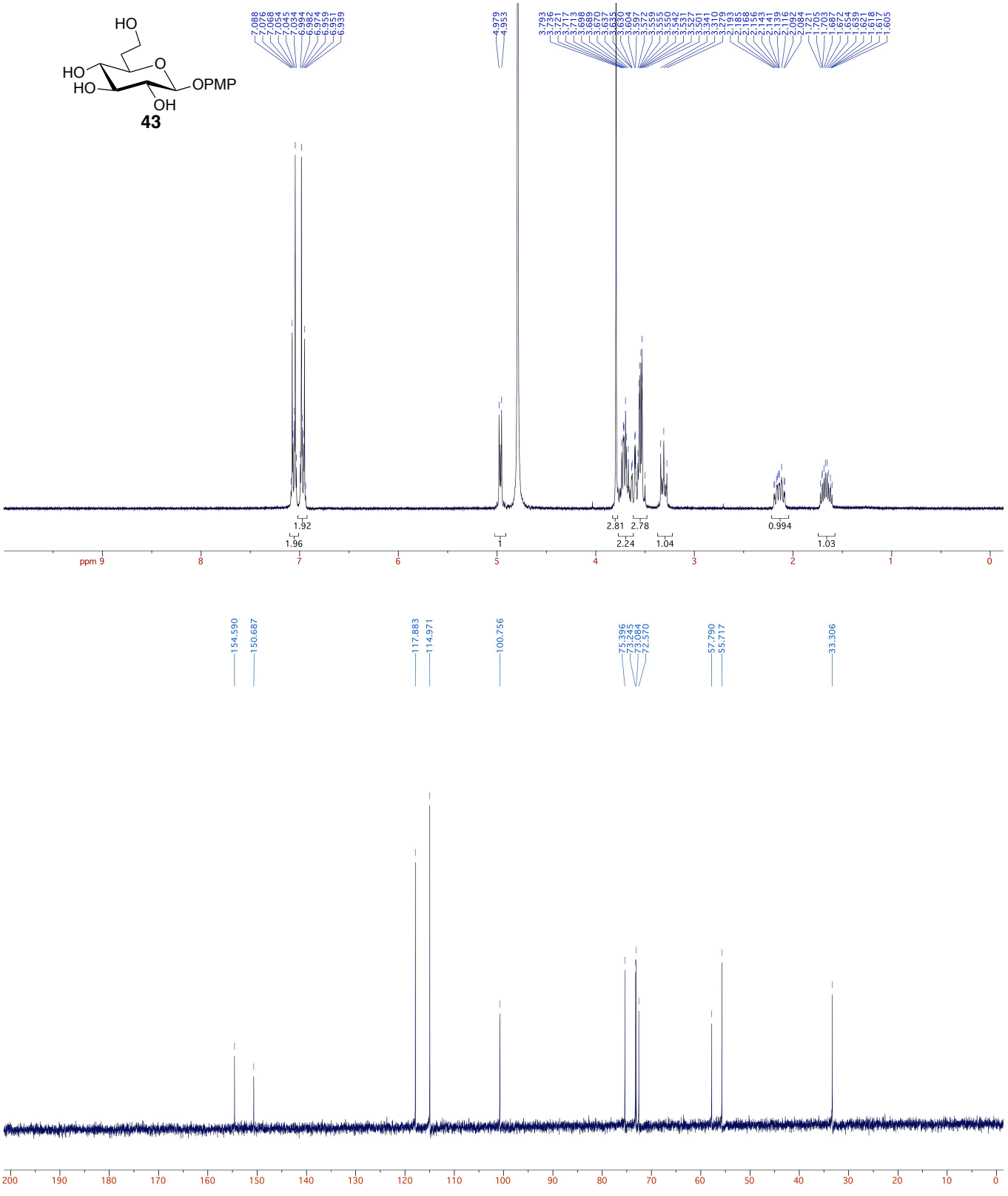





HO
O
BnO
BnO
OPMP
OBn
59






HO
HO
HO
O
OPMP
OH
43
7.088
7.076
7.066
7.054
7.045
7.034
6.982
6.974
6.959
6.951
6.939
4.979
4.953
3.793
3.716
3.721
3.717
3.713
3.688
3.689
3.670
3.657
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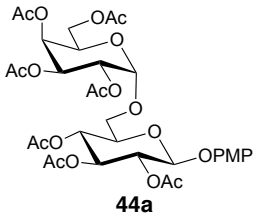
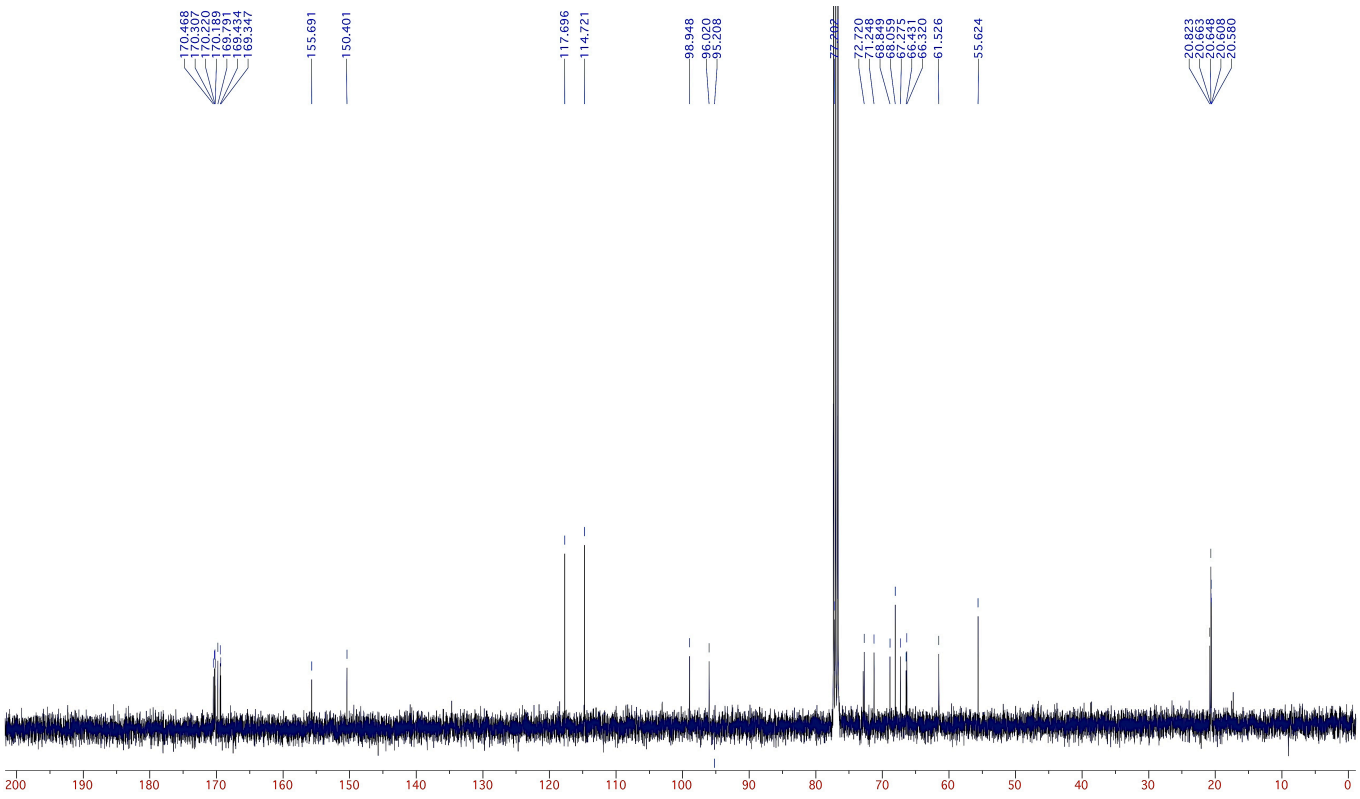
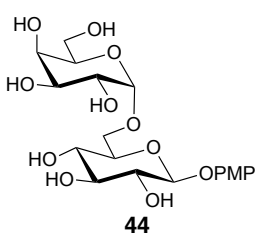
3.604
3.597
3.572
3.555
3.550
3.542
3.541
3.527
3.501
3.341
3.310
3.279
3.193
2.185
2.168
2.156
2.143
2.141
2.139
2.116
2.092
2.084
2.071
1.705
1.703
1.687
1.672
1.654
1.639
1.621
1.618
1.617
1.605
1.92
1.96
1
2.81
2.78
2.24
1.04
0.994
1.03
ppm 9
8
7
6
5
4
3
2
1
0
154.590
150.687
117.883
114.971
100.756
75.396
73.245
73.084
72.570
57.790
55.717
33.306
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


AcO
OAc
O
AcO
AcO
O
AcO
O
AcO
OPMP
OAc

**44a**

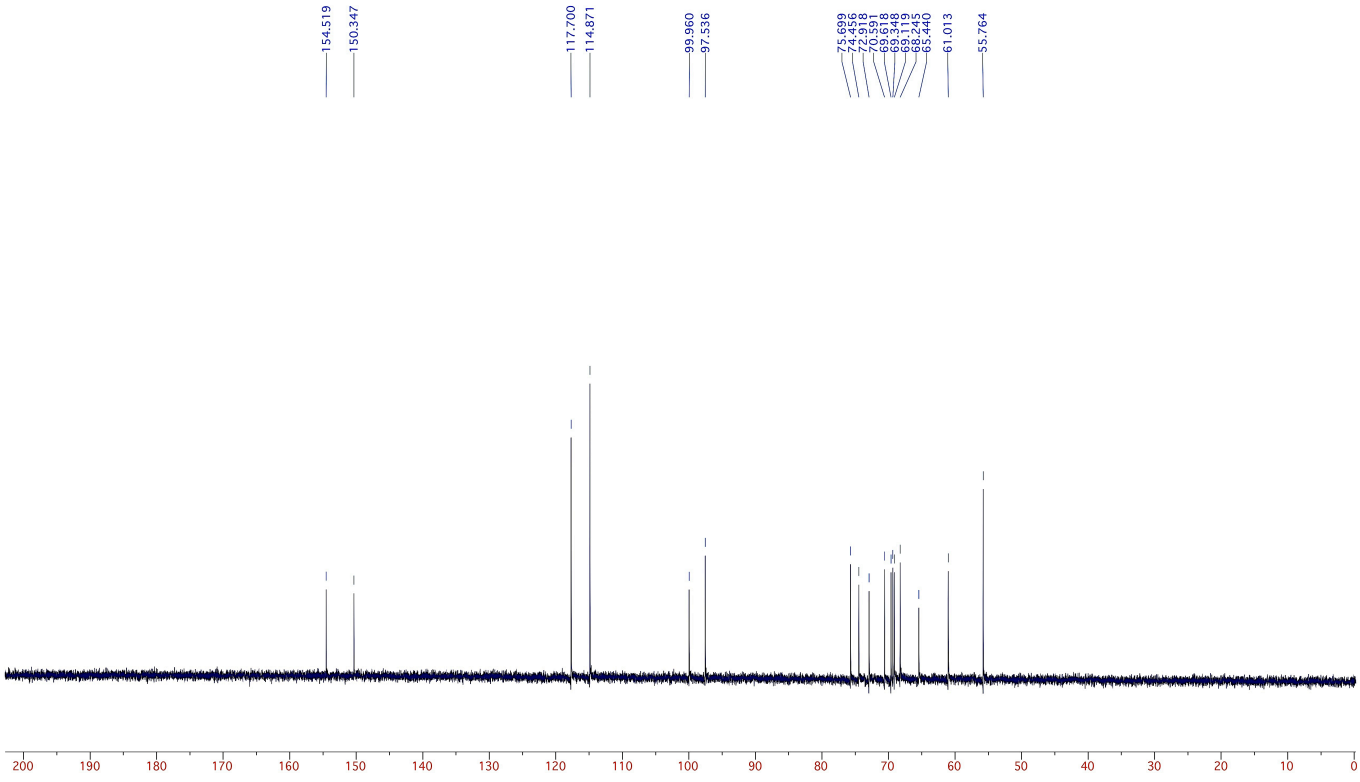

3.03
3.98
1.79
0.95
3.75
1.08
1
4.8
5.53
2.9
2.8

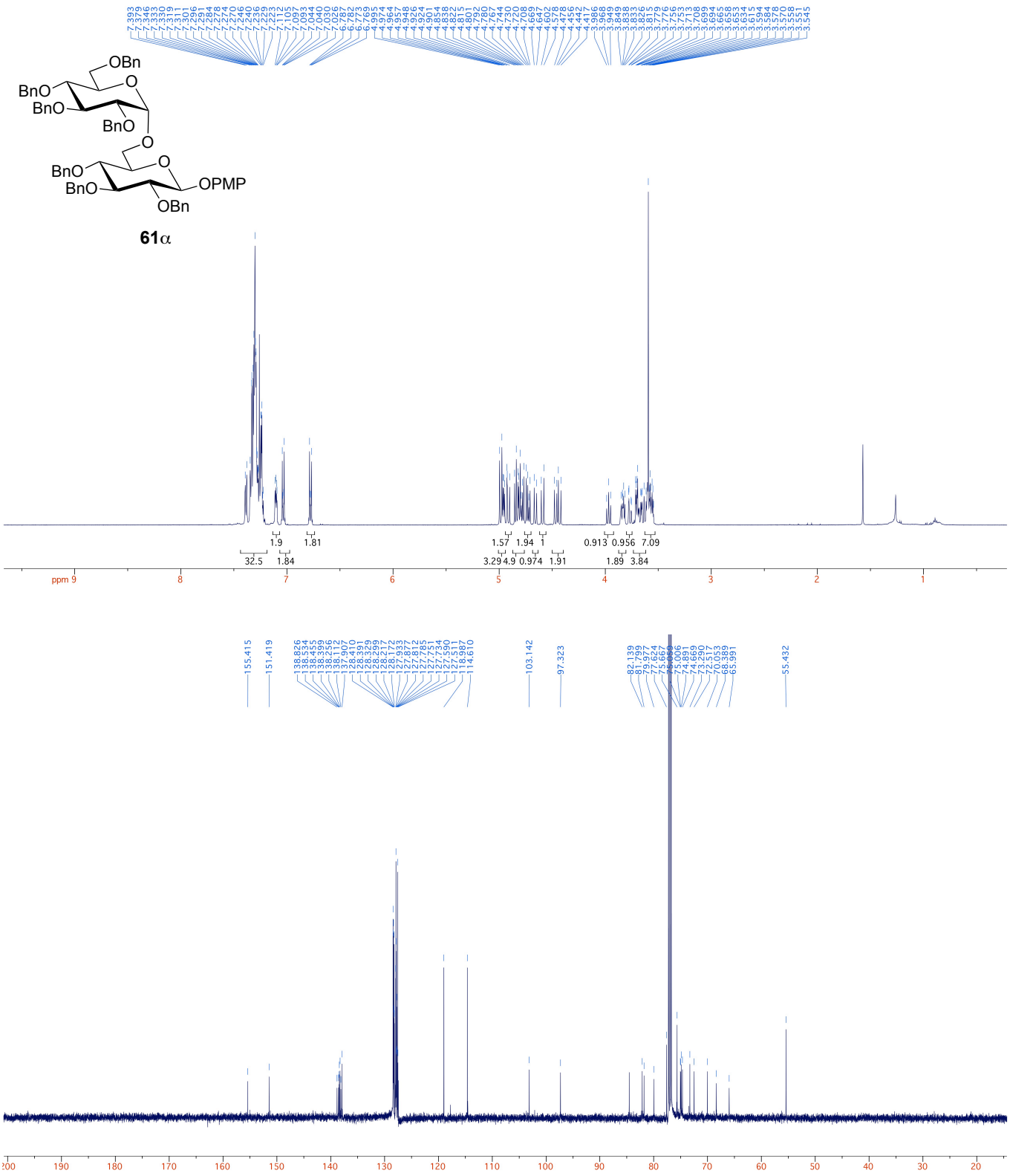


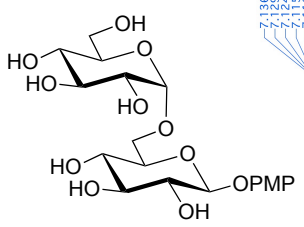

HO
OH
O
HO
HO
O
HO
O
HO
OPMP
OH

**44**


7.123
7.121
7.105
7.103
6.996
6.994
6.978
6.976
5.125
5.123
4.949
3.891
3.879
3.877
3.869
3.857
3.792
3.790
3.787
3.772
3.771
3.764
3.761
3.747
3.742
3.740
3.662
3.660
3.646
3.644
3.639
3.637
3.633
3.623
3.621
3.617
3.615
3.599
3.597
3.578
3.576
3.569
3.562
3.560
3.542
3.537
3.517
3.500
3.498
2.1
0.981
9.72
2.04
1
1.07
5.69
10
9
8
7
6
5
4
3
2
1
0

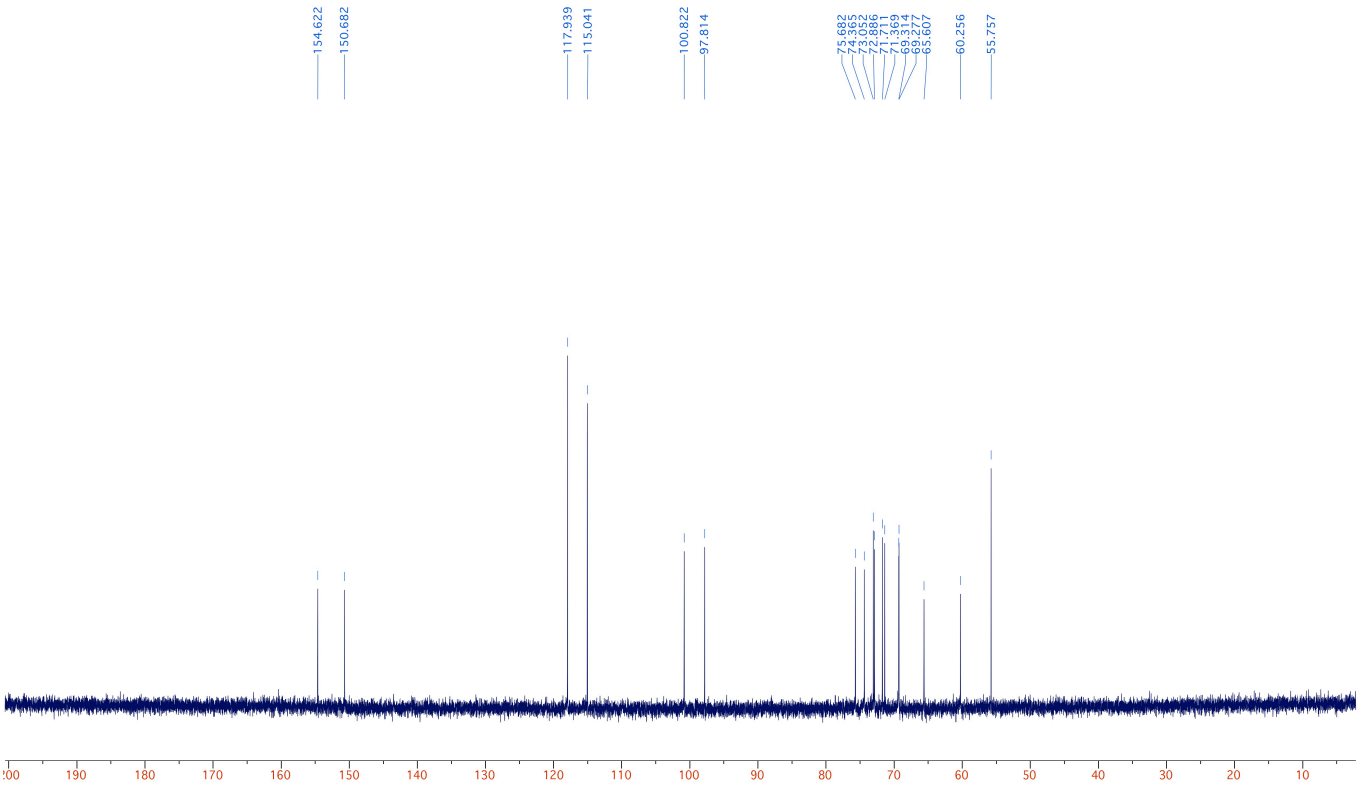

154.519
150.347
117.700
114.871
99.960
97.536
75.699
74.456
72.918
70.591
69.668
69.348
69.119
68.245
65.440
61.013
55.764
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

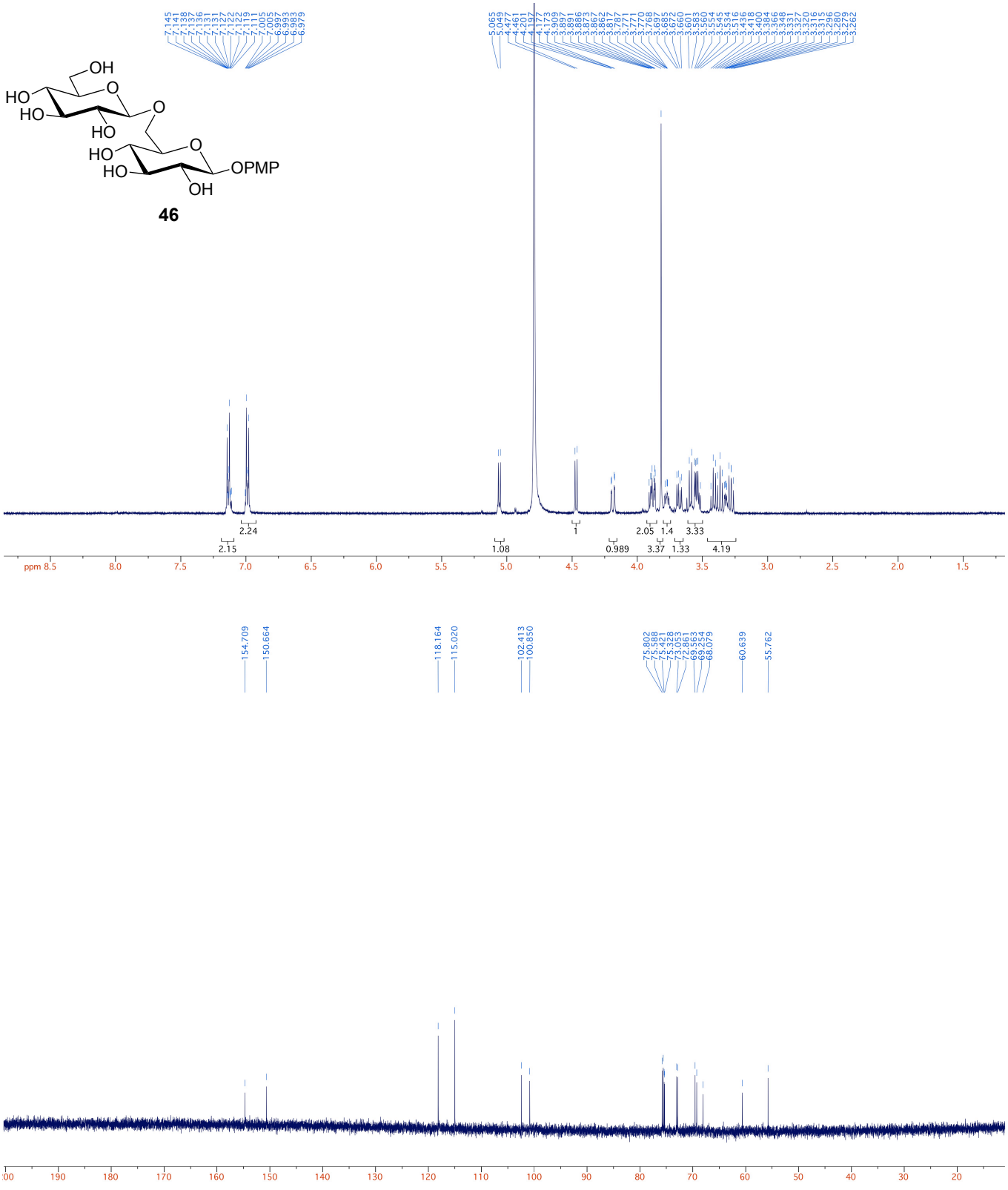

OBn
BnO
BnO
BnO
O
O
BnO
BnO
OBn
OPMP
61α
ppm 9
8
7
6
5
4
3
2
1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20


OH
HO
O
HO
HO
O
HO
HO
OPMP
OH

**45**


2.06
0.987
3.32
4.2
1.18
2.07
1
1.02
2.22
4.31
ppm 9
8
7
6
5
4
3
2
1


154.622
150.682
117.939
115.041
100.822
97.814
75.682
74.365
73.052
72.886
72.711
71.369
69.314
69.277
63.607
60.256
55.757
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


OH
HO
HO
O
O
HO
HO
O
HO
OPMP
OH
46
7.145
7.141
7.138
7.137
7.136
7.131
7.127
7.122
7.119
7.111
7.005
7.005
6.997
6.993
6.983
6.979
5.065
5.049
4.479
4.461
4.201
4.197
4.173
3.909
3.897
3.891
3.886
3.873
3.867
3.862
3.817
3.787
3.771
3.771
3.770
3.768
3.697
3.685
3.672
3.660
3.601
3.583
3.560
3.554
3.545
3.516
3.436
3.418
3.400
3.384
3.366
3.348
3.321
3.320
3.316
3.296
3.280
3.279
3.262
2.15
2.24
1.08
1
0.989
2.05
3.37
1.4
1.33
3.33
4.19
ppm 8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
154.709
150.664
118.164
115.020
102.413
100.850
75.802
75.588
75.421
75.328
73.053
72.861
69.563
69.254
68.079
60.639
55.762
190
180
170
160
150
140
130
120
110
100
90
80
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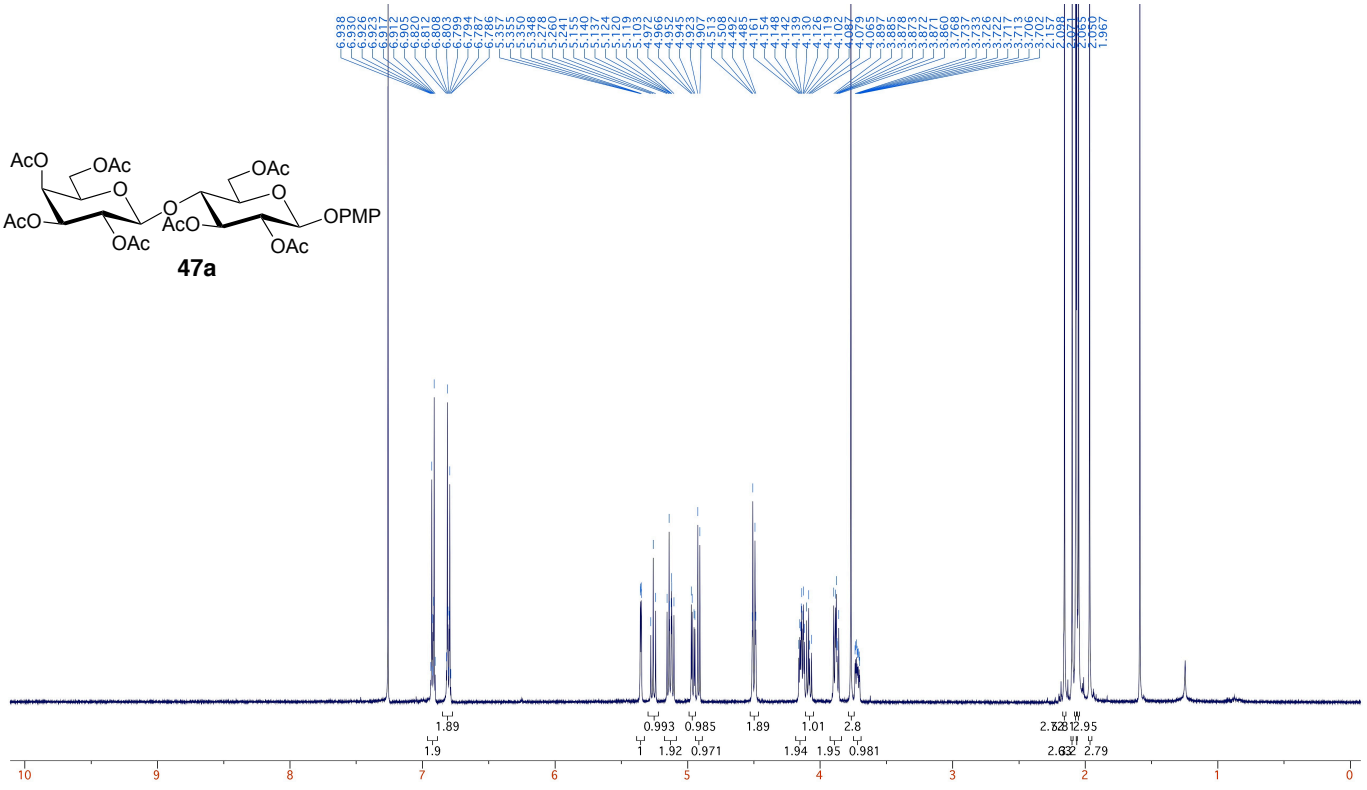
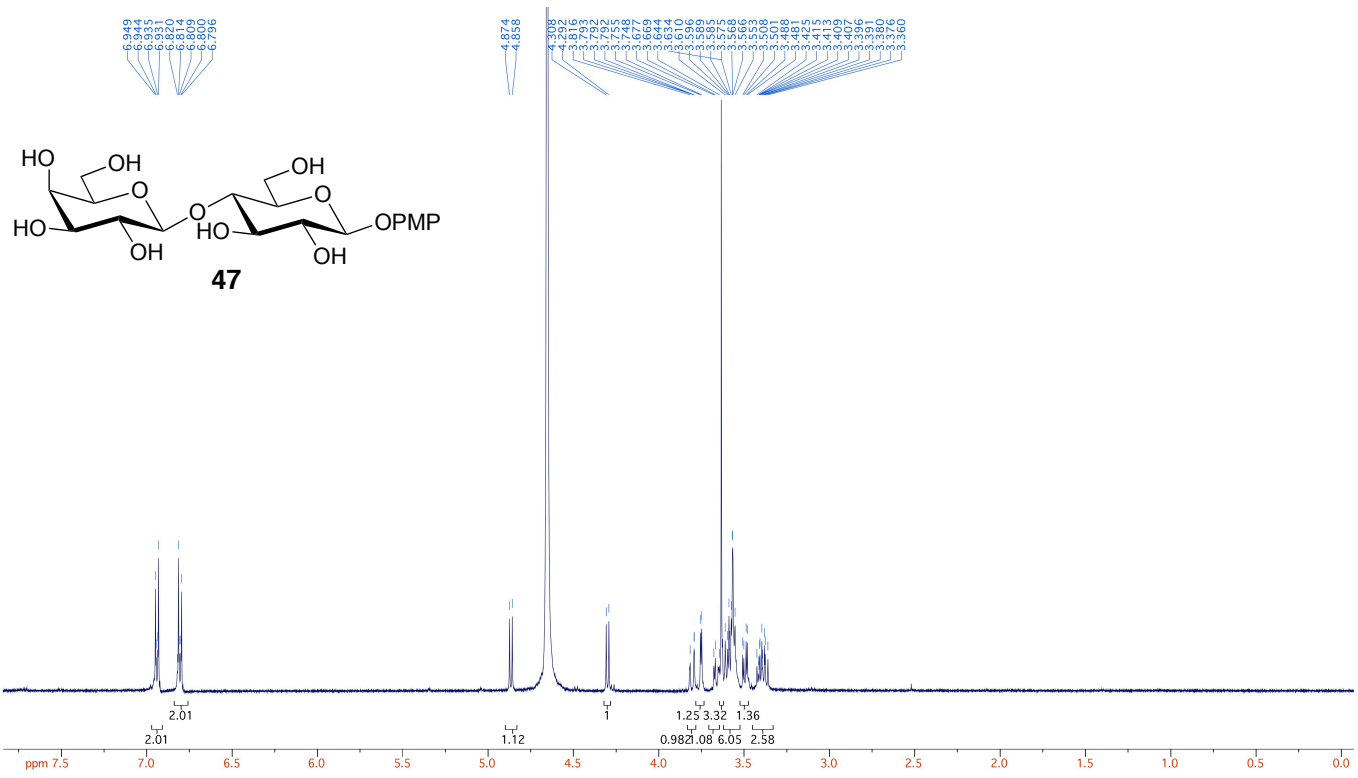
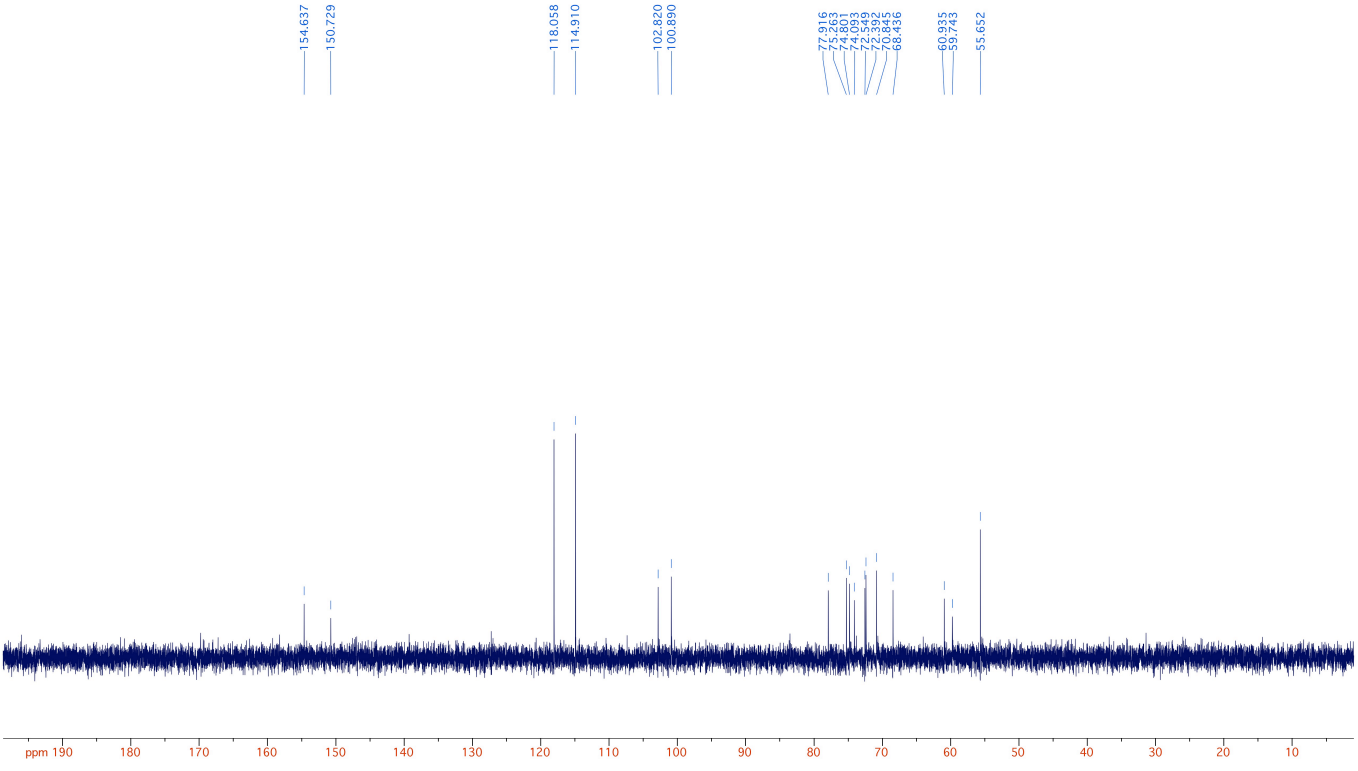
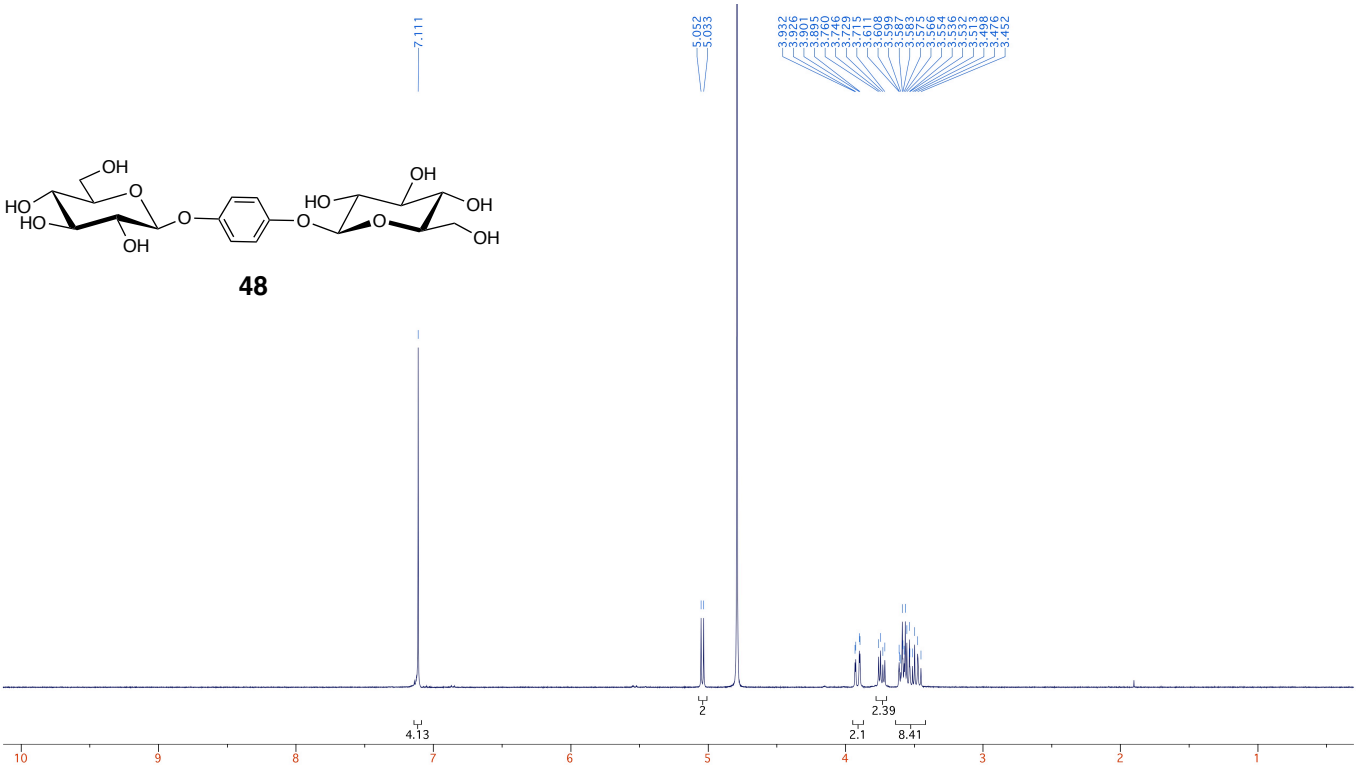
60
50
40
30
20



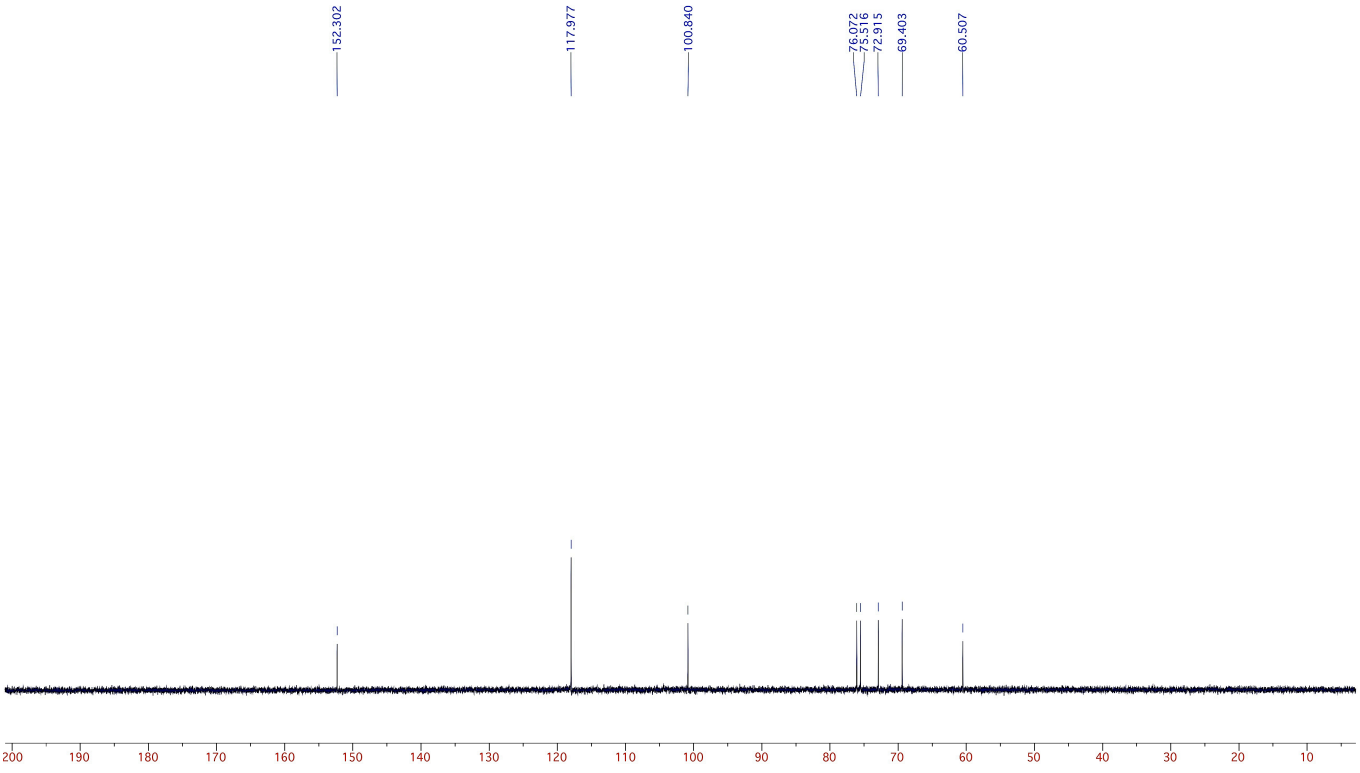

**47a**

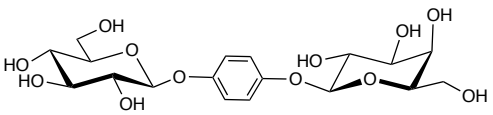

6.949
6.944
6.935
6.931
6.820
6.814
6.809
6.800
6.796
4.874
4.858
4.308
4.232
4.215
3.793
3.792
3.791
3.748
3.677
3.669
3.644
3.634
3.610
3.596
3.589
3.585
3.575
3.568
3.566
3.560
3.508
3.501
3.488
3.481
3.425
3.415
3.413
3.403
3.407
3.396
3.381
3.380
3.376
3.360
HO
OH
O
O
HO
OH
OH
O
HO
OPMP
OH
47
2.01
2.01
1.12
1
1.25
3.32
1.36
0.98
2.08
6.05
2.58
ppm 7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


154.637
150.729
118.058
114.910
102.820
100.890
77.916
75.263
74.801
74.043
72.049
72.392
70.845
68.436
60.935
59.743
55.652
ppm 190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


7.111
5.052
5.033
3.932
3.926
3.901
3.895
3.760
3.746
3.729
3.715
3.611
3.608
3.599
3.587
3.573
3.566
3.554
3.532
3.513
3.498
3.477
3.452
OH
HO
HO
OH
O
O
OH
HO
OH
O
OH
4.13
2
2.1
2.39
8.41
10
9
8
7
6
5
4
3
2
1

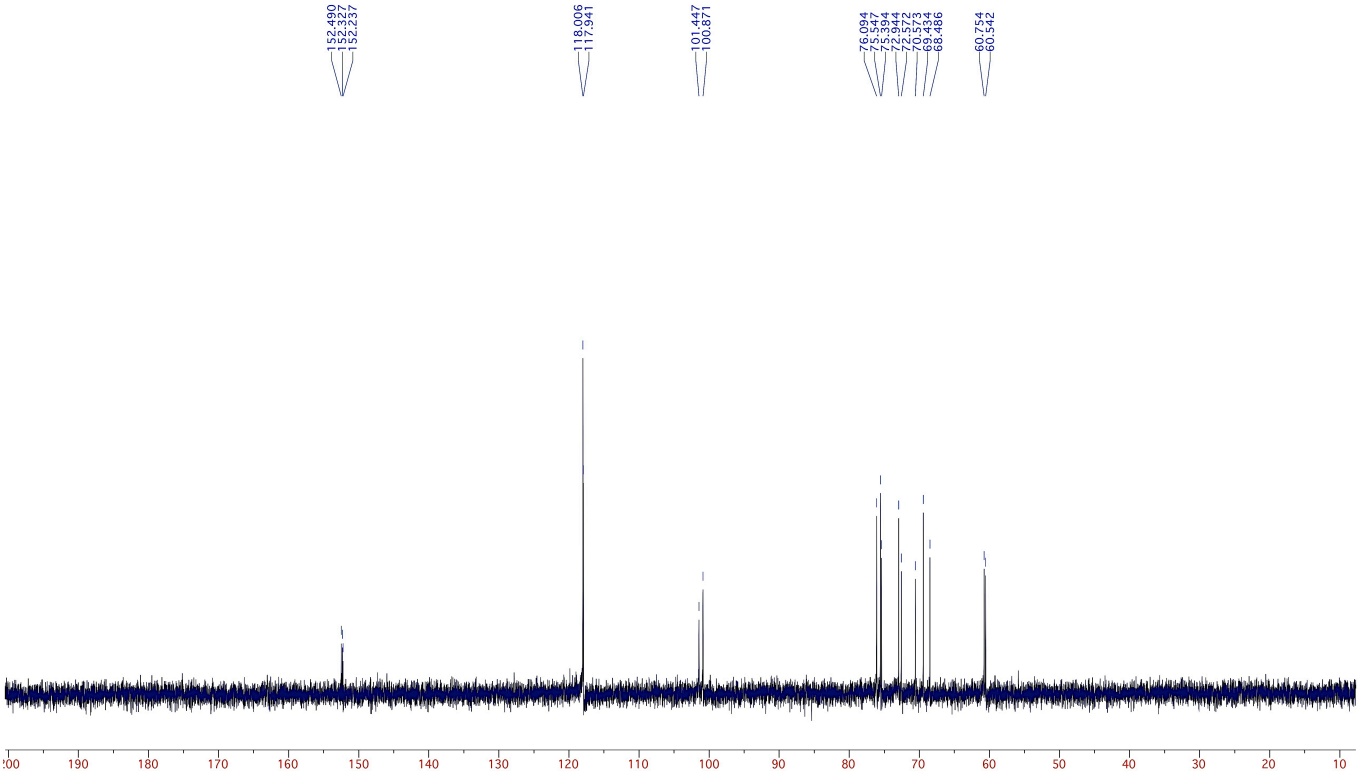
**48**

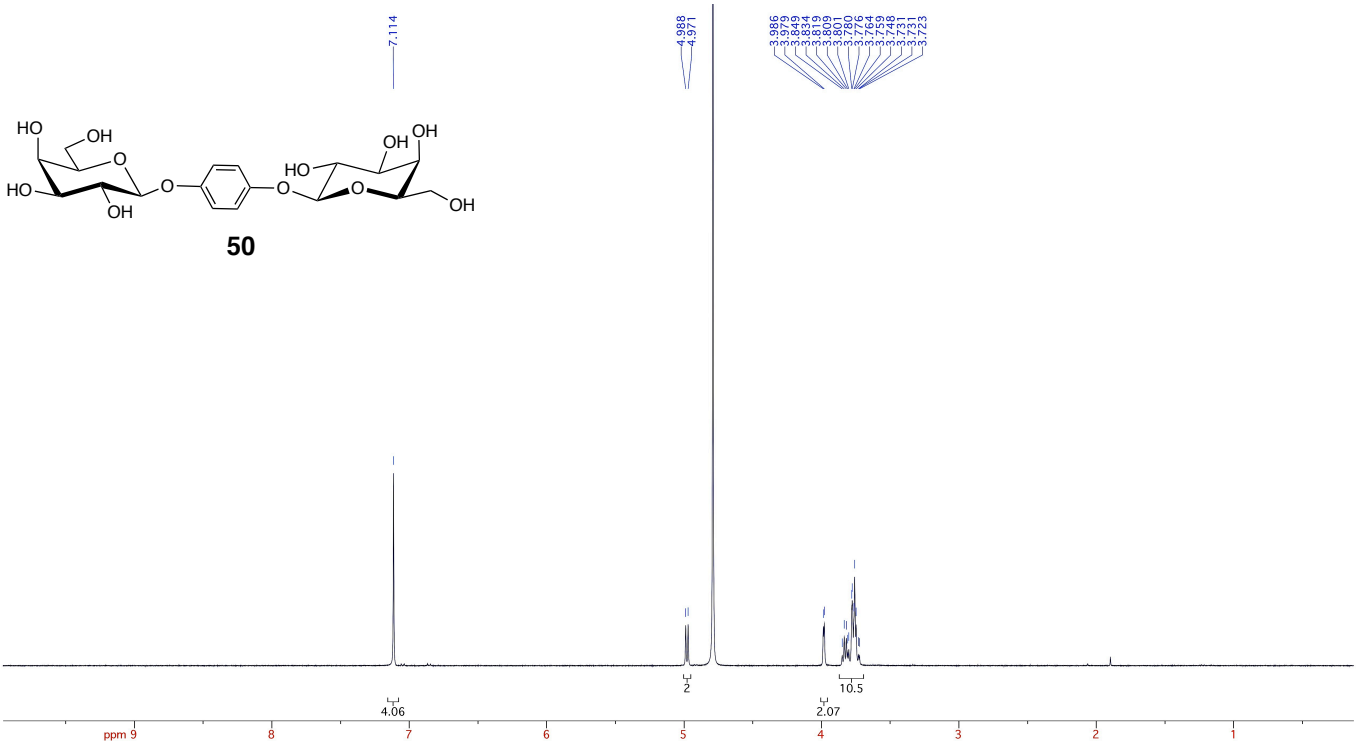

152.302
117.977
100.840
76.072
75.516
72.915
69.403
60.507
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


OH
HO
HO
O
OH
O
OH
HO
O
OH

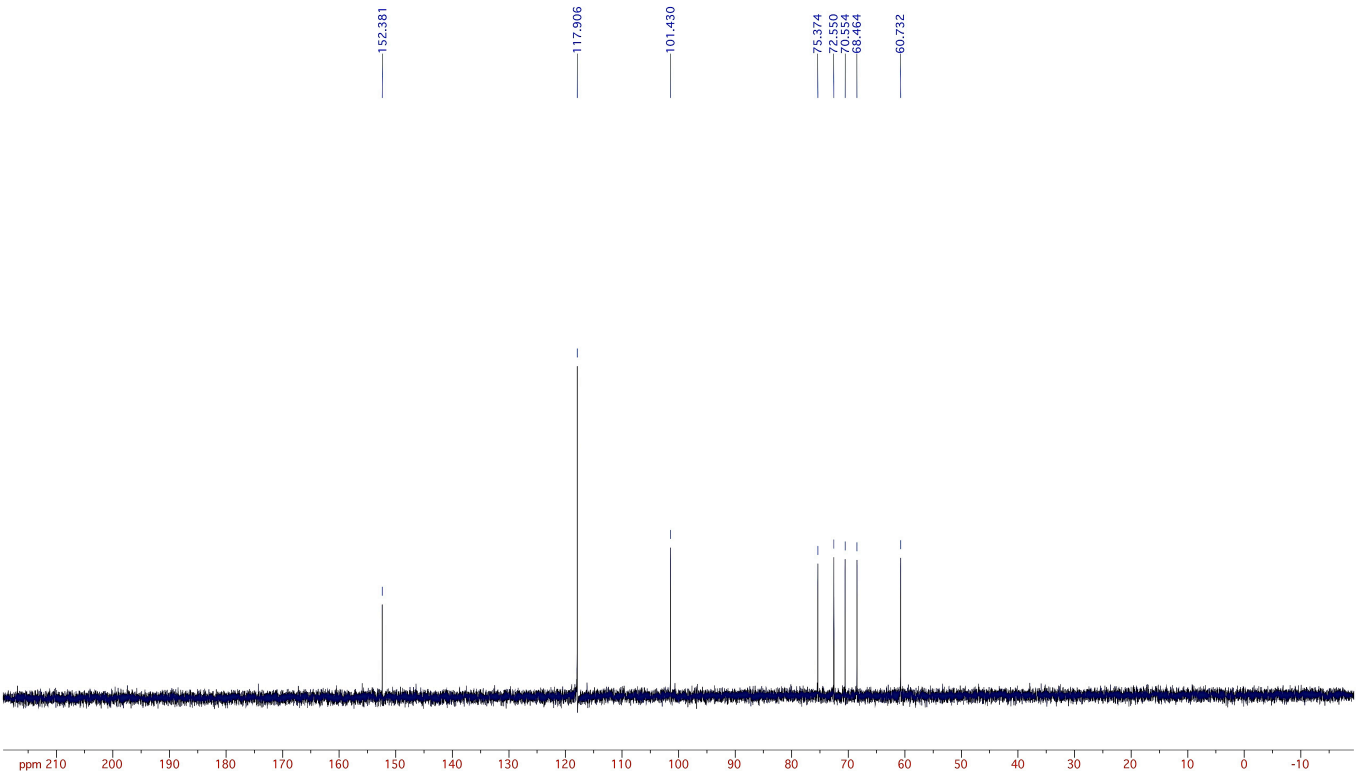
**49**


5.059
5.041
4.997
4.979
3.997
3.996
3.990
3.988
3.941
3.915
3.910
3.904
3.842
3.840
3.827
3.819
3.811
3.791
3.787
3.783
3.775
3.770
3.760
3.756
3.738
3.724
3.621
3.616
3.607
3.597
3.591
3.583
3.576
3.564
3.545
3.541
3.502
3.497
3.485
3.461
1.35
1
4.46
1.04
1.39
5.71
1.42
5.55
ppm 9
8
7
6
5
4
3
2
1


152.490
152.327
152.237
118.006
117.941
101.447
100.871
76.094
75.547
75.394
74.944
72.572
70.573
69.434
68.486
60.754
60.542
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


7.114
4.988
4.971
3.986
3.879
3.849
3.834
3.819
3.809
3.801
3.780
3.776
3.764
3.759
3.748
3.731
3.731
3.723
HO
OH
O
HO
OH
O
HO
OH
OH
O
OH
4.06
2
2.07
10.5
ppm 9
8
7
6
5
4
3
2
1

**50**


152.381
117.906
101.430
75.374
72.550
70.554
68.464
60.732
ppm 210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10