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1. General materials and methods.

- **1.1. General Materials.** Unless otherwise stated, all chemicals and reagents were purchased from Sigma-Aldrich (St. Louis, MO, USA) and utilized as received. Compound **1** was previously synthesized from glucose,^[S1] Compound **22**^[S2], **24**,^[S3] **26**,^[S4] **28**,^[S5] were synthesized following prior published protocols.
- **1.2. General Methods**. High resolution mass spectrometric data were obtained on a Waters (Milford, MA) LCT time-of-flight spectrometer for electrospray ionization (ESI) or AB SCIEX TripleTOF[®] 5600 System. NMR spectra were obtained on either a Varian Unity Inova 400 or 500 MHz instrument (Palo Alto, CA) using 99.8% CDCl₃ with 0.05% v/v TMS or 99.8% CD₃OD from Cambridge isotopes (Cambridge Isotope Laboratories, MA, USA). ¹H and ¹³C chemical shifts were referenced to internal solvent resonances. Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet) and br (broad). Chemical shifts are reported in parts per million (ppm) and coupling constants *J* are given in Hz. Routine ¹³C NMR spectra were fully decoupled by broad-broad WALTZ decoupling. All NMR spectra were recorded at ambient temperature. Normal phase flash chromatography was performed on 40 63 µm, 60 A silica gel (from Silicycle, Quebec, Canada). Analytical TLC was performed on silica gel glass TLC plates (from EMD chemical Inc). TLC visualization was accomplished with UV light (254 nm) followed by staining with diluted sulfuric acid (5% in ethanol) solution and heating.

2. Synthesis of 2-chloro-4-nitrophenyl glycosides (2-20).

- **2.1. General procedure of bromination with TiBr**₄/EtOAc. The per-O-acylated glycoside (1 eq) was dissolved in CH₂Cl₂/EtOAc (100/1) to a final concentration of 200 mM. To this solution was added TiBr₄ (2 eq) and the reaction was stirred under room temperature for 12 h or until TLC indicated completion of the reaction. The reaction was quenched by adding NaOAc (1 eq) and stirred for 15 mins, then filtered through celite and washed with CH₂Cl₂ (50 mL, x3). The brown filtrate was washed with water until the organic layer became colorless. The organic layer was then washed with brine and dried over Na₂SO₄. After the removal of the solvent, the per-O-acetylated-1-bromo-glycosides were purified by normal phase column chromatography (using a gradient from 100:0 to 40:60 hexanes:EtOAc) and subjected to glycosylation reaction immediately upon isolation.
- **2.2. General procedure for Koenigs-Knorr glycosylation reaction.** To the per-O-acylated glycosyl bromide (1.0 eq) in anhydrous 150 mM CH₃CN solution was added 2-chloro-4-nitrophenol (2.0 eq) and 4 Å molecular sieves. The mixture was stirred for 30 min before Ag₂O (1.5 eq) was added to the solution. The reaction was stirred under room temperature for 12 h or until TLC indicated the completion of the reaction. The reaction was quenched by filtering through celite and was subsequently washed with EtOAc to recover all material. After the removal of the solvent under vacuum, the 2-chloro-4-nitrophenyl glycoside was purified by normal phase column chromatography (using a gradient from 100:0 to 40:60 hexanes:EtOAc) to afford the desired per-O-acylated 2-chloro-nitrophenyl glycoside as the pure product.
- **2.3. General procedure for deacetylation.** A solution of per-O-acylated 2-chloro-4-nitrophenyl glycoside (100 mM) and NaOMe (2 eq) in MeOH was stirred at room temperature until the complete consumption of starting material (~ 2 h). The reaction was quenched by adding Amberlite 120 (H⁺) (4 eq) and stirred for 30 min. The reaction mixture was filtered through celite and and was subsequently washed with EtOAc to recover all material. After the removal of solvent under vacuum, the desired 2-chloro-4-nitrophenyl glycoside was purified by normal phase column chromatography (using a gradient from 100:0 to 80:20 CH₂Cl₂:MeOH) to afford the 2-chloro-4-nitrophenyl glycoside as the pure product.

- **2.4. General procedure for azide reduction.** To a 100 mM solution of 2-chloro-4-nitrophenyl azidosugar glycoside (1 eq) in THF was added PPh₃ (1.2 eq) or PMe₃ in THF (1.2 eq) and the reaction was stirred at 50 °C for 1 h. After removal of the solvent under reduced pressure, the residue was purified by normal-phase column chromatography (using a gradient from 100:0 CH₂Cl₂:MeOH to 80:20 CH₂Cl₂:MeOH) to afford the desired 2-chloro-4-nitrophenyl aminosugar glycoside as the pure product.
- **2.5. General procedure for 2-chloro-4-nitrophenyl aminosugar glycoside HCI formation.** The purified 2-chloro-4-nitrophenyl aminosugar glycoside was dissolved into water (4 mM) and acidified to pH 4 using 1 M HCI solution. After the removal of the solvent by reduced pressure, the 2-chloro-4-nitrophenyl aminosugar glycoside hydrochloride salt was obtained and used without further purification.
- **2.6. General procedure azidosugar formation.** Tf₂O (1.5 eq) was slowly added to a 125 mM CH₂Cl₂ solution of suitably-protected glycoside (1.0 eq) and pyridine (1.6 eq) under 0 °C and the reaction was stirred at 0 °C for 30 min. The reaction was diluted with CH₂Cl₂ and washed with water, sat. NaHCO₃, and brine and dried over Na₂SO₄. After filtration, the CH₂Cl₂ solution was concentrated in *vacu*o to less than 4 mL and transferred to 100 mL DMF solution containing NaN₃ (2.0 eq). The reaction mixture was stirred at room temperature for 12 h and filtered through a celite pad. The filtrate was concentrated under reduced pressure and purified by normal-phase column chromatography (using a gradient from 90:10 to 30:70 hexanes:EtOAc).

2.7. Synthesis of (2-chloro-4-nitrophenyl)-6-deoxy-6-amino-β-D-glucopyranoside (2).



(a) (1) PPh₃, CH₃CN/water=10/1, (2) NaOMe, MeOH; (b) (1) NaOMe, MeOH, (2) PMe₃ in toluene, THF; (c) HCl, Water

(2-chloro-4-nitrophenyl)-6-deoxy-6-amino-β-D-glucopyranoside (3). To a 10 mL MeOH solution of **21**^[S1] (58.3 mg, 0.12 mmol) was added 80 μl 1 M NaOMe/MeOH solution and according to general protocol **2.3**, (2-chloro-4-nitrophenyl)-6-deoxy-6-azido-β-D-glucopyranoside **2** ^[S1] (43.0 mg, 0.12 mmol) was obtained. The subsequent **2.4** general protocol for reduction of **2** yielded **3** (33.2 mg, 78% yield after 2 steps) as a white solid. ¹H NMR (CD₃OD, 500 MHz) δ ppm 8.32 (d, J = 2.7 Hz, 1 H), 8.19 (dd, J = 9.2, 2.8 Hz, 1 H), 7.41 (d, J = 9.3 Hz, 1 H), 5.20 (d, J = 7.6 Hz, 1 H), 3.57 (dd, J = 9.5, 7.6 Hz, 1 H), 3.42 - 3.52 (m, 3 H), 3.09 (dd, J = 13.6, 3.1 Hz, 1 H), 2.79 (dd, J = 13.7, 7.6 Hz, 1 H). ¹³C NMR (D₂O, 125 MHz) δ ppm 157.4, 142.7, 126.5, 124.5, 123.6, 115.6, 99.9, 76.1, 75.4, 72.8, 71.1, 41.5. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₁₂H₁₅CIN₂O₇Na, 357.0460; found 357.0457.

(2-chloro-4-nitrophenyl)-6-deoxy-6-amino-β-D-glucopyranoside hydrochloride (3a). According to general protocol **2.5**, **3** (30.0 mg, 0.08 mmol) yielded **3a** (33 mg, quantitative yield as a light yellow solid. ¹H NMR (D₂O, 500 MHz) δ ppm 8.48 (dd, *J* = 2.8, 1.3 Hz, 1 H), 8.27 (dd, *J* = 9.3, 2.9 Hz, 1 H), 7.41 (d, *J* = 9.3 Hz, 1 H), 5.44 (d, *J* = 7.8 Hz, 1 H), 3.8 - 4.0 (m, 1 H), 3.79 (t, *J* = 8.3 Hz, 1 H), 3.70 (t, *J*

= 9.3 Hz, 1 H), 3.5 (m, 2 H), 3.21 (dd, J = 13.7, 8.5 Hz, 1 H). ¹³C NMR (D₂O, 125 MHz) δ 157.3, 142.6, 126.5, 124.5, 123.6, 115.6, 99.9, 75.1, 72.6, 71.1, 62.8, 40.6. HRMS-ESI (m/z): [M]⁺ calcd for C₁₂H₁₆ClN₂O₇, 335.0646; found 335.0647.

 $(2-chloro-4-nitrophenyl)-6-deoxy-6-N-acetylamino-\beta-D-glucopyranoside$ То (19). а 10 mL CH₃CN/H₂O (10/1) solution of (2-chloro-4-nitrophenyl)-2,3,4-triacetyl-6-deoxy-6-azido-glucoside 21 ^[S1] (30 mg, 0.06 mmol) was added PPh₃ (25 mg, 0.09 mmol) and the reaction was stirred under room temperature for 12 h. The solvent was removed in vacuo and the residue was purified by column chromatography (using a gradient from 50:50 to 90:10 EtOAc:MeOH) to give the amine. To a 10 mL MeOH solution of this amine was added 60 µl 1 M NaOMe/MeOH solution and according to 2.3 general protocol for deacetylation reaction 19 (10 mg, 0.03 mmol) was obtained in 43% after two steps. ¹H NMR (CD₃OD 400 MHz) δ ppm 8.31 (d, J = 2.7 Hz, 1 H), 8.18 (dd, J = 9.5, 3.0 Hz, 1 H), 7.38 (d, J =9.4 Hz, 1 H), 5.18 (d, J = 7.6 Hz, 1 H), 3.5 - 3.6 (m, 3 H), 3.4 - 3.5 (m, 2 H), 3.25 (t, J = 9.0 Hz, 1 H), 1.94 (s, 3 H). ¹³C NMR (CD₃OD, 100 MHz) δ 172.5, 157.7, 142.1, 125.3, 123.34, 123.31, 115.2, 100.0, 75.9, 74.8, 73.1, 70.9, 39.9, 20.9. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₁₄H₁₇ClN₂O₈Na, 399.0566; found 399.0566.

2.8. Synthesis of (2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-glucopyranoside (5).



(a) (1) TiBr₄, CH₂Cl₂/EtOAc, (2) 2-chloro-4-nitrophenol, Ag₂O, CH₃CN, M.S., R. T., 12 hours; (b) NaOMe, MeOH; (c) PMe₃ in toluene, THF; (d) HCl, Water

(2-chloro-4-nitrophenyl)-3,4,6-tri-O-acetyl-2-deoxy-2-azido-β-D-glucopyranoside (23). According to general procedure **2.1** and **2.2**, **22** (1.42 g, 3.81 mmol) yielded **23** (0.33g, 18% yield after two steps) as a white solid. ¹H NMR (CDCl₃, 400 MHz) δ 8.35 (d, *J* = 2.7 Hz, 1 H), 8.15 (dd, *J* = 9.2, 2.7 Hz, 1 H), 7.18 (d, *J* = 9.2 Hz, 1 H), 5.1 (m, 2 H), 5.05 (d, *J* = 8.0 Hz, 1 H), 4.30 (dd, *J* = 12.4, 5.6 Hz, 1 H), 4.17 (dd, *J* = 12.4, 2.4 Hz, 1 H), 3.8 (m, 2 H), 2.13 (s, 3 H), 2.09 (s, 3 H), 2.05 - 2.07 (m, 3 H). ¹³C NMR (CDCl₃, 125 MHz) δ ppm 170.5, 170.0, 169.7, 157.0, 143.5, 126.6, 125.0, 123.7, 115.9, 99.9, 72.8, 72.2, 68.2, 64.0, 61.9, 20.9, 20.9, 20.8. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₁₈H₁₉ClN₄O₁₀Na, 509.0682; found 509.0679.

(2-chloro-4-nitrophenyl)-2-deoxy-2-azido-β-D-glucopyranoside (4). According to general procedure
2.3, 23 (0.16 g, 0.33 mmol) yielded 4 (0.13 g, 100% yield) as a light yellow solid. ¹H NMR (CD₃OD, 500 MHz) δ ppm 8.33 (d, J = 2.7 Hz, 1 H), 8.19 (dd, J = 9.0, 2.7 Hz, 1 H), 7.44 (d, J = 9.3 Hz, 1 H), 5.21 (d, J = 7.8 Hz, 1 H), 3.91 (dd, J = 12.2, 2.2 Hz, 1 H), 3.71 (dd, J = 12.2, 5.6 Hz, 1 H), 3.5 (m, 2 H), 3.4 - 3.5 (m, 2 H). ¹³C NMR (CD₃OD, 125 MHz) δ 157.5, 142.7, 125.5, 123.8, 123.4, 115.8, 99.4, 77.4, 75.0, 69.8, 66.9, 61.0. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₁₂H₁₃ClN₄O₇Na, 383.0365; found 383.0385.

- **(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-glucopyranoside (5).** According to general procedure **2.4**, **4** (62.3 mg, 0.17 mmol) yielded **5** (39.8 mg, 67% yield) as a yellow solid. ¹H NMR (CD₃OD, 400 MHz) δ ppm 8.33 (d, J = 2.7 Hz, 1 H), 8.20 (dd, J = 9.2, 2.7 Hz, 1 H), 7.49 (d, J = 9.4 Hz, 1 H), 5.05 (d, J = 8.0 Hz, 1 H), 3.92 (dd, J = 12.1, 2.1 Hz, 1 H), 3.72 (dd, J = 12.2, 5.8 Hz, 1 H), 3.5 (m, 1 H), 3.40 (dd, J = 9.4, 8.2 Hz, 2 H), 2.99 (dd, J = 9.4, 8.0 Hz, 1 H). ¹³C NMR (CD₃OD, 100 MHz) δ 157.9, 142.6, 125.4, 123.8, 123.5, 116.1, 101.9, 77.6, 75.8, 70.0, 61.1, 56.8. HRMS-ESI (m/z): [M+H]⁺ calcd for C₁₂H₁₆CIN₂O₇, 335.0641; found 335.0622.
- **(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-glucopyranoside hydrochloride (5a).** According to general procedure **2.5**, **5** (17 mg, 0.05 mmol) yielded **5a** (18.8 mg, quantitative yield) as a yellow oil. ¹H NMR (D₂O, 500 MHz) δ ppm 8.43 (d, J = 2.9 Hz, 1 H), 8.24 (dd, J = 9.3, 2.7 Hz, 1 H), 7.45 (d, J = 9.3 Hz, 1 H), 5.66 (d, J = 8.5 Hz, 1 H), 3.97 (dd, J = 12.5, 2.2 Hz, 1 H), 3.9 (m, 2 H), 3.77 (d, J = 2.2 Hz, 1 H), 3.65 (t, J = 9.8 Hz, 1 H), 3.57 (dd, J = 10.6, 8.4 Hz, 1 H). ¹³C NMR (D₂O, 125 MHz) δ 156.3, 143.2, 126.5, 124.5, 124.0, 116.6, 96.7, 77.0, 72.1, 69.6, 60.3, 55.5. HRMS-ESI (m/z): [M]⁺ calcd for C₁₂H₁₆CIN₂O₇, 335.0641; found 335.0642.
- **(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-α-D-glucopyranoside (20).** According to general procedure **2.1-2.4**, **22** (1.42 g, 3.81 mmol) yielded **20** (5.7 mg, 1% yield after three steps) as minor product. ¹H NMR (CD₃OD, 500 MHz) δ ppm 8.34 (d, J = 2.7 Hz, 1 H), 8.20 (dd, J = 9.3, 2.7 Hz, 1 H), 7.60 (d, J = 9.3 Hz, 1 H), 5.74 (d, J = 3.4 Hz, 1 H), 3.75 (dd, J = 12.2, 2.4 Hz, 1 H), 3.7 (m, 2 H), 3.57 (ddd, J = 5.2, 2.3,2.0 Hz, 1 H), 3.42 (dd, J = 10.0, 8.8 Hz, 1 H), 2.85 (dd, J = 10.0, 3.4 Hz, 1 H). ¹³C NMR (CD₃OD, 100 MHz) δ 157.1, 142.3, 125.2, 125.1, 123.6, 115.6, 99.3, 74.5, 74.4, 69.8, 60.8, 55.5. HRMS-ESI (m/z): [M+H]⁺ calcd for C₁₂H₁₆CIN₂O₇, 335.0641; found 335.0622.
- 2.9. Synthesis of (2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-glucopyranoside (7).



(a) (1) TiBr₄, CH₂Cl₂/EtOAc; (2) 2-chloro-4-nitrophenol, Ag₂O, CH₃CN, M.S., R. T., 12 hours; (b) NaOMe, MeOH; (c) PMe₃ in toluene, THF; (d) HCl, Water

(2-chloro-4-nitrophenyl)-2,4,6-tri-O-acetyl-3-deoxy-3-azido-β-D-glucopyranoside (25). According to general procedure **2.1** and **2.2**, **24** (0.40 g, 1.07 mmol) yielded **25** (0.19 g, 37% yield for two steps) as a white solid. ¹H NMR (CDCl₃, 400 MHz) δ 8.30 (d, J = 2.5 Hz, 1 H), 8.12 (dd, J = 9.0, 2.7 Hz, 1 H), 7.24 (d, J = 9.0 Hz, 1 H), 5.32 (dd, J = 10.2, 7.9 Hz, 1 H), 5.07 (d, J = 7.8 Hz, 1H), 5.09 (t, J = 9.2 Hz, 1H), , 4.1 - 4.2 (m, 2 H), 3.8 (m, 1 H), 3.77 (t, J = 10.0 Hz, 1 H), 2.17 (s, 3 H), 2.16 (s, 3 H), 2.11 (s, 3 H). ¹³C NMR (CDCl₃, 100 MHz) δ 170.6, 169.3, 168.9, 157.4, 143.5, 126.4, 125.3, 123.7, 116.8, 99.8, 73.6, 70.4, 68.3, 64.0, 61.9, 20.9, 20.82, 20.80. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₁₈H₁₉ClN₄O₁₀Na, 509.0682; found 509.0692.

(2-chloro-4-nitrophenyl)-3-deoxy-3-azido-β-D-glucopyranoside (6). According to general procedure **2.3**, **25** (0.19 g, 0.39 mmol) yielded **6** (0.09 g, 64% yield) as a white solid. ¹H NMR (CD₃OD, 400 MHz) δ ppm 8.30 (d, *J* = 2.7 Hz, 1 H), 8.18 (dd, *J* = 9.2, 2.7 Hz, 1 H), 7.43 (d, *J* = 9.2 Hz, 1 H), 5.24 (d, *J* = 7.6

Hz, 1 H), 3.88 (dd, J = 12.1, 2.1 Hz, 1 H), 3.70 (dd, J = 12.1, 5.5 Hz, 1 H), 3.5 (m, 2 H), 3.4 - 3.5 (m, 2 H). ¹³C NMR (CD₃OD, 100 MHz) δ 157.9, 142.4, 125.5, 123.7 (2 carbons), 115.6, 100.5, 77.8, 72.1, 69.9, 68.4, 60.8. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₁₂H₁₃CIN₄O₇Na, 383.0365; found 383.0348.

(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-glucopyranoside (7). According to general protocol **2.4**, **6** (35.7 mg, 0.096 mmol) yielded **7** (25.6 mg, 77% yield) as a yellow solid. ¹H NMR (CD₃OD, 400 MHz) δ ppm 8.28 (d, J = 2.7 Hz, 1 H), 8.14 (dd, J = 9.2, 2.7 Hz, 1 H), 7.42 (d, J = 9.4 Hz, 1 H), 5.18 (d, J = 7.8 Hz, 1 H), 4.66 (br. s., 1 H), 3.44 (t, J = 6.8 Hz, 3 H), 3.24 (t, J = 8.6 Hz, 1 H), 3.09 (t, J = 9.2 Hz, 1 H), 2.64 (t, J = 9.5 Hz, 1 H). ¹³C NMR (DMSO-d₆, 100 MHz) δ 158.3, 142.1, 126.1, 124.8, 122.9, 116.3, 100.7, 78.8, 73.3, 69.9, 61.0, 59.8. HRMS-ESI (m/z): [M+H]⁺ calcd for C₁₂H₁₆ClN₂O₇, 335.0641; found 335.0626.

(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-glucopyranoside hydrochloride (7a). According to general procedure **2.5**, **7** (8.9 mg, 0.03 mmol) yielded **7a** (12.0 mg, quantitative yield) as a white solid. ¹H NMR (D₂O, 500 MHz) δ ppm 8.43 (d, J = 2.7 Hz, 1 H), 8.24 (dd, J = 9.2, 2.8 Hz, 1 H), 7.43 (d, J = 9.3 Hz, 1 H), 5.44 (d, J = 7.6 Hz, 1 H), 3.9 (m, J = 10.5 Hz, 2 H), 3.8 - 3.9 (m, 3 H), 3.42 - 3.49 (m, 1 H). ¹³C NMR (D₂O, 100 MHz) δ 157.2, 142.8, 126.4, 124.5, 123.6, 115.9, 100.2, 77.4, 69.2, 65.7, 60.0, 57.7. HRMS-ESI (m/z): [M]⁺ calcd for C₁₂H₁₆CIN₂O₇, 335.0646; found 335.0628.





(a) (1) TiBr₄, CH₂Cl₂/EtOAc, (2) 2-chloro-4-nitrophenol, Ag₂O, CH₃CN, M.S., R. T., 12 hours; (b) NaOMe, MeOH; (c) PPh₃, THF; (d) HCl, Water

(2-chloro-4-nitrophenyl)-2,3,6-tri-O-acetyl-4-deoxy-4-azido-β-D-glucopyranoside (27). According to general procedure **2.1** and **2.2**, **26** (1.38 g, 3.7 mmol) yielded **27** (1.26 g, 70% yield for two steps) as a white solid. ¹H NMR (CDCl₃, 500 MHz) δ ppm 8.29 (d, J = 2.7 Hz, 1 H), 8.13 (dd, J = 9.2, 2.8 Hz, 1 H), 7.23 (d, J = 9.0 Hz, 1 H), 5.2 - 5.3 (m, 2 H), 5.13 (d, J = 7.6 Hz, 1 H), 4.50 (dd, J = 12.2, 2.2 Hz, 1 H), 4.31 (dd, J = 12.3, 5.0 Hz, 1 H), 3.81 (t, J = 10.0 Hz, 1 H), 3.70 (ddd, J = 5.1, 2.6, 1.8 Hz, 1 H), 2.15 (s, 3 H), 2.12 (s, 3 H), 2.09 (s, 3 H). ¹³C NMR (CDCl₃, 125 MHz) δ 170.5, 170.0, 169.5, 157.4, 143.5, 126.4, 125.2, 123.8, 116.7, 99.5, 73.3, 73.1, 71.0, 62.6, 59.8, 20.9, 20.83, 20.81. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₁₈H₁₉ClN₄O₁₀Na, 509.0682; found m/z 509.0699.

(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-β-D-glucopyranoside (8). According to general procedure **2.3**, **27** (1.26 g, 2.59 mmol) yielded **8** (0.80 g, 86% yield) as a white solid. ¹H NMR (CD₃OD, 400 MHz) δ ppm 8.33 (d, J = 2.7 Hz, 1 H), 8.17 (dd, J = 9.2, 3.7 Hz, 1 H), 7.40 (d, J = 8.8 Hz, 1 H), 5.18 (d, J = 7.0 Hz, 1 H), 3.8 (m, 1 H), 3.73 (dd, J = 12.1, 4.1 Hz, 1 H), 3.65 (t, J = 8.8 Hz, 1H), 3.61 (t, J = 9.2 Hz, 1 H), 3.4 - 3.5 (m, 2 H). ¹³C NMR (CD₃OD, 100 MHz) δ 157.9, 142.4, 125.5, 123.6 (2 carbons), 115.5, 100.3, 76.0, 75.4, 73.4, 61.5, 60.8. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₁₂H₁₃CIN₄O₆Na, 383.0365; found 383.0344.

(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-D-glucopyranoside (9). According to general procedure **2.4**, **8** (130 mg, 0.36 mmol) yielded **9** (62.1 mg, 52% yield) as a white solid. ¹H NMR (CD₃OD, 400 MHz) δ 8.30 (d, J = 2.7 Hz, 1 H), 8.18 (dd, J = 9.3, 2.8 Hz, 1 H), 7.42 (d, J = 9.2 Hz, 1 H), 5.17 (d, J = 7.8 Hz, 1 H), 3.85 (dd, J = 12.2, 2.8 Hz, 1 H), 3.71 (dd, J = 12.3, 5.3 Hz, 1 H), 3.57 (dd, J = 9.1, 7.7 Hz, 1 H), 3.48 (ddd, J = 8.0, 5.3, 2.7 Hz, 1 H), 3.38 (d, J = 9.7 Hz, 1 H), 2.79 (t, J = 9.8 Hz, 1 H). ¹³C NMR (CD₃OD, 100 MHz) δ 158.1, 142.3, 125.4, 123.6 (2 carbons), 115.5, 100.7, 77.6, 76.5, 73.6, 61.5, 53.0. HRMS-ESI (m/z): [M+H]⁺ calcd for C₁₂H₁₆CIN₂O₇, 335.0641; found 335.0626.

(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-D-glucopyranoside hydrochloride (9a). According to general procedure **2.5**, **9** (36.0 mg, 0.11 mmol) yielded **9a** (36.0 mg, 90% yield) as a yellow solid. ¹H NMR (D₂O, 500 MHz) δ ppm 8.32 (d, J = 2.7 Hz, 1 H), 8.15 (dd, J = 9.3, 2.7 Hz, 1 H), 7.35 (d, J = 9.3 Hz, 1 H), 5.36 (d, J = 7.6 Hz, 1 H), 4.07 (ddd, J = 10.3, 9.3, 4.9 Hz, 1 H), 3.97 (dd, J = 12.7, 3.9 Hz, 1 H), 3.8 - 3.9 (m, 2 H), 3.81 (t, J = 8.1 Hz, 1 H), 3.43 (t, J = 10.3 Hz, 1 H). ¹³C NMR (D₂O, 125 MHz) δ 157.3, 142.6, 126.4, 124.5, 123.6, 115.8, 100.0, 73.0, 72.7, 71.9, 60.7, 52.6. HRMS-ESI (m/z): [M]⁺) calcd for C₁₂H₁₆CIN₂O₇Na, 335.0646; found 335.0628.

2.11. Synthesis of (2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-xylopyranoside (11).



(a) TiBr₄, CH₂Cl₂/EtOAc; (b) 2-chloro-4-nitrophenol, Ag₂O, CH₃CN, M.S., R. T., 12 hours; (c) NaOMe, MeOH; (d) PMe₃ in toluene, THF; (e) HCl, Water

- **1-bromo-3,4-di-O-acetyl-2-deoxy-2-azido-α-D-xylopyranoside (29).** According to general procedure **2.1**, **28** (0.20 g, 0.66 mmol) yielded **29** (0.08 g, 38% yield) as a white solid. ¹H NMR (CDCl₃, 400 MHz) δ ppm 6.39 (d, *J* = 3.7 Hz, 1 H), 5.51 (t, *J* = 9.8 Hz, 1 H), 5.04 (ddd, *J* = 10.9, 9.4, 6.0 Hz, 1 H), 4.04 (dd, *J* = 11.5, 6.0 Hz, 1 H), 3.91 (t, *J* = 11.3 Hz, 1 H), 3.71 (dd, *J* = 10.1, 3.9 Hz, 1 H), 2.13 (s, 3 H), 2.06 (s, 3 H). ¹³C NMR (CDCl₃, 100 MHz) δ ppm 170.1, 169.7, 88.6, 71.1, 68.4, 63.0, 62.7, 20.8, 20.8. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₉H₁₂CIN₃O₅Na, 343.9853; found 343.9865.
- **(2-chloro-4-nitrophenyl)-3,4-di-***O***-acetyl-2-deoxy-2-azido-β-D-xylopyranoside (30).** According to general procedure **2.2**, **29** (80 mg, 0.25 mmol) yielded **30** (64.9 mg, 63% yield) as a white solid. ¹H NMR (CDCl₃, 400 MHz) δ ppm 8.34 (d, J = 2.7 Hz, 1 H), 8.15 (dd, J = 9.2, 2.7 Hz, 1 H), 7.21 (d, J = 9.2 Hz, 1 H), 5.15 (t, J = 6.44 Hz, 1H), 5.12 (d, J = 8.0 Hz, 1H), 5.03 (td, J = 7.8, 4.8 Hz, 1 H), 4.23 (dd, J = 12.2, 4.8 Hz, 1 H), 3.90 (dd, J = 9.0, 6.6 Hz, 1 H), 3.57 (dd, J = 12.1, 7.8 Hz, 1 H), 2.17 (s, 3 H), 2.09 (s, 3 H). ¹³C NMR (CDCl₃, 100 MHz) δ ppm 170.0, 169.8, 156.9, 143.2, 126.5, 124.7, 123.8, 115.9, 99.8, 70.7, 68.5, 62.8, 62.3, 20.92, 20.91. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₁₅H₁₅ClN₄O₈Na, 437.0471; found 437.0459.
- (2-chloro-4-nitrophenyl)-2-deoxy-2-azido-β-D-xylopyranoside (10). According to general procedure 2.3, 30 (65 mg, 0.16 mmol) yielded 10 (41.4 mg, 80% yield) as a light yellow solid. ¹H NMR (CD₃OD, 500 MHz) δ ppm 8.32 (d, J = 2.7 Hz, 1 H), 8.17 (dd, J = 9.2, 2.8 Hz, 1 H), 7.36 (d, J = 9.3 Hz, 1 H),

5.13 (d, J = 7.8 Hz, 1 H), 3.98 (dd, J = 11.5, 5.4 Hz, 1 H), 3.64 (ddd, J = 10.4, 8.9, 5.4 Hz, 1 H), 3.53 (dd, J = 9.8, 7.8 Hz, 1 H), 3.3 (m, 2 H). ¹³C NMR (CD₃OD, 125 MHz) δ ppm 157.4, 142.8, 125.6, 123.7 (2 carbons), 115.6, 100.0, 75.0, 69.5, 66.8, 66.1. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₁₁H₁₁ClN₄O₆Na, 353.0259; found 353.0276.

(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-xylopyranoside (11). According to general procedure **2.4**, **10** (26.5 mg, 0.08 mmol) yielded **11** (20.0 mg, 82% yield) as a white solid. ¹H NMR (CD₃OD, 400 MHz) δ ppm 8.32 (d, J = 2.7 Hz, 1 H), 8.19 (dd, J = 9.2, 2.9 Hz, 1 H), 7.41 (d, J = 9.2 Hz, 1 H), 5.04 (d, J = 7.8 Hz, 1 H), 4.00 (dd, J = 11.4, 5.2 Hz, 1 H), 3.6 (m, 1 H), 3.45 (dd, J = 11.4, 10.0 Hz, 1 H), 3.3 (m, 1 H), 2.98 (dd, J = 9.6, 7.7 Hz, 1 H). ¹³C NMR (CD₃OD, 100 MHz) δ ppm 157.7, 142.6, 125.5, 123.7 (2 carbons), 115.9, 102.3, 75.4, 69.6, 66.1, 56.5. HRMS-ESI (m/z): [M+H]⁺ calcd for C₁₁H₁₄CIN₂O₆, 305.0535; found 305.0543.

(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-xylopyranoside hydrochloride (11a). According to general procedure **2.5**, **11** (13.3 mg, 0.08 mmol) yielded **11a** (13.0 mg, 87% yield) as a white solid. ¹H NMR (D₂O, 400 MHz) δ ppm 8.36 (d, J = 2.7 Hz, 1 H), 8.16 (dd, J = 9.2, 2.7 Hz, 1 H), 7.37 (d, J = 9.2 Hz, 1 H), 5.56 (d, J = 7.8 Hz, 1 H), 4.11 (dd, J = 12.0, 4.2 Hz, 1 H), 3.7 (m, 2 H), 3.5 (m, 2 H). ¹³C NMR (D₂O, 100 MHz) δ ppm 156.1, 143.2, 126.5, 124.4, 124.0, 116.6, 97.1, 71.6, 69.1, 65.7, 55.0. HRMS-ESI (m/z): [M]⁺ calcd for C₁₁H₁₄ClN₂O₆Na, 305.0535; found 305.0544.

2.12. Synthesis of (2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-L-xylopyranoside (15).



(a) BzCl, Pyridine, -78°C-RT; (b) (1) Tf₂O, pyridine, CH₂Cl₂, (2) NaN₃, DMF; (c) NaOMe, MeOH; (d) Ac₂O, Et₃N, DMAP, CH₂Cl₂; (e) TiBr₄, CH₂Cl₂/EtOAc (f) 2-chloro-4-nitrophenol, Ag₂O, CH₃CN, M.S., R. T., 12 hours; (g) PPh₃, THF; (h) HCl, Water

1,2,3-tri-O-benzoyl-α-D-arabinopyranoside (32). To a solution of D-arabinose (1.0 g, 6.7 mmol) in anhydrous pyridine (20 mL) at -50 °C with stirring was added benzoyl chloride (2.48 mL, 21.3 mmol) in a dropwise fashion. The reaction was held below -20 °C for 2 h and then allowed to slowly warm to

room temperature. The reacion was quenched by removing pyridine in *vacuo* and the residue was diluted with EtOAc and washed with 1N HCl, NaHCO₃ (sat), water, and brine. The organic phase was dried over Na₂SO₄ and purified by normal-phase column chrotomagraphy (using a gradient from 100:0 Hexanes:EtOAc to 70:30 Hexanes:EtOAc). Compound **32** (0.76 g, 1.64 mmol) was obtained in 25% as a white solid along with **34** (1.62 g, 2.86 mmol, 43% yield). **32:** ¹H NMR (CDCl₃, 500 MHz) δ ppm 8.1 (m, 2 H), 8.0 (m, 2 H), 7.9 (m, 2 H), 7.6 (m, 2 H), 7.4 - 7.5 (m, 5 H), 7.3 (m, 2 H), 6.76 (d, *J* = 3.7 Hz, 1 H), 6.03 (dd, *J* = 10.5, 3.7 Hz, 1 H), 5.85 (dd, *J* = 10.5, 3.2 Hz, 1 H), 4.49 (br. s., 1 H), 4.26 (dd, *J* = 12.9, 1.2 Hz, 1 H), 4.04 (dd, *J* = 12.8, 2.1 Hz, 2 H). ¹³C NMR (CDCl₃, 100 MHz) δ ppm 166.14, 165.79, 164.96, 133.94, 133.84, 133.55, 130.09 (3 carbons), 130.05 (3 carbons), 129.95 (3 carbons), 128.91, 128.78 (2 carbons), 128.59 (3 carbons), 91.56, 71.08, 68.00, 67.58, 64.99. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₂₆H₂₂O₈Na, 485.1207; found 485.1232.

- **1,2,3,4-tetra-***O***-benzoyl-α-D-arabinopyranoside (34).** ¹H NMR (CDCl₃, 400 MHz) δ ppm 8.15 (ddd, J = 8.1, 4.0, 1.1 Hz, 3 H), 7.8 (m, 3 H), 7.5 7.6 (m, 2 H), 7.3 7.5 (m, 10 H), 7.26 (t, J = 7.6 Hz, 2 H), 6.95 (d, J = 2.3 Hz, 1 H), 6.3 (m, 2 H), 5.97 (s, 1 H), 4.46 (d, J = 12.5 Hz, 1 H), 4.21 (dd, J = 13.5, 1.9 Hz, 1 H). ¹³C NMR (CDCl₃, 100 MHz) δ ppm 165.97, 165.94, 165.83, 164.93, 134.08, 133.80, 133.70 (2 carbons), 133.65 (3 carbons), 130.15 (3 carbons), 129.98 (3 carbons), 129.41, 129.23, 129.07, 129.00 (2 carbons), 128.88 (2 carbons), 128.67 (2 carbons), 128.64 (2carbons), 91.41, 69.81, 68.53, 68.15, 63.34. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₃₃H₂₆O₉Na, 589.1469; found 589.1491.
- **1,2,3-tri-***O***-benzoyl-4-deoxy-4-azido-α-L-xylopyranoside (36).** According to general procedure **2.6**, **32** (0.76 g,1.64 mmol) yielded **36** (0.61 g, 76% yield) as a white oil. ¹H NMR (CDCl₃, 500 MHz) δ ppm 8.1 (m, 2 H), 8.0 (m, 2 H), 7.9 (m, 2 H), 7.63 (tt, J = 7.5, 1.3 Hz, 2 H), 7.4 7.6 (m, 5 H), 7.2 7.3 (m, 2 H), 6.70 (d, J = 3.7 Hz, 1 H), 6.01 (t, J = 9.6 Hz, 1 H), 5.50 (dd, J = 10.0, 3.7 Hz, 1 H), 4.0 (m, 2 H), 3.90 (d, J = 12.9 Hz, 1 H). ¹³C NMR (CDCl₃, 100 MHz) δ ppm 165.97, 165.70, 164.78, 134.18(3 carbons), 133.88 (3 carbons), 133.79, 130.23, 130.10, 129.17, 129.12, 129.04, 128.82 (2 carbons), 128.77 (2 carbons), 128.70 (2 carbons), 90.50, 71.33, 70.69, 62.26, 59.76. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₂₆H₂₁N₃O₇Na, 510.1272; found 510.1279.
- **1-bromo-2,3-di-***O*-**benzoyl-4-deoxy-4-azido**-α-**L-xylopyranoside (38).** According to general procedure **2.1**, **36** (27 mg, 0.054 mmol) yielded **38** (11 mg, 45 % yield) as a white oil. ¹H NMR (CDCl₃, 400 MHz) δ ppm 8.0 (m, 3 H), 7.6 (m, 3 H), 7.4 (m, 4 H), 6.74 (d, J = 3.9 Hz, 1 H), 5.96 (t, J = 9.6 Hz, 1 H), 5.15 (dd, J = 9.9, 3.9 Hz, 1 H), 4.0 (m, 1 H), 3.9 4.0 (m, 2 H). ¹³C NMR (CDCl₃, 100 MHz) δ ppm 165.56 (2 carbons), 134.02, 133.80, 130.27 (2 carbons), 130.03 (2 carbons), 129.02, 128.77 (2 carbons), 128.73 (2 carbons), 128.53, 87.83, 71.58, 71.36, 63.98, 59.07. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₁₉H₁₆BrN₃O₅Na, 468.0166; found 408.0176.
- **(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-2,3-di-***O***-benzoyl-β-L-xylopyranoside (40). According to general procedure 2.2**, **38** (11 mg, 0.025 mmol) yielded **40** (10.0 mg, 75% yield) as a white solid. ¹H NMR (CDCl₃ 500 MHz) δ ppm 8.26 (d, J = 2.7 Hz, 1 H), 8.0 8.1 (m, 5 H), 7.6 (m, 3 H), 7.4 (m, 3 H), 7.34 (d, J = 9.0 Hz, 1 H), 5.63 (dd, J = 5.9, 4.4 Hz, 1 H), 5.58 (t, J = 6.2 Hz, 1 H), 5.54 (d, J = 4.4 Hz, 1 H), 4.41 (dd, J = 12.5, 3.9 Hz, 1 H), 3.97 (td, J = 6.3, 3.9 Hz, 1 H), 3.80 (dd, J = 12.3, 6.2 Hz, 1 H). ¹³C NMR (CDCl₃, 125 MHz) δ ppm 167.32, 167.15, 159.23, 145.04, 135.91, 135.80, 132.18 (2 carbons), 132.15 (2 carbons), 132.03, 132.00, 130.83, 130.68, 130.65, 130.61, 128.28, 126.84, 125.79, 118.19, 100.54, 72.12, 71.12, 63.71, 59.00. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₂₅H₁₉ClN₄O₈Na, 561.0784; found 561.0802.
- **1,2,3-tri-O-acetyl-4-deoxy-4-azido-L-xylopyranoside (41).** To a solution of **36** (0.55g, 1.13 mmol) in 20 mL was added MeOH 1 M NaOMe in MeOH (2 mL, 2 mmol) and the reaction was stirred at room temperature for 2 h. The reaction was quenched by adding Amberlite 120 (H⁺) (0.1 g) and stirred for 30 min. The reaction mixture was filtered through celite and the celite subsequently washed with MeOH (5 mL, x3). After removal of solvent from collected organics, the residue was dried under vacuum. The

dried residue was dissolved into 40 mL CH₂Cl₂ solution and to this Et₃N (1.27 mL, 9.04 mmol), DMAP (34 mg, 0.28 mmol), Ac₂O (0.53 mL, 5.64 mmol) were added and the reaction was stirred at room temperature for 6 h. To the reaction was added 50 mL ethyl acetate and 50 mL NaHCO₃ (sat) solution and it was stirred vigorously until the evolution of gas halted. The organic layer was washed with water, brine and dried over Na₂SO₄. After the removal of the solvent under vacuum the recovered material was purified by normal phase column chromatography (using a gradient from 100:0 Hexanes:EtOAc to 70:30 Hexanes:EtOAc) to give **41** (0.30 g, 1.1 mmol, 97%) as a white powder. ¹H NMR (CDCl₃, 500 MHz) δ ppm 6.24 (d, *J* = 3.7 Hz, 1 H), 5.64 (d, *J* = 7.6 Hz, 1 H), 5.39 (t, *J* = 9.8 Hz, 1 H), 5.14 (t, *J* = 9.0 Hz, 1 H), 4.9 (m, 2 H), 4.09 (dd, *J* = 12.1, 5.2 Hz, 1 H), 3.88 (dd, *J* = 11.2, 5.4 Hz, 1 H), 3.7 (m, 2 H), 3.65 (t, *J* = 11.5 Hz, 1 H), 3.43 (dd, *J* = 12.0, 10.3 Hz, 1 H), 2.17 (s, 3 H), 2.12 (s, 3 H), 2.11 (s, 3 H), 2.10 (s, 3H), 2.05 (s, 3 H), 2.02 (s, 3 H). ¹³C NMR (CDCl₃, 125 MHz) δ ppm 170.11, 170.09, 170.01, 169.76, 169.26, 169.16, 92.45, 89.64, 73.29, 70.70, 70.33, 69.71, 64.29, 61.86, 59.36, 58.76, 21.13, 21.02, 20.98, 20.91, 20.83, 20.74. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₁₁H₁₅N₃O₇Na, 324.0802; found 324.0809.

- **1-bromo-2,3-di-O-acetyl-4-deoxy-4-azido-α-L-xylopyranoside (42).** According to general procedure **2.1**, **41** (0.30 g, 1.1 mmol) yielded **42** (80 mg, 23 % yield) as a white oil. ¹H NMR (CDCl₃, 400 MHz) δ ppm 6.55 (d, *J* = 3.9 Hz, 1 H), 5.50 (t, *J* = 9.7 Hz, 1 H), 4.75 (dd, *J* = 9.9, 3.9 Hz, 1 H), 4.00 (dd, *J* = 10.9, 5.5 Hz, 1 H), 3.84 (t, *J* = 11.5 Hz, 1 H), 37 (m, 1 H), 2.13 (s, 3 H), 2.10 (s, 3 H). ¹³C NMR (CDCl₃, 100 MHz) δ ppm 170.1, 169.6, 87.6, 71.0, 70.7, 63.7, 58.7, 20.8 (2 carbons). HRMS-ESI (m/z): [M+Na]⁺ calcd for C₉H₁₂BrN₃O₅Na, 343.9853; found 343.9863.
- **(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-2,3-di-***O*-acetyl-β-L-xylopyranoside **(43).** According to general procedure **2.2**, **42** (80 mg, 0.25 mmol) yielded **43** (100 mg, 97% yield) as a yellow solid. ¹H NMR (CDCl₃, 500 MHz) δ ppm 8.30 (d, J = 2.7 Hz, 1 H), 8.14 (dd, J = 9.0, 2.7 Hz, 2 H), 7.25 (d, J = 9.0 Hz, 1 H), 5.27 (d, J = 5.6 Hz, 1 H), 5.23 (dd, J = 7.3, 5.6 Hz, 1 H), 5.19 (d, J = 7.3 Hz, 1 H), 4.22 (dd, J = 12.2, 4.4 Hz, 1 H), 3.76 (td, J = 7.6, 4.6 Hz, 1 H), 3.57 (dd, J = 12.2, 8.1 Hz, 1 H), 2.16 (s, 3 H), 2.13 (s, 3 H). ¹³C NMR (CDCl₃, 125 MHz) δ ppm 169.95, 169.62, 157.23, 143.26, 126.48, 124.88, 123.99, 116.20, 98.78, 71.06, 69.45, 62.70, 57.46, 20.99, 20.91. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₁₅H₁₅CIN₄O₈Na, 437.0471; found 437.0485.
- **1-bromo-2,3,4-tri-***O***-benzoyl**-α**-D-arabinopyranoside (49).** According to general procedure **2.1**, **34** (0.40 g, 0.71 mmol) yielded **49** (0.47 g, quantitative yield) as a white solid. ¹H NMR (CDCl₃, 400 MHz) δ ppm 8.1 (m, 3 H), 8.0 (m, 2 H), 7.8 (m, 2 H), 7.4 7.6 (m, 6 H), 7.2 (m, 2 H), 6.96 (d, J = 3.9 Hz, 1 H), 6.04 (dd, J = 10.4, 3.4 Hz, 1 H), 5.9 (m, 1 H), 5.75 (dd, J = 10.5, 3.9 Hz, 1 H), 4.47 (d, J = 12.9 Hz, 1 H), 4.24 (dd, J = 13.5, 1.9 Hz, 1 H). ¹³C NMR (CDCl₃, 100 MHz) δ ppm 165.82, 165.78, 165.67, 133.99, 133.97, 133.87, 133.63, 130.44, 130.25 (2 carbons), 130.13 (2 carbons), 129.99 (2 carbons), 129.63, 129.49, 129.17, 128.89, 128.80, 128.71, 128.62, 90.14, 69.18, 68.98, 68.86, 65.29. HRMS-ESI (m/z): ([M+Na]⁺ calcd for C₂₆H₂₁ClO₇Na, 547.0363; compound decomposed during MS analysis.
- **(2-chloro-4-nitrophenyl)-2,3,4-tri-O-benzoyl-β-D-arabinopyranoside (51).** According to general procedure **2.2**, **49** (0.47 g, 0.90 mmol) yielded **51** (0.29 g, 57% yield) and **53** (0.12 g, 26%) both as white crystals. ¹H NMR (CDCl₃, 500 MHz) δ ppm 8.23 (d, J = 2.7 Hz, 1 H), 8.12 (dd, J = 9.3, 2.7 Hz, 1 H), 8.0 (m, 3 H), 7.5 7.6 (m, 4 H), 7.4 7.5 (m, 9 H), 5.98 (dd, J = 6.1, 4.2 Hz, 1 H), 5.8 (m, 2 H), 5.61 (d, J = 4.2 Hz, 1 H), 4.47 (dd, J = 12.2, 6.3 Hz, 1 H), 4.1 (m, 1 H). ¹³C NMR (CDCl₃, 125 MHz) δ ppm 165.84, 165.81, 165.34, 157.70, 143.12, 134.07, 133.90, 130.32 (2 carbons), 130.21 (2 carbons), 130.13 (2 carbons), 129.36, 129.25, 129.06, 128.89, 128.85 (2 carbons), 128.75 (2 carbons), 126.41, 124.99, 124.71, 124.01, 116.54, 116.45, 98.70, 69.56, 69.29, 67.09, 61.38. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₃₂H₂₄CINO₁₀Na, 640.0981; found 640.0989.
- **1,2,3,4-tetra-O-benzoyl-β-D-arabinopyranoside (53).** According to general procedure **2.2**, **49** (0.47 g, 0.90 mmol) yielded **51** (0.29 g, 57% yield) and **53** (0.12 g, 26%) both as white crystals. ¹H NMR (CDCl₃,

500 MHz) δ ppm 8.0 (m, 7 H), 7.5 - 7.6 (m, 4 H), 7.3 - 7.5 (m, 9 H), 6.27 (d, J = 5.4 Hz, 1 H), 5.95 (dd, J = 7.2, 5.5 Hz, 1 H), 5.8 (m, 2 H), 4.43 (dd, J = 12.5, 5.1 Hz, 1 H), 4.14 (dd, J = 12.6, 2.8 Hz, 1 H). ¹³C NMR (CDCl₃, 125 MHz) δ ppm 165.82, 165.73, 165.38, 165.00, 133.98, 133.87, 133.78, 133.76, 130.41, 130.17, 129.54, 129.35, 129.11, 129.05, 128.82 (2 carbons), 128.79 (2 carbons), 128.76 (2 carbons), 128.74, 92.68, 70.18, 69.17, 67.83, 63.01. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₃₃H₂₆O₉Na, 589.1469; found 589.1477.

- **(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-β-L-xylopyranoside (14).** According to general procedure **2.3**, **43** (100 mg, 0.24 mmol) yielded **14** (67 mg, 85% yield) or with **40** (10 mg,0.018 mmol) yielded **14** (5.8 mg, 95% yield) as a light yellow solid. ¹H NMR (CD₃OD, 400 MHz) δ ppm 8.29 (d, J = 2.7 Hz, 1 H), 8.16 (dd, J = 9.2, 2.7 Hz, 1 H), 7.35 (d, J = 9.4 Hz, 1 H), 5.12 (d, J = 7.0 Hz, 1 H), 4.00 (dd, J = 11.1, 4.9 Hz, 1 H), 3.5 3.6 (m, 3 H), 3.4 (m, 1 H). ¹³C NMR (CD₃OD, 100 MHz) δ ppm 157.8, 142.4, 125.5, 123.6 (2 carbons), 115.5, 101.0, 75.7, 73.3, 63.9, 61.3. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₁₁H₁₁CIN₄O₆Na, 353.0259; found 353.0270.
- **(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-L-xylopyranoside (15).** According to general procedure **2.4**, **14** (49.2 mg, 0.15 mmol) yielded **15** (25.6 mg, 57% yield) as a yellow solid. ¹H NMR (CD₃OD, 500 MHz) δ ppm 8.31 (d, J = 2.7 Hz, 1 H), 8.18 (dd, J = 9.2, 2.8 Hz, 1 H), 7.38 (d, J = 9.3 Hz, 1 H), 5.15 (d, J = 7.3 Hz, 1 H), 3.98 (dd, J = 11.5, 4.9 Hz, 1 H), 3.57 (dd, J = 8.7, 7.2 Hz, 1 H), 3.43 (dd, J = 11.6, 10.1 Hz, 1 H), 3.37 (t, J = 8.9 Hz, 1 H), 2.89 (ddd, J=10.0, 9.0, 5.1 Hz, 1 H). ¹³C NMR (CD₃OD, 100 MHz) δ ppm 157.9, 142.4, 125.5, 123.7, 123.6, 115.5, 101.3, 76.0, 73.3, 65.8, 52.1. HRMS-ESI (m/z): [M+H]⁺ calcd for C₁₁H₁₄CIN₂O₆, 305.0535; found m/z 305.0548.
- **(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-L-xylopyranoside hydrochloride (15a).** According to general procedure **2.5**, **15** (8.6 mg, 0.02 mmol) yielded **15a** (9.0 mg, 98% yield) as a yellow solid. ¹H NMR (D₂O, 400 MHz) δ ppm 8.3 (m, 1 H), 8.1 (m, 1 H), 7.34 (d, J = 9.4 Hz, 1 H), 5.33 (d, J = 5.5 Hz, 1 H), 4.26 (dd, J = 12.0, 4.8 Hz, 1 H), 3.7 3.8 (m, 3 H), 3.4 (m, 1 H). ¹³C NMR (DMSO-d₆, 100 MHz) δ ppm 157.9, 142.5, 126.3, 124.9, 123.2, 116.6, 100.9, 73.3, 72.3, 62.3, 51.2. HRMS-ESI (m/z): [M]⁺ calcd for C₁₁H₁₄CIN₂O₆Na, 305.0535; found 305.0550.
- **(2-chloro-4-nitrophenyl)-β-D-arabinopyranoside (18d).** According to general procedure **2.2**, **51** (140 mg, 0.25 mmol) yielded **18d** (30 mg, 40% yield) as a yellow solid. ¹H NMR (CD₃OD, 500 MHz) δ ppm 8.31 (d, J = 2.7 Hz, 1 H), 8.18 (dd, J = 9.2, 2.8 Hz, 1 H), 7.40 (d, J = 9.3 Hz, 1 H), 5.14 (d, J = 6.8 Hz, 1 H), 3.9 (m, 1 H), 3.9 (m, 2 H), 3.77 (dd, J = 12.0, 1.5 Hz, 1 H), 3.67 (m, J = 3.4 Hz, 1 H). ¹H NMR (500 MHz, DMSO- d_6) δ ppm 8.35 (d, J = 2.7 Hz, 1 H), 8.23 (dd, J = 9.3, 2.9 Hz, 1 H), 7.5 (m, 1 H), 5.37 (br. s., 1 H), 5.22 (d, J = 6.6 Hz, 1 H), 4.93 (br. s., 1 H), 4.77 (br. s., 1 H), 3.6 3.8 (m, 4 H), 3.53 (d, J = 8.1 Hz, 1 H). ¹³C NMR (DMSO- d_6 , 125 MHz) δ ppm 158.4, 142.1, 126.2, 124.9, 123.1, 116.4, 101.2, 72.9, 70.6, 67.8, 66.4. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₁₁H₁₂CINO₇Na 328.0195; found 328.0210.





(a) BzCl, Pyridine, -78°C-RT; (b) (1) Tf₂O, pyridine, CH₂Cl₂, (2) NaN₃, DMF; (c) TiBr₄, CH₂Cl₂/EtOAc; (d) 2-chloro-4-nitrophenol, Ag₂O, CH₃CN, M.S., R. T., 12 hours; (e) NaOMe, MeOH; (f) PMe₃ in toluene, THF; (g) HCl, Water

- **1,2,3-tri-O-benzoyl-β-L-arabinopyranoside (31).** To a magnetically-stirred solution of L-arabinose (2.0 g, 13.3 mmol) in anhydrous pyridine (40 mL) at -50 °C was added benzoyl chloride (4.64 mL, 40.0 mmol) in a dropwise fashion with stirring. The reaction temperature held below -20 °C for 2 h and was slowly allowed to room temperature. The reaction was quenched by removing pyridine in *vacuo* and the residue was diluted with EtOAc and was washed with 1N HCl, NaHCO₃ (sat), water, and brine. The organic phase was dried over Na₂SO₄ and resulting residue was purified by normal phase column chromatography (using a gradient from 100:0 to70:30 hexanes:EtOAc). Compound **31** (1.22 g, 2.64 mmol) was obtained with a yield of 20% as a white solid along with **33** (3.36 g, 5.94 mmol, 45% yield). **31**: ¹H NMR (CDCl₃, 500 MHz) δ ppm 8.12 (d, *J* = 7.3 Hz, 2 H), 8.03 (d, *J* = 7.3 Hz, 2 H), 7.87 (d, *J* = 7.3 Hz, 2 H), 7.5 (m, 1 H), 7.3 7.5 (m, 4 H), 7.2 7.3 (m, 4 H), 6.79 (d, *J* = 3.7 Hz, 1 H), 6.12 (dd, *J* = 10.5, 3.7 Hz, 1 H), 5.88 (dd, *J* = 10.5, 2.9 Hz, 1 H), 4.55 (br. s., 1 H), 4.26 (d, *J* = 12.5 Hz, 1 H), 4.0 4.1 (m, 2 H). ¹³C NMR (CDCl₃, 100 MHz) δ ppm 166.1, 165.6, 164.9, 133.7, 133.5, 133.3, 129.9 (2 carbons), 129.8 (2 carbons), 129.7 (2 carbons), 129.2, 129.0, 128.8, 128.7 (2 carbons), 128.4 (2 carbons), 128.3 (2 carbons), 91.4, 70.9, 67.6, 67.5, 65.0. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₂₆H₂₂O₈Na, 485.1207; found 485.1238.
- **1,2,3,4-tetra-O-benzoyl-β-L-arabinopyranoside (33).** ¹H NMR (CDCl₃, 500 MHz) δ ppm 8.28 (d, J = 2.0 Hz, 1 H), 7.9 8.2 (m, 8 H), 7.2 7.6 (m, 10 H), 7.11 (d, J = 9.0 Hz, 1 H), 6.27 (d, J = 5.4 Hz, 1 H), 5.95 (t, J = 6.0 Hz, 1 H), 5.7 (m, 2 H), 4.44 (dd, J = 12.3, 5.3 Hz, 1 H), 4.15 (m, 1 H). ¹³C NMR (CDCl₃, 100 MHz) δ ppm 165.75, 165.71, 165.6, 164.7, 133.8, 133.59, 133.49, 133.44, 129.9 (3 carbons), 129.7 (3 carbons), 129.3, 129.1, 128.9, 128.8 (2 carbons), 128.7 (2 carbons), 128.6 (3 carbons), 128.44 (2 carbons), 128.42 (2 carbons), 91.1, 69.5, 68.2, 67.9, 63.1. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₃₃H₂₆O₉Na, 589.1469; found 589.1481.

- **1,2,3-tri-O-benzoyl-4-deoxy-4-azido-α-D-xylopyranoside (35).** According to general procedure **2.6**, **31** (1.22 g,2.64 mmol) yielded **35** (0.67 g, 52% yield) as a white oil. ¹H NMR (CDCl₃, 500 MHz) δ ppm 8.1 (m, 2 H), 8.0 (m, 2 H), 7.8 7.9 (m, 2 H), 7.6 (m, 1 H), 7.5 (m, 3 H), 7.4 (m, 3 H), 7.30 (t, J = 7.8 Hz, 2 H), 6.73 (d, J = 3.7 Hz, 1 H), 6.04 (t, J = 9.7 Hz, 1 H), 5.53 (dd, J = 10.0, 3.7 Hz, 1 H), 4.0 4.2 (m, 2 H), 3.9 (m, 1 H). ¹³C NMR (CDCl₃, 100 MHz) δ ppm 165.7, 165.4, 164.5, 133.9, 133.6, 133.5, 129.94 (4 carbons), 129.81 (3 carbons), 128.77 (3 carbons), 128.8, 128.55 (2 carbons), 128.43 (2 carbons), 90.2, 71.0, 70.4, 61.9, 59.4. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₂₆H₂₁N₃O₇Na, 510.1272; found 510.1273.
- **1-bromo-2,3-di-***O***-benzoyl-4-deoxy-4-azido-α-D-xylopyranoside (37).** According to general procedure **2.1**, **35** (0.67 g, 1.18 mmol) yielded **37** (0.47 mg, 90 % yield) as a white oil. ¹H NMR (CD₃Cl 400 MHz) δ ppm 7.9 8.0 (m, 5 H), 7.5 (m, 2 H), 7.3 7.4 (m, 3 H), 6.74 (d, *J* = 3.9 Hz, 1 H), 5.9 (m, 1 H), 5.16 (dd, *J* = 9.8, 3.9 Hz, 1 H), 4.1 (m, 1 H), 3.9 4.0 (m, 2 H). ¹³C NMR (CDCl₃, 100 MHz) δ ppm 165.3, 133.8, 133.6, 130.0 (2 carbons), 129.8 (2 carbons), 128.7 (2 carbons), 128.6 (2 carbons), 128.5 (2 carbons), 128.2, 87.6, 71.3, 71.1, 63.7, 58.7. HRMS-ESI (m/z): compound decomposed during MS analysis.
- **(2-chloro-4-nitrophenyl)-2,3-di-O-benzoyl4-deoxy-4-azido-β-D-xylopyranoside (39).** According to general procedure **2.2**, **37** (0.38 mg, 0.85 mmol) yielded **39** (0.22 g, 48% yield) as a white solid. ¹H NMR (CDCl₃, 400 MHz) δ ppm 8.21 (dd, J = 2.7, 1.2 Hz, 1 H), 7.9 8.1 (m, 5 H), 7.5 7.6 (m, 2 H), 7.3 7.4 (m, 5 H), 5.63 (dd, J = 5.5, 4.3 Hz, 1 H), 5.58 (t, J = 6.3 Hz, 1 H), 5.53 (d, J = 4.3 Hz, 1 H), 4.39 (dd, J = 12.5, 3.5 Hz, 1 H), 3.9 4.0 (m, 1 H), 3.78 (dd, J = 12.5, 6.3 Hz, 1 H). ¹³C NMR (CDCl₃, 100 MHz) δ ppm 165.2, 165.0, 157.1, 142.8, 133.8, 133.7, 130.03 (2 carbons), 129.87 (2 carbons), 129.8, 129.8, 128.5 (2 carbons), 128.5 (2 carbons), 126.1, 124.6, 123.7, 116.0, 98.4, 70.1, 69.0, 61.6, 56.9. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₂₅H₁₉ClN₄O₈Na, 561.0784; found 561.1366.
- **1-bromo-2,3,4-tri-O-benzoyl-β-L-arabinopyranoside (48).** According to general procedure **2.1**, **33** (0.65 g, 1.15 mmol) yielded **48** (0.60 g, 100% yield) as a white solid. ¹H NMR (CDCl₃, 500 MHz) δ ppm 8.1 (m, 1 H), 8.05 (d, *J* = 8.3 Hz, 1 H), 7.88 (d, *J* = 8.3 Hz, 1 H), 7.62 (d, *J* = 0.7 Hz, 2 H), 7.3 7.6 (m, 8 H), 7.30 (t, *J* = 7.6 Hz, 2 H), 6.97 (d, *J* = 3.7 Hz, 1 H), 6.04 (dd, *J* = 10.5, 3.4 Hz, 1 H), 5.87 (d, *J* = 1.7 Hz, 1 H), 5.75 (dd, *J* = 10.3, 3.9 Hz, 1 H), 4.49 (d, *J* = 13.4 Hz, 1 H), 4.26 (d, *J* = 13.2 Hz, 1 H). ¹³C NMR (CDCl₃, 100 MHz) δ ppm 172.2, 165.6, 165.55, 165.4, 133.77, 133.6, 133.4, 130.20 (2 carbons), 130.0, 129.87 (2 carbons), 129.7, 129.3, 129.2, 128.9, 128.63, 128.58, 128.55, 128.47, 128.37, 89.8, 68.9, 68.9, 68.7, 65.0. HRMS-ESI (m/z): compound decomposed during MS analysis.
- **(2-chloro-4-nitrophenyl)-2,3,4-tri-***O***-benzoyl-α-L-arabinopyranoside (50).** According to general procedure **2.2**, **48** (0.60 g, 1.15 mmol) yielded **50** (0.22 g, 31% yield) and **52** (0.17 g, 26%) both as white crystals. ¹H NMR (CDCl₃, 500 MHz) δ ppm 8.2 8.3 (m, 1 H), 7.9 8.2 (m, 7 H), 7.3 7.6 (m, 9 H), 7.1 (m, 1 H), 5.96 (dd, J = 4.9, 3.7 Hz, 1 H), 5.8 (m, 2 H), 5.59 (d, J = 3.7 Hz, 1 H), 4.47 (dd, J = 11.7, 6.6 Hz, 1 H), 4.1 (m, 1 H). ¹³C NMR (CDCl₃, 100 MHz) δ ppm 165.54, 165.51, 165.0, 157.4, 156.9, 142.81, 133.79, 133.6, 130.02 (2 carbons), 129.90 (2 carbons), 129.85 (2 carbons), 129.8, 128.7, 128.6, 128.54, 128.50, 128.44, 126.1, 125.3, 124.7, 124.5, 123.7, 116.2, 116.1, 98.3, 69.2, 68.9, 66.7, 60.9. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₃₂H₂₄CINO₁₀Na, 640.0981; found 640.0995.
- **1,2,3,4-tetra-O-benzoyl-α-L-arabinopyranoside (52).** According to general procedure **2.2**, **48** (0.60 g, 1.15 mmol) yielded **50** (0.22 g, 31% yield) and **52** (0.17 g, 26%) both as white crystals. ¹H NMR (CDCl_{3,} 500 MHz) ¹H NMR δ ppm 8.2 (m, 1 H), 7.9 8.2 (m, 8 H), 7.2 7.6 (m, 10 H), 7.1 (m, 1 H), 6.27 (d, J = 5.4 Hz, 1 H), 5.95 (t, J = 6.0 Hz, 1 H), 5.7 5.8 (m, 2 H), 4.44 (dd, J = 12.6, 5.0 Hz, 1 H), 4.08 4.19 (m, 1 H). ¹³C NMR (CDCl₃, 100 MHz) δ ppm 165.6, 165.5, 165.2, 164.8, 156.9, 133.8, 133.64, 133.55, 133.53, 130.10 (2 carbons), 129.86 (3 carbons), 129.13 (2 carbons), 128.94 (2 carbons), 128.69 (2 carbons), 128.6, 128.5, 128.51, 128.48, 128.46, 125.4, 124.5, 116.2, 92.3, 69.9, 68.8, 67.5, 62.7. HRMS-ESI (m/z): [M]⁺ calcd for C₃₃H₂₆O₉Na, 589.1469; found m/z 589.1479.

- **(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-β-D-xylopyranoside (12).** According to general procedure **2.3**, **39** (0.22 g, 0.41 mmol) yielded **12** (0.13 g, 96% yield) as a light yellow solid. ¹H NMR (CD₃OD, 400 MHz) δ ppm 8.27 (d, *J* = 2.7 Hz, 1 H), 8.14 (dd, *J* = 9.0, 2.7 Hz, 1 H), 7.33 (d, *J* = 9.4 Hz, 1 H), 5.09 (d, *J* = 7.0 Hz, 1 H), 3.98 (dd, *J* = 11.5, 4.5 Hz, 1 H), 3.5 3.6 (m, 3 H), 3.3 (m, 1 H). ¹³C NMR (CD₃OD, 100 MHz) δ ppm 157.6, 142.2, 125.3, 123.4, 123.3, 115.2, 100.7, 75.5, 73.1, 63.6, 61.1. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₁₁H₁₁ClN₄O₆Na, 353.0259; found 353.0234.
- **(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-D-xylopyranoside (13).** According to general procedure **2.4**, **12** (70 mg, 0.19 mmol) yielded **13** (27.6 mg, 47% yield) as a yellow solid. ¹H NMR (CD₃OD, 400 MHz) δ ppm 8.29 (d, J = 2.7 Hz, 1 H), 8.16 (dd, J = 9.0, 2.7 Hz, 1 H), 7.36 (d, J = 9.4 Hz, 1 H), 5.12 (d, J = 7.0 Hz, 1 H), 3.95 (dd, J = 11.5, 4.9 Hz, 10 H), 3.54 (dd, J = 8.8, 7.2 Hz, 1 H), 3.40 (dd, J = 11.5, 10.4 Hz, 1 H), 3.3 (m, 1 H), 2.85 (ddd, J = 10.3, 9.3, 5.1 Hz, 1 H). ¹³C NMR (CD₃OD, 100 MHz) δ ppm 157.7, 142.1, 125.3, 123.4, 123.3, 115.2, 101.1, 76.1, 73.1, 65.8, 51.9. HRMS-ESI (m/z): [M+H]⁺ Calcd for C₁₁H₁₄CIN₂O₆, 305.0535; found 305.0545.
- (2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-D-xylopyranoside hydrochloride (13a). According to general procedure 2.5, 13 (8.3 mg, 0.03 mmol) yielded 13a (10.0 mg, 100% yield) as a yellow solid. ¹H NMR (D₂O, 400 MHz) δ ppm 8.22 (d, *J* = 2.7 Hz, 1 H), 8.03 (dd, *J* = 9.4, 2.7 Hz, 1 H), 7.22 (d, *J* = 9.0 Hz, 1 H), 5.21 (d, *J* = 6.7 Hz, 1 H), 4.15 (dd, *J* = 12.1, 4.7 Hz, 1 H), 3.6 3.7 (m, 3 H), 3.32 (td, *J*=9.3, 4.5 Hz, 1 H). ¹³C NMR (D₂O, 100 MHz) δ ppm 156.8, 142.3, 126.0, 124.1, 123.4, 115.5, 99.9, 71.8, 70.7, 61.4, 50.4. HRMS-ESI (m/z): [M]⁺ calcd for C₁₁H₁₄CIN₂O₆, 305.0535; found 305.0847.
- **(2-chloro-4-nitrophenyl)-α-L-arabinopyranoside (18).** According to general procedure **2.2**, **50** (0.22 g, 0.36 mmol) yielded **18** (0.10 g, 92% yield) as a yellow solid. ¹H NMR (CD₃OD, 400 MHz) δ ppm 8.32 (d, J = 2.4 Hz, 1 H), 8.18 (dd, J = 9.3, 2.4 Hz, 1 H), 7.41 (d, J = 8.8 Hz, 1 H), 5.14 (d, J = 6.6 Hz, 1 H), 3.9 (m, 3 H), 3.8 (m, 1 H), 3.67 (dd, J = 8.6, 2.9 Hz, 1 H). ¹³C NMR (DMSO-*d6*, 100 MHz) δ ppm 158.1, 141.8, 125.9, 124.6, 122.8, 116.0, 100.9, 72.6, 70.3, 67.5, 66.1. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₁₁H₁₂CINO₇Na, 328.0195; found 328.0192.

2.14. Synthesis of (2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-xylopyranoside (17).



(a) BzCl(3.2eq) , Pyridine, -50°C-R. T.; (b) (1) Tf₂O, Pyridine, CH₂Cl₂, (2) NaN₃, DMF; (c) (1) TiBr₄, CH₂Cl₂/EtOAc, (2) 2-chloro-4-nitrophenol, Ag₂O, CH₃CN, M.S., R. T., 12 hours; (d) NaOMe, MeOH; (e) PPh₃ THF, 50°C; (f) HCl, Water

1,2,3,4-tetra-O-benzoyl-α-D-ribopyranoside (44). To a solution of D-ribose (1.1 g, 7.33 mmol) in anhydrous pyridine (10 ml) at -50 °C with stirring was added benzoyl chloride (2.72 ml, 23.5 mmol) in

dropwise fashion. The reaction temperature held below -20 °C for 2 h and then allowed to slowly warm to room temperature. The solvent was removed in *vacu* and the residue was diluted with EtOAc and was washed with 1N HCl, NaHCO₃, water, and brine. The organic phase was dried over Na₂SO₄ and purified by normal phase chromotography (using a gradient of 100:0 Hexanes:EtOAc to 70:30 Hexanes:EtOAc) to afford **44** (0.56 g, 0.99 mmol, 14%) as a white solid, together with **45a** (0.82 g, 1.77 mmol, 24%), **45b** (0.37 g, 0.80 mmol, 11%), **45c** (0.82 g, 1.77 mmol, 24%), and **45d** (0.40 g, 0.86 mmol, 12%). **48**: ¹H NMR (CDCl₃, 500 MHz) δ ppm 8.1 (m, 3 H), 8.0 (m, 3 H), 7.8 - 7.9 (m, 3 H), 7.4 - 7.6 (m, 7 H), 7.3 - 7.4 (m, 4 H), 6.63 (d, *J* = 3.4 Hz, 1 H), 6.06 (t, *J* = 3.8 Hz, 1 H), 5.74 (td, *J* = 3.8, 0.7 Hz, 1 H), 5.71 (q, *J* = 3.3 Hz, 1 H), 4.41 (dd, *J* = 12.9, 2.9 Hz, 1 H), 4.29 (dd, *J* = 12.9, 4.2 Hz, 1 H). ¹³C NMR (CDCl₃, 100 MHz) δ ppm 166.18, 165.81, 165.57, 164.56, 134.17, 133.68, 133.65, 133.52 (2 carbons), 130.40 (2 carbons), 130.28 (4 carbons), 130.18 (3carbons), 130.02, 128.93, 128.72, 128.69, 128.64 (3 carbons), 128.61 (3 carbons), 92.39, 68.04, 67.38, 66.90, 63.41. HRMS-ESI (m/z): [M+H]⁺ calcd for C₃₃H₂₆O₉Na , 589.1469; found 589.1498.

- **1,2,4-tri-O-benzoyl-α-D-ribopyranoside (45a).** ¹H NMR (CDCl₃, 500 MHz) δ ppm 8.0 (m, 3 H), 7.5 (m, 5 H), 7.4 (m, 2 H), 7.3 7.4 (m, 5 H), 6.42 (d, J = 3.2 Hz, 1 H), 5.5 (m, 1 H), 5.34 (dt, J = 7.5, 3.9 Hz, 1 H), 4.65 (q, J = 3.6 Hz, 1 H), 4.41 (dd, J = 11.7, 7.8 Hz, 1 H), 4.20 (d, J = 3.2 Hz, 1 H), 3.92 (dd, J = 11.6, 3.8 Hz, 1 H). ¹³C NMR (CDCl₃, 100 MHz) δ ppm 166.10, 165.93, 165.04, 134.05, 133.86, 133.71, 133.67, 133.60, 130.34 (2 carbons), 130.25 (2 carbons), 130.19 (2 carbons), 130.15, 129.63, 129.43, 129.41, 128.87 (2 carbons), 128.79 (2 carbons), 128.69 (2 carbons), 128.65,128.59, 90.52, 69.42, 68.83, 67.55. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₂₆H₂₂O₈Na, 485.1207; found 485.1216.
- **1,3,4-tri-***O***-benzoyl-α-D-ribopyranoside (45b).** ¹H NMR (CDCl₃, 500 MHz) δ ppm 8.1 (m, 3 H), 8.0 (m, 3 H), 7.9 (m, 2 H), 7.3 7.7 (m, 7 H), 6.49 (d, J = 3.2 Hz, 1 H), 5.79 (t, J = 3.5 Hz, 1 H), 5.7 (m, 1 H), 4.32 (dd, J = 13.1, 2.3 Hz, 1 H), 4.25 (dt, J = 3.4, 1.7 Hz, 1 H), 4.20 (dd, J = 13.1, 3.5 Hz, 1 H). ¹³C NMR (CDCl₃, 125 MHz) δ ppm 165.85, 165.65, 164.71, 134.10, 133.90, 133.78, 130.36, 130.27, 130.20, 130.13, 130.10, 130.03, 129.91, 129.18 (2 carbons), 128.96 (2 carbons), 128.74 (2 carbons), 128.67, 128.63, 94.67, 69.25, 68.42, 68.04, 63.29. HRMS-ESI (m/z): [M+H]⁺ calcd for C₂₆H₂₂O₈Na, 485.1207; found 485.1212.
- **1,2,3-tri-***O***-benzoyl-α-D-ribofuranoside (45c).** ¹H NMR (CDCl₃, 500 MHz) δ ppm 7.9 8.1 (m, 3 H), 7.5 7.6 (m, 5 H), 7.4 (m, 2 H), 7.0 7.4 (m, 5 H), 6.57 (d, J = 3.2 Hz, 1 H), 5.50 (t, J = 3.8 Hz, 1 H), 5.45 (q, J = 3.2 Hz, 1 H), 4.66 (t, J = 3.8 Hz, 1 H), 4.20 (m, J=2.9 Hz, 2 H), 3.6 (s, broad, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ ppm 167.03, 166.63, 164.57, 134.10, 133.75, 133.64, 130.39 (3 carbons), 130.29 (3 carbons), 130.22, 129.86, 129.56, 129.24, 128.92 (2 carbons), 128.67 (2 carbons), 128.64, 92.29, 70.31, 69.95, 65.53, 63.18. HRMS-ESI (m/z): [M+H]⁺ calcd for C₂₆H₂₂O₈Na, 485.1207; found 485.1217.
- **1,2,3-tri-***O***-benzoyl-α-D-ribopyranoside (45d).** ¹H NMR (CDCl₃, 500 MHz) δ ppm 7.9 8.1 (m, 4 H), 7.5 7.8 (m, 4 H), 7.3 7.5 (m, 7 H), 6.53 (d, J = 3.9 Hz, 1 H), 5.81 (t, J = 3.4 Hz, 1 H), 5.66 (td, J = 3.8, 1.0 Hz, 1 H), 4.3 (m, 1 H), 4.23 (dd, J = 12.3, 2.6 Hz, 1 H), 4.1 (m, 1 H). ¹³C NMR (CDCl₃, 125 MHz) δ ppm 166.07, 165.46, 164.65, 134.19, 133.98, 133.84, 130.30 (2 carbons), 130.15 (2 carbons), 130.11 (2 carbons), 129.49, 129.26, 129.05, 128.96 (2 carbons), 128.95 (2 carbons), 128.82 (2 carbons), 92.20, 69.37, 69.03, 66.93, 66.08. HRMS-ESI (m/z): [M+H]⁺ calcd for C₂₆H₂₂O₈Na, 485.1207; found 485.1221.
- **3-deoxy-3-azido-1,2,4-tri-O-benzoyl-D-xylopyranoside (46).** According to general procedure **2.6**, **45a** (0.82 g, 1.77 mmol) yielded **46** (0.65 g, 75% yield) as a white solid. ¹H NMR (CDCl₃, 500 MHz) δ ppm ($\alpha/\beta=2/1$) ppm 8.1 (m, 5 H), 7.3 7.7 (m, 10 H), 6.70 (d, J = 3.7 Hz, 0.7 H), 6.21 (d, J = 6.1 Hz, 0.3 H), 5.46 (dd, J = 8.1, 6.1 Hz, 0.3 H), 5.34 (dd, J = 10.5, 3.7 Hz, 0.7 H), 5.27 (td, J = 10.3, 5.7 Hz, 0.7 H), 5.22 (td, J = 7.6, 4.4 Hz, 0.3 H), 4.4 (m, 1 H), 4.2 (m, 1 H), 3.94 (m, J = 11.0, 11.0 Hz, 0.7 H), 3.81 (dd, J = 12.2, 7.6 Hz, 0.3 H). ¹³C NMR (CDCl₃, 125 MHz) δ ppm 165.53, 165.42, 164.69, 134.18, 134.05, 133.95 (2 carbons), 130.39 (2 carbons), 130.19, 130.15, 129.03, 128.93, 128.91, 128.89, 128.86 (2

carbons), 128.83 (2 carbons), 128.80 (2 carbons), 89.89, 70.98, 70.20, 61.84, 61.32. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{26}H_{21}N_3O_7Na$, 510.1272; found 510.1281.

- **(2-chloro-4-nitrophenyl)-3-deoxy-3-azido-2,4-di-O-benzoyl-β-D-xylopyranoside (47).** According to general procedure **2.2**, **46** (0.26 g, 0.53 mmol) yielded **47** (0.27 g, 94% yield) as a white solid. ¹H NMR (CDCl₃, 500 MHz) δ ppm 8.28 (d, J = 2.7 Hz, 1 H), 8.13 (dd, J = 9.2, 2.8 Hz, 1 H), 7.9 (m, 2 H), 7.6 (m, 2 H), 7.4 (m, 3 H), 7.3 (m, 3 H), 7.32 (d, J = 9.3 Hz, 1 H), 5.60 (d, J = 4.4 Hz, 1 H), 5.52 (dd, J = 6.3, 4.2 Hz, 1 H), 5.14 (td, J = 5.9, 3.7 Hz, 1 H), 4.43 (dd, J = 12.5, 3.7 Hz, 1 H), 4.31 (t, J = 6.3 Hz, 1 H), 3.83 (dd, J = 12.5, 5.1 Hz, 1 H). ¹³C NMR (CDCl₃, 125 MHz) δ ppm 165.69, 165.23, 157.16, 143.20, 134.05, 134.01, 130.20 (2 carbons), 130.18 (2 carbons), 129.20, 128.95, 128.85 (2 carbons), 128.80 (2 carbons), 126.51, 125.26, 123.88, 116.26, 98.33, 69.10, 68.94, 61.72, 59.69. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₂₅H₁₉ClN₄O₈Na, 561.0784; found 561.0801.
- **(2-chloro-4-nitrophenyl)-3-deoxy-3-azido-β-D-xylopyranoside (16).** According to general procedure **2.3**, **47** (270 mg, 0.50 mmol) yielded **16** (119.5 mg, 66% yield) as a light yellow solid. ¹H NMR (CD₃OD, 500 MHz) δ ppm 8.31 (d, J = 2.7 Hz, 1 H), 8.18 (dd, J = 9.0, 2.7 Hz, 1 H), 7.38 (d, J = 9.3 Hz, 1 H), 5.18 (d, J = 7.6 Hz, 1 H), 3.95 (dd, J = 11.2, 5.1 Hz, 1 H), 3.5 (m, 2 H), 3.50 (dd, J = 11.2, 10.0 Hz, 1 H), 3.40 (t, J = 9.5 Hz, 1 H). ¹³C NMR (CD₃OD, 125 MHz) δ ppm 157.9, 142.5, 125.6, 123.7, 123.6, 115.6, 101.1, 71.9, 69.6, 68.3, 66.6. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₁₁H₁₁ClN₄O₆Na, 353.0259; found 353.0268.
- **(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-xylopyranoside (17).** According to general procedure **2.4**, **16** (56 mg, 0.16 mmol) yielded **17** (41.8 mg, 80% yield) as a white solid. ¹H NMR (CD₃OD, 500 MHz) δ ppm 8.32 (d, J = 2.7 Hz, 1 H), 8.19 (dd, J = 9.2, 2.8 Hz, 1 H), 7.40 (d, J = 9.3 Hz, 1 H), 5.17 (d, J = 7.3 Hz, 1 H), 3.94 (dd, J = 10.9, 4.5 Hz, 1 H), 3.4 3.5 (m, 3 H), 2.81 (t, J = 9.0 Hz, 1 H).¹H NMR (500 MHz, DMSO- d_6) δ ppm 8.35 (d, J = 2.9 Hz, 1 H), 8.22 (dd, J = 9.3, 2.7 Hz, 1 H), 7.51 (d, J = 9.3 Hz, 1 H), 5.49 (br. s., 1 H), 5.26 (d, J = 7.3 Hz, 1 H), 5.15 (br. s., 1 H), 3.79 (dd, J = 11.0, 5.1 Hz, 1 H), 3.43 (t, J = 10.5 Hz, 1 H), 3.3 (m, 1H), 3.29 (t, J = 8.5 Hz, 1 H), 3.19 (s, 1 H), 3.19 (s, 1 H), 2.64 (t, J = 9.3 Hz, 1 H), 1.84 (s, 1 H). ¹³C NMR (DMSO- d_6 , 125 MHz) δ ppm 158.3, 142.2, 126.2, 124.9, 123.1, 116.4, 101.4, 73.4, 70.0, 67.5, 60.0. HRMS-ESI (m/z): [M+H]⁺ calcd for C₁₁H₁₄CIN₂O₆, 305.0535; found 305.0536.
- (2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-xylopyranoside hydrochloride (17a). According to general procedure 2.5, 17 (2 mg, 0.006 mol) yielded 17a (2 mg, 98% yield) as a yellow solid. ¹H NMR (D₂O, 500 MHz) δ ppm 8.42 (d, *J* = 2.7 Hz, 1 H), 8.23 (dd, *J* = 9.2, 2.8 Hz, 1 H), 7.42 (d, *J* = 9.3 Hz, 1 H), 5.37 (d, *J* = 7.3 Hz, 1 H), 4.19 (dd, *J* = 11.5, 5.4 Hz, 1 H), 4.03 (td, *J* = 10.1, 5.4 Hz, 1 H), 3.97 (dd, *J* = 10.6, 7.4 Hz, 1 H), 3.68 (dd, *J* = 11.5, 10.5 Hz, 1 H), 3.38 (t, *J* = 10.4 Hz, 1 H). ¹³C NMR (D₂O, 125 MHz) δ ppm 157.2, 142.9, 126.5, 124.5, 123.7, 115.9, 100.7, 69.1, 66.6, 65.7, 57.8. HRMS-ESI (m/z): [M]⁺ calcd for C₁₁H₁₄ClN₂O₆, 305.0535; found 305.0539.

3. 2-chloro-4-nitrophenyl glycoside library screening

In Vitro 2-chloro-4-nitrophenyl glycoside screening with OleD variant Reactions containing 10 μM purified wtOleD, OleD TDP-16, or OleD Loki, 2 mM UDP or 5 mM TDP, and 2 mM of (2-chloro-4-nitophenol)-glycosides (1-20) in Tris-HCI (50 mM, pH 8.0) with a final volume of 100 μL were incubated at 25°C for 12 h and the absorbance of the reactions were monitored at 410 nm using a Fluostar Omega microplate reader (BMG LABTECH GmbH, Ortenberg, Germany). Reactions noted as positives based upon absorbance change where subsequently analyzed via HPLC as follows. To the reaction was added 50 μL MeOH and 50 μL H₂O and the mixture filtered through MultiScreen Filter Plate (from Millipore, Billerica, MA, USA) according to manufacturer's instructions. Sugar nucleotide formation was assessed by analytical reverse-phase HPLC using an Agilent 1260 system equipped with a DAD detector with a 250 mm x 4.6 mm Gemini-NX 5μ C18 column (Phenomenex, Torrance, CA, USA) and a

linear gradient of 1% B to 71% B over 30 min, 71% B for 5 min, 71% B to 1% B over 1 min, 1% B for 4 min (Solvent A = 50 mM PO₄²⁻, 5 mM tetrabutylammonium bisulfate, 2% acetonitrile, pH adjusted to 6.0 with KOH; Solvent B = acetonitrile); flow rate = 1 mL min⁻¹; A_{254} nm; injection volume 10 µL. The percent conversion was calculated based on the peak area of NDP and NDP-sugar integrated with Agilent 1260 workstation and each assay was repeated at least two times. The percentage conversion with the three enzymes and the retention time of the NDP-sugars are presented in Table S2. All 2-chloro-4-nitrophenyl aminosugar glycoside hydrochloride salts (**3a**, **5a**, **7a**, **9a**, **11a**, **13a**) were tested with OleD Loki iva the same protocol above and the percentage conversion was listed in Table S2.

Purification and characterization of NDP-sugars. Reactions containing 10 μ M purified OleD Loki, 2 mM UDP or 2 mM TDP, and 2 mM of 2-chloro-4-nitophenyl glycoside (**3**, **5**, **7**, **9**, **11**, **13**, **18**, **19**) in Tris-HCI (50 mM, pH 8.0) with a final volume of 100 μ L were incubated at 25°C for 6 h. To the reactions was added 50 μ L MeOH and 50 μ L H₂O and the mixtures filtered through Vivaspin 500 centrifugal concentrators. The recovered filtrate from each reaction was completely injected into reverse-phase HPLC using an Agilent 1260 system equipped with a DAD detector with a 250 mm x 4.6 mm Gemini-NX 5 μ C18 column (Phenomenex, Torrance, CA, USA) with a gradient of 1% B for 4min, 1% B to 20% B over 9 min, 20% B to 80% B over 2 min, 80% B for 7 min, 80% B to 1% B over 2 min, 1% B for 4 min (Solvent A = 50 mM triethylammonium acetate buffer, pH 7.0; Solvent B = acetonitrile; flow rate = 1 mL min⁻¹; A₂₅₄ nm). The sugar nucleotide peak was collected automatically by Agilent sample collector. The desired fractions were frozen at -80 °C, and lyophilized. The following samples were dissolved into 200 μ L 70% acetonitrile/ H₂O and submitted for mass analysis. The high resolution mass data are presented in Table S3.

4. Single enzyme coupled reaction of 4-methylumbelliferone 54. Reactions containing 10 µM of purified OleD Loki, 0.1 mM UDP, 1 mM 4-methylumbelliferone 54, and 1 mM 2-chloro-4-nitophenyl glycosides (1, 2, 3, 5, 7, 9, 11, 13, 18) in Tris-HCI (50 mM, pH 8.0) with a final volume of 100 µL were incubated at 25°C for 8 h and the fluorescence of the reactions were monitored (λ_{ex} =355 nm; I_{em} =460 nm) using a Fluostar Omega microplate reader (BMG LABTECH GmbH, Ortenberg, Germany). To the reaction was added 50 µL MeOH and 50 µL H₂O and the mixture filtered through a MultiScreen Filter Plate (from Millipore, Billerica, MA, USA) according to manufacturer's instructions. The filtrate was analyzed for the formation of related glycosylated 4-methylumbelliferone by analytical reverse-phase HPLC using an Agilent 1260 system equipped with a DAD detector with a 250 mm x 4.6 mm Gemini-NX 5µ C18 column (Phenomenex, Torrance, CA, USA) with a linear gradient of 1% B to 71% B over 30 min, 71% B for 5 min, 71% B to 1% B over 1 min, 1% B for 4 min (Solvent A = 50 mM $PO_4^{2^\circ}$, 5 mM tetrabutylammonium bisulfate, 2% acetonitrile, pH adjusted to 6.0 with KOH; Solvent B = acetonitrile; flow rate = 1 mL min⁻¹; A_{254} nm; injection volume 10 μ L). Percent conversion was calculated based on the peak area of glycosylated 4-methylumbelliferone and 4-methylumbelliferone integrated with Agilent 1260 workstation and was repeated at least two times for each glycoside donor. Retention times for the glycosylated 4-methylumbelliferones are listed in Table S4.

Purification and characterization of 4-methylumbelliferone glycosides. Reactions containing 2.6 μ M of purified OleD Loki, 0.2 mM UDP, 2 mM 4-methylumbelliferone **54**, and 2 mM of (2-chloro-4-nitophenyl)-glycoside (**1**, **2**, **3**, **5**, **7**, **9**, **13**) in Tris-HCl (50 mM, pH 8.0) with a final volume of 200 μ l were incubated at 25°C for 12 h. To the reactions was added 10 μ L 5/1 MeOH/HCl, 40 μ L MeOH and 50 μ L H₂O and the mixture filtered through Vivaspin 500 centrifugal concentrators. The entire filtrate was purified by semi-preparative reverse-phase HPLC with a Gemini C-18 (5 μ m, 250 × 10 mm) column (from Phenomenex, Torrance, California, USA) using a gradient of 5% B to 55% B over 27 min, 55% B to 100% B over 1 min, 100% B for 5 min, 100% B to 5% B over 1 min, 5% B for 4 min (A = ddH₂O with 0.1% TFA; B = acetonitrile; flow rate = 5 mL min⁻¹; A₂₅₄ nm). The desired fractions were collected, frozen at -80 °C, and lyophilized. The recovered samples were dissolved into 200 μ L 70% acetonitrile/H₂O and submitted for mass analysis. The high resolution mass data for all glycosylated 4-methylumbelliferones is presented in Table S4.

R=

NO2

CI



Figure S1. Library of synthesized 2-chloro-4-nitrophenyl glycoside donors (grey indicates no detectable turn-over in wtOleD-, OleD TDP-16-, or OleD Loki-catalyzed reactions).



Figure S2. HPLC chromatograms of UDP-sugar forming reactions. Reactions contained 10 μ M purified OleD Loki, 2 mM UDP, and 2 mM of 2-chloro-4-nitrophenyl glycoside in Tris-HCI (50 mM, pH 8.0) in a final volume of 100 μ I. (a) reaction of (2-chloro-4-nitrophenyl)- β -D-glucoside (1) and 2-chloro-4-nitrophenyl glucosamino/xylosaminosides (5, 7, 9, 3, 11, 13, 18) with UDP. (b) reaction of 2-chloro-4-nitrophenyl glucosamino/xylosaminoside hydrochloride salts (5a, 7a, 9a, 3a, 11a, 13a) with UDP. (\Diamond) denotes the corresponding phenolate by product.



Figure S3. HPLC chromatograms of TDP-sugar forming reactions. Reactions contained 10 μ M purified OleD Loki, 5 mM TDP, and 2 mM of 2-chloro-4-nitrophenyl glycoside in Tris-HCI (50 mM, pH 8.0) with a final volume of 100 μ I. (a) reaction of 2-chloro-4-nitrophenyl glucosamino/xylosaminosides (5, 7, 9, 3, 11) with TDP; (b) reaction of 2-chloro-4-nitrophenyl glucosamino/xylosaminoside hydrochloride salts (5a, 7a, 9a, 3a, 11a) with TDP. (\Diamond) denotes the phenolate by product.



Figure S4. HPLC of OleD Loki-catalyzed transglycosylation reactions. For each representative series: (i) control lacking enzyme; (ii) reaction of 2 mM 2-chloro-4-nitrophenyl glycoside, 2 mM UDP, 10 μ M Loki lacking 4-methylumbelliferone in 100 μ I Tris solution (50 mM, pH 8.0); (iii) full reaction of 2 mM 2-chloro-4-nitrophenyl glycoside, 0.2 mM UDP, 2 mM 4-methylumbelliferone, and 10 μ M Loki in 100 μ I Tris solution (50 mM, pH 8.0); (iii) full reaction of 2 mM 2-chloro-4-nitrophenyl glycoside, 0.2 mM UDP, 2 mM 4-methylumbelliferone, and 10 μ M Loki in 100 μ I Tris solution (50 mM, pH 8.0). The series includes: (a) β -D-glucoside (1); (b) 3-amino- β -D-glucoside (7); (c) 2-amino- β -D-glucoside (5); (d) 4-amino- β -D-glucoside (9); (e) 6-amino- β -D-glucoside (3); and (f) 4-amino- β -D-xyloside (13). Black closed diamonds (\blacklozenge) denote 2-chloro-4-nitrophenyl glycosides, black open diamonds (\diamondsuit) denote 2-chloro-4-nitrophenylate, red open circles (\circ) denote UDP sugar, red closed circles (\bullet) denote 4-methylumbelliferone (54) and green closed triangles (\blacktriangle) denote UDP.



Figure S5. HPLC of OleD Loki-catalyzed transglycosylation with 2-chloro-4-nitrophenyl glycoside HCI salts. For the representative reaction, (i) control lacking enzyme; (ii) reaction with 2 mM 2-chloro-4-nitrophenyl glycoside HCI, 2 mM UDP, 10 μ M Loki lacking 4-methylumbelliferone in 100 μ I 50 mM Tris, pH 8.0; (iii) full reaction with 2 mM 2-chloro-4-nitrophenyl glycoside HCI, 0.2 mM UDP, 2 mM 4-methylumbelliferone, and 10 μ M Loki in 100 μ I 50 mM Tris, pH 8.0. The series includes: (a) 2-amino- β -D-glucoside HCI (**5a**); (b) 3-amino- β -D-glucoside HCI (**7a**); (c) 4-amino- β -D-glucosidide HCI (**9a**); (d) 6-amino- β -D-glucoside HCI (**3a**); Black closed diamonds (\diamond) denote 2-chloro-4-nitrophenyl glycosides HCI, black open diamonds (\diamond) denote 2-chloro-4-nitrophenolate, red open circles (\circ) denote **UDP sugar**, and red closed circles (\bullet) denote **glycosylated-4-methylumbelliferone** in their respective panels. Green open triangle (Δ) denote 4-methylumbelliferone (**54**)and green closed triangle (Δ) denote UDP.

Table S1. Summary of 2-chloro-4-nitrophenyl aminosugar donors syntheses.



(a) (1) TiBr₄, CH₂Cl₂/EtOAc; (2) 2-chloro-4-nitrophenol, Ag₂O, CH₃CN, M.S., r t, 12 h; (b) NaOMe, MeOH; (c) PMe₃, THF, 50°C or PPh₃, THF, 50°C; (d) HCl, Water.

Entry	Starting material	:	step a ^a		step b ^a		step c ^a		step d ^a	
1	22: 2-deoxy-azido-D-glucoside (OAc)	23 :	18%	4:	99%	5 :	67%	5a :	99%	
2	24: 3-deoxy-3-azido-D-glucoside (OAc)	25 :	37%	6 :	64%	7 :	77%	7a :	99%	
3	26: 4-deoxy-4-azido-D-glucoside (OAc)	27 :	70%	8 :	86%	9 :	52%	9a :	90%	
4	28: 2-deoxy-2-azido-D-xyloside (OAc)	30 :	24%	10	: 80%	11:	82%	11a :	87%	
5	46: 3-deoxy-3-azido-D-xyloside (OBz)	47 :	94%	12	: 66%	13 :	80%	13a :	98%	
6	35: 4-deoxy-4-azido-D-xyloside (OBz)	39 :	43%	16	: 96%	17:	47%	17a :	99%	
7	36: 4-deoxy-4-azido-L-xyloside (OBz)	40 :	13%	14	: 95%	15 :	57%	15a :	98%	
18	41: 4-deoxy-4-azido-L-xyloside (OAc)	43 :	22%	14	: 85%	15 :	57%	15a :	98%	

^aisolated yield

 Table S2.
 Percentage conversion and retention time of the NDP-sugars.

Entry	Compound	OleD	Loki	OleD	wtOleD	Retention
,		A ^a	B ^D	- TDP-16		time (min)
1U	UDP-α -D-glucose	25%	-	97%	81%	4.9
2U	UDP-α-6-deoxy-6-azido-D-glucose	92%	-	96%	90%	11.7
3U	UDP-α-6-deoxy-6-amino-D-glucose	96%	100%	22%	77%	2.7
5U	UDP-α-2-deoxy-2-amino-D-glucose	100%	100%	72%	68%	2.7
7U	UDP-α-3-deoxy-3-amino-D-glucose	87%	90%	24%	1%	2.7
9U	UDP-α-4-deoxy-4-amino-D-glucose	96%	97%	58%	72%	2.8
11U	UDP-α-2-deoxy-2-amino-D-xylose	54%	54%	6%	28%	2.8
13U	UDP-α-4-deoxy-4-amino-D-xylose	88% 82%		1%	5%	2.8
18U	UDP-β-L-arabinose	13%	-	5%	7%	4.5
19U	UDP-α-6-deoxy-N-acetyamino-D-glucose	39%	-	11%	12%	5.8
1T	TDP-α -D-glucose	27%	-	87%	84%	7.7
2T	TDP-α-6-deoxy-6-azido-D-glucose	56%	-	93%	34%	11.9
3Т	TDP-α-6-deoxy-6-amino-D-glucose	92%	100%	21%	2%	4.9
5T	TDP-α-2-deoxy-2-amino-D-glucose	97%	89%	52%	61%	5.1
7T	TDP-α-3-deoxy-3-amino-D-glucose	64%	60%	9%	7%	5.2
9T	TDP-α-4-deoxy-4-amino-D-glucose	94%	88%	52%	14%	5.3
11T	TDP-α-2-deoxy-2-amino-D-xylose	72%	76%	2%	46%	5.2
13T	TDP-α-4-deoxy-4-amino-D-xylose	69%	47%	1%	9%	5.1
18T	TDP-β-L-arabinose	7%	-	2%	6%	8.4
19T	TDP-α-6-deoxy- <i>N</i> -acetyamino-D-glucose	48%	-	1%	4%	9.4

^a2-chloro-4-nitrophenyl aminosugar glycoside; ^b2-chloro-4-nitrophenyl aminosugar glycoside hydrochloride salt

Table S3. HRMS of the synthesized NDP-sugars.

		Elemental	Calculated	
		Composition	Theoretical Mass	Observed Mass
Entry	Compound	[M+Na]⁺	(m/z) [M+Na]⁺	(m/z) [M+Na]⁺
3U	UDP-α-6-deoxy-6-amino-D-glucose	C ₁₅ H ₂₅ N ₃ O ₁₆ P₂Na ⁺	588.0602	588.0600
5U	UDP-α-2-deoxy-2-amino-D-glucose	C ₁₅ H ₂₅ N ₃ O ₁₆ P₂Na⁺	588.0602	588.0601
7U	UDP-α-3-deoxy-3-amino-D-glucose	$C_{15}H_{25}N_{3}O_{16}P_{2}Na^{+}$	588.0602	588.0598
9U	UDP-α-4-deoxy-4-amino-D-glucose	C ₁₅ H ₂₅ N ₃ O ₁₆ P₂Na ⁺	588.0602	588.0600
11U	UDP-α-2-deoxy-2-amino-D-xylose	C ₁₄ H ₂₃ N ₃ O ₁₅ P₂Na⁺	558.0497	558.0493
13U	UDP-α-4-deoxy-4-amino-D-xylose	$C_{14}H_{23}N_{3}O_{15}P_{2}Na^{+}$	558.0497	558.0495
18U	UDP-β-L-arabinose	C ₁₄ H ₂₂ N ₂ O ₁₆ P ₂ Na ⁺	559.0337	559.0336
19U	UDP-α-6-deoxy-6-acetyamino-D-glucose	$C_{17}H_{27}N_3O_{17}P_2Na^+$	630.0708	630.0704
3T	TDP-α-6-deoxy-6-amino-D-glucose	C ₁₆ H ₂₇ N ₃ O ₁₅ P₂Na ⁺	586.0810	586.0797
5T	TDP-α-2-deoxy-2-amino-D-glucose	C ₁₆ H ₂₇ N ₃ O ₁₅ P ₂ Na ⁺	586.0810	586.0809
7T	TDP-α-3-deoxy-3-amino-D-glucose	$C_{16}H_{27}N_{3}O_{15}P_{2}Na^{+}$	586.0810	586.0811
9Т	TDP-α-4-deoxy-4-amino-D-glucose	C ₁₆ H ₂₇ N ₃ O ₁₅ P₂Na ⁺	586.0810	586.0795
11T	TDP-α-2-deoxy-2-amino-D-xylose	C ₁₅ H ₂₅ N ₃ O ₁₄ P₂Na⁺	556.0704	556.0692
13T	TDP-α-4-deoxy-4-amino-D-xylose	$C_{15}H_{25}N_{3}O_{14}P_{2}Na^{+}$	556.0704	556.0693
18T	TDP-β-L-arabinose	C ₁₅ H ₂₄ N ₂ O ₁₅ P ₂ Na ⁺	557.0544	557.0531
19T	TDP-α-6-deoxy-6-acetyamino-D-glucose	$C_{18}H_{29}N_3O_{16}P_2Na^+$	628.0915	628.0911

		Elemental	Calculated	
		Composition	Theoretical Mass	Observed Mass
	Compound	[M-H] ⁻	(m/z) [M-H] ⁻	(m/z) [M-H] ⁻
3U	UDP-α-6-deoxy-6-amino-D-glucose	$C_{15}H_{24}N_3O_{16}P_2^{-1}$	564.0637	564.0642
5U	UDP-α-2-deoxy-2-amino-D-glucose	C ₁₅ H ₂₄ N ₃ O ₁₆ P ₂	564.0637	564.0648
7U	UDP-α-3-deoxy-3-amino-D-glucose	$C_{15}H_{24}N_3O_{16}P_2^{-1}$	564.0637	564.0649
9U	UDP-α-4-deoxy-4-amino-D-glucose	$C_{15}H_{24}N_3O_{16}P_2$	564.0637	564.0642
11U	UDP-α-2-deoxy-2-amino-D-xylose	$C_{14}H_{22}N_{3}O_{15}P_{2}^{-1}$	534.0532	534.0534
13U	UDP-α-4-deoxy-4-amino-D-xylose	$C_{14}H_{22}N_{3}O_{15}P_{2}^{+}$	534.0532	534.0535
18U	UDP-β-L-arabinose	$C_{14}H_{21}N_2O_{16}P_2^{-1}$	535.0372	535.0372
19U	UDP-α-6-deoxy-6-acetyamino-D-glucose	C ₁₇ H ₂₆ N ₃ O ₁₇ P ₂	606.0743	606.0751
3T	TDP-α-6-deoxy-6-amino-D-glucose	$C_{16}H_{26}N_3O_{15}P_2$	562.0845	562.0853
5T	TDP-α-2-deoxy-2-amino-D-glucose	$C_{16}H_{26}N_3O_{15}P_2$	562.0845	562.0849
7T	TDP-α-3-deoxy-3-amino-D-glucose	$C_{16}H_{26}N_3O_{15}P_2^{-1}$	562.0845	562.0849
9T	TDP-α-4-deoxy-4-amino-D-glucose	$C_{16}H_{26}N_3O_{15}P_2$	562.0845	562.0851
11T	TDP-α-2-deoxy-2-amino-D-xylose	$C_{15}H_{24}N_3O_{14}P_2^{-1}$	532.0739	532.0746
13T	TDP-α-4-deoxy-4-amino-D-xylose	$C_{15}H_{24}N_3O_{14}P_2^{-1}$	532.0739	532.0747
18T	TDP-β-L-arabinose	$C_{15}H_{23}N_2O_{15}P_2$	533.0579	533.0586
19T	TDP-α-6-deoxy-6-acetyamino-D-glucose	$C_{18}H_{28}N_3O_{16}P_2^{-1}$	604.0950	604.0955

					HRMS-	ESI(m/z)
		Percentage	Retention	Chemical	Calculated	Observed Mass
Entry	Conjugated sugars	conversion	time(min)	formula	Theoretical Mass	(m/z)
54a	β-D-glucose	36%	10.4	$C_{16}H_{18}O_8$	339.1074 [M+H] ⁺	339.1072 [M+H] ⁺
54b	β-D-6-deoxy-6-amino- glucose	43%	8.1	$C_{16}H_{19}NO_7$	338.1234 [M+H] ⁺	338.1231 [M+H]⁺
54c	β-D-6-deoxy-6-azido- glucose	42%	15.8	$C_{16}H_{17}N_3O_7$	364.1139 [M+H]⁺	364.1144 [M+H]⁺
54d	β-D-2-deoxy-2-amino- glucose	53%	9.4	$C_{16}H_{19}NO_7$	338.1234 [M+H]⁺	338.1232 [M+H]⁺
54e	β-D-3-deoxy-3-amino- glucose	22%	9.1	$C_{16}H_{19}NO_7$	338.1234 [M+H] ⁺	338.1210 [M+H]⁺
54f	β-D-4-deoxy-4-amino- glucose	37%	9.4	$C_{16}H_{19}NO_7$	338.1234 [M+H]⁺	338.1231 [M+H]⁺
54g	β-D-4-deoxy-4-amino-	23%	10.4	$C_{15}H_{17}NO_6$	308.1129 [M+H]⁺	308.1126 [M+H]⁺

Table S4. Characterization data of the glycosylated 4-methylumbelliferone.

Table S5.	¹ H NMR.	aCOSY.	¹³ C NMR	of the s	vnthesized	compounds
					,	

Entry		Page
1	(2-chloro-4-nitrophenyl)-6-deoxy-6-amino-β-D-glucopyranoside (3): ¹ H NMR (CD ₃ OD, 500 MHz)	S32
2	(2-chloro-4-nitrophenyl)-6-deoxy-6-amino- β -D-glucopyranoside (3): gCOSY (CD ₃ OD, 500 MHz)	S33
3	(2-chloro-4-nitrophenyl)-6-deoxy-6-amino- β -D-glucopyranoside (3): ¹³ C NMR (D ₂ O, 125 MHz)	S34
4	(2-chloro-4-nitrophenyl)-6-deoxy-6-amino-β-D-glucopyranoside hydrochloride (3a): ¹ H NMR (D ₂ O, 500 MHz)	S35
5	(2-chloro-4-nitrophenyl)-6-deoxy-6-amino-β-D-glucopyranoside hydrochloride (3a): ¹³ C NMR (D ₂ O, 125 MHz)	S36
6	(2-chloro-4-nitrophenyl)-2-deoxy-2-azido-β-D-glucopyranoside (4): ¹ H NMR (CD ₃ OD, 500 MHz)	S37
7	(2-chloro-4-nitrophenyl)-2-deoxy-2-azido-β-D-glucopyranoside (4): ¹³ C NMR (CD ₃ OD, 125 MHz)	S38
8	(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-glucopyranoside (5): ¹ H NMR (CD ₃ OD, 400 MHz)	S39
9	(2-chloro-4-nitrophenyl)-2-deoxy-2-amino- β -D-glucopyranoside (5): gCOSY NMR (CD ₃ OD, 400 MHz)	S40
10	(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-glucopyranoside (5): ¹³ C NMR (CD ₃ OD, 100 MHz)	S41
11	(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-glucopyranoside hydrochloride (5a): ¹ H NMR (CD ₃ OD, 500 MHz)	S42
12	(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-glucopyranoside hydrochloride (5a): ¹³ C NMR (CD ₃ OD, 125 MHz)	S43
13	(2-chloro-4-nitrophenyl)-3-deoxy-3-azido- β -D-glucopyranoside (6): ¹ H NMR (CD ₃ OD, 400 MHz)	S44
14	(2-chloro-4-nitrophenyl)-3-deoxy-3-azido-β-D-glucopyranoside (6): ¹³ C NMR (CD ₃ OD, 100 MHz)	S45
15	(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-glucopyranoside (7): ¹ H NMR (CD ₃ OD, 400 MHz)	S46
16	(2-chloro-4-nitrophenyl)-3-deoxy-3-amino- β -D-glucopyranoside (7): gCOSY NMR (CD ₃ OD, 500 MHz)	S47
17	(2-chloro-4-nitrophenyl)-3-deoxy-3-amino- β -D-glucopyranoside (7): ¹³ C NMR (DMSO- d_6 , 100 MHz)	S48
18	(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-glucopyranoside hydrochloride (7a): ¹ H NMR (D ₂ O, 500 MHz)	S49
19	(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-glucopyranoside hydrochloride (7a): gCOSY NMR (D ₂ O, 500 MHz)	S50
20	(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-glucopyranoside hydrochloride (7a): ¹³ C NMR (D ₂ O, 100 MHz)	S51
21	(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-β-D-glucopyranoside (8): ¹ H NMR (CD ₃ OD, 400 MHz)	S52
22	(2-chloro-4-nitrophenyl)-4-deoxy-4-azido- β -D-glucopyranoside (8): gCOSY NMR (CD ₃ OD, 400 MHz)	S53
23	(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-β-D-glucopyranoside (8): ¹³ C NMR (CD ₃ OD, 100 MHz)	S54
24	(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-D-glucopyranoside (9): ¹ H NMR (CD ₃ OD, 400 MHz)	S55
25	(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-D-glucopyranoside (9): gCOSY NMR (CD₃OD, 400 MHz)	S56
26	(2-chloro-4-nitrophenyl)-4-deoxy-4-amino- β -D-glucopyranoside (9): ¹³ C NMR (CD ₃ OD, 100 MHz)	S57
27	(2-chloro-4-nitrophenyl)-4-deoxy-4-amino- β -D-glucopyranoside hydrochloride (9a): ¹ H NMR (D ₂ O, 500 MHz)	S58
28	(2-chloro-4-nitrophenyl)-4-deoxy-4-amino- β -D-glucopyranoside hydrochloride (9a): ¹³ C NMR (D ₂ O, 125 MHz)	S59
29	(2-chloro-4-nitrophenyl)-2-deoxy-2-azido-β-D-xylopyranoside (10): ¹ H NMR (CD ₃ OD, 500 MHz)	S60
30	(2-chloro-4-nitrophenyl)-2-deoxy-2-azido-β-D-xylopyranoside (10): gCOSY NMR (CD ₃ OD, 500 MHz)	S61
31	(2-chloro-4-nitrophenyl)-2-deoxy-2-azido-β-D-xylopyranoside (10): ¹³ C NMR (CD ₃ OD, 125 MHz)	S62
32	(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-xylopyranoside (11): ¹ H NMR (CD ₃ OD, 400 MHz)	S63
33	(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-xylopyranoside (11): gCOSY (CD ₃ OD, 400 MHz)	S64

34	(2-chloro-4-nitrophenyl)-2-deoxy-2-amino- β -D-xylopyranoside (11): ¹³ C NMR (CD ₃ OD, 100 MHz)	S65
35	(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-xylopyranoside hydrochloride (11a): ¹ H NMR (D ₂ O, 400 MHz)	S66
36	(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-xylopyranoside hydrochloride (11a): gCOSY NMR (D ₂ O, 400 MHz)	S67
37	(2-chloro-4-nitrophenyl)-2-deoxy-2-amino- β -D-xylopyranoside hydrochloride (11a) : ¹³ C NMR (D ₂ O, 100 MHz)	S68
38	(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-β-D-xylopyranoside (12): ¹ H NMR (CD ₃ OD, 400 MHz)	S69
39	(2-chloro-4-nitrophenyl)-4-deoxy-4-azido- β -D-xylopyranoside (12): gCOSY NMR (CD ₃ OD, 400 MHz)	S70
40	(2-chloro-4-nitrophenyl)-4-deoxy-4-azido- β -D-xylopyranoside (12): ¹³ C NMR (CD ₃ OD, 400 MHz)	S71
41	(2-chloro-4-nitrophenyl)-4-deoxy-4-amino- β -D-xylopyranoside (13): ¹ H NMR (CD ₃ OD, 400 MHz)	S72
42	(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-D-xylopyranoside (13): ¹³ C NMR (CD ₃ OD, 400 MHz)	S73
43	(2-chloro-4-nitrophenyl)-4-deoxy-4-amino- β -D-xylopyranoside hydrochloride (13a): ¹ H NMR (D ₂ O, 400 MHz)	S74
44	(2-chloro-4-nitrophenyl)-4-deoxy-4-amino- β -D-xylopyranoside hydrochloride (13a): ¹³ C NMR (D ₂ O, 100 MHz)	S75
45	(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-β-L-xylopyranoside (14): ¹ H NMR (CD ₃ OD, 400 MHz)	S76
46	(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-β-L-xylopyranoside (14): gCOSY NMR (CD ₃ OD, 400 MHz)	S77
47	(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-β-L-xylopyranoside (14): ¹³ C NMR (CD ₃ OD, 400 MHz)	S78
48	(2-chloro-4-nitrophenyl)-4-deoxy-4-amino- β -L-xylopyranoside (15): ¹ H NMR (CD ₃ OD, 500 MHz)	S79
49	(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-L-xylopyranoside (15): gCOSY NMR (CD ₃ OD, 500 MHz)	S80
50	(2-chloro-4-nitrophenyl)-4-deoxy-4-amino- β -L-xylopyranoside (15): ¹³ C NMR (CD ₃ OD, 100 MHz)	S81
51	(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-L-xylopyranoside hydrochloride (15a): ¹ H NMR (D ₂ O, 400 MHz)	S82
52	(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-L-xylopyranoside hydrochloride (15a): gCOSY NMR (DMSO-d6, 500 MHz)	S83
53	(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-L-xylopyranoside hydrochloride (15a): ¹³ C NMR (DMSO- <i>d6</i> , 500 MHz)	S84
54	(2-chloro-4-nitrophenyl)-3-deoxy-3-azido-β-D-xylopyranoside (16): ¹ H NMR (CD ₃ OD, 500 MHz)	S85
55	(2-chloro-4-nitrophenyl)-3-deoxy-3-azido- β -D-xylopyranoside (16): gCOSY NMR (CD ₃ OD, 500 MHz)	S86
56	(2-chloro-4-nitrophenyl)-3-deoxy-3-azido- β -D-xylopyranoside (16): ¹³ C NMR (CD ₃ OD, 125 MHz)	S87
57	(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-xylopyranoside (17): ¹ H NMR (CD₃OD, 500 MHz)	S88
58	(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-xylopyranoside (17): gCOSY NMR (DMSO-d6, 500 MHz)	S89
59	(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-xylopyranoside (17): ¹³ C NMR (DMSO- <i>d6</i> , 500 MHz)	S90
60	(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-xylopyranoside hydrochloride (17a): ¹ H NMR (D ₂ O, 500 MHz)	S91
61	(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-xylopyranoside hydrochloride (17a): gCOSY NMR (D ₂ O, 500 MHz)	S92
62	(2-chloro-4-nitrophenyl)-3-deoxy-3-amino- β -D-xylopyranoside hydrochloride (17a): ¹³ C NMR (D ₂ O, 125 MHz)	S93
63	(2-chloro-4-nitrophenyl)-α-D-arabinopyranoside (18d): ¹ H NMR (CD ₃ OD, 500 MHz)	S94
64	(2-chloro-4-nitrophenyl)-β-D-arabinopyranoside (18d): gCOSY NMR (DMSO-d6, 500 MHz)	S95
65	(2-chloro-4-nitrophenyl)-β-D-arabinopyranoside (18d): ¹³ C NMR (DMSO- <i>d</i> 6 500 MHz)	S96
66	(2-chloro-4-nitrophenyl)-α-L-arabinopyranoside (18): ¹ H NMR (CD₃OD, 400 MHz)	S97

67	(2-chloro-4-nitronhonyl)-g-L-arabinonyranocide (18): ¹³ C NMR (DMSO-d6 100 MHz)	202
67	(2-chloro-4-hittophenyl)-6-deoxy-6-aminoacetyl-8-D-dluconyranoside (19): 1H NMR (CD-OD, 400 MHz)	590
60	(2-chloro-4-nitrophenyl)-6-deoxy-6-aminoacetyl-6-D-dlucopyranoside (19): 11 NMR (CD-OD, 100 MHz)	S100
70	$(2 \text{ chloro-4-nitrophenyl}) = 4 \text{ conv} = 4 \text{ minor active provided (20):}^{1} + \text{NMR} (CD_{2}\text{OD} - 500 \text{ MHz})$	S101
70	(2 chlore 4 nitrophonyl) 2 amine a D glucopyranoside (20): a COSY NMR (CD-OD 500 MHz)	S102
71	(2 chlore 4 pitrophenyl)-2-amino-d-D-glucopyranoside (20). gCOST NNR (CD ₃ OD, 500 NHZ)	S102
72	(2 chlore 4-hittophenyl)-2-amino-d-D-glucopyranoside (20). C NMR (CD ₃ OD, 100 MHz)	5103
73	(2-chioro-4-nitrophenyi)-3,4,6-th-O-acetyi2-deoxy-2-azido-p-D-glucopyranoside (23): H NMR (CDCI3, 400 MHz)	5104
74	(2-chloro-4-nitrophenyl)-3,4,6-tri-O-acetyl2-deoxy-2-azido-β-D-glucopyranoside (23): °C NMR (CDCl ₃ , 125 MHz)	S105
75	(2-chloro-4-nitrophenyl)-2,4,6-tri-O-acetyl-3-deoxy-3-azido-β-D-glucopyranoside (25): 'H NMR (CDCl ₃ ,400 MHz)	S106
76	(2-chloro-4-nitrophenyl)-2,4,6-tri-O-acetyl-3-deoxy-3-azido-β-D-glucopyranoside (25): gCOSY NMR (CDCl ₃ , 400 MHz)	S107
77	(2-chloro-4-nitrophenyl)-2,4,6-tri-O-acetyl-3-deoxy-3-azido-β-D-glucopyranoside (25): ¹³ H NMR (CDCl ₃ , 100 MHz)	S108
78	(2-chloro-4-nitrophenyl)-2,3,6-tri-O-acetyl-4-deoxy-4-azido-β-D-glucopyranoside (27): ¹ H NMR (CDCl ₃ , 500 MHz)	S109
79	(2-chloro-4-nitrophenyl)-2,3,6-tri-O-acetyl-4-deoxy-4-azido-β-D-glucopyranoside (27): ¹³ C NMR (CDCl ₃ , 500 MHz)	S110
80	1-bromo-3,4-di-O-acetyl-2-deoxy-2-azido-α-D-xylopyranoside (29): ¹ H NMR (CDCl _{3,} 400 MHz)	S111
81	1-bromo-3,4-di-O-acetyl-2-deoxy-2-azido- α -D-xylopyranoside (29): gCOSY NMR (CDCl _{3,} 400 MHz)	S112
82	1-bromo-3,4-di-O-acetyl-2-deoxy-2-azido-α-D-xylopyranoside (29): ¹³ C NMR (CDCl _{3,} 100 MHz)	S113
83	(2-chloro-4-nitrophenyl)-3,4-di-O-acetyl-2-deoxy-2-azido-β-D-xylopyranoside (30): ¹ H NMR (CDCl _{3,} 400 MHz)	S114
84	(2-chloro-4-nitrophenyl)-3,4-di-O-acetyl-2-deoxy-2-azido-β-D-xylopyranoside (30): gCOSY NMR (CDCI _{3,} 400 MHz)	S115
85	(2-chloro-4-nitrophenyl)-3,4-di-O-acetyl-2-deoxy-2-azido-β-D-xylopyranoside (30): ¹³ C NMR (CDCI _{3,} 100 MHz)	S116
86	1,2,3-tri- <i>O</i> -benzoyl-β-L-arabinopyranoside (31): ¹ H NMR (CDCl _{3,} 500 MHz)	S117
87	1,2,3-tri- <i>O</i> -benzoyl-β-L-arabinopyranoside (31): ¹³ C NMR (CDCl ₃ , 100 MHz)	S118
88	1,2,3-tri- <i>O</i> -benzoyl-β-D-arabinopyranoside (32): ¹ H NMR (CDCl _{3,} 500 MHz)	S119
89	1,2,3-tri-O-benzoyl-β-D-arabinopyranoside (32): gCOSY NMR (CDCl _{3,} 500 MHz)	S120
90	1,2,3-tri-O-benzoyl-β-D-arabinopyranoside (32): ¹³ C NMR (CDCl ₃ , 100 MHz)	S121
91	1,2,3,4-tetra-O-benzoyl-β-L-arabinopyranoside (33): ¹ H NMR (CDCl₃, 500 MHz)	S122
92	1,2,3,4-tetra-O-benzoyl-β-L-arabinopyranoside (33): ¹³ C NMR (CDCl _{3,} 100 MHz)	S123
93	1,2,3,4-tetra-O-benzoyl-α-D-arabinopyranoside (34): ¹ H NMR (CDCl₃, 400 MHz)	S124
94	1,2,3,4-tetra- <i>O</i> -benzoyl-α-D-arabinopyranoside (34): gCOSY NMR (CDCl _{3,} 400 MHz)	S125
95	1,2,3,4-tetra- <i>O</i> -benzoyl-α-D-arabinopyranoside (34): ¹³ C NMR (CDCl _{3,} 100 MHz)	S126
96	1,2,3-tri-O-benzoyl-4-deoxy-4-azido-α-D-xylopyranoside (35): ¹ H NMR (CDCl ₃ 500 MHz)	S127
97	1,2,3-tri-O-benzoyl-4-deoxy-4-azido-α-D-xylopyranoside (35): ¹³ C NMR (CDCl ₃ 100 MHz)	S128
98	1.2.3-tri-O-benzoyl-4-deoxy-4-azido-α-L-xylopvranoside (36): ¹ H NMR (CDCI ₃ 500 MHz)	S129
99	1,2,3-tri-O-benzoyl-4-deoxy-4-azido-α-L-xylopvranoside (36): αCOSY NMR (CDCl₂ 500 MHz)	S130
100	1,2,3-tri-O-benzoyl-4-deoxy-4-azido-α-L-xylopyranoside (36): ¹³ C NMR (CDCl ₃ 125 MHz)	S131

101	1-bromo-2,3-di-O-benzoyl-4-deoxy-4-azido- α -D-xylopyranoside (37): ¹ H NMR (CD ₃ Cl 400 MHz)	S132
102	1-bromo-2,3-di-O-benzoyl-4-deoxy-4-azido- α -D-xylopyranoside (37): ¹³ C NMR (CD ₃ Cl, 100 MHz)	S133
103	1-bromo-2,3-di-O-benzoyl-4-deoxy-4-azido-α-L-xylopyranoside (38): ¹ H NMR (CDCl _{3,} 400 MHz)	S134
104	1-bromo-2,3-di-O-benzoyl-4-deoxy-4-azido- α -L-xylopyranoside (38): ¹³ C NMR (CDCl ₃ , 100 MHz)	S135
105	(2-chloro-4-nitrophenyl)-2,3-di-O-benzoyl4-deoxy-4-azido-β-D-xylopyranoside (39): ¹ H NMR (CDCl ₃ , 400 MHz)	S136
106	(2-chloro-4-nitrophenyl)-2,3-di-O-benzoyl4-deoxy-4-azido-β-D-xylopyranoside (39): ¹³ H NMR (CDCl _{3,} 100 MHz)	S137
107	(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-2,3-di-O-benzoyl-β-L-xylopyranoside (40): ¹ H NMR (CDCl _{3,} 500 MHz)	S138
108	(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-2,3-di-O-benzoyl-β-L-xylopyranoside (40): ¹³ C NMR (CDCl ₃ , 125 MHz)	S139
109	1,2,3-tri-O-acetyl-4-deoxy-4-azido-L-xylopyranoside (41): ¹ H NMR (CDCl _{3,} 500 MHz)	S140
110	1,2,3-tri-O-acetyl-4-deoxy-4-azido-L-xylopyranoside (41): gCOSY NMR (CDCl ₃ , 500 MHz)	S141
111	1,2,3-tri-O-acetyl-4-deoxy-4-azido-L-xylopyranoside (41): ¹³ C NMR (CDCl ₃ , 125 MHz)	S142
112	1-bromo-2,3-di-O-acetyl-4-deoxy-4-azido-α-L-xylopyranoside (42): ¹ H NMR (CDCl _{3,} 400 MHz)	S143
113	1-bromo-2,3-di-O-acetyl-4-deoxy-4-azido-α-L-xylopyranoside (42): gCOSY NMR (CDCl _{3,} 400 MHz)	S144
114	1-bromo-2,3-di-O-acetyl-4-deoxy-4-azido- α -L-xylopyranoside (42): ¹³ C NMR (CDCl ₃ , 100 MHz)	S145
115	(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-2,3-di-O-acetyl-β-L-xylopyranoside (43): ¹ H NMR (CDCl _{3,} 500 MHz)	S146
116	(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-2,3-di-O-acetyl-β-L-xylopyranoside (43): gCOSY NMR (CDCl _{3,} 500 MHz)	S147
117	(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-2,3-di-O-acetyl-β-L-xylopyranoside (43): ¹³ C NMR (CDCl _{3,} 125 MHz)	S148
118	1,2,3,4-tetra-O-benzoyl- α -D-ribopyranoside (44): ¹ H NMR (CDCl _{3,} 500 MHz)	S149
119	1,2,3,4-tetra-O-benzoyl-α-D-ribopyranoside (44): gCOSY NMR (CDCl _{3,} 500 MHz)	S150
120	1,2,3,4-tetra- <i>O</i> -benzoyl-α-D-ribopyranoside (44): ¹³ C NMR (CDCl _{3,} 100 MHz)	S151
121	1,2,4-tri- <i>O</i> -benzoyl-α-D-ribopyranoside (45a): ¹ H NMR (CDCl _{3,} 500 MHz)	S152
122	1,2,4-tri- <i>O</i> -benzoyl-α-D-ribopyranoside (45a): gCOSY NMR (CDCl₃, 500 MHz)	S153
123	1,2,4-tri- <i>O</i> -benzoyl-α-D-ribopyranoside (45a): ¹³ C NMR (CDCl ₃ , 100 MHz)	S154
124	1,3,4-tri- <i>O</i> -benzoyl-α-D-ribopyranoside (45b): ¹ H NMR (CDCl _{3,} 500 MHz)	S155
125	1,3,4-tri- <i>O</i> -benzoyl-α-D-ribopyranoside (45b): gCOSY NMR (CDCl _{3,} 500 MHz)	S156
126	1,3,4-tri- <i>O</i> -benzoyl-α-D-ribopyranoside (45b): ¹³ C NMR (CDCl ₃ , 125 MHz)	S157
127	1,2,3-tri-O-benzoyl-α-D-ribofuranoside (45c): ¹ H NMR (CDCl _{3,} 500 MHz)	S158
128	1,2,3-tri-O-benzoyl-α-D-ribofuranoside (45c): gCOSY NMR (CDCl _{3,} 500 MHz)	S159
129	1,2,3-tri-O-benzoyl-α-D-ribofuranoside (45c): ¹³ C NMR (CDCl _{3,} 125 MHz)	S160
130	1,2,3-tri- <i>O</i> -benzoyl-α-D-ribopyranoside (45d): ¹ H NMR (CDCl ₃ ,500 MHz)	S161
131	1,2,3-tri-O-benzoyl-α-D-ribopyranoside (45d): gCOSY NMR (CDCl _{3,} 125 MHz)	S162
132	1,2,3-tri- <i>O</i> -benzoyl-α-D-ribopyranoside (45d): ¹³ C NMR (CDCl _{3,} 125 MHz)	S163
133	3-deoxy-3-azido-1,2,4-tri-O-benzoyl-D-xylopyranoside (46): ¹ H NMR (CDCl _{3,} 500 MHz)	S164
134	3-deoxy-3-azido-1,2,4-tri-O-benzoyl-D-xylopyranoside (46): gCOSY NMR (CDCl ₃ , 500 MHz)	S165

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135	3-deoxy-3-azido-1,2,4-tri-O-benzoyl-D-xylopyranoside (46): ¹³ C NMR (CDCl _{3,} 125 MHz)	S166
136	(2-chloro-4-nitrophenyl)-3-deoxy-3-azido-2,4-di-O-benzoyl-β-D-xylopyranoside (47): ¹ H NMR (CDCl ₃ , 500 MHz)	S167
137	(2-chloro-4-nitrophenyl)-3-deoxy-3-azido-2,4-di-O-benzoyl-β-D-xylopyranoside (47): gCOSY NMR (CDCl _{3,} 500 MHz)	S168
138	(2-chloro-4-nitrophenyl)-3-deoxy-3-azido-2,4-di-O-benzoyl-β-D-xylopyranoside (47): ¹³ C NMR (CDCl ₃ , 125 MHz)	S169
139	1-bromo-2,3,4-tri- <i>O</i> -benzoyl-β-L-arabinopyranoside (48): ¹ H NMR (CDCl _{3,} 500 MHz)	S170
140	1-bromo-2,3,4-tri-O-benzoyl-β-L-arabinopyranoside (48): ¹³ C NMR (CDCl _{3,} 100 MHz)	S171
141	1-bromo-2,3,4-tri-O-benzoyl-α-D-arabinopyranoside (49): ¹ H NMR (CDCl _{3,} 400 MHz)	S172
142	1-bromo-2,3,4-tri-O-benzoyl-α-D-arabinopyranoside (49): gCOSY NMR (CDCl ₃ , 400 MHz)	S173
143	1-bromo-2,3,4-tri-O-benzoyl-α-D-arabinopyranoside (49): ¹³ C NMR (CDCl _{3,} 100 MHz)	S174
144	(2-chloro-4-nitrophenyl)-2,3,4-tri-O-benzoyl-α-L-arabinopyranoside (50): ¹ H NMR (CDCl ₃ , 500 MHz)	S175
145	(2-chloro-4-nitrophenyl)-2,3,4-tri-O-benzoyl-α-L-arabinopyranoside (50): ¹³ C NMR (CDCl _{3,} 100 MHz)	S176
146	(2-chloro-4-nitrophenyl)-2,3,4-tri-O-benzoyl-β-D-arabinopyranoside (51): ¹ H NMR (CDCl _{3,} 500 MHz)	S177
147	(2-chloro-4-nitrophenyl)-2,3,4-tri-O-benzoyl-β-D-arabinopyranoside (51): gCOSY (CDCl ₃ , 500 MHz)	S178
148	(2-chloro-4-nitrophenyl)-2,3,4-tri-O-benzoyl-β-D-arabinopyranoside (51): ¹³ C NMR (CDCl ₃ , 125 MHz)	S179
149	1,2,3,4-tetra-O-benzoyl-α-L-arabinopyranoside (52): ¹ H NMR (CDCl _{3,} 500 MHz)	S180
150	1,2,3,4-tetra-O-benzoyl-α-L-arabinopyranoside (52): ¹³ C NMR (CDCl _{3,} 100 MHz)	S181
151	1,2,3,4-tetra- <i>O</i> -benzoyl-β-D-arabinopyranoside (53): ¹ H NMR (CDCl _{3,} 500 MHz)	S182
152	1,2,3,4-tetra-O-benzoyl-β-D-arabinopyranoside (53): gCOSY NMR (CDCl _{3,} 500 MHz)	S183
153	1,2,3,4-tetra-O-benzoyl-β-D-arabinopyranoside (53): ¹³ C NMR (CDCl _{3,} 125 MHz)	S184

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8.322 8.316 8.185	7 415 7 396	5.205 5.190	4.852	3.568 3.553 3.345 3.345 3.345 3.309 3.309 3.309 3.309
$\forall 2$	\searrow	\checkmark		





S32



(2-chloro-4-nitrophenyl)-6-deoxy-6-amino- β -D-glucopyranoside (3): gCOSY (CD₃OD, 500 MHz)

 NH_2

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HO HO

S33

(2-chloro-4-nitrophenyl)-6-deoxy-6-amino- β -D-glucopyranoside (**3**): ¹³C NMR (D₂O, 125 MHz)

$$-157.401$$

$$-142.734$$

$$-142.734$$

$$-142.6573$$

$$-123.662$$

$$-115.621$$

$$-115.621$$

$$-99.979$$

$$-99.979$$

$$-99.979$$

$$-91.570$$









S35

(2-chloro-4-nitrophenyl)-6-deoxy-6-amino- β -D-glucopyranoside hydrochloride (**3a**): ¹³C NMR (D₂O, 125 MHz)

157.371	142.664	126.517 124.574 123.685	115.692	99.993	75 145 72 635 72 635 72 635 71 142 71 142 62 808	40.616
		512				1



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200 190 180 170 160) 150 140 130 120	0 110 100 90 80	70 60 50	40 30 20 10 0

S36


(2-chloro-4-nitrophenyl)-2-deoxy-2-azido-β-D-glucopyranoside (4): ¹H NMR (CD₃OD, 500 MHz)

(2-chloro-4-nitrophenyl)-2-deoxy-2-azido- β -D-glucopyranoside (4): ¹³C NMR (CD₃OD, 125 MHz)

















(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-glucopyranoside hydrochloride (**5a**): ¹³C NMR (CD₃OD, 125 MHz)

156.329	143.298	126.558 124.530 124.019	116.696	96.743	77.041	72 138 69 613	60.345	55.513
1		\leq				11		









(2-chloro-4-nitrophenyl)-3-deoxy-3-azido- β -D-glucopyranoside (6): ¹³C NMR (CD₃OD, 100 MHz)









(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-glucopyranoside (7): ¹H NMR (CD₃OD, 400 MHz)



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(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-glucopyranoside hydrochloride (**7a**): gCOSY NMR (D₂O, 500 MHz)

 $(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-\beta-D-glucopyranoside \ hydrochloride \ \textbf{(7a):}\ ^{13}C \ NMR \ \textbf{(D}_2O, \ 100 \ MHz)$







OH N3O OH OH OH OH NO₂







(2-chloro-4-nitrophenyl)-4-deoxy-4-amino- β -D-glucopyranoside (**9**): ¹H NMR (CD₃OD, 400 MHz)

304 297 193 186 169 163	433 410	177 158 848	727 684 566 566 499 481 481 481 3310 3310 298 298 298 790 765 765
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	\mathbf{Y}	\vee 1	











(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-D-glucopyranoside hydrochloride (**9a**): ¹H NMR (D₂O, 500 MHz)



(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-D-glucopyranoside hydrochloride (**9a**): ¹³C NMR (D₂O, 125 MHz)

157.338	142 <u>.</u> 664	126 424 124 539 123 669	115.880	100.052	73.079 72.799 71.929	60.761	52.604
		$\langle \langle \rangle$			$\langle \rangle$		





(2-chloro-4-nitrophenyl)-2-deoxy-2-azido- β -D-xylopyranoside (**10**): ¹H NMR (CD₃OD, 500 MHz)

483 317 143 143 143 143 355 3355 195 177 177	867	304 288 125 884 803 803	076 000 966	647 633 550 551 437 437 311 272 272	011 928
8 88800-8	2.2	000444	4 4 M		7 12
	Y	∇	5		57





(2-chloro-4-nitrophenyl)-2-deoxy-2-azido-β-D-xylopyranoside (**10**): gCOSY NMR (CD₃OD, 500 MHz)





(2-chloro-4-nitrophenyl)-2-deoxy-2-azido- β -D-xylopyranoside (**10**): ¹³C NMR (CD₃OD, 125 MHz)













(2-chloro-4-nitropher	nyl)-2-deox	y-2-amino-	β-D-xylop	yranoside (11): ¹³ C	; NMR (CD ₃ OD	100 MHz
•					J	/ -		- 0	

125.499 123.755	115.920	102.318	75.449	69.695	66.150	56.539
17						





(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-xylopyranoside hydrochloride (**11a**): ¹H NMR (D₂O, 400 MHz)



(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-xylopyranoside hydrochloride (**11a**): gCOSY NMR (D₂O, 400 MHz)

ĊI Ο HO `₩H₃CĪ NO₂



(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-xylopyranoside hydrochloride (**11a**): ¹³C NMR (D₂O, 100 MHz)

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HO HO





(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-β-D-xylopyranoside (**12**): ¹H NMR (CD₃OD, 400 MHz)





(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-β-D-xylopyranoside (**12**): gCOSY NMR (CD₃OD, 400 MHz)





(2-chloro-4-nitrophenyl)-4-deoxy-4-azido- β -D-xylopyranoside (**12**): ¹³C NMR (CD₃OD, 400 MHz)



(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-D-xylopyranoside (**13**): ¹H NMR (CD₃OD, 400 MHz)

87 82 030027	0 8 0	NU000000000000000000000000000000000000	\sim	4002
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33 20 77775	~ ~ ∞	തതതാന നെസസയയയയ	œ	7 7 7 10
888888	4 2	<i></i>	÷.	\leftarrow \leftarrow \leftarrow
	$\overline{\mathbf{v}}$			\searrow








(2-chloro-4-nitrophenyl)-4-deoxy-4-amino- β -D-xylopyranoside hydrochloride (**13a**): ¹³C NMR (D₂O, 100 MHz)

NO₂

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(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-β-L-xylopyranoside (**14**): ¹H NMR (CD₃OD, 400 MHz)

8 298 8 291 8 175 8 168 8 168 8 152 8 145	7 363 7 340	9015578 901
	\mathbf{Y}	









(2-chloro-4-nitrophenyl)-4-deoxy-4-azido- β -L-xylopyranoside (14): ¹³C NMR (CD₃OD, 400 MHz)







(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-L-xylopyranoside (**15**): ¹H NMR (CD₃OD, 500 MHz)



0.5

(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-L-xylopyranoside (**15**): gCOSY NMR (CD₃OD, 500 MHz)





.

(2-chloro-4-nitrophenyl)-4-deoxy-4-amino- β -L-xylopyranoside (**15**): ¹³C NMR (CD₃OD, 100 MHz)

— 157.993

^{125.556} ^{123.714} ^{123.616}		— 101.336	76.061 73.305		— 52.133
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Т



f1 (ppm)





(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-L-xylopyranoside hydrochloride (**15a**): gCOSY NMR (DMSO-*d6*, 500 MHz)







(2-chloro-4-nitrophenyl)-3-deoxy-3-azido-β-D-xylopyranoside (**16**): ¹H NMR (CD₃OD, 500 MHz)







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Z-Chioro-4-hitrophenvi)3-(1e0xv-3-azido-13-17-	-xviopvranoside (16		D 125 MHZ
				, 120 Mili 12





(2-chloro-4-nitrophenyl)-3-deoxy-3-amino- β -D-xylopyranoside (17): ¹H NMR (CD₃OD, 500 MHz)



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(2-chloro-4-nitrophenyl)-3-deoxy-3-amino- β -D-xylopyranoside (**17**): ¹³C NMR (DMSO-*d* β , 500 MHz)













(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-xylopyranoside hydrochloride (**17a**): gCOSY NMR (D₂O, 500 MHz)

_HO CIH₃N

 $(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-\beta-D-xylopyranoside hydrochloride (17a):$ ¹³C NMR (D₂O, 125 MHz)

157.202	142.908	126.519 124.562 123.772	115.960	100.711	39.153 36.645 35.762	57.805
		SYZ -			552	Ĩ







(2-chloro-4-nitrophenyl)-β-D-arabinopyranoside (**18d**): ¹H NMR (CD₃OD, 500 MHz)

10.0

9.5

9.0

8.5

8.0

7.5

6.5

7.0

S94

5.0

4.5

4.0

3.5

3.0

2.5

2.0

1.5

1.0

0.5

5.5

6.0



(2-chloro-4-nitrophenyl)-β-D-arabinopyranoside (**18d**): gCOSY NMR (DMSO-*d6*, 500 MHz)

(2-chloro-4-nitrophenyl)-β-D-arabinopyranoside (18d): ¹³C NMR (DMSO-*d*6, 500 MHz)

- 142.147	- 126.277 - 124.946 - 123.129	- 116.407	- 101.226	- 72.961 - 70.670 - 67.811
	\sim			





(2-chloro-4-nitrophenyl)-α-L-arabinopyranoside (**18**): ¹H NMR (CD₃OD, 400 MHz)



(2-chloro-4-nitrophenyl)- α -L-arabinopyranoside (**18**): ¹³C NMR (DMSO-*d6*, 100 MHz)









(2-chloro-4-nitrophenyl)-2-amino-α-D-glucopyranoside (**20**): ¹H NMR (CD₃OD 500 MHz)



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F1 (ppm)

D

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22



(2-chloro-4-nitrophenyl)-3,4,6-tri-O-acetyl-2-deoxy-2-azido-β-D-glucopyranoside (23): ¹H NMR (CDCl₃, 400 MHz)









(2-chloro-4-nitrophenyl)-2,4,6-tri-O-acetyl-3-deoxy-3-azido-β-D-glucopyranoside (25): ¹H NMR (CDCl₃, 400 MHz)

OAc

AcQ´







(2-chloro-4-nitrophenyl)-2,4,6-tri-O-acetyl-3-deoxy-3-azido-β-D-glucopyranoside (**25**): gCOSY NMR (CDCl₃, 400 MHz)

Ac








(2-chloro-4-nitrophenyl)-2,3,6-tri-O-acetyl-4-deoxy-4-azido-β-D-glucopyranoside (27): ¹³C NMR (CDCl₃, 500 MHz)

170.521 170.065 169.569	$<^{157441}_{157406}$	143.547	 126.469 125.224 123.875 116.776 	99.514	$\int 77.571$ $\int 77.316$ 77.062 77.062 73.363 77.73.166 71.011 -62.687 -59.898	$\bigwedge^{20.969}_{20.830}$
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1-bromo-3,4-di-O-acetyl-2-deoxy-2-azido-α-D-xylopyranoside (**29**): ¹H NMR (CDCl₃, 400 MHz)













 $(2-chloro-4-nitrophenyl)-3, 4-di-O-acetyl-2-deoxy-2-azido-\beta-D-xylopyranoside (\textbf{30}): {}^{1}H \text{ NMR (CDCl}_{3,} 400 \text{ MHz})$









(2-chloro-4-nitrophenyl)-3,4-di-O-acetyl-2-deoxy-2-azido-β-D-xylopyranoside (**30**): ¹³C NMR (CDCl₃, 100 MHz)

< 170.085 < 169.892	— 156.970	— 143.226	126.515 124.795 123.869 -115.910	99.840	∫ 77.563 ∫ 77.245 76.927				$\int_{-20.975}^{-21.258}$	
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1,2,3-tri-O-benzoyl- β -L-arabinopyranoside (**31**): ¹H NMR (CDCl₃, 500 MHz)

123 077 062 062 979 964 859 859 578	383 297 224 798 790	231 126 105 896 890 875 869	550 246 032 788	
88888877777	~ ~ ~ 99	ບ ບ ບ ບ ບ ບ	4 4 4 C	
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-------0.001

1,2,3-tri-O-benzoyl-β-L-arabinopyranoside (**31**): ¹³C NMR (CDCl₃, 100 MHz)

171.595	166.133 165.695 164.902	133.768 133.528 133.371 129.817	129.198 129.053 128.889 128.889 128.371 128.377 128.377	91.447	77 551 77 232 76 913	70.989	65.040	60.557	
					5				

--- 21.015 --- 14.138





1,2,3-tri-*O*-benzoyl-β-D-arabinopyranoside (**32**): ¹H NMR (CDCl₃, 500 MHz)











1,2,3-tri-O-benzoyl- β -D-arabinopyranoside (**32**): ¹³C NMR (CDCl₃, 100 MHz)

$ \begin{array}{c} 7.166.147 \\ 165.794 \\ 164.966 \\ 133.357 \\ 133.35$		()	ų -,	,		
	166.147 165.794 164.966		(129.164 128.910 128.510 128.581 128.592 128.592	— 91.560	$\frac{77.580}{77.680}$ $\frac{77.580}{76.944}$ $\frac{68.000}{64.993}$ -60.646	





1,2,3,4-tetra-O-benzoyl-β-L-arabinopyranoside (**33**): ¹H NMR (CDCl₃, 500 MHz)

8 281 8 046 8 045 7 345	7 421 7 406 7 359 7 260 7 115 7 115 7 097	6.277 6.266	5.954 5.805	C67 4	4.404	4 166 4 142
		\leq	11			





1,2,3,4-tetra-O-benzoyl-β-L-arabinopyranoside (**33**): ¹³C NMR (CDCl₃, 100 MHz)

- 165.600 - 165.501 - 165.153 - 164.783	- 156.937	- 133.758 - 133.645 - 133.549	- 128 464 - 125 353 - 124 531	- 116.228	- 92.344	- 77 332 - 77 014 - 76 696	- 69 847 - 68 831 - 67 491
							SIZ.





1,2,3,4-tetra-O-benzoyl- α -D-arabinopyranoside (**34**): ¹H NMR (CDCl₃, 400 MHz)

8.163 8.161 8.151 8.151 8.151 8.144 8.144 8.134 8.134	7.890	7 576 7 465 7 409 7 238	6 954 6 948 6 921	6.170 6.164 6.164 6.144 6.141 6.137 6.117 6.117 6.117 5.966	4.472 4.441 4.234 4.229 4.229 4.195
		5571	\checkmark		







1,2,3,4-tetra-O-benzoyl-α-D-arabinopyranoside (**34**): gCOSY NMR (CDCl₃, 400 MHz)

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1,2,3,4-tetra-O-benzoyl-α-D-arabinopyranoside (**34**): ¹³C NMR (CDCl₃, 100 MHz)

	— 171.231	165.974 165.942 164.930 164.930	134.079 133.807 133.700 123.500 123.566	129.416 129.078 129.0078 129.001 128.881 128.669 128.669	91.408	$ \frac{77\ 803}{77\ 165} $ $ \frac{77\ 68\ 533}{68\ 157} $	63.339 60.567		— 21.246	
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1,2,3-tri-O-benzoyl-4-deoxy-4-azido-α-D-xylopyranoside (**35**): ¹H NMR (CDCl₃, 500 MHz)

8 132 8 116 8 116 8 049 8 034 8 034 8 034 8 032 7 985 7 971 7 887 7 882 7 881 7 881	7 547 7 459 7 381 7 261 6 730 6 723	5.058 5.038 5.038 5.665 5.539 5.539 5.539 5.519	4 113 4 119 4 108 4 093 4 077 4 077 3 936 3 936 3 910 3 884 3 884
	11/ Y		

N₃ BzO BzÒ ÓВz



1,2,3-tri-*O*-benzoyl-4-deoxy-4-azido- α -D-xylopyranoside (**35**): ¹³C NMR (CDCl₃, 100 MHz)

165 691 165 421 164 529	133.943 133.645 133.546 133.546 129.946 128.806 128.806 128.806 128.437 128.416 128.416	90.168	77 395 77 077 76 759	70.991 70.350	. 61 946 . 59 434
\lor			5		1





1,2,3-tri-*O*-benzoyl-4-deoxy-4-azido-α-L-xylopyranoside (**36**): ¹H NMR (CDCl₃, 500 MHz)

115 100 098 013 013 876 859 859 859	521 449 393 250 250 699	033 014 995 516 508 495 488	093 087 064 068 0068 0069 0069 0038 0038 0038 0038 0038 0038 0038 003
2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	NNN 99	ນນນນ ນບບ	44444444000





1,2,3-tri-O-benzoyl-4-deoxy-4-azido-α-L-xylopyranoside (**36**): gCOSY NMR (CDCl₃, 500 MHz)





1,2,3-tri-O-benzoyl-4-deoxy-4-azido-α-L-xylopyranoside (**36**): ¹³C NMR (CDCl₃, 125 MHz)

					⁶² 2 ⁵⁹ 7 ⁵⁹ 7 ⁵⁹ 7 ⁵⁹ 7 ⁵⁹ 7 ⁵⁹ 7 ⁶² 3
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1-bromo-2,3-di-O-benzoyl-4-deoxy-4-azido-α-D-xylopyranoside (**37**): ¹H NMR (CD₃Cl, 400 MHz)

209/ 2012 2012 2012 2012 2012 2012 2012 201	5.743 5.733	5 980 5 976 5 956 5 951 5 932	5 174 5 164 5 149 5 139	1 151 1 106 1 106 1 106 1 106 1 1075 1 075 1 075 1 075 1 075 1 003 3 995 3 995 3 995 3 995 3 995 3 995 3 995 3 995 3 995 5 995
	$\overset{\circ}{\vee}$			





1-bromo-2,3-di-*O*-benzoyl-4-deoxy-4-azido-α-D-xylopyranoside (**37**): ¹³C NMR (CD₃Cl, 100 MHz)

165.341	133.825 133.610 130.040 128.752 128.551 128.551 128.557 128.577 128.577	87.681	77 392 77 073 76 755	71 336 71 112	63.752	58.797	22.665
		ţ	\sim	\lor			

— 14.162





1-bromo-2,3-di-O-benzoyl-4-deoxy-4-azido- α -L-xylopyranoside (38): ¹H NMR (CDCl₃, 400 MHz)

000040	6 6 9 7 7	<u><u> </u></u>	1 2 0		00-40010040
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— 1.256

1-bromo-2,3-di-O-benzoyl-4-deoxy-4-azido-α-L-xylopyranoside (38): ¹³C NMR (CDCl₃, 100 MHz)

134.022 133.801 130.275 130.037 129.028 128.538 128.538	87.834	77 542 77 225 76 907	71 585 71 353	63.982	59.069	
	ł	5	arphi			





(2-chloro-4-nitrophenyl)-2,3-di-O-benzoyl4-deoxy-4-azido-β-D-xylopyranoside (39): ¹H NMR (CDCl₃, 400 MHz)

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	2880 5030007/805007 53
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(2-chloro-4-nitrophenyl)-2,3-di-O-benzoyl4-deoxy-4-azido-β-D-xylopyranoside (**39**): ¹³H NMR (CDCl₃, 100 MHz)







(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-2,3-di-O-benzoyl-β-L-xylopyranoside (**40**): ¹H NMR (CDCl₃, 500 MHz)



(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-2,3-di-O-benzoyl-β-L-xylopyranoside (**40**): ¹³C NMR (CDCl₃, 125 MHz)







1,2,3-tri-O-acetyl-4-deoxy-4-azido-L-xylopyranoside (41): ¹H NMR (CDCl_{3,} 500 MHz)





N₃ AcO







1,2,3-tri-O-acetyl-4-deoxy-4-azido-L-xylopyranoside (41): ¹³C NMR (CDCl₃, 125 MHz)

70.115 69.7616 69.261 69.261 69.166	12.454 19.641	7 555 7 300 7 046	0.705 9.715	14 292 1865 1865 19364 18.767 18.767	11.138 11.019 0.982 0.915 0.832 0.742
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1-bromo-2,3-di-O-acetyl-4-deoxy-4-azido-α-L-xylopyranoside (42): ¹H NMR (CDCl₃, 400 MHz)






1-bromo-2,3-di-O-acetyl-4-deoxy-4-azido-α-L-xylopyranoside (42): ¹³C NMR (CDCl₃, 100 MHz)

170.134 169.681	87.619	77 243 76 924	70.998 70.719	63.711	58.776	
\mathbf{Y}		\leq	$\mathbf{\nabla}$			





(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-2,3-di-O-acetyl-β-L-xylopyranoside (**43**): ¹H NMR (CDCl₃, 500 MHz)







(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-2,3-di-O-acetyl-β-L-xylopyranoside (43): gCOSY NMR (CDCl₃, 500 MHz)

 $(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-2, 3-di-O-acetyl-\beta-L-xylopyranoside (\textbf{43}): {}^{13}C \text{ NMR (CDCl}_{3}, 125 \text{ MHz})$

< 169.952 < 169.623	— 157.236	— 143.266	 126.482 124.887 123.998 	— 116.201	98.785	77 554 77 300 77 045				∠ 20.997 20.910
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1,2,3,4-tetra-O-benzoyl- α -D-ribopyranoside (44): ¹H NMR (CDCl₃, 500 MHz)

117 105 105 105 105 105 105 105 105 105 105	634 627 230	949 949 803 803 803 803 803 803 803 803 807 108 108 007 108 007 108 007 108 007 108 007 108 007 108 007 108 007 108 007 108 108 108 108 108 108 108 108 108 108	940 883	039 036 036 630 616 602 586 573
88888877777777777777777777777777	9999	00 00004444444444	2 2	~~~~~~
	\mathcal{V}		57	









1,2,3,4-tetra-O-benzoyl- α -D-ribopyranoside (44): ¹³C NMR (CDCl₃, 100 MHz)

1/1.024	166 184 165 817 165 575 164 561	134 178 133 923 133 682 133 649 133 528	130.283 130.027 129.577 129.419 128.935 128.691 128.615	92.397	77 622 77 304 76 986	67 381 66 899 63 415
					\searrow	\leq

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1,2,4-tri-O-benzoyl-α-D-ribopyranoside (**45a**): ¹H NMR (CDCl₃, 500 MHz)

$\begin{array}{c} 112\\ 0.059\\ 0.031\\ 0.031\\ 0.032\\ 0.03$	504 345 256	829 820 559	421 415 021 513	450 350 335 335 320 652	307 201 059 059 031 031 928 928	316	825 759	122 000 994 863	556 328 200	965 952 927 912 897 879
88888888887777777	アファ	000	വായ	00004	4444400	e	2 2	N N		000000
	551	\checkmark	V1-			1	57	$\overline{4}$		









1,2,4-tri-O-benzoyl-α-D-ribopyranoside (**45a**): ¹³C NMR (CDCl₃, 100 MHz)

-171480 -166.044 -166.004 -166.004 -166.004 -166.004 -166.004 -166.004 -166.004 -166.004 -133.050 -133.050 -133.050 -133.050 -128.050 -128.650 -128.650 -128.650 -128.650	\sim 92.216 \sim 90.521 \sim 90.5216 \sim 90.5216 \sim 90.5216 \sim 90.5216 \sim 90.5216 \sim 90.5216 \sim 77.040 \sim 90.525 \sim 90.525 \sim 90.225 \sim 90.225 \sim 90.225 \sim 90.226 \sim 90.521 \sim	→ 21.225 19.331 14.396
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1,3,4-tri-*O*-benzoyl-α-D-ribopyranoside (**45b**): ¹H NMR (CDCl₃, 500 MHz)







1,3,4-tri-O-benzoyl- α -D-ribopyranoside (**45b**): gCOSY NMR (CDCl₃, 500 MHz)





1,3,4-tri-O-benzoyl-α-D-ribopyranoside (**45b**): ¹³C NMR (CDCl₃, 125 MHz)

166.108 165.858 165.657 165.361 164.717	$\int_{-1}^{-1} \frac{134.102}{133.782}$ $\int_{-1}^{-1} \frac{133.746}{133.648}$ $\int_{-1}^{-1} \frac{133.548}{33.509}$	L 129.915 L 129.915 L 128.967 L 128.793 L 128.670 L 128.637	~ 94.671 - 92.384 - 89.543	77.606 77.288 76.970 68.421 68.044 - 66.605 - 63.291
			1 I I	





1,2,3-tri-O-benzoyl-α-D-ribofuranoside (**45c**): ¹H NMR (CDCl₃, 500 MHz)









1,2,3-tri-O-benzoyl- α -D-ribofuranoside (**45c**): gCOSY NMR (CDCl₃, 500 MHz)



1,2,3-tri-O-benzoyl- α -D-ribofuranoside (**45c**): ¹³C NMR (CDCl₃, 125 MHz)

167.037 166.638 164.574	134.107 133.752 133.752 133.640 130.290 130.290 130.224 129.866 129.560 129.560 129.560 128.671 128.671 128.671	92.293	77 719 77 465 77 210	69.957 65.534 63.184 60.714	21.277	14.458
$\langle \rangle \rangle$			\sim	/ /		





1,2,3-tri-*O*-benzoyl-α-D-ribopyranoside (**45d**): ¹H NMR (CDCl₃, 500 MHz)

000000000000000000000000000000000000	4 4 4 5 5 5 5 5 5 5 5 5 5	535 506 448 354 354 3354 3354 670 670	419 235 110 070 029 928	135 877 815	034 020 015 884 603	559 559
888888888888888888888888888888888888888	000000VVVV	44 2222	4 44440	NN 3	7 7000	





1,2,3-tri-O-benzoyl-α-D-ribopyranoside (**45d**): gCOSY NMR (CDCl₃, 125 MHz)

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1,2,3-tri-O-benzoyl-α-D-ribopyranoside (45d): ¹³C NMR (CDCl₃, 125 MHz)

$\frac{166.072}{165.463}$	<pre>134.189 133.982 133.945 133.945 133.945 130.111 129.267 128.969 128.969 128.951 128.820</pre>	92.200 77.663 77.409	Z 69.372 69.033 C 66.087 66.087
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HO BZO OBZ



---- 14.482

3-deoxy-3-azido-1,2,4-tri-O-benzoyl-D-xylopyranoside (46): ¹H NMR (CDCl₃, 500 MHz)







3-deoxy-3-azido-1,2,4-tri-O-benzoyl-D-xylopyranoside (46): gCOSY NMR (CDCl₃, 500 MHz)





3-deoxy-3-azido-1,2,4-tri-O-benzoyl-D-xylopyranoside (46): ¹³C NMR (CDCl₃, 125 MHz)

165.685 165.670 165.537 165.534 165.427 165.427 165.427 165.427 165.427 165.427 165.427 165.378 165.378 165.378 165.378 165.378 165.378 165.378 165.378 165.358 133.959 133.959 133.959 133.959 133.158 133.959 133.158 133.959 133.158 133.959 133.158 133.959 133.158 133.959 133.158 133.959 133.158 133.959 133.158 133.959 133.158 135.158 135.15	128.999 128.966 128.866 128.866 128.866 91.795 89.897 89.897	77 651 77 396 77 142 70 207 68 856 61 324	56.773	34 968 31 875	25 588 22 951 21 015	14 436
		\vee \vee $ $			117	











(2-chloro-4-nitrophenyl)-3-deoxy-3-azido-2,4-di-O-benzoyl-β-D-xylopyranoside (47): gCOSY NMR (CDCl₃, 500 MHz)

(2-chloro-4-nitrophenyl)-3-deoxy-3-azido-2,4-di-O-benzoyl-β-D-xylopyranoside (47): ¹³C NMR (CDCl₃, 125 MHz)

165.693 165.236	157.167	143.208	134.052 134.015 130.206	128.858 126.509 123.880 116.263	98.336	77 564 77 310 77 055 69 102 68 949	61 723 59 690	31.866	14.403
\mathbf{Y}			\checkmark			\lor	17		





1-bromo-2,3,4-tri-O-benzoyl-β-L-arabinopyranoside (48): ¹H NMR (CDCl₃, 500 MHz)

154 152 137 137 137 111 111 054 037 893 893 837 637	451 261	969 961	055 048 034 034 027 865 765 758 745 737	507 480 270 146 1182 1132	061 659 266 251 251	974 899 872	021 020
8888888777	アア	o o	ນນູນນູບບູບ	44 44444	N NF F F F F	000	0 0
	11	\vdash					\triangleleft





1-bromo-2,3,4-tri-O-benzoyl-β-L-arabinopyranoside (**48**): ¹³C NMR (CDCl₃, 100 MHz)

				_/	
-172.226 -172.226 -165.581 -165.438	133.772 133.634 133.634 133.634 123.936 129.878 129.878 128.370 128.370	— 109.986	— 89.800	$ \begin{array}{c} 77.397 \\ 77.079 \\ 76.761 \\ 68.683 \\ 68.562 \\ -65.013 \\ \end{array} $	60.486





1-bromo-2,3,4-tri-O-benzoyl-α-D-arabinopyranoside (**49**): ¹H NMR (CDCl₃, 400 MHz)

0.110	8.104 8.098 8.098 8.098 8.098 8.098 8.098 8.098 8.098 8.098 8.098 8.044 8.043 8.043 8.044 8.033 8.034 8.035 8.035 8.036 8.037 8.037 8.038 8.037 8.037 8.037 8.037 8.037 8.037 8.038	- 7.506 - 7.404 - 7.229 - 6.963 ↓ 6.954	6.052 6.044 6.044 6.017 5.863 5.863 5.755 5.755 5.739 5.739	- 4.454 - 4.454 - 4.251 - 4.251 - 4.134 - 4.134 - 4.090 - 4.080 - 4.080 - 4.080	2.032 2.032 1.373 1.375 1.











1-bromo-2,3,4-tri-O-benzoyl-α-D-arabinopyranoside (**49**): ¹³C NMR (CDCl₃, 100 MHz)

172.135 165.829 165.676 165.676	133.997 133.976 133.875 138.632	129.631 129.498 129.177 128.890 128.805 128.805 128.621 128.621	90.145	77.706 77.388 77.069 68.979 68.863 65.296 60.683
$ \lor$				$\forall \vdash \forall \mid \mid$





(2-chloro-4-nitrophe	enyl)-2,3,4-tri-O-be	izoyl-α-L-arabinopyra	noside (50): ¹ H NM	R (CDCl _{3.} 500 MHz)
		JJJ J J J J J J J J			(= 0, = = =)

8.287 8.155 8.155 8.137 8.084 8.020 8.020 8.020 7.476 7.445 7.445 7.445 7.445 7.445 7.445 7.445 7.104 7.104	5.957 5.822 5.593	4 459 4 110	2.051 1.659 1.261	0.001
	1			







$ \underbrace{+}_{165.547}^{165.547} $ 165.510 165.030	— 157.375	— 142.810	$ \leq ^{133.792}_{133.609} $	7 129.856 128.685 126.132 123.702 116.218		77.323 77.005 76.687 76.687 76.509 69.194 68.873 66.873	60 917
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(2-chloro-4-nitrophenyl)-2,3,4-tri-*O*-benzoyl-β-D-arabinopyranoside (**51**): ¹H NMR (CDCl₃, 500 MHz)









(2-chloro-4-nitrophenyl)-2,3,4-tri-O-benzoyl-β-D-arabinopyranoside (**51**): ¹³C NMR (CDCl₃, 125 MHz)

 105.848 165.811 165.344 157.703 157.489 157.489 	- 143.128	$\frac{1}{7}$ 134.069 $\frac{1}{7}$ 138.991	 128 855 125 756 124 012 116 547 116 454 	- 98.705	77.636 77.381 77.126 69.566 69.289 67.088	- 61.381
YA Y		-	rrr Y	ł		ł





1,2,3,4-tetra-O-benzoyl- α -L-arabinopyranoside (**52**): ¹H NMR (CDCl₃, 500 MHz)




1,2,3,4-tetra-O-benzoyl- α -L-arabinopyranoside (**52**): ¹³C NMR (CDCl₃, 100 MHz)







S181

1,2,3,4-tetra-O-benzoyl-β-D-arabinopyranoside (**53**): ¹H NMR (CDCl₃, 500 MHz)

398 212 365	566 546 516 3399 350 253	272 261 340 304 778 318	451 441 426 416	356 356	119 055 042	307	258 936 923
∞ ∞∞ ~	ファファファ	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	4444	3.8	555	-	1 0 0 0
		\vee \vee \vee	<u> </u>		SK	1	$ \vee$





S182

1,2,3,4-tetra-O-benzoyl- β -D-arabinopyranoside (53): gCOSY NMR (CDCl₃, 500 MHz)





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1,2,3,4-tetra-O-benzoyl-β-D-arabinopyranoside (**53**): ¹³C NMR (CDCl₃, 125 MHz)

165.825 165.730 165.382 165.006	133.989 133.873 133.873 133.786 133.760 130.171	L 129.110 L 129.055 L 128.822 L 128.797 L 128.748 L 128.748	- 92.686	77.570 77.315 77.061 70.179 69.170 67.833	- 63.013



