Supporting Information
for
A stereoselective and flexible synthesis to access both enantiomers of N-acetylgalactosamine and peracetylated N-acetylglidosamine

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Experimental procedures, as well as $^1$H and $^{13}$C NMR spectra

Table of contents
General information and methods ................................................................. S3
Experimental procedures .............................................................................. S3

$(2R,3R,4S,5R)$-6-O-tert-Butyldimethylsilyl-2,3-epoxy-4,5-O-isopropylidene-hexan-1-ol (5a) ........................................................................................................................................ S3
$(2S,3S,4R,5S)$-6-O-tert-Butyldimethylsilyl-2,3-epoxy-4,5-O-isopropylidene-hexan-1-ol (5b) ........................................................................................................................................ S4
$(2S,3S,4S,5R)$-6-O-tert-Butyldimethylsilyl-2,3-epoxy-4,5-O-isopropylidene-hexan-1-ol (5c) ........................................................................................................................................ S5
Ethyl $(4R,5R,6S,7R)$-8-O-tert-butyldimethylsilyl-4,5-epoxy-6,7-O-isopropylidene-(2E)-octenoate (6a) ........................................................................................................ S5
Ethyl $(4S,5S,6R,7S)$-8-O-tert-butyldimethylsilyl-4,5-epoxy-6,7-O-isopropylidene-(2E)-octenoate (6b) ........................................................................................................ S6
Ethyl $(4S,5S,6S,7R)$-8-O-tert-butyldimethylsilyl-4,5-epoxy-6,7-O-isopropylidene-(2E)-octenoate (6c) ........................................................................................................ S7
Ethyl (4S,5R,6R,7R)-4-azido-8-O-tert-butyldimethylsilyl-6,7-O-isopropylidene-5-hydroxy-(2E)-octenoate (7a)........................................................................ S7
Ethyl (4R,5S,6S,7S)-4-azido-8-O-tert-butyldimethylsilyl-6,7-O-isopropylidene-5-hydroxy-(2E)-octenoate (7b) ................................................................................ S8
Ethyl (4R,5S,6R,7R)-4-azido-8-O-tert-butyldimethylsilyl-6,7-O-isopropylidene-5-hydroxy-(2E)-octenoate (7c) ................................................................................ S9
1,3,4,6-Tetra-O-acetyl-2-azido-2-deoxy-d-galactopyranose (8a) ............................................................. S9
1,3,4,6-Tetra-O-acetyl-2-azido-2-deoxy-l-galactopyranose (8b) ............................................................ S10
1,3,4,6-Tetra-O-acetyl-2-azido-2-deoxy-d-idopyranose (8c) .................................................................. S11
2-Acetamido-1,3,4,6-tetra-O-acetyl-2-deoxy-d-galactopyranose (2a) .................................................. S12
2-Acetamido-1,3,4,6-tetra-O-acetyl-2-deoxy-l-galactopyranose (2b) ..................................................... S13
2-Acetamido-1,3,4,6-tetra-O-acetyl-2-deoxy-d-idopyranose (2c) .......................................................... S13
2-Acetamido-2-deoxy-d-galactopyranose (1a) ..................................................................................... S14
2-Acetamido-2-deoxy-l-galactopyranose (1b) ..................................................................................... S15
NMR spectra........................................................................................................................................... S16
General information and methods

NMR spectra were recorded on a Bruker Avance DRX 400 (100.13 MHz for $^1$H, 100.61 MHz for $^{13}$C) or a Bruker Avance III 600 (600.13 MHz for $^1$H, 150.90 MHz for $^{13}$C) spectrometer. Chemical shifts (δ) are given in parts per million [ppm]. Abbreviations for the multiplicities are as followed: singlet (s), doublet (d), triplet (t), quadruplet (q), multiplet (m). MS experiments were performed on a Finnigan MAT 900 spectrometer in ESI mode. IR spectra were verified on an ELMER FT-IR spectrometer. Optical rotations were measured on a Perkin Elmer Polarimeter 341. For flash chromatography, Merck silica gel 60 (0.004–0.063 mm) was used. DCM, acetone, MeOH, EtOH, heptane and ethyl acetate were distilled before use. Dry DCM was prepared by filtration through an aluminium oxide column and stored over molecular sieves 4 Å. Other solvents and chemicals were purchased in reagent grade.

Experimental procedures

$\text{(2R,3R,4$^S$,5$^R$)}$-$6$^6$-$\text{O-tert-Butyldimethylsilyl-2,3-epoxy-4,5$^0$-isopropylidene-hexan-1-ol (5a)}$

Titanium(IV) isopropoxide (2.7 mL, 9.26 mmol, 1.4 equiv), was dissolved under argon in dry DCM (50 mL), containing 4 Å molecular sieves (1.5 g), and cooled to −78 °C. Diethyl-(L)-tartrate (1.6 mL, 9.26 mmol, 1.4 equiv) was added and the mixture stirred for 15 min. Ethyl 6-$\text{tert-butyldimethylsilyloxy-}\{4$^R$,5$^R$\}$-$isopropylidened dioxy-\{3$^E$\}$-hexenoate (4a, 2.00 g, 6.61 mmol, 1 equiv) in dry DCM (10 mL) was added dropwise followed by a 5.5 M solution of $\text{tert-buty1 hydroperoxide in nonane (2.4 mL, 13.22 mmol, 2 equiv). The solution was stirred for 18 h at −20 °C and quenched subsequently by the addition of 10% solution of tartaric acid in water (25 mL). After stirring for an additional hour at rt, the mixture was filtrated through a Celite pad, the layers separated and the organic layer washed with sat. NaHCO$_3$ solution. Drying over MgSO$_4$, removing of the solvent under reduced pressure and purification by flash chromatography (heptane/ethyl acetate 4:1) yielded 5a (1.86 g, 86%) as colorless oil: $[\alpha]_D^{20} = -16.19^\circ$ (c 1.1, CHCl$_3$); $^1$H NMR (600 MHz, CDCl$_3$) δ 4.01 – 3.92 (m, 3 H, H-2 and H-3 and H-6a), 3.79 – 3.71 (m, 2 H, H-1), 3.72 – 3.65 (m, 1 H, H-6b), 3.24 – 3.15 (m, 2 H, H-4 and H-5), 1.79 (dd, J = 7.5, 5.4 Hz, 1H, OH), 1.42 (s, 3 H, C(CH$_3$)$_2$), 1.41 (s, 3 H, C(CH$_3$)$_2$),
0.89 (s, 9 H, C(CH$_3$)$_3$), 0.07 (s, 6 H, Si(CH$_3$)$_2$); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 110.03 (C$_a$, C(CH$_3$)$_3$), 79.12 (CH, C-2), 77.02 (CH, C-3), 63.56 (CH$_2$, C-1), 61.10 (CH$_2$, C-6), 56.14 (CH, C-5), 55.29 (CH, C-4), 27.05 (CH$_3$, C(CH$_3$)$_2$), 26.89 (CH$_3$, C(CH$_3$)$_2$), 26.03 (3 x CH$_3$, C(CH$_3$)$_3$), 18.50 (C$_a$, C(CH$_3$)$_3$), -5.22 (CH$_3$, Si(CH$_3$)$_2$), -5.30 (CH$_3$, Si(CH$_3$)$_2$); HRMS (ESI) m/z [M + Na]$^+$ calcd for C$_{18}$H$_{30}$O$_5$SiNa 341.1755; found 341.1764.

(2S,3S,4R,5S)-6-O-tert-Butyldimethylsilyl-2,3-epoxy-4,5-O-isopropylidene-hexan-1-ol (5b)

Titanium(IV) isopropoxide (2.7 mL, 9.26 mmol, 1.4 equiv), was dissolved under argon in dry DCM (50 mL) containing 4 Å molecular sieves (1.5 g) and cooled to −78 °C. Diethyl-(D)-tartrate (1.6 mL, 9.26 mmol, 1.4 equiv) was added and the mixture stirred for 15 min. Ethyl 6-tert-butyldimethylsilyloxy-(4S,5S)-isopropylidenedioxy-(3E)-hexenoate (4b) (2.00 g, 6.61 mmol, 1 equiv) in dry DCM (10 mL) was added dropwise followed by a 5.5 M solution of tert-butyl hydroperoxide in nonane (2.4 mL, 13.22 mmol, 2 equiv). The solution was stirred for 18 h at −20 °C and quenched subsequently by the addition of 10 % solution of tartaric acid in water (25 mL). After stirring for an additional hour at rt, the mixture was filtrated through a Celite pad, the layers separated and the organic layer washed with sat. NaHCO$_3$ solution. Drying over MgSO$_4$, removing of the solvent under reduced pressure and purification by flash chromatography (heptane/ethyl acetate 4:1) yielded 5b (1.87 g, 89%) as colorless oil: [$\alpha$]$^2_0$ = +15.69° (c 1.1, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 4.02 (ddd, J = 7.8, 6.0, 4.0 Hz, 1 H, H-2), 3.96 (ddd, J = 12.8, 4.5, 2.4 Hz, 1 H, H-6a), 3.91 (dd, J = 7.9, 4.7 Hz, 1 H, H-3), 3.84 (dd, J = 10.6, 3.9 Hz, 1 H, H-1a), 3.72 (dd, J = 10.6, 6.0 Hz, 1 H, H-1b), 3.69 – 3.63 (m, 1 H, H-6b), 3.19 (dt, J = 3.8, 2.3 Hz, 1 H, H-5), 3.14 (dd, J = 4.7, 2.3 Hz, 1 H, H-4), 1.69 (dd, J = 7.6, 5.0 Hz, 1 H, OH), 1.40 (s, J = 0.7 Hz, 3 H, C(CH$_3$)$_2$), 1.39 (s, J = 0.7 Hz, 3 H, C(CH$_3$)$_2$), 0.89 (s, 9 H, C(CH$_3$)$_3$), 0.07 (s, 6 H, Si(CH$_3$)$_2$); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 109.99 (C$_a$, C(CH$_3$)$_3$), 78.41 (CH, C-2), 78.19 (CH, C-3), 63.65 (CH$_2$, C-1), 60.88 (CH$_2$, C-6), 55.77 (CH, C-5), 54.98 (CH, C-4), 27.16 (CH$_3$, C(CH$_3$)$_2$), 26.80 (CH$_3$, C(CH$_3$)$_2$), 26.05 (3 x CH$_3$, C(CH$_3$)$_3$), 18.51 (C$_a$, C(CH$_3$)$_3$), -5.22 (CH$_3$, Si(CH$_3$)$_2$), -5.27 (CH$_3$, Si(CH$_3$)$_2$); HRMS (ESI) m/z [M + Na]$^+$ calcd for C$_{18}$H$_{30}$O$_5$SiNa 341.1755; found 341.1758.
(2S,3S,4S,5R)-6-O-tert-Butyldimethylsilyl-2,3-epoxy-4,5-O-isopropylidene-hexan-1-ol (5c)

Compound 5c was synthesized from 4a (3.15 g, 10.41 mmol) according to the procedure for compound 5b: yield 2.97 g (89%); [α]$_D^{20}$ = +12.78° (c 1.6, CHCl$_3$); $^1$H NMR (600 MHz, CDCl$_3$) δ 3.99 – 3.91 (m, 3H, H-2 and H-3 and H-6a), 3.79 – 3.72 (m, 2H, H-1), 3.67 (ddd, $J = 12.8$, 7.4, 4.0 Hz, 1H, H-6b), 1.41 (s, 3H, C(CH$_3$)$_2$), 1.40 (s, 3H, C(CH$_3$)$_2$), 0.89 (s, 9H, C(CH$_3$)$_3$), 0.07 (s, 6H, Si(CH$_3$)$_2$); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 110.02 (C$_q$), 79.11 (CH), 76.99 (CH), 63.53 (CH$_2$), 61.11 (CH$_2$), 56.17 (CH), 55.29 (CH), 27.03 (CH$_3$), 26.87 (CH$_3$), 26.02 (3 x CH$_3$, C(CH$_3$)$_3$), 18.48 (C$_q$, C(CH$_3$)$_3$), -5.23 (CH$_3$, Si(CH$_3$)$_2$), -5.28 (CH$_3$, Si(CH$_3$)$_2$); HRMS (ESI) m/z [M + Na]$^+$ calcd for C$_{15}$H$_{30}$O$_5$SiNa 341.1755; found 341.1751.

Ethyl (4$R$,5$R$,6$S$,7$R$)-8-O-tert-butyldimethylsilyl-4,5-epoxy-6,7-O-isopropylidene-(2E)-octenoate (6a)

DMSO (2.9 mL, 41.33 mmol, 4 equiv) was added slowly to a solution of oxalyl chloride (1.8 mL, 20.66 mmol, 2 equiv) in dry DCM (35 mL) at −78 °C. After 15 min 5a (3.29 g, 10.33 mmol, 1 equiv) in DCM (30 mL) was added dropwise and stirring continued for an additional hour. The reaction was quenched by the addition of Et$_3$N (8.6 mL, 61.99 mmol, 6 equiv) and allowed to warm up to rt over 16 h. The mixture was washed with sat. NH$_4$Cl solution and brine. The organic phase was dried over MgSO$_4$, solvents removed under reduced pressure and the crude aldehyde used without further purification.

NaH (10% in mineral oil, 496 mg, 12.40 mmol, 1.2 equiv) was dissolved in dry DCM (35 mL) under argon and cooled to 0 °C. Triethyl phosphonoacetate (2.7 mL, 12.40 mmol, 1.2 equiv) was added slowly and the mixture stirred for 1 h at room temperature. Subsequently, the intermediate, dissolved in dry DCM (20 mL), was added and the solution stirred for 16 h. The
reaction was quenched at 0 °C by the slow addition of water. The phases were separated and the aqueous phase extracted 3× with DCM. The organic phase was washed with brine and dried over MgSO₄. Removing of the solvents under reduced pressure and purification by flash chromatography (heptane/ethyl acetate 9:1) yielded 6a (3.10 g, 78%) as a colorless oil: [α]D²⁰ = -7.57° (c 1.1, CHCl₃); ¹H NMR (600 MHz, CDCl₃) δ 6.67 (dd, J = 15.7, 7.1 Hz, 1 H, H-3), 6.15 (d, J = 15.7 Hz, 1 H, H-2), 4.19 (q, J = 7.1 Hz, 2 H, OCH₂CH₃), 3.98 (dt, J = 9.2, 4.7 Hz, 1 H, H-7), 3.93 (dd, J = 7.4, 4.5 Hz, 1 H, H-6), 3.78 (dd, J = 10.7, 4.0 Hz, 1 H, H-8a), 3.73 (dd, J = 10.7, 5.3 Hz, 1 H, H-8b), 3.52 – 3.49 (m, 1 H, H-4), 3.10 (dd, J = 4.2, 1.3 Hz, 1 H, H-5), 1.41 (s, 3 H, C(CH₃)₂), 1.40 (s, 3 H, C(CH₃)₂), 1.28 (t, J = 7.2 Hz, 3 H, OCH₂CH₃), 0.89 (s, 9 H, C(CH₃)₃), 0.07 (s, 6 H, Si(CH₃)₂); ¹³C NMR (150 MHz, CDCl₃) δ 165.60 (Cq, C-1), 143.44 (CH, C-3), 124.64 (CH, C-2), 110.20 (Cq, C(CH₃)₂), 79.02 (CH, C-7), 77.14 (CH, C-6), 63.47 (CH₂, C-8), 60.82 (CH, C-5), 60.80 (CH₂, OCH₂CH₃), 54.12 (CH, C-4), 27.02 (CH₃, C(CH₃)₂), 26.81 (CH₃, C(CH₃)₂), 26.02 (3 x CH₃, C(CH₃)₃), 18.48 (Cq, C(CH₃)₂), 14.33 (CH₃, OCH₂CH₃), -5.23 (CH₃, Si(CH₃)₂), -5.32 (CH₃, Si(CH₃)₂); HRMS (ESI) m/z [M + Na]⁺ calcd for C₁₉H₃₄O₆SiNa 409.2017; found 409.2016.

**Ethyl (4S,5S,6R,7S)-8-O-tert-butyldimethylsilyl-4,5-epoxy-6,7-O-isopropylidene-(2E)-octenoate (6b)**

Compound 6b was synthesized from 5b (1.31 g, 4.11 mol) according to the procedure for compound 6a: yield 1.15 g (72%); [α]D²⁰ = +6.80° (c 1.1, CHCl₃); ¹H NMR (600 MHz, CDCl₃) δ 6.67 (dd, J = 15.7, 7.1 Hz, 1 H, H-3), 6.15 (d, J = 15.6, 0.8 Hz, 1 H, H-2), 4.20 (q, J = 7.1 Hz, 2 H, OCH₂CH₃), 3.98 (ddd, J = 7.5, 5.3, 4.1 Hz, 1 H, H-7), 3.93 (dd, J = 7.5, 4.4 Hz, 1 H, H-6), 3.78 (dd, J = 10.7, 4.1 Hz, 1 H, H-8a), 3.74 (dd, J = 10.7, 5.4 Hz, 1 H, H-8b), 3.53 – 3.49 (m, 1 H, H-4), 3.11 (dd, J = 4.5, 2.0 Hz, 1 H, H-5), 1.41 (s, 3 H, C(CH₃)₂), 1.40 (s, 3 H, C(CH₃)₂), 1.28 (t, J = 7.1 Hz, 3 H, OCH₂CH₃), 0.89 (s, 9 H, C(CH₃)₃), 0.07 (s, 6 H, Si(CH₃)₂); ¹³C NMR (150 MHz, CDCl₃) δ 165.59 (Cq, C-1), 143.44 (CH, C-3), 124.65 (CH, C-2), 110.21 (Cq, C(CH₃)₂), 79.03 (CH, C-7), 77.15 (CH, C-6), 63.49 (CH₂, C-8), 60.83 (CH, C-5), 60.81 (CH₂, OCH₂CH₃), 54.13 (CH, C-4), 27.03 (CH₃, C(CH₃)₂), 26.82 (CH₃, C(CH₃)₂), 26.02 (3 x CH₃, C(CH₃)₃), 18.49 (Cq, C(CH₃)₂), 14.34 (CH₃, OCH₂CH₃), -5.22 (CH₃, Si(CH₃)₂), -5.31 (CH₃, Si(CH₃)₂); HRMS (ESI) m/z [M + Na]⁺ calcd for C₁₉H₃₄O₆SiNa 409.2017; found 409.2025.
Ethyl (4S,5S,6S,7R)-8-O-tert-butyldimethylsilyl-4,5-epoxy-6,7-O-isopropylidene-(2E)-octenoate (6c)

Compound 6c was synthesized from 5c (2.47 g, 7.76 mmol) according to the procedure for compound 6a: yield 2.37 g (79%); [α]$_{20}^{D}$ = +23.47° (c 1.0, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 6.66 (ddd, J = 15.7, 7.3, 0.7 Hz, 1 H, H-3), 6.15 (dd, J = 15.6, 0.8 Hz, 1 H, H-2), 4.20 (q, J = 7.1 Hz, 2 H, OCH$_2$CH$_3$), 4.05 (ddd, J = 7.6, 3.9 Hz, 1 H, H-7), 3.99 (dd, J = 7.7, 3.9 Hz, 1 H, H-6), 3.85 (dd, J = 10.6, 3.9 Hz, 1 H, H-8a), 3.72 (ddd, J = 10.6, 6.2 Hz, 1 H, H-8b), 3.53 (dt, J = 7.2, 1.3 Hz, 1 H, H-4), 3.05 (dd, J = 3.9, 2.0 Hz, 1 H, H-5), 1.39 (s, 6H, C(CH$_3$)$_2$), 1.29 (t, J = 7.1 Hz, 3 H, OCH$_2$CH$_3$), 0.89 (s, 9 H, Si(CH$_3$)$_2$); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 165.68 (C$q$, C-1), 143.74 (CH, C-3), 124.60 (CH, C-2), 110.15 (C$q$, C(CH$_3$)$_2$), 78.09 (CH, C-7), 77.72 (CH, C-6), 63.57 (CH$_2$, C-8), 60.82 (CH$_2$, OCH$_2$CH$_3$), 60.31 (CH, C-5), 53.80 (CH, C-4), 27.19 (CH$_3$, C(CH$_3$)$_2$), 26.64 (CH$_3$, C(CH$_3$)$_2$), 26.04 (3 x CH$_3$, C(CH$_3$)$_3$), 18.50 (C$q$, C(CH$_3$)$_3$), 14.35 (CH$_3$, OCH$_2$CH$_3$), -5.22 (CH$_3$, Si(CH$_3$)$_2$), -5.26 (CH$_3$, Si(CH$_3$)$_2$); HRMS (ESI) m/z [M + Na]$^+$ calcd for C$_{19}$H$_{34}$O$_6$SiNa 409.2017; found 409.2034.

Ethyl (4S,5R,6R,7R)-4-azido-8-O-tert-butyldimethylsilyl-6,7-O-isopropylidene-5-hydroxy-(2E)-octenoate (7a)

Compound 6a (1.00 g, 2.59, 1 equiv) was dissolved in dry and degassed EtOH under argon. Pd(PPh$_3$)$_4$ (0.30 g, 0.26 mmol, 0.1 equiv) and trimethylsilyl azide (0.7 mL, 5.17 mmol, 2 equiv) were added and the mixture stirred for 4 h. Subsequently, the orange solid was filtered off. The solvents were removed under reduced pressure and the crude product purified by flash chromatography (heptane/ethyl acetate 5:1) to receive compound 7a (0.99 g, 89%, 98% de) as a colorless oil: [α]$_{20}^{D}$ = +3.78° (c 1.0, CH$_2$Cl$_2$); $^1$H NMR (600 MHz, CDCl$_3$) δ 7.07 (dd, J = 15.7, 6.8 Hz, 1 H, H-3), 6.16 (dd, J = 15.7, 1.4 Hz, 1 H, H-2), 4.22 (q, J = 7.1 Hz, 2 H,
OCH₃CH₃), 4.19 (d, J = 6.8 Hz, 1 H, H-5), 3.98 (dd, J = 9.6, 3.6 Hz, 1 H, H-8a), 3.93 – 3.89 (m, 2 H, H-6 and H-7), 3.88 – 3.86 (m, 1 H, H-4), 3.68 (dt, J = 8.3, 2.5 Hz, 1 H, OH), 3.65 – 3.61 (m, 1 H, H-8b), 1.40 (s, 3 H, C(CH₃)₂), 1.38 (s, 3 H, C(CH₃)₂), 1.31 (t, J = 7.1 Hz, 3 H, OCH₂CH₃), 0.91 (s, 9 H, C(CH₃)₃), 0.12 (s, 6 H, Si(CH₃)₃); ¹³C NMR (150 MHz, CDCl₃) δ 165.86 (C₟, C-1), 142.22 (CH, C-3), 124.74 (CH, C-2), 109.77 (C₟, C(CH₃)₂), 80.25 (CH, C-6), 80.04 (CH, C-7), 74.94 (CH, C-4), 64.39 (CH₂, C-8), 62.93 (CH, C-5), 60.85 (CH₂, OCH₂CH₃), 26.93 (CH₃, C(CH₃)₂), 26.91 (CH₃, C(CH₃)₂), 25.99 (3 x CH₃, C(CH₃)₃), 18.52 (C₟, C(CH₃)₃), 14.37 (CH₃, OCH₂CH₃), -5.41 (CH₃, Si(CH₃)₃), -5.42 (CH₃, Si(CH₃)₃); HRMS (ESI) m/z [M + Na]⁺ calcd for C₁₉H₃₅N₅O₆SiNa 452.2193; found 452.2195; (IR) ν 3385 (OH), 2985 (CH), 2930 (CH), 2885 (CH), 2858 (CH), 2101 (N₃), 1722 (C=O) cm⁻¹.

Ethyl (4R,5S,6S,7S)-4-azido-8-O-tert-butyldimethylsilyl-6,7-O-isopropylidene-5-hydroxy-(2E)-octenoate (7b)

Compound 7b was synthesized from 6b (1.75 g, 4.53 mmol) according to the procedure for compound 7a: yield 1.57 g (80%, 95% de); [α]³⁰_D = -2.76° (c 1.25, CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃) δ 7.07 (dd, J = 15.7, 6.8 Hz, 1 H, H-3), 6.15 (dd, J = 15.7, 1.4 Hz, 1 H, H-2), 4.22 (q, J = 7.1 Hz, 2 H, OCH₂CH₃), 4.20 – 4.17 (m, 1 H, H-5), 4.00 – 3.96 (m, 1 H, H-8a), 3.94 – 3.88 (m, 2 H, H-6 and H-7), 3.86 (dd, J = 2.7, 1.0 Hz, 1H, H-4), 3.68 (dt, J = 8.2, 2.4 Hz, 1 H, OH), 3.65 – 3.60 (m, 1 H, H-8b), 1.40 (s, 3 H, C(CH₃)₂), 1.38 (s, 3 H, C(CH₃)₂), 1.30 (t, J = 7.1 Hz, 3 H, OCH₂CH₃), 0.91 (s, 9 H, C(CH₃)₃), 0.12 (s, 6 H, Si(CH₃)₃); ¹³C NMR (150 MHz, CDCl₃) δ 165.84 (C₟, C-1), 142.21 (CH, C-3), 124.73 (CH, C-2), 109.76 (C₟, C(CH₃)₂), 80.24 (CH, C-6), 80.04 (CH, C-7), 74.94 (CH, C-4), 64.39 (CH₂, C-8), 62.93 (CH, C-5), 60.83 (CH₂, OCH₂CH₃), 26.93 (CH₃, C(CH₃)₂), 26.90 (CH₃, C(CH₃)₂), 25.99 (3 x CH₃, C(CH₃)₃), 18.51 (C₟, C(CH₃)₃), 14.37 (CH₃, OCH₂CH₃), -5.42 (CH₃, Si(CH₃)₃), -5.43 (CH₃, Si(CH₃)₃); HRMS (ESI) m/z [M + Na]⁺ calcd for C₁₉H₃₅N₅O₆SiNa 452.2193; found 452.2186; (IR) ν 3385 (OH), 2931 (CH), 2101 (N₃), 1722 (C=O) cm⁻¹.
Ethyl (4R,5S,6R,7R)-4-azido-8-\textit{O}-tert-butyldimethylsilyl-6,7-\textit{O}-isopropylidene-5-hydroxy-(2\textit{E})-octenoate (7c)

Compound 7c was synthesized from 6c (2.20 g, 5.69 mmol) according to the procedure for compound 7a: yield 1.91 g (78%, 98% de); \([\alpha]_D^{20} = -14.64^\circ\) (c 1.20, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.85 (dd, \(J = 15.6, 7.5\) Hz, 1 H, H-3), 6.12 (dd, \(J = 15.6, 1.2\) Hz, 1 H, H-2), 4.26 – 4.20 (m, 2 H, OCH\(_2\)CH\(_3\)), 4.20 – 4.14 (m, 1 H, H-5), 4.10 (ddd, \(J = 7.9, 6.5, 3.9\) Hz, 1 H, H-7), 3.98 (dd, \(J = 8.0, 2.0\) Hz, 1 H, H-6), 3.83 (dd, \(J = 10.5, 3.9\) Hz, 1 H, H-8a), 3.70 – 3.63 (m, 2 H, H-4 and H-8b), 2.62 (d, \(J = 8.7\) Hz, 1 H, OH), 1.43 (s, 3 H, C(CH\(_3\))\(_2\)), 1.39 (s, 3 H, C(CH\(_3\))\(_2\)), 1.30 (t, \(J = 7.2\) Hz, 3 H, OCH\(_2\)C\(_\text{H}_3\)), 0.88 (s, 9 H, C(CH\(_3\))\(_3\)), -5.37 (CH\(_3\)), -5.40 (CH\(_3\)), Si(CH\(_3\))\(_2\)); \(^13\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 165.48 (C\(_q\), C-1), 140.87 (CH, C-3), 125.59 (CH, C-2), 109.98 (C\(_q\), C(CH\(_3\))\(_2\)), 78.47 (CH, C-6), 77.05 (CH, C-7), 71.99 (CH, C-4), 65.74 (CH, C-5), 63.57 (CH\(_2\), C-8), 60.92 (CH\(_2\), OCH\(_2\)CH\(_3\)), 27.22 (CH\(_3\), C(CH\(_3\))\(_2\)), 27.03 (CH\(_3\), C(CH\(_3\))\(_2\)), 25.97 (3 x CH\(_3\), C(CH\(_3\))\(_3\)), 18.39 (C\(_q\), C(CH\(_3\))\(_3\)), 14.33 (CH\(_3\), OCH\(_2\)CH\(_3\)), -5.37 (CH\(_3\), Si(CH\(_3\))\(_2\)), -5.40 (CH\(_3\), Si(CH\(_3\))\(_2\)); HRMS (ESI) \(m/z\) [M + Na]\(^+\) calcd for C\(_{19}\)H\(_{35}\)N\(_3\)O\(_6\)SiNa 452.2193; found 452.2188; (IR) \(\nu\) 3348 (OH), 2925 (CH), 2112 (N\(_3\)), 1738 (C=O) cm\(^{-1}\).

1,3,4,6-Tetra-\textit{O}-acetyl-2-azido-2-deoxy-\textit{D}-galactopyranose (8a)

1,3,4,6-Tetra-\textit{O}-acetyl-2-azido-2-deoxy-\textit{D}-galactopyranose (8a)

Compound 7a (2.00 g, 4.66 mmol, 1 equiv) was dissolved in 10 mL MeOH/H\(_2\)O (4:1). After the addition of DOWEX H\(^+\) (≈1 g), the mixture was heated to 40 °C for 16 h. DOWEX H\(^+\) was filtered off and the solvents removed under reduced pressure. The crude product was used for the next step without further purification.

The solid was dissolved in DCM/MeOH (9:1) and ozone was purged through at −78 °C until the solution turned blue. Subsequently, oxygen was purged through until the blue color disappeared, again. Dimethyl sulfide (0.7 mL, 9.31 mmol, 2 equiv) was added and the
solution stirred overnight. The solution, containing partly precipitated product, was evaporated and the product used without further purification.

The solid was dissolved in 10 mL Ac₂O/pyridine (1:1) under argon. Dimethylaminopyridine (57 mg, 0.47 mmol, 0.1 equiv) was added and the mixture stirred overnight. The solvents were removed under reduced pressure and the crude product purified by flash chromatography (heptane/ethyl acetate 3:1) to receive compound 8a (1.40 g, 81\%, \(\alpha\)-pyr/\(\beta\)-pyr 14:86): \(^1\)H NMR (600 MHz, CDCl₃) \(\delta\) \(\alpha\): 6.31 (d, \(J = 3.6\) Hz, 1 H, H-1), 5.47 (dd, \(J = 3.2, 1.3\) Hz, 1 H, H-4), 5.31 (dd, \(J = 11.1, 3.2\) Hz, 1 H, H-3), 4.30 – 4.25 (m, 1 H, H-5), 4.11 – 4.04 (m, 2 H, H-6), 3.93 (dd, \(J = 11.1, 3.6\) Hz, 1 H, H-2), 2.17 (s, 3 H; Ac), 2.16 (s, 3 H, Ac), 2.07 (s, 3 H, Ac), 2.03 (s, 3 H, Ac); \(\beta\): 5.54 (d, \(J = 8.5\) Hz, 1 H, H-1), 5.37 (dd, \(J = 3.3, 0.9\) Hz, 1 H, H-4), 4.88 (dd, \(J = 10.8, 3.3\) Hz, 1 H, H-3), 4.16 – 4.08 (m, 2 H, H-6), 4.00 (td, \(J = 6.7, 1.1\) Hz, 1 H, H-5), 3.83 (dd, \(J = 10.8, 8.5\) Hz, 1 H, H-2), 2.20 (s, 3 H, Ac), 2.16 (s, 3 H, Ac), 2.06 (s, 3 H, Ac), 2.03 (s, 3 H, Ac); \(^{13}\)C NMR (150 MHz, CDCl₃) \(\delta\) \(\alpha\): 170.48 (C\(_q\), Ac), 170.11 (C\(_q\), Ac), 169.99 (C\(_q\), Ac), 168.86 (C\(_q\), Ac), 90.52 (CH, C-1), 68.86 (CH, C-5), 68.77 (CH, C-3), 66.94 (CH, C-4), 61.21 (CH₂, C-6), 56.92 (CH, C-2), 21.08 (CH₃, Ac), 20.79 (3 x CH₃, Ac), 20.76 (CH₃, Ac); \(\beta\): 170.46 (C\(_q\), Ac), 170.07 (C\(_q\), Ac), 169.75 (C\(_q\), Ac), 168.70 (C\(_q\), Ac), 92.96 (CH, C-1), 71.82 (CH, C-5), 71.40 (CH, C-3), 66.25 (CH, C-4), 61.05 (CH₂, C-6), 59.75 (CH, C-2), 21.03 (CH₃, Ac), 20.79 (CH₃, Ac), 20.74 (CH₃, Ac), 20.72 (CH₃, Ac); HRMS (ESI) \(m/z\) [M + Na]⁺ calcd for C\(_{14}\)H\(_{19}\)N\(_3\)O\(_9\)Na 396.1019; found 396.1016; (IR) \(\nu\) 2970 (CH), 2114 (N\(_3\)) cm\(^{-1}\).

**1,3,4,6-Tetra-O-acetyl-2-azido-2-deoxy-L-galactopyranose (8b)**

Compound 8b was synthesized from 7b (1.56 g, 3.63 mmol) according to the procedure for compound 8a: yield 0.85 g (63\%, \(\alpha\)-pyr/\(\beta\)-pyr 19:81); \(^1\)H NMR (600 MHz, CDCl₃) \(\delta\) \(\alpha\): 6.31 (d, \(J = 3.6\) Hz, 1 H, H-1), 5.48 – 5.45 (m, 1 H, H-4), 5.30 (ddd, \(J = 11.0, 3.3, 1.1\) Hz, 1 H, H-3), 4.27 (t, \(J = 6.8\) Hz, 1 H, H-5), 4.11 – 4.06 (m, 2 H, H-6), 3.93 (dd, \(J = 11.0, 3.6\) Hz, 1 H, H-2), 2.17 (s, 3 H, Ac), 2.16 (s, 3 H, Ac), 2.06 (s, 3 H, Ac), 2.06 (s, 3 H, Ac); \(\beta\): 5.54 (d, \(J = 8.5\) Hz, 1 H, H-1), 5.38 – 5.35 (m, 1 H, H-4), 4.88 (dd, \(J = 10.8, 3.3\) Hz, 1 H, H-3), 4.15 – 4.09 (m, 2 H, H-6), 4.00 (td, \(J = 6.7, 1.2\) Hz, 1 H, H-5), 3.83 (ddd, \(J = 10.9, 8.5, 1.1\) Hz, 1 H, H-2), 2.19 (s, 3 H, Ac), 2.16 (s, 3 H, Ac), 2.05 (s, 3 H, Ac), 2.03 (s, 3 H, Ac); \(^{13}\)C NMR (150 MHz, CDCl₃)
δ α: 170.11 (Cq, Ac), 169.99 (Cq, Ac), 169.75 (Cq, Ac), 168.85 (Cq, Ac), 90.51 (CH, C-1), 68.86 (CH, C-5), 68.75 (CH, C-3), 66.94 (CH, C-4), 61.20 (CH₂, C-6), 56.91 (CH, C-2), 21.18 (CH₃, Ac), 20.06 (CH₃, Ac), 20.77 (CH₃, Ac), 20.72 (CH₃, Ac); β: 170.47 (Cq, Ac), 170.07 (Cq, Ac), 169.75 (Cq, Ac), 168.70 (Cq, C-1), 92.95 (CH, C-1), 71.81 (CH, C-5), 71.39 (CH, C-3), 66.26 (CH, C-4), 61.05 (CH₂, C-6), 59.74 (CH, C-2), 21.01 (CH₃, Ac), 20.77 (CH₃, Ac), 20.72 (CH₃, Ac); HRMS (ESI) m/z [M + Na]⁺ calcd for C₁₄H₁₉N₃O₉SiNa 396.1019; found 396.1013; (IR) ν 2969 (CH), 2113 (N₃), 1744 (C=O) cm⁻¹.

**1,3,4,6-Tetra-O-acetyl-2-azido-2-deoxy-β-idopyranose (8c)**

Compound 8c was synthesized from 7c (0.10 g, 0.23 mmol) according to the procedure for compound 8a: yield 32 mg (37%, α-pyr/β-pyr/α-fur 50:31:19); ¹H NMR (600 MHz, CDCl₃) δ α-pyr: 6.00 (d, J = 4.4 Hz, 1 H, H-1), 5.12 (dd, J = 6.4, 5.2 Hz, 1 H, H-3), 5.04 (dd, J = 5.2, 3.6 Hz, 1 H, H-4), 4.45 (ddd, J = 6.6, 5.2, 3.6 Hz, 1 H, H-5), 4.27 – 4.21 (m, 2 H, H-6), 3.65 (dd, J = 6.4, 4.4 Hz, 1 H, H-2), 2.12 (s, 3 H, Ac), 2.11 (s, 3 H, Ac), 2.11 (s, 3 H, Ac), 2.07 (s, 3 H, Ac); β-pyr: 6.06 (d, J = 2.4 Hz, 1 H, H-1), 5.25 (t, J = 4.6 Hz, 1 H, H-3), 4.87 (dd, J = 4.5, 3.0 Hz, 1 H, H-4), 4.35 (ddd, J = 7.2, 5.6, 3.1 Hz, 1 H, H-5), 4.19 – 4.13 (m, 2 H, H-6), 3.57 (dd, J = 4.6, 2.4 Hz, 1 H, H-2), 2.18 (s, 3 H, Ac), 2.13 (s, 3 H, Ac), 2.13 (s, 3 H, Ac), 2.04 (s, 3 H, Ac); α-fur: 6.02 (d, J = 1.8 Hz, 1 H, H-1), 5.32 (td, J = 6.3, 3.8 Hz, 1 H, H-3), 5.17 (dd, J = 6.0, 3.2 Hz, 1 H, H-4), 4.52 (t, J = 6.2 Hz, 1 H, H-2), 4.29 (dd, J = 12.0, 3.8 Hz, 1H, H-6a), 4.16 – 4.14 (m, 1H, H-5), 4.01 (dd, J = 12.0, 6.4 Hz, 1H, H-6b), 2.13 (s, 3 H, Ac), 2.11 (s, 3 H, Ac), 2.10 (s, 3 H, Ac), 2.03 (s, 3 H, Ac); ¹³C NMR (150 MHz, CDCl₃) δ α-pyr: 170.47 (Cq, Ac), 169.94 (Cq, Ac), 169.31 (Cq, Ac), 168.72 (Cq, Ac), 91.43 (CH, C-1), 68.94 (CH, C-3), 67.92 (CH, C-5), 67.63 (CH, C-4), 61.65 (CH₂, C-6), 58.27 (CH, C-2), 21.00 (CH₃, Ac), 20.85 (2 x CH₃, Ac), 20.69 (CH₃, Ac); β-pyr: 170.56 (Cq, Ac), 169.80 (Cq, Ac), 168.85 (Cq, Ac), 168.69 (Cq, Ac), 91.15 (CH, C-1), 72.29 (CH, C-5), 68.17 (CH, C-3), 66.04 (CH, C-4), 62.13 (CH₂, C-6), 57.49 (CH, C-2), 20.98 (CH₃, Ac), 20.89 (CH₃, Ac), 20.80 (CH₃, Ac), 20.71 (CH₃, Ac); α-fur: 170.53 (Cq, Ac), 170.10 (Cq, Ac), 169.94 (Cq, Ac), 169.58 (Cq, Ac), 98.68 (CH, C-1), 78.96 (CH, C-2), 75.09 (CH, C-4), 69.27 (CH, C-3 or C-5), 69.19 (CH, C-3 or C-5), 62.58 (CH₂, C-6), 21.13 (CH₃, Ac), 21.12 (CH₃, Ac), 20.78 (CH₃, Ac), 20.76 (CH₃, Ac); HRMS (ESI)
\[m/z\ [M + Na]^+\] calcd for C_{14}H_{19}N_{2}O_{5}SiNa 396.1019; found 396.1009; (IR) \nu (CH) 2969 cm\(^{-1}\), (N\(_3\)) 2113 cm\(^{-1}\), (C=O) cm\(^{-1}\).

**2-Acetamido-1,3,4,6-tetra-O-acetyl-2-deoxy-D-galactopyranose (2a)**

\[
\begin{array}{c}
\text{OAc} \\
\text{OAc} \\
\text{NHAc} \\
\text{OAc}
\end{array}
\]

8a (200 mg, 0.54 mmol, 1 equiv) was dissolved in 3 mL acetic anhydride. 20 mg Pd/C was added and a H\(_2\)-ballon attached to the flask. The mixture was stirred for 16 h before acetic anhydride was removed under reduced pressure. The mixture was dissolved in warm EtOH/H\(_2\)O (1:1) and filtered through a Celite pad. The solvents were removed under reduced pressure and the crude product purified by flash chromatography (DCM/ethyl acetate/MeOH 7/2.5/0.5) to receive compound 2a (108 mg, 52\%, \alpha-pyr/\beta-pyr 26:74) as a colorless solid: \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\): \(\alpha\) 6.21 (d, \(J = 3.6\) Hz, 1 H, H-1), 5.44 (d, \(J = 9.0\) Hz, 1 H, NH), 5.42 (dd, \(J = 3.1, 1.2\) Hz, 1 H, H-4), 5.22 (dd, \(J = 11.6, 3.1\) Hz, 1 H, H-3), 4.72 (ddd, \(J = 11.6, 9.2, 3.6\) Hz, 1 H, H-2), 4.25 – 4.22 (m, 1 H, H-5), 4.12 – 4.04 (m, 2 H, H-6), 2.17 (s, 6 H, Ac), 2.03 (s, 6 H, Ac), 1.95 (s, 3 H, Ac); \(\beta\): 5.69 (d, \(J = 8.9\) Hz, 1 H, H-1), 5.49 (d, \(J = 9.6\) Hz, 1 H, NH), 5.37 (dd, \(J = 3.4, 1.2\) Hz, 1 H, H-4), 5.08 (dd, \(J = 11.3, 3.4\) Hz, 1 H, H-3), 4.44 (dt, \(J = 11.3, 9.3\) Hz, 1 H, H-2), 4.18 – 4.08 (m, 2 H, H-6), 4.01 (td, \(J = 6.5, 1.2\) Hz, 1 H, H-5), 2.16 (s, 3 H, Ac), 2.12 (s, 3 H, Ac), 2.04 (s, 3 H, Ac), 2.01 (s, 3 H, Ac), 1.93 (s, 3 H, Ac); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\): \(\alpha\) 171.38 (C\(_q\), Ac), 170.56 (C\(_q\), Ac), 170.38 (C\(_q\), Ac), 170.21 (C\(_q\), Ac), 168.94 (C\(_q\), Ac), 91.49 (CH, C-1), 68.70 (CH, C-5), 67.97 (CH, C-3), 66.84 (CH, C-4), 61.45 (CH\(_2\), C-6), 47.14 (CH, C-2), 23.34 (CH\(_3\), Ac), 21.12 (CH\(_3\), Ac), 20.91 (CH\(_3\), Ac), 20.84 (CH\(_3\), Ac), 20.82 (CH\(_3\), Ac); \(\beta\): 170.90 (C\(_q\), Ac), 170.56 (C\(_q\), Ac), 170.43 (C\(_q\), Ac), 170.32 (C\(_q\), Ac), 169.72 (C\(_q\), Ac), 93.18 (CH, C-1), 72.00 (CH, C-5), 70.46 (CH, C-3), 66.48 (CH,C-4), 61.45 (CH\(_2\), C-6), 49.93 (CH, C-2), 23.46 (CH\(_3\), Ac), 21.05 (CH\(_3\), Ac), 20.82 (2 x CH\(_3\), Ac), 20.80 (CH\(_3\), Ac); HRMS (ESI) \(m/z\ [M + Na]^+\) calcd for C\(_{16}\)H\(_{23}\)NO\(_{10}\)Na 412.1220; found 412.1223.
2-Acetamido-1,3,4,6-tetra-O-acetyl-2-deoxy-L-galactopyranose (2b)

Compound 2b was synthesized from 8b (0.20 g, 0.54 mmol) according to the procedure for compound 2a: yield 0.11 g (56%, α-pyr/β-pyr 57:43); 1H NMR (600 MHz, CDCl3) δ α: 6.21 (d, J = 3.6 Hz, 1 H, H-1), 5.46 (d, J = 9.2 Hz, 1 H, NH), 5.42 (dd, J = 3.4, 1.3 Hz, 1 H, H-4), 5.21 (dd, J = 11.5, 3.3 Hz, 1 H, H-3), 4.72 (ddd, J = 11.6, 9.2, 3.7 Hz, 1 H, H-2), 4.23 (td, J = 6.8, 1.4 Hz, 1 H, H-5), 5.42 (dd, J = 11.3, 3.4 Hz, 1 H, H-4), 5.21 (dd, J = 11.3, 6.7 Hz, 2 H, H-6), 2.17 (s, 6H, Ac), 2.03 (s, 6H, Ac), 1.95 (s, 3H, Ac); β: 5.70 (d, J = 8.8 Hz, 1 H, H-1), 5.53 (d, J = 9.6 Hz, 1 H, NH), 5.37 (dd, J = 3.4, 1.1 Hz, 1 H, H-4), 5.08 (dd, J = 11.3, 3.4 Hz, 1 H, H-3), 4.44 (dt, J = 11.3, 9.2 Hz, 1 H, H-2), 4.16 (dd, J = 11.4, 6.6 Hz, 1 H, H-6a), 4.06 (dd, J = 11.3, 6.5 Hz, 1 H, H-6b), 4.02 (td, J = 6.5, 1.2 Hz, 1 H, H-5), 2.16 (s, 3H, Ac), 2.12 (s, 3H, Ac), 2.04 (s, 3H, Ac), 2.01 (s, 3H, Ac), 1.94 (s, 3H, Ac); 13C NMR (150 MHz, CDCl3) δ α: 171.35 (Cq, Ac), 170.54 (Cq, Ac), 170.37 (Cq, Ac), 170.21 (Cq, Ac), 168.94 (Cq, Ac), 91.49 (CH, C-1), 68.68 (CH, C-5), 67.96 (CH, C-3), 66.83 (CH, C-4), 61.43 (CH2, C-6), 47.12 (CH, C-2), 23.32 (CH3, Ac), 21.11 (CH3, Ac), 20.90 (CH3, Ac), 20.79 (2 x CH3, Ac); β: 170.87 (Cq, Ac), 170.53 (Cq, Ac), 170.44 (Cq, Ac), 170.37 (Cq, Ac), 169.70 (Cq, Ac), 93.17 (CH, C-1), 71.96 (CH, C-5), 70.46 (CH, C-3), 66.47 (CH, C), 61.45 (CH2, C-6), 49.88 (CH, C-2), 23.44 (CH3, Ac), 21.04 (CH3, Ac), 20.82 (2 x CH3, Ac), 20.79 (CH3, Ac); HRMS (ESI) m/z [M + Na]+ calcd for C16H23NO10Na 412.1220; found 412.1217.

2-Acetamido-1,3,4,6-tetra-O-acetyl-2-deoxy-β-idopyranose (2c)

Compound 2c was synthesized from 8c (30 mg, 0.08 mmol) according to the procedure for compound 2a: yield 18 mg (56%, α-pyr/β-pyr/α-fur 49:33:18); 1H NMR (600 MHz, CDCl3) δ α-pyr: 6.11 (d, J = 9.8 Hz, 1 H, NH), 5.93 (s, 1 H, H-1), 5.04 (t, J = 2.8 Hz, 1 H, H-4), 4.87 (t, J = 3.6 Hz, 1 H, H-3), 4.48 (td, J = 6.6, 2.1 Hz, 1 H, H-5), 4.31 (dt, J = 10.0, 2.9 Hz, 1 H, H-2), 4.11 (t, J = 6.2 Hz, 2 H, H-6), 2.14 (s, 3H, Ac), 2.11 (s, 3H, Ac), 2.10 (s, 3H, Ac), 2.09 (s, 3
H, Ac), 2.04 (s, 3 H, Ac); β-pyr: 6.06 (d, $J = 9.7$ Hz, 1 H, NH), 6.01 (d, $J = 2.4$ Hz, 1 H, H-1), 5.07 (t, $J = 4.2$ Hz, 1 H, H-4), 4.98 (t, $J = 3.3$ Hz, 1 H, H-3), 4.39 – 4.33 (m, 2 H, H-2 and H-5), 4.18 – 4.13 (m, 2 H, H-6), 2.12 (s, 3 H, Ac), 2.11 (s, 3 H, Ac), 2.04 (s, 3 H, Ac), 2.02 (s, 3 H, Ac), 1.99 (s, 3 H, Ac); α-fur: 6.27 (d, $J = 8.2$ Hz, 1 H, NH), 6.02 (d, $J = 3.2$ Hz, 1 H, H-1), 5.32 (dd, $J = 6.9$, 5.4 Hz, 1 H, H-3), 5.25 (dt, $J = 7.1$, 4.8 Hz, 1 H, H-5), 4.61 (ddd, $J = 8.3$, 5.4, 3.2 Hz, 1 H, H-2), 4.55 (dd, $J = 6.9$, 4.8 Hz, 1 H, H-4), 4.26 (dd, $J = 11.9$, 4.1 Hz, 1 H, H-6a), 4.05 (dd, $J = 11.9$, 7.1 Hz, 1 H, H-6b), 2.14 (s, 3 H, Ac), 2.10 (s, 3 H, Ac), 2.07 (s, 3 H, Ac), 2.04 (s, 3 H, Ac), 1.98 (s, 3 H, Ac); $^{13}$C NMR (150 MHz, CDCl₃) δ α-pyr: 170.59 (Cₐ, Ac), 169.71 (Cₐ, Ac), 169.04 (Cₐ, Ac), 168.68 (Cₐ, Ac), 168.66 (CH, Ac), 92.06 (CH, C-1), 67.36 (CH, C-3), 66.49 (CH, C-4), 66.04 (CH, C-5), 61.72 (CH₂, C-6), 46.32 (CH, C-2), 23.35 (CH₃, Ac), 20.99 (CH₃, Ac), 20.89 (CH₃, Ac), 20.84 (CH₃, Ac), 20.81 (CH₃, Ac); β-pyr: 170.34 (Cₐ, Ac), 170.17 (Cₐ, Ac), 170.02 (Cₐ, Ac), 168.76 (Cₐ, Ac), 168.57 (Cₐ, Ac), 90.80 (CH, C-1), 72.52 (CH, C-5), 68.48 (CH, C-4), 66.23 (CH, C-3), 61.94 (CH₂, C-6), 47.85 (CH, C-2), 23.35 (CH₃, Ac), 21.01 (CH₃, Ac), 20.91 (CH₃, Ac), 20.80 (CH₃, Ac), 20.74 (CH₃, Ac); α-fur: 170.62 (Cₐ, Ac), 170.55 (Cₐ, Ac), 170.36 (Cₐ, Ac), 169.89 (Cₐ, Ac), 168.93 (Cₐ, Ac), 98.76 (CH, C-1), 78.29 (CH, C-4), 75.05 (CH, C-3), 69.06 (CH, C-5), 62.70 (CH₂, C-6), 59.74 (CH, C-2), 23.18 (CH₃, Ac), 21.23 (CH₃, Ac), 21.16 (CH₃, Ac), 21.03 (CH₃, Ac), 20.87 (CH₃, Ac); HRMS (ESI) m/z [M + Na]$^+$ calc’d for C₁₆H₂₃NO₇Na 412.1220; found 412.1217.

2-Acetamido-2-deoxy-β-galactopyranose (1a)

2a (115 mg, 0.30 mmol, 1 equiv) was dissolved in 3 mL MeOH/H₂O/Et₃N (10:10:1) and stirred for 16 h. The solvents were removed under reduced pressure and the crude product was recrystallized from MeOH/Et₂O to receive compound 1a (57 mg, 88%, α-pyr/β-pyr 56:44) as a colorless solid: [$\alpha$]$^{20}_{D} = +80.0^\circ$ (c 1.0, H₂O); $^1$H NMR (600 MHz, D₂O) δ α: 5.20 (d, $J = 3.7$ Hz, 1 H, H-1), 4.12 – 4.06 (m, 2 H, H-2 and H-5), 3.97 (d, $J = 2.7$ Hz, 1 H, H-4), 3.91 (t, $J = 2.7$ Hz, 1 H, H-3), 3.11 – 3.03 (m, 2 H, H-6), 2.02 (s, 3 H, Ac); β: 4.62 (d, $J = 8.4$ Hz, 1 H, H-1), 3.88 (d, $J = 3.2$ Hz, 1 H, H-4), 3.85 (dd, $J = 10.8$, 8.5 Hz, 1 H, H-2), 3.79 – 3.69 (m, 2 H, H-6), 3.69 – 3.65 (m, 1 H, H-5), 2.02 (s, 3 H, Ac); $^{13}$C NMR (150 MHz, H₂O) δ α: 175.45 (Cₐ, Ac), 91.73 (CH, C-1), 71.28 (CH, C-5), 69.31 (CH, C-4), 68.12 (CH, C-3), 61.97 (CH₂, C-6), 51.00 (CH, C-2), 22.70 (CH₃, Ac); β: 175.72 (Cₐ, Ac), 96.14 (CH, C-1), 75.93
(CH, C-5), 71.87 (CH, C-3), 68.59 (CH, C-4), 61.74 (CH₂, C-6), 54.39 (CH, C-2), 22.95 (CH₃, Ac); HRMS (ESI) m/z [M + Na]⁺ calcd for C₈H₁₅NO₆Na 244.0797; found 244.0793.

2-Acetamido-2-deoxy-L-galactopyranose (1b)

Compound 1b was synthesized from 2b (31 mg, 0.08 mmol) according to the procedure for compound 1a: yield 16 mg (69%, α-pyr/β-pyr 68:32); [α]²⁰ D = -71.5° (c 1.0, H₂O); ¹H NMR (600 MHz, D₂O) δ α: 5.23 (d, J = 3.8 Hz, 1 H, H-1), 4.15 – 4.08 (m, 2 H, H-2 and H-5), 4.01 – 3.97 (m, 1 H, H-4), 3.93 (t, J = 3.4 Hz, 1 H, H-3), 3.74 (d, J = 6.1 Hz, 2 H, H-6), 2.05 (s, 3 H, Ac); β: 4.64 (d, J = 8.4 Hz, 1 H, H-1), 3.91 (d, J = 3.2 Hz, 1 H, H-4), 3.87 (dd, J = 10.9, 8.5 Hz, 1 H, H-2), 3.81 – 3.71 (m, 3 H, H-3 and H-6), 3.71 – 3.66 (m, 1H, H-5), 2.04 (s, 3 H, Ac); ¹³C NMR (150 MHz, H₂O) δ α: 175.44 (Cq, Ac), 91.74 (CH, C-1), 71.28 (CH, C-5), 69.32 (CH, C-4), 68.14 (CH, C-3), 61.98 (CH₂, C-6), 51.01 (CH, C-2), 22.72 (CH₃, Ac); β: 175.72 (Cq, Ac), 96.16 (CH, C-1), 75.93 (CH, C-5), 71.88 (CH, C-3), 68.60 (CH, C-4), 61.75 (CH₂, C-6), 54.41 (CH, C-2), 22.97 (CH₃, Ac); HRMS (ESI) m/z [M + Na]⁺ calcd for C₈H₁₅NO₆Na 244.0797; found 244.0788.
NMR spectra

5a
6a
8c