## Supporting Information

for

## A stereoselective and flexible synthesis to access both enantiomers of N -acetylgalactosamine and peracetylated N -acetylidosamine

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## General information and methods

NMR spectra were recorded on a Bruker Avance DRX 400 ( 100.13 MHz for ${ }^{1} \mathrm{H}, 100.61 \mathrm{MHz}$ for ${ }^{13} \mathrm{C}$ ) or a Bruker Avance III $600\left(600.13 \mathrm{MHz}\right.$ for ${ }^{1} \mathrm{H}, 150.90 \mathrm{MHz}$ for $\left.{ }^{13} \mathrm{C}\right)$ spectrometer. Chemical shifts ( $\delta$ ) 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 ( $0.004-0.063 \mathrm{~mm}$ ) 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 $4 \AA$ Å. Other solvents and chemicals were purchased in reagent grade.

## Experimental procedures

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



Titanium(IV) isopropoxide ( $2.7 \mathrm{~mL}, 9.26 \mathrm{mmol}, 1.4$ equiv), was dissolved under argon in dry DCM ( 50 mL ), containing $4 \AA$ molecular sieves ( 1.5 g ), and cooled to $-78{ }^{\circ} \mathrm{C}$. Diethyl-(L)tartrate ( $1.6 \mathrm{~mL}, 9.26 \mathrm{mmol}, 1.4$ equiv) was added and the mixture stirred for 15 min . Ethyl 6-tert-butyldimethylsilyloxy-( $4 R, 5 R$ )-isopropylidenedioxy-(3E)-hexenoate ( $4 \mathbf{a}, 2.00 \mathrm{~g}, 6.61$ mmol, 1 equiv) in dry DCM ( 10 mL ) was added dropwise followed by a 5.5 M solution of tertbutyl hydroperoxide in nonane ( $2.4 \mathrm{~mL}, 13.22 \mathrm{mmol}, 2$ equiv). The solution was stirred for 18 h at $-20^{\circ} \mathrm{C}$ 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. $\mathrm{NaHCO}_{3}$ solution. Drying over $\mathrm{MgSO}_{4}$, removing of the solvent under reduced pressure and purification by flash chromatography (heptane/ethyl acetate $4: 1$ ) yielded 5 a ( $1.86 \mathrm{~g}, 86 \%$ ) as colorless oil: $[\alpha]^{20}{ }_{\mathrm{D}}=-16.19^{\circ}\left(c 1.1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR $\left(600 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 4.01-3.92(\mathrm{~m}, 3 \mathrm{H}, \mathrm{H}-2$ and $\mathrm{H}-3$ and H-6a), $3.79-3.71$ (m, 2 H, H-1), $3.72-3.65(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-6 \mathrm{~b}), 3.24-3.15$ (m, $2 \mathrm{H}, \mathrm{H}-4$ and H-5), $1.79(\mathrm{dd}, \mathrm{J}=7.5,5.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OH}), 1.42\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.41\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}\right)$,
0.89 (s, $\left.9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 0.07\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right)$; ${ }^{13} \mathrm{C} \operatorname{NMR}\left(150 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 110.03\left(\mathrm{C}_{\mathrm{q}}\right.$, $\left.\underline{\mathrm{C}}\left(\mathrm{CH}_{3}\right)_{2}\right), 79.12(\mathrm{CH}, \mathrm{C}-2), 77.02(\mathrm{CH}, \mathrm{C}-3), 63.56\left(\mathrm{CH}_{2}, \mathrm{C}-1\right), 61.10\left(\mathrm{CH}_{2}, \mathrm{C}-6\right), 56.14(\mathrm{CH}$, C-5), $55.29(\mathrm{CH}, \mathrm{C}-4), 27.05\left(\mathrm{CH}_{3}, \mathrm{C}\left(\underline{\mathrm{C}} \mathrm{H}_{3}\right)_{2}\right), 26.89\left(\mathrm{CH}_{3}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}\right), 26.03\left(3 \times \mathrm{CH}_{3}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right)$, $18.50\left(\mathrm{C}_{\mathrm{q}}, \underline{\mathrm{C}}\left(\mathrm{CH}_{3}\right)_{3}\right),-5.22\left(\mathrm{CH}_{3}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right),-5.30\left(\mathrm{CH}_{3}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right) ;$ HRMS $(\mathrm{ESI}) \mathrm{m} / \mathrm{z}[\mathrm{M}+\mathrm{Na}]^{+}$ calcd for $\mathrm{C}_{15} \mathrm{H}_{30} \mathrm{O}_{5} \mathrm{SiNa} 341.1755$; 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 ( $2.7 \mathrm{~mL}, 9.26 \mathrm{mmol}$, 1.4 equiv), was dissolved under argon in dry DCM ( 50 mL ) containing $4 \AA$ molecular sieves ( 1.5 g ) and cooled to $-78^{\circ} \mathrm{C}$. Diethyl-(D)tartrate ( $1.6 \mathrm{~mL}, 9.26 \mathrm{mmol}, 1.4$ equiv) was added and the mixture stirred for 15 min . Ethyl 6-tert-buthyldimethylsilyloxy-(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 tertbutyl hydroperoxide in nonane ( $2.4 \mathrm{~mL}, 13.22 \mathrm{mmol}, 2$ equiv). The solution was stirred for 18 h at $-20^{\circ} \mathrm{C}$ 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. $\mathrm{NaHCO}_{3}$ solution. Drying over $\mathrm{MgSO}_{4}$, removing of the solvent under reduced pressure and purification by flash chromatography (heptane/ethyl acetate $4: 1$ ) yielded 5b ( $1.87 \mathrm{~g}, 89 \%$ ) as colorless oil: $[\alpha]^{20}{ }_{D}=+15.69^{\circ}\left(c 1.1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 4.02$ (ddd, $J=7.8,6.0,4.0 \mathrm{~Hz}$, $1 \mathrm{H}, \mathrm{H}-2$ ), 3.96 (ddd, $J=12.8,4.5,2.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6 \mathrm{a}$ ), 3.91 (dd, $J=7.9,4.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3$ ), 3.84 (dd, $J=10.6,3.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1 \mathrm{a}$ ), 3.72 (dd, $J=10.6,6.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1 \mathrm{~b}$ ), $3.69-3.63$ (m, $1 \mathrm{H}, \mathrm{H}-6 \mathrm{~b}), 3.19$ (dt, $J=3.8,2.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-5), 3.14$ (dd, $J=4.7,2.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4$ ), 1.69 (dd, $J=7.6,5.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OH}), 1.40\left(\mathrm{~s}, J=0.7 \mathrm{~Hz}, 3 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.39(\mathrm{~s}, J=0.7 \mathrm{~Hz}, 3 \mathrm{H}$, $\left.\mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}\right), 0.89\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 0.07\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right) ;{ }^{13} \mathrm{C}$ NMR ( $\left.100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ $109.99\left(\mathrm{C}_{\mathrm{q}}, \underline{\mathrm{C}}\left(\mathrm{CH}_{3}\right)_{2}\right), 78.41(\mathrm{CH}, \mathrm{C}-2), 78.19(\mathrm{CH}, \mathrm{C}-3), 63.65\left(\mathrm{CH}_{2}, \mathrm{C}-1\right), 60.88\left(\mathrm{CH}_{2}, \mathrm{C}-6\right)$, $55.77(\mathrm{CH}, \mathrm{C}-5), 54.98(\mathrm{CH}, \mathrm{C}-4), 27.16\left(\mathrm{CH}_{3}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}\right), 26.80\left(\mathrm{CH}_{3}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}\right), 26.05(3 \mathrm{x}$ $\left.\mathrm{CH}_{3}, \mathrm{C}\left(\underline{\mathrm{C}} \mathrm{H}_{3}\right)_{3}\right), 18.51\left(\mathrm{C}_{\mathrm{q}}, \underline{\mathrm{C}}\left(\mathrm{CH}_{3}\right)_{3}\right),-5.22\left(\mathrm{CH}_{3}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right),-5.27\left(\mathrm{CH}_{3}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right)$; HRMS (ESI) $\mathrm{m} / \mathrm{z}[\mathrm{M}+\mathrm{Na}]^{+}$calcd for $\mathrm{C}_{15} \mathrm{H}_{30} \mathrm{O}_{5} \mathrm{SiNa} 341.1755$; found 341.1758.
(2S,3S,4S,5R)-6-O-tert-Butyldimethylsilyl-2,3-epoxy-4,5-O-isopropylidene-hexan-1-ol (5c)


Compound $\mathbf{5 c}$ was synthesized from $\mathbf{4 a}(3.15 \mathrm{~g}, 10.41 \mathrm{mmol})$ according to the procedure for compound 5b: yield $2.97 \mathrm{~g}(89 \%)$; $[\alpha]^{20}{ }_{\mathrm{D}}=+12.78^{\circ}\left(\mathrm{c} 1.6, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR $\left(600 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ $\delta 3.99-3.91$ (m, 3H, H-2 and H-3 and H-6a), $3.79-3.72$ (m, 2H, H-1), 3.67 (ddd, $J=12.8$, $7.4,4.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6 \mathrm{~b}$ ), 3.19 (ddd, $J=7.7,4.1,2.2 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{H}-4$ and $\mathrm{H}-5$ ), 1.79 (dd, $J=7.5$, $5.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OH}$ ), $1.41\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.40\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}\right), 0.89\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 0.07(\mathrm{~s}$, $\left.6 \mathrm{H}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right) ;{ }^{13} \mathrm{C}$ NMR ( $\left.150 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 110.02\left(\mathrm{C}_{q}\right), 79.11(\mathrm{CH}), 76.99(\mathrm{CH}), 63.53$ $\left(\mathrm{CH}_{2}\right), 61.11\left(\mathrm{CH}_{2}\right), 56.17(\mathrm{CH}), 55.29(\mathrm{CH}), 27.03\left(\mathrm{CH}_{3}\right), 26.87\left(\mathrm{CH}_{3}\right), 26.02\left(3 \times \mathrm{CH}_{3}\right.$, $\left.\left.\mathrm{C}(\underline{\mathrm{CH}})_{3}\right)_{3}\right), 18.48\left(\mathrm{C}, \underline{\mathrm{C}}\left(\mathrm{CH}_{3}\right)_{3}\right),-5.23\left(\mathrm{CH}_{3}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right),-5.28\left(\mathrm{CH}_{3}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right)$; HRMS (ESI) m/z $[\mathrm{M}+\mathrm{Na}]^{+}$calcd for $\mathrm{C}_{15} \mathrm{H}_{30} \mathrm{O}_{5} \mathrm{SiNa} 341.1755$; found 341.1751.

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


DMSO ( $2.9 \mathrm{~mL}, 41.33 \mathrm{mmol}, 4$ equiv) was added slowly to a solution of oxalyl chloride $\left(1.8 \mathrm{~mL}, 20.66 \mathrm{mmol}, 2\right.$ equiv) in dry DCM $(35 \mathrm{~mL})$ at $-78^{\circ} \mathrm{C}$. After $15 \mathrm{~min} 5 \mathrm{a}(3.29 \mathrm{~g}, 10.33$ 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 $\mathrm{Et}_{3} \mathrm{~N}(8.6 \mathrm{~mL}, 61.99 \mathrm{mmol}, 6$ equiv) and allowed to warm up to rt over 16 h . The mixture was washed with sat. $\mathrm{NH}_{4} \mathrm{Cl}$ solution and brine. The organic phase was dried over $\mathrm{MgSO}_{4}$, solvents removed under reduced pressure and the crude aldehyde used without further purification.

NaH ( $10 \%$ in mineral oil, $496 \mathrm{mg}, 12.40 \mathrm{mmol}, 1.2$ equiv) was dissolved in dry DCM ( 35 mL ) under argon and cooled to $0^{\circ} \mathrm{C}$. Triethyl phosphonoacetate ( $2.7 \mathrm{~mL}, 12.40 \mathrm{mmol}, 1.2$ 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 $0^{\circ} \mathrm{C}$ by the slow addition of water. The phases were separated and the aqueous phase extracted $3 \times$ with DCM. The organic phase was washed with brine and dried over $\mathrm{MgSO}_{4}$. Removing of the solvents under reduced pressure and purification by flash chromatography (heptane/ethyl acetate 9:1) yielded $\mathbf{6 a}(3.10 \mathrm{~g}, 78 \%)$ as a colorless oil: $[\alpha]^{20}{ }_{D}=-7.57^{\circ}\left(c 1.1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR $\left(600 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 6.67(\mathrm{dd}, J=15.7,7.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-$ 3), $6.15(\mathrm{~d}, J=15.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2), 4.19\left(\mathrm{q}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OC} \underline{H}_{2} \mathrm{CH}_{3}\right), 3.98(\mathrm{dt}, J=9.2,4.7$ $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{H}-7$ ), 3.93 (dd, $J=7.4,4.5 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6$ ), 3.78 (dd, $J=10.7,4.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-8 \mathrm{a}$ ), 3.73 (dd, $J=10.7,5.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-8 \mathrm{~b}), 3.52-3.49$ (m, $1 \mathrm{H}, \mathrm{H}-4$ ), 3.10 (dd, J=4.2, $1.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-$ 5), 1.41 (s, $\left.3 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.40\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.28\left(\mathrm{t}, J=7.2 \mathrm{~Hz}, 3 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right), 0.89(\mathrm{~s}$, $\left.9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 0.07\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right) ;{ }^{13} \mathrm{C}$ NMR ( $\left.150 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 165.59(\mathrm{C}, \mathrm{C}-1), 143.44$ ( $\mathrm{CH}, \mathrm{C}-3$ ), $124.64(\mathrm{CH}, \mathrm{C}-2), 110.20\left(\mathrm{C}_{\mathrm{q}}, \underline{\mathrm{C}}\left(\mathrm{CH}_{3}\right)_{2}\right), 79.02(\mathrm{CH}, \mathrm{C}-7), 77.14(\mathrm{CH}, \mathrm{C}-6), 63.47$ $\left(\mathrm{CH}_{2}, \mathrm{C}-8\right), 60.82(\mathrm{CH}, \mathrm{C}-5), 60.80\left(\mathrm{CH}_{2}, \mathrm{O}_{\mathrm{CH}}^{2} \mathrm{CH}_{3}\right), 54.12(\mathrm{CH}, \mathrm{C}-4), 27.02\left(\mathrm{CH}_{3}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}\right)$, $26.81\left(\mathrm{CH}_{3}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}\right), 26.02\left(3 \times \mathrm{CH}_{3}, \mathrm{C}\left(\underline{\mathrm{CH}}_{3}\right)_{3}\right)$, $18.48\left(\mathrm{C}, \underline{\mathrm{C}}\left(\mathrm{CH}_{3}\right)_{3}\right)$, $14.33\left(\mathrm{CH}_{3}, \mathrm{OCH}_{2} \underline{\mathrm{CH}}_{3}\right)$, $-5.23\left(\mathrm{CH}_{3}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right),-5.32\left(\mathrm{CH}_{3}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right) ;$ HRMS (ESI) $\mathrm{m} / \mathrm{z}[\mathrm{M}+\mathrm{Na}]^{+}$calcd for $\mathrm{C}_{19} \mathrm{H}_{34} \mathrm{O}_{6} \mathrm{SiNa} 409.2017$; found 409.2016.

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



Compound $\mathbf{6} \mathbf{b}$ was synthesized from $\mathbf{5 b}(1.31 \mathrm{~g}, 4.11 \mathrm{~mol})$ according to the procedure for compound 6a: yield 1.15 g (72\%); $[\alpha]^{20}{ }_{\mathrm{D}}=+6.80^{\circ}\left(\mathrm{c} 1.1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 6.67$ (dd, $J=15.7,7.1 \mathrm{~Hz}, 1 \mathrm{H} . \mathrm{H}-3), 6.15(\mathrm{dd}, J=15.6,0.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2), 4.20(\mathrm{q}, J=7.1$ $\mathrm{Hz}, 2 \mathrm{H}, \mathrm{OCH} \underline{2}_{2} \mathrm{CH}_{3}$ ), 3.98 (ddd, $J=7.5,5.3,4.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-7$ ), 3.93 (dd, $J=7.5,4.4 \mathrm{~Hz}, 1 \mathrm{H}$, $\mathrm{H}-6$ ), 3.78 (dd, $J=10.7,4.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-8 \mathrm{a}$ ), 3.74 (dd, $J=10.7,5.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-8 \mathrm{~b}$ ), $3.53-$ 3.49 (m, $1 \mathrm{H}, \mathrm{H}-4), 3.11$ (dd, $J=4.5,2.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-5), 1.41\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.40(\mathrm{~s}, 3 \mathrm{H}$, $\left.\mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.28\left(\mathrm{t}, J=7.1 \mathrm{~Hz}, 3 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right), 0.89\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 0.07\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right)$; ${ }^{13} \mathrm{C}$ NMR ( $\left.150 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 165.60\left(\mathrm{C}_{\mathrm{q}}, \mathrm{C}-1\right)$, $143.44(\mathrm{CH}, \mathrm{C}-3), 124.65(\mathrm{CH}, \mathrm{C}-2), 110.21$ $\left(\mathrm{C}_{\mathrm{q}}, \underline{\mathrm{C}}\left(\mathrm{CH}_{3}\right)_{2}\right), 79.03(\mathrm{CH}, \mathrm{C}-7), 77.15(\mathrm{CH}, \mathrm{C}-6), 63.49\left(\mathrm{CH}_{2}, \mathrm{C}-8\right), 60.83(\mathrm{CH}, \mathrm{C}-5), 60.81$ $\left(\mathrm{CH}_{2}, \mathrm{O} \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 54.13(\mathrm{CH}, \mathrm{C}-4), 27.03\left(\mathrm{CH}_{3}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}\right), 26.82\left(\mathrm{CH}_{3}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}\right), 26.02(3 \mathrm{x}$ $\left.\mathrm{CH}_{3}, \mathrm{C}\left(\underline{\mathrm{C}} \mathrm{H}_{3}\right)_{3}\right), 18.49\left(\mathrm{C}, \underline{\mathrm{C}}\left(\mathrm{CH}_{3}\right)_{3}\right)$, $14.34\left(\mathrm{CH}_{3}, \mathrm{OCH}_{2} \underline{\mathrm{CH}}_{3}\right),-5.22\left(\mathrm{CH}_{3}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right),-5.31$ $\left(\mathrm{CH}_{3}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right)$; HRMS (ESI) $\mathrm{m} / \mathrm{z}[\mathrm{M}+\mathrm{Na}]^{+}$calcd for $\mathrm{C}_{19} \mathrm{H}_{34} \mathrm{O}_{6} \mathrm{SiNa} 409.2017$; found 409.2025.

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



Compound $\mathbf{6 c}$ was synthesized from $\mathbf{5 c}(2.47 \mathrm{~g}, 7.76 \mathrm{mmol})$ according to the procedure for compound 6a: yield $2.37 \mathrm{~g}(79 \%)$; $[\mathrm{d}]^{20} \mathrm{D}=+23.47^{\circ}\left(\mathrm{c} 1.0, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 6.66$ (ddd, $J=15.7,7.3,0.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3$ ), 6.15 (dd, $J=15.6,0.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2$ ), 4.20 (q, $J=$ $7.1 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}$ ), 4.05 (ddd, $J=7.6,6.2,3.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-7$ ), 3.99 (dd, $J=7.7,3.9 \mathrm{~Hz}, 1$ $\mathrm{H}, \mathrm{H}-6$ ), 3.85 (dd, $J=10.6,3.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-8 \mathrm{a}$ ), 3.72 (dd, $J=10.6,6.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-8 \mathrm{~b}$ ), 3.53 (dt, $J=7.2,1.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4), 3.05(\mathrm{dd}, J=3.9,2.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-5), 1.39\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.29$ ( $\mathrm{t}, \mathrm{J}=7.1 \mathrm{~Hz}, 3 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}$ ), $0.89\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 0.08\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{SI}\left(\mathrm{CH}_{3}\right)_{2}\right) ;{ }^{13} \mathrm{C}$ NMR (150 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 165.68\left(\mathrm{C}_{\mathrm{q}}, \mathrm{C}-1\right), 143.74(\mathrm{CH}, \mathrm{C}-3), 124.60(\mathrm{CH}, \mathrm{C}-2), 110.15\left(\mathrm{C}, \underline{\mathrm{C}}\left(\mathrm{CH}_{3}\right)_{2}\right)$, $78.09(\mathrm{CH}, \mathrm{C}-7), 77.72(\mathrm{CH}, \mathrm{C}-6), 63.57\left(\mathrm{CH}_{2}, \mathrm{C}-8\right), 60.82\left(\mathrm{CH}_{2}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right), 60.31(\mathrm{CH}, \mathrm{C}-$ 5), $53.80(\mathrm{CH}, \mathrm{C}-4), 27.19\left(\mathrm{CH}_{3}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}\right), 26.64\left(\mathrm{CH}_{3}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}\right), 26.04\left(3 \times \mathrm{CH}_{3}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right)$, $18.50\left(\mathrm{C}_{\mathrm{q}}, \underline{\mathrm{C}}\left(\mathrm{CH}_{3}\right)_{3}\right), \quad 14.35\left(\mathrm{CH}_{3}, \quad \mathrm{OCH}_{2} \mathrm{CH}_{3}\right), \quad-5.22\left(\mathrm{CH}_{3}, \quad \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right), \quad-5.26\left(\mathrm{CH}_{3}\right.$, $\left.\mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right) ; \mathrm{HRMS}(\mathrm{ESI}) \mathrm{m} / \mathrm{z}[\mathrm{M}+\mathrm{Na}]^{+}$calcd for $\mathrm{C}_{19} \mathrm{H}_{34} \mathrm{O}_{6} \mathrm{SiNa} 409.2017$; found 409.2034.

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


Compound $6 \mathbf{a}$ ( $1.00 \mathrm{~g}, 2.59$, 1 equiv) was dissolved in dry and degassed EtOH under argon. $\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{4}(0.30 \mathrm{~g}, 0.26 \mathrm{mmol}, 0.1$ equiv) and trimethylsilyl azide ( $0.7 \mathrm{~mL}, 5.17 \mathrm{mmol}, 2$ 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 7 a ( $0.99 \mathrm{~g}, 89 \%$, $98 \%$ de $)$ as a colorless oil: $[\alpha]^{20}{ }_{\mathrm{D}}=+3.78^{\circ}\left(\mathrm{c} 1.0, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right) ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(600 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.07$ (dd, $J=15.7,6.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3$ ), 6.16 (dd, $J=15.7,1.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2$ ), 4.22 ( $\mathrm{q}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}$,
$\mathrm{OCH}_{2} \mathrm{CH}_{3}$ ), $4.19(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-5), 3.98(\mathrm{dd}, J=9.6,3.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-8 \mathrm{a}), 3.93-3.89$ ( $\mathrm{m}, 2 \mathrm{H}, \mathrm{H}-6$ and H-7), $3.88-3.86(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-4$ ), $3.68(\mathrm{dt}, J=8.3,2.5 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OH}), 3.65-$ $3.61(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-8 \mathrm{~b}), 1.40\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}\right)$, $1.38\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.31(\mathrm{t}, \mathrm{J}=7.1 \mathrm{~Hz}, 3 \mathrm{H}$, $\left.\mathrm{OCH}_{2} \mathrm{CH}_{3}\right), 0.91\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 0.12\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right) ;{ }^{13} \mathrm{C}$ NMR $\left(150 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ $165.86\left(\mathrm{C}_{\mathrm{q}}, \mathrm{C}-1\right), 142.22(\mathrm{CH}, \mathrm{C}-3), 124.74(\mathrm{CH}, \mathrm{C}-2), 109.77\left(\mathrm{C}, \underline{\mathrm{C}}\left(\mathrm{CH}_{3}\right)_{2}\right), 80.25(\mathrm{CH}, \mathrm{C}-6)$, $80.04(\mathrm{CH}, \mathrm{C}-7), 74.94(\mathrm{CH}, \mathrm{C}-4), 64.39\left(\mathrm{CH}_{2}, \mathrm{C}-8\right), 62.93(\mathrm{CH}, \mathrm{C}-5), 60.85\left(\mathrm{CH}_{2}\right.$, $\left.\mathrm{O}_{\mathrm{CH}}^{2} \mathrm{CH}_{3}\right)$, $26.93\left(\mathrm{CH}_{3}, \mathrm{C}\left(\underline{\mathrm{C}}_{3}\right)_{2}\right), 26.91\left(\mathrm{CH}_{3}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}\right)$, $25.99\left(3 \times \mathrm{CH}_{3}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right)$, $18.52\left(\mathrm{C}_{\mathrm{q}}\right.$, $\left.\underline{\mathrm{C}}\left(\mathrm{CH}_{3}\right)_{3}\right), 14.37\left(\mathrm{CH}_{3}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right),-5.41\left(\mathrm{CH}_{3}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right),-5.42\left(\mathrm{CH}_{3}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right)$; HRMS (ESI) $\mathrm{m} / \mathrm{z}\left[\mathrm{M}+\mathrm{Na}^{+}\right.$calcd for $\mathrm{C}_{19} \mathrm{H}_{35} \mathrm{~N}_{3} \mathrm{O}_{6} \mathrm{SiNa} 452.2193$; found 452.2195; (IR) v 3385 (OH), 2985 (CH), $2930(\mathrm{CH}), 2885(\mathrm{CH}), 2858(\mathrm{CH}), 2101\left(\mathrm{~N}_{3}\right), 1722(\mathrm{C}=\mathrm{O}) \mathrm{cm}^{-1}$.

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



Compound $\mathbf{7 b}$ was synthesized from $\mathbf{6 b}(1.75 \mathrm{~g}, 4.53 \mathrm{mmol})$ according to the procedure for compound 7a: yield $1.57 \mathrm{~g}(80 \%, 95 \%$ de $) ;[\alpha]^{20} \mathrm{D}=-2.76^{\circ}$ (c 1.25, $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ); ${ }^{1} \mathrm{H}$ NMR ( 600 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.07(\mathrm{dd}, J=15.7,6.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3), 6.15(\mathrm{dd}, J=15.7,1.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2)$, $4.22\left(\mathrm{q}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right), 4.20-4.17(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-5), 4.00-3.96(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-8 \mathrm{a})$, $3.94-3.88(\mathrm{~m}, 2 \mathrm{H}, \mathrm{H}-6$ and H-7), $3.86(\mathrm{dd}, \mathrm{J}=2.7,1.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4), 3.68(\mathrm{dt}, J=8.2$, 2.4 $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{OH}$ ), $3.65-3.60(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-8 \mathrm{~b})$, $1.40\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.38\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.30$ ( $\mathrm{t}, \mathrm{J}=7.1 \mathrm{~Hz}, 3 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}$ ), $0.91\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 0.12\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right) ;{ }^{13} \mathrm{C}$ NMR (150 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 165.84\left(\mathrm{C}_{\mathrm{q}}, \mathrm{C}-1\right), 142.21(\mathrm{CH}, \mathrm{C}-3), 124.73(\mathrm{CH}, \mathrm{C}-2), 109.76\left(\mathrm{C}_{\mathrm{q}}, \underline{\mathrm{C}}\left(\mathrm{CH}_{3}\right)_{2}\right)$, $80.24(\mathrm{CH}, \mathrm{C}-6), 80.04(\mathrm{CH}, \mathrm{C}-7), 74.94(\mathrm{CH}, \mathrm{C}-4), 64.39\left(\mathrm{CH}_{2}, \mathrm{C}-8\right), 62.93(\mathrm{CH}, \mathrm{C}-5), 60.83$ $\left(\mathrm{CH}_{2}, \mathrm{O}_{2} \mathrm{CH}_{3}\right), 26.93\left(\mathrm{CH}_{3}, \mathrm{C}\left(\underline{\mathrm{C}} \mathrm{H}_{3}\right)_{2}\right), 26.90\left(\mathrm{CH}_{3}, \mathrm{C}\left(\underline{\mathrm{CH}}_{3}\right)_{2}\right), 25.99\left(3 \times \mathrm{CH}_{3}, \mathrm{C}\left(\underline{\mathrm{C}} \mathrm{CH}_{3}\right)_{3}\right)$, $18.51\left(\mathrm{C}_{\mathrm{q}}, \underline{\mathrm{C}}\left(\mathrm{CH}_{3}\right)_{2}\right), 14.37\left(\mathrm{CH}_{3}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right)$, $-5.42\left(\mathrm{CH}_{3}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right),-5.43\left(\mathrm{CH}_{3}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right)$; HRMS (ESI) $\mathrm{m} / \mathrm{z}[\mathrm{M}+\mathrm{Na}]^{+}$calcd for $\mathrm{C}_{19} \mathrm{H}_{35} \mathrm{~N}_{3} \mathrm{O}_{6} \mathrm{SiNa} 452.2193$; found 452.2186; (IR) $\vee 3385$ $(\mathrm{OH}), 2931(\mathrm{CH}), 2101\left(\mathrm{~N}_{3}\right), 1722(\mathrm{C}=\mathrm{O}) \mathrm{cm}^{-1}$.

## Ethyl (4R,5S,6R,7R)-4-azido-8-O-tert-butyldimethylsilyl-6,7-O-isopropylidene-5-

 hydroxy-(2E)-octenoate (7c)

Compound $7 \mathbf{c}$ was synthesized from $6 \mathbf{c}(2.20 \mathrm{~g}, 5.69 \mathrm{mmol})$ according to the procedure for compound 7a: yield $1.91 \mathrm{~g}(78 \%, 98 \% \mathrm{de})$; $[\alpha]^{20} \mathrm{D}=-14.64^{\circ}$ (c 1.20, $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ); ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 6.85(\mathrm{dd}, J=15.6,7.5 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3), 6.12(\mathrm{dd}, J=15.6,1.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-$ 2), $4.26-4.20\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right), 4.20-4.14(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-5), 4.10$ (ddd, $J=7.9,6.5,3.9 \mathrm{~Hz}$, $1 \mathrm{H}, \mathrm{H}-7$ ), 3.98 (dd, $J=8.0,2.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6$ ), 3.83 (dd, $J=10.5,3.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-8 \mathrm{a}$ ), $3.70-$ 3.63 (m, $2 \mathrm{H}, \mathrm{H}-4$ and H-8b), 2.62 (d, J=8.7 Hz, $1 \mathrm{H}, \mathrm{OH}$ ), $1.43\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.39(\mathrm{~s}, 3$ $\left.\mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.30\left(\mathrm{t}, J=7.2 \mathrm{~Hz}, 3 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right), 0.88\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 0.06(\mathrm{~s}, 6 \mathrm{H}$, $\left.\mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right) ;{ }^{13} \mathrm{C}$ NMR ( $150 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 165.48\left(\mathrm{C}_{\mathrm{q}}, \mathrm{C}-1\right), 140.87(\mathrm{CH}, \mathrm{C}-3), 125.59(\mathrm{CH}, \mathrm{C}-$ 2), $109.98\left(\mathrm{C}_{\mathrm{q}}, \underline{\mathrm{C}}\left(\mathrm{CH}_{3}\right)_{2}\right), 78.47(\mathrm{CH}, \mathrm{C}-6), 77.05(\mathrm{CH}, \mathrm{C}-7), 71.99(\mathrm{CH}, \mathrm{C}-4), 65.74(\mathrm{CH}, \mathrm{C}-$ 5), $63.57\left(\mathrm{CH}_{2}, \mathrm{C}-8\right), 60.92\left(\mathrm{CH}_{2}, \mathrm{O}_{2} \mathrm{CH}_{3}\right), 27.22\left(\mathrm{CH}_{3}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}\right), 27.03\left(\mathrm{CH}_{3}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}\right)$, $25.97\left(3 \times \mathrm{CH}_{3}, \mathrm{C}\left(\underline{\mathrm{C}} \mathrm{H}_{3}\right)_{3}\right), 18.39\left(\mathrm{C}, \underline{\mathrm{C}}\left(\mathrm{CH}_{3}\right)_{3}\right), 14.33\left(\mathrm{CH}_{3}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right),-5.37\left(\mathrm{CH}_{3}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right)$, $-5.40\left(\mathrm{CH}_{3}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right)$; HRMS (ESI) $\mathrm{m} / \mathrm{z}[\mathrm{M}+\mathrm{Na}]^{+}$calcd for $\mathrm{C}_{19} \mathrm{H}_{35} \mathrm{~N}_{3} \mathrm{O}_{6} \mathrm{SiNa} 452.2193$; found 452.2188; (IR) v $3348(\mathrm{OH}), 2925(\mathrm{CH}), 2112\left(\mathrm{~N}_{3}\right), 1738(\mathrm{C}=\mathrm{O}) \mathrm{cm}^{-1}$.

## 1,3,4,6-Tetra-O-acetyl-2-azido-2-deoxy-D-galactopyranose (8a)



Compound 7 a ( $2.00 \mathrm{~g}, 4.66 \mathrm{mmol}$, 1 equiv) was dissolved in $10 \mathrm{~mL} \mathrm{MeOH} / \mathrm{H}_{2} \mathrm{O}$ (4:1). After the addition of DOWEX $\mathrm{H}^{+}(\approx 1 \mathrm{~g})$, the mixture was heated to $40^{\circ} \mathrm{C}$ for 16 h . DOWEX $\mathrm{H}^{+}$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 $\mathrm{DCM} / \mathrm{MeOH}(9: 1)$ and ozone was purged through at $-78^{\circ} \mathrm{C}$ until the solution turned blue. Subsequently, oxygen was purged through until the blue color disappeared, again. Dimethyl sulfide ( $0.7 \mathrm{~mL}, 9.31 \mathrm{mmol}, 2$ 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 $10 \mathrm{~mL} \mathrm{Ac}_{2} \mathrm{O}$ pyridine (1:1) under argon. Dimethylaminopyridine ( $57 \mathrm{mg}, 0.47 \mathrm{mmol}, 0.1$ 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 8 a ( $1.40 \mathrm{~g}, 81 \%$, $\alpha$-pyr/ $\beta$-pyr 14:86): ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ a: $6.31(\mathrm{~d}, J=3.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1$ ), $5.47(\mathrm{dd}, J$ $=3.2,1.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4), 5.31$ (dd, J=11.1, $3.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3$ ), $4.30-4.25(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-5), 4.11$ - 4.04 (m, 2 H, H-6), 3.93 (dd, J=11.1, $3.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2$ ), 2.17 (s, $3 \mathrm{H} ; \mathrm{Ac}$ ), 2.16 (s, $3 \mathrm{H}, \mathrm{Ac}$ ), 2.07 (s, $3 \mathrm{H}, \mathrm{Ac}$ ), 2.03 (s, $3 \mathrm{H}, \mathrm{Ac}$ ); $\beta: 5.54$ (d, $J=8.5 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1$ ), 5.37 (dd, $J=3.3,0.9 \mathrm{~Hz}$, $1 \mathrm{H}, \mathrm{H}-4$ ), 4.88 (dd, $J=10.8,3.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3$ ), $4.16-4.08$ (m, $2 \mathrm{H}, \mathrm{H}-6$ ), 4.00 ( td, $J=6.7$, $1.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-5), 3.83$ (dd, $J=10.8,8.5 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2$ ), 2.20 (s, $3 \mathrm{H}, \mathrm{Ac}$ ), 2.16 (s, $3 \mathrm{H}, \mathrm{Ac}$ ), 2.06 (s, $3 \mathrm{H}, \mathrm{Ac}$ ), $2.03(\mathrm{~s}, 3 \mathrm{H}, \mathrm{Ac}) ;{ }^{13} \mathrm{C}$ NMR ( $150 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta \mathrm{a}: 170.48\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 170.11$ $\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 169.99\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 168.85\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 90.52(\mathrm{CH}, \mathrm{C}-1), 68.86(\mathrm{CH}, \mathrm{C}-5), 68.77(\mathrm{CH}, \mathrm{C}-$ 3), $66.94(\mathrm{CH}, \mathrm{C}-4), 61.21\left(\mathrm{CH}_{2}, \mathrm{C}-6\right), 56.92(\mathrm{CH}, \mathrm{C}-2), 21.08\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 20.79\left(3 \times \mathrm{CH}_{3}, \mathrm{Ac}\right)$, $20.76\left(\mathrm{CH}_{3}, \mathrm{Ac}\right) ; \beta: 170.46\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 170.07\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 169.75\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 168.70\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 92.96$ (CH, C-1), $71.82(\mathrm{CH}, \mathrm{C}-5), 71.40(\mathrm{CH}, \mathrm{C}-3), 66.25(\mathrm{CH}, \mathrm{C}-4), 61.05\left(\mathrm{CH}_{2}, \mathrm{C}-6\right), 59.75(\mathrm{CH}$, $\mathrm{C}-2), 21.03\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 20.79\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 20.74\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 20.72\left(\mathrm{CH}_{3}, \mathrm{Ac}\right)$; HRMS (ESI) m/z $[\mathrm{M}+\mathrm{Na}]^{+}$calcd for $\mathrm{C}_{14} \mathrm{H}_{19} \mathrm{~N}_{3} \mathrm{O}_{9} \mathrm{Na} 396.1019$; found 396.1016; (IR) $\vee 2970(\mathrm{CH}), 2114\left(\mathrm{~N}_{3}\right)$, 1747 ( $\mathrm{C}=\mathrm{O}$ ) $\mathrm{cm}^{-1}$.

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



Compound $\mathbf{8 b}$ was synthesized from $\mathbf{7 b}(1.56 \mathrm{~g}, 3.63 \mathrm{mmol})$ according to the procedure for compound 8a: yield $0.85 \mathrm{~g}(63 \%$, $\alpha-p y r / \beta-p y r 19: 81) ;{ }^{1} \mathrm{H}$ NMR $\left(600 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ a: 6.31 (d, $J=3.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1), 5.48-5.45(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-4), 5.30(\mathrm{ddd}, J=11.0,3.3,1.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3)$, 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, $1 \mathrm{H}, \mathrm{H}-2$ ), 2.17 (s, $3 \mathrm{H}, \mathrm{Ac}$ ), 2.16 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{Ac}$ ), 2.06 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{Ac}$ ), 2.06 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{Ac}$ ); $\beta: 5.54$ (d, $J=8.5 \mathrm{~Hz}$, $1 \mathrm{H}, \mathrm{H}-1), 5.38-5.35(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-4), 4.88$ (dd, $J=10.8,3.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3), 4.15-4.09$ ( $\mathrm{m}, 2$ $\mathrm{H}, \mathrm{H}-6), 4.00(\mathrm{td}, \mathrm{J}=6.7,1.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-5), 3.83$ (ddd, $J=10.9,8.5,1.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2$ ), 2.19 (s, $3 \mathrm{H}, \mathrm{Ac}$ ), $2.16(\mathrm{~s}, 3 \mathrm{H}, \mathrm{Ac}), 2.05(\mathrm{~s}, 3 \mathrm{H}, \mathrm{Ac}), 2.03(\mathrm{~s}, 3 \mathrm{H}, \mathrm{Ac}) ;{ }^{13} \mathrm{C}$ NMR ( $150 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )
$\delta$ a: $170.11\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 169.99\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 169.75\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 168.85\left(\mathrm{C}_{q}, \mathrm{Ac}\right), 90.51(\mathrm{CH}, \mathrm{C}-1)$, $68.86(\mathrm{CH}, \mathrm{C}-5), 68.75(\mathrm{CH}, \mathrm{C}-3), 66.94(\mathrm{CH}, \mathrm{C}-4), 61.20\left(\mathrm{CH}_{2}, \mathrm{C}-6\right), 56.91(\mathrm{CH}, \mathrm{C}-2), 21.18$ $\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 20.06\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 20.77\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 20.72\left(\mathrm{CH}_{3}, \mathrm{Ac}\right) ; \beta: 170.47\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 170.07\left(\mathrm{C}_{\mathrm{q}}\right.$, Ac), $169.75\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 168.70\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right)$, $92.95(\mathrm{CH}, \mathrm{C}-1), 71.81(\mathrm{CH}, \mathrm{C}-5), 71.39(\mathrm{CH}, \mathrm{C}-3)$, $66.26(\mathrm{CH}, \mathrm{C}-4), 61.05\left(\mathrm{CH}_{2}, \mathrm{C}-6\right), 59.74(\mathrm{CH}, \mathrm{C}-2), 21.01\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 20.77\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 20.72$ $\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 20.70\left(\mathrm{CH}_{3}, \mathrm{Ac}\right)$; HRMS (ESI) $\mathrm{m} / \mathrm{z}[\mathrm{M}+\mathrm{Na}]^{+}$calcd for $\mathrm{C}_{14} \mathrm{H}_{19} \mathrm{~N}_{3} \mathrm{O}_{9} \mathrm{SiNa} 396.1019$; found 396.1013; (IR) v 2969 (CH), $2113\left(\mathrm{~N}_{3}\right), 1744(\mathrm{C}=\mathrm{O}) \mathrm{cm}^{-1}$.

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



Compound $\mathbf{8 c}$ was synthesized from $7 \mathbf{c}(0.10 \mathrm{~g}, 0.23 \mathrm{mmol})$ according to the procedure for compound 8a: yield $32 \mathrm{mg}(37 \%$, $\alpha$-pyr/ $\beta$-pyr/ $\alpha$-fur $50: 31: 19)$; ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta \alpha-$ pyr: 6.00 (d, $J=4.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1$ ), 5.12 (dd, $J=6.4,5.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3$ ), 5.04 (dd, $J=5.2,3.6$ Hz, $1 \mathrm{H}, \mathrm{H}-4), 4.45$ (ddd, J = 6.6, 5.2, $3.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-5$ ), $4.27-4.21$ (m, $2 \mathrm{H}, \mathrm{H}-6$ ), 3.65 (dd, J $=6.4,4.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2$ ), $2.12(\mathrm{~s}, 3 \mathrm{H}, \mathrm{Ac}), 2.11(\mathrm{~s}, 3 \mathrm{H}, \mathrm{Ac}), 2.11(\mathrm{~s}, 3 \mathrm{H}, \mathrm{Ac}), 2.07(\mathrm{~s}, 3 \mathrm{H}$, Ac); $\beta$-pyr: 6.06 (d, $J=2.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1$ ), $5.25(\mathrm{t}, J=4.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3$ ), 4.87 (dd, $J=4.5,3.0$ $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{H}-4), 4.35$ (ddd, J=7.2, 5.6, 3.1 Hz, $1 \mathrm{H}, \mathrm{H}-5$ ), $4.19-4.13(\mathrm{~m}, 2 \mathrm{H}, \mathrm{H}-6), 3.57$ (dd, J = 4.6, $2.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2$ ), $2.18(\mathrm{~s}, 3 \mathrm{H}, \mathrm{Ac}), 2.13(\mathrm{~s}, 3 \mathrm{H}, \mathrm{Ac}), 2.13(\mathrm{~s}, 3 \mathrm{H}, \mathrm{Ac}), 2.04(\mathrm{~s}, 3 \mathrm{H}$, Ac); a-fur: 6.02 (d, $J=1.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1$ ), 5.32 (td, $J=6.3,3.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3$ ), 5.17 (dd, $J=6.0$, $3.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4), 4.52(\mathrm{t}, J=6.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2), 4.29$ (dd, $J=12.0,3.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6 \mathrm{a}), 4.16-$ 4.14 (m, 1H, H-5), 4.01 (dd, $J=12.0,6.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6 \mathrm{~b}$ ), 2.13 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{Ac}$ ), 2.11 (s, $3 \mathrm{H}, \mathrm{Ac}$ ), 2.10 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{Ac}$ ), 2.03 (s, $3 \mathrm{H}, \mathrm{Ac}$ ); ${ }^{13} \mathrm{C} \operatorname{NMR}\left(150 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ $\alpha$-pyr: $170.47\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right)$, $169.94\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 169.31\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 168.72\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 91.43(\mathrm{CH}, \mathrm{C}-1)$, $68.94(\mathrm{CH}, \mathrm{C}-3), 67.92$ (CH, C-5), 67.63 (CH, C-4), $61.65\left(\mathrm{CH}_{2}, \mathrm{C}-6\right), 58.27(\mathrm{CH}, \mathrm{C}-2), 21.00\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 20.85$ $\left(2 \times \mathrm{CH}_{3}, \mathrm{Ac}\right), 20.69\left(\mathrm{CH}_{3}, \mathrm{Ac}\right) ; \beta$-pyr: $170.56\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 169.80\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 168.85\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right)$, $168.69\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 91.15(\mathrm{CH}, \mathrm{C}-1), 72.29(\mathrm{CH}, \mathrm{C}-5), 68.17(\mathrm{CH}, \mathrm{C}-3), 66.04(\mathrm{CH}, \mathrm{C}-4), 62.13$ $\left(\mathrm{CH}_{2}, \mathrm{C}-6\right), 57.49(\mathrm{CH}, \mathrm{C}-2), 20.98\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 20.89\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 20.80\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 20.71\left(\mathrm{CH}_{3}\right.$, Ac); $\alpha$-fur: $170.53\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 170.10\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right)$, $169.94\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right)$, $169.58\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right)$, $98.68(\mathrm{CH}, \mathrm{C}-$ 1), 78.96 ( $\mathrm{CH}, \mathrm{C}-2$ ), $75.09(\mathrm{CH}, \mathrm{C}-4), 69.27(\mathrm{CH}, \mathrm{C}-3$ or $\mathrm{C}-5), 69.19(\mathrm{CH}, \mathrm{C}-3$ or $\mathrm{C}-5), 62.58$ $\left(\mathrm{CH}_{2}, \mathrm{C}-6\right), 21.13\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 21.12\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 20.78\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 20.76\left(\mathrm{CH}_{3}, \mathrm{Ac}\right)$; HRMS (ESI)
$\mathrm{m} / \mathrm{z}[\mathrm{M}+\mathrm{Na}]^{+}$calcd for $\mathrm{C}_{14} \mathrm{H}_{19} \mathrm{~N}_{3} \mathrm{O}_{9} \mathrm{SiNa} 396.1019$; found 396.1009; (IR) v 2969 (CH), 2113 $\left(\mathrm{N}_{3}\right), 1744(\mathrm{C}=\mathrm{O}) \mathrm{cm}^{-1}$.

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



8a ( $200 \mathrm{mg}, 0.54 \mathrm{mmol}, 1$ equiv) was dissolved in 3 mL acetic anhydride. $20 \mathrm{mg} \mathrm{Pd} / \mathrm{C}$ was added and a $\mathrm{H}_{2}$-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 $\mathrm{EtOH} / \mathrm{H}_{2} \mathrm{O}$ (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 $\mathbf{2 a}(108 \mathrm{mg}, 52 \%, \alpha-p y r / \beta-p y r 26: 74)$ as a colorless solid: ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ a: 6.21 (d, $J=3.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1$ ), 5.44 (d, J = $9.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}$ ), 5.42 (dd, $J=3.1,1.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4), 5.22$ (dd, $J=11.6,3.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3$ ), 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, $2 \mathrm{H}, \mathrm{H}-6$ ), 2.17 (s, $6 \mathrm{H}, \mathrm{Ac}$ ), 2.03 (s, $6 \mathrm{H}, \mathrm{Ac}$ ), 1.95 ( s, $3 \mathrm{H}, \mathrm{Ac}$ ); $\beta: 5.69$ (d, J = $8.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1$ ), 5.49 (d, J=9.6 Hz, 1 H , NH ), 5.37 (dd, $J=3.4,1.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4$ ), 5.08 (dd, $J=11.3,3.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3$ ), 4.44 (dt, $J=$ $11.3,9.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2), 4.18-4.08(\mathrm{~m}, 2 \mathrm{H}, \mathrm{H}-6), 4.01(\mathrm{td}, J=6.5,1.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-5)$, 2.16 (s, $3 \mathrm{H}, \mathrm{Ac}$ ), 2.12 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{Ac}$ ), 2.04 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{Ac}$ ), 2.01 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{Ac}$ ), 1.93 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{Ac}$ ); ${ }^{13} \mathrm{C}$ NMR ( $150 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ a: $171.38\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 170.56\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 170.38\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 170.21\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right)$, $168.94\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 91.49(\mathrm{CH}, \mathrm{C}-1), 68.70(\mathrm{CH}, \mathrm{C}-5), 67.97(\mathrm{CH}, \mathrm{C}-3), 66.84(\mathrm{CH}, \mathrm{C}-4), 61.45$ $\left(\mathrm{CH}_{2}, \mathrm{C}-6\right), 47.14(\mathrm{CH}, \mathrm{C}-2), 23.34\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 21.12\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 20.91\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 20.84\left(\mathrm{CH}_{3}\right.$, $\mathrm{Ac}), 20.82\left(\mathrm{CH}_{3}, \mathrm{Ac}\right) ; \beta: 170.90\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 170.56\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 170.43\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 170.32\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right)$, 169.72 ( $\mathrm{C}, \mathrm{Ac}$ ), $93.18(\mathrm{CH}, \mathrm{C}-1)$, $72.00(\mathrm{CH}, \mathrm{C}-5)$, $70.46(\mathrm{CH}, \mathrm{C}-3), 66.48(\mathrm{CH}, \mathrm{C}-4), 61.45$ $\left(\mathrm{CH}_{2}, \mathrm{C}-6\right), 49.93(\mathrm{CH}, \mathrm{C}-2), 23.46\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 21.05\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 20.82\left(2 \times \mathrm{CH}_{3}, \mathrm{Ac}\right), 20.80$ $\left(\mathrm{CH}_{3}, \mathrm{Ac}\right)$; HRMS (ESI) $\mathrm{m} / \mathrm{z}[\mathrm{M}+\mathrm{Na}]^{+}$calcd for $\mathrm{C}_{16} \mathrm{H}_{23} \mathrm{NO}_{10} \mathrm{Na} 412.1220$; found 412.1223.

## 2-Acetamido-1,3,4,6-tetra-O-acetyl-2-deoxy-L-galactopyranose (2b)



Compound $\mathbf{2 b}$ was synthesized from $\mathbf{8 b}(0.20 \mathrm{~g}, 0.54 \mathrm{mmol})$ according to the procedure for compound 2a: yield $0.11 \mathrm{~g}(56 \%, \alpha-p y r / \beta-p y r 57: 43)$; ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ a: $\alpha: 6.21$ (d, J = $3.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1$ ), $5.46(\mathrm{~d}, J=9.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}$ ), 5.42 (dd, $J=3.4,1.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4$ ), 5.21 (dd, $J=11.5,3.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3$ ), 4.72 (ddd, $J=11.6,9.2,3.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2$ ), 4.23 (td, $J=$ $6.8,1.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-5), 4.11$ (dd, $J=11.3,6.7 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{H}-6$ ), 2.17 (s, 6H, Ac), 2.03 (s, 6 H , Ac), 1.95 (s, $3 \mathrm{H}, ~ A c$ ); $\beta: 5.70$ (d, J = $8.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1$ ), 5.53 (d, J = $9.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}$ ), 5.37 (dd, $J=3.4,1.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4), 5.08$ (dd, $J=11.3,3.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3$ ), 4.44 (dt, $J=11.3,9.2$ $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{H}-2), 4.16$ (dd, $J=11.4,6.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6 \mathrm{a}), 4.06$ (dd, $J=11.3,6.5 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6 \mathrm{~b})$, 4.02 (td, J=6.5, 1.2 Hz, $1 \mathrm{H}, \mathrm{H}-5$ ), 2.16 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{Ac}$ ), 2.12 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{Ac}$ ), 2.04 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{Ac}$ ), 2.01 (s, $3 \mathrm{H}, \mathrm{Ac}$ ), $1.94(\mathrm{~s}, 3 \mathrm{H}, \mathrm{Ac}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(150 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta \mathrm{a}: 171.35\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 170.54\left(\mathrm{C}_{\mathrm{q}}\right.$, Ac), $170.37\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 170.21\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 168.94\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 91.49(\mathrm{CH}, \mathrm{C}-1), 68.68(\mathrm{CH}, \mathrm{C}-5)$, 67.96 (CH, C-3), $66.83(\mathrm{CH}, \mathrm{C}-4), 61.43\left(\mathrm{CH}_{2}, \mathrm{C}-6\right), 47.12(\mathrm{CH}, \mathrm{C}-2), 23.32\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 21.11$ $\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 20.90\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 20.79\left(2 \times \mathrm{CH}_{3}, \mathrm{Ac}\right) ; \beta: 170.87\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 170.53\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 170.44$ $\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right)$, $170.37\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right)$, $169.70\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right)$, $93.17(\mathrm{CH}, \mathrm{C}-1), 71.96(\mathrm{CH}, \mathrm{C}-5), 70.46(\mathrm{CH}$, $\mathrm{C}-3), 66.47(\mathrm{CH}, \mathrm{C}), 61.45\left(\mathrm{CH}_{2}, \mathrm{C}-6\right), 49.88(\mathrm{CH}, \mathrm{C}-2), 23.44\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 21.04\left(\mathrm{CH}_{3}, \mathrm{Ac}\right)$, $20.82\left(2 \times \mathrm{CH}_{3}, \mathrm{Ac}\right)$, $20.79\left(\mathrm{CH}_{3}, \mathrm{Ac}\right)$; HRMS (ESI) $\mathrm{m} / \mathrm{z}[\mathrm{M}+\mathrm{Na}]^{+}$calcd for $\mathrm{C}_{16} \mathrm{H}_{23} \mathrm{NO}_{10} \mathrm{Na}$ 412.1220; found 412.1217.

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



Compound $\mathbf{2 c}$ was synthesized from $\mathbf{8 c}(30 \mathrm{mg}, 0.08 \mathrm{mmol})$ according to the procedure for compound 2a: yield $18 \mathrm{mg}\left(56 \%\right.$, $\alpha$-pyr/ß-pyr/a-fur 49:33:18); ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ a-pyr. 6.11 (d, $J=9.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}$ ), $5.93(\mathrm{~s}, 1 \mathrm{H}, \mathrm{H}-1), 5.04(\mathrm{t}, J=2.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4), 4.87(\mathrm{t}$, $J=3.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3), 4.48(\mathrm{td}, J=6.6,2.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-5), 4.31(\mathrm{dt}, J=10.0,2.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2)$, 4.11 (t, J=6.2 Hz, $2 \mathrm{H}, \mathrm{H}-6$ ), $2.14(\mathrm{~s}, 3 \mathrm{H}, \mathrm{Ac}$ ), 2.11 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{Ac}$ ), 2.10 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{Ac}$ ), 2.09 ( $\mathrm{s}, 3$

H, Ac), 2.04 (s, $3 \mathrm{H}, \mathrm{Ac}$ ); $\beta$-pyr. 6.06 (d, J = $9.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}$ ), 6.01 (d, J=2.4 Hz, $1 \mathrm{H}, \mathrm{H}-1$ ), $5.07(\mathrm{t}, J=4.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4), 4.98(\mathrm{t}, J=3.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3), 4.39-4.33(\mathrm{~m}, 2 \mathrm{H}, \mathrm{H}-2$ and H5), 4.18 - 4.13 ( m, 2 H, H-6), 2.12 (s, $3 \mathrm{H}, \mathrm{Ac}$ ), 2.11 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{Ac}$ ), 2.04 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{Ac}$ ), 2.02 ( $\mathrm{s}, 3$ $\mathrm{H}, \mathrm{Ac}$ ), 1.99 (s, $3 \mathrm{H}, \mathrm{Ac}$ ); a-fur: 6.27 (d, J= $8.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}$ ), 6.02 (d, J=3.2 Hz, $1 \mathrm{H}, \mathrm{H}-1$ ), 5.32 (dd, $J=6.9,5.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3$ ), 5.25 (dt, $J=7.1,4.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-5$ ), 4.61 (ddd, $J=8.3$, $5.4,3.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2$ ), 4.55 (dd, $J=6.9,4.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4$ ), 4.26 (dd, $J=11.9,4.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-$ $6 \mathrm{a}), 4.05$ (dd, J=11.9, $7.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-6 \mathrm{~b}$ ), 2.14 (s, $3 \mathrm{H}, \mathrm{Ac}$ ), 2.10 (s, $3 \mathrm{H}, \mathrm{Ac}$ ), 2.07 (s, 3 H , Ac), 2.04 (s, $3 \mathrm{H}, \mathrm{Ac}$ ), 1.98 (s, $3 \mathrm{H}, \mathrm{Ac}$ ); ${ }^{13} \mathrm{C}$ NMR ( $150 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta \alpha$-pyr: $170.59\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right)$, 169.71 ( $\left.\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 169.04\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 168.68\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right)$, 168.66 (CH, Ac), 92.06 (CH, C-1), 67.36 (CH, C-3), $66.49(\mathrm{CH}, \mathrm{C}-4), 66.04(\mathrm{CH}, \mathrm{C}-5), 61.72\left(\mathrm{CH}_{2}, \mathrm{C}-6\right), 46.32(\mathrm{CH}, \mathrm{C}-2), 23.35\left(\mathrm{CH}_{3}\right.$, $\mathrm{Ac}), 20.99\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 20.89\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 20.84\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 20.81\left(\mathrm{CH}_{3}, \mathrm{Ac}\right) ; \beta-p y r: 170.34\left(\mathrm{C}_{\mathrm{q}}\right.$, Ac), $170.17\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 170.02\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right)$, $168.76\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 168.57\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 90.80(\mathrm{CH}, \mathrm{C}-1)$, $72.52(\mathrm{CH}, \mathrm{C}-5), 68.48(\mathrm{CH}, \mathrm{C}-4), 66.23(\mathrm{CH}, \mathrm{C}-3), 61.94\left(\mathrm{CH}_{2}, \mathrm{C}-6\right), 47.85(\mathrm{CH}, \mathrm{C}-2), 23.35$ $\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 21.01\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 20.91\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 20.80\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 20.74\left(\mathrm{CH}_{3}, \mathrm{Ac}\right)$; $\alpha$-fur: 170.62 ( $\left.\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 170.55\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right)$, $170.36\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 169.89\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right)$, $168.93\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 98.76(\mathrm{CH}, \mathrm{C}-1)$, 78.29 (CH, C-4), 75.05 (CH, C-3), 69.06 (CH, C-5), $62.70\left(\mathrm{CH}_{2}, \mathrm{C}-6\right), 59.74(\mathrm{CH}, \mathrm{C}-2), 23.18$ $\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 21.23\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 21.16\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 21.03\left(\mathrm{CH}_{3}, \mathrm{Ac}\right), 20.87\left(\mathrm{CH}_{3}, \mathrm{Ac}\right)$; HRMS (ESI) $\mathrm{m} / \mathrm{z}[\mathrm{M}+\mathrm{Na}]^{+}$calcd for $\mathrm{C}_{16} \mathrm{H}_{23} \mathrm{NO}_{10} \mathrm{Na} 412.1220$; found 412.1217.

## 2-Acetamido-2-deoxy-D-galactopyranose (1a)



2a ( $115 \mathrm{mg}, 0.30 \mathrm{mmol}, 1$ equiv) was dissolved in $3 \mathrm{~mL} \mathrm{MeOH} / \mathrm{H}_{2} \mathrm{O} / \mathrm{Et}_{3} \mathrm{~N}$ (10:10:1) and stirred for 16 h . The solvents were removed under reduced pressure and the crude product was recrystallized from $\mathrm{MeOH} / \mathrm{Et}_{2} \mathrm{O}$ to receive compound 1a ( $57 \mathrm{mg}, 88 \%$, $\alpha$-pyr/ $\beta$-pyr 56:44) as a colorless solid: $[\alpha]^{20}{ }_{D}=+80.0^{\circ}\left(c 1.0, \mathrm{H}_{2} \mathrm{O}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(600 \mathrm{MHz}, \mathrm{D}_{2} \mathrm{O}\right) \delta$ a: $5.20(\mathrm{~d}, \mathrm{~J}=$ $3.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1), 4.12-4.06(\mathrm{~m}, 2 \mathrm{H}, \mathrm{H}-2$ and $\mathrm{H}-5), 3.97(\mathrm{~d}, \mathrm{~J}=2.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4), 3.91(\mathrm{t}, \mathrm{J}$ $=2.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3), 3.77-3.69(\mathrm{~m}, 2 \mathrm{H}, \mathrm{H}-6), 2.02(\mathrm{~s}, 3 \mathrm{H}, \mathrm{Ac}) ; \beta: 4.62(\mathrm{~d}, \mathrm{~J}=8.4 \mathrm{~Hz}, 1 \mathrm{H}$, $\mathrm{H}-1$ ), 3.88 (d, J=3.2 Hz, $1 \mathrm{H}, \mathrm{H}-4$ ), 3.85 (dd, J=10.8, $8.5 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-2$ ), $3.79-3.69$ (m, 3 H , $\mathrm{H}-3$ and $\mathrm{H}-6$ ), $3.69-3.65(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-5)$, $2.02(\mathrm{~s}, 3 \mathrm{H}, \mathrm{Ac}) ;{ }^{13} \mathrm{C}$ NMR ( $150 \mathrm{MHz}, \mathrm{H}_{2} \mathrm{O}$ ) $\delta \mathrm{a}$ : $175.45\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 91.73(\mathrm{CH}, \mathrm{C}-1), 71.28(\mathrm{CH}, \mathrm{C}-5), 69.31(\mathrm{CH}, \mathrm{C}-4), 68.12(\mathrm{CH}, \mathrm{C}-3), 61.97$ $\left(\mathrm{CH}_{2}, \mathrm{C}-6\right), 51.00(\mathrm{CH}, \mathrm{C}-2), 22.70\left(\mathrm{CH}_{3}, \mathrm{Ac}\right) ; \beta: 175.72\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 96.14(\mathrm{CH}, \mathrm{C}-1), 75.93$
(CH, C-5), 71.87 (CH, C-3), $68.59(\mathrm{CH}, \mathrm{C}-4), 61.74\left(\mathrm{CH}_{2}, \mathrm{C}-6\right), 54.39(\mathrm{CH}, \mathrm{C}-2), 22.95\left(\mathrm{CH}_{3}\right.$, Ac); HRMS (ESI) $m / z[M+N a]^{+}$calcd for $\mathrm{C}_{8} \mathrm{H}_{15} \mathrm{NO}_{6} \mathrm{Na} 244.0797$; found 244.0793 .

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



Compound $\mathbf{1 b}$ was synthesized from $\mathbf{2 b}$ ( $31 \mathrm{mg}, 0.08 \mathrm{mmol}$ ) according to the procedure for compound 1a: yield $16 \mathrm{mg}(69 \%$, $\alpha-\operatorname{pyr} / \beta-p y r 68: 32)$; $[\alpha]^{20}{ }_{\mathrm{D}}=-71.5^{\circ}\left(c 1.0, \mathrm{H}_{2} \mathrm{O}\right) ;{ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{D}_{2} \mathrm{O}$ ) $\delta$ a: 5.23 (d, J=3.8 Hz, $1 \mathrm{H}, \mathrm{H}-1$ ), $4.15-4.08$ (m, $2 \mathrm{H}, \mathrm{H}-2$ and H-5), 4.01 3.97 (m, 1 H, H-4), 3.93 (t, J = $3.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-3$ ), 3.74 (d, J=6.1 Hz, $2 \mathrm{H}, \mathrm{H}-6$ ), 2.05 ( $\mathrm{s}, 3 \mathrm{H}$, Ac); ß: 4.64 (d, $J=8.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-1$ ), 3.91 (d, $J=3.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}-4$ ), 3.87 (dd, $J=10.9,8.5$ $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{H}-2$ ), $3.81-3.71$ (m, $3 \mathrm{H}, \mathrm{H}-3$ and H-6), $3.71-3.66$ (m, 1H, H-5), 2.04 (s, $3 \mathrm{H}, \mathrm{Ac}$ ); ${ }^{13} \mathrm{C}$ NMR ( $150 \mathrm{MHz}, \mathrm{H}_{2} \mathrm{O}$ ) $\delta$ a: $175.44\left(\mathrm{C}_{\mathrm{q}}, \mathrm{Ac}\right), 91.74(\mathrm{CH}, \mathrm{C}-1), 71.28(\mathrm{CH}, \mathrm{C}-5), 69.32(\mathrm{CH}$, $\mathrm{C}-4), 68.14(\mathrm{CH}, \mathrm{C}-3), 61.98\left(\mathrm{CH}_{2}, \mathrm{C}-6\right), 51.01(\mathrm{CH}, \mathrm{C}-2), 22.72\left(\mathrm{CH}_{3}, \mathrm{Ac}\right) ; \beta: 175.72\left(\mathrm{C}_{\mathrm{q}}\right.$, $\mathrm{Ac}), 96.16(\mathrm{CH}, \mathrm{C}-1), 75.93(\mathrm{CH}, \mathrm{C}-5), 71.88(\mathrm{CH}, \mathrm{C}-3), 68.60(\mathrm{CH}, \mathrm{C}-4), 61.75\left(\mathrm{CH}_{2}, \mathrm{C}-6\right)$, $54.41(\mathrm{CH}, \mathrm{C}-2), 22.97\left(\mathrm{CH}_{3}, \mathrm{Ac}\right)$; HRMS (ESI) $\mathrm{m} / \mathrm{z}[\mathrm{M}+\mathrm{Na}]^{+}$calcd for $\mathrm{C}_{8} \mathrm{H}_{15} \mathrm{NO}_{6} \mathrm{Na}$ 244.0797; found 244.0788 .

NMR spectra



5a












8a



## 


8b



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