## Supporting Information

for

# Indium-mediated allylation in carbohydrate synthesis: A short and efficient approach towards higher 2-acetamido-2-deoxy sugars 

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## Experimental section, spectral data and copies of ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra of compounds $2-8$

## General methods

NMR spectra were recorded on a Bruker Avance DRX 400 or Bruker Avance III 600 spectrometer using $\mathrm{CDCl}_{3}, \mathrm{D}_{2} \mathrm{O}$ or $\mathrm{CD}_{3} \mathrm{OD}$ for calibration. MS experiments were measured in the ESI mode on a Finnigan MAT 900 spectrometer. For chromatography Merck silica gel 60 ( $0.004-0.063 \mathrm{~mm}$ ) was used. For TLC monitoring Merck plates (silica gel 60 F254) were used; plates were stained by treatment with a solution of anis aldehyde (1 ml) in $\mathrm{AcOH}(100$ $\mathrm{ml})$ and $\mathrm{H}_{2} \mathrm{SO}_{4}(2 \mathrm{ml})$, followed by charring with a heat gun. All solvents were distilled before use. Ozonolysis was performed using an Anseros Generator COM-AD-04. Optical
rotations were measured on a Perkin-Elmer Polarimeter 341. IR spectra were recorded on a Bruker Vertex 70 FT-IR spectrometer. Chemicals were purchased in reagent grade.

## General Procedure for Allylation/Peracetylation of Aldoses. Synthesis of 2a-2c (Method

A): To a solution of the monosaccharide in the corresponding solvent indium powder and allyl bromide were added and the resulting suspension subjected to sonication for $2.5-7 \mathrm{~h}$. When TLC (acetone/2-propanol/ $/ \mathrm{H}_{2} \mathrm{O}=5 / 4 / 1$ ) indicated complete conversion of the starting material, the cloudy white to light blue reaction mixture was neutralized with 1 M NaOH , if necessary, and evaporated to dryness. The residue was redissolved in a mixture of pyridine (Pyr) and acetic anhydride $\left(\mathrm{Ac}_{2} \mathrm{O}\right)=1 / 1$ under argon and a catalytic amount of 4(dimethylamino)pyridine (DMAP) was added. The resulting reaction mixture was stirred at room temperature for 16 h and then poured into cooled $\left(0^{\circ} \mathrm{C}\right) 3 \mathrm{~m} \mathrm{HCl}$. The aqueous phase was extracted three times with dichloromethane (DCM) and the combined organic layers were dried over anhydrous $\mathrm{MgSO}_{4}$ and concentrated under reduced pressure. Purification by silica gel chromatography afforded olefins 2a-c as clear viscous oils.

General Procedure for Ozonolysis/Elimination. Synthesis of 3a-3c (Method B): A stirred solution of the olefin in dry DCM was cooled to $-78^{\circ} \mathrm{C}$ and ozone was bubbled through the reaction mixture until a blue color persisted, whereupon air was bubbled through the solution until the blue color vanished. Thiourea was then added and the reaction mixture was allowed to warm to room temperature and stirred for 16 h . The white precipitate formed was filtered off, TEA was added and the resulting light yellow solution stirred for $30-50 \mathrm{~min}$ at room temperature as judged by TLC (hexane/ethyl acetate $[\mathrm{HE} / \mathrm{EA}]=1 / 1$ ). The reaction mixture was then poured into cooled $\left(0^{\circ} \mathrm{C}\right) 1 \mathrm{~m} \mathrm{HCl}$. The aqueous phase was extracted three times with DCM and the combined organic layers were dried over anhydrous $\mathrm{MgSO}_{4}$ and
evaporated to dryness. Compounds 3a-c were obtained as white crystalline solids and used in the next step without further purification.

## General Procedure for Epoxidation/Wittig Reaction. Synthesis of 4a-4c (Method C): A

 stirred solution of the unsaturated aldehyde in dry DCM was cooled to $-20^{\circ} \mathrm{C}$ via a cryostat and (S)-(-)-alpha,alpha-diphenyl(pyrrolidin-2-yl)methanol trimethylsilyl ether was added followed by $\mathrm{H}_{2} \mathrm{O}_{2}(50 \%)$. The reaction mixture was stirred at $-20^{\circ} \mathrm{C}$ for 16 h after which water was added and the mixture stirred vigorously at room temperature for additional 10 min. The aqueous phase was extracted three times with DCM and the combined organic layers were dried over anhydrous $\mathrm{MgSO}_{4}$ and evaporated to dryness. The crude reaction product was redissolved in dry DCM and $\mathrm{Ph}_{3} \mathrm{P}\left(\mathrm{CHCO}_{2} \mathrm{Me}\right)$ was added. The resulting solution was stirred at room temperature for 1 h and then concentrated under reduced pressure. Purification by silica gel chromatography afforded epoxides 4a-c as white to light yellow crystalline solids.General Procedure for Epoxide Opening. Synthesis of 5a-5c (Method D): Dry tetrahydrofuran (THF) was degassed using the freeze-pump-thaw technique. Then the epoxide was added under argon followed by trimethylsilyl azide $\left(\mathrm{TMSN}_{3}\right)$ and tetrakis(triphenylphosphine)palladium $(0)\left(\operatorname{Pd}\left(\mathrm{PPh}_{3}\right)_{4}\right)$. The bright yellow reaction mixture was stirred at room temperature for 1 h , then quenched with a solution of citric acid in methanol and stirred for an additional hour at room temperature. The reaction mixture was concentrated under reduced pressure and purification by silica gel chromatography afforded azides 5a-c as colorless to light yellow viscous oils.

General Procedure for Deacetylation/Ozonolysis. Synthesis of 6a-6c (Method E): Acetyl chloride $(\mathrm{AcCl})$ was added to dry methanol $(\mathrm{MeOH})$ under argon and stirred at room temperature for 15 min . The resulting methanolic HCl solution was added to a solution of the
azide in dry MeOH under argon and stirred at room temperature for $16-24 \mathrm{~h}$ as judged by TLC $(\mathrm{DCM} / \mathrm{MeOH}=6 / 1)$. To avoid intramolecular 1,4 -addition, powdered MS $4 \AA$ was then added and the reaction mixture was stirred vigorously for 20 minutes. The molecular sieve was filtered off and the filtrate diluted with dry MeOH and a few ml of dry DCM. The resulting solution was cooled to $-78^{\circ} \mathrm{C}$ and ozone was bubbled through the reaction mixture until a blue color persisted, whereupon air was bubbled through the solution until the blue color vanished. Triphenylphosphine $\left(\mathrm{PPh}_{3}\right)$ was then added and the reaction mixture was allowed to warm to room temperature and stirred for 16 h . The solution was concentrated under reduced pressure and purification by silica gel chromatography afforded sugar azides 6a-c as light yellow viscous oils.

General Procedure for Azide Reduction. Synthesis of 7a-7c (Method F): The sugar azide was dissolved in $\mathrm{Pyr} / \mathrm{Ac}_{2} \mathrm{O}=1 / 1$ under argon and a catalytic amount of DMAP was added. The resulting reaction mixture was stirred at room temperature for 16 h and then evaporated to dryness. The crude reaction product was redissolved in dry acetonitrile (MeCN) under argon and DTT followed by DIPA were added. The resulting solution was stirred at room temperature for 2 h and then evaporated to dryness. The residue was redissolved in $\mathrm{Pyr} / \mathrm{Ac}_{2} \mathrm{O}$ $=1 / 1$ under argon and a catalytic amount of DMAP was added. The resulting reaction mixture was stirred at room temperature for 16 h and then evaporated to dryness. Purification by silica gel chromatography afforded peracetylated aminosugars 7a-c as colorless to light yellow viscous oils.

General Procedure for Zemplén Saponification. Synthesis of 8a-8c (Method G): Similar as described in [1]. To a solution of the peracetylated aminosugar in dry MeOH a catalytic amount of sodium methoxide ( NaOMe ) was added under argon and stirred at room temperature for $2-3 \mathrm{~h}$ as judged by TLC (acetone/2-propanol/ $/ \mathrm{H}_{2} \mathrm{O}=5 / 4 / 1$ ). Then a small
amount of acidic ion exchange resin was added and the reaction mixture stirred for additional 10 min at room temperature. After filtration, the solution was evaporated to dryness and the residue was redissolved in water, washed three times with ethyl acetate (EA) and evaporated to dryness. The aminosugars 8a-c obtained needed no further purification.

1,2,3,4,5-Penta-O-acetyl-6,7,8-trideoxy-L-gulo-7-octenitol (2a): D-arabinose (250 mg, 1.67 $\mathrm{mmol})$ in ethanol $/ \mathrm{H}_{2} \mathrm{O}=4 / 1(40 \mathrm{ml})$ was treated according to method A with indium (382 $\mathrm{mg}, 3.33 \mathrm{mmol}$ ) and allyl bromide ( $504 \mu \mathrm{l}, 5.83 \mathrm{mmol}$ ). Purification by silica gel chromatography was performed using $\mathrm{HE} / \mathrm{EA}=2 / 1$ as eluent; yield: $670 \mathrm{mg},(100 \%)$ as a mixture of diastereomers $(\mathrm{dr}=9 / 1) .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}, 25^{\circ} \mathrm{C}\right)$ (major diastereomer): $\delta=2.05,2.05,2.06,2.06,2.12(5 \mathrm{~s}, 15 \mathrm{H}, 5 \mathrm{OAc}), 2.34(\mathrm{~m}, 2 \mathrm{H}, 6 \mathrm{a}-\mathrm{H}, 6 \mathrm{~b}-\mathrm{H}), 4.12\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{\mathrm{la}, 2}=\right.$ $\left.5.4 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{\mathrm{la}, 1 \mathrm{~b}}=12.4 \mathrm{~Hz}, 1 \mathrm{H}, 1 \mathrm{a}-\mathrm{H}\right), 4.24\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{1 \mathrm{~b}, 2}=3.4 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{\mathrm{la}, 1 \mathrm{~b}}=12.4 \mathrm{~Hz}, 1 \mathrm{H}, 1 \mathrm{~b}-\mathrm{H}\right)$, $5.08(\mathrm{~m}, 4 \mathrm{H}, 2-\mathrm{H}, 5-\mathrm{H}, 8 \mathrm{a}-\mathrm{H}, 8 \mathrm{~b}-\mathrm{H}), 5.30\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{3,4}=4.0 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{4,5}=6.6 \mathrm{~Hz}, 1 \mathrm{H}, 4-\mathrm{H}\right), 5.42$ $\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{3,4}=4.0 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=6.9 \mathrm{~Hz}, 1 \mathrm{H}, 3-\mathrm{H}\right), 5.73(\mathrm{~m}, 1 \mathrm{H}, 7-\mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}\right.$, $\left.25^{\circ} \mathrm{C}\right): \delta=21.0,21.1,21.1,21.2,21.2$ (5 OAc), 35.6 (6-C), 61.9 (1-C), 68.7 (4-C), 68.9 (2C), 70.4 (3-C), 70.7 (5-C), 119.4 (8-C), 132.4 (7-C), 170.2, 170.2, 170.3, 170.6, 170.9 (5 COOAc); HRMS (ESI) $m / z[\mathrm{M}+\mathrm{Na}]^{+}$calculated 425.1424, found 425.1420.

1,2,3,4,5,6-Hexa-O-acetyl-7,8,9-trideoxy-L-galacto-D-glycero-8-octenitol (2b): D-galactose $(280 \mathrm{mg}, 1.55 \mathrm{mmol})$ in ethanol $/ 0,1 \mathrm{~m} \mathrm{HCl}=4 / 1(40 \mathrm{ml})$ was treated according to method A with indium ( $357 \mathrm{mg}, 3.11 \mathrm{mmol}$ ) and allyl bromide ( $470 \mu \mathrm{l}, 5.44 \mathrm{mmol}$ ). Purification by silica gel chromatography was performed using $\mathrm{HE} / \mathrm{EA}=1 / 1$ as eluent; yield: 737 mg $(100 \%)$ as a mixture of diastereomers $(\mathrm{dr}=7 / 1) .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}, 25^{\circ} \mathrm{C}\right)$ (major diastereomer): $\delta=2.00,2.01,2.06,2.08,2.10,2.12(6 \mathrm{~s}, 18 \mathrm{H}, 6 \mathrm{OAc}), 2.41(\mathrm{~m}, 2 \mathrm{H}, 7 \mathrm{a}-\mathrm{H}$, $7 \mathrm{~b}-\mathrm{H}), 3.83\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{\mathrm{la}, 2}=7.1 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{1 \mathrm{a}, 1 \mathrm{~b}}=11.6 \mathrm{~Hz}, 1 \mathrm{H}, 1 \mathrm{a}-\mathrm{H}\right), 4.28\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{\mathrm{lb}, 2}=4.6 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{\mathrm{la}, 1 \mathrm{~b}}=\right.$ $11.6 \mathrm{~Hz}, 1 \mathrm{H}, 1 \mathrm{~b}-\mathrm{H}), 4.94\left(\mathrm{ddd},{ }^{3} \mathrm{~J}_{6,7}=4.2 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=7.9 \mathrm{~Hz}, 1 \mathrm{H}, 6-\mathrm{H}\right), 5.13(\mathrm{~m}, 2 \mathrm{H}, 9 \mathrm{a}-\mathrm{H}$, $9 \mathrm{~b}-\mathrm{H}), 5.20\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{4,5}=2.1 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=7.9 \mathrm{~Hz}, 1 \mathrm{H}, 5-\mathrm{H}\right), 5.23(\mathrm{~m}, 2 \mathrm{H}, 3-\mathrm{H}, 2-\mathrm{H}), 5.36(\mathrm{dd}$,
$\left.{ }^{3} \mathrm{~J}_{4,5}=2.1 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{3,4}=9.4 \mathrm{~Hz}, 1 \mathrm{H}, 4-\mathrm{H}\right), 5.72(\mathrm{~m}, 1 \mathrm{H}, 8-\mathrm{H}) ;{ }^{13} \mathrm{C}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}, 25\right.$ $\left.{ }^{\circ} \mathrm{C}\right): \delta=21.0,21.0,21.0,21.1,21.1,21.2$ ( 6 OAc ), 35.5 (7-C), 62.6 (1-C), 67.7 (4-C), 68.1 (3-C), 68.3 (2-C), 70.2 (5-C), 71.1 (6-C), 119.2 (9-C), 132.5 (8-C), 170.2, 170.3, 170.3, 170.4, 170.6, 170.8 (6 CO-OAc); HRMS (ESI) $m / z[\mathrm{M}+\mathrm{Na}]^{+}$calculated 497.1635, found 497.1623.

## 1,2,3,4,5,6-Hexa-O-acetyl-7,8,9-trideoxy-L-gulo-D-glycero-8-octenitol (2c): D-glucose

 hydrate $(298 \mathrm{mg}, 1.50 \mathrm{mmol})$ in ethanol $/ 0,1 \mathrm{M} \mathrm{HCl}=4 / 1(40 \mathrm{ml})$ was treated according to method A with indium ( $344 \mathrm{mg}, 3.00 \mathrm{mmol}$ ) and allyl bromide ( $454 \mu \mathrm{l}, 5.25 \mathrm{mmol}$ ). Purification by silica gel chromatography was performed using HE/EA $=3 / 1$ as eluent; yield: $500 \mathrm{mg}(70 \%)$ as a mixture of diastereomers $(\mathrm{dr}=5 / 1) .{ }^{1} \mathrm{H} \mathrm{NMR}\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}, 25^{\circ} \mathrm{C}\right)$ (major diastereomer): $\delta=2.05,2.06,2.08,2.09,2.12,2.14(6 \mathrm{~s}, 18 \mathrm{H}, 6 \mathrm{OAc}), 2.28(\mathrm{~m}, 2 \mathrm{H}$, $7 \mathrm{a}-\mathrm{H}, 7 \mathrm{~b}-\mathrm{H}), 4.14\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{\mathrm{la}, 2}=5.0 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{\mathrm{la}, 1 \mathrm{~b}}=12.6 \mathrm{~Hz}, 1 \mathrm{H}, 1 \mathrm{a}-\mathrm{H}\right), 4.24\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{\mathrm{lb}, 2}=2.6 \mathrm{~Hz}\right.$, $\left.{ }^{2} \mathbf{J}_{\mathrm{la}, 1 \mathrm{~b}}=12.6 \mathrm{~Hz}, 1 \mathrm{H}, 1 \mathrm{~b}-\mathrm{H}\right), 4.98\left(\mathrm{ddd},{ }^{3} \mathrm{~J}_{2,3}=8.3 \mathrm{~Hz}, 1 \mathrm{H}, 2-\mathrm{H}\right), 5.11(\mathrm{~m}, 3 \mathrm{H}, 5-\mathrm{H}, 9 \mathrm{a}-\mathrm{H}, 9 \mathrm{~b}-$ H), $5.32(\mathrm{~m}, 2 \mathrm{H}, 4-\mathrm{H}, 6-\mathrm{H}), 5.43\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{3,4}=2.5 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=8.3 \mathrm{~Hz}, 1 \mathrm{H}, 3-\mathrm{H}\right), 5.69(\mathrm{~m}, 1 \mathrm{H}, 8-$ $\mathrm{H}) ;{ }^{13} \mathrm{C}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}, 25{ }^{\circ} \mathrm{C}\right): \delta=20.5,20.6,20.7,20.7,20.8,20.8(6 \mathrm{OAc}), 34.4$ (7-C), 61.4 (1-C), 68.4 (4-C), 68.9 (3-C), 69.2 (2-C), 69.9 (6-C), 70.9 (5-C), 118.6 (9-C), 132.6 (8-C), 169.7, 169.8, 170.0, 170.2, 170.4, 170.6 (6 CO-OAc); ESI-MS: $m / z 497.16$ $[\mathrm{M}+\mathrm{Na}]^{+}, 513.14[\mathrm{M}+\mathrm{K}]^{+}$.(2E)-4,5,6,7-Tetra-O-acetyl-2,3-dideoxy-D-arabino-hept-2-enose (3a): Olefin 2a (1340 $\mathrm{mg}, 3.33 \mathrm{mmol}$ ) was treated with ozone in 50 ml of dry DCM according to method B and quenched with thiourea ( $330 \mathrm{mg}, 4.34 \mathrm{mmol}$ ). For the elimination TEA $(1850 \mu \mathrm{l}, 13.35$ $\mathrm{mmol})$ was used; yield: $1146 \mathrm{mg},(100 \%) .[\alpha]^{\mathrm{D}}{ }_{20}=+49.5^{\circ}\left(11.0, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$; m.p. $75-77^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}, 25^{\circ} \mathrm{C}\right): \delta=2.05,2.06,2.08,2.15(4 \mathrm{~s}, 12 \mathrm{H}, 4 \mathrm{OAc}), 4.18\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{6,7 \mathrm{a}}\right.$ $\left.=4.7 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{7 \mathrm{a}, 7 \mathrm{~b}}=12.3 \mathrm{~Hz}, 1 \mathrm{H}, 7 \mathrm{a}-\mathrm{H}\right), 4.26\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{6,7 \mathrm{~b}}=2.2 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{7 \mathrm{a}, 7 \mathrm{~b}}=12.3 \mathrm{~Hz}, 1 \mathrm{H}, 7 \mathrm{~b}-\mathrm{H}\right)$,
$5.23\left(\mathrm{ddd},{ }^{3} \mathrm{~J}_{6,7 \mathrm{~b}}=2.2 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{6,7 \mathrm{a}}=4.7 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=9.1 \mathrm{~Hz}, 1 \mathrm{H}, 6-\mathrm{H}\right), 4.45\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{4,5}=2.5 \mathrm{~Hz}\right.$, $\left.{ }^{3} \mathrm{~J}_{5,6}=9.1 \mathrm{~Hz}, 1 \mathrm{H}, 5-\mathrm{H}\right), 5.82\left(\mathrm{ddd},{ }^{4} \mathrm{~J}_{2,4}=2.2 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{4,5}=2.5 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{3,4}=3.9 \mathrm{~Hz}, 1 \mathrm{H}, 4-\mathrm{H}\right)$, $6.17\left(\mathrm{ddd},{ }^{4} \mathrm{~J}_{2,4}=2.2 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{1,2}=7.7 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=15.8 \mathrm{~Hz}, 1 \mathrm{H}, 2-\mathrm{H}\right), 6.68\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{3,4}=3.9 \mathrm{~Hz}\right.$, $\left.{ }^{3} \mathrm{~J}_{2,3}=15.8 \mathrm{~Hz}, 1 \mathrm{H}, 3-\mathrm{H}\right), 9.54\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{1,2}=7.7 \mathrm{~Hz}, 1 \mathrm{H}, 1-\mathrm{H}\right) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}\right.$, $\left.25^{\circ} \mathrm{C}\right): \delta=20.9,20.9,21.0,21.1$ (4 OAc), 62.1 (7-C), 68.5 (6-C), 69.6 (5-C), 70.1 (4-C), 133.3 (2-C), 149.6 (3-C), 169.9, 170.0, 170.1, 170.9 (4 CO-OAc), 192.6 (1-C); HRMS (ESI) $m / z[\mathrm{M}+\mathrm{Na}]^{+}$calculated 367.1005, found 367.1006.
(2E)-4,5,6,7,8-Penta-O-acetyl-2,3-dideoxy-D-galacto-oct-2-enose (3b): Olefin 2b (1258 $\mathrm{mg}, 2.65 \mathrm{mmol}$ ) was treated with ozone in 50 ml of dry DCM according to method B and quenched with thiourea ( $277 \mathrm{mg}, 3.64 \mathrm{mmol}$ ). For the elimination TEA (1470 $\mu \mathrm{l}, 10.60$ $\mathrm{mmol})$ was used; yield: 1103 mg , $(100 \%) .[\alpha]^{\mathrm{D}}{ }_{20}=-1.4^{\circ}\left(7.6, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$; m.p. $154-156^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{CDCl}_{3}, 100 \mathrm{MHz}, 25^{\circ} \mathrm{C}\right): \delta=2.02,2.03,2.08,2.12,2.16(5 \mathrm{~s}, 15 \mathrm{H}, 5 \mathrm{OAc}), 3.86(\mathrm{dd}$, $\left.{ }^{3} \mathrm{~J}_{7,8 \mathrm{a}}=7.6 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{8 \mathrm{a}, 8 \mathrm{~b}}=11.6 \mathrm{~Hz}, 1 \mathrm{H}, 8 \mathrm{a}-\mathrm{H}\right), 4.28\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{7,8 \mathrm{~b}}=5.0 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{8 \mathrm{a}, 8 \mathrm{~b}}=11.6 \mathrm{~Hz}, 1 \mathrm{H}\right.$, $8 \mathrm{~b}-\mathrm{H}), 5.35\left(\mathrm{ddd},{ }^{3} \mathrm{~J}_{6,7}=1.9 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{7,8 \mathrm{~b}}=5.0 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{7,8 \mathrm{a}}=7.6 \mathrm{~Hz}, 1 \mathrm{H}, 7-\mathrm{H}\right), 5.38\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{4,5}=2.0\right.$ $\left.\mathrm{Hz},{ }^{3} \mathrm{~J}_{5,6}=10.1 \mathrm{~Hz}, 1 \mathrm{H}, 5-\mathrm{H}\right), 5.45\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{6,7}=1.9 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=10.1 \mathrm{~Hz}, 1 \mathrm{H}, 6-\mathrm{H}\right), 5.70(\mathrm{ddd}$, $\left.{ }^{4} \mathrm{~J}_{2,4}=1.8 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{4,5}=2.0 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{3,4}=4.0 \mathrm{~Hz}, 1 \mathrm{H}, 4-\mathrm{H}\right), 6.13\left(\mathrm{ddd},{ }^{4} \mathrm{~J}_{2,4}=1.8 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{1,2}=7.7 \mathrm{~Hz}\right.$, $\left.{ }^{3} \mathrm{~J}_{2,3}=15.7 \mathrm{~Hz}, 1 \mathrm{H}, 2-\mathrm{H}\right), 6.65\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{3,4}=4.0 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=15.7 \mathrm{~Hz}, 1 \mathrm{H}, 3-\mathrm{H}\right), 9.52\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{1,2}=\right.$ $7.7 \mathrm{~Hz}, 1 \mathrm{H}, 1-\mathrm{H}) ;{ }^{13} \mathrm{C}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}, 25{ }^{\circ} \mathrm{C}\right): \delta=20.5,20.5,20.5,20.6,20.6(5$ OAc), 62.4 (8-C), 67.6 (6-C), 67.6 (7-C), 68.3 (5-C), 69.4 (4-C), 133.2 (2-C), 149.7 (3-C), $170.0,170.1,170.2,170.5,170.8$ (5 CO-OAc), 192.5 (1-C); HRMS (ESI) $m / z[\mathrm{M}+\mathrm{Na}]^{+}$ calculated 439.1216, found 439.1220.
(2E)-4,5,6,7,8-Penta-O-acetyl-2,3-dideoxy-D-gluco-oct-2-enose (3c): Olefin 2c (917 mg, 1.93 mmol ) was treated with ozone in 40 ml of dry DCM according to method B and quenched with thiourea ( $191 \mathrm{mg}, 2.51 \mathrm{mmol}$ ). For the elimination TEA ( $1070 \mu \mathrm{l}, 7.72 \mathrm{mmol}$ )
was used; yield: $804 \mathrm{mg}(100 \%) .[\alpha]^{\mathrm{D}} 20=+9.4^{\circ}\left(5.9, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$; m.p. $83-85^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}, 25^{\circ} \mathrm{C}\right): \delta=2.06,2.06,2.09,2.11,2.15(5 \mathrm{~s}, 15 \mathrm{H}, 5 \mathrm{OAc}), 4.11\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{7,8 \mathrm{a}}=\right.$ $\left.5.3 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{8 \mathrm{a}, 8 \mathrm{~b}}=12.4 \mathrm{~Hz}, 1 \mathrm{H}, 8 \mathrm{a}-\mathrm{H}\right), 4.27\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{7,8 \mathrm{~b}}=3.1 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{8 \mathrm{a}, 8 \mathrm{~b}}=12.4 \mathrm{~Hz}, 1 \mathrm{H}, 8 \mathrm{~b}-\mathrm{H}\right)$, $5.07\left(\mathrm{ddd},{ }^{3} \mathrm{~J}_{7,8 \mathrm{~b}}=3.1 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{7,8 \mathrm{a}}=5.3 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{6,7}=7.3 \mathrm{~Hz}, 1 \mathrm{H}, 7-\mathrm{H}\right), 5.38\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{5,6}=3.84 \mathrm{~Hz}\right.$, $\left.{ }^{3} \mathrm{~J}_{4,5}=6.3 \mathrm{~Hz}, 1 \mathrm{H}, 5-\mathrm{H}\right), 5.43\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{5,6}=3.84 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{6,7}=7.3 \mathrm{~Hz}, 1 \mathrm{H}, 6-\mathrm{H}\right), 5.65\left(\mathrm{ddd},{ }^{4} \mathrm{~J}_{2,4}=\right.$ $\left.1.6 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{3,4}=4.6 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{4,5}=6.3 \mathrm{~Hz}, 1 \mathrm{H}, 4-\mathrm{H}\right), 6.21\left(\mathrm{ddd},{ }^{4} \mathrm{~J}_{2,4}=1.6 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{1,2}=7.6 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=\right.$ $15.8 \mathrm{~Hz}, 1 \mathrm{H}, 2-\mathrm{H}), 6.76\left(\mathrm{dd}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{3,4}=4.6 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=15.8 \mathrm{~Hz}, 3-\mathrm{H}\right), 9.59\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{1,2}=7.6 \mathrm{~Hz}\right.$, $1 \mathrm{H}, 1-\mathrm{H}) ;{ }^{13} \mathrm{C}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}, 25{ }^{\circ} \mathrm{C}\right): \delta=20.9,21.0,21.1,21.1,21.1$ ( 5 OAc ), 61.9 (8-C), 68.8 (6-C), 68.9 (7-C), 70.1 (5-C), 70.7 (4-C), 133.8 (2-C), 148.4 (3-C), 169.7, 169.9, 170.0, 170.2, 170.9 (5 CO-OAc), 192.6 (1-C); HRMS (ESI) $m / z[\mathrm{M}+\mathrm{Na}]^{+}$calculated 439.1216, found 439.1212.

## Methyl (2E)-6,7,8,9-Tetra-O-acetyl-2,3-dideoxy-4R,5S-epoxy-D-arabino-nona-2-enonate

 (4a): Aldehyde 3a ( $500 \mathrm{mg}, 1.45 \mathrm{mmol}$ ) was epoxidized with the catalyst ( $71 \mathrm{mg}, 0.22$ $\mathrm{mmol})$ and $\mathrm{H}_{2} \mathrm{O}_{2} 50 \%(108 \mu \mathrm{l}, 1.88 \mathrm{mmol})$ in 25 ml of dry DCM according to method C. For the Wittig reaction $\mathrm{Ph}_{3} \mathrm{P}\left(\mathrm{CHCO}_{2} \mathrm{Me}\right)(970 \mathrm{mg}, 2.90 \mathrm{mmol})$ was used. Purification by silica gel chromatography was performed using $\mathrm{HE} / \mathrm{EA}=3 / 1$ as eluent; yield: 435 mg , $(72 \%)$. $[\alpha]^{\mathrm{D}}{ }_{20}=+20.7^{\circ}\left(4.5, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$; m.p. $82-84^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}, 25^{\circ} \mathrm{C}\right): \delta=2.06$, 2.06, 2.12, $2.13(4 \mathrm{~s}, 12 \mathrm{H}, 4 \mathrm{OAc}), 3.02\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{4,5}=2.0 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=4.8 \mathrm{~Hz}, 1 \mathrm{H}, 5-\mathrm{H}\right), 3.35$ (ddd, ${ }^{4} \mathrm{~J}_{2,4}=0.7 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{4,5}=2.0 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{3,4}=6.7 \mathrm{~Hz}, 1 \mathrm{H}, 4-\mathrm{H}$ ), $3.75(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OMe}), 4.18(\mathrm{dd}$, $\left.{ }^{3} \mathrm{~J}_{8,9 \mathrm{a}}=4.6 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{9 \mathrm{a}, 9 \mathrm{~b}}=12.5 \mathrm{~Hz}, 1 \mathrm{H}, 9 \mathrm{a}-\mathrm{H}\right), 4.26\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{8,9 \mathrm{~b}}=2.9 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{9 \mathrm{a}, 9 \mathrm{~b}}=12.5 \mathrm{~Hz}, 1 \mathrm{H}\right.$, $9 \mathrm{~b}-\mathrm{H}), 5.15\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{5,6}=2.7 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{6,7}=4.8 \mathrm{~Hz}, 1 \mathrm{H}, 6-\mathrm{H}\right), 5.16\left(\mathrm{ddd},{ }^{3} \mathrm{~J}_{8,9 \mathrm{~b}}=2.9 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{8,9 \mathrm{a}}=4.6\right.$ $\left.\mathrm{Hz},{ }^{3} \mathrm{~J}_{7,8}=8.7 \mathrm{~Hz}, 1 \mathrm{H}, 8-\mathrm{H}\right), 5.48\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{6,7}=4.8 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{7,8}=8.7 \mathrm{~Hz}, 1 \mathrm{H}, 7-\mathrm{H}\right), 6.15\left(\mathrm{dd},{ }^{4} \mathrm{~J}_{2,4}\right.$ $\left.=0.6 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=15.7 \mathrm{~Hz}, 1 \mathrm{H}, 2-\mathrm{H}\right), 6.62\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{3,4}=6.7 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=15.7 \mathrm{~Hz}, 1 \mathrm{H}, 3-\mathrm{H}\right),{ }^{13} \mathrm{C}$ NMR ( $\left.\mathrm{CDCl}_{3}, 100 \mathrm{MHz}, 25^{\circ} \mathrm{C}\right): \delta=21.0,21.0,21.1,21.2$ (4 OAc), 52.2 (OMe), 53.7 (4-C), 59.8 (5-C), 61.9 (9-C), 68.4 (8-C), 69.5 (6-C), 69.8 (7-C), 125.0 (2-C), 142.8 (3-C), 166.1 (1-C), 170.1, 170.2, 170.3, 170.9 (4 CO-OAc); HRMS (ESI) $m / z[\mathrm{M}+\mathrm{Na}]^{+}$calculated 439.1216, found 439.1218 .

Methyl (2E)-6,7,8,9,10-Penta-O-acetyl-2,3-dideoxy-4R,5S-epoxy-d-galacto-deca-2enonate (4b): Aldehyde 3b ( $500 \mathrm{mg}, 1.20 \mathrm{mmol}$ ) was epoxidized with the catalyst ( 59 mg , $0.18 \mathrm{mmol})$ and $\mathrm{H}_{2} \mathrm{O}_{2} 50 \%(90 \mu \mathrm{l}, 1.57 \mathrm{mmol})$ in 25 ml of dry DCM according to method C. For the Wittig reaction $\mathrm{Ph}_{3} \mathrm{P}\left(\mathrm{CHCO}_{2} \mathrm{Me}\right)(802 \mathrm{mg}, 2.40 \mathrm{mmol})$ was used. Purification by silica gel chromatography was performed using $\mathrm{HE} / \mathrm{EA}=2 / 1$ as eluent; yield: 437 mg , $(75 \%)$. $[\alpha]^{\mathrm{D}}{ }_{20}=+31.8^{\circ}\left(4.5, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right) ;$ m.p. $182-184^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}, 25^{\circ} \mathrm{C}\right): \delta=2.02$, 2.08, 2.08, 2.08, $2.10(5 \mathrm{~s}, 15 \mathrm{H}, 5 \mathrm{OAc}), 2.94\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{4,5}=1.9 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=4.3 \mathrm{~Hz}, 1 \mathrm{H}, 5-\mathrm{H}\right)$, $3.44\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{4,5}=1.9 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{3,4}=7.3 \mathrm{~Hz}, 1 \mathrm{H}, 4-\mathrm{H}\right), 3.73(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OMe}), 3.85\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{9,10 \mathrm{a}}=7.5 \mathrm{~Hz}\right.$, $\left.{ }^{2} \mathrm{~J}_{10 \mathrm{a}, 10 \mathrm{~b}}=11.6 \mathrm{~Hz}, 1 \mathrm{H}, 10 \mathrm{a}-\mathrm{H}\right), 4.27\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{9,10 \mathrm{~b}}=4.9 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{10 \mathrm{a}, 10 \mathrm{~b}}=11.6 \mathrm{~Hz}, 1 \mathrm{H}, 10 \mathrm{~b}-\mathrm{H}\right)$, $5.10\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{6,7}=1.8 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=4.3 \mathrm{~Hz}, 1 \mathrm{H}, 6-\mathrm{H}\right), 5.33\left(\mathrm{ddd},{ }^{3} \mathrm{~J}_{8,9}=2.0 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{9,10 \mathrm{~b}}=4.9 \mathrm{~Hz}\right.$, $\left.{ }^{3} \mathrm{~J}_{9,10 \mathrm{a}}=7.5 \mathrm{~Hz}, 1 \mathrm{H}, 9-\mathrm{H}\right), 5.37\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{8,9}=2.0 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{7,8}=10.0 \mathrm{~Hz}, 1 \mathrm{H}, 8-\mathrm{H}\right), 5.43\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{6,7}=\right.$ $\left.1.8 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{7,8}=10.0 \mathrm{~Hz}, 1 \mathrm{H}, 7-\mathrm{H}\right), 6.13\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{2,3}=15.7 \mathrm{~Hz}, 1 \mathrm{H}, 2-\mathrm{H}\right), 6.55\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{3,4}=7.3 \mathrm{~Hz}\right.$, $\left.{ }^{3} \mathrm{~J}_{2,3}=15.7 \mathrm{~Hz}, 1 \mathrm{H}, 3-\mathrm{H}\right) ;{ }^{13} \mathrm{C}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}, 25{ }^{\circ} \mathrm{C}\right): \delta=20.9,20.9,21.0,21.0$, 21.1 (5 OAc), 52.2 (OMe), 54.0 (4-C), 58.0 (5-C), 62.5 (10-C), 67.4 (7-C), 67.5 (8-C), 67.5 (9-C), 67.5 (6-C), 125.0 (2-C), 143.3 (3-C), 166.0 (1-C), 169.9, 170.1, 170.2, 170.7, 170.8 (5 CO-OAc); HRMS (ESI) $m / z[\mathrm{M}+\mathrm{Na}]^{+}$calculated 511.1428, found 511.1439.

## Methyl (2E)-6,7,8,9,10-Penta-O-acetyl-2,3-dideoxy-4R,5S-epoxy-d-gluco-deca-2-enonate

 (4c): Aldehyde 3c ( $350 \mathrm{mg}, 0.84 \mathrm{mmol}$ ) was epoxidized with the catalyst ( $41 \mathrm{mg}, 0.13 \mathrm{mmol}$ ) and $\mathrm{H}_{2} \mathrm{O}_{2} 50 \%(63 \mu \mathrm{l}, 1.10 \mathrm{mmol})$ in 20 ml of dry DCM according to method C. For the Wittig reaction $\mathrm{Ph}_{3} \mathrm{P}\left(\mathrm{CHCO}_{2} \mathrm{Me}\right)(562 \mathrm{mg}, 1.68 \mathrm{mmol})$ was used. Purification by silica gel chromatography was performed using HE/EA $=2 / 1$ as eluent; yield $296 \mathrm{mg}(72 \%) \cdot[\alpha]^{\mathrm{D}}{ }_{20}=$ $+34.3^{\circ}\left(2.7, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right) ;$ m.p. $112-114^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}, 25^{\circ} \mathrm{C}\right): \delta=2.04,2.07$,2.09, 2.10, $2.12(5 \mathrm{~s}, 15 \mathrm{H}, 5 \mathrm{OAc}), 2.98\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{5,6}=1.8 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{4,5}=5.4 \mathrm{~Hz}, 1 \mathrm{H}, 5-\mathrm{H}\right), 3.52(\mathrm{dd}$, $\left.{ }^{3} \mathrm{~J}_{4,5}=5.4 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{3,4}=7.2 \mathrm{~Hz}, 1 \mathrm{H}, 4-\mathrm{H}\right), 3.74(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OMe}), 4.11\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{9,10 \mathrm{a}}=5.8 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{10 \mathrm{a}, 10 \mathrm{~b}}\right.$ $=12.3 \mathrm{~Hz}, 1 \mathrm{H}, 10 \mathrm{a}-\mathrm{H}), 4.30\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{9,10 \mathrm{~b}}=4.0 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{10 \mathrm{a}, 10 \mathrm{~b}}=12.3 \mathrm{~Hz}, 1 \mathrm{H}, 10 \mathrm{~b}-\mathrm{H}\right), 5.01(\mathrm{dd}$, $\left.{ }^{3} \mathrm{~J}_{5,6}=1.8 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{6,7}=4.8 \mathrm{~Hz}, 1 \mathrm{H}, 6-\mathrm{H}\right), 5.04\left(\mathrm{ddd},{ }^{3} \mathrm{~J}_{9,10 \mathrm{~b}}=4.0 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{8,9}=5.7 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{9,10 \mathrm{a}}=5.8\right.$ $\mathrm{Hz}, 1 \mathrm{H}, 9-\mathrm{H}), 5.45\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{7,8}=5.4 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{8,9}=5.7 \mathrm{~Hz}, 1 \mathrm{H}, 8-\mathrm{H}\right), 5.47\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{6,7}=4.8 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{7,8}\right.$ $=5.4 \mathrm{~Hz}, 1 \mathrm{H}, 7-\mathrm{H}), 6.16\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{2,3}=15.7 \mathrm{~Hz}, 1 \mathrm{H}, 2-\mathrm{H}\right), 6.59\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{3,4}=7.2 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=15.7\right.$ $\mathrm{Hz}, 1 \mathrm{H}, 3-\mathrm{H}) ;{ }^{13} \mathrm{C}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}, 2{ }^{\circ} \mathrm{C}\right): \delta=20.9,21.0,21.1,21.1,21.1$ (5 OAc), 52.2 (OMe), 55.0 (4-C), 57.8 (5-C), 61.8 (10-C), 69.2 (9-C), 69.4 (7-C), 69.8 (8-C), 70.4 ( $6-$ C), 125.1 (2-C), 143.1 (3-C), 166.1 (1-C), 170.0, 170.0, 170.0, 170.2, 170.8 ( 5 CO-OAc); HRMS (ESI) $m / z[\mathrm{M}+\mathrm{Na}]^{+}$calculated 511.1428, found 511.1432.

## Methyl (2E)-6,7,8,9,10-Tetra-O-acetyl-4-azido-2,3,4-trideoxy-d-glycero-d-ido-nona-2-

 enonate (5a): Epoxide 4a ( $100 \mathrm{mg}, 0.24 \mathrm{mmol}$ ) was opened with $\mathrm{TMSN}_{3}(64 \mu \mathrm{l}, 0.48 \mathrm{mmol})$ and $\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{4}(28 \mathrm{mg}, 0.02 \mathrm{mmol})$ in 3 ml of degassed THF according to method D . Purification by silica gel chromatography was performed using HE/EA $=2 / 1$ as eluent; yield: $92 \mathrm{mg},(83 \%)$ as a mixture of acetate migration products ( $\sim 2 / 1 / 1$ ). IR (neat): 3475, 2923, $2109,1748,1437,1373,1223,1044 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR ( $\mathrm{CDCl}_{3}, 400 \mathrm{MHz}, 25^{\circ} \mathrm{C}$ ): (main product) $\delta=2.05,2.06,2.09,2.12(4 \mathrm{~s}, 12 \mathrm{H}, 4 \mathrm{OAc}), 2.93\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{5,5-\mathrm{OH}}=8.6 \mathrm{~Hz}, 1 \mathrm{H}, 5-\mathrm{OH}\right), 3.70(\mathrm{ddd}$, $\left.{ }^{3} \mathrm{~J}_{4,5}=4.4 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=4.5 \mathrm{~Hz}, 1 \mathrm{H}, 5-\mathrm{H}\right), 3.78(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OMe}), 4.09-4.48(\mathrm{~m}, 3 \mathrm{H}, 4-\mathrm{H}, 9 \mathrm{a}-\mathrm{H}, 9 \mathrm{~b}-$ H), $5.12\left(\mathrm{ddd},{ }^{3} \mathrm{~J}_{8,9 \mathrm{a}}=2.9 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{8,9 \mathrm{~b}}=4.2 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{7,8}=8.3 \mathrm{~Hz}, 1 \mathrm{H}, 8-\mathrm{H}\right), 5.26\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{5,6}=2.0\right.$ $\left.\mathrm{Hz},{ }^{3} \mathrm{~J}_{6,7}=7.0 \mathrm{~Hz}, 1 \mathrm{H}, 6-\mathrm{H}\right), 5.38\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{6,7}=7.0 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{7,8}=8.3 \mathrm{~Hz}, 1 \mathrm{H}, 7-\mathrm{H}\right), 6.16\left(\mathrm{dd},{ }^{4} \mathrm{~J}_{2,4}\right.$ $\left.=1.3 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=15.8 \mathrm{~Hz}, 1 \mathrm{H}, 2-\mathrm{H}\right), 6.83\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{3,4}=6.1 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=15.8 \mathrm{~Hz}, 1 \mathrm{H}, 3-\mathrm{H}\right) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}, 25^{\circ} \mathrm{C}\right): \delta=20.93,20.96,21.10,21.19\left(4 \mathrm{CH}_{3}\right), 52.41(\mathrm{OMe}), 62.83$ (9-C), 68.58 (4-C), 70.57 (8-C), 71.03 (7-C), 72.58 (6-C), 73.68 (5-C), 125.84 (2-C), 139.86 (3-C), 165.63 (1-C), $170.19,170.27,170.35,170.66(4 \mathrm{C}=\mathrm{O})$; HRMS (ESI) $m / z[\mathrm{M}+\mathrm{Na}]^{+}$ calculated 482.1387, found 482.1400.
## Methyl (2E)-6,7,8,9,10-Penta-O-acetyl-4-azido-2,3,4-trideoxy-d-threo-L-galacto-deca-2-

 enonate (5b): Epoxide 4b ( $100 \mathrm{mg}, 0.20 \mathrm{mmol}$ ) was opened with $\mathrm{TMSN}_{3}(54 \mu \mathrm{l}, 0.41 \mathrm{mmol})$ and $\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{4}(24 \mathrm{mg}, 0.02 \mathrm{mmol})$ in 3 ml of degassed THF according to method D . Purification by silica gel chromatography was performed using HE/EA $=3 / 2$ as eluent; yield: $83 \mathrm{mg},(76 \%) .[\alpha]^{\mathrm{D}}{ }_{20}=+12.1^{\circ}\left(9.0, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$; IR (neat): 3483, 2957, 2106, 1744, 1437, 1371, 1210, 1033, 734, $630 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}, 25^{\circ} \mathrm{C}\right): \delta=2.02,2.08,2.10,2.14$, $2.18(5 \mathrm{~s}, 15 \mathrm{H}, 5 \mathrm{OAc}), 3.44\left(\mathrm{ddd},{ }^{3} \mathrm{~J}_{4,5}=2.8 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,5-\mathrm{OH}}=5.4 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=9.4 \mathrm{~Hz}, 1 \mathrm{H}, 5-\mathrm{H}\right)$, $3.63\left(\mathrm{dd},{ }^{4} \mathrm{~J}_{4,5-\mathrm{OH}}=0.5 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,5-\mathrm{OH}}=5.4 \mathrm{~Hz}, 1 \mathrm{H}, 5-\mathrm{OH}\right), 3.78(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OMe}), 3.78(\mathrm{~m}, 1 \mathrm{H}, 4-$ H), $3.82\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{9,10 \mathrm{a}}=5.4 \mathrm{~Hz}, 8.0 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{10 \mathrm{a}, 10 \mathrm{~b}}=11.9 \mathrm{~Hz}, 1 \mathrm{H}, 10 \mathrm{a}-\mathrm{H}\right), 4.33\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{9,10 \mathrm{~b}}=4.1\right.$ $\left.\mathrm{Hz},{ }^{2} \mathrm{~J}_{10 \mathrm{a}, 10 \mathrm{~b}}=11.9 \mathrm{~Hz}, 1 \mathrm{H}, 10 \mathrm{~b}-\mathrm{H}\right), 5.22\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{8,9}=1.9 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{7,8}=10.2 \mathrm{~Hz}, 1 \mathrm{H}, 8-\mathrm{H}\right), 5.25$ $\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{6,7}=1.3 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=9.4 \mathrm{~Hz}, 1 \mathrm{H}, 6-\mathrm{H}\right), 5.36\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{6,7}=1.3 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{7,8}=10.2 \mathrm{~Hz}, 1 \mathrm{H}, 7-\right.$ H), $5.36\left(\mathrm{ddd},{ }^{3} \mathrm{~J}_{8,9}=1.9 \mathrm{~Hz},{ }^{3} \mathbf{J}_{9,10 \mathrm{~b}}=4.1 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{9,10 \mathrm{a}}=5.4 \mathrm{~Hz}, 1 \mathrm{H}, 9-\mathrm{H}\right), 6.10\left(\mathrm{dd},{ }^{4} \mathrm{~J}_{2,4}=1.1\right.$ $\left.\mathrm{Hz},{ }^{3} \mathrm{~J}_{2,3}=15.7 \mathrm{~Hz}, 1 \mathrm{H}, 2-\mathrm{H}\right), 6.97\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{3,4}=7.3 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=15.7 \mathrm{~Hz}, 1 \mathrm{H}, 3-\mathrm{H}\right) ;{ }^{13} \mathrm{C}-\mathrm{NMR}$ $\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}, 25^{\circ} \mathrm{C}\right): ~ \delta=20.6,20.6,20.7,20.7,20.9$ (5 OAc), 51.9 (OMe), 62.1 (4-C), 62.7 (10-C), 67.3 (7-C), 68.0 (9-C), 68.6 (6-C), 68.9 (8-C), 70.2 (5-C), 124.8 (2-C), 141.4 (3C), 165.9 (1-C), 169.7, 170.1, 170.4, 170.4, 172.5 (5 CO-OAc); HRMS (ESI) $m / z[\mathrm{M}+\mathrm{Na}]^{+}$ calculated 554.1598, found 554.1595.
## Methyl (2E)-6,7,8,9,10-Penta-O-acetyl-4-azido-2,3,4-trideoxy-D-erythro-L-galacto-deca-

2-enonate (5c): Epoxide $\mathbf{4 c}\left(100 \mathrm{mg}, 0.20 \mathrm{mmol}\right.$ ) was opened with $\mathrm{TMSN}_{3}(54 \mu \mathrm{l}, 0.41$ $\mathrm{mmol})$ and $\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{4}(24 \mathrm{mg}, 0.02 \mathrm{mmol})$ in 3 ml of degassed THF according to method D . Purification by silica gel chromatography was performed using $\mathrm{HE} / \mathrm{EA}=3 / 2$ as eluent; yield $93 \mathrm{mg},(85 \%) \cdot[\alpha]^{\mathrm{D}}{ }_{20}=-17.2^{\circ}\left(1.5, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$; IR (neat): 3482, 2957, 2109, 1750, 1654, 1374, 1219, 1047, $717 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}, 25^{\circ} \mathrm{C}\right): \delta=2.03,2.10,2.11,2.12,2.15$
( $5 \mathrm{~s}, 15 \mathrm{H}, 5 \mathrm{OAc}$ ), $3.16\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{5,5-\mathrm{OH}}=7.6 \mathrm{~Hz}, 1 \mathrm{H}, 5-\mathrm{OH}\right), 3.63\left(\mathrm{ddd},{ }^{3} \mathrm{~J}_{4,5}=2.7 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,5-\mathrm{OH}}=\right.$ $7.6 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=8.8 \mathrm{~Hz}, 1 \mathrm{H}, 5-\mathrm{H}$ ), $3.77(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OMe}), 3.95\left(\mathrm{ddd},{ }^{4} \mathrm{~J}_{2,4}=1.0 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{4,5}=2.7 \mathrm{~Hz}\right.$, $\left.{ }^{3} \mathrm{~J}_{3,4}=7.4 \mathrm{~Hz}, 1 \mathrm{H}, 4-\mathrm{H}\right), 4.13\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{9,10 \mathrm{a}}=5.4 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{10 \mathrm{a}, 10 \mathrm{~b}}=12.2 \mathrm{~Hz}, 1 \mathrm{H}, 10 \mathrm{a}-\mathrm{H}\right), 4.29(\mathrm{dd}$, $\left.{ }^{3} \mathrm{~J}_{9,10 \mathrm{~b}}=4.6 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{10 \mathrm{a}, 10 \mathrm{~b}}=12.2 \mathrm{~Hz}, 1 \mathrm{H}, 10 \mathrm{~b}-\mathrm{H}\right), 5.12\left(\mathrm{ddd},{ }^{3} \mathrm{~J}_{9,10 \mathrm{~b}}=4.6 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{9,10 \mathrm{a}}=5.4 \mathrm{~Hz}\right.$, $\left.{ }^{3} \mathbf{J}_{8,9}=10.7 \mathrm{~Hz}, 1 \mathrm{H}, 9-\mathrm{H}\right), 5.24\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{6,7}=3.4 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=8.8 \mathrm{~Hz}, 1 \mathrm{H}, 6-\mathrm{H}\right), 5.47\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{6,7}=\right.$ $\left.3.4 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{7,8}=5.9 \mathrm{~Hz}, 1 \mathrm{H}, 7-\mathrm{H}\right), 5.50\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{7,8}=5.9 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{8,9}=10.7 \mathrm{~Hz}, 1 \mathrm{H}, 8-\mathrm{H}\right), 6.11(\mathrm{dd}$, $\left.{ }^{4} \mathrm{~J}_{2,4}=1.0 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=15.7 \mathrm{~Hz}, 1 \mathrm{H}, 2-\mathrm{H}\right), 6.94\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{3,4}=7.4 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=15.7 \mathrm{~Hz}, 1 \mathrm{H}, 3-\mathrm{H}\right) ;$ ${ }^{13} \mathrm{C}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}, 25{ }^{\circ} \mathrm{C}\right): \delta=20.6,20.6,20.6,20.7,20.7$ (5 OAc), 52.3 (OMe), 61.7 (10-C), 63.2 (4-C), 69.3 (9-C), 69.8 (6-C), 70.2 (7-C), 70.6 (8-C), 71.9 (5-C), 125.4 (2C), 141.4 (3-C), 166.1 (1-C), 170.1, 170.1, 170.6, 170.9, 171.5 (5 CO-OAc); HRMS (ESI) $m / z[\mathrm{M}+\mathrm{Na}]^{+}$calculated 554.1598, found 554.1609.

2-Azido-2-deoxy-D-glycero-D-ido-heptose (6a): Azide 5a (157 mg, 0.34 mmol ) was deacetylated in a methanolic HCl solution using $\mathrm{AcCl}(73 \mu \mathrm{l}, 1.03 \mathrm{mmol})$ in 9 ml of dry MeOH according to method E. After ozonolysis, the reaction was quenched with $\mathrm{PPh}_{3}$ (108 $\mathrm{mg}, 0.41 \mathrm{mmol})$. Purification by silica gel chromatography was performed using $\mathrm{DCM} / \mathrm{MeOH}=6 / 1$ as eluent; yield: 66 mg (mixture of anomers/conformers), $(82 \%) .[\alpha]^{\mathrm{D}}{ }_{20}=$ $-26.3^{\circ}\left(4.2, \mathrm{H}_{2} \mathrm{O}\right)$; IR (neat): $3340,2926,2117,1641,1263,1042,813,737,631 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{D}_{2} \mathrm{O}, 600 \mathrm{MHz}, 25^{\circ} \mathrm{C}\right):(1-\mathrm{H}) \delta=4.98\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{1,2}=8.7 \mathrm{~Hz}\right), 5.01\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{1,2}=4.9 \mathrm{~Hz}\right), 5.18$ $\left(\mathrm{d},{ }^{3} \mathrm{~J}_{1,2}=1.4 \mathrm{~Hz}\right), 5.25\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{1,2}=3.5 \mathrm{~Hz}\right), 5.52\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{1,2}=4.7 \mathrm{~Hz}\right),{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{D}_{2} \mathrm{O}, 150 \mathrm{MHz}\right.$, $25^{\circ} \mathrm{C}$ ): (1-C) $\delta=92.4,93.1,93.3,94.8,99.0$; HRMS (ESI) $m / z[\mathrm{M}+\mathrm{Na}]^{+}$calculated 258.0702, found 258.0701.

2-Azido-2-deoxy-D-threo-L-galacto-octose (6b): Azide 5b (155 mg, 0.29 mmol ) was deacetylated in a methanolic HCl solution using $\mathrm{AcCl}(62 \mu \mathrm{l}, 0.87 \mathrm{mmol})$ in 9 ml of dry MeOH according to method E . Since the deacetylation product was not completely soluble in

MeOH about 1.5 mmol of ozone were bubbled through the suspension. After 1 h at $-78^{\circ} \mathrm{C}$ additional 0.75 mmol of ozone were added. After 1 h at $-78^{\circ} \mathrm{C}$ the reaction was quenched with $\mathrm{PPh}_{3}$ ( $92 \mathrm{mg}, 0.35 \mathrm{mmol}$ ). Purification by silica gel chromatography was performed using $\mathrm{DCM} / \mathrm{MeOH}=6 / 1$ as eluent; yield: 55 mg (mixture of anomers, $\alpha / \beta=1 / 2$ ), (71\%), 3 $\mathrm{mg}(3 \%)$ of not ozonolyzed deacetylation product were recovered. $[\alpha]^{\mathrm{D}}{ }_{20}=+17.9^{\circ}\left(2.9, \mathrm{H}_{2} \mathrm{O}\right)$; IR (neat): 3341, 2927, 2118, 1591, 1350, 1064, 770, $630 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR ( $\mathrm{D}_{2} \mathrm{O}, 600 \mathrm{MHz}, 25$ $\left.{ }^{\circ} \mathrm{C}\right):(\beta$-anomer $) \delta=3.49\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{2,3}=10.6 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{1,2}=8.1 \mathrm{~Hz}, 1 \mathrm{H}, 2-\mathrm{H}\right), 3.61\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{5,6}=9.4 \mathrm{~Hz}\right.$, $\left.{ }^{3} \mathrm{~J}_{4,5}=0.9 \mathrm{~Hz}, 1 \mathrm{H}, 5-\mathrm{H}\right), 3.71(\mathrm{~m}, 3 \mathrm{H}, 8 \mathrm{a}-\mathrm{H}, 8 \mathrm{~b}-\mathrm{H}, 3-\mathrm{H}), 3.83\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{6,7}=1.5 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=9.4\right.$ $\mathrm{Hz}, 1 \mathrm{H}, 6-\mathrm{H}), 3.92\left(\mathrm{ddd},{ }^{3} \mathrm{~J}_{6,7}=1.5 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{7,8 \mathrm{a}}=5.6 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{7,8 \mathrm{~b}}=7.2 \mathrm{~Hz}, 1 \mathrm{H}, 7-\mathrm{H}\right), 4.09(\mathrm{dd}$, $\left.{ }^{3} \mathrm{~J}_{4,5}=0.9 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{3,4}=3.4 \mathrm{~Hz}, 1 \mathrm{H}, 4-\mathrm{H}\right), 4.65\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{1,2}=8.1 \mathrm{~Hz}, 1 \mathrm{H}, 1-\mathrm{H}\right),(\alpha-$ anomer $) \delta=3.71$ $(\mathrm{m}, 3 \mathrm{H}, 8 \mathrm{a}-\mathrm{H}, 8 \mathrm{~b}-\mathrm{H}, 2-\mathrm{H}), 3.81\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{5,6}=9.6 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{6,7}=1.7 \mathrm{~Hz}, 1 \mathrm{H}, 6-\mathrm{H}\right), 3.87\left(\mathrm{ddd},{ }^{3} \mathrm{~J}_{6,7}=\right.$ $\left.1.7 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{7,8 \mathrm{~b}}=5.4 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{7,8 \mathrm{a}}=7.3 \mathrm{~Hz}, 1 \mathrm{H}, 7-\mathrm{H}\right), 4.02\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{3,4}=3.2 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=10.8 \mathrm{~Hz}, 1 \mathrm{H}\right.$, $3-\mathrm{H}), 4.04\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{4,5}=0.9 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=9.6 \mathrm{~Hz}, 1 \mathrm{H}, 5-\mathrm{H}\right), 4.18\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{4,5}=0.9 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{3,4}=3.2 \mathrm{~Hz}\right.$, $1 \mathrm{H}, 4-\mathrm{H}), 5.37\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{1,2}=3.8 \mathrm{~Hz}, 1 \mathrm{H}, 1-\mathrm{H}\right),{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{D}_{2} \mathrm{O}, 150 \mathrm{MHz}, 25^{\circ} \mathrm{C}\right):(\beta$-anomer $) \delta$ $=63.0$ ( $8-\mathrm{C}$ ), 64.7 (2-C), 67.0 (4-C), 67.4 (6-C), 70.0 (7-C), 72.0 (3-C), 73.0 (5-C), 95.6 ( 1 C), ( $\alpha$-anomer): 60.5 (2-C), 63.0 ( $8-\mathrm{C}$ ), 67.7 ( $6-\mathrm{C}), 67.9$ (4-C), 68.4 (3-C), 68.4 (5-C), 70.1 (7-C), 91.4 (1-C); HRMS (ESI) $m / z[\mathrm{M}+\mathrm{Na}]^{+}$calculated 288.0808, found 288.0791.

2-Azido-2-deoxy-D-erythro-L-galacto-octose (6c): Azide 5c (102 mg, 0.19 mmol ) was deacetylated in a methanolic HCl solution using $\mathrm{AcCl}(41 \mu \mathrm{l}, 0.58 \mathrm{mmol})$ in 6 ml of dry MeOH according to method E . After ozonolysis the reaction was quenched with $\mathrm{PPh}_{3}$ (60 $\mathrm{mg}, 0.23 \mathrm{mmol}$ ). Purification by silica gel chromatography was performed using $\mathrm{DCM} / \mathrm{MeOH}=6 / 1$ as eluent; yield: 38 mg (mixture of anomers, $\alpha / \beta=1 / 2$ ), $(75 \%) .[\alpha]_{20}^{\mathrm{D}}=-$ $35.6^{\circ}\left(12.9, \mathrm{H}_{2} \mathrm{O}\right)$; IR (neat): $3339,2923,2121,1641,1252,1017,723,633 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR ( $\mathrm{D}_{2} \mathrm{O}, 600 \mathrm{MHz}, 25^{\circ} \mathrm{C}$ ): $\left(\beta\right.$-anomer) $\delta=3.52$ (dd, ${ }^{3} \mathrm{~J}_{1,2}=8.1 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=10.4 \mathrm{~Hz}, 1 \mathrm{H}, 2-\mathrm{H}$ ), $3.66\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{7,8 \mathrm{a}}=6.5 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{8 \mathrm{a}, 8 \mathrm{~b}}=11.8 \mathrm{~Hz}, 1 \mathrm{H}, 8 \mathrm{a}-\mathrm{H}\right), 3.67\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{3,4}=3.3 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=10.4 \mathrm{~Hz}\right.$,
$1 \mathrm{H}, 3-\mathrm{H}), 3.69\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{4,5}=0.9 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=5.3 \mathrm{~Hz}, 1 \mathrm{H}, 5-\mathrm{H}\right), 3.77\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{7,8 \mathrm{~b}}=3.3 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{8 \mathrm{a}, 8 \mathrm{~b}}=\right.$ $11.8 \mathrm{~Hz}, 1 \mathrm{H}, 8 \mathrm{~b}-\mathrm{H}), 3.82\left(\mathrm{ddd},{ }^{3} \mathrm{~J}_{7,8 \mathrm{~b}}=3.3 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{6,7}=5.9 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{7,8 \mathrm{a}}=6.5 \mathrm{~Hz}, 1 \mathrm{H}, 7-\mathrm{H}\right), 3.94$ (dd, $\left.{ }^{3} \mathrm{~J}_{5,6}=5.3 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{6,7}=5.9 \mathrm{~Hz}, 1 \mathrm{H}, 6-\mathrm{H}\right), 4.04\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{3,4}=3.3 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{4,5}=0.9 \mathrm{~Hz}, 1 \mathrm{H}, 4-\mathrm{H}\right.$ ), $4.65\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{1,2}=8.1 \mathrm{~Hz}, 1 \mathrm{H}, 1-\mathrm{H}\right),(\alpha-\mathrm{anomer}) \delta=3.67\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{7,8 \mathrm{a}}=6.5 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{8 \mathrm{a}, 8 \mathrm{~b}}=11.8 \mathrm{~Hz}, 1\right.$ $\mathrm{H}, 8 \mathrm{a}-\mathrm{H}), 3.77\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{7,8 \mathrm{~b}}=3.3 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{8 \mathrm{a}, 8 \mathrm{~b}}=11.8 \mathrm{~Hz}, 1 \mathrm{H}, 8 \mathrm{~b}-\mathrm{H}\right), 3.73\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{1,2}=3.8 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}\right.$ $=10.7 \mathrm{~Hz}, 1 \mathrm{H}, 2-\mathrm{H}), 3.80\left(\mathrm{ddd},{ }^{3} \mathrm{~J}_{7,8 \mathrm{~b}}=3.3 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{6,7}=5.9 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{7,8 \mathrm{a}}=6.5 \mathrm{~Hz}, 1 \mathrm{H}, 7-\mathrm{H}\right), 3.93$ (dd, ${ }^{3} \mathrm{~J}_{5,6}=5.3 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{6,7}=5.9 \mathrm{~Hz}, 1 \mathrm{H}, 6-\mathrm{H}$ ), $4.01\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{3,4}=3.1 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=10.7 \mathrm{~Hz}, 1 \mathrm{H}, 3-\right.$ H), $4.13\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{3,4}=3.1 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{4,5}=0.9 \mathrm{~Hz}, 1 \mathrm{H}, 4-\mathrm{H}\right), 4.13\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{4,5}=0.9 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=5.3 \mathrm{~Hz}, 1\right.$ $\mathrm{H}, 5-\mathrm{H}), 5.42\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{1,2}=3.8 \mathrm{~Hz}, 1 \mathrm{H}, 1-\mathrm{H}\right),{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 150 \mathrm{MHz}, 25^{\circ} \mathrm{C}\right):(\beta$-anomer $) \delta$ $=61.9$ ( $8-\mathrm{C}$ ), 64.5 (2-C), 69.5 (4-C), 70.8 (7-C), 71.7 (3-C), 72.3 ( $6-\mathrm{C}), 73.3$ (5-C), 95.6 ( 1 C), $(\alpha-$ anomer $) \delta=60.3$ (2-C), 62.1 ( $8-\mathrm{C}), 68.1$ (3-C), $68.4(5-\mathrm{C}), 70.7$ ( $4-\mathrm{C}), 70.8$ (7-C), 72.5 (6-C), 91.3 (1-C); HRMS (ESI) $m / z[\mathrm{M}+\mathrm{Na}]^{+}$calculated 288.0808, found 288.0808 .

2-Acetamido-1,3,4,6,7-penta-O-acetyl-2-deoxy-d-glycero-d-ido-heptose (7a): Sugar azide $\mathbf{6 a}(31 \mathrm{mg}, 0.13 \mathrm{mmol})$ was peracetylated and reduced with DTT ( $82 \mathrm{mg}, 0.53 \mathrm{mmol}$ ) and DIPA ( 1 ml ) in 4 ml of dry MeCN according to method F. Purification by silica gel chromatography was performed using $\mathrm{HE} / \mathrm{EA}=1 / 3$ as eluent; yield: $20 \mathrm{mg},\left({ }^{4} \mathrm{C}_{1}\right.$-pyranoid form, mixture of anomers, $\alpha / \beta=3 / 2$ ), ( $33 \%$ ), $16 \mathrm{mg}\left(\beta\right.$-furanoid form $/{ }^{1} \mathrm{C}_{4} \alpha$-pyranoid form $=$ $5 / 2),(26 \%) .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 600 \mathrm{MHz}, 25^{\circ} \mathrm{C}\right):\left({ }^{4} \mathrm{C}_{1}\right.$-pyranoid form), $(\alpha$-anomer) $\delta=2.01$, 2.02, 2.05, 2.10, 2.12, $2.14(6 \mathrm{~s}, 18 \mathrm{H}, 6 \mathrm{Ac}), 4.10\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{6,7 \mathrm{a}}=4.6 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{7 \mathrm{a}, 7 \mathrm{~b}}=12.4 \mathrm{~Hz}, 1 \mathrm{H}\right.$, $7 \mathrm{a}-\mathrm{H}), 4.33$ (dddd, ${ }^{4} \mathrm{~J}_{2,4}=1.0 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{1,2}=1.8 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=3.1 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,2-\mathrm{NH}}=9.8 \mathrm{~Hz}, 1 \mathrm{H}, 2-\mathrm{H}$ ), $4.38\left(\mathrm{ddd},{ }^{4} \mathrm{~J}_{5,1}=0.6 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{4,5}=1.9 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=9.9 \mathrm{~Hz}, 1 \mathrm{H}, 5-\mathrm{H}\right), 4.46\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{6,7 \mathrm{~b}}=2.4 \mathrm{~Hz}\right.$, $\left.{ }^{2} \mathrm{~J}_{7 \mathrm{a}, 7 \mathrm{~b}}=12.4 \mathrm{~Hz}, 1 \mathrm{H}, 7 \mathrm{~b}-\mathrm{H}\right), 4.84\left(\mathrm{ddd},{ }^{4} \mathrm{~J}_{3,1}=1.1 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=3.1 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{3,4}=3.1 \mathrm{~Hz}, 1 \mathrm{H}, 3-\mathrm{H}\right)$, 5.08 (dddd, ${ }^{5} \mathrm{~J}_{4,1}=0.7 \mathrm{~Hz},{ }^{4} \mathrm{~J}_{2,4}=1.0 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{4,5}=1.9 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{3,4}=3.1 \mathrm{~Hz}, 1 \mathrm{H}, 4-\mathrm{H}$ ), 5.12 (ddd, $\left.{ }^{3} \mathrm{~J}_{6,7 \mathrm{~b}}=2.4 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{6,7 \mathrm{a}}=4.6 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=9.9 \mathrm{~Hz}, 1 \mathrm{H}, 6-\mathrm{H}\right), 5.92\left(\mathrm{dddd},{ }^{4} \mathrm{~J}_{5,1}=0.6 \mathrm{~Hz},{ }^{5} \mathrm{~J}_{4,1}=0.7\right.$ $\left.\mathrm{Hz},{ }^{4} \mathrm{~J}_{3,1}=1.1 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{1,2}=1.8 \mathrm{~Hz}, 1 \mathrm{H}, 1-\mathrm{H}\right), 6.05\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{2,2-\mathrm{NH}}=9.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}\right),\left({ }^{4} \mathrm{C}_{1}\right.$-pyranoid
form), $(\beta$-anomer $) \delta=2.01,2.05,2.09,2.09,2.10,2.17,(6 s, 18 \mathrm{H}, 6 \mathrm{Ac}), 4.13\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{6,7 \mathrm{a}}=5.0\right.$ $\left.\mathrm{Hz},{ }^{2} \mathrm{~J}_{7 \mathrm{a}, 7 \mathrm{~b}}=12.4 \mathrm{~Hz}, 1 \mathrm{H}, 7 \mathrm{a}-\mathrm{H}\right), 4.20\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{4,5}=1.8 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=9.8 \mathrm{~Hz}, 1 \mathrm{H}, 5-\mathrm{H}\right), 4.35$ (dddd, $\left.{ }^{4} \mathrm{~J}_{2,4}=1.0 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{1,2}=2.1 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=2.9 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,2-\mathrm{NH}}=9.7 \mathrm{~Hz}, 1 \mathrm{H}, 2-\mathrm{H}\right), 4.43\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{6,7 \mathrm{~b}}=2.3\right.$ $\left.\mathrm{Hz},{ }^{2} \mathrm{~J}_{7 \mathrm{a}, 7 \mathrm{~b}}=12.4 \mathrm{~Hz}, 1 \mathrm{H}, 7 \mathrm{~b}-\mathrm{H}\right), 4.97\left(\mathrm{ddd},{ }^{4} \mathrm{~J}_{2,4}=1.0 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{3,4}=2.9 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=2.9 \mathrm{~Hz}, 1 \mathrm{H}, 4-\right.$ H), $5.00\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{2,3}=2.9 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{3,4}=2.9 \mathrm{~Hz}, 1 \mathrm{H}, 3-\mathrm{H}\right), 5.18\left(\mathrm{ddd},{ }^{3} \mathrm{~J}_{6,7 \mathrm{~b}}=2.3 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{6,7 \mathrm{a}}=5.0 \mathrm{~Hz}\right.$, $\left.{ }^{3} \mathrm{~J}_{5,6}=9.8 \mathrm{~Hz}, 1 \mathrm{H}, 6-\mathrm{H}\right), 5.94\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{1,2}=2.1 \mathrm{~Hz}, 1 \mathrm{H}, 1-\mathrm{H}\right), 6.10\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{2,2-\mathrm{NH}}=9.7 \mathrm{~Hz}, 1 \mathrm{H}, 2-\right.$ NH ), ( $\beta$-furanoid form) $\delta=2.00,2.04,2.04,2.10,2.12,2.16(6 \mathrm{~s}, 18 \mathrm{H}, 6 \mathrm{Ac}), 4.10\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{6,7 \mathrm{a}}\right.$ $\left.=6.7 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{7 \mathrm{a}, 7 \mathrm{~b}}=12.4 \mathrm{~Hz}, 1 \mathrm{H}, 7 \mathrm{a}-\mathrm{H}\right), 4.37\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{6,7 \mathrm{~b}}=3.0 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{7 \mathrm{a}, 7 \mathrm{~b}}=12.4 \mathrm{~Hz}, 1 \mathrm{H}, 7 \mathrm{~b}-\mathrm{H}\right)$, $4.55\left(\mathrm{ddd},{ }^{3} \mathrm{~J}_{1,2}=3.1 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=5.1 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,2-\mathrm{NH}}=8.1 \mathrm{~Hz}, 1 \mathrm{H}, 2-\mathrm{H}\right), 4.59\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{4,5}=5.1 \mathrm{~Hz}\right.$, $\left.{ }^{3} \mathrm{~J}_{3,4}=6.8 \mathrm{~Hz}, 1 \mathrm{H}, 4-\mathrm{H}\right), 5.13$ (ddd, ${ }^{3} \mathrm{~J}_{6,7 \mathrm{~b}}=3.0 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=5.1 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{6,7 \mathrm{a}}=6.7 \mathrm{~Hz}, 1 \mathrm{H}, 6-\mathrm{H}$ ), $5.32\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{3,4}=2.9 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=2.9 \mathrm{~Hz}, 1 \mathrm{H}, 3-\mathrm{H}\right), 5.36\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{4,5}=5.1 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=9.8 \mathrm{~Hz}, 1 \mathrm{H}\right.$, $5-\mathrm{H}), 5.93\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{2,2-\mathrm{NH}}=8.1 \mathrm{~Hz}, 1 \mathrm{H}, 2-\mathrm{NH}\right), 6.03\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{1,2}=2.1 \mathrm{~Hz}, 1 \mathrm{H}, 1-\mathrm{H}\right),\left({ }^{1} \mathrm{C}_{4} \alpha\right.$-pyranoid form) $\delta=1.95,2.01,2.07,2.12,2.13,2.22(6 \mathrm{~s}, 18 \mathrm{H}, 6 \mathrm{Ac}), 4.11\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{4,5}=1.5 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=9.6\right.$ $\mathrm{Hz}, 1 \mathrm{H}, 5-\mathrm{H}), 4.14\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{6,7 \mathrm{a}}=5.1 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{7 \mathrm{a}, 7 \mathrm{~b}}=12.3 \mathrm{~Hz}, 1 \mathrm{H}, 7 \mathrm{a}-\mathrm{H}\right), 4.42\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{6,7 \mathrm{~b}}=2.4 \mathrm{~Hz}\right.$, $\left.{ }^{2} \mathrm{~J}_{7 \mathrm{a}, 7 \mathrm{~b}}=12.3 \mathrm{~Hz}, 1 \mathrm{H}, 7 \mathrm{~b}-\mathrm{H}\right), 4.54\left(\mathrm{ddd},{ }^{3} \mathrm{~J}_{2,3}=3.4 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{1,2}=9.3 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,2-\mathrm{NH}}=9.3 \mathrm{~Hz}, 1 \mathrm{H}, 2-\right.$ H), $5.04\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{4,5}=1.5 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{3,4}=3.6 \mathrm{~Hz}, 1 \mathrm{H}, 4-\mathrm{H}\right), 5.15\left(\mathrm{ddd},{ }^{3} \mathrm{~J}_{6,7 \mathrm{~b}}=2.4 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{6,7 \mathrm{a}}=5.1 \mathrm{~Hz}\right.$, $\left.{ }^{3} \mathrm{~J}_{5,6}=9.6 \mathrm{~Hz}, 1 \mathrm{H}, 6-\mathrm{H}\right), 5.16\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{2,3}=3.4 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{3,4}=3.6 \mathrm{~Hz}, 1 \mathrm{H}, 3-\mathrm{H}\right), 5.47\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{2,2-\mathrm{NH}}=\right.$ $9.3 \mathrm{~Hz}, 1 \mathrm{H}, 2-\mathrm{NH}), 5.84\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{1,2}=9.3 \mathrm{~Hz}, 1 \mathrm{H}, 1-\mathrm{H}\right),{ }^{13} \mathrm{C} \mathrm{NMR}\left(\mathrm{CDCl}_{3}, 150 \mathrm{MHz}, 25^{\circ} \mathrm{C}\right)$ : $\left({ }^{4} \mathrm{C}_{1}\right.$-pyranoid form), ( $\alpha$-anomer) $\delta=20.6,20.7,20.7,20.7,20.8,23.2\left(6 \mathrm{CH}_{3}\right), 45.7(2-\mathrm{C})$, 62.2 (7-C), 65.0 (4-C), 65.2 (5-C), 67.1 (3-C), $67.2(6-\mathrm{C}), 91.8\left({ }^{1} \mathrm{~J}_{1 \mathrm{C}, 1 \mathrm{H}}=177 \mathrm{~Hz}, 1-\mathrm{C}\right), 168.1$, 168.5, 168.8, 168.8, 169.7, 170.3 (6 CO-Ac), ( ${ }^{4} \mathrm{C}_{1}$-pyranoid form), ( $\beta$-anomer) $\delta=20.6,20.7$, 20.7, 20.6, 20.8, 23.3 ( 6 Ac ), 47.0 (2-C), 62.4 (7-C), 64.2 (4-C), 67.0 (6-C), 68.7 (3-C), 72.3 $(5-\mathrm{C}), 90.7\left({ }^{1} \mathrm{~J}_{1 \mathrm{C}, 1 \mathrm{H}}=166 \mathrm{~Hz}, 1-\mathrm{C}\right), 168.2,168.3,168.6,169.4,169.8,170.6(6 \mathrm{CO}-\mathrm{Ac}),(\beta-$ furanoid form) $\delta=20.6,20.7,20.8,20.9,21.1,23.1$ ( 6 Ac ), 60.0 (2-C), 61.8 (7-C), 69.2 (5C), 70.1 (6-C), 74.8 (4-C), 78.3 (3-C), $98.5\left({ }^{1} \mathrm{~J}_{1 \mathrm{C}, 1 \mathrm{H}}=179 \mathrm{~Hz}, 1-\mathrm{C}\right), 169.5,169.8,170.0$,
170.1, 170.3, 170.7 (6 CO-Ac), $\left({ }^{1} \mathrm{C}_{4} \alpha\right.$-pyranoid form) $\delta=20.7,20.7,20.7,20.9,21.0,23.2(6$ Ac), 47.3 (2-C), 62.5 (7-C), 64.8 (4-C), 67.3 (6-C), $70.0(3-C), 71.1(5-C), 91.4\left({ }^{1} \mathrm{~J}_{1 \mathrm{C}, 1 \mathrm{H}}=166\right.$ $\mathrm{Hz}, 1-\mathrm{C}), 168.8,169.4,169.6,169.6,170.0,170.6$ (6 CO-Ac); HRMS (ESI) $m / z[\mathrm{M}+\mathrm{Na}]^{+}$ calculated 484.1431, found (7a) 484.1419, (7a) 484.1425.

2-Acetamido-1,3,4,6,7,8-hexa-O-acetyl-2-deoxy-D-threo-L-galacto-octose (7b): Sugar azide $\mathbf{6 b}(55 \mathrm{mg}, 0.21 \mathrm{mmol})$ was peracetylated and reduced with DTT ( $128 \mathrm{mg}, 0.83 \mathrm{mmol}$ ) and DIPA ( 1.5 ml ) in 6 ml of dry MeCN according to method F. Purification by silica gel chromatography was performed using $\mathrm{HE} / \mathrm{EA}=1 / 4$ as eluent; yield 73 mg (mixture of anomers, $\alpha / \beta=1 / 1),(66 \%) .{ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}, 25^{\circ} \mathrm{C}\right):(\beta$-anomer $) \delta=1.93,2.00$, 2.01, 2.01, 2.04, 2.12, $2.13(7 \mathrm{~s}, 21 \mathrm{H}, 7 \mathrm{Ac}), 3.87\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{4,5}=1.1 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=9.5 \mathrm{~Hz}, 1 \mathrm{H}, 5-\mathrm{H}\right), 3.96$ $\left(\mathrm{dd},{ }^{2} \mathrm{~J}_{8 \mathrm{a}, 8 \mathrm{~b}}=11.8 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{7,8 \mathrm{a}}=5.8 \mathrm{~Hz}, 1 \mathrm{H}, 8 \mathrm{a}-\mathrm{H}\right), 4.17\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{7,8 \mathrm{~b}}=4.8 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{8 \mathrm{~B}, 8 \mathrm{~b}}=11.8 \mathrm{~Hz}, 1 \mathrm{H}, 8 \mathrm{~b}-\mathrm{H}\right)$, $4.36\left(\mathrm{ddd},{ }^{3} \mathrm{~J}_{1,2}=9.0 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,2-\mathrm{NH}}=9.1 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=11.3 \mathrm{~Hz}, 1 \mathrm{H}, 2-\mathrm{H}\right), 5.12\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{3,4}=3.5 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=\right.$ $11.3 \mathrm{~Hz}, 1 \mathrm{H}, 3-\mathrm{H}), 5.30\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{2,2-\mathrm{NH}}=9.1 \mathrm{~Hz}, 1 \mathrm{H}, 2-\mathrm{NH}\right), 5.35(\mathrm{~m}, 3 \mathrm{H}, 4-\mathrm{H}, 6-\mathrm{H}, 7-\mathrm{H}), 5.62\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{1,2}\right.$ $=9.0 \mathrm{~Hz}, 1 \mathrm{H}, 1-\mathrm{H}),(\alpha$-anomer) $\delta=1.94,2.01,2.02,2.10,2.12,2.12,2.15(7 \mathrm{~s}, 21 \mathrm{H}, 7 \mathrm{Ac}), 3.94(\mathrm{dd}$, $\left.{ }^{3} \mathbf{J}_{7,8 \mathrm{a}}=7.1 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{8 \mathrm{a}, 8 \mathrm{~b}}=11.8 \mathrm{~Hz}, 1 \mathrm{H}, 8 \mathrm{a}-\mathrm{H}\right), 4.06\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{4,5}=0.9 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=9.7 \mathrm{~Hz}, 1 \mathrm{H}, 5-\mathrm{H}\right), 4.21(\mathrm{dd}$, $\left.{ }^{3} \mathrm{~J}_{7,8 \mathrm{~b}}=5.6 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{8 \mathrm{Ba}, 8 \mathrm{~b}}=11.8 \mathrm{~Hz}, 1 \mathrm{H}, 8 \mathrm{~b}-\mathrm{H}\right), 4.72\left(\mathrm{ddd},{ }^{3} \mathrm{~J}_{1,2}=3.7 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,2-\mathrm{NH}}=9.3 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=11.5 \mathrm{~Hz}\right.$, $1 \mathrm{H}, 2-\mathrm{H}), 5.15\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{6,7}=2.0 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=9.7 \mathrm{~Hz}, 1 \mathrm{H}, 6-\mathrm{H}\right), 5.18\left(\mathrm{dd}, \mathrm{J}_{3,4}=3.3 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=11.5 \mathrm{~Hz}, 1\right.$ $\mathrm{H}, 3-\mathrm{H}), 5.31\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{2,2-\mathrm{NH}}=9.3 \mathrm{~Hz}, 1 \mathrm{H}, 2-\mathrm{NH}\right), 5.35(\mathrm{~m}, 2 \mathrm{H}, 4-\mathrm{H}, 7-\mathrm{H}), 6.23\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{1,2}=3.7 \mathrm{~Hz}, 1 \mathrm{H}, 1-\right.$ H); ${ }^{13} \mathrm{C}$-NMR $\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}, 25{ }^{\circ} \mathrm{C}\right):(\beta$-anomer $) \delta=20.5,20.6,20.6,20.7,20.7,20.8,23.7(7$ Ac), 50.1 (2-C), 62.9 (8-C), 65.1 (6-C), 65.6 (4-C), 68.7 (7-C), 70.3 (3-C), 71.6 (5-C), 93.2 (1-C), $169.2,169.5,169.9,170.2,170.4,170.7,171.2(7 \mathrm{CO}-\mathrm{Ac}),(\alpha-$ anomer $) \delta=20.4,20.6,20.6,20.6$, 20.7, 20.8, 23.6 ( 7 Ac ), 47.1 (2-C), 62.1 (8-C), 67.1 (4-C), 67.4 ( $6-\mathrm{C}), 68.1$ (3-C), 68.2 (5-C), 68.2 (7C), 91.2 (1-C), $168.5,169.4,169.5,169.6,170.2,170.4,170.6$ (7 CO-Ac); HRMS (ESI) $m / z[\mathrm{M}+\mathrm{Na}]^{+}$ calculated 556.1642, found 556.1633.

2-Acetamido-1,3,4,6,7,8-hexa-O-acetyl-2-deoxy-D-erythro-L-galacto-octose (7c): Sugar azide $\mathbf{6 c}(38 \mathrm{mg}, 0.14 \mathrm{mmol})$ was peracetylated and reduced with DTT ( $88 \mathrm{mg}, 0.57 \mathrm{mmol}$ )
and DIPA ( 1 ml ) in 4 ml of dry MeCN according to method F. Purification by silica gel chromatography was performed using $\mathrm{HE} / \mathrm{EA}=1 / 4$ as eluent; yield: 51 mg , (mixture of anomers, $\alpha / \beta=1 / 2),(67 \%) .[\alpha]^{\mathrm{D}}{ }_{20}=-12.0^{\circ}\left(1.0, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right) ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}\right.$, $25^{\circ} \mathrm{C}$ :, ( $\beta$-anomer) $\delta=1.94,2.01,2.01,2.07,2.11,2.11,2.23(7 \mathrm{~s}, 21 \mathrm{H}, 7 \mathrm{Ac}), 3.90\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{4,5}\right.$ $\left.=0.5 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=7.6 \mathrm{~Hz}, 1 \mathrm{H}, 5-\mathrm{H}\right), 4.17\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{7,8 \mathrm{a}}=5.9 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{8 \mathrm{a}, 8 \mathrm{~b}}=11.9 \mathrm{~Hz}, 1 \mathrm{H}, 8 \mathrm{a}-\mathrm{H}\right), 4.28$ $\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{7,8 \mathrm{~b}}=5.1 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{8 \mathrm{a}, 8 \mathrm{~b}}=11.9 \mathrm{~Hz}, 1 \mathrm{H}, 8 \mathrm{~b}-\mathrm{H}\right), 4.32\left(\mathrm{ddd},{ }^{3} \mathrm{~J}_{1,2}=8.8 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,2-\mathrm{NH}}=9.4 \mathrm{~Hz}\right.$, $\left.{ }^{3} \mathrm{~J}_{2,3}=11.1 \mathrm{~Hz}, 1 \mathrm{H}, 2-\mathrm{H}\right), 4.95\left(\mathrm{ddd},{ }^{3} \mathrm{~J}_{6,7}=3.5 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{7,8 \mathrm{~b}}=5.1 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{7,8 \mathrm{a}}=5.9 \mathrm{~Hz}, 1 \mathrm{H}, 7-\mathrm{H}\right)$, $5.14\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{3,4}=3.3 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=11.1 \mathrm{~Hz}, 1 \mathrm{H}, 3-\mathrm{H}\right), 5.32\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{2,2-\mathrm{NH}}=9.4 \mathrm{~Hz}, 1 \mathrm{H}, 2-\mathrm{NH}\right), 5.46$ $\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{6,7}=3.5 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=7.6 \mathrm{~Hz}, 1 \mathrm{H}, 6-\mathrm{H}\right), 5.52\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{4,5}=0.5 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{3,4}=3.3 \mathrm{~Hz}, 1 \mathrm{H}, 4-\mathrm{H}\right)$, $5.65\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{1,2}=8.8 \mathrm{~Hz}, 1 \mathrm{H}, 1-\mathrm{H}\right),(\alpha$-anomer $) \delta=1.95,2.02,2.02,2.07,2.08,2.18,2.21(7 \mathrm{~s}$, $21 \mathrm{H}, 7 \mathrm{Ac}), 4.05\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{4,5}=1.0 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=6.6 \mathrm{~Hz}, 1 \mathrm{H}, 5-\mathrm{H}\right), 4.14\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{7,8 \mathrm{a}}=6.3 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{8 \mathrm{a}, 8 \mathrm{~b}}\right.$ $=12.0 \mathrm{~Hz}, 1 \mathrm{H}, 8 \mathrm{a}-\mathrm{H}), 4.28\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{7,8 \mathrm{~b}}=5.1 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{8 \mathrm{a}, 8 \mathrm{~b}}=12.0 \mathrm{~Hz}, 1 \mathrm{H}, 8 \mathrm{~b}-\mathrm{H}\right), 4.72\left(\mathrm{ddd},{ }^{3} \mathrm{~J}_{1,2}\right.$ $\left.=3.7 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,2-\mathrm{NH}}=9.2 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=11.6 \mathrm{~Hz}, 1 \mathrm{H}, 2-\mathrm{H}\right), 5.00\left(\mathrm{ddd},{ }^{3} \mathrm{~J}_{6,7}=4.1 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{7,8 \mathrm{~b}}=5.1 \mathrm{~Hz}\right.$, $\left.{ }^{3} \mathrm{~J}_{7,8 \mathrm{a}}=6.3 \mathrm{~Hz}, 1 \mathrm{H}, 7-\mathrm{H}\right), 5.16\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{3,4}=3.3 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=11.6 \mathrm{~Hz}, 1 \mathrm{H}, 3-\mathrm{H}\right), 5.32\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{2,2-\mathrm{NH}}=\right.$ $9.2 \mathrm{~Hz}, 1 \mathrm{H}, 2-\mathrm{NH}), 5.37\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{6,7}=4.1 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=6.6 \mathrm{~Hz}, 1 \mathrm{H}, 6-\mathrm{H}\right), 5.53\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{4,5}=1.0 \mathrm{~Hz}\right.$, $\left.{ }^{3} \mathrm{~J}_{3,4}=3.3 \mathrm{~Hz}, 1 \mathrm{H}, 4-\mathrm{H}\right), 6.19\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{1,2}=3.7 \mathrm{~Hz}, 1 \mathrm{H}, 1-\mathrm{H}\right) ;{ }^{13} \mathrm{C}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}, 25\right.$ $\left.{ }^{\circ} \mathrm{C}\right):(\beta$-anomer $) \delta=20.6,20.6,20.7,20.7,20.8,20.9,23.4$ (7 Ac), 50.2 (2-C), 61.1 (8-C), 66.2 (4-C), 69.2 (7-C), 69.9 (6-C), 70.3 (3-C), 73.3 (5-C), 93.2 (1-C), 169.6, 169.8, 170.1, 170.2, 170.5, 170.6, 170.9 (7 CO-OAc), ( $\alpha$-anomer) $\delta=20.6,20.6,20.7,20.7,20.8,20.9$, 23.2 (7 Ac), 46.9 (2-C), 61.4 (8-C), 67.0 (4-C), 68.1 (3-C), 69.0 (5-C), 69.5 (6-C), 69.6 (7-C), 91.6 (1-C), 169.7, 169.8, 170.9, 170.3, 170.5, 170.52, 170.5 (7 CO-OAc); HRMS (ESI) $\mathrm{m} / \mathrm{z}$ $[\mathrm{M}+\mathrm{Na}]^{+}$calculated 556.1642, found 556.1638.

2-Acetamido-2-deoxy-D-glycero-D-ido-heptose (8a): Peracetylated amino sugar 7a (20 mg, 0.04 mmol ) was deacetylated according to method G in 3 ml of dry MeOH ; yield: 11 mg , $(100 \%) \cdot[\alpha]^{\mathrm{D}}{ }_{20}=-12.8^{\circ}\left(2.5, \mathrm{H}_{2} \mathrm{O}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{D}_{2} \mathrm{O}, 600 \mathrm{MHz}, 25^{\circ} \mathrm{C}\right):(1-\mathrm{H}) \delta=4.92\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{1,2}\right.$
$=8.9 \mathrm{~Hz}), 5.05\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{1,2}=3.0 \mathrm{~Hz}\right), 5.15\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{1,2}=3.8 \mathrm{~Hz}\right), 5.19\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{1,2}=1.9 \mathrm{~Hz}\right), 5.45\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{1,2}\right.$ $=4.9 \mathrm{~Hz}),{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{D}_{2} \mathrm{O}, 150 \mathrm{MHz}, 25^{\circ} \mathrm{C}\right):(1-\mathrm{C}) \delta=91.4,91.8,92.9,93.5,93.6$; HRMS (ESI) $m / z[\mathrm{M}+\mathrm{Na}]^{+}$calculated 274.0903, found 274.0905.

2-Acetamido-2-deoxy-D-threo-L-galacto-octose (8b): Peracetylated amino sugar 7b (44 mg, 0.08 mmol ) was deacetylated according to method G in 4 ml of dry methanol; yield: 23 mg , (mixture of anomers, $\alpha / \beta=1 / 1$ ), $(100 \%) .[\alpha]^{\mathrm{D}}{ }_{20}=-30^{\circ}\left(5.0, \mathrm{H}_{2} \mathrm{O}\right),{ }^{1} \mathrm{H}$ NMR (MeOD, 600 $\left.\mathrm{MHz}, 25^{\circ} \mathrm{C}\right):\left(\beta\right.$-anomer) $\delta=2.00(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NHAc}), 3.52\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{4,5}=1.0 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=9.0 \mathrm{~Hz}, 1 \mathrm{H}\right.$, $5-\mathrm{H}), 3.58\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{3,4}=3.4 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=10.8 \mathrm{~Hz}, 1 \mathrm{H}, 3-\mathrm{H}\right), 3.65(\mathrm{~m}, 2 \mathrm{H}, 8 \mathrm{a}-\mathrm{H}, 8 \mathrm{~b}-\mathrm{H}), 3.88(\mathrm{~m}$, $3 \mathrm{H}, 2-\mathrm{H}, 6-\mathrm{H}, 7-\mathrm{H}), 4.04\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{4,5}=1.0 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{3,4}=3.4 \mathrm{~Hz}, 1 \mathrm{H}, 4-\mathrm{H}\right), 4.55\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{1,2}=8.4 \mathrm{~Hz}\right.$, $1 \mathrm{H}, 1-\mathrm{H}),\left(\alpha\right.$-anomer) $\delta=2.00(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NHAc}) 3.65(\mathrm{~m}, 2 \mathrm{H}, 8 \mathrm{a}-\mathrm{H}, 8 \mathrm{~b}-\mathrm{H}), 3.83\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{3,4}=\right.$ $3.2 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=10.9 \mathrm{~Hz}, 1 \mathrm{H}, 3-\mathrm{H}$ ), 3.83 (ddd, ${ }^{3} \mathrm{~J}_{6,7}=1.6 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{7,8 \mathrm{a}}=6.5 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{7,8 \mathrm{~b}}=6.5 \mathrm{~Hz}, 1$ $\mathrm{H}, 7-\mathrm{H}), 3.85\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{6,7}=1.6 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=9.2 \mathrm{~Hz}, 1 \mathrm{H}, 6-\mathrm{H}\right), 4.03\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{4,5}=1.2 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=9.2\right.$ $\mathrm{Hz}, 1 \mathrm{H}, 5-\mathrm{H}), 4.10\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{4,5}=1.2 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{3,4}=3.2 \mathrm{~Hz}, 1 \mathrm{H}, 4-\mathrm{H}\right), 4.22\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{1,2}=3.7 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}\right.$ $=10.9 \mathrm{~Hz}, 1 \mathrm{H}, 2-\mathrm{H}), 5.14\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{1,2}=3.7 \mathrm{~Hz}, 1 \mathrm{H}, 1-\mathrm{H}\right),{ }^{13} \mathrm{C}$ NMR ( $\mathrm{MeOD}, 150 \mathrm{MHz}, 25^{\circ} \mathrm{C}$ ): ( $\beta$-anomer) $\delta=22.9$ (NHAc), 55.9 (2-C), 64.8 ( $8-\mathrm{C}$ ), 68.7 (4-C), 69.1 (6-C), 71.7 (7-C), 73.6 (3-C), 74.8 ( $5-\mathrm{C}$ ), 97.6 (1-C), 174.7 (CO-NHAc), ( $\alpha$-anomer) $\delta=22.7$ (NHAc), 52.1 (2-C), 64.8 (8-C), 69.5 (6-C), 69.6 (4-C), 69.9 (3-C), 70.0 (5-C), 71.8 (7-C), 93.0 (1-C), 174.0 (CONHAc); HRMS (ESI) $m / z[\mathrm{M}+\mathrm{Na}]^{+}$calculated 304.1008, found 304.1003.

## 2-Acetamido-2-deoxy-D-erythro-L-galacto-octose (8c):

Peracetylated amino sugar $7 \mathbf{c}(51 \mathrm{mg}, 0.10 \mathrm{mmol})$ was deacetylated according to method G in 5 ml of dry methanol; yield: 27 mg , (mixture of anomers, $\alpha / \beta=1 / 1$ ), $(100 \%) .[\alpha]^{\mathrm{D}}{ }_{20}=-31.6^{\circ}$ (7.9, $\left.\mathrm{H}_{2} \mathrm{O}\right) ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{D}_{2} \mathrm{O}, 600 \mathrm{MHz}, 25^{\circ} \mathrm{C}\right):(\beta$-anomer) $\delta=2.06(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NHAc}), 3.67(\mathrm{dd}$, $\left.{ }^{3} \mathrm{~J}_{7,8 \mathrm{a}}=6.7 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{8 \mathrm{a}, 8 \mathrm{~b}}=12.0 \mathrm{~Hz}, 1 \mathrm{H}, 8 \mathrm{a}-\mathrm{H}\right), 3.70\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{4,5}=1.1 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{5,6}=5.3 \mathrm{~Hz}, 1 \mathrm{H}, 5-\mathrm{H}\right)$, $3.72\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{3,4}=3.3 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=10.8 \mathrm{~Hz}, 1 \mathrm{H}, 3-\mathrm{H}\right), 3.78\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{7,8 \mathrm{~b}}=3.5 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{8 \mathrm{a}, 8 \mathrm{~b}}=12.0 \mathrm{~Hz}\right.$,
$1 \mathrm{H}, 8 \mathrm{~b}-\mathrm{H}), 3.83\left(\mathrm{ddd},{ }^{3} \mathrm{~J}_{7,8 \mathrm{~b}}=3.5 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{6,7}=6.1 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{7,8 \mathrm{a}}=6.7 \mathrm{~Hz}, 1 \mathrm{H}, 7-\mathrm{H}\right), 3.92\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{1,2}\right.$ $\left.=8.5 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=10.8 \mathrm{~Hz}, 1 \mathrm{H}, 2-\mathrm{H}\right), 3.96\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{5,6}=5.3 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{6,7}=6.1 \mathrm{~Hz}, 1 \mathrm{H}, 6-\mathrm{H}\right), 4.06$ $\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{4,5}=1.1 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{3,4}=3.3 \mathrm{~Hz}, 1 \mathrm{H}, 4-\mathrm{H}\right), 4.66\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{1,2}=8.5 \mathrm{~Hz}, 1 \mathrm{H}, 1-\mathrm{H}\right),(\alpha$-anomer) $\delta=$ $2.06(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NHAc}) 3.67\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{7,8 \mathrm{a}}=6.5 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{8 \mathrm{a}, 8 \mathrm{~b}}=11.9 \mathrm{~Hz}, 1 \mathrm{H}, 8 \mathrm{a}-\mathrm{H}\right), 3.78\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{7,8 \mathrm{~b}}=\right.$ $\left.3.5 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{8 \mathrm{a}, 8 \mathrm{~b}}=11.9 \mathrm{~Hz}, 1 \mathrm{H}, 8 \mathrm{~b}-\mathrm{H}\right), 3.81\left(\mathrm{ddd},{ }^{3} \mathrm{~J}_{7,8 \mathrm{~b}}=3.5 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{6,7}=6.2 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{7,8 \mathrm{a}}=6.5 \mathrm{~Hz}\right.$, $1 \mathrm{H}, 7-\mathrm{H}), 3.92\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{3,4}=3.2 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=10.9 \mathrm{~Hz}, 1 \mathrm{H}, 3-\mathrm{H}\right), 3.94\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{5,6}=5.0 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{6,7}=\right.$ $6.2 \mathrm{~Hz}, 1 \mathrm{H}, 6-\mathrm{H}), 4.12\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{4,5}=1.3 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{3,4}=3.2 \mathrm{~Hz}, 1 \mathrm{H}, 4-\mathrm{H}\right), 4.14\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{4,5}=1.3 \mathrm{~Hz}\right.$, $\left.{ }^{3} \mathrm{~J}_{5,6}=5.0 \mathrm{~Hz}, 1 \mathrm{H}, 5-\mathrm{H}\right), 4.18\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{1,2}=3.8 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{2,3}=10.9 \mathrm{~Hz}, 1 \mathrm{H}, 2-\mathrm{H}\right), 5.28\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{1,2}=\right.$ $3.8 \mathrm{~Hz}, 1 \mathrm{H}, 1-\mathrm{H}),{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{D}_{2} \mathrm{O}, 150 \mathrm{MHz}, 25^{\circ} \mathrm{C}\right):(\beta$-anomer $) \delta=22.2(\mathrm{NHAc}), 53.5(2-$ C), 61.8 (8-C), 69.4 (4-C), 70.1 (7-C), 71.2 (3-C), 72.4 (6-C), 73.2 (5-C), 95.5 (1-C), 175.0 (CO-NHAc), $(\alpha-$ anomer $) ~ \delta=22.0$ (NHAc), 50.1 (2-C), 62.1 (8-C), 67.5 (3-C), 68.4 (5-C), 70.3 (4-C), 71.0 (7-C), 72.6 (6-C), 91.0 (1-C), 174.7 (CO-NHAc), HRMS (ESI) $m / z[\mathrm{M}+\mathrm{Na}]^{+}$ calculated 304.1008, found 304.1002.

## References

1. Albler, C.; Schmid, W. Eur. J. Org. Chem. 2014, 2451-2459.

Copies of ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra

(2a)



(2b)






(2c)



(3a)



[^0]
(3b)




(4a)



(4b)




(5a)


(5b)





























[^0]:    

