A concise *C*-glycosyl amino acid synthesis by alkenyl *C*-glycoside–vinyloxazolidine cross-metathesis. Synthesis of glycosyl serine, asparagine and hydroxynorvaline isosteres

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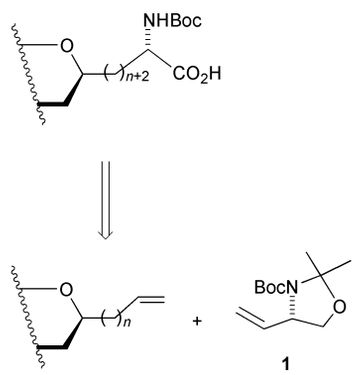
A convergent synthesis has been developed to afford *C*-linked glycosyl amino acids by cross-metathesis of vinyl, allyl, and butenyl *C*-glycosides with *N*-Boc-vinyloxazolidine using the Grubbs 1,3-dimesityl-4,5-dihydroimidazol-2-ylideneruthenium carbene. The method has been employed to introduce through an α-linkage, an α-aminopentanoic acid chain at the anomeric carbon of β-D-*C*-gentiobiose to give a totally artificial glycosyl α-amino acid of a disaccharide. This compound represents the isostere of the α-linked glycosylasparagine moiety of the natural glycopeptide nephritogenoside.

Introduction

The current interest in synthetic methods leading to *C*-glycosyl amino acids, primarily isosteres of *O*-serine, *O*-threonine and *N*-asparagine glycoconjugates, is mainly due to the need of usable quantities of these building blocks in studies of the complex biological machinery involving glycoproteins[1] as well as the development of glycosidase inhibitors and lead compounds for drug design.[2] The stereoselective introduction of amino acid moieties at the anomeric carbon of sugars has been described *via* various carbon–carbon bond-forming processes.[3] Substantial efforts in our laboratory have been recently focused toward the synthesis of *C*-glycosyl serines and asparagines *via* either direct *C*-glycosidation reaction or coupling of functionalized *C*-glycosides (methylenephosphorane, formyl, ethynyl) with amino acid equivalents.[4] Nevertheless further innovations are still required focusing mainly on the search for methods endowed with conciseness and simplicity. Hence, we have been stimulated to develop a convergent synthetic approach to *C*-glycosyl amino acids *via* cross-metathesis (CM) reaction of the *N*-Boc-vinyloxazolidine[5] **1**, a vinylglycine equivalent, with sugar olefins whose double bond was linked to the anomeric carbon of the glycoside moiety through alkyl chains of variable length. We sought the α-amino acid equivalence of **1** on the basis of the racemization-free one-step oxidative cleavage of the *N*-Boc-oxazolidine ring into the glycinyl moiety [$CH(NH_2)$-CO_2H] using the Jones reagent.[6] A single example of the CM-based approach to *C*-glycosyl amino acids has been recently reported using racemic allylglycine and an allyl D-*C*-mannoside derivative.[7] The resulting mixture of *E* and *Z* alkenes containing epimeric glycinyl moieties was not transformed into usable building blocks for glycopeptide synthesis. Hence, we have carried out a wider investigation into this synthetic approach directed toward this main objective and report here the relevant results of our study.

As compared with the metal (Mo, W, Ru) alkylidene-promoted ring-closing metathesis (RCM) of alkenes employed for the synthesis of carbo- and heterocyclic systems,[8] the CM reaction in which two different alkenes are used to form a new acyclic product has so far found much less application. The limited scope of the latter intermolecular process appears to be due to concomitant self-metathesis reactions leading to homocoupling products as main reaction products. The recent advent of tetracoordinated ruthenium carbene complexes reported by Grubbs and co-workers[9] has considerably expanded the scope of all types of alkene metathesis reactions. These pre-catalysts show both high tolerance toward various heteroatoms, particularly oxygen-containing functional groups, and ability to suppress the formation of self-metathesis products. Hence, some examples of selective CM reactions have recently appeared in the literature.[7,10]



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Results and discussion

Heating a mixture of the allyl β-D-*C*-glucopyranoside **3a**, the vinyloxazolidine **1** (2 equiv.) and the 'second generation' Grubbs 1,3-dimesityl-4,5-dihydroimidazol-2-ylideneruthenium carbene[11] **2** (0.2 equiv.) in CCl_4 at 100 °C (screw-capped vial) afforded after 3.5 h the corresponding CM product **4a** as a mixture of *E* and *Z* isomers in 50% isolated yield by column chromatography (Scheme 1). A substantial amount of unchanged **3a** (*ca.* 30%) was also isolated whereas the mixture of homodimers did not exceed 10%. On the other hand the homodimers were the only products obtained by the use of the 'standard' Grubbs ruthenium carbene complex [$RuCl_2$-(=CHPh)$(PCy_3)_2$]. Comparable yields of CM products **4b**–**e** and unchanged sugar alkenes were obtained in reactions of **1** with the allyl *C*-pyranosides **3b** and **3c** as well as the *C*-butenyl derivatives **3d** and **3e** whereas the yield of **4f** from the reaction with the vinyl β-D-*C*-glucopyranoside **3f** was much lower (Table

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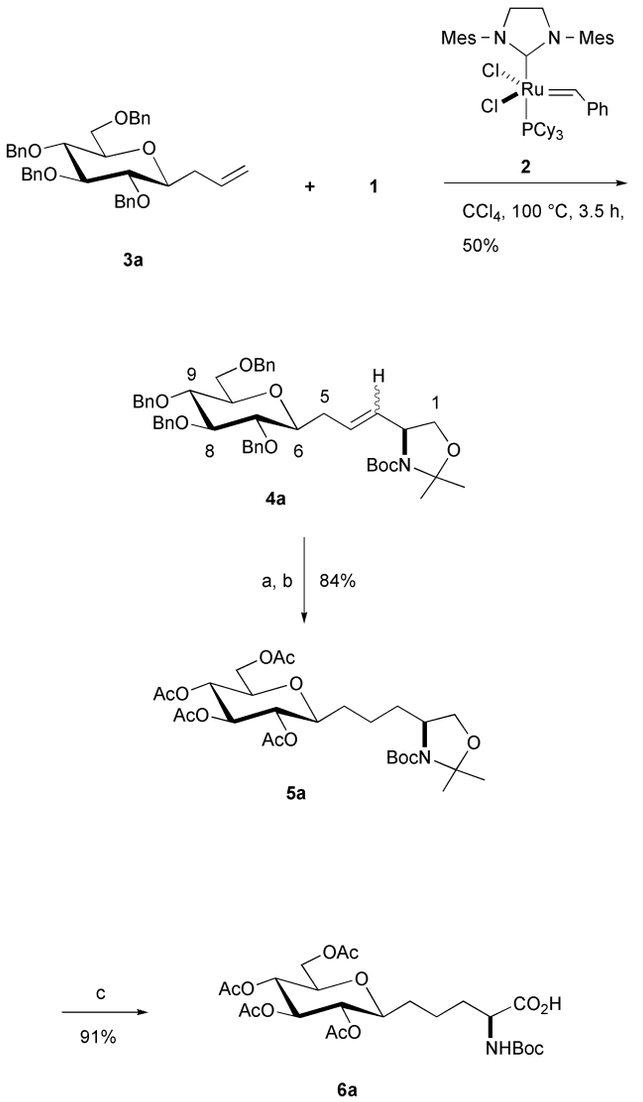


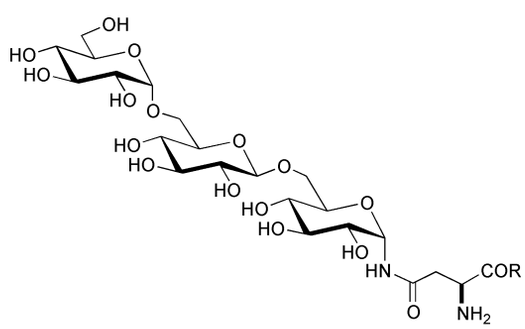
Scheme 1 *Reagents and conditions*: a) H_2, $Pd(OH)_2$, *t*-BuOH–THF, 1 bar, rt, 3 h; b) Ac_2O, pyridine, rt, 3 h; c) 1 M Jones, acetone, 0 °C to rt, 3.5 h.

1). Very likely the well known instability[12] of vinyl *C*-glycosides constitutes a serious limitation on the use of these compounds as partners in CM reactions. However in order to elaborate upon this methodology, all alkenes **4a**–**f** were transformed into the corresponding peracetylated *N*-Boc-oxazolidine derivatives **5a**–**f** by hydrogenation over $Pd(OH)_2$ and acetylation. Finally, oxidative cleavage of the oxazolidine ring by the Jones reagent afforded the α-amino acids **6a**–**f**. Based on precedent examples of the latter transformation in our[6] and others' laboratory,[13] the same configuration for the resulting glycinyl moiety as that for the precursor *N*-Boc-oxazolidine ring was assigned. All compounds **6a**–**f** were adequately characterized through their corresponding methyl ester. It has to be noted that compounds **6a**–**c** are ethylene isosteres of *N*-glycosylasparagines and **6f** is the methylene isostere of *O*-glycosylserine. Of the two α-aminohexanoic acids **6d** and **6e**, the latter compound has recently attracted some attention in immunological studies as the *C*-linked isostere of β-D-galactosyl hydroxynorvaline.[14] All compounds **5a**–**f** with *O*-acetyl[15] and *N*-Boc[16] protecting groups appear to be orthogonally protected building blocks suitable for glycopeptide synthesis.

As an expanded scope of the methodology we considered the introduction of the *C*-tethered α-amino acid group in a more complex carbohydrate moiety such as a *C*-disaccharide to give a totally artificial *C*-glycoconjugate. For this endeavour we started from the sugar alkene **7** (Scheme 2) which was available in our laboratory by Wittig-type coupling of perbenzylated formyl *C*-glucopyranoside with glucose 6-phosphorane.[17] Treatment of **7** with the *in situ* generated diimide from *p*-tolylsulfonyl hydrazine and sodium acetate[17] allowed the reduction of the double bond without removal of the *O*-benzyl groups. The resulting perbenzylated *O*-methyl β-D-*C*-gentiobioside **8** was then transformed by hydrolysis and acetylation into the acetate **9** and this product was glycosidated with allyltrimethylsilane to give the corresponding α-linked *C*-allyl derivative **10**. The cross-metathesis of **10** with **1** under the activation of the Grubbs ruthenium carbene **2** gave the alkene **11** as an *E*,*Z* mixture in 40% isolated yield. Also this mixture of alkenes was suitably elaborated as described for the CM products in Table 1 to give the oxazolidine derivative **12** and then the glycosyl α-amino acid **13** in 67% overall yield. This compound represents, to our knowledge, the first example of a *C*-glycosyl α-amino acid of a *C*-disaccharide.

Quite interestingly compound **13** appears to be the isostere of the major fragment of the asparagine-linked core trisaccharide **14** of the natural glycopeptide nephritogenoside **15**. The name of this compound stems from its activity to induce a progressive chronic glomerulonephritis in animals.[18] The glycopeptide **15** is uniquely distinct from common glycoproteins as it contains an α-D-glucopyranose as the glycan linker to the amide group of L-asparagine.[19] Hence compound **13** can be used as a probe in recognition-specificity studies regarding the biological activity of **15**.

In conclusion, the methodology *via* olefin CM reaction described above appears to be a viable route to various *C*-glycosyl amino acids with a great degree of structural diversity. The products of this synthetic approach can be transformed into suitable building blocks for the synthesis of modified glycopeptides possessing enhanced stability and eventually different biological activity with respect to the natural analogues.



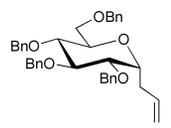
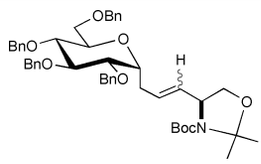
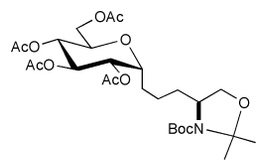
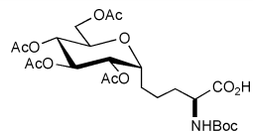
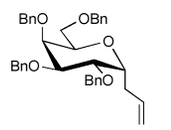
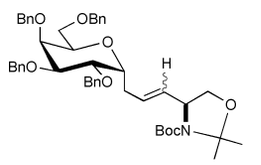
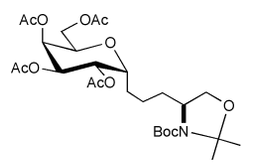
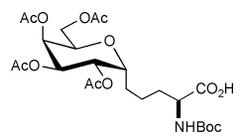
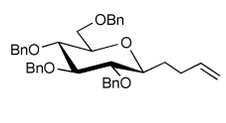
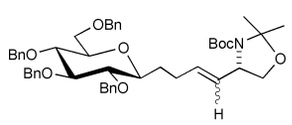
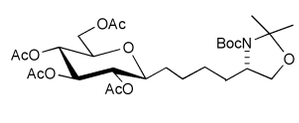
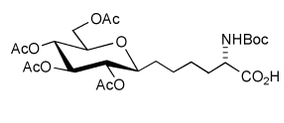
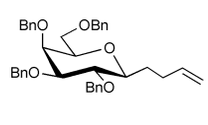
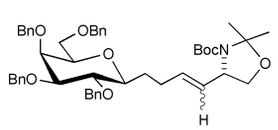
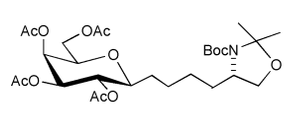
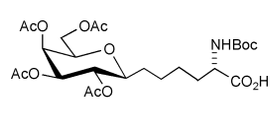
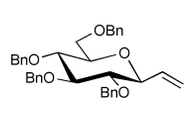
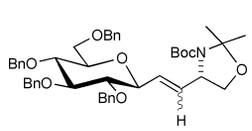
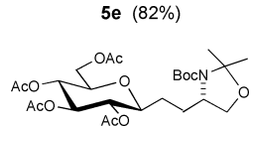
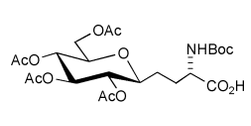
14 R = OH

15 R = peptide (nephrotogenoside)

Experimental

All moisture-sensitive reactions were performed under a nitrogen atmosphere using oven-dried glassware. Anhydrous solvents were dried over standard drying agents[20] and freshly distilled prior to use. Commercially available powdered 4 Å molecular sieves (5 μm average particle size) were used without further activation. Reactions were monitored by TLC on silica gel 60 F_{254} with detection by charring with sulfuric acid. Flash column chromatography[21] was performed on silica gel 60 (230–400 mesh). Melting points were determined with a capillary apparatus and are uncorrected. Optical rotations were measured at 20 ± 2 °C in the stated solvent; $[\alpha]_D$-values are given in 10^{-1} deg cm^2 g^{-1}. ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded at room temperature unless otherwise specified; chemical shifts are in ppm (δ) from $SiMe_4$ (TMS) as internal standard; *J*-values are given in Hz; assignments were aided by homo- and heteronuclear two-dimensional experiments. MALDI-TOF mass spectra were acquired using

Table 1 Other *C*-glycosyl amino acids prepared by cross-metathesis reactions of sugar alkenes and the vinyloxazolidine **1**[a]

Sugar alkene	CM-Product	Oxazolidine	Amino acid
 **3b**	 **4b** (51%)	 **5b** (81%)	 **6b** (92%)
 **3c**	 **4c** (47%)	 **5c** (82%)	 **6c** (90%)
 **3d**	 **4d** (42%)	 **5d** (81%)	 **6d** (94%)
 **3e**	 **4e** (41%)	 **5e** (82%)	 **6e** (94%)
 **3f**	 **4f** (16%)	 **5f** (74%)	 **6f** (91%)

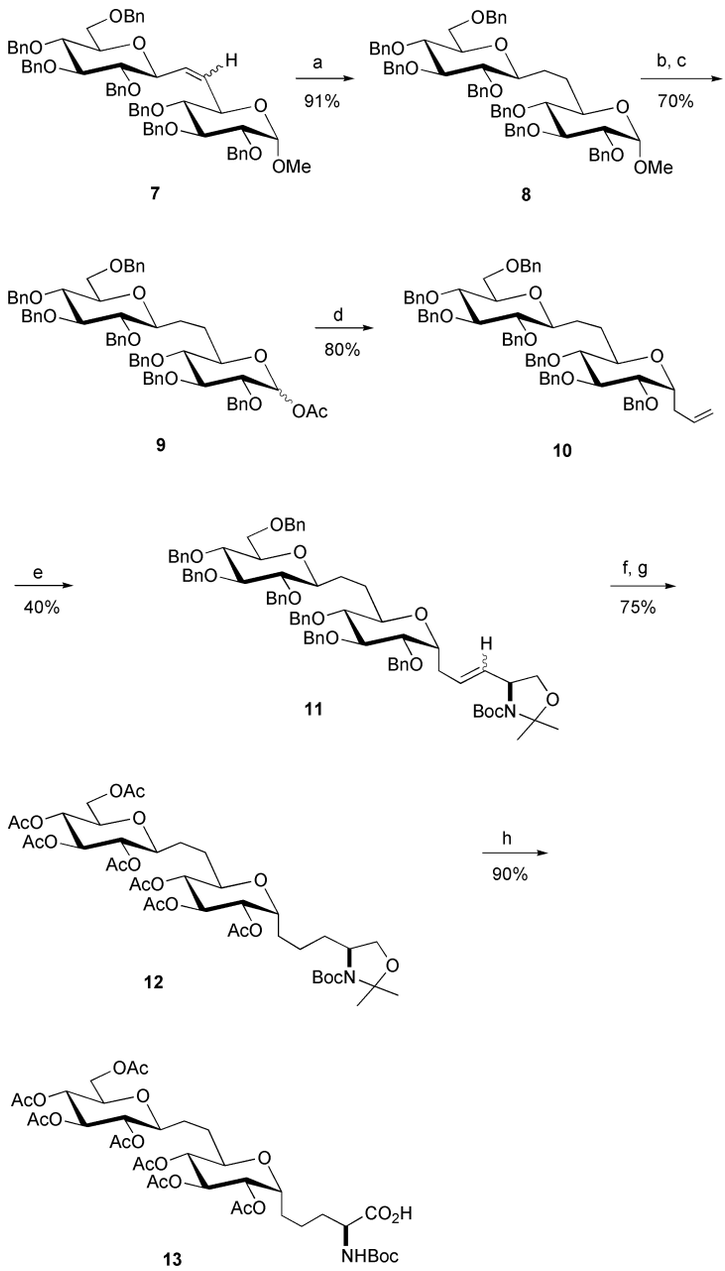
[a] For the catalyst and reaction conditions, see Scheme 1. Yields in parentheses refer to isolated products.

α-cyano-4-hydroxycinnamic acid as the matrix. The allyl β-*C*-glucoside **3a**, α-*C*-glucoside **3b** and α-*C*-galactoside **3c** were prepared as described.[22] The butenyl β-*C*-glucoside **3d**, prepared as reported,[23] had mp 87–88 °C (from MeOH); $[\alpha]_D$ 0.0 (*c* 1.4 in $CHCl_3$) {lit.,[23] mp 83–84 °C (from Et_2O); $[\alpha]_D$ +3 (*c* 1.2 in $CHCl_3$); lit.,[24] mp 84–85 °C (from light petroleum); $[\alpha]_D$ −1.7}. The butenyl β-*C*-galactoside **3e**, prepared as described,[25] had $[\alpha]_D$ −3.0 (*c* 1.0 in $CHCl_3$) {lit.[25] $[\alpha]_D$ not reported}. The preparation of the vinyl *C*-glucoside **3f** was previously described by Kraus and Molina[26] but the physical data of this compound were not reported. Hence, our synthesis and the full characterization of **3f** are described below. The Grubbs catalyst, tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene][benzylidene]ruthenium(IV) dichloride, was purchased from Strem Chemicals, Inc., Bischheim, France.

3,7-Anhydro-4,5,6,8-tetra-*O*-benzyl-1,2-dideoxy-D-*glycero*-D-*gulo*-oct-1-enitol 3f

To a cooled (−70 °C), stirred solution of 2,3,4,6-tetra-*O*-benzyl-D-gluconolactone (1.61 g, 3.0 mmol) in anhydrous Et_2O (30 cm^3) was added commercially available vinylmagnesium bromide (4.5 cm^3, 4.5 mmol; a 1.0 M solution in THF) over a 20 min period. The reaction mixture was allowed to warm to −55 °C in 1.5 h, then was diluted with 1 M phosphate buffer at pH 7 (60 cm^3) and extracted with Et_2O (2 × 100 cm^3). The combined organic phases were dried (Na_2SO_4) and concentrated. The residue was eluted from a column of silica gel with cyclohexane–AcOEt (from 5 : 1 to 4 : 1) to give 2,3,4,6-tetra-*O*-benzyl-1-*C*-vinyl-D-glucopyranose (1.00 g, 59%) as a syrup.

To a cooled (−40 °C), stirred solution of the hemiketal and triethylsilane (1.40 cm^3, 8.8 mmol) in anhydrous acetonitrile (17 cm^3) was slowly added freshly distilled boron trifluoride–diethyl ether (0.22 cm^3, 1.76 mmol). The solution was stirred for 2 h at −40 °C, then diluted with triethylamine (0.5 cm^3), warmed to room temperature, and concentrated. The residue was eluted from a column of silica gel with 10 : 1 cyclohexane–AcOEt (containing 0.3% of triethylamine) to give **3f** (0.53 g, 55%) as a white solid; mp 68–69 °C (from pentane); $[\alpha]_D$ +28.0 (*c* 0.2 in $CHCl_3$) (Found: C, 78.70; H, 7.03. Calc. for $C_{36}H_{38}O_5$: C, 78.52; H, 6.96%); ^{1}H NMR ($CDCl_3$) δ 7.40–7.17 (m, 20 H, 4 × Ph), 6.00 (ddd, 1 H, $J_{1a,2}$ 17.0, $J_{1b,2}$ 10.6, $J_{2,3}$ 6.5, H-2), 5.49 (ddd, 1 H, $J_{1a,1b}$ 1.6, $J_{1a,3}$ 1.2, H-1a), 5.32 (ddd, 1 H, $J_{1b,3}$ 0.8, H-1b), 4.95 and 4.90 (2 d, 2 H, *J* 11.2, PhCH_2), 4.85 and 4.59 (2 d, 2 H, *J* 10.8, PhCH_2), 4.78 and 4.68 (2 d, 2 H, *J* 10.8, PhCH_2), 4.66 and 4.58 (2 d, 2 H, *J* 11.2, PhCH_2), 3.80 (dddd, 1 H, $J_{3,4}$ 9.6, H-3), 3.76–3.64 (m, 4 H, H-5, H-6, 2 × H-8), 3.50 (ddd, 1 H, $J_{6,7}$ 9.2, $J_{7,8a} = J_{7,8b} = 3.2$, H-7), 3.36 (dd, 1 H, $J_{4,5}$ 8.5, H-4); MALDI-TOF MS (550.7) *m*/*z*, 573.6 (M + Na), 589.9 (M + K).



Scheme 2 *Reagents and conditions*: a) $TsNHNH_2$, AcONa, DME–water, 85 °C, 4 h; b) 10 : 1 AcOH–1 M H_2SO_4, 100 °C, 75 min; c) Ac_2O, pyridine, rt; d) $AllSiMe_3$, TMSOTf, CH_2Cl_2, rt, 1 h; e) **1** (2 equiv.), **2** (0.2 equiv.), CCl_4, 100 °C, 3.5 h; f) H_2, $Pd(OH)_2$, *t*-BuOH–THF, 1 bar, rt; g) Ac_2O, pyridine, rt; h) 1 M Jones, acetone, 0 °C to rt, 3.5 h.

6,10-Anhydro-7,8,9,11-tetra-*O*-benzyl-2,3,4,5-tetradeoxy-1-*O*,2-*N*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*erythro*-L-*galacto*-undec-3-enitol 4a

A solution of the allyl β-*C*-glucopyranoside **3a** (282 mg, 0.50 mmol), the vinyloxazolidine **1** (227 mg, 1.00 mmol), and the Grubbs catalyst **2** (85 mg, 0.10 mmol) in anhydrous CCl_4 (10 cm^3) was stirred in a screw-capped vial at 100 °C (oil-bath temperature) for 3.5 h, then cooled to room temperature and concentrated. The residue was eluted from a column of silica gel with cyclohexane–AcOEt (from 9 : 1 to 5 : 1) to give, first, unchanged **3a** (84 mg, 30% recovery). Eluted second was the dimer of **3a** slightly contaminated by uncharacterized by-products (27 mg, *ca.* 10%); MALDI-TOF MS (1101.5) *m*/*z*, 1124.4 (M + Na), 1140.9 (M + K). Eluted third was **4a** (191 mg, 50%) as a *ca.* 5 : 1 *E* : *Z* mixture (Found: C, 74.08; H, 7.66; N, 2.01. Calc. for $C_{47}H_{57}NO_8$: C, 73.89; H, 7.52; N, 1.83%); ^{1}H NMR (DMSO-d_6; 140 °C) selected data of the *E* isomer: δ 5.69 (ddd, 1 H, $J_{3,4}$ 15.6, $J_{4,5a} = J_{4,5b}$ = 6.7, H-4), 5.51 (dd, 1 H, $J_{2,3}$ 6.8, H-3), 4.83 (s, 2 H, PhCH_2), 4.80 and 4.66 (2 d, 2 H, *J* 11.6, PhCH_2), 4.75 and 4.62 (2 d, 2 H, *J* 11.5, PhCH_2), 4.57 and 4.52 (2 d, 2 H, *J* 12.2, PhCH_2), 4.27 (ddd, 1 H, $J_{1a,2}$ 6.3, $J_{1b,2}$ 2.5, H-2), 3.98 (dd, 1 H, $J_{1a,1b}$ 8.8, H-1a); MALDI-TOF MS (764.0) *m*/*z*, 787.1 (M + Na), 803.2 (M + K).

6,10-Anhydro-7,8,9,11-tetra-*O*-benzyl-2,3,4,5-tetradeoxy-1-*O*,2-*N*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*erythro*-L-*gulo*-undec-3-enitol 4b

Cross-metathesis of the allyl α-*C*-glucopyranoside **3b** (226 mg, 0.40 mmol) with the vinyloxazolidine **1** (182 mg, 0.80 mmol) as described for the preparation of **4a** afforded, after column chromatography with cyclohexane–AcOEt (from 8 : 1 to 5 : 1), **4b** (156 mg, 51%) as a *ca.* 5 : 1 *E* : *Z* mixture (Found: C, 73.78; H, 7.76; N, 1.94. Calc. for $C_{47}H_{57}NO_8$: C, 73.89; H, 7.52; N, 1.83%); ^{1}H NMR (DMSO-d_6; 160 °C) selected data of the *E* isomer: δ 5.65 (ddd, 1 H, $J_{3,4}$ 15.6, $J_{4,5a} = J_{4,5b}$ = 6.3 Hz, H-4), 5.56 (dd, 1 H, $J_{2,3}$ 5.9, H-3), 4.27 (ddd, 1 H, $J_{1a,2}$ 6.4, $J_{1b,2}$ 3.0, H-2), 4.03 (ddd, 1 H, $J_{5a,6}$ 9.1, $J_{5b,6} = J_{6,7}$ = 5.0, H-6), 3.98 (dd, 1 H, $J_{1a,1b}$ 8.8, H-1a); MALDI-TOF MS (764.0): *m*/*z*, 787.3 (M + Na), 803.1 (M + K).

6,10-Anhydro-7,8,9,11-tetra-*O*-benzyl-2,3,4,5-tetradeoxy-1-*O*,2-*N*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*threo*-L-*gulo*-undec-3-enitol 4c

Cross-metathesis of the allyl α-*C*-galactopyranoside **3c** (226 mg, 0.40 mmol) with the vinyloxazolidine **1** (182 mg, 0.80 mmol) as described for the preparation of **4a** afforded, after column chromatography with cyclohexane–AcOEt (from 8 : 1 to 5 : 1), **4c** (144 mg, 47%) as a *ca.* 5 : 1 *E* : *Z* mixture (Found: C, 73.67; H, 7.62; N, 1.98. Calc. for $C_{47}H_{57}NO_8$: C, 73.89; H, 7.52; N, 1.83%); ^{1}H NMR ($CDCl_3$) selected data: δ 5.62–5.40 (m, 2 H, H-3, H-4), 2.48–2.30 (m, 2 H, 2 × H-5); MALDI-TOF MS (764.0): *m*/*z*, 787.6 (M + Na), 803.6 (M + K).

7,11-Anhydro-8,9,10,12-tetra-*O*-benzyl-2,3,4,5,6-pentadeoxy-1-*O*,2-*N*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*erythro*-L-*galacto*-dodec-3-enitol 4d

Cross-metathesis of the butenyl β-*C*-glucopyranoside **3d** (289 mg, 0.50 mmol) with the vinyloxazolidine **1** (227 mg, 1.00 mmol) as described for the preparation of **4a** afforded, after column chromatography with cyclohexane–AcOEt (from 9 : 1 to 6 : 1), **4d** (163 mg, 42%) as a *ca.* 5 : 1 *E* : *Z* mixture (Found: C, 74.38; H, 7.69; N, 1.68. Calc. for $C_{48}H_{59}NO_8$: C, 74.10; H, 7.64; N, 1.80%); ^{1}H NMR (DMSO-d_6; 120 °C) selected data of the *E* isomer: δ 5.60 (ddd, 1 H, $J_{3,4}$ 15.5, $J_{4,5a} = J_{4,5b} = 6.5$, H-4), 5.40 (dd, 1 H, $J_{2,3}$ 7.0, H-3), 4.83 (s, 2 H, PhCH_2), 4.80 and 4.61 (2 d, 2 H, *J* 11.2, PhCH_2), 4.76 and 4.64 (2 d, 2 H, *J* 11.6, PhCH_2), 4.57 and 4.53 (2 d, 2 H, *J* 12.0, PhCH_2), 4.25 (ddd, 1 H, $J_{1a,2}$ 6.3, $J_{1b,2}$ 2.6, H-2), 3.99 (dd, 1 H, $J_{1a,1b}$ 8.8, H-1a); MALDI-TOF MS (778.0): *m*/*z*, 800.8 (M + Na), 817.0 (M + K).

7,11-Anhydro-8,9,10,12-tetra-*O*-benzyl-2,3,4,5,6-pentadeoxy-1-*O*,2-*N*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*threo*-L-*galacto*-dodec-3-enitol 4e

Cross-metathesis of the butenyl β-*C*-galactopyranoside **3e** (174 mg, 0.30 mmol) with the vinyloxazolidine **1** (136 mg, 0.60 mmol) as described for the preparation of **4a** afforded, after column chromatography with cyclohexane–AcOEt (from 10 : 1 to 6 : 1), **4e** (96 mg, 41%) as a *ca.* 5 : 1 *E* : *Z* mixture (Found: C, 74.34; H, 7.75; N, 1.67. Calc. for $C_{48}H_{59}NO_8$: C, 74.10; H, 7.64; N, 1.80%); ^{1}H NMR (DMSO-d_6; 120 °C) selected data of the *E* isomer: δ 5.58 (ddd, 1 H, $J_{3,4}$ 15.8, $J_{4,5a} = J_{4,5b} = 6.5$, H-4), 5.40 (dd, 1 H, $J_{2,3}$ 7.0, H-3), 4.84 and 4.62 (2 d, 2 H, *J* 11.4, PhCH_2), 4.84 and 4.56 (2 d, 2 H, *J* 11.6, PhCH_2), 4.79 and 4.67 (2 d, 2 H, *J* 12.0, PhCH_2), 4.54 and 4.48 (2 d, 2 H, *J* 12.2, PhCH_2), 4.23 (ddd, 1 H, $J_{1a,2}$ 6.4, $J_{1b,2}$ 2.5, H-2), 4.04 (dd, 1 H, $J_{9,10}$ 2.6, $J_{10,11}$ 0.5, H-10), 3.98 (dd, 1 H, $J_{1a,1b} = 8.9$, H-1a), 3.23 (ddd, 1 H, $J_{6a,7}$ 3.0, $J_{6b,7} = J_{7,8} = 9.0$, H-7); MALDI-TOF MS (778.0): *m*/*z*, 801.4 (M + Na), 817.2 (M + K).

5,9-Anhydro-6,7,8,10-tetra-*O*-benzyl-2,3,4-trideoxy-1-*O*,2-*N*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*erythro*-L-*galacto*-dec-3-enitol 4f

Cross-metathesis of the vinyl β-*C*-glucopyranoside **3f** (275 mg, 0.50 mmol) with the vinyloxazolidine **1** (227 mg, 1.00 mmol) as described for the preparation of **4a** afforded, after column chromatography with cyclohexane–AcOEt (from 9 : 1 to 6 : 1), **4f** (60 mg, 16%) as a *ca.* 5 : 1 *E* : *Z* mixture (Found: C, 73.40; H, 7.53; N, 1.70. Calc. for $C_{46}H_{55}NO_8$: C, 73.67; H, 7.39; N, 1.87%); ^{1}H NMR ($CDCl_3$) selected data: δ 5.70–5.42 (m, 2 H, H-3, H-4); MALDI-TOF MS (749.9): *m*/*z*, 772.9 (M + Na), 789.4 (M + K).

7,8,9,11-Tetra-*O*-acetyl-6,10-anhydro-2,3,4,5-tetradeoxy-1-*O*,2-*N*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*erythro*-L-*galacto*-undecitol 5a

A vigorously stirred mixture of **4a** (153 mg, 0.20 mmol), 20% palladium hydroxide on carbon (75 mg), and 1 : 1 *t*-BuOH–THF (10 cm^3) was degassed under vacuum and saturated with hydrogen (by an H_2-filled balloon) three times. The suspension was stirred at room temperature for 3 h under a slightly positive pressure of hydrogen (balloon), then filtered through a plug of cotton and concentrated. A solution of the residue in pyridine (3 cm^3) and acetic anhydride (3 cm^3) was kept at room temperature for 3 h, then concentrated. The residue was eluted from a column of silica gel with 2 : 1 cyclohexane–AcOEt to give **5a** (96 mg, 84%) as a syrup; $[\alpha]_D$ +3.4 (*c* 1.2 in $CHCl_3$) (Found: C, 56.40; H, 7.61; N, 2.28. Calc. for $C_{27}H_{43}NO_{12}$: C, 56.53; H, 7.56; N, 2.44%); ^{1}H NMR ($CDCl_3$): δ 5.18 (dd, 1 H, $J_{7,8}$ 9.4, $J_{8,9}$ 9.3, H-8), 5.07 (dd, 1 H, $J_{9,10}$ 10.0, H-9), 4.89 (dd, 1 H, $J_{6,7}$ 9.3, H-7), 4.26 (dd, 1 H, $J_{10,11a}$ 4.9, $J_{11a,11b}$ 12.2, H-11a), 4.09 (dd, 1 H, $J_{10,11b}$ 2.2, H-11b), 3.94 (dd, 1 H, $J_{1a,2}$ 6.4, $J_{1a,1b}$ 8.6, H-1a), 3.90–3.72 (m, 2 H, H-1b, H-2), 3.63 (ddd, 1 H, H-10), 3.45–3.35 (m, 1 H, H-6), 2.11, 2.07, 2.04, and 2.02 (4 s, 12 H, 4 × Ac), 1.83–1.28 (m, 6 H, 2 × H-3, 2 × H-4, 2 × H-5), 1.58 and 1.52 (2 s, 6 H, 2 × CH_3), 1.51 (s, 9 H, *t*-Bu); MALDI-TOF MS (573.6): *m*/*z*, 596.8 (M + Na), 612.9 (M + K).

7,8,9,11-Tetra-*O*-acetyl-6,10-anhydro-2,3,4,5-tetradeoxy-1-*O*,2-*N*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*erythro*-L-*gulo*-undecitol 5b

Hydrogenation and acetylation of **4b** (153 mg, 0.20 mmol) as described for the preparation of **5a** afforded, after column chromatography with 1.5 : 1 cyclohexane–AcOEt, **5b** (93 mg, 81%) as a syrup; $[\alpha]_D$ +62.6 (*c* 1.0 in $CHCl_3$) (Found: C, 56.31; H, 7.70; N, 2.41. Calc. for $C_{27}H_{43}NO_{12}$: C, 56.53; H, 7.56; N, 2.44%); ^{1}H NMR (DMSO-d_6; 140 °C): δ 5.22 (dd, 1 H, $J_{7,8}$ 8.6, $J_{8,9}$ 8.2, H-8), 4.94 (dd, 1 H, $J_{6,7}$ 5.4, H-7), 4.86 (dd, 1 H, $J_{9,10}$ 8.7, H-9), 4.18 (dd, 1 H, $J_{10,11a}$ 5.8, $J_{11a,11b}$ 12.0, H-11a), 4.09 (dd, 1 H, $J_{10,11b}$ 3.3, H-11b), 4.11–4.05 (m, 1 H, H-6), 3.95 (dd, 1 H, $J_{1a,2}$ 6.0, $J_{1a,1b}$ 8.7, H-1a), 3.92 (ddd, 1 H, H-10), 3.82 (dddd, 1 H, $J_{1b,2}$ 2.0, $J_{2,3a}$ 3.8, $J_{2,3b}$ 8.2, H-2), 3.69 (dd, 1 H, H-1b), 2.03, 2.02, 2.01, and 1.99 (4 s, 12 H, 4 × Ac), 1.86–1.24 (m, 6 H, 2 × H-3, 2 × H-4, 2 × H-5), 1.52 and 1.46 (2 s, 6 H, 2 × CH_3), 1.47 (s, 9 H, *t*-Bu); MALDI-TOF MS (573.6): *m*/*z*, 596.6 (M + Na), 612.8 (M + K).

7,8,9,11-Tetra-*O*-acetyl-6,10-anhydro-2,3,4,5-tetradeoxy-1-*O*,2-*N*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*threo*-L-*gulo*-undecitol 5c

Hydrogenation and acetylation of **4c** (153 mg, 0.20 mmol) as described for the preparation of **5a** afforded, after column chromatography with 1.5 : 1 cyclohexane–AcOEt, **5c** (94 mg, 82%) as a syrup; $[\alpha]_D$ +70.2 (*c* 1.2 in $CHCl_3$) (Found: C, 56.46; H, 7.65; N, 2.31. Calc. for $C_{27}H_{43}NO_{12}$: C, 56.53; H, 7.56; N, 2.44%); ^{1}H NMR ($CDCl_3$): δ 5.42 (dd, 1 H, $J_{8,9}$ 3.0, $J_{9,10}$ 2.3, H-9), 5.29 (dd, 1 H, $J_{6,7}$ 5.1, $J_{7,8}$ 9.6, H-7), 5.20 (dd, 1 H, H-8), 4.26–4.15 (m, 2 H, H-6, H-11a), 4.10 (dd, 1 H, $J_{10,11b}$ 5.2, $J_{11a,11b}$ 11.4, H-11b), 4.02 (ddd, 1 H, $J_{10,11a}$ 7.0, H-10), 3.94 (dd, 1 H, $J_{1a,2}$ 6.0, $J_{1a,1b}$ 8.3, H-1a), 3.93–3.86 (m, 1 H, H-2), 3.74 (d, 1 H, H-1b), 2.14, 2.09, 2.07, and 2.04 (4 s, 12 H, 4 × Ac), 1.85–1.46 (m, 6 H, 2 × H-3, 2 × H-4, 2 × H-5), 1.49 and 1.44 (2 s, 6 H, 2 × CH_3), 1.49 (s, 9 H, *t*-Bu); MALDI-TOF MS (573.6): *m*/*z*, 597.3 (M + Na), 613.4 (M + K).

8,9,10,12-Tetra-*O*-acetyl-7,11-anhydro-2,3,4,5,6-pentadeoxy-1-*O*,2-*N*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*erythro*-L-*galacto*-dodecitol 5d

Hydrogenation and acetylation of **4d** (156 mg, 0.20 mmol) as described for the preparation of **5a** afforded, after column chromatography with 1.5 : 1 cyclohexane–AcOEt, **5d** (95 mg, 81%) as a syrup; $[\alpha]_D$ +5.0 (*c* 0.5 in $CHCl_3$) (Found: C, 57.40; H, 7.79; N, 2.25. Calc. for $C_{28}H_{45}NO_{12}$: C, 57.23; H, 7.72; N, 2.38%); ^{1}H NMR (DMSO-d_6; 160 °C): δ 5.16 (dd, 1 H, $J_{8,9}$ 9.2, $J_{9,10}$ 9.4, H-9), 4.88 (dd, 1 H, $J_{10,11}$ 9.6, H-10), 4.74 (dd, 1 H, $J_{7,8}$ 9.6, H-8), 4.14 (dd, 1 H, $J_{11,12a}$ 5.0, $J_{12a,12b}$ 12.0, H-12a), 4.09 (dd, 1 H, $J_{11,12b}$ 3.2, H-12b), 3.94 (dd, 1 H, $J_{1a,2}$ 6.0, $J_{1a,1b}$ 8.6, H-1a),

3.82–3.77 (m, 1 H, H-2), 3.81 (ddd, 1 H, H-11), 3.68 (dd, 1 H, $J_{1b,2}$ 2.3 Hz, H-1b), 3.62–3.54 (m, 1 H, H-7), 2.01, 2.00, 1.99, and 1.94 (4 s, 12 H, 4 × Ac), 1.72–1.25 (m, 8 H, 2 × H-3, 2 × H-4, 2 × H-5, 2 × H-6), 1.51 and 1.45 (2 s, 6 H, 2 × CH_3), 1.47 (s, 9 H, *t*-Bu); MALDI-TOF MS (587.7): *m*/*z*, 611.2 (M + Na), 627.3 (M + K).

8,9,10,12-Tetra-*O*-acetyl-7,11-anhydro-2,3,4,5,6-pentadeoxy-1-*O*,2-*N*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*threo*-L-*galacto*-dodecitol 5e

Hydrogenation and acetylation of **4e** (117 mg, 0.15 mmol) as described for the preparation of **5a** afforded, after column chromatography with 2 : 1 cyclohexane–AcOEt, **5e** (72 mg, 82%) as a syrup; $[\alpha]_D$ +12.5 (*c* 1.0 in $CHCl_3$) (Found: C, 57.01; H, 7.86; N, 2.28. Calc. for $C_{28}H_{45}NO_{12}$: C, 57.23; H, 7.72; N, 2.38%); ^{1}H NMR (DMSO-d_6; 120 °C): δ 5.33 (dd, 1 H, $J_{9,10}$ 3.5, $J_{10,11}$ 0.5, H-10), 5.11 (dd, 1 H, $J_{8,9}$ 9.9, H-9), 4.92 (dd, 1 H, $J_{7,8}$ 9.6, H-8), 4.08–4.00 (m, 3 H, H-11, 2 × H-12), 3.92 (dd, 1 H, $J_{1a,2}$ 6.0, $J_{1a,1b}$ 8.6, H-1a), 3.82–3.74 (m, 1 H, H-2), 3.68 (dd, 1 H, $J_{1b,2}$ 2.1, H-1b), 3.59–3.52 (m, 1 H, H-7), 2.10, 2.02, 1.98, and 1.93 (4 s, 12 H, 4 × Ac), 1.70–1.22 (m, 8 H, 2 × H-3, 2 × H-4, 2 × H-5, 2 × H-6), 1.51 and 1.45 (2 s, 6 H, 2 × CH_3), 1.49 (s, 9 H, *t*-Bu); MALDI-TOF MS (587.7): *m*/*z*, 610.9 (M + Na), 627.0 (M + K).

6,7,8,10-Tetra-*O*-acetyl-5,9-anhydro-2,3,4-trideoxy-1-*O*,2-*N*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*erythro*-L-*galacto*-decitol 5f

Hydrogenation and acetylation of **4f** (75 mg, 0.10 mmol) as described for the preparation of **5a** afforded, after column chromatography with 1.5 : 1 cyclohexane–AcOEt, **5f** (42 mg, 74%) as a syrup; $[\alpha]_D$ +8.1 (*c* 0.6 in $CHCl_3$) (Found: C, 55.73; H, 7.47; N, 2.17. Calc. for $C_{26}H_{41}NO_{12}$: C, 55.80; H, 7.38; N, 2.50%); ^{1}H NMR (DMSO-d_6; 120 °C): δ 5.17 (dd, 1 H, $J_{6,7}$ 9.4, $J_{7,8}$ 9.2, H-7), 4.88 (dd, 1 H, $J_{8,9}$ 10.0, H-8), 4.72 (dd, 1 H, $J_{5,6}$ 9.6, H-6), 4.13 (dd, 1 H, $J_{9,10a}$ 5.6, $J_{10a,10b}$ 12.0, H-10a), 4.07 (dd, 1 H, $J_{9,10b}$ 2.8, H-10b), 3.91 (dd, 1 H, $J_{1a,2}$ 6.5, $J_{1a,1b}$ 8.7, H-1a), 3.86–3.78 (m, 2 H, H-2, H-9), 3.66 (dd, 1 H, $J_{1b,2}$ 1.8, H-1b), 3.58 (ddd, 1 H, $J_{4a,5}$ 2.8, $J_{4b,5}$ 8.1, H-5), 2.05–1.80 and 1.66–1.30 (2 m, 4 H, 2 × H-3, 2 × H-4), 2.00 and 1.95 (2 s, 12 H, 4 × Ac), 1.50 and 1.43 (2 s, 6 H, 2 × CH_3), 1.45 (s, 9 H, *t*-Bu); MALDI-TOF MS (559.6): *m*/*z*, 583.0 (M + Na), 598.8 (M + K).

7,8,9,11-Tetra-*O*-acetyl-6,10-anhydro-2,3,4,5-tetradeoxy-1-*O*,2-*N*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*erythro*-L-*galacto*-undeconic acid 6a

To a cooled (0 °C), stirred solution of **5a** (115 mg, 0.20 mmol) in acetone (4 cm^3) was added freshly prepared 1 M Jones reagent (0.60 cm^3, 0.6 mmol). The mixture was allowed to warm to room temperture during 30 min, then was stirred for an additional 3 h. To the orange suspension was added dropwise propan-2-ol until a green colour was observed, then the reaction mixture was diluted with CH_2Cl_2 (60 cm^3) and washed with brine (3 × 20 cm^3). The organic phase was dried (Na_2SO_4) and concentrated to afford **6a** (99 mg, *ca.* 91%) as a syrup *ca.* 95% pure by ^{1}H NMR analysis. ^{1}H NMR ($CDCl_3$): δ 5.18 (dd, 1 H, $J_{7,8}$ 9.1, $J_{8,9}$ 9.5, H-8), 5.08 (d, 1 H, $J_{2,NH}$ 8.0, NH), 5.06 (dd, 1 H, $J_{9,10}$ 9.9 Hz, H-9), 4.88 (dd, 1 H, $J_{6,7}$ 9.9, H-7), 4.33–4.26 (m, 1 H, H-2), 4.26 (dd, 1 H, $J_{10,11a}$ 4.9, $J_{11a,11b}$ 12.3, H-11a), 4.11 (dd, 1 H, $J_{10,11b}$ 2.3, H-11b), 3.64 (ddd, 1 H, H-10), 3.42 (ddd, 1 H, $J_{5a,6}$ 3.3, $J_{5b,6}$ 7.8, H-6), 2.11, 2.06, 2.04, and 2.01 (4 s, 12 H, 4 × Ac), 1.93–1.48 (m, 6 H, 2 × H-3, 2 × H-4, 2 × H-5), 1.46 (s, 9 H, *t*-Bu).

7,8,9,11-Tetra-*O*-acetyl-6,10-anhydro-2,3,4,5-tetradeoxy-1-*O*,2-*N*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*erythro*-L-*gulo*-undeconic acid 6b

Treatment of the oxazolidine derivative **5b** (115 mg, 0.20 mmol) as described for the preparation of **6a** gave **6b** (101 mg, *ca.* 92%) as a syrup *ca.* 95% pure by ^{1}H NMR analysis. ^{1}H NMR ($CDCl_3$): δ 5.32 (dd, 1 H, $J_{7,8}$ 9.5, $J_{8,9}$ 8.9, H-8), 5.08 (dd, 1 H, $J_{6,7}$ 5.8, H-7), 5.08 (d, 1 H, $J_{2,NH}$ 8.5, NH), 4.99 (dd, 1 H, $J_{9,10}$ 9.5, H-9), 4.38–4.30 (m, 1 H, H-2), 4.26 (dd, 1 H, $J_{10,11a}$ 5.4, $J_{11a,11b}$ 12.0, H-11a), 4.18 (ddd, 1 H, $J_{5a,6}$ 2.7, $J_{5b,6}$ 8.5, H-6), 4.09 (dd, 1 H, $J_{10,11b}$ 2.5, H-11b), 3.84 (ddd, 1 H, H-10), 2.12, 2.08, 2.06, and 2.05 (4 s, 12 H, 4 × Ac), 1.98–1.41 (m, 6 H, 2 × H-3, 2 × H-4, 2 × H-5), 1.46 (s, 9 H, *t*-Bu).

7,8,9,11-Tetra-*O*-acetyl-6,10-anhydro-2,3,4,5-tetradeoxy-1-*O*,2- *N*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*threo*-L-*gulo*-undeconic acid 6c

Treatment of the oxazolidine derivative **5c** (86 mg, 0.15 mmol) as described for the preparation of **6a** gave **6c** (74 mg, *ca.* 90%) as a syrup *ca.* 95% pure by ^{1}H NMR analysis. ^{1}H NMR ($CDCl_3$): δ 5.42 (dd, 1 H, $J_{8,9}$ 3.1, $J_{9,10}$ 2.0, H-9), 5.27 (dd, 1 H, $J_{6,7}$ 4.9, $J_{7,8}$ 9.5, H-7), 5.20 (dd, 1 H, H-8), 5.14 (d, 1 H, $J_{2,NH}$ 8.0, NH), 4.38–4.17 and 4.12–4.02 (2 m, 5 H, H-2, H-6, H-10, 2 × H-11), 2.15, 2.10, 2.09, and 2.04 (4 s, 12 H, 4 × Ac), 1.93–1.40 (m, 6 H, 2 × H-3, 2 × H-4, 2 × H-5), 1.46 (s, 9 H, *t*-Bu).

8,9,10,12-Tetra-*O*-acetyl-7,11-anhydro-2,3,4,5,6-pentadeoxy-1-*O*,2-*N*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*erythro*-L-*galacto*-dodeconic acid 6d

Treatment of the oxazolidine derivative **5d** (117 mg, 0.20 mmol) as described for the preparation of **6a** gave **6d** (105 mg, *ca.* 94%) as a syrup *ca.* 95% pure by ^{1}H NMR analysis. ^{1}H NMR ($CDCl_3$): δ 5.17 (dd, 1 H, $J_{8,9}$ 9.3, $J_{9,10}$ 9.5, H-9), 5.06 (dd, 1 H, $J_{10,11}$ 9.8, H-10), 5.04 (d, 1 H, $J_{2,NH}$ 8.0, NH), 4.89 (dd, 1 H, $J_{7,8}$ 9.5, H-8), 4.34–4.26 (m, 1 H, H-2), 4.26 (dd, 1 H, $J_{11,12a}$ 5.0, $J_{12a,12b}$ 12.4, H-12a), 4.13 (dd, 1 H, $J_{11,12b}$ 2.1, H-12b), 3.63 (ddd, 1 H, H-11), 3.43–3.36 (m, 1 H, H-7), 2.11, 2.06, 2.04, and 2.02 (4 s, 12 H, 4 × Ac), 1.84–1.30 (m, 8 H, 2 × H-3, 2 × H-4, 2 × H-5, 2 × H-6), 1.46 (s, 9 H, *t*-Bu).

8,9,10,12-Tetra-*O*-acetyl-7,11-anhydro-2,3,4,5,6-pentadeoxy-1-*O*,2-*N*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*threo*-L-*galacto*-dodeconic acid 6e

Treatment of the oxazolidine derivative **5e** (88 mg, 0.15 mmol) as described for the preparation of **6a** gave **6e** (79 mg, *ca.* 94%) as a syrup *ca.* 95% pure by ^{1}H NMR analysis. ^{1}H NMR ($CDCl_3$): δ 5.43 (dd, 1 H, $J_{9,10}$ 3.1, $J_{10,11}$ 0.8, H-10), 5.10 (dd, 1 H, $J_{7,8}$ 9.0, $J_{8,9}$ 9.6, H-8), 5.01 (d, 1 H, $J_{2,NH}$ 8.0, NH), 5.01 (dd, 1 H, H-9), 4.31 (ddd, 1 H, $J_{2,3a}$ 5.5, $J_{2,3b}$ 8.0, H-2), 4.17 (dd, 1 H, $J_{11,12a}$ 6.8, $J_{12a,12b}$ 11.4, H-12a), 4.06 (dd, 1 H, $J_{11,12b}$ 6.6, H-12b), 3.85 (ddd, 1 H, H-11), 3.43–3.35 (md, 1 H, H-7), 2.18, 2.07, and 2.00 (3 s, 12 H, 4 × Ac), 1.85–1.34 (m, 8 H, 2 × H-3, 2 × H-4, 2 × H-5, 2 × H-6), 1.47 (s, 9 H, *t*-Bu).

6,7,8,10-Tetra-*O*-acetyl-5,9-anhydro-2,3,4-trideoxy-1-*O*,2-*N*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*erythro*-L-*galacto*-deconic acid 6f

Treatment of the oxazolidine derivative **5f** (56 mg, 0.10 mmol) as described for the preparation of **6a** gave **6f** (49 mg, *ca.* 91%) as a syrup *ca.* 95% pure by ^{1}H NMR analysis. ^{1}H NMR ($CDCl_3$): δ 5.19 (dd, 1 H, $J_{6,7}$ 9.4, $J_{7,8}$ 9.3, H-7), 5.17 (d, 1 H, $J_{2,NH}$ 9.0, NH), 5.05 (dd, 1 H, $J_{8,9}$ 10.0, H-8), 4.90 (dd, 1 H, $J_{5,6}$ 9.9, H-6), 4.33–4.25 (m, 1 H, H-2), 4.23 (dd, 1 H, $J_{9,10a}$ 5.1, $J_{10a,10b}$ 12.3, H-10a), 4.13 (dd, 1 H, $J_{9,10b}$ 2.2, H-10b), 3.66 (ddd, 1 H, H-9), 3.50 (ddd, 1 H, $J_{4a,5}$ 2.6, $J_{4b,5}$ 8.0, H-5), 2.11, 2.06, 2.04, and 2.02 (4 s, 12 H, 4 × Ac), 2.01–1.44 (m, 4 H, 2 × H-3, 2 × H-4), 1.46 (s, 9 H, *t*-Bu).

Methyl 7,8,9,11-tetra-*O*-acetyl-6,10-anhydro-2,3,4,5-tetradeoxy-1-*O*,2-*N*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*erythro*-L-*galacto*-undeconate 6a Me ester

Treatment of a solution of crude acid **6a** in 1 : 1 Et_2O–MeOH

with ethereal diazomethane at 0 °C for 5 min gave, after column chromatography on silica gel (1 : 1 cyclohexane–AcOEt), **6a Me ester** as a syrup; $[\alpha]_D$ −1.5 (*c* 1.0 in $CHCl_3$) (Found: C, 53.69; H, 7.10; N, 2.41. Calc. for $C_{25}H_{39}NO_{13}$: C, 53.47; H, 7.00; N, 2.49%); ^{1}H NMR ($CDCl_3$): δ 5.18 (dd, 1 H, $J_{7,8}$ 9.1, $J_{8,9}$ 9.5, H-8), 5.06 (dd, 1 H, $J_{9,10}$ 9.9, H-9), 5.03 (d, 1 H, $J_{2,NH}$ 8.0, NH), 4.88 (dd, 1 H, $J_{6,7}$ 9.9, H-7), 4.33–4.26 (m, 1 H, H-2), 4.26 (dd, 1 H, $J_{10,11a}$ 4.9, $J_{11a,11b}$ 12.3, H-11a), 4.10 (dd, 1 H, $J_{10,11b}$ 2.3, H-11b), 3.76 (s, 3 H, OCH_3), 3.63 (ddd, 1 H, H-10), 3.40 (ddd, 1 H, $J_{5a,6}$ 3.3, $J_{5b,6}$ 7.8, H-6), 2.11, 2.06, 2.04, and 2.01 (4 s, 12 H, 4 × Ac), 1.86–1.34 (m, 6 H, 2 × H-3, 2 × H-4, 2 × H-5), 1.46 (s, 9 H, *t*-Bu); ^{13}C NMR ($CDCl_3$): δ_C 173.2, 170.7, 170.4, 169.7, and 155.3 (C=O), 79.9 (*C*Me_3), 77.5 (C-6), 75.7 (C-10), 74.3 (C-8), 71.8 (C-7), 68.6 (C-9), 62.3 (C-11), 53.3 (C-2), 52.2 (OMe), 32.3, 30.7, and 21.0 (C-3, C-4, C-5), 28.3 (C*Me*$_3$), 20.7 and 20.6 (*Me*CO); MALDI-TOF MS (561.6): *m*/*z*, 584.1 (M + Na), 600.2 (M + K).

Methyl 7,8,9,11-tetra-*O*-acetyl-6,10-anhydro-2,3,4,5-tetradeoxy-1-*O*,2-*N*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*erythro*-L-*gulo*-undeconate 6b Me ester

Treatment of a solution of crude acid **6b** in 1 : 1 Et_2O–MeOH with ethereal diazomethane at 0 °C for 5 min gave, after column chromatography on silica gel (1 : 1 cyclohexane–AcOEt), **6b Me ester** as a syrup; $[\alpha]_D$ +54.9 (*c* 1.0 in $CHCl_3$) (Found: C, 53.31; H, 7.19; N, 2.30. Calc. for $C_{25}H_{39}NO_{13}$: C, 53.47; H, 7.00; N, 2.49%); ^{1}H NMR ($CDCl_3$): δ 5.32 (dd, 1 H, $J_{7,8}$ 9.5, $J_{8,9}$ 8.9, H-8), 5.07 (dd, 1 H, $J_{6,7}$ 5.8, H-7), 5.04 (d, 1 H, $J_{2,NH}$ 8.5, NH), 4.94 (dd, 1 H, $J_{9,10}$ 9.5, H-9), 4.38–4.30 (m, 1 H, H-2), 4.27 (dd, 1 H, $J_{10,11a}$ 5.4, $J_{11a,11b}$ 12.0, H-11a), 4.16 (ddd, 1 H, $J_{5a,6}$ 2.7, $J_{5b,6}$ 8.5, H-6), 4.08 (dd, 1 H, $J_{10,11b}$ 2.5, H-11b), 3.83 (ddd, 1 H, H-10), 3.77 (s, 3 H, OCH_3), 2.13, 2.09, 2.06, and 2.05 (4 s, 12 H, 4 × Ac), 1.94–1.36 (m, 6 H, 2 × H-3, 2 × H-4, 2 × H-5), 1.46 (s, 9 H, *t*-Bu); ^{13}C NMR ($CDCl_3$): δ_C 173.1, 170.7, 170.1, 169.7, and 155.3 (C=O), 80.0 (*C*Me_3), 72.5 (C-6), 70.3 (C-7, C-8), 68.8 (C-9), 68.7 (C-10), 62.3 (C-11), 53.0 (C-2), 52.3 (OMe), 32.4, 24.7, and 20.9 (C-3, C-4, C-5), 28.3 (C*Me*$_3$), 20.7 (*Me*CO); MALDI-TOF MS (561.6): *m*/*z*, 584.6 (M + Na), 600.7 (M + K).

Methyl 7,8,9,11-tetra-*O*-acetyl-6,10-anhydro-2,3,4,5-tetradeoxy-1-*O*,2-*N*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*threo*-L-*gulo*-undeconate 6c Me ester

Treatment of a solution of crude acid **6c** in 1 : 1 Et_2O–MeOH with ethereal diazomethane at 0 °C for 5 min gave, after column chromatography on silica gel (1 : 1 cyclohexane–AcOEt), **6c Me ester** as a syrup; $[\alpha]_D$ +67.7 (*c* 0.9 in $CHCl_3$) (Found: C, 53.70; H, 7.11; N, 2.36. Calc. for $C_{25}H_{39}NO_{13}$: C, 53.47; H, 7.00; N, 2.49%); ^{1}H NMR ($CDCl_3$): δ 5.42 (dd, 1 H, $J_{8,9}$ 3.1, $J_{9,10}$ 2.0, H-9), 5.27 (dd, 1 H, $J_{6,7}$ 4.9, $J_{7,8}$ 9.5, H-7), 5.20 (dd, 1 H, H-8), 5.06 (d, 1 H, $J_{2,NH}$ 8.5, NH), 4.37–4.28 (m, 1 H, H-2), 4.27 (dd, 1 H, $J_{10,11a}$ 6.7, $J_{11a,11b}$ 10.8, H-11a), 4.24–4.16 (m, 1 H, H-6), 4.11–4.01 (m, 2 H, H-10, H-11b), 3.77 (s, 3 H, OCH_3), 2.15, 2.10, 2.09, and 2.04 (4 s, 12 H, 4 × Ac), 1.93–1.31 (m, 6 H, 2 × H-3, 2 × H-4, 2 × H-5), 1.46 (s, 9 H, *t*-Bu); ^{13}C NMR ($CDCl_3$): δ_C 173.1, 170.6, 170.1, 169.9, and 155.3 (C=O), 79.9 (*C*Me_3), 71.9 (C-6), 68.3 (C-7), 68.1 (C-10), 67.9 (C-8), 67.6 (C-9), 61.5 (C- 11), 53.1 (C-2), 52.3 (OMe), 32.3, 25.1, and 21.2 (C-3, C-4, C-5), 28.3 (C*Me*$_3$), 20.7 (*Me*CO); MALDI-TOF MS (561.6): *m*/*z*, 584.2 (M + Na), 600.4 (M + K).

Methyl 8,9,10,12-tetra-*O*-acetyl-7,11-anhydro-2,3,4,5,6-pentadeoxy-1-*O*,2-*N*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*erythro*-L-*galacto*-dodeconate 6d Me ester

Treatment of a solution of crude acid **6d** in 1 : 1 Et_2O–MeOH with ethereal diazomethane at 0 °C for 5 min gave, after column chromatography on silica gel (1.5 : 1 cyclohexane–AcOEt), **6d Me ester** as a syrup; $[\alpha]_D$ −4.4 (*c* 1.0 in $CHCl_3$) (Found: C, 54.52; H, 7.29; N, 2.36. Calc. for $C_{26}H_{41}NO_{13}$: C, 54.25; H, 7.18; N, 2.43%); ^{1}H NMR ($CDCl_3$): δ 5.17 (dd, 1 H, $J_{8,9}$ 9.3, $J_{9,10}$ 9.5, H-9), 5.06 (dd, 1 H, $J_{10,11}$ 9.8, H-10), 5.03 (d, 1 H, $J_{2,NH}$ 8.0, NH), 4.88 (dd, 1 H, $J_{7,8}$ 9.5, H-8), 4.34–4.26 (m, 1 H, H-2), 4.26 (dd, 1 H, $J_{11,12a}$ 5.0, $J_{12a,12b}$ 12.4, H-12a), 4.10 (dd, 1 H, $J_{11,12b}$ 2.1, H-12b), 3.76 (s, 3 H, OCH_3), 3.63 (ddd, 1 H, H-11), 3.43–3.36 (m, 1 H, H-7), 2.11, 2.06, 2.04, and 2.01 (4 s, 12 H, 4 × Ac), 1.84–1.26 (m, 8 H, 2 × H-3, 2 × H-4, 2 × H-5, 2 × H-6), 1.46 (s, 9 H, *t*-Bu); ^{13}C NMR ($CDCl_3$): δ_C 173.3, 170.7, 170.4, 169.7, 169.5, and 155.3 (C=O), 79.9 (*C*Me_3), 77.7 (C-7), 75.6 (C-11), 74.4 (C-9), 71.9 (C-8), 68.7 (C-10), 62.3 (C-12), 53.3 (C-2), 52.2 (OMe), 32.7, 31.0, 25.1, and 24.7 (C-3, C-4, C-5, C-6), 28.3 (C*Me*$_3$), 20.7 and 20.6 (*Me*CO); MALDI-TOF MS (575.6): *m*/*z*, 598.6 (M + Na), 614.9 (M + K).

Methyl 8,9,10,12-tetra-*O*-acetyl-7,11-anhydro-2,3,4,5,6-pentadeoxy-1-*O*,2-*N*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*threo*-L-*galacto*-dodeconate 6e Me ester

Treatment of a solution of crude acid **6e** in 1 : 1 Et_2O–MeOH with ethereal diazomethane at 0 °C for 5 min gave, after column chromatography on silica gel (1.5 : 1 cyclohexane–AcOEt), **6e Me ester** as a syrup; $[\alpha]_D$ +5.8 (*c* 1.0 in $CHCl_3$) (Found: C, 54.16; H, 7.36; N, 2.31. Calc. for $C_{26}H_{41}NO_{13}$: C, 54.25; H, 7.18; N, 2.43%); ^{1}H NMR ($CDCl_3$): δ 5.43 (dd, 1 H, $J_{9,10}$ 3.1, $J_{10,11}$ 0.8, H-10), 5.09 (dd, 1 H, $J_{7,8}$ 9.0, $J_{8,9}$ 9.6, H-8), 5.02 (d, 1 H, $J_{2,NH}$ 8.0, NH), 5.01 (dd, 1 H, H-9), 4.31 (ddd, 1 H, $J_{2,3a}$ 5.5, $J_{2,3b}$ 8.0, H-2), 4.16 (dd, 1 H, $J_{11,12a}$ 6.8, $J_{12a,12b}$ 11.4, H-12a), 4.08 (dd, 1 H, $J_{11,12b}$ 6.6, H-12b), 3.85 (ddd, 1 H, H-11), 3.76 (s, 3 H, OCH_3), 3.37 (ddd, 1 H, $J_{6a,7}$ 6.0, $J_{6b,7}$ 9.1, H-7), 2.18, 2.07, and 2.00 (3 s, 12 H, 4 × Ac), 1.85–1.34 (m, 8 H, 2 × H-3, 2 × H-4, 2 × H-5, 2 × H-6), 1.46 (s, 9 H, *t*-Bu); ^{13}C NMR ($CDCl_3$): δ_C 173.3, 170.4, 170.3, 170.2, 169.8, and 155.3 (C=O), 79.9 (*C*Me_3), 78.1 (C-7), 74.1 (C-11), 72.2 (C-9), 69.4 (C-8), 67.7 (C-10), 61.6 (C- 12), 53.3 (C-2), 52.2 (OMe), 32.7, 31.2, 25.1, and 24.7 (C-3, C-4, C-5, C-6), 28.3 (C*Me*$_3$), 20.8, 20.7, and 20.6 (*Me*CO); MALDI-TOF MS (575.6): *m*/*z*, 598.6 (M + Na), 614.7 (M + K).

Methyl 6,7,8,10-tetra-*O*-acetyl-5,9-anhydro-2,3,4-trideoxy-1-*O*,2-*N*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*erythro*-L-*galacto*-deconate 6f Me ester

Treatment of a solution of crude acid **6f** in 1 : 1 Et_2O–MeOH with ethereal diazomethane at 0 °C for 5 min gave, after column chromatography on silica gel (1 : 1 cyclohexane–AcOEt), **6f Me ester** as a white solid; mp 109–111 °C (from AcOEt–cyclohexane); $[\alpha]_D$ −4.0 (*c* 0.6 in $CHCl_3$) (Found: C, 52.80; H, 6.76; N, 2.46. Calc. for $C_{24}H_{37}NO_{13}$: C, 52.64; H, 6.81; N, 2.56%); ^{1}H NMR ($CDCl_3$): δ 5.19 (dd, 1 H, $J_{6,7}$ 9.4, $J_{7,8}$ 9.3, H-7), 5.06 (d, 1 H, $J_{2,NH}$ 8.0, NH), 5.05 (dd, 1 H, $J_{8,9}$ 10.0, H-8), 4.89 (dd, 1 H, $J_{5,6}$ 9.9, H-6), 4.33–4.25 (m, 1 H, H-2), 4.24 (dd, 1 H, $J_{9,10a}$ 5.1, $J_{10a,10b}$ 12.3, H-10a), 4.11 (dd, 1 H, $J_{9,10b}$ 2.2, H-10b), 3.76 (s, 3 H, OCH_3), 3.65 (ddd, 1 H, H-9), 3.48 (ddd, 1 H, $J_{4a,5}$ 2.6, $J_{4b,5}$ 8.0, H-5), 2.11, 2.06, 2.04, and 2.02 (4 s, 12 H, 4 × Ac), 2.01–1.44 (m, 4 H, 2 × H-3, 2 × H-4), 1.46 (s, 9 H, *t*-Bu); ^{13}C NMR ($CDCl_3$): δ_C 175.0, 173.0, 170.7, 170.3, 169.7, 169.5, and 155.5 (C=O), 80.0 (*C*Me_3), 76.8 (C-5), 75.7 (C-9), 74.2 (C-7), 71.6 (C-6), 68.7 (C-8), 62.3 (C-10), 52.9 (C-2), 52.3 (OMe), 28.3 (C*Me*$_3$), 27.7 and 27.0 (C-3, C-4), 20.7, and 20.6 (*Me*CO); MALDI-TOF MS (547.6): *m*/*z*, 570.7 (M + Na), 587.0 (M + K).

Methyl 8,12-anhydro-2,3,4,9,10,11,13-hepta-*O*-benzyl-6,7-dideoxy-α-D-*glycero*-D-*gulo*-D-*gluco*-tridecopyranoside 8

To a warmed (85 °C), stirred solution of alkene **7** (590 mg, 0.60 mmol) and freshly recrystallized toluene-*p*-sulfonylhydrazide (335 mg, 1.80 mmol) in 1,2-dimethoxyethane (12 cm^3) was added 1 M aq. sodium acetate (1.8 cm^3) by a syringe-pump apparatus during 4 h. After an additional 1 h at 85 °C the

mixture was cooled to room temperature, diluted with water (15 cm^3), and extracted with CH_2Cl_2 (2 × 60 cm^3). The combined organic phases were dried (Na_2SO_4) and concentrated. The residue was eluted from a column of silica gel with 5 : 1 cyclohexane–AcOEt to give **8** (538 mg, 91%) as a white solid; mp 161–162 °C (from CH_3CN); $[\alpha]_D$ +9.0 (*c* 1.0 in $CHCl_3$) (Found: C, 76.98; H, 7.11. Calc. for $C_{63}H_{68}O_{10}$: C, 76.80; H, 6.96%); ^{1}H NMR ($CDCl_3$) selected data: δ 4.54 (d, 1 H, $J_{1,2}$ 3.6, H-1), 3.96 (dd, 1 H, $J_{2,3}$ 9.6, $J_{3,4}$ 9.0, H-3), 3.52 (dd, 1 H, H-2), 3.31 (s, 3 H, OCH_3), 3.18 (dd, 1 H, $J_{4,5}$ 9.5, H-4), 2.17–2.06 (m, 2 H, 2 × H-7), 1.50–1.40 (m, 2 H, 2 × H-6); MALDI-TOF MS (985.2): *m*/*z*, 1007.5 (M + Na), 1024.0 (M + K).

1-*O*-Acetyl-8,12-anhydro-2,3,4,9,10,11,13-hepta-*O*-benzyl-6,7-dideoxy-α,β-D-*glycero*-D-*gulo*-D-*gluco*-tridecopyranose 9

To a warmed (100 °C), stirred solution of **8** (591 mg, 0.60 mmol) in acetic acid (24 cm^3) was added dropwise 1 M aq. H_2SO_4 (2.4 cm^3). The solution was stirred at 100 °C for an additional 75 min, then cooled to room temperature, diluted with CH_2Cl_2 (100 cm^3), and washed with saturated aq. Na_2CO_3 (5 × 20 cm^3). The combined organic phases were dried (Na_2SO_4) and concentrated. A solution of the crude hemiacetal in pyridine (5 cm^3) and acetic anhydride (5 cm^3) was kept at room temperature for 3 h, then concentrated. The residue was eluted from a column of silica gel with 6 : 1 cyclohexane–AcOEt to give **9** (425 mg, 70%) as an amorphous solid (Found: C, 75.59; H, 6.89. Calc. for $C_{64}H_{68}O_{11}$: C, 75.86; H, 6.76%); ^{1}H NMR ($CDCl_3$) selected data: δ 6.30 (d, 0.5 H, $J_{1,2}$ 3.5, H-1α), 5.59 (d, 0.5 H, $J_{1,2}$ 8.2, H-1β), 2.14 and 2.02 (2 s, 3 H, Ac); MALDI-TOF MS (1013.2): *m*/*z*, 1036.7 (M + Na), 1052.5 (M + K).

4,8:11,15-Dianhydro-5,6,7,12,13,14,16-hepta-*O*-benzyl-1,2,3,9,10-pentadeoxy-D-*erythro*-L-*talo*-D-*ido*-hexadec-1-enitol 10

A mixture of acetate **9** (811 mg, 0.8 mmol), allyltrimethylsilane **3** (0.38 cm^3, 2.4 mmol), activated 4 Å powdered molecular sieves (0.8 g), and anhydrous CH_2Cl_2 (8 cm^3) was stirred at room temperature for 15 min, then trimethylsilyl triflate (0.29 cm^3, 1.6 mmol) was added dropwise. The suspension was stirred at room temperature for 1 h, then treated with an excess of Et_3N, diluted with CH_2Cl_2, filtered through Celite, and concentrated. The residue was eluted from a column of silica gel with 8 : 1 cyclohexane–AcOEt (containing 5% of CH_2Cl_2) to give **10** (637 mg, 80%) as a white solid; mp 147–148 °C (from cyclohexane); $[\alpha]_D$ +19.0 (*c* 1.0 in $CHCl_3$) (Found: C, 78.29; H, 7.01. Calc. for $C_{65}H_{70}O_9$: C, 78.44; H, 7.09%); ^{1}H NMR ($CDCl_3$) selected data: δ 5.76 (dddd, 1 H, *J* 6.5, 6.5, 10.2, 17.0, H-2), 5.10 (dddd, 1 H, *J* 1.7, 1.7, 2.0, 17.0, H-1a), 4.99 (dddd, 1 H, *J* 1.3, 1.3, 2.0, 10.2, H-1b), 4.93 and 4.81 (2 d, 2 H, *J* 10.8, PhCH_2), 4.90 (s, 2 H, PhCH_2), 4.87 and 4.63 (2 d, 2 H, *J* 10.8, PhCH_2), 4.84 and 4.62 (2 d, 2 H, *J* 10.7, PhCH_2), 4.84 and 4.59 (2 d, 2 H, *J* 11.0, PhCH_2), 4.72 and 4.65 (2 d, 2 H, *J* 11.8, PhCH_2), 4.62 and 4.52 (2 d, 2 H, *J* 12.2, PhCH_2); MALDI-TOF MS (995.3): *m*/*z*, 1018.2 (M + Na), 1034.4 (M + K).

6,10:13,17-Dianhydro-7,8,9,14,15,16,18-hepta-*O*-benzyl-2,3,4,5,11,12-hexadeoxy-1-*O*,2-*N*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*arabino*-D-*allo*-L-*gulo*-octadec-3-enitol 11

Cross-metathesis of allyl α-*C*-glycoside **10** (298 mg, 0.30 mmol) with the vinyloxazolidine **1** (136 mg, 0.60 mmol) as described for the preparation of **4a** afforded, after column chromatography with cyclohexane–AcOEt (from 7 : 1 to 4 : 1), **11** (143 mg, 40%) as a *ca.* 5 : 1 *E* : *Z* mixture (Found: C, 75.15; H, 7.51; N, 1.38. Calc. for $C_{75}H_{87}NO_{12}$: C, 75.41; H, 7.34; N, 1.17%); ^{1}H NMR ($CDCl_3$) selected data: δ 5.63–5.40 (m, 2 H, H-3, H-4), 2.47–2.32 (m, 2 H, 2 × H-5), 1.58 and 1.46 (2 s, 6 H, 2 × CH_3), 1.46 (s, 9 H, *t*-Bu); MALDI-TOF MS (1194.5): *m*/*z*, 1217.7 (M + Na), 1233.2 (M + K).

7,8,9,14,15,16,18-Hepta-*O*-acetyl-6,10:13,17-dianhydro-2,3,4,5,11,12-hexadeoxy-1-*O*,2-*N*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*arabino*-D-*allo*-L-*gulo*-octadecitol 12

Hydrogenation and acetylation of **11** (179 mg, 0.15 mmol) as described for the preparation of **5a** afforded, after column chromatography with 1.5 : 1 cyclohexane–AcOEt, **12** (97 mg, 75%) as a syrup; $[\alpha]_D$ +36.2 (*c* 0.8 in $CHCl_3$) (Found: C, 56.07; H, 7.21; N, 1.88. Calc. for $C_{40}H_{61}NO_{19}$: C, 55.87; H, 7.15; N, 1.63%); ^{1}H NMR (DMSO-d_6; 140 °C): δ 5.17 (dd, 1 H, $J_{7,8}$ 9.0, $J_{8,9}$ 8.6, H-8), 5.16 (dd, 1 H, $J_{14,15} = J_{15,16}$ = 9.4, H-15), 4.92 (dd, 1 H, $J_{6,7}$ 5.6, H-7), 4.87 (dd, 1 H, $J_{16,17}$ 9.8, H-16), 4.72 (dd, 1 H, $J_{13,14}$ 9.7, H-14), 4.68 (dd, 1 H, $J_{9,10}$ 9.0, H-9), 4.14 (dd, 1 H, $J_{17,18a}$ 5.3, $J_{18a,18b}$ 12.0, H-18a), 4.07 (dd, 1 H, $J_{17,18b}$ 3.0, H-18b), 4.05–3.99 (m, 1 H, H-6), 3.95 (dd, 1 H, $J_{1a,2}$ 6.0, $J_{1a,1b}$ 9.0, H-1a), 3.86–3.78 (m, 1 H, H-2), 3.81 (ddd, 1 H, H-17), 3.68 (dd, 1 H, $J_{1b,2}$ 2.0, H-1b), 3.67–3.55 (m, 2 H, H-10, H-13), 2.02, 2.01, 2.00, 1.99, 1.97, and 1.94 (6 s, 21 H, 7 × Ac), 1.85–1.26 (m, 10 H, 2 × H-3, 2 × H-4, 2 × H-5, 2 × H-11, 2 × H-12), 1.52 and 1.46 (2 s, 6 H, 2 × CH_3), 1.48 (s, 9 H, *t*-Bu); MALDI-TOF MS (859.9): *m*/*z*, 883.6 (M + Na), 900.0 (M + K).

7,8,9,14,15,16,18-Hepta-*O*-acetyl-6,10:13,17-dianhydro-2,3,4,5,11,12-hexadeoxy-2-(*tert*-butoxycarbonylamino)-D-*arabino*-D-*allo*-L-*gulo*-octadeconic acid 13

Treatment of the oxazolidine derivative **12** (86 mg, 0.10 mmol) as described for the preparation of **6a** gave **13** (75 mg, *ca.* 90%) as a syrup *ca.* 95% pure by ^{1}H NMR analysis. ^{1}H NMR ($CDCl_3$) selected data: δ 5.30–5.26 (m, 1 H, NH), 5.26 (dd, 1 H, $J_{7,8}$ 9.9, $J_{8,9}$ 9.0, H-8), 5.20 (dd, 1 H, $J_{14,15} = J_{15,16}$ = 9.4, H-15), 5.03 (dd, 1 H, $J_{16,17}$ 9.1, H-16), 5.02 (dd, 1 H, $J_{6,7}$ 6.0, H-7), 4.90 (dd, 1 H, $J_{13,14}$ 9.9, H-14), 4.76 (dd, 1 H, $J_{9,10}$ 9.5, H-9), 4.47–4.40 (m, 1 H, H-2), 4.22 (dd, 1 H, $J_{17,18a}$ 5.1, $J_{18a,18b}$ 12.4, H-18a), 3.61 (ddd, 1 H, $J_{17,18b}$ 2.0, H-17), 3.51–3.44 (m, 1 H, H-10), 3.36–3.29 (m, 1 H, H-13), 1.46 (s, 9 H, *t*-Bu).

Methyl 7,8,9,14,15,16,18-hepta-*O*-acetyl-6,10:13,17-dianhydro-2,3,4,5,11,12-hexadeoxy-2-(*tert*-butoxycarbonylamino)-D-*arabino*-D-*allo*-L-*gulo*-octadeconate 13 Me ester

Treatment of a solution of crude acid **13** in 1 : 1 Et_2O–MeOH with ethereal diazomethane at 0 °C for 5 min gave, after column chromatography on silica gel (1 : 1 cyclohexane–AcOEt), **13 Me ester** as a syrup; $[\alpha]_D$ +29.8 (*c* 0.9 in $CHCl_3$) (Found: C, 54.11; H, 7.00; N, 1.51. Calc. for $C_{38}H_{57}NO_{20}$: C, 53.83; H, 6.78; N, 1.65%); ^{1}H NMR ($CDCl_3$): δ 5.28 (dd, 1 H, $J_{7,8}$ 9.9, $J_{8,9}$ 9.0, H-8), 5.18 (dd, 1 H, $J_{14,15} = J_{15,16}$ = 9.4, H-15), 5.17 (d, 1 H, $J_{2,NH}$ 8.0, NH), 5.04 (dd, 1 H, $J_{16,17}$ 9.1, H-16), 5.02 (dd, 1 H, $J_{6,7}$ 6.0, H-7), 4.88 (dd, 1 H, $J_{13,14}$ 9.9, H-14), 4.79 (dd, 1 H, $J_{9,10}$ 9.5, H-9), 4.37–4.30 (m, 1 H, H-2), 4.25 (dd, 1 H, $J_{17,18a}$ 5.1, $J_{18a,18b}$ 12.4, H-18a), 4.09 (dd, 1 H, $J_{17,18b}$ 2.3, H-18b), 4.09–4.04 (m, 1 H, H-6), 3.78 (s, 3 H, OCH_3), 3.62 (ddd, 1 H, H-17), 3.54–3.48 (m, 1 H, H-10), 3.42–3.36 (m, 1 H, H-13), 2.11, 2.07, 2.04, 2.03, and 2.01 (5 s, 21 H, 7 × Ac), 1.88–1.70 (m, 6 H, 2 × H-3, 2 × H-4, 2 × H-5), 1.53–1.32 (m, 4 H, 2 × H-11, 2 × H-12), 1.46 (s, 9 H, *t*-Bu); ^{13}C NMR ($CDCl_3$): δ_C 173.0, 170.6, 170.3, 170.2, 169.5, and 155.3 (C=O), 79.8 (*C*Me_3), 77.7 (C-13), 75.7 (C-17), 74.2 (C-15), 72.5 (C-6, C-9), 71.6 (C-14), 70.7 (C-7), 70.5 (C-8), 69.7 (C-10), 68.7 (C-16), 62.3 (C-18), 53.0 (C-2), 52.3 (OMe), 32.3, 27.1, 24.6, and 21.0 (C-3, C-4, C-5, C-11, C-12), 28.3 (C*Me*$_3$), 20.7 (*Me*CO); MALDI-TOF MS (847.9): *m*/*z*, 870.6 (M + Na), 886.6 (M + K).

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