

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

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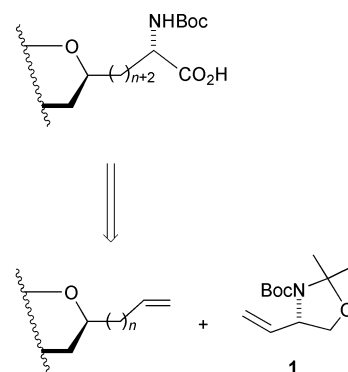
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A convergent synthesis has been developed to afford C-linked glycosyl amino acids by cross-metathesis of vinyl, allyl, and butenyl C-glycosides with *N*-Boc-vinylloxazolidine using the Grubbs 1,3-dimesityl-4,5-dihydroimidazol-2-ylideneruthenium carbene. 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 glycoproteins¹ 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-vinylloxazolidine⁵ **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 glycyl moiety [CH(NH₂)-CO₂H] 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 glycyl 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.

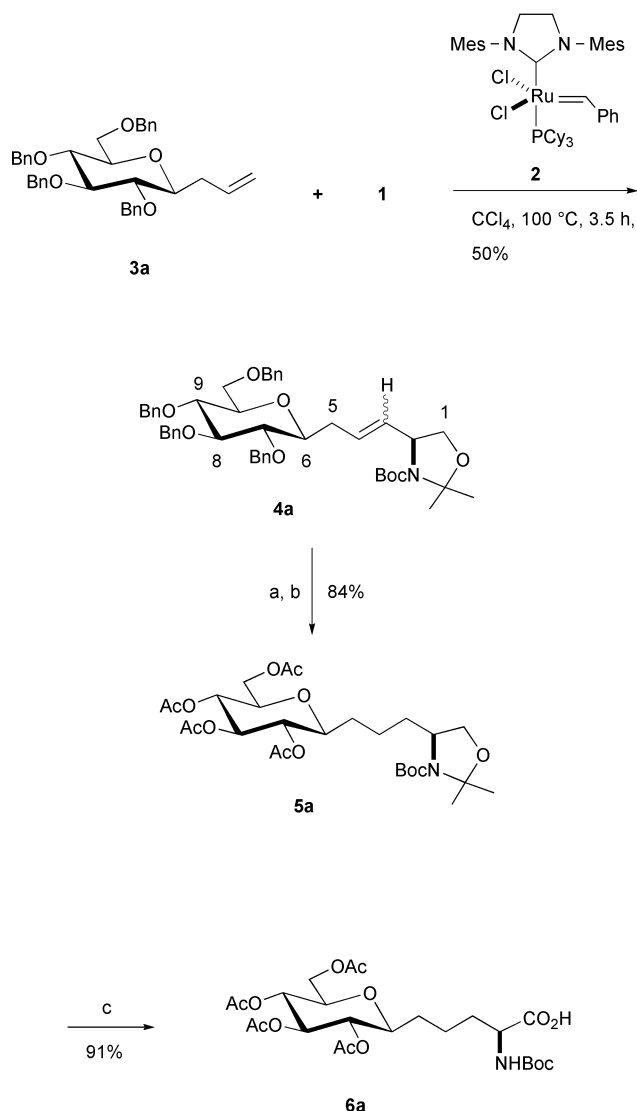
As compared with the metal (Mo, W, Ru) alkylidene-promoted ring-closing metathesis (RCM) of alkenes employed for the synthesis of carbo- and heterocyclic systems,⁸ the CM reaction in which two different alkenes are used to form a new acyclic product has so far found much less application. The limited 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-workers⁹ 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}

Results and discussion

Heating a mixture of the allyl β -D-C-glucopyranoside **3a**, the vinylloxazolidine **1** (2 equiv.) and the 'second generation' Grubbs 1,3-dimesityl-4,5-dihydroimidazol-2-ylideneruthenium carbene¹¹ **2** (0.2 equiv.) in CCl₄ 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 [RuCl₂(=CHPh)(PCy₃)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



Scheme 1 Reagents and conditions: a) H_2 , $\text{Pd}(\text{OH})_2$, $t\text{-BuOH}$ – 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.

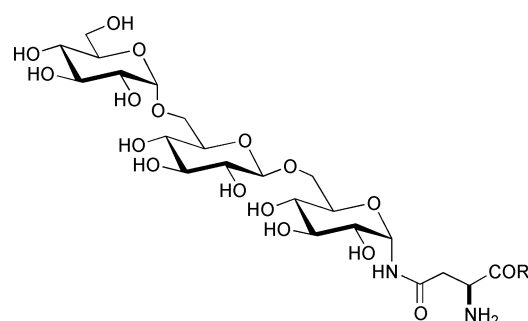
1). Very likely the well known instability¹² of vinyl *C*-glycosides constitutes a serious limitation on the use of these compounds as partners in CM reactions. However in order to elaborate upon this methodology, all alkenes **4a–f** were transformed into the corresponding peracetylated *N*-Boc-oxazolidine derivatives **5a–f** by hydrogenation over $\text{Pd}(\text{OH})_2$ 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 our⁶ and others' laboratory,¹³ the same configuration for the resulting glycyl 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*-acetyl¹⁵ and *N*-Boc¹⁶ 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 acetate¹⁷ 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.



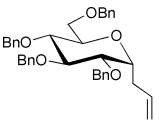
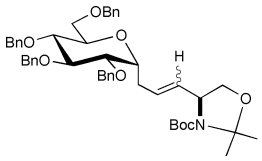
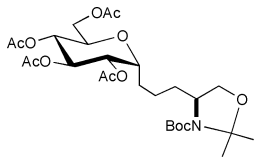
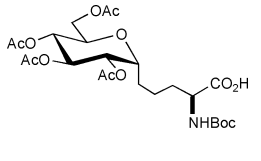
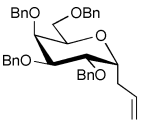
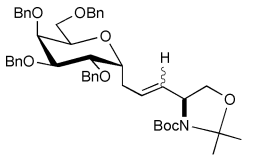
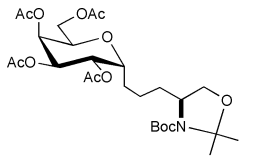
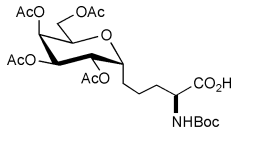
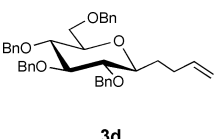
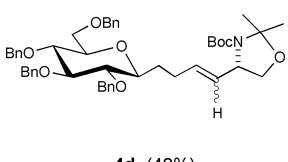
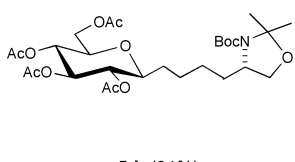
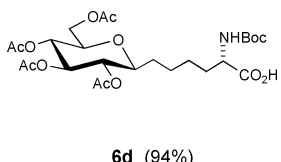
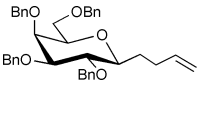
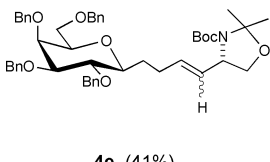
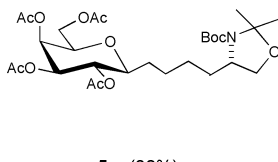
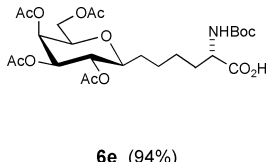
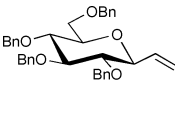
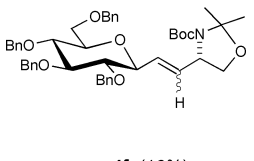
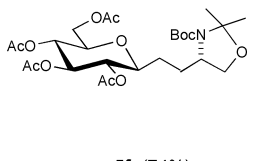
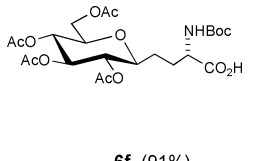
14 R = OH

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 agents²⁰ 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 F₂₅₄ with detection by charring with sulfuric acid. Flash column chromatography²¹ 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 $\text{cm}^2 \text{g}^{-1}$. ^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.

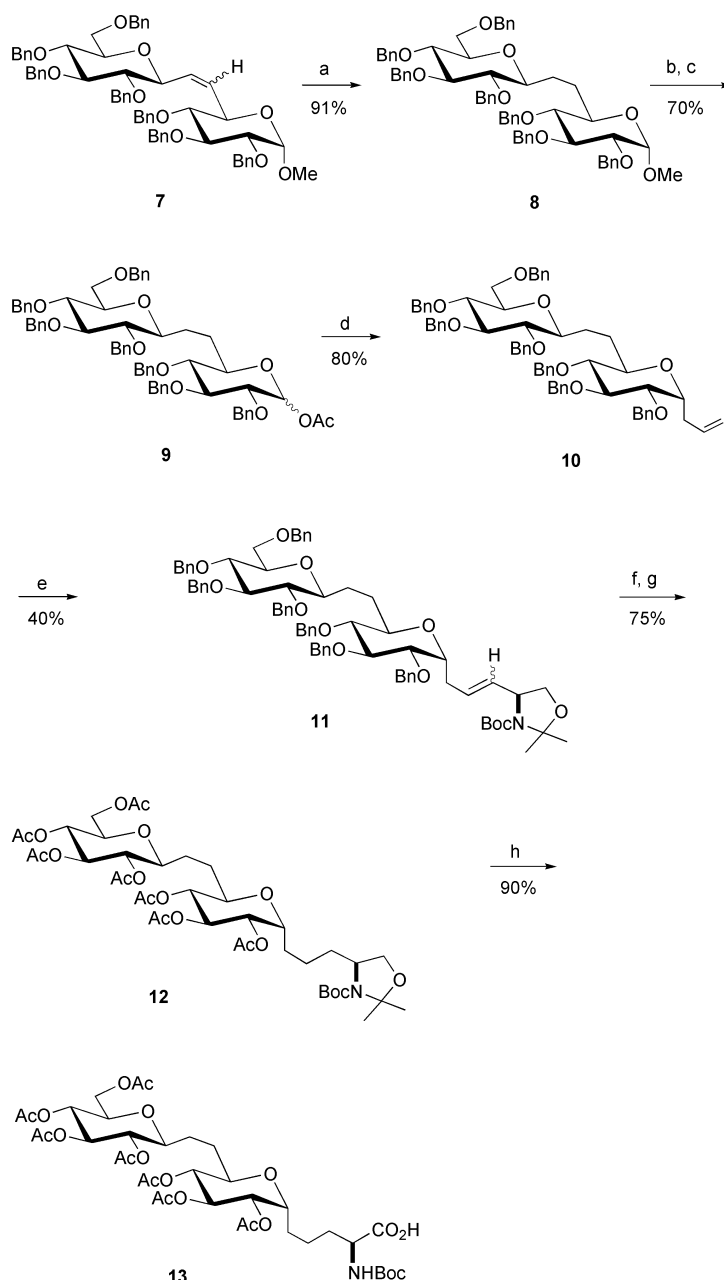
α -cyano-4-hydroxycinnamic acid as the matrix. The allyl β -C-glucoside **3a**, α -C-glucoside **3b** and α -C-galactoside **3c** were prepared as described.²² The butenyl β -C-glucoside **3d**, prepared as reported,²³ had mp 87–88 °C (from MeOH); [α]_D 0.0 (*c* 1.4 in CHCl₃) {lit.,²³ mp 83–84 °C (from Et₂O); [α]_D +3 (*c* 1.2 in CHCl₃); lit.,²⁴ mp 84–85 °C (from light petroleum); [α]_D –1.7}. The butenyl β -C-galactoside **3e**, prepared as described,²⁵ had [α]_D –3.0 (*c* 1.0 in CHCl₃) {lit.²⁵ [α]_D not reported}. The preparation of the vinyl C-glucoside **3f** was previously described by Kraus and Molina²⁶ 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., Bischoheim, 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 Et₂O (30 cm³) was added commercially available vinylmagnesium bromide (4.5 cm³, 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 cm³) and extracted with Et₂O (2 × 100 cm³). The combined organic phases were dried (Na₂SO₄) 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 cm³, 8.8 mmol) in anhydrous acetonitrile (17 cm³) was slowly added freshly distilled boron trifluoride-diethyl ether (0.22 cm³, 1.76 mmol). The solution was stirred for 2 h at –40 °C, then diluted with triethylamine (0.5 cm³), 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); [α]_D +28.0 (*c* 0.2 in CHCl₃) (Found: C, 78.70; H, 7.03. Calc. for C₃₆H₃₈O₅: C, 78.52; H, 6.96%); ¹H NMR (CDCl₃) 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, PhCH₂), 4.85 and 4.59 (2 d, 2 H, *J* 10.8, PhCH₂), 4.78 and 4.68 (2 d, 2 H, *J* 10.8, PhCH₂), 4.66 and 4.58 (2 d, 2 H, *J* 11.2, PhCH₂), 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) AlSiMe_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 , $\text{Pd}(\text{OH})_2$, 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-tetradecoxy-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 ($M + \text{Na}$), 1140.9 ($M + \text{K}$). 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 $\text{C}_{47}\text{H}_{57}\text{NO}_8$: C, 73.89; H, 7.52; N, 1.83%); ^1H NMR ($\text{DMSO}-d_6$; 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 ($M + \text{Na}$), 803.2 ($M + \text{K}$).

6,10-Anhydro-7,8,9,11-tetra-*O*-benzyl-2,3,4,5-tetradecoxy-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 $\text{C}_{47}\text{H}_{57}\text{NO}_8$: C, 73.89; H, 7.52; N, 1.83%); ^1H NMR ($\text{DMSO}-d_6$; 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 ($M + \text{Na}$), 803.1 ($M + \text{K}$).

6,10-Anhydro-7,8,9,11-tetra-*O*-benzyl-2,3,4,5-tetradecoxy-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%); 1H NMR ($CDCl_3$) selected data: δ 5.62–5.40 (m, 2 H, H-3, H-4), 2.48–2.30 (m, 2 H, $2 \times$ 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%); 1H NMR (DMSO- d_6 ; 120 $^\circ C$) 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%); 1H NMR (DMSO- d_6 ; 120 $^\circ C$) 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%); 1H 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-tetradecoxy-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; $[a]_D +3.4$ (*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%); 1H 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, $4 \times$ Ac), 1.83–1.28 (m, 6 H, $2 \times$ H-3, $2 \times$ H-4, $2 \times$ H-5), 1.58 and 1.52 (2 s, 6 H, $2 \times$ 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-tetradecoxy-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; $[a]_D +62.6$ (*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%); 1H NMR (DMSO- d_6 ; 140 $^\circ C$): 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, $4 \times$ Ac), 1.86–1.24 (m, 6 H, $2 \times$ H-3, $2 \times$ H-4, $2 \times$ H-5), 1.52 and 1.46 (2 s, 6 H, $2 \times$ 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-tetradecoxy-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; $[a]_D +70.2$ (*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%); 1H 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, $4 \times$ Ac), 1.85–1.46 (m, 6 H, $2 \times$ H-3, $2 \times$ H-4, $2 \times$ H-5), 1.49 and 1.44 (2 s, 6 H, $2 \times$ 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; $[a]_D +5.0$ (*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%); 1H NMR (DMSO- d_6 ; 160 $^\circ C$): 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 × CH₃), 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; $[\alpha]_D^{25} +12.5$ (*c* 1.0 in CHCl₃) (Found: C, 57.01; H, 7.86; N, 2.28. Calc. for C₂₈H₄₅NO₁₂: C, 57.23; H, 7.72; N, 2.38%); ¹H 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 × CH₃), 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; $[\alpha]_D^{25} +8.1$ (*c* 0.6 in CHCl₃) (Found: C, 55.73; H, 7.47; N, 2.17. Calc. for C₂₆H₄₁NO₁₂: C, 55.80; H, 7.38; N, 2.50%); ¹H 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 × CH₃), 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-tetradecoxy-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 cm³) was added freshly prepared 1 M Jones reagent (0.60 cm³, 0.6 mmol). The mixture was allowed to warm to room temperature 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 CH₂Cl₂ (60 cm³) and washed with brine (3 × 20 cm³). The organic phase was dried (Na₂SO₄) and concentrated to afford **6a** (99 mg, *ca.* 91%) as a syrup *ca.* 95% pure by ¹H NMR analysis. ¹H NMR (CDCl₃): 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-tetradecoxy-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 ¹H NMR analysis. ¹H NMR (CDCl₃): 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-tetradecoxy-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 ¹H NMR analysis. ¹H NMR (CDCl₃): 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 ¹H NMR analysis. ¹H NMR (CDCl₃): 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 ¹H NMR analysis. ¹H NMR (CDCl₃): 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 ¹H NMR analysis. ¹H NMR (CDCl₃): 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-tetradecoxy-1-*O*,2-*N*-isopropylidene-2-(*tert*-butoxycarbonylamino)-*D*-erythro-*L*-galacto-undecionate 6a Me ester

Treatment of a solution of crude acid **6a** in 1 : 1 Et₂O–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; $[a]_D -1.5$ (*c* 1.0 in CHCl₃) (Found: C, 53.69; H, 7.10; N, 2.41. Calc. for C₂₅H₃₉NO₁₃: C, 53.47; H, 7.00; N, 2.49%); ¹H NMR (CDCl₃): 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, OCH₃), 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); ¹³C NMR (CDCl₃): δ_C 173.2, 170.7, 170.4, 169.7, and 155.3 (C=O), 79.9 (CMe₃), 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 (CMe₃), 20.7 and 20.6 (MeCO); 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-tetra-deoxy-1-*O*,2-*N*-isopropylidene-2-(*tert*-butoxycarbonylamino)-*D*-erythro-*L*-gulo-undecionate 6b Me ester

Treatment of a solution of crude acid **6b** in 1 : 1 Et₂O–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; $[a]_D +54.9$ (*c* 1.0 in CHCl₃) (Found: C, 53.31; H, 7.19; N, 2.30. Calc. for C₂₅H₃₉NO₁₃: C, 53.47; H, 7.00; N, 2.49%); ¹H NMR (CDCl₃): 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, OCH₃), 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); ¹³C NMR (CDCl₃): δ_C 173.1, 170.7, 170.1, 169.7, and 155.3 (C=O), 80.0 (CMe₃), 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 (CMe₃), 20.7 (MeCO); 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-tetra-deoxy-1-*O*,2-*N*-isopropylidene-2-(*tert*-butoxycarbonylamino)-*D*-threo-*L*-gulo-undecionate 6c Me ester

Treatment of a solution of crude acid **6c** in 1 : 1 Et₂O–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; $[a]_D +67.7$ (*c* 0.9 in CHCl₃) (Found: C, 53.70; H, 7.11; N, 2.36. Calc. for C₂₅H₃₉NO₁₃: C, 53.47; H, 7.00; N, 2.49%); ¹H NMR (CDCl₃): 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, OCH₃), 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); ¹³C NMR (CDCl₃): δ_C 173.1, 170.6, 170.1, 169.9, and 155.3 (C=O), 79.9 (CMe₃), 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 (CMe₃), 20.7 (MeCO); 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-penta-deoxy-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 Et₂O–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; $[a]_D -4.4$ (*c* 1.0 in CHCl₃) (Found: C,

54.52; H, 7.29; N, 2.36. Calc. for C₂₆H₄₁NO₁₃: C, 54.25; H, 7.18; N, 2.43%); ¹H NMR (CDCl₃): 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, OCH₃), 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); ¹³C NMR (CDCl₃): δ_C 173.3, 170.7, 170.4, 169.7, 169.5, and 155.3 (C=O), 79.9 (CMe₃), 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 (CMe₃), 20.7 and 20.6 (MeCO); 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-penta-deoxy-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 Et₂O–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; $[a]_D +5.8$ (*c* 1.0 in CHCl₃) (Found: C, 54.16; H, 7.36; N, 2.31. Calc. for C₂₆H₄₁NO₁₃: C, 54.25; H, 7.18; N, 2.43%); ¹H NMR (CDCl₃): 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, OCH₃), 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); ¹³C NMR (CDCl₃): δ_C 173.3, 170.4, 170.3, 170.2, 169.8, and 155.3 (C=O), 79.9 (CMe₃), 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 (CMe₃), 20.8, 20.7, and 20.6 (MeCO); 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 Et₂O–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); $[a]_D -4.0$ (*c* 0.6 in CHCl₃) (Found: C, 52.80; H, 6.76; N, 2.46. Calc. for C₂₄H₃₇NO₁₃: C, 52.64; H, 6.81; N, 2.56%); ¹H NMR (CDCl₃): 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, OCH₃), 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); ¹³C NMR (CDCl₃): δ_C 175.0, 173.0, 170.7, 170.3, 169.7, 169.5, and 155.5 (C=O), 80.0 (CMe₃), 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 (CMe₃), 27.7 and 27.0 (C-3, C-4), 20.7, and 20.6 (MeCO); 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 cm³) was added 1 M aq. sodium acetate (1.8 cm³) 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 cm³), and extracted with CH₂Cl₂ (2 × 60 cm³). The combined organic phases were dried (Na₂SO₄) 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 CH₃CN); [α]_D +9.0 (*c* 1.0 in CHCl₃) (Found: C, 76.98; H, 7.11. Calc. for C₆₃H₆₈O₁₀: C, 76.80; H, 6.96%); ¹H NMR (CDCl₃) 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, OCH₃), 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 cm³) was added dropwise 1 M aq. H₂SO₄ (2.4 cm³). The solution was stirred at 100 °C for an additional 75 min, then cooled to room temperature, diluted with CH₂Cl₂ (100 cm³), and washed with saturated aq. Na₂CO₃ (5 × 20 cm³). The combined organic phases were dried (Na₂SO₄) and concentrated. A solution of the crude hemiacetal in pyridine (5 cm³) and acetic anhydride (5 cm³) 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 C₆₄H₆₈O₁₁: C, 75.86; H, 6.76%); ¹H NMR (CDCl₃) 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 cm³, 2.4 mmol), activated 4 Å powdered molecular sieves (0.8 g), and anhydrous CH₂Cl₂ (8 cm³) was stirred at room temperature for 15 min, then trimethylsilyl triflate (0.29 cm³, 1.6 mmol) was added dropwise. The suspension was stirred at room temperature for 1 h, then treated with an excess of Et₃N, diluted with CH₂Cl₂, filtered through Celite, and concentrated. The residue was eluted from a column of silica gel with 8 : 1 cyclohexane–AcOEt (containing 5% of CH₂Cl₂) to give **10** (637 mg, 80%) as a white solid; mp 147–148 °C (from cyclohexane); [α]_D +19.0 (*c* 1.0 in CHCl₃) (Found: C, 78.29; H, 7.01. Calc. for C₆₅H₇₀O₉: C, 78.44; H, 7.09%); ¹H NMR (CDCl₃) 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, PhCH₂), 4.90 (s, 2 H, PhCH₂), 4.87 and 4.63 (2 d, 2 H, *J* 10.8, PhCH₂), 4.84 and 4.62 (2 d, 2 H, *J* 10.7, PhCH₂), 4.84 and 4.59 (2 d, 2 H, *J* 11.0, PhCH₂), 4.72 and 4.65 (2 d, 2 H, *J* 11.8, PhCH₂), 4.62 and 4.52 (2 d, 2 H, *J* 12.2, PhCH₂); 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 vinylloxazolidine **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 C₇₅H₈₇NO₁₂: C, 75.41; H, 7.34; N, 1.17%); ¹H NMR (CDCl₃) 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 × CH₃), 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; [α]_D +36.2 (*c* 0.8 in CHCl₃) (Found: C, 56.07; H, 7.21; N, 1.88. Calc. for C₄₀H₆₁NO₉: C, 55.87; H, 7.15; N, 1.63%); ¹H 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 (dd, 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 × CH₃), 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 ¹H NMR analysis. ¹H NMR (CDCl₃) 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-octadecionate 13 Me ester

Treatment of a solution of crude acid **13** in 1 : 1 Et₂O–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; [α]_D +29.8 (*c* 0.9 in CHCl₃) (Found: C, 54.11; H, 7.00; N, 1.51. Calc. for C₃₈H₅₇NO₂₀: C, 53.83; H, 6.78; N, 1.65%); ¹H NMR (CDCl₃): 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, OCH₃), 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); ¹³C NMR (CDCl₃): δ_C 173.0, 170.6, 170.3, 170.2, 169.5, and 155.3 (C=O), 79.8 (CMe₃), 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 (CMe₃), 20.7 (MeCO); MALDI-TOF MS (847.9): *m/z*, 870.6 (M + Na), 886.6 (M + K).

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