Synthesis of α- and β-D-(1→6)-*C*-Disaccharides by Wittig Olefination of Formyl *C*-Glycosides with Glycopyranose 6-Phosphoranes

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The synthesis of (1→6)-*C*-disaccharides by Wittig condensation of formyl *C*-glycofuranosides and pyranosides with galacto- and glucopyranose 6-phosphoranes is described herein. The method involves the coupling of the sugar aldehydes with the ylides and the reduction of the double bond of the resulting sugar alkenes, in most of the cases by catalytic hydrogenation. The reduction with nickel boride or diimide is employed in some special cases. *O*-Benzyl protective groups are removed by catalytic hydrogenation either in the course of the reduction of the double bond or in a subsequent step, while *O*-isopropylidene groups are cleaved by treatment with Amberlite IR-120. In this way, eight free β-D-(1→6)-*C*-disaccharides have been prepared in 26−61% overall yield starting from β-linked formyl *C*-glycosides. These include *C*-linked analogues of the biologically active disaccharides allolactose (Galβ1,6Glc), gentiobiose (Glcβ1,6Glc), and *N*-acetylamino disaccharides (GalNHAcβ1,6Gal and GalNHAcβ1,6Glc). Moreover, the synthesis of two α-D-(1→6)-*C*-disaccharides is described from formyl *C*-furanosides. The limiting condition of the synthesis of these stereoisomers is the configurational instability of the α-linked formyl *C*-glycosides under the basic conditions of the Wittig olefination.

Introduction

The coupling of two or more monosaccharides by the stereoselective formation of *O*- or *C*-glycosidic linkage is a fundamental process in carbohydrate chemistry[1] and a key operation in numerous totally synthetic routes to biologically active natural products and their analogues.[2] Owing to intense work over the years, several methods are available that permit the synthesis of oxygen-linked disaccharides and trisaccharides (*O*-glycosides) of either aldoses and ketoses in good yield and high stereocontrol at the anomeric center.[1,3] Various approaches have been also developed in more recent times toward the synthesis of carbon-linked isosteres (*C*-glycosides) of naturally occurring *O*-glycosides and structurally related analogues.[4,5] The main purpose is to create stable carbohydrate mimics that may serve as glycosidase and glycosyltransferase inhibitors[6] and as models for the study of carbohydrate recognition in biological systems.[7] For the same reasons, suitably tailored *C*-disaccharides and *C*-trisaccharides have been synthesized and their conformational properties have been compared with their *O*-glycosidic counterparts.[8] The most straightforward *C*-glycoside syntheses occur through the coupling of anomeric carbocations, radicals, carbanions, and carbenes with suitable glycosyl partners. In all cases, the main problem consists in the control of the stereochemistry at the anomeric center of the sugar moiety serving as glycosyl donor. A remarkable improvement in this rather difficult task has been recently achieved by Sinaÿ[5a] and Beau[5h] and their co-workers by an intramolecular delivery strategy through ketal- or silaketal-tethered monosaccharides.[9,10] The coupling through the reaction of a carbon-linked anomeric functionality with the desired stereochemistry already in place is an attractive approach to this chemistry. For instance, Martin and Lai have followed this concept in their nitroaldol-based synthesis of one (1→6)-*C*-disaccharide by the use of an anomeric glycosylnitromethane derivative and a C-5 substituted sugar aldehyde.[11] A conceptually similar approach to *C*-disaccharides has been described more recently by others[5m] who, however, employed anomeric *C*-glycosyl aldehydes and nitro sugars for the nitroaldol

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(3) (a) For reviews on classical and improved methods, see: Paulsen, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 155. Schmidt, R. R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 212. Toshima, T.; Tatsuta, K. *Chem. Rev. (Washington, D.C.)* **1993**, *93*, 1503. Boons, G. J. *Tetrahedron* **1996**, *52*, 1095. Boons, G. J. *Contemp. Org. Synth.* **1996**, *3*, 173. (b) For innovative methods, see: Boger, D. L.; Honda, T. *J. Am. Chem. Soc.* **1994**, *116*, 5647. Kondo, H.; Aoki, S.; Ichikawa, Y.; Halcomb, R. L.; Ritzen, H.; Wong, C.-H. *J. Org. Chem.* **1994**, *59*, 864. Nuller, T.; Schneider, R.; Schmidt, R. R. *Tetrahedron Lett.* **1994**, *35*, 4763. Watanabe, Y.; Nakamoto, C.; Yammamoto, S.; Ozaki, S. *Tetrahedron* **1994**, *50*, 6523. Yamanoi, T.; Nakamura, K.; Takeyama, H.; Yanagihara, Y. *Bull. Chem. Soc. Jpn* **1994**, *67*, 1359. Muller, T.; Fernandez-Mayoralas, A.; Martín-Lomas, M. *J. Chem. Soc., Chem. Commun.* **1994**, 775. Lin, C.-C.; Shimazaki, M.; Heck, M.-P.; Aoki, S.; Wang, R.; Kimura, T.; Ritzèn, H.; Takayama, S.; Wu, S.-H.; Weitz-Schmidt, G.; Wong, C.-H. *J. Am. Chem. Soc.* **1996**, *118*, 6826. Capozzi, G.; Dios, A.; Franck, R. W.; Geer, A.; Marzabadi, C.; Menichetti, S.; Nativi, C.; Tamarez, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 777. Marzabadi, C. H.; Franck, R. W. *Chem. Commun.* **1996**, 2651. Fraser-Reid, B. *Acc. Chem. Res.* **1996**, *29*, 57. Liu, K. K.-C.; Danishefsky, S. J. *Chem. Eur. J.* **1996**, *2*, 1359. Dondoni, A.; Marra, A.; Rojo, I.; Scherrmann, M.-C. *Tetrahedron* **1996**, *52*, 3057. Seeberger, P. H.; Beebe, X.; Sukenick, G. D.; Pochapsky, S.; Danishefsky, S. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 491.

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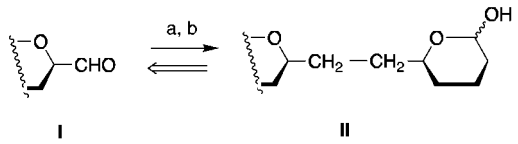
condensation. At the same time, we reported[5n] the synthesis of (1→6)-*C*-disaccharides via Wittig olefination of two model formyl *C*-glycosides with a protected galactose 6-phosphorane followed by reduction of the resulting alkenes. We have now considered the use of various aldehydes (**I**) in this sugar coupling toward ethylene bridged disaccharides (**II**) (Scheme 1) and have obtained results that confirm the efficiency of the method particularly for the assembly through β-linkage. Herein the results of earlier[5n] and recent work are presented in full.

Results and Discussion

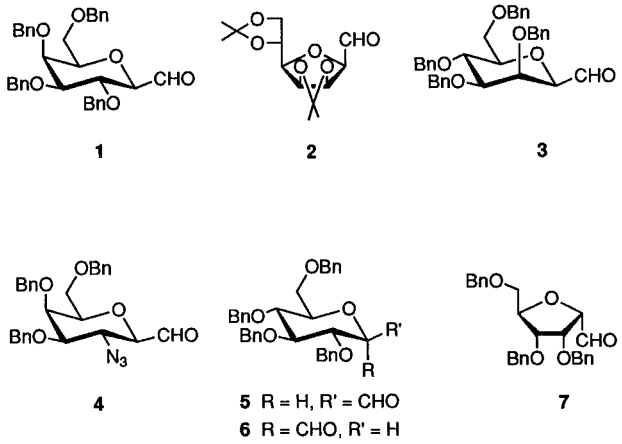
The opportunity for a Wittig olefination approach toward the synthesis of *C*-disaccharides was provided by the ready access to various anomeric formyl *C*-glycopyranosides and furanosides **1**−**7** (Chart 1) through the thiazole-based formylation of sugars that has been recently developed in our laboratory.[12] The synthetic value of this one-carbon extension of carbohydrates[13] stems from both the ease of installation of the thiazole ring at the anomeric carbon by addition of 2-lithiothiazole to sugar lactones and the conversion of the heterocycle into the formyl group under mild and neutral conditions[14] that are tolerant to various common hydroxyl protective groups employed in carbohydrate chemistry. In addition, the method is amenable for the gram-scale synthesis of all formyl *C*-glycosides shown in Chart 1[15] and therefore provides the material for the preparation of *C*-disaccharides on a similar scale.

Scheme 1[a]

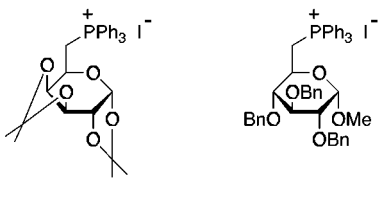


[a] Key: (a) Wittig with sugar ylide; (b) reduction of the alkene.

Chart 1



As the other partner of the Wittig condensation with the aldehydes **1**−**7**, we chose the ylides from the galactopyranose and glucopyranose phosphonium iodides **8** and **9**. The preparation of **8** from the corresponding iodogalactose and the conditions for the generation of the ylide and the reaction with nonanomeric aldehyde sugars were originally described by Secrist and Wu.[16] It has been reported that this ylide is generated without epimerization at C-5, a rather common process for carbohydrate phosphoranes as a consequence of ring opening and reclosure.[17] In a similar fashion to **8**, we have prepared the hitherto unreported phosphonium salt **9** from the known methyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-iodo-α-D-glucopyranoside.[18]



Synthesis of β-D-(1→6)-*C*-Disaccharides. Among the *C*-glycosyl aldehydes shown in Chart 1, the β-linked

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(9) The "stereocontrolled synthesis of disaccharides via the temporary silicon connection" was originally described by Stork, G.; Suh, H. S.; Kim, G. *J. Am. Chem. Soc.* **1991**, *113*, 7054.

(10) For a review of silicon-based methods for tethering, see: Bols, M.; Skrydstrup, T. *Chem. Rev. (Washington, D.C.)* **1995**, *95*, 1253.

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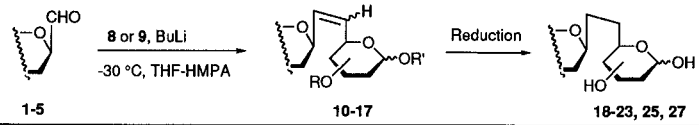
(12) Dondoni, A.; Scherrmann, M.-C. *J. Org. Chem.* **1994**, *59*, 6404.

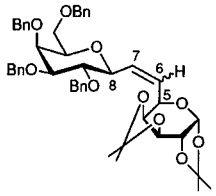
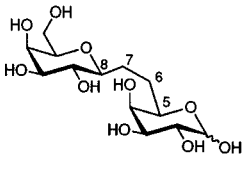
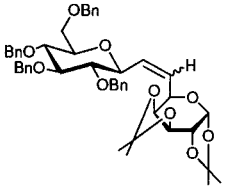
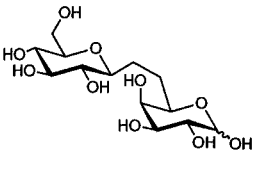
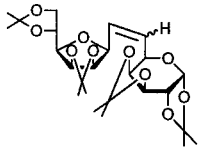
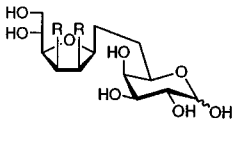
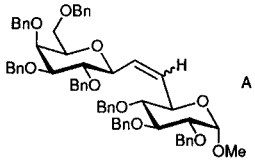
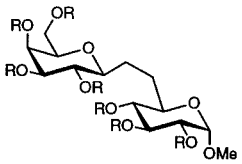
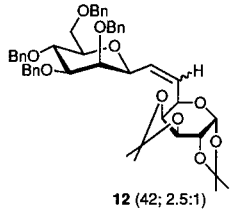
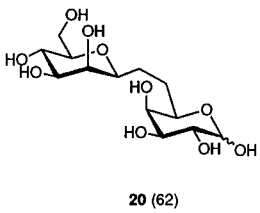
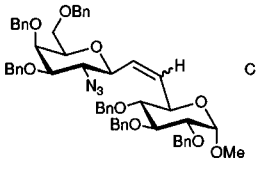
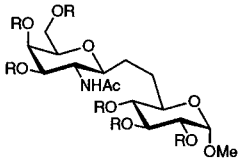
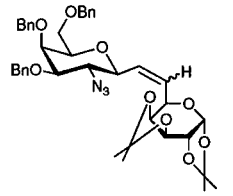
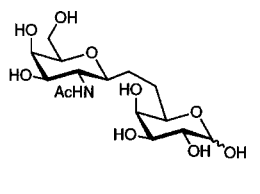
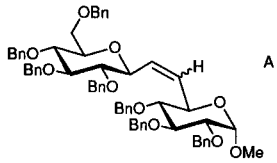
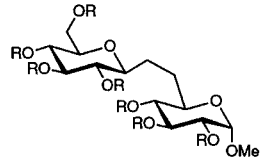
(13) For an account of this and other methods, see: Dondoni, A.; Marra, A. In ref 1b, p 173.

(14) Dondoni, A.; Marra, A.; Perrone, D. *J. Org. Chem.* **1993**, *58*, 275.

Table 1. Condensation of Aldehydes 1−5 with the Ylides from the Phosphonium Salts 8 and 9 and Reduction of the Olefins 10−17 to *C*-Disaccharides 18−23, 25, and 27



1-5 10-17 18-23, 25, and 27

Condensation	Olefin (% yield; *Z* : *E*)	Reduction[a]	*C*-Disaccharide (% yield)	Condensation	Olefin (% yield; *Z* : *E*)	Reduction[a]	*C*-Disaccharide (% yield)
1 + 8	 **10** (76; 1:0)	A	 **18** (81)	5 + 8	 **14** (77; 1:0)	A	 **22** (65)
2 + 8	 **11** (67; 7:3)	A	 **19** R = OH (72)	1 + 9	 **15** (56; 7:3)	A	 Ac_2O/Py → **23** (82) R = H, **24** (70) R = Ac
3 + 8	 **12** (42; 2.5:1)	A	 **20** (62)	4 + 9	 **16** (55; 1:1)	C	 Ac_2O/Py → **25** (60) R = H, **26** (77) R = Ac
4 + 8	 **13** (80; 1:0)	B	 **21** (40)	5 + 9	 **17** (53; 4:1)	A	 Ac_2O/Py → **27** (85) R = H, **28** (67) R = Ac

[a] Method A: (1) H_2, $Pd(OH)_2$, 3 bar; (2) Amberlite IR-120, H_2O, 70 °C. Method B: (1) $NiCl_2 \cdot 6H_2O$ + $NaBH_4$ then Ac_2O, pyridine; H_2, $Pd(OH)_2$, 3 bar; (2) Amberlite IR-120, H_2O, 70 °C. Method C: $NiCl_2 \cdot 6H_2O$ + $NaBH_4$ then Ac_2O, pyridine; H_2, $Pd(OH)_2$, 3 bar.

galactopyranosyl and mannofuranosyl derivatives **1** and **2** were considered as model substrates for the Wittig coupling with the galactose 6-phosphorane from **8**. Following the procedure of Secrist and Wu,[16] the red-colored ylide was generated by the addition of 1 equiv of *n*-BuLi to the salt dissolved in 2:1 THF−HMPA in the presence of activated molecular sieves at −30 °C under nitrogen. A THF solution of the freshly purified aldehyde (1.0−1.5 equiv)[19] was then added, and the reaction mixture was allowed to warm slowly to 0 °C and then to room temperature before workup. Under these conditions, the alkenes **10** and **11** (Table 1) were isolated by chromatography in 76 and 67% yields, respectively. Along with **10** was also obtained the *C*-formyl glycal **30** in 5% yield (Chart 2). The formation of the byproduct **30** may be ascribed to the base-induced β-elimination of the benzyloxy group at C-2 of the aldehyde **1**.[12] On the other hand, reactions carried out in the absence of molecular sieves and at a lower temperature (−60 °C) afforded the alkenes **10** and **11** in much lower yield (ca. 20%). In these cases, the hydrolysis of the unreacted phosphorane[20] produced the sugar diphenylphosphine oxide **29** as the main product (Chart 2). Compound **10** was obtained as a

(15) For instance, the aldehyde **1** is currently prepared in our laboratory in stocks of 5.5−6.0 g (ca. 65% yield) starting from 9.0 g of the tetrabenzyl galactonolactone.

(16) Secrist, J. A., III; Wu, S.-R. *J. Org. Chem.* **1979**, *44*, 1434.

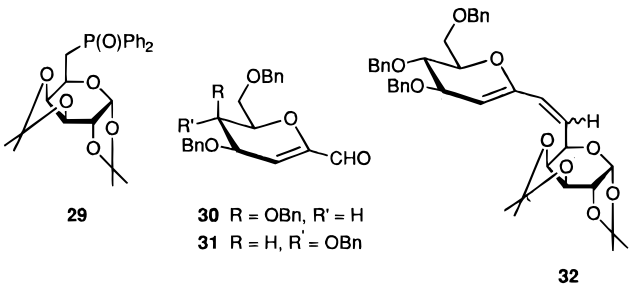
(17) (a) Secrist, J. A., III; Wu, S.-R. *J. Org. Chem.* **1977**, *42*, 4084. (b) For an authorative review on the stereochemistry, mechanism, and synthetic applications of the Wittig olefination, see: Maryanoff, B. E.; Reitz, A. B. *Chem. Rev. (Washington, D.C.)* **1989**, *89*, 863.

(18) Sakairi, N.; Kuzuhara, H. *Tetrahedron Lett.* **1982**, *23*, 5327.

(19) These aldehydes were isolated in the form of hydrates as shown by the complexity of their ^1H NMR spectra in $CDCl_3$ at room temperature. However, a filtration over a short column of silica gel just prior to use gave pure products showing simple NMR spectra.

(20) (a) Warren, S.; Clayden, J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 241. (b) Smith, D. J. H. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. D., Eds.; Pergamon Press Ltd: Oxford, 1979; p 1301.

Chart 2



29 **30** R = OBn, R' = H
31 R = H, R' = OBn
32

single *Z*-isomer ($J_{6,7}$ = 12 Hz),[21] while **11** was a 2.3:1 mixture of (*Z*)- and (*E*)-alkenes. While the stereoselectivity of the Wittig condensation[17b] was unimportant in view of the subsequent reduction of the resulting olefin, the preservation of the original configuration of the two sugar moieties was a key issue in the context of the planned synthesis. This was readily confirmed by ^{1}H NMR analysis. The spectrum of **10** showed a $J_{8,9}$ value of 9.0 Hz, indicating the β-configuration at the anomeric center of one sugar moiety and a $J_{4,5}$ value of 2.0 Hz consistent with the α-D-*galacto* configuration in the other moiety. The individual isomers (*Z*)-**11** and (*E*)-**11** were separated, and in both cases the NMR spectra[22] provided evidence that the original β-D-*manno* configuration was retained in the furanose ring and the α-D-*galacto* configuration was retained in the pyranose ring. Encouraged by these results, the other β-linked *C*-glycopyranosyl aldehydes **3**−**5** were subjected to the Wittig olefination with the ylide from **8**. The reaction of the mannopyranosyl aldehyde **3** afforded the corresponding alkene **12**, although in much lower yield (42%) than **10** and **11**, along with compound **32** as a side product (Chart 2). In agreement with the above isolation of the *C*-formyl glycal **30**, the formation of the minor product **32** is likely to occur via olefination of the corresponding glycal **31** that in turn is easily produced by the aldehyde **3** under basic conditions because of the favorable *trans*-diaxal disposition between the C-1 hydrogen and C-2 *O*-benzyl group. On the other hand, the condensation of the 2-azidogalactopyranosyl **4** and glucopyranosyl derivative **5** afforded the corresponding alkenes **13** and **14** as *Z*-isomers ($J_{6,7}$ = 11.0 and 12.0 Hz, respectively)[21] in good yields (Table 1). Also for these compounds, the integrity of the configuration at C-5 and C-8[23] was demonstrated by ^{1}H NMR analysis as described for compounds **10** and **11**. In the case of compound **12** bearing the mannopyranosyl ring, the β-linkage was supported by the substantial NOE between H-8 and H-12.

Next, we examined the condensation with the glucose 6-phosphorane from **9** to give a new set of (1→6)-*C*-disaccharides bearing the glucopyranosyl moiety at one side. Application of the above ylide generation procedure and the coupling with the sugar aldehydes **1**, **4**, and **5** afforded the corresponding alkenes **15**, **16**, and **17** as mixtures of *E*- and *Z*-isomers in 53−56% yields (Table 1). Unfortunately, the separation of these stereoisomers by column chromatography turned out to be quite difficult, and therefore, the configuration at C-5 and C-8 was confirmed by ^{1}H NMR analysis of the corresponding alkanes (see below).

The second key operation required the reduction of the double bond of the sugar alkenes **10**−**17**. With the exception of compounds **13** and **16** bearing the azido group, all the other alkenes, either as a single isomer or as a mixture of *E*- and *Z*-isomers, were readily reduced by mild-pressure hydrogenation over $Pd(OH)_2$ on carbon. Also, the *O*-benzyl protective groups were removed in this single step while the cleavage of the *O*-isopropylidene groups required the treatment with Amberlite IR-120 at 70 °C.[11b] Under these conditions, the sugar rings remained unaffected, while under different conditions, such as in refluxing 80% acetic acid, the C-1 unprotected sugar moieties equilibrate into furanose and pyranose forms. In this way, the free β-D-(1→6)-*C*-disaccharides **18**−**20**, **22**, **23**, and **27** were isolated in good to excellent yields (Table 1). The conversion of the alkenes **13** and **16** to the corresponding *C*-disaccharides required a different procedure since the above catalytic hydrogenation did not proceed in the presence of the azido group as shown by the recovery of unreacted starting material even after longer reaction time (24 h). Therefore, following an earlier report by Paulsen and Hölck[24] and recent work from this laboratory,[25] we attempted the reduction of the azido function and the alkene double bond in a single step by the use of nickel boride generated *in situ*[26] from $NiCl_2$ hexahydrate and $NaBH_4$. This method appeared to work quite well as shown by TLC analysis of the reaction mixture. Then, after protection of the amino group as *N*-acetyl derivative, the *O*-benzyl and *O*-isopropylidene protective groups were removed by sequential catalytic hydrogenation and treatment with Amberlite IR-120 as described above to give the *N*-acetylamino *C*-disaccharides **21** and **25** in satisfactory overall yields. To confirm the assigned configuration at C-5 and C-8, compounds **23**, **25**, and **27** were converted into the corresponding peracetylated derivatives **24**, **26**, and **28**, which showed highly resolved ^{1}H NMR spectra suitable for structural assignment. In all cases, the $J_{8,9}$ and $J_{4,5}$ values were in the range of 9−11 Hz in agreement with the β-linkage at the anomeric center of one sugar unit and the α-D-*gluco* configuration in the other. These examples also show that the glucose 6-phosphorane generated from **9** reacted with sugar aledehydes without apparent epimerization at C-5.

A brief recapitulation and few comments may help to better evaluate the above results. Eight β-D-(1→6)-*C*-disaccharides have been prepared from *C*-formyl glycosides by an olefination−reduction sequence. The overall yield of isolated products ranged from 26 to 61%. The method is compatible with *O*-benzyl and *O*-isopropylidene protective groups and is tolerant to the presence of the azido group as a substituent. Various β-linked *C*-formyl glycosides with different structural arrays were efficiently employed, and in all cases there were no

(21) In this and in the other cases where only one isomer was obtained, the *Z* configuration was assigned with enough confidence since the observed $J_{6,7}$ values (11−12 Hz) were in the range of cis ethylenic coupling constants. See: Jackman, L. M.; Sternhell, S. In *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*; Barton, D., Ed.; Pergamon Press Ltd: Oxford, 1969; p 301. Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. In *Spectrometric Identification of Organic Compounds*; John Wiley & Sons, Inc.: New York, 1991; p 221.

(22) Both the (*E*)-**11** and (*Z*)-**11** ($J_{6,7}$ = 15.0 and 12.0 Hz, respectively) showed a substantial NOE between H-8 and H-11 and a $J_{4,5}$ value of 2.0 Hz.

(23) For all sugar olefins and the corresponding alkanes the same conventional numbering system outlined for **10** and **18** was adopted; i.e., counting starts from the reducing end of the disaccharide.

(24) Paulsen, H.; Hölck, J.-P. *Carbohydr. Res.* **1982**, *109*, 89.

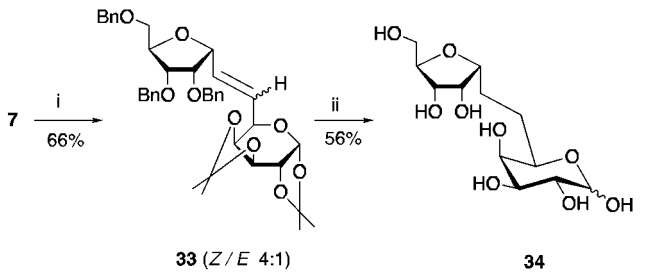
(25) Dondoni, A.; Perrone, D.; Semola, M. T. *J. Org. Chem.* **1995**, *60*, 7927.

(26) Brown, H. C.; Brown, C. A. *J. Am. Chem. Soc.* **1963**, *85*, 1003.

indications that the configuration at the anomeric carbon was changed. The same conclusion was drawn for the configuration at C-5 of the two 6-phosphoranes employed. This method appears to be more practical and to give higher yields than the nitroaldol (Henry) condensation wherein the removal of the hydroxyl and nitro groups in the adduct is a troublesome operation requiring several steps.[5m,11b] In contrast, in our Wittig olefination-based method, the reduction of the ethylenic double bond is a high-yield one-step process that in addition offers the opportunity for the concomitant removal of the hydroxyl protective groups. The higher efficiency of this method is substantiated by the 46% overall yield of isolated methyl *β*-*C*-allolactoside **23** (*C*-Gal*β*1,6Glc) from the aldehyde **1** in comparison to the reported 5% yield through the Henry route.[5m] It has been suggested[5m] that this *C*-analogue of allolactose due to its resistance to enzymatic hydrolysis by *β*-galactosidase could serve as a potent inducer of the *lac* repressor protein and therefore may exert control over the lactose operon. Also, the isomer **22** (*C*-Glc*β*1,6Gal) was isolated in good yield (50% from the aldehyde **5**), while a significantly lower value (17%) was obtained from an earlier synthesis by condensation of peracetylated glucosylnitromethane with a galactose-derived aldehyde.[11b] A satisfactory yield (45%) was also registered for the methyl *β*-*C*-gentiobioside **27** (*C*-Glc*β*1,6Glc), the first example of a *C*-disaccharide described in 1983 by Rouzaud and Sinaÿ.[27] Noteworthy are the hitherto unreported amino *C*-disaccharides **21** (*C*-GalNHAc*β*1,6Gal) and **25** (*C*-GalNHAc*β*1,6Glc), which may bear significant relevance to biological systems wherein 2-amino-2-deoxy sugars are involved such as aminoglycosidic antibiotics[28] and antigenic determinant on cell surfaces.[29] It is in this context that recent reports have stressed the importance of the synthesis of alkyl *C*-glycosides derived from D-glucosamine[30] and D-galactosamine.[31]

Synthesis of α-D-(1→6)-*C*-Disaccharides. The α-linked formyl *C*- glucopyranoside **6** and *C*-ribofuranoside **7** (Chart 1) were at our disposal from previous work.[12] While the configurational stability at C-1 of **7** was supported by the well-known preference for a 1,2-*cis* arrangement in ribofuranoses,[32] the isomerization of the sugar aldehyde **6** to the *β*-linked isomer **5** was likely to occur under the basic conditions[12] of the Wittig olefination. Indeed, upon treatment of **6** with the galactose 6-phosphorane from **8** under the above standard conditions (*n*-BuLi, THF−HMPA, −30 °C), the main isolated products were the alkenes **14** (*Z*-isomer) and **32** (*Z*/*E*, 2:1) in 43% overall yield. In contrast, the condensation of the aldehyde **7** with the same ylide from **8** (Scheme 2) afforded the corresponding sugar alkene **33** (66%) as a 4:1 mixture of *Z*- and *E*-isomers. For these

Scheme 2



33 (*Z*/*E* 4:1) **34**

[a] Key: (i) **8**, *n*-BuLi, −30 °C, THF−HMPA; (ii) *p*-MeC$_6$H$_4$SO$_2$-NHNH$_2$, AcONa, DME−H$_2$O, then H$_2$, Pd(OH)$_2$, 3 atm, then Amberlite IR-120, H$_2$O, 70 °C.

compounds, in agreement with the original α-linkage at C-1 of the furanose ring, no NOE was observed between H-8 and H-11 by irradiation of the latter. The reduction of the double bond of **33** by catalytic hydrogenation over either Pd(OH)$_2$ or Pd was hampered by the elimination of the benzyloxy group from the furanose ring.[33] Instead, a clean reduction was carried out under mild conditions by the use of diimide generated in situ from (*p*-toluenesulfonyl)hydrazine and sodium acetate.[34] Then, the *O*-benzyl and *O*-isopropylidene protective groups were removed in the usual manner to give the final α-linked *C*-disaccharide **34** in 56% isolated yield.

Since recent work from this laboratory has provided access to the α-linked formyl *C*-mannofuranoside diacetonide **39** from the corresponding thiazolyl *C*-glycoside **38**[35] (Scheme 3), the condensation of this aldehyde with the galactose 6-phosphorane from **8** was carried out as well. The reaction afforded the alkene **40** exclusively as *Z*-isomer ($J_{6,7}$ = 11.5 Hz) in 62% yield after purification by chromatography. The α-linkage at C-8 of **40** was easily confirmed by the $J_{8,9}$ value of 1.0 Hz in comparison to the 4.0 Hz of the *β*-linked isomer **11**. Moreover, the α-D-*galacto* configuration of the pyranose ring was proved

(27) Rouzaud, D.; Sinaÿ, P. *J. Chem. Soc., Chem. Commun.* **1983**, 1353.

(28) Umezawa, S. In *Advances In Carbohydrate Chemistry and Biochemistry*; Tipson, R. S., Horton, D., Eds.; Academic Press: London, 1974.

(29) Kabut, E. A. In *Blood and Tissue Antigens*, Aminoff, D., Ed.; Academic Press: New York, 1970.

(30) Hoffmann, M.; Kessler, H. *Tetrahedron Lett.* **1994**, *35*, 6067.

(31) Ayadi, E.; Czernecki, S.; Xie, J. *Chem. Commun.* **1996**, 347. The key reaction in this paper is the addition of alkyllithium reagents to 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-galactonolactone. It is worth pointing out that the original synthesis of the azido sugar lactone and its reaction with a *C*-nucleophile (2-lithiothiazole) described by one of us in a much earlier report (ref 12) were not acknowledged.

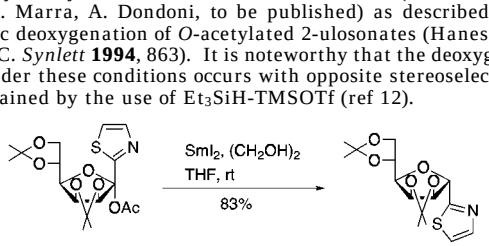
(32) Ohrui, H.; Jones, G. H.; Moffatt, J. G.; Maddox, M. L.; Christensen, A. T.; Byram, S. K. *J. Am. Chem. Soc.* **1975**, *97*, 4602.

(33) In addition to the expected debenzylated *C*-disaccharide **35**, also the deoxy derivative **36** (Gal = galoctopyranoside diacetonide moiety as in **33**) was obtained in a 1:1 ratio (86% overall yield). Compound **36** showed the following data: $[\alpha]_D = -50$ (*c* 0.3, CHCl$_3$); ^{1}H NMR (CD$_3$OD) δ 1.30, 1.32, 1.40, 1.50 (4 × s, 2 × C(CH$_3$)$_2$), 1.41−1.72 (m, 6H, H-6, H-6′, H-7, H-7′, H-9, H-9′), 3.43 (t, 1H, H-10, $J_{10,9} \approx J_{10,11} \approx$ 6.0 Hz), 3.59 (t, 1H, H-12, $J_{12,11} \approx J_{12,12'} \approx$ 4.5 Hz), 3.62−3.70 (m, 2H, H-8, H-11), 3.74−3.80 (m, 2H, H-5, H-12′), 4.16 (dd, 1H, H-4, $J_{4,3}$ = 8.0 Hz, $J_{4,5}$ = 2.0 Hz), 4.31 (dd, 1H, H-2, $J_{2,3}$ = 2.5 Hz, $J_{2,1}$ = 5.0 Hz), 4.59 (dd, 1H, H-3), 5.50 (d, 1H, H-1); ^{13}C NMR (CD$_3$OD) δ 22.8, 24.5, 25.1, 26.3, 31.3, 33.2, 64.6, 68.7, 71.9, 72.3, 73.9, 74.0, 74.4, 76.0, 98.0, 109.6, 110.0.

35 **36**

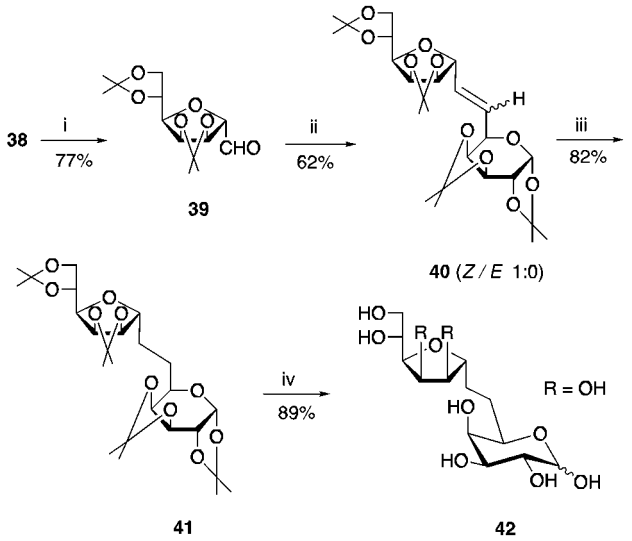
(34) van Tamelen, E. E.; Dewey, R. S. *J. Am. Chem. Soc.* **1961**, *83*, 3729.

(35) The thiazolyl *C*-glycoside **38** (oil, $[\alpha]_D = +22$ (*c* 0.9, CHCl$_3$), ^{1}H NMR (300 MHz, CDCl$_3$) δ 5.31 (s, 1H, H-1)) was obtained in 83% isolated yield by reduction of the ketol acetate **37** (see ref 12) using SmI$_2$ (A. Marra, A. Dondoni, to be published) as described for the anomeric deoxygenation of *O*-acetylated 2-ulosonates (Hanessian, S.; Girard, C. *Synlett* **1994**, 863). It is noteworthy that the deoxygenation of **37** under these conditions occurs with opposite stereoselectivity to that obtained by the use of Et$_3$SiH-TMSOTf (ref 12).



37 **38**

Scheme 3



[a] Key: (i) MeOTf, MeCN, then $NaBH_4$, MeOH, then $HgCl_2$, MeCN−H_2O; (ii) **8**, *n*-BuLi, −30 °C, THF−HMPA; (iii) H_2, $Pd(OH)_2$, 3 atm; (iv) Amberlite IR-120, H_2O, 70 °C.

by the $J_{4,5}$ value of 2.0 Hz. The reduction of the double bond of **40** was carried out by catalytic hydrogenation over $Pd(OH)_2$ without any appreciable side reaction to give **41** (82%), which upon treatment with Amberlite IR-120 afforded the free α-D-(1→6) *C*-disaccharide **42** in 89% yield.

Conclusion

Collectively, these examples show that β-linked formyl *C*-glycosides can be effectively employed in a Wittig olefination route to β-D-(1→6)-*C*-disaccharides. This successful approach relies on the fact that the stereochemistry of the formyl group already in place in β-linked sugar aldehydes is unaffected by the reaction conditions. Since pyranose 6-phosphoranes may be prepared from other sugars, this expeditious method should constitute a general entry to various (1→6)-*C*-disaccharide linkages. Of course, the availability of furanose 5-phosphoranes[17a] may extend the scope of the synthesis to β-(1→5)-*C*-disaccharides. On the other hand, the configurational instability of α-linked formyl *C*-glycosides does not permit the same wide scope synthesis of α-D-(1→6)-*C*-disaccharides. Nevertheless, once stable sugar aldehydes are available such as the α-linked formyl *C*-ribofuranoside **7** and mannofuranoside **39**, the corresponding *C*-disaccharide linkage can be effectively constructed.

Experimental Section

All moisture-sensitive reactions were performed under a nitrogen atmosphere using oven-dried glassware. All solvents were dried over standard drying agents[36] and freshly distilled prior to use. Commercially available powdered 4-Å molecular sieves (50 μm average particle size) were used without further activation. Flash chromatography[37] was performed on silica gel 60 (230−400 mesh). Reactions were monitored by TLC on silica gel 60 F_{254} with detection by charring with sulfuric acid. Melting points were determined with a capillary apparatus and are uncorrected. Optical rotations were measured at 20 ± 2 °C in $CHCl_3$ unless stated otherwise. ^{1}H (300 MHz) and ^{13}C NMR (75 MHz) were recorded at room temperature for $CDCl_3$ solutions, unless otherwise specified. Assignments were aided by homo- and heteronuclear two-dimensional experiments. Stocks of crude sugar aldehydes **1**−**7** were prepared as described[12] and stored at −20 °C without any apparent decomposition for several days. The required amount of aldehyde for immediate reaction was purified by elution through a short column of silica gel with 1:2 ethyl acetate−cyclohexane. The phosphonium iodide **8** was prepared on a multigram scale (10 g) as described[16] and stored at −20 °C.

Methyl 2,3,4-Tri-*O*-benzyl-6-deoxy-6-(triphenylphosphonio)-α-D-glucopyranoside iodide (9). A degassed solution of methyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-iodo-α-D-glucopyranoside[18] (1.9 g, 3.3 mmol) and triphenylphosphine (914 mg; 3.5 mmol) in tetramethylenesulfolane (2.5 mL) was heated under nitrogen at 120 °C for 3 days. The mixture was diluted with CH_2Cl_2 (20 mL), refluxed with activated carbon (1 g) for 10 min, and filtered over Celite. The resulting yellow solution was dropped slowly into diethyl ether (1.2 L) to give a slightly yellow precipitate, which was filtered, immediately washed with diethyl ether (3 × 50 mL), and dried in vacuo to give 2.5 g (90%) of the phosphonium iodide **9** as a slightly yellow solid: mp 178−179 °C (from chloroform−diethyl ether); $[\alpha]_D$ = +62 (*c* 0.8, CH_3OH); ^{1}H NMR δ 2.62 (s, 3H, OCH_3), 3.47 (m, 1H, H-5), 3.61 (dd, H-2, $J_{2,1}$ = 3.5 Hz, $J_{2,3}$ = 9.5 Hz), 3.80−3.91 (m, 3H, H-3, H-4, H-6), 4.40 (d, 1H, H-1), 4.51−4.63 (m, 1H, H-6), 4.62 and 4.76 (2d, 2H, *J* = 12.0 Hz), 4.79 and 4.95 (2d, 2H, *J* = 12.0 Hz), 5.05 and 5.10 (2d, 2H, *J* = 12.0 Hz), 7.20−7.40 (m, 15H, H_{arom}), 7.55−7.80 (m, 15H, H_{arom}). Anal. Calcd for $C_{46}H_{46}IO_5P$: C, 66.03, H, 5.54. Found: C, 66.00, H, 5.70.

(*Z*)-8,12-Anhydro-9,10,11,13-tetra-*O*-benzyl-6,7-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-L-*manno*-D-*galacto*-tridec-6-eno-1,5-pyranose (10). A mixture of the phosphonium salt **8** (350 mg; 0.55 mmol), activated 4-Å powdered molecular sieves (480 mg), anhydrous THF (2 mL), and HMPA (1 mL) was cooled to −30 °C. To this suspension was added *n*-BuLi (346 μL, 0.55 mmol of 1.6 M solution in hexane), followed by the aldehyde **1** (0.55 mmol; 150 mg) in anhydrous THF (1.2 mL). The suspension was allowed to slowly warm to room temperature (about 2.5 h), maintained for an additional 30 min at the same temperature, and then filtered through Celite. The filtrate was diluted with diethyl ether (20 mL), and the organic layer was washed with water (10 mL), 5% sodium thiosulfate solution (10 mL) and water (10 mL), dried (Na_2SO_4), and concentrated. Flash chromatography (4:1 cyclohexane−ethyl acetate) of the residue gave 325 mg (76%) of the oily olefin **10** (only *Z*-isomer): $[\alpha]_D$ = −5 (*c* 0.4); ^{1}H NMR δ 1.07, 1.25, 1.36, 1.43 (4 × s, 12H, 2 × $C(CH_3)_2$), 3.62 (m, 4H, H-10, H-12, H-13, H-13′), 3.66 (dd, 1H, H-4, $J_{4,3}$ = 8.0 Hz, $J_{4,5}$ = 2.0 Hz), 3.70 (t, 1H, H-9, $J_{9,8} \approx J_{9,10} \approx$ 9.0 Hz), 3.97 (d, 1H, H-11, $J_{11,10}$ = 3.0 Hz), 4.00 (dd, 1H, H-8, $J_{8,7}$ = 7.5 Hz), 4.16 (dd, 1H, H-2, $J_{2,1}$ = 5.0 Hz, $J_{2,3}$ = 2.2 Hz), 4.21 (dd, 1H, H-3, $J_{3,2}$ = 2.2 Hz, $J_{3,4}$ = 8.0 Hz), 4.34 and 4.42 (2d, 2H, *J* = 11.0 Hz, OCH_2Ph), 4.56 and 4.85 (2d, 2H, *J* = 11.0 Hz, OCH_2Ph), 4.57 and 4.87 (2d, 2H, *J* = 11.0 Hz, OCH_2Ph), 4.59 (dd, 1H, H-5, $J_{5,4}$ = 2.0 Hz, $J_{5,6}$ = 8.0 Hz), 4.60 and 4.68 (2d, 2H, *J* = 11.0 Hz, OCH_2Ph), 5.44 (d, 1H, H-1), 5.66 (dd, 1H, H-7, $J_{7,6}$ = 11.0 Hz), 5.74 (dd, 1H, H-6), 7.15−7.30 (m, 20H, H_{arom}); ^{13}C NMR δ 24.5, 25.2, 26.4, 26.5, 66.7, 70.9, 71.1, 72.0, 73.6, 74.8, 75.2, 75.3, 75.6, 76.7, 77.7, 79.8, 85.0, 97.1, 108.5, 109.2, 127.2, 128.7, 127.7−128.7, 138.8, 139.1, 139.2, 139.4. Anal. Calcd for $C_{47}H_{54}O_{10}$: C, 72.47, H, 6.99. Found: C, 72.23, H, 7.18.

(*Z*/*E*)-8,11-Anhydro-1,2:3,4:9,10:12,13-tetra-*O*-isopropylidene-6,7-dideoxy-α-D-*glycero*-D-*galacto*-D-*galacto*-tridec-6-eno-1,5-pyranose (11). The phosphonium salt **8** (350 mg; 0.55 mmol) was reacted with the aldehyde **2** (150 mg; 0.55 mmol) as described for the preparation of **10** to afford, after chromatography (5:2 cyclohexane−ethyl acetate), the olefin **11** (184 mg; 67%) as a mixture of *E* and *Z* isomers in a 3:7 ratio. Pure samples of these compounds were obtained by flash chromatography (4:1 cyclohexane−ethyl acetate). Eluted first was (*Z*)-**11** as an oil: $[\alpha]_D$ = −32 (*c* 0.2); ^{1}H NMR (C_6D_6) δ 1.06, 1.14, 1.18, 1.32, 1.40, 1.47, 1.48, 1.50 (8 × s, 24H, 4 × $C(CH_3)_2$), 3.38 (dd, 1H, H-11, $J_{11,10}$ = 3.5 Hz, $J_{11,12}$ = 8.0 Hz),

(36) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, 1988.

(37) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

4.09 (dd, 1H, H-4, $J_{4,3}$ = 8.0 Hz, $J_{4,5}$ = 2.0 Hz), 4.11−4.12 (m, 2H, H-13, H-13′), 4.17 (dd, 1H, H-2, $J_{2,1}$ = 5.0 Hz, $J_{2,3}$ = 2.0 Hz), 4.37 (ddd, 1H, H-8, $J_{8,6}$ = 1.0 Hz, $J_{8,7}$ = 6.5 Hz, $J_{8,9}$ = 4.0 Hz), 4.40 (dd, 1H, H-9, $J_{9,10}$ = 6.0 Hz), 4.48 (dd, 1H, H-10), 4.53 (dd, 1H, H-3), 4.63 (dt, H-12, $J_{12,13} \approx J_{12,13'} \approx$ 6.0 Hz), 4.82 (dd, 1H, H-5, $J_{5,6}$ = 6.4 Hz), 5.56 (d, 1H, H-1), 5.98 (ddd, 1H, H-7, $J_{7,5}$ = 1.0 Hz, $J_{7,6}$ = 12.0 Hz), 6.06 (ddd, 1H, H-6); ^{13}C NMR δ 24.3, 24.7, 24.9, 25.2, 25.8, 25.9, 26.3, 27.0, 65.1, 67.2, 70.2, 70.8, 72.9, 73.4, 78.8, 80.8, 81.9, 82.7, 96.4, 108.4, 109.2, 109.3, 112.6, 127.5, 128.9. Anal. Calcd for $C_{25}H_{38}O_{10}$: C, 60.23; H, 7.68. Found: C, 59.74, H, 7.67.

Eluted second was (*E*)-**11** as an oil: $[\alpha]_D$ = −36 (*c* 0.2); ^{1}H NMR (C_6D_6) δ 1.13, 1.15, 1.16, 1.32, 1.40, 1.48, 1.50 (7 × s, 24H, 4 × $C(CH_3)_2$), 3.32 (dd, 1H, H-11, $J_{11,10}$ = 3.5 Hz, $J_{11,12}$ = 7.0 Hz), 3.60 (dd, 1H, H-8, $J_{8,7}$ = 6.0 Hz, $J_{8,9}$ = 4.0 Hz), 3.91 (dd, 1H, H-4, $J_{4,3}$ = 8.0 Hz, $J_{4,5}$ = 2.0 Hz), 4.02 (dd, 1H, H-9, $J_{9,10}$ = 6.0 Hz), 4.05 (dd, 1H, H-13, $J_{13,12}$ = 6.0 Hz, $J_{13,13'}$ = 8.0 Hz), 4.14 (dd, 1H, H-2, $J_{2,1}$ = 5.0 Hz, $J_{2,3}$ = 2.0 Hz), 4.18 (dd, H-13′, $J_{13',12}$ = 5.7 Hz, $J_{13',13}$ = 8.0 Hz), 4.26 (dd, 1H, H-10), 4.43 (dd, 1H, H-3), 4.52 (dd, 1H, H-5, $J_{5,6}$ = 5.7 Hz), 4.56 (dt, 1H, H-12), 6.24 (2H, H-6, H-7, $J_{6,7}$ = 15.3 Hz, $J_{8,7}$ = 6.0 Hz); ^{13}C NMR δ 24.3, 24.6, 24.9, 25.1, 25.8, 26.0, 26.1, 27.0, 67.1, 68.5, 70.3, 70.8, 73.1, 73.3, 76.0, 80.8, 81.8, 82.5, 96.4 108.5, 109.2, 112.5, 127.6, 131.5. Anal. Calcd for $C_{25}H_{38}O_{10}$: C, 60.23; H, 7.68. Found: C, 60.49; H, 7.42.

(*Z*/*E*)-8,12-Anhydro-9,10,11,13-tetra-*O*-benzyl-6,7-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-D-*galacto*-tridec-6-eno-1,5-pyranose (12). The phosphonium salt **8** (330 mg; 0.52 mmol) was reacted with the aldehyde **3** (287 mg; 0.52 mmol) as described for the preparation of **10**. Flash chromatography (5:1 cyclohexane−ethyl acetate) of the residue gave first a 1:2 mixture of (*E*)-**32** and (*Z*)-**32** (70 mg, 20%). Flash chromatography (30:1 toluene−acetone) afforded almost pure samples of these isomers. (*Z*)-**32**: ^{1}H NMR (C_6D_6) δ 1.10, 1.15, 1.50, 1.55 (4 × s, 12H, 2 × $C(CH_3)_2$), 3.65 (dd, 1H, H-13, $J_{13,12}$ = 7.5 Hz, $J_{13,13'}$ = 10.0 Hz), 3.77 (dd, 1H, H-11, $J_{11,12}$ = 9.0 Hz, $J_{11,10}$ = 6.5 Hz), 3.92 (dd, 1H, H-13′, $J_{13',12}$ = 2.5 Hz), 4.15 (ddd, 1H, H-12), 4.21 (m, 2H, H-2, H-10), 4.25 and 4.50 (2 × d, 2H, *J* = 12.0 Hz, OCH_2Ph), 4.34 and 4.41 (2 × d, 2H, *J* = 12.0 Hz, OCH_2Ph), 4.40 (m, 1H, H-3); 4.41 and 4.77 (2 × d, 2H, *J* = 12.0 Hz, OCH_2Ph), 4.90 (m, 2H, H-4, H-9), 5.55 (d, 1H, H-5, $J_{5,6}$ = 7.0 Hz), 5.64 (d, 1H, H-7, $J_{6,7}$ = 12.0 Hz), 5.65 (d, 1H, H-1, $J_{1,2}$ = 5.0 Hz), 5.97 (dd, 1H, H-6); 7.00−7.35 (m, 15H, H_{arom}); ^{13}C NMR (C_6D_6) δ 24.6, 25.1, 26.5, 26.7, 67.0, 70.2, 70.8, 71.6, 73.3, 73.5, 74.7, 75.1, 77.7, 78.0, 97.1, 103.0, 108.2, 108.8, 123.1, 126.9−128.5, 138.9, 139.1, 153.1. (*E*)-**32**: ^{1}H NMR δ 1.34, 1.35, 1.45, 1.52 (4 × s, 12H, 2 × $C(CH_3)_2$), 3.82 (dd, 1H, H-13′, $J_{13,12}$ = 3.0 Hz, $J_{13,13'}$ = 11.0 Hz), 3.86 (dd, 1H, H-13, $J_{13,12}$ = 5.5 Hz), 3.92 (dd, 1H, H-11, $J_{11,10}$ = 6.5 Hz, $J_{11,12}$ = 9.0 Hz), 4.40 (ddd, 1H, H-12), 4.25 (dd, 1H, H-4, $J_{4,3}$ = 8.0 Hz, $J_{4,5}$ = 2.0 Hz), 4.32 (dd, 1H, H-10, $J_{10,9}$ = 3.0 Hz), 4.33 (dd, 1H, H-2, $J_{2,1}$ = 5.0 Hz, $J_{2,3}$ = 2.0 Hz), 4.40 (d, 1H, H-5, $J_{5,6}$ = 5.0 Hz), 4.56 and 4.63 (2 × d, 2H, *J* = 12.0 Hz, OCH_2Ph), 4.60 and 4.64 (2 × d, 2H, *J* = 12.0 Hz, OCH_2-Ph), 4.65 (dd, 1H, H-3), 4.68 and 4.85 (2 × d, 2H, *J* = 12.0 Hz, OCH_2Ph), 4.95 (d, 1H, H-9), 5.60 (d, 1H, H-1), 6.10 (d, 1H, H-7, $J_{7,6}$ = 15.0 Hz), 6.20 (dd, 1H, H-6), 7.20−7.40 (m, 15H, H_{arom}); ^{13}C NMR ($CDCl_3$) δ 24.3, 24.9, 26.0, 26.1, 67.9, 68.5, 70.2, 70.6, 73.1, 73.4, 73.7, 74.4, 77.2, 96.5, 101.1, 108.4, 109.2, 126.6, 127.2−128.4, 151.3.

Eluted second was a 1:2.5 mixture of (*E*)-**12** and (*Z*)-**12** (170 mg, 42%). Flash chromatography (30:1 toluene−acetone) gave pure samples of these isomers. Eluted first was (*Z*)-**12** as an oil: $[\alpha]_D$ = −27 (*c* 0.4); ^{1}H NMR δ 1.25, 1.30, 1.45, 1.46 (4 × s, 12H, 2 × $C(CH_3)_2$), 3.47 (ddd, 1H, H-12, $J_{12,11}$ = 9.5 Hz, $J_{12,13}$ = 6.0 Hz, $J_{12,13'}$ = 10.0 Hz), 3.59 (dd, 1H, H-10, $J_{10,9}$ = 2.6 Hz, $J_{10,11}$ = 9.5 Hz), 3.68 (dd, 1H, H-13, $J_{13,13'}$ = 11.0 Hz), 3.76 (dd, 1H, H-13′), 3.80 (d, 1H, H-9), 3.82 (t, 1H, H-11), 4.19 (d, 1H, H-8, $J_{8,7}$ = 5.8 Hz), 4.23 (dd, 1H, H-4, $J_{4,3}$ = 8.0 Hz, $J_{4,5}$ = 2.0 Hz), 4.28 (dd, 1H, H-2, $J_{2,1}$ = 5.0 Hz, $J_{2,3}$ = 2.5 Hz), 4.50 (dd, 1H, H-3), 4.53 and 4.89 (2 × d, 2H, *J* = 10.5 Hz, OCH_2Ph), 4.62 and 4.68 (2 × d, 2H, *J* = 12.0 Hz, OCH_2Ph), 4.75 (dd, 1H, H-5, $J_{5,6}$ = 6.8 Hz), 4.76 and 4.84 (2 × d, 2H, *J* = 12.0 Hz, OCH_2Ph), 5.53 (d, 1H, H-1), 5.61 (dd, 1H, H-6, $J_{6,7}$ = 12.0 Hz), 5.72 (dd, 1H, H-7), 7.10−7.42 (m, 20H, H_{arom}); ^{13}C NMR (C_6D_6) δ 24.5, 25.2, 26.4, 26.5, 66.7, 70.9, 71.1, 72.0, 73.6, 74.8, 75.2, 75.3, 75.6, 76.7, 77.7, 79.8, 85.0, 97.1, 108.5, 109.0, 127.2, 128.7, 127.7−128.7, 138.8, 139.1, 139.2, 139.4. Anal. Calcd for $C_{47}H_{54}O_{10}$: C, 72.47, H, 6.99. Found: C, 71.73, H, 7.20.

Eluted second was (*E*)-**12** as a syrup: $[\alpha]_D$ = −47 (*c* 0.4); ^{1}H NMR δ 1.26, 1.30, 1.35, 1.45 (4 × s, 12H, 2 × $C(CH_3)_2$), 3.42 (ddd, 1H, H-12, $J_{12,11}$ = 10.0 Hz, $J_{12,13}$ = 5.0 Hz, $J_{12,13'}$ = 2.0 Hz), 3.63 (dd, 1H, H-10, $J_{10,9}$ = 3.0 Hz, $J_{10,11}$ = 10.0 Hz), 3.76 (m, 2H, H-13, H-13′), 3.83 (d, 1H, H-9), 3.94 (d, 1H, H-8, $J_{8,7}$ = 5.0 Hz), 3.95 (t, 1H, H-11), 4.22 (dd, 1H, H-4, $J_{4,3}$ = 8.0 Hz, $J_{4,5}$ = 2.0 Hz), 4.32 (dd, 1H, H-2, $J_{2,1}$ = 5.0 Hz, $J_{2,3}$ = 3.0 Hz), 4.34 (d, 1H, H-5, $J_{5,6}$ = 5.0 Hz), 4.56 and 4.89 (2 × d, 2H, *J* = 10.0 Hz, OCH_2Ph), 4.57 and 4.66 (2 × d, 2H, *J* = 12.0 Hz, OCH_2Ph), 4.61 (dd, 1H, H-3), 4.62 and 4.65 (2 × d, 2H, *J* = 12.0 Hz, OCH_2Ph), 4.78 and 4.85 (2 × d, H, *J* = 12.0 Hz, OCH_2-Ph), 5.59 (d, 1H, H-1), 5.91 (dd, 1H, H-6, $J_{6,7}$ = 16.0 Hz), 6.00 (dd, 1H, H-7), 7.05−7.40 (m, 20H, H_{arom}); ^{13}C NMR (C_6D_6) δ 24.3, 24.9, 26.3, 69.0, 70.3, 71.0, 71.3, 71.9, 73.7, 73.8, 75.1, 75.2, 75.5, 77.6, 78.9, 80.2, 85.0, 97.0, 108.3, 109.1, 127.2, 131.7, 127.5−128.3, 139.3, 139.7. Anal. Calcd for $C_{47}H_{54}O_{10}$: C, 72.47, H, 6.99. Found: C, 72.07, H, 7.44.

(*Z*)-8,12-Anhydro-9-azido-10,11,13-tri-*O*-benzyl-6,7,9-trideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-L-*manno*-D-*galacto*-tridec-6-eno-1,5-pyranose (13). The phosphonium salt **8** (209 mg; 0.33 mmol) was reacted with the aldehyde **4** (161 mg; 0.33 mmol) as described for the preparation of **10** to afford, after flash chromatography (4:1 cyclohexane−ethyl acetate), 192 mg (80%) of the olefin **13**, exclusively in the form of the *Z*-isomer, as a syrup: $[\alpha]_D$ = −20 (*c* 0.5); ^{1}H NMR (C_6D_6) δ 1.07, 1.15, 1.50, 1.55 (4 × s, 12H, 2 × $C(CH_3)_2$), 3.32 (dd, 1H, H-10, $J_{10,9}$ = 10.0 Hz, $J_{10,11}$ = 3.0 Hz), 3.49 (dd, 1H, H-13′, $J_{13',12}$ = 5.0 Hz, $J_{13',13}$ = 8.0 Hz), 3.58 (dd, 1H, H-12, $J_{12,13}$ = 8.0 Hz), 3.74 (t, 1H, H-13), 3.88 (t, 1H, H-9, $J_{9,8}$ = 10.0 Hz), 3.92 (1H, H-11), 4.14−4.26 (m, 4H, H-8, H-2, OCH_2Ph), 4.29 (dd, 1H, H-4, $J_{4,3}$ = 8.0 Hz, $J_{4,5}$ = 2.0 Hz), 4.32 and 4.38 (2d, 2H, *J* = 12.0 Hz, OCH_2Ph), 4.96 (dd, 1H, H-5, $J_{5,6}$ = 8.0 Hz), 5.55 (d, 1H, H-1, $J_{2,1}$ = 5.0 Hz), 5.64 (ddd, 1H, H-7, $J_{7,5}$ = 1.0 Hz, $J_{7,6}$ = 11.0 Hz, $J_{7,8}$ = 8.0 Hz), 6.18 (ddd, 1H, H-6, $J_{6,8}$ = 2.0 Hz), 7.05−7.40 (m, 15H, H_{arom}); ^{13}C NMR (C_6D_6) δ 23.5, 24.0, 25.4, 25.5, 62.7, 63.7, 67.8, 70.5, 70.8, 71.9, 72.6, 72.8, 74.2, 75.3, 76.3, 82.2, 96.2, 107.3, 108.3, 126.2−127.7 129.5, 129.9, 137.3, 137.7, 138.2. Anal. Calcd for $C_{40}H_{47}N_3O_{10}$: C, 67.30, H, 6.64, N, 5.89. Found: C, 67.46, H, 6.84, N, 5.97.

(*Z*)-8,12-Anhydro-9,10,11,13-tetra-*O*-benzyl-6,7-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*gulo*-D-*galacto*-tridec-6-eno-1,5-pyranose (14). The phosphonium salt **8** (209 mg; 0.33 mmol) was reacted with aldehyde **5** (183 mg; 0.33 mmol) as described for the preparation of **10** to afford, after flash chromatography (4:1 cyclohexane−ethyl acetate), 198 mg (77%) of the olefin **14** exclusively as *Z*-isomer, as a syrup: $[\alpha]_D$ = +5 (*c* 0.5); ^{1}H NMR (C_6D_6) δ 1.06, 1.10, 1.50, 1.64 (4 × s, 12H, 2 × $C(CH_3)_2$), 3.33 (t, H, H-9, $J_{9,8} \approx J_{9,10} \approx$ 10.0 Hz), 3.51 (ddd, 1H, H-12, $J_{12,11}$ = 9.0 Hz, $J_{12,13}$ = 1.0 Hz, $J_{12,13'}$ = 3.5 Hz), 3.56 (dd, 1H, H-13, $J_{13,13'}$ = 11.0 Hz), 3.70 (dd, 1H, H-13′), 3.79 (t, 1H, H-10, $J_{10,11}$ = 9.0 Hz), 3.92 (t, 1H, H-11), 3.91 (dd, 1H, H-4, $J_{4,3}$ = 8.0 Hz, $J_{4,5}$ = 2.0 Hz, $J_{4,3}$ = 8.0 Hz), 4.17 (dd, 1H, H-2, $J_{2,1}$ = 5.0 Hz, $J_{2,3}$ = 2.5 Hz), 4.34 and 4.47 (2 × d, 2H, *J* = 12.0 Hz, OCH_2Ph), 4.39 (dd, 1H, H-3, $J_{3,4}$ = 8.0 Hz), 4.40 (t, 1H, H-8, $J_{8,7}$ = 9.0 Hz), 4.51 and 4.74 (2 × d, 2H, *J* = 11.0 Hz, OCH_2Ph), 4.72 and 4.92 (2 × d, 2H, *J* = 11.0 Hz, OCH_2Ph), 4.91 (s, 2H, OCH_2Ph), 4.98 (d, 1H, H-5, $J_{5,6}$ = 8.0 Hz), 5.54 (d, 1H, H-1), 5.76 (dd, 1H, H-7, $J_{7,6}$ = 12.0 Hz), 6.21 (dd, 1H, H-6), 7.00−7.32 (m, 20H, H_{arom}); ^{13}C NMR (C_6D_6) δ 24.4, 24.9, 26.3, 26.5, 64.5, 69.3, 70.7, 71.5, 73.5, 73.6, 75.1, 75.6, 76.7, 78.6, 79.7, 82.9, 87.4, 97.2, 108.3, 109.0, 127.2−128.3, 130.1, 131.8, 139.1, 139.2, 139.3, 139.4. Anal. Calcd for $C_{47}H_{54}O_{10}$: C, 72.47, H, 6.99. Found: C, 72.17, H, 6.93.

(*Z*/*E*)-Methyl 8,12-Anhydro-2,3,4,9,10,11,13-hepta-*O*-benzyl-6,7-dideoxy-α-D-*glycero*-L-*manno*-D-*gluco*-tridec-6-enopyranoside (15). A mixture of phosphonium salt **9** (226 mg; 0.27 mmol), activated 4-Å powdered molecular sieves (240 mg), anhydrous THF (1 mL), and HMPA (0.5 mL) was cooled to −30 °C. To this suspension was added *n*-BuLi (169 μL, 0.27 mmol of 1.6 M solution in hexane), followed by the aldehyde **1** (210 mg; 0.38 mmol) in anhydrous THF (1.0 mL). The

suspension was allowed to slowly warm to room temperature over 2.5 h, maintained at this temperature for additional 30 min, and then filtered through Celite. The filtrate was diluted with diethyl ether (15 mL), and the organic layer was washed with water (5 mL), 5% aqueous sodium thiosulfate (5 mL), and water (5 mL), dried (Na_2SO_4), and concentrated. Flash chromatography (6:1 cyclohexane−ethyl acetate) of the residue afforded 149 mg (56%) of the olefin **15** as a 3:7 mixture of *E*- and *Z*-isomer. (*Z*)-**15**: ^{1}H NMR (selected data) δ 5.54 and 5.56 (2 × dd, 2H, H-6, H-7, $J_{6,7}$ = 12.0 Hz). (*E*)-**15**: ^{1}H NMR (selected data) δ 5.95 (2 × dd, 2H, H-6, H-7, $J_{6,7}$ = 16.0 Hz).

(*Z*/*E*)-Methyl 8,12-Anhydro-9-azido-2,3,4,10,11,13-hexa-*O*-benzyl-6,7,9-trideoxy-α-D-*glycero*-L-*manno*-D-*gluco*-tridec-6-enopyranoside (16). The phosphonium salt **9** (151 mg; 0.18 mmol) was reacted with the aldehyde **4** (117 mg; 0.24 mmol) as described for the preparation of **15** to afford, after flash chromatography (6:1 cyclohexane−ethyl acetate), 91 mg (55%) of the olefin **16** as a 1:1 mixture of *E*- and *Z*-isomers. (*Z*)-**16**: ^{1}H NMR (C_6D_6) (selected data) δ 5.74 and 5.83 (2 × dd, 2H, H-6, H-7, $J_{6,7}$ = 11.0 Hz). (*E*)-**16**: ^{1}H NMR (C_6D_6) (selected data) δ 6.25 (2 × dd, 2H, H-6, H-7, $J_{6,7}$ = 16.0 Hz).

(*Z*/*E*)-Methyl 8,12-Anhydro-2,3,4,9,10,11,13-hepta-*O*-benzyl-6,7-dideoxy-α-D-*glycero*-D-*gulo*-D-*gluco*-tridec-6-enopyranoside (17). The phosphonium salt **9** (142 mg; 0.17 mmol) was reacted with the aldehyde **5** (127 mg; 0.23 mmol) as described for the preparation of **15** to afford, after flash chromatography (6:1 cylohexane−ethyl acetate), 92 mg (55%) of the olefin **17** as 1:4 mixture of *E*- and *Z*-isomer. (*Z*)-**17**: ^{1}H NMR (selected data) δ 5.70 (2 × dd, 2H, H-6, H-7, $J_{6,7}$ = 12.0 Hz). (*E*)-**17**: ^{1}H NMR (selected data) δ 6.00 (2 × dd, 2H, H-6, H-7, $J_{6,7}$ = 16.0 Hz).

8,12-Anhydro-6,7-dideoxy-D-*glycero*-L-*manno*-D-*galacto*-tridecose (18). To a solution of the alkene **10** (111 mg; 0.14 mmol) in 1:1 ethyl acetate−ethanol (5 mL) was added $Pd(OH)_2$ (20%, 20 mg). The reaction mixture was stirred under an atmosphere of hydrogen for 4 h at 3 atm. The catalyst was removed by filtration and the filtrate concentrated. The residue was purified by flash chromatography (9:1 ethyl acetate−methanol) to afford 57 mg (95%) of oily 8,12-anhydro-6,7-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-L-*manno*-D-*galacto*-trideco-1,5-pyranose, which showed the following data: $[\alpha]_D$ = −38 (*c* 1.2); ^{1}H NMR (CD_3OD) δ 1.34, 1.43, 1.56 (3 × s, 12H, 2 × $C(CH_3)_2$), 1.57 (m, 1H, H-7′), 1.70 (m, 1H, H-6′), 1.80 (m, 1H, H-6), 2.14 (m, 1H, H-7), 3.10 (dt, 1H, H-8, $J_{8,7'} \approx 2.0$ Hz, $J_{8,7} \approx J_{8,9} \approx 9.0$ Hz), 3.45 (t, 1H, H-9, $J_{9,10}$ = 9.0 Hz), 3.46 (dd, 1H, H-10, $J_{10,11}$ = 3.5 Hz), 3.47 (m, 1H, H-12), 3.70 (dd, 1H, H-13, $J_{13,13'}$ = 12.0 Hz, $J_{13,12}$ = 5.5 Hz), 3.72 (dd, 1H, H-13′, $J_{13',12}$ = 7.0 Hz), 3.80 (ddd, H, H-5, $J_{5,4}$ = 2.0 Hz, $J_{5,6}$ = 8.0 Hz, $J_{5,6'}$ = 5.5 Hz), 3.92 (d, 1H, H-11), 4.20 (dd, 1H, H-4, $J_{4,3}$ = 8.0 Hz), 4.36 (dd, 1H, H-2, $J_{2,3}$ = 2.5 Hz, $J_{2,1}$ = 5.0 Hz), 4.62 (dd, 1H, H-3), 5.48 (d, 1H, H-1); ^{13}C NMR (CD_3OD) δ 22.0, 22.7, 23.8, 23.9, 25.0, 27.0, 60.2, 66.8, 68.3, 69.4, 69.7, 70.3, 71.5, 73.9, 77.6, 79.0, 95.4, 107.1, 107.5. Anal. Calcd for $C_{19}H_{32}O_{10}$: C, 54.27, H, 7.67. Found: C, 54.41, H, 7.81. This product (57 mg; 0.136 mmol) was dissolved in water (3 mL), and then Amberlite IR-120 (H^+) ion-exchange resin, previously washed with hot water (70 °C), was added, and the mixture was heated at 70 °C for 2 h. After the misture was cooled to room temperature, the resin was removed by filtration and the filtrate was concentrated to give 39 mg (85%) of the free *C*-disaccharide **18** as an oil: $[\alpha]_D$ = +39 (*c* 0.9, CH_3OH); ^{1}H NMR (CD_3OD) (selected data) δ 4.52 (d, 1H, H-1β, $J_{1,2}$ = 7.6 Hz), 5.20 (d, 1H, H-1α, $J_{1,2}$ = 3.7 Hz), relative intensity β/α 2:1; ^{13}C NMR (CD_3OD, some signals are overlapping) δ 28.0, 29.2, 62.8, 70.5, 70.9, 71.1, 71.3, 72.0, 72.6, 72.7, 73.8, 75.2, 76.4, 80.0, 81.6, 81.6, 81.7, 94.1, 98.6. Anal. Calcd for $C_{13}H_{24}O_{10}$: C, 45.88, H, 7.11. Found: C, 45.73, H, 7.09.

8,11-Anhydro-6,7-dideoxy-D-*glycero*-D-*galacto*-D-*galacto*-tridecose (19). The alkene **11** (mixture of *E*- and *Z*-isomers) (50 mg; 0.10 mmol) was reduced for 1.5 h as described for the preparation of **18** to afford, after flash chromatography (4:1 cyclohexane−ethyl acetate), 42 mg (83%) of 8,11-anhydro-6,7-dideoxy-1,2:3,4:9,10;12,13-tetra-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-D-*galacto*-trideco-1,5-pyranose as a syrup: $[\alpha]_D$ = −43 (*c* 0.6); ^{1}H NMR δ 1.31, 1.32, 1.34, 1.42, 1.43, 1.51 (6 × s, 24H, 4 × $C(CH_3)_2$), 1.74 (m, 2H, H-7, H-7′), 1.90 (m, 2H, H-6, H-6′), 3.41 (dd, 1H, H-11, $J_{11,10}$ = 3.5 Hz, $J_{11,12}$ = 8.0 Hz), 3.44 (m, 1H, H-8), 3.71 (m, 1H, H-5), 4.06 (m, 2H, H-13, H-13′), 4.14 (dd, 1H, H-4, $J_{4,3}$ = 7.5 Hz, $J_{4,5}$ = 1.5 Hz), 4.28 (dd, 1H, H-2, $J_{2,3}$ = 2.5 Hz, $J_{2,1}$ = 5.0 Hz), 4.38 (dt, 1H, H-12, $J_{12,13} \approx J_{12,13'} \approx 6.5$ Hz), 4.58 (dd, 1H, H-3), 4.59 (dd, 1H, H-9, $J_{9,8}$ = 4.0 Hz, $J_{9,10}$ = 6.5 Hz), 4.72 (dd, 1H, H-10); 5.52 (d, 1H, H-1); ^{13}C NMR ($CDCl_3$) δ 24.3, 24.6, 24.7, 25.0, 25.2, 25.7, 26.0, 26.1, 27.0, 27.3, 67.0, 67.7, 70.5, 70.9, 72.7, 73.1, 80.7, 81.3, 81.6, 82.4, 96.5, 108.3, 109.0, 109.1, 112.1. Anal. Calcd for $C_{25}H_{40}O_{10}$: C, 59.98, H, 8.05. Found: C, 59.46, H, 7.59. This product (22 mg; 0.044 mmol) dissolved in 1:1 methanol−water (2 mL) was treated with Amberlite IR-120 (H^+) ion-exchange resin as described for compound **18** to give after 4 h 12 mg (87%) of the free *C*-disaccharide **19** as a white foam: $[\alpha]_D$ = +18 (*c* 0.5, H_2O); ^{1}H NMR (D_2O) (selected data) δ 4.52 (d, 1H, H-1β, $J_{1,2}$ = 7.6 Hz), 5.20 (d, 1H, H-1α, $J_{1,2}$ = 3.7 Hz), relative intensity β/α 2:1; ^{13}C NMR (D_2O, some signals are overlapping) δ 25.2, 26.6, 62.9, 69.2, 69.9, 71.5, 71.7, 72.9, 74.6, 78.3, 80.4, 92.1, 96.2. Anal. Calcd for $C_{13}H_{24}O_{10}$: C, 45.88, H, 7.11. Found: C, 45.97, H, 7.31.

8,12-Anhydro-6,7-dideoxy-D-*glycero*-D-*galacto*-D-*galacto*-tridecose (20). The olefin **12** (mixture of *E*- and *Z*-isomers) (50 mg; 0.06 mmol) was treated for 5 h as described for the preparation of **18** to afford, after flash chromatography (9:1 ethyl acetate−methanol), 20 mg (76%) of oily 8,12-anhydro-6,7-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-L-*galacto*-D-*galacto*-trideco-1,5-pyranose: $[\alpha]_D$ = −53 (*c* 0.8); ^{1}H NMR (CD_3OD) δ 1.50, 1.55, 1.59 (3 × s, 12H, 2 × $C(CH_3)_2$), 1.66 (m, 4H, H-6, H-6′, H-7, H-7′), 3.18 (ddd, 1H, H-12, $J_{12,11}$ = 10.0 Hz, $J_{12,13'}$ = 5.5 Hz, $J_{12,13}$ = 2.5 Hz), 3.42 (m, 1H, H-8), 3.44 (dd, 1H, H-10, $J_{10,9}$ = 3.5 Hz, $J_{10,11}$ = 9.5 Hz), 3.58 (t, 1H, H-11), 3.70 (dd, 1H, H-13′, $J_{13',13}$ = 12.0 Hz), 3.70−3.74 (m, 2H, H-9, H-5), 3.85 (dd, 1H, H-13), 4.16 (dd, 1H, H-4, $J_{4,3}$ = 8.0 Hz, $J_{4,5}$ = 2.0 Hz), 4.30 (dd, 1H, H-2, $J_{2,1}$ = 5.0 Hz, $J_{2,3}$ = 2.5 Hz), 4.58 (dd, 1H, H-3), 5.48 (d, 1H, H-1); ^{13}C NMR (CD_3OD) δ 24.5, 25.1, 26.3, 27.6, 28.5, 63.1, 68.9, 69.1, 71.9, 72.2, 72.5, 74.1, 76.7, 79.6, 82.0, 97.9, 109.6, 110.1. Anal. Calcd for $C_{19}H_{32}O_{10}$: C, 54.27, H, 7.67. Found: C, 54.39, H, 7.56. This product (15 mg; 0.036 mmol) dissolved in water (1 mL) was treated with Amberlite 120-IR (H^+) ion-exchange resin as described for compound **18** for 1.5 h to give 10 mg (82%) of the *C*-disaccharide **20** as an oil: $[\alpha]_D$ = +27 (*c* 0.5, H_2O); ^{1}H NMR (D_2O) (selected data) δ 4.50 (d, 1H, H-1β, $J_{1,2}$ = 7.5 Hz), 5.20 (d, 1H, H-1α, $J_{1,2}$ = 3.7 Hz), relative intensity β/α 2:1; ^{13}C NMR (D_2O, some signals are overlapping) δ 26.2, 26.5, 61.3, 67.3, 68.3, 69.3, 70.2, 70.5, 71.8, 73.0 74.2, 74.7, 78.0, 80.0, 92.2, 96.3. Anal. Calcd for $C_{13}H_{24}O_{10}$: C, 45.88, H, 7.11. Found: C, 45.69, H, 7.37.

9-Acetamido-8,12-anhydro-6,7,9-trideoxy-D-*glycero*-L-*manno*-D-*galacto*-tridecose (21). The alkene **13** (52 mg, 0.074 mmol) was dissolved in ethanol (2 mL) together with nickel(II) chloride (6 mg) and H_3BO_3 (3 mg). To this solution was added dropwise a suspension of sodium borohydride (1.5 mg) in ethanol (0.5 mL). The mixture was concentrated, dissolved in anhydrous pyridine (2 mL), and treated with acetic anhydride (1 mL). The mixture was stirred at room temperature for 2 h and then was concentrated. Flash chromatography (2:1 ethyl acetate−cyclohexane) of the residue gave the alkane, which was hydrogenated for 3 h as described for the preparation of **18**. Flash chromatography (9:1 ethyl acetate−methanol) gave 17 mg (50%) of 9-acetamido-8,12-anhydro-6,7,9-trideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-L-*manno*-D-*galacto*-trideco-1,5-pyranose as an oil: $[\alpha]_D$ = −61 (*c* 0.4), ^{1}H NMR (CD_3OD) δ 1.32, 1.33, 1.40, 1.43 (4 × s, 12H, 2 × $C(CH_3)_2$), 1.50 (m, 1H, H-7′), 1.61 (m, 1H, H-6′), 1.82 m, 2H, H-6, H-7), 2.98 (s, 3H, CH_3CONH), 3.20 (dt, 1H, H-8, $J_{8,7'}$ 2.0 Hz, $J_{8,9} \approx J_{8,7} \approx 9.0$ Hz), 3.40 (dt, 1H, H-12, $J_{12,11}$ = 1.0 Hz, $J_{12,13} \approx J_{12,13'} \approx 6.0$ Hz), 3.48 (dd, 1H, H-10, $J_{10,9}$ = 10.0 Hz, $J_{10,11}$ = 3.5 Hz), 3.66 (dd, 1H, H-13, $J_{13,12}$ = 6.0 Hz, $J_{13,13'}$ = 12.0 Hz), 3.72 (m, 1H, H-5), 3.73 (dd, 1H, H-13′), 3.82 (d, 1H, H-11), 3.87 (t, 1H, H-9), 4.14 (dd, 1H, H-4, $J_{4,3}$ = 8.0 Hz, $J_{4,5}$ = 1.5 Hz), 4.29 (dd, 1H, H-2, $J_{2,1}$ = 5.0 Hz, $J_{2,3}$ = 2.0 Hz), 4.58 (dd, 1H, H-3), 5.46 (d, 1H, H-1); ^{13}C NMR (CD_3OD) δ 19.3, 24.5, 25.1, 26.2, 26.3, 27.5, 29.7, 53.6, 62.8, 69.4, 70.1, 71.9,

72.2, 74.6, 80.2, 80.3, 97.9, 109.6, 110.0. Anal. Calcd for $C_{21}H_{35}NO_{10}$: C, 54.65, H, 7.64, N, 3.03. Found: C, 54.85, H, 7.51, N, 2.65. This product (17 mg: 0.037 mmol) dissolved in water (1 mL) was treated with Amberlite IR-120 (H^+) ion-exchange resin for 1 h as described for the preparation of **18** to afford 11 mg (80%) of the *C*-disaccharide **21** as an oil: $[\alpha]_D = +14$ (*c* 0.7, CH_3OH); ^1H NMR (D_2O) (selected data) δ 4.50 (d, 1H, H-1β, $J_{1,2} = 7.6$ Hz), 5.17 (d, 1H, H-1α, $J_{1,2} = 3.7$ Hz), relative intensity β/α 2:1; ^{13}C NMR (D_2O, some signals are overlapping) δ 21.2, 25.3, 26.7, 51.1, 60.5, 67.3, 68.4, 69.2, 69.7, 70.9, 71.3, 72.0, 73.9, 77.5, 77.8, 91.2, 95.4. Anal. Calcd for $C_{15}H_{27}NO_{10}$: C, 47.24, H, 7.14. Found: 47.52, H, 7.16.

8,12-Anhydro-6,7-dideoxy-D-*glycero*-D-*gulo*-D-*galacto*-tridecose (22). The olefin **14** (59 mg; 0.076 mmol) was reduced for 5 h as described for the preparation of **18** to afford, after flash chromatography (9:1 ethyl acetate−methanol), 24 mg (75%) of 8,12-anhydro-6,7-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*gulo*-D-*galacto*-trideco-1,5-pyranose as a syrup: $[\alpha]_D = -53$ (*c* 1.1); ^1H NMR (CD_3OD) δ 1.30, 1.31, 1.40, 1.43 (4 × s, 12H, 2 × $C(CH_3)_2$), 1.43 (m, 1H, H-7), 1.65 (m, 1H, H-6), 1.85 (m, 1H, H-6′), 2.08 (m, 1H, H-7′), 3.05 (t, 1H, H-9, $J_{9,8} \approx J_{9,10} \approx 9.0$ Hz), 3.12 (m, 1H, H-8), 3.18 (dt, 1H, H-12, $J_{12,11} = 9.0$ Hz, $J_{12,13} = 2.0$ Hz, $J_{12,13'} = 5.0$ Hz), 3.24 (t, 1H, H-11, $J_{11,10} = 9.0$ Hz), 3.31 (t, 1H, H-10), 3.62 (dd, 1H, H-13′, $J_{13',13} = 12.0$ Hz), 3.75 (ddd, 1H, H-5, $J_{5,4} = 2.0$ Hz, $J_{5,6} = 5.0$ Hz, $J_{5,6'} = 9.0$ Hz), 4.18 (dd, 1H, H-4, $J_{4,3} = 7.5$ Hz), 4.31 (dd, 1H, H-2, $J_{2,1} = 5.0$ Hz, $J_{2,3} = 2.5$ Hz), 4.59 (dd, 1H, H-3), 5.45 (d, 1H, H-1); ^{13}C NMR (CD_3OD) δ 24.5, 25.2, 26.3, 26.4, 27.3, 29.5, 63.2, 69.3, 71.9, 72.0, 72.2, 74.0, 75.5, 79.8, 80.8, 81.7, 97.9, 109.6, 110.0. Anal. Calcd for $C_{19}H_{32}O_{10}$: C, 54.27, H, 7.67. Found: C, 54.52, H, 7.61. This product (17 mg; 0.04 mmol) dissolved in water (1 mL) was treated with Amberlite IR-120 (H^+) ion-exchange resin as described for compound **18** for 1.5 h to give 12 mg (86%) of the *C*-disaccharide **22** as an oil: $[\alpha]_D = +18$ (*c* 0.7, CH_3OH) (lit.[11b] $[\alpha]_D = +12$ (*c* 1, H_2O)); ^1H NMR (D_2O) (selected data) δ 4.52 (d, 1H, H-1β, $J_{1,2} = 7.6$ Hz), 5.17 (d, 1H, H-1α, $J_{1,2} = 3.5$ Hz), relative intensity β/α 2:1; ^{13}C NMR (D_2O, some signals are overlapping) δ 24.9, 26.3, 60.1, 67.4, 68.4, 69.1, 69.1, 69.7, 70.9, 72.1, 72.5, 73.8, 76.4, 78.2, 78.5, 78.6, 91.2, 95.4. Anal. Calcd for $C_{13}H_{24}O_{10}$: C, 45.88, H, 7.11. Found: C, 45.52, H, 7.56.

Methyl 8,12-Anhydro-6,7-dideoxy-α-D-*glycero*-L-*manno*-D-*gluco*-tridecopyranoside (23). To a solution of the alkene **15** (mixture of *E*- and *Z*-isomers) (39 mg; 0.04 mmol) in 1:1 ethyl acetate−ethanol (2 mL) was added $Pd(OH)_2$ (20%, 10 mg). The reaction mixture was stirred under an atmosphere of hydrogen for 4 h at 3 atm. The catalyst was removed by filtration and the filtrate concentrated to afford 12 mg (82%) of methyl *C*-disaccharide **23** as a white foam: $[\alpha]_D = +83$ (*c* 0.4, CH_3OH); ^1H NMR (CD_3OD) δ 1.40 (m, 2H, H-6, H-7), 2.20 (m, 2H, H-6′, H-7′), 3.04 (dd, 1H, H-4, $J_{4,3} \approx J_{4,5} \approx 9.0$ Hz), 3.08 (ddd, 1H, H-8, $J_{8,7} = 9.0$ Hz, $J_{8,7'} = 1.0$ Hz, $J_{8,9} = 10.0$ Hz), 3.37 (dd, 1H, H-2, $J_{2,1} = 4.0$ Hz, $J_{2,3} = 9.5$ Hz), 3.38 (s, 3H, OCH_3), 3.39 (m, 2H, H-9, H-10), 3.43 (ddd, 1H, H-12, $J_{12,11} = 1.0$ Hz, $J_{12,13'} = 7.0$ Hz, $J_{12,13} = 5.5$ Hz), 3.44 (ddd, 1H, H-5, $J_{5,6} = 9.5$ Hz, $J_{5,6'} = 1.5$ Hz), 3.55 (dd, 1H, H-3), 3.64 (dd, 1H, H-13′, $J_{13',13} = 11.5$ Hz), 3.71 (dd, 1H, H-13), 3.85 (dd, 1H, $J_{11,10} = 2.5$ Hz), 4.60 (d, 1H, H-1); ^{13}C NMR (CD_3OD) δ 29.0, 29.2, 55.5, 62.9, 70.9, 72.8, 73.8, 75.1, 75.9, 76.5, 80.2, 81.9, 101.10. Anal. Calcd for $C_{14}H_{26}O_{10}$: C, 47.45, H, 7.40. Found: C, 47.40, H, 7.64.

Methyl 2,3,4,9,10,11,13-Hepta-*O*-acetyl-8,12-anhydro-6,7-dideoxy-α-D-*glycero*-L-*manno*-D-*gluco*-tridecopyranoside (24). Compound **23** (20 mg; 0.056 mmol) was dissolved in 2:1 pyridine−acetic anhydride (3 mL), and the solution was allowed to stand overnight at room temperature. The mixture was concentrated in vacuo, and the traces of acetic anhydride were removed by evaporation with toluene (3 × 5 mL). The residue was purified by flash chromatography (1:1 ethyl acetate−cyclohexane) to afford 25 mg (70%) of the acetylated compound **24** as a white foam: $[\alpha]_D = +69$ (*c* 0.7); ^1H NMR δ 1.36−1.54 (m, 2H, H-6, H-7), 1.76−1.84 (m, 2H, H-7′, H-6′), 1.97−2.14 (7 × s, 21H, 7 × $OCOCH_3$), 3.38 (s, 3H, OCH_3), 3.18 (ddd, 1H, H-8, $J_{8,7} = 7.3$ Hz, $J_{8,7'} = 2.7$ Hz, $J_{8,9} = 9.0$ Hz), 3.74 (ddd, 1H, H-5, $J_{5,4} = 10.0$ Hz, $J_{5,6} = 8.5$ Hz, $J_{5,6'} = 1.5$ Hz), 3.84 (ddd, 1H, H-12, $J_{12,11} = 1.0$ Hz, $J_{12,13} = 6.5$ Hz, $J_{12,13'} = 7.0$ Hz), 4.04 (dd, 1H, H-13, $J_{13,13'} = 11.0$ Hz), 4.12 (dd, 1H, H-13′), 4.83 (dd, 1H, H-4, $J_{4,3} = 9.5$ Hz), 4.84 (dd, 1H, H-2, $J_{2,1} = 4.0$ Hz, $J_{2,3} = 10.0$ Hz), 4.88 (d, 1H, H-1), 5.00 (dd, 1H, H-10, $J_{10,9} = 10.0$ Hz, $J_{10,11} = 3.0$ Hz), 5.07 (dd, 1H, H-9), 5.41 (dd, 1H, H-11), 5.42 (dd, 1H, H-3); ^{13}C NMR δ 20.7, 26.9, 27.2, 55.2, 61.6, 67.7, 68.4, 69.3, 70.1, 71.1, 72.1, 72.2, 74.2, 78.3, 96.4, 169.9−170.5. Anal. Calcd for $C_{28}H_{40}O_{17}$: C, 51.80, H, 6.17. Found: C, 51.53, H, 6.21.

Methyl 9-Acetamido-8,12-anhydro-6,7,9-trideoxy-α-D-*glycero*-L-*manno*-D-*gluco*-tridecopyranoside (25). The olefin **16** (mixture of *E*- and *Z*-isomers) was dissolved in ethanol (2 mL) together with nickel(II) chloride (6 mg) and H_3BO_3 (3 mg). To this solution was added dropwise a suspension of sodium borohydride (1.5 mg) in ethanol (0.5 mL). The mixture was concentrated, dissolved in anhydrous pyridine (2 mL), and treated with acetic anhydride (1 mL). The mixture was stirred at room temperature for 2 h and then was concentrated. Flash chromatography (2:1 ethyl acetate−cyclohexane) of the residue gave the alkane, which was hydrogenated for 3 h as described for the preparation of **23** to afford 10 mg (60%) of methyl *C*-disaccharide **25** as a white foam: $[\alpha]_D = +63$ (*c* 0.4, CH_3OH); ^1H NMR (CD_3OD) δ 1.40 (m, 2H, H-6′, H-7′), 1.88 (m, 1H, H-6), 1.96 (s, 3H, CH_3CONH), 2.18 (m, 1H, H-7), 3.01 (dd, 1H, H-4, $J_{4,3} = 9.5$ Hz, $J_{4,5} = 9.0$ Hz), 3.14 (dd, 1H, H-8, $J_{8,7} = 9.0$ Hz, $J_{8,7'} = 1.5$ Hz, $J_{8,9} = 9.5$ Hz), 3.34 (dd, 1H, H-2, $J_{2,1} = 1.0$ Hz, $J_{2,3} = 9.5$ Hz), 3.35 (s, 3H, OCH_3), 3.40 (m, 2H, H-5, H-12), 3.48 (dd, 1H, H-10, $J_{10,9} = 10.5$ Hz, $J_{10,11} = 3.0$ Hz), 3.53 (dd, 1H, H-3), 3.66 (dd, 1H, H-13′, $J_{13',12} = 5.5$ Hz, $J_{13,13'} = 11.5$ Hz), 3.73 (dd, 1H, H-13, $J_{13,12} = 6.5$ Hz), 3.84 (dd, 1H, H-11, $J_{11,12} = 0.5$ Hz), 3.87 (dd, 1H, H-9), 4.58 (d, 1H, H-1); ^{13}C NMR (CD_3OD) δ 20.2, 26.6, 27.0, 51.3, 52.7, 60.4, 67.5, 70.1, 71.1, 71.8, 72.4, 73.2, 77.6, 78.1, 78.4, 171.4. Anal. Calcd for $C_{16}H_{29}NO_{10}$: C, 48.60, H, 7.39, N, 3.54. Found: C, 48.83, H, 7.37, N, 3.08.

Methyl 9-Acetamido-2,3,4,10,11,13-hexa-*O*-acetyl-8,12-anhydro-6,7,9-trideoxy-α-D-*glycero*-L-*manno*-D-*gluco*-tridecopyranoside (26). Compound **25** (8 mg, 0.02 mmol) was acetylated as described for **24**. Flash chromatography (7:2 ethyl acetate−cyclohexane) of the residue gave 10 mg (77%) of acetylated product **26** as a white foam: $[\alpha]_D = +63$ (*c* 0.4); ^1H NMR δ 1.25−1.40 (m, 1H, H-5), 1.60−1.45 (m, 1H, H-7), 1.80−2.00 (m, 2H, H-7′, H-6′), 1.94−2.16 (7 × s, 21H, 7 × $OCOCH_3$), 3.18 (ddd, 1H, H-8, $J_{8,7} = 10.0$ Hz, $J_{8,7'} = 1.0$ Hz, $J_{8,9} = 11.0$ Hz), 3.36 (s, 3H, OCH_3), 3.73 (ddd, 1H, H-5, $J_{5,4} = 9.5$ Hz, $J_{5,6} = 9.0$ Hz, $J_{5,6'} = 2.0$ Hz), 3.78 (ddd, 1H, $J_{12,11} = 1.0$ Hz, $J_{12,13} = 6.0$ Hz, $J_{12,13'} = 7.0$ Hz), 4.04 (dd, 1H, H-13, $J_{13,13'} = 11.0$ Hz), 4.11 (dd, 1H, H-13′), 4.18 (ddd, 1H, $J_{9,NHAc} = 10.0$ Hz, $J_{9,10} = 11.0$ Hz), 4.78−4.88 (m, 3H, H-2, H-4, H-1), 5.26 (d, 1H, CH_3CONH), 5.34 (dd, 1H, H-11), 5.42 (dd, 1H, H-3, $J_{3,2} = 10.5$ Hz, $J_{3,4} = 9.0$ Hz); ^{13}C NMR δ 19.8, 22.4, 26.4, 42.2, 54.3, 60.9, 66.2, 67.4, 69.2, 70.2, 70.9, 71.2, 73.3, 79.3, 95.4, 169.2, 169.3, 169.4, 169.5, 170.2. Anal. Calcd for $C_{28}H_{41}NO_{16}$: C, 51.88, H, 6.33, N, 2.16. Found: C, 51.58, H, 6.26, N, 1.83.

Methyl 8,12-Anhydro-6,7-dideoxy-α-D-*glycero*-D-*gulo*-D-*gluco*-tridecopyranoside (27). The olefin **17** (*E*/*Z* mixture) (70 mg; 0.07 mmol) was hydrogenated as described for the preparation of **23** to afford 21 mg (85%) of methyl *C*-disaccharide **27** as a white foam: $[\alpha]_D = +61$ (*c* 0.6, CH_3OH) (lit.[27] $[\alpha]_D = +88$ (*c* 1, CH_3OH)); ^1H NMR (CD_3OD) δ 1.38 (m, 2H, H-6, H-7), 2.19 (m, 2H, H-6′, H-7′), 3.04 (dd, 1H, H-4, $J_{4,3} = 9.0$ Hz, $J_{4,5} = 9.5$ Hz), 3.05 (dd, 1H, H-9, $J_{9,8} = 9.5$ Hz, $J_{9,10} = 10$ Hz), 3.12 (dd, 1H, H-8, $J_{8,7} = 9.0$ Hz, $J_{8,7'} = 1.5$ Hz), 3.18 (ddd, 1H, H-12, $J_{12,11} = 9.0$ Hz, $J_{12,13'} = 5.5$ Hz, $J_{12,13} = 2.0$ Hz), 3.23 (dd, 1H, H-10, $J_{10,11} = 9.5$ Hz), 3.30 (dd, 1H, H-11), 3.37 (dd, 1H, H-2, $J_{2,1} = 4.0$ Hz, $J_{2,3} = 9.5$ Hz), 3.38 (s, 3H, OCH_3), 3.44 (ddd, 1H, H-5, $J_{5,4} = 9.5$ Hz, $J_{5,6} = 9.0$ Hz, $J_{5,6'} = 1.0$ Hz), 3.55 (dd, 1H, H-3), 3.62 (dd, 1H, H-13′, $J_{13,13'} = 12.0$ Hz), 3.83 (dd, 1H, H-13), 4.61 (d, 1H, H-1); ^{13}C NMR (CD_3OD) δ 26.2, 26.8 52.9, 60.7, 69.5, 70.1, 71.1, 72.4, 72.9, 73.1, 77.2, 78.5, 78.9, 98.4. Anal. Calcd for $C_{14}H_{26}O_{10}$: C, 47.45, H, 7.40. Found: C, 47.65, H, 7.59.

Methyl 2,3,4,9,10,11,13-Hepta-*O*-acetyl-8,12-anhydro-6,7-dideoxy-α-D-*glycero*-D-*gulo*-D-*gluco*-tridecopyranoside (28). Compound **27** (14 mg, 0.04 mmol) was acetylated

as described for **24**. Flash chromatography (4:5 ethyl acetate−cyclohexane) of the residue gave 17 mg (67%) of the acetylated product **28** as a white foam: $[\alpha]_D = +63$ (*c* 0.7) (lit.[27] $[\alpha]_D = +55$ (*c* 1)); ^{1}H NMR δ 1.46−1.38 (m, 2H, H-6, H-7), 1.84−1.74 (m, 2H, H-6′, H-7′), 1.99−2.10 (7 × s, 21H, 7 × $OCOCH_3$), 3.35 (s, 3H, OCH_3), 3.38 (ddd, 1H, H-8, $J_{8,7} = 10.0$ Hz, $J_{8,7'} = 1.0$ Hz, $J_{8,9} = 9.0$ Hz), 3.61 (ddd, 1H, H-12, $J_{12,11} = 9.7$ Hz, $J_{12,13} = 5.5$ Hz, $J_{12,13'} = 2.0$ Hz), 3.73 (dd, 1H, H-5, $J_{5,4} = 9.5$ Hz, $J_{5,6} = 7.0$ Hz, $J_{5,6'} = 1.5$ Hz), 4.07 (dd, 1H, H-13′, $J_{13',13} = 12.5$ Hz), 4.23 (dd, 1H, H-13), 4.79−4.90 (m, 4H, H-1, H-2, H-9, H-4), 5.02 (dd, H-11, $J_{11,10} = 9.5$ Hz), 5.16 (dd, 1H, H-10, $J_{10,9} = 9.5$ Hz), 5.42 (t, 1H, H-3, $J_{3,2} \approx J_{3,4} \approx 9.8$ Hz); ^{13}C NMR δ 20.6, 26.7, 26.9, 55.2, 62.2, 68.3, 68.6, 70.0, 71.1, 71.7, 72.1, 74.2, 75.6, 77.8, 96.4, 169.5, 169.2, 169.9, 170.0, 170.2, 170.3, 170.6. Anal. Calcd for $C_{28}H_{40}O_{17}$: C, 51.80, H, 6.17. Found: C, 51.71, H, 6.12.

(*E*/*Z*)-8,11-Anhydro-9,10,12-tri-*O*-benzyl-6,7-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*altro*-D-*galacto*-tridec-6-eno-1,5-pyranose (33). The phosphonium salt **8** (130 mg; 0.21 mmol) was reacted with the aldehyde **7** (91 mg; 0.21 mmol) as described for the preparation of **10** to afford, after flash chromatography (4:1 cyclohexane−ethyl acetate), a 1:4 mixture of (*E*)-**33** and (*Z*)-**33** (91 mg; 66%). Pure samples of these compounds were obtained by flash chromatography (30:1 toluene−acetone). Eluted first was (*Z*)-**33** as an oil: $[\alpha]_D = -18$ (*c* 1.1); ^{1}H NMR δ 1.15, 1.32, 1.45, 1.54 (4 × s, 12H, 2 × $C(CH_3)_2$), 3.49 (dd, 1H, H-12, $J_{12,11} = 5.0$ Hz, $J_{12,12'} = 11.0$ Hz), 3.53 (dd, 1H, H-12′, $J_{12',11} = 4.0$ Hz), 3.68 (dd, 1H, H-9, $J_{9,8} = 8.0$ Hz, $J_{9,10} = 5.0$ Hz), 3.97 (dd, 1H, H-4, $J_{4,3} = 8.0$ Hz, $J_{4,5} = 2.0$ Hz), 3.98 (dd, 1H, H-10, $J_{10,11} = 2.0$ Hz), 4.24 (m, 2H, H-2, H-11), 4.32 (dd, 1H, H-3, $J_{3,2} = 2.0$ Hz), 4.43 and 4.59 (2 × d, 2H, $J = 12.0$ Hz, OCH_2Ph), 4.51 and 4.56 (2 × d, 2H, $J = 12.0$ Hz, OCH_2Ph), 4.56 and 4.61 (2 × d, 2H, $J = 12.0$ Hz, OCH_2Ph), 4.64 (dd, H-5, $J_{5,6} = 8.5$ Hz), 4.75 (t, 1H, H-8, $J_{8,7} = 8.0$ Hz), 5.51 (d, 1H, H-1, $J_{1,2} = 5.0$ Hz), 5.61 (dd, 1H, H-7, $J_{7,6} = 11.0$ Hz), 5.75 (dd, 1H, H-6), 7.21−7.39 (m, 15H, H_{arom}); ^{13}C NMR (C_6D_6) δ 24.4, 25.0, 25.8, 26.4, 64.7, 67.8, 70.6, 71.2, 71.6, 72.2, 73.6, 74.6, 77.2, 78.2, 82.8, 83.3, 97.1, 108.4, 108.9, 127.7−128.6, 130.6, 132.0, 138.8. Anal. Calcd for $C_{39}H_{46}O_9$: C, 71.10, H, 7.04. Found: C, 70.93, 6.95.

Eluted second was (*E*)-**33** as an oil: $[\alpha]_D = -32$ (*c* 0.2); ^{1}H NMR δ 1.32, 1.37, 1.43, 1.54 (4 × s, 12H, 2 × $C(CH_3)_2$), 3.52 (dd, 1H, H-12, $J_{12,12'} = 11.0$ Hz, $J_{12,11} = 5.0$ Hz), 3.57 (dd, 1H, H-12′, $J_{12',11} = 4.5$ Hz), 3.75 (t, 1H, H-9, $J_{9,8} \approx J_{9,10} \approx 5.5$ Hz), 3.91 (t, 1H, H-10, $J_{10,11} = 5.5$ Hz), 4.16 (dd, 1H, H-4, $J_{4,3} = 8.0$ Hz, $J_{4,5} = 2.0$ Hz), 4.20 (q, 1H, H-11), 4.29 (dd, 1H, H-5, $J_{5,6} = 5.5$ Hz), 4.31 (dd, 1H, H-2, $J_{2,1} = 5.0$ Hz, $J_{2,3} = 2.1$ Hz), 4.49 and 4.64 (2 × d, 2H, $J = 12.0$ Hz, OCH_2Ph), 4.52 and 4.62 (2 × d, 2H, $J = 12.0$ Hz, OCH_2Ph), 4.55 and 4.60 (2 × d, 2H, $J = 12.0$ Hz, OCH_2Ph), 4.54 (m, 1H, H-8), 4.59 (dd, 1H, H-3), 5.58 (d, 1H, H-1), 5.79 (ddd, 1H, H-7, $J_{7,5} = 1.0$ Hz, $J_{7,6} = 16.0$ Hz, $J_{7,8} = 7.0$ Hz), 5.95 (ddd, 1H, H-6, $J_{6,8} = 1.0$ Hz), 7.22−7.40 (m, 15H, H_{arom}); ^{13}C NMR δ 24.3, 24.9, 25.9, 26.1, 68.0, 70.2, 70.4, 70.7, 72.0, 73.1, 73.4, 76.0, 77.7, 81.1, 81.7, 96.4, 108.4, 109.1, 127.7−128.3, 129.2, 131.4, 138.0. Anal. Calcd for $C_{39}H_{46}O_9$: C, 71.10, H, 7.04. Found: C, 71.23, H, 7.21.

8,11-Anhydro-6,7-dideoxy-D-*altro*-Dd-*galacto*-tridecose (34). A solution of the alkene **33** (mixture of *E*- and *Z*-isomers) (48 mg; 0.073 mmol) and (*p*-toluenesulfonyl)hydrazine (40 mg; 0.22 mmol) in dimethoxyethane (7.6 mL) was heated to reflux. A solution of NaOAc (18.0 mg; 0.22 mmol) in water (4 mL) was added dropwise over a 6 h period. The reaction was stirred for an additional 12 h at reflux and then cooled to room temperature. The solution was diluted with diethyl ether, and the organic layer washed with water and brine, dried (Na_2SO_4), and concentrated. Flash chromatography (4:1 cyclohexane−ethyl acetate) of the residue gave the reduced product, which was hydrogenated for 3 h as described for the preparation of **18**. Flash chromatography (9:1 ethyl acetate−methanol) gave 21 mg (73%) of oily 8,11-anhydro-6,7-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*altro*-D-*galacto*-trideco-1,5-pyranose that showed: $[\alpha]_D = -47$ (*c* 0.6); ^{1}H NMR (CD_3OD) δ 1.32, 1.33, 1.40, 1.50 (4 × s, 12H, 2 × $C(CH_3)_2$), 1.52 (m, 2H, H-6, H-6′), 1.70 (m, 2H, H-7, H-7′), 3.54 (dd, 1H, H-12, $J_{12,11} = 5.0$ Hz, $J_{12,12'} = 12.0$ Hz), 3.66 (dd, 1H, H-12′, $J_{12',11} = 3.5$ Hz), 3.67 (t, 1H, H-9, $J_{9,8} \approx J_{9,10} \approx 5.5$ Hz), 3.70−3.80 (m, 3H, H-5, H-8, H-11), 3.91 (t, 1H, H-10, $J_{10,11} = 5.5$ Hz), 4.16 (dd, 1H, H-4, $J_{4,3} = 8.0$ Hz, $J_{4,5} = 2.0$ Hz), 4.31 (dd, 1H, H-2, $J_{2,3} = 2.5$ Hz, $J_{2,1} = 5.0$ Hz), 4.59 (dd, 1H, H-3), 5.45 (d, 1H, H-1); ^{13}C NMR (CD_3OD) δ 26.4, 27.5, 27.8, 28.8, 31.0, 53.6, 63.6, 69.0, 71.9, 72.3, 72.8, 74.0, 76.3, 84.2, 85.6, 97.7, 109.6, 110.1. Anal. Calcd for $C_{18}H_{30}O_9$: C, 55.37, H, 7.74. Found: 54.81, H, 7.26. This product (21 mg; 0.051 mmol) dissolved in water (1 mL) was treated with Amberlite IR-120 (H^+) ion-exchange resin as described for compound **18** for 2 h to give free *C*-disaccharide **34** as an oil: $[\alpha]_D = -16$ (*c* 0.5, H_2O); ^{1}H NMR (D_2O) (selected data) δ 4.50 (d, 1H, H-1β, $J_{1,2} = 7.6$ Hz), 5.20 (d, 1H, H-1α, $J_{1,2} = 3.7$ Hz), relative intensity β/α 2:1; ^{13}C NMR (D_2O, some signals are overlapping) δ 26.1, 28.9, 61.6, 68.3, 69.3, 69.9, 70.1, 70.5, 70.6, 71.0, 71.7, 71.8, 72.9, 74.3, 74.6, 82.6, 83.1, 92.1, 96.3. Anal. Calcd for $C_{12}H_{22}O_9$: C, 46.45, H, 7.15. Found: C, 46.01, H, 7.32.

2,5-Anhydro-3,4:6,7-di-*O*-isopropylidene-*aldehydo*-D-*glycero*-D-*talo*-heptafuranose (39). A mixture of **38** (128 mg; 0.39 mmol) and activated 4-Å powdered molecular sieves (780 mg) in dry CH_3CN (3.6 mL) was stirred at room temperature for 10 min, and then methyl triflate (58 μL, 0.50 mmol) was added. The suspension was stirred for 15 min and then concentrated to dryness. The crude *N*-methylthiazolium salt was suspended in MeOH (3.6 mL), cooled to 0 °C, and then treated with $NaBH_4$ (34 mg; 0.88 mmol). The mixture was stirred at room temperature for an additional 10 min, diluted with acetone (5.2 mL), filtered through Celite, and concentrated. To the solution of the crude thiazolidine in 10:1 CH_3CN-H_2O (3.6 mL) was added $HgCl_2$ (107 mg, 0.39 mmol). The mixture was stirred for 15 min and then filtered through Celite. The solvent was evaporated and the residue suspended in CH_2Cl_2 (10 mL) and washed with 20% aqueous KI (3 × 10 mL) and water (10 mL). The organic layer was dried (Na_2SO_4) and concentrated to give a syrup, which was diluted with diethyl ether (10 mL) and filtered through a short pad of Florisil (100−200 mesh) to afford a colorless solution. After a further washing of the Florisil pad with AcOEt (3 mL), the filtrate was concentrated to give 82 mg (77%) of almost pure (NMR analysis) aldehyde **39** as an oil; ^{1}H NMR (DMSO-d_6, 120 °C) δ 1.30, 1.32, 1.33, 1.38 (4 × s, 12H, 2 × $C(CH_3)_2$, 3.84 (dd, 1H, H-5, $J_{5,4} = 3.5$ Hz, $J_{5,6} = 6.3$ Hz), 3.98 (dd, 1H, H-7, $J_{7,6} = 6.3$ Hz, $J_{7,7'} = 8.3$ Hz), 4.05 (dd, 1H, H-7′, $J_{7',6} = 6.3$ Hz), 4.31 (q, 1H, H-6), 4.42 (d, 1H, H-2), 4.73 (dd, 1H, H-4, $J_{4,3} = 5.6$ Hz), 5.01 (dd, 1H, H-3, $J_{3,2} = 1.4$ Hz), 9.62 (s, 1H, H-1).

(*Z*)-8,11-Anhydro-1,2:3,4:9,10:12,13-tetra-*O*-isopropylidene-6,7-dideoxy-α-D-*glycero*-D-*talo*-D-*galacto*-tridec-6-eno-1,5-pyranose (40). The phosphonium salt **8** (189 mg; 0.30 mmol) was reacted with the aldehyde **39** (82 mg; 0.30 mmol) as described for the preparation of **10** to afford, after flash chromatography (3:1 cyclohexane−ethyl acetate), 92 mg (62%) of the (*Z*)-alkene **40** as an oil: $[\alpha]_D = -43$ (*c* 1.3); ^{1}H NMR δ 1.32, 1.35, 1.39, 1.45, 1.50, 1.59 (6 × s, 24H, 4 × $C(CH_3)_2$), 3.79 (dd, 1H, H-11, $J_{11,10} = 3.5$ Hz, $J_{11,12} = 7.5$ Hz), 4.04 (dd, 1H, H-13, $J_{13,12} = 4.5$ Hz, $J_{13,13'} = 9.0$ Hz), 4.08 (dd, 1H, H-13′, $J_{13',12} = 6.0$ Hz), 4.26 (dd, 1H, H-4, $J_{4,3} = 8.0$ Hz, $J_{4,5} = 2.0$ Hz), 4.32 (dd, 1H, H-2, $J_{2,1} = 5.0$ Hz, $J_{2,3} = 2.5$ Hz), 4.40 (ddd, 1H, H-12), 4.62 (dd, 1H, H-3), 4.70 (d, 1H, H-9, $J_{9,10} = 6.0$ Hz), 4.73−4.78 (m, 2H, H-5, H-10), 4.81 (dd, 1H, H-8, $J_{8,6} = 1.5$ Hz, $J_{8,7} = 6.0$ Hz), 5.66 (d, 1H, H-1), 5.61 (ddd, 1H, H-7, $J_{7,5} = 1.0$ Hz, $J_{7,6} = 11.5$ Hz), 5.77 (dd, 1H, H-6, $J_{6,5} = 8.5$ Hz); ^{13}C NMR δ 24.4, 24.7, 24.9, 25.2, 26.1, 26.2, 26.3, 26.9, 66.4, 67.1, 70.4, 70.9, 72.8, 73.4, 80.0, 80.7, 83.6, 85.4, 96.5, 108.3, 109.1, 109.2, 112.5. Anal. Calcd for $C_{25}H_{38}O_{10}$: C, 60.23, H, 7.68. Found: C, 60.10, H, 8.27.

8,11-Anhydro-1,2:3,4:9,10:12,13-tetra-*O*-isopropylidene-6,7-dideoxy-α-D-*glycero*-D-*talo*-D-*galacto*-tridec-1,5-pyranose (41). The olefin **40** (34 mg; 0.068 mmol) was reduced for 1.5 h as described for the preparation of **18** to afford, after flash chromatography (3:1 cyclohexane−ethyl acetate), 28 mg (82%) of the reduced product **41** as an oil: $[\alpha]_D = -34$ (*c* 0.5); ^{1}H NMR ($CDCl_3$) δ 1.33, 1.34, 1.38, 1.45, 1.49, 1.52 (6 × s, 24H, 4 × $C(CH_3)_2$), 1.44 (m, 1H, H-7′), 1.54−1.68 (m, 2H, H-7, H-6), 1.74−1.86 (m, 1H, H-6′), 3.72 (dd, 1H, H-11, $J_{11,10} = 4.0$ Hz, $J_{11,12} = 8.0$ Hz), 3.76 (ddd, 1H, H-5, $J_{5,4} = 1.5$ Hz, $J_{5,6} = 4.0$ Hz, $J_{5,6'} = 9.0$ Hz), 4.02 (dd, 1H, H-13, $J_{13,12} = 4.5$ Hz, $J_{13,13'} = 8.5$ Hz), 4.07 (m, 1H, H-8), 4.10 (dd, 1H, H-4, $J_{4,3} = 8.0$ Hz),

4.13 (dd, 1H, H-13′, $J_{13',12}$ = 7.0 Hz), 4.30 (dd, 1H, H-2, $J_{2,1}$ = 5.0 Hz, $J_{2,3}$ = 2.5 Hz), 4.38 (ddd, 1H, H-12), 4.52 (d, 1H, H-9, $J_{9,10}$ = 6.0 Hz), 4.59 (dd, 1H, H-3), 4.76 (dd, 1H, H-10), 5.51 (d, 1H, H-1). Anal. Calcd for $C_{25}H_{40}H_{10}$: C, 59.98, H, 8.05. Found: C, 60.32, H, 8.62.

8,11-Anhydro-6,7-dideoxy-D-*glycero*-D-*talo*-D-*galacto*-tridecose (42). Compound **41** (20 mg; 0.04 mmol) dissolved in 1:1 ethyl acetate−water (2 mL) was treated with Amberlite IR-120 (H^+) ion-exchange resin as described for compound **18** for 5 h to give 12 mg (89%) of the free *C*-disaccharide **42**: $[\alpha]_D$ = +30 (*c* 0.2, CH_3OH); ^1H NMR (D_2O) (selected data) δ 4.38 (d, 1H, H-1β, $J_{1,2}$ = 7.6 Hz), 5.02 (d, 1H, H-1α, $J_{1,2}$ = 3.7 Hz), relative intensity β/α 2:1; ^{13}C NMR (CD_3OD, some signals are overlapping) δ 27.1, 29.8, 64.0, 69.5, 70.7, 70.9, 71.6, 72.5, 72.8, 74.3, 74.7, 77.2, 79.7, 80.8, 93.1, 97.7. This compound was highly hygroscopic, thus preventing a satisfactory elemental analysis.

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