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Carbohydrate Research 341 (2006) 2487–2497
Carbohydrate RESEARCH

Synthesis of α-D-Gal*f*-(1→2)-D-galactitol and α-D-Gal*f*-(1→2)[β-D-Gal*f*-(1→3)]-D-galactitol, oligosaccharide derivatives from *Bacteroides cellulosolvens* glycoproteins

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Received 8 June 2006; received in revised form 4 July 2006; accepted 18 July 2006
Available online 1 September 2006

Abstract—The synthesis of α-D-galactofuranosyl-(1→2)-D-galactitol, which has been isolated by reductive β-elimination from glycoproteins of *Bacteroides cellulosolvens* and *Clostridium thermocellum*, is described. The approach of selective glycosylation of an aldono-1,4-lactone by the trichloroacetimidate method was employed. The synthesis of α-D-Gal*f*-(1→2)[β-D-Gal*f*-(1→3)]-D-Galol, that contains Gal*f* units in both anomeric configurations, is also reported. These are the first synthetic oligosaccharides with α-D-Gal*f*, previously found in natural products.

Keywords: α-D-Galactofuranosyl; Aldonolactone; Trichloroacetimidate; 1,2-cis-Glycosylation; *Bacteroides cellulosolvens*; *Clostridium thermocellum*

1. Introduction

The occurrence of galactose in the furanose form, absent in mammals, is limited to bacteria,[1] protozoa,[2] and fungi.[3] Although both anomeric configurations have been described, these studies were mainly concerned with β-galactofuranose because of its presence in pathogenic microorganisms like *Mycobacterium tuberculosis*,[4] *Leishmania*,[5] and *Trypanosoma cruzi*.[6] Therefore, galactofuranose metabolism arises as a potential target for antimicrobial chemotherapy,[7] and Gal*f* biosynthetic studies are currently being performed. It was proved that two enzymes are required for β-Gal*f* incorporation into glycoconjugates: (1) a low-efficiency mutase that transforms UDP-Gal*p* into UDP-Gal*f*,[8] and (2) a UDP-Gal*f* transferase,[9] which transfers the Gal*f* unit to the sugar chain.

However, there are several reported examples in which galactofuranose occurs in the α-configuration. In fungi, α-D-Gal*f* was found together with β-D-Gal*f* in varianose, a complex extracellular polysaccharide produced by *Penicillium varians*. This was the first natural carbohydrate in which both α- and β-Gal*f* residues have been observed.[10] Similar structures have been found in the cell-wall polysaccharides of *Talaromyces flavus*[11] and in the extracellular polysaccharide of *P. vermiculatum*.[12] The cell-wall polysaccharide isolated from *Apodus deciduus* has Gal*f* only in the α-configuration.[13] N-Linked mannose-type oligosaccharides from *Aspergillus niger* α-glucosidase also contain α-Gal*f* linkages.[14] More recently, α-Gal*f* was found in the cell wall of the fungus *Paracoccidioides brasiliensis*,[15] the etiological agent of paracoccidioidomycosis, the most common systemic mycosis in Latin America. Interestingly, the presence of α-Gal*f* units in the polysaccharide structures differs in the mycelial and yeast phases. Other fungi belonging to Onygenales have related structures.[16]

In bacteria, α-Gal*f* is also found in the capsular polysaccharide of *Streptococcus pneumoniae* 22F,[17] in the O-antigenic polysaccharide from *Escherichia coli* O167,[18]

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doi:10.1016/j.carres.2006.07.013

as well as in part of the lipopolysaccharide of a plant-growth-promoting rhizobacteria.[19]

The anaerobic eubacteria *Clostridium thermocellum*[20] and *Bacteroides cellulosolvens*[21] produce cellulosomes for the degradation of cellulose. These multienzyme complexes contain oligosaccharides O-linked to threonine or serine via galactopyranose. The disaccharide alditol, α-D-Gal*f*-(1→2)-GalOH (**1**), was isolated by reductive β-elimination.[20b,21a] Interestingly, in *C. thermocellum* Gal*f* appears only in the α-configuration, whereas both configurations α and β coexist in *B. cellulosolvens* as α-D-Gal*f*-(1→2)[β-D-Gal*f*-(1→3)]-D-Gal, which is a part of higher oligosaccharides.[21b]

Since biosynthesis of the α-D-Gal*f* linkage has not been studied, the synthesis of oligosaccharides containing α-galactofuranose is useful for confirming the assigned structures and as tools for biosynthetic studies.

The preparation of 1,2-*trans* β-galactofuranosides can be selectively accomplished by neighboring group participation through the use of galactofuranosyl donors containing acyl protecting groups at O-2.[22] In our laboratory, we have extensively employed the trichloroacetimidate method[23] for β-galactofuranosyl linkage construction,[24,25] including the synthesis of internal β-D-Gal*f*-containing oligosaccharides.[26,27] However, no successful general method is available for 1,2-cis glycosylation. A procedure that introduces a chiral auxiliary at C-2 acting as a neighboring participating group has recently been described for pyranoses.[28] The advances in strategies for 1,2-cis-O-glycosylation have been reviewed.[29] The construction of a 1,2-cis α-galactofuranosidic linkage requires a galactofuranosyl derivative with a non-participating group at the C-2 position, which is the case of 2,3,5,6-tetra-*O*-benzyl-α,β-D-galactofuranose. However, activation of this compound as the *n*-pentenyl glycoside gave mainly the β-D-galactofuranosyl linkage.[30] On the other hand, moderate diastereoselectivities were obtained with the trichloroacetimidate method.[31] Also, encouraging results for 1,2-cis glycosylation have been described starting from 2-O-benzylated 1,2-*trans*-thiogalactofuranoside derivatives.[32]

Taking into account the stereochemical relationship between arabinose and galactose, two recently developed methods should be mentioned. The preparation of 1,2-*cis*-β-D-arabinofuranosides from 2,3-anhydrothiofuranosides or glycosyl sulfoxides has been developed.[33] A stereoselective β-arabinofuranosylation employing 2′-carboxybenzyl arabinofuranoside derivatives as glycosyl donors has been reported.[34]

In this paper, we describe the synthesis of α-D-Gal*f*-(1→2)-D-Galol (**1**), which has been isolated by reductive β-elimination from glycoproteins of *B. cellulosolvens* and *C. thermocellum*. We also report the challenging synthesis of α-D-Gal*f*-(1→2)[β-D-Gal*f*-(1→3)]-D-Galol (**2**) that contains the Gal*f* units in both anomeric configurations (Fig. 1).

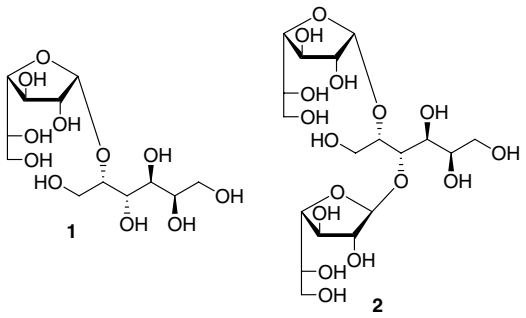


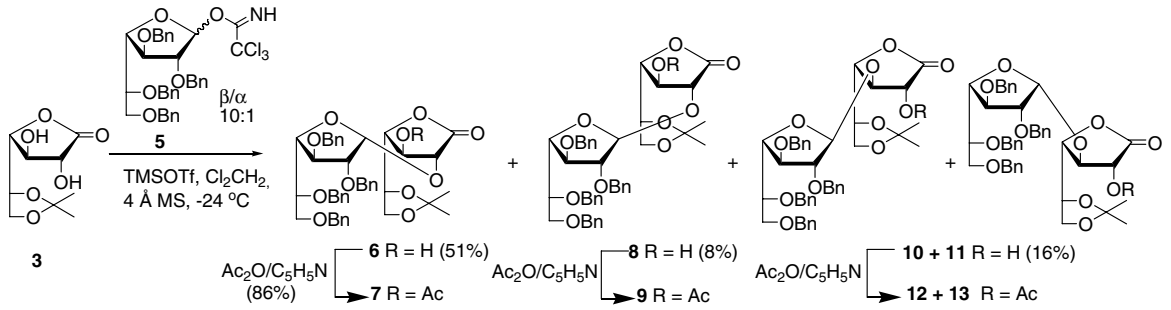
Figure 1.

2. Results and discussion

The common feature of the target alditols **1** and **2** is that the α-galactofuranosyl moiety is linked to the OH-2 of galactitol. We have previously used D-galactono-1,4-lactone as a precursor of D-galactofuranose[26,27] and D-galactopyranose[25] derivatives, taking advantage of the different hydroxyl group reactivities. The primary OH-6 and secondary OH-2 are easily substituted. Selective acylation of D-galactono-1,4-lactone gave 2,6-di-*O*-acyl derivatives in high yield.[35] Moreover, selective pivaloylation of 5,6-*O*-isopropylidene-D-galactono-1,4-lactone gave the 2-*O*-pivaloyl derivative as the only product.[26] This fact suggested that OH-2 would also be sterically less demanding than OH-3 for glycosylation. For that reason, we employed 5,6-*O*-isopropylidene-D-galactono-1,4-lactone[36] (**3**) as the precursor for the downstream end unit of the natural disaccharide.

The construction of the 1,2-cis α-galactofuranosidic linkage requires a galactofuranosyl derivative with a non-participating group at the C-2 position, which is the case of 2,3,5,6-tetra-*O*-benzyl-α,β-D-galactofuranose (**4**). Compound **4** is easily synthesized in three steps from galactose via its allyl α-glycoside obtained by direct anomeric O-alkylation.[37,38] The glycosylation step was performed by the trichloroacetimidate method, previously communicated for the construction of α-galactofuranosyl linkages.[31] Treatment of 2,3,5,6-tetra-*O*-benzyl-α,β-D-galactofuranose (**4**) with trichloroacetonitrile and DBU gave 2,3,5,6-tetra-*O*-benzyl-D-galactofuranosyl trichloroacetimidate (**5**) in 93% yield, as a 10:1 β:α anomeric mixture established by the integration of the anomeric signals in the ^{1}H NMR spectrum.

Glycosidation of the 2,3-diol **3** with 1 equiv of imidate **5** afforded crystalline 2,3,5,6-tetra-*O*-benzyl-α-D-galactofuranosyl-(1→2)-5,6-*O*-isopropylidene-D-galactono-1,4-lactone (**6**) as the main component in 51% yield (Scheme 1). The α-anomeric configuration of the glycosidic linkage of **6** was established by the coupling constants in the ^{1}H NMR spectrum. Thus, the resonance for H-1′ appeared at 5.12 ppm with a $J_{1',2'}$ 4.1 Hz. The ^{13}C NMR spectrum showed the C-1′ at 99.9 ppm that confirmed the α-furanosidic linkage. Further acetylation



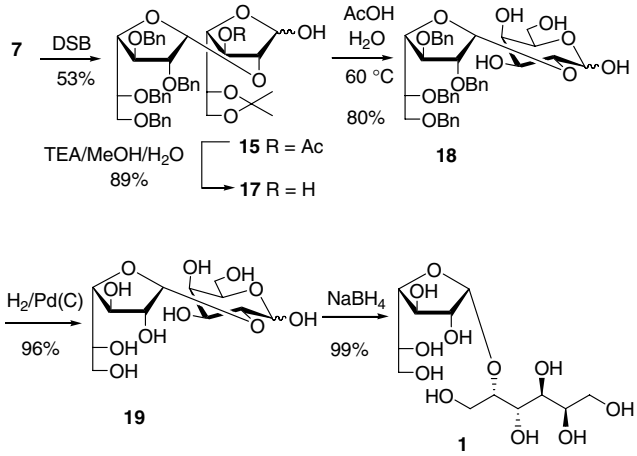
Scheme 1.

of **6** to give **7** confirmed the site of glycosylation. In the ^{1}H NMR spectrum of **6**, H-3 of the galactone moiety appeared as a doublet of triplets at 3.78 ppm, and it shifted 1.61 ppm downfield in the acetylated compound **7**, indicating that the coupling occurred with OH-2.

Other products were observed in the glycosidation reaction. The crystalline β-(1→2) disaccharide **8** was recovered in 8% yield. The anomeric configuration was established from the ^{1}H NMR (δ 5.31 ppm, J 1.3 Hz for H-1′) and ^{13}C NMR (δ 104.6 ppm for C-1′) parameters. Acetylation of **8** gave **9** and confirmed the site of glycosylation, as shown by the downfield shift (0.88 ppm) of H-3 in the ^{1}H NMR spectrum compared to the same signal in **8**. On the other hand, byproducts resulting from 3-O-glycosylation of the lactone were also obtained. An inseparable mixture of the α-(1→3) and β-(1→3) disaccharides **10** and **11** was obtained in 16% yield. The anomeric signals in the ^{1}H NMR spectrum appeared as doublets at 4.92 ppm (J 4.4 Hz) and 5.28 ppm (J 1.3 Hz), indicating a 7:3 α/β ratio. Acetylation of the mixture allowed further separation and characterization of the acetylated products **12** and **13**, which showed in their ^{1}H NMR spectra deshielded doublets at 5.58 ppm (J 7.1 Hz) and 5.71 ppm (J 8.0 Hz), respectively, due to acetylation of lactonic OH-2 confirming the glycosylation site.

Finally, the rearranged imidate byproduct 2,3,5,6-tetra-*O*-benzyl-*N*-trichloroacetyl-β-D-galactofuranosylamine (**14**) was also recovered in 13% yield and was fully characterized. *N*-Glycosyl trichloroacetamides as byproducts of the glycosylation reaction have been described.[39]

Diisoamylborane reduction of the lactone function of **7** gave the corresponding hemiacetal, α-D-Gal*f*-(1→2)-D-Gal*f* (**15**), as a 4:1 β/α mixture in 53% yield (Scheme 2). Compound **15** is a synthon for the construction of the branching unit α-D-Gal*f*-(1→2)-Gal*f*, found in varianose, a complex carbohydrate elaborated by *P. varians* and other fungi.[10–14] The moderate yield obtained in the reduction reaction would be due to partial hydrolysis of the isopropylidene group of **15**, probably during workup of the reaction. In fact, 2,3,5,6-tetra-*O*-benzyl-α-D-galactofuranosyl-(1→2)-3-*O*-acetyl-D-galactose (**16**)



Scheme 2.

was obtained (14%) as a mixture of the four anomers, β-pyranose/α-pyranose/β-furanose/α-furanose in 33:29:14:24 ratio as indicated by the integration of the anomeric protons in the ^{1}H NMR spectrum. Deprotection of the acetyl group of the isopropylidene derivative **15** was smoothly performed with triethylamine–MeOH–water to give **17** that crystallized from the reaction mixture in 89% yield. Aqueous acetic acid hydrolysis of the *O*-isopropylidene group of **17** gave **18** in 80% yield, as a mixture of β/α pyranose anomers in a 85:15 ratio. Catalytic hydrogenation of **18** afforded the free disaccharide, α-D-Gal*f*-(1→2)-D-Gal (**19**), in 96% yield. The galactose reducing end was in the pyranose form in a 5:1 β:α ratio.

Further borohydride reduction of the anomeric center gave the alditol, α-D-Gal*f*-(1→2)-GalOH (**1**). The chemical shifts in the ^{1}H NMR spectrum matched with those reported for the alditol released by reductive β-elimination from glycoproteins of *C. thermocellum*[20b] and *B. cellulosolvens*,[21a] confirming the unusual structure. The ^{13}C NMR spectrum was also recorded and showed the resonance for the anomeric center at 100.8 ppm.

In order to obtain alditol **2** that contains Gal*f* in both α and β configurations, a second glycosylation step was performed on acceptor **6**. Thus, the imidate procedure was again used, employing in this case tetra-*O*-ben-

zoyl-β-D-galactofuranose trichloroacetimidate (**20**).[31] The anchimeric assistance of the benzoyl group in position-2 favors β-glycosylation. We had previously used donor **20** for glycosylation of the 4-OH in *N*-acetylglucosamine derivatives with high yield.[25] In the present case, glycosylation of disaccharide lactone **6** with imidate **20** gave the expected β-(1→3) linkage of trisaccharide lactone **21** in a 46% yield (Scheme 3). In the ^{1}H NMR spectrum, the H-1 signal for the new glycosidic linkage appeared at 5.64 ppm as a broad singlet and correlated with the C-1 signal at 106.3 ppm in the ^{13}C NMR spectrum, indicating the β configuration. The moderate yield could be related to the steric hindrance exerted by the substituent at O-2. In fact, the corresponding imidate transposition product, 2,3,5,6-tetra-*O*-benzoyl-*N*-trichloroacetyl-β-D-galactofuranosylamine (**22**), was also obtained in 38% yield, and unreacted starting material **6** (27%) was also recovered. Glycosylation using the thioglycoside procedure (phenyl tetra-*O*-benzoyl-1-thio-D-galactofuranoside[40] activated by NIS) was attempted, but lower yields of **21** were achieved.

Removal of the *O*-isopropylidene group of **21** gave syrupy **23**. In order to obtain the corresponding alditol derivative, sodium borohydride reduction, followed by methanolysis, was performed to give alditol **24**. Hydrogenolysis of the benzyl groups afforded the target alditol **2**. The ^{1}H NMR spectrum showed the anomeric protons in the α (δ 5.21, J 4.4 Hz) and β configurations (δ 5.06 ppm, J 2.6 Hz) of the furanose form. The ^{13}C NMR spectrum was also recorded and full assignment was performed, showing the signals at 110.5 and 102.1 ppm for C-1β and C-1α, respectively.

In conclusion, we report the first synthesis of a trisaccharide containing galactofuranose in both anomeric configurations. Moreover, this is the first synthesis of α-D-galactofuranosyl-containing moieties of bacterial glycoproteins. The approach of selective glycosylation of an aldono-1,4-lactone was used for the synthesis. Analysis by NMR spectroscopy confirmed the presence of the disaccharide and trisaccharide in the structure of *B. cellulosolvens* glycoproteins.

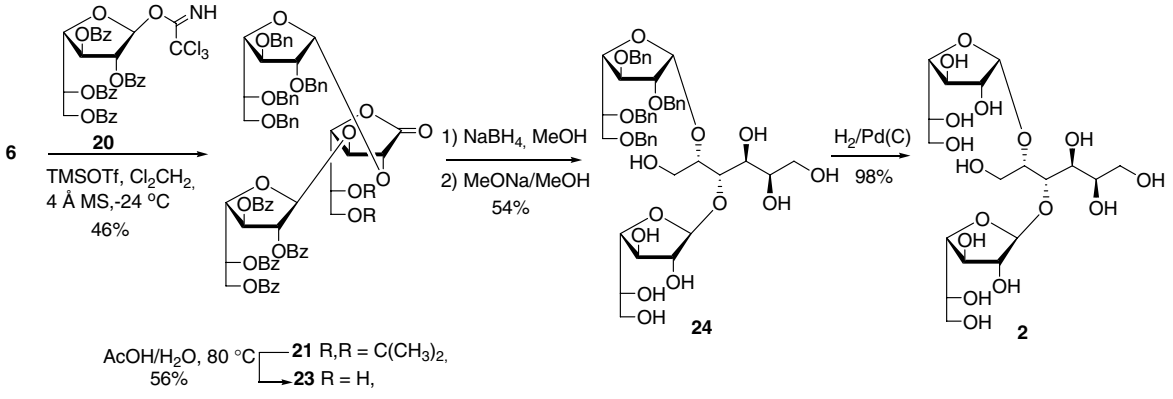
3. Experimental

3.1. General methods

Melting points were determined with a Thomas–Hoover apparatus and are uncorrected. Optical rotations were measured with a Perkin–Elmer 343 polarimeter at 25 °C. TLC was performed on 0.2 mm Silica Gel 60 F254 (E. Merck) aluminum supported plates. When TEA was added to the solvent system, a previous TLC elution was performed. Detection was effected by exposure to UV light or by spraying with 5% (v/v) H_2SO_4 in EtOH and charring. Column chromatography was performed on Silica Gel 60 (230–400 mesh, E. Merck). NMR spectra were recorded with a Bruker AM 500 spectrometer at 500 MHz (^{1}H) and 125.8 MHz (^{13}C) or with a Bruker AC 200 at 200 MHz (^{1}H) and 50.3 MHz (^{13}C). Chemical shifts are given relative to the signal of internal acetone standard at 2.16 and 30.8 ppm for ^{1}H NMR and ^{13}C NMR spectra when recorded in D_2O. ^{1}H and ^{13}C assignments were supported by DEPT 135, homonuclear COSY and HETCOR experiments. High-resolution mass spectra (HRMS) were recorded on a Micromass Q-TOF Ultima Tandem Quadrupole/Time-of-Flight Instrument equipped with an electrospray-ionisation (ESI) source, or in a PE BIOSYSTEMS DE-STR-MALDI TOF System (2000).

3.2. Preparation of 2,3,5,6-tetra-*O*-benzyl-D-galactofuranosyl trichloroacetimidate[31] (5)

To a stirred solution of 2,3,5,6-tetra-*O*-benzyl-D-galactofuranose[38] (1.64 g, 3.04 mmol) and trichloroacetonitrile (1.50 mL, 14.9 mmol) in CH_2Cl_2 (20 mL) cooled to 0 °C was slowly added DBU (0.181 mL, 1.21 mmol). After 1 h TLC monitoring showed the consumption of the starting material. The solution was concentrated at room temperature under reduced pressure, and the residue was purified by column chromatography (6:1:0.06 hexane–EtOAc–TEA) to give an amorphous solid of 2,3,5,6-tetra-*O*-benzyl-D-galactofuranosyl trichloroace-



Scheme 3.

timidate (**5**) as 10:1 β:α anomeric mixture (1.94 g, 93%) that showed R_f 0.59 (β anomer); 0.50 (α anomer) (3:1:0.03 hexane–EtOAc–TEA); ^{1}H NMR ($CDCl_3$, 500 MHz): δ (for the β anomer, only diagnostic signals are listed for the α anomer) 8.50 (N*H*, 0.91H), 8.44 (N*H*, 0.09H α anomer), 7.41–7.34 (m, 20H), 6.44 (d, 0.09H, *J* 4.2 Hz, H-1α), 6.38 (d, 0.91H, *J* 0.8 Hz, H-1), 4.73, 4.40 (2d, 1.82H, *J* 11.7 Hz), 4.68, 4.57 (2d, 1.82H, *J* 11.8 Hz), 4.53, 4.32 (2d, 1.82H, *J* 11.8 Hz), 4.51–4.45 (m, 1.82H), 4.42 (dd, 0.91H, *J* 6.1, 4.2 Hz), 4.21 (dd, 0.91H, *J* 0.8, 2.3 Hz), 4.12 (dd, 0.91H, *J* 2.3, 6.1 Hz), 4.83 (ddd, 0.91H, *J* 4.2, 5.5, 5.8 Hz), 3.72–3.65 (m, 1.82H); ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ (for the β anomer, only the anomeric carbon is listed for the α anomer) 160.9 (C=NH), 138.4–127.5, 104.2 (C-1), 98.2 (C-1 α anomer), 91.2, 86.7, 84.3, 82.8, 76.5; 73.4, 73.2, 71.9, 70.5. The anomeric resonances are in agreement with literature values.[31]

3.3. 2,3,5,6-Tetra-*O*-benzyl-α-D-galactofuranosyl-(1→2)-5,6-*O*-isopropylidene-D-galactono-1,4-lactone (6)

3.3.1. 2,3,5,6-Tetra-*O*-benzyl-*N*-trichloroacetyl-β-D-galactofuranosylamine (14). A vigorously stirred suspension of dried trichloroacetimidate **5** (1.90 g, 2.78 mmol), 5,6-*O*-isopropylidene-D-galactono-1,4-lactone[36] (**3**, 0.86 g, 3.89 mmol) and dried 4 Å powdered molecular sieves (0.9 g) in anhyd CH_2Cl_2 (50 mL) was cooled to −27 °C. After 10 min, TMSOTf (0.131 mL, 0.74 mmol) was slowly added. After 1 h, TLC monitoring showed consumption of imidate **5**, the mixture was rapidly filtered and quenched by the addition of satd aq $NaHCO_3$ (25 mL). After dilution with CH_2Cl_2 (220 mL) and additional satd aq $NaHCO_3$, the organic phase was separated and washed with water, dried ($MgSO_4$), and concentrated. The oily residue was purified by column chromatography (9:1 toluene–EtOAc and then 4:1 toluene–EtOAc). The fastest migrating component (R_f 0.76, 4:1 toluene–EtOAc) was identified as 2,3,5,6-tetra-*O*-benzyl-*N*-trichloroacetyl-β-D-galactofuranosylamine (**14**, 0.24 g, 13%): $[\alpha]_D$ +5.6 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.02 (d, 1H, *J* 8.8 Hz, N*H*), 7.35–7.22 (m, 20H), 5.88 (dd, 1H, *J* 5.7, 8.8 Hz, H-1), 4.70, 4.61 (2d, 2H, *J* 11.4 Hz), 4.55, 4.50 (2d, 2H, *J* 12.0 Hz), 4.46, 4.44 (2d, 2H, *J* 11.7 Hz), 4.46, 4.30 (2d, 2H, *J* 11.9 Hz), 4.24 (t, 1H, *J* 5.7 Hz), 4.15–4.10 (m, 2H), 3.71 (dd, 1H, *J* 6.1, 9.2 Hz), 3.63 (dd, 1H, *J* 5.4, 9.2 Hz), 3.63 (m, 1H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 161.3 (NH*C*OCl_3), 137.9–127.6, 83.8, 82.1, 81.4, 81.3, 76.7, 73.9, 73.6, 72.9, 72.0, 70.4. HRMS (MALDI) Calcd for $C_{36}H_{36}Cl_3NO_6$ $[M+Na]^+$ 706.1506. Found: $[M+Na]^+$ 706.1499. The second fraction from the column (R_f 0.48, 4:1 toluene–EtOAc) afforded crystalline **6** (1.05 g, 51%): mp 101–102 °C (9:1 hexane–EtOAc); $[\alpha]_D$ +17.4 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.47–7.18 (m, 20H, aromatic), 5.12 (d, 1H, *J* 4.1 Hz, H-1′), 4.92, 4.66 (2d, 2H, *J* 11.6 Hz, C*H*$_2$Ph), 4.83, 4.59 (2d, 2H, *J* 12.1 Hz, C*H*$_2$Ph), 4.69 (d, 1H, *J* 2.3 Hz, OH), 4.54, 4.51 (2d, 2H, *J* 12.1 Hz, C*H*$_2$Ph), 4.48, 4.13 (2d, 2H, *J* 11.2 Hz, C*H*$_2$Ph), 4.45 (t, 1H, *J* 8.2 Hz, H-3′), 4.24 (d, 1H, *J* 8.4 Hz, H-2), 4.12 (dd, *J* 4.1, 7.8 Hz, H-2′), 3.98 (d, 1H, *J* 8.2, H-4′), 3.91 (dd, 1H, *J* 5.7, 8.5 Hz, H-4), 3.91–3.86 (m, 1H, H-5), 3.78 (dt, 1H, *J* 8.5, 2.3 Hz, H-3), 3.78–3.74 (m, 2H, H-6a, H-6b), 3.66–3.63 (m, 3H, H-5′, H-6a′, H-6b′), 1.38, 1.36 (2s, 6H, (C*H*$_3$)$_2$C). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 171.4 (C-1), 137.9–127.6 (aromatic), 109.9 ((CH$_3$)$_2$*C*), 100.0 (C-1′), 83.0 (C-2′), 79.9 (C-4′), 79.2 (C-2), 79.1 (C-4), 77.7 (C-3′), 76.0 (C-5′), 75.6 (C-5); 74.6, 73.6 (*C*H$_2$Ph), 72.5 (C-3); 72.2, 72.0 (*C*H$_2$Ph), 70.3 (C-6′), 64.8 (C-6), 26.3, 25.7 ((*C*H$_3$)$_2$C). Anal. Calcd for $C_{43}H_{48}O_{11}$: C, 69.71; H, 6.53. Found: C, 69.87; H, 6.50.

3.3.2. Mixture of 2,3,5,6-tetra-*O*-benzyl-β-D-galactofuranosyl-(1→3)-5,6-*O*-isopropylidene-D-galactono-1,4-lactone (10) and 2,3,5,6-tetra-*O*-benzyl-α-D-galactofuranosyl-(1→3)-5,6-*O*-isopropylidene-D-galactono-1,4-lactone (11). The third fraction from the column (R_f 0.31, 4:1 toluene–EtOAc) was identified as a mixture of 2,3,5,6-tetra-*O*-benzyl-β-D-galactofuranosyl-(1→3)-5,6-*O*-isopropylidene-D-galactono-1,4-lactone (**10**) and 2,3,5,6-tetra-*O*-benzyl-α-D-galactofuranosyl-(1→3)-5,6-*O*-isopropylidene-D-galactono-1,4-lactone (**11**) (330 mg, 16%): ^{1}H NMR ($CDCl_3$, 500 MHz, anomeric region): δ 5.28 (d, *J* 1.3 Hz, 0.3H, β anomer, H-1′), 4.92 (d, *J* 4.4 Hz, 0.7H, α anomer, H-1′); ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 171.5 (C-1 of α and β anomer), 138.2–127.5, 110.4, 110.2, 106.0 (C-1′β), 99.9 (C-1′α), 88.3, 83.4, 82.7, 81.8, 81.7, 80.0, 79.8, 79.4, 78.2, 76.1, 76.0, 74.8, 74.3, 73.6, 73.4, 73.3, 73.2, 73.1, 72.8, 72.7, 72.6, 72.2, 70.0, 69.6, 65.1, 65.0, 25.9, 25.8, 25.7, 25.6.

3.3.3. 2,3,5,6-Tetra-*O*-benzyl-β-D-galactofuranosyl-(1→2)-5,6-*O*-isopropylidene-D-galactono-1,4-lactone (8). The lowest migrating component from the column (R_f 0.12, 4:1 toluene–EtOAc) was identified as 2,3,5,6-tetra-*O*-benzyl-β-D-galactofuranosyl-(1→2)-5,6-*O*-isopropylidene-D-galactono-1,4-lactone (**8**) (165 mg, 8%). Compound **8** was crystallized from 6:1 hexane–EtOAc, mp 105–107 °C; $[\alpha]_D$ −66.1 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.38–7.20 (m, 20H, aromatic), 5.31 (d, 1H, *J* 1.3 Hz, H-1′), 4.64, 4.54 (2d, 2H, *J* 12.0 Hz, C*H*$_2$Ph), 4.62, 4.47 (2d, 2H, *J* 11.8 Hz, C*H*$_2$Ph), 4.58 (ddd, 1H, *J* 3.5, 8.4, 9.5 Hz, H-3), 4.52, 4.49 (2d, 2H, *J* 12.0 Hz, C*H*$_2$Ph), 4.46 (d, 1H, *J* 9.5 Hz, H-2), 4.45, 4.32 (2d, 2H, *J* 11.6 Hz, C*H*$_2$Ph), 4.39 (dd, 1H, *J* 3.2, 7.6 Hz, H-3′), 4.27 (dt, 1H, *J* 3.8, 6.9 Hz, H-5), 4.14 (dd, *J* 1.3, 3.2 Hz, H-2′), 4.07 (dd, 1H, *J* 3.6, 7.6 Hz, H-4′), 4.04 (dd, 1H, *J* 6.9, 8.6 Hz, H-6a), 3.99 (dd, 1H, *J* 3.8, 8.4 Hz, H-4), 3.95 (dd, 1H, *J* 6.9, 8.6 Hz, H-6b), 3.76–3.71 (m, 2H, H-5′, H-6a′), 3.73 (dd, 1H, *J* 5.5,

12.0 Hz, H-6a′), 3.63 (dd, 1H, *J* 7.7, 12.0 Hz, H-6b′), 3.45 (d, 1H, *J* 3.5 Hz, O*H*), 1.41, 1.38 (2s, 6H, (CH_3)$_2$C). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 170.4 (C-1), 137.9–127.6 (aromatic), 110.0 ((CH$_3$)$_2$*C*), 104.6 (C-1′), 88.1 (C-2′), 82.3 (C-4′), 80.9 (C-3′), 78.7 (C-2), 78.3 (C-4), 75.4 (C-5′), 73.8 (C-5); 73.5, 73.2 (*C*H$_2$Ph), 72.5 (C-3); 72.1, 72.1 (*C*H$_2$Ph), 70.0 (C-6′), 64.9 (C-6), 26.1, 25.6 ((*C*H$_3$)$_2$C). Anal. Calcd for $C_{43}H_{48}O_{11}$: C, 69.71; H, 6.53. Found: C, 69.73; H, 6.73.

3.4. 2,3,5,6-Tetra-*O*-benzyl-α-D-galactofuranosyl-(1→2)-3-*O*-acetyl-5,6-*O*-isopropylidene-D-galactono-1,4-lactone (7)

To a stirred solution of 2,3,5,6-tetra-*O*-benzyl-α-D-galactofuranosyl-(1→2)-5,6-*O*-isopropylidene-D-galactono-1,4-lactone (**6**, 255 mg, 0.34 mmol) in dry pyridine (2.6 mL), cooled to 0 °C was added dropwise Ac_2O (2.6 mL). After 30 min at 0 °C and another 30 min at room temperature, the mixture was cooled to 0 °C, and MeOH (3 mL) was added. The solution was diluted with CH_2Cl_2 (50 mL), and the organic layer was sequentially washed with 5% HCl (50 mL), water (50 mL), satd aq $NaHCO_3$ (50 mL), and water (2 × 50 mL), dried ($MgSO_4$), and concentrated. Purification of the crude product by column chromatography (9:1 toluene–EtOAc) gave **7** (218 mg, 86%) as a syrup: R_f 0.38 (5:1 toluene–EtOAc); $[\alpha]_D$ +48.2 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.31–7.22 (20H, aromatic), 5.55 (d, 1H, *J* 4.3 Hz, H-1′), 5.39 (t, 1H, *J* 4.7 Hz, H-3), 4.76, 4.35 (2d, 2H, *J* 11.9 Hz, C*H*$_2$Ph), 4.69, 4.65 (2d, 2H, *J* 11.8 Hz, C*H*$_2$Ph), 4.61 (d, 1H, *J* 4.8 Hz, H-2), 4.53 (m, 2H, C*H*$_2$Ph), 4.49, 4.45 (2d, 2H, *J* 12.1 Hz, C*H*$_2$Ph), 4.38 (dt, 1H, *J* 4.1, 6.6 Hz, H-5), 4.30 (t, 1H, *J* 7.6 Hz, H-3′), 4.17 (t, 1H, *J* 4.1 Hz, H-4), 4.10 (dd, *J* 4.3, 7.7 Hz, H-2′), 4.01 (dd, 1H, *J* 7.0, 8.5 Hz, H-6a), 4.00 (dd, 1H, *J* 7.8, 4.7 Hz, H-4′), 3.89 (dd, 1H, *J* 6.4, 8.5 Hz, H-6b), 3.65–3.62 (m, 1H, H-5′), 3.59–3.57 (m, 2H, H-6a′, H-6b′), 1.94 (COC*H*$_3$), 1.30, 1.26 (2s, 6H, (C*H*$_3$)$_2$C). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 171.7 (C-1), 169.9 (*C*OCH$_3$), 138.6–127.5 (aromatic), 110.4 ((CH$_3$)$_2$*C*), 99.3 (C-1′), 83.5 (C-2′), 81.6 (C-4′), 80.9, 79.9 (C-2, C-4), 78.2 (C-3′); 75.0, 74.9 (C-5′, C-5), 74.0 (C-3); 73.4, 72.9, 72.2, 72.0 (*C*H$_2$Ph), 70.3 (C-6′), 65.2 (C-6), 26.0, 25.4 ((*C*H$_3$)$_2$C), 20.5 (COCH$_3$). Anal. Calcd for $C_{45}H_{50}O_{12}$: C, 69.04; H, 6.44. Found: C, 69.10; H, 6.37.

3.5. 2,3,5,6-Tetra-*O*-benzyl-β-D-galactofuranosyl-(1→2)-3-*O*-acetyl-5,6-*O*-isopropylidene-D-galactono-1,4-lactone (9)

2,3,5,6-Tetra-*O*-benzyl-β-D-galactofuranosyl-(1→2)-5,6-*O*-isopropylidene-D-galactono-1,4-lactone (**8**, 31 mg, 0.042 mmol) was acetylated as described for **6**. Purification of the crude product by column chromatography (2:1 hexane–EtOAc) gave **9** (30 mg, 91%) as a syrup: R_f 0.32 (2:1 hexane–EtOAc); $[\alpha]_D$ −47.0 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.28–7.13 (m, 20H, aromatic), 5.46 (dd, 1H, *J* 5.3, 5.7 Hz, H-3), 5.19 (br s, 1H, H-1′), 4.74, 4.42 (2d, 2H, *J* 11.8 Hz), 4.60, 4.50 (2d, 2H, *J* 11.6 Hz), 4.58 (d, 1H, *J* 5.7 Hz), 4.51, 4.30 (2d, 2H, *J* 12.0 Hz), 4.49, 4.47 (2d, 2H, *J* 9.7 Hz), 4.40 (dd, 1H, *J* 2.9, 6.9 Hz), 4.38 (ddd, 1H, *J* 3.1, 6.3, 6.9 Hz), 4.25 (dd, 1H, *J* 5.3, 3.1 Hz), 4.09 (dd, 1H, *J* 1.2, 2.9 Hz), 4.08 (dd, 1H, *J* 2.9, 6.9 Hz), 4.07 (dd, 1H, *J* 6.9, 8.6 Hz), 3.93 (dd, 1H, *J* 6.3, 8.6 Hz), 3.81 (ddd, 1H, *J* 2.9, 4.8, 6.3 Hz), 3.76 (dd, 1H, *J* 6.3, 10.1 Hz), 3.73 (dd, 1H, *J* 4.8, 10.1 Hz), 2.08 (s, 3H), 1.40, 1.36 (2s, 6H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 170.4, 169.8, 138.4–127.6, 110.5, 105.5 (C-1′), 88.1, 82.7, 81.5, 79.2, 76.0, 75.0, 74.8, 74.4, 73.5, 73.4, 72.0, 71.9, 71.7, 65.0, 25.9, 25.4, 20.7.

3.6. 2,3,5,6-Tetra-*O*-benzyl-β-D-galactofuranosyl-(1→3)-2-*O*-acetyl-5,6-*O*-isopropylidene-D-galactono-1,4-lactone (12) and 2,3,5,6-tetra-*O*-benzyl-α-D-galactofuranosyl-(1→3)-2-*O*-acetyl-5,6-*O*-isopropylidene-D-galactono-1,4-lactone (13)

The crude mixture of 2,3,5,6-tetra-*O*-benzyl-β-D-galactofuranosyl-(1→3)-5,6-*O*-isopropylidene-D-galactono-1,4-lactone and 2,3,5,6-tetra-*O*-benzyl-α-D-galactofuranosyl-(1→3)-5,6-*O*-isopropylidene-D-galactono-1,4-lactone (**10** and **11**, 110 mg, 0.15 mmol) was acetylated as described for **6**. The residue was purified by column chromatography (4:1 hexane–EtOAc). The first fraction (R_f 0.85, 3:1 toluene–EtOAc) afforded syrupy **12** (11 mg, 9%): $[\alpha]_D$ −41.6 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.42–7.18 (m, 20H, aromatic), 5.58 (d, 1H, *J* 7.1 Hz, H-2), 5.18 (d, 1H, *J* 1.3 Hz, H-1′), 4.66, 4.47 (2d, 2H, *J* 11.8 Hz, C*H*$_2$Ph), 4.60 (t, *J* 6.8 Hz, H-3), 4.58, 4.43 (2d, 2H, *J* 11.8 Hz, C*H*$_2$Ph), 4.50, 4.29 (2d, 2H, *J* 11.6 Hz, C*H*$_2$Ph), 4.51, 4.45 (2d, 2H, *J* 12.2 Hz, C*H*$_2$Ph), 4.31 (dt, 1H, *J* 2.8, 6.7 Hz, H-5), 4.20 (dd, 1H, *J* 2.8, 6.7 Hz, H-4), 4.10 (dd, 1H, *J* 3.4, 6.9 Hz, H-3′), 4.02 (dd, 1H, *J* 3.3, 6.9 Hz, H-4′), 4.00 (dd, 1H, *J* 1.3, 3.4 Hz, H-2′), 3.88 (dd, 1H, *J* 6.8, 8.5 Hz, H-6a), 3.86 (dd, 1H, *J* 6.7, 8.5 Hz, H-6b), 3.73 (dt, 1H, *J* 3.3, 6.1 Hz, H-5′), 3.64–3.62 (m, 2H, H-6a, H-6b), 2.16 (s, 3H, COC*H*$_3$), 1.37, 1.30 (2s, 6H, (C*H*$_3$)$_2$C). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 169.5 (C-1), 169.2 (CH$_3$*C*O), 138.1–127.5 (aromatic), 110.2 ((CH$_3$)$_2$*C*), 105.9 (C-1′), 87.9 (C-2′), 82.5 (C-4′), 81.8 (C-3′), 79.7 (C-4), 75.9 (C-3), 75.9 (C-5′), 73.9 (C-5), 73.7 (C-2); 73.4, 73.3, 72.2, 72.0 (*C*H$_2$Ph), 70.1 (C-6′), 65.0 (C-6), 25.9, 25.6 ((*C*H$_3$)$_2$C), 20.5 (*C*H$_3$CO). The second fraction was a mixture of **12** and **13** (67 mg, 57%). The last fraction (R_f 0.80, 3:1 toluene–EtOAc) afforded crystalline **13** (18.5 mg, 16%): mp 107 °C (8:1 hexane–EtOAc); $[\alpha]_D$ +4.6 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.37–7.20 (m, 20H, aromatic), 5.71 (d,

1H, *J* 8.0 Hz, H-2), 4.77, 4.51 (2d, 2H, *J* 11.8 Hz, CH_2Ph), 4.73 (d, 1H, *J* 4.4 Hz, H-1′), 4.67, 4.05 (2d, 2H, *J* 10.0 Hz, CH_2Ph), 4.61, 4.60 (2d, 2H, *J* 12.0 Hz, CH_2Ph), 4.59, 4.52 (2d, 2H, *J* 12.0 Hz, CH_2Ph), 4.34 (t, *J* 8.1 Hz, H-3), 4.22 (t, 1H, *J* 8.0 Hz, H-3′), 4.12 (dt, 1H, *J* 2.7, 6.9 Hz, H-5), 4.00 (dd, 1H, *J* 4.4, 8.2 Hz, H-2′), 3.94 (dd, 1H, *J* 1.5, 7.8 Hz, H-4′), 3.91 (dd, 1H, *J* 6.9, 8.5 Hz, H-6a), 3.78 (dd, 1H, *J* 6.9, 8.5 Hz, H-6b), 3.74 (dd, 1H, *J* 5.6, 9.3 Hz, H-6a′), 3.59 (dd, 1H, *J* 6.2, 9.3 Hz, H-6b′), 3.55 (dt, 1H, *J* 1.5, 6.0 Hz, H-5′), 3.28 (dd, 1H, *J* 2.7, 8.0 Hz, H-4), 2.04 (s, 3H, CH_3), 1.37, 1.34 (2s, 6H, (CH_3)$_2$C). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 169.6 (C-1), 169.1 (CH_3CO), 138.3–127.6 (aromatic), 110.1 ((CH_3)$_2$*C*), 99.8 (C-1′), 83.7 (C-2′), 79.7 (C-4′), 78.5 (C-3′), 77.7 (C-3), 77.3 (C-4), 76.0 (C-5′), 73.8 (C-2); 73.5, 73.4 (*C*H$_2$Ph), 73.1 (C-5); 72.6, 72.5 (*C*H$_2$Ph), 70.0 (C-6′), 64.9 (C-6), 26.0, 25.6 ((*C*H$_3$)$_2$C), 20.5 (*C*H$_3$CO). Anal. Calcd for $C_{45}H_{50}O_{12}$: C, 69.04; H, 6.44. Found: C, 69.02; H, 6.77.

3.7. 2,3,5,6-Tetra-*O*-benzyl-α-D-galactofuranosyl-(1→2)-3-*O*-acetyl-5,6-*O*-isopropylidene-D-galactofuranose (15)

A solution of bis(isoamyl)borane (0.84 mmol) in anhyd THF (0.25 mL) cooled to 0 °C and under an argon atmosphere was added to a flask containing dry compound **7** (168 mg, 0.21 mmol). The resulting solution was stirred for 20 h at room temperature and then processed as already described.[41] The organic layer was washed with water, dried ($MgSO_4$), and concentrated. Boric acid was eliminated by co-evaporation with MeOH (5 × 5 mL) at room temperature. Purification of the crude product by column chromatography gave **15** (88 mg, 53%) as a syrup: R_f 0.25 (2:1 hexane–EtOAc); $[\alpha]_D$ +28.5 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): (for the β anomer, only the anomeric proton is listed for the α anomer) δ 7.26–7.18 (m, 20H, aromatic), 5.45 (dd, 0.77H, *J* 1.2, 3.9 Hz (interchangeable with D_2O), H-1, β anomer), 5.40 (dd, 0.23H, *J* 4.4, 10.9 Hz (interchangeable with D_2O), H-1, α anomer), 5.11 (dd, 0.77H, *J* 2.0, 3.7 Hz, H-3), 5.08 (d, 0.77H, *J* 4.6 Hz, H-1′), 4.67, 4.54 (2d, 1.54H, *J* 11.9 Hz, CH_2Ph), 4.64, 4.34 (2d, 1.54H, *J* 11.5 Hz, CH_2Ph), 4.60, 4.52 (2d, 1.54H, *J* 11.7 Hz, CH_2Ph), 4.50, 4.47 (2d, 1.54H, *J* 11.9 Hz, CH_2Ph), 4.29 (m, 0.77H, H-5), 4.27 (t, 0.77H, *J* 7.6 Hz, H-3′), 4.21 (dd, 0.77H, *J* 1.2, 2.0 Hz, H-2), 4.11 (dd, 0.77H, *J* 3.7, 7.3 Hz, H-4), 4.05 (dd, 0.77H, *J* 4.6, 7.7 Hz, H-2′), 3.96 (dd, 0.77H, *J* 4.6, 7.5 Hz, H-4′), 3.95 (dd, 0.77H, *J* 6.5, 8.7 Hz, H-6a), 3.80 (dd, 0.77H, *J* 6.4, 8.7 Hz, H-6b), 3.69 (ddd, 0.77H, *J* 4.6, 5.0, 6.4 Hz, H-5′), 3.64 (dd, 0.77H, *J* 5.0, 10.0 Hz, H-6a′), 3.65 (dd, 0.77H, *J* 6.4, 10.0 Hz, H-6b′), 2.92 (d, 0.77H, *J* 3.9 Hz, OH) 1.98 (s, 2.31H, $COCH_3$), 1.42, 1.28 (2s, 4.62H, (CH_3)$_2$C). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ for the β anomer 169.1 (CH_3CO), 138.5–127.7 (aromatic), 109.7 ((CH_3)$_2$*C*), 100.7 (C-1), 99.7 (C-1′ for α anomer), 99.1 (C-1′), 96.1 (C-1 α anomer), 84.7 (C-4), 84.0 (C-2′), 80.4 (C-5), 80.3 (C-4′), 79.9 (C-2), 78.9 (C-5′), 78.0 (C-3), 76.2 (C-3′); 73.4, 72.8, 72.3, 72.2 (*C*H$_2$Ph), 70.2 (C-6′), 65.7 (C-6); 26.6, 25.3 ((*C*H$_3$)$_2$C), 20.8 (*C*H$_3$CO). Anal. Calcd for $C_{45}H_{52}O_{12}$: C, 68.86; H, 6.68. Found: C, 68.64; H, 6.75.

3.7.1. 2,3,5,6-Tetra-*O*-benzyl-α-D-galactofuranosyl-(1→2)-3-*O*-acetyl-D-galactose (16).

A second fraction from the column afforded syrupy 2,3,5,6-tetra-*O*-benzyl-α-D-galactofuranosyl-(1→2)-3-*O*-acetyl-D-galactose (**16**, 22 mg, 14%): R_f 0.67 (1:1 toluene–EtOAc), $[\alpha]_D$ +48.2 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): (only the values for the anomeric and H-3 protons, and the protecting groups are listed) δ 7.35–7.18 (m, 20H, aromatic), 5.44 (t, 0.24H, *J* 3.5 Hz, H-3, α furanose anomer), 5.38 (d, 0.29H, *J* 3.5 Hz, H-1, α pyranose anomer), 5.37 (d, 0.24H, *J* 4.7 Hz, H-1, α furanose anomer), 5.34 (br s, 0.14H, H-1, β furanose anomer), 5.32 (d, 0.33H, *J* 4.5 Hz, H-1′, β pyranose anomer), 5.30 (dd, 0.14H, *J* 1.5, 3.4 Hz, H-3, β furanose anomer), 5.18 (dd, 0.29H, *J* 3.2, 10.0 Hz, H-3, α pyranose anomer), 5.10 (d, 0.29H, *J* 4.5 Hz, H-1′, α pyranose anomer), 5.00 (d, 0.14H, *J* 4.5 Hz, H-1′, β furanose anomer), 4.98 (d, 0.24H, *J* 4.6 Hz, H-1′, α furanose anomer), 4.88 (dd, 0.33H, *J* 3.2, 10.2 Hz, H-3, β pyranose anomer), 4.65 (d, 0.33H, *J* 7.7 Hz, H-1, β pyranose anomer), 2.02, 2.00, 1.99, 1.97 (4s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 125.8 MHz): (only the values for the anomeric region and the protecting groups are listed) δ 170.5, 170.4, 170.3 (CH_3CO); 138.3–127.5 (aromatic), 100.7 (C-1, β furanose anomer), 100.1 (C-1′, α furanose anomer), 99.3 (C-1′, β pyranose anomer), 99.2 (C-1′, β furanose anomer), 98.8, (C-1′, α pyranose anomer), 96.9 (C-1, β pyranose anomer), 96.3 (C-1, α furanose anomer), 91.6 (C-1, α pyranose anomer); 73.4, 72.9, 72.7, 72.3, 72.4 (*C*H$_2$Ph), 21.1, 21.0, 20.8, 20.7 (CH_3). HRMS (MALDI) Calcd for $C_{42}H_{48}O_{12}$ $[M+Na]^+$ 767.3044. Found: $[M+Na]^+$ 767.3018.

3.8. 2,3,5,6-Tetra-*O*-benzyl-α-D-galactofuranosyl-(1→2)-5,6-*O*-isopropylidene-D-galactofuranose (17)

Compound **15** (45 mg, 0.057 mmol) was suspended in 5:2:1 MeOH–TEA–H_2O (3.0 mL). After 20 h of stirring at room temperature, compound **17** precipitated in situ. The precipitate was filtered and washed with 5:1 MeOH–H_2O affording 2,3,5,6-tetra-*O*-benzyl-α-D-galactofuranosyl-(1→2)-5,6-*O*-isopropylidene-D-galactofuranose (**17**) (38 mg, 89%): R_f 0.40 (1:1 hexane–EtOAc); mp 70–77 °C (MeOH–water); $[\alpha]_D$ +17.8 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): (for the β anomer, only the anomeric protons are listed for the α anomer) δ 7.35–7.19 (m, 20H, aromatic), 5.23 (t, 0.7H, *J* 4.2 Hz, H-1), 5.15 (dd, 0.3H, *J* 4.8, 7.5 Hz, H-1, α anomer), 4.95 (d, 0.7H, *J* 4.4 Hz, H-1′), 4.81 (d, 0.3H, *J* 4.8 Hz, H-1′, α

anomer), 4.78, 4.53 (2d, 1.4H, *J* 11.8 Hz, CH_2Ph), 4.68, 4.59 (2d, 1.4H, *J* 11.8 Hz, CH_2Ph), 4.55–4.51 (m, 1.4H, CH_2Ph), 4.49, 4.18 (2d, 1.4H, *J* 10.8 Hz, CH_2Ph), 4.40 (t, 0.7H, *J* 8.3 Hz, H-3′), 4.10 (d, 0.7H, *J* 2.6 Hz, OH-3), 4.05 (dd, 0.7H, *J* 4.4, 8.3 Hz, H-2′), 3.94 (dd, 0.7H, *J* 1.5, 8.1 Hz, H-4′), 3.89–3.84 (m, 1H, H-4), 3.86 (dd, 0.7H, *J* 4.2, 7.0 Hz, H-2), 3.74 (m, 0.7H, H-5′), 3.70–3.58 (m, 4.2H, H-3, H-5, H-6a, H-6b, H-6a′, H-6b′), 2.69 (d, *J* 4.2 Hz, OH-1, β anomer), 1.37, 1.36 (2s, 4.2H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): (for the β anomer, only the anomeric signals are listed for the α anomer) δ 138.0–127.0 (aromatic), 109.3 ($(CH_3)_2C$), 100.3 (C-1), 99.8 (C-1′), 99.3 (C-1′ for α anomer), 94.7 (C-1 α anomer), 89.7 (C-2 or C-4), 83.4 (C-2′), 80.5 (C-4 or C-2), 79.4 (C-4′), 78.3 (C.3′), 77.4 (C-5′), 76.0, 75.2 (C-5, C-3); 73.9, 72.5, 72.4, 72.3 (*C*H_2Ph); 70.2 (C-6′), 65.1 (C-6); 26.5, 25.7 (CH_3). Anal. Calcd for $C_{43}H_{50}O_{11}$: C, 69.52; H, 6.78. Found: C, 69.63; H, 6.91.

3.9. 2,3,5,6-Tetra-*O*-benzyl-α-D-galactofuranosyl-(1→2)-D-galactose (18)

To a stirred solution of **17** (35 mg, 0.047 mmol) in HOAc (0.40 mL) at 80 °C, H_2O (0.13 mL) was slowly added until turbidity, and heating was continued for 1.5 h. The solution was cooled and concentrated, and the residue was subjected to successive dissolution and evaporation with toluene (3 × 3 mL). Column chromatography (1:2 hexane–EtOAc) of the residue afforded **18** (25.8 mg, 80%) as a hygroscopic syrup: R_f 0.25 (1:5 toluene–EtOAc), $[\alpha]_D$ +39.2 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, D_2O interchanged, 500 MHz): (for the β pyranose anomer, only the anomeric protons are listed for the α anomer) δ 7.40–7.11 (m, 20H, aromatic), 5.35 (d, 0.85H, *J* 4.8 Hz, H-1′), 5.21 (d, 0.15H, *J* 3.8 Hz, H-1 α pyranose anomer), 4.90 (d, 0.15H, *J* 4.5 Hz, H-1′, α pyranose anomer), 4.85, 4.51 (2d, 1.7H, *J* 11.7 Hz, CH_2Ph), 4.66, 4.29 (2d, 1.7H, *J* 11.7 Hz, CH_2Ph), 4.61, 4.34 (2d, 1.7H, *J* 11.5 Hz, CH_2Ph), 4.60 (d, 0.85H, *J* 7.5 Hz, H-1), 4.47 (br s, 1.7H, CH_2Ph), 4.32 (t, 0.85H, *J* 8.4 Hz, H-3′), 3.99 (dd, 0.85H, *J* 4.5, 8.6 Hz, H-2′), 3.91 (dd, 0.85H, *J* 7.5, 12.0 Hz, H-6a), 3.89 (dd, 0.85H, *J* 1.4, 8.2 Hz, H-4′), 3.76 (dd, 0.85H, *J* 1.0, 3.4 Hz, H-4), 3.71–3.67 (m, 0.85H, H-6a′), 3.67 (dd, 0.85H, *J* 3.8, 12.0 Hz, H-6b), 3.65–3.61 (m, 1.7H, H-5′, H-6b′), 3.58 (dd, 0.85H, *J* 7.5, 9.3 Hz, H-2), 3.42 (ddd, 0.85H, *J* 1.0, 3.8, 7.5 Hz, H-5), 3.28 (dd, 0.85H, *J* 3.4, 9.3 Hz, H-3). ^{13}C NMR ($CDCl_3$, 125.8 MHz): (for the β pyranose anomer, only the anomeric signals are listed for the α anomer) δ 138.0–127.6 (aromatic), 100.7 (C-1′, β pyranose anomer), 99.6 (C-1′, α pyranose anomer), 97.0 (C-1, β pyranose anomer), 91.2 (C-1, α pyranose anomer), 83.1 (C-2′), 80.3 (C-2), 79.3 (C-4′), 78.5 (C-3′), 74.9, 74.8 (C-5, C-5′), 73.5 (2 × *C*H_2Ph); 72.4, 71.7 (*C*H_2Ph), 71.1 (C-3), 70.6 (C-6′), 69.2 (C-4), 62.6 (C-6). Anal. Calcd for $C_{40}H_{46}O_{11}$: C, 68.36; H, 6.60. Found: C, 68.24; H, 6.75.

3.10. α-D-Galactofuranosyl-(1→2)-D-galactose (19)

A suspension of compound **18** (55 mg, 0.078 mmol) in MeOH (1.5 mL) and 10% Pd/C (8 mg) was hydrogenated at 45 psi (3 atm) for 4 h at room temperature. The catalyst was filtered off, and the filtrate was evaporated under vacuum to give an amorphous solid, which was dissolved in water (1 mL), passed through a C8-Maxi-Clean and lyophilized. Disaccharide **19** (25.6 mg, 96%) was obtained as a highly hygroscopic syrup: R_f 0.46 (7:1:1 *n*-propanol–MeOH–H_2O), $[\alpha]_D$ +97.6 (*c* 1, H_2O); ^{1}H NMR (D_2O, 500 MHz): (for the β pyranose anomer, only the anomeric protons are listed for the α anomer) δ 5.30 (d, 0.3H, *J* 3.7 Hz, H-1, α pyranose anomer), 5.21 (d, 0.7H, *J* 4.7 Hz, H-1′), 5.07 (d, 0.3H, *J* 4.7 Hz, H-1′, α pyranose anomer), 4.61 (d, 0.7H, *J* 7.7 Hz, H-1), 4.20 (dd, 0.7H, *J* 7.7, 8.8 Hz, H-3′), 4.07 (dd, 0.7H, *J* 4.7, 8.8 Hz, H-2′), 3.89 (dd, 0.7H, *J* 1.0, 3.5 Hz, H-4), 3.79 (dd, 0.7H, *J* 2.5, 7.7 Hz, H-4′), 3.73–3.65 (m, H-5′, H-6a, H-6b), 3.64 (dd, 0.7H, *J* 3.5, 9.8 Hz, H-3), 3.61 (ddd, 0.7H, *J* 1.0, 5.0, 7.7 Hz, H-5), 3.58 (dd, 0.7H, *J* 4.4, 11.6 Hz, H-6a′), 3.48 (dd, 0.7H, *J* 6.6, 11.6 Hz, H-6b′), 3.47 (dd, 0.7H, *J* 7.7, 9.8 Hz, H-2). ^{13}C NMR (D_2O, 125.8 MHz): (for the β pyranose anomer, only the anomeric signals are listed for the α anomer) δ 102.1 (C-1′), 101.0 (C-1′ for α pyranose anomer), 96.8 (C-1), 90.9 (C-1, α pyranose anomer), 81.2 (C-4′), 79.8 (C-2), 76.4 (C-2′), 75.6 (C-5), 73.8 (C-3′), 72.0 (C-3), 70.8 (C-5′), 68.9 (C-4), 63.1 (C-6′), 61.5 (C-6). HRMS (ESI) Calcd for $C_{12}H_{23}O_{11}$ $[M+H]^+$ 343.1240. Found: $[M+H]^+$ 343.1253.

3.11. Preparation of α-D-galactofuranosyl-(1→2)-D-galactitol[20b] (1)

To a solution of **19** (13 mg, 0.037 mmol) in 9:1 MeOH–H_2O (1 mL) cooled to 0 °C, $NaBH_4$ (15 mg, 0.39 mmol) was added. After 1 h of stirring at 0 °C and then 30 min at room temperature, the solution was neutralized by elution through a column containing BIO-RAD AG 50W-X12, 100–200 mesh, H^+ form (2.7 mL), washed with 9:1 MeOH–H_2O, and concentrated to dryness. The residue was co-evaporated with MeOH (4 × 1 mL), dissolved in water, passed through a C8-Maxi-Clean cartridge, and lyophilized. Alditol **1** (13 mg, 99%) was obtained as a hygroscopic syrup: R_f 0.40 (7:1:1 *n*-propanol–MeOH–H_2O), $[\alpha]_D$ +45.4 (*c* 1, H_2O). ^{1}H NMR (D_2O, 500 MHz): δ 5.20 (d, 1H, *J* 4.7 Hz, H-1′), 4.13 (dd, 1H, *J* 7.5, 8.6 Hz, H-3′), 4.07 (dd, 1H, *J* 4.7, 8.6 Hz, H-2′), 4.01 (br t, 1H, *J* 6.1 Hz, H-2), 3.91 (br t, 1H, *J* 6.5 Hz, H-5), 3.75 (dd, 1H, *J* 6.5, 11.9 Hz, H-1a), 3.74–3.68 (m, 5H, H-1b, H-3, H-4, H-4′, H-5′), 3.60–3.64 (m, 3H, H-6a, H-6b, H-6a′),

3.55 (dd, 1H, *J* 7.2, 11.6 Hz, H-6b′). The data agree with the literature.[20b] ^{13}C NMR (D_2O, 125.8 MHz): δ 100.8 (C-1′), 80.8 (C-4′), 77.6 (C-2), 76.7 (C-2′), 74.0 (C-3′), 71.4 (C-5′), 70.6 (C-5), 69.9, 69.7 (C-3, C-4), 63.8 (C-6′), 63.2 (C-6), 62.0 (C-1).

3.12. 2,3,5,6-Tetra-*O*-benzyl-α-D-galactofuranosyl-(1→2)[2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→3)]-D-galactono-1,4-lactone (23)

A vigorously stirred suspension of dried trichloroacetimidate **20**[31] (1.17 g, 1.58 mmol), 2,3,5,6-tetra-*O*-benzyl-α-D-galactofuranosyl-(1→2)-5,6-*O*-isopropylidene-D-galactono-1,4-lactone (**6**, 0.84 g, 1.13 mmol), and 4 Å powdered molecular sieves (0.9 g) in anhyd CH_2Cl_2 (60 mL) was cooled to −27 °C and TMSOTf (73 μL, 0.41 mmol) was slowly added. After 2 h, the mixture was filtered and quenched by the addition of satd aq $NaHCO_3$ (30 mL). After dilution with CH_2Cl_2 (250 mL) and additional satd aq $NaHCO_3$, the organic phase was separated and washed with water, dried ($MgSO_4$), and concentrated. Column chromatography (20:1 toluene–EtOAc and then 4:1 toluene–EtOAc) of the residue afforded a first fraction of crystalline 2,3,5,6-tetra-*O*-benzoyl-*N*-trichloroacetyl-β-D-galactofuranosylamine (**22**, 445 mg, 38%); R_f 0.64 (5:1 toluene–EtOAc), mp 156–158 °C (EtOH), $[\alpha]_D$ −7.2 (*c* 1, $CHCl_3$), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.10–8.04 (8H, aromatic), 7.81 (d, 1H, *J* 8.5 Hz, N*H*), 7.65–7.26 (12H, aromatic), 6.10 (dd, 1H, *J* 2.5, 8.5 Hz, H-1), 6.01 (ddd, 1H, *J* 4.1, 4.7, 6.7 Hz, H-5), 5.80 (t, 1H, *J* 2.5 Hz, H-2), 5.69 (dd, 1H, *J* 2.4, 3.7 Hz, H-3), 4.82 (dd, 1H, *J* 4.1, 11.9 Hz, H-6a), 4.80 (dd, 1H, *J* 3.7, 4.7 Hz, H-4), 4.71 (dd, 1H, *J* 6.7, 11.9 Hz, H-6b). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 166.1–165.3 (*C*OPh), 161.4 (NH*C*OCl_3), 134.1–128.2 (aromatic), 86.2 (C-1), 82.5, 79.8, 78.5, 71.0, 63.4. HRMS (MALDI) Calcd for $C_{36}H_{28}Cl_3NO_{10}$ $[M+Na]^+$ 762.0677. Found: $[M+Na]^+$ 762.0688. The second fraction gave 2,3,5,6-tetra-*O*-benzyl-α-D-galactofuranosyl-(1→2)[2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→3)]-5,6-*O*-isopropylidene-D-galactono-1,4-lactone (**21**) (686 mg, 46%) as a hygroscopic syrup: R_f 0.48 (5:1 toluene–EtOAc), $[\alpha]_D$ +22.4 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.07–7.09 (m, 40H, aromatic), 5.97 (dt, 1H, *J* 4.4, 6.8 Hz, H-5″), 5.64 (br s, 1H, H-1″), 5.64–5.62 (m, 2H, H-1′, H-3″), 5.56 (d, 1H, *J* 1.8 Hz, H-2″), 4.77, 4.55 (2d, 2H, *J* 11.6 Hz, CH_2Ph), 4.71 (t, 1H, *J* 5.9 Hz, H-4″), 4.70 (d, 1H, *J* 5.7 Hz, H-2), 4.67, 4.40 (2d, 2H, *J* 11.8 Hz, CH_2Ph), 4.66 (dd, 1H, *J* 4.4, 11.4 Hz, H-6a″), 4.64 (m, 1H, H-3), 4.65, 4.27 (2d, 2H, *J* 11.6 Hz, CH_2Ph), 4.64 (m, 1H, H-3), 4.63 (dd, 1H, *J* 6.8, 11.4 Hz, H-6b″), 4.34 (t, 1H, *J* 7.8 Hz, H-3′), 4.34 (m, 1H, H-5), 4.25–4.20 (m, 3H, CH_2Ph, H-4), 4.08 (dd, 1H, *J* 4.3, 8.0 Hz, H-2′), 3.94 (dd, 1H, *J* 4.8, 7.7 Hz, H-4′), 3.88 (dd, 1H, *J* 6.2, 11.2 Hz, H-6a), 3.85 (dd, 1H, *J* 6.8, 11.2 Hz, H-6b), 3.66 (m, 1H, H-5′), 3.58 (dd, 1H, *J* 5.6, 10.0 Hz, H-6a′), 3.42 (dd, 1H, *J* 5.7, 10.0 Hz, H-6b′), 1.34, 1.26 (2s, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 171.8 (C-1), 165.6–165.1 (*C*OPh), 138.5–128.2 (aromatic), 110.3 ((CH$_3$)$_2$*C*), 106.3 (C-1″), 99.2 (C-1′), 83.5 (C-2′), 82.0 (C-2″, C-4″), 80.4 (C-4), 80.2 (C-4′), 79.9 (C-3′), 78.7 (C-2), 77.8 (C-5′), 77.3 (C-3″), 75.8 (C-3), 73.9 (C-5); 73.2, 72.6, 72.3, 72.2 (*C*H$_2$Ph), 70.5 (C-5″), 69.6 (C-6′), 65.0 (C-6), 63.2 (C-6″), 26.0, 25.4 ((*C*H$_3$)$_2$C).

Unreacted **6** was recovered (224 mg, 27%, R_f 0.30 (5:1 toluene–EtOAc)).

To a stirred solution of **21** (327 mg, 0.25 mmol) in HOAc (2 mL) at 80 °C, H_2O (0.65 mL) was slowly added until turbidity and the heating was continued for 2.5 h. The mixture was cooled and concentrated, and the residue subjected to successive dissolution and evaporation with toluene (3 × 5 mL). Column chromatography (5:1 toluene–EtOAc) of the residue afforded **23** (180 mg, 56%) as a hygroscopic syrup: R_f 0.66 (1:1 toluene–EtOAc), $[\alpha]_D$ +23.2 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.07–7.09 (m, 40H, aromatic), 5.99 (m, 1H, H-5″), 5.61 (dd, 1H, *J* 2.2, 5.3 Hz, H-3″), 5.59 (br s, 1H, H-1″), 5.50 (d, 1H, *J* 4.5 Hz, H-1′), 5.51 (d, 1H, *J* 2.2 Hz, H-2″), 4.81 (dd, 1H, *J* 4.3, 12.0 Hz, H-6a″), 4.76 (t, 1H, *J* 4.7 Hz, H-3), 4.72, 4.54 (2d, 2H, *J* 11.6 Hz, CH_2Ph), 4.67, 4.37 (2d, 2H, *J* 11.6 Hz, CH_2Ph), 4.65 (dd, 1H, *J* 3.9, 5.3 Hz, H-4″), 4.62 (dd, 1H, *J* 5.0, 11.8 Hz, H-6b″), 4.61, 4.25 (2d, 2H, *J* 12.0 Hz, CH_2Ph), 4.55 (d, 1H, *J* 4.8 Hz, H-2), 4.43 (dd, 1H, *J* 2.8, 4.5 Hz, H-4), 4.31 (t, 1H, *J* 7.8 Hz, H-3′), 4.29–4.23 (m, 2H, CH_2Ph), 4.07 (dd, 1H, *J* 4.5, 7.9 Hz, H-2′), 3.95 (dd, 1H, *J* 3.9, 7.7 Hz, H-4′), 3.86 (dt, 1H, *J* 2.8, 5.7 Hz, H-5), 3.67 (dd, 1H, *J* 6.2, 11.5 Hz, H-6a′), 3.64 (m, 1H, H-5′), 3.60 (dd, 1H, *J* 5.9, 9.7 Hz, H-6a), 3.57 (dd, 1H, *J* 5.6, 11.5 Hz, H-6b′), 3.48 (dd, 1H, *J* 5.7, 9.7 Hz, H-6b). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 172.0 (C-1), 166.3–165.2 (*C*OPh), 138.2–127.4 (aromatic), 106.0 (C-1″), 99.4 (C-1′), 83.4 (C-2′), 82.6 (C-4), 82.1 (C-2″), 81.9 (C-4″), 80.2 (C-4′), 79.5 (C-3′), 78.4 (C-3), 77.2 (C-3″), 77.0 (C-5′), 75.7 (C-2); 73.2, 72.7, 72.4, 72.3 (*C*H$_2$Ph); 70.3 (C-5″), 70.0 (C-5), 69.7 (C-6′), 63.5, 62.6 (C-6, C-6″). Anal. Calcd for $C_{74}H_{70}O_{20}$: C, 69.4; H, 5.52. Found: C, 69.12; H, 5.40.

3.13. 2,3,5,6-Tetra-*O*-benzyl-α-D-galactofuranosyl-(1→2)[β-D-galactofuranosyl-(1→3)]-D-galactitol (24)

To a solution of **23** (140 mg, 0.11 mmol) in MeOH (11 mL) cooled to 0 °C, $NaBH_4$ (45 mg, 1.2 mmol) was added. After 1 h of stirring at 0 °C, 0.43 M NaOMe in MeOH (1 mL) was added, and stirring was continued for additional 4 h. The solution was neutralized by elution through a column containing Bio-Rad AG 50W-X12, 100–200 mesh, H^+ form (1.6 mL), washed with

MeOH and concentrated to dryness. The residue was co-evaporated with MeOH (4 × 1 mL). Purification by column chromatography (9:1 $CHCl_3$–MeOH) afforded **24** (51.4 mg, 54%) as a hygroscopic syrup: R_f 0.61 (3:1 EtOAc–MeOH), $[\alpha]_D$ +6.4 (*c* 1, $CHCl_3$); ^1H NMR (CD_3OD, 500 MHz): δ 7.45–7.10 (m, 20H), 5.48 (d, 1H, *J* 4.8 Hz, H-1′), 5.15 (d, 1H, *J* 2.3 Hz, H-1″), 4.82, 4.59 (2d, 2H, *J* 11.6 Hz, CH_2Ph), 4.73, 4.60 (2d, 2H, *J* 11.8 Hz, CH_2Ph), 4.56, 4.28 (2d, 2H, *J* 11.6 Hz, CH_2Ph), 4.55–451 (m, 2H, CH_2PH), 4.25 (t, 1H, *J* 7.5 Hz, H-3′), 4.19 (ddd, 1H, *J* 2.9, 5.4, 6.6 Hz, H-2), 4.11 (dd, 1H, *J* 4.8, 7.5 Hz, H-2′), 4.10–4.08 (m, 3H, H-2″, H-3″, H-4″), 4.09 (dd, 1H, *J* 2.9, 8.5 Hz, H-3), 4.03 (ddd, 1H, *J* 1.5, 5.0, 6.6 Hz, H-5), 3.98 (dd, 1H, *J* 1.5, 8.5 Hz, H-4), 3.97 (dd, 1H, *J* 6.6, 11.4 Hz, H-1a), 3.92 (dd, 1H, *J* 3.7, 7.6 Hz, H-4′), 3.88 (dd, 1H, *J* 5.4, 11.4 Hz, H-1b), 3.77–3.74 (m, 2H, H-5′, H-5″), 3.72–3.66 (m, 4H, H-6′a, H-6′b, H-6a″, H-6b″), 3.66 (dd, 1H, *J* 6.6, 10.9 Hz, H-6a), 3.58 (dd, 1H, *J* 5.0, 10.9 Hz, H-6b). ^{13}C NMR (CD_3OD, 500 MHz, 125.8 MHz): δ 138.1–127.6 (aromatic), 110.4 (C-1″), 101.2 (C-1′), 84.7, 84.2 (C-2″, C-4″), 83.4 (C-2′), 81.0 (C-3′), 80.8 (C-4′), 79.2 (C-2), 78.6 (C-3″), 78.0 (C-3), 77.6 (C-5′), 74.4, 73.7, 73.5, 73.3 (*C*H_2Ph), 72.0, (C-5″), 71.4 (C-5), 71.0 (C-6′), 70.8 (C-4), 65.2 (C-6), 64.2 (C-6″), 61.9 (C-1). Anal. Calcd for $C_{46}H_{58}O_{16}$: C, 63.73; H, 6.74. Found: C, 63.62; H, 6.69. HRMS (ESI) Calcd for $C_{46}H_{59}O_{16}$ $[M+H]^+$ 867.3803. Found: $[M+H]^+$ 867.3794.

3.14. α-D-Galactofuranosyl-(1→2)[β-D-galactofuranosyl-(1→3)]-D-galactitol (2)

A suspension of compound **24** (21 mg, 0.024 mmol) in MeOH (1 mL) and 10% Pd/C (8 mg) was hydrogenated at 45 psi (3 atm) for 3 h at room temperature. The catalyst was filtered off with a 0.2 μm Nylon filter, and the filtrate was evaporated under vacuum to give alditol **2** (12 mg, 98%) as an amorphous solid: R_f 0.28 (7:1:1 *n*-propanol–EtOH–H_2O), $[\alpha]_D$ −11.2 (*c* 1, H_2O); ^1H NMR (D_2O, 500 MHz): δ 5.21 (d, 1H, *J* 4.4 Hz, H-1′), 5.06 (d, 1H, *J* 2.6 Hz, H-1″), 4.12 (dd, 1H, *J* 7.3, 8.5 Hz, H-3′), 4.09 (ddd, 1H, *J* 1.9, 5.5, 6.6 Hz, H-2), 4.06 (dd, 1H, *J* 4.4, 8.5 Hz, H-2′), 4.06 (dd, 1H, *J* 2.6, 4.8 Hz, H-2″), 4.02 (dd, 1H, *J* 4.8, 6.9 Hz, H-3″), 3.97 (m, 1H, H-5), 3.96 (dd, 1H, *J* 3.7, 6.9 Hz, H-4″), 3.92 (dd, 1H, *J* 1.9, 9.3 Hz, H-3), 3.82 (dd, 1H, *J* 6.6, 11.6 Hz, H-1a), 3.78 (dd, 1H, *J* 1.1, 9.3 Hz, H-4), 3.76–3.72 (m, 2H, H-5′, H-5″), 3.72 (dd, 1H, *J* 3.8, 7.3 Hz, H-4′), 3.71 (dd, 1H, *J* 5.5, 11.6 Hz, H-1b), 3.66 (dd, 1H, *J* 4.8, 11.7 Hz, H-6a″), 3.66 (dd, 1H, *J* 5.9, 11.8 Hz, H-6a′), 3.64–3.59 (m, 3H, H-6a, H-6b, H-6b′), 3.57 (dd, 1H, *J* 7.0, 11.7 Hz, H-6b″). ^{13}C NMR (D_2O, 500, 125.8 MHz): δ 110.5 (C-1″), 102.1 (C-1′), 84.1 (C-4″), 82.7 (C-2″), 81.9 (C-4′), 78.8 (C-2), 78.7 (C-3), 77.7 (C-2′), 77.3 (C-3″), 75.0 (C-3′), 72.5 (C-5″), 71.9 (C-5′), 71.3 (C-5), 69.9 (C-4), 64.6 (C-6′), 64.2 (C-6), 64.2 (C-6″), 61.8 (C-1). HRMS (ESI) Calcd for $C_{18}H_{35}O_{16}$ $[M+H]^+$ 507.1925. Found: $[M+H]^+$ 507.1920.

Acknowledgements

This work was supported by grants from Agencia Nacional de Promoción Científica y Tecnológica, Universidad de Buenos Aires, CONICET and Fundación Antorchas. R. M. de Lederkremer and C. Gallo-Rodriguez are research members of CONICET. L. Gandolfi-Donadio is a research fellow from CONICET.

Supplementary data

^1H NMR and ^{13}C spectra of **14**, **16**, and **22**, ^1H–^1H and/or ^1H–^{13}C 2D correlation spectra of **6**, **8**, **12**, **13**, **15**, **16**, **17**, **18**, **19**, **1**, **21**, **23**, **24**, and **2** are included. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2006.07.013.

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