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PAPER

Synthesis of arabinofuranose branched galactofuran tetrasaccharides, constituents of mycobacterial arabinogalactan†

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Mycolyl-arabinogalactan (mAG) complex is a major component of the cell wall of *Mycobacterium tuberculosis*, the causative agent of tuberculosis disease. Due to the essentiality of the cell wall for mycobacterium viability, knowledge of the biosynthesis of the arabinogalactan is crucial for the development of new therapeutic agents. In this context, we have synthesized two new branched arabinogalactafuranose tetrasaccharides, decenyl β-D-Gal*f*-(1→5)-β-D-Gal*f*-(1→6)[α-D-Ara*f*-(1→5)]-β-D-Gal*f* (**1**) and decenyl β-D-Gal*f*-(1→6)-[α-D-Ara*f*-(1→5)]-β-D-Gal*f*-(1→5)-β-D-Gal*f* (**2**), as interesting tools for arabinofuranosyl transferase studies. The aldonolactone strategy for the introduction of the internal D-Gal*f* was employed, allowing the construction of oligosaccharides from the non-reducing to the reducing end. Moreover, a one-pot procedure was developed for the synthesis of trisaccharide lactone **21**, precursor of **2**, which involved a glycosylation-deprotection-glycosylation sequence, through the use of TMSOTf as catalyst of the trichloroacetimidate method as well as promoter of TBDMS deprotection.

Introduction

Among the worldwide infectious diseases, tuberculosis causes the second most deaths after HIV/AIDS.[1] There were 9.4 million new cases in 2008, and although the estimated incidence rates are falling very slowly, that year showed the highest multidrug-resistant tuberculosis rate ever recorded.[2] In fact, the emergence of drug-resistant strains of *Mycobacterium tuberculosis*, together with the widespread dissemination by global travel, encouraged the search for new drugs. Better understanding the biology of Mycobacteria will help in the development of better diagnosis and more efficient drugs.[3] There are gaps in the knowledge of the biology of this pathogen, connected also with the life cycle.[4] In this context, *M. tuberculosis* presents a complex cell wall, rich in lipids and diverse polysaccharides,[5–7] which acts as a robust barrier that is difficult to penetrate. Recently, cryo-electron microscopy showed that the outer membrane is a thick and morphologically symmetrical lipid bilayer, despite the presence of mycolic acids with asymmetrical hydrocarbon chains.[8,9] Mycolic acids are covalently linked to the arabinogalactan, which is covalently linked to peptidoglycan through a phosphate ester *via* a linker disaccharide α-D-GlcNAc-(1→3)-α-L-Rha*p*.[10] This entity is termed as the mycolyl-arabinogalactan-peptidoglycan complex (mAG-P). The sugar constituents of the AG are in the furanose form; both are absent in mammals. The galactan region consists of a 30 unit linear polymer of alternating β-(1→5) and β-(1→6)Gal*f*, which are further branched by three arabinan chains located at positions 8, 10 and 12 from the galactan reducing end, through an α-D-Ara*f*-(1→5)-D-Gal*f* linkage.[11] The 31 unit long arabinan includes α-(1→5), α-(1→3) and β-(1→2) linkages. Recently, a model of the entire primary structure of the mycobacterial mycolyl-arabinogalactan was proposed which includes the localization of a succinyl ester residue and the identification of an inner 14 unit linear arabinan region.[12] Understanding the biosynthesis of the arabinogalactan is important in the context of new drug development against tuberculosis,[13] taking into account that the integrity of the mycobacterial cell wall is essential for the viability of mycobacteria.[14] Although extensive research has been performed on the biosynthesis of the arabinogalactan, the assembly of the polysaccharide was not fully elucidated. Questions arise on the nature of the assembly that could be on a lipid carrier, or by introduction of each Ara*f* step-by-step from the reducing to the non-reducing end or *vice versa*, or by attachment of preformed oligosaccharide building blocks, *etc.*[7] The assembly of the mycolyl-arabinogalactan is sustained by an array of glycosyltranferases, some of which have been identified and partially characterized.[15,16]

The arabinosyltransferases already characterized are: AftA that transfers the first Ara*f* to the galactan,[17] AftB that completes the arabinan synthesis by adding a terminal cap of β-Ara*f*-(1→2);[18] AftC involved in internal α-1,3-branching of AG[19] and very recently, AftD which also is an α-(1→3) branching enzyme of AG and lipoarabinomannan (LAM);[20] EmbA and EmbB proteins

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involved in the formation of the Ara_6 motif of AG,[21] and EmbC required for the elongation of the arabinan domain in LAM.[22]

Synthetic oligosaccharides have been used as tools for the characterization of these enzymes. For example, the use of synthetic trisaccharides, constituents of galactofuranan (octyl β-D-Gal*f*-(1→6)-β-D-Gal*f*-(1→5)-β-D-Gal*f* and octyl β-D-Gal*f*-(1→5)-β-D-Gal*f*-(1→6)-β-D-Gal*f*) were useful as substrates for the transfer of the first Ara*f* residue of the galactan backbone, by demonstration that the transference occurred not on the *O*-5 of the non-reducing terminal Gal*f*, but on the 6-*O*-linked internal Gal*f*.[23] The enzymatic products, octyl glycosides of β-D-Gal*f*-(1→5)-β-D-Gal*f*-(1→6)[α-D-Ara*f*(1→5)]-β-D-Gal*f* and β-D-Gal*f*-(1→6)-[α-D-Ara*f*-(1→5)]-β-D-Gal*f*-(1→5)-β-D-Gal*f*, were characterized by MALDI-TOF/TOF MS/MS analysis of their methylated derivatives. Synthetic branched arabinose acceptor constituents of AG and LAM arabinan domains were used to identify a novel arabinofuranosyl transferase activity of internal α-D-Ara*f*(1→5)transferase that follows an α-3,5-branch in the acceptor.[24] Recently, synthetic oligosaccharides allowed the development of a plate-based assay to screen inhibitors of AftB.[25]

The galactan domain of AG is apparently biosynthesized by two bifunctional galactosyl transferases (GlfT1 and GlfT2).[26] By the use of synthetic acceptors such as galactofuranose trisaccharides containing β-(1→6) and β-(1→5) linkages, the characterization of the dual functionality of galactofuranosyl transferase GlfT2 was possible.[27,28] Also, the galactofuranosyl transferase (GlfT1) responsible for attaching the first unit of Gal*f* to decaprenyl-P-P-GlcNAc-Rha was characterized using synthetic acceptors.[26]

Additional arabinofuranosyl transferases involved in AG biosynthesis still remain to be identified and characterized. The synthesis of oligosaccharides which would allow the characterization of these enzymes is required. Our laboratory and other groups have been involved in the synthesis of oligosaccharide constituents of the AG of *M. tuberculosis*, such as arabinan fragments,[29,30] galactan fragments,[31,32] and more recently, galactan-linker-disaccharide fragments.[32,33] However, there are few reports on the synthesis of oligosaccharides containing both units, Ara*f* and Gal*f*.[34–36] We have synthesized the galactofuranose trisaccharides with alternating linkages of mycobacterial galactan,[31] and we have incorporated an Ara*f*[37] in the synthesis of lineal α-D-Ara*f*-(1→5)-β-D-Gal*f*-(1→5)-β-D-Gal*f*-(1→6)-D-Gal*f*.[36] We now report the synthesis of two branched arabinogalactofuranose tetrasaccharides, decenyl β-D-Gal*f*-(1→5)-β-D-Gal*f*-(1→6)[α-D-Ara*f*(1→5)]-β-D-Gal*f* (**1**) and decenyl β-D-Gal*f*-(1→6)-[α-D-Ara*f*-(1→5)]-β-D-Gal*f*-(1→5)-β-D-Gal*f* (**2**) (Scheme 1), as useful tools to investigate the influence of the position of the Ara*f* on the transfer of another Ara*f* or Gal*f* in the galactan. Compounds **1** and **2** are analogous structures of those already isolated from the AfTA-promoted glycosylation of a galactofuranose trisaccharide acceptor.[23] In addition, we also report a one-pot procedure for the preparation of a branched trisaccharide precursor of **2**.

Results and discussion

Synthetic strategies

The synthesis of galactofuranosyl-containing oligosaccharides involves the choice of convenient galactofuranosyl precursors as well as glycosylation methods,[38,39] and the difficulty is increased when internal galactofuranosyl linkages are required. In this sense, the following methods have been employed for internal linkage construction of several oligosaccharides:[31–33,36,40–46] Koenings–Knörr,[40a] cyanoorthoester,[40b–d] anomeric acetate,[40e] trichloroacetimidate,[31,36,41–43] and more recently, thioglycoside,[32,44] 2′-carboxybenzyl-glycosides[33,45,46] and glycosyl fluoride.[33,46] Recently, several galactofuranosyl trisaccharides have been obtained as by-products by enzymatic procedures.[47]

From all the galactofuranosyl precursors used to date,[32,39,48] we have chosen D-galactone-1,4-lactone as the template for the internal galactofuranoses in oligosaccharides **1** and **2**. We have succeeded in the use of the glycosyl aldonolactone approach for the synthesis of oligosaccharides which are constituents of *Leishmania*,[41] and *Trypanosoma cruzi*,[43] as well as *M. tuberculosis*.[31,36] As is known, D-galactono-1,4-lactone can be selectively substituted and can act as an acceptor in a glycosylation reaction, with the anomeric carbon virtually protected as a lactone. After reduction of the lactone function, activation of the anomeric center can be accomplished by the trichloroacetimidate method. This strategy allows oligosaccharide construction from the non-reducing to the reducing end.

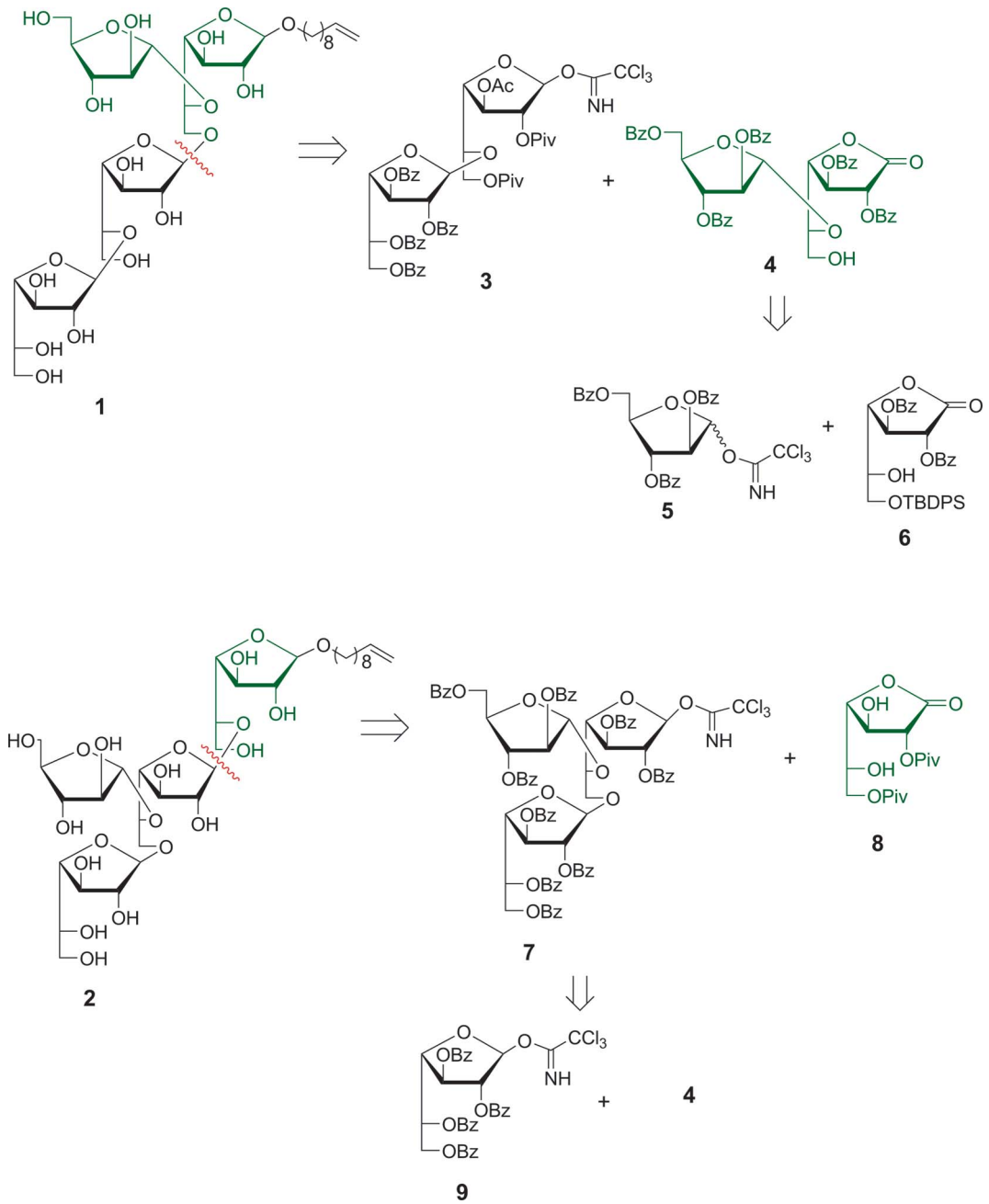
We chose to synthethize **1** and **2** as decenyl glycosides because the double bound could be further functionalized. In this sense, recently, galactofuranose-based acceptors for carbohydrate polymerase GlfT2 have been synthetized by Grubbs olefin cross metathesis from the corresponding allyl glycosides.[49]

Retrosynthetic analysis for tetrasaccharide **1** indicated a 2 + 2 retroglycosylation between the already synthesized disaccharide trichoroacetimidate **3**[31] and disaccharide lactone **4** (Scheme 1). Compound **4** could be obtained by glycosylation of D-galacto-1,4-lactone derivative **6** with *O*-2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl trichloroacetimidate (**5**), to give the desired 1,2-*trans* α-linkage by anchimeric assistance.

On the other hand, retrosynthetic analysis for oligosaccharide **2** indicated a 3 + 1 retroglycosylation between trisaccharide imidate **7** and the already synthesized lactone **8**[31] (Scheme 1). Moreover, trisaccharide **7** could be synthesized from disaccharide **4**, also a synthon for **1**, and 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl trichloroacetimidate (**9**).[50] It is important to mention that once the tetrasaccharide lactone was in hand, reduction of the lactone function would allow either further elongation or decenyl glycoside derivatization.

Synthesis of decenyl β-D-Gal*f*-(1→5)-β-D-Gal*f*-(1→6)[α-D-Ara*f*-(1→5)]-β-D-Gal*f* (1)

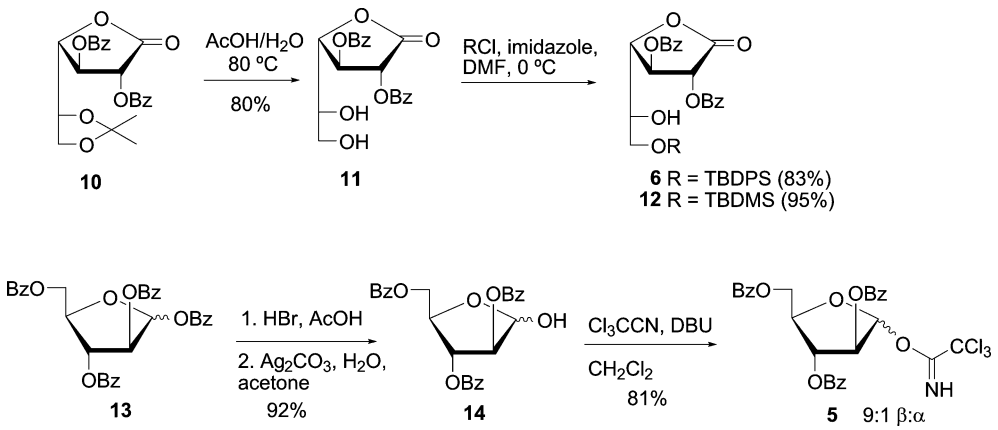
For the synthesis of disaccharide lactone **4**, we have chosen to start with the 6-*O* silyl derivative **6** (Scheme 2), taking into account that it is a common intermediate for trisaccharide **7** (Scheme 1), precursor of oligosaccharide **2**. Compound **6** was synthesized from 2,3-di-*O*-benzoyl-5,6-*O*-isopropylidene-D-galactono-1,4-lactone (**10**).[41,51] Hydrolysis of the isopropylidene of **10** gave **11** (80%) which was selectively silylated on the primary 6-position with 1.2 equiv. of *t*-butyldiphenylchlorosilane and imidazole in DMF to yield **6** (83%). The TBDPS group was used due to its resistance to acid hydrolysis. On the other hand, arabinofuranosyl imidate **5** was synthesized from 1,2,3,5-tetra-*O*-benzoyl-α,β-D-arabinose (**13**), which is obtained in one step by



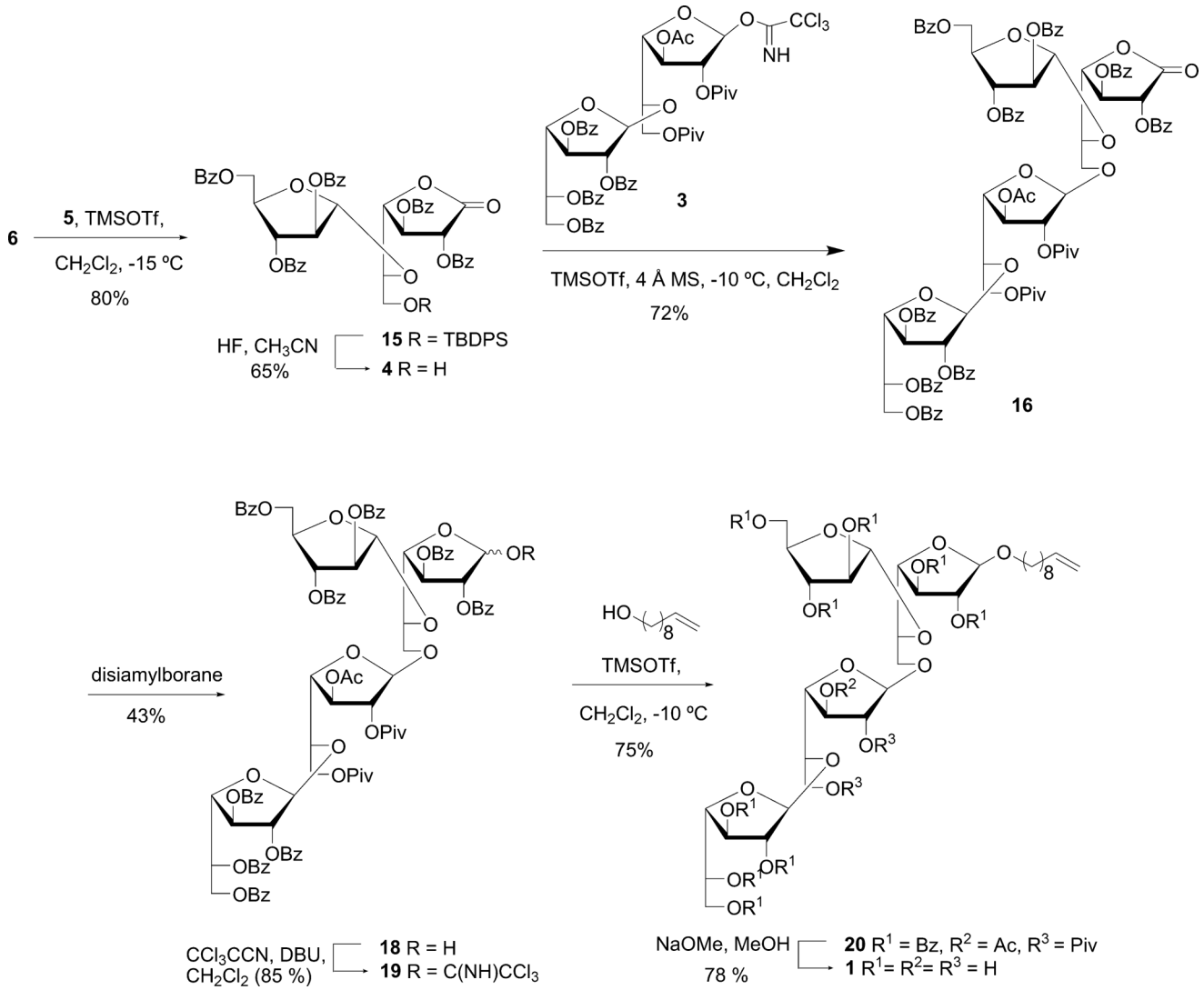
Scheme 1 Retrosynthesis of the target tetrasaccharides **1** and **2**.

benzoylation of arabinose in hot pyridine.[37,52] Treatment of **13** with 32% HBr in AcOH, followed by bromide hydrolysis with the assistance of Ag_2CO_3[53] gave the already described **14**[54] (92%), which was activated as the trichloroacetimidate **5**[54] by reaction with trichloroacetonitrile and DBU.

Glycosylation of **6** with imidate **5** in the presence of TMSOTf afforded disaccharide lactone **15** in 80% yield (Scheme 3). The ^{1}H NMR spectrum showed the resonance of H-1′ as a singlet and H-2 as a doublet with a small coupling constant (J = 1.7 Hz) which are characteristic signals for α-D-Ara*f*, with a 1,2-*trans* disposition. The signal at 107.5 ppm in the ^{13}C NMR spectrum was assigned to the anomeric center (C-1′), and together with the downfield signals for C-2′ and C-4′ at 82.7 and 81.1 ppm, confirmed the α furanosic linkage. In order to glycosidate the 6-position in this convergent synthesis, the TBDPS group was removed by treatment of **15** with HF in CH_3CN to give **4** in 65% yield. Glycosylation of **4** with disaccharide imidate **3**[31] with TMSOTf as catalyst in Cl_2CH_2 at −10 °C gave tetrasaccharide lactone **16** in 58% yield after column chromatography. The stereochemistry of the new glycosidic linkage was established as β as indicated by the ^{13}C NMR spectrum that showed the anomeric new carbon at 105.3 ppm (internal Gal*f* C-1′), together with the signals at 107.7 (Ara*f* C-1‴) and 106.2 (terminal Gal*f* C-1″) ppm. The ^{1}H NMR spectrum showed three singlets assigned by HETCOR and COSY experiments to the anomeric hydrogen of terminal Ara*f* (δ 5.77, H-1‴), terminal



Scheme 2 Synthesis of tetrasaccharide **1** building blocks **5** and **6**.



Scheme 3 Synthesis of tetrasaccharide **1**.

Gal*f* (δ 5.61, H-1″) and the internal Gal*f* (δ 4.98, H-1′) which confirmed the β configuration. A second fraction from the column (34%) was identified as the corresponding opened lactone 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→5)-3-*O*-acetyl-2,6-di-*O*-pivaloyl-β-D-galactofuranosyl-(1→6)-[2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2,3-di-*O*-benzoyl-D-galactonic acid (**17**) which was converted into **16** upon warming in Cl_3CH at 50 °C for 5 h, raising the total glycosylation yield to 72%. The opened

lactone byproduct **17** from the glycosylation reaction could not be avoided even by quenching the reaction with 1 equivalent of triethylamine. As shown by tlc, the opening occurred on column purification of the crude mixture.

With tetrasaccharide lactone **16** in hand, reduction of the lactone function with disiamylborane gave tetrasaccharide **18** in a moderate yield of 43% as an α : β anomeric mixture in 0.23 : 0.77 ratio, as indicated by the integration of the H-5α (δ 6.09) and H-3β (δ 5.83) signals in the ^{1}H NMR spectrum. Activation of the anomeric center of **18** with trichloroacetonitrile and DBU at rt gave trichloroacetimidate **19** in 85% as a 9 : 1 β : α anomeric mixture, as indicated by the integration of the anomeric signals at 6.91 (J = 4.5 Hz) and 6.66 ppm in the ^{1}H NMR spectrum. On reaction of tetrasaccharide imidate **19** with 9-decen-1-ol in Cl_2CH_2 with TMSOTf as catalyst, decenyl glycoside **20** was obtained as a single diastereomer β (75%). In the ^{1}H NMR spectrum, the anomeric hydrogen of the new glycosidic bond resonated at 5.24 ppm as a singlet in agreement with the β-configuration. Accordingly, in the ^{13}C NMR spectrum, the new anomeric C-1 appeared at 105.3 ppm, corroborating the diastereoselectivity of the reaction. The other furanose anomeric centers appeared at 106.7 (C-1‴), 106.0 (C-1′) and 105.8 (C-1″). Assignments were supported by COSY and HETCOR experiments. Deacylation of **20** by sodium methoxide in methanol yielded the desired decenyl β-D-Gal*f*-(1→5)-β-D-Gal*f*-(1→6)[α-D-Ara*f*(1→5)]-β-D-Gal*f* (**1**) (78%).

Synthesis of tetrasaccharide 2

For the synthesis of tetrasaccharide **2**, our first target was the synthesis of imidate **7**, as shown in the retrosynthetic analysis (Scheme 1). Whereas several groups have synthesized oligosaccharide fragments from arabinan or galactan, few oligosaccharides containing both units have been synthesized. This is the case for α-D-Ara*f*-(1→5)-[β-D-Gal*f*-(1→6)]-D-Gal*f*, which has been synthesized by two different methodologies. The first involved a sequential strategy with the introduction of the Ara*f* moiety by the trichloroacetimidate method at *O*-5 of a Gal*f* derivative, then deprotection of the 6-*O* position, followed by the introduction of the galactofuranosyl moiety by the pentenyl method at position 6.[34] This trisaccharide was obtained as its ethyl glycoside, which is difficult to hydrolyze for further elongation. On the other hand, this trisaccharide was also synthesized by a one-pot strategy from 3-*O*-benzoyl-1,2-*O*-isopropylidene-D-galactofuranose by selective glycosylation of the primary OH-6 with Gal*f* imidate **9**, followed by glycosylation with Ara*f* imidate **5**.[35] In this case, further elongation of the product would imply hydrolysis of the isopropylidene group, and differentiation of OH-1 and OH-2.

Considering the aldonolactone approach, our first attempt was the use of 2,3-di-*O*-benzoyl-D-galactono-1,4-lactone (**11**, Scheme 2) in order to introduce the Gal*f* at the primary 6-O position, followed by the Ara*f* at 5-position, taking into account the previous report.[35] However, in our hands, glycosylation of **11** with 1 equiv. of Gal*f* imidate **9** resulted in low regioselectivity. The disaccharide lactone obtained by monoglycosylation at OH-6, and the corresponding monoglycosylation by-product at OH-5, as well as the trisaccharide lactone, product of diglycosylation, were obtained, even at temperatures as low as −78 °C. For that reason, following the Gurjar strategy,[34] we chose to use compound **4** which was already employed for the synthesis of tetrasaccharide **1**.

Glycosylation of **4** with 2,3,4,5-tetra-*O*-benzoyl-D-galactofuranosyl trichloroacetimidate **9** yielded the crystalline trisaccharide lactone **21** in 84% yield (Scheme 4). The two singlets at 5.78 (Ara*f* H-1″) and 5.27 ppm (Gal*f* H-1′) in the ^{1}H NMR spectrum, as well as the anomeric signals at 107.7 (Ara*f* C-1″) and 105.2 ppm (Gal*f* C-1′) indicated the 1,2-*trans* disposition for the furanose moieties.

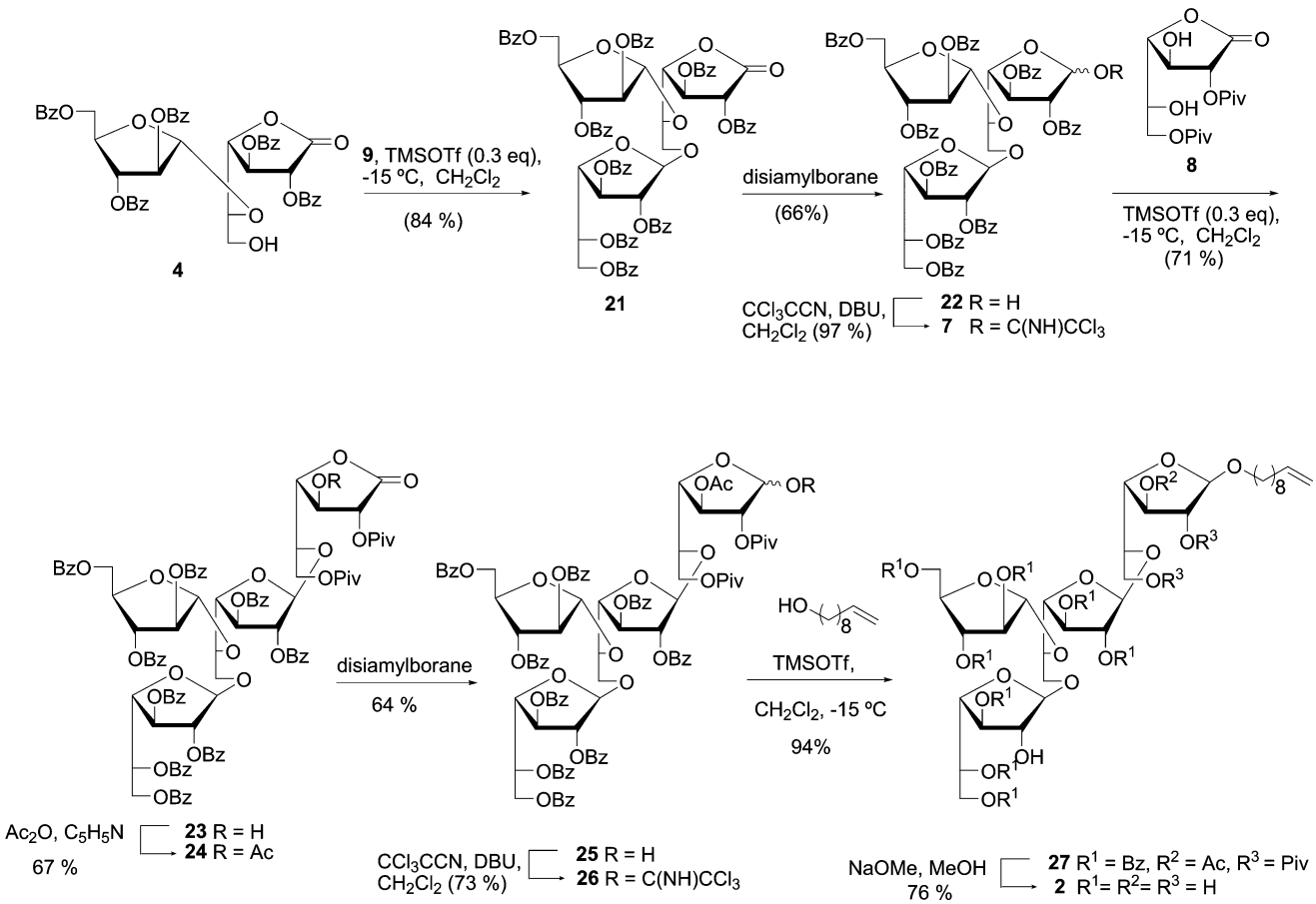
One-pot synthesis of trisaccharide lactone 21

Considerable efforts are being pursued to simplify the preparation of complex oligosaccharides by one-pot multi-step approaches involving different glycosylation strategies as well as minimizing protective group manipulation.[55] An interesting strategy combines deprotection or manipulation of protecting groups with glycosylation reactions employing the same catalyst, thus obtaining branched oligosaccharides.[56] In this sense, we envisioned the synthesis of trisaccharide lactone **21** in a one-pot procedure by the use of TMSOTf as glycosylation catalyst as well as promoter for the removal of the silyl protecting group. Glycosylation by the trichloroacetimidate method followed by silyl deprotection with TMSOTf in a one-pot procedure was previously described.[57] In our case, we planned the following one-pot procedure: (1) glycosylation at O-5 of a D-galactone-1,4-lactone derivative with Ara*f* imidate **5**, (2) removal of the silyl group at the 6-*O* position and (3) glycosylation with Gal*f* imidate **9** at the 6-*O* position (Scheme 5). In this case, acid resistant 6-*O*-TBDPS in **6** was replaced by TBDMS which can be removed by Lewis acids.[58] Treatment of **11** with 1.2 equiv. of *t*-butyldimethylchlorosilane and imidazole in DMF gave the acceptor **12** (95%, Scheme 2). We first assayed the resistance to acid of the TBDMS group of **12**, and under standard glycosylation conditions (0.3 equiv. TMSOTf, Cl_2CH_2, −15 °C), no product **11** was observed which would result from silyl removal. However, on addition of 1 equiv. of TMSOTf, and after 1.5 h reaction, **11** was obtained as the only product as shown by TLC. The resistance of the arabinofuranosyl linkage to the TBDMS removal conditions was also evaluated. On treatment of 2,3,5-tri-*O*-benzoyl-α-D-Ara*f*-(1→5)-2,6-di-*O*-pivaloyl-D-galactono-1,4-lactone[37] with 1.3 equiv. TMSOTf for 2.5 h at −15 °C, no decomposition was observed.

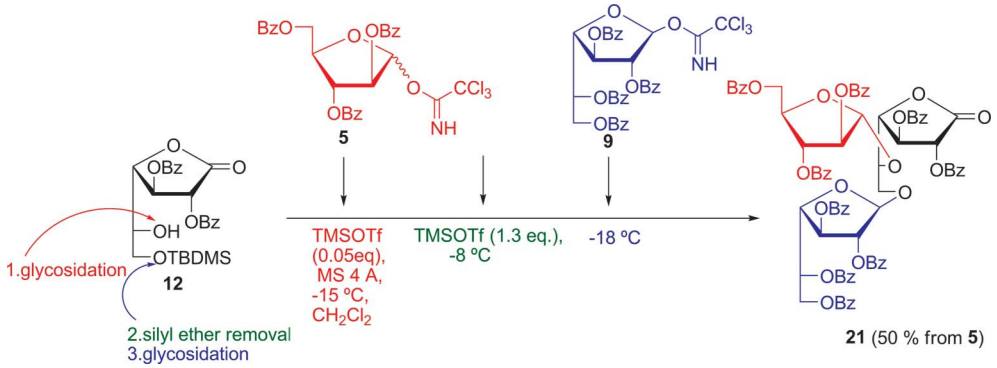
With these results, and after several assays, we found that the best one-pot conditions were: (1) glycosylation of **12** with 1 equiv. of Ara*f* imidate **5** using a small amount of TMSOTf (0.05 equiv.) at −15 °C, which gave the corresponding disaccharide, (2) after 1.5 h, the temperature was raised to −8 °C and 1.3 equiv. of TMSOTf were added, (3) after 1 h more, the mixture was cooled to −18 °C and Gal*f* imidate **9** was added. Under this procedure, trisaccharide lactone **21** was obtained crystalline from the crude reaction mixture in 50% overall yield.

It is important to mention that deprotection of the TBDMS group required a short time. Longer times resulted in the formation of the transglycosylation by-product, 5,6-di-*O*-(2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl)-2,3-di-*O*-benzoyl-D-galactono-1,4-lactone (data not shown).

The next step was the reduction of the lactone function followed by activation of the furanose center. Treatment of **21**



Scheme 4 Synthesis of tetrasaccharide **2**.



Scheme 5 One-pot strategy for the synthesis of **21**.

with disiamylborane gave trisaccharide **22** as a 0.6 : 0.4 β : α anomeric mixture. Activation of the anomeric center of **22** with trichloroacetonitrile and DBU gave trichloroacetimidate **7** as a 9 : 1 β : α anomeric mixture, which was condensed with 2,6-di-*O*-pivaloyl-D-galactono-1,4-lactone (**8**)[31] (Scheme 4). The reaction was carried out with TMSOTf as catalyst in Cl_2CH_2 and the product of glycosylation on exocyclic OH-5 **23** was obtained regioselectively as expected in 71% yield. Prior to disiamylborane reduction, **23** was acetylated to give **24**. In the ^{1}H NMR spectrum of **24**, the H-3 signal appeared shifted 1 ppm downfield compared to the same signal in **23**, confirming the regioselectivity of the glycosylation. Reduction of the lactone function of **24** with disiamylborane gave **25** as a β : α (0.7 : 0.3) anomeric mixture (64%). Its imidate **26** (73%) was reacted with 9-decenol to yield tetrasaccharide **27** in 94% yield. The ^{1}H NMR spectrum of **27** showed the new anomeric center at 4.92 ppm as a singlet due to the β-stereochemistry, together with the other anomeric signals at 5.78 (Ara*f* H-1‴), 5.58 (internal Gal*f* H-1′), and 5.35 ppm (terminal Gal*f* H-1″). In the ^{13}C NMR spectrum, the anomeric centers appeared at 106.5 (C-1″), 106.0 (C-1‴), 105.0 (C-1′) and 105.4 ppm, the latter assigned to the new glycosidic center (C-1). With tetrasaccharide **27** in hand, the last step was the total deprotection by Zemplen procedure to afford the desired decenyl glycoside **2** with 76% yield.

Conclusions

We have synthesized two branched arabinogalactan derivatives as their decenyl glycosides **1** and **2**, which constitute interesting substrates for studies on arabinofuranosyl transferases. The aldonolactone strategy was employed as the template of the furanose ring, by sequential construction of the oligosaccharides from the non-reducing end to the reducing end. The synthesis of trisaccharide lactone **21**, precursor of **2**, was extended to a one-pot procedure. The glycosylation-deprotection-glycosylation strategy was possible by the use of TMSOTf as the catalyst for the trichloroacetimidate method as well as the promoter for silyl removal.

Experimental

General

TLC was performed on 0.2 mm silica gel 60 F254 aluminium supported plates. Detection was effected by exposure to UV light or by spraying with 5% (v/v) sulfuric acid in EtOH and charring. Column chromatography was performed on silica gel 60 (230–400 mesh). NMR spectra were recorded with a Bruker AVANCE II 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 an internal acetone standard at 2.16 ppm 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 COSY and HSQC experiments. High resolution mass spectra (HRMS) were recorded on an Agilent LCTOF with Windows XP-based OS and a APCI/ESI ionization high resolution mass spectrometer analyzer or in a BRUKER micrOTOF-Q II spectrometer. Melting points were determined with a Fisher–Johns apparatus and are uncorrected. Optical rotations were measured with a path length of 1 dm at 25 °C.

2,3-Di-*O*-benzoyl-D-galactono-1,4-lactone (11). To a stirred solution of 2,3-di-*O*-benzoyl-5,6-*O*-isopropylidene-D-galactono-1,4-lactone[51] (**10**, 1.6 g, 3.8 mmol) in HOAc (15 mL) at 80 °C was slowly added H_2O (2 mL) until turbidity, and heating was continued for 1 h. The mixture was cooled and concentrated, and the residue was subjected to successive dissolution and evaporation with toluene (3 × 10 mL). Column chromatography (3 : 1 toluene–EtOAc) of the residue afforded **11** (1.17 g, 80%) as a solid which after recrystallization from hexane–EtOAc (1.5 : 1) gave mp 118–120 °C, $[\alpha]_D$ +89.1 (*c* 1, $CHCl_3$), R_f 0.38 (1 : 1 hexane–EtOAc); ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.07–7.18 (m. 10 H, aromatic), 6.08 (m, 2 H, H-2, H-3), 4.66 (m, 1 H, H-4), 4.13 (m, 1 H, H-5), 3.86 (dd, 1H, *J* = 6.2, 11.2 Hz, H-6a), 3.75 (dd, 1H, *J* = 5.9, 11.2 Hz, H-6b), 3.60 (bs, 1H, O*H*), 2.91 (bs, 1H, O*H*). ^{13}C NMR ($CDCl_3$, 25.3 MHz): δ 169.0 (C-1), 165.8 (*C*OPh), 165.3 (*C*OPh), 133.9–128.5 (CO*Ph*), 80.3, 73.4, 72.7, 70.2, 62.9. Anal. Calcd for $C_{20}H_{18}O_8$: C 62.17; H 4.70; Found: C 62.11, H 4.46.

2,3-Di-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-D-galactono-1,4-lactone (6). To a stirred solution of 2,3-di-*O*-benzoyl-D-galactono-1,4-lactone (**11**, 400 mg, 0.99 mmol) and imidazole (115 mg, 1.7 mmol) in DMF (4 mL) cooled to 0 °C, *tert*-butyldiphenylchlorosilane (0.3 mL, 1.15 mmol) was slowly added. After 2 h, the mixture was quenched by addition of water (10 mL). After dilution with CH_2Cl_2 (70 mL) and additional water (60 mL), the organic phase was separated and washed with water (4 × 70 mL), dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography (toluene) to give 0.532 g of **6** (83% yield) as an amorphous solid: R_f 0.61 (2 : 1 hexane–EtOAc), $[\alpha]_D$ +41.6 (*c* 1, $CHCl_3$),^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.12–7.37 (m, 20 H, aromatic), 6.14 (d, 1 H, *J* = 6.6 Hz, H-2), 6.13 (dd, 1 H, *J* = 6.6, 6.2 Hz, H-3), 4.73 (dd, 1 H, *J* = 6.2, 1.9 Hz, H-4), 4.12 (m, 1 H, H-5), 3.91 (dd, 1 H, *J* = 6.6, 10.3 Hz, H-6a), 3.85 (dd, 1 H, *J* = 6.4, 10.3 Hz, H-6b), 1.09 (s, 9H, C(CH_3)$_3$); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 168.7 (C-1), 165.6 (*C*OPh), 165.2 (*C*OPh), 135.5–127.8 (aromatic), 79.3 (C-4); 73.4, 72.6 (C-2, C-3); 69.9 (C-5), 63.8 (C-6), 26.8 (C(*C*H_3)$_3$), 19.2 (*C*(CH$_3$)$_3$). Anal. Calcd for $C_{36}H_{36}O_8Si$: C 69.21; H 5.81; Found: C 69.15, H 5.71.

2,3-Di-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl-D-galactono-1,4-lactone (12). To a stirred suspension of 2,3-di-*O*-benzoyl-D-galactono-1,4-lactone (**10**) (577 mg, 1.44 mmol) and imidazole (170 mg, 2.5 mmol) in DMF (7 mL) cooled to 0 °C, *tert*-butyldimethylchlorosilane (262 mg, 1.74 mmol) was slowly added. After 1.5 h, the mixture was quenched by addition of water (10 mL). After dilution with CH_2Cl_2 (70 mL) and additional water (60 mL), the organic phase was separated and washed with water (4 × 70 mL), dried (Na_2SO_4) and concentrated. The solid residue was purified by recrystallization from 7 : 1 hexane–EtOAc to give the first crop of **12** (0.623 g, 87% yield). The mother liquors were concentrated under reduced pressure and the solid recrystallized from 7 : 1 hexane–EtOAc to give a second crop of crystalline **12** (61 mg, 8% yield): mp 118 °C, R_f 0.61 (2 : 1 hexane–EtOAc), $[\alpha]_D$ +68.1 (*c* 1, $CHCl_3$), ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.10–7.43 (m, 10 H, aromatic), 6.13 (t, 1 H, *J* = 6.6 Hz, H-3), 6.09 (d, 1 H, *J* = 7.1 Hz, H-2), 4.66 (dd, 1 H, *J* = 6.2, 2.2 Hz, H-4), 4.07 (m, 1 H, H-5), 3.83 (dd, 1 H, *J* = 6.6, 10.0 Hz, H-6a), 3.77 (dd, 1 H, *J* = 6.3, 10.0 Hz, H-6b), 0.89 (s, 9H, C(CH_3)$_3$); 0.09, 0.08 (2 × CH_3); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 168.8 (C-1), 165.7 (*C*OPh), 165.2 (*C*OPh), 133.9–128.3 (aromatic), 79.4, 73.4, 72.6, 69.9, 62.9, 25.8 (C(*C*H_3)$_3$), 18.2 (*C*(CH$_3$)$_3$), −5.5 (CH$_3$). Anal. Calcd for $C_{26}H_{32}O_8Si$: C 62.38, H 6.44; Found: C 62.37, H 6.43.

2,3,5-Tri-*O*-benzoyl-α,β-D-arabinofuranose (14). A solution of 1,2,3,5-tetra-*O*-benzoyl-α,β-D-arabinofuranose[37,52] (**13**) (455 mg, 0.80 mmol) in 32% (w/w) hydrogen bromide–glacial acetic acid (1.5 mL) was stirred for 1 h at room temperature until the tlc showed consumption of the starting material. The solution was concentrated under reduced pressure and the residue coevaporated with toluene (5 × 5 mL). The crude solid was diluted in 10 : 1 acetone–water and the resulting solution was then warmed to 40 °C and Ag_2CO_3 (171 mg, 1.01 mmol) was slowly added. After stirring at 50 °C for 1.5 h, the reaction mixture was diluted with CH_2Cl_2 (50 mL) and filtered through Celite. The filtrate was washed with water (3 × 50 mL), the organic layer was dried (Na_2SO_4), filtered and concentrated. The crude product was purified by column chromatography (20 : 1 toluene–EtOAc) to give 0.339 g of **14** (92%) as an amorphous solid: R_f 0.19 (7 : 1 toluene–EtOAc), $[\alpha]_D$ −34.7 (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 200 MHz, mixture of α and β anomers, 0.76 : 0.24, in accordance with lit.[54]); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 166.5–165.5 (COPh), 133.6–128.3 (aromatic), 100.9 (C-1α), 95.5 (C-1β), 82.5, 81.3, 78.9, 77.9, 76.5, 65.8 (C-5α), 63.9 (C-5β).

2,3,5-Tri-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-D-galactono-1,4-lactone (15). A vigorously stirred solution of dried 2,3,5-tri-*O*-benzoyl-D-arabinofuranosyl trichloroacetimidate[54] (**5**, 1.26 g, 2.07 mmol), 2,3-di-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-D-galactono-1,4-lactone (**6**, 1.12 g, 1.75 mmol), and activated 4 Å powdered molecular sieves (0.7 g) in anhydr. CH_2Cl_2 (90 mL) was cooled to −15 °C, and TMSOTf (105 μL, 0.58 mmol) was slowly added. After 2 h of stirring, the mixture was filtered into saturated aqueous $NaHCO_3$ (200 mL) and then extracted with CH_2Cl_2 (2 × 200 mL). The organic layer was washed with water (3 × 150 mL), dried (Na_2SO_4), filtered and concentrated under reduced pressure. The residue was purified by column chromatography (80 : 1 toluene–EtOAc) to give **15** (1.50 g, 80%) as a syrup: R_f 0.68 (7 : 1 toluene–EtOAc); $[\alpha]_D$ −24.2 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) *δ*: 8.09–7.24 (m, 35 H, aromatic), 6.24 (d, 1 H, *J* = 6.7 Hz, H-2), 6.15 (t, 1 H, *J* = 6.4 Hz, H-3), 5.61 (d, 1 H, *J* = 1.7, 5.2 Hz, H-3′), 5.58 (s, 1 H, H-1′), 5.53 (d, 1 H, *J* = 1.7 Hz, H-2′), 5.01 (dd, 1 H, *J* = 1.9, 6.1 Hz, H-4), 4.55 (dd, 1 H, *J* = 3.8, 12.0 Hz, H-5a′), 4.49 (dd, 1 H, *J* = 4.4, 12.0 Hz, H-5b′), 4.36 (m, 1 H, H-4′), 4.23 (ddd, 1 H, *J* = 1.9, 5.2, 9.3 Hz, H-5), 4.03 (dd, 1 H, *J* = 5.2, 10.0 Hz, H-6a), 3.97 (t, 1 H, *J* = 9.8 Hz, H-6b), 1.0 (s, 9 H, $((CH_3)_3CSi)$; ^{13}C NMR ($CDCl_3$, 125.8 MHz) *δ*: 168.9 (C-1), 166.1, 165.7 (x2), 165.4, 165.2 (*C*OPh), 135.4–127.8 (aromatic), 107.5 (C-1′), 82.7 (C-2′), 81.0 (C-4′), 79.3 (C-4), 77.5 (C-5), 77.0 (C-3′), 73.9 (C-3), 72.4 (C-2), 63.4 (C-5′), 61.9 (C-6), 26.8 ($(CH_3)_3C$), 19.1 ($(CH_3)_3C$). HRMS (ESI) *m*/*z* calcd for $C_{62}H_{56}O_{15}SiNa$ (M+Na$^+$) 1091.3281, found 1091.3268.

2,3,5-Tri-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-D-galactono-1,4-lactone (4). A solution of 5% HF (48 wt% in H_2O) in acetonitrile (30 mL) was added to **15** (1.16 g, 1.01 mmol), and the resulting solution was stirred at 5 °C for 16 h, and 20 °C for additional 3 h. The reaction mixture was poured into saturated aq. $NaHCO_3$ (150 mL), and extracted with CH_2Cl_2 (2 × 100 mL). The organic layer was washed with water (3 × 100 mL) until pH 7, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification by column chromatography (10 : 1 toluene–EtOAc) yielded **4** (595 mg, 65%) as a foamy solid: R_f 0.39 (4 : 1 toluene–EtOAc); $[\alpha]_D$ +43.7 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) *δ*: 8.09–7.16 (m, 25 H, aromatic), 6.17 (m, 2 H, H-2, H-3), 5.73 (bs, 1 H, H-1), 5.68 (dd, 1 H, *J* = 1.9, 4.9 Hz, H-3′), 5.66 (dd, 1 H, *J* = 0.6, 1.9 Hz, H-2′), 4.80 (dd, 1 H, *J* = 3.4, 11.5 Hz, H-5a′), 4.76 (m, 2 H, H-4, H-4′), 4.66 (dd, 1 H, *J* = 5.55, 11.5 Hz, H-5b′), 4.33 (ddd, 1 H, *J* = 2.4, 4.7, 7.7 Hz, H-5), 4.04 (dd, 1 H, *J* = 7.7, 12.0 Hz, H-6a), 3.86 (ddd, 1 H, *J* = 2.4, 8.0, 12.0 Hz, H-6b), 2.88 (d, 1 H, *J* = 8.0 Hz, O*H*); ^{13}C NMR ($CDCl_3$, 125.8 MHz) *δ*: 168.7 (C-1), 166.1, 165.8, 165.7, 165.2 (*C*OPh), 133.7–125.3 (aromatic), 107.7 (C-1′), 82.4 (C-2′), 81.5 (C-4′), 80.5 (C-4), 80.1 (C-5), 76.8 (C-3′), 74.0, 72.1 (C-3 and C-2), 63.7 (C-5′), 62.8 (C-6). Anal. Calcd for $C_{46}H_{38}O_{15}$: C 66.50; H 4.61; Found: C 66.62, H 4.42.

2,3,5,6-Tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→5)-3-*O*-acetyl-2,6-di-*O*-pivaloyl-β-D-galactofuranosyl-(1→6)-[2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2,3-di-*O*-benzoyl-D-galactono-1,4-lactone (16). A vigorously stirred suspension of 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→5)-3-*O*-acetyl-2,6-di-*O*-pivaloyl-β-D-galactofuranosyl trichloroacetimidate[31] (**3**, 592 mg, 0.53 mmol), disaccharide lactone **4** (391 mg, 0.47 mmol), and 4 Å powdered molecular sieves (0.5 g) in anhydr. CH_2Cl_2 (8 mL) was cooled to −10 °C and then, TMSOTf (29 μL, 0.16 mmol) was slowly added. After 1 h of stirring, tlc monitoring showed a main spot (R_f 0.47, 7 : 1 toluene–EtOAc) and consumption of the starting materials. The mixture was filtered into saturated aqueous $NaHCO_3$ (100 mL) and then extracted with CH_2Cl_2 (2 × 100 mL). The organic layer was washed with water (3 × 100 mL), dried (Na_2SO_4), filtered and concentrated under reduced pressure. The syrupy residue was purified by column chromatography (80 : 1 toluene–EtOAc).

The first fraction of the column (R_f 0.47, 7 : 1 toluene–EtOAc) was concentrated to give an amorphous solid identified as **16** (484 mg, 58%): $[\alpha]_D$ +1.2 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) *δ*: 8.09-7.23 (m, 45 H, aromatic), 6.29 (d, 1 H, *J* = 6.7 Hz, H-2), 6.19 (dd, 1H, *J* = 6.7, 6.0 Hz, H-3), 6.08 (m, 1 H, H-5″), 5.77 (bs, 1 H, H-1‴), 5.72 (m, 2 H, H-3‴, H-3″), 5.61 (bs, 1 H, H-1″), 5.60 (d, 1 H, *J* = 2.1 Hz, H-2″), 5.58 (d, 1 H, *J* = 2.1 Hz, H-2‴), 5.31 (dd, 1 H, *J* = 2.3, 6.2 Hz, H-3′), 5.01 (d, 1 H, *J* = 2.3 Hz, H-2′), 4.98 (s, 1 H, H-1′), 4.87 (dd, 1 H, *J* = 1.6, 6.0 Hz, H-4), 4.83 (dd, 1 H, *J* = 3.6, 5.2 Hz, H-4″), 4.78 (dd, 1 H, *J* = 5.4, 13.0 Hz, H-5a‴), 4.77 (dd, 1 H, *J* = 3.9, 12.0 Hz, H-6a″), 4.73 (dd, 1 H, *J* = 7.3, 12.0 Hz, H-6b″), 4.68 (m, 2 H, H-4‴, H-5b‴), 4.42 (m, 2 H, H-6a′, H-5), 4.37 (dd, 1 H, *J* = 3.2, 6.2 Hz, H-4′), 4.30 (m, 2 H, H-5′, H-6b′), 4.01 (t, *J* = 9.4 Hz, H-6a), 3.91 (dd, 1 H, *J* = 6.0, 9.4 Hz, H-6b); ^{13}C NMR ($CDCl_3$, 125.8 MHz) *δ*: 177.8, 177.3 ($COC(CH_3)_3$), 169.7 ($COCH_3$), 168.8 (C-1), 166.1–165.1 (*C*OPh), 133.8–128.2 (aromatic), 107.7 (C-1‴), 106.2 (C-1″), 105.3 (C-1′), 82.9 (C-2″), 82.0 (C-2‴), 81.7 (C-4″), 81.3 (C-2′), 80.9 (C-4′), 80.8 (C-4‴), 79.6 (C-4), 77.6 (C-3″), 76.9 (C-3‴), 75.9 (C-3′), 75.6 (C-5), 73.8 (C-3), 73.4 (C-5′), 72.2 (C-2), 70.2 (C-5″), 64.7 (C-6), 63.9 (C-6′); 63.6, 63.4 (C-5‴, C-6″); 38.6 ($C(CH_3)_3$), 38.4 ($C(CH_3)_3$), 27.0 ($C(CH_3)_3$), 27.8($C(CH_3)_3$), 20.3(CH_3). Anal. Calcd for $C_{98}H_{92}O_{32}$: C 66.06; H 5.20; Found: C 65.81, H 5.08.

The lowest migrating component from the column (R_f 0.65, EtOAc) was eluted with EtOAc and identified as 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→5)-3-*O*-acetyl-2,6-di-*O*-pivaloyl-β-D-galactofuranosyl-(1→6)-[2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2,3-di-*O*-benzoyl-D-galactonic acid (**17**, 287 mg, 34%): $[\alpha]_D$ −27.9 (*c* 1, $CHCl_3$), ^{13}C NMR ($CDCl_3$, 125.8 MHz) *δ*: 178.2 (C-1 and $COC(CH_3)_3$), 177.4 ($COC(CH_3)_3$, 170.0 ($COCH_3$), 166.3, 166.1, 165.9, 165.8, 165.7, 165.6, 165.5, 165.4, 165.2 (9 x *C*OPh), 133.8–128.2 (aromatic), 107.0 (C-1‴), 105.9 (C-1″), 105.4 (C-1′), 82.3, 82.0, 81.9, 81.4, 81.2, 80.8, 77.9, 77.4, 75.9, 75.6, 72.9, 71.7, 70.3, 68.4, 65.6, 64.7, 63.9, 63.5; 38.7 ($C(CH_3)_3$), 38.5 ($C(CH_3)_3$), 27.0 ($C(CH_3)_3$), 26.8 ($C(CH_3)_3$), 20.2 (CH_3). HRMS (ESI) *m*/*z* calcd for $C_{98}H_{94}O_{33}Na$ (M+Na$^+$) 1821.5570, found 1821.5617.

This fraction was concentrated, the residue was dissolved in $CHCl_3$ (15 mL) and the solution was heated for 5 h at 50 °C. Tlc monitoring showed almost total conversion into **16** (R_f 0.47, 7 : 1 toluene–EtOAc). The solution was evaporated to dryness and the resulting residue was purified by a short column chromatography (40 : 1, toluene–EtOAc) to provide 116 mg of a product with the same spectroscopic and physical data as **16** (14%).

2,3,5,6-Tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→5)-3-*O*-acetyl-2,6-di-*O*-pivaloyl-β-D-galactofuranosyl-(1→6)-[2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2,3-di-*O*-benzoyl-D-galactofuranose (18). A solution of bis(2-butyl-3-methyl)borane

(1.28 mmol) in anhydr. THF (0.4 mL), cooled to 0 °C under an argon atmosphere, was added to a flask containing previously dried compound **16** (381 mg, 0.21 mmol). The solution was allowed to reach room temperature and stirring continued for 16 h. Tlc showed partial consumption of compound **16**, the mixture was cooled to 0 °C and a solution of bis(2-butyl-3-methyl)borane (1.55 mmol) in anhydr. THF (2.2 mL) was added. The resulting solution was stirred at room temperature for additional 12 h; tlc showed total consumption of compound **16** and the mixture was processed as previously described.[59] The organic layer was washed with water, dried (Na_2SO_4), and concentrated. Boric acid was eliminated by coevaporation with MeOH (5 × 3 mL) at rt. The residue was purified by column chromatography (15 : 1, toluene–EtOAc) to give 162 mg (43%) of syrupy **18** as a 0.77 : 0.23 β : α anomeric mixture: R_f 0.6 (5 : 1 toluene–EtOAc); $[\alpha]_D$ +2.9 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz), only the assigned δ are listed: 8.17–7.16 (m, 45 H, aromatic), 6.09 (m, 0.23 H, H-5″α anomer), 6.04 (m, 0.77 H, H-5″ β anomer), 5.87 (bs, 0.23 H, H-1‴ α anomer), 5.83 (dd, 0.77 H, *J* = 1.8, 5.9 Hz, H-3), 5.77 (bs, 0.77 H, H-1‴ β anomer), 5.75 (d, 0.77 H, *J* = 4.6 Hz, H-1 β anomer), 5.70 (dd, 0.23 H, *J* = 5.0, 11.7 Hz, H-1 α anomer), 5.67 (bs, 0.77 H, H-1″), 5.66–5.63 (m, 2.31 H, H-2, H-3″, H-3‴), 5.59 (d, 0.77 H, *J* = 1.6 Hz, H-2″), 5.56 (d, 0.77 H, *J* = 2.3 Hz, H-2‴), 5.25 (dd, 0.77 H, *J* = 5.6, 1.6 Hz, H-3′), 5.06 (d, 0.77 H, *J* = 1.6 Hz, H-2′), 5.03 (d, 0.77 H, *J* = 5.0 Hz, OH), 4.98 (bs, 0.23 H, H-1′α anomer), 4.96 (dd, 0.77 H, *J* = 1.7, 5.7 Hz, H-4″), 4.95 (bs, 0.77 H, H-1′), 4.79 (dd, 0.77 H, *J* = 3.7, 12.4 Hz, H-6a″), 4.76–4.70 (m, 1.54 H, H-6a′, H-5a‴), 4.67 (dd, 0.77 H, *J* = 7.6, 12.1 Hz, H-6b″), 4.65 (m, 0.77 H, H-4‴), 4.63 (dd, 0.77 H, *J* = 5.0, 11.0 Hz, H-5b‴), 4.59 (dd, 0.77 H, *J* = 1.8, 5.9 Hz, H-4), 4.47 (dd, 0.77 H, *J* = 3.4, 5.9 Hz, H-4′), 4.44 (m, 0.77 H, H-5), 4.40 (m, 0.77 H, H-5′), 4.22 (dd, 0.77 H, *J* = 7.5, 12.6 Hz, H-6b′), 4.09 (dd, 0.77 H, *J* = 8.3, 9.9 Hz, H-6a), 3.84 (dd, 0.77 H, *J* = 5.45, 8.3 Hz, H-6b), 1.88 (s, 0.69 H, CH_3 α anomer), 1.83 (s, 2.31 H, CH_3 β anomer); 1.15, 1.04 (2 s, 13.9 H, $C(CH_3)_3$);1.14, 1.00 (2 s, 4.1 H, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ: 179.7 ($COC(CH_3)_3$), 177.3 ($COC(CH_3)_3$), 170.2 ($COCH_3$), 166.3–165.2 (*C*OPh), 133.5–125.3 (aromatic), 107.6 (C-1‴ β anomer), 107.3 (C-1‴ α anomer), 105.8 (C-1″ α anomer), 105.4 (C-1′ α anomer), 105.1 (C-1″ β anomer), 103.9 (C-1′ β anomer), 100.5 (C-1 β anomer), 95.1 (C-1 α anomer), 83.6 (C-2), 82.6 (C-2‴), 82.3 (C-2″), 82.1 (C-4′), 81.4 (C-4″), 81.2 (C-4), 80.9 (C-2′), 80.1 (C-4‴), 77.9 (C-3‴*), 77.5 (C-3), 77.4 (C-3‴*), 76.0 (C-3′), 75.4 (C-5), 72.6 (C-5′), 70.5 (C-5″), 66.9 (C-6′), 63.7 (C-6″, C-6, C-5‴), 38.9, 39.5, ($COC(CH_3)_3$), 27.1, 27.0, 26.9, 26.8 ($COC(CH_3)_3$), 21.5, 20.3 (CH_3). HRMS (ESI) *m*/*z* calcd for $C_{98}H_{94}O_{32}Na$ ($M+Na^+$) 1805.5620, found 1805.5684.

9-Decenyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→5)-3-*O*-acetyl-2,6-di-*O*-pivaloyl-β-D-galactofuranosyl-(1→6)-[2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2,3-di-*O*-benzoyl-β-D-galactofuranoside (20). To a stirred solution of **18** (146 mg, 0.082 mmol) and trichloroacetonitrile (42 µL, 0.41 mmol) in anhydr. CH_2Cl_2 (5 mL) cooled to 0 °C, DBU (6.1 µL, 0.041 mmol) was slowly added. After 1 h, the solution was carefully concentrated under reduced pressure at rt and the residue was purified by column chromatography (20 : 1 : 0.2 toluene–EtOAc–TEA) to give 131 mg (85%) of syrupy trichloroacetimidate **19** as a 9 : 1 β : α anomeric mixture: R_f 0.68 (5 : 1 : 0.05 toluene–EtOAc–TEA);^{1}H NMR ($CDCl_3$, 200 MHz) for the β anomer, only diagnostic signals are listed for the α anomer, δ 9.01 (N*H*, 0.10 H), 8.82 (N*H*, 0.90 H), 8.07–7.14 (m, 45 H), 6.91 (d, 0.10 H, *J* = 4.5 Hz, H-1 α anomer), 6.66 (bs, 0.9 H, H-1 β anomer), 6.07 (m, 0.9 H, H-5″), 5.87 (dd, 0.9 H, *J* = 0.9, 4.6 Hz), 5.85 (bs, 0.9 H), 5.73 (bs, 0.9 H), 5.66–5.63 (m, 3.6 H), 6.39 (d, 0.9 H, *J* = 1.9 Hz), 5.29 (dd, 0.9 H, *J* = 2.7, 7.1 Hz), 5.02 (dd, 0.9 H, *J* = 0.5, 2.8 Hz), 4.96 (bs, 0.9 H), 4.86 (dd, 0.9 H, *J* = 3.6, 4.8 Hz), 4.72–4.65 (m, 7.2 H), 4.62 (dd, 0.9 H, *J* = 4.0, 11.4 Hz), 4.53 (m, 0.9 H), 4.49 (dd, 0.9 H, *J* = 3.1, 12.0), 4.32–4.25 (m, 1.8 H), 4.21 (m, 0.9 H), 4.09 (dd, 0.9 H, *J* = 8.1, 9.2), 3.93 (dd, *J* = 6.3, 9.2 Hz), 1.86 (s, 3 H), 1.24, 0.95 (2 s, 18 H), ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ: 177.9 ($COC(CH_3)_3$), 177.3 ($COC(CH_3)_3$), 170.0 ($COCH_3$), 166.1–165.1 (*C*OPh), 160.2 (*C*ONH), 133.5–125.3 (CO*Ph*), 107.1, 106.1, 105.7, 103.1, 85.6, 82.6, 82.4, 82.0, 81.7, 81.2, 80.6, 80.4, 77.9, 77.2, 76.9, 76.1, 75.3, 72.7, 70.4, 66.0, 65.4, 63.9, 63.5, 38.7, 38.3, 27.1, 26.8, 20.5.

A vigorously stirred suspension of trichloroacetimidate **19** (100 mg, 0.052 mmol), 9-decen-1-ol (12.6 µL, 0.068 mmol), and 4 Å powdered molecular sieves (0.2 g) in freshly anhydr. CH_2Cl_2 (2 mL) was cooled to −15 °C and TMSOTf (2.8 µL, 0.016 mmol) was slowly added. After 30 min of stirring, the mixture was diluted with CH_2Cl_2 (10 mL) and filtered into saturated aq. $NaHCO_3$ (10 mL). The organic layer was washed with water (3 × 10 mL), filtered, and evaporated under reduced pressure. The product was washed with cold hexane (2 × 0.7 mL) to eliminate the alcohol affording **20** as a chromatographically homogeneous syrup (75 mg, 75%): R_f 0.49 (7 : 1, toluene–EtOAc); $[\alpha]_D$ −14.1 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.09–7.24 (m, 45 H, aromatic), 6.07 (ddd, 1 H, *J* = 3.5, 3.8, 7.7 Hz, H-5″), 5.78 (ddt, 1 H, *J* = 6.6, 10.3, 16.9 Hz, C*H*-ethylenic), 5.79 (bs, 1 H, H-1‴), 5.75 (dd, 1 H, *J* = 1.6, 5.4 Hz, H-3), 5.68 (dd, 1 H, *J* = 1.6, 5.5 Hz, H-3‴), 5.66 (dd, 1 H, *J* = 1.7, 5.4 Hz, H-3″), 5.64 (s, 1 H, H-1″), 5.60 (d, 1 H, *J* = 1.6 Hz, H-2‴), 5.59 (d, 1 H, *J* = 1.7 Hz, H-2″), 5.52 (d, 1 H, *J* = 1.6 Hz, H-2), 5.32 (dd, 1 H, *J* = 2.4, 6.6 Hz, H-3′), 5.24 (s, 1 H, H-1), 5.05 (d, 1 H, *J* = 2.4 Hz, H-2′), 5.01 (s, 1 H, H-1′), 4.96 (ddt, 1 H, *J* = 1.6, 2.2, 17.2 Hz, CH_2-ethylenic), 4.90 (ddt, 1 H, *J* = 1.3, 2.0, 10.2 Hz, CH_2-ethylenic), 4.88 (dd, 1 H, *J* = 3.5, 5.4 Hz, H-4″), 4.79 (m, 1 H, H-4‴), 4.77 (dd, 1 H, *J* = 3.4, 11.9 Hz, H-5a‴), 4.74 (dd, 1 H, *J* = 3.8, 12.1 Hz, H-6a″), 4.69 (dd, 1 H, *J* = 7.7, 12.1 Hz, H-6b″), 4.65 (dd, 1 H, *J* = 3.8, 11.9 Hz, H-5b‴), 4.47 (ddd, 1 H, *J* = 3.7, 6.2, 6.8 Hz, H-5), 4.41 (dd, 1 H, *J* = 3.7, 5.4 Hz, H-4), 4.39 (dd, 1 H, *J* = 3.4, 11.4 Hz, H-6a′), 4.31 (dd, 1 H, *J* = 3.0, 6.5 Hz, H-4′), 4.28 (dd, 1 H, *J* = 7.1, 11.4 Hz, H-6b′), 4.26 (m, 1 H, H-5′), 4.04 (dd, 1 H, *J* = 6.2, 10.1 Hz, H-6a), 3.81 (dd, 1 H, *J* = 6.8, 10.1 Hz, H-6b), 3.74 (dt, 1 H, *J* = 6.7, 9.7 Hz, CH_2O), 3.49 (dt, 1 H, *J* = 6.5, 9.7 Hz, CH_2O), 2.01 (m, 2 H, CH_2), 1.89 (s, 3 H, CH_3), 1.61 (m, 2 H, CH_2), 1.38–1.22 (m, 10 H, CH_2), 1.12, 0.96 (2 s, 18 H, ($(CH_3)_3CCO$); ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 177.8, 177.1 ($(CH_3)_3CCO$), 170.0 (CH_3CO), 166.1–165.1 (*C*OPh), 139.2 (*C*H-ethylenic), 133.5–128.3 (aromatic), 114.1 (CH_2-ethylenic), 106.7 (C-1‴), 106.0 (C-1′), 105.8 (C-1″), 105.3 (C-1), 82.7 (C-2″), 82.3 (C-2), 82.2 (C-4), 82.1 (C-4″), 82.0 (C-2‴), 81.6 (C-4‴), 80.8 (C-2′), 80.2 (C-4′), 77.9 (C-3″), 77.5 (C-3‴), 77.3 (C-3), 76.1 (C-3′), 75.3 (C-5), 72.7 (C-5′), 70.3 (C-5″), 67.6 (CH_2O), 67.0 (C-6), 64.5 (C-6′), 63.8 (C-6″), 63.4 (C-5‴), 38.7 (2 x $(CH_3)_3CCO$), 29.7, 29.5, 29.4, 29.1, 28.9, 26.1 (7 × CH_2), 27.0, 26.7 ($(CH_3)_3CCO$), 20.4 (CH_3). HRMS (ESI) *m*/*z* calcd for $C_{108}H_{113}O_{32}$ ($M+H^+$) 1921.7210, found 1921.7251.

9-Decenyl β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→6)-[α-D-arabinofuranosyl-(1→5)]-β-D-galactofuranoside (1).

Compound **20** (57 mg, 0.030 mmol) was suspended in 0.52 M sodium methoxide in methanol (0.83 mL) and then cooled at 0 °C. After stirring for 1 h at 0 °C, the resulting solution was warmed to room temperature, stirred for 2 h, and a 9 : 1 MeOH–H_2O solution (2 mL) was added. The solution was passed through a column containing (H^+) resin (1.5 mL) and the column washed with MeOH–H_2O (9 : 1). The combined eluates were evaporated and the remaining methyl benzoate eliminated by five successive coevaporations with water. The residue was dissolved in water and purified through a C18-cartridge. Evaporation of solvent gave **1** (18 mg, 78%) as a hygroscopic syrup. R_f 0.79 (n-propanol–EtOH–H_2O, 7 : 1 : 1); $[\alpha]_D$ −52.6 (*c* 1, H_2O); ^{1}H NMR (D_2O, 500 MHz) δ: 5.86 (ddt, 1 H, *J* = 6.2, 10.0, 16.9 Hz, C*H*-ethylenic), 5.15 (bs, 1 H), 5.14 (bs, 1 H), 4.99 (ddt, 1 H, *J* = 1.5, 1.9, 17.1 Hz, CH_2-ethylenic), 4.94 (bs, 1 H), 4.92 (bs, 1 H), 4.91 (ddt, 1 H, *J* = 1.3, 2.6, 10.4 Hz, CH_2-ethylenic), 4.10–3.83 (14 H), 3.79–3.59 (8 H), 3.51 (ddt, 1 H, *J* = 6.2, 9.4 Hz, CH_2O), 2.00 (m, 2 H, CH_2), 1.55 (m, 2 H, CH_2), 1.34–1.29 (m, 10 H, $CH_2 \times 5$). ^{13}C NMR (D_2O, 125.8 MHz): δ 139.8 (*C*H-ethylenic), 114.5 (*C*H_2-ethylenic), 109.2 (C-1‴), 108.2, 107.7, 107.4, 84.4, 83.2, 82.4, 82.3, 81.8, 81.7 (x 3), 77.3, 77.1, 77.0 (x 2), 76.9, 76.8, 76.4, 71.1 (CH_2O), 69.2, 67.9, 63.4, 61.8, 61.7, 33.7, 29.2, 29.1, 28.9, 28.8, 28.7, 25.7.

HRMS (ESI) *m*/*z* calcd for $C_{33}H_{58}O_{20}Na$ (M+Na^+) 797.34137, found 797.34138.

2,3,5,6-Tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-[2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2,3-di-*O*-benzoyl-D-galactono-1,4-lactone (21). A vigorously stirred suspension of 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl trichloroacetimidate[50] (**9**, 877 mg, 1.18 mmol), disaccharide lactone **4** (820 mg, 0.99 mmol), and 4 Å powdered molecular sieves (1.2 g) in anhydr. CH_2Cl_2 (70 mL) was cooled to −15 °C and TMSOTf (64 µL, 0.35 mmol) was slowly added. After 1.5 h of stirring, the mixture was diluted with CH_2Cl_2 (50 mL) and filtered into saturated aq. $NaHCO_3$ (120 mL). The organic layer was washed with water (3 × 150 mL), dried (Na_2SO_4), filtered, and evaporated under reduced pressure. The residue was purified by column chromatography (30 : 1, toluene–EtOAc) to give 1.22 g (84%) of **21** as an amorphous solid which crystallized from hot EtOH: mp 89–90 °C, R_f 0.58 (7 : 1, toluene–EtOAc); $[\alpha]_D$ +9.23 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.12–7.14 (m, 45 H, aromatic), 6.18 (dd, 1 H, *J* = 6.2, 7.1 Hz, H-3), 6.10 (ddd, 1 H, *J* = 4.0, 4.4, 7.2 Hz, H-5′), 6.06 (dd, 1 H, *J* = 7.1 Hz, H-2), 5.78 (bs, 1 H, H-1″), 5.69 (dd, 1 H, *J* = 2.1, 5.2 Hz, H-3″), 5.61 (d, 1 H, *J* = 2.1 Hz, H-2″), 5.59 (dd, 1 H, *J* = 1.3, 4.8 Hz, H-3′), 5.42 (d, 1 H, *J* = 1.3 Hz, H-2′), 5.27 (bs, 1 H, H-1′), 4.88 (dd, 1 H, *J* = 1.9, 6.2 Hz, H-4), 4.78 (dd, 1 H, *J* = 7.2, 12.2 Hz, H-6a′), 4.75 (dd, 1 H, *J* = 4.0, 5.2 Hz, H-4′), 4.75 (dd, 1 H, *J* = 4.4, 12.2 Hz, H-6b′), 4.74 (dd, 1 H, *J* = 5.6, 8.6 Hz, H-5a″), 4.70–4.66 (m, 2 H, H-4″, H-5b″), 4.46 (ddd, 1 H, *J* = 1.9, 5.9, 9.5 Hz, H-5), 4.09 (t, 1 H, *J* = 9.5 Hz, H-6a), 3.97 (dd, 1 H, *J* = 5.9, 9.5 Hz, H-6b). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 168.5 (C-1), 166.1–165.2 (*C*OPh), 133.8–125.3 (aromatic), 107.7 (C-1″), 105.2 (C-1′), 82.9 (C-2″), 82.0 (C-4′), 81.7 (C-2′), 80.7 (C-4″), 79.3 (C-4), 77.6 (C-3′), 76.9 (C-3″), 75.2 (C-5), 73.5 (C-3), 72.0 (C-2), 70.4 (C-5′), 64.5 (C-6), 63.7 (C-6′), 63.6 (C-5″). Anal. Calcd for $C_{80}H_{64}O_{24}$. 1/2H_2O: C 67.74; H 4.62; Found: C 67.65, H 4.45.

One-pot preparation of trisaccharide lactone 21. A suspension of 2,3,5-tri-*O*-benzoyl-D-arabinofuranosyl trichloroacetimidate (**5**, 501 mg, 0.83 mmol), 2,3-di-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl-D-galactono-1,4-lactone (**12**, 413 mg, 0.83 mmol) and 4 Å powdered molecular sieves (1.2 g) in anhydr. CH_2Cl_2 (40 mL) was cooled to −15 °C. The mixture was stirred for 5 min and TMSOTf (7.5 µL, 0.041 mmol) was slowly added. After stirring for 1.5 h, tlc showed almost total consumption of **5** and the appearance of a main spot (R_f 0.74; 10 : 1 toluene–EtOAc) of 2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl-D-galactono-1,4-lactone. The reaction mixture was warmed to −8 °C and additional TMSOTf (195.4 µL, 1.08 mmol) was slowly added. Silyl ether hydrolysis was monitored by tlc and after 1 h of stirring at −8 °C showed total disappearance of the silylated disaccharide and the appearance of disaccharide **4** (R_f 0.09; toluene–EtOAc, 10 : 1). Therefore, the mixture was cooled to −18 °C and a solution of donor **9** (764 mg, 1.03 mmol) in anhydr. CH_2Cl_2 (40 mL) was slowly added. The stirring continued for 2 h at −15 °C and 12 h at −30 °C. The reaction mixture was diluted with CH_2Cl_2 (50 mL) and filtered into saturated aq. $NaHCO_3$ (150 mL). The organic layer was washed with water (3 × 150 mL), filtered, and evaporated under reduced pressure to give a syrupy product which was dissolved in boiling EtOH (185 mL). After the first crystals appeared at room temperature, the mixture was kept at 2 °C for 12 h and **21** was obtained (452 mg, 39%). The mother liquors were kept at 2 °C for additional 12 h and a second crop of crystals (123 mg, 11%) was filtered and characterized as **21**.

2,3,5,6-Tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-[2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2,3-di-*O*-benzoyl-D-galactofuranose (22). A solution of bis(2-butyl-3-methyl)borane (4.64 mmol) in anhydr. THF (1.55 mL), cooled to 0 °C and under an argon atmosphere, was added to a flask containing previously dried **21** (493 mg, 0.35 mmol). The solution was allowed to reach room temperature and stirring continued for 16 h. The tlc showed total consumption of **21** and the mixture was processed as previously described.[59] The product was purified by column chromatography (25 : 1, toluene–EtOAc) to give 326 mg (66%) of syrupy **22** as a 0.59 : 0.41 β : α anomeric mixture: R_f 0.38 (7 : 1 toluene–EtOAc); $[\alpha]_D$ +14.4 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.18–7.17 (m, 45 H, aromatic), 6.11 (m, 0.4 H, H-5′ α anomer), 6.07 (dd, 0.4 H, *J* = 5.3, 6.6 Hz, H-3α), 6.01 (m, 0.6 H, H-5′ β anomer), 5.88 (dd, 0.6 H, *J* = 2.1, 6.0 Hz, H-3β), 5.87 (s, 0.4 H, H-1″α), 5.82 (d, 0.6 H, *J* = 2.3 Hz, H-1β), 5.80 (s, 0.6 H, H-1″β), 5.76 (dd, 0.4 H, *J* = 2.7, 6.2 Hz, H-3″α), 5.66 (dd, 0.4 H, *J* = 4.9, 12.0 Hz, H-1α), 5.65–5.55 (m, 3.6 H, H-2 αβ, H-2″αβ, H-3β, H-3′αβ), 5.42 (d, 0.4 H, *J* = 0.9 Hz, H-2′α), 5.40 (d, 0.6 H, *J* = 0.9 Hz, H-2′β), 5.26 (s, 0.4 H, H-1′α), 5.21 (s, 0.6 H, H-1′β), 5.05 (dd, 0.6 H, *J* = 3.4, 5.6 Hz, H-4′β), 5.01 (dd, 0.4 H, *J* = 2.7, 12.3 Hz), 4.81–4.59 (m, 6,6 H, H-4αβ, H-4″αβ, H-6a′αβ, H-6b′αβ, H-5a″αβ, H-5b″ αβ, OH-β), 4.53–4.44 (m, 1.4 H, H-4′α, H-5αβ), 4.29 (d, 0.4 H, *J* = 12.0 Hz, OH-α), 4.21 (t, 0.6 H, *J* = 8.3 Hz, H-6a β), 4.14 (m, 0.4 H, H-6a α), 3.91 (dd, 0.6 H, *J* = 5.4, 8.3 Hz, H-6bβ), 3.87 (dd, 0.4 H, *J* = 5.9, 9.1 Hz, H-6bα). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 167.0–165.3 (*C*OPh), 133.4–128.3 (aromatic), 107.6 (C-1″ β anomer), 107.4 (C-1′ α anomer), 105.0 (C-1′ α anomer), 105.0 (C-1′ α anomer), 104.3 (C-1′ β anomer), 100.6 (C-1 β anomer), 95.1 (C-1 α anomer), 83.7, 83.5, 82.6, 81.7,

81.6, 81.5, 81.3, 80.2, 80.1, 80.0, 77.7, 77.5, 77.3, 76.3, 75.8, 75.4, 70.8, 70.4, 64.8, 64.5, 63.9, 63.8, 63.5. Anal. Calcd for $C_{80}H_{66}O_{24}$: C 68.08; H 4.71; Found: C 67.56, H 4.50.

2,3,5,6-Tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-[2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2,3-di-*O*-benzoyl-β-D-galactofuranosyl-(1→5)-2,6-di-*O*-pivaloyl-D-galactono-1,4-lactone (23). To a stirred solution of **22** (490 mg, 0.35 mmol) and trichloroacetonitrile (0.17 mL, 1.74 mmol) in anhydr. CH_2Cl_2 (20 mL) cooled to 0 °C, DBU (26 μL, 0.17 mmol) was slowly added. After 1 h, the solution was carefully concentrated under reduced pressure at rt and the residue was purified by column chromatography (20 : 1 : 0.2 toluene–EtOAc–TEA) to give *O*-(2,3,5,6-*O*-(tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-[2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2,3-di-*O*-benzoyl-D-galactofuranosyl) trichloroacetimidate (**7**) as a syrup (522 mg, 97%): R_f 0.70 (5 : 1 : 0.05 toluene–EtOAc–TEA); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.77 (s, 0.88 H, N*H*), 8.55 (s, 0.12 H, N*H*), 8.11–7.14 (m, 45 H), 6.68 (bs, 0.88 H, H-1 β anomer), 6.65 (d, 0.12 H, J = 4.5 Hz, H-1 α anomer), 6.25 (m, 0.12 H), 6.17 (m, 0.12 H, H-5″), 6.06 (m, 0.88 H, H-5″), 5.89 (d, 0.88 H, J = 4.2 Hz), 5.83 (d, 0.88 H, J = 1.1 Hz), 5.74 (s, 0.88 H), 5.61 (dd, 0.88 H, J = 1.7, 4.9 Hz), 5.58 (dd, 0.88 H, J = 1.5, 5.6 Hz), 5.39 (d, 0.9 H, J = 1.7 Hz), 5.38 (d, 0.88 H, J = 1.5 Hz), 5.28 (s, 0.88 H), 4.81–4.49 (m, 8 H), 4.24 (dd, 0.88 H, J = 7.8, 9.4 Hz), 3.95 (dd, 0.88 H, J = 5.7, 9.4 Hz), ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ: 166.1–165.2 (*C*OPh), 160.5 (*C*ONH), 133.5–125.3 (CO*Ph*), 107.0, 105.6, 103.3, 86.0, 82.5, 82.1, 81.4, 81.1, 80.8, 77.2, 76.8, 75.4, 70.1, 66.0, 64.1, 63.6.

A vigorously stirred suspension of trichloroacetimidate **7** (340 mg, 0.22 mmol), 2,6-di-*O*-pivaloyl-D-galactono-1,4-lactone[31] (**8**, 91.4 mg, 0.26 mmol), and 4 Å powdered molecular sieves (0.5 g) in freshly anhydr. CH_2Cl_2 (18 mL) was cooled to −15 °C and TMSOTf (12 μL, 0.066 mmol) was slowly added. After 2 h of stirring, the mixture was diluted with CH_2Cl_2 (25 mL) and processed as usual. The product was purified by a short column chromatography (20 : 1, toluene–EtOAc and then 10 : 1, toluene–EtOAc) to give 270 mg (71%) of syrupy **23**: R_f 0.46 (5 : 1, toluene–EtOAc); $[\alpha]_D$ −21.4 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.07–7.19 (m, 45 H, aromatic), 6.13 (m, 1 H, H-5″), 5.84 (dd, 1 H, J = 1.2, 3.8 Hz, H-3′), 5.75 (bs, 1 H, H-1‴), 5.70 (dd, 1 H, J = 1.6, 5.5 Hz, H-3‴), 5.56 (dd, 1 H, J = 1.4, 5.0 Hz, H-3″), 5.52 (d, 1 H, J = 8.7 Hz, H-2), 5.49 (s, 1 H, H-1″), 5.47 (d, 1 H, J = 1.2 Hz, H-2′), 5.43 (d, 1 H, J = 1.6 Hz, H-2‴), 5.42 (d, 1 H, J = 1.4 Hz, H-2″), 5.37 (s, 1 H, H-1″), 4.87 (dd, 1 H, J = 3.2, 5.0 Hz, H-4″), 4.85–4.82 (m, 2 H, H-3, H-4‴), 4.80–4.74 (m, 2 H, H-5a‴, H-6a″), 4.72 (dd, 1 H, J = 7.6, 11.9 Hz, H-6b″), 4.69 (dd, 1 H, J = 4.4, 12.1 Hz, H-5b‴), 4.62 (dd, 1 H, J = 3.8, 7.2 Hz, H-4′), 4.40 (dd, 1 H, J = 6.9, 10.7 Hz, H-6a), 4.38–4.34 (m, 2 H, H-5′, H-6b), 4.33 (dd, 1 H, J = 2.1, 8.0 Hz, H-4), 4.22 (ddd, 1 H, J = 2.1, 6.3, 6.9 Hz, H-5), 4.18 (dd, 1 H, J = 6.4, 10.7 Hz, H-6a′), 3.79 (dd, 1 H, J = 5.6, 10.7 Hz, H-6b′), 1.18, 0.98 (2 s, 18 H, ((C*H*$_3$)$_3$CCO)). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 177.3, 177.1 ((CH$_3$)$_3$*C*CO), 168.8 (C-1), 166.6–165.0 (*C*OPh), 133.5–128.3 (aromatic), 106.7 (C-1′), 106.4 (C-1‴), 106.2 (C-1″), 86.8 (C-4′), 83.4 (C-2‴), 81.8 (C-4″, C-2″), 81.4 (C-2′), 80.5 (C-4‴), 79.5 (C-4), 77.7 (C-3″), 77.2 (C-3″), 76.1 (C-3′, C-5′), 74.6 (C-2), 73.2 (C-5), 71.5 (C-3), 70.3 (C-5″), 67.2 (C-6′), 63.8, 63.3 (C-5‴, C-6″), 63.0 (C-6); 38.7, 38.4 (CO*C*(CH$_3$)$_3$); 27.0, 26.7 (COC(*C*H$_3$)$_3$).

HRMS (ESI) *m*/*z* calcd for $C_{96}H_{91}O_{31}$ (M+H$^+$) 1739.5539, found 1739.5543.

2,3,5,6-Tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-[2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2,3-di-*O*-benzoyl-β-D-galactofuranosyl-(1→5)-3-*O*-acetyl-2,6-di-*O*-pivaloyl-D-galactono-1,4-lactone (24). To a solution of **23** (259 mg, 0.15 mmol) in dry pyridine (1.2 mL), cooled at 0 °C, was added acetic anhydride (1.2 mL) dropwise and the mixture was stirred at room temperature for 40 min. After cooling to 0 °C, the reaction was quenched by slow addition of MeOH (2.7 mL) and the stirring continued for 30 min at room temperature. The solution was diluted with CH_2Cl_2 (30 mL) and then sequentially washed with 10% HCl (2 × 40 mL), water (2 × 40 mL), satd. aq. $NaHCO_3$ (2 × 40 mL), water (2 × 40 mL), dried (Na_2SO_4), filtered, and then concentrated. The crude product was purified by column chromatography (30 : 1, toluene–EtOAc) to give **24** (174 mg, 67%) as a syrup; R_f 0.58 (5 : 1 toluene–EtOAc); $[\alpha]_D$ −22.0 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.05–7.17 (m, 45 H, aromatic), 6.10 (m, 1 H, H-5″), 5.81 (dd, 1 H, J = 1.5, 4.5 Hz, H-3′), 5.77 (t, 1 H, J = 7.7 Hz, H-3), 5.73 (bs, 1 H, H-1‴), 5.63 (dd, 1 H, J = 1.5, 6.0 Hz, H-3‴), 5.61 (d, 1 H, J = 8.0 Hz, H-2), 5.57 (dd, 1 H, J = 1.5, 5.3 Hz, H-3″), 5.53 (d, 1 H, J = 1.5 Hz, H-2‴), 5.49 (bs, 1 H, H-1′), 5.48 (d, 1 H, J = 1.5 Hz, H-2′), 5.43 (d, 1 H, J = 1.5 Hz, H-2″), 5.35 (s, 1 H, H-1″), 4.86 (m, 1 H, H-4‴), 4.78 (dd, 1 H, J = 3.2, 5.3 Hz, H-4″), 4.75 (dd, 1 H, J = 3.7, 12.0 Hz, H-5a‴), 4.72–4.65 (m, 4 H, H-4′, H-5b‴, H-6a″, H-6b″), 4.55 (dd, 1 H, J = 3.4, 7.8 Hz, H-4), 4.41 (m, 1 H, H-5′), 4.35 (dd, 1 H, J = 6.1, 10.9 Hz, H-6a), 4.30 (m, 2 H, H-5, H-6b), 4.17 (dd, 1 H, J = 4.6, 10.8 Hz, H-6a′), 3.81 (dd, 1 H, J = 6.5, 10.8 Hz, H-6b′), 2.00 (s, 3 H, CH_3), 1.14, 0.97 (2 s, 18 H, ((C*H*$_3$)$_3$CCO)). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 177.8 ((CH$_3$)$_3$*C*CO); 169.4, 168.8 (C-1, *C*OCH$_3$), 165.7–165.1 (*C*OPh), 133.5–125.3 (aromatic), 106.4 (C-1″), 106.3 (C-1‴), 105.5 (C-1′), 85.0 (C-4′), 82.5 (C-2‴), 81.9 (C-2′, C-2″), 81.6 (C-4″), 80.8 (C-4‴), 77.7 (C-3‴), 77.6 (C-3″), 77.2 (C-4), 76.6 (C-3′), 76.2 (C-5′), 72.3 (C-2, C-5), 72.1 (C-3), 70.3 (C-5″), 67.8 (C-6′), 63.8 (C-6″), 63.5 (C-5‴), 62.2 (C-6); 38.7, 38.4 (CO*C*(CH$_3$)$_3$); 27.0, 26.6 (COC(*C*H$_3$)$_3$), 20.4 (CH$_3$).

HRMS (ESI) *m*/*z* calcd for $C_{98}H_{93}O_{32}$ (M+H$^+$) 1781.5645, found 1781.5631.

2,3,5,6-Tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-[2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2,3-di-*O*-benzoyl-β-D-galactofuranosyl-(1→5)-3-*O*-acetyl-2,6-di-*O*-pivaloyl-α,β-D-galactofuranose (25). A solution of bis(2-butyl-3-methyl)borane (0.47 mmol) in anhydr. THF (0.13 mL), cooled to 0 °C and under an argon atmosphere, was added to a flask containing previously dried compound **24** (70 mg, 0.04 mmol). The solution was allowed to reach room temperature and stirring continued for 16 h when tlc showed partial consumption of **24**. The mixture was cooled to 0 °C and more solution of bis(2-butyl-3-methyl)borane (0.47 mmol) in anhydr. THF (0.13 mL) was added. The resulting solution was allowed to reach room temperature and the stirring continued for additional 16 h. The tlc showed total consumption of **24** and the mixture was processed as previously described.[59] The product was purified by column chromatography (12 : 1, toluene–EtOAc) to give 64 mg (64%) of syrupy **25** as a 0.71 : 0.29 β : α anomeric mixture: R_f 0.52 (5 : 1 toluene–EtOAc); $[\alpha]_D$ − 6.3 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz), only the assigned value are listed, δ: 8.106–7.18 (m, 45 H, aromatic), 6.11 (m, 0.71 H, H-5″β anomer),

6.05 (m, 0.29 H, H-5″ α anomer), 5.84 (dd, 0.29 H, J = 1.9, 5.6 Hz, H-3‴), 5.82 (bs, 1 H, H-1‴), 5.79 (dd, 0.79 H, J = 1.3, 5.6 Hz, H-3‴ β anomer), 5.66 (m, 0.71 H, H-3″ β anomer), 5.61 (bs, 0.29 H, H-1′ α anomer), 5.51 (s, 0.71 H, H-1′), 5.36 (bs, 0.29 H, H-1′ α anomer), 5.33 (m, 1.71 H, H-1″ β anomer, H-1 β anomer, H-1 α anomer), 5.23 (dd, 0.71 H, J = 1.4, 5.1 Hz, H-3 β anomer), 1.96, 1.32 (2 s, CH_3), 1.14, 1.13, 1.11, 1.06 (4 s, 18 H, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ: 178.0 ($COC(CH_3)_3$), 177.1 ($COC(CH_3)_3$), 169.8 ($COCH_3$), 166.4–165.3 (COPh), 133.4–128.2 (aromatic), 106.5 (C-1‴ β anomer), 106.3 (C-1‴ α anomer), 105.7 (C-1″), 105.4 (C-1′ α anomer), 105.6 (C-1′ β anomer), 105.0 (C-1′ α anomer), 100.5 (C-1 β anomer), 95.3 (C-1 α anomer), 82.9, 82.7, 82.3, 82.1, 82.0, 81.7 (x 2), 81.5, 81.3, 80.8, 80.4, 79.1, 77.6, 76.4, 75.3, 74.7, 70.1, 66.8, 64.2, 63.8, 63.5; 38.7, 38.5, 38.4 ($CO\mathit{C}(CH_3)_3$); 27.1, 27.0, 26.9, ($COC(\mathit{C}H_3)_3$); 21.5, 20.3 (CH_3). HRMS (ESI) m/z calcd for $C_{98}H_{94}O_{32}Na$ (M+Na$^+$) 1805.5620, found 1805.5573.

9-Decenyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-[2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2,3-di-*O*-benzoyl-β-D-galactofuranosyl-(1→5)-3-*O*-acetyl-2,6-di-*O*-pivaloyl-β-D-galactofuranoside (27). To a stirred solution of **25** (86 mg, 0.048 mmol) and trichloroacetonitrile (36 μL, 0.36 mmol) in anhydr. CH_2Cl_2 (5 mL) cooled to 0 °C, DBU (5.4 μL, 0.036 mmol) was slowly added. After 2 h, the solution was carefully concentrated under reduced pressure at rt and the residue was purified by column chromatography (25 : 1 : 0.2 toluene–EtOAc–TEA) to give trichloroacetimidate **26** (68 mg, 73%) as a syrup: R_f 0.45 (5 : 1 : 0.05 toluene–EtOAc–TEA); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.54 (s, 1 H, NH), 8.07-7.15 (m, 45 H), 6.26 (s, 1 H, H-1 β anomer), 6.04 (m, 1 H, H-5″), 5.78 (m, 2 H), 5.62 (m, 2 H), 5.55 (d, 1 H, J = 1.8 Hz), 5.53 (s, 1 H), 5.51 (d, 1 H, J = 1.3 Hz), 5.45 (d, 1 H, J = 1.5 Hz), 5.36 (m, 2 H), 5.33 (dd, 1 H, J = 0.5, 2.0 Hz), 4.88 (m, 1 H), 4.75–4.68 (m, 5 H), 4.64 (dd, 1 H, J = 4.1, 12.0 Hz), 4.53 (m, 1 H), 4.47 (t, 1 H, J = 5.3 Hz), 4.37 (dd, 1 H, J = 3.9, 11.4 Hz), 4.32 (m, 1 H), 4.25 (dd, 1 H, J = 6.6, 1.4 Hz), 4.17 (dd, 1 H, J = 3.7, 11.0 Hz), 4.89 (dd, 1 H, J = 7.1, 11.0 Hz), 1.93 (s, 3 H), 1.25, 1.22 (2 s, 18 H).

A vigorously stirred suspension of trichloroacetimidate **26** (63 mg, 0.033 mmol), 9-decen-1-ol (8.1 μL, 0.044 mmol), and 4 Å powdered molecular sieves (0.2 g) in freshly anhydr. CH_2Cl_2 (2 mL) was cooled to −15 °C and TMSOTf (1.8 μL, 0.010 mmol) was slowly added. After 2 h of stirring, the mixture was diluted with CH_2Cl_2 (10 mL) and processed as above. The product was washed with cold hexane (6 × 0.7 mL) to eliminate the alcohol to afford **27** as a chromatographically homogeneous syrup (60 mg, 94%): R_f 0.62 (7 : 1, toluene–EtOAc); $[\alpha]_D$ −14.9 (c 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.06—7.17 (m, 45 H, aromatic), 6.03 (m, 1 H, H-5″), 5.80 (ddt, 1 H, J = 6.7, 10.8, 17.0 Hz, CH-ethylenic), 5.78 (bs, 1 H, H-1‴), 5.63 (dd, 1 H, J = 1.6, 5.3 Hz, H-3‴), 5.61 (dd, 1 H, J = 1.6, 5.4 Hz, H-3″), 5.58 (m, 2H, H-1′, H-2′), 5.50 (d, 1H, J = 1.6 Hz, H, H-2‴), 5.45 (d, 1H, J = 1.6 Hz, H, H-2″), 5.35 (m, 1 H, H-1″), 5.31 (dd, 1 H, J = 2.5, 6.5 Hz, H-3), 5.06 (dd, 1 H, J = 1.0, 2.5 Hz, H-2), 4.98 (ddt, 1 H, J = 1.6, 2.2, 17.0 Hz, CH_2-ethylenic), 4.92 (ddt, 1 H, J = 1.2, 2.2, 10.3 Hz, CH_2-ethylenic), 4.92 (bs, 1 H, H-1), 4.88 (dt, 1 H, J = 3.8, 5.9 Hz, H-5′), 4.74 (dd, 1 H, J = 3.6, 12.0 Hz, H-6a″), 4.71 (dd, 1 H, J = 3.3, 5.4 Hz, H-4″), 4.70–4.67 (m, 3 H, H-5a″, H-5b″, H-4‴), 4.65 (dd, 1 H, J = 4.1, 12.0 Hz, H-6b‴), 4.51 (m, 1 H, H-5′), 4.37 (m, H-6a), 4.31 (m, 2 H, H-5, H-6b), 4.27 (dd, 1 H, J = 3.6, 6.5 Hz, H-4), 4.14 (dd, 1 H, J = 3.8, 10.8 Hz, H-6a′), 3.87 (dd, 1 H, J = 7.2, 10.9 Hz, H-6b′), 3.62 (dt, 1 H, J = 6.8, 9.6 Hz, CH_2O), 3.36 (dt, 1 H, J = 6.6, 9.6 Hz, CH_2O), 2.01 (m, 2 H, CH_2), 1.93 (s, 3 H, CH_3), 1.50 (m, 2 H, CH_2), 1.36–1.22 (m, 10 H, CH_2), 1.11, 1.07 (2 s, 18 H, ($(C\mathit{H}_3)_3CCO$)). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 177.9, 177.4 ($(CH_3)_3\mathit{C}CO$), 169.9 ($CH_3\mathit{C}O$), 166.0–165.2 ($\mathit{C}O$Ph), 139.2 (CH-ethylenic), 133.4–128.2 (aromatic), 114.1 ($\mathit{C}H_2$-ethylenic), 106.5 (C-1″), 106.0 (C-1‴), 105.4 (C-1), 105.0 (C-1′), 83.2 (C-4′), 82.6 (C-2‴), 82.2 (C-2′), 82.0 (C-2″), 81.7 (C-2), 81.5 (C-4″), 80.7 (C-4‴), 80.2 (C-4), 77.7 (C-3″), 77.4 (C-3′), 77.2 (C-3‴), 76.2 (C-3), 75.4 (C-5′), 72.5 (C-5), 70.3 (C-5″), 68.0 (C-6′), 67.6 (CH_2O), 63.8 (C-6), 63.7 (C-6′), 63.4 (C-5‴), 38.6 (2 x $(CH_3)_3\mathit{C}CO$), 33.8, 29.4, 29.5, 29.3, 29.1, 28.9, 27.0, 26.8, 26.0; 27.0, 26.7 ($(\mathit{C}H_3)_3CCO$), 26.0, 20.6 (CH_3).

HRMS (ESI) m/z calcd for $C_{108}H_{112}O_{32}Na$ (M+Na$^+$) 1943.7029, found 1943.7091.

9-Decenyl β-D-galactofuranosyl-(1→6)-[α-D-arabinofuranosyl-(1→5)]-β-D-galactofuranosyl-(1→5)-β-D-galactofuranoside (2). Compound **27** (52 mg, 0.027 mmol) was suspended in 0.49 M sodium methoxide in methanol solution (0.79 mL) and then cooled at 0 °C. After stirring for 1 h at 0 °C, the resulting solution was warmed to room temperature, stirred for 2.5 h, and 9 : 1 MeOH–H_2O solution (2 mL) was added. The solution was passed through a column containing Amberlite IR-120 plus (H$^+$) resin (1.5 mL) and the column washed with MeOH–H_2O (9 : 1). The combined eluates were evaporated and the remaining methyl benzoate was eliminated by five successive coevaporations with water (1 mL). The residue was dissolved in water, further purified through a Strata™ C18-E cartridge, and the solution evaporated. Glycoside **2** (16 mg, 76%) was obtained as a hygroscopic syrup. R_f 0.62 (n-propanol–EtOH–H_2O, 7 : 1 : 1); $[\alpha]_D$ −37.9 (c 1, H_2O); ^{1}H NMR (D_2O, 500 MHz) δ: 5.78 (m, 1 H, CH-ethylenic), 5.20 (bs, 1 H), 5.18 (bs, 1 H), 4.98 (bs, 1 H), 4.97 (m, 1 H, CH_2-ethylenic), 4.87 (bs, 1 H), 4.90 (m, 1 H, CH_2-ethylenic), 4.58–3.88 (14 H), 3.80–3.60 (8 H), 3.43 (m, 1 H, CH_2O), 2.00 (m, 2 H, CH_2), 1.53 (m, 2 H, CH_2), 1.33–1.25 (m, 10 H, CH_2 × 5). ^{13}C NMR (D_2O, 125.8 MHz): δ 139.7 (CH-ethylenic), 114.7 ($\mathit{C}H_2$-ethylenic), 109.1, 108.3, 107.9 (x 2), 84.4, 83.5, 83.2, 82.1 (x 2), 82.0, 81.7, 81.6, 77.4, 77.3, 77.2, 77.0, 76.4, 71.4, 68.8 (CH_2O), 68.2, 63.4, 62.7, 61.8, 34.2, 30.8, 30.3, 29.8, 29.5, 29.3, 26.3. HRMS (ESI) m/z calcd for $C_{33}H_{58}O_{20}Na$ (M+Na$^+$) 797.3414, found 797.3416.

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