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Note

Synthetic tools for the characterization of galactofuranosyl transferases: glycosylations via acylated glycosyl iodides

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ABSTRACT

With the aim of developing synthetic tools for the characterization of galactofuranosyltransferases, the synthesis of 9-decenyl glycosides of D-Man*p*, D-Gal*f*, and β-D-Gal*f*-(1→3)-D-Man*p* was targeted. The interest in the alkenyl aglycone arises via potential conjugation reactions, once the terminal double bond has been conveniently functionalized. The glycosylation of β-D-Gal*f*-(1→3)-D-Man*p* was attempted by two different approaches: the trichloroacetimidate method and the glycosylation via the glycosyl iodide. The conditions for the latter were established on the basis of glycosylation assays of per-*O*-acetylmannose. On the other hand, the study of glycosylation reactions via per-O-benzoylated galactofuranosyl iodide confirms the versatility of glycosyl iodides as donors.

Among the numerous structures of pathogenic microorganisms in which D-galactofuranose occurs,[1] the disaccharide β-D-Gal*f*-(1→3)-D-Man*p* (**1**, Fig. 1) is found in glycoconjugates of protozoa (*Trypanosoma cruzi* and *Leishmania* spp.) and in fungi, as *Aspergillus fumigatus*.[2,3] In *T. cruzi*, motif **1** is present as non-reducing terminal units of the glycoinositolphospholipids (GIPLs),[4–6] which are important for the interaction with the intestine of the insect vector.[7] In *Leishmania*, disaccharide **1** is present as an internal unit in the lipophosphoglycan (LPG),[8] which was also shown to play a critical role in the attachment of *Leishmania* promastigotes to the fly midgut.[9]

For elucidating the biosynthesis of D-Gal*f* containing glycoconjugates, synthetic substrates of the involved enzymes are required.[10–12] Oligosaccharides containing the β-D-Gal*f*-(1→3)-D-Man*p* (**1**) motif have been synthesized,[13,14] as well as some derivatives of **1**, which were afforded by different approaches.[15] We have described the synthesis of free disaccharide **1** using the glycosyl-aldonolactone approach, and we have shown that it is hydrolyzed by the *exo* β-D-galactofuranosidase of *Penicillium fellutanum*, our non-pathogenic model to evaluate the synthetic tools developed for studying the D-Gal*f* related enzymes.[16]

With the aim of obtaining a derivative of **1** for the characterization of the galactofuranosyltransferases of *P. fellutanum* and *T. cruzi*, we have now targeted the synthesis of 9-decenyl β-D-Gal*f*-(1→3)-D-Man*p* (**2**, Fig. 1), which is expected to be an acceptor of D-Gal*f* units and as precursor of other derivatives designed to study the immunogenic activity of **1**. For the synthesis of **2** it was necessary to introduce the alkenyl moiety with a glycosylation method that would preserve the Gal*f*-(1→3)-Man*p* linkage. We decided to carry on this synthesis by two alternative approaches: one based on the trichloroacetimidate method, which required transformations that we have previously applied,[17,18] and the other involving a glycosyl iodide donor (Scheme 1). In this case, the conditions for the glycosylation of the acetylated mannose unit must be established. For the glycobiological studies, we have also decided to synthesize acceptors **3** and **4** (Fig. 1). The optimized conditions for the synthesis of **3** would be useful for the glycosylation of **1**. On the other hand, as continuation of our studies on the scope of glycosylations via galactofuranosyl iodides,[18–20] this reaction was investigated for the synthesis of compound **4** from acylated precursors of D-Gal*f*. Thus, we report here the studies of glycosylations of per-*O*-acetylmannose via glycosyl iodides, the exploration of the galactofuranosylation via iodides prepared from per-O-acylated precursors, and the synthesis of glycosyl disaccharide **2**.

For the synthesis of mannopyranoside **3** we used the glycosyl iodide method starting from penta-*O*-acetyl-α,β-D-mannopyranose (**5**). In the first instance, we established the reaction conditions for the formation of the mannopyranosyl iodide and its subsequent glycosylation, in order to apply similar conditions to the synthesis of disaccharide **2**. According to the reported conditions for similar substrates,[21,22] compound **5** was treated with TMSI (2.4 equiv) at room temperature and after 2 h, the medium was neutralized with EtN(*i*Pr)$_2$, and 9-decen-1-ol was added as an acceptor (Scheme 2). Under these conditions, starting compound **5** was not completely consumed, and the reaction proceeded slowly toward the

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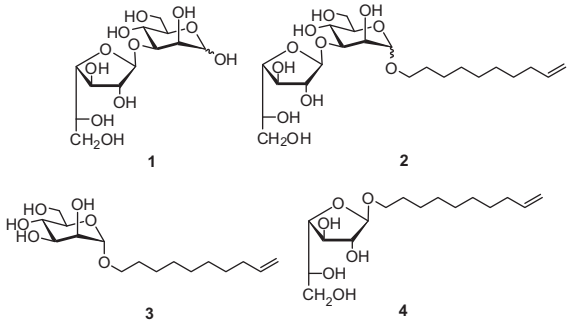
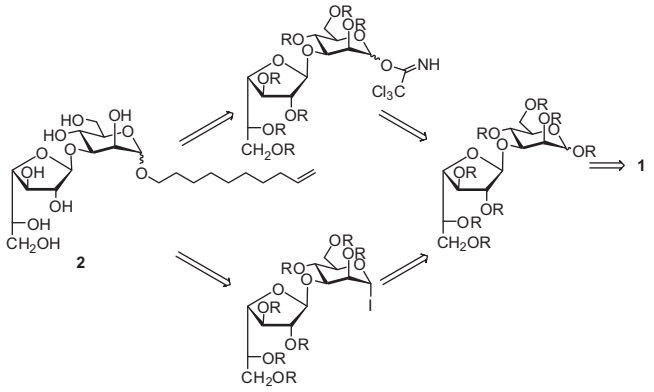


Figure 1. Synthetic targets.

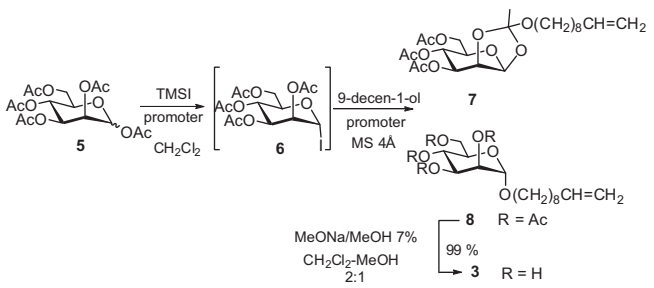


Scheme 1. Retrosynthetic approaches for 9-decenyl β-D-Gal*f*-(1→3)-D-Man*p* (**2**).

formation of a main product, but on the basis of the ^{13}C NMR spectrum, this compound was identified as the orthoesther **7** (Table 1, entry 1).[23,24]

Attempts to rearrange the orthoesther **7** with TMSOTf[25,26] were not satisfactory; although the NMR spectra of the crude product showed the formation of **8**, a complex mixture of products has been obtained as result of partial O-deacetylation.

It has been reported that ZnI_2 accelerates the formation of peracylated glycosyl iodides and prevents the formation of the orthoesther.[21,22] The ZnI_2 also acted as iodide source and in this way the halogen exchange in the anomeric carbon, that would occur with other halogenated Lewis acids, was avoided. Hence, ZnI_2 was added in a substoichiometric amount and iodide **6** was formed in just 0.5 h (Table 1, entry 2). As the glycosylation of acylated iodides generally requires a promoter,[23,24] after the complete transformation of **5** into **6**, an additional amount of ZnI_2 was added together with the 4 Å powdered molecular sieves. They were not used in the first step because it has been reported that they retard the iodide formation.[23,24] Under these conditions the 9-decenyl



Scheme 2. Synthesis of 9-decenyl α-D-mannopyranoside (**3**).

glycoside **8** was obtained as major product (46%), along with an important amount of partially de-O-acylated products. Therefore, after reacetylation, compound **8** was obtained in 80% combined yield (Table 1, entry 2). The NMR spectra of **8** showed that the glycosylation occurred with complete 1,2-*trans* stereoselectivity, due to participation of the neighboring acetyl group on O-2. O-Deacetylation of crude compound **8** afforded **3** in 80% overall yield from **5**.

The synthesis of **8** and **3** as precursors of oligosaccharides present in the antigenic lipophosphoglycan of *Leishmania donovani*, had been previously accomplished by the Koenigs–Knorr method from acetobromomannose.[27] The glycosyl iodide method here described, besides avoiding the use of mercuric salts, affords **8** in higher yield, and the complete NMR spectroscopic characterization of both **8** and **3** is now provided.

Previously, we have described the synthesis of per-*O*-TBS-β-D-galactofuranose (**9**) and its glycosylation by in situ activation with TMSI as the galactofuranosyl iodide **12** (Scheme 3). Compound **12** was effectively glycosylated to afford *O*-,[18] *S*-, *C*-galactofuranosides,[20] and some nitrogenated derivatives,[19] under mild conditions compatible with labile acceptors. Recently, the lipoteichoic acid from *Streptococcus* sp. DSM 8747 has been synthesized by glycosylation of **9** via the galactofuranosyl iodide, and the method showed to be significantly more efficient than those using traditional glycosyl donors.[28] Condensation of persilylated **9** with 9-decen-1-ol under the conditions previously described,[18] afforded glycoside **14** in 83% yield as an anomeric mixture β/α in a 3:1 ratio. A similar diastereoselectivity was observed with simple acceptors, which was increased when bulky acceptors were used.[18] O-Desilylation of **14** with TBAF afforded the free galactofuranoside **4** in 66% yield.

Although β-D-galactofuranosides can be stereoselectively obtained by neighboring-group participation from acylated precursors using $SnCl_4$ or other Lewis acids[3] as promoters, the glycosyl acceptors are limited to acid stable derivatives. We aimed to investigate the scope of the galactofuranosyl iodide glycosylations from the easily available peracylated Gal*f* derivatives **10**[29] and **11**,[30] which are expected to give glycosides with higher diastereoselectivity than **9**, due to the anchimeric effect. In order to optimize the reaction conditions, *n*BuOH was employed as a model acceptor. As peracylated precursors are less reactive than persilylated,[31–33] more drastic conditions than those employed for **9** would be required. The assayed conditions involving variations in the amounts of TMSI, temperature, and reaction time are summarized in Table 2. The effect of molecular sieves and promoters was also examined. As expected, **11** was more reactive than **10**, but less than **9** (Table 2, entries 1–3). The best condition for the preparation of iodide **13**, in the absence of a catalyst or a promoter, was the treatment of **11** with 3 equiv of TMSI (Table 2, entry 5). Compound **10** required 4.5 equiv of TMSI to complete the reaction (Table 2, entry 4). Iodide **13** was not stable enough to be isolated.

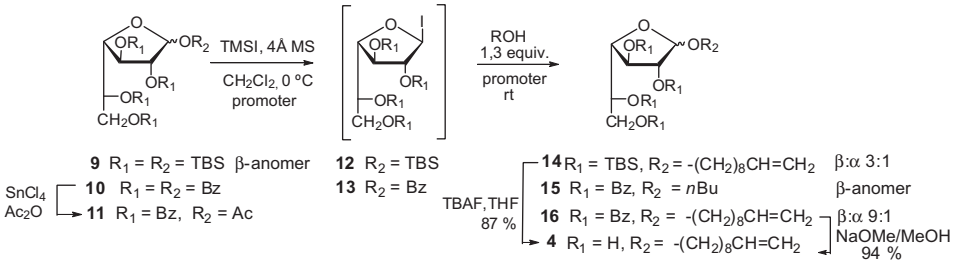
The addition of powdered molecular sieves during the second step of the reaction avoided the formation of TMSOAc and TMSOBz[23,34] and the subsequent reaction with **13**, which would afford **10** and **11** as recombination products.

The effect of the addition of ZnI_2 during the iodide formation was also studied (Table 2, entries 6–8). In the presence of 0.6 equiv of ZnI_2, compound **13** was formed at room temperature with only 1.2 equiv of TMSI and in 0.5 h (Table 2, entry 8). When the amount of ZnI_2 was reduced, the consumption of acetate **11** was not complete, although the formed iodide was consumed in 1 h (Table 2, entries 7 and 8). The best results were obtained conducting the reactions at room temperature, without the need of heating to 45 °C, as in the case of the mannopyranosyl iodide **6**.

Under the optimized conditions established for the synthesis of **15** (Table 2, entry 8), the analogous decenyl glycoside **16** was obtained in 66% yield, mainly in the β-configuration (9:1). O-Debenzoylation of **16**

Table 1
Reaction conditions assayed for glycosylation of penta-*O*-acetyl-D-mannopyranose (**5**) via mannosyl iodide

Entry	Iodide **6** formation			Glycosylation			
	TMSI (equiv)	ZnI_2 (equiv)	Conditions	Base/promoter (equiv)	MS 4 Å	Conditions	Products/observations
1	2.4		25 °C, 2 h	$EtN(iPr)_2$ (2.4)	—	25 °C, 144 h	**7** (50%)
2	1.5	0.4	45 °C, 0.5 h	ZnI_2 (1.0)	Yes	45 °C, 3.5 h	**8** (46%) (80% after reacetylation)



Scheme 3. Synthesis of *O*-galactofuranosides via in situ formed galactofuranosyl iodides.

Table 2
Reaction conditions assayed for O-glycosylations via in situ formed galactofuranosyl iodides. Compound numbers in bold.

Entry	Precursor	TMSI (equiv)	ZnI_2 (equiv)	Conditions	MS 4 Å	Conversion to iodide[a] (%)	Products/observations
1	**9**	1.2	—	0 °C, 0.5 h	Yes	100	**14β**:**α** 3:1
2	**10**	1.2	—	0 °C, 0.5 h	Yes	0	—
3	**10**	1.2	—	0 °C, 0.5 h	Yes	20	**15β**
4	**10**	4.5	—	0→25 °C, 1 h	Yes	100	**15β**
5	**11**	3.0	—	0→25 °C, 1.5 h	Yes	100	**15β**
6	**11**	1.2	0.6	0→25 °C, 0.5 h	Yes	100	**15β** in 1 h (80%)
7	**11**	1.2	0.4	0→25 °C, 1-2 h	Yes	80	**15β** in 1 h
8	**11**	1.2	0.2	0→25 °C, 1-2 h	Yes	60	**15β** in 1 h

[b]Isolated by column chromatography.
[a] Estimated by TLC.

with NaOMe/MeOH in CH_2Cl_2 afforded **4** in almost quantitative yield. The β-configuration of the major component of **16** and **4** was confirmed on the basis of the ^{13}C NMR spectra, which showed characteristic resonances for C-1 (105.6 and 109.4 ppm, respectively) and signals corresponding to C-2 and C-4 above 80 ppm, also characteristic of the β-D-Gal*f* configuration.

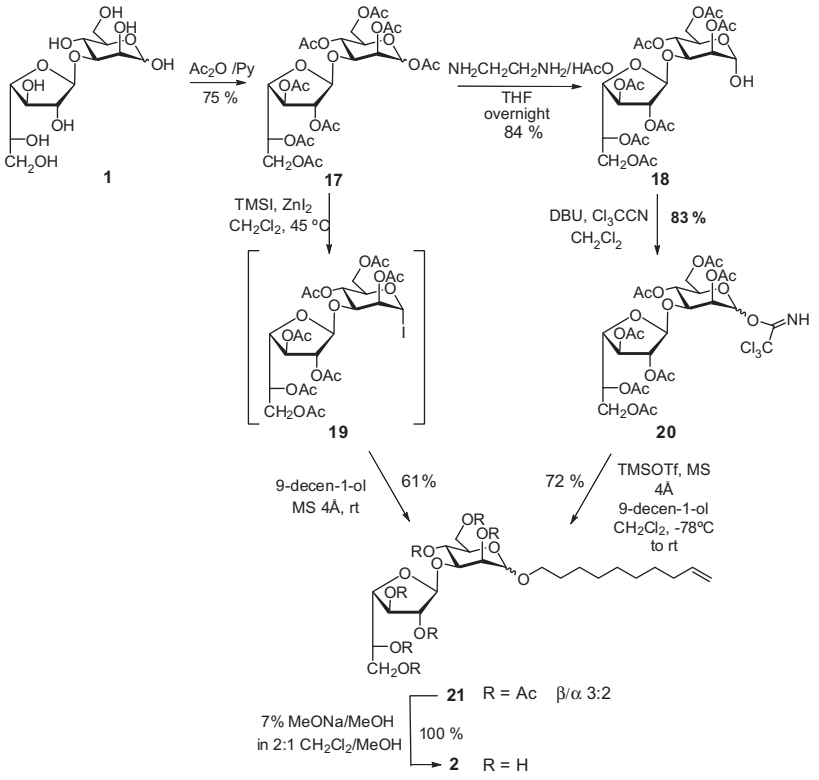
Despite the convenience of the use of iodide 13 to achieve stereoselectively β-D-galactofuranosides, the disarmed character of this benzoylated iodide was evidenced when allyl TMS, $(TMS)_2S$, or 2,4,6-tri-*O*-benzoyl-D-manono-1,4-lactone were used as acceptors. While these compounds were effectively coupled with **9**,[18,20] the glycosylation of **13** failed.

Both strategies designed to accomplish the synthesis of the decenyl glycoside **2**, required per-O-acetylated disaccharide **17**, which was afforded as an anomeric mixture in 75% yield by treatment of **1**[16] with Ac_2O/py (Scheme 4). The approach involving a trichloroacetimidate donor required the selective anomeric O-deacetylation of **17**. Hence, **17** was treated with ethylenediamine and acetic acid to afford the hemiacetal **18** in 84% yield (Scheme 4), exclusively in the α-configuration as indicated by the ^1H NMR spectrum. Treatment of **18** with trichloroacetonitrile and DBU afforded the trichloroacetimidate **20** (83%). Glycosylation of **20** with 1.5 equiv of 9-decen-1-ol in CH_2Cl_2 using TMSOTf as catalyst gave **21** in 72% yield. The NMR spectra showed that, despite the anchimeric assistance from the participating acetyl group at O-2, compound **21** was obtained as an inseparable mixture of β/α anomers, in a 3:2 ratio. The ^{13}C NMR spectrum showed resonances at 102.7 and 102.5 ppm corresponding to C-1′ of the β- and the α-anomers, respectively, and signals at δ 99.6 (C-1β) and 99.2 (C-1α) due to the mannopyranosyl unit. The ^1H NMR spectrum showed singlets at 5.19 and 5.13 ppm for H-1′ of the β- and the α-anomers, respectively, and doublets at 4.90 (H-1α) and 4.52 ppm (H-1β) for the mannopyranosyl unit.

On the other hand, peracetylated compound **17** was treated with TMSI/ZnI_2, according to the conditions optimized for the formation and glycosylation of iodide **6** (Table 1, entry 2), although a greater amount of ZnI_2 (0.7 equiv) was necessary to obtain iodide **19**. Then, 9-decen-1-ol and 4 Å powdered molecular sieves were added (Scheme 4). Compound **21** (78%) was obtained, along with a small amount of **18**.

In the ^1H NMR spectrum of **21** obtained in this way, it was observed that an anomeric mixture in a β/α ratio of 3:2 was actually obtained. This ratio was almost equal to that obtained in the glycosylation via the trichloroacetimidate **20**, suggesting that the stereoselectivity depends on the substrate itself rather than the glycosylation method used. Probably, the β-D-Gal*f* unit as substituent on the O-3 of D-Man*p* would be responsible for a distortion in the intermediate bicyclic 1,2-acyloxonium ion, making the anchimeric participation less efficient.

Finally, de-O-acetylation of **21** with NaOMe/MeOH in CH_2Cl_2 afforded **2** in quantitative yield (Scheme 4). The ^1H NMR spectrum of **2**, showed signals corresponding to H-1′ (δ 5.04 and 5.00) of both anomers, which correlated with signals at 104.3 and 105.4 ppm in the HSQC experiment. The broad singlets at δ 4.74 (H-1α) and 4.47 (H-1β) corresponding to the Man*p* unit, correlated with signals at 99.9 (C-1β) and 99.7 (C-1α) ppm. The assignment of the anomeric configuration in the Man*p* moiety was confirmed by a 2D NOESY experiment which showed cross peaks between H-1/ H-3 and H-1/H-5 for the β-anomer.



Scheme 4. Synthesis of 9-decenyl β-D-Gal*f*-(1→3)-D-Man*p* (**2**).

Since its development, the trichloroacetimidate glycosylation method has been widely used as it has the advantage of being mild enough to preserve other glycosidic linkages present in the acceptor or in the donor.[35] This aspect is particularly critical in the case of furanosyl units, due to their lability. Glycosyl iodides have long been underused as they were considered too reactive to be of synthetic utility. However, their use as glycosyl donors has been revalued over the past 15 years mainly due to the development of new methods of preparation.[36] Our studies on the glycosylation via the benzoylated galactofuranosyl iodide **13** confirm once more the versatility of glycosyl iodides as donors**.**

For the synthesis of **2** by the trichloroacetimidate approach compound **21** was obtained from **17** in three steps with the corresponding column chromatography purifications in 50% overall yield. The synthesis of **21** from **17** by means of the glycosyl iodide strategy involved two reaction steps and two column chromatography purifications, in 78% overall yield. Beyond the yield, the advantage of the iodide approach was that the sequence was shorter and the reaction times were significantly reduced. On the other hand, in the synthesis of **2** via a mannosyl iodide, we demonstrated that a β-D-Gal*f* unit in the glycosyl donor resists the glycosylation, without degradation.

1. Experimental section

1.1. General synthetic methods

Analytical thin layer chromatography (TLC) was performed on Silica Gel 60 F254 (Merck) aluminum supported plates (layer thickness 0.2 mm) with solvent systems given in the text. Visualization of the spots was effected by exposure to UV light and charring with a solution of 10% (v/v) sulfuric acid in EtOH, containing 0.5% *p*-anisaldehyde. Column chromatography was carried out with Silica Gel 60 (230–400 mesh, Merck). Optical rotations were measured with a Perkin–Elmer 343 digital polarimeter. Nuclear magnetic resonance (NMR) spectra were recorded with a Bruker AMX 500 spectrometer. Assignments of ^{1}H and ^{13}C were assisted by 2D ^{1}H-COSY and HSQC experiments. High resolution mass spectra (HRMS ESI$^+$) were recorded in a Bruker micrOTOF-Q II spectrometer.

1.2. 9-Decenyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyanoside (8)

A suspension of **5** (0.1 g, 0.25 mmol) and ZnI_2 (0.4 equiv, 0.032 g, 0.1 mmol) in anhydrous CH_2Cl_2 (10.0 mL) was stirred under argon atmosphere at 0 °C for 15 min. TMSI (1.5 equiv, 50.0 μL, 0.375 mmol) was slowly added and the stirring was continued for another 15 min. The suspension was allowed to reach room temperature and then heated at 45 °C. After 30 min of stirring TLC analysis showed total consumption of the starting material (R_f = 0.36, 1:1 hexane/EtOAc) and a single spot of R_f = 0.52 (1:1 hexane/EtOAc). Powdered molecular sieves 4 Å and 9-decen-1-ol (0.14 mL, 0.75 mmol, 3.0 equiv) were added. After 3 h of stirring at 45 °C and 18 h at room temperature, the solution was diluted with CH_2Cl_2 (250 mL), washed with $NaHCO_3$ (ss) (2 × 140 mL) and water (3 × 100 mL), dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography (3:1→3:2 hexane/EtOAc) affording syrupy compound **8** (0.056 g, 46%), R_f = 0.70 (1:1 hexane/EtOAc), $[\alpha]_D$ +38.4 (*c* 0.9, $CHCl_3$). Lit.:[27] $[\alpha]_D$ +40 (*c* 1, $CHCl_3$). Fractions of R_f = 0.34 (1:1 hexane/EtOAc) were reacetylated affording **195** in 80% overall yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.80 (m, 1H, C*H*=CH_2), 5.34 (dd, *J* = 3.4, 10.0 Hz, 1H, H-3, 5.26 (at, *J* = 10.0 Hz, 1H, H-4), 5.22 (dd, *J* = 1.7, 3.4 Hz, 1H, H-2), 4.96 (m, 1H, CH=CH_aH), 4.92 (m, 1H, CH=CHH_b), 4.79 (d, *J* = 1.7 Hz, 1H, H-1), 4.27 (dd, *J* = 5.3, 12.2 Hz, 1H, H-6), 4.09 (dd, *J* = 2.3, 12.2 Hz, 1H, H-6′), 3.97 (ddd, *J* = 2.3, 5.2, 10.0 Hz, 1H, H-5), 3.67 (m, 1H, OCH_aH), 3.43 (dt, *J* = 6.6, 9.6 Hz, 1H, OCHH_b), 2.14, 2.09, 2.03, 1.98, (4s, $COCH_3$), 1.58 (CH_2), 1.28 (CH_2). ^{13}C NMR ($CDCl_3$, 125,8 MHz) δ 170.6, 170.1, 169.9, 169.7 (*C*OCH_3), 139.1

(*C*H=CH_2), 114.1 (CH=*C*H_2), 97.5 (C-1), 69.7 (C-2), 69.1 (C-3), 68.5 (OCH_2), 68.3 (C-5), 66.2 (C-4), 63.0 (OCH_2), 62.5 (C-6), 33.7, 32.7, 29.3, 29.2, 29.0, 28.8, 26.0 (CH_2), 20.9, 20.72, 20.67 × 2 ($COCH_3$). ^{1}H NMR data match with data reported in the lit.[27] HRMS (ESI) *m*/*z* calcd for $C_{24}H_{38}NaO_{10}$ [M+Na]$^+$: 509.2357. Found: 509.2376.

1.3. 9-Decenyl α-D-mannopyranoside (3)

To a solution of **8** (0.05 g, 0.1 mmol) in anhydrous 2:1 CH_2Cl_2/MeOH (10 mL) at 0 °C, 1.3 M NaOMe/MeOH (0.5 mL) was added. After 1 h of stirring at 0 °C, the mixture was concentrated to 3 mL and deionized by elution with MeOH through a column of strongly acidic cation exchange resin (H^+). The eluate was evaporated under reduced pressure to afford compound **3** (0.032 g, 99%) as a syrup, R_f = 0.65 (7:1:2 *n*PrOH/NH_3/H_2O), $[\alpha]_D$ +50 (*c* 0.9, MeOH). Lit.:[27] $[\alpha]_D$ +56 (*c* 0.5, MeOH). ^{1}H NMR (CD_3OD, 500 MHz) δ 5.81 (ddt, *J* = 6.8, 10.2, 13.9 Hz, 1H, C*H*=CH_2), 4.98 (ddt, *J* = 1.6, 2.2, 17.1 Hz, 1H, CH=CH_aH), 4.91 (ddt, *J* = 1.2, 2.3, 10.2 Hz, 1H, CH=CHH_b), 4.73 (d, *J* = 1.6 Hz, 1H, H-1), 3.82 (dd, *J* = 2.4, 11.8 Hz, 1H, H-6), 3.78 (dd, *J* = 1.7, 3.4 Hz, 1H, H-2), 3.73 (dt, *J* = 6.7, 9.6 Hz, 1H, OCH_aH partially overlapped with H-6′), 3.71 (dd, *J* = 5.8, 11.8 Hz, 1H, H-6′), 3.69 (dd, *J* = 3.4, 9.2 Hz, 1H, H-3), 3.61 (at, *J* = 9.5 Hz, 1H, H-4), 3.52 (ddd, *J* = 2.4, 5.8, 9.6 Hz, 1H, H-5), 3.41 (dt, *J* = 6.3, 9.7 Hz, 1H, OCHH_b), 2.08–1.27 (CH_2). ^{13}C NMR (CD_3OD, 125.8 MHz) δ 140.1 (*C*H=CH_2), 114.7 (CH=*C*H_2), 101.5 (C-1), 74.5 (C-5), 72.7 (C-3), 72.3 (C-2), 68.63 (OCH2), 68.56 (C-4), 62.9 (C-6), 34.9, 30.6, 30.53, 30.50, 30.2, 30.1, 27.3 (CH_2). ^{13}C NMR data match with data reported in the lit.[27] HRMS (ESI) *m*/*z* calcd for $C_{16}H_{30}NaO_6$ [M+Na]$^+$: 341.19346. Found: 341.19476.

1.4. 9-Decenyl 2,3,5,6-tetra-*O*-*tert*-butyldimethylsilyl-α,β-D-galactofuranoside (14)

A solution of **9** (0.20 g, 0.26 mmol) in anhydrous CH_2Cl_2 (10.0 mL) containing dry 4 Å powdered molecular sieves was cooled to 0 °C and stirred for 10 min under Ar. Then, TMSI (1.2 equiv, 0.042 mL, 0.32 mmol) was added and the solution was stirred at 0 °C until TLC monitoring showed complete transformation of **9** into two lower moving products, the 1-iodo intermediate **12** (R_f = 0.70, 10:1 hexane/EtOAc) and some 2,3,5,6-tetra-*O*-TBS-α,β-D-galactofuranose (R_f = 0.54), formed as a result of the hydrolysis of **12** on the silica gel plate.[16] 9-Decen-1-ol (1.3 equiv, 0.34 mmol, 0.061 mL) and EtN(*i*Pr)$_2$ (0.054 mL, 0.32 mmol), were added by syringe. After stirring at room temperature for 2 h the solution was diluted with CH_2Cl_2 (250 mL), washed with $NaHCO_3$ (ss) (2 × 140 mL) and water (3 × 100 mL), dried (Na_2SO_4), and concentrated. The syrup obtained was purified by column chromatography (99.7:0.3→99.5:0.5 hexane/EtOAc) affording syrupy compound **14** (0.167 g, 83%) as an inseparable βα mixture in a 3:1 ratio, which gave R_f = 0.40 (7:0.1 hexane/EtOAc twice developed), $[\alpha]_D$ −11.7 (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.81 (m, 1.29H, C*H*=CH_2α,β), 4.99 (m, 1.29H, CH=CH_aHα,β), 4.92 (m, 1.29H, CH=CHH_bα,β), 4.84 (d, *J* = 4.2 Hz, 0.36H, H-1α), 4.79 (d, *J* = 2.6 Hz, 1H, H-1β), 4.20 (apparent t, *J* = 5.0 Hz, 0.36 H, H-3α), 4.13 (dd, *J* = 3.6, 6.0 Hz, 1H, H-3β), 3.98 (dd, *J* = 2.5, 3.5 Hz, 1H, H-2β), 3.94 (dd, *J* = 2.5, 6.0 Hz, 1H, H-4β), 3.90 (dd, *J* = 4.0, 5.2 Hz, 0.36H, H-2α), 3.75 (m, 2.3H, H-5β, H-4α, H-5α, OCH_aHα), 3.67 (m, 2.6H, H-6α,β, OCH_aHβ), 3.57 (m, 1.43H, H-6′α,β), 3.35 (dt, *J* = 6.7, 9.6 Hz, 1H, OCHH_bβ), 3.28 (m, 0.32H, OCHH_bα), 2.04–1.28 (CH_2α,β), 0.91–0.87 ($SiC(CH_3)_3$), 0.11–0.05 ($Si(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 139.2 (2C, *C*H=CH_2α,β), 114.1 (2C, CH=*C*H_2α,β), 108.0 (C-1β), 102.2 (C-1α), 84.7 (C-2β), 83.8 (C-4β), 79.5 (C-3β), 78.8 (C-2α), 76.4 (C-3α), 73.5 (C-5α), 73.3 (C-5β), 68.7 (OCH_2α), 68.0 (OCH_2β), 65.2 (C-6α), 64.5 (C-6β), 33.8, 29.7, 29.6, 29.5, 29.44, 29.42, 29.1, 29.08, 28.94, 28.92 (CH_2), 26.2–25.7 ($SiC(CH_3)_3$), 18.4–17.8 ($SiC(CH_3)_3$), −3.5–(−5.4) ($Si(CH_3)_2$). HRMS (ESI) *m*/*z* calcd for $C_{40}H_{86}NaO_6Si_4$ [M+Na]$^+$: 797.53937. Found: 797.54188.

1.5. 9-Decenyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranoside (16)

A suspension of **11** (0.20 g, 0.31 mmol) in anhydrous CH_2Cl_2 (10.0 mL) containing dry 4 Å powdered molecular sieves was cooled to 0 °C and stirred for 10 min under Ar. TMSI (1.2 equiv, 0.048 mL, 0.37 mmol) and ZnI_2 (0.6 equiv, 0.059 g, 0.18 mmol) were added and the stirring was continued at 0 °C for 15 min and then the suspension was allowed to reach room temperature. After 0.5 h TLC monitoring showed complete transformation of **11** (R_f = 0.61, 9:1 toluene/EtOAc) into a lower moving product (R_f = 0.27), presumably 2,3,5,6-tetra-*O*-benzoyl-D-Gal*f*. 9-Decen-1-ol (1.3 equiv, 0.40 mmol, 0.072 mL) was added and the stirring was continued for 1 h. Then, the suspension was filtered and the filtrate was diluted with CH_2Cl_2 (250 mL), washed with $NaHCO_3$ (ss) (2 × 140 mL) and water (3 × 100 mL), dried (Na_2SO_4), and concentrated. After purification by column chromatography (95:5 toluene/EtOAc) fractions of R_f = 0.67 (9:1 toluene/EtOAc) afforded syrupy compound **16** (0.15 g, 66%), $[\alpha]_D$ +10.3 (*c* 1.2, $CHCl_3$). For the β anomer: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.16–7.21 (aromatic), 6.08 (m, 1H, H-5), 5.81 (m, 1H, C*H*=CH_2), 5.63 (d, *J* = 5.2 Hz, 1H, H-3), 5.47 (s, 1H, H-2), 5.30 (s, 1H, H-1), 5.01–4.90 (m, 2H, CH=CH_2), 4.79–4.72 (m, 2H, H-6,6′), 4.64 (m, 1H, H-4), 3.75 (m, 1H, OCH_aH), 3.54 (m, 1H, OCHH_b), 1.72–1.57 (CH_2), 1.51–1.47 (CH_2), 1.41–1.22 (CH_2). ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 166.1, 165.7, 165.6, 165.4 (*C*OPh), 139.1 (*C*H=CH_2), 133.42, 133.40, 133.29, 133.28, 133.2, 133.04, 133.03 (C-aromatic), 114.1 (CH=*C*H_2), 105.6 (C-1), 82.0 (C-2), 81.2 (C-4), 77.6 (C-3), 70.3 (C-5), 67.6 (OCH_2), 63.5 (C-6), 40.3, 33.7, 29.3, 29.04, 29.02, 28.9, 26.6 (CH_2). HRMS (ESI) *m*/*z* calcd for $C_{44}H_{46}NaO_{10}$ [M+Na]$^+$: 757.2983. Found: 757.2999.

1.6. 9-Decenyl α,β-D-galactofuranoside (4)

1.6.1. From 14

To a solution of compound **14** (0.077 g, 0.1 mmol) in freshly distilled THF (10.0 mL) cooled at 0 °C, TBAF (0.209 g, 0.8 mmol) was added.[18] The stirring was continued for 10 min at 0 °C and then at room temperature for 1 h. The solution was evaporated and the residue was purified by column chromatography (EtOAc). Fractions of R_f = 0.85 (7:1:2 *n*PrOH/NH_3/H_2O) gave compound **4** (0.028 g, 87%) as β/α mixture in a 3:1 ratio, $[\alpha]_D$ −34.3 (*c* 0.8, CH_3OH). ^{1}H NMR (CD_3OD, 500 MHz) δ 5.81 (ddt, *J* = 6.7, 10.3, 17.1 Hz, 1.23H, C*H*=CH_2α,β), 4.98 (m, 2H, CH=CH_2β), 4.91 (m, 0.89H, CH=CH_2α), 4.85–4.83 (m, 1.44H, H-1α,β), 4.08 (at, *J* = 7.3 Hz, 0.44H, H-3α), 4.00 (dd, *J* = 4.0, 6.7 Hz, 1H, H-3β), 3.94 (m, 0.44H, H-2α), 3.93 (dd, *J* = 2.0, 4.0 Hz, 1H, H-2β), 3.91 (dd, *J* = 3.3, 6.7 Hz, 1H, H-4β), 3.80 (dt, *J* = 6.9, 9.6 Hz, 0.44H, OCH_aHα), 3.74–3.67 (m, 2.44H, H-4α, H-5β, OCH_aHβ), 3.65–3.58 (m, 2.88H, H-5α, H-6α, H-6β, H-6′β), 3.55 (m, 0.44H, H-6′α), 3.46 (dt, *J* = 6.7, 9.4 Hz, 0.44H, OCHH_bα), 3.41 (dt, *J* = 6.6, 9.6 Hz, 1H, OCHH_bβ), 2.08–1.27 (7 CH_2). ^{13}C NMR (CD_3OD, 125.8 MHz) δ 140.1 (*C*H=CH_2), 114.7 (CH=*C*H_2), 109.4 (C-1β), 102.8 (C-1α), 84.1 (C-4β), 83.5 (C-4α), 83.4 (C-2β), 78.9 (C-2α), 78.7 (C-3β), 76.4 (C-3α), 74.5 (C-5α), 72.4 (C-5β), 69.7 (OCH_2α), 68.9 (OCH_2β), 64.6 (C-6β), 64.2 (C-6α), 34.9, 30.7, 30.6, 30.55, 30.49, 30.2, 30.1, 27.2 (CH_2). HRMS (ESI) *m*/*z* calcd for $C_{16}H_{30}NaO_6$ [M+Na]$^+$: 341.19346. Found: 341.19470.

1.6.2. From 16

To a solution of compound **16** (0.073 g, 0.1 mmol) in anhydrous 3:2 CH_2Cl_2/MeOH (10 mL) at 0 °C, 1.3 M NaOMe/MeOH (0.4 mL)

was added. After 1 h of stirring at 0 °C, the mixture was concentrated to 4 mL and deionized by elution with MeOH through a column of strongly acidic cation exchange resin (H^+). The eluate was evaporated under reduced pressure to afford compound **4** (0.030 g, 94%) as a syrup, R_f = 0.9 (7:1:2 *n*PrOH/NH_3/H_2O), $[\alpha]_D$ −25.6 (*c* 1.1, MeOH). The NMR spectra showed that compound **4** was a mixture of anomers in 9:1 ratio.

1.7. 1,2,4,6-Tetra-*O*-acetyl-3-*O*-(2,3,5,6-tetra-*O*-acetyl-β-D-galactofuranosyl)-α,β-D-mannopyranose (17)

To a solution of **1** (1.43 g, 4.19 mmol)[19] in dry pyridine (10 mL) cooled at 0 °C, Ac_2O (4.74 mL, 50.26 mmol) was added dropwise, and the mixture was stirred overnight at 5 °C. After cooling to 0 °C, the reaction was quenched by slow addition of water (0.5 mL) and the stirring continued for 30 min at room temperature. The solution was diluted with CH_2Cl_2 (250 mL) and then successively washed with HCl 10% (150 mL), $NaHCO_3$ ss (150 mL), and water (3 × 150 mL). The organic layer was dried (Na_2SO_4), filtered, and then concentrated under reduced pressure. Purification of the crude mixture by column chromatography (8:1 →1:1 hexane/EtOAc) afforded compound **17** (2.13 g, 75%) as an anomeric mixture in 2:1 α/β ratio, R_f = 0.55 (1:3 hexane/EtOAc), $[\alpha]_D$ −20.1 (*c* 0.9, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.09 (d, 1H, *J* = 2.0 Hz, H-1α), 5.80 (d, 0.4H, *J* = 1.2 Hz, H-1β), 5.51 (dd, 0.4H, *J* = 1.2, 3.7 Hz, H-2β), 5.40–5.33 (m, 1.4H, H-5′α,β), 5.29 (m, 1H, H-2α), 5.27–5.17 (m, 1.4H, H-4α,β), 5.14 (s, 1H, H-1′α), 5.11 (s, 0.4H, H-1′β), 4.97–4.95 (m, 2.8H, H-2′α,β, H-3′α,β), 4.39 (dd, 1H, *J* = 4.5, 11.6 Hz, H-6′aα), 4.37–4.25 (m, 1.8H, H-6aα,β, H-6′aβ), 4.20–4.12 (m, 4.2H, H-4′α,β, H-6′bα,β, H-6bβ, H-3α), 4.09 (dd, 1H, *J* = 2.5, 12.2 Hz, H-6bα), 4.03–3.97 (m, 1.4H, H-3β, H-5α), 3.77–3.73 (m, 0.4H, H-5β), 2.17–2.05 (*CH*$_3$CO). ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 170.7, 170.4, 170.3, 169.96, 169.9, 169.2, 169.1, 169.06, 169.03 (CH_3CO), 102.5 (C-1′α), 102.2 (C-1′β), 90.9 (C-1α), 90.8 (C-1β), 80.8, 80.7 (C-2′α,β), 80.6 (2C, C-4′α,β), 76.4 (2C, C-3′α,β), 73.4 (C-5β), 72.3 (C-3β), 70.6 (C-5α), 70.5 (C-3α), 69.3 (2C, C-5′α,β), 66.0 (C-2α), 65.9 (2C, C-4α,β), 65.8 (C-2β), 62.5 (2C, C-6′α,β), 62.2 (2C, C-6α,β), 20.9, 20.8, 20.79, 20.77, 20.73, 20.71, 20.67, 20.66, 20.5 (*C*H_3CO). HRMS (ESI) calcd for $C_{28}H_{38}NaO_{19}$ $[M+Na]^+$: 701.1900. Found 701.1897.

1.8. 2,4,6-Tri-*O*-acetyl-3-*O*-(2,3,5,6-tetra-*O*-acetyl-β-D-galactofuranosyl)-α-D-mannopyranose (18)

To a stirred solution of ethylendiamine (0.025 mL, 0.38 mmol) in THF (5 mL) cooled to 0 °C glacial acetic acid (0.025 mL, 0.46 mmol) was added dropwise. Immediately, this mixture was transferred to a flask containing compound **17** (0.23 g, 0.34 mmol) and the solution was stirred for 21 h at room temperature. The mixture was diluted with CH_2Cl_2 (50 mL), washed with 5% HCl (30 mL), $NaHCO_3$ ss (30 mL), and water (3 × 30 mL). The organic layer was dried (Na_2SO_4), filtered, and evaporated under reduced pressure. Purification by column chromatography (2:3 hexane/EtOAc) gave compound **18** in 84% yield (0.17 g), R_f = 0.28 (1:3 hexane/EtOAc), $[\alpha]_D$ −12.7 (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.35 (dt, 1H, *J* = 2.9, 4.1 Hz, H-5′), 5.30 (dd, 1H, *J* = 1.9, 3.5 Hz, H-2), 5.23 (s, 1H, H-1), 5.21 (at, *J* = 9.9 Hz, 1H, H-4), 5.12 (s, 1H, H-1′), 4.96–4.93 (m, 2H, H-2′, H-3′), 4.33 (dd, 1H, *J* = 4.2, 11.9 Hz, H-6′a), 4.25–4.08 (m, 6H, H-3, H-6a, H-6′b, H-4′, H-5, H-6b). ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 170.8, 170.5, 170.3, 169.9, 169.3, 169.28, 169.25 (CH_3CO), 102.2 (C-1′), 92.4 (C-1), 80.8 (C-2′), 80.5 (C-4′), 76.5 (C-3′), 70.3 (C-3), 69.3 (C-5′), 68.5 (C-5), 67.5 (C-2), 66.6 (C-4), 62.6, 62.5 (C-6, C-6′), 20.9, 20.79, 20.76, 20.75, 20.7, 20.5 (*C*H_3CO). HRMS (ESI) calcd for $C_{26}H_{36}NaO_{18}$ [M+Na] 659.1794. Found 659.1776.

1.9. 9-Decenyl 2,4,6-tri-*O*-acetyl-3-*O*-(2,3,5,6-tetra-*O*-acetyl-β-D-galactofuranosyl)-α,β-D-mannopyranoside (21)

1.9.1. Trichloroacetimidate method

To a stirred solution of **18** (0.16 g, 0.25 mmol) and trichloroacetonitrile (0.174 mL, 1.75 mmol) in anhydrous CH_2Cl_2 (15 mL) cooled to 0 °C, DBU (15.5 μL, 0.1 mmol) was slowly added. After 1 h, the solution was carefully concentrated under reduced pressure, and the residue was purified by column chromatography (2:3 hexane/EtOAc) to give 0.163 g (83.4%) of the trichloroacetimidate of **20** as a syrup, R_f = 0.63 (1:3 hexane/EtOAc). A stirred suspension of **20** (163 mg, 0.208 mmol), 9-decen-1-ol (55 μL, 0.313 mmol), and 4 Å powdered molecular sieves (0.5 g) in anhydrous CH_2Cl_2 (15 mL) was cooled to −78 °C, and TMSOTf (11.3 μL, 0.062 mmol) was slowly added. After 48 h of stirring at room temperature, the mixture was quenched by addition of $NaHCO_3$ ss (10 mL) and then extracted with CH_2Cl_2. Purification by column chromatography (2:1→1:1 hexane/EtOAc), afforded syrupy **21** (0.11 g, 72%) as an anomeric mixture in 2:3 α/β ratio, R_f = 0.58 (1:3 hexane/EtOAc), $[\alpha]_D$ −31.9 (*c* 1.2, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.79 (m, 2.5H, C*H*=CH_2α,β), 5.38–5.34 (m, 2.5H, H-5′α,β), 5.30 (at, *J* = 8.5 Hz, 1.5H, H-4β), 5.28 dd, *J* = 9.0, 10.0 Hz, 1H, H-4α), 5.19 (s, 1.5H, H-1′β), 5.13 (s, 1H, H-1′α), 5.06 (dd, *J* = 2.1, 6.1 Hz, 1H, H-3′α), 5.02–4.99 (m, 4.5H, H-2′β, CH=C*H*$_a$Hβ, H-3′β, 4.97 (m, 1H, CH=C*H*$_a$Hα), 4.94 (dd, *J* = 0.6, 2.3 Hz, 1H, H-2′α, 4.93 (m, 1H, CH=CH*H*$_b$α), 4.92–4.90 (m, 2.5H, CH=CH*H*$_b$β, H-1α), 4.52 (d, *J* = 1.3 Hz, 1.5H, H-1β), 4.37–4.15 (m, 11.5H, H-6′aα,β, H-6aα,β, H-4′α,β, H-6′bα,β, H-6bβ), 4.11 (dd, *J* = 1.4, 3.1 Hz, 1.5H, H-2β), 4.08 (dd, *J* = 2.4, 12.3 Hz, 1H, H-6bα), 4.04–4.00 (m, 2H, H-2α, H-3α), 3.91 (dt, *J* = 6.8, 9.5 Hz, 1.5H, OC*H*$_a$Hβ), 3.87 (ddd, *J* = 2.8, 5.3, 10.3 Hz, 1H, H-5α), 3.82 (dd, *J* = 3.1, 9.0 Hz, 1.5H, H-3β), 3.65 (dt, *J* = 6.8, 9.8 Hz, 1H, OC*H*$_a$Hα), 3.59 (m, 1.5H, H-5β), 3.50 (dt, *J* = 6.8, 9.5 Hz,1.5H, OCH*H*$_b$β), 3.42 (dt, *J* = 6.8, 9.8 Hz, 1H, OCH*H*$_b$α), 2.13–2.06 (*CH*$_3$CO, CH_2), 1.64–1.54 (CH_2), 1.40–1.27 (CH_2). ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 170.88, 170.84, 170.5, 170.4, 170.0, 169.99, 169.97, 169.7, 169.4, 169.1 (CH_3CO), 139.2 (2C, *C*H=CH_2α,β), 114.2, 114.1 (CH=CH_2α,β), 102.7 (C-1′β), 102.5 (C-1′α), 99.6 (C-1β), 99.2 (C-1α), 82.4 (C-2′α), 81.6 (C-2′β), 80.5 (C-4′β), 80.1 (C-4′α), 76.1 (C-3′β), 75.7 (C-3′α), 75.0 (C-3β, 74.5 (C-3α), 72.2 (C-5β), 70.1 (OCH_2), 69.28, 69.27 (C-5′α,β), 68.3 (C-5α), 68.1 (OCH_2), 67.3 (C-2α), 66.9 (C-4β), 66.8 (C-2β), 66.4 (C-4α), 62.8 (C-6′α), 62.7 (C-6α), 62.6 (C-6β), 62.4 (C-6′β), 33.8–25.9 (CH_2), 20.9–20.6 (*C*H_3CO).

1.9.2. Glycosyl iodide method

A suspension of **17** (0.050 g, 0.074 mmol) and ZnI_2 (0.038 g, 0.12 mmol) in anhydrous CH_2Cl_2 (10.0 mL) was stirred at 0 °C under argon atmosphere. After 15 min TMSI (35 μL, 0.26 mmol) was slowly added and the reaction was allowed to reach room temperature. After 30 min of stirring at 45 °C TLC analysis showed total consumption of starting material (R_f = 0.51, 1:3 hexane/EtOAc) and a new compound of R_f = 0.64 (1:3 hexane/EtOAc), presumably **19**. Powdered molecular sieves 4 Å (0.5 g) and 9-decen-1-ol (0.04 mL, 0.22 mmol) were then added. After 17 h of stirring at room temperature the reaction mixture was diluted with CH_2Cl_2 (250 mL), washed with $NaHCO_3$ ss (2 × 140 mL), and H_2O (3 × 100 mL), dried (Na_2SO_4), and concentrated under reduced pressure. The syrup was purified by silica gel column chromatography (2:1→1:1 hexane/EtOAc) and fractions of R_f = 0.59 (1:3 hexane/EtOAc) afforded compound **21** (0.034 g, 61%). By reacetylation of the partial deprotected products formed during the purification by column chromatography the yield was improved (78%).

1.10. 9-Decenyl 3-*O*-(β-D-galactofuranosyl)-α,β-D-mannopyranoside (2)

To a solution of **21** (0.05 g, 0.064 mmol) in 2:1 anhydrous CH_2Cl_2/MeOH (6 mL) stirred at 0 °C, 1.3 M NaOMe/MeOH (0.75 mL) was added. After 1 h the solution was deionized by elution with MeOH through a column of strongly acidic cation exchange resin (H^+). The eluate was evaporated and the residue was dissolved in water and further purified through a RP18 cartridge. Compound **2** (0.031 g, 100%) was obtained as a 2:3 αβ anomeric mixture, R_f = 0.62 (7:1:2 *n*PrOH/NH_3/H_2O), $[\alpha]_D$ −12.7 (*c* 1, MeOH). ^{1}H NMR (D_2O, 500 MHz) δ 5.68 (m, 2.5H, C*H*=CH_2α,β), 5.04 (s, 1.5H, H-1′β), 5.00 (s, 1H, H-1′α), 4.89 (dd, 2.5H, *J* = 6.5, 16.7 Hz, CH=CH_aHα,β), 4.82 (m, 2.5H, CH=CHH_bα,β), 4.74 (s, 1H, H-1α), 4.47 s, 1.5H, H-1β), 4.076 m, 1.5H, H-2′β), 4.05 (m, 2.5H, H-2′α, H-2β), 4.03–3.96 (m, 6H, H-3′α,β, H-4′α,β, H-2α, 3.81–3.66 (m, 11H, OCH_aHβ, H-5′α,β, H-6aα,β, H-6bα,β, H-3α, H-4α), 3.64–3.51 (m, 9H, OCH_aHα, H-6′aα,β, H-6′bα,β, H-3β, H-4β, 3.50–3.43 (m, 2.5H, OCHH_bβ, H-5α), 3.33 (m, 1H, OCHH_bα), 3.24 (m, 1.5H, H-5β), 1.98–1.88, 1.57–1.45, 1.34–1.13 (7CH_2). ^{13}C NMR (D_2O, 125.8 MHz) δ 139.0, 138.8 (CH=*C*H_2), 114.16, 114.15 (*C*H=CH_2), 105.4 (C-1′α), 104.3 (C-1′β), 99.9(C-1β), 99.7 (C-1α), 83.3 (C-4′α), 83.1 (C-4′β), 81.3 (C-2′β), 81.1 (C-2′α), 77.5 (C-3β), 77.1 (2C, C-3′α,β), 76.9 (C-3α),76.1 (C-5β), 72.5 (C-5α), 70.8, 70.7 (2C, C-5′α,β), 69.8 (O*C*H_2β), 67.7 (O*C*H_2α), 67.6 (C-2α), 67.3 (C-2β), 64.8 (C-4β), 64.6 (C-4α), 62.8 (2C, C-6′α,β), 60.9 (2C, C-6α,β), 33.7, 33.6 (*C*H_2CH=CH_2α,β), 29.4–25.7 (CH_2). HRMS (ESI) calcd for $C_{22}H_{41}O_{11}$ $[M+H]^+$ 481.26434. Found 481.26331.

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Supplementary data

Supplementary data associated with this article (^{1}H and ^{13}C NMR spectra for compounds **2-4**, **8**, **14-18** and **21**) can be found, in the online version, at http://dx.doi.org/10.1016/j.carres.2013.03.032.

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