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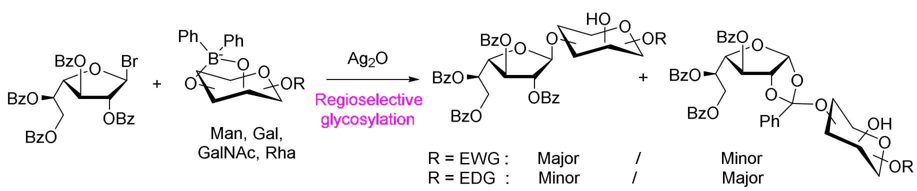


Abstract: Koenigs-Knorr glycosylation of acceptors with more than one free hydroxyl group by 2,3,5,6-tetrabenzoyl galactofuranosyl bromide was performed using diphenylborinic acid 2-aminoethyl ester (DPBA) as inducer of regioselectivity. High regioselectivity for the glycosylation on the equatorial hydroxyl group of the acceptor was obtained thanks to the transient formation of a borinate adduct of the corresponding 1,2-*cis* diol. Nevertheless formation of orthoester by-products hampered the efficiency of the method. Interestingly electron-withdrawing groups on *O*-6 or on *C*-1 of the acceptor displaced the reaction in favour of the desired galactofuranosyl containing disaccharide. The best yield was obtained for the furanosylation of *p*-nitrophenyl 6-*O*-acetyl mannopyranoside. Precursors of other disaccharides, found in the glycocalix of some pathogens, were synthesized according to the same protocol with yields ranging from 45 to 86%. This is a good alternative for the synthesis of biologically relevant glycoconjugates.

Introduction

The significant discoveries on the organization of the cell, either from prokaryote or eukaryote origin, have pointed out the key role of the glycocalix, the complex layer of hetero- and oligosaccharides that surrounds the cell wall.[1-4] Even if most cells use common sugars to build this glycocalix, they manage to differentiate from each other thanks to the infinite possibilities of sequence and the nature of the linkages involved. Intriguingly some microorganisms incorporate carbohydrates in their furanose form rather than in their pyranose one in order to further differentiate themselves from other organisms.[5,6] In particular D-galactofuranose (D-Gal*f*) containing glycoconjugates are found in large amount in pathogenic microorganisms like *Mycobacteria* or *Leishmania* but are absent in the mammalian kingdom.[7] Owing to the key role played by such motifs in the virulence or survival of the parasite or bacteria, numerous groups have developed evolved synthetic pathways to access to such Gal*f*-containing oligosaccharides.[8-13] Alternatively galactofuranosyl-transferases isolated from mycobacteria or furanosylhydrolases involved in the degradation of biomass have been used to obtain either oligomers of Gal*f*[14,15] or heterodisaccharides.[16,17] These last strategies involve a minimum of protecting group manipulation as biocatalysts are able to selectively transfer a furanosyl entity on a specific position of an acceptor.

Attempt to mimic such selectivity remains the grail for glycochemists. Already, regioselective glycosylation of naked acceptors could be performed thanks to transient selective activation of one hydroxyl group against the others using for example dibutyltin(IV) oxide[18,19] or aryl borinic acid[20,21] as inducers of regioselectivity. More recently, Taylor and coworkers developed new diarylborinic acid derivatives for the regioselective acylation,[22] alkylation[23] or tosylation[24] of the secondary alcohol of various alkyl glycosides. They postulated that diarylborinic acid could form tetracoordinate adducts with 1,3-diols and 1,2-*cis* diols thus increasing the nucleophilicity of either the primary hydroxyl group or the least hindered equatorial one. The methodology was recently extended to the glycosylation of thiophenyl mannopyranoside using D-arabinofuranosyl methanesulfonate as a donor.[25] It is the first example of the synthesis of furanosyl containing disaccharides obtained by this methodology and works remain to be done to apply such process to the synthesis of hexofuranosyl-containing conjugates.

After having proposed to work with unprotected thioimidates as donors,[26] we now report on the use of diphenylborinic acid 2-aminoethyl ester (DPBA) to induce regioselectivity for galactofuranosylation of various glycosidic acceptors: D-mannopyranosides (D-Man*p*), D-galactopyranoside (D-Gal*p*), *N*-acetyl-D-galactopyranoside (D-Gal*p*NAc), L-rhamnopyranoside (L-Rha*p*) and D-Gal*f*. The target compounds are disaccharidic parts of biomolecules anchored to the cell wall of pathogenic microorganisms (Figure 1).[5,6] Representative examples include β-(1→3) and (1→6)-D-Man*p* linkage found in *Aspergillus*, *Trypanosoma* or *Leishmania* sp.; β-(1→3)-D-Gal*p* or β-(1→3)-D-Gal*p*NAc linkage identified in *Bacteroides*, *Fibrobacter* or *Agelas sp.* for the first one or *Bacteroides* and *Shigella* for the second one; β-(1→4)-L-Rha*p* bond presented by *Mycobacterium*.[6,27] Wide ligation diversity was also established between two D-Gal*f* entities: β-(1→5) and β-(1→6) found in particular in *Mycobacterium tuberculosis*, *Cryphonectria parasitica* and *Aspergillus*.[28]

Some of these disaccharides linked the Gal*f* non-reducing end to the most nucleophilic equatorial oxygen of the sugar at the reducing end. This oxygen is in addition in a 1,2-*cis* configuration with one of the proximal hydroxyl group. Such glycosidic bonds could therefore be selectively obtained thanks to glycosylation in presence of diarylborinic inducer. First the conditions of glycosylation were optimized with mannopyranosidic acceptor using peracylated galactofuranosyl bromide as donor. Different groups were introduced on the acceptor either on the primary hydroxyl group or at the anomeric position in order to investigate the influence of the inductive effect on the glycosylation. An attempt of rationalization of the results was performed thanks to *ab initio* calculation. Finally the methodology was extended to the other relevant acceptors.

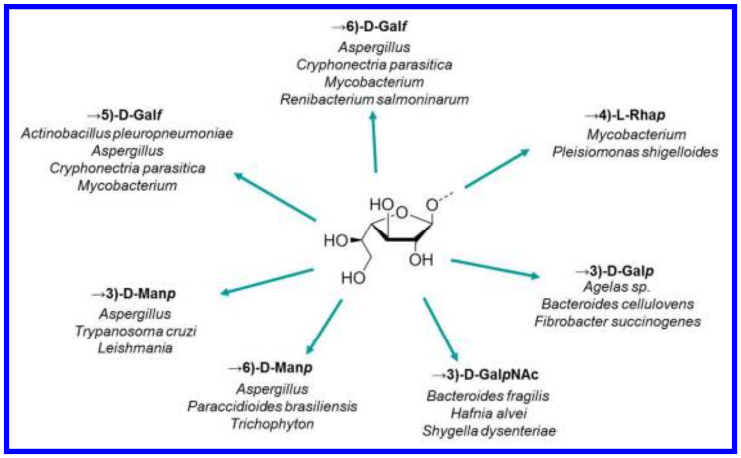


FIGURE 1. Natural occurrence of galactofuranose in some glycocalix of selected organisms.

Results and discussion

Our aim is to develop a regio- and stereoselective glycosylation to obtain Gal*f*-containing disaccharides. The conditions developed by Taylor[29] were first applied on a model reaction between various Gal*f* donors and Man*p* acceptors (Figure 2). Different activating groups were introduced from peracylated derivatives of galactofuranose, namely the bromide,[30] the thiophenyl[31] or the trichloroacetimidate[32] according to available protocols to give **1a**, **1b** and **1c** respectively. As for the acceptors, we decided to evaluate the influence of the protecting group on both positions *C*-1 and *O*-6. The primary position has to be masked anyway in order to avoid glycosylation at this position. Starting from commercially available *p*-nitrophenyl mannopyranoside (*p*NP Man*p*) **2a**, the electron-donating group *tert*-butyldimethylsilyl was first introduced on position *O*-6 by action of the corresponding silylating agent TBSCl in presence of imidazole and DMAP with a moderate 40% yield. The electron-withdrawing group acetyl on the other hand was added using vinyl acetate in THF in presence of the supported lipase from *Candida antartica* (CAL-B). This last strategy was also applied to the octyl and thiotolyl α-Man*p* **3a** and **3b** to obtain the corresponding 6-*O*Ac mannoside **4a** and **4b** with 89% and 69% yields respectively.

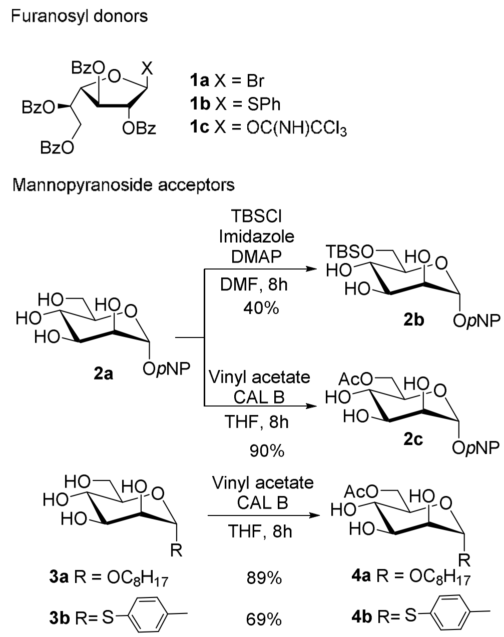


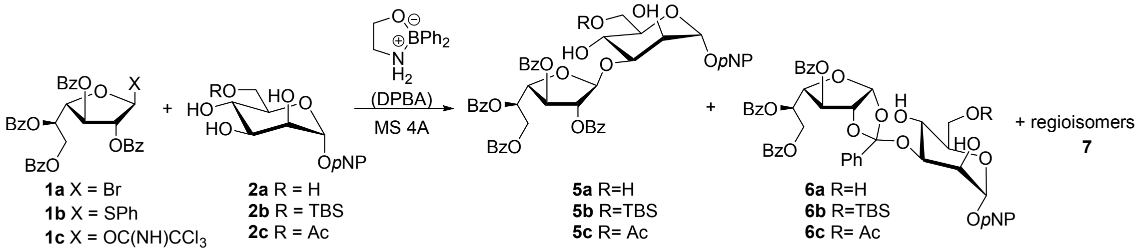
FIGURE 2. Building blocks used in the regioselective glycosylation.

With the donors **1** and acceptors **2** in hand, different attempts of glycosylation were implemented (Table 1). Following the findings of Taylor and coworkers, a catalytic amount of diphenylborinic acid 2-aminoethyl ester (DPBA) was used first (Entries 1, 3 to 7). The reactions proceeded in acetonitrile in presence of molecular sieves 4Å in order to limit the hydrolysis of the donors **1**. These donors were used also in excess in the case where the hydrolysis is too high. With TBS Man*p* **2b** as acceptor and bromide **1a** as donor, the reaction proceeded quickly in presence of both silver oxide and the borinic acid to give the target disaccharide **5b** in 36% yield (Entry 1). It was unambiguously characterized thanks to ^{1}H and ^{13}C NMR spectroscopy. The isolated disaccharide presented an anomeric proton at 5.55 ppm associated with a carbon at 103.8 ppm. Coupling constant $J_{H1,H2}$ was almost zero, a typical value for an anomeric proton of a furanoside in 1,2-*trans* configuration. The regioisomery of the disaccharide was further confirmed by 2D-NMR HMBC experiments. A long range correlation between C_{Galf}-1 and H_{Manp}-3 indicated a (1→3)-glycosidic bond. The other product of the reaction, and the major one, was identified as the orthoester **6b**. It showed a characteristic signal in ^{1}H NMR at 6.47 ppm associated with a carbon at 105.3 ppm. The related coupling constant $J_{H1,H2}$ reached 4.4 Hz thus indicating a 1,2-*cis* configuration. In addition ^{13}C NMR showed a carbon at 123.3 ppm assigned to the quaternary carbon of the orthoester function.

For comparative purpose, we tested the absence of DPBA (Entry 2) or of TBS on the primary hydroxyl group of the acceptor (Entry 3). Both conditions led to a complex mixture of products. As expected when no borinic acid was added the glycosylation occurred on different positions of the acceptor and the disaccharide **5b** was isolated in only 10% yield. Also no protecting group on *O*-6 resulted in the concomitant glycosylation of both positions 3 and 6, the two positions that were activated by the inducers of regioselectivity.[29] In these conditions only trisaccharide 3,6-di-*O*-(β-D-Gal*f*)-D-Man*p* could be isolated.

Then we tried to isomerize the orthoester **6b** into **5a** by heating the reaction media or by the addition of a Lewis acid but only the degradation of the orthoester occurred. Alternatively another halogenophile, the silver triflate was used as promoter as it is known to avoid orthoester formation. However in these acidic conditions, the TBS group has been cleaved and again the trisaccharide 3,6-di-*O*-(β-D-Gal*f*)-D-Man*p* was obtained. Therefore the silyl group was swapped by an acetyl one. After reaction between **1a** and **2c** (Entry 4), the major product remained the orthoester **6c** and **5c** was obtained only in 19% yield. As the acetyl group is tolerant to acidic condition, silver triflate was this time used successfully as promoter (Entry 5). It allowed to access to **5c** with a better yield and no orthoester was isolated. However other regioisomers, the *p*NP β-D-Gal*f*-(1→2)-D-Man*p* and *p*NP β-D-Gal*f*-(1→4)-D-Man*p* were formed as well. It confirms that acidic conditions are detrimental to the formation of the borinate complex.[24] Finally, when other Gal*f* donors **1b** and **1c** were used (Entries 6 and 7), the yield did not improve and the regioselectivity was poorer as previously reported.[29]

TABLE 1. Optimization of the conditions for the regioselective galactofuranosylation of *p*NP Man*p* derivatives.



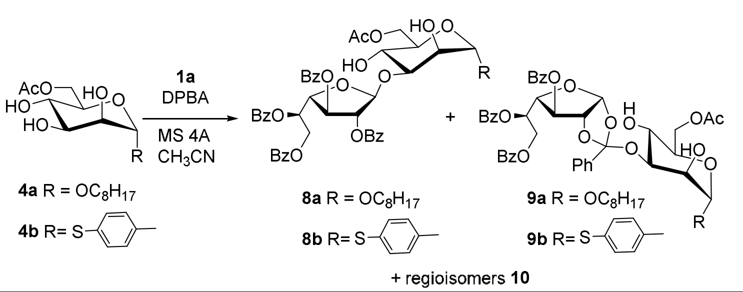
Entry	Donor (2 eq.)	Acceptor (1 eq.)	Promoter (1 eq.)	DPBA (eq.)	Solvent	Time (h)	**5** (Yield %)	Ratio **5**:**6**:**7**
1	**1a**	**2b**	Ag_2O	0.1	CH_3CN	2	**5b** (36)	5:6:0
2	**1a**	**2b**	Ag_2O	-	CH_3CN	28	**5b** (10)	Mixture
3	**1a**	**2a**	Ag_2O	0.1	CH_3CN	2	**-**	Trisac-charide[a]
4	**1a**	**2c**	Ag_2O	0.1	CH_3CN	19	**5c** (19)	1:2.4:0
5	**1a**	**2c**	AgOTf	0.1	CH_3CN	19	**5c** (33)	13:0:2[b]
6	**1b**	**2c**	NIS, AgOTf	0.1	CH_3CN	19	-	-
7	**1c**	**2c**	TMSOTf	0.1	CH_3CN	19	**5c** (25)	8:0:2[c]
8	**1a**	**2b**	Ag_2O	1	CH_3CN	6	**5b** (46)	7:3:0
9	**1a**	**2b**	Ag_2O	1	CH_2Cl_2	8	**5b** (40)	1:0:0
10	**1a**	**2b**	Ag_2O	1	THF	8	**5b** (25)	1:1:0
11	**1a**	**2c**	Ag_2O	1	CH_3CN	2	**5c** (85)	1:0:0
12	**1a**	**2c**	AgOTf	1	CH_3CN	19	**5c** (80)	1:0:tr[c]

[a] Mainly *p*NP 3,6-di-O-(β-D-Gal*f*)-D-Man*p*. [b] Mainly *p*NP β-D-Gal*f*-(1→2)-D-Man*p* and *p*NP β-D-Gal*f*-(1→4)-D-Man*p*. [c] Mainly *p*NP β-D-Gal*f*-(1→4)-D-Man*p*

Interestingly, when a stoichiometric amount of DPBA was used, the yield greatly improved and no or trace amount of orthoester was formed (Entries 8 to 12). In addition the use of alternative solvents like THF or dichloromethane decreased either the yields or the selectivity (Entries 9 and 10). Also, the glycosylation of 6-*O*-TBS Man*p* **2b** proceeded with lower yields than with 6-*O*-Ac Man*p* **2c**, and a higher amount of orthoester **6b** was isolated (Entries 8 *vs.* 11). As for the promoter, the acidic AgOTf can be used but trace amount of regioisomers (mainly β-(1→4)-) contaminated again the disaccharide **5c** (Entry 12). The best result was obtained using the bromide **1a** as donor, activated by one molar ratio of silver oxide, the 6-*O*-acetyl acceptor **2c**, DPBA (one equivalent), in acetonitrile. Under these conditions, the *p*NP β-D-Gal*f*-(1→3)-α-D-Man*p* compound **5c** was obtained in a quite worthy yield of 85% with no contamination by the orthoester (Entry 11).

Following this optimization, the methodology was then applied to 6-*O*-acetylated mannosidic acceptors **4a** and **4b** (Table 2) that differ on the nature of the substituent attached to the anomeric position. On one hand, the presence of the electron-donating group octyl at the anomeric position seemed to favour greatly the formation of the orthoester **9a** (Entry 1). Solely the use of silver trifluoromethanesulfonate instead of silver oxide allowed isolating the target compound **8a** with 57% yield (Entry 2). Once again, contamination by other regioisomers hampered the use of such acidic promoter. On the other hand, a completely different outcome arose with a thiotolyl group on *C*-1 of the mannose as the donor **1a** easily glycosylated the position 3 of the mannoside **4b.** Formation of the orthoester **9b** was low and no other regioisomers were isolated (Entry 3 and 4). It confirms the great influence of the electron-density of the substituent on both position *O*-6 and *C*-1.

TABLE 2. Extension to octyl and thiotolyl mannoside.



Entry	Acceptor	Promoter	Time (h)	Disaccharide (Yield %)	Ratio **8**:**9**:**10**
1	**4a**	Ag_2O	2	**8a** (40)	45:55:0
2	**4a**	AgOTf	5	**8a** (57)	4:0:1[a]
3	**4b**	Ag_2O	2	**8b** (96)	95:5:0
4	**4b**	AgOTf	6	**8b** (69)	1:0:0

[a] Mainly octyl β-D-Gal*f*-(1→4)-D-Man*p*.

To explain these results, we decided to compare the difference of reactivity of the tested acceptors **2b**, **2c**, **4a** and **4b** in complex with diphenylborinic acid using DFT calculation in the gas-phase (B3LYP/6-31+G*) (Table 3 and Supporting Information).

TABLE 3. Calculated Mulliken charges and Fukui indexes of diphenylborinate adduct of 2b, 2c, 4a and 4b (B3LYP/6-31+G*).

Entry	Mannoside acceptor	Mulliken charge at *O*-3	f_k at *O*-3
1	**2b**	-0.35	0.180
2	**2c**	-0.31	0.115
3	**4a**	-0.32	0.135
4	**4b**	-0.33	0.115

Surprisingly, the estimation of the Mulliken charges on the most reactive equatorial oxygen *O*-3 did not vary much between the different mannosides. Only the Fukui index f_k, a measure of the strength of the nucleophile,[33] decreased significantly with the presence of electron-withdrawing groups either on *O*-6 or on *C*-1. Interestingly, those molecules **2c** and **4b** also formed no or trace amount of orthoesters. On the contrary, electron-donating groups like the TBS (**2b**) or the alkyl (**4a**) one reinforced the nucleophilicity on *O*-3. Those acceptors generated after glycosylation the largest amount of orthoester. Orthoesters are known to form in various amounts during Koenigs-Knorr glycosylation.[34] According to Taylor *et al*'s work on pyranosyl bromide,[29] the formation of such orthoester is not favoured because the reaction pathway follows a pure S_N2 mechanism. Here, the presence of the bromide in a 1,2-*trans* configuration and the assistance of the benzoyl group on *O*-2 favour the transient acyloxonium specie and not the oxonium intermediate (Figure 3). The formation of such intermediate is in addition predominant in the furanose series.[35] The attack of the nucleophile could then occur either at the quaternary carbon or at the anomeric one *via* an S_N2

mechanism. Strong nucleophiles like **4a** or **2b** reacted first at the quaternary carbon and then at the anomeric position leading to a mixture of orthoester and disaccharide. The resulting orthoesters were stable enough to be isolated by silica gel chromatography.[36] On the contrary, if less nucleophilic acceptors **2c** and **4b** were used, the attack occured only at the anomeric center to give the corresponding disaccharides **5c** and **8b**. For the moment we are not able to decide if such selectivity is under kinetic or thermodynamic control. Nevertheless these results could be compared with the armed/disarmed effect linked with the nature of the substituent on the donor. Such activating/deactivating effects are however rarely reported when dealing with the acceptor and thus pave the way to a new understanding of the acceptor reactivity.

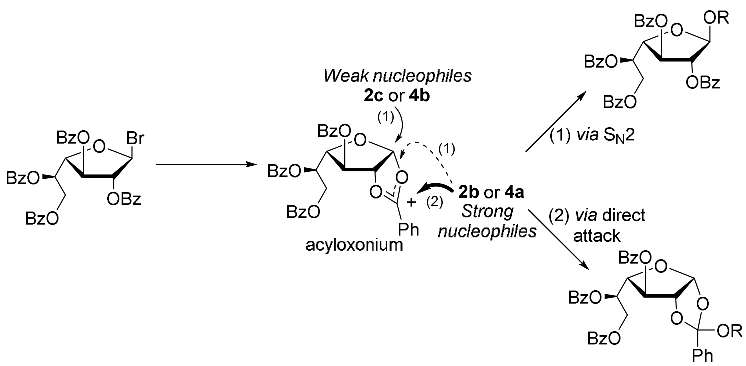


FIGURE 3. Mechanism of the formation of the orthoester and the disaccharide according to the nucleophilicity of the acceptor.

The same trend of reactivity was observed when the furanosylation assisted by DPBA was extended to the acceptors *p*NP galactopyranoside **12**, *N*-acetyl-galactosamine **14**, L-rhamnoside **15** and galactofuranoside **16** (Table 4). The building blocks **12** and **14** were obtained through biocatalysed acetylation as before (Figure 4)[21,37,38] while **15** and **16** came from commercial sources.

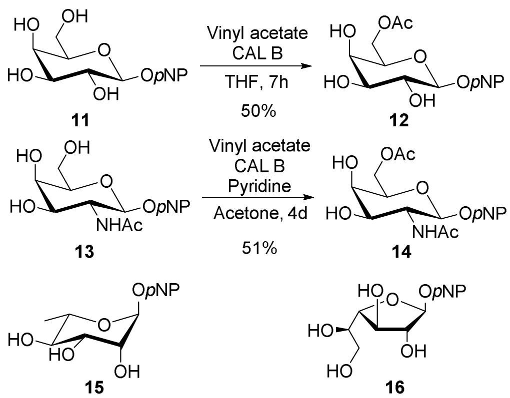
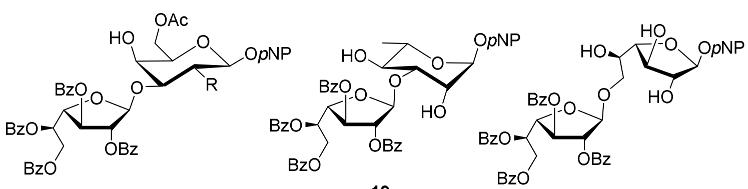


FIGURE 4. Acceptors used to obtain Gal*f*-containing disaccharides found in various microorganisms.

On one hand **12** that bears electron-withdrawing groups on *O*-6 and *C*-1 and shows a low Fukui index at *O*-3, gave the corresponding disaccharide **17** with excellent yield and without formation of the orthoester (Entry 1). On the other hand the 6-deoxy-hexose **15** is rather nucleophilic and during the regioselective furanosylation catalysed by silver oxide, more than 30% of orthoester was formed (Entry 4). Alternative silver triflate protocol allowed to increase the yield for disaccharide **19** to 59% but the regioselectivity was decreased and 20% of the regiosiomer *p*NP β-Gal*f*-(1→4)-L-Rha*p* was obtained as well (Entry 5). Surprisingly, *p*NP *N*-acetyl-galactosamine **14** whose calculated Fukui index was very low, gave the corresponding disaccharide **18** with poor yield (Entry 2). The amount of the corresponding orthoester was also low. The low nucleophilicity of *O*-3, due to the presence of the acetamide group on *C*-2 could explain the poor yield for the glycosylation.[39] However 55% yield could be reached with silver triflate as promoter with the downside formation of regioisomers (Entry 3).

The last acceptor tested in the regioselective glycosylation was the *p*NP Gal*f* **16**. In presence of the DPBA, we were expecting to form the diphenylborinate adduct between the *O*-6 and the *O*-5 and thus exacerbating the nucleophilicity of the primary hydroxyl group. Indeed the reaction between the bromide furanosyl **1a** and *p*NP Gal*f* **16** in presence of the borinic acid and silver oxide led quickly to the total conversion of the acceptor (Entry 6). The minor product of the reaction was then identified as the targeted *p*NP β-Gal*f*-(1→6)-Gal*f* **20** thanks to 2D-NMR experiments. The major one was the orthoester derivative isolated in 56% yield. This was expected as primary hydroxyl groups are much more reactive than secondary hydroxyl groups thus leading to high Fukui index and therefore to a high ratio of orthoester. It is worth to mention nevertheless that no other regioisomer was isolated which means that DPBA indeed formed a complex with *O*-6 and *O*-5 of the Gal*f* moiety. Finally to prevent from the formation of the orthoester, silver triflate was used and allowed to obtain **20** with 45% yield in mixture with the regioisomer *p*NP β-Gal*f*-(1→5)-Gal*f* (Entry 7).

TABLE 4. Extension to relevant acceptors to obtain Gal*f*-containing disaccharides.



17 R = OH
18 R = NHAc
19
20

Entry	Acceptor	f_k	Promoter	Product (Yield %)	By-product (%)
1	**12**	0.121[a]	Ag_2O	**17** (86)	None
2	**14**	0.101[a]	Ag_2O	**18** (10)	Orthoester (37)
3			AgOTf	**18** (55[c])	β-Gal*f*-(1→4)-Gal*p*NHAc (20)
4	**15**	0.134[a]	Ag_2O	**19** (45)	Orthoester (33)
5			AgOTf	**19** (59[c])	β-Gal*f*-(1→4)-L-Rha*p* (20)
6	**16**	0.157[b]	Ag_2O	**20** (12)	Orthoester (56)
7			AgOTf	**20** (45[c])	β-Gal*f*-(1→5)-Gal*f* (10)

[a] Fukui index at *O*-3. [b] Fukui index at *O*-6. [c] As an inseparable mixture. Yield and ratio determined by ^{1}H NMR.

Conclusion

As a conclusion, the high potential of diphenylborinic acid 2-aminoethyl ester as inducer of regioselective galactofuranosylation of various acceptors was confirmed. In this study we have validated the extension of Taylor's methodology from hexopyranosyl bromide to a 1,2-*trans* hexofuranosyl bromide unable to react in a pure S_N2 glycosylation pathway. When using silver oxide as promoter, only one regioisomer was formed as expected. High amount of orthoester however was formed when the *O*-6 or *C*-1 position of the acceptor possessed an electron-donating group. Silver triflate could be used instead but such an acidic catalyst destabilized the borinate adduct and the resulting regioselectivity dropped. The role of the substituents on the acceptor was partly explained thanks to *ab initio* calculation of the Fukui index of all borinate complexes. Electron-donating groups at primary and anomeric positions significantly increased the Fukui indexes and borinate adducts with high Fukui index on the equatorial oxygen generated the greater amount of orthoester. This is a confirmation that the electron-density of the substituent at the anomeric position of the acceptor can modulate the glycosylation reaction. Finally, despite these limitations, we managed to obtain quickly and efficiently galactofuranosyl containing disaccharides found in the glycocalix of pathogenic microorganisms. The minimum protecting group manipulation and the simplicity of the method represent an attractive alternative to biocatalysed process that still suffer from too strong specificity and low conversion yields.

Experimental Section

General Experimental Details

All reactions were carried out in oven-dried glassware. All reagents were purchased from commercial sources and were used without further purification unless noted. Dried acetonitrile, dichloromethane and THF were purchased sealed on molecular sieves. Unless otherwise stated, all reactions were monitored by TLC on Silica Gel 60 F_{254}. TLC spots were detected under 254 nm UV-light or by staining with cerium ammonium molybdate solution. Column chromatography was performed on Silica Gel (25 or 50 µm). Optical rotations were measured at 20 °C on a Perkin-Elmer 341 polarimeter. NMR spectra were recorded at 400 MHz for ^{1}H and 100 MHz for ^{13}C. Chemical shifts are given in δ units (ppm) and referenced to either $CDCl_3$ or CD_3OD. Coupling constants J were calculated in Hertz (Hz). Proton and carbon NMR peaks were unambiguously assigned by COSY (double quantum filtered with gradient pulse for selection), HSQC (gradient echo-anti echo selection and shape pulse) and HMBC (echo-anti echo gradient selection, magnitude mode) correlation experiments. For each isolated oligosaccharide, the reducing end (bearing *p*NP or alkyl chain) was quoted as "a", and the letter increased toward the non-reducing end (for example the sugar after was quoted as "b"). High Resolution Masses were) were recorded in positive mode using direct Electrospray ionization on a Waters Q-Tof 2 spectrometer.

4-Nitrophenyl 6-*O*-*tert*-butyldimethylsilyl-α-D-mannopyranoside (2b): To a solution of 4-Nitrophenyl α-D-mannopyranoside **2a** (1.5 g, 4.98 mmol) in DMF (30 mL) were added imidazole (1.02 g, 14.94 mmol), a catalytic amount of DMAP (30 mg, 0.25 mmol) followed by TBSCl (901 mg, 5.98 mmol). The reaction mixture was stirred at room temperature until no evolution was observed through TLC monitoring (8 h). The reaction mixture was diluted into CH_2Cl_2 (100 mL) and washed with water (100 mL). The organic layer was washed twice with a saturated aq NH_4Cl solution, water and brine. The resulting organic layer was dried with $MgSO_4$, filtered and concentrated under reduced pressure. The remaining silane was removed by submitting the crude material to vacuum during several hours. The 6-*O*-protected mannopyranoside **2b** was obtained as a white solid (829 mg, 40%) and could be used without further purification. $[\alpha]_D^{20}$ + 115 (c 1, MeOH). ^{1}H NMR (CD_3OD): δ_H 8.20 (2H, d, J = 9.3 Hz, H_{Ar}), 7.28 (2H, d, J = 9.3 Hz, H_{Ar}), 5.64 (1H, d, $J_{1,2}$ = 1.8 Hz, H-1), 4.04 (1H, dd, $J_{2,3}$ = 3.4

Hz, H-2), 3.92 (1H, dd, $J_{6,5}$ = 2 Hz, $J_{6,6'}$ = 11.2 Hz, H-6), 3.87 (1H, dd, $J_{3,4}$ = 9.3 Hz, H-3), 3.74 (1H, dd, $J_{6',5}$ = 6.8 Hz, H-6'), 3.65 (1H, app. t, $J_{4,5}$ = 9.5 Hz, H-4), 3.50 (1H, ddd, H-5), 0.8 (9H, s, $C(CH_3)_3$), 0.02 (3H, s, $OSi(CH_3)_2$), 0.00 (3H, s, $OSi(CH_3)_2$). ^{13}C NMR (CD_3OD): δ_C 162.7 (C_{Ar}), 143.8 (C_{Ar}), 126.7 (C_{Ar}), 118.0 (C_{Ar}), 100.0 (C-1), 76.6 (C-5), 72.4 (C-3), 71.5 (C-2), 68.4 (C-4), 64.3 (C-6), 26.3 [$SiC(CH_3)_3$], 19.1 [$SiC(CH_3)_3$], -5.15 [$OSi(CH_3)_2$], -5.17 [$OSi(CH_3)_2$]. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{29}NO_8SiNa$ 438.1560; Found 438.1560.

General procedure for the regioselective acetylation of pyranosides: A solution (0.1 M) of 4-nitrophenyl glycopyranoside in THF was heated to 45 °C until complete dissolution. Then vinyl acetate (3 equiv.) and Novozym®435 were added (Lipase acrylic resin *Candida antartica* from Novozymes) in a w/w ratio 1:1.2 [glycoside : immobilized enzyme]. The reaction mixture was stirred at 45 °C until complete conversion of starting material (≈ 7 h). The enzyme was filtered off and rinsed with MeOH. The resulting filtrate was then concentrated under reduced pressure and purified by column chromatography on silica gel (DCM/MeOH ratio 95:5).

4-Nitrophenyl 6-*O*-acetyl-α-D-mannopyranoside (2c): Synthesized according to general procedure from *p*NP α-D-mannopyranoside **2a** (1.0 g, 3.32 mmol), vinyl acetate (918 µL, 9.96 mmol) and Novozym®435 (1.2 g) to afford **2c** as a pale yellow solid (1.03 g, 90%). $[\alpha]_D^{20}$ + 128 (c 1, MeOH). ^{1}H NMR (CD_3OD): δ_H 8.24 (2H, d, ^3J = 9.3 Hz, H_{Ar}), 7.27 (2H, d, H_{Ar}), 5.63 (1H, d, $J_{1,2}$ = 1.7 Hz, H-1), 4.33 (1H, dd, $J_{6,6'}$ = 11.8 Hz, $J_{6a,5}$ = 2 Hz, H-6), 4.19 (1H, dd, $J_{6',5}$ = 6.4, H-6'), 4.05 (1H, dd, $J_{2,3}$ = 3.4 Hz, H-2), 3,88 (1H, dd, $J_{3,4}$ = 9 Hz, H-3), 3.73 (1H, app. t, $J_{4,5}$ = 9.8 Hz, H-4), 3.61 (1H, ddd, H-5), 1.94 (3H, s, CH_3CO). ^{13}C NMR (CD_3OD): δ_C 172.7 (CO), 162.6 (C_{Ar}), 144.0 (C_{Ar}), 126.7 (C_{Ar}), 117.9 (C_{Ar}), 100 (C-1); 73.5 (C-4), 72.2 (C-3), 71.5 (C-2), 68.3 (C-5), 64.8 (C-6), 20.7 (CH_3CO). HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{17}NO_9Na$ 366.0801 ; Found 366.0797.

Octyl 6-*O*-acetyl-α-D-mannopyranoside (4a): Synthesized according to general procedure from octyl α-D-mannopyranoside **3a**[40] (300 mg, 1 mmol), vinyl acetate (284 μL, 3.31 mmol) and Novozym®435 (400 mg) to afford **2c** as a colorless oil (305 mg, 90%). $[\alpha]_D^{20}$ + 43 (c 1, MeOH). ^{1}H NMR (CD_3OD): δ_H 4.70 (1H, d, $J_{1,2}$ = 1.6 Hz, H-1), 4.39 (1H, dd, $J_{6,6'}$ = 11.7 Hz, $J_{6,5}$ = 2.0 Hz, H-6), 4.20 (1H, dd, $J_{6',5}$ = 6.4 Hz, H-6'), 3.79 (1H, dd, $J_{2,3}$ = 3.2 Hz, H-2), 3.73–3.65 (3H, m, H-5, H-3, OCH_2), 3.60 (1H, t, $J_{4,5}$ = 9.4 Hz, H-4), 3.42 (1H, dt, ^2J = 9.6 Hz, ^3J = 6.3 Hz, OCH_2), 2.06 (3H, s, COCH_3), 1.66–1.54 (2H, m, OCH_2CH_2), 1.45–1.27 (10H, m, $(CH_2)_5CH_3$), 0.91 (3H, t, ^3J = 6.8 Hz, CH_2CH_3). ^{13}C NMR (CD_3OD): δ_C 172.8 (CO), 101.7 (C-1), 72.6 (C-3), 72.1, 72.1 (C-2, C-5), 68.7, 68.7 (C-4, OCH_2), 65.3 (C-6), 33.0, 30.6, 30.5, 30.4, 27.4, 23.7[$(CH_2)_5CH_3$], 20.8 (COCH_3), 14.4 (CH_2CH_3). HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{30}O_7Na$ 357.18837 ; Found 357.1882.

Thiotolyl 6-*O*-acetyl-α-D-mannopyranoside (4b): Synthesized according to general procedure from thiotolyl α-D-mannopyranoside **3b**[41] (780 mg, 2.7 mmol), vinyl acetate (750 μL, 8.2 mmol) and Novozym®435 (1 g) to afford **4b** as a colorless oil (624 mg, 69%). $[\alpha]_D^{20}$ +244 (c 1.25, MeOH). ^{1}H NMR (CD_3OD): δ_H 7.40 (2H, d, ^3J = 8.1 Hz, H_{Ar}), 7.14 (2H, d, H_{Ar}), 5.35 (1H, d, $J_{1,2}$ = 1.5 Hz, H-1), 4.43-4.35 (1H, m, H-6), 4.29-4.20 (2H, m, H-5, H-6'), 4.07 (1H, dd, $J_{2,3}$ = 2.9 Hz, H-2), 3.72-3.64 (2H, m, H-3, H-4), 2.32 (3H, s, CH_3), 2.00 (3H, s, $COCH_3$). ^{13}C NMR (CD_3OD): δ_C 172.7 (CO), 139.0, 133.5, 131.7, 130.7 (C_{Ar}), 90.3 (C-1), 73.4 (C-2), 73.0, 72.9 (C-4, C-5), 69.0 (C-3), 65.0 (C-6), 21.1 (CH_3), 20.8 (COCH_3). HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{20}O_6SNa$ 351.08728 ; Found 351.0872.

4-Nitrophenyl 6-*O*-acetyl-β-D-galactopyranoside (12): Synthesized according to general procedure from *p*NP β-D-galactopyranoside **11** (100 mg, 0.3 mmol), vinyl acetate (100 μL, 1mmol) and Novozym®435 (120 mg) to afford **12** as a colorless oil (56 mg, 50%). ^{1}H NMR ($CD_3OD+CDCl_3$): δ_H 8.20 (2H, d, ^3J = 9.3 Hz, H_{Ar}), 7.19 (2H, d, H_{Ar}), 4.99 (1H, d, $J_{1,2}$ = 7.7 Hz, H-1), 4.34 (1H, dd, $J_{6,6'}$ = 11.5 Hz, $J_{6,5}$ = 7.8 Hz, H-6), 4.25 (1H, dd, $J_{6',5}$ = 4.5 Hz, H-6'), 3.99–3.91 (1H, m, H-5), 3.90 (1H, dt, $J_{4,3}$ = 3.5 Hz, $J_{4,5}$ = 0.9 Hz, H-4), 3.85 (1H, dd, $J_{2,3}$ = 9.7 Hz, H-2), 3.61 (1H, dd, H-3), 2.07 (3H, s, CH_3). ^{13}C NMR (CD_3OD): δ_C 172.2 (CO), 163.4, 143.5, 126.3, 117.4 (C_{Ar}), 101.6 (C-1), 74.1 (C-3, C-5), 71.4 (C-2), 69.5 (C-4), 64.4 (C-6), 20.9 (CH_3). HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{17}NO_9Na$ 366.0801 ; Found 366.0804.

4-Nitrophenyl 6-*O*-acetyl-2-deoxy-β-D-*N*-acetylgalactosamine (14): Synthesized according to described procedure[38] from *p*NP β-D-*N*-acetylgalactosamine **13** (280 mg, 0.8 mmol), vinyl acetate (10 mL) Novozym®435 (350 mg) in a mixture of acetone/pyridine (29/21 mL) to afford **14** as a white solid (161 mg, 51%). Spectroscopic data were in accordance with previous report.

General procedure for the 2-ADPB-assisted glycosidic coupling: Bromide donor **1a**[30] (2 equiv.), acceptor (1 equiv.) and 2-aminoethyl diphenylborinate (2-DPBA, 1 equiv.) were suspended in dry CH_3CN (40 mM) with activated 4 Å molecular sieves (100 mg / mL) and under a nitrogen atmosphere. The mixture was stirred for 30 min and Ag_2O (1 equiv.) was added. Alternatively, the mixture was protected from light and AgOTf (1 equiv.) was used. After stirring at room temperature, when no evolution was observed through TLC monitoring, the reaction mixture was diluted with EtOAc and filtered through a plug of Celite. In the case of AgOTf-promoted reactions, a few drops of Et_3N were added to neutralize the reaction prior to dilution and filtration. The filtrate was concentrated under reduced pressure and the resulting crude material was purified by column chromatography on silica gel (cyclohexane/ ethyl acetate ratio 4:1).

4-Nitrophenyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→3)-6-*O*-*tert*-butyldimethylsilyl-α-D-mannopyranoside (5b): Synthesized according to general procedure starting from 6-*O*-TBS-mannopyranoside **2b** (63 mg, 0.15 mmol), galactofuranosyl bromide

1a (200 mg, 0.30 mmol), 2-DPBA (34 mg, 0.15 mmol) and Ag_2O (35 mg, 0.15 mmol). Reaction reached completion after 6 h. Purification by column chromatography on silica gel afforded **5b** (70 mg, 46%) as a white solid. Further elution allowed isolating the corresponding orthoester **6b** (37 mg, 24%).

5b: $[\alpha]_D^{20}$ + 12 (c 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ_H 8.19 (2H, d, J = 9.3 Hz, H_{Ar}), 8.10, 8.04, 7.99, 7.93 (8H, 4dd, J = 8.3 Hz, J = 1.2 Hz, H_{Ar}), 7.61-7.29 (12H, m, H_{Ar}), 7.15 (2H, d, H_{Ar}), 6.03-5.98 (1H, m, H-5b), 5.76 (1H, dd, $J_{3b,4b}$ = 5.8 Hz, $J_{3b,2b}$ = 2 Hz, H-3b), 5.70 (1H, d, $J_{1a,2a}$ = 1.5 Hz, H-1a), 5.55 (1H, bs, H-1b), 5.49 (1H, dd, $J_{2b,1b}$ = 0.7 Hz, H-2b), 4.95 (1H, dd, $J_{4b,5b}$ = 3.6 Hz, H-4b), 4.80 (2H, d, $J_{6b,5b}$ = 4.9 Hz, H-6b), 4.28 (1H, bs, H-2a), 4.14 (1H, dd, $J_{3a,2a}$ = 3.3 Hz, $J_{3a,4a}$ = 9.3 Hz, H-3a), 4.02 (1H, app. td, $J_{4a,5a}$ = 9.6 Hz, $J_{4a,OH}$ = 2.7 Hz, H-4), 3.87 (1H, dd, $J_{6a,6'a}$ = 11 Hz, $J_{6a,5a}$ = 4.2 Hz, H-6a), 3.81 (1H, dd, $J_{6'a,5a}$ = 5.4 Hz, H-6'a), 3.65-3.58 (1H, m, H-5a), 3.17 (1H, d, OH), 2.94 (1H, d, $J_{OH,2a}$ = 2.5 Hz, OH), 0.84 (9H, s, ^{t}*Bu*-Si), 0.04 [6H, s, OSi*(CH$_3$)$_2$*]. ^{13}C NMR ($CDCl_3$): δ_C 166.3, 166.2, 165.7, 165.6 (*C*OPh), 160.8, 142.6 (C_{pNP}), 133.8, 133.7, 133.4, 133.2, 130.2, 129.9, 129.8, 129.4, 129.3, 128.8, 128.5, 128.4 (C_{Ph}), 125.8, 116.5 (C_{pNP}), 103.8 (C-1b), 97.7 (C-1a), 83.1 (C-2b), 81.2 (C-4b), 77.3 (C-3a), 76.8 (C-3b), 73.0 (C-5a), 70.1 (C-5b), 67.5 (C-2a), 66.8 (C-4a), 63.6 (C-6a), 63.3(C-6b), 25.8 [SiC(*C*H$_3$)$_3$], 18.2 [Si*C*(CH$_3$)$_3$], -5.5, -5.4 [OSi(*C*H$_3$)$_2$]. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ Calcd for $C_{52}H_{55}NO_{17}SiNa$ 1016.3137 ; Found 1016.3134.

6b: $[\alpha]_D^{20}$ + 65 (c 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ_H 8.16 (2H, d, J = 9.3 Hz, H_{Ar}), 7.97, 7.93, 7.86, 7.76 (8H, 4dd, J = 8.5 Hz, J = 1.3 Hz, H_{Ar}), 7.61-7.30 (12H, m, H_{Ar}), 7.06 (2H, d, J = 9.3 Hz, H_{Ar}), 6.47 (1H, d, $J_{1b,2b}$ = 4.4 Hz, H-1b), 5.56 (1H, dd, $J_{3b,4b}$ = 3.5 Hz, $J_{3b,2b}$ = 0.9 Hz, H-3b), 5.47 (1H, d, $J_{2a,1a}$ = 1.8 Hz, H-1a), 5.37-5.32 (1H, m, H-5b), 5.30 (1H, dd, H-2b), 4.69 (1H, dd, $J_{4b,5b}$ = 8.0 Hz, H-4b), 4.56 (1H, dd, $J_{6b,6'b}$ = 12.5 Hz, $J_{6b,5b}$ = 3.9 Hz, H-6b), 4.38 (1H, dd, $J_{6'b,5b}$ = 4.9 Hz, H-6'b), 4.08 (1H, dd, $J_{3a,2a}$ = 3,3 Hz, $J_{3a,4a}$ = 9.4 Hz, H-3a), 3.93 (1H, app.td, $J_{4a,5a}$ = 9.5 Hz, $J_{4a,OH}$ = 2 Hz, H-4a), 3.78 (2H, d, $J_{6a,5a}$ = 4.3 Hz, H-6a), 3.64 (1H, br s, H-2a), 3.58-3.53 (1H, m, H-5a), 3.04 (1H, d, OH), 2.37(1H, d, $J_{OH,2a}$ = 2.8 Hz, OH), 0.83 (9H, s, ^{t}Bu-Si), 0.02 [6H, s, OSi$(CH_3)_2$]. ^{13}C NMR ($CDCl_3$): δ_C 165.6, 165.3, 165.2 (*C*OPh), 160.8, 142.6 (C_{pNP}), 136.1, 133.7, 133.4, 133.2, 133.1, 130.0, 129.9, 129.8, 129.6, 129.5, 129.4, 128.6, 128.5, 128.3, 128.2, 125.8 (C_{Ph}), 125.7 (C_{pNP}), 123.3 (Ph*C*O_3), 116.3 (C_{pNP}), 105.3 (C-1b), 97.4 (C-1a), 85.7 (C-2b), 83.9 (C-4b), 76.8 (C-3b), 73.7 (C-3a), 72.7 (C-5a), 71.2 (C-5b), 69.0 (C-2a), 67.3 (C-4a), 64.0 (C-6a), 62.8 (C-6b), 25.8 [SiC$(CH_3)_3$], 18.3 [Si*C*$(CH_3)_3$], -5.5, -5.6 [OSi$(CH_3)_2$]. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ Calcd for $C_{52}H_{55}NO_{17}SiNa$ 1016.3137 ; Found 1016.3130.

4-Nitrophenyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→3)-6-*O*-acetyl-α-D-mannopyranoside (5c): Synthesized according to general procedure starting from 6-*O*-Ac-mannopyranoside **2c** (52 mg, 0.15 mmol), galactofuranosyl bromide **1a** (200 mg, 0.30 mmol), 2-DPBA (34 mg, 0.15 mmol) and Ag_2O (35 mg, 0.15 mmol). Reaction reached completion after 2 h. Purification by column chromatography on silica gel afforded **5c** (119 mg, 85%) as a white solid. $[\alpha]_D^{20}$ + 37.5 (c 0.8, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ_H 8.20 (2H, d, J = 9.3 Hz, H_{Ar}), 8.11, 8.02, 7.99, 7.93 (8H, 4 dd, J = 1.3 Hz, J = 8.4 Hz, H_{Ar}), 7.60-7.32 (12H, m, H_{Ar}), 7.14 (2H, d, H_{Ar}), 5.99-5.94 (1H, m, H-5b), 5.77 (1H, dd, $J_{3b,2b}$ = 2.2 Hz, $J_{3b,4b}$ = 6.0 Hz, H-3b), 5.71 (1H, d, $J_{1a,2a}$ = 1.5 Hz, H-1a), 5.54 (1H, br s, H-1b), 5.49 (1H, dd, $J_{2b,1b}$ = 0.7 Hz, H-2b), 4.95 (1H, dd, $J_{4b,5b}$ = 3.7 Hz, H-4b), 4.83 (1H, dd, $J_{6b,6'b}$ = 11.9 Hz, $J_{6b,5b}$ = 4.8 Hz, H-6b), 4.78 (1H, dd, $J_{6'b,5b}$ = 6.1 Hz, H-6‘b), 4.39 (1H, dd, $J_{6a,5a}$ = 5.2 Hz, $J_{6a,6'a}$ = 12.2 Hz, H-6a), 4.31 (1H, br s, H-2a), 4.27 (1H, dd, $J_{6'a,5a}$ = 2.2 Hz, H-6‘a), 4.13 (1H, dd, $J_{3a,2a}$ = 3.3 Hz, $J_{3a,4a}$ = 9.3 Hz, H-3), 3.96 (1H, app. td, $J_{4a,OH}$ = 3.4 Hz, $J_{4a,5a}$ = 9.7Hz, H-4a), 3.74 (1H, ddd, H-5a), 3.24 (1H, d, OH), 3.08 (1H, d, $J_{2a,OH}$ = 1.9 Hz, OH), 2.04 (3H, s, CH_3CO). ^{13}C NMR ($CDCl_3$): δ_C 171.3 (*C*OCH_3), 166.3, 165.6 (*C*OPh), 160.6, 142.8, 133.8, 133.7, 133.5, 133.3, 130.0, 129.9, 129.8, 129.4, 129.3, 128.7, 128.6, 128.5, 128.4, 125.7, 116.4 (C_{Ar}), 103.9 (C-1b), 97.8 (C-1a), 83.3 (C-2b), 81.0 (C-4b), 77.0 (C-3a),76.7 (C-3b), 71.7 (C-5a), 70.0 (C-5b), 67.6 (C-2a), 65.3

(C-4a), 63.1, 63.0 (C-6a, C-6b), 20.8 (CH_3CO). HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ Calcd for $C_{48}H_{43}NO_{18}Na$ 944.23723 ; Found 944.2391.

Octyl 2,3,5,6-*O*-benzoyl-β-D-galactofuranosyl)-(1→3)-6-*O*-acetyl-α-D-mannopyranoside (8a): Synthesized according to general procedure starting from 6-*O*-Ac-mannopyranoside **4a** (51 mg, 0.15 mmol), galactofuranosyl bromide **1a** (200 mg, 0.30 mmol), 2-DPBA (34 mg, 0.15 mmol) and Ag_2O (35 mg, 0.15 mmol). Reaction reached completion after 2 h. Purification by column chromatography on silica gel afforded **8a** (56 mg, 40%) as a white solid. Further elution allowed isolating the corresponding orthoester **9a** (68 mg, 49%).

Alternative protocol using **4a** (44 mg, 0.13 mmol), **1a** (176 mg, 0.27 mmol), 2-DPBA (30 mg, 0.13 mmol) and AgOTf (34 mg, 0.13 mmol) as promoter gave **8a** (70 mg, 57%) in mixture with the octyl β-D-Gal*f*-(1→4)-D-Man*p* regioisomer (ratio 4:1).

8a: $[\alpha]_D^{20}$ + 6 (c 1.5, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ_H 8.13-7.88 (8H, m, H_{Ar}), 7.62-7.47 (4H, m, H_{Ar}), 7.46-7.28 (8H, m, H_{Ar}), 5.96 (1H, dt, $J_{5b,6'b}$ = 6.2 Hz, $J_{5b,6b}$ = 4.7 Hz, $J_{5b,4b}$ = 3.8 Hz, H-5b), 5.73 (1H, dd, $J_{3b,4b}$ = 5.8 Hz, $J_{3b,2b}$ = 1.9 Hz, H-3b), 5.51-5.46 (2H, m, H-1b, H-2b), 4.91 (1H, dd, H-4b), 4.89 (1H, d, $J_{1a,2a}$ = 1.6 Hz, H-1a), 4.80 (1H, dd, $J_{6b,6'b}$ = 11.9 Hz, H-6b), 4.74 (1H, dd, H-6'b), 4.40 (1H, dd, $J_{6a,6'a}$ = 11.9 Hz, $J_{6a,5a}$ = 4.7 Hz, H-6a), 4.36 (1H, dd, $J_{6'a,5a}$ = 2.8 Hz, H-6'a), 4.07 (1H, dd, $J_{2a,3a}$ = 3.3 Hz, H-2a), 3.95 (1H, dd, $J_{3a,4a}$ = 9.2 Hz, H-3a), 3.86 (1H, dd, $J_{4a,5a}$ = 9.7 Hz, H-4a), 3.77 (1H, ddd, H-5a), 3.66 (1H, dt, ^2J = 9.7 Hz, ^3J = 6.8 Hz, OCH_2), 3.42 (1H, dt, ^3J = 6.6 Hz, OCH_2), 2.11 (3H, s, $COCH_3$) 1.56 (2H, m, OCH_2CH_2), 1.36–1.20 (10H, m, $(CH_2)_5CH_3$), 0.87 (3H, t, ^3J = 6.9, CH_2CH_3). ^{13}C NMR ($CDCl_3$): δ_C 171.5, 166.4, 166.2, 165.8, 165.7 (CO), 134.8, 133.8, 133.5, 133.3, 130.1, 130.1, 130.0, 129.9, 129.6, 129.5, 128.9, 128.7, 128.6, 128.6, 128.5, 128.0 (C_{Ar}), 104.4 (C-1b), 99.5 (C-1a), 83.1 (C-2b), 81.2 (C-4b), 78.8 (C-3a), 77.0 (C-3b), 70.4 (C-5a), 70.3 (C-5b), 68.6 (C-2a), 68.1 (OCH_2), 66.0 (C-4a), 63.8 (C-6a), 63.2 (C-6b), 32.0, 29.5, 29.5, 29.3, 26.2, 22.8 $[(CH_2)_6CH_3]$, 21.1 (COCH_3), 14.2 (CH_2CH_3). HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ Calcd for $C_{50}H_{56}O_{16}Na$ 935.34606 ; Found 935.3467.

9a: ^{1}H NMR ($CDCl_3$): δ_H 7.97-7.91 (2H, m, H_{Ar}), 7.91- 7.83 (4H, m, H_{Ar}), 7.75-7.70 (2H, m, H_{Ar}), 7.60- 7.54 (1H, m, H_{Ar}), 7.53-7.46 (2H, m, H_{Ar}), 7.42-7.36 (5H, m, H_{Ar}), 7.36-7.28 (4H, m, H_{Ar}), 6.36 (1H, d, $J_{1b,2b}$ = 4.4 Hz, H-1b), 5.51 (1H, dd, $J_{3b,4b}$ = 4.2 Hz, $J_{3b,2b}$ = 1.5 Hz, H-3b), 5.28 (1H, ddd, $J_{5b,4b}$ = 7.6 Hz, $J_{5b,6'b}$ = 5.0 Hz, $J_{5b,6b}$ = 3.9 Hz, H-5b), 5.23 (1H, dd, H-2b), 4.71 (1H, d, $J_{1a,2a}$ = 1.7 Hz, H-1a), 4.62 (1H, dd, H-4b), 4.51 (1H, dd, $J_{6b,6'b}$ = 12.4 Hz, H-6b), 4.42 (1H, dd, $J_{6a,6'a}$ = 12.1 Hz, $J_{6a,5a}$ = 4.6 Hz, H-6a), 4.33 (1H, dd, H-6'b), 4.27 (1H, dd, $J_{6'a,5a}$ = 2.1 Hz, H-6'a), 3.90 (1H, dd, $J_{3a,4a}$ = 8.8 Hz, $J_{3a,2a}$ = 3.3 Hz, H-3a), 3.79-3.67 (2H, m, H-4a, H5a), 3.63-3.55 (2H, m, H-2a, OCH_2), 3.33 (1H, dt, ^2J = 9.7 Hz, ^3J = 6.6 Hz, OCH_2), 2.87 (1H, d, $J_{OH,4a}$ = 2.8 Hz, OH), 2.17 (1H, d, $J_{OH,2a}$ = 3.2 Hz, OH), 2.09 (3H, s, $COCH_3$), 1.56-1.46 (2H, m, OCH_2CH_2), 1.31-1.23 (10H, m, $(CH_2)_5CH_3$), 0.88 (3H, t, ^3J = 6.9 Hz, $(CH_2)_5CH_3$). ^{13}C NMR ($CDCl_3$): δ_C 171.7 ($COCH_3$), 165.8, 165.4, 165.3 (COPh), 136.6, 133.8, 133.2, 133.2, 130.1, 130.0, 129.9, 129.8, 129.6, 128.7, 128.6, 128.5, 128.4, 126.2 (C_{Ar}), 123.9 ($PhCO_3$), 105.1 (C-1b), 99.3 (C-1a), 86.0 (C-2b), 83.1 (C-4b), 76.7 (C-3b), 74.5 (C-3a), 71.2 (C-5b), 70.6 (C-5a), 70.2 (C-2a), 68.0 (OCH_2), 65.6 (C-4a), 63.7 (C-6a), 62.9 (C-6b), 31.9, 29.4, 29.4, 29.4, 26.2, 22.8 [$(CH_2)_6CH_3$], 21.0 ($COCH_3$), 14.2 [$(CH_2)_6CH_3$]. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ Calcd for $C_{50}H_{56}O_{16}Na$ 935.34606 ; Found 935.3465.

Thiotolyl 2,3,5,6-*O*-benzoyl-β-D-galactofuranosyl)-(1→3)-6-*O*-acetyl-α-D-mannopyranoside (8b): Synthesized according to general procedure starting from thiotolyl 6-*O*-Ac-mannopyranoside **4b** (50 mg, 0.15 mmol), galactofuranosyl bromide **1a** (200 mg, 0.30 mmol), 2-DPBA (34 mg, 0.15 mmol) and Ag_2O (35 mg, 0.15 mmol). Reaction reached completion after 2 h. Purification by column chromatography on silica gel afforded **8b** (131 mg, 96%) as a white solid.

Alternative protocol using **4b** (50 mg, 0.15 mmol), **1a** (200 mg, 0.30 mmol), 2-DPBA (34 mg, 0.14 mmol) and AgOTf (39 mg, 0.15 mmol) as promoter gave **8b** (94 mg, 69%).

8b: $[\alpha]_D^{20}$ + 60 (c 1.15, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ_H 8.11 (2H, dd, ^3J = 8.4 Hz, ^4J = 1.3 Hz, H_{Ar}), 8.02 (4H, dd, ^3J = 8.4 Hz, ^4J = 1.3 Hz, H_{Ar}), 7.93 (2H, dd, ^3J = 8.4 Hz, ^4J = 1.3 Hz, H_{Ar}), 7.61-7.51 (4H, m, H_{Ar}), 7.46-7.31 (10H, m, H_{Ar}), 7.12 (2H, d, ^3J = 8.0 Hz, H_{Tol}), 5.94 (1H, td, $J_{5b,6b}$ = 5.3 Hz, $J_{5b,4b}$ = 3.6 Hz, H-5b), 5.73 (1H, dd, $J_{3b,4b}$ = 5.9 Hz, $J_{3b,2b}$ = 2.2 Hz, H-3b), 5.54 (1H, d, $J_{1a,2a}$ = 1.4 Hz, H-1a), 5.48 (1H, d, $J_{1b,2b}$ = 0.8 Hz, H-1b), 5.48 (1H, dd, H-2b), 4.92 (1H, dd, H-4b), 4.80 (2H, d, H-6b), 4.41 (1H, dd, $J_{6a,6'a}$ = 12.1 Hz, $J_{6a,5a}$ = 5.9 Hz, H-6a), 4.37-4.30 (3H, m, H-2a, H-5a, H-6'a), 3.98-3.88 (2H, m, H-3a, H-4a), 3.19 (1H, d, $J_{OH,4a}$ = 3.8 Hz, OH), 2.33 (3H, s, CH_3), 2.07 (3H, s, $COCH_3$). ^{13}C NMR ($CDCl_3$): δ_C 171.4, 166.5, 166.2, 165.8, 165.7 (CO), 138.1, 133.9, 133.6, 133.4, 132.5, 130.1, 130.0, 129.6, 129.5, 128.9, 128.7, 128.6 (C_{Ar}), 104.1 (C-1b), 87.8 (C-1a), 83.2 (C-2b), 81.4 (C-4b), 78.3 (C-3a), 77.0 (C-3b), 71.4 (C-5a), 70.2 (C-5b), 69.6 (C-2a), 66.4 (C-4a), 63.8 (C-6a), 63.2 (C-6b), 21.3 (CH_3), 21.0 ($COCH_3$). HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ Calcd for $C_{49}H_{46}O_{15}SNa$ 929.24496 ; Found 929.2455.

***p*-Nitrophenyl (2, 3, 5, 6-*O*-tetrabenzoyl-β-D-galactofuranosyl)-(1→3)-6-*O*-acetyl-β-D-galactopyranoside (17):** Synthesized according to general procedure starting from *p*NP 6-*O*-Ac-galactopyranoside **12** (52 mg, 0.15 mmol), galactofuranosyl bromide **1a** (200 mg, 0.30 mmol), 2-DPBA (34 mg, 0.15 mmol) and Ag_2O (35 mg, 0.15 mmol). Reaction reached completion after 2 h. Purification by column chromatography on silica gel afforded **17** (121 mg, 86%) as a white solid. $[\alpha]_D^{20}$ - 26.5 (c 1, $CHCl_3$). ^1H NMR ($CDCl_3$): δ_H 8.20 (2H, d, J = 9.4 Hz, H_{pNP}), 8.12-8.06 (2H, m, H_{Bz}), 8.04-7.97 (4H, m, H_{Bz}), 7.95-7.89 (2H, m, H_{Bz}), 7.62-7.51 (3H, m, H_{Bz}), 7.47-7.29 (9H, m, H_{Bz}), 7.12 (2H, d, H_{pNP}), 5.97 (1H, ddd, $J_{5b,6'b}$ = 6.3 Hz, $J_{5b,6'b}$ = 5.0 Hz, $J_{5b,4b}$ = 3.8 Hz, H-5b), 5.75 (1H, dd, $J_{3b,4b}$ = 5.8 Hz, $J_{3b,2b}$ = 2.2 Hz, H-3b), 5.69 (1H, d, $J_{1b,2b}$ = 0.9 Hz H-1b), 5.56 (1H, dd, H-2b), 4.99 (1H, d, $J_{1a,2a}$ = 7.8 Hz, H-1a), 4.83 (1H, dd,

$J_{6b,6'b}$ = 11.8, H-6b), 4.80 (1H, dd, H-4b), 4.71 (1H, dd, H-6'b), 4.34 (1H, dd, $J_{6a,6'a}$ = 11.7 Hz, $J_{6a,5a}$ = 7.6 Hz, H-6a), 4.24 (1H, dd, $J_{6'a,5a}$ = 4.8 Hz, H-6'a), 4.22 (1H, dd, $J_{2a,3a}$ = 9.4 Hz, H-2a), 4.10 (1H, dd, $J_{4a,3a}$ = 3.4 Hz, $J_{4a,5a}$ = 1.1 Hz, H-4a), 3.86 (1H, ddd, H-5a), 3.79 (1H, dd, H-3a), 2.08 (3H, s, CH_3). ^{13}C NMR ($CDCl_3$): δ_C 170.8, 166.3, 166.3, 165.8, 165.7 (*C*OPh), 161.8 (C_{pNP}), 142.9 (C_{pNP}), 133.9, 133.6, 133.5, 130.1, 130.0, 129.9, 129.4, 128.7, 128.6, 128.5 (C_{Bz}), 125.7 (C_{pNP}), 116.7 (C_{pNP}), 107.9 (C-1b), 100.2 (C-1a), 83.1 (C-2b), 81.6 (C-4b), 80.7 (C-3a), 77.0 (C-3b), 72.9 (C-5a), 70.2 (C-2a, C-5b), 68.5 (C-4a), 63.0 (C-6a, C-6b), 20.9 (CH_3). HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ Calcd for $C_{48}H_{43}NO_{18}Na$ 944.23723 ; Found 944.2368.

***p*-Nitrophenyl (2, 3, 5, 6-tetra-*O*-benzoyl-β-D-galactofuranosyl)-(1→3)-2-acetamido-6-*O*-acetyl-2-deoxy-β-D-galactopyranoside (18):** Synthesized according to general procedure starting from *p*NP 6-O-acetyl-β-D-*N*-acetylgalactosamine **14** (58 mg, 0.15 mmol), galactofuranosyl bromide **1a** (200 mg, 0.30 mmol), 2-DPBA (34 mg, 0.15 mmol) and Ag_2O (35 mg, 0.15 mmol). Reaction reached completion after 2 h. Purification by column chromatography on silica gel afforded **18** (14 mg, 10%) as a light brown solid. Further elution allowed isolating the corresponding orthoester **18'** (54 mg, 37%).

Alternative protocol using **14** (58 mg, 0.15 mmol), **1a** (200 mg, 0.30 mmol), 2-DPBA (34 mg, 0.15 mmol) and AgOTf (39 mg, 0.15 mmol) as promoter gave **18** (80 mg, 55%) in mixture with the *p*NP β-D-Gal*f*-(1→4)-D-GalNHAc regioisomer (ratio 4:1).

18: ^{1}H NMR (CD_3OD+$CDCl_3$): δ_H 8.15 (2H, d, ^3J = 9.2 Hz, H_{pNP}), 8.10-8.03 (2H, m, H_{Bz}), 8.02-7.93 (4H, m, H_{Bz}), 7.87-7.81 (2H, m, H_{Bz}), 7.57-7.50 (3H, m, H_{Bz}), 7.44-7.27 (9H, m, H_{Bz}), 7.06 (2H, d, H_{pNP}), 5.95 (1H, ddd, $J_{5b,6'b}$ = 6.7 Hz, $J_{5b,6b}$ = 4.4 Hz, $J_{5b,4b}$ = 4.0 Hz, H-5b), 5.68 (1H, d, $J_{1a,2a}$ = 8.2 Hz, H-1a), 5.66 (1H, dd, $J_{3b,4b}$ = 5.4 Hz, $J_{3b,2b}$ = 1.9 Hz, H-3b), 5.43 (1H, d, H-2b), 5.37 (1H, s, H-1b), 4.84 (1H, dd, H-4b), 4.76 (1H, dd, $J_{6b,6'b}$ = 11.8 Hz, H-6b), 4.67 (1H, dd, H-6'b), 4.49 (1H, dd, $J_{3a,2a}$ = 10.8 Hz, $J_{3a,4a}$ = 3.3 Hz, H-3a), 4.30 (1H, dd, $J_{6a,6'a}$ = 11.7 Hz, $J_{6a,5a}$ = 7.9 Hz, H-6a), 4.16 (1H, dd, $J_{6'a,5a}$ = 4.5 Hz, H-6'a), 4.09 (1H, d, H-4a), 3.89 (1H, dd, H-5a), 3.80 (1H, dd, H-2a), 2.03 (3H, s, CH_3), 1.93 (3H, s, CH_3). ^{13}C NMR ($CD_3OD+CDCl_3$): δ_C 172.4, 171.0 (*C*OCH_3), 166.4, 166.2, 165.9, 165.9 (*C*OPh), 161.9 (C_{pNP}), 142.8 (C_{pNP}), 133.9, 133.6, 133.5, 130.1, 130.0, 129.9, 129.8, 129.4, 128.7, 128.6, 128.5 (C_{Bz}), 125.7 (C_{pNP}), 116.7 (C_{pNP}), 107.9 (C-1b), 97.0 (C-1a), 83.0 (C-2b), 81.2 (C-4b), 77.4 (C-3b), 76.8 (C-3a), 72.8 (C-5a), 70.3 (C-5b), 68.2 (C-4a), 63.3 (C-6a, C-6b), 53.4 (C-2a), 23.3, 20.8 (CO*C*H_3). HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ Calcd for $C_{50}H_{46}N_2O_{18}Na$ 985.26378 ; Found 985.2646.

18': ^{1}H NMR ($CDCl_3$): δ_H 8.14 (2H, d, ^3J = 9.3 Hz, H_{pNP}), 7.93-7.88 (2H, m, H_{Bz}), 7.86-7.80 (4H, m, H_{Bz}), 7.73-7.68 (2H, m, H_{Bz}), 7.59-7.46 (3H, m, H_{Bz}), 7.43-7.27 (9H, m, H_{Bz}), 7.04 (2H, d, H_{pNP}), 6.21 (1H, d, $J_{1b,2b}$ = 4.3 Hz, H-1b), 5.84 (1H, d, $J_{1a,2a}$ = 8.3 Hz, H-1a), 5.76 (1H, d, J=7.0, NH), 5.40 (1H, dd, $J_{3b,4b}$ = 5.4 Hz, $J_{3b,2b}$ = 1.8 Hz, H-3b), 5.19 (1H, ddd, $J_{5b,4b}$ = 7.0 Hz, $J_{5b,6'b}$ = 5.3 Hz, $J_{5b,6b}$ = 3.7 Hz, H-5b), 5.10 (1H, dd, H-2b), 4.63 (1H, dd, $J_{3a,2a}$ = 10.6 Hz, $J_{3a,4a}$ = 3.0 Hz, H-3a), 4.51 (1H, dd, H-4b), 4.42 (1H, dd, $J_{6b,6'b}$ = 12.4 Hz, H-6b), 4.32 (2H, d, $J_{6a,\ 5a}$ = 6.2 Hz, H-6a), 4.24 (1H, dd, H-6'b), 4.10 (1H, t, $J_{4a,3a}$ = $J_{4a,OH}$ = 3.0 Hz, H-4a), 3.92 (1H, t, H-5a), 3.54 (1H, ddd, $J_{2a,NH}$ = 7.0 Hz, H-2a), 2.46 (1H, d, OH), 2.07 (3H, s, $OCOCH_3$), 1.98 (3H, s, NHCOC*H_3*). ^{13}C NMR ($CDCl_3$): δ_C 171.9 (NHCO), 170.9 (OCO), 165.8, 165.4 (COPh), 161.9 (C_{pNP}), 142.9 (C_{pNP}), 137.4, 133.9, 133.3, 133.2, 130.2, 129.9, 129.8, 129.5, 128.7, 128.6, 128.5, 128.4, 126.2 (C_{Ar}), 125.8 (C_{pNP}), 124.8 ($PhCO_3$), 116.7 (C_{pNP}), 104.5 (C-1b), 96.6 (C-1a), 86.4 (C-2b), 81.2 (C-4b), 76.4 (C-3b), 72.7 (C-5a), 71.0 (C-5b), 70.0 (C-3a), 68.2 (C-4a), 63.2 (C-6a), 62.7 (C-6b), 53.9 (C-2a), 24.0 (NHCO*C*H_3), 21.0 (OCO*C*H_3). HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ Calcd for $C_{50}H_{46}N_2O_{18}Na$ 985.26378 ; Found 985.2632.

***p*-Nitrophenyl (2, 3, 5, 6-tetra-*O*-benzoyl-β-D-galactofuranosyl)-(1→3)-α-L-rhamnopyranoside (19):** Synthesized according to general procedure starting from *p*NP α-L-rhamnopyranoside **15** (43 mg, 0.15 mmol), galactofuranosyl bromide **1a** (200 mg, 0.30 mmol), 2-DPBA (34 mg, 0.15 mmol) and Ag_2O (35 mg, 0.15 mmol). Reaction reached completion after 2 h. Purification by column chromatography on silica gel afforded **19** (58 mg, 45%) as a light brown foam. Further elution allowed isolating the corresponding orthoester **19'** (43 mg, 33%).

Alternative protocol using **15** (43 mg, 0.15 mmol), **1a** (200 mg, 0.30 mmol), 2-DPBA (34 mg, 0.15 mmol) and AgOTf (39 mg, 0.15 mmol) as promoter gave **19** (77 mg, 59%) in mixture with the *p*NP β-D-Gal*f*-(1→4)-L-Rha*p* regioisomer (ratio 9:1).

19: $[\alpha]_D^{20}$ -90 (c 0.8, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ_H 8.20 (2H, d, ^3J = 9.3 Hz, H_{pNP}), 8.10 (2H, dd, ^3J = 8.4 Hz, ^4J = 1.3 Hz, H_{Bz}), 8.05-7.90 (6H, m, H_{Bz}), 7.62-7.48 (4H, m, H_{Bz}), 7.47-7.40 (2H, m, H_{Bz}), 7.39-7.31 (6H, m, H_{Bz}), 7.11 (2H, d, H_{pNP}), 5.94 (1H, ddd, $J_{5b,6'b}$ = 6.2 Hz, $J_{5b,6b}$ = 5.6 Hz, $J_{5b,4b}$ = 3.5 Hz, H-5b), 5.78 (1H, dd, $J_{3b,4b}$ = 6.2 Hz, $J_{3b,2b}$ = 2.7 Hz, H-3b), 5.65 (1H, d, $J_{1b,2b}$ = 1.1 Hz, H-1b), 5.54 (1H, dd, H-2b), 5.49 (1H, d, $J_{1a,2a}$ = 1.9 Hz, H-1a), 4.87 (1H, dd, $J_{6b,6'b}$ = 11.8 Hz, H-6b), 4.84 (1H, dd, H-4b), 4.69 (1H, dd, H-6'b), 4.26 (1H, dd, $J_{2a,3a}$ = 3.4 Hz, H-2a), 4.05 (1H, dd, $J_{3a,4a}$ = 9.3 Hz, H-3a), 3.81 (1H, t, $J_{4a,3a}$ = $J_{4a,5a}$ = 9.3 Hz, H-4a), 3.71 (1H, qd, $J_{5a,CH3}$ = 6.2 Hz, H-5a), 3.12 (1H, s, OH), 2.86 (1H, s, OH), 1.31 (3H, d, CH_3). ^{13}C NMR ($CDCl_3$): δ_C 166.6, 166.5, 165.8, 165.7 (COPh), 161.0 (C_{pNP}), 142.7 (C_{pNP}), 134.9, 134.0, 133.9, 133.7, 133.5, 130.2, 130.1, 130.0, 129.9, 129.4, 128.7, 128.7, 128.7, 128.6, 128.5, 128.1 (CPh), 125.9 (C_{pNP}), 116.4 (C_{pNP}), 108.6 (C-1b), 97.8 (C-1a), 83.9 (C-2b), 81.0 (C-3a,C-4b), 76.7 (C-3b), 71.3 (C-4a), 70.3 (C-2a), 70.1 (C-5b), 69.4 (C-5a), 63.0 (C-6b), 17.8. (CH_3). HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ Calcd for $C_{46}H_{41}NO_{16}Na$ 886.23175 ; Found 886.2322.

19': ^{1}H NMR ($CDCl_3$): δ_H 8.14 (2H, d, ^3J = 9.2 Hz, H_{pNP}), 7.96-7.91 (2H, m, H_{Bz}), 7.89-7.84 (4H, m, H_{Bz}), 7.79-7.73 (2H, m, H_{Bz}), 7.61-7.55 (1H, m, H_{Bz}), 7.54-7.48 (2H, m, H_{Bz}), 7.44-

7.30 (9H, m, H_{Bz}), 7.05 (2H, d, H_{pNP}), 6.36 (1H, d, $J_{1b,2b}$ = 4.2 Hz, H-1b), 5.53-5.49 (2H, m, H-1a, H-3b), 5.28-5.23 (1H, m, H-5b), 5.25 (1H, dd, $J_{2b,3b}$ = 1.5 Hz, H-2b), 4.63 (1H, dd, $J_{4b,3b}$ = 7.5 Hz, $J_{4b,5b}$ = 4.6 Hz, H-4b), 4.51 (1H, dd, $J_{6b,6'b}$ = 12.5 Hz, $J_{6b,5b}$ = 3.7 Hz, H-6b), 4.32 (1H, dd, $J_{6'b,5b}$ = 5.3 Hz, H-6'b), 4.06 (1H, t, $J_{OH,2a} = J_{2a,3a}$ = 3.1 Hz, H-2a), 4.00 (1H, dd, $J_{3a,4a}$ = 8.8 Hz, H-3a), 3.69-3.57 (2H, m, H-4a, H-5a), 2.59 (1H, d, OH), 2.52 (1H, d, $J_{OH,4a}$ = 2.4 Hz, OH), 1.26 (3H, d, $J_{CH3,5a}$ = 1.0 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ_C 165.8, 165.5, 165.4 (COPh), 161.0 (C_{pNP}), 142.7 (C_{pNP}), 136.6, 134.0, 133.3, 130.1, 129.9, 129.8, 128.7, 128.6, 128.5, 128.4, 126.2 (C_{Bz}), 125.9 (C_{pNP}), 124.3 ($PhCO_3$), 116.3 (C_{pNP}), 104.8 (C-1b), 97.7 (C-1a), 86.2 (C-2b), 82.4 (C-4b), 76.6 (C-3b), 74.4 (C-3a), 71.1 (C-5b), 70.5 (C-4a), 70.0 (C-5a), 69.7 (C-2a), 62.9 (C-6b), 17.8 (CH_3). HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ Calcd for $C_{46}H_{41}NO_{16}Na$ 886.23175 ; Found 886.2318.

4-Nitrophenyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-β-D-galactofuranoside (20): Synthesized according to general procedure starting from *p*NP β-D-galactofuranoside **16** (20 mg, 67 μmol), galactofuranosyl bromide **1a** (88 mg, 0.13 mmol), 2-DPBA (15 mg, 67 μmol) and Ag_2O (15 mg, 67 μmol). Reaction reached completion after 2 h. Purification by column chromatography on silica gel afforded **20** (7 mg, 12%) as a white solid. Further elution allowed isolating the corresponding orthoester **20'** (35 mg, 56%).

Alternative protocol using **16** (20 mg, 67 μmol), **1a** (88 mg, 0.13 mmol), 2-DPBA (15 mg, 65 μmol) and AgOTf (16 mg, 65 μmol) as promoter yielded a 7:1 inseparable mixture of 20 and *p*NP β-D-Gal*f*-(1→5)-D-Gal*f* (51% overall yield, 30 mg, 34 μmol).

20: ^1H NMR (CD_3OD): δ_H 8.11-8.06 (4H, m, H_{pNP}, H_{Bz}), 7.93-7.81 (6H, 3 dd, ^3J = 8.3 Hz, ^4J = 1.2 Hz, H_{Bz}), 7.66 (1H, td, ^3J = 7.3 Hz, ^4J = 1.2 Hz, H_{Bz}), 7.56-7.22 (11H, m, H_{Bz}), 7.03 (2H, d, ^3J = 9.3 Hz, H_{pNP}), 5.77 (1H, ddd, $J_{5b,6b}$ = 7.1 Hz, $J_{5b,4b} = J_{5b,6'b}$ = 3.5 Hz, H-5b), 5.61 (1H, d, $J_{1a,2a}$ = 2.4 Hz, H-1a), 5.51 (1H, d, $J_{3b,4b}$ = 4.7 Hz, H-3b), 5.41 (1H, s, H-1b), 5.39 (1H, s, H-2b), 4.60 (1H, dd, $J_{6b,6'b}$ = 12.1 Hz, H-6b), 4.42-4.36 (2H, m, H-6'b, H-4b), 4.34 (1H, dd, $J_{4a,3a}$ = 7.1 Hz, $J_{4a,5a}$ = 1.9 Hz, H-4a), 4.27 (1H, dd, $J_{3a,2a}$ = 4.9 Hz, H-3a), 4.15 (1H, dd, H-2a), 4.04 (1H, ddd, $J_{5a,6'a}$ = 8.6 Hz, $J_{5a,6a}$ = 6.2 Hz, H-5a), 3.92 (1H, app. t., $J_{6a,6'a}$ = 8.6 Hz, H-6a), 3.63 (1H, ddd, H-6'a). ^{13}C NMR ($CDCl_3$) δ_C 167.6, 167.2, 167.1, 166.8 (*C*OPh), 163.4 (C_{pNP}), 143.6 (C_{pNP}), 134.9, 134.7, 134.6, 134.4, 131.1, 130.8, 130.7, 130.4, 130.3, 129.9, 129.7, 129.5 (C_{Bz}), 126.7, 117.4 (C_{pNP}), 107.6 (C-1a), 106.3 (C-1b), 84.5 (C-4a), 83.4 (C-2a), 83.3 (C-4b), 83.2 (C-2b), 79.0 (C-3b), 77.1 (C-3a), 71.7 (C-5b), 68.8 (C-5a), 67.4 (C-6a), 64.9 (C-6b).

20': ^{1}H NMR (CD_3OD) δ_H 8.14 (2H, d, ^3J = 9.3 Hz, H_{pNP}), 7.96, 7.83, 7.62 (8H, 3 d, ^3J = 7.9 Hz, H_{Ar}), 7.54-7.27 (12H, m, H_{Ar}), 7.18 (2H, d, H_{pNP}), 6.06 (1H, d, $J_{1b,2b}$ = 4.2 Hz, H-1b), 5.64 (1H, d, $J_{1a,2a}$ = 1.8 Hz, H-1a), 5.51 (1H, d, $J_{3b,4b}$ = 3.3 Hz, H-3b), 5.43-5.38 (1H, m, H-5b), 5.10 (1H, d, H-2b), 4.66-4.59 (2H, m, H-4b, H-6b), 4.43 (1H, dd, $J_{6'b,6b}$ = 12.4 Hz, $J_{6'b,5b}$ = 5.5 Hz, H-6'b), 4.27 (1H, dd, $J_{2a,3a}$ = 4.0 Hz, H-2a), 4.18 (1H, dd, $J_{3a,4a}$ = 6.4 Hz, H-3a), 4.11 (1H, dd, $J_{4a,5a}$ = 2.5 Hz, H-4a), 3.86 (1H, app. td., $J_{5a,6a}$ = 6.8 Hz, H-5a), 3.51 (1H, dd, $J_{6a,6'a}$ = 9.4 Hz, H-6a), 3.40 (1H, dd, H-6'a). ^{13}C NMR ($CDCl_3$) δ_C 167.1, 166.7, 166.7 (*C*OPh), 163.2, 143.5 (C_{pNP}), 137.2, 134.7, 134.2, 130.7, 130.6, 130.5, 130.5, 130.3, 130.1, 129.6, 129.4, 129.3, 129.1, 127.5 (C_{Ar}), 126.5 (C_{pNP}), 124.6 (*C*O_3Ph), 117.5 (C_{pNP}), 107.5 (C-1a), 106.5(C-1b), 86.8 (C-2b), 85.2 (C-4a), 84.6 (C-4b), 83.3 (C-2a), 77.9, 77.8(C-3b, C-3a), 72.7 (C-5b), 69.2 (C-5a), 64.9 (C-6a), 64.0 (C-6b).

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Supporting Information Available: Details of the computational calculations and ^{1}H and ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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