Ionic Liquid [bmim]PF_6-Mediated Synthesis of 1,2-Orthoesters of Carbohydrates and the Glycosidation Reactions of 4-Pentenyl Orthoesters

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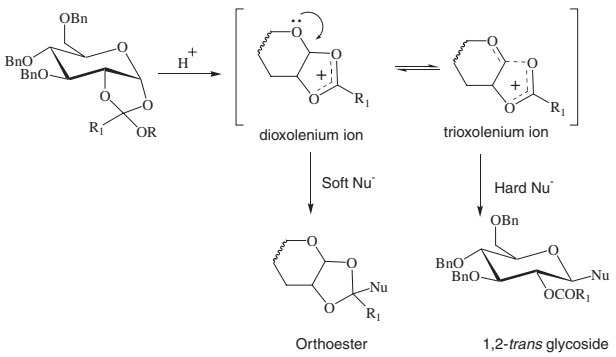
A facile synthesis of the 1,2-orthoesters of carbohydrates in the ionic liquid [bmim]PF_6 without a quaternary ammonium salt like tetrabutylammonium iodide, is described. The glycosidation reactions of 4-pentenyl orthoesters (NPOEs) with different alcohols are also discussed. The work described in this paper showed that [bmim]PF_6 is an efficient and recyclable solvent for the synthesis and glycosidation reaction of orthoesters.

In recent years, ionic liquids have been described as one of the most promising environmentally benign reaction media in organic synthesis.[1] They have several benefits over conventional organic solvents and show better process performance in reactions.[2] Ionic liquids possess fundamentally unique combinations of properties, such as being non-volatile and able to dissolve both ionic and non-ionic species. Room temperature ionic liquids are being applied to a wide range of syntheses and their usefulness in a number of reactions, both catalytic and stoichiometric, have been demonstrated recently.[3] However, there is little understanding of how the ionic liquids might affect reactivity when used as a reaction medium.

Due to their high polarity, ionic liquids can coordinate with polar molecules very easily, thereby solubilizing the organic compounds. Among polar organic molecules, carbohydrates have gained much attention.[4] The current developments and trends in glycobiology[5] stress the prime importance of carbohydrate chemistry. One of the major challenges for carbohydrate chemists is to avoid the environmental problems caused by the extensive use of the solvents, such as DMF, pyridine, MeOH, etc. It is, therefore, of great interest to develop practical and environmentally benign methods for synthetic carbohydrate chemistry, especially for glycosidation, which is one of the most important and fundamental transformation involving carbohydrates. There are only few reports in the literature, that describe the use of ionic liquid as solvent in carbohydrate chemistry. Ionic liquids have been used for the acetylation of sugars[6] and for the synthesis of various glycosides and disaccharides from trichloroacetimidate donors.[7] Toshima et al. have reported the glycosidation of glucopyranosyl phosphates and glycosyl fluorides in ionic liquid.[8] Very recently, Poletti et al. have studied the influence of the reaction medium on the stereochemical outcome of the glycosylation with trichloroacetimidate donors in ionic liquids.[9]

1,2-Orthoesters are valuable intermediates in synthetic carbohydrate chemistry.[10] Among various 1,2-orthoesters of carbohydrates, 4-pentenyl orthoesters (NPOEs) have received much attention. This interest is based on the fact that orthoesters typically undergo facile acid-catalyzed rearrangement, in which the alkoxy group is transferred to the anomeric centre, resulting in the formation of the glycosidic products (Scheme 1).[11]



Scheme 1.

The interesting reactivity of NPOEs have been well utilized in the pioneering works of Fraser-Reid and co-workers in synthesizing oligosaccharides of biological importance.[12] For example, NPOEs have been used for the preparation of the oligosaccharide portion of the viral coat of HIV1, known as GP-120,[13] and in the preparation of glycolipids for multivalent presentation (Fig. 1).[14] Synthesis of lipoarabinomannan component of the cell wall of *Mycobacterium tuberculosis* using NPOE donors have also been achieved by Fraser-Reid et al.[15] Very recently, Seeberger et al. have explored the utility of 1,2-orthoesters as important precursors for the synthesis of glycosylphosphates (Scheme 2).[16]

As part of our program on the synthesis of neoglycoconjugates for pharmaceutical applications, we have been interested in utilizing 1,2-orthoesters of carbohydrates as monomers for oligosaccharide synthesis. In this context, we have previously reported a facile method for the synthesis of 1,2-orthoesters of carbohydrates in [bmim]PF_6 without quaternary ammonium

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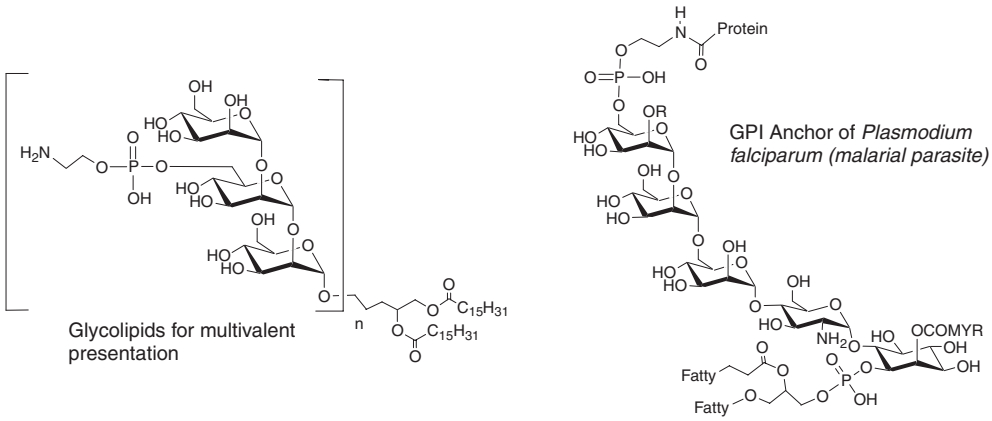
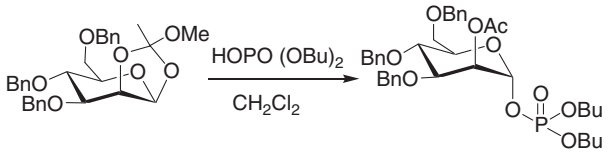
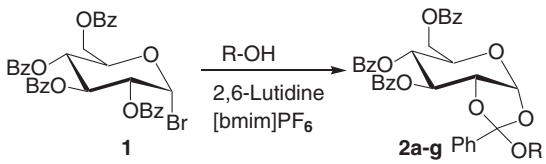


Fig. 1. Some NPOE derived oligosaccharides.



Scheme 2.



Scheme 3.

salts as promoters.[17] The details of this work and the glycosidation reactions of NPOEs in ionic liquid are presented in this paper. To the best of our knowledge this is the first report on the glycosidation of NPOEs in an ionic liquid.

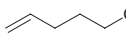
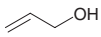
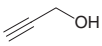
Results and Discussion

Synthesis of 1,2-Orthoesters in [bmim]PF_6. The classical method for the preparation of orthoesters involves refluxing the anomeric bromide in dry dichloromethane with a base-like 2,6-lutidine for five days.[18] The modified method using tetrabutylammonium iodide also requires refluxing the bromide in dry dichloromethane for 24 h. Other methods available for the synthesis of 1,2-orthoesters include the treatment of peracetylated or perbenzoylated glycosyl bromides with quaternary ammonium salts[19] or silver triflate[20] and a base or with alcohol and potassium fluoride.[21] The reaction of 1-hydroxy sugars with tetramethyl-α-chloroenamine and alcohol in presence of triethylamine[22] also results in the formation of orthoesters. These methods suffer from some major drawbacks, like long reaction time, need for dry solvents and cumbersome work-up.

Our studies began with the reaction of perbenzoylated glucopyranosyl bromide with 4-penten-1-ol in presence of 2,6-lutidine in [bmim]PF_6 without using tetrabutylammonium iodide. The reaction proceeded smoothly at room temperature (8 h) affording the glucose NPOE in 80% yield (Scheme 3).

The product was separated from the reaction mixture by extraction with ether and purified by silica-gel column chromatography (if needed). The water and ether insoluble ionic liquid was washed with water, followed by ether, dried in vacuo and reused. Similar results were obtained with various other alcohols, and the results obtained with glucopyranosyl bromide are summarized in Table 1.

Table 1. Synthesis of 1,2-Orthoesters of Glucose in Ionic Liquid

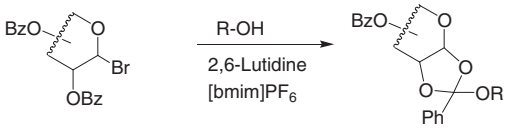
Entry	Alcohol (R–OH)	Yield/%	
1		**2a**	80[a]
2		**2b**	64[a]
3		**2c**	58[a]
4	1-Butanol	**2d**	60[a]
5	Propan-2-ol	**2e**	52[b]
6	Isooctyl alcohol	**2f**	77[b]
7	Benzyl alcohol	**2g**	59[a]

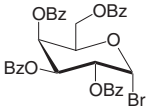
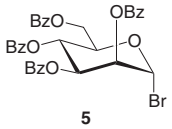
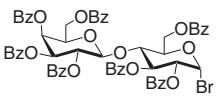
a) Alcohol (1.5 equiv), 2,6-lutidine (2 equiv), [bmim]PF_6, rt, 8 h. b) Alcohol (1.5 equiv), 2,6-lutidine (2 equiv), [bmim]PF_6, 45 °C, 3 h.

To establish the feasibility of this reaction as a general method for the synthesis of 1,2-orthoesters, we prepared galactose, mannose, and lactose orthoesters in the ionic liquid, and the results are summarized in Table 2. The reaction proceeded smoothly without any quaternary ammonium salt as promoter, and it was complete in 8 h at room temperature. At 45 °C, it took only 3 h for completion. However, in the case of lactosyl bromide, the reactions took 8 h at 45 °C for completion. The reaction time was found to be considerably reduced even in the absence of quaternary ammonium salts. This shows that the ionic liquid has the ability to enhance the reaction rate without affecting the yield of the reaction. In some cases, it was found that the yields were better than those obtained from the existing methods. It is noteworthy that the ionic liquid can be reused several times, and purification of the product is also easier.

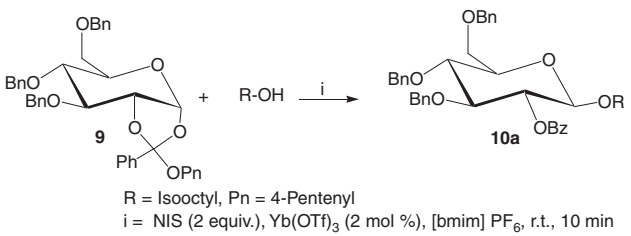
Glycosidation Reactions in Ionic Liquid, [bmim]PF_6. Though trichloroacetimidate,[7] glycosyl phosphates,[8] and fluorides[9] have been utilized in glycosidation reactions in ionic liquids, to the best of our knowledge, there is no report on the use of ionic liquid as a solvent for NPOE-mediated glycosidations. Owing to the increased attention towards NPOEs[11–15] in oligosaccharide synthesis and our sustained interest in using NPOEs

Table 2. Synthesis of 1,2-Orthoesters of Galactose, Mannose, and Lactose in an Ionic Liquid



Entry	Sugar bromide	Alcohol (R–OH)		Yield/%
1			**4a**	75[a]
2			**4b**	68[a]
3		Propan-2-ol	**4c**	69[a]
4	**3**	Isooctyl alcohol	**4d**	82[a]
5			**6a**	70[a]
6			**6b**	90[a]
7		Propan-2-ol	**6c**	59[a]
8	**5**	Isooctyl alcohol	**6d**	53[a]
9		Benzyl alcohol	**6e**	35[b]
10			**8a**	80[b]
11			**8b**	49[b]
12	**7**	Propan-2-ol	**8c**	20[b]
13		Isooctyl alcohol	**8d**	43[b]

a) Alcohol (1.5 equiv), 2,6-lutidine (2 equiv), [bmim]PF_6, rt, 8 h. b) Alcohol (1.5 equiv), 2,6-lutidine (2 equiv), [bmin]PF_6, 45 °C, 8 h.



Scheme 4.

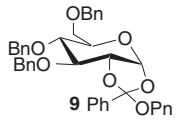
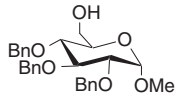
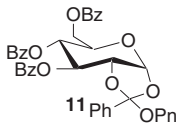
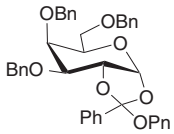
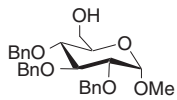
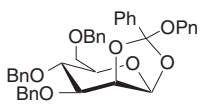
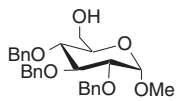
as glycoside donors, we decided to investigate its glycosidation reactions in [bmim]PF_6. Our preliminary experiments involved the reaction of 3,4,6-tribenzyl-NPOE of glucose **9** with isooctyl alcohol. The reaction afforded the corresponding β-glycoside **10a** in 79% yield (Scheme 4).

To prove the generality of the method, we have carried out the coupling reactions of mannose and galactose using NPOE donors with various alcohols including carbohydrate derived alcohol. Results of our investigations are summarized in Table 3.

The configurations of the products were assigned on the basis of the coupling pattern in the proton NMR data. In the case of glucose and galactose-based donors, the β-glycosides were formed exclusively, while the mannose orthoester gave the corresponding α-glycosides. Thus, this method can be efficiently used in the synthesis of oligosaccharides. The recovered ionic liquid was purified and reused for the above experiments.

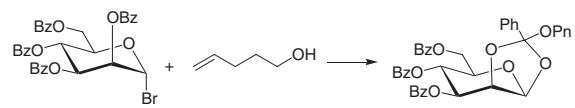
Studies on the Reusability of the Ionic Liquid [bmim]-PF_6. We have carried out experimental studies on the reusability of [bmim]PF_6 in the reactions described above. The results of our investigations in the case of NPOE synthesis and glycosidation reactions are summarized in Tables 4 and 5 respectively. The ionic liquid [bmim]PF_6 was recovered and reused for each cycle, and the isolated yield for each cycle is shown in the tables. As is clear from the results, there is no appreciable change in the yield of the products even after the fifth cycle using the recovered ionic liquid. This clearly establishes the reusability of [bmim]PF_6.

Table 3. Glycosidation of NPOEs with Various Alcohols in Ionic Liquid[a]

Entry	Donor	Acceptor (R–OH)		Yield/%
1		Isooctyl alcohol	**10a**	79
2		2-Adamantanol	**10b**	71
3	**9**		**10c**	62
4		Isooctyl alcohol	**12a**	60
5	**11**	Cyclohexanol	**12b**	84
6		Isooctyl alcohol	**14a**	78
7		Cyclohexanol	**14b**	67
8		2-Adamantanol	**14c**	74
9	**13**		**14d**	82
10		Isooctyl alcohol	**16a**	72
11		Cyclohexanol	**16b**	66
12	**15**		**16c**	77

a) Reaction conditions: donor (2 equiv), acceptor (1 equiv), NIS (2 equiv), $Yb(OTf)_3$ (2 mol %), [bmim]PF_6, rt, 10 min.

Table 4. Synthesis of NPOE of Mannose to Study the Reusability of [bmim]PF_6[a]



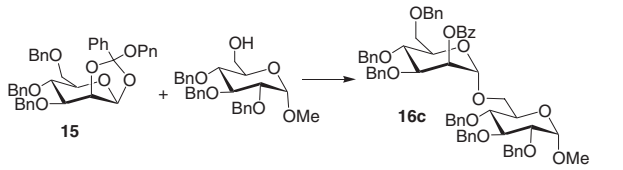
Cycle	1	2	3	4	5
Yield/%	70	70	67	68	67

a) Reaction conditions: alcohol (1.5 equiv), 2,6-lutidine (2 equiv), [bmim]PF_6, rt, 8 h.

Conclusion

In conclusion, we developed a facile and eco-friendly method for the synthesis of 1,2-orthoesters in ionic liquid. Our method did not need quaternary ammonium salts, thus simplifying the reaction. The ionic liquid used as a solvent could be

Table 5. Glycosidation Reactions to Study the Reusability of [bmim]PF_6[a)]



Cycle	1	2	3	4	5
Yield/%	77	76	74	76	74

a) Reaction conditions: donor (2 equiv), acceptor (1 equiv), NIS (2 equiv), $Yb(OTf)_3$ (2 mol %), [bmim]PF_6, rt, 10 min.

reused several times. The reaction is faster and high yielding. We also efficiently performed the glycosidation reactions of NPOEs of carbohydrates in an ionic liquid. Thus, we proved that [bmim]PF_6 can be used as an efficient and recyclable solvent for the synthesis and glycosidation of NPOEs. This method can be applied to the synthesis of oligosaccharides of biological importance.

Experimental

General. All reactions were conducted in oven-dried glassware. Solvents used for the experiments were distilled and dried as specified. All other reagents were purchased from local supplier. All reactions were monitored by TLC (Silica gel 60 F_{254}, 0.25 mm, Merck); visualization was done with UV, by developing in iodine or by staining with McGill solution. Chromatography was performed on a silica-gel column (100–200 mesh). NMR spectra were recorded at 300 (^{1}H) and 75 (^{13}C) MHz respectively on a Bruker Advance DPX-300 MHz. Chemical shifts are reported in δ (ppm) relative to TMS (^{1}H) or $CDCl_3$ (^{13}C) as internal standards. IR spectra were recorded on a Bomem MB series FT-IR spectrometer; absorptions are reported in cm^{-1}. Mass spectra were recorded using JEOL JMS 600H mass spectrometer. Abbreviations used in ^{1}H NMR are: s = singlet, t = triplet, d = doublet, dd = doublet of a doublet, and m = multiplet.

Typical Procedure for the Synthesis of 3,4,6-Tribenzoylglucose Pentenyl Orthoester. 2,3,4,6-Tetra-*O*-benzoyl-α-D-glucopyranosyl bromide (**1**) (0.20 g, 0.30 mmol) was dissolved in [bmim]PF_6 (2 mL). 2,6-Lutidine (0.07 mL, 0.60 mmol) was added to the solution followed by 4-penten-1-ol (0.05 mL, 0.46 mmol). The reaction mixture was stirred at room temperature for 8 h. The reaction mixture was extracted with ether and dried over Na_2SO_4 and the solvent was evaporated off completely. The crude sample on purification by silica-gel column chromatography afforded pure **2a** as a viscous liquid (0.16 g, 80%).

Data for 3,4,6-Tri-*O*-benzoylglucose 4-Pentenyl Orthoester (2a): R_f: 0.29 (25% EtOAc–Hexane). IR (Neat) ν_{max} 3070, 2449, 1740, 1644, 1612, 1460, 1275, 1109, 976, 925, 708 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06–7.24 (m, 20H), 6.01 (d, 1H, J = 5.2 Hz), 5.84–5.67 (m, 3H), 5.47 (d, 1H, J = 8.7 Hz), 4.97 (d, 1H, J = 1.5 Hz), 4.92 (d, 1H, J = 1.3 Hz), 4.74 (dd, 1H, J_1 = 3.4 Hz, J_2 = 7.2 Hz), 4.51 (dd, 1H, J_1 = 4.8 Hz, J_2 = 12.0 Hz), 4.14–4.10 (m, 1H), 3.37–3.29 (m, 2H), 2.09–2.01 (m, 2H), 1.62–1.57 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.7, 164.9, 164.4, 137.7, 135.5, 133.5, 133.3, 132.8, 129.9, 129.8, 129.7, 129.6, 129.5, 129.1, 129.0, 128.5, 128.3, 128.2, 128.1, 126.3, 121.2, 120.0, 115.0, 97.4, 72.1, 69.2, 68.5, 67.4, 63.9, 63.3, 30.1, 28.6. LR-FAB-MS: Calcd for $C_{39}H_{36}O_{10}$: 664.23; Found: 579.82 ($M^+ - C_5H_9O$).

Data for 3,4,6-Tri-*O*-benzoylglucose Allyl Orthoester (2b): R_f: 0.27 (25% EtOAc–Hexane). IR (Neat) ν_{max} 2351, 1722, 1547, 1511, 1264, 1099, 1022, 713 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08–7.36 (m, 20H), 6.04 (d, 1H, J = 5.3 Hz), 5.84–5.81 (m, 1H), 5.79–5.74 (m, 2H), 5.48 (d, 1H, J = 8.7 Hz), 5.31 (dd, 1H, J_1 = 4 Hz, J_2 = 9.9 Hz), 5.09 (d, 2H, J = 10.4 Hz), 4.39 (d, 2H, J = 3.3 Hz), 4.14 (dd, 1H, J_1 = 3.3 Hz, J_2 = 8.3 Hz), 3.83 (dd, 1H, J_1 = 6.3 Hz, J_2 = 7.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8, 164.9, 164.4, 157.6, 136.4, 133.7, 132.9, 130.1, 128.5, 126.4, 120.1, 116.7, 97.5, 72.7, 70.6, 69.2, 68.5, 67.5, 64.0, 24.4. LR-FAB-MS: Calcd for $C_{37}H_{32}O_{10}$: 636.20; Found: 579.82 ($M^+ - C_3H_5O$).

Data for 3,4,6-Tri-*O*-benzoylglucose 2-Propargyl Orthoester (2c): R_f: 0.15 (25%, EtOAc–Hexane). IR (Neat) ν_{max} 2351, 1735, 1624, 1352, 1511, 1454, 1253, 881, 707, 517 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00–7.32 (m, 20H), 5.99 (d, 1H, J = 5.3 Hz), 5.41 (d, 1H, J = 8.7 Hz), 4.78 (d, 1H, J = 1.9 Hz), 4.47 (dd, 1H, J_1 = 2.8 Hz, J_2 = 9.4 Hz), 4.30 (dd, 1H, J_1 = 4.8 Hz, J_2 = 12.0 Hz), 4.06 (m, 2H), 3.89 (s, 2H), 2.06 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.7, 165.0, 134.4, 134.2, 133.6, 132.9, 130.0, 129.9, 126.5, 121.1, 97.7, 79.2, 73.9, 72.1, 69.0, 68.4, 67.5, 63.9, 52.3. LR-FAB-MS: Calcd for $C_{37}H_{30}O_{10}$: 634.18; Found: 579.82 ($M^+ - C_3H_3O$).

Data for 3,4,6-Tri-*O*-benzoylglucose Butyl Orthoester (2d): R_f: 0.37 (25% EtOAc–Hexane). IR (Neat) ν_{max} 2351, 1728, 1624, 1451, 1553, 1259, 512 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18–7.32 (m, 20H), 5.95 (d, 1H, J = 5.2 Hz), 5.40 (d, 1H, J = 8.7 Hz), 4.68 (m, 2H), 4.44 (dd, 1H, J_1 = 2.8 Hz, J_2 = 12.0 Hz), 4.29 (dd, 1H, J_1 = 4.8 Hz, J_2 = 12.1 Hz), 4.05 (dd, 1H, J_1 = 3.4 Hz, J_2 = 8.3 Hz), 3.27–3.16 (m, 2H), 1.43–1.38 (m, 2H), 1.27–1.10 (m, 2H), 0.82–0.75 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.3, 164.8, 164.5, 133.6, 133.4, 132.8, 130.1, 129.9, 129.7, 129.6, 128.5, 128.4, 128.35, 128.3, 128.2, 126.4, 97.5, 72.1, 69.3, 68.6, 67.5, 64.0, 52.0, 31.5, 19.2, 13.8. LR-FAB-MS: Calcd for $C_{38}H_{36}O_{10}$: 652.23; Found: 579.81 ($M^+ - C_4H_9O$).

Data for 3,4,6-Tri-*O*-benzoylglucose Isopropyl Orthoester (2e): R_f: 0.29 (25% EtOAc–Hexane). IR (Neat) ν_{max} 2345, 1732, 1624, 1516, 1457, 1253, 1109, 805, 707 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01–7.14 (m, 20H), 6.00 (d, 1H, J = 3.6 Hz), 5.66 (m, 1H), 5.39 (m, 1H), 4.68 (m, 1H), 4.42 (dd, 1H, J_1 = 2.6 Hz, J_2 = 11.9 Hz), 4.27 (dd, 1H, J_1 = 4.8 Hz, J_2 = 12.0 Hz,), 4.03–3.98 (m, 1H), 3.61 (m, 1H), 1.02 (d, 3H, J = 6.1 Hz), 0.95 (d, 3H, J = 6.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8, 165.1, 164.5, 136.5, 136.3, 133.6, 133.4, 132.8, 130.0, 129.9, 129.7, 129.6, 129.5, 128.5, 128.4, 128.3, 128.2, 97.4, 69.3, 68.6, 67.4, 67.2, 63.9, 32.0, 29.7, 24.3, 23.2. LR-FAB-MS: Calcd for $C_{37}H_{34}O_{10}$: 638.22; Found: 579.82 ($M^+ - C_3H_7O$).

Data for 3,4,6-Tri-*O*-benzoylglucose Isooctyl Orthoester (2f): R_f: 0.39 (25% EtOAc–Hexane). IR (Neat) ν_{max} 2959, 2925, 2856, 2346, 1722, 1542, 1511, 1449, 1253, 1104, 707, 507 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01–7.32 (m, 20H), 5.93 (d, 1H, J = 5.1 Hz), 4.66 (d, 2H, J = 3.0 Hz), 4.43 (m, 1H), 4.28 (dd, 1H, J_1 = 4.7 Hz, J_2 = 12.0 Hz), 4.13 (m, 1H), 3.43 (d, 1H, J = 4.1 Hz), 3.14–3.04 (m, 2H), 1.27–1.20 (m, 15H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8, 165.0, 164.4, 135.6, 133.7, 132.8, 130.0, 129.6, 129.4, 129.0, 128.5, 126.3, 97.4, 72.1, 69.2, 68.5, 66.1, 63.9, 41.9, 39.3, 30.2, 28.8, 23.6, 23.3, 22.9, 14.1, 10.9. LR-FAB-MS: Calcd for $C_{42}H_{44}O_{10}$: 708.29; Found: 579.69 ($M^+ - C_8H_{17}O$).

Data for 3,4,6-Tri-*O*-benzoylglucose Benzyl Orthoester (2g): R_f: 0.30 (25% EtOAc–Hexane). IR (Neat) ν_{max} 3063,

2625, 2360, 1728, 1607, 1452, 1276, 1182, 1115, 1034, 987 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.08–7.39 (m, 25H), 6.03 (d, 1H, $J = 5.2$ Hz), 5.49 (m, 1H), 4.78 (d, 2H, $J = 3.0$ Hz), 4.66 (s, 2H), 4.53 (dd, 1H, $J_1 = 9.3$ Hz, $J_2 = 12.1$ Hz), 4.38 (dd, 1H, $J_1 = 6.2$ Hz, $J_2 = 10.9$ Hz), 4.17 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8, 165.1, 164.5, 137.1, 135.2, 133.6, 132.9, 130.06, 129.9, 129.1, 128.4, 126.5, 121.4, 97.6, 72.2, 69.2, 68.5, 67.5, 66.4, 63.9. LR-FAB-MS: Calcd for $C_{41}H_{34}O_{10}$: 686.22; Found: 579.78 ($M^+ - C_7H_7O$).

Data for 3,4,6-Tri-*O*-benzoylgalactose 4-Pentenyl Orthoester (4a): R_f: 0.37 (25% EtOAc–Hexane). IR (Neat) ν_{max} 2917, 1723, 1452, 1269, 1091, 708, 496 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.10–7.21 (m, 20H), 6.19 (d, 1H, $J = 5.0$ Hz), 5.92–5.75 (m, 2H), 5.74–5.69 (m, 1H), 5.54 (dd, 1H, $J_1 = 4.2$ Hz, $J_2 = 5.9$ Hz), 4.93 (m, 2H), 4.76 (m, 2H), 4.62–4.59 (m, 1H), 4.37 (dd, 1H, $J_1 = 5.0$ Hz, $J_2 = 10.7$ Hz), 3.40 (m, 2H), 1.63–1.57 (m, 2H), 1.27–1.24 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.5, 165.2, 137.9, 136.6, 133.5, 133.3, 133.1, 129.86, 129.8, 129.7, 129.5, 129.4, 129.1, 128.5, 128.5, 128.4, 128.35, 128.3, 126.0, 120.2, 114.9, 98.2, 73.7, 72.0, 70.1, 68.8, 66.5, 63.1, 62.3, 30.2, 29.7. LR-FAB-MS: Calcd for $C_{39}H_{36}O_{10}$: 664.23; Found: 579.81 ($M^+ - C_5H_9O$).

Data for 3,4,6-Tri-*O*-benzoylgalactose Allyl Orthoester (4b): R_f: 0.29 (25% EtOAc–Hexane). IR (Neat) ν_{max} 2917, 2366, 1721, 1452, 1263, 1086, 708 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.97–7.35 (m, 20H), 6.21 (d, 1H, $J = 5.0$ Hz), 5.98–5.96 (m, 1H), 5.92–5.80 (m, 2H), 5.56 (dd, 1H, $J_1 = 4.3$ Hz, $J_2 = 5.1$ Hz), 5.12 (d, 2H, $J = 10.5$ Hz), 4.79 (dd, 1H, $J_1 = 7.1$ Hz, $J_2 = 12.3$ Hz), 4.64–4.50 (m, 1H), 4.38 (dd, 1H, $J_1 = 4.9$ Hz, $J_2 = 10.6$ Hz), 3.93 (d, 2H, $J = 4.9$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.2, 164.9, 164.3, 136.3, 133.8, 133.5, 133.3, 133.1, 129.83, 129.8, 129.7, 129.6, 129.4, 129.1, 128.9, 128.5, 128.37, 128.3, 126.1, 125.9, 120.3, 116.7, 98.5, 98.2, 73.4, 70.1, 68.9, 66.5, 64.9, 62.35, 29.7. LR-FAB-MS: Calcd for $C_{37}H_{32}O_{10}$: 636.20; Found: 579.80 ($M^+ - C_3H_5O$).

Data for 3,4,6-Tri-*O*-benzoylgalactose Isopropyl Orthoester (4c): R_f: 0.30 (25% EtOAc–Hexane). IR (Neat) ν_{max} 2920, 1725, 1630, 1587, 1517, 1459, 1110, 808, 702 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.02–7.20 (m, 20H), 6.03 (d, 1H, $J = 5.0$ Hz), 5.60–5.57 (m, 1H), 5.27 (m, 2H), 4.82 (dd, 1H, $J_1 = 7.2$ Hz, $J_2 = 12.4$ Hz), 4.63–4.51 (m, 1H), 4.35 (dd, 1H, $J = 4.9, 10.8$ Hz), 3.59 (m, 1H), 1.05 (d, 3H, $J = 6.1$ Hz), 1.01 (d, 3H, $J = 6.1$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8, 165.7, 165.32, 136.6, 136.3, 136.0, 133.4, 132.8, 130.0, 129.9, 129.8, 129.7, 129.5, 128.9, 128.5, 128.4, 128.3, 128.2, 127.9, 98.8, 70.0, 68.9, 66.6, 65.1, 65.0, 62.6, 32.0, 29.7, 24.5, 23.3. LR-FAB-MS: Calcd for $C_{37}H_{34}O_{10}$: 638.22; Found: 579.78 ($M^+ - C_3H_7O$).

Data for 3,4,6-Tri-*O*-benzoylgalactose Isooctyl Orthoester (4d): R_f: 0.16 (25% EtOAc–Hexane). IR (Neat) ν_{max} 2923, 1721, 1595, 1446, 1263, 1091, 1017, 771, 702 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.10–7.21 (m, 20H), 6.08 (d, 1H, $J = 5.0$ Hz), 5.83 (d, 1H, $J = 3.4$ Hz), 5.64 (dd, 1H, $J_1 = 3.5$ Hz, $J_2 = 12.0$ Hz), 4.90–4.87 (m, 1H), 4.63–4.59 (m, 2H), 4.35–4.32 (m, 1H), 3.62 (t, 2H, $J = 6.5$ Hz), 1.40–0.86 (m, 15H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8, 165.5, 165.4, 136.9, 133.3, 133.1, 133.0, 130.0, 129.9, 129.9, 129.8, 129.7, 129.5, 129.4, 128.7, 128.6, 128.34, 128.2, 120.5, 117.5, 98.2, 90.7, 69.9, 69.6, 68.5, 66.5, 62.4, 42.3, 38.4, 29.8, 23.9, 14.2, 10.4. LR-FAB-MS: Calcd for $C_{42}H_{44}O_{10}$: 708.29; Found: 579.82 ($M^+ - C_8H_{17}O$).

Data for 3,4,6-Tri-*O*-benzoylmannose NPOE (6a): R_f: 0.38 (25% EtOAc–Hexane). IR (Neat) ν_{max} 2935, 2357, 1721, 1447, 1263, 1092, 702 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.01–7.27 (m, 20H), 5.75 (d, 1H, $J = 2.9$ Hz), 5.71–5.60 (m, 1H), 5.02 (m, 1H), 4.94–4.82 (m, 1H), 4.49 (dd, 1H, $J_1 = 3.2$ Hz, $J_2 = 11.9$ Hz), 4.33 (dd, 1H, $J_1 = 4.6$ Hz, $J_2 = 12.0$ Hz), 4.07 (dd, 1H, $J_1 = 3.7$ Hz, $J_2 = 10.6$ Hz), 3.48–3.45 (m, 2H), 3.43–3.35 (m, 1H), 2.06–2.01 (m, 2H), 1.64–1.55 (m, 2H), 1.28–1.16 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9, 165.6, 165.1, 137.8, 136.6, 133.4, 133.3, 132.9, 130.1, 129.8, 129.7, 129.2, 128.9, 128.5, 128.4, 128.2, 128.1, 127.6, 127.0, 126.5, 122.8, 115.0, 97.9, 72.2, 71.1, 66.5, 65.3, 63.4, 63.1, 30.1, 29.7. LR-FAB-MS: Calcd for $C_{39}H_{36}O_{10}$: 664.23; Found: 579.82 ($M^+ - C_5H_9O$).

Data for 3,4,6-Tri-*O*-benzoylmannose Allyl Orthoester (6b): R_f: 0.32 (25% EtOAc–Hexane). IR (Neat) ν_{max} 2917, 2356, 1723, 1452, 508 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.01–7.25 (m, 20H), 5.86 (m, 1H), 5.78 (d, 1H, $J = 2.7$ Hz), 5.65 (d, 2H, $J = 3.9$ Hz), 5.04 (m, 1H), 4.51 (dd, 1H, $J_1 = 3.2$ Hz, $J_2 = 11.5$ Hz), 4.35 (m, 2H), 4.12–4.08 (m, 1H), 3.90 (d, 2H, $J = 5.1$ Hz), 3.45 (dd, 1H, $J_1 = 6.4$ Hz, $J_2 = 13.9$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9, 133.8, 133.4, 133.3, 132.8, 130.1, 129.8, 129.75, 129.7, 129.4, 129.1, 128.9, 128.4, 128.3, 128.2, 126.6, 122.9, 116.8, 98.0, 83.9, 72.3, 71.0, 65.5, 63.1, 32.0, 29.7. LR-FAB-MS: Calcd for $C_{37}H_{32}O_{10}$: 636.20; Found: 579.82 ($M^+ - C_3H_5O$).

Data for 3,4,6-Tri-*O*-benzoylmannose Isopropyl Orthoester (6c): R_f: 0.29 (25% EtOAc–Hexane). IR (Neat) ν_{max} 2917, 2849, 2356, 1716, 1458, 1269, 1086 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.01–7.23 (m, 20H), 5.74 (d, 1H, $J = 3.0$ Hz), 5.62 (dd, 1H, $J_1 = 3.6$ Hz, $J_2 = 10.0$ Hz), 5.04 (t, 1H, $J = 3.4$ Hz), 4.47 (dd, 1H, $J_1 = 3.4$ Hz, $J_2 = 12.0$ Hz), 4.31 (dd, 1H, $J_1 = 4.8$ Hz, $J_2 = 12.0$ Hz), 4.09–4.01 (m, 2H), 3.73 (m, 1H), 1.07 (d, 3H, $J = 6.1$ Hz), 1.03 (d, 3H, $J = 6.1$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8, 165.7, 165.0, 145.4, 137.3, 133.3, 133.2, 132.8, 130.1, 129.9, 129.8, 129.25, 129.2, 128.47, 128.4, 128.2, 128.1, 126.6, 124.3, 123.6, 123.0, 119.2, 97.9, 75.7, 72.4, 71.2, 67.3, 66.8, 63.3, 23.5, 23.4. LR-FAB-MS: Calcd for $C_{37}H_{34}O_{10}$: 638.25; Found: 579.81 ($M^+ - C_3H_7O$).

Data for 3,4,6-Tri-*O*-benzoylmannose Isooctyl Orthoester (6d): R_f: 0.39 (30% EtOAc–Hexane). IR (Neat) ν_{max} 3070, 2968, 2939, 2866, 1737, 1718, 1601, 1543, 1455, 1363, 1270, 1178, 1095, 1022, 978, 891, 793, 764, 706 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.03–7.27 (m, 20H), 5.93 (t, 1H, $J = 10.2$ Hz), 5.78 (d, 1H, $J = 2.6$ Hz), 5.65 (dd, 1H, $J_1 = 10.0$ Hz, $J_2 = 3.9$ Hz), 5.04 (t, 1H, $J = 3.0$ Hz), 4.50 (dd, 1H, $J_1 = 12.1$ Hz, $J_2 = 3.4$ Hz), 4.35 (dd, 1H, $J_1 = 12.1$ Hz, $J_2 = 6.0$ Hz), 4.13–4.07 (m, 1H), 3.25–3.23 (m, 2H), 1.30–1.16 (m, 8H), 0.83–0.74 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 165.9, 165.1, 136.7, 133.4, 133.3, 132.9, 130.1, 129.8, 129.7, 129.2, 129.1, 129.0, 128.4, 128.2, 128.1, 126.5, 122.8, 97.9, 76.0, 72.3, 71.2, 66.6, 66.1, 63.2, 39.6, 39.4, 31.5, 30.3, 29.7, 29.0, 28.9, 23.7, 23.6, 22.9, 14.1, 10.9, 10.8. LR-FAB-MS: Calcd for $C_{42}H_{44}O_{10}$: 708.29; Found: 731.43 $(M + Na)^+$.

Data for 3,4,6-Tri-*O*-benzoylmannose Benzyl Orthoester (6e): R_f: 0.39 (30% EtOAc–Hexane). IR (Neat) ν_{max} 3070, 2963, 1731, 1716, 1605, 1548, 1494, 1460, 1275, 1182, 1109, 1071, 1032, 978, 852, 798, 710 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.01–7.19 (m, 25H), 5.90 (t, 1H, $J = 9.5$ Hz), 5.77 (d, 1H, $J = 3.0$ Hz), 5.64 (dd, 1H, $J_1 = 10.0$ Hz, $J_2 = 3.9$ Hz), 5.01 (t, 1H, $J = 3.5$ Hz), 4.53 (dd, 1H, $J_1 = 15.4$ Hz, $J_2 = 3.4$ Hz), 4.43 (d, 2H, $J = 3.3$ Hz), 4.35 (dd, 1H, $J_1 = 12.1$ Hz, $J_2 = 4.8$ Hz), 4.14–4.07 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 165.8, 165.1, 137.3, 136.3, 133.4, 133.3, 132.9, 130.0, 129.73, 129.7, 129.6, 129.4, 128.94, 128.9, 128.4, 128.3, 127.64, 127.6, 126.6, 122.9, 98.0, 76.1, 72.2, 70.9, 66.5, 63.1. LR-FAB-MS: Calcd for

$C_{41}H_{34}O_{10}$: 686.22; Found: 709.52 $(M + Na)^+$.

Data for 3,6,2′,3′,4′,6′-Hexa-*O*-benzoyllactose 4-Pentenyl Orthoester (8a): R_f: 0.37 (30% EtOAc–Hexane) IR (Neat) ν_{max} 3070, 2944, 2666, 2545, 2097, 1971, 1918, 1737, 1713, 1698, 1649, 1542, 1494, 1455, 1314, 1265, 1173, 1100, 1027, 969, 910, 847, 774, 706 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.13–7.09 (m, 35H), 6.10 (d, 1H, $J = 2.6$ Hz), 6.00 (d, 1H, $J = 3.0$ Hz), 5.95–5.87 (m, 2H), 5.75–5.69 (m, 1H), 5.60 (dd, 1H, $J_1 = 10.5$ Hz, $J_2 = 3.6$ Hz), 5.12 (d, 1H, $J = 8.1$ Hz), 5.00–4.90 (m, 2H), 4.67–4.62 (m, 2H), 4.47–4.37 (m, 2H), 4.14–4.10 (m, 3H), 3.80 (d, 1H, $J = 9.0$ Hz), 3.43–3.40 (m, 1H), 3.26–3.23 (m, 1H), 2.10–2.05 (m, 2H), 1.66–1.61 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9, 165.7, 165.6, 165.5, 165.1, 164.7, 137.9, 133.6, 133.5, 130.1, 130.0, 129.86, 129.8, 129.6, 129.5, 129.4, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 121.3, 114.9, 103.0, 97.6, 72.1, 71.8, 71.6, 69.9, 69.7, 68.2, 67.6, 63.6, 62.1, 30.2, 30.0, 28.7, 20.1. LR-FAB-MS: Calcd for $C_{66}H_{58}O_{18}$: 1138.36; Found: 1161.70 $(M + Na)^+$.

Data for 3,6,2′,3′,4′,6′-Hexa-*O*-benzoyllactose Allyl Orthoester (8b): R_f: 0.34 (30% EtOAc–Hexane). IR (Neat) ν_{max} 3070, 2934, 1727, 1649, 1542, 1455, 1265, 1173, 1095, 1022, 968, 769, 706 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.11–7.09 (m, 35H), 6.10 (d, 1H, $J = 2.5$ Hz), 5.99 (d, 1H, $J = 3.1$ Hz), 5.95–5.94 (m, 1H), 5.90–5.87 (m, 1H), 5.85–5.80 (m, 1H), 5.60 (dd, 1H, $J_1 = 10.4$ Hz, $J_2 = 3.3$ Hz), 5.25 (dd, 1H, $J_1 = 17.2$ Hz, $J_2 = 1.5$ Hz), 5.15–5.10 (m, 2H), 4.69–4.63 (m, 2H), 4.48–4.39 (m, 2H), 4.14–4.08 (m, 3H), 3.93–3.91 (m, 1H), 3.83–3.79 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9, 165.7, 165.6, 164.9, 157.8, 136.8, 135.1, 134.1, 133.7, 133.5, 133.4, 133.1, 132.9, 130.3, 130.1, 130.0, 129.9, 129.8, 129.7, 129.56, 129.5, 129.1, 128.9, 128.7, 128.6, 128.5, 128.3, 127.8, 127.2, 127.1, 127.0, 126.4, 121.6, 120.5, 116.9, 103.3, 98.0, 77.7, 72.2, 72.0, 70.1, 69.9, 68.5, 67.8, 65.6, 63.5, 62.4, 29.9. LR-FAB-MS: Calcd for $C_{64}H_{54}O_{18}$: 1110.33; Found: 1133.69 $(M + Na)^+$.

Data for 3,6,2′,3′,4′,6′-Hexa-*O*-benzoyllactose Isopropyl Orthoester (8c): R_f: 0.29 (30% EtOAc–Hexane). IR (Neat) ν_{max} 3066, 2973, 2929, 2861, 1971, 1913, 1728, 1621, 1601, 1577, 1489, 1450, 1348, 1265, 1173, 1100, 1066, 1022, 968, 847, 789, 764, 706 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.11–7.12 (m, 35H), 6.07 (d, 1H, $J = 2.5$ Hz), 5.98 (d, 1H, $J = 3.0$ Hz), 5.88 (d, 1H, $J = 2.1$ Hz), 5.57 (dd, 1H, $J_1 = 10.4$ Hz, $J_2 = 3.4$ Hz), 5.12 (d, 1H, $J = 8.1$ Hz), 4.68–4.58 (m, 2H), 4.47–4.41 (m, 1H), 4.34–4.30 (m, 1H), 4.13–4.03 (m, 3H), 3.78–3.65 (m, 3H), 1.13 (d, 3H, $J = 6.1$ Hz), 1.04 (d, 3H, $J = 6.2$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.5, 165.4, 165.1, 164.9, 164.5, 133.4, 133.2, 132.9, 132.7, 130.1, 129.9, 129.8, 129.7, 129.6, 129.5, 129.3, 128.9, 128.7, 128.5, 128.4, 128.3, 128.1, 126.9, 126.8, 102.8, 97.6, 71.8, 71.6, 70.0, 69.7, 68.3, 67.3, 63.2, 62.1, 24.7, 23.6, 23.2. LR-FAB-MS: Calcd for $C_{64}H_{56}O_{18}$: 1112.35; Found: 1135.53 $(M + Na)^+$.

Data for 3,6,2′,3′,4′,6′-Hexa-*O*-benzoyllactose Isooctyl Orthoester (8d): R_f: 0.38 (30% EtOAc–Hexane). IR (Neat) ν_{max} 3070, 2959, 2929, 2871, 1971, 1917, 1732, 1601, 1514, 1494, 1450, 1270, 1178, 1100, 1071, 1027, 973, 857, 793, 769, 710 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.12–7.12 (m, 35H), 6.07 (d, 1H, $J = 2.6$ Hz), 5.99 (d, 1H, $J = 3.0$ Hz), 5.94–5.86 (m, 2H), 5.58 (dd, 1H, $J_1 = 10.4$ Hz, $J_2 = 3.3$ Hz), 5.10 (d, 1H, $J = 8.0$ Hz), 4.68–4.59 (m, 2H), 4.46–4.41 (m, 1H), 4.34–4.32 (m, 1H), 4.14–4.10 (m, 3H), 3.82 (d, 1H, $J = 8.9$ Hz), 3.32–3.25 (m, 1H), 3.17–3.10 (m, 1H), 1.43–1.21 (m, 8H), 0.87–0.78 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 165.5, 165.4, 165.3, 164.9, 164.5, 135.3, 133.4, 133.2, 133.1, 132.8, 132.7, 130.0, 129.8, 129.7, 129.6, 129.58, 129.52, 129.5, 129.4, 129.2, 128.8, 128.6, 128.4, 128.3, 128.2, 128.0, 126.8, 126.6, 121.3, 116.1, 102.9, 97.5, 76.5, 71.7, 71.6, 69.6, 68.2, 67.5, 61.9, 39.5, 30.2, 28.9, 28.8, 23.6, 22.9, 14.0, 10.9. LR-FAB-MS: Calcd for $C_{69}H_{66}O_{118}$: 1182.42; Found: 1205.38 $(M + Na)^+$.

Typical Procedure for the Glycosidation of NPOE of Glucose with Isooctyl Alcohol. Isooctyl alcohol (0.020 g, 0.16 mmol) and the NPOE **9** (0.20 g, 0.32 mmol) in $[bmim]PF_6$ (2 mL) were combined, rotoevaporated twice with dry toluene and then vacuum dried for 3 h. This mixture, cooled with ice, was treated under argon with NIS (0.72 g, 0.32 mmol) followed by catalytic addition of $Yb(OTf)_3$ (2 mg, 2 mol %). After 10 min, TLC showed the reaction to be complete; the mixture was extracted with Et_2O and washed successively with sodium thiosulphate solution and sodium hydrogen carbonate solution. The organic layer was dried over anhydrous Na_2SO_4, and the solvent was removed completely. The crude sample on purification by column chromatography afforded pure **10a** as a viscous liquid (0.084 g, 79%). The 4-pentenyl glycoside (NPG) formed from excess NPOE was also isolated as a viscous liquid (0.063 g, 0.10 mmol).

Data for 2-*O*-Benzoyl-1-*O*-isooctyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (10a): R_f: 0.49 (25% EtOAc–Hexane). IR (Neat) ν_{max} 2928, 1729, 1640, 1449, 1265, 1088, 732, 691 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, 2H, $J = 7.55$ Hz), 7.54 (t, 1H, $J = 7.1$ Hz), 7.44–7.11 (m, 17H), 5.26 (t, 1H; C_2, $J = 8.5$ Hz), 4.82 (d, 1H; C_1, $J = 10.2$ Hz), 4.74–4.56 (m, 6H), 4.45 (dd, 1H, $J_1 = 1.5$ Hz, $J_2 = 7.9$ Hz), 3.84–3.68 (m, 4H), 3.53–3.51 (m, 1H), 3.25 (dd, 1H, $J_1 = 6.4$ Hz, $J_2 = 9.3$ Hz), 1.40–1.09 (m, 9H), 0.75–0.67 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.2, 138.5, 138.3, 138.2, 133.1, 130.5, 130.0, 128.65, 128.6, 128.57, 128.5, 128.2, 128.0, 127.8, 101.8, 83.0, 78.4, 75.6, 75.1, 74.1, 73.8, 72.5, 69.1, 39.7, 30.7, 29.4, 29.0, 23.8, 23.1, 14.3, 11.0. LR-FAB-MS: Calcd for $C_{42}H_{50}O_7$: 666.36; Found: 689.88 $(M + Na)^+$.

Data for 2-*O*-Benzoyl-1-*O*-adamantyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (10b): R_f: 0.47 (25% EtOAc–Hexane). IR (Neat) ν_{max} 2903, 2361, 1721, 1456, 1268, 1099, 1068, 726, 692 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.03 (d, 2H, $J = 7.6$ Hz), 7.53 (t, 1H, $J = 7.2$ Hz), 7.43–7.12 (m, 17H), 5.31–5.27 (m, 1H), 5.10 (s, 1H; C_2), 4.84–4.80 (m, 2H), 4.70–4.50 (m, 6H), 4.26–4.21 (m, 1H), 4.04–3.93 (m, 2H), 3.85–3.66 (m, 1H), 2.00–1.30 (m, 14H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.4, 138.1, 133.7, 132.7, 130.7, 129.7, 128.7, 128.5, 128.4, 127.8, 127.7, 127.65, 127.6, 127.5, 125.9, 99.1 (C_1), 94.3, 79.8, 75.1, 74.7, 73.9, 73.3, 68.9, 38.7, 37.3, 36.4, 36.0, 33.3, 31.4, 30.3, 27.2, 23.7. LR-FAB-MS: Calcd for $C_{44}H_{48}O_7$ 688.34; Found: 711.84 $(M + Na)^+$.

Data for 2,3,4-Tri-*O*-benzyl-1-*O*-methyl-6-*O*-(2-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-α-D-glucopyranoside (10c): R_f: 0.23 (25% EtOAc–Hexane). IR (Neat) ν_{max} 2926, 1724, 1493, 1451, 1360, 1262, 1099, 1024, 735, 697 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, 2H, $J = 7.2$ Hz), 7.55–7.14 (m, 33H), 5.53 (t, 1H, $J = 8.1$ Hz), 5.10 (dd, 1H, $J_1 = 3.5$ Hz, $J_2 = 10.1$ Hz), 4.96 (d, 1H, $J = 10.9$ Hz), 4.88–4.72 (m, 7H), 4.66–4.50 (m, 6H), 4.20 (t, 1H, $J = 9.3$ Hz), 4.16–4.08 (m, 1H), 3.98 (t, 1H, $J = 9.3$ Hz), 3.79–3.59 (m, 6H), 3.53–3.45 (m, 2H), 3.36 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.5, 138.8, 138.3, 137.6, 137.4, 133.0, 129.6, 129.4, 128.9, 128.2, 106.1, 98.3, 90.7, 81.9, 80.0, 79.2, 78.1, 78.0, 77.3, 77.0, 76.5, 75.0, 74.2, 73.4, 70.7, 70.5, 61.8, 55.2, 52.8. LR-FAB-MS: Calcd for $C_{44}H_{48}O_7$: 1000.44; Found: 1023.76 $(M + Na)^+$.

Data for 2,3,4,6-Tetra-*O*-benzoyl-1-*O*-isooctyl-β-D-glucopyranoside (12a): R_f: 0.18 (25% EtOAc–Hexane). IR (Neat)

ν_{max} 2903, 1723, 1452, 1265, 1097, 1071, 729, 693 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, 2H, $J = 7.8$ Hz), 8.0 (d, 2H, $J = 7.7$ Hz), 7.97 (d, 2H, $J = 7.7$ Hz), 7.81 (d, 2H, $J = 7.8$ Hz), 7.59–7.18 (m, 12H), 5.98 (d, 1H, $J = 3.0$ Hz), 5.76 (dd, 1H, $J_1 = 10.5$ Hz, $J_2 = 7.5$ Hz), 5.59 (dd, 1H, $J_1 = 3.3$ Hz, $J_2 = 7.2$ Hz), 4.77–4.67 (m, 2H), 4.43–4.36 (m, 1H), 4.32–4.25 (m, 1H), 3.90 (dd, 1H, $J_1 = 4.8$ Hz, $J_2 = 9.6$ Hz), 3.39–3.34 (m, 1H), 1.27–1.19 (m, 9H), 0.75–0.64 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 166.9, 165.7, 164.7, 133.7, 133.4, 133.3, 130.3, 130.1, 129.9, 129.8, 129.7, 129.6, 129.5, 129.0, 128.6, 128.5, 128.4, 128.35, 128.3, 128.0, 101.3 (C_1), 90.4, 77.7, 71.4, 70.1, 62.1, 30.3, 30.0, 29.3, 28.9, 23.1, 14.3, 11.3. LR-FAB-MS: Calcd for $C_{42}H_{44}O_{10}$: 708.29; Found: 731.68 $(M + Na)^+$.

Data for 2,3,4,6-Tetra-*O*-benzoyl-1-*O*-cyclohexyl-β-D-glucopyranoside (12b): R_f: 0.20 (25% EtOAc–Hexane). IR (Neat) ν_{max} 3067, 2961, 1729, 1600, 1449, 1264, 1108, 708 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.10–7.75 (m, 8H), 7.61–7.26 (m, 12H), 6.24 (t, 1H; C_2, $J = 9.9$ Hz), 5.75–5.70 (m, 2H), 5.29 (dd, 1H, $J_1 = 3.5$ Hz, $J_2 = 10.2$ Hz), 4.67–4.55 (m, 2H), 4.49–4.38 (m, 1H), 3.89 (s, 1H), 2.03–1.23 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 165.8, 165.7, 165.2, 133.8, 133.5, 133.3, 133.1, 130.1, 129.9, 129.82, 129.8, 129.7, 129.6, 129.5, 129.4, 129.1, 129.0, 128.9, 128.7, 128.4, 128.3, 128.2, 98.4 (C_1), 90.4, 74.0, 70.2, 67.5, 62.8, 36.5, 33.4, 32.3, 32.1, 31.0, 29.8. LR-FAB-MS: Calcd for $C_{40}H_{38}O_{10}$: 678.25; Found: 701.36 $(M + Na)^+$.

Data for 2-*O*-Benzoyl-3,4,6-Tri-*O*-benzyl-1-*O*-isooctyl-β-D-galactopyranoside (14a): R_f: 0.48 (25% EtOAc–Hexane). IR (Neat) ν_{max} 2923, 2368, 1726, 1449, 1265, 1092, 732, 691 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, 2H, $J = 7.2$ Hz), 7.60 (t, 1H, $J = 7.2$ Hz), 7.48–7.11 (m, 17H), 5.60 (dd, 1H; C_2, $J_1 = 8.1$ Hz, $J_2 = 10.2$ Hz), 4.97 (d, 1H; C_1, $J = 11.7$ Hz), 4.70–4.54 (m, 3H), 4.50–4.37 (m, 3H), 3.99 (d, 1H, $J = 2.4$ Hz), 3.83–3.75 (m, 2H), 3.72–3.56 (m, 3H), 3.24–3.21 (m, 1H), 1.41–1.10 (m, 9H), 0.76–0.67 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.1, 138.3, 138.1, 137.8, 132.8, 130.4, 129.7, 128.4, 128.3, 128.0, 127.9, 127.6, 127.5, 99.3 (C_1), 81.5, 77.7, 75.3, 74.8, 73.8, 72.2, 72.0, 69.2, 39.2, 30.5, 29.1, 28.6, 23.4, 22.6, 14.2, 11.1. LR-FAB-MS: Calcd for $C_{42}H_{50}O_7$: 666.36; Found: 689.66 $(M + Na)^+$.

Data for 2-*O*-Benzoyl-1-*O*-cyclohexyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranoside (14b): R_f: 0.40 (25% EtOAc–Hexane). IR (Neat) ν_{max} 2934, 2361, 1722, 1527, 1346, 1265, 1065, 803, 694 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, 2H, $J = 7.5$ Hz), 7.56 (t, 1H, $J = 7.5$ Hz), 7.46–7.10 (m, 17H), 5.57 (dd, 1H; C_2, $J_1 = 8.1$ Hz, $J_2 = 9.9$ Hz), 4.97 (d, 1H; C_1, $J = 11.7$ Hz), 4.68–4.60 (m, 2H), 4.53 (d, 1H, $J = 8.1$ Hz), 4.48–4.41 (m, 3H), 3.98 (d, 1H, $J = 2.1$ Hz), 3.68–3.53 (m, 5H), 1.92–1.10 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.7, 133.5, 133.4, 133.1, 130.8, 129.7, 128.6, 128.4, 128.2, 128.0, 127.9, 127.7, 127.64, 127.6, 99.1 (C_1), 81.3, 75.0, 74.4, 73.6, 72.5, 71.6, 68.9, 36.6, 33.6, 32.4, 32.2, 30.9, 28.5. LR-FAB-MS: Calcd for $C_{40}H_{44}O_7$: 636.31; Found: 659.77 $(M + Na)^+$.

Data for 2-*O*-Benzoyl-1-*O*-adamantyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranoside (14c): R_f: 0.45 (25% EtOAc–Hexane). IR (Neat) ν_{max} 2903, 1723, 1452, 1265, 1097, 1071, 728, 693 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, 2H, $J = 7.6$ Hz), 7.53 (t, 1H, $J = 7.3$ Hz), 7.50–7.10 (m, 17H), 5.64 (dd, 1H; C_2, $J_1 = 8.1$ Hz, $J_2 = 9.9$ Hz), 4.98 (d, 1H; C_1, $J = 12$ Hz), 4.71–4.58 (m, 2H), 4.54 (d, 1H, $J = 7.8$ Hz), 4.49–4.41 (m, 3H), 3.99 (d, 1H, $J = 2.4$ Hz), 3.75 (s, 1H), 3.66–3.55 (m, 4H), 2.09–1.67 (m, 10H), 1.43–0.69 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.7, 133.5, 133.4, 133.2, 130.9, 129.7, 128.5, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 99.5 (C_1), 80.8, 74.5, 73.6, 72.4, 71.7, 68.8, 37.7, 37.5, 36.7, 36.3, 34.6, 33.3, 31.1, 31.0, 27.2. LR-FAB-MS: Calcd for $C_{44}H_{48}O_7$: 688.34; Found: 711.79 $(M + Na)^+$.

Data for 2,3,4-Tri-*O*-benzyl-1-*O*-methyl-6-*O*-(2-benzoyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-α-D-glucopyranoside (14d): R_f: 0.25 (25% EtOAc–Hexane). IR (Neat) ν_{max} 2926, 1724, 1493, 1451, 1262, 1099, 735, 697 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, 2H, $J = 7.3$ Hz), 7.46 (t, 1H, $J = 7.4$ Hz), 7.43–7.20 (m, 32H), 5.65 (dd, 1H; C'_2, $J_1 = 9.9$ Hz, $J_2 = 7.9$ Hz), 4.94 (d, 1H; C'_1, $J = 11.5$ Hz), 4.84 (d, 1H, $J = 10.9$ Hz), 4.70–4.55 (m, 6H), 4.48–4.40 (m, 6H), 4.30 (d, 1H, $J = 11.3$ Hz), 4.05 (d, 1H, $J = 9.3$ Hz), 3.82 (t, 1H, $J = 9.2$ Hz), 3.64–3.56 (m, 6H), 3.39–3.28 (m, 2H), 3.15 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.1, 133.5, 133.4, 133.2, 130.9, 129.7, 128.5, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 101.9 (C_1), 98.0, 82.3, 80.1, 79.4, 78.3, 77.3, 76.4, 75.3, 74.9, 74.5, 74.8, 73.8, 71.9, 62.3, 56.3, 52.2. LR-FAB-MS: Calcd for $C_{62}H_{64}O_{12}$: 1000.44; Found: 1023.26 $(M + Na)^+$.

Data for 2-*O*-Benzoyl-3,4,6-tri-*O*-benzyl-1-*O*-isooctyl-α-D-mannopyranoside (16a): R_f: 0.49 (25% EtOAc–Hexane). IR (Neat) ν_{max} 2931, 1728, 1643, 1494, 1263, 1096, 1087, 732, 698, 459 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, 2H, $J = 7.6$ Hz), 7.51 (t, 1H, $J = 7.3$ Hz), 7.49–7.16 (m, 17H), 5.54 (s, 1H), 4.84 (s, 1H; C_1), 4.83–4.70 (m, 3H), 4.56–4.50 (m, 3H), 4.03 (d, 2H, $J = 5.5$ Hz), 3.90–3.66 (m, 4H), 3.34–3.29 (m, 1H), 1.47–1.13 (m, 9H), 0.76–0.65 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.7, 137.6, 133.1, 129.9, 129.8, 128.5, 128.4, 128.3, 128.2, 127.9, 127.5, 127.4, 98.2 (C_1), 77.7, 73.6, 71.6, 71.4, 70.7, 69.9, 68.5, 67.2, 39.6, 32.0, 30.6, 29.2, 23.9, 23.1, 14.2, 11.3. LR-FAB-MS: Calcd for $C_{42}H_{50}O_7$: 666.36; Found: 689.46 $(M + Na)^+$.

Data for 2-*O*-Benzoyl-3,4,6-tri-*O*-benzyl-1-*O*-cyclohexyl-α-D-mannopyranoside (16b): R_f: 0.52 (25% EtOAc–Hexane). IR (Neat) ν_{max} 3030, 2925, 1720, 1605, 1497, 1452, 1358, 1261, 1104, 974, 907, 732 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.98 (d, 2H, $J = 7.5$ Hz), 7.47 (t, 1H, $J = 7.2$ Hz), 7.47–7.11 (m, 18H), 5.56 (s, 1H), 4.96 (s, 1H; C_1), 4.80–4.64 (m, 4H), 4.49–4.44 (m, 3H), 4.08–3.96 (m, 2H), 3.82–3.79 (d, 2H, $J = 6.0$ Hz), 3.67–3.64 (m, 1H), 2.01–1.18 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.5, 138.5, 138.4, 138.0, 133.1, 130.0, 129.9, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 127.5, 127.4, 97.2 (C_1), 78.4, 75.3, 74.3, 73.5, 71.9, 71.6, 69.4, 69.0, 36.6, 33.6, 32.4, 32.2, 31.0, 29.7. LR-FAB-MS: Calcd for $C_{40}H_{44}O_7$: 636.31; Found: 659.68 $(M + Na)^+$.

Data for 2,3,4-Tri-*O*-benzyl-1-*O*-methyl-6-*O*-(2-benzoyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-α-D-glucopyranoside (16c): R_f: 0.40 (25% EtOAc–Hexane). IR (Neat) ν_{max} 3037, 2927, 1724, 1456, 1356, 1277, 1024, 738, 694 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, 2H, $J = 8.1$ Hz), 7.48 (t, 1H, $J = 7.3$ Hz), 7.36–7.16 (m, 32H), 5.61 (s, 1H), 4.98 (d, 2H, $J = 9.6$ Hz), 4.86 (d, 2H, $J = 11.1$ Hz), 4.80–4.73 (m, 3H), 4.70–4.64 (m, 2H), 4.59–4.56 (m, 2H), 4.52–4.42 (m, 3H), 4.04–3.94 (m, 3H), 3.83 (dd, 1H, $J_1 = 3.6$ Hz, $J_2 = 10.9$ Hz), 3.75–3.72 (m, 3H), 3.64 (d, 1H, $J = 11.4$ Hz), 3.54 (dd, 2H, $J_1 = 3.3$ Hz, $J_2 = 9.7$ Hz), 3.43 (t, 1H, $J = 9.5$ Hz), 3.32 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.5, 138.8, 138.6, 138.5, 138.3, 138.2, 137.8, 133.0, 130.1, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.5, 127.4, 98.2 (C'_1), 97.9 (C''_1), 82.1, 80.2, 77.6, 77.5, 77.2, 75.8, 75.2, 74.9, 74.2, 73.4, 71.8, 71.4, 69.8, 68.9, 68.7, 66.2, 55.1. LR-FAB-MS: Calcd for $C_{62}H_{64}O_{12}$: 1000.44; Found: 1023.69 $(M + Na)^+$.

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