Sulfide-Mediated Dehydrative Glycosylation

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Abstract: The development of a new method for glycosylation with 1-hydroxy glycosyl donors employing dialkyl sulfonium reagents is described. The process employs the reagent combination of a dialkyl sulfide and triflic anhydride to effect anomeric bond constructions. This controlled dehydrative coupling of various C(1)-hemiacetal glycosyl donors and nucleophilic acceptors proceeds by way of a sulfide-to-sulfoxide oxidation process in which triflic anhydride serves as the oxidant.

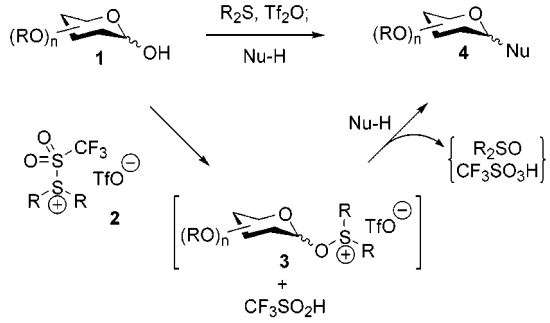
Introduction

The development of new methods for glycosylation has been an intensive area of investigation owing to the varied and important biological functions of complex oligosaccharides and glycoconjugates.[1] The bulk of the efforts in this area have focused on the invention of new methods and reagents for the generation of isolable glycosyl donors which can subsequently undergo anomeric bond formation with a nucleophilic glycosyl acceptor.[2] On the other hand, methods for dehydrative glycosylation with 1-hydroxy glycosyl donors have been the subject of comparatively fewer investigations, despite the fact that this approach combines the operations of anomeric derivatization, anomeric activation, and anomeric bond formation into a one-pot procedure.[3] We report herein a new method for dehydrative glycosylation employing activated sulfide reagents. This coupling method employs an in situ sulfide-to-sulfoxide oxidation process that mediates the dehydrative condensation of 1-hydroxyl glycosyl donors, allowing for the formation of a variety of glycoconjugates.

Results and Discussion

The key to establishing a successful dehydrative glycosylation reaction lies in the development of a suitable reagent for controlled activation of the C(1)-hemiacetal functionality of the glycosyl donor. We have recently established that oxosulfonium reagents derived from the reagent combination of a diaryl sulfoxide and triflic anhydride serve as effective hemiacetal activating agents for anomeric bond construction. It was envisioned that a complementary method for hemiacetal activation would arise from the combination of a dialkyl sulfide reagent (R_2S) and triflic anhydride (Scheme 1), leading to the in situ generation of the thiosulfonium intermediate **2**. Subsequent addition of the hemiacetal donor **1** to **2** would generate an anomeric oxosulfonium intermediate **3** via expulsion of trifluoromethanesulfinic acid (CF_3SO_2H). The resultant glycosyl oxosulfonium species **3** should function as an effective in situ glycosyl donor; consequently, introduction of a nucleophilic acceptor (Nu-H) would lead to displacement of the anomeric sulfoxide (R_2SO) with concomitant formation of the glycosidic bond in **4**.

Scheme 1



It is worth noting that in this process for anomeric bond construction (Scheme 1), the sulfide reagent is also oxidized to the corresponding sulfoxide, with triflic anhydride serving as the oxidant.[4] Such a redox process is certainly plausible, especially in light of the recent work of Balenkova and co-

(1) (a) Dwek, R. A. *Chem. Rev.* **1996**, *96*, 683−720. (b) Bertozzi, C. R.; Kiessling, L. L. *Science* **2001**, *291*, 2357−2364. (c) Helenius, A.; Aebi, M. *Science* **2001**, *291*, 2364−2369.

(2) (a) Toshima, K.; Tatsuta, K. *Chem. Rev.* **1993**, *93*, 1503−1531. (b) Schmidt, R. R.; Kinzy, W. *Adv. Carbohydr. Chem. Biochem.* **1994**, *50*, 21−123. (c) Davis, B. G. *J. Chem. Soc., Perkin Trans. 1* **1999**, 3215−3237. (d) Davis, B. G. *J. Chem. Soc., Perkin Trans. 1* **2000**, 2137−2160. (e) Hinklin, R. J.; Kiessling, L. L. *J. Am. Chem. Soc.* **2001**, *123*, 3379−3380.

(3) (a) Szarek, W. A.; Jarrell, H. C.; Jones, J. K. N. *Carbohydr. Res.* **1977**, *57*, C13−C16. (b) Koto, S.; Sato, T.; Morishima, N.; Zen, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1761−1762. (c) Pavia, A. A.; Ung-Chhun, S. N. *Can. J. Chem.* **1981**, *59*, 482−489. (d) Mukaiyama, T.; Suda, S. *Chem. Lett.* **1990**, 1143−1146. (e) Mukaiyama, T.; Matsubara, K.; Suda, S. *Chem. Lett.* **1991**, 981−984. (f) Inanaga, J.; Yokoyama, Y.; Hanamoto, T. *J. Chem. Soc., Chem. Commun.* **1993**, 1090−1091. (g) Susaki, H. *Chem. Pharm. Bull.* **1994**, *42*, 1917−1918. (h) Uchiro, H.; Mukaiyama, T. *Chem. Lett.* **1996**, 79−80, and references therein. (i) Garcia, B. A.; Poole, J. L.; Gin, D. Y. *J. Am. Chem. Soc.* **1997**, *119*, 7597−7598. (j) Hirooka, M.; Koto, S. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2893−2902. (k) Toshima, K.; Nagai, H.; Matsumura, S. *Synlett* **1999**, 1420−1422. (l) Wakao, M.; Nakai, Y.; Fukase, K.; Kusumoto, S. *Chem. Lett.* **1999**, 27−28. (m) Garcia, B. A.; Gin, D. Y. *J. Am. Chem. Soc.* **2000**, *122*, 4269−4279. (n) Garcia, B. A.; Gin, D. Y. *Org. Lett.* **2000**, *2*, 2135−2138.

(4) For examples of the oxidative properties of triflic anhydride, see: (a) Maas, G.; Stang, P. J. *J. Org. Chem.* **1981**, *46*, 1606−1610. (b) Binkley, R. W.; Ambrose, M. G. *J. Org. Chem.* **1983**, *48*, 1776−1777. (c) Hendrickson, J. B.; Judelson, D. A.; Chancellor, T. *Synthesis* **1984**, 320−322. (d) Creary, X.; Wang, Y. X.; Gill, W. *Tetrahedron Lett.* **1991**, *32*, 729−732. (e) Netscher, T.; Bohrer, P. *Tetrahedron Lett.* **1996**, *37*, 8359−8362. (f) Billard, T.; Langlois, B. R.; Large, S.; Anker, D.; Roidot, N.; Roure, P. *J. Org. Chem.* **1996**, *61*, 7545−7550. (g) Baraznenok, I. L.; Nenajdenko, V. G.; Balenkova, E. S. *Tetrahedron* **2000**, *56*, 3077−3119.

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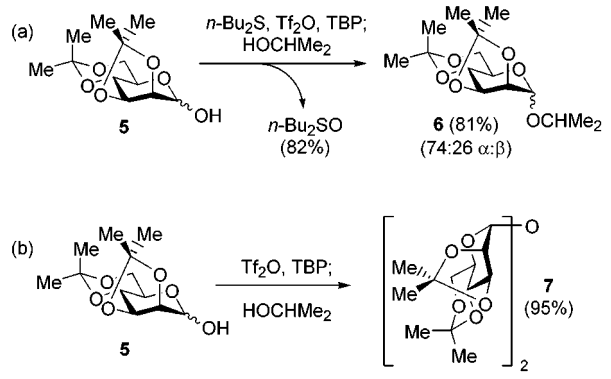
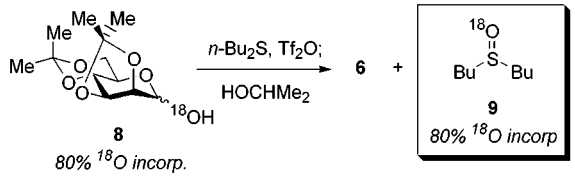
Scheme 2



workers,[5] wherein sulfonium species such as **2** are invoked as intermediates in the triflic anhydride-mediated oxidation of sulfides to sulfoxides.

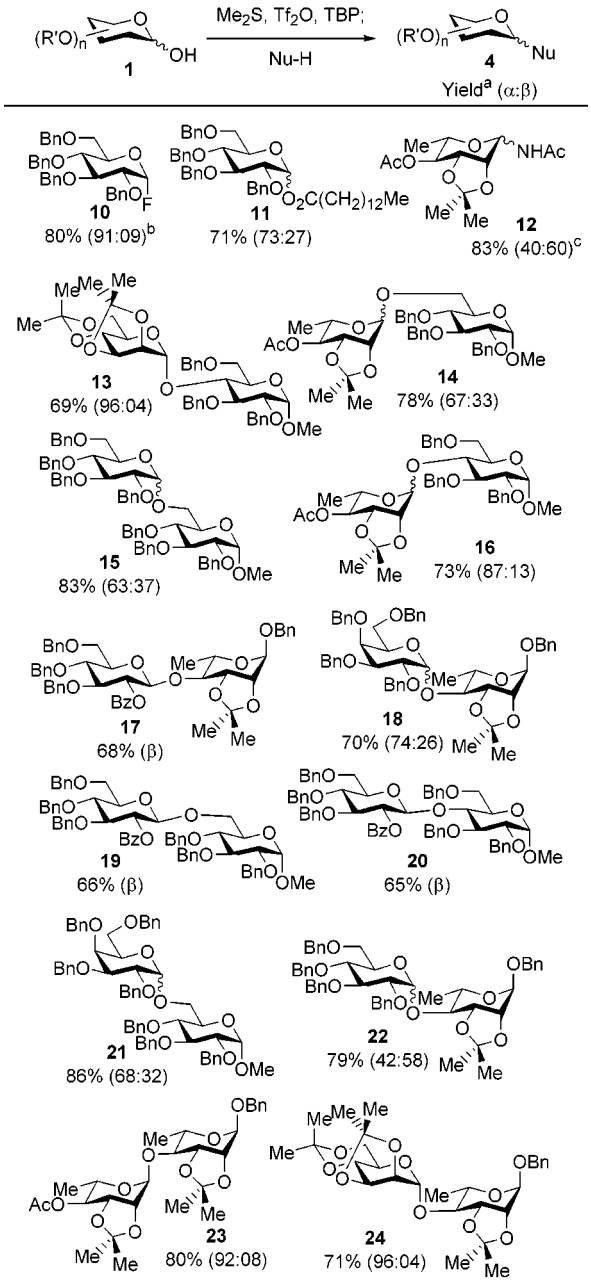
The key model investigations to establish the feasibility of the method outlined in Scheme 1 involved a series of glycosylations of 2-propanol with 2,3,4,6-bis(di-*O*-isopropylidene)-D-mannopyranose[6] (**5**, Scheme 2), employing di-*n*-butyl sulfide and triflic anhydride as the activating agent and 2,4,6-tri-*tert*-butylpyridine (TBP) as an acid scavenger. First, a mixture of the hemiacetal **5** (1 equiv) and Bu_2S (2 equiv) was treated with Tf_2O (1.5 equiv) at −45 °C (Scheme 2a). Subsequent addition of excess 2-propanol (3 equiv) led to the formation of the isopropyl mannopyranoside **6** in 81% yield along with 82% of Bu_2SO, indicating that dehydrative glycosylation proceeds efficiently and that it does so with concomitant oxidation of the sulfide reagent. As a control experiment, a similar dehydrative glycosylation was attempted in the absence of the sulfide reagent (Scheme 2b); however, this led only to the formation of the symmetrical α,α′-1,1′-linked disaccharide **7** in 95% yield. Thus, the rate of self-condensation of hemiacetal **5** with its corresponding glycosyl triflate is greater than that of hemiacetal activation with triflic anhydride alone. This experiment highlights the critical role of the sulfide reagent in this dehydrative glycosylation process.

Scheme 3



During the course of the sulfide oxidation process outlined in Scheme 1, a dehydrative coupling occurs in which the hemiacetal C(1)-oxygen atom of the glycosyl donor is presumed to be transferred to the sulfoxide byproduct. To verify this hypothesis, the glycosylation of 2-propanol was performed with the hemiacetal donor **8** (Scheme 3), incorporating an ^{18}O-label at the hemiacetal hydroxyl (80% ^{18}O incorp.).[7] In the event, the formation of the isopropyl glycoside **6** from **8** proceeded in comparable yield to that of Scheme 2a, with the recovered sulfoxide **9** possessing 80% ^{18}O incorporation. The observed quantitative transfer of ^{18}O from the hemiacetal donor to the sulfoxide byproduct is consistent with the activation pathway proposed in Scheme 1 in which the anomeric oxosulfonium species **3** is the first glycosyl intermediate formed upon hemiacetal activation.

Chart 1[a]



[a] 1.5 equiv of the glycosyl donor was employed with the glycosyl acceptor serving as the limiting reagent. [b] Tetrabutylammonium triphenyldifluorosilicate (TBAT) was employed as the glycosyl acceptor. [c] *N*-TMS-acetamide was employed as the glycosyl acceptor.

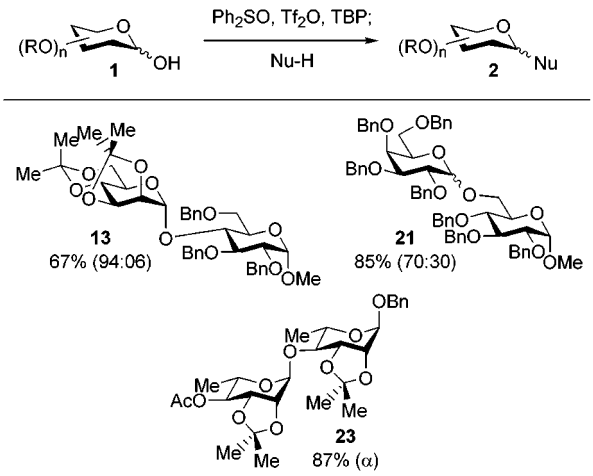
To assess the potential utility of this novel sulfide-mediated dehydrative glycosylation in carbohydrate synthesis, a number of coupling reactions were performed to prepare a variety of glycoconjugates and oligosaccharides (Chart 1). It is worth noting that in the initial exploratory investigations (Schemes 2 and 3), Bu_2S was employed as the sulfide reagent to allow for facile isolation of the sulfoxide byproduct to gain mechanistic insight into the dehydrative coupling process. However, to illustrate the scope of this new dehydrative coupling reaction for generalized glycosylation, dimethyl sulfide is employed as

(5) (a) Nenajdenko, V. G.; Vertelezkij, P. V.; Koldobskij, A. B.; Alabugin, I. V.; Balenkova, E. S. *J. Org. Chem.* **1997**, *62*, 2483−2486. For the preparation of a related thiosulfonium salt, see: (b) Minato, H.; Yamaguchi, K.; Miura, T.; Kobayashi, M. *Chem. Lett.* **1976**, 593−596.

(6) Gelas, J.; Horton, D. *Carbohydr. Res.* **1978**, *67*, 371−387.

(7) Preparation of **8** was accomplished by the glycosylation of 95% $H_2{}^{18}O$ with **5**. See ref 3m.

Chart 2



the sulfide reagent (Chart 1). One advantage of using this volatile sulfide reagent lies in the fact that the sulfoxide byproduct, DMSO, can easily be removed after the oxidation/coupling event by either aqueous partition or evaporation, thereby facilitating purification of the glycoside products.

With the $Me_2S{\cdot}Tf_2O$ reagent combination, the glycosylation reaction is amenable to a variety of nucleophilic acceptors including fluoride, carboxylic acids, and amides. Primary and hindered secondary hydroxyls of carbohydrate nucleophiles are suitable glycosyl acceptors for the preparation of various disaccharides. In addition, the couplings proceed with glycosyl donors incorporating a variety of protective groups, such as alkyl ethers, isopropylidene ketals, and ester functionalities, including C(2)-acyl protective groups that engage in neighboring group participation to generate 1,2-*trans*-linked glycosides. Although DMSO is generated in these reactions, attempts to accurately quantify the DMSO byproduct were difficult due to its volatility, a fact that only underscores the added convenience of employing Me_2S as the sulfide reagent in this dehydrative coupling reaction.

The results arising from the dialkyl sulfide-mediated dehydrative glycosylations are similar to those of our previously reported $Ph_2SO{\cdot}Tf_2O$ glycosylation method. For example, dehydrative glycosylations employing $Ph_2SO{\cdot}Tf_2O$ afford the glycoside products **13**, **21**, and **23** (Chart 2) with efficiencies that are comparable to the corresponding results listed in Chart 1. Nevertheless, the methods are notably distinct in that anomeric bond formation proceeds more rapidly with $Ph_2SO{\cdot}Tf_2O$ compared to that employing $Me_2S{\cdot}Tf_2O$ following hemiacetal activation.[8] In a previous study,[3m] we have established the intermediacy of an anomeric diphenyloxosulfonium species in the Ph_2SO-mediated glycosylation method. It is therefore likely that the relative attenuation in the rate of glycosylation in the Me_2S-mediated coupling arises from the generation of a less reactive anomeric dimethyloxosulfonium intermediate (i.e., **3**, R = Me) as an in situ glycosyl donor.[9] However, it is worth noting that the coupling process is not complicated by Moffatt−Swern oxidation of the hemiacetal donor via ylide generation from **3**. Moreover, the good yields obtained in Chart 1 indicate that Pummerer rearrangement of the sulfonium intermediates is not likely to be a significant competitive pathway. This highlights the opportunity for further development of the method by assessing the influence of dialkyl sulfide structure on anomeric selectivity in dehydrative glycosylation.

(8) Anomeric bond formation with the $Ph_2SO{\cdot}Tf_2O$ reagent combination typically proceeds to completion within a few hours at temperatures between 0 °C and 23 °C (depending on the nature of the coupling partners), whereas glycosylation with $Me_2S{\cdot}Tf_2O$ typically proceeds to completion only after 5−8 h at 23 °C.

(9) Although the ^{18}O-labeling study is consistent with the formation of the anomeric oxosulfonium species **3**, the mechanistic details of the anomeric bond forming event remain in question.

Conclusions

A new method for dehydrative glycosylation is described, employing a dialkyl sulfide reagent and triflic anhydride to induce a controlled dehydrative condensation between a 1-hydroxy glycosyl donor and a nucleophilic acceptor. The reaction involves a novel process for hemiacetal activation and anomeric bond formation with concomitant oxidation of the sulfide species to the corresponding sulfoxide by triflic anhydride. Efforts are currently underway to explore various sulfide structures to modulate anomeric selectivity in the glycosylation reaction as well as to adapt this method to iterative chemoselective dehydrative glycosylation for oligosaccharide synthesis.[10]

Experimental Section

Reagents and Methods. All reactions were performed in flame-dried modified Schlenk (Kjeldahl shape) flasks fitted with a glass stopper or rubber septa under a positive pressure of argon, unless otherwise noted. Air- and moisture-sensitive liquids and solutions were transferred via syringe or stainless steel cannula. Organic solutions were concentrated by rotary evaporation below 30 °C at ca. 25 Torr. Flash column chromatography was performed, employing 230−400 mesh silica gel. Thin-layer chromatography (analytical and preparative) was performed using glass plates precoated to a depth of 0.25 mm with 230−400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Tetrahydrofuran, dichloromethane, toluene, and ether were purified by passage through two packed columns of neutral alumina under an argon atmosphere. Triethylamine and 2-propanol were distilled from calcium hydride at 760 Torr. The carbohydrate hemiacetals and acceptors were dried by azeotropic removal of water with toluene in vacuo prior to use. Trifluoromethanesulfonic anhydride was triply distilled from phosphorus pentoxide. Infrared (IR) spectra were obtained using a Perkin-Elmer Spectrum BX spectrophotometer referenced to a polystyrene standard. Data are presented as frequency of absorption (cm^{-1}). Proton and carbon-13 nuclear magnetic resonance (^1H NMR or ^{13}C NMR) spectra were recorded on a Varian 400, a Varian 500, or a Varian Inova 500 NMR spectrometer; chemical shifts are expressed in parts per million (δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$: δ 7.26; C_6HD_5: δ 7.15). Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or multiple resonances), integration, coupling constant in hertz (Hz) and assignment.

General Glycosylation Procedure with $Me_2S{\cdot}Tf_2O$: Methyl *O*-2,3,4,6-Bis(di-*O*-isopropylidene)-α-D-mannopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (13). Trifluoromethanesulfonic anhydride (34 μL, 0.20 mmol, 1.5 equiv) was added to a solution of 2,3,4,6-bis(di-*O*-isopropylidene)-D-mannopyranose (53 mg, 0.20 mmol, 1.5 equiv), 2,4,6-tri-*tert*-butylpyridine (151 mg, 0.61 mmol, 4.5 equiv), and dimethyl sulfide (20 μL, 0.27 mmol, 2 equiv) in dichloromethane (3 mL) at −45 °C. The resulting mixture was stirred at this temperature for 1 h, then at 0 °C for 15 min, and finally at 23 °C for 15 min. A solution of methyl 2,3,6-tri-*O*-benzyl-D-glucopyranoside[11] (63 mg, 0.13 mmol, 1 equiv) in dichloromethane (3 mL) was then added via cannula. The resulting solution was stirred at 23 °C for 8 h. The reaction mixture was diluted with dichloromethane (200 mL) and was washed sequentially with saturated aqueous sodium bicarbonate solution (2 × 100 mL) and water (100 mL). The organic layer was dried (sodium sulfate), filtered, and concentrated. The residue was purified by silica gel flash chromatography (8% acetonitrile in benzene) to afford the (1→4)-

(10) Nguyen, H. M.; Poole, J. L.; Gin, D. Y. *Angew. Chem., Int. Ed.* **2001**, *40*, 414−417.

(11) DeNinno, M. P.; Etienne, J. B.; Duplantier, K. C. *Tetrahedron Lett.* **1995**, *36*, 669−672.

disaccharide **13** (66 mg, 96:04 α:*β*, 69% total). R_f = 0.48 (9% acetonitrile in benzene); $[\alpha]^{24}_D = +39.1°$ (c = 2.7, $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6) δ 7.49−7.05 (m, 15H, ArH), 5.78 (s, 1H, H-1), 4.98 (d,1 H, J = 10.9 Hz, OBn), 4.80 (d,1 H, J = 10.7 Hz, OBn), 4.69 (s, 2H, OBn), 4.62 (d,1 H, J = 3.4 Hz, H-1′), 4.54 (m,1 H, H-5), 4.51 (d, 1H, J = 5.9 Hz, H-2), 4.47 (dd, 1H, J = 5.6, 3.2 Hz, H-3), 4.44 (d, 1H, J = 11.9 Hz, OBn), 4.37 (d, 1H, J = 11.9 Hz, OBn), 4.23 (dd, 1H, J = 8.5, 5.4 Hz, H-6), 4.18 (t, 1H, J = 9.3 Hz, H-3′), 4.12 (dd, 1H, J = 6.6, 3.2 Hz, H-4), 4.06 (dd, 1H, J = 8.5, 6.3 Hz, H-6), 3.98 (ddd, 1H, J = 10.0, 6.1, 1.5 Hz, H-5′), 3.87 (dd, 1H, J = 10.7, 1.7 Hz, H-6′), 3.78 (dd, 1H, J = 10.7, 6.3 Hz, H-6′), 3.73 (t, 1H, J = 9.0 Hz, H-4′), 3.42 (dd, 1H, J = 9.5, 3.4 Hz, H-2′), 3.18 (s, 3H, OMe), 1.46 (s, 3H), 1.32 (s, 3H), 1.31 (s, 3H), 1.09 (s, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 139.4, 139.1, 139.0, 128.9, 128.6, 128.5, 128.4, 127.8, 127.7, 127.6, 112.5, 109.0, 108.9, 97.9, 86.0, 81.5, 81.4, 81.2, 80.1, 76.2, 75.6, 73.7, 73.6, 72.6, 70.7, 70.5, 66.9, 54.9, 27.2, 26.1, 25.6, 24.8; FTIR (neat film) 2987, 2934, 1454, 1371, 1259, 1210, 1161, 1072, 849, 738, 698 cm^{-1}; HRMS (FAB) *m/z*: Calcd for $C_{40}H_{51}O_{11}Na$ (M + Na) 729.3252, found 729.3251. Anal. Calcd for $C_{40}H_{50}O_{11}$: C, 67.97; H, 7.13. Found: C, 67.63; H, 7.16.

2-Propyl 2,3,4,6-bis(di-*O*-isopropylidene)-D-mannopyranoside (6): α: R_f = 0.44 (9% acetonitrile in benzene); $[\alpha]^{22}_D = +37.4°$ (c = 3.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.08 (s, 1H, H-1), 4.77 (dd, 1H, J = 5.8, 3.6 Hz, H-3), 4.55 (d,1 H, J = 6.0 Hz, H-2), 4.38 (ddd,1 H, J = 7.7, 6.4, 4.5 Hz, H-5), 4.10 (dd, 1 H, J = 8.8, 6.4 Hz, H-6), 4.01 (dd, 1H, J = 8.8, 4.5 Hz, H-6), 3.93 (dd, 1H, J = 7.7, 3.6 Hz, H-4), 3.84 (sept, 1H, J = 6.0 Hz, $CHMe_2$), 1.45 (s, 3H), 1.44 (s, 3H), 1.37 (s, 3H), 1.31 (s, 3H), 1.15 (d, 3H, J = 6.2 Hz), 1.12 (d, 3H, J = 6.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 112.4, 109.2, 104.6, 85.4, 80.1, 79.6, 73.2, 69.2, 66.9, 26.8, 25.8, 25.1, 24.4, 23.4, 21.4; FTIR (neat film) 2980, 2937, 1371, 1261, 1210, 1162, 1117, 1082, 1002, 979, 850 cm^{-1}; HRMS (FAB) *m/z*: Calcd for $C_{15}H_{26}O_6Na$ (M + Na) 325.1628, found 325.1627. *β*: R_f = 0.24 (9% acetonitrile in benzene); $[\alpha]^{22}_D = -27.2°$ (c = 1.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.77 (d, 1H, J = 3.7 Hz, H-1), 4.68 (dd, 1H, J = 6.1, 3.9 Hz, H-3), 4.57 (dd, 1H, J = 6.1, 3.7 Hz, H-2), 4.45 (dt,1 H, J = 7.6, 5.4 Hz, H-5), 4.10−4.05 (m, 2H, H-6), 3.95 (sept, 1H, J = 6.0 Hz, $CHMe_2$), 3.54 (dd,1 H, J = 7.8, 3.9 Hz, H-4), 1.53 (s, 3H), 1.44 (s, 3H), 1.37 (s, 3H), 1.35 (s, 3H), 1.27 (d, 3H, J = 6.1 Hz), 1.21 (d, 3H, J = 6.1 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 113.5, 109.2, 101.2, 79.9, 78.9, 76.7, 73.3, 72.4, 66.9, 26.9, 25.6, 25.3, 25.1, 23.1, 21.8; FTIR (neat film) 2982, 2936, 1370, 1252, 1215, 1123, 1103, 1068, 1017, 974, 847 cm^{-1}; HRMS (FAB) *m/z*: Calcd for $C_{15}H_{26}O_6Na$ (M + Na) 325.1628, found 325.1627.

***O*-2,3,4,6-Bis(di-*O*-isopropylidene)-α-D-mannopyranosyl-(1→1′)-2,3,4,6-bis(di-*O*-isopropylidene)-α-D-mannopyranoside (7):** R_f = 0.38 (17% ethyl acetate in benzene); $[\alpha]^{24}_D = +67.3°$ (c = 1.9, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.22 (s, 1H, H-1), 4.79 (dd, 1H, J = 5.9, 3.7 Hz, H-3), 4.56 (d, 1 H, J = 5.9 Hz, H-2), 4.38 (ddd, 1 H, J = 7.8, 6.1, 4.4 Hz, H-5), 4.10 (dd, 1 H, J = 8.8, 6.3 Hz, H-6), 4.01 (dd, 1H, J = 8.8, 4.4 Hz, H-6), 3.89 (dd, 1H, J = 7.8, 3.7 Hz, H-4), 1.48 (s, 3H), 1.44 (s, 3H), 1.37 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 112.8, 109.3, 101.4, 84.9, 80.9, 79.4, 72.9, 66.9, 26.9, 25.8, 25.1, 24.5; FTIR (neat film) 2986, 2921, 1372, 1210, 1162, 1118, 1079, 997, 977, 850 cm^{-1}; HRMS (FAB) *m/z*: Calcd for $C_{24}H_{38}O_{11}Na$ (M + Na) 525.2313, found 525.2312. Anal. Calcd for $C_{24}H_{38}O_{11}$: C, 57.36; H, 7.62. Found: C, 57.48; H, 7.58.

2,3,4,6-Tetra-*O*-benzyl-1-deoxy-1-fluoro-α-D-glucopyranoside (10):[12] R_f = 0.34 (3% ethyl acetate in benzene); $[\alpha]^{23}_D = +15.5°$ (c = 2.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.1−7.4 (m, 20 H), 5.56 (dd, 1 H, J = 53.2, 2.7 Hz, H-1), 4.96 (d, 1 H, J = 10.9 Hz, OBn), 4.86 (d, 1 H, J = 10.9 Hz, OBn), 4.84 (d, 1 H, J = 10.9 Hz, OBn), 4.81 (d, 1 H, J = 12.0 Hz, OBn), 4.60 (d, 1 H, J = 12.0 Hz, OBn), 4.52 (d, 1 H, J = 10.8 Hz, OBn), 4.48 (d, 1 H, J = 12.1 Hz, OBn), 3.99 (t, 1 H, J = 9.5 Hz, H-3), 3.95 (dt, 1 H, J = 10.2, 2.5 Hz, H-5), 3.76 (dd, 1 H, J = 10.8, 2.9 Hz, H-6) 3.74 (t, 1 H, J = 9.5 Hz, H-4), 3.67 (dd, 1 H, J = 10.9, 2.0 Hz, H-6), 3.57 (ddd, 1 H, J = 25.7, 9.7, 2.7 Hz, H-2); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.8, 138.3, 138.0, 128.9, 128.80, 128.78, 128.77, 128.73, 128.68, 128.43, 128.38, 128.36, 128.32, 128.29, 128.27, 128.22, 128.19, 128.17, 128.13, 128.10, 106.8, 105.0, 81.8, 79.7, 79.5, 76.9, 76.2, 75.5, 73.90, 73.86, 73.20, 73.00, 72.97, 68.1; FTIR (neat film) 3031, 2918, 1952, 1874, 1806, 1609, 1496, 1454, 1362, 1210, 1161, 1072, 736, 697 cm^{-1}; HRMS (FAB) *m/z*: Calcd for $C_{34}H_{35}F_1O_5Na$ (M + Na) 565.2366, found 565.2364.

1-*n*-Tetradecanoyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (11): R_f = 0.32 (3% acetonitrile in benzene); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.1−7.4 (m, 20 H), 6.41 (d, 1 H, J = 3.6 Hz, H-1)[1], 4.97 (d, 1 H, J = 11.0 Hz, OBn), 4.86 (d, 1 H, J = 10.8 Hz, OBn), 4.83 (d, 1 H, J = 11.1 Hz, OBn), 4.71 (d, 1 H, J = 11.2 Hz, OBn), 4.64 (d, 1 H, J = 11.2 Hz, OBn), 4.62 (d, 1 H, J = 12.1 Hz, OBn), 4.52 (d, 1 H, J = 10.5 Hz, OBn), 4.49 (d, 1 H, J = 12.3 Hz, OBn), 3.95 (t, 1 H, J = 9.4 Hz, H-3), 3.88 (dt, 1 H, J = 10.1, 2.0 Hz, H-5), δ 3.72−3.78 (m, 2 H, H-4, H-6), 3.71 (dd, 1 H, J = 9.5, 3.5 Hz, H-2), 3.66 (dd, 1 H, J = 10.7, 1.8 Hz, H-6), 2.39 (t, 2 H, J = 7.4 Hz), 1.65 (quint., 2 H, J = 7.4 Hz), 1.25 (m, 20 H), 0.90 (t, 3 H, J = 7.1 Hz).

3-*O*-Acetyl-2,3-di-*O*-isopropylidene-1-deoxy-1-*N*-acetylamino-L-rhamnopyranoside (12):[13] α: R_f = 0.28 (33% acetonitrile in benzene); $[\alpha]^{23}_D = +19.6°$ (c = 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.49 (d, 1 H, J = 9.4 Hz, NH), 5.49 (dd, 1 H, J = 9.6, 2.3 Hz, H-1), 4.83 (dd, 1H, J = 8.3, 6.8 Hz, H-4), 4.20 (dd, 1 H, J = 6.7, 5.9 Hz, H-3), 4.15 (dd, 1 H, J = 5.6, 2.3 Hz, H-2), 3.55 (dq, 1 H, J = 8.3, 6.3 Hz, H-5), 2.09 (s, 3 H), 2.06 (s, 3 H), 1.36 (s, 3. H), 1.22 (d, 3 H, J = 6.3 Hz, H-6); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.4, 170.2, 111.0, 77.0, 75.1, 74.6, 73.7, 72.0, 27.7, 26.7, 23.8, 21.4, 18.2; FTIR (neat film) 3306, 2986, 1742, 1678, 1525, 1454, 1375, 1232, 1128, 1080, 865, 732 cm^{-1}; HRMS (FAB) *m/z*: Calcd for $C_{13}H_{21}N_1O_6Na$ (M + Na) 310.1267, found 310.1268. *β*: R_f = 0.22 (33% acetonitrile in benzene); $[\alpha]^{23}_D = -7.7°$ (c = 0.9, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.23 (d, 1 H, J = 8.5 Hz, NH), 5.49 (dd, 1 H, J = 8.7, 5.3 Hz, H-1), 4.96 (t, 1 H, J = 5.6 Hz, H-4), 4.31 (t, 1 H, J = 5.4 Hz, H-3), 4.10 (t, 1 H, J = 5.4 Hz, H-2), 3.87 (quint., 1 H, J = 6.5 Hz, H-5), 2.10 (s, 3 H), 2.04 (s, 3 H), 1.54 (s, 3 H), 1.34 (s, 3 H), 1.34 (d, 1 H, J = 6.7 Hz, H-6); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 170.2, 110.5, 75.9, 75.3, 74.2, 72.8, 70.2, 27.9, 26.3, 21.4, 17.2; FTIR (neat film) 3293, 2986, 1742, 1666, 1546, 1374, 1232, 1130, 1077, 1029, 860, 733 cm^{-1}; HRMS (FAB) *m/z*: Calcd for $C_{13}H_{21}N_1O_6Na$ (M + Na) 310.1267, found 310.1268.

Methyl *O*-3-*O*-acetyl-2,3-di-*O*-isopropylidene-L-rhamnopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (14):[14] α: R_f = 0.39 (13% acetonitrile in benzene); $[\alpha]^{24}_D = +23.9°$ (c = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6) δ 7.39−7.05 (m, 15H, ArH), 5.30 (dd, 1H, J = 10.3, 8.1 Hz, H-4), 5.09 (s, 1H, H-1), 5.04 (d, 1 H, J = 11.2 Hz, OBn), 4.93 (d, 1 H, J = 11.5 Hz, OBn), 4.79 (d, 1H, J = 11.2 Hz, OBn), 4.61 (d, 1 H, J = 3.4 Hz, H-1′), 4.58 (d, 1 H, J = 11.5 Hz, OBn), 4.48 (d, 1H, J = 11.9 Hz, OBn), 4.40 (d, 1H, J = 11.9 Hz, OBn), 4.28−4.23 (m, 2H, H-3, H-3′), 4.17 (d, 1H, J = 5.4 Hz, H-2), 3.92−3.87 (m, 3H, H-5, H-5′, H-6′), 3.61 (t, 1H, J = 9.0 Hz, H-4′), 3.55−3.52 (m, 2H, H-2′, H-6′), 3.13 (s, 3H, OMe), 1.62 (s, 3H), 1.61 (s, 3H), 1.21 (s, 3H), 1.19 (d, 3H, J = 6.3 Hz); ^{13}C NMR (126 MHz, C_6D_6) δ 169.5, 139.6, 139.0, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.6, 109.9, 98.2, 97.5, 82.4, 81.1, 77.7, 76.5, 76.3, 75.6, 74.8, 74.7, 72.8, 70.5, 66.3, 64.3, 54.9, 27.9, 26.6, 20.4, 17.2; FTIR (neat film) 2985, 2934, 1742, 1455, 1374, 1232, 1139, 1086, 1052, 1029, 859, 737, 698 cm^{-1}; HRMS (FAB) *m/z*: Calcd for $C_{39}H_{48}O_{11}Na$ (M + Na) 715.3096, found 715.3094. *β*: R_f = 0.29 (13% acetonitrile in benzene); $[\alpha]^{24}_D = +27.8°$ (c = 2.8, $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6) δ 7.43−7.05 (m, 15H, ArH), 5.47 (dd, 1H, J = 9.5, 7.3 Hz, H-4), 5.06 (d, 1 H, J = 11.2 Hz, OBn), 5.01 (d, 1 H, J = 11.2 Hz, OBn), 4.92 (d, 1H, J = 11.2 Hz, OBn), 4.85 (d, 1H, J = 11.5 Hz, OBn), 4.76 (d, 1 H, J = 3.4 Hz, H-1′), 4.59 (d, 1H, J = 2.2 Hz, H-1), 4.49 (d, 1H, J = 11.9 Hz, OBn), 4.39 (d, 1H, J = 11.9 Hz, OBn), 4.31 (dd, 1H, J = 10.7, 4.2 Hz, H-6′), 4.26 (t, 1H, J = 9.0 Hz, H-3′), 4.02 (dd, 1H, J = 6.1, 2.4 Hz, H-2), 3.98−3.93 (m, 2H, H-3, H-5′), 3.90 (t,

(12) For preparation of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose, see: Perrine, T. D.; Glaudemans, C. P. J.; Ness, R. K.; Kyle, J.; Fletcher, H. G., Jr. *J. Org. Chem.* **1967**, *32*, 664−669.

(13) For preparation of 4-*O*-acetyl-2,3-di-*O*-isopropylidene-L-rhamnopyranose, see: Pozsgay, V.; Neszmelyi, A. *Carbohydr. Res.* **1980**, *80*, 196−202.

(14) For preparation of methyl 2,3,4,-tri-*O*-benzyl-α-D-glucopyranoside, see: Hashimoto, H.; Asano, K.; Fujii, F.; Yoshimura, J. *Carbohydr. Res.* **1982**, *104*, 87−104.

1H, J = 10.0 Hz, H-4′), 3.70 (dd, 1H, J = 10.5, 1.5 Hz, H-6′), 3.50 (dd, 1H, J = 9.5, 3.4 Hz, H-2′), 3.28 (s, 3H, OMe), 3.22 (dq, 1H, J = 9.8, 6.3 Hz, H-5), 1.62 (s, 3H), 1.57 (s, 3H), 1.21 (d, 3H, J = 6.3 Hz), 1.19 (s, 3H); ^{13}C NMR (126 MHz, C_6D_6) δ 169.2, 139.8, 139.7, 139.3, 128.4, 128.3, 128.2, 128.1, 127.9, 127.6, 127.5, 127.4, 110.9, 98.5, 98.4, 82.3, 81.1, 78.3, 77.3, 75.5, 75.1, 74.7, 74.4, 72.9, 70.7, 70.0, 67.6, 55.0, 27.5, 26.2, 20.5, 18.4; FTIR (neat film) 2985, 2932, 1745, 1455, 1374, 1230, 1191, 1162, 1075, 1048, 1029, 866, 738, 698 cm^{-1}; HRMS (FAB) *m*/*z*: Calcd for $C_{39}H_{48}O_{11}Na$ (M + Na) 715.3096, found 715.3094.

Methyl *O*-2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (15): α: R_f = 0.43 (9% acetonitrile in benzene); $[\alpha]^{25}_D$ = +50.2° (c = 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6) δ 7.38−7.06 (m, 35H, ArH), 5.19 (d, 1H, J = 3.4 Hz, H-1), 5.10 (d, 1H, J = 11.5 Hz, OBn), 5.05 (d, 1H, J = 11.2 Hz, OBn), 5.01 (d, 1H, J = 11.0 Hz, OBn), 4.99 (d, 1H, J = 11.0 Hz, OBn), 4.86 (d, 1H, J = 11.5 Hz, OBn), 4.82 (t, 2H, J = 11.5 Hz, OBn), 4.64 (d, 1H, J = 11.5 Hz, OBn), 4.61 (d, 1H, J = 3.4 Hz, H-1′), 4.56 (d, 1H, J = 11.9 Hz, OBn), 4.50−4.44 (m, 4H, OBn), 4.39 (d, 1H, J = 12.2 Hz, OBn), 4.37 (d, 1H, J = 11.9 Hz, OBn), 4.31−4.23 (m, 2H, H-3, H-3′), 4.08−4.05 (m, 1H, H-5), 4.03 (dd, 1H, J = 11.7, 3.7 Hz, H-6′), 3.97−3.89 (m, 2H, H-4′, H-5′), 3.83 (t, 1H, J = 9.8 Hz, H-4), 3.79 (dd, 1H, J = 11.7, 2.4 Hz, H-6′), 3.72 (dd, 1H, J = 11.0, 4.1 Hz, H-6), 3.64 (dd, 1H, J = 10.7, 1.7 Hz, H-6), 3.59 (dd, 1H, J = 9.5, 3.4 Hz, H-2), 3.50 (dd, 1H, J = 9.5, 3.4 Hz, H-2′), 3.15 (s, 3H, OMe); ^{13}C NMR (126 MHz, C_6H6) δ 139.7, 139.6, 139.5, 139.4, 139.2, 139.1, 128.6, 128.5, 128.48, 128.44, 128.4, 128.3, 128.1, 127.9, 127.7, 127.64, 127.63, 127.6, 127.5, 98.4, 97.4, 82.4, 82.1, 81.2, 81.1, 78.4, 78.1, 75.6, 75.4, 75.1, 73.4, 72.9, 72.4, 71.2, 69.4, 66.0, 54.9; FTIR (neat film) 3030, 2923, 2860, 1496, 1453, 1360, 1159, 1089, 1072, 1028, 736, 697 cm^{-1}; HRMS (FAB) *m*/*z*: Calcd for $C_{62}H_{66}O_{11}Na$ (M + Na) 1009.4505, found 1009.4503. β: R_f = 0.35 (9% acetonitrile in benzene); $[\alpha]^{24}_D$ = +19.3° (c = 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6) δ 7.44−7.04 (m, 35 H, ArH), 5.15 (d, 1H, J = 11.2 Hz, OBn), 5.03 (d, 1 H, J = 11.2 Hz, OBn), 5.01 (d, 1H, J = 11.0 Hz, OBn), 4.91 (d, 1H, J = 11.5 Hz, OBn), 4.85 (d, 1H, J = 11.5 Hz, OBn), 4.82 (d, 1H, J = 11.2 Hz, OBn), 4.78 (t, 2H, J = 10.7 Hz, OBn), 4.68 (d, 1H, J = 3.4 Hz, H-1′), 4.65 (d, 1H, J = 11.7 Hz, OBn), 4.56 (d, 1H, J = 11.2 Hz, OBn), 4.53 (d, 1H, J = 11.9 Hz, OBn), 4.48 (d, 1H, J = 8.1 Hz, H-1), 4.47−4.44 (m, 2H, OBn), 4.40 (d, 1H, J = 12.2 Hz, OBn), 4.34 (dd, 1H, J = 11.0, 1.7 Hz, H-6′), 4.28 (t, 1H, J = 9.0 Hz, H-3′), 4.05 (ddd, 1H, J = 10.0, 5.4, 1.5 Hz, H-5′), 3.79 (dd, 1H, J = 11.0, 5.4 Hz, H-6′), 3.75−3.71 (m, 2H, H-3, H-6), 3.69−3.66 (m, 3H, H-4, H-6, H-4′), 3.64−3.59 (m, 2H, H-2, H-2′), 3.36 (dt, 1H, J = 9.3, 2.4 Hz, H-5), 3.16 (s, 3H, OMe); ^{13}C NMR (126 MHz, C_6D_6) δ 139.7, 139.5, 139.4, 139.3, 139.2, 139.1, 139.0, 128.6, 128.5, 128.47, 128.45, 128.4, 128.3, 128.2, 128.1, 127.9, 127.7, 127.6, 127.5, 127.4, 104.4, 98.2, 85.1, 82.6, 82.2, 81.1, 78.6, 78.3, 75.6, 75.5, 75.4, 74.9, 74.8, 73.5, 72.7, 70.8, 69.3, 69.0, 54.9; FTIR (neat film) 3030, 2905, 2860, 1496, 1454, 1359, 1093, 1072, 1028, 735, 687 cm^{-1}; HRMS (FAB) *m*/*z*: Calcd for $C_{62}H_{66}O_{11}$-Na (M + Na) 1009.4505, found 1009.4503.

Methyl *O*-3-*O*-acetyl-2,3-di-*O*-isopropylidene-L-rhamnopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (16): α: R_f = 0.33 (13% acetonitrile in benzene); $[\alpha]^{24}_D$ = +4.5° (c = 3.1, $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6) δ 7.36−7.03 (m, 15H, ArH), 5.56 (s, 1H, H-1), 5.30−5.26 (m, 1H, H-4), 5.08 (d, 1H, J = 11.0 Hz, OBn), 4.71 (d, 1H, J = 11.2 Hz, OBn), 4.56 (d, 1H, J = 3.7 Hz, H-1′), 4.44 (d, 1H, J = 11.9 Hz, OBn), 4.39−4.32 (m, 3H, OBn), 4.30−4.21 (m, 2H, H-2, H-3), 4.23 (t, 1H, J = 9.5 Hz, H-4′), 4.14 (dq, 1H, J = 10.3, 6.3 Hz, H-5), 4.08 (t, 1H, J = 9.5 Hz, H-3′), 3.80 (dt, 1H, J = 9.8, 2.7 Hz, H-5′), 3.58−3.53 (m, 2H, H-6′), 3.46 (dd, 1H, J = 9.5, 3.7 Hz, H-2′), 3.11 (s, 3H, OMe), 1.66 (s, 3H), 1.62 (s, 3H), 1.26 (s, 3H), 1.00 (d, 3H, J = 6.1 Hz); ^{13}C NMR (126 MHz, C_6D_6) δ 169.5, 139.3, 138.9, 138.5, 128.6, 128.5, 128.3, 128.1,127.9, 127.8, 127.7, 127.4, 109.8, 98.1, 96.9, 81.6, 80.1, 76.8, 76.4, 75.7, 74.6, 73.8, 73.5, 72.9, 70.9, 69.3, 65.0, 54.9, 27.9, 26.7, 20.5, 16.9; FTIR (neat film) 3031, 2986, 2935, 1742, 1454, 1373, 1233, 1086, 1049, 859, 737, 698 cm^{-1}; HRMS (FAB) *m*/*z*: Calcd for $C_{39}H_{48}O_{11}Na$ (M + Na) 715.3096, found 715.3094. β: R_f = 0.20 (13% acetonitrile in benzene); $[\alpha]^{23}_D$ = +16.4° (c = 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6) δ 7.40−7.05 (m, 15H, ArH), 5.21 (dd, 1H, J = 9.3, 7.1 Hz, H-4), 5.14 (d, 1H, J = 1.9 Hz, H-1), 5.08 (d, 1H, J = 11.7 Hz, OBn), 4.71 (d, 1H, J = 11.5 Hz, OBn), 4.69 (d, 1H, J = 3.7 Hz, H-1′), 4.57 (d, 1H, J = 12.2 Hz, OBn), 4.50 (d, 1H, J = 12.2 Hz, OBn), 4.41 (s, 2H, OBn), 4.29 (t, 1H, J = 8.5 Hz, H-3′), 4.07−4.01 (m, 3H, H-4′, H-5′, H-6′), 3.96 (dd, 1H, J = 10.3, 4.6 Hz, H-6′), 3.86 (dd, 1H, J = 5.4, 1.9 Hz, H-2), 3.83 (dd, 1H, J = 7.1, 5.6 Hz, H-3), 3.55 (dd, 1H, J = 9.5, 3.4 Hz, H-2′), 3.16 (s, 3H, OMe), 3.04 (dq, 1H, J = 9.3, 6.3 Hz, H-5), 1.60 (s, 6H), 1.23 (s, 3H), 1.14 (d, 3H, J = 6.1 Hz); ^{13}C NMR (126 MHz, C_6D_6) δ 169.4, 139.8, 139.7, 138.9, 128.52, 128.5, 128.4, 128.3, 128.1, 127.9, 127.7, 127.6, 127.3, 110.7, 99.7, 97.7, 82.4, 81.3, 77.5, 76.5, 75.6, 74.9, 74.3, 73.2, 72.5, 70.3, 70.2, 69.0, 54.7, 27.9, 26.5, 20.4, 17.8; FTIR (neat film) 2927, 1744, 1454, 1374, 1187, 1077, 1045, 738, 698 cm^{-1}; HRMS (FAB) *m*/*z*: Calcd for $C_{39}H_{48}O_{11}Na$ (M + Na) 715.3096, found 715.3094.

Benzyl *O*-3,4,6-tri-*O*-benzyl-2-*O*-benzoyl-β-D-glucopyranosyl-(1→4)-2,3-di-*O*-isopropylidene-α-L-rhamnopyranoside (17):[15] R_f = 0.56 (9% acetonitrile in benzene); $[\alpha]^{24}_D$ = +4.7° (c = 1.3, $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6) δ 8.25−8.22 (m, 2H, ArH), 7.33−6.95 (m, 23H, ArH), 5.78 (dd, 1H, J = 9.3, 8.1 Hz, H-2), 5.34 (d, 1 H, J = 8.1 Hz, H-1), 5.10 (s, 1 H, H-1′), 4.74 (d, 1H, J = 11.5 Hz, OBn), 4.66 (s, 2H, OBn), 4.50 (d, 1H, J = 11.5 Hz, OBn), 4.49 (d, 1H, J = 12.5 Hz, OBn), 4.44 (d, 1H, J = 11.9 Hz, OBn), 4.43 (d, 1H, J = 12.5 Hz, OBn), 4.20 (dd, 1H, J = 7.6, 5.9 Hz, H-3′), 4.15 (d, 1H, J = 11.9 Hz, OBn), 4.04 (d, 1H, J = 5.9 Hz, H-2′), 3.99 (dd, 1H, J = 10.0, 7.6 Hz, H-4′), 3.83 (t, 1H, J = 8.8 Hz, H-3), 3.78 (dq, 1H, J = 10.0, 6.1 Hz, H-5′), 3.73 (t, 1H, J = 8.8 Hz, H-4), 3.70−3.64 (m, 2H, H-6), 3.59 (ddd, 1H, J = 9.8, 4.4, 2.2 Hz, H-5), 1.53 (d, 3H, J = 6.1 Hz), 1.49 (s, 3H), 1.15 (s, 3H); ^{13}C NMR (126 MHz, C_6D_6) δ 165.4, 139.1, 138.9, 138.7, 137.8, 132.8, 131.1, 130.2, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.7, 127.67, 127.6, 109.2, 100.8, 96.6, 83.6, 80.0, 78.9, 78.4, 76.7, 75.9, 75.0, 74.7, 74.6, 73.5, 69.1, 68.9, 64.7, 28.1, 26.3, 18.0; FTIR (neat film) 3031, 2925, 2860, 1730, 1453, 1372, 1268, 1218, 1093, 1062, 1027, 862, 763, 698 cm^{-1}; HRMS (FAB) *m*/*z*: Calcd for $C_{50}H_{54}O_{11}Na$ (M + Na) 853.3561, found 853.3563.

Benzyl *O*-2,3,4,6-tetra-*O*-benzyl-D-galactopyranosyl-(1→4)-2,3-di-*O*-isopropylidene-α-L-rhamnopyranoside (18):[16] α: R_f = 0.36 (5% acetonitrile in benzene); $[\alpha]^{24}_D$ = +24.9° (c = 3.2, $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6) δ 7.48−7.47 (m, 2H, ArH), 7.33−7.05 (m, 23H, ArH), 5.16 (s, 1H, H-1′), 5.14 (d, 1H, J = 3.2 Hz, H-1), 5.12 (d, 1H, J = 12.2 Hz, OBn), 4.74 (d, 1H, J = 11.2 Hz, OBn), 4.70 (d, 1H, J = 11.5 Hz, OBn), 4.60 (d, 1H, J = 11.7 Hz, OBn), 4.58−4.56 (m, 1H, H-5), 4.51 (d, 1H, J = 11.9 Hz, OBn), 4.48−4.37 (m, 4H, OBn), 4.29−4.26 (m, 2H, H-2, H-3′), 4.24−4.22 (m, 2H, H-4, H-2′), 4.18 (d, 1H, J = 11.9 Hz, OBn), 4.11 (dd, 1H, J = 10.3, 2.9 Hz, H-3), 4.04 (t, 1H, J = 8.5 Hz, H-6), 3.89 (dq, 1H, J = 10.0, 6.3 Hz, H-5′), 3.78 (dd, 1H, J = 8.3, 4.9 Hz, H-6), 3.62 (dd, 1H, J = 10.0, 7.3 Hz, H-4′), 1.53 (s, 3H), 1.38 (d, 3H, J = 6.3 Hz), 1.22 (s, 3H); ^{13}C NMR (126 MHz, C_6D_6) δ 139.9, 139.5, 139.3, 139.0, 137.9, 128.6, 128.5, 128.47, 128.41, 128.3, 128.13, 128.1, 127.9, 127.6, 127.5, 109.1, 99.5, 96.8, 81.3, 79.5, 77.8, 77.6, 76.7, 75.7, 75.4, 74.2, 73.6, 72.7, 69.5, 69.1, 68.6, 65.7, 28.3, 26.5, 17.6; FTIR (neat film) 3031, 2933, 2866, 1497, 1454, 1372, 1243, 1220, 1139, 1096, 1049, 1028, 997, 862, 735, 697 cm^{-1}; HRMS (FAB) *m*/*z*: Calcd for $C_{50}H_{56}O_{10}Na$ (M + Na) 839.3775, found 839.3771. β: R_f = 0.27 (5% acetonitrile in benzene); $[\alpha]^{25}_D$ = −21.2° (c = 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6) δ 7.44−7.42 (m, 2H, ArH), 7.36−7.07 (m, 23H, ArH), 5.19 (d, 1H, J = 8.1 Hz, H-1), 5.18 (s, 1H, H-1′), 5.03 (d, 1H, J = 11.5 Hz, OBn), 5.02 (d, 1H, J = 11.2 Hz, OBn), 4.75 (d, 1H, J = 11.2 Hz, OBn), 4.62 (d, 1H, J = 11.9 Hz, OBn), 4.61 (d, 1H, J = 11.5 Hz, OBn), 4.53 (d, 1H, J = 11.9 Hz, OBn), 4.47−4.43 (m, 2H, H-3, OBn), 4.31−4.21 (m, 4H, H-4, OBn), 4.10−4.07 (m, 2H, H-2, H-4′), 3.92 (dq, 1H, J = 9.8, 6.3 Hz, H-5′), 3.80−3.76 (m, 2H, H-6, H-2′), 3.68 (dd, 1H, J = 9.0, 5.6 Hz, H-6), 3.58−3.56 (m, 1H, H-5), 3.40 (dd, 1H, J = 9.8, 3.2 Hz, H-3′), 1.53 (s, 3H), 1.51 (d, 3H, J = 5.9 Hz), 1.21 (s, 3H); ^{13}C NMR (126 MHz,

(15) For preparation of 3,4,6-tri-*O*-benzyl-2-*O*-benzoyl-D-glucopyranose, see: Shi, L.; Kim. Y.-J.; Gin, D. Y. *J. Am. Chem. Soc.* **2001**, *123*, 6939−6940.

(16) For preparation of 2,3,4,6-tetra-*O*-benzyl-D-galactopyranose, see: Marco-Contelles, J.; Gallego, P.; Rodriguez-Fernandez, M.; Khiar, N.; Destabel, C.; Bernabe, M.; Martinez-Grau, A.; Chiara, J. L. *J. Org. Chem.* **1997**, *62*, 7397−7412.

C_6D_6) δ 139.9, 139.6, 139.4, 138.8, 137.9, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.7, 127.6, 127.5, 127.4, 109.2, 102.7, 96.8, 82.9, 80.4, 79.3, 78.9, 76.6, 75.3, 75.2, 74.9, 73.9, 73.5, 73.3, 69.2, 69.1, 64.9, 28.1, 26.3, 18.4; FTIR (neat film) 2907, 2853, 2360, 2334, 1454, 1143, 1085, 1068, 1026, 735, 697 cm^{-1}; HRMS (FAB) *m/z*: Calcd for $C_{50}H_{56}O_{10}Na$ (M + Na) 839.3775, found 839.3771.

Methyl *O*-3,4,6-tri-*O*-benzyl-2-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (19): R_f = 0.35 (9% acetonitrile in benzene); $[\alpha]^{25}_D$ = +20° (*c* = 1.8, $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6) δ 8.09−8.07 (m, 2H, ArH), 7.30−6.91 (m, 33H, ArH), 5.75 (dd, 1H, *J* = 9.5, 7.8 Hz, H-2), 4.90 (d, 1H, *J* = 11.5 Hz, OBn), 4.69−4.65 (m, 5H, OBn), 4.50 (d, 1H, *J* = 3.4 Hz, H-1′), 4.48 (d, 1H, *J* = 7.8 Hz, H-1), 4.46−4.38 (m, 5H, OBn), 4.30 (d, 1H, *J* = 11.9 Hz, OBn), 4.25 (dd, 1H, *J* = 10.5, 1.7 Hz, H-6′), 4.14 (t, 1H, *J* = 9.3 Hz, H-3′), 3.87 (ddd, 1H, *J* = 10.3, 4.4, 1.5 Hz, H-5), 3.77 (t, 1H, *J* = 9.3 Hz, H-3), 3.71−3.61 (m, 5H, H-4, H-5, H-6, H-4′, H-6′), 3.47−3.43 (m, 2H, H-6, H-2′), 3.04 (s, 3H, OMe); ^{13}C NMR (126 MHz, C_6D_6) δ 165.2, 139.8, 139.5, 139.3, 139.0, 138.9, 138.7, 132.9, 130.9, 130.1, 128.6, 128.56, 128.50, 128.4, 128.35, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.68, 127.67, 127.6, 127.5, 127.4, 127.3, 101.8, 98.1, 82.9, 82.1, 81.1, 78.5, 78.1, 75.9, 75.3, 74.9, 74.8, 74.6, 74.3, 73.5, 72.8, 70.3, 69.1, 68.5, 54.8; FTIR (neat film) 3030, 2925, 1729, 1453, 1267, 1093, 1065, 1028, 736, 697 cm^{-1}; HRMS (FAB) *m/z*: Calcd for $C_{62}H_{64}O_{12}Na$ (M + Na) 1023.4291, found 1023.4295. Anal. Calcd for $C_{62}H_{64}O_{12}$: C, 74.38; H, 6.44. Found: C, 74.25; H, 6.48.

Methyl *O*-3,4,6-tri-*O*-benzyl-2-*O*-benzoyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (20). R_f = 0.28 (9% acetonitrile in benzene); $[\alpha]^{25}_D$ = +22.4° (*c* = 2.4, $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6) δ 8.09−8.07 (m, 2H, ArH), 7.49−6.97 (m, 33H, ArH), 5.76 (dd, 1H, *J* = 9.5, 8.1 Hz, H-2), 5.30 (d, 1H, *J* = 11.9 Hz, OBn), 5.07 (d, 1H, *J* = 8.1 Hz, H-1), 4.94 (d, 1H, *J* = 11.9 Hz, OBn), 4.72 (d, 1H, *J* = 11.5 Hz, OBn), 4.71 (d, 1H, *J* = 11.2 Hz, OBn), 4.64 (d, 1H, *J* = 11.2 Hz, OBn), 4.57 (d, 1H, *J* = 12.5 Hz, OBn), 4.55 (d, 1H, *J* = 3.2 Hz, H-1′), 4.55−4.48 (m, 2H, OBn), 4.43−4.36 (m, 3H, OBn), 4.32−4.28 (m, 2H, H-4′, OBn), 4.23 (t, 1H, *J* = 9.3 Hz, H-3′), 3.93 (dd, 1H, *J* = 11.0, 3.7 Hz, H-6′), 3.78−3.69 (m, 4H, H-3, H-4, H-6, H-5′), 3.59−3.55 (m, 2H, H-5, H-6), 3.53 (dd, 1H, *J* = 11.0, 1.5 Hz, H-6′), 3.49 (dd, 1H, *J* = 9.3, 3.7 Hz, H-2′), 2.94 (s, 3H, OMe); ^{13}C NMR (126 MHz, C_6D_6) δ 164.9, 140.6, 139.3, 139.2, 139.03, 139.0, 138.7, 133.0, 130.7, 130.0, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 127.93, 127.9, 127.7, 127.6, 127.54, 127.5, 127.1, 101.1, 98.4, 83.5, 80.5, 80.4, 78.5, 77.7, 76.1, 75.2, 75.0, 74.9, 74.8, 73.7, 73.6, 73.1, 70.7, 69.1, 68.7, 54.8; FTIR (neat film) 3030, 2901, 2860, 1731, 1496, 1453, 1362, 1266, 1096, 1070, 1048, 1027, 736, 698 cm^{-1}; HRMS (FAB) *m/z*: Calcd for $C_{62}H_{64}O_{12}Na$ (M + Na) 1023.4291, found 1023.4295. Anal. Calcd for $C_{62}H_{64}O_{12}$: C, 74.30; H, 6.44. Found: C, 74.17; H, 6.45.

Methyl *O*-2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (21). α: R_f = 0.49 (5% acetonitrile in benzene); $[\alpha]^{24}_D$ = +41.1° (*c* = 2.4, $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6) δ 7.40−7.32 (m, 10H, ArH), 7.27−7.24 (m, 4H, ArH), 7.18−7.04 (m, 21H, ArH), 5.28 (d, 1H, *J* = 3.7 Hz, H-1), 5.10 (d, 1H, *J* = 11.2 Hz, OBn), 5.05 (d, 1H, *J* = 11.5 Hz, OBn), 5.01 (d, 1H, *J* = 11.2 Hz, OBn), 4.82 (d, 1H, *J* = 11.0 Hz, OBn), 4.80 (d, 1H, *J* = 11.2 Hz, OBn), 4.71 (d, 1H, *J* = 12.2 Hz, OBn), 4.63 (d, 1H, *J* = 11.2 Hz, OBn), 4.60 (d, 1H, *J* = 3.4 Hz, H-1′), 4.58 (d, 1H, *J* = 11.9 Hz, OBn), 4.55 (s, 2H, OBn), 4.49 (d, 1H, *J* = 12.2 Hz, OBn), 4.37 (d, 1H, *J* = 11.9 Hz, OBn), 4.34 (d, 1H, *J* = 11.9 Hz, OBn), 4.29−4.27 (m, 2H, H-2, OBn), 4.26−4.20 (m, 2H, H-5, H-3′), 4.10 (dd, 1H, *J* = 10.0, 2.7 Hz, H-3), 4.01 (dd, 1H, *J* = 11.9, 3.7 Hz, H-6′), 3.98 (d, 1H, *J* = 1.7 Hz, H-4), 3.94−3.87 (m, 2H, H-4′, H-5′), 3.86−3.80 (m, 2H, H-6,H-6′), 3.73 (dd, 1H, *J* = 9.0, 5.9 Hz, H-6), 3.49 (dd, 1H, *J* = 9.5, 3.4 Hz, H-2′), 3.11 (s, 3H, OMe); ^{13}C NMR (126 MHz, C_6D_6) δ 139.8, 139.7, 130.6, 139.59, 139.5, 139.3, 138.9, 128.6, 128.5, 128.49, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.58, 127.5, 127.4, 98.4, 98.3, 82.4, 81.2, 78.6, 78.3, 77.7, 76.2, 75.5, 75.3, 75.0, 73.5, 73.0, 72.9, 72.7, 71.3, 70.1, 69.5, 66.3, 54.9; FTIR (neat film) 3030, 2914, 2866, 1496, 1453, 1160, 1134, 1099, 1056, 1028, 736, 697 cm^{-1}; HRMS (FAB) *m/z*: Calcd for $C_{62}H_{66}O_{11}Na$ (M + Na) 1009.4505, found 1009.4503. Anal. Calcd for $C_{62}H_{66}O_{11}$: C, 75.43; H, 6.74. Found: C, 75.11; H, 6.73. β: R_f = 0.42 (5% acetonitrile in benzene); $[\alpha]^{24}_D$ = +10.4° (*c* = 1.4, $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6) δ 7.43−7.33 (m, 4H, ArH), 7.31−7.23 (m, 9H, ArH), 7.17−7.06 (m, 22H, ArH), 5.07 (d, 1H, *J* = 11.5 Hz, OBn), 5.04 (d, 1H, *J* = 11.5 Hz, OBn), 5.01 (d, 1H, *J* = 11.2 Hz, OBn), 4.90 (d, 1H, *J* = 11.7 Hz, OBn), 4.78 (d, 1H, *J* = 11.2 Hz, OBn), 4.77 (d, 1H, *J* = 11.2 Hz, OBn), 4.68 (d, 1H, *J* = 3.4 Hz, H-1′), 4.66 (d, 1H, *J* = 10.3 Hz, OBn), 4.61 (d, 1H, *J* = 11.2 Hz, OBn), 4.60 (d, 1H, *J* = 12.2 Hz, OBn), 4.51 (t, 2H, *J* = 12.2 Hz, OBn), 4.46 (d, 1H, *J* = 11.9 Hz, OBn), 4.44 (d, 1H, *J* = 7.6 Hz, H-1), 4.37 (dd, 1H, *J* = 10.7, 1.7 Hz, H-6′), 4.31−4.23 (m, 3H, H-5, OBn), 4.14 (dd, 1H, *J* = 9.8, 7.6 Hz, H-2), 4.04 (ddd, H, *J* = 10.0, 4.9, 1.5 Hz, H-5′), 3.84−3.81 (m, 2H, H-4, H-6′), 3.78−3.73 (m, 2H, H-6, H-4′), 3.64−3.60 (m, 2H, H-6, H-2′), 3.41 (t, 1H, *J* = 6.6 Hz, H-3′), 3.37 (dd, 1H, *J* = 9.8, 2.9 Hz, H-3), 3,12 (s, 3H, OMe); ^{13}C NMR (126 MHz, C_6D_6) δ 139.8, 139.7, 139.6, 139.2, 139.1, 138.8, 128.6, 128.5, 128.49, 128.46, 128.42, 128.4, 128.3, 128.1, 128.0, 127.9, 127.7, 127.6, 127.5, 127.4, 104.7, 98.2, 82.7, 82.3, 81.1, 79.9, 76.6, 75.5, 75.3, 75.2, 74.8, 74.6, 73.7, 73.5, 72.9, 72.7, 70.7, 69.0, 68.7, 54.9; FTIR (neat film) 3030, 2921, 2870, 1496, 1454, 1361, 1093, 1068, 1028, 735, 697 cm^{-1}; HRMS (FAB) *m/z*: Calcd for $C_{62}H_{66}O_{11}Na$ (M + Na) 1009.4505, found 1009.4503. Anal. Calcd for $C_{62}H_{66}O_{11}$: C, 75.43; H, 6.74. Found: C, 75.16; H, 6.73.

Benzyl *O*-2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl-(1→4)-2,3-di-*O*-isopropylidene-α-L-rhamnopyranoside (22): α: R_f = 0.41 (9% acetonitrile in benzene); $[\alpha]^{24}_D$ = +24.2° (*c* = 0.9, $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6) δ 7.36−7.17 (m, 8H, ArH), 7.16−7.06 (m, 17H, ArH), 5.14 (s, 1H, H-1′), 5.05 (d, 1H, *J* = 11.0 Hz, OBn), 5.04 (d, 1H, *J* = 3.4 Hz, H-1), 5.01 (d, 1H, *J* = 11.5 Hz, OBn), 4.92 (d, 1H, *J* = 11.5 Hz, OBn), 4.81 (d, 1H, *J* = 11.5 Hz, OBn), 4.59 (d, 1H, *J* = 11.4 Hz, OBn), 4.54−4.47 (m, 3H, H-2′, OBn), 4.45 (d, 1H, *J* = 11.5 Hz, OBn), 4.39−4.37 (m, 1H, H-5), 4.30 (t, 1H, *J* = 9.5 Hz, H-3), 4.21−4.16 (m, 3H, H-3′, OBn), 4.10 (dd, 1H, *J* = 10.0, 9.3 Hz, H-4), 4.01 (dd, 1H, *J* = 11.0, 2.7 Hz, H-6), 3.89 (dq, 1H, *J* = 10.0, 6.1 Hz, H-5′), 3.85 (dd, 1H, *J* = 11.0, 1.9 Hz, H-6), 3.58−3.55 (m, 2H, H-2, H-4′), 1.53 (s, 3H), 1.40 (d, 3H, *J* = 6.3 Hz), 1.18 (s, 3H); ^{13}C NMR (126 MHz, C_6D_6) δ 139.8, 139.6, 139.3, 138.8, 137.8, 128.6, 128.4, 128.3, 128.1, 127.9, 127.8, 127.6, 127.5, 127.4, 109.0, 99.0, 96.7, 82.6, 82.4, 81.2, 78.6, 77.6, 76.7, 75.5, 75.1, 74.1, 73.5, 71.6, 69.1, 68.9, 65.6, 28.4, 26.5, 17.6; FTIR (neat film) 3030, 2933, 2866, 1454, 1139, 1083, 1044, 1027, 735, 697 cm^{-1}; HRMS (FAB) *m/z*: Calcd for $C_{50}H_{56}O_{10}$-Na (M + Na) 839.3775, found 839.3771. β: R_f = 0.50 (9% acetonitrile in benzene); $[\alpha]^{24}_D$ = −15.3° (*c* = 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6) δ 7.41−7.21 (m, 6H, ArH), 7.19−7.07 (m, 19H, ArH), 5.23 (d, 1H, *J* = 7.8 Hz, H-1), 5.19 (s, 1H, H-1′), 5.0 (d, 1H, *J* = 11.2 Hz, OBn), 4.96 (d, 1H, *J* = 11.2 Hz, OBn), 4.87 (d, 1H, *J* = 11.5 Hz, OBn), 4.76 (d, 1H, *J* = 11.5 Hz, OBn), 4.73 (d, 1H, *J* = 11.5 Hz, OBn), 4.57 (d, 2H, *J* = 11.4 Hz, OBn), 4.46 (d, 1H, *J* = 12.4 Hz, OBn), 4.41−4.38 (m, 2H, H-3′, OBn), 4.26 (d, 1H, *J* = 11.9 Hz, OBn), 4.21 (d, 1H, *J* = 5.6 Hz, H-2′), 4.10 (dd, 1H, *J* = 9.8, 7.3 Hz, H-4′), 3.93 (dq, 1H, *J* = 10.0, 6.1 Hz, H-5′), 3.76−3.66 (m, 4H, H-3, H-4, H-6), 3.57 (t, 1H, *J* = 8.3 Hz, H-2), 3.50−3.48 (m, 1H, H-5), 1.58 (d, 3H, *J* = 6.3 Hz), 1.50 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (126 MHz, C_6D_6) δ 139.6, 139.5, 139.3, 139.0, 137.9, 128.6, 128.5, 128.4, 128.3, 128.1, 127.9, 127.6, 127.59, 127.5, 127.4, 109.4, 102.2, 96.9, 85.2, 83.0, 78.84, 78.8, 78.3, 76.7, 75.5, 74.9, 74.7, 73.4, 69.2, 69.1, 64.9, 28.1, 26.4, 18.2; FTIR (neat film) 2905, 2860, 1453, 1082, 1065, 1027,-735, 697 cm^{-1}; HRMS (FAB) *m/z*: Calcd for $C_{50}H_{56}O_{10}Na$ (M + Na) 839.3775, found 839.3771.

Benzyl *O*-3-*O*-acetyl-2,3-di-*O*-isopropylidene-α-L-rhamnopyranosyl-(1→4)-2,3-di-*O*-isopropylidene-α-L-rhamnopyranoside (23): R_f = 0.38 (9% acetonitrile in benzene); $[\alpha]^{24}_D$ = −41.3° (*c* = 3.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38−7.31 (m, 5H, ArH), 5.63 (s, 1H, H-1), 5.06 (s, 1H, H-1′), 4.88 (dd, 1H, *J* = 10.0, 7.8 Hz, H-4), 4.70 (d, 1H, *J* = 11.7 Hz, OBn), 4.52 (d, 1H, *J* = 11.7 Hz, OBn), 4.23 (dd, 1H, *J* = 7.1, 5.6 Hz, H-3′), 4.16−4.14 (m, 2H, H-2, H-2′), 4.11 (dd, 1H, *J* = 7.8, 5.1 Hz, H-3), 3.73 (dq, 2H, *J* = 10.0, 6.1 Hz, H-5, H-5′), 3.59 (dd, 1H, *J* = 9.8, 7.3 Hz, H-4′), 2.10 (s, 3H), 1.56 (s, 3H), 1.54 (s, 3H), 1.35 (s, 3H), 1.32 (s, 3H), 1.26 (d, 3H, *J* = 6.1 Hz), 1.15 (d, 3H, *J* = 6.3 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.0, 136.9, 128.5, 128.2, 127.9, 109.6, 109.5, 96.1, 95.5, 78.5, 76.7, 76.2, 76.1, 75.5, 74.2, 69.1, 64.3, 64.0, 27.9, 27.6, 26.4, 26.3, 21.0, 17.8, 16.7; FTIR (neat

film) 2985, 2936, 1744, 1376, 1220, 1140, 1082, 1047, 1028, 991, 860 cm^{-1}; HRMS (FAB) *m*/*z*: Calcd for $C_{27}H_{38}O_{10}Na$ (M + Na) 545.2365, found 545.2363.

Benzyl *O*-2,3,4,6-bis(di-*O*-isopropylidene)-α-D-mannopyranosyl-(1→4)-2,3-di-*O*-isopropylidene-α-L-rhamnopyranoside (24): R_f = 0.49 (13% acetonitrile in benzene); $[\alpha]^{24}_D = +10.6°$ (*c* = 2.3, $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6) δ 7.37−7.29 (m, 5H, ArH), 5.12 (s, 1H, H-1), 5.02 (s, 1H, H-1′), 4.80 (dd, 1H, *J* = 5.9, 3.7 Hz, H-3), 4.68 (d, 1H, *J* = 11.9 Hz, OBn), 4.57 (d, 1H, *J* = 6.1 Hz, H-2), 4.50 (d, 1H, *J* = 11.7 Hz, OBn), 4.40 (ddd, 1H, *J* = 8.3, 6.3, 4.9 Hz, H-5), 4.15−4.13 (m, 2H, H-6), 4.12−4.08 (m, 2H, H-4, H-2′), 4.06 (dd, 1H, *J* = 9.7, 5.9 Hz, H-3′), 3.68 (dq, 1H, *J* = 10.0, 6.3 Hz, H-5′), 3.38 (dd, 1H, *J* = 10.0, 7.3 Hz, H-4′), 1.55 (s, 3H), 1.47 (s, 3H), 1.44 (s, 3H), 1.38 (s, 3H), 1.32 (s, 6H), 1.27 (d, 3H, *J* = 6.1 Hz); ^{13}C NMR (126 MHz, C_6D_6) δ 137.1, 128.5, 128.2, 127.9, 112.6, 109.24, 109.2, 106.2, 96.3, 85.0, 80.3, 79.5, 79.4, 77.1, 75.8, 73.1, 69.1, 66.9, 64.9, 27.9, 26.8, 26.2, 25.8, 25.3, 24.4, 17.8; FTIR (neat film) 2985, 2937, 1372, 1217, 1089, 1058, 1036, 859 cm^{-1}; HRMS (FAB) *m*/*z*: Calcd for $C_{28}H_{840}O_{10}Na$ (M + Na) 559.2519, found 559.2519.

General Glycosylation Procedure with $Ph_2SO{\cdot}Tf_2O$: Methyl *O*-2,3,4,6-bis(di-*O*-isopropylidene)-α-D-mannopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (13). Trifluoromethanesulfonic anhydride (48 μL, 0.28 mmol, 1.4 equiv) was added to a solution of 2,3,4,6-bis(di-*O*-isopropylidene)-D-mannopyranose (53 mg, 0.20 mmol, 1 equiv), 2,4,6-tri-*tert*-butylpyridine (200 mg, 0.81 mmol, 4 equiv), and diphenyl sulfoxide (115 mg, 0.57 mmol, 2.8 equiv) in dichloromethane (3 mL) at −78 °C. The resulting mixture was stirred at this temperature for 10 min and then at −45 °C for 1 h. A solution of methyl 2,3,6-tri-*O*-benzyl-D-glucopyranoside (141 mg, 0.30 mmol, 1.5 equiv) in dichloromethane (3 mL) was then added via cannula. The resulting solution was stirred at −45 °C for 30 min, then at 0 °C for 30 min, and finally at 23 °C for 5 h. The reaction mixture was quenched with triethylamine (0.4 mL), diluted with dichloromethane (50 mL), and concentrated in vacuo. The residue was purified by silica gel flash chromatography (8% acetonitrile in benzene) to afford the (1,4)-disaccharide **13** (97 mg, 94:06 α:*β*, 67% total).

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Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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